Supplementary Information

Synthetic trisaccharides reveal discrimination of endo-glycosidic linkages by exo-acting α-1,2-mannosidases in the endoplasmic reticulum

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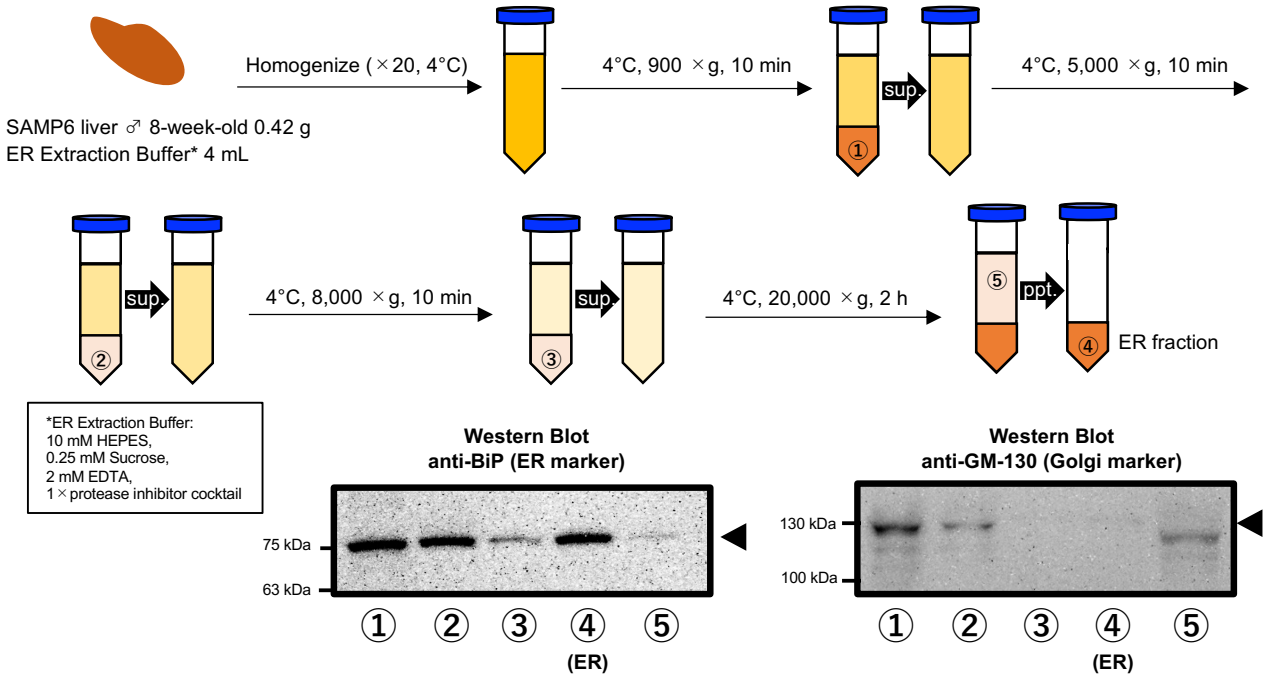

Fig. S1 Extraction of ER fraction from SAMP6 liver.

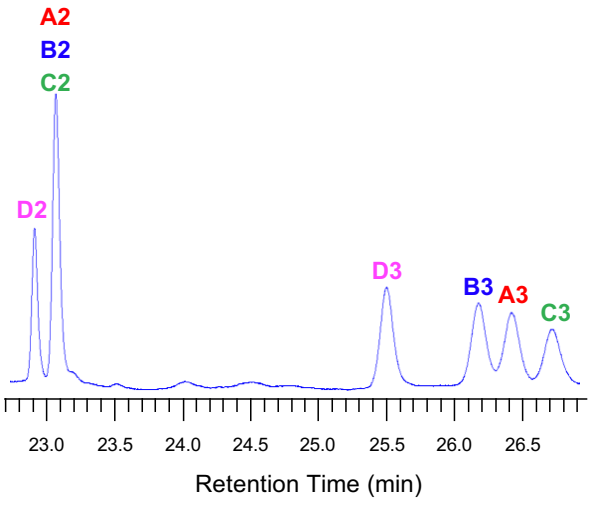

Fig. S2 HPLC chromatogram of the substrates (**A3**, **B3**, **C3** and **D3**) and the products (**A2**, **B2**, **C2** and **D2**).

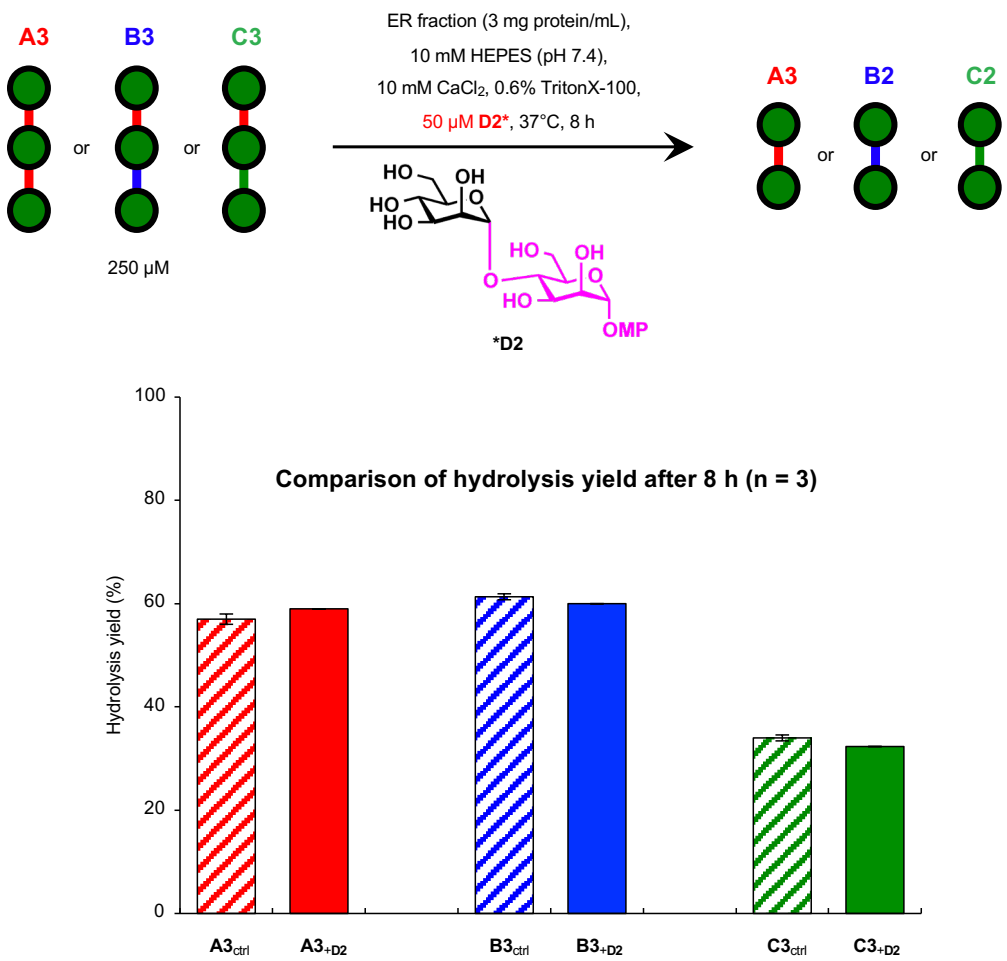

Fig. S3 Influence on the hydrolysis yield of **A3** (250 µM), **B3** (250 µM) or **C3** (250 µM) by adding internal standard **D2** (50 µM). Each data point represents the mean value with the standard deviation (n = 3).

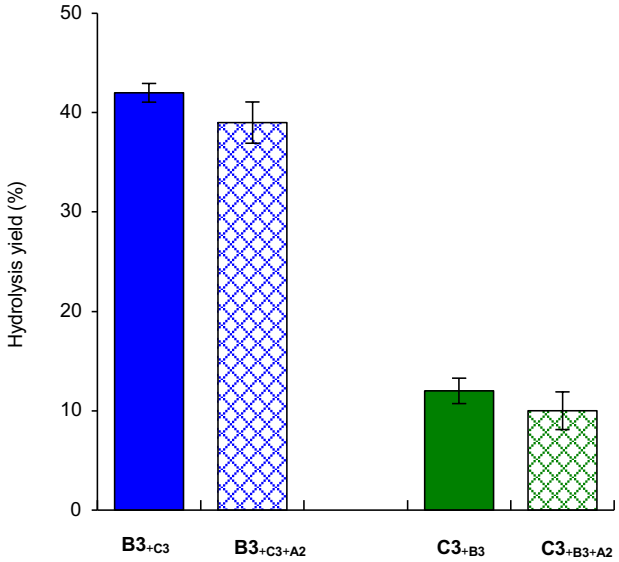

Fig. S4 Influence on the hydrolysis yield after 6h from competitive assay of **B3** (250 µM) with **C3** (250 µM) in the ER fraction (3 mg/mL) by adding **A2** (250 µM). Each data point represents the mean value with the standard deviation (n = 3).

General methods & materials for chemical synthesis

Unless otherwise indicated, all reactions were performed under an argon atmosphere in oven-dried glassware. All reagents and dry solvents were used as purchased without further purification. Column chromatography on silica gel was carried out with silica gel 60N (40-50 μm) or silica gel 60N (40-100 μm) from Kanto Chemical Co. Column chromatography was also carried out using Automated Flash Chromatography System Smart Flash EPCLC AI-580S (Yamazen Co.) with Hi-Flash column or Ultrapack column. Gel filtration chromatography was carried out with Sephadex G-10 or Sephadex LH-20 from GE Healthcare. TLC was performed on pre-coated glass plates using silica gel (Merck, 60, F254) and detected by UV light (254 nm) and/or by staining reagents such as Orcinol/H_2SO_4. Molecular sieves AW-300 used in the reactions, were activated for 12 h *in vacuo* at 180 °C. ^{1}H NMR spectra were recorded on a JEOL JNM-ECA500 (500 MHz) spectrometer using $CDCl_3$ (δ_H 7.26), D_2O (δ_H 4.79) or CD_3OD [δ_H 3.31 (central line of a quintet)] as the NMR solvents, whereby the spectra were referenced to the corresponding residual protonated solvent signals. ^{13}C NMR spectra were recorded on a JEOL JNM-ECA500 (125 MHz) spectrometer with $CDCl_3$ [δ_C 77.2 (central line of a triplet)] or CD_3OD [δ_C 49.2 (central line of a septet)], whereby the spectra were referenced to the solvent signals. High-resolution mass spectra (HRMS) were obtained from a Thermo SCIENTIFIC Q-Exactive (ESI-TOF) mass spectrometer.

Chemical synthesis

2-*O*-Acetyl-3,4,6-tri-*O*-benzyl-1-deoxy-α-D-mannopyranosyl fluoride (2).

DAST (10.5 μL, 0.0801 mmol) was added to a cold (-40°C) solution of **1** (24.4 mg, 0.0482 mmol) in CH_2Cl_2 (0.500 mL). After stirring the reaction mixture for 3 h at 0°C, another portion of DAST (10.5 μL, 0.0801 mmol) was added at -40°C. After stirring the reaction mixture for 80 min at 0°C, the reaction was quenched with MeOH (0.200 mL, 4.94 mmol) at -20°C. The mixture was diluted with EtOAc (100 mL) and washed with saturated aq. $NaHCO_3$ (100 mL × 2) and brine (100 mL × 2). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:3, v/v) to give **2** (18.9 mg, 80%). Physical data were consistent with those reported previously[1]: TLC, R_f 0.44 (EtOAc/hexane, 1:3, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.14 (m, 15H, (-CH_2<u>Ph</u>)$_3$), 5.61 (dd, J = 2.3, 2.3 Hz, $J_{H\text{-}F}$ = 49.3 Hz, 1H, H-1), 5.47 (t, J = 2.3 Hz, 1H, H-2), 4.86, 4.71 (ABq, J = 10.9 Hz, 2H, -(<u>CH_2</u>Ph)$_3$), 4.68, 4.51 (ABq, J = 12.6 Hz, 2H, -(<u>CH_2</u>Ph)$_3$), 4.56, 4.50 (ABq, J = 11.5 Hz, 2H, -(<u>CH_2</u>Ph)$_3$), 3.97-3.94 (m, 3H, H-3, H-5, H-6), 3.81 (dd, J = 3.4, 10.6 Hz, 1H, H-6'), 3.71 (dd, J = 1.2, 10.9 Hz, 1H, H-4), 2.16 (s, 3H, -CH_3 of Ac).

1,2-di-*O*-Acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranose (3).

Compound **1** (67.1 mg, 0.133 mmol) was diluted in AcOH (1.30 mL, 22.7 mmol) at 0°C. After stirring the reaction mixture for 2 h at 0°C, Ac_2O (1.30 mL, 1.38 mmol) and DMAP (32.3 mg, 0.264 mmol) were added at 0°C. After stirring the reaction mixture for 2 h at room temperature, another portion of Ac_2O (1.30 mL, 1.38 mmol) was added at 0°C. After stirring the reaction mixture for 40 min at room temperature, the reaction was quenched with MeOH (2.6 mL, 6.42 mmol) at 0°C. The mixture was diluted with EtOAc (100 mL) and washed with saturated aq. $NaHCO_3$ (65 mL × 3) and brine (65 mL × 3). The organic layer was dried over Na_2SO_4,

filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:2, v/v) to give **3** (57.0 mg, 80%). Physical data were consistent with those reported previously[2]: TLC, R_f 0.44 (EtOAc/toluene, 6:1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) (α -isomer) δ 7.36-7.13 (m, 15H, (-CH_2Ph)$_3$), 6.13 (d, J = 1.7 Hz, 1H, H-1), 5.37 (dd, J = 1.7, 2.6 Hz, 1H, H-2), 4.86, 4.73 (ABq, J = 10.9 Hz, 2H, -(CH_2Ph)$_3$), 4.68, 4.51 (ABq, J = 12.6 Hz, 2H, -(CH_2Ph)$_3$), 4.56, 4.51 (ABq, J = 11.5 Hz, 2H, -(CH_2Ph)$_3$), 4.00-3.96 (m, 2H, H-3, H-6), 3.88-3.83 (m, 1H, H-5), 3.81 (dd, J = 3.4, 10.6 Hz, 1H, H-4), 3.69 (dd, J = 1.7, 10.9 Hz, 1H, H-6'), 2.16 (s, 3H, -CH_3 of Ac) , 2.07 (s, 3H, -CH_3 of Ac).

4-Methoxyphenyl 2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (4).

p-Methoxyphenol (372 mg, 3.00 mmol), Et_3N (0.140 mL, 1.00 mmol), and BF_3•Et_2O (0.520 mL, 4.14 mmol) were added to a cold (0°C) solution of **3** (1.10 g, 2.06 mmol) in CH_2Cl_2 (20.0 mL). After stirring the reaction mixture for 4 h at room temperature, another portion of Et_3N (35.0 μL, 0.250 mmol) and BF_3•Et_2O (0.130 mL, 1.03 mmol) were added at 0°C. After stirring the reaction mixture for 30 min at room temperature, another portion of *p*-Methoxyphenol (93.5 mg, 0.750 mmol) was added at 0°C. After stirring the reaction mixture for 30 min at room temperature, the mixture was diluted with EtOAc (200 mL) and washed with saturated aq. $NaHCO_3$ (200 mL) and brine (200 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/toluene, 1:20, v/v) to give **4** (1.15 g, 94%). Physical data were consistent with those reported previously[3]: TLC, R_f 0.60 (EtOAc/toluene, 6:1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.16 (m, 15H, (-CH_2Ph)$_3$), 6.99 (dd, J = 2.3, 6.9 Hz, 2H, Ph of MP), 6.79 (dd, J = 2.3, 6.9 Hz, 2H, Ph of MP), 5.54 (dd, J = 1.7, 3.4 Hz, 1H, H-2), 5.46 (d, J = 1.7 Hz, 1H, H-1), 4.89, 4.51 (ABq, J = 10.9 Hz, 2H, -(CH_2Ph)$_3$), 4.77, 4.61 (ABq, J = 10.9 Hz, 2H, -(CH_2Ph)$_3$), 4.66, 4.45 (ABq, J = 12.0 Hz, 2H, -(CH_2Ph)$_3$), 4.18 (dd, J = 3.4, 9.2 Hz, 1H, H-3), 4.00 (t, J = 9.2 Hz, 1H, H-4), 3.96-3.94 (m, 1H, H-5), 3.81 (dd, J = 4.0, 10.9 Hz, 1H, H-6), 3.75 (s, 3H, -OCH_3 of MP), 3.68 (dd, J = 1.7, 10.9 Hz, 1H, H-6), 2.18 (s, 3H, -CH_3 of Ac).

4-Methoxyphenyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (5).

NaOMe (28% in MeOH; 1.00 mL, 5.19 mmol) was added to a cold (0°C) solution of **4** (1.12 g, 1.88 mmol) in MeOH/THF (1:1, v/v, 20.0 mL). After stirring the reaction mixture for 30 min at room temperature, the reaction mixture was neutralized with Amberlyst 15E at 0°C. The mixture was filtered and concentrated *in vacuo*, before the residue was purified by column chromatography on silica gel (EtOAc/toluene, 1:6, v/v) to give **5** (0.979 g, 94%). Physical data were consistent with those reported previously[4]: TLC, R_f 0.26 (EtOAc/toluene, 1:6, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.17 (m, 15H, (-CH_2Ph)$_3$), 7.00 (dd, J = 2.3, 6.9 Hz, 2H, Ph of MP), 6.79 (dd, J = 2.3, 6.6 Hz, 2H, Ph of MP), 5.52 (d, J = 1.4 Hz, 1H, H-1), 4.85, 4.54 (ABq, J = 10.9 Hz, 2H, -(CH_2Ph)$_3$), 4.78, 4.75 (ABq, J = 11.5 Hz, 2H, -(CH_2Ph)$_3$), 4.62, 4.45 (ABq, J = 12.0 Hz, 2H, -(CH_2Ph)$_3$), 4.22 (m, 1H, H-2), 4.08 (dd, J = 3.4, 8.6 Hz, 1H, H-3), 3.97 (t, J = 8.6 Hz, 1H, H-4), 3.93-3.90 (m, 1H, H-5), 3.78-3.73 (m, 4H, -OCH_3 of MP, H-6), 3.66 (dd, J = 1.7, 10.9 Hz, 1H, H-6').

4-Methoxyphenyl 3,4,6-tri-*O*-benzyl-2-*O*-pivaloyl-α-D-mannopyranoside (6).

PivCl (45.0 μL, 0.343 mmol), Et_3N (95.0 μL, 0.744 mmol), and DMAP (43.5 mg, 0.356 mmol) were added to

a cold (0°C) solution of **5** (82.5 mg, 0.148 mmol) in CH_2Cl_2 (3.00 mL). After stirring the reaction mixture for 90 min at 50°C, another portion of PivCl (45.0 μL, 0.343 mmol) and Et_3N (95.0 μL, 0.744 mmol) were added at 0°C. After stirring the reaction mixture for 40 min at 50°C, the mixture was diluted with EtOAc (200 mL) and washed with saturated aq. $NaHCO_3$ (200 mL) and brine (200 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*, before the residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:10, v/v) to give **6** (87.0 mg, 92%): TLC, R_f 0.75 (EtOAc/toluene, 1:6, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.16 (m, 15H, (-CH_2Ph)$_3$), 7.01 (dd, J = 2.3, 7.2 Hz, 2H, Ph of MP), 6.79 (dd, J = 2.3, 6.9 Hz, 2H, Ph of MP), 5.54 (dd, J = 2.3, 3.2 Hz, 1H, H-2), 5.43 (d, J = 2.3 Hz, 1H, H-1), 4.87, 4.53 (ABq, J = 10.9 Hz, 2H, -(CH_2Ph)$_3$), 4.75, 4.58 (ABq, J = 10.9 Hz, 2H, -(CH_2Ph)$_3$), 4.62, 4.46 (ABq, J = 12.0 Hz, 2H, -(CH_2Ph)$_3$), 4.19 (m, 1H, H-3), 4.02-3.94 (m, 2H, H-4, H-5), 3.80 (dd, J = 3.4, 10.9 Hz, 1H, H-6), 3.75 (s, 3H, -OCH_3 of MP), 3.71 (dd, J = 1.5, 10.9 Hz, 1H, H-6'), 1.24 (s, 3H, -(CH_3)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.80, 155.21, 150.11, 138.44, 138.34, 138.23, 128.42×2, 128.38×2, 128.30×2, 128.16×2, 128.02×2, 127.78, 127.70, 127.55×2, 127.52, 118.09×2, 114.64×2, 97.11, 78.33, 75.32, 74.17, 73.22, 71.96, 71.63, 68.95, 68.12, 55.71, 39.13, 27.27×3; HRMS calcd. for $C_{39}H_{44}NaO_8$ $(M+Na)^+$ *m/z* 663.2934, found 663.2921.

4-Methoxyphenyl 4,6-*O*-benzylidene-2-*O*-pivaloyl-α-D-mannopyranoside (8).

$Pd(OH)_2$ (20% on carbon, 64.0 mg) was added to a solution of **6** (87.0 mg, 0.136 mmol) in MeOH (2.00 mL). After stirring the reaction mixture under H_2 atmosphere for 17 h at room temperature, the mixture was filtered through a pad of celite. The filtrate and washings were concentrated *in vacuo* to give **7**. BDA (0.200 mL, 1.34 mmol) was added to a cold (0°C) solution of unpurified **7** in MeCN (2.00 mL). After stirring the reaction mixture for 5 min at 0°C, CSA (49.0 mg, 0.211 mmol) was added at 0°C. After stirring the reaction mixture for 90 min at room temperature, the mixture was diluted with EtOAc (100 mL) and washed with saturated aq. $NaHCO_3$ (100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:6, v/v) to give **8** (61.6 mg, 99%): TLC, R_f 0.46 (EtOAc/hexane, 1:3, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.34 (m, 5H, Ph of Bzl), 6.99 (dd, J = 2.3, 6.9 Hz, 2H, Ph of MP), 6.83 (dd, J = 2.3, 6.9 Hz, 2H, Ph of MP), 5.62 (s, 1H, H of Bzl), 5.38 (dd, J = 1.7, 3.4 Hz, 1H, H-2), 5.35 (d, J = 1.7 Hz, 1H, H-1), 4.44 (dd, J = 3.4, 9.7 Hz, 1H, H-3), 4.23 (dd, J = 5.2, 10.3 Hz, 1H, H-6), 4.06-4.01 (m, 1H, H-5), 3.92 (t, J = 9.7 Hz, 1H, H-4), 3.80 (t, J = 10.3 Hz, 1H, H-6'), 3.77 (s, 3H, -OCH_3 of MP), 1.30 (s, 9H, -(CH_3)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.03, 155.43, 149.91, 137.13, 129.41, 128.44×2, 126.40×2, 118.07×2, 114.77×2, 102.40, 97.69, 79.41, 71.74, 68.79, 67.46, 64.04, 55.75, 39.22, 27.29×3; HRMS calcd. for $C_{25}H_{30}NaO_8$ $(M+Na)^+$ *m/z* 481.1838, found 481.1833.

4-Methoxyphenyl 4,6-*O*-benzylidene-2,3-di-*O*-pivaloyl-α-D-mannopyranoside (9).

PivCl (37.0 μL, 0.301 mmol), Et_3N (77.0 μL, 0.603 mmol) and DMAP (31.2 mg, 0.255 mmol) were added to a cold (0°C) solution of **8** (55.0 mg, 0.120 mmol) in CH_2Cl_2 (3.00 mL). After stirring the reaction mixture for 80 min at 50°C, second portion of PivCl (19.0 μL, 0.154 mmol) and Et_3N (30.0 μL, 0.235 mmol) were added at 0°C. After stirring the reaction mixture for 80 min at 50°C, third portion of PivCl (19.0 μL, 0.154 mmol) and Et_3N (30.0 μL, 0.235 mmol) were added at 0°C. After stirring the reaction mixture for 50 min at 50°C, the

mixture was diluted with EtOAc (50 mL) and washed with saturated aq. $NaHCO_3$ (50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:10, v/v) to give **9** (63.7 mg, 98%): TLC, R_f 0.73 (EtOAc/toluene, 1:6, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.30 (m, 5H, Ph of Bzl), 7.00 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.83 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 5.68 (dd, *J* = 3.4, 9.8 Hz, 1H, H-3), 5.61 (s, 1H, H of Bzl), 5.48 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 5.34 (d, *J* = 1.7 Hz, 1H, H-1), 4.25 (dd, *J* = 4.6, 10.3 Hz, 1H, H-6), 4.16-4.07 (m, 2H, H-4, H-5), 3.83 (t, *J* = 10.3 Hz, 1H, H-6'), 3.77 (s, 3H, -O$\underline{CH_3}$ of MP), 1.30 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv), 1.19 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv);^{13}C NMR (125 MHz, $CDCl_3$) δ 177.24, 177.03, 155.31, 149.72, 137.11, 128.89, 128.17×2, 125.88×2, 117.88×2, 114.64×2, 101.45, 97.52, 76.72, 70.02, 68.69, 68.03, 64.43, 55.64, 38.95, 38.88, 27.18×3, 27.07×3; HRMS calcd. for $C_{30}H_{38}NaO_9$ $(M+Na)^+$ *m/z* 565.2414, found 565.2397.

4-Methoxyphenyl 4-*O*-benzyl-2,3-di-*O*-pivaloyl-α-D-mannopyranoside (10).

Compound **9** (59.9 mg, 0.110 mmol) was dissolved in CH_2Cl_2 (2.00 mL). After stirring the reaction mixture for 20 min at -100°C, $PhBCl_2$ (46.0 μL, 0.353 mmol) was added at -100C. After stirring the reaction mixture for 10 min at -100 °C, Et_3SiH (52.0 μL, 0.328 mmol) was added at -100°C. After stirring the reaction mixture for 10 min at -100 °C, the mixture was diluted with EtOAc (50 mL) and washed with saturated aq. $NaHCO_3$ (50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by Flash chromatography system (EtOAc/toluene, 2:98 → 24:76, v/v) to give **10** (55.3 mg, 92%): TLC, R_f 0.34 (EtOAc/toluene, 1:6, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.26 (m, 5H, -$CH_2\underline{Ph}$), 6.98 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.81 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.63 (dd, *J* = 2.9, 9.7 Hz, 1H, H-3), 5.42 (t, *J* = 2.9 Hz, 1H, H-2), 5.34 (d, *J* = 2.9 Hz, 1H, H-1), 4.78, 4.65 (ABq, *J* = 10.9 Hz, 2H, -$\underline{CH_2}$Ph), 4.10 (t, *J* = 9.7 Hz, 1H, H-4), 3.94-3.90 (m, 1H, H-5), 3.83-3.74 (m, 5H, H-6, H-6', -O$\underline{CH_3}$ of MP), 1.28 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv), 1.21 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.43, 177.15, 155.36, 149.98, 137.72, 128.60×2, 128.05, 127.74×2, 118.06×2, 114.72×2, 96.90, 75.03, 72.58, 72.43, 71.91, 69.78, 61.59, 55.72, 39.05, 38.92, 27.28×6; HRMS calcd. for $C_{30}H_{40}NaO_9$ $(M+Na)^+$ *m/z* 567.2570, found 567.2556.

4-Methoxyphenyl 6-*O*-benzyl-2,3-di-*O*-pivaloyl-α-D-mannopyranoside (11).

Compound **9** (247 mg, 0.455 mmol) was dissolved in CH_2Cl_2 (5.00 mL). After stirring the reaction mixture for 10 min at -20°C, BF_3•Et_2O (0.100 mL, 0.910 mmol) was added at -20°C. After stirring the reaction mixture for 5 min at -20°C, Et_3SiH (0.800 mL, 0.328 mmol) was added at -100°C. After stirring the reaction mixture for 4h at -100°C followed by 1h at 0°C, the mixture was diluted with EtOAc (100 mL) and washed with saturated aq. $NaHCO_3$ (100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by Flash chromatography system (EtOAc/hexane, 21:79, v/v) to give **11** (222 mg, 89%): TLC, R_f 0.44 (EtOAc/toluene, 1:6, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.26 (m, 5H, -$CH_2\underline{Ph}$), 7.03 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.80 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.44 (dd, *J* = 2.9, 9.7 Hz, 1H, H-3), 5.35 (m, 2H, H-1, H-2), 4.62, 4.54 (ABq, *J* = 11.5 Hz, 2H, -$\underline{CH_2}$Ph), 4.13 (ddd, *J* = 4.6, 9.7, 9.7 Hz, 1H, H-4), 4.02-3.98 (m, 1H, H-5), 3.84 (dd, *J* = 4.6, 10.9 Hz, 1H, H-6), 3.79-3.75 (m, 2H, H-6', -O$\underline{CH_3}$ of MP), 1.25 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv), 1.21 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ

178.83, 177.26, 155.33, 150.15, 138.07, 128.45×2, 127.72, 127.57×2, 118.12×2, 114.69×2, 96.92, 73.63, 72.01, 71.93, 69.98, 69.63, 67.60, 55.71, 39.07, 39.03, 27.21×6; HRMS calcd. for $C_{30}H_{40}NaO_9$ $(M+Na)^+$ *m/z* 567.2570, found 567.2564.

4-Methoxyphenyl *O*-(2-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (12).

AgOTf (100 mg, 0.389 mmol), Cp_2HfCl_2 (77.6 mg, 0.204 mmol), DTBMP (6.00 mg, 0.0292 mmol) and MS AW-300 (1.25 g) were dissolved in toluene (2.00 mL). After stirring the mixture for 20 min at -20°C, the solution of **2** (128 mg, 0.259 mmol) and **5** (78.5 mg, 0.141 mmol) in toluene (2.20 mL) was added at -20°C. After stirring the reaction mixture for 70 min at 0°C, the reaction was quenched with Et_3N (0.100 mL, 0.783 mmol) at -20°C. The mixture was filtered through a pad of celite. The filtrate and washings (200 mL of EtOAc) were combined and washed with saturated aq. $NaHCO_3$ (100 mL) and brine (100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:5, v/v) to give **12** (135 mg, 93%, α only): TLC, R_f 0.44 (EtOAc/toluene, 1:4, v/v, double development); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.11 (m, 30H, -($\underline{CH_2}Ph)_6$), 6.95 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.73 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.57 (dd, *J* = 1.7, 3.2 Hz, 1H, H'-2), 5.54 (d, *J* = 2.3 Hz, 1H, H-1), 5.12 (d, *J* = 1.7 Hz, 1H, H'-1), 4.88, 4.59 (ABq, *J* = 10.9 Hz, 2H, -($\underline{CH_2}Ph)_6$), 4.83, 4.44 (ABq, *J* = 10.3 Hz, 2H, -($\underline{CH_2}Ph)_6$), 4.77, 4.73 (ABq, *J* = 12.0 Hz, 2H, -($\underline{CH_2}Ph)_6$), 4.77, 4.41 (ABq, *J* = 10.9 Hz, 2H, -($\underline{CH_2}Ph)_6$), 4.62, 4.45 (ABq, *J* = 12.0 Hz, 2H, -($\underline{CH_2}Ph)_6$), 4.60, 4.46 (ABq, *J* = 12.6 Hz, 2H, -($\underline{CH_2}Ph)_6$), 4.18 (dd, *J* = 2.3, 2.9 Hz, 1H, H-2), 4.11 (dd, *J* = 2.9, 9.2 Hz, 1H, H-3), 4.01-3.94 (m, 3H, H'-3, H'-5, H-4), 3.91-3.87 (m, 1H, H-5), 3.81 (t, *J* = 9.7 Hz, 1H, H'-4), 3.76 (dd, *J* = 6.3, 11.7 Hz, 1H, H-6), 3.74-3.71 (m, 4H, H'-6, -O$\underline{CH_3}$ of MP), 3.69-3.66 (m, 2H, H'-6', H-6'), 2.13 (s, 3H, -$\underline{CH_3}$ of Ac); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.25, 154.97, 150.11, 138.54, 138.44×2, 138.39, 138.17, 138.06, 128.53×2, 128.44×4, 128.40×2, 128.38×2, 128.34×2, 128.27×2, 128.11×2, 127.92×2, 127.83×2, 127.78, 127.75, 127.70, 127.64×3, 127.59×4, 127.46, 117.86×2, 114.59×2, 99.72, 97.72, 79.53, 78.25, 75.29, 75.20, 74.71, 74.55, 74.42, 73.42, 73.28, 72.39, 72.32, 72.05, 69.16, 68.99, 68.77, 55.69, 21.25; HRMS calcd. for $C_{90}H_{94}NaO_{18}$ $(M+Na)^+$ *m/z* 1053.439,6 found 1053.4397.

4-Methoxyphenyl *O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (13).

NaOMe (28% in MeOH; 0.135 mL, 0.701 mmol) was added to a cold (0°C) solution of **12** (135 mg, 0.131 mmol) in MeOH/THF (1:1, v/v, 2.70 mL). After stirring the reaction mixture for 20 min at room temperature, the reaction mixture was neutralized with Amberlyst 15E at 0°C. The mixture was filtered and concentrated *in vacuo*, before the residue was purified by column chromatography on silica gel (EtOAc/toluene, 1:10, v/v) to give **13** (115 mg, 89%). Physical data were consistent with those reported previously[5]: TLC, R_f 0.24 (EtOAc/hexane, 1:2, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.13 (m, 30H, -($\underline{CH_2}Ph)_6$), 6.96 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.72 (dd, *J* = 2.3, 6.3 Hz, 2H, Ph of MP), 5.60 (d, *J* = 1.7 Hz, 1H, H-1), 5.19 (d, *J* = 1.7 Hz, 1H, H'-1), 4.88, 4.59 (ABq, *J* = 10.9 Hz, 2H, -($\underline{CH_2}Ph)_6$), 4.80, 4.49 (ABq, *J* = 10.9 Hz, 2H, -($\underline{CH_2}Ph)_6$), 4.76, 4.73 (ABq, *J* = 12.0 Hz, 2H, -($\underline{CH_2}Ph)_6$), 4.66, 4.46 (ABq, *J* = 12.0 Hz, 2H, -($\underline{CH_2}Ph)_6$), 4.57, 4.48 (ABq,

J = 12.0 Hz, 2H, -(CH$_2$Ph)$_6$), 4.54, 4.54 (ABq, *J* = 11.5 Hz, 2H, -(CH$_2$Ph)$_6$), 4.22 (m, 1H, H-2), 4.16 (dd, *J* = 1.7, 2.9 Hz, 1H, H'-2), 4.13 (dd, *J* = 2.9, 9.7 Hz, 1H, H-3), 4.01-3.97 (m, 1H, H'-5), 3.97 (t, *J* = 9.7 Hz, 1H, H-4), 3.90-3.87 (m, 2H, H'-3, H-5), 3.82 (dd, *J* = 3.4, 10.9 Hz, 1H, H-6), 3.79 (t, *J* = 9.2 Hz, 1H, H'-4), 3.72 (s, 3H, -OCH$_3$ of MP) 3.71-3.66 (m, 3H, H'-6, H'-6', H-6').

4-Methoxyphenyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-*O*-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (14).

AgOTf (8.20 mg, 0.0319 mmol), Cp_2HfCl_2 (6.00 mg, 0.0158 mmol), and MS AW-300 (340 mg) were dissolved in toluene (0.500 mL). After stirring the mixture for 10 min at room temperature and for 10 min at -20°C, the solution of **2** (10.6 mg, 0.0214 mmol) and **13** (11.0 mg, 0.0111 mmol) in toluene (0.6 mL) was added at -20°C. After stirring the reaction mixture for 80 min at gradually heated from -20 to 0°C, the reaction was quenched with Et_3N (5.00 μL, 0.0359 mmol) at -20°C. The mixture was filtered through a pad of celite. The filtrate and washings (200 mL of EtOAc) were combined and washed with saturated aq. $NaHCO_3$ (200 mL) and brine (200 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by Flash Chromatography System (UltraPack B, EtOAc/hexane, 12:88→26:74→51:49, v/v) to give **14** (16.1 mg, 99%, α:β = 99:1): TLC, R_f 0.42 (EtOAc/hexane, 1:3, v/v, double development); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.12 (m, 45H, -(CH$_2$Ph)$_9$), 6.95 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 6.71 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.60 (d, *J* = 2.3 Hz, 1H, H-1), 5.53 (dd, *J* = 1.7, 3.4 Hz, 1H, H"-2), 5.23 (d, *J* = 1.7 Hz, 1H, H'-1), 5.05 (d, *J* = 2.3 Hz, 1H, H"-1), 4.86-4.30 (m, 18H, -(CH$_2$Ph)$_9$), 4.14 (t, *J* = 2.3 Hz, 1H, H-2), 4.11 (t, *J* = 2.5 Hz, 1H, H'-2), 4.05 (dd, *J* = 2.9, 8.6 Hz, 1H, H-3), 4.00-3.96 (m, 2H, H"-3, H'-5), 3.94-3.84 (m, 5H, H'-3, H-5, H-4, H"-4, H"-5), 3.80-3.75 (m, 2H, H''-6, H'-4), 3.72 (s, 3H, -OCH$_3$ of MP), 3.70-3.64 (m, 4H, H'-6, H-6, H"-6', H'-6'), 3.54 (dd, *J* = 1.2, 10.6 Hz, 1H, H-6'), 2.13 (s, 3H, -CH$_3$ of Ac); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.15, 154.82, 150.05, 138.54, 138.40, 138.35, 138.33, 138.31, 138.15, 138.01, 128.45×2, 128.33×5, 128.29×8, 128.24×5, 128.18×2, 128.00×2, 127.93×2, 127.83×2, 127.79×3, 127.76×2, 127.65, 127.57, 127.55, 127.49×4, 127.45×3, 127.38, 127.34, 117.78×2, 114.57×2, 114.47, 99.43, 97.60, 79.22, 78.08, 75.16, 75.11×2, 74.99, 74.95, 74.75, 74.65, 74.25, 73.36×2, 73.20×2, 73.16×2, 72.34, 72.30, 72.15, 72.02, 71.87×2, 69.39, 69.16, 68.84, 68.71, 55.60, 21.19; HRMS calcd. for $C_{90}H_{94}NaO_{18}$ $(M+Na)^+$ *m/z* 1485.6338, found 1485.6345.

4-Methoxyphenyl *O*-(3,4,6-tri-*O*-benzyl–α-D-mannopyranosyl-(1→2)-*O*-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (15).

NaOMe (28% in MeOH; 50.0 μL, 0.260 mmol) was added to a cold (0°C) solution of **14** (42.9 mg, 0.0293 mmol) in MeOH/THF (1:1, v/v, 1.00 mL). After stirring the reaction mixture for 60 min at room temperature, the reaction mixture was neutralized with Amberlyst 15E at 0°C. The mixture was filtered and concentrated *in vacuo*, before the residue was purified by column chromatography on silica gel (EtOAc/toluene, 1:2, v/v) to give **15** (39.8 mg, 97%): TLC, R_f 0.49 (EtOAc/toluene, 1:6, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.14 (m, 45H, -(CH$_2$Ph)$_9$), 6.96 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.71 (dd, *J* = 2.3, 5.7 Hz, 2H, Ph of MP), 5.62 (d, *J* = 1.7 Hz, 1H, H-1), 5.27 (d, *J* = 1.7 Hz, 1H, H'-1), 5.12 (d, *J* = 1.2 Hz, 1H, H"-1), 4.85-4.32 (m, 18H, -(CH$_2$Ph)$_9$), 4.13 (m, 3H, H-2, H'-2, H"-2), 4.05 (dd, *J* = 2.9, 8.6 Hz, 1H, H-3), 4.01-3.97 (m, 1H, H"-5), 3.93 (dd, *J* = 2.9, 8.6 Hz, 1H, H'-3), 3.92-3.84 (m, 5H,H-4, H"-3, H'-5, H"-6), 3.78 (dd, *J* = 4.0, 11.5 Hz, 1H, H'-

4), 3.76 (t, *J* = 9.2 Hz, 1H, H"-4) 3.94-3.84 (m, 5H, H'-3, H-5, H-4, H"-4, H"-5), 3.80-3.75 (m, 2H, H''-6, H'-4), 3.72 (s, 3H, -O$\underline{CH_3}$ of MP), 3.72-3.63 (m, 4H, H'-6, H-6, H"-6', H'-6'), 3.57 (dd, *J* = 1.2, 10.9 Hz, 1H, H-6'); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.90, 150.17, 138.63, 138.54×2, 138.51×2, 138.39×2, 138.26, 138.12, 138.01, 128.60×2, 128.57×2, 128.49×2, 128.45×2, 128.41×6, 128.39×6, 128.33×2, 128.04×2, 127.99×8, 127.95, 127.90×2, 127.81×2, 127.73, 127.68, 127.63, 127.54×5, 127.46, 127.42, 117.88×2, 114.58×2, 101.13, 101.03, 97.69, 80.03, 79.24, 75.38, 75.26, 75.15, 75.10, 75.03, 74.72, 74.41, 73.45, 73.26×2, 72.46, 72.36, 72.21, 72.03, 71.66, 69.54, 69.27, 69.12, 69.64, 55.69; HRMS calcd. for $C_{88}H_{92}NaO_{17}$ $(M+Na)^+$ *m/z* 1443.6232, found 1443.6235.

4-Methoxyphenyl *O*-(α-D-mannopyranosyl-(1→2)-*O*-α-D-mannopyranosyl)-(1→2)-α-D-mannopyranoside (16) = (A3).

$Pd(OH)_2$ (20% on carbon, 94.2 mg) was added to a solution of **15** (39.8 mg, 0.0280 mmol) in MeOH/THF (2:1, v/v, 2.00 mL). After stirring the reaction mixture under H_2 atmosphere for 17.5 h at room temperature, the mixture was filtered through a pad of celite. The filtrate and washings were concentrated *in vacuo.* The residue was purified by gel filtration chromatography on Sephadex G-10 (3 cm*Φ* × 80 cm) (20% EtOH) to give **16** (17.8 mg, quant.): TLC, R_f 0.68 (H_2O/2-PrOH, 1:2, v/v); ^{1}H NMR (500 MHz, D_2O) δ 7.11 (dd, *J* = 2.3, 6.3 Hz, 2H, Ph of MP), 6.96 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.75 (d, *J* = 1.2 Hz, 1H, H-1), 5.34 (d, *J* = 1.2 Hz, 1H, H'-1), 5.05 (d, *J* = 1.7 Hz, 1H, H"-1), 4.15 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 4.13-4.10 (m, 2H,H'-2, H-3), 4.06 (dd, *J* = 1.7, 3.4 Hz, 1H, H"-2), 3.96 (dd, *J* = 3.4, 9.4 Hz, 1H, H'-3), 3.89 (t, *J* = 1.7 Hz, 1H, H'-6), 3.87 (t, *J* = 1.7 Hz, 1H, H'-6'), 3.84-3.81 (m, 2H, H"-3. H-6), 3.79-3.68 (m, 8H,H-5'', -O$\underline{CH_3}$ of MP, H-4, H"-6, H-6', H''-6', H-5, H'-5), 3.64 (t, *J* = 9.4 Hz, H'-4) 3.60 (t, *J* = 9.7 Hz, H"-4); ^{13}C NMR (125 MHz, D_2O) δ 154.70, 149.70, 118.93×2, 115.03×2, 102.30, 100.85, 97.83, 79. 24, 78.68, 73.40, 73.38, 73.29, 70.34, 69.98×2, 69.95, 67.18, 66.90, 66.82, 61.23, 61.17, 60.70, 55.80; HRMS calcd. for $C_{25}H_{38}NaO_{17}$ $(M+Na)^+$ *m/z* 633.2007, found 633.1993.

4-Methoxyphenyl 2-*O*-pivaroyl-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-*O*-4,6-benzylidene-α-D-mannopyranoside (17).

AgOTf (40.4 mg, 0.157 mmol), Cp_2HfCl_2 (29.9 mg, 0.0788 mmol), DTBMP (3.00 mg, 0.0146 mmol) and MS AW-300 (901 mg) were dissolved in toluene (1.25 mL). After stirring the mixture for 10 min at room temperature and for 20 min at -40°C, the solution of **2** (45.0 mg, 0.0910 mmol) and **8** (27.3 mg, 0.0595 mmol) in CH_2Cl_2/toluene (2.5:1, v/v, 1.75 mL) was added at -40°C. After stirring the reaction mixture for 70 min at -40°C, the reaction was quenched with Et_3N (0.100 mL, 0.783 mmol) at -40°C. The mixture was filtered through a pad of celite. The filtrate and washings (200 mL of EtOAc) were combined and washed with saturated aq. $NaHCO_3$ (200 mL) and brine (200 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by Flash Chromatography System (EtOAc/hexane, 8:92→20:80, v/v) to give **17** (55.1 mg, 99%, α only): TLC, R_f 0.67 (EtOAc/toluene, 1:4, v/v, triple development); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.14 (m, 20H, Ph of Bzl, -($\underline{CH_2}$Ph)$_3$), 6.93 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 6.80 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 5.64 (s, 1H, H of Bzl), 5.52 (dd, *J* = 1.7, 2.9 Hz, 1H, H'-2), 5.36 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 5.33 (d, *J* = 1.7 Hz, 1H, H-1), 5.31 (d, *J* = 1.7 Hz, 1H, H'-1), 4.85, 4.49 (ABq, *J* = 10.9 Hz,

2H, -($\underline{CH_2}$Ph)$_3$), 4.71, 4.49 (ABq, J = 12.0 Hz, 2H, -($\underline{CH_2}$Ph)$_3$), 4.66, 4.44 (ABq, J = 11.5 Hz, 2H, -($\underline{CH_2}$Ph)$_3$), 4.53 (dd, J = 3.4, 9.2 Hz, 1H, H-3), 4.23 (dd, J = 4.6, 10.6 Hz, 1H, H-6), 4.07 (t, J = 9.2 Hz, 1H, H-4), 4.05-4.01 (m, 1H, H-5), 3.90-3.85 (m, 3H, H'-3, H'-6, H'-4), 3.84-3.78 (m, 2H, H-6', H'-5), 3.76 (s, 3H, -O$\underline{CH_3}$ of MP), 4.53 (dd, J = 1.2, 10.8 Hz, 1H, H'-6'), 2.10 (s, 3H, -$\underline{CH_3}$ of Ac), 1.24 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.43, 170.30, 155.44, 149.70, 138.76, 138.37, 138.02, 137.16, 129.01, 128.46×2, 128.38×2, 128.29×2, 128.25×2, 128.00×2, 127.89×2, 127.76, 127.65×2, 127.59, 127.48, 126.11×2, 118.16×2, 114.72×2, 101.54, 99.19, 97.61, 79.28, 78.18, 74.83, 74.17, 73.50, 72.07, 71.81, 71.40, 71.30, 68.80, 68.71, 68.48, 64.20, 55.74, 39.11, 27.27×3, 21.19; HRMS calcd. for $C_{54}H_{60}NaO_{14}$ $(M+Na)^+$ *m/z* 955.3881, found 955.3879.

4-Methoxyphenyl 2-*O*-pivaroyl-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-*O*-4,6-benzylidene-α-D-mannopyranoside (18).

H_2O_2 (35% in water, 58.0 μL, 0.600 mmol) and $LiOH \cdot H_2O$ (2.70 mg, 0.0643 mmol) were added to a cold (0°C) solution of **17** (14.1 mg, 0.151 mmol) in THF (2.00 mL). After stirring the reaction mixture for 2 h at room temperature, second portion of H_2O_2 (35% in water, 58.0 μL, 0.600 mmol) was added at 0°C. After stirring the reaction mixture for 26 h at room temperature, the mixture was diluted with EtOAc (50 mL) and washed with saturated aq. $NaHCO_3$ (50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:3, v/v) to give **18** (10.4 mg, 78%): TLC, R_f 0.56 (EtOAc/hexane, 1:1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.18 (m, 20H, Ph of Bzl, -($\underline{CH_2}$Ph)$_3$), 6.93 (dd, J = 2.3, 6.9 Hz, 2H, Ph of MP), 6.80 (dd, J = 2.3, 6.9 Hz, 2H, Ph of MP), 5.61 (s, 1H, H of Bzl), 5.37 (dd, J = 1.7, 3.4 Hz, 1H, H-2), 5.33 (d, J = 1.7 Hz, 1H, H-1), 5.31 (d, J = 1.7 Hz, 1H, H'-1), 4.81, 4.51 (ABq, J = 11.5 Hz, 2H, -($\underline{CH_2}$Ph)$_3$), 4.68, 4.50 (ABq, J = 12.0 Hz, 2H, -($\underline{CH_2}$Ph)$_3$), 4.63, 4.60 (ABq, J = 11.5 Hz, 2H, -($\underline{CH_2}$Ph)$_3$), 4.55 (dd, J = 3.4, 9.5 Hz, 1H, H-3), 4.21 (dd, J = 4.6, 8.0 Hz, 1H, H-6), 4.08-4.03 (m, 2H, H'-2, H-5), 4.02 (t, J = 9.5 Hz, 1H, H-4), 3.89 (t, J = 9.7 Hz, 1H, H'-4), 3.80 (dd, J = 2.3, 4.6 Hz, 1H, H-6'), 3.79-3.71 (m, 7H, H-3', -O$\underline{CH_3}$ of MP, H-5', H'-6, H'-6'), 1.24 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.43, 155.39, 149.74, 138.74, 138.35, 137.97, 137.24, 129.17, 128.57×2, 128.42×2, 128.37×2, 128.29×2, 127.96×3, 127.78×2, 127.61×2, 127.57, 127.48, 126.14×2, 118.09×2, 114.71×2, 101.86, 100.90, 97.50, 79.94, 79.13, 74.71, 74.10, 73.51, 72.02, 71.87, 71.76, 71.60, 68.80, 68.74, 68.40, 64.23, 55.74, 39.10, 27.26×3; HRMS calcd. for $C_{52}H_{58}NaO_{13}$ $(M+Na)^+$ *m/z* 913.3775, found 913.3773.

4-Methoxyphenyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-*O*-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→3)-*O*-2-*O*-pivaroyl-4,6-benzylidene-α-D-mannopyranoside (19).

AgOTf (9.60 mg, 0.0374 mmol), Cp_2HfCl_2 (7.10 mg, 0.0187 mmol) and MS AW-300 (360 mg) were dissolved in CH_2Cl_2/toluene (1:1, v/v, 0.600 mL). After stirring the mixture for 10 min at room temperature and for 20 min at -20°C, the solution of **2** (11.7 mg, 0.0237 mmol) and **18** (10.5 mg, 0.0118 mmol) in CH_2Cl_2/toluene (1:1, v/v, 0.600 mL) was added at -20°C. After stirring the reaction mixture for 50 min at 0°C, the reaction was quenched with Et_3N (10.0 μL, 0.0718 mmol) at -20°C. The mixture was filtered through a pad of celite. The filtrate and washings (200 mL of EtOAc) were combined and washed with saturated aq. $NaHCO_3$ (200 mL)

and brine (200 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by Flash Chromatography System (UltraPack B, EtOAc/hexane, 15:85→30:70→50:50, v/v) to give **19** (16.2 mg, quant., α/β=99:1): TLC, R_f 0.43 (EtOAc/toluene, 1:3, v/v, triple development); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.09 (m, 35H, Ph of Bzl, -(CH_2Ph)$_6$), 6.90 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.78 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.51 (m, 2H, H 0f Bzl, H''-2), 5.37 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 5.33 (d, *J* = 1.7 Hz, 1H, H-1), 5.27 (d, *J* = 2.3 Hz, 1H, H'-1), 5.11 (d, *J* = 1.7 Hz, 1H, H''-1), 4.83, 4.38 (ABq, *J* = 10.9 Hz, 4H, -(CH_2Ph)$_9$), 4.69-4.49 (m, 6H, -(CH_2Ph)$_9$), 4.53 (dd, *J* = 3.4, 9.7 Hz, 1H, H-3), 4.47, 4.24 (ABq, *J* = 12.0 Hz, 2H, -(CH_2Ph)$_9$), 4.17 (dd, *J* = 3.4, 10.0 Hz, 1H, H-6), 4.11 (t, *J* = 2.3 Hz, 1H, H'-2), 4.03-3.98 (m, 2H, H-4, H-6'), 3.96 (dd, *J* = 3.4, 9.5 Hz, 1H, H''-3), 3.91-3.86 (m, 2H, H''-4, H'-4), 3.81 (dd, *J* = 2.3, 9.2 Hz, 1H, H'-3), 3.80-3.67 (m, 8H, H'-6, H-5, -OCH_3 of MP, H'-6', H'-5, H''-5), 3.70-3.64 (m, 4H, H'-6, H-6, H''-6', H'-6'), 3.40 (dd, *J* = 3.4, 10.9 Hz, 1H, H''-6), 3.21 (dd, *J* = 1.2, 10.9 Hz, 1H, H''-6'), 2.08 (s, 3H, -CH_3 of Ac), 1.26 (s, 9H, -(CH_3)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.32, 170.01, 155.27, 149.64, 138.69, 138.65, 138.47, 138.44, 138.27, 138.02, 137.20, 128.98, 128.35×2, 128.30×2, 128.27×2, 128.24×2, 128.18×8, 128.15×2, 127.75×2, 127.63×4, 127.54×2 127.50×2, 127.46, 127.39, 127.35, 127.32×2, 127.03×2, 126.02×2, 118.02×2, 101.73, 100.25, 99.08, 97.42, 79.62, 78.91, 78.14, 75.00, 74.54, 74.24, 73.99, 73.66, 73.29, 73.08, 71.97, 71.90, 71.52, 71.40, 69.06, 68.67, 68.58, 68.23, 64.13, 55.63, 38.99, 38.94, 27.18×3, 21.12; HRMS calcd. for $C_{81}H_{88}NaO_{19}$ $(M+Na)^+$ *m/z* 1387.5818, found 1387.5825.

4-Methoxyphenyl *O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-*O*-3,4,6-tri-*O*-benzyl–α-D-mannopyranosyl)-(1→3)-*O*-4,6-benzylidene-α-D-mannopyranoside (20).

NaOMe (28% in MeOH; 100.0 μL, 0.520 mmol) was added to a cold (0°C) solution of **19** (41.3 mg, 0.0302 mmol) in MeOH/THF (1:1, v/v, 1.00 mL). After stirring the reaction mixture for 17 h at room temperature, the reaction mixture was neutralized with Amberlyst 15E at 0°C. The mixture was filtered and concentrated *in vacuo*, before the residue was purified by Flash Chromatography System (UltraPack B, EtOAc/toluene, 14:86→44:56, v/v) to give **20** (29.0 mg, 77%): TLC, R_f 0.31 (EtOAc/toluene, 1:4, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.12 (m, 42H, Ph of Bzl, -(CH_2Ph)$_6$), 6.84 (dd, *J* = 2.2, 7.0 Hz, 2H, Ph of MP), 6.77 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 5.51 (s, 1H, H 0f Bzl), 4.79-4.43 (m, 12H, -(CH_2Ph)$_9$), 4.29-4.24 (m, 2H, H'-2, H-3), 4.15-4.06 (m, 5H, H'-5, H-4, H-2, H''-4, H''-2), 4.01-3.97 (m, 1H, H"-5), 3.94 (dd, *J* = 2.9, 8.0 Hz, 1H, H'-4), 3.92-3.87 (m, 2H, H-5, H'-3), 3.83-3.70 (m, 7H, H"-3, H-6, -OCH_3 of MP, H''-6, H-6'), 3.60-3.53 (m, 3H, H'-6, H'-6', H''-6'); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.90, 149.87, 138.19, 138.15, 138.00×2, 137.95, 137.62, 137.56, 129.01, 128.87, 128.46×4, 128.40×4, 128.38×3, 128.34×2, 128.24×2, 128.08×2, 127.91×2, 127.86×8, 127.77×8, 127.53, 126.13×2, 117.62×2, 114.50×2, 101.57, 99.53, 99.31, 79.90, 75.26, 75.21, 74.90, 74.42, 73.56, 73.33, 72.42, 71.95, 71.92, 71.50, 69.84, 69.76, 68.86, 68.66, 68.36, 64.29, 55.62; HRMS calcd. for $C_{74}H_{78}NaO_{17}$ $(M+Na)^+$ *m/z* 1261.5137, found 1261.5127.

4-Methoxyphenyl *O*-(α-D-mannopyranosyl-(1→2)-*O*-α-D-mannopyranosyl)-(1→3)-*O*-α-D-mannopyranoside (21) = (B3).

$Pd(OH)_2$ (20% on carbon, 94.2 mg) was added to a solution of **20** (28.7 mg, 0.0232 mmol) in MeOH/THF (1:1, v/v, 1.00 mL). After stirring the reaction mixture under H_2 atmosphere for 4 h at room temperature, the mixture

was filtered through a pad of celite. The filtrate and washings were concentrated *in vacuo.* The residue was purified by gel filtration chromatography on Sephadex LH-20 (3 cmΦ × 80 cm) (20% EtOH) to give **21** (12.0 mg, 85%): TLC, R_f 0.63 (H_2O/2-PrOH, 1:3, v/v); ^{1}H NMR (500 MHz, D_2O) δ 7.10 (dd, *J* = 2.3, 4.6 Hz, 2H, Ph of MP), 6.96 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.46 (d, *J* = 2.3 Hz, 1H, H'-1), 5.42 (d, *J* = 1.2 Hz, 1H, H''-1), 5.05 (d, *J* = 1.7 Hz, 1H, H-1), 4.29 (dd, *J* = 2.3, 3.4 Hz, 1H, H'-2), 4.11 (dd, *J* = 1.7, 3.4 Hz, 1H, H''-2), 4.10 (dd, *J* = 3.4, 9.5 Hz, 1H, H'-3), 4.06 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 4.00 (dd, *J* = 3.4, 9.7 Hz, 1H, H''-3), 3.90-3.83 (m, 4H, H'-6, H'-4, H-5, H-3), 3.80-3.72 (m, 9H, H'-6', -O$\underline{CH_3}$ of MP, H-6, H'-5, H''-6, H''-6', H-6'), 3.70 (t, *J* = 9.4 Hz, 1H, H''-4), 3.70 (t, *J* = 9.7 Hz, 1H, H-4); ^{13}C NMR (125 MHz, D_2O) δ 154.66, 149.59, 118.71×2, 115.09×2, 102.36, 100.82, 99.06, 78.53, 78.24, 73.56, 73.46, 73.28, 70.36, 69.99, 69.57, 66.97, 66.76, 65.97, 61.01, 60.96, 60.58, 55.82; HRMS calcd. for $C_{25}H_{38}NaO_{17}$ $(M+Na)^+$ *m/z* 633.2007, found 633.2008.

4-Methoxyphenyl 2,3-di-*O*-pivaroyl-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-4-benzyl-α-D-mannopyranoside (22).

AgOTf (49.3 mg, 0.192 mmol), Cp_2HfCl_2 (36.8 mg, 0.0969 mmol), DTBMP (4.70 mg, 0.0229 mmol) and MS AW-300 (606 mg) were dissolved in toluene (1.00 mL). After stirring the mixture for 10 min at room temperature and for 15 min at -20°C, the solution of **2** (58.0 mg, 0.0117 mmol) and **10** (50.5 mg, 0.0927 mmol) in toluene (1.00 mL) was added at -20°C. After stirring the reaction mixture for 90 min at 0°C, the reaction was quenched with Et_3N (28.0 μL, 0.201 mmol) at 0°C. The mixture was filtered through a pad of celite. The filtrate and washings (200 mL of EtOAc) were combined and washed with saturated aq. $NaHCO_3$ (200 mL) and brine (200 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:3, v/v) to give **22** (85.2 mg, 90%, α only): TLC, R_f 0.47 (EtOAc/toluene, 1:3, v/v, double development); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.14 (m, 20H, -($CH_2\underline{Ph}$)$_4$), 7.00 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.78 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.62 (dd, *J* = 3.4, 9.7 Hz, 1H, H-3), 5.42 (dd, *J* = 1.7, 3.4 Hz, 1H, H'-2), 5.40 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 5.30 (d, *J* = 1.7 Hz, 1H, H-1), 4.95 (d, *J* = 1.7 Hz, 1H, H'-1), 4.86, 4.46 (ABq, *J* = 10.9 Hz, 2H, -($\underline{CH_2}$Ph)$_4$), 4.73, 4.52 (ABq, *J* = 11.5 Hz, 2H, -($\underline{CH_2}$Ph)$_4$), 4.69, 4.47 (ABq, *J* = 11.5 Hz, 2H, -($\underline{CH_2}$Ph)$_4$), 4.65, 4.45 (ABq, *J* = 12.0 Hz, 2H, -($\underline{CH_2}$Ph)$_4$), 4.03-4.00 (m, 1H, H-5), 3.94 (t, *J* = 9.7 Hz, 1H, H-4), 3.92 (dd, *J* = 3.4, 9.2 Hz, 1H, H'-3), 3.89 (t, *J* = 9.2 Hz, 1H, H'-4), 3.86 (dd, *J* = 4.0, 11.5 Hz, 1H, H-6), 3.79-3.77 (m, 1H, H'-5), 3.73 (dd, *J* = 4.0, 10.3 Hz, 1H, H'-6), 3.68 (dd, *J* = 1.2, 11.5 Hz, 1H, H-6'), 3.64 (s, 1H, -O$\underline{CH_3}$ of MP), 3.60 (dd, *J* = 1.7, 10.3 Hz, 1H, H'-6'), 2.14 (s, 3H, -$\underline{CH_3}$ of Ac), 1.28 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv), 1.20 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.26, 176.99, 170.15, 155.08, 149.96, 138.44, 138.06, 137.86, 137.48, 128.40×2, 128.37×2, 128.28×2, 128.25×2, 128.04×2, 127.78×5, 127.57, 127.34×2, 117.65×2, 114.59×2, 97.98, 96.37, 78.36×2, 75.21, 74.66, 74.12, 73.35×2, 72.94, 71.94, 71.72, 71.53, 71.24, 69.67, 68.50, 68.19, 65.54, 55.47, 33.90, 38.79, 27.17×3, 27.15×3, 21.09; HRMS calcd. for $C_{59}H_{70}NaO_{15}$ $(M+Na)^+$ *m/z* 1041.4612, found 1041.4607.

4-Methoxyphenyl 2,3-di-*O*-pivaroyl-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-4-benzyl-α-D-mannopyranoside (23).

H_2O_2 (35% in water, 140 μL, 0.144 mmol) and $LiOH \cdot H_2O$ (4.90 mg, 0.117 mmol) were added to a cold (0°C) solution of **22** (37.2 mg, 0.0365 mmol) in THF (1.00 mL). After stirring the reaction mixture for 2 h at room temperature, second portion of H_2O_2 (35% in water, 58.0 μL, 0.600 mmol) was added at 0°C. After stirring the reaction mixture for 5 h at room temperature, the mixture was diluted with EtOAc (50 mL) and washed with saturated aq. $NaHCO_3$ (50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 1:3, v/v) to give **23** (29.7 mg, 83%): TLC, R_f 0.44 (EtOAc/hexane, 1:1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.16 (m, 20H, -(CH_2Ph)$_4$), 7.00 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 6.78 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 5.62 (dd, *J* = 3.4, 9.7 Hz, 1H, H-3), 5.40 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 5.30 (d, *J* = 1.7 Hz, 1H, H-1), 5.01 (d, *J* = 1.2 Hz, 1H, H'-1), 4.86, 4.46 (ABq, *J* = 10.9 Hz, 2H, -(CH_2Ph)$_4$), 4.73, 4.52 (ABq, *J* = 11.5 Hz, 2H, -(CH_2Ph)$_4$), 4.69, 4.47 (ABq, *J* = 11.5 Hz, 2H, -(CH_2Ph)$_4$), 4.65, 4.45 (ABq, *J* = 12.0 Hz, 2H, -(CH_2Ph)$_4$), 4.02-4.00 (m, 2H, H-5, H'-2), 3.92 (t, *J* = 9.7 Hz, 1H, H-4), 3.88-3.85 (m, 2H,H-6, H'-4), 3.82 (dd, *J* = 3.4, 9.2 Hz, 1H, H'-3), 3.80-3.77 (m, 1H, H'-5), 3.79-3.77 (m, 1H, H'-5), 3.73-3.68 (m, 2H, H-6', H'-6), 3.64 (s, 1H, -OCH_3 of MP), 3.61 (dd, *J* = 1.7, 10.9 Hz, 1H, H'-6'), 1.26 (s, 9H, -(CH_3)$_3$ of Piv), 1.20 (s, 9H, -(CH_3)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.23, 176.90, 155.09, 149.95, 138.34, 138.11, 137.86, 137.49, 128.51×2, 128.40×2, 128.29×4, 127.92, 127.83×5, 127.71×2, 127.62, 127.53, 127.35×2, 117.73×2, 114.57×2, 99.29, 96.38, 80.11, 75.15, 74.68, 74.22, 73.35, 73.03, 71.94, 71.89, 71.47, 71.18, 69.68, 68.59, 68.18, 65.54, 55.47, 38.90, 38.78, 27.17×3, 27.14×3; HRMS calcd. for $C_{57}H_{68}NaO_{14}$ $(M+Na)^+$ *m/z* 999.4507, found 999.4524.

4-Methoxyphenyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-*O*-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-2,3-di-*O*-pivaroyl-4-benzyl-α-D-mannopyranoside (24)

AgOTf (8.10 mg, 0.0315 mmol), Cp_2HfCl_2 (6.00 mg, 0.0158 mmol), DTBMP (0.65 mg, 0.0032 mmol) and MS AW-300 (302 mg) were dissolved in toluene (0.500 mL). After stirring the mixture for 10 min at room temperature and for 10 min at -20°C, the solution of **2** (10.1 mg, 0.0204 mmol) and **23** (9.6 mg, 0.00982 mmol) in toluene (0.500 mL) was added at -20°C. After stirring the reaction mixture for 50 min at 0°C, the reaction was quenched with Et_3N (10.0 μL, 0.0718 mmol) at -20°C. The mixture was filtered through a pad of celite. The filtrate and washings (200 mL of EtOAc) were combined and washed with saturated aq. $NaHCO_3$ (200 mL) and brine (200 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 2:7, v/v) to give **24** (14.4 mg, quant., α only): TLC, R_f 0.49 (EtOAc/hexane, 1:3, v/v, double development); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.12 (m, 35H, -(CH_2Ph)$_7$), 6.99 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.76 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.61 (dd, *J* = 3.4, 9.7 Hz, 1H, H-3), 5.52 (dd, *J* = 1.7, 3.4 Hz, 1H, H''-2), 5.38 (dd, *J* = 1.7, 3.2 Hz, 1H, H-2), 5.27 (d, *J* = 1.7 Hz, 1H, H-1), 5.06 (d, *J* = 1.2 Hz, 1H, H''-1), 4.93 (d, *J* = 1.7 Hz, 1H, H'-1), 4.88-4.37 (m, *J* = 11.5 Hz, 2H, -(CH_2Ph)$_7$), 4.02-3.98 (m, 2H, H'-2, H-5), 3.97 (dd, *J* = 3.4, 9.5 Hz, 1H, H''-3), 3.94-3.91 (m, 1H, H''-5), 3.88-3.83 (m, 5H, H-4, H-6, H''-6, H'-3, H''-4), 3.79-3.76 (m, 1H, H'-5), 3.77 (dd, *J* = 4.0, 10.9 Hz, 1H, H'-4), 3.68 (dd, *J* = 4.6, 10.9 Hz, 1H, H'-6), 3.63 (dd, *J* = 1.7, 10.6 Hz, 1H, H''-6'), 3.60-3.58 (m, 4H, H'-6', -OCH_3 of MP), 3.53 (dd, *J* = 1.2, 10.9 Hz, 1H, H-6'), 2.11 (s, 3H, -CH_3 of Ac), 1.25 (s, 9H, -(CH_3)$_3$ of Piv), 1.19 (s, 9H, -(CH_3)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.28, 176.94, 170.14, 155.09, 150.10, 138.53, 138.45, 138.39, 138.24, 137.98, 137.51, 128.37×4, 128.31×2, 128.26×10, 128.15×2,

127.91×2, 127.79×4, 127.75, 127.63, 127.57, 127.52×2, 127.47×2, 127.37, 127.26×3, 117.73×2, 114.57×2, 99.29, 96.38, 80.11, 75.15, 74.68, 74.22, 73.35, 73.03, 71.94, 71.89, 71.47, 71.18, 69.68, 68.59, 68.18, 65.54, 55.47, 38.90, 38.78, 27.17×3, 27.14×3; HRMS calcd. for $C_{86}H_{98}NaO_{20}$ $(M+Na)^+$ *m/z* 1473.6549, found 1473.6544.

4-Methoxyphenyl *O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-*O*-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-4-benzyl-α-D-mannopyranoside (25).

NaOMe (28% in MeOH; 0.300 mL, 1.56 mmol) was added to a cold (0°C) solution of **24** (71.8 mg, 0.0495 mmol) in MeOH/THF (1:1, v/v, 3.00 mL). After stirring the reaction mixture for 24 h at room temperature, second portion of NaOMe (28% in MeOH; 0.200 mL, 1.04 mmol) was added at 0°C. After stirring the reaction mixture for 1 h at room temperature, third portion of NaOMe (28% in MeOH; 0.300 mL, 1.56 mmol) was added at 0°C. After stirring the reaction mixture for 2 h at room temperature, the reaction mixture was neutralized with Amberlyst 15E at 0°C. The mixture was filtered and concentrated *in vacuo*, before the residue was purified by Flash Chromatography System (EtOAc/toluene, 22:78→42:58, v/v) to give **25** (52.8 mg, 86%): TLC, R_f 0.43 (EtOAc/toluene, 1:1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.14 (m, 35H, -(CH_2Ph)$_7$), 6.93 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.75 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.30 (d, *J* = 1.7 Hz, 1H, H'-1), 5.22 (d, *J* = 1.7 Hz, 1H, H''-1), 5.11 (d, *J* = 1.7 Hz, 1H, H-1), 4.86-4.45 (m, 14H, -(CH_2Ph)$_7$), 4.14-4.07 (m, 3H, H''-2, H-2, H-5), 3.96-3.93 (m, 2H, H'-2, H-3), 3.90 (dd, *J* = 3.4, 9.2 Hz, 1H, H-4), 3.88-3.74 (m, 7H, H''-3, H'-4, H-6, H''-4, H'-3, H'-5, H''-5), 3.70-3.62 (m, 5H, H-6', H'-6, H''-6, H'-6', H''-6'), 3.61 (s, 3H, -OCH_3 of MP); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.91, 150.29, 138.64, 138.37, 138.34, 138.30, 138.07, 137.99, 128.61×2, 128.56×2, 128.54×2, 128.46×2, 128.41×2, 128.39×2, 128.35×2, 128.03×2, 127.96×2, 127.93×2, 127.86×2, 127.84×2, 127.78×2, 127.73, 127.65, 127.58×2, 127.46×2, 117.50×2, 114.70×2, 100.38, 99.23, 98.18, 80.00, 75.83, 75.09, 74.91, 74.86, 74.55, 73.95, 73.52, 73.33, 72.17×2, 72.05, 71.74, 71.64, 71.53, 70.78, 69.57, 69.34, 68.50, 65.85, 55.56; HRMS calcd. for $C_{74}H_{80}NaO_{17}$ $(M+Na)^+$ *m/z*1263.5293, found 1263.5294.

4-Methoxyphenyl *O*-(α-D-mannopyranosyl-(1→2)-*O*-α-D-mannopyranosyl)-(1→6)-*O*-α-D-mannopyranoside (26) = (C3).

$Pd(OH)_2$ (20% on carbon, 94.2 mg) was added to a solution of **25** (52.8 mg, 0.0425 mmol) in MeOH/THF (1:1, v/v, 3.00 mL). After stirring the reaction mixture under H_2 atmosphere for 4 h at room temperature, the mixture was filtered through a pad of celite. The filtrate and washings were concentrated *in vacuo.* The residue was purified by gel filtration chromatography on Sephadex LH-20 (3 cm*Φ* × 80 cm) (20% EtOH) to give **26** (25.2 mg, 97%): TLC, R_f 0.72 (H_2O/2-PrOH, 1:3, v/v); ^{1}H NMR (500 MHz, D_2O) δ 7.12 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.99 (dd, *J* = 2.9, 6.9 Hz, 2H, Ph of MP), 5.50 (d, *J* = 1.7 Hz, 1H, H-1), 5.02 (d, *J* = 1.7 Hz, 1H, H'-1), 4.79 (s, 1H, H''-1 in ddH_2O), 4.16 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 4.01 (dd, *J* = 1.7, 3.4 Hz, 1H, H''-2), 4.00 (dd, *J* = 3.4, 9.7 Hz, 1H, H-3), 3.87-3.80 (m, 7H, H'-6, H'-4, H''-6, -OCH_3 of MP, H'-6), 3.79 (dd, *J* = 3.4, 10.0 Hz, 1H, H''-3), 3.78-3.60 (m, 9H, H'-3, H-6, H'-5, H''-5, H-4, H-6', H'-2, H''-6', H-5), 3.58 (t, *J* = 9.7 Hz, 1H, H''-4); ^{13}C NMR (125 MHz, D_2O) δ 154.55, 149.28, 118.49×2, 115.09×2, 102.26, 98.56, 97.65, 78.91, 73.11, 72.63, 71.44, 70.57, 70.34, 70.05, 69.95, 69.86, 66.96, 66.87, 66.75, 66.07, 61.11, 60.92, 55.81;

HRMS calcd. for $C_{25}H_{38}NaO_{17}$ $(M+Na)^+$ *m/z* 633.2007 found 633.1998.

4-Methoxyphenyl 2,3-di-*O*-pivaroyl-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-6-benzyl-α-D-mannopyranoside (27).

AgOTf (115 mg, 0.448 mmol), Cp_2HfCl_2 (84.5 mg, 0.0223 mmol), DTBMP (10.2 mg, 0.0498 mmol) and MS AW-300 (1.51 g) were dissolved in toluene (2.50 mL). After stirring the mixture for 20 min at room temperature and for 30 min at -20°C, the solution of **2** (149 mg, 0.302 mmol) and **11** (90.4 mg, 0.166 mmol) in toluene (2.50 mL) was added at -20°C. After stirring the reaction mixture for 70 min at 0°C, the reaction was quenched with Et_3N (65.0 μL, 0.467 mmol) at 0°C. The mixture was filtered through a pad of celite. The filtrate and washings (200 mL of EtOAc) were combined and washed with saturated aq. $NaHCO_3$ (200 mL) and brine (200 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by Flash Chromatography System (UltraPack B, EtOAc/hexane, 14:86→28:72, v/v) to give **27** (169 mg, 90%, α only): TLC, R_f 0.47 (EtOAc/hexane, 1:3, v/v, double development); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.10 (m, 20H, -(CH_2Ph)$_4$), 7.04 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.79 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.56 (dd, *J* = 3.4, 9.7 Hz, 1H, H-3), 5.37 (dd, *J* = 2.3, 3.4 Hz, 1H, H-2), 5.34-5.33 (m, 2H, H-1, H'-2), 5.15 (d, *J* = 2.3 Hz, 1H, H'-1), 4.79, 4.40 (ABq, *J* = 10.9 Hz, 2H, -(CH_2Ph)$_4$), 4.71, 4.47 (ABq, *J* = 10.9 Hz, 2H, -(CH_2Ph)$_4$), 4.59, 4.33 (ABq, *J* = 12.0 Hz, 2H, -(CH_2Ph)$_4$), 4.53, 4.48 (m, 2H, -(CH_2Ph)$_4$), 4.39-4.34 (m, 1H, H-4), 4.01-3.98 (m, 1H, H-5), 3.90-3.87 (m, 2H, H-6, H'-3), 3.84 (t, *J* = 9.2 Hz, 1H, H'-4), 3.79-3.76 (m, 2H, H'-5, -OCH_3 of MP), 3.71 (dd, *J* = 1.7, 11.2 Hz, 1H, H-6'), 3.63 (dd, *J* = 4.0, 10.9 Hz, 1H, H'-6), 3.49 (dd, *J* = 1.7, 10.9 Hz, 1H, H-6), 3.79-3.77 (m, 1H, H'-5), 3.73 (dd, *J* = 4.0, 10.9 Hz, 1H, H'-6), 3.68 (dd, *J* = 1.2, 11.5 Hz, 1H, H-6'), 2.10 (s, 3H, -CH_3 of Ac), 1.22 (s, 9H, -(CH_3)$_3$ of Piv), 1.20 (s, 9H, -(CH_3)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.46, 177.16, 169.85, 155.23, 150.07, 138.45, 138.31, 138.06, 137.86, 128.35×2, 128.36×2, 128.24×2, 128.21×2, 128.12×2, 127.85×2, 127.81×2, 127.70, 127.58×2, 127.27, 127.11×2, 118.13×2, 114.54×2, 99.54, 96.49, 78.07, 75.02, 73.80, 73.39, 72.98, 72.50, 72.46, 72.22, 71.82, 71.52, 69.31, 69.05, 68.66, 68.54, 55.61, 38.89, 27.10×3, 26.94×3, 21.01; HRMS calcd. for $C_{59}H_{70}NaO_{15}$ $(M+Na)^+$ *m/z* 1041.4612, found 1041.4611.

4-Methoxyphenyl 2,3-di-*O*-pivaroyl-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-6-benzyl-α-D-mannopyranoside (28).

H_2O_2 (35% in water, 500 μL, 0.514 mmol) and $LiOH \cdot H_2O$ (18.1 mg, 0.432 mmol) were added to a cold (0°C) solution of **28** (138 mg, 0.136 mmol) in THF (2.60 mL). After stirring the reaction mixture for 4.5 h at room temperature, second portion of H_2O_2 (35% in water, 100 μL, 0.103 mmol) was added at 0°C. After stirring the reaction mixture for 30 min at room temperature, the mixture was diluted with EtOAc (150 mL) and washed with saturated aq. $NaHCO_3$ (150 mL) and brine (150 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by Flash Chromatography System (EtOAc/hexane, 16:84→30:70, v/v) to give **28** (120 mg, 90%): TLC, R_f 0.41 (EtOAc/hexane, 1:1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.12 (m, 20H, -(CH_2Ph)$_4$), 7.06 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.79 (dd, *J* = 2.3, 6.3 Hz, 2H, Ph of MP), 5.55 (dd, *J* = 3.4, 9.7 Hz, 1H, H-3), 5.35 (dd, *J* = 2.3, 3.4 Hz, 1H, H-2), 5.32 (d, *J* = 2.3 Hz, 1H, H-1), 5.17 (d, *J* = 1.7 Hz, 1H, H'-1), 4.78, 4.45 (ABq, *J* = 10.9 Hz, 2H, -(CH_2Ph)$_4$), 4.66 (ABq, *J* = 12.0

Hz, 2H, -($\underline{CH_2}$Ph)$_4$), 4.57, 4.38 (ABq, *J* = 12.0 Hz, 2H, -($\underline{CH_2}$Ph)$_4$), 4.48 (ABq, *J* = 12.0 Hz, 2H, -($\underline{CH_2}$Ph)$_4$), 4.25 (t, *J* = 9.7 Hz, 1H, H-4), 4.04-4.01 (m, 1H,H-5), 3.90 (dd, *J* = 1.7, 4.6 Hz, 1H, H'-2), 3.85 (t, *J* = 9.2 Hz, 1H, H'-4), 3.82-3.72 (m, 7H, H-6, H-6', H'-3, -O$\underline{CH_3}$ of MP, H'-5), 3.61 (dd, *J* = 4.0, 10.3 Hz, 1H, H'-6), 3.50 (dd, *J* = 1.7, 10.3 Hz, 1H, H'-6'), 1.23 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv), 1.21 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.58, 177.21, 155.28, 150.14, 138.37, 138.22, 138.05, 137.78, 128.54×2, 128.28×4, 128.13×2, 127.95, 127.90×2, 127.88×2, 127.73×2, 127.65, 127.57, 127.29, 127.22×2, 118.34×2, 114.53×2, 101.15, 96.71, 79.76, 75.00, 73.89, 73.44, 73.07, 72.97, 72.30, 72.10, 72.06, 71.33, 69.36, 69.33, 68.60, 68.52, 55.60, 38.96, 38.89, 27.12×3, 27.09×3; HRMS calcd. for $C_{57}H_{68}NaO_{14}$ $(M+Na)^+$ *m/z* 999.4507, found 999.4497.

4-Methoxyphenyl *O*-(2-*O*-acetyl-3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-*O*-3,4,6-tri-*O*-benzyl–α-D-mannopyranosyl)-(1→4)-*O*-2,3-di-*O*-pivaroyl-6-benzyl-α-D-mannopyranoside (29)

AgOTf (7.70 mg, 0.0300 mmol), Cp_2HfCl_2 (5.60 mg, 0.0148 mmol) and MS AW-300 (295 mg) were dissolved in toluene (0.500 mL). After stirring the mixture for 10 min at room temperature and for 10 min at -20°C, the solution of **2** (9.80 mg, 0.0198 mmol) and **28** (9.4 mg, 0.00962 mmol) in toluene (0.500 mL) was added at -20°C. After stirring the reaction mixture for 50 min at 0°C, the reaction was quenched with Et_3N (10.0 μL, 0.0718 mmol) at -20°C. The mixture was filtered through a pad of celite. The filtrate and washings (200 mL of EtOAc) were combined and washed with saturated aq. $NaHCO_3$ (200 mL) and brine (200 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc/hexane, 2:7, v/v) to give **29** (11.7 mg, 84%, α only): TLC, R_f 0.59 (EtOAc/hexane, 1:3, v/v, double development); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33-7.12 (m, 35H, -($CH_2\underline{Ph}$)$_7$), 7.03 (dd, *J* = 1.7, 6.9 Hz, 2H, Ph of MP), 6.78 (dd, *J* = 1.7, 6.9 Hz, 2H, Ph of MP), 5.57-5.56 (m, 1H, H''-2), 5.49 (dd, *J* = 2.9, 9.2 Hz, 1H, H-3), 5.34-5.32 (m, 2H, H-2, H-1), 5.12 (d, *J* = 1.2 Hz, 1H, H''-1), 5.05 (d, *J* = 1.4 Hz, 1H, H'-1), 4.88-4.37 (m, 14H, -($\underline{CH_2}$Ph)$_7$), 4.24 (t, *J* = 9.2 Hz, 1H, H-4), 3.96-3.93 (m, 4H, H-5, H'-2, H''-3, H-6), 3.90-3.81 (m, 4H,H'-3, H''-4, H''-5, H'-4), 3.80 (dd, *J* = 2.3, 11.2 Hz, 1H, H''-6), 3.78-3.74 (m, 4H, -O$\underline{CH_3}$ of MP, H'-5), 3.70 (dd, *J* = 1.2, 10.9 Hz, 1H, H-6'), 3.57-3.48 (m, 3H, H''-6', H'-6, H'-6'), 2.09 (s, 3H, -$\underline{CH_3}$ of Ac), 1.20 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv), 1.17 (s, 9H, -($\underline{CH_3}$)$_3$ of Piv); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.34, 177.12, 170.09, 155.24, 150.13, 138.65, 138.49, 138.27×2, 138.15, 138.02×2, 128.37×2, 128.27×8, 128.15×2, 128.14×2, 128.08×2, 127.95×2, 127.82×2, 127.72×2, 127.57×4, 127.53×2, 127.45×3, 127.40, 127.19, 127.09×2, 118.25×2, 114.52×2, 78.14, 75.01, 74.84, 74.71, 74.38, 73.85, 73.40, 73.28, 72.78, 72.17, 71.98, 71.76, 71.64, 71.47, 69.37, 69.11, 69.06, 68.56, 68.35, 55.62, 38.88, 38.84, 27.24×3, 27.10×3, 21.16; HRMS calcd. for $C_{86}H_{98}NaO_{20}$ $(M+Na)^+$ *m/z* 1473.6549, found 1473.6552.

4-Methoxyphenyl *O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl-(1→2)-*O*-3,4,6-tri-*O*-benzyl–α-D-mannopyranosyl)-(1→4)-*O*-6-benzyl-α-D-mannopyranoside (30).

NaOMe (28% in MeOH; 0.100 mL, 0.520 mmol) was added to a cold (0°C) solution of **29** (59.8 mg, 0.0412 mmol) in MeOH/THF (1:1, v/v, 1.00 mL). After stirring the reaction mixture for 5.5 h at room temperature, second portion of NaOMe (28% in MeOH; 0.0500 mL, 0.260 mmol) was added at 0°C. After stirring the reaction mixture for 15.5 h at room temperature, the reaction mixture was neutralized with Amberlyst 15E at 0°C. The mixture was filtered and concentrated *in vacuo*, before the residue was purified by Flash

Chromatography System (EtOAc/toluene, 31:69→61:39, v/v) to give **30** (47.6 mg, 93%): TLC, R_f 0.24 (EtOAc/toluene, 1:1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.16 (m, 35H, -(CH_2Ph)$_7$), 7.02 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.78 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.45 (d, *J* = 1.7 Hz, 1H, H''-1), 5.38 (d, *J* = 1.7 Hz, 1H, H-1), 5.31 (d, *J* = 1.3 Hz, 1H, H'-1), 4.85-4.39 (m, 14H, -(CH_2Ph)$_7$), 4.28 (dd, *J* = 1.7, 2.6 Hz, 1H, H''-2), 4.13 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 4.02-3.95 (m, 2H, H-5, H-6), 3.92 (dd, *J* = 3.4, 9.2 Hz, 1H, H-3), 3.89-3.75 (m, 6H, H'-4, H''-3, H-4, H'-3, H''-5, H'-5), 3.74 (s, 1H, -OCH_3 of MP), 3.70-3.54 (m, 8H, H-6', H''-6, H''-6', H'-6', H-4, H''-4, H'-2, H-6); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.97, 150.38, 138.42, 138.38, 138.34, 138.14, 138.05, 137.78, 137.39, 128.64×2, 128.49×2, 128.46×2, 128.37×2, 128.27×6, 128.14×6, 127.97×2, 127.89×2, 127.87×2, 127.74×2, 127.71, 127.60×3, 127.45×2, 127.27, 118.06×2, 114.53×2, 99.83, 99.47, 98.33, 79.97, 75.02, 74.98, 74.63, 74.51, 74.10, 73.97, 73.40, 73.13, 72.80, 72.40, 72.16, 71.74, 71.41, 71.37, 70.94, 70.78, 70.39, 69.71, 69.14, 68.19, 55.58; HRMS calcd. for $C_{74}H_{80}NaO_{17}$ $(M+Na)^+$ *m/z*1263.5293, found 1263.5284.

4-Methoxyphenyl *O*-(α-D-mannopyranosyl-(1→2)-*O*-α-D-mannopyranosyl)-(1→4)-*O*-α-D-mannopyranoside (31) = (D3).

$Pd(OH)_2$ (20% on carbon, 83.4 mg) was added to a solution of **30** (47.6 mg, 0.0383 mmol) in MeOH/THF (1:1, v/v, 1.00 mL). After stirring the reaction mixture under H_2 atmosphere for 25 h at room temperature, the mixture was filtered through a pad of celite. The filtrate and washings were concentrated *in vacuo.* The residue was purified by gel filtration chromatography on Sephadex LH-20 (3 cm*Φ* × 80 cm) (20% EtOH) to give **31** (19.6 mg, 84%): TLC, R_f 0.64 (H_2O/2-PrOH, 1:3, v/v); ^{1}H NMR (500 MHz, D_2O) δ 7.09 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.96 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 5.50 (d, *J* = 1.7 Hz, 1H, H'-1), 5.46 (d, *J* = 1.7 Hz, 1H, H''-1), 5.04 (d, *J* = 1.7 Hz, 1H, H-1), 4.13 (dd, *J* = 3.4, 9.2 Hz, 1H, H'-3), 4.11-4.10 (m, 2H,H'-2, H''-2), 4.06 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 3.97 (dd, *J* = 3.4, 9.7 Hz, 1H, H''-3), 3.89-3.83 (m, 4H, H'-6, H'-4, H-5, H-3), 3.81-3.80 (m, 1H, H'-5), 3.79 (s, 1H, -OCH_3 of MP), 3.78-3.73 (m, 5H, H-6, H'-6', H'-6, H''-6, H''-6', H-6'), 3.71 (t, *J* = 9.4 Hz, 1H, H''-4), 3.67-3.63 (m, 2H, H-4, H''-5); ^{13}C NMR (125 MHz, D_2O) δ 154.65, 149.63, 118.75×2, 115.05×2, 102.26, 100.00, 99.09, 78.79, 74.39, 73.79, 73.74, 73.23, 71.85, 70.97, 70.49, 70.36, 70.09, 70.01, 66.77, 66.75, 61.04, 60.90, 60.81, 55.80; HRMS calcd. for $C_{25}H_{38}NaO_{17}$ $(M+Na)^+$ *m/z* 633.2007, found 633.1997.

4-Methoxyphenyl *O*-(α-D-mannopyranosyl)-(1→2)-*O*-α-D-mannopyranoside (32) = (A2).

$Pd(OH)_2$ (20% on carbon, 41.2 mg) was added to a solution of **13** (23.7 mg, 0.0240 mmol) in MeOH (2.00 mL). After stirring the reaction mixture under H_2 atmosphere for 21 h at room temperature, the mixture was filtered through a pad of celite. The filtrate and washings were concentrated *in vacuo.* The residue was purified by gel filtration chromatography on Sephadex G-10 (3 cm*Φ* × 80 cm) (20% EtOH) to give **32** (8.13 mg, 76%). Physical data were consistent with those reported previously[6]: TLC, R_f 0.67 (H_2O/2-PrOH, 2:3, v/v); ^{1}H NMR (500 MHz, D_2O) δ 7.05 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 6.90 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.69 (d, *J* = 2.3 Hz, 1H, H-1), 5.00 (d, *J* = 2.3 Hz, 1H, H'-1), 4.11 (dd, *J* = 2.3, 3.4 Hz, 1H, H-2), 4.06 (dd, *J* = 3.4, 8.3 Hz, 1H, H'-6), 4.03 (dd, *J* = 2.3, 3.4 Hz, 1H, H'-2), 3.81 (dd, *J* = 2.3, 12.0 Hz, 1H, H-6), 3.79-3.75 (m, 2H, H'-3, H'-6'), 3.74-3.72 (m, 4H, H-4, -OCH_3 of MP), 3.71-3.65 (m, 3H, H-3, H-5, H'-5) 3.62 (dd, *J* = 6.9, 12.0

Hz, 1H, H-6'), 3.53 (t, *J* = 9.7 Hz, H'-4).

4-Methoxyphenyl *O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→2)-*O*-4,6-benzylidene-α-D-mannopyranoside (33).

NaOMe (28% in MeOH; 0.100 mL, 0.520 mmol) was added to a cold (0°C) solution of **18** (15.6 mg, 0.0175 mmol) in MeOH/THF (1:1, v/v, 1.00 mL). After stirring the reaction mixture for 5 h at room temperature, the reaction mixture was neutralized with Amberlyst 15E at 0°C. The mixture was filtered and concentrated *in vacuo*, before the residue was purified by Flash Chromatography System (EtOAc/toluene, 34:66→45:55, v/v) to give **33** (11.7 mg, 83%): TLC, R_f 0.49 (EtOAc/hexane, 1:1, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.19 (m, 20H, -(CH_2Ph)$_3$, Ph of Bzl), 6.92 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.83 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.56 (s, 1H, Ph of Bzl), 5.16 (d, *J* = 1.2 Hz, 1H, H-1), 5.14 (d, *J* = 1.7 Hz, 1H, H'-1), 4.83, 4.48 (ABq, *J* = 10.9 Hz, 2H, -(CH_3Ph)$_3$), 4.70-4.66 (m, 2H, -(CH_2Ph)$_3$), 4.57, 4.51 (ABq, *J* = 11.5 Hz, 2H, -(CH_3Ph)$_3$), 4.38-4.36 (m, 1H, H'-2), 4.23 (dd, *J* = 3.4, 9.7 Hz, 1H, H'-3), 4.21-4.19 (m, 1H, H-5), 4.16 (dd, *J* = 4.6, 10.3 Hz, 1H, H'-6), 4.08 (t, *J* = 9.7 Hz, 1H, H'-4), 3.97-3.93 (m, 1H, H'-5), 3.93 (dd, *J* = 3.4, 8.6 Hz, 1H, H-3), 3.85-3.81 (m, 2H, H-4, H'-6'), 3.78 (s, 1H, -OCH_3 of MP), 3.62 (dd, *J* = 8.6, 9.7 Hz, 1H, H-6), 3.62 (dd, *J* = 8.6, 9.7 Hz, 1H, H-6'); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.96, 149.91, 137.93, 137.65, 137.52, 137.24, 128.97, 128.54×2, 128.47×2, 128.41×2, 128.23×2, 128.14×2, 128.04, 127.94×3, 128.88×2, 127.81, 126.17×2, 117.53×2, 114.58×2, 101.78, 100.39, 99.57, 79.88, 77.17, 74.90, 74.63, 73.75, 72.18, 71.56, 69.65×2, 68.70, 68.60, 64.30, 55.64; HRMS calcd. for $C_{47}H_{50}NaO_{12}$ $(M+Na)^+$ *m/z* 829.3200, found 829.3203.

4-Methoxyphenyl *O*-(α-D-mannopyranosyl)-(1→3)-*O*-α-D-mannopyranoside (34) = (B2).

$Pd(OH)_2$ (20% on carbon, 14.4 mg) was added to a solution of **33** (11.7 mg, 0.0145 mmol) in THF/MeOH (1:1, v/v, 1.00 mL). After stirring the reaction mixture under H_2 atmosphere for 26 h at room temperature, the mixture was filtered through a pad of celite. The filtrate and washings were concentrated *in vacuo.* The residue was purified by gel filtration chromatography on Sephadex G-10 (3 cm*Φ* × 80 cm) (20% EtOH) to give **34** (6.00 mg, 92%): TLC, R_f 0.73 (H_2O/2-PrOH, 2:3, v/v); ^{1}H NMR (500 MHz, D_2O) δ 7.12 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.98 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.47 (d, *J* = 1.7 Hz, 1H, H-1), 5.18 (d, *J* = 1.7 Hz, 1H, H'-1), 4.31 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 4.13 (dd, *J* = 3.4, 9.2 Hz, 1H, H-3), 4.09 (dd, *J* = 1.7, 3.4 Hz, 1H, H'-2), 3.90 (dd, *J* = 3.4, 9.7 Hz, 1H, H'-3), 3.91-3.89 (m, 1H, H-5), 3.86 (t, *J* = 9.2 Hz, 1H, H-4), 3.81-3.72 (m, 8H, H'-5, -OCH_3 of MP, H-6, H-6', H'-6, H'-6') 3.67 (dd, *J* = 9.7 Hz, 1H, H'-4); ^{13}C NMR (125 MHz, D_2O) δ 154.66, 149.60, 118.73×2, 115.09×2, 102.43, 99.13, 77.93, 73.56, 73.43, 70.42, 70.09, 69.60, 66.82, 66.00, 61.02, 60.59, 55.82; HRMS calcd. for $C_{19}H_{28}NaO_{12}$ $(M+Na)^+$ *m/z* 471.1478, found 471.1470.

4-Methoxyphenyl *O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→6)-*O*-4-benzyl-α-D-mannopyranoside (35).

NaOMe (28% in MeOH; 0.0500 mL, 0.260 mmol) was added to a cold (0°C) solution of **23** (33.0 mg, 0.0338 mmol) in MeOH/THF (1:1, v/v, 1.00 mL). After stirring the reaction mixture for 12 h at room temperature, the reaction mixture was neutralized with Amberlyst 15E at 0°C. The mixture was filtered and concentrated *in vacuo*, before the residue was purified by Flash Chromatography System (EtOAc/hexane, 29:71→8:92, v/v)

to give **35** (30.5 mg, quant.): TLC, R_f 0.37 (EtOAc/hexane, 1:2, v/v); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.17 (m, 20H, -(CH_2Ph)$_4$), 6.96 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.76 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 5.42 (d, *J* = 1.7 Hz, 1H, H-1), 4.98 (d, *J* = 1.2 Hz, 1H, H'-1), 4.83, 4.50 (ABq, *J* = 10.9 Hz, 2H, -(CH_2Ph)$_4$), 4.78-4.44 (m, 6H, -(CH_2Ph)$_4$), 4.12 (dd, *J* = 3.4, 9.2 Hz, 1H, H-3), 4.05 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 4.02 (dd, *J* = 1.7, 2.9 Hz 1H, H'-2), 3.90-3.83 (m, 3H, H-5, H'-6, H'-6'), 3.83-3.80 (m, 1H, H'-5), 3.80 (dd, *J* = 2.9, 9.2 Hz 1H, H'-3), 3.73-3.68 (m, 2H, H-6, H'-4), 3.65 (t, *J* = 9.2 Hz, 1H, H-4), 3.62-3.59 (m, 2H, H-6' -OCH_3 of MP); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.82, 150.04, 138.42, 138.09, 137.96×2, 128.56×2, 128.47×2, 128.33×2, 128.28×2, 127.94×2, 127.92, 127.84×5, 127.73×2, 126.64, 127.58, 117.36×2, 114.61×2, 99.44, 97.98, 79.80, 75.75, 75.06, 74.76, 74.14, 73.40, 71.81, 71.65, 71.12, 71.07, 70.87, 68.78, 68.11, 65.92, 55.42; HRMS calcd. for $C_{47}H_{52}NaO_{12}$ $(M+Na)^+$ *m/z* 831.3356, found 831.3342.

4-Methoxyphenyl *O*-(α-D-mannopyranosyl)-(1→6)-*O*-α-D-mannopyranoside (36) = (C2).

$Pd(OH)_2$ (20% on carbon, 36.2 mg) was added to a solution of **35** (30.5 mg, 0.0377 mmol) in THF/MeOH (1:1, v/v, 1.00 mL). After stirring the reaction mixture under H_2 atmosphere for 21.5 h at room temperature, the mixture was filtered through a pad of celite. The filtrate and washings were concentrated *in vacuo.* The residue was purified by gel filtration chromatography on Sephadex G-10 (3 cm*Φ* × 80 cm) (20% EtOH) to give **36** (16.9 mg, quant.): TLC, R_f 0.69 (H_2O/2-PrOH, 1:2, v/v); ^{1}H NMR (500 MHz, D_2O) δ 7.11 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.98 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 5.51 (d, *J* = 1.7 Hz, 1H, H-1), 4.73 (d, *J* = 1.7 Hz, 1H, H'-1), 4.17 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 4.01 (dd, *J* = 3.4, 9.2 Hz, 1H, H-3), 3.90-3.88 (m, 1H, H-5), 3.87-3.82 (m, 2H, H-6, H'-3), 3.81 (s, 1H, -OCH_3 of MP), 3.75-3.67 (m, 5H, H-4, H-6', H'-4, H'-5, H'-2), 3.64-3.59 (m, 2H, H'-6, H'-6'); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.64, 149.21, 118.67×2, 115.06×2, 98.90, 98.71, 72.66, 71.18, 70.62, 70.54, 69.95, 69.87, 66.81, 66.71, 65.52, 60.94, 55.83; HRMS calcd. for $C_{19}H_{28}NaO_{12}$ $(M+Na)^+$ *m/z* 471.1478, found 471.1469.

4-Methoxyphenyl *O*-(3,4,6-tri-*O*-benzyl-α-D-mannopyranosyl)-(1→4)-*O*-6-benzyl-α-D-mannopyranoside (37).

NaOMe (28% in MeOH; 0.0500 mL, 0.260 mmol) was added to a cold (0°C) solution of **28** (16.1 mg, 0.0158 mmol) in MeOH/THF (1:1, v/v, 1.00 mL). After stirring the reaction mixture for 13 h at room temperature, second portion NaOMe (28% in MeOH; 0.0500 mL, 0.260 mmol) was added at 0°C. After stirring the reaction mixture for 3 h at room temperature, the reaction mixture was neutralized with Amberlyst 15E at 0°C. The mixture was filtered and concentrated *in vacuo*, before the residue was purified by column chromatography on silica gel (MeOH/$CHCl_3$, 1:25, v/v) to give **37** (11.8 mg, 77%): TLC, R_f 0.33 (EtOAc); ^{1}H NMR (500 MHz, CD_3OD); δ 7.42-7.17 (m, 20H, -(CH_2Ph)$_4$), 7.04 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.82 (dd, *J* = 2.3, 6.6 Hz, 2H, Ph of MP), 5.36 (d, *J* = 2.3 Hz, 1H, H-1), 5.34 (d, *J* = 1.7 Hz, 1H, H'-1), 4.81, 4.48 (ABq, *J* = 10.9 Hz, 2H, -(CH_2Ph)$_4$), 4.77, 4.59 (ABq, *J* = 11.5 Hz, 2H, -(CH_2Ph)$_4$), 4.49, 4.38 (ABq, *J* = 10.9 Hz, 2H, -(CH_2Ph)$_4$), 4.38, 4.36 (ABq, *J* = 11.5 Hz, 2H, -(CH_2Ph)$_4$), 4.23 (t, *J* = 2.3 Hz, 1H, H-2), 4.00 (dd, *J* = 3.4, 9.2 Hz, 1H, H'-3), 3.95 (dd, *J* = 1.7, 3.4 Hz, 1H, H'-2), 3.92 (t, *J* = 9.2 Hz, 1H, H'-4), 3.84-3.74 (m, 4H, H'-5, H-3, H-4, H-5), 3.72 (s, 3H, -OCH_3 of MP), 3.71-3.70 (m, 2H, H-6, H'-6, H'-6'), 3.56 (dd, *J* = 5.2, 10.6 Hz, 1H, H-6), 3.51 (dd, *J* = 2.3, 10.6 Hz, 1H, H-6'); ^{13}C NMR (125 MHz, CD_3OD) δ 156.62, 151.75, 139.86, 139.83, 139.57,

139.14, 129.40×2, 129.33×2, 129.29×4, 129.13×4, 129.13×2, 128.89×2, 128.74, 128.68, 128.65, 128.55, 119.24×2, 115.60×2, 102.93, 100.75, 80.83, 75.96, 75.52, 75.47, 74.40, 74.05, 73.42, 73.08, 72.49, 72.46, 72.26, 70.97, 70.51, 69.06, 56.01 ; HRMS calcd. for $C_{47}H_{52}NaO_{12}$ $(M+Na)^+$ *m/z* 831.3356, found 831.3357.

4-Methoxyphenyl *O*-(α-D-mannopyranosyl)-(1→4)-*O*-α-D-mannopyranoside (38) = (D2).

$Pd(OH)_2$ (20% on carbon, 11.2 mg) was added to a solution of **37** (11.8 mg, 0.0121 mmol) in THF/MeOH (1:1, v/v, 1.00 mL). After stirring the reaction mixture under H_2 atmosphere for 4.5 h at room temperature, the mixture was filtered through a pad of celite. The filtrate and washings were concentrated *in vacuo.* The residue was purified by gel filtration chromatography on Sephadex LH-20 (3 cmΦ × 80 cm) (20% EtOH) to give **38** (5.00 mg, 92%): TLC, R_f 0.64 (H_2O/2-PrOH, 1:4, v/v); ^{1}H NMR (500 MHz, D_2O) δ 7.10 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 6.96 (dd, *J* = 2.3, 6.9 Hz, 2H, Ph of MP), 5.47 (d, *J* = 1.7 Hz, 1H, H-1), 5.25 (d, *J* = 1.7 Hz, 1H, H'-1), 4.14 (dd, *J* = 3.4, 9.2 Hz, 1H, H-3), 4.10 (dd, *J* = 1.7, 3.4 Hz, 1H, H-2), 4.06 (dd, *J* = 1.7, 3.4 Hz, 1H, H'-2), 3.88 (t, *J* = 9.2 Hz, 1H, H-4), 3.87 (t, *J* = 9.2 Hz, 1H, H'-4), 3.82-3.78 (m, 5H, H-5, H'-3, -O$\underline{CH_3}$ of MP), 3.76-3.72 (m, 3H, H-6, H'-6, H'-5), 3.68-3.63 (m, 2H, H-6', H'-6'); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.65, 149.57, 118.77×2, 115.05×2, 101.56, 99.07, 74.12, 73.72, 71.86, 70.93, 70.42, 70.36, 70.30, 66.55, 60.91, 60.79, 55.78; HRMS calcd. for $C_{19}H_{28}NaO_{12}$ $(M+Na)^+$ *m/z* 471.1478, found 471.1468.

General methods & materials for enzymatic assay

Reagents were purchased from suppliers and used without further purification. SAMP6 livers were purchased from Sankyo Labo Service. Anti-GM130 (610822) and anti-BiP (ab21685) antibodies were obtained from BD Biosciences and abcam, respectively. Anti-rabbit IgG (goat), HRP-labeled antibody (NEF812001EA) was purchased from perkinelmer and anti-mouse IgG (H+L) antibody (A4416) was obtained from Sigma Aldrich. HPLC was performed by a JASCO LC-2000 system with TSK-GEL Amide-80 column (5 μm, 4.6 mm I.D. × 25 cm) from TOSOH Co.

Enzymatic assay

Extraction of ER fraction from SAMP6 livers (Figure S1).

SAMP6 livers (8-week-old, male, 0.4 g) were minced by a surgical scissors, and the paste was transferred to a motor-driven tight fitting glass/Teflon Potter-Elvehjem homogenizer. ER Extraction Buffer (4 mL) [Sucrose (0.25 M), EDTA (2 mM), HEPES (10 mM, pH 7.4), EDTA-free protease inhibitor cocktail (1 tablet per 50 mL, Poche)] was added to the homogenizer and the suspension was crushed (20 strokes, 4°C). Resulting homogenates were centrifuged (900 *g*, 4°C) for 10 min. Subsequently, recovered supernatant was centrifuged (5,000 *g*, 4°C) for 10 min. Then the supernatant was centrifuged (8,000 *g*, 4°C) for 10 min. After further centrifugation step (20000 *g*, 4°C, 120 min), the recovered pellet was obtained as the ER fraction. ER-solubilization Buffer (10 μL per 1 mg of the ER pellet) [Sucrose (0.25 M), EDTA (2 mM), HEPES (10 mM, pH 7.4), EDTA-free protease inhibitor cocktail (1 tablet per 50 mL, Roche), TritonX-100 (0.6%)] was added to the pellet and the suspension was incubated at 4°C for 2 h. The protein concentration of the ER fraction was measured using a bicinchoninic acid (BCA) assay kit (Thermo Fisher Scientific) according to the manufacturers' instructions. Each purity of the preparations was analyzed by western blotting using anti-BiP

and anti-GM130 antibodies as ER and Golgi apparatus marker proteins, respectively.

Validation and assessment of purity of the ER fraction (Figure S1).

Each protein sample (40 μL) was added to the 5× SDS-PAGE sample buffer [Tris-HCl (250 mM, pH 6.8), DTT (375 mM), SDS (10%), glycelol (50%), Bromophenol Blue (0.1%)] and heated at 100°C for 3 min. The samples were centrifuged (15000 *g,* 4°C, 3 min). The recovered supernatant (5 μL for anti-BiP antibody or 15 μL for anti-GM130 antibody) was resolved on SDS-PAGE (7.5% Tris/HCl gel) and transferred onto polyvinylidene difluoride (PVDF) membranes. The membranes were incubated with Blocking One (Nacalai Tesque) at room temperature for 1 h. Then anti-BiP antibody (5000-fold dilution) or anti-GM130 antibody (500-fold dilution) was added to the membrane and it was incubated at 4°C for 16 h. After wash steps of membranes by TBS-T (5, 10, 15 min), secondary antibody solutions [anti-rabbit IgG (Goat) or anti-mouse IgG (H+L)] were added to the membranes and reacted with the membranes at room temperature for 30 min. After the same wash steps, the membranes were reacted by a chemiluminescent reagent (Immobilon Western, Millipore). The bands were detected using FluoroChemQ image analyzer (protein simple).

Individual glycohydrolysis assay of the synthetic trimmannosides in the ER fraction (Figure 4).

Reaction mixtures (20 μL) contained the ER fraction (3 mg/mL), TritonX-100 (0.6%), $CaCl_2$ (10 mM), HEPES (10 mM, pH 7.4), and each trimannosides (**A3**, **B3**, **C3** or **D3**) (250 μM). The mixtures were incubated for 1, 2, 4, 6 and 8 h at 37°C. After incubation, CH_3CN (45 μL) and ddH_2O (42 μL) were added to the mixture (3 μL) to stop enzymatic reaction. The samples were centrifuged (20,000 × g, 4°C, 20 min) and the recovered supernatant (50 μL) was analyzed by HPLC [TSK-GEL Amide-80 column 5 μm (4.6 mm I.D. × 25 cm); mobile phase: CH_3CN/ddH_2O; linear gradients: 98:2 to 90:10 over 10 min and 90:10 to 65:35 over 10 min; flow rate: 1.0 mL/min; temperature: 40°C; detection: 284 nm].

Influence of D2 on the hydrolysis of the synthetic trimannnosides in the ER fraction (Figure S3).

Reaction mixtures (20 μL) contained ER fraction (3 mg/mL), TritonX-100 (0.6%), $CaCl_2$ (10 mM), HEPES (10 mM, pH 7.4), trimannosides (**A3**, **B3** or **C3**) (250 μM) and **D2** (50 μM). The mixtures were incubated for 1, 2, 4, 6 and 8 h at 37°C. After incubation, CH_3CN (45 μL) and ddH_2O (42 μL) were added to the mixture (3 μL) to stop enzymatic reaction. The samples were centrifuged (20,000 × g, 4°C, 20 min) and the recovered supernatant (50 μL) was analyzed by HPLC [TSK-GEL Amide-80 column 5 μm (4.6 mm I.D. × 25 cm); mobile phase: CH_3CN/ddH_2O; linear gradients: 98:2 to 90:10 over 10 min and 90:10 to 65:35 over 10 min; flow rate: 1.0 mL/min; temperature: 40°C; detection: 284 nm].

Competitive glycohydrolysis assay of synthetic trimannsosides in the ER fraction (Figure 5 and 9).

Reaction mixtures (25 μL) contained the ER fraction (3 mg/mL), TritonX-100 (0.6%), $CaCl_2$ (10 mM), HEPES (10 mM, pH 7.4) and [**A3** (250 μM), **B3** (250 μM), **C3** (250 μM) and **D2** (50 μM)] or [**A3** (250 μM), **B3** (250 μM) and **D2** (50 μM)] or [**A3** (250 μM), **C3** (250 μM) and **D2** (50 μM)] or [**B3** (250 μM), **C3** (250 μM) and **D2** (50 μM)]. The mixtures were incubated at 37°C for 1, 2, 4, 6 and 8 h. After incubation, CH_3CN (45 μL) and ddH_2O (42 μL) were added to the mixture (3 μL) to stop enzymatic reaction. The samples were centrifuged

(20,000 × g, 4°C, 20 min) and the recovered supernatant (50 μL) was analyzed by HPLC [TSK-GEL Amide-80 column 5 μm (4.6 mm I.D. × 25 cm); mobile phase: CH_3CN/ddH_2O; linear gradients: 98:2 to 90:10 over 10 min and 90:10 to 65:35 over 10 min; flow rate: 1.0 mL/min; temperature: 40°C; detection: 284 nm].

Influence of A2 on the hydrolysis of B3/C3 mixture in the ER fraction (Figure S4).

Reaction mixtures (25 μL) contained the ER fraction (3 mg/mL), TritonX-100 (0.6%), $CaCl_2$ (10 mM), HEPES (10 mM, pH 7.4) and [**B3** (250 μM), **C3** (250 μM), **A2** (250 μM) and **D2** (50 μM)]. The mixtures were incubated at 37°C for 1, 2, 4, 6 and 8 h. After incubation, CH_3CN (45 μL) and ddH_2O (42 μL) were added to the mixture (3 μL) to stop enzymatic reaction. The samples were centrifuged (20,000 × g, 4°C, 20 min) and the recovered supernatant (50 μL) was analyzed by HPLC [TSK-GEL Amide-80 column 5 μm (4.6 mm I.D. × 25 cm); mobile phase: CH_3CN/ddH_2O; linear gradients: 98:2 to 90:10 over 10 min and 90:10 to 65:35 over 10 min; flow rate: 1.0 mL/min; temperature: 40°C; detection: 284 nm].

Glycohydrolysis assay of A2 in the ER fraction (Figure 7 and 8).

Reaction mixtures (25 μL) contained ER fraction (3 mg/mL), TritonX-100 (0.6%), $CaCl_2$ (10 mM), HEPES (10 mM, pH 7.4), and **A2** (250 μM) or **A3** (250 μM). The mixtures were incubated for 1, 2, 4, 6 and 8 h at 37°C. After incubation, CH_3CN (45 μL) and ddH_2O (42 μL) were added to the mixture (3 μL) to stop enzymatic reaction. The samples were centrifuged (20,000 × g, 4°C, 20 min) and the recovered supernatant (50 μL) was analyzed by HPLC [TSK-GEL Amide-80 column 5 μm (4.6 mm I.D. × 25 cm); mobile phase: CH_3CN/ddH_2O; linear gradients: 98:2 to 90:10 over 10 min and 90:10 to 65:35 over 10 min; flow rate: 1.0 mL/min; temperature: 40°C; detection: 284 nm].

Competitive glycohydrolysis assay of natural A3, B3 or C3 with unnatural D3 in the ER fraction (Figure 10).

Reaction mixtures (20 μL) contained ER fraction (3 mg/mL), TritonX-100 (0.6%), $CaCl_2$ (10 mM), HEPES (10 mM, pH 7.4) and [**A3** (250 μM) and **D3** (250 μM)] or [**B3** (250 μM) and **D3** (250 μM)] or [**C3** (250 μM) and **D3** (250 μM)]. The mixtures were incubated for 1, 2, 4, 6 and 8 h at 37°C. After incubation, CH_3CN (45 μL) and ddH_2O (42 μL) were added to the mixture (3 μL) to stop enzymatic reaction. The samples were centrifuged (20,000 × g, 4°C, 20 min) and the recovered supernatant (50 μL) was analyzed by HPLC [TSK-GEL Amide-80 column 5 μm (4.6 mm I.D. × 25 cm); mobile phase: CH_3CN/ddH_2O; linear gradients: 98:2 to 90:10 over 10 min and 90:10 to 65:35 over 10 min; flow rate: 1.0 mL/min; temperature: 40°C; detection: 284 nm].

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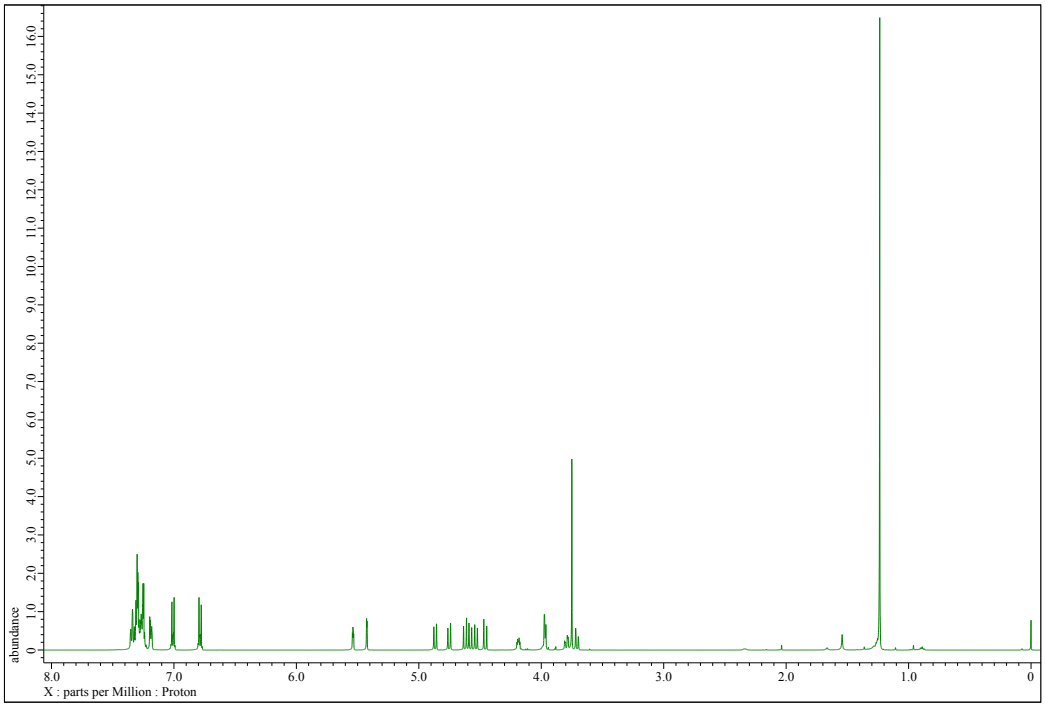
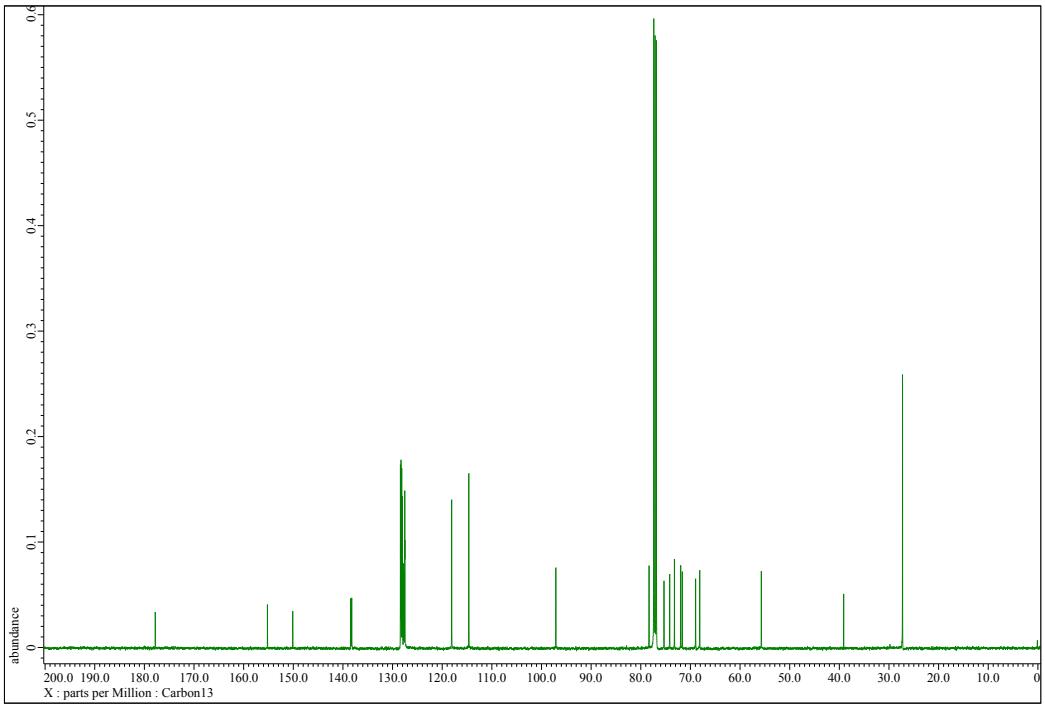
^{1}H NMR & ^{13}C-NMR spectra for the novel compounds

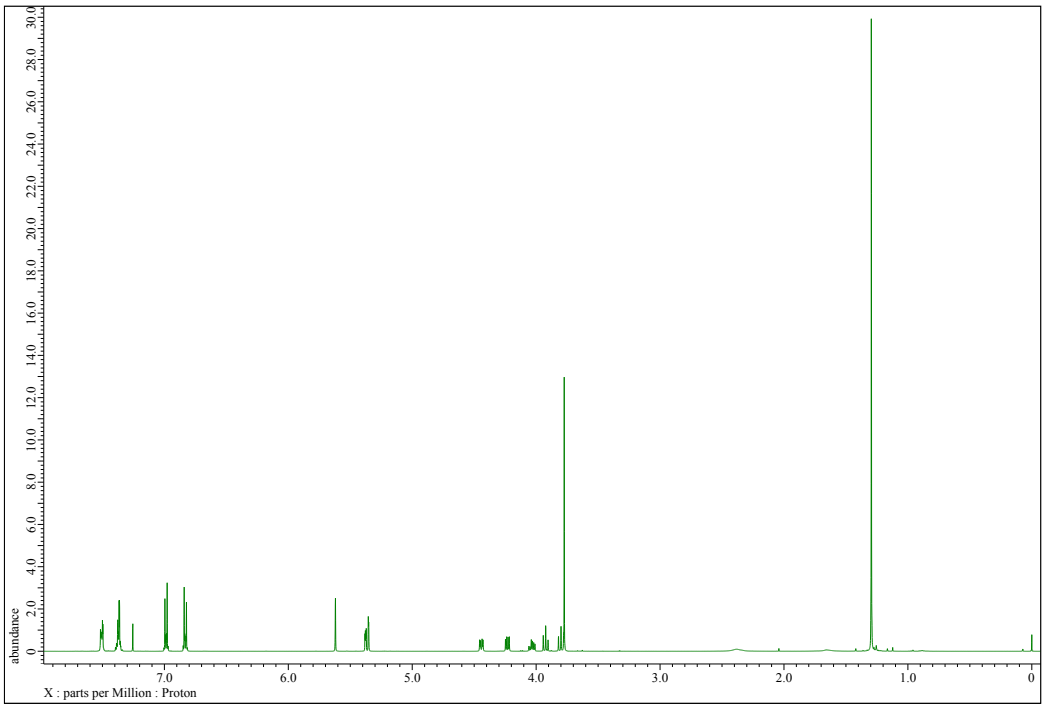
Compound **6** (^{1}H NMR) in $CDCl_3$



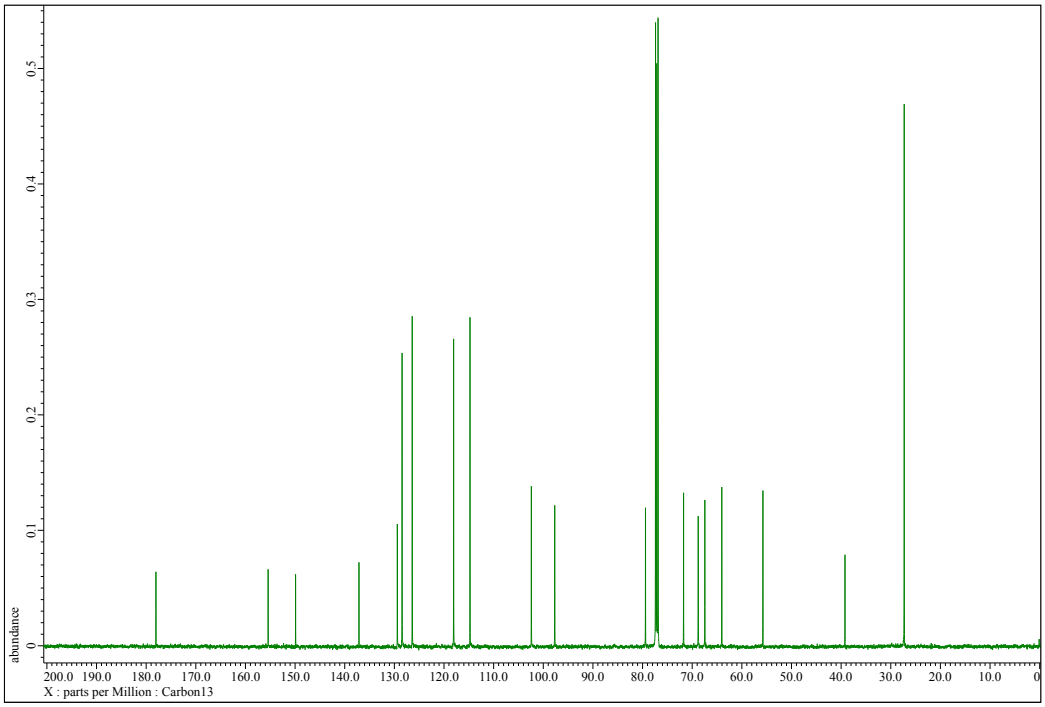
Compound **6** (^{13}C NMR) in $CDCl_3$



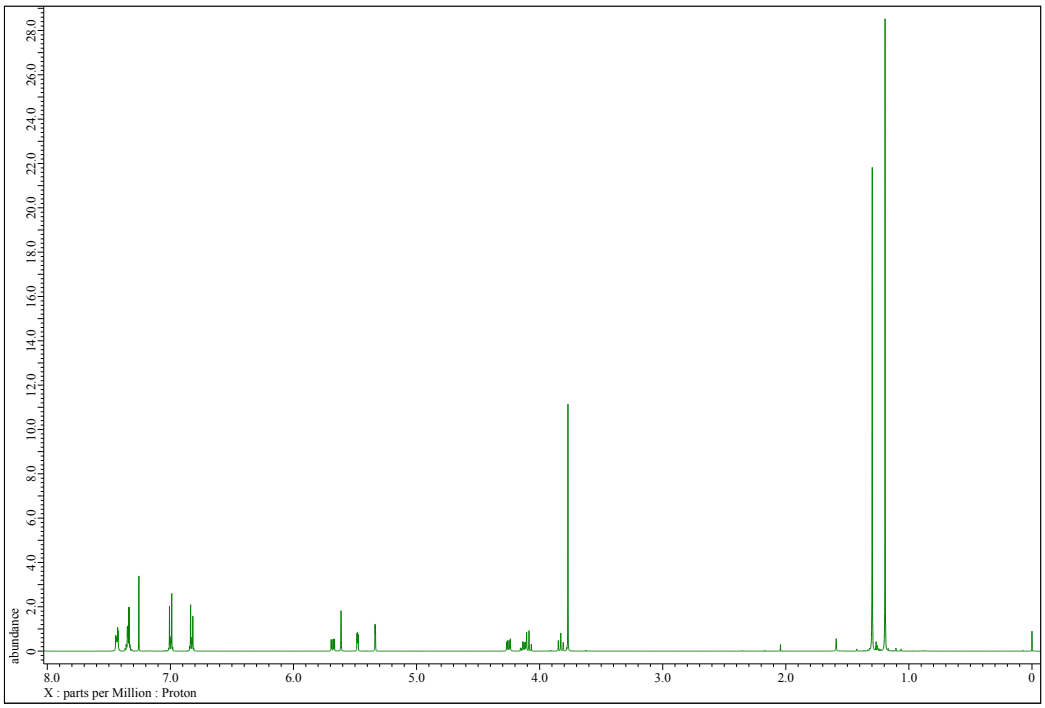
Compound **8** (^{1}H NMR) in $CDCl_3$



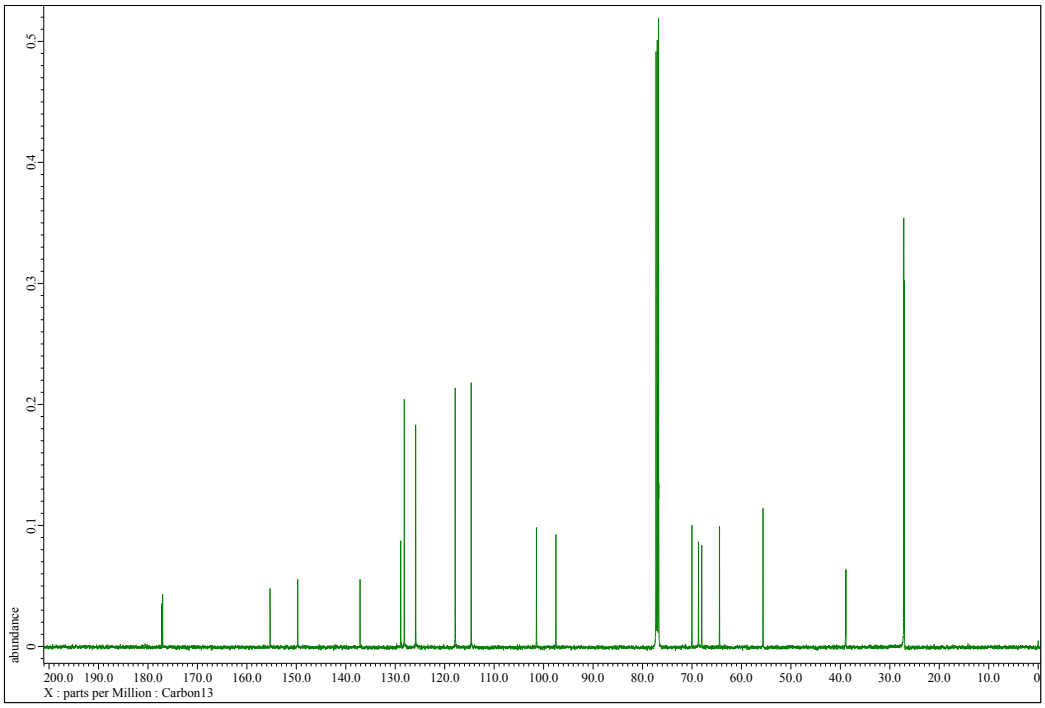
Compound **8** (^{13}C NMR) in $CDCl_3$



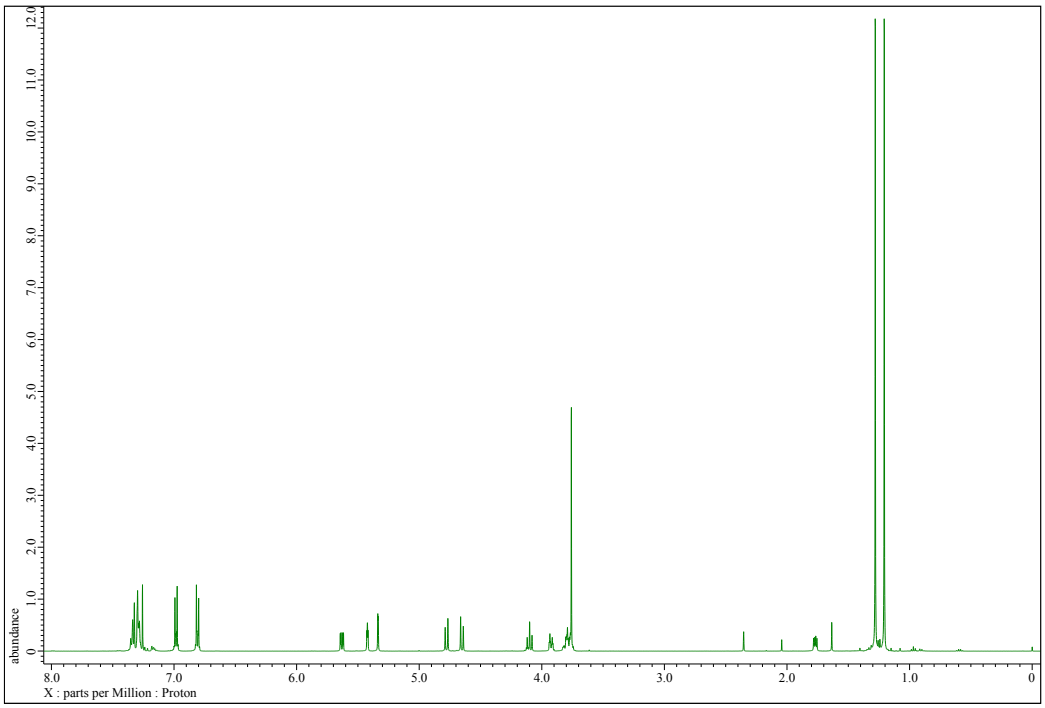
Compound **9** (^{1}H NMR) in $CDCl_3$



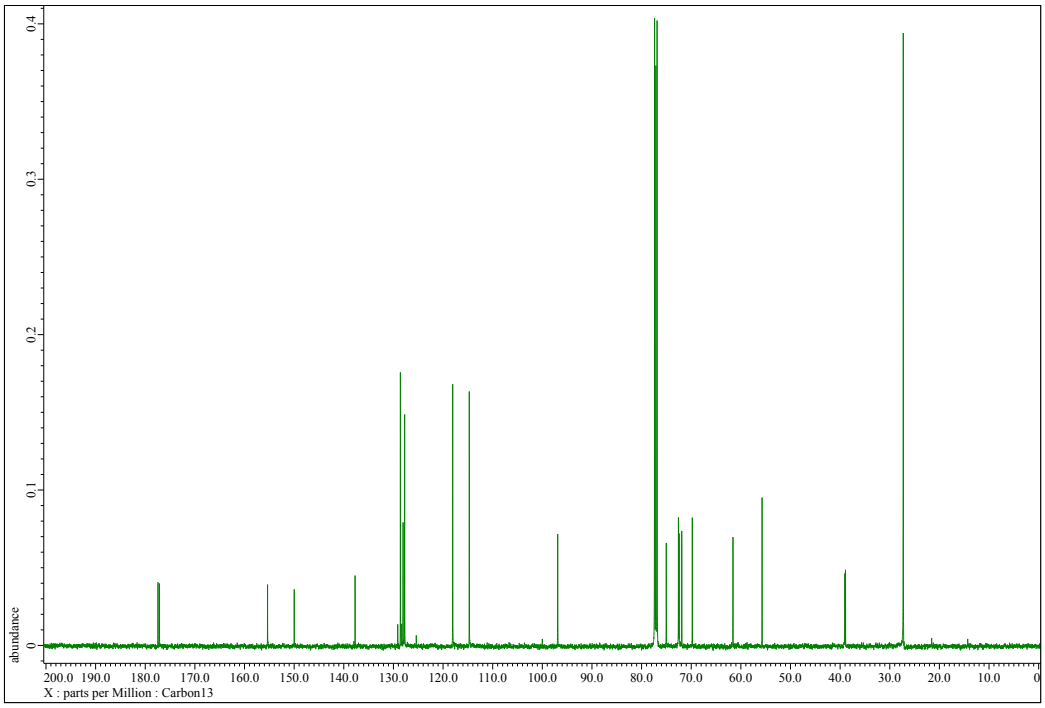
Compound **9** (^{13}C NMR) in $CDCl_3$



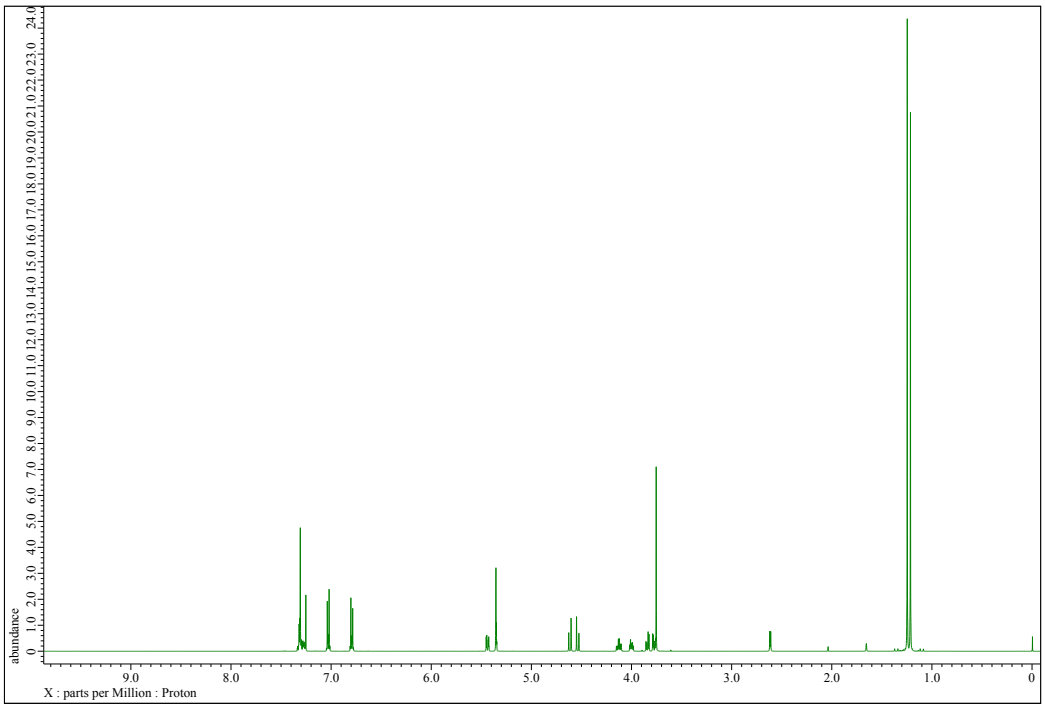
Compound **10** (^{1}H NMR) in $CDCl_3$



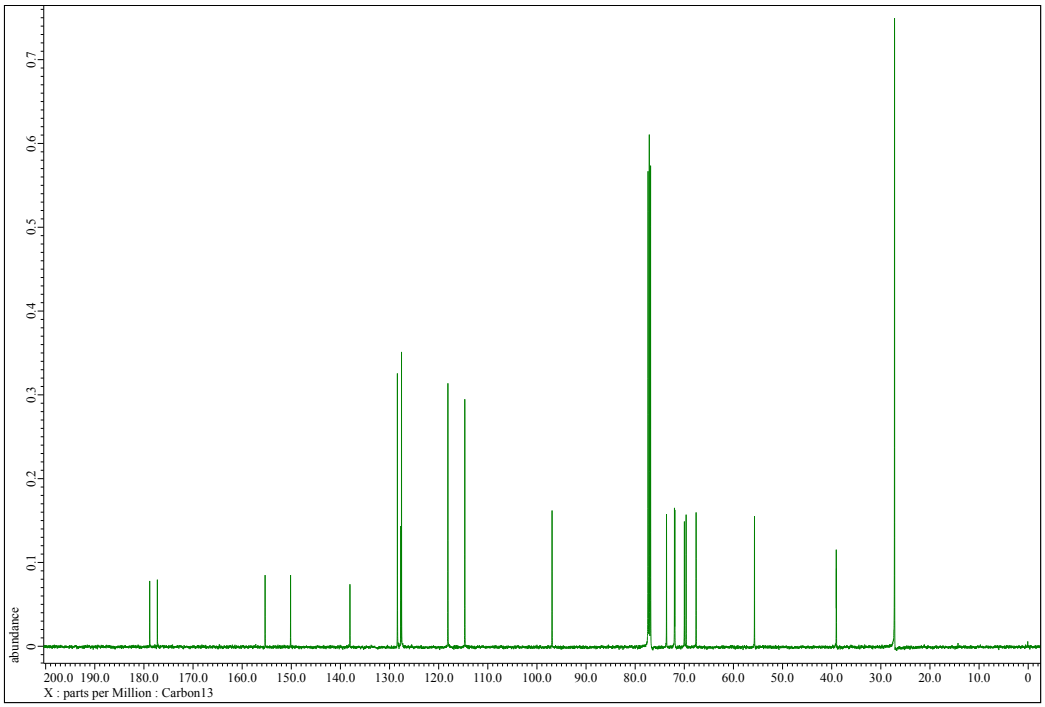
Compound **10** (^{13}C NMR) in $CDCl_3$



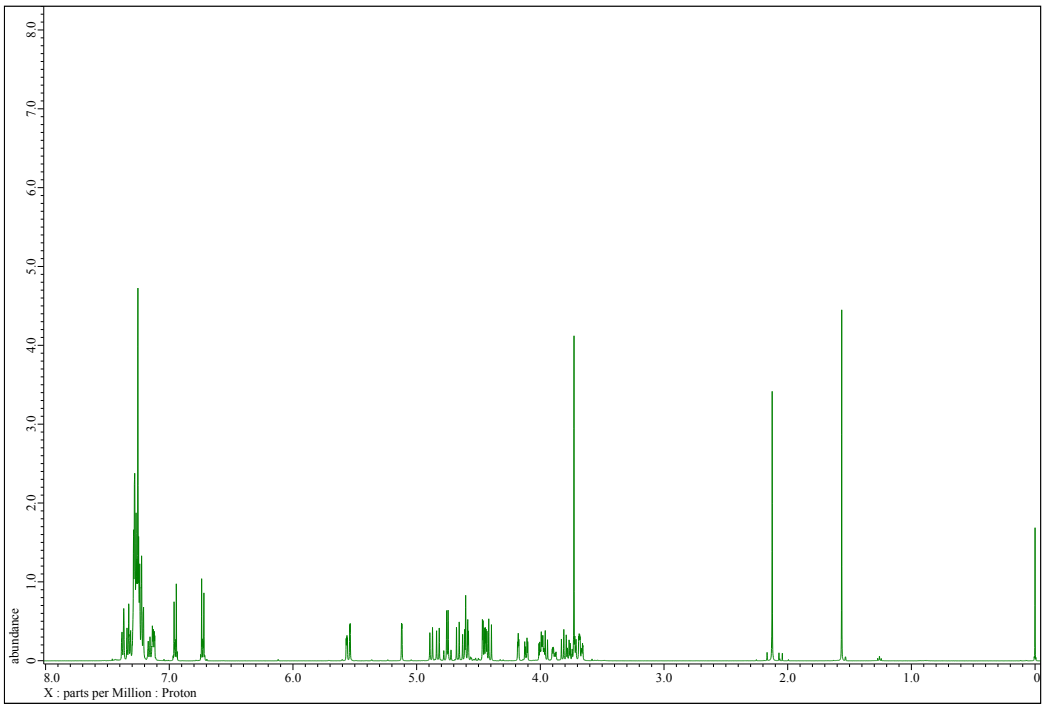
Compound **11** (^{1}H NMR) in $CDCl_3$



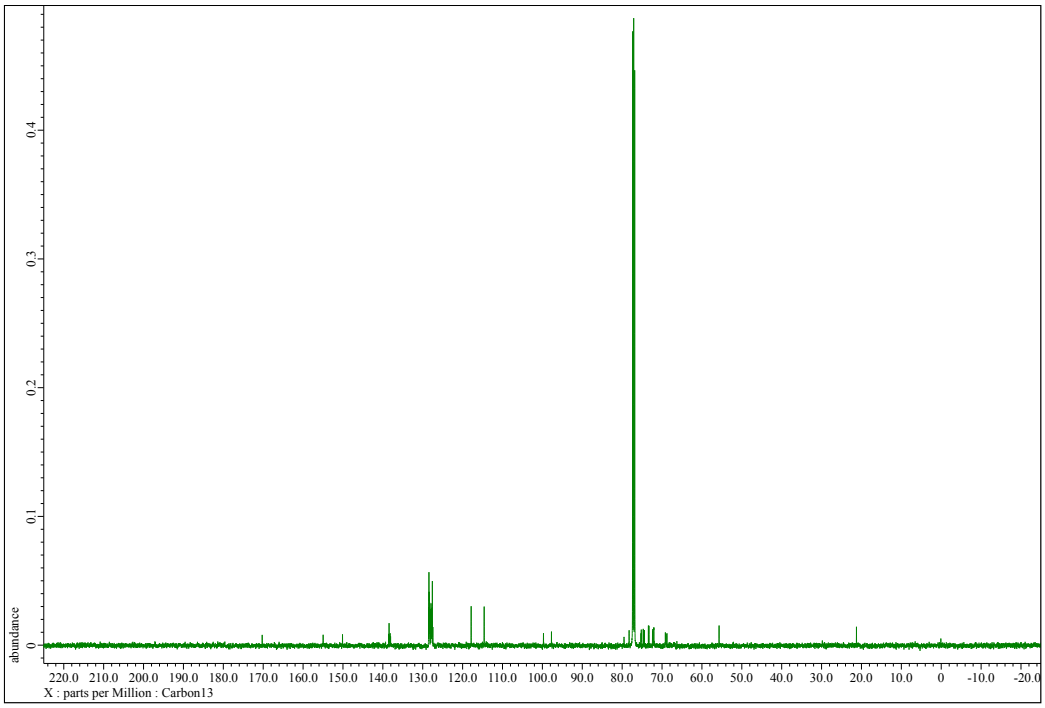
Compound **11** (^{13}C NMR) in $CDCl_3$



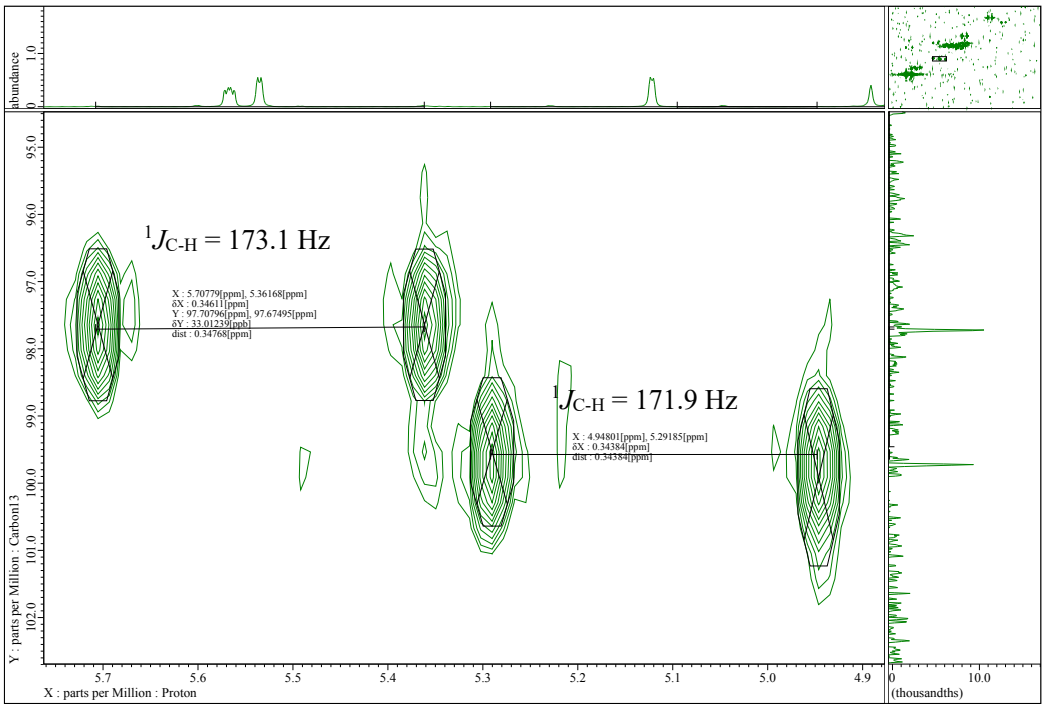
Compound **12** (^{1}H NMR) in $CDCl_3$



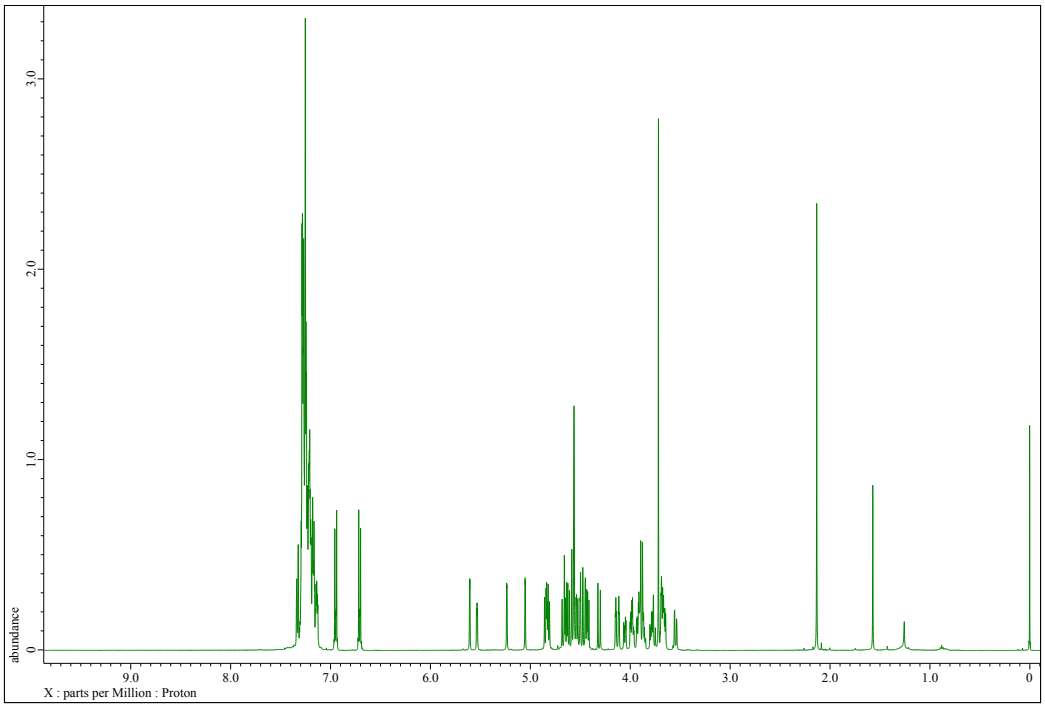
Compound **12** (^{13}C NMR) in $CDCl_3$



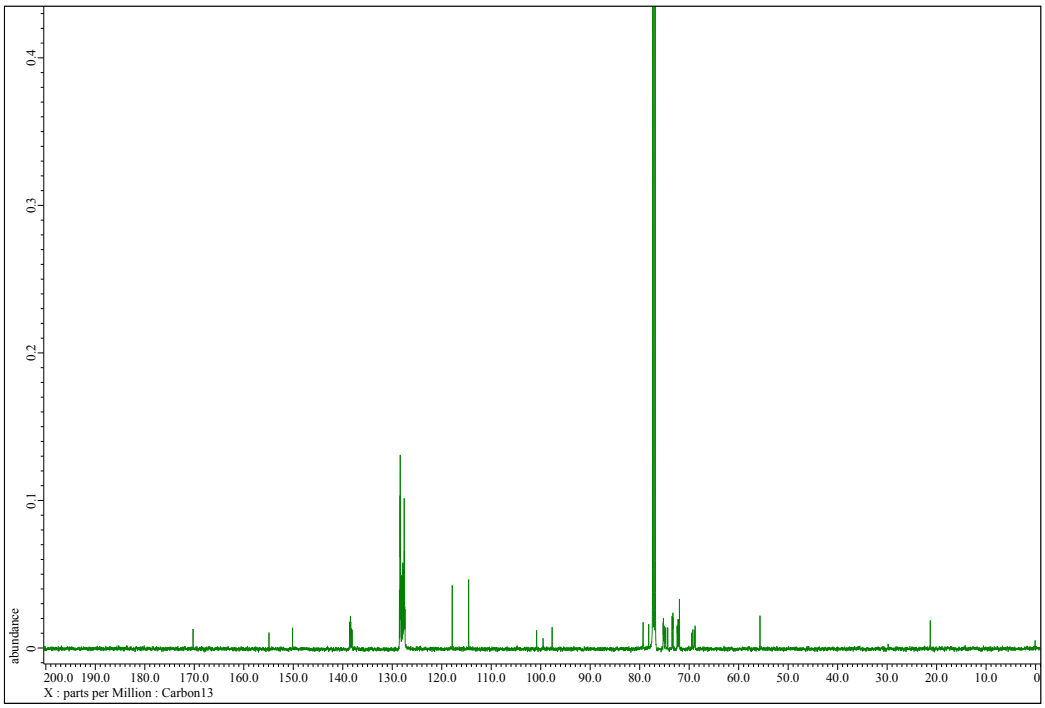
Compound **12** (Non-decoupling HMQC) in $CDCl_3$



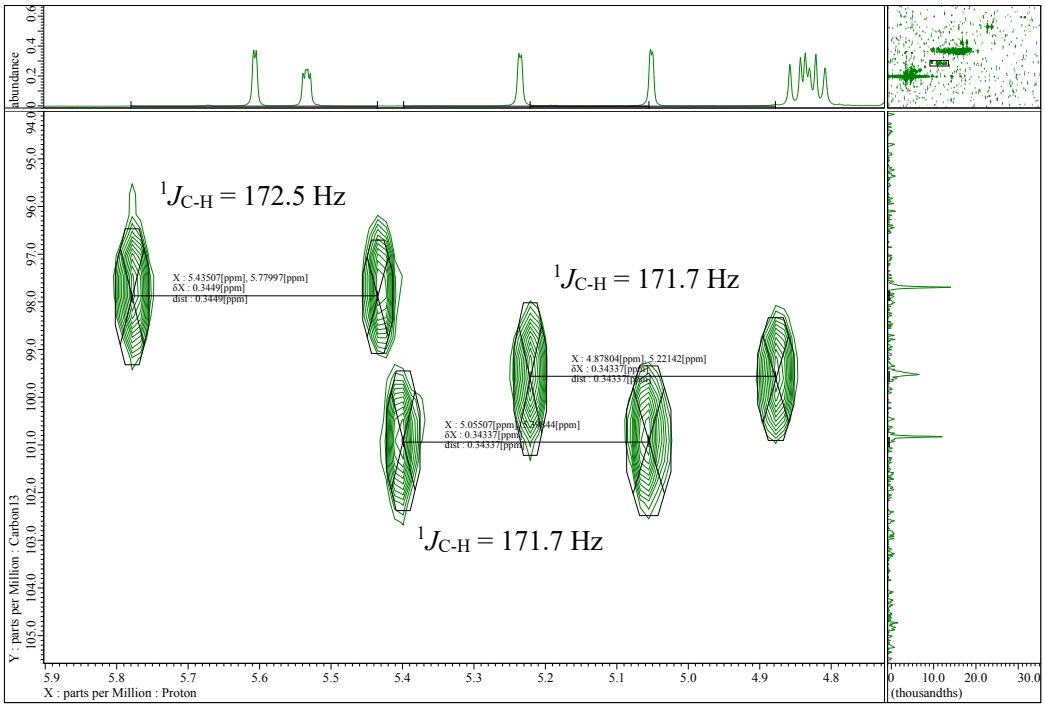
Compound **14** (^{1}H NMR) in $CDCl_3$



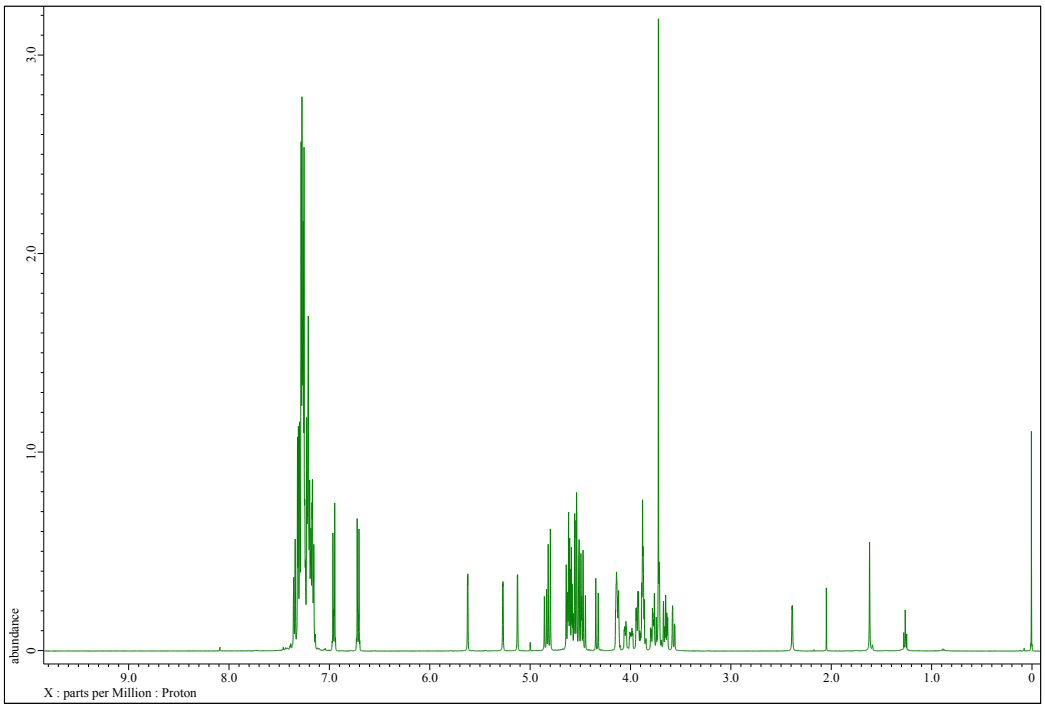
Compound **14** (^{13}C NMR) in $CDCl_3$



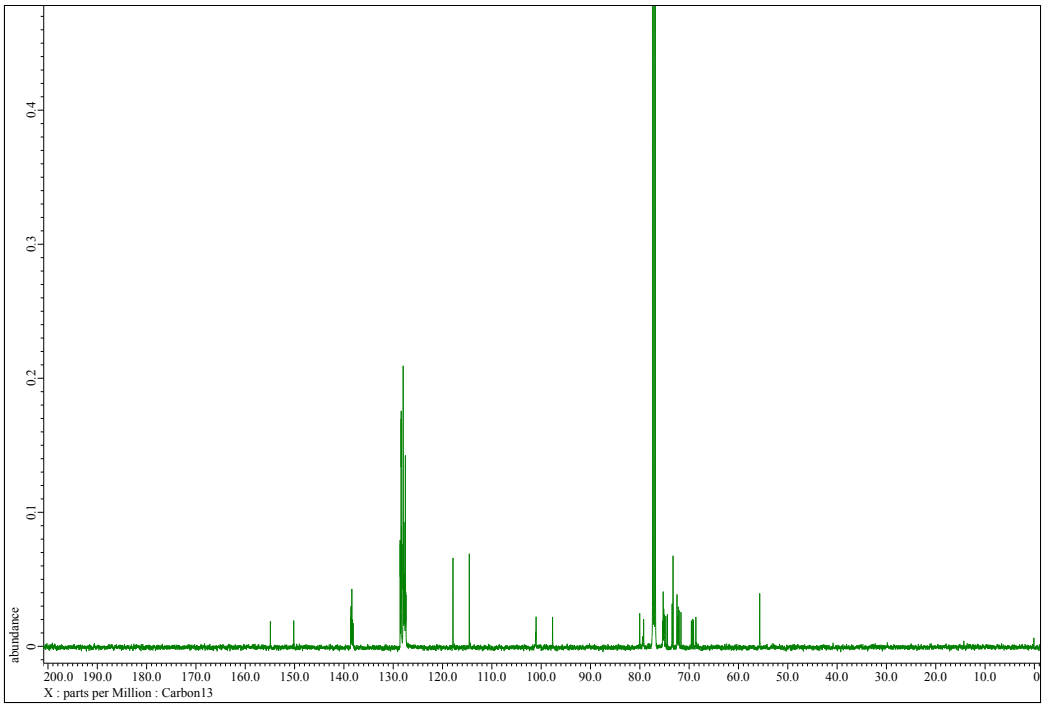
Compound **14** (Non-decoupling HMQC) in $CDCl_3$



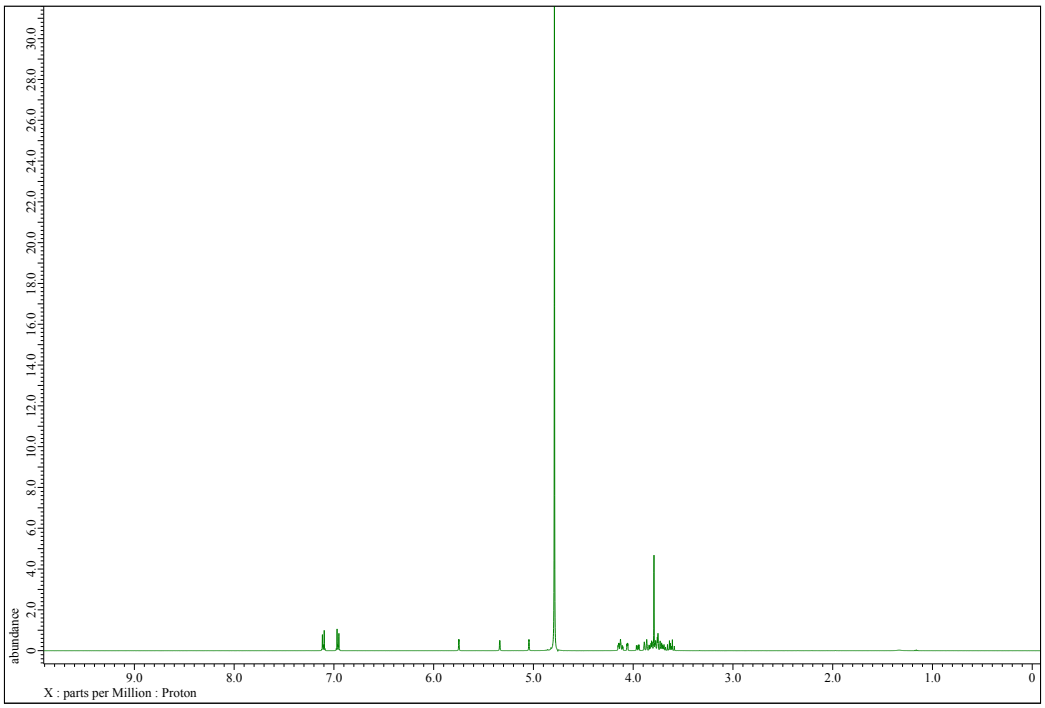
Compound **15** (^{1}H NMR) in $CDCl_3$



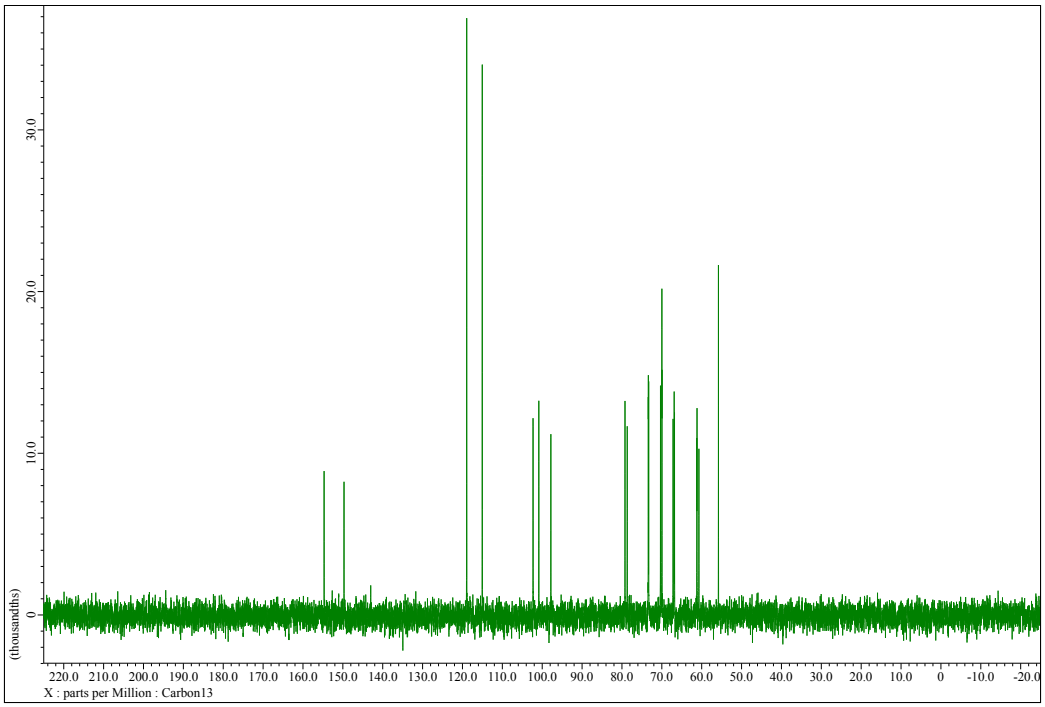
Compound **15** (^{13}C NMR) in $CDCl_3$



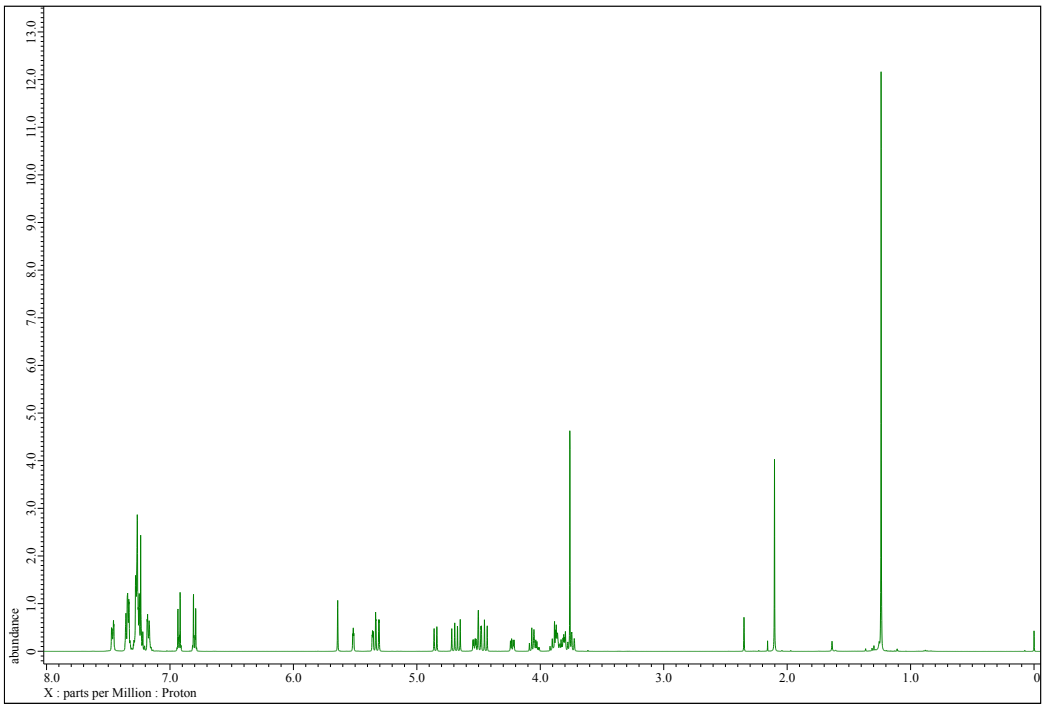
Compound **16** (^{1}H NMR) in D_2O



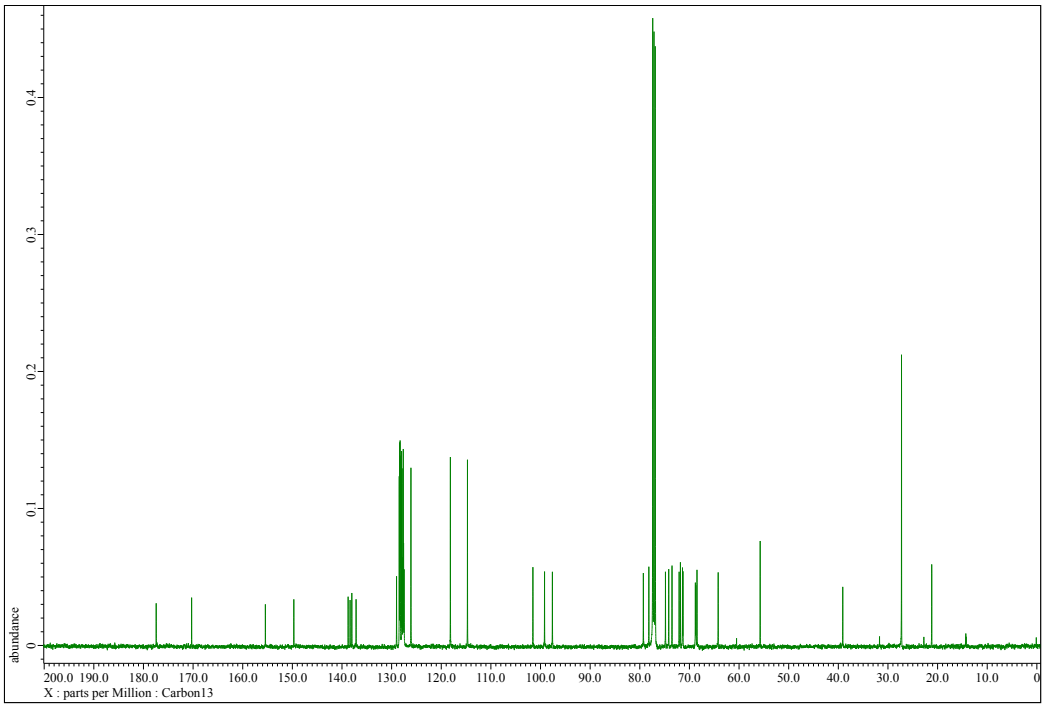
Compound **16** (^{13}C NMR) in D_2O



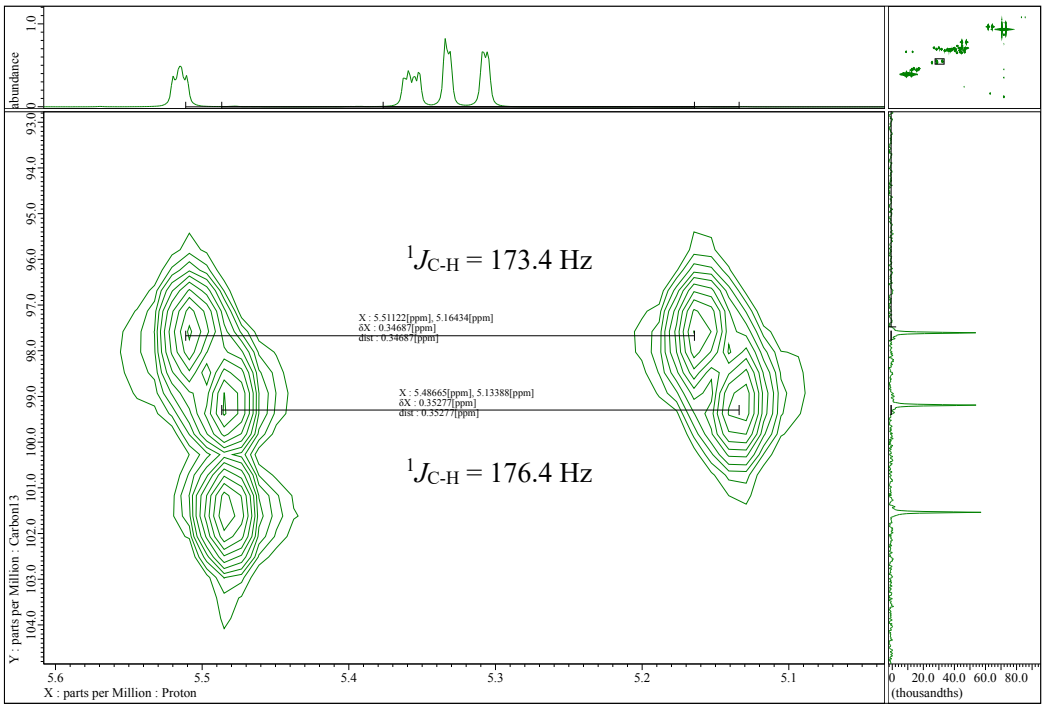
Compound **17** (^{1}H NMR) in $CDCl_3$



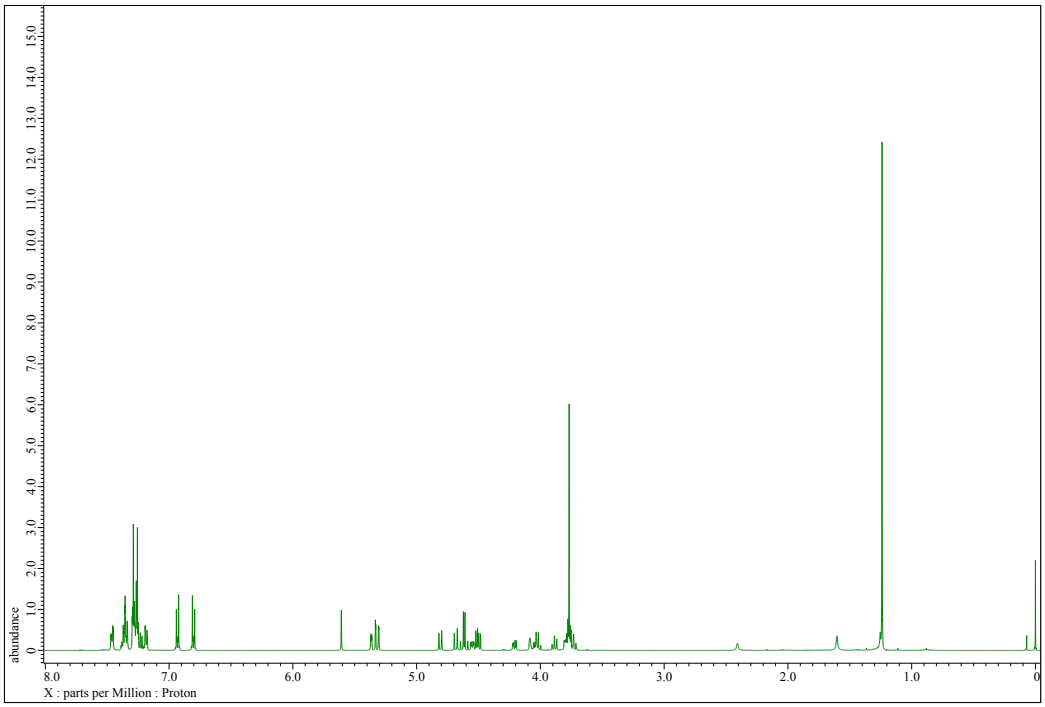
Compound **17** (^{13}C NMR) in $CDCl_3$



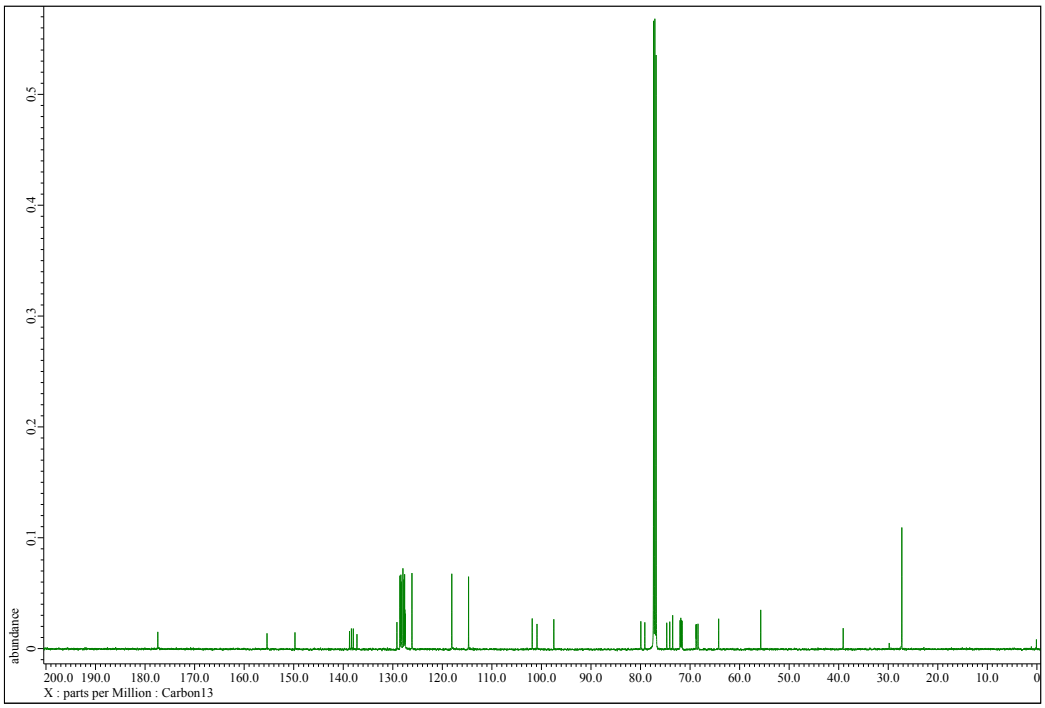
Compound **17** (Non-decoupling HMQC) in $CDCl_3$



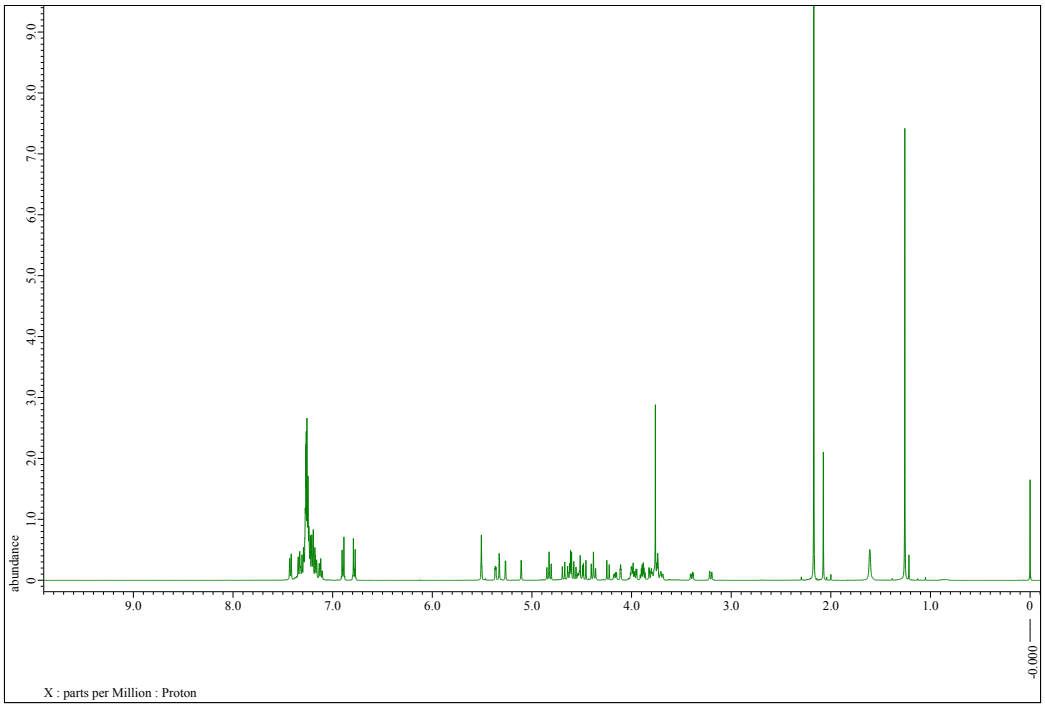
Compound **18** (^{1}H NMR) in $CDCl_3$



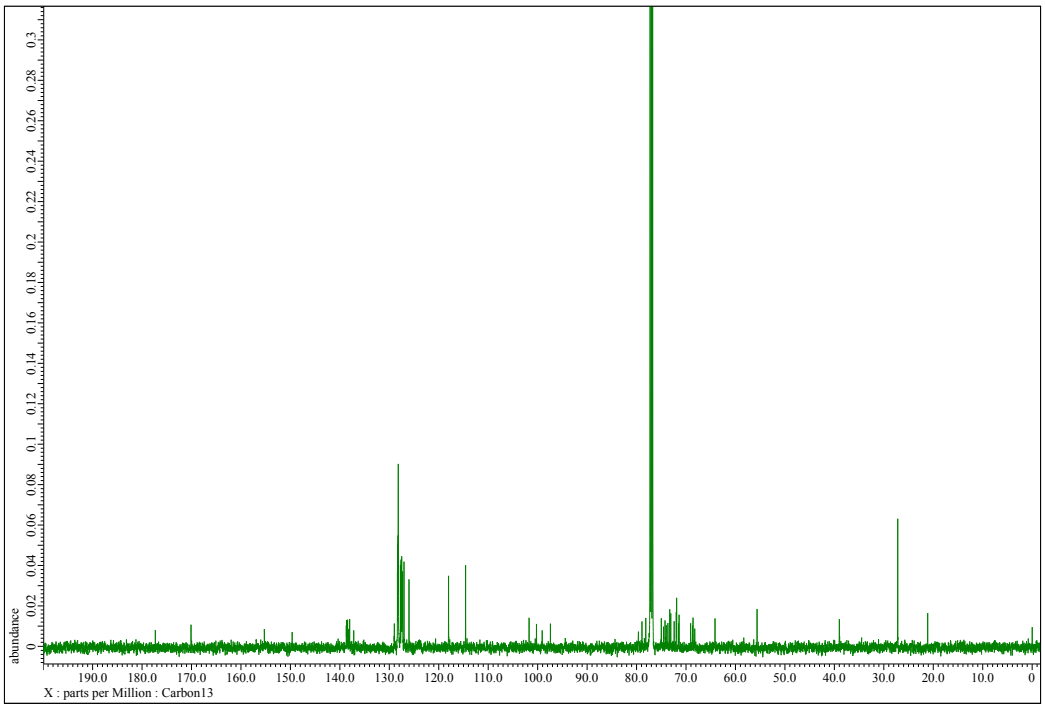
Compound **18** (^{13}C NMR) in $CDCl_3$



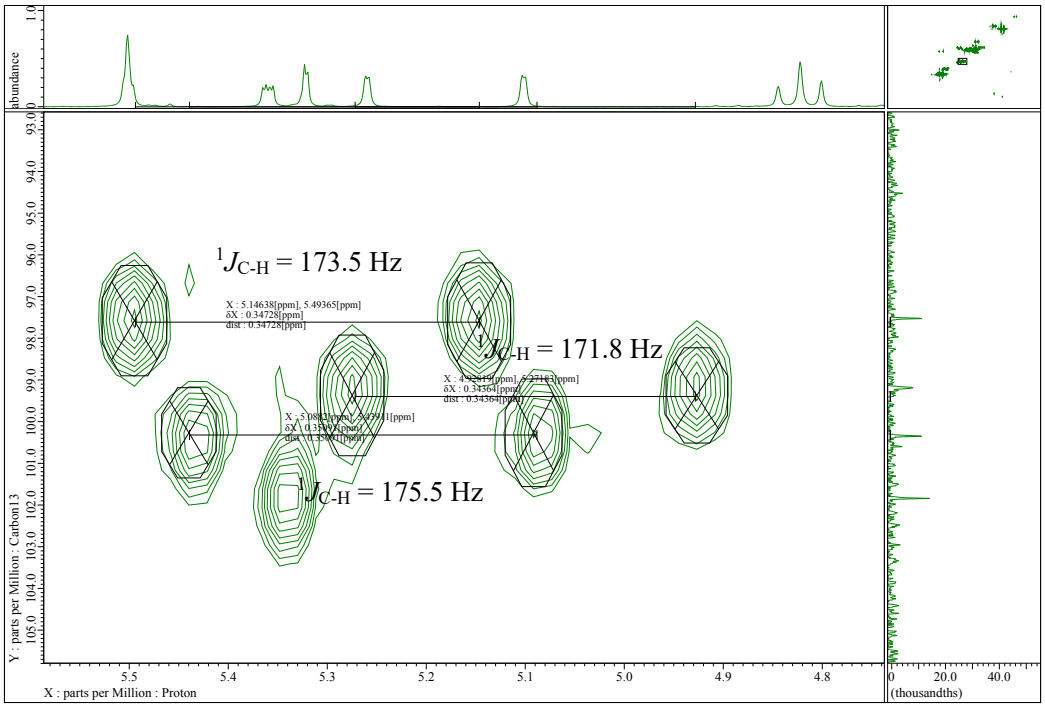
Compound **19** (^{1}H NMR) in $CDCl_3$



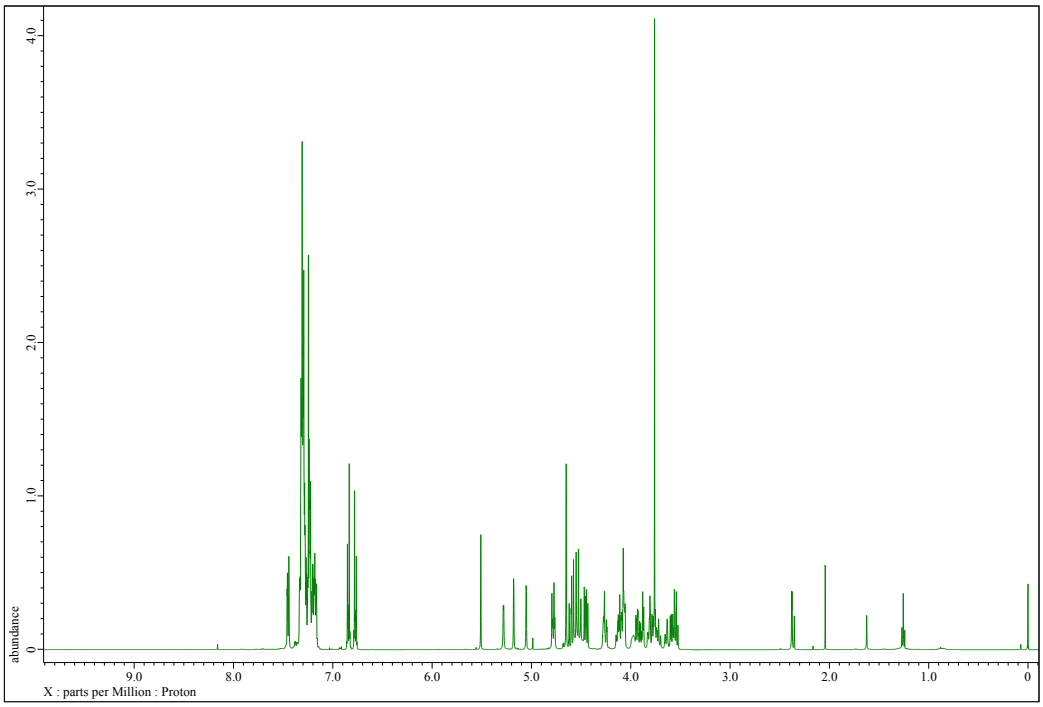
Compound **19** (^{13}C NMR) in $CDCl_3$



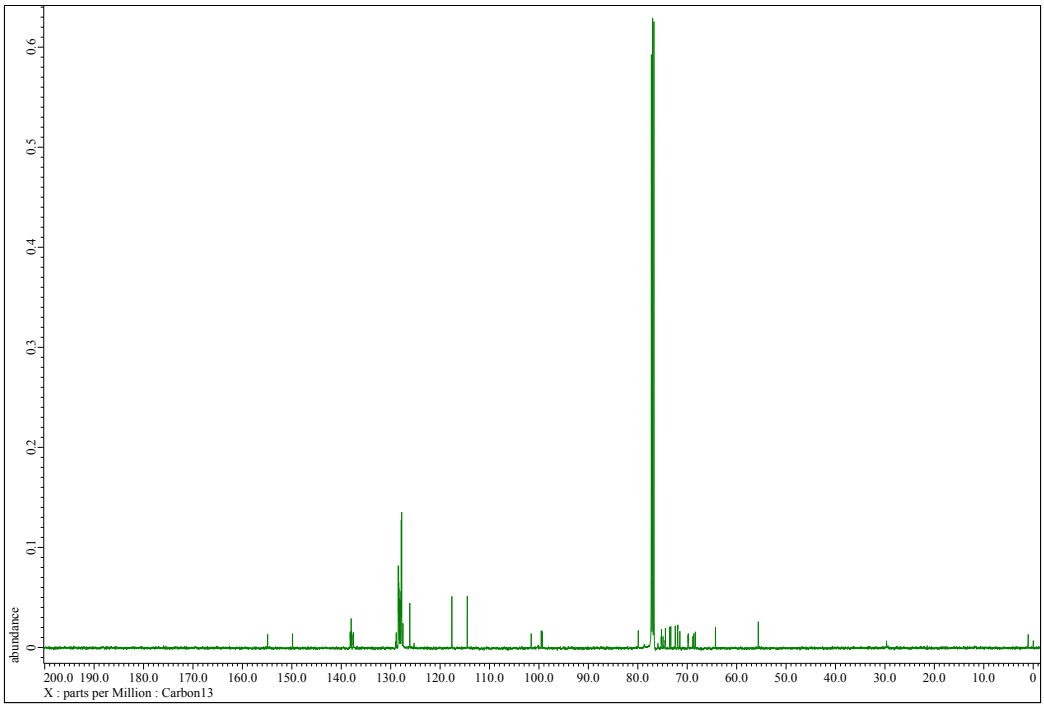
Compound **19** (Non-decoupling HMQC) in $CDCl_3$



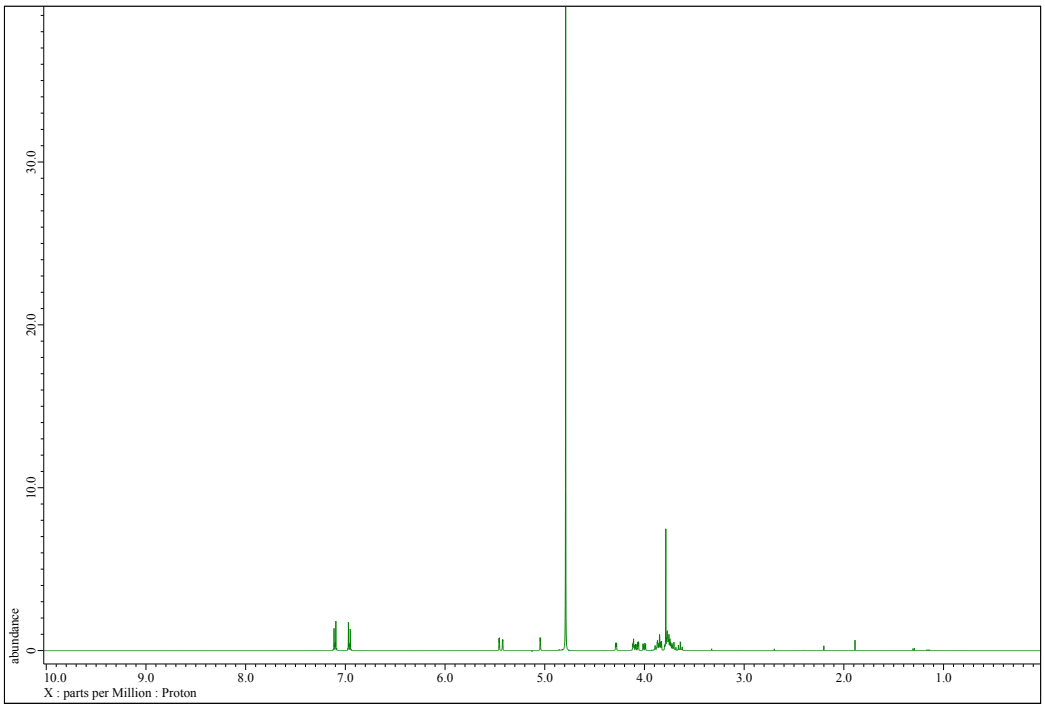
Compound **20** (^{1}H NMR) in $CDCl_3$



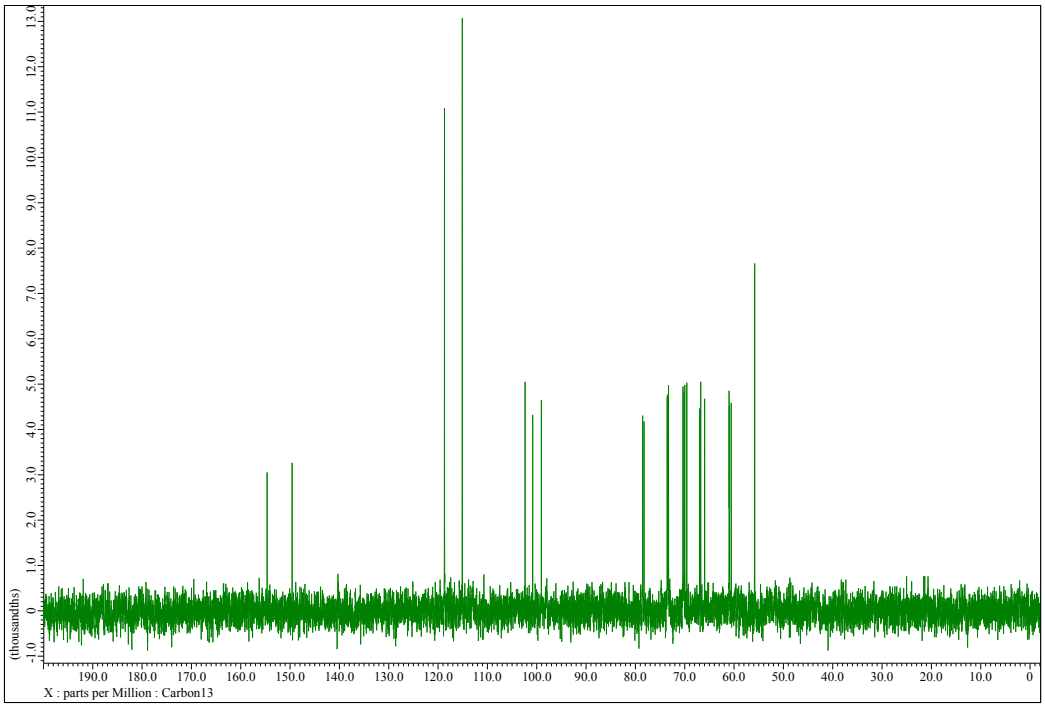
Compound **20** (^{13}C NMR) in $CDCl_3$



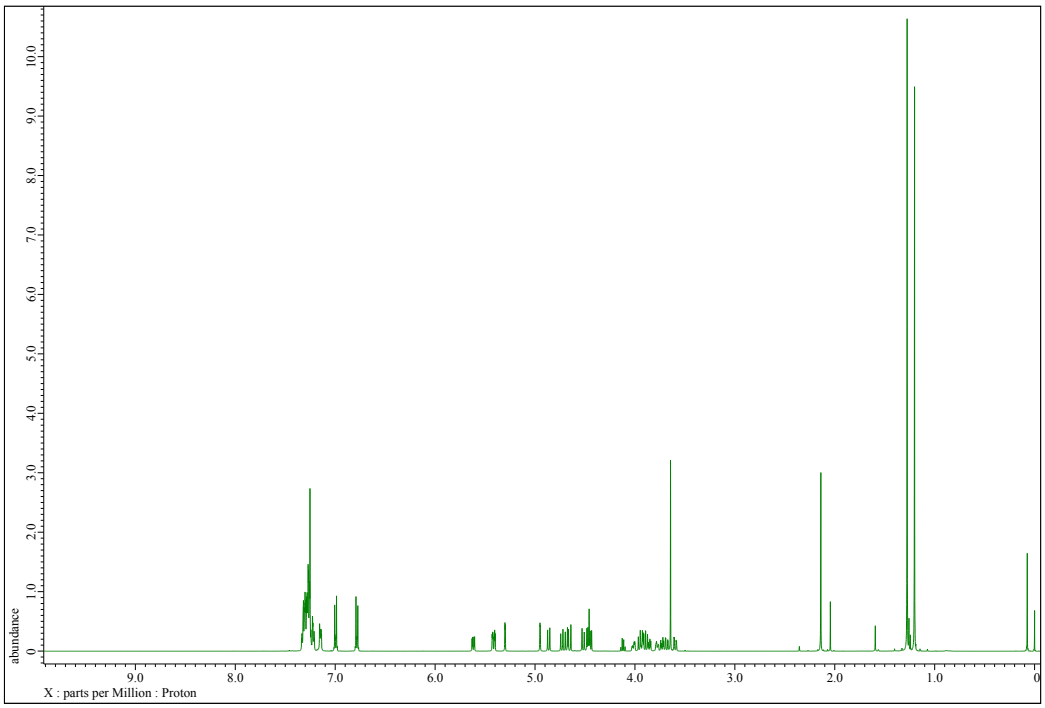
Compound **21** (^{1}H NMR) in $CDCl_3$



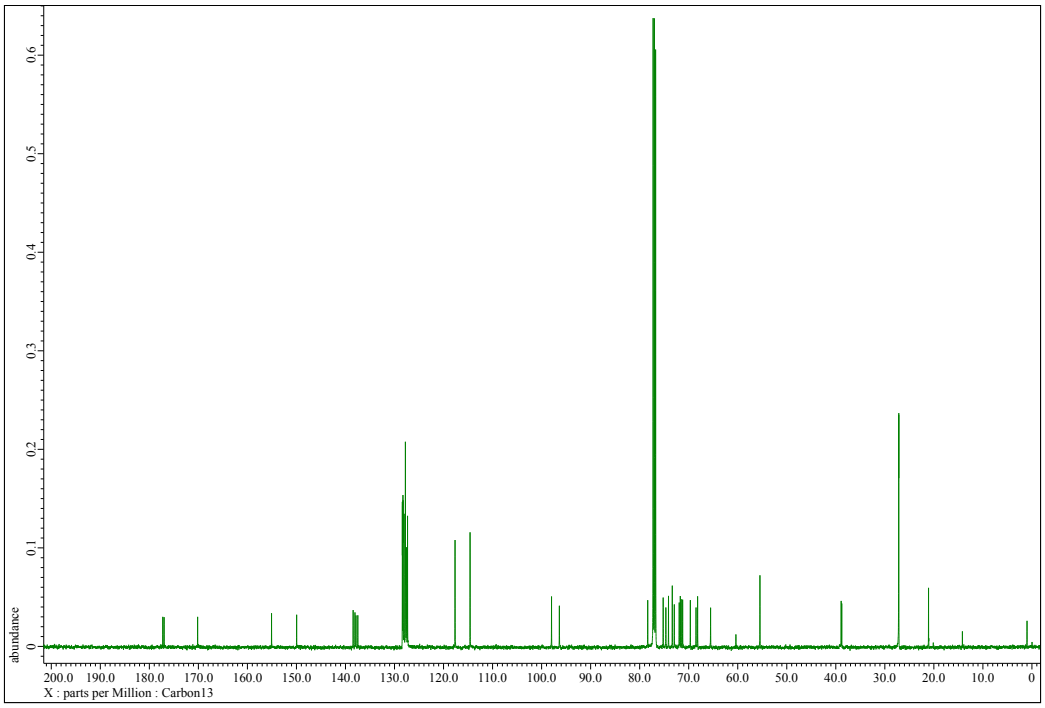
Compound **21** (^{13}C NMR) in $CDCl_3$



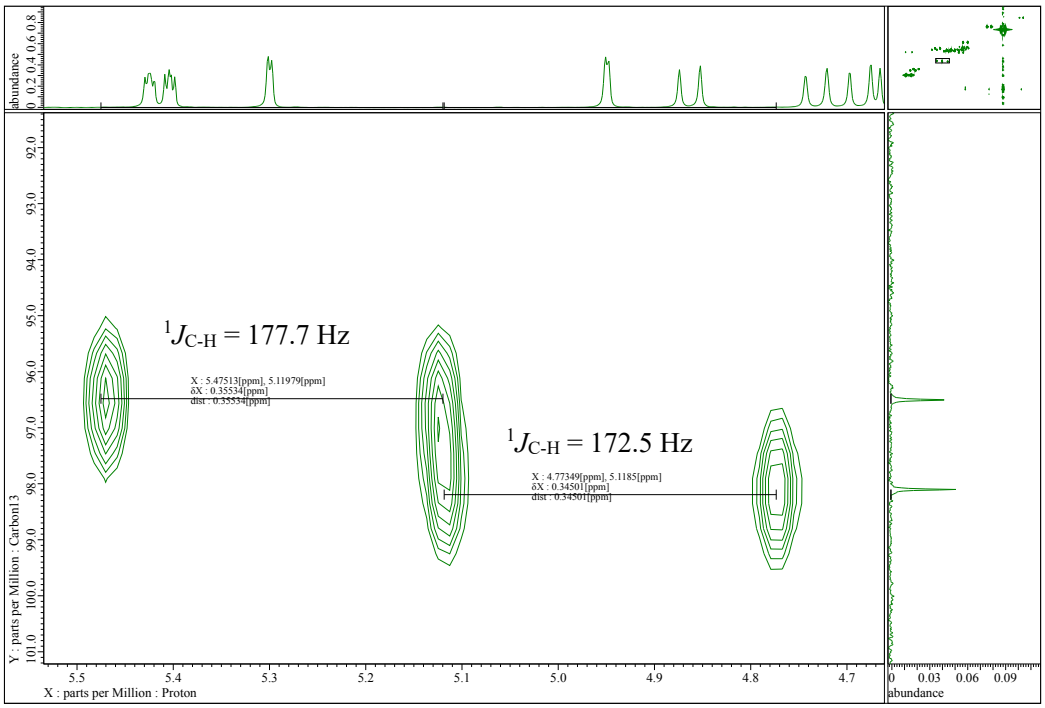
Compound **22** (^{1}H NMR) in $CDCl_3$



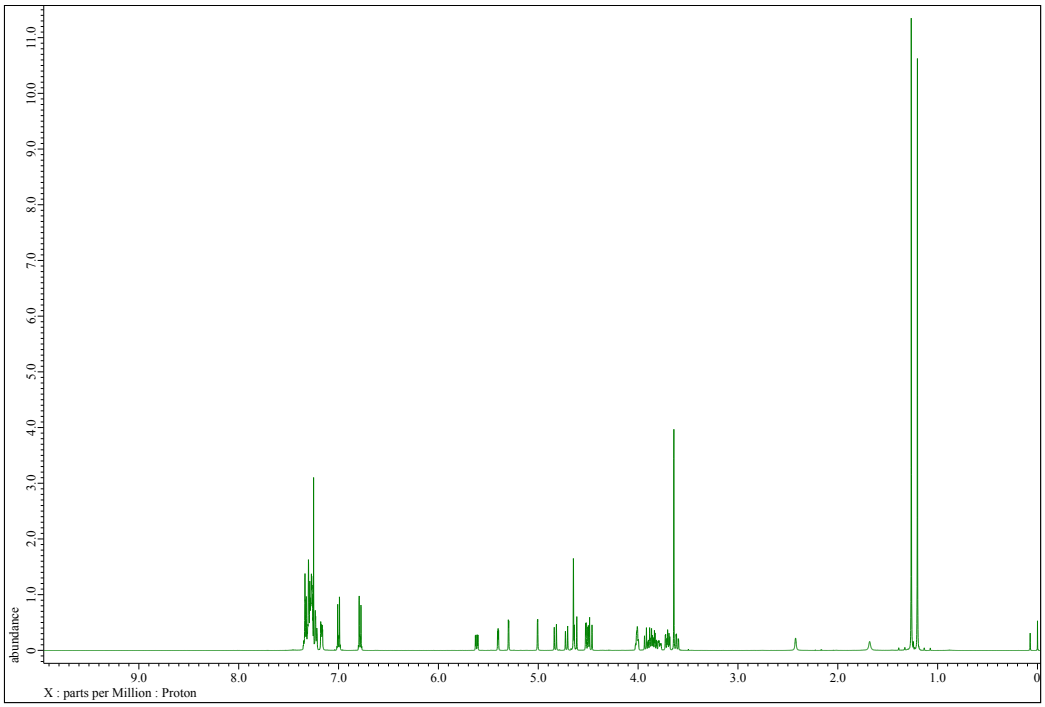
Compound **22** (^{13}C NMR) in $CDCl_3$



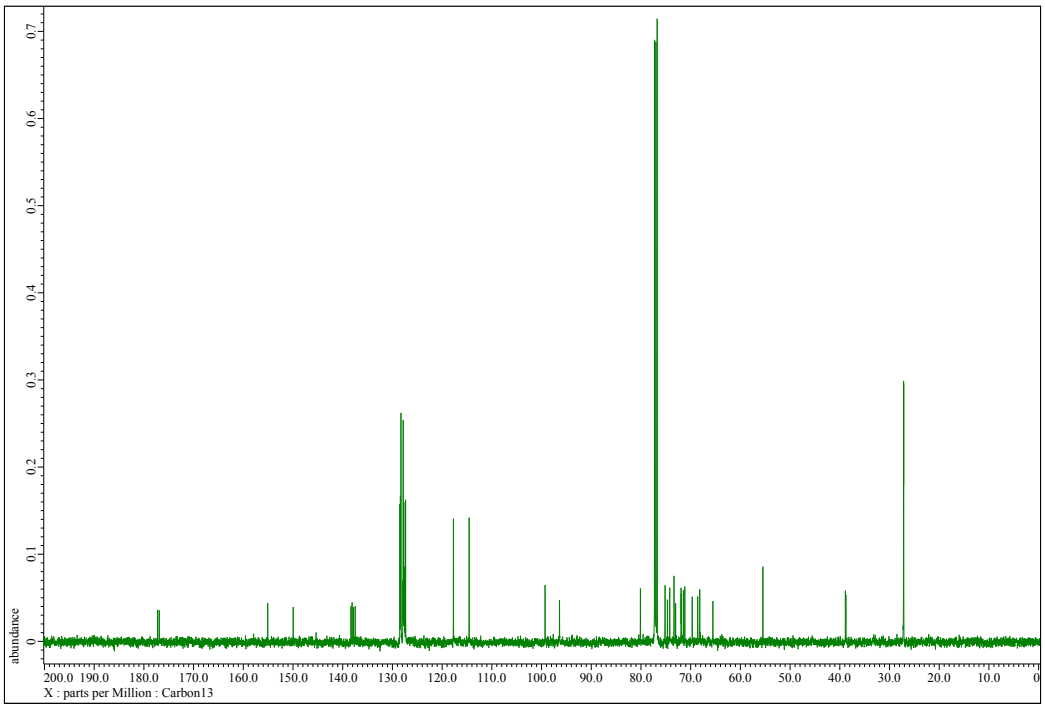
Compound **22** (Non-decoupling HMQC) in $CDCl_3$



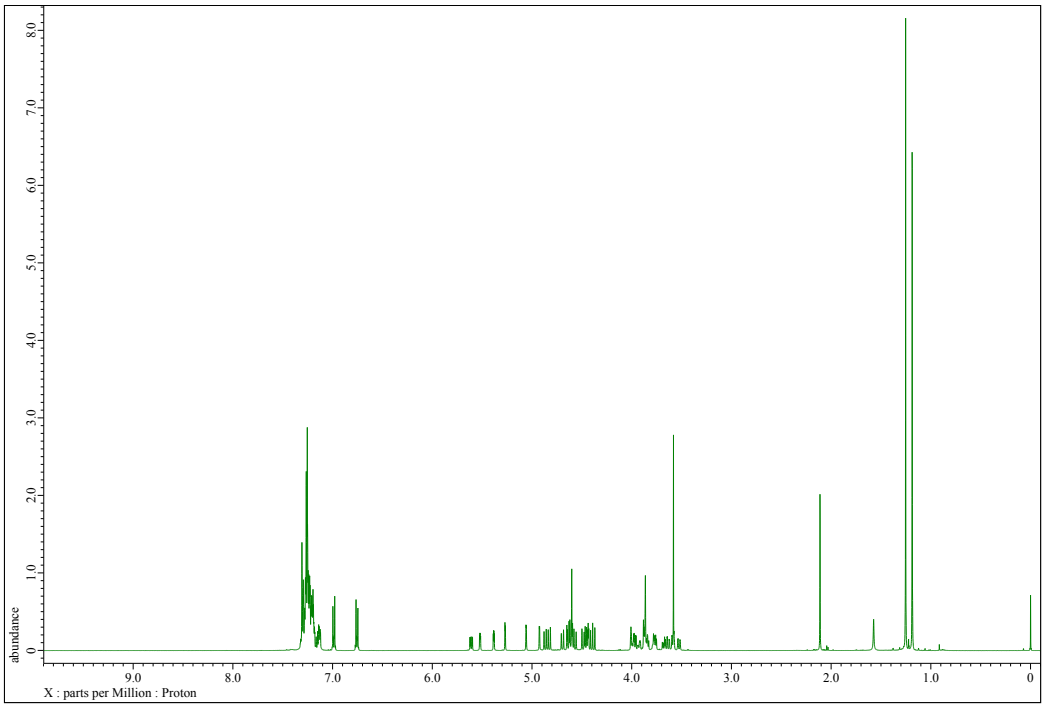
Compound **23** (^{1}H NMR) in $CDCl_3$



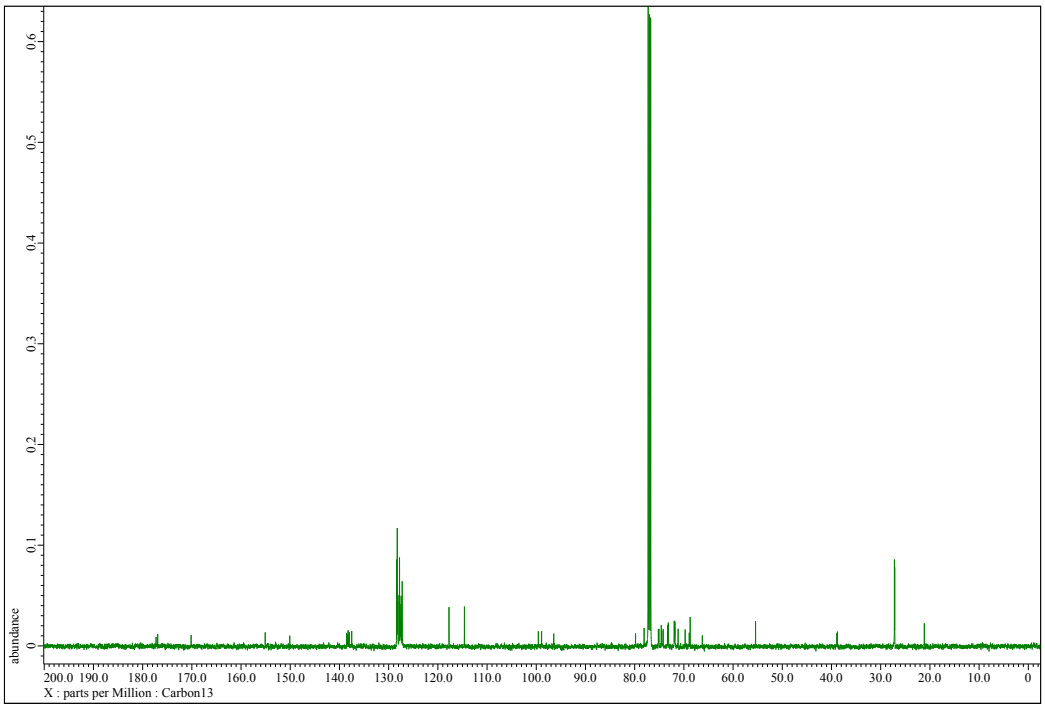
Compound **23** (^{13}C NMR) in $CDCl_3$



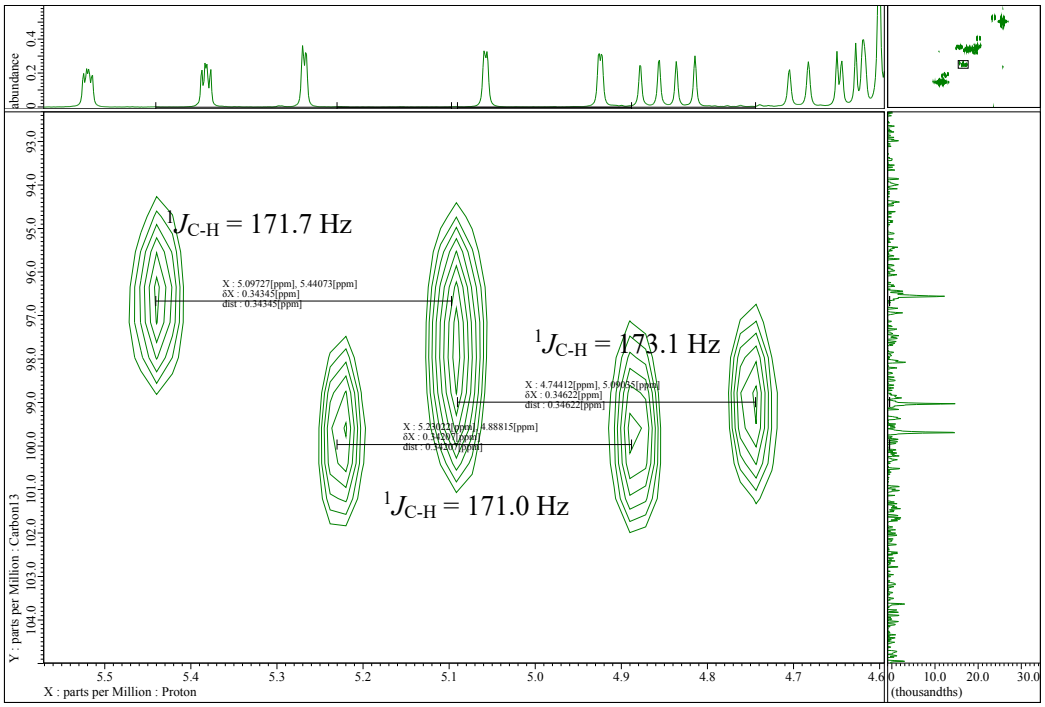
Compound **24** (^{1}H NMR) in $CDCl_3$



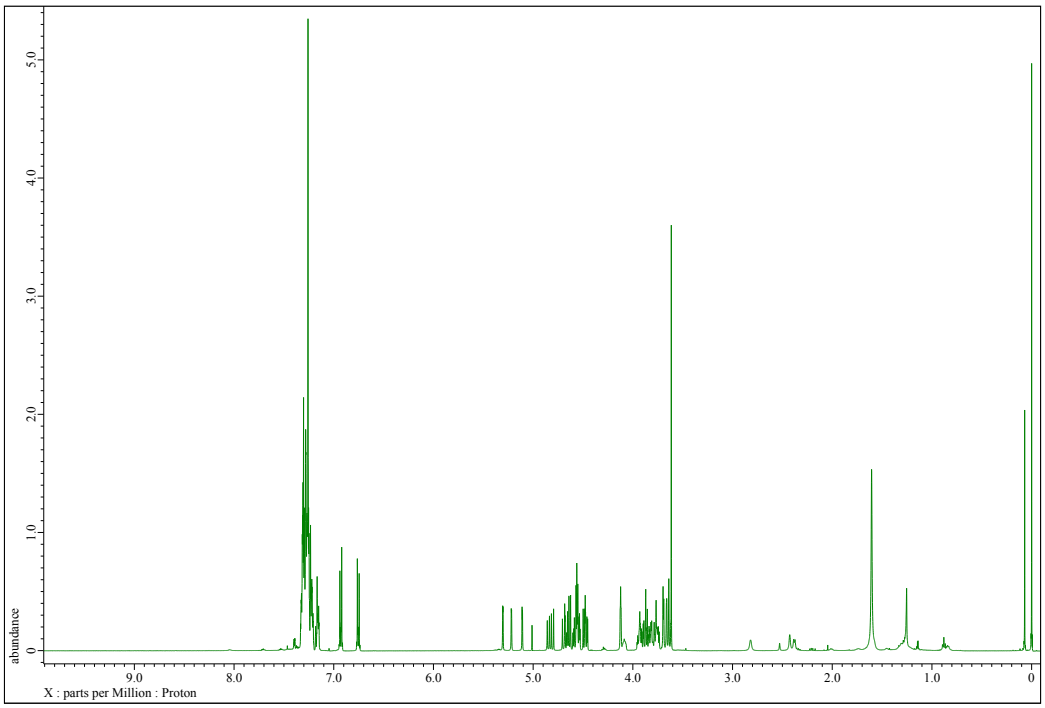
Compound **24** (^{13}C NMR) in $CDCl_3$



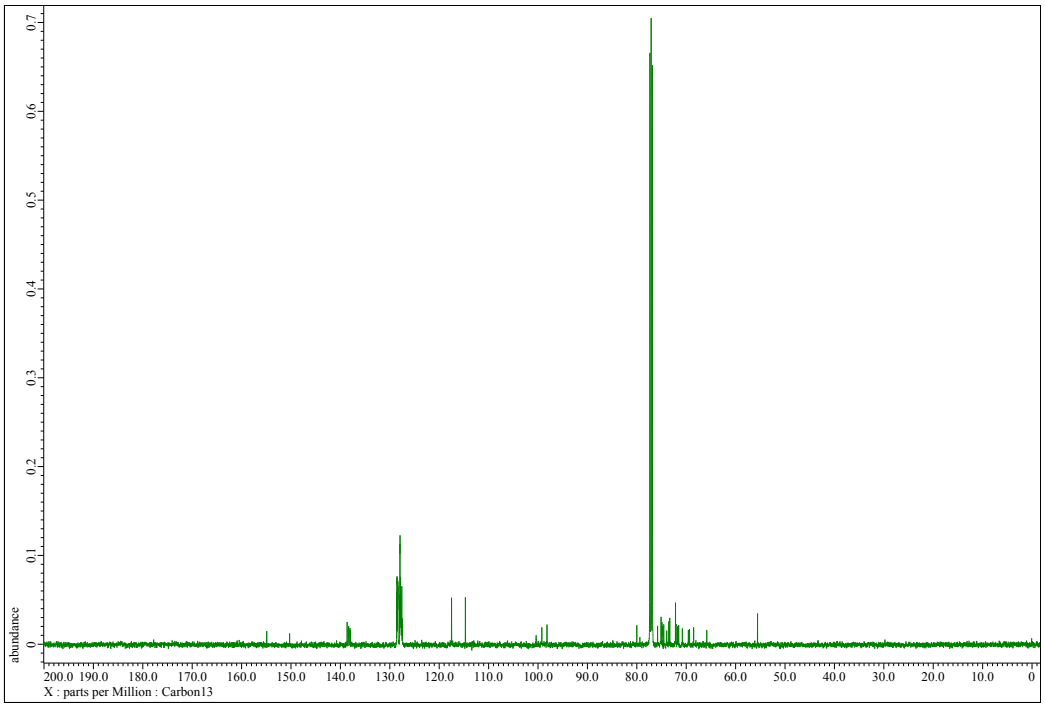
Compound **24** (Non-decoupling HMQC) in $CDCl_3$



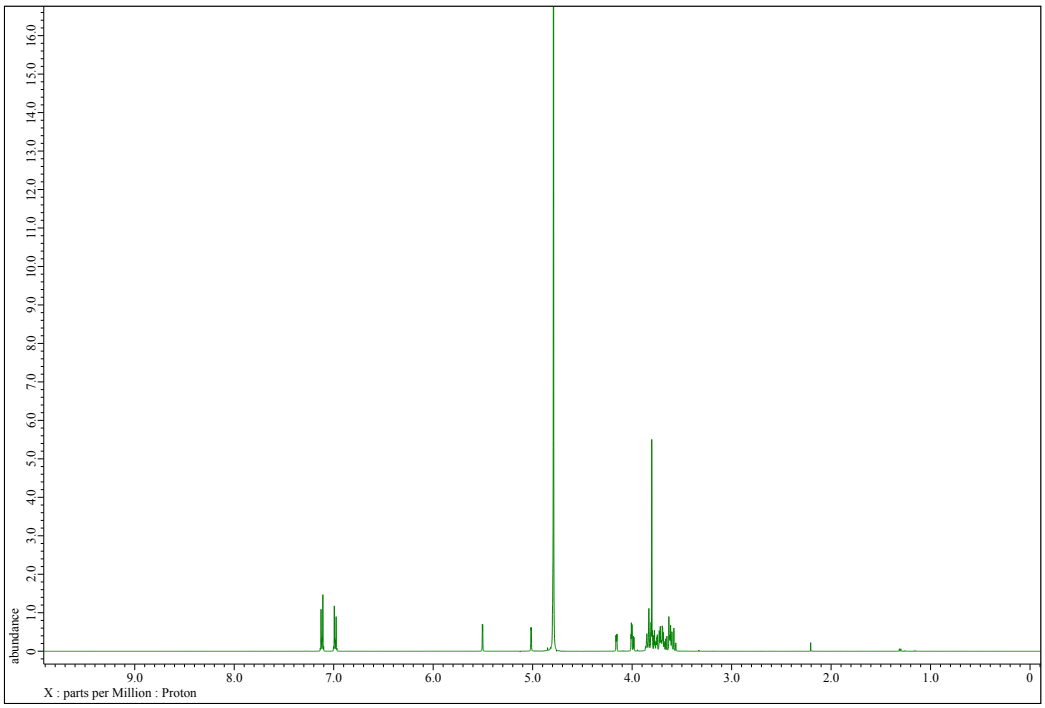
Compound **25** (^{1}H NMR) in $CDCl_3$



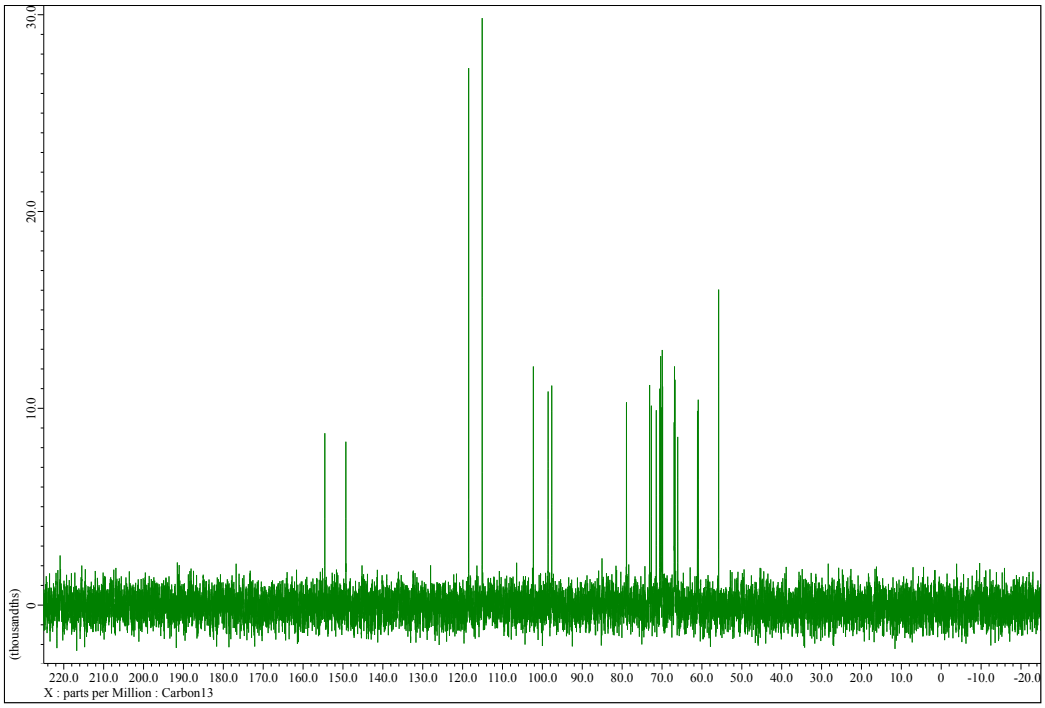
Compound **25** (^{13}C NMR) in $CDCl_3$



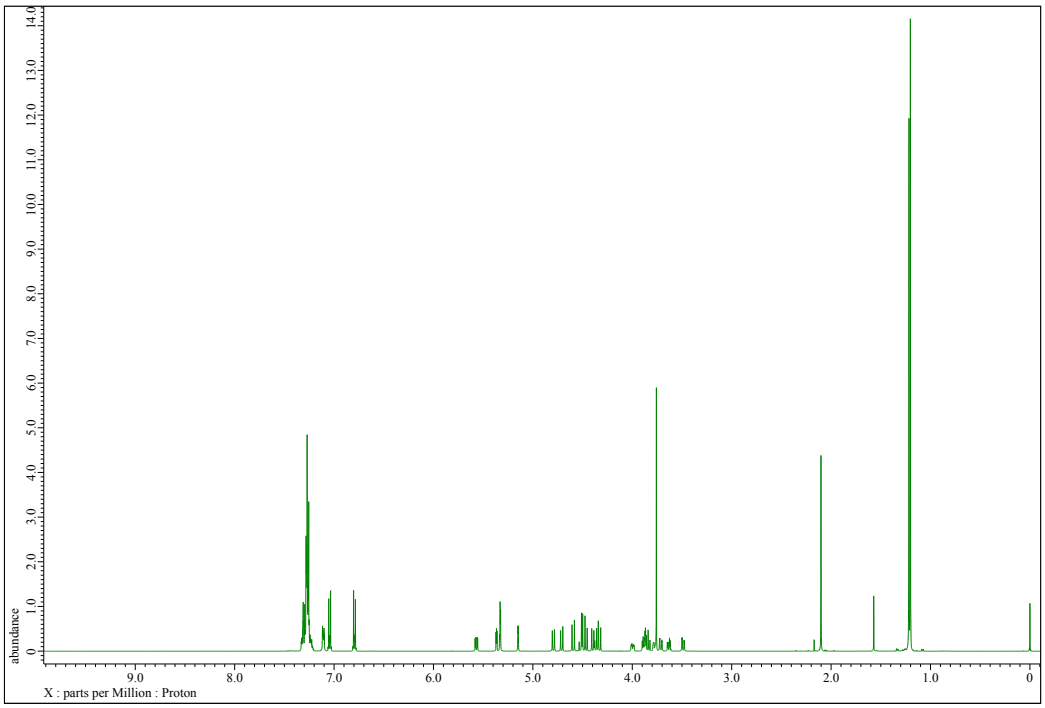
Compound **26** (^{1}H NMR) in $CDCl_3$



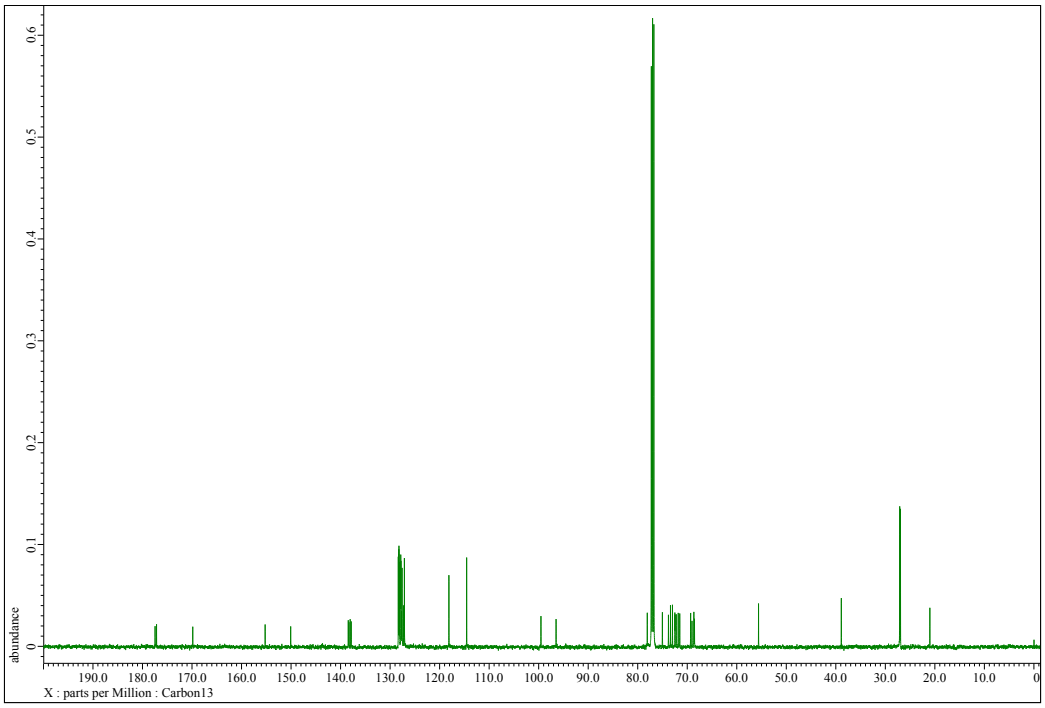
Compound **26** (^{13}C NMR) in $CDCl_3$



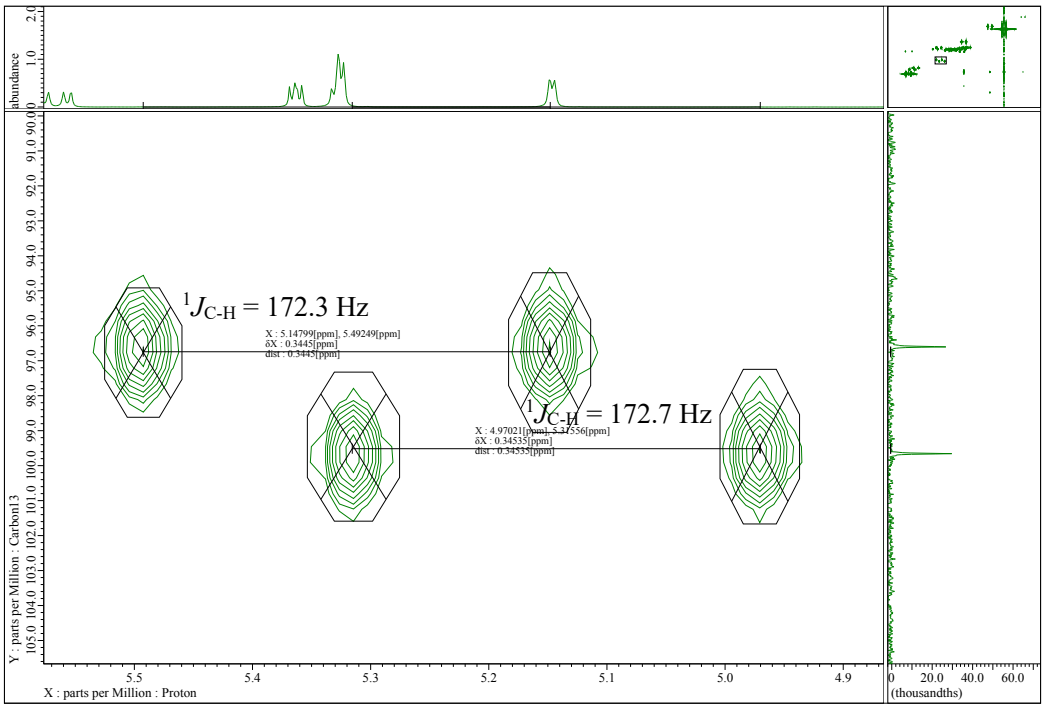
Compound **27** (^{1}H NMR) in $CDCl_3$



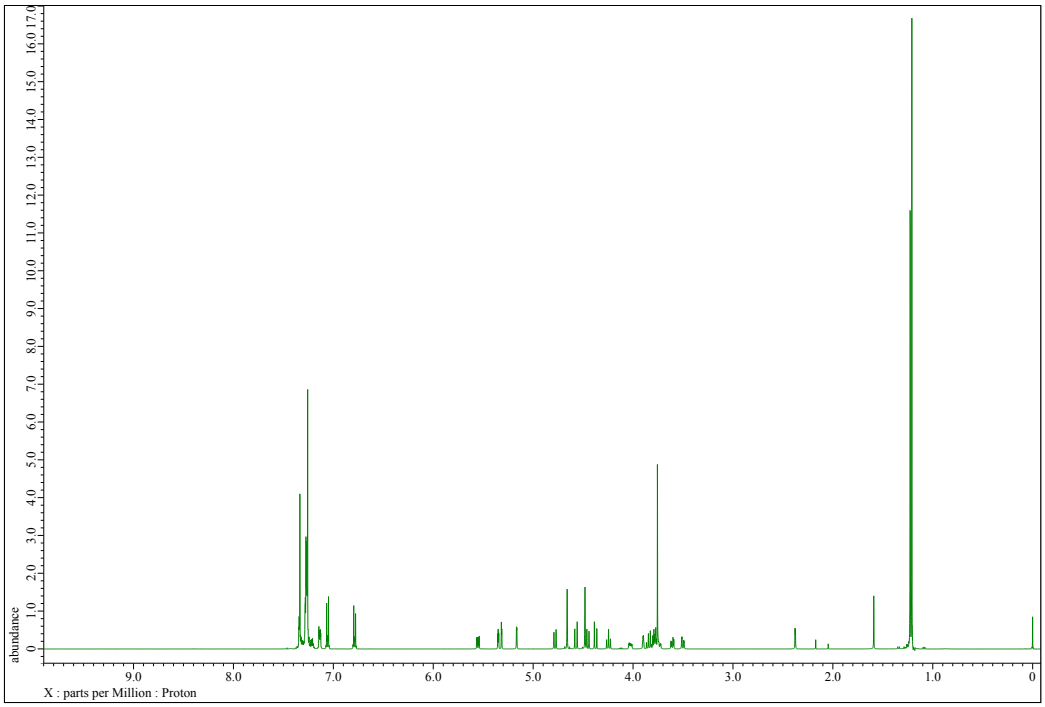
Compound **27** (^{13}C NMR) in $CDCl_3$



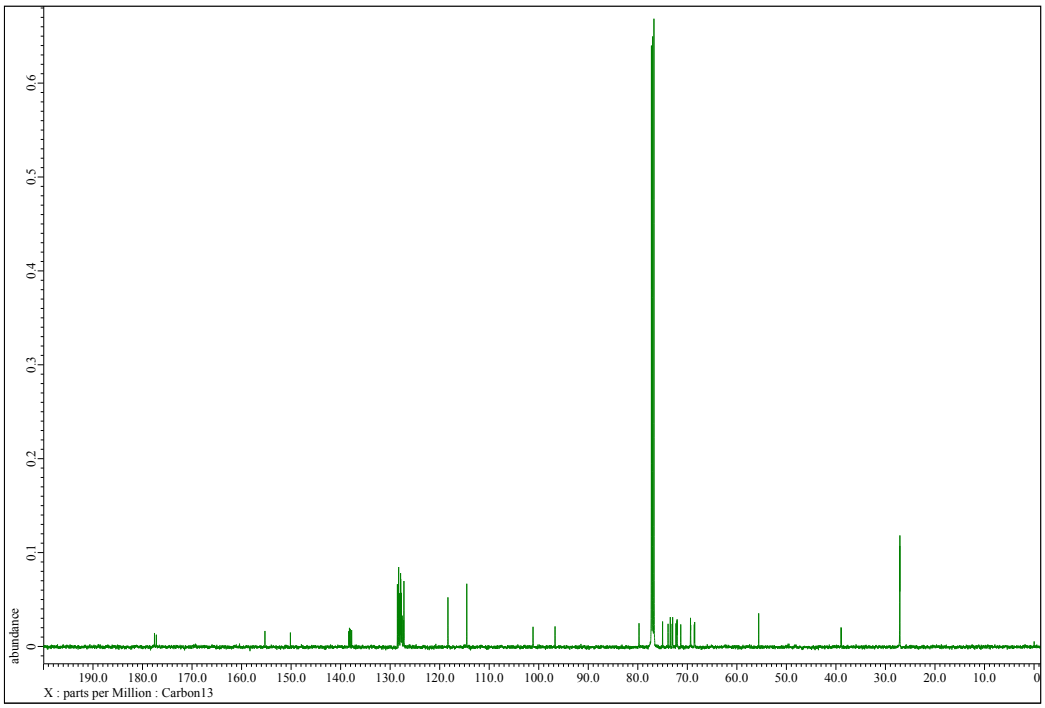
Compound **27** (Non-decoupling HMQC) in $CDCl_3$



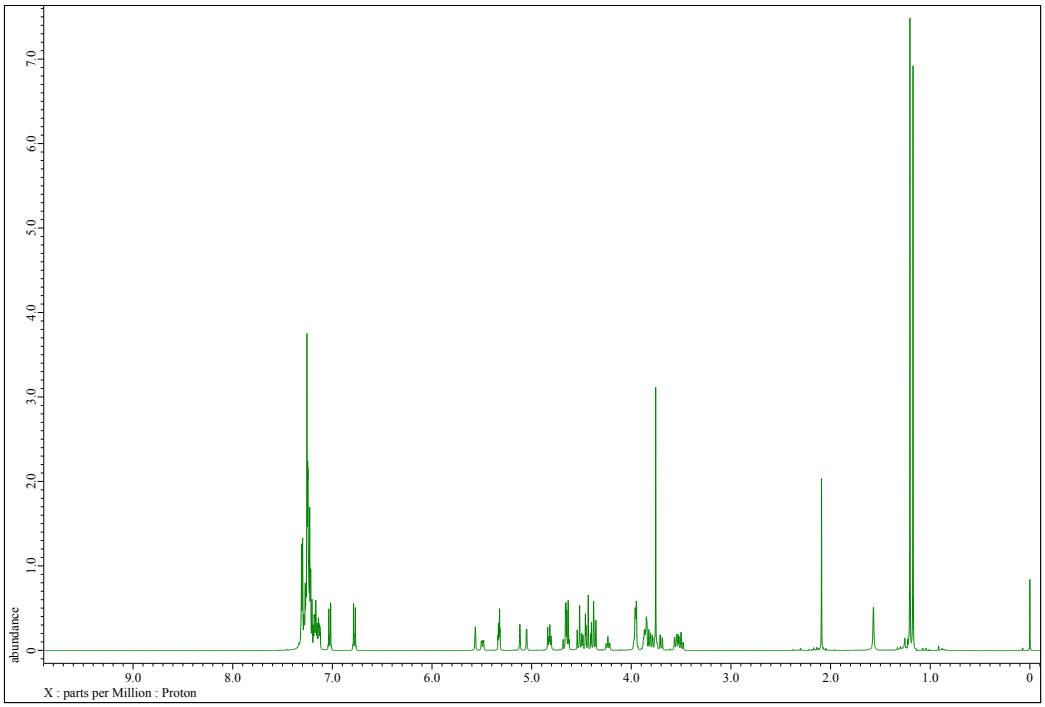
Compound **28** (^{1}H NMR) in $CDCl_3$



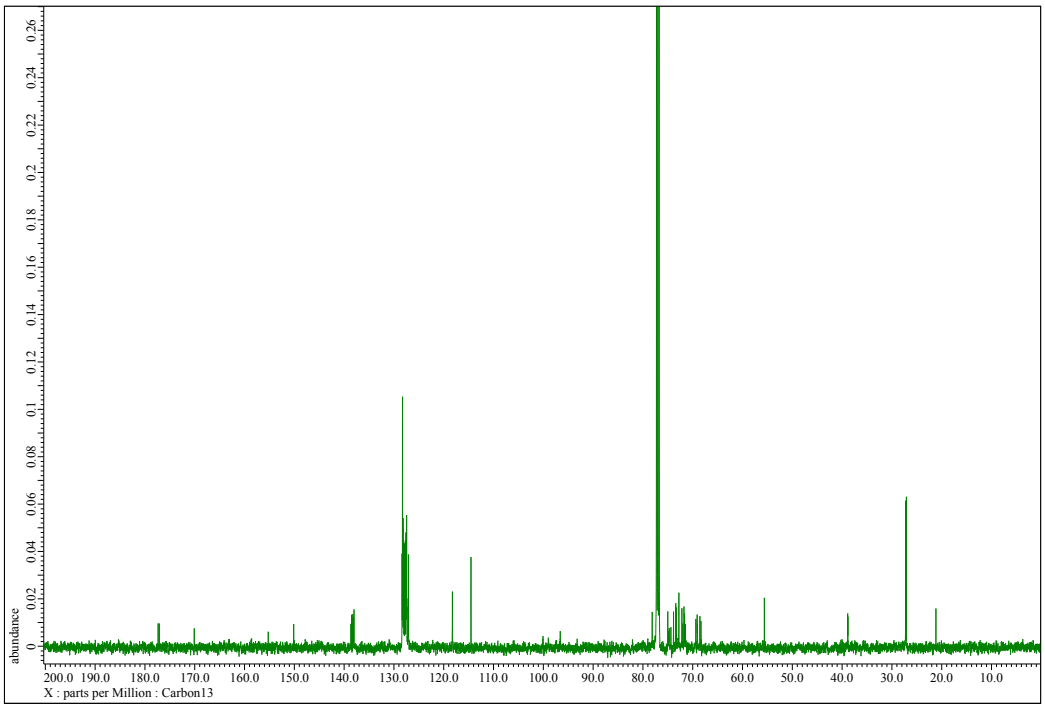
Compound **28** (^{13}C NMR) in $CDCl_3$



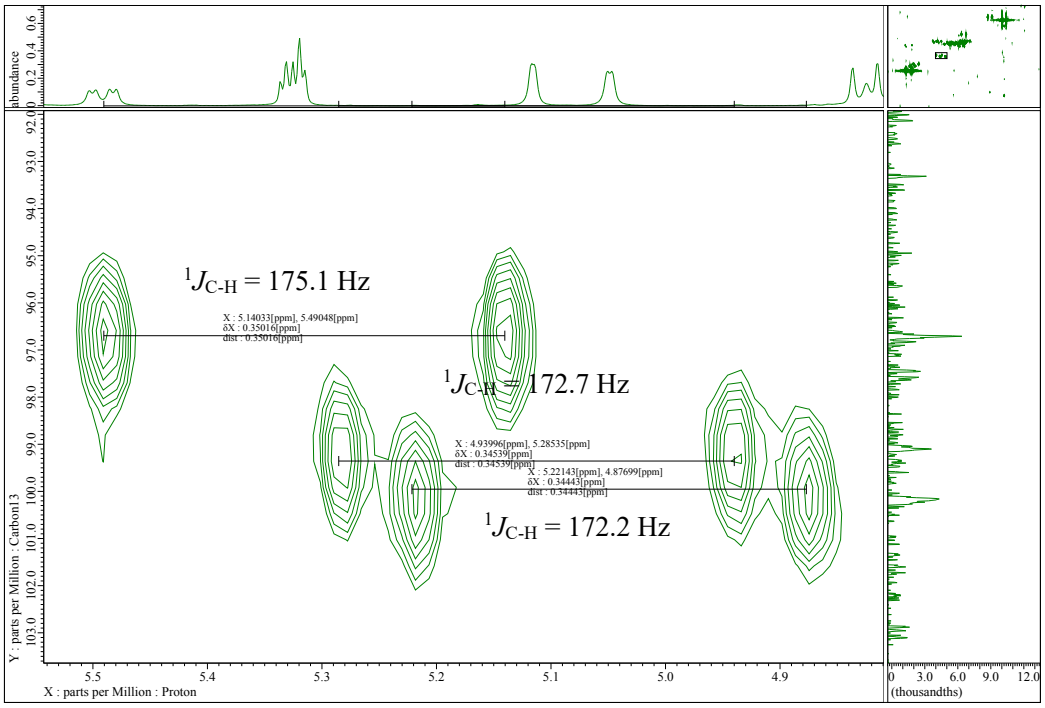
Compound **29** (^{1}H NMR) in $CDCl_3$



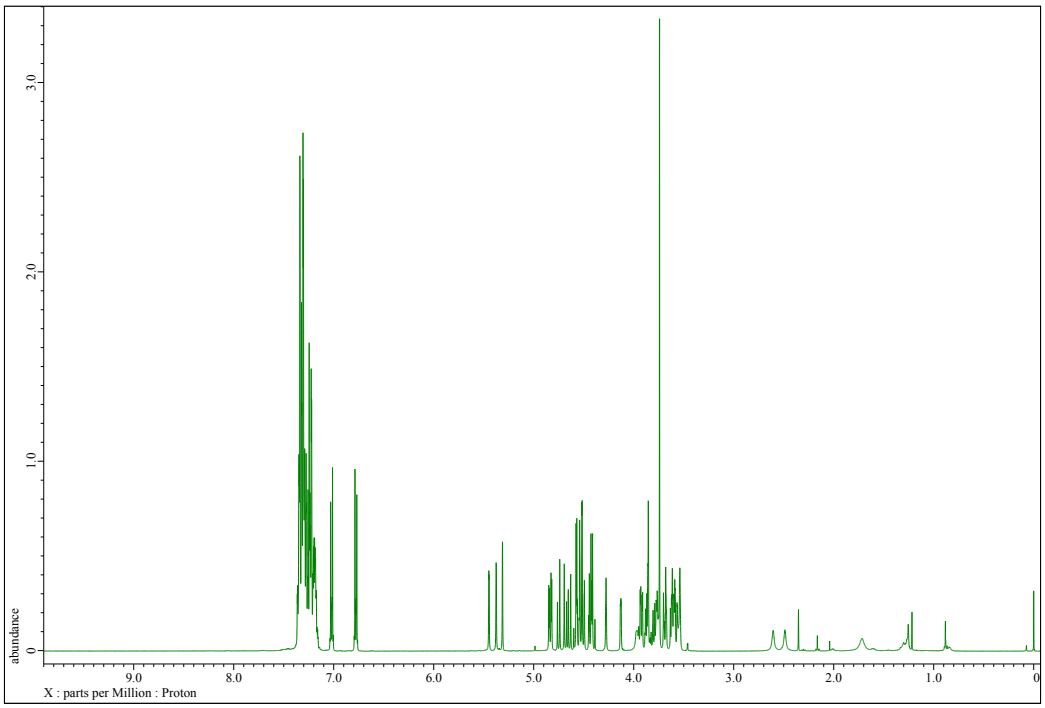
Compound **29** (^{13}C NMR) in $CDCl_3$



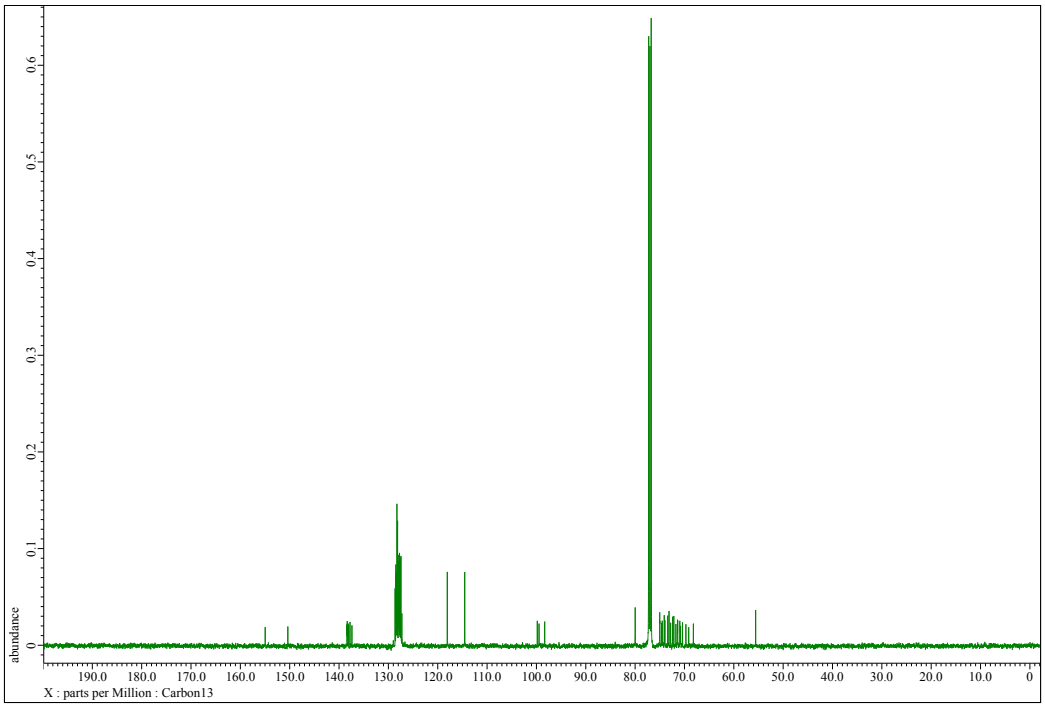
Compound **29** (Non-decoupling HMQC) in $CDCl_3$



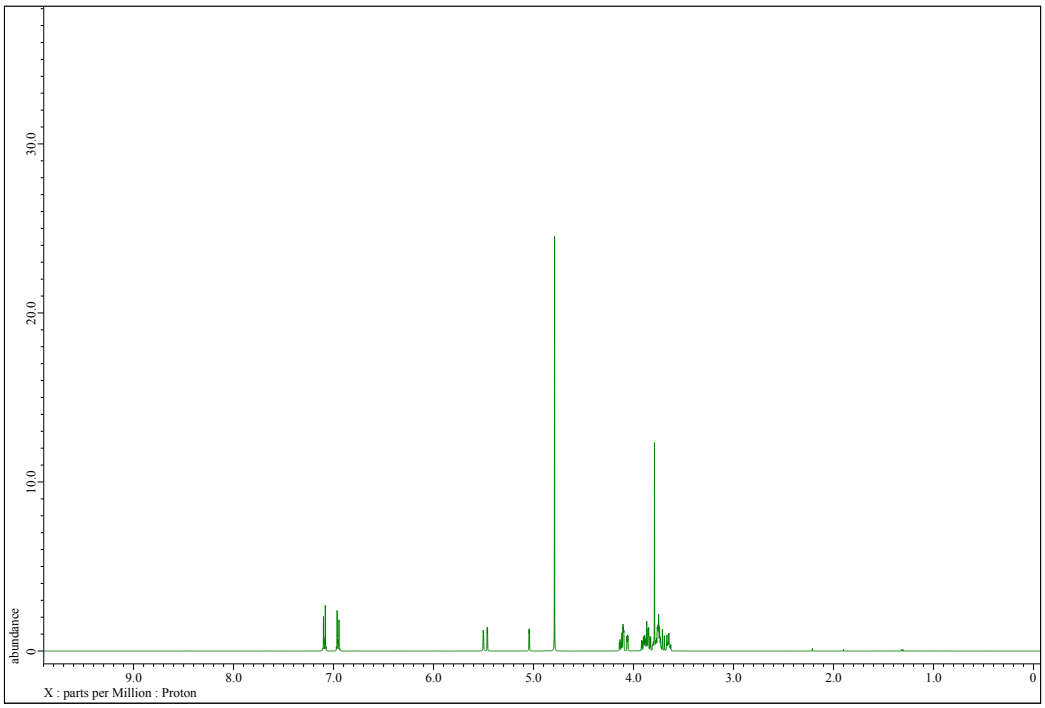
Compound **30** (^{1}H NMR) in $CDCl_3$



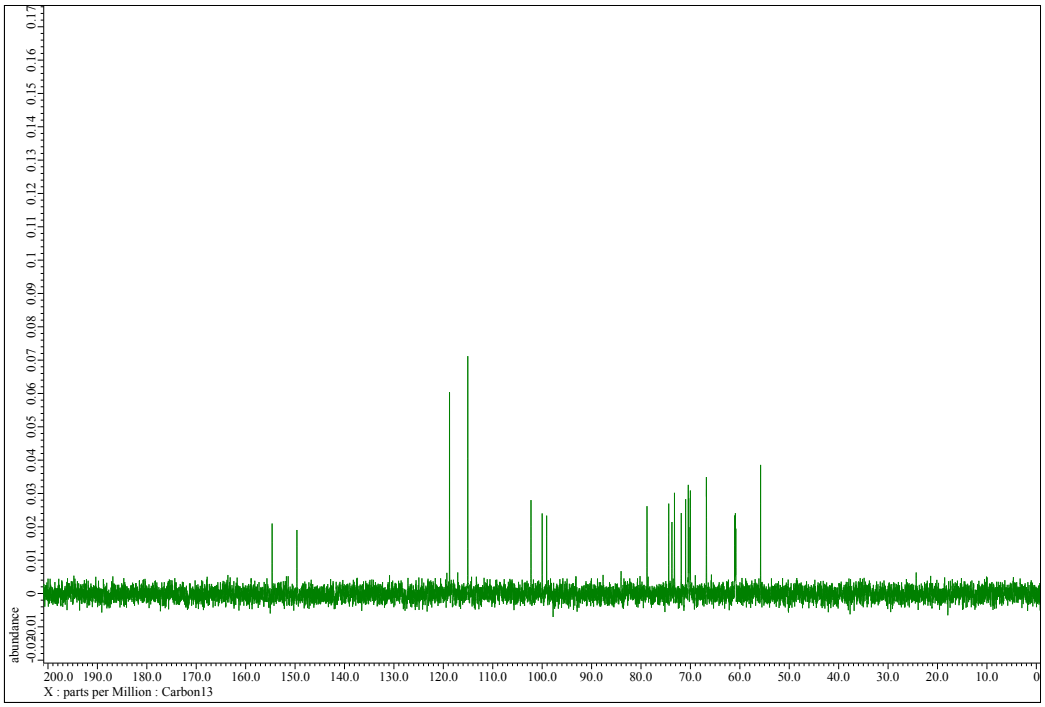
Compound **30** (^{13}C NMR) in $CDCl_3$



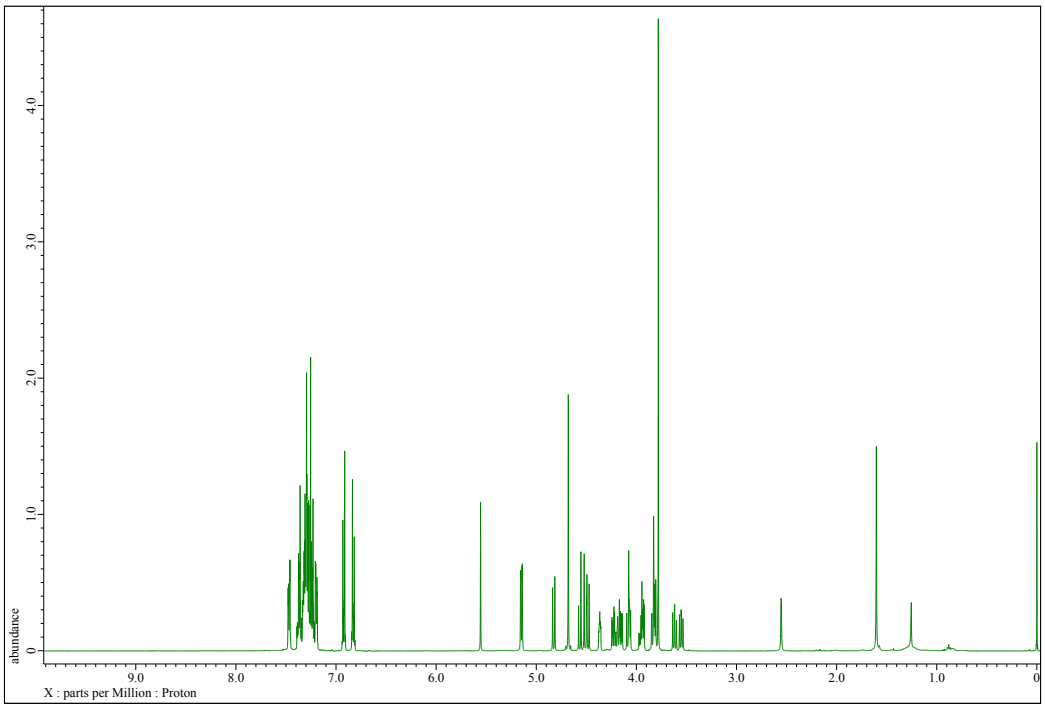
Compound **31** (^{1}H NMR) in D_2O



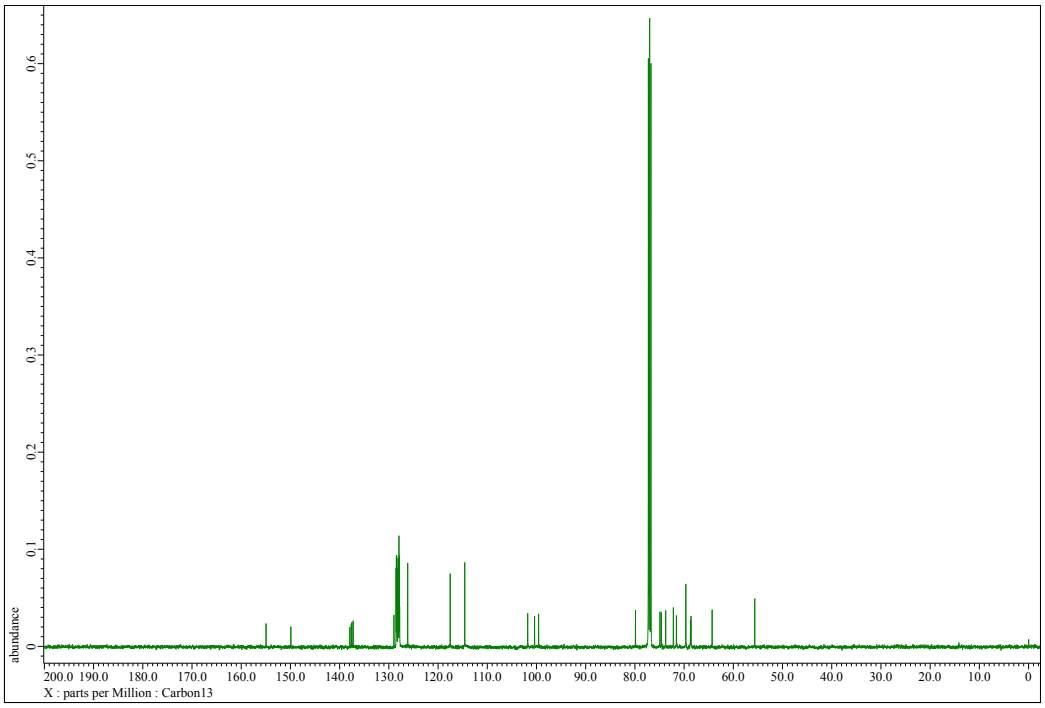
Compound **31** (^{13}C NMR) in D_2O



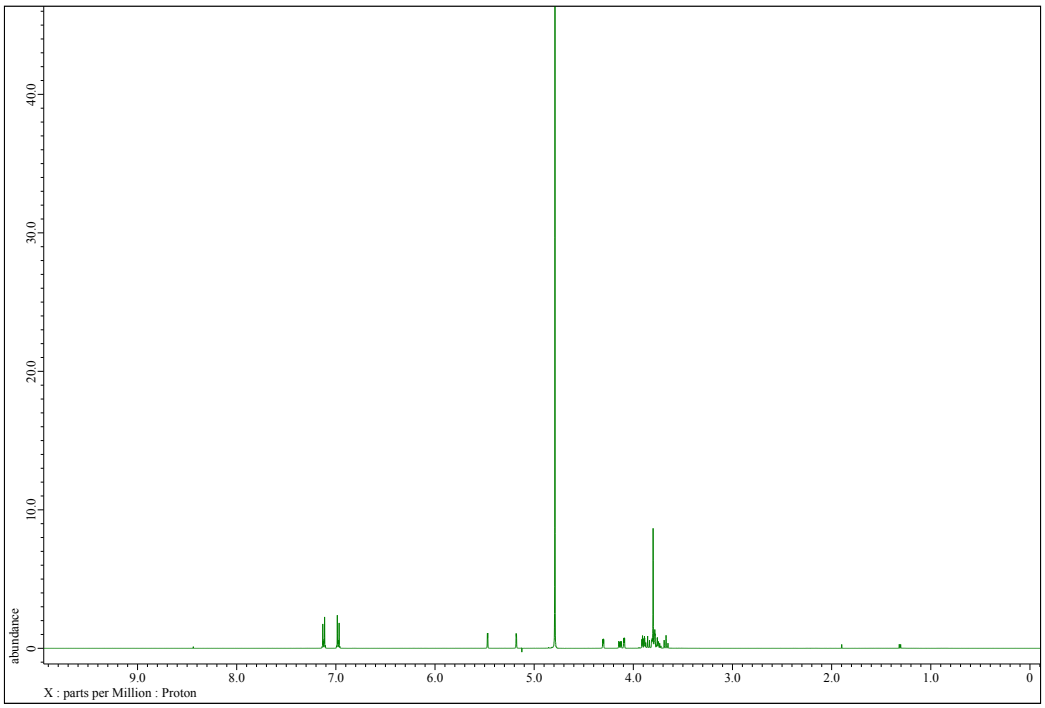
Compound **33** (^{1}H NMR) in $CDCl_3$



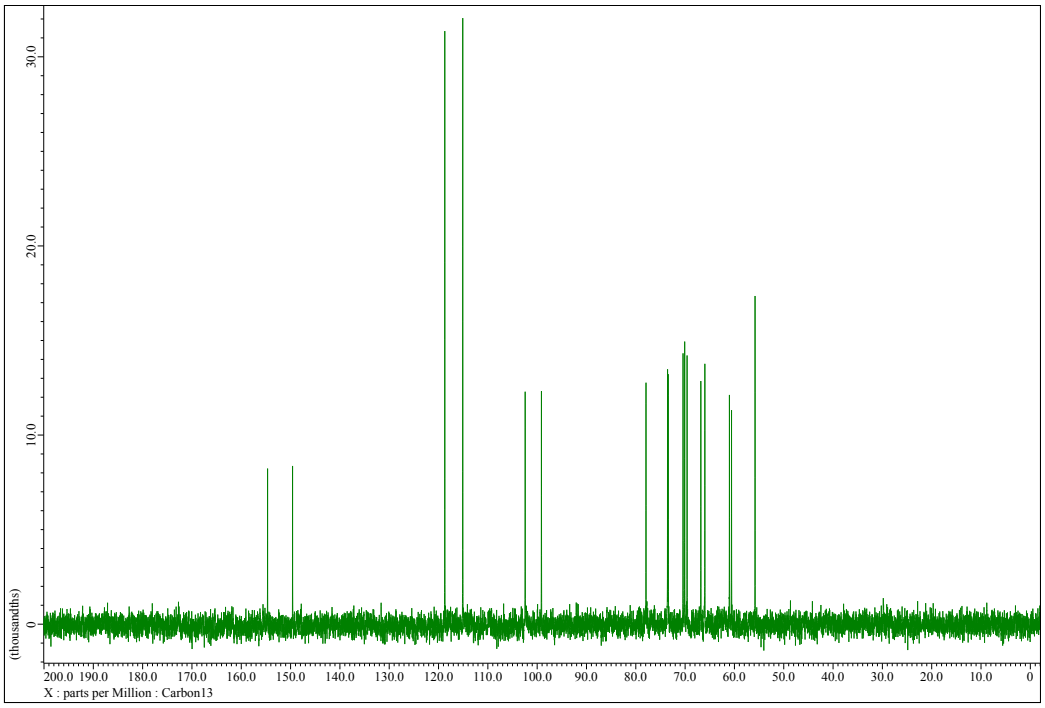
Compound **33** (^{13}C NMR) in $CDCl_3$



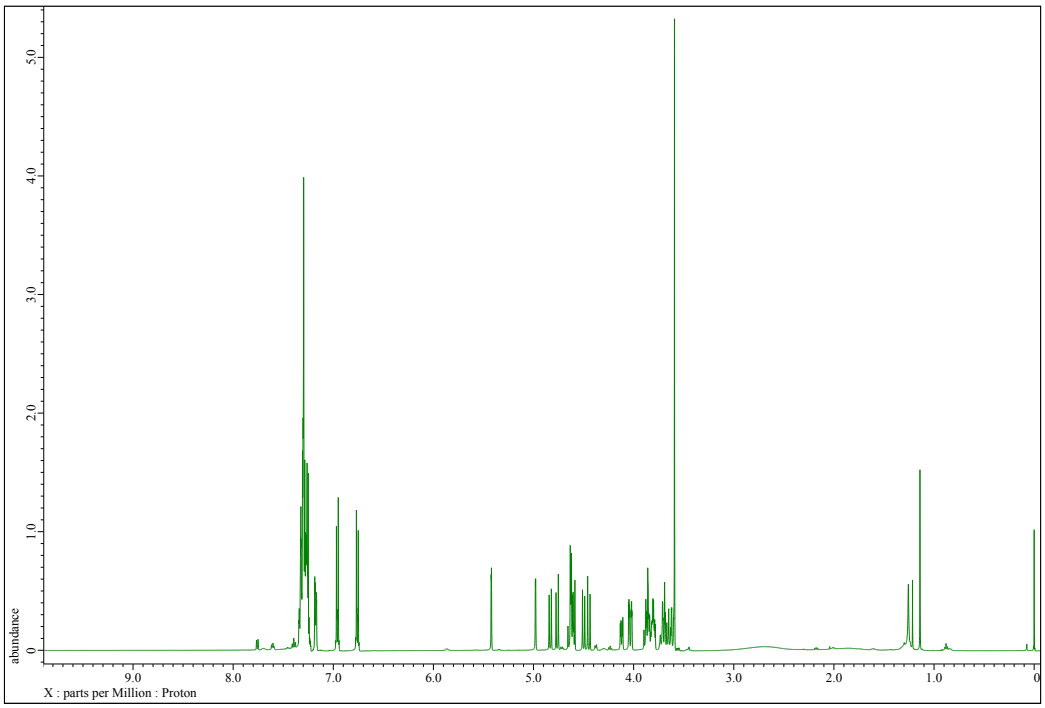
Compound **34** (^{1}H NMR) in D_2O



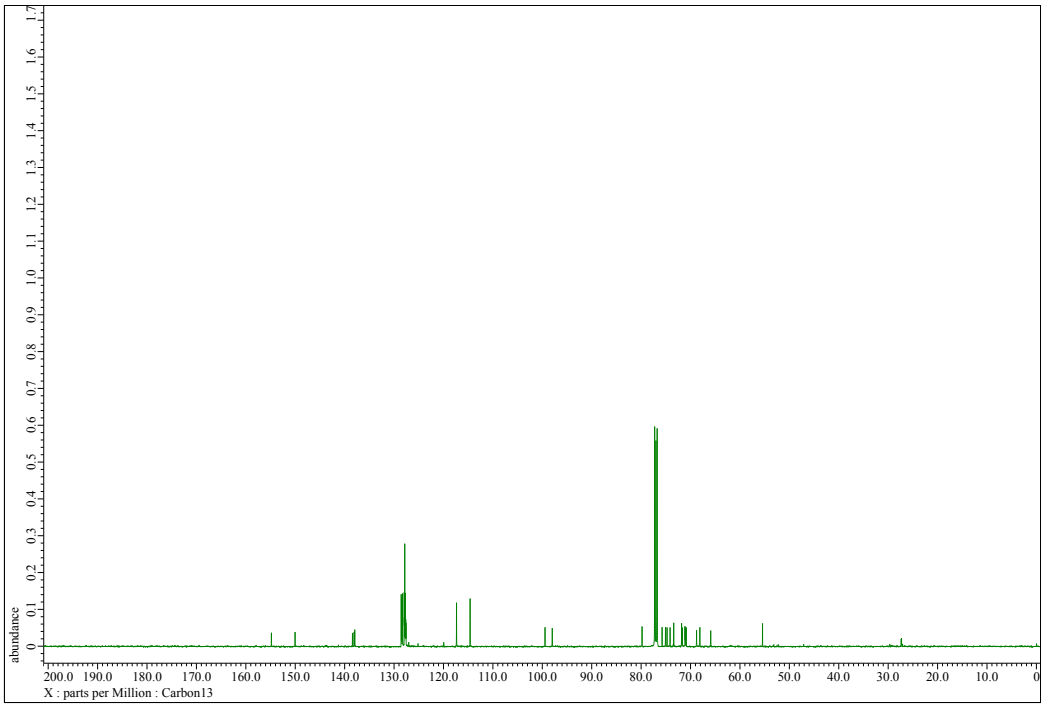
Compound **34** (^{13}C NMR) in D_2O



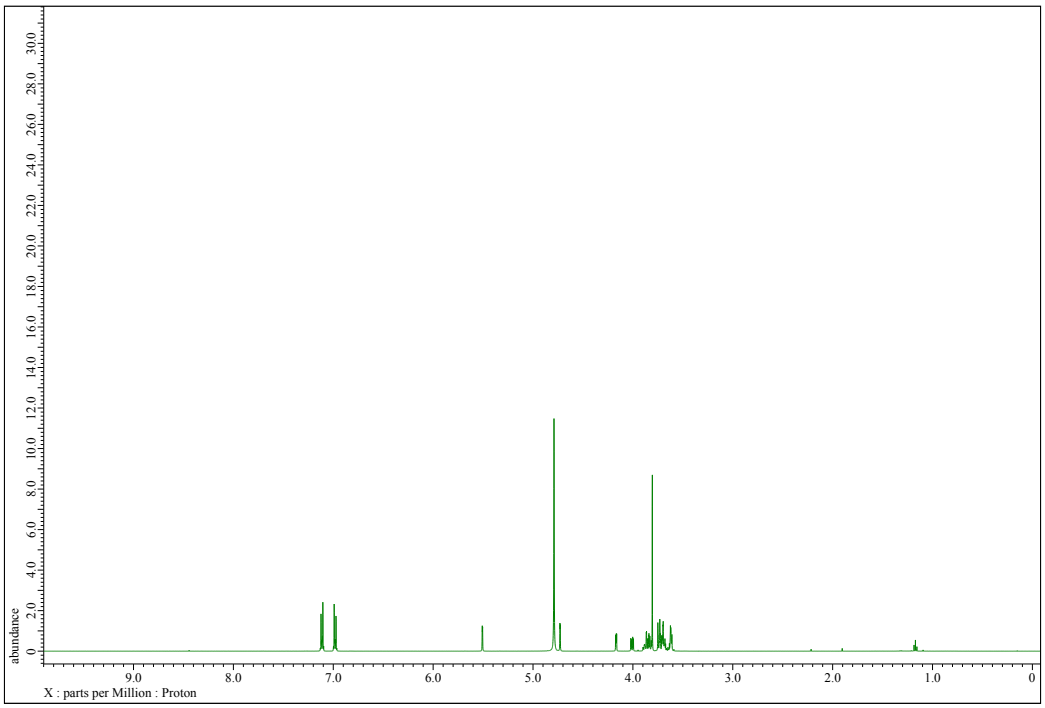
Compound **35** (^{1}H NMR) in $CDCl_3$



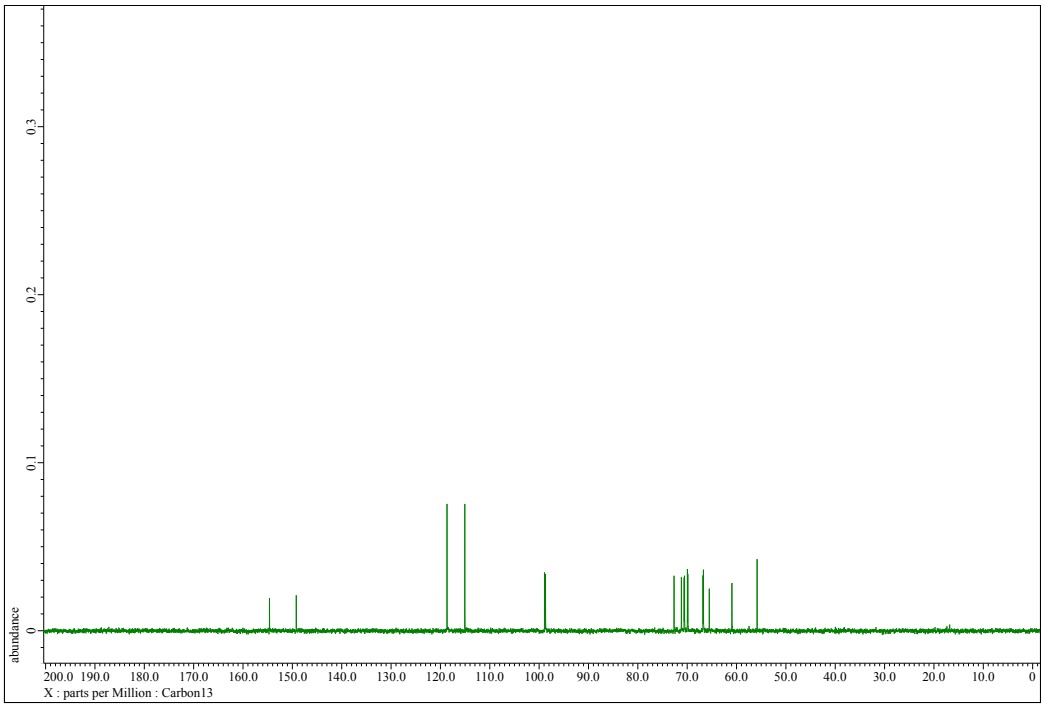
Compound **35** (^{13}C NMR) in $CDCl_3$



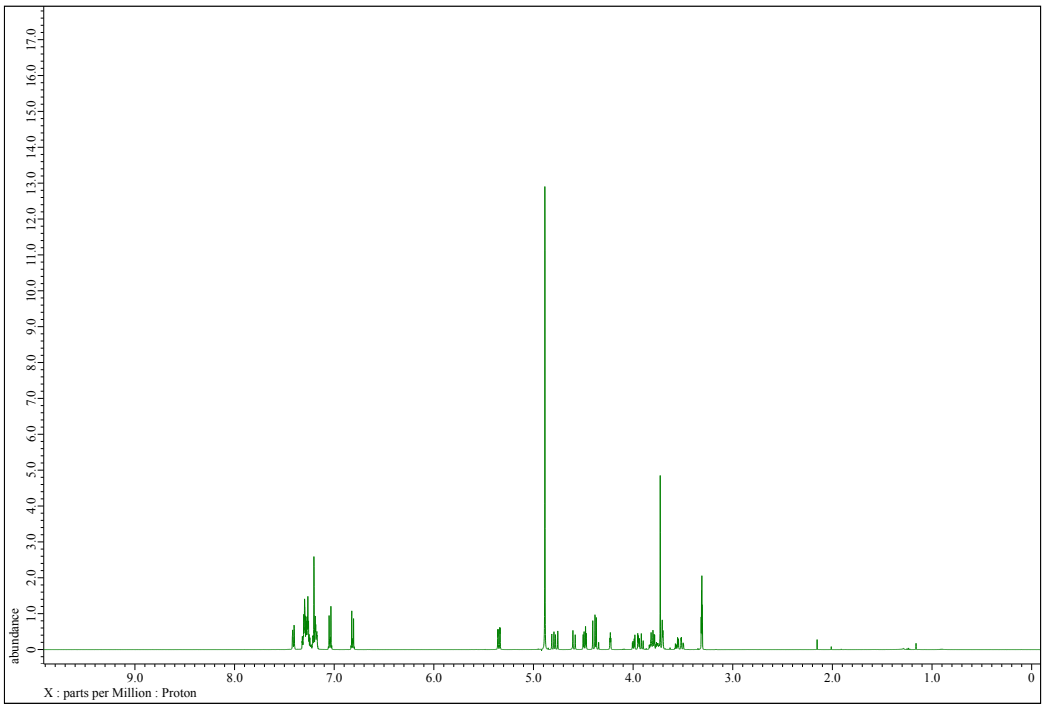
Compound **36** (^{1}H NMR) in D_2O



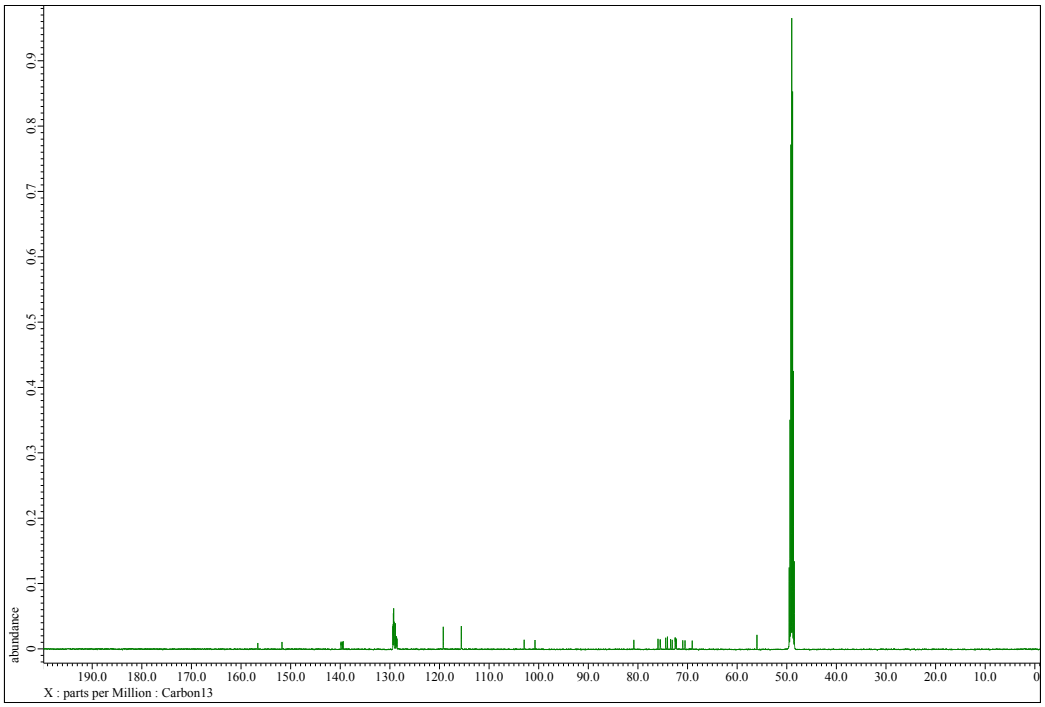
Compound **36** (^{13}C NMR) in D_2O



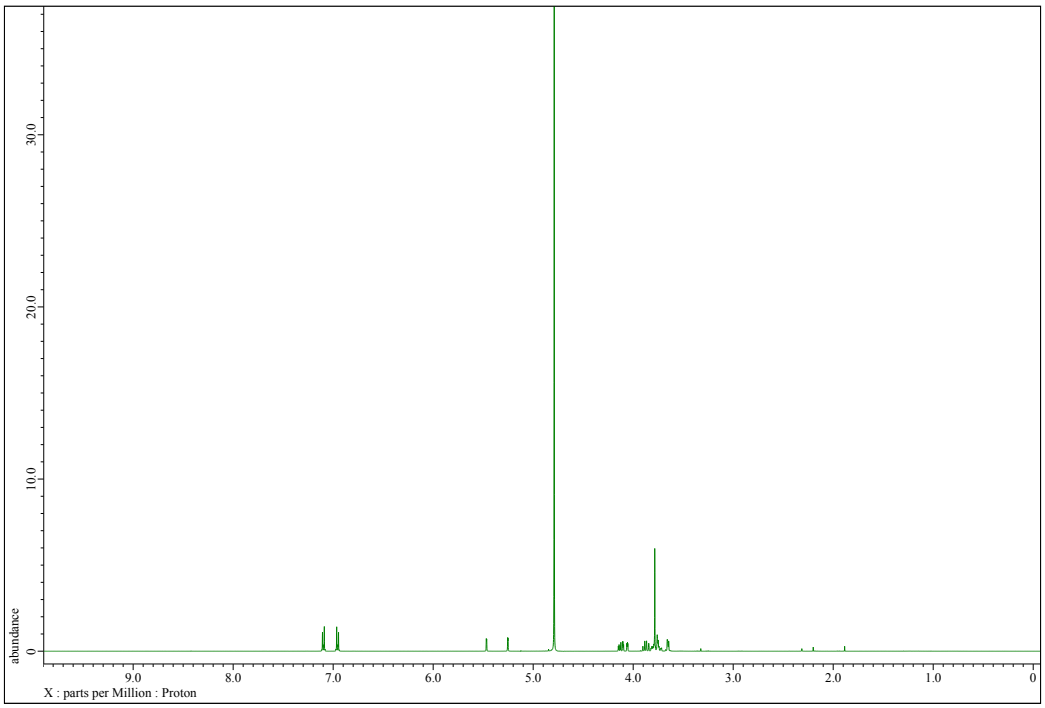
Compound **37** (^{1}H NMR) in CD_3OD



Compound **37** (^{13}C NMR) in CD_3OD



Compound **38** (^{1}H NMR) in D_2O



Compound **38** (^{13}C NMR) in D_2O