Supporting information

Pd-Catalyzed S-glycosylation of cysteine-containing peptides at room temperature

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1. General information

Solvents and reagents are obtained from commercial suppliers and were used without further purification. Analytical TLC was performed using Merck silica gel F254 (230-400 mesh) plates and analyzed by UV light or by staining upon heating with vanilin solution (15 g of vanilin in 250 mL ethanol and 2.5 mL of concentrated sulfuric acid). For silica gel chromatography, the flash chromatography technique was used, with Merck silica gel 60 (230-400 mesh) and p.a. grade solvents unless otherwise noted. The ^{1}H NMR and ^{13}C NMR spectra were recorded in either acetone or MeOD-d4 on Bruker Avance 300 spectrometers. The chemical shifts of ^{1}H and ^{13}C are reported in ppm relative to the solvent residual peaks. IR spectra were measured on a Bruker Vector 22 spectrophotometer. Merck silica gel 60 (0.015–0.040 mm) was used for column chromatography. Melting points were recorded on a Büchi B-450 apparatus and are uncorrected. High resolution mass spectra (HR-MS) were recorded on a MicroMass LCT Premier Spectrometer spectrometer, mass analyzer type: Time of Flight Mass Spectrometer (TOF). Optical rotations were obtained with a PolAAr 32 polarimeter.
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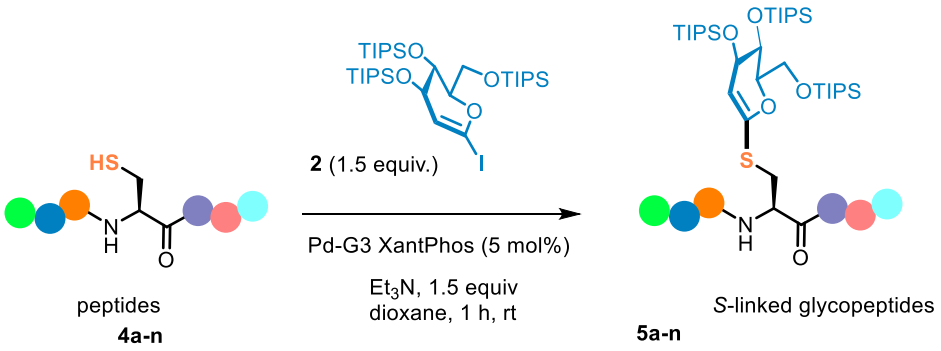
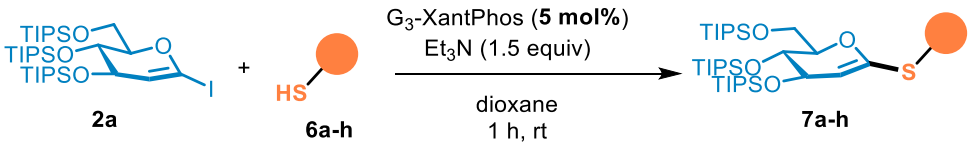
2. General Procedure for the coupling of iodoglycals with Cysteine containing peptides



All 1-iodine sugars were synthesized according to previously reported protocols.[1,2]
All cysteine-containing peptides were synthesized according to literature procedures.[3,4,5]

3. General Procedure for the coupling of iodoglycals with other thiols

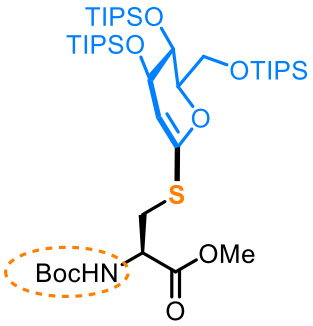
A vial (5 mL) with a stir bar was charged with iodoglycal (0.12 mmol), cysteine-containing peptide (0.1 mmol), Xantphos Pd-G_3 (0.005 mmol). The vial was then evacuated and backfilled with an argon balloon. Dry 1,4-dioxane (1 mL) was added and the mixture stirred at room temperature for 1 min. Et_3N (0.15 mmol) was added and the reaction mixture stirred intensely under Ar at room temperature for one hour. The reaction mixture was extracted with DCM, and the organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography.



A vial (5 mL) with a stir bar was charged with iodglycal (0.12 mmol), thiol (0.1 mmol), Xantphos Pd-G_3 (0.005 mmol). The vial was then evacuated and backfilled with an argon balloon. Dry 1,4-dioxane (1 mL) was added and the mixture stirred at room temperature for 1 min. Et_3N (0.15 mmol) was added and the reaction mixture stirred intensely under Ar at room temperature for one hour. The reaction mixture was extracted with DCM, and the organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by flash chromatography.

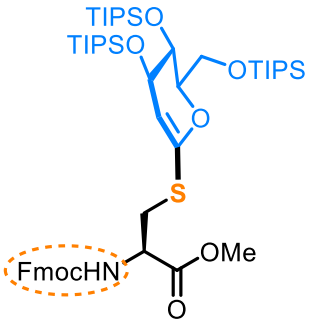
3. Experimental data

Methyl-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-N-(tert-butoxycarbonyl)-L-cysteinate



Following the general procedure, starting from cysteine (23.5 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (PE) to provide compound **3a** (75.3 mg, 89 %) as a colorless liquid. Rf = 0.5 (cyclohexane); $[\alpha]_D^{22}$ = - 14.8 (c, 0.5, DCM); ^{1}H NMR (300 MHz, acetone-*d6*): δ 6.20 (bd, *J* = 9.0 Hz, 1 H), 5.20 (dd, *J* = 5.1, 1.5 Hz, 1H), 4.48-4.32 (m, 2 H), 4.24-4.10 (m, 3 H), 4.02 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.70 (S, 3 H), 3.27 (dd, *J* = 13.8, 5.4 Hz, 1H), 3.10 (dd, *J* = 13.8, 8.4 Hz, 1H), 1.42 (s, 9 H), 1.24-0.99 (m, 63H); ^{13}C NMR (75 MHz, acetone-*d6*) 172.5, 156.3, 149.45, 103.4, 84.5, 79.8, 71.1, 68.5, 62.7, 54.9, 52.7, 33.7, 28.9, 18.8, 13.6, 13.5, 13.14; IR (neat): 2943, 2891, 2362, 1749, 1653, 1463, 1213, 1064, 1059, 1030, 881, 752, 657 cm^{-1}; HRMS (ESI): m/z calc. for $C_{42}H_{85}NNaO_8SSi_3$ $[M+Na]^+$ 870.5196; found 870.5199.

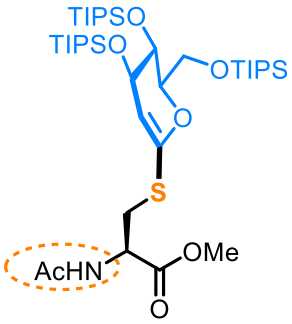
Methyl-N-(((9H-fluoren-9-yl)methoxy)carbonyl)-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)- L-cysteinate.



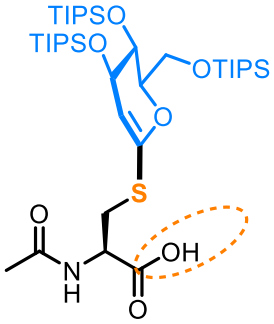
Following the general procedure, starting from cysteine **2b** (35.8 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (PE) to provide compound **3b** (83.4 mg, 84 %) as a colorless liquid. Rf = 0.5 (cyclohexane); $[\alpha]_D^{22}$ = - 15.6 (c, 0.4, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 7.87 (d, *J* = 7.2 Hz, 2H), 7.79–7.65 (m, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 6.89 (bd, *J* = 7.9 Hz, 1H), 5.23 (d, *J* = 5.0 Hz, 1H), 4.57–4.42 (m, 2H), 4.39–4.25 (m, 3H), 4.25–4.00 (m, 4H), 3.73 (s, 3H), 3.38 (dd, *J* = 13.7, 5.0 Hz, 1H), 3.14 (dd, *J* = 13.6, 8.8 Hz, 1H), 1.24–0.98

(m, 63H); ^{13}C NMR (75 MHz, acetone-*d6*) δ 172.1, 156.7, 148.8, 145.4, 142.4, 142.1, 128.8, 128.2, 126.4, 126.4,121.1, 102.4, 84.5, 70.9, 68.3, 67.7, 62.7, 55.4, 52.8, 48.3, 33.2, 18.9, 18.8, 18.8, 13.5, 12.4, 13.1; IR (neat): 2943, 2891, 2866, 2372, 2324, 1749, 1653, 1508, 1458, 1246, 1085, 881, 790, 756, 681 cm^{-1}; HRMS (ESI): m/z calc. for $C_{52}H_{87}NNaO_8SSi_3$ $[M+Na]^+$ 992.5352; found 992.5359.

Methyl-N-acetyl-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)- L-cysteinate

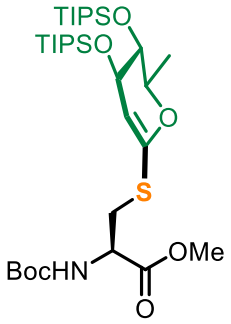


Following the general procedure, starting from cysteine **2c** (18 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (PE) to provide compound **3c** (64.7 mg, 82 %) as a colorless liquid. Rf = 0.5 (cyclohexane); $[\alpha]_D^{22}$ = - 13.1 (c, 0.5, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 7.35 (bd, J = 7.8 Hz, 1 H), 5.17 (dd, *J* = 5.1, 1.2 Hz, 1H), 4.68-4.61 (m, 1H), 4.44-4.42 (m, 1H), 4.22-4.11 (m, 3 H), 4.01 (dd, *J* = 11.4, 4.5 Hz, 1H), 3.68 (s, 3 H), 3.25 (dd, *J* = 13.5, 5.1 Hz, 1H), 3.11 (dd, *J* = 13.5, 7.8 Hz, 1H), 1.93 (s, 3H), 1.13-1.10 (m, 63 H); ^{13}CNMR (75 MHz, acetone-*d6*) δ 172.1, 169.7, 149.0, 103.1, 84.5, 71.0, 68.3, 62.6, 53.5, 52.6, 33.5, 22.9, 18.7, 13.4, 13.1; IR (neat): 2943, 2891, 2866, 2360, 1749, 1653, 1463, 1085, 1059, 1030, 881, 790, 752, 680 cm^{-1}; HRMS (ESI): m/z calc. for $C_{39}H_{79}NNaO_7SSi_3$ $[M+Na]^+$ 812.4777; found 812.4795.



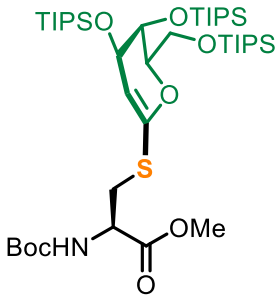
Following the general procedure, starting from cysteine **2d** (16.2 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (DCM/MeOH = 99/1) to provide compound **3d** (54.4 mg, 62 %) as a colorless liquid. Rf = 0.2 (DCM/MeOH=99/1); $[\alpha]_D^{22}$ = - 18.9 (c, 0.6, DCM); ^{1}H NMR (300 MHz, Methanol-d_4) δ 5.00 (dd, *J* = 5.1, 1.5 Hz, 1H), 4.37 (dd, *J* = 7.4, 4.3 Hz, 1H), 4.24 (m, 1H), 4.12 – 3.91 (m, 3H), 3.84 (dd, *J* = 11.3, 4.6 Hz, 1H), 3.35 – 3.23 (m, 1H), 1.89 (s, 3H), 1.07 – 0.79 (m, 63H). ^{13}CNMR (75 MHz, Methanol-d_4) δ 150.5, 84.6, 71.4, 68.8, 63.0, 55.0, 47.8, 35.2, 22.9, 18.6, 13.8, 13.1, 9.23; IR (neat): 2949, 2891, 2866, 2360, 1765, 1653, 1467, 1097, 1067, 881, 790, 752, 680, 485 cm^{-1}; HRMS (ESI): m/z calc. for $C_{38}H_{77}NNaO_7SSi_3$ $[M+H]^+$ 776.4801; found 776.4797.

Methyl-N-(tert-butoxycarbonyl)-S-((2S,3S,4S)-2-methyl-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-L-cysteinate.



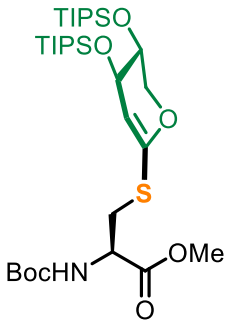
Following the general procedure, starting from cysteine **2a** (23.5 mg, 0.1 mmol) and iodosugar (68.5 mg, 0.12 mmol), the residue was purified by flash chromatography (PE) to provide compound **3f** (58.7 mg, 85 %) as a colorless liquid. Rf = 0.5 (cyclohexane); $[\alpha]_D^{22}$ = - 30.7 (c, 0.4, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 6.16 (bd, *J* = 7.3 Hz, 1H), 5.29–5.03 (m, 1H), 4.61–4.29 (m, 2H), 4.21–4.10 (m, 1H), 4.05 (d, *J* = 1.5 Hz, 1H), 3.72 (s, 3H), 3.36 (dd, *J* = 14.0, 4.3 Hz, 1H), 2.91 (dd, *J* = 13.9, 8.9 Hz, 1H), 1.49 (d, *J* = 7.1 Hz, 3H), 1.43 (s, 9H), 1.19–1.03 (m, 42H); ^{13}C NMR (75 MHz, acetone-*d6*) δ 171.3, 155.2, 146.8, 102.8, 78.6, 77.4, 73.3, 68.0, 66.7, 53.9, 51.5, 32.5, 27.4, 17.7, 15.1, 12.4, 12.3; IR (neat): 2943, 2891, 2866, 2359, 2324, 1749, 1717, 1624, 1463, 1338, 1167, 1085, 10498, 881, 756, 680 cm^{-1}; HRMS (ESI): m/z calc. for $C_{33}H_{65}NNaO_7SSi_2$ $[M+Na]^+$ 698.3912; found 698.3910.

Methyl-S-((2R,3R,4S)-2,4-bis((triisopropylsilyl)oxy)-3-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-N-(tert-butoxycarbonyl)- L-cysteinate.



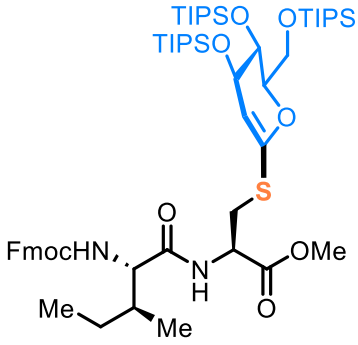
Following the general procedure, starting from cysteine **2a** (23.5 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (PE) to provide compound **3g** (75.8 mg, 87 %) as a colorless liquid. Rf = 0.5 (cyclohexane); $[\alpha]_D^{22}$ = - 48.3 (c, 0.5, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 6.22 (bd, *J* = 9.0 Hz, 1H), 5.20 (dd, *J* = 5.1, 1.5 Hz, 1 H), 4.53-4.47 (m, 2 H), 4.25-4.09 (m, 3 H), 4.02 (dd, *J* = 11.4, 4.5 Hz, 1 H), 3.70 (s, 3 H), 3.27 (dd, *J* = 13.5, 5.1 Hz, 1H), 3.00 (dd, *J* = 13.5, 8.4 Hz, 1 H), 1.42 (s, 9H), 1.22-1.10 (m, 63 H); ^{13}C NMR (75 MHz, acetone-*d6*) δ 171.8, 161.9, 149.0, 103.3, 84.5, 79.8, 71.1, 68.4, 62.7, 54.9, 52.7, 33.7, 28.9, 18.8, 13.6, 13.5, 13.1; IR (neat): 2943, 2891, 2362, 1749, 1653, 1463, 1213, 1064, 1059, 1030, 881, 752, 657 cm^{-1}; HRMS (ESI): m/z calc. for $C_{42}H_{85}NNaO_8SSi_3$ $[M+Na]_+$ 870.5196; found 870.5198.

Methyl-S-((3S,4S)-3,4-bis((triisopropylsilyl)oxy)-3,4-dihydro-2H-pyran-6-yl)-N-(tert-butoxycarbonyl)-L-cysteinate.



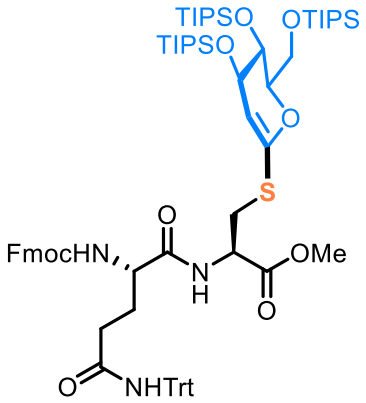
Following the general procedure, starting from cysteine **2a** (23.5 mg, 0.1 mmol) and iodosugar (66.5 mg, 0.12 mmol), the residue was purified by flash chromatography (PE) to provide compound **3h** (53.5 mg, 81 %) as a colorless liquid. Rf = 0.5 (cyclohexane); colorless liquid; $[\alpha]_D^{22}$ = - 60.8 (c, 0.53, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 6.20 (bd, *J* = 6.9 Hz, 1H), 5.21 (dd, *J* = 5.2, 1.3 Hz, 1H), 4.42 (d, *J* = 6.8 Hz, 1H), 4.22 (dt, *J* = 13.2, 2.1 Hz, 1H), 4.14 (bd, *J* = 10.7 Hz, 1H), 4.08–4.04 (m, 1H), 4.01–3.95 (m, 1H), 3.72 (s, 3H), 3.17 (d, *J* = 6.3 Hz, 2H), 1.43 (s, 9H), 1.27–0.96 (m, 42H). ^{13}C NMR (75 MHz, acetone-*d6*) δ 171.6, 156.0, 150.8, 104.3, 79.5, 70.1, 68.9, 67.0, 54.5, 52.0, 33.6, 28.6, 18.5, 13.3, 13.2; IR (neat): 2943, 2891, 2866, 2362, 1749, 1718, 1622, 1506, 1436, 1365, 1114, 1097, 1049, 914, 881, 752, 680 cm^{-1}; HRMS (ESI): m/z calc. for $C_{32}H_{63}NNaO_7SSi_2$ $[M+Na]^+$ 684.3756; found 684.3757.

methyl N-(((9H-fluoren-9-yl)methoxy)carbonyl)-S-((2R,3R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-L-cysteinyl-L-isoleucinate.



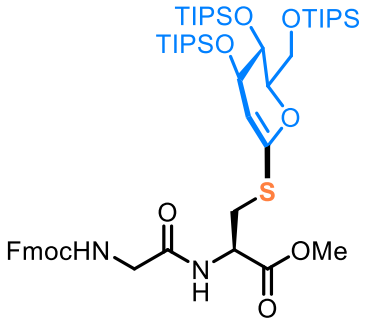
Following the general procedure, starting from cysteine containing peptide (46.9 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (PE) to provide compound **5a** (90.1 mg, 84 % yield) as a colorless liquid. Rf = 0.4 ((EtOAc /cyclohexane = 1:9); $[\alpha]_D^{22}$ = - 67 (c, 0.7, DCM 1H NMR (300 MHz, Acetone-d6) δ 7.86 (d, J = 7.5 Hz, 2H), 7.77 – 7.67 (m, 2H), 7.62 (d, J = 7.5 Hz, 1H), 7.48 – 7.32 (m, 4H), 6.40 (d, J = 8.8 Hz, 1H), 5.19 (d, J = 5.2 Hz, 1H), 4.75 – 4.52 (m, 1H), 4.46 – 4.02 (m, 10H), 3.70 (s, 3H), 3.35 (dd, J = 13.6, 5.3 Hz, 1H), 3.15 (dd, J = 13.6, 8.2 Hz, 1H), 1.93 (m, 1H), 1.23 – 0.87 (m, 69H); ^{13}C NMR (75 MHz, acetone-*d6*) δ 133.8, 130.9, 128.5, 127.9, 126.1, 120.8, 84.3, 70.7, 68.0, 67.4, 62.4, 55.1, 48.1, 33.1, 25.3, 18.4, 13.3, 12.8; IR (neat): 2978, 2889, 2389, 2330, 1749, 1547, 1508, 1467, 1246, 1085, 897, 756, 787, 687 cm^{-1}; HRMS (ESI): m/z calc. for $C_{58}H_{98}N_2NaO_9SSi_3$ $[M+Na]^+$ 1105.6193; found 1105.6190.

Methyl-N-(N2-(((9H-fluoren-9-yl)methoxy)carbonyl)-N5-trityl-L-glutaminyl)-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-L-cysteinate.



Following the general procedure, starting from cysteine containing peptide (72.7 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (PE) to provide compound **5b** (70.5 mg, 53 %) as a colorless liquid. Rf = 0.4 (EtOAc/cyclohexane = 1:9); $[\alpha]_D^{22}$ = -25.3 (c, 0.5, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 7.92–7.81 (m, 3H), 7.85-7.5 (m, 3H), 7.48 (bt, *J* = 7.5 Hz, 2H), 7.43–7.24 (m, 15H), 6.67 (bd, *J* = 12.3 Hz, 1H), 5.25 (bd, *J* = 5.1 Hz, 1H), 4.71 (bq, *J* = 5.2 Hz, 1H), 4.54–4.46 (m, 1H), 4.46–3.96 (m, 8H), 3.74 (s, 3H), 3.42 (dd, *J* = 13.6, 5.1 Hz, 1H), 3.10 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.69–2.55 (m, 2H), 2.25–2.10 (m, 2H), 1.26–0.95 (m, 63H); ^{13}C NMR (75 MHz, acetone-*d6*) δ 172.9, 172.8, 172.0, 157.4, 149.1, 146.7, 145.6, 142.6, 130.3, 129.1, 128.9, 127.9, 125.7, 121.4, 103.8, 84.8, 71.5, 71.2, 68.5, 67.9, 63.0, 55.6, 53.8, 53.1, 48.6, 34.0, 33.6 , 19.0, 13.8, 13.7,13.3; HRMS (ESI): m/z calc. for $C_{76}H_{109}N_3NaO_{10}SSi_3$ $[M+Na]^+$ 1362.7034; found 1362.7049.

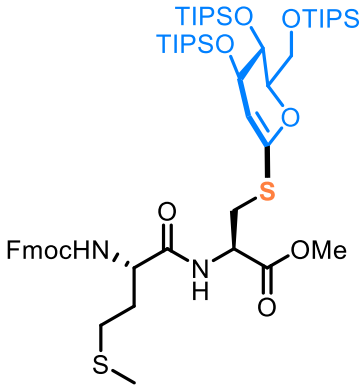
Methyl-N-((((9H-fluoren-9-yl)methoxy)carbonyl)glycyl)-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-L-cysteinate.



Following the general procedure, starting from cysteine containing peptide (41.5 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc /cyclohexane = 10:90) to provide compound **5c** (74.7 mg, 73%) as a colorless liquid Rf = 0.3 (EtOAc/cyclohexane = 2:8); $[\alpha]_D^{22}$ = - 14.9 (c, 0.5, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 7.95 (d, *J* = 7.0 Hz, 2H), 7.81 (dd, *J* = 6.9, 4.1 Hz, 1H), 7.48 (t, *J* = 7.0 Hz, 1H), 7.42 (t, *J* = 7.0 Hz, 1H), 6.96 (bd, *J* = 7.6 Hz, 1H), 5.31 (d, *J* = 5.1 Hz, 1H), 4.66–4.48 (m, 2H), 4.47–4.33 (m, 3H), 4.32–4.18 (m, 3H), 4.17–4.06 (m, 1H), 3.81 (s, 3H), 3.57–3.35 (m, 1H), 3.22 (dd, *J* = 13.8, 8.8 Hz, 1H), 1.29–1.05 (m, 63H); ^{13} C NMR (75 MHz, acetone-*d6*) δ 172.2, 148.9, 145.3, 142.5, 128.9, 128.3, 126.5, 121.1, 103.9, 84.6, 71.1, 68.4, 67.8,62.8, 55.3, 52.9, 48.4, 33.7, 18.8, 13.6, 13.5,13.2; IR (neat): 2943, 2891,

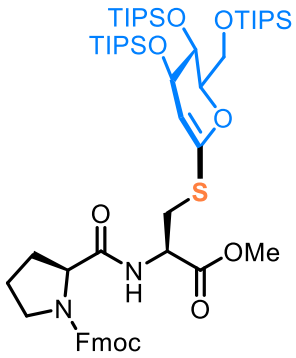
2866, 2372, 2324, 1683, 1508, 1458, 1246, 1085, 881, 756, 740, 680 cm^{-1}; HRMS (ESI): m/z calc. for $C_{54}H_{90}N_2NaO_9SSi_3$ $[M+Na]^+$ 1049.5567; found 1049.5570.

Methyl-N-((((9H-fluoren-9-yl)methoxy)carbonyl)-L-methionyl)-S-((2S,3S,4S)-3,4-bis ((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-L-cysteinate.



Following the general procedure, starting from cysteine containing peptide (48.8 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (PE) to provide compound **5d** (83.4 mg, 76 % yield) as a colorless liquid. Rf = 0.4 ((EtOAc /cyclohexane = 1:9); $[\alpha]_D^{22}$ = - 32.7 (c, 0.4, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 7.87 (d, *J* = 7.3 Hz, 1H), 7.79–7.62 (m, 3H), 7.47–7.26 (m, 4H), 6.63 (bd, *J* = 7.6 Hz, 1H), 5.19 (dd, *J* = 5.2, 1.3 Hz, 1H), 4.80–4.57 (m, 1H), 4.47–4.24 (m, 5H), 4.22–4.07 (m, 3H), 4.03 (dd, *J* = 11.2, 4.7 Hz, 1H), 3.71 (s, 3H), 3.36 (dd, *J* = 13.6, 5.2 Hz, 1H), 3.14 (dd, *J* = 13.6, 8.3 Hz, 1H), 2.60 (t, *J* = 7.7 Hz, 2H), 2.15–2.04 (m, 6H), 1.25–0.99 (m, 63H); ^{13}C NMR (75 MHz, acetone-*d6*) δ 172.2, 171.7, 148.8, 142.4, 128.8, 128.2, 126.4, 121.0, 103.7, 84.5, 70.9, 68.3, 67.5, 62.7, 55.1, 53.4, 52.8, 48.3, 33.5, 33.4, 18.7, 15.5, 13.5, 13.4,13.0; IR (neat): 2943, 2891, 2866, 2374, 2330, 1749, 1683, 1541, 1508, 1458, 1246, 1085, 883, 756, 740, 681 cm^{-1}; HRMS (ESI): m/z calc. for $C_{57}H_{96}N_2NaO_9S_2Si_3$ $[M+Na]^+$ 1123.5757; found 1123.5760.

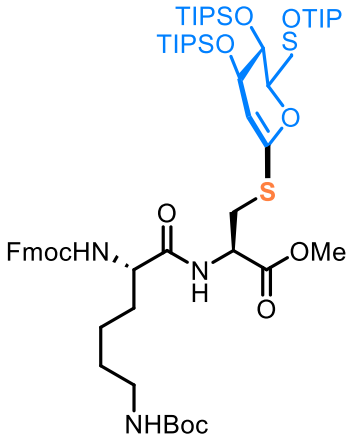
(9H-fluoren-9-yl)methyl-(S)-2-(((R)-3-(((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)thio)-1-methoxy-1-oxopropan-2-yl)glycyl)pyrrolidine-1-carboxylate



Following the general procedure, starting from cysteine containing peptide (46.8 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (PE) to provide compound **5e** (73.1 mg, 68 %) as a colorless liquid. Rf = 0.3 (EtOAc/cyclohexane = 2:8); $[\alpha]_D^{22}$ = - 23.1 (c, 0.5, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 7.91 (bd, *J* = 7.3 Hz, 2H), 7.78–7.63 (m, 2H), 7.53-7.23 (m, 3H), 5.19 (bs, 1H), 4.90–4.65 (m, 1H), 4.58–4.30 (m, 4H), 4.26–4.02 (m, 4H), 3.80–

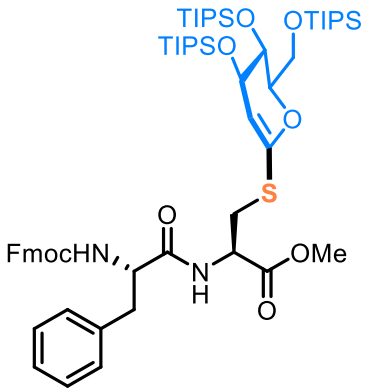
3.69 (m, 1H), 3.69–3.58 (m, 3H), 3.58–3.46 (m, 1H), 3.43–3.31 (m, 1H), 3.16 (dd, *J* = 13.4, 8.6 Hz, 1H), 2.44–2.18 (m, 2H), 2.04–1.85 (m, 2H), 1.44–0.92 (m, 63H); ^{13}C NMR (75 MHz, acetone-*d6*) δ 171.9, 149.0, 142.5, 128.9, 128.3, 126.5, 121.1, 103.9, 84.5, 71.0, 68.7, 68.4,62.8, 61.7, 53.3, 52.8, 53.1, 48.5, 34.9, 33.8, 26.9, 26.0, 18.8, 13.6, 13.5,13.1; IR (neat): 2943, 2891, 2866, 2359, 1734, 1508, 1463, 1365, 1247, 1170, 1083, 1064, 1014, 883, 792, 683, 657 cm^{-1}; HRMS (ESI): m/z calc. for $C_{57}H_{94}N_2NaO_9SSi_3$ $[M+Na]^+$ 1089.5880.

Methyl-N-(N2-((((9H-fluoren-9-yl)methoxy)carbonyl)-N6-(tert-butoxycarbonyl)-L-lysyl)-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-L-cysteinate



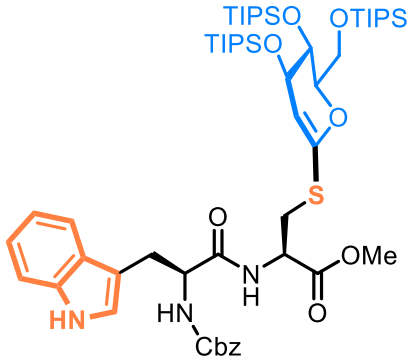
Following the general procedure, starting from cysteine containing peptide (58.7 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc /cyclohexane = 10:90) to provide compound **5f** (81.9 mg, 66%) as a colorless liquid. Rf = 0.3 ((EtOAc/cyclohexane = 2:8); $[\alpha]_D^{22}$ = - 3.2(c, 0.4, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 7.94-7.81 (m, 2H), 7.78–7.63 (m, 3H), 7.39 (dt, *J* = 24.1, 7.4 Hz, 4H), 6.53 (bd, *J* = 7.5 Hz, 1H), 5.89 (bs, 1H), 5.18 (d, *J* = 5.0 Hz, 1H), 4.67 (bd, *J* = 5.6 Hz, 1H), 4.48–3.97 (m, 9H), 3.71 (s, 1H), 3.35 (dd, *J* = 13.5, 5.1 Hz, 1H), 3.17–3.00 (m, 3H), 2.84 (bs, 1H), 1.93–1.78 (m, 2H), 1.81–1.62 (m, 1H), 1.64–1.47 (m, 4H), 1.41 (s, 9H), 1.18–1.01 (m, 63H); ^{13}CNMR (75 MHz, acetone-*d6*) δ 171.6, 170.6, 147.7, 141.2, 127.6, 127.0, 125.2, 119.9, 102.4, 83.4, 69.8, 67.2, 66.4, 61.6, 54.7, 52.3, 51.6, 47.2, 40.0, 33.7, 32.3, 29.7, 27.8, 24.8, 22.5, 17.7, 12.4, 12.3,11.9; IR (neat): 3315, 2943, 2866, 2362, 1717, 1522, 1463, 1365, 1247, 1170, 1066, 1014, 883, 790, 682 cm^{-1}; HRMS (ESI): m/z calc. for $C_{63}H_{107}N_3NaO_{11}SSi_3$ $[M+Na]^+$ 1220.6826; found 1220.6839.

Methyl-N-((((9H-fluoren-9-yl)methoxy)carbonyl)-L-phenylalanyl)-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-L-cysteinate.



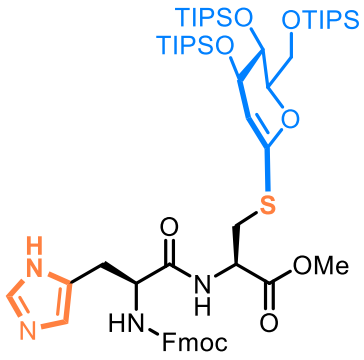
Following the general procedure, starting from cysteine containing peptide (50.6 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc/cyclohexane = 5:95) to provide compound **5g** (91.5 mg, 82%) as a colorless liquid. Rf = 0.4 ((EtOAc /cyclohexane = 1:9), $[\alpha]_D^{22}$ = - 22.7 (c, 0.4, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 7.86 (d, *J* = 7.2 Hz, 2H), 7.75–7.58 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.37–7.18 (m, 7H), 6.53 (bd, *J* = 8.2 Hz, 1H), 5.22–5.14 (m, 1H), 4.78–4.62 (m, 1H), 4.59–4.48 (m, 1H), 4.47–4.38 (m, 1H), 4.37–4.27 (m, 1H), 4.27–3.99 (m, 6H), 3.71 (s, 3H), 3.41–3.07 (m, 3H), 3.06–2.82 (m, 1H), 1.26–0.92 (m, 63H); 13 CNMR (75 MHz, acetone-*d6*) δ 172.1, 171.7, 172.0, 148.9, 145.3, 142.4, 138.8, 134.9, 130.6, 129.4, 128.8, 128.2, 127.6, 125.4, 121.0, 103.6, 84.5, 71.0, 68.4, 67.6, 62.7, 57.2, 53.5, 52.8, 48.3, 39.2, 33.5, 18.9, 13.6, 13.5, 13.0; IR (neat): 3315, 2943, 2891, 2866, 2372, 2322, 1683, 1541, 1458, 1209, 1087, 883, 788, 756, 681 cm^{-1}; HRMS (ESI): m/z calc. for $C_{61}H_{96}N_2NaO_9SSi_3$ $[M+Na]^+$ 1139.6037; found 1139.6036.

Methyl-N-(((benzyloxy)carbonyl)-D-tryptophyl)-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-L-cysteinate



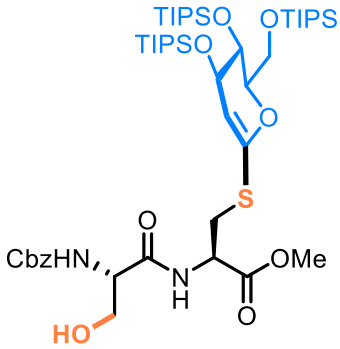
Following the general procedure, starting from cysteine containing peptide (45.5 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc/cyclohexane = 5:95) to provide compound **5h** (78.8 mg) as a colorless liquid. Rf = 0.4 (EtOAc/cyclohexane = 1:9); $[\alpha]_D^{22}$ = - 20.4 (c, 0.6, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 10.01 (bs, 1H), 7.62 (bs, 2H), 7.45–7.15 (m, 7H), 7.16–6.85 (m, 2H), 6.26 (bs, 1H), 5.24–5.16 (m, 1H), 5.04 (s, 2H), 4.76–4.35 (m, 3H), 4.28–3.97 (m, 4H), 3.69 (s, 3H), 3.55–2.93 (m, 4H), 1.24–0.90 (m, 63H); ^{13} CNMR (75 MHz, acetone-*d6*) δ 172.4, 171.7, 148.9, 137.8, 129.4, 129.0, 128.7, 124.8, 122.3, 119.8, 119.5, 112.3, 111.3, 103.5, 84.4, 70.9, 68.3, 67.0, 62.6, 55.7, 53.4, 52.7, 33.4, 18.7, 13.5, 13.4, 13.0; IR (neat): 3363, 2943, 2891, 2866, 2376, 2322, 1743, 1670, 1506, 1458, 1232, 1232, 1087, 883,740, 681 cm^{-1}; HRMS (ESI): m/z calc. for $C_{56}H_{93}N_3NaO_9SSi_3$ $[M+Na]^+$ 1090.5833; found 1090.5839.

Methyl-N-((((9H-fluoren-9-yl)methoxy)carbonyl)-D-histidyl)-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-L-cysteinate



Following the general procedure, starting from cysteine containing peptide (49.5 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc/cyclohexane = 5:95) to provide compound **5i** (78.9 mg, 71%) as a colorless liquid. Rf = 0.4 (EtOAc/cyclohexane = 1:9); $[\alpha]_D^{22}$ = - 26.8 (c, 0.5, DCM); ^{1}H NMR (300 MHz, MeOD) δ 7.85 (bd, *J* = 7.3 Hz, 2H), 7.77–7.56 (m, 3H), 7.58–7.24 (m, 4H), 6.96 (s, 1H), 5.19 (bs, 1H), 4.71–4.59 (m, 1H), 4.58–4.49 (m, 1H), 4.49–4.41 (m, 1H), 4.40–4.33 (m, 2H), 4.28 (d, *J* = 6.4 Hz, 1H), 4.22–4.08 (m, 3H), 4.09–3.90 (m, 1H), 3.78 (s, 3H), 3.51–3.33 (m, 3H), 3.30–3.05 (m, 3H), 3.05–2.92 (m, 1H), 1.20–0.85 (m, 63H); (75 MHz, MeOD) δ 173.8, 172.2, 158.1, 148.8, 145.3, 142.5, 138.8, 128.2, 126.3, 120.9, 104.0, 84.7, 71.1, 68.4, 68.2, 63.0, 56.3, 53.9, 52.9, 48.4, 33.2, 30.8), 18.6, 13.7, 13.6, 13.3; IR (neat): 3308, 2868, 2891, 2480, 2071, 1674, 1458, 1120, 1026, 975, 883, 790, 681 cm^{-1}; HRMS (ESI): m/z calc. for $C_{58}H_{94}N_4NaO_9SSi_3$ $[M+Na]^+$ 1129.5942; found 1129.5941.

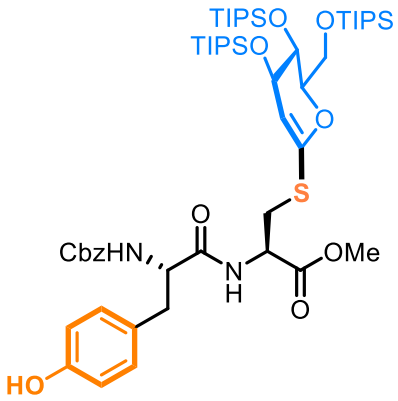
Methyl N-(((benzyloxy)carbonyl)-L-seryl)-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triiso propylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-L-cysteinate



Following the general procedure, starting from cysteine containing peptide (35.7 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc/cyclohexane = 5:95) to provide compound **5j** (69.7 mg, 72%) as a colorless liquid. Rf = 0.3 (EtOAc/cyclohexane = 1:9); $[\alpha]_D^{22}$ = - 57 (c, 0.7, DCM); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (bd, *J* = 7.6 Hz, 1H), 7.53–7.19 (m, 5H), 6.29 (bs, 1H), 5.20 (dd, *J* = 5.2, 1.4 Hz, 1H), 5.10 (s, 2H), 4.78–4.58 (m, 1H), 4.51–4.35 (m, 1H), 4.34–4.25 (m, 1H), 4.24–4.19 (m, 1H), 4.18–4.10 (m, 2H), 4.10–4.00 (m, 2H), 3.88–3.75 (m, 2H), 3.70 (s, 3H), 3.32 (dd, *J* = 13.6, 5.5 Hz, 1H), 3.14 (dd, *J* = 13.6, 7.8 Hz, 1H), 1.16–1.00 (m, 63H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 171.3, 148.9, 138.3, 129.4, 128.9, 126.8, 103.6, 84.5, 71.0, 68.3, 67.2, 63.7, 62.7, 57.7, 53.5, 52.9, 33.4, 18.7, 13.5, 13.4, 13.0; IR (neat): 3367, 2943, 2891, 2866, 2376, 2322, 1743, 1670, 1506, 1465, 1232, 1087,740, 681 cm^{-1}; HRMS (ESI): m/z calc. for $C_{48}H_{88}N_2NaO_{10}SSi_3$

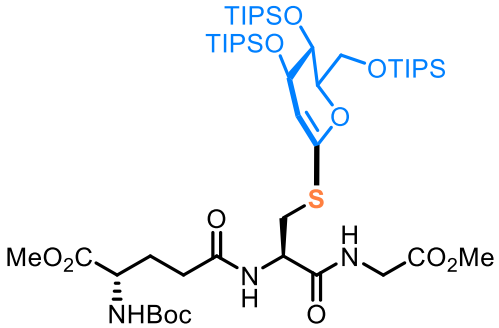
$[M+Na]^+$ 991.5360; found 991.5367.

Methyl-(R,E)-11-((S)-2-(((benzyloxy)carbonyl)amino)-3-(4-hydroxyphenyl)propanamido)-3,3-diisopropyl-2-methyl-8-(2-((triisopropylsilyl)oxy)ethylidene)-6-(((triisopropylsilyl)oxy)methyl)-4,7-dioxa-9-thia-3-siladodecan-12-oate



Following the general procedure, starting from cysteine containing peptide (43.3 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc/cyclohexane = 5:95) to provide compound **5k** (82.3 mg, 74%) as a colorless liquid. Rf = 0.4 (EtOAc/cyclohexane = 1:9); $[\alpha]_D^{22}$ = - 16.9 (c, 0.4, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ: 8.09 (s, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.43–7.18 (m, 5H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.86–6.49 (m, 2H), 6.25 (bs, 1H), 5.21 (dd, *J* = 5.2, 1.4 Hz, 1H), 5.13–4.88 (m, 2H), 4.77–4.58 (m, 1H), 4.52–4.32 (m, 2H), 4.32–3.97 (m, 4H), 3.71 (s, 3H), 3.30 (dd, *J* = 13.6, 5.7 Hz, 1H), 3.19–3.02 (m, 2H), 2.97–2.85 (m, 4H), 1.25–0.87 (m, 63H); ^{13} CNMR (75 MHz, acetone-*d6*) δ 172.5, 171.9, 157.5, 149.2, 131.8, 129.7, 129.5, 129.0, 128.9, 116.5, 103.9, 84.7, 71.3, 68.6, 67.2, 63.0, 57.7, 53.7, 53.1, 38.7, 33.8, 19.0, 13.8, 13.7,13.3; IR (neat): 3503, 2945, 2891, 2868, 2376, 2322, 1705, 1683, 1508, 1419, 1361, 1220, 1091, 883, 681 cm^{-1}; HRMS (ESI): m/z calc. for $C_{61}H_{96}N_2O_9SSi_3$ $[M+Na]^+$ 1067.5673; found 1067.5676.

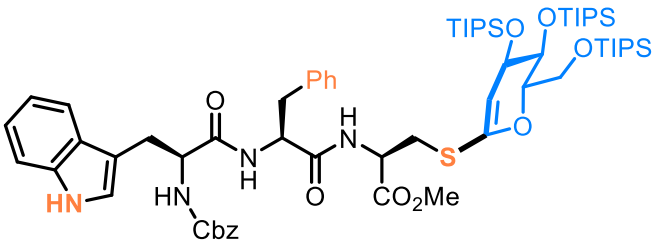
Methyl-N-((R)-4-acetoxy-4-((tert-butoxycarbonyl)amino)butanoyl)-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-L-cysteinylglycinate.



Following the general procedure, starting from cysteine containing peptide (43.6 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc/cyclohexane = 10:90) to provide compound **5l** (64.7 mg, 71%) as a colorless liquid. Rf = 0.3 ((EtOAc/cyclohexane = 2:8); $[\alpha]_D^{22}$ = - 6.3 (c, 0.6, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 7.55 (bs, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 6.34 (bd, *J* = 7.8 Hz, 1H), 5.19 (dd, *J* = 5.1, 1.4 Hz, 1H), 4.63 (d, *J* = 6.0 Hz, 1H), 4.50–4.31 (m, 1H), 4.27–4.17 (m, 2H), 4.17–4.07 (m, 2H), 4.07–3.91 (m, 3H), 3.70 (s, 3H), 3.68 (s, 3H), 3.30

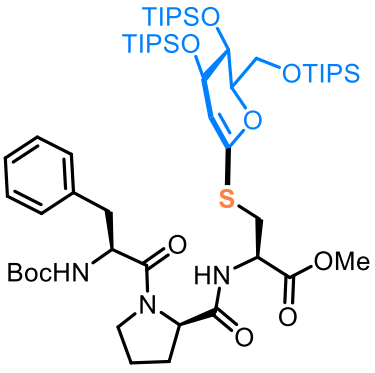
(dd, *J* = 13.5, 5.7 Hz, 1H), 3.20–3.01 (m, 1H), 2.41 (t, *J* = 7.4 Hz, 2H), 2.21–2.01 (m, 2H), 1.42 (s, 9H), 1.22–0.93 (m, 63H); ^{13}C NMR (75 MHz, acetone-*d6*) δ 173.7, 172.8, 171.3, 170.8, 149.4, 102.8, 84.3, 79.5, 70.9, 68.3, 62.4, 54.3, 53.7, 52.4, 52.3, 41.7, 33.2, 32.7, 28.7, , 28.3, 18.6, 13.4, 13.3, 12.9; IR (neat): 3304, 2943, 2891, 2866, 2480, 1745, 1642, 1502, 1436, 1367, 1254, 1209, 1160, 1052, 1026, 975, 883, 802, 772, 730, 680 cm^{-1}; HRMS (ESI): m/z calc. for $C_{50}H_{97}N_3NaO_{12}SSi_3$ $[M+Na]^+$ 1070.5993; found 1070.5990.

Methyl-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-N-(tert-butoxycarbonyl)-L-tryptophyl-D-phenylalanyl-D-cysteinate



Following the general procedure, starting from cysteine containing peptide (57.1 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc /cyclohexane = 10:90) to provide compound **5m** (67.1 mg, 54%) as a colorless liquid. Rf = 0.3 (EtOAc /cyclohexane: 3/7); $[\alpha]_D^{22}$ = - 11.6 (c, 0.3, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 10.00 (bs, 1H), 7.62 (t, *J* = 7.4 Hz, 2H), 7.43–7.35 (m, 1H), 7.28–6.98 (m, 8H), 5.87 (bs, 1H), 5.22 (dd, *J* = 5.2, 1.4 Hz, 1H), 4.83–4.51 (m, 2H), 4.48–4.29 (m, 2H), 4.25–3.94 (m, 4H), 3.70 (s, 3H), 3.39–3.19 (m, 3H), 3.10 (dd, *J* = 13.6, 7.9 Hz, 2H), 3.00 (d, *J* = 6.5 Hz, 2H), 1.34 (s, 9H), 1.27–0.92 (m, 63H); ^{13}C NMR (75 MHz, acetone-*d6*) δ 172.5, 171.7, 171.5, 148.9, 138.2, 137.9, 130.6, 129.3, 127.5, 124.8, 122.4, 119.8, 119.7, 112.4, 111.6, 103.5, 84.4, 79.8, 70.9, 68.3, 62.7, 54.9, 53.6, 52.8, 38.6, 33.3, 28.8, , 18.4, 13.5, 13.4, 13.0; IR (neat): 3311, 2943, 2891, 2866, 2372, 2324, 1749, 1647, 1508, 1458, 1247, 1089, 883, 742, 682 cm^{-1}; HRMS (ESI): m/z calc. for $C_{62}H_{104}N_4NaO_{10}SSi_3$ $[M+Na]^+$ 1203.6673; found 1203.6676.

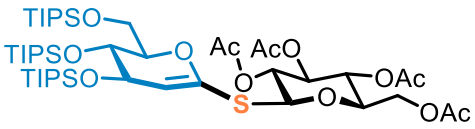
Methyl-S-((2S,3S,4S)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)-N-(tert-butoxycarbonyl)-D-phenylalanylprolyl-L-cysteinate.



Following the general procedure, starting from cysteine containing peptide (47.5 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc /cyclohexane = 10:90) to provide compound **5n** (80.7 mg, 74%) as a colorless liquid. $[\alpha]_D^{22}$ = - 13.3 (c, 0.2, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 7.68 (bd, *J* = 6.9 Hz, 1H), 7.51–7.13 (m, 5H), 5.96 (bd, *J* = 8.6 Hz, 1H), 5.48–5.08 (m, 1H), 4.79–4.33 (m, 4H), 4.34–3.97 (m, 4H), 3.78 (s, 3H), 3.52 (d,

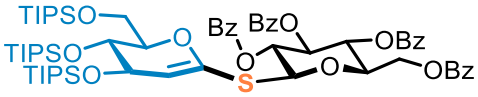
J = 8.9 Hz, 2H), 3.34–2.92 (m, 4H), 2.27–2.09 (m, 4H), 1.42 (d, *J* = 6.0 Hz, 9H), 1.26–1.07 (m, 63H); ^{13}C NMR (75 MHz, acetone-*d6*) δ 171.4, 170.9, 170.5, 129.6, 129.5, 128.5, 128.1, 126.4, 102.5, 83.2, 83.0, 69.7, 67.2, 61.4, 59.7, 53.6, 52.3, 51.6, 47.0, 38.0, 32.4, 27.6, 24.7, 17.6, 12.4, 12.3, 11.9; IR (neat): 3311, 2943, 2891, 2866, 2372, 1758, 1683, 1541, 1458, 1209, 1087, 883, 788, 756, 680 cm^{-1}; HRMS (ESI): m/z calc. for $C_{56}H_{101}N_3NaO_{10}SSi_3$ $[M+Na]^+$ 1114.6408; found 1114.6409.

(2S,3S,4R,5S,6R)-2-(acetoxymethyl)-6-(((2R,3R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropyl silyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl triacetate



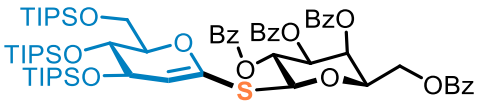
Following the general procedure, starting from thiosugar (36.3 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc/cyclohexane = 10:90) to provide compound **7a** (113.5 mg, 93% yield) as a colorless liquid. Rf = 0.2 ((EtOAc/cyclohexane = 1/9); $[\alpha]_D^{22}$ = - 10.8 (c, 0.5, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 5.42–5.17 (m, 2H), 5.18 – 4.81 (m, 3H), 4.55 – 4.38 (m, 1H), 4.34 – 3.97 (m, 6H), 3.97 – 3.80 (m, 1H), 2.03 (s, 3H), 2.01 (s, 3H), 2.00 (s, 3H), 1.96 (s, 3H), 1.22 – 1.04 (m, 63H); ^{13} CNMR (75 MHz, acetone-*d6*) δ 169.6, 169.2, 168.9, 168.9, 168.6, 147.0, 103.6, 83.6, 83.0, 75.7, 73.6, 70.0, 68.2, 67.2, 61.9, 61.5, 19.8, 19.7, 19.6, 19.6, 17.6, 12.4, 12.3,11.9; IR (neat): 2943, 2894, 2865, 2364, 2327, 1759, 1627, 1463, 1340, 1229, 1109, 1085, 881, 830, 670 cm^{-1}; HRMS (ESI): m/z calc. for $C_{67}H_{96}NO_{13}SSi_3$ $[M+Na]^+$ 999.5146; found 999.5151.

(2R,3R,4S,5R,6S)-2-((benzoyloxy)methyl)-6-(((2R,3R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate



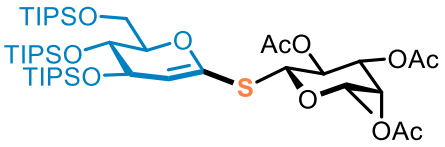
Following the general procedure, starting from thiosugar (61.3 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc/cyclohexane = 10:90) to provide compound **7b** (64.7 mg, 71%) as a colorless liquid. Rf = 0.3 ((EtOAc/cyclohexane = 1:9); $[\alpha]_D^{22}$ = - 32.4 (c, 0.6, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 8.08–8.02 (m, 2H), 8.00–7.89 (m, 4H), 7.87–7.77 (m, 2H), 7.67–7.53 (m, 3H), 7.53–7.32 (m, 9H), 6.05 (t, *J* = 9.3 Hz, 1H), 5.84 (t, *J* = 9.7 Hz, 1H), 5.73–5.42 (m, 2H), 5.29 (dd, *J* = 5.1, 1.4 Hz, 1H), 4.68–4.55 (m, 2H), 4.52–4.37 (m, 2H), 4.25–4.10 (m, 3H), 4.04 (dd, *J* = 11.2, 4.2 Hz, 1H), 1.36–0.81 (m, 63H); ^{13} CNMR (75 MHz, acetone-*d6*) δ 165.4, 165.3, 164.8, 164.7, 146.7, 133.4, 133.3, 133.1, 129.9, 129.5, 129.4, 129.2, 129.1, 128.5, 128.4, 104.1, 83.7, 83.3, 75.8, 74.5, 70.6, 70.0, 69.7, 67.3, 63.2, 61.5, 17.6, 12.4, 12.3, 11.9; IR (neat): 2943, 2893, 2866, 2370, 2322, 1743, 1458, 1109, 1066, 830, 680 cm^{-1}; HRMS (ESI): m/z calc. for $C_{67}H_{96}NaO_{13}SSi_3$ $[M+Na]^+$ 1247.5772; found 1247.5771.

Tribenzyl-((2R,3S,4S,5R,6S)-2-((((benzyloxy)carbonyl)oxy)methyl)-6-(((2R,3R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)thio)tetrahydro-2H-pyran-3,4,5-triyl) tricarbonate



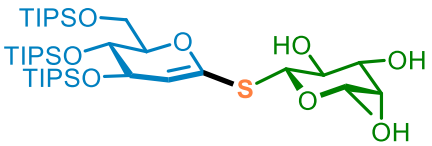
Following the general procedure, starting from thiosugar (61 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc/cyclohexane = 10:90) to provide compound **7c** (103.1 mg, 84%) as a colorless liquid. Rf = 0.3 (EtOAc/cyclohexane = 2:8); $[\alpha]_D^{22}$ = 12.3 (c, 0.4, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 8.10–7.99 (m, 2H), 8.01–7.88 (m, 4H), 7.84 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.67–7.53 (m, 3H), 7.517.30 (m, 9H), 6.19–5.95 (m, 1H), 5.83 (dd, *J* = 23.4, 13.8 Hz, 1H), 5.70–5.48 (m, 2H), 5.30 (dd, *J* = 5.1, 1.3 Hz, 1H), 4.74–4.55 (m, 2H), 4.52–4.39 (m, 2H), 4.25–4.12 (m, 3H), 4.08–3.97 (m, 1H), 1.27–0.93 (m, 63H); ^{13} CNMR (75 MHz, acetone-*d6*) δ 165.4, 165.3, 164.8, 164.7, 146.7, 133.4, 133.3, 133.1, 129.9, 129.5, 129.4, 129.2, 129.1, 128.5, 128.4, 104.2, 83.5, 83.3, 75.9, 74.5, 70.6, 70.0, 69.7, 67.3, 66.7, 63.2, 61.6, 17.7, 12.5, 12.3,12.0; IR (neat): 2943, 2893, 2866, 2363, 2322, 1743, 2362, 1749, 1653, 1463, 1066, 881, 757 680, 658 cm^{-1}; HRMS (ESI): m/z calc. for $C_{67}H_{96}O_{13}SSi_3$ $[M+Na]^+$ 1247.5772; found 1247.5771.

(2S,3R,4S,5S,6R)-2-(((2R,3R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)thio)-6-methyltetrahydro-2H-pyran-3,4,5-triyl triacetate



Following the general procedure, starting from thiosugar (30.6 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc /cyclohexane = 10:90) to provide compound **7d** (80.1 mg, 87%) as a colorless liquid. Rf = 0.3 ((EtOAc/cyclohexane = 1:9); $[\alpha]_D^{22}$ = - 17.8 (c, 0.4, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 5.34–5.23 (m, 2H), 5.21–5.13 (m, 1H), 5.13–4.99 (m, 2H), 4.49–4.36 (m, 1H), 4.25 (d, *J* = 1.7 Hz, 1H), 4.17–4.05 (m, 3H), 4.06–3.94 (m, 1H), 2.16 (s, 3H), 2.02 (s, 3H), 1.93 (s, 3H), 1.18 (d, *J* = 3.6 Hz, 3H), 1.18 – 1.06 (m, 63H); ^{13} CNMR (75 MHz, acetone-*d6*) δ 170.0, 169.2, 169.1, 146.0, 105.2, 83.3, 82.2, 73.0, 72.0, 70.4, 70.0, 67.2, 67.1, 61.5, 19.6, 17.7, 17.6, 15.7, 12.4, 12.3, 11.9; IR (neat): 2943, 2893, 2866, 2370, 2322, 1743, 1720, 1628, 1458, 1336, 1109, 1066, 880, 830, 680 cm^{-1}; HRMS (ESI): m/z calc. for $C_{45}H_{86}NaO_{11}SSi_3$ $[M+Na]^+$ 941.5091; found 941.5089.

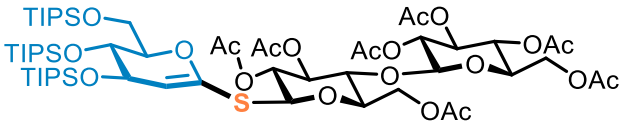
(2S,3R,4S,5R,6R)-2-(((2R,3R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)thio)-6-methyltetrahydro-2H-pyran-3,4,5-triol



Following the general procedure, starting from thiosugar (18 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc/cyclohexane = 10:90) to provide compound **7e** (44.5 mg, 57%) as a colorless liquid. Rf = 0.3 ((MeOH/cyclohexane = 5:95); colorless liquid; $[\alpha]_D^{22}$ = - 15.7 (c, 0.3, DCM); ^{1}H NMR (300 MHz, MeOD) δ 5.30 (d, *J* = 3 Hz, 1H), 4.97-4.87 (m, 1H), 4.42 (bs, 1H), 4.26 (s, 1H), 4.22–4.03 (m, 3H), 3.76-3.65 (m, 2H), 3.62–3.47 (m,

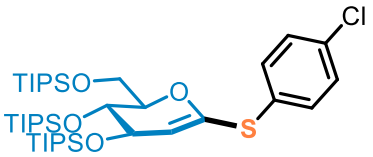
2H), 3.46–3.42 (m, 3H), 1.31(d, *J* = 6 Hz, 3H), 1.26–0.96 (m, 63H); ^{13} CNMR (75 MHz, MeOD) δ 145.5, 103.5, 83.4, 81.9, 74.0, 73.4, 70.5, 68.8, 68.1, 66.0, 60.4, 16.0, 14.5, 11.1, 11.0, 10.7; IR (neat): 3310, 2943, 2893, 2866, 2370, 2322, 11759, 1627, 1463, 1340, 1219, 1109, 1085, 881, 830, 655 cm^{-1}; HRMS (ESI): m/z calc. for $C_{39}H_{80}NaO_8SSi_3$ $[M+Na]^+$ 815.4774; found 815.4777.

(2R,3S,4R,5R)-5-(acetoxymethyl)-6-(((2R,3R,4S,5R,6S)-4,5-diacetoxy-2-(acetoxymethyl)-6-(((2R,3R)-3,4-bis((triisopropylsilyl)oxy)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-6-yl)thio)tetrahydro-2H-pyran-3-yl)oxy)tetrahydro-2H-pyran-2,3,4-triyl triacetate



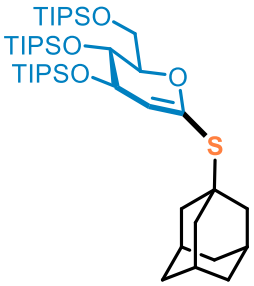
Following the general procedure, starting from thiodisaccharde (65 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (EtOAc/cyclohexane = 10:90) to provide compound **7f** (88.4 mg, 70%) as a colorless liquid. Rf = 0.3 (EtOAc/cyclohexane = 3:7); $[\alpha]_D^{22}$ = - 37.1 (c, 0.5, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 5.28–5.12 (m, 2H), 5.06 (d, *J* = 9.9, 1H), 5.02 (d, *J* = 8.1, 1H), 4.95-4.77 (m, 3H), 4.58–4.27 (m, 3H), 4.26–3.89 (m, 9H), 3.83–3.70 (m, 1H), 2.17–1.85 (m, 21H), 1.23–1.01 (m, 63H); ^{13}CNMR (75 MHz, acetone-*d6*) δ 170.0, 169.8, 169.7, 169.4, 169.1, 168.9, 168.8, 168.6, 147.2, 103.2, 100.4, 83.6, 83.0, 76.6, 76.0, 73.4, 72.7, 71.4, 68.0, 67.3, 62.0, 61.5, 19.7, 17.7, 17.6, 12.4, 12.3,11.9; IR (neat): 2943, 2891, 2866, 2360, 2341, 1746, 1380, 1366, 1228, 1216, 1097, 1043, 830, 774, 680 cm^{-1}; HRMS (ESI): m/z calc. for $C_{59}H_{104}O_{21}SSi_3$ $[M+Na]^+$ 1287.5991; found 1287.5994.

(((2R,3R)-6-((4-chlorophenyl)thio)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-3,4-diyl) bis(oxy))bis(triisopropylsilane)



Following the general procedure, starting from 4-chlorobenzenethiol (14.3 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (cyclohexane) to provide compound **7g** (31.6 mg, 42%) as a colorless liquid. Rf = 0.5 (cyclohexane); $[\alpha]_D^{22}$ = - 25.6 (c, 0.4, DCM); ^{1}H NMR (300 MHz, acetone-*d6*) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 5.44 (d, *J* = 5.3 Hz, 1H), 4.53–4.34 (m, 1H), 4.28–4.09 (m, 2H), 4.08–3.93 (m, 2H), 1.22–0.84 (m, 63H); ^{13} CNMR (75 MHz, acetone-*d6*) δ 131.3, 128.9, 106.8, 83.8, 83.0, 69.4, 67.1, 61.8, 17.5, 12.3, 12.2, 11.9; IR (neat): 2943, 2891, 2866, 2364, 2322, 1744, 1463, 1232, 1107, 1066, 1014, 881, 806, 678 cm^{-1}; HRMS (ESI): m/z calc. for $C_{39}H_{73}ClNaO_4SSi_3$ $[M+Na]^+$ 779.4118; found 779.4116.

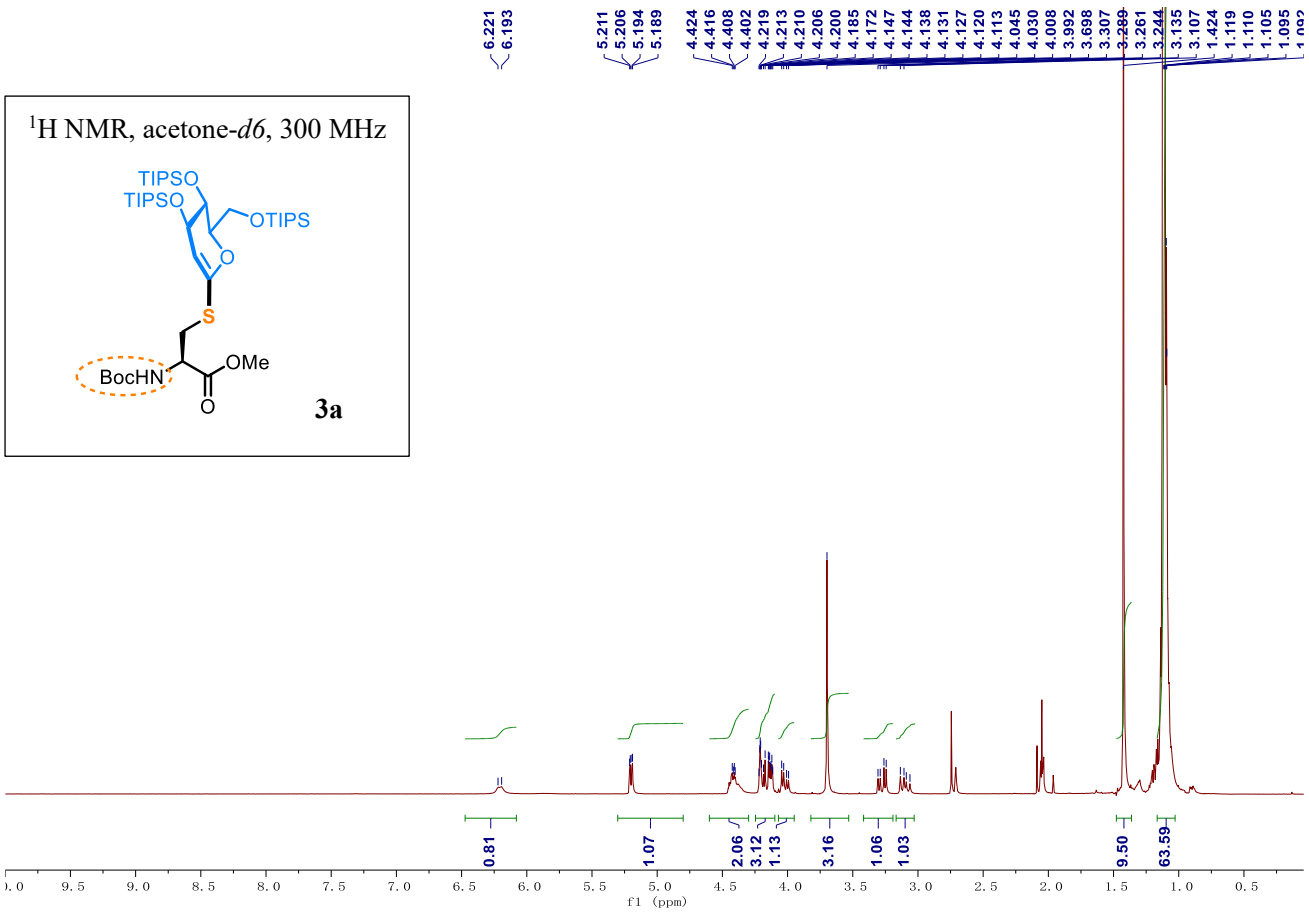
(((2R,3R)-6-(((3S,5S,7S)-adamantan-1-yl)thio)-2-(((triisopropylsilyl)oxy)methyl)-3,4-dihydro-2H-pyran-3,4-diyl)bis(oxy))bis(triisopropylsilane)



Following the general procedure, starting from adamantane-1-thiol (16.8 mg, 0.1 mmol) and iodosugar (89 mg, 0.12 mmol), the residue was purified by flash chromatography (cyclohexane) to provide compound **7h** (69.7 mg, 89%) as a colorless liquid. Rf = 0.5 (cyclohexane); $[\alpha]_D^{22}$ = - 56.8 (c, 0.8, DCM); ^{1}H NMR (300 MHz, Acetone-*d*6) δ 5.31 (dd, J = 5.3, 1.6 Hz, 1H), 4.39 (m, *J* = 7.5, 1H), 4.20 – 4.07 (m, 3H), 4.02 (dd, *J* = 11.2, 4.4 Hz, 1H), 2.80 – 2.56 (m, 1H), 2.03 – 1.92 (m, 9H), 1.71 (m, 6H), 1.21 – 1.02 (m, 63H). ^{13} CNMR (75 MHz, acetone-*d6*) δ 149.8, 125.9, 84.1, 70.2, 68.0, 63.1, 44.8, 36.9, 31.0, 30.3, 18.5, 13.2, 12.8; IR (neat): 2947, 2888, 2379, 2341, 1767, 1366, 1228, 1216, 1087, 1043, 830, 795, cm^{-1}; HRMS (ESI): m/z calc. for $C_{43}H_{84}O_4SSi_3$ $[M+Na]^+$ 803.5290; found 803.5297.

4. Referecnce

1. M. Liu, Y. Niu, Y. F. Wu, X. S. Ye. *Org. Lett.* **2017**, 19, *13*, 3608
2. S. ZHANG, Y. H. Niu, X. S. Ye. *Org. Lett.* **2016**, 18, *8*, 1836
3. S. Verhoog, C. W. Kee, Y. Wang, T. Khotavivattana, T. C. Wilson, V. Kersemans, S. Smart, M. Tredwell, B. G. Davis and V. Gouverneur. *J. Am. Chem. Soc*., **2018**, 140, *5*, 1572–1575
4. R. Frei, J. Waser, *J. Am. Chem. Soc*., **2013**, *135*, 9620.
5. J. M. Chalker, C. S. C. Wood, B. G. Davis, J. *Am. Chem. Soc*., **2009**, *131*, 16346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TIPSO
TIPSO
OTIPS
O
S
BocHN
OMe
O
3a
6.221
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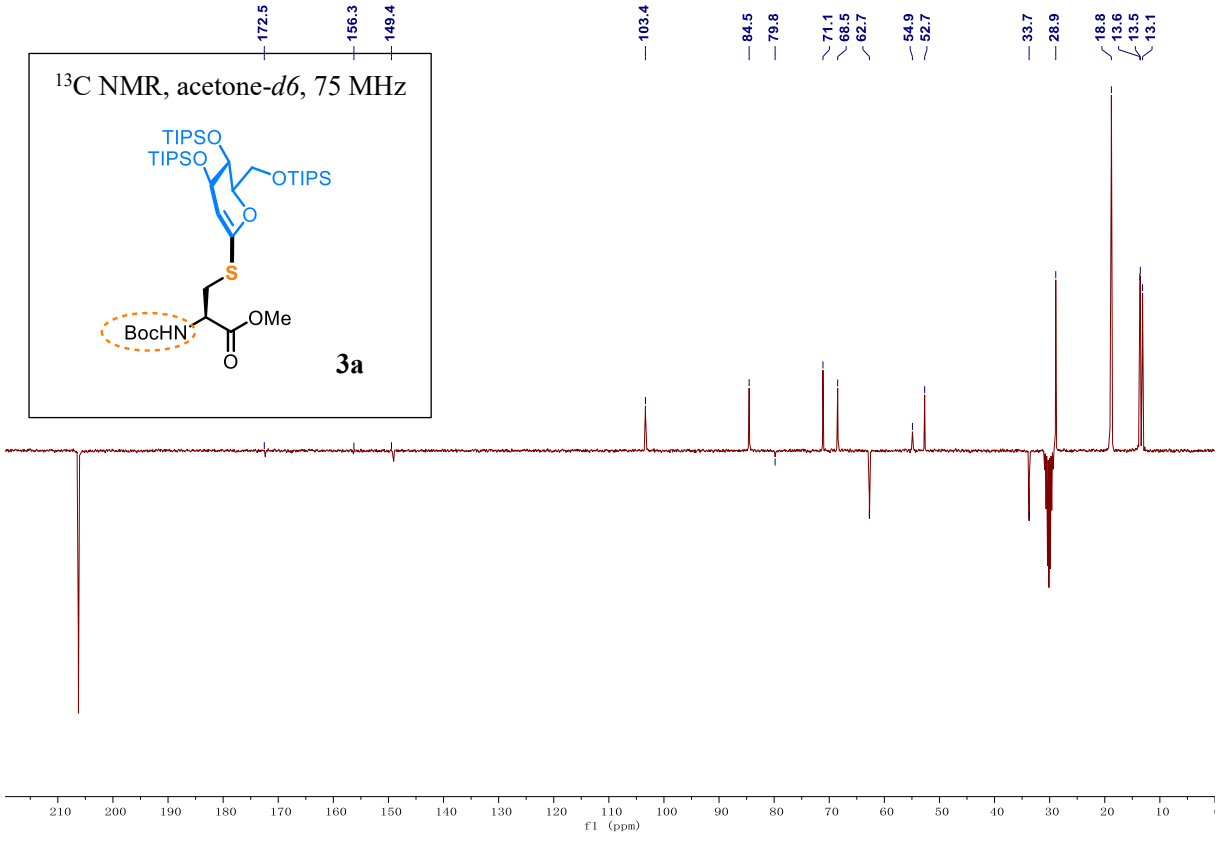
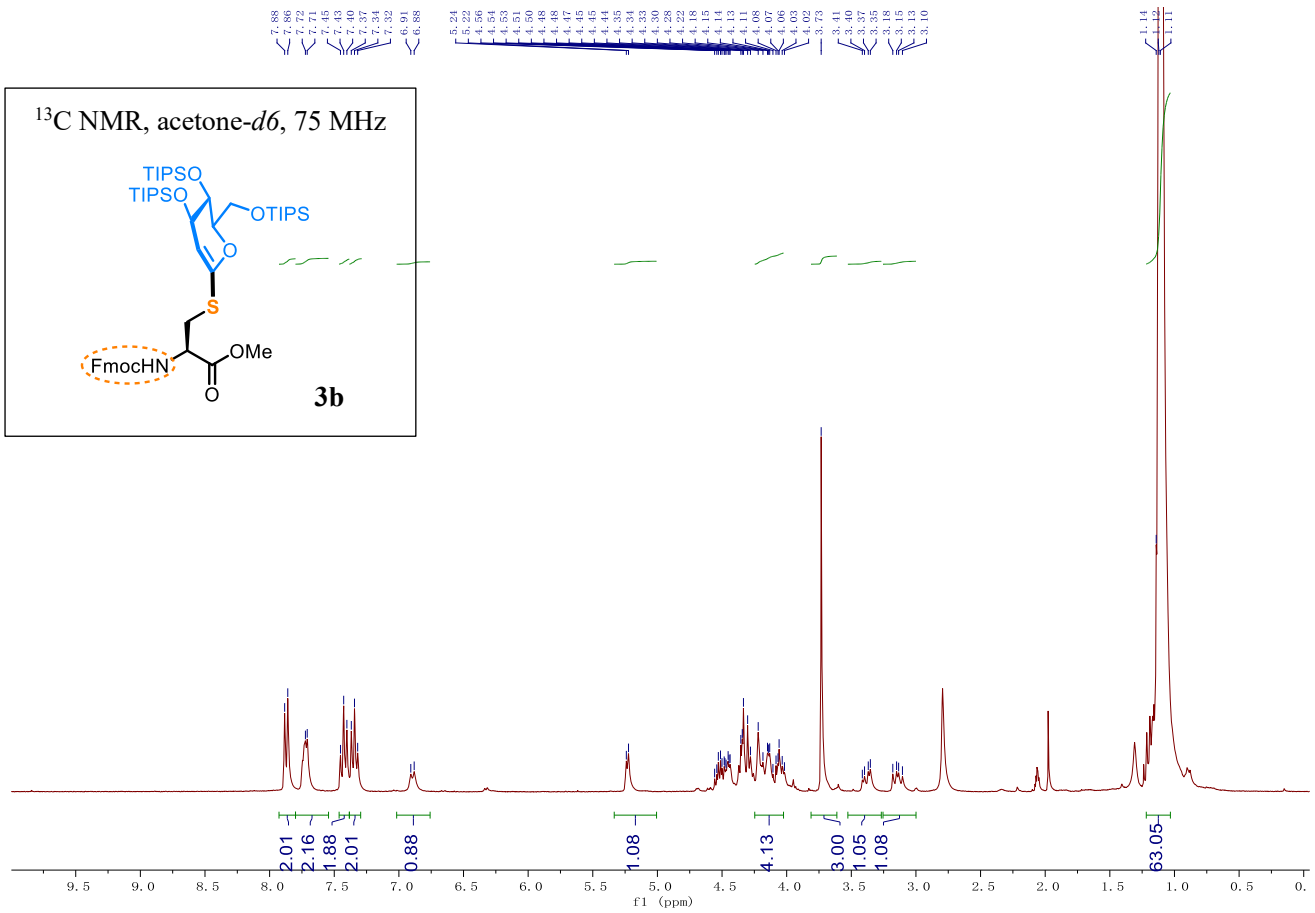
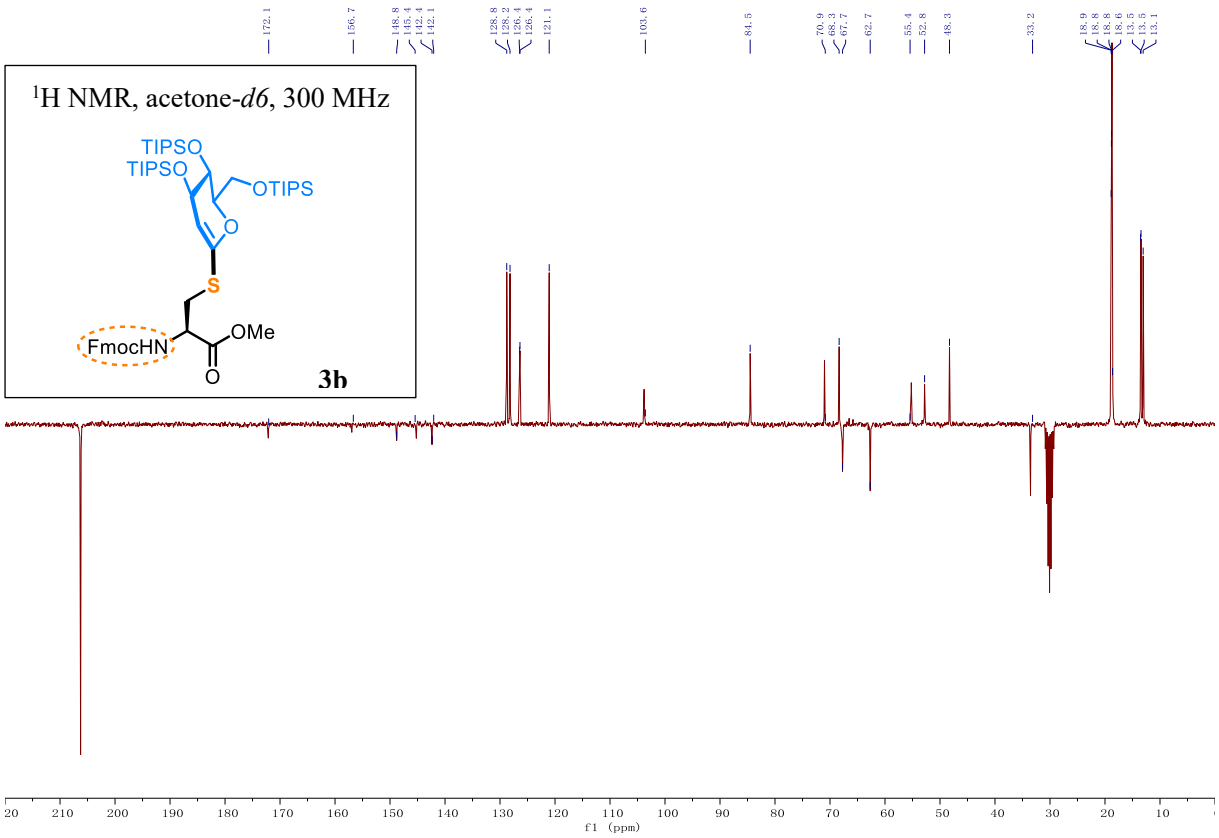
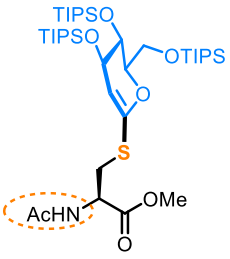
5.211
5.206
5.194
5.189
4.424
4.416
4.408
4.402
4.219
4.213
4.210
4.206
4.200
4.185
4.172
4.147
4.144
4.138
4.131
4.127
4.120
4.113
4.045
4.030
4.008
3.992
3.698
3.307
3.289
3.261
3.244
3.135
3.107
1.424
1.119
1.110
1.105
1.095
0.81
1.07
2.06
3.12
1.13
3.16
1.06
1.03
9.50
63.59
f1 (ppm)


[13]C NMR, acetone-d6, 75 MHz
TIPSO
TIPSO
OTIPS
O
S
BocHN
OMe
O
3a
172.5
156.3
149.4
103.4
84.5
79.8
71.1
68.5
62.7
54.9
52.7
33.7
28.9
18.8
13.6
13.5
13.1
f1 (ppm)


^{13}C NMR, acetone-*d6*, 75 MHz
TIPSO
TIPSO
OTIPS
O
S
FmocHN
OMe
O
3b
f1 (ppm)

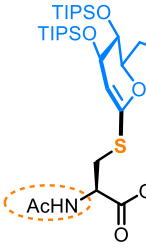

^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
TIPSO
OTIPS
O
S
FmocHN
OMe
O
3b
f1 (ppm)

^{1}H NMR, acetone-*d6*, 300 MHz

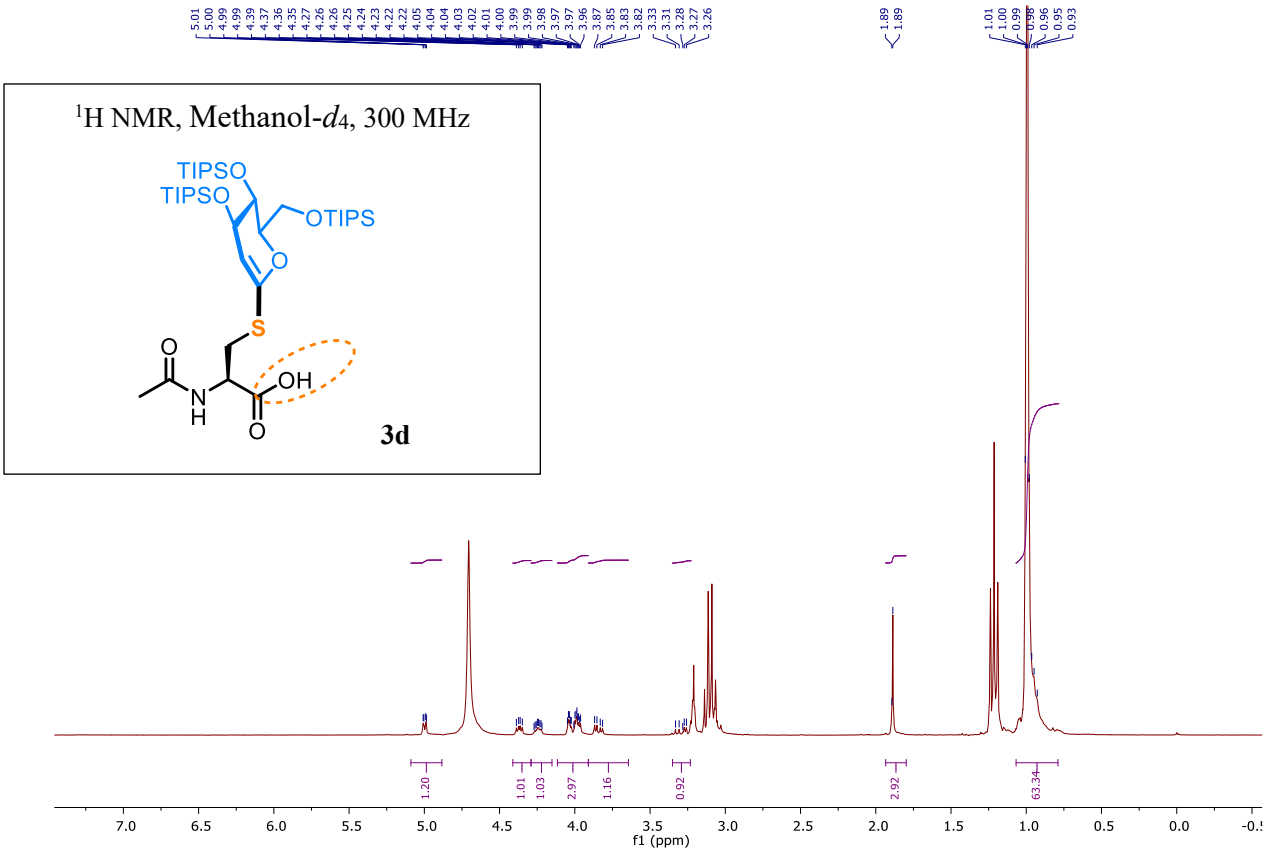


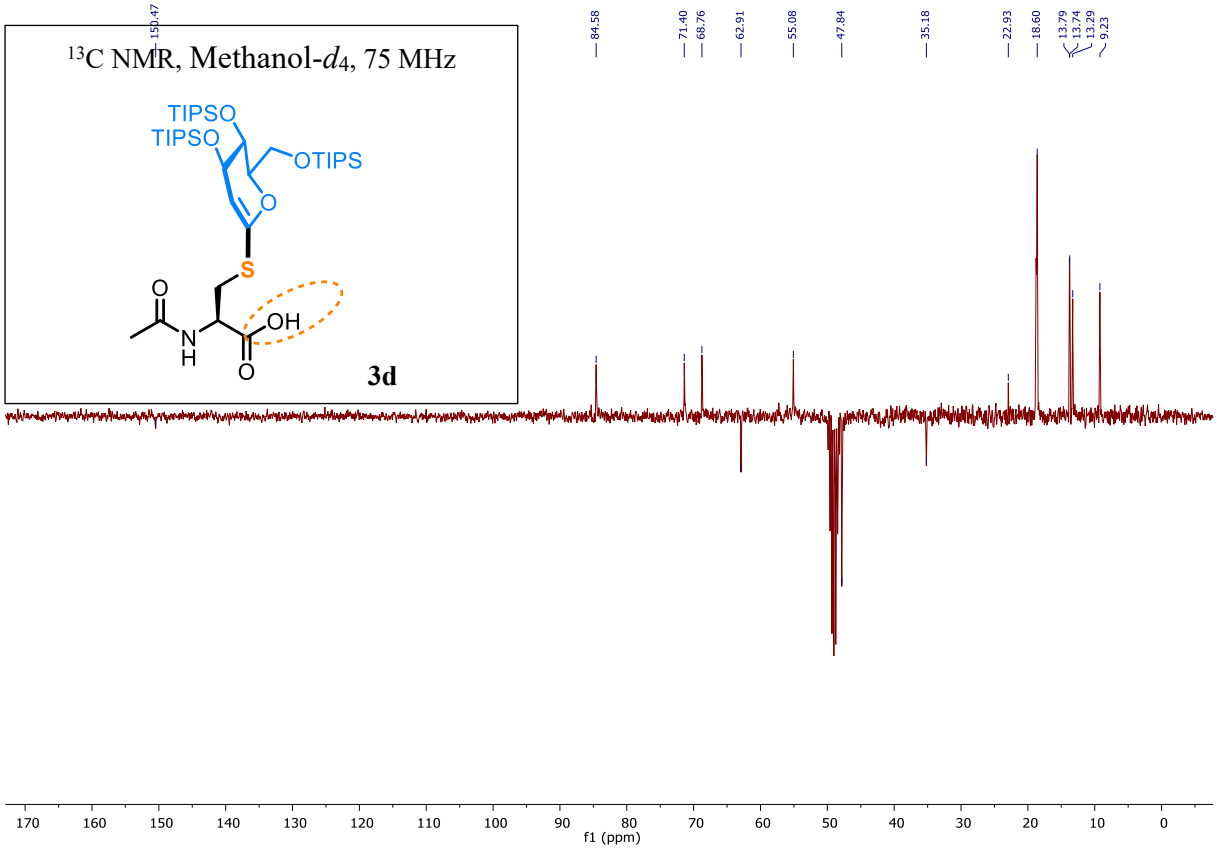
3c

^{13}C NMR, acetone-*d6*, 75 MHz

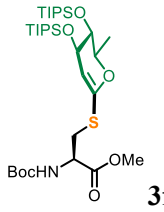


3c


^{1}H NMR, Methanol-d_4, 300 MHz
TIPSO
TIPSO
OTIPS
O
S
O
N
H
OH
O
3d
f1 (ppm)

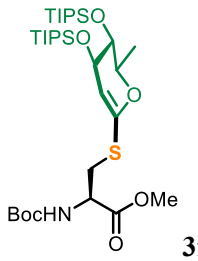

^{13}C NMR, Methanol-d_4, 75 MHz
TIPSO
TIPSO
OTIPS
O
S
O
N
H
OH
O
3d
f1 (ppm)

^{1}H NMR, acetone-*d6*, 300 MHz



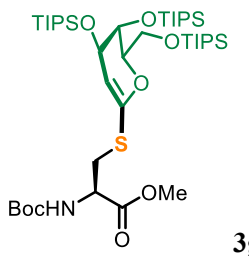
3f

^{13}C NMR, acetone-*d6*, 75 MHz



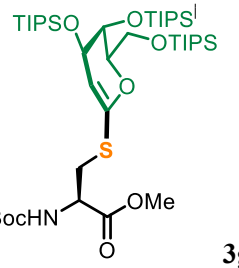
3f

^{1}H NMR, acetone-*d6*, 300 MHz



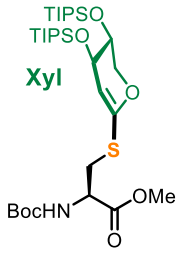
3g

^{13}C NMR, acetone-*d6*, 75 MHz



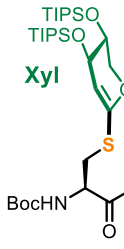
3g

^{1}H NMR, acetone-*d6*, 300 MHz

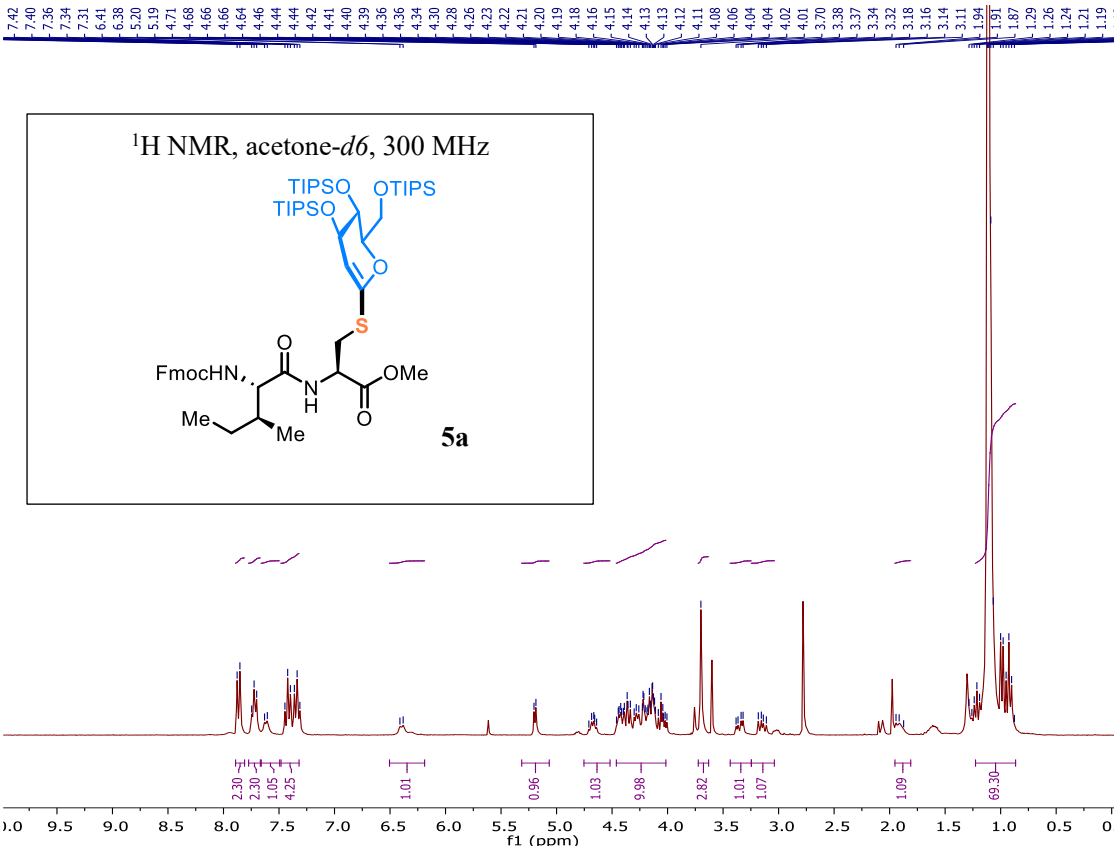


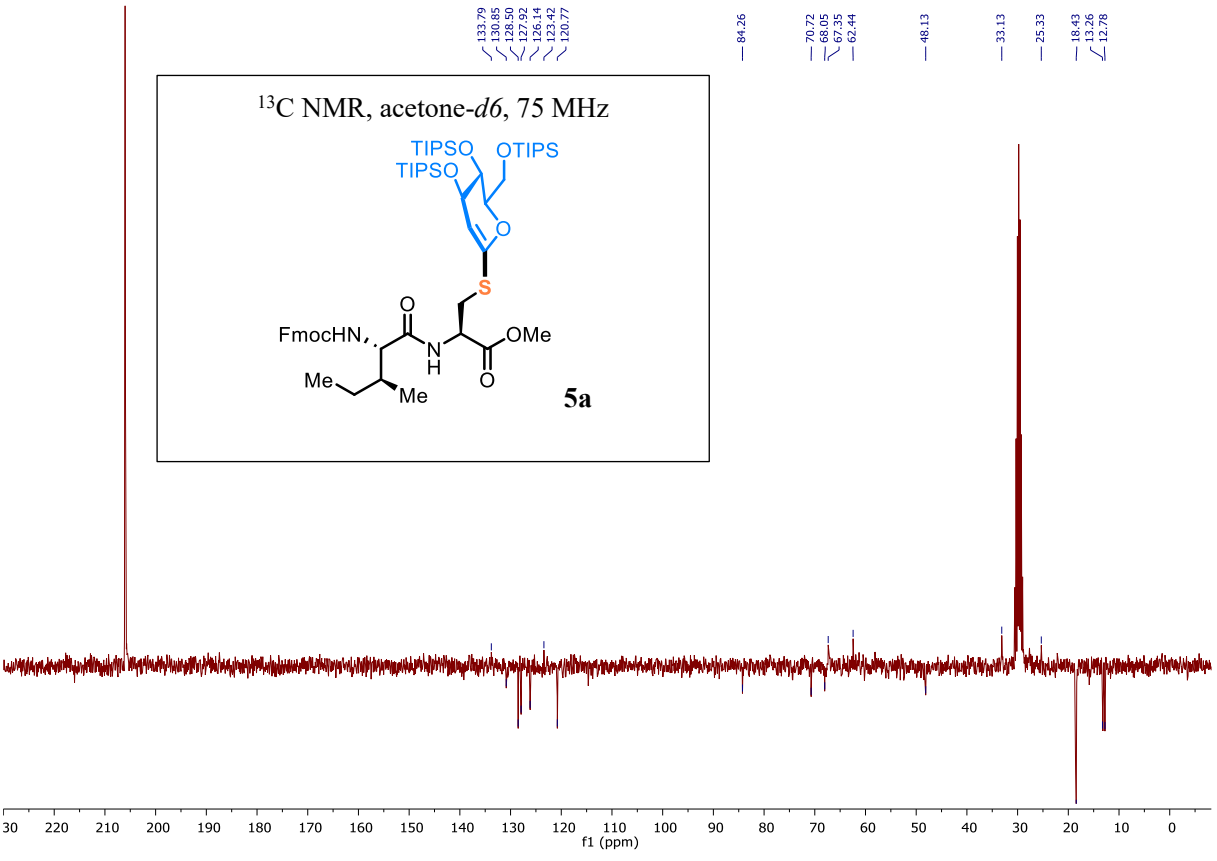
3h

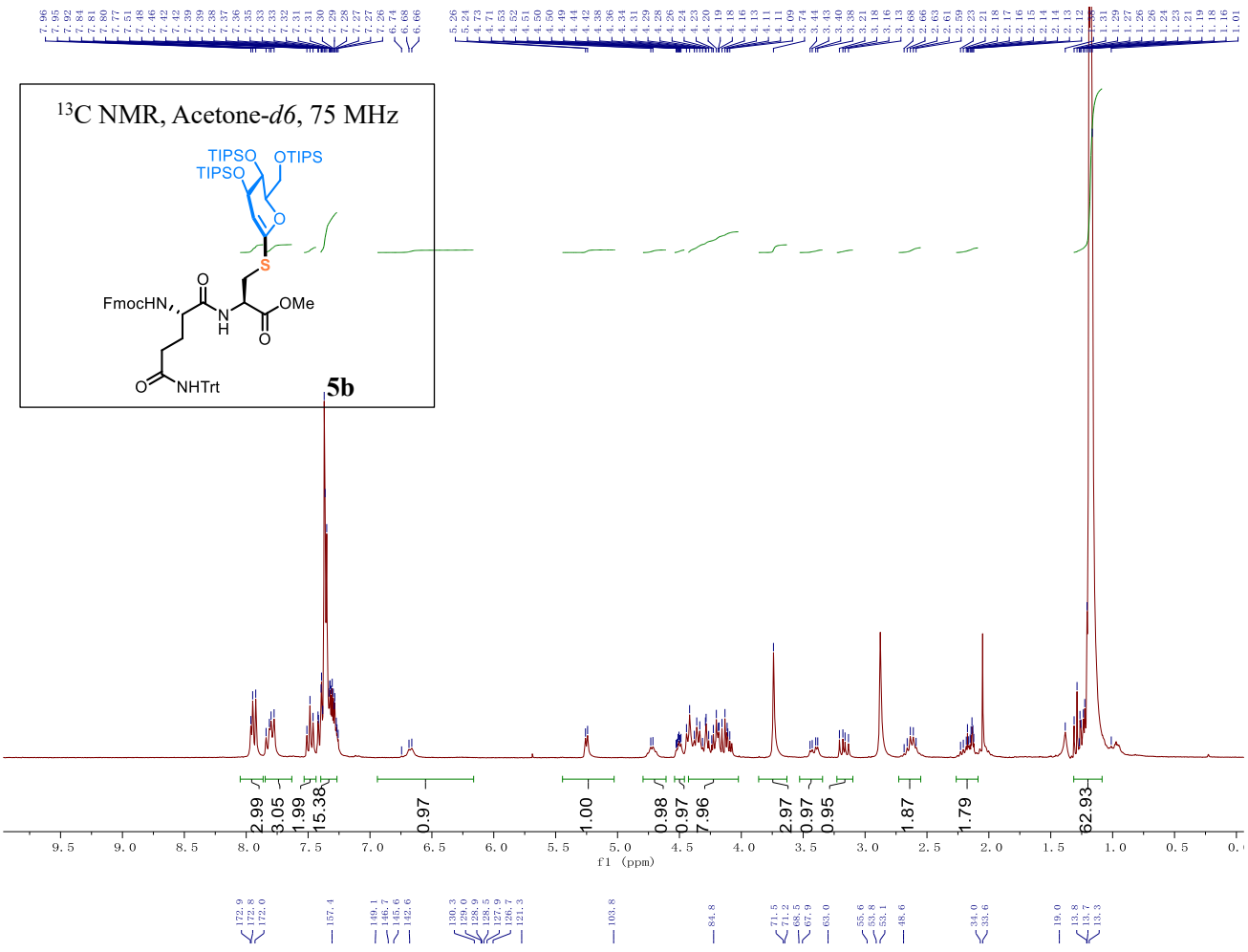
^{13}C NMR, acetone-*d6*, 75 MHz

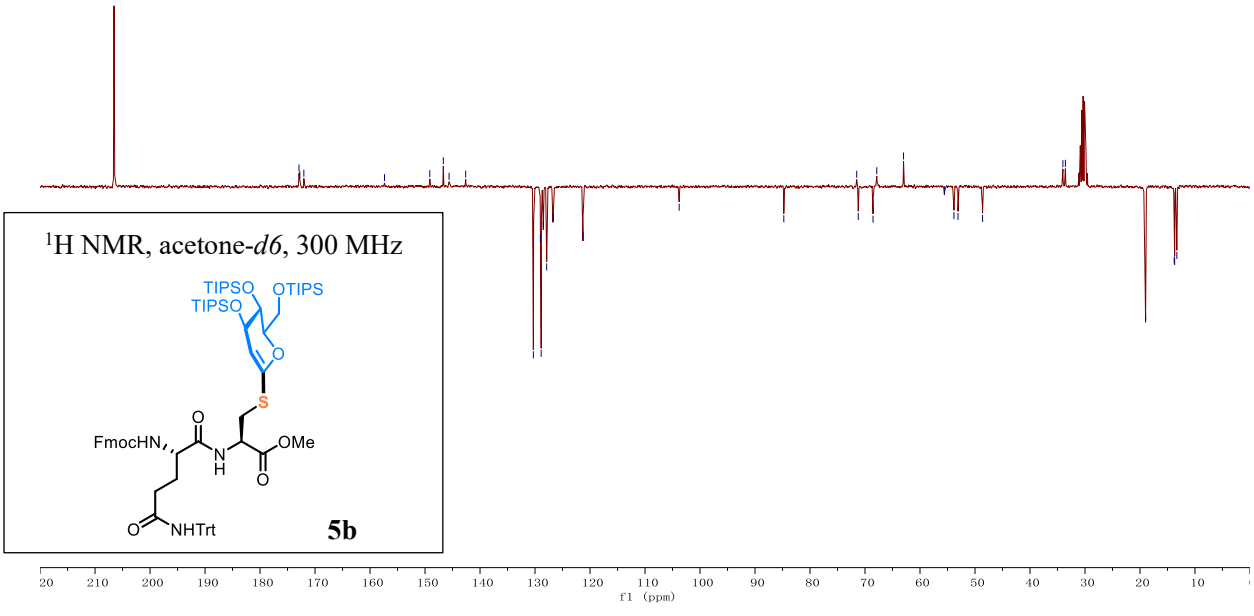


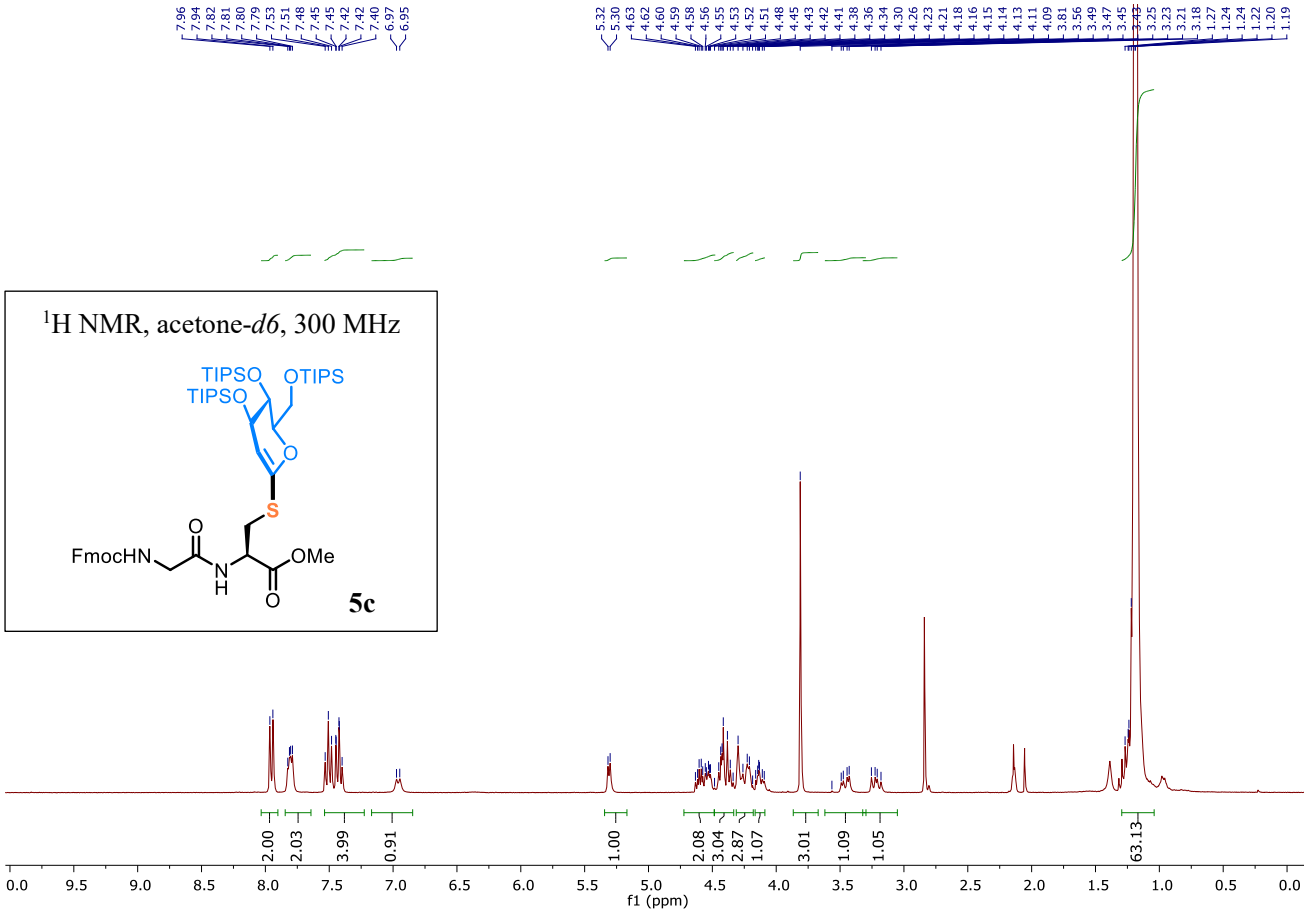
3h

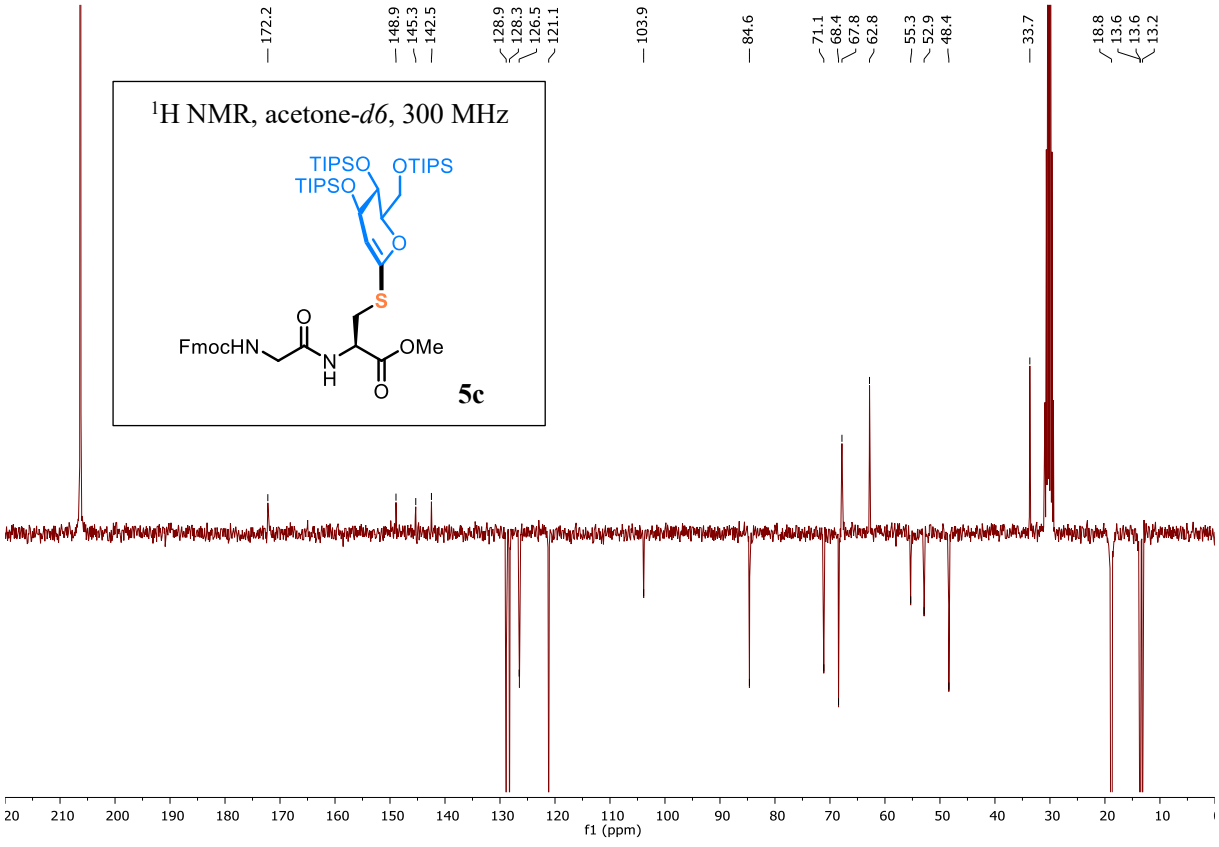

7.42 7.40 7.36 7.34 7.31 6.41 6.38 5.20 5.19 4.71 4.68 4.66 4.66 4.64 4.46 4.44 4.44 4.42 4.41 4.40 4.39 4.36 4.36 4.34 4.30 4.28 4.26 4.23 4.22 4.21 4.20 4.19 4.18 4.16 4.15 4.14 4.13 4.13 4.12 4.11 4.08 4.06 4.04 4.04 4.02 4.01 3.70 3.38 3.37 3.34 3.32 3.18 3.16 3.14 3.11 1.94 1.91 1.87 1.29 1.26 1.24 1.21 1.19
1H NMR, acetone-d6, 300 MHz
TIPSO
TIPSO
OTIPS
O
S
FmocHN
O
N
H
OMe
O
Me
Me
5a
2.30 2.30 1.05 4.25 1.01 0.96 1.03 9.98 2.82 1.01 1.07 1.09 69.30
f1 (ppm)

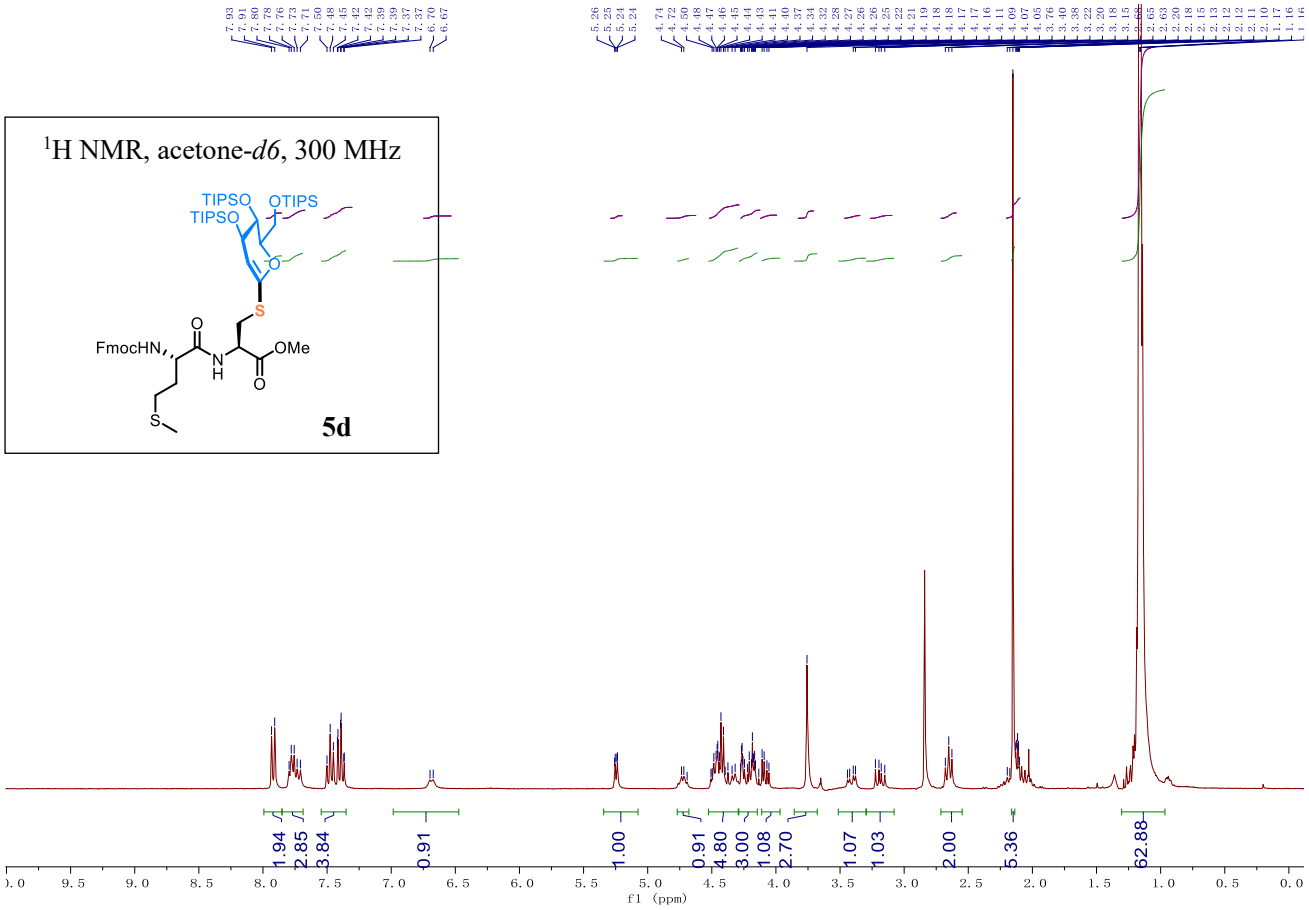

133.79 130.85 128.50 127.92 126.14 123.42 120.77 84.26 70.72 68.05 67.35 62.44 48.13 33.13 25.33 18.43 13.26 12.78
13C NMR, acetone-d6, 75 MHz
TIPSO
TIPSO
OTIPS
O
S
FmocHN
O
N
H
OMe
O
Me
Me
5a
f1 (ppm)

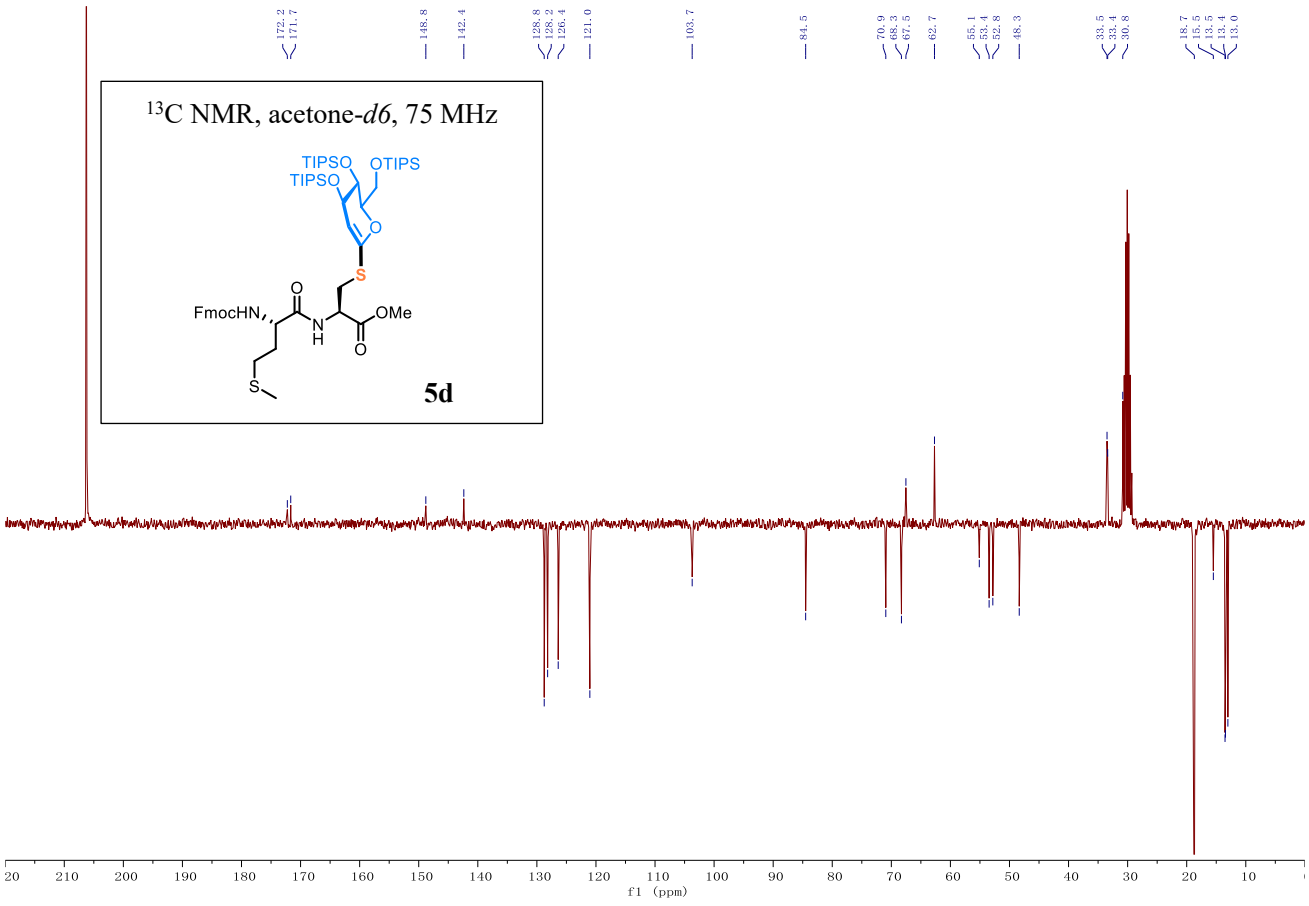

^{13}C NMR, Acetone-*d6*, 75 MHz
TIPSO
TIPSO
OTIPS
O
S
FmocHN
O
N
H
OMe
O
O
NHTrt
5b
f1 (ppm)

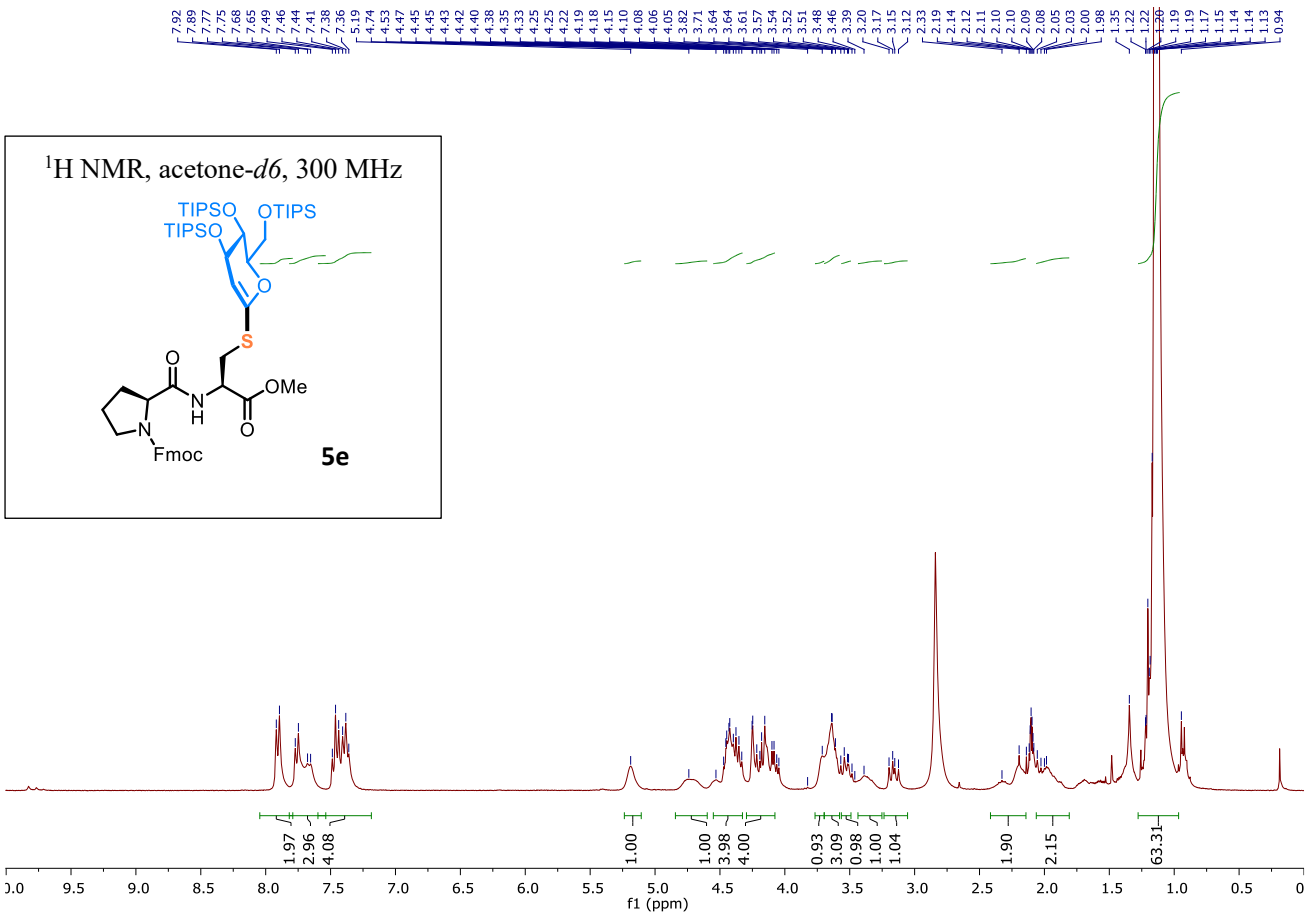

^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
TIPSO
OTIPS
O
S
FmocHN
O
N
H
OMe
O
O
NHTrt
5b
f1 (ppm)

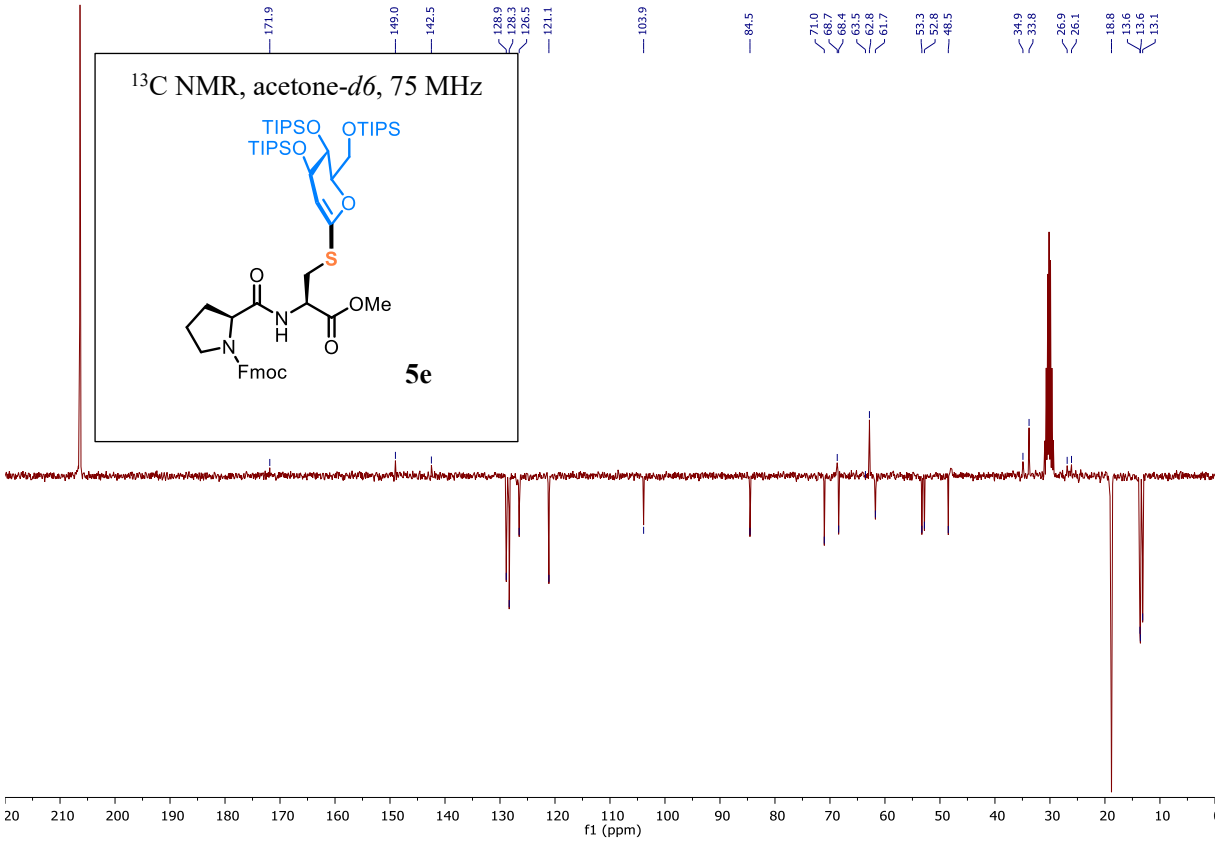

7.96 7.94 7.82 7.81 7.80 7.79 7.53 7.51 7.48 7.45 7.45 7.42 7.42 7.40 6.97 6.95
5.32 5.30 4.63 4.62 4.60 4.59 4.58 4.56 4.55 4.53 4.52 4.51 4.48 4.45 4.43 4.42 4.41 4.38 4.36 4.34 4.30 4.26 4.23 4.21 4.18 4.16 4.15 4.14 4.13 4.11 4.09 3.81 3.56 3.49 3.47 3.45 3.25 3.23 3.21 3.18 1.27 1.24 1.24 1.22 1.20 1.19
1H NMR, acetone-d6, 300 MHz
TIPSO
TIPSO
OTIPS
O
S
FmocHN
O
N
H
O
OMe
O
5c
2.00 2.03 3.99 0.91 1.00 2.08 3.04 2.87 1.07 3.01 1.09 1.05 63.13
0.0 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 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

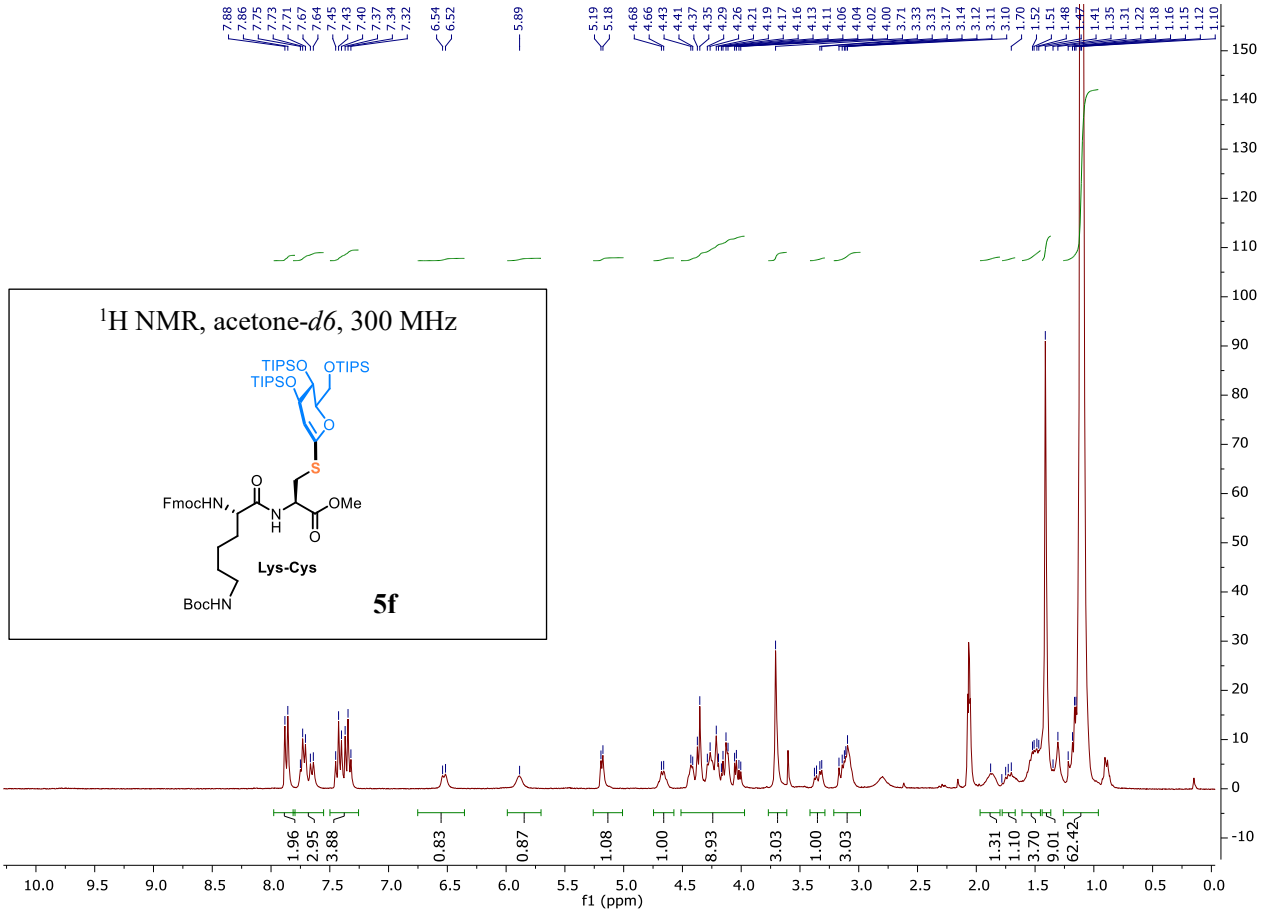

172.2
148.9 145.3 142.5
128.9 128.3 126.5 121.1
103.9
84.6
71.1 68.4 67.8 62.8
55.3 52.9 48.4
33.7
18.8 13.6 13.6 13.2
1H NMR, acetone-d6, 300 MHz
TIPSO
TIPSO
OTIPS
O
S
FmocHN
O
N
H
O
OMe
O
5c
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

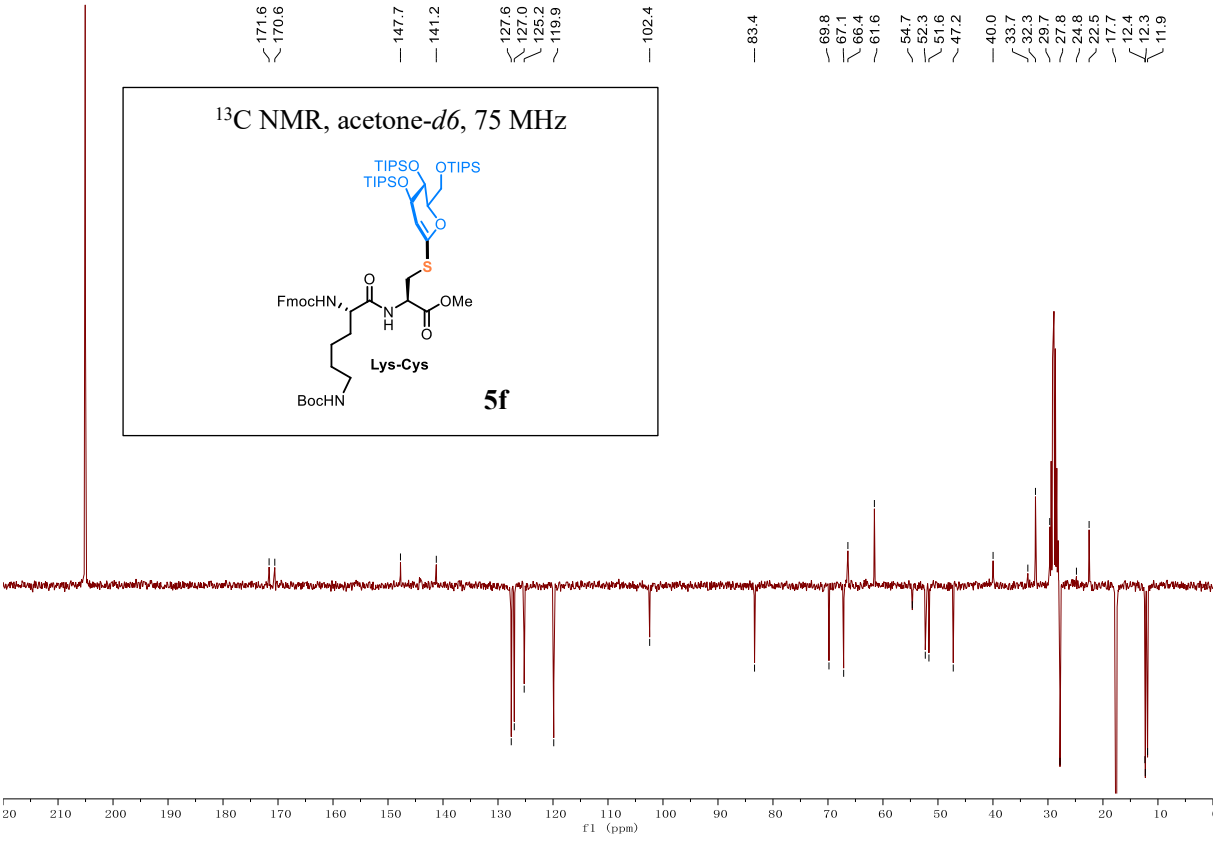

^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
OTIPS
TIPSO
O
S
FmocHN
O
N
H
OMe
O
S
5d
f1 (ppm)

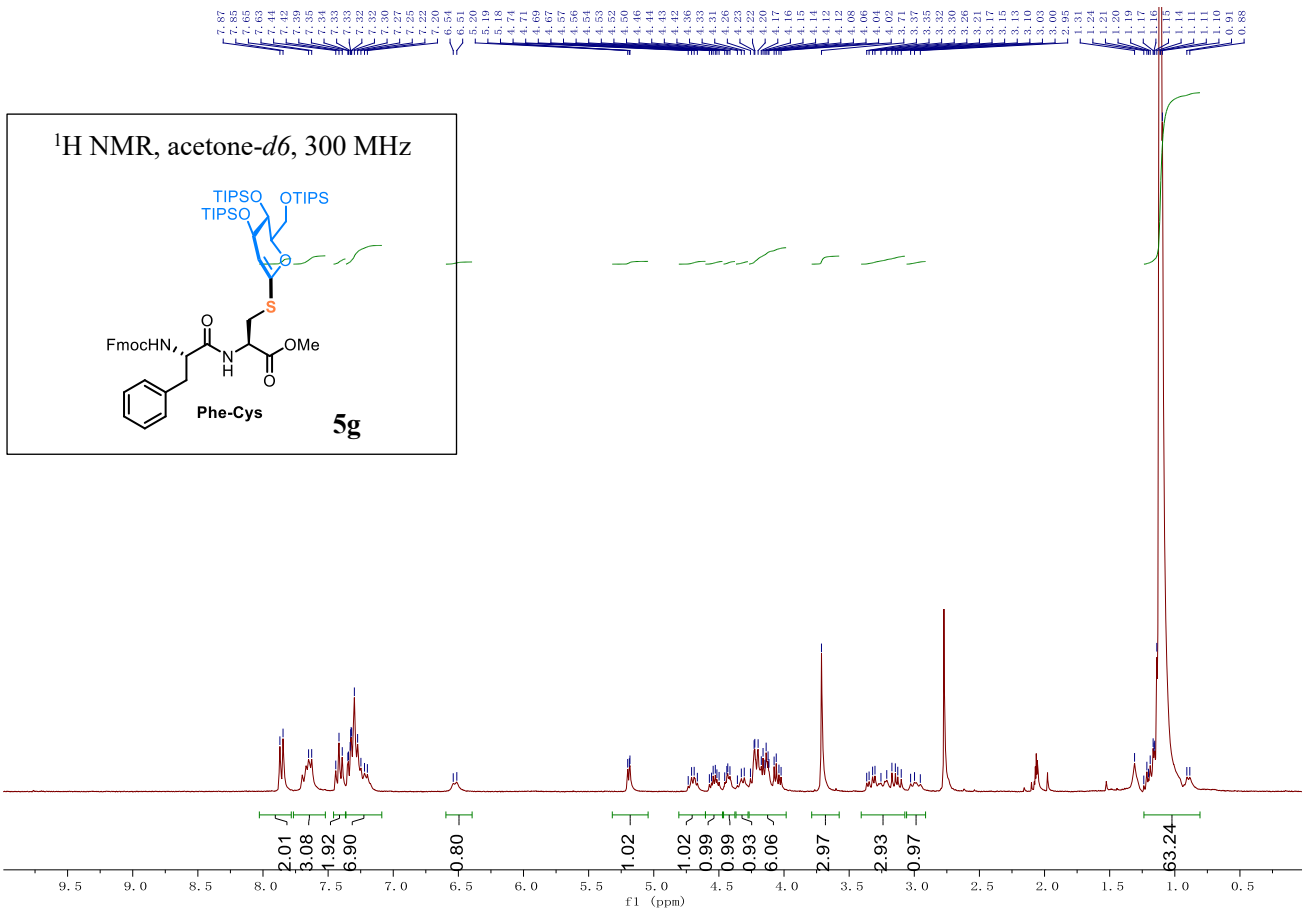

^{13}C NMR, acetone-*d6*, 75 MHz
TIPSO
OTIPS
TIPSO
O
S
FmocHN
O
N
H
OMe
O
S
5d
f1 (ppm)

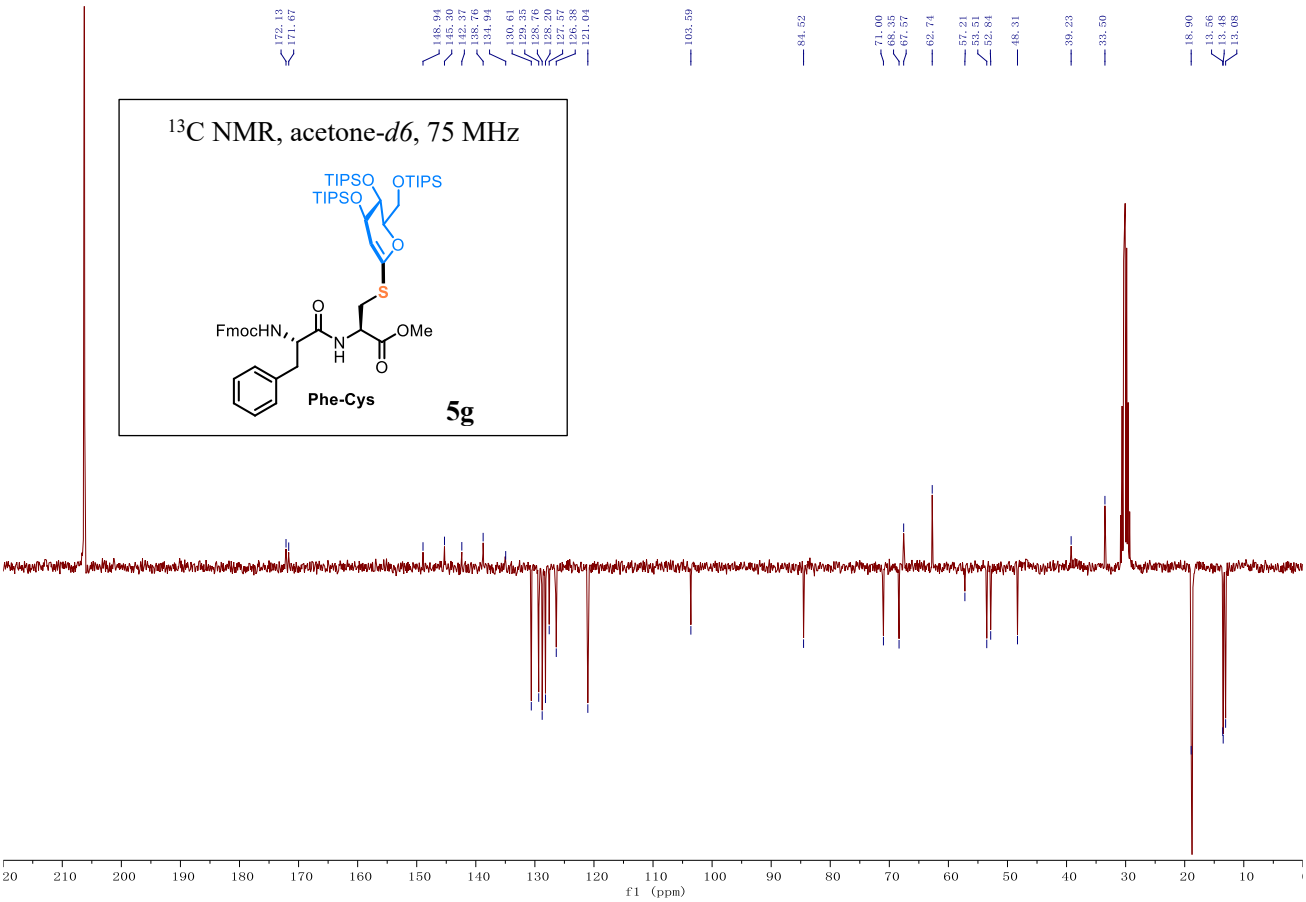

^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
TIPSO
OTIPS
O
S
O
N
H
OMe
O
N
Fmoc
5e
f1 (ppm)

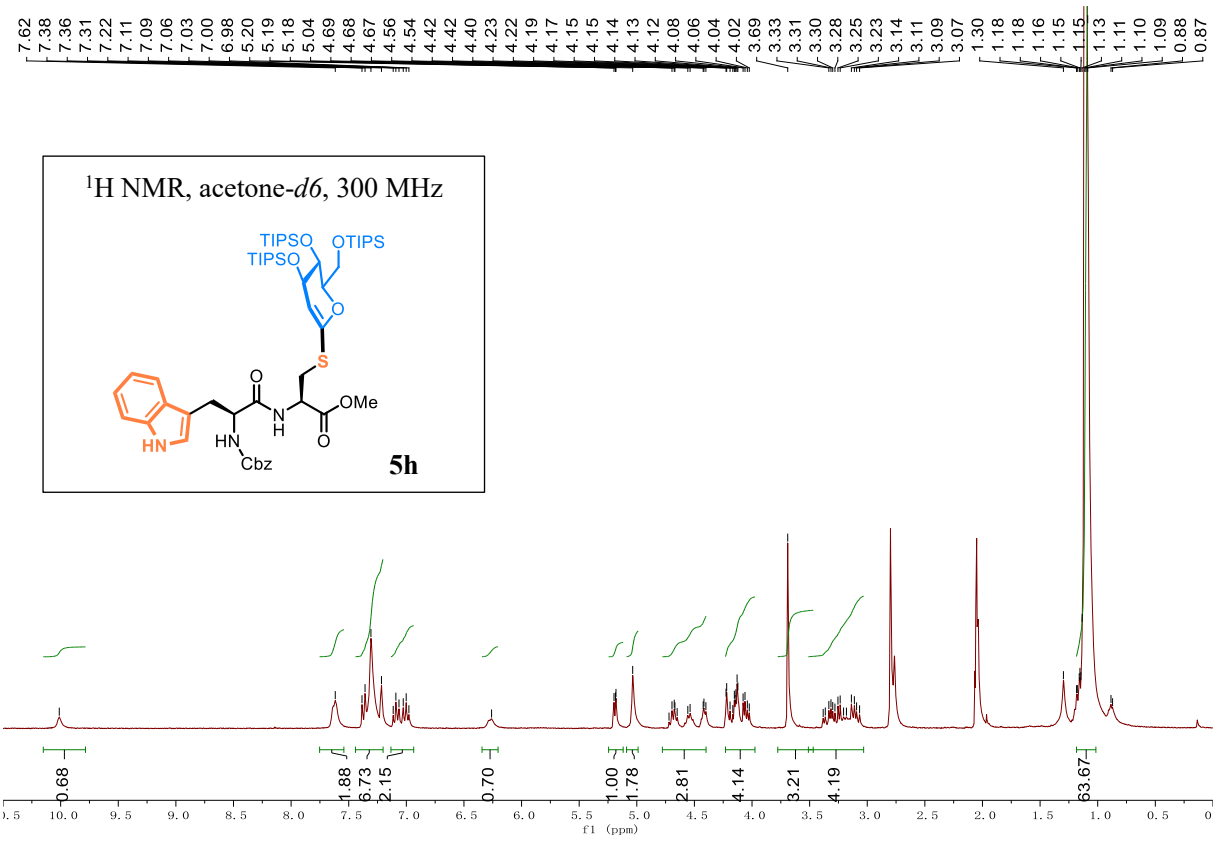

^{13}C NMR, acetone-*d6*, 75 MHz
TIPSO
TIPSO
OTIPS
O
S
O
N
H
OMe
O
N
Fmoc
5e
f1 (ppm)


^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
TIPSO
OTIPS
O
S
FmocHN
O
N
H
OMe
O
Lys-Cys
BocHN
5f
f1 (ppm)


^{13}C NMR, acetone-*d6*, 75 MHz
TIPSO
TIPSO
OTIPS
O
S
FmocHN
O
N
H
OMe
O
Lys-Cys
BocHN
5f
f1 (ppm)

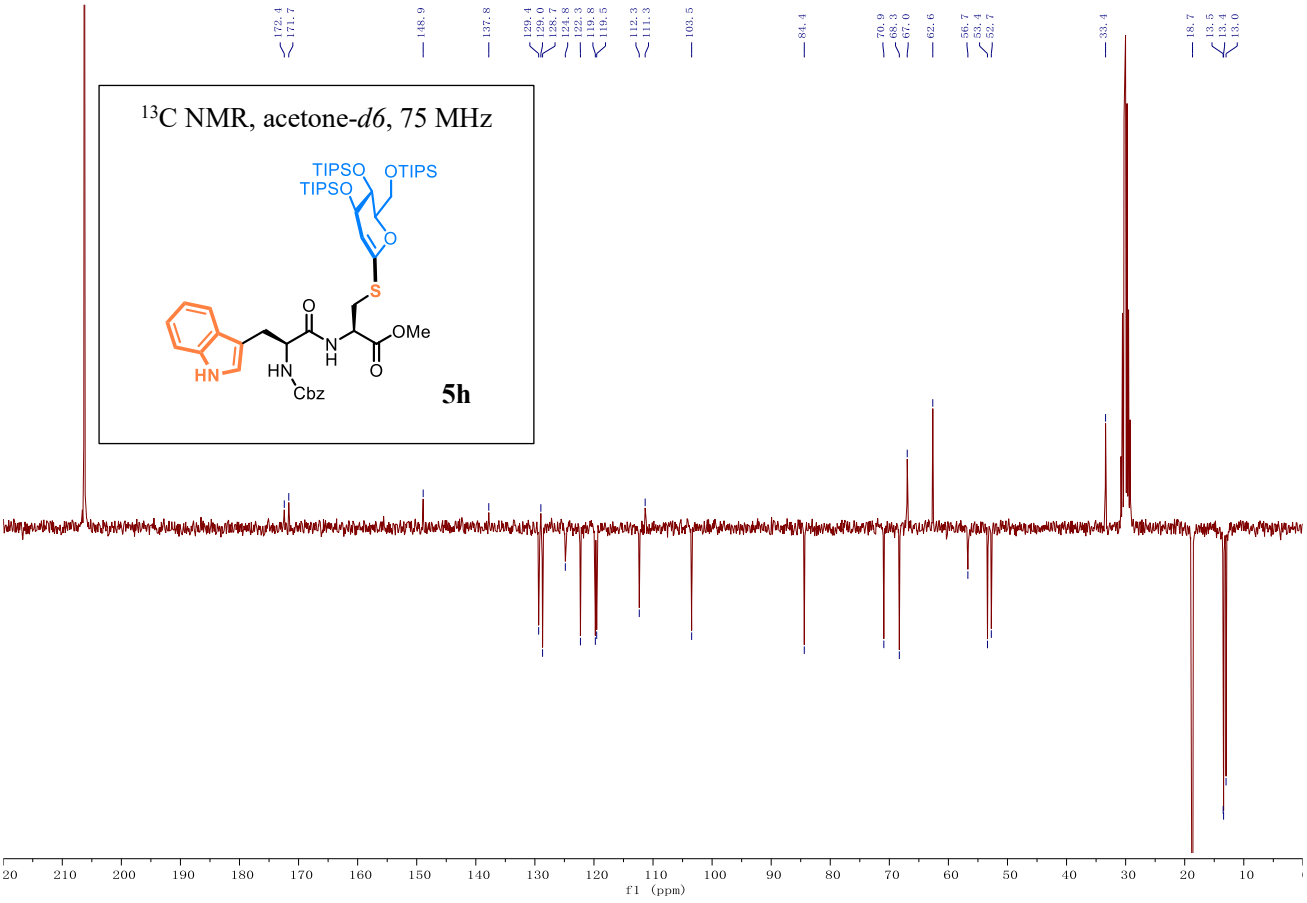

^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
TIPSO
OTIPS
S
FmocHN
O
N
H
OMe
O
Phe-Cys
5g
2.01
3.08
1.92
6.90
0.80
1.02
1.02
0.99
0.99
0.93
6.06
2.97
2.93
0.97
63.24
f1 (ppm)


^{13}C NMR, acetone-*d6*, 75 MHz
TIPSO
TIPSO
OTIPS
S
FmocHN
O
N
H
OMe
O
Phe-Cys
5g
f1 (ppm)



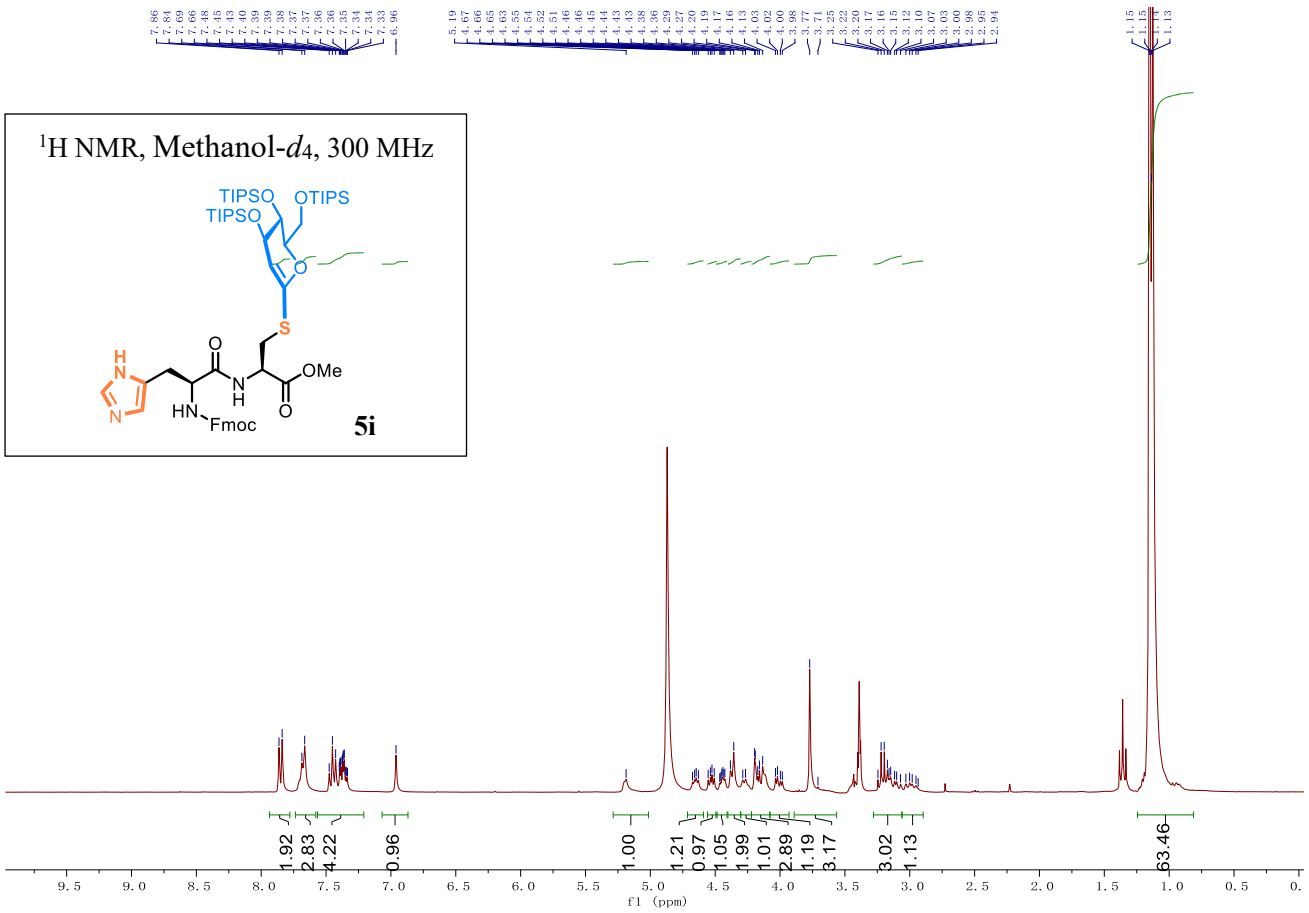
^{1}H NMR, acetone-*d6*, 300 MHz

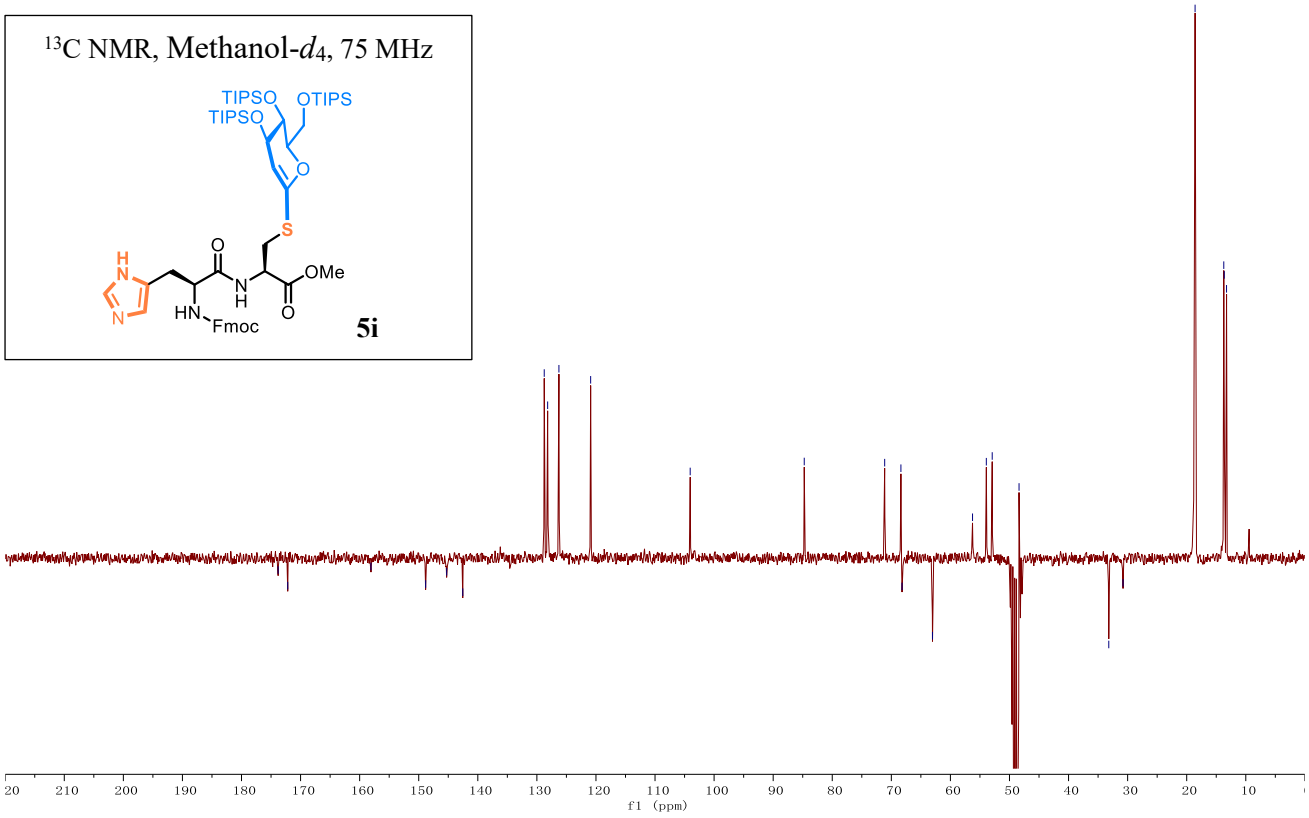
5h

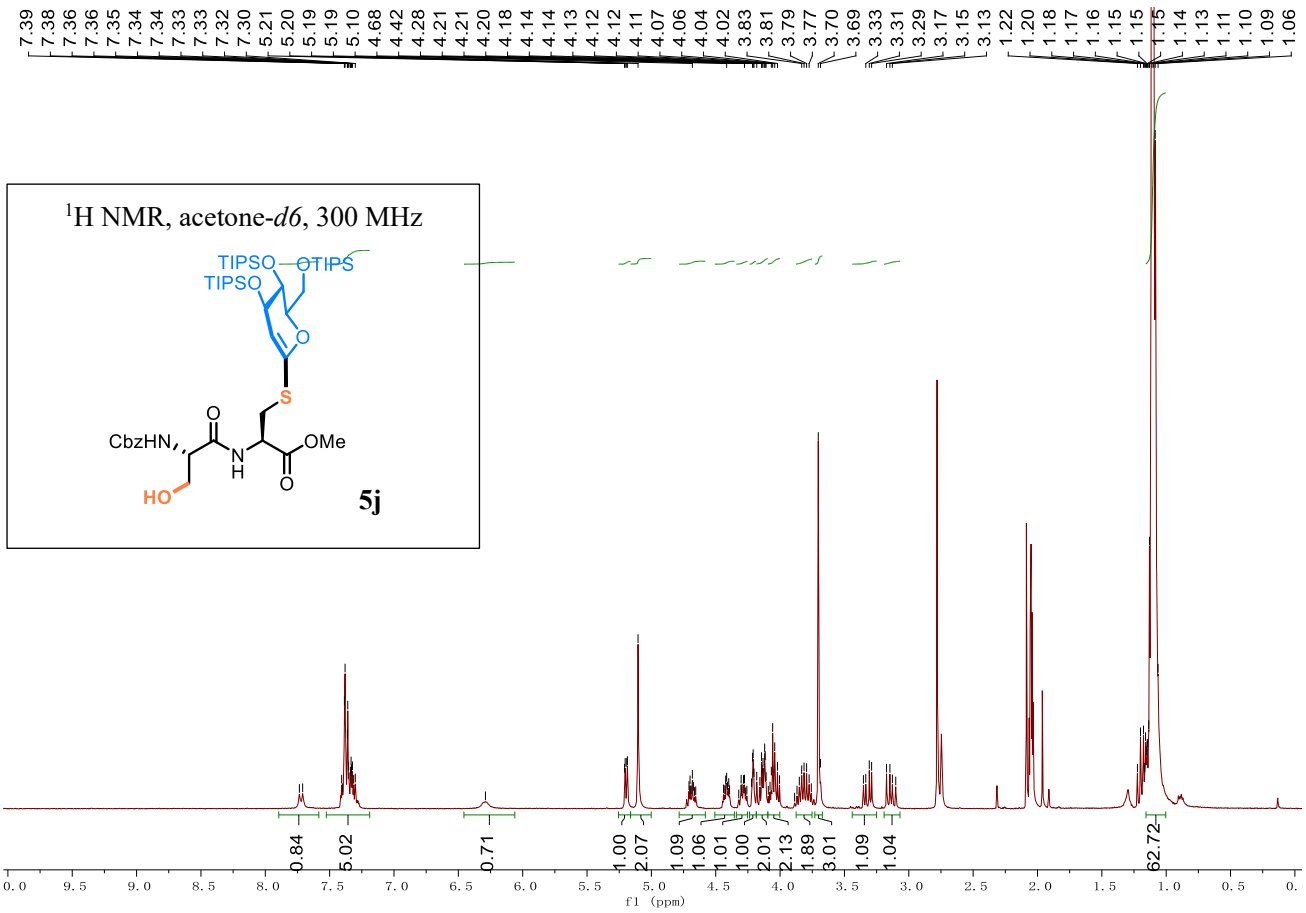


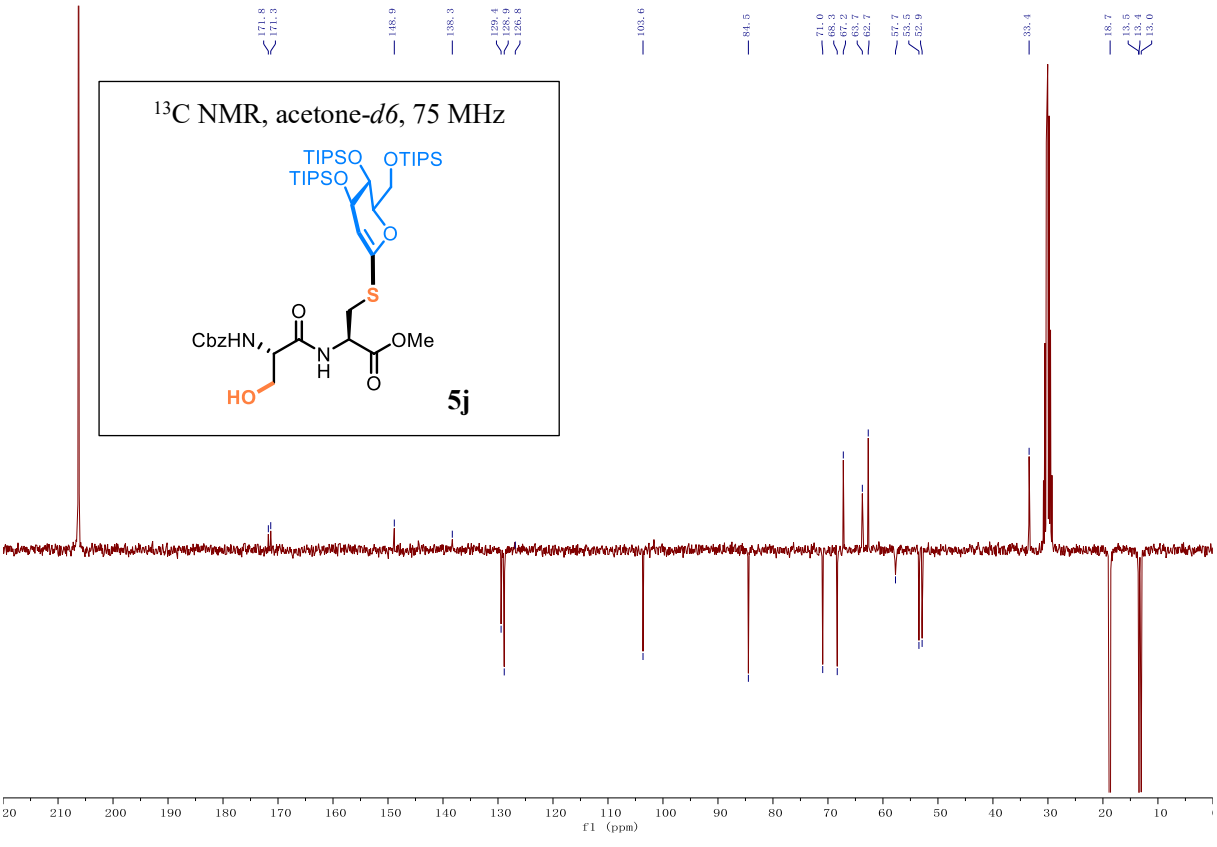
^{13}C NMR, acetone-*d6*, 75 MHz

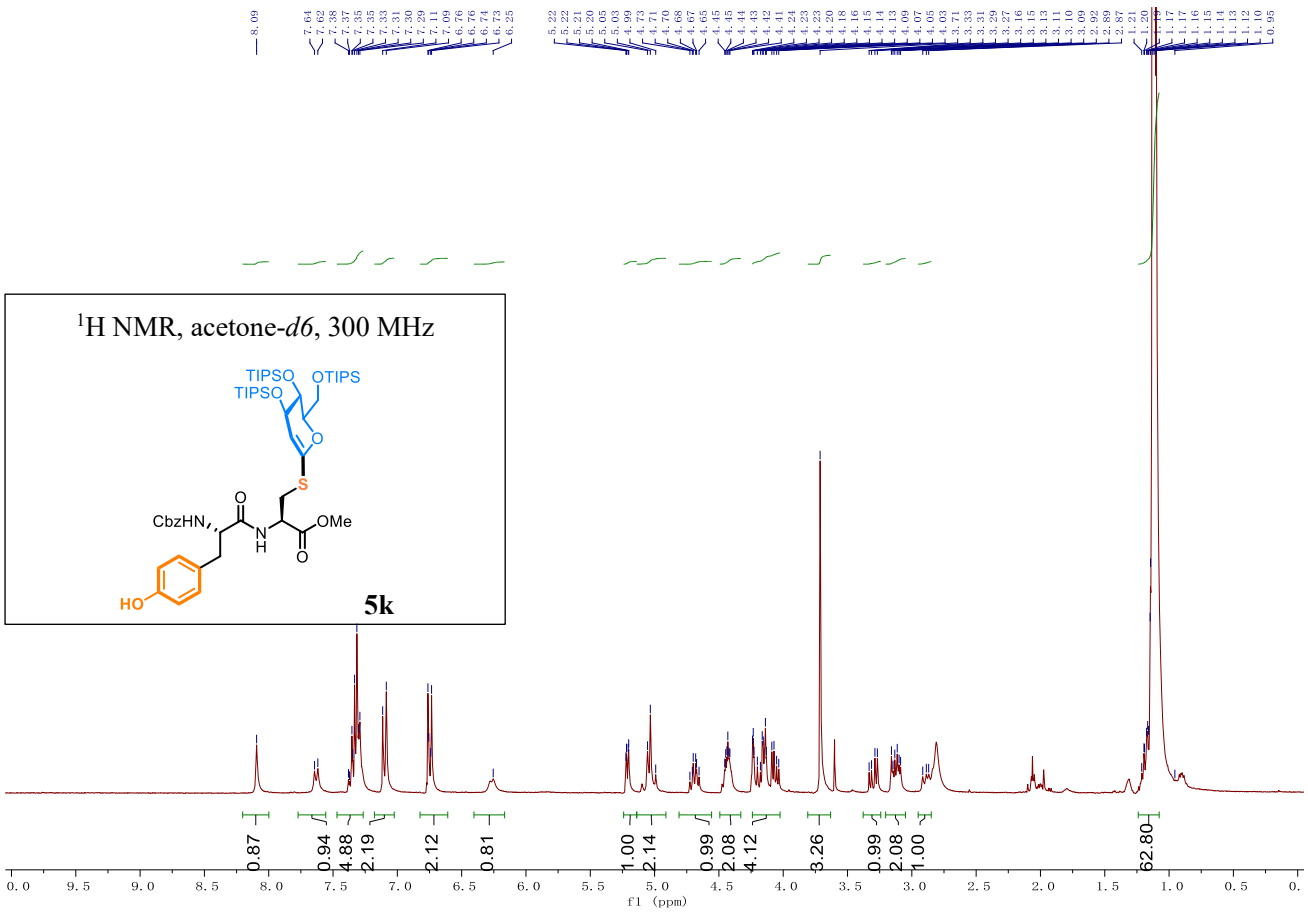
5h

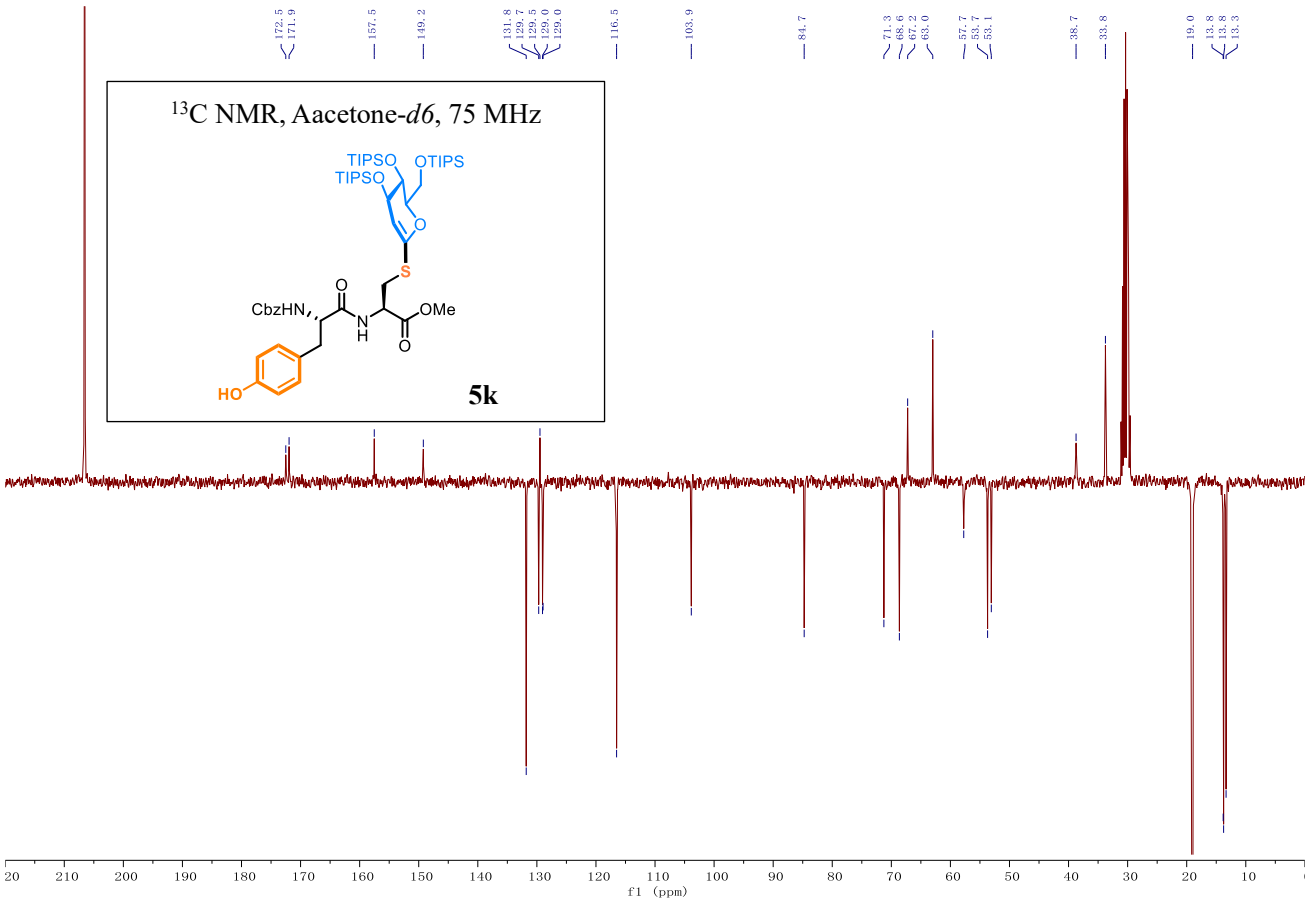

^{1}H NMR, Methanol-d_4, 300 MHz
TIPSO
OTIPS
TIPSO
O
S
H
N
N
O
N
H
OMe
O
HN
Fmoc
5i
1.92
2.83
4.22
0.96
1.00
1.21
0.97
1.05
1.99
1.01
2.89
1.19
3.17
3.02
1.13
63.46
f1 (ppm)

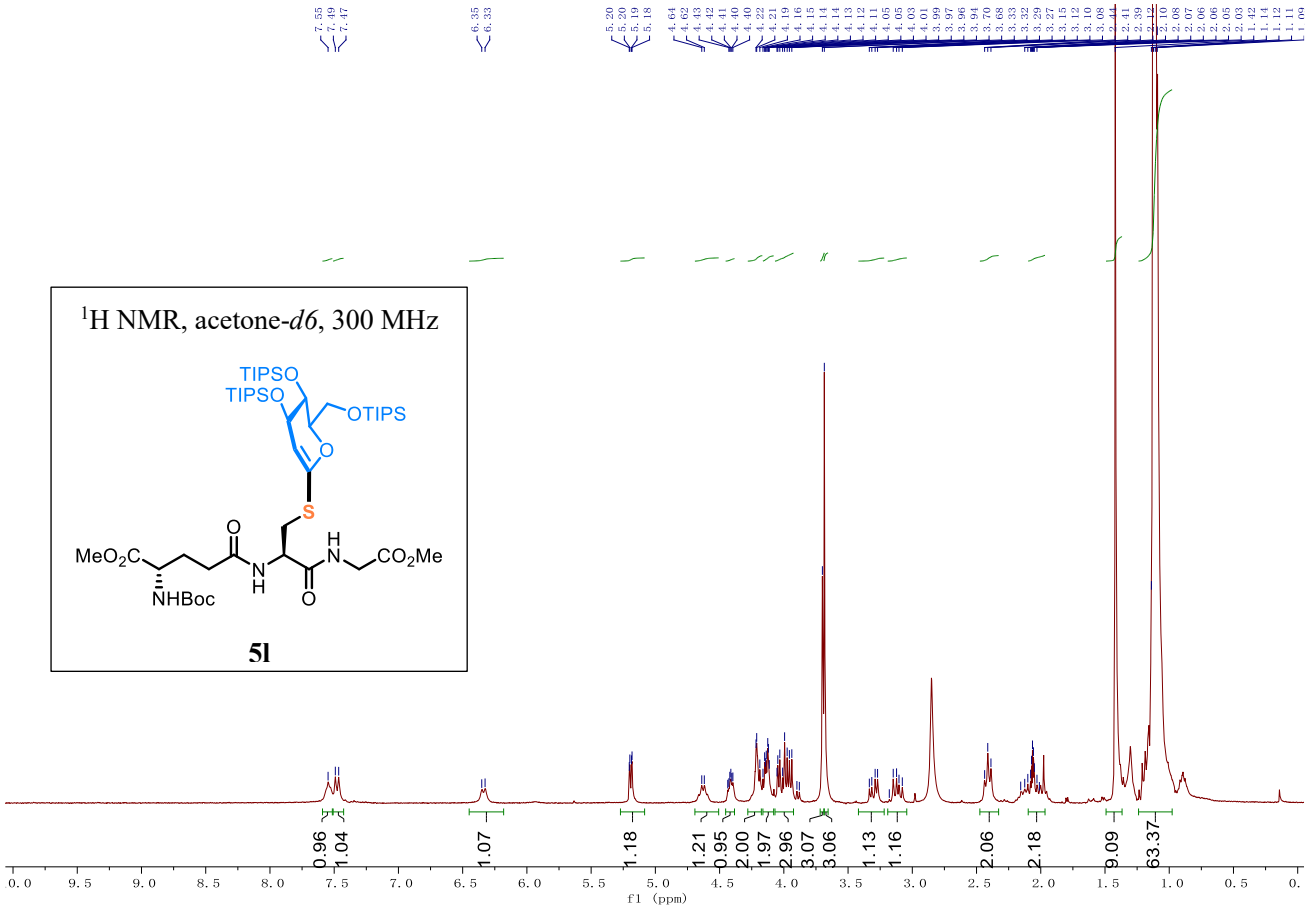

^{13}C NMR, Methanol-d_4, 75 MHz
TIPSO
OTIPS
TIPSO
O
S
H
N
N
O
N
H
OMe
O
HN
Fmoc
5i
f1 (ppm)

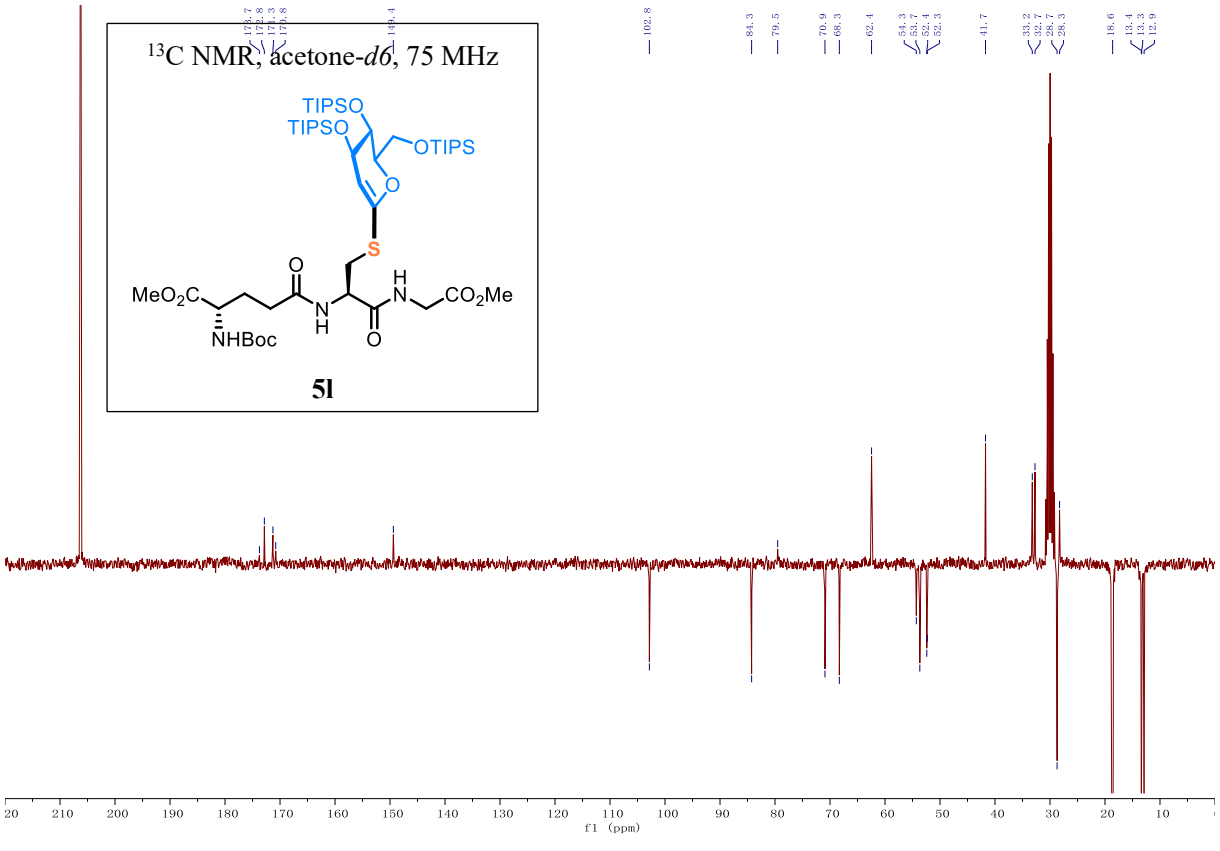

^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
OTIPS
TIPSO
O
S
CbzHN
O
N
H
OMe
O
HO
5j
f1 (ppm)

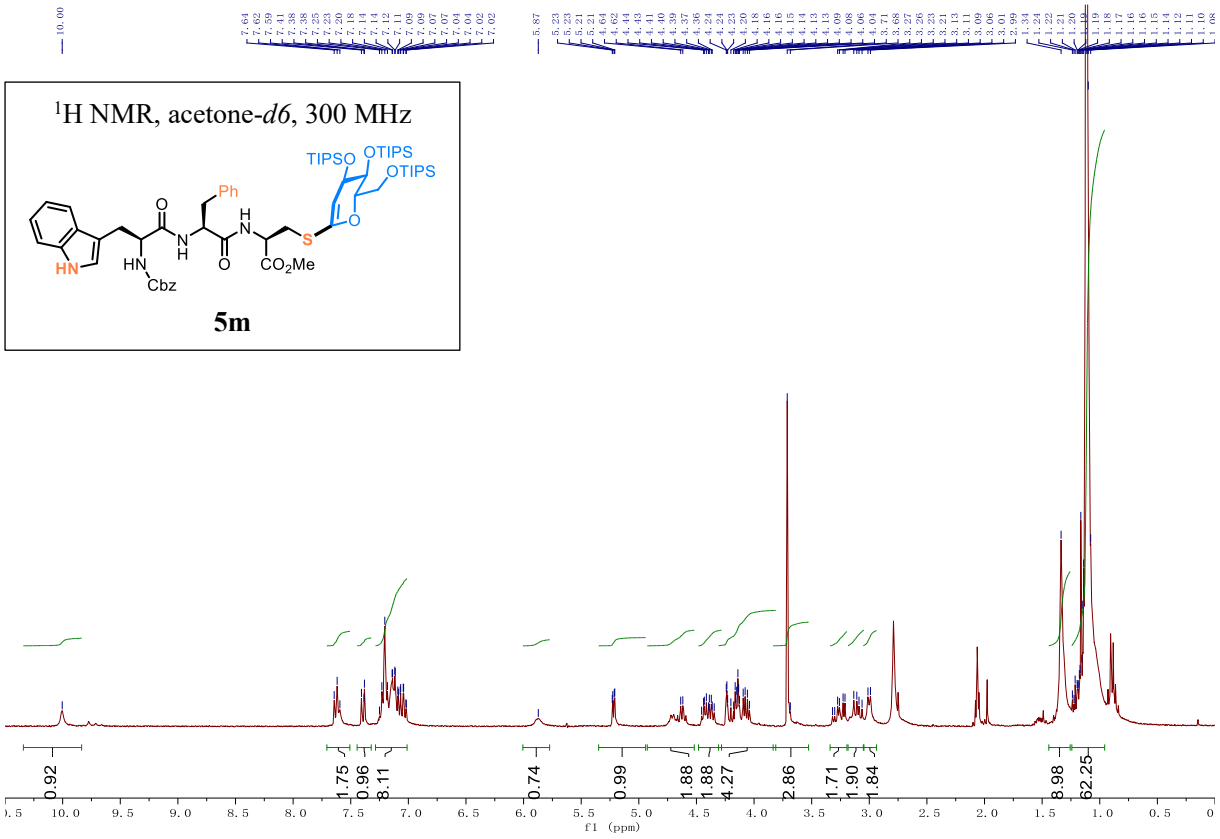

^{13}C NMR, acetone-*d6*, 75 MHz
TIPSO
OTIPS
TIPSO
O
S
CbzHN
O
N
H
OMe
O
HO
5j
f1 (ppm)

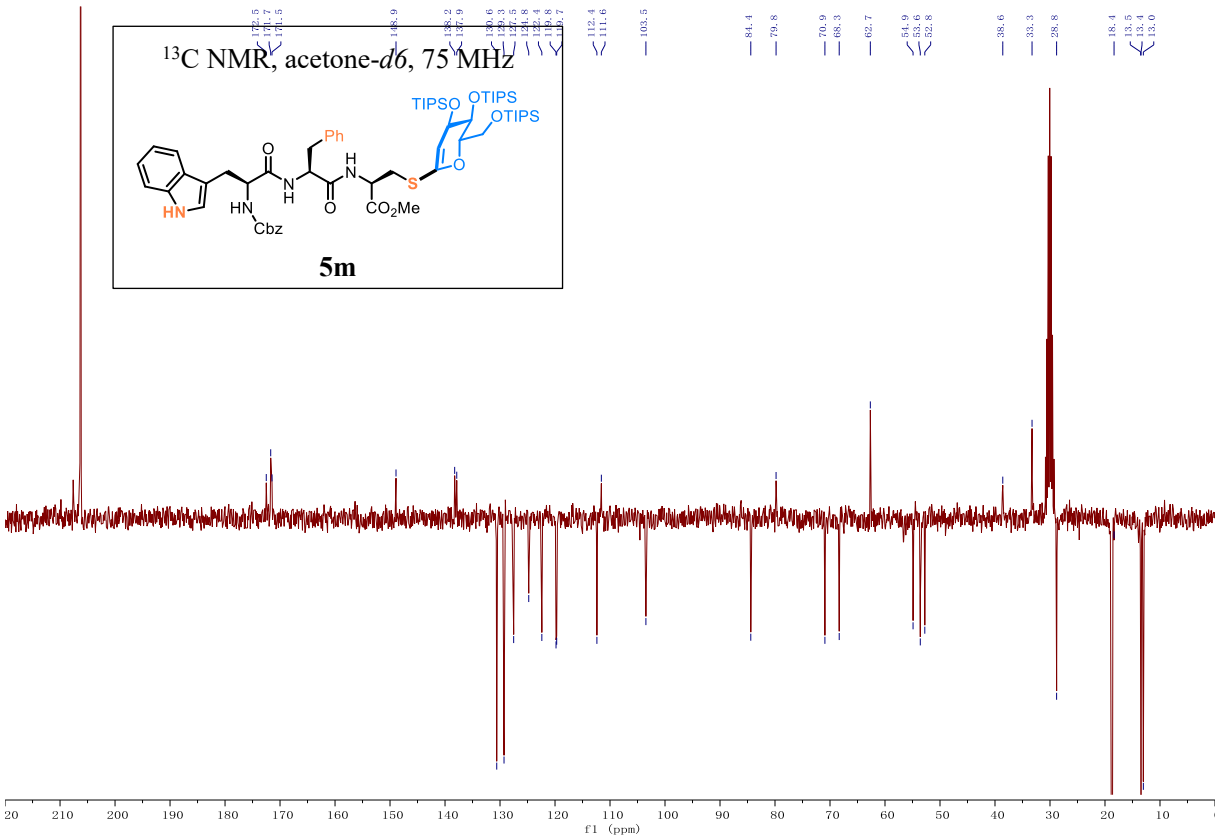

^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
TIPSO
OTIPS
O
S
CbzHN
O
N
H
OMe
O
HO
5k
0.87
0.94
4.88
2.19
2.12
0.81
1.00
2.14
0.99
2.08
4.12
3.26
0.99
2.08
1.00
62.80
f1 (ppm)

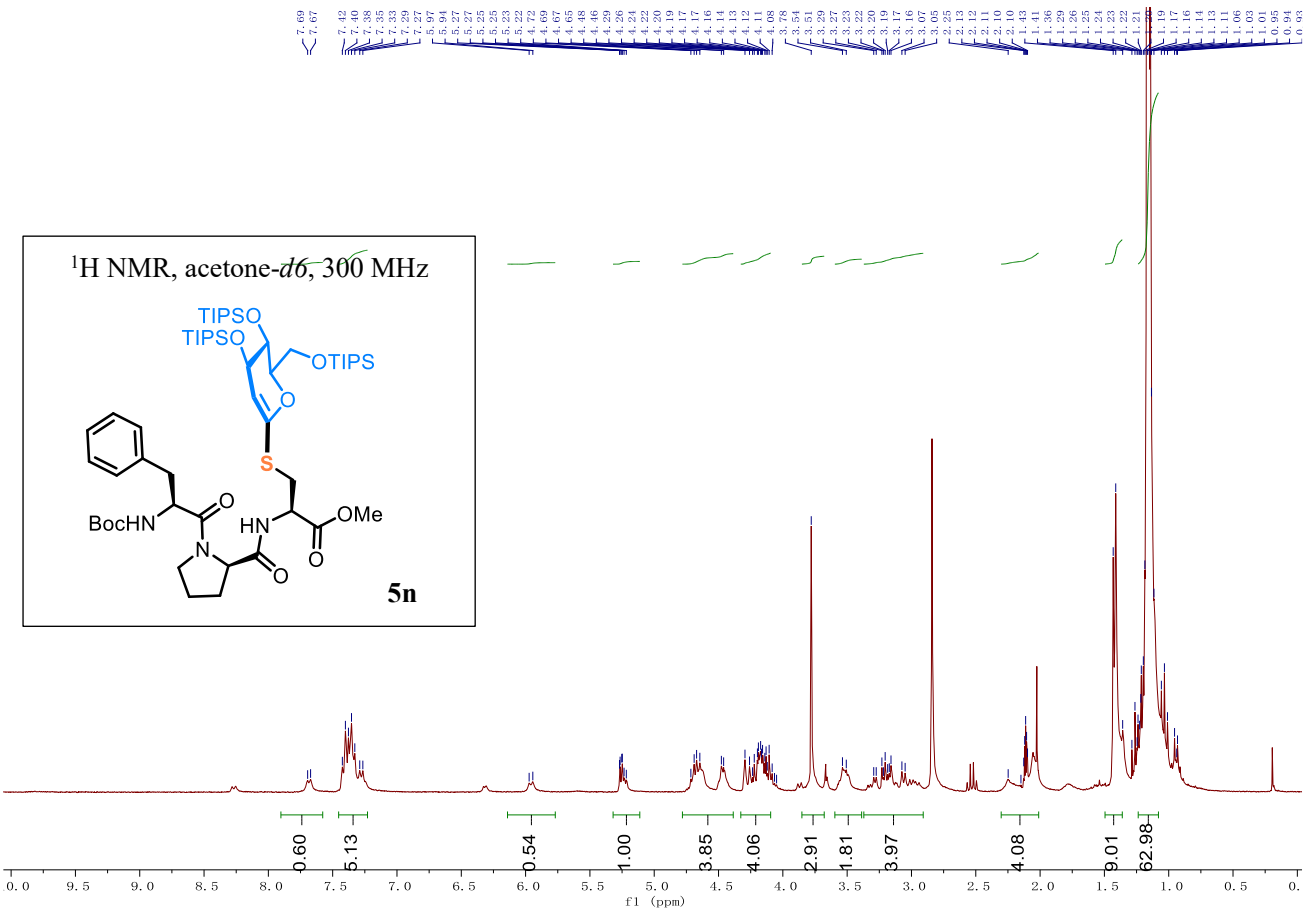

^{13}C NMR, Aacetone-*d6*, 75 MHz
TIPSO
TIPSO
OTIPS
O
S
CbzHN
O
N
H
OMe
O
HO
5k
f1 (ppm)

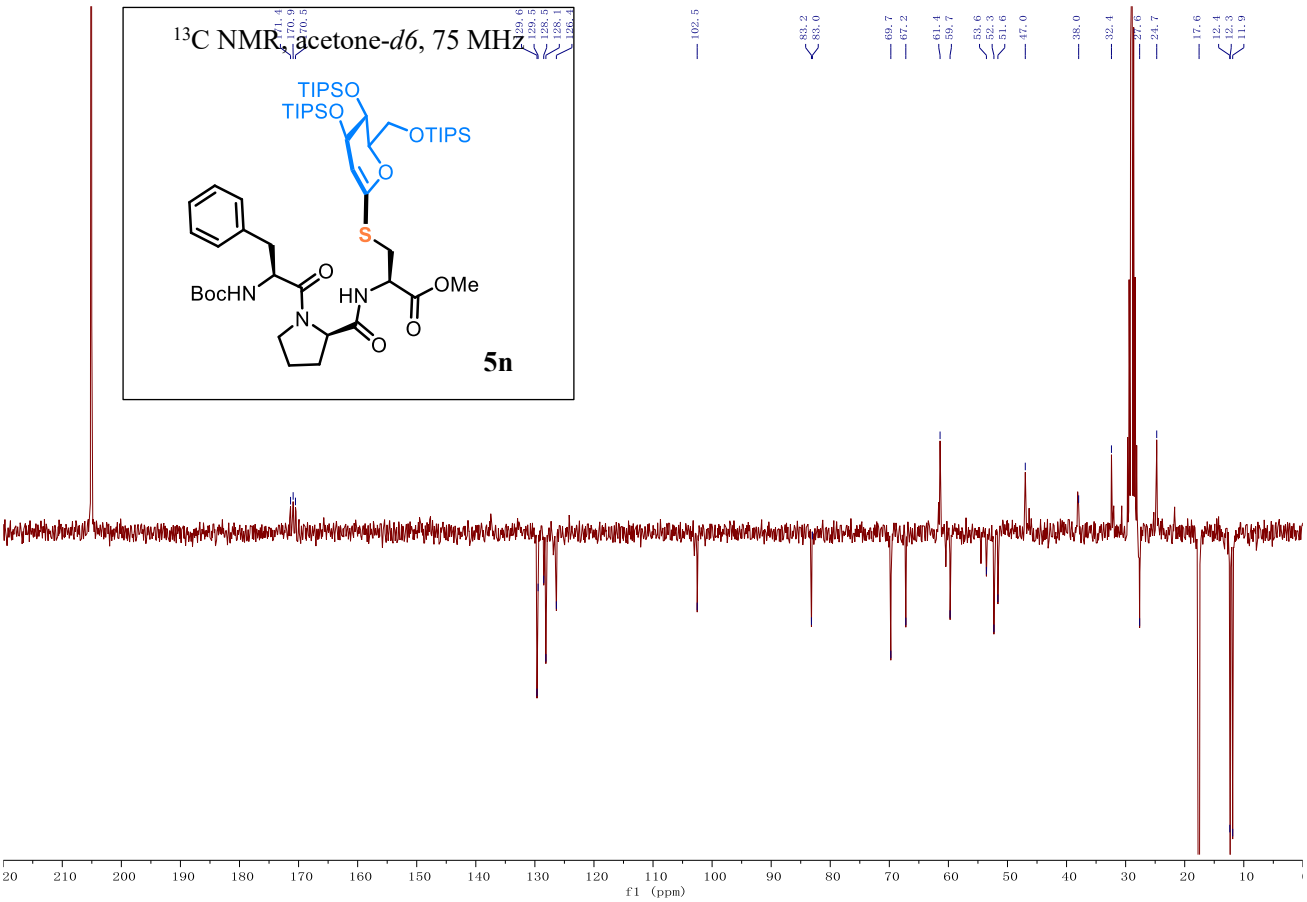

^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
TIPSO
OTIPS
O
S
MeO2C
O
N
H
H
N
CO2Me
NHBoc
O
5l


^{13}C NMR, acetone-*d6*, 75 MHz
TIPSO
TIPSO
OTIPS
O
S
MeO2C
O
N
H
H
N
CO2Me
NHBoc
O
5l

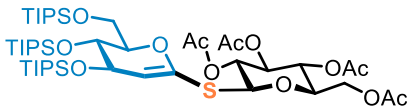

^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
OTIPS
OTIPS
Ph
HN
Cbz
CO2Me
5m
f1 (ppm)


^{13}C NMR, acetone-*d6*, 75 MHz
TIPSO
OTIPS
OTIPS
Ph
HN
Cbz
CO2Me
5m
f1 (ppm)


^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
TIPSO
OTIPS
O
S
BocHN
O
HN
OMe
N
O
O
5n
0.60
5.13
0.54
1.00
3.85
4.06
2.91
1.81
3.97
4.08
9.01
62.98
f1 (ppm)

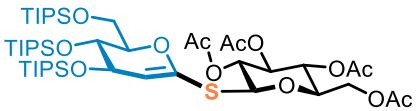

^{13}C NMR, acetone-*d6*, 75 MHz
TIPSO
TIPSO
OTIPS
O
S
BocHN
O
HN
OMe
N
O
O
5n
f1 (ppm)

^{1}H NMR, acetone-*d6*, 300 MHz

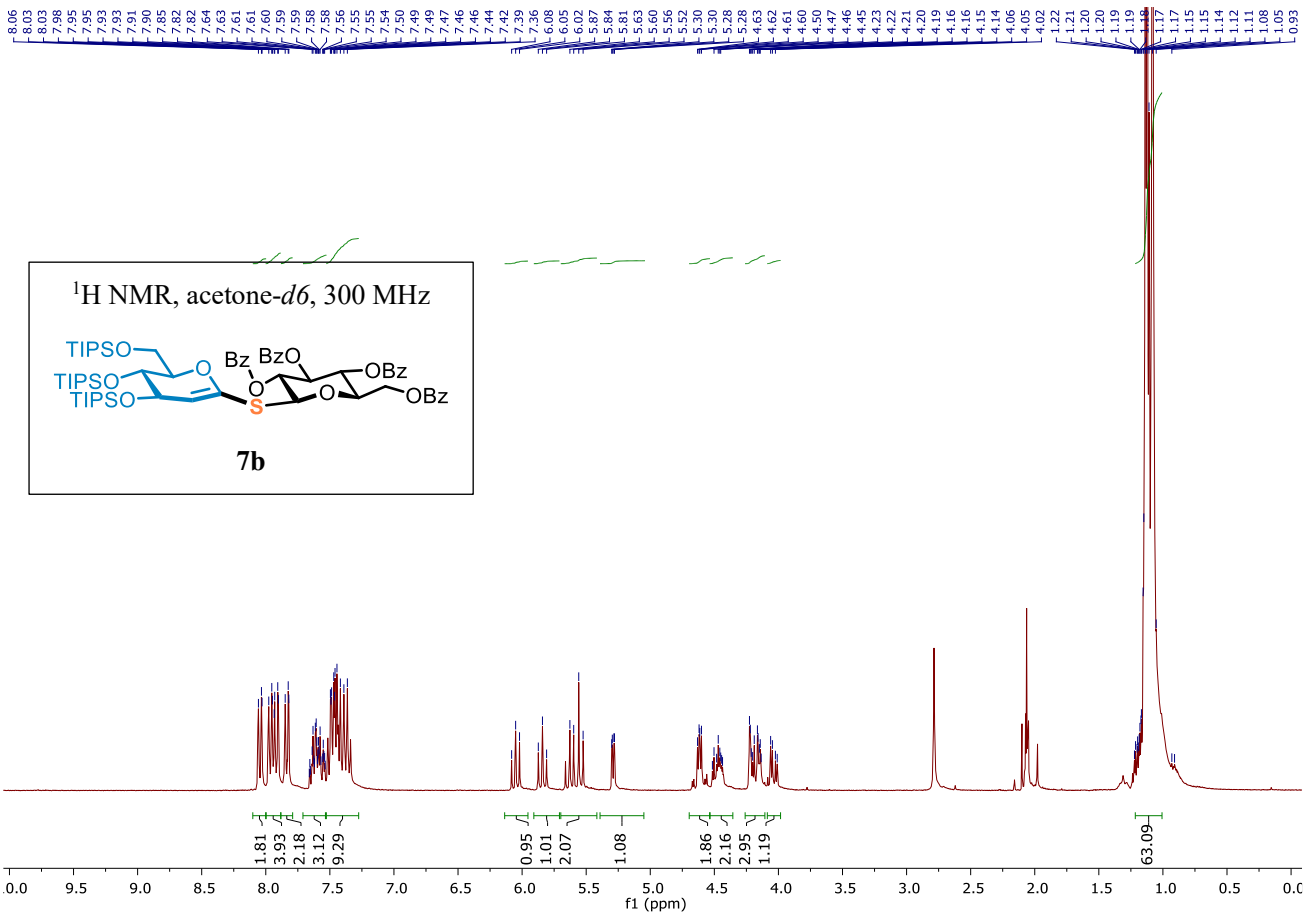


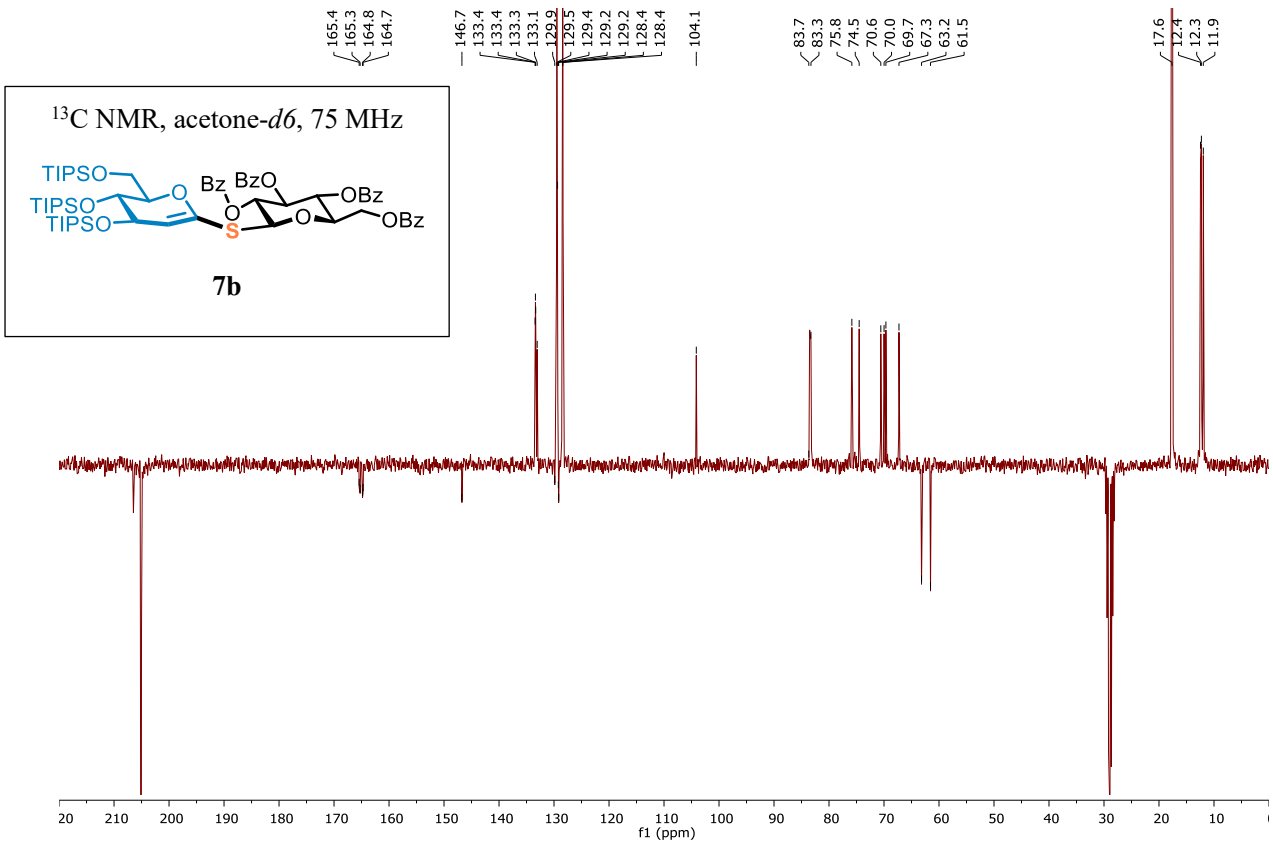
7a

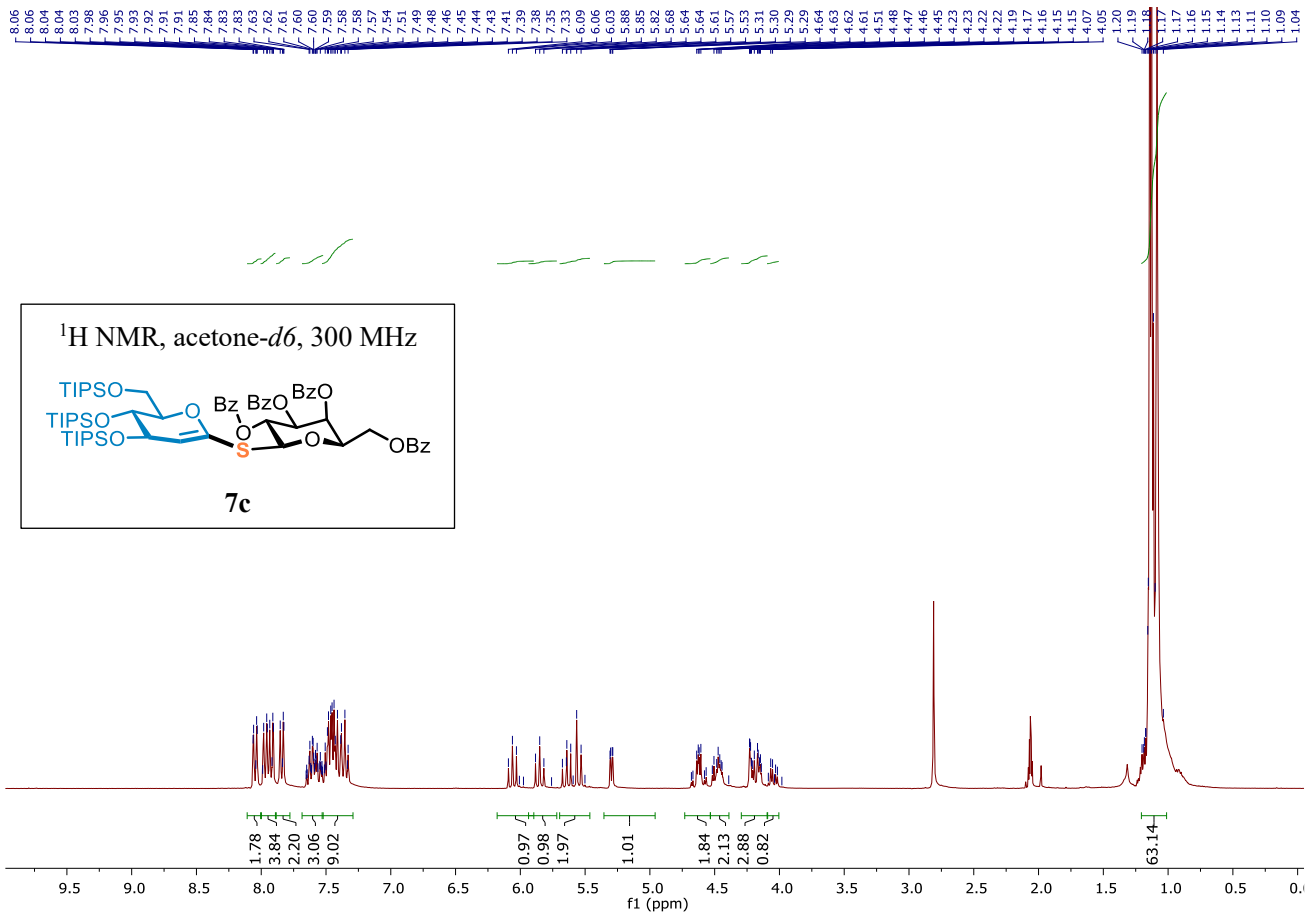
^{13}C NMR, acetone-*d6*, 75 MHz



7a

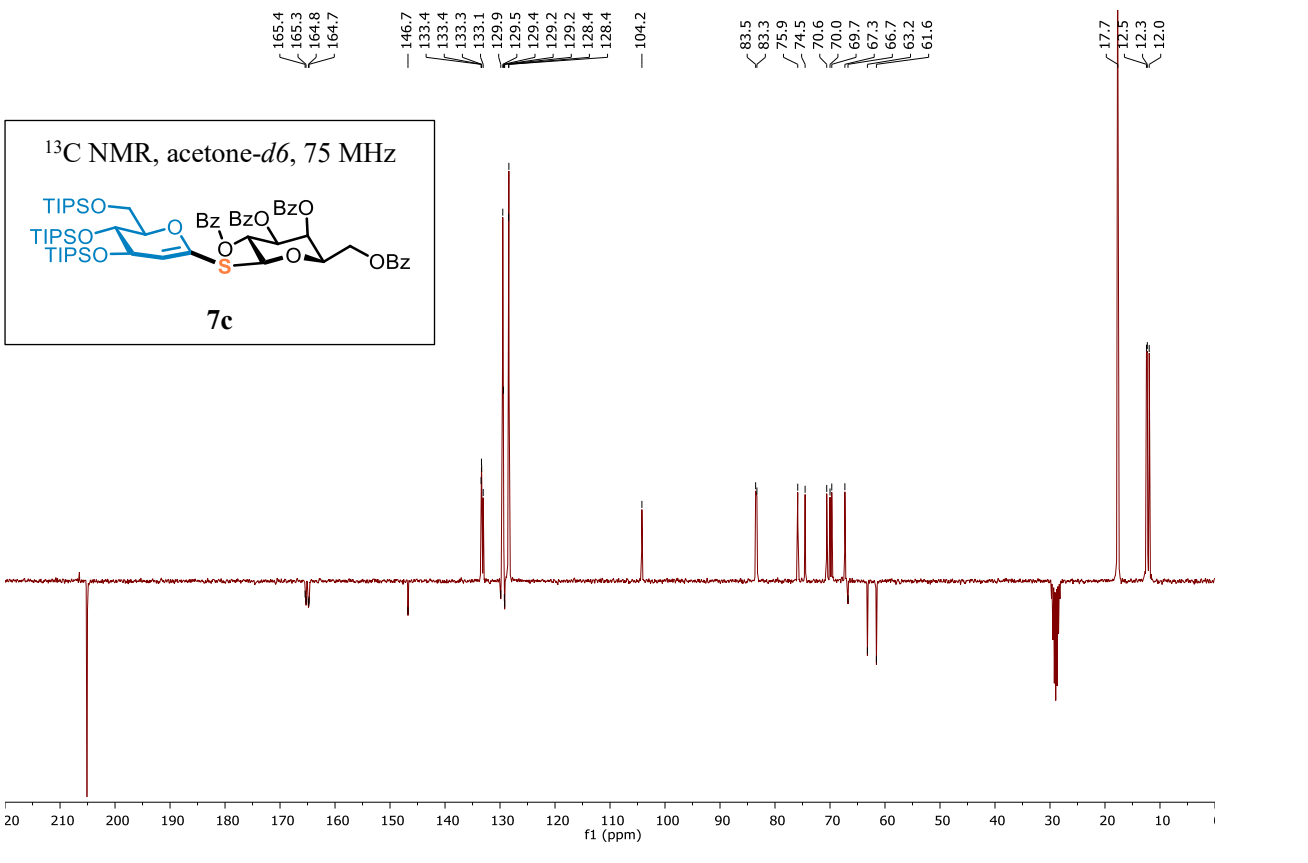

^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
TIPSO
TIPSO
O
Bz
BzO
O
S
O
OBz
OBz
7b
1.81
3.93
2.18
3.12
9.29
0.95
1.01
2.07
1.08
1.86
2.16
2.95
1.19
63.09
f1 (ppm)


^{13}C NMR, acetone-*d6*, 75 MHz
TIPSO
TIPSO
TIPSO
O
Bz
BzO
O
S
O
OBz
OBz
7b
165.4
165.3
164.8
164.7
146.7
133.4
133.4
133.3
133.1
129.9
129.5
129.4
129.2
129.2
128.4
128.4
104.1
83.7
83.3
75.8
74.5
70.6
70.0
69.7
67.3
63.2
61.5
17.6
12.4
12.3
11.9
f1 (ppm)



^{1}H NMR, acetone-*d6*, 300 MHz

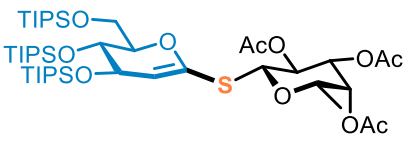
7c



^{13}C NMR, acetone-*d6*, 75 MHz

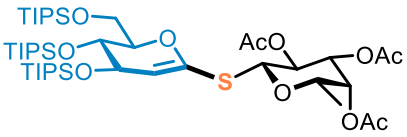
7c

^{1}H NMR, acetone-*d6*, 300 MHz



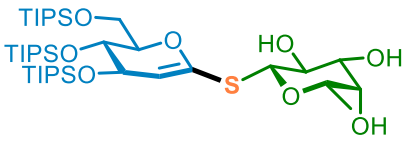
7d

^{13}C NMR, acetone-*d6*, 75 MHz



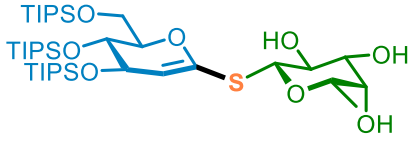
7d

^{1}H NMR, Methanol-d_4, 300 MHz



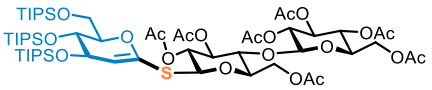
7e

^{13}C NMR, Methanol-d_4, 75 MHz



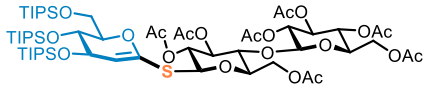
7e

^{13}C NMR, acetone-*d6*, 75 MHz

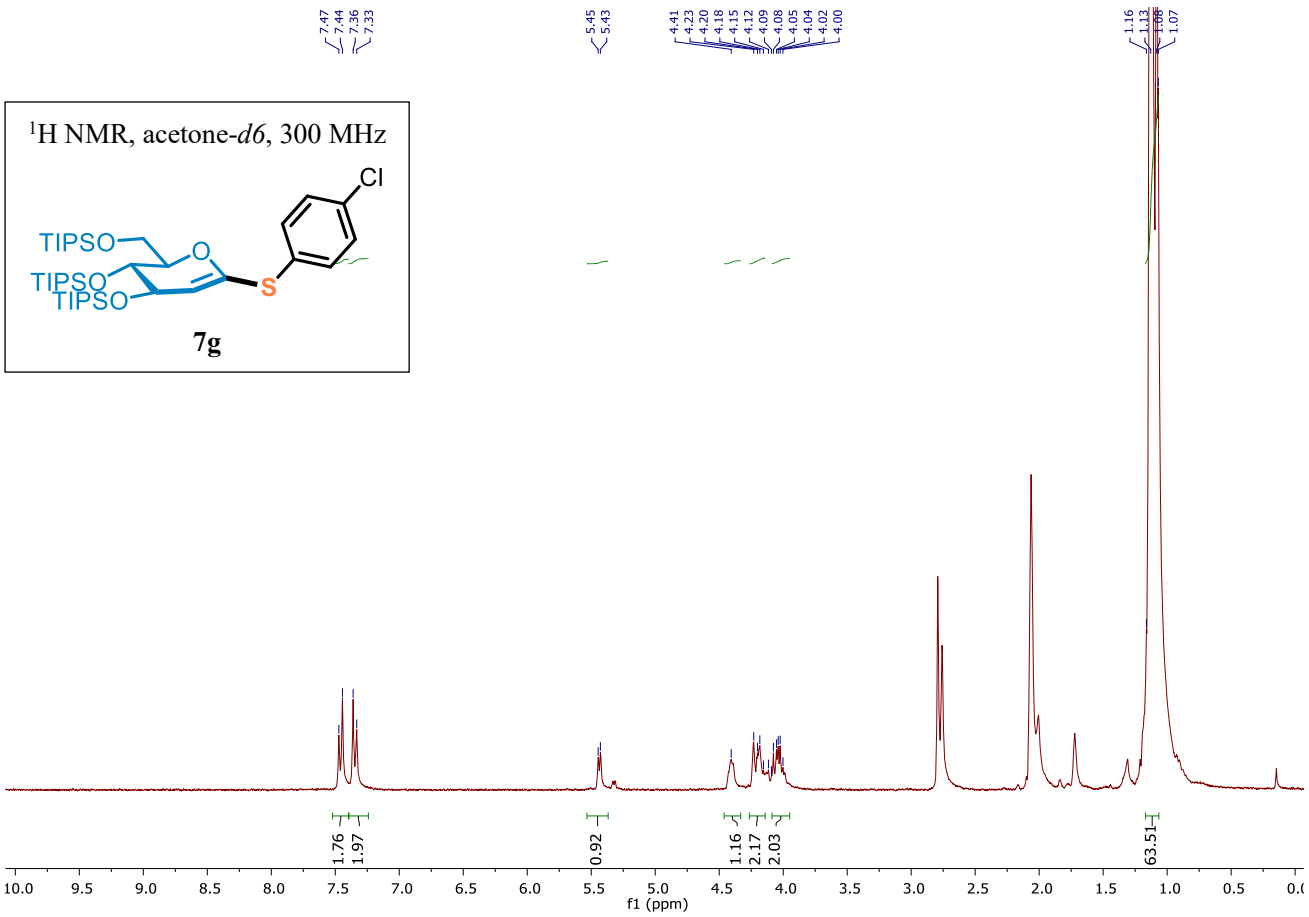


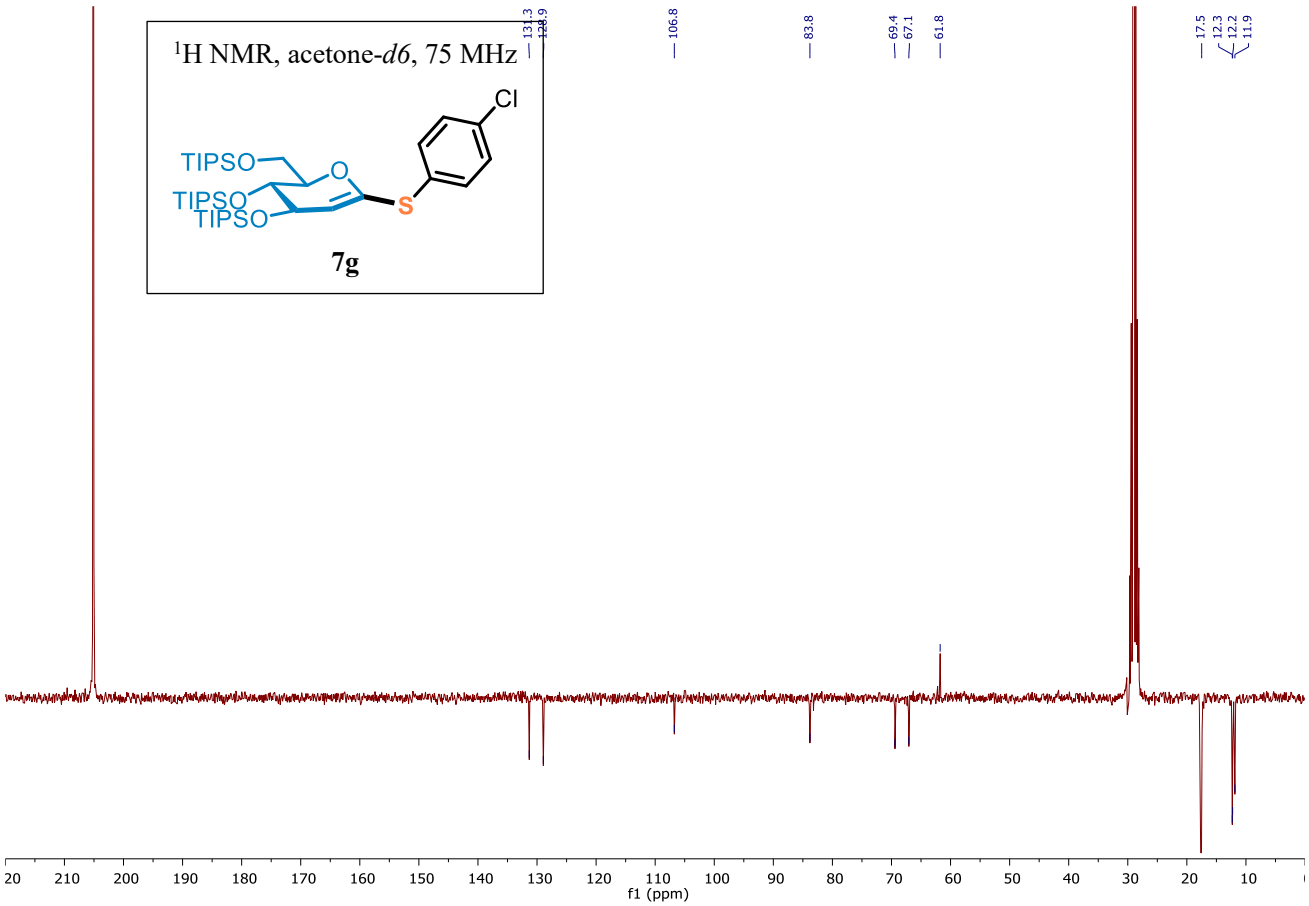
7f

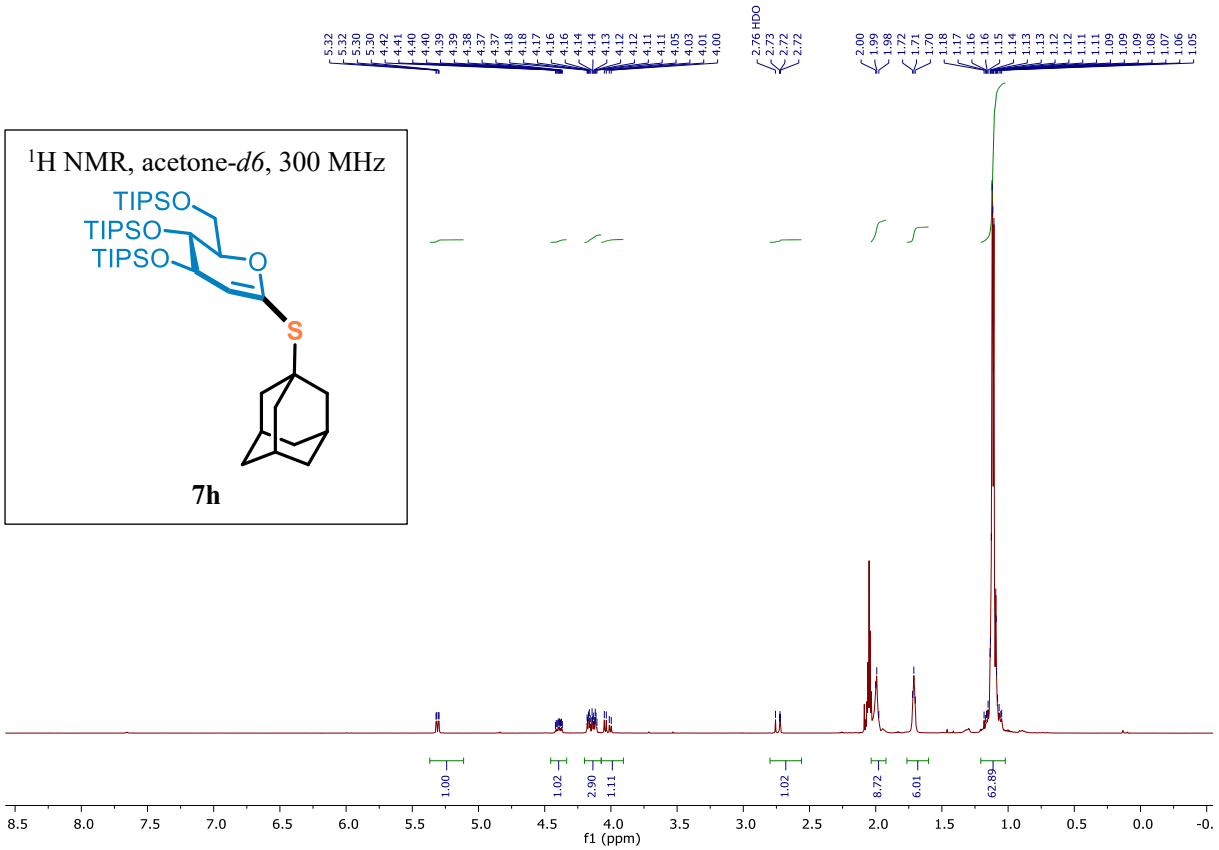
^{1}H NMR, acetone-*d6*, 300 MHz

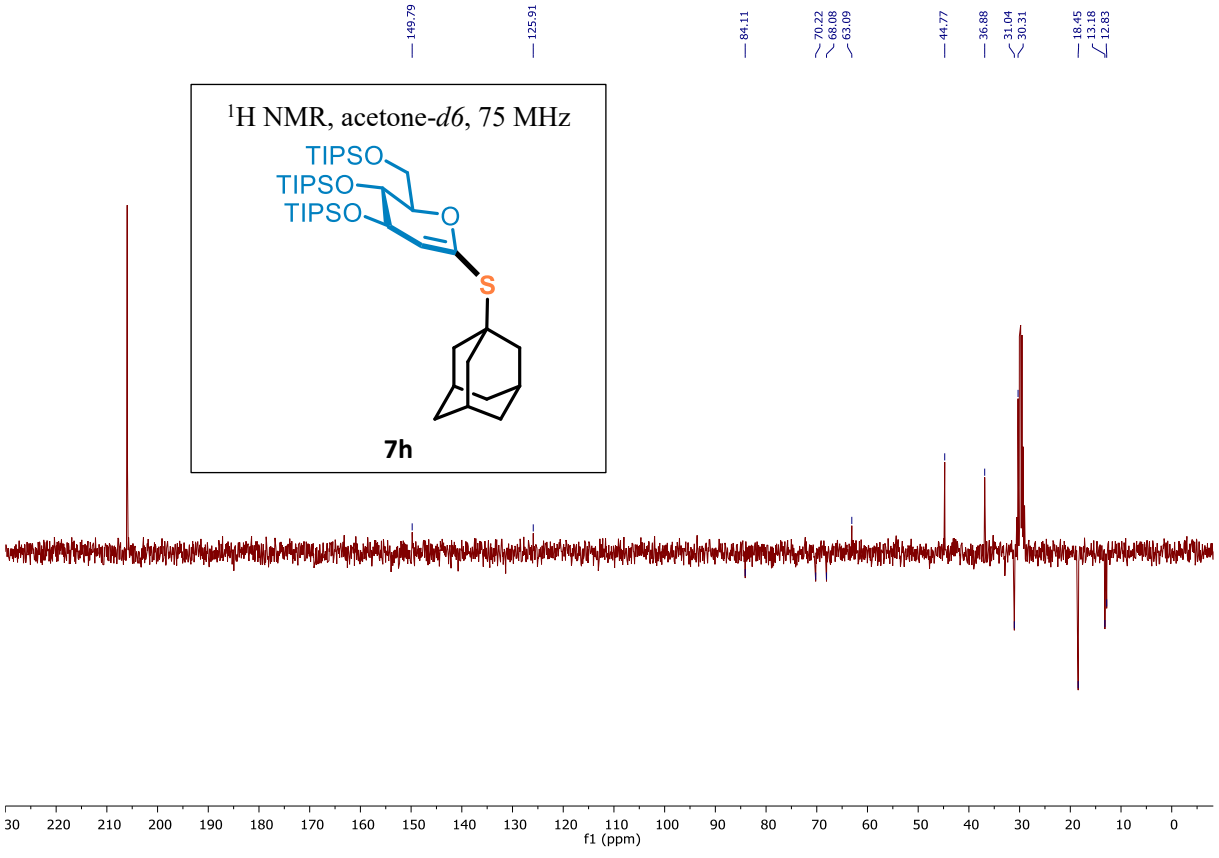


7f


^{1}H NMR, acetone-*d6*, 300 MHz
TIPSO
TIPSO
TIPSO
O
S
Cl
7g
7.47
7.44
7.36
7.33
5.45
5.43
4.41
4.23
4.20
4.18
4.15
4.12
4.09
4.08
4.05
4.04
4.02
4.00
1.16
1.13
1.08
1.07
1.76
1.97
0.92
1.16
2.17
2.03
63.51
f1 (ppm)


^{1}H NMR, acetone-*d6*, 75 MHz
TIPSO
TIPSO
TIPSO
O
S
Cl
7g
131.3
128.9
106.8
83.8
69.4
67.1
61.8
17.5
12.3
12.2
11.9
f1 (ppm)


[1]H NMR, acetone-d6, 300 MHz
TIPSO
TIPSO
TIPSO
O
S
7h
f1 (ppm)


[1]H NMR, acetone-d6, 75 MHz
TIPSO
TIPSO
TIPSO
O
S
7h
f1 (ppm)