Supplementary Information

Modifying the phenyl group of PUGNAc: Reactivity tuning to deliver selective inhibitors for *N*-acetyl-D-glucosaminidases

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Experimental

General

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were obtained on Bruker ARX500 (500 MHz for ^{1}H and 126 MHz for ^{13}C) or Bruker AV600 or AV600III HD (600 MHz for ^{1}H and 151 MHz for ^{13}C) spectrometers. Solvents used for NMR were: deuteriochloroform ($CDCl_3$) with $CHCl_3$ (^{1}H, δ, 7.26 $CDCl_3$ (^{13}C, δ 77.16) used as an internal standard, tetradeuteriomethanol (CD_3OD) with CD_2HOD (^{1}H, δ 3.31) or CD_3OD (^{13}C, δ 49.00) used as an internal standard, hexadeuteriodimethyl sulfoxide (d_6-DMSO) with $CD_3S(O)CD_2H$ (^{1}H, δ 2.50) or $(CD_3)_2SO$ (^{13}C, δ 39.52) used as an internal standard, deuterium oxide (D_2O) with DHO (^{1}H, δ 4.79) or CH_3OH (^{13}C, δ 49.50) used as an internal standard.[1] All compounds were dried under vacuum to constant weight before analysis. High resolution mass spectra (HR-MS) were recorded with a Waters LCT Premier XE spectrometer, run in W-mode, using ESI or APCI ionisation methods as indicated, with MeCN:water (9:1) as a matrix. Flash chromatography was performed on BDH silica gel with the specified solvents. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F254 aluminium-backed plates that were stained by heating (>200 °C) with 5% solution of sulfuric acid in EtOH.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *O′*-(4-nitrophenyl)carbonate **1**

N,*N*-Diisopropylethylamine (37 μL, 0.21 mmol) and 4-nitrophenylchloroformate (0.21 mmol) were added to a stirred solution of hydroximolactone **2**[2] (70 mg, 0.19 mmol) in THF (3.5 mL) at 0°C. After 1.5 h., the reaction mixture was concentrated. Flash chromatography (EtOAc:hexane 7:3) of the residue afforded the carbonate **1** as a colourless oil (43 mg, 36%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.27 (AA′BB′, 2H), 7.41 (AA′BB′, 2H), 7.07 (d, J = 8.0 Hz, 1H), 5.43 (dd, J = 9.2, 9.2 Hz, 1H), 5.32 (dd, J = 8.8, 8.8 Hz, 1H), 4.80 (dd, J = 8.2, 9.2 Hz, 1H), 4.59 (ddd, J = 2.5, 3.5, 8.6 Hz, 1H), 4.46 (dd, J = 3.5, 13.0 Hz, 1H), 4.31 (dd, J = 2.5, 13.0 Hz, 1H), 2.12 (s, 3H), 2.05 (s, 3H), 2.00 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 171.1, 170.3, 170.0, 169.2, 158.8, 155.0, 151.1, 145.6, 125.4, 121.6, 77.6, 71.3, 67.0, 61.2, 49.8, 22.6, 20.6, 20.44, 20.4. HR-MS (APCI) *m/z* 548.1138; $[M+Na]^+$ requires 548.1129.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-phenyl carbamate **3**

Method 1: Aniline (21 μL, 0.23 mmol) was added to a stirred solution of DIPEA (13 μL, 0.080 mmol) and the 4-nitrophenylcarbonate **1** (40 mg, 0.076 mmol) in THF (2.0 mL) at 0°C. After 24 h., the reaction mixture was concentrated and the residue dissolved in CH_2Cl_2, washed with water (15 mL), brine (15 mL), dried ($MgSO_4$), filtered and concentrated. Flash chromatography (EtOAc:hexane 7:3) of the residue yielded the triacetate **3** as a colourless oil (30 mg, 50%). The ^{1}H and ^{13}C NMR spectra was consistent with that found in the literature.[2]

Method 2: N,*N*-Diisopropylethylamine (37 μL, 0.21 mmol) and 4-nitrophenylchloroformate (43 mg, 0.21 mmol) were added to a stirred solution of hydroximolactone **2**[2] (70 mg, 0.19 mmol) in THF (3.5 mL) at 0°C. After 1.5 h., aniline (0.21 mmol) and DIPEA (37 μL, 0.21 mmol) were added at 0°C and the reaction mixture was concentrated once all the *in situ* carbonate **1** was consumed, as judged by TLC. Flash chromatography of the resultant residue (EtOAc:hexane 7:3) yielded the triacetate **3** as a colourless oil (56 mg, 69%).

*General preparation of 3,4,6-tri-O-acetyl carbamates **4-33**, using the in situ method.*

Procedure 1

N,*N*-Diisopropylethylamine (1.1 equiv) and 4-nitrophenylchloroformate (1.1 equiv) were added to a stirred solution of **2**[2] (1.0 equiv) in THF (20 mL/mmol) at 0°C. After 1.5 h., the appropriate amine (1.1 equiv) and DIPEA (1.5 equiv) were added at 0°C and the reaction mixture was concentrated once all the *in situ* carbonate **1** was consumed, as judged by TLC.

Procedure 2

N,*N*-Diisopropylethylamine (1.1 equiv) and 4-nitrophenylchloroformate (1.1 equiv) were added to a stirred solution of **2**[2] (1.0 equiv) in THF (20 mL/mmol) at 0°C. After 1.5 h., the appropriate amine hydrochloride (1.1 equiv) and DIPEA (2.5 equiv) were added at 0°C and the reaction mixture was concentrated once all the *in situ* carbonate **1** was consumed, as judged by TLC.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(4-methylphenyl) carbamate **4**

Using **2** and 4-methylaniline according to Procedure 1 and flash chromatography (EtOAc:hexane 3:1) yielded the triacetate **4** as a colourless oil (60 mg, 64%). R_f 0.32 (EtOAc:hexane 7:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51 (*br* s, 1H), 7.29 (AA′BB′, 2H), 7.13 (AA′BB′, 2H), 6.41 (d, *J* = 8.0 Hz, 1H), 5.36-5.32 (m, 2H), 4.96 (dd, *J* = 8.5, 9.0 Hz, 1H), 4.47-4.41 (m, 2H), 4.33 (dd, *J* = 2.0, 12.5 Hz, 1H), 2.31 (s, 3H), 2.14 (s, 3H), 2.08 (s, 6H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.5, 170.4, 170.3, 169.1, 154.8, 151.7, 134.2, 134.0, 129.9, 119.4, 77.4, 71.3, 67.2, 61.3, 49.5, 23.0, 20.8, 20.7, 20.6, 20.5. HR-MS (APCI) *m/z* 494.1775; $[M+H]^+$ requires 494.1775.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(4-methoxyphenyl) carbamate **5**

Using **2** and 4-anisidine according to Procedure 1 and flash chromatography (EtOAc:hexane 4:1) yielded the triacetate **5** as a colourless oil (60 mg, 95%). R_f 0.30 (EtOAc:hexane, 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (*br* s, 1H), 7.32 (AA′BB′, 2H), 6.87 (AA′BB′, 2H), 6.44 (d, *J* = 8.5 Hz, 1H), 5.37-5.31 (m, 2H), 4.97 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.46-4.32 (m, 3H), 3.79 (s, 3H), 2.14 (s, 3H), 2.08 (s, 6H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.5, 170.4, 170.3, 169.1, 156.6, 154.7, 152.1, 129.7, 121.4, 114.4, 77.4, 71.3, 67.2, 61.3, 55.5, 49.5, 23.0, 20.7, 20.6, 20.5. HR-MS (APCI) *m/z* 532.1525; $[M+Na]^+$ requires 532.1543.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(4-bromophenyl)carbamate **6**

Using **2** and 4-bromoaniline according to Procedure 1 and flash chromatography (EtOAc:hexane 7:3) yielded the triacetate **6** as a colourless oil (20 mg, 23%). R_f 0.27 (EtOAc:hexane 7:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (*br* s, 1H), 7.42 (AA′BB′, 2H), 7.33 (AA′BB′, 2H), 6.87 (d, *J* = 7.5 Hz, 1H), 5.39 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.33 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.84 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.51 (ddd, *J* = 2.5, 3.0, 8.5 Hz, 1H), 4.41 (dd, *J* = 3.5, 13.0 Hz, 1H), 4.31 (dd, *J* = 2.5, 13.0 Hz, 1H), 2.11 (s, 3H), 2.06 (s, 3H), 2.04, (s, 3H), 2.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.6, 170.4, 170.2, 169.1, 155.6, 154.7, 151.2, 136.1, 132.1, 120.1, 116.8, 77.2, 71.3, 67.1, 61.2,

49.7, 22.9, 20.62, 20.6, 20.5. HR-MS (APCI) *m/z* 558.0717; $[M+H]^+$ requires 558.0723.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-benzyl carbamate **7**

Using **2** and $BnNH_2$ according to Procedure 1 and flash chromatography (EtOAc:hexane 9:1) yielded the triacetate **7** as a colourless oil (54 mg, 55%). R_f 0.35 (EtOAc:hexane 9:1).^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36-7.27 (m, 5H), 6.14 (d, *J* = 9.0 Hz, 1H), 5.97 (t, *J* = 5.0 Hz, 1H), 5.34 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.26 (dd, *J* = 10.0, 10.0 Hz, 1H), 4.97 (dd, *J* = 8.5, 10.0 Hz, 1H), 4.49-4.37 (m, 3H), 4.29 (dd, *J* = 1.5, 12.5 Hz, 1H), 2.13 (s, 3H), 2.07 (s, 3H), 2.06, (s, 3H), 1.95 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.5, 170.4, 170.1, 169.1, 154.6, 154.1, 137.7, 128.8, 127.8, 127.6, 77.5, 71.4, 67.3, 61.4, 49.4, 45.3, 22.9, 20.64, 20.6, 20.5. HR-MS (APCI) *m/z* 516.1590; $[M+Na]^+$ requires 516.1594.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-cyclo-propylcarbamate **8**

Using **2** and cyclopropylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 3:1) yielded the triacetate **8** as a colourless oil (68 mg, 89%). R_f 0.28 (EtOAc:hexane 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.52 (d, *J* = 6.0 Hz, 1H), 5.49 (s, 1H), 5.34-5.27 (m, 2H), 5.28 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.94 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.45-4.39 (m, 2H), 4.29 (dd, *J* = 3.0, 13.0 Hz, 1H), 2.67-2.61 (m, 1H), 2.12 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.03, (s, 3H), 0.79-0.73 (m, 2H), 0.58-0.54 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.4, 170.3, 169.1, 155.5, 154.3, 71.5, 67.3, 61.4, 49.3, 22.9, 22.6, 20.63, 20.6, 20.5, 6.8. HR-MS (APCI) *m/z* 444.1603; $[M+H]^+$ requires 444.1618.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-cyclo-butylcarbamate **9**

Using **2** and cyclobutylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 9:1) yielded the triacetate **9** as a colourless oil (72 mg, 53%). R_f 0.29 (EtOAc:hexane 9:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.40 (d, *J* = 8.5 Hz, 1H), 5.78 (d, *J* = 7.5 Hz, 1H), 5.33 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.28 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.96

(dd, *J* = 8.5, 8.5 Hz, 1H), 4.43-4.40 (m, 2H), 4.30 (dd, *J* = 3.5, 13.5 Hz, 1H), 4.22-4.19 (m, H), 2.37-2.32 (m 2H), 2.13 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.04, (s, 3H), 1.94-1.95 (m, 2H), 1.76-1.68 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.4, 170.3, 169.1, 154.0, 153.5, 71.5, 67.3, 61.3, 49.4, 46.3, 31.0, 23.0, 20.64, 20.6, 20.5, 14.9. HR-MS (APCI) *m/z* 458.1765; $[M+H]^+$ requires 458.1775.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-cyclopentylcarbamate **10**

Using **2** and cyclopentylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 9:1) yielded the triacetate **10** as a colourless oil (70 mg, 79%). R_f 0.33 (EtOAc:hexane 9:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.30 (d, *J* = 7.5 Hz, 1H), 5.60 (d, *J* = 7.5 Hz, 1H), 5.34 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.27 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.96 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.43-4.37 (m, 2H), 4.30 (dd, *J* = 2.5, 12.5 Hz, 1H), 4.05-4.01 (m, 1H), 2.13 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.03, (s, 3H), 1.99-1.95 (m, 2H), 1.70-1.58 (m, 4H), 1.47-1.42 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.4, 170.3, 169.0, 154.1, 153.7, 71.4, 67.3, 61.4, 53.0, 49.4, 33.1, 33.0, 23.5, 23.0, 20.64, 20.6, 20.5. HR-MS (APCI) *m/z* 472.1915; $[M+H]^+$ requires 472.1931.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-cyclohexylcarbamate **11**

Using **2** and cyclohexylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 3:1) yielded the triacetate **11** as a colourless oil (67 mg, 76%). R_f 0.25 (EtOAc:hexane 7:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.18 (d, *J* = 8.5 Hz, 1H), 5.54 (d, *J* = 8.0 Hz,1H), 5.35 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.25 (dd, *J* = 10.0, 10.0 Hz, 1H), 5.00 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.41 (dd, *J* = 3.5, 12.5 Hz, 1H), 4.35 (ddd, *J* = 2.5, 3.5, 12.5 Hz, 1H), 4.30 (dd, *J* = 2.5, 12.5 Hz, 1H), 3.58-3.56 (m, 1H), 2.14 (s, 3H), 2.08 (*br* s, 2H), 2.07 (s, 3H), 2.03, (s, 3H), 1.97-1.94 (m, 2H), 1.72-1.68 (m, 2H), 1.41-1.31 (m, 3H), 1.22-1.15 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.44, 170.4, 170.1, 169.1, 153.6, 153.4, 71.4, 67.3, 61.4, 50.1, 49.5, 33.0, 25.4, 24.6, 23.0, 20.7, 20.6, 20.5. HR-MS (APCI) *m/z* 486.2081; $[M+H]^+$ requires 486.2088.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(adamant-1-yl)carbamate **12**

Using **2** and adamant-1-ylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 3:1) yielded the triacetate **12** as a colourless oil (99 mg, 86%). R_f 0.29 (EtOAc:hexane 3:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.22 (d, *J* = 7.0 Hz, 1H), 5.44 (*br* s, 1H), 5.36 (dd, *J* = 9.0, 9.0 Hz, 1H), 5.25 (dd, *J* = 10.0, 10.0 Hz, 1H), 5.00 (dd, *J* = 9.0, 10.0 Hz, 1H), 4.40 (dd, *J* = 3.0, 12.0 Hz, 1H), 4.35-4.29 (m, 2H), 2.14 (s, 3H), 2.09 (*br* s, 2H), 2.07 (s, 3H), 2.06, (s, 3H), 2.03 (s, 3H), 1.96 (*br* s, 6H), 1.68 (*br* s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.43, 170.4, 170.3, 169.1, 153.2, 152.0, 77.4, 71.5, 67.3, 61.4, 51.4, 49.4, 41.5, 36.2, 29.4, 23.0, 20.7, 20.6, 20.5. HR-MS (APCI) *m/z* 538.2423; $[M+H]^+$ requires 538.2401.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(2-amino-2-oxoeth-1-yl)carbamate **13**

Using **2** and glycinamide[3] according to Procedure 1 and flash chromatography (MeOH:EtOAc 1:9) yielded the triacetate **13** as a colourless oil (43 mg, 61%). R_f 0.15 (EtOAc:hexane:MeOH 75:23:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.17 (d, *J* = 8.4 Hz, 1H), 7.15 (dd, *J* = 5.4, 6.0 Hz, 1H), 6.62 (*br* s, 1H), 6.17 (*br* s, 1H), 5.38 (dd, *J* = 9.0, 9.0 Hz, 1H), 5.34 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.98 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.58-4.55 (m, 1H), 4.41 (dd, *J* = 2.4, 12.6 Hz, 1H), 4.31 (dd, *J* = 1.8, 12.6 Hz, 1H), 3.96 (dd, *J* = 6.0, 16.2 Hz, 1H), 3.82 (dd, *J* = 5.4, 16.2 Hz, 1H), 2.12 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02, (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 171.9, 171.1, 170.6, 170.4, 169.2, 155.8, 154.8, 71.4, 67.2, 61.2, 49.2, 43.9, 22.8, 20.6, 20.5. HR-MS (APCI) *m/z* 461.1514; $[M+H]^+$ requires 461.1520.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *(S)-N*-(1-amino-1-oxoprop-2-yl)carbamate **14**

Using **2** and (*S*)-alaninamide[4] according to Procedure 1 and flash chromatography (MeOH:EtOAc 3:97) yielded the triacetate **14** as a colourless oil (90 mg, 89%). R_f 0.40 (MeOH:EtOAc 1:19). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00-6.98 (m, 2H), 6.12 (*br* s, 1H), 5.71 (*br* s, 1H), 5.39 (dd, *J* = 9.0, 9.0 Hz, 1H), 5.33 (dd, *J* = 10.0, 10.0 Hz, 1H), 5.01 (dd, *J* = 9.5, 9.5 Hz, 1H), 4.67-4.64 (m, 1H), 4.40 (dd, *J* = 2.5, 13.0 Hz, 1H), 4.30 (dd, *J* = 1.5, 13.0 Hz, 1H), 4.22 (quintet, *J* = 6.5 Hz, 1H), 2.12 (s, 3H), 2.07

(s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 1.47 (d, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 175.3, 170.7, 170.6, 170.5, 169.1, 155.2, 154.1, 71.7, 66.8, 61.0, 50.7, 49.4, 22.8, 20.7, 20.6, 20.5, 17.9. HR-MS (APCI) *m/z* 475.1682; $[M+H]^+$ requires 475.1676.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(*(S)*-1-amino-3-hydroxy-1-oxo-prop-2-yl) carbamate **15**

Using **2** and (*S*)-2-amino-3-hydroxypropanamide[5] according to Procedure 1 and flash chromatography (MeOH/EtOAc 3:47) gave the triacetate **15** as a colourless oil (70 mg, 64%). R_f 0.15 (MeOH/EtOAc 3:47). ^{1}H NMR (500 MHz, CD_3OD) δ 5.44 (dd, J = 8.9, 8.9 Hz, 1H), 5.34 (dd, J = 8.9, 8.9 Hz, 1H), 4.87 (dd, J = 9.1, 9.1 Hz, 1H), 4.60-4.56 (m, 3H), 4.45 (dd, J = 4.0, 12.9 Hz, 1H), 4.41-4.28 (m, 2H), 4.25 (dd, J = 4.6, 4.6 Hz, 1H), 3.85 (dd, J = 4.7, 11.2 Hz, 1H), 3.80 (dd, J = 4.7, 11.2 Hz, 1H), 2.10 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (126 MHz, CD_3OD) δ 174.6, 173.7, 172.1, 171.4, 171.0, 156.9, 156.4, 78.4, 72.5, 62.7, 57.8, 50.6, 22.6, 20.6, 20.5, 20.5. HR-MS (APCI) *m/z* 491.1619; $[M+H]^+$ requires 491.1625.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *(S)*-*N*-(1-amino-1-oxo-3-phenylprop-2-yl)carbamate **16**

Using **2** and (*S*)-phenylalaninamide[6] according to Procedure 1 and flash chromatography (MeOH:EtOAc 1:39) yielded the triacetate **16** as a colourless oil (83 mg, 78%). R_f 0.17 (EtOAc:hexane:MeOH 75:23:2). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31-7.24 (m, 6H), 7.02 (d, J = 8.4 Hz, 1H), 5.95 (*br* s, 1H), 5.72 (*br* s, 1H), 5.38 (dd, J = 9.0, 9.0 Hz, 1H), 5.28 (dd, J = 9.6, 9.6 Hz, 1H), 5.01 (dd, J = 9.0, 9.0 Hz, 1H), 4.68-4.66 (m, 1H), 4.39-4.34 (m, 2H), 4.29 (dd, J = 2.4, 12.0 Hz, 1H), 3.20 (dd, J = 7.2, 14.8 Hz, 1H), 3.10 (dd, J = 7.8, 13.8 Hz, 1H), 2.11 (s, 3H), 2.03 (s, 3H), 2.02 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 174.2, 170.7, 170.6, 170.4, 169.1, 155.4, 154.3, 72.0, 66.7, 60.8, 57.1, 49.2, 38.0, 22.8, 20.7, 20.6, 20.5. HR-MS (APCI) *m/z* 551.1979; $[M+H]^+$ requires 551.1989.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(2-hexylamino-2-oxoeth-1-yl) carbamate **17**

Using **2** and the hydrochloride[7] according to Procedure 2 and flash chromatography

(MeOH/EtOAc 1:19) gave the triacetate **17** as a white solid (85 mg, 70%). R_f 0.35 (EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (t, *J* = 5.7 Hz, 1H), 6.91 (d, *J* = 8.5 Hz, 1H), 6.21 (t, *J* = 5.6, Hz, 1H), 5.38 (dd, *J* = 9.0, 9.0 Hz, 1H), 5.33 (dd, *J* = 8.6, 8.6 Hz, 1H), 4.98 (dd, *J* = 8.9, 8.9 Hz, 1H), 4.58 (ddd, *J* = 2.9, 2.9, 8.7 Hz, 1H), 4.42 (dd, *J* = 3.3, 12.9 Hz, 1H), 4.28 (dd, *J* = 2.5, 12.9 Hz, 1H), 3.94 (dd, *J* = 5.9, 16.4 Hz, 1H), 3.77 (dd, *J* = 5.2, 16.3 Hz, 1H), 3.36-3.12 (m, 2H), 2.12 (s, 3H), 2.05 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.52-1.47 (m, 2H), 1.38-1.18 (m, 6H), 0.88 (app t, *J* = 6.8 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 170.6, 170.3, 169.3, 169.01, 155.8, 154.7, 77.4, 71.6, 67.4, 61.3, 49.4, 44.6, 40.0, 31.6, 29.5, 26.7, 23.0, 22.7, 20.8, 20.7, 14.1. HR-MS (APCI) *m/z* 545.2458; $[M+H]^+$ requires 545.2459.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-methyl carbamate **18**

Using **2** and methylamine hydrochloride according to Procedure 2 and flash chromatography (MeOH/EtOAc 3:97) gave the triacetate **18** as a white solid (40 mg, 57%). The ^{1}H NMR spectrum was consistent with that found in the literature.[8]

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-ethyl carbamate **19**

Using **2** and ethylamine hydrochloride according to Procedure 2 and flash chromatography (EtOAc) gave the triacetate **19** as a colourless oil (59 mg, 83%). R_f 0.32 (EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.54 (d, *J* = 8.5 Hz, 1H), 5.69 (br s, 1H), 5.46-5.22 (m, 2H), 4.97 (dd, *J* = 8.9, 8.9 Hz, 1H), 4.45-4.26 (m, 3H), 3.36 – 3.25 (m, 2H), 2.13 (s, 3H), 2.07 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.18 (app t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.5, 170.5, 169.3, 154.8, 154.2, 71.7, 67.5, 61.5, 49.4, 36.3, 23.1, 20.8, 20.8, 20.7, 15.1. HR-MS (APCI) *m/z* 432.1621; $[M+H]^+$ requires 432.1618.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(prop-1-yl)carbamate **20**

Using **2** and 1-propylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 17:3) yielded the triacetate **20** as a colourless oil (64 mg, 71%). R_f 0.26 (EtOAc:hexane 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.01 (d, *J* = 8.5 Hz, 1H),

5.93 (t, *J* = 5.5 Hz, 1H), 5.32 (dd, *J* = 8.0, 8.0 Hz, 1H), 5.28 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.88 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.50 (ddd, *J* = 2.5, 3.5, 8.0 Hz, 1H), 4.40 (dd, *J* = 3.5, 12.5 Hz, 1H), 4.27 (dd, *J* = 2.5, 13.0 Hz, 1H), 3.19-3.15 (m, 2H), 2.09 (s, 3H), 2.04 (s, 6H), 1.99 (s, 3H), 1.54 (heptet, *J* = 7.5 Hz, 2H) 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.4, 170.4, 170.0, 169.1, 155.1, 154.1, 76.7, 71.4, 67.3, 61.2, 49.3, 42.8, 22.8, 22.76, 20.5, 20.55, 20.5, 11.1. HR-MS (APCI) *m/z* 446.1781; $[M+H]^+$ requires 446.1775.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(but-1-yl)carbamate **21**

Using **2** and 1-butylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 9:1) yielded the triacetate **21** as a colourless oil (67 mg, 71%). R_f 0.28 (EtOAc:hexane 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (d, *J* = 8.0 Hz, 1H), 5.87 (t, *J* = 5.5 Hz, 1H), 5.32 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.29 (dd, *J* = 8.0, 8.0 Hz, 1H), 4.89 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.90 (ddd, *J* = 2.5, 3.5, 8.0 Hz, 1H), 4.40 (dd, *J* = 3.5, 12.5 Hz, 1H), 4.28 (dd, *J* = 2.5, 12.5 Hz, 1H), 3.23-3.18 (m, *2*H), 2.10 (s, 3H), 2.04 (s, 6H), 2.00 (s, 3H), 1.52-1.47 (m, 2H), 1.37-1.31 (m, 2H), 0.91 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.41, 170.4, 170.0, 169.1, 155.0, 154.1, 71.4, 67.3, 61.2, 49.3, 40.9, 31.6, 22.8, 20.6, 20.56, 20.5, 19.8, 13.6. HR-MS (APCI) *m/z* 460.1938; $[M+H]^+$ requires 460.1931.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(hex-1-yl)carbamate **22**

Using **2** and 1-hexylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 4:1) yielded the triacetate **22** as a colourless oil (69 mg, 69%). R_f 0.33 (EtOAc:hexane 4:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.99 (d, *J* = 8.4 Hz, 1H), 5.88 (t, *J* = 5.4 Hz, 1H), 5.32 (dd, *J* = 8.4, 8.4 Hz, 1H), 5.28 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.87 (dd, *J* = 7.8, 7.8 Hz, 1H), 4.99 (ddd, *J* = 2.4, 3.0, 8.4 Hz, 1H), 4.40 (dd, *J* = 3.0, 12.6 Hz, 1H), 4.28 (dd, *J* = 2.4, 12.6 Hz, 1H), 3.24-3.17 (m, *2*H), 2.09 (s, 3H), 2.04 (s, 6H), 1.99 (s, 3H), 1.51-1.49 (m, 2H), 1.33-1.23 (m, 6H), 0.86 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.4, 170.0, 169.1, 155.0, 154.1, 76.7, 71.4, 67.3, 61.2, 49.3, 41.2, 31.3, 29.5, 26.3, 22.8, 22.5, 20.6, 20.54, 20.5, 13.9. HR-MS (APCI) *m/z* 488.2259; $[M+H]^+$ requires 488.2244.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(prop-2-yl)carbamate **23**

Using **2** and 2-propylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 4:1) yielded the triacetate **23** as a colourless oil (48 mg, 67%). R_f 0.34 (EtOAc:hexane 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.23 (d, *J* = 8.0 Hz, 1H), 5.47 (d, *J* = 7.0 Hz, 1H), 5.34 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.27 (dd, *J* = 9.5, 9.5 Hz, 1H), 4.97 (dd, *J* = 9.5, 9.5 Hz, 1H), 4.43-4.37 (m, 2H), 4.30 (dd, *J* = 2.5, 12.5 Hz, 1H), 3.92-3.84 (m, 1H), 2.13 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.20 (t, *J* = 6.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.4, 170.2, 169.1, 153.7, 153.7, 71.5, 67.3, 61.4, 49.4, 43.5, 23.0, 22.8, 22.7, 20.7, 20.6, 20.5. HR-MS (APCI) *m/z* 446.1776; $[M+H]^+$ requires 446.1775.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(2-methylprop-1-yl)carbamate **24**

Using **2** and 2-methylpropylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 4:1) yielded the triacetate **24** as a colourless oil (73 mg, 74%). R_f 0.23 (EtOAc:hexane 4:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.22 (d, *J* = 8.5 Hz, 1H), 5.78 (t, *J* = 5.5 Hz, 1H), 5.35 (dd, *J* = 8.5, 8.5 Hz, 1H), 5.27 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.98 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.44-4.38 (m, 2H), 4.30 (dd, *J* = 2.0, 12.5 Hz, 1H), 3.13-3.04 (m, *2*H), 2.13 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.81 (septet, *J* = 7.5 Hz, 1H) 0.93 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.4, 170.4, 170.2, 169.1, 154.8, 153.7, 77.3, 71.4, 67.3, 61.4, 49.4, 48.5, 28.5, 23.0, 20.6, 20.6, 20.5, 19.9. HR-MS (APCI) *m/z* 460.1943; $[M+H]^+$ requires 460.1931.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(2-methylprop-2-yl)carbamate **25**

Using **2** and 2-methylprop-2-ylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 7:3) yielded the triacetate **25** as a colourless oil (62 mg, 62%). R_f 0.45 (EtOAc:hexane 7:3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.84 (d, *J* = 6.5 Hz, 1H), 5.61 (*br* s, 1H), 5.32-5.30 (m, 2H), 4.93 (dd, *J* = 9.0, 9.0 Hz, 1H), 4.43-4.38 (m, 2H), 4.28 (dd, *J* = 2.0, 12.5 Hz, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 2.00 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 170.7, 170.4, 170.2, 169.1, 153.7, 153.1, 77.1, 71.5, 67.3, 61.3, 51.1, 49.4, 28.6, 22.8, 20.6, 20.5, 20.5. HR-MS

(APCI) *m/z* 460.1926; $[M+H]^+$ requires 460.1931.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(prop-2-en-1-yl)carbamate **26**

Using **2** and allylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 4:1) yielded the triacetate **26** as a colourless oil (66 mg, 63%). R_f 0.32 (EtOAc:hexane 4:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 6.94 (d, *J* = 8.4 Hz, 1H), 6.00 (t, *J* = 5.4 Hz, 1H), 5.83 (ddt, *J* = 5.2, 10.2, 16.8 Hz, 1H), 5.33 (dd, *J* = 8.4, 8.4 Hz, 1H), 5.29 (dd, *J* = 8.4, 8.4 Hz, 1H), 5.19 (dd, *J* = 1.2, 16.8 Hz, 1H), 5.14 (dd, *J* = 1.2, 10.2 Hz, 1H), 4.88 (dd, *J* = 8.4, 8.4 Hz, 1H), 4.51 (ddd, *J* = 2.4, 3.6, 16.8 Hz, 1H), 4.41 (dd, *J* = 3.6, 13.2 Hz, 1H), 4.28 (dd, *J* = 2.4, 13.2 Hz, 1H), 3.84 (dd, *J* = 5.2, 5.4 Hz, 2H) 2.10 (s, 3H), 2.04 (s, 6H), 1.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.4, 170.4, 170.0, 169.1, 154.9, 154.4, 133.6, 116.5, 71.4, 67.2, 61.2, 49.3, 43.4, 22.9, 20.6, 20.6, 20.5. HR-MS (APCI) *m/z* 444.1619; $[M+H]^+$ requires 444.1618.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(prop-2-yn-1-yl)carbamate **27**

Using **2** and propargylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 17:3) yielded the triacetate **27** as a colourless oil (65 mg, 79%). R_f 0.39 (EtOAc:hexane 9:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.11 (d, *J* = 8.1 Hz, 1H), 6.32 (t, *J* = 5.4 Hz, 1H), 5.34 (dd, *J* = 8.6, 8.6 Hz, 1H), 5.28 (dd, *J* = 8.6, 8.6 Hz, 1H), 4.89 (dd, *J* = 8.5, 8.5 Hz, 1H), 4.51 (ddd, *J* = 2.5, 3.4, 8.8 Hz, 1H), 4.40 (dd, *J* = 3.4, 12.8 Hz, 1H), 4.27 (dd, *J* = 2.5, 12.8 Hz, 1H), 4.08-3.91 (m, 2H), 2.28 (t, *J* = 2.5 Hz, 1H), 2.09 (s, 3H), 2.03 (s, 6H), 2.00 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 170.6, 170.4, 169.9, 169.1, 154.9, 154.8, 79.2, 76.9, 72.0, 71.3, 67.2, 61.2, 49.1, 30.8, 22.8, 20.5, 20.5, 20.4. HR-MS (APCI) *m/z* 442.1447; $[M+H]^+$ requires 442.1462.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N*-(2-chloroethyl) carbamate **28**

Using **2** and 2-chloroethanolamine hydrochloride according to Procedure 2 and flash chromatography (EtOAc:hexane 9:1) gave the triacetate **28** as a colourless oil (65 mg, 64%). R_f 0.35 (EtOAc:hexane 9:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.26 (s, 1H), 6.14 (d, *J* = 8.6 Hz, 1H), 5.35 (dd, *J* = 8.3, 8.3 Hz, 1H), 5.28 (dd, *J* = 9.3, 9.3 Hz, 1H), 4.99

(dd, *J* = 9.2, 9.2 Hz, 1H), 4.48 – 4.38 (m, 2H), 4.32-4.29 (m, 1H), 3.72-3.52 (m, 4H), 2.14 (s, 3H), 2.08 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.6, 170.5, 170.4, 169.3, 154.7, 154.3, 77.7, 71.4, 67.5, 61.6, 49.5, 44.2, 43.0, 23.2, 20.8, 20.8, 20.7. HR-MS (APCI) *m/z* 466.1235; $[M+H]^+$ requires 466.1228.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N,N*-(dimethyl) carbamate **29**

Using **2** and dimethylamine hydrochloride according to Procedure 2 and flash chromatography (EtOAc) gave the triacetate **29** as a colourless oil (77 mg, 88%). R_f 0.34 (EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.2 Hz, 1H), 5.38 (dd, *J* = 9.4. 9.4 Hz, 1H), 5.31 (dd, *J* = 9.1, 9.1 Hz, 1H), 4.88 (dd, *J* = 8.2, 9.6 Hz, 1H), 4.41 (ddd, *J* = 2.4, 4.0, 9.0 Hz, 1H), 4.37 (dd, *J* = 4.0, 12.6 Hz, 1H), 4.29 (dd, *J* = 2.4, 12.6 Hz, 1H), 2.96 (s, 6H), 2.11 (s, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 170.5, 170.3, 169.4, 156.4, 154.8, 77.4, 72.2, 67.6, 61.7, 49.8, 37.0, 36.1, 23.0, 20.8, 20.7, 20.7. HR-MS (APCI) *m/z* 432.1638; $[M+H]^+$ requires 432.1618.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N,N*-(diethyl) carbamate **30**

Using **2** and diethylamine according to Procedure 2 and flash chromatography (EtOAc) gave the triacetate **30** as a colourless oil (64 mg, 63%). R_f 0.37 (EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.03 (s, 1H), 5.46-5.26 (m, 2H), 4.99 – 4.85 (m, 1H), 4.39 (ddd, *J* = 2.4, 3.9, 8.6 Hz, 1H), 4.34 (dd, *J* = 4.1, 12.5 Hz, 1H), 4.28 (dd, *J* = 2.4, 12.7 Hz, 1H), 3.31 (br s, 4H), 2.11 (s, 3H), 2.05 (s, 6H), 1.99 (s, 3H), 1.16 (app t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 170.5, 170.3, 169.3, 156.3, 154.2, 77.4, 72.3, 67.5, 61.8, 49.8, 42.7, 41.9, 23.1, 20.8, 20.8, 20.7, 14.1, 13.5. HR-MS (APCI) *m/z* 460.1922; $[M+H]^+$ requires 460.1931.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N,N*-(dibutyl) carbamate **31**

Using **2** and dibutylamine according to Procedure 1 and flash chromatography (EtOAc:hexane 17:3) gave the triacetate **31** as a white solid (69 mg, 60%). R_f 0.59 (EtOAc). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 5.44 (dd, *J* = 9.3,

9.3 Hz, 1H), 5.29 (dd, *J* = 9.4, 9.4 Hz, 1H), 4.79 (dd, *J* = 8.6, 8.6 Hz, 1H), 4.44 (ddd, *J* = 3.0, 3.0, 9.4 Hz, 1H), 4.35 (dd, *J* = 3.6, 12.7 Hz, 1H), 4.23 (dd, *J* = 2.4, 12.7 Hz, 1H), 3.33-3.11 (m, 4H), 2.08 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.93 (s, 3H), 1.51 (br s, 4H), 1.29 (br s, 4H), 0.90 (app t, *J* = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.0, 170.4, 170.1, 169.3, 156.5, 154.5, 76.4, 72.4, 67.3, 61.4, 49.9, 47.9, 47.1, 30.8, 30.2, 22.8, 20.7, 20.7, 20.6, 20.1, 13.9, 13.9. HR-MS (APCI) *m/z* 516.2574; $[M+H]^+$ requires 516.2557.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N,N*-(pentylene) carbamate **32**

Using **2** and piperidine according to Procedure 1 and flash chromatography (EtOAc) gave the triacetate **32** as a colourless oil (90 mg, 86%). R_f 0.35 (EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 1H), 5.39 (dd, *J* = 9.4, 9.4 Hz, 1H), 5.30 (dd, *J* = 9.1, 9.1 Hz, 1H), 4.83 (dd, *J* = 8.2, 9.5 Hz, 1H), 4.42 (ddd, *J* = 2.4, 4.1, 9.0 Hz, 1H), 4.37 (dd, *J* = 4.1, 12.6 Hz, 1H), 4.28 (dd, *J* = 2.4, 12.7 Hz, 1H), 3.44 (br s, 4H), 2.11 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.97 (s, 3H), 1.69-1.46 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.0, 170.5, 170.3, 169.4, 156.3, 153.7, 77.4, 72.2, 67.5, 61.7, 49.8, 45.3, 25.7, 24.3, 22.9, 20.8, 20.8, 20.7. HR-MS (APCI) *m/z* 472.1984; $[M+H]^+$ requires 472.1931.

O-(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-D-glucopyranosylidene)amino *N,N*-(ethyleneoxyethylene) carbamate **33**

Using **2** and morpholine according to Procedure 1 and flash chromatography (MeOH/EtOAc 1:24) gave the triacetate **33** as a colourless oil (71 mg, 68%). R_f 0.41 (MeOH/EtOAc 1:19). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, *J* = 8.1 Hz, 1H), 5.40 (dd, *J* = 9.4, 9.4 Hz, 1H), 5.30 (dd, *J* = 9.1, 9.1 Hz, 1H), 4.82 (dd, *J* = 8.1, 9.5 Hz, 1H), 4.44 (ddd, *J* = 2.4, 3.8, 8.9 Hz, 1H), 4.37 (dd, *J* = 3.9, 12.7 Hz, 1H), 4.31 (dd, *J* = 2.5, 12.7 Hz, 1H), 3.69 (s, 4H), 3.51 (s, 4H), 2.11 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 170.4, 170.2, 169.4, 156.7, 153.5, 72.0, 67.5, 66.6, 61.6, 49.9, 44.4, 44.2, 23.0, 20.8, 20.8, 20.7. HR-MS (APCI) *m/z* 474.1725; $[M+H]^+$ requires 474.1724.

*General preparation of carbamates **34-63***

A saturated solution of NH_3 in MeOH (10 mL) prepared at 0°C was added to a solution of the appropriate 3,4,6-tri-*O*-acetyl carbamate (1.0 equiv) in MeOH (25 mL/mmol) at 0°C. After 2 h. at 0°C, the reaction mixture was concentrated.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(4-methylphenyl) carbamate **34**

Using **4** and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **34** as a white solid (15 mg, 26%). m.p. 182-184°C (dec.). R_f 0.21 (MeOH:EtOAc 3:17). ^{1}H NMR (500 MHz, CD_3OD): δ 7.31 (AA′BB′, 2H), 7.10 (AA′BB′, 2H), 4.57 (d, J = 9.0 Hz, 1H), 3.97-3.94 (m, 2H), 3.85 (dd, J = 4.5, 13.0 Hz, 1H), 3.75 (dd, J = 8.5, 8.5 Hz, 1H), 3.73 (dd, J = 8.5, 8.5 Hz, 1H), 2.28 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, CD_3OD): δ 173.8, 159.3, 154.8, 136.7, 134.4, 130.4, 120.4, 84.1, 74.5, 69.8, 61.7, 52.9, 22.8, 20.8. HR-MS (APCI) *m/z* 368.1462; $[M+H]^+$ requires 368.1458.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(4-methoxyphenyl) carbamate **35**

Using **5** and flash chromatography (MeOH:EtOAc 9:91) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **5** as a white solid (20 mg, 28%). m.p. 136-140°C (dec.). R_f 0.15 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD): δ 7.34 (AA′BB′, 2H), 6.88 (AA′BB′, 2H), 4.59 (d, J = 9.6 Hz, 1H), 4.57 (s, 1H), 3.98-3.95 (m, 2H), 3.86 (dd, J = 4.8, 13.2 Hz, 1H), 3.80-3.72 (m, 5H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, CD_3OD): δ 173.8, 159.2, 157.7, 155.1, 132.1, 122.2, 115.1, 84.1, 74.5, 69.8, 61.7, 55.9, 52.9, 22.8. HR-MS (APCI) *m/z* 384.1418; $[M+H]^+$ requires 384.1407.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(4-bromophenyl) carbamate **36**

Using **6** and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **36** as a white solid (30 mg, 43%). m.p. 176-180°C (dec.). R_f 0.30 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, $(CD_3)_2SO$): δ 9.81 (s, 1H), 8.32 (d, J = 8.0 Hz, 1H), 7.53-7.39 (m,

6H), 5.50 (t, *J* = 4.8 Hz, 2H), 4.90 (t, *J* = 5.1 Hz 1H), 4.52 (dd, *J* = 6.5, 14.2 Hz, 1H), 4.37 (t, *J* = 8.2 Hz, 1H), 3.97-3.91 (m, 1H), 3.79-3.74 (m, 1H), 3.70-3.61 (m, 2H), 3.58 (t, *J* = 7.3 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (151 MHz, $(CD_3)_2SO$): δ 169.2, 158.4, 151.7, 138.1, 131.6, 120.5, 114.4, 82.4, 72.2, 68.6, 60.0, 51.1, 22.7. HR-MS (APCI) *m/z* 432.0414; $[M+H]^+$ requires 432.0406.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-benzylcarbamate **37**
Using **7** and flash chromatography (MeOH:EtOAc 1:9) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **37** as a white solid (15 mg, 40%). m.p. 150-156°C (dec.). R_f 0.23 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD): δ 7.33-7.25 (m, 5H), 4.57 (s, 1H), 4.54 (d, *J* = 9.3 Hz, 1H), 4.39-4.34 (m, 2H), 3.95-3.91 (m, 2H) 3.84 (dd, *J* = 4.4, 12.9 Hz, 1H), 3.75 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.71 (dd, *J* = 8.4, 8.4 Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (126 MHz, CD_3OD): δ 173.8, 158.6, 158.1, 140.0, 129.6, 128.4, 84.1, 74.4, 69.7, 61.6, 52.8, 45.6, 22.7. HR-MS (APCI) *m/z* 368.1460; $[M+H]^+$ requires 368.1458.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-cyclopropylcarbamate **38**
Using **8** and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **38** as a white solid (21 mg, 46%). m.p. 148-152°C (dec.). R_f 0.15 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD): δ 4.57 (s, 1H), 4.53 (d, *J* = 9.0 Hz, 1H), 3.93-3.91 (m, 2H), 3.84 (dd, *J* = 4.2, 12.6 Hz, 1H), 3.74 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.70 (dd, *J* = 9.0, 9.0 Hz, 1H), 2.59 (tt, *J* = 3.8, 7.2 Hz, 1H), 2.04 (s, 3H), 0.73-0.71 (m, 2H), 0.53-0.51 (m, 2H). ^{13}C NMR (126 MHz, CD_3OD): δ 173.8, 158.7, 158.6, 84.0, 74.5, 69.7, 61.6, 52.8, 24.0, 22.8, 6.8. HR-MS (APCI) *m/z* 318.1297; $[M+H]^+$ requires 318.1301.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-cyclobutylcarbamate **39**
Using **9** and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **39** as a white solid (38 mg, 77%). m.p. 130-134°C (dec.). R_f 0.17 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD): δ 4.57 (s, 1H), 4.54 (d, *J* = 9.6 Hz, 1H), 4.12 (q, *J* = 8.3 Hz, 1H), 3.94-3.92 (m, 2H), 3.84 (dd, *J* = 3.6, 12.6 Hz, 1H), 3.75 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.71 (dd, *J* = 9.0, 9.0 Hz, 1H), 2.31-2.25 (m, 2H), 2.05 (s, 3H), 2.01-1.96 (m,

2H), 1.75-1.67 (m, 2H). ^{13}C NMR (151 MHz, CD_3OD): δ 173.8, 158.5, 156.7, 84.0, 74.2, 69.8, 61.7, 52.9, 47.5, 31.5, 22.8, 15.6. HR-MS (APCI) *m/z* 332.1473; $[M+H]^+$ requires 332.1458.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-cyclopentylcarbamate **40**
Using **10** and flash chromatography (MeOH:EtOAc 3:22) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **40** as a white solid (24 mg, 50%). m.p. 140-144°C (dec.). R_f 0.17 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD): δ 4.56 (s, 1H), 4.52 (d, *J* = 9.6 Hz, 1H), 3.97-3.90 (m, 3H), 3.84 (dd, *J* = 4.2, 12.6 Hz, 1H), 3.75 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.71 (dd, *J* = 9.0, 9.0 Hz, 1H), 2.04 (s, 3H), 1.96-1.91 (m, 2H), 1.75-1.68 (m, 2H), 1.65-1.58 (m, 2H), 1.53-1.47 (m, 2H). ^{13}C NMR (151 MHz, CD_3OD): δ 173.7, 158.2, 157.3, 84.0, 74.3, 69.8, 61.6, 54.1, 52.9, 33.7, 24.5, 22.8. HR-MS (APCI) *m/z* 346.1611; $[M+H]^+$ requires 346.1614.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-cyclohexylcarbamate **41**
Using **11** and flash chromatography (MeOH:EtOAc 1:9) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **41** as a white solid (32 mg, 66%). m.p. 158-162°C (dec.). R_f 0.24 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD): δ 4.57 (s, 1H), 4.53 (d, *J* = 8.0 Hz, 1H), 3.94-3.90 (m, 2H), 3.84 (dd, *J* = 4.2, 12.6 Hz, 1H), 3.75 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.70 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.49-3.42 (m, 1H), 2.04 (s, 3H), 1.92-1.86 (m, 2H), 1.76-1.71 (m, 2H), 1.64-1.60 (m, 1H), 1.41-1.34 (m, 2H), 1.31-1.22 (m, 3H). ^{13}C NMR (126 MHz, CD_3OD): δ 173.7, 158.2, 157.0, 84.0, 74.3, 69.8, 61.6, 52.9, 51.4, 33.8, 26.6, 25.9, 22.8. HR-MS (APCI) *m/z* 360.1765; $[M+H]^+$ requires 360.1771.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(adamant-1-yl)carbamate **42**
Using **12** and flash chromatography (MeOH:EtOAc 1:9) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **42** as a white solid (46 mg, 63%). m.p. 154-160°C (dec.). R_f 0.19 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD): δ 4.57 (s, 1H), 4.51 (d, *J* = 10.2 Hz, 1H), 3.93 (dd, *J* = 2.4, 12.6 Hz, 1H), 3.89 (ddd, *J* = 2.4, 3.6, 9.0 Hz, 1H), 3.84 (dd, *J* = 3.6, 12.6 Hz, 1H),

3.74 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.70 (dd, *J* = 9.0, 9.0 Hz, 1H), 2.08 (*br* s, 3H), 2.04 (s, 3H), 2.00-1.97 (m, 6H), 1.75-1.70 (m, 6H). ^{13}C NMR (126 MHz, CD_3OD): δ 174.0, 157.6, 155.4, 84.0, 74.2, 69.8, 61.7, 52.9, 52.0, 42.5, 37.4, 30.9, 22.8. HR-MS (APCI) *m/z* 412.2077; $[M+H]^+$ requires 412.2084.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(2-amino-2-oxoeth-1-yl)carbamate **43**

Using **13** and flash chromatography (MeOH:EtOAc 3:7) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **43** as a white solid (16 mg, 55%). m.p. 136-140°C (dec.). R_f 0.17 (MeOH:EtOAc 3:7). ^{1}H NMR (600 MHz, CD_3OD): δ 4.55 (d, *J* = 9.0 Hz, 1H), 3.96-3.93 (m, 2H), 3.89-3.83 (m, 3H), 3.76 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.72 (dd, *J* = 9.0, 9.0 Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, CD_3OD): δ 173.91, 173.86, 158.7, 158.0, 84.2, 74.3, 69.7, 61.6, 52.8, 44.4, 22.8. HR-MS (APCI) *m/z* 335.1200; $[M+H]^+$ requires 335.1203.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino (*S*)-*N*-(1-amino-1-oxoprop-2-yl)carbamate **44**

Using **14** and flash chromatography (MeOH:EtOAc 1:4) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **44** as a white solid (35 mg, 56%). m.p. 108-112°C (dec.). R_f 0.24 (MeOH:EtOAc 3:7). ^{1}H NMR (600 MHz, CD_3OD): δ 4.57 (s, 1H), 4.53 (d, *J* = 9.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 1H), 3.97-3.92 (m, 2H), 3.85 (dd, *J* = 3.6, 12.4 Hz, 1H), 3.75 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.72 (dd, *J* = 9.0, 9.0 Hz, 1H), 2.07 (s, 3H), 1.39 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, CD_3OD): δ 177.1, 173.9, 158.4, 157.0, 84.2, 74.1, 69.7, 61.6, 52.9, 51.4, 22.8, 19.2. HR-MS (APCI) *m/z* 349.1352; $[M+H]^+$ requires 349.1359.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(*(S)*-1-amino-3-hydroxy-1-oxo-prop-2-yl) carbamate **45**

Using **15** and flash chromatography (MeOH/EtOAc 3:7) of the resultant residue gave a colourless oil which was treated with EtOAc to give **45** as a white solid (16 mg, 31%). R_f 0.26 (MeOH/EtOAc 7:13). ^{1}H NMR (600 MHz, D_2O) δ 4.62 (d, *J* = 9.9 Hz, 1H), 4.30 (dd, *J* = 4.6, 4.6 Hz, 1H), 4.13-4.07 (m, 1H), 4.01 (dd, *J* = 2.2, 12.9 Hz, 1H), 3.94-3.77 (m, 5H), 2.09 (s, 3H). ^{13}C NMR (151 MHz, D_2O) δ 175.5, 175.3,

158.8, 157.4, 83.2, 72.8, 68.6, 62.4, 60.9, 57.3, 52.2, 22.9. HR-MS (APCI) *m/z* 365.1309; $[M+H]^+$ requires 365.1309.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino (*S*)-*N*-(1-amino-1-oxo-3-phenylprop-2-yl)carbamate **46**

Using **16** and flash chromatography (MeOH:EtOAc 3:7) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **46** as a white solid (28 mg, 46%). m.p. 118-122°C (dec.). R_f 0.32 (MeOH:EtOAc 3:7). ^{1}H NMR (600 MHz, CD_3OD): δ 7.29-7.18 (m, 5H), 4.57 (s, 1H), 4.53 (d, *J* = 9.6 Hz, 1H), 4.46 (dd, *J* = 5.4, 7.8 Hz, 1H), 3.93-3.89 (m, 2H), 3.83 (dd, *J* = 4.2, 12.6 Hz, 1H), 3.75 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.69 (dd, *J* = 9.6, 9.6 Hz, 1H), 3.14 (dd, *J* = 5.4, 13.8 Hz, 1H), 2.94 (dd, *J* = 8.4, 13.8 Hz, 1H), 2.01 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD): δ 175.7, 173.8, 158.4, 157.0, 137.9, 130.4, 129.5, 127.9, 84.2, 74.2, 69.7, 61.6, 57.1, 52.8, 39.6, 22.8. HR-MS (APCI) *m/z* 425.1679; $[M+H]^+$ requires 425.1672.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(2-hexylamino-2-oxoeth-1-yl) carbamate **47**

Using **17** and flash chromatography (MeOH/EtOAc 1:3) of the resultant residue gave a colourless oil which was treated with EtOAc to give **47** as a white solid (21 mg, 34%). R_f 0.33 (MeOH/EtOAc 1:3). ^{1}H NMR (600 MHz, CD_3OD) δ 4.56 (d, *J* = 9.3 Hz, 1H), 3.99-3.91 (m, 2H), 3.88-3.68 (m, 5H), 3.20 (app t, *J* = 7.2 Hz, 2H), 2.06 (s, 3H), 1.55-1.45 (m, 2H), 1.39-1.23 (m, 6H), 0.91 (app t, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 173.8, 171.1, 158.7, 158.0, 84.1, 74.3, 69.7, 61.6, 52.8, 44.7, 40.5, 32.7, 30.4, 27.6, 23.6, 22.8, 14.4. HR-MS (APCI) *m/z* 419.2124; $[M+H]^+$ requires 419.2142.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-methyl carbamate **48**

Using **18** and flash chromatography (MeOH/EtOAc 1:3) of the resultant residue gave a colourless oil which was treated with EtOAc to give **48** as a white solid (18 mg, 65%). The ^{1}H NMR spectrum was consistent with that found in the literature.[8]

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-ethyl carbamate **49**

Using **19** and flash chromatography (MeOH/EtOAc 1:4) of the resultant residue gave

a colourless oil which was treated with EtOAc to give **49** as a white solid (9 mg, 22%). R_f 0.26 (MeOH/EtOAc 1:4). ^{1}H NMR (600 MHz, CD_3OD) δ 4.61-4.48 (m, 2H), 3.99-3.89 (m, 2H), 3.84 (dd, *J* = 4.5, 13.0 Hz, 1H), 3.75 (dd, *J* = 8.7, 8.7 Hz, 1H), 3.71 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.21 (q, *J* = 7.2 Hz, 2H), 2.04 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 173.8, 158.4, 157.8, 84.0, 74.4, 69.7, 61.6, 52.8, 36.8, 22.8, 15.2. HR-MS (APCI) *m/z* 306.1311; $[M+H]^+$ requires 306.1301.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(prop-1-yl)carbamate **50**
Using **20** and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **50** as a white solid (31 mg, 72%). m.p. 130-136°C (dec.). R_f 0.11 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD): δ 4.54 (d, *J* = 9.6 Hz, 1H), 3.94-3.91 (m, 2H), 3.84 (dd, *J* = 4.2, 13.2 Hz, 1H), 3.75 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.71 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.14 (t, *J* = 7.2 Hz, 2H), 2.04 (s, 3H), 1.54 (tq, *J* = 7.2, 7.2 Hz, 2H), 0.93 (t, *J* = 7.2, Hz, 3H). ^{13}C NMR (151 MHz, CD_3OD): δ 173.7, 158.3, 158.0, 84.0, 74.4, 69.7, 61.6, 52.8, 43.7, 23.9, 22.8, 11.5. HR-MS (APCI) *m/z* 320.1453; $[M+H]^+$ requires 320.1458.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(but-1-yl)carbamate **51**
Using **21** and flash chromatography (MeOH:EtOAc 3:22) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **51** as a white solid (32 mg, 68%). m.p. 84-88°C. R_f 0.24 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD): δ 4.54 (d, *J* = 9.3 Hz, 1H), 3.94-3.91 (m, 2H), 3.84 (dd, *J* = 3.6, 12.0 Hz, 1H), 3.75 (dd, *J* = 8.6, 8.6 Hz, 1H), 3.71 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.18 (t, *J* = 7.0 Hz, 2H), 2.04 (s, 3H), 1.51 (tt, *J* = 7.0, 7.0 Hz, 2H), 1.36 (tq, *J* = 7.0, 7.4 Hz, 2H), 0.94 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, CD_3OD): δ 173.7, 158.3, 158.0, 84.0, 74.4, 69.7, 61.6, 52.8, 41.6, 32.8, 22.8, 20.9, 14.0. HR-MS (APCI) *m/z* 334.1611; $[M+H]^+$ requires 334.1614.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(hex-1-yl)carbamate **52**
Using **22** and flash chromatography (MeOH:EtOAc 3:22) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **52** as a

white solid (30 mg, 62%). m.p. 134-138°C (dec.). R_f 0.14 (MeOH:EtOAc 3:22). ^{1}H NMR (600 MHz, CD_3OD): δ 4.54 (d, *J* = 9.0 Hz, 1H), 3.94-3.91 (m, 2H), 3.84 (dd, *J* = 4.2, 13.2 Hz, 1H), 3.75 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.71 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.18 (t, *J* = 6.6 Hz, 2H), 2.04 (s, 3H), 1.54-1.49 (m, 2H), 1.38-1.29 (m, 6H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, CD_3OD): δ 173.7, 158.3, 158.0, 84.0, 74.4, 69.7, 61.6, 52.8, 42.0, 32.7, 30.7, 27.5, 23.6, 22.8, 14.4. HR-MS (APCI) *m/z* 362.1915; $[M+H]^+$ requires 362.1927.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(prop-2-yl)carbamate **53**

Using **23** and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **53** as a white solid (23 mg, 71%). m.p. 132-136°C (dec.). R_f 0.14 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD): δ 4.56 (s, 1H), 4.53 (d, *J* = 8.4 Hz, 1H), 3.94-3.91 (m, 2H), 3.84 (dd, *J* = 3.6, 12.6 Hz, 1H), 3.80-3.69 (m, 3H), 2.04 (s, 3H), 1.17 (d, *J* = 6.6, Hz, 6H). ^{13}C NMR (151 MHz, CD_3OD): δ 173.7, 158.3, 157.0, 84.0, 74.4, 69.8, 61.7, 52.9, 44.5, 22.8. HR-MS (APCI) *m/z* 320.1464; $[M+H]^+$ requires 320.1458.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(2-methylprop-1-yl)carbamate **54**

Using **24** and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **54** as a white solid (32 mg, 63%). m.p. 120-124°C (dec.). R_f 0.18 (MeOH:EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD): δ 4.54 (d, *J* = 9.6 Hz, 1H), 3.97-3.93 (m, 2H), 3.84 (dd, *J* = 3.0, 12.0 Hz, 1H), 3.75 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.71 (dd, *J* = 8.4, 8.4 Hz, 1H), 3.01 (d, *J* = 6.0 Hz, 2H), 2.04 (s, 3H), 1.81-1.76 (m, 1H), 0.91 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (151 MHz, CD_3OD): δ 173.7, 158.3, 158.1, 84.0, 74.3, 69.7, 61.6, 52.9, 49.4, 29.9, 22.8, 20.2. HR-MS (APCI) *m/z* 334.1605; $[M+H]^+$ requires 334.1614.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(2-methylprop-2-yl)carbamate **55**

Using **25** and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **55** as a white solid (23 mg, 51%). m.p. 112-116°C (dec.). R_f 0.15 (MeOH:EtOAc 4:21). ^{1}H

NMR (600 MHz, CD_3OD): δ 4.52 (d, *J* = 9.6 Hz, 1H), 3.93 (dd, *J* = 2.4, 12.6 Hz, 1H), 3.90 (ddd, *J* = 2.4, 3.6, 9.0 Hz, 1H), 3.84 (dd, *J* = 3.6, 12.6 Hz, 1H), 3.74 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.70 (dd, *J* = 9.6, 9.6 Hz, 1H), 2.04 (s, 3H), 1.33 (s, 9H). ^{13}C NMR (151 MHz, CD_3OD): δ 173.7, 157.7, 155.9, 84.0, 74.3, 69.8, 61.7, 52.9, 51.6, 28.9, 22.7. HR-MS (APCI) *m/z* 334.1627; $[M+H]^+$ requires 334.1614.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(prop-2-en-1-yl)carbamate **56**

Using **26** and flash chromatography (MeOH:EtOAc 3:22) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **56** as a white solid (28 mg, 58%). m.p. 80-84°C. R_f 0.14 (MeOH:EtOAc 9:41). ^1H NMR (600 MHz, CD_3OD): δ 5.87 (ddt, *J* = 4.8, 10.8, 17.4 Hz, 1H), 5.20 (dd, *J* = 1.2, 17.4 Hz, 1H), 5.11 (dd, *J* = 1.2, 10.8 Hz, 1H), 4.54 (d, *J* = 9.6 Hz, 1H), 3.94-3.92 (m, 2H), 3.84 (dd, *J* = 4.2, 13.2 Hz, 1H), 3.80 (d, *J* = 4.8 Hz, 2H), 3.76 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.71 (dd, *J* = 9.0, 9.0 Hz, 1H), 2.03 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD): δ 173.7, 158.5, 157.8, 135.6, 116.1, 84.1, 74.4, 69.7, 61.6, 52.8, 44.2, 22.8. HR-MS (APCI) *m/z* 318.1297; $[M+H]^+$ requires 318.1301.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(prop-2-yn-1-yl) carbamate **57**

Using **27** and flash chromatography (MeOH:EtOAc 3:17) of the resultant residue gave a clear oil which was precipitated with EtOAc to yield the title compound **57** as a white solid (26 mg, 56%). m.p. 104-110°C (dec.). R_f 0.19 (MeOH:EtOAc 4:21). ^1H NMR (600 MHz, CD_3OD): δ 4.56 (d, *J* = 9.0 Hz, 1H), 3.96 (d, *J* = 3.0 Hz, 2H), 3.95-3.92 (m, 2H), 3.85 (dd, *J* = 4.8, 13.2 Hz, 1H), 3.76 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.72 (dd, *J* = 9.0, 9.0 Hz, 1H), 2.61 (t, *J* = 2.5 Hz, 1H), 2.05 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD): δ 173.8, 158.9, 157.5, 84.1, 80.6, 74.4, 72.4, 69.7, 61.6, 52.8, 31.2, 22.8. HR-MS (APCI) *m/z* 316.1137; $[M+H]^+$ requires 316.1145.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*-(2-chloroethyl) carbamate **58**

Using **28** and flash chromatography (MeOH/EtOAc 3:17) of the resultant residue gave a colourless oil which was treated with EtOAc to give **58** as a white solid (27 mg,

59%). R_f 0.18 (MeOH/EtOAc 3:17). ^{1}H NMR (600 MHz, CD_3OD) δ 4.55 (d, J = 10.3 Hz, 1H), 3.91-3.95 (m, 2H), 3.85 (dd, J = 4.3, 13.1 Hz, 1H), 3.77-3.71 (m, 2H), 3.65-3.63 (m, 2H), 3.52-3.50 (m, 2H), 2.04 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 173.7, 158.6, 157.8, 84.0, 74.3, 69.7, 61.6, 52.8, 44.0, 43.9, 22.8. HR-MS (APCI) *m/z* 340.0900; $[M+H]^+$ requires 340.0912.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*,*N*-(dimethyl) carbamate **59** Using **29** and flash chromatography (MeOH/EtOAc 1:3) of the resultant residue gave a colourless oil which was treated with EtOAc to give **59** as a white solid (37 mg, 74%). R_f 0.16 (MeOH/EtOAc 4:21). ^{1}H NMR (600 MHz, CD_3OD) δ 4.58 (d, J = 9.8 Hz, 1H), 3.93 (dd, J = 2.2, 12.3 Hz, 1H), 3.90 (ddd, J = 2.2, 3.9, 9.2 Hz, 1H), 3.85 (dd, J = 4.0, 12.3 Hz, 1H), 3.76 (dd, J = 9.0, 9.0 Hz, 1H), 3.69 (dd, J = 9.6, 9.6 Hz, 1H), 2.96 (m, 6H), 2.04 (s, 3H). ^{13}C NMR (151 MHz, CD_3OD) δ 173.8, 160.1, 157.1, 84.0, 74.8, 69.8, 61.7, 52.8, 36.9, 36.1, 22.8. HR-MS (APCI) *m/z* 306.1301; $[M+H]^+$ requires 306.1301.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*,*N*-(diethyl) carbamate **60** Using **30** and flash chromatography (MeOH/EtOAc 4:21) of the resultant residue gave a colourless oil which was treated with EtOAc to give **60** as a white solid (37 mg, 85%). R_f 0.23 (MeOH/EtOAc 4:21). ^{1}H NMR (600 MHz, CD_3OD) δ 4.59 (d, J = 9.9 Hz, 1H), 3.93-3.83 (m, 3H), 3.77 (dd, J = 8.9, 8.9 Hz, 1H), 3.69 (dd, J = 9.6, 9.6 Hz, 1H), 3.41-3.32 (m, 4H), 2.04 (s, 3H), 1.17 (br s, 6H). ^{13}C NMR (151 MHz, CD_3OD) δ 173.8, 160.2, 156.5, 84.0, 74.8, 69.8, 61.7, 52.8, 43.5, 42.9, 22.8, 14.3, 13.7. HR-MS (APCI) *m/z* 334.1619; $[M+H]^+$ requires 334.1614.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*,*N*-(dibutyl) carbamate **61** Using **31** and flash chromatography (MeOH/EtOAc 3:17) of the resultant residue gave a colourless oil which was treated with EtOAc to give **61** as a white solid (38 mg, 79%). R_f 0.22 (MeOH/EtOAc 7:43). ^{1}H NMR (600 MHz, CD_3OD) δ 4.59 (d, J = 10.0 Hz, 1H), 4.02-3.84 (m, 3H), 3.80 (dd, J = 8.8, 8.8 Hz, 1H), 3.69 (dd, J = 9.4, 9.4 Hz, 1H), 3.29-3.13 (m, 2H), 2.04 (s, 3H), 1.62-1.49 (m, 4H), 1.41-1.23 (m, 4H), 0.95 (ap t, J = 7.3 Hz, 6H). ^{13}C NMR (151 MHz, CD_3OD) δ 173.8, 160.1, 156.9, 83.9, 74.8, 69.7, 61.6, 52.8, 48.1, 31.8, 31.2, 22.8, 21.0, 14.2. HR-MS (APCI) *m/z* 390.2236; $[M+H]^+$ requires 390.2240.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*,*N*-(pentylene) carbamate **62**

Using **32** and flash chromatography (MeOH/EtOAc 1:4) of the resultant residue gave a colourless oil which was treated with EtOAc to give **62** as a white solid (45 mg, 72%). R_f 0.21 (MeOH/EtOAc 1:4). ^{1}H NMR (600 MHz, D_2O) δ 4.68 (d, *J* = 8.8 Hz, 1H), 4.10-4.07 (m, 1H), 4.05-3.98 (m, 1H), 3.95-3.84 (m, 3H), 3.57-3.42 (m, 4H), 2.12 (s, 3H), 1.70-1.44 (m, 6H). ^{13}C NMR (151 MHz, D_2O) δ 175.1, 159.9, 155.8, 82.5, 72.8, 68.4, 60.5, 51.8, 46.0, 25.8, 24.1, 22.7. HR-MS (APCI) *m/z* 346.1625; $[M+H]^+$ requires 346.1614.

O-(2-Acetamido-2-deoxy-D-glucopyranosylidene)amino *N*,*N*-(ethyleneoxyethylene) carbamate **63**

Using **33** and flash chromatography (MeOH/EtOAc 3:17) of the resultant residue gave a colourless oil which was treated with EtOAc to give **63** as a white solid (20 mg, 42%). R_f 0.25 (MeOH/EtOAc 1:4). ^{1}H NMR (600 MHz, D_2O) δ 4.68 (d, *J* = 9.6 Hz, 1H), 4.10 (ddd, *J* = 2.2, 4.3, 9.4 Hz, 1H), 4.02 (dd, *J* = 2.3, 13.0 Hz, 1H), 3.95-3.84 (m, 3H), 3.77 (br s, 4H), 3.57 (br s, 4H), 2.12 (s, 3H). ^{13}C NMR (151 MHz, D_2O) δ 175.2, 160.2, 155.6, 82.6, 72.7, 68.3, 66.7, 60.5, 51.8, 44.6, 22.7. HR-MS (APCI) *m/z* 348.1396; $[M+H]^+$ requires 348.1407.

Kinetic Analysis of Inhibitiors

Assays against β-hexosaminidase B and NAGLU were carried out in triplicate at 37 °C for 30 minutes using a stopped assay procedure in which the enzymatic reactions were quenched by the addition of a 4-fold excess of quenching buffer (200 mM glycine, pH 10.75). Assays against OGA were carried out in triplicate at 37°C for 20 minutes using a continuous assay procedure where reactions were initiated by the addition of substrate. Assays against β-hexosaminidase B were conducted in buffer (50 mM citrate, 100 mM NaCl, pH 4.25) and OGA (PBS, pH 7.4 buffer, 0.03% BSA) using 4-methylumbelliferyl *N*-acetyl-β-D-glucosaminide as substrate. For NAGLU, assays were performed in acetate buffer (100 mM, pH 4.3), containing bovine serum albumin (0.5 mg ml^{-1}) using 4-methylumbelliferyl *N*-acetyl-α-D-glucosaminide as substrate. For β-hexosaminidase B and NAGLU assays, release of 4-methylumbelliferone was monitored using a Varian CARY Eclipse Fluorescence Spectrophotometer 96-well plate system with readings taken at excitation and

emission wavelengths of 368 nm and 450 nm respectively, with 5 mm slit openings. For OGA the extent of 4-methylumbelliferone release was determined using a BioTek Synergy Plate Reader at excitation and emission wavelengths of 350 and 445 nm respectively. Assays contained substrate at the previously determined K_m value of the substrate for the enzyme, and the enzyme was at a concentration of 0.5-10 nM for β-hexosaminidase B, 10-100 nM for NAGLU and 10 nM for OGA. For K_I analysis, inhibitors were tested at a range of concentrations that encompassed their K_I values. The rates at each inhibitor concentration were plotted and a best fit line through the points was ascertained. The $-1/K_I$ was taken as the point where the line of best fit intersected with $1/V_{max}$.

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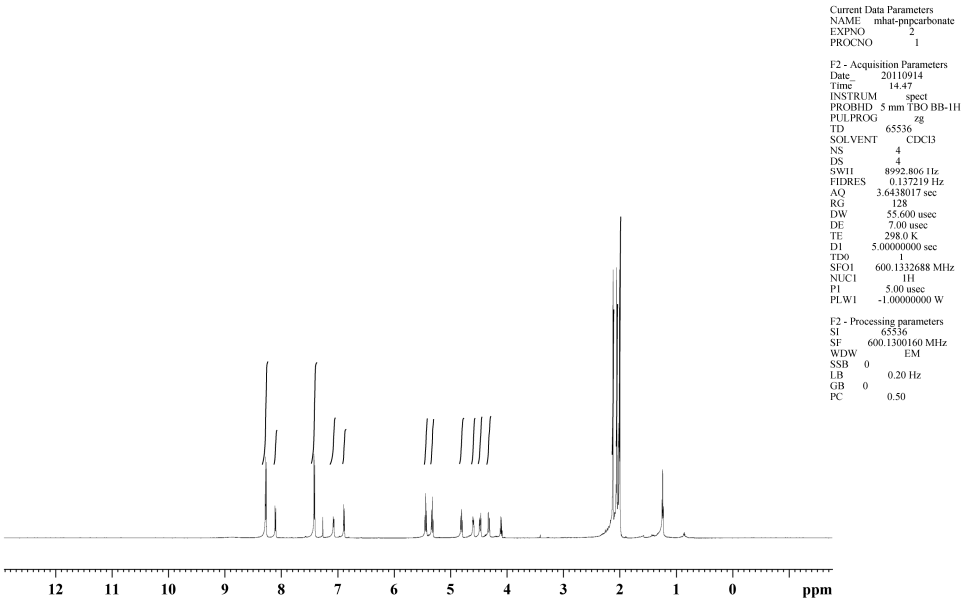
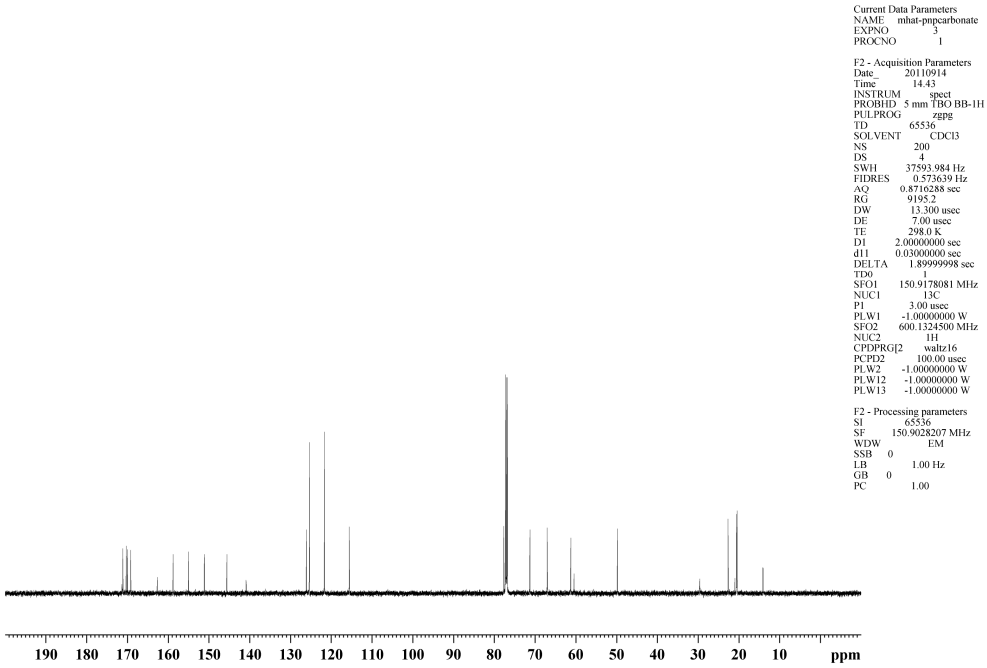
^{1}H NMR spectrum of **1**



^{13}C NMR spectrum of **1**



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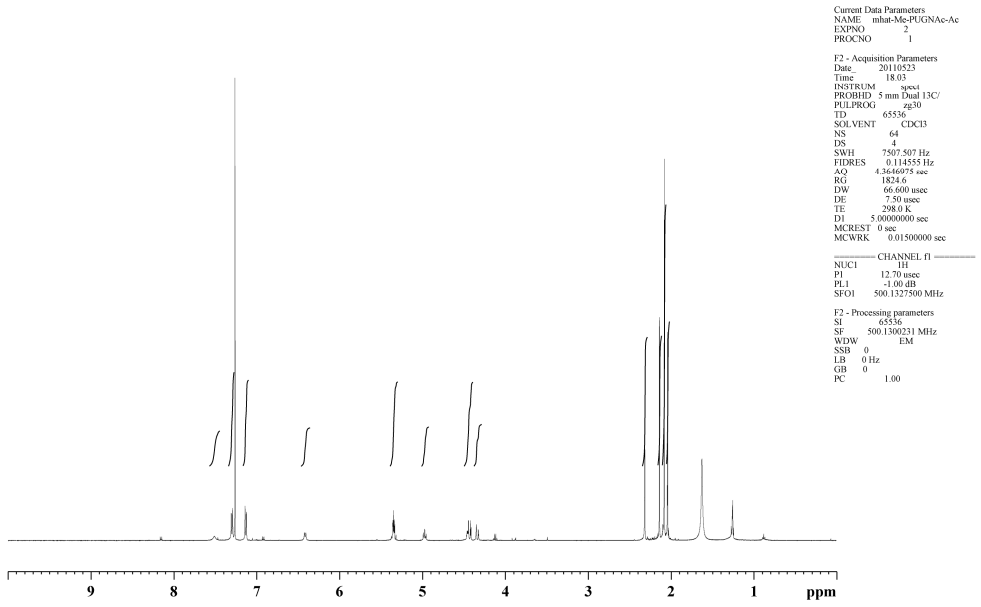

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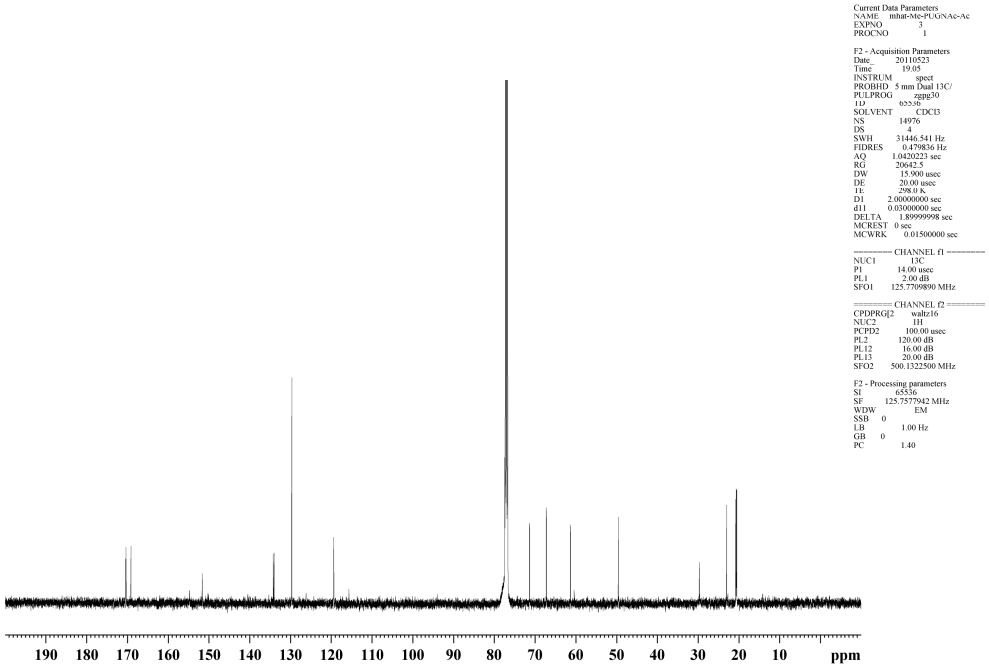
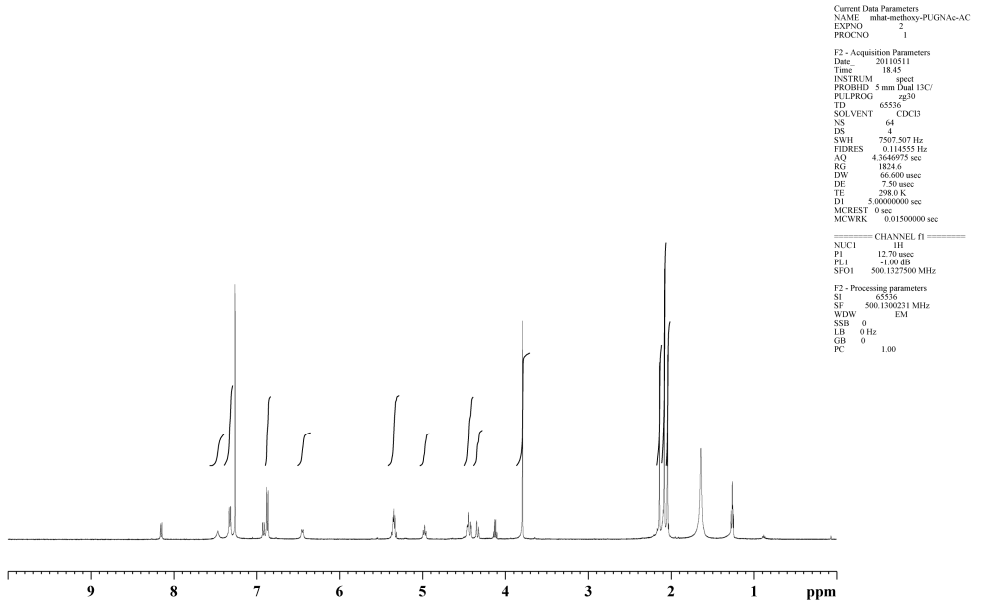


^{1}H NMR spectrum of **5**



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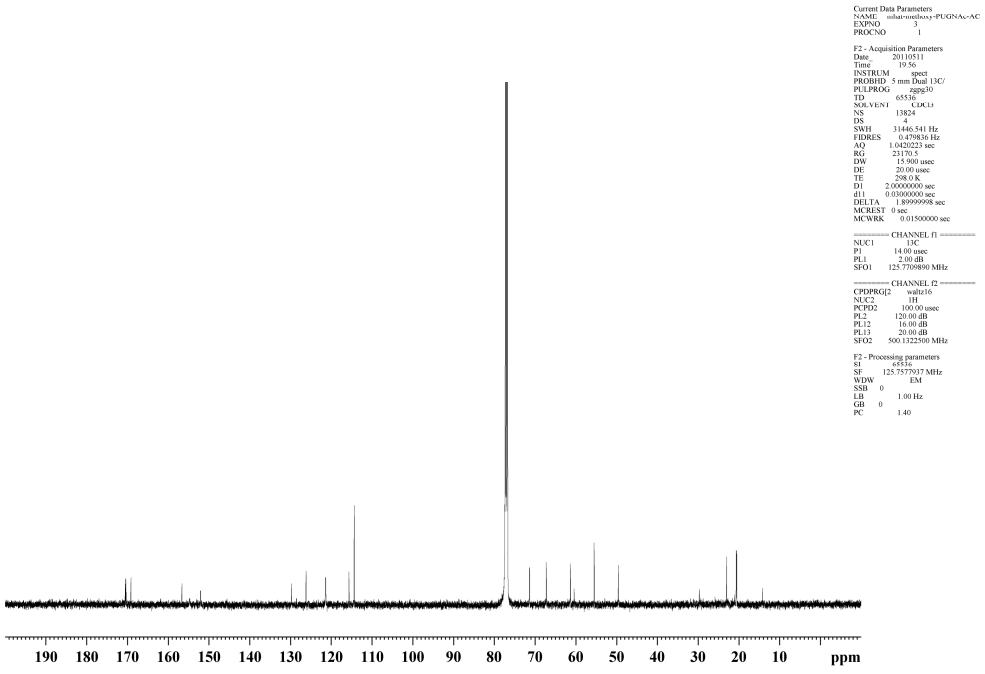

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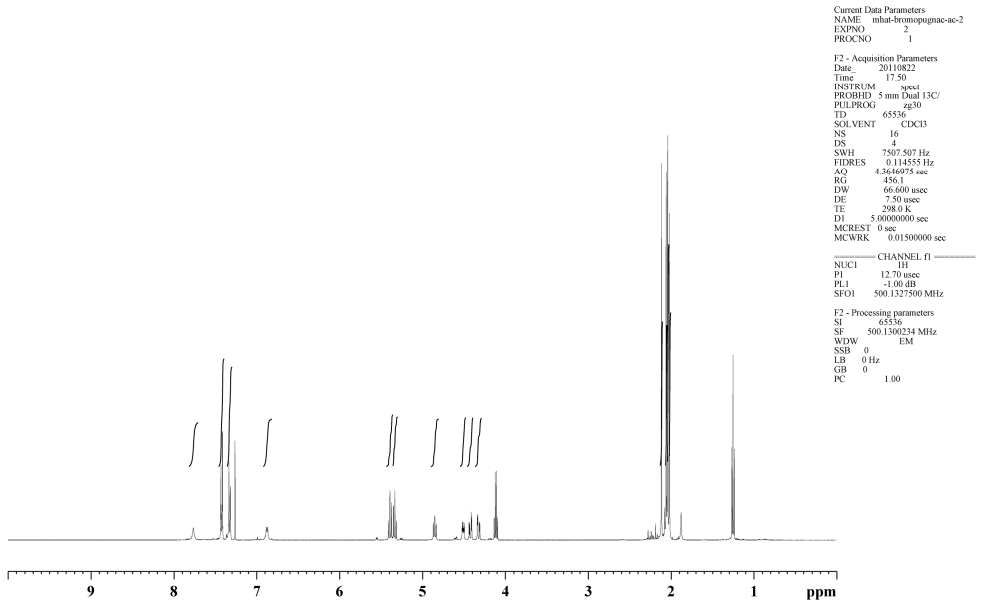
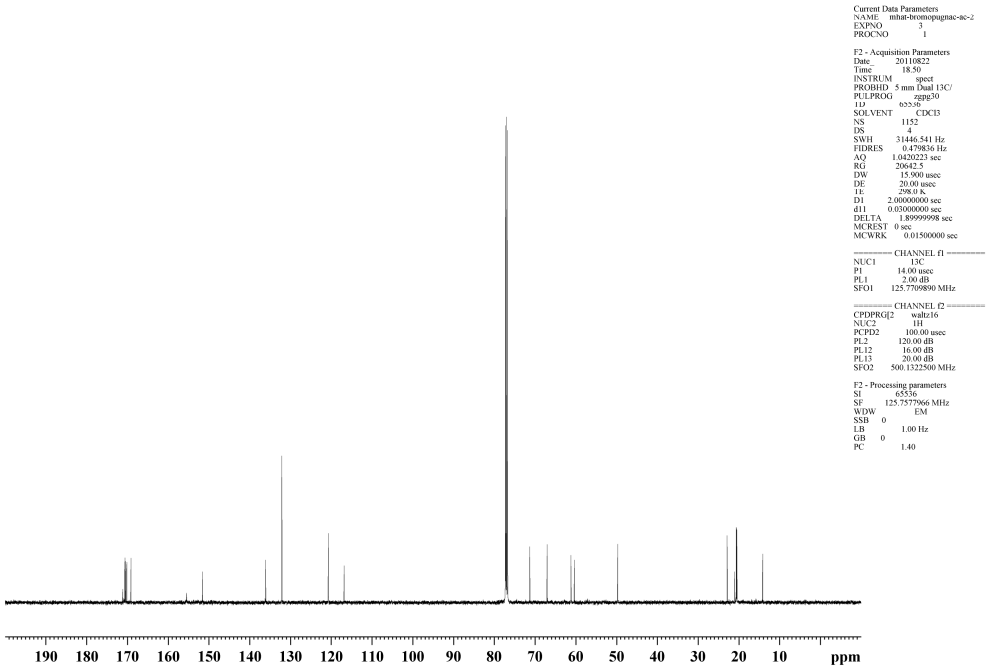


^{13}C NMR spectrum of **6**



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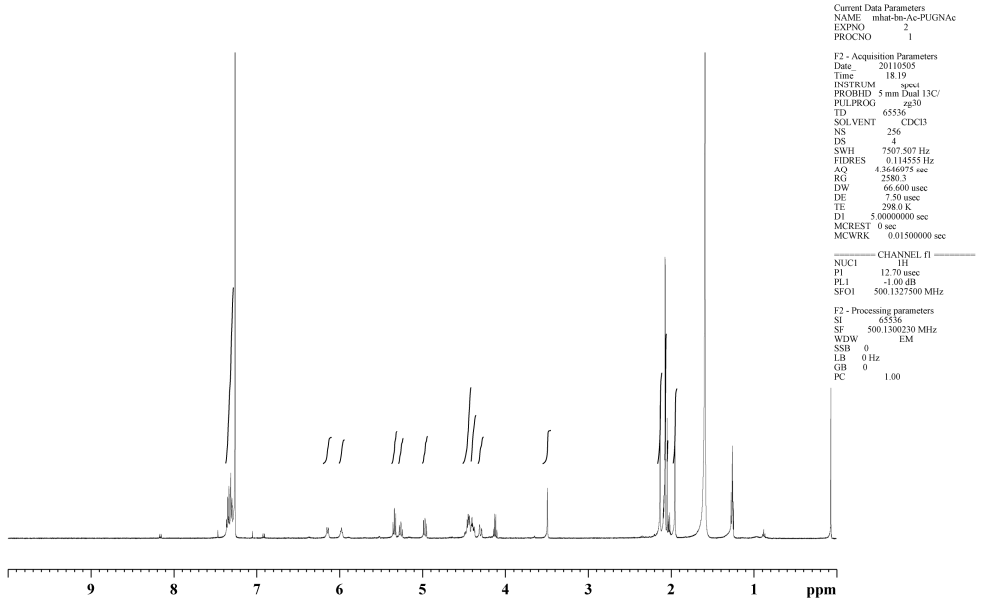
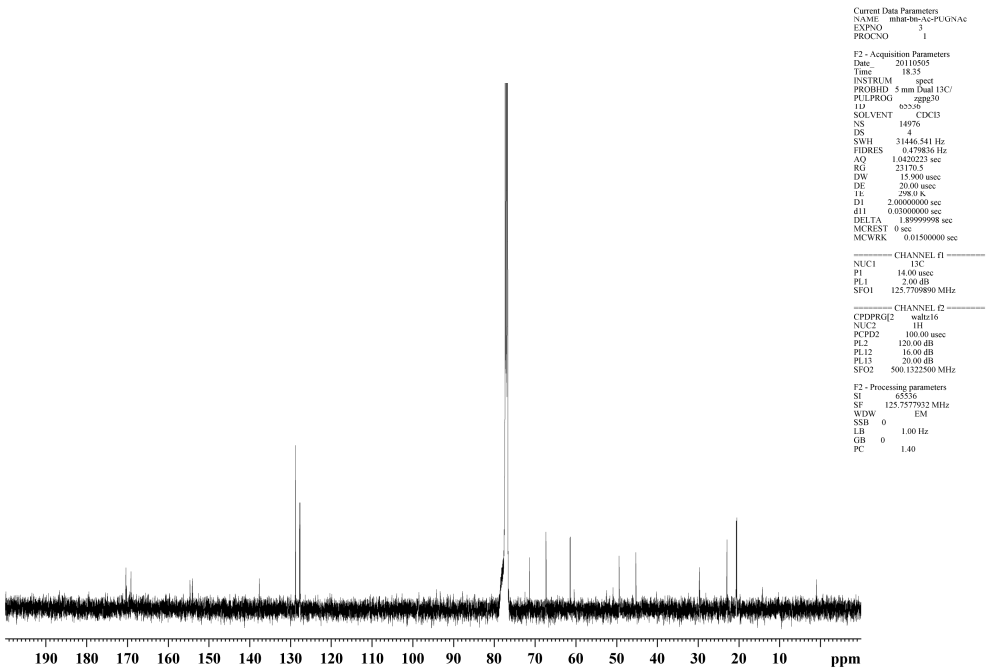


^{13}C NMR spectrum of **7**



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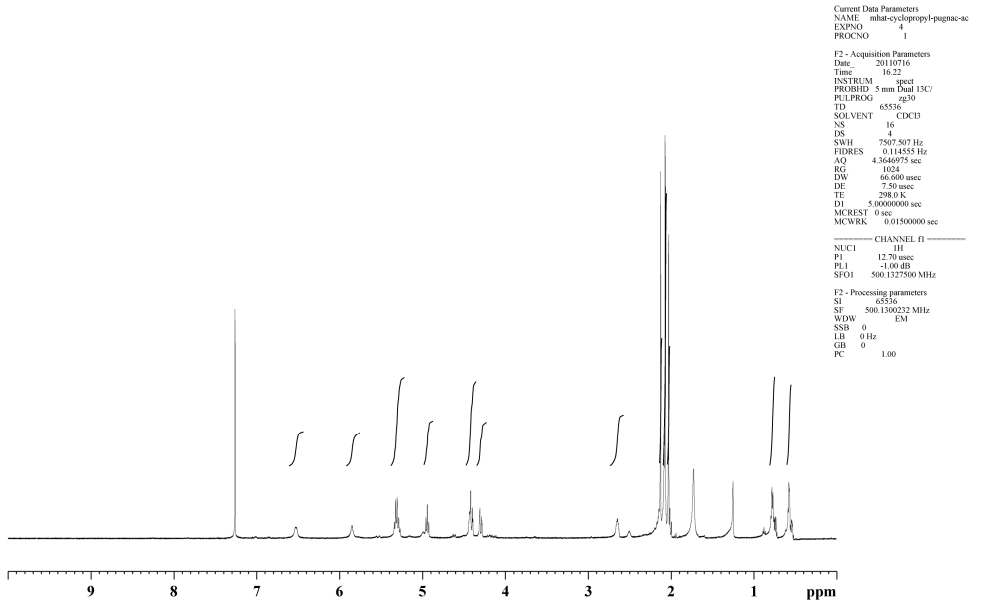

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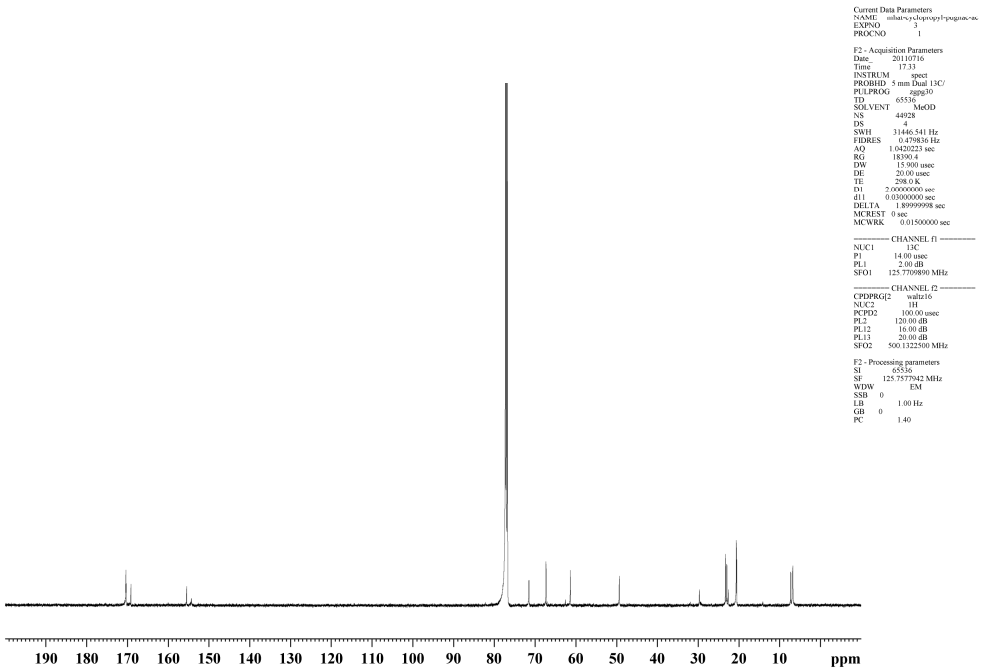
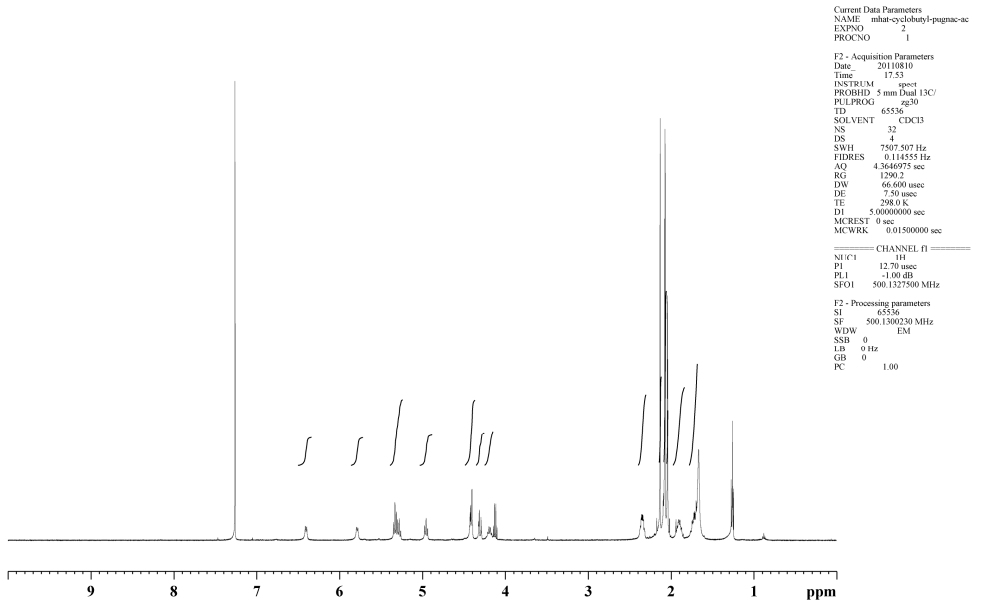


^{1}H NMR spectrum of **9**



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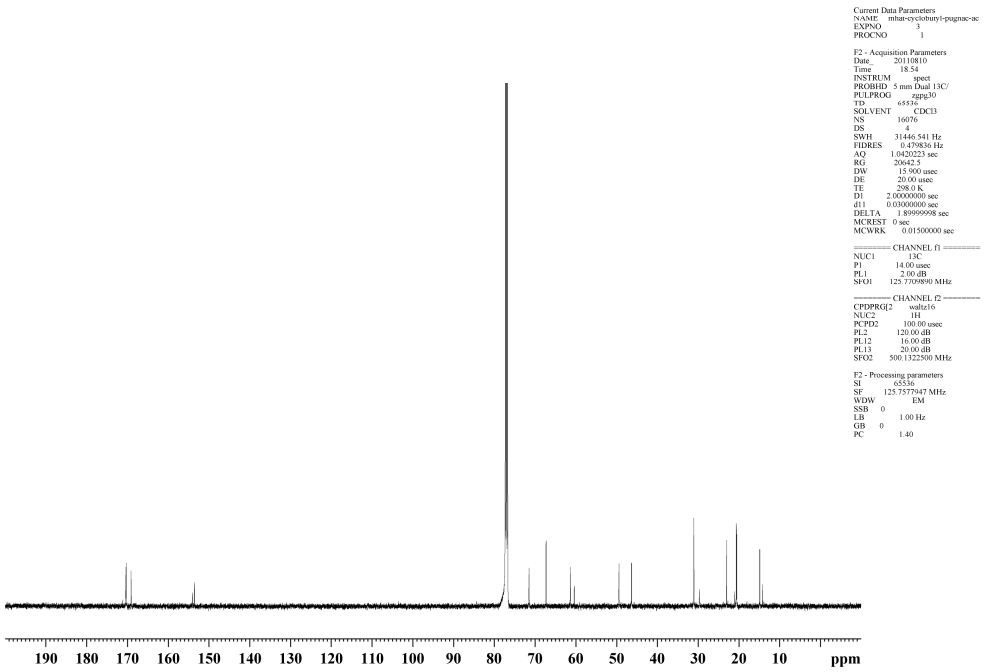
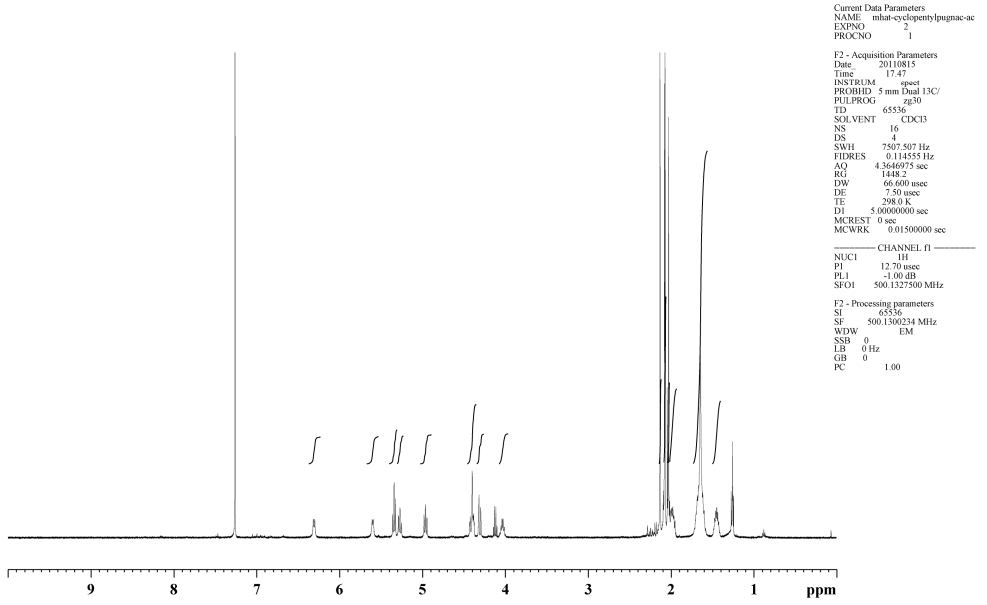


^{1}H NMR spectrum of **10**



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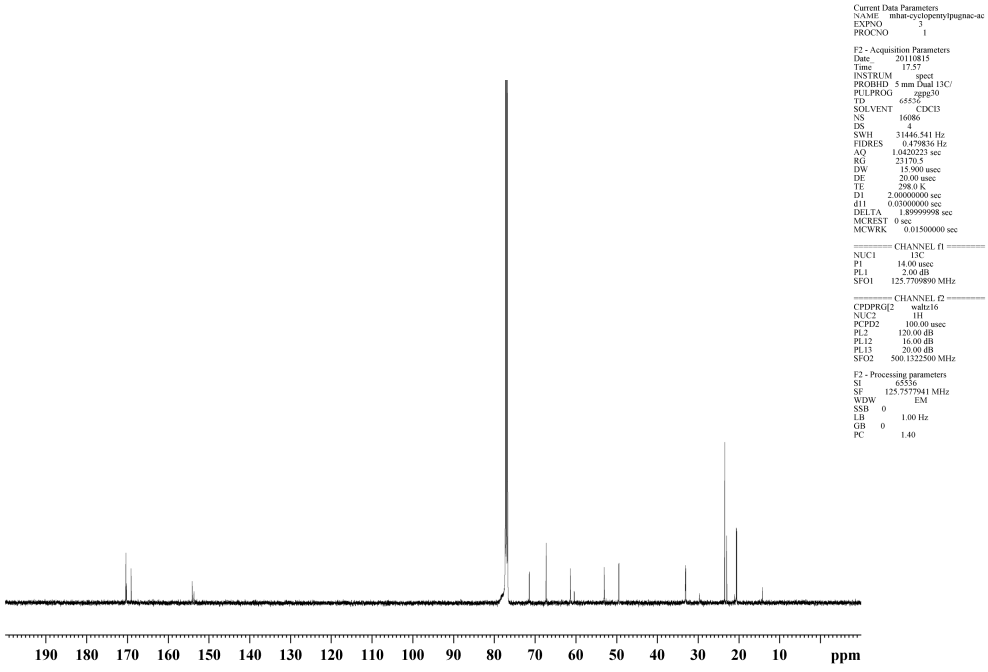

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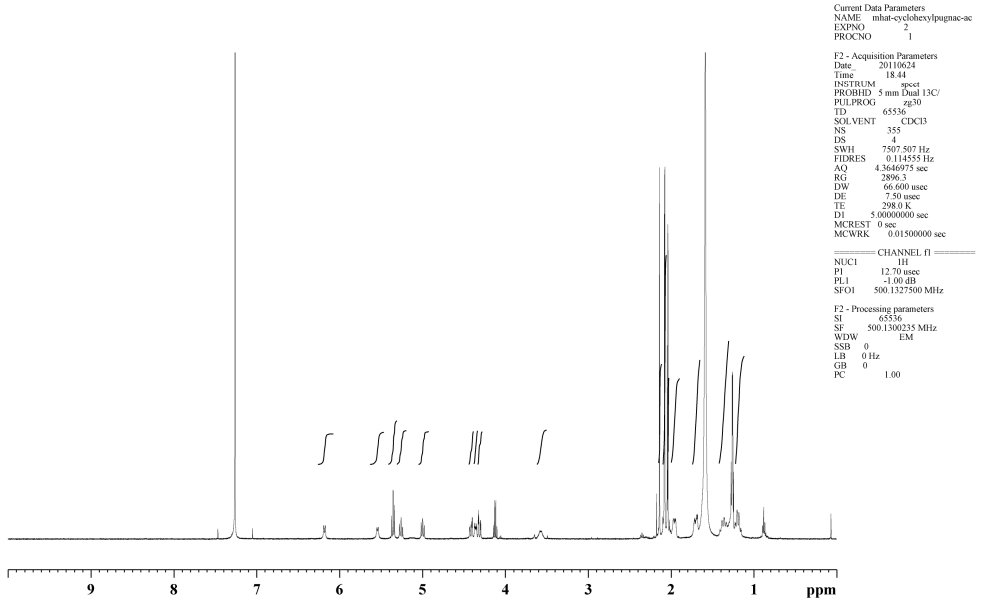
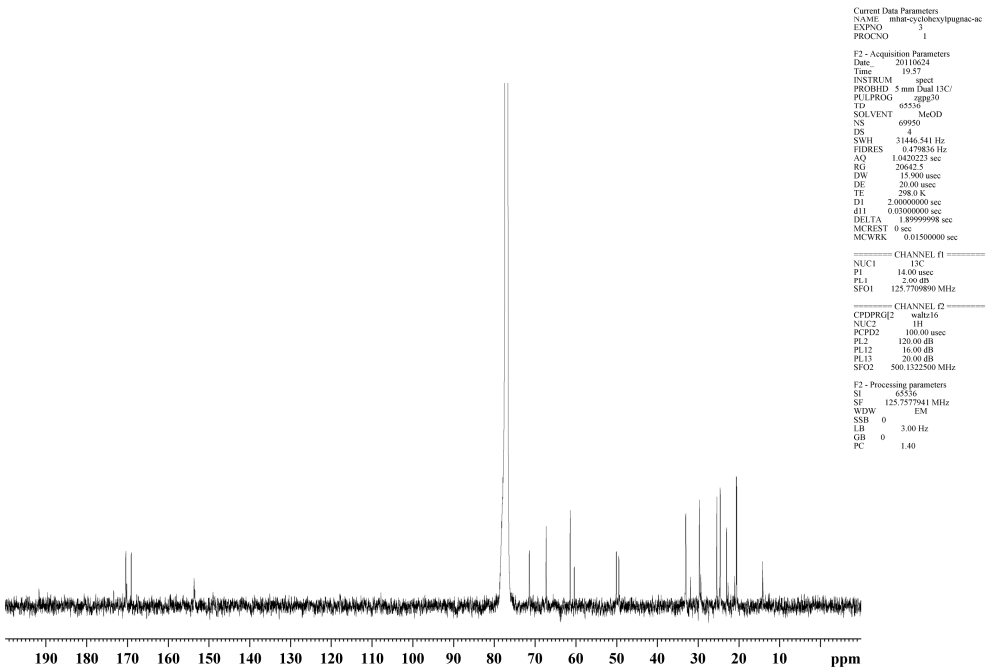
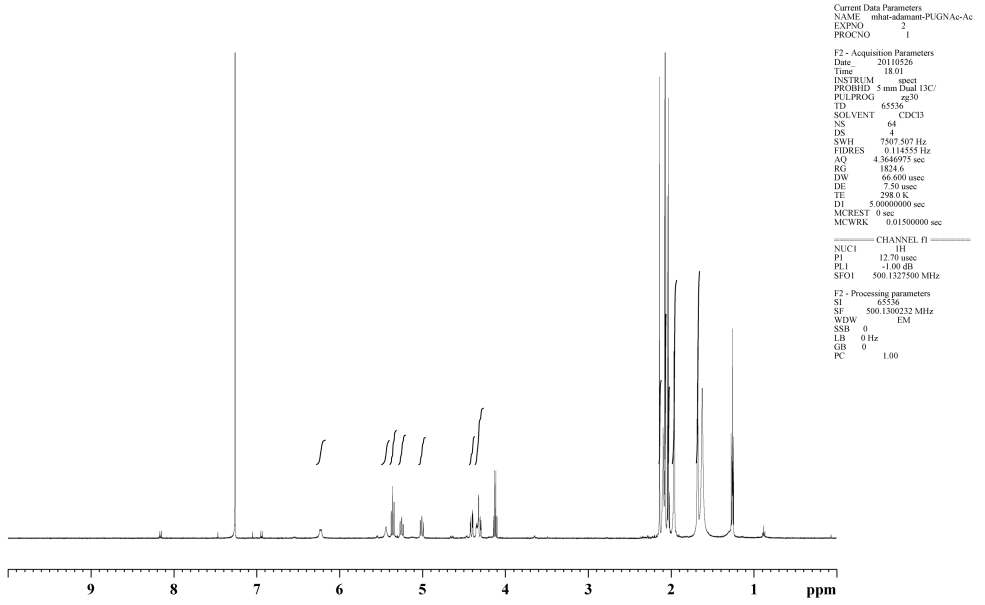


^{13}C NMR spectrum of **11**



^{1}H NMR spectrum of **12**



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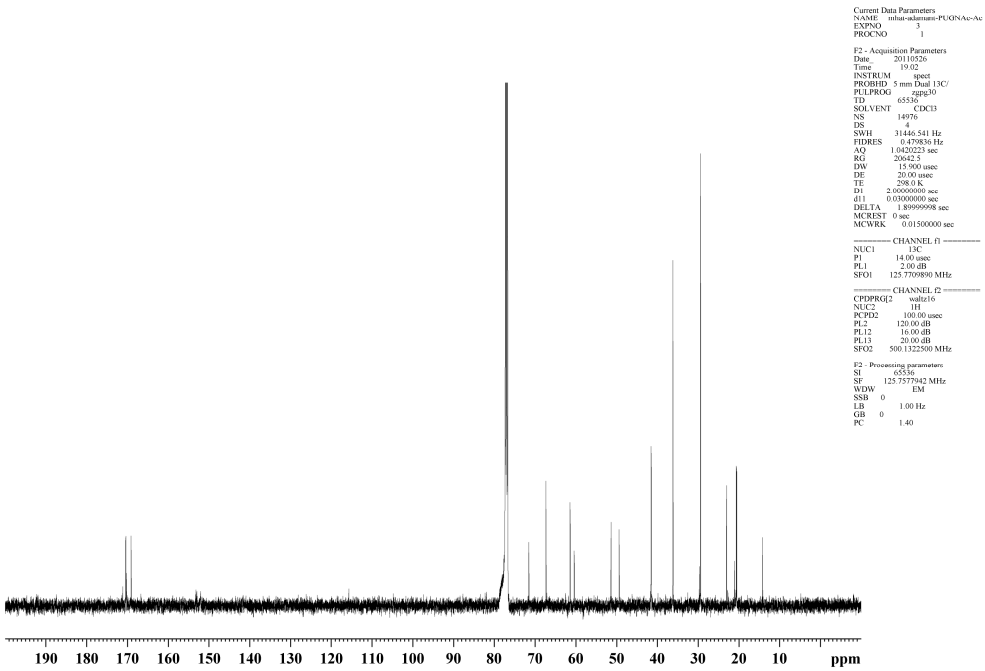
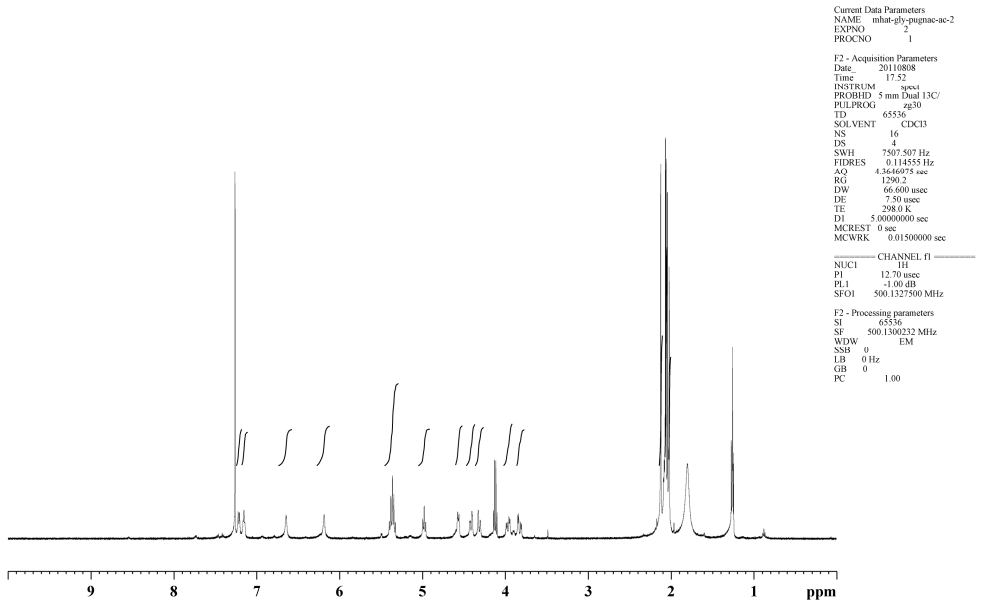


^{1}H NMR spectrum of **13**



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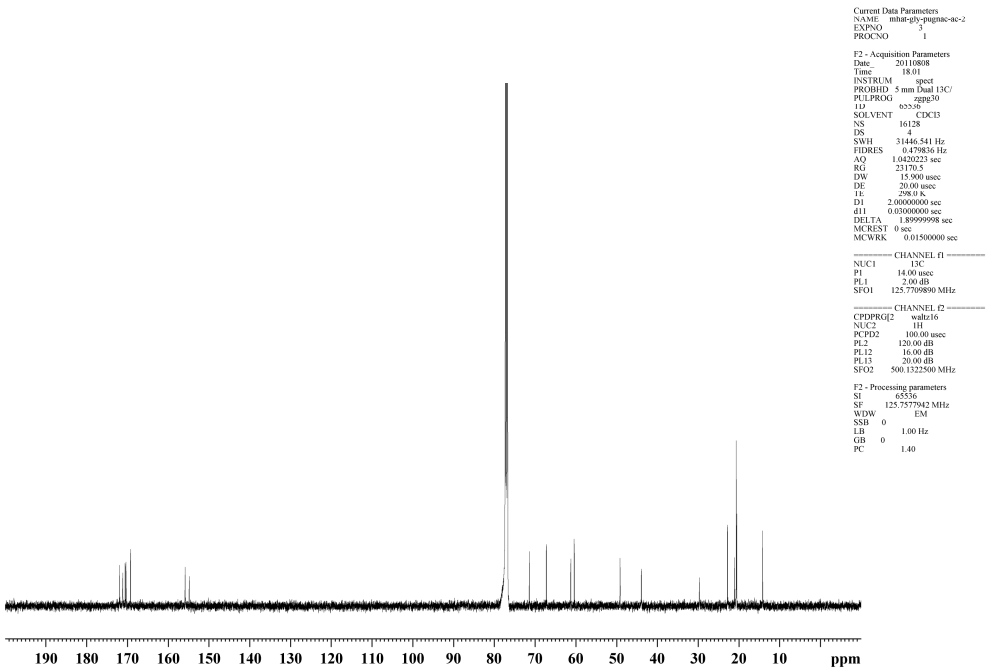

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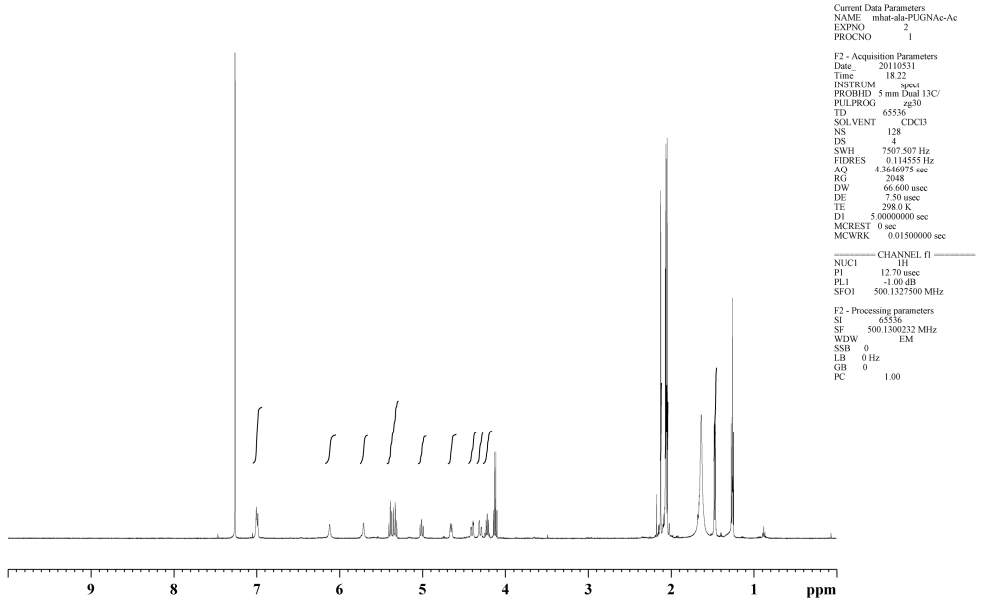

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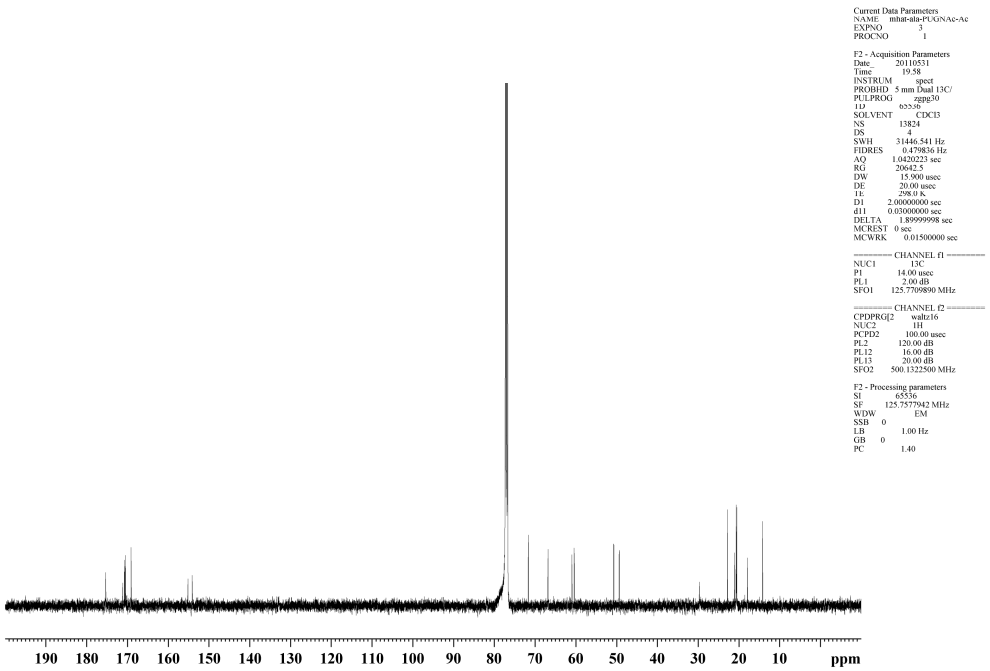
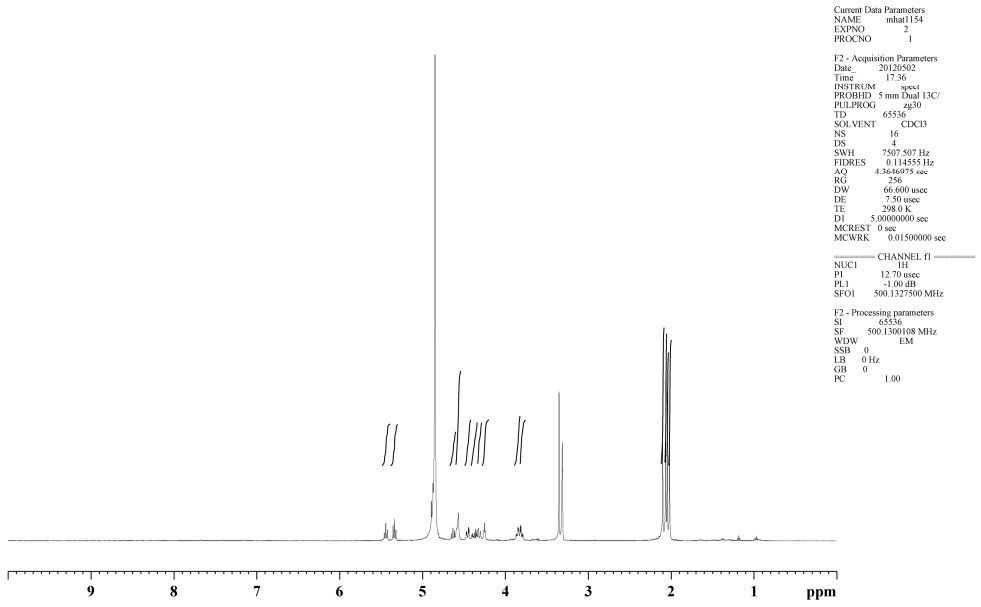


^{1}H NMR spectrum of **15**



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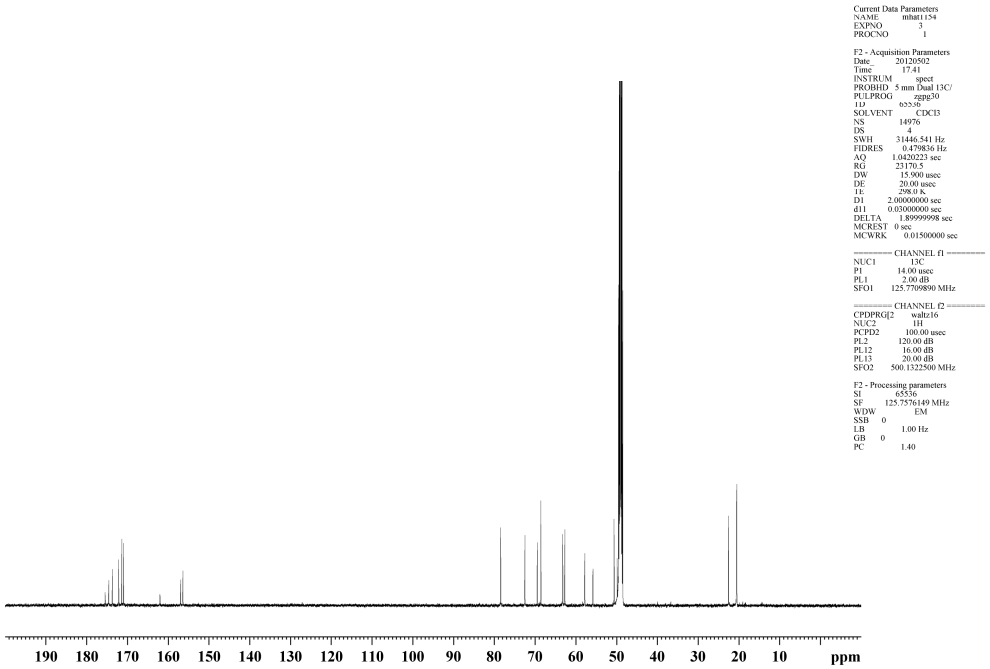

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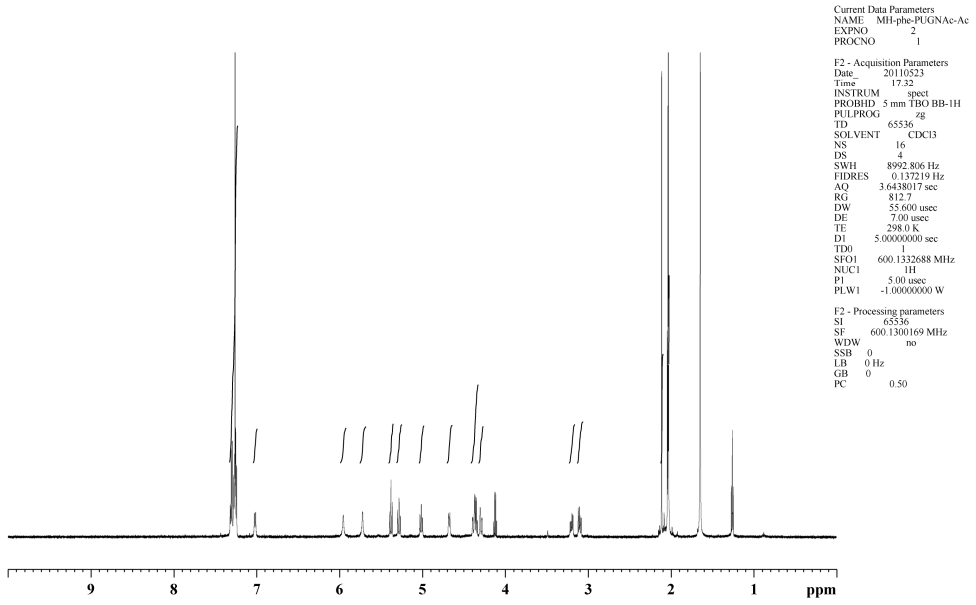

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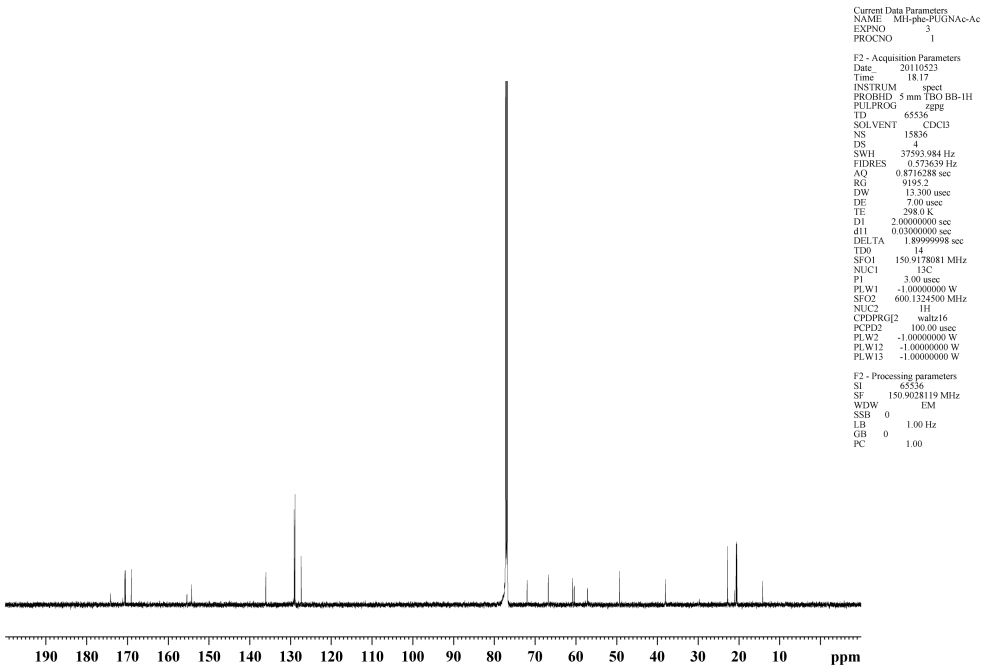

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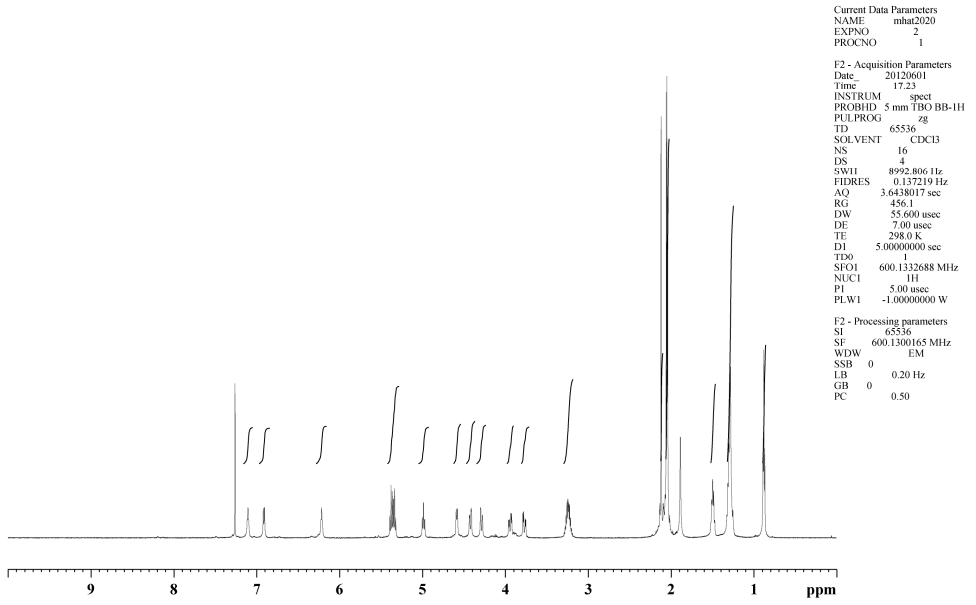

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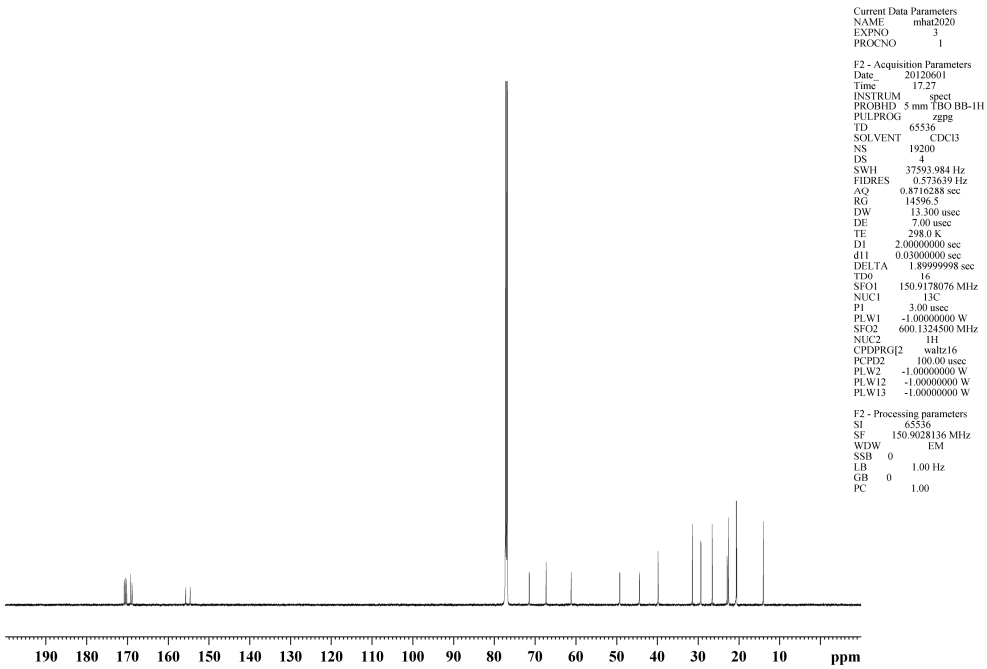
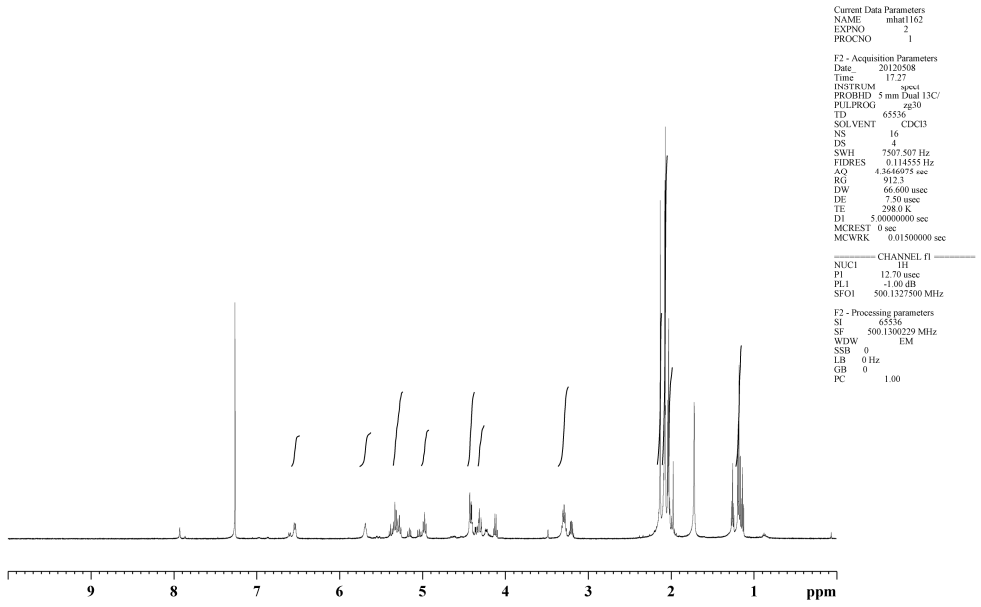
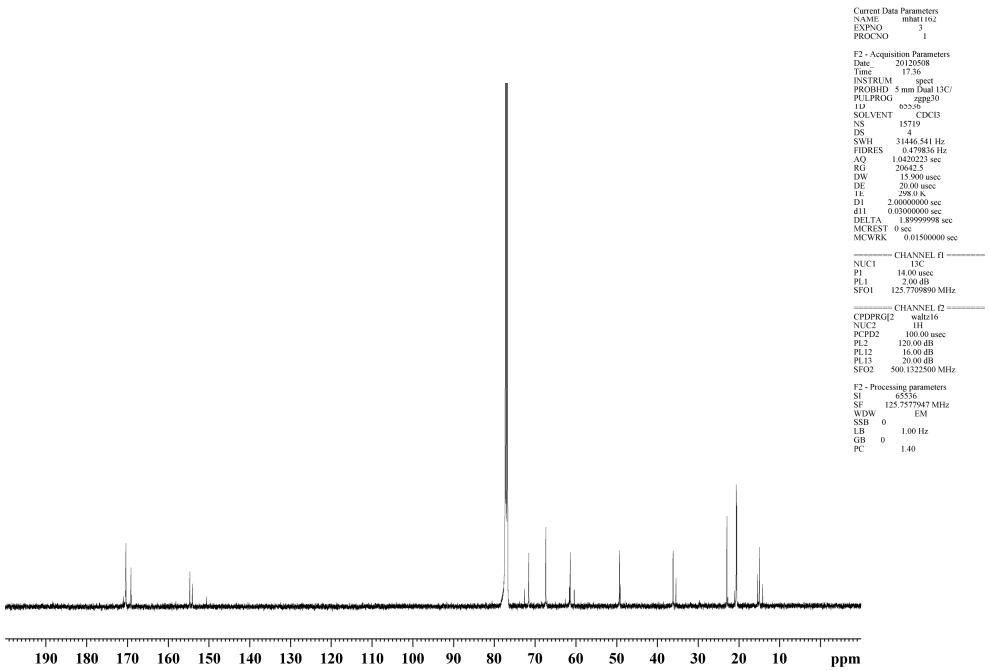


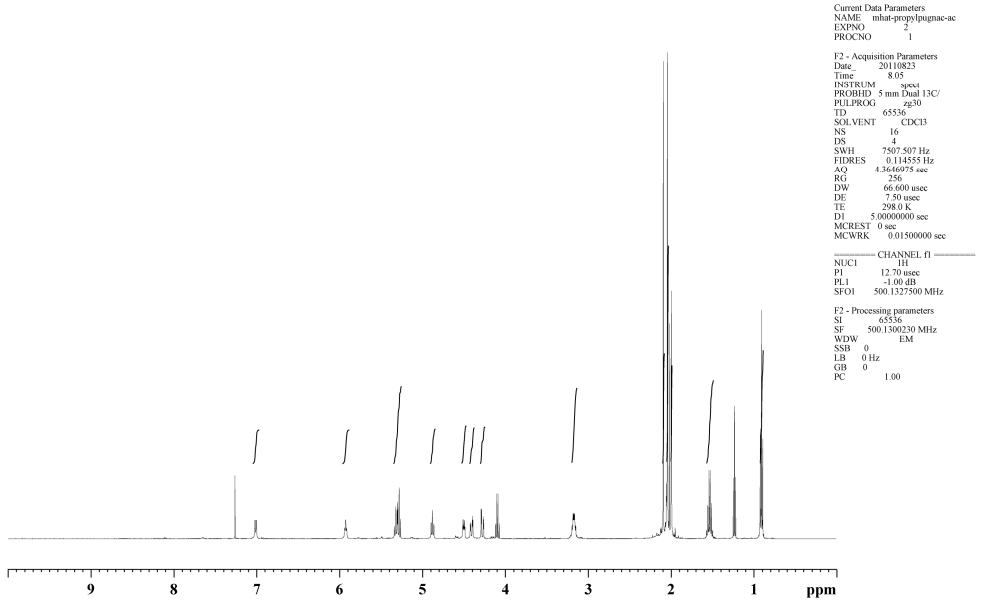
^{1}H NMR spectrum of **19**



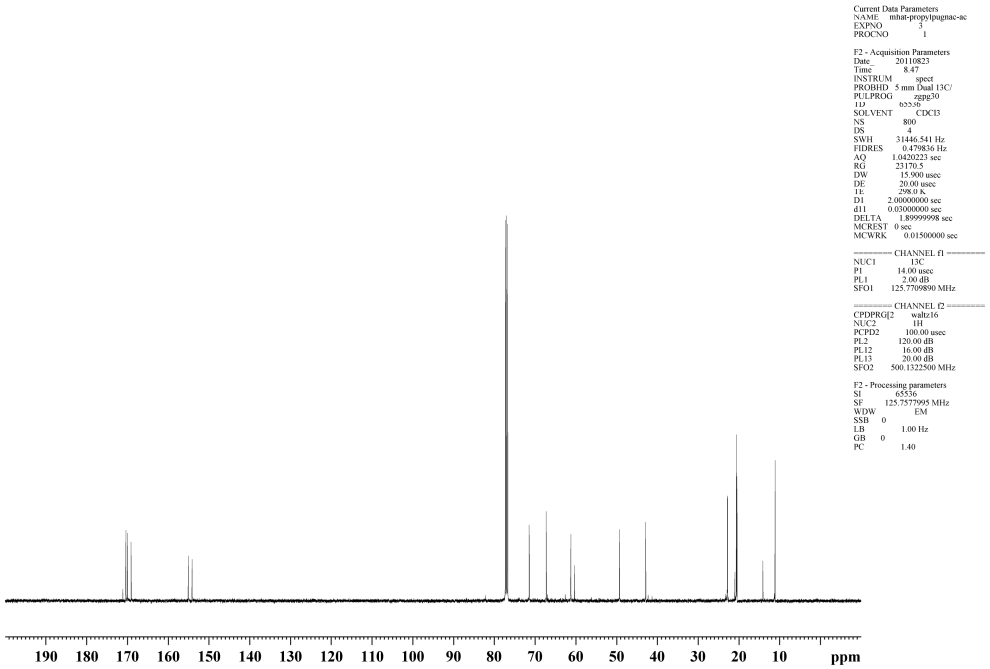
^{13}C NMR spectrum of **19**



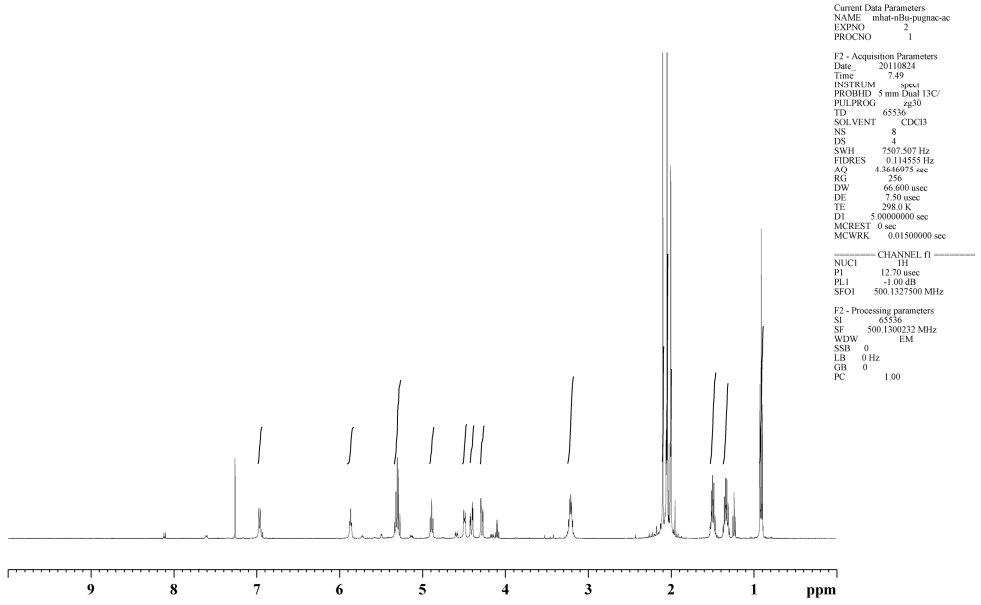
^{1}H NMR spectrum of **20**



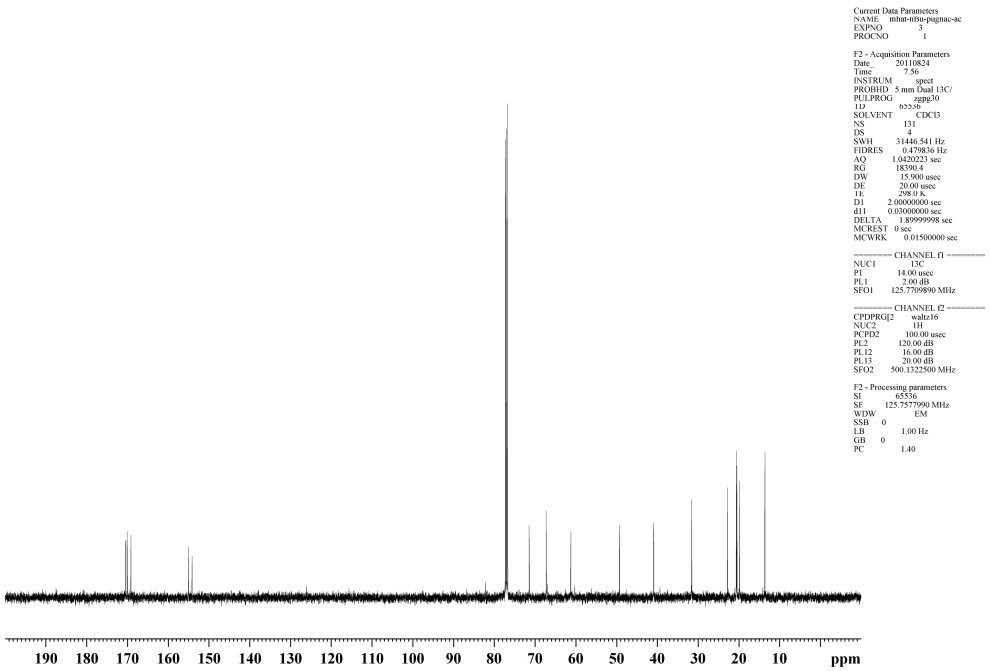
^{13}C NMR spectrum of **20**



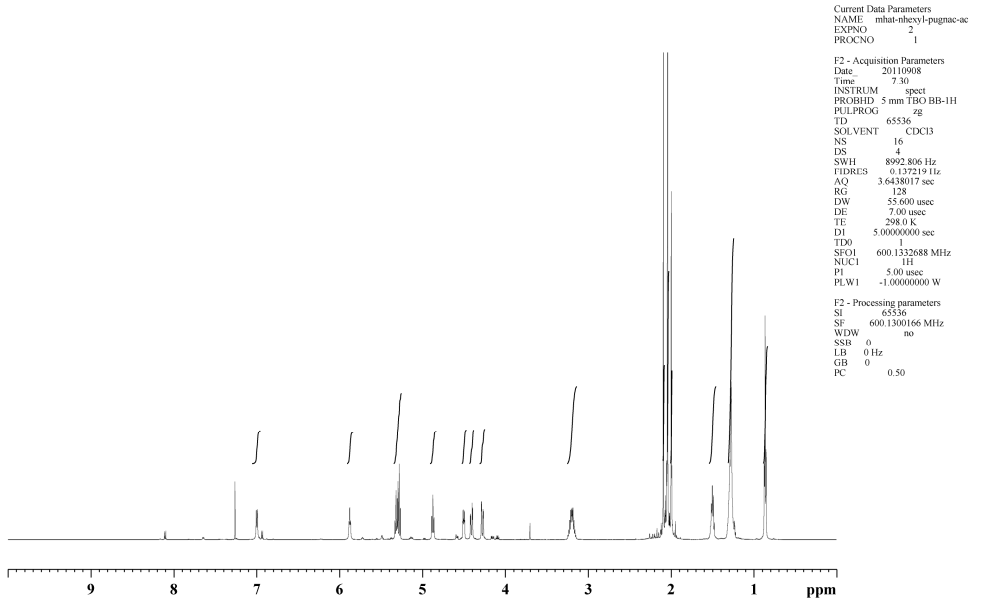
^{1}H NMR spectrum of **21**



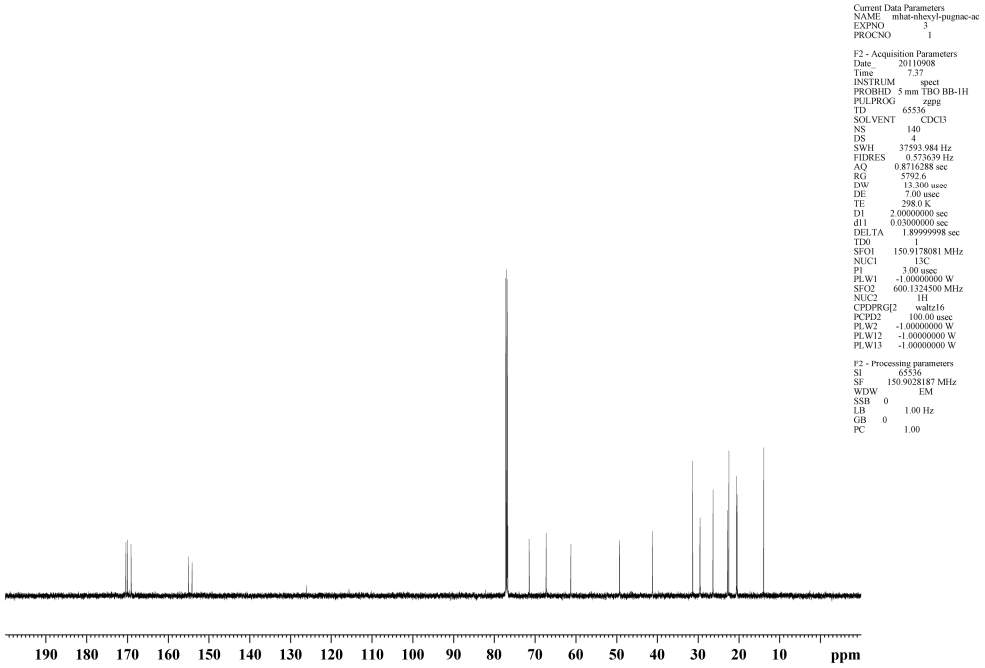
^{13}C NMR spectrum of **21**



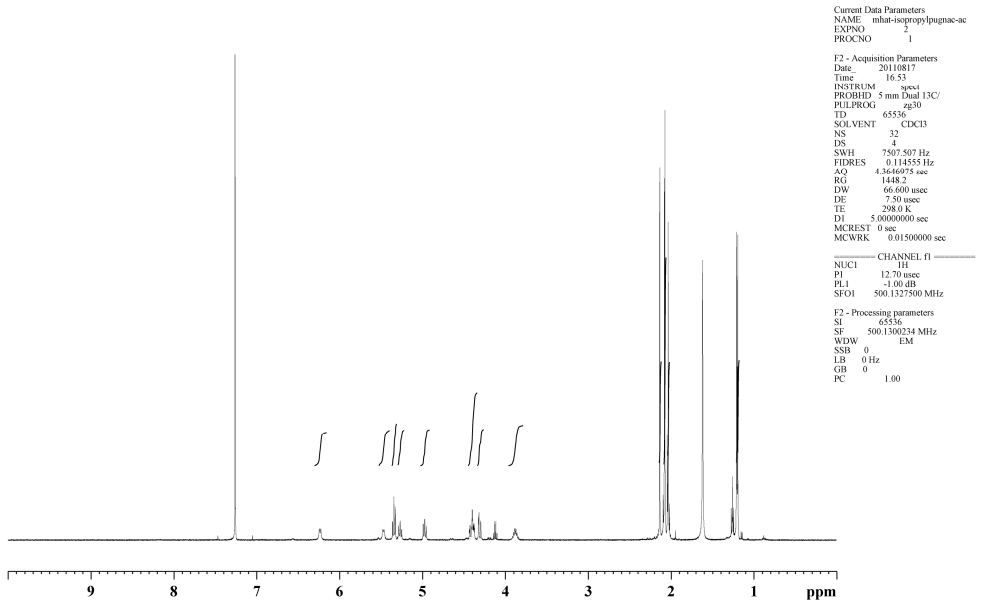
^{1}H NMR spectrum of **22**



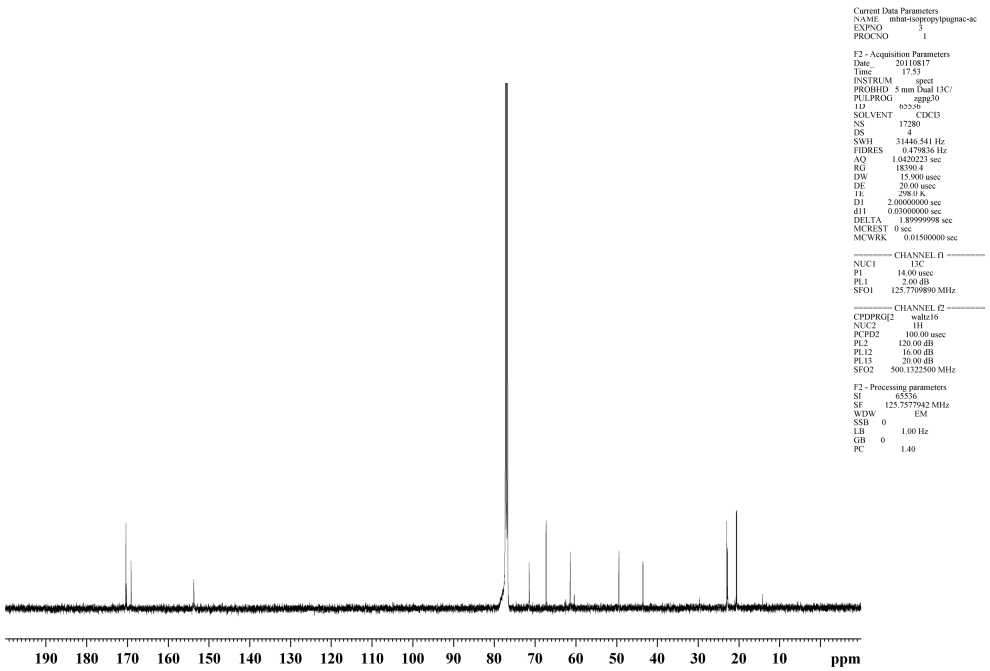
^{13}C NMR spectrum of **22**



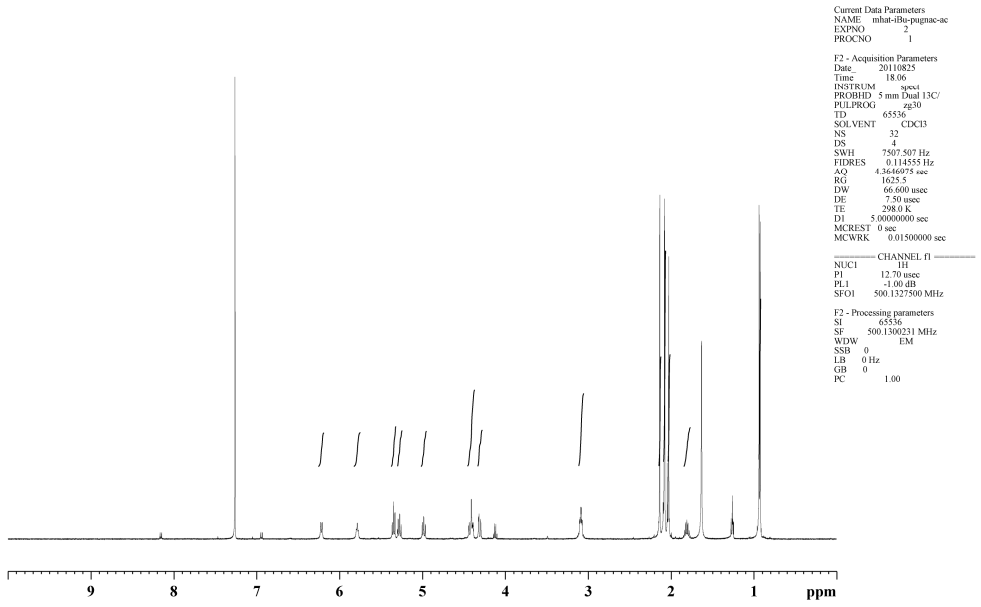
^{1}H NMR spectrum of **23**



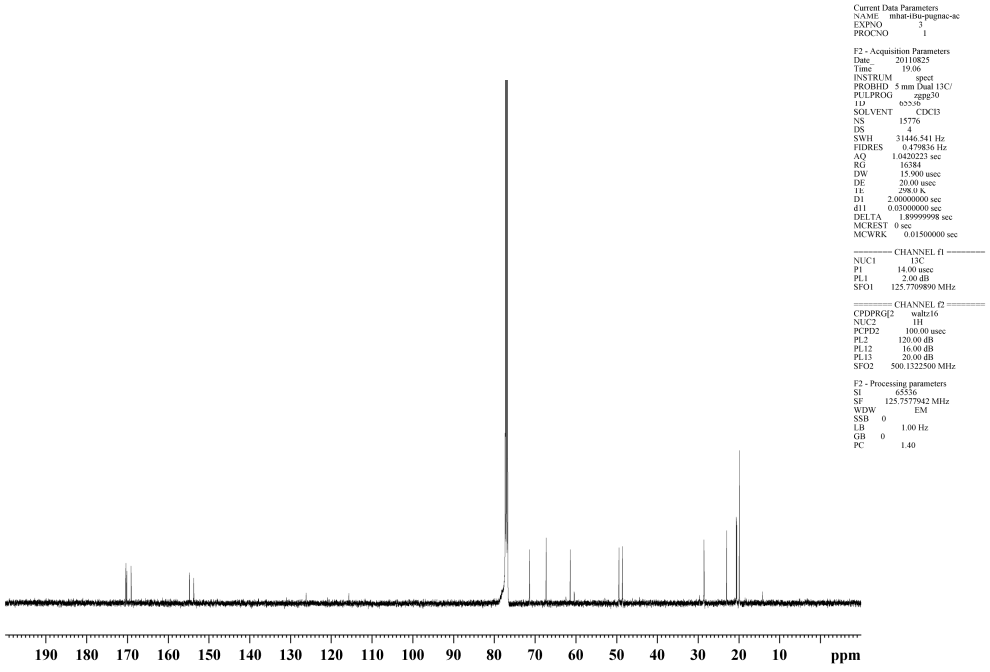
^{13}C NMR spectrum of **23**



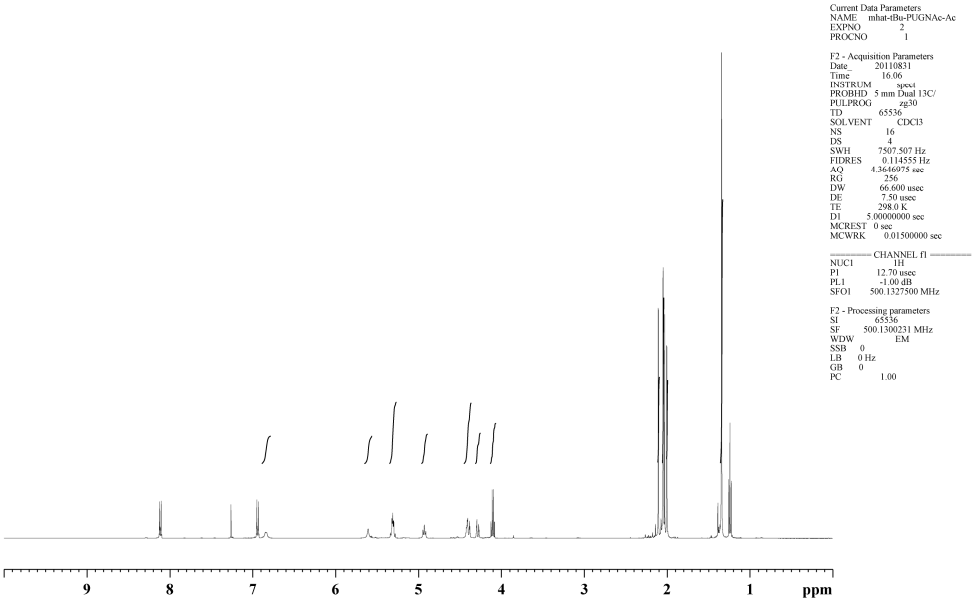
^{1}H NMR spectrum of **24**



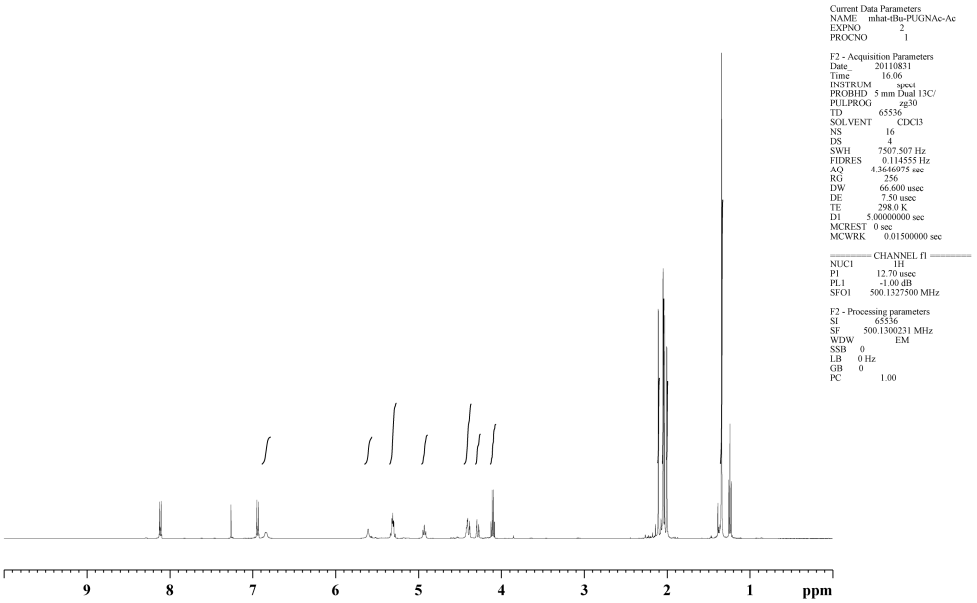
^{13}C NMR spectrum of **24**



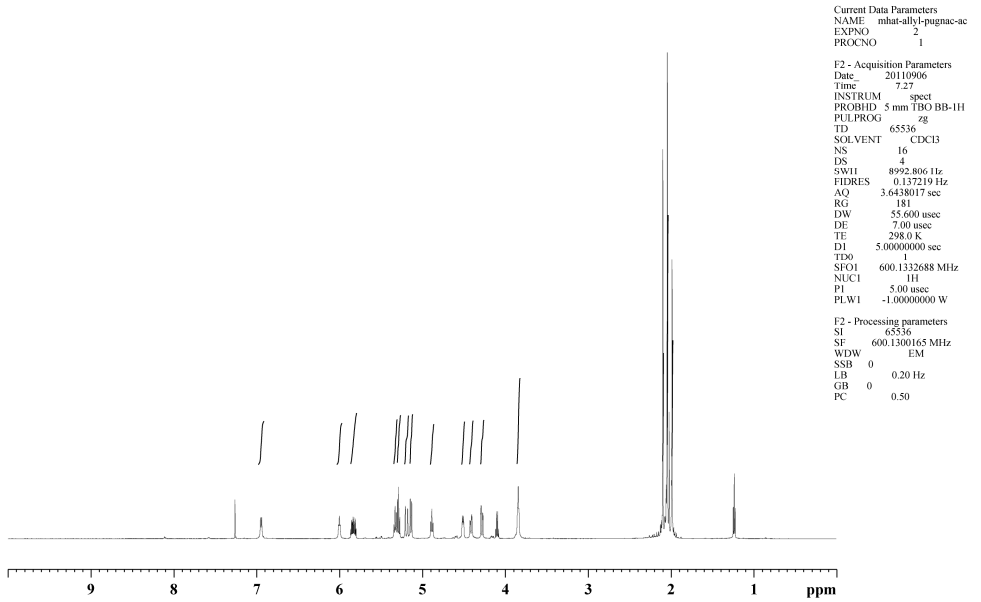
^{1}H NMR spectrum of **25**



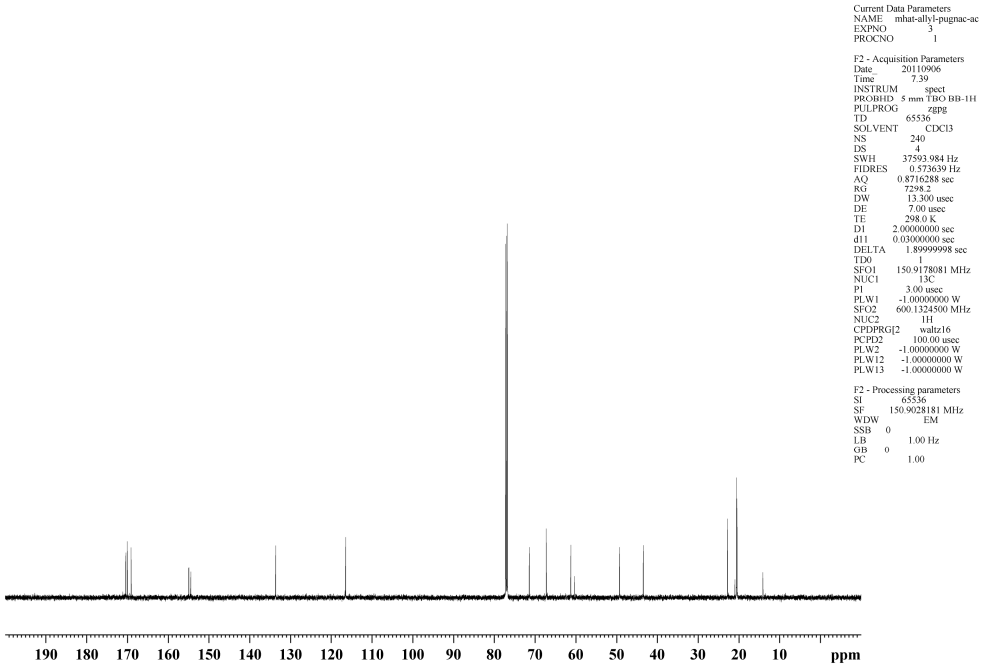
^{13}C NMR spectrum of **25**



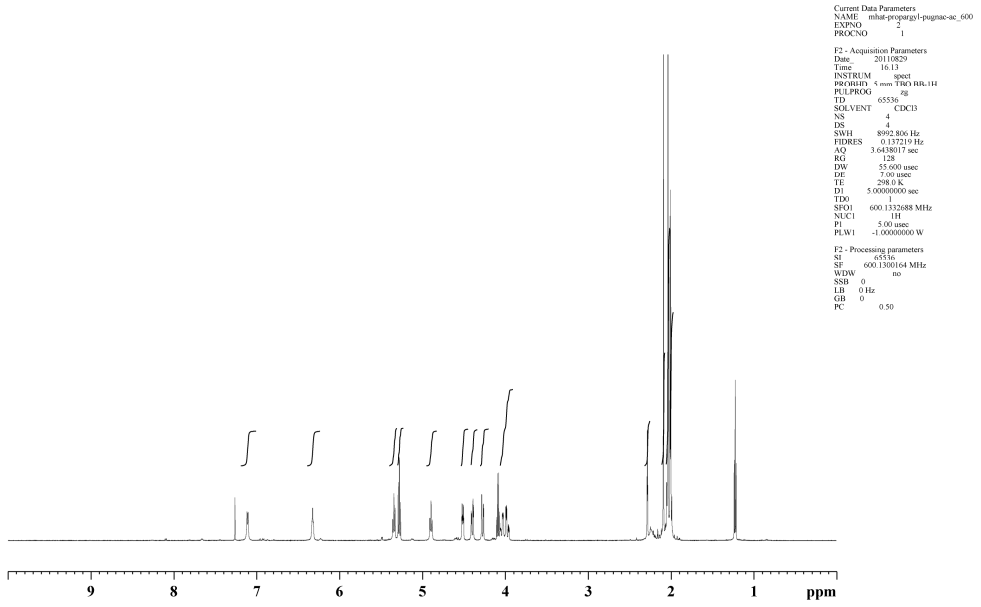
^{1}H NMR spectrum of **26**



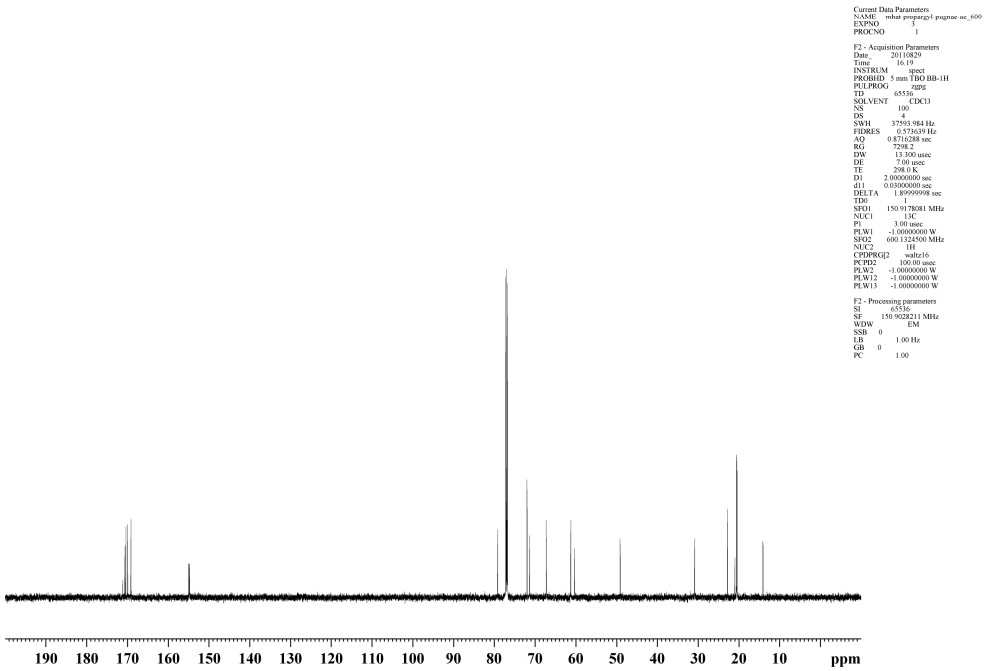
^{13}C NMR spectrum of **26**



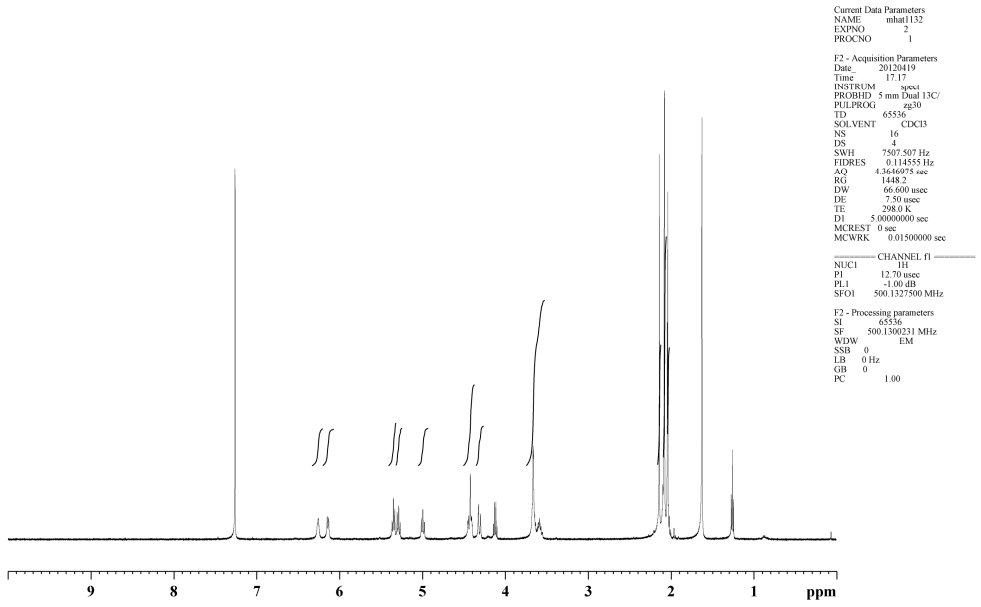
^{1}H NMR spectrum of **27**



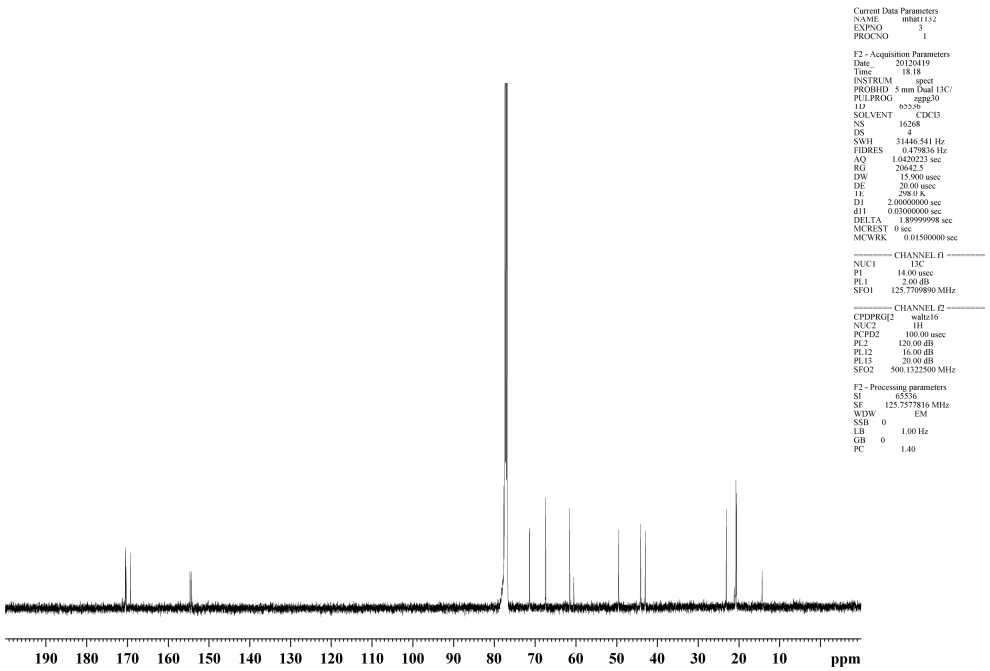
^{13}C NMR spectrum of **27**



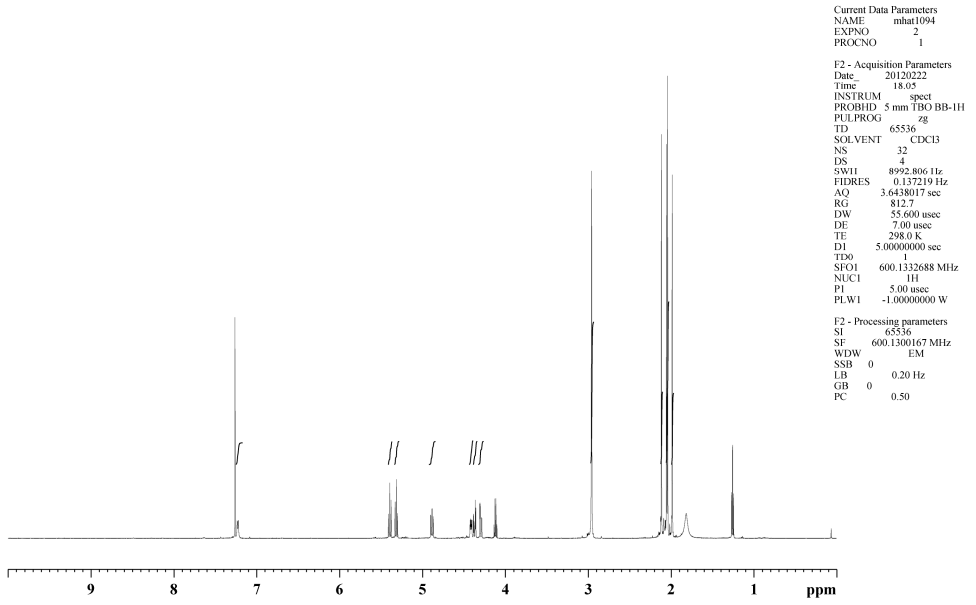
^{1}H NMR spectrum of **28**



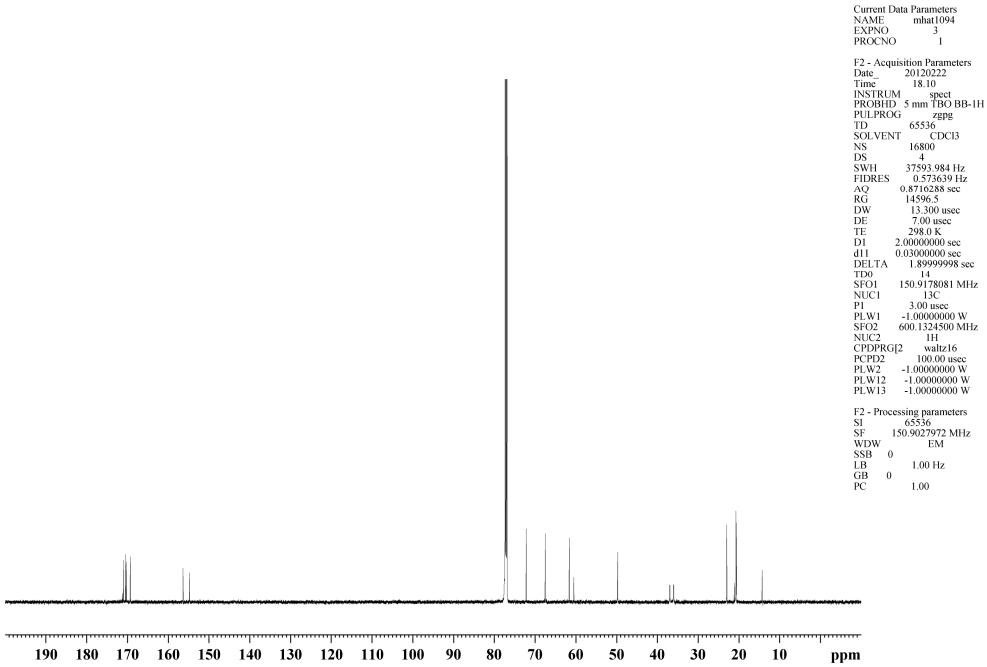
^{13}C NMR spectrum of **28**



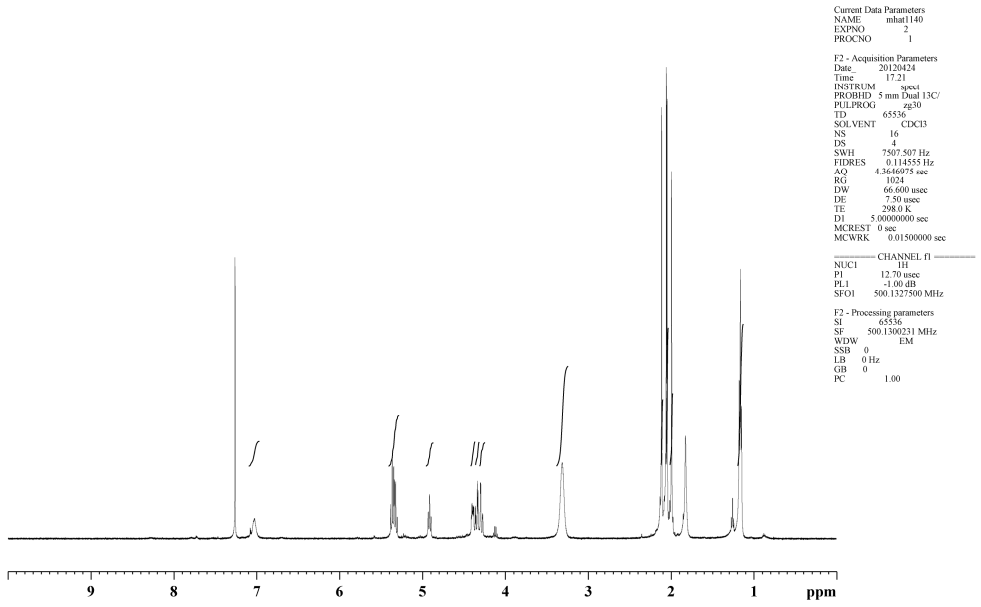
^{1}H NMR spectrum of **29**



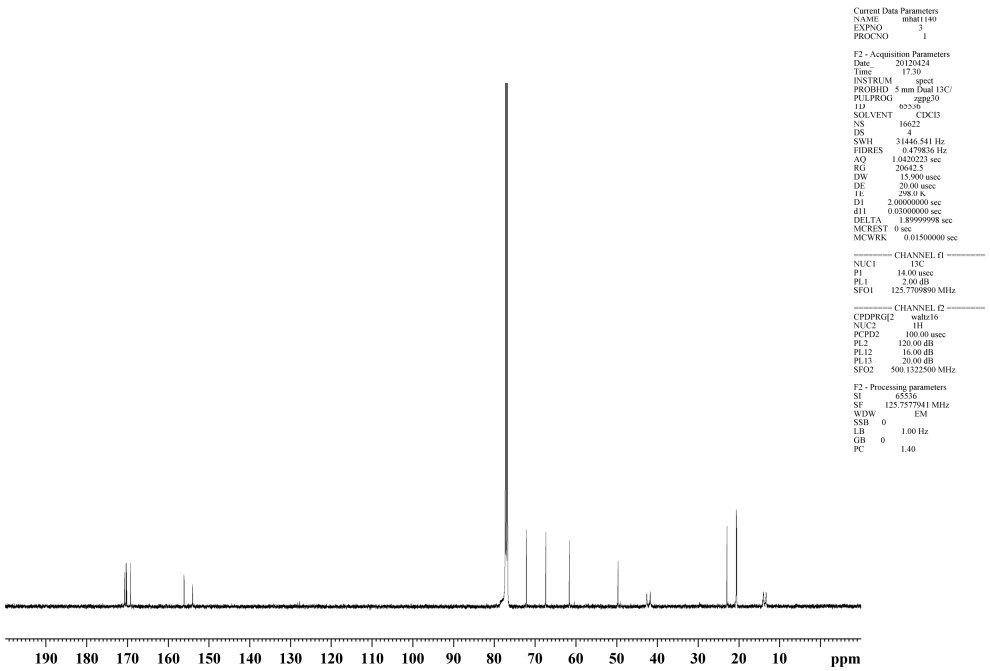
^{13}C NMR spectrum of **29**



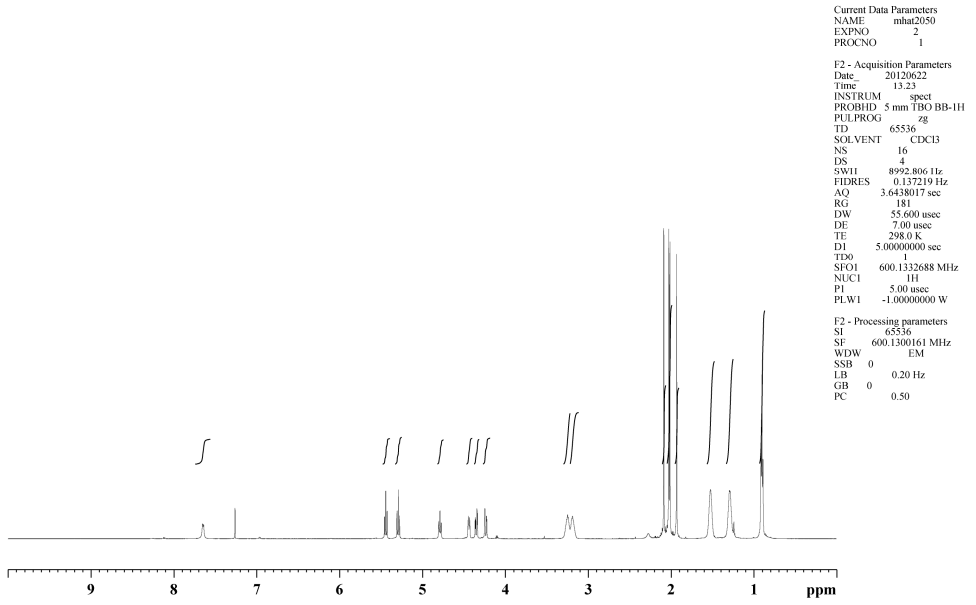
^{1}H NMR spectrum of **30**



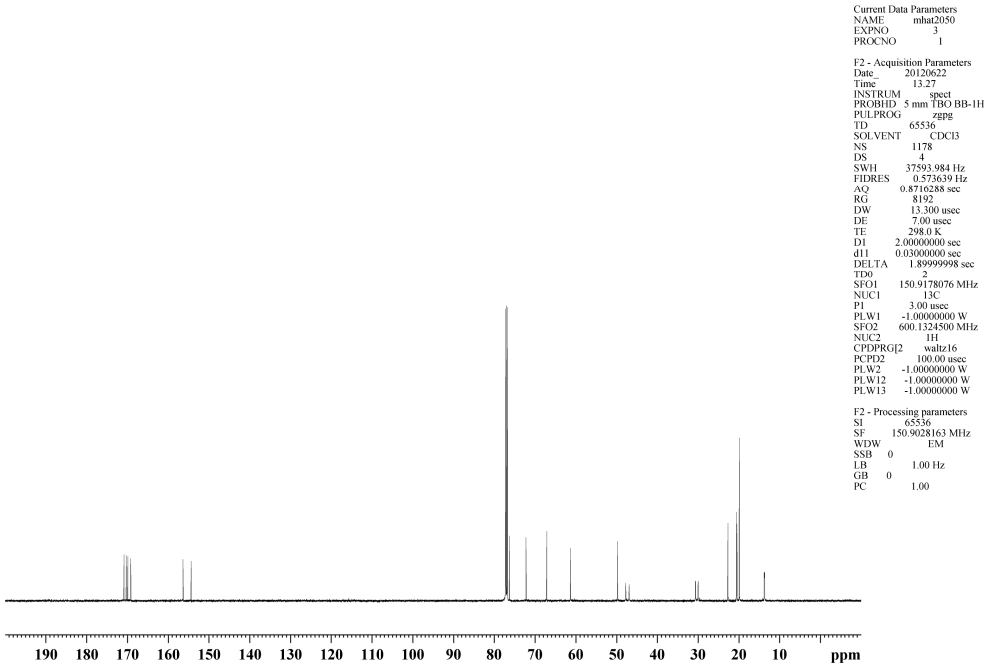
^{13}C NMR spectrum of **30**



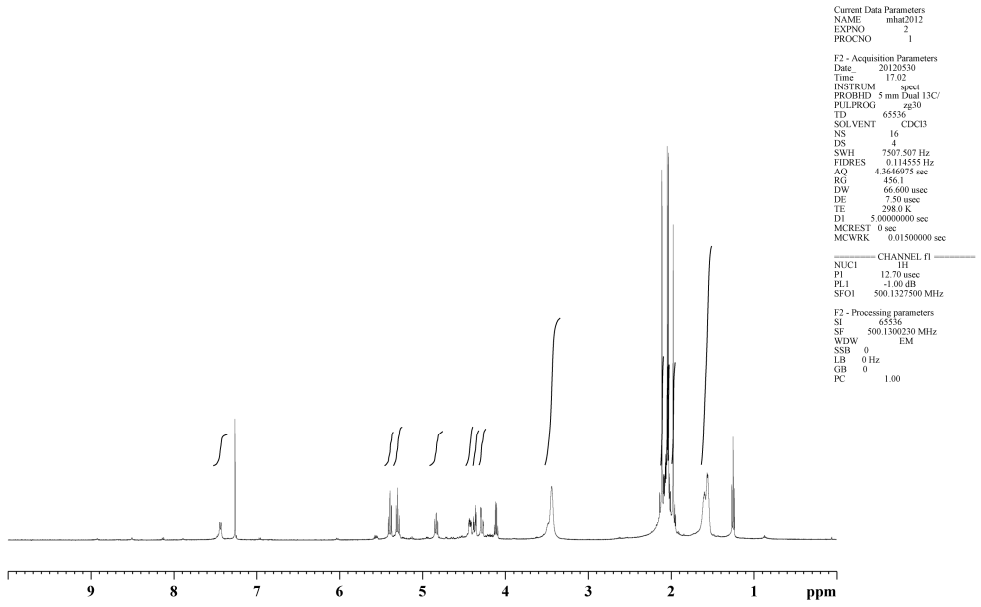
^{1}H NMR spectrum of **31**



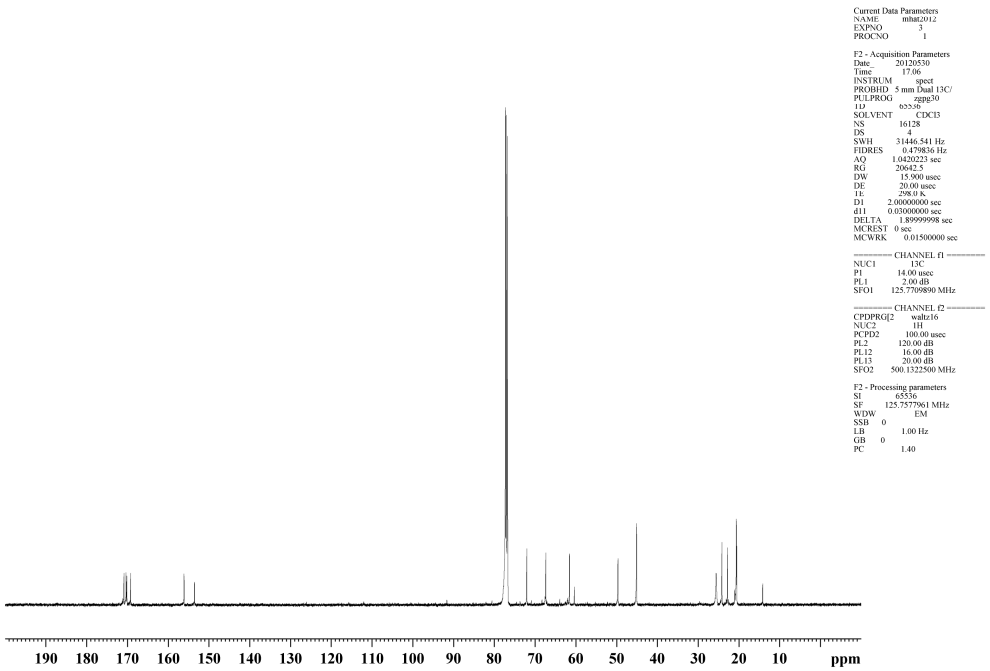
^{13}C NMR spectrum of **31**



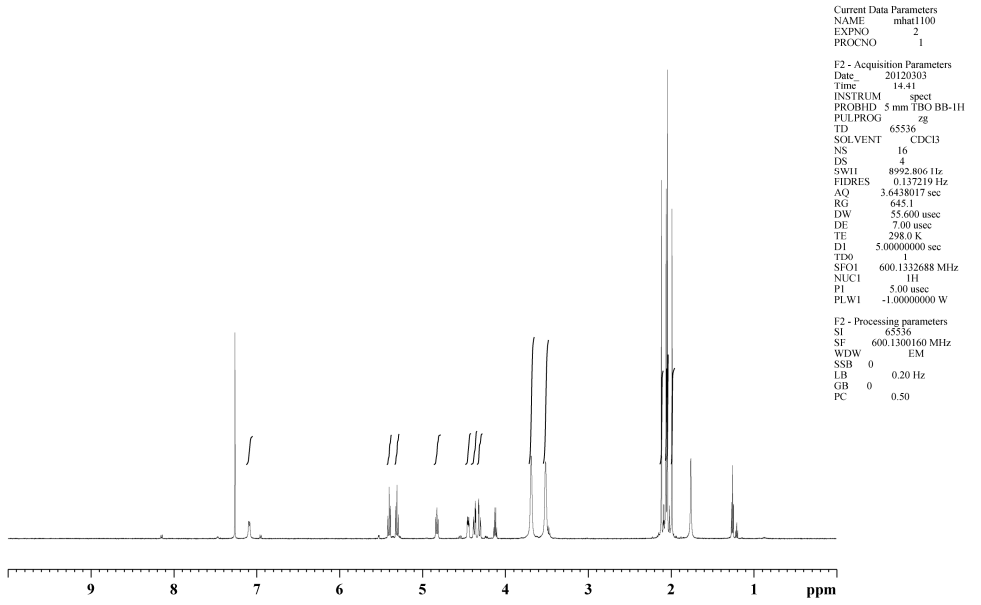
^{1}H NMR spectrum of **32**



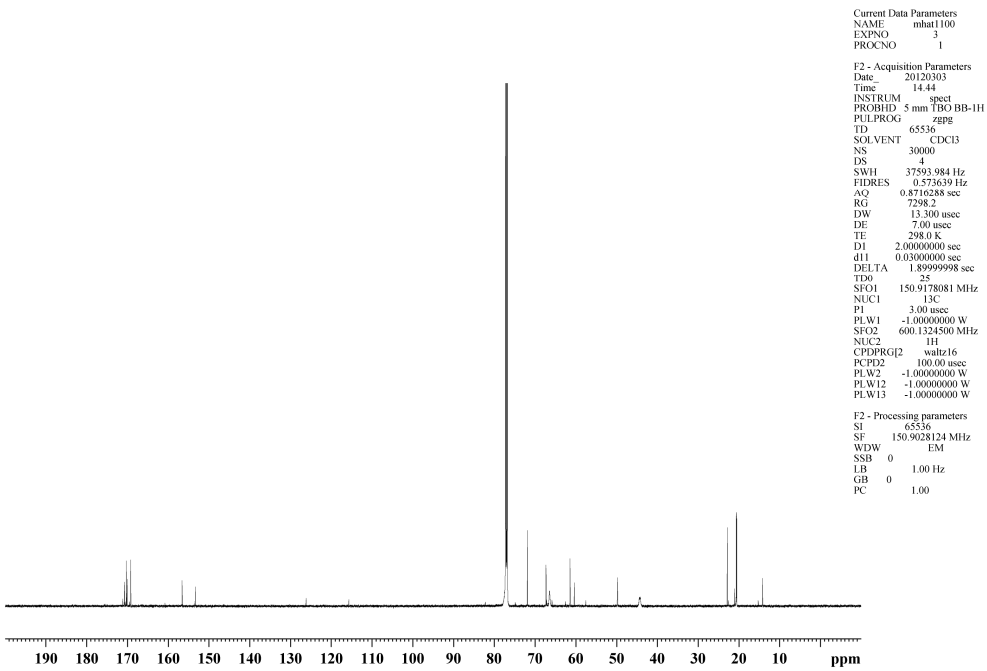
^{13}C NMR spectrum of **32**



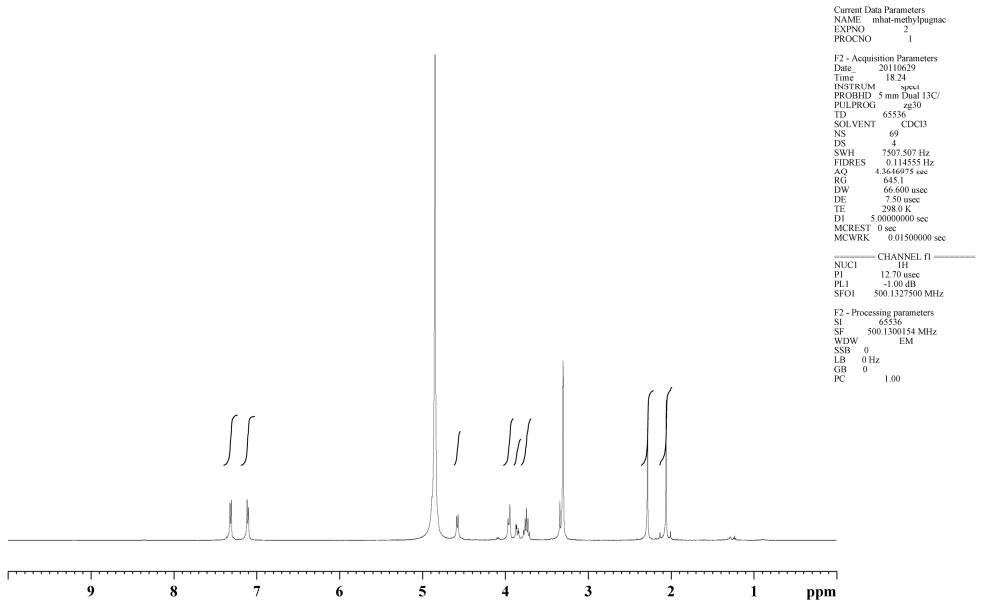
^{1}H NMR spectrum of **33**



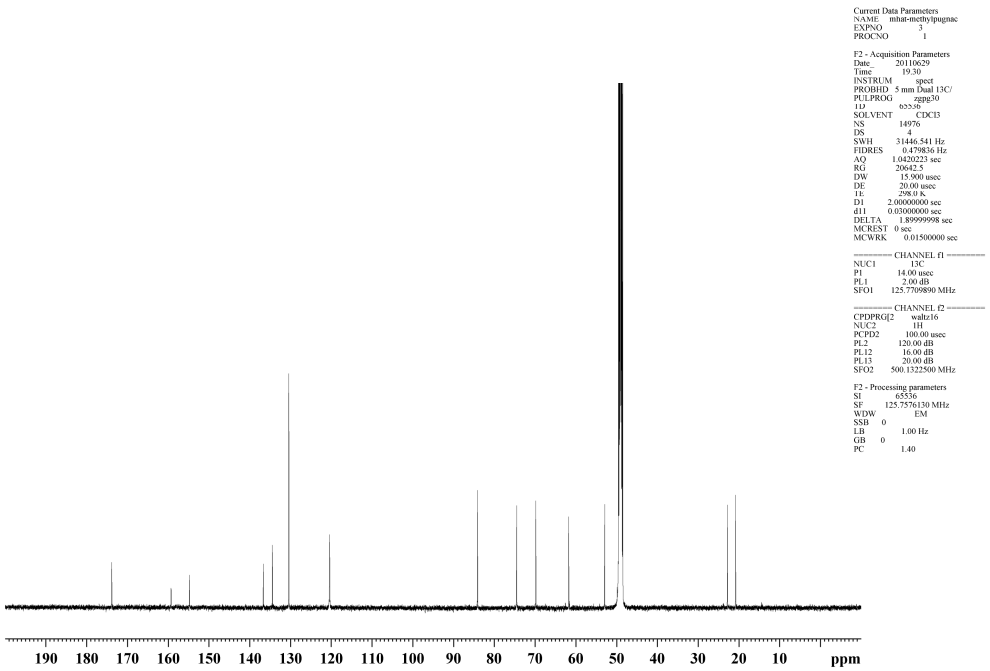
^{13}C NMR spectrum of **33**



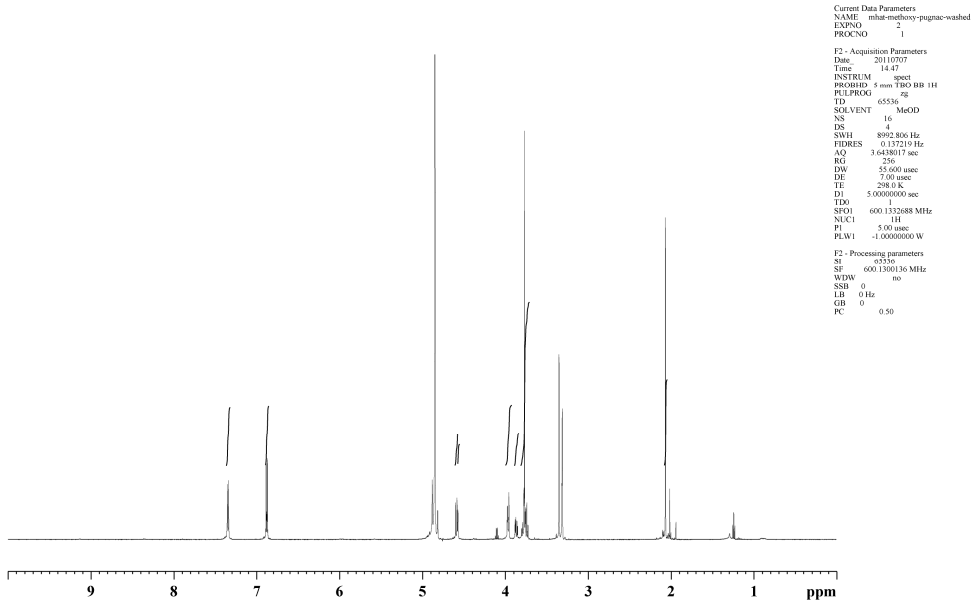
^{1}H NMR spectrum of **34**



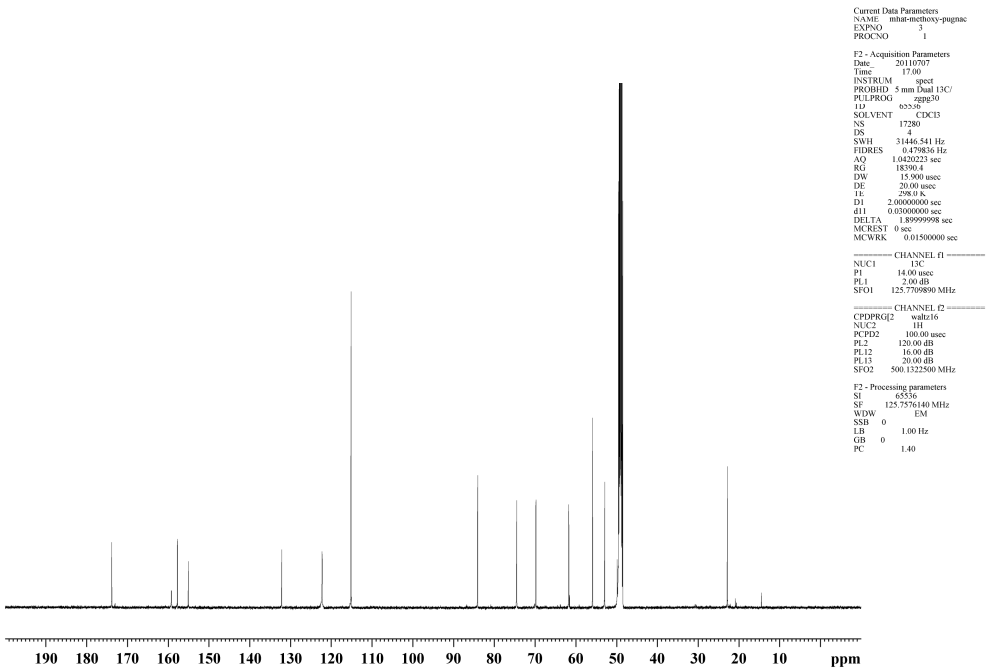
^{13}C NMR spectrum of **34**



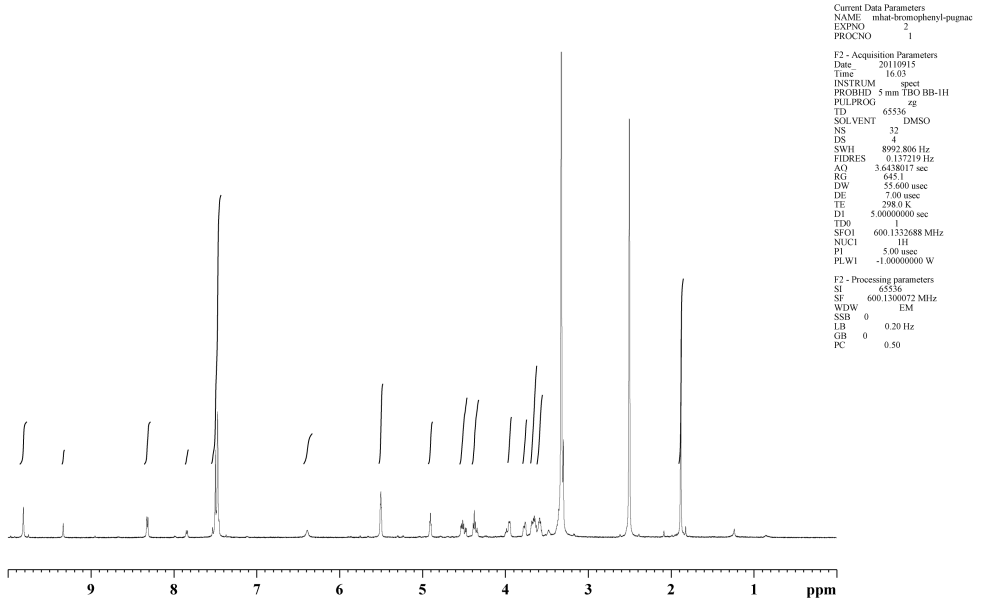
^{1}H NMR spectrum of **35**



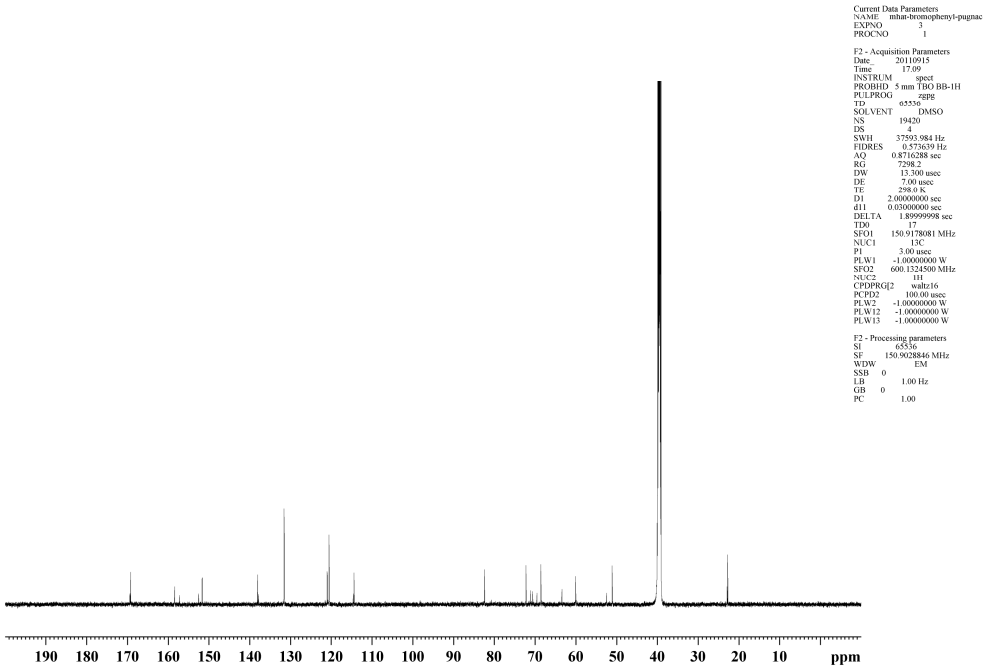
^{13}C NMR spectrum of **35**



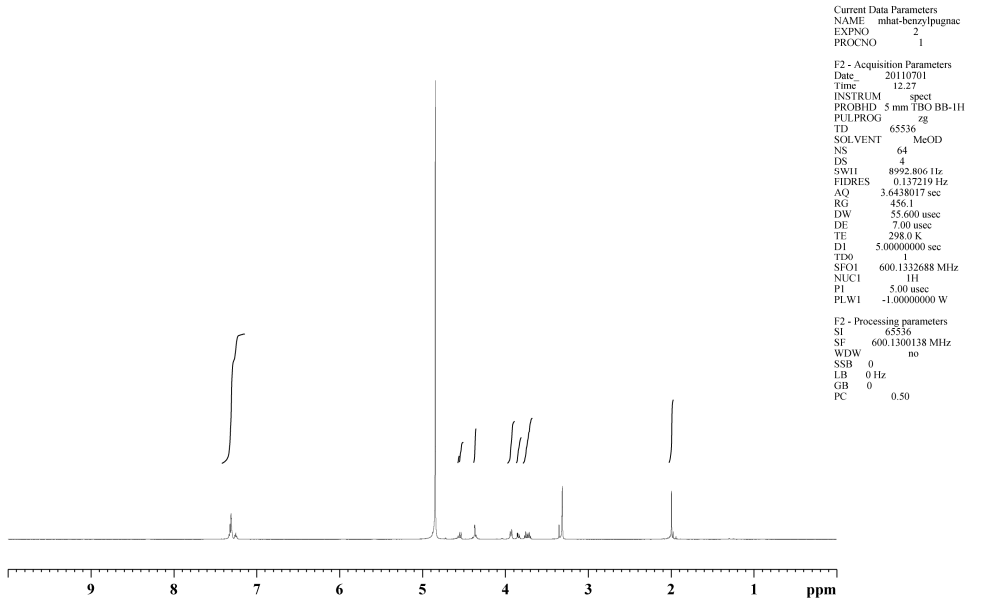
^{1}H NMR spectrum of **36**



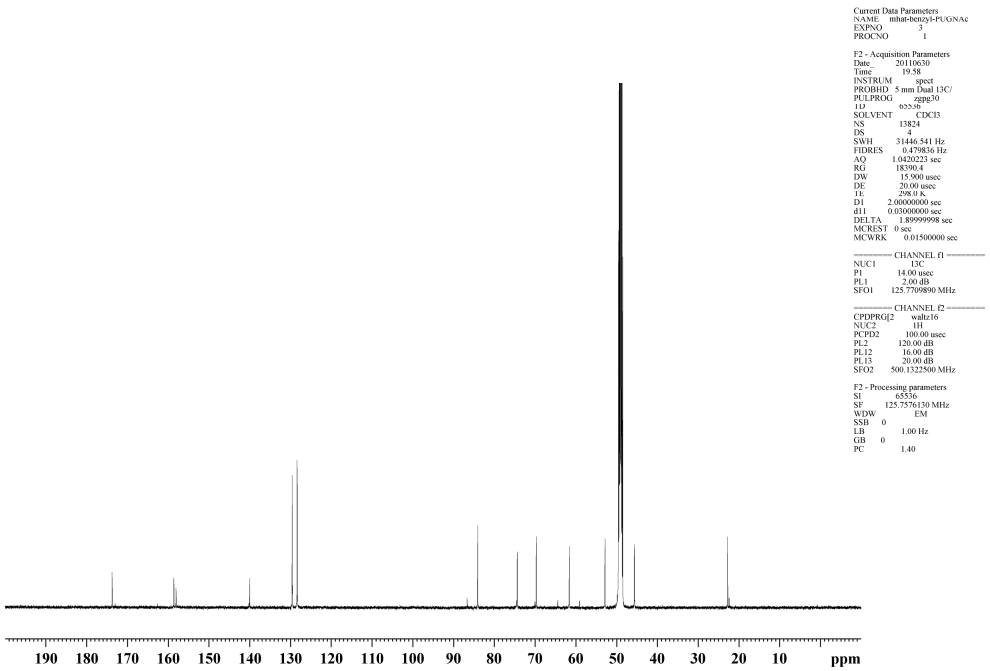
^{13}C NMR spectrum of **36**



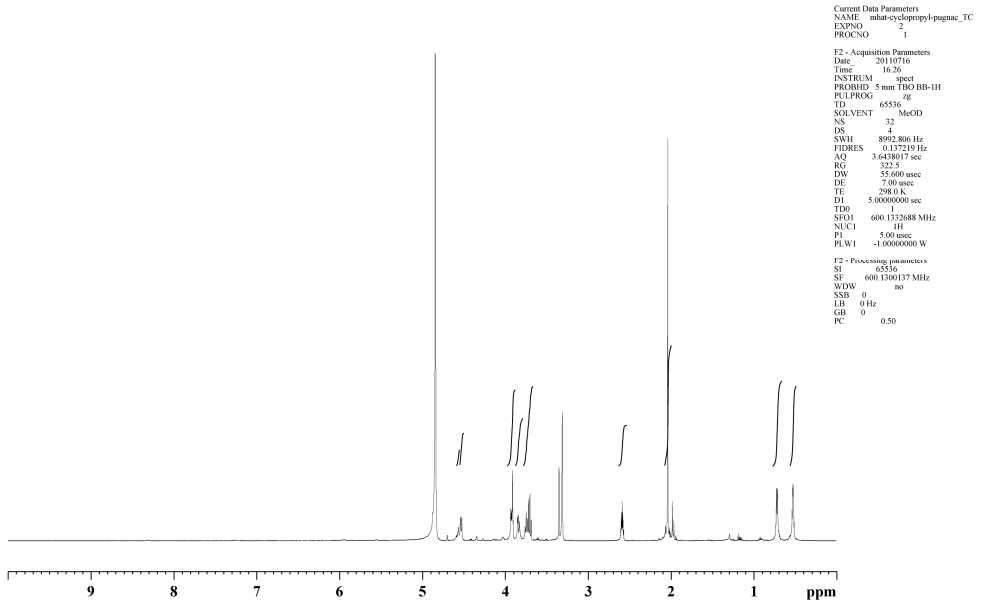
^{1}H NMR spectrum of **37**



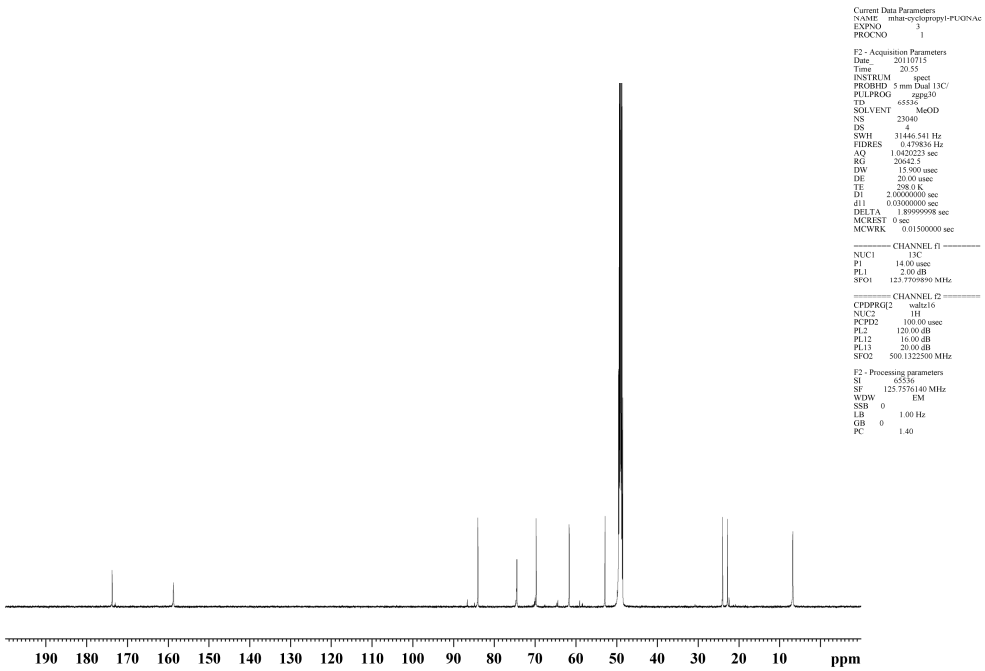
^{13}C NMR spectrum of **37**



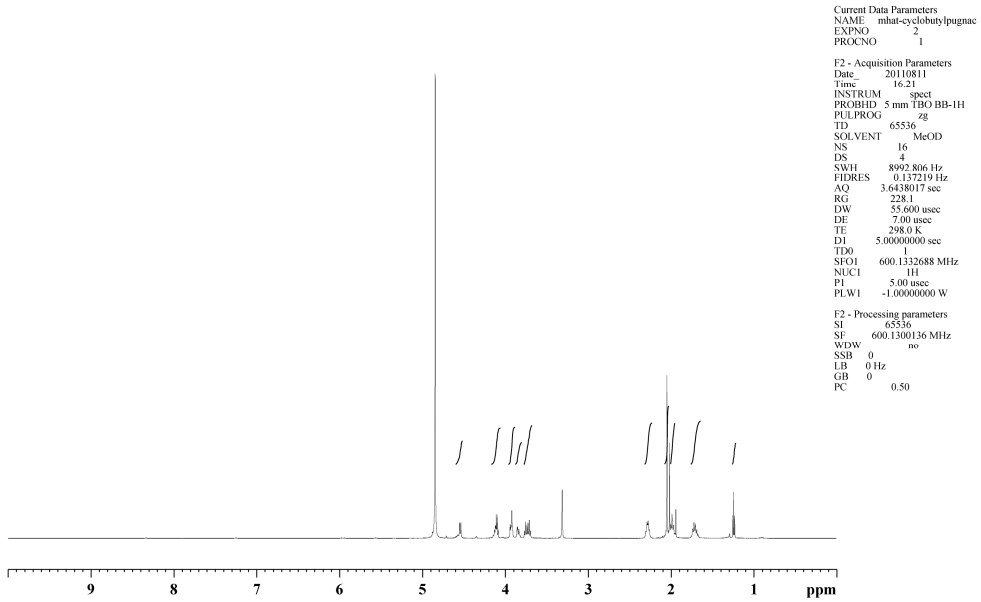
^{1}H NMR spectrum of **38**



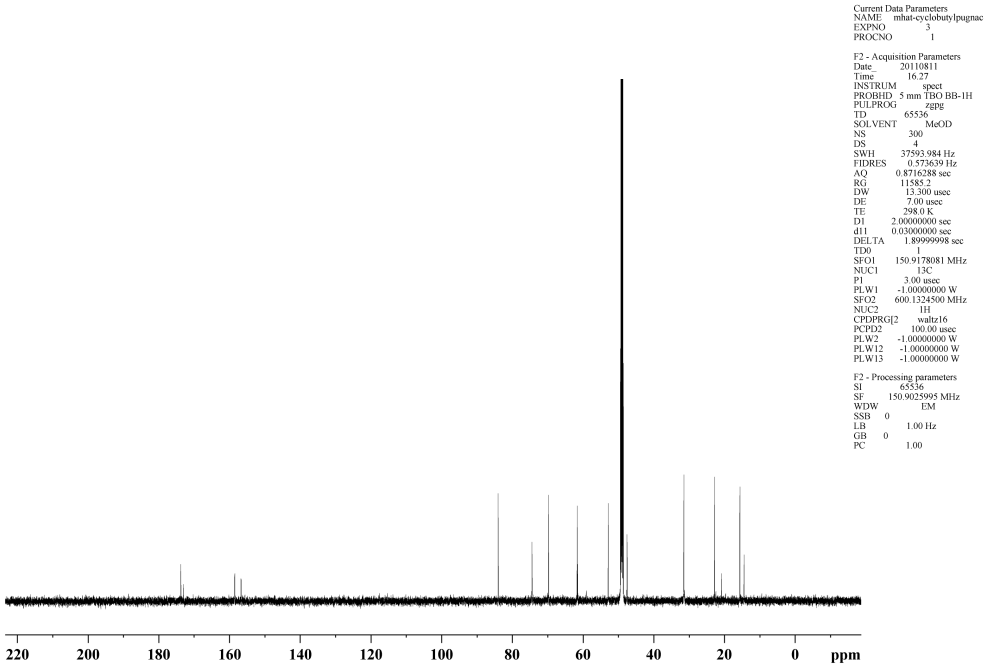
^{13}C NMR spectrum of **38**



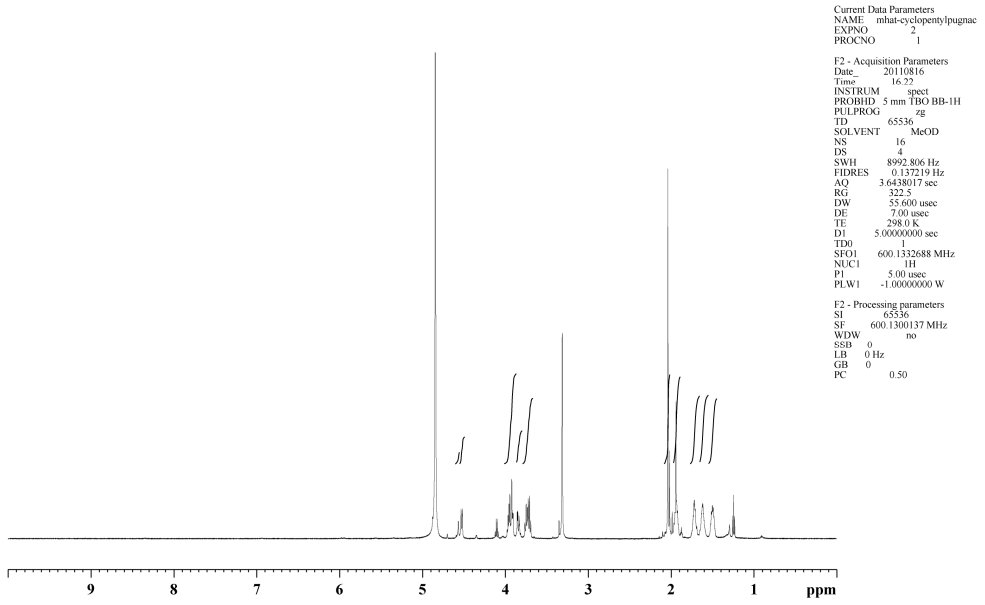
^{1}H NMR spectrum of **39**



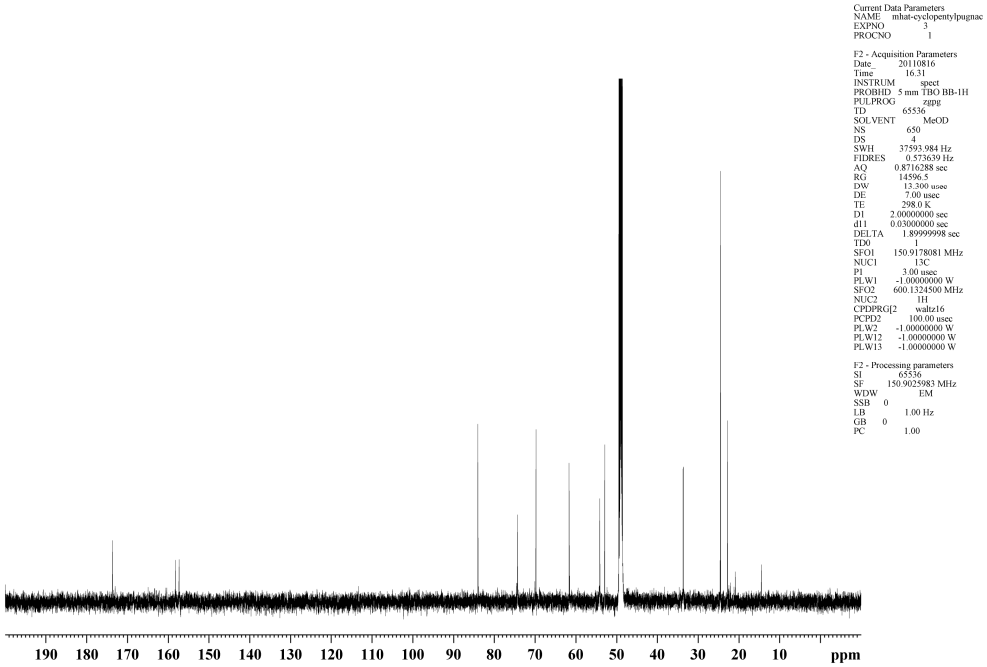
^{13}C NMR spectrum of **39**



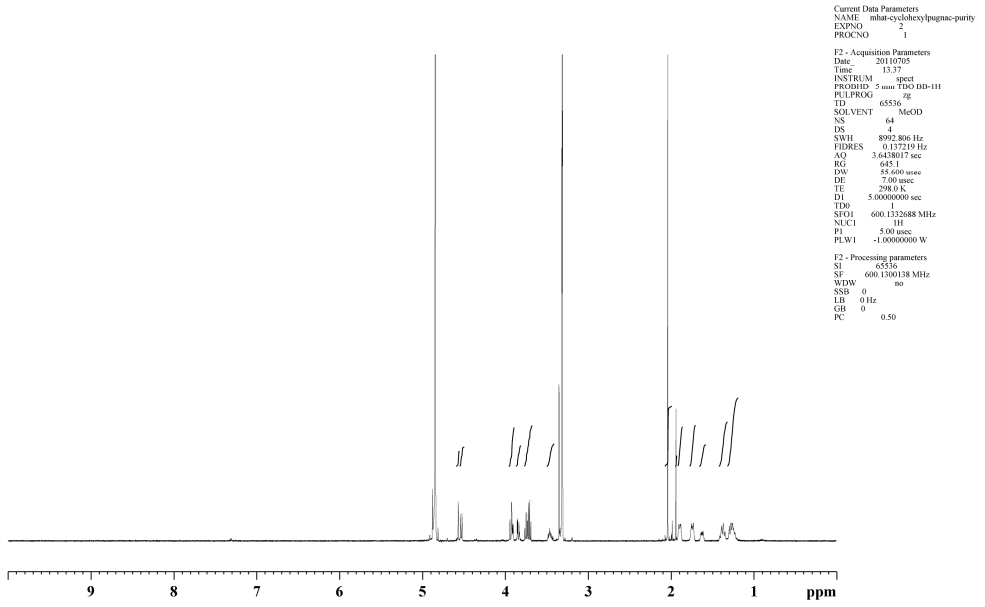
^{1}H NMR spectrum of **40**



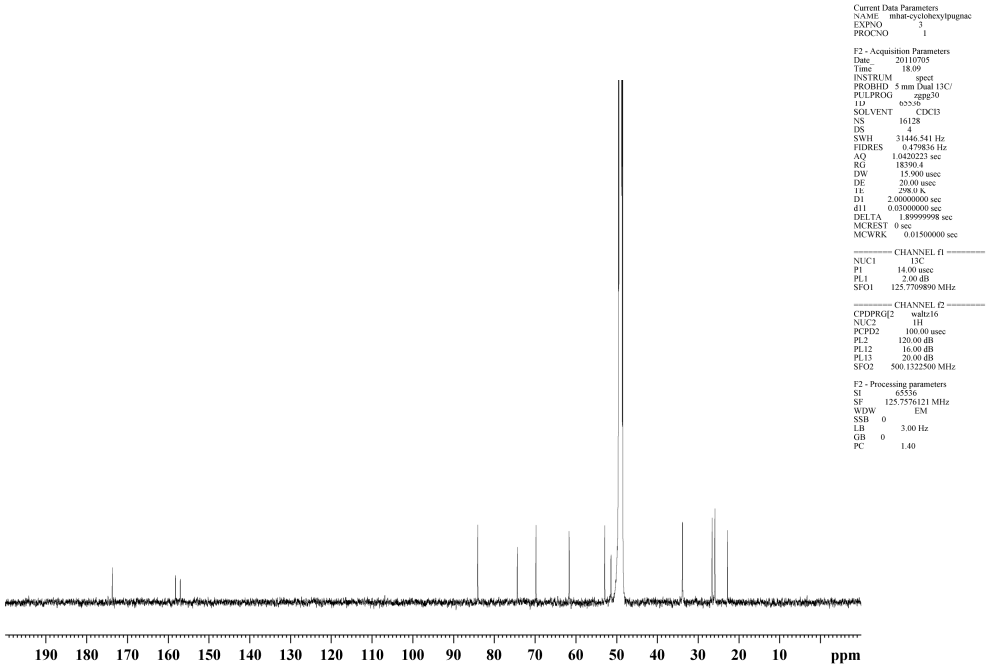
^{13}C NMR spectrum of **40**



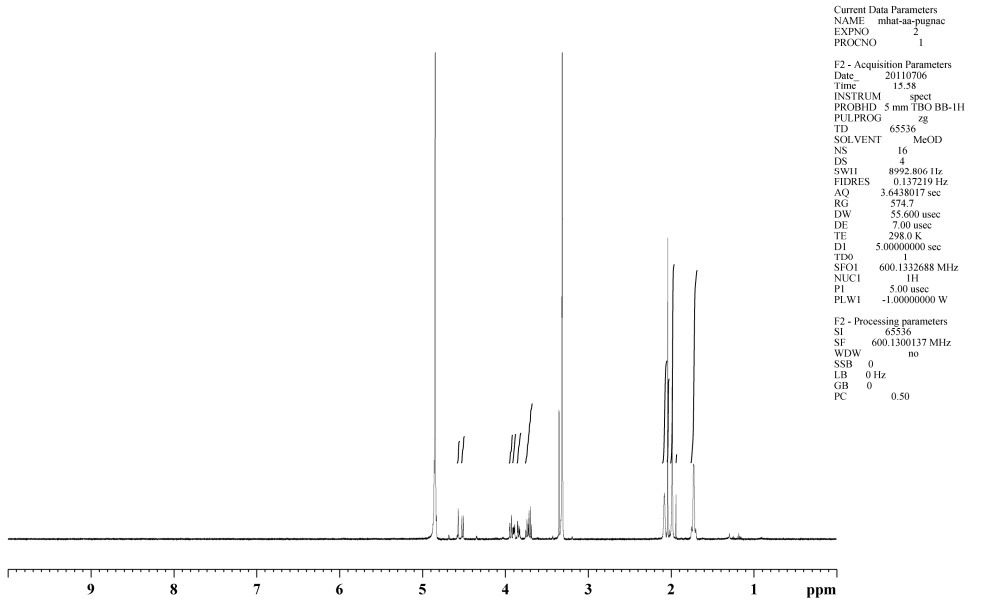
^{1}H NMR spectrum of **41**



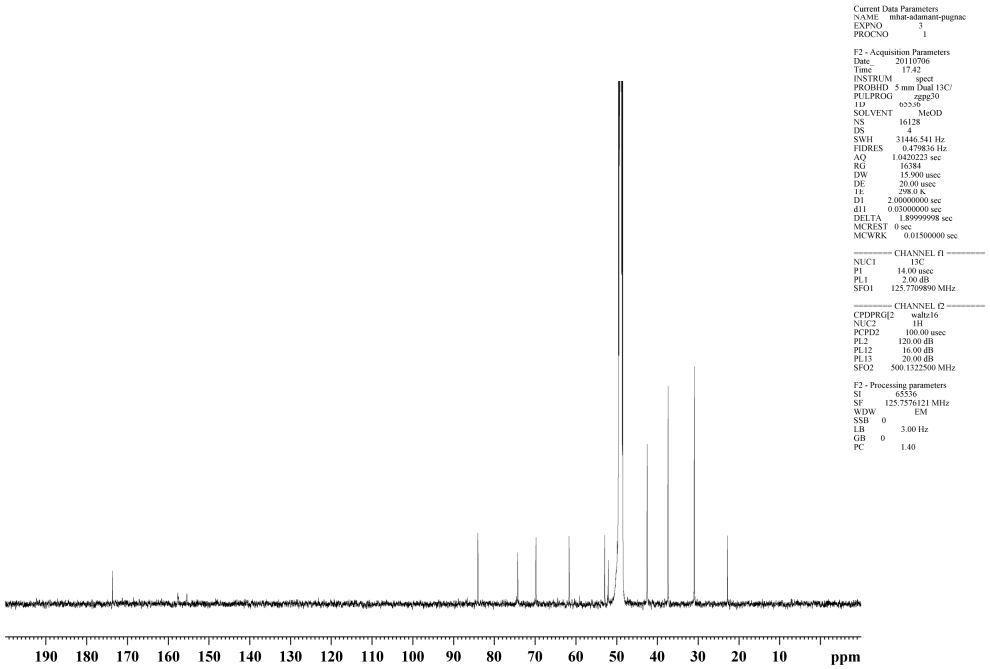
^{13}C NMR spectrum of **41**



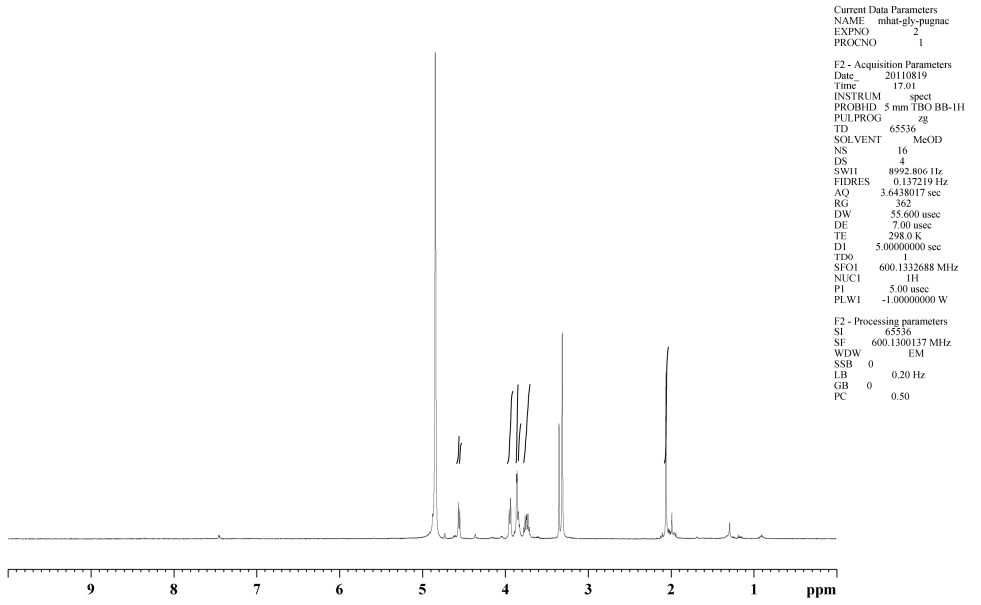
^{1}H NMR spectrum of **42**



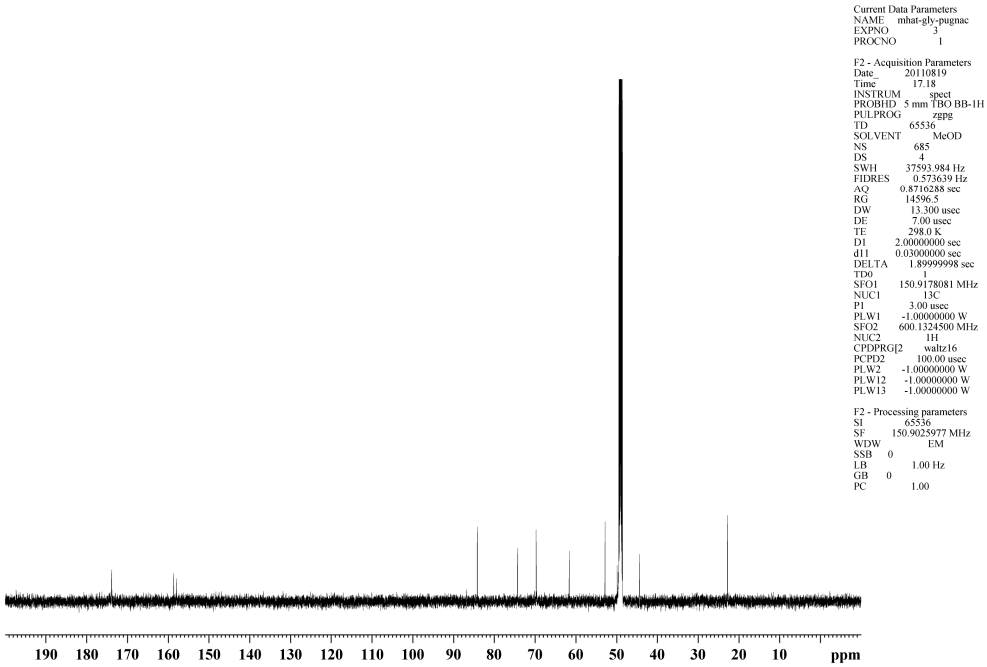
^{13}C NMR spectrum of **42**



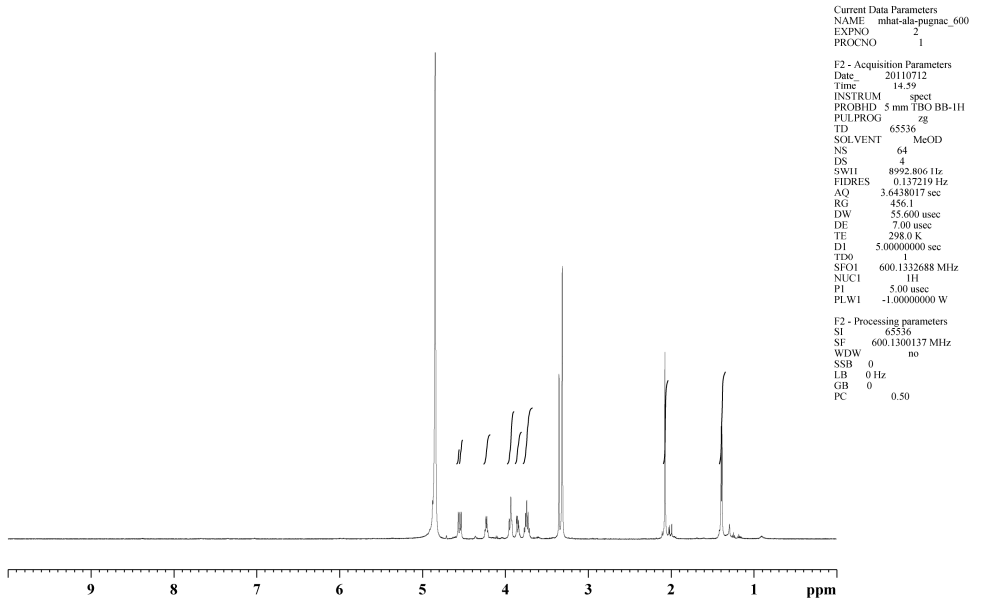
^{1}H NMR spectrum of **43**



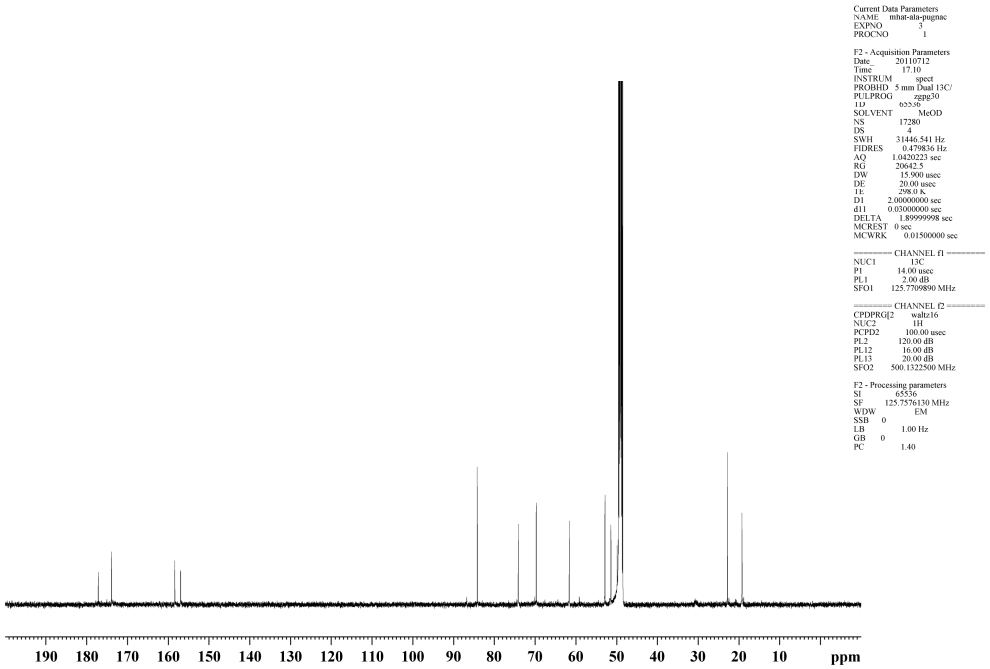
^{13}C NMR spectrum of **43**



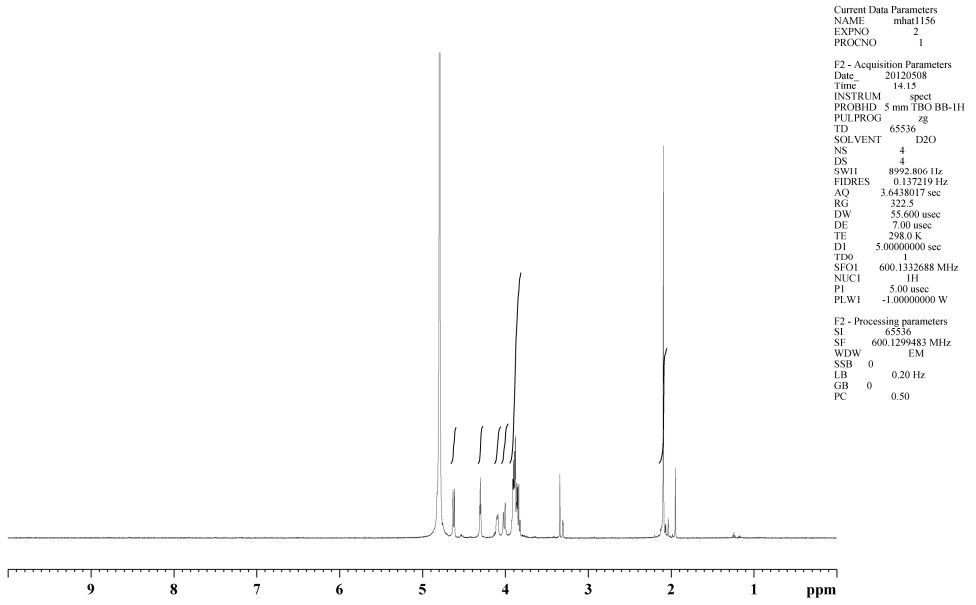
^{1}H NMR spectrum of **44**



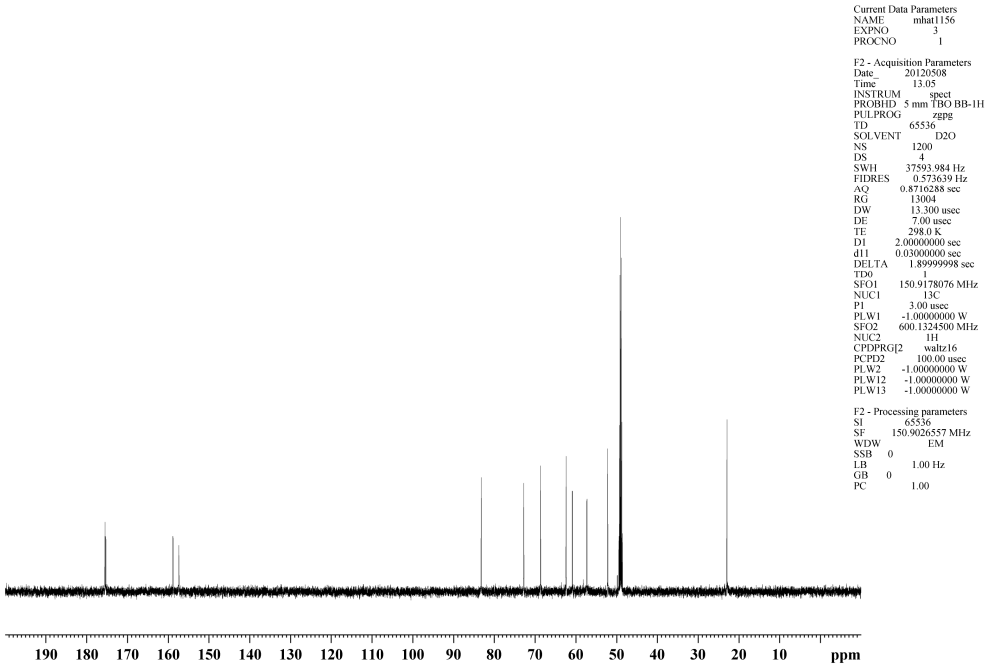
^{13}C NMR spectrum of **44**



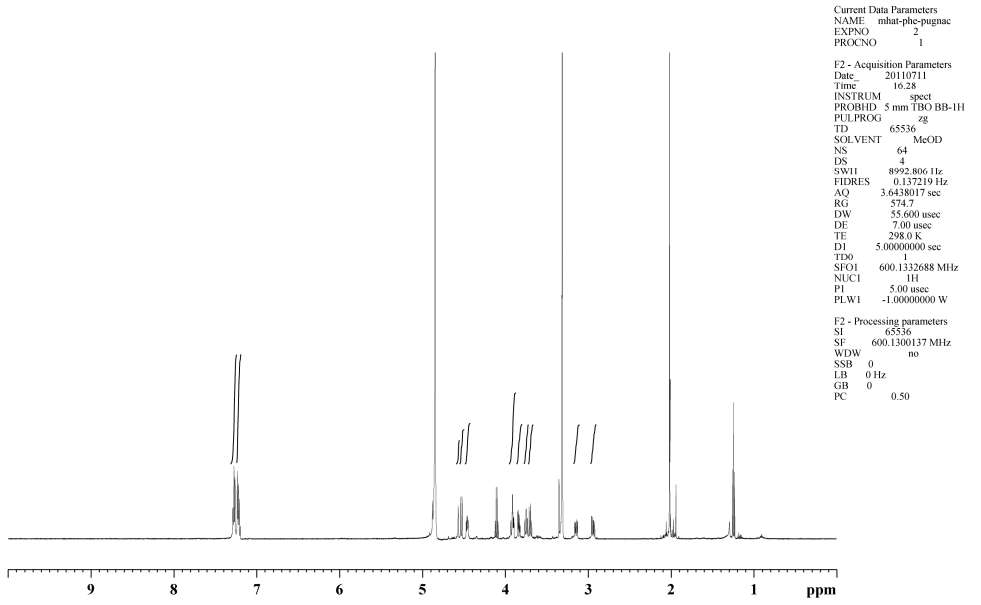
^{1}H NMR spectrum of **45**



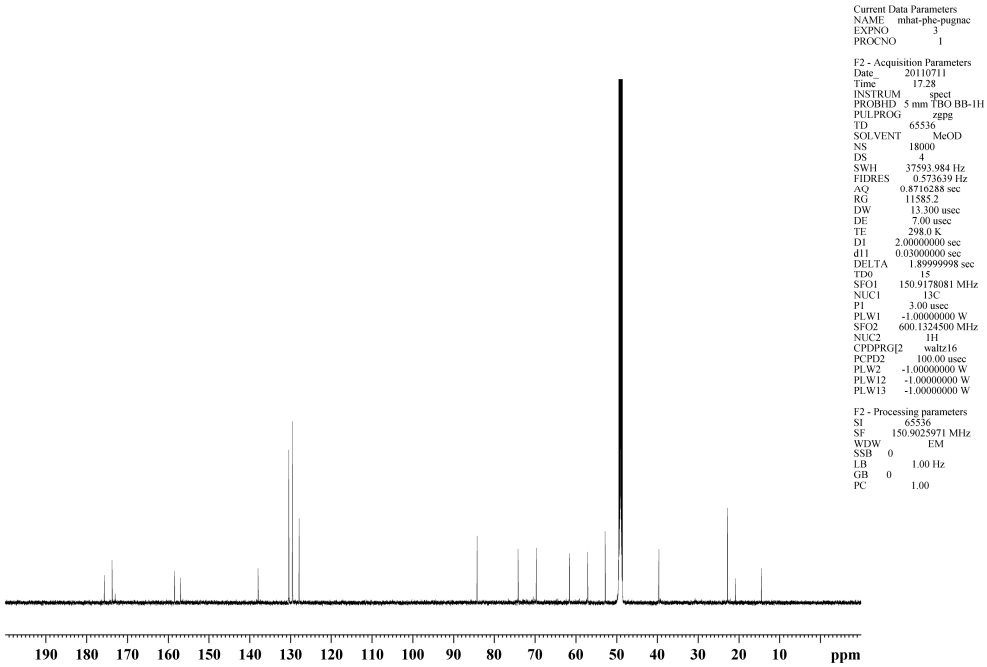
^{13}C NMR spectrum of **45**



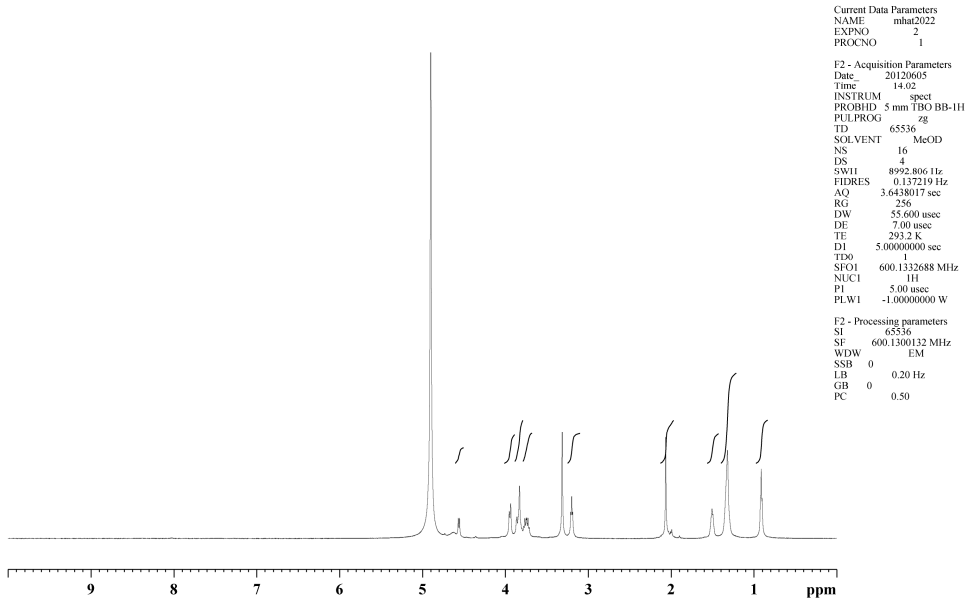
^{1}H NMR spectrum of **46**



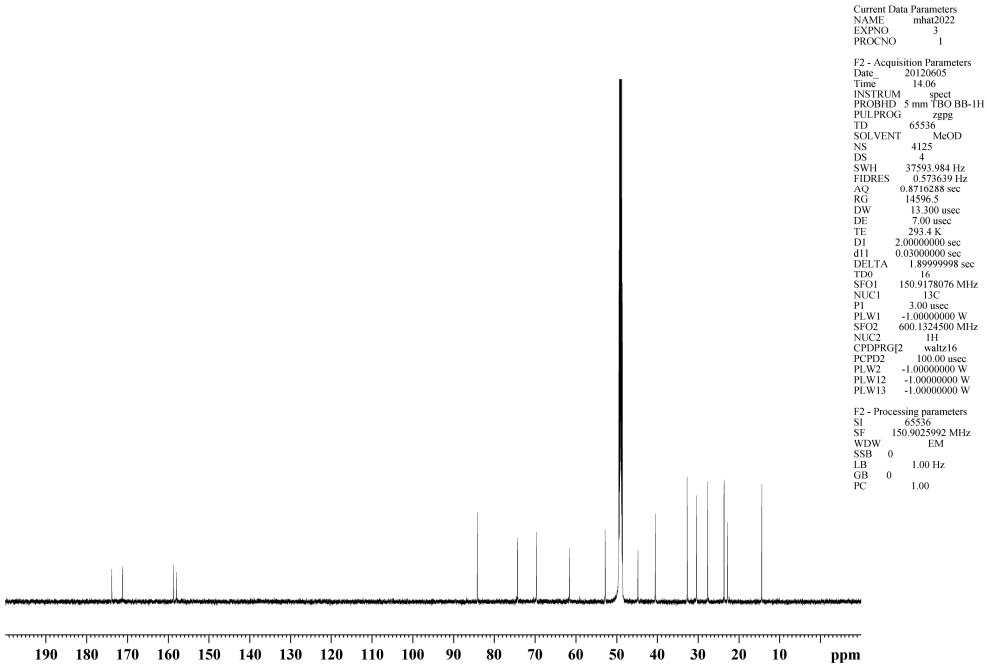
^{13}C NMR spectrum of **46**



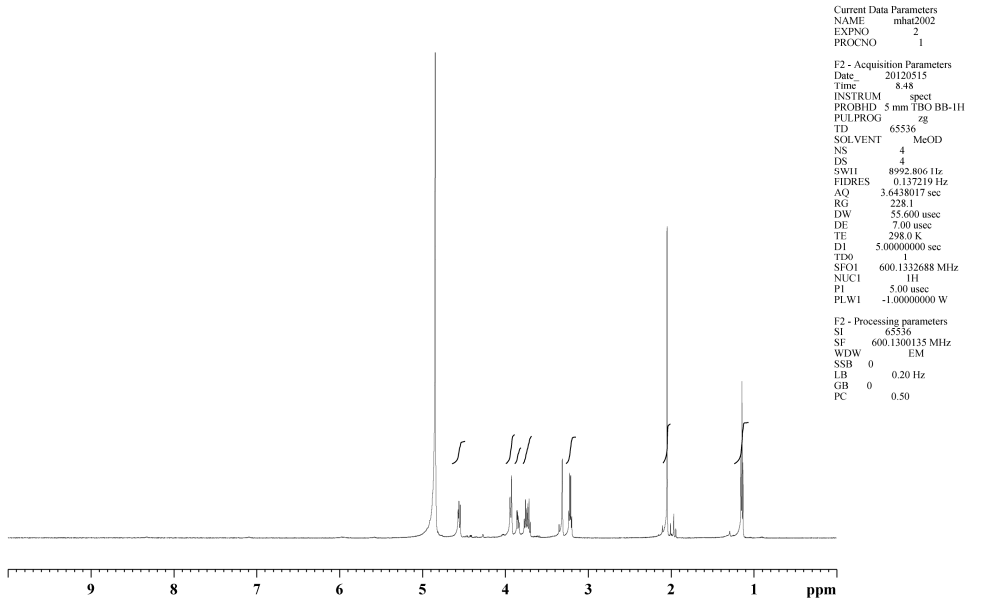
^{1}H NMR spectrum of **47**



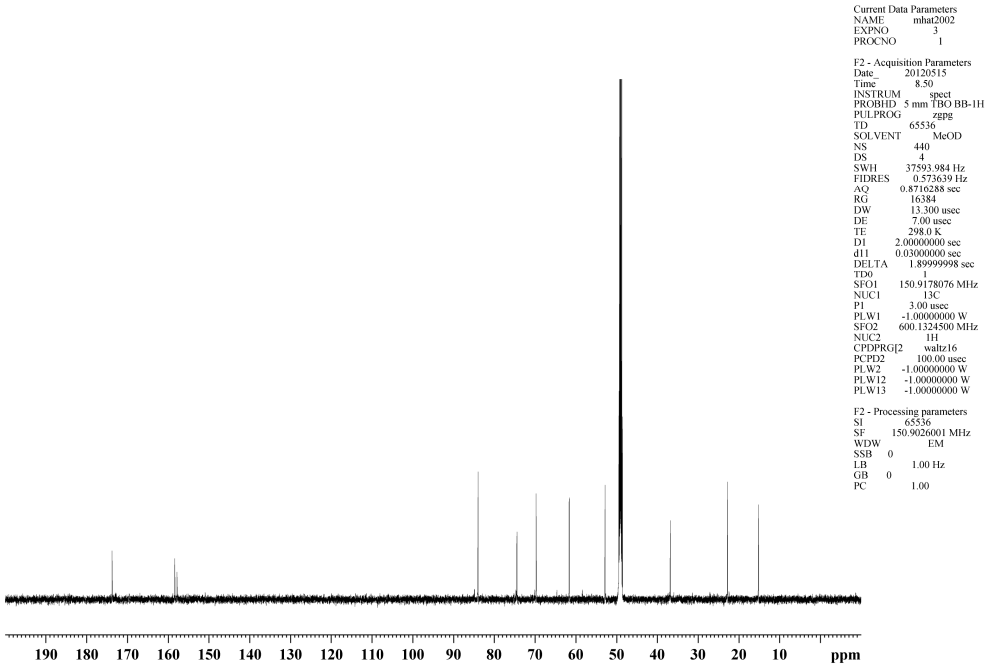
^{13}C NMR spectrum of **47**



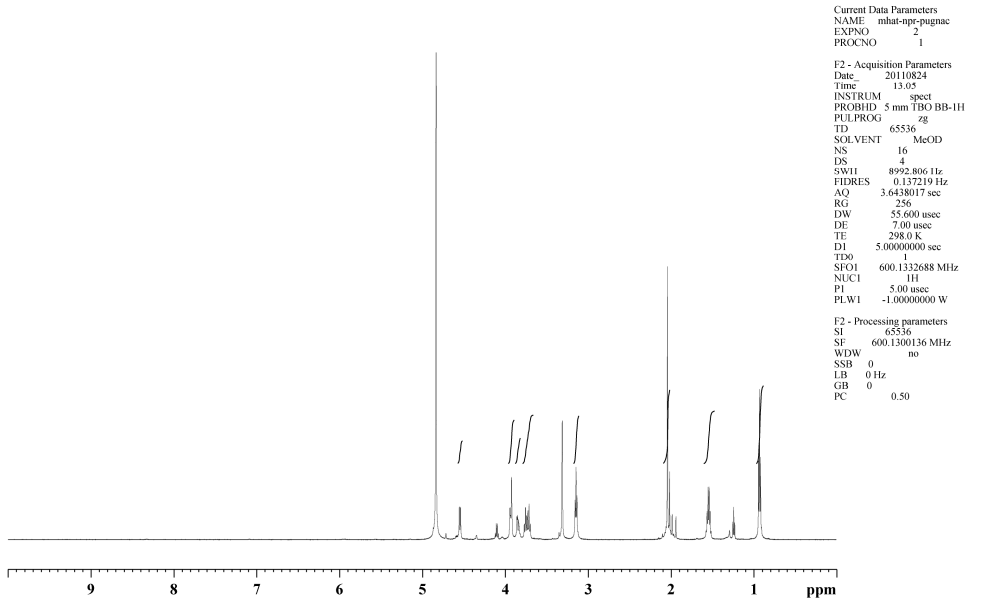
^{1}H NMR spectrum of **49**



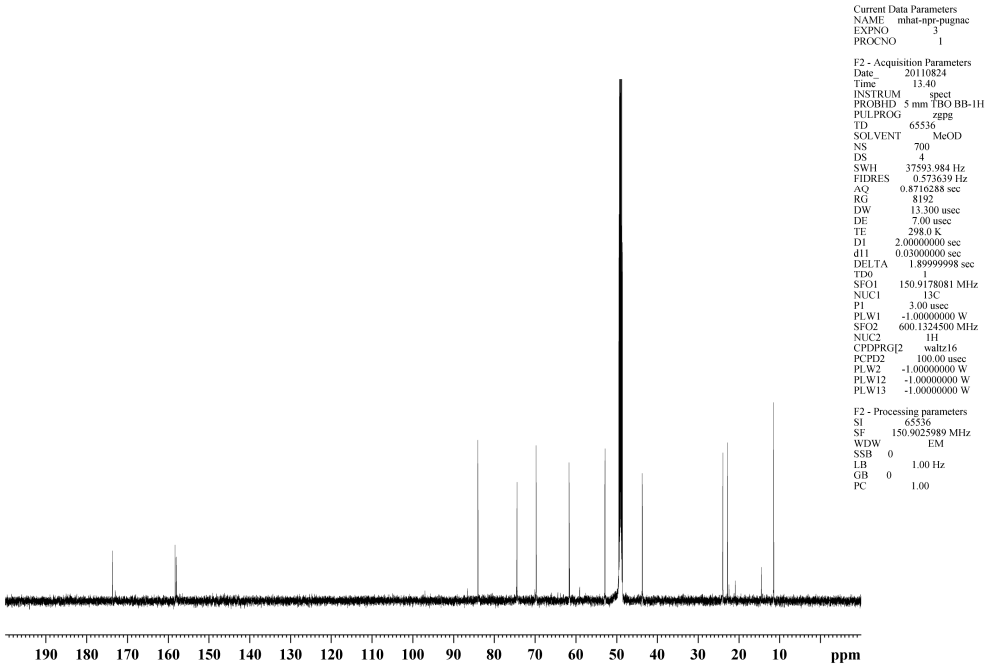
^{13}C NMR spectrum of **49**



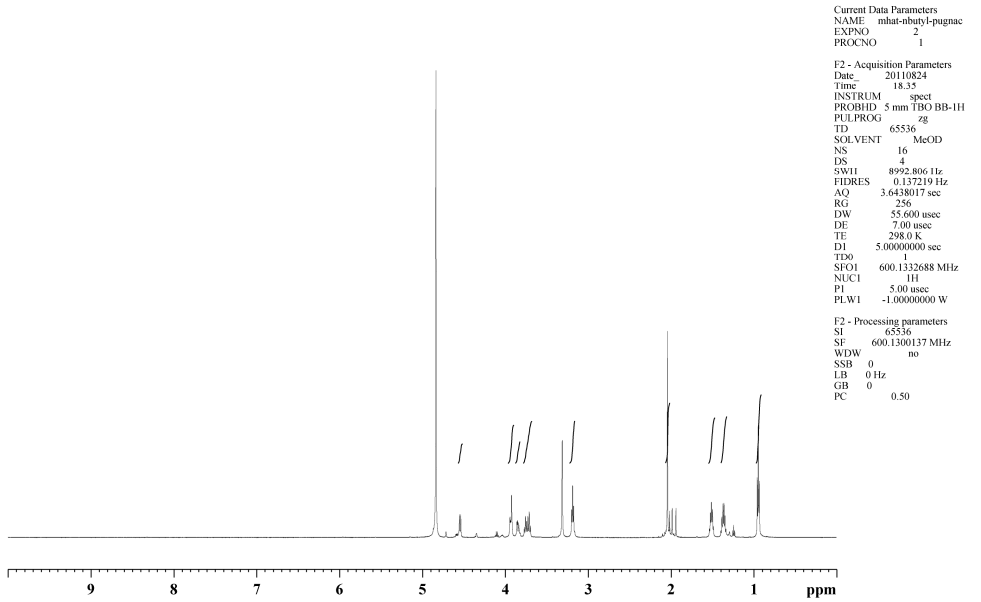
^{1}H NMR spectrum of **50**



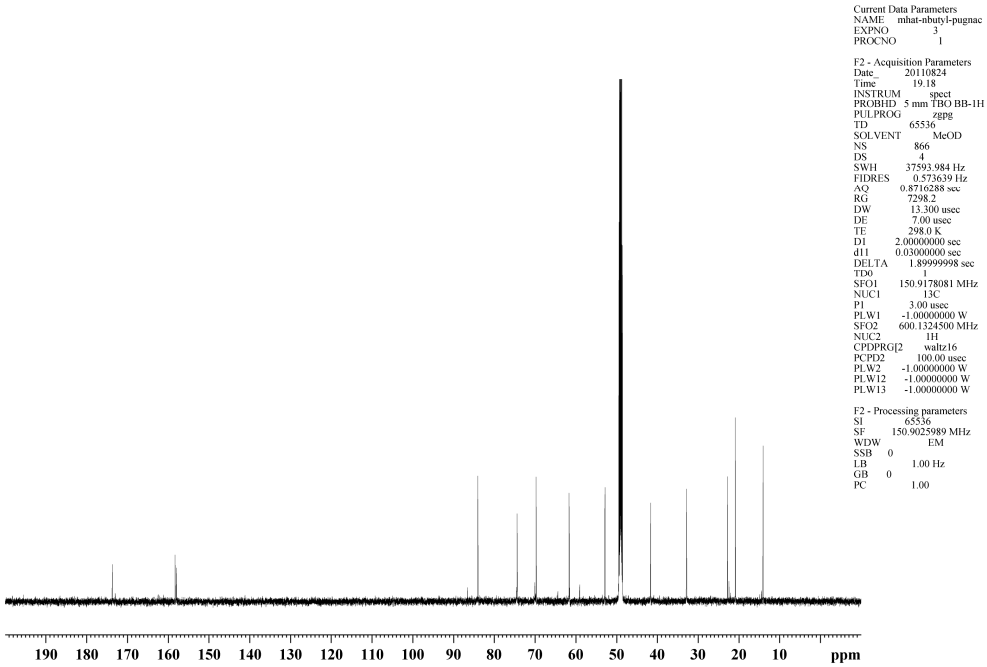
^{13}C NMR spectrum of **50**



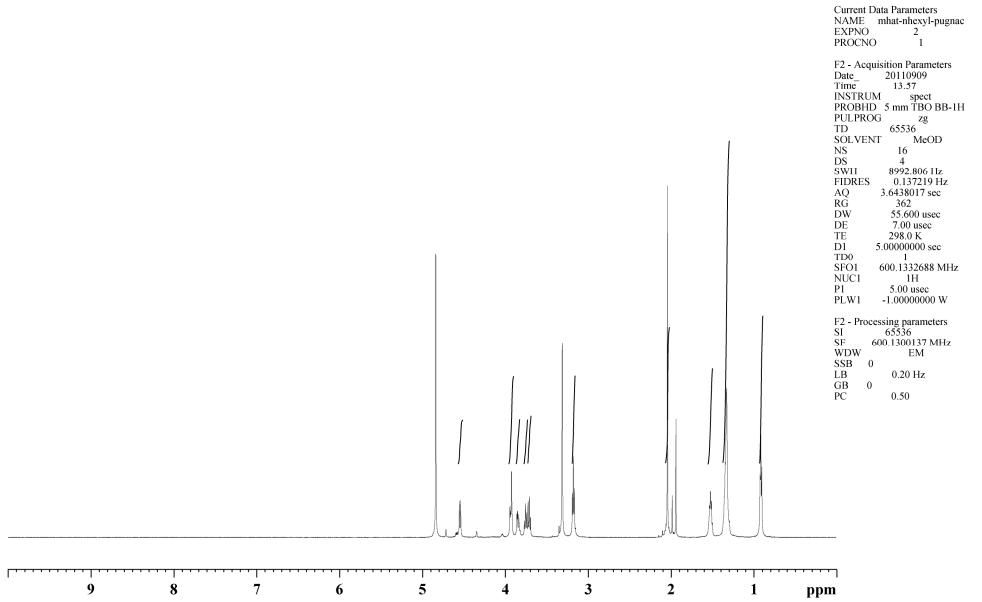
^{1}H NMR spectrum of **51**



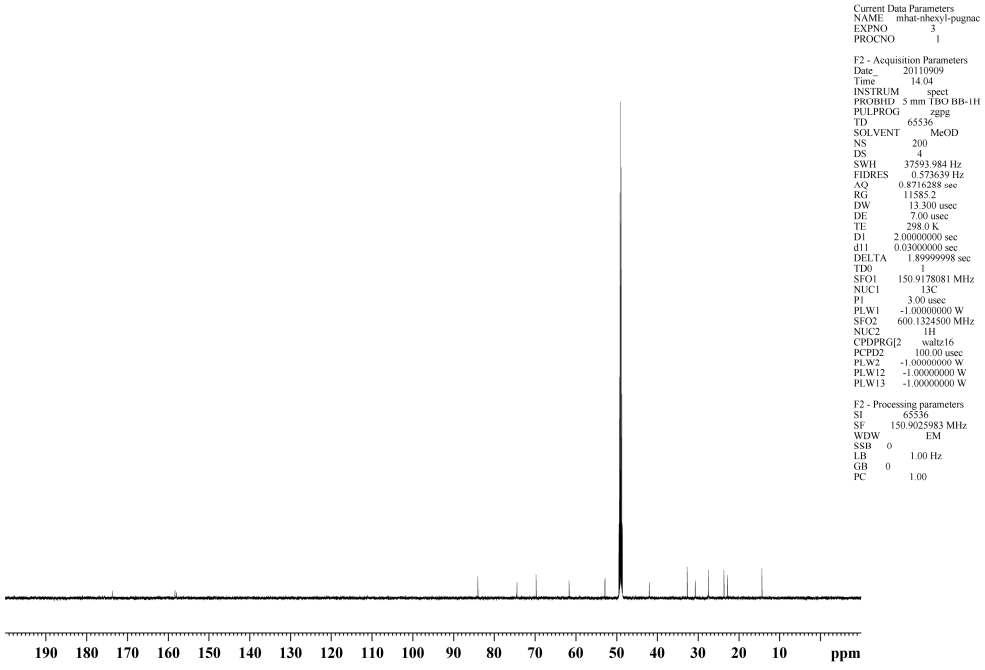
^{13}C NMR spectrum of **51**



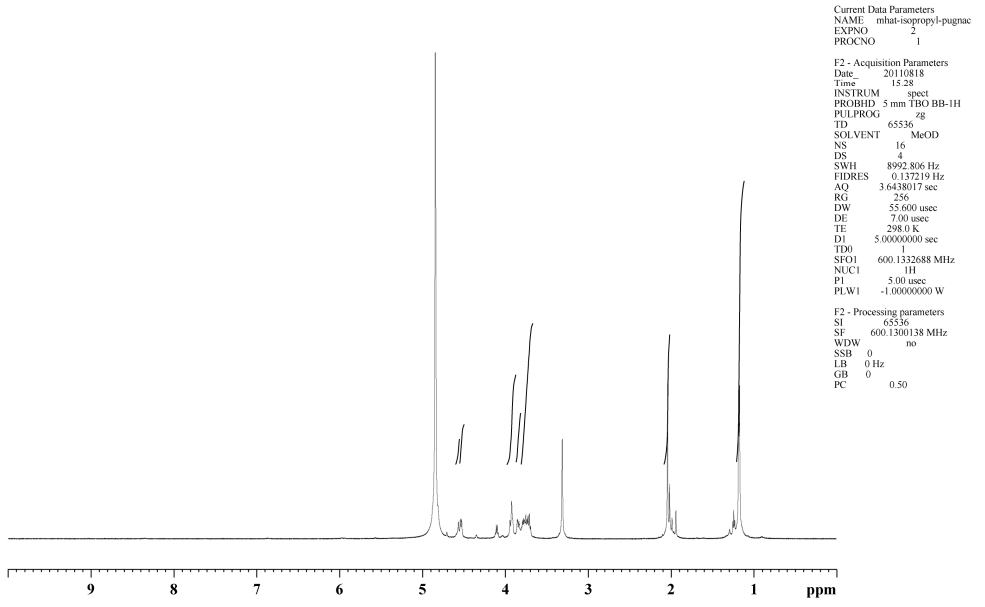
^{1}H NMR spectrum of **52**



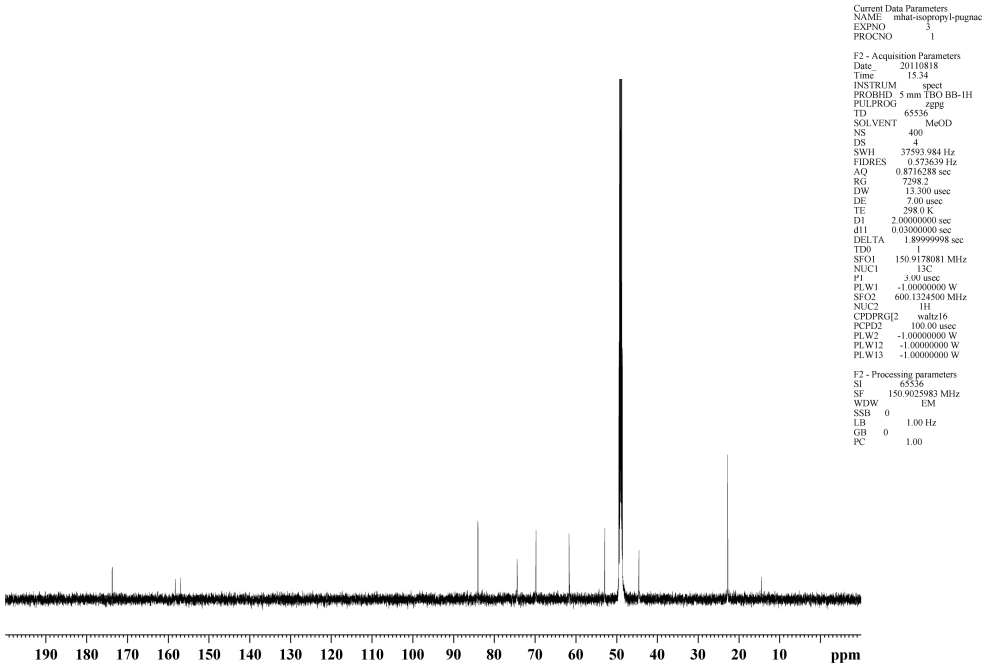
^{13}C NMR spectrum of **52**



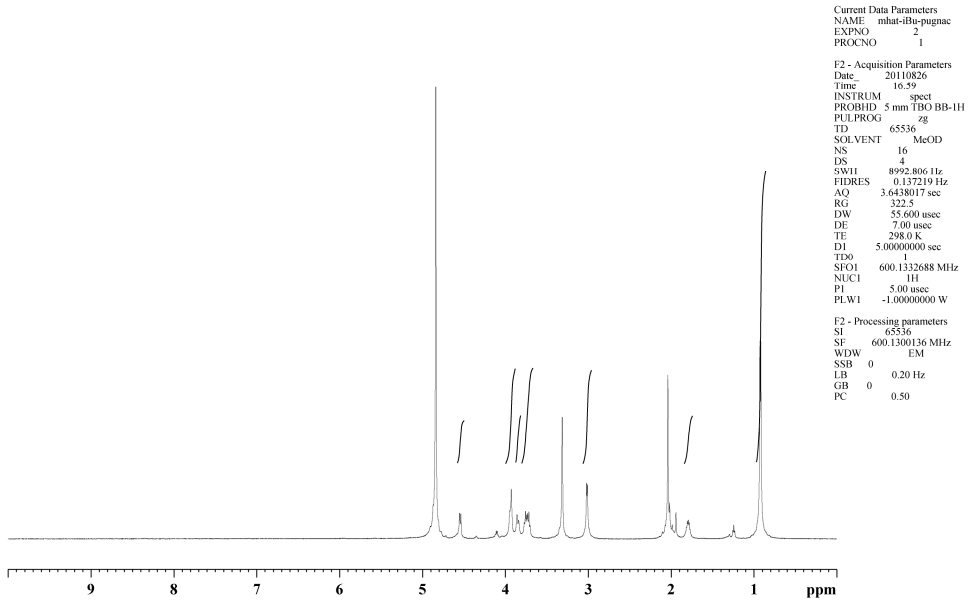
^{1}H NMR spectrum of **53**



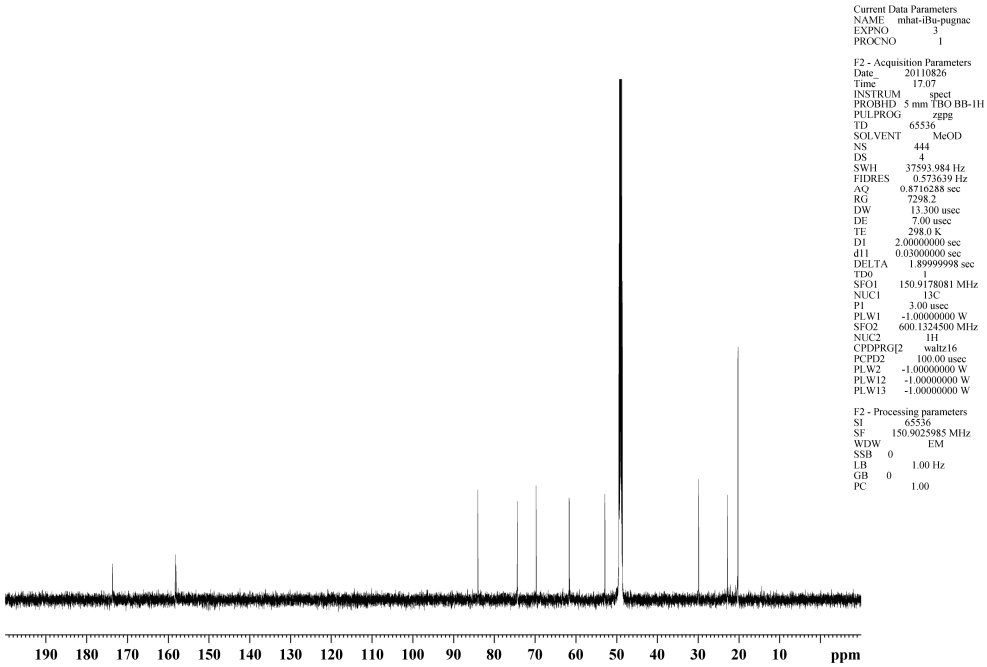
^{13}C NMR spectrum of **53**



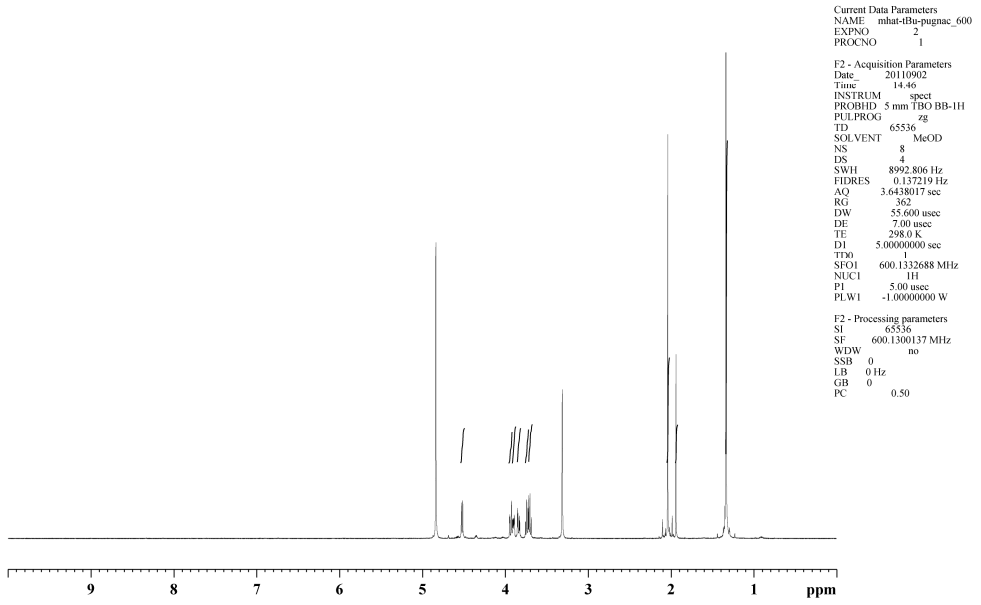
^{1}H NMR spectrum of **54**



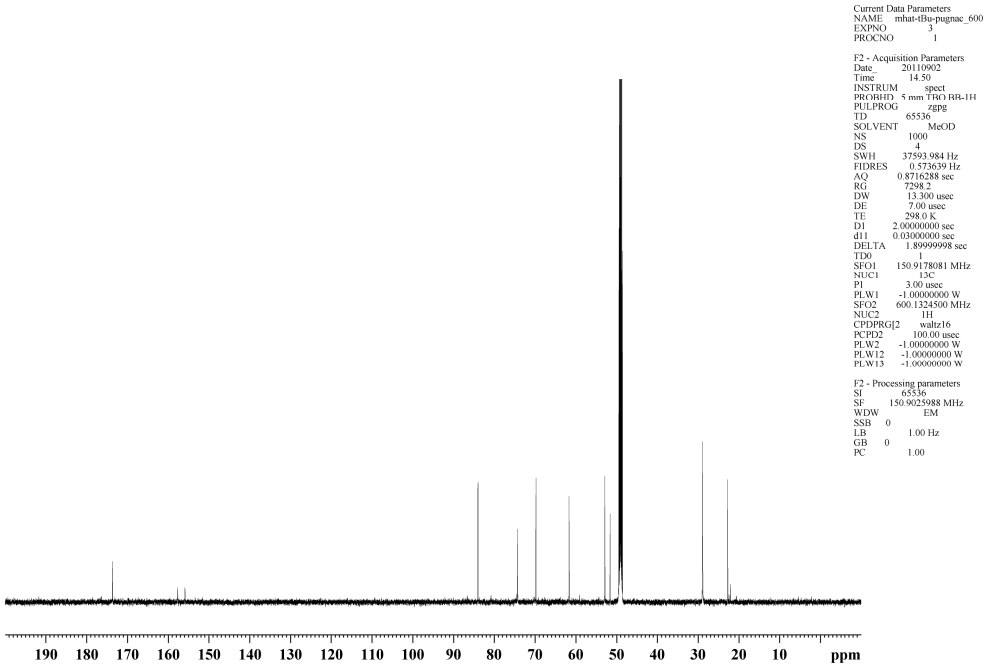
^{13}C NMR spectrum of **54**



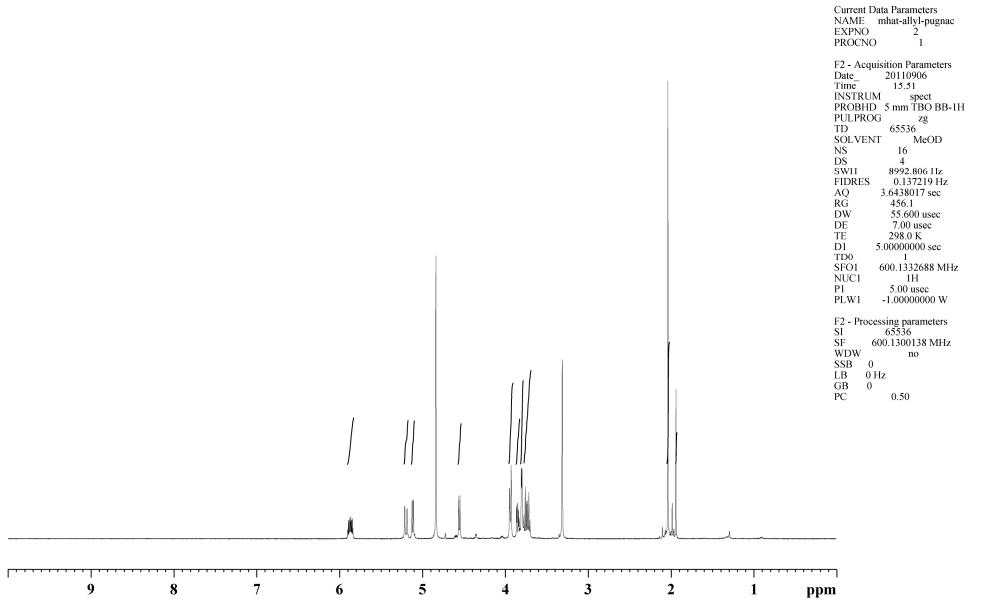
^{1}H NMR spectrum of **55**



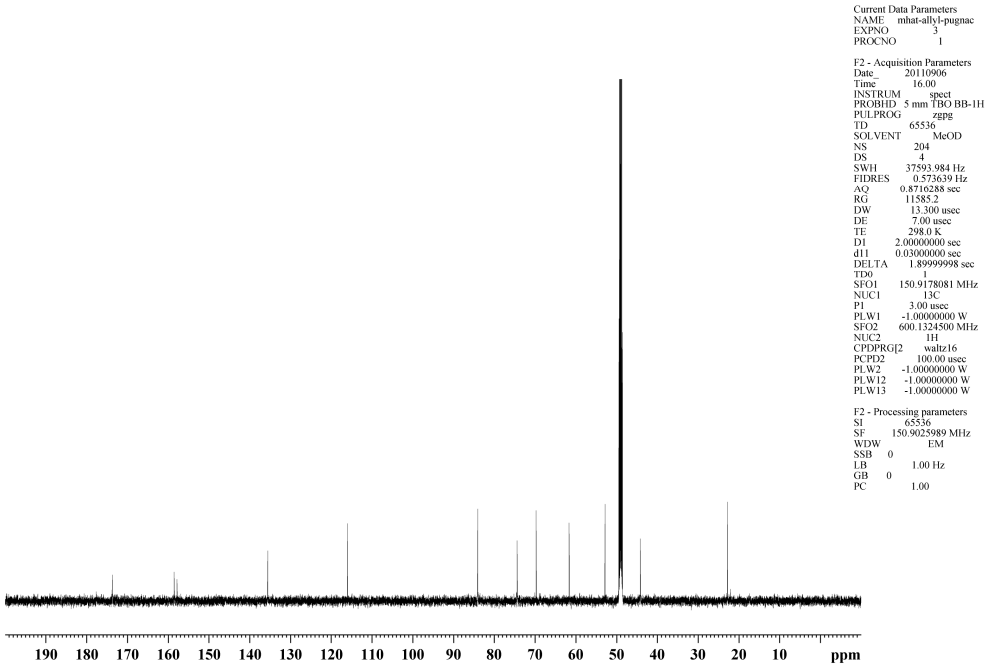
^{13}C NMR spectrum of **55**



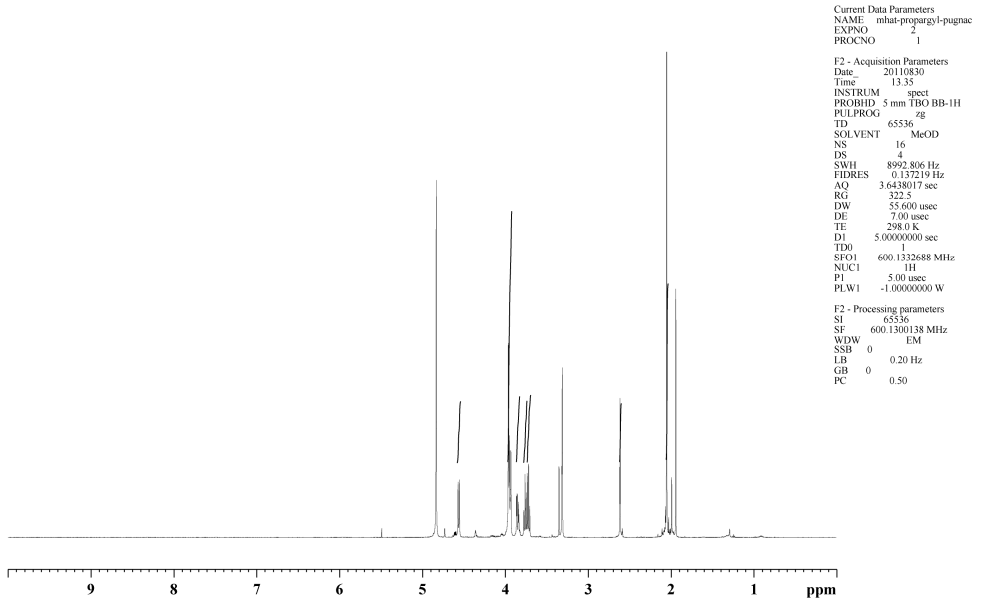
^{1}H NMR spectrum of **56**



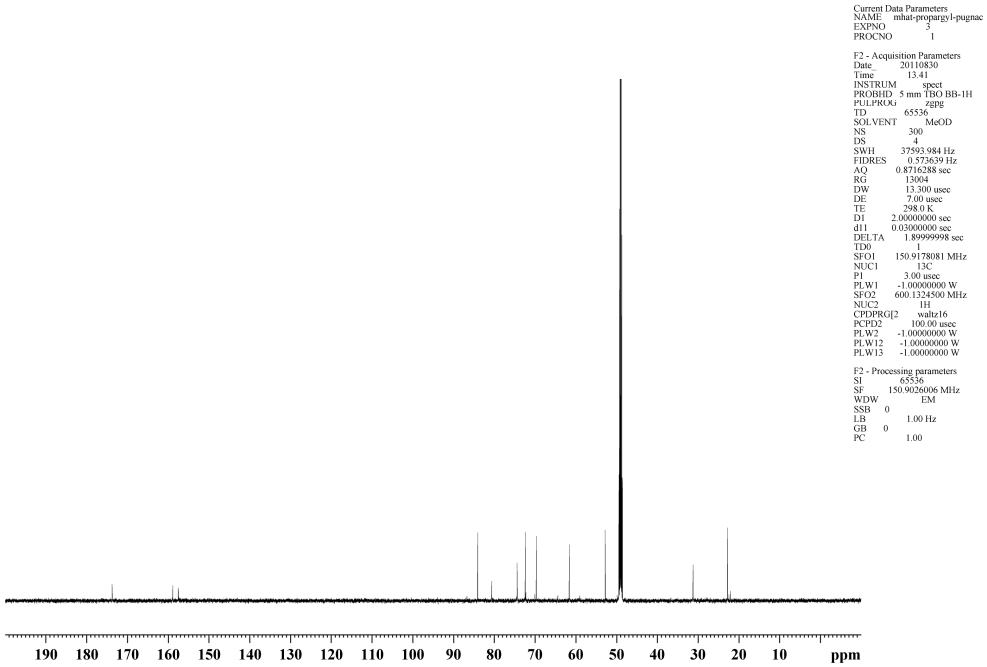
^{13}C NMR spectrum of **56**



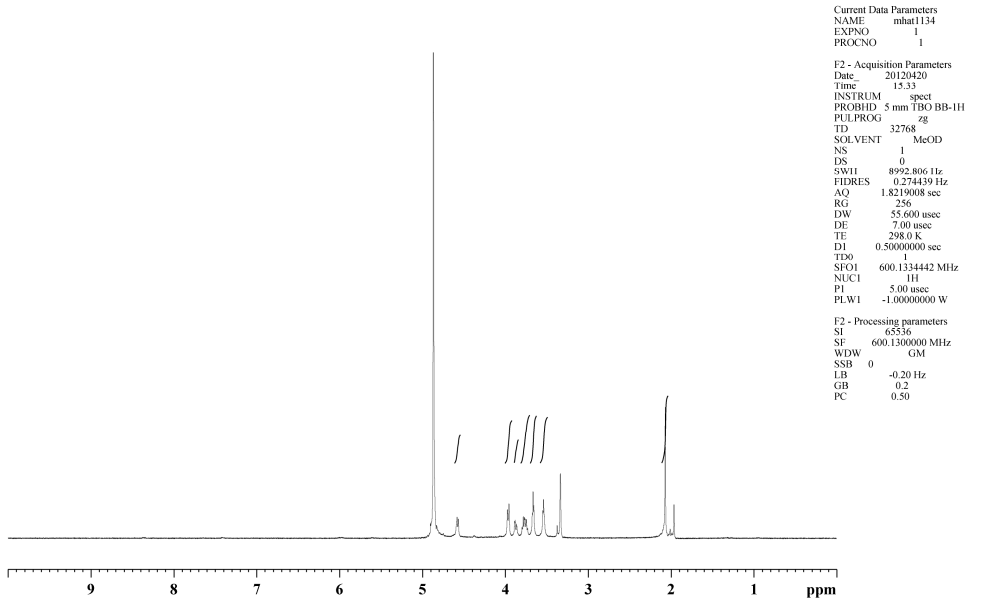
^{1}H NMR spectrum of **57**



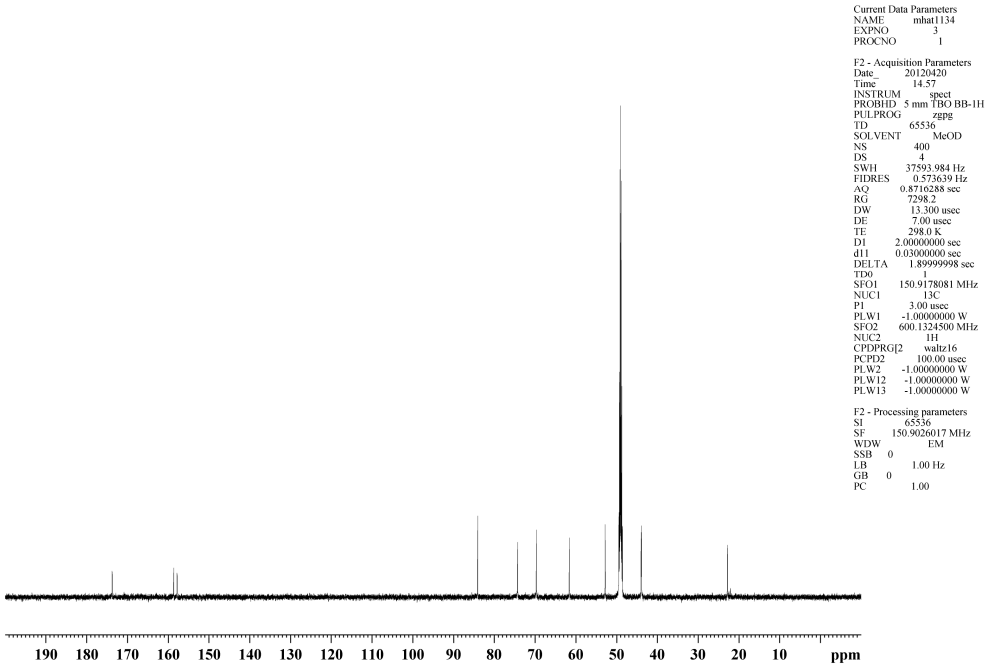
^{13}C NMR spectrum of **57**



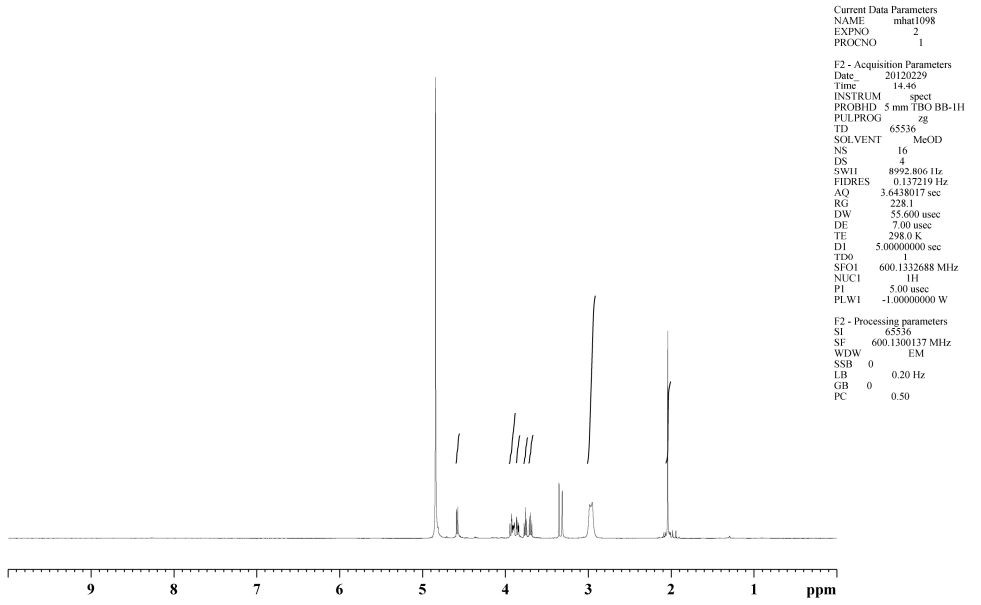
^{1}H NMR spectrum of **58**



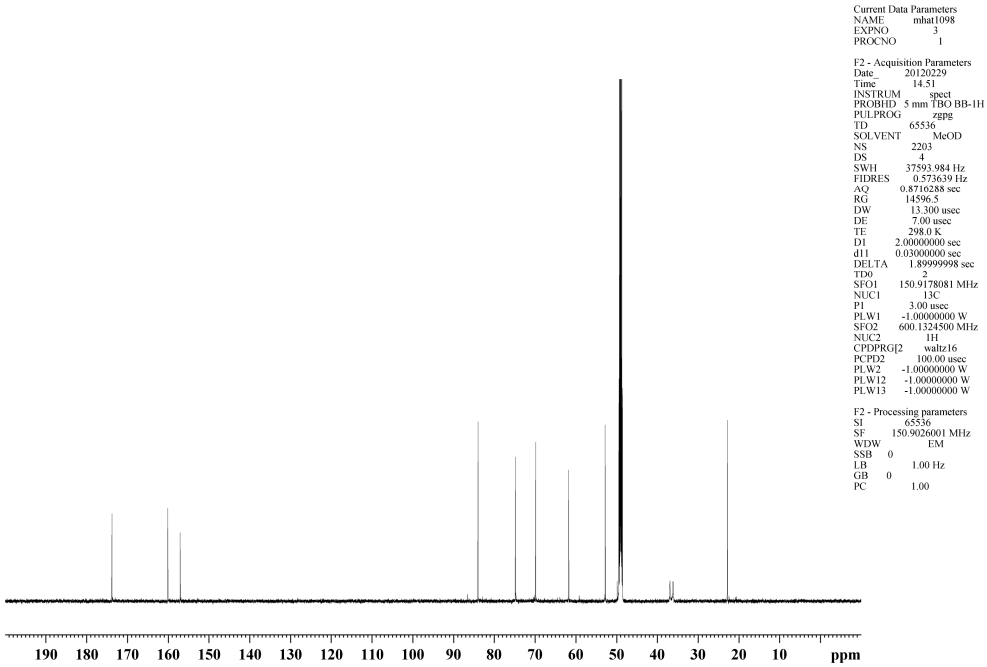
^{13}C NMR spectrum of **58**



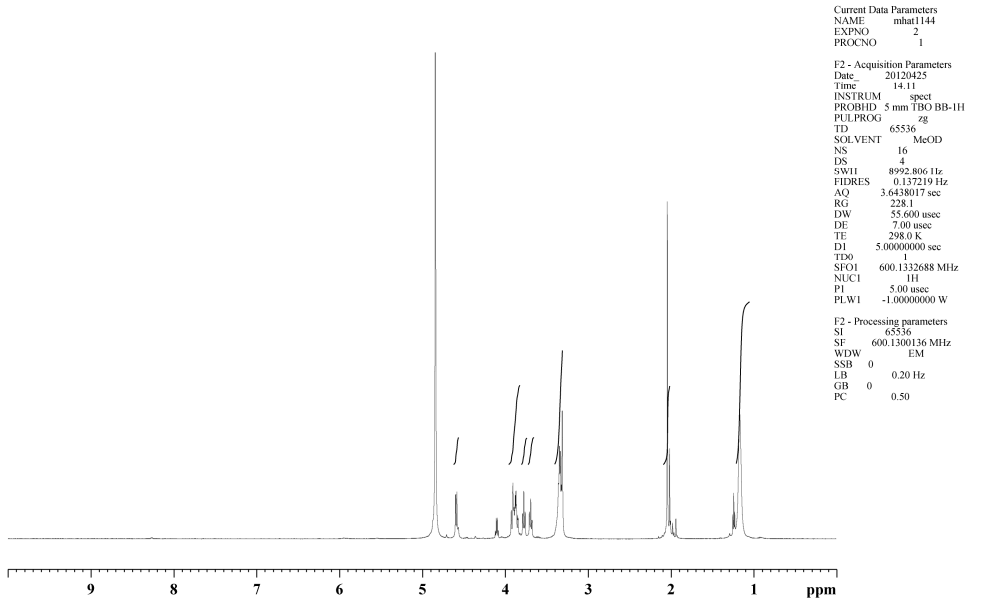
^{1}H NMR spectrum of **59**



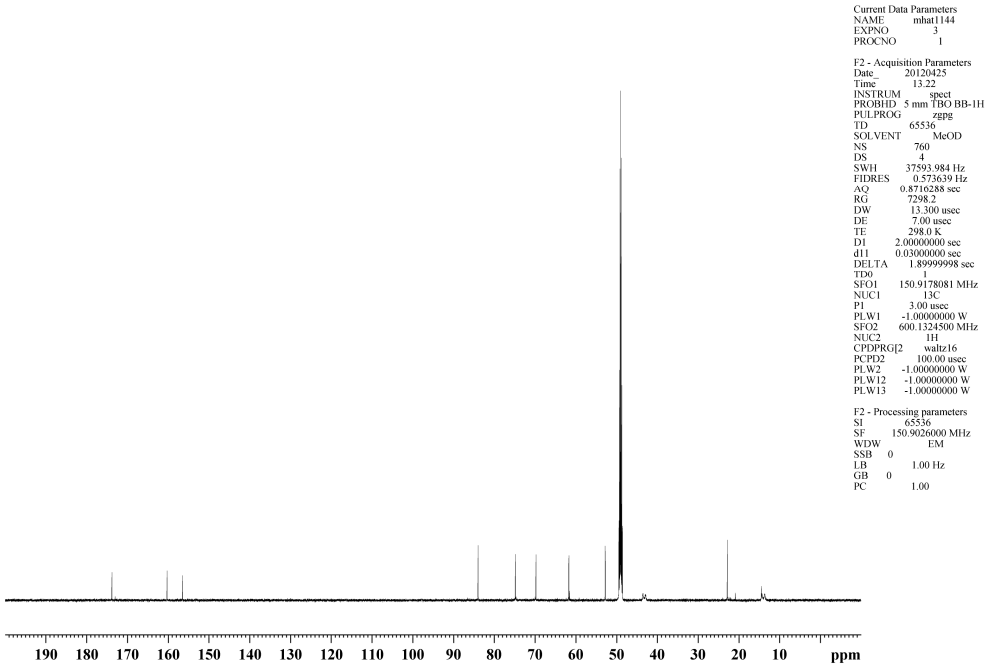
^{13}C NMR spectrum of **59**



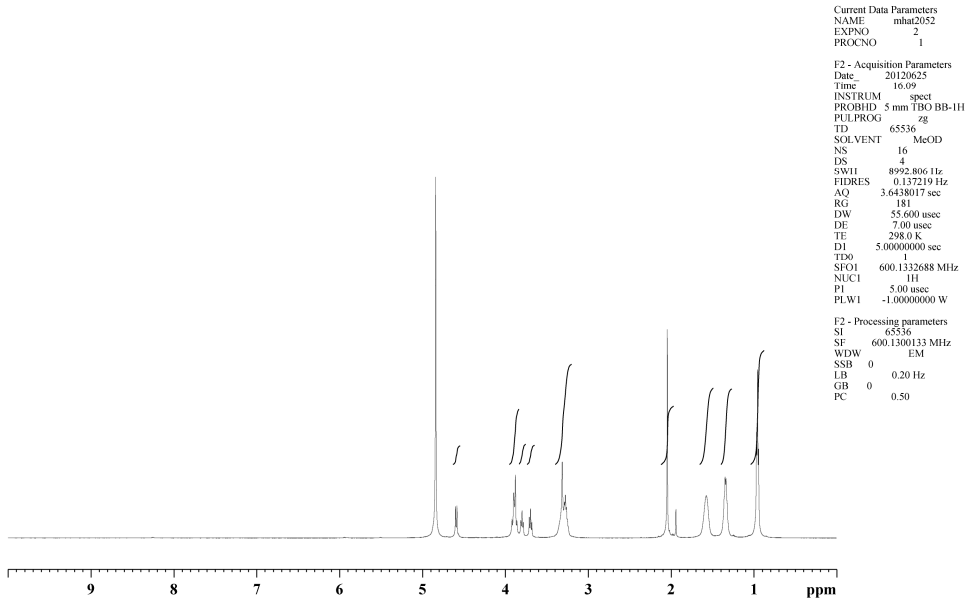
^{1}H NMR spectrum of **60**



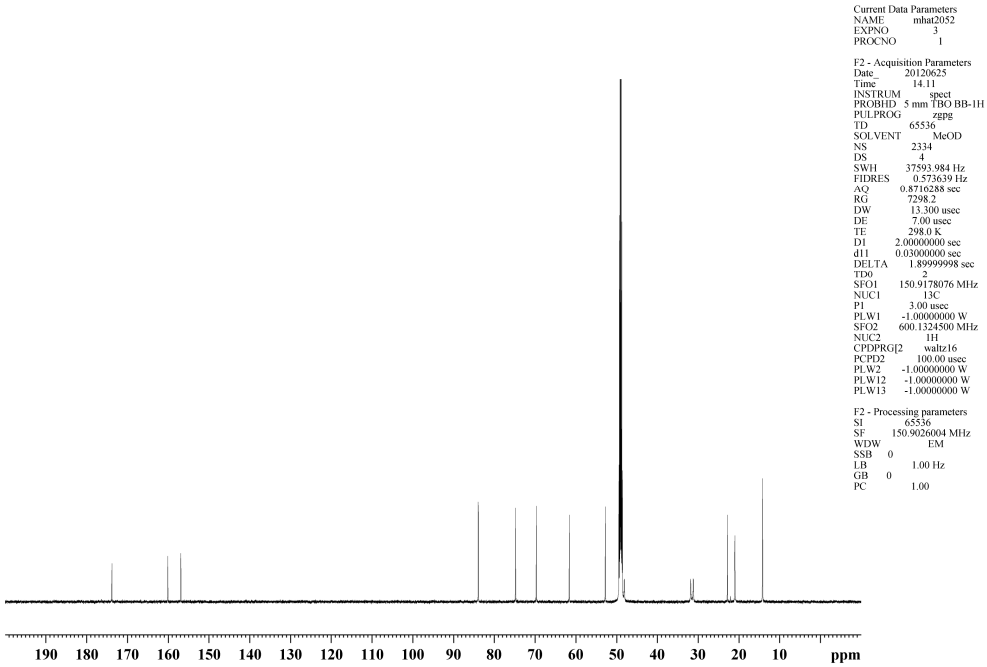
^{13}C NMR spectrum of **60**



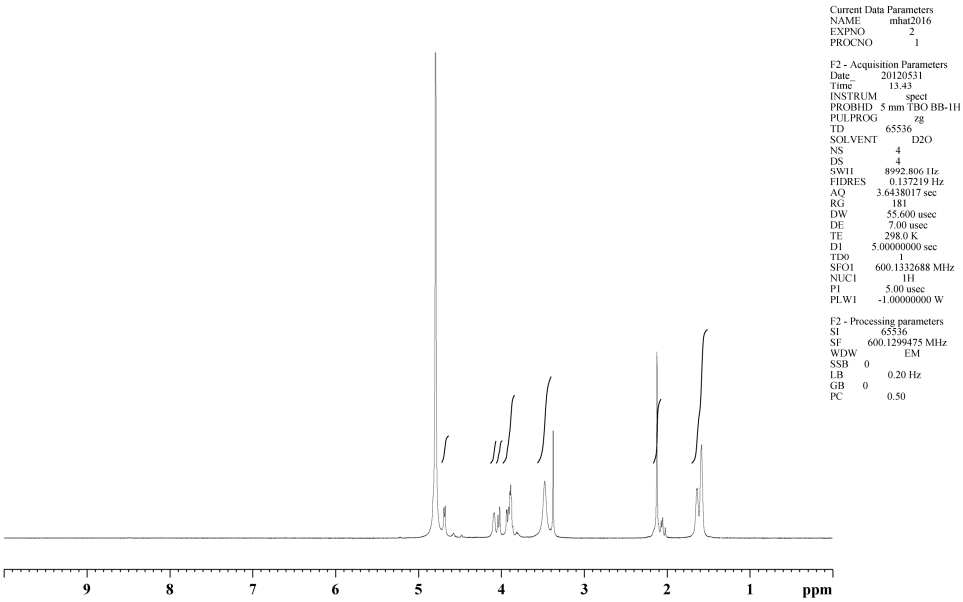
^{1}H NMR spectrum of **61**



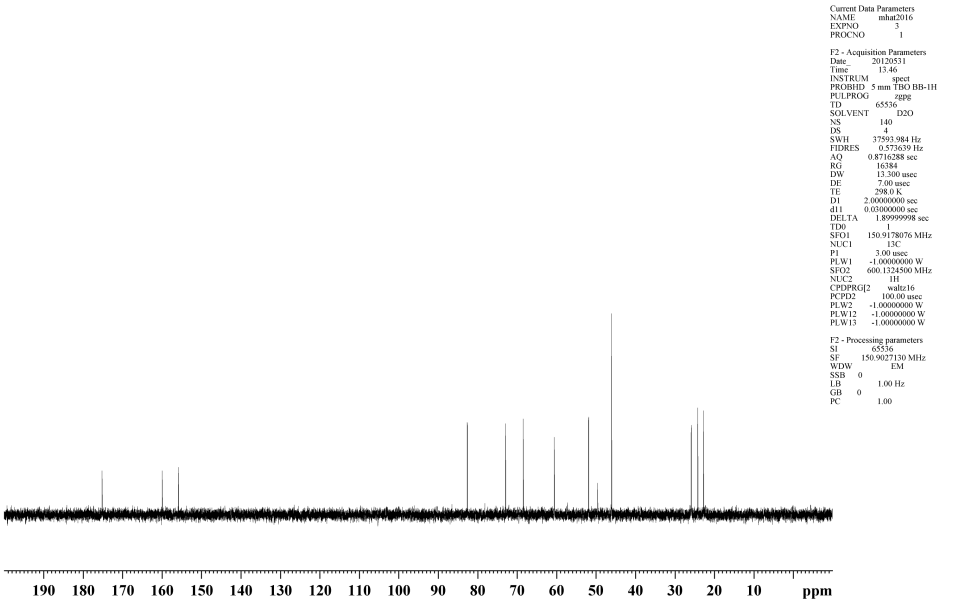
^{13}C NMR spectrum of **61**



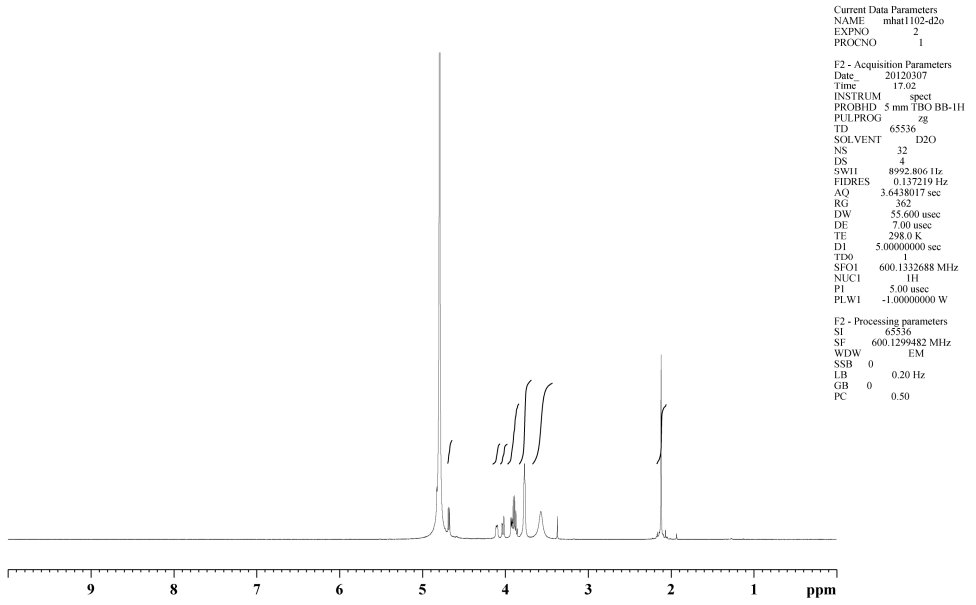
^{1}H NMR spectrum of **62**



^{13}C NMR spectrum of **62**



^{1}H NMR spectrum of **63**



^{13}C NMR spectrum of **63**