

Transition Metal-Catalyzed Synthesis of Pyrroles from Dienyl Azides

Huijun Dong, Meihua Shen, Joanne E. Redford, Benjamin J. Stokes,
Ashley L. Pumphrey, and Tom G. Driver*

Department of Chemistry, University of Illinois at Chicago,
845 West Taylor Street, Chicago, Illinois, 60607-7061

Supporting Information 1

Contents

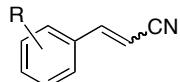
I.	Preparation of α,β -unsaturated nitriles.....	s-2
II.	Preparation of cinnamaldehydes.....	s-5
III.	Preparation of dienyl azides.....	s-8
IV.	Metal-catalyzed synthesis of pyrroles from dienyl azides.....	s-15
V.	References.....	s-22
VI.	^1H and ^{13}C NMR Spectra of Pyrroles.....	s-23

General. ^1H NMR and ^{13}C NMR spectra were recorded at ambient temperature using Bruker DRX 500 or Varian DRX 300 spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were acquired on a JEOL GC Mate II or Thermo Finnigan LTQ FT spectrometer, and were obtained by peak matching. Melting points were acquired on a Thomas Hoover Uni-Melt, capillary melting point apparatus and are reported uncorrected. Analytical thin layer chromatography was performed on Sorbent Technologies 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on Sorbent Technologies 60 \AA (40 – 60 μm) mesh silica gel (SiO_2). Medium pressure liquid chromatography (MPLC) was performed using Thomson SINGLE StEP pumps to force flow the indicated solvent system down columns that had been packed with Sorbent Technologies 60 \AA (40 – 60 μm) mesh silica gel (SiO_2). All reactions were carried out under an atmosphere of nitrogen in glassware, which had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Acetonitrile, Methanol, Toluene, THF, Et_2O , and CH_2Cl_2 were dried by filtration through alumina according to the procedure of Grubbs.¹ Metal salts were stored in an MBraun labmaster nitrogen atmosphere dry box.

I. Preparation of α,β -unsaturated nitriles

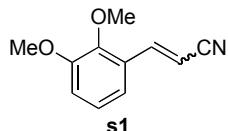
A. General procedure for the preparation of α,β -unsaturated nitriles

The requisite α,β -unsaturated nitriles were prepared from acetonitrile and aromatic or heteroaromatic aldehydes following the method reported by DiBiase and co-workers.²

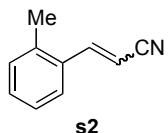


In a 100 mL, three-necked round bottom flask, equipped with a pressure equalizing addition funnel, reflux condenser, N₂ purge, powdered KOH was added to dry acetonitrile. The mixture was heated to reflux (internal temperature 83 ± 3°C), and a solution of the aldehyde in acetonitrile was added at once. After the addition was complete, stirring was continued for the specified time and then the hot solution was poured onto cracked ice. This mixture was extracted with 3 × 20 mL of CH₂Cl₂. The combined organic phases were washed with brine. The resulting organic phase was dried over Na₂SO₄ and filtered. The filtrate was concentrated *in vacuo* and purified via MPLC (0:100 – 30:70 EtOAc:hexanes) to afford the product.

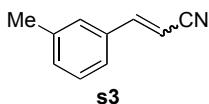
B. α,β -Unsaturated nitrile syntheses



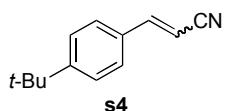
Nitrile (s1).² The general procedure was followed using a solution of 4.98 g of 2,3-dimethoxybenzaldehyde (30 mmol) in 12 mL of acetonitrile and 20 mL of a 1.78 M solution of KOH in acetonitrile. The mixture was refluxed for 3.5 min. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s1**, an inseparable mixture of regioisomers [*E*:*Z* = 88:12 (NMR)], as a white solid (4.33 g, 76%). The spectral data matched that reported by DiBiase and co-workers.² *E*-isomer: ¹H NMR (CDCl₃, 500 MHz): δ 7.68 (d, *J* = 17.0 Hz, 1H), 7.06 (m, 1H), 7.02 (m, 1H), 6.97 (m, 1H), 5.98 (d, *J* = 16.5 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H); *Z*-isomer: ¹H NMR (CDCl₃, 500 MHz) δ 7.74 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.0 Hz, 1H), 7.56 (d, *J* = 12.5 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.03-7.01 (m, 1H), 5.48 (d, *J* = 12.5 Hz, 1H), 3.84 (s, 6H); IR (thin film): 2216, 1576, 1480, 1267, 1071, 748 cm⁻¹.



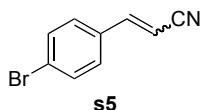
Nitrile (s2).² The general procedure was followed using a solution of 3.60 g of *o*-tolualdehyde (30 mmol) in 12 mL of acetonitrile and 20 mL of a 1.78 M solution of KOH in acetonitrile. The mixture was refluxed for 9 min. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s2**, an inseparable mixture of regioisomers [*E*:*Z* = 82:18 (NMR)], as a pale waxy solid (2.15 g, 51%). The spectral data matched that reported by DiBiase and co-workers.² *E*-isomer: ¹H NMR (CDCl₃, 300 MHz) δ 7.70 (d, *J* = 16.2 Hz, 1H), 7.47-7.43 (m, 1H), 7.35-7.29 (m, 1H), 7.28-7.21 (m, 2H), 5.81 (d, *J* = 16.5 Hz, 1H), 2.42 (s, 3H); *Z*-isomer: ¹H NMR (CDCl₃, 300 MHz) δ 7.93 (d, *J* = 7.5, 1H), 7.43-7.39 (m, 1H), 7.35-7.32 (m, 1H), 7.29-7.23 (m, 2H), 5.53 (d, *J* = 12, 1H), 2.36 (s, 3H).



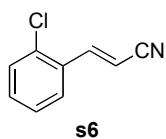
Nitrile (s3).³ The general procedure was followed using a solution of 3.60 g of *m*-tolualdehyde (30 mmol) in 12 mL of acetonitrile and 20 mL of a 1.78 M solution of KOH in acetonitrile. The mixture was refluxed for 9 min. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s3**, an inseparable mixture of regioisomers [*E*:*Z* = 82:18 (NMR)], as a white solid (1.92 g, 45%). The spectral data matched that reported by Andrus and co-workers.³ *E*-isomer: ¹H NMR (CDCl_3 , 300 MHz) δ 7.66–7.58 (m, 1H), 7.40–7.28 (m, 4H), 5.86 (d, J = 16.8 Hz, 1H), 2.38 (s, 3H); *Z*-isomer: ¹H NMR (CDCl_3 , 300 MHz) δ 7.66–7.58 (m, 1H), 7.36–7.29 (m, 3H), 7.09 (d, J = 12.0 Hz, 1H), 5.42 (d, J = 12.0 Hz, 1H), 2.40 (s, 3H).



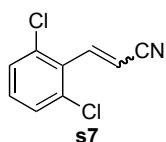
Nitrile (s4).⁴ The general procedure was followed using a solution of 5.00 mL of 4-*tert*-butylbenzaldehyde (30 mmol) in 12 mL of acetonitrile and 20 mL of 1.78 M solution of KOH in acetonitrile. The mixture was refluxed for 8 min. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s4**, an inseparable mixture of regioisomers [*E*:*Z* = 83:17 (NMR)], as yellow oil (4.83 g, 87%). The spectral data matched that reported by Fairhurst and co-workers:⁴ *E*-isomer: ¹H NMR (CDCl_3 , 500 MHz) δ 7.37–7.44 (m, 5H), 5.84 (d, J = 16.5 Hz, 1H), 1.33 (s, 9H); ¹³C NMR (CDCl_3 , 125 MHz) δ 155.0, 150.5, 129.0, 127.3, 126.1, 118.5, 95.3, 35.0, 31.1. *Z*-isomer: ¹H NMR (CDCl_3 , 500 MHz) δ 7.77 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.10 (d, J = 12.0 Hz, 1H), 5.39 (d, J = 12.0 Hz, 1H), 1.34 (s, 9H); ¹³C NMR (CDCl_3 , 125 MHz) δ 154.7, 148.6, 130.9, 127.3, 125.9, 117.8, 94.0, 35.0, 31.1.



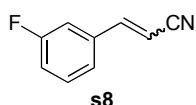
Nitrile (s5).⁵ The general procedure was followed using a solution of 5.55 g of 4-bromo-benzaldehyde (30 mmol) in 12 mL of acetonitrile and 20 mL of 1.78 M solution of KOH in acetonitrile. The mixture was refluxed for 2 min. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s5**, an inseparable mixture of regioisomers [*E*:*Z* = 93:7 (NMR)], as a white solid (3.50 g, 63%). The spectral data matched that reported by Peppe and co-workers:⁵ *E*-isomer: ¹H NMR (CDCl_3 , 500 MHz) δ 7.56 (dd, J_1 = 14.0 Hz, J_2 = 1.5 Hz, 2H), 7.31–7.35 (m, 3H), 5.88 (d, J = 16.5 Hz, 1H); ¹³C NMR (CDCl_3 , 125 MHz) δ 149.2, 132.4 (2C), 130.4, 128.7, 117.8, 97.0. *Z*-isomer: ¹H NMR (CDCl_3 , 500 MHz) δ 7.66–7.68 (m, 2H), 7.56–7.58 (m, 2H), 7.07 (d, J = 12.0 Hz, 1H), 5.49 (d, J = 12.0 Hz, 1H).



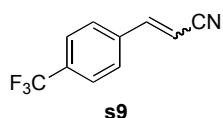
Nitrile (s6).² The general procedure was followed using a solution of 5.68 mL of 2-chloro-benzaldehyde (50 mmol) in 20 mL of acetonitrile and 30 mL of 1.78 M solution of KOH in acetonitrile. The mixture was refluxed for 1 min. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s6** as a white solid (2.52 g, 31%). The spectral data matched that reported by DiBiase and co-workers:² ¹H NMR (CDCl_3 , 500 MHz) δ 7.78 (d, J = 16.5 Hz, 1H), 7.52 (dd, J_1 = 12.8 Hz, J_2 = 1.8 Hz, 1H), 7.40 (dd, J_1 = 8.0 Hz, J_2 = 8.0 Hz, 1H), 7.35 (td, J = 1.7, 7.6 Hz, 1H), 7.28–7.31 (m, 1H), 5.88 (d, J = 16.5 Hz, 1H); ¹³C NMR (CDCl_3 , 125 MHz) δ 146.5, 134.5, 132.1, 131.7, 127.4, 126.9, 117.8, 99.0.



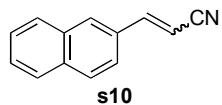
Nitrile (s7). The general procedure was followed using a solution of 5.25 g of 2,6-dichlorobenzaldehyde (30 mmol) in 12 mL of acetonitrile and 20 mL of a 1.78 M solution of KOH in acetonitrile. The mixture was refluxed for 2 min. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s7**, an inseparable mixture of regioisomers [*E*:*Z* = 87:13 (NMR)], as a white solid (1.75 g, 29%): ¹H NMR (CDCl₃, 500 MHz) *E*-isomer: δ 7.54 (d, *J* = 17.0 Hz, 1 H), 7.38 (m, 2 H), 7.24 (m, 1 H), 6.20 (d, *J* = 17.0 Hz, 1H); *Z*-isomer: δ 5.87 (d, *J* = 11.5 Hz, 1H), other resonances obscured by *E*-isomer. ¹³C NMR (CDCl₃, 125 MHz): δ 144.2, 134.9, 130.8, 130.6, 129.1, 117.2, 105.8.



Nitrile (s8).⁶ The general procedure was followed using a solution of 5.25 mL of 3-fluoro-benzaldehyde (50 mmol) in 20 mL acetonitrile and 30 mL of a 1.78 M solution of KOH in acetonitrile. The mixture was refluxed for 20 sec. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s8** as a white solid (2.91 g, 40%). The spectral data matched that reported by Happer and co-workers:⁶ ¹H NMR (CDCl₃, 500 MHz) δ 7.35-7.41 (m, 2H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 8.5 Hz, 2H), 5.90 (d, *J* = 17.0 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 163.0 (d, *J*_{CF} = 246 Hz), 149.2, 135.6 (d, *J*_{CF} = 6.2 Hz), 130.8 (d, *J*_{CF} = 7.5 Hz), 123.5, 118.2 (d, *J*_{CF} = 21.2 Hz), 117.7, 113.7 (d, *J*_{CF} = 21.2 Hz), 98.0.

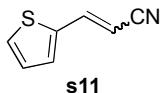


Nitrile (s9).^{6,7} The general procedure was followed using a solution of 9.09 g of *p*-trifluoromethylbenzaldehyde (51.1 mmol) in 21 mL acetonitrile and 40 mL of a 1.28 M solution of KOH in acetonitrile. The mixture was refluxed for 30 sec. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s9**, an inseparable mixture of regioisomers [*E*:*Z* = 98:2 (NMR)], as an off-white solid (1.88 g, 19%). The spectral data for the *E*-isomer matched that reported by Happer and co-workers,⁶ and the spectral data for the *Z*-isomer matched that reported by Nakao and co-workers.⁷ Selected spectral data for *E*-isomer: ¹H NMR (CDCl₃, 500 MHz) δ 7.66 (d, *J* = 8.0 Hz, 2 H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 16.5 Hz, 1H), 5.99 (d, *J* = 16.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 147.0, 136.7, 132.6 (q, *J* = 32.5 Hz), 129.2, 125.9, 123.6 (q, *J* = 270 Hz), 116.7, 98.0. Selected spectral data for *Z*-isomer: ¹H NMR (CDCl₃, 500 MHz) δ 7.85 (d, *J* = 8 Hz, 2H), 7.20 (d, *J* = 12 Hz, 1H), 5.61 (d, *J* = 12 Hz, 1H) other peaks obscured by *E* isomer; ¹³C NMR (CDCl₃, 125 MHz) δ 148.8, 127.6, 126.1, 120.4, 99.3. Selected spectral data for the mixture: IR (thin film) 3030, 2219, 1621, 1416, 1322, 1113, 1066, 1015, 970, 851, 813 cm⁻¹.



Nitrile (s10).^{8,9} The general procedure was followed using a solution of 2.50 g of 2-naphthaldehyde (15.7 mmol) in 7 mL acetonitrile and 18 mL of a 0.87 M solution of KOH in acetonitrile. The mixture was refluxed for 3 min. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s10**, an inseparable mixture of regioisomers [*E*:*Z* = 75:25 (NMR)], as an off-white solid (1.07 g, 38%). The spectral data for the *E*-isomer matched that reported by Addrus and co-workers,⁸ and the spectral data for the *Z*-isomer matched that reported by

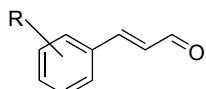
Nenajdenko and co-workers:⁹ Selected spectral data for *E* isomer: ¹H NMR (CDCl₃, 500 MHz) δ 7.81–7.91 (m, 4H), 7.49–7.58 (m, 4H), 5.96 (d, *J* = 16.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 150.6, 134.6, 133.1, 131.0, 130.5, 129.7, 129.1, 128.8, 127.9, 127.8, 127.1, 122.2, 96.3. Selected spectral data for *Z* isomer: ¹H NMR (CDCl₃, 500 MHz) δ 8.16 (s, 1H), 8.03 (dd, *J₁* = 8 Hz, *J₂* = 2.0 Hz, 1H), 7.25 (d, *J* = 16 Hz, 1H), 5.50 (d, *J* = 12.0 Hz, 1H), other peaks obscured by *E* isomer; ¹³C NMR (CDCl₃, 125 MHz) δ 148.7, 134.3, 133.0, 131.2, 128.9, 126.9, 124.8, 118.4, 117.6, 95.1, other peaks obscured by *E* isomer. Selected spectral data for the mixture: IR (thin film) 2220, 1623, 1416, 1325, 1266, 1113, 1067, 971, 815, 739 cm⁻¹.



Nitrile (s11).¹⁰ The general procedure was followed using 4.5 mL of thiophene-2-carboxaldehyde (48.1 mmol) in 20 mL acetonitrile and 30 mL of a 1.60 M solution of KOH in acetonitrile. The mixture was refluxed for 1 min. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded the product **s11**, an inseparable mixture of isomers [*E*:*Z* = 72:28 (NMR)], as a beige liquid (3.62 g, 56%). The spectral data matched that reported by Morton and co-workers.¹⁰ Selected spectral data for *E* isomer: ¹H NMR (CDCl₃, 500 MHz) δ 7.34–7.41 (m, 2H), 7.16–7.19 (m, 1H), 7.00–7.03 (m, 1H), 5.56 (d, *J* = 16.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 142.8, 138.4, 131.5, 129.5, 128.5, 118.2, 94.3. Selected spectral data for *Z* isomer: ¹H NMR (CDCl₃, 500 MHz) δ 7.53–7.57 (m, 2H), 7.24 (d, *J* = 11.5 Hz, 1H), 7.11–7.14 (m, 1H), 5.27 (d, *J* = 11.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 140.8, 137.8, 132.4, 130.3, 127.7, 117.6, 91.8. Selected spectral data for the mixture: IR (thin film) 3106, 2213, 1604, 1420, 1361, 1218, 1049, 954, 857, 802 cm⁻¹.

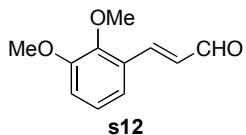
II. Preparation of cinnamaldehydes

C. General procedure for the preparation of cinnamaldehyde



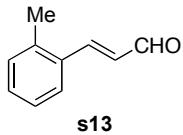
To a solution of the α,β -unsaturated nitrile (1.0 equiv) in anhydrous THF at -78 °C was slowly added DIBAL-H (1.0 M in hexanes, 1.2 equiv). The mixture was kept cold for an additional 2 hours, and then warmed gradually to room temperature for 2 hours. The remaining alkyl aluminum salts were quenched at 0°C slowly through addition of a 10% aqueous solution of HCl. The resulting mixture then diluted with 20 mL of water and 20 mL of Et₂O. The phases were separated and the resulting aqueous phase was extracted with an additional 2 × 20 mL of Et₂O. The combined organic phases were washed with 2 × 20 mL of distilled water and 1 × 20 mL of brine. The resulting organic phase was dried over Na₂SO₄ and the heterogeneous mixture was filtered. The filtrate was concentrated *in vacuo*. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded the product.

D. Cinnamaldehyde syntheses

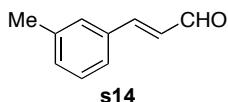


Cinnamaldehyde (s12). The general procedure was followed using 2.00 g of 2,3-dimethoxy-*trans*-cinnamic acid nitrile (10.6 mmol), 12.7 mL of DIBAL-H (12.7 mmol), and 30 mL of THF. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s12** as a white solid (0.98 g, 49%): ¹H NMR (CDCl₃, 500 MHz): δ 9.73 (d, *J* = 16.5 Hz, 1H), 7.81 (d, *J* = 16.5 Hz, 1H), 7.49 (d, *J* = 16.5 Hz, 1H), 7.16 (d, *J* = 16.5 Hz, 1H), 7.00 (d, *J* = 16.5 Hz, 1H), 5.56 (d, *J* = 16.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 142.8, 138.4, 131.5, 129.5, 128.5, 118.2, 94.3.

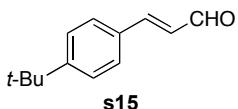
δ = 8.0 Hz, 1H), 7.86 (d, J = 16.0 Hz, 1H), 7.19 (m, 1H), 7.10 (t, J = 8 Hz, 1H), 7.0 (m, 1H), 6.75 (dd, J_1 = 16 Hz, J_2 = 7.5 Hz, 1H), 3.90 (m, 6H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 194.3, 153.1, 148.5, 147.4, 129.7, 128.1, 124.4, 119.2, 114.9, 61.4, 55.9; IR (thin film): 1676, 1480, 1270, 1124, 1003 cm^{-1} .



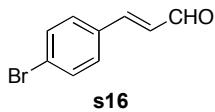
Cinnamaldehyde (s13).¹¹ The general procedure was followed using 2.00 g of nitrile **s2** (10.6 mmol), 12.7 mL of DIBAL-H (12.7 mmol), and 30 mL of THF. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s13** as a white solid (0.98 g, 49%). The spectral data matched that reported by Battistuzzi and co-workers:¹¹ ^1H NMR (CDCl_3 , 500 MHz): δ 9.73 (d, J = 7.5 Hz, 1H), 7.78 (d, J = 15.5 Hz, 1H), 7.60 (d, J = 7.5 Hz, 1H), 7.35-7.32 (m, 1H), 7.27-7.24 (m, 2H), 6.67 (dd, J_1 = 16 Hz, J_2 = 7.5 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 193.8, 150.2, 137.9, 132.8, 131.1, 131.0, 129.6, 126.8, 126.6, 19.7.



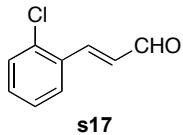
Cinnamaldehyde (s14).¹¹ The general procedure was followed using 2.00 g of nitrile **s3** (13.97 mmol), 16.8 mL of DIBAL-H (16.8 mmol), and 30 mL of THF. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s14** as a white solid (0.98 g, 49%). The spectral data matched that reported by Battistuzzi and co-workers:¹¹ ^1H NMR (CDCl_3 , 300 MHz): δ 9.70 (d, J = 7.8, 1H), 7.46 (d, J = 15.9, 1H), 7.38 (m, 2H), 7.33 (m, 1H), 7.27 (m, 1H), 6.71 (dd, J_1 = 16.1 Hz, J_2 = 7.5 Hz, 1H), 2.40 (s, 3H); IR (thin film): 1679, 1290, 1125, 972, 119 cm^{-1} .



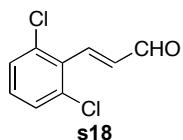
Cinnamaldehyde (s15).¹¹ The general procedure was followed using 4.83 g of nitrile **s4** (26 mmol), 30 mL of DIBAL-H (30 mmol), and 70 mL of THF. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s15** as a light yellow solid (2.90 g, 59%). The spectral data matched that reported by Battistuzzi and co-workers:¹¹ ^1H NMR (CDCl_3 , 300 MHz) δ 9.68 (d, J = 7.5 Hz, 1H), 7.44-7.53 (m, 5H), 6.70 (dd, J_1 = 15.9 Hz, J_2 = 7.8 Hz, 1H), 1.34 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 193.7, 155.0, 152.7, 131.2, 128.3, 127.8, 126.0, 34.9, 31.0.



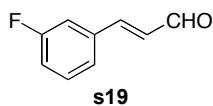
Cinnamaldehyde (s16).¹² The general procedure was followed using 3.45 g of nitrile **s5** (17 mmol), 20 mL of DIBAL-H (20 mmol), and 50 mL of THF. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s16** as a light yellow solid (2.06 g, 59%). The spectral data matched that reported by Avery and co-workers:¹² ^1H NMR (CDCl_3 , 300 MHz) δ 9.71 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.39-7.44 (m, 3H), 6.70 (dd, J_1 = 16.0 Hz, J_2 = 7.6 Hz, 1H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 193.7, 155.0, 152.7, 131.2, 128.3, 127.8, 126.0.



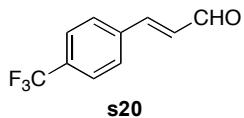
Cinnamaldehyde (s17).¹² The general procedure was followed using 1.64 g of 2-chloro-*trans*-cinnamic acid nitrile (10 mmol), 12 mL of DIBAL-H (12 mmol), and 30 mL of THF. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s17** as a light yellow solid (0.95 g, 57%). The spectral data matched that reported by Avery and co-workers:¹² ¹H NMR (CDCl₃, 500 MHz) δ 9.70–9.75 (m, 1H), 7.86–7.93 (m, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.29–7.45 (m, 3H), 6.64–6.71 (m, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 193.5, 147.9, 135.1, 131.9, 130.4, 130.3 (2C), 127.8, 127.2.



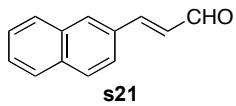
Cinnamaldehyde (s18).¹³ The general procedure was followed using 1.75 g of nitrile **s7** (8.85 mmol), 10.2 mL of DIBAL-H (10.2 mmol), and 25 mL of THF. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s18** as a pale yellow solid (0.62 g, 23%). The spectral data matched that reported by Hashem and co-workers:¹³ ¹H NMR (CDCl₃, 500 MHz): δ 9.77 (d, *J* = 7.0 Hz, 1H), 7.64 (d, *J* = 16 Hz, 1H), 7.39 (m, 2H), 7.24 (m, 1H), 6.91 (dd, *J*₁ = 16 Hz, *J*₂ = 7 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz): 193.8, 145.8, 136.3, 135.1, 131.2, 130.6, 129.0; IR (thin film): 1686, 1431, 1117, 975, 776 cm⁻¹.



Cinnamaldehyde (s19).¹¹ The general procedure was followed using 2.91 g of nitrile **s8** (20 mmol), 22 mL of DIBAL-H (22 mmol), and 60 mL of THF. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s19** as a light yellow oil (2.0 g, 67%). The spectral data matched that reported by Battistuzzi and co-workers:¹¹ ¹H NMR (CDCl₃, 300 MHz) δ 9.71 (d, *J* = 7.5 Hz, 1H), 7.33–7.46 (m, 3H), 7.26–7.28 (m, 1H), 7.10–7.17 (m, 1H), 6.69 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 193.4, 163.0 (d, *J*_{CF} = 246 Hz), 151.0, 136.2 (d, *J*_{CF} = 7.5 Hz), 130.7 (d, *J*_{CF} = 7.5 Hz), 129.6, 124.4, 118.1 (d, *J*_{CF} = 21.2 Hz), 114.7 (d, *J*_{CF} = 21.2 Hz).

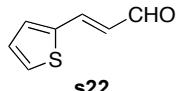


Cinnamaldehyde (s20).¹⁴ The general procedure was followed using 1.80 g of nitrile **s9** (10.1 mmol), 12 mL of DIBAL-H (11.8 mmol), and 30 mL of THF. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **s20** as a white solid (0.719 g, 39%). The spectral data matched that reported by He and co-workers:¹⁴ ¹H NMR (CDCl₃, 500 MHz) δ 9.75 (d, *J* = 7.5 MHz, 1H), 7.69 (m, 4H), 7.51 (d, *J* = 16.0 Hz, 1H), 6.77 (dd, *J*₁ = 16.0 Hz, *J*₂ = 7.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 193.2, 150.3, 137.3, 132.6 (q, *J*_{CF} = 32.5), 130.5, 128.6, 126.1, 126.1; IR (thin film) 2821, 1680, 1324, 1173, 1122, 1066, 982, 822 cm⁻¹.



Cinnamaldehyde (s21).¹² The general procedure was followed using 0.490 g of nitrile **s10** (2.73 mmol), 3.6 mL of DIBAL-H (3.55 mmol), and 9.1 mL of THF. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes)

afforded the product **s21** as a flocculent light yellow powder (0.200 g, 40%). The spectral data matched that reported by Avery and co-workers:¹² ¹H NMR (CDCl₃, 500 MHz) δ 9.76 (d, *J* = 7.5 Hz, 1H), 7.99 (s, 1H), 7.87 (q, *J* = 8.5 Hz, 3H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.63 (d, *J* = 16 Hz, 1H), 7.52-7.59 (m, 2H), 6.83 (dd, *J*₁ = 16.0 Hz, *J*₂ = 7.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 193.7, 152.8, 134.7, 133.2, 131.6, 130.8, 129.0, 128.8, 128.7, 127.9, 127.8, 127.0, 123.6; IR (thin film) 1668, 1618, 1122, 829, 751 cm⁻¹.

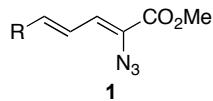


Cinnamaldehyde (s22).¹⁵ The general procedure was followed using 2.00 g of nitrile **s11** (14.8 mmol), 19 mL of DIBAL-H (19.2 mmol), and 50 mL of THF. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded the product **s22** as a yellow oil (0.980 g, 48%). The spectral data matched that reported by Krasnaya and co-workers:¹⁵ ¹H NMR (CDCl₃, 500 MHz) δ 9.63 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 15.5 Hz, 1H), 7.50 (d, *J* = 5.0 Hz, 1H), 7.35 (d, *J* = 3.5 Hz, 1H), 7.11 (dd, *J*₁ = 5.0, *J*₂ = 3.5 Hz, 1H), 6.51 (dd, *J*₁ = 11.0 Hz, *J*₂ = 8.0 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 192.9, 144.4, 139.3, 132.1, 130.4, 128.7, 127.4; IR (thin film) 2820, 1670, 1612, 1421, 1360, 1226, 1118, 1045, 961, 858, 817 cm⁻¹.

III. Preparation of dienyl azides

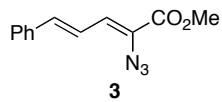
E. General procedure for the preparation of dienyl azide

The requisite dienyl azides were prepared in one step from the condensation of methyl azidoacetate and aromatic or heteroaromatic cinnamaldehyde following the method reported by Moody and co-workers.¹⁶ The yields were not optimized.



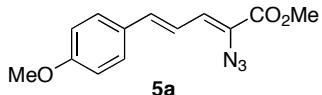
To a cooled (-22°C) solution of NaOMe (1.52 equiv) in MeOH was added a solution of cinnamaldehyde (1 equiv) and methyl azidoacetate (3 – 4 equiv) dropwise over 1 hour. The resulting reaction mixture was warmed to -10°C . After four hours, the heterogeneous mixture was diluted with 20 mL of water and 20 mL of Et₂O. The phases were separated, and the resulting aqueous phase was extracted with an additional 2×20 mL of Et₂O. The combined organic phases were washed with 2×20 mL of distilled water and 1×20 mL of brine. The resulting organic phase was dried over MgSO₄, and the heterogeneous mixture was filtered. The filtrate was concentrated *in vacuo*. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded the product.

F. Dienyl azide syntheses

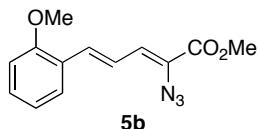


Dienyl azide (3).¹⁷ The general procedure was followed using 0.493 g of sodium methoxide (9.13 mmol), 3 mL of methanol, 1.00 mL of cinnamaldehyde (7.94 mmol), and 3.66 g of methyl azidoacetate (31.8 mmol). Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **3** as a yellow solid (0.836 g, 46%). The spectral data matched that reported by Geist and co-workers:¹⁷ ¹H NMR (CDCl₃, 500 MHz): δ 7.49-7.48 (m, 2H), 7.37-7.34 (m, 2H), 7.32-7.30 (m, 1H), 7.17 (dd, *J*₁ = 11 Hz, *J*₂ = 15.7 Hz, 1H), 6.83-6.75 (m, 2H), 3.88 (s,

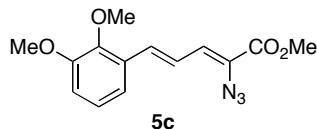
3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 163.6, 139.1, 136.3, 129.0, 128.8, 127.2, 127.1, 125.4, 122.1, 52.6; IR (thin film): 2125, 1711, 1370, 1234, 1072, 970, 748 cm^{-1} .



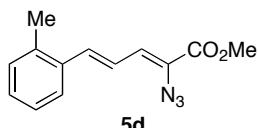
Dienyl azide (5a). The general procedure was followed using 0.749 g of sodium methoxide (13.9 mmol), 3.5 mL of methanol, 1.50 g of 4-methoxy-*trans*-cinnamaldehyde (9.25 mmol), and 3.19 g of methyl azidoacetate (27.7 mmol). Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **5a** as a yellow solid (1.20 g, 50%); ^1H NMR (CDCl_3 , 500 MHz): δ 7.44–7.42 (m, 2H), 7.05–7.00 (m, 1H), 6.90–6.87 (m, 2H), 6.87–6.74 (m, 2H), 3.87 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 163.7, 160.4, 139.0, 129.1, 128.8, 127.8, 124.2, 120.1, 114.2, 55.3, 52.6; IR (thin film): 2118, 1710, 1510, 1252, 1174, 971 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{N}_3\text{O}_3$: 259.0957, found 259.0959.



Dienyl azide (5b). The general procedure was followed using 0.499 g of sodium methoxide (9.23 mmol), 3.0 mL of methanol, 1.00 g of 2-methoxy-*trans*-cinnamaldehyde (6.17 mmol), and 2.82 g of methyl azidoacetate (24.6 mmol). Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **5b** as a yellow solid (0.81 g, 50%); ^1H NMR (CDCl_3 , 500 MHz): δ 7.56 (d, $J = 8.0$ Hz, 1H), 7.27 (q, $J = 7.5$ Hz, 1H), 7.19 (m, 2H), 6.95 (t, $J = 7.5$ Hz, 1H), 6.88 (d, $J = 8.5$ Hz, 1H), 6.80 (dd, $J_1 = 4.0$ Hz, $J_2 = 6.0$ Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 163.7, 157.4, 134.2, 130.2, 128.3, 127.3, 125.3, 124.7, 122.5, 120.8, 111.0, 55.5, 52.6; IR (thin film): 2116, 1709, 1588, 1434, 1246, 752 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{O}_3\text{N}_3$: 259.0957, found 259.0958.

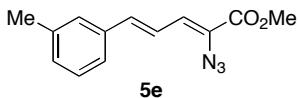


Dienyl azide (5c). The general procedure was followed using 0.316 g of sodium methoxide (5.85 mmol), 2.25 mL of methanol, 0.75 g of 2,3-dimethoxy-*trans*-cinnamaldehyde (3.90 mmol), and 1.80 g of methyl azidoacetate (15.6 mmol). Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **5c** as a yellow solid (0.12 g, 11%); ^1H NMR (CDCl_3 , 500 MHz): δ 7.20 (m, 3H), 7.04 (t, $J = 8.0$ Hz, 1H), 6.87 (m, 1H), 6.81 (m, 1H), 3.87 (m, 6H), 3.83 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 163.6, 153.0, 147.5, 133.4, 130.5, 127.7, 125.3, 124.2, 123.2, 118.2, 112.7, 61.2, 55.8, 52.6; IR (thin film): 2129, 1711, 1481, 1271, 1080 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}_4\text{N}_3$: 289.1063, found 289.1061.

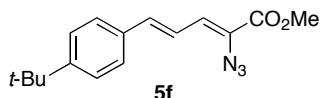


Dienyl azide (5d). The general procedure was followed using 0.277 g of sodium methoxide (5.13 mmol), 1.5 mL of methanol, 0.5 g of 2-methyl-*trans*-cinnamaldehyde (3.42 mmol), and 1.57 g of methyl azidoacetate (13.7 mmol). Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **5d** as a yellow solid (0.754 g, 91%); ^1H NMR (CDCl_3 , 500 MHz): δ 7.63–7.60 (m, 1H), 7.22–7.16 (m, 3H), 7.11–7.05 (m, 2H), 6.80 (d, $J = 10.0$ Hz,

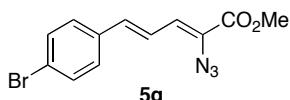
1H), 3.87 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 163.6, 136.6, 136.5, 135.0, 130.6, 128.8, 127.5, 126.3, 125.7, 125.2, 123.0, 52.6, 19.7; IR (thin film): 2114, 1711, 1370, 1232, 1072, 970, 754 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}_3$: 243.1008, found 243.1009.



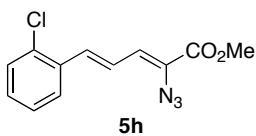
Dienyl azide (5e). The general procedure was followed using 0.277 g of sodium methoxide (5.13 mmol), 1.5 mL of methanol, 0.500 g of 3-methyl-*trans*-cinnamaldehyde (3.42 mmol), and 1.57 g of methyl azidoacetate (13.7 mmol). Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **5e** as a yellow solid (0.248 g, 30%); ^1H NMR (CDCl_3 , 500 MHz): δ 7.30 (m, 2H), 7.24 (m, 1H), 7.18-7.11 (m, 2H), 6.76 (m, 2H), 3.88 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 163.6, 139.3, 138.4, 136.2, 129.9, 128.7, 127.8, 127.3, 125.2, 124.6, 122.0, 52.6, 21.3; IR (thin film): 2123, 1711, 1369, 1227, 970 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{N}_3$: 243.1008, found: 243.1010.



Dienyl azide (5f). The general procedure was followed using 0.84 g of sodium methoxide (15 mmol), 5 mL of methanol, 1.88 g of 4-*tert*-butyl-*trans*-cinnamaldehyde (10.0 mmol), and 3.89 mL of methyl azidoacetate (40.0 mmol). Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **5f** as a yellow oil (1.94 g, 68%); ^1H NMR (CDCl_3 , 500 MHz) δ 7.38-7.44 (m, 4H), 7.14 (dd, $J_1 = 15.8$ Hz, $J_2 = 11.2$ Hz, 1H), 6.76-6.82 (m, 2H), 3.88 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.6, 152.4, 139.1, 133.6, 127.5, 127.1, 125.7, 124.9, 121.4, 52.6, 34.7, 31.2; IR (thin film): 2961, 2905, 2120, 1713, 1605, 1371, 1235, 972 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}_3$: 285.1477, found: 285.1478.

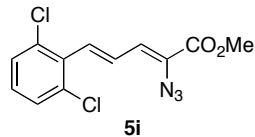


Dienyl azide (5g). The general procedure was followed using 0.80 g of sodium methoxide (14 mmol), 5 mL of methanol, 2.00 g of 4-bromo-*trans*-cinnamaldehyde (9.5 mmol), and 3.70 mL of methyl azidoacetate (38 mmol). Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **5g** as a yellow solid (1.48 g, 50%); ^1H NMR (CDCl_3 , 500 MHz) δ 7.47 (d, $J = 8.5$ Hz, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.14 (dd, $J_1 = 15.5$ Hz, $J_2 = 7.6$ Hz, 1H), 6.70-6.74 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.5, 137.5, 135.2, 132.0, 128.6, 126.5, 126.0, 122.9, 122.8, 52.7; IR (thin film): 2125, 2105, 1710, 1438, 1260, 1234, 1069, 967 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{12}\text{H}_{10}\text{O}_2\text{N}_3\text{Br}$: 306.9956, found 306.9956.

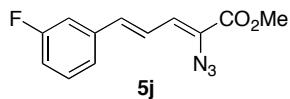


Dienyl azide (5h). The general procedure was followed using 0.80 g of sodium methoxide (14 mmol), 5 mL of methanol, 1.57 g of 2-chloro-*trans*-cinnamaldehyde (9.50 mmol), and 3.70 mL of methyl azidoacetate (38.0 mmol). Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **5h** as a yellow solid (0.98 g, 39%); ^1H NMR (CDCl_3 , 500 MHz) δ 7.68 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, 1H), 7.37 (dd, $J_1 = 7.5$ Hz, $J_2 = 1.5$ Hz, 1H), 7.13-7.28 (m, 4H), 6.80 (d, $J = 5.5$ Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.4, 134.3, 134.2, 133.9, 130.0, 129.7, 127.0, 126.8, 126.6, 126.3, 124.3, 52.7; IR (thin film): 2121, 1716, 1641, 1436, 1368, 1235,

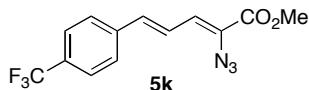
967, 750 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₁₀O₂N₃Cl: 263.0462, found: 263.0465.



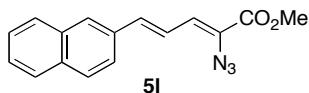
Dienyl azide (5i). The general procedure was followed using 0.078 g of sodium methoxide (1.44 mmol), 1.0 mL of methanol, 0.168 g of 2,6-dichloro-*trans*-cinnamaldehyde (0.959 mmol), and 0.473 g of methyl azidoacetate (4.11 mmol). Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **5i** as a pale yellow solid (0.280 g, 98%): ¹H NMR (CDCl₃, 500 MHz): δ 7.37–7.31 (m, 3H), 7.12 (t, *J* = 8 Hz, 1H), 6.91 (d, *J* = 16 Hz, 1H), 6.76 (d, *J* = 11 Hz, 1H), 3.89 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 163.4, 134.6, 133.3, 132.1, 130.4, 128.82, 128.76, 127.2, 126.2, 52.8; IR (thin film): 2129, 1715, 1232, 973, 773 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₉Cl₂N₃O₂: 297.0072, found: 297.0070.



Dienyl azide (5j). The general procedure was followed using 1.12 g of sodium methoxide (20 mmol), 7 mL of methanol, 2.00 g of 3-fluoro-*trans*-cinnamaldehyde (13.3 mmol), and 5.18 mL of methyl azidoacetate (53.0 mmol). Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **5j** as a yellow solid (1.58 g, 48%): ¹H NMR (CDCl₃, 500 MHz) δ 7.11–7.32 (m, 4H), 6.98 (t, *J* = 7.2 Hz, 1H), 6.69–6.75 (m, 2H), 3.87 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 163.3, 163.0 (d, *J*_{CF} = 244 Hz), 138.6 (d, *J*_{CF} = 7.5 Hz), 137.3, 130.2 (d, *J*_{CF} = 8.8 Hz), 126.2 (2C), 123.3, 123.1, 115.6 (d, *J*_{CF} = 21.2 Hz), 113.3 (d, *J*_{CF} = 22.5 Hz), 52.6; IR (thin film): 2127, 1709, 1576, 1435, 1374, 1230, 973, 757 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₁₀O₂N₃F: 247.0757, found: 247.0760.

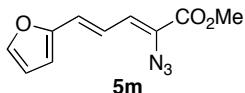


Dienyl azide (5k). The general procedure was followed using 0.320 g of sodium methoxide (5.98 mmol), 2.7 mL of methanol, 0.719 g of aldehyde **s20** (3.99 mmol), and 1.6 mL of methyl azidoacetate (16.0 mmol). Purification via MPLC (0:2:98 – 10:2:88 EtOAc:Et₃N:hexanes) afforded **5k**, an inseparable mixture of regioisomers (94:6, *E*:*Z*), as a flocculent off-white solid (0.060 g, 5%): Selected spectral data for *E*-isomer: ¹H NMR (CDCl₃, 500 MHz) δ 7.59 (d, *J* = 8.5, 1H), 7.56 (d, *J* = 8.5, 1H), 7.23 (dd, *J*₁ = 16.0 Hz, *J*₂ = 11.0 Hz, 1H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.73 (d, *J* = 11.0 Hz, 1H), 3.89 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 163.4, 139.7, 136.9, 130.3 (q, *J*_{CF} = 20.0 Hz), 127.3, 127.0, 125.9, 125.8, 125.7, 124.5, 52.8. Selected spectral data for *Z* isomer: ¹H NMR (CDCl₃, 500 MHz) δ 7.87 (dd, *J*₁ = 15.0, *J*₂ = 6.0 Hz, 1H), 6.49 (d, *J* = 12.0 Hz, 1H), 3.93 (s, 3H), other peaks obscured by *E* isomer; ¹³C NMR δ 130.5, 130.2, 128.5, 127.0, 126.0, 125.1, 122.9, 52.8. Selected spectral data for mixture: IR (thin film) 2121, 1716, 1331, 1286, 1246, 1108, 820, 758 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₃H₁₀O₂NF₃: 269.06636, found 269.06615.

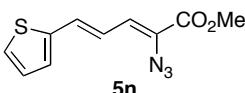


Dienyl azide (5l). The general procedure was followed using 0.251 g of aldehyde **s21** (1.38 mmol), 0.54 mL of methyl azidoacetate (5.51 mmol), 0.112 g of sodium methoxide (2.07 mmol), 0.92 mL of methanol, and 2 mL of DMF. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded the product **5l**, an inseparable mixture of isomers (95:5 *E*:*Z*) an off-white solid (0.102 g, 26%). Spectral data for *E*-isomer: ¹H NMR (CDCl₃, 500

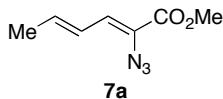
MHz) δ 7.77–7.84 (m, 4H), 7.68 (dd, $J_1 = 8.5$ Hz, $J_2 = 1.5$ Hz, 1H), 7.44–7.51 (m, 2H), 7.27 (dd, $J_1 = 14.0$ Hz, $J_2 = 11.0$ Hz, 1H), 6.96 (d, $J = 16.0$ Hz, 1H), 6.80 (dd, $J_1 = 11.0$ Hz, $J_2 = 1.0$ Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.6, 139.2, 133.9, 133.7, 133.5, 128.6, 128.3, 128.2, 127.8, 127.2, 126.7, 126.6, 125.5, 123.5, 122.5, 52.7. Selected spectral data for Z-isomer: ^1H NMR (CDCl_3 , 500 MHz) δ 7.93 (dd, $J_1 = 16.0$ Hz, $J_2 = 11.5$ Hz, 1H), 6.55 (d, $J = 11.5$ Hz, 1H), 3.95 (s, 3H), other peaks obscured by E isomer. Data for the mixture: IR (thin film) 2123, 1697, 1334, 1279, 1232 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$: 251.0946, found: 251.0948.



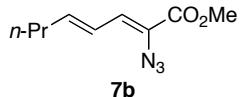
Dienyl azide (5m). The general procedure was followed using 0.663 g of sodium methoxide (12.3 mmol), 3.0 mL of methanol, 1.00 g of *trans*-3-(2-furyl)acrolein (8.19 mmol), and 3.77 g of methyl azidoacetate (32.8 mmol). Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **5m** as a brown solid (0.70 g, 39%): ^1H NMR (CDCl_3 , 500 MHz): δ 7.43 (m, 1H), 7.02 (dd, $J_1 = 15.5$ Hz, $J_2 = 11.5$ Hz, 1H), 6.68 (d, $J = 11.5$ Hz, 1H), 6.58 (d, $J = 15.5$ Hz, 1H), 6.44 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz): δ 163.5, 152.6, 143.7, 126.6, 125.4, 125.3, 120.6, 112.1, 111.7, 52.6; IR (thin film): 2123, 1709, 1364, 1236, 755 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{10}\text{H}_9\text{O}_3\text{N}_3$: 219.06440, found 219.06440.



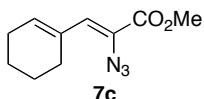
Dienyl azide (5n). The general procedure was followed using 0.947 g of aldehyde **s22** (6.86 mmol), 3.15 g of methyl azidoacetate (27.4 mmol), 0.557 g of sodium methoxide (10.3 mmol), and 4.5 mL of methanol. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded the product **5n** as a bold yellow solid (0.480 g, 30%). ^1H NMR (CDCl_3 , 500 MHz) δ 7.28 (d, $J = 5.0$ Hz, 1H), 7.10 (d, $J = 3.5$ Hz, 1H), 7.00 (dd, $J_1 = 5.0$ Hz, $J_2 = 3.5$ Hz, 1H), 6.93 (d, $J = 4.0$ Hz, 1H), 6.92 (s, 1H), 6.68 (dd, $J_1 = 7.0$, $J_2 = 3.0$ Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.5, 142.0, 131.6, 128.4, 128.0, 126.9, 126.7, 125.1, 121.8, 52.7; IR (thin film) 1679, 1323, 1172, 1122, 1066, 982, 822 cm^{-1} ; HRMS (EI) m/z calcd for $\text{C}_{10}\text{H}_9\text{O}_2\text{NS}$: 207.0354, found 207.0356.



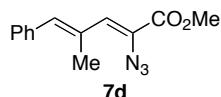
Dienyl azide (7a). To a cooled (-78°C) solution of lithium diisopropylamide [2.95 mL of diisopropylamine (21.00 mmol), 9.24 mL of *n*-butyllithium (2.5 M solution in hexanes, 23.00 mmol) stirred at -78°C for 0.5 hour] in 10 mL of THF was added a solution of 1.66 mL of crotonaldehyde (20.0 mmol) and 7.78 mL of methyl azidoacetate (80 mmol) dropwise over 1 hour. The resulting reaction mixture was warmed to -10°C . After four hours, the heterogeneous mixture was diluted with 20 mL of water and 20 mL of Et_2O . The phases were separated and the resulting aqueous phase was extracted with an additional 2×20 mL of Et_2O . The combined organic phases were washed with 2×20 mL of distilled water and 1×20 mL of brine. The resulting organic phase was dried over Na_2SO_4 , and the heterogeneous mixture was filtered. The filtrate was concentrated *in vacuo*. Purification by flash chromatography (with 2% Et_3N) afforded **7a** as yellow oil (1.84 g, 55%, with 5% another isomer): ^1H NMR (CDCl_3 , 500 MHz) δ 6.52 (d, $J = 11.5$ Hz, 1H), 6.39–6.44 (m, 1H), 6.00–6.07 (m, 1H), 3.80 (s, 3H), 1.83 (dd, $J_1 = 7.0$ Hz, $J_2 = 1.0$ Hz, 3H); ^{13}C NMR (CDCl_3 , 125 MHz) δ 163.6, 138.3, 127.4, 125.6, 123.4, 52.3, 18.8; IR (thin film): 2122, 1716, 1635, 1436, 1372, 1238, 1072, 974; HRMS (EI) m/z calcd for $\text{C}_7\text{H}_9\text{O}_2\text{N}_3$: 167.0695, found 167.0696.



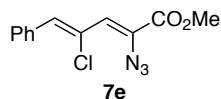
Dienyl azide (7b). The same procedure as **7a** was followed for **7b** using 2.21 mL of diisopropylamine (15.75 mmol), 6.6 mL of *n*-butyllithium (2.5 M solution in hexanes, 16.5 mmol), 7.5 mL of THF, 1.74 mL of *trans*-2-hexen-1-al (15.0 mmol) and 6.90 g of methyl azidoacetate (60.0 mmol). Purification using MPLC (0:2:98 – 10:2:88 EtOAc:Et₃N:hexanes) afforded the product as yellow oil (1.91 g, 65%): ¹H NMR (CDCl₃, 500 MHz): δ 6.59–6.57 (m, 1H), 6.46–6.40 (m, 1H), 6.09–6.03 (m, 1H), 3.84 (s, 3H), 2.18–2.14 (m, 2H), 1.49 (m, 2H), 0.93–0.89 (m, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 163.8, 143.8, 127.8, 124.4, 123.6, 52.5, 35.3, 22.0, 13.7; IR (thin film): 2122, 1716, 1437, 1240, 974, 760 cm⁻¹; HRMS (EI) *m/z* calcd for C₉H₁₃O₂N₃: 195.1008, found: 195.1010.



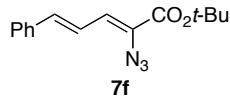
Dienyl azide (7c). The same procedure as **7a** was followed for **7c** using 1.11 mL of diisopropylamine (7.89 mmol), 3.4 mL of *n*-butyllithium (2.5 M solution in hexanes, 8.68 mmol), 4 mL of THF, 0.6 mL of 1-cyclohexene-1-carboxaldehyde (5.26 mmol) and 2.42 g of methyl azidoacetate (21.0 mmol). Purification using MPLC (0:2:98 – 10:2:88 EtOAc:Et₃N:hexanes) afforded **7c** as yellow oil, (with 10% starting material): ¹H NMR (CDCl₃, 500 MHz): δ 6.45 (s, 1H), 6.17–6.16 (m, 1H), 3.82 (s, 3H), 2.43–2.41 (m, 2H), 2.19–2.17 (m, 2H), 1.66–1.61 (m, 2H), 1.59–1.55 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz): δ 164.5, 138.2, 134.3, 130.2, 122.0, 52.6, 27.6, 26.6, 22.6, 21.3; HRMS (EI) *m/z* calcd for C₁₀H₁₃O₂N: 179.0946, found: 179.0946.



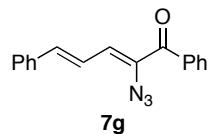
Dienyl azide (7d). The general procedure was followed using 5.00 mL of α -methyl-*trans*-cinnamaldehyde (35.1 mmol), 2.84 g of sodium methoxide (53.0 mmol), 14.0 mL of methyl azidoacetate (140 mmol), and 23 mL of methanol. Purification using MPLC (0:2:98 – 10:2:88 EtOAc:Et₃N:hexanes) afforded **7d** as an 88:12 mixture of stereoisomers as a yellow-orange, low-melting solid (0.939 g, 11%). Spectral data for the *E*-isomer: ¹H NMR (CDCl₃, 500 MHz) δ 7.31–7.39 (m, 4H), 7.28 (d, *J* = 7.0 Hz, 1H), 6.86 (s, 1H), 6.69 (s, 1H), 3.88 (s, 3H), 2.25 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 164.3, 138.2, 136.9, 133.5, 131.2, 129.5, 128.3, 127.6, 124.2, 52.8, 17.3.; Selected spectral data for the *Z*-isomer: ¹H NMR (CDCl₃, 500 MHz) δ 7.22 (d, *J* = 7.5 Hz, 2H), 6.94 (s, 1H), 6.61 (s, 1H), 3.82 (s, 3H), other peaks obscured by *E* isomer. Spectral data for the mixture: IR (thin film) 2122, 1715, 1375, 1271, 1254 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₃H₁₃N₃O₂: 243.10078, found 243.10072.



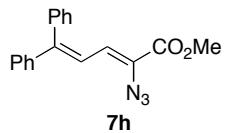
Dienyl azide (7e). The same procedure as **7a** was followed for **7e** using 2.95 mL of diisopropylamine (21.0 mmol), 9.24 mL of *n*-butyllithium (2.5 M solution in hexanes, 23.0 mmol), 10 mL of THF, 3.33 g of α -chlorocinnam-aldehyde (20.0 mmol) and 7.78 mL of methyl azidoacetate (80.0 mmol). Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **7e** as yellow solid (0.15 g, 3%): ¹H NMR (CDCl₃, 500 MHz) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.53 (s, 1H), 7.32–7.41 (m, 3H), 6.56 (s, 1H), 3.90 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 163.2, 134.4, 133.8, 129.9, 128.9, 128.3, 125.9, 124.6, 124.3, 53.1; IR (thin film): 2130, 1721, 1605, 1436, 1381, 1247, 1088, 732 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₁₀O₂N₃Cl: 263.0462, found: 263.0465.



Dienyl azide (7f). To a cooled (-30°C) solution of *t*-BuOK (1.06 g, 9 mmol, 1.5 equiv) in 4 mL of THF was added a solution of cinnamaldehyde (0.76 mL, 6.0 mmol, 1 equiv) and *tert*-butyl azidoacetate (3.76 g, 24.0 mmol, 4 equiv) dropwise over 1 hour. The resulting reaction mixture was warmed to -10°C . After six hours, the heterogeneous mixture was diluted with 20 mL of water and 20 mL of Et₂O. The phases were separated and the resulting aqueous phase was extracted with an additional 2 \times 20 mL of Et₂O. The combined organic phases were washed with 2 \times 20 mL of distilled water and 1 \times 20 mL of brine. The resulting organic phase was dried over Na₂SO₄, and the mixture was filtered. The filtrate was concentrated *in vacuo*. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **7f** as yellow oil (0.53 g, 38%): ¹H NMR (CDCl₃, 500 MHz) δ 7.49 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.30–7.31 (m, 1H), 7.18 (dd, *J*₁ = 15.8 Hz, *J*₂ = 11.2 Hz, 1H), 6.80 (d, *J* = 16.0 Hz, 1H), 6.69 (dd, *J*₁ = 11.2 Hz, *J*₂ = 0.8 Hz, 1H), 1.59 (s, 9H); ¹³C NMR (CDCl₃, 125 MHz): δ 162.0, 138.3, 136.4, 128.7 (2C), 127.1, 126.7, 126.1, 122.3, 83.0, 28.0; IR (thin film): 2139, 2106, 1702, 1369, 1242, 1151, 969, 748 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₅H₁₇O₂N: 271.1321, found 271.1298.



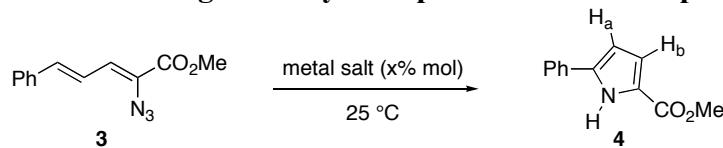
Dienyl azide (7g). To a cooled (-78°C) solution of 1 mL of cinnamaldehyde (3.78 mmol), 2.44 g of α -azidoacetophenone (15.13 mmol) and 5 mL THF was added a solution of 0.943 g of KHMDS (4.73 mmol) in 4 mL of THF dropwise over 1 hour. The resulting reaction mixture was kept cold in -78°C . After four hours, the heterogeneous mixture was diluted with 20 mL of methanol and 20 mL of water. The resulting aqueous solution was extracted with 3 \times 20 mL of Et₂O. The combined organic phases were washed with 2 \times 20 mL of distilled water and 1 \times 20 mL of brine. The resulting organic phase was dried over MgSO₄, and the heterogeneous mixture was filtered. The filtrate was concentrated *in vacuo*. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **7g** as a brown solid (0.056 g, 5%). ¹H NMR (CDCl₃, 500 MHz) δ 7.51–7.50 (m, 2H), 7.27 (dd, *J*₁ = 16 Hz, *J*₂ = 11 Hz, 1H), 7.20–7.13 (m, 2H), 7.11–7.00 (m, 6H), 6.14 (d, *J* = 15.5 Hz, 1H), 6.10 (d, *J* = 11 Hz, 1H); ¹³C NMR (CD₃COCD₃, 125 MHz) δ 191.1, 140.3, 137.1, 136.5, 133.7, 132.3, 131.3, 129.3, 129.2, 128.9, 128.5, 127.4, 122.2; IR (thin film): 2106, 1644, 1366, 1279, 971 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₇H₁₃ON₃: 275.1059, found 275.1036.



Dienyl azide (7h).¹⁷ The general procedure was followed using 0.272 g of sodium methoxide (5.04 mmol), 2.0 mL of methanol, 0.70 g of β -phenylcinnamaldehyde (0.959 mmol), and 0.473 g of methyl azidoacetate (4.11 mmol). Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded **7h** as a pale yellow solid (0.280 g, 98%). The spectral data matched that reported by Geist and co-workers:¹⁷ ¹H NMR (CDCl₃, 500 MHz): δ 7.45–7.41 (m, 3H), 7.33 (m, 5H), 7.23–7.21 (m, 2H), 7.11 (dd, *J*₁ = 1Hz, *J*₂ = 11.5 Hz, 1H), 6.68 (dd, *J*₁ = 1Hz, *J*₂ = 11.5 Hz, 1H), 3.782–3.779 (m, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 163.6, 149.7, 141.4, 138.7, 130.5 (2C), 128.6, 128.3 (2C), 128.2, 126.2, 124.6, 121.1, 52.6; IR (thin film): 2122, 1712, 1378, 1075, 768 cm⁻¹.

IV. Metal-catalyzed synthesis of pyrroles from dienyl azides

A. General procedure for the screening of catalysts to promote the decomposition of vinyl azides



To a mixture of 0.010 g of dienyl azide **3** (0.044 mmol) and metal salt (2 - 100% mol) was added 0.100 – 0.200 mL of solvent. After 16h, the heterogenous mixture was filtered through SiO_2 . The filtrate was concentrated *in vacuo*. The resulting mixture was dissolved in 1.5 mL of CDCl_3 and 0.007 mL of dibromomethane (0.1 mmol) was added. The area of H_a or H_b peak in pyrrole was compared with the area of the peak of dibromomethane to derive a ^1H NMR yield.

Table s1. Optimization of reaction conditions

entry	metal salt (mol, %)	yield, % ^a	entry	metal salt (mol, %)	yield, % ^a
1	$\text{Rh}_2(\text{OAc})_4$ (10) ^b	22	11	$\text{Cu}(\text{OTf})_2$ (5)	>95
2	$\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ (2) ^b	42	12	CuCl_2 (5)	19
3	$\text{Rh}_2(\text{O}_2\text{CC}_3\text{F}_7)_4$ (2) ^b	>95	13	ZnCl_2 (5)	86
4	$\text{Pd}(\text{OTf})_2$ (10) ^b	50	14	SiO_2 (50) ^b	15
5	HOTf (2) ^b	n.a.	15	AuOTf (10) ^b	5
6	FeCl_3 (10)	54	16	MgBr_2 (5)	12
7	FeBr_3 (15)	76	17	Ti(O'Pr)_4 (5)	n.a.
8	FeCl_2 (15)	86	18	TiCl_4 (5)	n.a.
9	CuCl (5)	5	19	$\text{Hg}(\text{OTf})_2$ (5)	39
10	$(\text{CuOTf})_2\text{PhH}$ (5)	95	20	$\text{Hg}(\text{OTf})_2$ (100)	55

^a As determined using ^1H NMR spectroscopy. ^b PhMe as solvent, 40 °C.

B. Scope of pyrrole formation using ZnI_2 , $\text{Rh}_2(\text{O}_2\text{CC}_3\text{F}_7)_4$, and $\text{Cu}(\text{OTf})_2$ as catalyst

Table s2. Comparison of ZnI_2 -, $\text{Rh}_2(\text{O}_2\text{CC}_3\text{F}_7)_4$ -, and $\text{Cu}(\text{OTf})_2$ - mediated processes

Entry	substrate	product	ZnI_2 yield, %	$\text{Rh}_2(\text{O}_2\text{CC}_3\text{F}_7)_4$ yield, %	$\text{Cu}(\text{OTf})_2$ yield, %
1			>95 ^a (93) ^b	>95 (96)	>95 ^a
2			>95 (83)	90 (71)	88
3			>95 (96)	84 (66)	87
4			>95 (92)	67	>95
5			>95 (90)	>95 (88)	72
6			>95 (77)	>95	>95
7			>95 (90)	75(66)	69

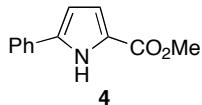
Table s2 (continued). Comparison of ZnI₂--, Rh₂(O₂CC₃F₇)₄-, and Cu(OTf)₂-mediated processes

Entry	substrate	product	ZnI ₂ yield, %	Rh ₂ (O ₂ CC ₃ F ₇) ₄ yield, %	Cu(OTf) ₂ yield, %
8			>95 (82)	>95 (93)	68
9			89 (80)	>95 (97)	52
10			>95 (70)	>95 (97)	92
11			83 (70) ^c	>95 (98)	61
12			38 (37)	>95 (85)	10
13			85 (71) ^c	33	10
14			21 (n.a.)	72	23
15			47 (41) ^e	47	25
16			60 (59)	65 (51)	64
17			85 (72)	n.a.	83
18			73 (71)	n.a.	n.a.
19			>95 (86)	>95	82
20			94 (75)	82	88
21			93 (89)	53	78
22			43 (n.a.)	29	93 (72) ^d
23			0 (n.a.) ^d	0	0

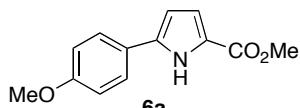
^aAs determined using ¹H NMR spectroscopy. ^bIsolated yield after flash chromatography over SiO₂. ^cZnI₂ (10% mol) employed. ^dStarting material was recovered. ^eZnI₂ (10% mol), 40 °C.

C. Optimized general procedure

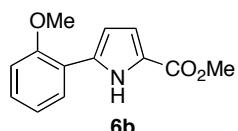
To a mixture of 0.100 g of dienyl azide **3** (0.436 mmol) and 0.007 g of ZnI₂ (5% mol) was added 0.300 mL of solvent (1.5 M). The resulting mixture was stirred at room temperature for 15 h. The heterogeneous mixture was filtered through SiO₂. The filtrate was concentrated *in vacuo*. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) provided the pyrrole. For more electron deficient arenes, increased catalyst loading (10% mol) was required.



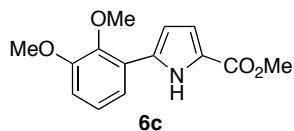
Pyrrole (4).¹⁸ The general procedure was followed with 0.100 g of dienyl azide **3** (0.436 mmol), 0.007 g of ZnI₂ (0.022 mmol), and 0.300 mL of CH₂Cl₂. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole as a white solid (0.082 g, 93%): mp 145-146 °C. The spectral data matched that reported by Knight and co-workers:¹⁸ ¹H NMR (CDCl₃, 500 MHz): δ 9.78 (br s, 1H), 7.63-7.61 (m, 2H), 7.42-7.39 (m, 2H), 7.32-7.29 (m, 1H), 6.99-6.97 (m, 1H), 6.56-6.54 (m, 1H), 3.88 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 161.8, 137.1, 131.3, 128.9, 127.7, 124.8, 123.0, 116.9, 108.0, 51.6; IR (thin film): 3307, 1680, 1275, 1004 cm⁻¹.



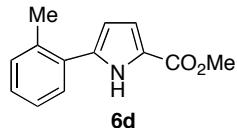
Pyrrole (6a). The general procedure was followed with 0.100 g of dienyl azide **5a** (0.386 mmol), 0.006 g of ZnI₂ (0.019 mmol), and 0.260 mL of CH₂Cl₂. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **6a** as a white solid (0.074 g, 83%): mp 144-146 °C; ¹H NMR (CDCl₃, 500 MHz): δ 9.32 (br s, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 6.97-6.93 (m, 3H), 6.44-6.43 (m, 1H), 3.87 (s, 3H), 3.84 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 161.8, 159.3, 137.2, 126.2, 124.2, 122.3, 117.0, 114.3, 107.1, 55.3, 51.5; IR (thin film): 3323, 1686, 1477, 1275, 1006, 762 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₃H₁₃O₃N: 231.08955, found: 231.08963.



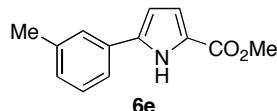
Pyrrole (6b). The general procedure was followed with 0.100 g of dienyl azide **5b** (0.386 mmol), 0.006 g of ZnI₂ (0.019 mmol), and 0.260 mL of CH₂Cl₂. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **6b** as a white solid (0.086 g, 96%): ¹H NMR (CDCl₃, 500 MHz): δ 10.41 (br s, 1H), 7.68 (dd, *J*₁ = 7.8 Hz, *J*₂ = 1.5 Hz, 1H), 7.25 (dt, *J*₁ = 7.9 Hz, *J*₂ = 1.5 Hz, 1H), 7.01 (m, 2H), 6.96 (dd, *J*₁ = 3.8 Hz, *J*₂ = 3.0 Hz, 1H), 6.63 (dd, *J*₁ = 3.8 Hz, *J*₂ = 3.0 Hz, 1H), 3.99 (s, 3H), 3.88 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 161.5, 155.4, 134.5, 128.4, 127.4, 121.8, 121.3, 119.4, 115.7, 111.6, 108.1, 55.7, 51.3; IR (thin film): 3442, 1699, 1476, 1259, 1146, 758 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₃H₁₃O₃N: 231.0895, found 231.0898.



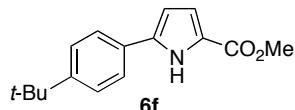
Pyrrole (6c). The general procedure was followed with 0.100 g of dienyl azide **5c** (0.346 mmol), 0.0055 g of ZnI₂ (0.017 mmol), and 0.230 mL of CH₂Cl₂. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **6c** as a white solid (0.083 g, 92%): mp 69-70 °C; ¹H NMR (CDCl₃, 500 MHz): δ 10.47 (br s, 1H), 7.24-7.22 (m, 1H), 7.08 (td, *J*₁ = 8 Hz, *J*₂ = 1 Hz, 1H), 6.96-6.94 (m, 1H), 6.85-6.83 (m, 1H), 6.62-6.60 (m, 1H), 3.90-3.87 (m, 9H); ¹³C NMR (CDCl₃, 125 MHz): δ 161.4, 153.3, 145.4, 133.8, 124.7, 124.3, 122.5, 119.2, 115.8, 111.4, 108.9, 60.6, 55.9, 51.4; IR (thin film): 3439, 1700, 1262, 1005, 762 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₄H₁₅O₄N: 261.1001, found: 261.0989.



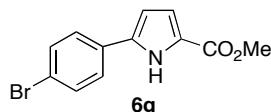
Pyrrole (6d). The general procedure was followed with 0.100 g of dienyl azide **5b** (0.411 mmol), 0.007 g of ZnI₂ (0.021 mmol), and 0.280 mL of CH₂Cl₂. Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **6d** as a colorless oil (0.083 g, 92%): ¹H NMR (CDCl₃, 500 MHz): δ 9.42 (br s, 1H), 7.41–7.39 (m, 1H), 7.27–7.24 (m, 3H), 6.98 (dd, *J*₁ = 4 Hz, *J*₂ = 2.5 Hz, 1H), 6.35 (dd, *J*₁ = 3.8 Hz, *J*₂ = 3 Hz, 1H), 3.82 (s, 3H), 2.45 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 161.6, 136.4, 135.7, 131.5, 131.1, 128.5, 128.1, 126.2, 122.3, 116.0, 110.9, 51.5, 21.0; HRMS (EI) *m/z* calcd for C₁₃H₁₃O₂N: 215.0946, found: 215.0947.



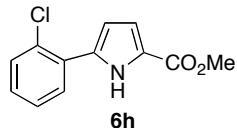
Pyrrole (6e). The general procedure was followed with 0.096 g of dienyl azide **5e** (0.40 mmol), 0.006 g of ZnI₂ (0.020 mmol), and 0.260 mL of CH₂Cl₂. Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **6e** as a white solid (0.083 g, 92%): mp 118–119 °C; ¹H NMR (CDCl₃, 500 MHz): δ 9.69 (br s, 1H), 7.42–7.40 (m, 2H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.13–7.11 (m, 1H), 6.99 (m, 1H), 6.54 (m, 1H), 3.88 (s, 3H), 2.40 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 161.9, 138.7, 137.3, 131.3, 128.9, 128.6, 125.6, 122.9, 122.0, 116.9, 108.0, 51.6, 21.5; IR (thin film): 3330, 1694, 1439, 1275, 1148, 762 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₃H₁₃O₂N: 215.0946, found 215.0947.



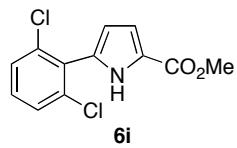
Pyrrole (6f). The general procedure was followed with 0.055 g of dienyl azide **5f** (0.193 mmol), 0.003 g of ZnI₂ (0.010 mmol), and 0.130 mL of CH₂Cl₂. Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **6f** as a white solid (0.045 g, 90%): mp 149–150 °C; ¹H NMR (CDCl₃, 500 MHz) δ 9.65 (br s, 1H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 6.97 (dd, *J*₁ = 3.5 Hz, *J*₂ = 2.5 Hz, 1H), 6.52 (t, *J* = 3.0 Hz, 1H), 3.88 (s, 3H), 1.35 (s, 9H); ¹³C NMR (CDCl₃, 125 MHz) δ 161.8, 150.9, 137.2, 128.6, 125.9, 124.6, 122.6, 116.9, 107.7, 51.5, 34.6, 31.2; IR (thin film): 3294, 3259, 2955, 1691, 1479, 1292, 1266, 799 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₆H₁₉O₂N: 257.1416, found 257.1418.



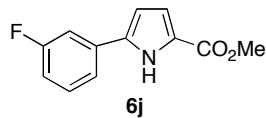
Pyrrole (6g). The general procedure was followed with 0.086 g of dienyl azide **5g** (0.279 mmol), 0.005 g of ZnI₂ (0.016 mmol), and 0.190 mL of CH₂Cl₂. Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **6g** as a white solid (0.064 g, 82%): mp 182–183 °C; ¹H NMR (CDCl₃, 500 MHz) δ 9.43 (br s, 1H), 7.52–7.54 (m, 2H), 7.43–7.45 (m, 2H), 6.95 (dd, *J*₁ = 3.8, *J*₂ = 2.2 Hz, 1H), 6.53 (t, *J* = 3.2 Hz, 1H), 3.88 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 161.7, 135.7, 132.1, 130.3, 126.2, 123.4, 121.6, 116.9, 108.4, 51.7; IR (thin film): 3311, 1687, 1461, 1440, 1284, 1268, 794, 758 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₁₀O₂NBr: 278.9895, found 278.9895.



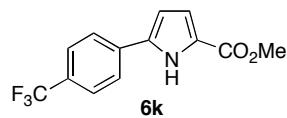
Pyrrole (6h). The general procedure was followed with 0.056 g of dienyl azide **6g** (0.212 mmol), 0.003 g of ZnI₂ (0.010 mmol), and 0.140 mL of CH₂Cl₂. Purification using MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **6h** as a white solid (0.040 g, 80%): mp 88-89 °C; ¹H NMR (CDCl₃, 500 MHz) δ 9.85 (br s, 1H), 7.57 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.45 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.30 (td, *J* = 7.5, 1.5 Hz, 1H), 7.23 (td, *J* = 7.6, 1.6 Hz, 1H), 6.97 (dd, *J*₁ = 4.0 Hz, *J*₂ = 2.5 Hz, 1H), 6.53 (dd, *J*₁ = 6.0, *J*₂ = 3.0 Hz, 1H), 3.86 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 161.5, 133.6, 130.9, 130.8, 129.9 (2C), 128.7, 127.2, 123.1, 115.7, 111.4, 51.6; IR (thin film): 3300, 1686, 1458, 1442, 1290, 1248, 1154, 756 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₁₀O₂NCl: 235.0400, found 235.0403.



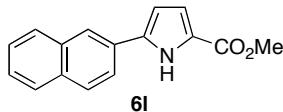
Pyrrole (6i). The general procedure was followed with 0.059 g of dienyl azide **5i** (0.198 mmol), 0.003 g of ZnI₂ (0.010 mmol), and 0.140 mL of CH₂Cl₂. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **6i** as a white solid (0.036 g, 70%): mp 110-112 °C; ¹H NMR (CDCl₃, 500 MHz): δ 9.23 (br s, 1H), 7.41-7.39 (m, 2H), 7.27-7.24 (m, 1H), 7.01-6.99 (m, 1H), 6.40-6.38 (m, 1H), 3.83 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 161.5, 135.9, 130.4, 130.1, 129.8, 128.4, 122.9, 115.2, 113.0, 51.5; IR (thin film): 3299, 1698, 1558, 1251 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₉Cl₂NO₂: 269.0010, found 269.0011.



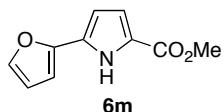
Pyrrole (6j). The general procedure was followed with 0.058 g of dienyl azide **5j** (0.234 mmol), 0.008 g of ZnI₂ (0.025 mmol), and 0.160 mL of CH₂Cl₂. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **6j** as a white solid (0.036 g, 70%): mp 121-123 °C; ¹H NMR (CDCl₃, 500 MHz) δ 9.92 (br s, 1H), 7.34-7.40 (m, 3H), 6.96-7.01 (m, 2H), 6.56 (dd, *J*₁ = 3.8 Hz, *J*₂ = 2.8 Hz, 1H), 3.90 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 163.1 (d, *J*_{CF} = 242 Hz), 162.2, 136.2, 133.6 (d, *J*_{CF} = 8.8 Hz), 130.3 (d, *J*_{CF} = 8.8 Hz), 123.5, 120.7, 117.1, 114.3 (d, *J*_{CF} = 8.8 Hz), 111.9 (d, *J*_{CF} = 22.5 Hz), 108.6, 51.8; IR (thin film): 3318, 1691, 1474, 1286, 1201, 1153, 780, 762 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₁₀O₂NF: 219.0696, found 219.0696.



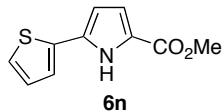
Pyrrole (6k). The general procedure was followed using 0.016 g of dienyl azide **5k** (0.005 mmol), 0.002 g of Rh₂(pfb)₄, and 0.036 mL of toluene. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded the pyrrole **6k** as a white solid (0.013 g, 88%): mp 196-197 °C; ¹H NMR (CDCl₃, 500 MHz) δ 9.67 (br s, 1H), 7.64-7.71 (m, 4H), 6.96-7.00 (m, 1H), 6.62-6.65 (m, 1H), 3.89 (s, 3H); ¹³C NMR δ (CDCl₃, 125 MHz) 161.7, 134.9 (d, 68.75 Hz), 129.5 (d, 32.50 Hz), 126.1, 126.0, 125.1 (t, 268.75 Hz), 124.8, 124.1, 117.0, 109.3, 51.8; IR (thin film) 3313, 1692, 1279, 1158, 1116, 845, 798, 759 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₃H₁₀O₂NF₃: 269.0664, found 269.0663.



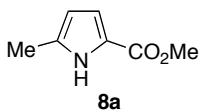
Pyrrole (6l). The general procedure at 40 °C was followed using 0.065 g dienyl azide **5l** (0.232 mmol), 0.008 mg ZnI₂ (0.025 mmol), and 0.160 mL of CH₂Cl₂. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded the product **6l** as a yellow solid (0.041 g, 71%): mp 150–152 °C; ¹H NMR (CDCl₃, 500 MHz) δ 9.85 (br s, 1H), 8.02 (s, 1H), 7.81–7.88 (m, 3H), 7.73 (dd, *J*₁ = 8.5 Hz, *J*₂ = 2.0 Hz, 1H), 7.46–7.53 (m, 2H), 7.02–7.05 (m, 1H), 6.66–6.69 (m, 1H), 3.89 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 161.8, 137.0, 133.5, 132.8, 128.8, 128.7, 128.0, 127.8, 126.8, 126.2, 123.3, 123.2, 123.1, 117.1, 108.6, 51.7; IR (thin film) 3323, 1687, 1278, 1233, 1148, 791, 753 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₆H₁₃O₂N: 251.0946, found 251.0946.



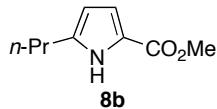
Pyrrole (6m).¹⁸ To a mixture of 0.041 g of dienyl azide **5m** (0.188 mmol) and 0.003 g of ZnI₂ (0.009 mmol) was added 0.140 mL of CH₂Cl₂. The resulting mixture was stirred at room temperature. After 15h, the heterogenous mixture was filtered through SiO₂. The filtrate was concentrated *in vacuo*. The resulting mixture was dissolved in 1.5 mL of CDCl₃ and 0.007 mL of dibromomethane (0.1 mmol) was added. The areas of the MeO peaks were compared with the area of the peak of dibromomethane to derive a 1H NMR yield: 21%. The spectral data matched that reported by Knight and co-workers:¹⁸ ¹H NMR (CDCl₃, 500 MHz): δ 9.45 (br s, 1H), 7.42–7.41 (m, 1H), 6.92 (dd, *J*₁ = 4.0 Hz, *J*₂ = 2.5 Hz, 1H), 6.54 (m, 1H), 6.45 (m, 2H), 3.88 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 161.4, 146.8, 141.7, 128.3, 122.3, 116.6, 111.7, 107.0, 105.3, 51.6; IR (thin film): 3296, 1693, 1280, 1146, 756 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₀H₉O₃N: 191.0582, found 191.0584.



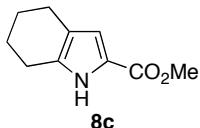
Pyrrole (6n). The general procedure was followed using 0.100 g of dienyl azide **5n** (0.42 mmol), 0.014 g of ZnI₂ (0.04 mmol), and 0.280 mL of CH₂Cl₂. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded the product **6n** as a yellow solid (0.036 g, 41%): mp 105–106 °C; ¹H NMR (CDCl₃, 500 MHz) δ 9.41 (br s, 1H), 7.22–7.26 (m, 2H), 7.04–7.07 (m, 1H), 6.91–6.94 (m, 1H), 6.42–6.44 (m, 1H), 3.88 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 161.6, 134.5, 131.5, 127.9, 124.6, 123.1, 122.7, 116.9, 108.6, 51.7; IR (thin film) 3313, 1686, 1481, 1323, 1269, 1223, 1143, 760 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₀H₉O₂NS: 207.0354, found 207.0356.



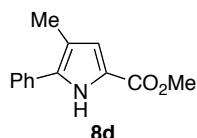
Pyrrole (8a).¹⁹ The general procedure was followed with 0.079 g of dienyl azide **7a** (0.473 mmol), 0.008 g of ZnI₂ (0.025 mmol), and 0.320 mL of CH₂Cl₂. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **8a** as a white solid (0.039 g, 59%): mp 93–94 °C. The spectral data matched that reported by Yoshida and co-workers:¹⁹ ¹H NMR (CDCl₃, 500 MHz) δ 9.26 (br s, 1H), 6.81 (t, *J* = 3.0 Hz, 1H), 5.95 (t, *J* = 2.8 Hz, 1H), 3.83 (s, 3H), 2.31 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 161.8, 134.0, 121.0, 116.2, 109.0, 51.3, 13.2; IR (thin film): 3310, 2922, 1680, 1492, 1330, 1267, 1041, 771 cm⁻¹.



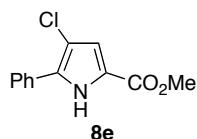
Pyrrole (8b).¹⁸ The general procedure was followed with 0.100 g of dienyl azide **7a** (0.512 mmol), 0.008 g of ZnI₂ (0.026 mmol), and 0.320 mL of CH₂Cl₂. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **8b** as a colorless oil (0.062 g, 72%). The spectral data matched that reported by Knight and co-workers:¹⁸ ¹H NMR (CDCl₃, 500 MHz): δ 8.98 (br s, 1H), 6.83–6.82 (m, 1H), 5.98–5.96 (m, 1H), 3.83 (s, 3H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.69–1.64 (m, 2H), 0.97–0.94 (m, 3H); ¹³C NMR (CDCl₃, 125 MHz): δ 161.7, 138.7, 120.8, 116.0, 108.1, 51.2, 29.8, 22.5, 13.8; IR (thin film): 3308, 1684, 1494, 1226, 769 cm⁻¹.



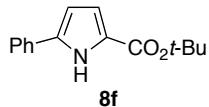
Pyrrole 8c.²⁰ The general procedure was followed with 0.100 g of crude dienyl azide **7c**, 0.008 g of ZnI₂ (0.026 mmol), and 0.320 mL of CH₂Cl₂. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **8c** as a white solid (0.053 g, 70%): mp 150–152 °C. The spectral data matched that reported by May and co-workers:²⁰ ¹H NMR (CDCl₃, 500 MHz): δ 9.00 (br s, 1H), 6.65 (d, *J* = 2 Hz, 1H), 3.82 (s, 3H), 2.60 (t, *J* = 6 Hz, 2H), 2.50 (t, *J* = 6 Hz, 2H), 1.82–1.79 (m, 2H), 1.76–1.73 (m, 2H); ¹³C NMR (CDCl₃, 125 MHz): δ 162.0, 133.6, 120.1, 119.7, 114.4, 51.2, 23.5, 22.93, 22.89, 22.7.



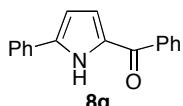
Pyrrole (8d).²¹ The general procedure was followed using 0.101 g of dienyl azide **7d** (0.413 mmol), 0.007 g of ZnI₂ (0.021 mmol) and 0.28 mL of CH₂Cl₂. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) over neutral alumina afforded the product **8d** as a white powder (0.076 g, 86%): mp 110–111 °C. The spectral data matched that reported by Lakhlifi and co-workers:²¹ ¹H NMR (CDCl₃, 500 MHz) δ 9.22 (br s, 1H), 7.50 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.44 (t, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 2.5 Hz, 1H), 3.84 (s, 3H), 2.26 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 161.7, 133.8, 132.3, 128.8, 127.5, 127.0, 121.2, 118.4, 118.2, 51.5, 12.5; IR (thin film) 3303, 1696, 1445, 1266, 1217, 1184, 762 cm⁻¹.



Pyrrole (8e). The general procedure was followed using 0.101 g of dienyl azide **7d** (0.413 mmol), 0.007 g of ZnI₂ (0.021 mmol) and 0.28 mL of CH₂Cl₂. Purification via MPLC (0:100 – 30:70 EtOAc:hexanes) over neutral alumina afforded the product **8d** as a white powder (0.076 g, 86%): mp 145–146 °C; ¹H NMR (CDCl₃, 500 MHz) δ ¹H NMR (CDCl₃, 500 MHz) δ 9.70 (br s, 1H), 7.72 (dd, *J*₁ = 8.8 Hz, *J*₂ = 1.0 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 3.82 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 161.3, 132.3, 129.9, 128.7, 128.3, 127.0, 120.9, 116.5, 111.3, 51.9; IR (thin film): 3291, 3271, 1699, 1448, 1221, 1154, 828, 769 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₂H₁₀O₂NCl: 235.0400, found 235.0403.



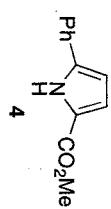
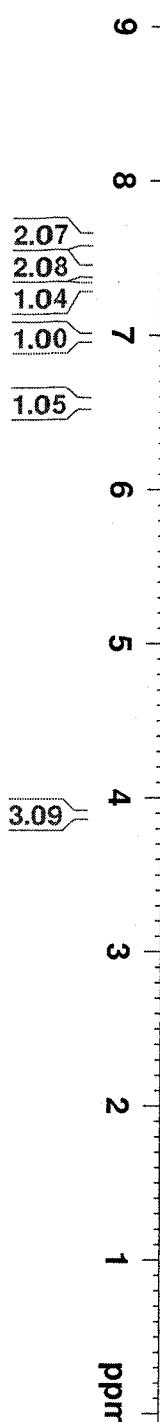
Pyrrole (8f). The general procedure was followed with 0.084 g of dienyl azide **7f** (0.310 mmol), 0.005 g of ZnI₂ (0.016 mmol), and 0.200 mL of CH₂Cl₂. Purification by flash chromatography (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **8f** as a white solid (0.067 g, 89%): mp 90–91 °C; ¹H NMR (CDCl₃, 500 MHz): δ 9.47 (br s, 1H), δ 7.55–7.57 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.26–7.30 (m, 1H), 6.90 (dd, *J*₁ = 4.0 Hz, *J*₂ = 2.5 Hz, 1H), 6.53 (t, *J* = 3.2 Hz, 1H), 1.58 (s, 9H); ¹³C NMR (CDCl₃, 125 MHz): δ 160.8, 136.2, 131.5, 128.9, 127.5, 124.8, 124.6, 116.1, 107.7, 80.9, 28.3; IR (thin film): 3320, 2977, 1669, 1464, 1275, 1149, 980, 759 cm⁻¹; HRMS (EI) *m/z* calcd for C₁₅H₁₇O₂N: 243.1259, found 243.1256.



Pyrrole (8g).²² The general procedure was followed with 0.040 g of dienyl azide **7g** (0.145 mmol), 0.003 g of Cu(OTf)₂ (0.007 mmol), and 0.100 mL of CH₂Cl₂. Purification MPLC (0:100 – 30:70 EtOAc:hexanes) afforded pyrrole **8g** as a white solid (0.026 g, 72%): mp 163–164 °C. The spectral data matched that reported by Pale-Grosdemange and co-workers:²² ¹H NMR (CDCl₃, 500 MHz): δ 10.11 (br s, 1H), 9.94–9.20 (m, 2H), 7.70–7.68 (m, 2H), 7.60–7.57 (m, 1H), 7.52–7.49 (m, 2H), 7.42–7.40 (m, 2H), 7.36–7.32 (m, 1H), 6.95 (dd, *J*₁ = 4.0 Hz, *J*₂ = 2.5 Hz, 1H), 6.65 (dd, *J*₁ = 4.0 Hz, *J*₂ = 2.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz): δ 184.5, 139.1, 138.4, 131.8, 131.7, 130.9, 129.1, 129.0, 128.4, 128.3, 125.2, 121.2, 108.8; IR (thin film): 3303, 1615, 1559, 1471, 1276, 1160, 762 cm⁻¹.

V. References

- (1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
- (2) DiBiase S., Lipisko B., Haag A., Wolak R., Gokel G., *J. Org. Chem.* **1979**, *44*, 4640.
- (3) Andrus M., Song C., Zhang J., *Org. Lett.*, **2002**, *4*, 2079.
- (4) Fairhurst, J.; Horwell, D. C.; Timms, G. H. *Tetrahedron Lett.* **1975**, *44*, 3843.
- (5) Peppe, C.; Mello, P. A.; Chagas, R. P. *J. Organomet. Chem.* **2006**, *691*, 2335.
- (6) Happer, D. A. R.; Steenson, B. E. *J. Chem. Soc. Perkin Trans. 2* **1988**, 19.
- (7) Nakao, Y.; Yada, A.; Satoh, J.; Ebata, S.; Oda, S.; Hiyama, T. *Chem. Lett.* **2006**, *35*, 790.
- (8) Andrus, M. B.; Song, C.; Zhang, J. *Org. Lett.* **2002**, *4*, 2079.
- (9) Nenajdenko, V. G.; Golubinskii, I. V.; Lenkova, O. N.; Shastin, A. V.; Balenkova, E. S. *Russ. Chem. Bull. Int. Ed.* **2005**, *54*, 252.
- (10) Morton, C. J. H.; Gilmour, R.; Smith, D. M.; Lightfoot, P.; Slawin, A. M. Z.; MacLean, E. J. *Tetrahedron* **2002**, *58*, 5547.
- (11) Battistuzzi G., Cacchi S., Fabrizi G., *Org. Lett.*, **2003**, *5*, 777.
- (12) Avery, T. D.; Caiazza, D.; Culbert, J. A.; Taylor, D. K.; Tiekkink, E. R. T. *J. Org. Chem.* **2005**, *70*, 8344.
- (13) Hashem A., Weyerstahl P. and Green B. S., *Tetrahedron*, **1984**, *40*, 203.
- (14) He, M.; Bode, J. W. *Org. Lett.* **2005**, *7*, 3131.
- (15) Krasnaya, Z. A.; Burova, S. A.; Bogdanov, V. S.; Smirnova, Y. V. *Chem. Heterocycl. Compd.* **1997**, *33*, 410.
- (16) Henn, L.; Hickey, D. M. B.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2189.
- (17) Geist B., Knittel D., *Monatsh. Chem.*, **1988**, *119*, 571.
- (18) Knight D. W., Redfern A. L., Gilmore J., *J. Chem. Soc., Perkin Trans. 1*, **2001**, *21*, 2874.
- (19) Yoshida, M.; Uchiyama, K.; Narasaka, K. *Heterocycles* **2000**, *52*, 681
- (20) May D. A., Lash T. D., *J. Org. Chem.* **1992**, *57*, 4820.
- (21) Lakhlifi, T.; Sedqui, A.; Fathi, T.; Laude, B.; Robert, J.-F. *Can. J. Chem.* **1994**, *72*, 1417.
- (22) Pale-Grosdemange C., Chuche J., *Tetrahedron*, **1989**, *45*, 3397.

0.98

standard parameters, BBO probe
 7.630
 7.627
 7.624
 7.613
 7.611
 7.421
 7.418
 7.406
 7.390
 7.319
 7.317
 7.304
 7.301
 7.290
 7.260
 6.985
 6.980
 6.977
 6.972
 6.560
 6.557
 6.553
 6.553
 6.549
 6.547
 6.544

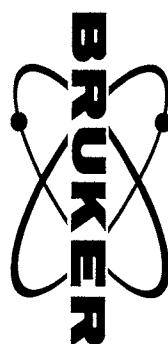
3.882
 3.878

Current Data Parameters
 NAME hjd123.001
 EXPNO 1
 PROCNO 1

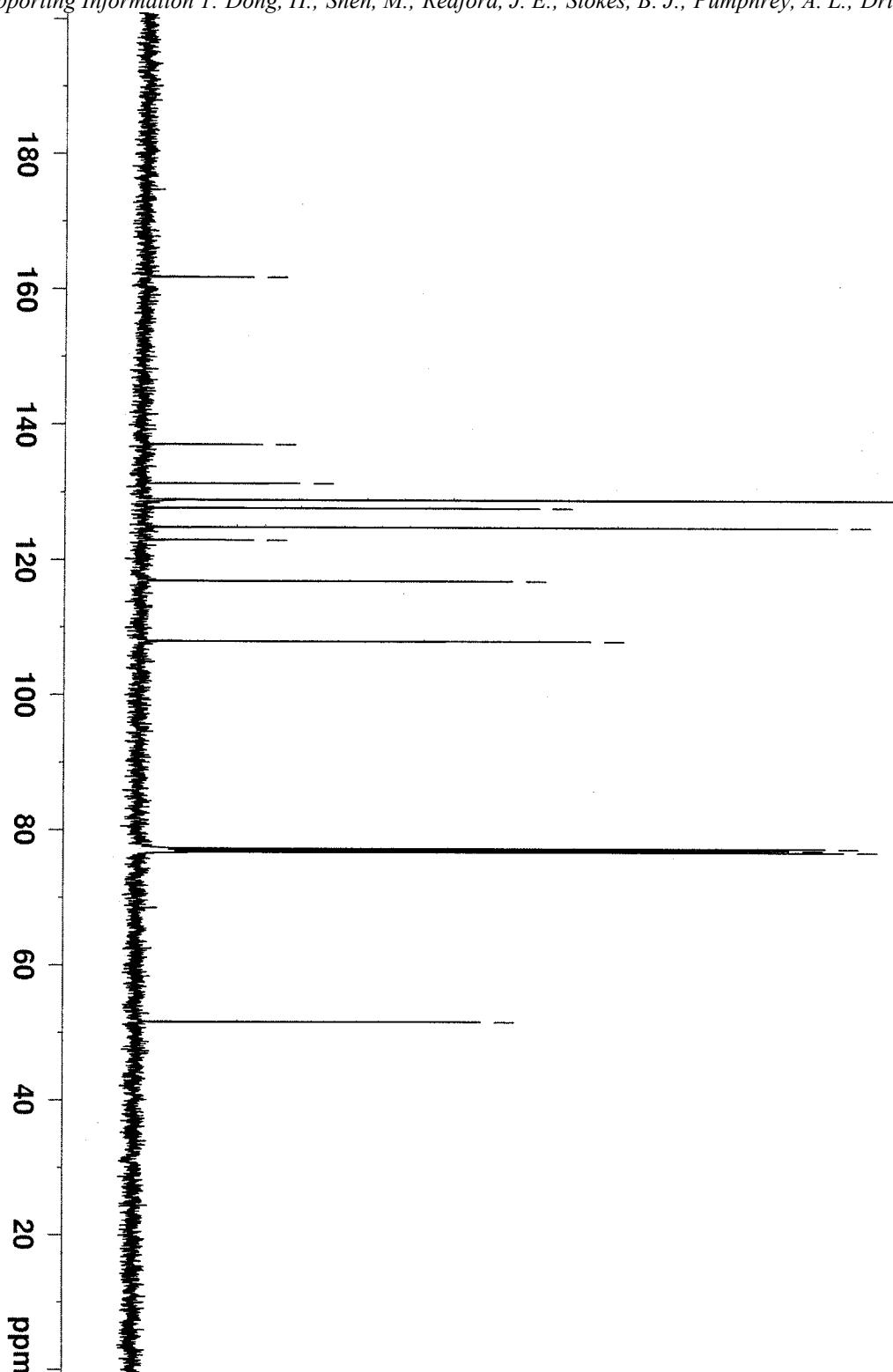
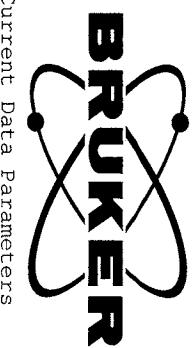
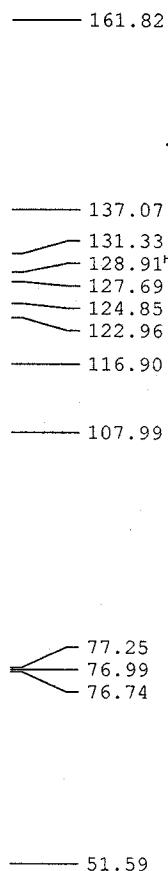
F2 - Acquisition Parameters
 Date 20070613
 Time 18.35
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg
 TD 32768
 SOLVENT CDCl3
 NS 8
 DS 2
 SWH 6009.615 Hz
 FIDRES 0.183399 Hz
 AQ 2.7264309 sec
 RG 143.7
 DW 83.200 use
 DE 6.00 use
 TE 300.0 K
 D1 1.0000000 sec
 MCREST 0.0000000 sec
 MCWRK 0.0150000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 3.50 use
 PLL -2.00 dB
 SFO1 500.6427535 MHz

F2 - Processing parameters
 SI 32768
 SF 500.6400128 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



13 standard parameters, BBO probe.



Current Data Parameters
NAME hjid123.001
EXPNO 2
PROCNO 1

F2 - Acquisition parameters
Date_ 20070613
Time 18.40
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg
TD 32768
SOLVENT CDCl3
NS 108
DS 2
SWH 30303.031 Hz
FIDRES 0.924775 Hz
AQ 0.5407385 sec
RG 2298.8
DW 16.500 usec
DE 6.00 usec
TE 300.0 K
D1 2.0000000 sec
d11 0.03000000 sec
delta 1.89999998 sec
MCREST 0.0000000 sec
MCWRK 0.01500000 sec

===== CHANNEL f1 =====

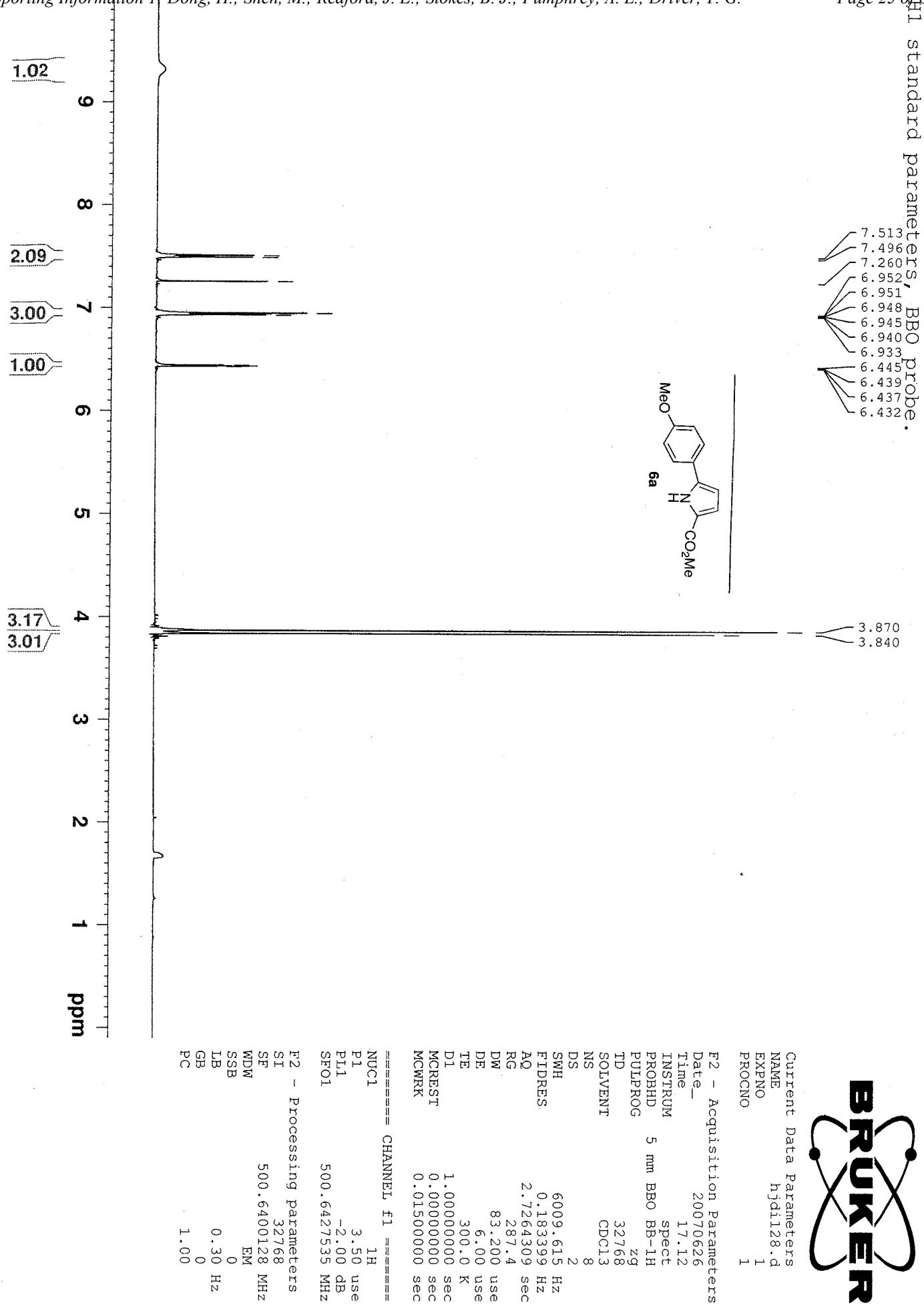
NUC1 13C
P1 2.70 usec
PL1 1.00 dB
SFO1 125.8998755 MHz

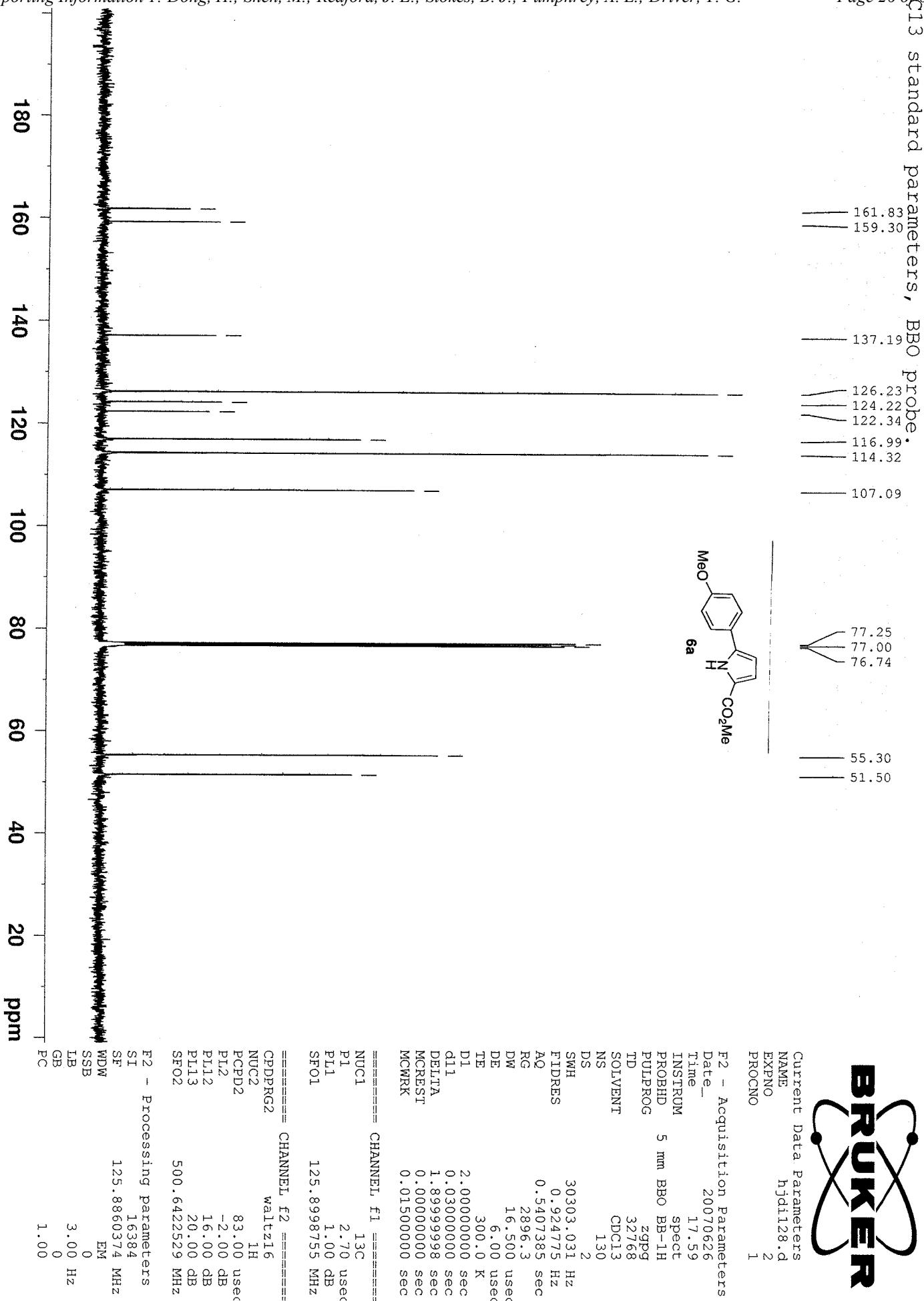
===== CHANNEL f2 =====

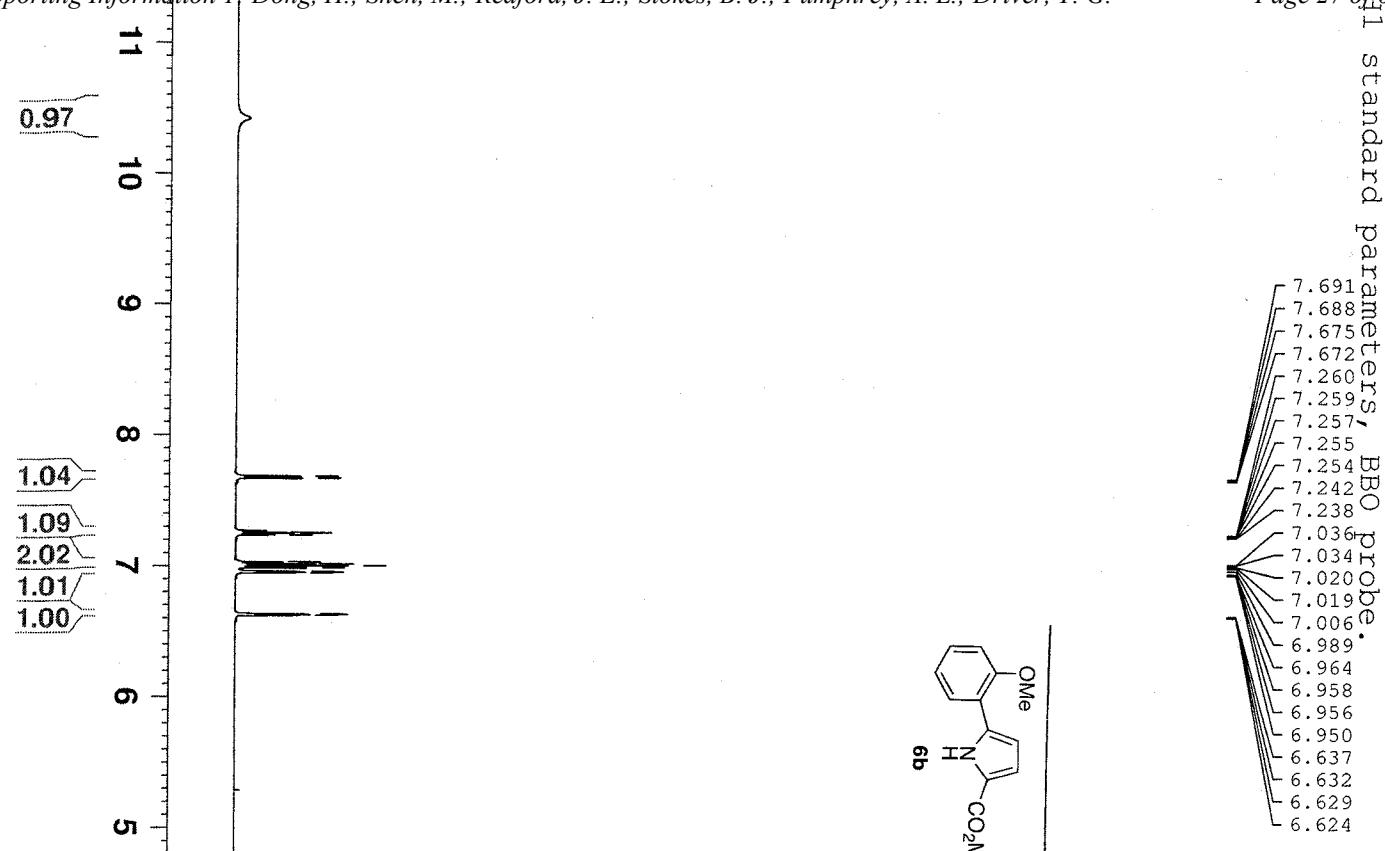
CPDPRG2 waltz16
NUC2 1H
PCPD2 83.00 usec
PL2 -2.00 dB
PL12 16.00 dB
PL13 20.00 dB
SF02 500.6422529 MHz

F2 - Processing parameters

SI 16384
SF 125.8860374 MHz
WDW 0
SSB 0
LB 3.00 Hz
GB 0
PC 1.00







F2 - Acquisition Parameters

NAME	hjdil45.a_1	PROCNO
EXPNO	1	
INSTRUM	spec	
PROBHD	5 mm BBO BB-1H	
PULPROG	pulprog	
TD	32768	
SOLVENT	CDCl ₃	
NS	8	
DS	2	
SWH	6009.615 Hz	
FIDRES	0.183399 Hz	
AQ	2.7264309 sec	
RG	114	
DW	83.200 use	
DE	6.00 use	
TE	300.0 K	
D1	1.0000000 sec	
MCREST	0.0000000 sec	
MCWRK	0.0150000 sec	

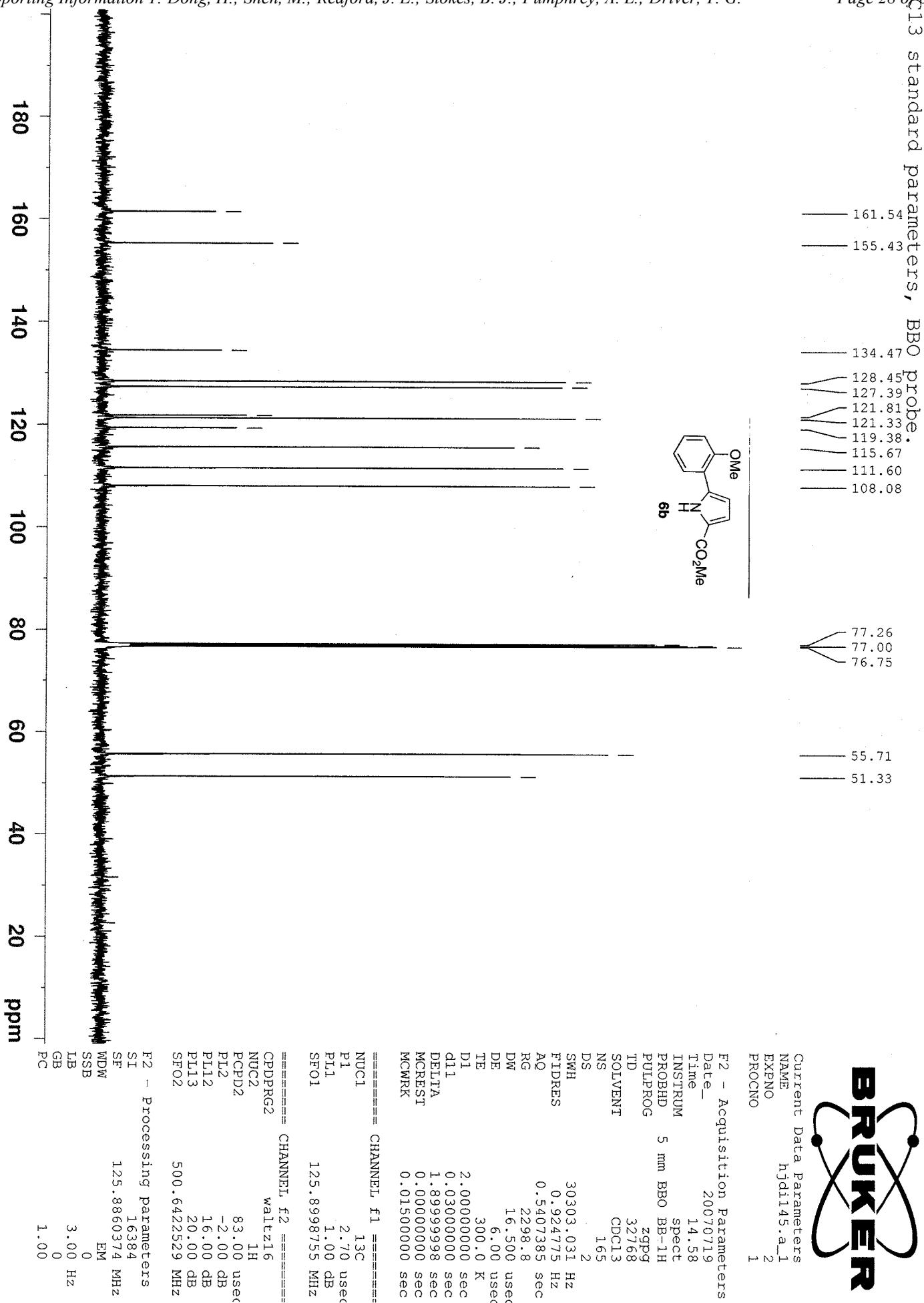
===== CHANNEL f1 =====

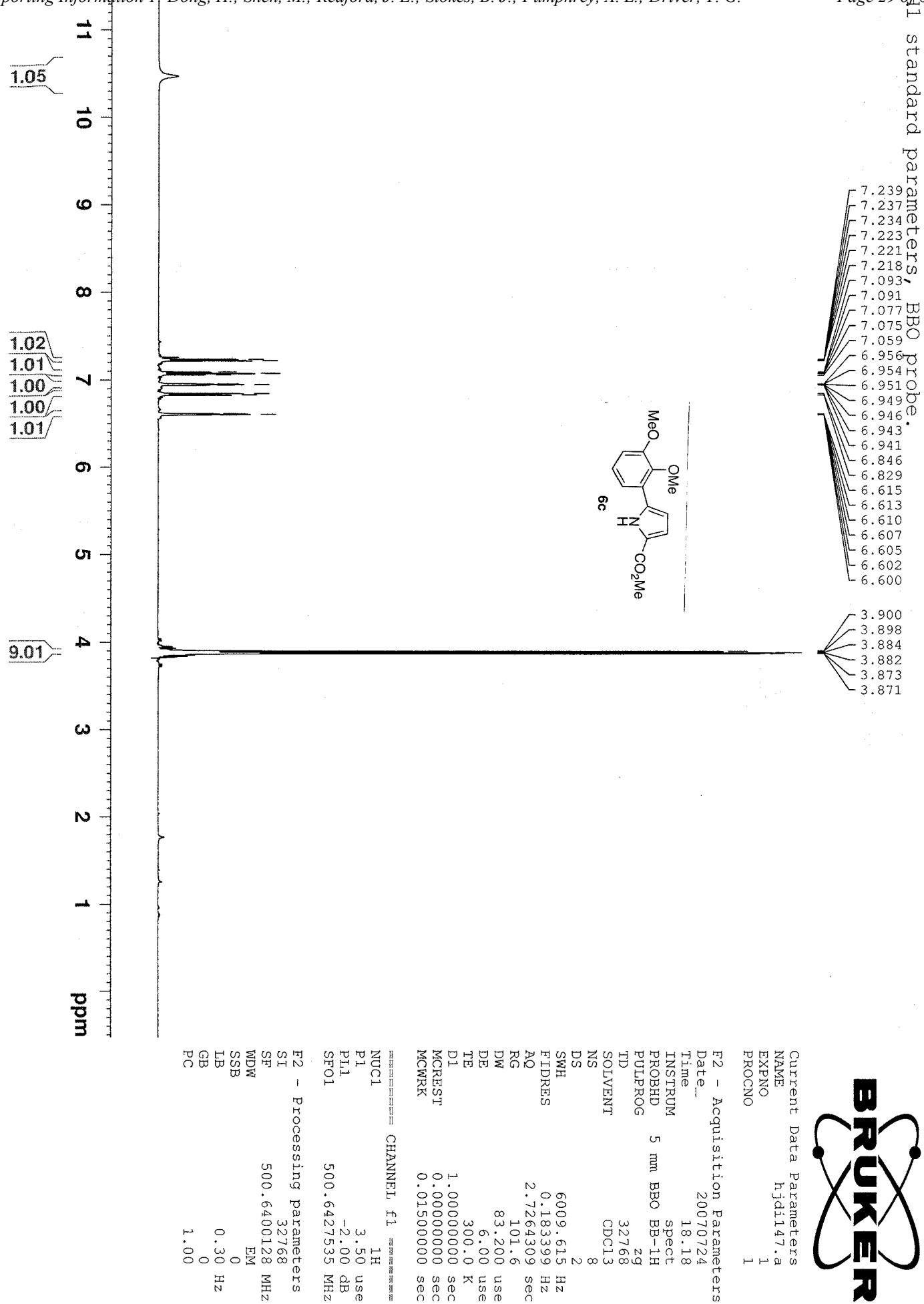
NUC1	1H
P1	3.50 use
PL1	-2.00 dB
SFO1	500.6427535 MHz

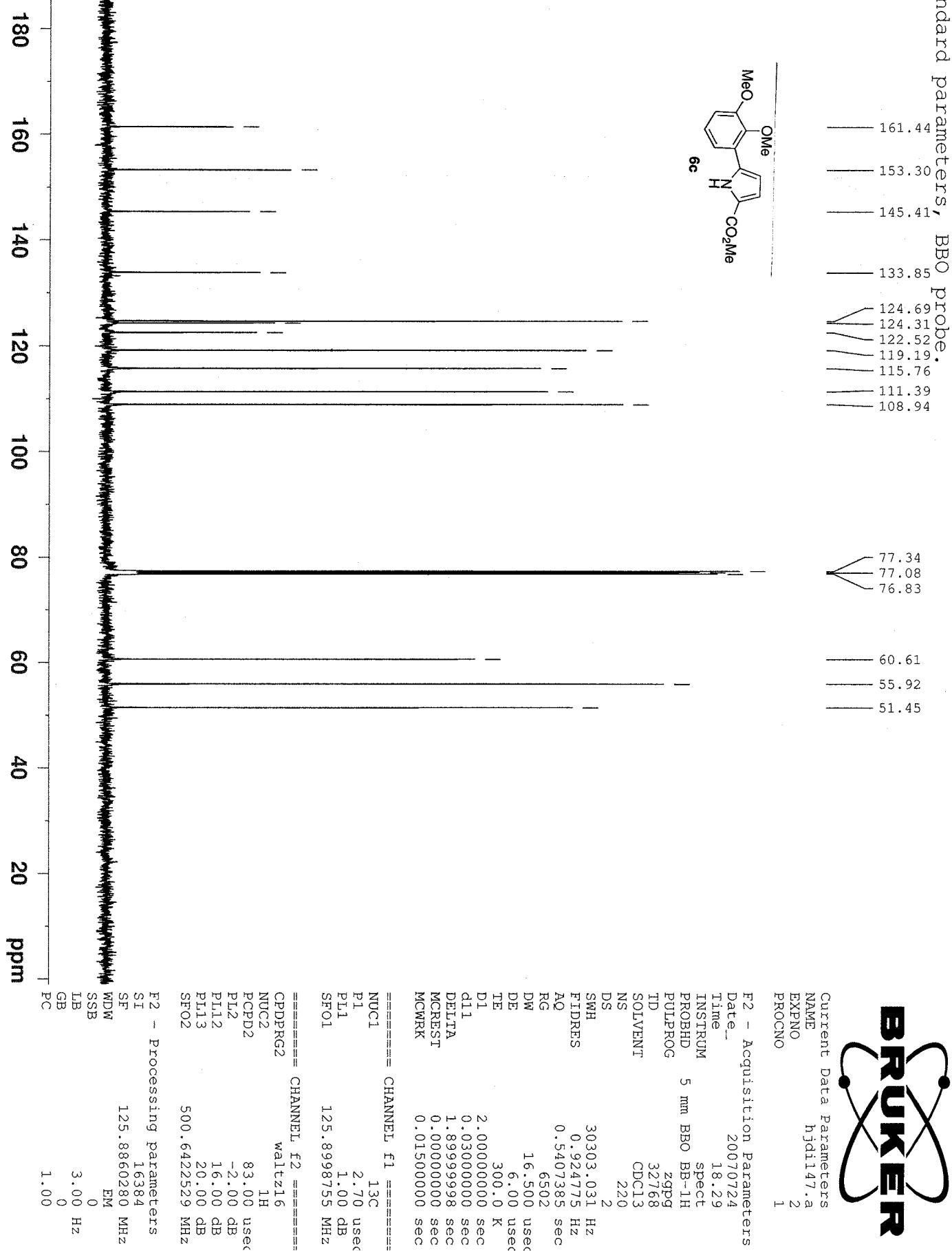
F2 - Processing parameters

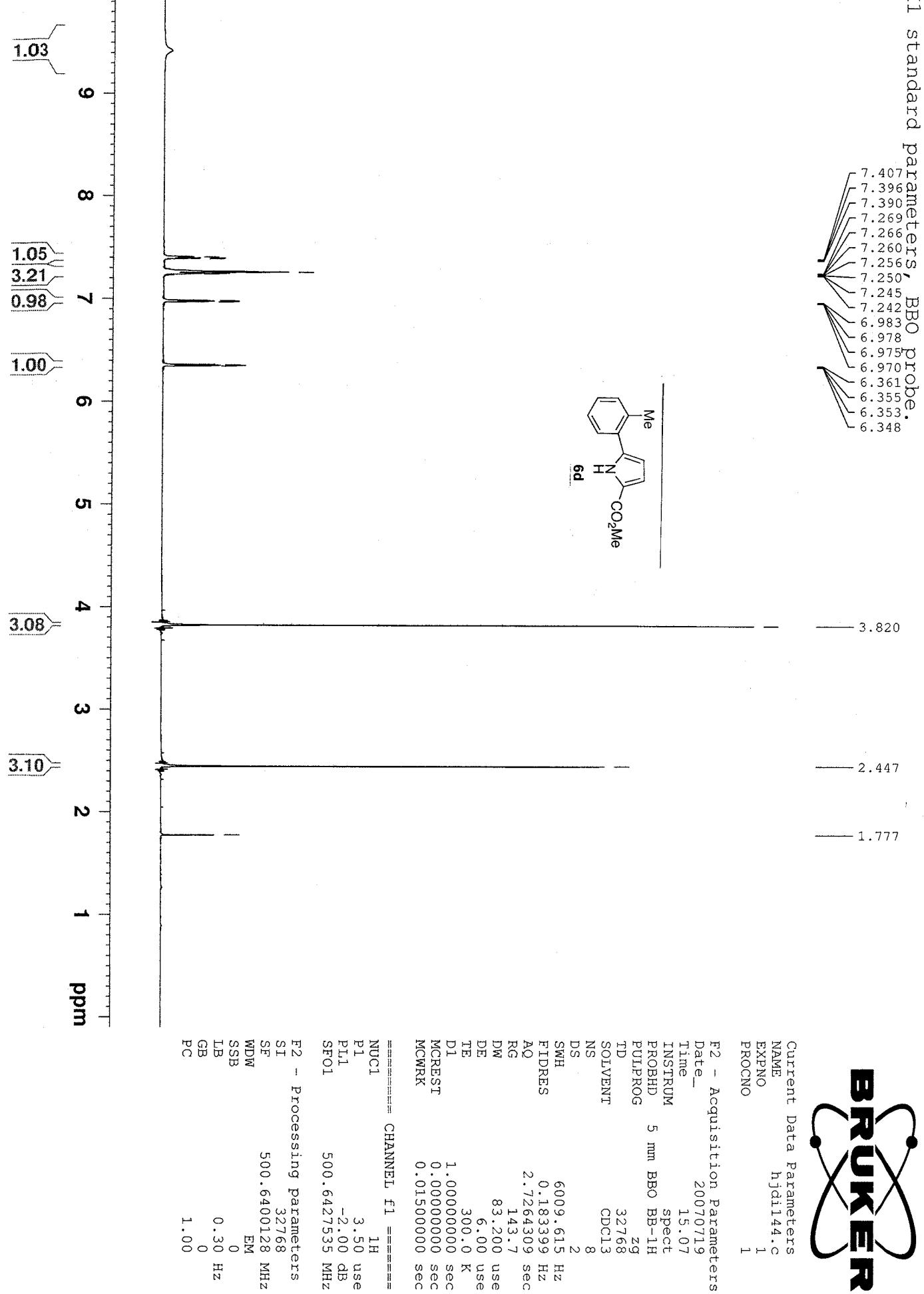
SI	32768
SF	500.6400128 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

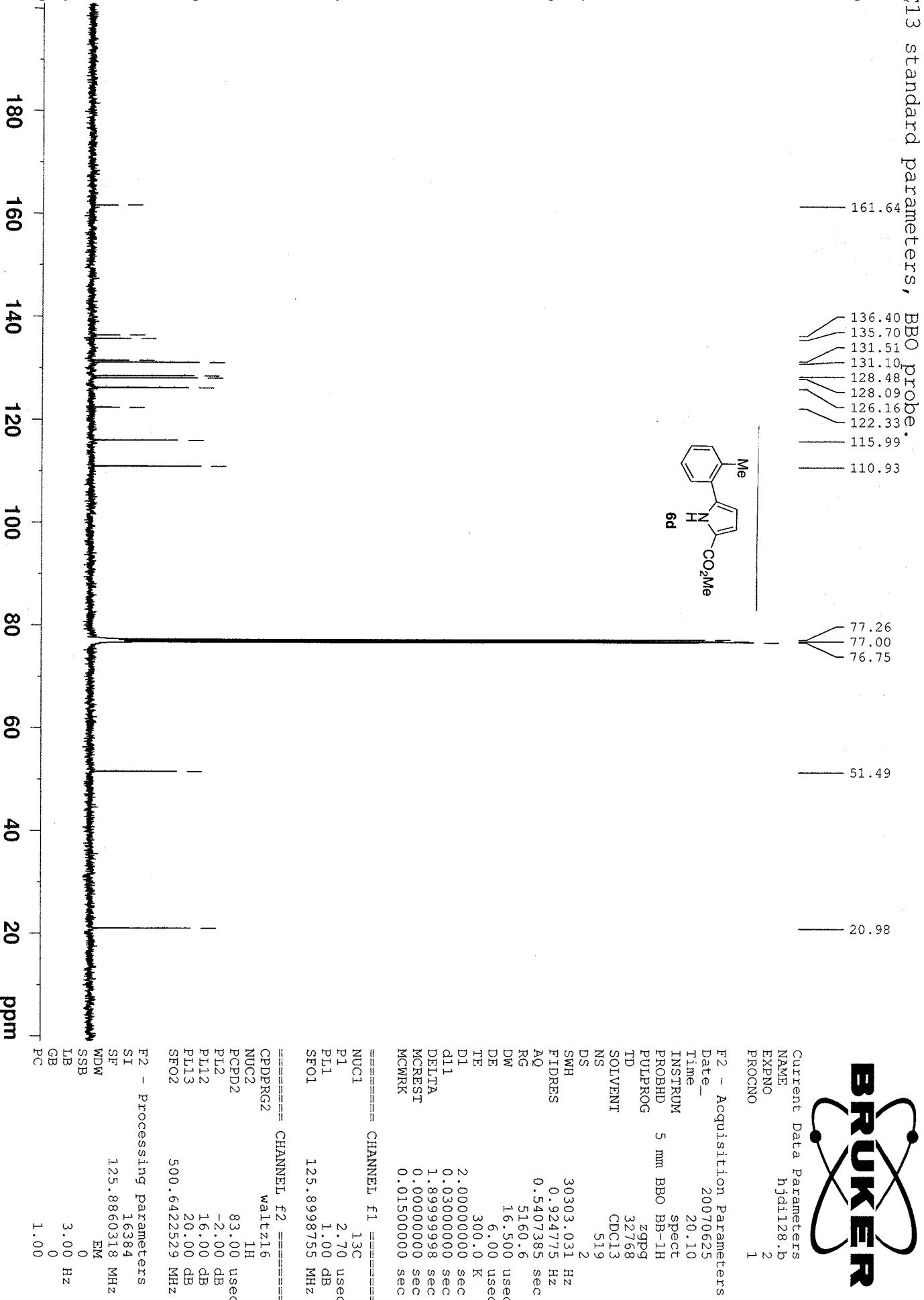


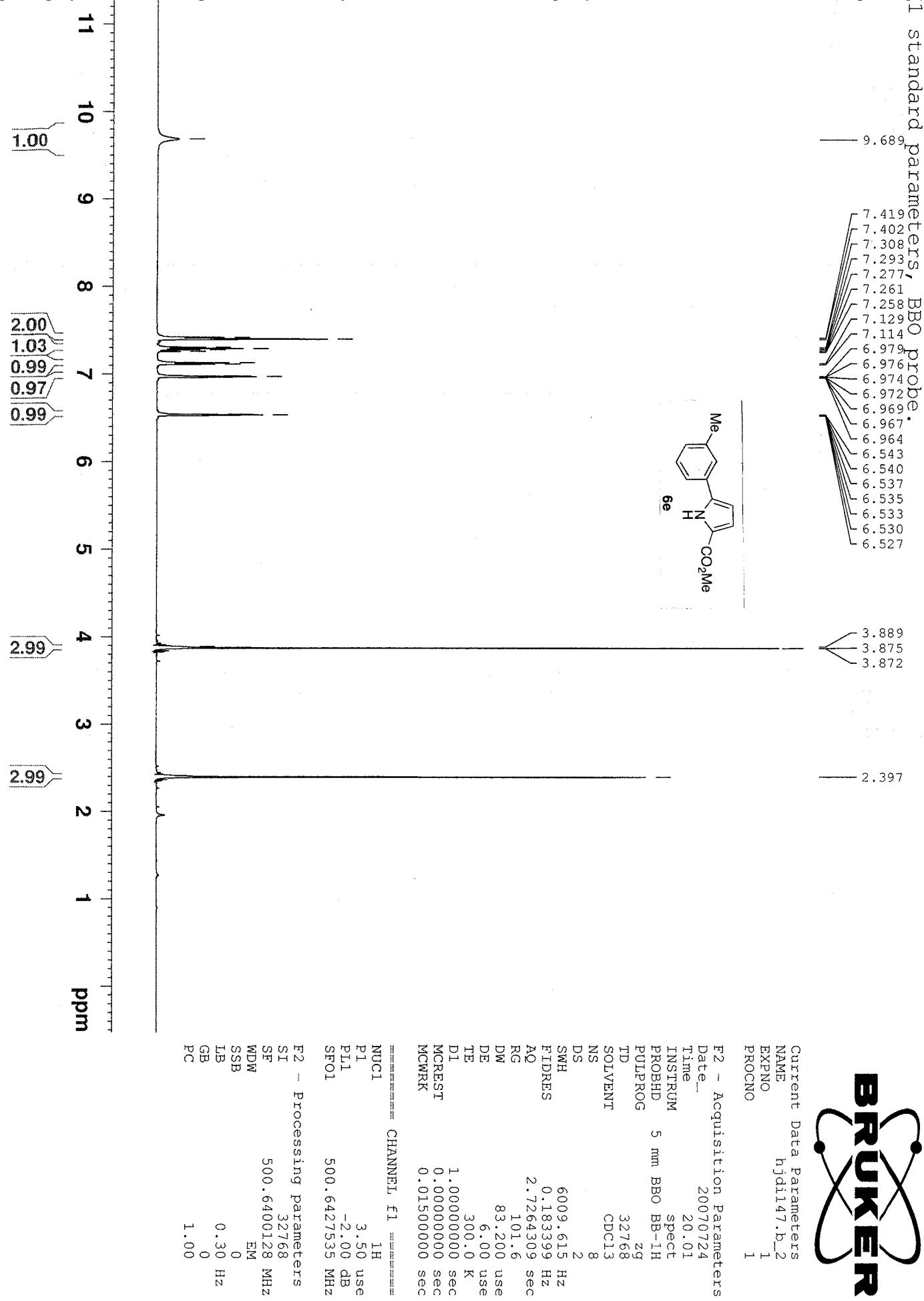


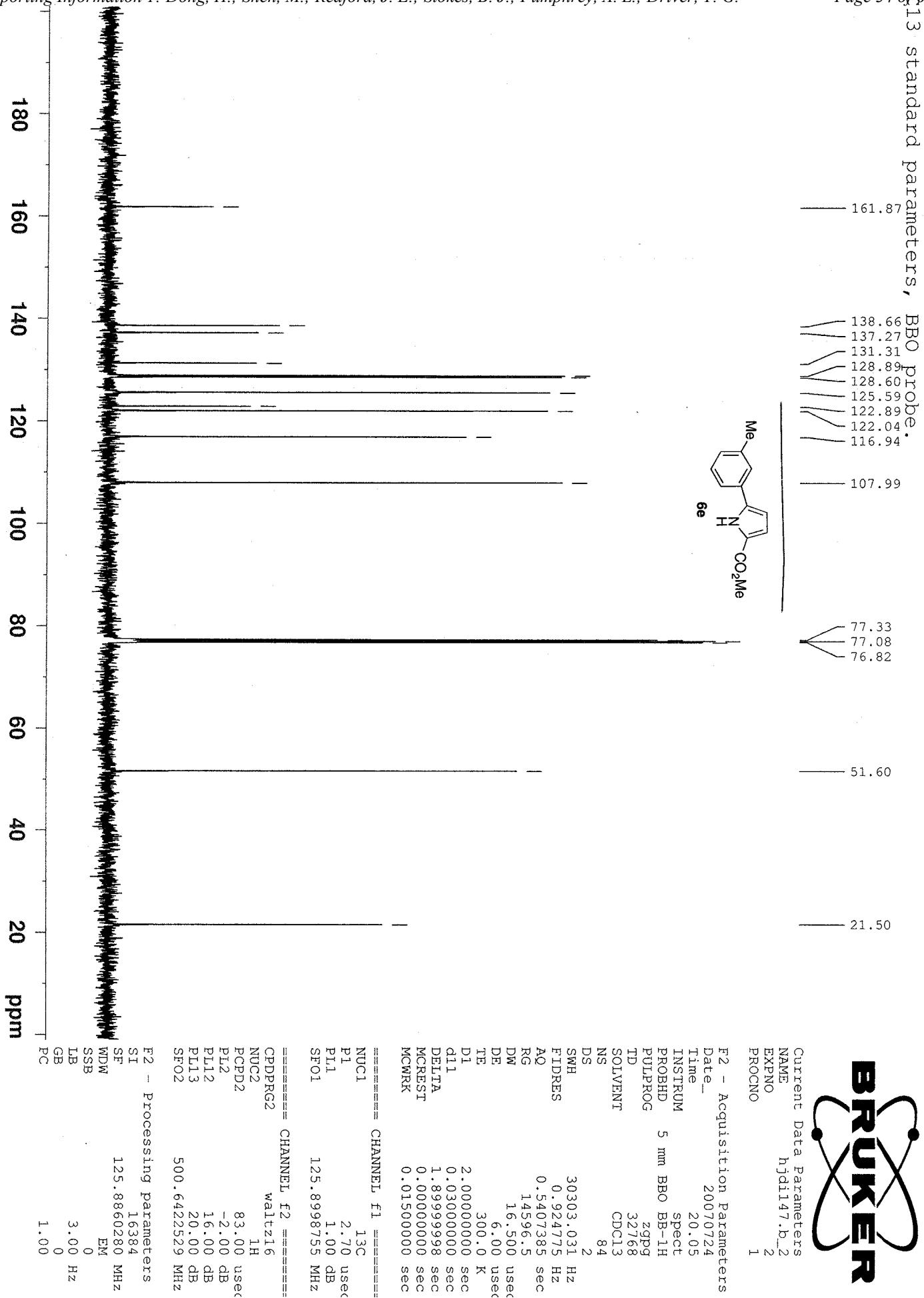


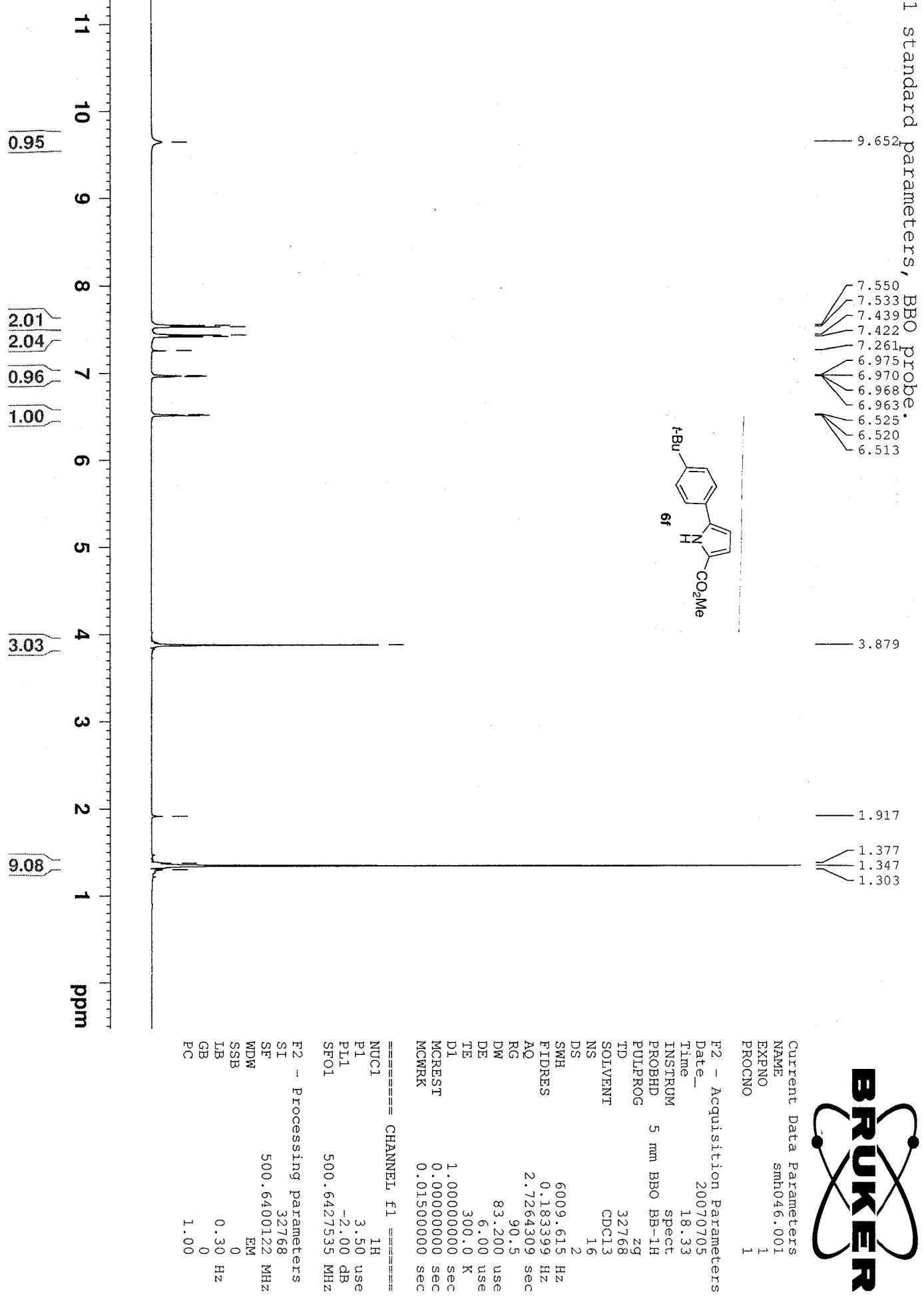


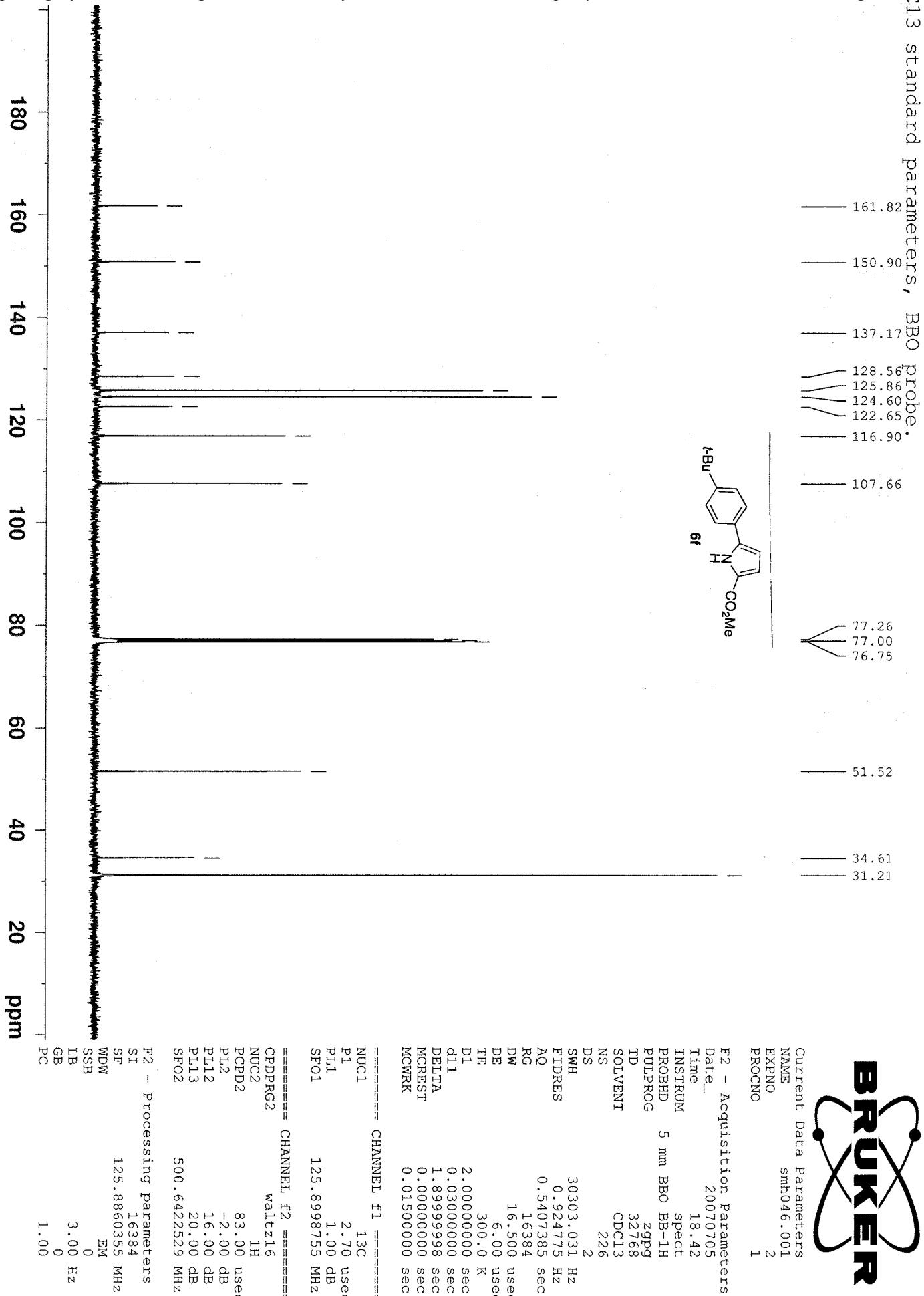


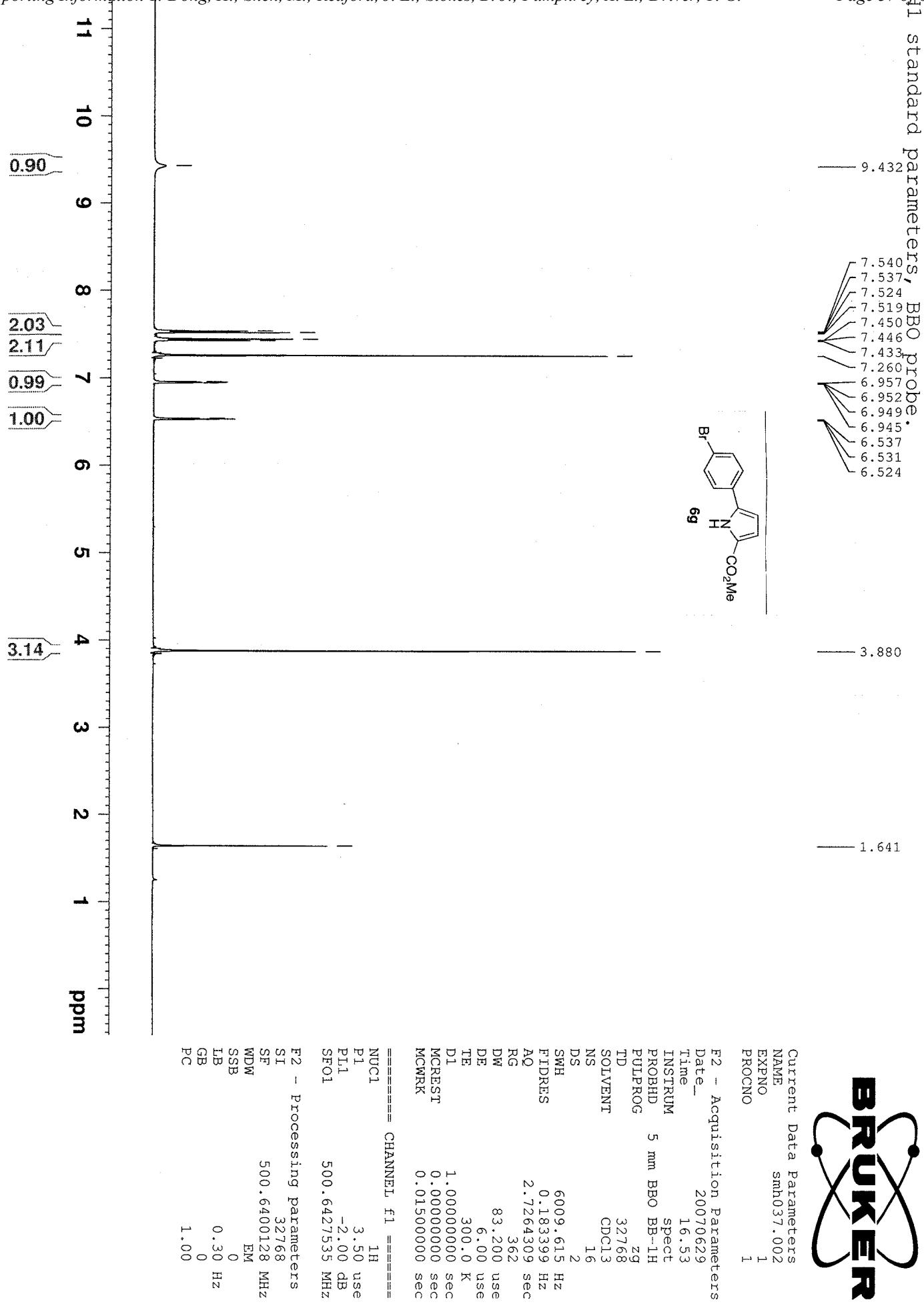


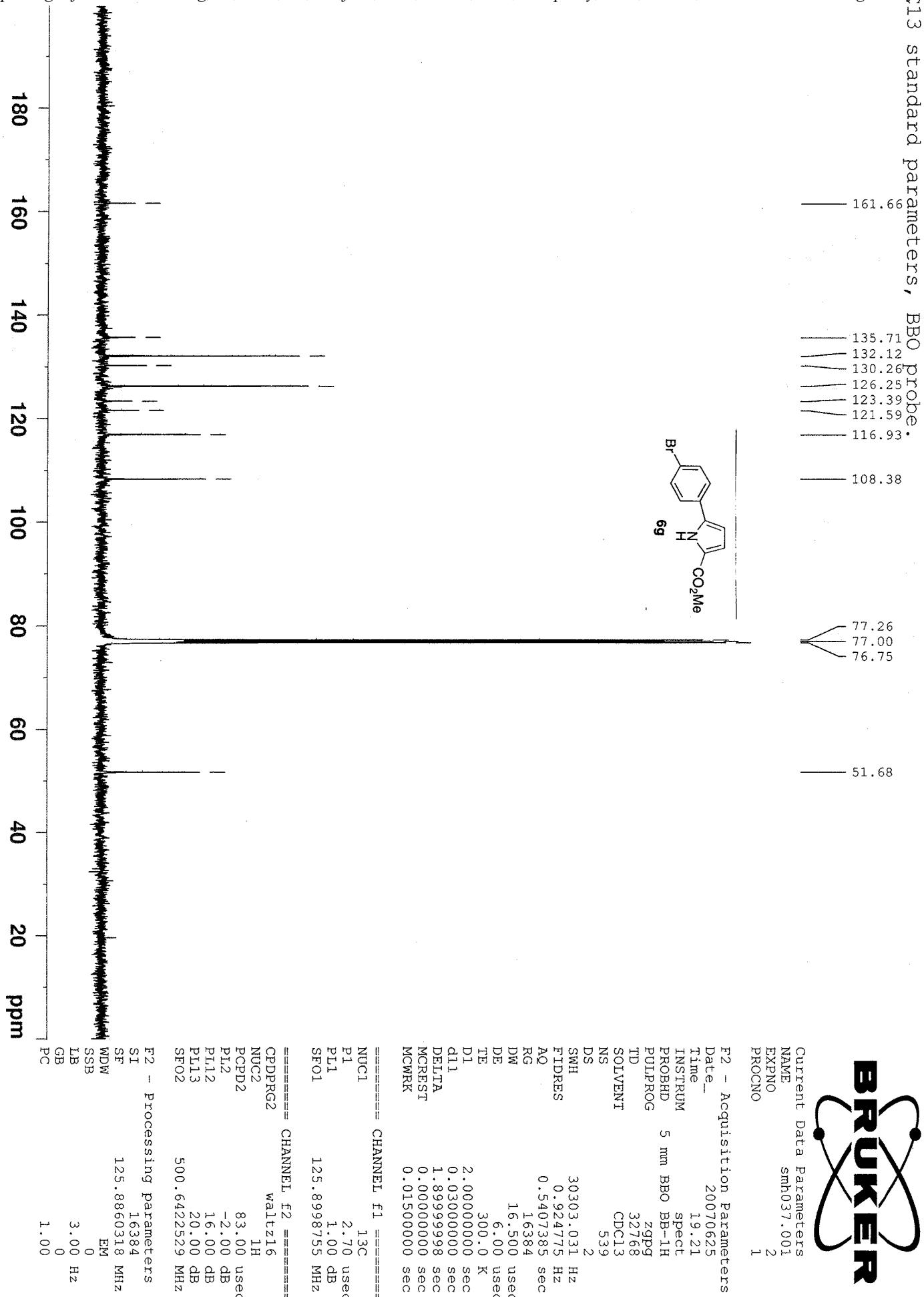


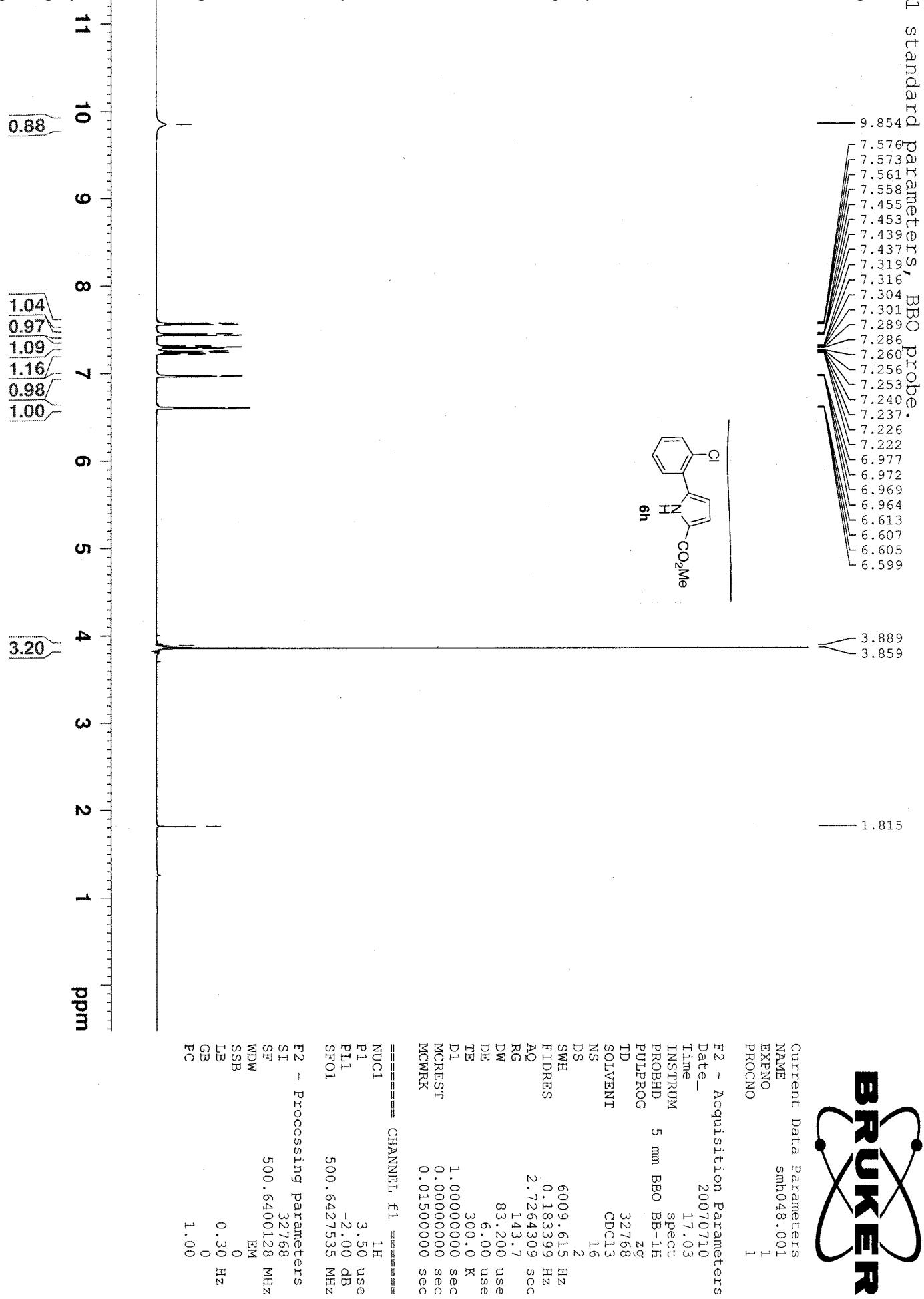


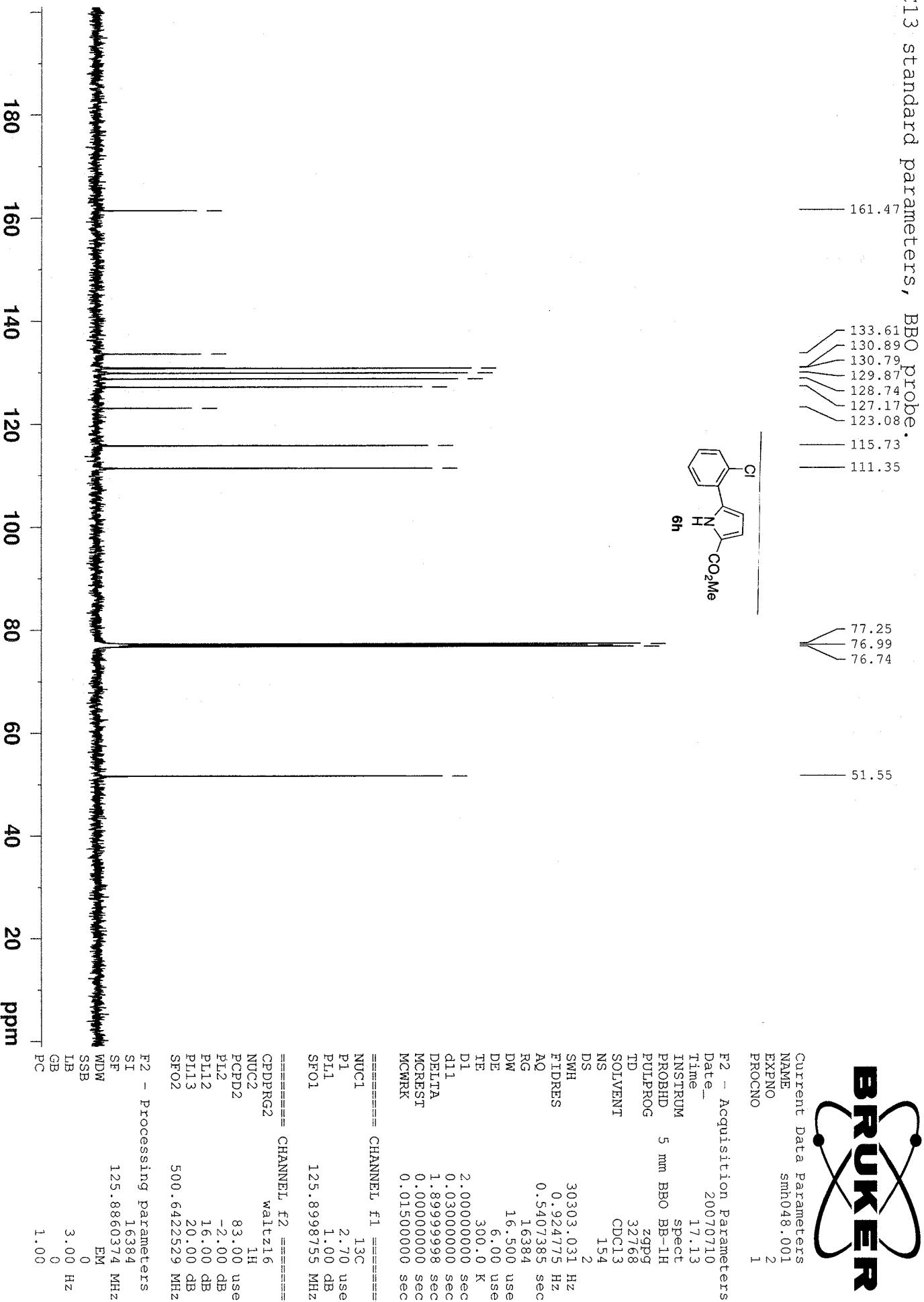


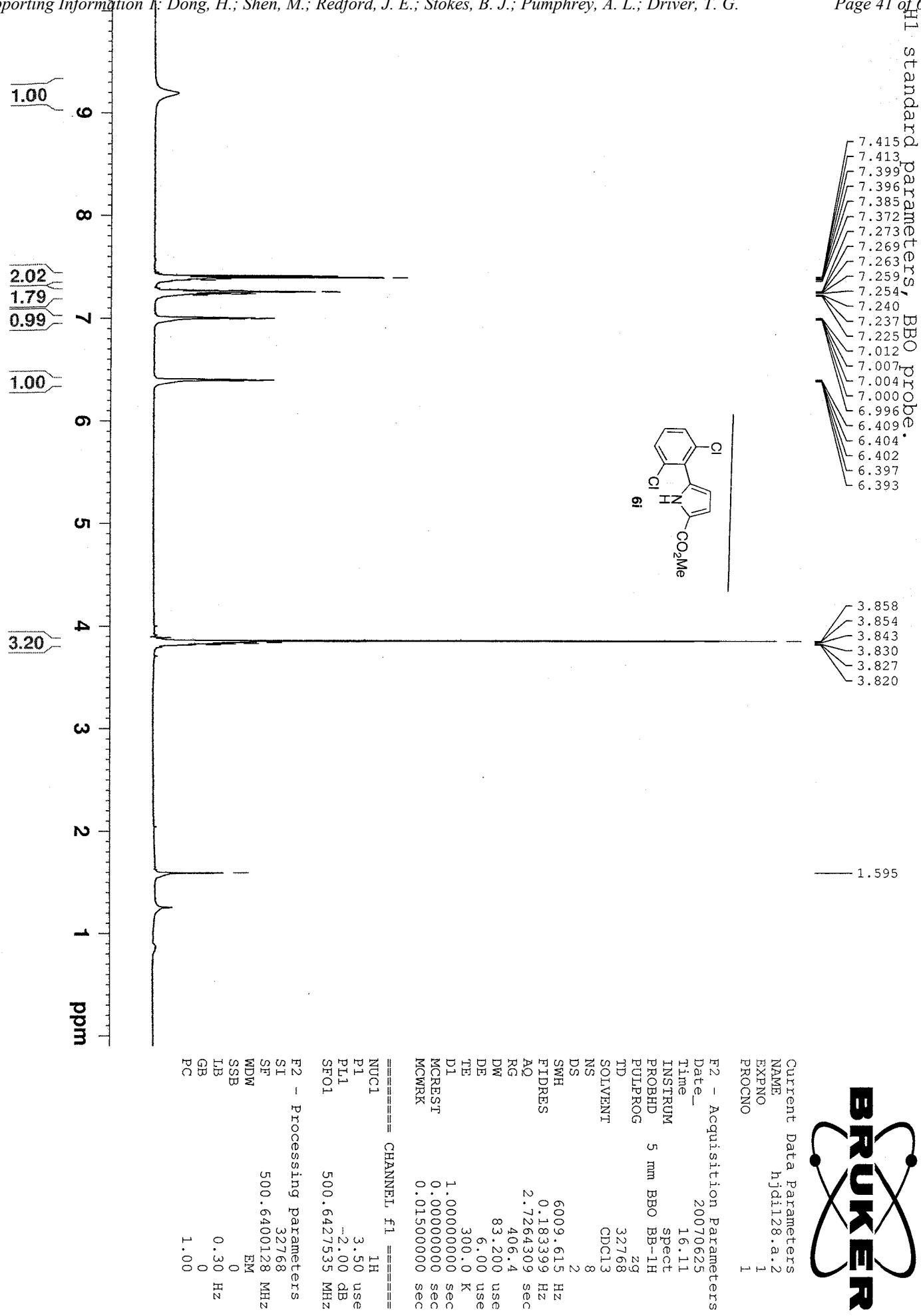


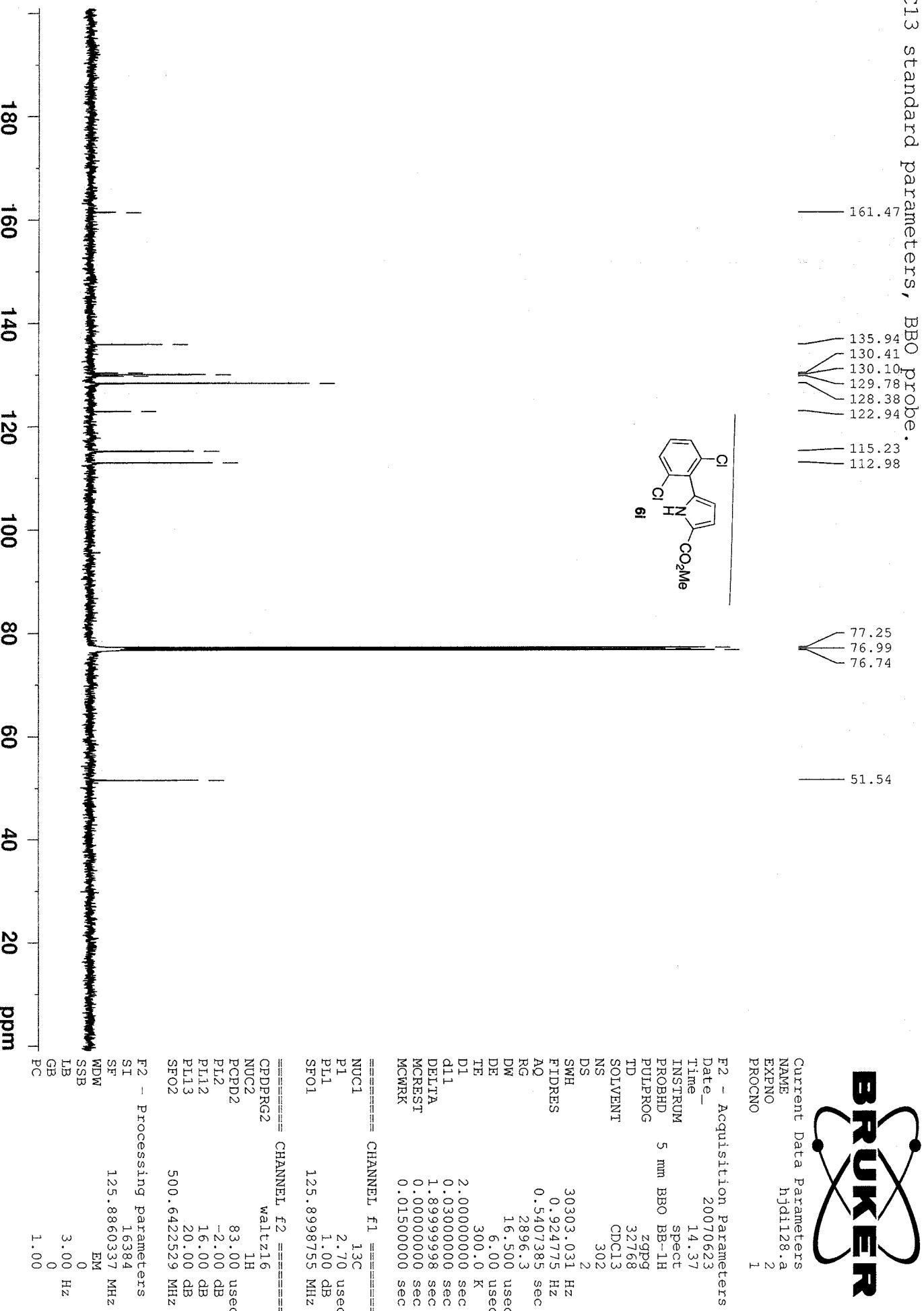


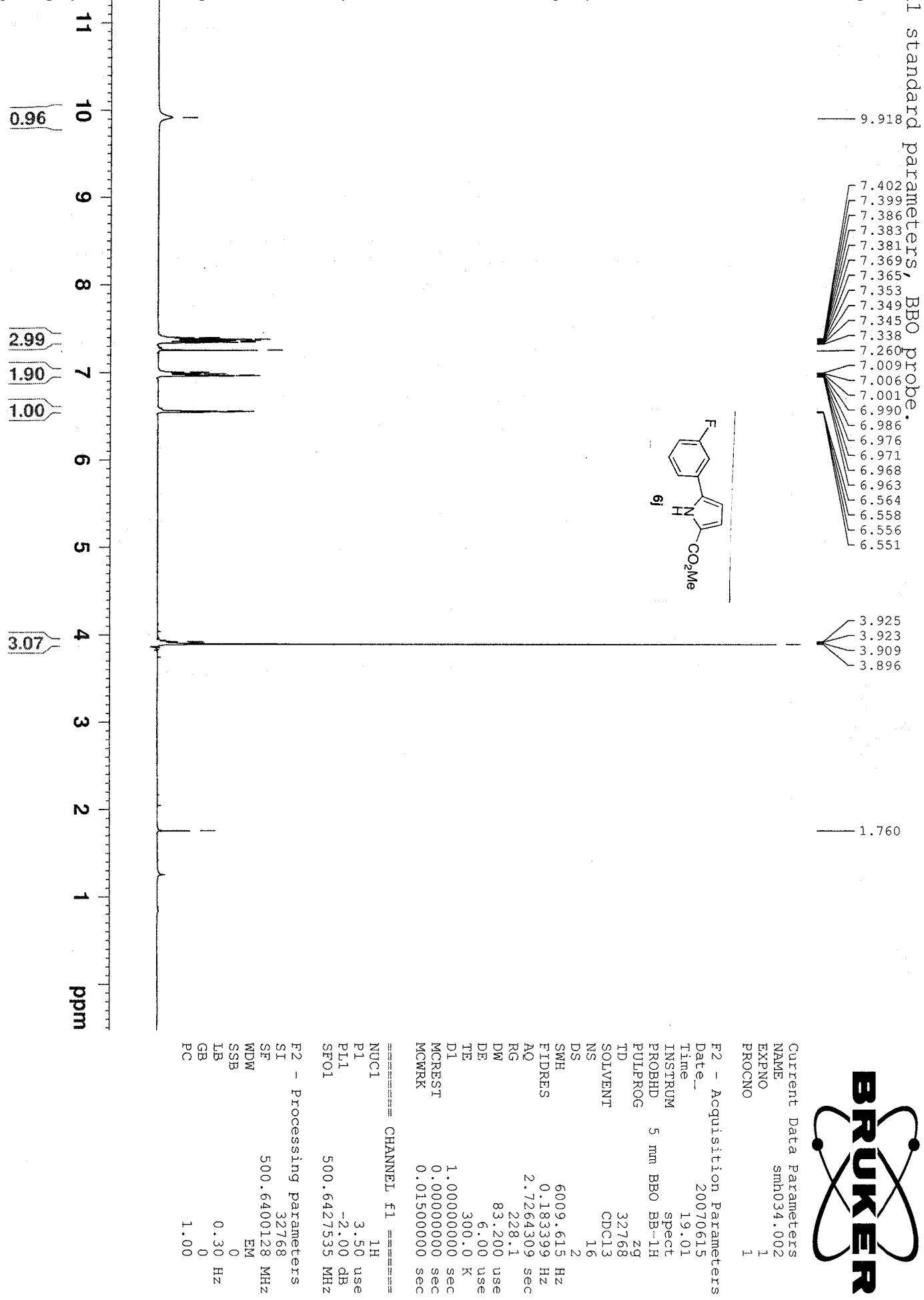




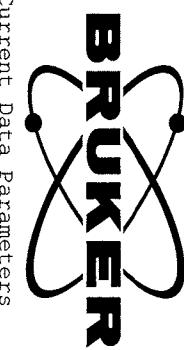
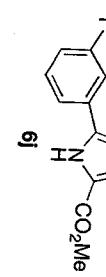
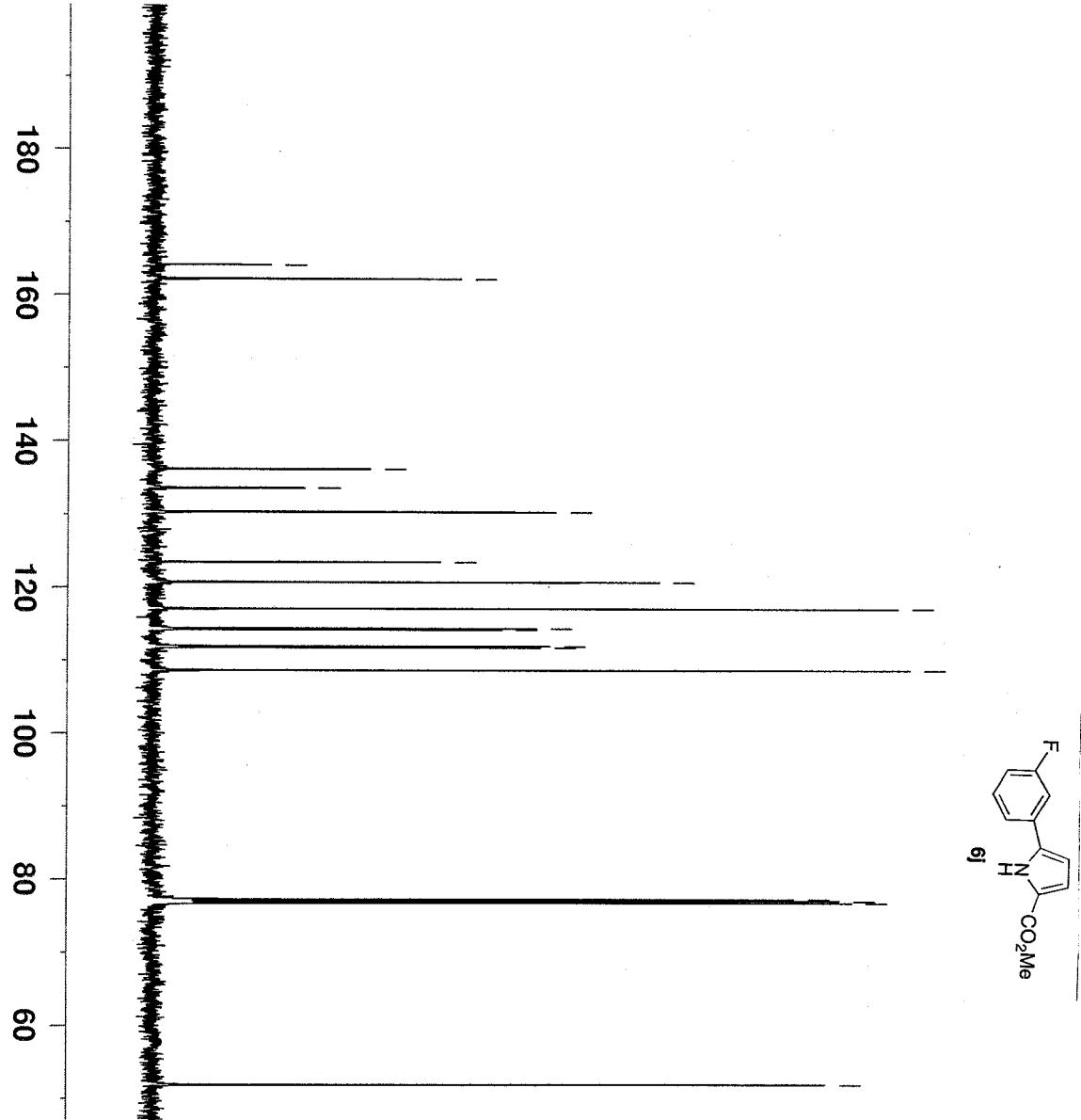
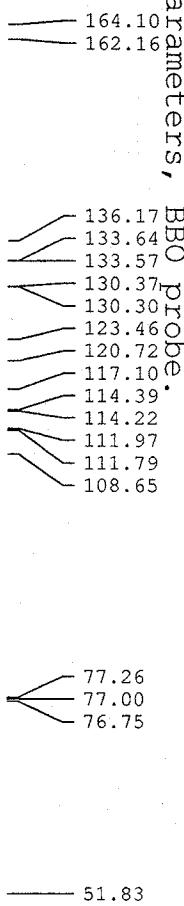








13 standard parameters, BBO probe.

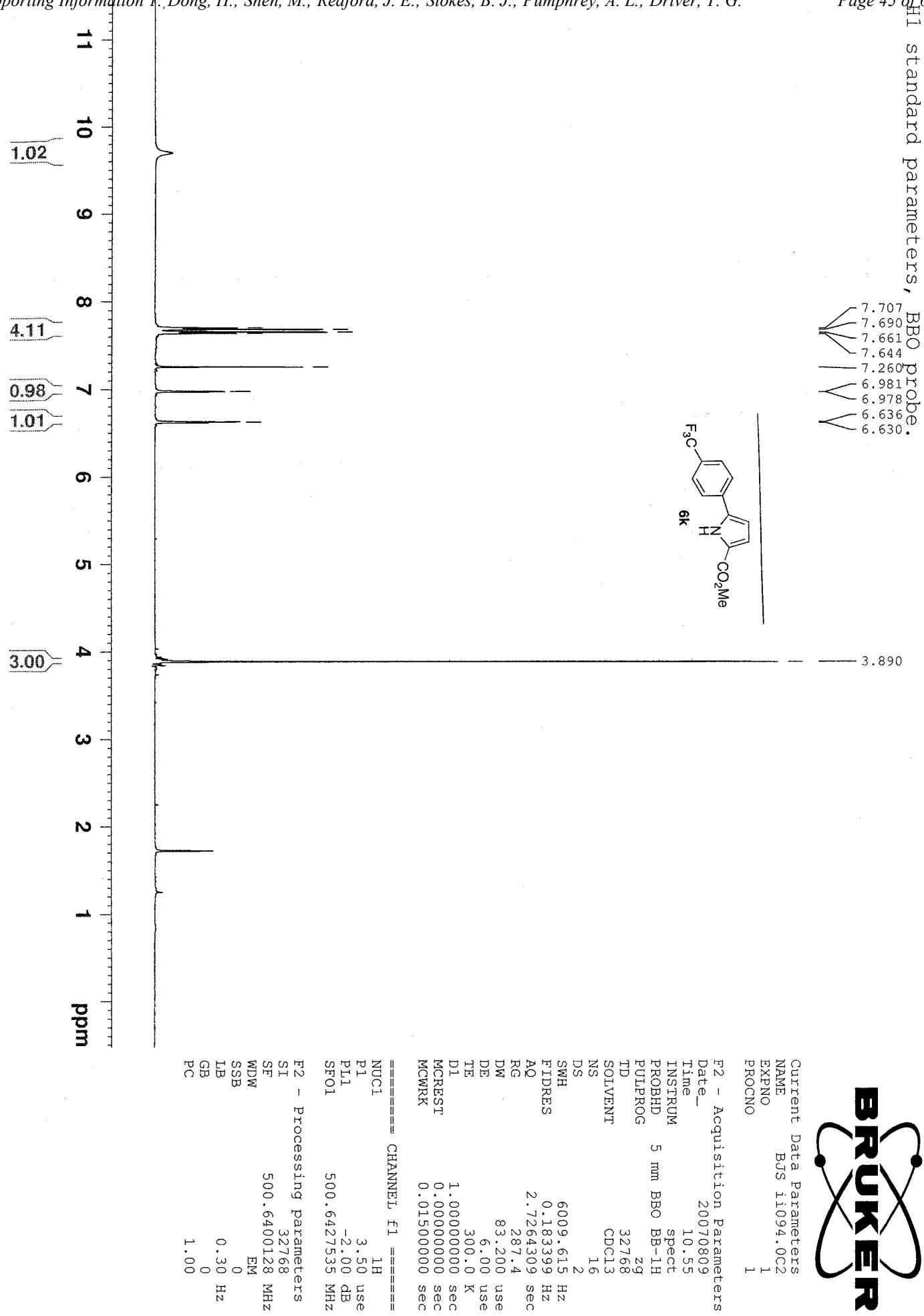


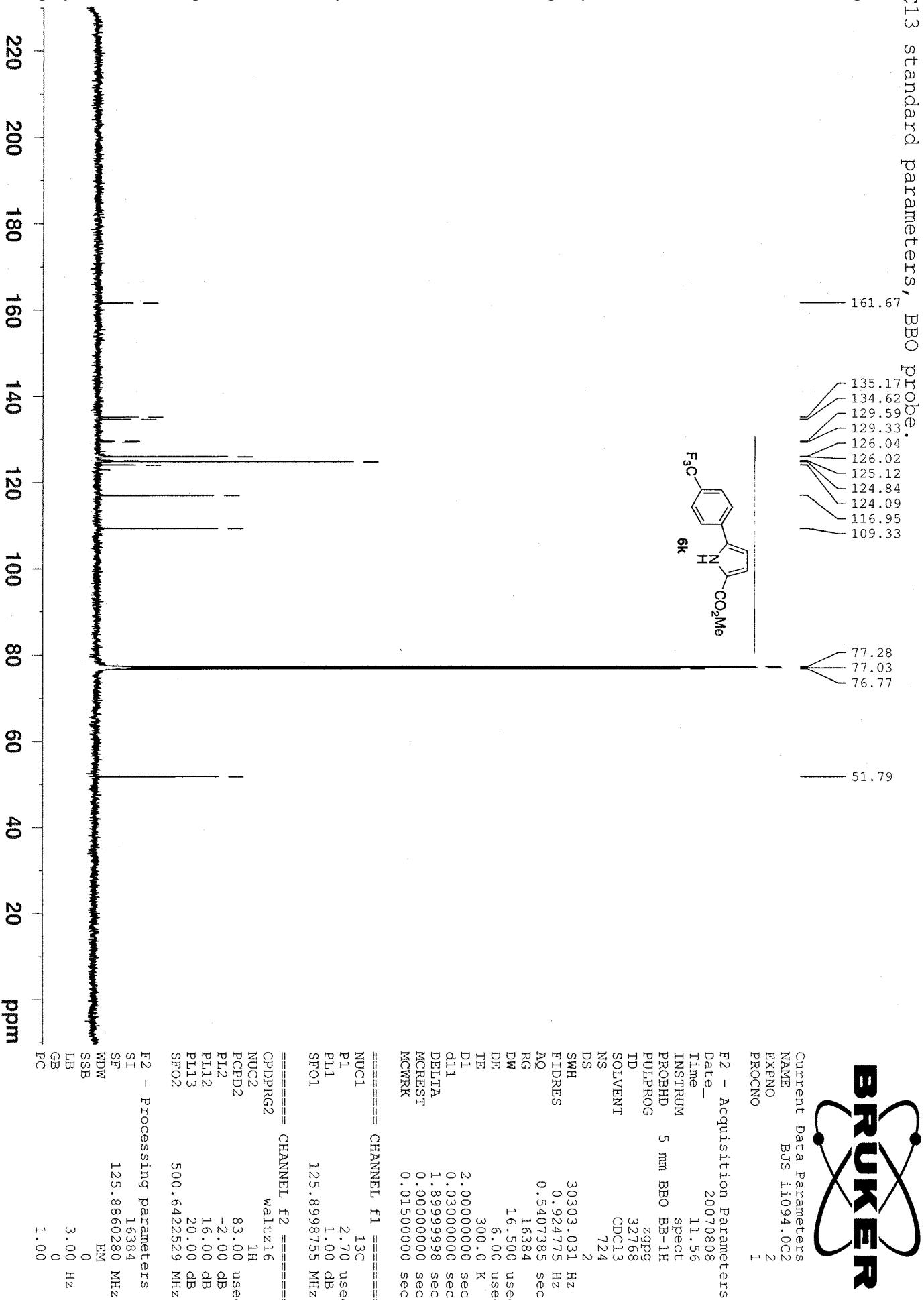
Current Data Parameters
NAME smh047.002
EXPNO 2
PROCNO 1

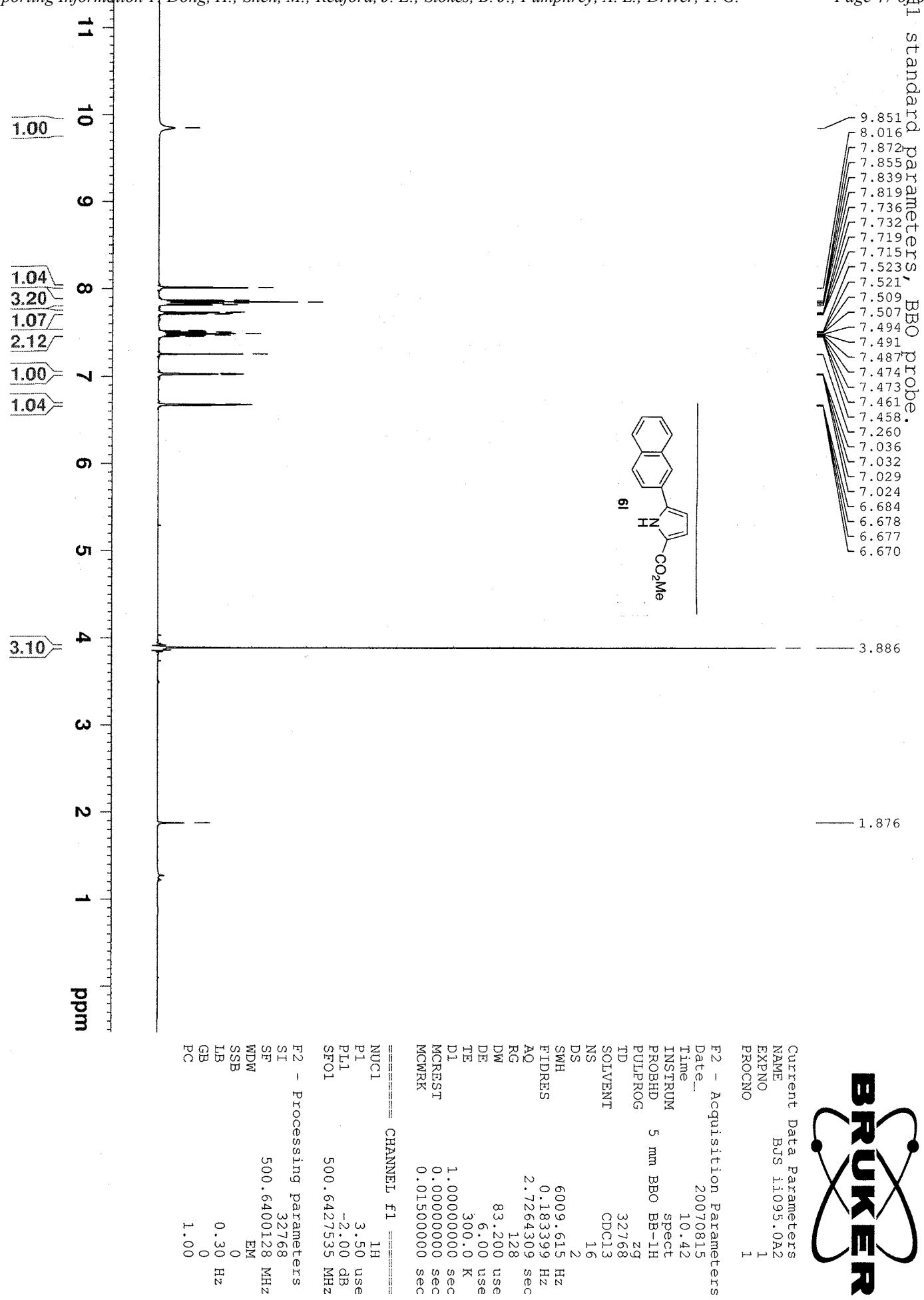
F2 - Acquisition Parameters
Date_ 20070629
Time 17.09
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zpgq
TD 32768
SOLVENT CDCl3
NS 93
DS 2
SWH 30.303-0.031 Hz
FIDRES 0.924775 Hz
AQ 0.5407385 sec
RG 4096
DW 16.500 usec
DE 6.00 usec
TE 300.0 K
D1 2.0000000 sec
d11 0.03000000 sec
DELTA 1.8999999 sec
MCREST 0.000000 sec
MCWRK 0.01500000 sec

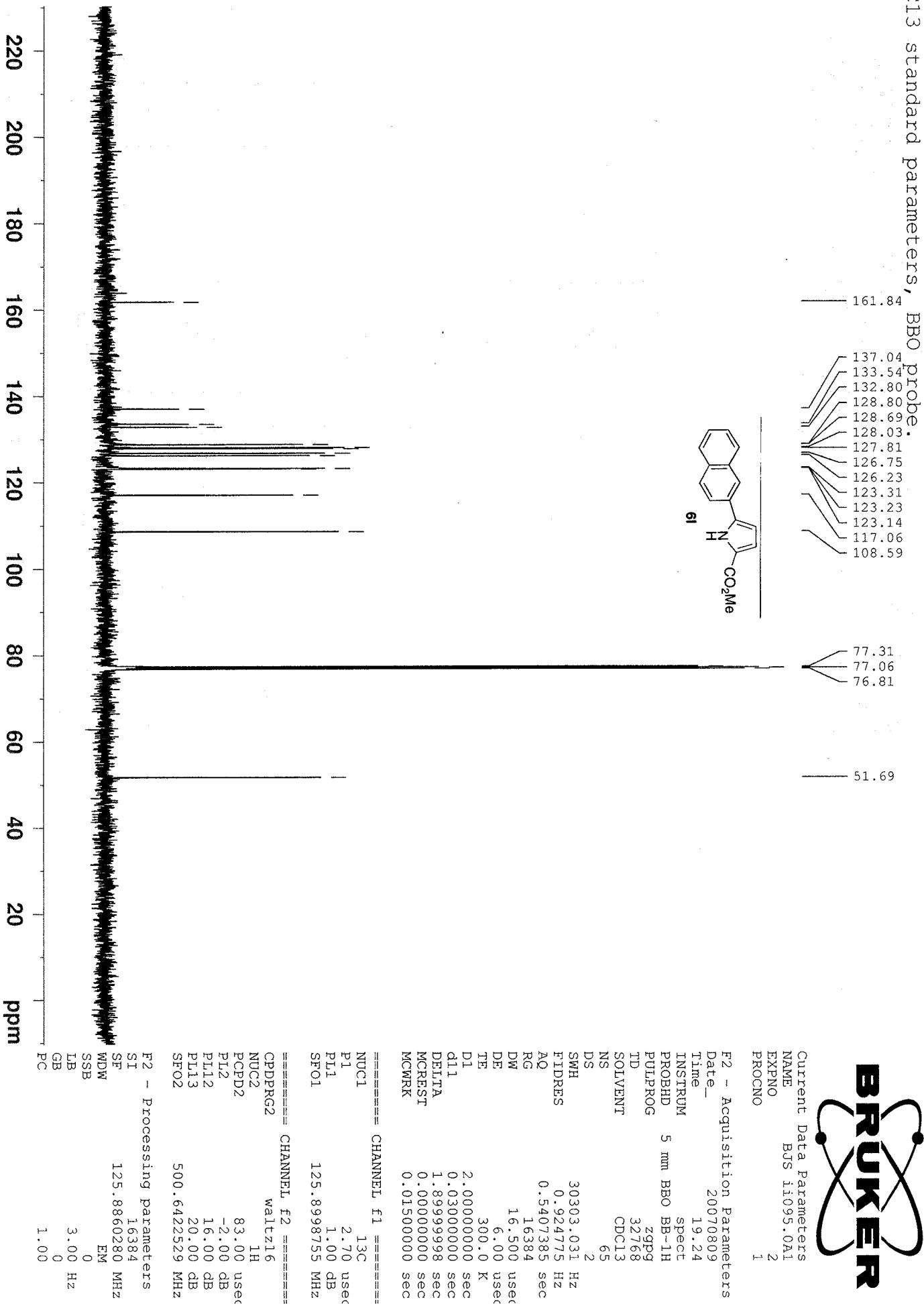
===== CHANNEL f1 ======
NUC1 13C
P1 2.70 usec
PL1 1.00 dB
SFO1 125.8998755 MHz
===== CHANNEL f2 ======
CPDPRG2 waltz16
NUC2 1H
PCPD2 83.00 usec
PL2 -2.00 dB
PL12 16.00 dB
PL13 20.00 dB
SFO2 500.6422529 MHz

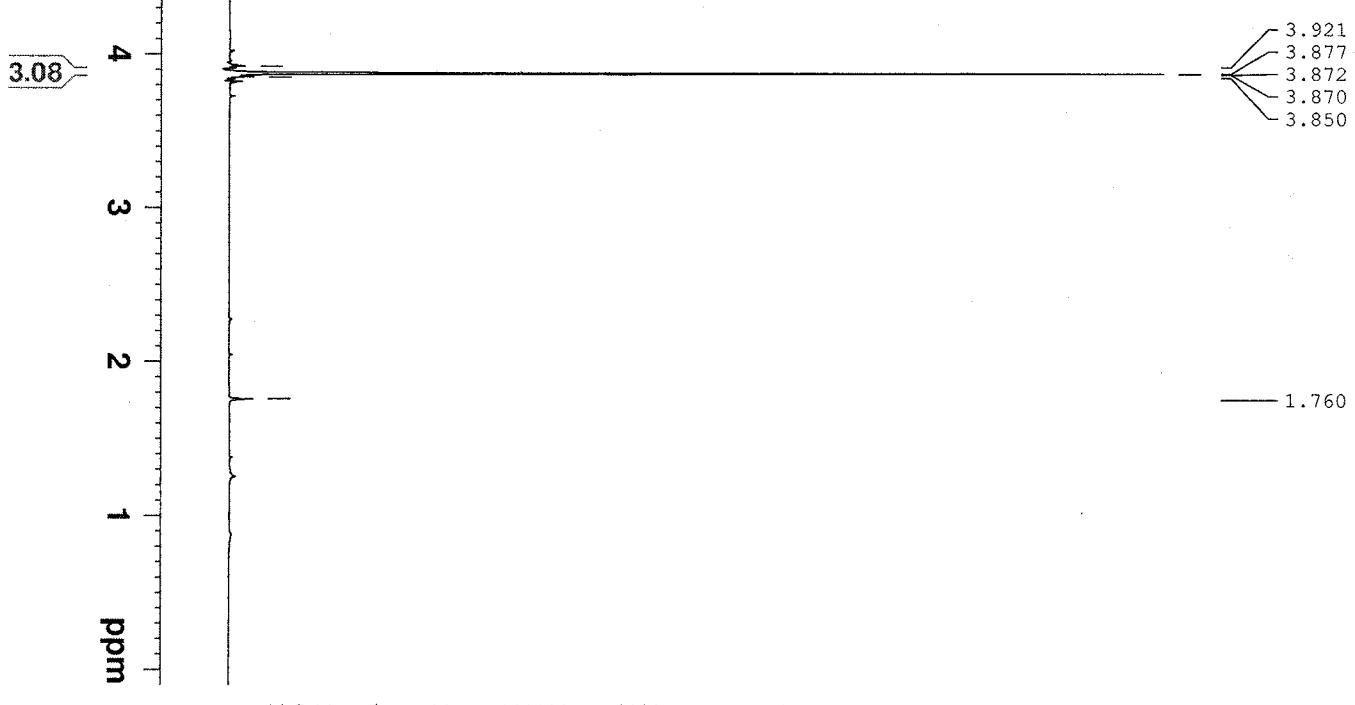
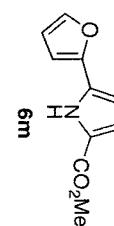
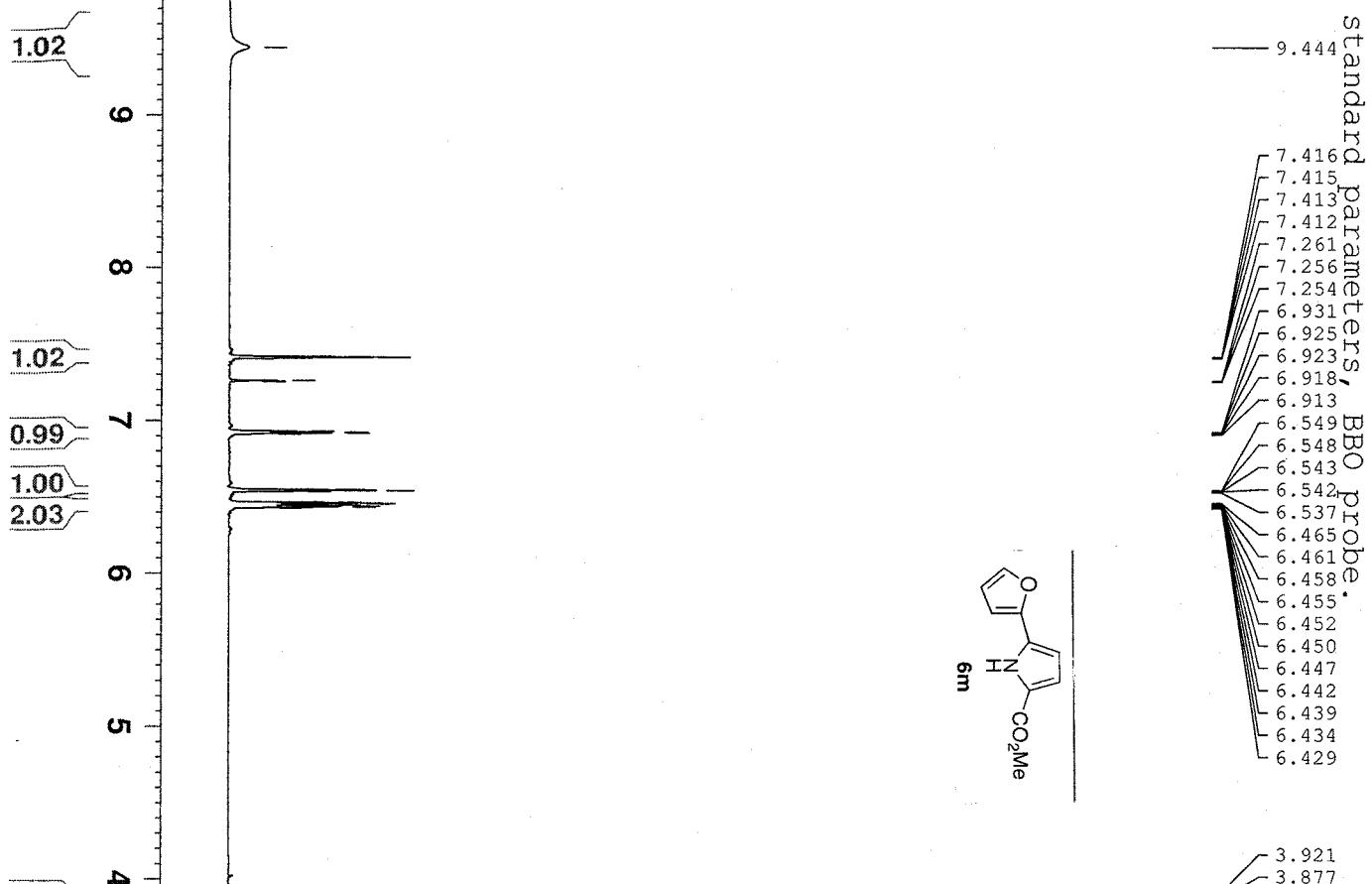
F2 - Processing parameters
SI 16384
SF 125.8860374 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.00











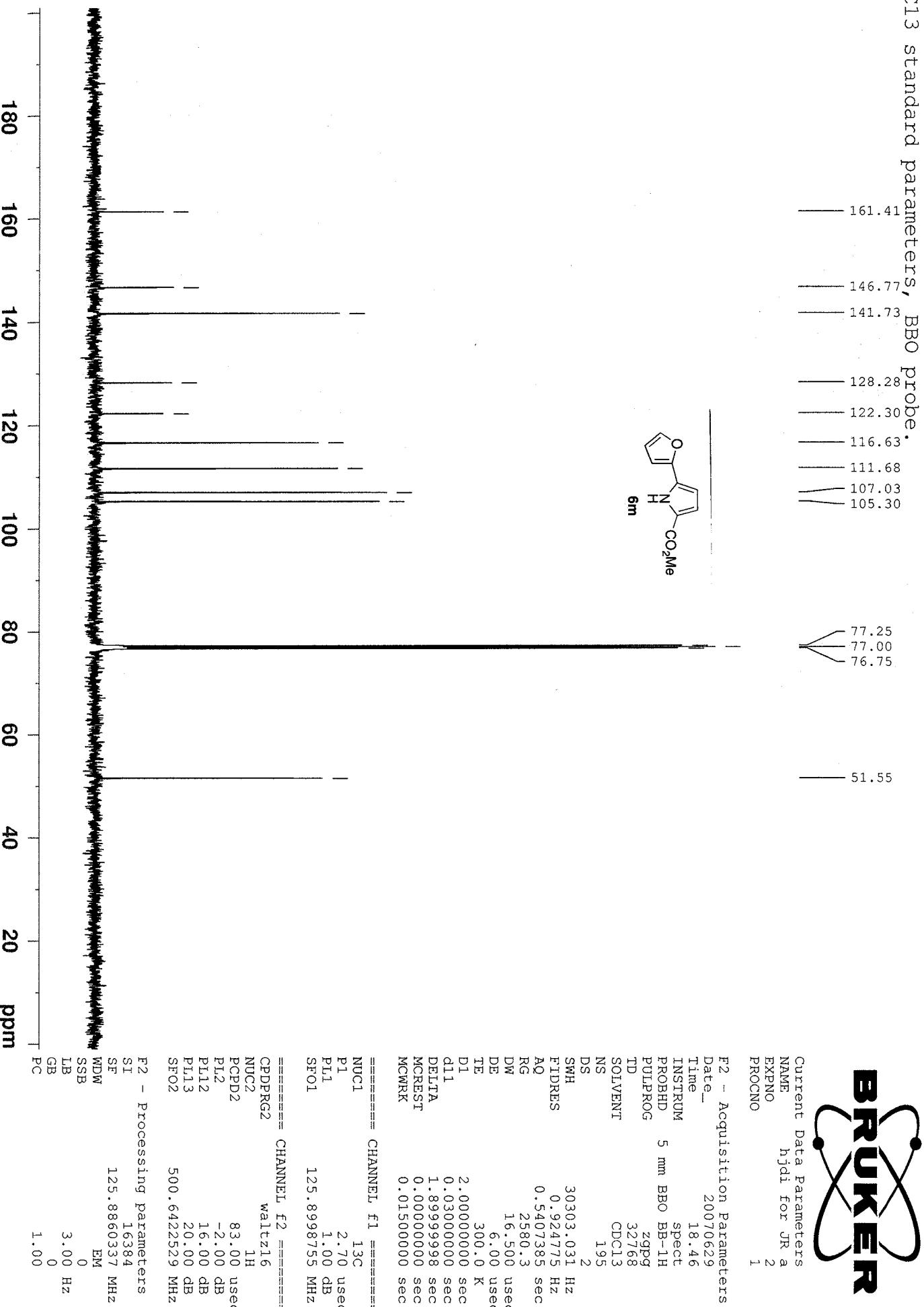
Current Data Parameters
NAME hди for JR a
EXPNO 1
PROCNO 1

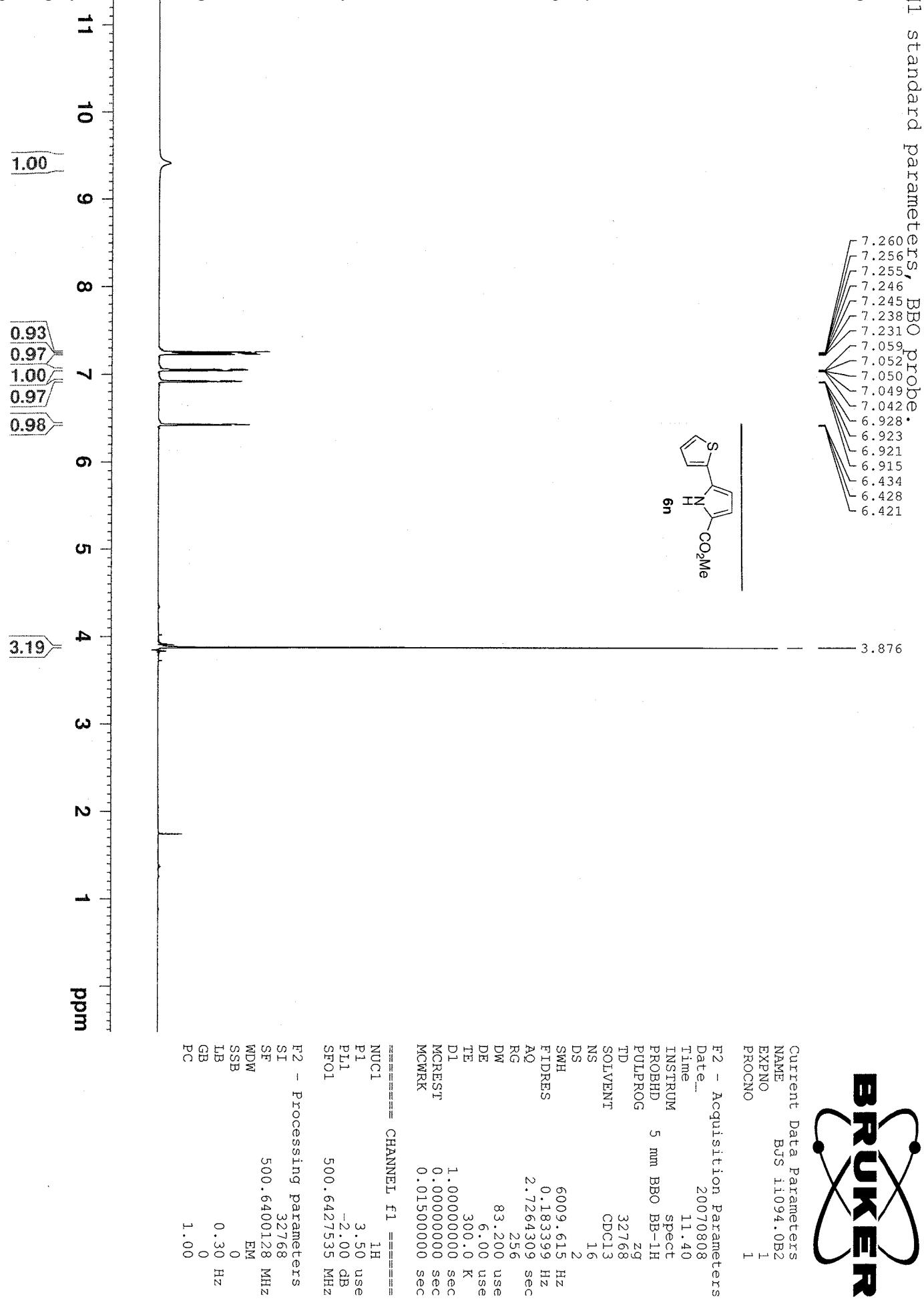
F2 - Acquisition Parameters
Date_ 20070629
Time 18.37
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg32768
TD 32768
SOLVENT CDCl3
NS 8
DS 2
SWH 6009.615 Hz
FIDRES 0.183399 Hz
AQ 2.7264309 sec
RG 203.2
DW 83.200 usec
DE 6.00 usec
TE 300.0 K
D1 1.0000000 sec
MCREST 0.0000000 sec
MCWRK 0.0150000 sec

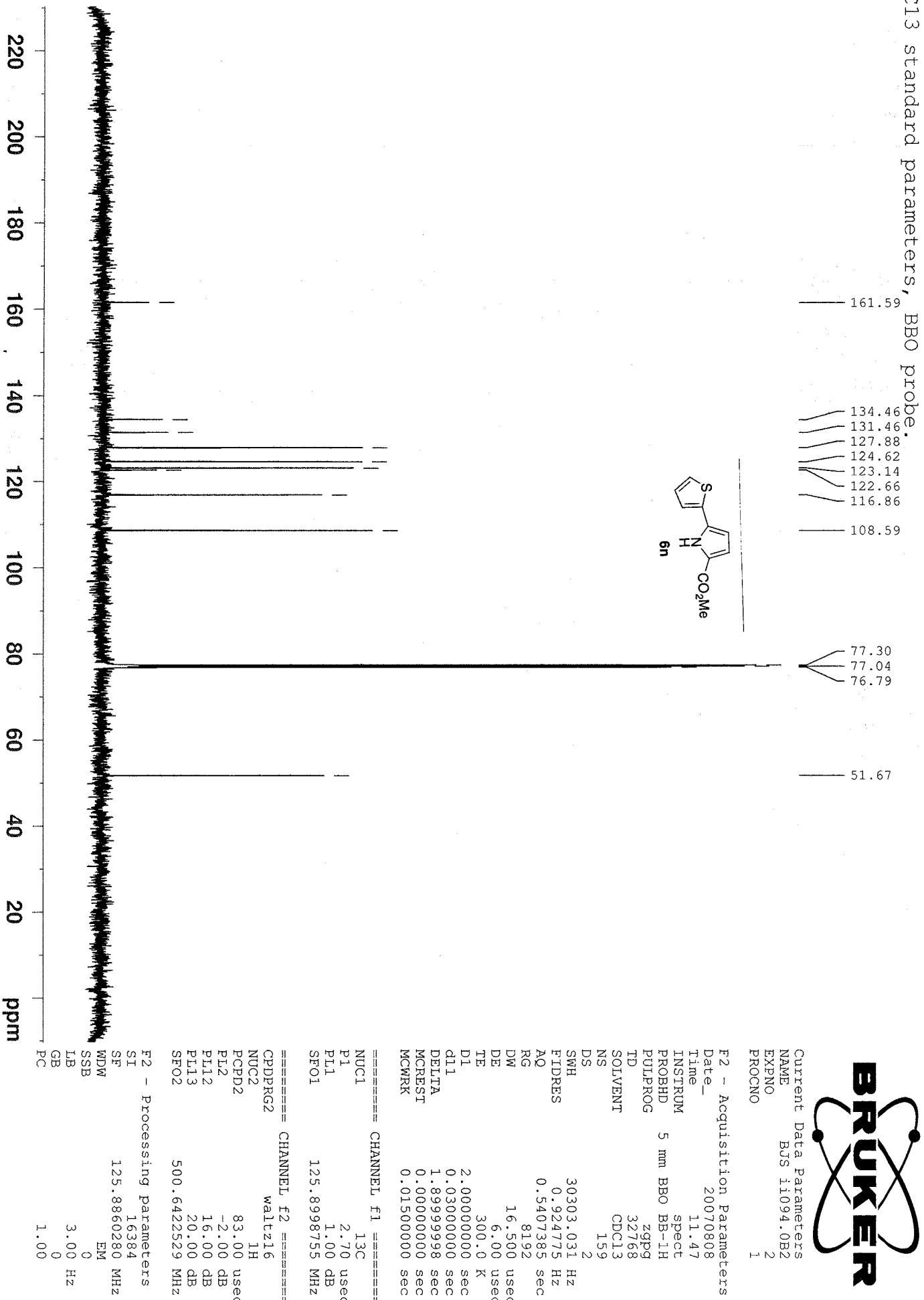
===== CHANNEL f1 =====
NUC1 1H
P1 3.50 usec
PL1 -2.00 dB
SF01 500.6427535 MHz

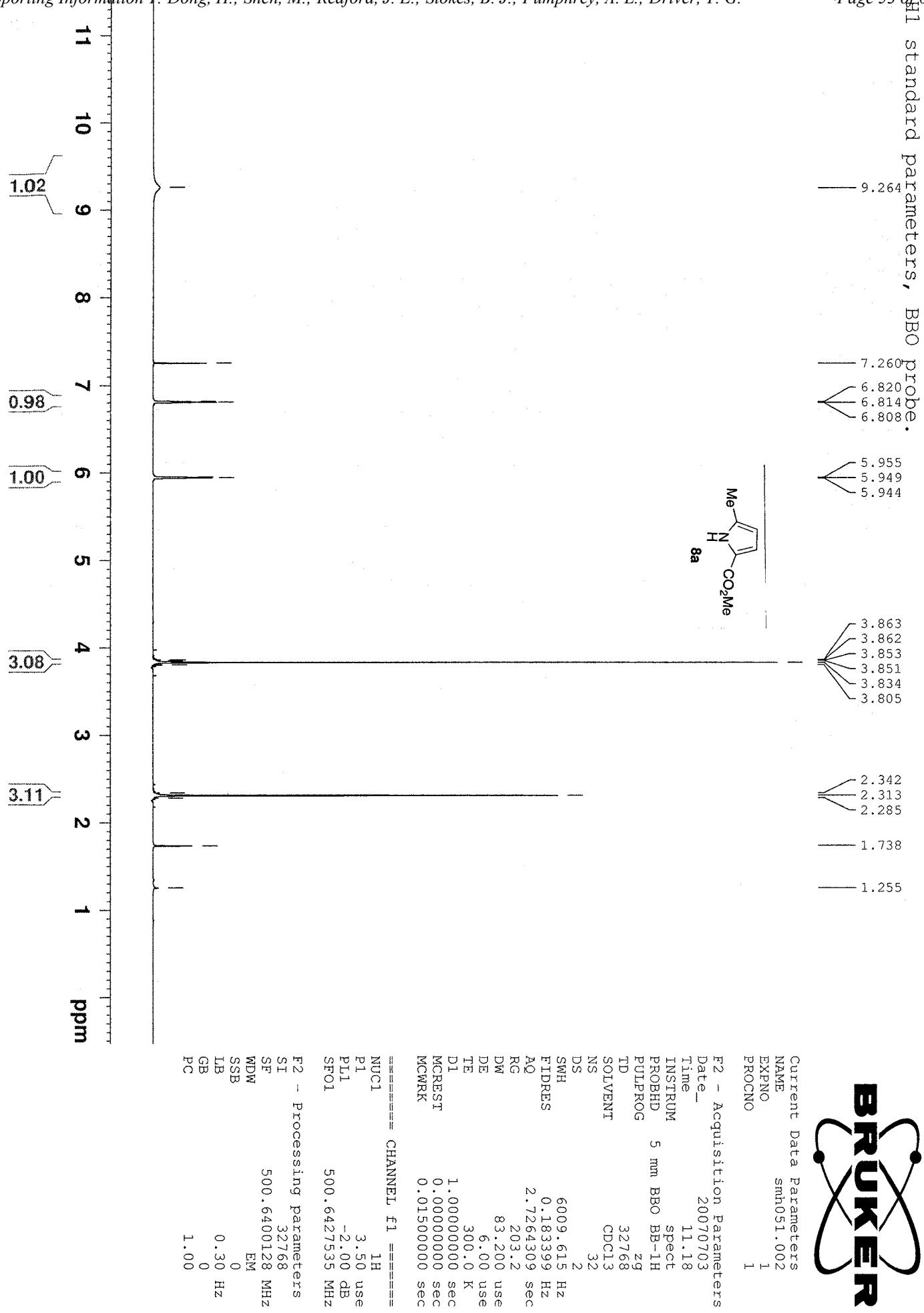
F2 - Processing parameters
SI 32768
SF 500.6400128 MHz
WDW EM
SSB 0
LB 0 Hz
GB 0
PC 1.00



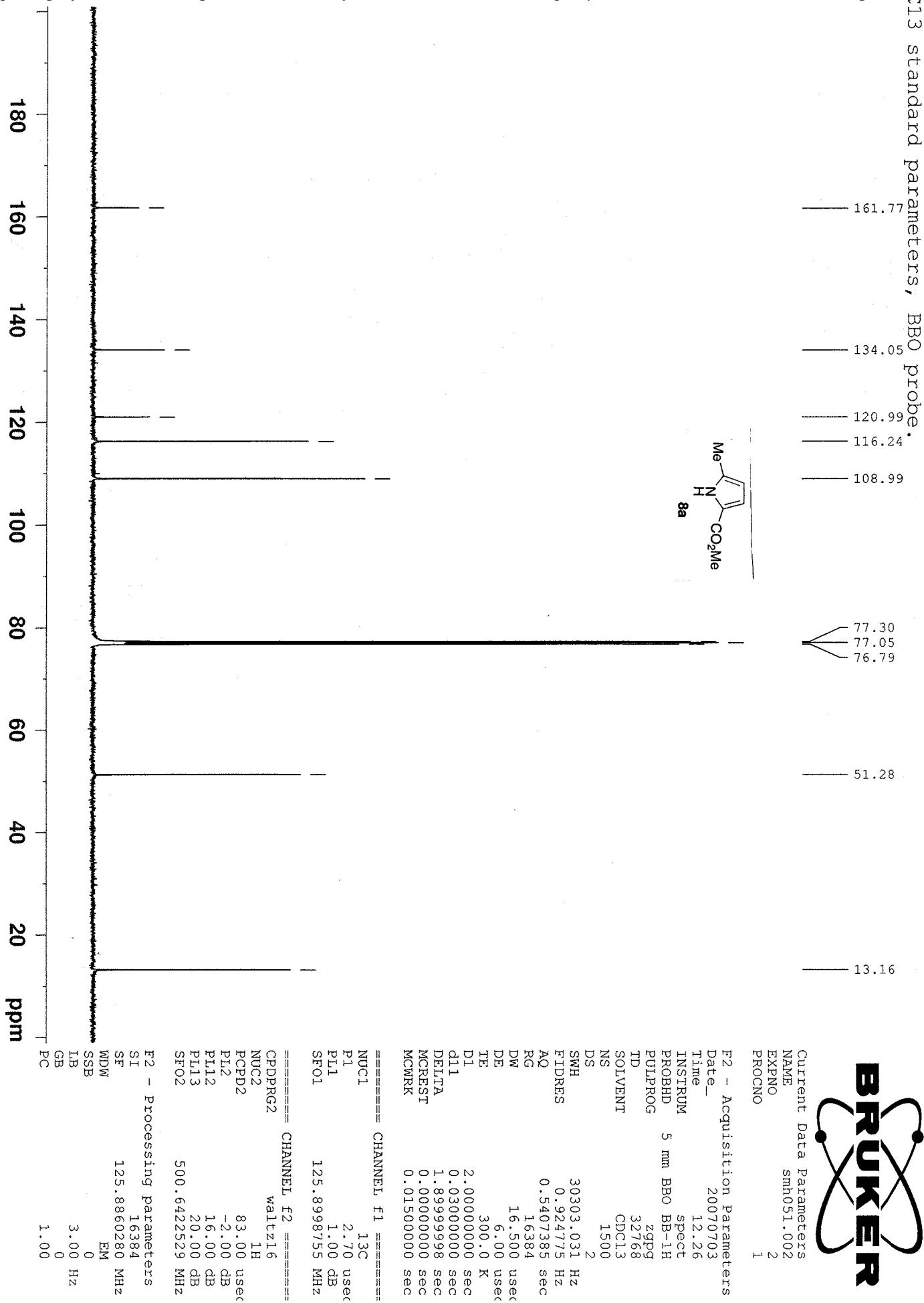


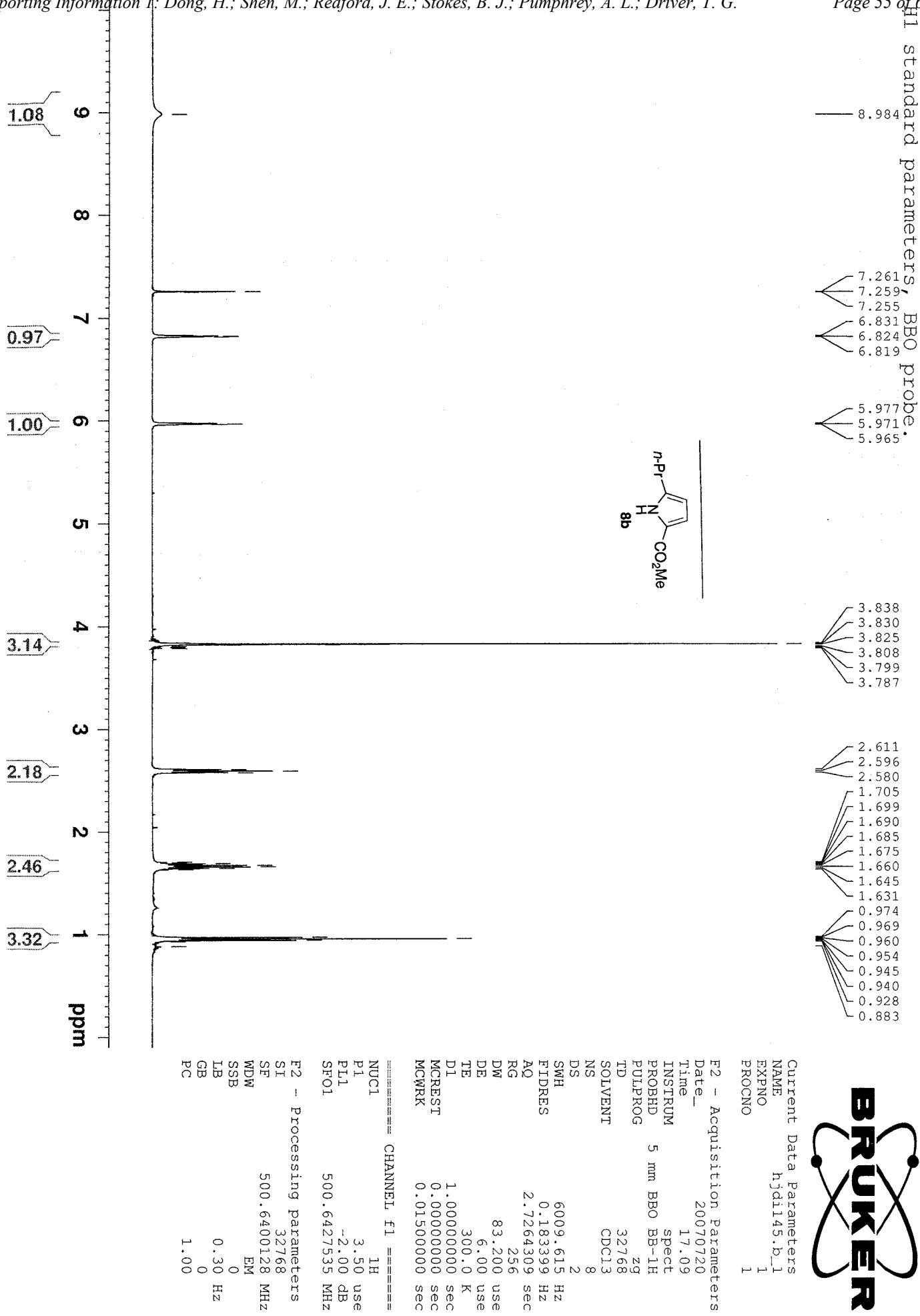


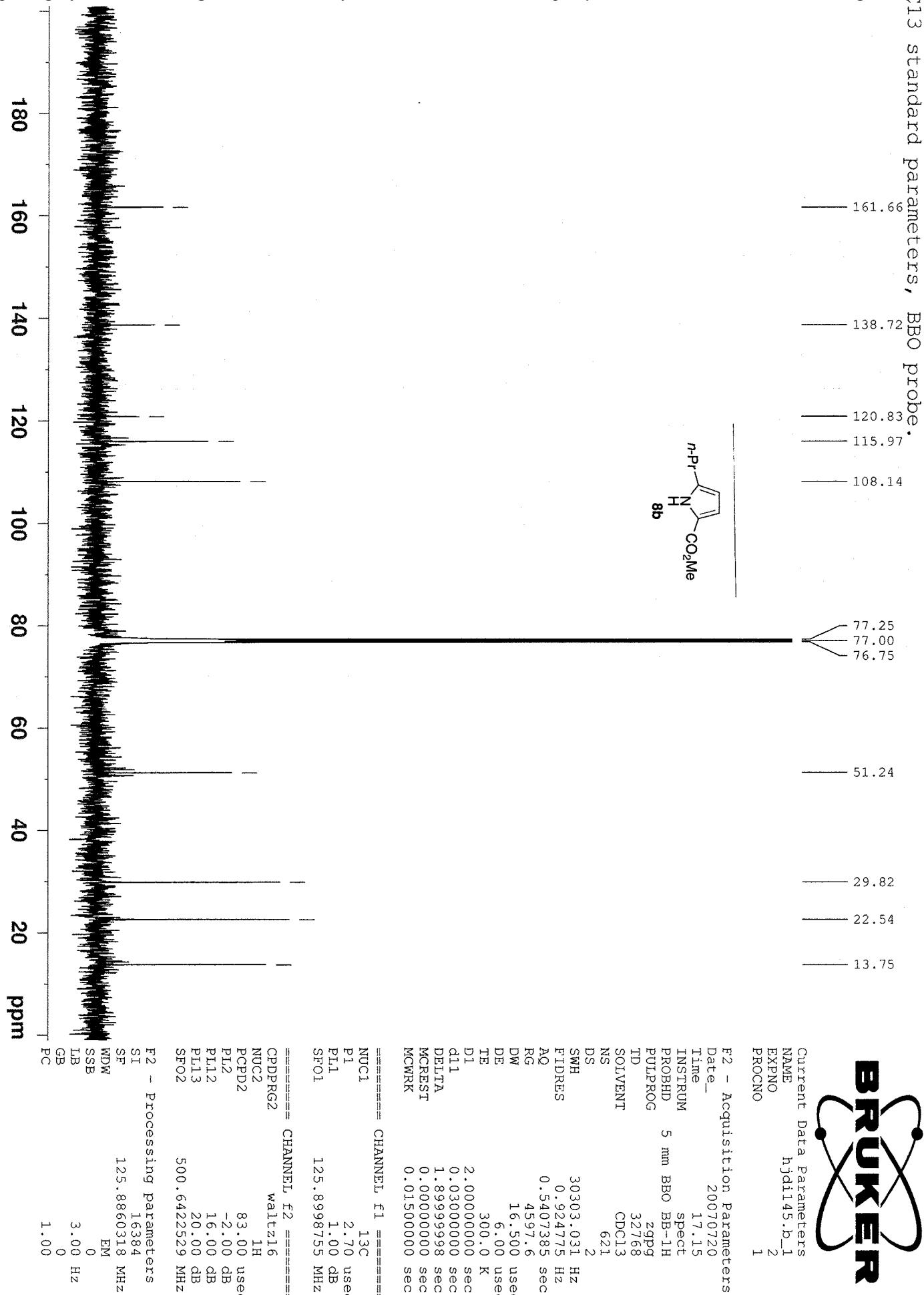




13 standard parameters, BBO probe.



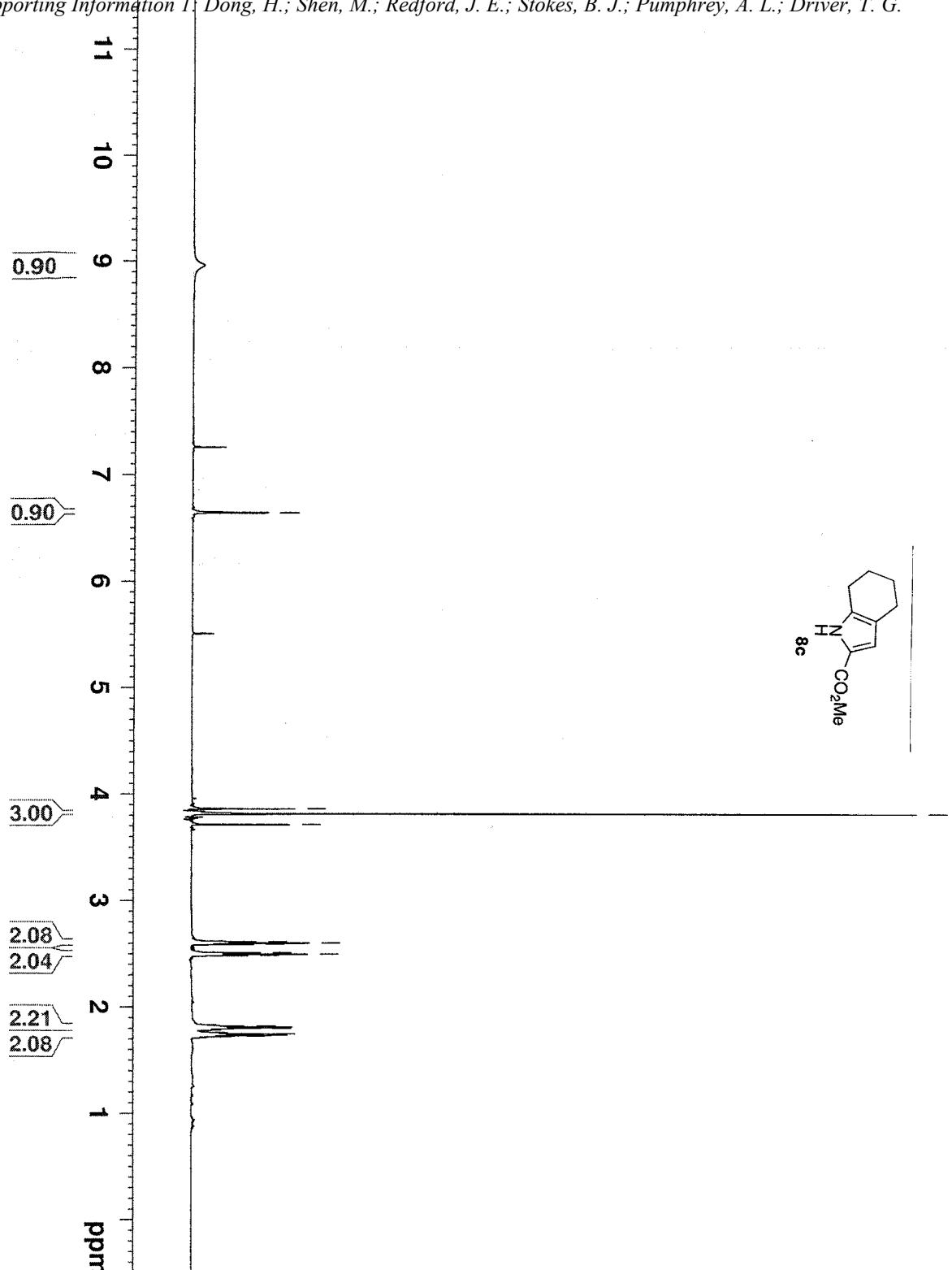




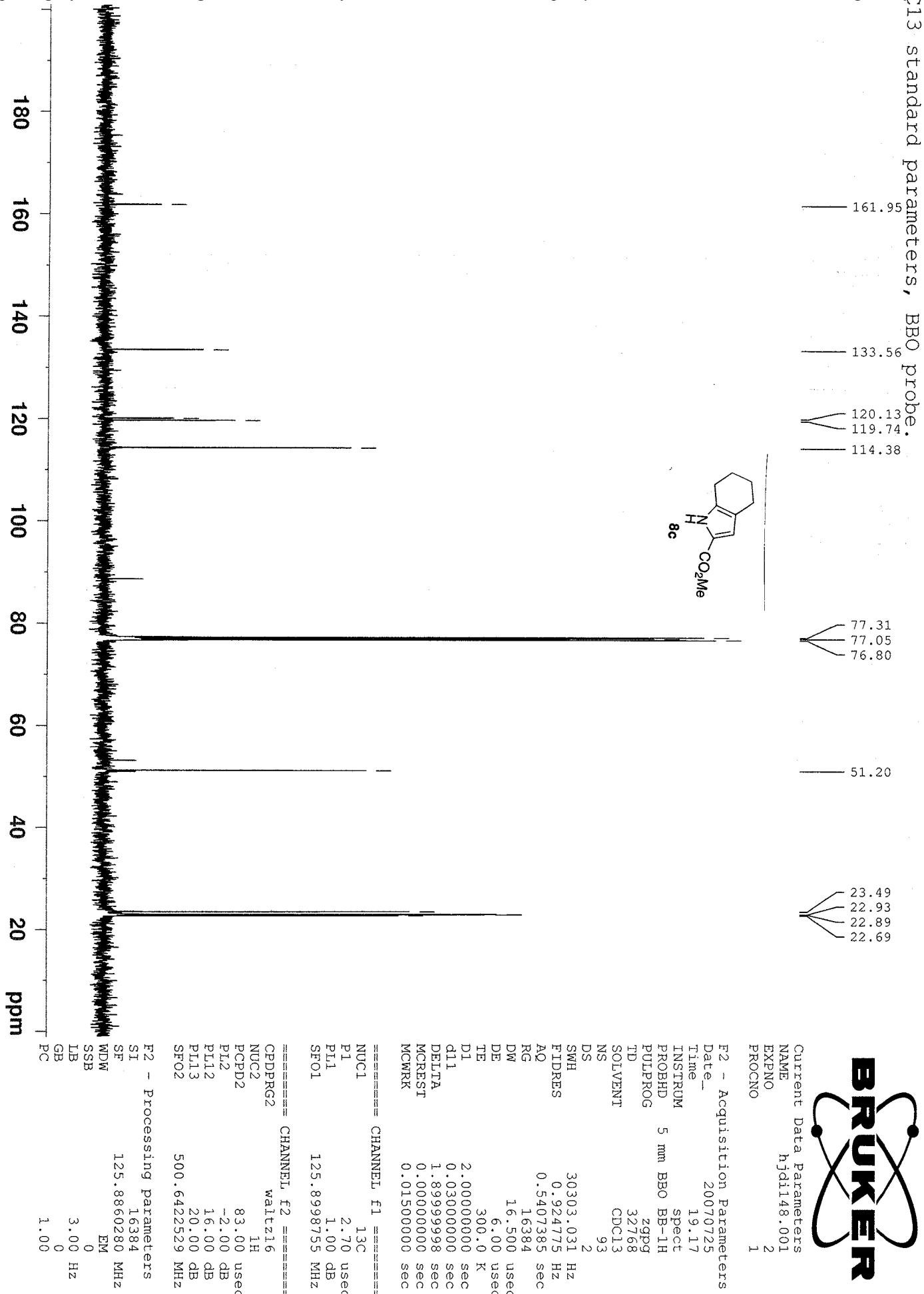
¹H standard parameters, BBO probe.

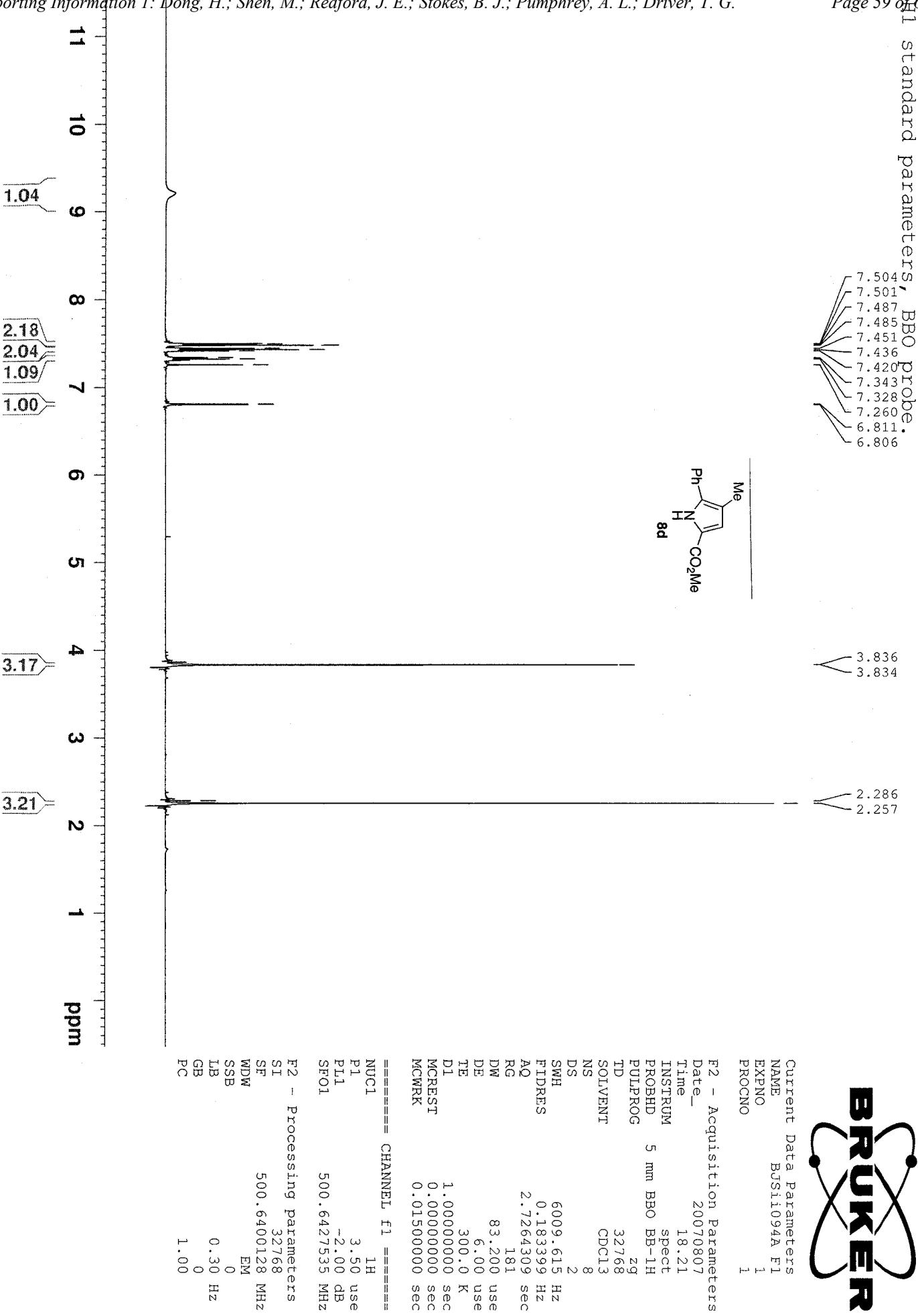
6.648
6.644

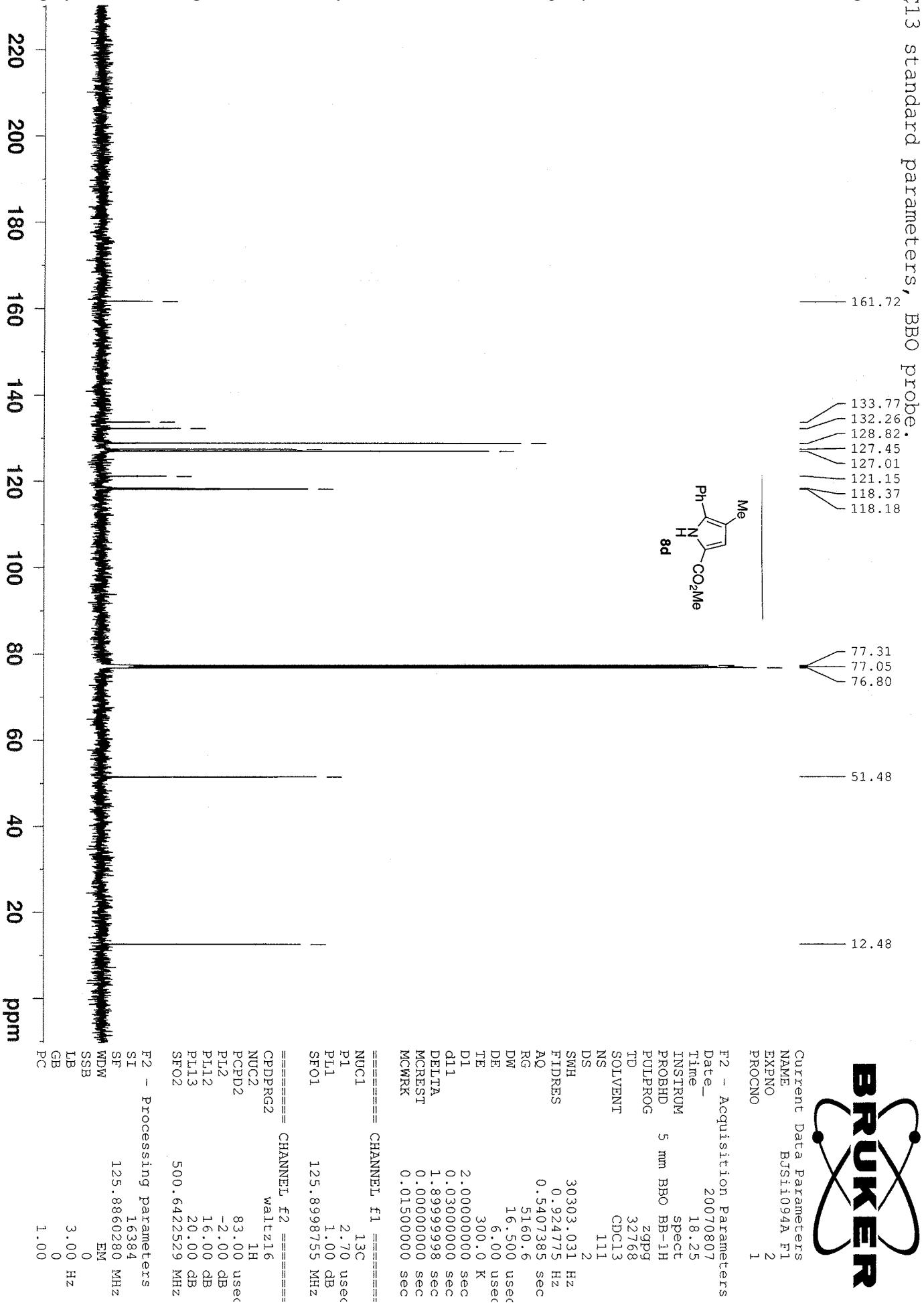
3.865
3.863
3.817
3.815
3.716
3.714
2.616
2.604
2.592
2.510
2.498
2.487
1.822
1.816
1.812
1.804
1.800
1.748
1.745
1.737
1.733
1.726

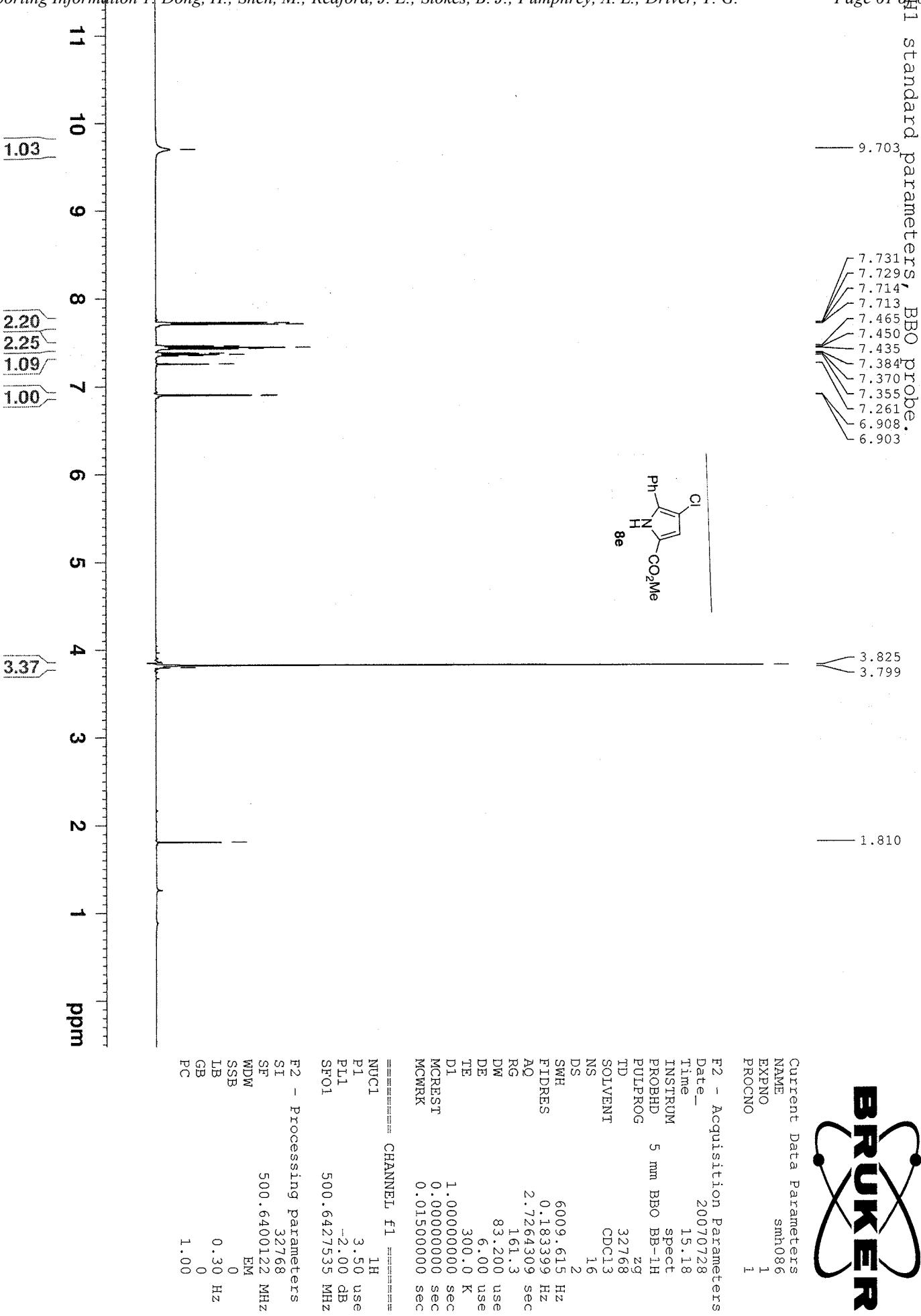


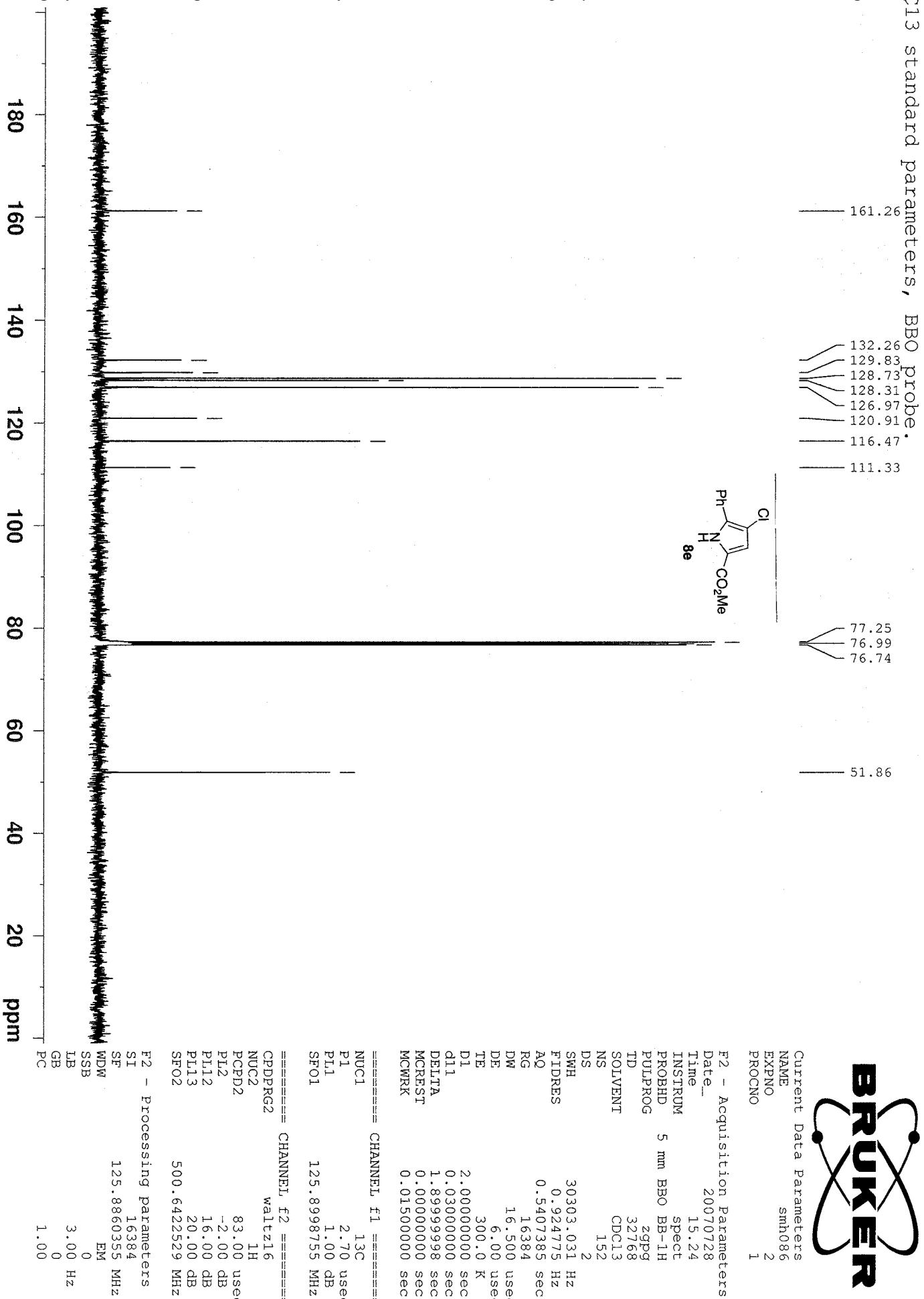
Current Data Parameters	
NAME	hjdl148.001
EXPNO	1
PROCNO	1
F2 - Acquisition Parameters	
DATE	20070725
TIME	19.12
INSTRUM	spec
PROBHD	5 mm BBO BB-1H
PULPROG	zg
ID	32768
SOLVENT	CDCl ₃
NS	8
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7264309 sec
RG	128
DW	83.200 use
DE	6.00 use
TE	300.0 K
DI	1.00000000 sec
MOREST	0.00000000 sec
MCWRK	0.01500000 sec
===== CHANNEL f1 =====	
NUC1	1H
P1	3.50 use
PL1	-2.00 dB
SFO1	500.6427535 MHz
F2 - Processing parameters	
ST	32768
SF	500.6400128 MHz
WDW	EM
SSB	0
LB	0
GB	0.30 Hz
PC	1.00

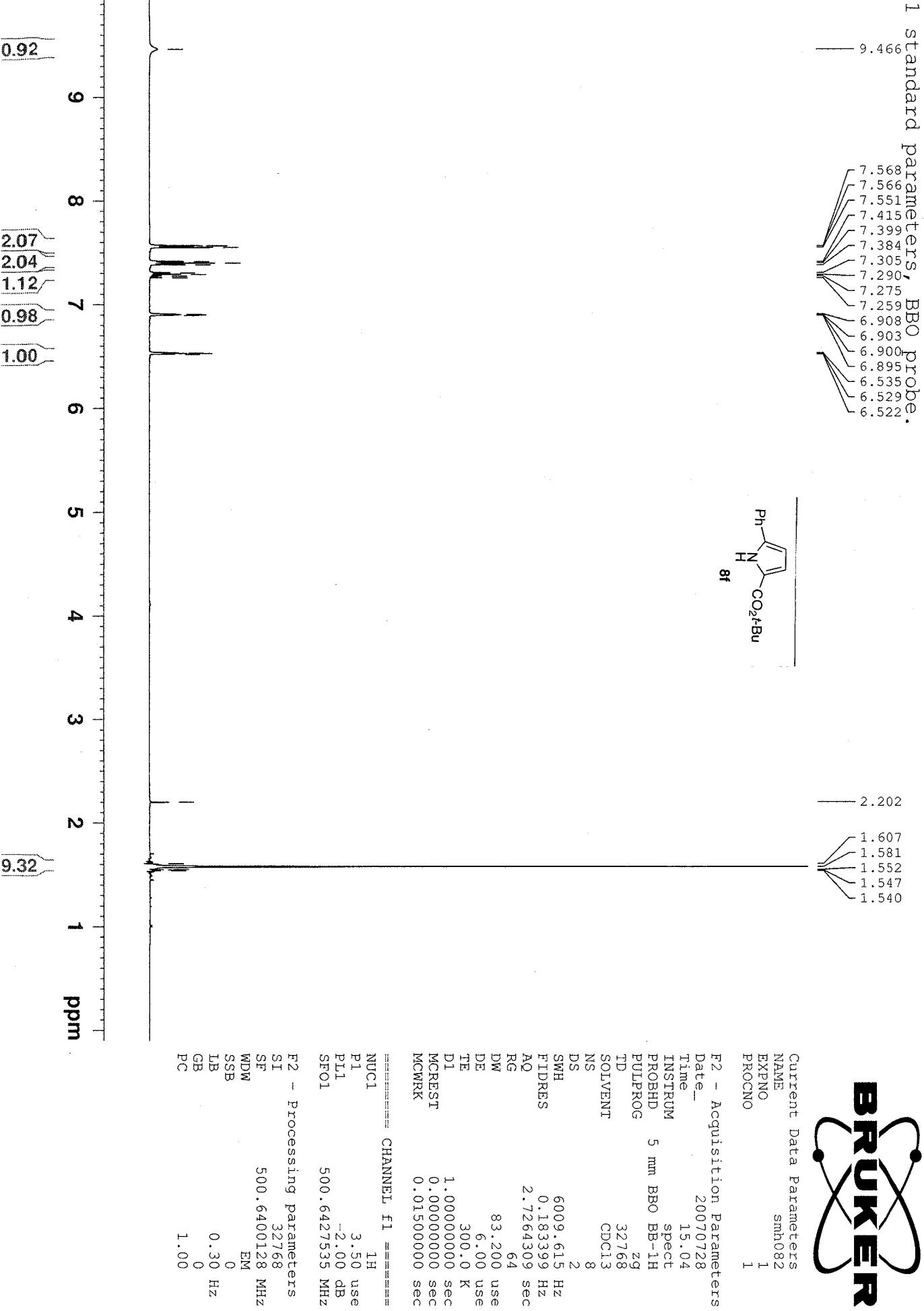


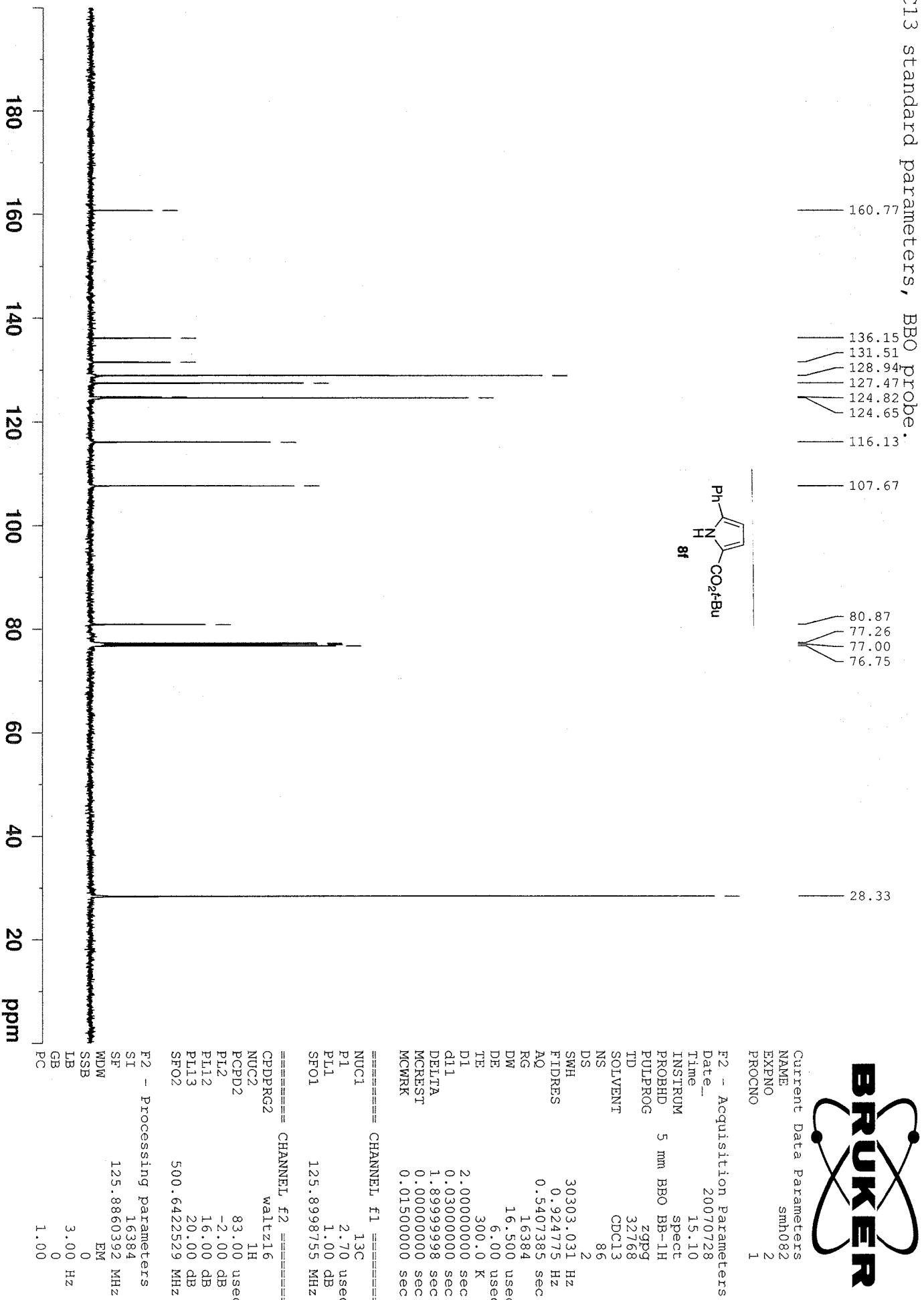


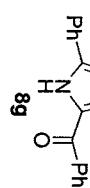
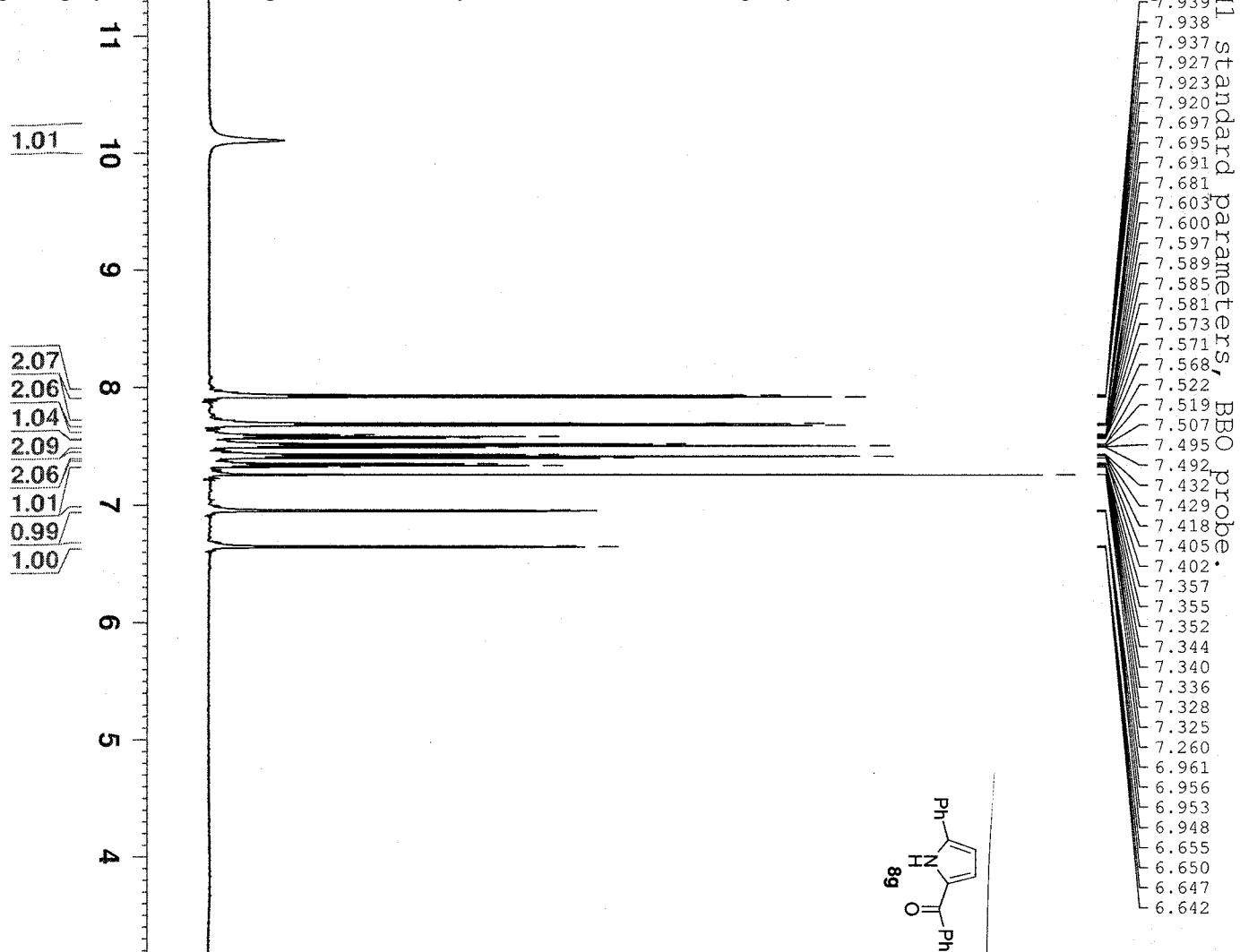












Current	Data	Parameters
NAME	hjdi163.a	
EXPNO	1	
PROCNO	1	

F2 - Acquisition Parameters

DATE	20070911
TIME	17.26
INSTRUM	spec
PROBHD	5 mm BBO BB-1H
PULPROG	zg
ID	32768
SOLVENT	CDCl ₃
NS	8
DS	2
SWH	6009.615 Hz
FIDRES	0.183399 Hz
AQ	2.7264309 sec
RG	362
DW	83.200 use
DE	6.00 use
TE	300.0 K
DI	1.0000000 sec
MREST	0.0150000 sec
MCWRK	0.0150000 sec

===== CHANNEL f1 =====

NUC1	1H
P1	3.50 use
PL1	-2.00 dB
SFO1	500.6427535 MHz

F2 - Processing parameters

ST	32768
SF	500.6400126 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00



C13 standard parameters, BBO probe.

