Supporting Information

Gold(I)-promoted α-Selective Sialylation of Glycosyl *ortho*-Hexynylbenzoates for Latent-active Synthesis of Oligosialic Acids

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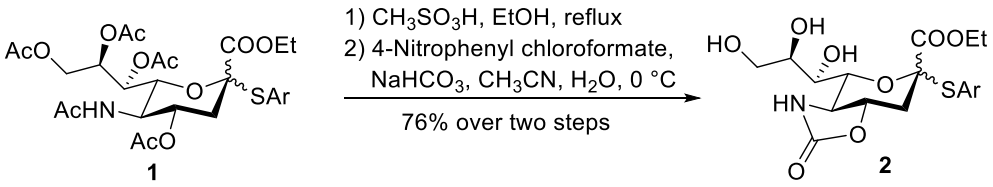
Contents

1. General Information. Commercial reagents were used without further purification except where noted. Solvents were dried and redistilled prior to use in the usual way. All reactions were performed in oven-dried glassware with magnetic stirring under an inert atmosphere unless noted otherwise. Analytical thin layer chromatography (TLC) was performed on precoated plates of silica gel (0.25 - 0.3 mm, Shanghai, China). The TLC plates were visualized with UV light and by staining with a solution of ammonium molybdate and ammonium ceric nitrate in aqueous sulfuric acid or sulfuric acid-ethanol solution. Silica gel column chromatography was performed on Silica Gel AR (100-200 mesh, Shanghai, China). Optical rotations (OR) were measured with a Rudolph Research Analytical Autopol I automatic polarimeter at a concentration (c) expressed in g/100 mL. NMR spectra were measured with a Bruker Avance III 400 or Bruker Avance III 500 spectrometer. The ^{1}H and ^{13}C NMR spectra were calibrated against the residual proton and carbon signals of the solvents as internal references ($CDCl_3$: δ_H = 7.26 ppm and δ_C = 77.2 ppm). Multiplicities are quoted as singlet (s), broad singlet (br s), doublet (d), doublet of doublets (dd), triplet (t), doublet of triplets (dt), or multiplet (m). Spectra were assigned using HMBC. All NMR chemical shifts (δ) were recorded in ppm and coupling constants (J) were reported in Hz. High resolution ESI mass spectra were recorded on an LCT Premier XE FTMS instrument.

2. Experimental details and characterization data of new compounds

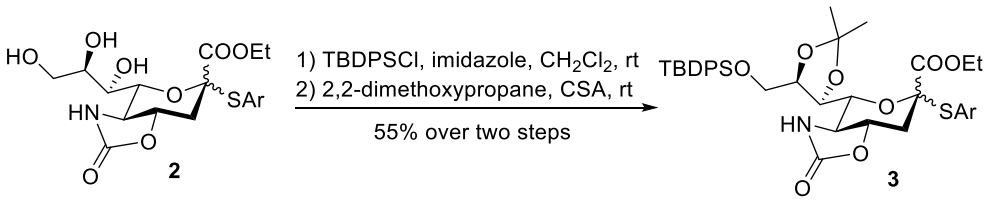
2.1. Synthesis of ethyl (5-*tert*-butyl-2-methylbenzene 5-amido-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 2



To a solution of thioglycoside **1**[1] (32.8 g, 49.1 mmol) in EtOH (500 mL) at room temperature was added methanesulfonic acid (9.6 mL, 147.3 mmol). After refluxing at 100 ℃ for 24 h, the cooling mixture was neutralized with Et_3N and evaporated to give the corresponding unprotected sialic acid for the next step without further purification. To a solution of the above residue and $NaHCO_3$ (20.6 g, 245.5 mmol) in acetonitrile/water (1/2, v/v, 600 mL) at 0 ℃ was added a solution of 4-nitrophenyl chloroformate (24.7 g, 122.7 mmol) in CH_3CN (100 mL) dropwise. After stirring at

0 ℃ for 3 h, the mixture was diluted with EtOAc, washed with brine. The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a yellow residue, which was purified by silica gel column chromatography (CH_2Cl_2/MeOH: 100/1 → 50/1) to afford the 5-*N*,4-*O*-oxazolidinone protected sialyl thioglycoside **2** (18.1 g, 76% over two steps) as a pale yellow foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 2.0 Hz, 1 H), 7.27 (m, 1 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 6.60 (br s, 1 H, N*H*), 4.72 (dt, *J* = 3.2, 12.0 Hz, 1 H), 4.42 (dd, *J* = 3.6, 9.6 Hz, 1 H), 4.04–3.98 (m, 2 H), 3.76–3.69 (m, 4 H), 3.55 (t, *J* = 10.4 Hz, 1 H), 2.93 (dd, *J* = 3.2, 12.4 Hz, 1 H, H-3*e*), 2.42–2.33 (m, 4 H) , 1.28 (s, 9 H), 1.10 (t, *J* = 7.2 Hz, 3 H); HRMS (ESI) *m/z* calcd for $C_{23}H_{33}NO_8SNa$ $[M + Na]^+$ 506.1819, found 506.1826.

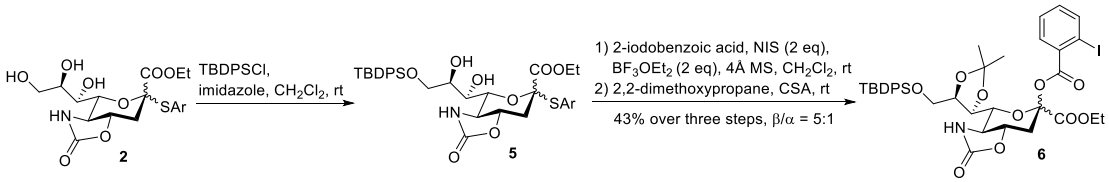
2.2. Synthesis of ethyl (5-*tert*-butyl-2-methylbenzene 5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-2-thio-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 3



To a solution of **2** (1.0 g, 2.1 mmol), imidazole (282 mg, 4.1 mmol) in anhydrous CH_2Cl_2 (8.0 mL) at room temperature was slowly added TBDPSCl (645 μL, 2.5 mmol) under argon. After stirring at room temperature for 6 h, the solvent was evaporated *in vacuo* to give a residue, which was diluted with EtOAc and washed with 1 M aq. HCl, sat. aq. $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the corresponding diol. To a solution of the above diol in 2,2-dimethoxypropane (4.0 mL) at room temperature was added CSA (98 mg, 0.42 mmol) under argon. After TLC showed complete conversion of starting material, Et_3N (58 μL, 0.42 mmol) was added and the solvent was evaporated *in vacuo* to give a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc: 6/1 → 3/1) to afford **3** (861 mg, 55% over two steps) as a white foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63–7.57 (m, 4 H), 7.43–7.30 (m, 5 H), 7.25–7.09 (m, 4 H), 5.16 (s, 1 H, N*H*), 4.93–4.85 (m, 1 H), 4.66–4.59 (m, 2 H), 4.32 (m, 1 H), 4.24 (d-like, *J* = 6.4 Hz, 1 H), 4.15–4.11 (m, 1 H), 4.01–3.89 (m, 2 H), 3.56 (t, *J* = 10.8 Hz, 1 H), 2.79–2.74 (m, 1 H, H-3*e*), 2.32–2.18 (m, 4 H), 1.52–1.46 (m, 3 H), 1.33 (m, 3 H), 1.27–1.20 (m, 12 H), 1.03 (m, 9 H); ^{13}C NMR

(150 MHz, $CDCl_3$) δ 168.0, 167.8, 159.8, 159.7, 149.9, 149.8, 138.1, 138.0, 135.8, 135.7, 135.0, 133.5, 133.3, 133.2, 131.6, 131.5, 130.5, 130.4, 130.2, 130.1, 130.0, 129.9, 128.6, 128.4, 128.1, 127.9, 127.8, 126.2, 110.5, 89.3, 89.2, 78.0, 77.9, 77.3, 76.2, 76.1, 74.0, 73.9, 67.7, 62.8, 62.7, 62.1, 58.8, 58.7, 37.6, 37.3, 34.7, 31.6, 31.4, 31.3, 29.9, 27.1, 26.4, 25.8, 20.5, 20.4, 19.4, 13.8; HRMS (ESI) *m/z* calcd for $C_{42}H_{55}NO_8SSiNa$ $[M + Na]^+$ 784.3315, found 784.3306.

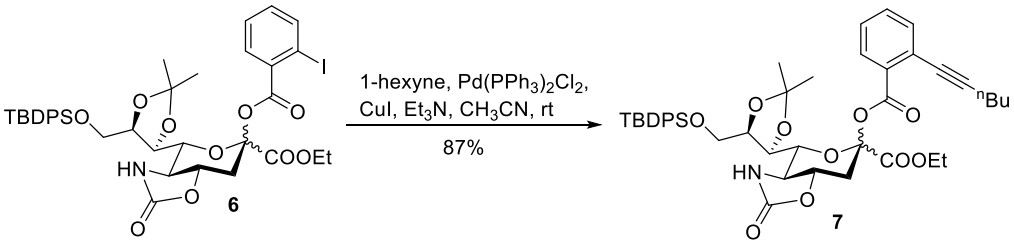
2.3. Synthesis of ethyl (*ortho*-iodobenzoyl 5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 6



To a solution of **2** (7.25 g, 15.0 mmol), imidazole (2.04 g, 30.0 mmol) in anhydrous CH_2Cl_2 (300 mL) at room temperature was slowly added TBDPSCl (4.30 mL, 18.0 mmol) under argon. After stirring at room temperature for 6 h, the mixture was diluted with CH_2Cl_2 and washed with 1 M aq. HCl, sat. aq. $NaHCO_3$, and brine. The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to give the corresponding diol **5** without further purification. HRMS (ESI) *m/z* calcd for $C_{39}H_{51}NO_8SSiNa$ $[M + Na]^+$ 744.3002, found 744.3000. To a solution of the above diol **5** in anhydrous CH_2Cl_2 (4.0 mL) was added 2-iodobenzoic acid (11.16 g, 45.0 mmol) and freshly activated 4Å MS (22.0 g) under argon. After stirring at room temperature for 15 min, $BF_3{\cdot}Et_2O$ (3.70 mL, 30.0 mmol) and NIS (6.75 g, 30.0 mmol) was added. After being stirred for 5 min, the mixture was filtered and the filtrate was washed with sat. aq. $Na_2S_2O_3$ and sat. aq. $NaHCO_3$. The organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a residue for the next step without further purification. To a solution of the above residue in 2,2-dimethoxypropane (30 mL) at room temperature was added camphorsulfonic acid (697 mg, 3.0 mmol). After stirring at room temperature for 3 h, the reaction was quenched with Et_3N (416 μL, 3.0 mmol) and evaporated *in vacuo* to give a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc: 6/1 → 5/1) to afford **6** (5.30 g, 43% over three steps, β/α = 5/1) as a pale yellow foam. **6β:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.0 Hz, 1 H), 7.67 (dd, *J* = 1.5, 8.0 Hz, 1 H), 7.58 (d, *J* = 6.5 Hz, 2 H),

7.51 (d, *J* = 7.0 Hz, 2 H), 7.41–7.25 (m, 6 H), 7.19 (dt, *J* = 1.0, 8.0 Hz, 1 H), 7.13 (dt, *J* = 1.5, 7.5 Hz, 1 H), 5.67 (s, 1 H, N*H*), 4.69 (dt, *J* = 4.0, 12.5 Hz, 1 H, H-4), 4.30–4.24 (m, 3 H), 4.19 (dd, *J* = 7.0, 13.0 Hz, 1 H), 4.13–4.05 (m, 3 H), 3.75 (t, *J* = 11.0 Hz, 1 H, H-5), 3.01 (dd, *J* = 3.5, 12.5 Hz, 1 H, H-3*e*), 2.46 (t, *J* = 12.5 Hz, 1 H, H-3*a*), 1.49 (s, 3 H), 1.27 (s, 3 H), 1.26 (t, *J* = 7.0 Hz, 3 H), 0.94 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4 (C-1, $^3J_{C1,H3ax}$ = 0 Hz), 164.1, 160.0, 141.8, 135.7, 135.5, 133.7, 133.5, 133.4, 131.7, 130.0, 129.9, 128.3, 127.9, 127.8, 110.3, 100.1 (C-2), 94.2, 77.1, 76.8, 75.8, 75.6, 62.8, 62.6, 58.0, 35.8, 27.0, 26.3, 25.6, 19.3, 14.1; HRMS (ESI) *m/z* calcd for $C_{38}H_{44}NO_{10}ISiNa$ $[M + Na]^+$ 852.1677, found 852.1687.

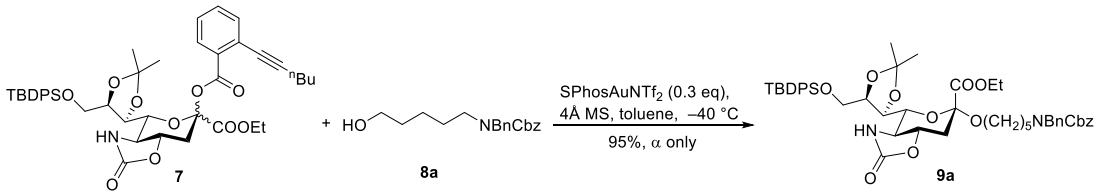
2.4. Synthesis of ethyl (*ortho*-hexynylbenzoyl 5-amido-9-*O*-*tert*-butyldiphenyl silyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 7



To a solution of compound **6** (997 mg, 1.2 mmol), $Pd(PPh_3)_2Cl_2$ (42 mg, 0.06 mmol) and CuI (23 mg, 0.12 mmol) in anhydrous acetonitrile (30 mL) was added Et_3N (333 μL, 2.4 mmol) and 1-hexyne (205 μL, 1.8 mmol) at room temperature under argon. After being stirred overnight, the mixture was quenched with sat. aq. NH_4Cl and extracted with CH_2Cl_2 for three times. The combined organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc: 5/1) to afford **7** (820 mg, 87%) as a yellow foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 1 H), 7.56 (d, *J* = 6.8 Hz, 2 H), 7.51–7.16 (m, 11 H), 5.20 (s, 1 H), 4.81 (dt, *J* = 4.0, 12.4 Hz, 1 H), 4.28 (d, *J* = 9.6 Hz, 1 H), 4.22 (q, *J* = 7.2 Hz, 2 H), 4.10 (m, 1 H), 4.05 (m, 3 H), 3.72 (t, *J* = 10.8 Hz, 1 H), 2.96 (dd, *J* = 3.6, 12.4 Hz, 1 H, H-3*e*), 2.43 (dt, *J* = 1.6, 7.2 Hz, 2 H), 2.36 (t, *J* = 12.4 Hz, 1 H, H-3*a*), 1.63–1.56 (m, 2 H), 1.52–1.45 (m, 5 H), 1.23 (s, 3 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 0.94 (t, *J* = 7.2 Hz, 3 H), 0.88 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 164.1, 159.9, 135.7, 135.6, 135.3, 133.8, 133.3, 132.5, 131.1, 130.0, 129.9, 129.8, 128.0, 127.9, 127.7, 127.6, 124.9, 110.3, 99.2, 96.8, 80.2, 77.0, 76.8, 75.7, 75.3, 62.5, 58.1, 36.3, 30.9, 27.0, 26.9, 26.3, 25.6,

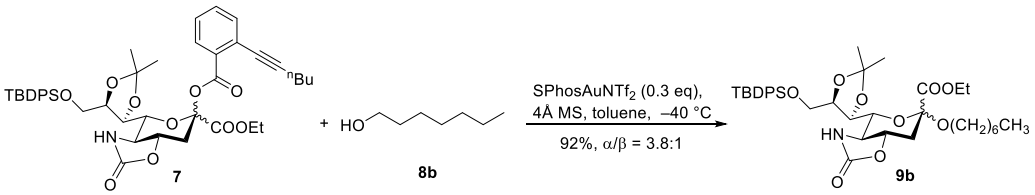
19.8, 19.2, 14.1, 13.8; HRMS (ESI) *m/z* calcd for $C_{44}H_{54}NO_{10}Si$ $[M + H]^+$ 784.3517, found 784.3518.

2.5. Synthesis of ethyl (*N*-benzyl–benzyloxycarbonyl-5-aminopentyl 5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)onate 9a



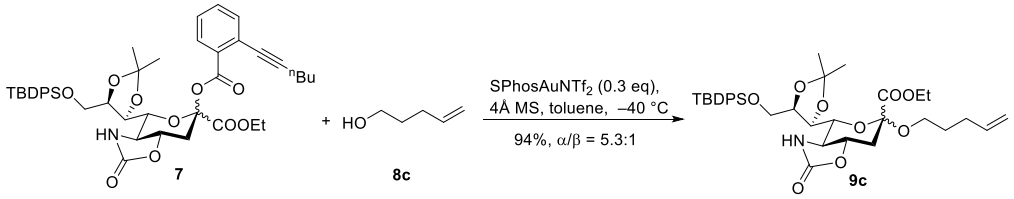
To a solution of compound **7** (78.3 mg, 0.10 mmol) in anhydrous toluene (2.0 mL) was added **8a**[2] (65.4 mg, 0.20 mmol) and freshly activated 4Å MS (200 mg) under argon. After stirring at – 40 °C for 1 h, freshly prepared $SPhosAuNTf_2$ (0.6 mL, 0.05 M in CH_2Cl_2)[3] was added dropwise and the solution was stirred overnight. The mixture was then warmed to room temperature and filtered. The filtrate was evaporated *in vacuo* and purified by silica gel column chromatography (petroleum ether/EtOAc: 5/1 → 3/1) to afford **9a** (86.4 mg, 95%, α only) as a colorless syrup**:** $[\alpha]_D^{25}$ = –19.1 (*c* 0.64, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73–7.69 (m, 4 H), 7.42–7.26 (m, 15 H), 7.17 (m, 1 H), 5.37 (s, 1 H, N*H*), 5.17 (d-like, *J* = 18.6 Hz, 2 H), 4.48 (d-like, *J* = 14.4 Hz, 2 H), 4.41 (dd, *J* = 6.6, 12.0 Hz, 1 H), 4.25 (dd, *J* = 4.8, 11.4 Hz, 1 H), 4.14–4.07 (m, 3 H), 4.03 (dd, *J* = 1.2, 7.2 Hz, 1 H), 4.00 (d-like, *J* = 7.2 Hz, 1 H), 3.89 (m, 1 H), 3.56 (m, 2 H), 3.23 (m, 1 H), 3.15 (m, 1 H), 2.90 (m, 1 H), 2.83 (dd, *J* = 3.0, 12.0 Hz, 1 H, H-3*e*), 1.97 (t, *J* = 12.0 Hz, 1 H, H-3*a*), 1.49–1.33 (m, 11 H), 1.20 (t, *J* = 6.6 Hz, 3 H), 1.06 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6 (C-1, $^3J_{C1,H3ax}$ = 4.8 Hz), 160.1, 138.1, 136.9, 135.9, 133.9, 133.7, 129.8, 129.7, 128.7, 128.6, 128.1, 127.9, 127.7, 127.4, 127.3, 109.9, 100.3, 78.5, 75.8, 75.2, 67.4, 65.2, 63.1, 62.1, 58.2, 50.6, 50.3, 47.2, 46.3, 38.0, 29.3, 28.2, 27.7, 27.0, 26.4, 25.8, 23.5, 19.4, 14.4; HRMS (ESI) *m/z* calcd for $C_{51}H_{65}N_2O_{11}Si$ $[M + H]^+$ 909.4358, found 909.4350.

2.6. Synthesis of ethyl (*n*-heptanyl 5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 9b



To a solution of compound **7** (78.3 mg, 0.10 mmol) in anhydrous toluene (2.0 mL) was added **8b** (28.3 μL, 0.20 mmol) and freshly activated 4Å MS (102 mg) under argon. After stirring at – 40 °C for 1 h, freshly prepared SPhosAuNTf$_2$ (0.6 mL, 0.05 M in CH_2Cl_2) was added dropwise and the solution was stirred overnight. The mixture was then warmed to room temperature and filtered. The filtrate was evaporated *in vacuo* and purified by silica gel column chromatography (petroleum ether/EtOAc: 9/1) to afford **9b** (64.3 mg, 92%, α/β = 3.8/1) as a white foam**. 9bα:** $[\alpha]_D^{25}$ = –28.9 (*c* 0.93, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74–7.70 (m, 4 H), 7.42–7.34 (m, 6 H), 5.42 (s, 1 H, N*H*), 4.41 (dd, *J* = 6.6, 12.0 Hz, 1 H), 4.26 (dd, *J* = 6.0, 10.8 Hz, 1 H), 4.17–4.13 (m, 2 H), 4.11–4.08 (m, 1 H), 4.04 (d, *J* = 6.6 Hz, 1 H), 4.01 (d, *J* = 10.8 Hz, 1 H), 3.90 (dt, *J* = 3.0, 13.8 Hz, 1 H), 3.59–3.55 (m, 2 H), 2.94 (dd, *J* = 6.6, 15.6 Hz, 1 H), 2.86 (dd, *J* = 3.0, 12.0 Hz, 1 H, H-3*e*), 2.00 (t, *J* = 12.4 Hz, 1 H, H-3*a*), 1.45 (s, 3 H), 1.39 (m, 2 H), 1.34 (s, 3 H), 1.29–1.21 (m, 11 H), 1.06 (s, 9 H), 0.88 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7 (C-1, $^3J_{C1,H3ax}$ = 5.5 Hz), 160.2, 135.9, 133.9, 133.8, 129.8, 129.7, 127.7, 109.9, 100.4 (C-2), 78.6, 77.3, 75.8, 75.2, 65.4, 63.2, 62.0, 58.2, 38.0, 31.9, 29.6, 29.2, 27.0, 26.4, 26.1, 25.8, 22.8, 19.4, 14.3, 14.2; HRMS (ESI) *m/z* calcd for $C_{38}H_{54}NO_9Si$ $[M - H]^-$ 696.3568, found 696.3569.

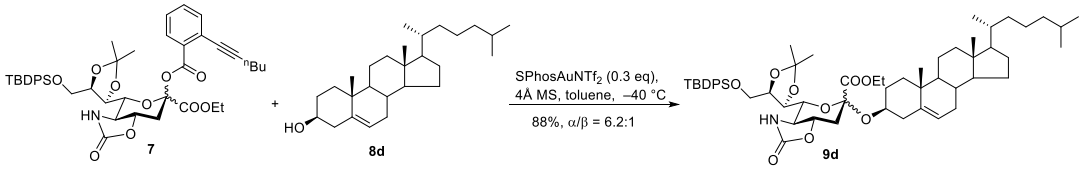
2.7. Synthesis of ethyl (4-penten-1-yl 5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 9c



To a solution of compound **7** (78.3 mg, 0.10 mmol) in anhydrous toluene (2.0 mL) was added **8c** (20.6 mg, 0.20 mmol) and freshly activated 4Å MS (100 mg) under argon. After stirring at – 40 °C for 1 h, freshly prepared SPhosAuNTf$_2$ (0.6 mL, 0.05 M in CH_2Cl_2) was added dropwise and the solution was stirred overnight. The mixture was then warmed to room temperature and filtered. The filtrate was evaporated *in*

vacuo and purified by silica gel column chromatography (petroleum ether/EtOAc: 9/1 → 8/1) to afford **9c** (62.7 mg, 94%, α/β = 5.3/1) as a white foam**. 9cα:** $[\alpha]_D^{25}$ = –24.1 (*c* 1.01, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74–7.71 (m, 4 H), 7.42–7.34 (m, 6 H), 5.78–5.71 (m, 1 H), 5.58 (s, 1 H, N*H*), 4.98–4.92 (m, 2 H), 4.42 (dd, *J* = 6.0, 11.4 Hz, 1 H), 4.25 (dd, *J* = 4.8, 11.4 Hz, 1 H), 4.17–4.08 (m, 3 H), 4.05 (d, *J* = 6.6 Hz, 1 H), 4.00 (d, *J* = 9.6 Hz, 1 H), 3.90 (dt, *J* = 3.0, 13.8 Hz, 1 H), 3.60–3.56 (m, 2 H), 2.96 (dd, *J* = 6.6, 15.6 Hz, 1 H), 2.86 (dd, *J* = 3.0, 11.4 Hz, 1 H, H-3*e*), 2.03–1.98 (m, 3 H), 1.50 (m, 2 H), 1.45 (s, 3 H), 1.35 (s, 3 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 1.06 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.6 (C-1, $^3J_{C1,H3ax}$ = 5.7 Hz), 160.2, 138.2, 135.9, 133.9, 133.8, 129.8, 129.7, 127.7, 114.9, 109.9, 100.4 (C-2), 78.6, 77.2, 75.8, 75.2, 64.6, 63.2, 62.1, 58.2, 38.0, 30.2, 28.7, 27.0, 26.4, 25.8, 19.4, 14.3; HRMS (ESI) *m/z* calcd for $C_{36}H_{48}NO_9Si$ $[M - H]^-$ 666.3098, found 666.3100.

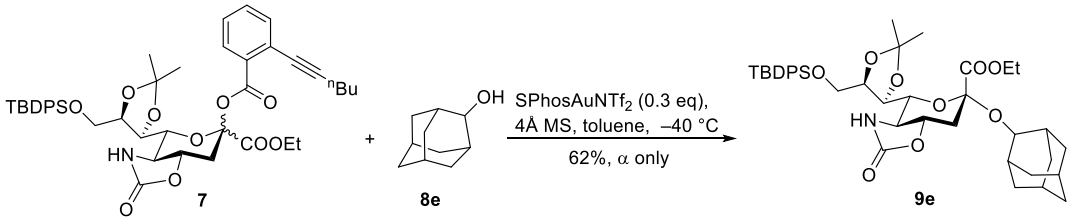
2.8. Synthesis of ethyl (cholesteryl 5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 9d



To a solution of compound **7** (78.3 mg, 0.10 mmol) in anhydrous toluene (2.0 mL) was added **8d** (77.3 mg, 0.20 mmol) and freshly activated 4Å MS (160 mg) under argon. After stirring at – 40 °C for 1 h, freshly prepared $SPhosAuNTf_2$ (0.6 mL, 0.05 M in CH_2Cl_2) was added dropwise and the solution was stirred overnight. The mixture was then warmed to room temperature and filtered. The filtrate was evaporated *in vacuo* and purified by silica gel column chromatography (petroleum ether/EtOAc: 10/1) to afford **9d** (85.2 mg, 88%, α/β = 6.2/1) as a white foam**. 9dα:** $[\alpha]_D^{25}$ = –25.8 (*c* 1.02, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 1.2, 6.6 Hz, 4 H), 7.42–7.34 (m, 6 H), 5.31 (m, 1 H), 5.20 (s, 1 H, N*H*), 4.43 (dd, *J* = 6.6, 11.4 Hz, 1 H), 4.27 (dd, *J* = 4.8, 11.4 Hz, 1 H), 4.20–4.14 (m, 2 H), 4.08 (m, 1 H), 4.03 (d-like, *J* = 7.8 Hz, 2 H), 3.87 (m, 1 H), 3.59 (t, *J* = 10.2 Hz, 1 H), 3.29 (m, 1 H), 2.86 (dd, *J* = 3.6, 12.0 Hz, 1 H, H-3*e*), 2.66 (m, 1 H), 2.14 (m, 1 H), 2.05–1.98 (m, 2 H, H-3*a*), 1.83–1.73 (m, 3 H), 1.63–0.65 (m, 56 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0 (C-1, $^3J_{C1,H3ax}$ = 4.6 Hz), 160.0, 140.5, 135.9, 135.8, 134.0, 129.8, 129.7, 127.8, 127.7,

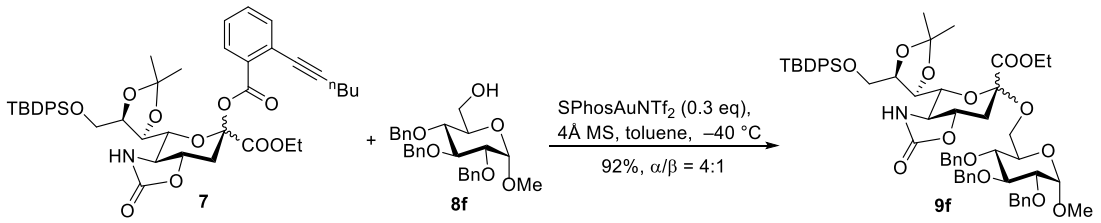
122.3, 109.6, 101.3 (C-2), 78.9, 75.8, 75.3, 63.2, 62.0, 58.4, 57.0, 56.3, 50.2, 42.5, 40.7, 40.0, 39.7, 38.4, 37.6, 36.5, 36.4, 36.0, 32.0, 31.9, 30.4, 29.9, 29.4, 28.4, 28.2, 27.1, 27.0, 26.7, 25.4, 24.4, 24.0, 23.0, 22.7, 21.2, 19.5, 19.4, 18.9, 14.3, 12.0; HRMS (ESI) *m/z* calcd for $C_{58}H_{84}NO_9Si$ $[M - H]^-$ 966.5915, found 966.5914.

2.9. Synthesis of ethyl (adamantan-2-yl 5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)onate 9e



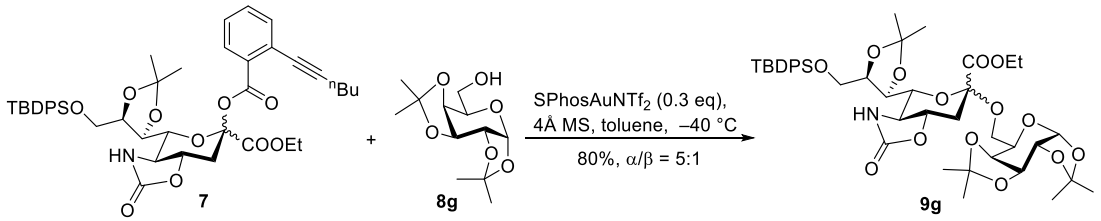
To a solution of compound **7** (78.3 mg, 0.10 mmol) in anhydrous toluene (2.0 mL) was added **8e** (30.4 mg, 0.20 mmol) and freshly activated 4Å MS (110 mg) under argon. After stirring at – 40 °C for 1 h, freshly prepared $SPhosAuNTf_2$ (0.6 mL, 0.05 M in CH_2Cl_2) was added dropwise and the solution was stirred overnight. The mixture was then warmed to room temperature and filtered. The filtrate was evaporated *in vacuo* and purified by silica gel column chromatography (petroleum ether/EtOAc: 9/1) to afford **9e** (45.5 mg, 62%, α only) as a white foam**:** $[\alpha]_D^{25} = -25.3$ (*c* 1.14, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.72 (t, *J* = 7.2 Hz, 4 H), 7.42–7.35 (m, 6 H), 5.30 (s, 1 H, N*H*), 4.39 (dd, *J* = 6.6, 12.0 Hz, 1 H), 4.33 (dd, *J* = 5.4, 11.4 Hz, 1 H), 4.15–4.02 (m, 5 H), 3.88 (dt, *J* = 3.0, 13.8 Hz, 1 H), 3.63 (br s, 1 H), 3.59 (t, *J* = 10.2 Hz, 1 H), 2.90 (dd, *J* = 3.0, 11.4 Hz, 1H, H-3*e*), 2.06–2.02 (m, 2 H), 1.98 (t, *J* = 12.6 Hz, 2 H), 1.72–1.57 (m, 8 H), 1.40–1.33 (m, 9 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 1.07 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.0 (C-1, $^3J_{C1,H3ax}$ = 5.3 Hz), 160.2, 135.9, 135.8, 134.0, 133.9, 130.0, 129.8, 127.8, 127.7, 109.4, 101.0 (C-2), 79.2, 78.9, 75.8, 75.0, 63.3, 61.9, 58.4, 38.4, 37.6, 36.8, 36.5, 33.3, 33.1, 31.6, 27.3, 27.0, 26.9, 26.5, 25.5, 19.4, 14.3; HRMS (ESI) *m/z* calcd for $C_{41}H_{54}NO_9Si$ $[M - H]^-$ 732.3568, found 732.3567.

2.10. Synthesis of ethyl (5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate-(2→6)-2,3,4-tri-*O*-benzyl-1-methyl-α-D-glucopyranoside 9f



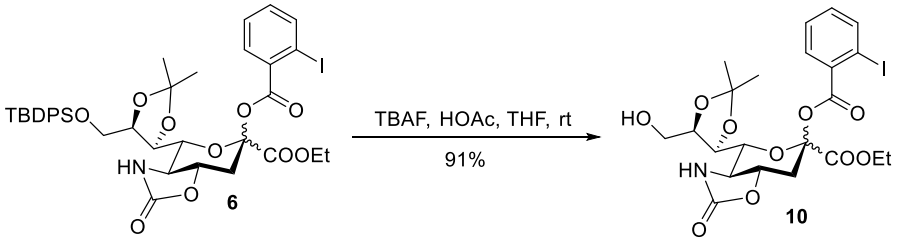
To a solution of compound **7** (78.3 mg, 0.10 mmol) in anhydrous toluene (2.0 mL) was added **8f**[4] (92.8 mg, 0.20 mmol) and freshly activated 4Å MS (180 mg) under argon. After stirring at – 40 °C for 1 h, freshly prepared $SPhosAuNTf_2$ (0.6 mL, 0.05 M in CH_2Cl_2) was added dropwise and the solution was stirred overnight. The mixture was then warmed to room temperature and filtered. The filtrate was evaporated *in vacuo* and purified by silica gel column chromatography (petroleum ether/EtOAc: 8/1 → 5/1) to afford **9f** (96.6 mg, 92%, α/β = 4/1) as a white foam**:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73–7.68 (m, 4 H), 7.40–7.19 (m, 21 H), 5.13 (s, 1 H), 4.94 (d-like, *J* = 10.8 Hz, 1 H), 4.78–4.75 (m, 3 H), 4.64 (d-like, *J* = 12.0 Hz, 1 H), 4.50 (d-like, *J* = 10.8 Hz, 1 H), 4.44 (d, *J* = 3.6 Hz, 11 H), 4.35 (dd, *J* = 6.6, 12.6 Hz, 1 H), 4.29 (dd, *J* = 5.4, 10.8 Hz, 1 H), 4.16 (dd, *J* = 6.6, 11.4 Hz, 1 H), 4.06–3.88 (m, 6 H), 3.75 (dd, *J* = 5.4, 11.4 Hz, 1 H), 3.58–3.52 (m, 2 H), 3.46–3.42 (m, 2 H), 3.36 (t, *J* = 10.2 Hz, 1 H), 3.28 (s, 3 H), 2.92 (dd, *J* = 3.0, 11.4 Hz, 1 H, H-3*e*), 1.98 (t, *J* = 12.0 Hz, 1 H, H-3*a*), 1.35 (s, 3 H), 1.29 (s, 3 H), 1.12 (t, *J* = 7.2 Hz, 3 H), 1.04 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.8 (C-1, $^3J_{C1,H3ax}$ = 5.9 Hz), 159.9, 138.9, 138.5, 138.4, 135.9, 133.8, 133.7, 130.0, 129.8, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.7, 109.9, 100.6, 98.0, 82.3, 80.0, 78.2, 77.7, 77.3, 75.9, 75.8, 75.0, 74.8, 73.5, 69.5, 64.6, 62.9, 62.6, 58.3, 55.2, 37.7, 27.0, 26.4, 25.7, 19.4, 14.2; HRMS (ESI) *m/z* calcd for $C_{59}H_{71}NO_{14}SiNa$ $[M + Na]^+$ 1068.4542, found 1068.4550.

2.11. Synthesis of ethyl (5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate-(2→6)-1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranoside 9g



To a solution of compound **7** (78.3 mg, 0.10 mmol) in anhydrous toluene (2.0 mL) was added **8g**[5] (52.0 mg, 0.20 mmol) and freshly activated 4Å MS (140 mg) under argon. After stirring at – 40 °C for 1 h, freshly prepared SPhosAuNTf$_2$ (0.6 mL, 0.05 M in CH_2Cl_2) was added dropwise and the solution was stirred overnight. The mixture was then warmed to room temperature and filtered. The filtrate was evaporated *in vacuo* and purified by silica gel column chromatography (petroleum ether/EtOAc: 8/1 → 4/1) to afford **9g** (67.6 mg, 80%, α/β = 5/1) as a colorless syrup**:** ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74–7.68 (m, 4 H), 7.42–7.37 (m, 6 H), 5.59 (s, 1 H, N*H*), 5.48 (d, *J* = 4.8 Hz, 1 H), 4.58 (dd, *J* = 2.4, 7.8 Hz, 1 H), 4.33 (dd, *J* = 6.6, 12.6 Hz, 1 H), 4.30–4.26 (m, 2 H), 4.21 (dd, *J* = 1.2, 7.8 Hz, 1 H), 4.18–4.12 (m, 2 H), 4.07 (m, 1 H), 4.03 (m, 2 H), 3.95–3.85 (m, 3 H), 3.58 (t, *J* = 10.8 Hz, 1 H), 3.43 (dd, *J* = 6.0, 7.2 Hz, 1 H), 2.91 (dd, *J* = 3.0, 11.4 Hz, 1 H, H-3*e*), 2.06 (t, *J* = 12.6 Hz, 1 H), 1.50 (s, 3 H), 1.46 (s, 3 H), 1.39 (s, 3 H), 1.32 (s, 6 H), 1.31 (s, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 1.06 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.1 (C-1, $^3J_{C1,H3ax}$ = 5.0 Hz), 160.2, 135.9, 135.8, 133.8, 133.7, 129.8, 128.7, 127.9, 127.8, 110.1, 109.4, 108.7, 100.2, 96.4, 78.0, 77.3, 75.9, 75.3, 70.9, 70.8, 70.7, 66.5, 63.4, 62.7, 62.1, 58.1, 37.7, 31.7, 30.3, 29.9, 27.0, 26.3, 26.2, 26.1, 25.8, 25.1, 24.9, 19.4, 14.2; HRMS (ESI) *m/z* calcd for $C_{43}H_{59}NO_{14}SiNa$ $[M + Na]^+$ 864.3603, found 864.3607.

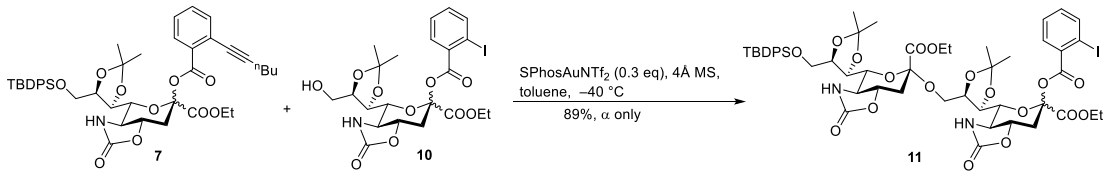
2.12. Synthesis of ethyl (*ortho*-iodobenzoyl 5-amido-7,8-*O*-isopropylidene-5-*N*, 4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 10



To a solution of compound **6** (165.8 mg, 0.2 mmol) in anhydrous THF (2.8 mL) at room temperature was slowly added TBAF (1.2 mL, 1.2 mmol, 1M in THF) and AcOH (137 μL, 2.4 mmol). After being stirred overnight, the mixture was quenched with sat. aq. $NaHCO_3$ and extracted with ethyl acetate for three times. The combined organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a

residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc: 1/1) to afford **10** (107.2 mg, 91%) as a white foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1 H), 7.81 (d, *J* = 8.0 Hz, 1 H), 7.46 (t, *J* = 7.6 Hz, 1 H), 7.23 (t, *J* = 7.6 Hz, 1 H), 5.43 (s, 1 H, N*H*), 4.69 (dt, *J* = 4.0, 12.0 Hz, 1 H), 4.38–4.29 (m, 3 H), 4.25–4.18 (m, 2 H), 3.94 (m, 1 H), 3.88–3.77 (m, 2 H), 2.98 (dd, *J* = 3.6, 12.4 Hz, 1 H, H-3*e*), 2.37 (t, *J* = 12.4 Hz, 1H, H-3*a*), 2.24 (dd, *J* = 5.2, 6.0 Hz, 1 H), 1.57 (s, 3 H), 1.38 (s, 3 H), 1.31 (t, *J* = 7.2 Hz, 3 H); HRMS (ESI) *m/z* calcd for $C_{22}H_{26}O_{10}NINa$ $[M + Na]^+$ 614.0499, found 614.0503.

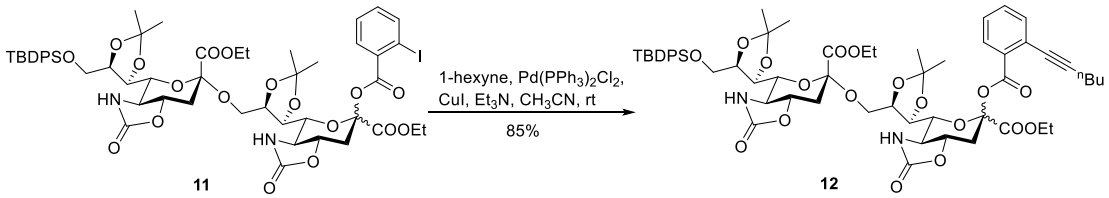
2.13. Synthesis of ethyl (5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropyli dene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)o nate-(2→9)-ethyl (*ortho*-iodobenzoyl 5-amido-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 11



To a solution of compound **7** (78.3 mg, 0.10 mmol) in anhydrous toluene (2.0 mL) was added **10** (118.2 mg, 0.20 mmol) and freshly activated 4Å MS (200 mg) under argon. After stirring at – 40 °C for 1 h, freshly prepared $SPhosAuNTf_2$ (0.6 mL, 0.05 M in CH_2Cl_2) was added dropwise and the solution was stirred overnight. The mixture was then warmed to room temperature and filtered. The filtrate was evaporated *in vacuo* and purified by silica gel column chromatography (petroleum ether/EtOAc: 2/1 → 1/1) to afford **11** (103.8 mg, 89%) as a white foam**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.0 Hz, 1 H), 7.80 (d, *J* = 7.5 Hz, 1 H), 7.68 (t, *J* = 7.5 Hz, 4 H), 7.44–7.36 (m, 7 H), 7.22 (t, *J* = 7.5 Hz, 1 H), 5.52 (s, 1 H, N*H*), 5.49 (s, 1 H, N*H*), 4.72 (dt, *J* = 4.0, 12.0 Hz, 1 H), 4.59 (m, 1 H), 4.34–4.27 (m, 4 H), 4.15–3.96 (m, 7 H), 3.91–3.66 (m, 4 H), 3.42 (t, *J* = 10.5 Hz, 1 H), 2.95 (dd, *J* = 3.5, 12.5 Hz, 1 H, H-3′*e*), 2.59 (dd, *J* = 3.0, 11.5 Hz, 1 H, H-3*e*), 2.37 (t, *J* = 12.5, 1 H, H-3′*a*), 1.86 (t, *J* = 12.5 Hz, 1 H, H-3*a*), 1.50 (s, 3 H), 1.43 (s, 3 H), 1.33–1.29 (m, 9 H), 1.04 (s, 9 H), 1.02 (t, *J* = 7.0 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.8 (C-1, $^3J_{C1,H3ax}$ = 5.7 Hz), 165.5, 164.2, 160.0, 141.7, 135.8, 135.7, 134.3, 133.7, 133.5, 131.9, 129.9, 129.8, 128.2, 128.1, 127.9, 127.8, 110.4, 109.1, 101.6, 99.5, 94.0, 78.4, 76.6, 75.7, 75.6, 75.4, 75.2, 74.7, 64.5, 62.8, 62.7, 62.4, 58.3, 58.0, 37.5, 36.3, 27.0, 26.9, 26.8,

26.3, 25.7, 25.2, 19.3, 14.2, 14.1; HRMS (ESI) *m/z* calcd for $C_{53}H_{65}O_{18}N_2ISiNa$ [M + Na]$^+$ 1195.2944, found 1195.2957.

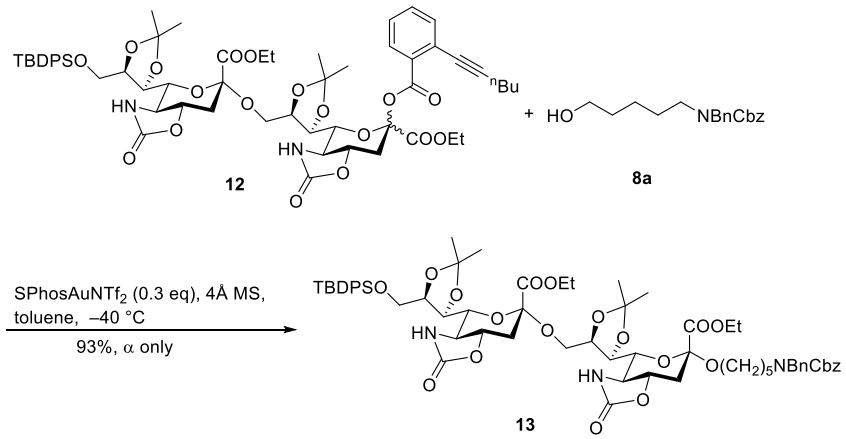
2.14. Synthesis of ethyl (5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)onate-(2→9)-ethyl (*ortho*-hexynylbenzoyl 5-amido-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 12



To a solution of compound **11** (523 mg, 0.45 mmol), $Pd(PPh_3)_2Cl_2$ (32 mg, 0.045 mmol) and CuI (8.6 mg, 0.045 mmol) in anhydrous acetonitrile (9 mL) was added Et_3N (125 μL, 0.90 mmol) and 1-hexyne (76 μL, 0.675 mmol) at room temperature under argon. After being stirred overnight, the mixture was quenched with sat. aq. NH_4Cl and extracted with CH_2Cl_2 for three times. The combined organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc: 3/1 → 2/1) to afford **12** (425 mg, 85%) as a pale brown foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 1.2, 8.0 Hz, 1 H), 7.67 (dt, *J* = 1.6, 7.6 Hz, 4 H), 7.54 (dd, *J* = 0.8, 8.0 Hz, 1 H), 7.48 (dt, *J* = 1.2, 7.6 Hz, 1 H), 7.43–7.32 (m, 7 H), 5.40 (s, 1 H, N*H*), 5.34 (s, 1 H, N*H*), 4.82 (dt, *J* = 4.0, 12.0 Hz, 1 H), 4.57 (dd, *J* = 6.8, 15.2 Hz, 1 H), 4.33–4.23 (m, 4 H), 4.13 (dd, *J* = 5.6, 11.2 Hz, 1 H), 4.08–4.03 (m, 2 H), 4.01–3.86 (m, 5 H), 3.81–3.65 (m, 3 H), 3.33 (t, *J* = 10.8 Hz, 1 H), 2.92 (dd, *J* = 4.0, 12.4 Hz, 1H, H-3′*e*), 2.46–2.42 (m, 3 H, H-3*e*), 2.30 (t, *J* = 12.4 Hz, 1 H, H-3′*a*), 1.82 (t, *J* = 12.4 Hz, 1 H, H-3*a*), 1.62–1.56 (m, 2 H), 1.51 (s, 3 H), 1.49–1.45 (m, 2 H), 1.42 (s, 3 H), 1.30–1.27 (m, 9 H), 1.06–1.03 (m, 12 H), 0.95 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 166.0, 164.2, 159.8, 135.8, 135.3, 133.5, 132.6, 131.1, 130.4, 129.9, 129.8, 127.9, 127.8, 127.5, 124.7, 110.4, 109.1, 101.5, 98.7, 96.7, 80.2, 78.3, 77.4, 77.0, 76.6, 75.8, 75.5, 75.3, 75.1, 74.8, 64.5, 62.7, 62.6, 62.4, 58.4, 58.2, 37.0, 36.7, 30.9, 27.0, 26.9, 26.4, 25.7, 25.2, 22.3, 19.9, 19.4, 14.2, 13.9; HRMS (ESI) *m/z* calcd for $C_{59}H_{74}O_{18}N_2SiNa$ [M + Na]$^+$ 1149.4604, found 1149.4598.

2.15. Synthesis of ethyl (5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropyli

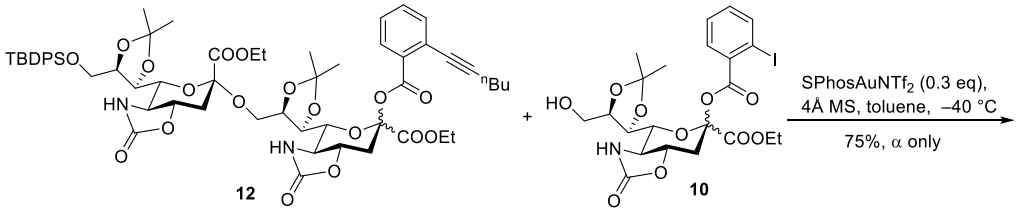
dene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)onate-(2→9)-ethyl (*N*-Benzyl-benzyloxycarbonyl-5-aminopentyl 5-amido-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)onate 13

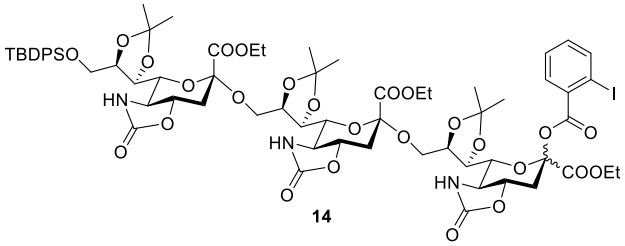


To a solution of compound **12** (56.3 mg, 0.05 mmol) in anhydrous toluene (1.0 mL) was added **8a** (32.7 mg, 0.10 mmol) and freshly activated 4Å MS (100 mg) under argon. After stirring at – 40 °C for 1 h, freshly prepared $SPhosAuNTf_2$ (0.3 mL, 0.05 M in CH_2Cl_2) was added dropwise and the solution was stirred overnight. The mixture was then warmed to room temperature and filtered. The filtrate was evaporated *in vacuo* and purified by silica gel column chromatography (petroleum ether/EtOAc: 3/1 → 3/2) to afford **13** (58.4 mg, 93%, α only) as a white foam**:** $[\alpha]_D^{25}$ = –40.8 (*c* 0.88, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 6.5 Hz, 2 H), 7.67 (d, *J* = 6.5 Hz, 2 H), 7. 43–7.24 (m, 15 H), 7.15 (m, 1 H), 5.70 (s, 1 H, N*H*), 5.68 (s, 1 H, N*H*), 5.16 (d-like, *J* = 16.0 Hz, 2 H), 4.49–4.41 (m, 3 H), 4.34–4.25 (m, 2 H), 4.20 (q, *J* = 7.0 Hz, 2 H), 4.12–3.86 (m, 11 H), 3.70 (m, 1 H), 3.60 (t, *J* = 10.5 Hz, 1 H), 3.54 (t, *J* = 10.5 Hz, 1 H), 3.22–3.15 (m, 2 H), 3.05 (m, 1 H), 2.92 (dd, *J* = 3.0, 11.5 Hz, 1 H, H-3′*e*), 2.86 (dd, *J* = 2.0, 11.5 Hz, 1 H, H-3*e*), 2.11 (t, *J* = 12.5 Hz, 1 H, H-3′*a*), 1.99 (t, *J* = 12.5 Hz, 1 H, H-3*a*), 1.48–1.39 (m, 10 H), 1.33–1.23 (m, 11 H), 1.19 (t, *J* = 7.0 Hz, 3 H), 1.04 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.6 (C-1, $^3J_{C1,H3ax}$ = 5.2 Hz), 168.0 (C-1′, $^3J_{C1',H3'ax}$ = 5.4 Hz), 160.2, 156.3, 138.0, 135.9, 135.8, 135.6, 133.7, 133.6, 123.0, 129.9, 128.7, 128.6, 128.1, 127.9, 127.8, 127.5, 127.3, 110.0, 109.7, 100.9, 100.4, 77.7, 77.3, 76.2, 76.0, 75.6, 75.2, 67.3, 65.2, 64.0, 62.5, 62.4, 62.2, 58.3, 58.1, 50.6, 50.3, 47.2, 46.3, 38.0, 37.4, 29.3, 28.2, 27.8, 27.0, 26.6,

26.3, 25.7, 25.5, 23.6, 19.4, 14.3; HRMS (ESI) *m/z* calcd for $C_{66}H_{85}N_3O_{19}SiK$ $[M + K]^+$ 1290.5184, found 1290.5164.

2.16. Synthesis of ethyl (5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)onate-(2→9)-ethyl (5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)onate-(2→9)-ethyl (*ortho*-iodobenzoyl 5-amido-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 14

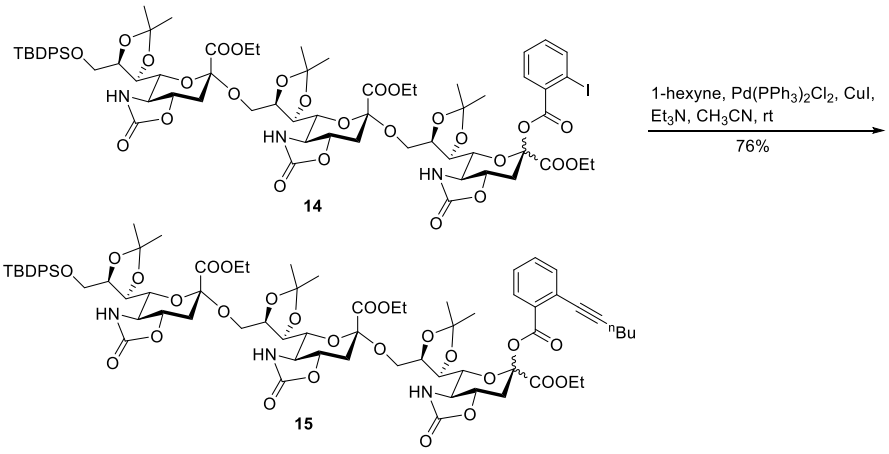




To a solution of compound **12** (56.3 mg, 0.05 mmol) in anhydrous toluene (1.0 mL) was added **10** (59.1 mg, 0.10 mmol) and freshly activated 4Å MS (100 mg) under argon. After stirring at – 40 °C for 1 h, freshly prepared $SPhosAuNTf_2$ (0.3 mL, 0.05 M in CH_2Cl_2) was added dropwise and the solution was stirred overnight. The mixture was then warmed to room temperature and filtered. The filtrate was evaporated *in vacuo* and purified by silica gel column chromatography (petroleum ether/EtOAc: 2/1 → 1/1) to afford **14** (57.2 mg, 75%, α only) as a white foam**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 1 H), 7.80 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.71–7.66 (m, 4 H), 7.48–7.35 (m, 7 H), 7.23 (dd, *J* = 1.6, 8.0 Hz, 1 H), 5.38 (s, 1 H, NH), 5.33 (s, 1 H, N*H*), 5.30 (s, 1H, N*H*), 4.74 (dt, *J* = 4.0, 12.0 Hz, 1 H), 4.56 (dd, *J* = 6.4, 14.8 Hz, 1 H), 4.42 (dd, *J* = 6.4, 12.8 Hz, 1 H), 4.33–4.23 (m, 5 H), 4.19–3.79 (m, 16 H), 3.73 (t, *J* = 11.2 Hz, 1 H), 3.58 (t, *J* = 10.4 Hz, 1 H), 3.42 (t, *J* = 10.8 Hz, 1 H), 2.95 (dd, *J* = 3.6, 12.4 Hz, 1 H, H-3″*e*), 2.89 (dd, *J* = 3.6, 12.0 Hz, 1 H, H-3′*e*), 2.65 (dd, *J* = 3.6, 12.0 Hz, 1 H, H-3*e*), 2.35 (t, *J* = 12.4 Hz, 1 H, H-3″*a*), 2.04 (t, *J* = 12.0 Hz, 1 H, H-3′*a*), 1.88 (t, *J* = 12.4 Hz, 1 H, H-3*a*), 1.50 (s, 3 H), 1.42 (s, 3 H),

1.38 (s, 3 H), 1.32–1.25 (m, 12 H), 1.21 (t, *J* = 6.8 Hz, 3 H), 1.14 (t, *J* = 7.2 Hz, 3 H), 1.05 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 167.8, 165.6, 164.3, 159.9, 159.7, 159.6, 141.8, 135.9, 135.8, 134.3, 133.8, 133.6, 132.0, 130.0, 129.9, 128.3, 128.0, 127.9, 110.4, 109.5, 109.2, 101.4, 101.2, 99.5, 94.0, 78.1, 76.5, 76.0, 75.9, 75.6, 75.5, 75.2, 75.1, 74.8, 64.4, 63.7, 62.9, 62.7, 62.6, 58.4, 58.3, 58.0, 37.5, 37.4, 36.5, 27.0, 26.9, 26.7, 26.3, 25.8, 25.4, 25.3, 19.4, 14.3, 14.2; HRMS (ESI) *m/z* calcd for $C_{68}H_{86}O_{26}N_3ISiNa$ $[M + Na]^+$ 1538.4211, found 1538.4205.

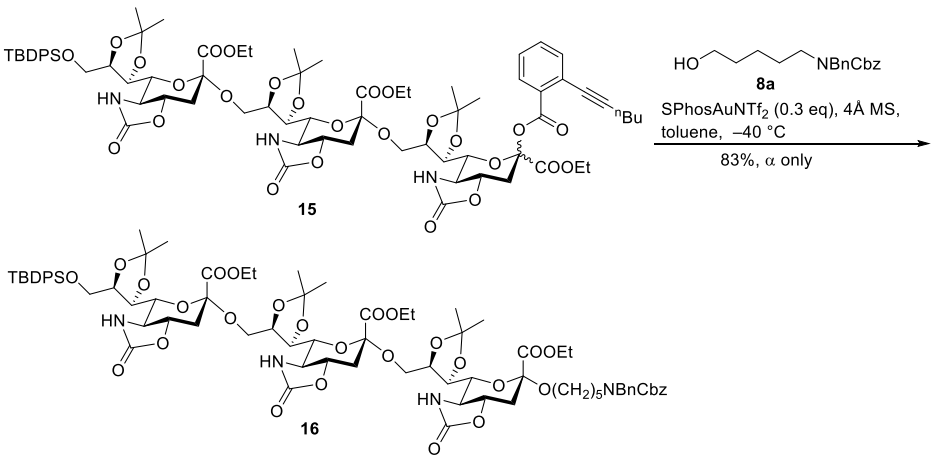
2.17. Synthesis of ethyl (5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropyli dene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)o nate-(2→9)-ethyl (5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)onate-(2→9)-ethyl (*ortho*-hexynylbenzoyl 5-amido-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-D-*galacto*-non-2-ulopyranoside)onate 15



To a solution of compound **14** (57.2 mg, 0.038 mmol), $Pd(PPh_3)_2Cl_2$ (2.7 mg, 0.0038 mmol) and CuI (0.8 mg, 0.0038 mmol) in anhydrous acetonitrile (1 mL) was added Et_3N (10.6 μL, 0.076 mmol) and 1-hexyne (6.5 μL, 0.057 mmol) at room temperature under argon. After being stirred overnight, the mixture was quenched with sat. aq. NH_4Cl and extracted with CH_2Cl_2 for three times. The combined organic layer was dried over Na_2SO_4, filtered and concentrated *in vacuo* to give a residue, which was purified by silica gel column chromatography (petroleum ether/EtOAc: 3/1 → 1/1) to afford **15** (42.1 mg, 76%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 1 H), 7.71–7.66 (m, 4 H), 7.56 (dd, *J* = 0.8, 7.6 Hz, 1 H), 7.50 (dt, *J* = 1.2, 7.6 Hz, 1 H), 7.44–7.34 (m, 7 H), 5.28 (s, 1 H, N*H*), 5.25 (s, 1 H, N*H*), 5.18 (s, 1 H, N*H*), 4.83 (dt, *J* = 3.6, 11.6 Hz, 1 H), 4.54 (dd, *J* = 6.8, 14.0 Hz, 1 H), 4.39 (dd, *J*

= 6.4, 12.4 Hz, 1 H), 4.33–4.23 (m, 5 H), 4.20–3.96 (m, 11 H), 3.93–3.77 (m, 5 H), 3.71 (t, *J* = 11.2 Hz, 1 H), 3.58 (t, *J* = 10.4 Hz, 1 H), 3.31 (t, *J* = 10.8 Hz, 1 H), 2.93 (dd, *J* = 3.6, 12.4 Hz, 1 H, H-3″*e*), 2.87 (dd, *J* = 3.6, 12.0 Hz, 1 H, H-3′*e*), 2.50 (dd, *J* = 3.2, 11.6 Hz, 1 H, H-3*e*), 2.46–2.42 (m, 2 H), 2.29 (t, *J* = 12.4 Hz, 1 H, H-3″*a*), 2.05 (t, *J* = 12.4 Hz, 1 H, H-3′*a*), 1.86 (t, *J* = 12.4 Hz, 1 H, H-3*a*), 1.58 (m, 2 H), 1.50 (s, 3 H), 1.46 (m, 2 H), 1.41 (s, 3 H), 1.37 (s, 3 H), 1.29–1.25 (m, 12 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 1.14 (t, *J* = 7.2 Hz, 3 H), 1.05 (s, 9 H), 0.95 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 167.8, 165.9, 164.3, 159.9, 159.7, 159.6, 147.3, 135.9, 135.3, 133.6, 133.0, 132.7, 132.3, 132.2, 132.1, 131.1, 130.4, 130.0, 129.9, 128.7, 128.6, 127.9, 127.8, 127.6, 124.7, 124.6, 124.2, 119.3, 110.4, 109.5, 109.2, 101.3, 101.1, 98.8, 96.7, 80.2, 78.0, 76.6, 75.9, 75.7, 75.5, 75.2, 75.1, 74.9, 74.8, 64.3, 63.8, 62.6, 62.5, 62.4, 58.4, 58.3, 58.1, 37.3, 36.9, 36.8, 35.0, 32.1, 31.6, 30.9, 30.4, 29.9, 29.5, 27.0, 26.9, 26.7, 26.4, 25.7, 25.4, 25.3, 22.9, 22.3, 19.8, 19.4, 14.3, 14.2, 13.9; HRMS (ESI) *m/z* calcd for $C_{74}H_{95}O_{26}N_3SiNa$ $[M + Na]^+$ 1492.5871, found 1492.5874.

2.18. Synthesis of ethyl (5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropyli dene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)o nate-(2→9)-ethyl (5-amido-9-*O*-*tert*-butyldiphenylsilyl-7,8-*O*-isopropylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranoside)onate-(2→9)-ethyl (*N*-Benzyl-benzyloxycarbonyl-5-aminopentyl 5-amido-7,8-*O*-isopro pylidene-5-*N*,4-*O*-carbonyl-3,5-dideoxy-D-*glycero*-α-D-*galacto*-non-2-ulopyranosi de)onate 16



To a solution of compound **15** (41.0 mg, 0.028 mmol) in anhydrous toluene (0.6 mL) was added **8a** (18.3 mg, 0.056 mmol) and freshly activated 4Å MS (60 mg) under argon. After stirring at – 40 °C for 1 h, freshly prepared $SPhosAuNTf_2$ (0.3 mL,

0.028 M in CH_2Cl_2) was added dropwise and the solution was stirred overnight. The mixture was then warmed to room temperature and filtered. The filtrate was evaporated *in vacuo* and purified by silica gel column chromatography (petroleum ether/EtOAc: 3/2) to afford **16** (36.9 mg, 83%) as a colorless syrup**:** $[\alpha]_D^{25} = -47.1$ (*c* 0.77, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72–7.67 (m, 4 H), 7.43–7.24 (m, 15 H), 7.15 (m, 1 H), 5.62 (s, 1 H, N*H*), 5.60 (s, 1 H, N*H*), 5.57 (s, 1 H, N*H*), 5.16 (d-like, *J* = 21.0 Hz, 2 H), 4.48 (d-like, *J* = 12.6 Hz, 2 H), 4.45–4.39 (m, 2 H), 4.32–4.09 (m, 12 H), 4.04–3.87 (m, 10 H), 3.73 (m, 1 H), 3.61–3.57 (m, 2 H), 3.52 (t, *J* = 10.2 Hz, 1 H), 3.24 (m, 1 H), 3.17 (m, 1 H), 3.11 (m, 1 H), 2.95 (dd, *J* = 3.0, 11.4 Hz, 1 H, H-3″*e*), 2.91–2.88 (m, 2 H, H-3′*e*, H-3*e*), 2.13–2.08 (m, 2 H, H-3″*a*, H-3′*a*), 2.00 (t, *J* = 12.0 Hz, 1 H, H-3*a*), 1.52–1.46 (m, 4 H), 1.45–1.41 (m, 8 H), 1.32–1.25 (m, 18 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 1.05 (s, 9 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.7 (C-1, $^3J_{C1,H3ax}$ = 5.1 Hz), 168.1 (C-1′, $^3J_{C1',H3'ax}$ = 5.4 Hz), 167.8 (C-1″, $^3J_{C1'',H3''ax}$ = 5.2 Hz), 160.1, 160.0, 138.0, 135.8, 133.6, 133.5, 130.0, 129.9, 128.7, 128.6, 128.1, 128.0, 127.9, 127.4, 127.3, 110.1, 109.6, 109.5, 101.1, 100.6, 100.4, 77.9, 77.3, 75.9, 75.8, 75.7, 75.6, 75.2, 75.1, 67.3, 65.1, 63.6, 62.6, 62.5, 62.3, 58.3, 58.2, 58.0, 50.6, 50.3, 47.2, 46.3, 37.9, 37.2, 37.1, 29.3, 28.2, 27.8, 27.0, 26.7, 26.6, 26.2, 25.8, 25.5, 25.4, 23.6, 19.4, 14.4, 14.3; HRMS (ESI) *m/z* calcd for $C_{81}H_{106}O_{27}N_4SiNa$ $[M + Na]^+$ 1617.6711, found 1617.6694.

3. References

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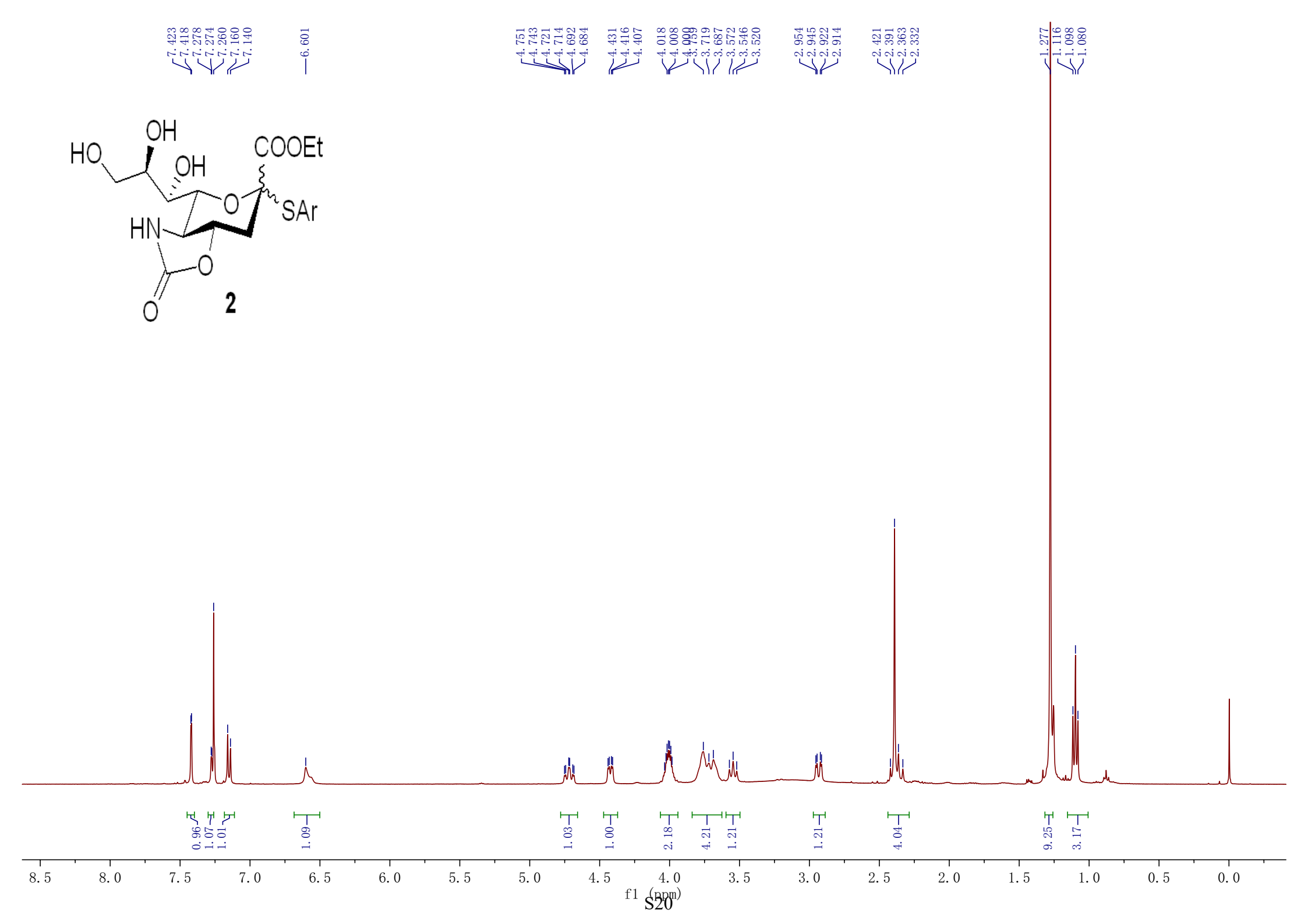
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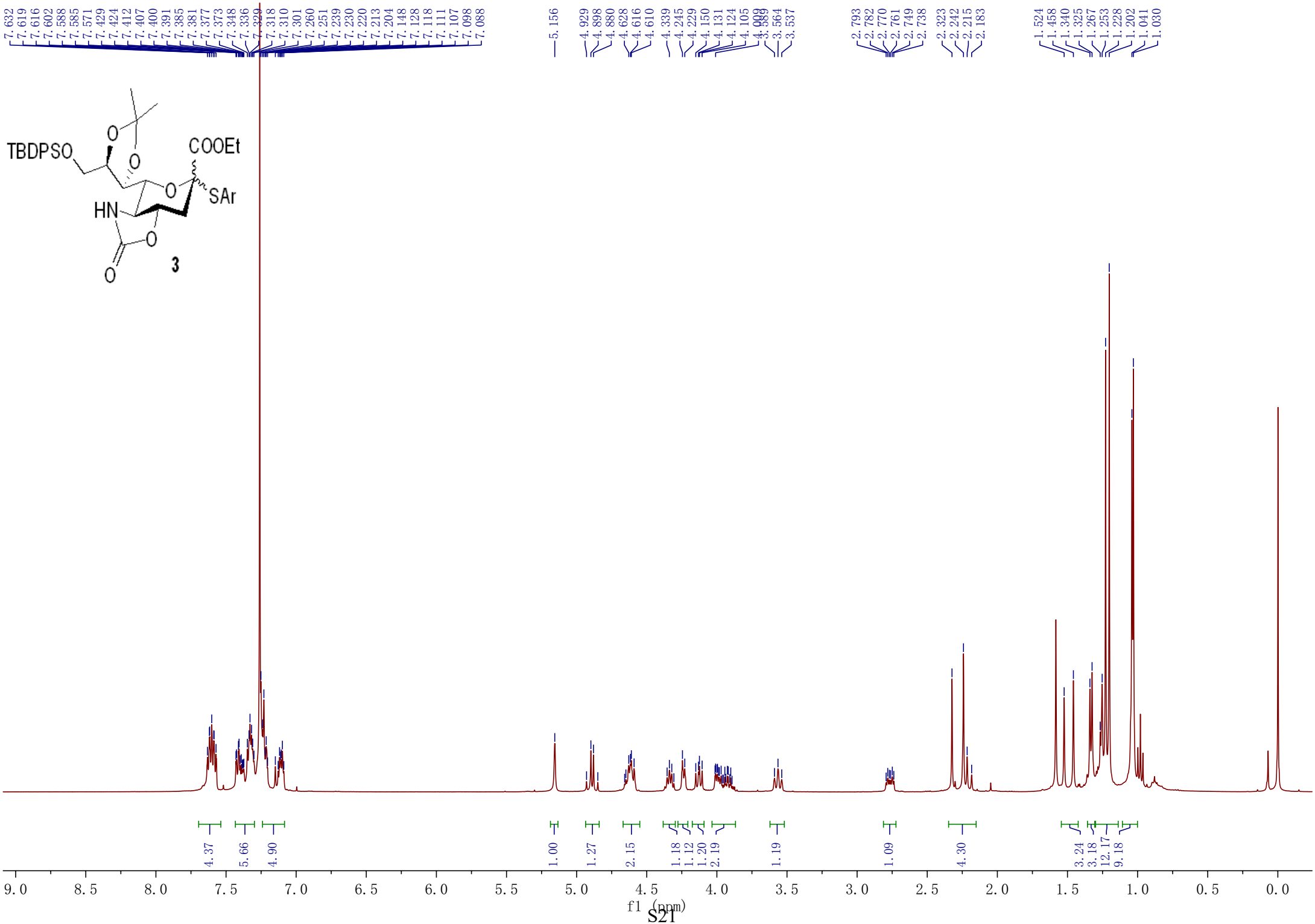
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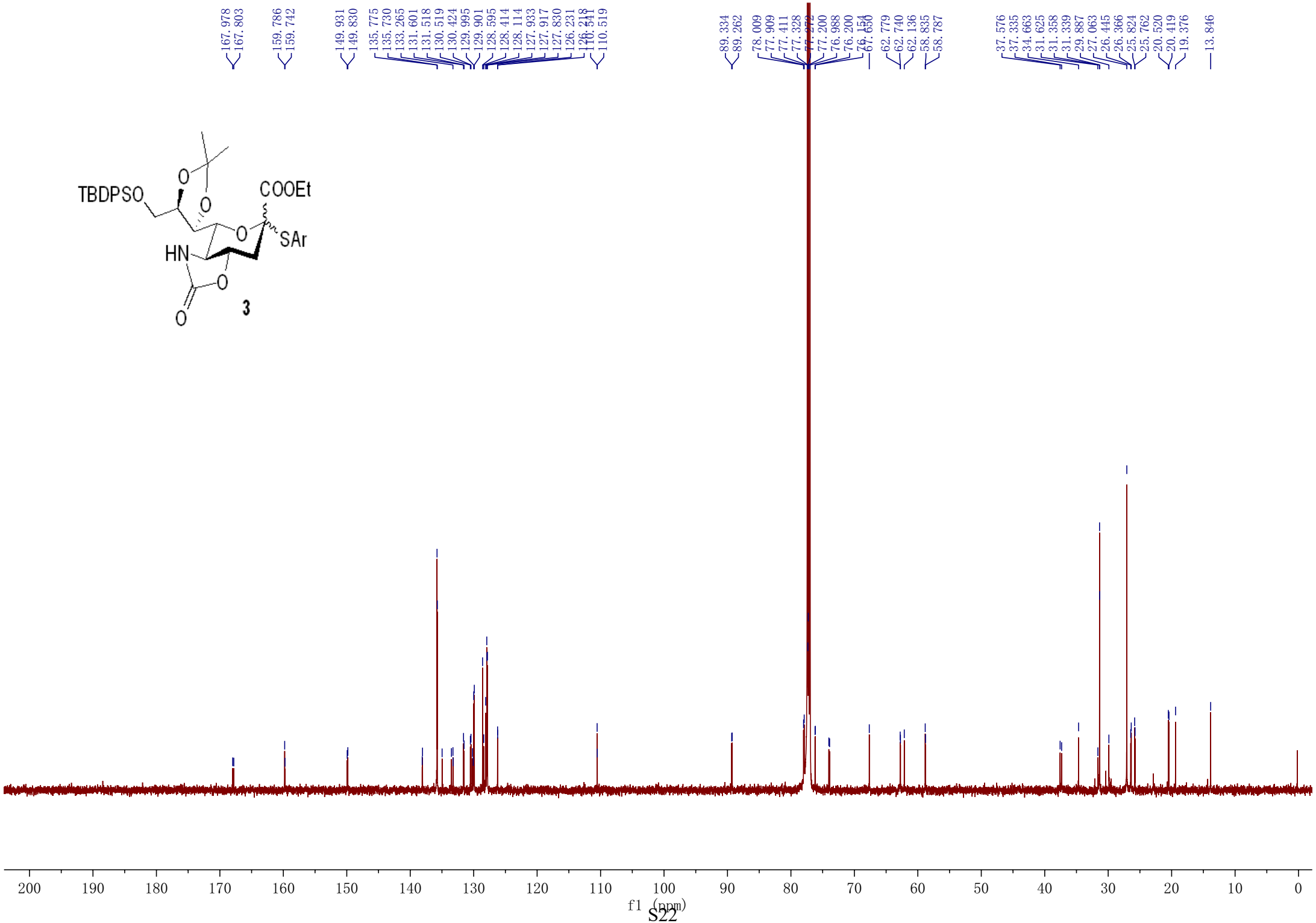
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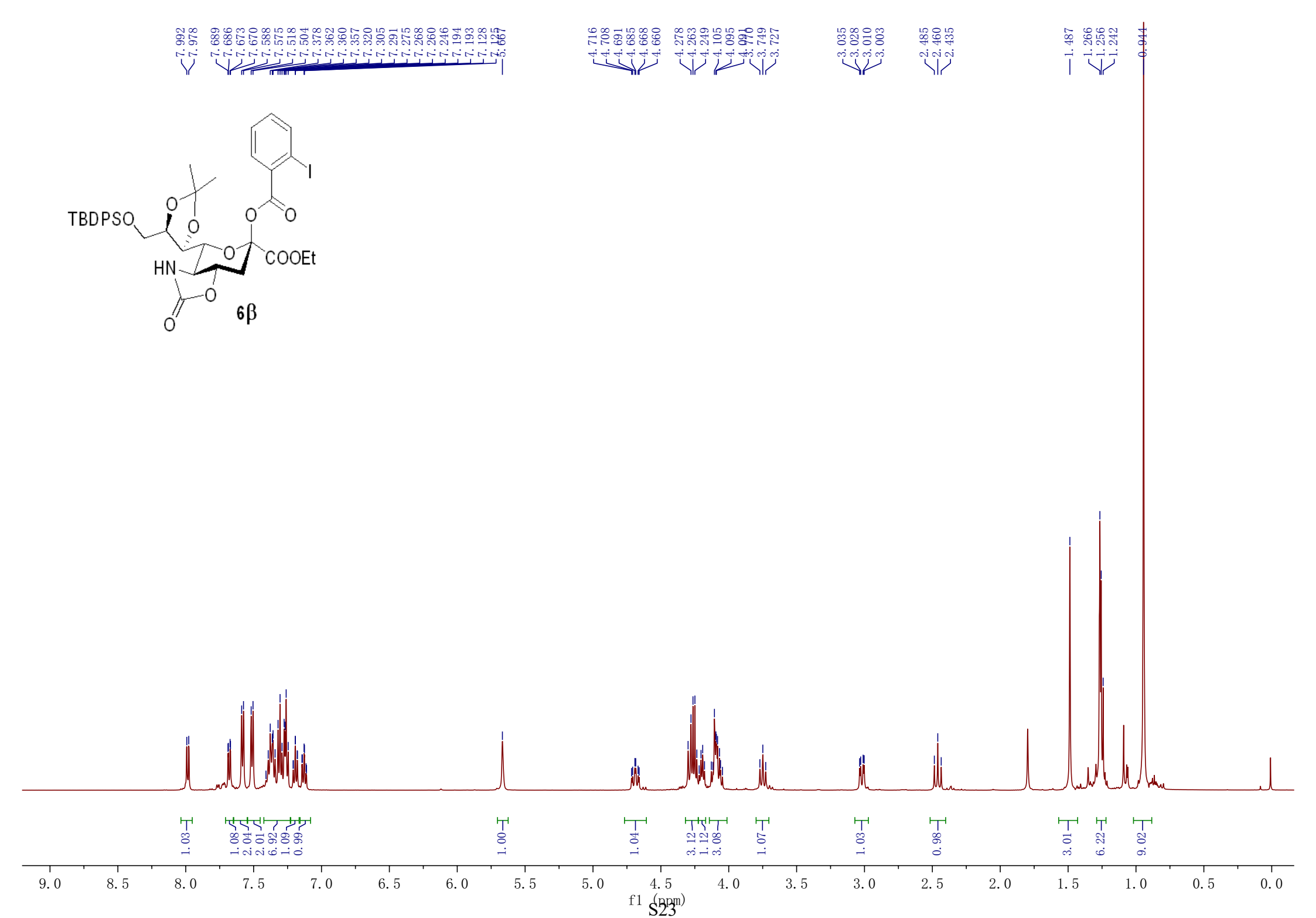
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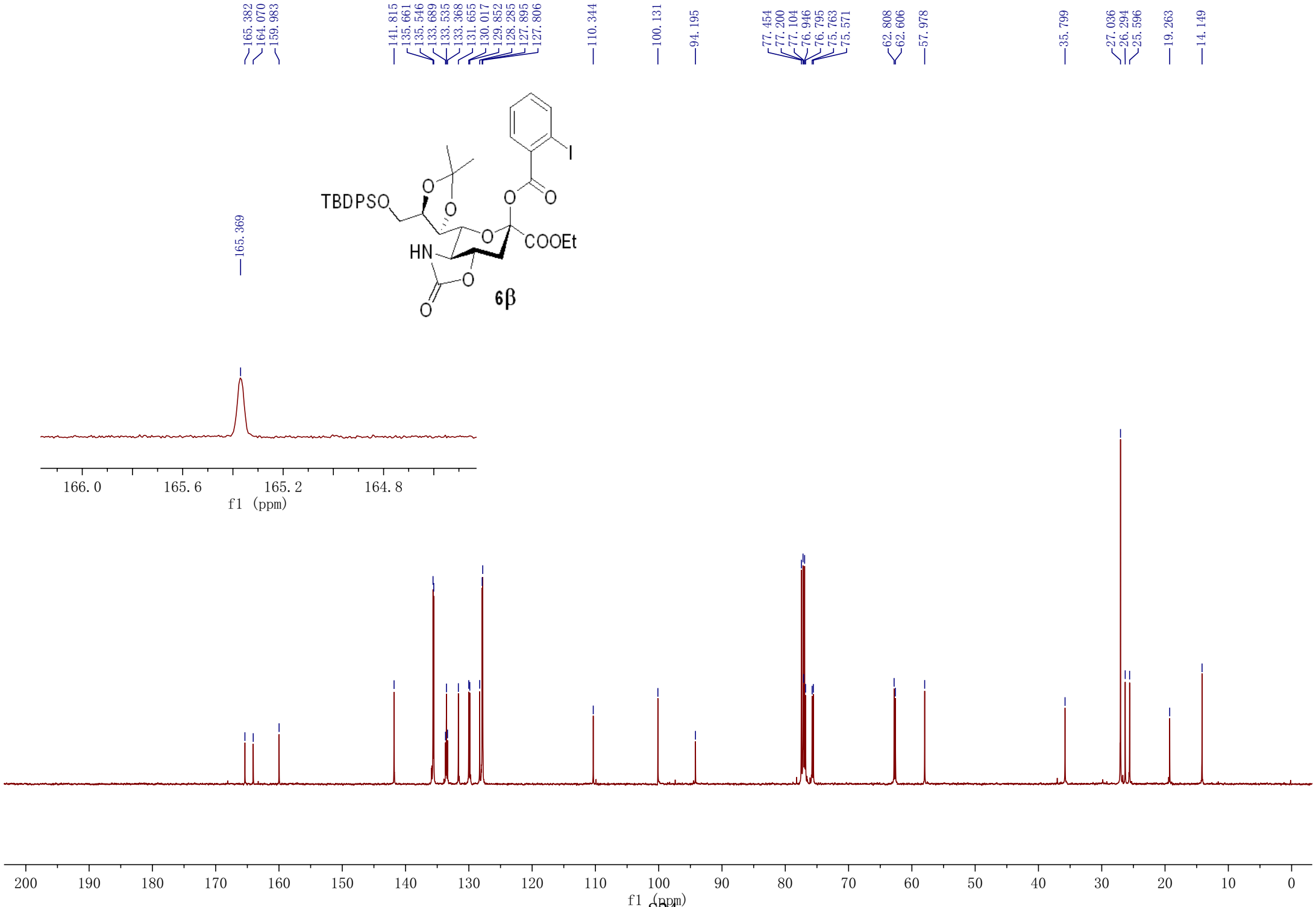
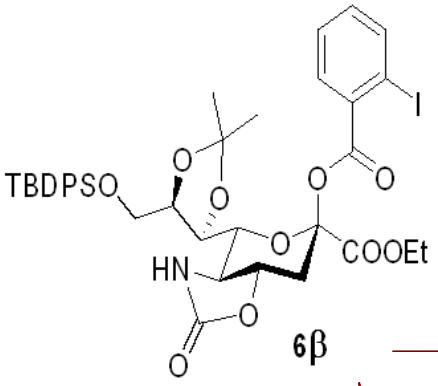
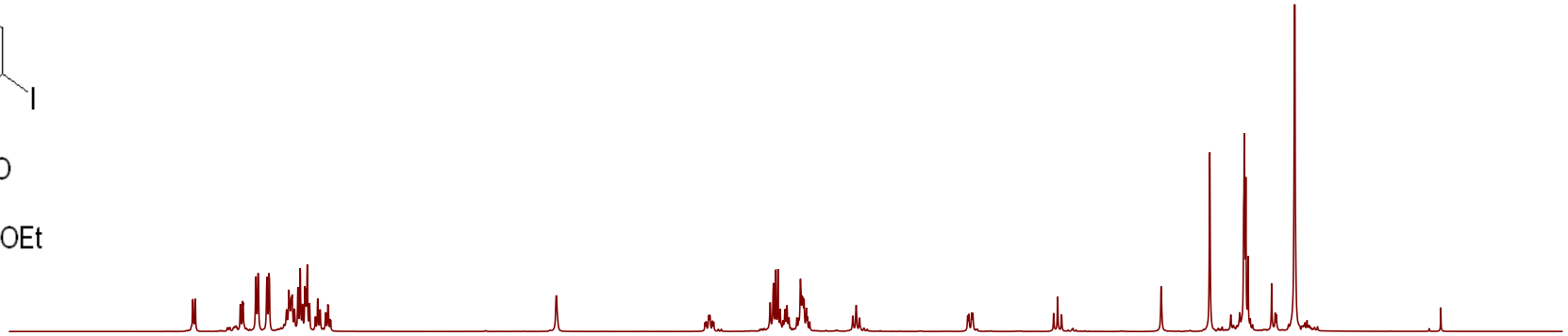
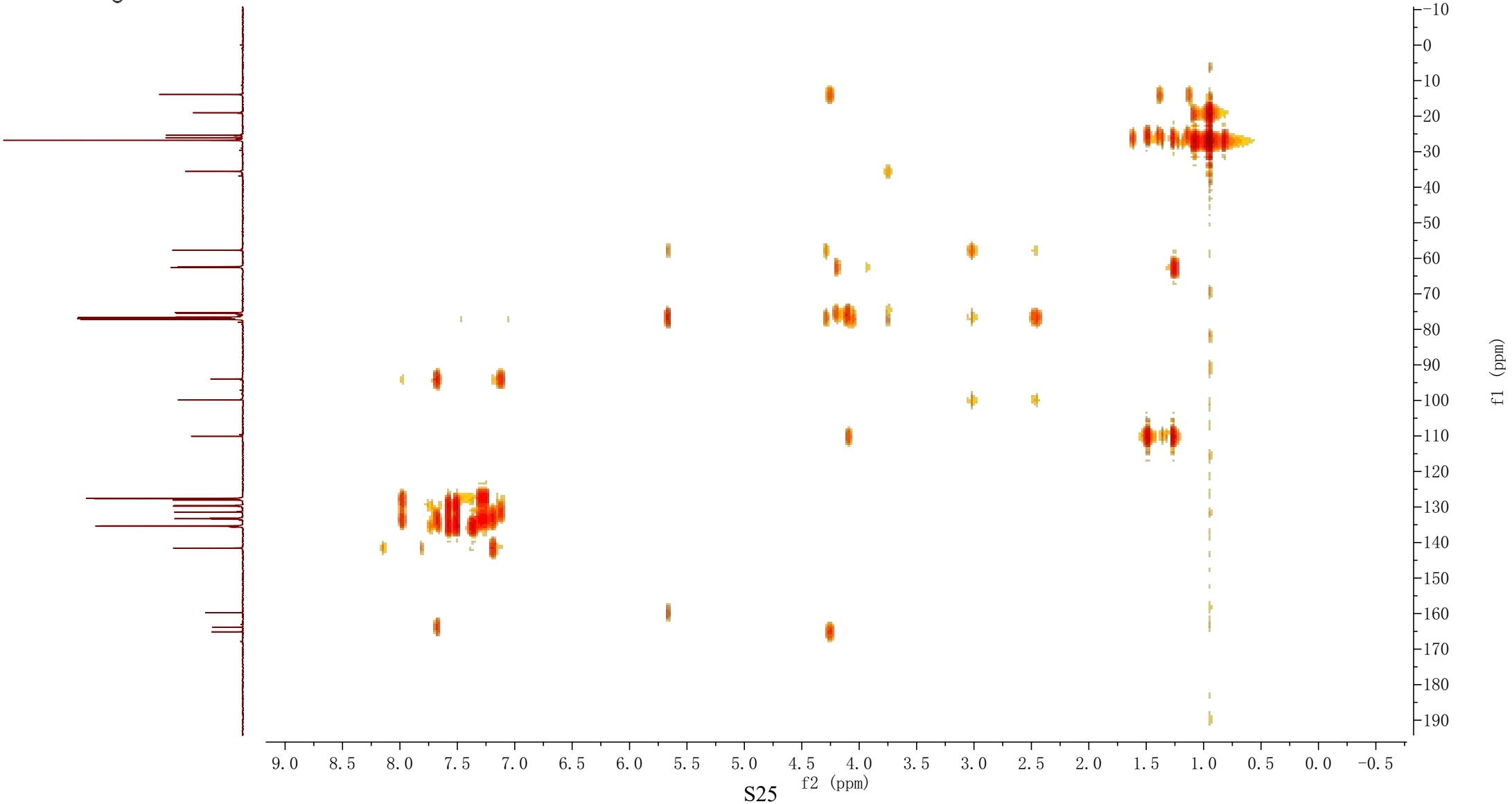
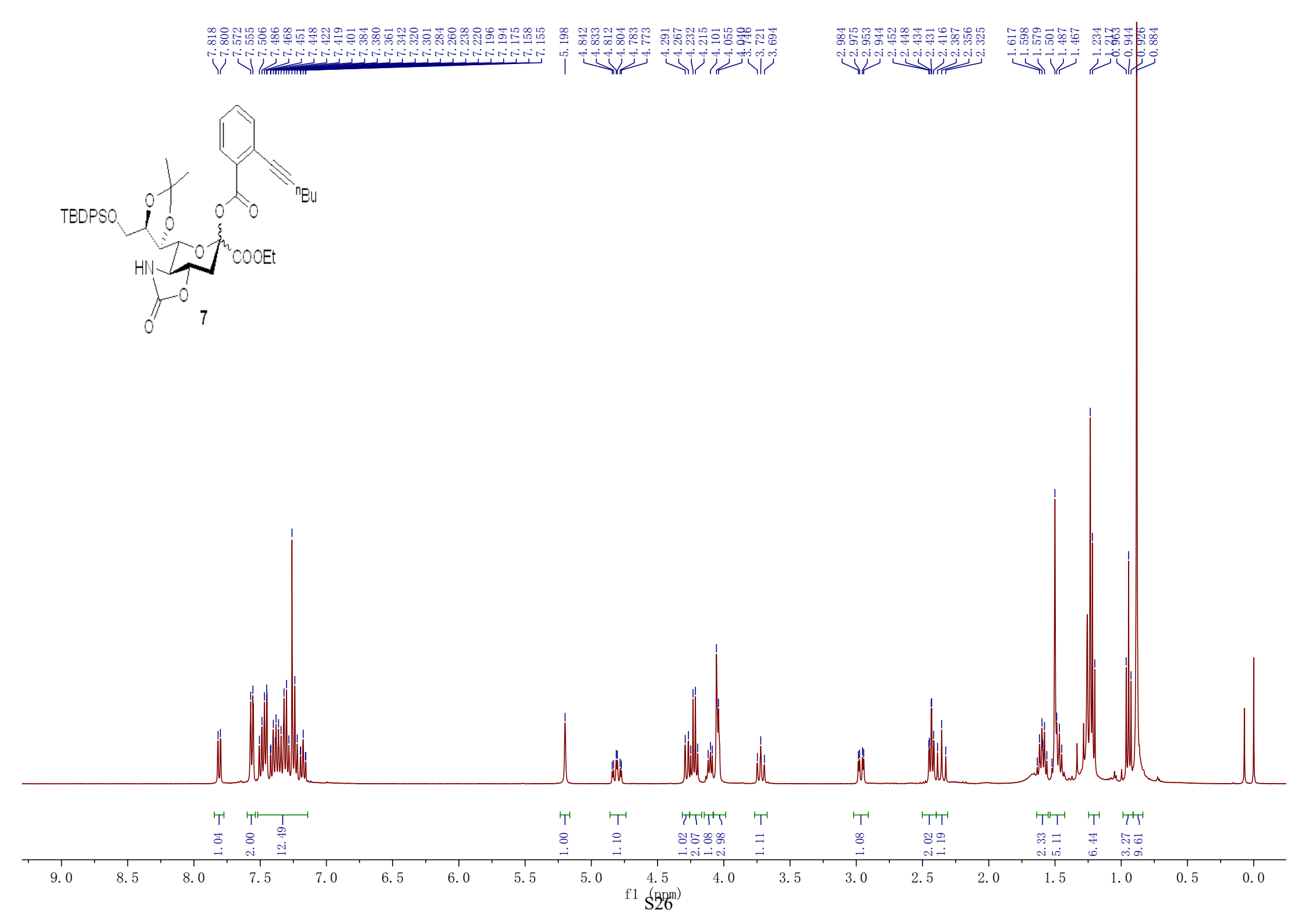
f1 (ppm)

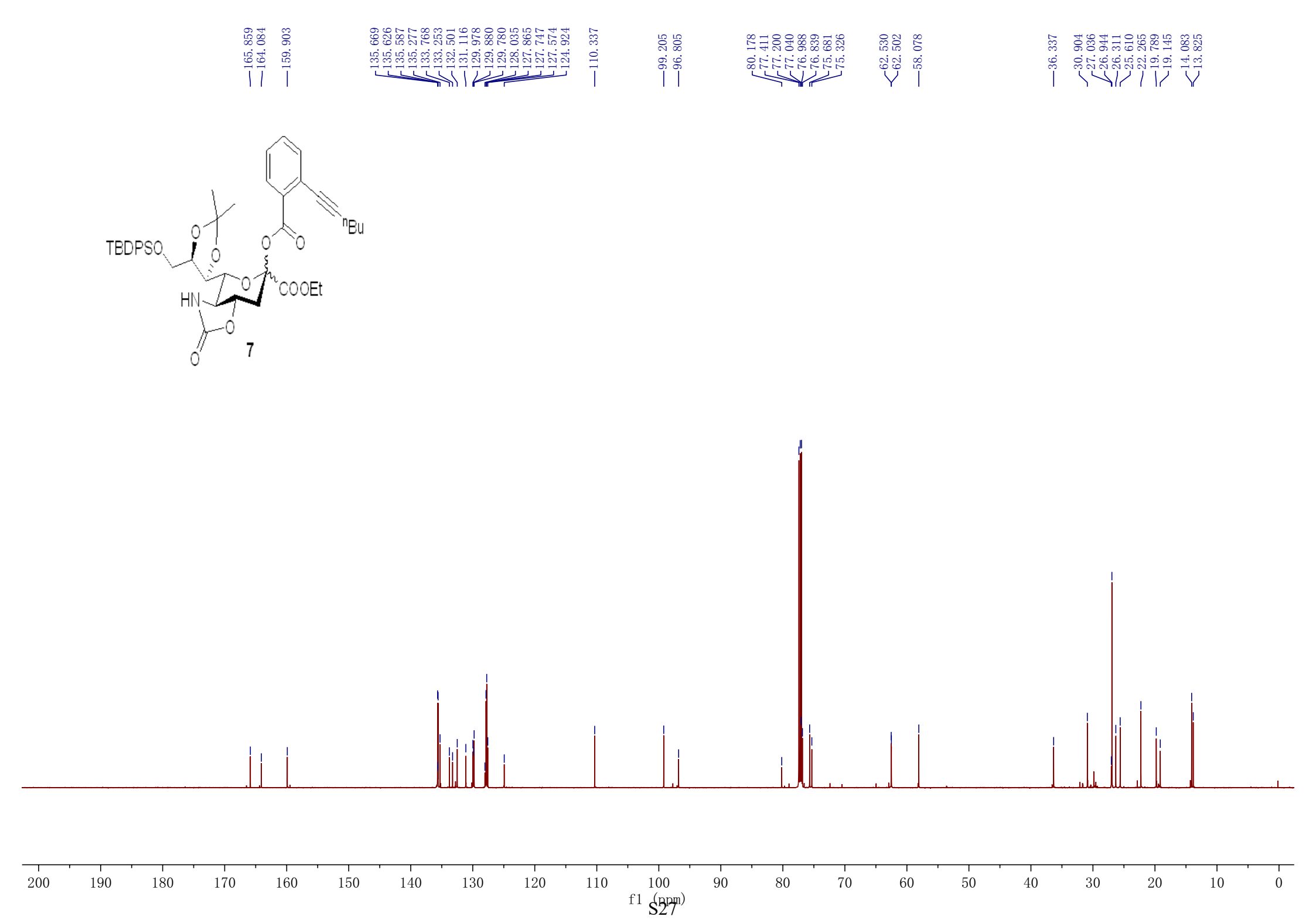

165.382
164.070
159.983
141.815
135.661
135.546
133.689
133.535
133.368
131.655
130.017
129.852
128.285
127.895
127.806
110.344
100.131
94.195
77.454
77.200
77.104
76.946
76.795
75.763
75.571
62.808
62.606
57.978
35.799
27.036
26.294
25.596
19.263
14.149
165.369
TBDPSO
O
O
O
O
O
HN
O
O
I
COOEt
6β
166.0
165.6
165.2
164.8
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

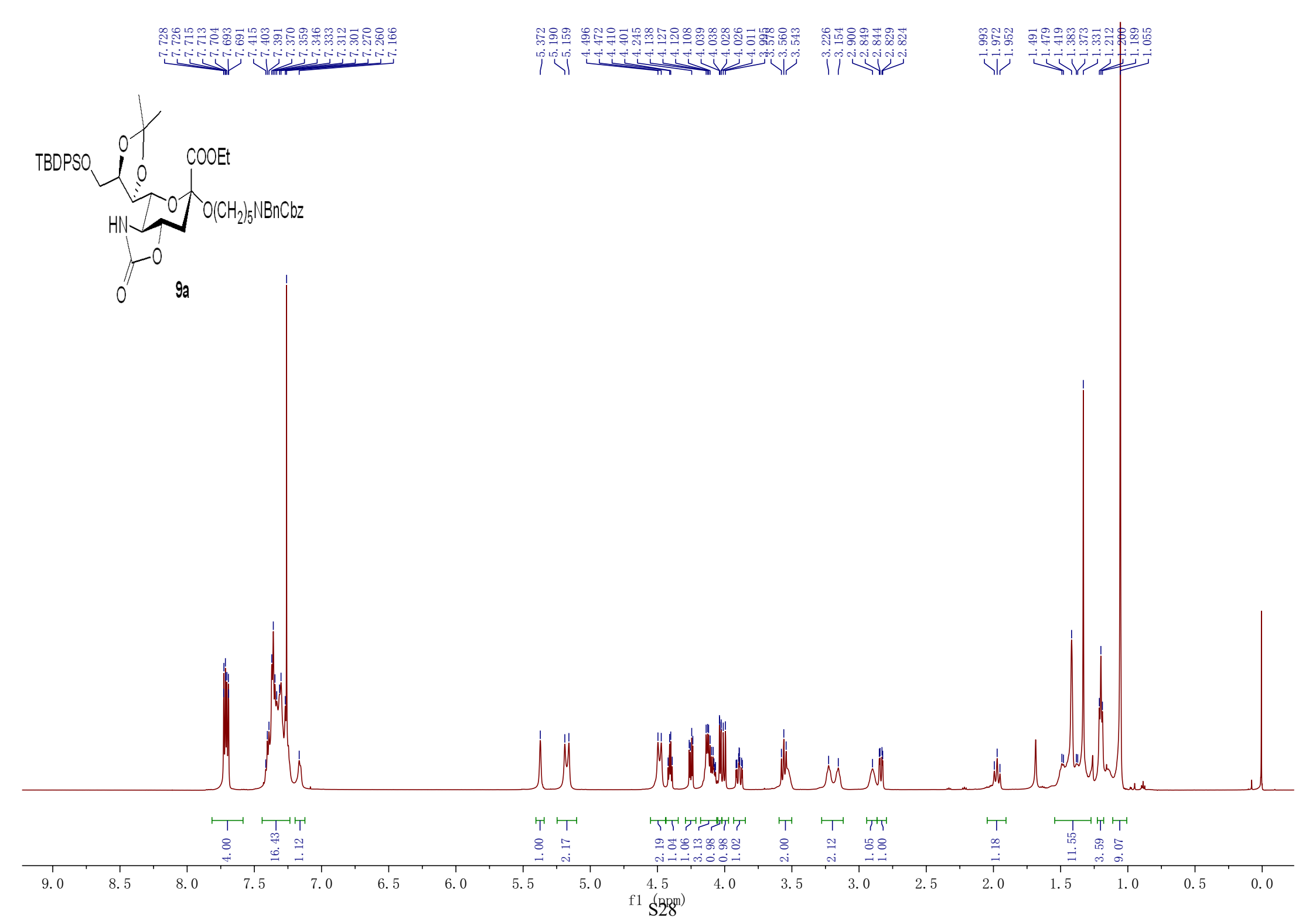

TBDPSO
O
O
O
O
O
I
O
O
COOEt
HN
O
O
6β

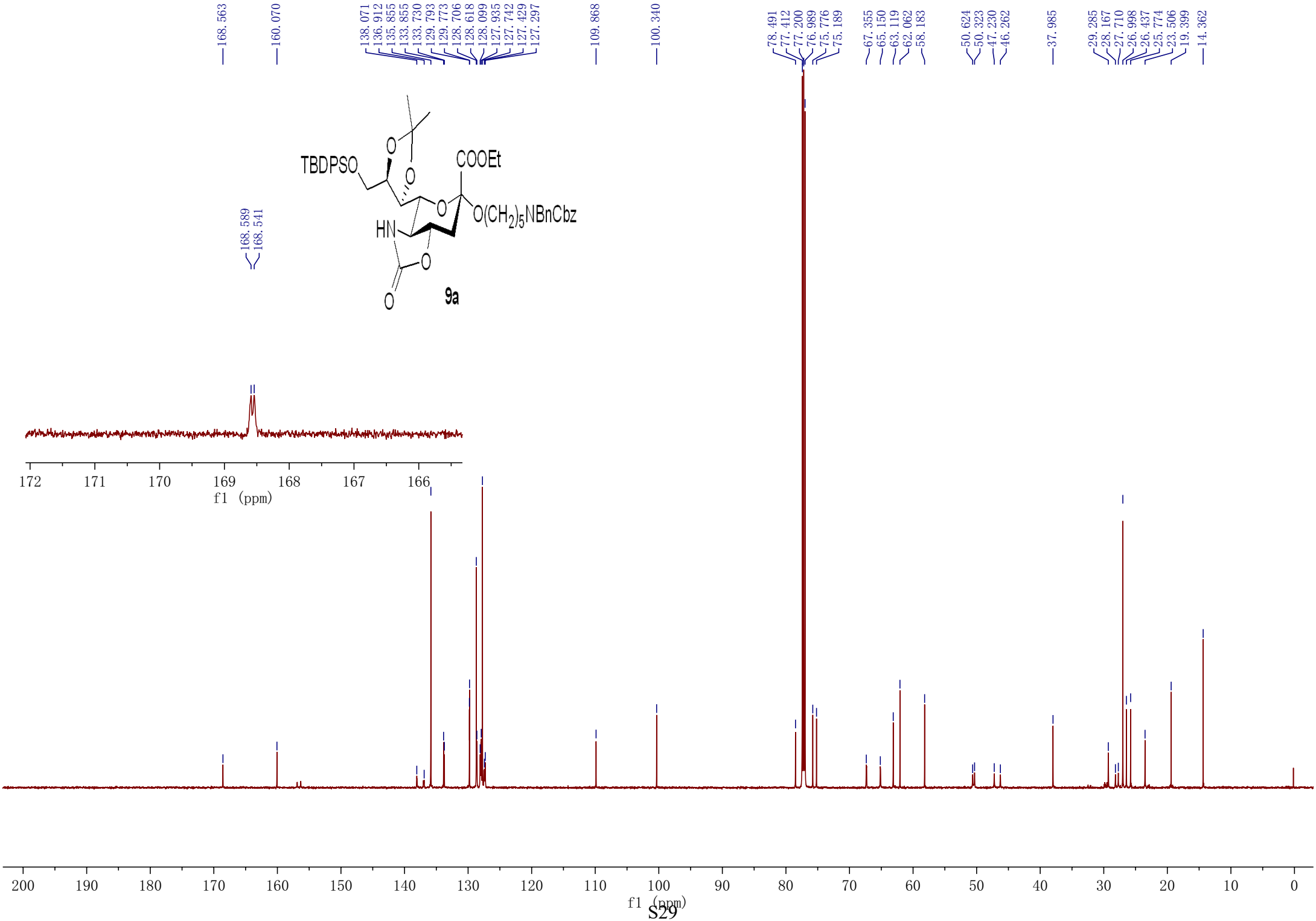


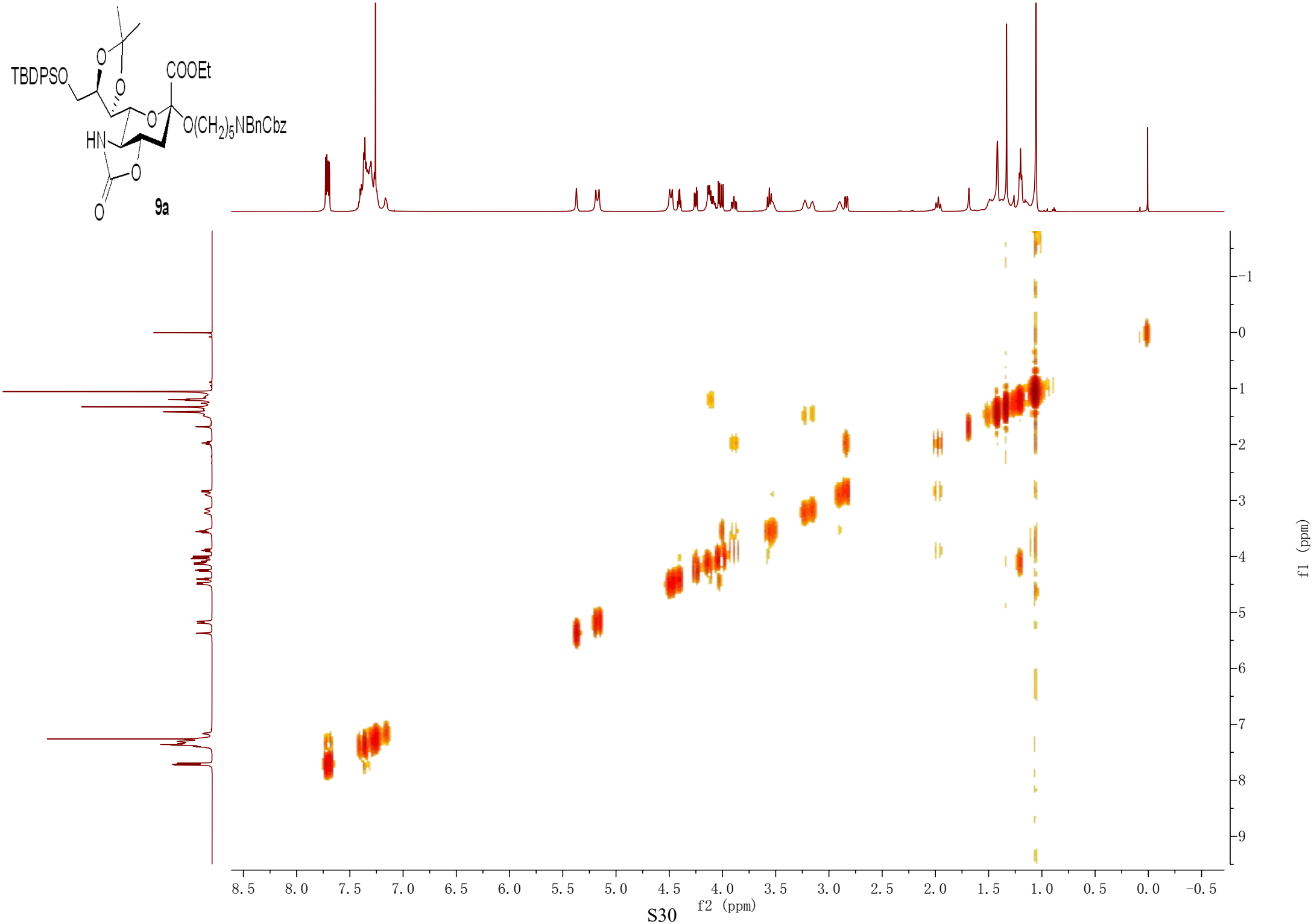

−10
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f2 (ppm)

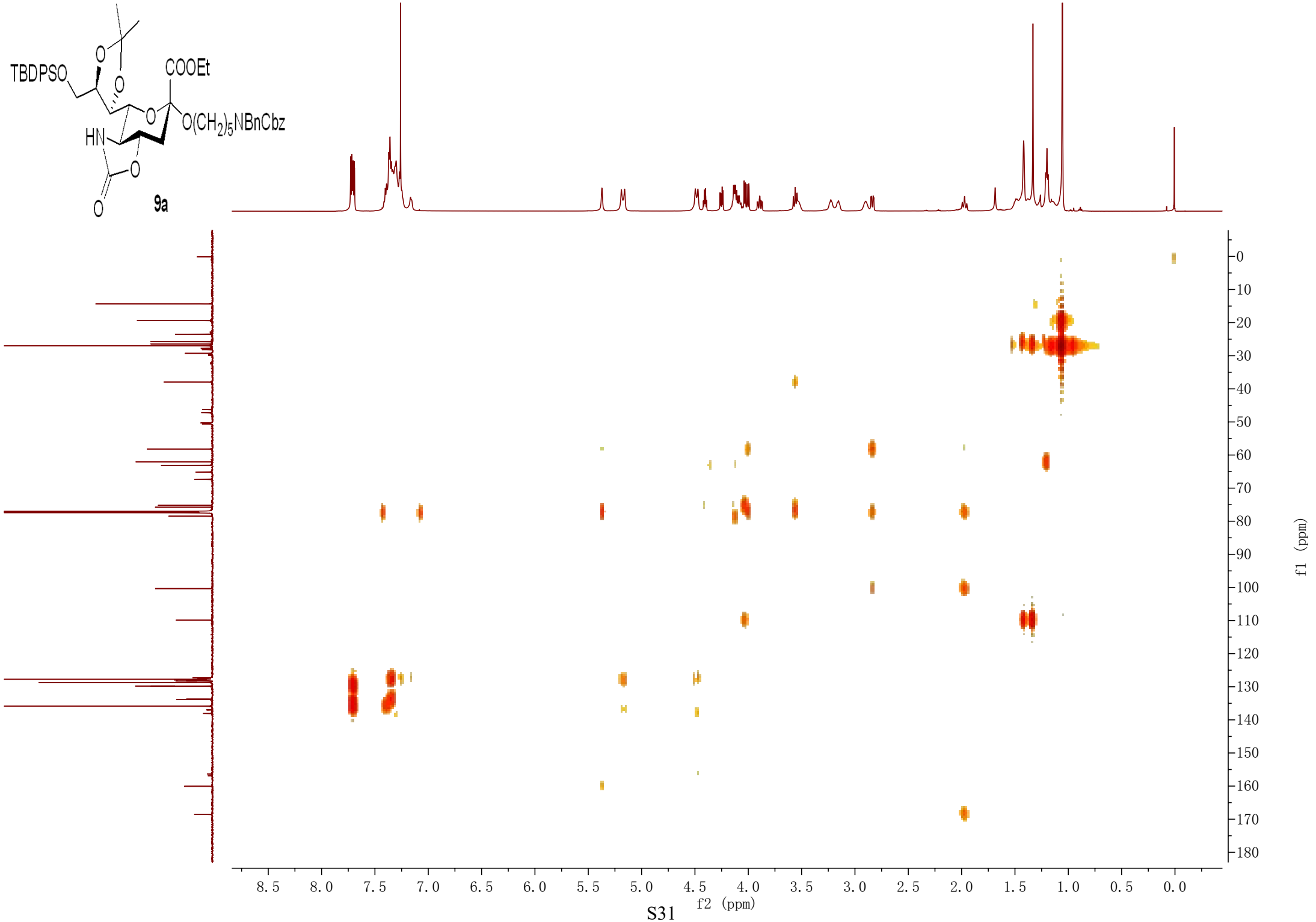

7.818
7.800
7.572
7.555
7.506
7.486
7.468
7.451
7.448
7.422
7.419
7.401
7.384
7.380
7.361
7.342
7.320
7.301
7.284
7.260
7.238
7.220
7.196
7.194
7.175
7.158
7.155
5.198
4.842
4.833
4.812
4.804
4.783
4.773
4.291
4.267
4.232
4.215
4.101
4.055
3.721
3.694
2.984
2.975
2.953
2.944
2.452
2.448
2.434
2.431
2.416
2.387
2.356
2.325
1.617
1.598
1.579
1.501
1.487
1.467
1.234
1.217
0.963
0.944
0.926
0.884
TBDPSO
nBu
COOEt
HN
7
1.04
2.00
12.49
1.00
1.10
1.02
2.07
1.08
2.98
1.11
1.08
2.02
1.19
2.33
5.11
6.44
3.27
9.61
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
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

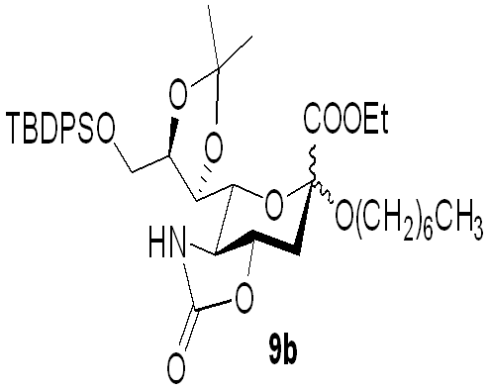

165.859
164.084
159.903
135.669
135.626
135.587
135.277
133.768
133.253
132.501
131.116
129.978
129.880
129.780
128.035
127.865
127.747
127.574
124.924
110.337
99.205
96.805
80.178
77.411
77.200
77.040
76.988
76.839
75.681
75.326
62.530
62.502
58.078
36.337
30.904
27.036
26.944
26.311
25.610
22.265
19.789
19.145
14.083
13.825
TBDPSO
nBu
COOEt
HN
7
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

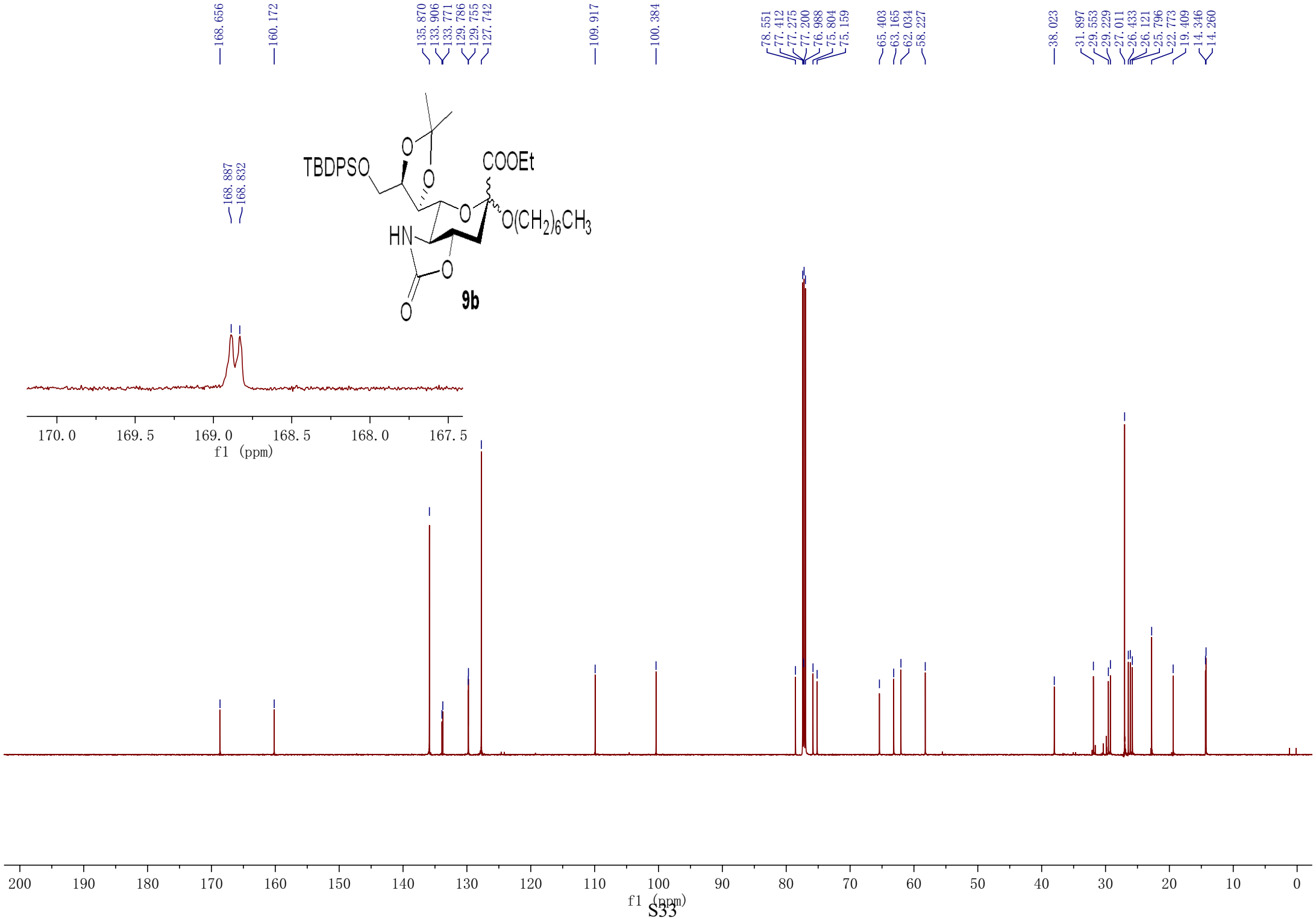

7.728
7.726
7.715
7.713
7.704
7.693
7.691
7.415
7.403
7.391
7.370
7.359
7.346
7.333
7.312
7.301
7.270
7.260
7.166
5.372
5.190
5.159
4.496
4.472
4.410
4.401
4.245
4.138
4.127
4.120
4.108
4.039
4.038
4.028
4.026
4.011
3.995
3.578
3.560
3.543
3.226
3.154
2.900
2.849
2.844
2.829
2.824
1.993
1.972
1.952
1.491
1.479
1.419
1.383
1.373
1.331
1.212
1.200
1.189
1.055
TBDPSO
COOEt
O(CH2)5NBnCbz
HN
9a
4.00
16.43
1.12
1.00
2.17
2.19
1.04
1.06
3.13
0.98
0.98
1.02
2.00
2.12
1.05
1.00
1.18
11.55
3.59
9.07
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
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

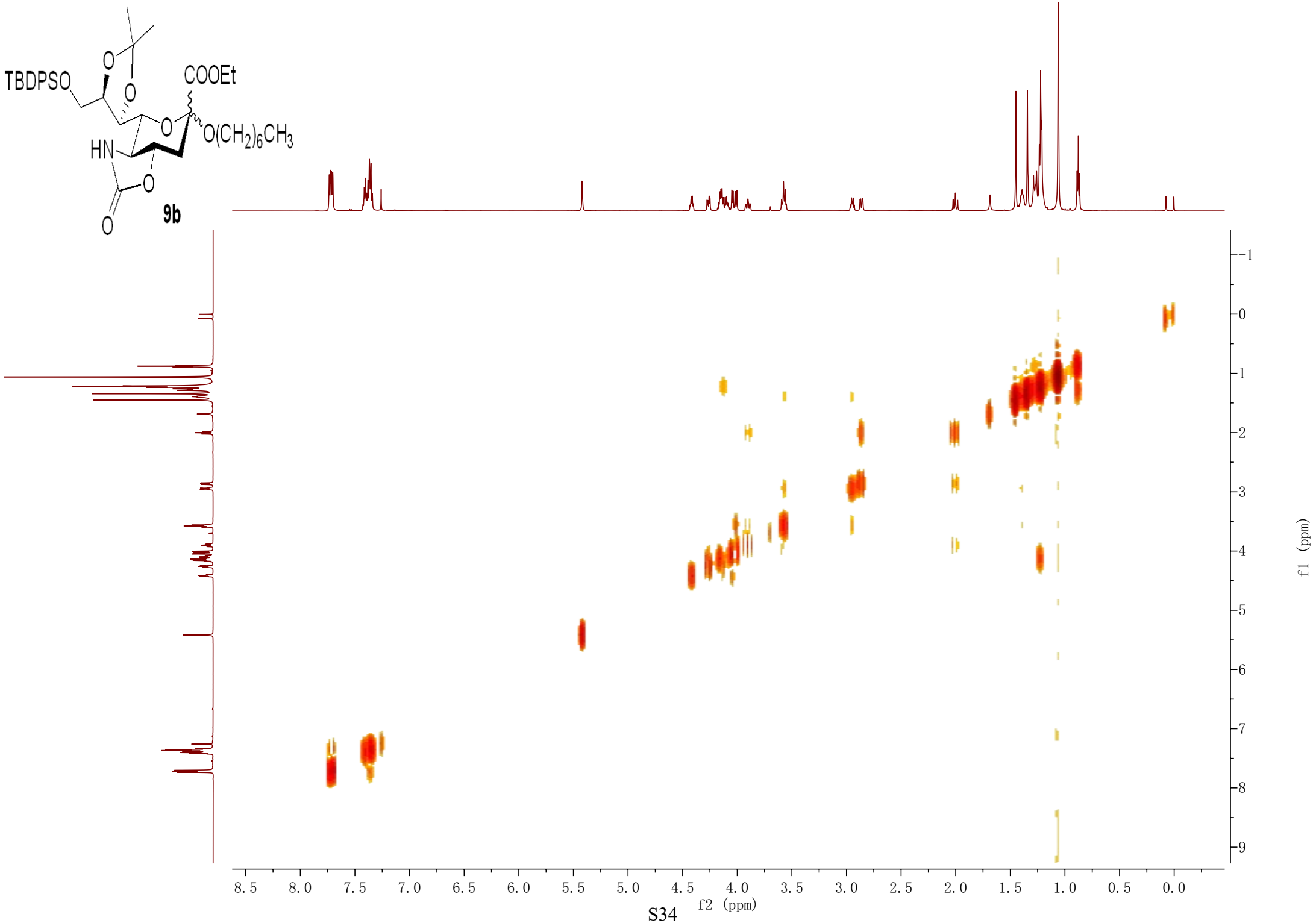

168.563
160.070
138.071
136.912
135.855
133.855
133.730
129.793
129.773
128.706
128.618
128.099
127.935
127.742
127.429
127.297
109.868
100.340
78.491
77.412
77.200
76.989
75.776
75.189
67.355
65.150
63.119
62.062
58.183
50.624
50.323
47.230
46.262
37.985
29.285
28.167
27.710
26.998
26.437
25.774
23.506
19.399
14.362
168.589
168.541
TBDPSO
COOEt
O(CH2)5NBnCbz
HN
9a
f1 (ppm)
f1 (ppm)

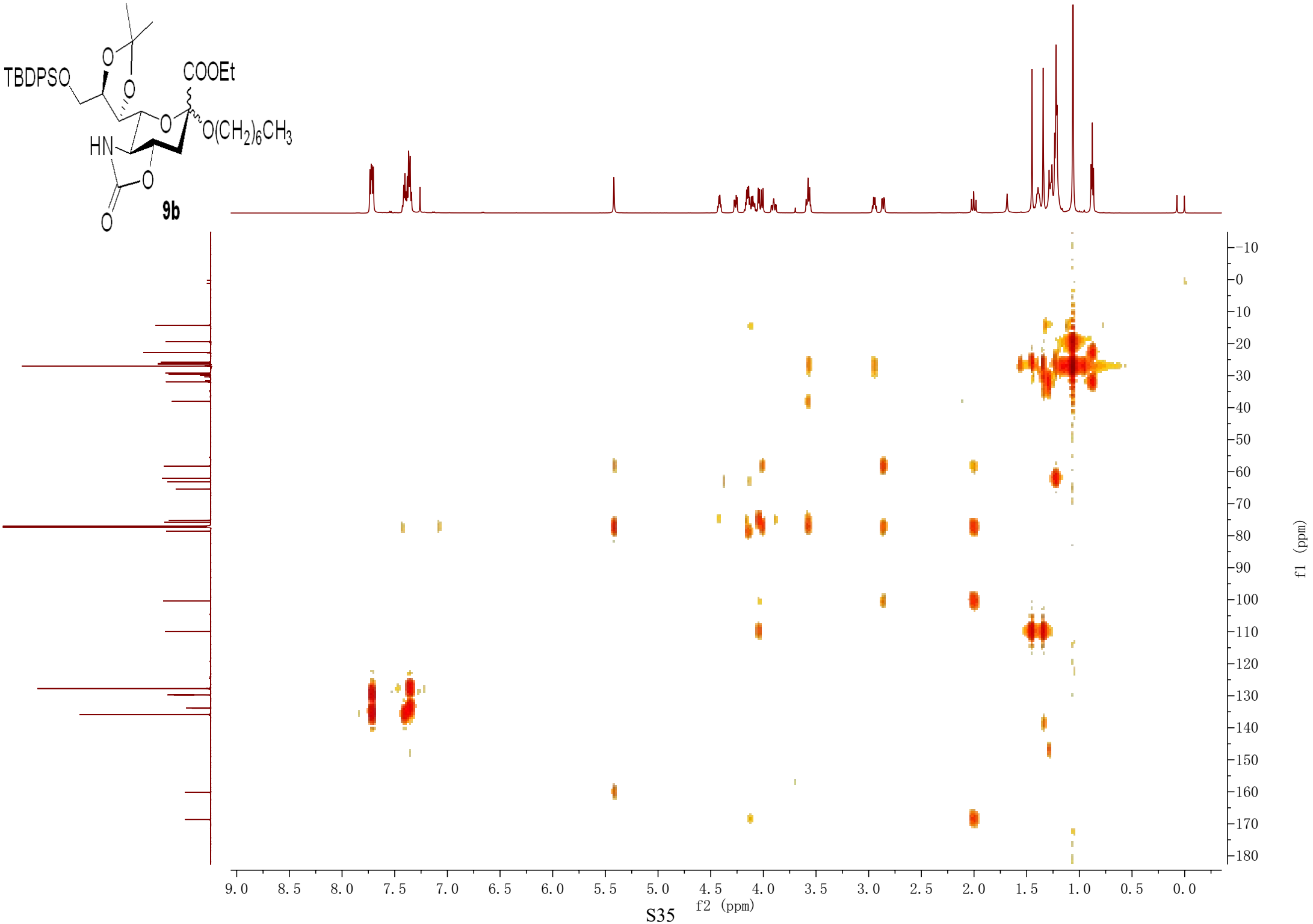

TBDPSO
COOEt
O(CH2)5NBnCbz
HN
O
9a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
f1 (ppm)

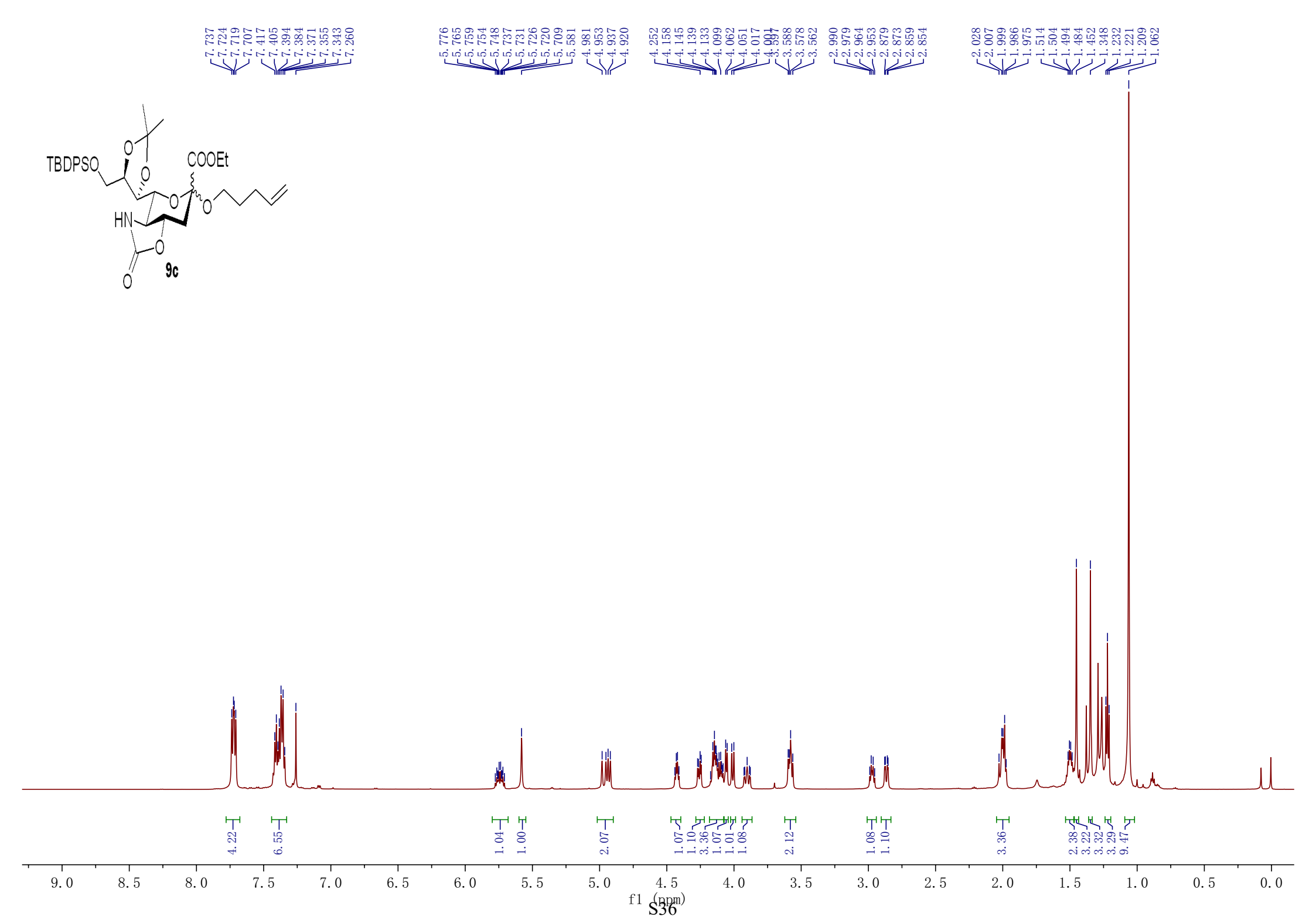

TBDPSO
COOEt
O(CH2)5NBnCbz
HN
9a
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

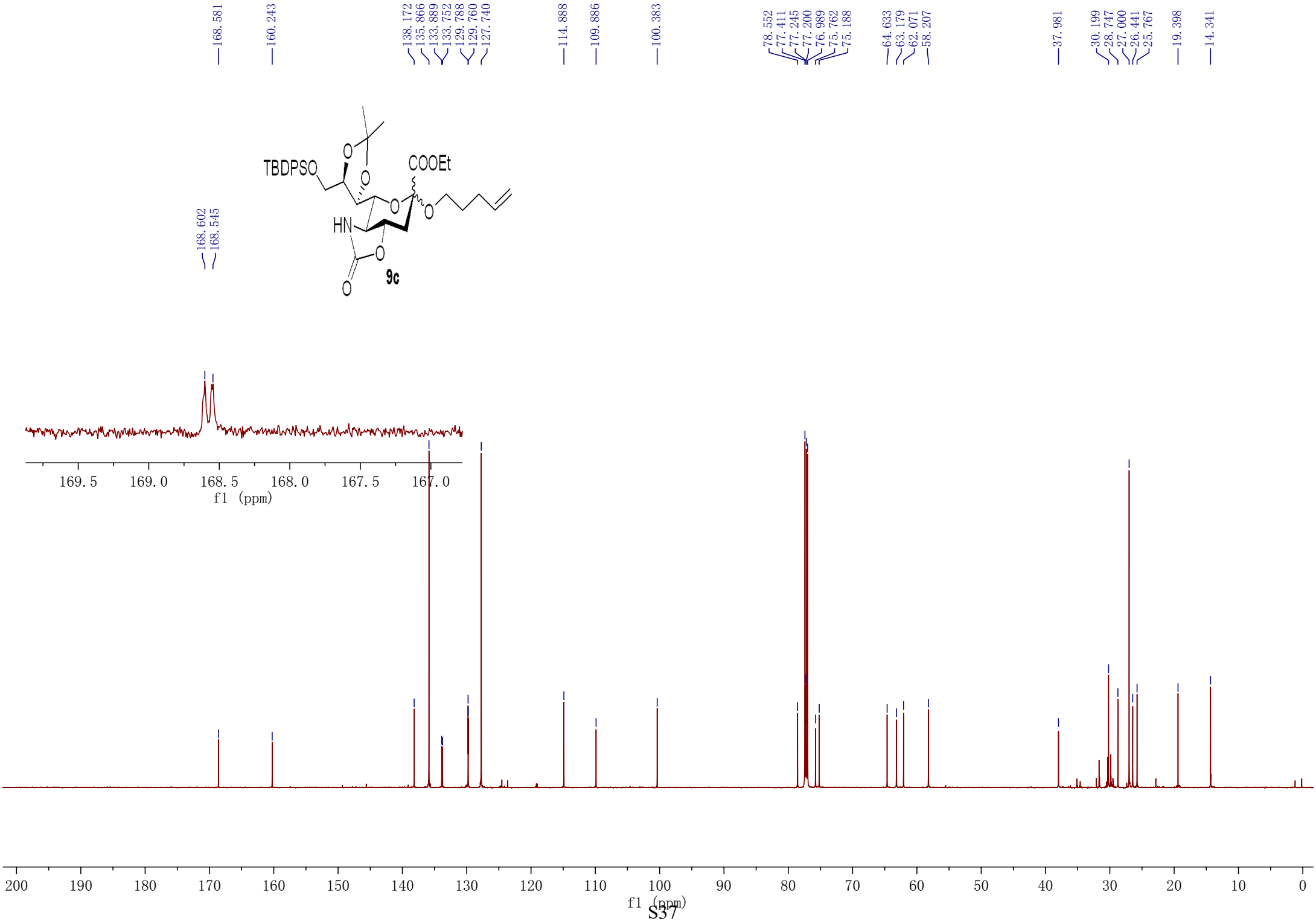

TBDPSO
COOEt
O(CH2)6CH3
HN
9b

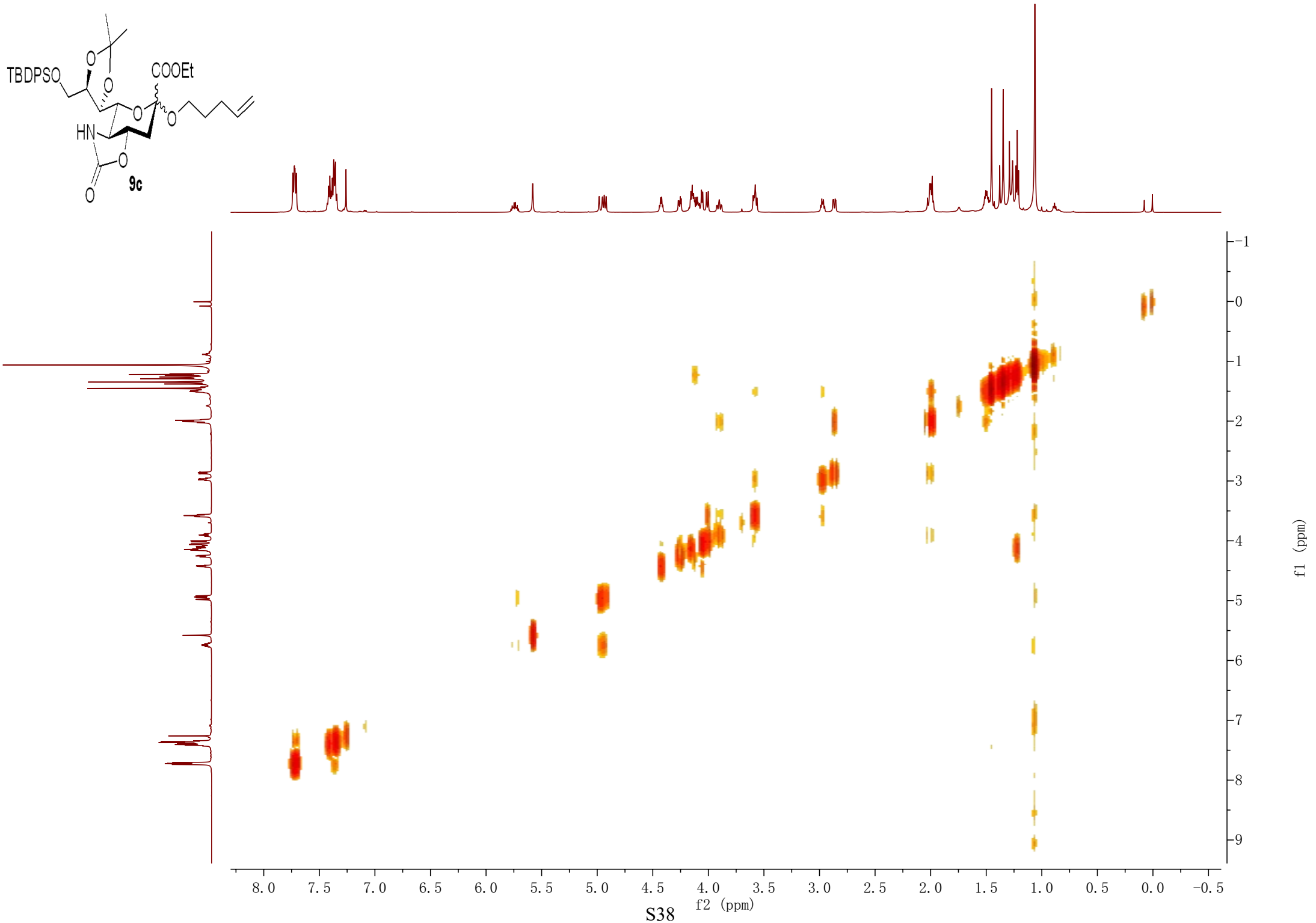

168.656
160.172
135.870
133.906
133.771
129.786
129.755
127.742
109.917
100.384
78.551
77.412
77.275
77.200
76.988
75.804
75.159
65.403
63.165
62.034
58.227
38.023
31.897
29.553
29.229
27.011
26.433
26.121
25.796
22.773
19.409
14.346
14.260
168.887
168.832
TBDPSO
COOEt
O(CH2)6CH3
HN
9b
170.0
169.5
169.0
168.5
168.0
167.5
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

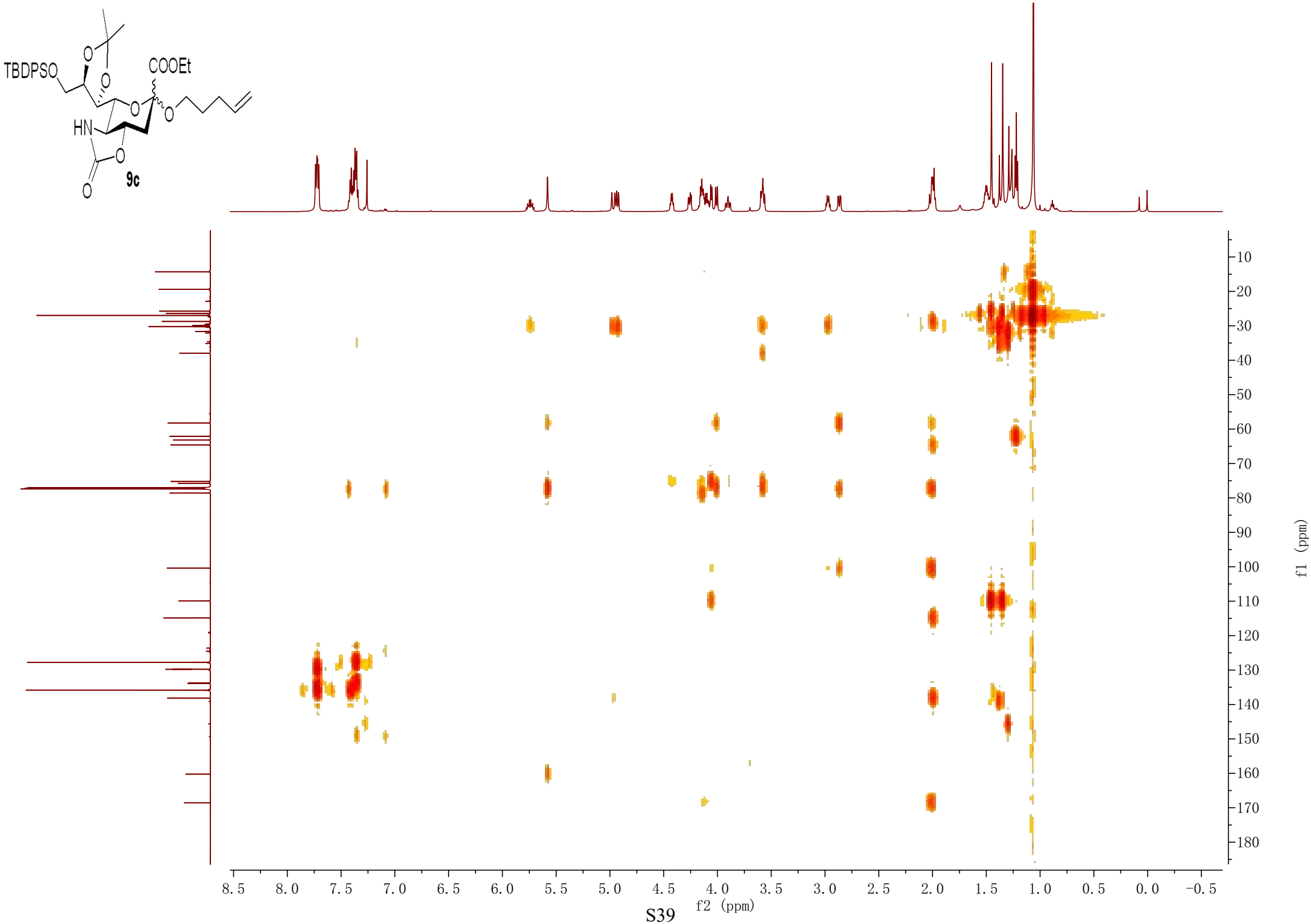

TBDPSO
COOEt
O(CH2)6CH3
HN
9b
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
f1 (ppm)

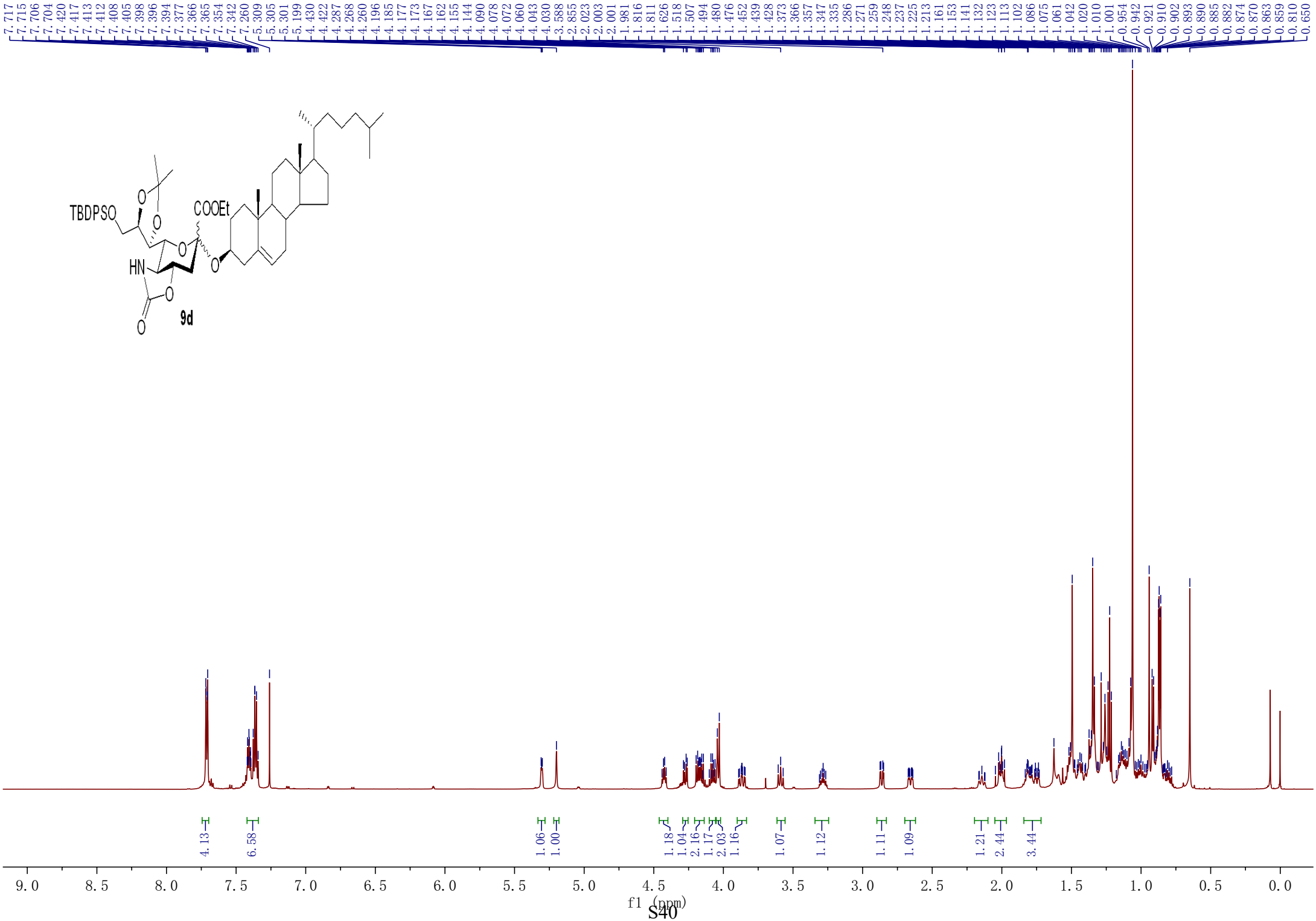

TBDPSO
COOEt
O(CH2)6CH3
HN
9b
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
f1 (ppm)

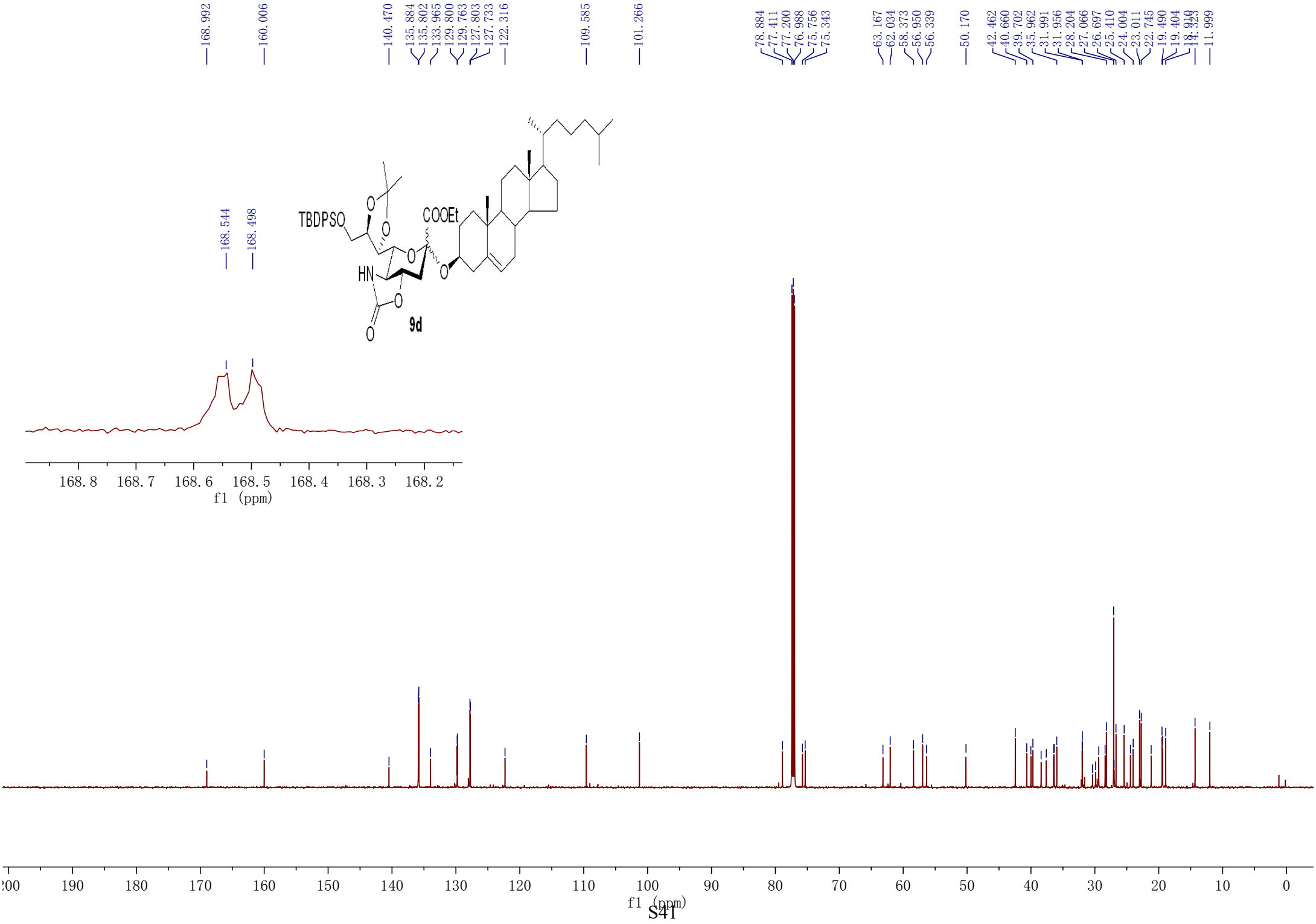

7.737
7.724
7.719
7.707
7.417
7.405
7.394
7.384
7.371
7.355
7.343
7.260
5.776
5.765
5.759
5.754
5.748
5.737
5.731
5.726
5.720
5.709
5.581
4.981
4.953
4.937
4.920
4.252
4.158
4.145
4.139
4.133
4.099
4.062
4.051
4.017
3.588
3.578
3.562
2.990
2.979
2.964
2.953
2.879
2.873
2.859
2.854
2.028
2.007
1.999
1.986
1.975
1.514
1.504
1.494
1.484
1.452
1.348
1.232
1.221
1.209
1.062
TBDPSO
COOEt
HN
O
9c
4.22
6.55
1.04
1.00
2.07
1.07
1.10
3.36
1.07
1.01
1.08
2.12
1.08
1.10
3.36
2.38
3.22
3.32
3.29
9.47
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
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

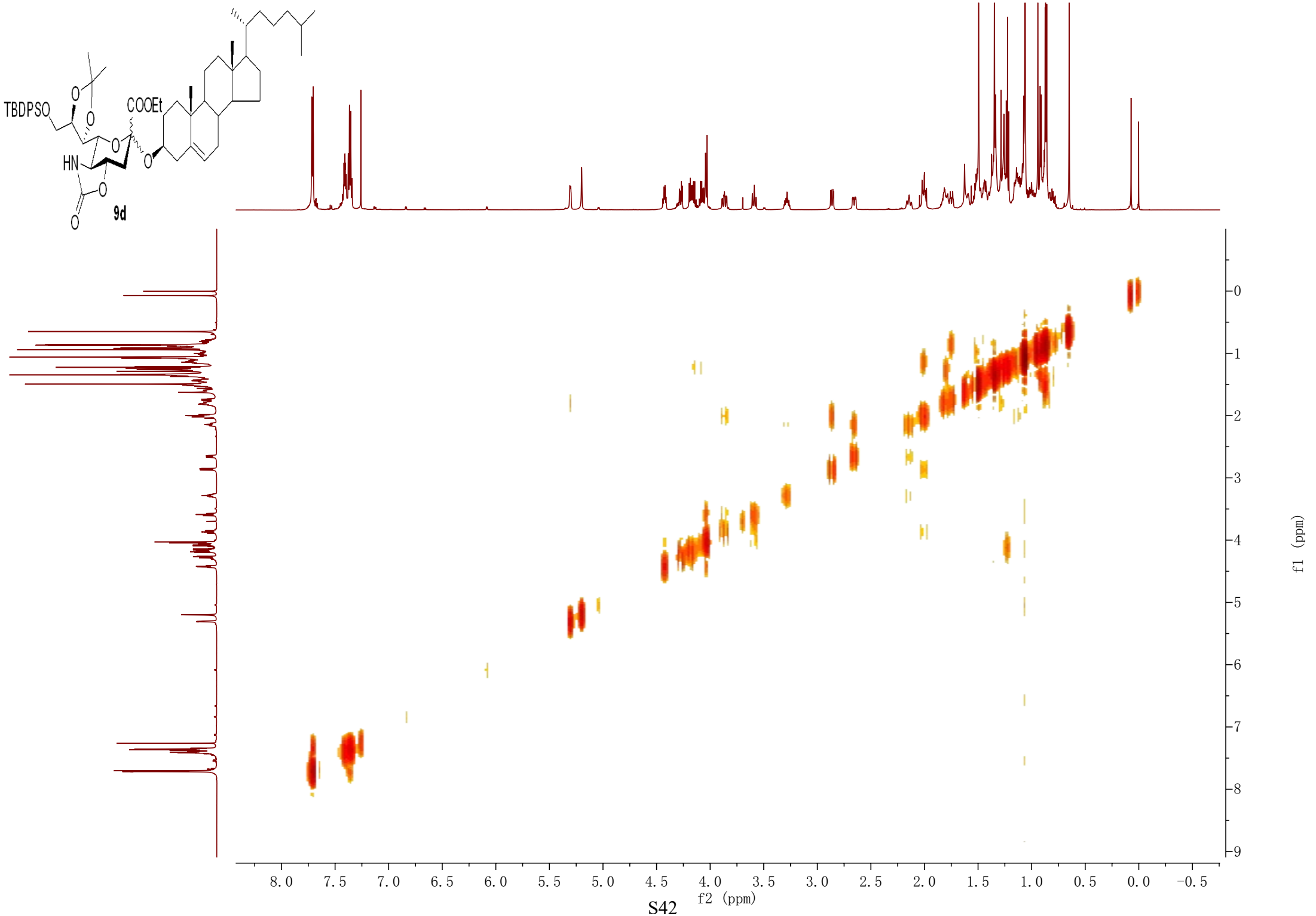

168.581
160.243
138.172
135.866
133.889
133.752
129.788
129.760
127.740
114.888
109.886
100.383
78.552
77.411
77.245
77.200
76.989
75.762
75.188
64.633
63.179
62.071
58.207
37.981
30.199
28.747
27.000
26.441
25.767
19.398
14.341
168.602
168.545
TBDPSO
COOEt
HN
O
9c
169.5
169.0
168.5
168.0
167.5
167.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

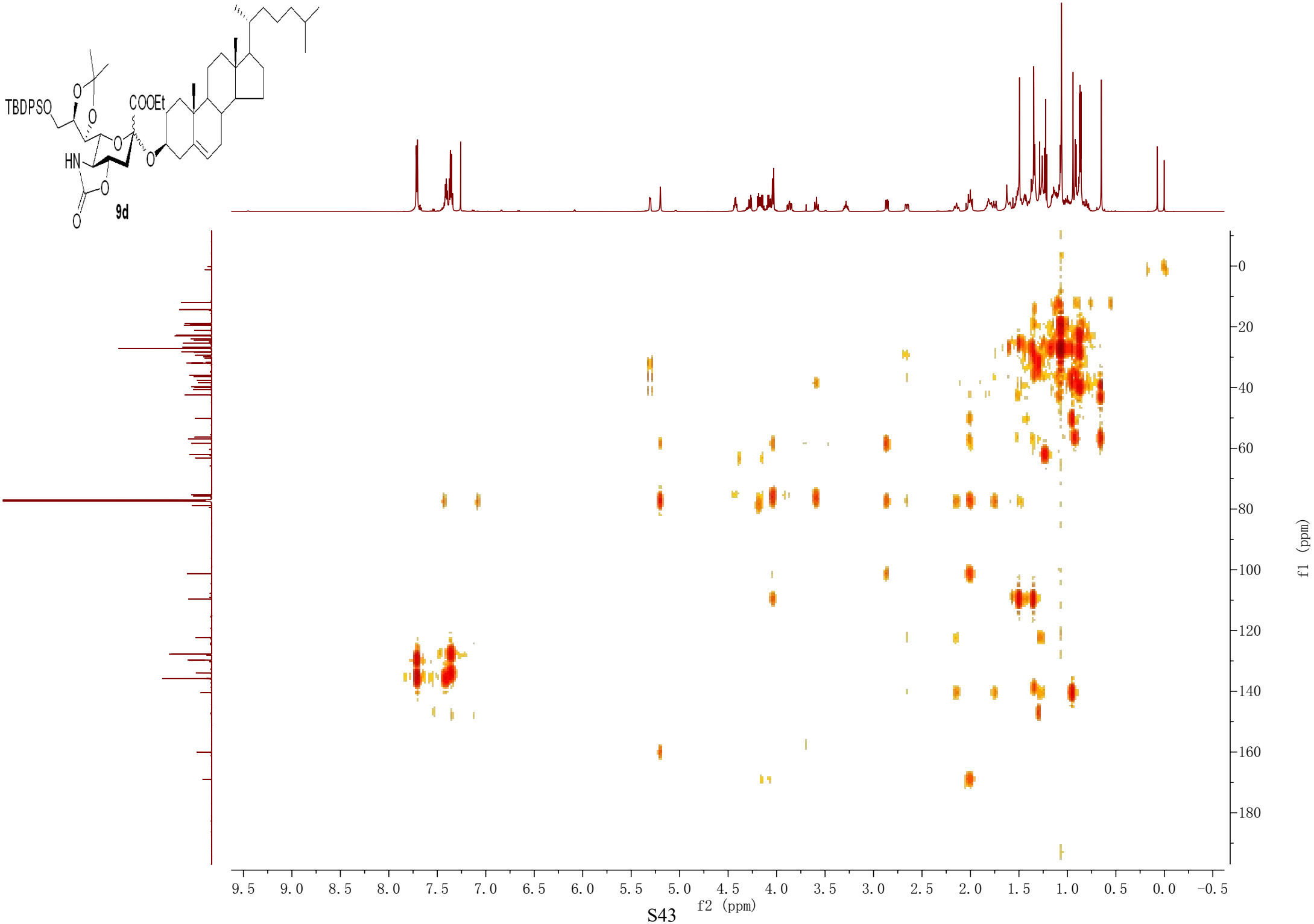

TBDPSO
COOEt
HN
O
9c
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
9
f1 (ppm)

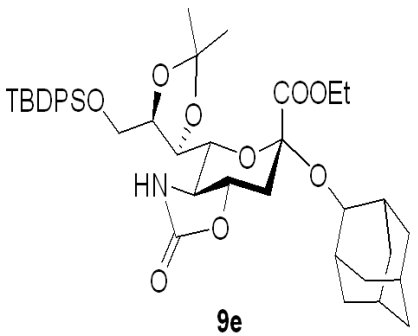

TBDPSO
COOEt
HN
9c
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)


7.717 7.715 7.706 7.704 7.420 7.417 7.413 7.412 7.408 7.405 7.398 7.396 7.394 7.377 7.366 7.365 7.354 7.342 7.260 5.309 5.305 5.301 5.199 4.430 4.422 4.287 4.268 4.260 4.196 4.185 4.177 4.173 4.167 4.162 4.155 4.144 4.090 4.078 4.072 4.060 4.043 4.030 3.588 2.855 2.023 2.003 2.001 1.981 1.816 1.811 1.626 1.518 1.507 1.494 1.480 1.476 1.452 1.439 1.428 1.373 1.366 1.357 1.347 1.335 1.286 1.271 1.259 1.248 1.237 1.225 1.213 1.161 1.153 1.141 1.132 1.123 1.113 1.102 1.086 1.075 1.061 1.042 1.020 1.010 1.001 0.954 0.942 0.921 0.910 0.902 0.893 0.890 0.885 0.882 0.874 0.870 0.863 0.859 0.810 0.650
TBDPSO
COOEt
HN
O
9d
4.13 6.58 1.06 1.00 1.18 1.04 2.16 1.17 2.03 1.16 1.07 1.12 1.11 1.09 1.21 2.44 3.44
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 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.992
160.006
140.470
135.884
135.802
133.965
129.800
129.763
127.803
127.733
122.316
109.585
101.266
78.884
77.411
77.200
76.988
75.756
75.343
63.167
62.034
58.373
56.950
56.339
50.170
42.462
40.660
39.702
35.962
31.991
31.956
28.204
27.066
26.697
25.410
24.004
23.011
22.745
19.490
19.404
18.910
14.323
11.999
168.544
168.498
TBDPSO
COOEt
HN
9d
168.8
168.7
168.6
168.5
168.4
168.3
168.2
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

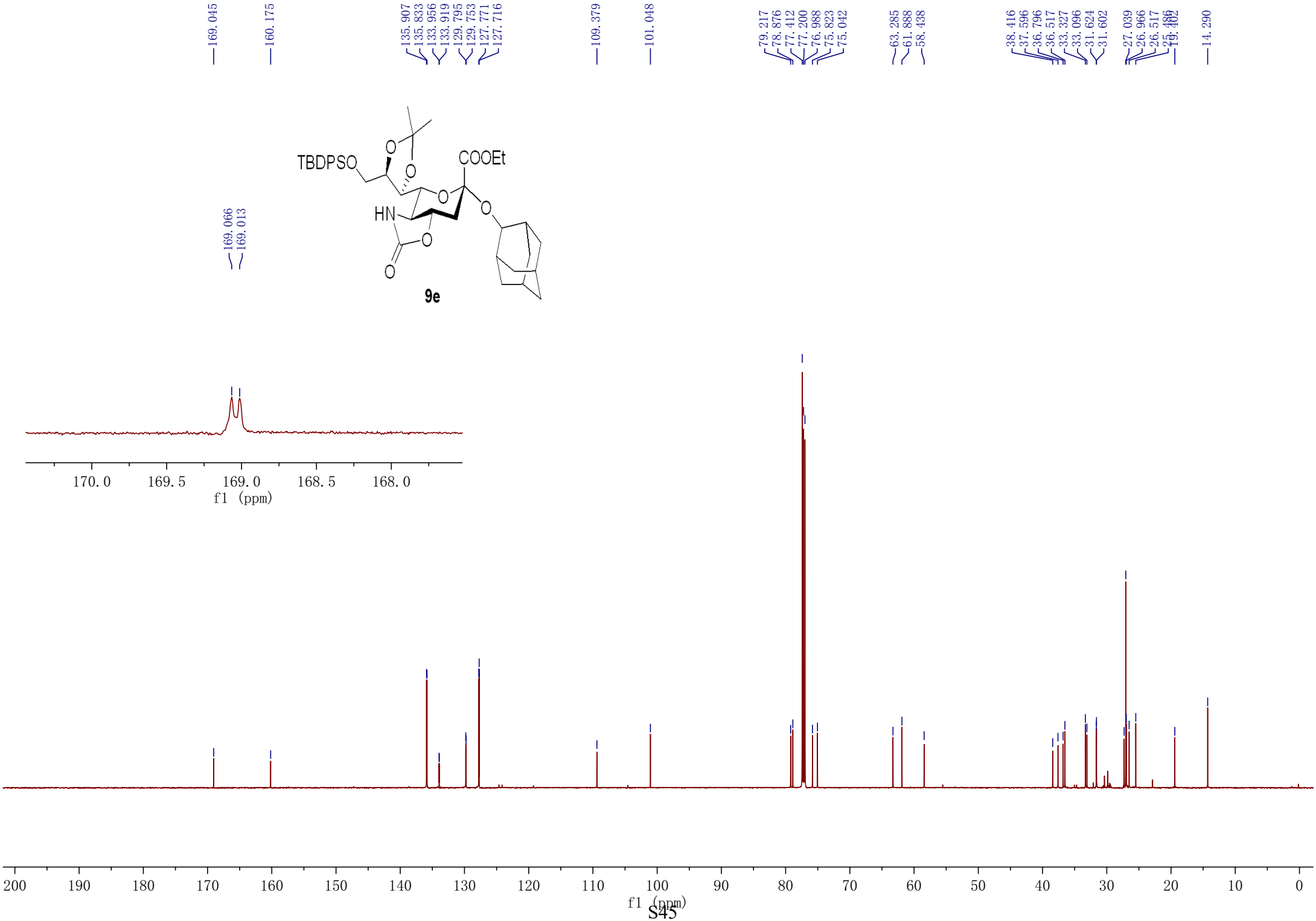

TBDPSO
COOEt
HN
O
9d
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)

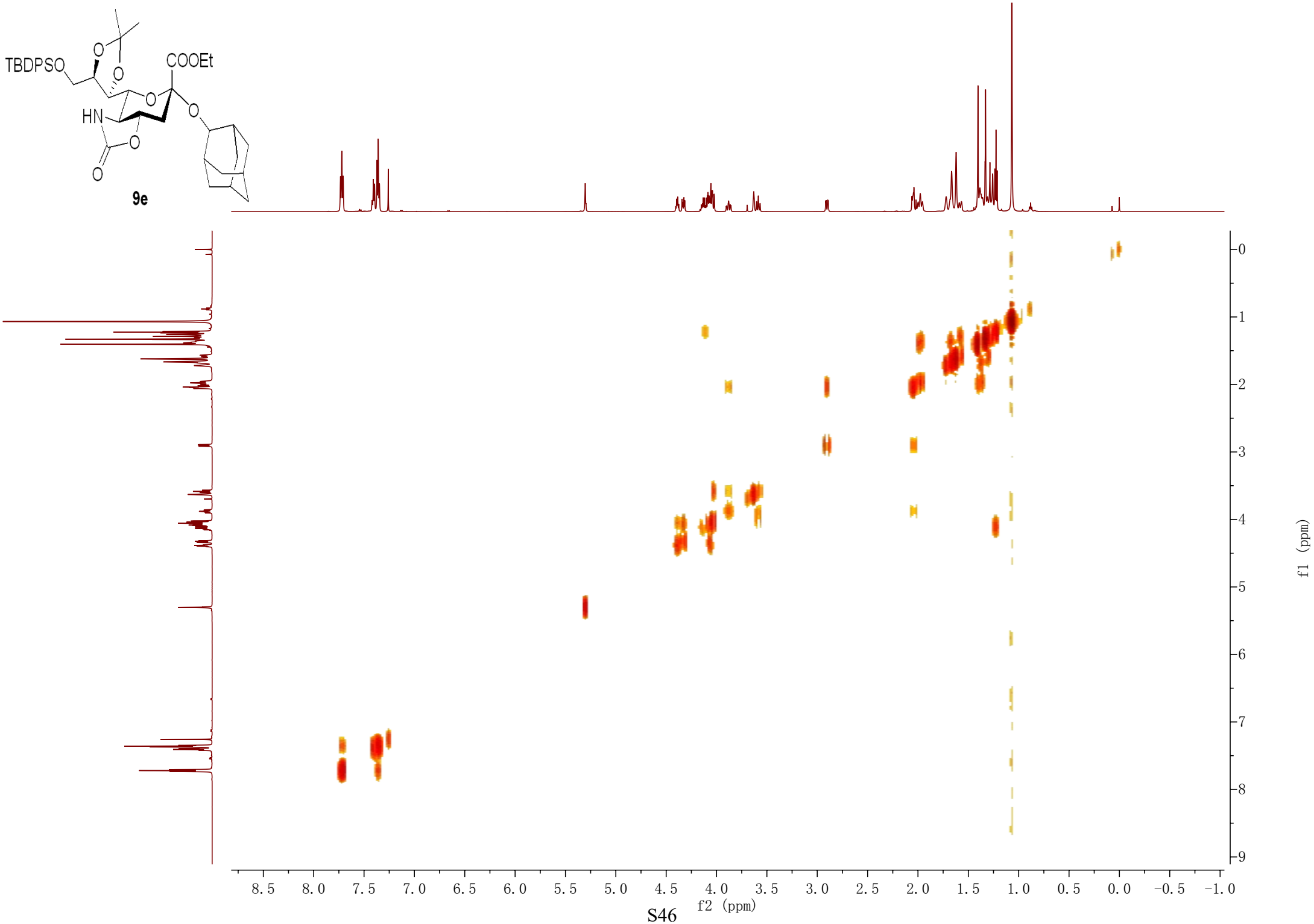

TBDPSO
COOEt
HN
O
9d
f2 (ppm)
f1 (ppm)

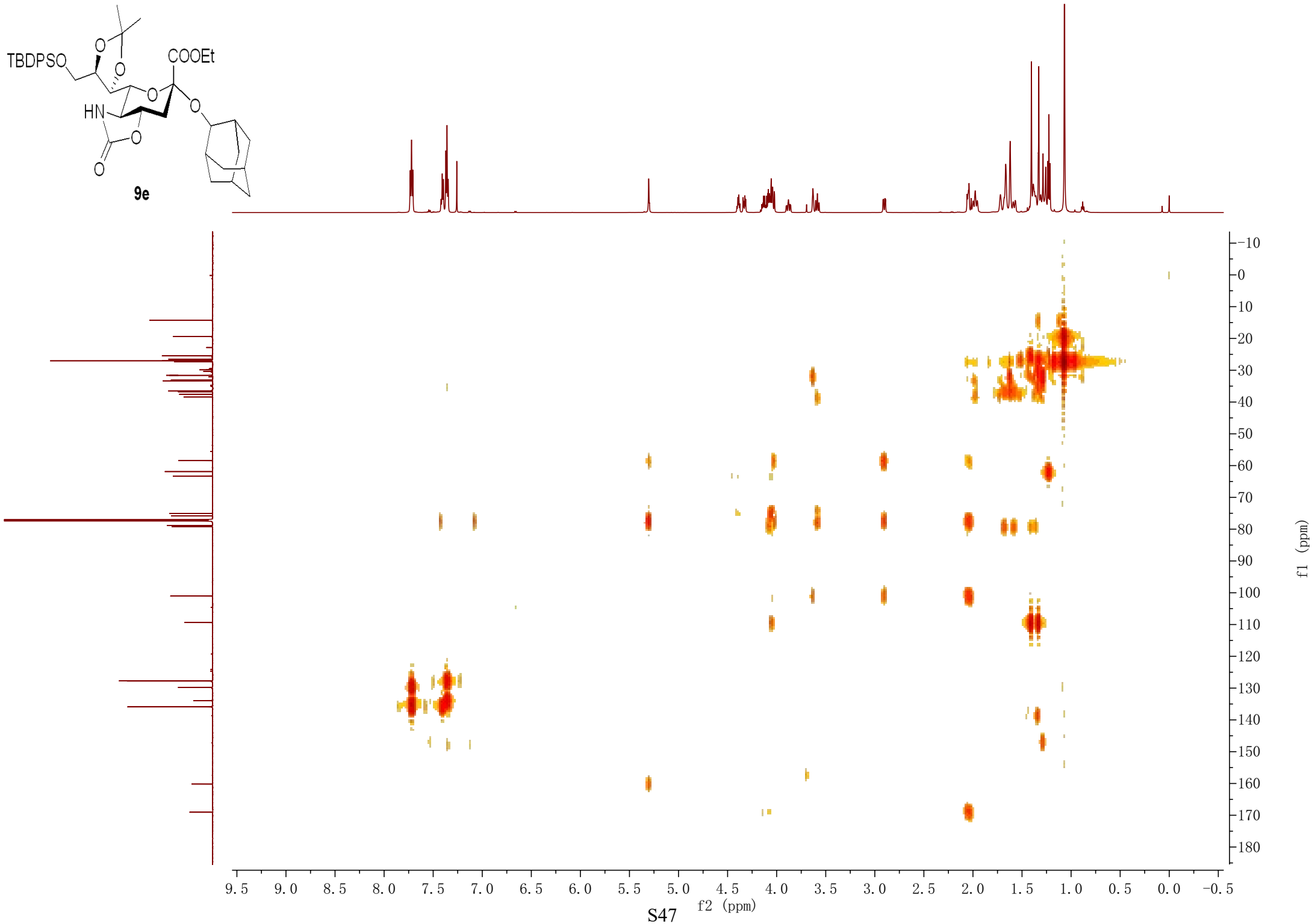

TBDPSO
COOEt
HN
O
O
O
O
O
O
O

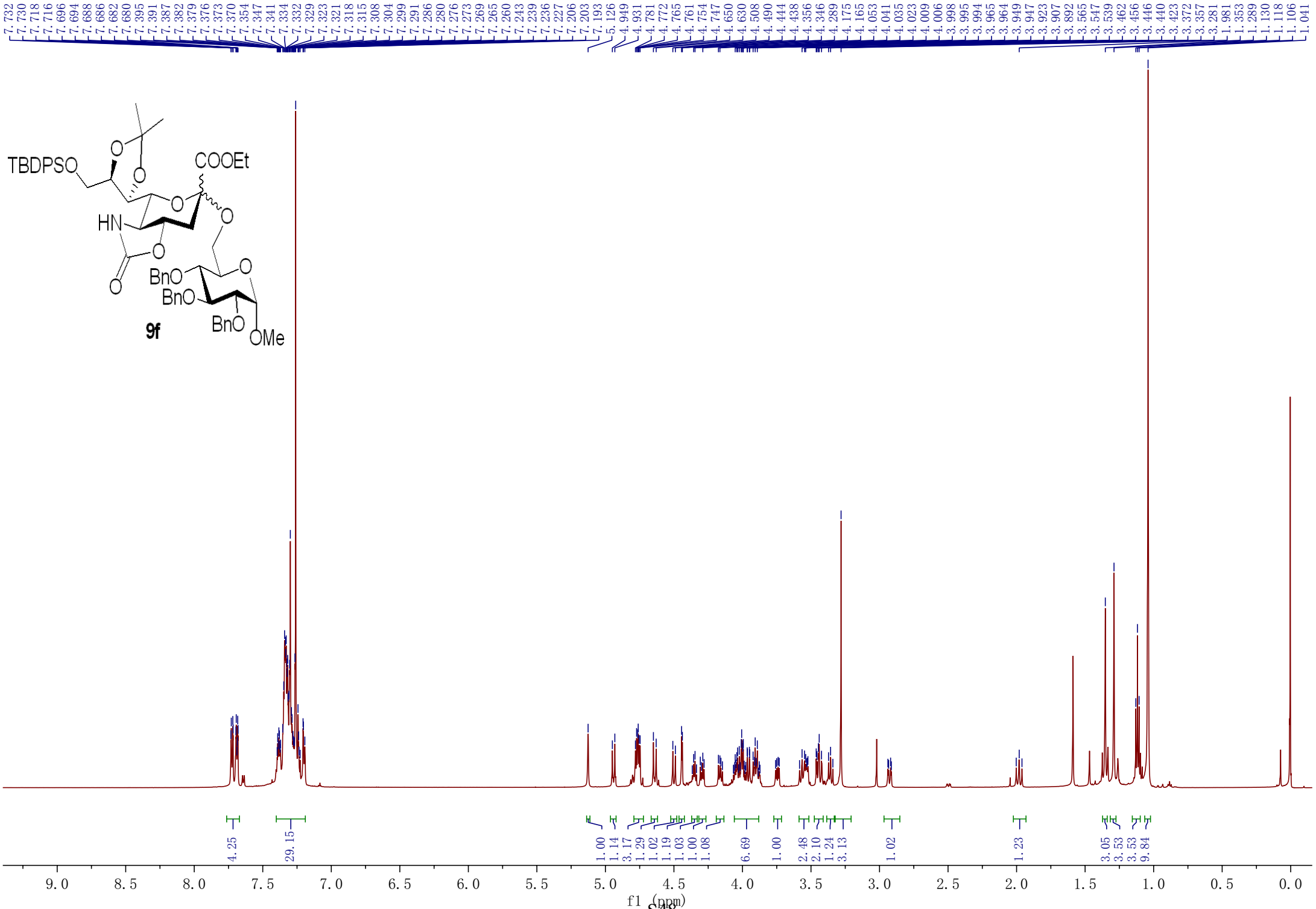
9e

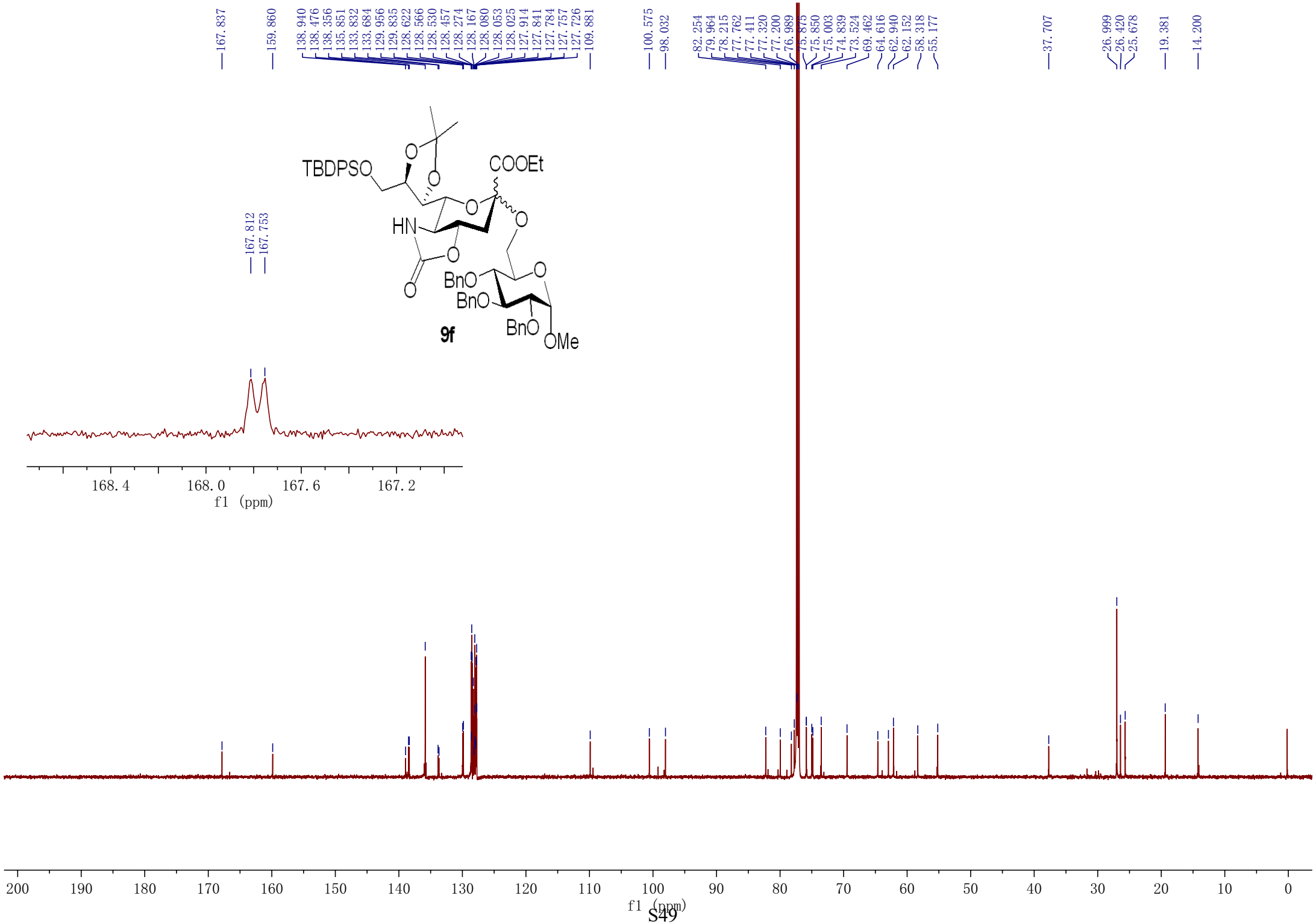
7.734
7.720
7.708
7.420
7.408
7.396
7.371
7.359
7.347
7.260
5.304
4.395
4.386
4.342
4.324
4.133
4.121
4.102
4.090
4.084
4.075
4.066
4.056
4.044
4.040
3.630
3.603
3.585
3.568
2.916
2.910
2.896
2.891
2.060
2.045
2.040
2.018
1.998
1.977
1.956
1.720
1.681
1.666
1.621
1.591
1.569
1.404
1.384
1.373
1.358
1.334
1.329
1.237
1.225
1.213
1.067
4.03
6.20
1.00
1.00
1.00
5.12
1.02
1.01
1.02
1.01
2.11
2.12
8.42
9.97
3.30
9.36
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
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

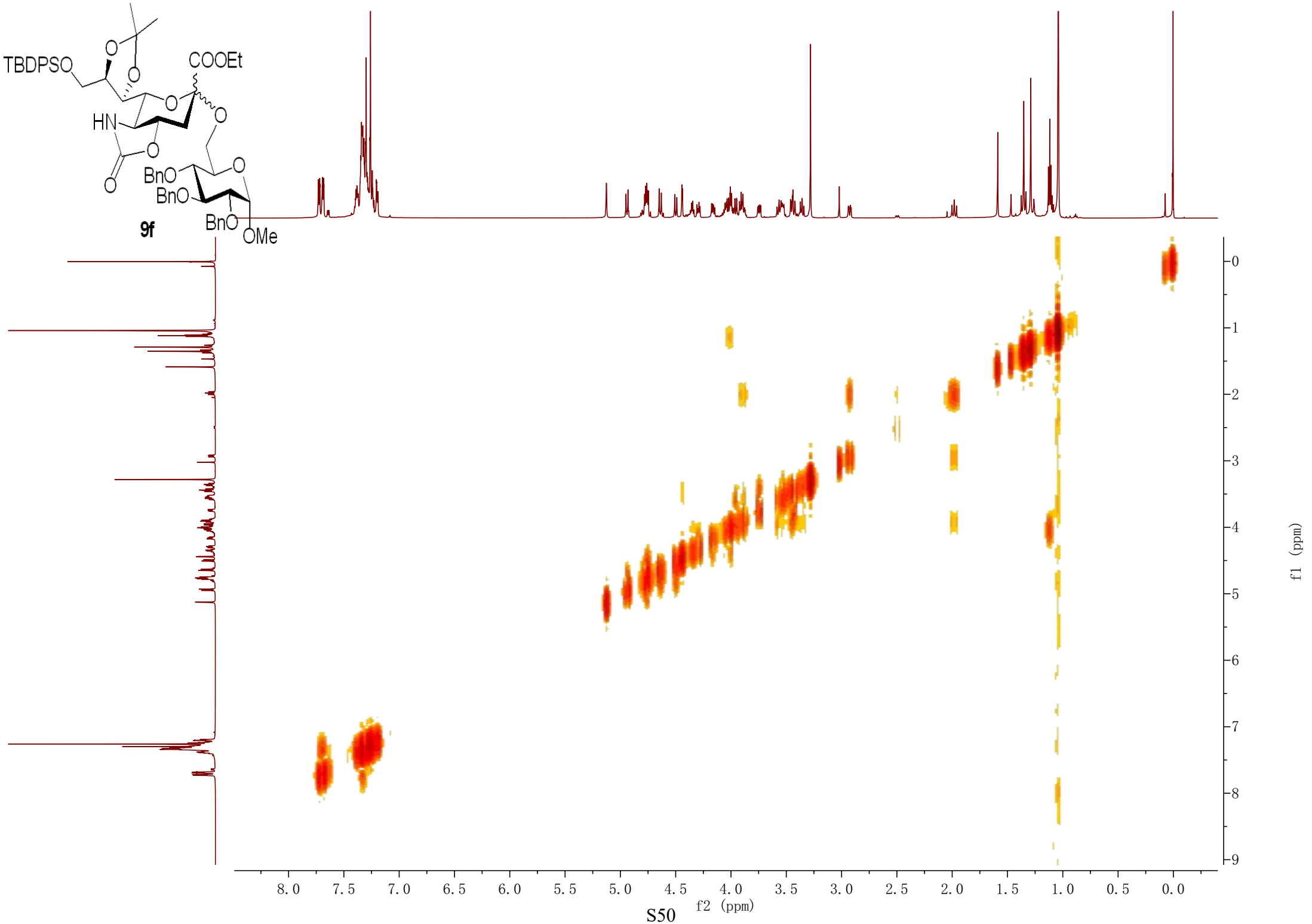

169.045
160.175
135.907
135.833
133.956
133.919
129.795
129.753
127.771
127.716
109.379
101.048
79.217
78.876
77.412
77.200
76.988
75.823
75.042
63.285
61.888
58.438
38.416
37.596
36.796
36.517
33.327
33.096
31.624
31.602
27.039
26.966
26.517
14.290
169.066
169.013
TBDPSO
COOEt
HN
O
9e
170.0
169.5
169.0
168.5
168.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

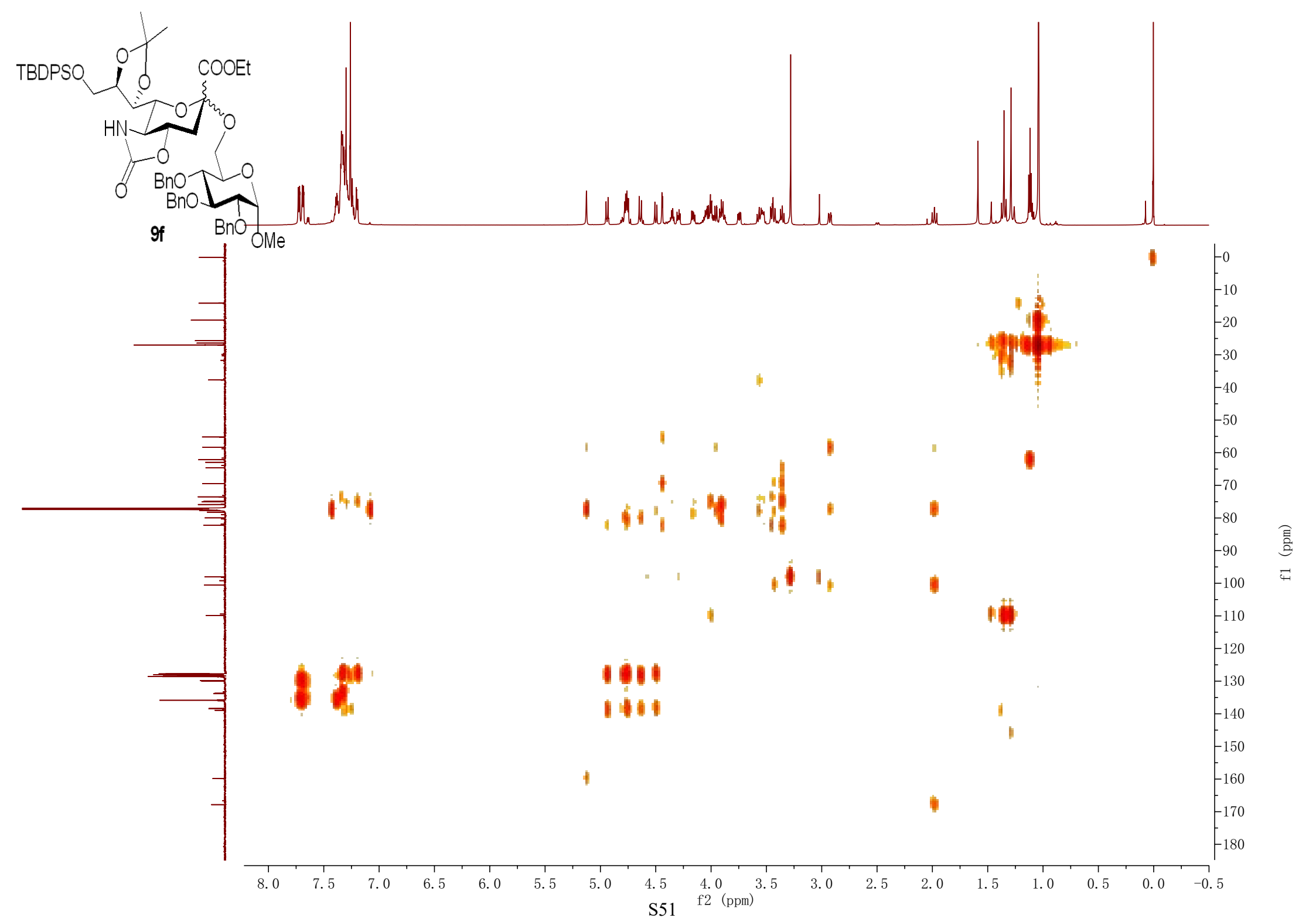

TBDPSO
COOEt
HN
O
9e
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)

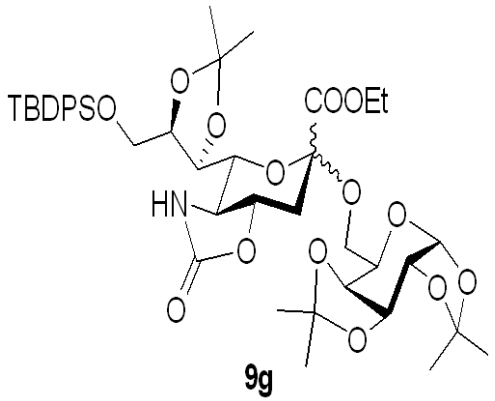

TBDPSO
COOEt
HN
O
9e
f2 (ppm)
f1 (ppm)


TBDPSO
COOEt
HN
BnO
BnO
BnO
OMe
9f
f1 (ppm)

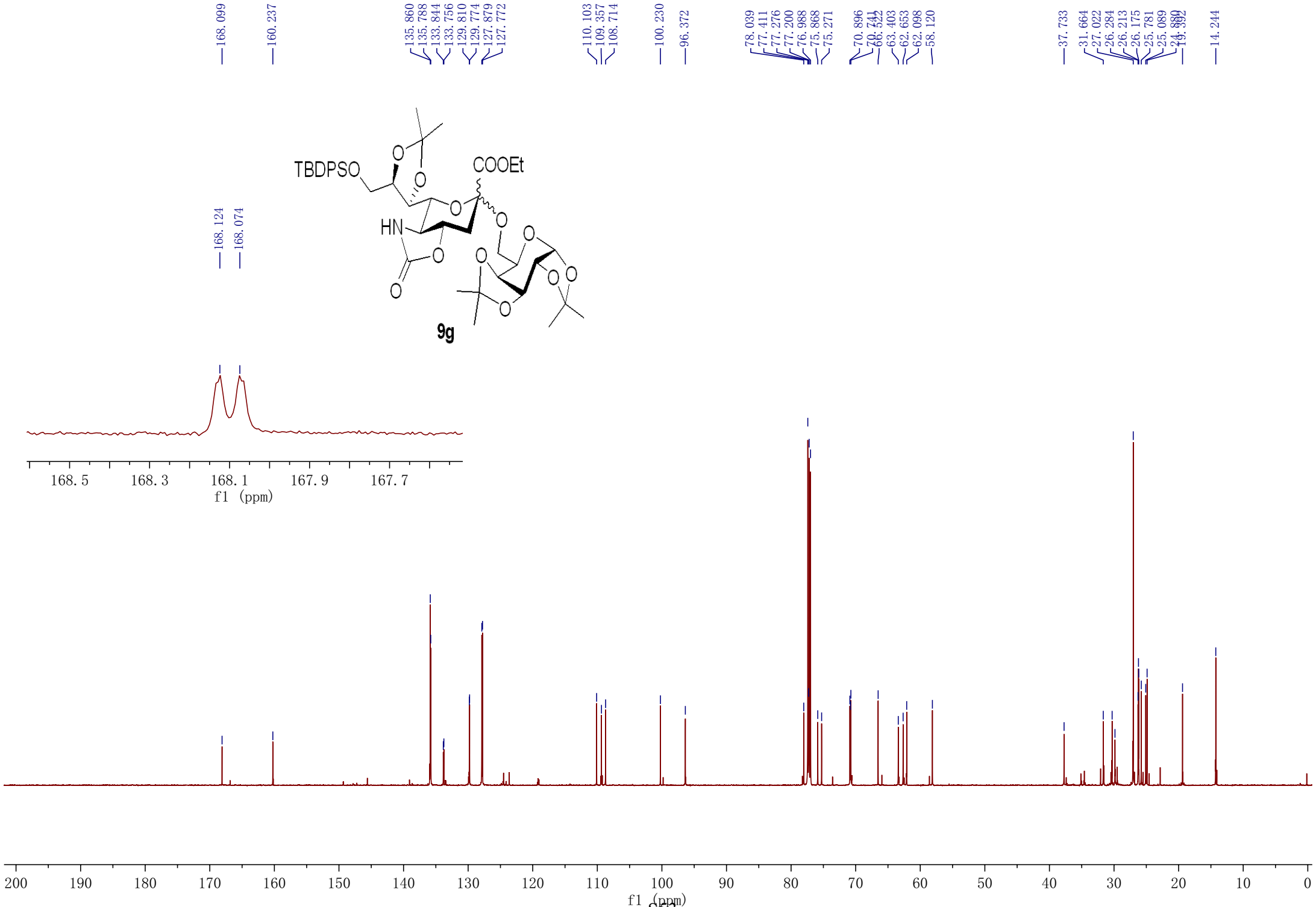

167.837
159.860
138.940
138.476
138.356
135.851
133.832
133.684
129.956
129.835
128.622
128.566
128.530
128.457
128.274
128.167
128.080
128.053
128.025
127.914
127.841
127.784
127.757
127.726
109.881
100.575
98.032
82.254
79.964
78.215
77.762
77.411
77.320
77.200
76.989
75.875
75.850
75.003
74.839
73.524
69.462
64.616
62.940
62.152
58.318
55.177
37.707
26.999
26.420
25.678
19.381
14.200
167.812
167.753
TBDPSO
COOEt
HN
BnO
BnO
BnO
OMe
9f
168.4
168.0
167.6
167.2
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

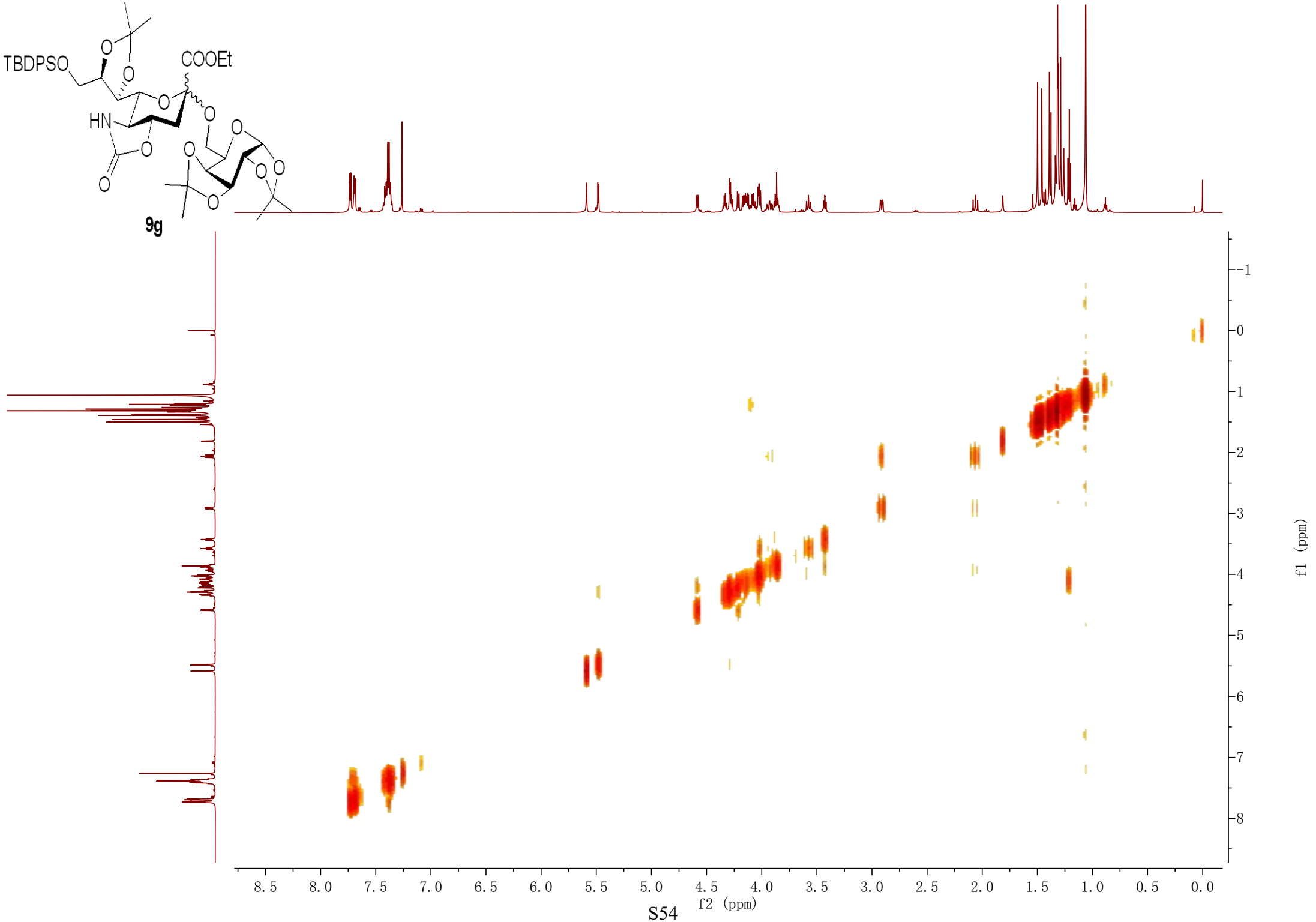

TBDPSO
COOEt
HN
BnO
BnO
BnO
OMe
9f
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
1
2
3
4
5
6
7
8
9
f1 (ppm)

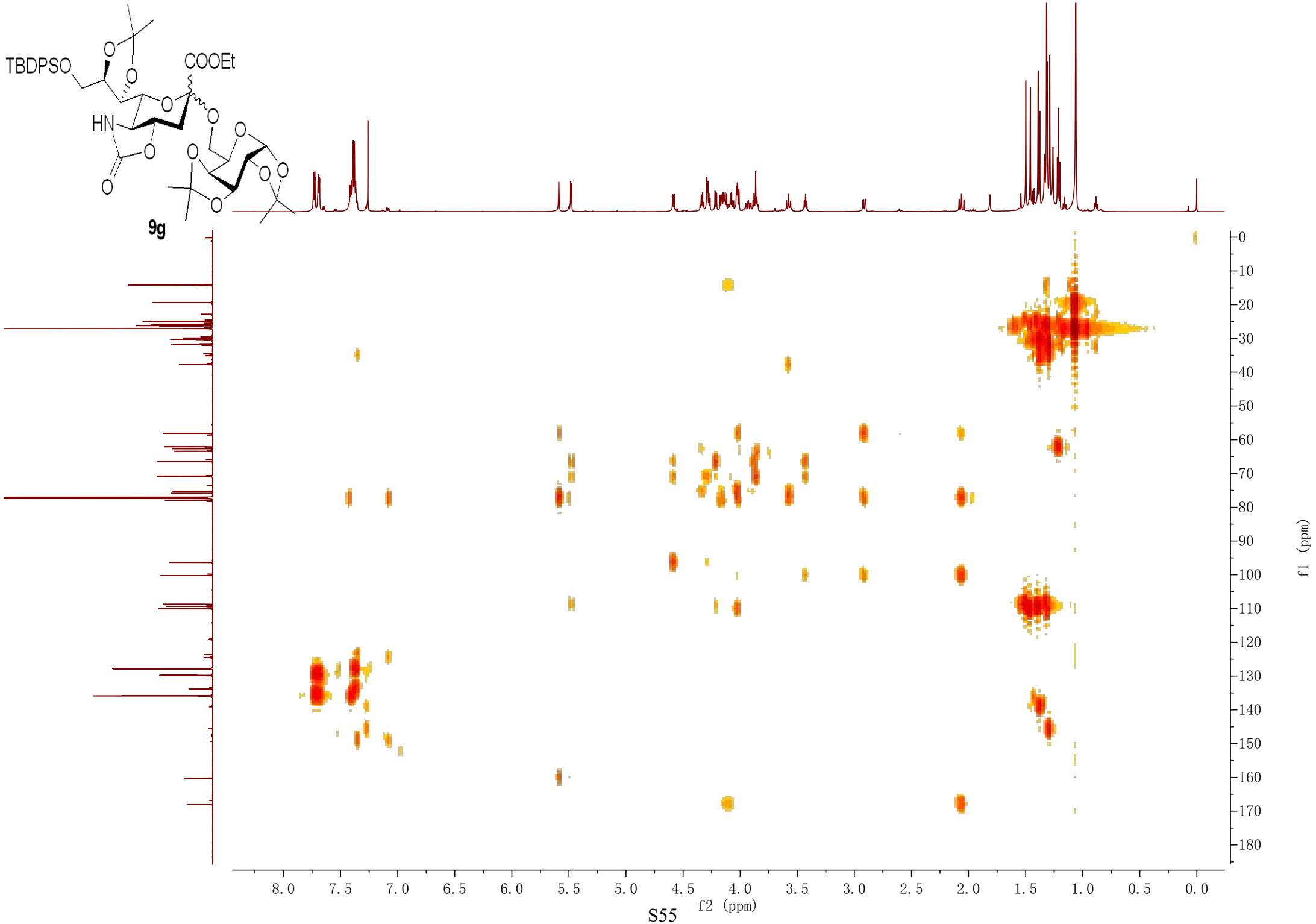

TBDPSO
COOEt
HN
BnO
BnO
BnO
OMe
9f
f2 (ppm)
f1 (ppm)

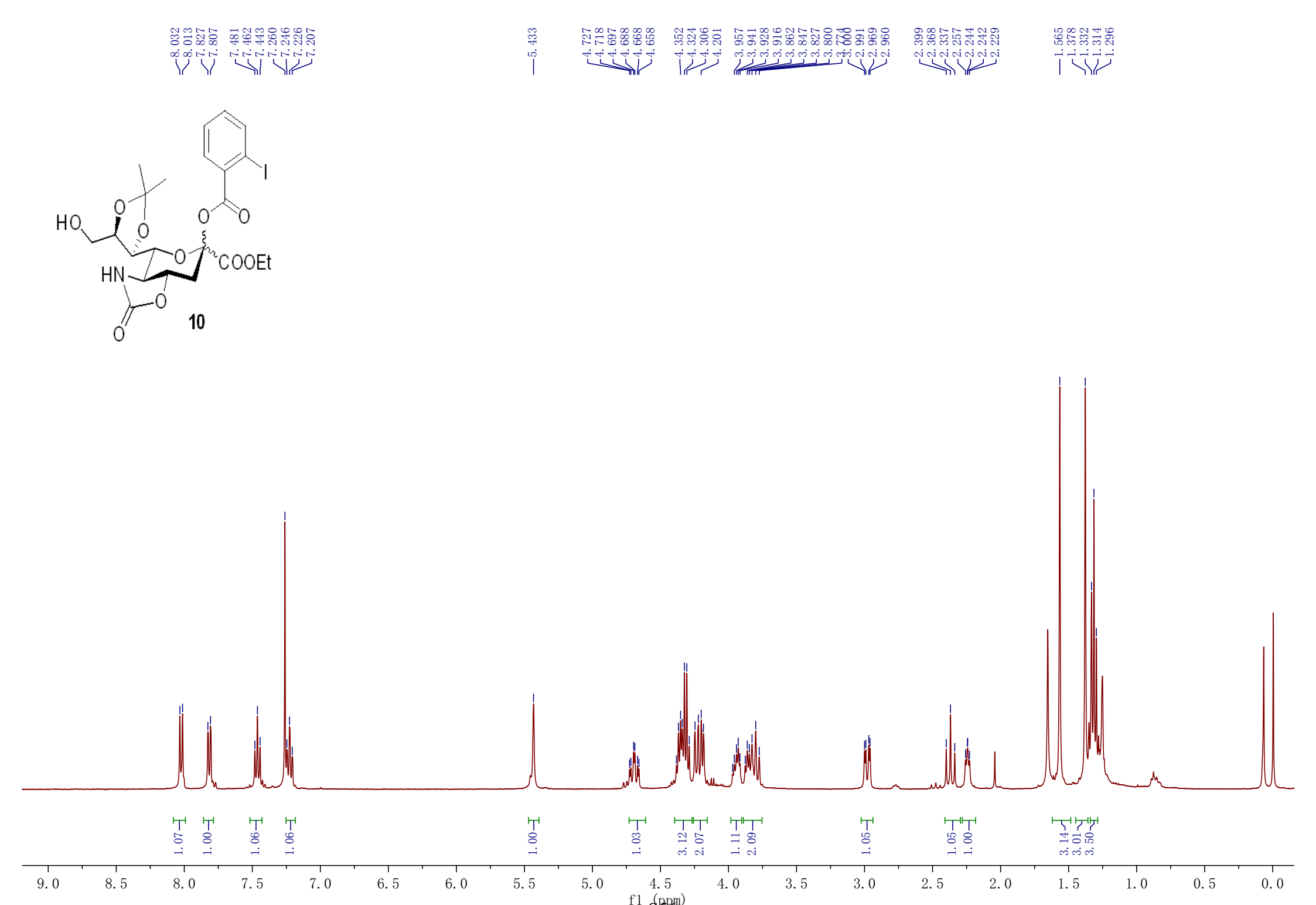


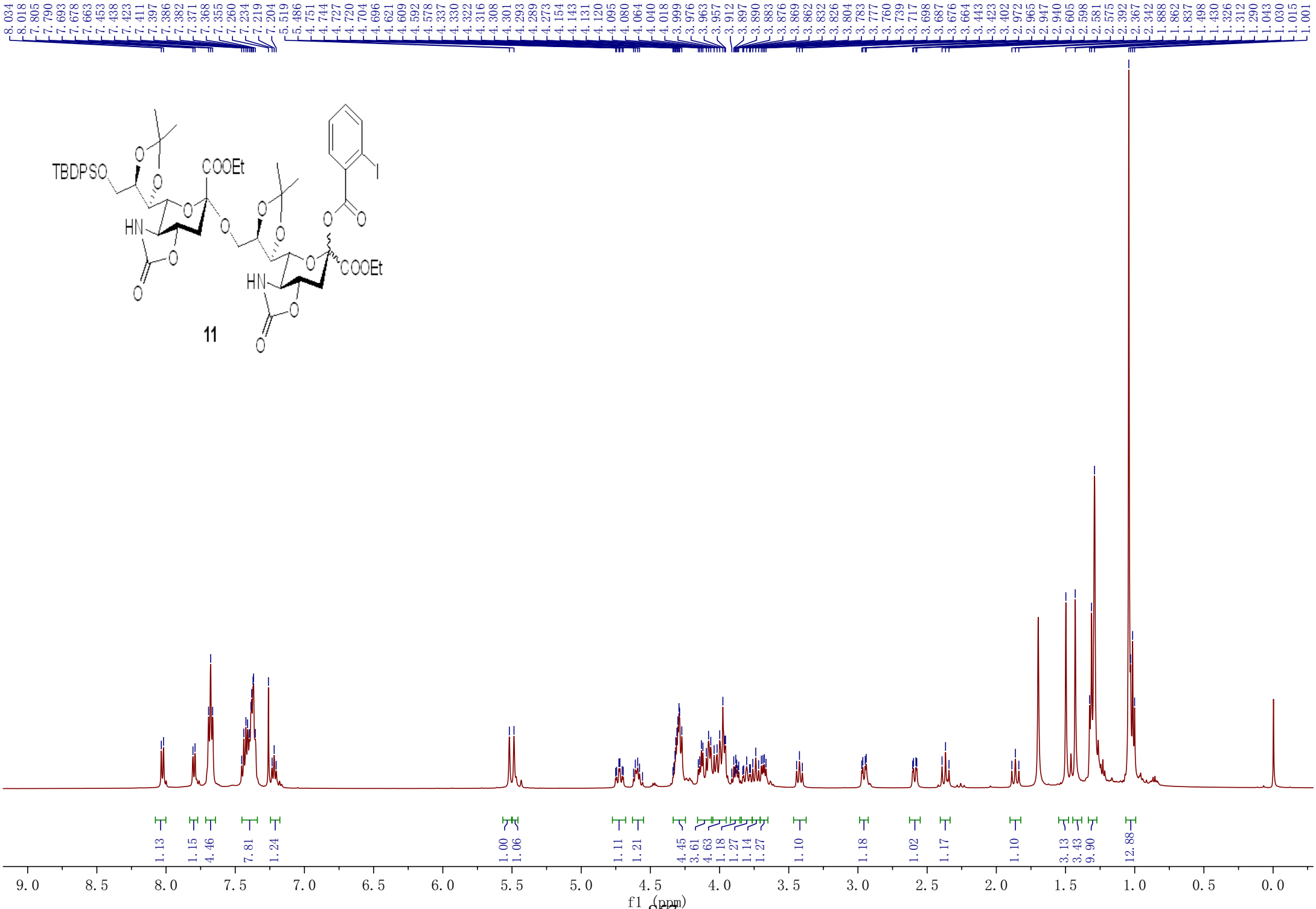
9g

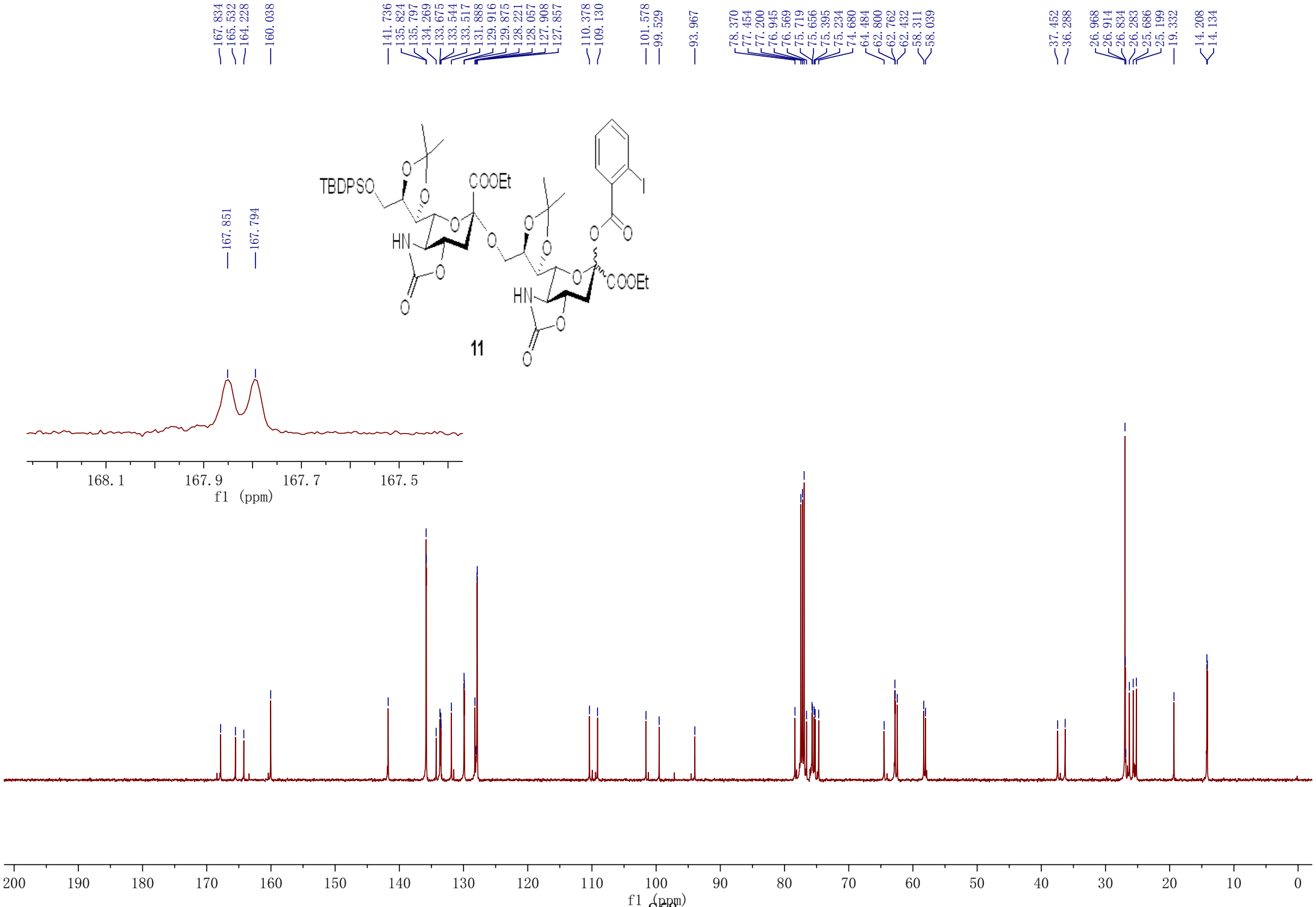

168.099
160.237
135.860
135.788
133.844
133.756
129.810
129.774
127.879
127.772
110.103
109.357
108.714
100.230
96.372
78.039
77.411
77.276
77.200
76.988
75.868
75.271
70.896
63.403
62.653
62.098
58.120
37.733
31.664
27.022
26.284
26.213
26.175
25.781
25.089
14.244
168.124
168.074
TBDPSO
COOEt
HN
9g
168.5
168.3
168.1
167.9
167.7
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

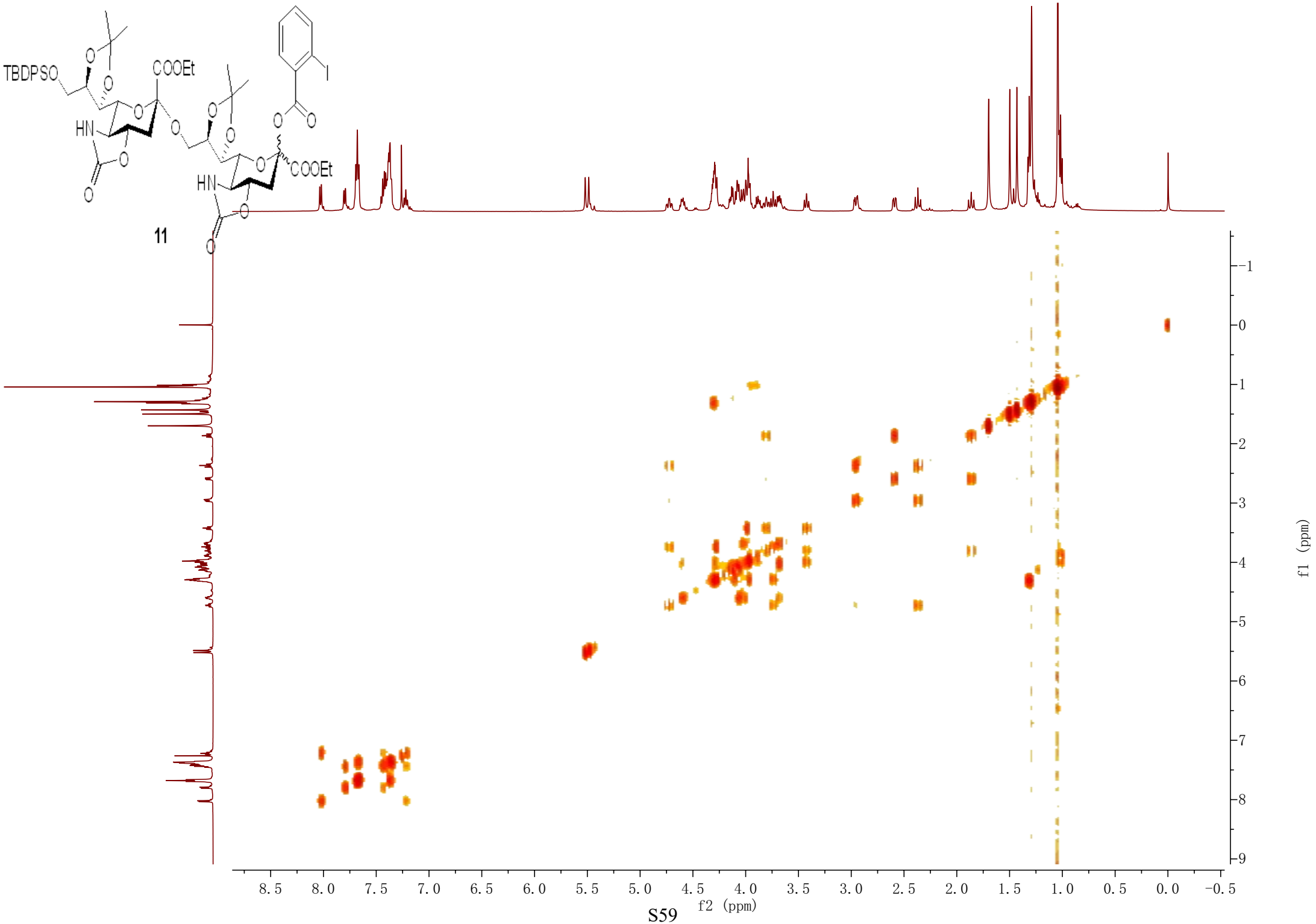

TBDPSO
COOEt
HN
O
9g
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
-1
0
1
2
3
4
5
6
7
8
f1 (ppm)

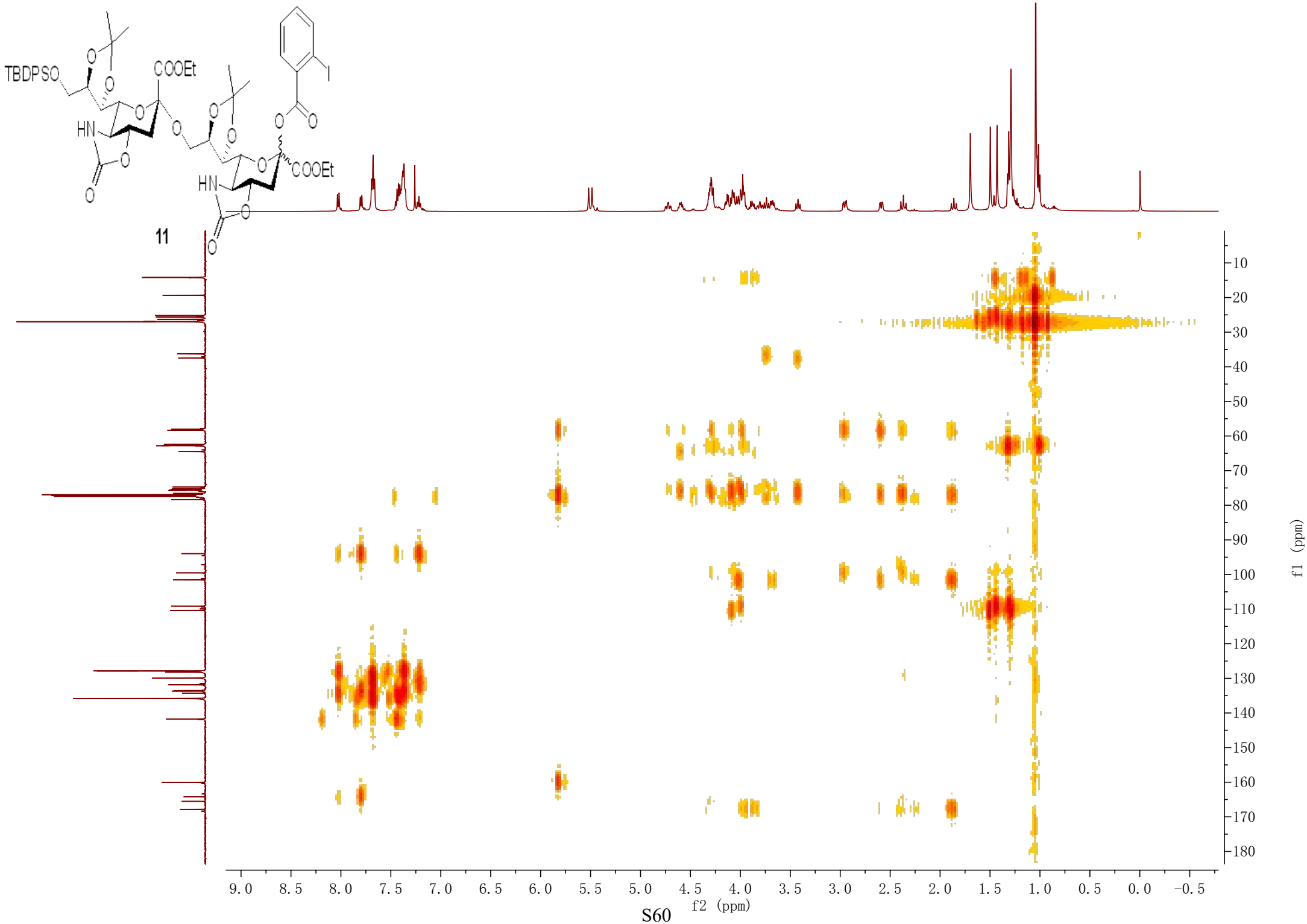

TBDPSO
COOEt
HN
O
9g
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)

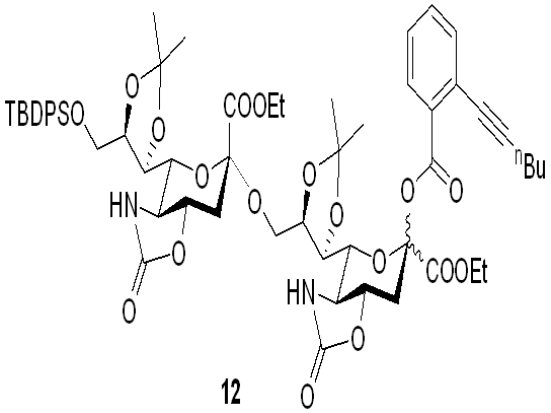

8.032
8.013
7.827
7.807
7.481
7.462
7.443
7.260
7.246
7.226
7.207
5.433
4.727
4.718
4.697
4.688
4.668
4.658
4.352
4.324
4.306
4.201
3.957
3.941
3.928
3.916
3.862
3.847
3.827
3.800
2.991
2.969
2.960
2.399
2.368
2.337
2.257
2.244
2.242
2.229
1.565
1.378
1.332
1.314
1.296
HO
O
O
O
O
O
I
HN
O
O
COOEt
10
1.07
1.00
1.06
1.06
1.00
1.03
3.12
2.07
1.11
2.09
1.05
1.05
1.00
3.14
3.01
3.50
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
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


TBDPSO
COOEt
HN
O
I
COOEt
HN
11
f1 (ppm)

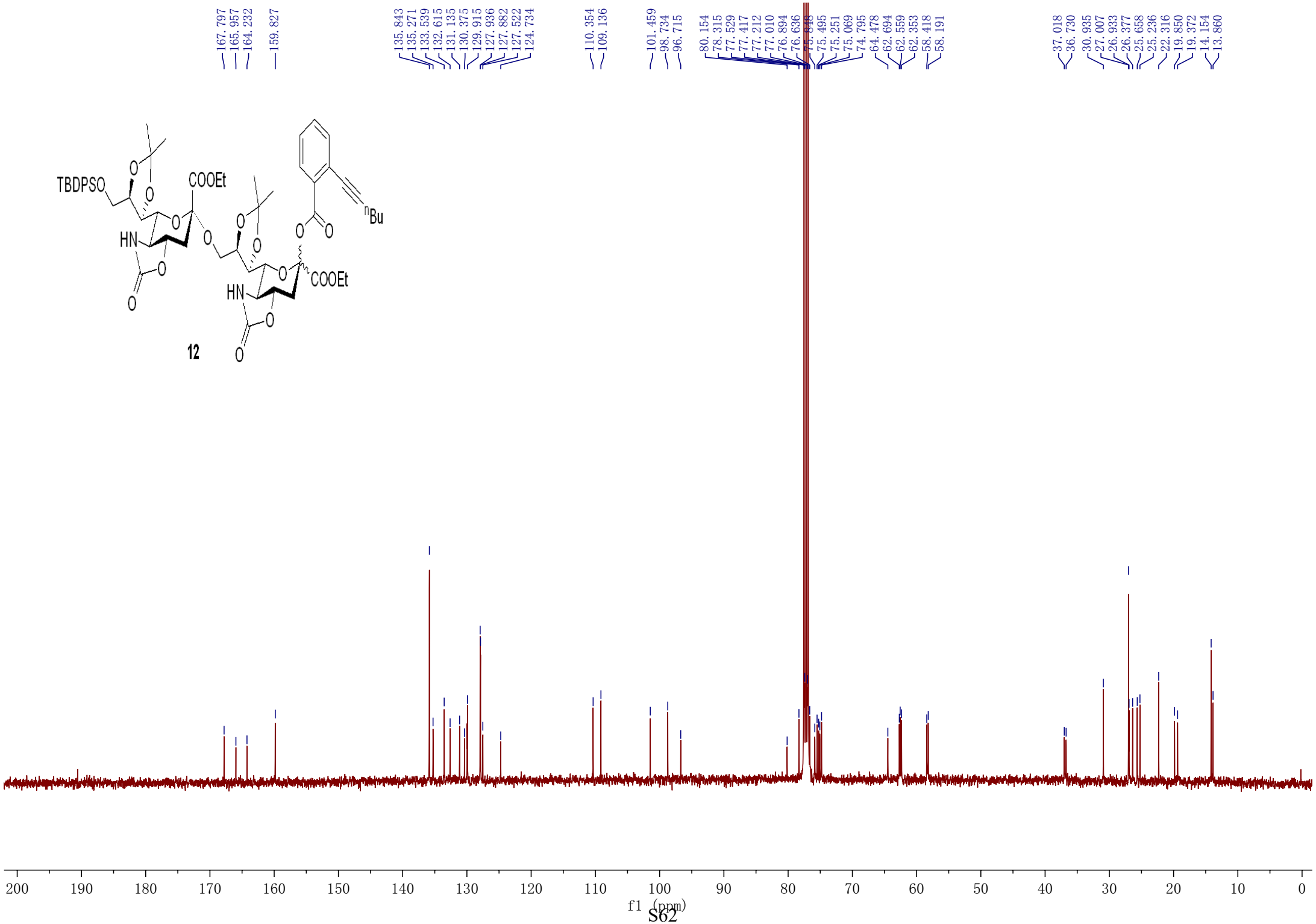

167.834
165.532
164.228
160.038
141.736
135.824
135.797
134.269
133.675
133.544
133.517
131.888
129.916
129.875
128.221
128.057
127.908
127.857
110.378
109.130
101.578
99.529
93.967
78.370
77.454
77.200
76.945
76.569
75.719
75.656
75.395
75.234
74.680
64.484
62.800
62.762
62.432
58.311
58.039
37.452
36.288
26.968
26.914
26.834
26.283
25.686
25.199
19.332
14.208
14.134
167.851
167.794
TBDPSO
COOEt
HN
HN
COOEt
I
11
168.1
167.9
167.7
167.5
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

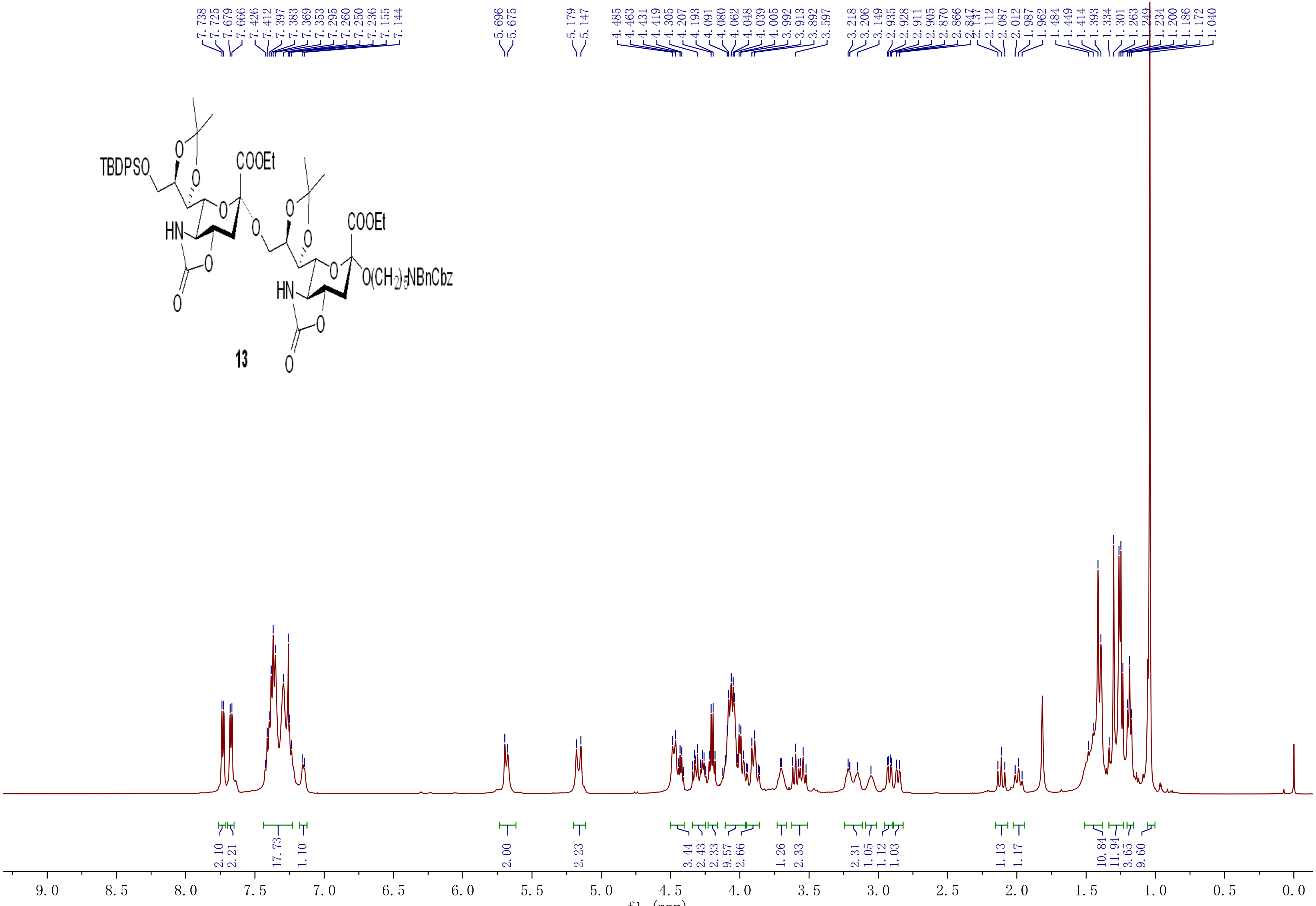

TBDPSO
COOEt
HN
O
I
COOEt
HN
11
f2 (ppm)
f1 (ppm)


TBDPSO
COOEt
HN
O
I
COOEt
HN
11
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
2.0
1.5
1.0
0.5
0.0
-0.5
f2 (ppm)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
f1 (ppm)



12


167.797
165.957
164.232
159.827
135.843
135.271
133.539
132.615
131.135
130.375
129.915
127.936
127.882
127.522
124.734
110.354
109.136
101.459
98.734
96.715
80.154
78.315
77.529
77.417
77.212
77.010
76.894
76.636
75.495
75.251
75.069
74.795
64.478
62.694
62.559
62.353
58.418
58.191
37.018
36.730
30.935
27.007
26.933
26.377
25.658
25.236
22.316
19.850
19.372
14.154
13.860
TBDPSO
COOEt
HN
O
nBu
COOEt
12
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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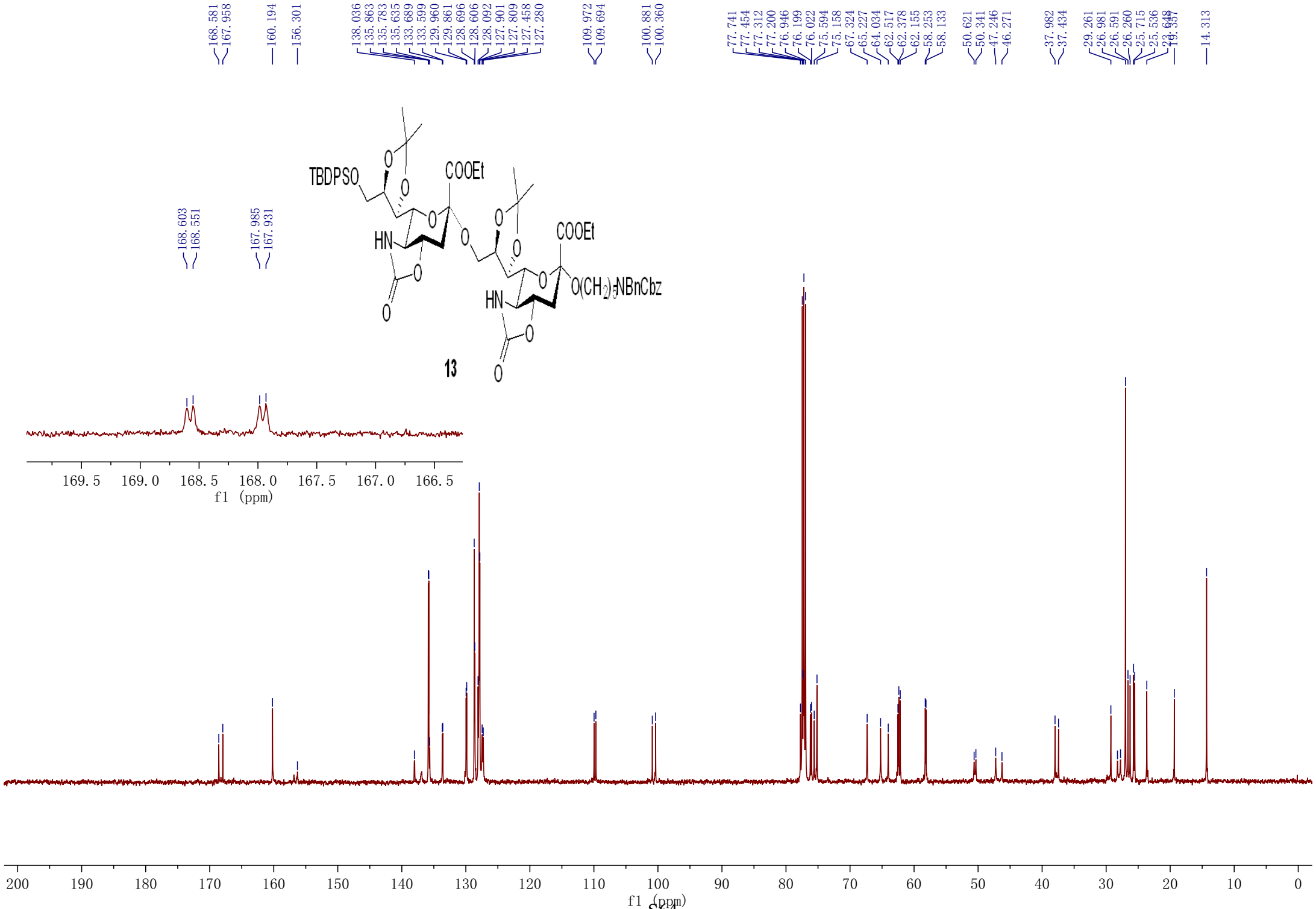
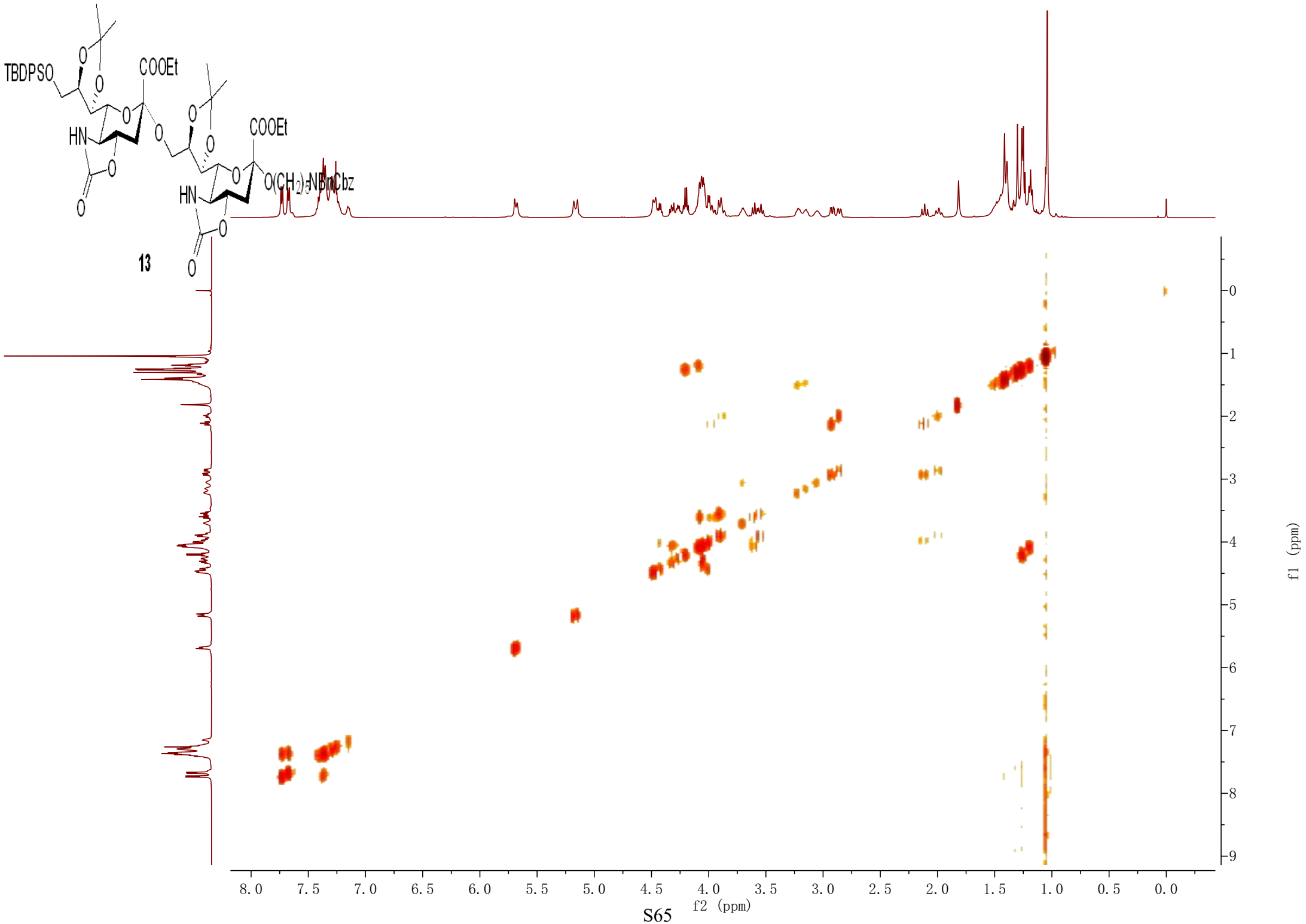
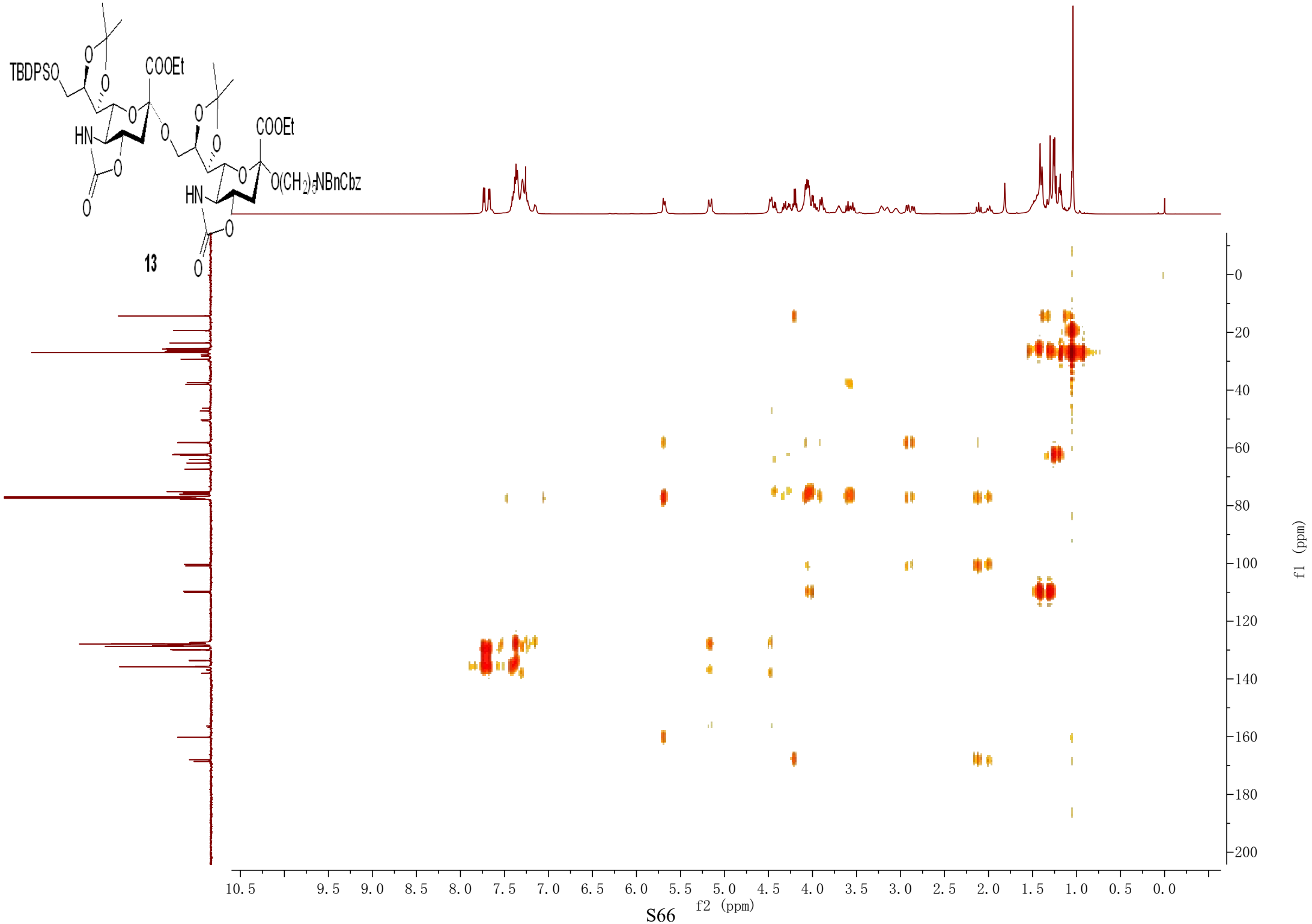
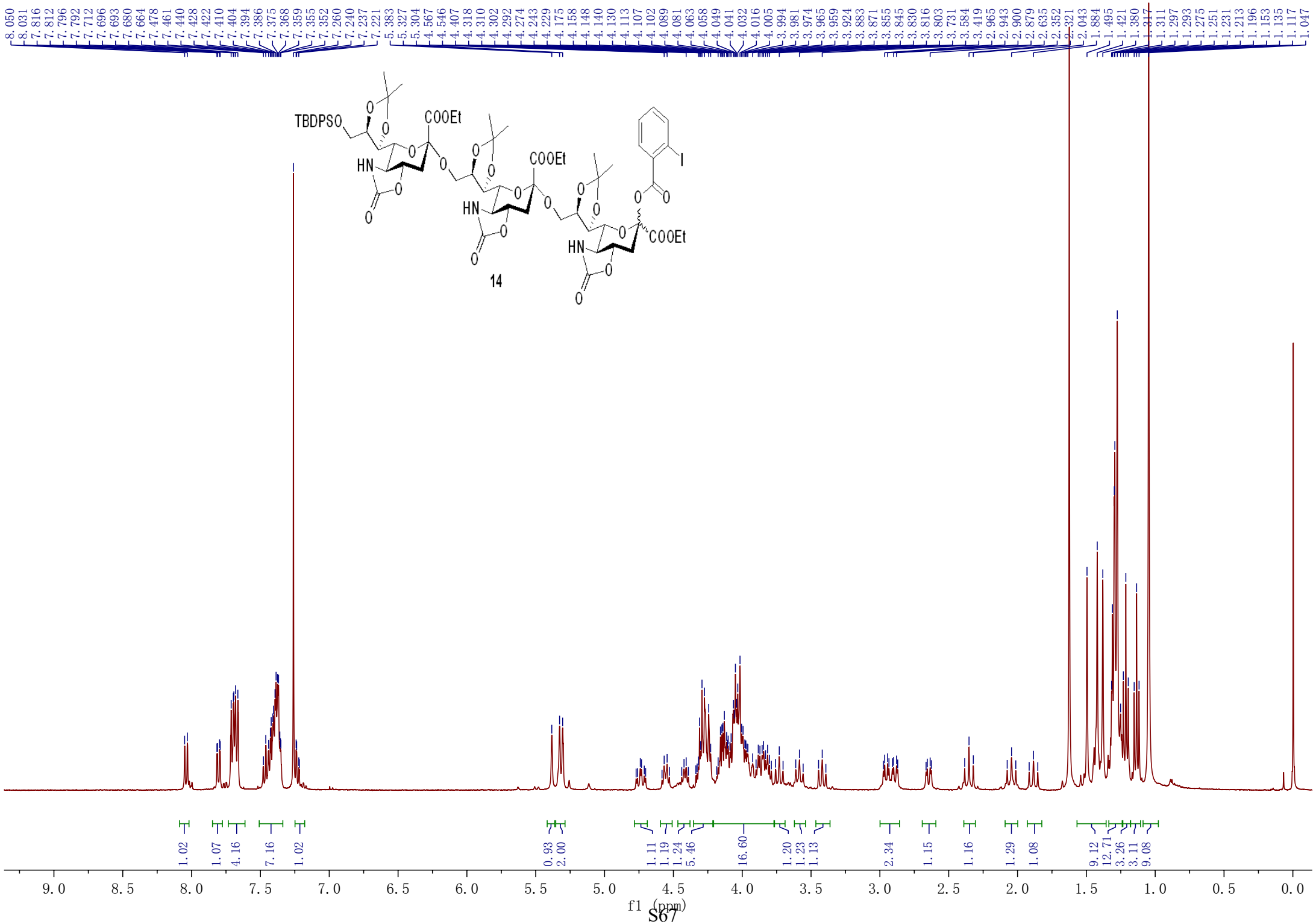
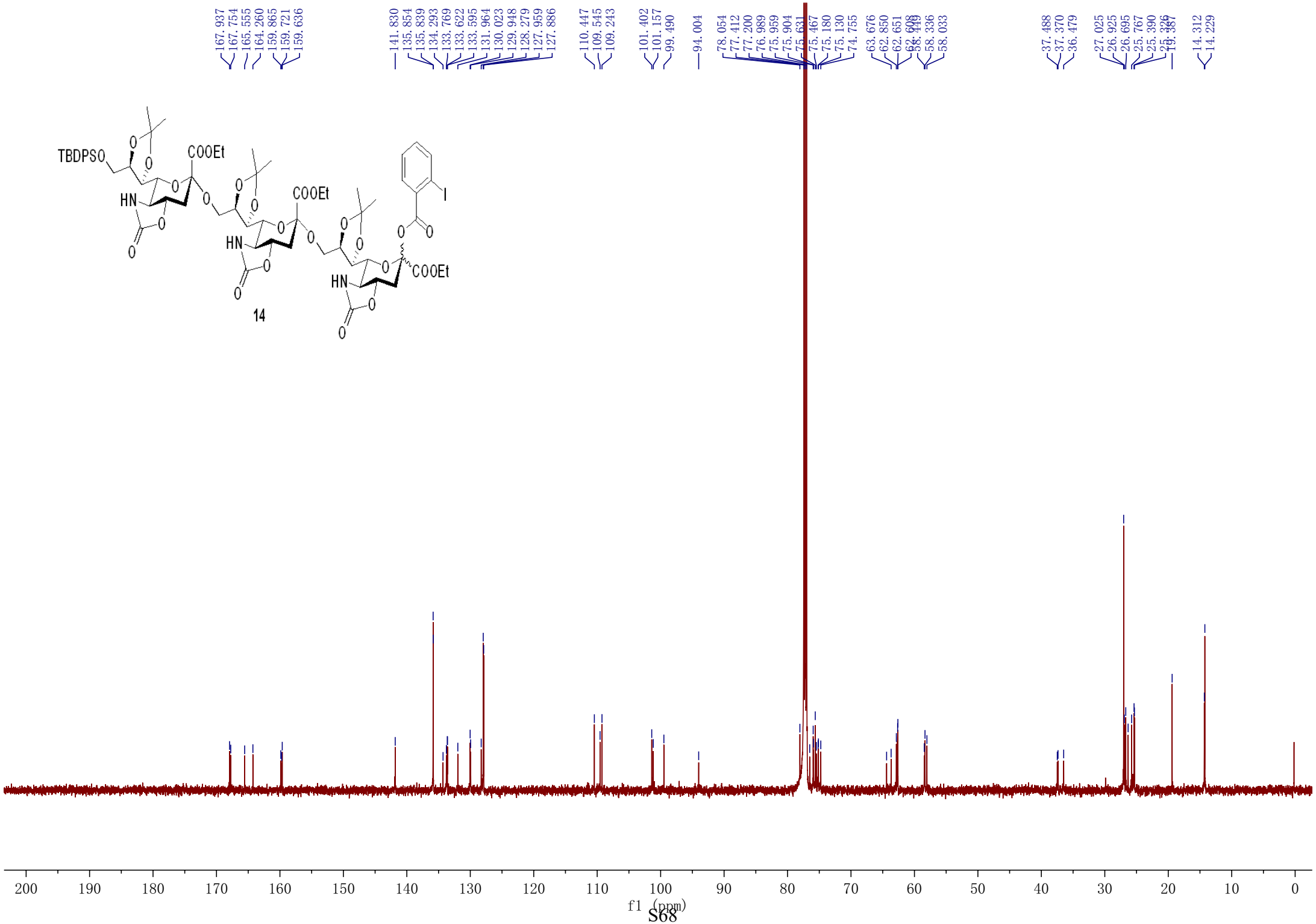
7.725
7.679
7.666
7.426
7.412
7.397
7.383
7.369
7.353
7.295
7.260
7.250
7.236
7.155
7.144
5.696
5.675
5.179
5.147
4.485
4.463
4.431
4.419
4.305
4.207
4.193
4.091
4.080
4.062
4.048
4.039
4.005
3.992
3.913
3.892
3.597
3.218
3.206
3.149
2.935
2.928
2.911
2.905
2.870
2.866
2.847
2.137
2.112
2.087
2.012
1.987
1.962
1.484
1.449
1.414
1.393
1.334
1.301
1.263
1.249
1.234
1.200
1.186
1.172
1.040
TBDPSO
COOEt
HN
O
COOEt
O(CH2)5NBnCbz
HN
O
13
2.10
2.21
17.73
1.10
2.00
2.23
3.44
2.43
2.33
9.57
2.66
1.26
2.33
2.31
1.05
1.12
1.03
1.13
1.17
10.84
11.94
3.65
9.60
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
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

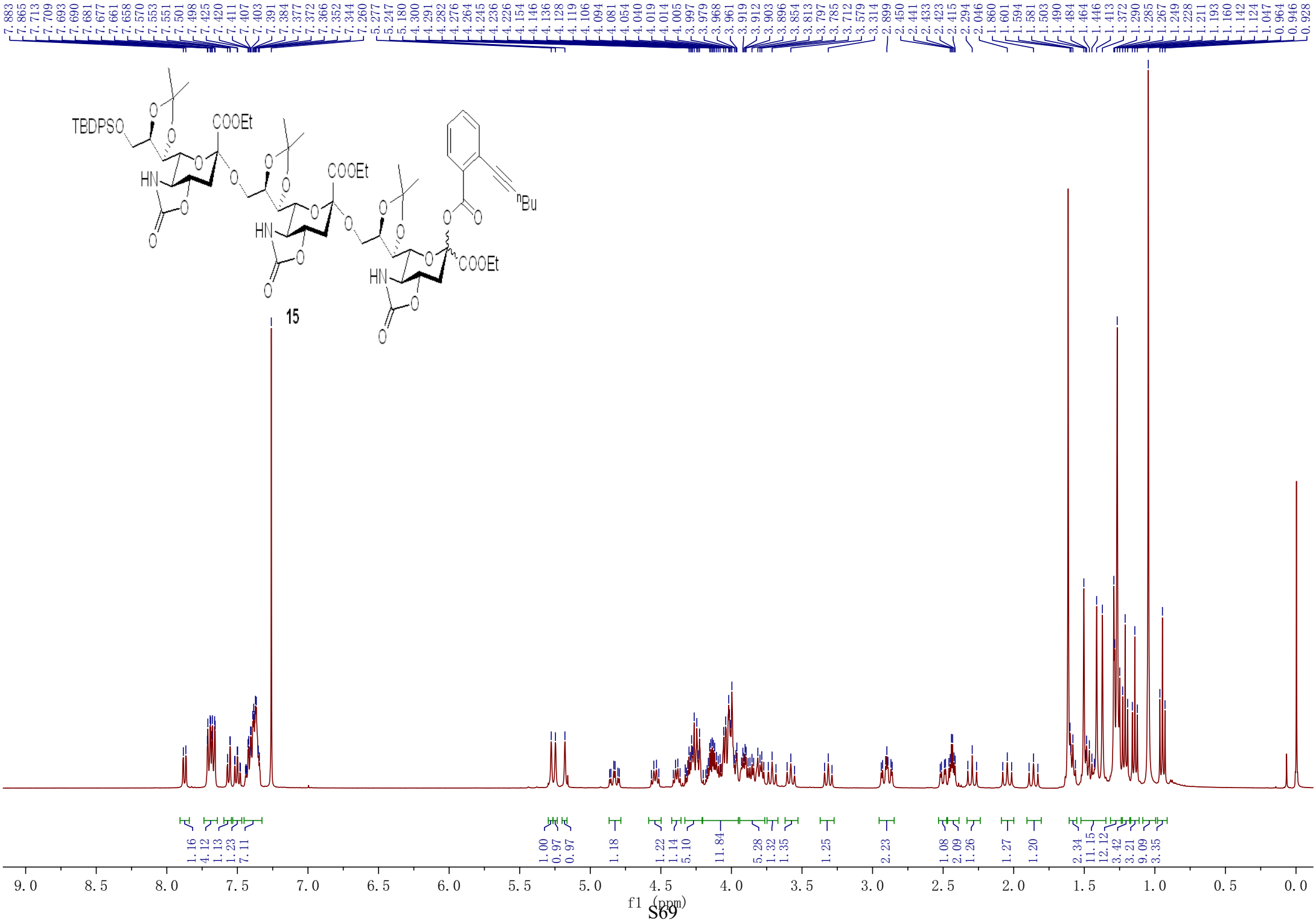

168.581
167.958
160.194
156.301
138.036
135.863
135.783
135.635
133.689
133.599
129.960
129.861
128.696
128.606
128.092
127.901
127.809
127.458
127.280
109.972
109.694
100.881
100.360
77.741
77.454
77.312
77.200
76.946
76.199
76.022
75.594
75.158
67.324
65.227
64.034
62.517
62.378
62.155
58.253
58.133
50.621
50.341
47.246
46.271
37.982
37.434
29.261
26.981
26.591
26.260
25.715
25.536
14.313
168.603
168.551
167.985
167.931
TBDPSO
COOEt
HN
O
O(CH2)3NBnCbz
13
169.5
169.0
168.5
168.0
167.5
167.0
166.5
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

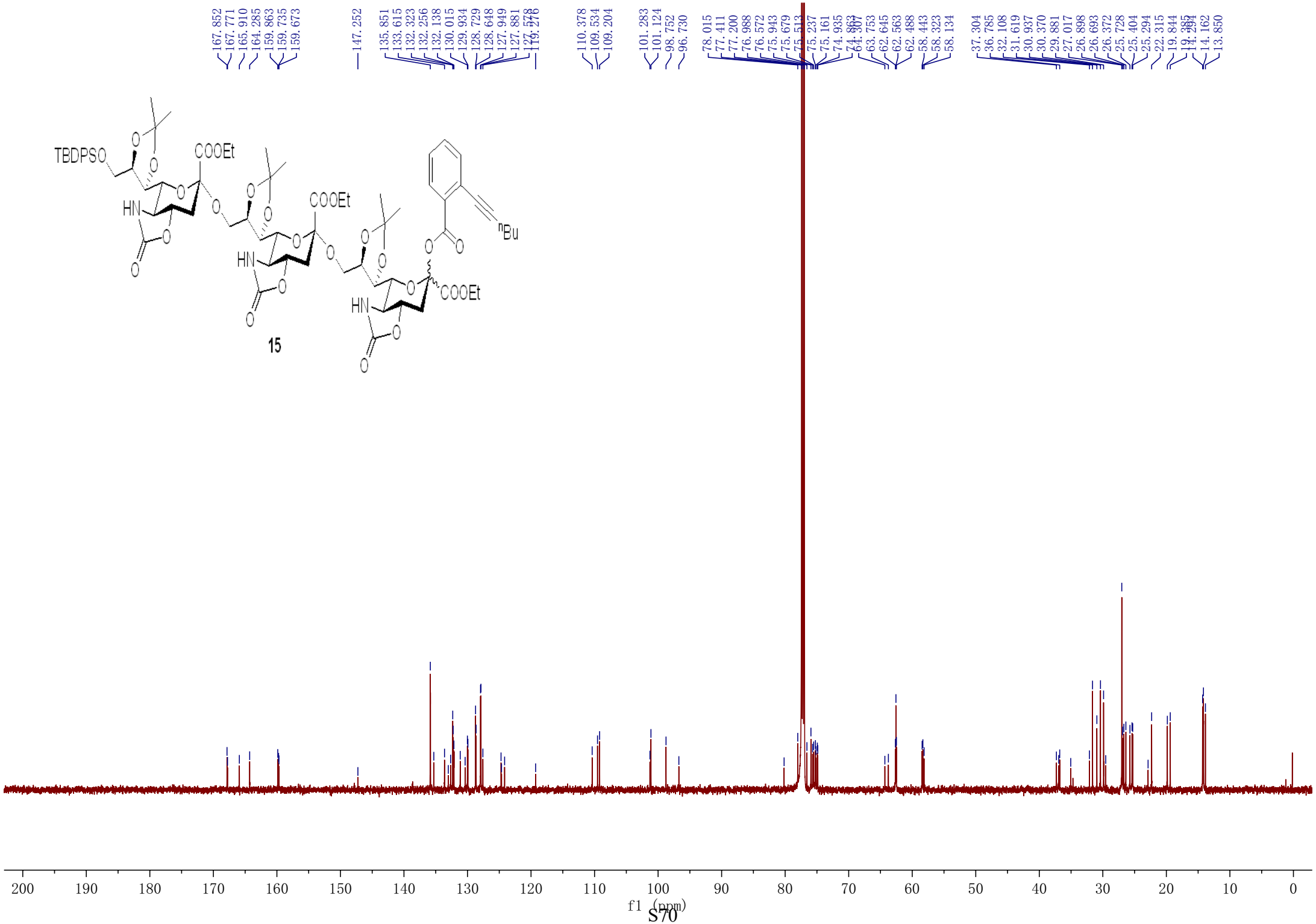

TBDPSO
COOEt
HN
O
COOEt
HN
O(CH2)5NBnCbz
13
f2 (ppm)
f1 (ppm)

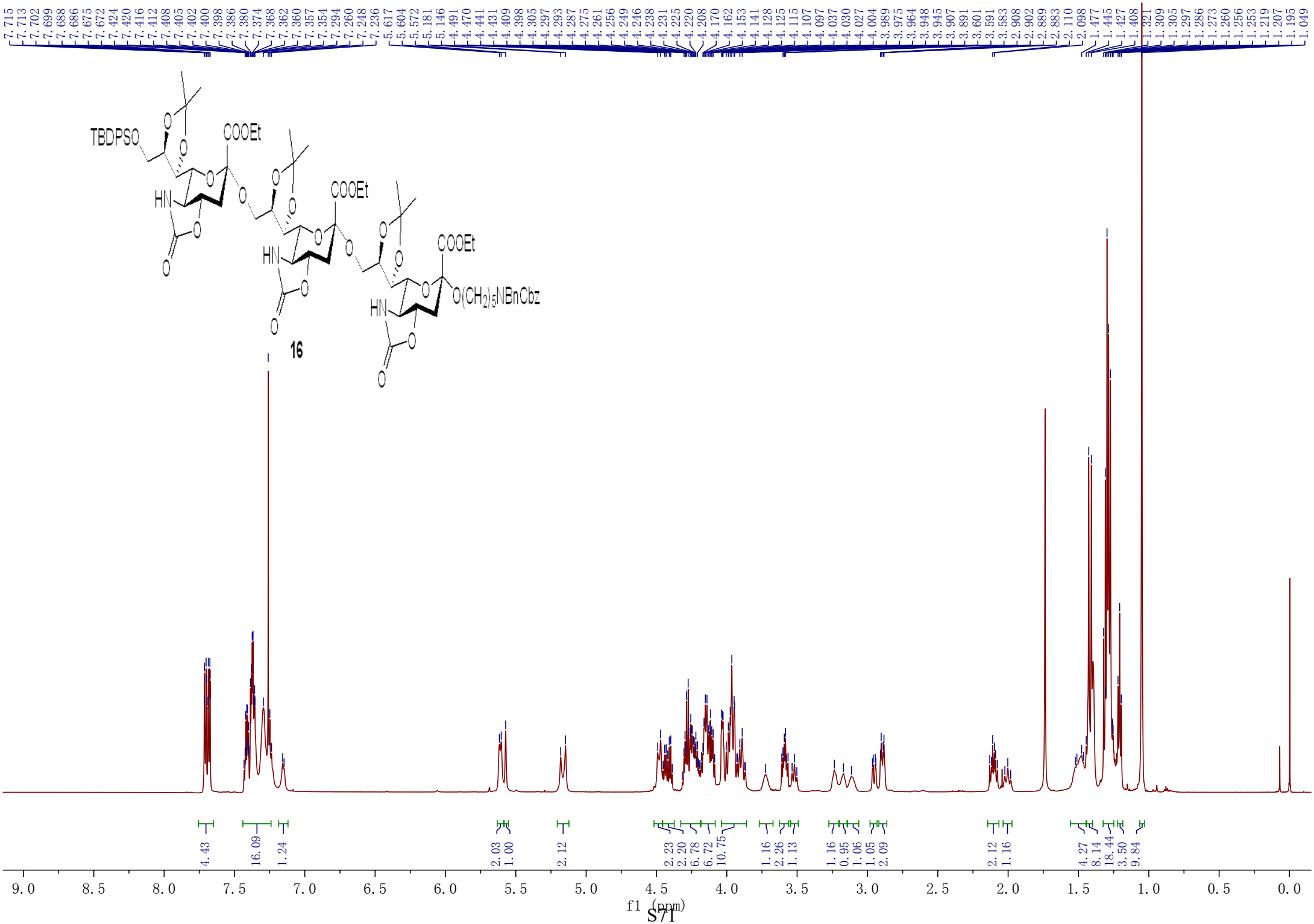

TBDPSO
COOEt
HN
O
COOEt
O(CH2)5NBnCbz
HN
13
f2 (ppm)
f1 (ppm)

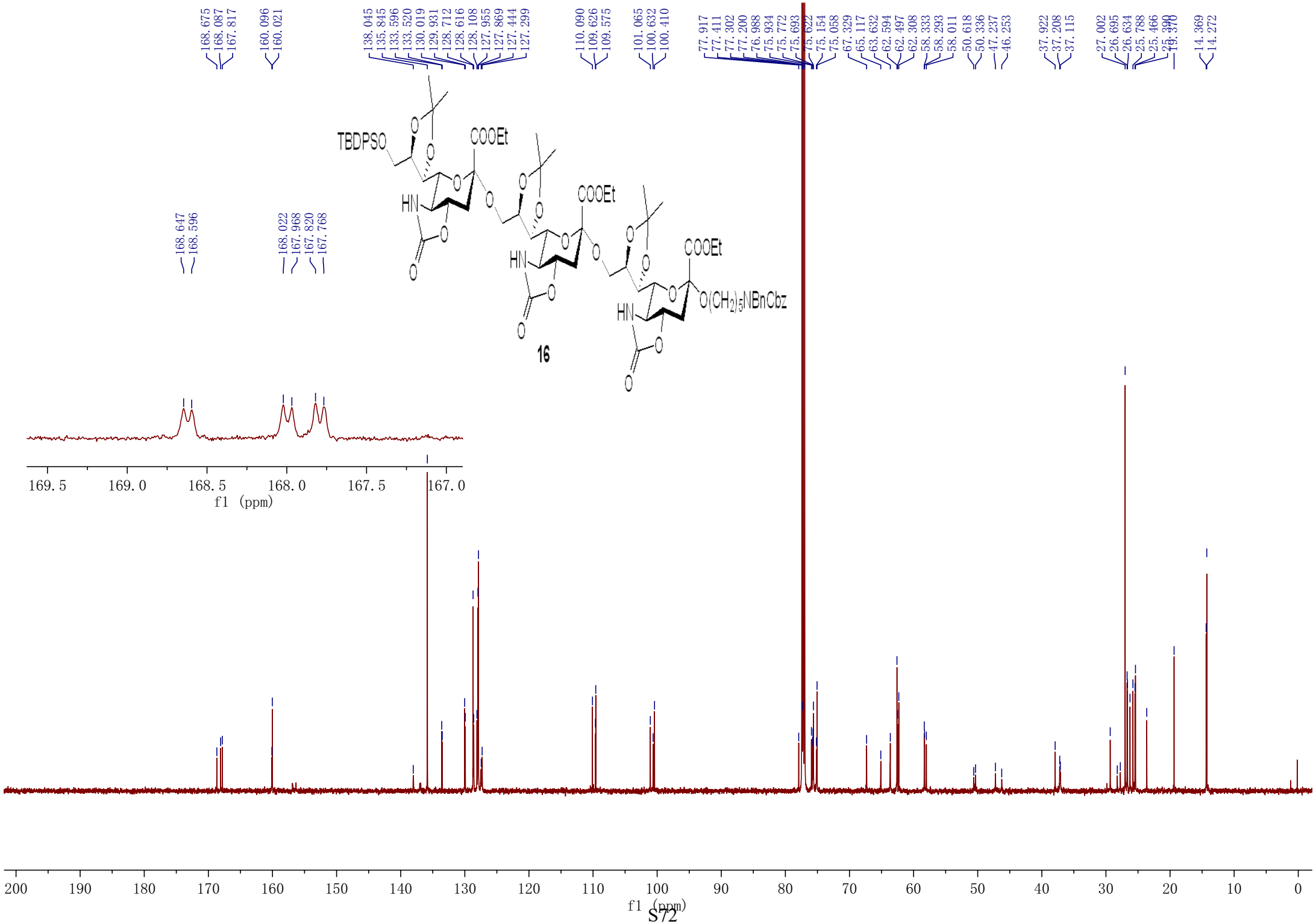

TBDPSO
COOEt
HN
O
I
14
f1 (ppm)

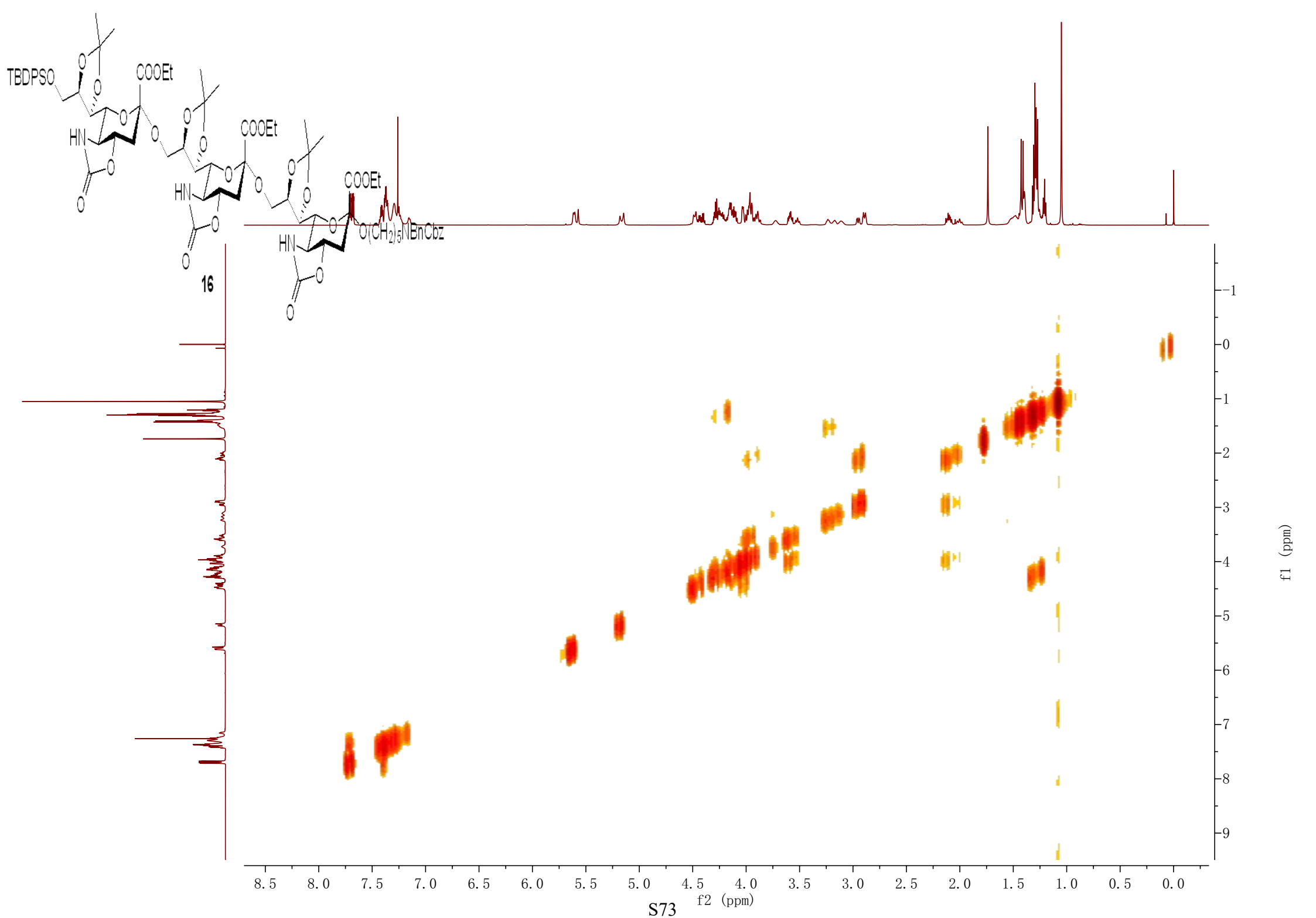

167.937
167.754
165.555
164.260
159.865
159.721
159.636
141.830
135.854
135.839
134.293
133.769
133.622
133.595
131.964
130.023
129.948
128.279
127.959
127.886
110.447
109.545
109.243
101.402
101.157
99.490
94.004
78.054
77.412
77.200
76.989
75.959
75.904
75.631
75.467
75.180
75.130
74.755
63.676
62.850
62.651
58.449
58.336
58.033
37.488
37.370
36.479
27.025
26.925
26.695
25.767
25.390
19.387
14.312
14.229
TBDPSO
COOEt
HN
O
I
14
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

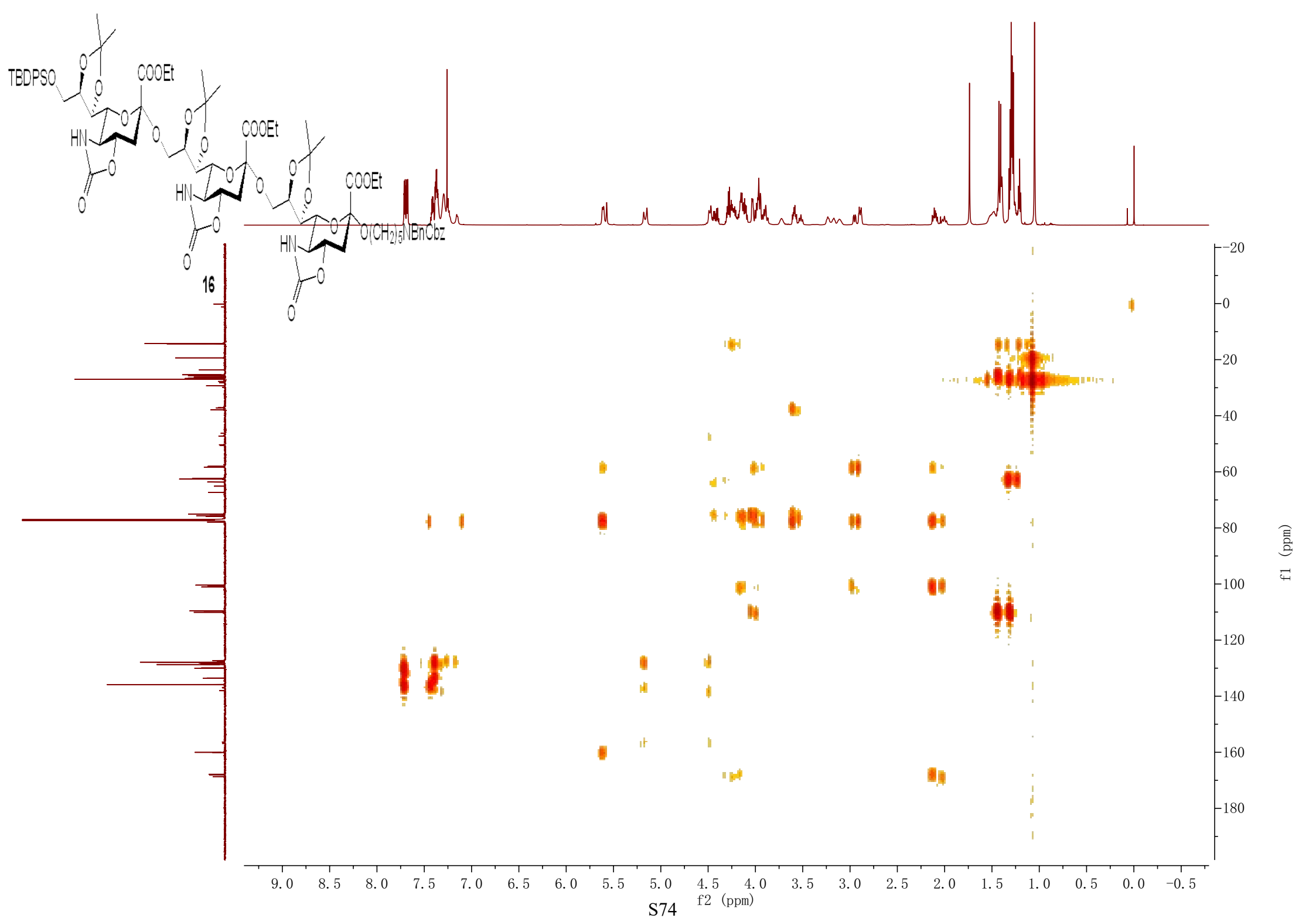

TBDPSO
COOEt
HN
O
COOEt
HN
O
COOEt
HN
O
nBu
15
f1 (ppm)


167.852
167.771
165.910
164.285
159.863
159.735
159.673
147.252
135.851
133.615
132.323
132.256
132.138
130.015
129.934
128.729
128.648
127.949
127.881
110.378
109.534
109.204
101.283
101.124
98.752
96.730
78.015
77.411
77.200
76.988
76.572
75.943
75.679
75.513
75.237
75.161
74.935
63.753
62.645
62.563
62.488
58.443
58.323
58.134
37.304
36.785
32.108
31.619
30.937
30.370
29.881
27.017
26.898
26.693
26.372
25.728
25.404
25.294
22.315
19.844
14.162
13.850
TBDPSO
COOEt
COOEt
COOEt
HN
HN
HN
nBu
15
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TBDPSO
COOEt
HN
O
O(CH2)5NBnCbz
16
f1 (ppm)


168.675
168.087
167.817
160.096
160.021
138.045
135.845
133.596
133.520
130.019
129.931
128.712
128.616
128.108
127.955
127.869
127.444
127.299
110.090
109.626
109.575
101.065
100.632
100.410
77.917
77.411
77.302
77.200
76.988
75.934
75.772
75.693
75.622
75.154
75.058
67.329
65.117
63.632
62.594
62.497
62.308
58.333
58.293
58.011
50.618
50.336
47.237
46.253
37.922
37.208
37.115
27.002
26.695
26.634
25.788
25.466
19.370
14.369
14.272
168.647
168.596
168.022
167.968
167.820
167.768
TBDPSO
COOEt
COOEt
COOEt
HN
HN
HN
O(CH2)5NBnCbz
16
169.5
169.0
168.5
168.0
167.5
167.0
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


TBDPSO
COOEt
HN
O
O(CH2)5NBnCbz
16
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
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
f1 (ppm)


TBDPSO
COOEt
HN
O
16
O(CH2)5NBnCbz
f2 (ppm)
f1 (ppm)