SUPPORTING INFORMATION

Investigation of the Remote Acyl Group Participation in Glycosylation from Conformational Perspectives by Using Trichloroacetimidate as the Acetyl Surrogate

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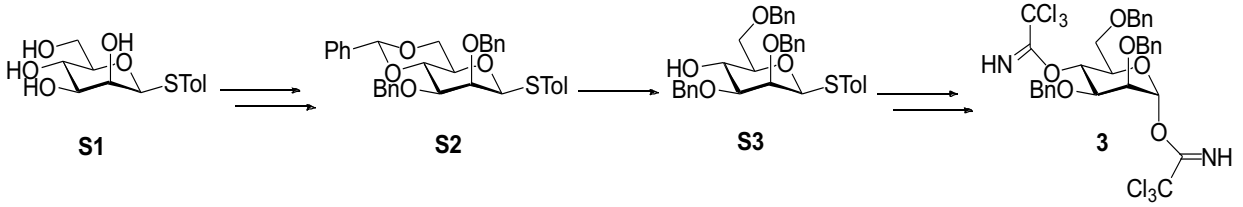
1. General Information

Unless otherwise noted, all materials and dry solvents were used as received from Adamas-beta® without further purification. ^{1}H and ^{13}C (data from HSQC) NMR spectra were recorded on Varian Mercury 300 MHz, 400 MHz or Bruker 600 MHz spectrometers. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) ($\delta = 0$). NMR data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet and/or multiple resonances), coupling constant in hertz (Hz), integration. All NMR signals were assigned on the basis of ^{1}H NMR, ^{13}C NMR, COSY, HSQC and HMBC experiments. Mass spectra were recorded on a Q-Tof Ultima Global mass spectrometer or a Shimadzu LCMS-IT-TOF mass spectrometer. TLC-analysis was performed on silica gel 60 F_{254} (Huang Hai Inc.) with detection by UV-absorption (254 nm) when applicable, and by spraying with a solution of $(NH_4)_6Mo_7O_{24}{\cdot}H_2O$ (25 g L^{-1}) in 5% sulfuric acid in ethanol followed by charring. All reactions were carried out under an argon atmosphere.

2. Preparation of *bis*- and *tris*- trichloroacetimidates

Scheme S1. Synthesis of Compound 3



p-Methylphenyl 2,3-*O*-di-Benzyl-4,6-*O*-benzylidene-1-thio-β-D-mannopyranoside (S2)

To a solution of **S1**[1] (3.1 g, 11.0 mmol) in CH_3CN (100 mL), CSA (511.1 mg, 2.2 mmol) was added. The mixture was kept stirring at r.t. for 6 h. Upon completion, the solvent was evaporated to form a residue as a yellow solid.

The above residue was dissolved in DMF (250 mL), NaH (60% dispersion in oil, 3.5 g, 88.0 mmol) was added at 0 °C. After stirred at 0 °C for 30 min, benzyl bromide was added to the above solution. The reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by water (100 mL), and then diluted by ethyl acetate (500 mL). The organic phase was separated and then washed with brine (200 mL). The organic phase was separated, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S2** as a white solid (5.6 g, 92%). The physical data matched those previously reported.[2]

p-Methylphenyl 2,3,6-*O*-tri-benzyl-1-thio-β-D-mannopyranoside (S3)

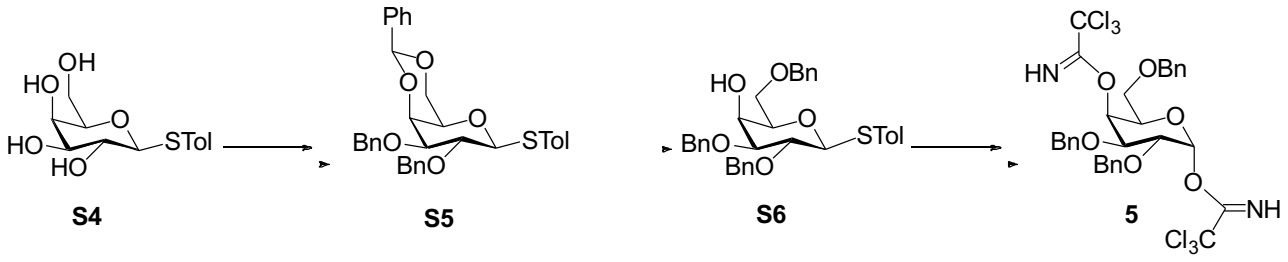
To a solution of **S2** (2.0 g, 3.6 mmol) in THF at 0 °C was added borane-trimethylamine complex (1.0 g, 14.4 mmol), $AlCl_3$ (2.88 g, 21.6 mmol) and H_2O (130 μL, 7.2 mmol), the reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by H_2O/1 M HCl (*v*:*v* = 1:1), and then neutralized by saturated aqueous $NaHCO_3$. The above mixture was diluted by ethyl acetate. The organic phase was separated, washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S3** as a white solid (1.8 g, 92%). The physical data matched those previously reported.[3]

1 2,3,6-tri-*O*-benzyl-4-*O*-trichloroacetimidoyl-α-D-mannopyranosyl trichloroacetimidate (3)

To a solution of **S3** (1.0 g, 1.8 mmol) in DCM (50 mL) at 0 ℃ was added NIS (445.5 mg, 2.0 mmol), TFA (154 μL) and H_2O (1.0 mL), the reaction mixture was kept stirring at r.t. for 6 h. upon completion, the above solution was quenched by $NaHSO_3$ and then diluted by DCM. The organic phase was separated and then washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow oil. The residue was purified by silica gel column chromatography to afford a colorless oil.

The above residue was dissolved in anhydrous DCM (50 mL) containing DBU (134 μL, 0.9 mmol) and trichloroacetonitrile (900 μL, 9.0 mmol), the reaction mixture was kept stirring at r.t. for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **3** as a colorless oil (543 mg, 41%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.55 (s, 1H), 7.35 (d, *J* = 5.7 Hz, 2H), 7.29 – 7.24 (m, 13H), 6.32 (s, 1H), 5.77 (t, *J* = 9.8 Hz, 1H), 4.71 (d, *J* = 4.5 Hz, 2H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.55 – 4.48 (m, 3H), 4.16 (s, 1H), 3.98 (d, *J* = 9.3 Hz, 1H), 3.80 (s, 1H), 3.69 – 3.63 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.19 (*C*=N-H), 159.63 (*C*=N-H), 137.42 – 126.92, 95.36, 90.64, 90.31, 75.91, 72.99, 72.95, 72.74, 72.15, 72.02, 71.81, 68.11, 65.26. ESI-MS: m/z calcd for $C_{31}H_{30}Cl_6N_2NaO_6^+$ $[M+Na]^+$ 759.0, found 759.0.

Scheme S2. Synthesis of Compound 5



***p*-Methylphenyl 2,3-*O*-di-Benzyl-4,6-*O*-benzylidene-1-thio-β-D-galactopyranoside (S5)**

To a solution of **S4**[2] (3.1 g, 11.0 mmol) in CH_3CN (100 mL), CSA (511.1 mg, 2.2 mmol) was added. The mixture was kept stirring at r.t. for 6 h. Upon completion, the solvent was evaporated to form a residue as a yellow solid.

The above residue was dissolved in DMF (250 mL), NaH (60% dispersion in oil, 3.5 g, 88.0 mmol) was added at 0 °C. After stirred at 0 ℃ for 30min, benzyl bromide was added to the above solution. The reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by water (100 mL), and then diluted by ethyl acetate (500 mL). The organic phase was separated and then washed with brine (200 mL). The organic phase was separated, dried ($MgSO_4$) and concentrated in vacuo

to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S5** as a white solid (5.8 g, 95%). The physical data matched those previously reported.[2]

***p*-Methylphenyl 2,3,6-*O*-tri-benzyl-1-thio-β-D-galactopyranoside (S6)**

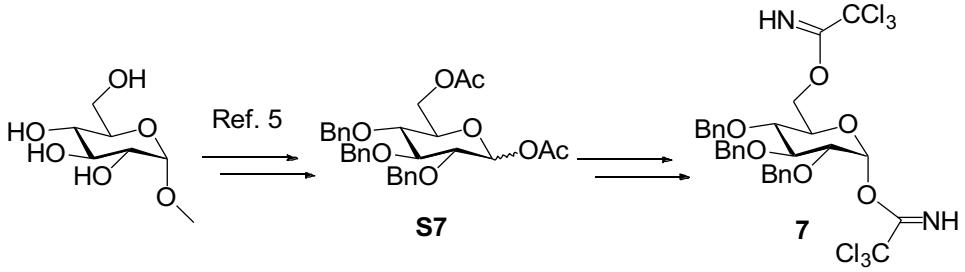
To a solution of **S5** (2.0 g, 3.6 mmol) in THF at 0 ℃ was added borane-trimethylamine complex (1.0 g, 14.4 mmol), $AlCl_3$ (2.88 g, 21.6 mmol) and H_2O (130 μL, 7.2 mmol), the reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by H_2O/1 M HCl (*v:v* = 1:1), and then neutralized by saturated aqueous $NaHCO_3$. The above mixture was diluted by ethyl acetate. The organic phase was separated, washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S6** as a white solid (1.6 g, 82%). The physical data matched those previously reported.[4]

2,3,6-tri-*O*-benzyl-4-*O*-trichloroacetimidoyl-α-D-galactopyranosyl trichloroacetimidate (5)

To a solution of **S6** (1.0 g, 1.8 mmol) in DCM (50 mL) at 0 ℃ was added NIS (445.5 mg, 2.0 mmol), TFA (154 μL) and H_2O (1.0 mL), the reaction mixture was kept stirring at r.t. for 6 h. upon completion, the above solution was quenched by $NaHSO_3$ and then diluted by DCM. The organic phase was separated and then washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow oil. The residue was purified by silica gel column chromatography to afford a colorless oil.

The above residue was dissolved in anhydrous DCM (50 mL) containing DBU (134 μL, 0.9 mmol) and trichloroacetonitrile (900 μL, 9.0 mmol), the reaction mixture was kept stirring at r.t, for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **5** as a colorless oil (596 mg, 45%). ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.59 (s, 1H, C=N*H*), 8.44 (s, 1H, C=N*H*), 7.31 – 7.27 (m, 13H), 7.25 – 7.24 (m, 2H), 6.53 (d, *J* = 2.9 Hz, 1H), 5.99 (s, 1H), 4.89 (d, *J* = 11.7 Hz, 1H), 4.73 (d, *J* = 2.5 Hz, 2H), 4.62 (d, *J* = 11.7 Hz, 1H), 4.51 (s, 1H), 4.46 (d, *J* = 11.7 Hz, 1H), 4.38 (t, *J* = 6.6 Hz, 1H), 4.11 (dd, *J* = 4.3, 2.8 Hz, 2H), 3.62 (dd, *J* = 6.7, 3.0 Hz, 2H). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 162.19 (*C*=NH), 161.25 (*C*=NH), 138.31 – 127.25, 95.06, 91.47 (-*C*Cl_3), 91.31 (-*C*Cl_3), 75.98, 73.83, 73.63, 73.01, 71.75, 71.68, 70.82, 67.77. ESI-MS: m/z calcd for $C_{31}H_{30}Cl_6N_2NaO_6^+$ $[M+Na]^+$ 759.0, found 759.0.

Scheme S3. Synthesis of Compound 7

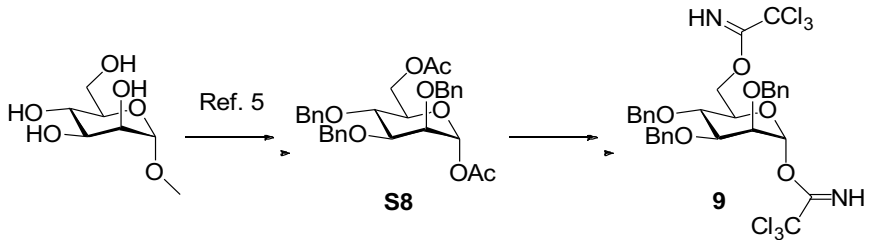


2,3,4-tri-*O*-benzyl-6-*O*-trichloroacetimidoyl-α-D-glucopyranosyl trichloroacetimidate (7)

To a solution of **S7**[5] (2.8 g, 5.3 mmol) in CH_3OH at r.t. was added sodium methanolate, the mixture was kept stirring for 12 h. then the mixture was neutralized by amberlite 120 [H^+] and concentrated *in vacuo* to form a yellow solid.

The above residue was dissolved in anhydrous DCM containing DBU (387 μL, 2.6 mmol) and trichloro-acetonitrile (2.7 mL, 26.5 mmol), the reaction mixture was kept stirring at r,t, for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **7** as a colorless oil (1.8 g, 45%, two steps). ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.60 (s, 1H, C=N-*H*), 8.36 (s, 1H, C=N-*H*), 7.35 – 7.27 (m, 15H, Ar-*H*), 6.51 (d, *J* = 3.5 Hz, 1H, H1), 4.98 (d, *J* = 10.8 Hz, 1H), 4.93 (d, *J* = 10.5 Hz, 1H), 4.85 (d, *J* = 10.8 Hz, 1H), 4.76 (d, *J* = 11.6 Hz, 1H), 4.71 (d, *J* = 11.6 Hz, 1H), 4.63 (d, *J* = 10.5 Hz, 1H), 4.58 (dd, *J* = 12.0, 1.8 Hz, 1H), 4.53 (dd, *J* = 12.0, 3.8 Hz, 1H), 4.18 (ddd, *J* = 10.2, 3.6, 1.7 Hz, 1H), 4.10 (t, *J* = 9.3 Hz, 1H), 3.79 – 3.75 (m, 2H). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 162.54 (*C*=NH), 161.26 (*C*=NH), 138.3 – 127.61, 94.01, 91.18 (-*C*Cl_3), 91.17 (-*C*Cl_3), 81.37, 79.50, 75.86, 75.60, 72.99, 71.55, 67.23. ESI-MS: m/z calcd for $C_{31}H_{30}Cl_6N_2NaO_6^+$ $[M+Na]^+$ 759.0, found 759.0.

Scheme S4. Synthesis of Compound 9

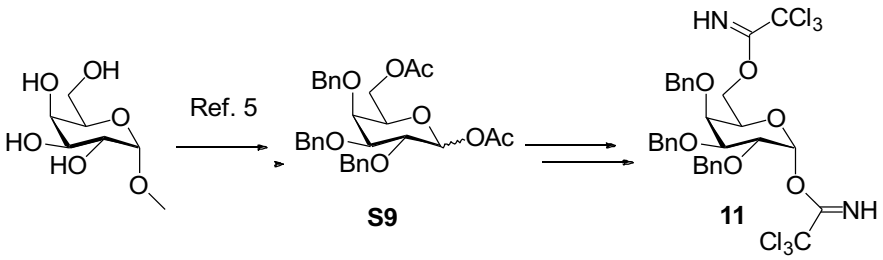


2,3,4-tri-*O*-benzyl-6-*O*-trichloroacetimidoyl-α-D-mannopyranosyl trichloroacetimidate (9)

To a solution of **S8**[5] (2.7 g, 5.1 mmol) in CH_3OH at r.t. was added sodium methanolate, the mixture was kept stirring for 12 h. then the mixture was neutralized by amberlite 120 [H^+] and concentrated *in vacuo* to form a yellow solid.

The above residue was dissolved in anhydrous DCM containing DBU (372 µL, 2.5 mmol) and trichloroacetonitrile (2.6 mL, 25.5 mmol), the reaction mixture was kept stirring at r,t, for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **9** as a colorless oil (1.8 g, 44%, two steps). ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.56 (s, 1H, C=N-*H*), 8.35 (s, 1H, C=N-*H*), 6.35 (s, 1H), 4.98 (d, *J* = 10.5 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.74 – 4.69 (m, 2H), 4.67 – 4.63 (m, 4H), 4.56 (dd, *J* = 11.8, 4.1 Hz, 1H), 4.24 (t, *J* = 9.7 Hz, 1H), 4.11 (dd, *J* = 9.9, 3.5 Hz, 1H), 3.99 (dd, *J* = 9.5, 2.9 Hz, 1H), 3.87 (s, 1H). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 162.73 (*C*=NH), 160.38 (*C*=NH), 138.00 – 127.63, 95.63, 91.28 (-*C*Cl_3), 90.91 (-*C*Cl_3), 78.92, 75.60, 73.96, 73.94, 72.95, 72.68, 72.47, 67.48. ESI-MS: m/z calcd for $C_{31}H_{30}Cl_6N_2NaO_6^+$ [M+Na] $^+$ 759.0, found 759.0.

Scheme S5. Synthesis of Compound 11

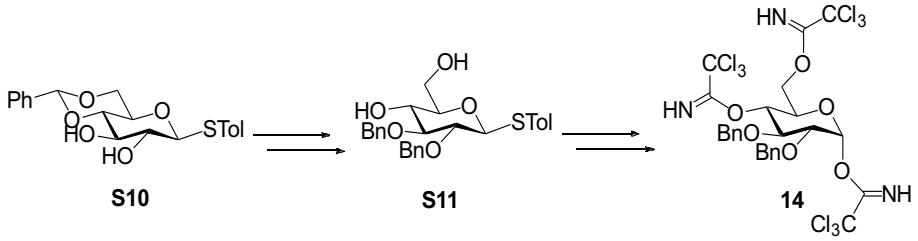


2,3,4-tri-*O*-benzyl-6-*O*-trichloroacetimidoyl-α-D-galactopyranosyl trichloroacetimidate (11)

To a solution of **S9**[5] (2.6 g, 4.9 mmol) in CH_3OH at r.t. was added sodium methanolate, the mixture was kept stirring for 12 h. Then the mixture was neutralized by amberlite 120 [H^+] and concentrated *in vacuo* to form a yellow solid.

The above residue was dissolved in anhydrous DCM containing DBU (357 µL, 2.4 mmol) and trichloroacetonitrile (2.5 mL, 24.5 mmol), the reaction mixture was kept stirring at r,t, for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **11** as a colorless oil (1.6 g, 42%, two steps). ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.48 (s, 1H, C=N-*H*), 8.25 (s, 1H, C=N-*H*), 7.29 - 7.18 (m, 15H, Ar-*H*), 6.47 (d, *J* = 3.4 Hz, 1H), 4.96 (d, *J* = 11.2 Hz, 1H), 4.83 (d, *J* = 11.8 Hz, 1H), 4.71 (d, *J* = 11.9 Hz, 1H), 4.69 (s, 2H), 4.57 (d, *J* = 11.2 Hz, 1H), 4.40 – 4.37 (m, 1H), 4.30 – 4.26 (m, 2H), 4.21 (dd, *J* = 10.0, 3.5 Hz, 1H), 3.99 (dd, *J* = 10.0, 2.6 Hz, 1H), 3.96 (s, 1H). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 161.65 (*C*=NH), 160.47 (*C*=NH), 137.83 – 126.88, 94.27, 90.75 (-*C*Cl_3), 90.48 (-*C*Cl_3), 77.41, 75.14, 74.32, 74.31, 72.81, 72.37, 69.97, 66.78. ESI-MS: m/z calcd for $C_{31}H_{30}Cl_6N_2NaO_6^+$ [M+Na] $^+$ 759.0, found 759.0.

Scheme S6. Synthesis of Compound 14



To a solution of **S10**[2] (2.0 g, 5.3 mmol) was dissolved in DMF (250 mL), NaH (60% dispersion in oil, 3.5 g, 88.0 mmol) was added at 0 °C. After stirred at 0 ℃ for 30min, benzyl bromide was added to the above solution. The reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by water (100 mL), and then diluted by ethyl acetate (500 mL). The organic phase was separated and then washed with brine (200 mL). The organic phase was separated, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow solid.

The above residue was dissolved in DCM (100 mL) at 0 ℃ was added TFA (16 mL) and H_2O (4 mL), the reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by saturated aqueous $NaHCO_3$, and then diluted by DCM. The organic phase was separated, washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S11** as a white solid (2.3 g, 92%). The physical data matched those previously reported.[6]

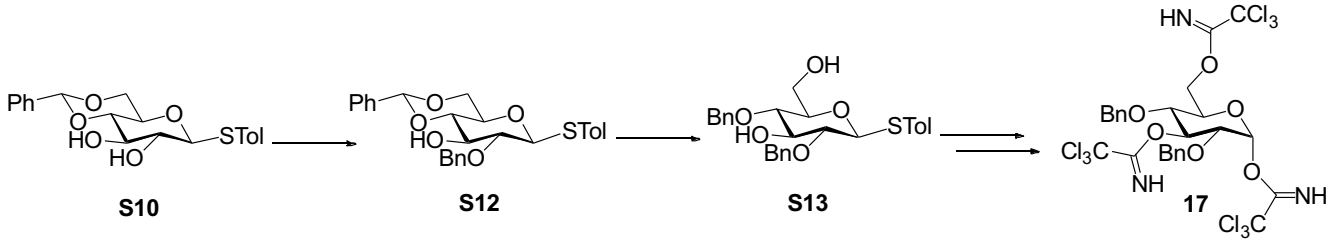
2,3-di-*O*-benzyl-4,6-di-*O*-trichloroacetimidoyl-α-D-glucopyranosyl trichloroacetimidate (15)

To a solution of **S11** (1.0 g, 2.1 mmol) in DCM (50 mL) at 0 ℃ was added NIS (512.0 mg, 2.3 mmol), TFA (177 μL, 2.3 mmol) and H_2O (1.0 mL), the reaction mixture was kept stirring at r.t. for 6 h. upon completion, the above solution was quenched by $NaHSO_3$ and then diluted by DCM. The organic phase was separated and then washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow oil. The residue was purified by silica gel column chromatography to afford a colorless oil.

The above residue was dissolved in anhydrous DCM (50 mL) containing DBU (150 μL, 1.0 mmol) and trichloroacetonitrile (3.2 mL, 31.5 mmol), the reaction mixture was kept stirring at r,t, for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **15** as a colorless oil (530 mg, 32%). ^{1}H NMR: (400 MHz, $CDCl_3$): δ 8.65 (s, 1H, C=N*H*), 8.64 (s, 1H, C=N*H*), 8.29 (s, 1H, C=N*H*), 7.31 – 7.25 (m, 10H), 6.48 (s, 1H), 5.49 (t, *J* = 9.4 Hz, 1H), 4.87

(d, J = 10.8 Hz, 1H), 4.78 (d, J = 10.6 Hz, 1H), 4.72 (s, 2H), 4.48 (d, J = 10.7 Hz, 1H), 4.40 (d, J = 10.8 Hz, 2H), 4.17 (t, J = 9.3 Hz, 1H), 3.87 (d, J = 8.2 Hz, 1H). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 162.49 (*C*=NH), 161.79 (*C*=NH), 161.02 (*C*=NH), 137.99 – 127.64, 93.69, 91.08 (-*C*Cl_3), 91.04 (-*C*Cl_3), 79.00, 78.98, 75.58, 73.89, 73.27, 70.45, 67.01. ESI-MS: m/z calcd for $C_{26}H_{24}Cl_9N_3NaO_6^+$ $[M+Na]^+$ 811.9, found 811.9.

Scheme S7. Synthesis of Compound 17



***p*-Methylphenyl 2-*O*-Benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (S12)**

S10[2] (2.0 g, 5.3 mmol) were allowed to react with benzyl bromide (1.1 equiv) in dry acetonitrile (1 mL) at 80 ℃ for 12 h, in the presence of $[Fe(dibm)_3]$[7] (0.1 equiv) and K_2CO_3 (1.5 equiv). The reaction mixture was directly purified by silica gel column chromatography to afford **S12** (2.1g, 85%) as a white solid. The physical data matched those previously reported.[7]

***p*-Methylphenyl 2,4-di-*O*-Benzyl-1-thio-β-D-glucopyranoside (S13)**

To a solution of **S12** (2.0 g, 4.3 mmol) in anhydrous DCM (20 mL) at r.t. was added 1 M borane-tetrahydrofuran complex (21.5 mL, 21.5 mmol) and $Cu(OTf)_2$ (234 mg, 0.65 mmol), the reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by saturated aqueous $NaHCO_3$, and then diluted by ethyl acetate. The organic phase was separated, washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S13** as a colorless oil (2.0 g, 99%). The physical data matched those previously reported.[3]

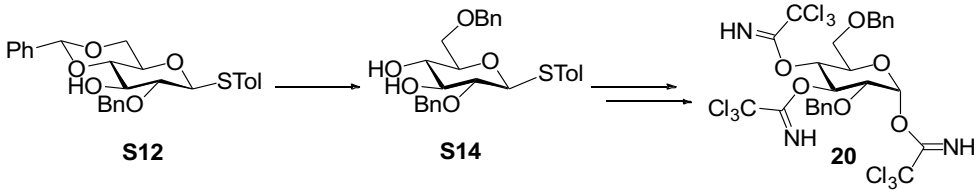
2,4-di-*O*-benzyl-3,6-di-*O*-trichloroacetimidoyl-α-D-glucopyranosyl trichloroacetimidate (17)

To a solution of **S13** (1.0 g, 2.1 mmol) in DCM (50 mL) at 0 ℃ was added NIS (512.0 mg, 2.3 mmol), TFA (177 μL, 2.3 mmol) and H_2O (1.0 mL), the reaction mixture was kept stirring at r.t. for 6 h. upon completion, the above solution was quenched by $NaHSO_3$ and then diluted by DCM. The organic phase

was separated and then washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow oil. The residue was purified by silica gel column chromatography to afford a colorless oil.

The above residue was dissolved in anhydrous DCM (50 mL) containing DBU (150 μL, 1.0 mmol) and trichloroacetonitrile (3.2 mL, 31.5 mmol), the reaction mixture was kept stirring at r,t, for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **17** as a colorless oil (148 mg, 9%). ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.66 (s, 1H, C=N*H*), 8.58 (s, 1H, C=N*H*), 8.38 (s, 1H, C=N*H*), 7.29 – 7.27 (m, 10H, Ar-*H*), 6.44 (d, *J* = 3.6 Hz, 1H), 5.99 (t, *J* = 9.6 Hz, 1H), 4.82 (d, *J* = 10.4 Hz, 1H), 4.71 (d, *J* = 11.8 Hz, 1H), 4.65 (s, 1H), 4.59 (dd, *J* = 12.7, 2.4 Hz, 2H), 4.52 – 4.49 (m, 1H), 4.29 (ddd, *J* = 10.1, 3.8, 1.7 Hz, 1H), 3.94 (d, *J* = 9.7 Hz, 1H), 3.91 (dd, *J* = 8.5, 4.8 Hz, 1H). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 162.43 (*C*=NH), 162.16 (*C*=NH), 161.13 (*C*=NH), 137.44 – 127.65, 93.65, 91.55 (-*C*Cl_3), 91.16 (-*C*Cl_3), 90.97 (-*C*Cl_3), 78.51, 77.54, 75.90, 75.01, 73.32, 71.29, 67.07. ESI-MS: m/z calcd for $C_{26}H_{24}Cl_9N_3NaO_6^+$ $[M+Na]^+$ 811.9, found 811.9.

Scheme S8. Synthesis of Compound 20



***p*-Methylphenyl 2,6-di-*O*-Benzyl-1-thio-β-D-glucopyranoside (S14)**

To a solution of **S12** (2.0 g, 4.3 mmol) in THF (100 mL) at 0 ℃ was added borane-trimethylamine complex (1.25 g, 17.2 mmol), $AlCl_3$ (3.4 g, 25.8 mmol) and H_2O (155 μL, 7.2 mmol), the reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by H_2O/1 M HCl (*v*:*v* = 1:1), and then neutralized by saturated aqueous $NaHCO_3$. The above mixture was diluted by ethyl acetate. The organic phase was separated, washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S14** (1.7 g, 85%) as a white solid. The physical data matched those previously reported.[3]

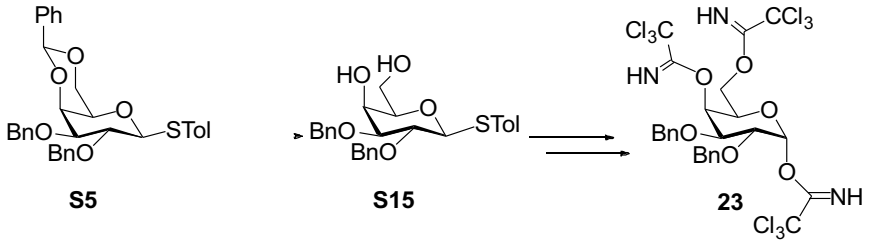
2,6-di-*O*-benzyl-3,4-di-*O*-trichloroacetimidoyl-α-D-glucopyranosyl trichloroacetimidate (20)

To a solution of **S14** (1.0 g, 2.1 mmol) in DCM (50 mL) at 0 ℃ was added NIS (512.0 mg, 2.3 mmol), TFA (177 μL, 2.3 mmol) and H_2O (1.0 mL), the reaction mixture was kept stirring at r.t. for 6 h. upon completion, the above solution was quenched by $NaHSO_3$ and then diluted by DCM. The organic phase

was separated and then washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow oil. The residue was purified by silica gel column chromatography to afford a colorless oil.

The above residue was dissolved in anhydrous DCM (50 mL) containing DBU (150μL, 1.0 mmol) and trichloroacetonitrile (3.2 mL, 31.5 mmol), the reaction mixture was kept stirring at r,t, for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **20** as a colorless oil (115 mg, 7%). ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.64 (s, 1H), 8.53 (s, 2H), 7.37 – 7.28 (m, 11H), 6.47 (s, 1H), 6.07 (t, *J* = 9.7 Hz, 1H), 5.72 (t, *J* = 9.9 Hz, 1H), 4.71 (d, *J* = 12.2 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 11.3 Hz, 2H), 4.29 (d, *J* = 9.8 Hz, 1H), 3.99 (d, *J* = 9.7 Hz, 1H), 3.62 (dd, *J* = 24.7, 11.2 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.39 (*C*=NH), 160.74 (*C*=NH), 160.42 (*C*=NH), 136.96 – 127.18, 93.20, 90.64 (-*C*Cl_3), 90.38 (-*C*Cl_3), 90.27 (-*C*Cl_3), 75.26, 72.88, 72.77, 71.48, 71.15, 66.92. ESI-MS: m/z calcd for $C_{26}H_{24}Cl_9N_3NaO_6^+$ $[M+Na]^+$ 811.9, found 811.9.

Scheme S9. Synthesis of Compound 23



***p*-Methylphenyl 2,3-*O*-di-Benzyl-1-thio-β-D-galactopyranoside (S15)**

To a solution of **S5** (2.0 g, 3.6 mmol) in DCM (100 mL) at 0 ℃ was added TFA (16 mL) and H_2O (4 mL), the reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by saturated aqueous $NaHCO_3$, and then diluted by DCM. The organic phase was separated, washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S15** as a white solid (1.3 g, 81%). The physical data matched those previously reported.[6]

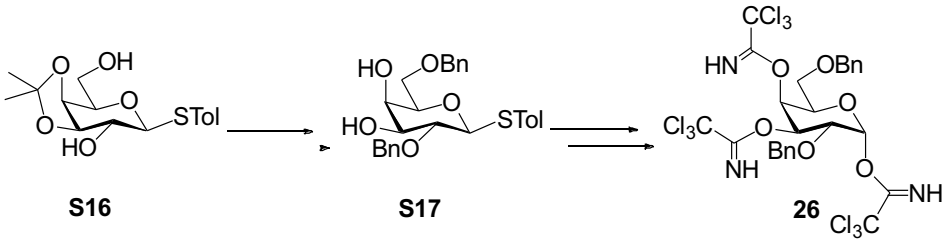
2,3-di-*O*-benzyl-4,6-di-*O*-trichloroacetimidoyl-α-D-galactopyranosyl trichloroacetimidate (23)

To a solution of **S15** (1.0 g, 2.1 mmol) in DCM (50 mL) at 0 ℃ was added NIS (512.0 mg, 2.3 mmol), TFA (177 μL, 2.3 mmol) and H_2O (1.0 mL), the reaction mixture was kept stirring at r.t. for 6 h. upon completion, the above solution was quenched by $NaHSO_3$ and then diluted by DCM. The organic phase

was separated and then washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow oil. The residue was purified by silica gel column chromatography to afford a colorless oil.

The above residue was dissolved in anhydrous DCM (50 mL) containing DBU (150 μL, 1.0 mmol) and trichloroacetonitrile (3.2 mL, 31.5 mmol), the reaction mixture was kept stirring at r,t, for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **23** as a colorless oil (430 mg, 26%). ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.55 (s, 1H, C=N*H*), 8.47 (s, 1H, C=N*H*), 8.36 (s, 1H, C=N*H*), 7.34 – 7.27 (m, 10H, Ar-*H*), 6.39 (s, 1H), 5.80 – 5.77 (m, 1H), 4.71 (d, *J* = 11.9 Hz, 1H), 4.64 (dd, *J* = 11.6, 4.6 Hz, 1H), 4.62 – 4.59 (m, 2H), 4.55 (d, *J* = 11.9 Hz, 1H), 4.51 (d, *J* = 6.8 Hz, 2H), 4.27 (d, *J* = 2.3 Hz, 1H), 4.19 – 4.17 (m, 1H). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 161.72 (*C*=NH), 161.47 (*C*=NH), 160.21 (*C*=NH), 136.64, 136.54, 127.84, 127.76, 127.37, 127.33, 127.29, 103.34, 90.48 (-*C*Cl_3), 90.40 (-*C*Cl_3), 90.36 (-*C*Cl_3), 86.01, 82.13, 81.28, 72.75, 71.85, 71.58, 66.05. ESI-MS: m/z calcd for $C_{26}H_{24}Cl_9N_3NaO_6^+$ $[M+Na]^+$ 811.9, found 811.9.

Scheme S10. Synthesis of Compound 26



***p*-Methyphenyl 2,6-*O*-di-Benzyl-1-thio-β-D-galactopyranoside (S17)**

To a solution of **S16**[7] (510 mg, 1.56 mmol) in DMF (20 mL) at 0 °C was added NaH (60% dispersion in oil, 500 mg, 12.5 mmol). After stirred at 0 ℃ for 30 min, benzyl bromide (950 μL, 7.82 mmol) was added to the above solution. The reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by water (20 mL), and then diluted by ethyl acetate (50 mL). The organic phase was separated and then washed with brine (20 mL). The organic phase was separated, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow solid.

The above residue was dissolved in AcOH/H_2O (*v*:*v* = 4:1, 10 mL). The solution was kept stirring at 80 ℃ for 3 h. Upon completion, the reaction mixture was quenched by saturated aqueous $NaHCO_3$, and then diluted by ethyl acetate. The organic phase was separated, washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow solid. The residue was purified by silica gel column

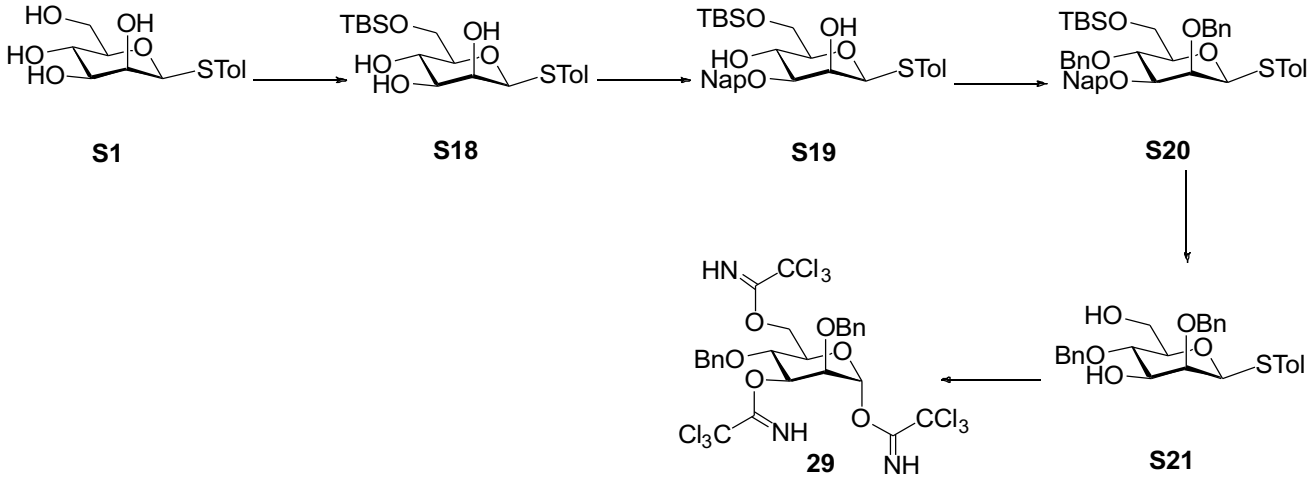
chromatography to afford **S17** (545 mg, 75%) as a colorless oil. The physical data matched those previously reported.[7]

2,6-di-*O*-benzyl-3,4-di-*O*-trichloroacetimidoyl-α-D-galactopyranosyl trichloroacetimidate (26)

To a solution of **S17** (545 mg, 1.17 mmol) in DCM (20 mL) was added NIS (200.0 mg, 1.20 mmol), TFA (90 μL, 1.20 mmol) and H_2O (0.5 mL). The reaction mixture was kept stirring at r.t. for 6 h. upon completion, the above solution was quenched by $NaHSO_3$ and then diluted by DCM. The organic phase was separated and then washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow oil. The residue was purified by silica gel column chromatography to afford a colorless oil.

The above residue was dissolved in anhydrous DCM (10 mL) containing DBU (75 μL, 0.5 mmol) and trichloroacetonitrile (1.6 mL, 16.4 mmol), the reaction mixture was kept stirring at r,t, for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **26** as a colorless oil (172 mg, 11%, 2 steps). ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.66 (s, 1H, C=N*H*), 8.58 (s, 1H, C=N*H*), 8.49 (s, 1H, C=N*H*), 7.35 – 7.30 (m, 10H, Ar-*H*), 6.46 (d, *J* = 1.6 Hz, 1H), 6.23 (dd, *J* = 9.7, 1.6 Hz, 1H), 5.79 (t, *J* = 5.8 Hz, 1H), 4.83 (dd, *J* = 9.7, 1.5 Hz, 1H), 4.75 (s, 1H), 4.60 (s, 1H), 4.56 (d, *J* = 11.9 Hz, 1H), 4.54 (s, 1H), 3.96 (t, *J* = 1.6 Hz, 1H), 3.85 (dd, *J* = 9.9, 5.9 Hz, 1H), 3.74 (dd, *J* = 9.9, 7.3 Hz, 1H). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 160.60 (*C*=NH), 159.61 (*C*=NH), 157.29 (*C*=NH), 137.04 – 127.10, 90.60 (-*C*Cl_3), 90.23 (-*C*Cl_3), 89.77 (-*C*Cl_3), 76.85, 73.06, 72.81, 72.21, 71.34, 70.55, 66.83, 65.58. ESI-MS: m/z calcd for $C_{26}H_{24}Cl_9N_3NaO_6^+$ $[M+Na]^+$ 811.9, found 811.9.

Scheme S11. Synthesis of Compound 29



***p*-Methylphenyl 6-*O*-*tert*-butyldimethylsilyl-1-thio-β-D-mannopyranoside (S18)**

To a solution of **S1** (3.1 g, 11.0 mmol), TEA (5.0 mL, 36.3 mmol) and DMAP (67 mg, 0.5 mmol) in anhydrous DMF (30 mL) was added dropwise TBDMSCl (2.0 g, 13.2 mmol) solution of DMF (10 mL) at 0 ℃. The reaction mixture was kept stirring at r.t. for 24 h. Upon completion, the reaction mixture was concentrated *in vacuo* to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S18** as a colorless oil (3.3g, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 2H, 2 Ar-H), 7.11 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 4.46 (d, *J* = 9.6 Hz, 1H), 4.08 (s, 1H), 3.96 – 3.85 (m, 2H), 3.66 (t, *J* = 9.2 Hz, 1H), 3.58 (d, *J* = 6.4 Hz, 1H), 3.51 (d, *J* = 4.7 Hz, 1H), 2.33 (s, 3H, PhC*H*$_3$), 0.90 (s, 9H, -C(C*H*$_3$)$_3$), 0.11 (s, 3H, -C*H*$_3$), 0.09 (s, 3H, -C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.22 – 128.35, 88.77, 78.01, 74.97, 69.85, 69.40, 63.18, 25.82, 21.17, 18.22, -5.45, -5.46. ESI-MS: m/z calcd for $C_{19}H_{32}NaO_5SSi^+$ $[M+Na]^+$ 423.2, found 423.2.

_p_-Methylphenyl 3-_O_-(2-methyl-naphthyl)-6-_O-tert_-butyldimethylsilyl-1-thio-β-D-mannopyranoside (S19)

To a solution of **S18** (1.0 g, 2.5 mmol) in toluene (50 mL) was added dibutyltin oxide (685 mg, 2.7 mmol), the mixture was refluxed for 6 h in Dean-Stark tube. After cooled to 60 ℃, tetrabutylammonium bromide (890 mg, 2.7 mmol) and NapBr (830 mg, 3.7 mmol) were added to the mixture and stirred at 60 ℃ for 24h. Upon completion, the reaction mixture was concentrated *in vacuo* to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S19** as a colorless oil (700 mg, 52%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 10.4, 6.5 Hz, 4H, Ar-*H*), 7.52 – 7.44 (m, 5H, Ar-*H*), 7.09 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 4.91 (s, 2H), 4.44 (d, *J* = 9.7 Hz, 1H), 4.10 (s, 1H), 3.93 – 3.79 (m, 3H), 3.50 – 3.42 (m, 2H), 2.71 (d, *J* = 1.9 Hz, 1H, -O*H*), 2.49 (d, *J* = 2.0 Hz, 1H, -O*H*), 2.32 (s, 3H, PhC*H*$_3$), 0.89 (s, 9H, -C(C*H*$_3$)$_3$), 0.08 (s, 3H, -C*H*$_3$), 0.07 (s, 3H, -C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.22 – 128.35, 88.77, 78.01, 74.97, 69.85, 69.40, 63.18, 25.82, 21.17, 18.22, -5.45, -5.46. ESI-MS: m/z calcd for $C_{30}H_{40}NaO_5SSi^+$ $[M+Na]^+$ 563.2, found 563.2.

_p_-Methylphenyl 2,4-di-_O_-Benzyl-3-_O_-(2-methyl-naphthyl)-6-_O-tert_-butyldimethylsilyl-1-thio-β-D-mannopyranoside (S20)

To a solution of **S19** (540 mg, 1.0 mmol) in DMF (100 mL) at 0 °C was added NaH (60% dispersion in oil, 320 mg, 8.0 mol). After stirred at 0 ℃ for 30min, benzyl bromide (0.6 mL, 5.0 mmol) was added to the above solution. The reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by water (100 mL), and then diluted by ethyl acetate (500 mL). The organic phase was separated and then washed with brine (200 mL). The organic phase was separated, dried ($MgSO_4$)

and concentrated *in vacuo* to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S20** as a white solid (450 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 3H, Ar-*H*), 7.73 – 7.68 (m, 1H, Ar-*H*), 7.47 (dd, *J* = 8.6, 3.0 Hz, 5H, Ar-*H*), 7.41 – 7.29 (m, 10H, Ar-*H*), 7.01 (d, *J* = 7.9 Hz, 2H, Ar-*H*), 5.02 (d, *J* = 11.4 Hz, 1H), 4.89 (s, 2H), 4.78 (q, *J* = 10.3 Hz, 2H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.59 (d, *J* = 9.6 Hz, 1H), 3.97 (d, *J* = 2.3 Hz, 1H), 3.93 (d, *J* = 9.4 Hz, 1H), 3.74 (dd, *J* = 6.7, 3.6 Hz, 2H), 3.65 (dd, *J* = 9.2, 2.7 Hz, 1H), 3.43 (t, *J* = 6.7 Hz, 1H), 2.30 (s, 3H, PhC*H*$_3$), 0.85 (s, 9H, -C(C*H*$_3$)$_3$), 0.02 (s, 3H, -C*H*$_3$), 0.01 (s, 3H, -C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.99 – 125.67, 88.01, 84.09, 78.79, 75.59, 74.49, 73.49, 72.80, 61.42, 25.86, 21.11, 18.17, -5.39, -5.48. ESI-MS: m/z calcd for $C_{44}H_{52}NaO_5SSi^+$ $[M+Na]^+$ 743.3, found 743.3.

_p_-Methylphenyl 2,4-di-_O_-Benzyl-1-thio-β-D-mannopyranoside (S21)

S20 (450 mg, 0.6 mmol) was dissolved in TFA/toluene (*v:v* = 10:1). The solution was kept stirring at 0 ℃ for 3h. Upon completion, the reaction mixture was concentrated in vacuo to form a residue as a yellow solid. The residue was dissolved in DCM/MeOH (*v:v* = 2:1) containing MeONa and stirred at r.t. for 2 h. the reaction mixture was concentrated *in vacuo* and purified by silica gel column chromatography to afford **S21** as a colorless oil (200 mg, 72%). ^{1}H NMR (400 MHz, $CDCCl_3$) δ 7.45 – 7.32 (m, 12H, Ar-*H*), 7.10 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 5.71 (d, *J* = 5.0 Hz, 1H), 4.92 (d, *J* = 11.5 Hz, 1H), 4.81 (d, *J* = 11.1 Hz, 1H), 4.66 (d, *J* = 11.6 Hz, 1H), 4.57 (d, *J* = 11.1 Hz, 1H), 4.30 (d, *J* = 5.3 Hz, 1H), 4.18 (dd, *J* = 9.7, 5.3 Hz, 1H), 4.00 (d, *J* = 9.6 Hz, 1H), 3.92 (s, 1H), 3.77 – 3.70 (m, 1H), 3.52 (s, 1H), 2.32 (s, 3H, -C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.97 – 127.98, 86.90, 76.63, 75.78, 74.90, 71.99, 71.39, 71.24, 62.35, 21.05. ESI-MS: m/z calcd for $C_{27}H_{30}NaO_5S^+$ $[M+Na]^+$ 489.2, found 489.2.

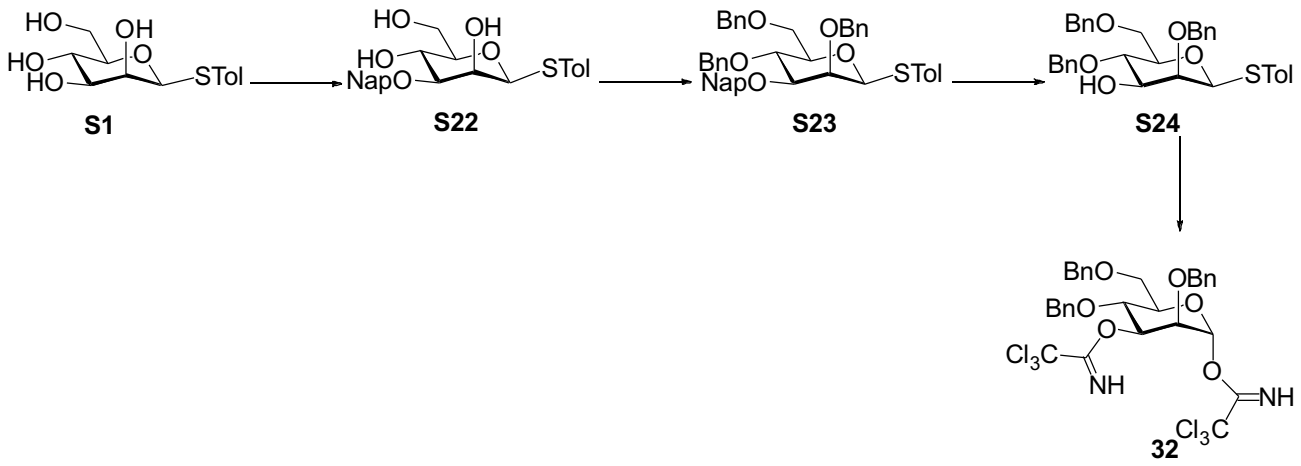
2,4-di-_O_-benzyl-3,6-di-_O_-trichloroacetimidoyl-α-D-mannopyranosyl trichloroacetimidate (29)

S29 (200 mg, 0.4 mmol) was dissolved in DCM (10 mL), NIS (100 mg, 0.44 mmol), TFA (34μL, 0.44 mmol) and H_2O (0.1 mL) was added at 0 ℃. The reaction mixture was kept stirring at r.t. for 6 h. upon completion, the above solution was quenched by $NaHSO_3$ and then diluted by DCM. The organic phase was separated and then washed with brine, dried ($MgSO_4$) and concentrated *in vacuo* to form a residue as a yellow oil. The residue was purified by silica gel column chromatography to afford a colorless oil.

The above residue was dissolved in anhydrous DCM (5 mL) containing DBU (120μL, 0.2 mmol) and trichloroacetonitrile (0.6 mL, 6.0 mmol), the reaction mixture was kept stirring at r,t, for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **29** as a colorless oil (150 mg, 48%, 2 steps). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (s, 1H, C=N*H*),

8.56 (s, 1H, C=N*H*), 8.35 (s, 1H, C=N*H*), 6.50 (d, *J* = 2.1 Hz, 1H), 7.35 – 7.28 (m, 10H, Ar-*H*), 5.54 (d, *J* = 10.3 Hz, 1H), 4.93 (d, *J* = 10.8 Hz, 1H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.71 (d, *J* = 11.8 Hz, 1H), 4.55 (d, *J* = 10.8 Hz, 1H), 4.51 (t, *J* = 6.1 Hz, 1H), 4.48 – 4.43 (m, 2H), 4.39 (dd, *J* = 10.0, 2.6 Hz, 1H), 4.34 (dd, *J* = 10.7, 6.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.19 (*C*=NH), 162.09 (*C*=NH), 161.10 (*C*=NH), 137.78, 137.64, 128.45, 128.32, 127.96, 127.73, 127.60, 94.65, 91.24 (-*C*Cl_3), 91.14 (-*C*Cl_3), 90.98 (-*C*Cl_3), 77.75, 75.24, 73.91, 73.36, 73.27, 69.99, 66.97. ESI-MS: m/z calcd for $C_{26}H_{24}Cl_9N_3NaO_6^+$ [M+Na]$^+$ 811.9, found 811.9.

Scheme S12. Synthesis of Compound 32



***p*-Methylphenyl 3-*O*-(2-methyl-naphthyl)-1-thio-β-D-galactopyranoside (S22)**

To a solution of **S1** (3.1 g, 11.0 mmol) in toluene (100 mL) was added dibutyltin oxide (3.0 g, 12.1 mmol), the mixture was refluxed for 6 h in Dean-Stark tube. After cooled to 60 ℃， tetrabutylammonium bromide (3.9 mg, 12.1 mmol) and NapBr (3.6 g, 16.5 mmol) were added to the mixture and stirred at 60 ℃ for 24 h. Upon completion, the reaction mixture was concentrated in vacuo to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S22** as a colorless oil (2.4 g, 52%). The physical data matched those previously reported.[8]

***p*-Methylphenyl 2,4,6-tri-*O*-Benzyl-3-*O*-(2-methyl-naphthyl)-1-thio-β-D-galactopyranoside (S23)**

To a solution of **S22** (426 mg, 1.0 mmol) in DMF (50 mL) at 0 ℃ was added NaH (60% dispersion in oil, 320 mg, 8.0 mol). After stirred at 0 ℃ for 30 min, benzyl bromide (0.6 mL, 5.0 mmol) was added to the above solution. The reaction mixture was kept stirring at r.t. for 6 h. Upon completion, the reaction mixture was quenched by water (100 mL), and then diluted by ethyl acetate (500 mL). The organic phase was

separated and then washed with brine (200 mL). The organic phase was separated, dried ($MgSO_4$) and concentrated in vacuo to form a residue as a yellow solid. The residue was purified by silica gel column chromatography to afford **S23** as a white solid (510 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (t, *J* = 15.7 Hz, 4H, Ar-*H*), 7.45 (d, *J* = 9.1 Hz, 3H, Ar-*H*), 7.34 – 7.20 (m, 17H, Ar-*H*), 7.02 (d, *J* = 7.1 Hz, 2H, Ar-*H*), 5.55 (s, 1H), 4.94 (d, *J* = 10.6 Hz, 1H), 4.73 (d, *J* = 7.2 Hz, 3H), 4.63 (t, *J* = 12.7 Hz, 2H), 4.55 (d, *J* = 10.4 Hz, 1H), 4.49 (d, *J* = 11.6 Hz, 1H), 4.30 (dd, *J* = 8.1, 3.7 Hz, 1H), 4.09 (t, *J* = 9.2 Hz, 1H), 4.02 (s, 1H), 3.94 (d, *J* = 9.3 Hz, 1H), 3.85 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.76 (d, *J* = 10.6 Hz, 1H), 2.30 (s, 3H, -C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.45 – 125.86, 85.96, 80.17, 76.13, 75.20, 75.01, 73.28, 72.72, 72.11, 71.80, 69.21, 21.10. ESI-MS: m/z calcd for $C_{45}H_{44}NaO_5S^+$ $[M+Na]^+$ 719.3, found 719.3.

***p*-Methylphenyl 2,4,6-tri-*O*-Benzyl-1-thio-β-D-galactopyranoside (S24)**

S23 (420 mg, 0.6 mmol) was dissolved in TFA/toluene (*v:v* = 10:1). The solution was kept stirring at 0 ℃ for 3h. Upon completion, the reaction mixture was concentrated in vacuo to form a residue as a yellow solid. The residue was dissolved in DCM/MeOH (*v:v* = 2:1) containing MeONa and stirred at r.t. for 2 h. the reaction mixture was concentrated in vacuo and purified by silica gel column chromatography to afford **S24** as a colorless oil (227 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 17H, Ar-*H*), 7.04 (d, *J* = 6.9 Hz, 2H, Ar-*H*), 5.61 (s, 1H), 4.87 (d, *J* = 10.9 Hz, 1H), 4.75 (d, *J* = 11.4 Hz, 1H), 4.65 (d, *J* = 11.6 Hz, 1H), 4.57 – 4.46 (m, 3H), 4.34 – 4.26 (m, 1H), 3.99 (s, 2H), 3.83 – 3.73 (m, 3H), 2.30 (s, 3H, -C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.35 – 127.48, 85.24, 79.64, 74.91, 73.32, 72.28, 72.09, 71.90, 69.14, 21.11. ESI-MS: m/z calcd for $C_{34}H_{36}NaO_5S^+$ $[M+Na]^+$ 579.2, found 579.2.

2,4,6-tri-*O*-benzyl-3-*O*-trichloroacetimidoyl-α-D-galactopyranosyl trichloroacetimidate (32)

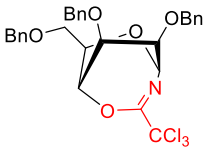
S24 (227 mg, 0.4 mmol) was dissolved in DCM (10 mL), NIS (100 mg, 0.44 mmol), TFA (34 μL, 0.44 mmol) and H_2O (0.1 mL) was added at 0 ℃. The reaction mixture was kept stirring at r.t. for 6 h. upon completion, the above solution was quenched by $NaHSO_3$ and then diluted by DCM. The organic phase was separated and then washed with brine, dried ($MgSO_4$) and concentrated in vacuo to form a residue as a yellow oil. The residue was purified by silica gel column chromatography to afford a colorless oil.

The above residue was dissolved in anhydrous DCM (5 mL) containing DBU (120 μL, 0.2 mmol) and trichloroacetonitrile (0.4 mL, 4.0 mmol), the reaction mixture was kept stirring at r,t, for 2 h. Upon completion, the solvent was evaporated and the residue was purified by silica gel column chromatography to afford **32** as a colorless oil (166 mg, 56%, 2 steps). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.59 (s, 1H, C=N*H*), 8.45 (s, 1H, C=N*H*), 7.38 (d, *J* = 7.1 Hz, 2H, Ar-*H*), 7.34 – 7.26 (m, 11H, Ar-*H*), 7.19 – 7.17 (m, 2H, Ar-

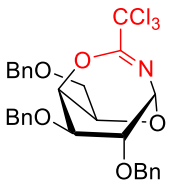
H), 6.41 (d, *J* = 2.0 Hz, 1H), 5.44 (dd, *J* = 9.7, 3.2 Hz, 1H), 4.91 (d, *J* = 10.6 Hz, 1H), 4.73 (s, 2H), 4.68 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 10.6 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.47 – 4.45 (m, 1H), 4.36 (t, *J* = 9.8 Hz, 1H), 4.09 (ddd, *J* = 9.9, 4.0, 1.5 Hz, 1H), 3.85 (dd, *J* = 11.3, 4.2 Hz, 1H), 3.74 (dd, *J* = 11.3, 1.7 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.58, (*C*=NH), 160.42 (*C*=NH), 138.10 – 127.44, 95.83, 91.16 (-*C*Cl_3), 90.85 (-*C*Cl_3), 78.80, 74.92, 74.51, 73.39, 73.15, 73.04, 72.38, 68.44. ESI-MS: m/z calcd for $C_{31}H_{30}Cl_6N_2NaO_6^+$ $[M+Na]^+$ 759.0, found 759.0.

3. Formation of bridging intermediates

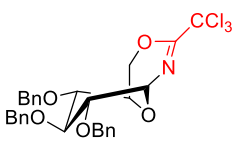
General procedures for Formation of bridging intermediates **4**, **6**, **8**, **10**, **12**, **15**, **16**, **18**, **19**, **21**, **24**, **25**, **28**, **33** and by-products **13, 22** based on the '*bis*-trichloroacetimidates method' and '*tris*-trichloroacetimidates method': *bis*-trichloroacetimidates **3**, **5**, **7**, **9**, **11**, **32** or *tris*-trichloroacetamides **14**, **17**, **20**, **23**, **26**, **29** (50 mg, 0.06 mmol) was dissolved in anhydrous DCM (5 mL) and cooled to 0 °C. 4 Å molecular sieves (fresh activated) and TfOH or TBSOTf (0.1 equiv.) were then added. The reaction mixture was stirred at 0 °C for 3 h and then quenched with Et_3N. The solvent was evaporated and the residue was purified by silica gel column chromatography to afford the corresponding bridging intermediate **4**, **6**, **8**, **10**, **12**, **15**, **16**, **18**, **19**, **21**, **24**, **25**, **28**, **33** or by-products **13**, **22**.



Compound **4**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 7.33 – 7.29 (m, 13H, Ar-*H*), 7.25 (m, 2H, Ar-*H*), 5.34 (d, *J* = 1.7 Hz, 1H, H1), 4.71 – 4.65 (m, 5H, H4, H5 and 3 × PhC*H*-), 4.62 (d, *J* = 11.5 Hz, 1H, PhC*H*-), 4.50 (d, *J* = 11.8 Hz, 1H, PhC*H*-), 4.46 (d, *J* = 11.8 Hz, 1H, PhC*H*-), 4.24 (dt, *J* = 7.7, 1.7 Hz, 1H, H3), 4.13 (dd, *J* = 7.7, 1.6 Hz, 1H, H2), 4.09 (m, 1H, H6a), 3.75 (dd, *J* = 9.6, 5.7 Hz, 1H, H6b). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 155.52 (*C*=N-), 137.89 – 127.61, 81.37 (C1), 76.07, 75.19, 73.83 (C2), 73.33 (Ph*C*H_2-), 73.08 (C3), 72.77, 72.61, 69.32 (C6). ESI-HRMS: m/z calcd. for $C_{29}H_{29}Cl_3NO_5^+$ $[M+H]^+$ 576.1106, found 576.1120.

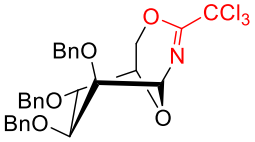


Compound **6**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 7.39 – 7.26 (m, 15H, Ar-*H*), 5.80 (d, *J* = 5.5 Hz, 1H, H1), 4.68 (d, *J* = 11.2 Hz, 1H, PhC*H*-), 4.63 (td, *J* = 6.8, 1.5 Hz, 1H, H5), 4.58 (d, *J* = 11.6 Hz, 1H, PhC*H*-), 4.53 (m, 3H, H4 and PhC*H*-), 4.49 (d, *J* = 11.6 Hz, 1H, PhC*H*-), 4.39 (d, *J* = 11.2 Hz, 1H, PhC*H*-), 4.30 (dd, *J* = 5.4, 3.8 Hz, 1H, H2), 4.10 (dd, *J* = 3.4, 1.7 Hz, 1H, H3), 3.72 (dd, *J* = 9.8, 6.3 Hz, 1H, H6a), 3.66 (dd, *J* = 9.7, 7.0 Hz, 1H, H6b). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 151.51 (*C*=N-), 137.50 – 127.76, 93.64 (-*C*Cl_3), 87.94 (C1), 86.62 (C2), 85.36 (C3), 82.85 (C5), 81.71 (C4), 73.63 (Ph*C*H_2-), 72.46 (Ph*C*H_2-), 71.92 (Ph*C*H_2-), 67.61 (C6). ESI-HRMS: m/z calcd. for $C_{29}H_{29}Cl_3NO_5^+$ $[M+H]^+$ 576.1106, found 576.1094.

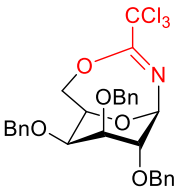


Compound **8**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 7.39 (d, *J* = 7.0 Hz, 2H), 7.36 – 7.27 (m, 13H), 5.51 (d, *J* = 1.5 Hz, 1H), 4.88 (d, *J* = 11.2 Hz, 2H, 2 × PhC*H*-), 4.80 (m, 2H, 2 × PhC*H*-), 4.59 (m, 2H, 2 × PhC*H*-), 4.15 – 4.08 (m, 3H, H5 and H6a and H6b), 3.89 (dd, *J* = 10.0, 7.6 Hz, 1H, H3), 3.57 (dd, *J* = 10.0, 5.8 Hz, 1H, H4), 3.52 (dd, *J* = 7.6, 1.7 Hz, 1H, H2). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 148.91 (*C*=N-), 138.24 – 127.80, 93.69 (-*C*Cl_3), 89.31 (C1), 84.34

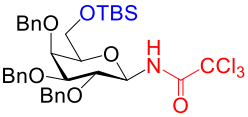
(C2), 81.43 (C3), 77.42 (C5), 75.26 (Ph*C*H$_2$-), 74.84 (C6), 74.65 (Ph*C*H$_2$-), 74.31 (C4), 72.14 (Ph*C*H$_2$-). ESI-HRMS: m/z calcd. for $C_{29}H_{28}Cl_3NNaO_5^+$ [M+Na] $^+$ 598.0925, found 598.0932.



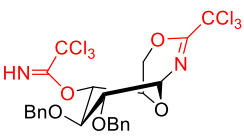
Compound **10**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 7.40 – 7.27 (m, 15H, Ar-*H*), 5.65 (d, *J* = 6.4 Hz, 1H, H1), 4.83 (dd, *J* = 12.5, 8.9 Hz, 1H, H6a), 4.74 (d, *J* = 11.9, 1H, PhC*H*-), 4.69 (d, *J* = 11.8, 1H, PhC*H*-), 4.63 (d, *J* = 12.0 Hz, 1H, PhC*H*-), 4.59 (d, *J* = 12.0 Hz, 1H, PhC*H*-), 4.55 – 4.50 (m, 2H, 2 × PhC*H*-), 4.31 – 4.26 (m, 1H, H5), 4.20 (dd, *J* = 6.4, 3.5 Hz, 1H, H2), 4.13 (dd, *J* = 12.5, 6.7 Hz, 1H, H6b), 3.84 (dd, *J* = 6.8, 3.4 Hz, 1H, H3), 3.62 (bd, *J* = 6.8 Hz, 1H, H4). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 153.69 (*C*=N-), 138.17 – 127.78, 93.32 (-*C*Cl_3), 86.36 (C1), 77.63 (C3), 75.68 (C5), 73.91, 73.01, 72.90, 72.71. ESI-HRMS: m/z calcd. for $C_{29}H_{28}Cl_3NNaO_5^+$ [M+Na] $^+$ 598.0925, found 598.0934.



Compound **12**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 7.35 – 7.27 (m, 13H, Ar-*H*), 7.23 (d, *J* = 7.1 Hz, 2H, Ar-*H*), 5.48 (s, 1H, H1), 5.00 (dd, *J* = 11.9, 3.3 Hz, 1H, H6a), 4.61-4.51 (m, 4H, 4 × PhC*H*-), 4.44 (dd, *J* = 12.0, 3.2 Hz, 2H, 2 × PhC*H*-), 4.33-4.27 (m, 2H, H5 and H6b), 4.09 (d, *J* = 5.4 Hz, 1H, H4), 3.88 (bs, 2H, H2 and H3). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 151.43 (*C*=N-), 137.83 – 127.76, 93.97(-*C*Cl_3), 85.64 (C1), 74.34, 72.92, 72.73 (Ph*C*H$_2$-), 72.37 (Ph*C*H$_2$-), 72.13 (C6), 71.60 (Ph*C*H$_2$-), 71.45 (C4), 70.05 (C5). ESI-HRMS: m/z calcd. for $C_{29}H_{28}Cl_3NNaO_5^+$ [M+Na] $^+$598.0925, found 598.0932.

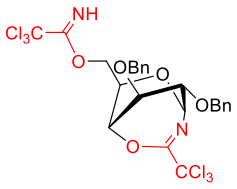


Compound **13**:^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 15H, Ar-*H*), 7.03 (d, *J* = 9.2 Hz, 1H, H1), 5.08 (t, *J* = 9.0 Hz, 1H, H2), 4.94 (d, *J* = 11.0 Hz, 1H, PhC*H*-), 4.84 (d, *J* = 11.2 Hz, 1H, PhC*H*-), 4.77 – 4.75 (m, 3H, 3 × PhC*H*-), 4.65 (d, *J* = 11.0 Hz, 1H, PhC*H*-), 3.99 (d, *J* = 1.6 Hz, 1H, H5), 3.84 (t, *J* = 9.0 Hz, 1H, H3), 3.70 (dd, *J* = 10.8, 4.9 Hz, 2H, H4 and H6a), 3.55 (t, *J* = 6.9 Hz, 1H, H6b), 0.89 (s, 9H, -C(C*H*$_3$)$_3$), 0.05 (s, 3H, Si-C*H*$_3$), 0.05 (s, 3H, Si-C*H*$_3$). ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.63 (*C*=O), 137.40 – 126.69, 91.22 (*C*Cl_3), 82.39 (C4), 80.02 (C1), 74.21 (Ph*C*H$_2$-), 73.91 (Ph*C*H$_2$-), 72.57 (C5), 71.76 (Ph*C*H$_2$-), 59.87 (C6), 24.87(3×-*C*H$_3$), 17.17 (Si-*C*Me$_3$), -6.34 (Si-*C*H$_3$), -6.42 (Si-*C*H$_3$). ESI-MS: m/z calcd for $C_{35}H_{44}Cl_3NNaO_6Si^+$ [M+Na] $^+$ 730.2, found 730.2.

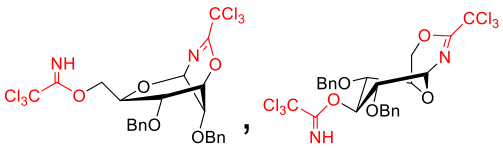


Compound **15**:^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.45 (s, 1H, C=N*H*), 7.37 – 7.27 (m, 10H, Ar-*H*), 5.57 (d, *J* = 3.6 Hz, 1H, H1), 5.02 (dd, *J* = 8.4, 2.8 Hz, 1H, H4), 4.84-4.79 (m, 3H, 3 × PhC*H*-), 4.66 (dd, *J* = 12.5, 4.3 Hz, 1H, H6a), 4.62 (d, *J* = 11.8 Hz, 1H, PhC*H*-), 4.33 (m, 1H, H5), 4.26 (dd, *J* = 12.5, 3.4 Hz, 1H, H6b), 4.08 (t, *J* = 8.6 Hz, 1H, H3), 3.54

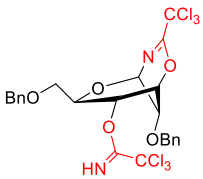
(dd, *J* = 8.8, 3.6 Hz, 1H, H2). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 162.30 (*C*=NH), 153.60 (*C*=N-), 137.92 – 127.81, 93.14 (-*C*Cl_3), 90.84 (-*C*Cl_3), 89.80 (C1), 81.70 (C2), 77.66 (C3), 77.58 (C4), 76.48 (C5), 75.46 (C6), 75.28 (Ph*C*H_2-), 72.58 (Ph*C*H_2-). ESI-HRMS: m/z calcd. for ^{37}Cl $C_{24}H_{23}Cl_5N_2O_5^+$ [M+H]$^+$ 630.9705, found 630.9717.



Compound **16**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.40 (s, 1H, C=N*H*), 7.35 – 7.27 (m, 10H, Ar-*H*), 5.47 (d, *J* = 4.0 Hz, 1H, H1), 4.91 (bt, *J* = 7.3 Hz, 1H, H5), 4.70 (d, J = 11.8 Hz, 1H, PhC*H*-), 4.68 (bs, 1H, H4), 4.64 (d, J = 11.6 Hz, 1H, PhC*H*-), 4.55 (m, 2H, 2 × PhC*H*-), 4.50 (dd, *J* = 10.9, 8.6 Hz, 1H, H6a), 4.46 (dd, *J* = 10.9, 6.3 Hz, 1H, H6b), 4.20 (dd, *J* = 3.7,1.9, 1H, H3), 4.14 (t, *J* = 3.8 Hz, 1H, H2). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 162.05 (*C*=NH), 154.63 (*C*=N-), 137.30 – 127.84, 91.98 (-*C*Cl_3), 90.91 (-*C*Cl_3), 83.28 (C2), 79.57 (C1), 79.48 (C3), 75.84 (C4), 73.81(C5), 72.22 (Ph*C*H_2-), 71.47 (Ph*C*H_2-), 67.33 (C6). ESI-HRMS: m/z calcd. for ^{37}Cl$C_{24}H_{22}Cl_5N_2NaO_5^+$ [M+Na]$^+$ 652.9525, found 652.9542.

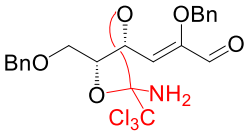


Compound **18** and **19**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.65 (s, 1H, 19-C=N*H*), 8.28 (s, 1.5*H*, 18-C=NH), 7.37 – 7.27 (m, 25H, 18-Ar-*H* and 19-Ar-*H*), 5.77 (dd, *J* = 10.2, 8.5 Hz, 1H, 19-H3), 5.56 (d, *J* = 1.9 Hz, 1H, 19-H1), 5.43 (t, *J* = 2.3 Hz, 1.5H, 18-H3), 4.83 (d, *J* = 11.8 Hz, 1H, 19-PhC*H*-), 4.78 (d, *J* = 11.7 Hz, 1.5H, 18-PhC*H*-), 4.75 (d, *J* = 4.1 Hz, 1H, 19-PhC*H*-), 4.73 (m, 3H, 18-H1 and 18-H4), 4.71 (d, *J* = 11.9 Hz, 1.5H, 18-H2), 4.60 (d, *J* = 9.8 Hz, 1.5H, 18-PhC*H*-), 4.58 (d, *J* = 9.8 Hz, 1H, 19-PhC*H*-), 4.55 (dd, *J* = 11.6, 1.8 Hz, 1.5H, 18-H6a), 4.49 (d, *J* = 11.8 Hz, 1H, 19-PhC*H*-), 4.36 – 4.32 (m, 3H, 18-PhC*H*- and 18-H6b), 4.21 – 4.19 (m, 1H, 19-H5), 4.06 (dd, *J* = 12.6, 2.0 Hz, 1H, 19-H6a), 4.00 (d, *J* = 10.0 Hz, 1.5H, 18-PhC*H*-), 3.91 (dd, *J* = 12.6, 2.8 Hz, 1H, 19-H6b), 3.87 (t, *J* = 2.5 Hz, 1.5H, 18-H5), 3.72 (dd, *J* = 10.3, 6.0 Hz, 1H, 19-H4), 3.58 (dd, *J* = 8.4, 2.0 Hz, 1H, 19-H2). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 162.72 (18-*C*=NH), 162.52 (19-*C*=NH), 153.66 (18-*C*=N-), 149.87 (19-*C*=N-), 137.39 – 127.94, 93.55 (-*C*Cl_3), 91.46 (-*C*Cl_3), 91.42 (-*C*Cl_3), 91.17 (-*C*Cl_3), 89.51 (19-C1), 82.39 (19-C2), 78.53 (19-C3), 78.48, 77.66 (19-C5), 75.73 (18-C3), 74.62 (19-C6), 74.60 (19-Ph*C*H_2-), 73.65 (19-C4), 73.49, 72.13 (19-Ph*C*H_2-), 72.03, 71.96, 70.78 (18-C5), 67.34 (18-C6), 66.14. ESI-HRMS: m/z calcd. for ^{37}Cl$C_{24}H_{23}Cl_5N_2O_5^+$ [M+H]$^+$ 630.9705, found 630.9725.

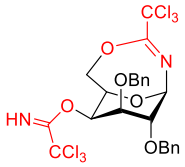


Compound **21**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.70 (s, 1H, C=N*H*), 7.35 – 7.26 (m, 10H, Ar-*H*), 5.61-5.59 (m, 1H, H4), 5.48 (d, *J* = 4.3 Hz, 1H, H1), 4.82 (d, *J* = 1.2 Hz, 1H, H3), 4.75 (bt, *J* = 7.2 Hz, 1H, H5), 4.70 – 4.66 (m, 2H, 2 × PhC*H*-), 4.51 (s, 2H, 2 × PhC*H*-), 4.17 (t, *J* = 3.7 Hz, 1H, H2), 3.71 – 3.63 (m, 2H, H6a and H6b). ^{13}C NMR:

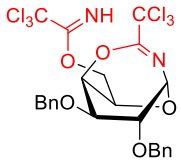
(151 MHz, $CDCl_3$): δ 160.67 (*C*=NH), 155.26 (*C*=N-), 137.33 – 127.65, 91.77 (-*C*Cl_3), 90.39 (-*C*Cl_3), 80.97 (C2), 79.61 (C1), 77.68 (C4), 75.06 (C5), 75.00 (C3), 73.42 (Ph*C*H_2-), 71.48 (Ph*C*H_2-), 69.06 (C6). ESI-HRMS: m/z calcd. for $^{37}ClC_{24}H_{23}Cl_5N_2O_5^+$ $[M+H]^+$ 630.9705, found 630.9717.



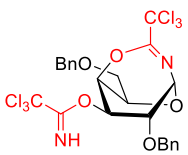
Compound **22**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 9.24 (s, 1H, O=C*H*), 7.32 (m, 10H), 5.99 (d, *J* = 8.7 Hz, 1H, C=C*H*-), 5.55 (t, *J* = 8.2 Hz, 1H, H4), 5.16 – 5.09 (m, 2H, 2 × PhC*H*-), 4.77 (dd, *J* = 7.3, 2.8 Hz, 1H, H5), 4.48 (m, 2H, 2 × PhC*H*-), 3.48 (dd, *J* = 10.4, 6.9 Hz, 1H, H6a), 3.34 (dd, *J* = 10.4, 4.5 Hz, 1H, H6b). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 188.48 (O=*C*H, 154.40 (C2), 137.49 – 127.63, 114.65 (H_2N-*C*), 102.23 (-*C*Cl_3), 79.48 (C5), 73.98 (C4), 73.44 (Ph*C*H_2-), 73.00 (Ph*C*H_2-), 67.88 (C6). ESI-HRMS: m/z calcd. for $C_{22}H_{23}Cl_3NO_5^+$ $[M+H]^+$ 486.0636, found 486.0649.



Compound **24**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.61 (s, 1H, C=N*H*), 7.40 – 7.26 (m, 10H, Ar-*H*), 6.08 (d, *J* = 6.7 Hz, 1H, H1), 5.47 (td, *J* = 6.9, 3.0 Hz, 1H, H5), 4.78 (d, *J* = 11.2 Hz, 1H, PhC*H*-), 4.66 (dd, *J* = 6.2, 3.2 Hz, 1H, H4), 4.59 (m, 1H, H6a), 4.57 – 4.55 (m, 3H, 2 × PhC*H*- and H3), 4.52 (dd, *J* = 6.8, 4.0 Hz, 1H, H2), 4.46 – 4.42 (m, 2H, H6b and PhC*H*-). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 161.32 (*C*=NH), 152.77 (*C*=N-), 137.61 – 127.65, 94.02 (-*C*Cl_3), 90.72 (-*C*Cl_3), 89.24 (C1), 86.57 (C2), 85.51 (C3), 79.96 (C4), 73.47 (C5), 73.16 (Ph*C*H_2-), 72.17 (Ph*C*H_2-), 71.07 (C6). ESI-HRMS: m/z calcd. for $^{37}ClC_{24}H_{23}Cl_5N_2O_5^+$ $[M+H]^+$ 630.9705, found 630.9732.

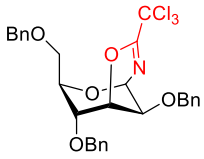


Compound **25**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.42 (s, 1H, C=N*H*), 7.38 – 7.29 (m, 10H, Ar-*H*), 5.83 (d, J = 5.4 Hz, 1H, H1), 4.84 (t, *J* = 5.8 Hz, 1H, H5), 4.69 (d, *J* = 11.2 Hz, 1H, PhC*H*-), 4.62 (d, *J* = 11.6 Hz, 1H, PhC*H*-), 4.54 – 4.44 (m, 4H, H4, H6a, H6b and PhC*H*-), 4.40 (d, *J* = 11.2 Hz, 1H, PhC*H*-), 4.32 – 4.29 (m, 1H, H2), 4.14 (bs, 1H, H3). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 162.24 (*C*=NH), 150.96 (*C*=N-), 137.23 – 127.97, 93.43 (-*C*Cl_3), 90.80 (-*C*Cl_3), 88.01 (C1), 86.56 (C2), 85.17 (C3), 81.93 (C4), 81.06(C5), 72.50 (Ph*C*H_2-), 72.11 (Ph*C*H_2-), 66.42(C6). ESI-HRMS: m/z calcd. for $^{37}ClC_{24}H_{23}Cl_5N_2O_5^+$ $[M+H]^+$ 630.9705, found 630.9711.



Compound **28**: ^{1}H NMR: (600 MHz, $CDCl_3$): δ 8.47 (s, 1H, C=N*H*), 7.39 – 7.27 (m, 10H, Ar-*H*), 5.83 (d, *J* = 5.7 Hz, 1H, H1), 5.22 – 5.19 (m, 1H, H3), 5.14 (bt, *J* = 6.0 Hz, 1H, H5), 4.72 – 4.68 (m, 1H, PhC*H*-), 4.58 – 4.52 (m, 4H, H2, H4 and 2 × PhC*H*-), 4.51 (d, *J* = 11.5 Hz, 1H, PhC*H*-), 3.74 (dd, *J* = 9.9, 6.5 Hz, 1H, H6a), 3.68 (dd, *J* = 10.0, 6.9 Hz, 1H, H6b). ^{13}C NMR: (151 MHz, $CDCl_3$): δ 162.51 (*C*=NH), 152.00 (*C*=N-), 137.46 – 127.86, 93.60 (-*C*Cl_3), 90.59 (-*C*Cl_3), 87.16

(C1), 85.12 (C3), 84.43 (C2), 82.35 (C5), 81.48 (C4), 73.71 (Ph*C*H$_2$-), 72.45 (Ph*C*H$_2$-), 67.50 (C6). ESI-HRMS: m/z calcd. for $^{37}ClC_{24}H_{23}Cl_5N_2O_5^+$ [M+H]$^+$ 630.9705, found 630.9720.



Compound **33**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 15H, Ar-*H*), 5.35 (t, *J* = 2.4 Hz, 1H, H1), 4.86-4.84 (m, 1H, H3), 4.64 – 4.57 (m, 3H, 3 × PhC*H*-), 4.55 (d, *J* = 11.9 Hz, 1H, PhC*H*-), 4.50 (d, *J* = 12.0 Hz, 1H, PhC*H*-), 4.44 (d, *J* = 12.0 Hz, 1H, PhC*H*-), 4.08 (t, *J* = 2.1 Hz, 1H, H2), 4.03 – 3.99 (m, 1H, H5), 3.96 (t, *J* = 2.8 Hz, 1H, H4), 3.45 (dd, *J* = 9.7, 4.7 Hz, 1H, H6a), 3.40 – 3.36 (m, 1H, H6b). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.65(*C*=N), 137.84 – 127.67, 91.72(-*C*Cl_3), 76.39(C4), 75.47(C1), 73.38(C3), 73.34(Ph*C*H$_2$-), 71.81(Ph*C*H$_2$-), 71.58(C5), 70.68(Ph*C*H$_2$-), 70.58(C6), 65.58(C2). ESI-HRMS: m/z calcd. for $C_{29}H_{29}Cl_3NO_5^+$ [M+H]$^+$ 576.1106, found 576.1105.

4. Details for DFT calculations

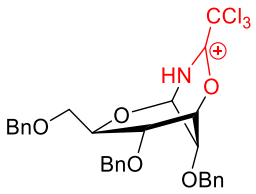
Computational methods

The energy calculation of the intermediate was carried out in two stages. In the first stage, the initial structure of each intermediate was built by Spartan software (Spartan' 18 for Windows).[9] The structure was then subjected to a conformation distribution calculation at MMFF level to determine all low energy conformations. The remaining conformations were optimized with semi-empirical and H-F level by Spartan' 18 software.[9] Then was deleted according to Boltzmann Weights proportion. In the second stage, the coordinates of these lowest energy structure were then moved to Gaussian 09 Rev.A.01 [10] and further optimized at B3LYP/6-311+G (d, p). Optimization was done in gas-phase and subsequently re-optimization in combination with a PCM model to include solvent effects, using dichloromethane as the solvent parameter. The denoted free Gibbs energy was calculated using Equation (1) in which E_{gas} is the electronic energy in gas-phase, $\Delta G^{T}_{\text{gas}}$ (T=273.15k, p=1atm and C=1M) is thermal correction to Gibbs Free Energy, ΔG_{solv} is solvation free energy and $G^{T}_{\text{in solution}}$ is the free Gibbs energy in solvation. Molecular structures of all intermediates were illustrated using CYLview.[11]

$$G^{T}_{\text{in solution}} = E_{gas} + \Delta G^{T}_{\text{gas}} + \Delta G_{solv} \qquad (1)$$

Computational results

Cartesian coordinates, absolute energy values and the number of imaginary frequencies for intermediates:



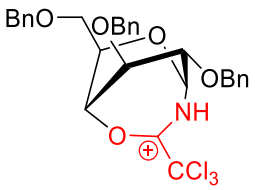
E_{gas}(B3LYP)=-2934.19523624 a.u.

E_{solv}(B3LYP)=-2934.25374853 a.u.

Thermal correction to Gibbs Free Energy= 0.465488 a.u.

C	-1.295928	-0.849346	-1.384489
C	-2.248278	0.136565	-0.709081
C	-1.408632	0.822824	0.369680
C	-0.142232	1.517649	-0.174320
C	0.436958	0.903531	-1.481871
O	-0.242984	-0.262254	-2.039453
O	-1.003122	-0.221352	1.360610
O	-0.457433	2.872391	-0.441450
O	-2.678490	1.027472	-1.693722
C	1.902722	0.539741	-1.329866
C	1.291418	3.996792	0.891125
C	-5.098416	0.898380	-1.210333
C	1.861069	3.650770	2.119213
C	3.222353	3.850876	2.353647
C	4.026054	4.396663	1.356230
C	3.465869	4.746499	0.125596
C	2.107758	4.549761	-0.104490
C	-0.183217	3.798673	0.635058
O	2.033657	-0.399066	-0.267827
C	4.189256	-1.399381	-0.970908
C	5.188901	-0.742762	-1.693677
C	5.910306	-1.413372	-2.681246
C	-5.757730	0.834332	0.020653
C	-6.880351	0.021889	0.184890
C	-7.348750	-0.738781	-0.883120
C	-6.697789	-0.681094	-2.117117
N	-0.797252	-1.770142	-0.292924
C	-5.581914	0.133853	-2.280477
C	-3.886797	1.776884	-1.394145
C	5.635883	-2.750483	-2.956821
C	-0.206477	-2.354483	2.051776
C	4.642876	-3.417749	-2.238330

C	3.927387	-2.745681	-1.251903	H	-5.406376	1.437954	0.852377
C	-0.671277	-1.392347	0.942626	H	-7.389405	-0.010685	1.141182
C	3.404305	-0.675288	0.097081	H	-8.223631	-1.366541	-0.760344
Cl	0.540299	-3.823499	1.347066	H	-7.070217	-1.261116	-2.953621
Cl	0.951052	-1.534479	3.118317	H	-0.405681	-2.669215	-0.556363
Cl	-1.697566	-2.801282	2.944399	H	-5.087211	0.187387	-3.244731
H	-1.813808	-1.485879	-2.100854	H	-3.724866	2.409729	-0.515468
H	-3.083576	-0.411027	-0.253349	H	-3.991210	2.429382	-2.260833
H	-1.976513	1.519226	0.979752	H	6.198243	-3.274538	-3.720815
H	0.624071	1.449094	0.603483	H	4.437300	-4.462655	-2.441103
H	0.333192	1.673470	-2.246176	H	3.167454	-3.273162	-0.684076
H	2.274557	0.122659	-2.270960	H	3.898538	0.267179	0.360854
H	2.467993	1.455420	-1.105751	H	3.328398	-1.283075	0.999934
H	1.235937	3.239141	2.905903				
H	3.650077	3.588766	3.314510				
H	5.081772	4.561395	1.538273				
H	4.086268	5.186255	-0.646948				
H	1.673231	4.835109	-1.056906				
H	-0.653283	4.725127	0.302141				
H	-0.689814	3.478436	1.554467				
H	5.413473	0.296986	-1.477230				
H	6.686503	-0.893440	-3.230720				



E_{gas}(B3LYP)=-2934.19312932 a.u.

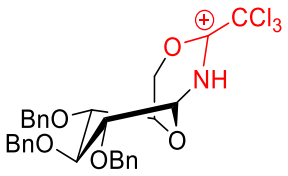
E_{solv}(B3LYP)= -2934.25029159 a.u.

Thermal correction to Gibbs Free Energy= 0.464903 a.u.

C	-0.306590	1.032778	-2.244826
C	-1.075934	-0.220627	-1.793035
C	-0.733616	-0.570426	-0.317014

C	0.309845	0.411127	0.247247	N	-0.890601	2.258630	-1.570876
C	1.481610	0.738974	-0.665668	C	-0.913810	2.471995	-0.289173
O	1.056615	0.951182	-2.036637	C	-1.578071	3.734478	0.303425
O	-2.450014	0.042008	-1.992048	C	-0.686276	-2.293725	2.174284
C	2.563941	-0.340447	-0.679164	C	0.561162	-2.320211	2.811776
C	-3.562585	-2.178311	-2.040124	C	0.692190	-1.889222	4.128568
O	3.104208	-0.377429	0.624822	C	-0.424773	-1.431412	4.830077
C	5.432335	-0.929017	0.001812	C	-1.671458	-1.409800	4.210102
C	5.912505	-1.758360	-1.014699	C	-1.799336	-1.838407	2.888374
C	7.058900	-1.414650	-1.731694	C	-0.830264	-2.756665	0.745527
C	-4.497738	-2.135167	-0.997509	Cl	-2.895230	3.185286	1.373321
C	-4.858552	-3.297968	-0.323159	Cl	-0.326872	4.621873	1.211694
C	-4.292226	-4.521725	-0.686723	Cl	-2.246875	4.784489	-0.989223
C	-3.365522	-4.575585	-1.724851	H	-0.461993	1.209042	-3.307503
C	-3.002576	-3.407744	-2.396852	H	-0.721695	-1.046162	-2.417463
C	-3.199316	-0.917347	-2.783160	H	-1.649072	-0.468236	0.272460
C	7.732171	-0.231397	-1.439794	H	0.673349	0.084333	1.216843
C	7.259598	0.604965	-0.426835	H	1.943106	1.667572	-0.315629
C	6.119403	0.256671	0.290922	H	3.312171	-0.046545	-1.424227
C	4.196493	-1.302937	0.786343	H	2.140341	-1.310312	-0.965715
O	-0.406374	1.698592	0.599020	H	5.394231	-2.684799	-1.242433
O	-0.206921	-1.875535	-0.232461	H	7.424749	-2.070500	-2.513295

H	-4.955224	-1.189228	-0.725713
H	-5.593555	-3.256217	0.472600
H	-4.582612	-5.428886	-0.169592
H	-2.931973	-5.524569	-2.018399
H	-2.291190	-3.459910	-3.215013
H	-4.095481	-0.367192	-3.073233
H	-2.634744	-1.153144	-3.691806
H	8.624702	0.037004	-1.993079
H	7.787575	1.521942	-0.191120
H	5.760709	0.904509	1.084151
H	4.397176	-1.291573	1.858960
H	3.862845	-2.310961	0.508966
H	-1.348286	2.952705	-2.153859
H	1.430191	-2.685997	2.275251
H	1.660776	-1.920845	4.614146
H	-0.323088	-1.104767	5.858497
H	-2.544132	-1.068922	4.755257
H	-2.776407	-1.838696	2.415265
H	-0.320829	-3.706808	0.584084
H	-1.884007	-2.880814	0.482652



E_{gas}(B3LYP)=-2934.18785740 a.u.

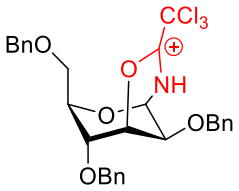
E_{solv}(B3LYP)= -2934.24643684 a.u.

Thermal correction to Gibbs Free Energy= 0.466361 a.u.

C	-0.122355	0.824466	2.445097
C	1.023194	0.578257	1.437669
C	1.245318	-0.932285	1.282649
C	-0.035668	-1.582291	0.723207
C	-1.305780	-0.980638	1.423745
O	-1.037396	-0.277886	2.579138
O	2.136320	1.254486	1.981196
C	2.499834	3.033755	0.307601
C	2.323679	3.008120	-1.078747
C	1.816403	4.121028	-1.752374
C	1.473034	5.268539	-1.042221
C	1.645658	5.305398	0.343406
C	2.158444	4.197007	1.011579
C	3.069864	1.839209	1.035123
O	2.321769	-1.148009	0.399048

C	4.414424	-2.171941	-0.172822	Cl	-4.450350	2.551427	-0.049818
C	4.343116	-2.858521	-1.389021	H	0.340164	0.938709	3.428146
C	5.406674	-2.821658	-2.287272	H	0.778746	0.998224	0.451592
C	6.557368	-2.098070	-1.975730	H	1.451923	-1.366234	2.268210
C	6.641279	-1.415307	-0.763481	H	-0.070269	-1.372216	-0.352976
C	5.574068	-1.452801	0.131661	H	-1.972133	-1.794682	1.700444
C	3.255548	-2.191834	0.783338	H	2.606346	2.121229	-1.637201
O	0.043139	-2.969798	0.954982	H	1.703617	4.094484	-2.830417
N	-2.115985	-0.155677	0.442891	H	1.089451	6.137793	-1.564003
C	-0.930250	2.072460	2.192966	H	1.401101	6.205698	0.895811
O	-1.621974	2.084323	0.883148	H	2.319466	4.238623	2.084459
C	-2.204609	1.128972	0.253232	H	3.912253	2.133253	1.662851
C	-3.116673	1.688281	-0.873678	H	3.405835	1.075210	0.333699
C	-2.007540	-3.802224	-0.163491	H	3.453806	-3.432014	-1.630177
C	-2.650562	-3.331910	-1.313414	H	5.343357	-3.363146	-3.224185
C	-4.045829	-3.330967	-1.399143	H	7.388879	-2.075109	-2.670616
C	-4.809751	-3.789613	-0.328950	H	7.538970	-0.862028	-0.512560
C	-4.176428	-4.261899	0.823159	H	5.646891	-0.928887	1.079450
C	-2.786833	-4.273261	0.902670	H	3.594962	-1.998632	1.806770
C	-0.497471	-3.824843	-0.072438	H	2.740267	-3.156161	0.763735
Cl	-2.152181	2.793070	-1.881034	H	-2.659683	-0.724364	-0.209745
Cl	-3.792155	0.379897	-1.895454	H	-0.308538	2.963894	2.144809

H	-1.721237	2.189440	2.934024
H	-2.059361	-3.001047	-2.162479
H	-4.532013	-2.993677	-2.307709
H	-5.891326	-3.797664	-0.396231
H	-4.767419	-4.637632	1.650415
H	-2.299522	-4.659618	1.791978
H	-0.052497	-3.555570	-1.037222
H	-0.144281	-4.820340	0.200068



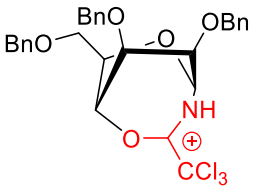
E_{gas}(B3LYP)=-2934.20463382 a.u.

E_{solv}(B3LYP)= -2934.25982903 a.u.

Thermal correction to Gibbs Free Energy= 0.466974 a.u.

C	1.551600	-0.442140	-0.924386
C	1.629763	-1.804403	-0.217030
C	0.396787	-1.860353	0.661296
C	-0.897001	-1.790620	-0.173114
C	-0.861276	-0.778345	-1.350039
O	0.462836	-0.340725	-1.775546
O	-1.070340	-3.090416	-0.719286
C	-3.373308	-3.553795	0.035410
C	-4.082370	-3.493489	-1.171441
C	-5.418808	-3.107047	-1.185932
C	-6.065976	-2.779508	0.007534
C	-5.371400	-2.841066	1.212589
C	-4.029512	-3.224773	1.224507
C	-1.925948	-3.980670	0.039488
O	2.769127	-1.949264	0.590414
C	4.641519	-1.636136	-1.006102
C	4.633871	-1.904001	-2.378046
C	5.273542	-1.045047	-3.273133
C	5.926539	0.090858	-2.801056
C	5.948037	0.362199	-1.431146
C	5.312212	-0.497394	-0.539805
C	3.935109	-2.548765	-0.033879
C	-1.775884	0.421888	-1.170881
O	-1.437457	1.158254	-0.003698
O	0.448360	-0.747198	1.644078
N	1.524995	0.593814	0.156692
C	0.999633	0.367310	1.322377
C	1.113794	1.378250	2.477462
C	-2.570495	3.248692	-0.720784

C	-3.751036	3.354021	-1.460960	H	5.266571	-1.267506	-4.333766
C	-3.899717	4.348691	-2.427340	H	6.429508	0.755477	-3.493733
C	-2.862898	5.246969	-2.665966	H	6.475680	1.233380	-1.059816
C	-1.680099	5.152566	-1.931266	H	5.346415	-0.294003	0.525755
C	-1.537643	4.162042	-0.964211	H	3.635404	-3.482152	-0.522352
C	-2.414079	2.173448	0.328926	H	4.577046	-2.795614	0.812052
Cl	-0.364469	1.374377	3.457892	H	-1.707692	1.052117	-2.063467
Cl	1.430362	3.026723	1.843819	H	-2.807035	0.046691	-1.098027
Cl	2.516889	0.822637	3.447525	H	1.885189	1.522523	-0.034645
H	2.439918	-0.233893	-1.515373	H	-4.565247	2.660640	-1.274928
H	1.542205	-2.590644	-0.974305	H	-4.823369	4.422243	-2.989582
H	0.389470	-2.738348	1.301493	H	-2.976745	6.022721	-3.414175
H	-1.728872	-1.527815	0.486142	H	-0.876342	5.858597	-2.106478
H	-1.236273	-1.330627	-2.212584	H	-0.621848	4.102431	-0.385503
H	-3.585742	-3.759839	-2.098655	H	-2.058039	2.596178	1.268807
H	-5.961431	-3.073842	-2.123724	H	-3.378127	1.685708	0.516781
H	-7.109753	-2.487747	-0.003662				
H	-5.872066	-2.597510	2.142543				
H	-3.497115	-3.284109	2.169044				
H	-1.793923	-4.944127	-0.454551				
H	-1.557805	-4.078050	1.068072				
H	4.137807	-2.794599	-2.751334				



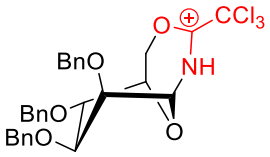
E_{gas}(B3LYP)=-2934.17885950 a.u.

E_{solv}(B3LYP)= -2934.23879223 a.u.

Thermal correction to Gibbs Free Energy= 0.465750 a.u.

				C	-5.665818	-1.036529	-1.685839
C	0.532682	-0.242393	1.573474	C	-3.646510	0.132769	-2.661726
C	1.586433	-0.761929	0.558449	O	0.657625	-1.384762	-1.626577
C	1.186480	-0.309818	-0.897102	N	0.862512	1.199580	1.907185
C	0.127634	0.803400	-0.815048	O	0.783976	2.033543	-0.226211
C	-1.112370	0.461741	0.004980	C	1.002936	2.154988	1.033295
O	-0.784624	-0.351845	1.149975	C	1.485579	3.562128	1.445477
O	1.888411	-2.117244	0.684600	C	2.417711	-1.406128	-3.378420
C	0.502409	-3.396259	2.267510	C	2.969818	-0.419209	-4.200060
C	1.528348	-3.634932	3.191326	C	4.325021	-0.446461	-4.530688
C	1.228015	-3.942458	4.515511	C	5.141104	-1.458323	-4.032008
C	-0.101829	-4.024375	4.932493	C	4.599266	-2.445156	-3.206230
C	-1.127906	-3.794683	4.019296	C	3.245969	-2.422010	-2.884554
C	-0.825870	-3.477750	2.694177	C	0.945296	-1.391676	-3.051703
C	0.830540	-3.101618	0.819688	Cl	1.704087	3.676235	3.222882
C	-2.189957	-0.268467	-0.796734	Cl	3.050582	3.825766	0.626729
O	-2.528284	0.586099	-1.870364	Cl	0.261610	4.740309	0.912356
C	-4.959243	0.146669	-1.915191	H	0.615298	-0.783385	2.513739
C	-5.492967	1.356082	-1.452440	H	2.530142	-0.263409	0.800844
C	-6.705663	1.377979	-0.770281	H	2.080333	0.085857	-1.389085
C	-7.404822	0.190303	-0.547421	H	-0.171198	1.166190	-1.794275
C	-6.885384	-1.016533	-1.008142	H	-1.554687	1.399812	0.361261

H	2.562067	-3.581350	2.867708
H	2.029632	-4.131554	5.220464
H	-0.334498	-4.272192	5.961642
H	-2.162564	-3.860502	4.335836
H	-1.630076	-3.294565	1.989278
H	1.241212	-3.990055	0.335368
H	-0.056198	-2.797741	0.264990
H	-3.041687	-0.444173	-0.129789
H	-1.813218	-1.232534	-1.154791
H	-4.958334	2.282506	-1.635464
H	-7.113990	2.320255	-0.423071
H	-8.353555	0.209063	-0.023702
H	-7.427688	-1.940522	-0.843893
H	-5.268353	-1.979369	-2.048860
H	-3.669259	0.822939	-3.506579
H	-3.435757	-0.872723	-3.046260
H	1.024103	1.444050	2.880335
H	2.336414	0.367928	-4.597943
H	4.739220	0.319188	-5.176360
H	6.193797	-1.483430	-4.288605
H	5.231349	-3.237611	-2.822423
H	2.828335	-3.191608	-2.245167
H	0.452024	-2.300980	-3.398402
H	0.454573	-0.538874	-3.534451



E_{gas}(B3LYP)=-2934.18780364 a.u.

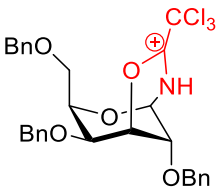
E_{solv}(B3LYP)= -2934.24431630 a.u.

Thermal correction to Gibbs Free Energy= 0.467918 a.u.

C	-0.252317	0.401101	1.161691
C	-1.117263	-0.060540	-0.050752
C	-1.109822	-1.599894	-0.052134
C	0.316904	-2.151304	-0.237266
C	1.325416	-1.293115	0.581886
O	0.658019	-0.539511	1.613846
O	-0.610970	0.476159	-1.260384
C	-2.199918	2.303408	-1.704945
C	-1.450444	3.485793	-1.779708
C	-1.974874	4.690075	-1.317609
C	-3.259862	4.729114	-0.772685
C	-4.017204	3.562531	-0.700531
C	-3.489806	2.357173	-1.166210
C	-1.608950	1.000179	-2.183188

O	-1.959785	-2.055906	-1.084093	Cl	2.932964	3.600138	-0.946708
O	0.312393	-3.503158	0.178895	C	2.116117	-0.354558	-0.335907
N	0.477777	1.693762	0.900088	H	-0.898734	0.632173	2.010178
O	2.567200	0.874891	0.362470	H	-2.139428	0.283709	0.118567
C	1.747974	1.821897	0.664817	H	-1.467574	-1.934707	0.927966
C	2.428350	3.208177	0.726473	H	0.556774	-2.085827	-1.304363
Cl	1.304458	4.469040	1.328179	H	1.994049	-1.947049	1.134176
C	-2.874264	-3.122541	-0.724367	H	-0.461157	3.465776	-2.226789
C	-3.983193	-2.666326	0.193523	H	-1.393633	5.601425	-1.400969
C	-4.020356	-3.070407	1.531446	H	-3.673189	5.667966	-0.422865
C	-5.041780	-2.637516	2.378645	H	-5.021248	3.590937	-0.293332
C	-6.038529	-1.795379	1.892868	H	-4.093808	1.456362	-1.125087
C	-6.015778	-1.391493	0.556364	H	-2.374898	0.239743	-2.342640
C	-4.995707	-1.824595	-0.285633	H	-1.057291	1.135898	-3.113939
C	1.081601	-4.412319	-0.635732	H	-0.044616	2.557352	1.032943
C	2.573541	-4.166044	-0.594716	H	-3.274150	-3.455794	-1.683019
C	3.252685	-3.701948	-1.725445	H	-2.312292	-3.946097	-0.276934
C	4.628452	-3.465353	-1.684380	H	-3.256466	-3.742403	1.910191
C	5.337254	-3.688717	-0.506418	H	-5.063136	-2.966573	3.411260
C	4.669765	-4.159475	0.626741	H	-6.838740	-1.466676	2.545920
C	3.299410	-4.399660	0.580945	H	-6.804080	-0.755358	0.169647
Cl	3.831471	3.085367	1.812745	H	-4.993048	-1.525743	-1.329267

H	0.839270	-5.397057	-0.233790
H	0.717781	-4.364192	-1.668577
H	2.708537	-3.545468	-2.652076
H	5.144833	-3.121081	-2.573335
H	6.406537	-3.514616	-0.473455
H	5.221966	-4.353184	1.539228
H	2.787621	-4.778847	1.459688
H	1.531367	-0.010246	-1.186729
H	3.043871	-0.813416	-0.667392



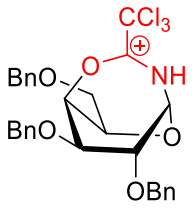
E_{gas}(B3LYP)=-2934.19691393 a.u.

E_{solv}(B3LYP)= -2934.25289872 a.u.

Thermal correction to Gibbs Free Energy= 0.468566 a.u.

C	-0.316394	0.115729	-1.925099
C	0.833277	-0.870949	-1.549730
C	1.516452	-0.586923	-0.202578
C	1.860184	0.895166	-0.079933
C	0.504060	1.623061	-0.152372
O	-0.162156	1.445431	-1.351561
N	-0.285272	1.112250	1.015571
O	2.704316	1.223064	-1.148708
O	0.651238	-0.962337	0.946585
C	-0.171465	-0.112541	1.442838
C	-1.746721	-0.381039	-1.772882
C	3.162971	3.593285	-0.565835
C	2.506988	4.330439	-1.560675
C	-0.884839	-0.591771	2.720741
C	1.977700	5.585275	-1.275020
C	2.102497	6.122707	0.007997
C	2.761502	5.402440	1.001442
C	3.288317	4.142299	0.714154
C	3.719574	2.225955	-0.874632
C	2.459364	-3.507888	-1.512074
O	0.359627	-2.190816	-1.652826
C	2.329073	-4.227142	-0.316630
C	3.452643	-4.560078	0.434004
C	4.724164	-4.183656	-0.004151
C	4.865456	-3.477941	-1.196457
C	3.736767	-3.141634	-1.945595
C	1.233512	-3.137744	-2.313040
O	-2.123270	-0.608596	-0.420563

C	-4.562256	-0.478629	-0.859427	H	3.817988	3.593478	1.487097
C	-5.323202	-0.969785	-1.922973	H	4.352590	1.870873	-0.054062
C	-6.405977	-0.243402	-2.419363	H	4.314558	2.235599	-1.787930
C	-6.733954	0.987964	-1.858440	H	1.343527	-4.530149	0.021253
C	-5.980012	1.488411	-0.795760	H	3.341140	-5.125045	1.352429
C	-4.904980	0.757770	-0.299075	H	5.599646	-4.452218	0.575633
C	-3.400046	-1.275395	-0.310849	H	5.851171	-3.197077	-1.549133
Cl	-1.321961	-2.301345	2.600367	H	3.855195	-2.603152	-2.880773
Cl	0.331244	-0.340788	4.027702	H	1.520531	-2.738627	-3.292602
Cl	-2.334495	0.406242	3.054731	H	0.595287	-4.007851	-2.472401
H	-0.209585	0.302053	-2.996561	H	-5.073900	-1.929919	-2.363801
H	1.641934	-0.692219	-2.267861	H	-6.989954	-0.639378	-3.242085
H	2.376100	-1.237369	-0.072737	H	-7.574836	1.553981	-2.241934
H	2.332626	1.100035	0.888785	H	-6.238359	2.442702	-0.350951
H	0.606167	2.696353	-0.008374	H	-4.328780	1.147140	0.533755
H	-1.036986	1.679385	1.393409	H	-3.336093	-2.247606	-0.813366
H	-2.402652	0.371777	-2.223440	H	-3.527426	-1.455371	0.757073
H	-1.836687	-1.307994	-2.349754				
H	2.412882	3.918652	-2.559939				
H	1.478506	6.150789	-2.053313				
H	1.699034	7.104662	0.226226				
H	2.875912	5.823027	1.993832				



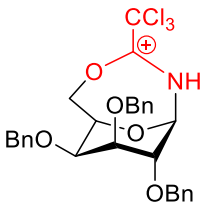
E_{gas}(B3LYP)=-2934.1972601 a.u.

E_{solv}(B3LYP)= -2934.25472122 a.u.

Thermal correction to Gibbs Free Energy= 0.465703 a.u.

C	0.303605	-1.734002	-1.531323
C	0.309358	-0.218463	-1.436708
C	-1.111999	0.362862	-1.598873
C	-2.160677	-0.543962	-0.904380
C	-1.449498	-1.481115	0.093805
O	-0.500205	-2.310818	-0.477378
O	-2.825061	-1.304334	-1.884082
C	1.686497	-2.371059	-1.435125
C	-4.564902	-2.373106	-0.470530
C	-4.239978	-3.736125	-0.459969
C	-4.511893	-4.518377	0.658782
C	-5.118917	-3.949840	1.780680
C	-5.456616	-2.598330	1.776531
C	-5.179297	-1.814614	0.654996
C	-4.244124	-1.522439	-1.675320
O	2.467292	-1.799273	-2.461491
C	4.669767	-1.883524	-1.355680
C	5.064453	-2.808058	-0.384671
C	5.841383	-2.410069	0.703889
C	6.230617	-1.078419	0.830673
C	5.844930	-0.147351	-0.135725
C	5.071415	-0.548628	-1.221003
C	3.817662	-2.303212	-2.530852
O	-1.237157	1.662500	-1.075696
N	-0.793857	-0.623621	1.162693
O	0.898537	0.220452	-0.132658
C	0.285462	0.078472	0.987161
C	0.984476	0.792181	2.164601
C	-1.021476	4.049771	-1.316245
C	-2.361327	4.435311	-1.197705
C	-2.691467	5.682934	-0.677712
C	-1.685227	6.563887	-0.278631
C	-0.349071	6.191297	-0.400836
C	-0.020225	4.936673	-0.913990
C	-0.663379	2.709967	-1.896422
Cl	1.031255	2.532695	1.802654
Cl	0.094911	0.519510	3.703263
Cl	2.624936	0.100031	2.286643
H	-0.148142	-1.986264	-2.497531
H	1.020795	0.191806	-2.147649
H	-1.332512	0.337248	-2.673849

H	-2.848755	0.107309	-0.355293
H	-2.155335	-2.112377	0.628326
H	2.118426	-2.186726	-0.444132
H	1.582636	-3.456573	-1.563722
H	-3.775746	-4.183720	-1.332520
H	-4.263915	-5.573499	0.653143
H	-5.340282	-4.562631	2.646801
H	-5.946301	-2.156934	2.637006
H	-5.463149	-0.766534	0.649508
H	-4.743241	-0.549758	-1.604015
H	-4.565173	-2.006782	-2.597665
H	4.775374	-3.849615	-0.485586
H	6.149628	-3.140060	1.443579
H	6.845946	-0.769157	1.667942
H	6.162604	0.885709	-0.050210
H	4.785671	0.175086	-1.977621
H	3.791121	-3.395809	-2.618938
H	4.208248	-1.895103	-3.463714
H	-1.173714	-0.649345	2.104892
H	-3.146506	3.757899	-1.515662
H	-3.731946	5.974291	-0.592230
H	-1.943371	7.538642	0.118517
H	0.436251	6.875344	-0.100668
H	1.022881	4.653142	-1.013594
H	0.425398	2.598427	-1.940683
H	-1.063181	2.599130	-2.912867



E_{gas}(B3LYP)=-2934.19473831 a.u.

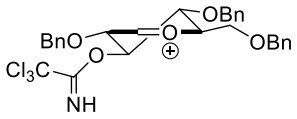
E_{solv}(B3LYP)= -2934.24984989 a.u.

Thermal correction to Gibbs Free Energy= 0.468181 a.u.

C	-1.879483	0.122897	-0.904965
C	-1.772126	-0.738180	0.376770
C	-0.342568	-0.838717	0.921477
C	0.595932	-1.259939	-0.222163
C	0.399002	-0.362923	-1.473709
O	-0.912838	-0.255383	-1.899632
O	0.286042	-2.585730	-0.596074
O	-0.676233	2.352203	-0.438064
N	1.026953	0.988050	-1.247102
C	-1.924060	1.634114	-0.776982
C	2.345118	-3.129174	-1.858538
C	3.634219	-2.651979	-1.601959

C	0.530701	2.085471	-0.756210	C	-3.873740	-0.975834	1.575856
C	1.457888	3.317129	-0.565629	Cl	1.054579	4.434106	-1.908793
C	4.487166	-2.304650	-2.651624	Cl	3.193819	2.862325	-0.666041
C	4.054351	-2.429201	-3.969617	Cl	1.135820	4.072208	1.008889
C	2.770654	-2.910228	-4.236792	H	-2.845924	-0.114768	-1.357111
C	1.923673	-3.259955	-3.188873	H	-2.058086	-1.752239	0.077151
C	1.412272	-3.486363	-0.725335	H	-0.305789	-1.619556	1.685639
O	0.129259	0.398295	1.441752	H	1.629112	-1.166199	0.126525
O	-2.642132	-0.238942	1.375363	H	0.958374	-0.787640	-2.305965
C	1.026846	-0.355865	3.613724	H	2.031076	1.017627	-1.409879
C	2.408380	-0.177113	3.463498	H	-2.606150	1.940424	0.011126
C	3.306944	-1.004117	4.130424	H	-2.219585	2.072306	-1.730759
C	2.835655	-2.023198	4.960635	H	3.984405	-2.573721	-0.577125
C	1.465132	-2.205944	5.122841	H	5.489767	-1.951170	-2.439380
C	0.566609	-1.375826	4.450943	H	4.717075	-2.168408	-4.786614
C	0.057800	0.543417	2.884761	H	2.437327	-3.024680	-5.261854
C	-4.871489	-0.800248	0.456779	H	0.930552	-3.642494	-3.401028
C	-5.560881	0.411213	0.312554	H	0.948038	-4.459251	-0.889315
C	-6.460770	0.594237	-0.733641	H	1.955818	-3.520197	0.225344
C	-6.686259	-0.435123	-1.649689	H	2.779525	0.624202	2.832455
C	-6.016118	-1.647922	-1.508679	H	4.373873	-0.848071	4.017398
C	-5.114478	-1.828699	-0.458939	H	3.535494	-2.662615	5.486034

H	1.094147	-2.989253	5.773648
H	-0.500852	-1.515217	4.590379
H	-0.968324	0.368750	3.213511
H	0.299021	1.594358	3.052194
H	-5.403322	1.206884	1.034177
H	-6.998647	1.530754	-0.827439
H	-7.392571	-0.295703	-2.459808
H	-6.200715	-2.455623	-2.207468
H	-4.609626	-2.782970	-0.344593
H	-4.266310	-0.580176	2.513448
H	-3.639078	-2.035786	1.721847



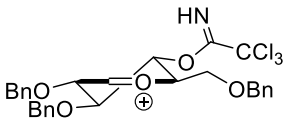
E_{gas}(B3LYP)= -2934.14884308 a.u.

E_{solv}(B3LYP)= -2934.21931740 a.u.

Thermal correction to Gibbs Free Energy= 0.459390 a.u.

C	-0.428207	-2.402540	-0.920487
C	0.637337	-0.238228	-0.229661
C	-1.861895	-0.505823	-0.371028
C	-0.670626	0.402173	-0.714840
O	-1.573470	-1.962331	-0.696328
C	0.841052	-1.61458900	-0.87094400
O	-0.909573	1.612167	-0.030177
O	1.738482	0.587123	-0.629373
O	1.751611	-2.389245	-0.122900
C	-3.152058	-0.184447	-1.091917
C	-1.229598	3.986865	0.023781
C	2.585250	1.054816	0.318241
C	-2.548782	4.444967	0.103626
C	-2.876200	5.522341	0.925567
C	-1.884859	6.151399	1.678318
C	-0.566179	5.701510	1.604714
N	2.411572	0.887905	1.549551
C	-0.241429	4.625494	0.781170
C	-0.878150	2.814829	-0.848419
C	3.755776	1.783201	-0.385036
C	3.671601	-3.812975	0.048307
C	4.685955	-3.074162	0.669114
C	5.556213	-3.687624	1.566475
C	5.421755	-5.047547	1.851232
C	4.415436	-5.790731	1.235642
C	3.542972	-5.174314	0.339410
C	2.726661	-3.143219	-0.905443

O	-4.186974	-0.91831800	-0.47817800	H	0.208110	6.19105600	2.18435500
C	-6.508521	-1.466608	-0.304951	H	0.785444	4.281578	0.721991
C	-6.893949	-2.724727	-0.778188	H	0.122020	2.924859	-1.273683
C	-7.819984	-3.493966	-0.074430	H	-1.598419	2.709092	-1.665882
H	-0.383028	-3.473399	-1.117262	H	4.795743	-2.018829	0.444810
H	0.629331	-0.330878	0.856679	H	6.340681	-3.108365	2.039783
H	-2.025399	-0.535612	0.706342	H	6.101475	-5.525938	2.547099
H	-0.621824	0.565437	-1.797601	H	4.309950	-6.847638	1.451628
H	1.174077	-1.479619	-1.912839	H	2.761830	-5.755659	-0.139040
H	-3.317271	0.896644	-0.997024	H	2.207149	-3.881101	-1.523971
H	-3.062739	-0.424481	-2.160865	H	3.245955	-2.436099	-1.560024
C	-8.369841	-3.010289	1.112614	H	-6.469977	-3.102410	-1.702980
C	-7.993039	-1.754826	1.591175	H	-8.113391	-4.466588	-0.452960
C	-7.068411	-0.987999	0.884631	H	-9.091791	-3.606091	1.659562
C	-5.484298	-0.651501	-1.045930	H	-8.422175	-1.372527	2.510425
Cl	4.636355	0.604678	-1.425968	H	-6.781142	-0.010292	1.257481
Cl	3.114623	3.119200	-1.405694	H	-5.698426	0.420569	-0.956866
H	3.146210	1.302718	2.116358	H	-5.474014	-0.914678	-2.110162
Cl	4.894201	2.464032	0.815089				
H	-3.323287	3.961575	-0.482823				
H	-3.901181	5.871654	0.975887				
H	-2.137454	6.991194	2.315649				



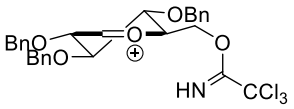
E_{gas}(B3LYP)= -2934.14910469 a.u.

E_{solv}(B3LYP)= -2934.21900233 a.u.

Thermal correction to Gibbs Free Energy= 0.459751 a.u.

C	0.123542	2.535188	-0.612741
C	-0.929535	0.323433	-0.036691
C	1.608129	0.638258	-0.219690
C	0.403682	-0.267383	-0.511064
O	1.276492	2.101115	-0.406119
C	-1.117945	1.710348	-0.686850
O	0.655981	-1.463103	0.239838
O	-1.955158	-0.547247	-0.438840
O	-2.133248	2.437974	-0.036815
C	2.816186	0.378698	-1.093958
C	-4.027515	-1.689863	-0.083064
C	-3.971610	3.978139	-0.062368
C	-5.199459	3.424620	0.315020
C	-6.076324	4.140118	1.128573
C	-5.731676	5.416760	1.572425
C	-4.510100	5.977540	1.198321
C	-3.635727	5.261033	0.384003
C	-3.014256	3.200165	-0.917020
O	3.915991	1.063659	-0.543769
C	6.248191	1.599698	-0.603175
C	6.548313	2.92589700	-0.93023200
C	7.565961	3.607505	-0.263978
C	8.294750	2.966376	0.737757
C	8.004190	1.642512	1.068912
C	6.986483	0.963983	0.400724
C	5.129757	0.874721	-1.299515
C	-5.000695	-1.217947	-0.971176
C	-5.916311	-2.093409	-1.550909
C	-5.869555	-3.454521	-1.246027
C	-4.904159	-3.934319	-0.361709
C	-3.987271	-3.055415	0.214369
C	-3.028502	-0.742480	0.521527
C	0.758840	-2.643668	-0.414721
N	0.676029	-2.754475	-1.662045
C	1.033630	-3.754825	0.624877
Cl	2.654480	-3.451993	1.353724
H	0.058731	3.620619	-0.690588
H	-0.911561	0.444142	1.052249
H	1.879671	0.599668	0.835045
H	0.340830	-0.515816	-1.571842
H	-1.337924	1.553142	-1.755740
H	2.608261	0.700447	-2.124343

H	2.985398	-0.706598	-1.110371
H	-5.473002	2.434369	-0.032718
H	-7.027331	3.704169	1.412139
H	-6.414613	5.974694	2.202833
H	-4.242040	6.971905	1.536329
H	-2.689264	5.702324	0.089242
H	-2.411917	3.872395	-1.536713
H	-3.534910	2.492920	-1.570205
H	5.985551	3.425426	-1.712091
H	7.791953	4.634339	-0.528262
H	9.088652	3.493826	1.254372
H	8.572278	1.138865	1.842810
H	6.765785	-0.067057	0.657108
H	5.343500	-0.198619	-1.367257
H	4.984566	1.263117	-2.314514
H	-5.042853	-0.160158	-1.208422
H	-6.667795	-1.715298	-2.234781
H	-6.584526	-4.136028	-1.692874
H	-4.865624	-4.990232	-0.119204
H	-3.237601	-3.432427	0.901308
H	-2.605249	-1.154385	1.442683
H	-3.487319	0.224221	0.743672
H	0.777147	-3.71308100	-1.98472700
Cl	1.031836	-5.365052	-0.153869
Cl	-0.219701	-3.723292	1.911621



E_{gas}(B3LYP)= -2934.15088690 a.u.

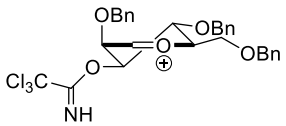
E_{solv}(B3LYP)= -2934.22144122 a.u.

Thermal correction to Gibbs Free Energy= 0.461157 a.u.

C	0.087405	-2.355519	-0.408857
C	1.174019	-0.129887	-0.007832
C	-1.347765	-0.408476	-0.100431
C	-0.152468	0.465281	-0.509795
O	-1.052561	-1.890727	-0.190996
C	1.330627	-1.551887	-0.591977
O	-0.419227	1.714392	0.089706
O	2.225622	0.696702	-0.437462
O	2.381104	-2.254145	0.027711
C	-2.585242	-0.187751	-0.936611
C	4.318209	1.814799	-0.066570
C	4.271814	-3.730404	-0.066209
C	5.513092	-3.112388	0.117364
C	6.502118	-3.727501	0.882816

C	6.257074	-4.967389	1.472941	H	1.145962	-0.194149	1.085918
C	5.022317	-5.591770	1.293037	H	-1.562750	-0.280450	0.959830
C	4.035751	-4.975859	0.525845	H	-0.108695	0.556503	-1.602710
C	3.199964	-3.058604	-0.873130	H	1.486812	-1.448985	-1.678810
O	-3.673961	-0.823209	-0.255585	H	-2.473213	-0.601463	-1.941102
C	-4.879777	-0.746161	-0.843351	H	-2.768087	0.885513	-1.014897
N	-5.067816	-0.162059	-1.942295	H	5.708548	-2.150470	-0.344568
C	-5.917535	-1.467195	0.046859	H	7.462232	-3.242250	1.015440
C	-0.585113	4.102928	0.022264	H	7.026684	-5.447738	2.066260
C	-1.932100	4.478670	0.083577	H	4.830614	-6.558146	1.745031
C	4.496176	3.093974	0.467167	H	3.079007	-5.466901	0.381749
C	5.443330	3.964617	-0.073586	H	2.565789	-3.798438	-1.372145
C	6.217010	3.564113	-1.161169	H	3.624663	-2.392607	-1.630784
C	6.045873	2.288013	-1.701803	H	-6.038183	-0.195683	-2.244175
C	5.105911	1.418529	-1.154472	Cl	-5.966421	-0.667021	1.658239
C	3.301372	0.875146	0.521193	Cl	-5.430634	-3.190133	0.239950
C	-2.321684	5.601280	0.810656	Cl	-7.546904	-1.399408	-0.689640
C	-1.365466	6.364271	1.482794	H	-2.678184	3.892882	-0.443287
C	-0.020749	6.000685	1.423525	H	3.897350	3.409055	1.315285
C	0.365602	4.874331	0.697438	H	5.574525	4.952397	0.353402
C	-0.168913	2.879279	-0.745144	H	6.952318	4.239160	-1.584104
H	0.136898	-3.444551	-0.405383	H	6.649574	1.970211	-2.544429

H	4.982969	0.425236	-1.572969
H	2.886507	1.286295	1.446501
H	3.744841	-0.100306	0.738618
H	-3.367426	5.884535	0.848662
H	-1.667351	7.240600	2.045140
H	0.726206	6.593707	1.938905
H	1.412861	4.595905	0.648947
H	-0.753142	2.779098	-1.666470
H	0.891754	2.912164	-0.999320



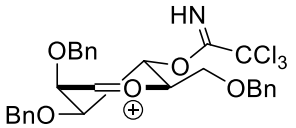
E_{gas}(B3LYP)= -2934.13682826 a.u.

E_{solv}(B3LYP)= -2934.20185440 a.u.

Thermal correction to Gibbs Free Energy= 0.463652 a.u.

C	1.053185	-1.419637	-1.668802
C	0.407310	-0.673305	-0.488994
C	-1.100067	-0.539251	-0.738266
C	-1.735092	-1.925745	-0.854285
C	-0.921832	-2.851885	-1.695935
O	0.285937	-2.689074	-1.986375
O	1.014001	0.598823	-0.449209
C	2.351505	2.26590300	0.68618000
C	3.037432	2.749847	1.807393
C	3.680951	3.983451	1.766782
C	3.647563	4.753441	0.602209
C	2.965993	4.277475	-0.515096
C	2.319579	3.039689	-0.474887
C	1.672255	0.921576	0.789248
O	-1.606699	-2.669832	0.357442
C	-2.770888	-3.455853	0.790551
C	-3.963048	-2.606025	1.124109
C	-5.106019	-2.640786	0.318062
C	-6.220973	-1.865273	0.636801
C	-6.197506	-1.046043	1.763469
C	-5.060548	-1.006165	2.574289
C	-3.950695	-1.782693	2.257955
O	-1.734630	0.119532	0.357004
C	-1.921062	1.465369	0.448147
C	-2.685109	2.155079	-0.722644
N	-1.560426	2.030182	1.510292
C	2.482295	-1.865118	-1.466534
Cl	-1.516267	2.596394	-2.028832
Cl	-3.484512	3.658857	-0.156387
Cl	-3.944634	1.061281	-1.393426

O	2.553932	-2.627040	-0.279513	H	-5.130706	-3.287138	-0.553681
C	4.968029	-2.392634	0.190616	H	-7.103498	-1.903550	0.008779
C	5.058281	-1.732843	1.423007	H	-7.063104	-0.443685	2.014402
C	6.118890	-0.870712	1.689319	H	-5.044093	-0.374418	3.454855
C	7.107800	-0.659663	0.726088	H	-3.071694	-1.754829	2.892290
C	7.030494	-1.315357	-0.501012	H	-1.848639	3.005505	1.553057
C	5.964161	-2.176122	-0.765955	H	2.797065	-2.453799	-2.337331
C	3.806094	-3.316817	-0.093269	H	3.108107	-0.965611	-1.423398
H	0.968702	-0.834259	-2.585526	H	4.297008	-1.901491	2.177740
H	0.573467	-1.228663	0.436752	H	6.179980	-0.368877	2.648386
H	-1.266257	-0.008877	-1.678284	H	7.935483	0.008635	0.934721
H	-2.769238	-1.862112	-1.197770	H	7.797441	-1.158707	-1.251075
H	-1.330342	-3.816825	-1.990035	H	5.910318	-2.687352	-1.721926
H	3.067498	2.158340	2.717286	H	4.012331	-3.931457	-0.977153
H	4.207714	4.344483	2.643013	H	3.623226	-3.980387	0.752643
H	4.147972	5.714521	0.569431				
H	2.932894	4.869037	-1.423369				
H	1.788444	2.677115	-1.344756				
H	2.410000	0.144983	1.020767				
H	0.928694	0.940868	1.593080				
H	-3.014291	-4.193156	0.022286				
H	-2.383682	-3.979332	1.663680				



E_{gas}(B3LYP)= -2934.14707738 a.u.

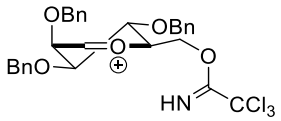
E_{solv}(B3LYP)= -2934.21285622 a.u.

Thermal correction to Gibbs Free Energy= 0.464678 a.u.

C	-0.244225	-1.066298	-2.088628

C	0.507036	-0.236269	-1.030124	C	-1.495115	-3.860521	-0.049593
C	0.320277	1.271370	-1.264892	O	1.070527	2.120342	-0.432072
C	-1.177859	1.609225	-1.290606	C	2.613358	-1.144611	-0.278186
C	-1.968066	0.661246	-2.130506	C	4.032727	-1.429490	-0.822546
O	-1.607694	-0.507011	-2.404590	N	2.160466	-1.387263	0.867661
O	1.888365	-0.566259	-1.261222	C	1.877206	3.042711	1.613401
O	-1.834163	1.328906	-0.049477	C	3.256709	2.838269	1.728712
C	-2.775155	2.337977	0.445286	C	4.076521	3.827589	2.268028
C	-4.068087	2.380519	-0.323979	C	3.524241	5.034402	2.699650
C	-4.367958	3.460753	-1.160573	C	2.150440	5.247129	2.589633
C	-5.560324	3.483401	-1.885202	C	1.333224	4.255515	2.047773
C	-6.461707	2.426116	-1.777236	C	0.993359	1.981613	1.016627
C	-6.174276	1.347609	-0.937524	Cl	3.905657	-2.551971	-2.226232
C	-4.986830	1.326737	-0.211674	Cl	5.054447	-2.184540	0.437372
C	-0.495266	-2.510689	-1.714648	Cl	4.786888	0.114422	-1.348101
O	-1.205407	-2.538371	-0.498131	H	0.273571	-1.008923	-3.046714
C	-2.265136	-3.824270	1.249471	H	0.213648	-0.542070	-0.028205
C	-2.737201	-2.632984	1.803454	H	0.694534	1.494052	-2.270643
C	-3.457324	-2.649290	3.000149	H	-1.327827	2.641125	-1.613871
C	-3.712992	-3.853024	3.652912	H	-2.983154	0.905972	-2.437548
C	-3.242188	-5.046885	3.102852	H	-2.937061	2.026250	1.476964
C	-2.522363	-5.031041	1.911088	H	-2.271818	3.307649	0.436497

H	-3.675897	4.292670	-1.239343
H	-5.784319	4.326395	-2.528404
H	-7.389158	2.444331	-2.337872
H	-6.879572	0.530188	-0.842399
H	-4.771103	0.493244	0.448533
H	0.478203	-3.011872	-1.631496
H	-1.056965	-2.999289	-2.520597
H	-2.539072	-1.694957	1.301176
H	-3.816431	-1.717044	3.422088
H	-4.271235	-3.863479	4.582101
H	-3.432762	-5.989351	3.603778
H	-2.156773	-5.963761	1.492557
H	-2.079966	-4.384857	-0.818357
H	-0.557143	-4.415674	0.085043
H	2.843030	-1.824119	1.481446
H	3.689771	1.900837	1.396718
H	5.143515	3.656638	2.355620
H	4.161049	5.802741	3.123271
H	1.715814	6.181249	2.927090
H	0.263975	4.423049	1.966719
H	1.335750	0.985321	1.305532
H	-0.035911	2.108326	1.350272



E_{gas}(B3LYP)= -2934.14559245 a.u.

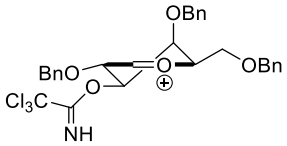
E_{solv}(B3LYP)= -2934.21388019 a.u.

Thermal correction to Gibbs Free Energy= 0.464076 a.u.

C	0.637474	-0.626725	-0.198401
C	-0.626236	0.035135	0.398271
C	-1.656572	0.306161	-0.711513
C	-2.001595	-1.038287	-1.380592
C	-0.816068	-1.887414	-1.683386
O	0.298627	-1.772117	-1.120053
O	-2.581194	-1.964879	-0.456695
C	-3.880238	-2.531853	-0.838536
C	-4.343675	-3.406657	0.285546
C	-4.945922	-2.840703	1.415776
C	-5.360094	-3.649363	2.471118
C	-5.177371	-5.031530	2.405052
C	-4.580389	-5.602915	1.281470
C	-4.163872	-4.792509	0.226815
C	1.545339	-1.224555	0.859721

O	2.749197	-1.767568	0.297237	Cl	5.463844	-2.897050	0.753693
C	4.958593	-1.725535	-0.511220	H	1.187770	0.051711	-0.848827
C	3.743201	-0.915132	-0.004114	H	-1.084521	-0.653983	1.112615
O	-2.793053	0.896768	-0.131625	H	-1.220953	0.955883	-1.482279
C	-3.193774	2.834924	-1.627423	H	-2.618939	-0.908529	-2.271182
C	-3.213432	4.010777	-0.866172	H	-0.911293	-2.761379	-2.324567
C	-2.724938	5.204235	-1.391614	H	-4.562046	-1.694889	-1.009195
C	-2.210762	5.238554	-2.689222	H	-3.763544	-3.098946	-1.764535
C	-2.193352	4.076912	-3.458929	H	-5.093222	-1.767225	1.466343
C	-2.685174	2.882749	-2.930118	H	-5.828683	-3.204182	3.341151
C	-3.718522	1.546587	-1.041683	H	-5.503929	-5.661119	3.224826
O	-0.240207	1.145990	1.176369	H	-4.442157	-6.676444	1.225484
N	3.642161	0.334251	0.117763	H	-3.703229	-5.238276	-0.648532
C	0.678877	3.313980	1.546751	H	1.060532	-2.065699	1.353325
C	2.013747	3.248419	1.961640	H	1.777565	-0.447582	1.587288
C	2.489614	4.110762	2.947695	H	-3.621052	3.989586	0.139133
C	1.634395	5.047898	3.529170	H	-2.751069	6.108319	-0.794135
C	0.302742	5.119154	3.121090	H	-1.833983	6.168410	-3.099691
C	-0.171544	4.255151	2.134539	H	-1.804680	4.100112	-4.470616
C	0.161685	2.365091	0.499128	H	-2.684568	1.986930	-3.543031
Cl	6.332599	-0.643594	-0.891640	H	-4.011731	0.8569500	-1.839596
Cl	4.477604	-2.611157	-2.005569	H	-4.595269	1.732876	-0.422043

H	4.493436	0.824464	-0.145159
H	2.676918	2.518266	1.509625
H	3.526154	4.054439	3.260723
H	2.004968	5.720821	4.294213
H	-0.364796	5.846974	3.568353
H	-1.207135	4.313911	1.817786
H	-0.700454	2.793087	-0.016538
H	0.946199	2.150961	-0.232542



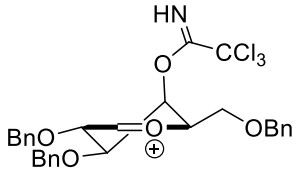
E_{gas}(B3LYP)= -2934.15844527 a.u.

E_{solv}(B3LYP)= -2934.22411410 a.u.

Thermal correction to Gibbs Free Energy= 0.459161 a.u.

C	-0.680808	1.345448	1.186893
C	0.645782	0.199519	-0.590102
C	-1.835632	0.175046	-0.612619
C	-0.595080	-0.708656	-0.671656
O	-1.754465	1.099302	0.600464
C	0.681607	0.873747	0.777981
O	-0.650509	-1.621280	0.407512
O	1.869681	-0.534583	-0.717964
O	1.473992	2.041664	0.757860
C	-3.153188	-0.551805	-0.473757
C	-0.503952	-3.825430	1.330333
C	2.387969	-0.662753	-1.959851
C	0.439546	-3.981592	2.351216
C	0.145710	-4.752203	3.475224
C	-1.096788	-5.376106	3.587606
C	-2.042888	-5.228798	2.572596
N	1.779911	-0.287711	-2.994006
C	-1.746604	-4.457103	1.450651
C	-0.192677	-2.974372	0.131948
C	3.784087	-1.319471	-1.860763
C	3.134572	3.482909	1.714809
C	4.191942	3.581662	0.802641
C	4.869494	4.787079	0.636914
C	4.497979	5.906187	1.383869
C	3.447457	5.815686	2.296210
C	2.768415	4.608829	2.458677
C	2.394547	2.188630	1.881735
O	-4.187536	0.384317	-0.684174
C	-6.523099	0.906004	-0.697223
C	-6.905309	1.739255	0.359520

C	-7.831300	2.761137	0.156895	H	0.880406	-2.957628	-0.065934
H	-0.768811	2.026591	2.033329	H	4.486949	2.712706	0.224737
H	0.600829	0.955282	-1.376125	H	5.689196	4.853137	-0.069288
H	-1.876055	0.878793	-1.443814	H	5.028540	6.843073	1.257890
H	-0.608094	-1.216251	-1.642064	H	3.158454	6.681166	2.881279
H	1.015063	0.148250	1.533425	H	1.953274	4.540095	3.171403
H	-3.224761	-1.023961	0.512097	H	1.828574	2.183175	2.817357
H	-3.169670	-1.347407	-1.232793	H	3.071031	1.328315	1.871054
C	-8.386951	2.958755	-1.107628	H	-6.479137	1.584278	1.345387
C	-8.014474	2.130746	-2.166567	H	-8.122466	3.398726	0.984002
C	-7.087225	1.110011	-1.960505	H	-9.110111	3.750907	-1.265510
C	-5.499833	-0.175222	-0.482633	H	-8.447385	2.277306	-3.149640
Cl	3.616101	-2.957674	-1.132820	H	-6.801719	0.464963	-2.785073
Cl	4.524886	-1.476018	-3.481625	H	-5.651512	-1.000481	-1.188640
H	2.314542	-0.438450	-3.845604	H	-5.564483	-0.576434	0.535963
Cl	4.847233	-0.306529	-0.822216				
H	1.409805	-3.504107	2.262318				
H	0.886145	-4.870474	4.258153				
H	-1.324438	-5.980087	4.458584				
H	-3.006453	-5.719012	2.652625				
H	-2.481735	-4.350758	0.659624				
H	-0.714202	-3.342159	-0.757532				



E_{gas}(B3LYP)= -2934.15723376 a.u.

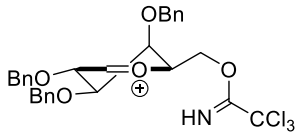
E_{solv}(B3LYP)= -2934.22420288 a.u.

Thermal correction to Gibbs Free Energy= 0.458233 a.u.

C	0.623116	1.646704	-1.030613

C	-0.698965	0.448252	0.742119	C	8.049236	2.491046	-0.126671
C	1.815077	0.320093	0.631581	C	7.041695	1.567754	-0.403052
C	0.533813	-0.479891	0.764751	C	5.441529	-0.244632	0.312126
O	1.713362	1.314549	-0.517917	C	-4.833888	-0.311039	2.297062
C	-0.732989	1.194912	-0.594468	C	-6.118387	-0.848375	2.225011
O	0.449815	-1.398240	-0.341271	C	-6.291163	-2.215761	2.010454
O	-1.914420	-0.241487	0.852436	C	-5.176476	-3.043486	1.872116
O	-1.504245	2.371776	-0.504736	C	-3.893714	-2.503816	1.947267
C	3.078543	-0.469917	0.370094	C	-2.326896	-0.548076	2.208815
C	-3.711041	-1.133063	2.158243	C	0.135517	-2.690691	-0.089925
C	-3.315988	3.763432	-1.224872	N	-0.005857	-3.150070	1.069337
C	-4.373335	3.681899	-0.311372	C	0.013875	-3.438867	-1.436039
C	-5.114966	4.815849	0.011823	Cl	1.590572	-3.345299	-2.301843
C	-4.806423	6.043160	-0.576797	H	0.704734	2.382778	-1.830573
C	-3.756215	6.132387	-1.490042	H	-0.586804	1.184833	1.548818
C	-3.014418	4.996560	-1.811316	H	1.952697	0.972450	1.493862
C	-2.505156	2.544583	-1.552592	H	0.576761	-1.036371	1.701666
O	4.175390	0.390975	0.579687	H	-1.106337	0.505124	-1.367024
C	6.545991	0.733383	0.603989	H	3.069895	-0.877999	-0.647611
C	7.078209	0.836129	1.893700	H	3.093197	-1.314410	1.074079
C	8.084979	1.758473	2.173577	H	-4.618782	2.727067	0.141161
C	8.571879	2.588150	1.162957	H	-5.935485	4.742523	0.716378

H	-5.386089	6.924953	-0.328550
H	-3.517064	7.082866	-1.952987
H	-2.200127	5.067041	-2.524885
H	-2.001044	2.656488	-2.516794
H	-3.124061	1.642570	-1.576390
H	6.705624	0.188365	2.680499
H	8.492183	1.826516	3.176031
H	9.358221	3.302703	1.378406
H	8.428464	3.129679	-0.916381
H	6.640955	1.490821	-1.408504
H	5.534084	-1.135236	0.945159
H	5.467951	-0.562298	-0.736896
H	-4.701650	0.752203	2.468116
H	-6.981689	-0.202729	2.339480
H	-7.289338	-2.635362	1.956692
H	-5.306708	-4.107575	1.710691
H	-3.027950	-3.149306	1.845334
H	-1.622981	-1.260203	2.650162
H	-2.314349	0.376196	2.796028
H	-0.231319	-4.141143	1.080691
Cl	-0.407221	-5.156209	-1.171199
Cl	-1.268754	-2.662819	-2.430202



E_{gas}(B3LYP)= -2934.15704596 a.u.

E_{solv}(B3LYP)= -2934.22480239 a.u.

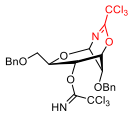
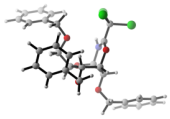
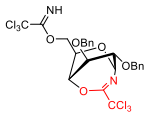
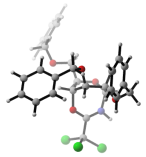
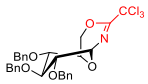
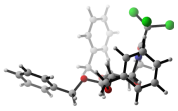
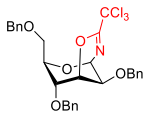
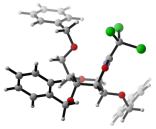
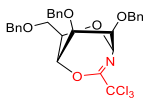
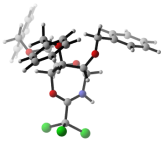
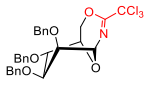
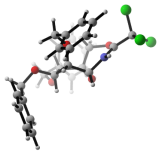
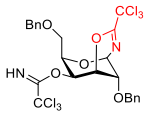
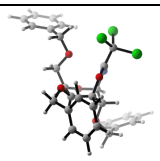
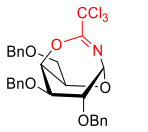
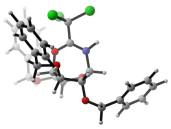
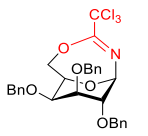
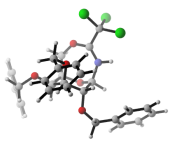
Thermal correction to Gibbs Free Energy= 0.459417 a.u.

C	-0.089624	-1.557188	-0.863962
C	1.126329	-0.190228	0.852243
C	-1.381577	-0.233197	0.722478
C	-0.155483	0.665910	0.826043
O	-1.202214	-1.285355	-0.362027
C	1.216983	-0.936723	-0.492784
O	-0.172516	1.559611	-0.269881
O	2.234050	0.654237	1.039676
O	2.158234	-1.986185	-0.446034
C	-2.660584	0.489452	0.374219
C	4.330594	1.198136	2.055495
C	3.858179	-3.340083	-1.461370
C	5.109878	-3.199531	-0.852628
C	5.927460	-4.310291	-0.653118
C	5.500162	-5.573683	-1.062318
C	4.255292	-5.722334	-1.674190

C	3.439741	-4.609992	-1.872519	H	-0.232471	1.198135	1.781522
C	2.963751	-2.149506	-1.650569	H	1.447779	-0.191109	-1.270041
O	-3.733638	-0.435691	0.599113	H	-2.661162	0.835694	-0.658157
C	-4.971119	-0.003735	0.304658	H	-2.769455	1.355708	1.030949
N	-5.205030	1.149528	-0.142253	H	5.448548	-2.217903	-0.539254
C	-5.981772	-1.133032	0.609949	H	6.897101	-4.189889	-0.183841
C	0.038390	3.745196	-1.223673	H	6.136990	-6.437660	-0.910397
C	1.078326	4.052258	-2.106117	H	3.922670	-6.701242	-1.999856
C	5.382875	1.353217	1.147102	H	2.474994	-4.727567	-2.354740
C	6.317254	2.374607	1.311035	H	2.301542	-2.293930	-2.509825
C	6.208529	3.252703	2.389402	H	3.538924	-1.230367	-1.801379
C	5.164623	3.104162	3.302889	H	-6.194419	1.311864	-0.311391
C	4.231715	2.081989	3.135395	Cl	-5.577978	-2.571704	-0.394888
C	3.305697	0.115749	1.858675	Cl	-5.873248	-1.563571	2.354885
C	0.836086	4.813602	-3.249738	Cl	-7.653246	-0.612065	0.240750
C	-0.452079	5.271906	-3.521952	H	2.082262	3.699017	-1.894804
C	-1.496637	4.970842	-2.645848	H	5.474044	0.670182	0.309171
C	-1.251005	4.213826	-1.502767	H	7.130377	2.482342	0.602119
C	0.297104	2.910568	-0.000896	H	6.936536	4.045268	2.520375
H	-0.113849	-2.364181	-1.597026	H	5.079982	3.780191	4.146160
H	1.051022	-0.926077	1.662589	H	3.423334	1.967218	3.850228
H	-1.508736	-0.844333	1.615097	H	2.886725	-0.203033	2.819039

H	3.739102	-0.753496	1.358391
H	1.651214	5.049523	-3.924406
H	-0.641500	5.865532	-4.409123
H	-2.498284	5.331429	-2.850672
H	-2.063705	3.988369	-0.819863
H	-0.254110	3.297937	0.863162
H	1.359917	2.879927	0.241474

5. Table S1. The matchings of calculated and NMR data-suggested conformations

	Compd.	Optimized structure [a]		Position	dihedral angle [b]	Calcul. ^3J (Hz) [c]	Found ^3J (Hz) [d]
Glu	21			H1-H2	60.6	1.6	4.3
				H2-H3	-108.6	0.8	3.7
				H3-H4	46.3	3.7	1.2
				H4-H5	-69.4	0.7	bs, bt
	16			H1-H2	57.1	2.1	4.0
				H2-H3	-127.9	3.4	3.8
				H3-H4	71.2	0.5	1.9
				H4-H5	-71.7	0.4	bs, bt
	8			H1-H2	107.3	0.7	1.5
				H2-H3	-163.7	8.5	7.6
				H3-H4	-177.8	9.2	10.0
				H4-H5	-148.0	6.6	5.8
Man	33			H1-H2	-70.6	0.6	2.4
				H2-H3	70.8	0.5	2.1
				H3-H4	71.6	0.5	2.1
				H4-H5	-106.1	0.6	2.8
	4			H1-H2	-81.7	-0.2	1.7
				H2-H3	18.7	7.3	7.7
				H3-H4	60.9	1.6	1.7
				H4-H5	-76.6	0.1	m, m
	10			H1-H2	19.4	7.3	6.4
				H2-H3	-60.5	1.7	3.5
				H3-H4	163.1	8.4	6.8
				H4-H5	-108.6	0.8	bd, m
	27			H1-H2	57.7	2.0	NA[e]
				H2-H3	-56.8	2.2	NA[e]
				H3-H4	-58.2	2.0	NA[e]
				H4-H5	27.5	6.4	NA[e]
Gal	6			H1-H2	60.6	1.6	5.5
				H2-H3	-108.6	0.8	3.8
				H3-H4	46.3	3.7	1.7
				H4-H5	-69.4	0.7	1.5
	12			H1-H2	69.4	0.7	s
				H2-H3	-71.3	0.5	bs
				H3-H4	-52.5	2.8	bs
				H4-H5	47.7	3.5	5.4

Note: [a]The conformations were first optimized by computational calculations according to the procedure described in the experimental section. In each case, the final conformation was selected from the conformations with the lowest calculated energy but matching best to the corresponding NMR data. according to the matching degree to the corresponding NMR data. [b] Dihedral angles were generated through CYLview. [c] ^3J was calculated according to Karplus formula. [d] The real ^3J found in NMR. [e] This compound was not synthesized.

6. References

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C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J.; Gaussian Inc., Wallingford CT, **2009**.

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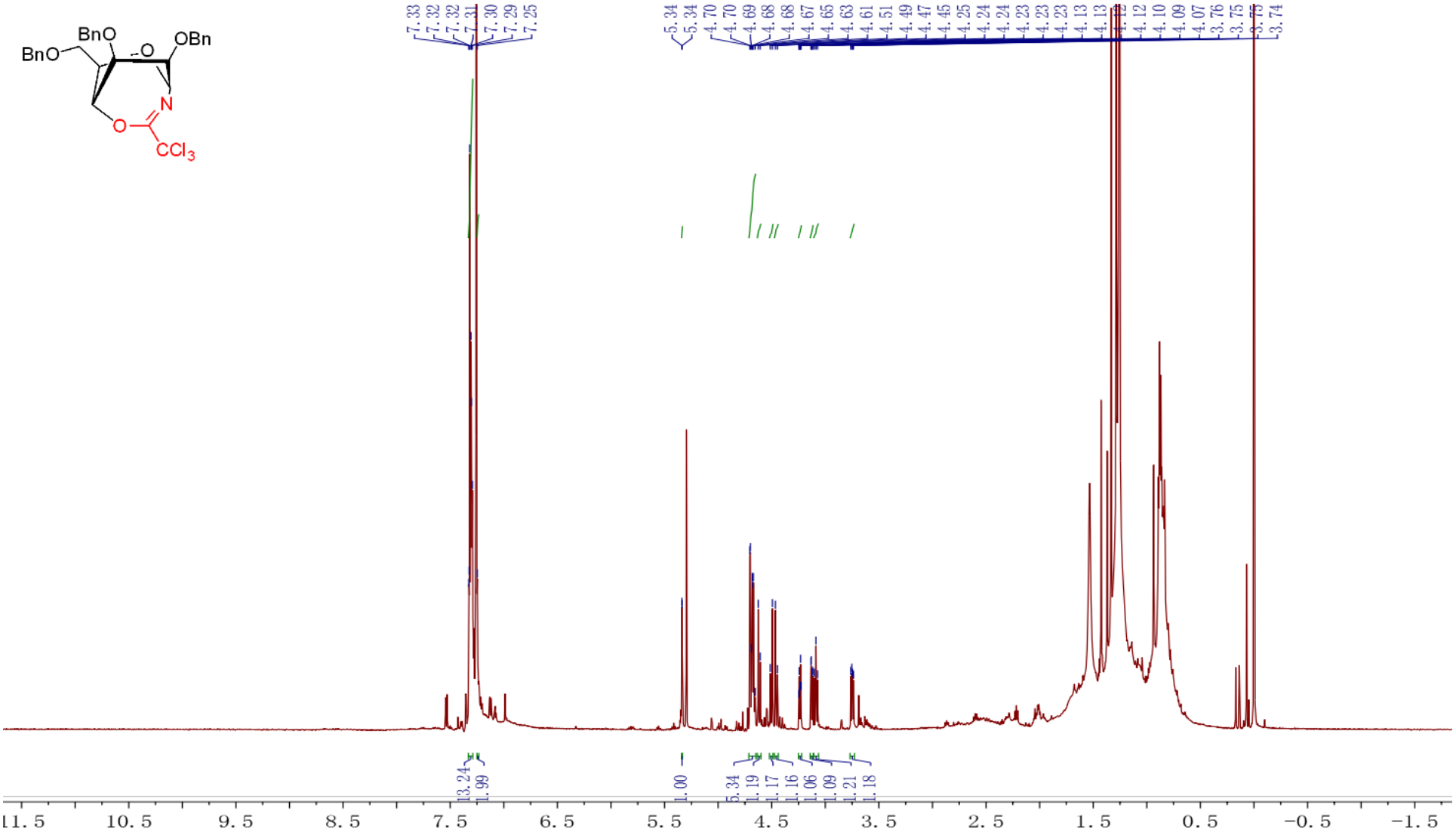
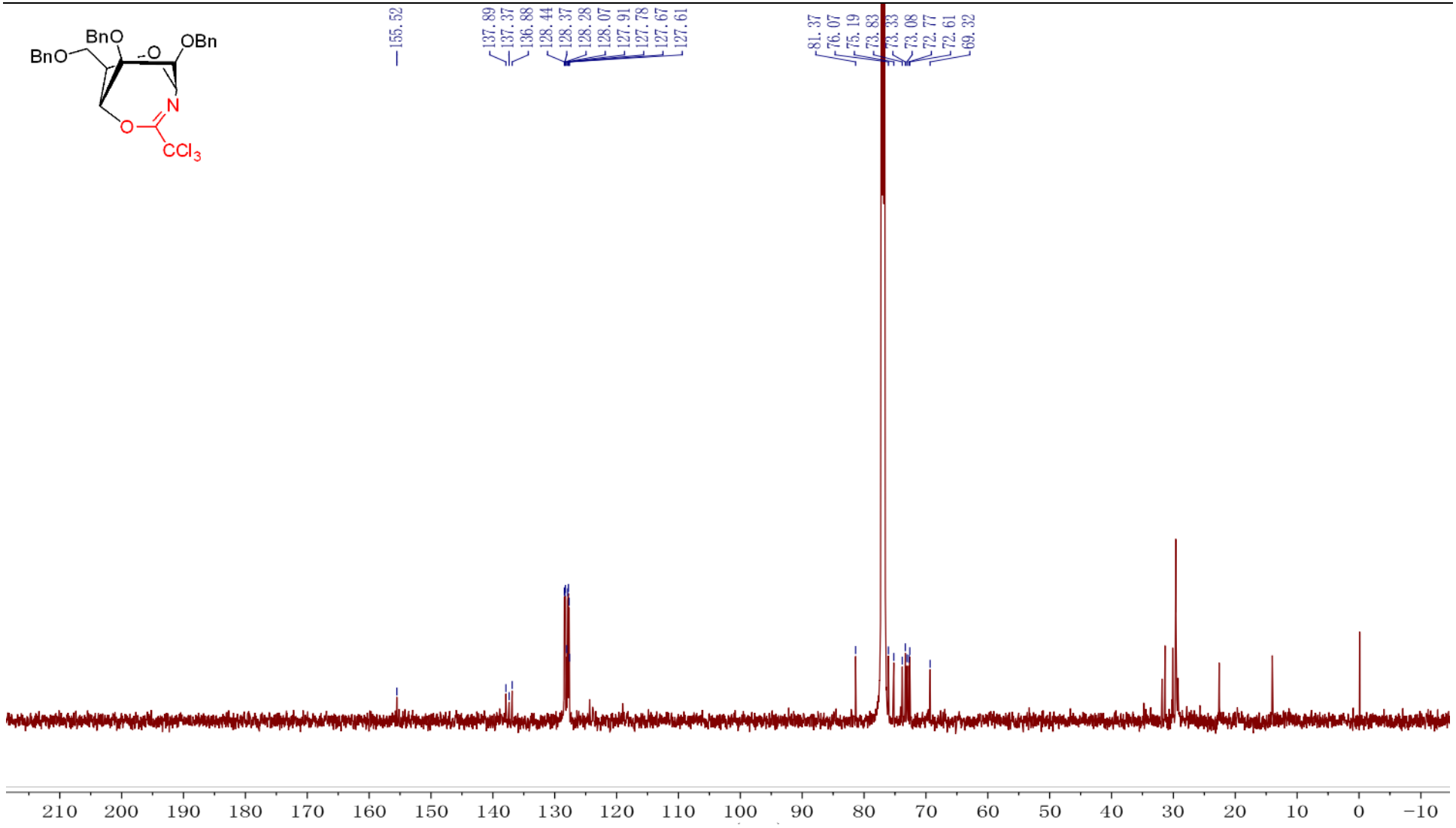
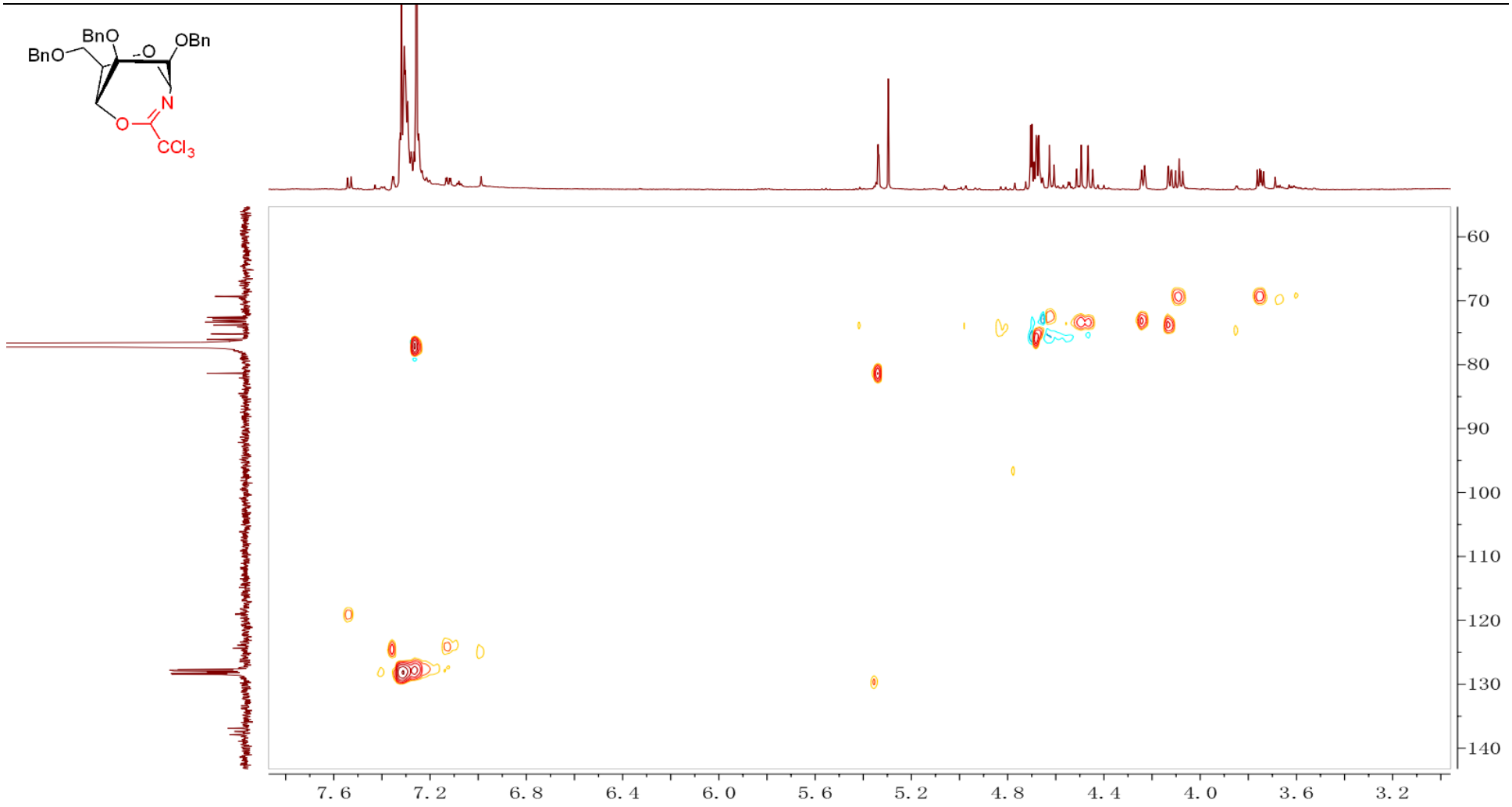
7. NMR Spectra



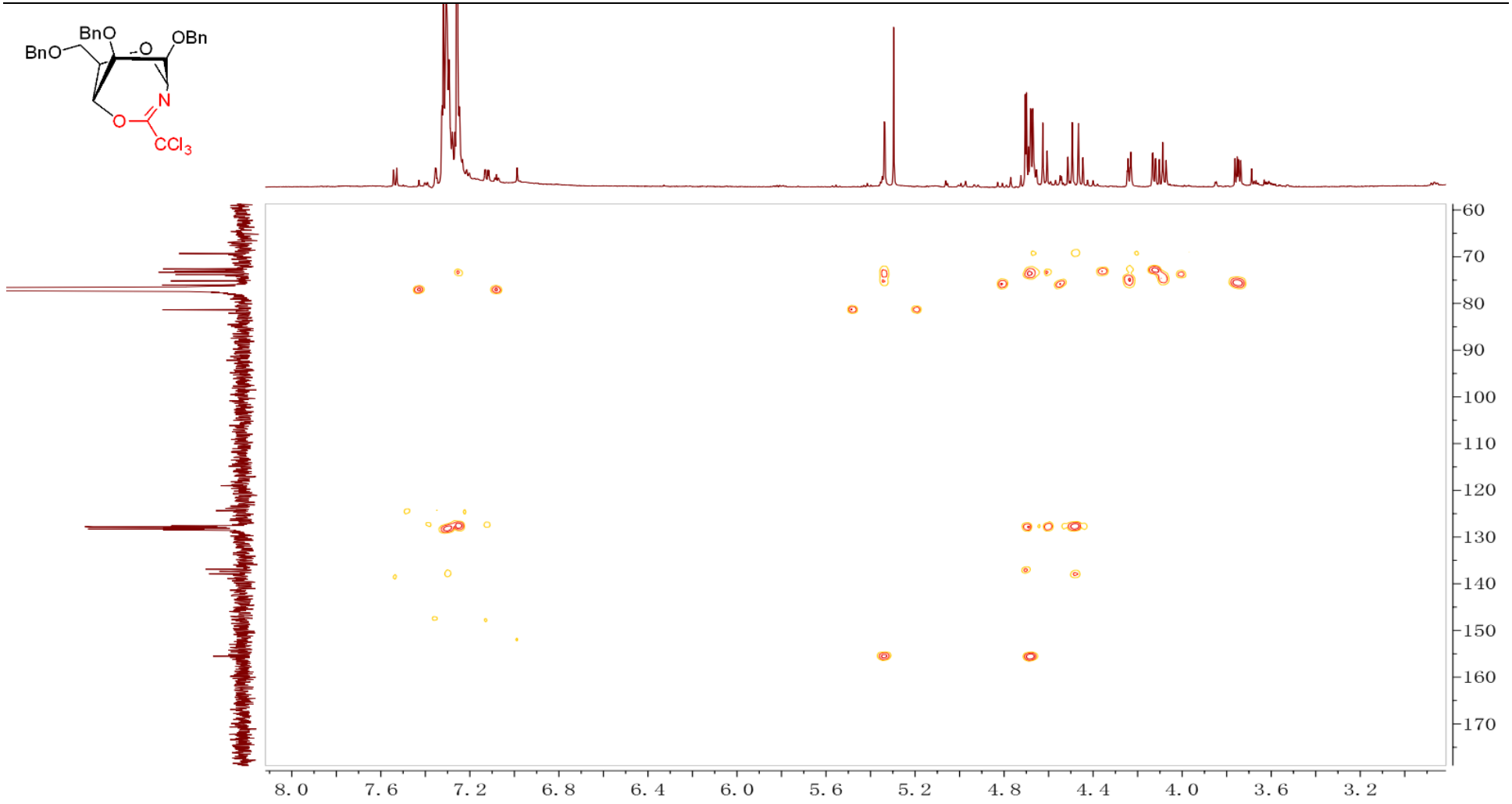
^{1}H NMR of **4** (600 M, $CDCl_3$)



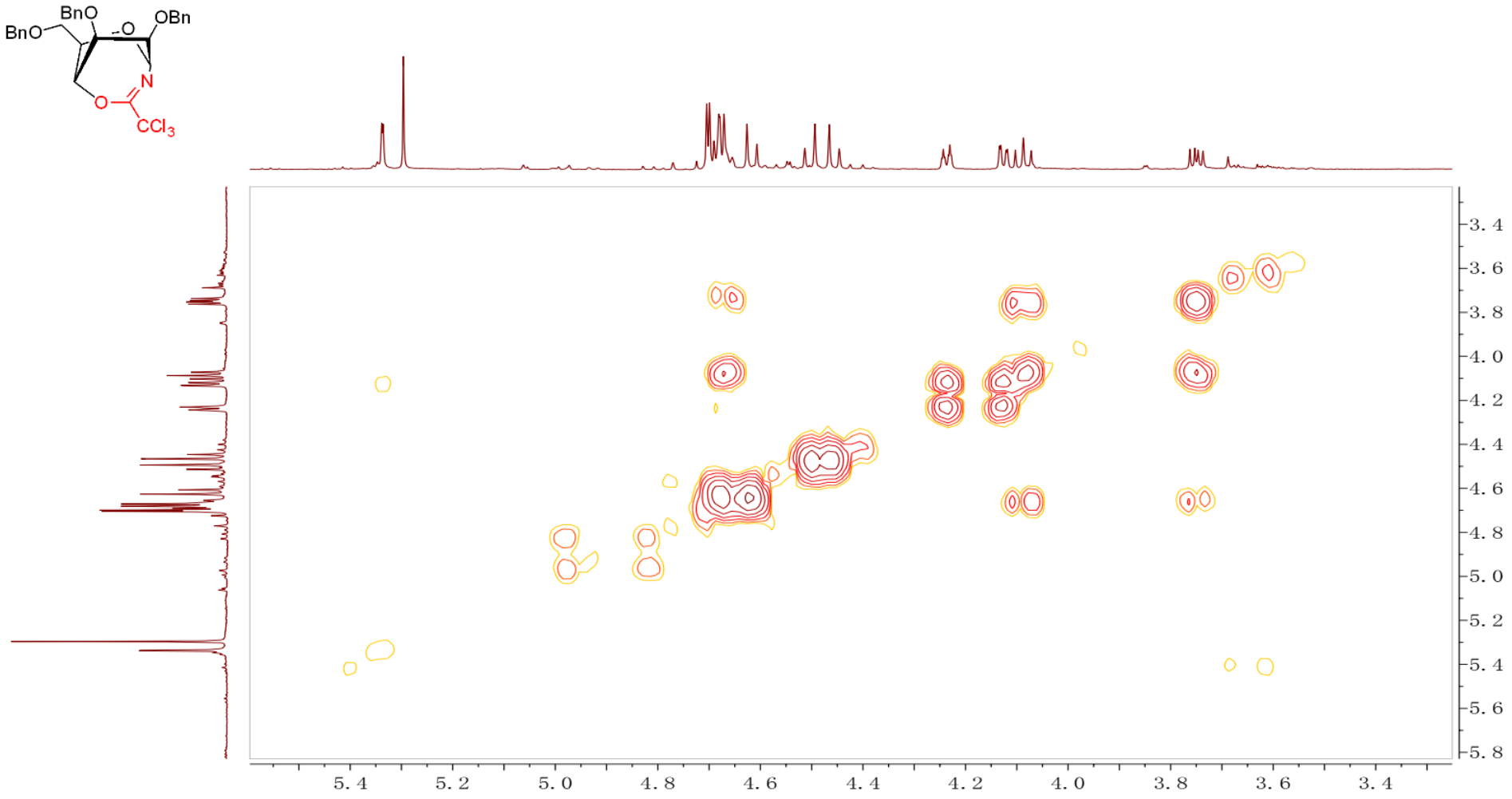
^{13}C NMR of **4** (151 M, $CDCl_3$)


BnO
OBn
BnO
O
N
O
CCl3
60
70
80
90
100
110
120
130
140
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2

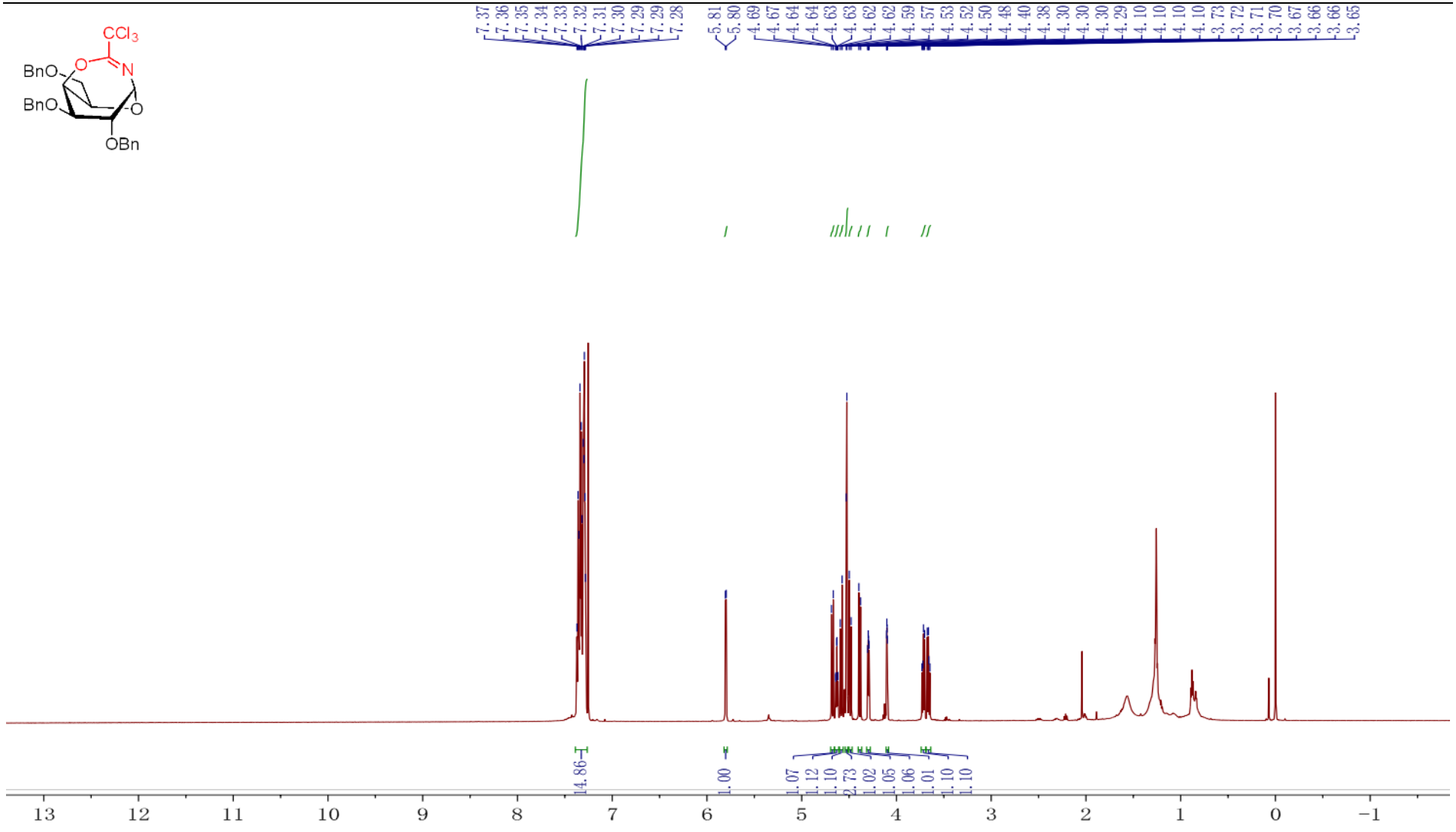
HSQC of **4**


BnO
OBn
BnO
O
N
O
CCl3
60
70
80
90
100
110
120
130
140
150
160
170
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2

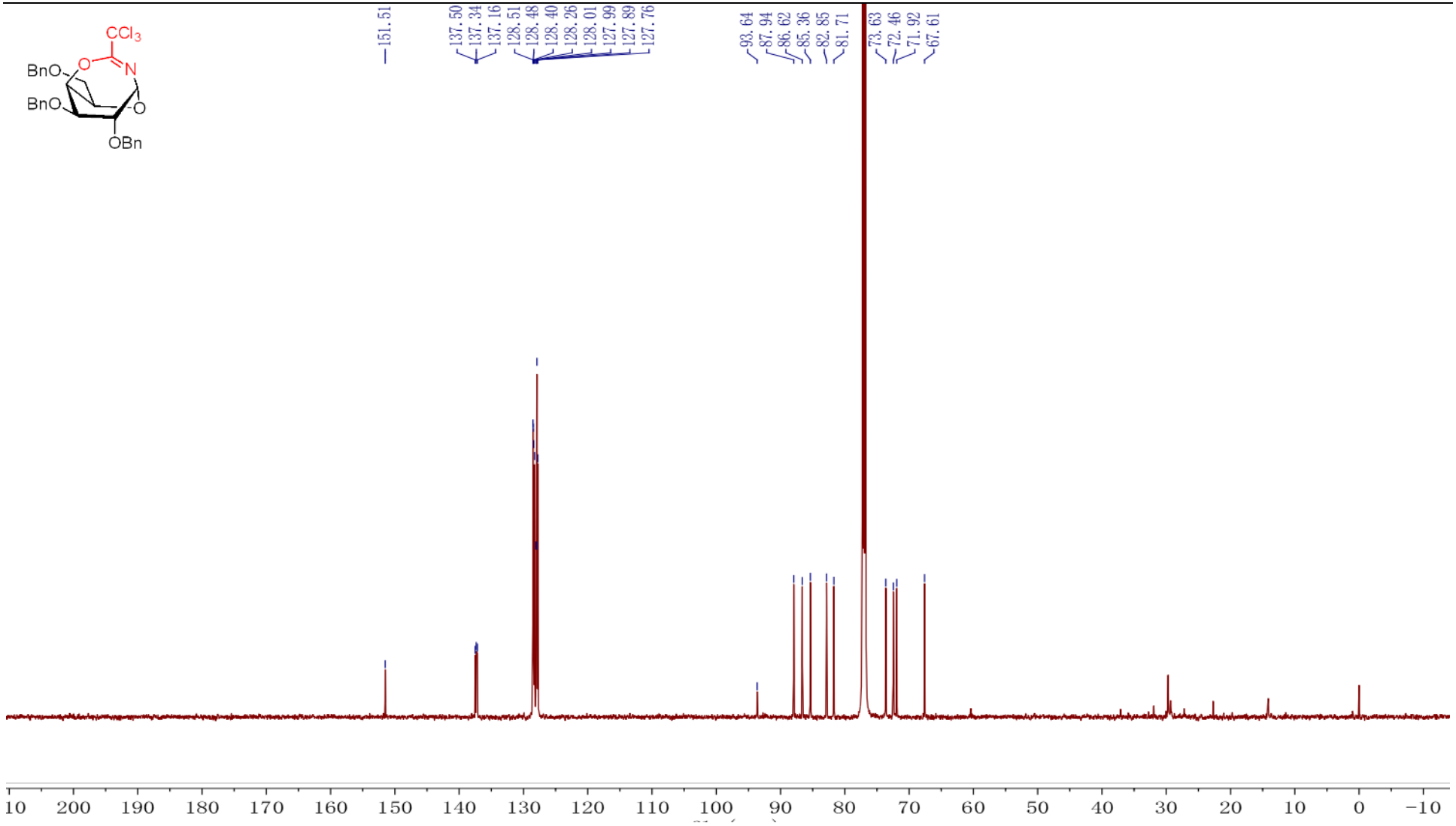
HMBC of **4**



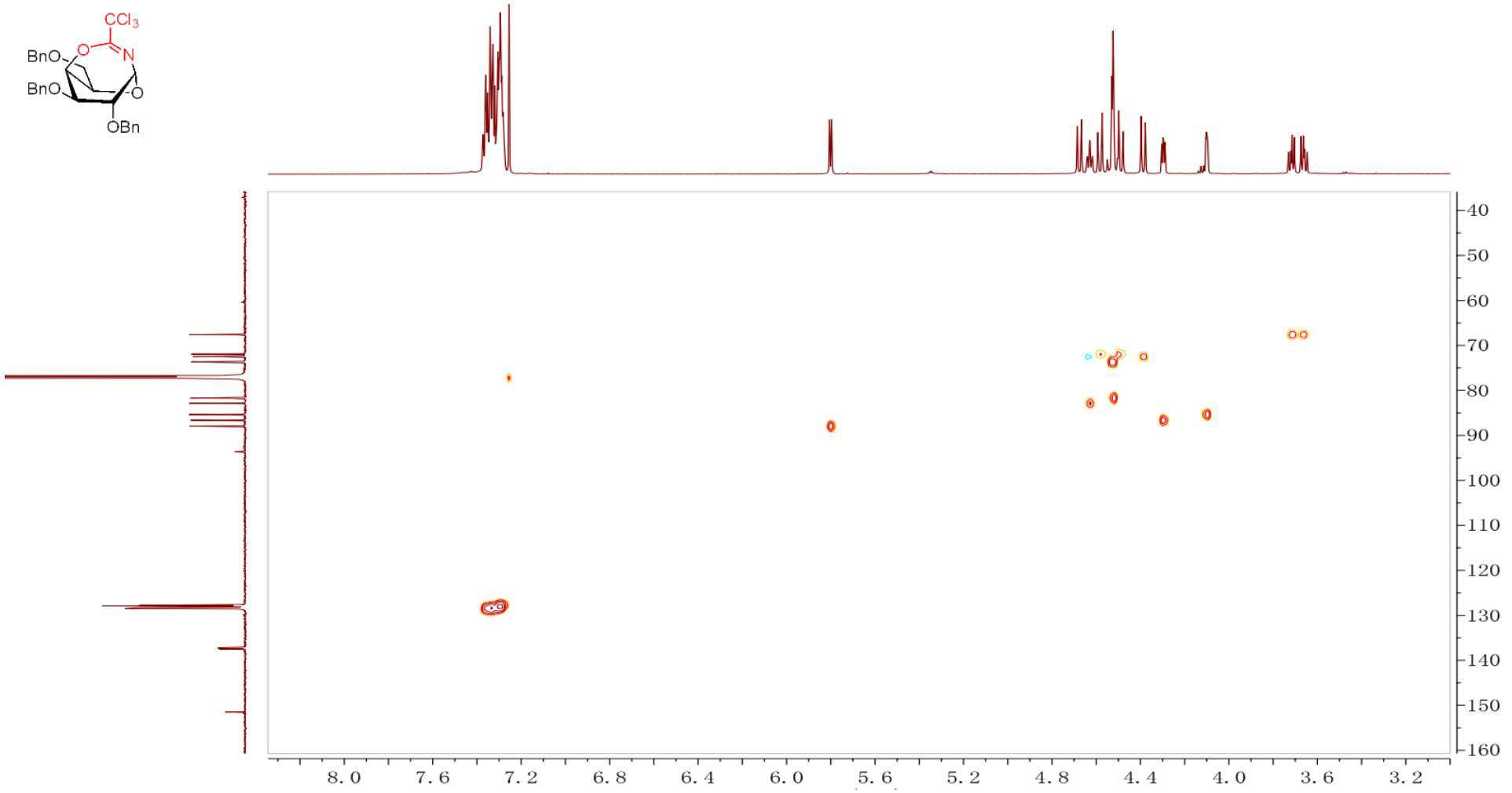
$^{1}H - {}^{1}H$ COSY of **4**



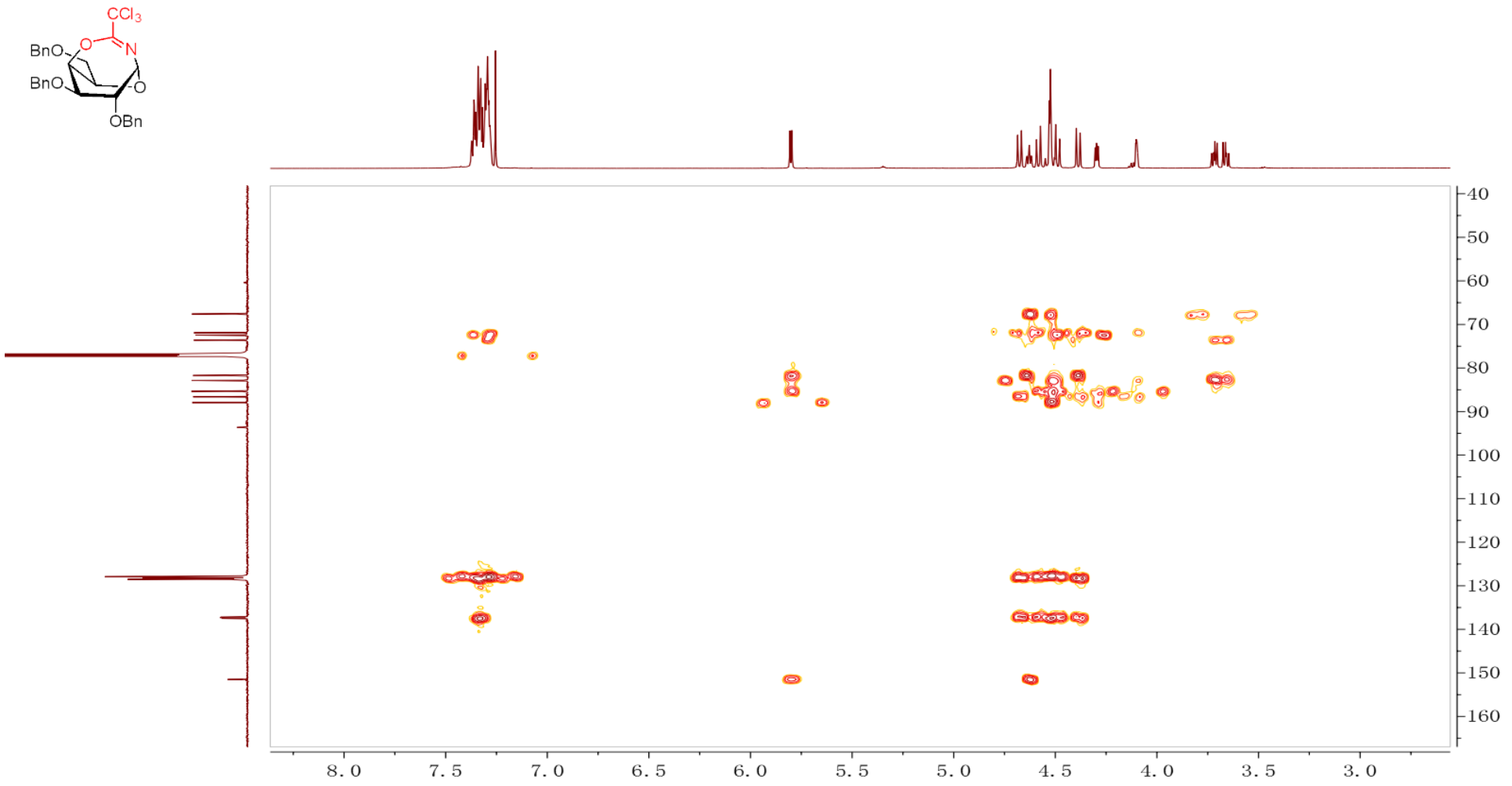
^{1}H NMR of **6** (600 M, $CDCl_3$)



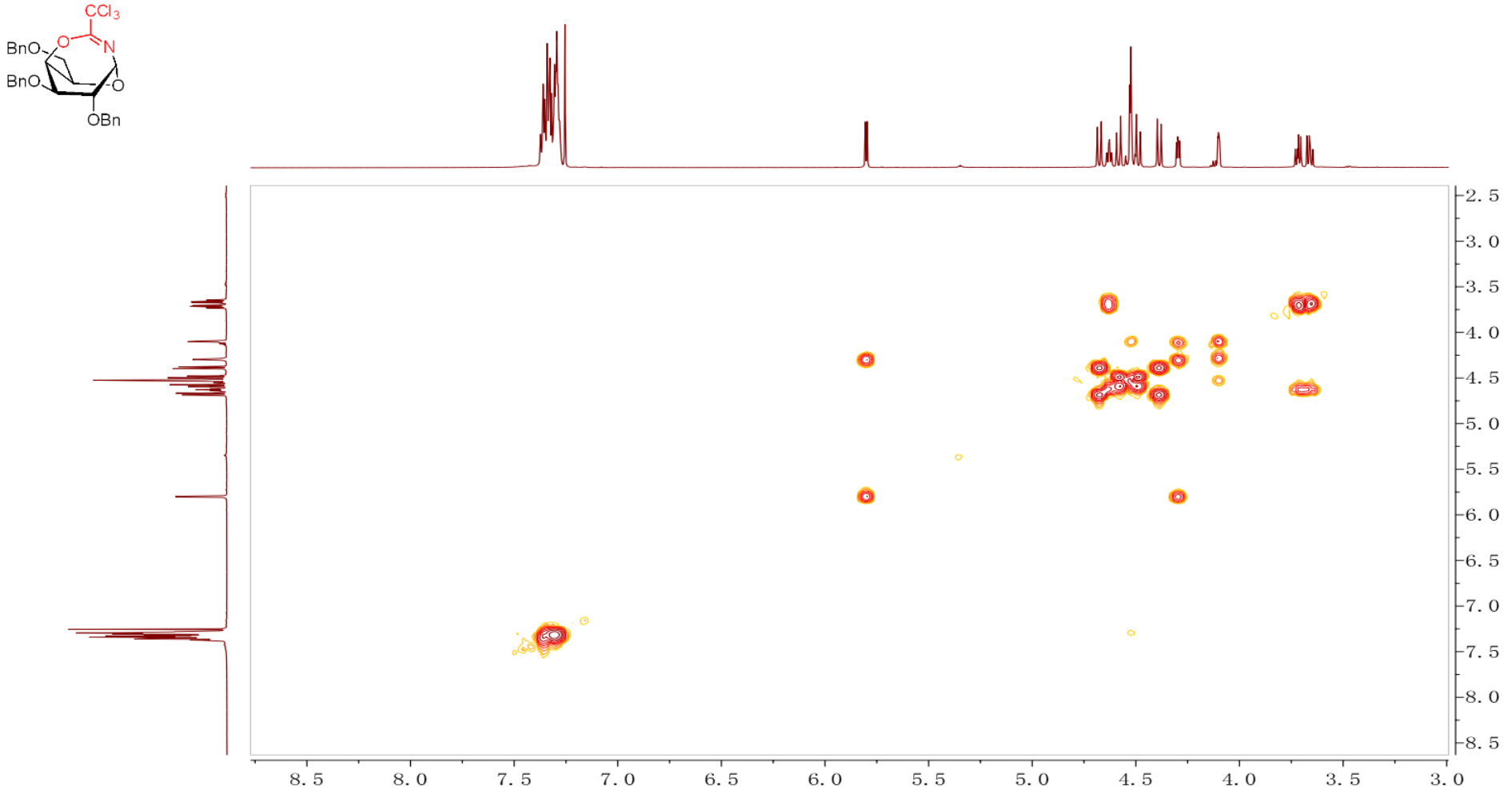
^{13}C NMR of **6** (151 M, $CDCl_3$)


CCl3
BnO
O
N
BnO
O
OBn
40
50
60
70
80
90
100
110
120
130
140
150
160
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2

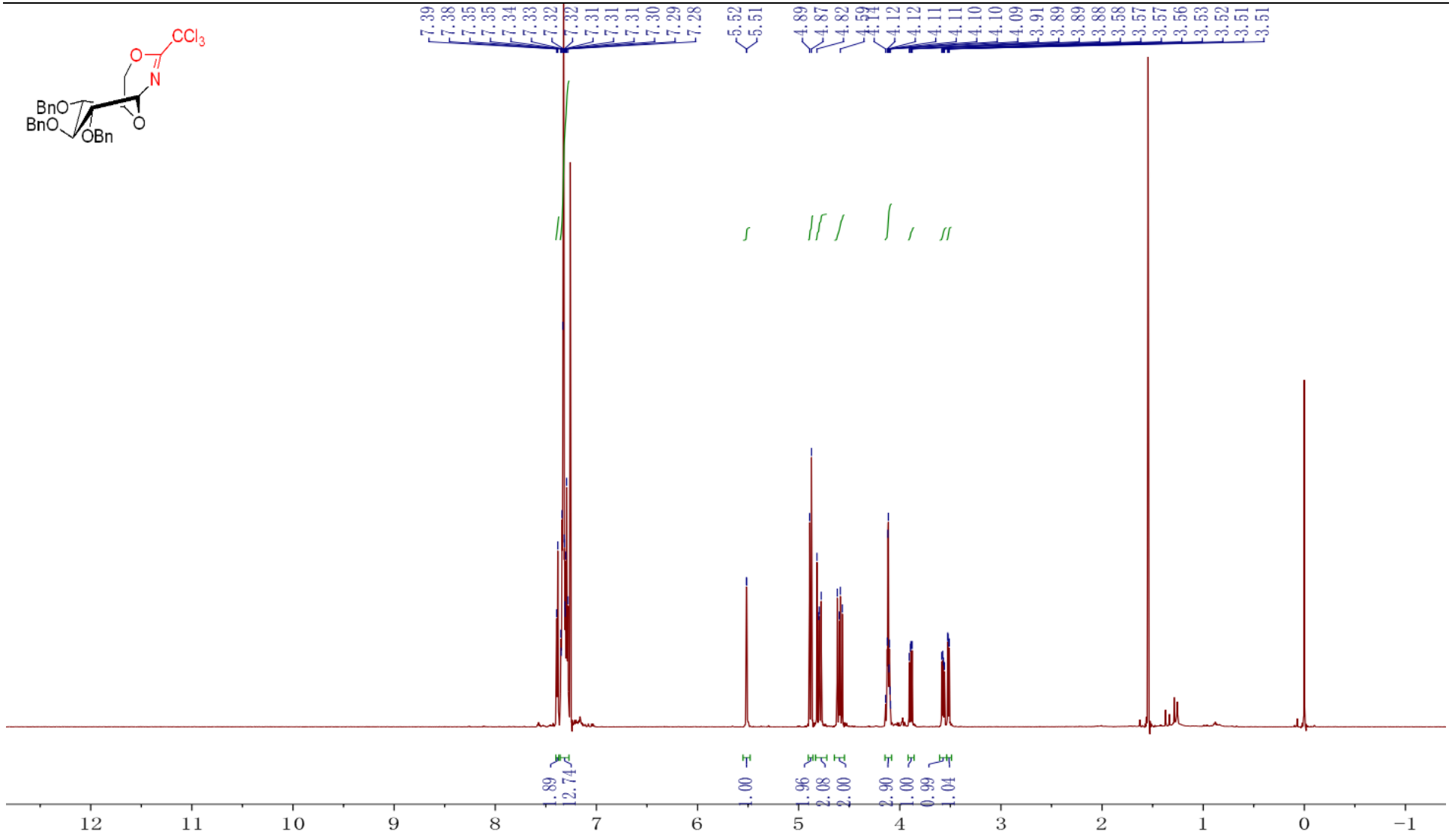
HSQC of **6**


CCl3
BnO
BnO
O
N
O
OBn
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
40
50
60
70
80
90
100
110
120
130
140
150
160

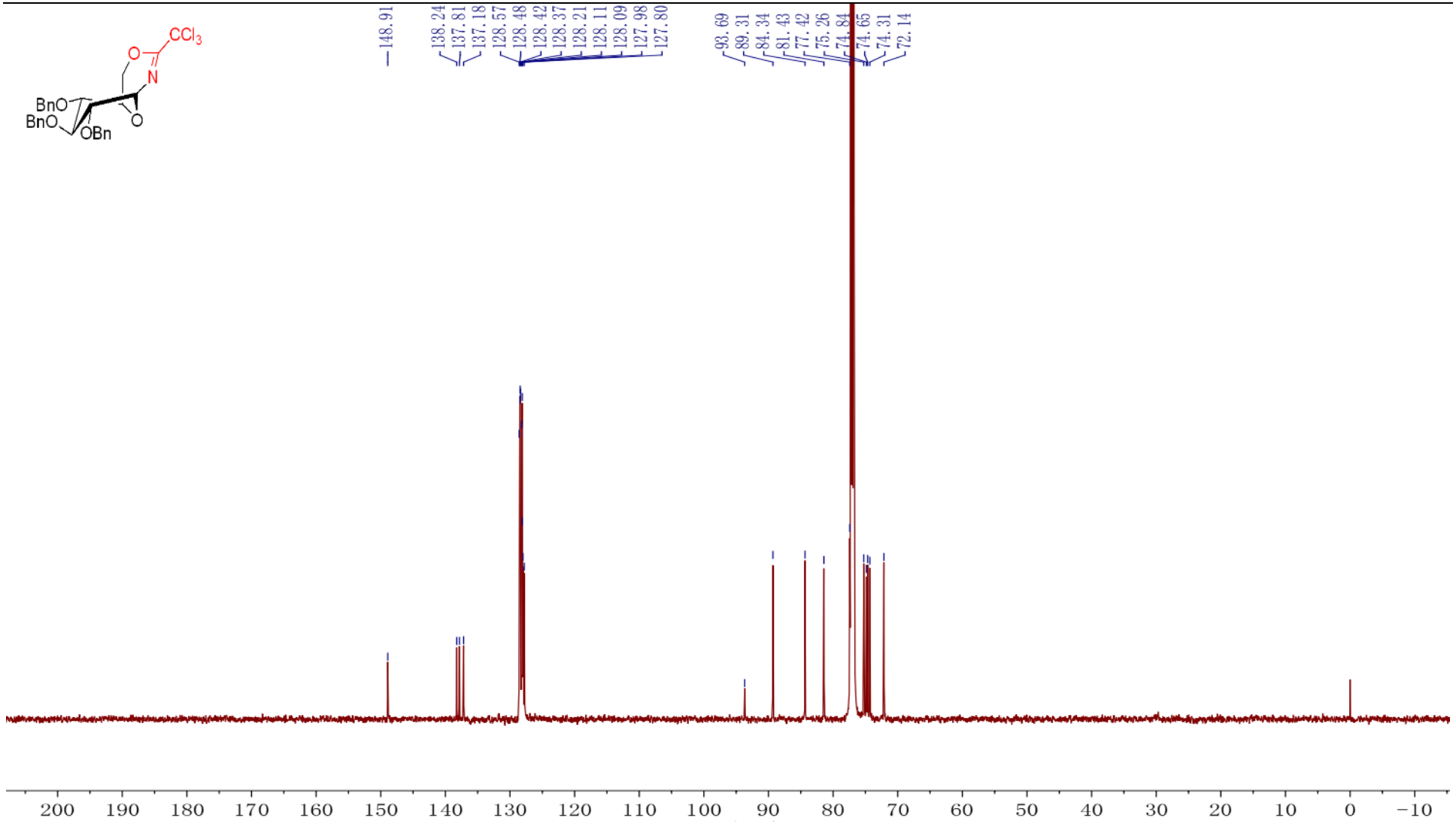
HMBC of **6**



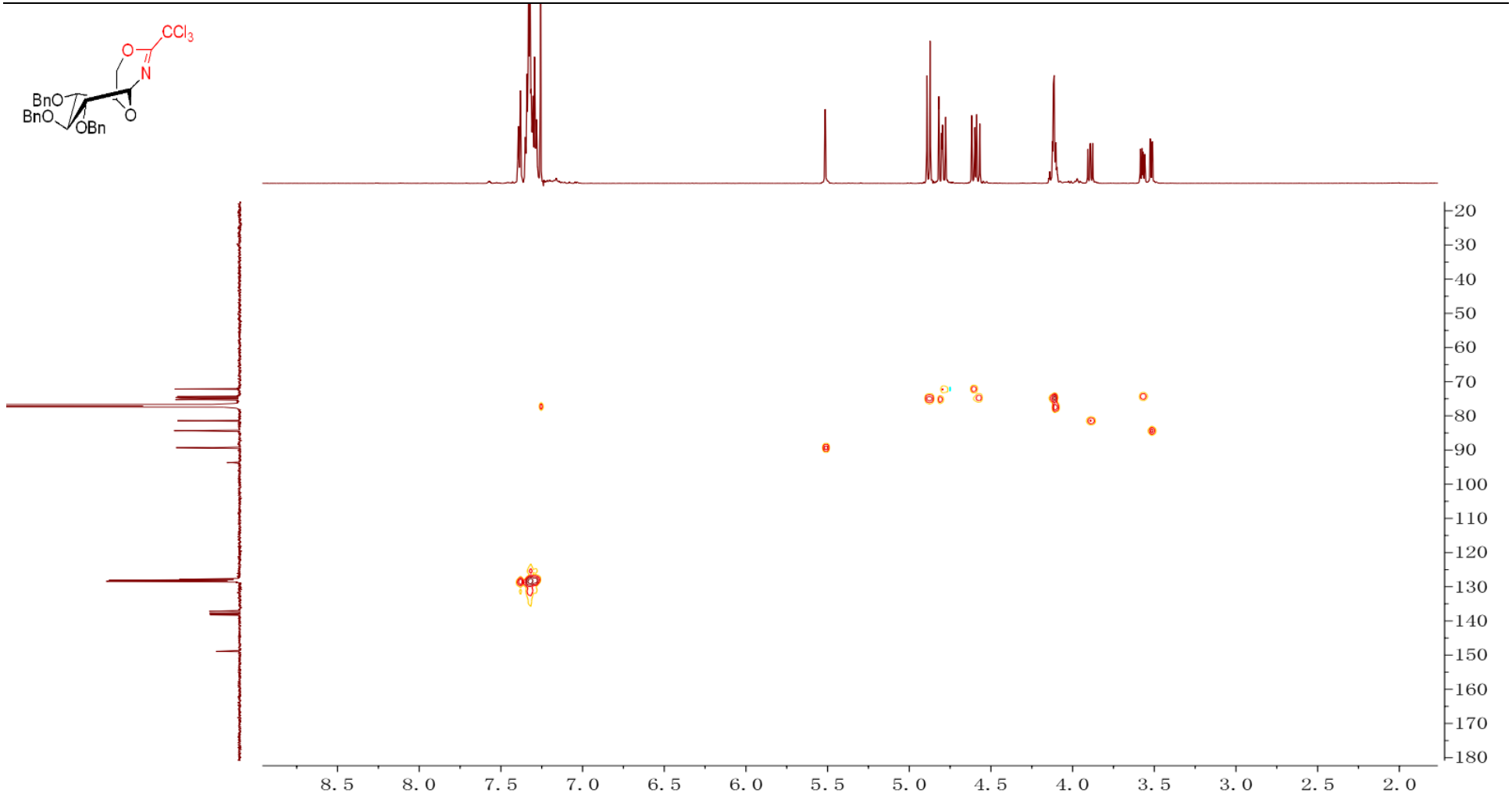
$^{1}H - {}^{1}H$ COSY of **6**



^{1}H NMR of **8** (600 M, $CDCl_3$)



^{13}C NMR of **8** (151 M, $CDCl_3$)


CCl3
O
N
BnO
BnO
OBn
O
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
8.5
8.0
7.5
7.0
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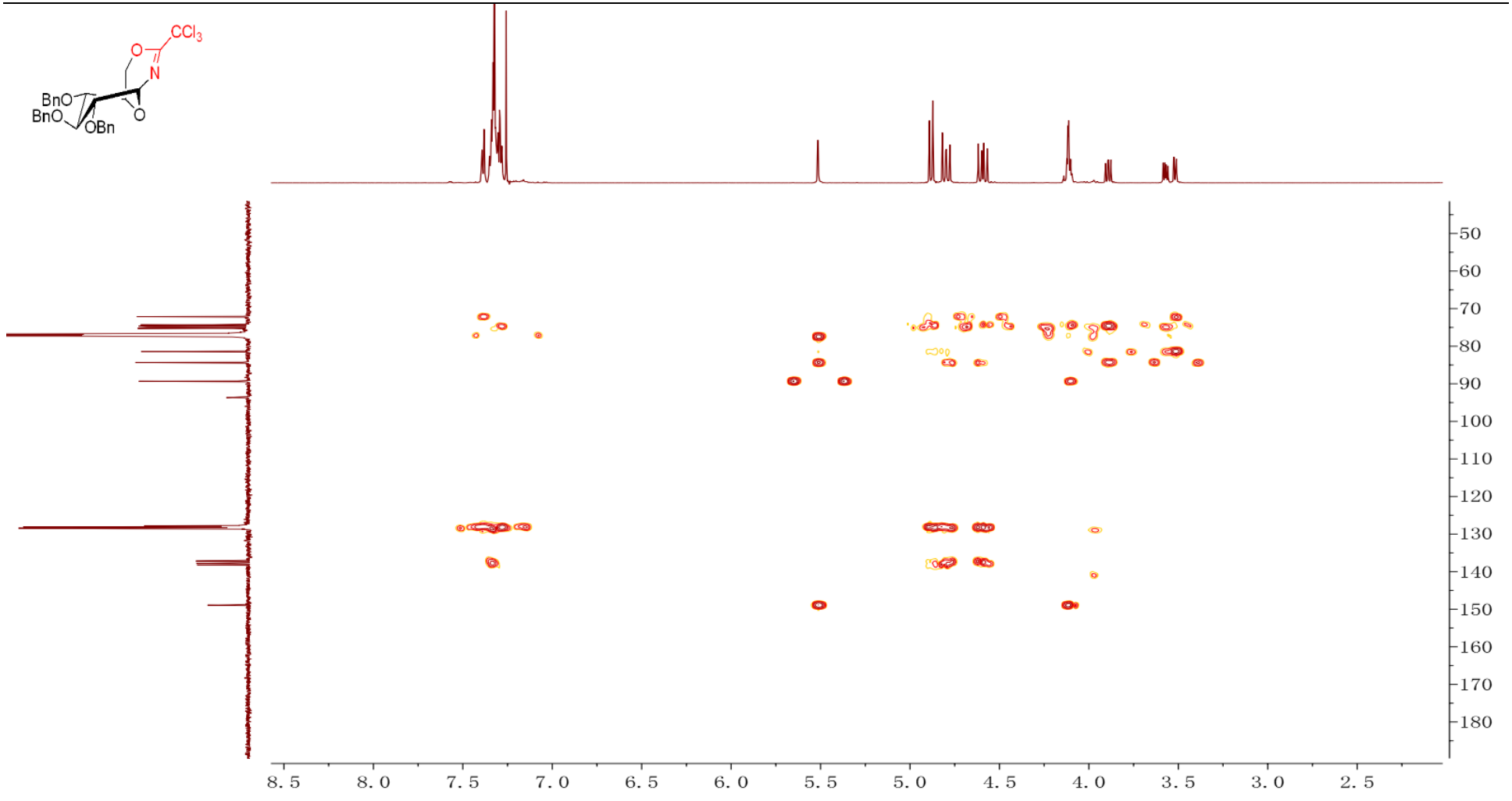
3.5
3.0
2.5
2.0

HSQC of **8**


CCl3
O
N
BnO
BnO
OBn
O
50
60
70
80
90
100
110
120
130
140
150
160
170
180
8.5
8.0
7.5
7.0
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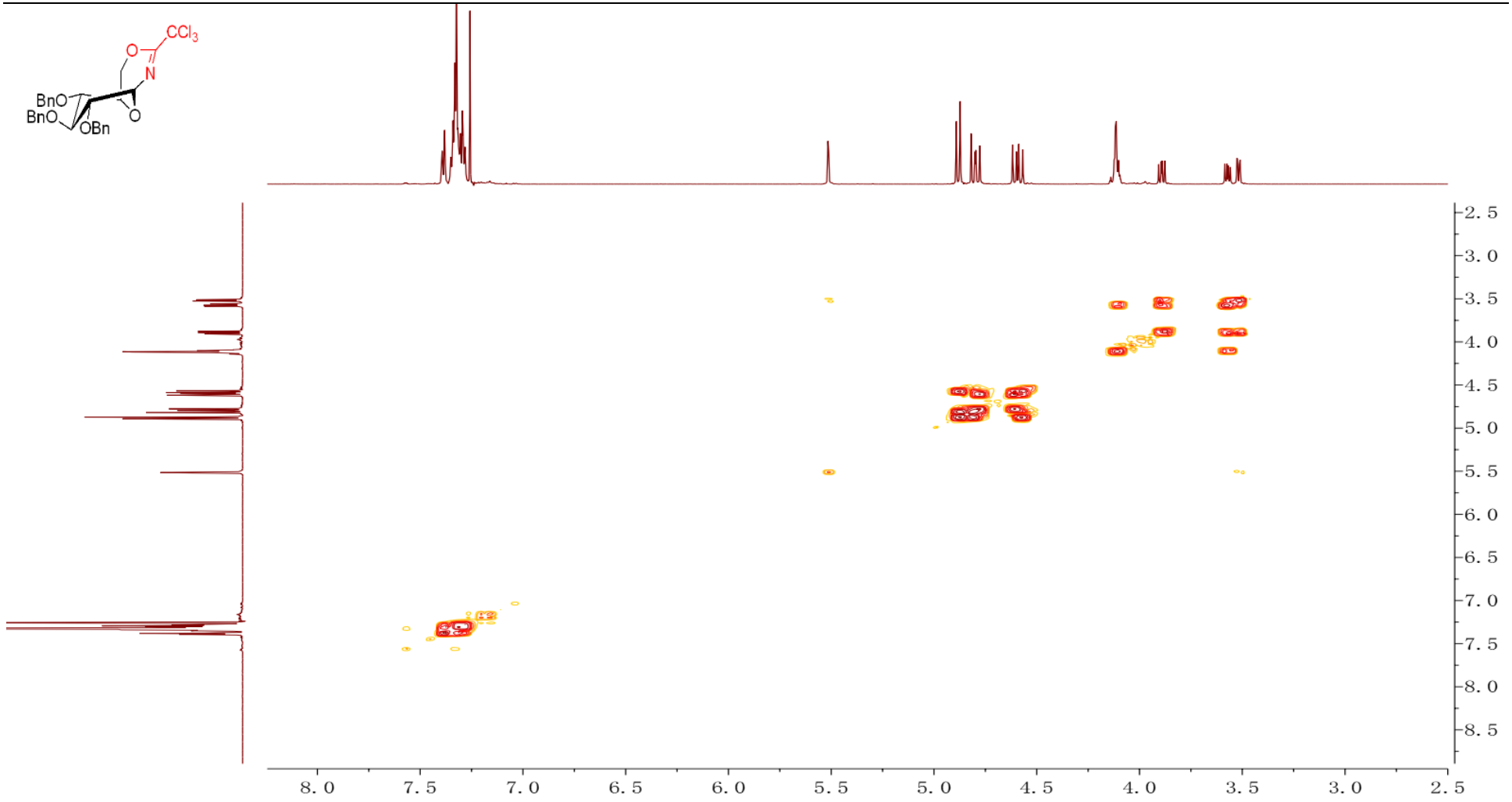
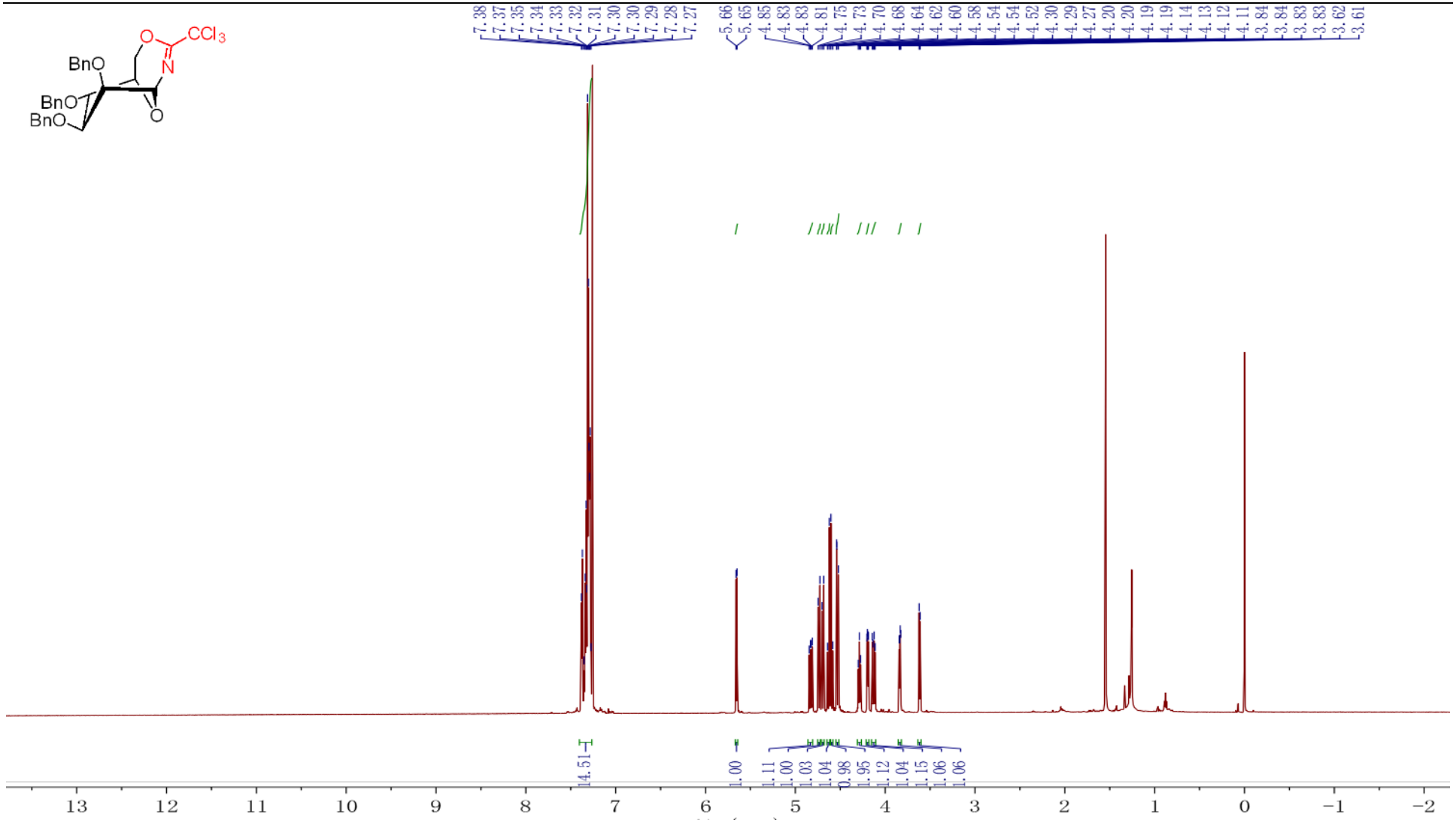
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

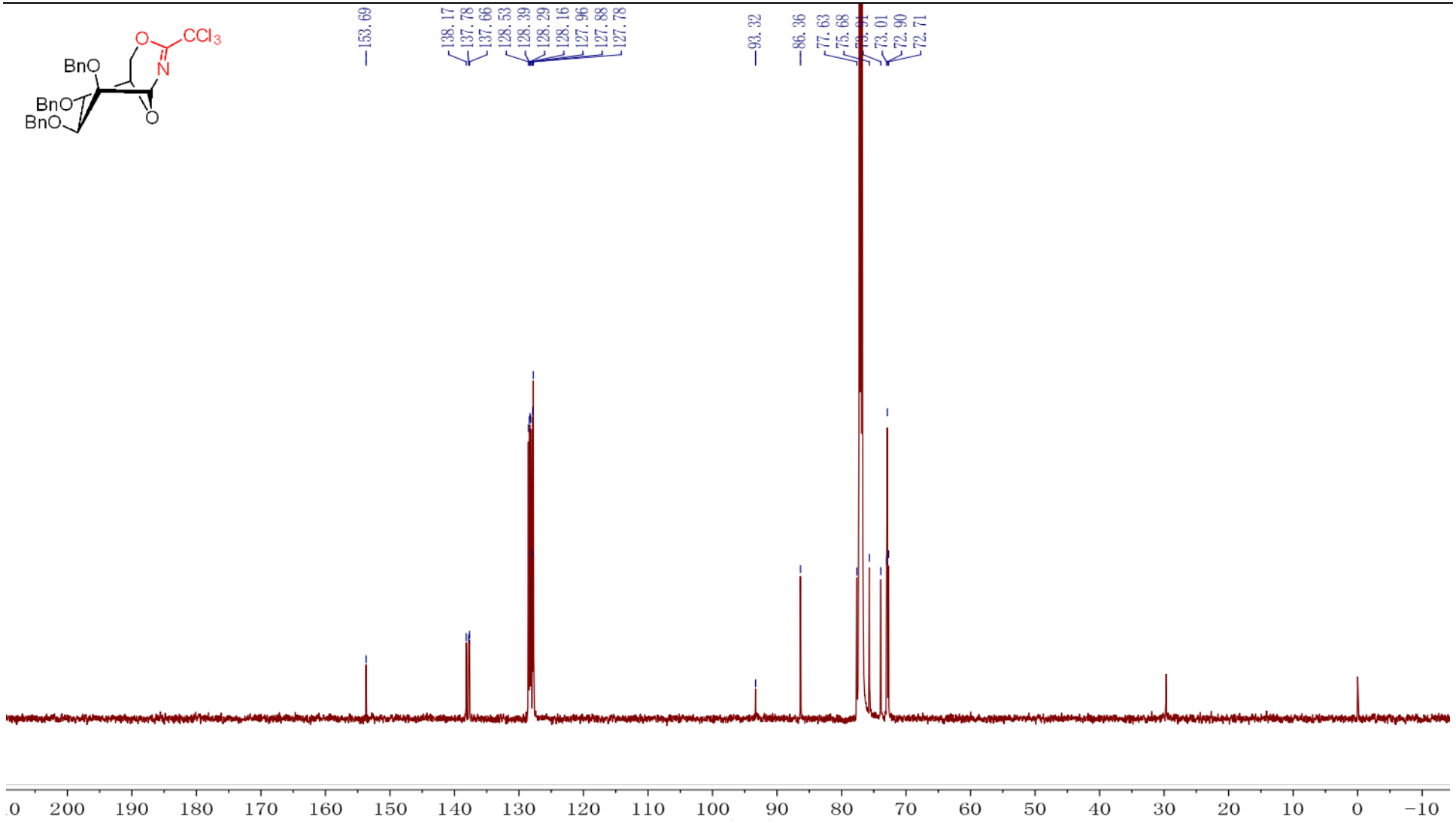
HMBC of **8**



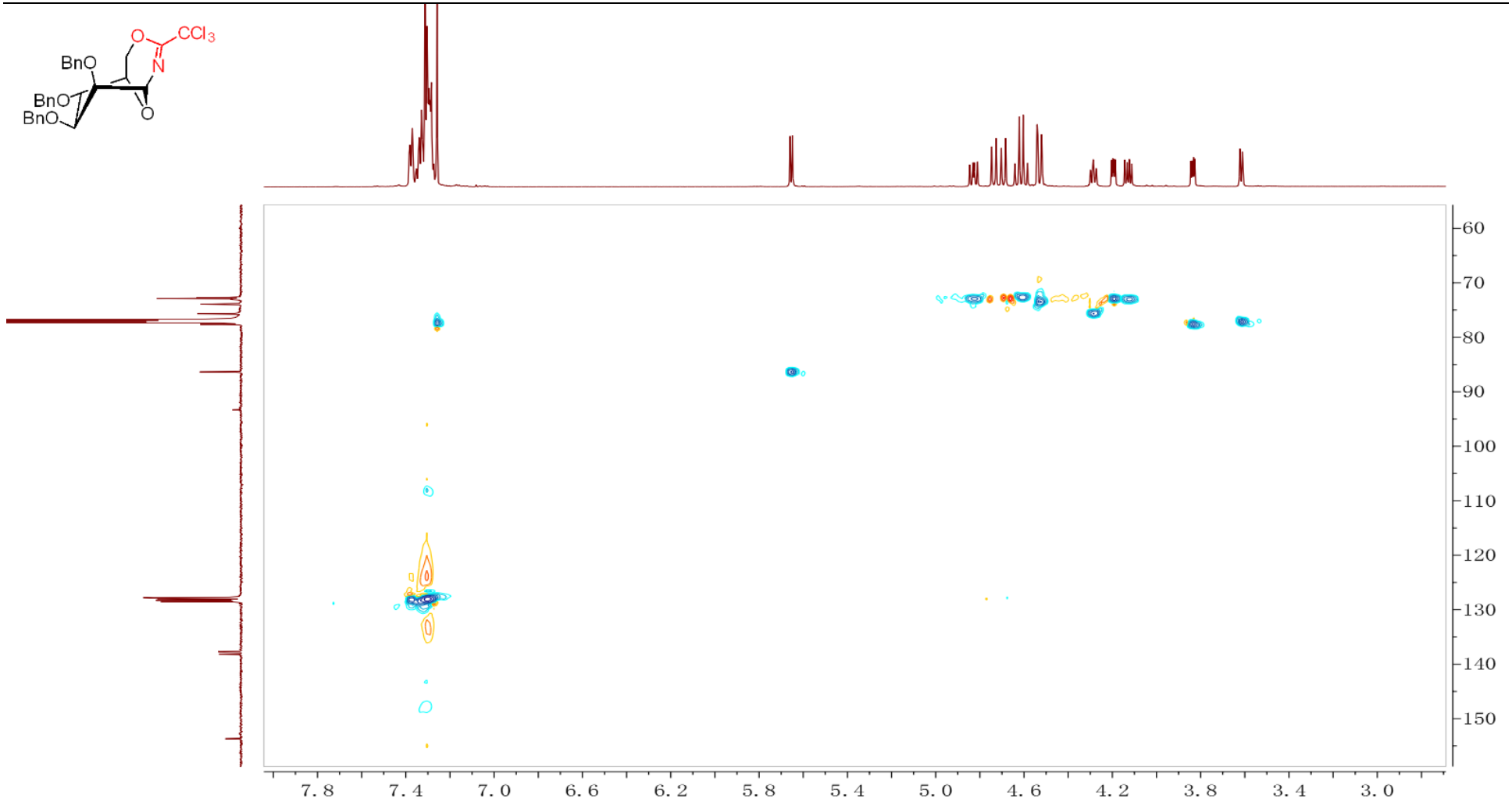
$^{1}H - {}^{1}H$ COSY of **8**



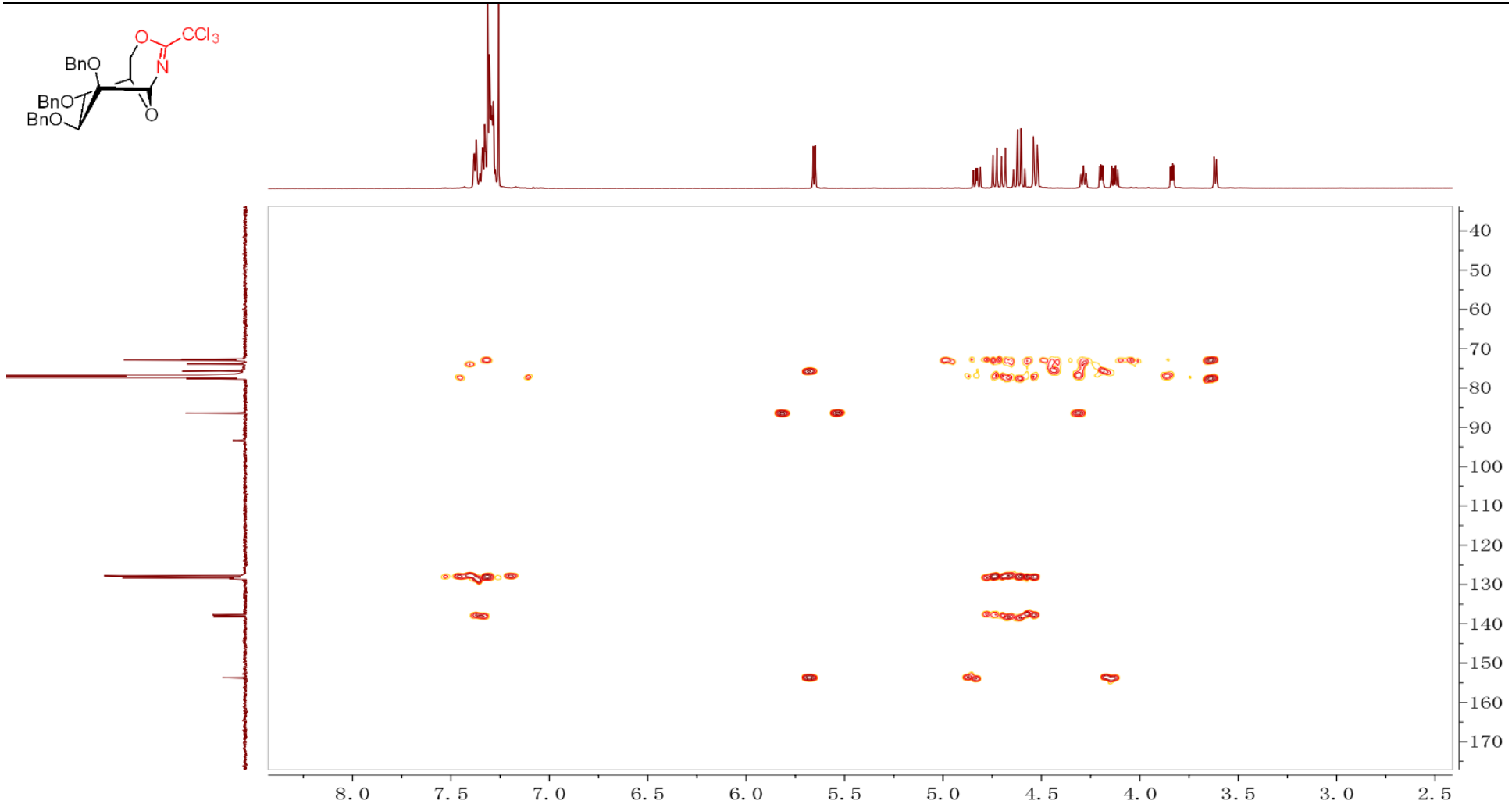
^{1}H NMR of **10** (600 M, $CDCl_3$)



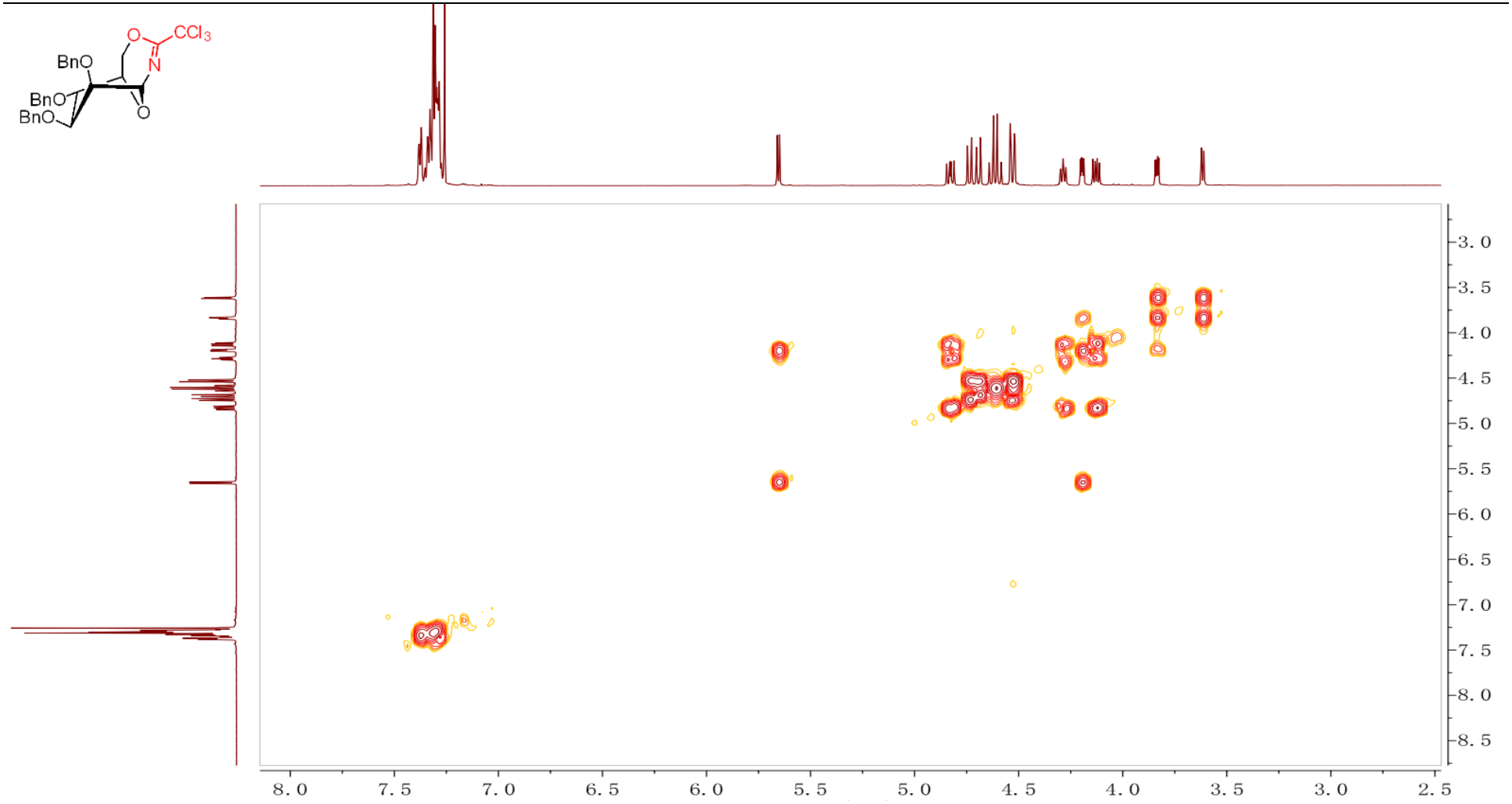
^{13}C NMR of **10** (151 M, $CDCl_3$)


BnO
BnO
BnO
O
N
CCl3
O
60
70
80
90
100
110
120
130
140
150
7.8
7.4
7.0
6.6
6.2
5.8
5.4
5.0
4.6
4.2
3.8
3.4
3.0

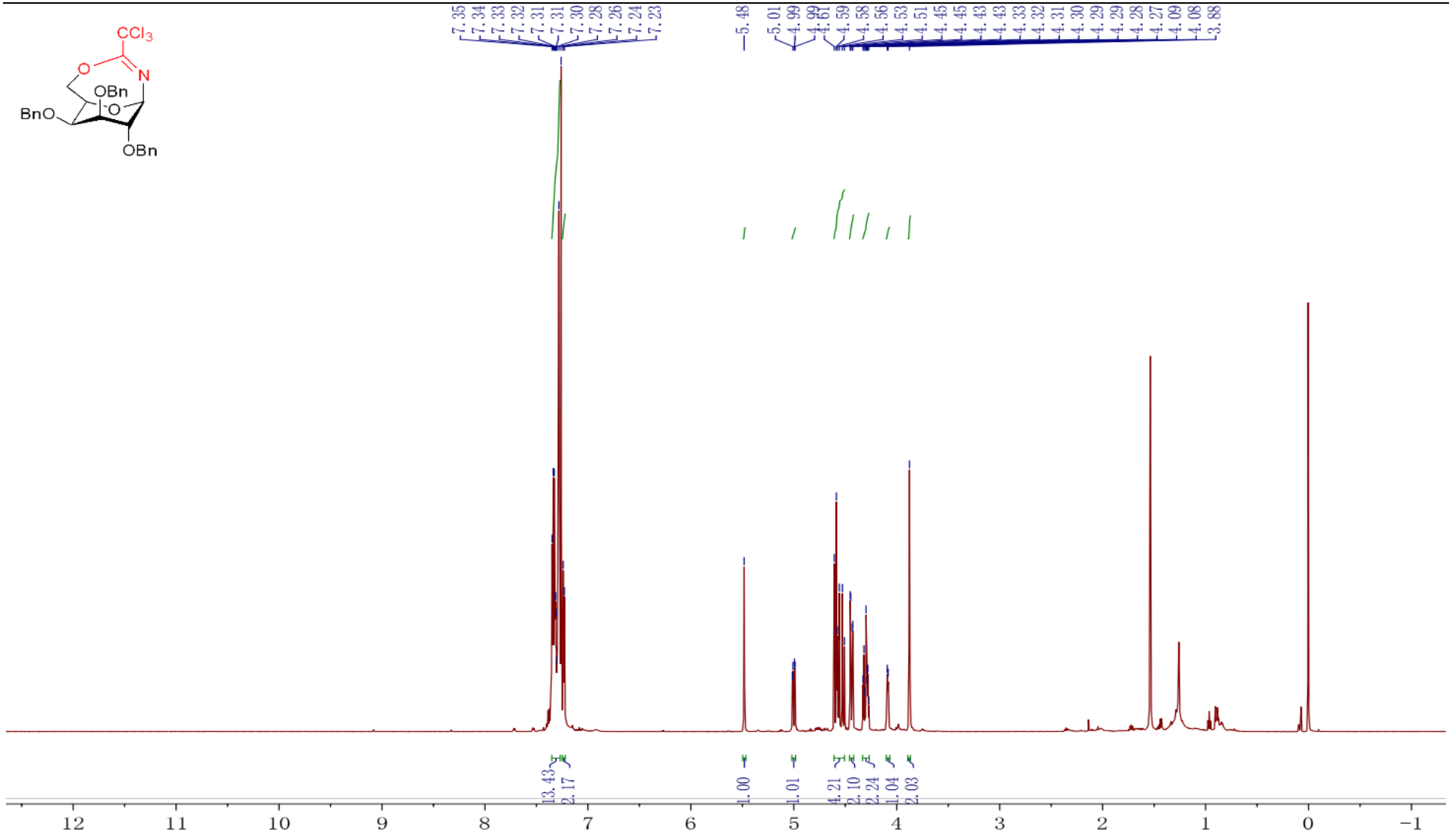
HSQC of **10**


BnO
BnO
BnO
O
CCl3
N
O
40
50
60
70
80
90
100
110
120
130
140
150
160
170
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

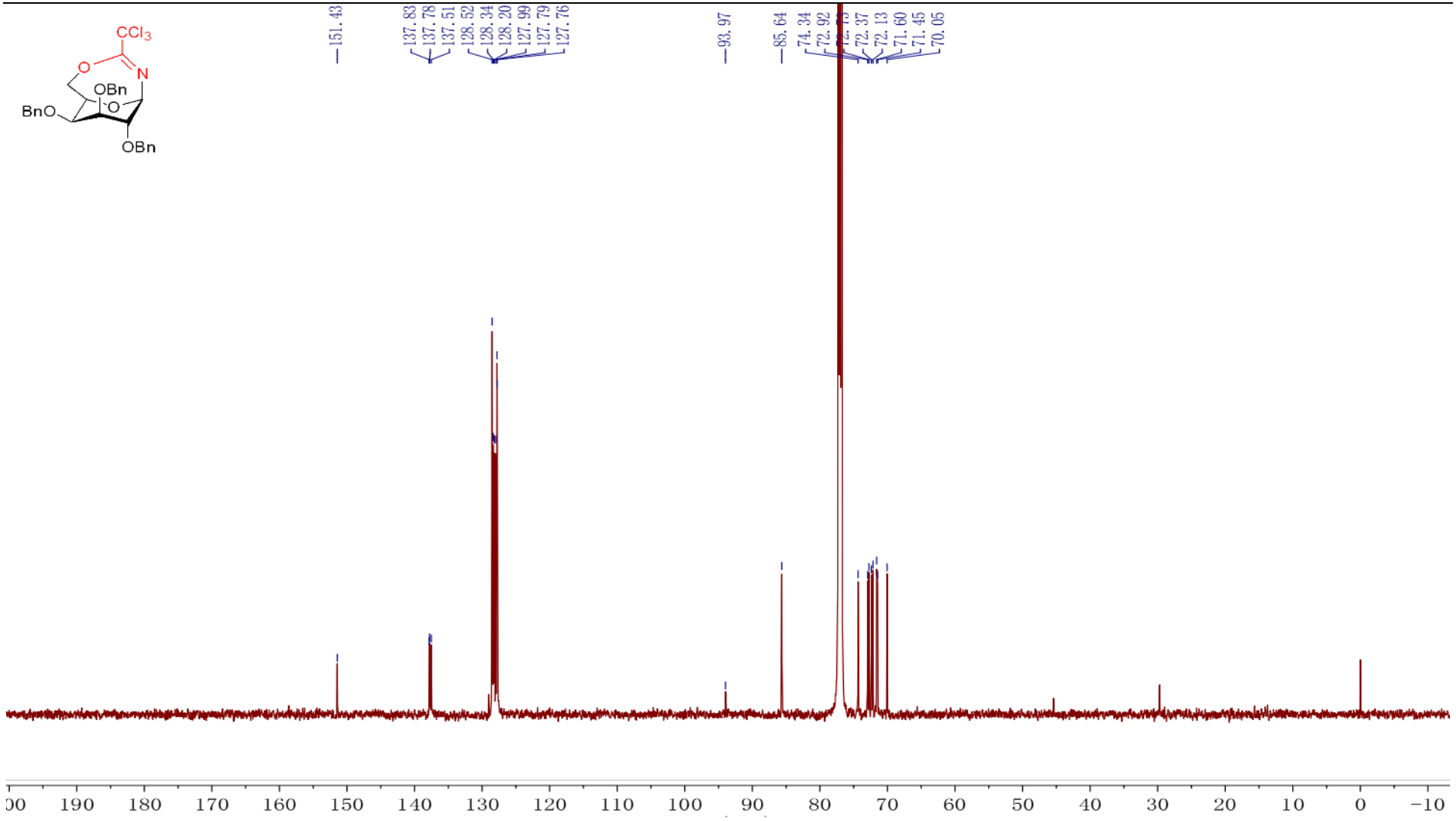
HMBC of **10**



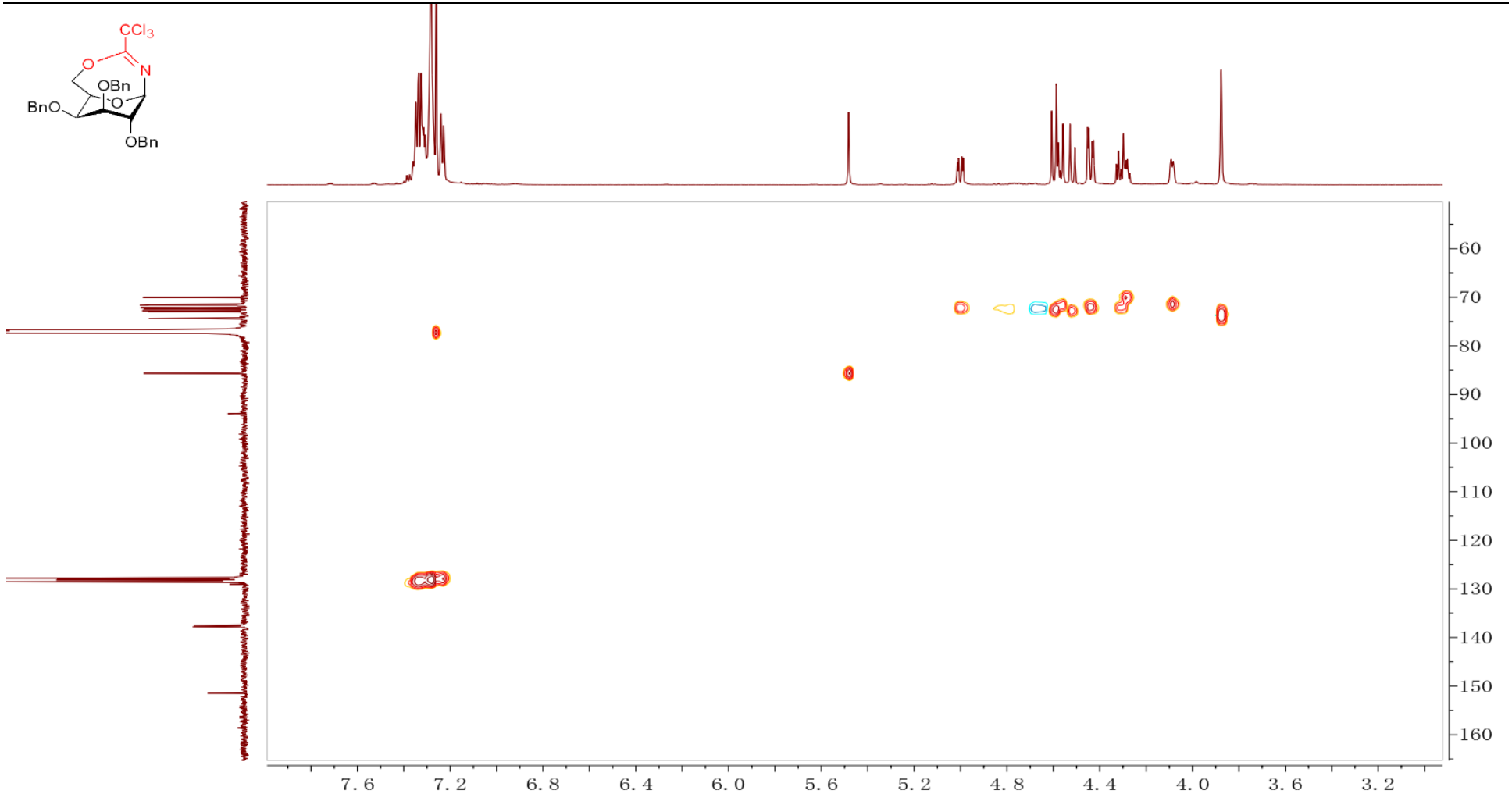
^{1}H – ^{1}H COSY of **10**



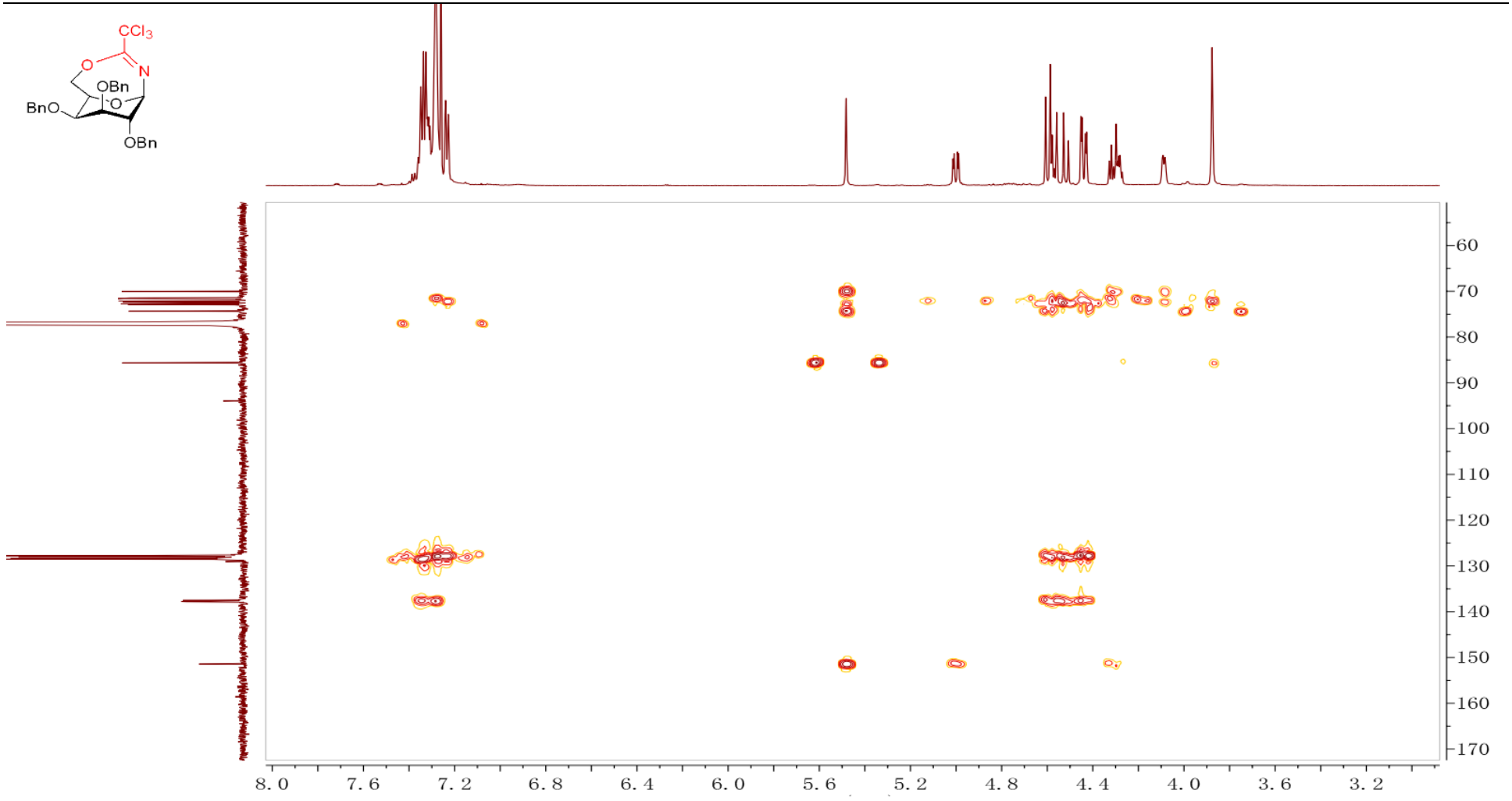
^{1}H NMR of **12** (600 M, $CDCl_3$)



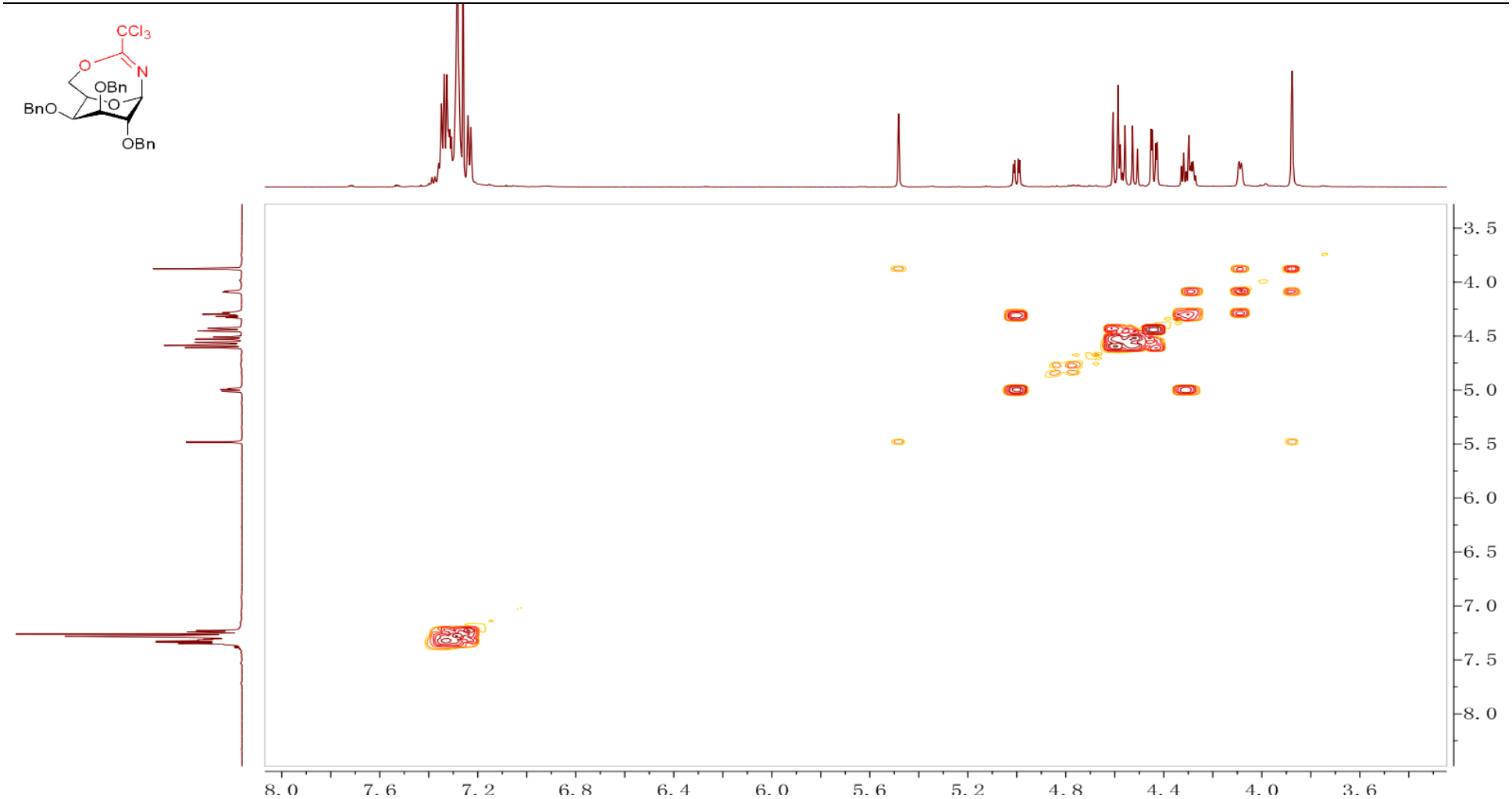
^{13}C NMR of **12** (151 M, $CDCl_3$)


CCl3
O
N
OBn
BnO
O
OBn
60
70
80
90
100
110
120
130
140
150
160
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2

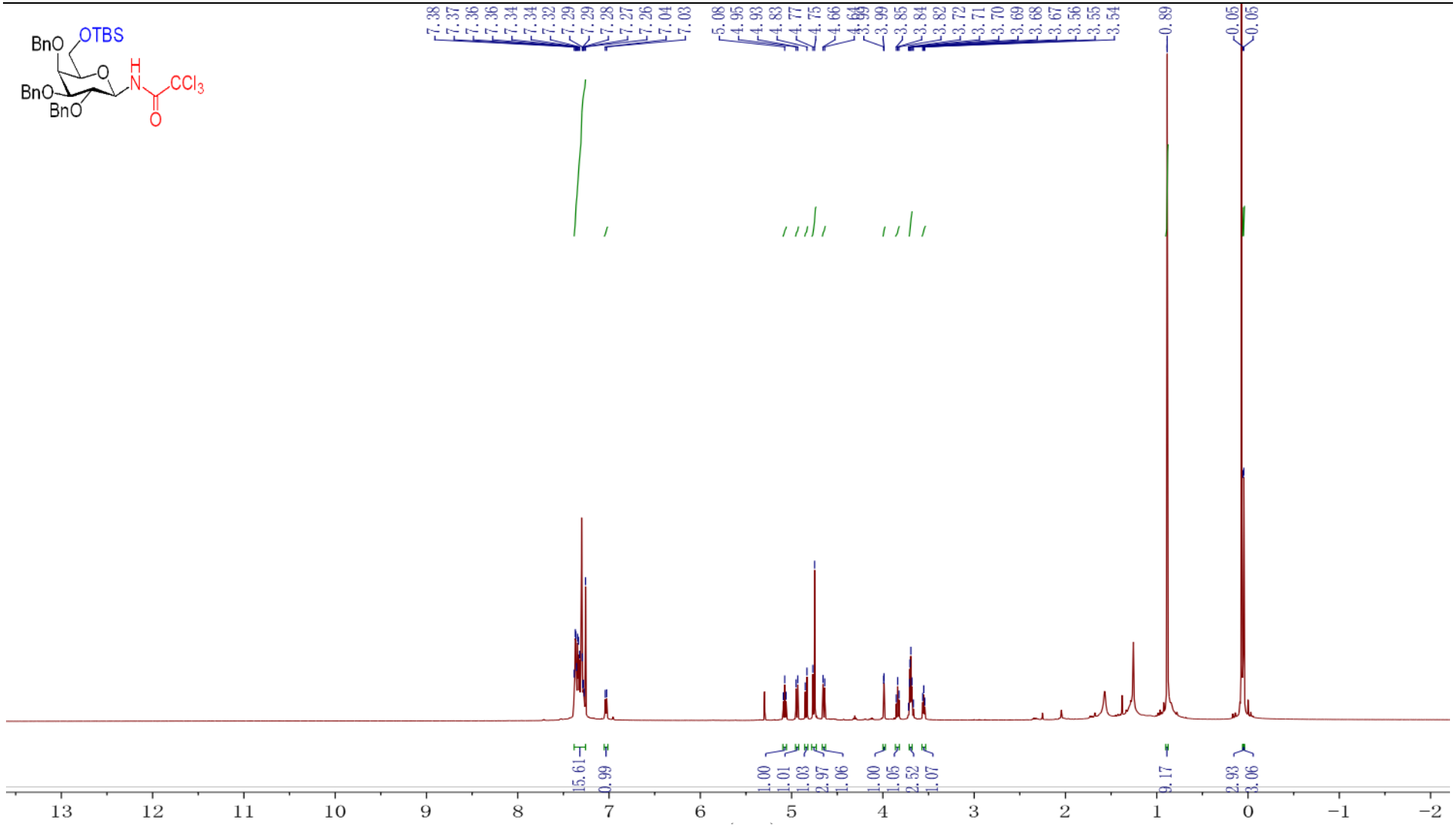
HSQC of **12**


CCl3
O
N
OBn
BnO
O
OBn
60
70
80
90
100
110
120
130
140
150
160
170
8.0
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2

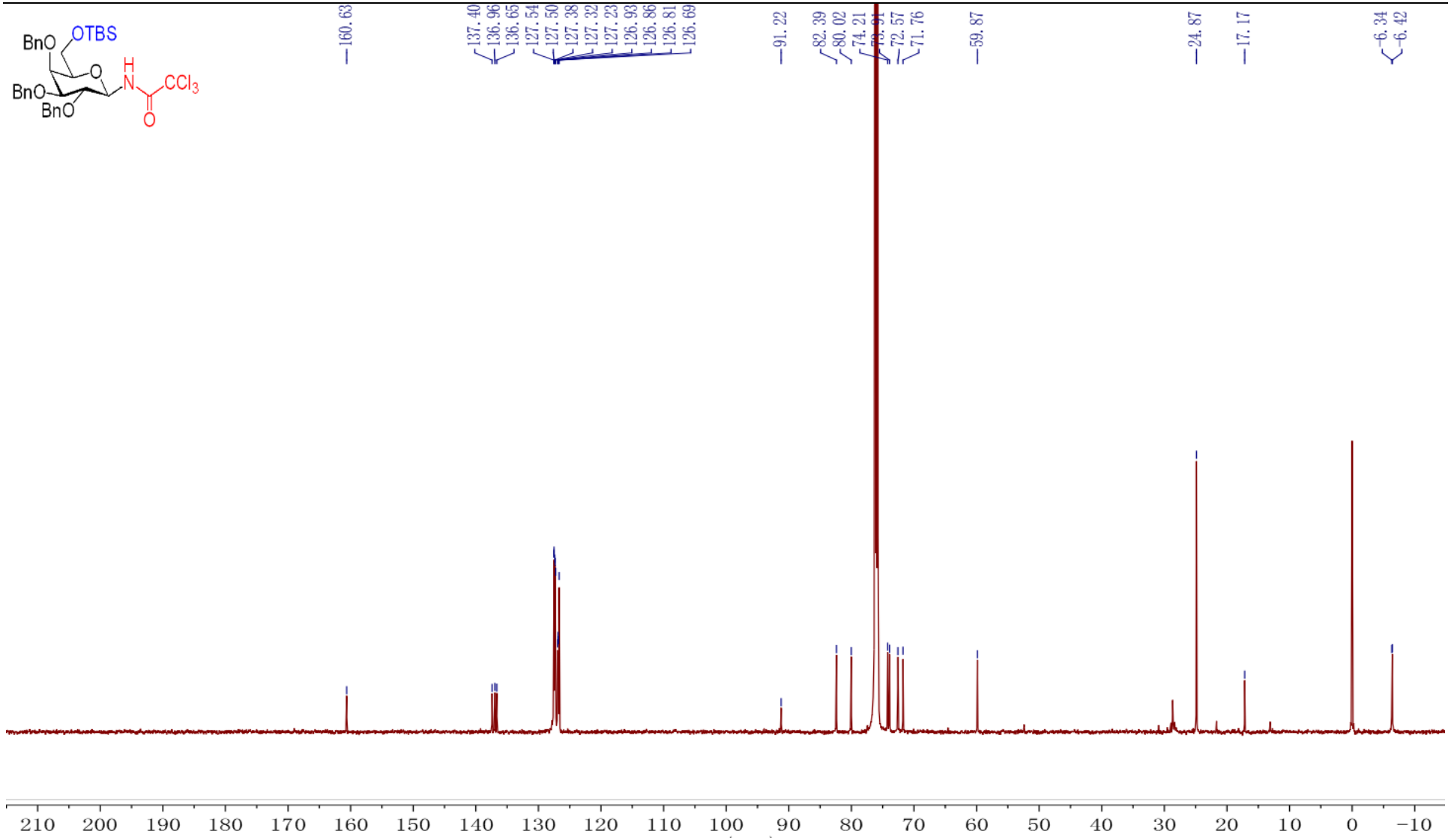
HMBC of **12**



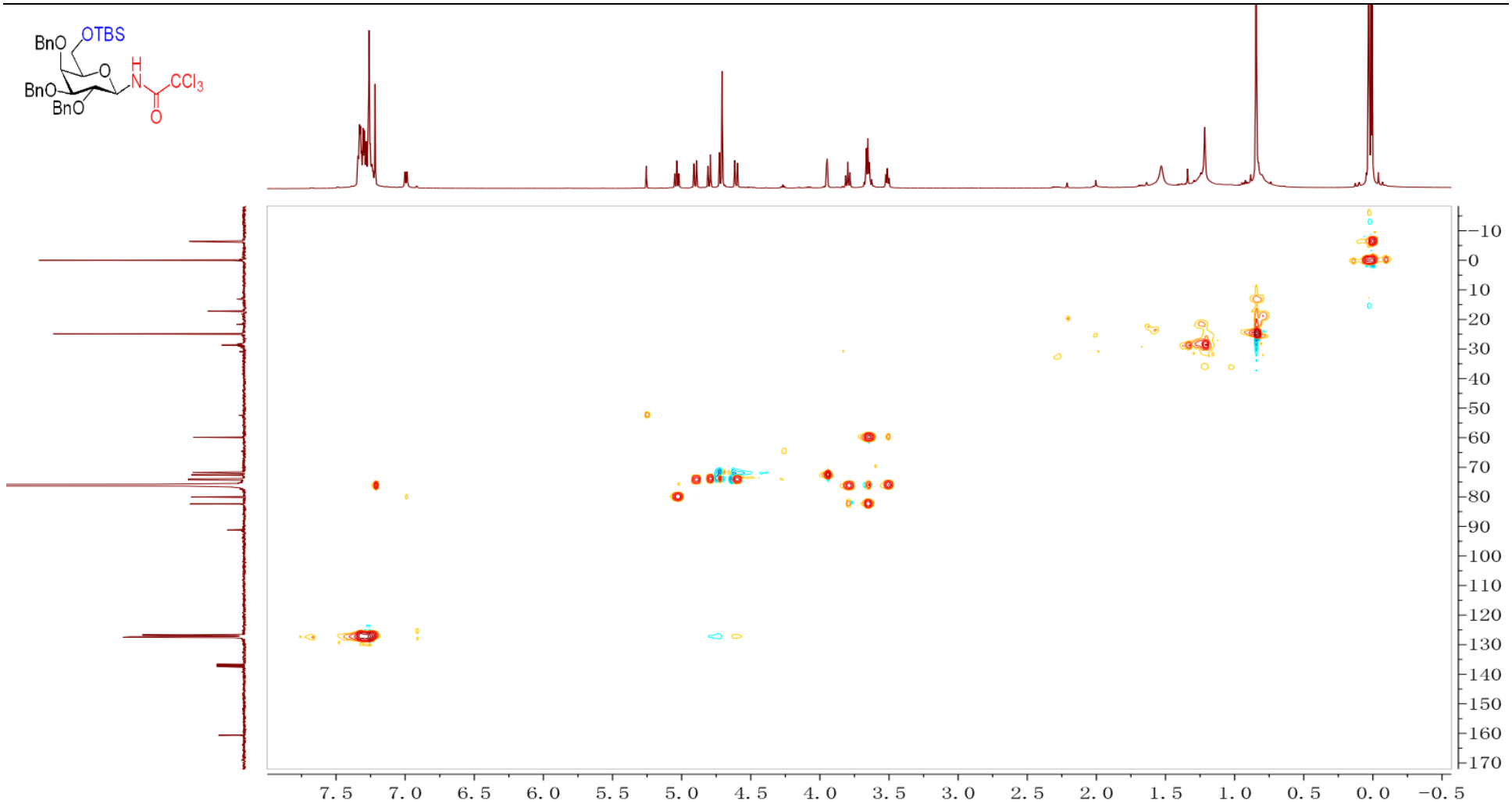
^{1}H – ^{1}H COSY of **12**



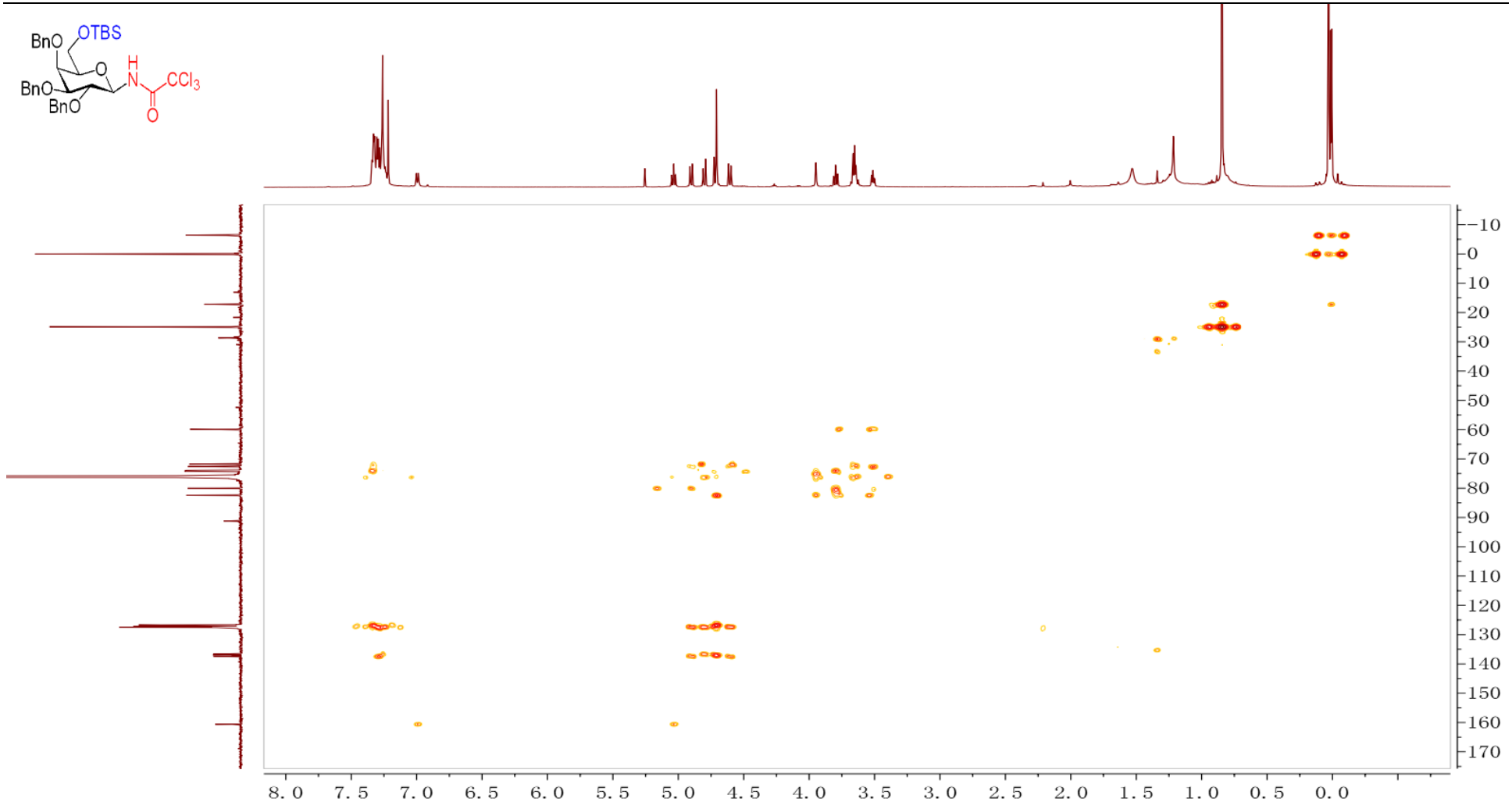
^{1}H NMR of **13** (600 M, $CDCl_3$)



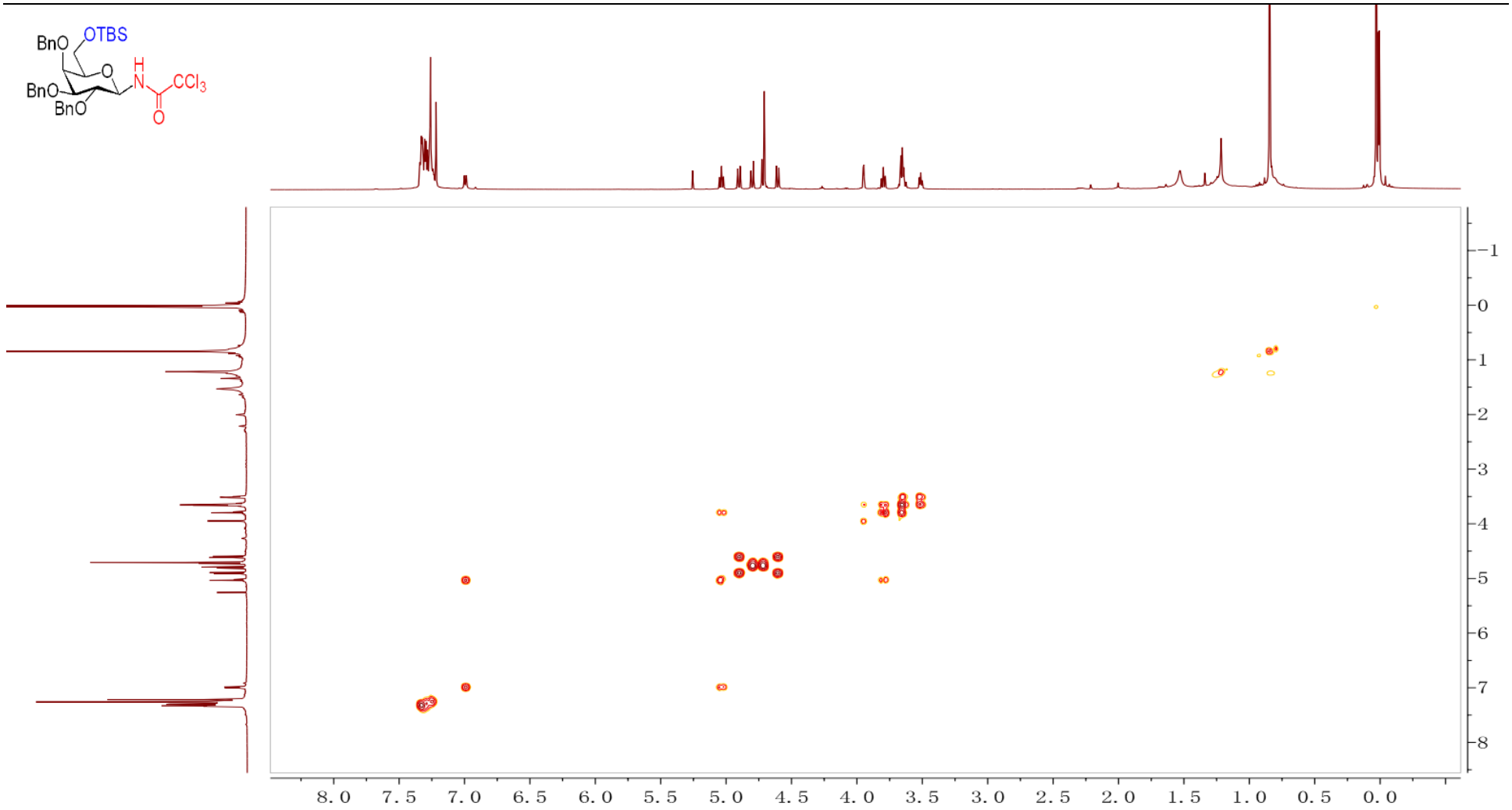
^{13}C NMR of **13** (151 M, $CDCl_3$)


BnO
OTBS
BnO
BnO
H
N
CCl3
O
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

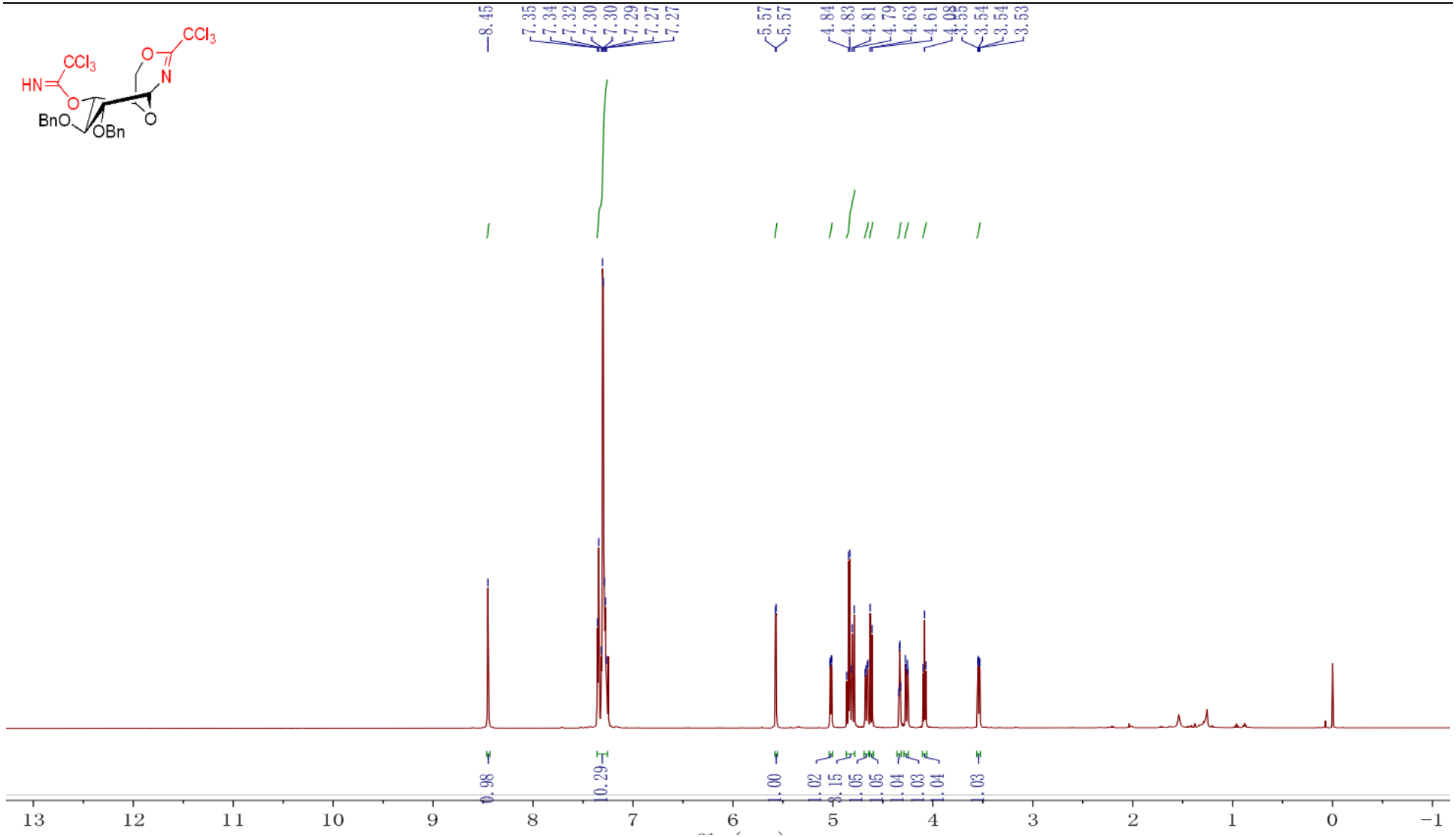
HSQC of **13**


BnO
OTBS
BnO
BnO
H
N
CCl3
O
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170

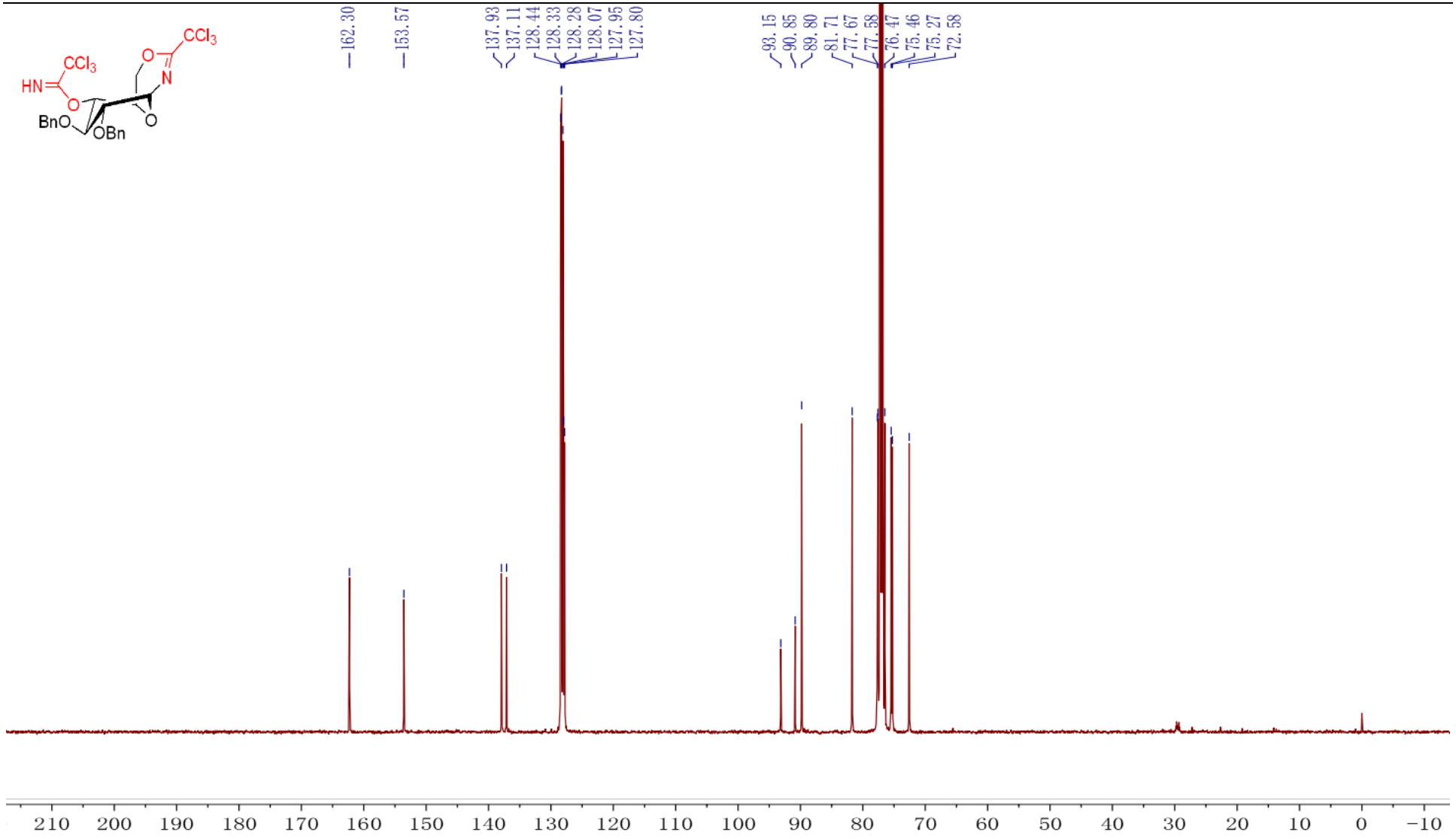
HMBC of **13**



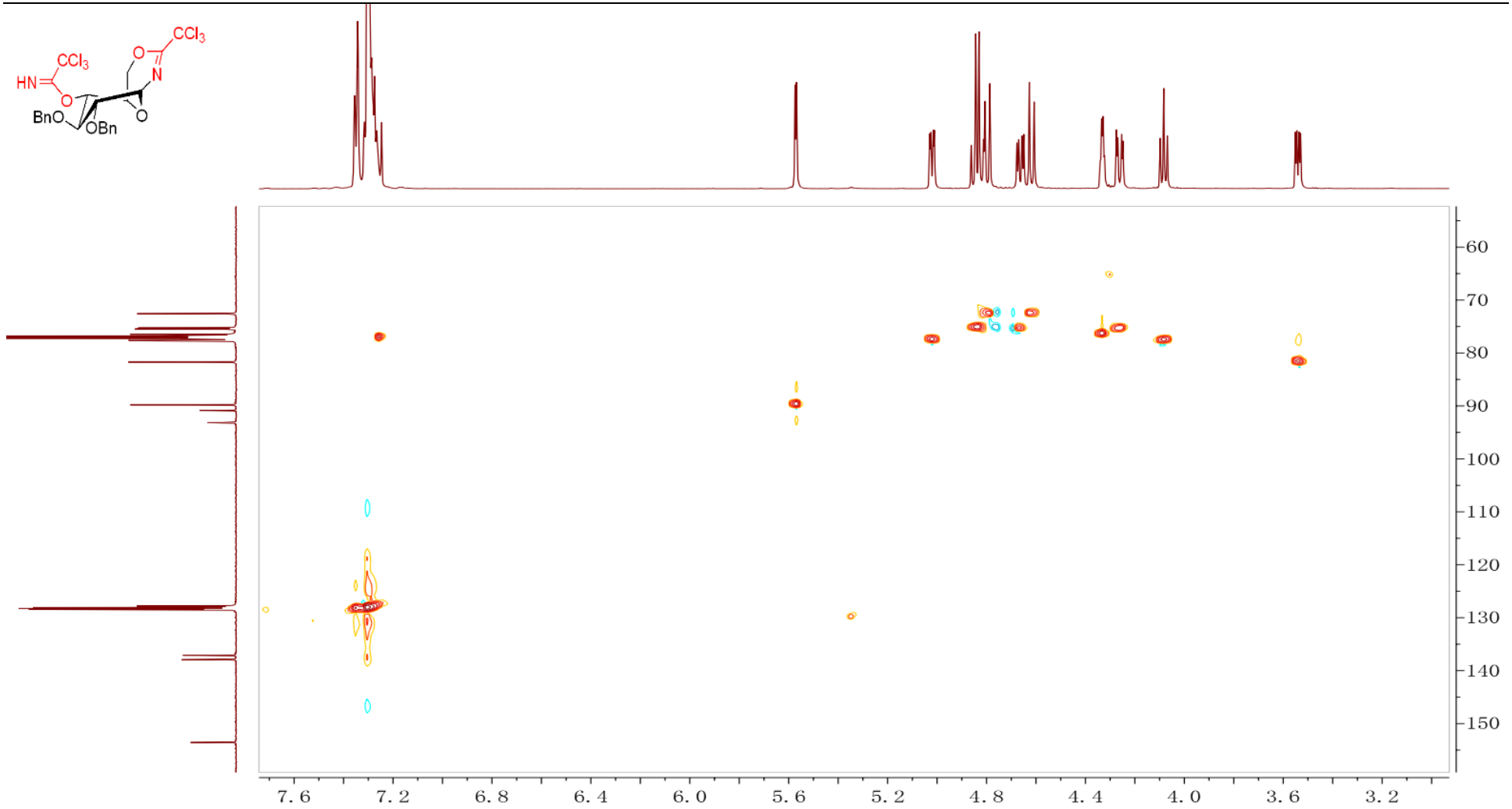
^{1}H – ^{1}H COSY of **13**



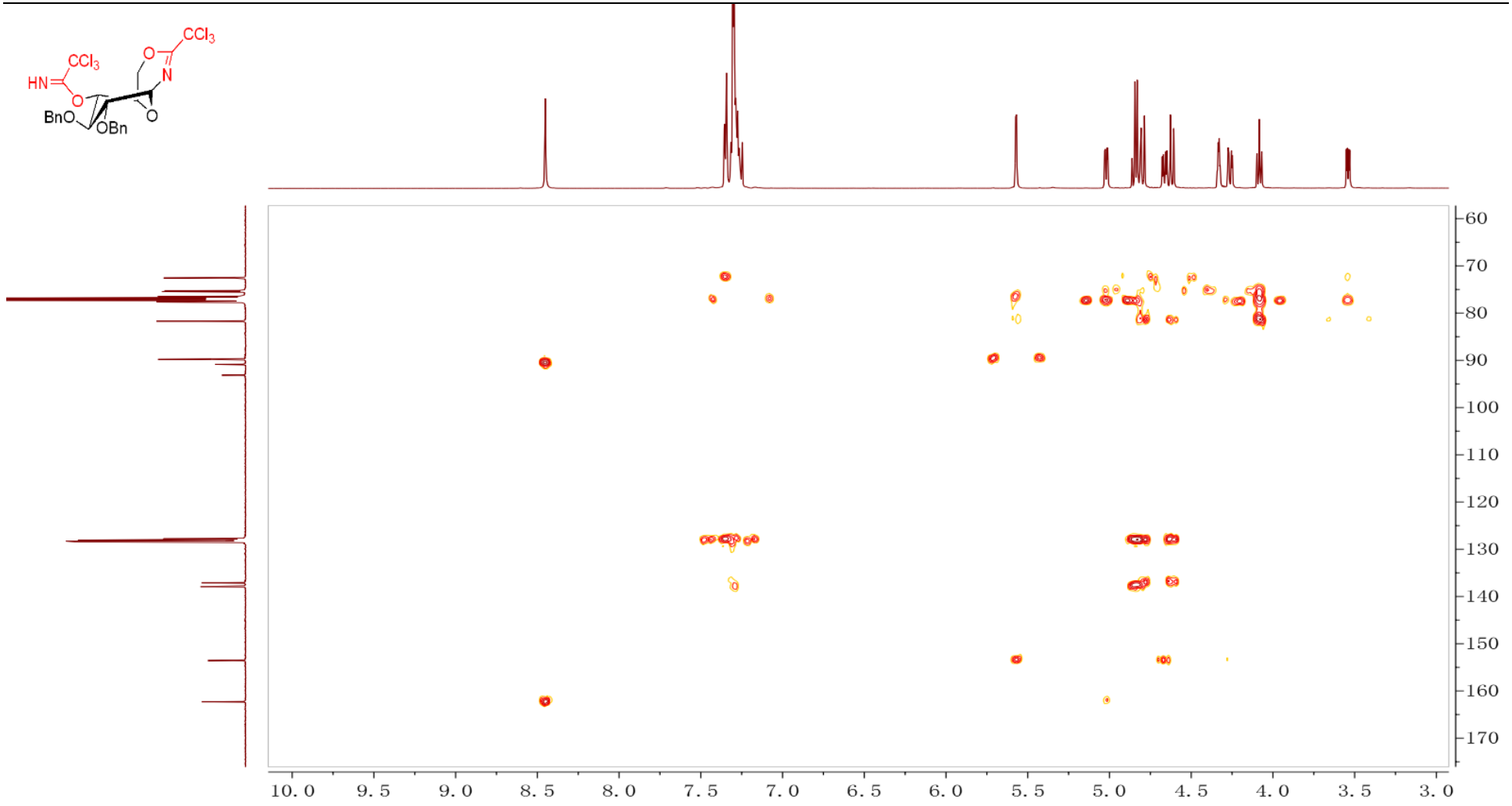
^{1}H NMR of **15** (600 M, $CDCl_3$)



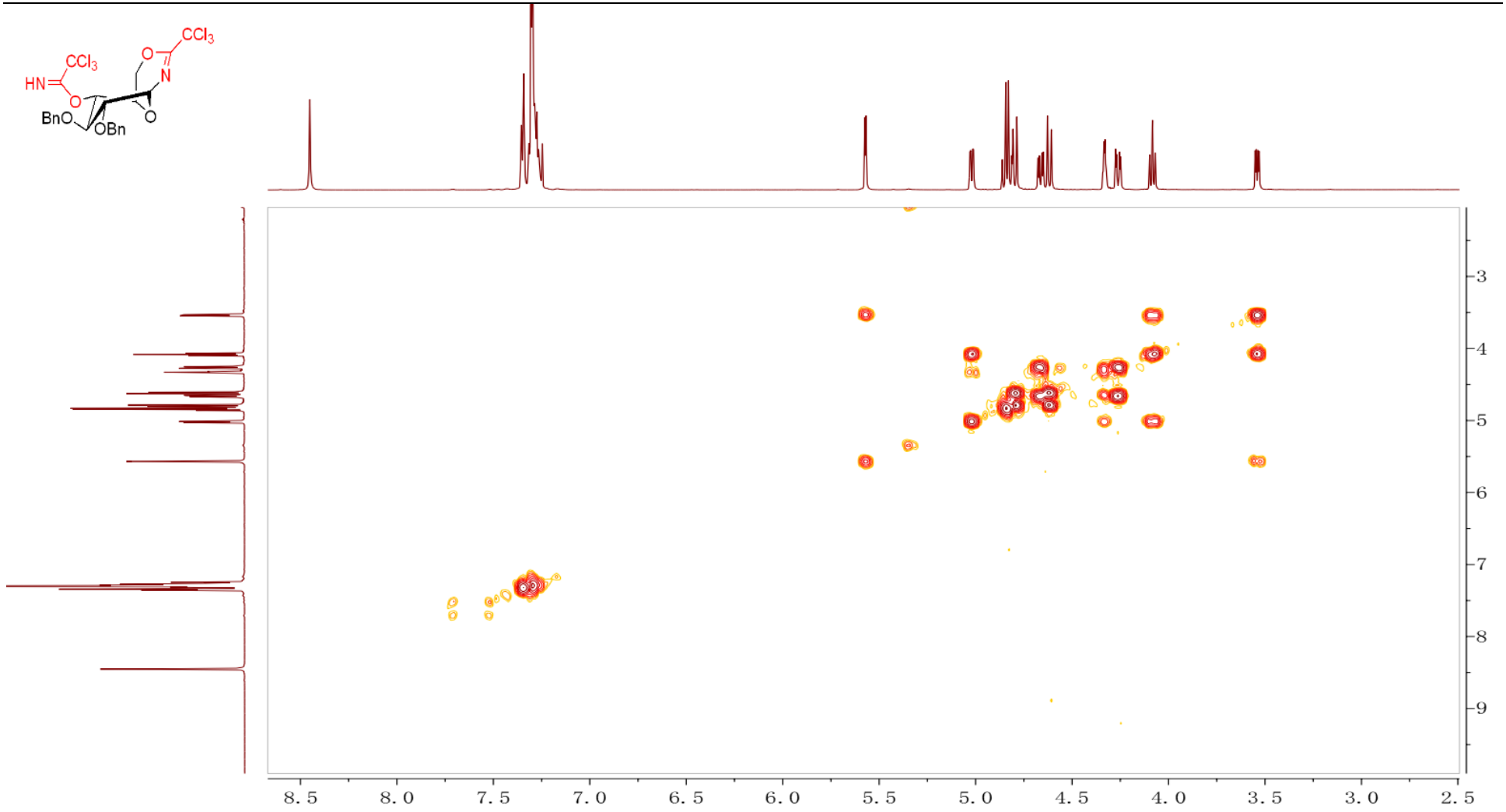
^{13}C NMR of **15** (151 M, $CDCl_3$)


CCl3
HN
O
CCl3
O
N
BnO
OBn
O
60
70
80
90
100
110
120
130
140
150
7.6
7.2
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2

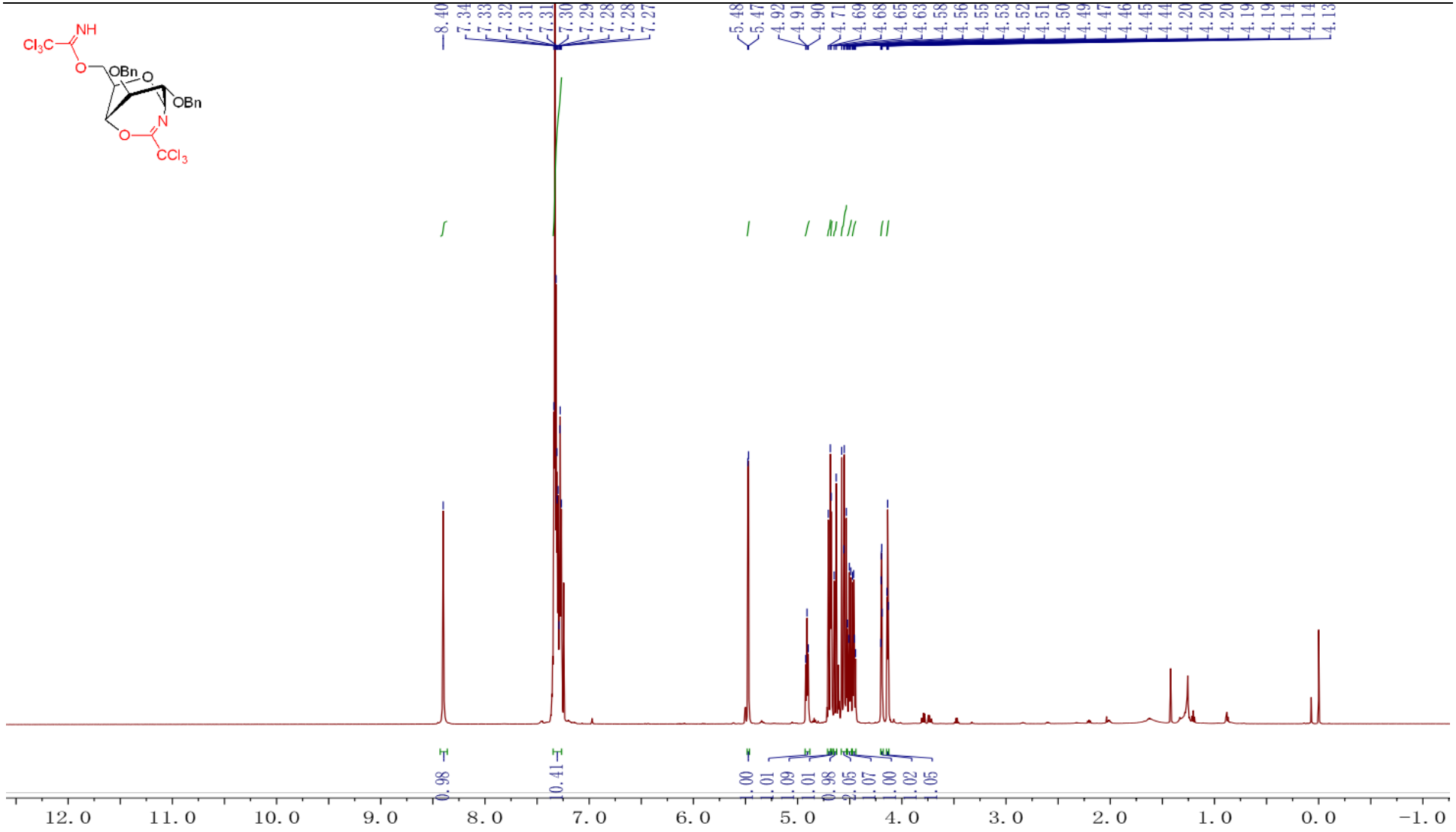
HSQC of **15**


CCl3
HN
O
BnO
OBn
O
O
N
CCl3
60
70
80
90
100
110
120
130
140
150
160
170
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0

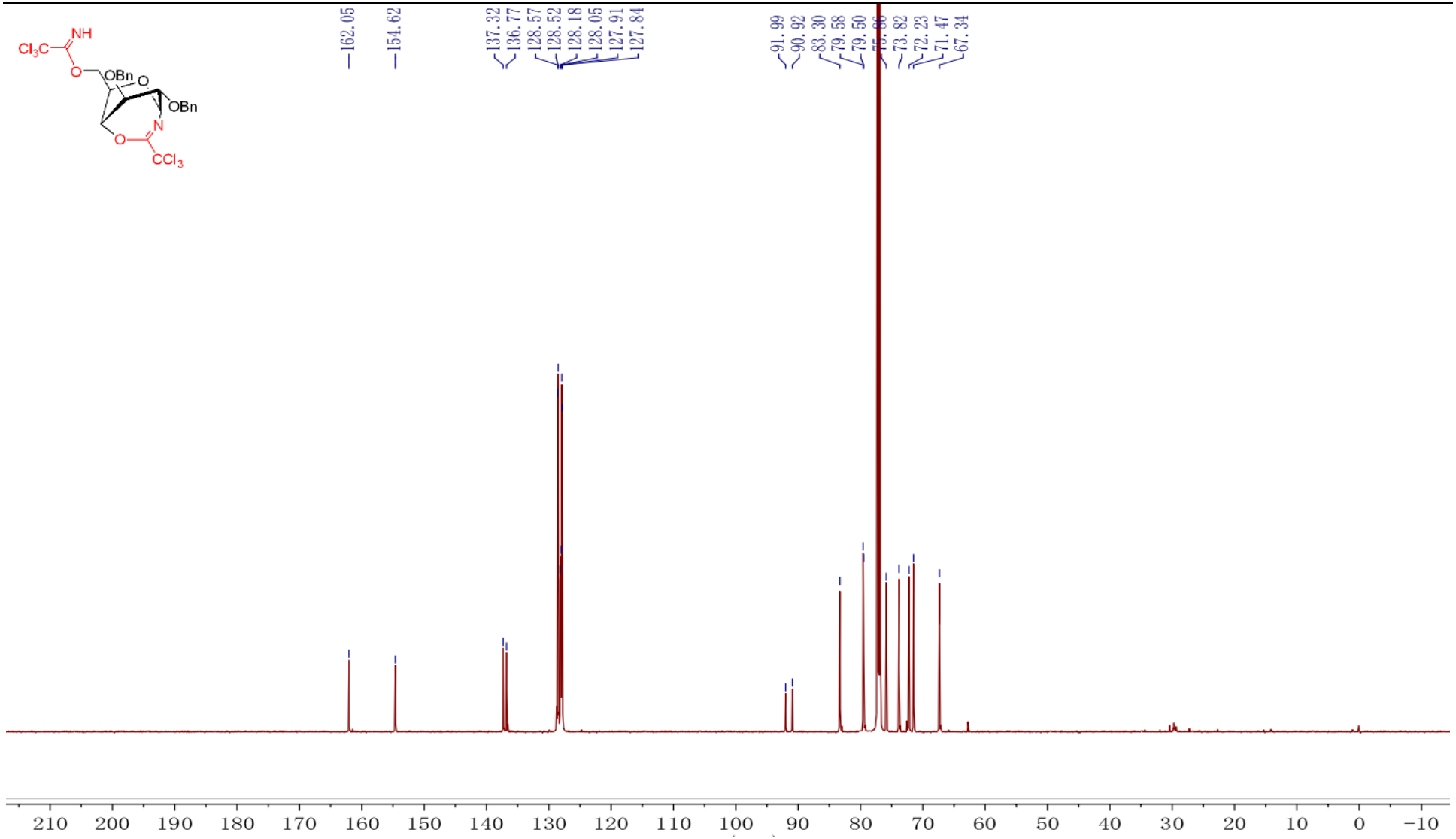
HMBC of **15**



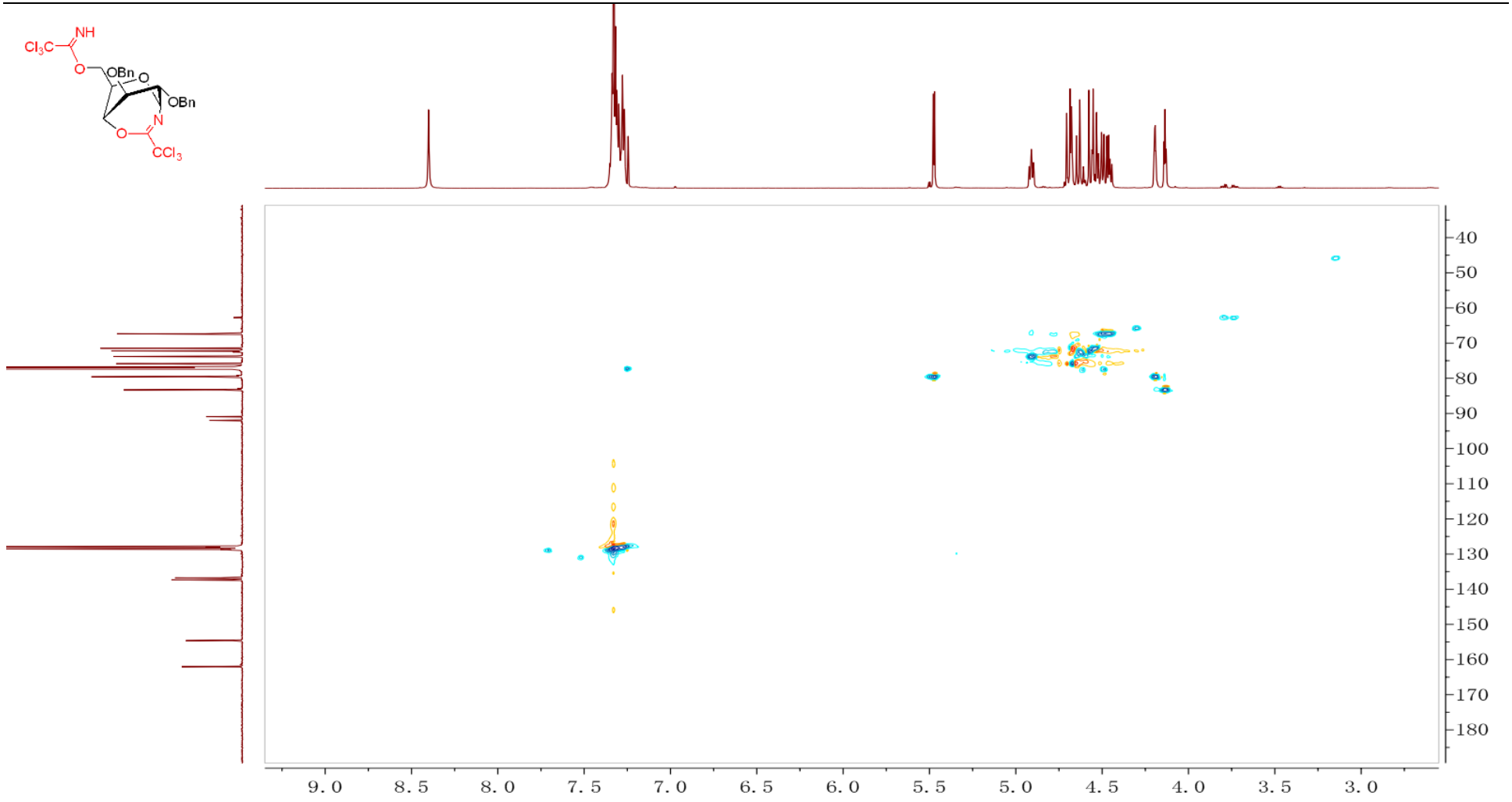
^{1}H – ^{1}H COSY of **15**



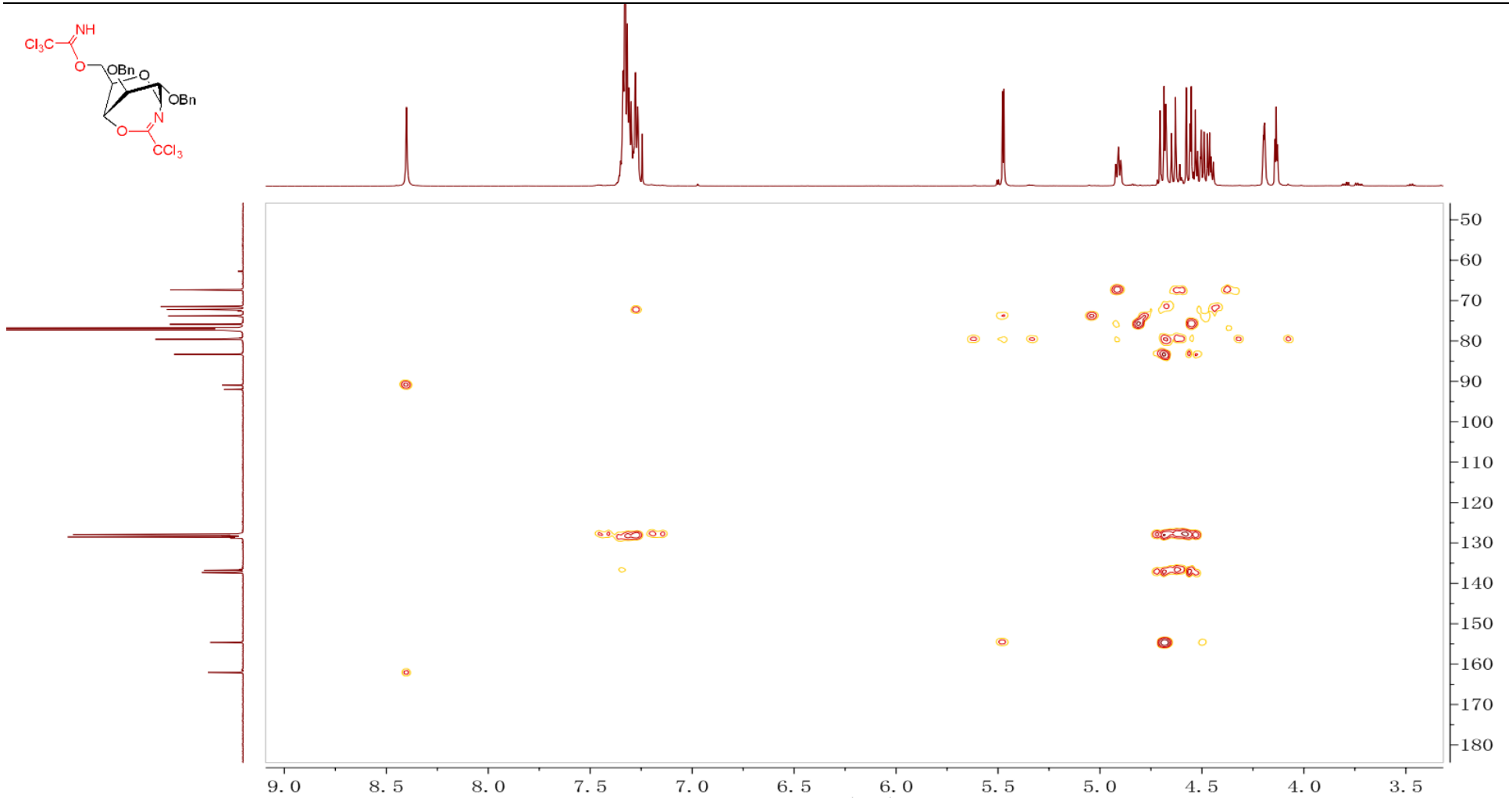
^{1}H NMR of **16** (600 M, $CDCl_3$)



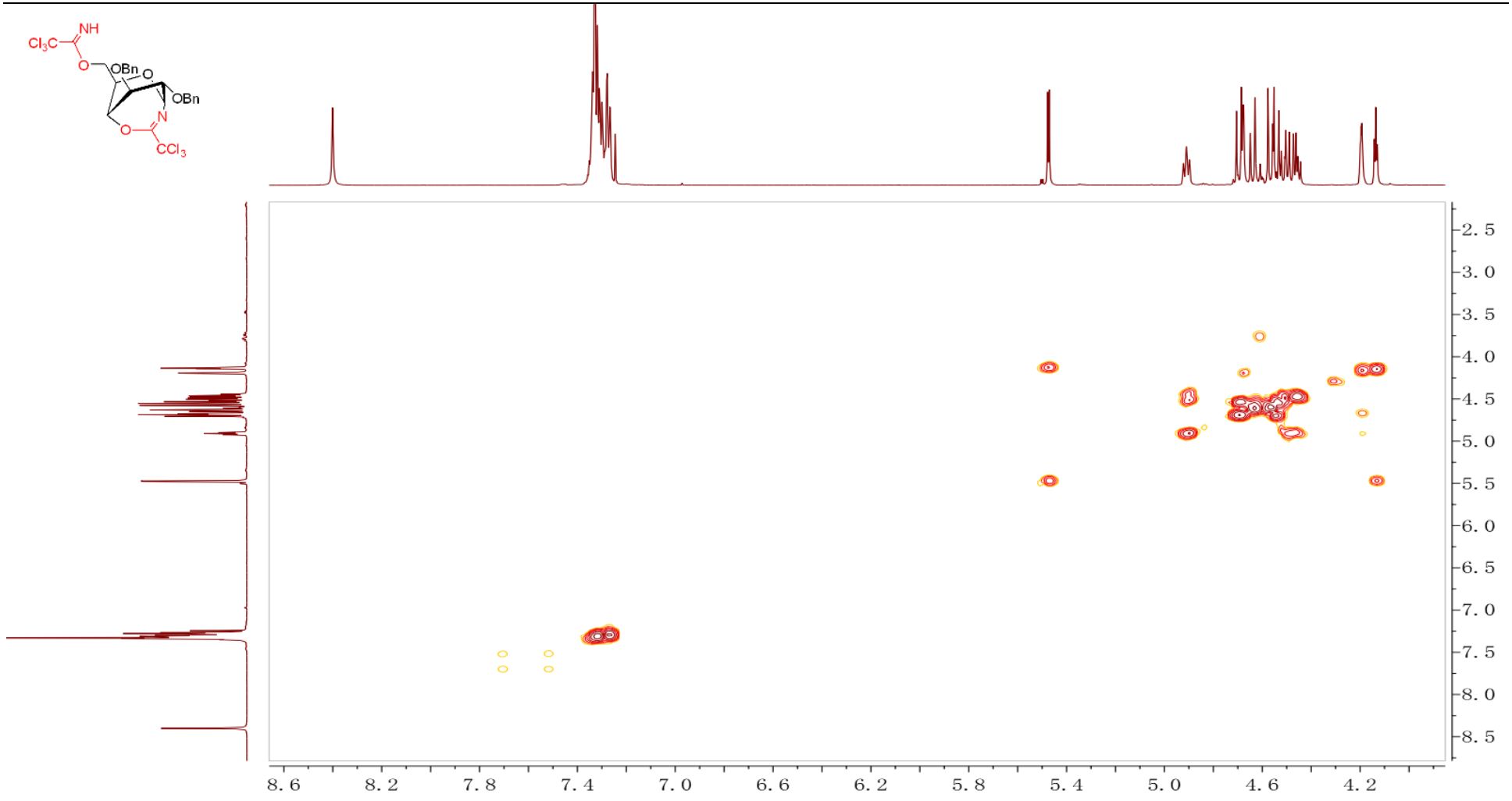
^{13}C NMR of **16** (151 M, $CDCl_3$)


NH
Cl3C
O
OBn
O
OBn
N
O
CCl3
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0

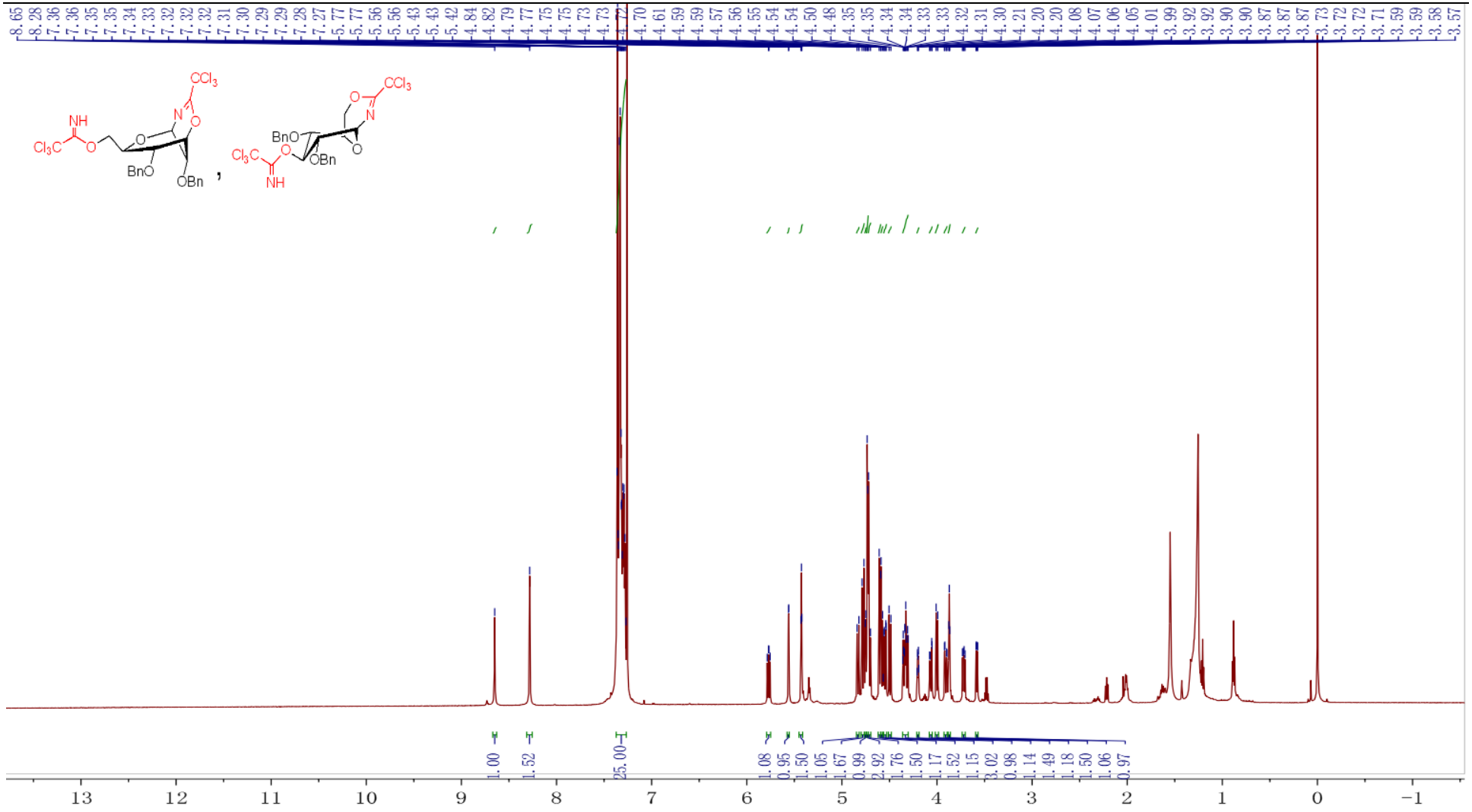
HSQC of **16**


NH
Cl3C
O
OBn
O
OBn
N
O
CCl3
50
60
70
80
90
100
110
120
130
140
150
160
170
180
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

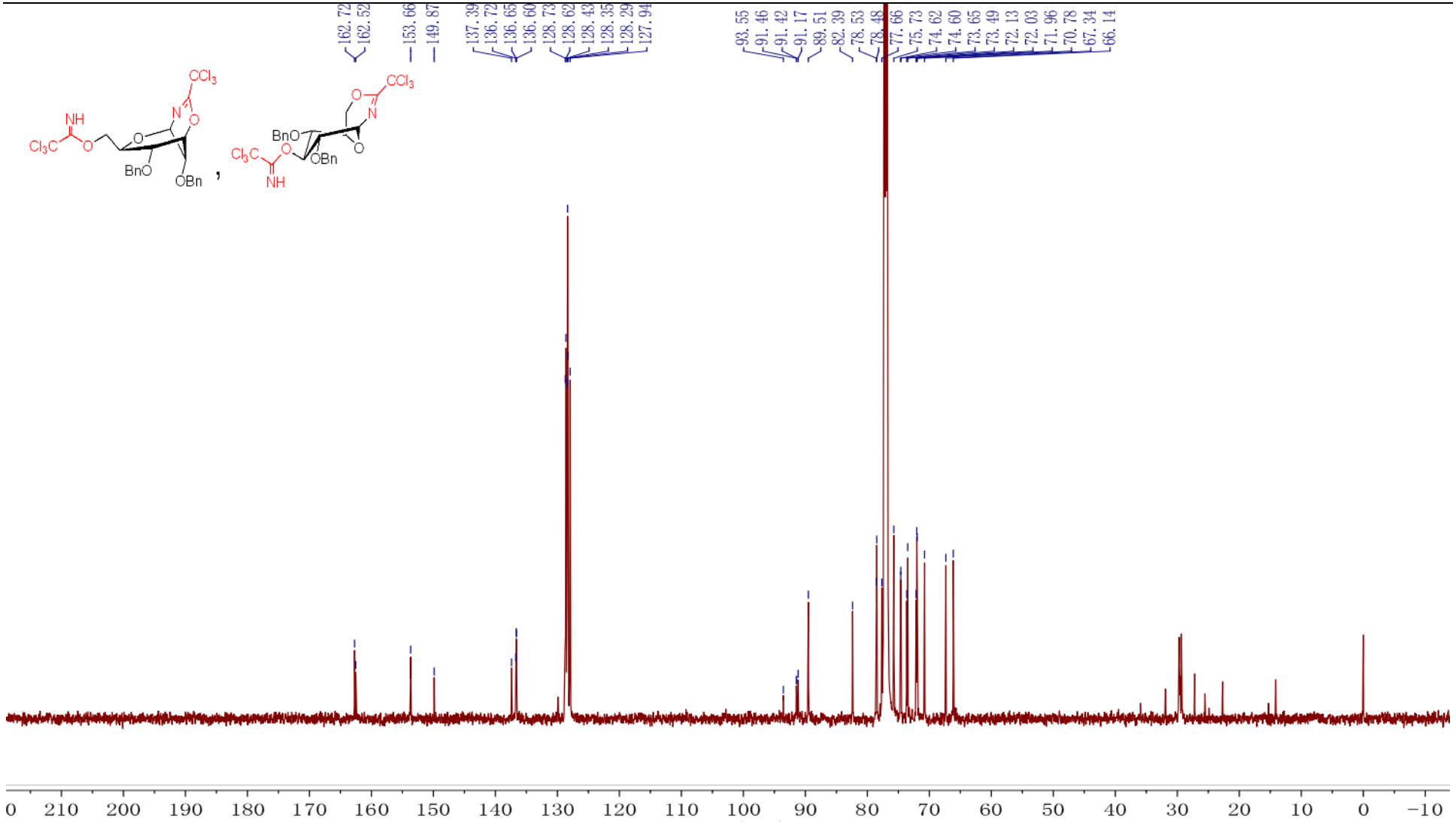
HMBC of **16**



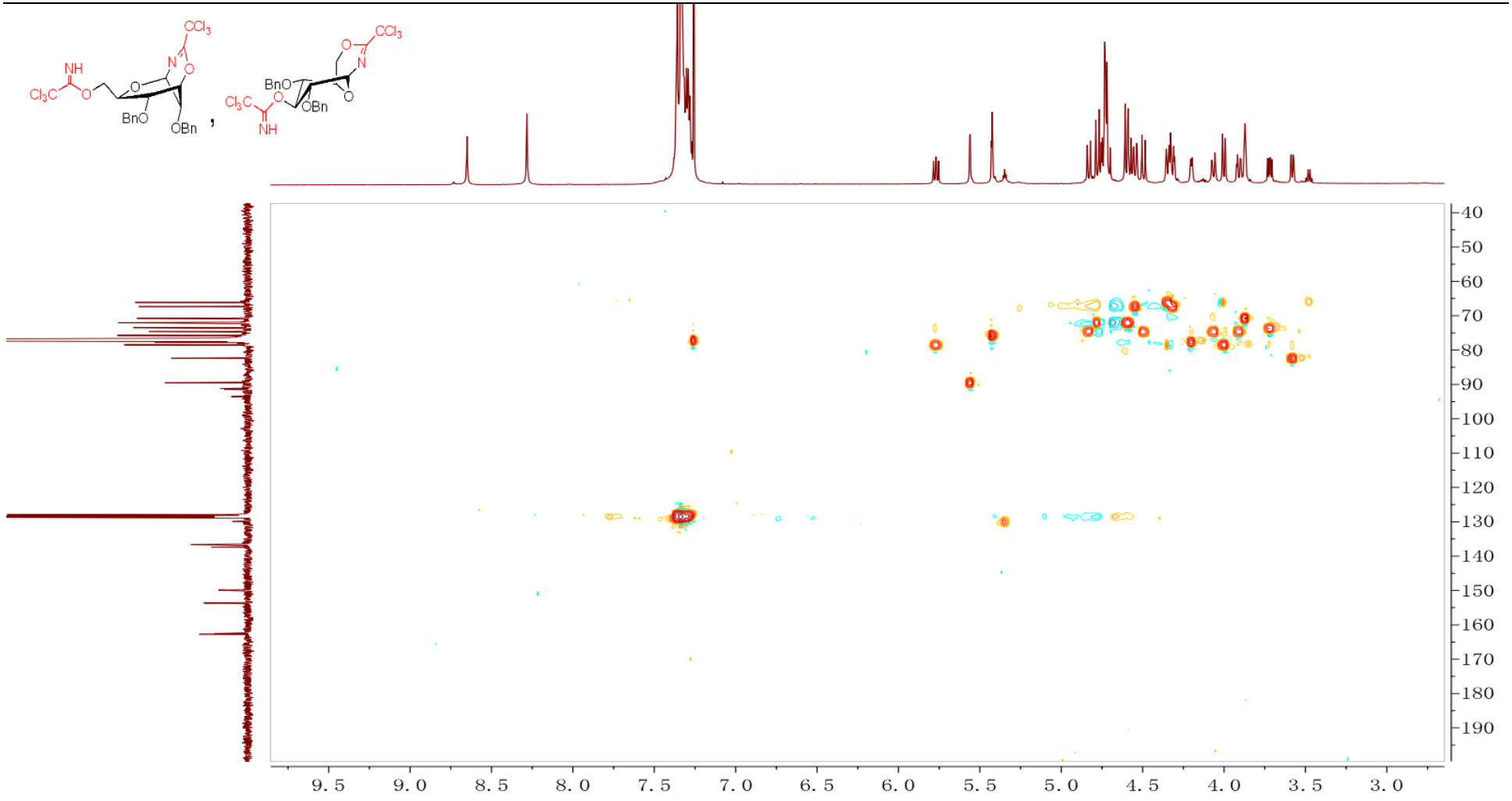
$^{1}H - {}^{1}H$ COSY of **16**



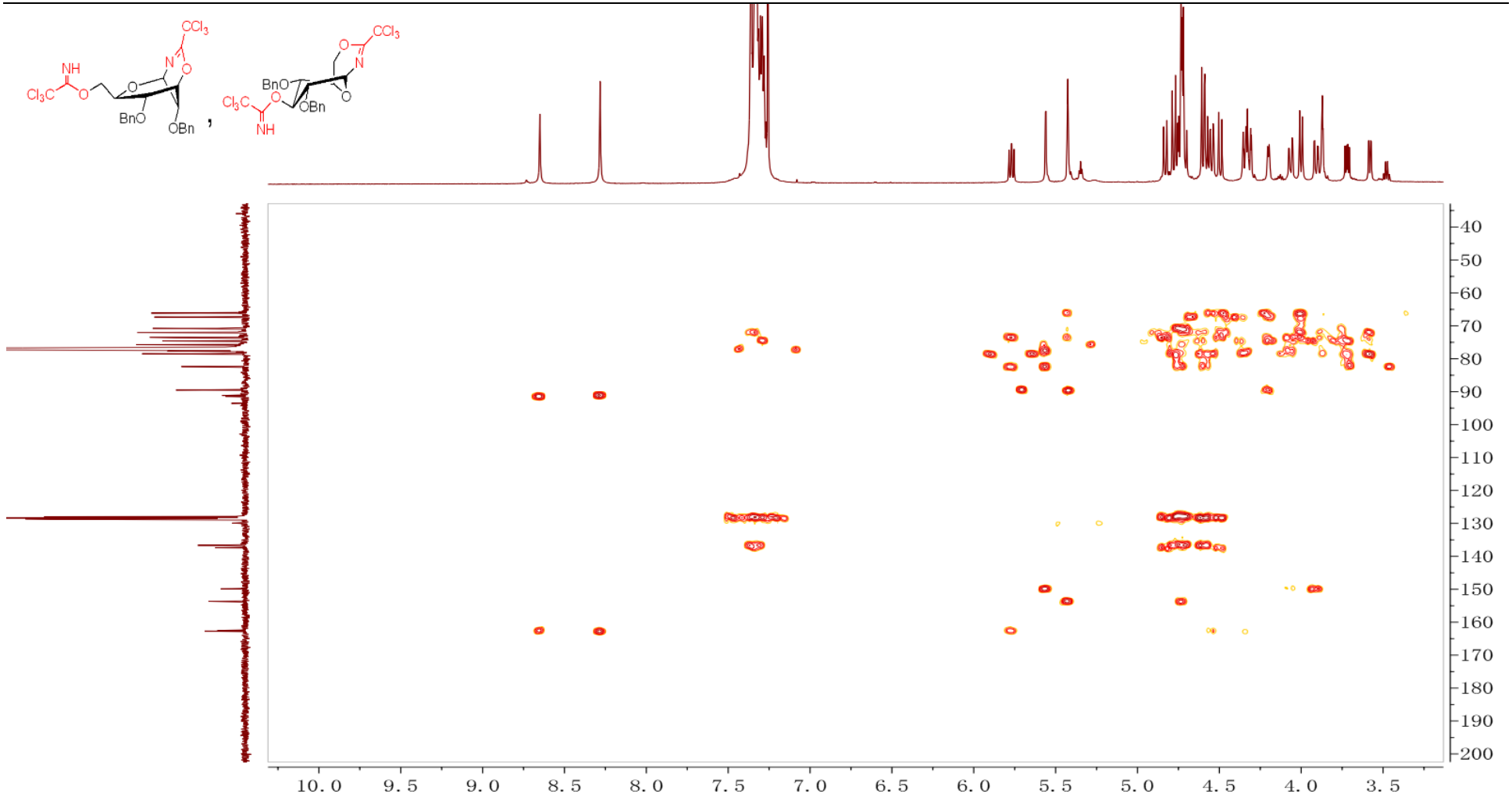
^{1}H NMR of **18** and **19** (600 M, $CDCl_3$)



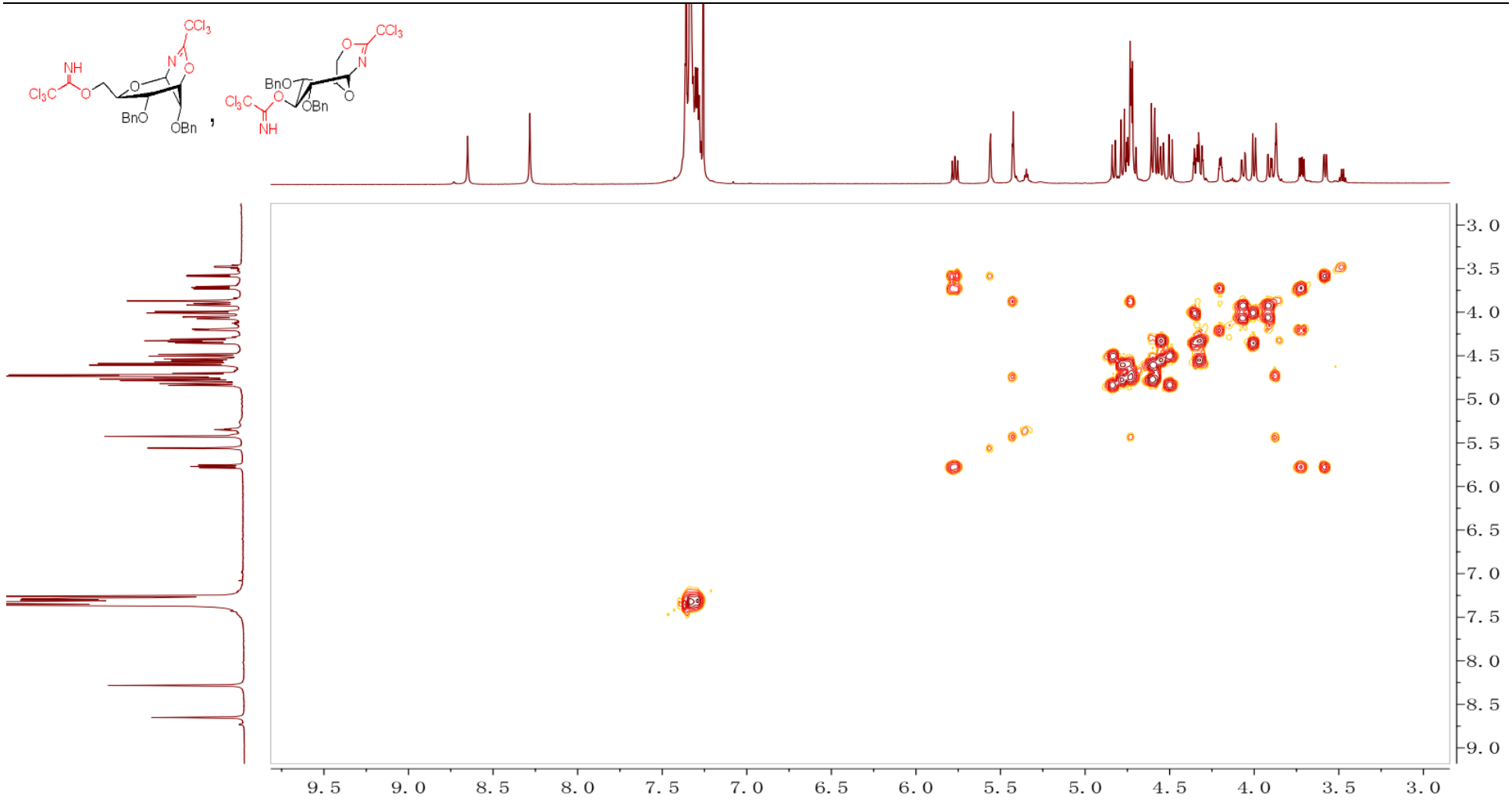
^{13}C NMR of **18** and **19** (151 M, $CDCl_3$)



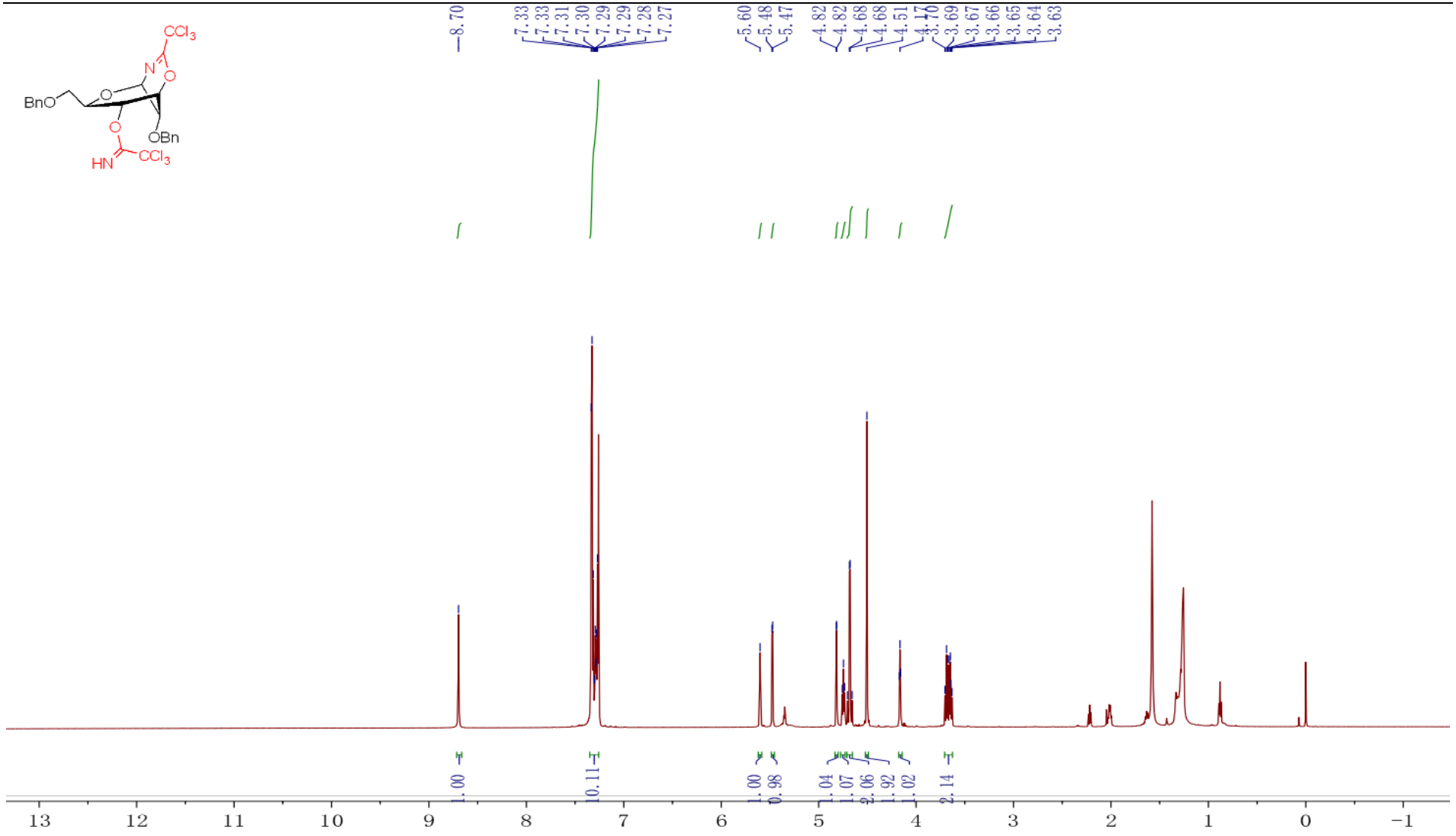
HSQC of **18** and **19**



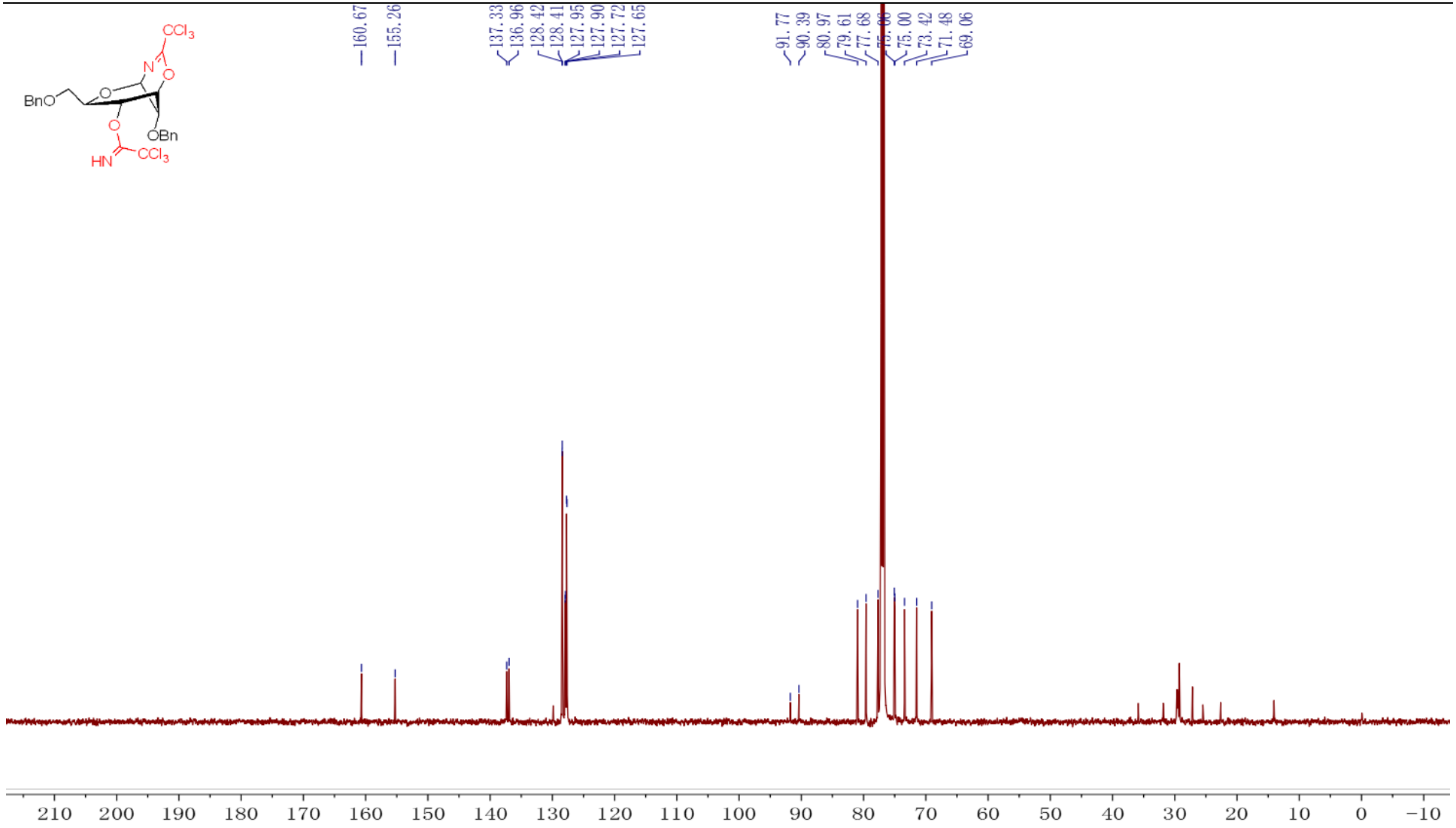
HMBC of **18** and **19**



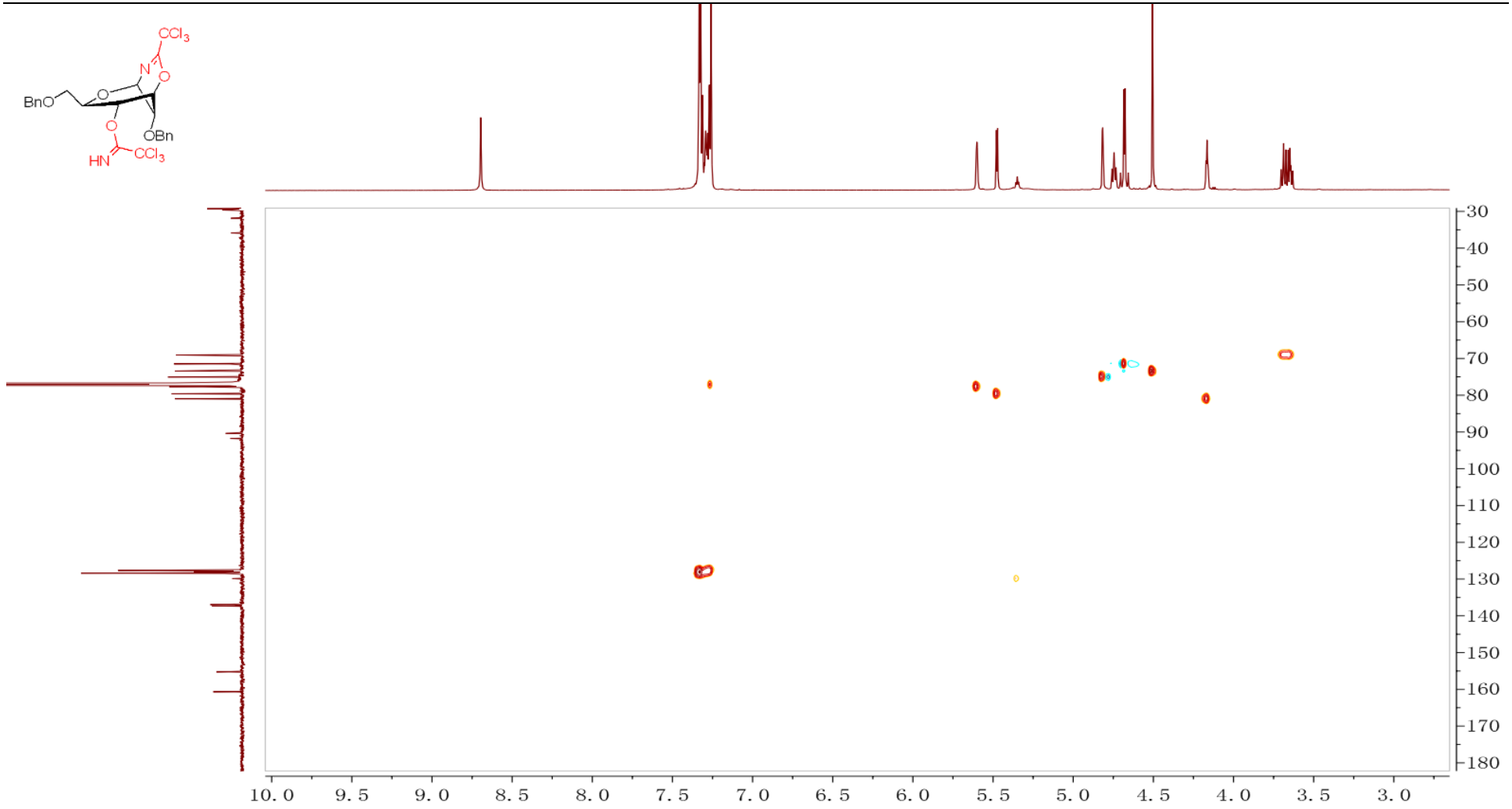
$^{1}H - {}^{1}H$ COSY of **18** and **19**



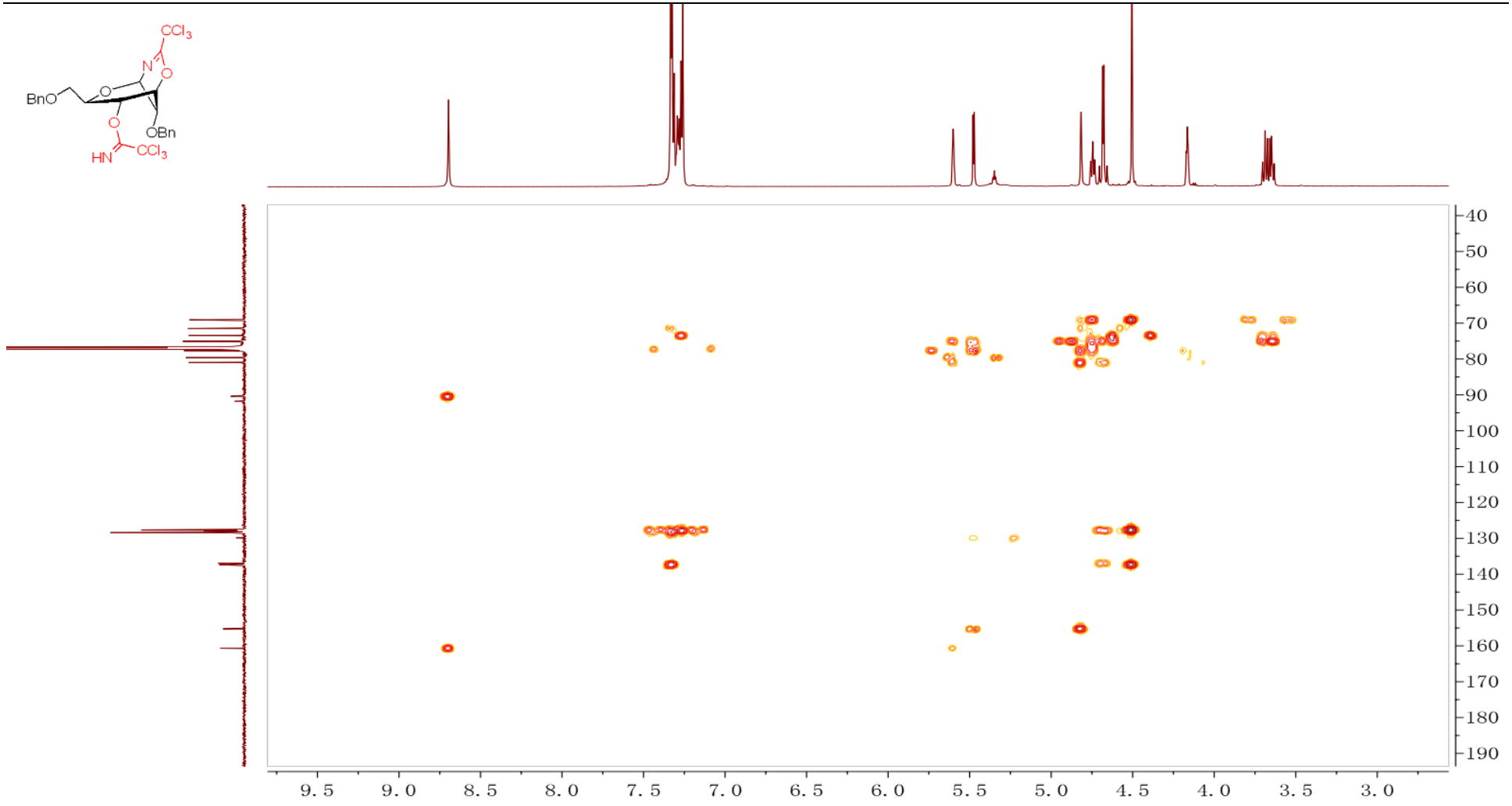
^{1}H NMR of **21** (600 M, $CDCl_3$)



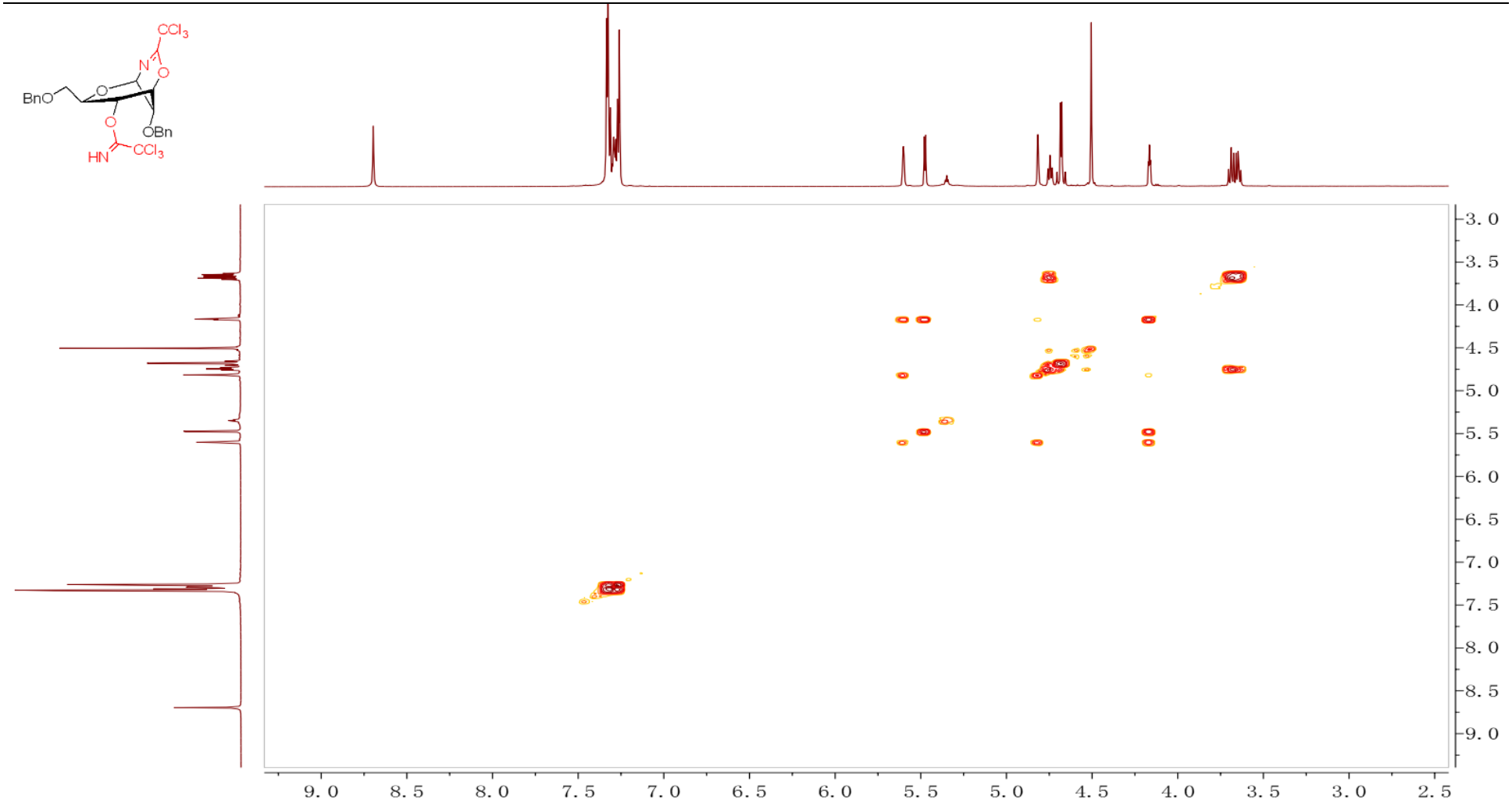
^{13}C NMR of **21** (151 M, $CDCl_3$)


CCl3
N
O
BnO
O
OBn
HN
CCl3
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0

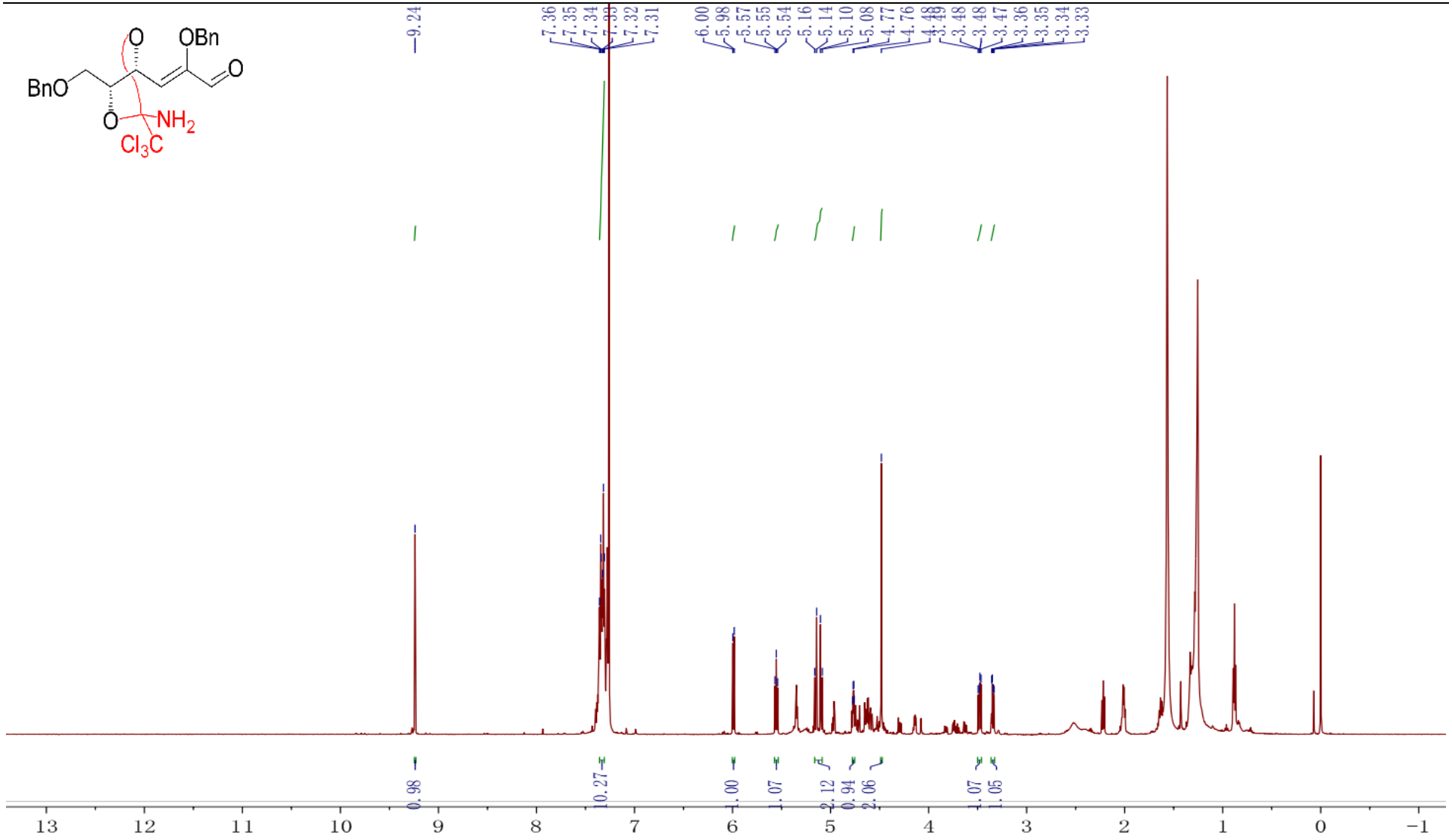
HSQC of **21**


CCl3
N
O
BnO
O
OBn
O
HN
CCl3
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0

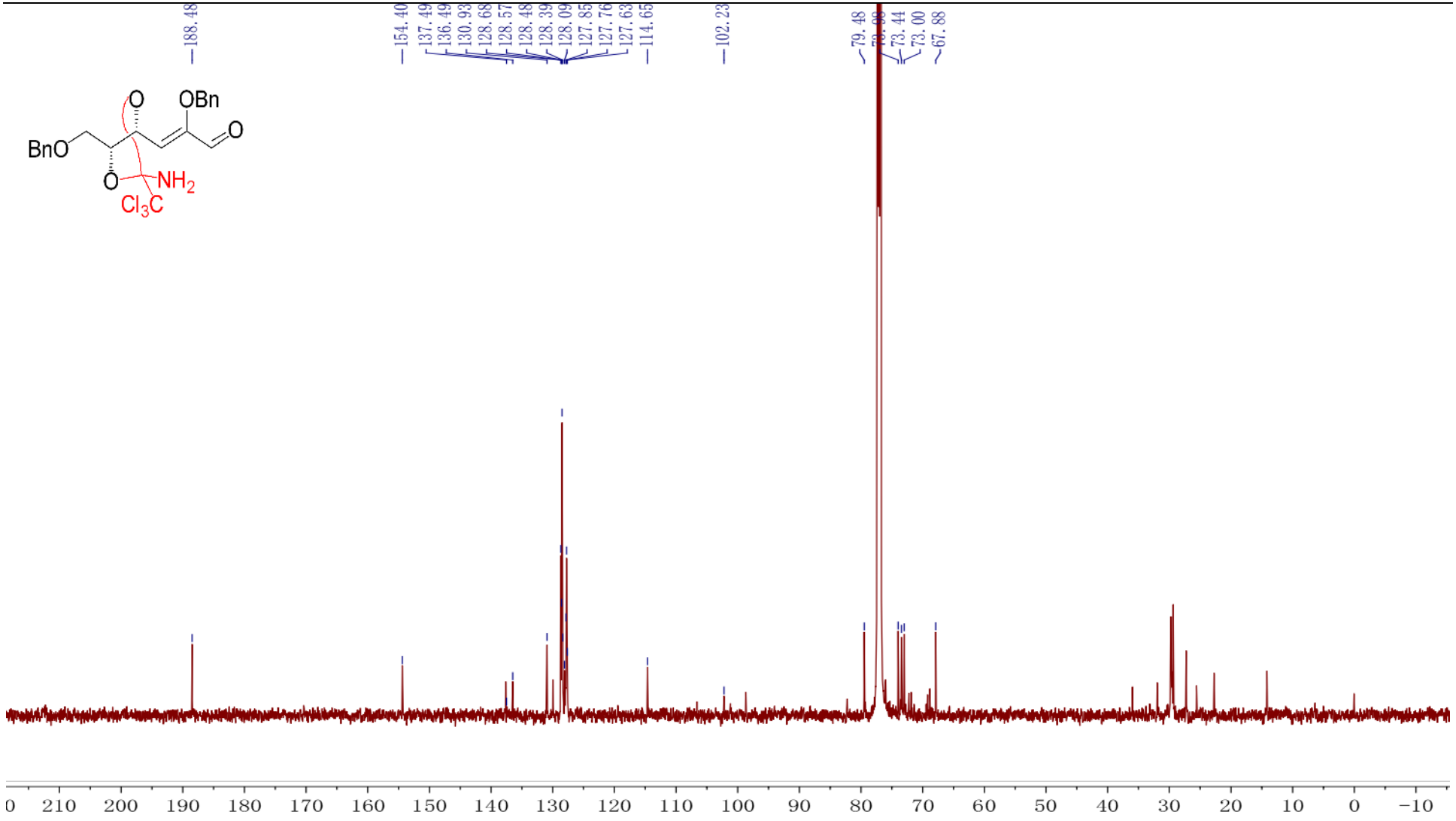
HMBC of **21**



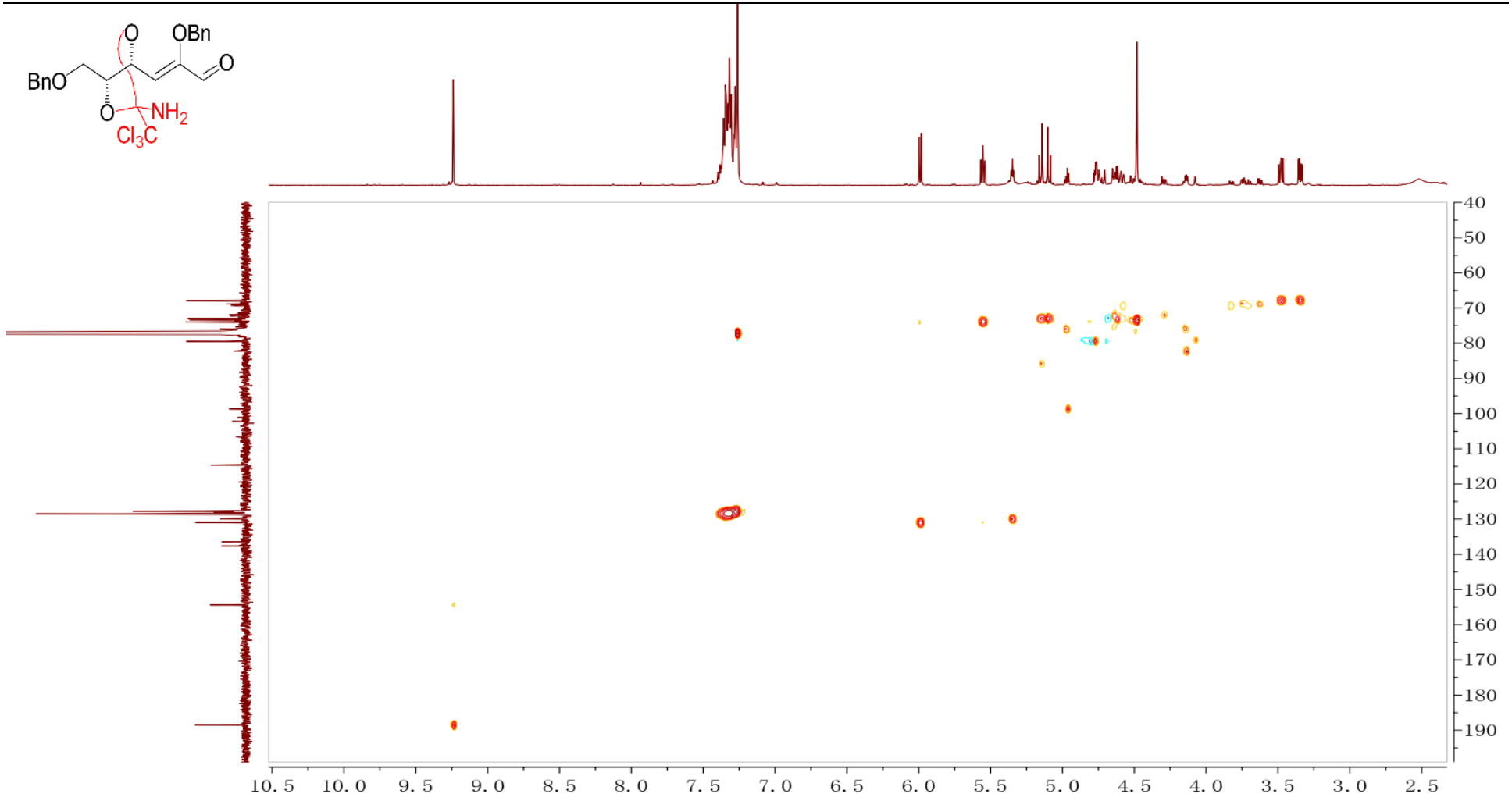
^{1}H – ^{1}H COSY of **21**



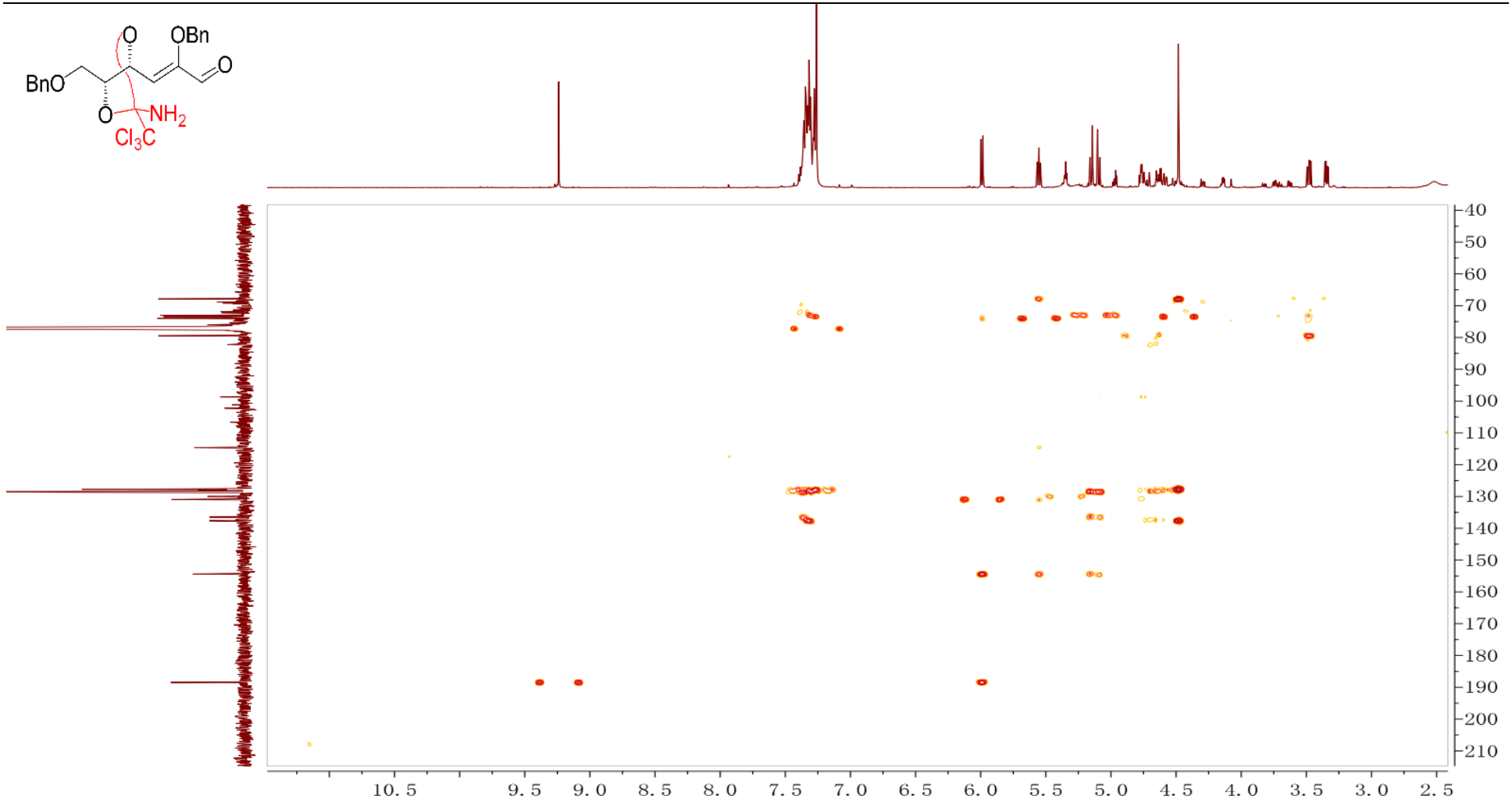
^{1}H NMR of **22** (600 M, $CDCl_3$)



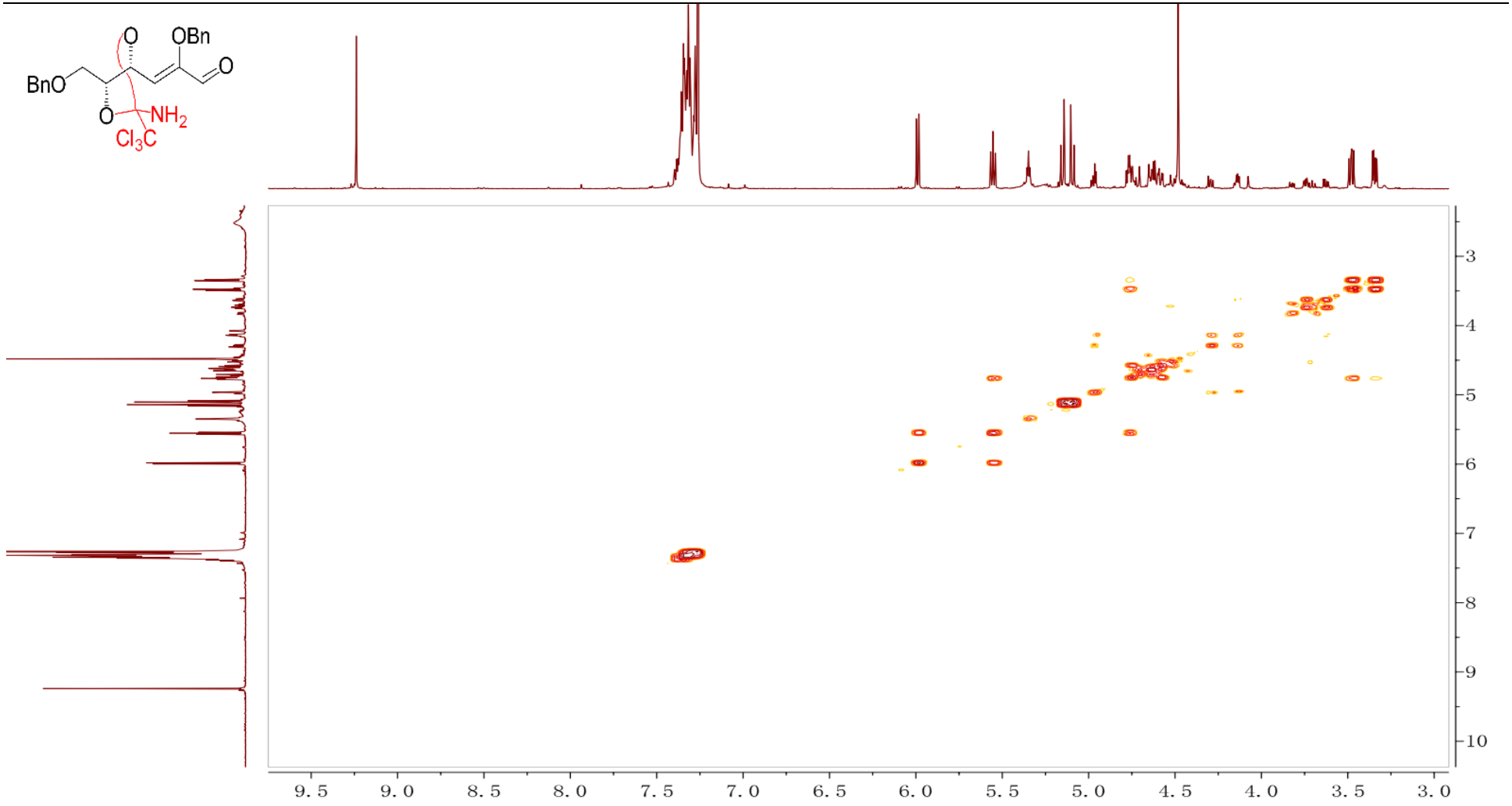
^{13}C NMR of **22** (151 M, $CDCl_3$)


O
OBn
BnO
O
O
NH2
Cl3C
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

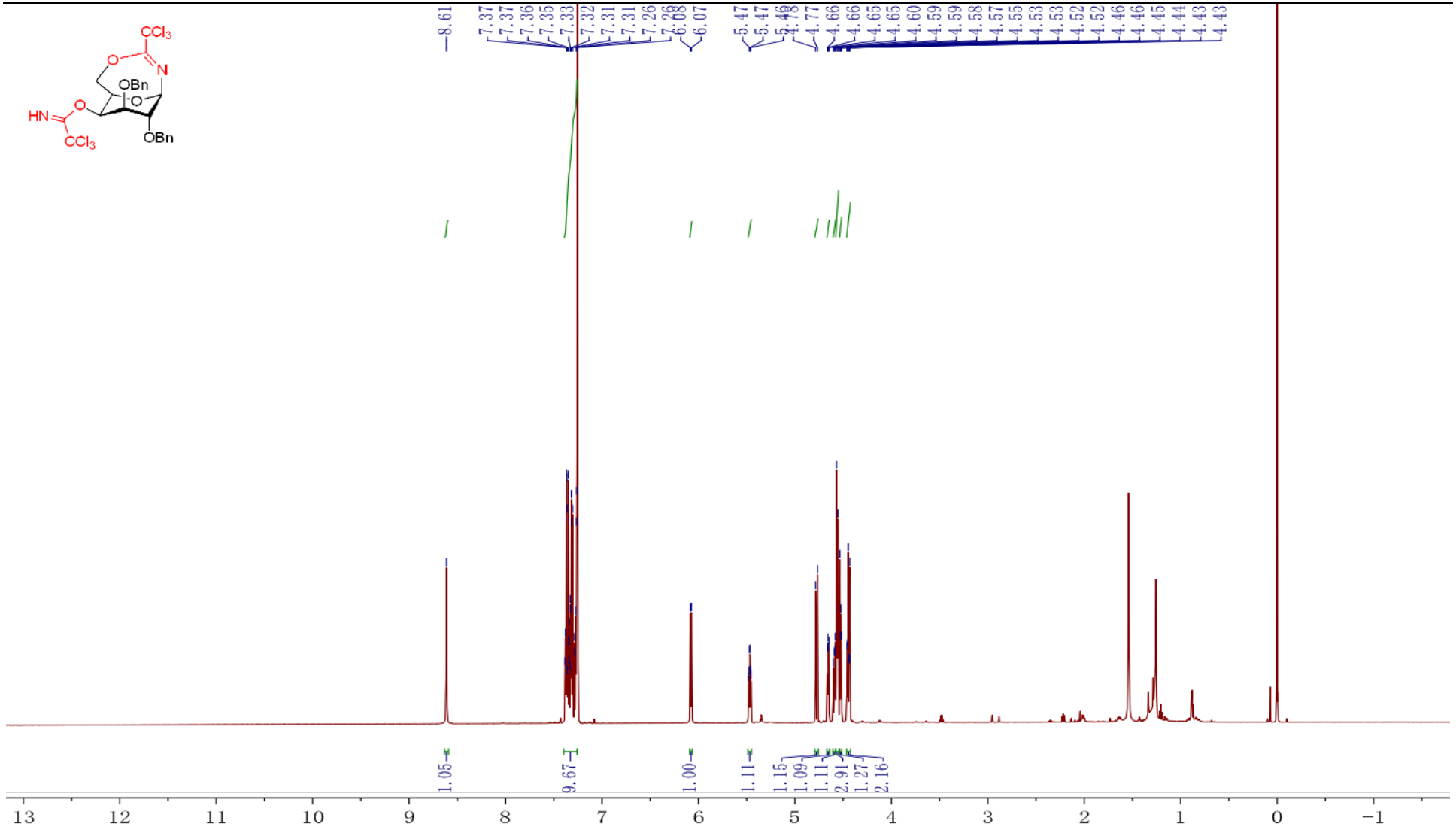
HSQC of **22**


BnO
O
OBn
O
O
NH2
Cl3C
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

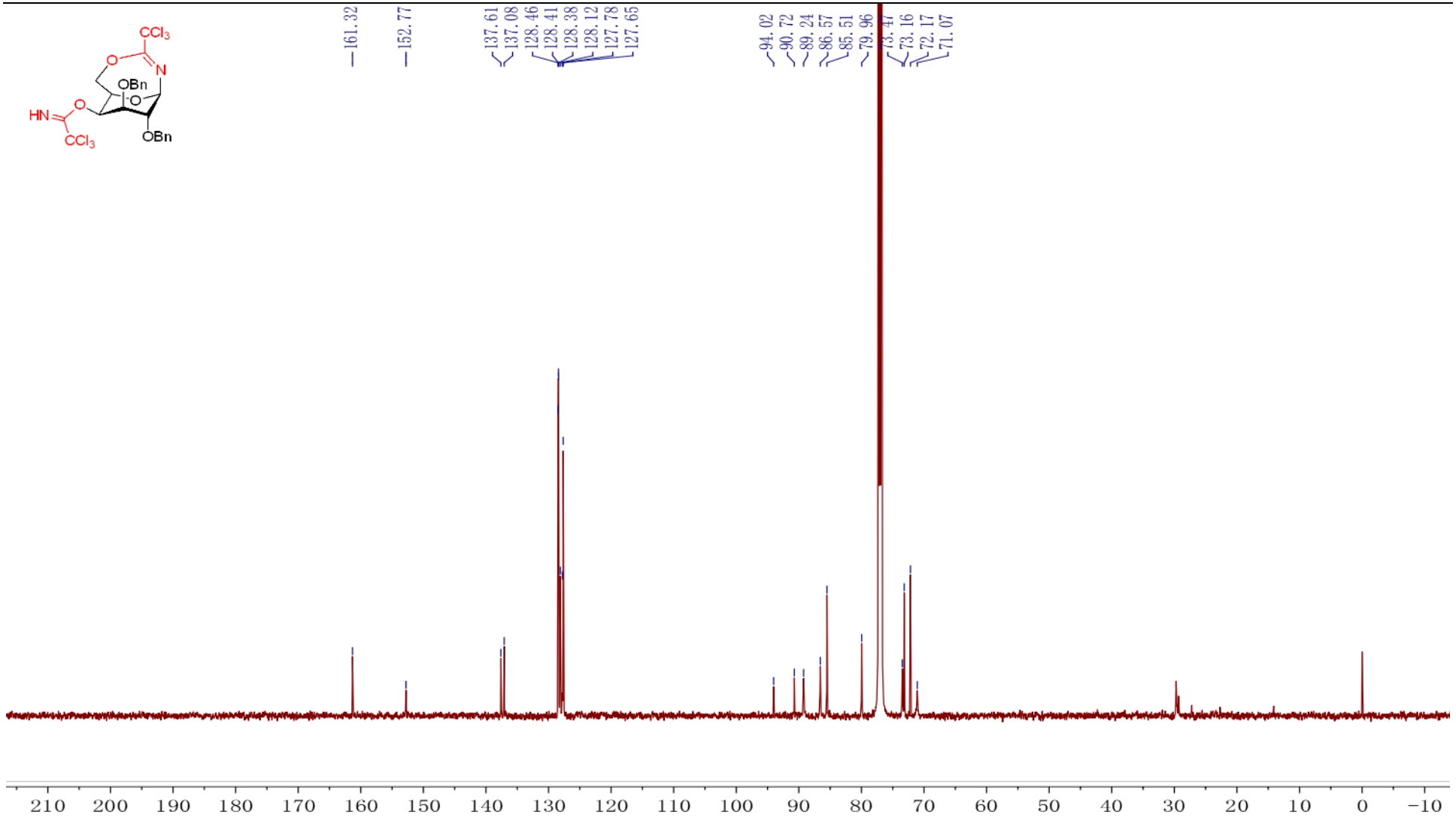
HMBC of **22**



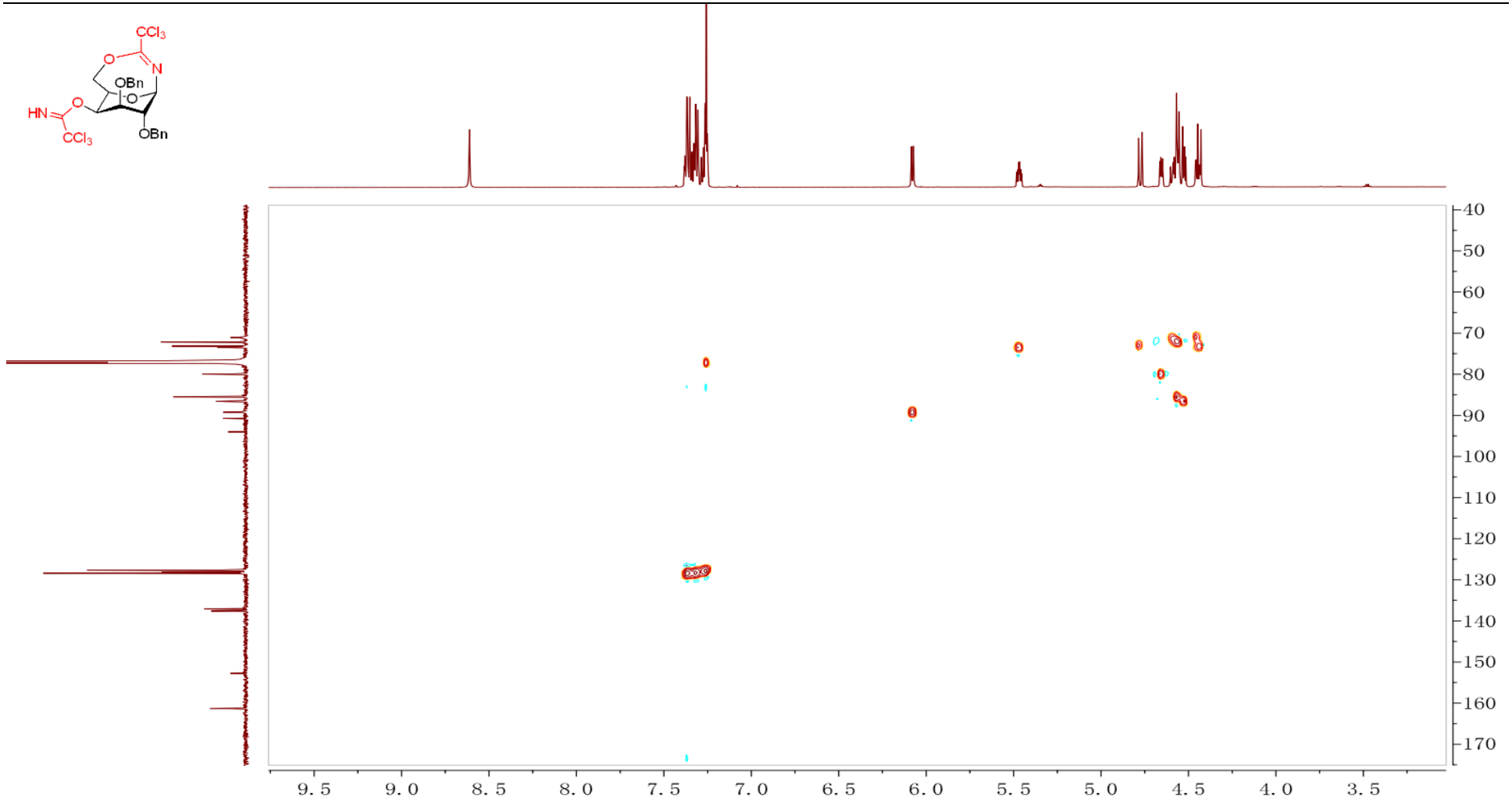
^{1}H – ^{1}H COSY of **22**



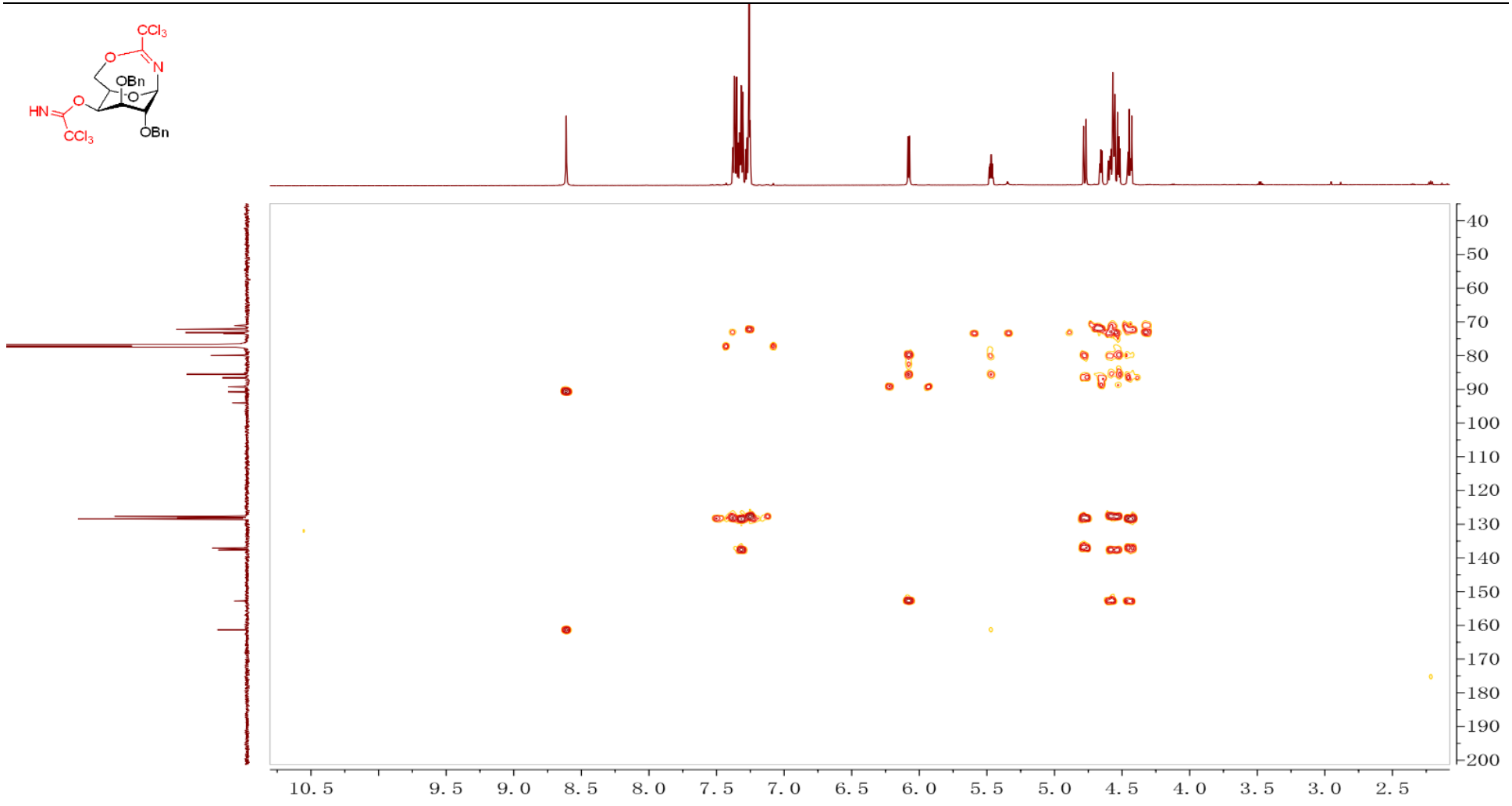
^{1}H NMR of **24** (600 M, $CDCl_3$)



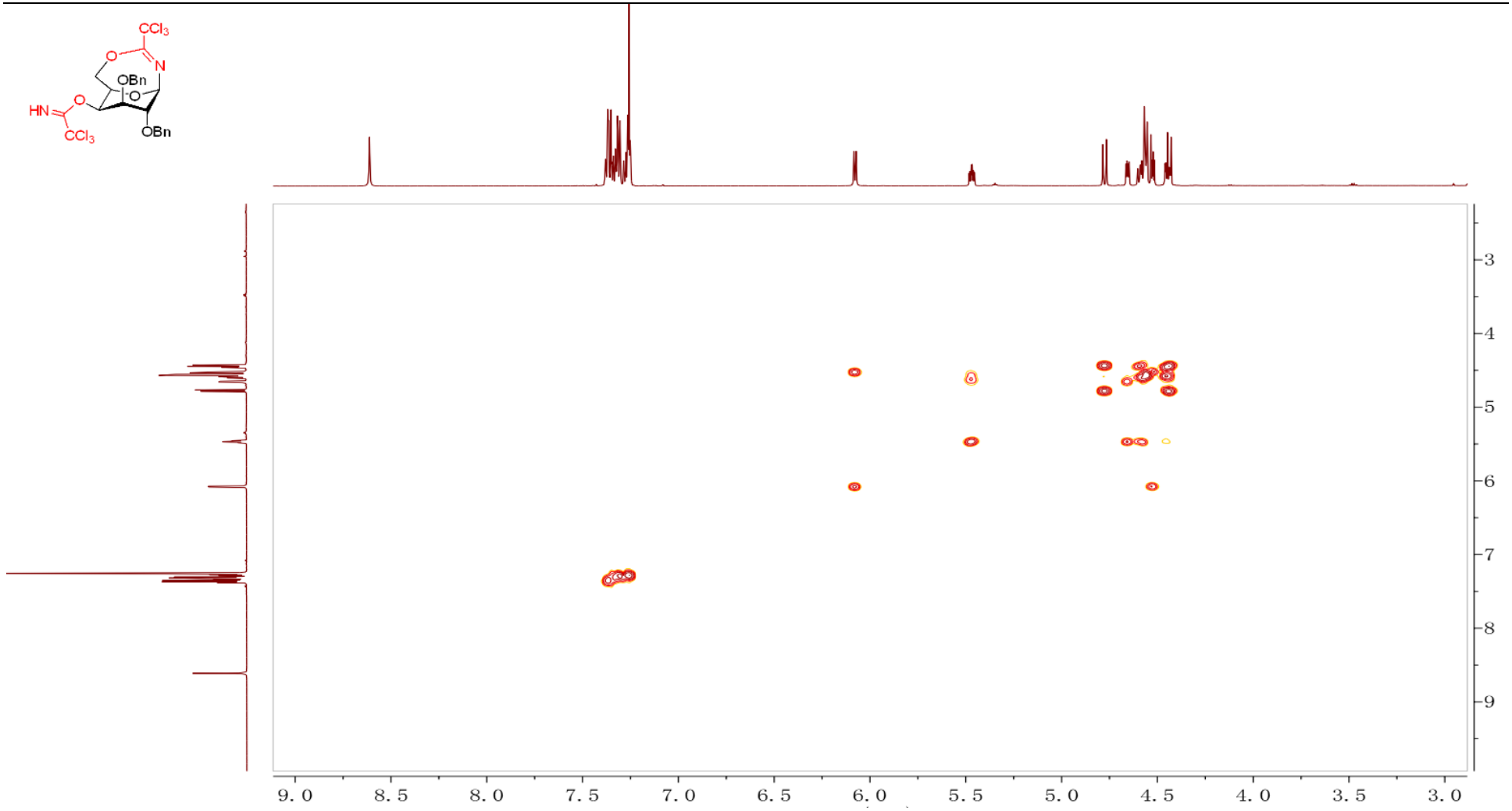
^{13}C NMR of **24** (151 M, $CDCl_3$)


CCl3
O
N
OBn
O
HN
O
CCl3
OBn
40
50
60
70
80
90
100
110
120
130
140
150
160
170
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

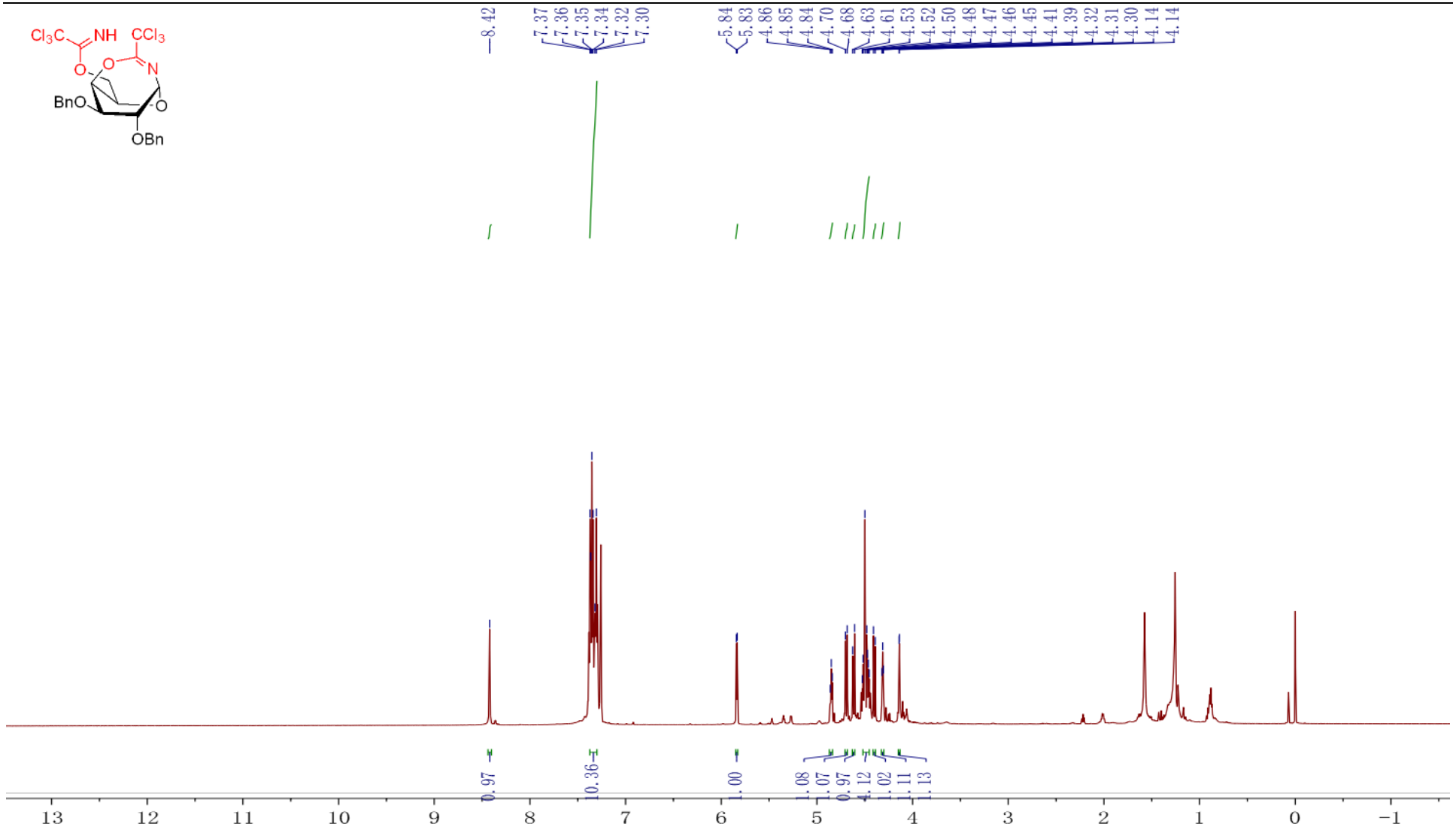
HSQC of **24**


CCl3
O
N
OBn
HN
O
O
CCl3
OBn
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5

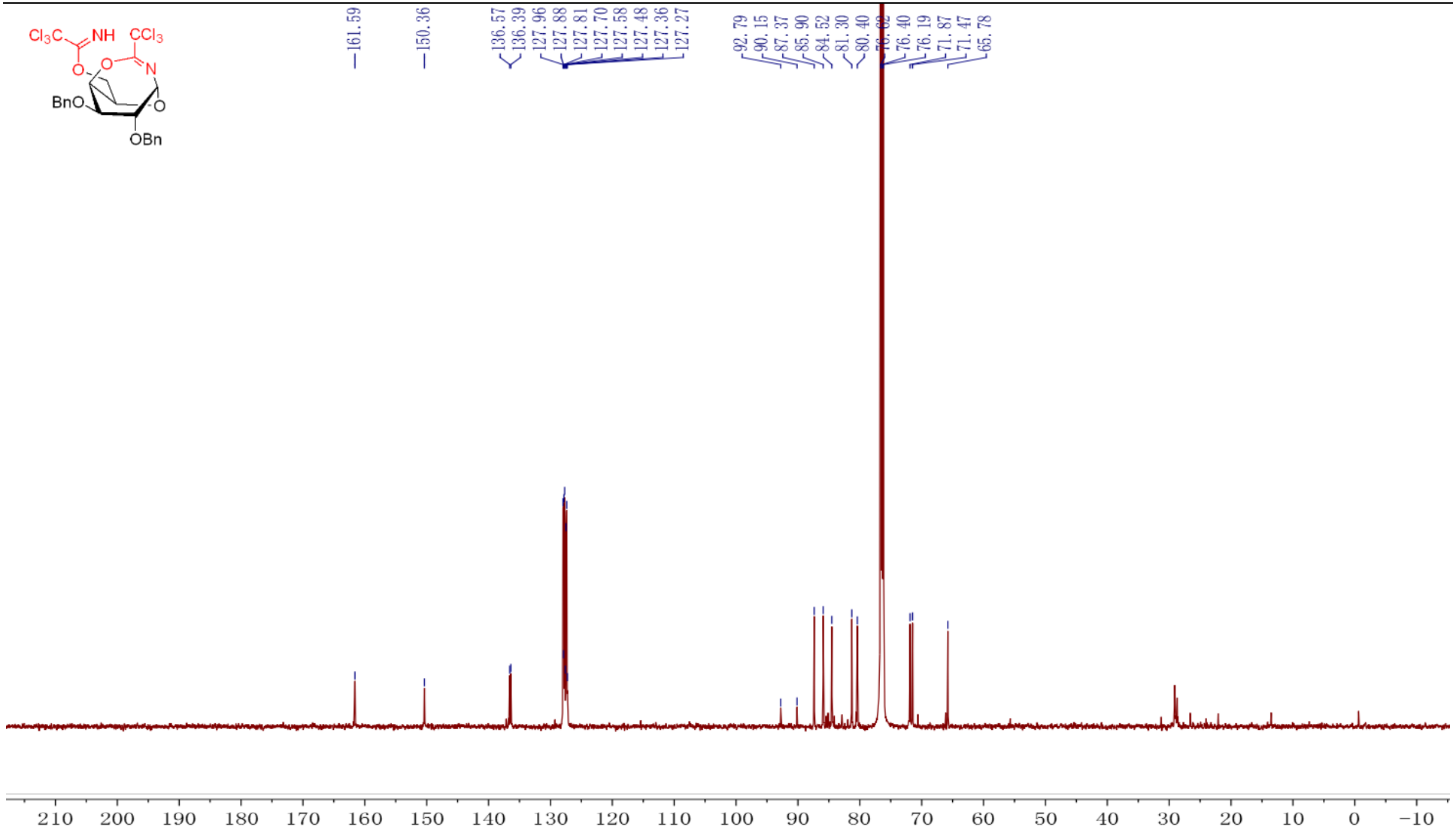
HMBC of **24**



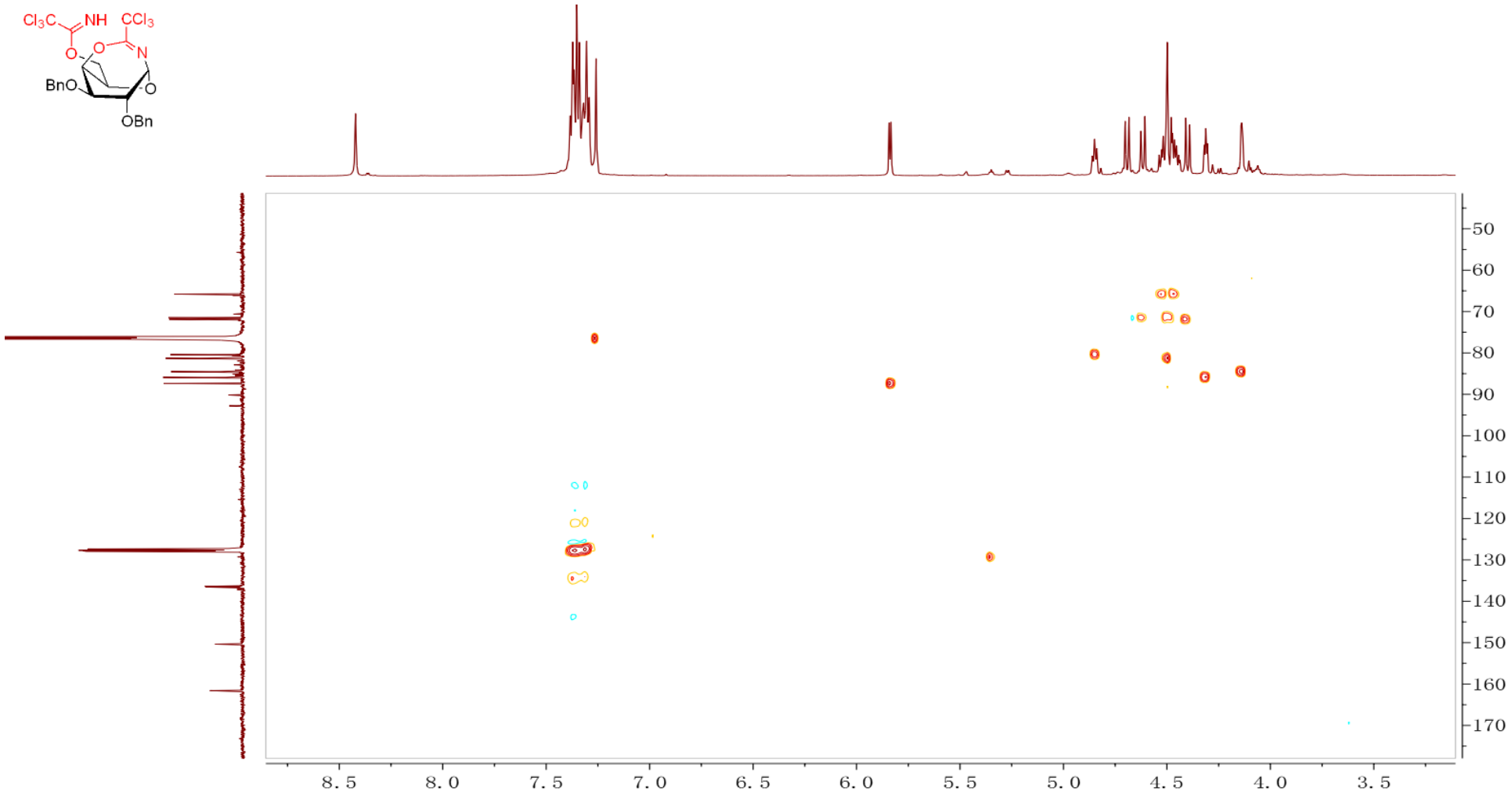
^{1}H – ^{1}H COSY of **24**



^{1}H NMR of **25** (600 M, $CDCl_3$)



^{13}C NMR of **25** (151 M, $CDCl_3$)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NH
CCl3
O
O
N
BnO
O
OBn
8.5
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
50
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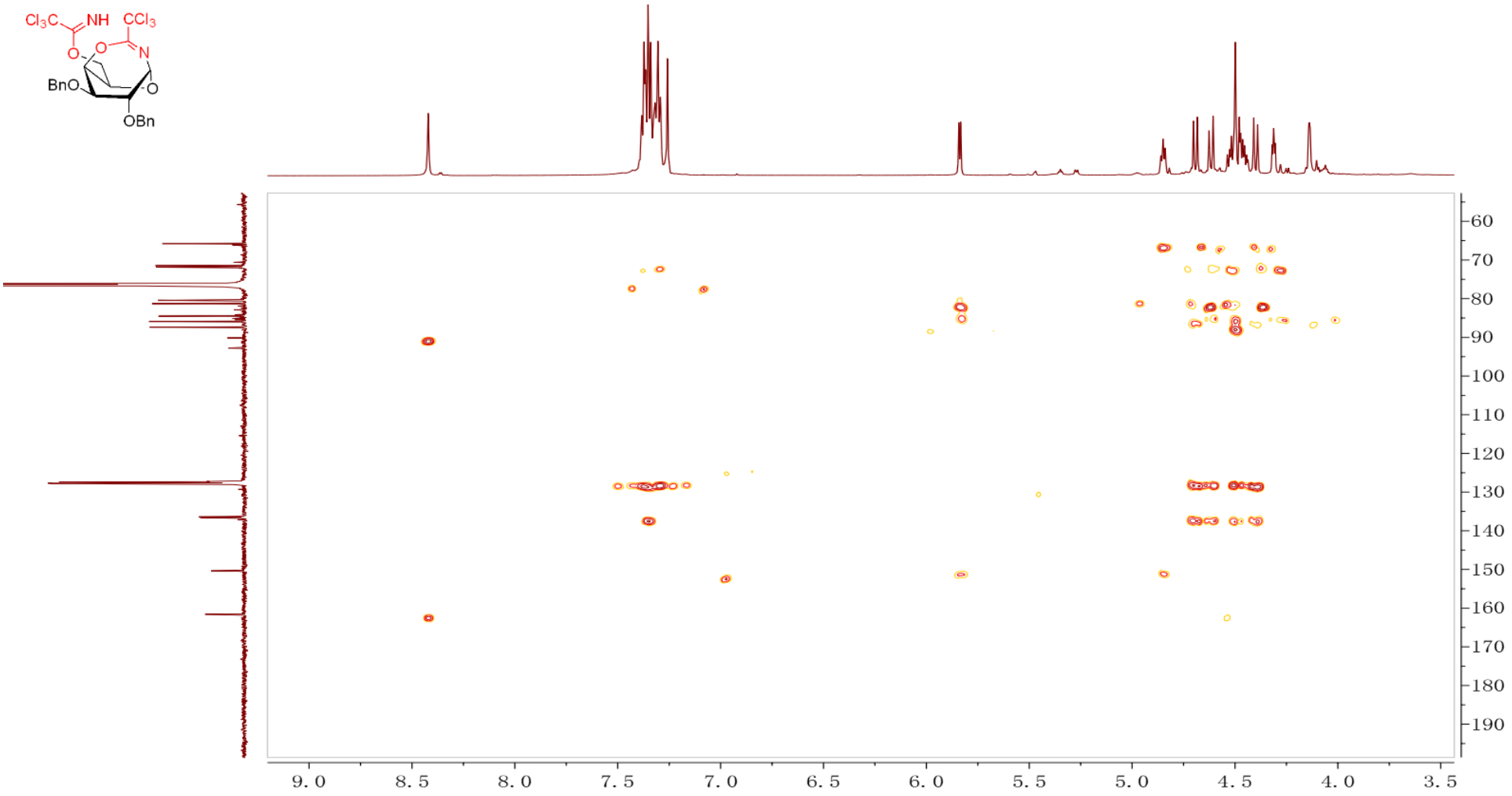
80
90
100
110
120
130
140
150
160
170

HSQC of **25**


Cl3C
NH
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O
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N
BnO
O
OBn
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120
130
140
150
160
170
180
190
9.0
8.5
8.0
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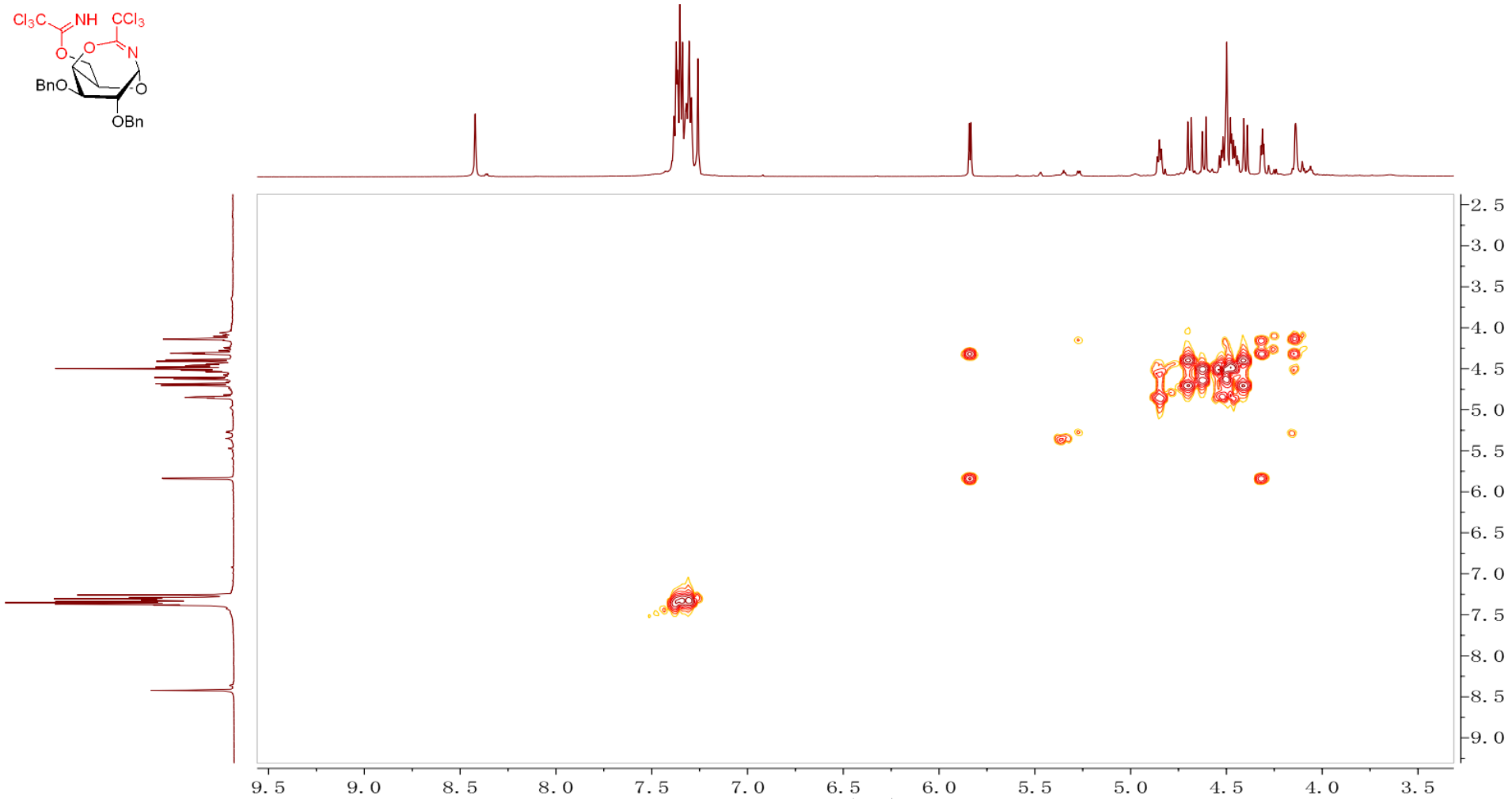
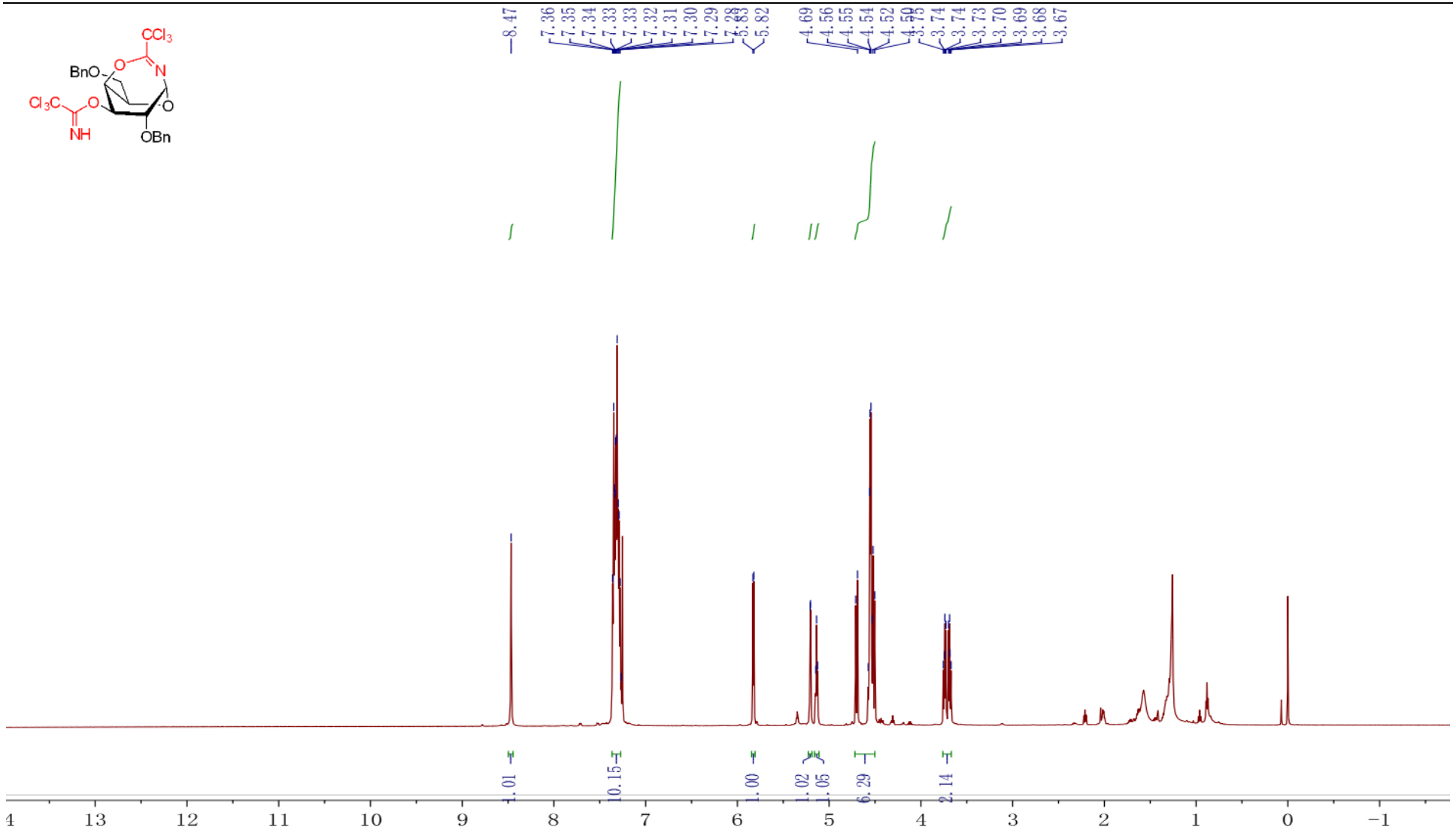
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5

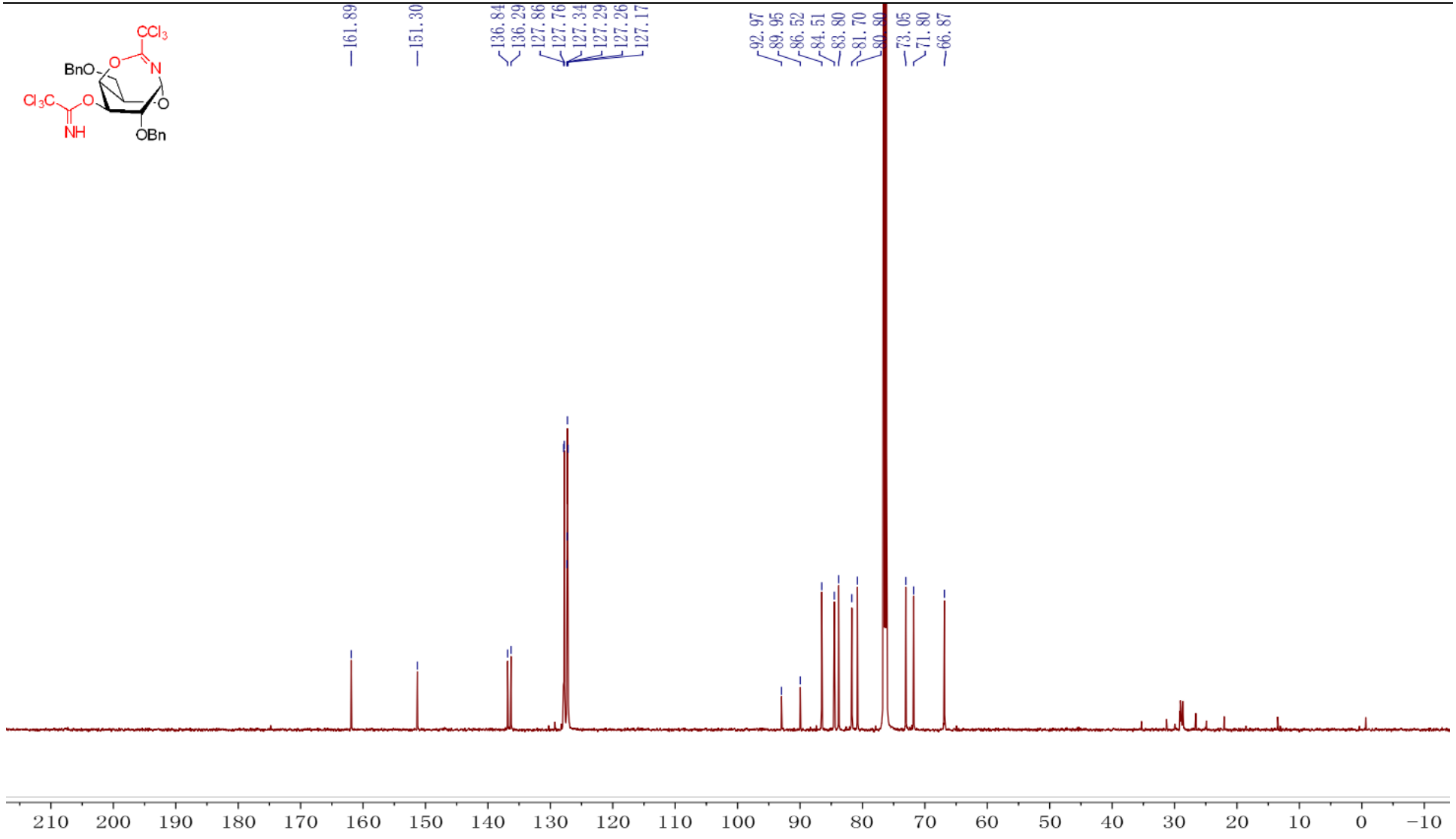
HMBC of **25**



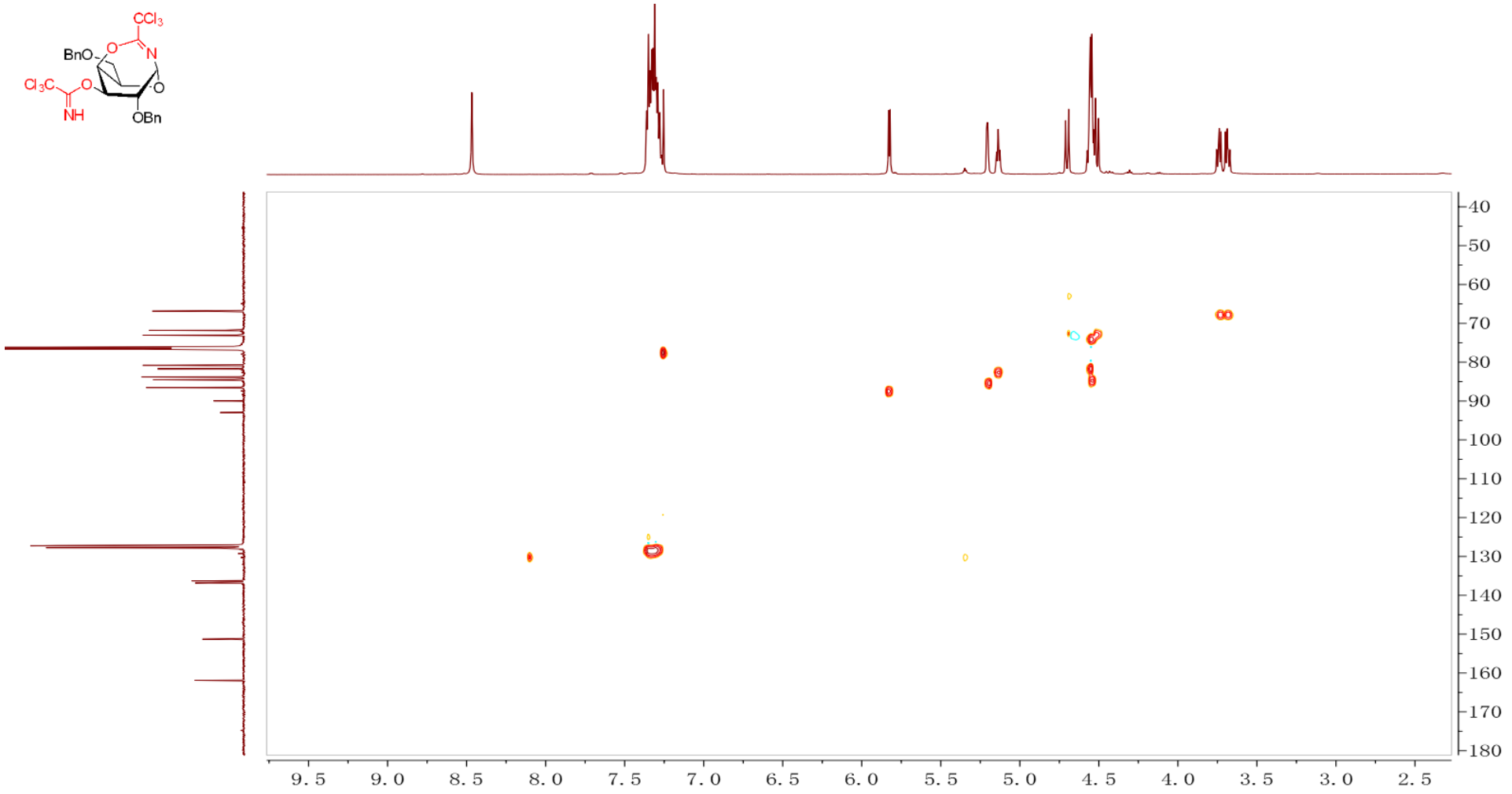
$^{1}H - {}^{1}H$ COSY of **25**



^{1}H NMR of **28** (600 M, $CDCl_3$)



^{13}C NMR of **28** (151 M, $CDCl_3$)


CCl3
BnO
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N
Cl3C
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NH
O
OBn
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50
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110
120
130
140
150
160
170
180
9.5
9.0
8.5
8.0
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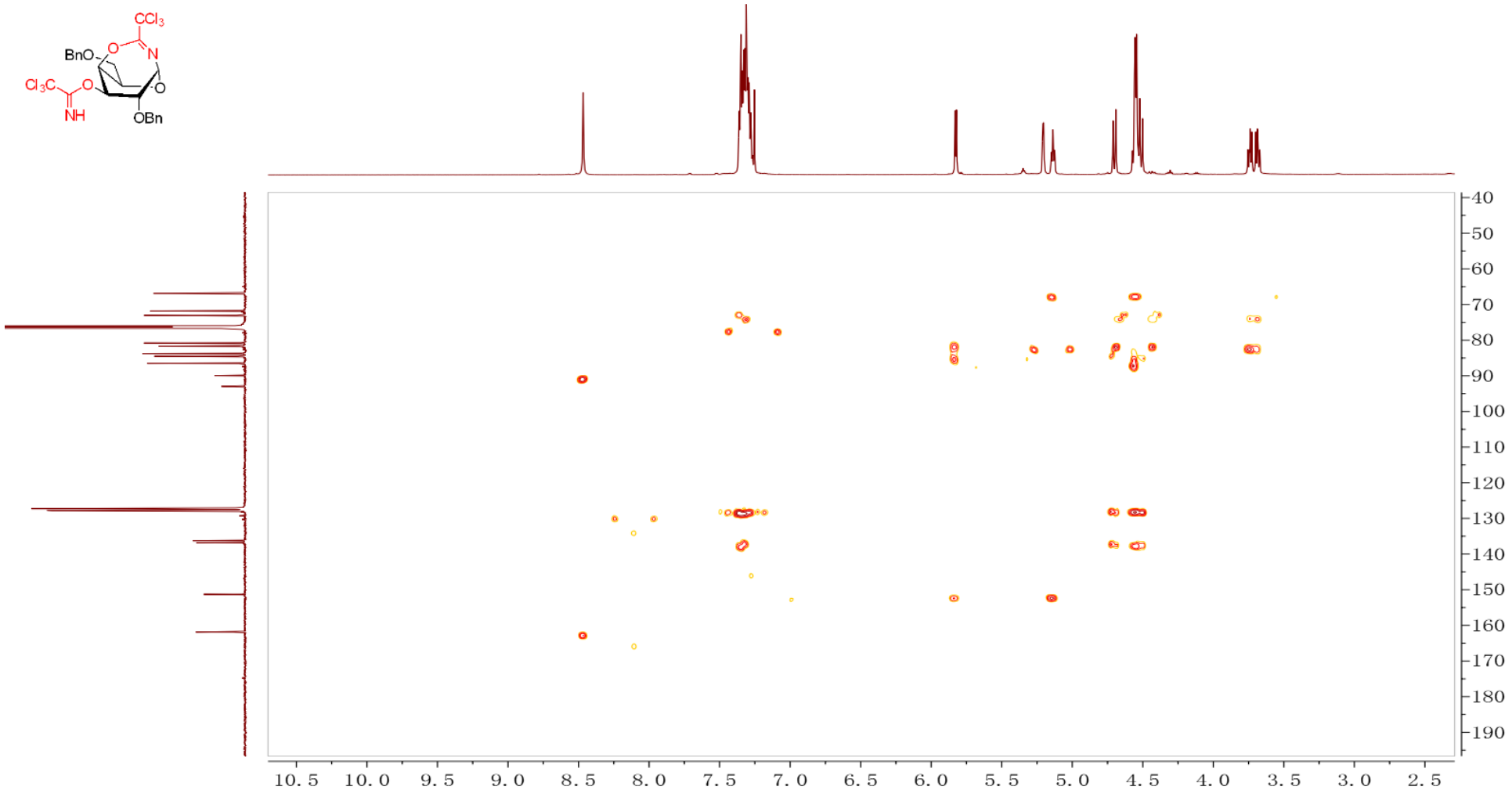
3.5
3.0
2.5

HSQC of **28**


CCl3
BnO
O
N
Cl3C
O
NH
O
OBn
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130
140
150
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10.5
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8.0
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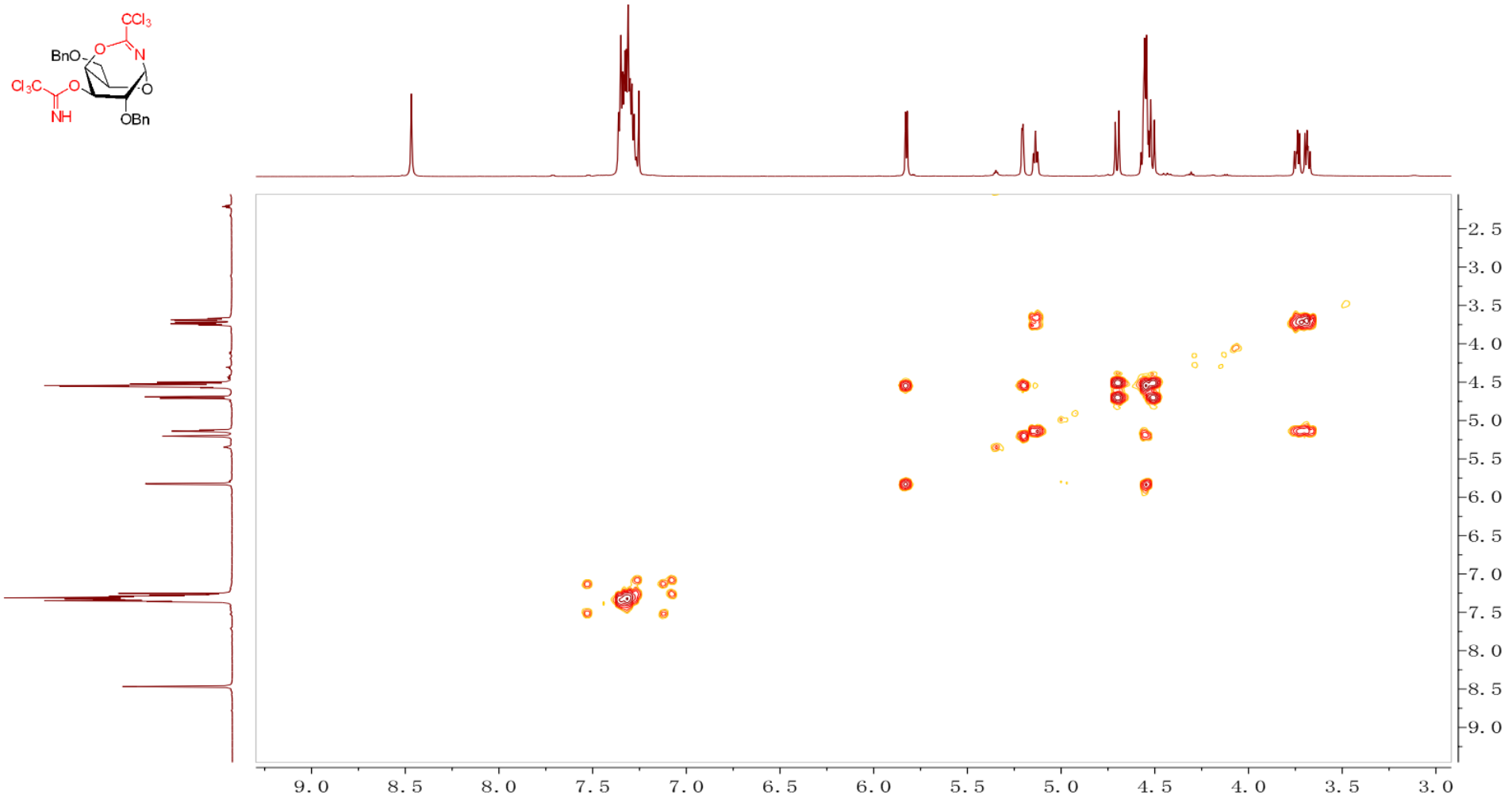
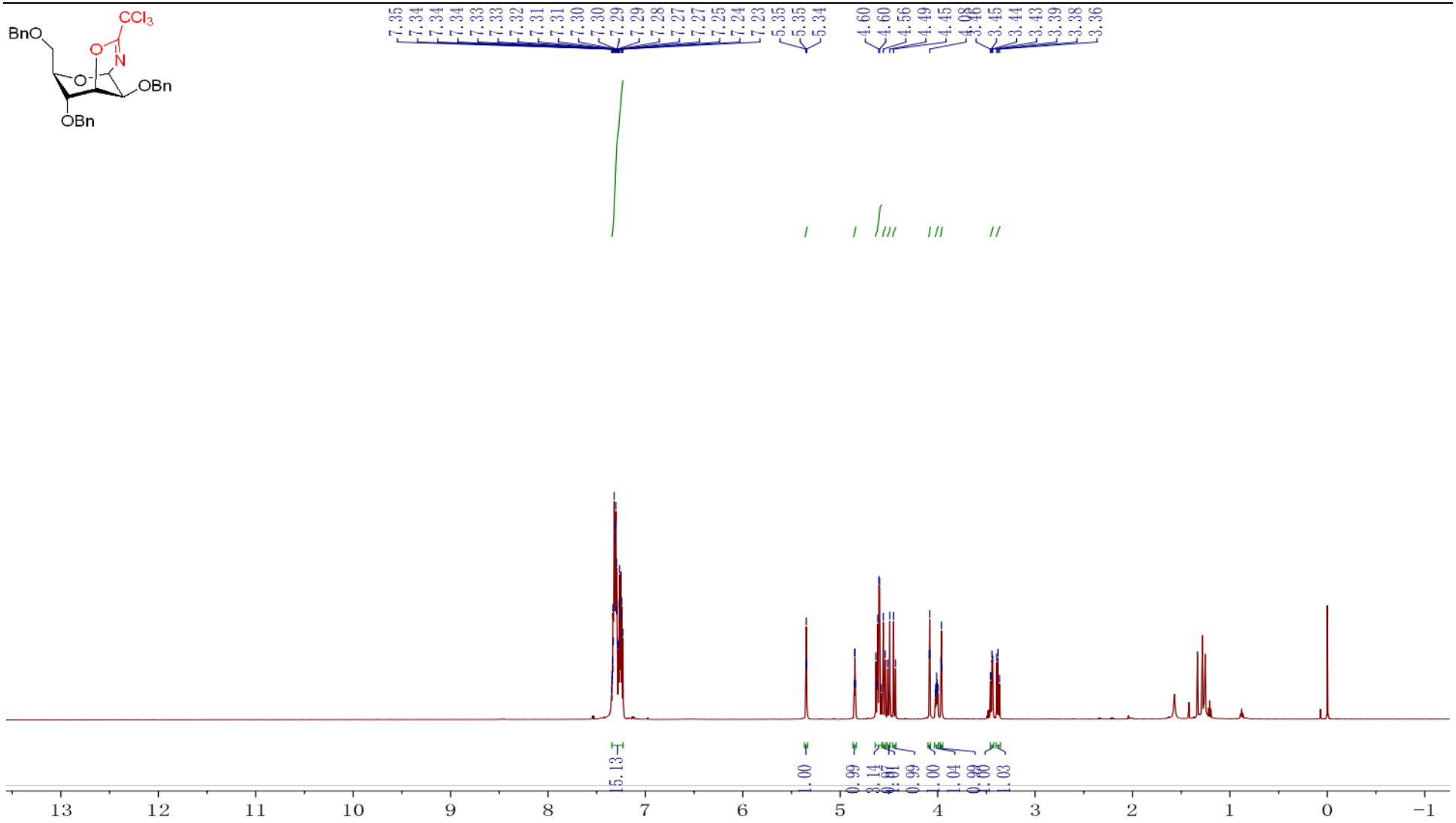
2.5

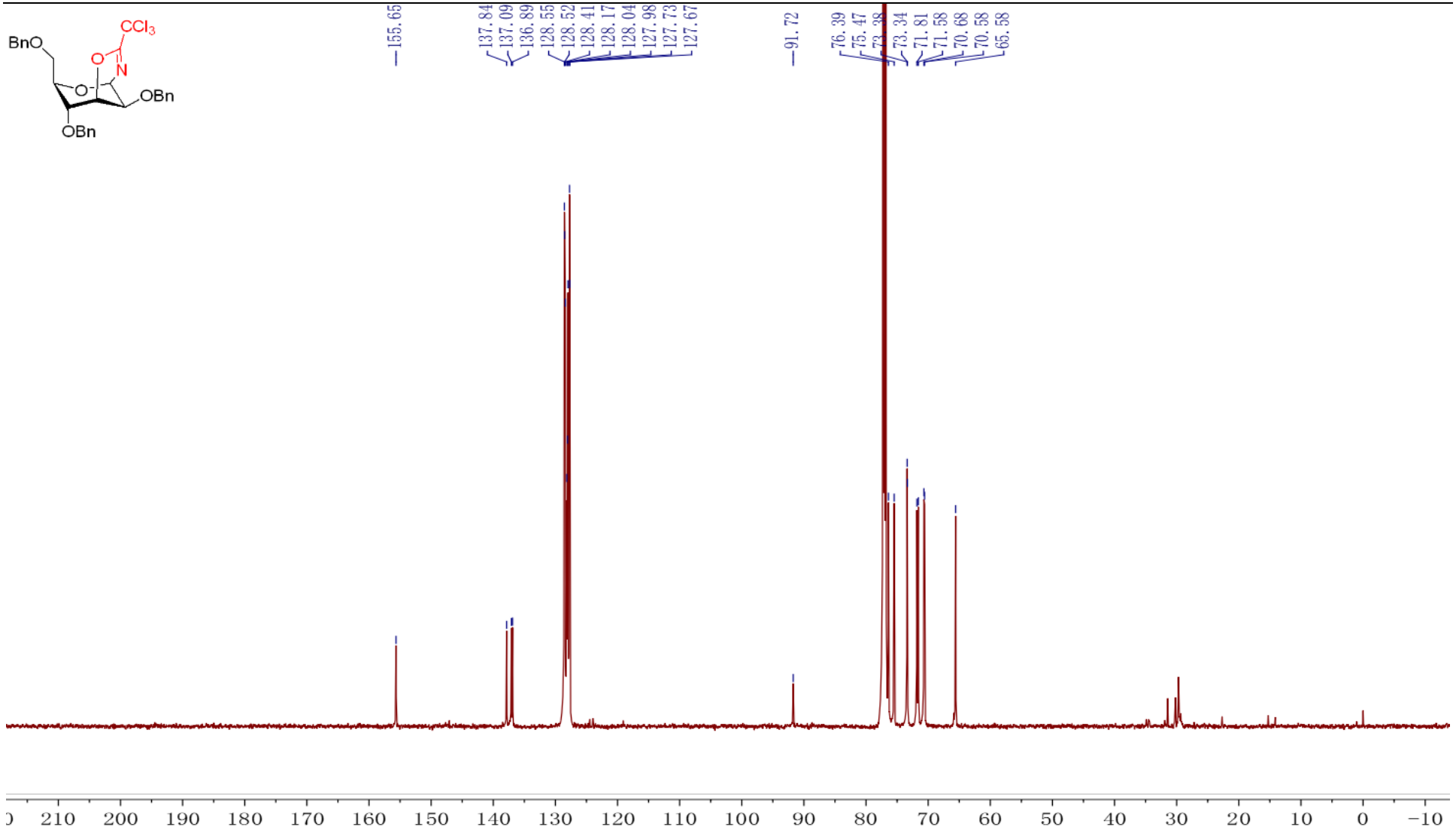
HMBC of **28**



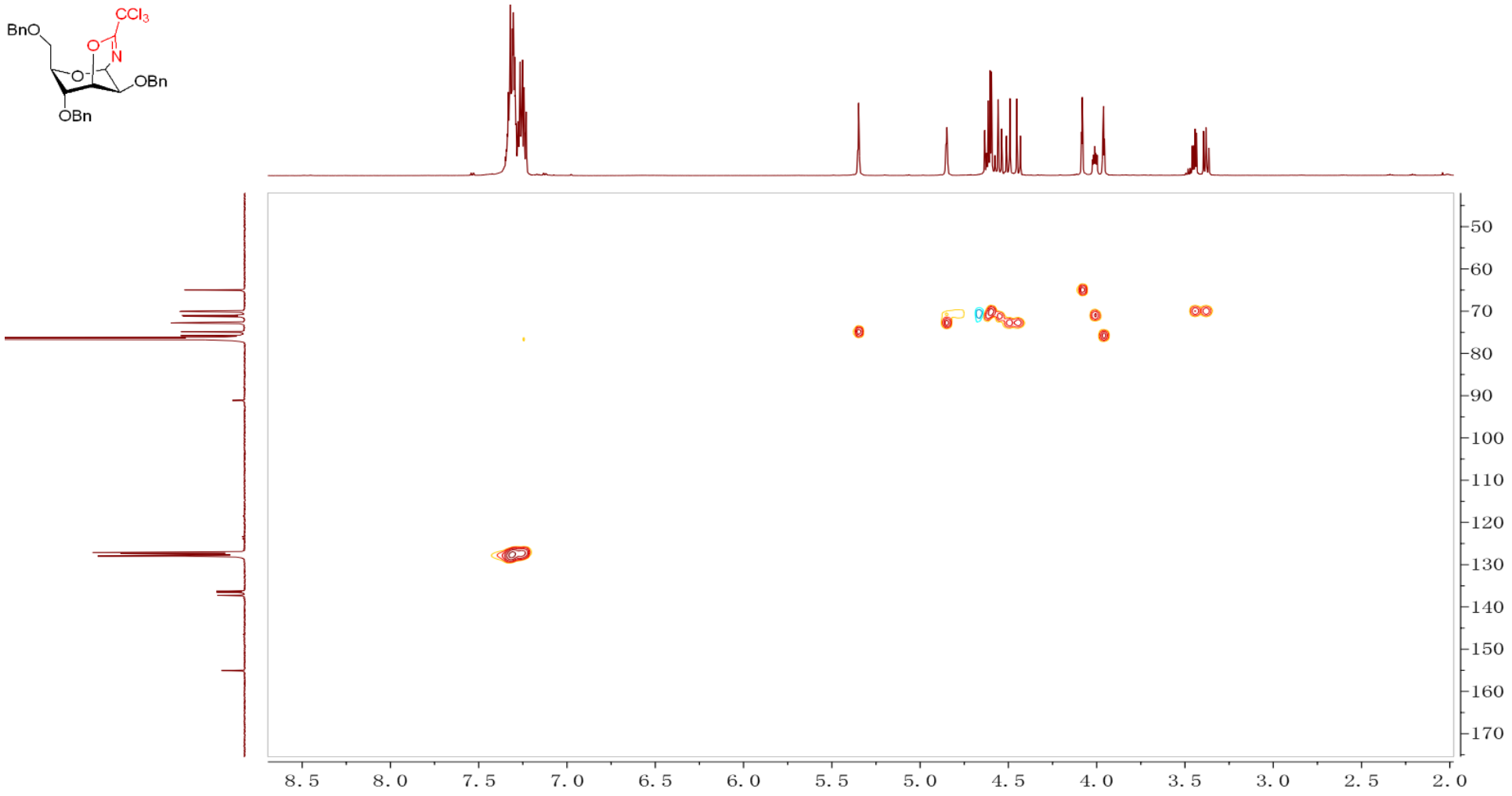
$^{1}H - {}^{1}H$ COSY of **28**



^{1}H NMR of **33** (600 M, $CDCl_3$)



^{13}C NMR of **33** (151 M, $CDCl_3$)


BnO
CCl3
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OBn
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170
8.5
8.0
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4.5
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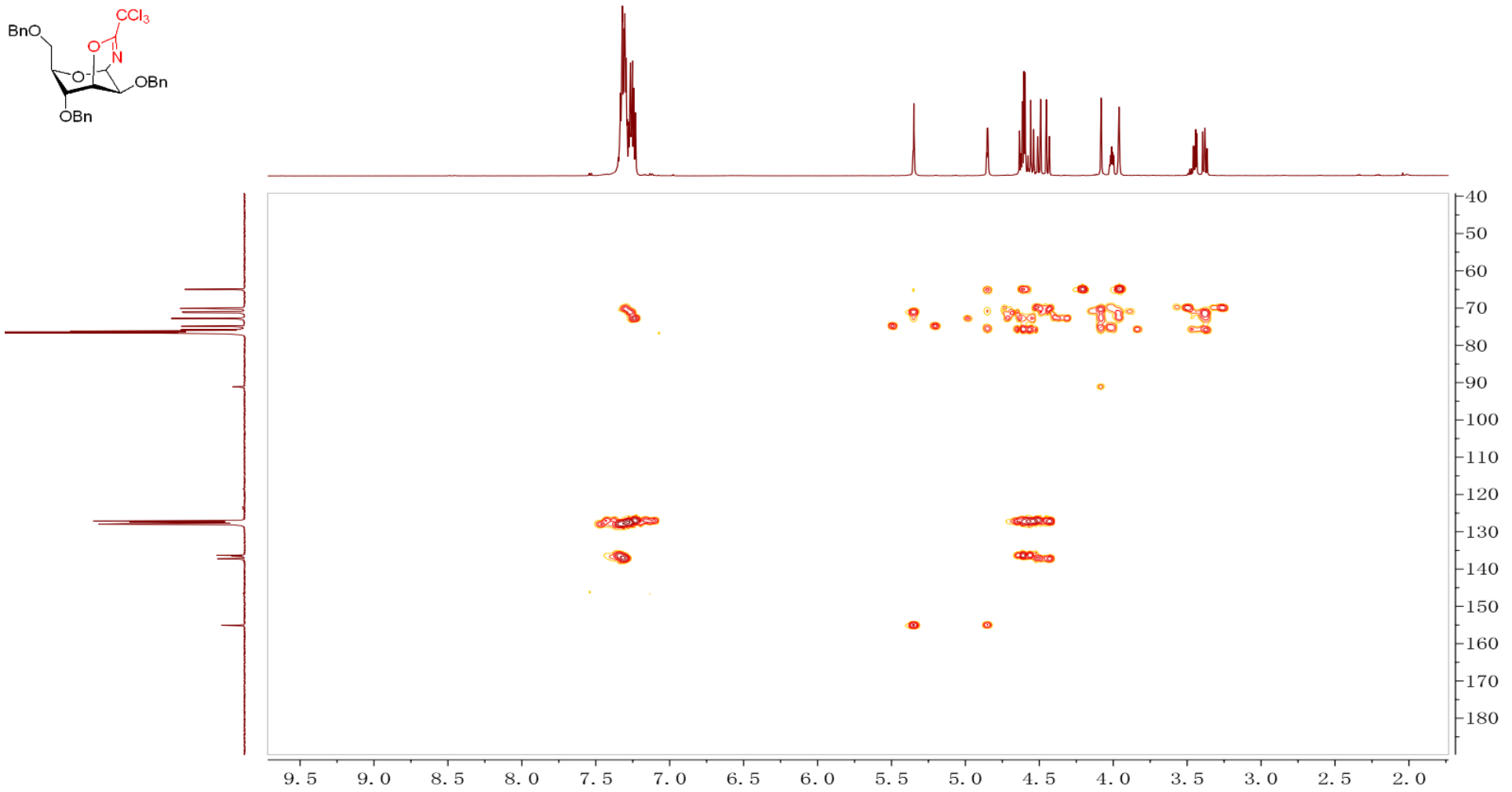
3.0
2.5
2.0

HSQC of **33**


BnO
CCl3
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OBn
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150
160
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8.0
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5.5
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4.5
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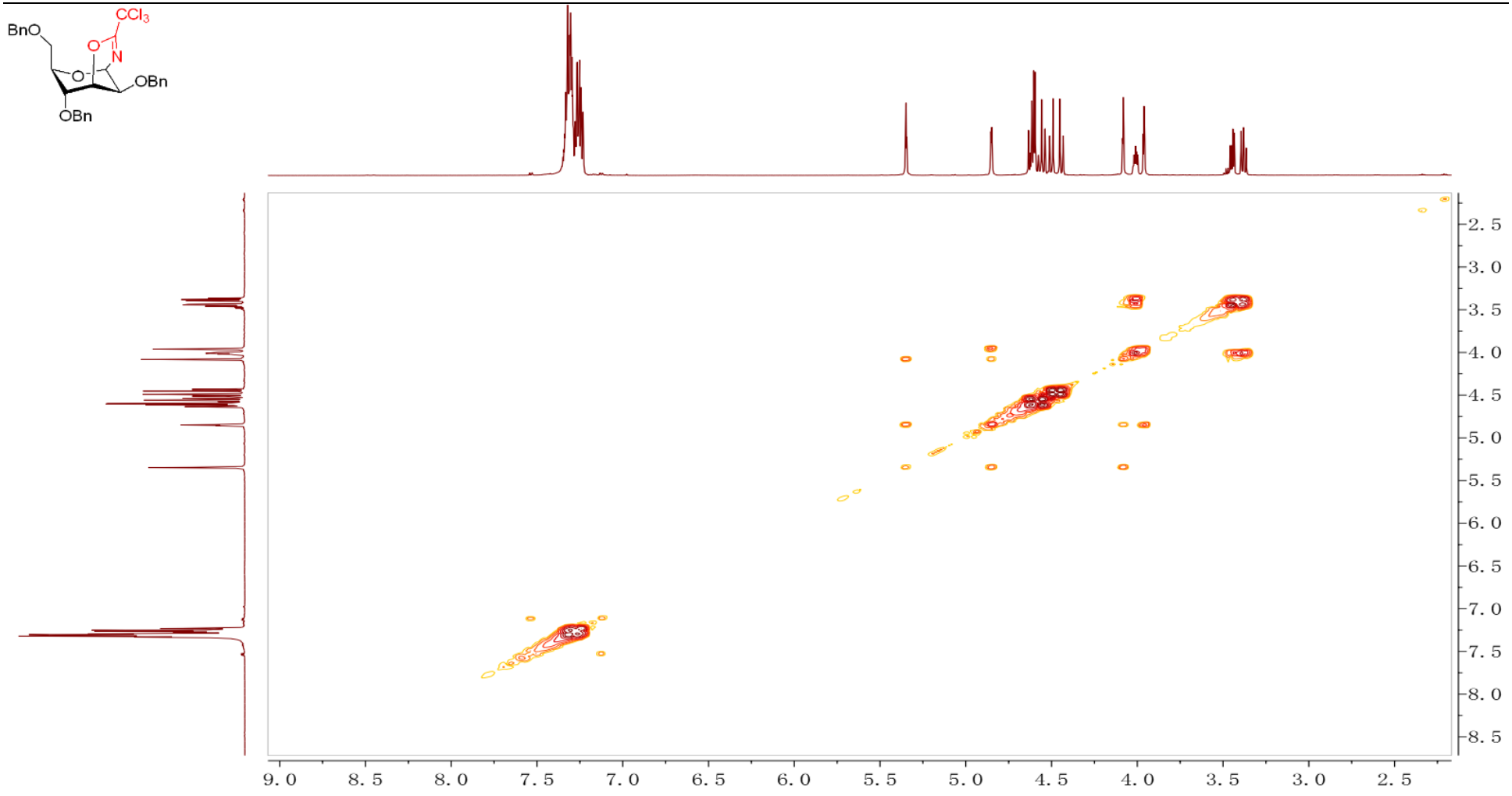
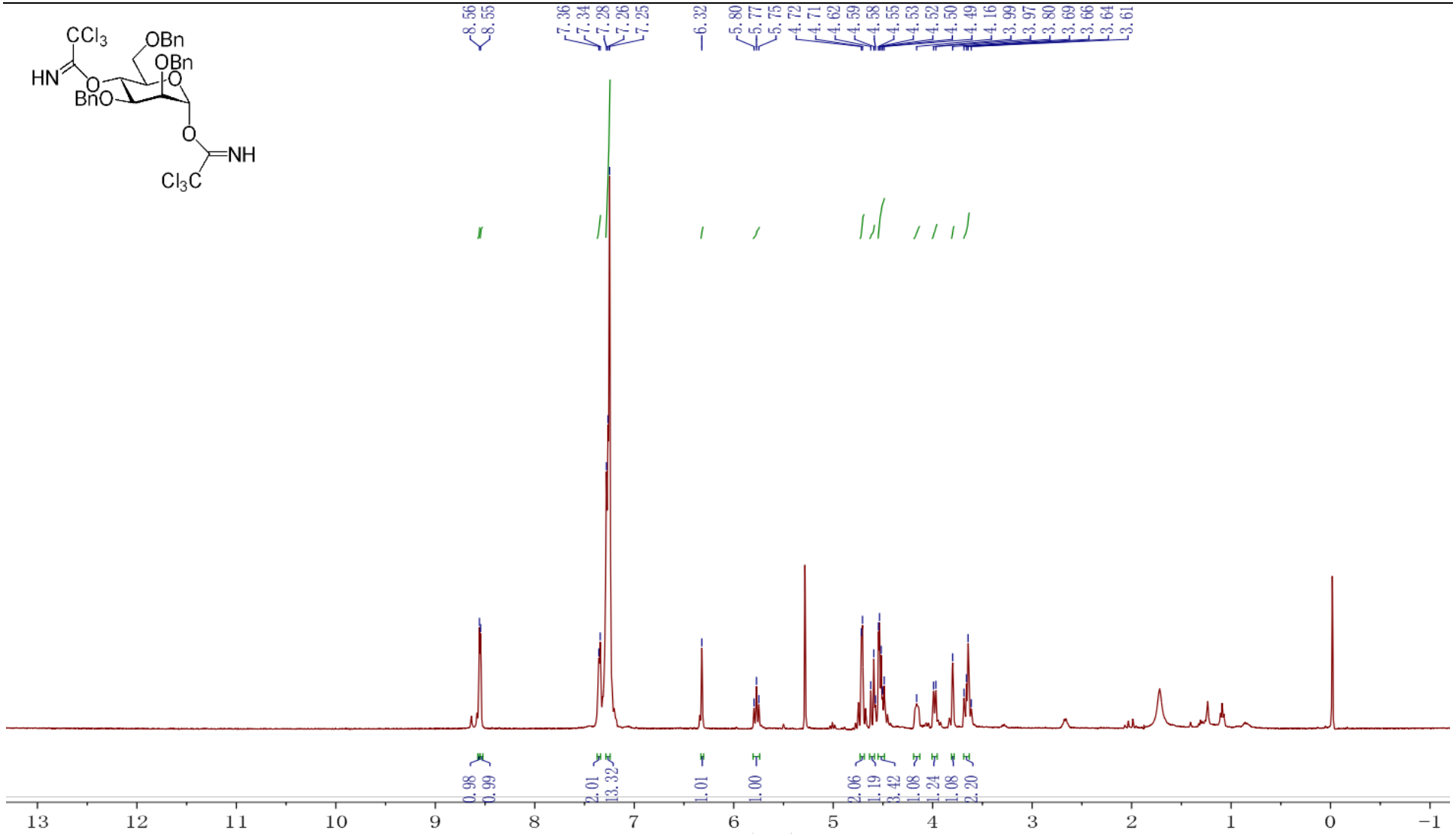
3.0
2.5
2.0

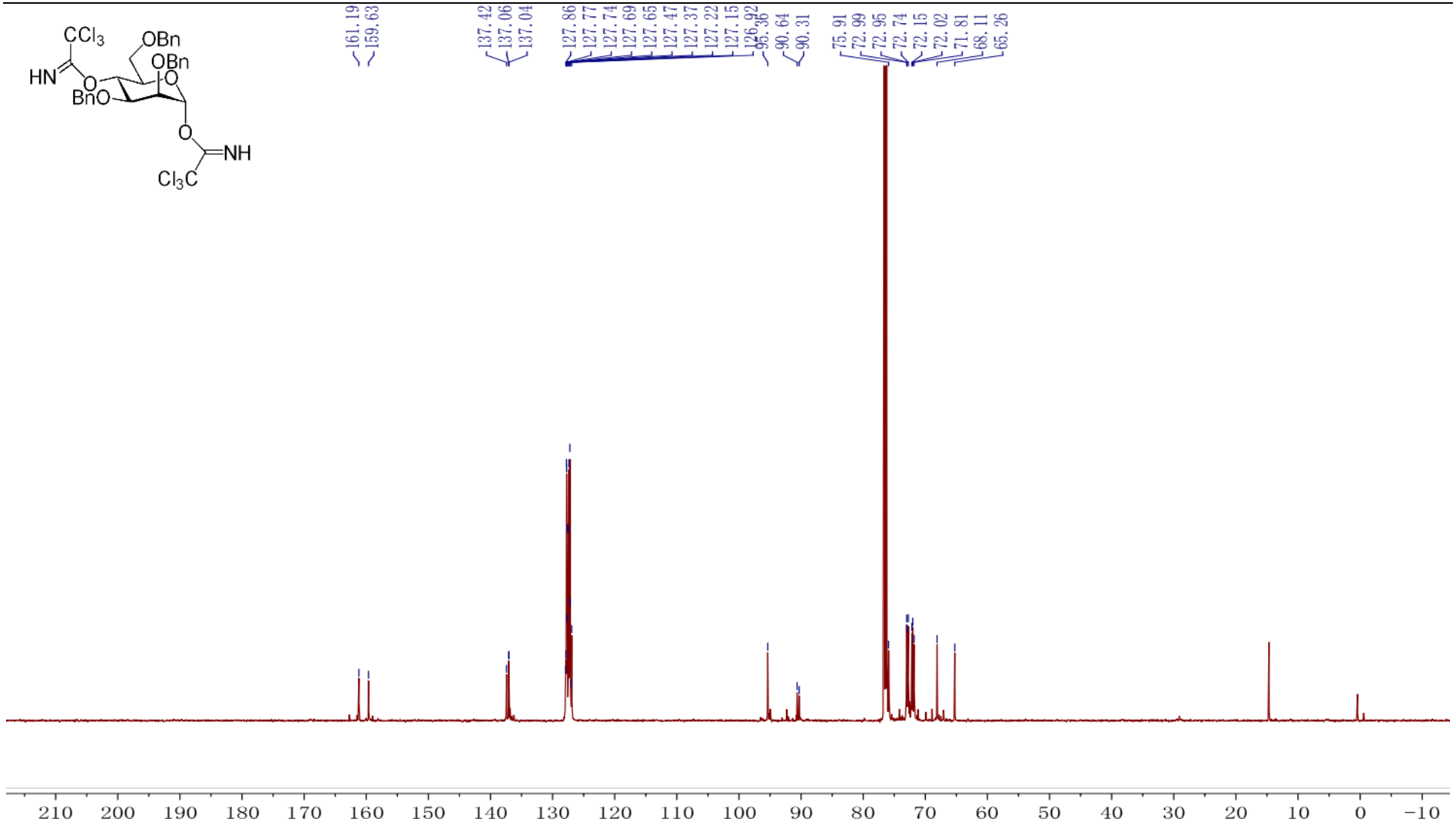
HMBC of **33**



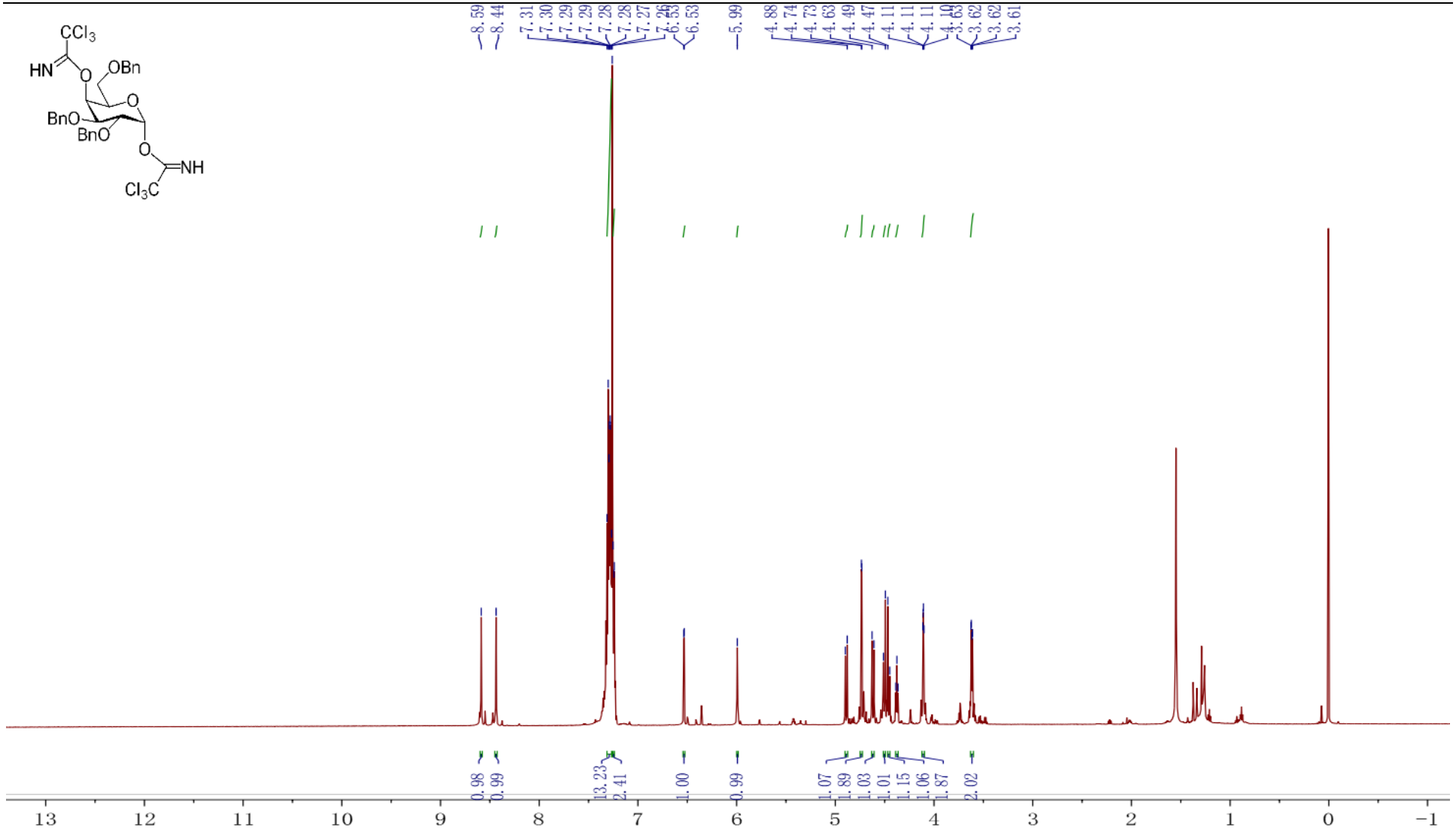
^{1}H – ^{1}H COSY of **33**



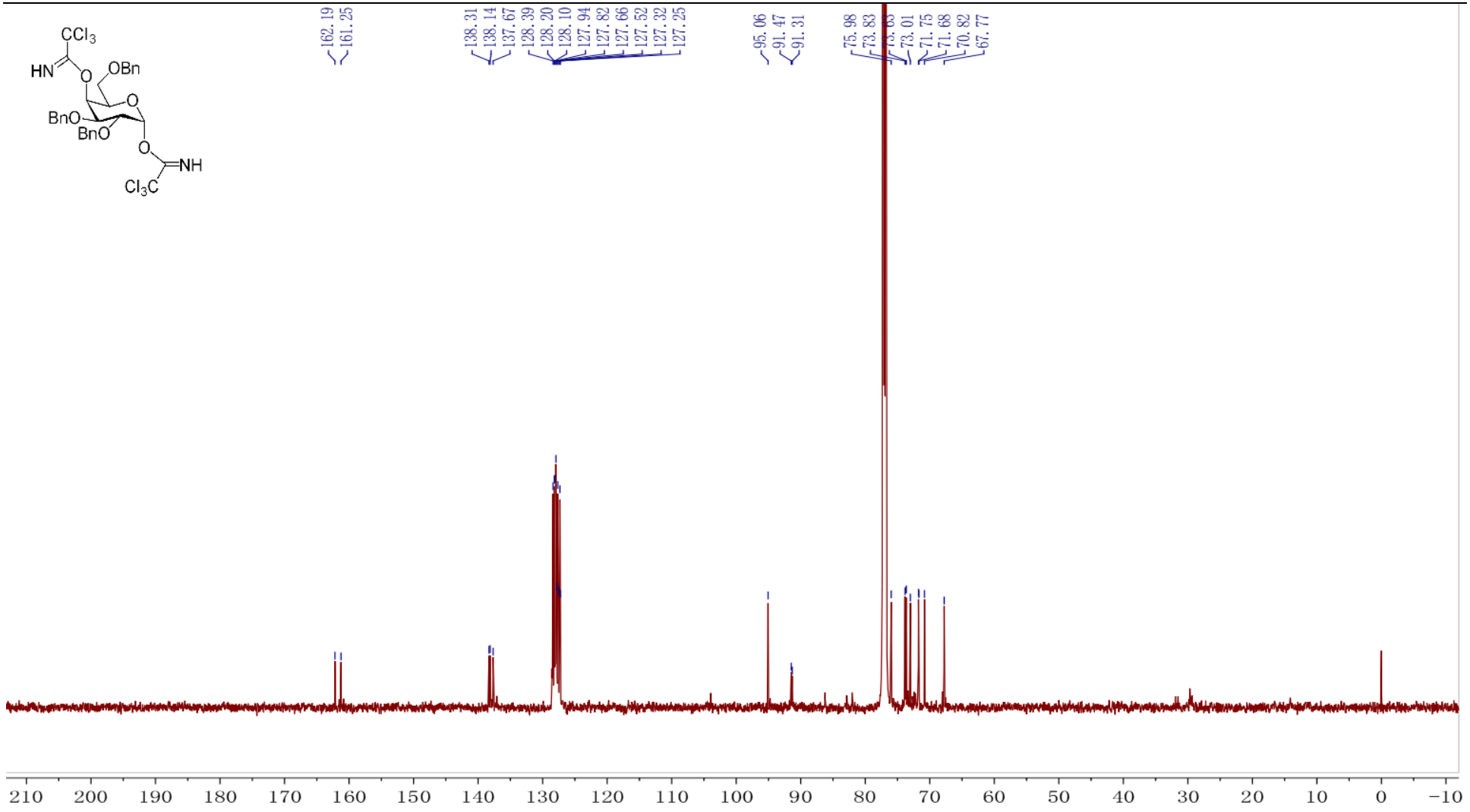
^{1}H NMR of **3** (600 M, $CDCl_3$)



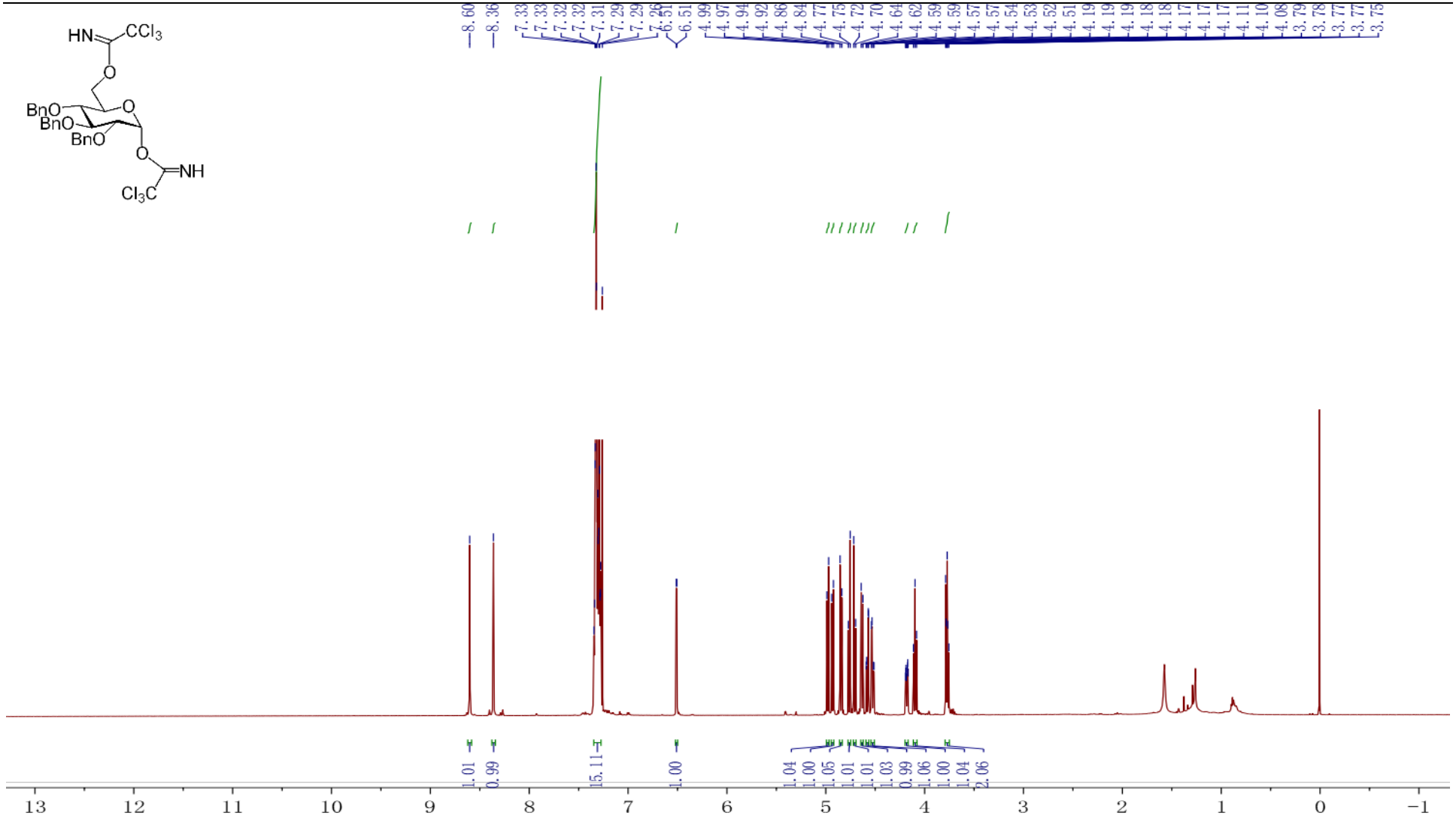
^{13}C NMR of **3** (151 M, $CDCl_3$)



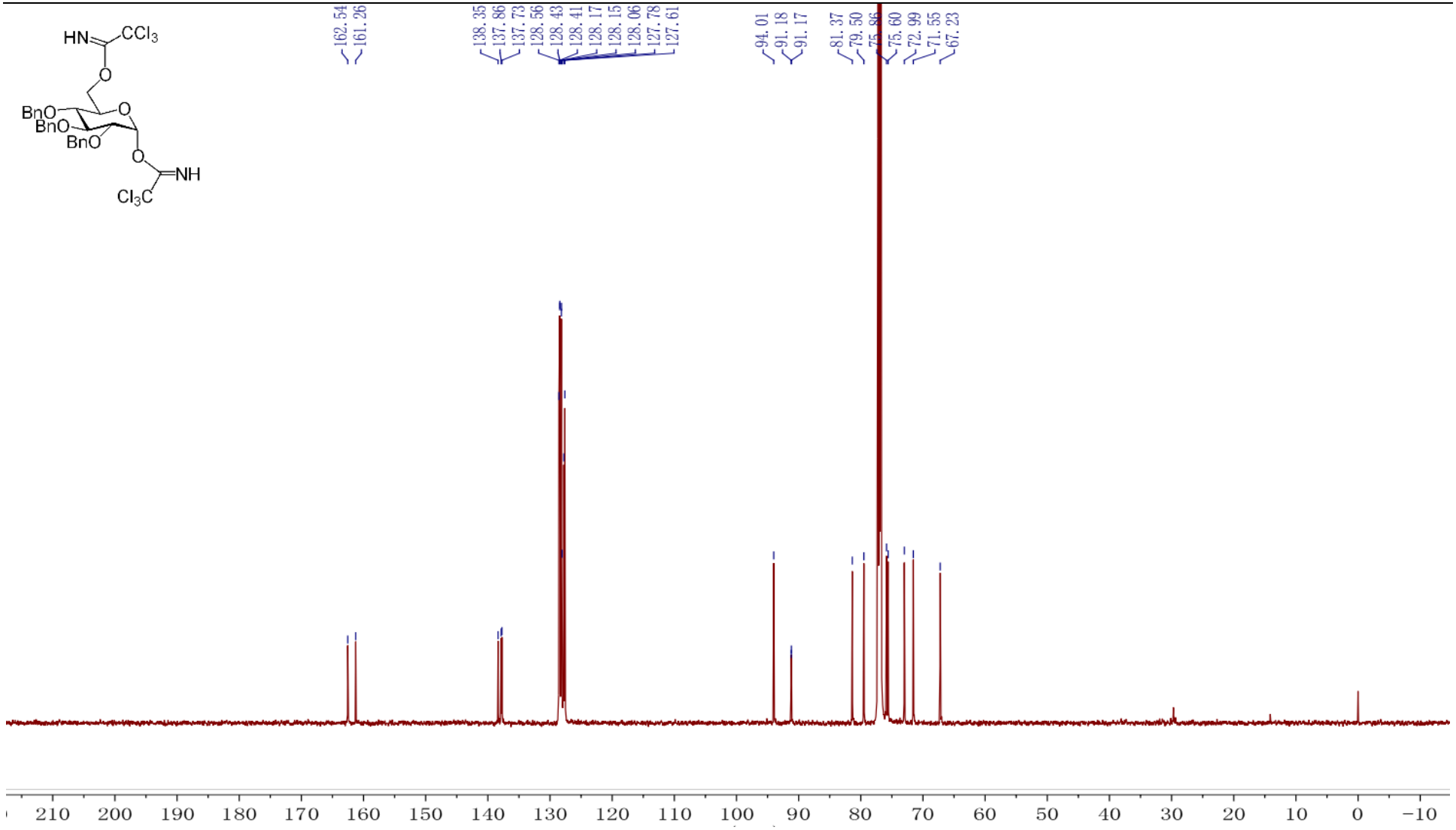
^{1}H NMR of **5** (600 M, $CDCl_3$)



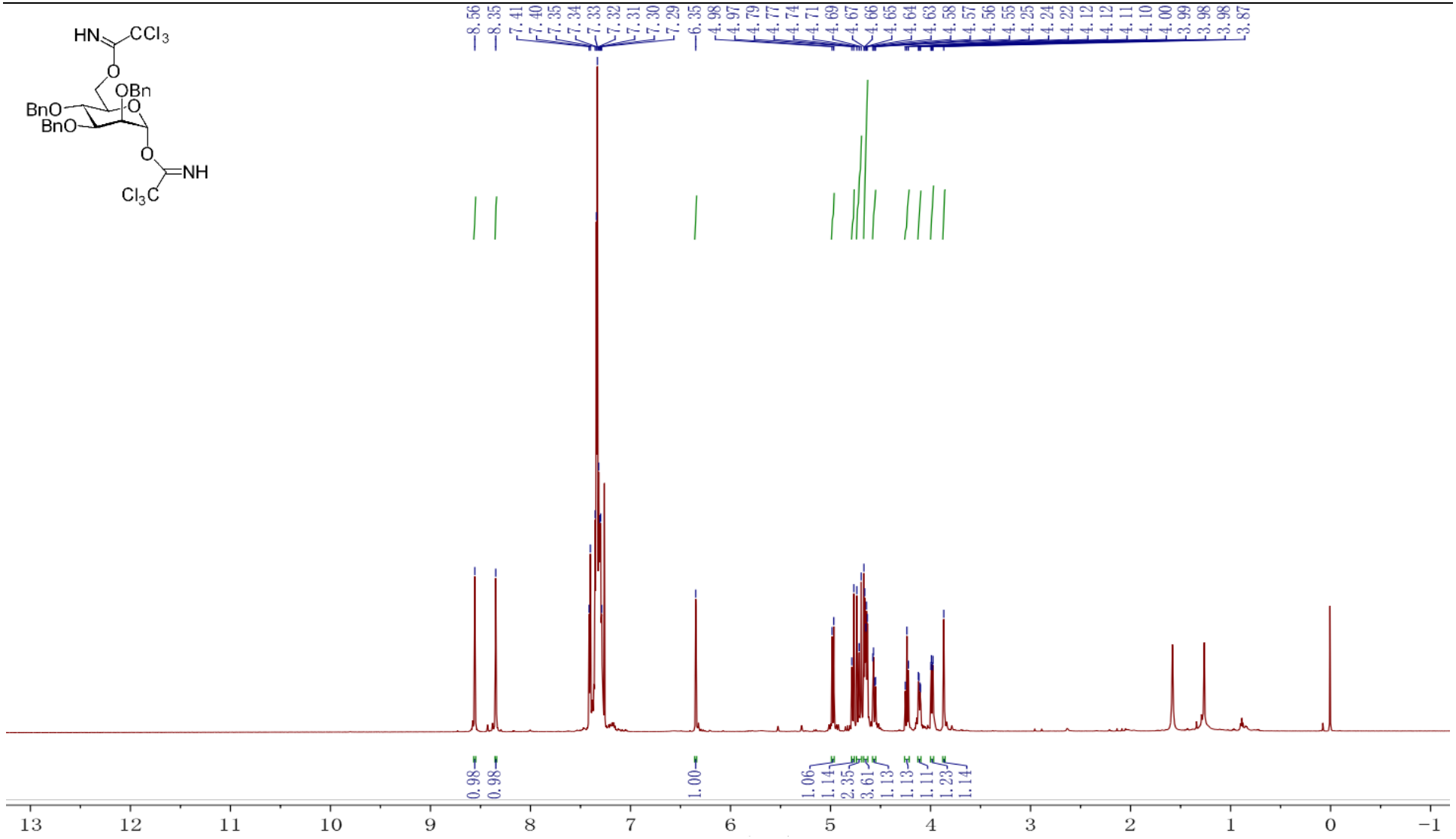
^{13}C NMR of **5** (151 M, $CDCl_3$)



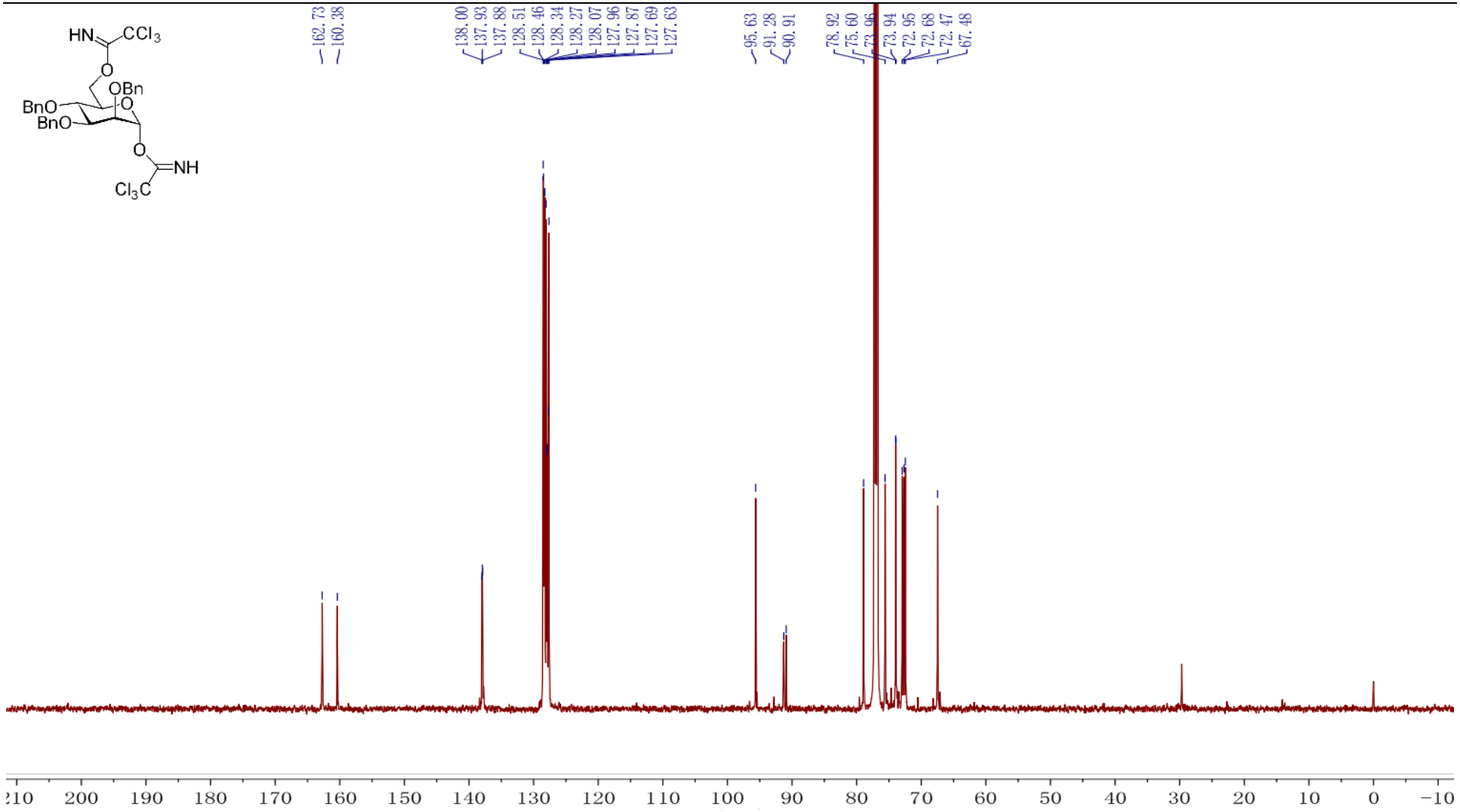
^{1}H NMR of **7** (600 M, $CDCl_3$)



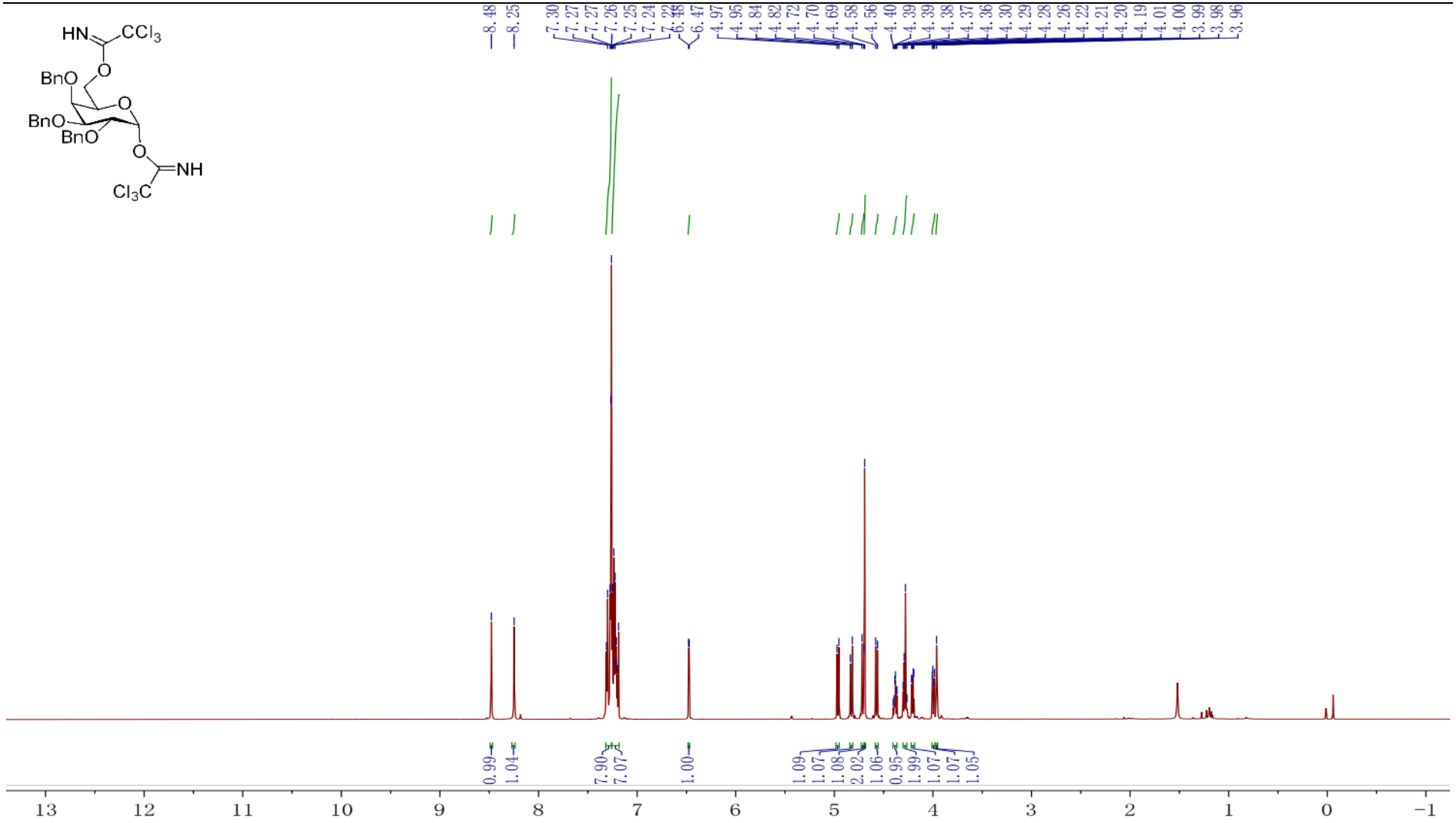
^{13}C NMR of **7** (151 M, $CDCl_3$)



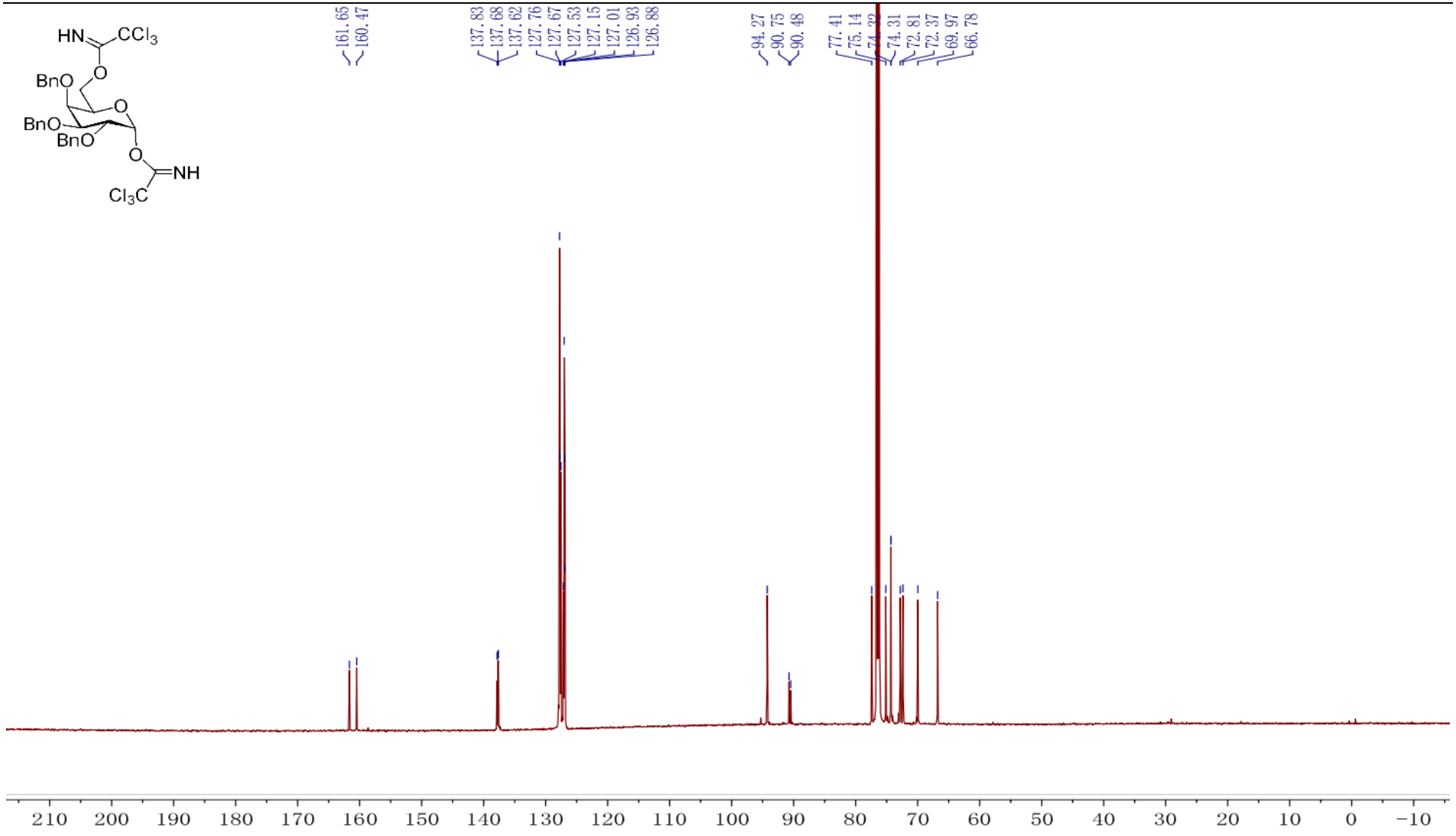
^{1}H NMR of **9** (600 M, $CDCl_3$)



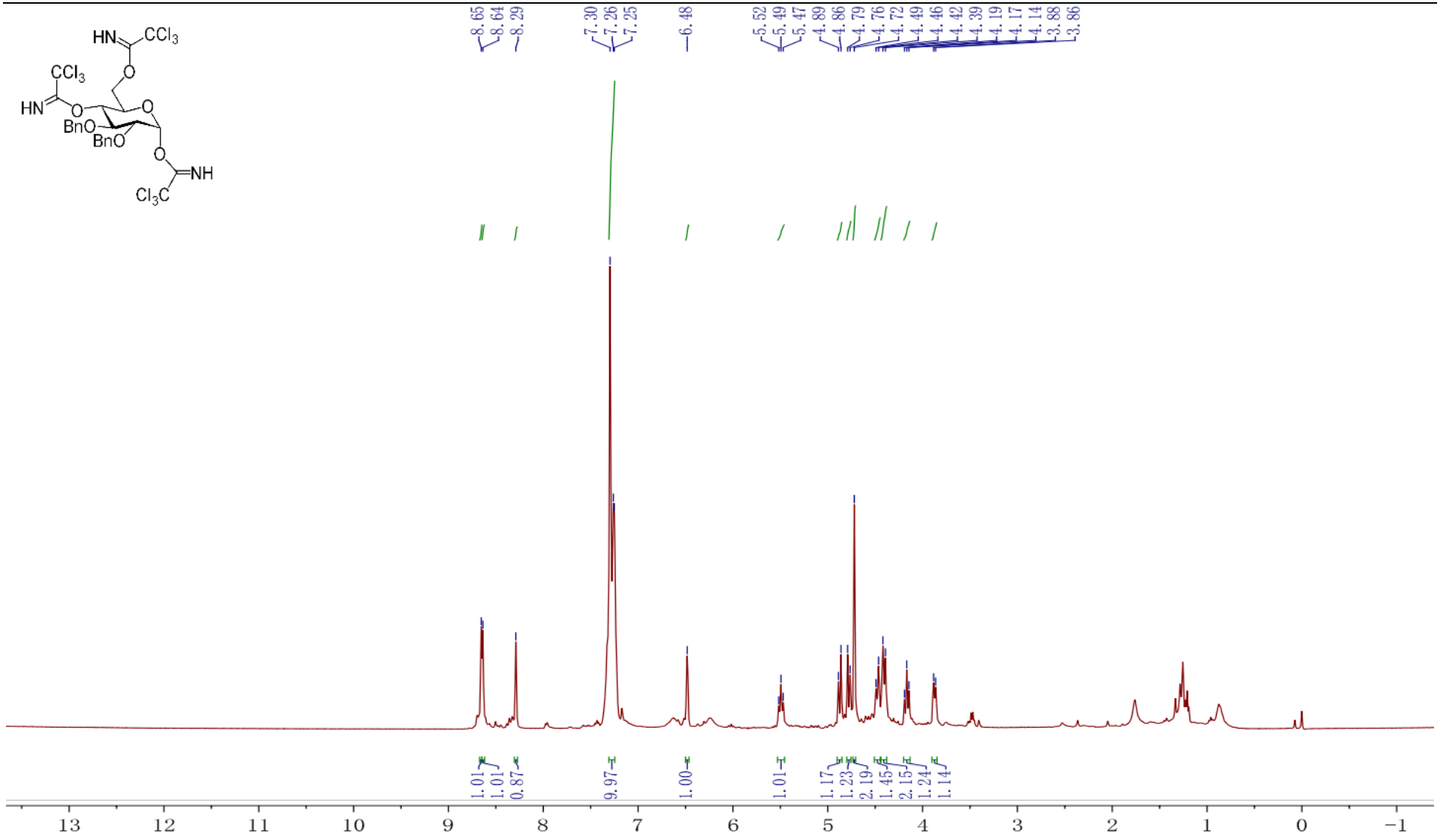
^{13}C NMR of **9** (151 M, $CDCl_3$)



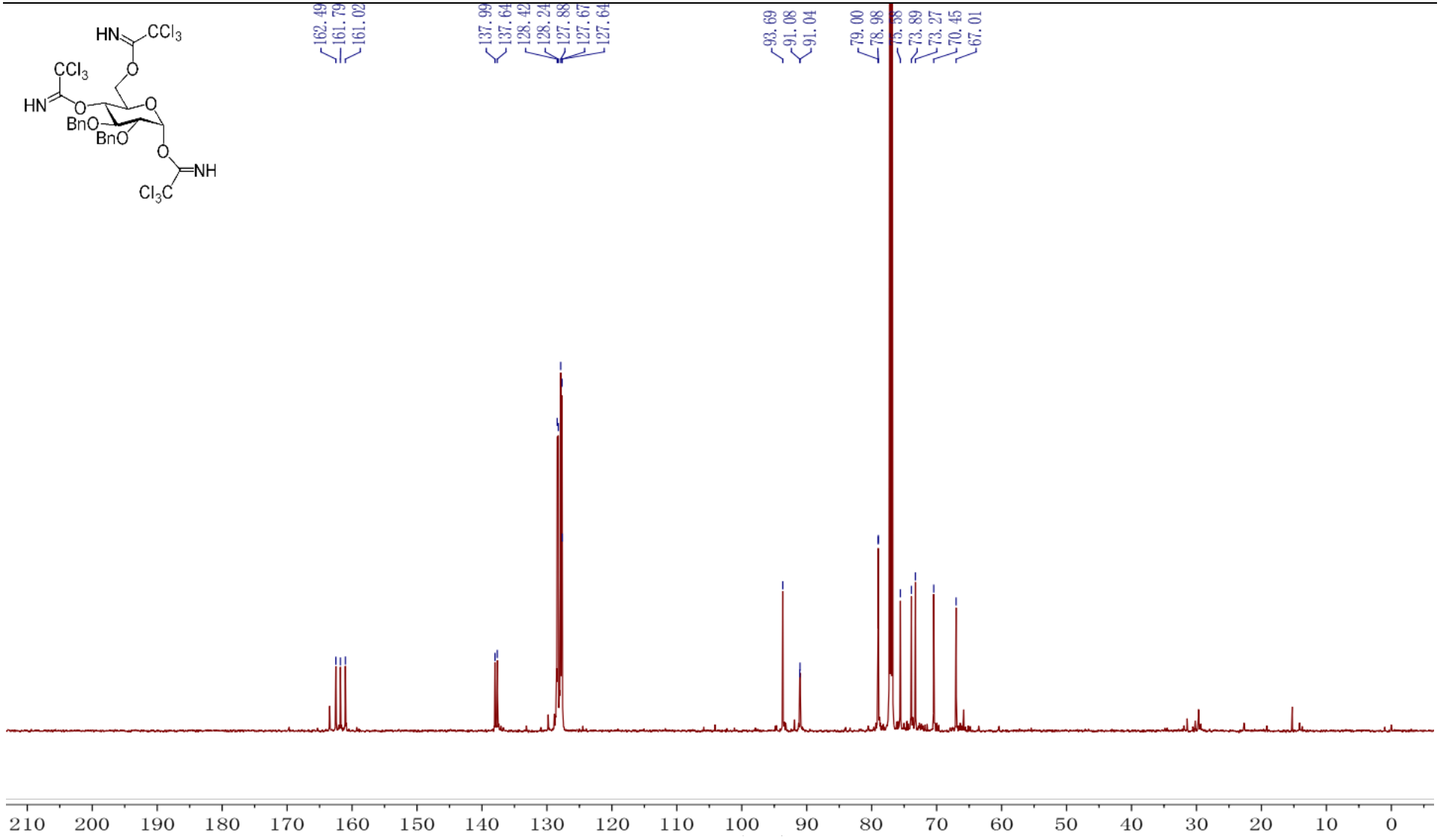
^{1}H NMR of **11** (600 M, $CDCl_3$)



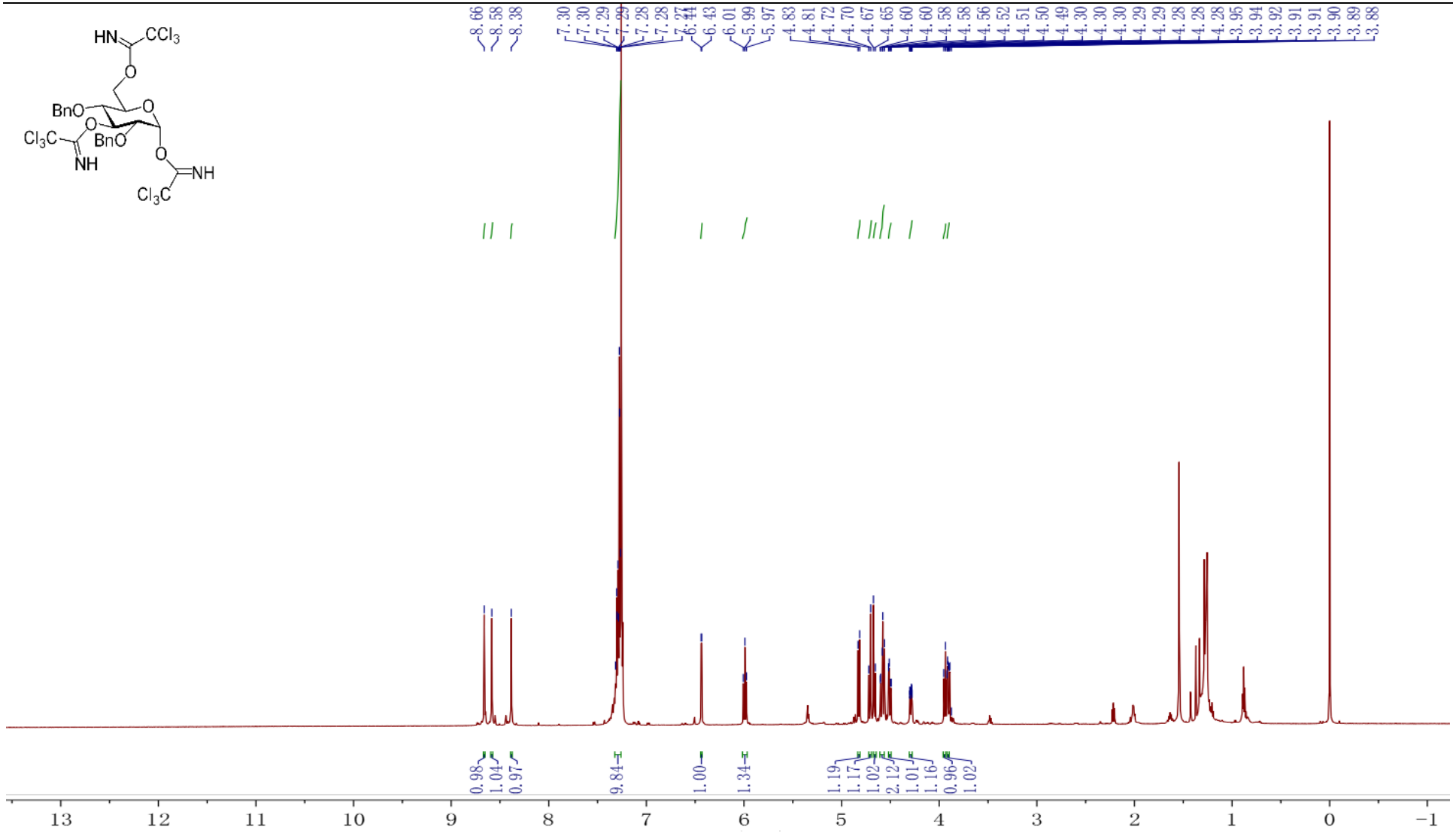
^{13}C NMR of **11** (151 M, $CDCl_3$)



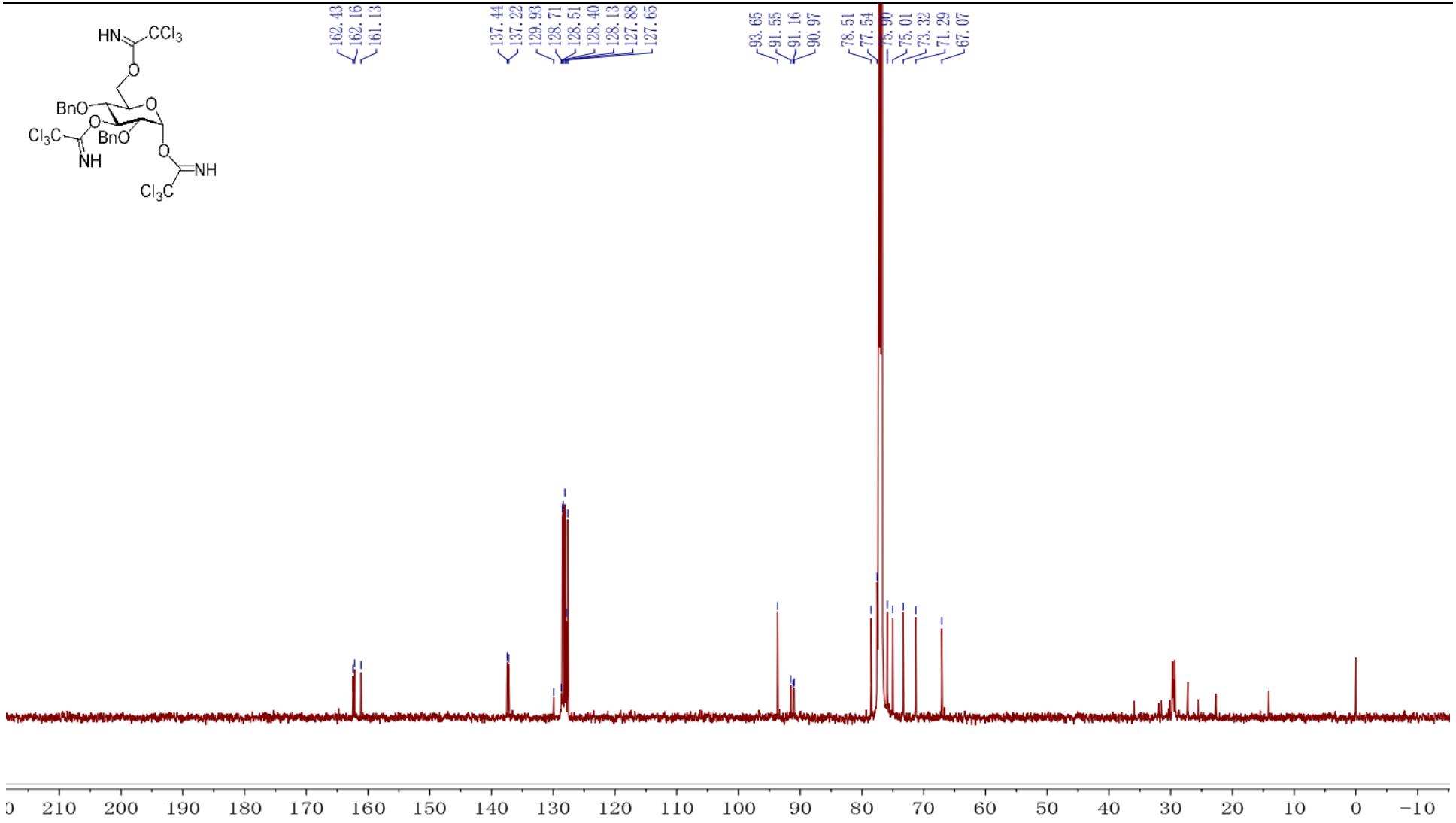
^{1}H NMR of **14** (600 M, $CDCl_3$)



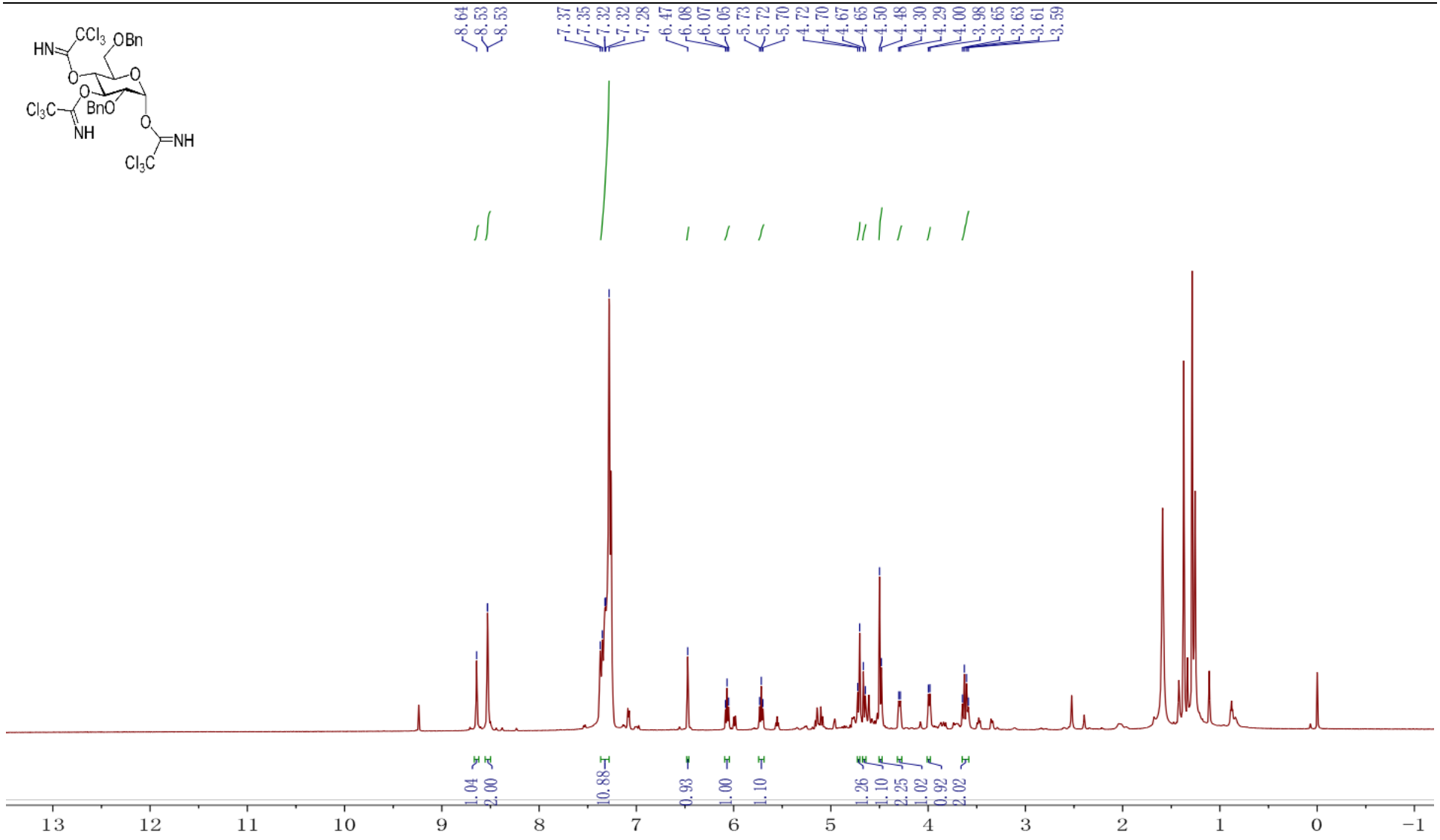
^{13}C NMR of **14** (151 M, $CDCl_3$)



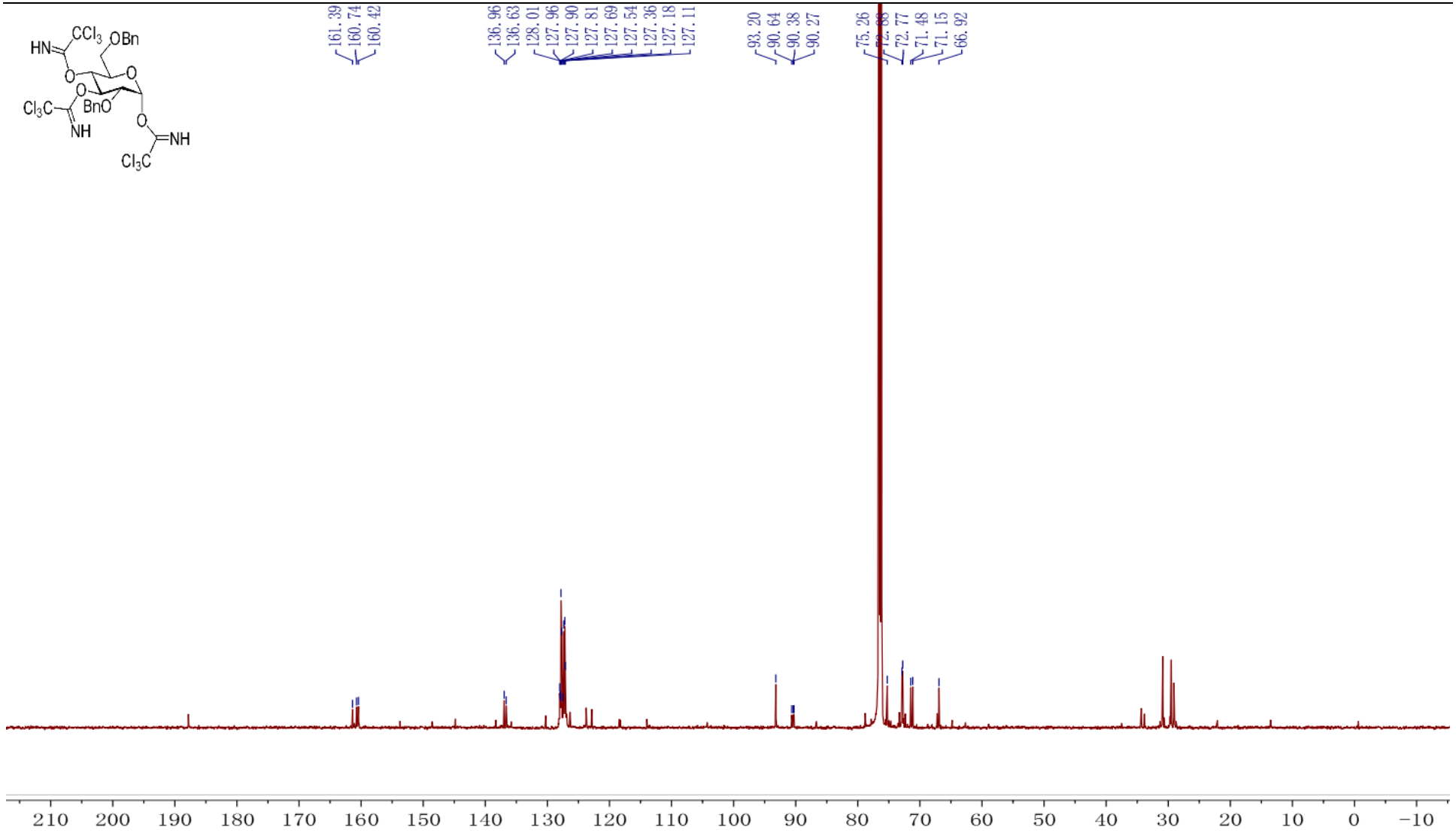
^{1}H NMR of **17** (600 M, $CDCl_3$)



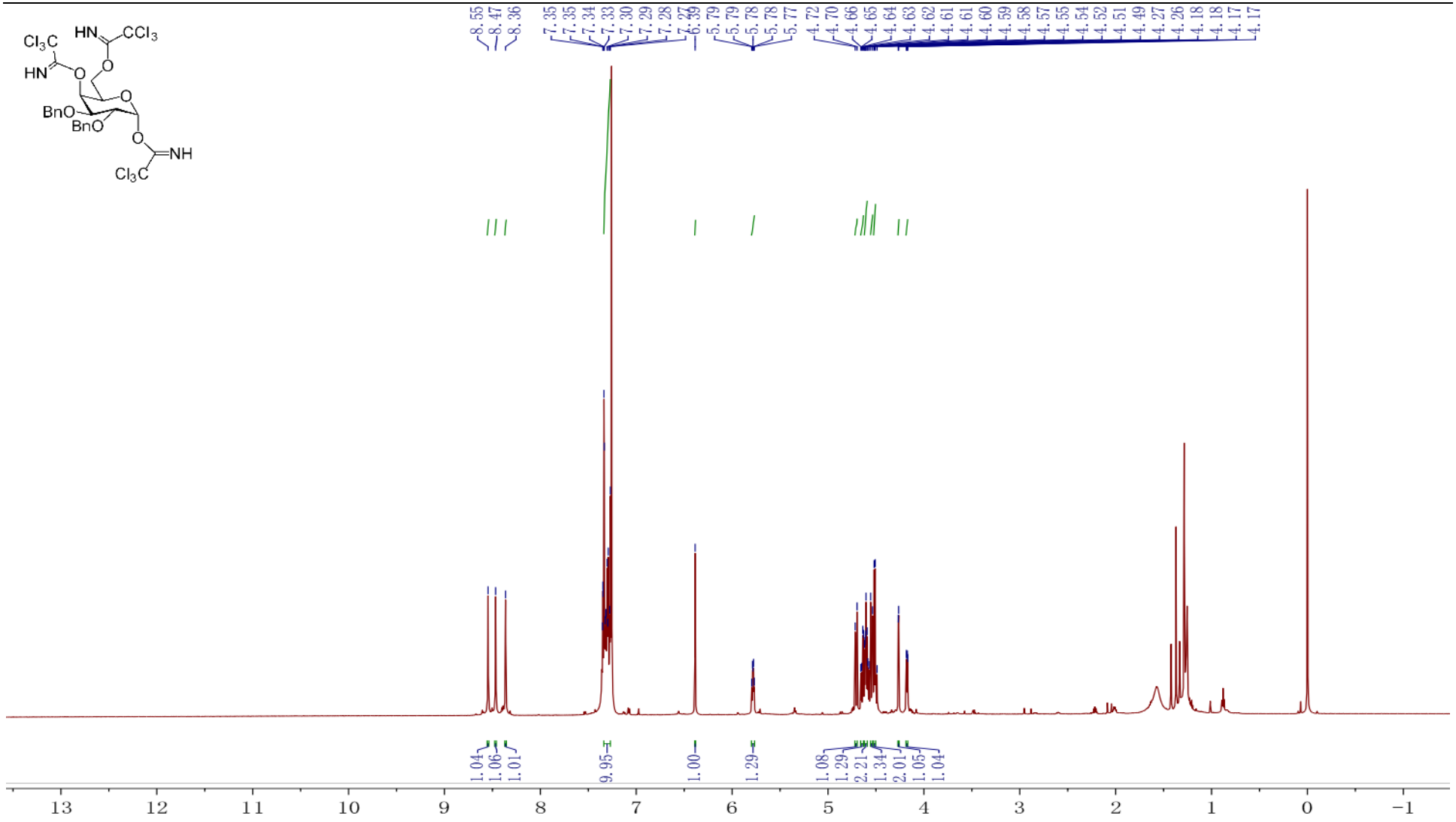
^{13}C NMR of **17** (151 M, $CDCl_3$)



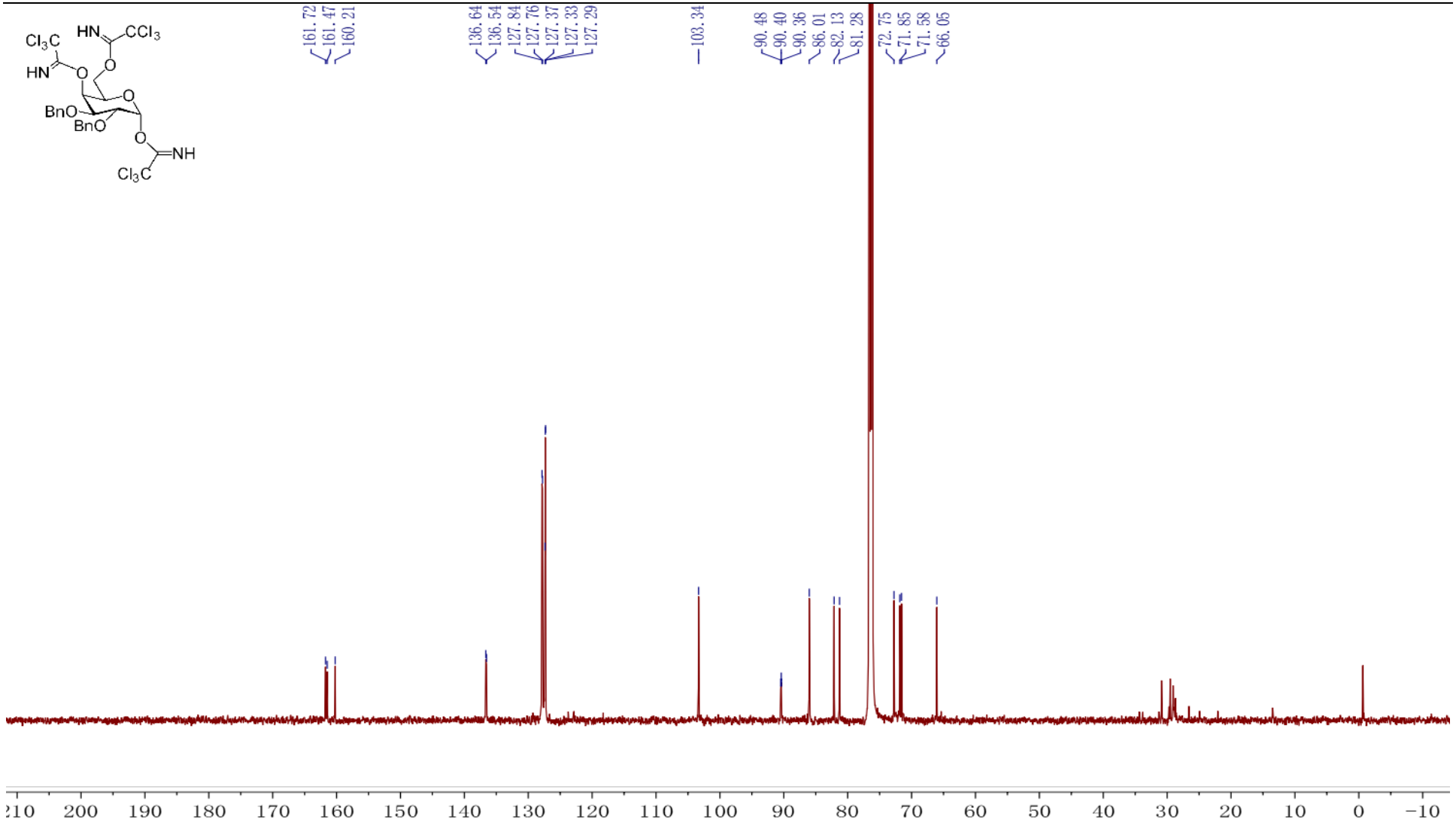
^{1}H NMR of **20** (600 M, $CDCl_3$)



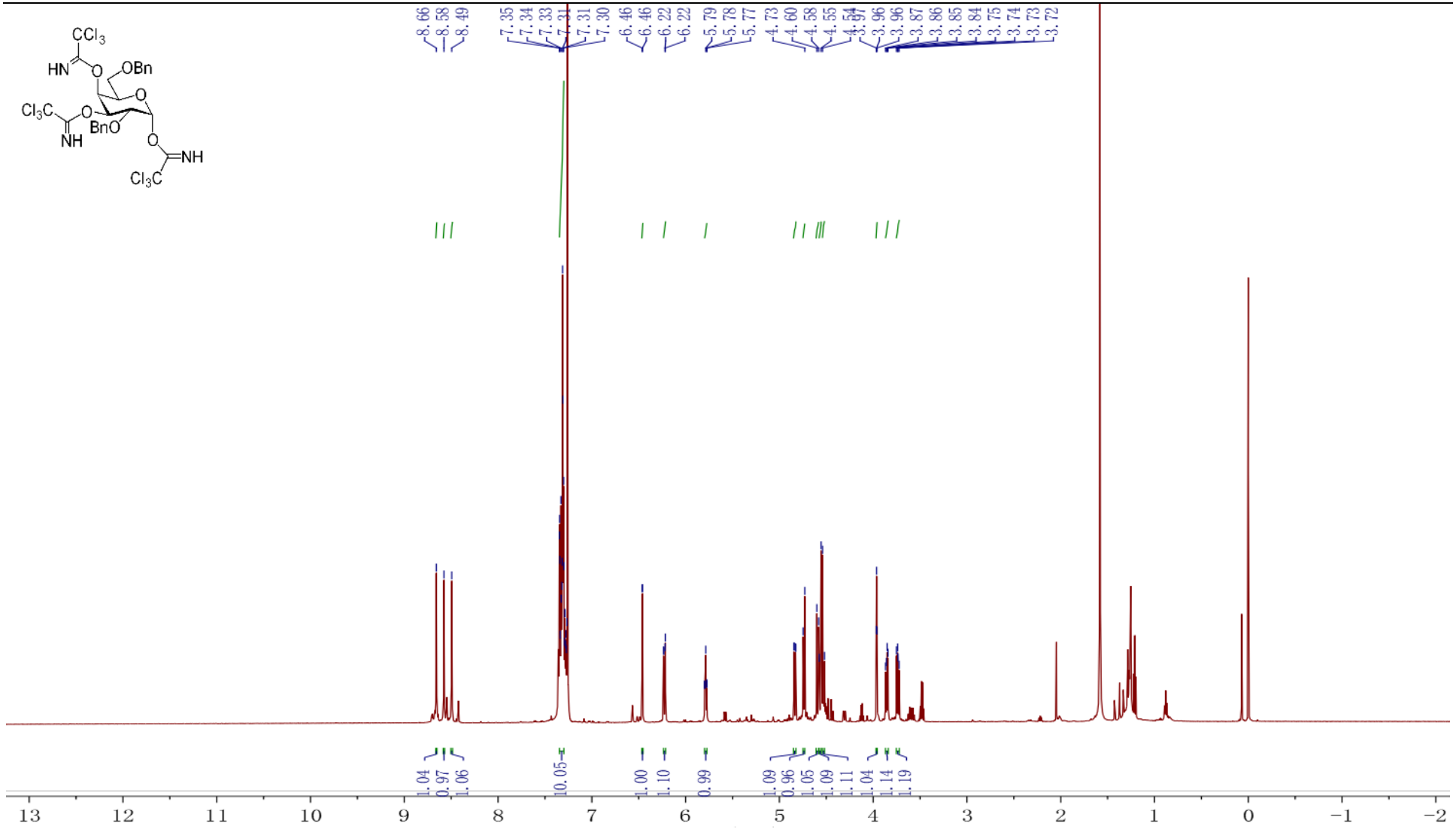
^{13}C NMR of **20** (151 M, $CDCl_3$)



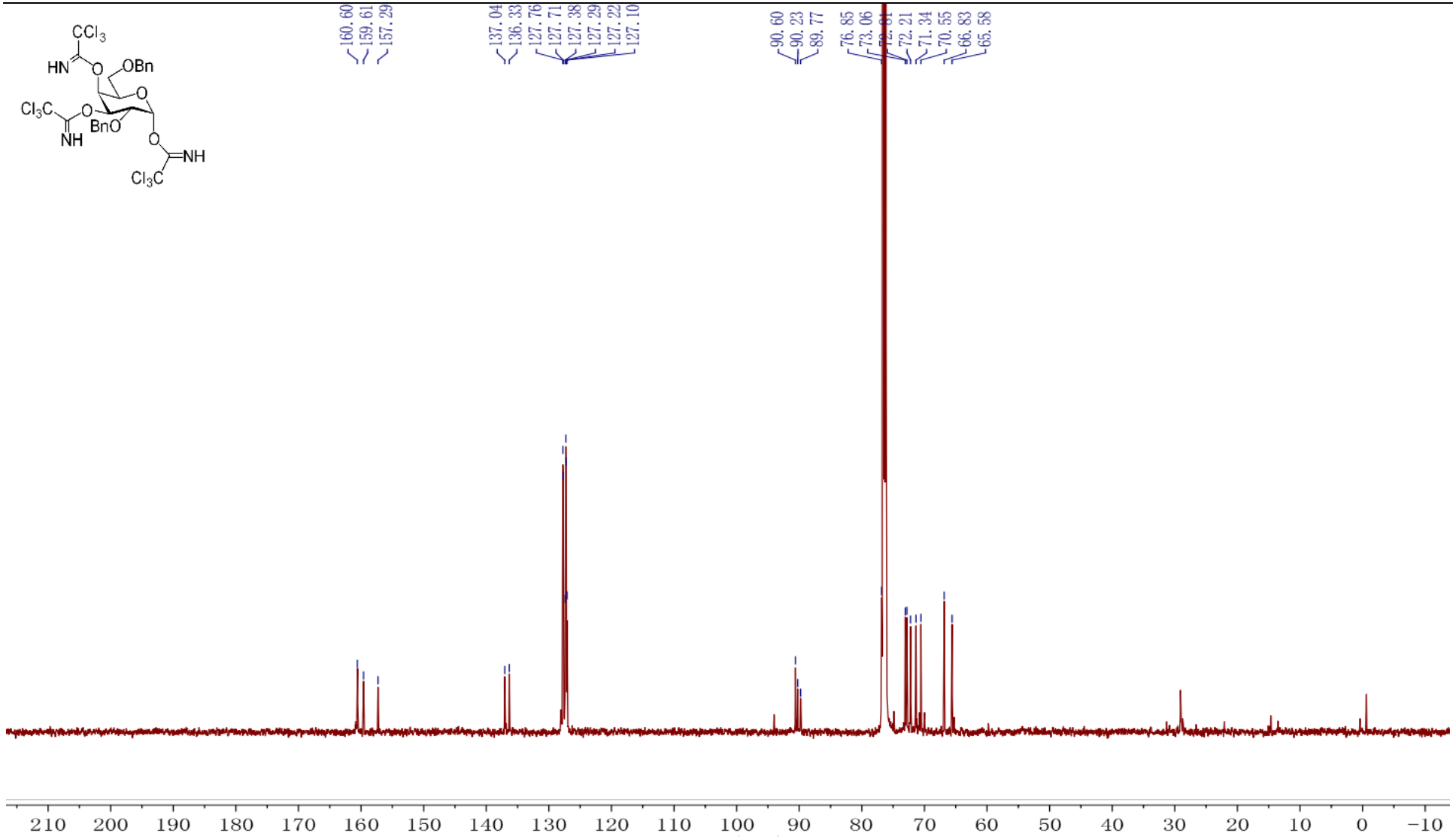
^{1}H NMR of **23** (600 M, $CDCl_3$)



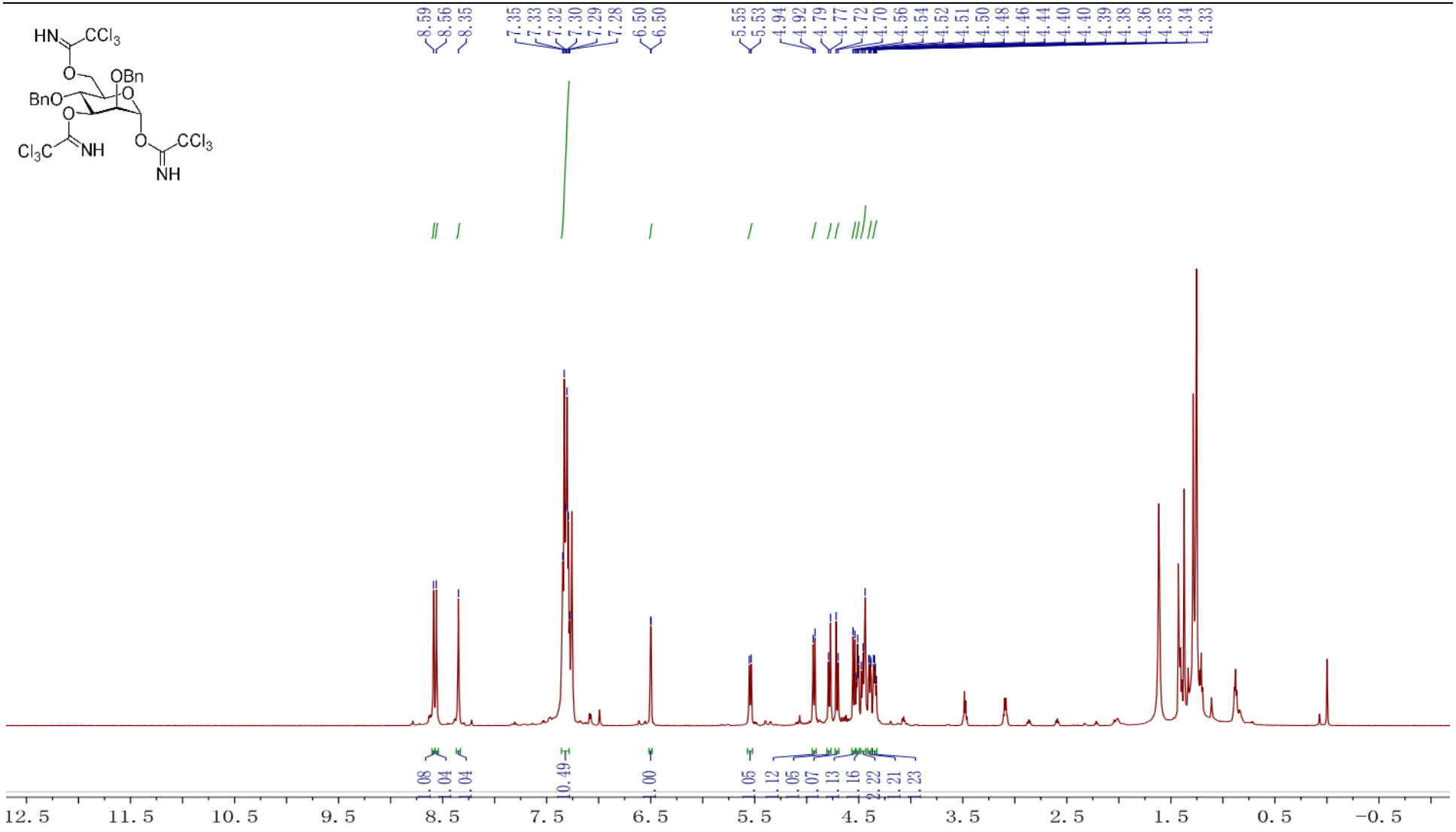
^{13}C NMR of **23** (151 M, $CDCl_3$)



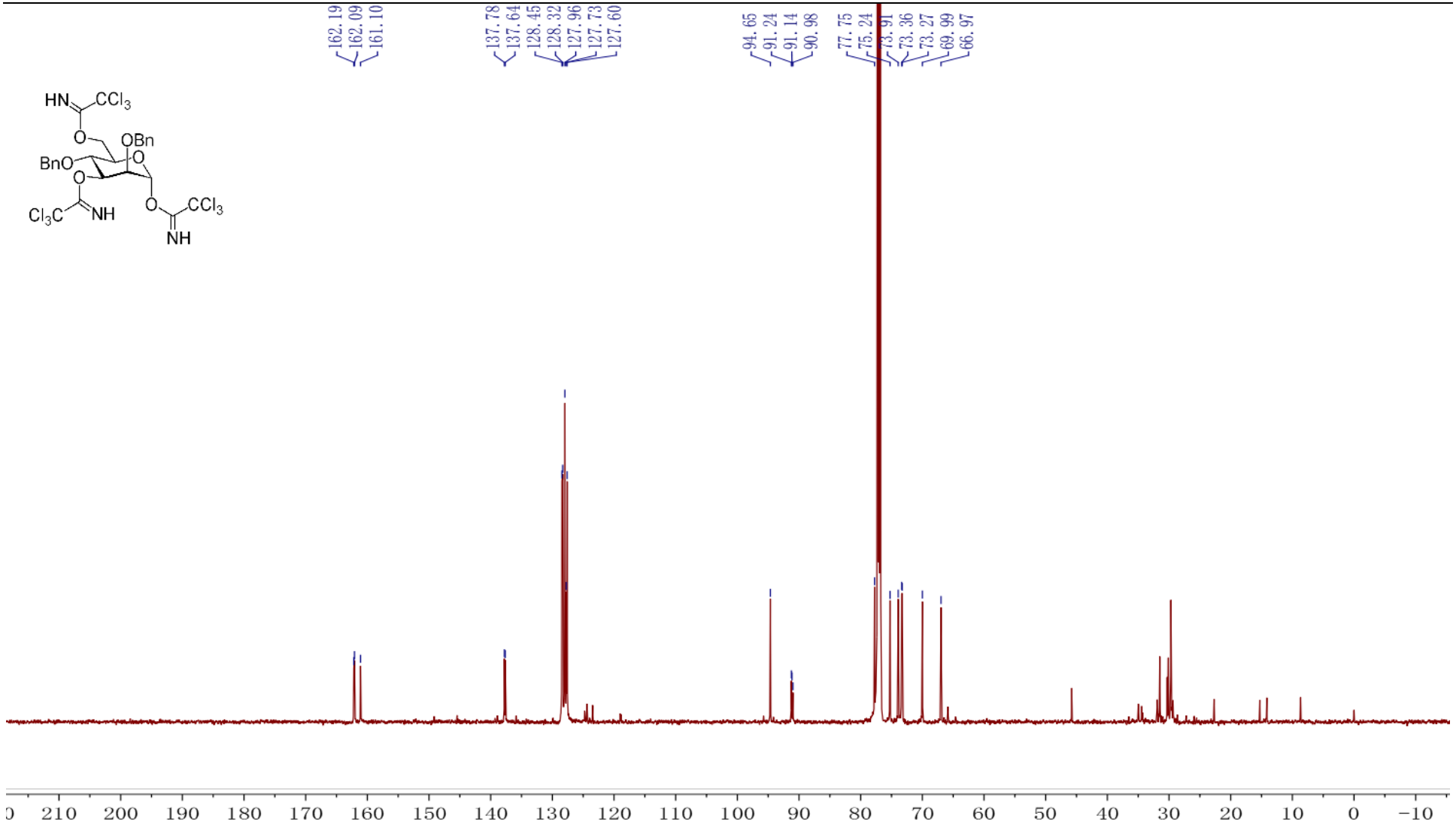
^{1}H NMR of **26** (600 M, $CDCl_3$)



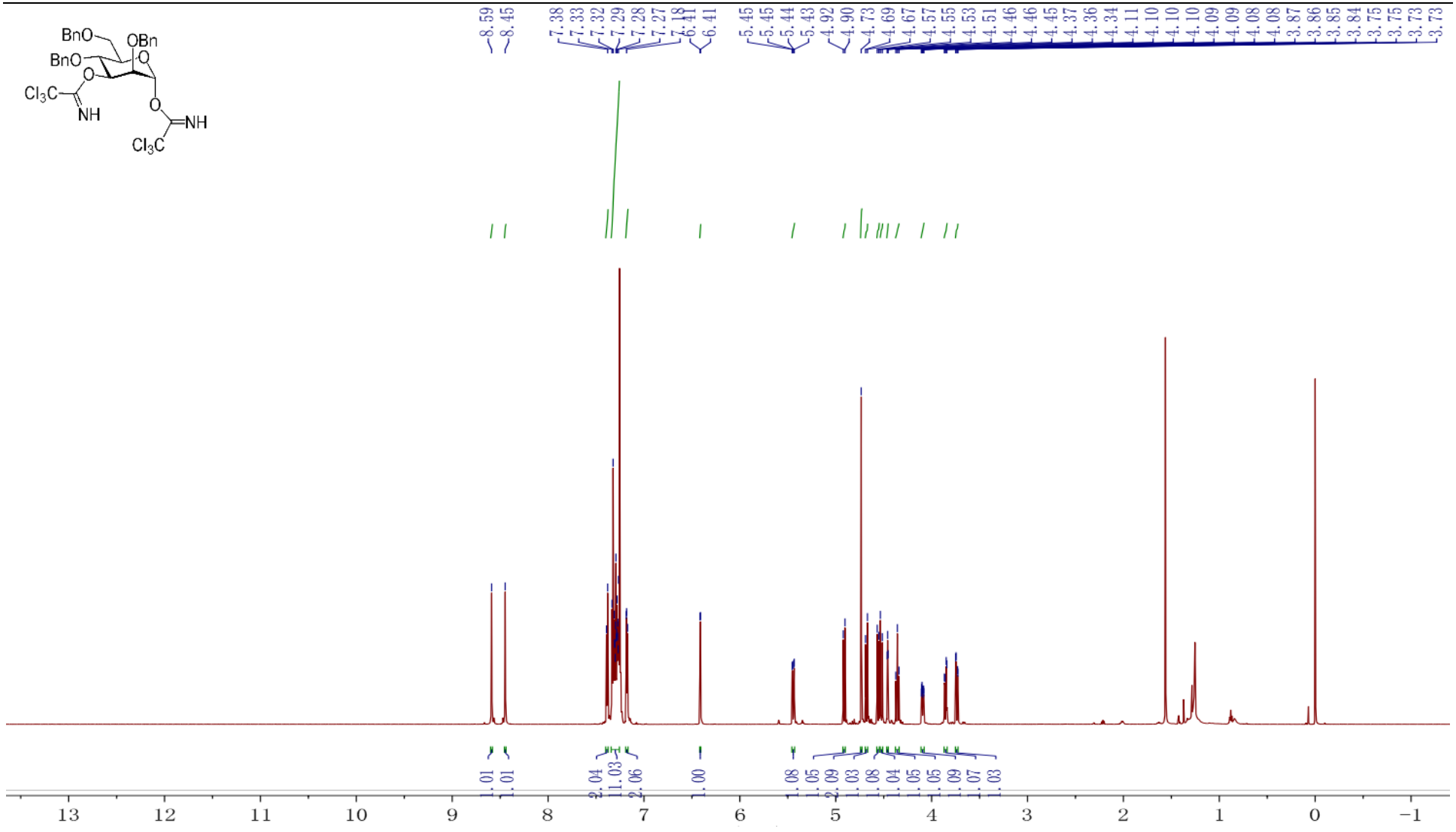
^{13}C NMR of **26** (151 M, $CDCl_3$)



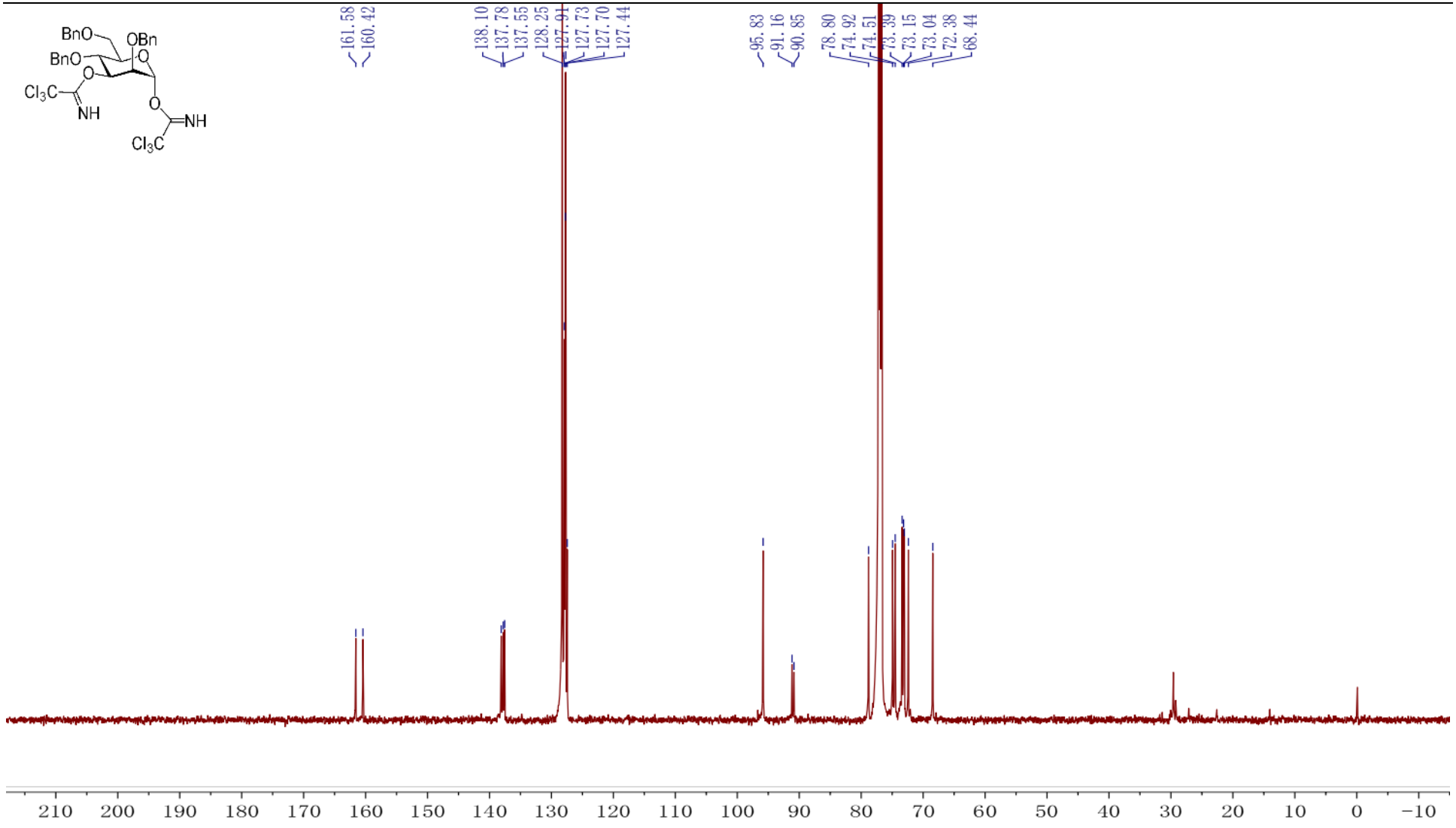
^{1}H NMR of **29** (600 M, $CDCl_3$)



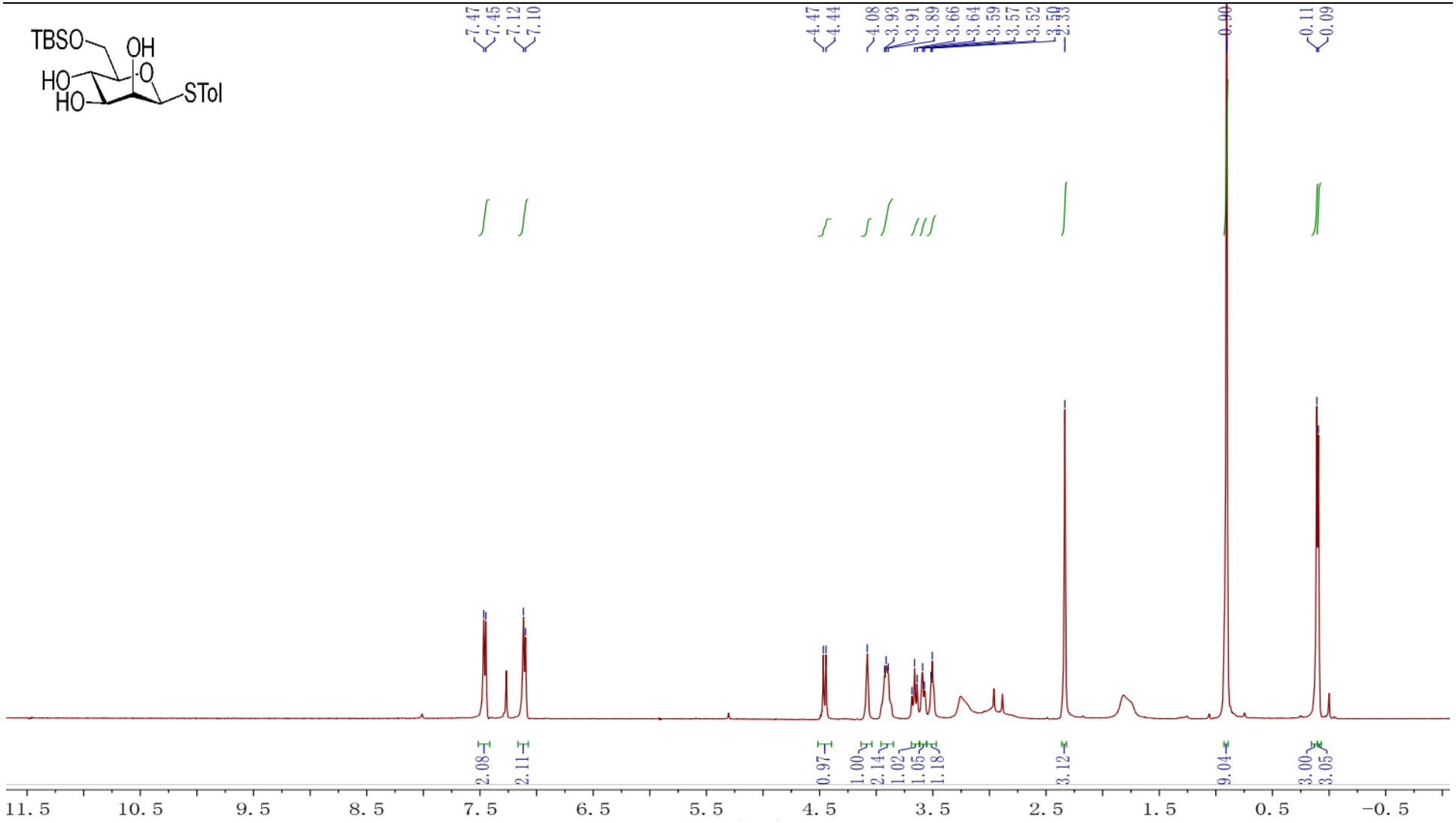
^{13}C NMR of **29** (151 M, $CDCl_3$)



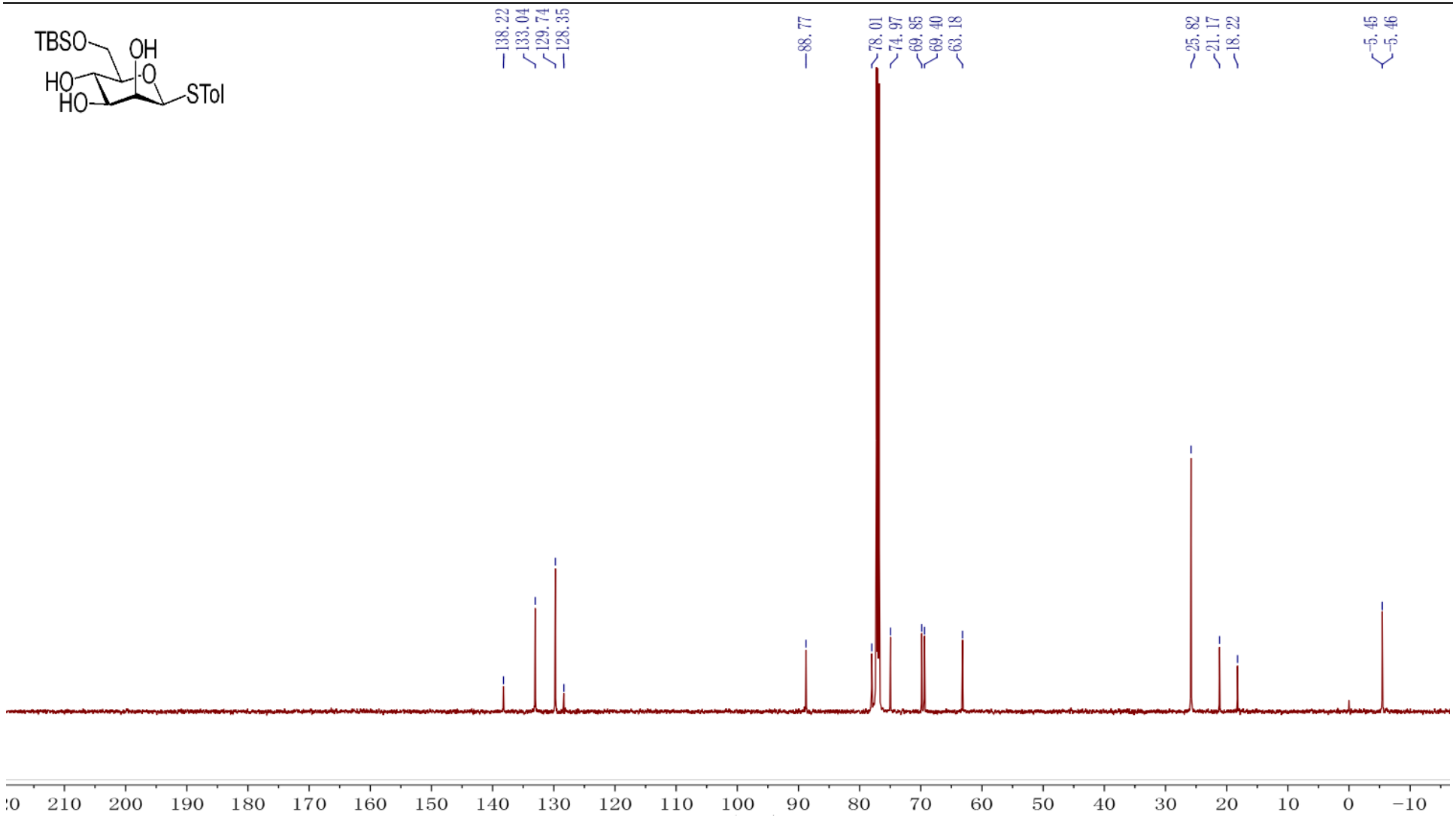
^{1}H NMR of **32** (600 M, $CDCl_3$)



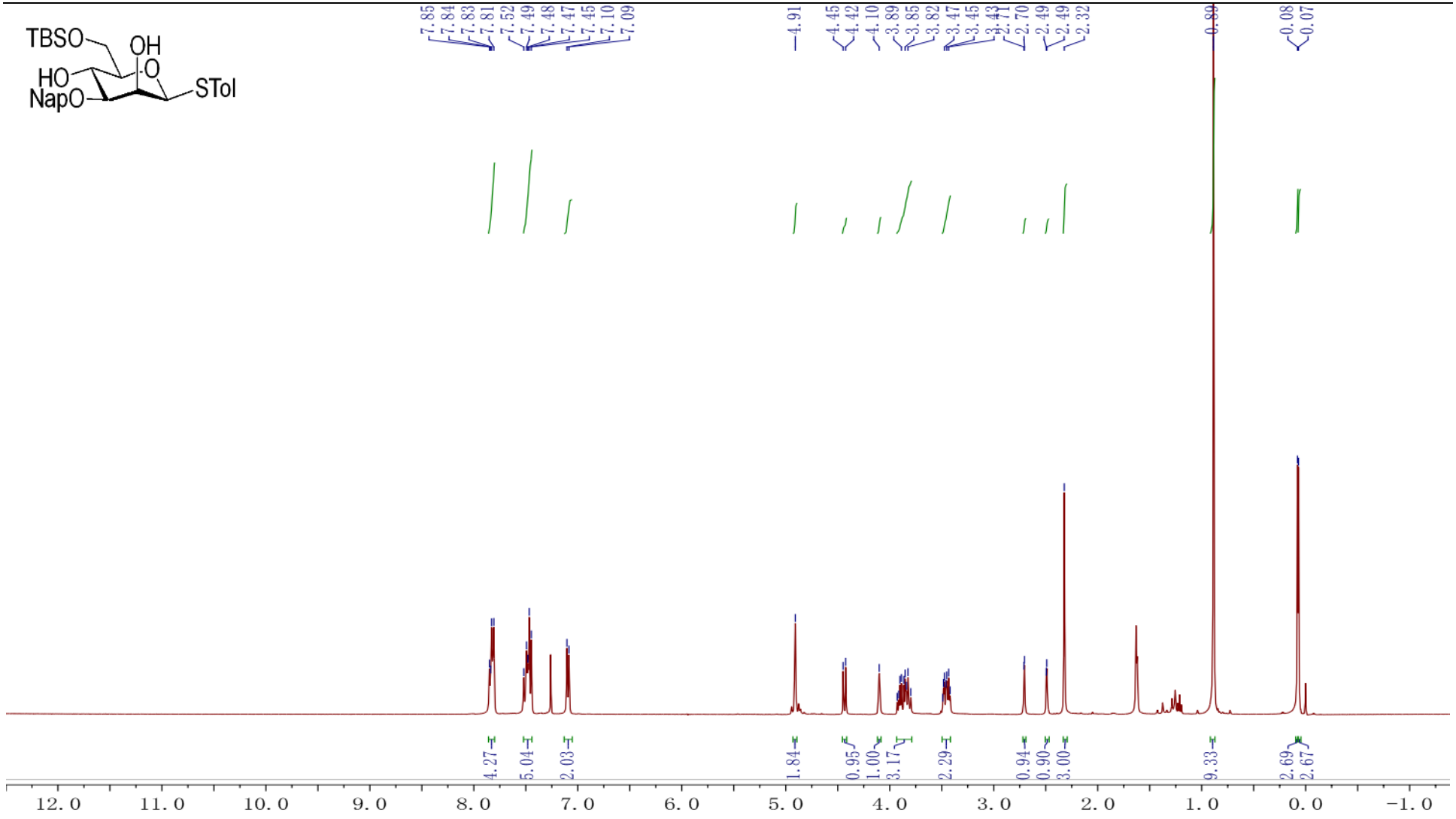
^{13}C NMR of **32** (151 M, $CDCl_3$)



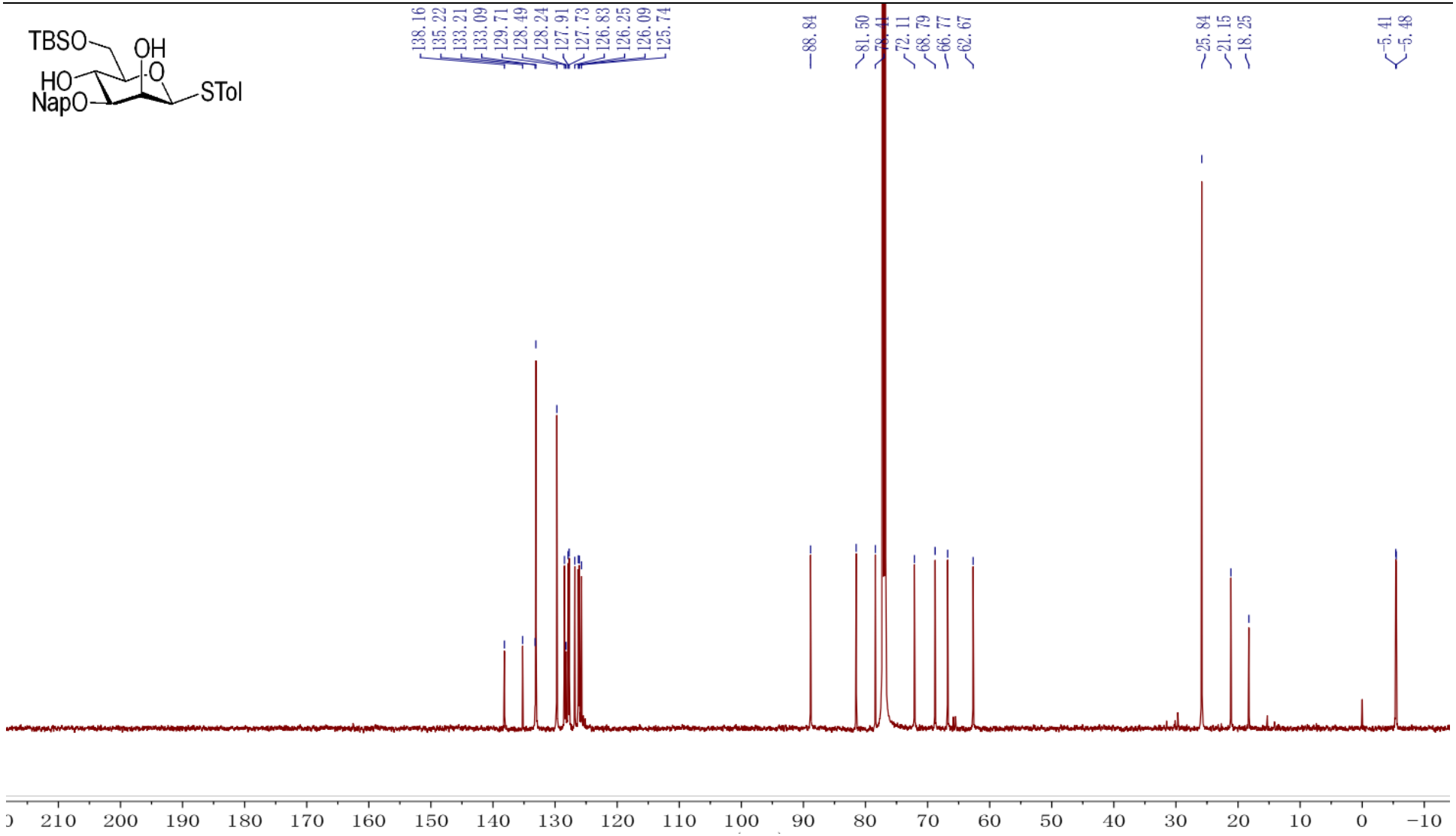
^{1}H NMR of **S18** (400 M, $CDCl_3$)



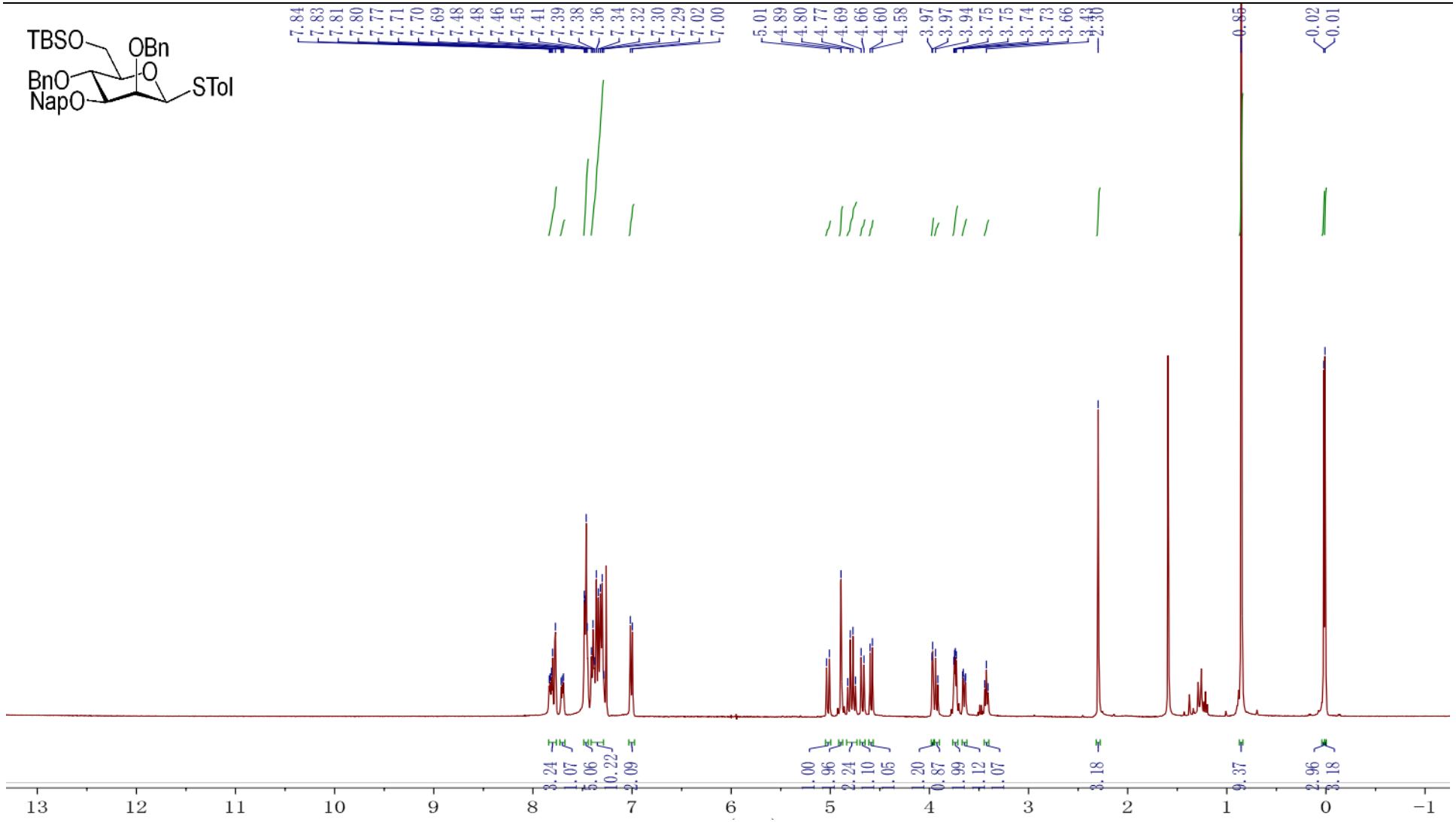
^{13}C NMR of **S18** (151 M, $CDCl_3$)



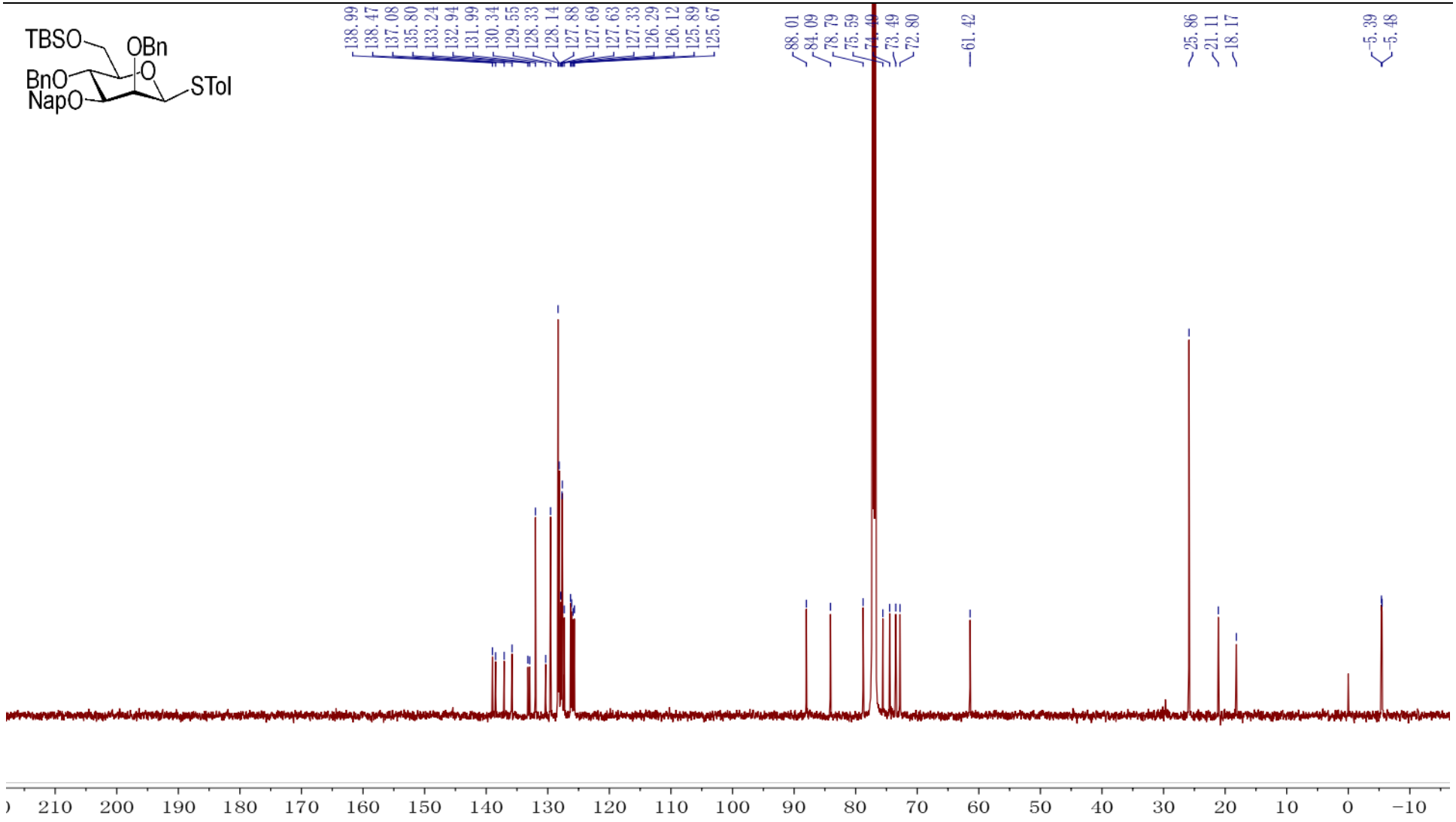
^{1}H NMR of **S19** (400 M, $CDCl_3$)



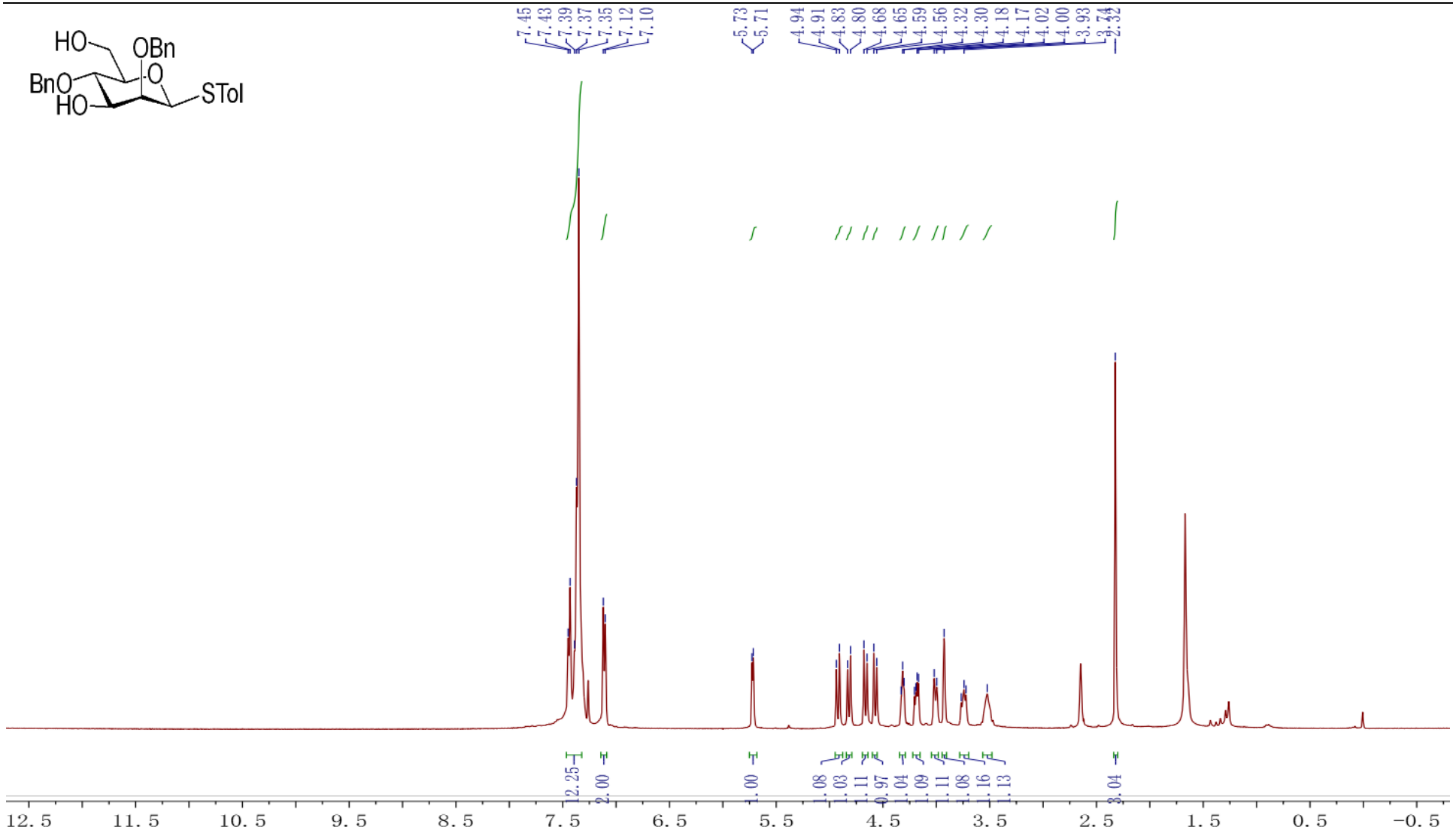
^{13}C NMR of **S19** (151 M, $CDCl_3$)



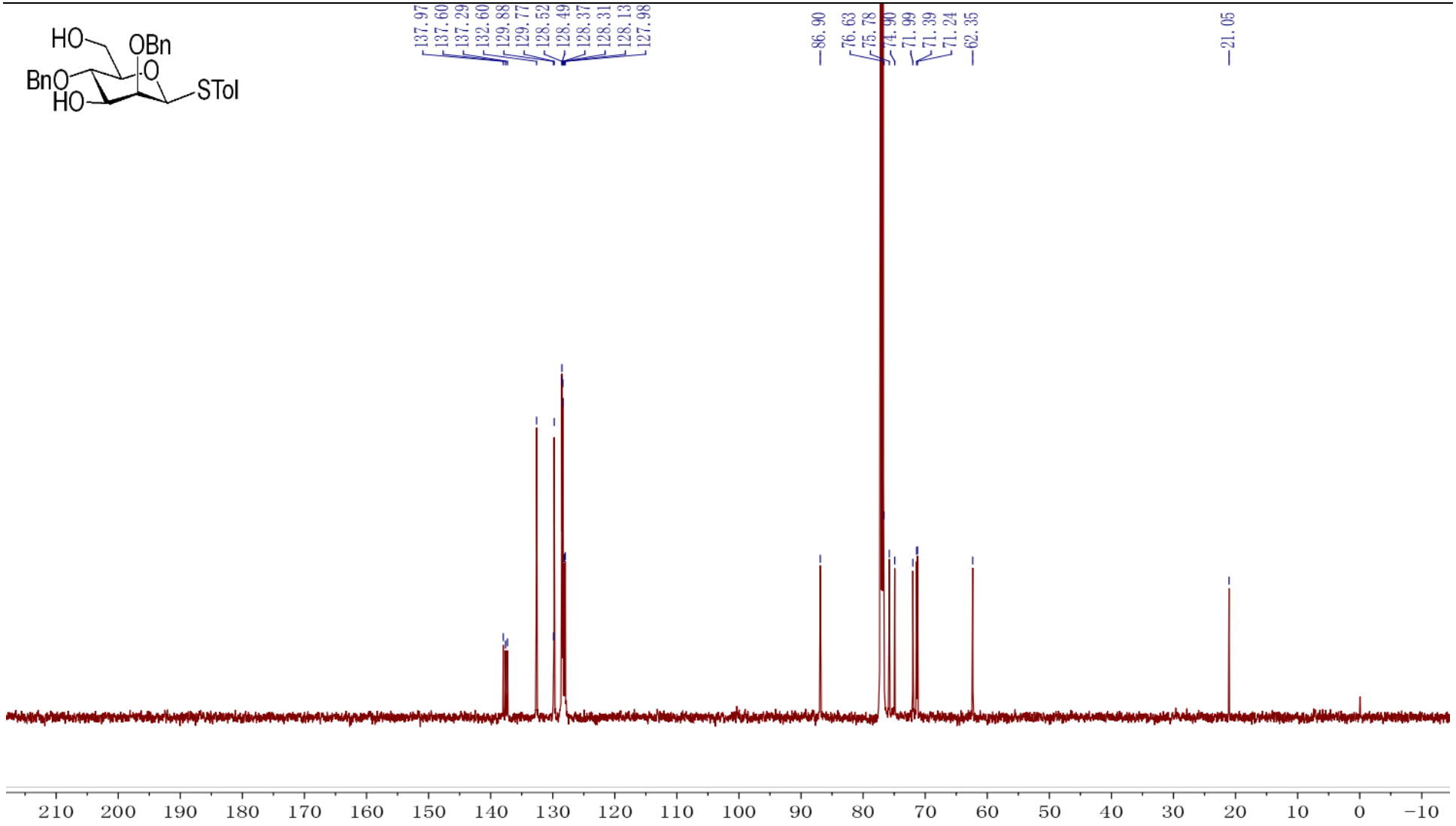
^{1}H NMR of **S20** (400 M, $CDCl_3$)



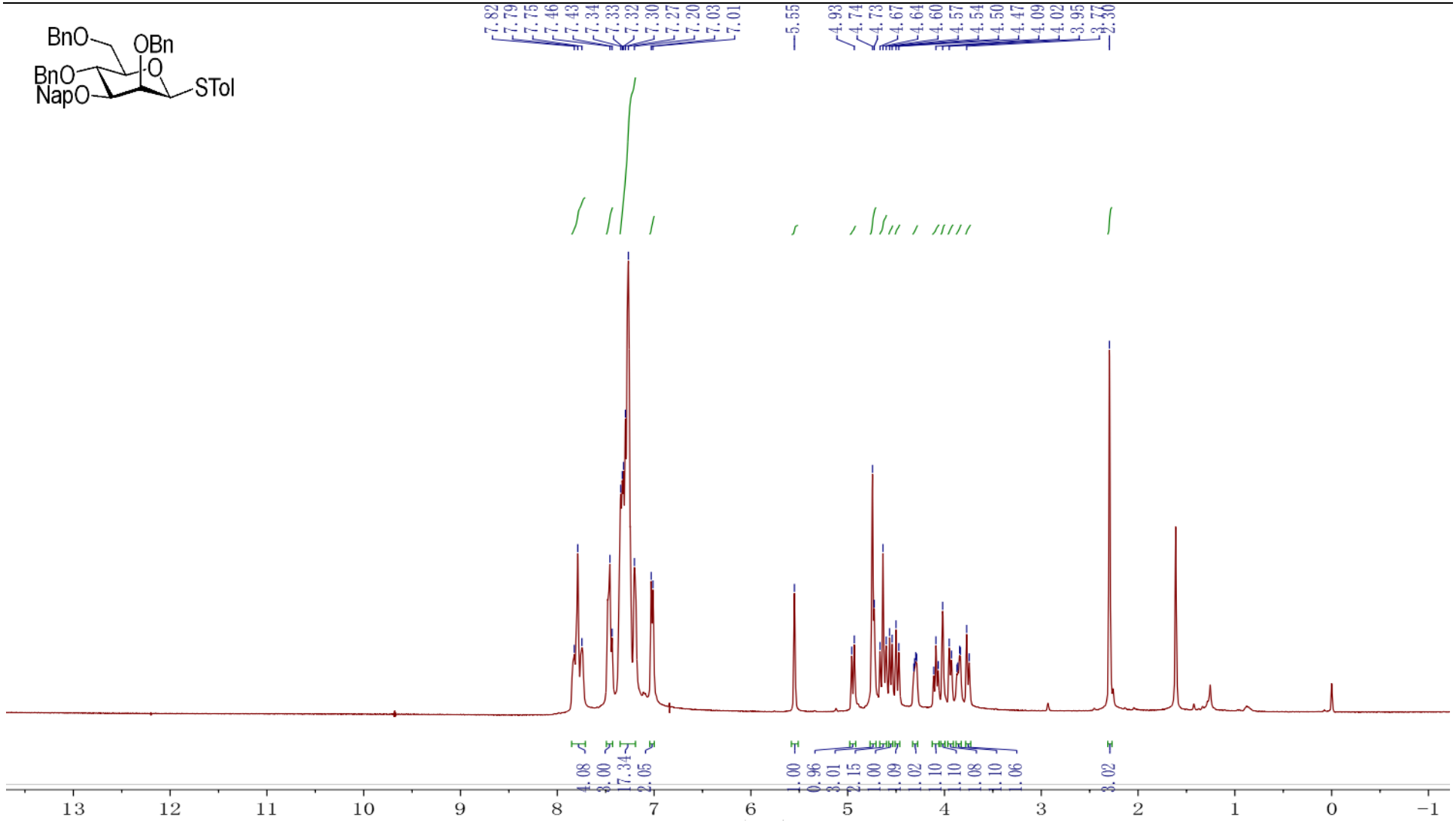
^{13}C NMR of **S20** (151 M, $CDCl_3$)



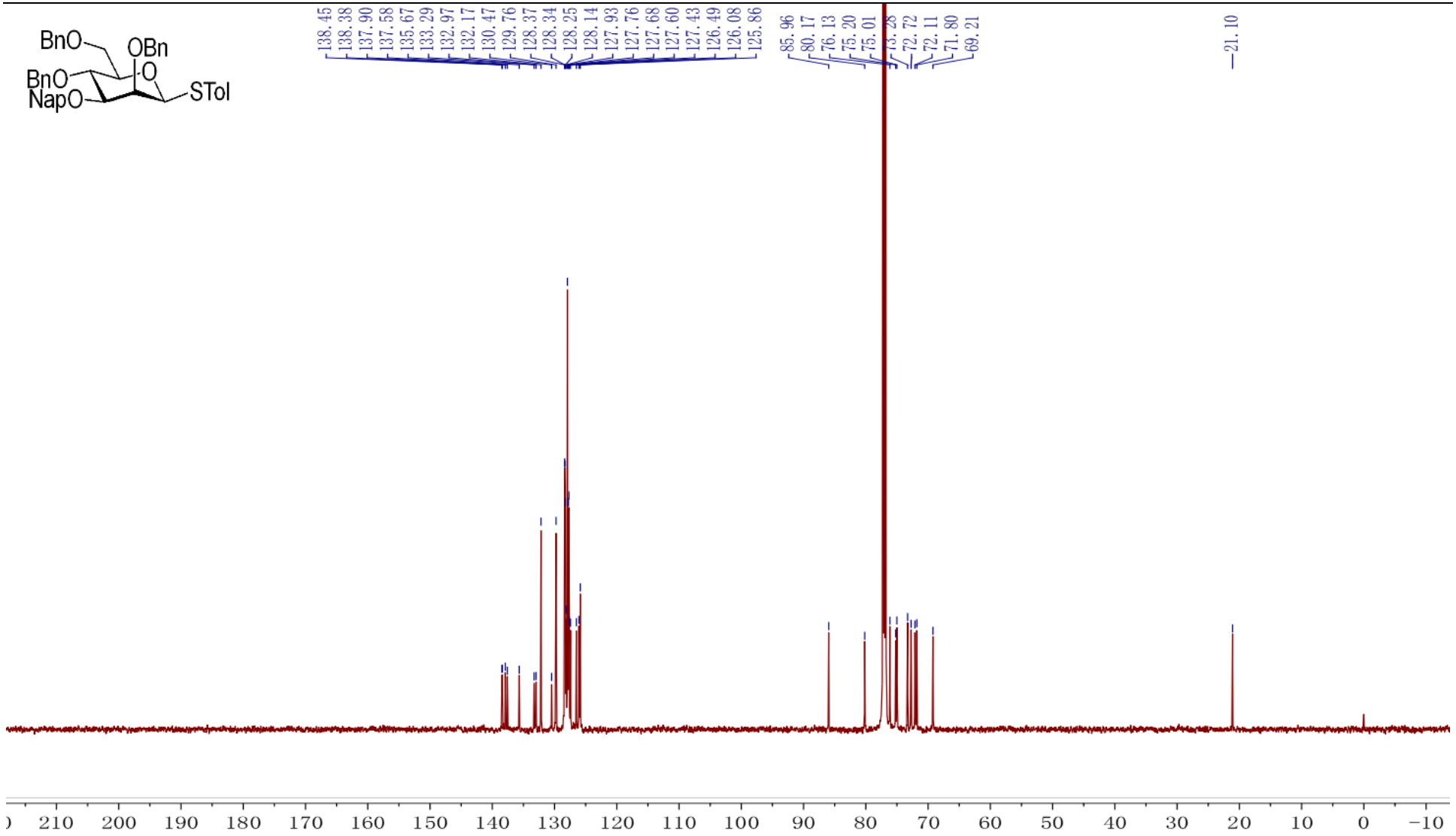
^{1}H NMR of **S21** (400 M, $CDCl_3$)



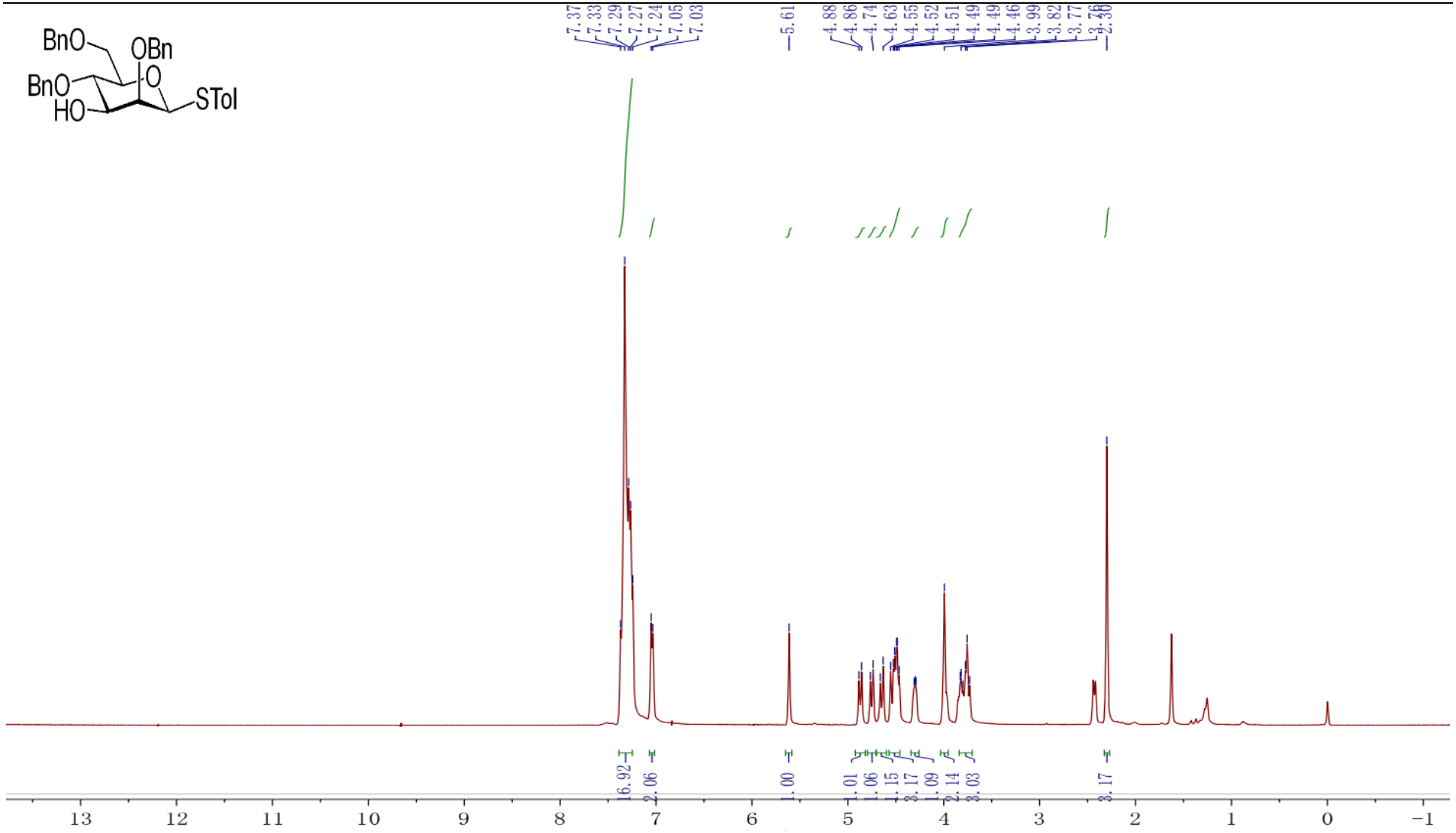
^{13}C NMR of **S21** (151 M, $CDCl_3$)



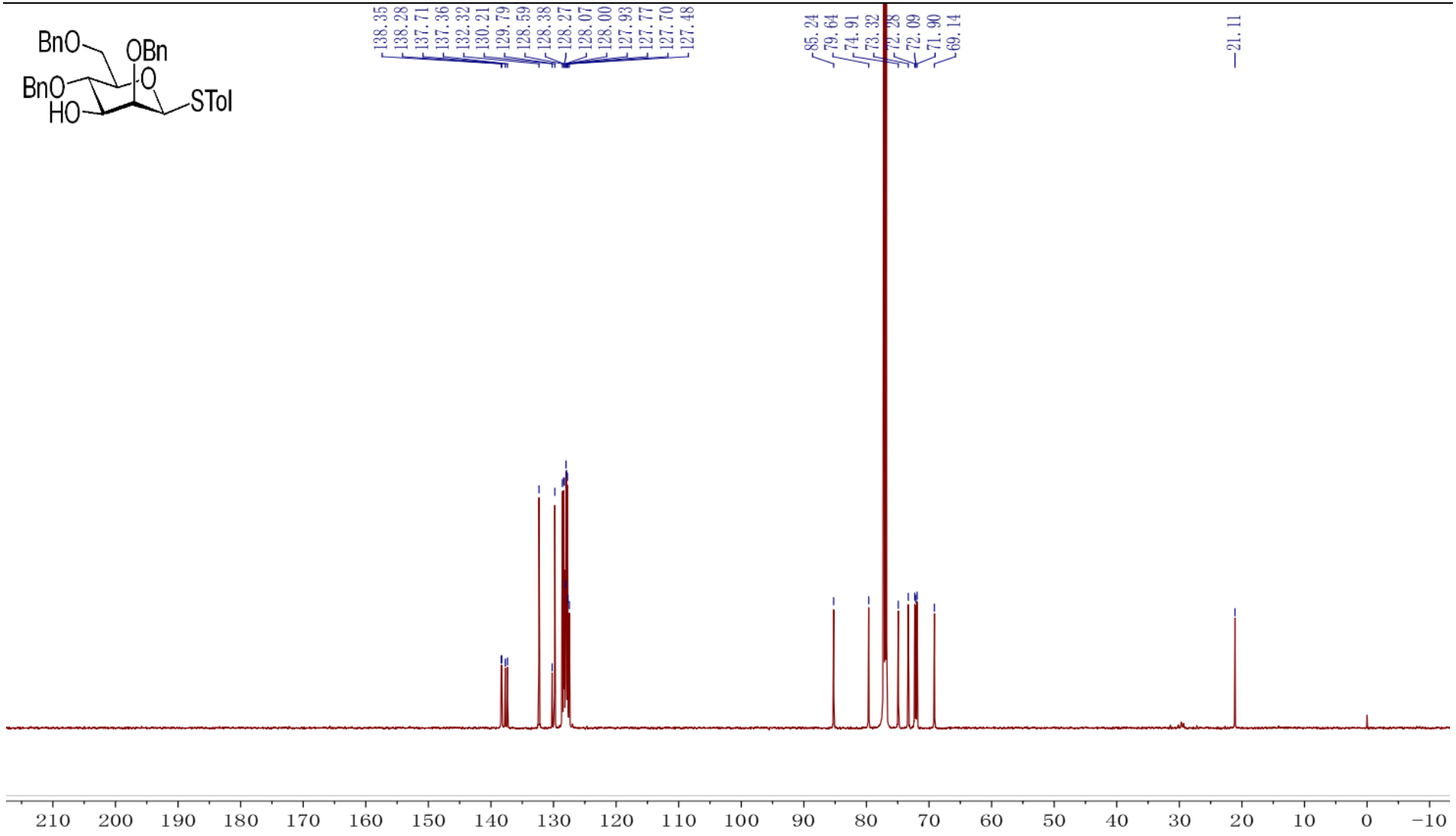
^{1}H NMR of **S23** (400 M, $CDCl_3$)



^{13}C NMR of **S23** (151 M, $CDCl_3$)



^{1}H NMR of **S24** (400 M, $CDCl_3$)



^{13}C NMR of **S24** (151 M, $CDCl_3$)