Convergent Palladium Catalyzed Stereospecific Arginine Glycosylation Using Glycals

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1 General Information

Air- and moisture-sensitive reactions were carried out in oven-dried glassware sealed with rubber septa under a positive pressure of nitrogen. Reactions were stirred using Teflon coated magnetic stir bars. Organic solutions were concentrated using a rotary evaporator with a desktop vacuum pump. All reagents were purchased from Sigma-Aldrich, Tokyo Chemical Industry, Acros, Alfa Aesar, Chemimpex, and Oakwood Chemicals which were used without further purification. The catalyst $Pd(PPh_3)_4$ was purchased from Strem and $Pd_2(dba)_3 \cdot CHCl_3$ from Ark Pharm, Inc. All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen gas with anhydrous solvents unless otherwise noted. Analytical TLC was performed with 0.25 mm silica gel G plates with a 254 nm fluorescent indicator. The TLC plates were visualized by ultraviolet light and treatment with iodine/silica-gel followed by water washing. Purification of products was accomplished by flash chromatography on silica gel, and the purified compounds showed a single spot by analytical TLC if not special instructions. NMR spectra were recorded at 500 MHz for ^1H and 125 MHz for ^{13}C using $CDCl_3$ (^1H, 7.26 ppm; ^{13}C, 77.16 ppm), CD_3OD (^1H, 3.31 ppm; ^{13}C, 49.00 ppm) and DMSO-d_6 (^1H, 2.50 ppm; ^{13}C, 39.52 ppm) as internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration. High-resolution mass spectra were obtained at the University at Albany-SUNY Core Facility Center using an Agilent 6530B Q-TOF mass spectrometer. Optical rotations were obtained by a PerkinElmer 243 B polarimeter with a sodium lamp and are reported as follows: $[\alpha]_\lambda T$ ℃ (c = g/100 mL solvent).

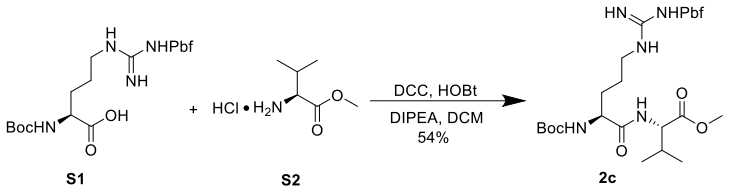
Abbreviations:

Bn = benzyl	Boc = *tert*-butoxycarbonyl	Bz = benzoyl
DCM = dichloromethane	DCC= *N*,*N*'-dicyclohexylcarbodiimide	EA = ethyl acetate
DIPEA = *N*,*N*-Diisopropylethylamine	dba = dibenzylideneacetone	TBS = *tert*-butyldimethylsilyl
Fmoc = fluorenylmethoxycarbonyl	HOBt = hydroxybenzotriazole	TBDPS = *tert*-butyldiphenylsilyl
NMO = *N*-Methylmorpholine *N*-oxide	Ts = 4-toluenesulfonyl	TIPS = triisopropylsilyl
Pbf = 2,2,4,6,7-pentamethyldihydrobenzofuran-5-sulfonyl		TFA = trifluoroacetic acid
Xantphos = (9,9-dimethyl-9*H*-xanthene-4,5-diyl)bis(diphenylphosphane)		Mp = melting point

2 Experimental Procedures

2.1 Substrate syntheses

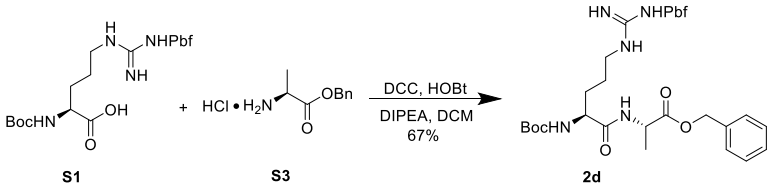
Substrate (2c)



To a solution of **S1** (526.9 mg, 1.0 mmol), **S2** (167.5 mg, 1.0 mmol), HOBt (162.2 mg, 1.2 mmol) and DCC (248.0 mg, 1.2 mmol) in DCM (50 mL) was added DIPEA (0.2 mL, 1.2 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexane/EA 1:1 then 1:1.5) to give **2c** (347.9 mg, 54% yield) as a white solid.

2c: Mp = 95−97 ℃. TLC Rf (Hexane/EA 1:3) = 0.23. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.06 (s, 1H), 6.28 (s, 2H), 6.14 (brs, 1H), 5.57 (s, 1H), 4.41 (dd, J = 8.0, 5.5 Hz, 1H), 4.18 (s, 1H), 3.70 (s, 3H), 3.22 (s, 2H), 2.94 (s, 2H), 2.57 (s, 3H), 2.50 (s, 3H), 2.20-2.10 (m, 1H), 2.08 (s, 3H), 1.90-1.80 (m, 1H), 1.72-1.63 (m, 1H), 1.62-1.55 (m, 1H), 1.45 (s, 6H), 1.41 (s, 9H), 0.90 (d, J = 8.0 Hz, 3H), 0.89 (d, J = 8.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.7, 172.6, 158.9, 156.4, 156.1, 138.5, 133.0, 132.4, 124.7, 117.6, 86.5, 80.2, 57.8, 54.0, 52.3, 43.4, 40.8, 30.8, 29.7, 28.7, 28.4, 25.4, 19.4, 19.1, 18.1, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{50}N_5O_8S$ 640.3375; Found 640.3370. $[\alpha]_D^{20}$: − 9.5° (c 0.4, CH_3OH).

Substrate (2d)

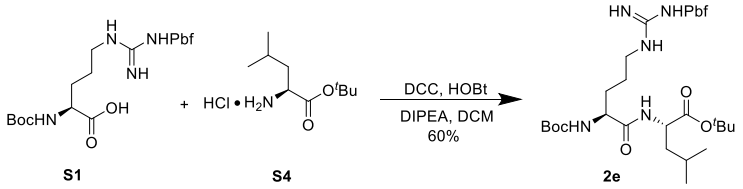


To a solution of **S1** (526.4 mg, 1.0 mmol), **S3** (215.1 mg, 1.0 mmol), HOBt (162.1 mg, 1.2 mmol) and DCC (247.9 mg, 1.2 mmol) in DCM (50 mL) was added DIPEA (0.2 mL, 1.2 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered,

concentrated and purified by column chromatography (Hexane/EA 1:1, 1:1.5 then 1:2) to give **2d** (460.6 mg, 67% yield) as a white solid.

2d: Mp = 80−83 ℃. TLC R_f (Hexane/EA 1:3) = 0.25. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.39-7.27 (s, 5H), 6.27 (s, 2H), 6.11 (brs, 1H), 5.55 (brs, 1H), 5.15 (d, J = 12.3 Hz, 1H), 5.08 (d, J = 12.3 Hz, 1H), 4.60-4.47 (m, 1H), 4.29 (s, 1H), 3.19 (s, 2H), 2.94 (s, 2H), 2.57 (s, 3H), 2.51 (s, 3H), 2.08 (s, 3H), 1.88-1.77 (m, 1H), 1.66-1.54 (m, 3H), 1.45 (s, 6H), 1.40 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.1, 172.5, 158.9, 156.5, 156.1, 138.6, 135.5, 132.8, 132.5, 128.7, 128.5, 128.2, 124.8, 117.7, 86.5, 80.0, 67.2, 53.5, 48.5, 43.4, 40.6, 30.6, 28.7, 28.5, 25.3, 19.5, 18.1, 17.4, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{50}N_5O_8S$ 688.3375; Found 688.3368. $[\alpha]_D^{20}$: − 14.8° (c 0.21, CH_3OH).

Substrate (2e)

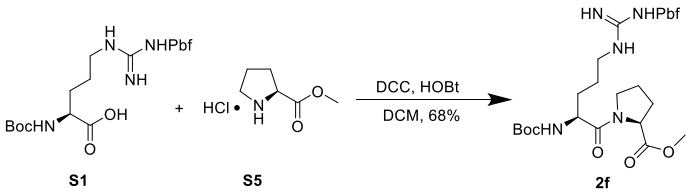


S1 S4 2e

To a solution of **S1** (525.9 mg, 1.0 mmol), **S4** (223.6 mg, 1.0 mmol), HOBt (162.4 mg, 1.2 mmol) and DCC (248.6 mg, 1.2 mmol) in DCM (50 mL) was added DIPEA (0.2 mL, 1.2 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexane/EA 1:1 then 1:2) to give **2e** (416.3 mg, 60% yield) as a white solid.

2e: Mp = 89−92 ℃. TLC R_f (Hexane/EA 1:3) = 0.49. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99 (s, 1H), 6.28 (s, 2H), 6.13 (brs, 1H), 5.48 (s, 1H), 4.37 (dd, J = 7.0, 6.5 Hz, 1H), 4.21 (s, 1H), 3.24 (s, 2H), 2.95 (s, 2H), 2.57 (s, 3H), 2.51 (s, 3H), 2.08 (s, 3H), 1.94-1.82 (m, 1H), 1.74-1.50 (m, 6H), 1.45 (s, 6H), 1.42 (s, 9H), 1.40 (s, 9H), 0.88 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ172.4, 172.3, 158.9, 156.4, 156.0, 138.5, 133.1, 132.4, 124.7, 117.6, 86.5, 82.0, 80.0, 53.5, 51.8, 43.4, 40.9, 34.0, 30.3, 28.7, 28.5, 28.1, 25.7, 25.1, 24.9, 22.9, 21.9, 19.4, 18.1, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{58}N_5O_8S$ 696.4001; Found 696.3992. $[\alpha]_D^{20}$: − 15.6° (c 0.4, CH_3OH).

Substrate (2f)

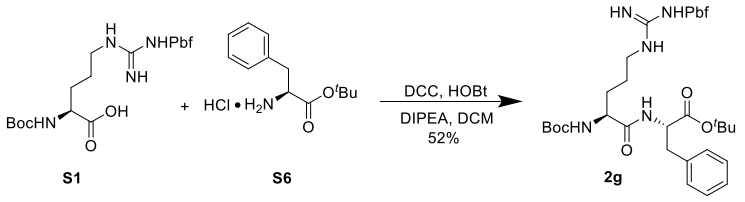


S1 S5 2f

To a solution of **S1** (525.9 mg, 1.0 mmol), **S5** (163.2 mg, 1.0 mmol), HOBt (162.8 mg, 1.2 mmol) and DCC (248.6 mg, 1.2 mmol) in DCM (50 mL) was added DIPEA (0.2 mL, 1.2 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexane/EA 1:1, 1:3, 1:4 then 1:5) to give **2f** (430.6 mg, 68% yield) as a white solid.

2f: Mp = 98−101 ℃. TLC R_f (DCM/MeOH 8:1) = 0.60. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.14 (s, 2H), 6.01 (brs, 1H), 5.52 (d, J = 8.0 Hz, 1H), 4.50 (dd, J = 8.5, 4.5 Hz, 1H), 4.48-4.39 (m, 1H), 3.70 (s, 3H), 3.69 -3.65 (m, 1H), 3.62-3.53 (m, 1H), 3.33-3.13 (m, 2H), 2.94 (s, 2H), 2.59 (s, 3H), 2.51 (s, 3H), 2.26-2.17 (m, 1H), 2.08 (s, 3H), 2.06-1.93 (m, 3H), 1.89-1.78 (m, 2H), 1.67-1.58 (m, 2H), 1.45 (s, 6H), 1.40 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.2, 171.0, 158.7, 156.3, 156.0, 138.5, 133.3, 132.4, 124.6, 117.5, 86.4, 80.2, 59.0, 52.7, 51.3, 47.2, 43.4, 40.9, 29.7, 29.1, 28.7, 28.5, 25.1, 24.1, 22.4, 19.4, 18.0, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{48}N_5O_8S$ 638.3218; Found 638.3210. $[\alpha]_D^{20}$: − 31.8° (c 0.22, CH_3OH).

Substrate (2g)



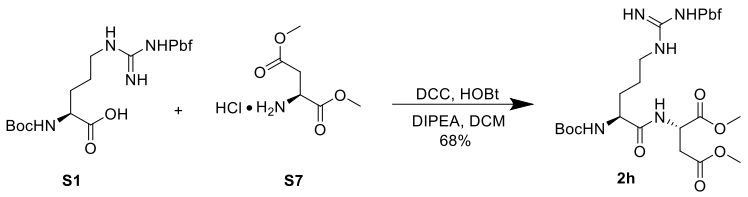
S1 S6 2g

To a solution of **S1** (264.5 mg, 0.5 mmol), **S6** (128.1 mg, 0.5 mmol), HOBt (80.9 mg, 0.6 mmol) and DCC (123.4 mg, 0.6 mmol) in DCM (25 mL) was added DIPEA (0.1 mL, 0.6 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexanes/EA 1:1, 1:1.2 then 1:1.5) to give **2g** (188.7 mg, 52% yield) as a white solid.

2g: Mp = 89−92 ℃. TLC R_f (Hexane/EA 1:2) = 0.29. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 (dd, J = 7.0 Hz, 2H), 7.19 (d, J = 6.5 Hz, 1H), 7.13 (d, J = 7.5 Hz, 2H), 6.97 (brs, 1H), 6.23 (s, 2H), 6.12 (brs, 1H), 5.42 (s, 1H), 4.64 (dd, J = 13.5, 6.5 Hz, 1H), 4.12 (s, 1H), 3.20 (s, 2H), 3.10-2.98 (m, 2H), 2.94 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.08 (s, 3H), 1.86-1.74 (m, 1H), 1.67-1.49 (m, 3H), 1.45 (s, 6H), 1.40 (s, 9H), 1.36 (s, 9H), 0.88 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.0, 170.9, 158.9, 156.4, 155.9, 138.5, 136.4, 133.1, 132.5, 129.5, 128.5, 127.0, 124.7, 117.6, 86.5, 82.5, 80.2, 54.1, 53.9, 43.4,

40.8, 37.9, 30.2, 28.7, 28.4, 28.0, 25.2, 19.4, 18.1, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{37}H_{56}N_5O_8S$ 730.3844; Found 730.3842. $[\alpha]_D^{20}$: − 4.7° (*c* 0.87, CH_3OH).

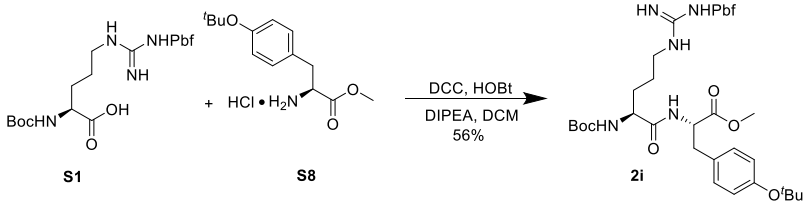
Substrate (2h)



To a solution of **S1** (263.0 mg, 0.5 mmol), **S7** (99.4 mg, 0.5 mmol), HOBt (81.0 mg, 0.6 mmol) and DCC (124.7 mg, 0.6 mmol) in DCM (25 mL) was added DIPEA (0.1 mL, 0.6 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexanes/EA 1:1.5, 1:2 then 1:3) to give **2h** (226.5 mg, 68% yield) as a white solid.

2h: Mp = 78−80 ℃. TLC R_f (Hexane/EA 1:3) = 0.14. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 (s, 1H), 6.28 (s, 2H), 6.11 (brs, 1H), 5.52 (s, 1H), 4.85 (s, 1H), 4.22 (s, 1H), 3.71 (s, 3H), 3.66 (s, 3H), 3.38-3.14 (m, 2H), 3.02-2.90 (m, 1H), 2.95 (s, 2H), 2.86 (d, *J* = 16.5 Hz, 1H), 2.57 (s, 3H), 2.51 (s, 3H), 2.08 (s, 3H), 1.93-1.79 (m, 1H), 1.72-1.55 (m, 3H), 1.45 (s, 6H), 1.40 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4, 171.4, 158.9, 156.5, 155.9, 138.5, 133.0, 132.4, 124.7, 117.6, 86.5, 80.1, 53.8, 53.0, 52.3, 48.8, 43.4, 40.6, 35.9, 30.2, 28.7, 28.4, 25.2, 19.4, 18.1, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{48}N_5O_{10}S$ 670.3116; Found 670.3105. $[\alpha]_D^{20}$: − 4.4° (*c* 0.34, CH_3OH).

Substrate (2i)

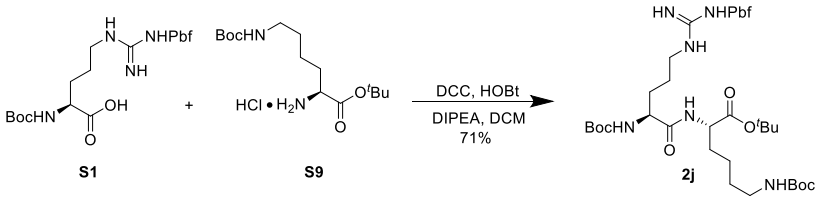


To a solution of **S1** (262.9 mg, 0.5 mmol), **S8** (143.8 mg, 0.5 mmol), HOBt (81.8 mg, 0.6 mmol) and DCC (124.9 mg, 0.6 mmol) in DCM (25 mL) was added DIPEA (0.1 mL, 0.6 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered,

concentrated and purified by column chromatography (Hexanes/EA 1:1.5, 1:2 then 1:3) to give **2i** (211.5 mg, 56% yield) as a white solid.

2i: Mp = 98−99 ℃. TLC R_f (Hexane/EA 1:2) = 0.19. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22-7.06 (m, 1H), 7.02 (d, J = 7.5 Hz, 2H), 6.86 (dd, J = 8.5, 2.0 Hz, 2H), 6.28 (s, 2H), 5.54-5.32 (m, 1H), 4.71 (s, 1H), 4.16 (s, 1H), 3.63 (d, J = 5.0 Hz, 3H), 3.19 (s, 2H), 3.11-3.02 (m, 1H), 3.02-2.96 (m, 1H), 2.94 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.08 (s, 3H), 1.83-1.69 (m, 1H), 1.66-1.54 (m, 1H), 1.55-1.47 (m, 2H), 1.45 (s, 6H), 1.40 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4, 158.9, 156.40, 156.35, 155.9, 154.3, 138.5, 133.0, 132.5, 131.3, 129.8, 124.7, 124.3, 117.6, 86.5, 80.2, 78.7, 53.9, 52.41, 52.39, 43.4, 40.7, 37.1, 30.2, 29.0, 28.7, 28.4, 25.2, 19.4, 18.1, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{38}H_{58}N_5O_9S$ 760.3950; Found 760.3941. $[\alpha]_D^{20}$: − 3.1° (c 0.23, CH_3OH).

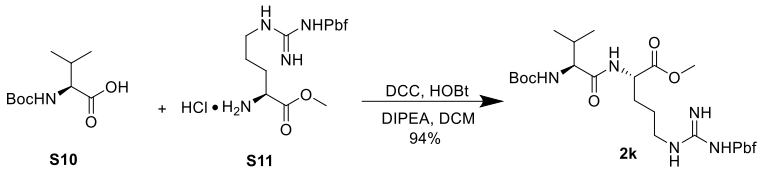
Substrate (2j)



To a solution of **S1** (265.0 mg, 0.5 mmol), **S9** (169.7 mg, 0.5 mmol), HOBt (81.6 mg, 0.6 mmol) and DCC (124.0 mg, 0.6 mmol) in DCM (25 mL) was added DIPEA (0.1 mL, 0.6 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexanes/EA 1:1.5, then 1:2) to give **2j** (288.2 mg, 71% yield) as a white solid.

2j: Mp = 92−94 ℃. TLC R_f (Hexane/EA 1:3) = 0.43. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 (s, 1H), 6.29 (s, 2H), 6.09 (brs, 1H), 5.51 (s, 1H), 4.80 (s, 1H), 4.36 (s, 1H), 4.21 (s, 1H), 3.39-3.14 (m, 2H), 3.05 (d, J = 6.0 Hz, 2H), 2.95 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.09 (s, 3H), 1.92-1.76 (m, 2H), 1.74-1.62 (m, 2H), 1.63-1.52 (m, 2H), 1.50-1.45 (m, 1H), 1.45 (s, 6H), 1.43 (s, 9H), 1.41 (s, 18H), 1.36-1.27 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.3, 171.7, 158.8, 156.43, 156.37, 156.0, 138.5, 133.1, 132.5, 124.7, 117.6, 86.5, 82.2, 80.1, 79.3, 53.8, 53.1, 43.4, 40.7, 40.3, 31.5, 30.3, 29.6, 28.7, 28.6, 28.5, 28.1, 25.3, 22.7, 19.5, 18.1, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{39}H_{67}N_6O_{10}S$ 811.4634; Found 811.4627. $[\alpha]_D^{20}$: − 4.8° (c 0.31, CH_3OH).

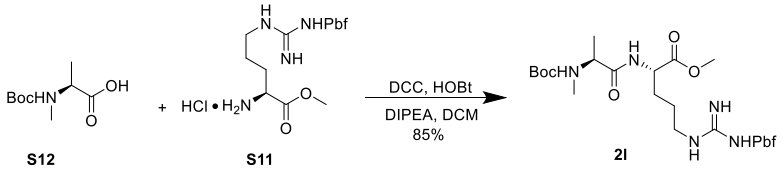
Substrate (2k)



To a solution of **S10** (108.5 mg, 0.5 mmol), **S11** (239.0 mg, 0.5 mmol), HOBt (82.1 mg, 0.6 mmol) and DCC (125.8 mg, 0.6 mmol) in DCM (25 mL) was added DIPEA (0.1 mL, 0.6 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexanes/EA 1:1, 1:1.5 then 1:2) to give **2k** (301.1 mg, 94% yield) as a white solid.

2k: Mp = 80−83 ℃. TLC R_f (Hexane/EA 1:3) = 0.40. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (s, 1H), 6.31 (s, 2H), 6.14 (brs, 1H), 5.41 (brs, 1H), 4.44 (s, 1H), 4.13-3.95 (m, 1H), 3.70 (s, 3H), 3.20 (s, 2H), 2.94 (s, 2H), 2.57 (s, 3H), 2.50 (s, 3H), 2.13-2.04 (m, 1H), 2.08 (s, 3H), 1.91-1.79 (m, 1H), 1.78-1.68 (m, 1H), 1.64-1.49 (m, 2H), 1.45 (s, 6H), 1.39 (s, 9H),0.93 (d, J = 7.0 Hz, 3H), 0.90 (d, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.7, 172.4, 158.8, 156.5, 156.4, 138.5, 133.1, 132.4, 124.7, 117.6, 86.5, 80.1, 59.8, 52.5, 52.3, 43.4, 40.7, 31.2, 29.4, 28.7, 28.5, 25.4, 19.4, 19.2, 18.1, 17.8, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{30}H_{50}N_5O_8S$ 640.3375; Found 640.3374. $[\alpha]_D^{20}$: − 16.5˚ (*c* 0.41, CH_3OH).

Substrate (2l)

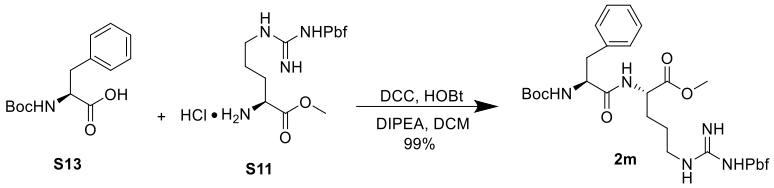


To a solution of **S12** (103.4 mg, 0.5 mmol), **S11** (238.8 mg, 0.5 mmol), HOBt (81.6 mg, 0.6 mmol) and DCC (122.4 mg, 0.59 mmol) in DCM (25 mL) was added DIPEA (0.1 mL, 0.6 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexanes/EA 1:1.5, 1:2 then 1:3) to give **2l** (266.6 mg, 85% yield) as a white solid.

2l: Mp = 72−74 ℃. TLC R_f (Hexane/EA 1:3) = 0.18. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.84 (brs, 1H), 6.21 (s, 2H), 6.16 (brs, 1H), 4.59 (q, J = 7.0 Hz, 1H), 4.51 (s, 1H), 3.72 (s, 3H), 3.40-3.10 (m, 2H), 2.95 (s, 2H), 2.80 (s, 3H), 2.56 (s, 3H), 2.50 (s, 3H), 2.09 (s, 3H), 1.92-1.82 (m, 1H), 1.71-1.61 (m, 1H), 1.58-1.49 (m, 2H), 1.45 (s, 15H), 1.35 (d, J = 7.0 Hz, 3H). ^{13}C

NMR (125 MHz, $CDCl_3$): δ 172.6, 172.4, 158.8, 156.2, 138.5, 133.2, 132.4, 124.7, 117.6, 86.5, 81.0, 52.7, 51.6, 43.4, 40.7, 30.3, 28.7, 28.5, 25.2, 19.4, 18.0, 14.2, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{48}N_5O_8S$ 626.3218; Found 626.3222. $[\alpha]_D^{20}$: − 18.9° (*c* 0.41, CH_3OH).

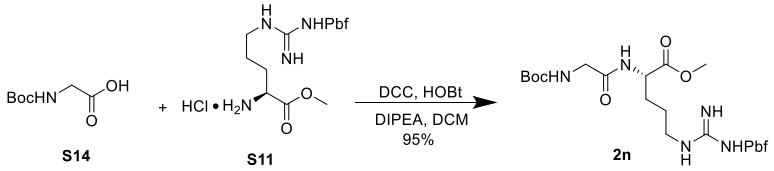
Substrate (2m)



To a solution of **S13** (133.5 mg, 0.5 mmol), **S11** (237.4 mg, 0.5 mmol), HOBt (80.9 mg, 0.6 mmol) and DCC (122.8 mg, 0.6 mmol) in DCM (25 mL) was added DIPEA (0.1 mL, 0.6 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexanes/EA 1:1, 1:1.5 then 1:2) to give **2m** (340.0 mg, 99% yield) as a white solid.

2m: Mp = 88−92 ℃. Mp = 80−83 ℃. TLC R_f (Hexane/EA 1:3) = 0.32. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (brs, 1H), 7.24-7.11 (m, 5H), 6.32 (s, 1H), 6.29 (s, 1H), 6.14 (brs, 1H), 5.62-5.32 (m, 1H), 4.46 (s, 2H), 3.69 (s, 3H), 3.30-3.12 (m, 2H), 3.14 (dd, *J* = 15.0, 5.0 Hz, 1H), 2.94 (s, 2H), 2.88 (dd, *J* = 13.5, 10.0 Hz, 1H), 2.58 (s, 3H), 2.50 (s, 3H), 2.09 (s, 3H), 1.90-1.80 (m, 1H), 1.78-1.68 (m, 1H), 1.63-1.50 (m, 2H), 1.45 (s, 6H), 1.32 (s, 3H), 1.31 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.7, 172.2, 158.9, 156.4, 156.0, 138.5, 136.8, 133.1, 132.4, 129.5, 128.6, 126.9, 124.7, 117.6, 86.5, 80.2, 55.8, 52.6, 52.3, 43.4, 40.8, 38.6, 29.5, 28.7, 28.4, 25.3, 19.4, 18.1, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{34}H_{50}N_5O_8S$ 688.3375; Found 688.3381. $[\alpha]_D^{20}$: − 5.1° (*c* 0.39, CH_3OH).

Substrate (2n)

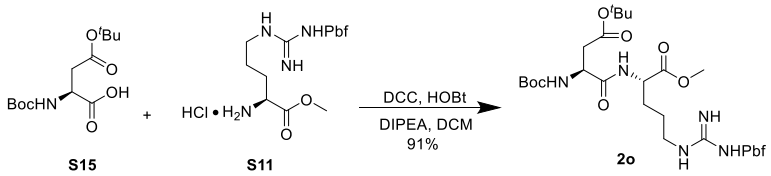


To a solution of **S14** (88.7 mg, 0.5 mmol), **S11** (238.3 mg, 0.5 mmol), HOBt (81.7 mg, 0.6 mmol) and DCC (123.6 mg, 0.6 mmol) in DCM (25 mL) was added DIPEA (0.1 mL, 0.6 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered,

concentrated and purified by column chromatography (Hexanes/EA 1:2, 1:3 then EA) to give **2n** (282.3 mg, 95% yield) as a white solid.

2n: Mp = 88−91 ℃. TLC R_f (EA) = 0.18. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (s, 1H), 6.30 (s, 2H), 6.20 (brs, 1H), 5.64 (s, 1H), 4.52 (s, 1H), 3.87 (dd, J = 17.5, 4.5 Hz, 1H), 3.76 (dd, J = 17.5, 4.5 Hz, 1H), 3.70 (s, 3H), 3.19 (s, 2H), 2.95 (s, 2H), 2.56 (s, 3H), 2.49 (s, 3H), 2.08 (s, 3H), 1.92-1.82 (m, 1H), 1.78-1.66 (m, 1H), 1.62-1.48 (m, 2H), 1.45 (s, 6H), 1.41 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4, 170.3, 158.9, 156.6, 156.4, 138.4, 132.9, 132.4, 124.8, 117.7, 86.5, 80.4, 52.7, 52.1, 44.1, 43.4, 40.7, 29.5, 28.7, 28.4, 25.3, 19.4, 18.1, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{44}N_5O_8S$ 598.2905; Found 598.2898. $[\alpha]_D^{20}$: − 3.5° (c 0.23, CH_3OH).

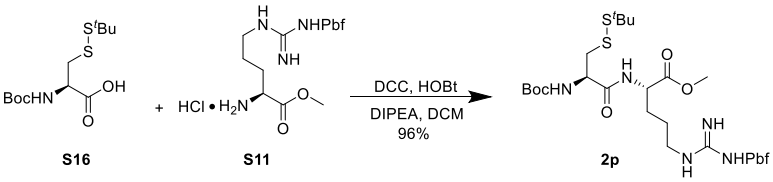
Substrate (2o)



To a solution of **S15** (146.5 mg, 0.5 mmol), **S11** (238.3 mg, 0.5 mmol), HOBt (81.3 mg, 0.6 mmol) and DCC (124.7 mg, 0.6 mmol) in DCM (25 mL) was added DIPEA (0.1 mL, 0.6 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexanes/EA 1:1, 1:2 then1:3) to give **2o** (325.0 mg, 91% yield) as a white solid.

2o: Mp = 83−84 ℃. TLC R_f (Hexane/EA 1:3) = 0.35. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 (d, J = 7.0 Hz, 1H), 6.18 (s, 2H), 6.12 (brs, 1H), 5.80 (s, 1H), 4.60-4.40 (m, 2H), 3.71 (s, 3H), 3.30-3.10 (m, 2H), 2.94 (s, 2H), 2.83 (dd, J = 13.5, 3.5 Hz, 1H), 2.64 (dd, J = 17.0, 6.0 Hz, 1H), 2.56 (s, 3H), 2.50 (s, 3H), 2.08 (s, 3H), 1.92-1.80 (m, 1H), 1.74-1.63 (m, 1H), 1.60-1.50 (m, 2H), 1.45 (s, 6H), 1.43 (s, 9H), 1.41 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.1, 171.7, 171.1, 158.8, 156.2, 155.8, 138.5, 133.2, 132.4, 124.7, 117.5, 86.5, 82.1, 80.7, 52.7, 51.9, 51.0, 43.4, 40.8, 37.4, 30.2, 28.7, 28.4, 28.1, 24.9, 19.4, 18.0, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{33}H_{54}N_5O_{10}S$ 712.3586; Found 712.3578. $[\alpha]_D^{20}$: − 8.4° (c 0.39, CH_3OH).

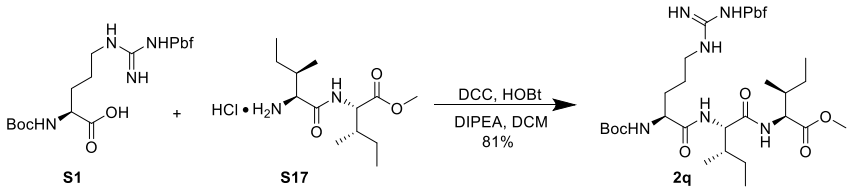
Substrate (2p)



To a solution of **S16** (155.2 mg, 0.5 mmol), **S11** (239.0 mg, 0.5 mmol), HOBt (80.5 mg, 0.6 mmol) and DCC (123.9 mg, 0.6 mmol) in DCM (25 mL) was added DIPEA (0.1 mL, 0.6 mmol). The reaction mixture was stirred for 6 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexanes/EA 1:1, 1:1.2 then 1:1.5) to give **2p** (350.8 mg, 96% yield) as a white solid.

2p: Mp = 87−89 ℃. TLC R_f (Hexane/EA 1:3) = 0.32. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13 (s, 1H), 6.18 (s, 2H), 6.17 (brs, 1H), 5.57 (s, 1H), 4.55 (dd, J = 12.0, 7.5 Hz, 1H), 4.40 (dd, J = 13.5, 6.5 Hz, 1H), 3.74 (s, 3H), 3.32-3.14 (m, 2H), 3.09 (d, J = 5.5 Hz, 2H), 2.95 (s, 2H), 2.57 (s, 3H), 2.51 (s, 3H), 2.09 (s, 3H), 1.95-1.84 (m, 1H), 1.77-1.67 (m, 1H), 1.65-1.52 (m, 2H), 1.46 (s, 6H), 1.44 (s, 9H), 1.32 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.2, 171.2, 158.8, 156.3, 155.9, 138.5, 133.1, 132.4, 124.7, 117.6, 86.5, 80.8, 54.6, 52.7, 52.0, 48.5, 43.4, 42.4, 40.8, 30.0, 28.7, 28.4, 25.2, 24.1, 19.4, 18.1, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{54}N_5O_8S_3$ 732.3129; Found 732.3131. $[\alpha]_D^{20}$: − 47.5˚ (*c* 0.32, CH_3OH).

Substrate (2q)

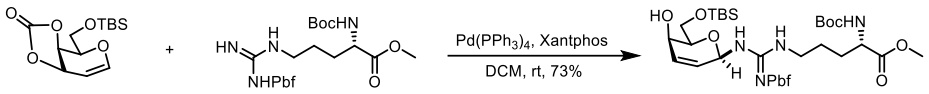


To a solution of **S1** (233.5 mg, 0.44 mmol), **S17** (103.0 mg, 0.35 mmol), HOBt (57.3 mg, 0.42 mmol) and DCC (87.9 mg, 0.43 mmol) in DCM (18 mL) was added DIPEA (0.07 mL, 0.42 mmol). The reaction mixture was stirred for 24 h at ambient temperature. Remove DCM via rotary evaporator, add EA (100 mL), then filter the white precipitate. The filtrate was washed sequentially with saturated sodium carbonate solution, water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexanes/EA 1:1.5, 1:2 then 1:3) to give **2q** (215.9 mg, 81% yield) as a white solid.

2q: Mp = 101−106 ℃. TLC R_f (Hexane/EA 1:3) = 0.29. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (s, 1H), 6.99 (s, 1H), 6.38 (s, 2H), 5.56 (s, 1H), 4.52 (s, 1H), 4.45-4.25 (s, 2H), 3.67 (s, 3H), 3.50-3.05 (m, 2H), 2.95 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.09 (s, 3H), 1.88-1.76 (m, 1H), 1.74-1.50 (m, 10H), 1.45 (s, 6H), 1.41 (s, 9H), .0.87 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.5, 172.7, 158.9, 156.7, 156.0, 138.5, 132.9, 132.4, 124.8, 117.7, 86.5, 80.0, 53.0, 52.4, 50.9, 43.4, 41.1, 40.8, 28.7, 28.5, 25.3, 24.82, 24.75, 22.9, 22.8, 22.1, 21.9, 19.5, 18.1, 17.6, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{37}H_{63}N_6O_9S$ 767.4372; Found 767.4361. $[\alpha]_D^{20}$: − 24.9˚ (*c* 0.25, CH_3OH).

2.2 Glycosylation

Product (3a)

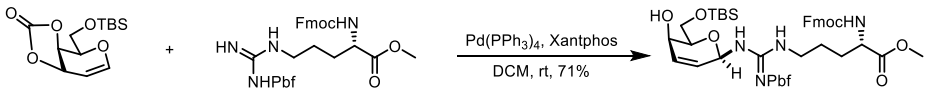


1a **2a** **3a**

To a solution of **1a**[1] (43.6 mg, 0.15 mmol), **2a**[2] (27.7 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.9 mg, 0.005 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1 then 1:1.5) afforded the **3a** (29.1 mg, 73%) as a yellow solid.

3a: Mp = 73−75 ℃. TLC R_f (Hexane/EA 1:2) = 0.50. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 6.26 (s, 1H), 6.13 (s, 1H), 5.75 (d, J = 10.5 Hz, 1H), 5.19 (d, J = 7.5 Hz, 2H), 4.23 (s, 1H), 4.08 (s, 1H), 3.83 (d, J = 4.0 Hz, 2H), 3.71 (s, 3H), 3.67 (t, J = 5.5 Hz, 1H), 3.27 (s, 1H), 3.20-3.11 (m, 1H), 2.95 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.09 (s, 3H), 1.90 (s, 1H), 1.76 (brs, 1H), 1.66-1.49 (m, 3H), 1.45 (s, 6H), 1.42 (s, 9H), 0.88 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.2, 158.7, 155.6, 154.4, 138.5, 133.3, 132.4, 131.3, 129.9, 124.6, 117.5, 86.5, 80.2, 78.9, 76.5, 63.1, 61.7, 53.2, 52.5, 43.3, 40.9, 30.2, 28.7, 28.4, 25.9, 25.0, 19.4, 18.3, 18.1, 12.6, -5.26, -5.32. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{37}H_{63}N_4O_{10}SSi$ 783.4029; Found 783.4021. $[\alpha]_D^{20}$: − 3.2˚ (*c* 0.56, CH_3OH).

Product (3b)



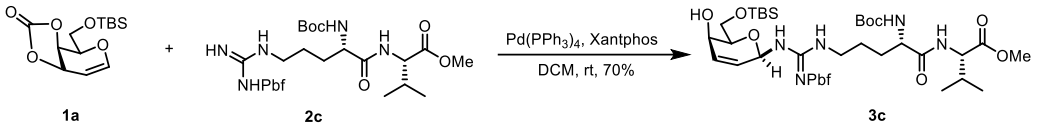
1a **2b** **3b**

To a solution of **1a** (42.9 mg, 0.15 mmol), **2b**[3] (33.1 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1.2 then 1:1.5) afforded the **3b** (32.0 mg, 71%) as a yellow solid.

3b: Mp = 85−87 ℃. TLC R_f (Hexane/EA 1:2) = 0.54. ^{1}H NMR (500 MHz, CD_3OD): δ 7.77 (d, J = 7.5 Hz, 2H), 7.64 (t, J = 7.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 7.5 Hz, 2H), 7.28 (t, J = 7.0 Hz, 2H), 6.16 (dd, J = 8.5, 5.5 Hz, 1H), 5.65 (s, 1H), 4.47-4.29 (m, 2H), 4.20 (t, J = 6.5 Hz, 1H), 4.16-4.04 (m, 1H), 3.89 (d, J = 5.5 Hz, 1H), 3.86-3.72 (m, 2H), 3.68 (s, 3H), 3.26-3.19 (m, 1H), 2.95 (s, 2H), 2.58 (s, 3H), 2.50 (s, 3H), 2.06 (s, 3H), 1.83-1.73 (m, 1H), 1.67-1.49 (m, 3H), 1.41 (s, 6H), 0.89 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (125 MHz, d^6-DMSO): δ 172.7, 157.6, 156.1, 153.8, 143.8, 143.7, 140.7, 137.4, 133.7, 131.5, 127.6, 127.0, 125.2, 124.4, 120.1, 116.4, 86.3, 79.2, 76.9, 65.6, 62.1, 59.5, 53.6, 51.8, 46.7, 42.4, 40.4, 28.2,

28.0, 25.8, 25.6, 19.0, 18.0, 17.6, 12.2, -5.3, -5.4. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{47}H_{65}N_4O_{10}SSi$ 905.4185; Found 905.4189. $[\alpha]_D^{20}$: − 4.8° (*c* 0.58, CH_3OH).

Product (3c)

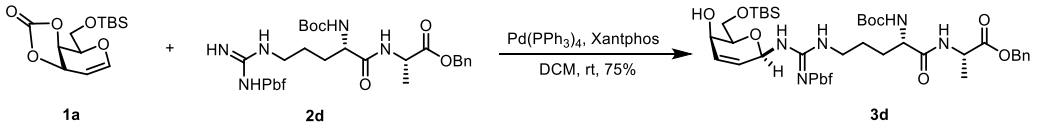


1a 2c 3c

To a solution of **1a** (42.9 mg, 0.15 mmol), **2c** (31.6 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.9 mg, 0.005 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1 then 1:2) afforded the **3c** (30.6 mg, 70%) as a pale yellow solid.

3c: Mp = 63−64 ℃. TLC R_f (Hexane/EA 1:2) = 0.56. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (s, 1H), 6.92 (d, *J* = 7.0 Hz, 1H), 6.45-6.15 (m, 2H), 5.75 (d, *J* = 10.0 Hz, 1H), 5.21 (s, 1H), 5.09 (d, *J* = 8.0 Hz, 1H), 4.48 (dd, *J* = 8.5, 5.0 Hz, 1H), 4.26-4.03 (m, 2H), 3.99-3.79 (m, 3H), 3.72 (s, 3H), 3.68 (t, *J* = 5.5 Hz, 1H), 3.38 (brs, 1H), 3.21-3.04 (m, 1H), 2.95 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.23-2.13 (m, 1H), 2.12 (s, 1H), 2.09 (s, 3H), 1.91-1.81 (m, 2H), 1.64-1.49 (m, 3H), 1.45 (s, 6H), 1.43 (s, 9H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.89 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 175.1, 173.4, 160.0, 157.8, 155.9, 139.5, 134.1, 133.6, 132.9, 129.9, 126.1, 118.5, 87.7, 80.6, 78.9, 78.4, 64.0, 61.8, 59.0, 55.5, 52.6, 44.0, 42.0, 32.0, 30.4, 28.7, 26.8, 26.5, 19.7, 19.5, 19.3, 18.5, 18.4, 12.6, -5.05, -5.13. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{72}N_5O_{11}SSi$ 882.4713; Found 882.4712. $[\alpha]_D^{20}$: − 24.6° (*c* 0.50, CH_3OH).

Product (3d)



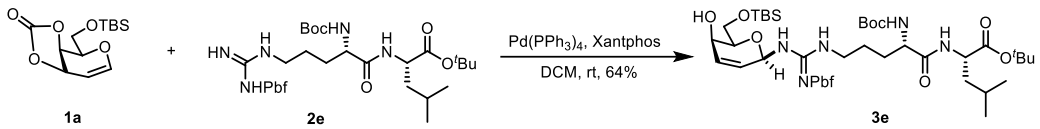
1a 2d 3d

To a solution of **1a** (43.0 mg, 0.15 mmol), **2d** (34.4 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1 then 1:1.2) afforded the **3d** (34.9 mg, 75%) as a while solid.

3d: Mp = 69−72 ℃. TLC R_f (Hexane/EA 1:2) = 0.53. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.38-7.28 (m, 5H), 7.10 (d, *J* = 7.0 Hz, 1H), 6.32-6.15 (m, 2H), 5.71 (d, *J* = 10.0 Hz, 1H), 5.25-5.05 (m, 2H), 5.18 (d, *J* = 12.5 Hz, 1H), 5.13 (d, *J* = 12.5 Hz, 1H), 4.61-4.51 (m, 1H), 4.10 (s, 2H), 3.85 (d, *J* = 4.0 Hz, 2H), 3.80 (brs, 1H), 3.67 (t, *J* = 6.0 Hz, 1H), 3.31 (s, 1H), 3.20 (s, 1H), 2.95 (s, 2H), 2.58 (s, 3H), 2.52 (s, 3H), 2.09 (s, 3H), 1.92-1.78 (m, 2H), 1.62-1.50 (m, 2H), 1.45 (s, 6H), 1.42

(d, *J* = 6.5 Hz, 3H), 1.41 (s, 9H), 0.88 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.7, 173.8, 160.0, 157.7, 155.9, 139.5, 137.2, 134.1, 133.6, 129.6, 129.4, 129.3, 126.1, 118.5, 87.7, 80.6, 79.0, 78.4, 68.0, 64.1, 61.8, 55.2, 49.6, 44.0, 41.9, 30.8 28.7, 26.7, 26.5, 23.2, 19.7, 19.3, 18.5, 17.4, 12.6, -5.05, -5.12. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{46}H_{72}N_5O_{11}SSi$ 930.4713; Found 930.4715. $[\alpha]_D^{20}$: − 10.0˚ (*c* 0.30, CH_3OH).

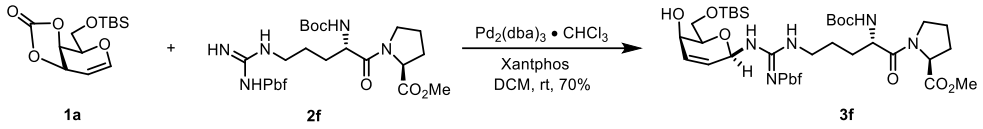
Product (3e)



To a solution of **1a** (43.1 mg, 0.15 mmol), **2e** (34.4 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and Xantphos (3.0 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1) afforded the **3e** (29.9 mg, 64%) as a yellow solid.

3e: Mp = 76−78 ℃. TLC R_f (Hexane/EA 1:2) = 0.61. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (s, 1H), 6.77 (s, 1H), 6.27 (s, 2H), 5.72 (d, *J* = 10.0 Hz, 1H), 5.20 (s, 1H), 5.08 (d, *J* = 7.0 Hz, 1H), 4.40 (d, *J* = 4.5 Hz, 1H), 4.25-3.94 (m, 3H), 3.90-3.77 (m, 2H), 3.67 (t, *J* = 5.5 Hz, 1H), 3.37 (brs, 1H), 3.22-3.04 (m, 1H), 2.94 (s, 2H), 2.57 (s, 3H), 2.51 (s, 3H), 2.08 (s, 3H), 1.93-1.81 (m, 1H), 1.71-1.55 (m, 3H), 1.55-1.46 (m, 3H), 1.45 (s, 6H), 1.44 (s, 9H), 1.41 (s, 9H), 0.91 (t, *J* = 6.5 Hz, 6H), 0.88 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4, 172.1, 158.7, 155.8, 154.2, 138.5, 133.5, 132.4, 131.3, 130.0, 124.5, 117.4, 86.4, 82.1, 80.2, 79.0, 62.9, 61.2, 53.6, 51.6, 43.3, 41.5, 40.2, 29.4, 28.7, 28.4, 28.1, 26.0, 24.9, 23.0, 22.0, 19.4, 18.4, 18.1, 12.6, -5.2, -5.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{46}H_{80}N_5O_{11}SSi$ 938.5339; Found 938.5346. $[\alpha]_D^{20}$: − 13.2˚ (*c* 0.63, CH_3OH).

Product (3f)

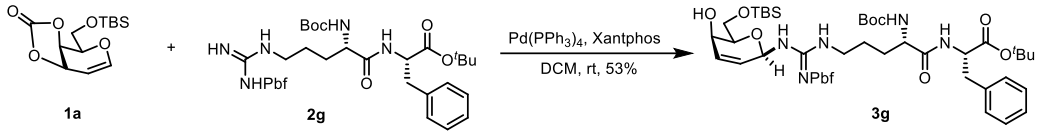


To a solution of **1a** (43.0 mg, 0.15 mmol), **2f** (31.9 mg, 0.05 mmol), $Pd_2(dba)_3 \bullet CHCl_3$ (2.7 mg, 0.0026 mmol) and Xantphos (3.0 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 24 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1, 1:2 then 1:3) afforded the **3f** (30.9 mg, 70%) as a white solid.

3f: Mp = 80−83 ℃. TLC R_f (Hexane/EA 1:3) = 0.35. ^{1}H NMR (500 MHz, CD_3OD): δ 6.21 (s, 1H), 5.67 (s, 1H), 4.45 (dd, *J* = 8.5, 5.0 Hz, 1H), 4.26 (s, 1H), 3.92 (d, *J* = 5.5 Hz, 1H), 3.84 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.80-3.62 (m, 3H), 3.68 (s, 3H),

3.53 (brs, 1H), 3.26-3.13 (m,1H), 3.08-2.94 (m, 2H), 2.59 (s, 3H), 2.52 (s, 3H), 2.32-2.16 (m, 1H), 2.09 (s, 3H), 2.04-1.87 (m, 3H), 1.82-1.53 (m, 4H), 1.46 (s, 6H), 1.43 (s, 9H), 0.91 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.0, 173.3, 160.0, 157.8, 155.9, 139.4, 134.2, 133.6, 133.1, 129.8, 126.1, 118.5, 87.8, 80.6, 78.9, 78.4, 64.0, 61.8, 60.4, 53.1, 52.7, 48.3, 43.9, 42.0, 30.0, 29.8, 28.7, 26.5, 26.2, 26.0, 19.7, 19.3, 18.5, 12.6, -5.07, -5.14. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{70}N_5O_{11}SSi$ 880.4556; Found 880.4574. $[\alpha]_D^{20}$: − 18.0° (*c* 0.36, CH_3OH).

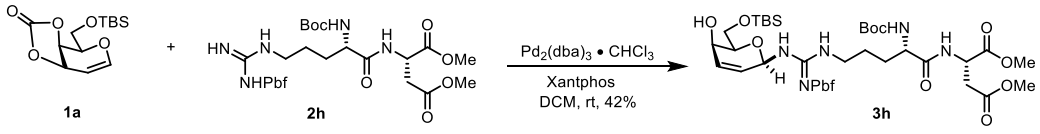
Product (3g)



To a solution of **1a** (42.9 mg, 0.15 mmol), **2g** (36.4 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1) afforded the **3g** (25.9 mg, 53%) as a white solid.

3g: Mp = 78−81 ℃. TLC R_f (Hexane/EA 1:1) = 0.33. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.31-7.19 (m, 4H), 7.10 (d, *J* = 7.0 Hz, 2H), 6.83 (s, 1H), 6.38-6.26 (m, 1H), 6.23 (dd, *J* = 8.5, 5.5 Hz, 1H), 5.72 (d, *J* = 10.0 Hz, 1H), 5.20 (s, 1H), 4.98 (s, 1H), 4.68 (dd, *J* = 13.0, 6.5 Hz, 1H), 4.16-3.98 (m, 2H), 3.92-3.78 (m, 2H), 3.67 (t, *J* = 5.5 Hz, 1H), 3.37 (s, 1H), 3.18-2.98 (m, 3H), 2.95 (s, 2H), 2.59 (s, 3H), 2.52 (s, 3H), 2.09 (s, 3H), 1.95-1.70 (m, 2H), 1.66-1.48 (m, 2H), 1.46 (s, 6H), 1.42 (s, 9H), 1.39 (s, 9H), 0.90 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.6, 171.9, 160.0, 157.7, 155.9, 139.5, 138.0, 134.1, 133.6, 130.5, 129.4, 127.9, 126.1, 118.5, 96.6, 87.7, 83.1, 80.7, 79.0, 78.4, 64.1, 61.8, 55.6, 44.0, 41.9, 38.6, 30.6, 28.7, 28.2, 26.8, 26.5, 23.2, 19.7, 19.3, 18.5, 12.6, -5.05, -5.13. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{49}H_{78}N_5O_{11}SSi$ 972.5182; Found 972.5182. $[\alpha]_D^{20}$: − 5.7° (*c* 0.32, CH_3OH).

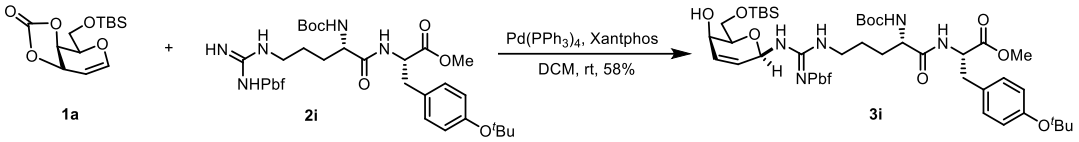
Product (3h)



To a solution of **1a** (42.8 mg, 0.15 mmol), **2h** (33.5 mg, 0.05 mmol), $Pd_2(dba)_3 \bullet CHCl_3$ (2.6 mg, 0.0025 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 24 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1.5, 1:2 then 1:2.5) afforded the **3h** (19.1 mg, 42%) as a pale yellow solid.

3h: Mp = 65−66 ℃. Mp = 83−84 ℃. TLC R_f (Hexane/EA 1:3) = 0.33. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.29 (d, J = 7.5 Hz, 1H), 6.32 (s, 1H), 6.29-6.17 (m, 1H), 5.76 (d, J = 10.5 Hz, 1H), 5.21 (s, 1H), 5.13 (d, J = 7.5 Hz, 1H), 4.91-4.78 (m, 1H), 4.15 (s, 1H), 4.11 (s, 1H), 3.85 (d, J = 5.0 Hz, 2H), 3.74 (s, 3H), 3.71-3.65 (m, 1H), 3.68 (s, 3H), 3.34 (s, 1H), 3.22-3.12 (m, 1H), 3.00 (dd, J = 17.0, 5.0 Hz, 1H), 2.95 (s, 2H), 2.84 (dd, J = 17.0, 5.0 Hz, 1H), 2.58 (s, 3H), 2.51 (s, 3H), 2.12 (s, 1H), 2.09 (s, 3H), 1.92-1.82 (m, 1H), 1.63-1.48 (m, 3H), 1.45 (s, 6H), 1.42 (s, 9H), 0.89 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 172.5, 172.4, 160.0, 157.7, 156.0, 139.5, 134.1, 133.6, 126.1, 118.5, 87.7, 80.7, 79.0, 78.4, 64.1, 61.8, 55.5, 53.1, 52.5, 50.1, 43.9, 41.8, 36.7, 30.5, 28.7, 26.8, 26.5, 19.7, 19.3, 18.5, 12.6, -5.1, -5.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{70}N_5O_{13}SSi$ 912.4455; Found 912.4456. $[\alpha]_D^{20}$: − 12.4˚ (*c* 0.31, CH_3OH).

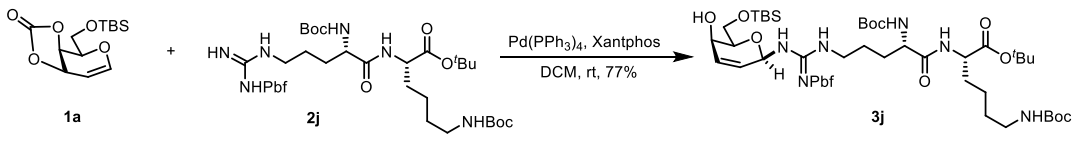
Product (3i)



To a solution of **1a** (43.0 mg, 0.15 mmol), **2i** (38.0 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.7 mg, 0.005 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1.2 then 1:1.5) afforded the **3i** (29.1 mg, 58%) as a yellow solid.

3i: Mp = 85−88 ℃. TLC R_f (Hexane/EA 1:3) = 0.53. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.00 (d, J = 7.0 Hz, 2H), 6.94-6.85 (m, 1H), 6.89 (d, J = 8.0 Hz, 2H), 6.32-6.16 (m, 2H), 5.73 (d, J = 10.0 Hz, 1H), 5.28-5.13 (m, 1H), 5.02 (d, J = 6.5 Hz, 1H), 4.77 (dd, J = 13.5, 6.5 Hz, 1H), 4.16-3.90 (m, 3H), 3.85 (d, J = 5.0 Hz, 1H), 3.67 (s, 3H), 3.35 (brs, 1H), 3.19-2.99 (m, 3H), 2.94 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.11 (s, 1H), 2.09 (s, 3H), 1.92-1.78 (m, 1H), 1.64-1.48 (m, 2H), 1.45 (s, 7H), 1.41 (s, 9H), 1.31 (s, 9H), 0.89 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 173.3, 171.8, 158.6, 156.3, 154.5, 154.1, 138.1, 132.7, 132.2, 131.6, 129.5, 124.7, 123.8, 117.1, 86.3, 79.3, 78.1, 77.6, 77.0, 62.7, 60.4, 54.2, 53.7, 51.3, 42.6, 40.5, 36.4, 29.2, 27.9, 27.38, 27.35, 25.4, 25.1, 18.3, 17.9, 17.1, 11.2, -6.4, -6.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{50}H_{80}N_5O_{12}SSi$ 1002.5288; Found 1002.5299. $[\alpha]_D^{20}$: − 14.8˚ (*c* 0.49, CH_3OH).

Product (3j)

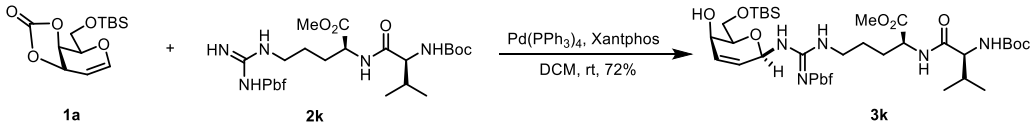


To a solution of **1a** (43.1 mg, 0.15 mmol), **2j** (40.4 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.7 mg, 0.005 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room

temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1.2 then 1:1.5) afforded the **3j** (40.7 mg, 77%) as a white solid.

3j: Mp = 87−91 ℃. TLC R_f (Hexane/EA 1:2) = 0.42. ^{1}H NMR (500 MHz, CD_3OD): δ 6.52 (s, 1H), 6.30-6.13 (m, 1H), 5.65 (s, 1H), 5.34 (brs, 1H), 4.32-4.19 (m, 1H), 4.14-3.99 (m, 1H), 3.92 (d, J = 5.0 Hz, 1H), 3.84 (dd, J = 10.5, 5.5 Hz, 1H), 3.79 (s, 1H), 3.73-3.63 (m, 1H), 3.36-3.24 (m, 2H), 3.24-3.13 (m, 1H), 3.03 (dd, J = 12.5, 6.0 Hz, 2H), 3.01 (s, 2H), 2.58 (s, 3H), 2.52 (s, 3H), 2.09 (s, 3H), 1.86-1.73 (m, 2H), 1.73-1.53 (m, 4H), 1.49-1.39 (m, 37H), 0.91 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.8, 172.6, 159.9, 158.4, 157.7, 155.9, 139.4, 134.1, 133.5, 132.9, 129.9, 126.0, 118.5, 87.7, 82.8, 80.6, 79.8, 78.9, 78.4, 64.1, 61.8, 55.4, 54.3, 44.0, 41.9, 41.1, 32.3, 30.6, 30.4, 28.83, 28.78, 28.76, 28.3, 26.8, 26.5, 23.9, 19.7, 19.3, 18.5, 12.6, -5.0, -5.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{51}H_{89}N_6O_{13}SSi$ 1053.5972; Found1053.5985. $[\alpha]_D^{20}$: − 6.6° (c 0.74, CH_3OH).

Product (3k)

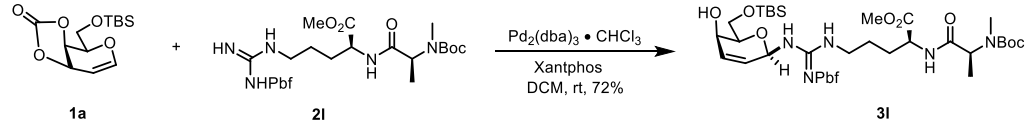


1a **2k** **3k**

To a solution of **1a** (43.0 mg, 0.15 mmol), **2k** (32.0 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1.2 then 1:1.5) afforded the **3k** (31.6 mg, 72%) as a white solid.

3k: Mp = 98−102 ℃. TLC R_f (Hexane/EA 1:2) = 0.34. ^{1}H NMR (500 MHz, CD_3OD): δ 6.52 (d, J = 8.5 Hz, 1H), 6.20 (s, 1H), 5.66 (s, 1H), 4.37 (s, 1H), 3.93 (d, J = 5.0 Hz, 1H), 3.90-3.73 (m, 3H), 3.72-3.62 (m, 1H), 3.67 (s, 3H), 3.29-3.16 (m, 2H), 3.01 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.08 (s, 3H), 2.06-1.95 (m, 1H), 1.87-1.77 (m, 1H), 1.70-1.52 (m, 3H), 1.46 (s, 6H), 1.43 (s, 9H), 0.96 (d, J = 6.5 Hz, 3H), 0.93 (d, J = 6.5 Hz, 3H), 0.91 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.6, 173.5, 159.9, 157.9, 155.9, 139.4, 134.1, 133.5, 132.7, 129.9, 126.0, 118.5, 87.7, 80.5, 79.0, 78.4, 64.1, 61.7, 61.3, 53.4, 52.7, 43.9, 41.8, 32.0, 29.7, 28.7, 26.7, 26.5, 19.73, 19.67, 19.3, 18.6, 18.5, 12.6, -5.06, -5.13. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{42}H_{72}N_5O_{11}SSi$ 882.4713; Found 882.4721. $[\alpha]_D^{20}$: − 8.9° (c 0.80, CH_3OH).

Product (3l)

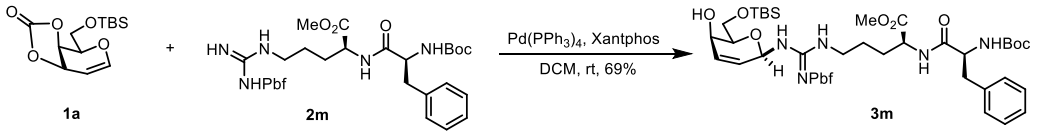


1a **2l** **3l**

To a solution of **1a** (43.0 mg, 0.15 mmol), **2l** (31.3 mg, 0.05 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (2.7 mg, 0.0026 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 24 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1.5, 1:2 then 1:3) afforded the **3l** (31.3 mg, 72%) as a pale yellow solid.

3l: Mp = 67−70 ℃. TLC R_f (Hexane/EA 1:3) = 0.52. ^{1}H NMR (500 MHz, CD_3OD): δ 6.27-6.12 (m, 1H), 5.66 (brs, 1H), 5.44-5.20 (m, 1H), 4.58 (s, 1H), 4.34 (s, 1H), 3.92 (d, J = 5.5 Hz, 1H), 3.84 (dd, J = 10.5, 5.5 Hz, 1H), 3.78 (s, 1H), 3.69 (s, 4H), 3.28-3.16 (m, 2H), 3.01 (s, 2H), 2.84 (s, 3H), 2.57 (s, 3H), 2.51 (s, 3H), 2.09 (s, 3H), 1,91-1.78 (m, 1H), 1.70-1.52 (m, 3H), 1.46 (s, 6H), 1.45 (s, 9H), 1.35 (dd, J = 10.0, 7.0 Hz, 4H), 0.91 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.7, 173.7, 160.0, 157.5, 155.9, 139.4, 134.2, 133.5, 132.9, 129.8, 126.1, 118.5, 99.4, 96.6, 87.7, 81.6, 79.0, 78.5, 64.1, 61.7, 53.5, 52.8, 44.0, 41.8, 31.0, 29.6, 28.7, 27.0, 26.5, 23.2, 19.7, 19.3, 18.5, 12.5, -5.07, -5.14. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{41}H_{70}N_5O_{11}SSi$ 868.4556; Found 868.4564. $[\alpha]_D^{20}$: − 11.8° (c 0.34, CH_3OH).

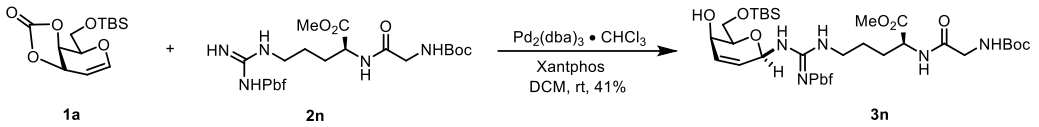
Product (3m)



To a solution of **1a** (43.0 mg, 0.15 mmol), **2m** (34.4 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and Xantphos (2.8 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1 then 1:1.2) afforded the **3m** (32.1 mg, 69%) as a white solid.

3m: Mp = 88−90 ℃. TLC R_f (Hexane/EA 1:3) = 0.52. ^{1}H NMR (500 MHz, CD_3OD): δ 7.31-7.15 (m, 5H), 6.63 (d, J = 8.0 Hz, 1H), 6.28-6.13 (m, 1H), 5.66 (s, 1H), 5.46-5.18 (m, 1H), 4.38 (dd, J = 7.0, 5.0 Hz, 1H), 4.35-4.29 (m, 1H), 3.92 (d, J = 5.5 Hz, 1H), 3.84 (dd, J = 10.5, 6.5 Hz, 1H), 3.83-3.73 (m, 1H), 3.69 (s, 1H), 3.66 (s, 3H), 3.23 (t, J = 6.0 Hz, 2H), 3.09 (dd, J = 14.0, 5.0 Hz, 1H), 3.00 (s, 2H), 2.82 (dd, J = 13.5, 9.5 Hz, 1H), 2.58 (s, 3H), 2.51 (s, 3H), 2.08 (s, 3H), 1.88-1.75 (m, 1H), 1.67-1.59 (m, 1H), 1.58-1.51 (m, 2H), 1.45 (s, 6H), 1.35 (s, 9H), 0.91 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.4, 173.5, 160.0, 157.5, 155.9, 139.4, 138.5, 134.1, 133.5, 130.4, 129.4, 127.7, 126.1, 118.5, 87.7, 80.6, 79.0, 78.5, 64.1, 61.8, 57.2, 53.4, 52.8, 43.9, 41.8, 39.2, 29.9, 28.73, 28.69, 26.6, 26.5, 19.7, 19.3, 18.5, 12.6, -5.06, -5.14. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{46}H_{72}N_5O_{11}SSi$ 930.4713; Found 930.4721. $[\alpha]_D^{20}$: − 3.6° (c 0.44, CH_3OH).

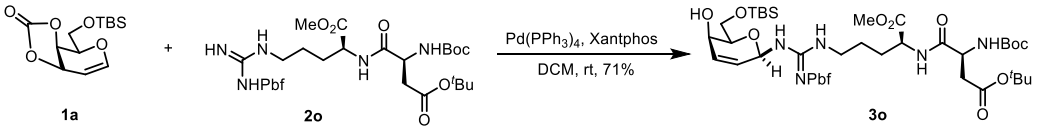
Product (3n)



To a solution of **1a** (43.1 mg, 0.15 mmol), **2n** (29.8 mg, 0.05 mmol), $Pd_2(dba)_3 \bullet CHCl_3$ (2.6 mg, 0.0025 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 24 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1.5, 1:2) afforded the **3n** (17.2 mg, 41%) as a pale yellow solid.

3n: Mp = 74−77 ℃. TLC R_f (Hexane/EA 1:3) = 0.22. ^{1}H NMR (500 MHz, CD_3OD): δ 6.27-6.14 (m, 1H), 5.66 (s, 1H), 4.40 (s, 1H), 3.92 (d, J = 5.5 Hz, 1H), 3.85 (dd, J = 10.0, 6.0 Hz, 1H), 3.82-3.75 (m, 1H), 3.92 (d, J = 5.5 Hz, 2H), 3.69 (s, 4H), 3.23 (t, J = 5.0 Hz, 1H), 3.01 (s, 2H), 2.84 (s, 3H), 2.57 (s, 3H), 2.51 (s, 3H), 2.09 (s, 3H), 1.88-1.76 (m, 1H), 1.70-1.61 (m, 1H), 1.59-1.52 (m, 2H), 1.46 (s, 6H), 1.44 (s, 9H), 0.91 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 173.7, 172.4, 160.0, 158.4, 155.9, 139.4, 134.1, 133.5, 126.1, 118.5, 99.4, 87.8, 80.7, 78.5, 64.1, 61.8, 53.3, 52.8, 44.0, 43.9, 41.8, 29.9, 28.7, 26.4, 21.1, 19.6, 19.3, 18.5, 17.5, 12.5, -5.1, -5.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{39}H_{66}N_5O_{11}SSi$ 840.4243; Found 840.4241. $[\alpha]_D^{20}$: − 8.8° (c 0.24, CH_3OH).

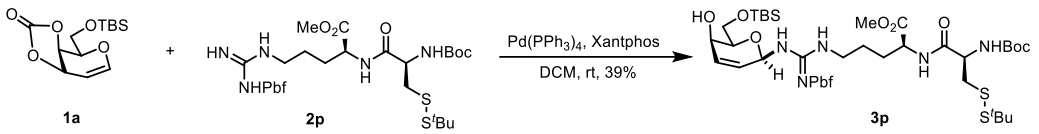
Product (3o)



To a solution of **1a** (43.0 mg, 0.15 mmol), **2o** (35.7 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.9 mg, 0.005 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1 then 1:2) afforded the **3o** (34.1 mg, 71%) as a pale yellow solid.

3o: Mp = 70−74 ℃. TLC R_f (Hexane/EA 1:3) = 0.62. ^{1}H NMR (500 MHz, CD_3OD): δ 6.20 (s, 1H), 5.66 (s, 1H), 5.46-5.20 (m, 1H), 4.44 (t, J = 6.5 Hz, 1H), 4.37 (s, 1H), 3.93 (d, J = 5.0 Hz, 1H), 3.85 (dd, J = 10.5, 5.5 Hz, 1H), 3.83-3.73 (m, 1H), 3.68 (s, 4H), 3.22 (t, J = 6.0 Hz, 2H), 3.01 (s, 2H), 2.73 (dd, J = 16.0, 5.5 Hz, 1H), 2.57 (s, 3H), 2.57-2.52 (m, 1H), 2.51 (s, 3H), 2.09 (s, 3H), 1.89-1.77 (m, 1H), 1.71-1.61 (m, 1H), 1.61-1.51 (m, 2H), 1.46 (s, 6H), 1.45 (s, 9H), 1.44 (s, 9H), 0.91 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 173.6, 173.5, 171.3, 160.0, 157.5, 155.9, 139.4, 134.1, 133.5, 132.9, 129.9, 126.1, 118.5, 87.7, 82.4, 80.8, 79.0, 78.4, 64.1, 61.8, 53.4, 52.8, 52.6, 44.0, 41.8, 38.7, 29.8, 28.7, 28.3, 26.6, 26.5, 26.4, 19.7, 19.3, 18.5, 12.6, -5.06, -5.13. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{45}H_{76}N_5O_{13}SSi$ 954.4924; Found 954.4919. $[\alpha]_D^{20}$: − 5.9° (c 0.44, CH_3OH).

Product (3p)

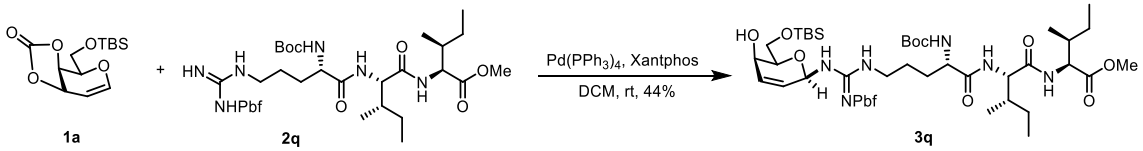


1a 2p 3p

To a solution of **1a** (43.0 mg, 0.15 mmol), **2p** (36.6 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.9 mg, 0.005 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1 then 1:1.2) afforded the **3p** (19.0 mg, 39%) as a yellow solid.

3p: Mp = 76−79 ℃. TLC R_f (Hexane/EA 1:3) = 0.64. ^{1}H NMR (500 MHz, CD_3OD): δ 6.20 (s, 1H), 5.66 (s, 1H), 5.50-5.15 (m, 1H), 4.38 (s, 1H), 4.34 (dd, J = 8.5, 5.0 Hz, 1H), 3.92 (d, J = 5.5 Hz, 1H), 3.85 (dd, J = 10.0, 6.0 Hz, 1H), 3.82-3.74 (m, 1H), 3.69 (s, 4H), 3.22 (t, J = 6.0 Hz, 2H), 3.12 (dd, J = 13.5, 5.0 Hz, 1H), 3.01 (s, 2H), 2.93 (dd, J = 13.0, 9.5 Hz, 1H), 2.57 (s, 3H), 2.51 (s, 3H), 2.09 (s, 3H), 1.90-1.76 (m, 1H), 1.73-1.61 (m, 1H), 1.61-1.51 (m, 2H), 1.46 (s, 6H), 1.44 (s, 9H), 1.34 (s, 9H), 0.91 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 173.4, 173.2, 160.0, 157.6, 155.9, 139.4, 134.1, 133.5, 126.1, 118.5, 87.7, 80.9, 79.0, 78.4, 64.1, 61.8, 55.5, 53.5, 52.8, 44.0, 43.6, 41.8, 30.2, 29.8, 28.8, 26.7, 26.5, 26.4, 19.7, 19.3, 18.5, 12.6, -5.04, -5.12. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{44}H_{76}N_5O_{11}S_3Si$ 974.4467; Found 974.4459. $[\alpha]_D^{20}$: −42.0˚ (*c* 0.35, CH_3OH).

Product (3q)



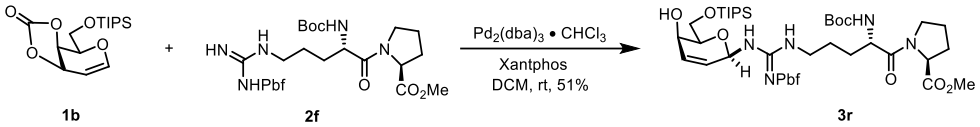
1a 2q 3q

To a solution of **1a** (43.0 mg, 0.15 mmol), **2q** (38.3 mg, 0.05 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1.2 then 1:1.5) afforded the **3q** (22.0 mg, 44%) as a white solid.

3q: Mp = 68−72 ℃. TLC R_f (Hexane/EA 1:3) = 0.51. ^{1}H NMR (500 MHz, CD_3OD): δ 6.29-6.14 (m, 1H), 5.65 (s, 1H), 5.45-5.23 (m, 1H), 4.51-4.38 (m, 2H), 4.02 (t, J = 7.0 Hz, 1H), 3.92 (d, J = 5.0 Hz, 1H), 3.84 (dd, J = 10.0, 5.5 Hz, 1H), 3.79 (s, 1H), 3.69 (s, 4H), 3.27 (brs, 1H), 3.22-3.13 (m, 1H), 3.01 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.09 (s, 3H), 1.77-1.66 (m, 3H), 1.62-1.54 (m, 6H), 1.46 (s, 6H), 1.44 (s, 9H), 0.96 (d, J = 6.5 Hz, 3H), 0.94-0.88 (m, 16H), 0.88 (d, J = 6.5 Hz, 3H). 0.09 (s, 6H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.7, 174.6, 174.4, 160.0, 157.8, 155.9, 139.5, 134.1, 133.6, 126.1, 118.5, 87.7, 80.6, 79.0, 78.4, 64.0, 61.8, 55.5, 52.9, 52.7, 52.1, 44.0, 42.0, 41.4, 30.3, 28.7, 26.8, 26.5, 25.9, 25.7, 23.43,

23.35, 22.2, 21.9, 19.7, 19.3, 18.5, 12.6, -5.05, -5.12. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{49}H_{85}N_6O_{12}SSi$ 1009.5710; Found 1009.5707. $[\alpha]_D^{20}$: − 23.8° (*c* 0.31, CH_3OH).

Product (3r)

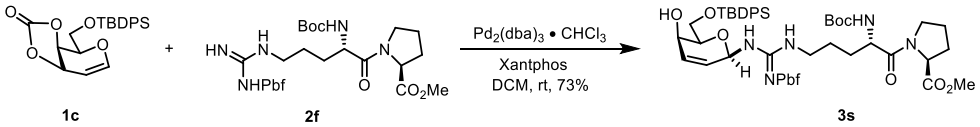


1b **2f** **3r**

To a solution of **1b**[1] (49.9 mg, 0.15 mmol), **2f** (31.9 mg, 0.05 mmol), $Pd_2(dba)_3$ • $CHCl_3$ (2.7 mg, 0.0026 mmol) and Xantphos (3.0 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 24 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1, 1:2) afforded the **3r** (23.6 mg, 51%) as a yellow solid.

3r: Mp = 73−75 ℃. TLC R_f (EA) = 0.69. ^{1}H NMR (500 MHz, CD_3OD): δ 6.22 (s, 1H), 5.68 (s, 1H), 4.45 (dd, *J* = 8.5, 5.0 Hz, 1H), 4.27 (s, 1H), 3.95 (d, *J* = 5.5 Hz, 1H), 3.93 (dd, *J* = 10.0, 6.0 Hz, 1H), 3.87 (s, 1H), 3.78-3.71 (m, 2H), 3.68 (s, 3H), 3.64-3.45 (m,1H), 3.25-3.17 (m, 1H), 3.04 (d, *J* = 15.8 Hz, 1H), 2.99 (d, *J* = 15.8 Hz, 1H), 2.59 (s, 3H), 2.52 (s, 3H), 2.29-2.16 (m, 1H), 2.09 (s, 3H), 2.05-1.88 (m, 3H), 1.75-1.51 (m, 4H), 1.46 (s, 6H), 1.43 (s, 9H), 1.16-1.05 (m, 21H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.0, 173.3, 159.9, 157.8, 155.9, 139.4, 134.2, 133.6, 133.0, 129.8, 126.1, 118.5, 87.7, 80.6, 79.0, 78.5, 64.3, 61.8, 60.4, 53.1, 52.7, 48.2, 43.9, 42.1, 30.0, 29.8, 28.7, 26.2, 26.0, 19.70, 19.67, 18.5, 13.2, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{45}H_{76}N_5O_{11}SSi$ 922.5026; Found 922.5029. $[\alpha]_D^{20}$: − 13.8° (*c* 0.43, CH_3OH).

Product (3s)



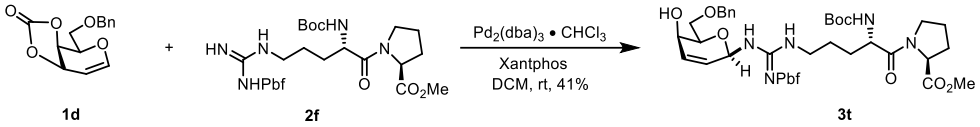
1c **2f** **3s**

To a solution of **1c**[1] (61.6 mg, 0.15 mmol), **2f** (31.8 mg, 0.05 mmol), $Pd_2(dba)_3$ • $CHCl_3$ (2.6 mg, 0.0025 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 24 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1, 1:2) afforded the **3s** (36.4 mg, 73%) as a pale yellow solid.

3s: Mp = 96−99 ℃. TLC R_f (EA) = 0.59. ^{1}H NMR (500 MHz, CD_3OD): δ 7.72 (td, *J* = 8.0, 1.0 Hz, 4H), 7.46-7.29 (m, 6H), 6.20 (dd, *J* = 8.5, 5.5 Hz, 1H), 5.68 (s, 1H), 4.41 (dd, *J* = 7.5, 4.5 Hz, 1H), 4.19 (s, 1H), 3.97 (d, *J* = 4.5 Hz, 1H), 3.94-3.88 (m, 1H), 3.84 (s, 2H), 3.74-3.60 (m, 1H), 3.64 (s, 3H), 3.43 (brs,1H), 3.21 (s, 1H), 3.16-3.06 (m, 1H), 2.95 (s, 2H), 2.59 (s, 3H), 2.51 (s, 3H), 2.24-2.14 (m, 1H), 2.06 (s, 3H), 1.92 (s, 3H), 1.70-1.46 (m, 4H), 1.44-1.36 (m, 15H), 1.04 (s, 9H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.0, 173.2, 159.9, 157.7, 155.9, 139.4, 136.7, 134.6, 134.5, 134.2, 133.6, 132.8, 130.9, 129.9,

128.9, 128.8, 126.1, 118.5, 87.7, 80.6, 78.9, 78.6, 65.1, 61.9, 60.4, 53.1, 52.7, 48.2, 43.9, 42.1, 29.9, 29.8, 28.7, 27.4, 26.1, 25.9, 20.1, 19.7, 18.5, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{52}H_{74}N_5O_{11}SSi$ 1004.4869; Found 1004.4876. $[\alpha]_D^{20}$: −15.6° (*c* 0.67, CH_3OH).

Product (3t)

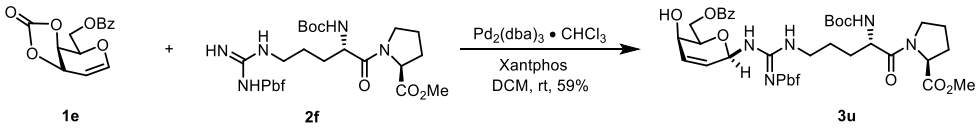


1d 2f 3t

To a solution of **1d**[1] (39.3 mg, 0.15 mmol), **2f** (31.9 mg, 0.05 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (2.6 mg, 0.0025 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:2, 1:3), concentration and then further purification by a big TLC (EA) afforded the **3t** (17.4 mg, 41%) as a white solid.

3t: Mp = 75−78 ℃. TLC R_f (EA) = 0.42. ^{1}H NMR (500 MHz, CD_3OD): δ 7.41-7.24 (m, 5H), 6.18 (s, 1H), 5.68 (s, 1H), 5.31 (s, 1H), 4.85 (s, 2H), 4.57 (s, 2H), 4.44 (dd, *J* = 8.5, 4.5 Hz, 1H), 4.23 (s, 1H), 3.90 (d, *J* = 5.0 Hz, 1H), 3.86 (t, *J* = 4.5 Hz, 1H), 3.71 (s, 2H), 3.66 (s, 3H), 3.50 (s,1H), 3.24-3.17 (m, 1H), 2.99 (s, 2H), 2.59 (s, 3H), 2.52 (s, 3H), 2.29-2.17 (m, 1H), 2.08 (s, 3H), 2.02-1.87 (m, 3H), 1.75-1.65 (m, 1H), 1.65-1.50 (m, 3H), 1.44 (s, 6H), 1.42 (s, 9H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.0, 173.4, 159.9, 157.8, 156.0, 139.4, 139.3, 134.2, 133.6, 132.9, 129.5, 129.1, 128.9, 126.1, 118.5, 87.7, 80.6, 78.7, 76.9, 74.5, 71.4, 62.4, 60.4, 53.2, 52.7, 48.2, 43.9, 42.0, 29.9, 29.8, 28.7, 26.3, 26.0, 19.70, 19.68, 18.5, 12.6, 12.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{43}H_{62}N_5O_{11}S$ 856.4161; Found 856.4168. $[\alpha]_D^{20}$: − 22.7° (*c* 0.33, CH_3OH).

Product (3u)



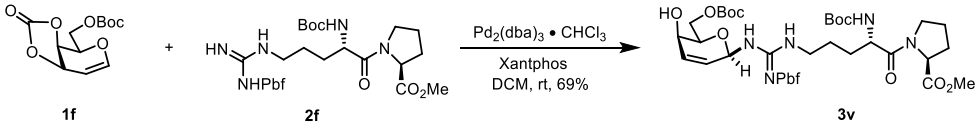
1e 2f 3u

To a solution of **1e**[1] (41.3 mg, 0.15 mmol), **2f** (31.9 mg, 0.05 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (2.6 mg, 0.0025 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 1 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:2, 1:3), concentration and then further purification by a big TLC (EA) afforded the **3u** (25.9 mg, 59%) as a white solid.

3u: Mp = 96−100 ℃. TLC R_f (EA) = 0.40. ^{1}H NMR (500 MHz, CD_3OD): δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.41-7.24 (m, 5H), 6.23 (s, 1H), 5.74 (s, 1H), 5.43 (brs, 1H), 4.48 (s, 2H), 4.43 (dd, *J* = 8.5,

5.0 Hz, 1H), 4.23 (brs, 1H), 4.08 (t, *J* = 5.0 Hz, 1H), 4.04 (d, *J* = 4.5 Hz, 1H), 3.71 (s, 1H), 3.66 (s, 3H), 3.51 (brs,1H), 3.28-3.14 (m, 2H), 2.96 (s, 2H), 2.57 (s, 3H), 2.51 (s, 3H), 2.28-2.17 (m, 1H), 2.05 (s, 3H), 2.01-1.95 (m, 2H), 1.94-1.86 (m, 1H), 1.75-1.65 (m, 1H), 1.64-1.49 (m, 3H), 1.44 (s, 6H), 1.42 (s, 9H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.0, 173.3, 167.8, 160.0, 157.8, 156.0, 139.4, 134.4, 134.1, 133.6, 131.3, 130.7, 129.7, 126.1, 118.5, 87.8, 80.6, 78.9, 75.8, 65.4, 62.1, 60.4, 53.1, 52.8, 48.3, 43.9, 42.0, 29.9, 29.7, 28.7, 26.2, 26.0, 19.7, 18.5, 12.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{43}H_{60}N_5O_{12}S$ 870.3954, found 870.3956. $[\alpha]_D^{20}$: + 4.0° (*c* 0.30, CH_3OH).

Product (3v)

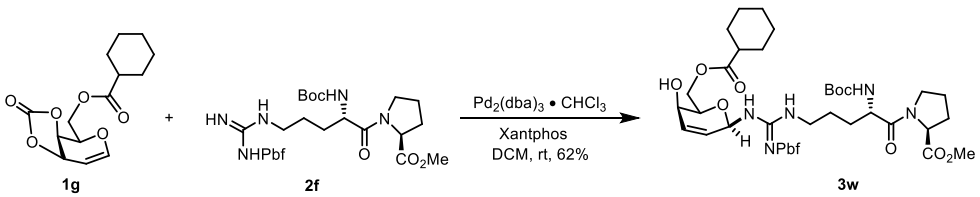


1f 2f 3v

To a solution of **1f**[4] (40.8 mg, 0.15 mmol), **2f** (31.8 mg, 0.05 mmol), $Pd_2(dba)_3$ • $CHCl_3$ (2.6 mg, 0.0025 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:2, 1:2.5 and 1:3) afforded the **3v** (30.0 mg, 69%) as a white solid.

3v: Mp = 93−96 ℃. TLC R_f (EA) = 0.26. ^{1}H NMR (500 MHz, CD_3OD): δ 6.66 (s, 1H), 6.19 (s, 1H), 5.71 (s, 1H), 5.35 (brs, 1H), 4.45 (dd, *J* = 9.0, 5.0 Hz, 1H), 4.26 (s, 1H), 4.24 (dd, *J* = 11.3, 4.0 Hz, 1H), 4.18 (s, 1H), 3.92 (d, *J* = 4.5 Hz, 1H), 3.89 (t, *J* = 6.5 Hz, 1H), 3.75 (s, 1H), 3.68 (s, 3H), 3.55 (brs,1H), 3.26 (s, 1H), 3.04 (d, *J* = 15.5 Hz, 1H), 3.00 (d, *J* = 15.5 Hz, 1H), 2.60 (s, 3H), 2.53 (s, 3H), 2.31-2.17 (m, 1H), 2.09 (s, 3H), 2.03-1.88 (m, 3H), 1.78-1.70 (m, 1H), 1.69-1.53 (m, 3H), 1.47 (s, 9H), 1.46 (s, 6H), 1.43 (s, 9H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.0, 173.3, 159.9, 157.7, 155.9, 154.9, 139.5, 134.1, 133.6, 132.5, 129.6, 126.1, 118.5, 87.8, 83.2, 80.6, 78.9, 75.8, 67.4, 61.9, 60.4, 53.1, 52.8, 48.3, 43.9, 42.0, 30.0, 29.8, 28.7, 28.0, 26.1, 26.0, 19.7, 18.5, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{41}H_{64}N_5O_{13}S$ 866.4216; Found 866.4269. $[\alpha]_D^{20}$: − 7.6° (*c* 0.82, CH_3OH).

Product (3w)



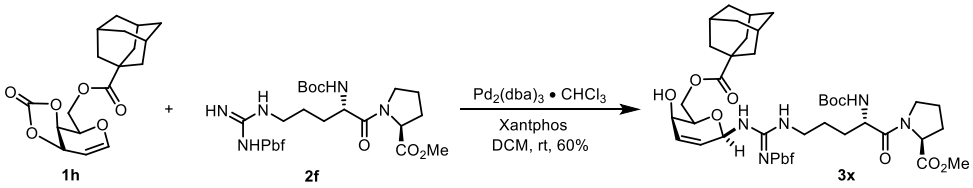
1g 2f 3w

To a solution of **1g**[4] (42.4 mg, 0.15 mmol), **2f** (31.8 mg, 0.05 mmol), $Pd_2(dba)_3$ • $CHCl_3$ (2.7 mg, 0.0026 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at

room temperature for 1 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:2, 1:3) afforded the **3w** (27.0 mg, 62%) as a yellow solid.

3w: Mp = 86−90 ℃. TLC R_f (EA) = 0.41. ^{1}H NMR (500 MHz, CD_3OD): δ 6.20 (s, 1H), 5.74 (s, 1H), 4.45 (dd, *J* = 8.5, 5.0 Hz, 1H), 4.34-4.25 (m, 1H), 4.23 (d, *J* = 5.0 Hz, 2H), 3.92 (d, *J* = 4.5 Hz, 1H), 3.89 (t, *J* = 5.5 Hz, 1H), 3.75 (s, 1H), 3.68 (s, 3H), 3.62-3.51 (m,1H), 3.30-3.16 (m, 2H), 3.04 (d, *J* = 16.0 Hz, 1H), 3.00 (d, *J* = 16.0 Hz, 1H), 2.59 (s, 3H), 2.52 (s, 3H), 2.34 (tt, *J* = 11.0, 3.5 Hz, 1H), 2.29-2.20 (m, 1H), 2.09 (s, 3H), 2.05-1.93 (m, 3H), 1.89 (dd, *J* = 13.0, 3.0 Hz, 1H), 1.79-1.69 (m, 3H), 1.68-1.52 (m, 4H), 1.46 (s, 6H), 1.43 (s, 9H), 1.37-1.21 (m, 5H). ^{13}C NMR (125 MHz, CD_3OD): δ 177.4, 174.0, 173.3, 160.0, 157.8, 155.9, 139.4, 134.2, 133.6, 132.6, 129.6, 126.1, 118.5, 87.8, 80.6, 78.9, 75.7, 64.5, 61.9, 60.4, 53.1, 52.8, 48.3, 44.2, 43.9, 42.0, 30.2, 30.1, 30.0, 29.8, 28.7, 26.9, 26.5, 26.4, 26.2, 26.0, 19.7, 18.5, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{43}H_{66}N_5O_{12}S$ 876.4423; Found 876.4424. $[\alpha]_D^{20}$: − 12.8˚ (*c* 0.49, CH_3OH).

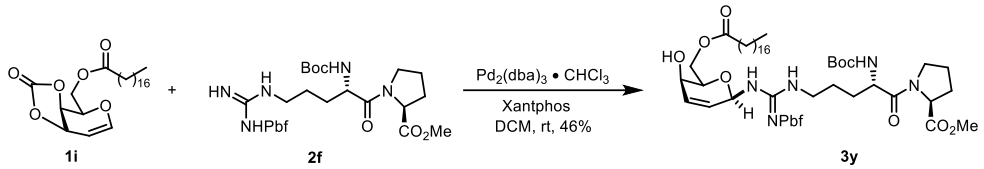
Product (3x)



To a solution of **1h**[4] (50.1 mg, 0.15 mmol), **2f** (31.9 mg, 0.05 mmol), $Pd_2(dba)_3$ • $CHCl_3$ (2.6 mg, 0.0025 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:2, 1:3) afforded the **3x** (27.6 mg, 60%) as a white solid.

3x: Mp = 109−114 ℃. TLC R_f (EA) = 0.47. ^{1}H NMR (500 MHz, CD_3OD): δ 6.69 (d, *J* = 6.0 Hz, 1H), 6.20 (s, 1H), 5.71 (s, 1H), 5.35 (brs, 1H), 4.45 (dd, *J* = 9.0, 5.0 Hz, 1H), 4.34-4.24 (m, 1H), 4.21 (d, *J* = 4.5 Hz, 2H), 3.92 (d, *J* = 4.0 Hz, 1H), 3.89 (t, *J* = 6.0 Hz, 1H), 3.75 (s, 1H), 3.68 (s, 3H), 3.63-3.49 (m,1H), 3.26-3.18 (m, 1H), 3.04 (d, *J* = 15.5 Hz, 1H), 3.00 (d, *J* = 15.5 Hz, 1H), 2.59 (s, 3H), 2.52 (s, 3H), 2.30-2.19 (m, 1H), 2.09 (s, 3H), 2.04-1.97 (m, 5H), 1.93-1.85 (m, 7H), 1.77 (d, *J* = 12.0 Hz, 3H), 1.72 (d, *J* = 12.0 Hz, 4H), 1.68-1.55 (m, 3H), 1.46 (s, 3H), 1.45 (s, 3H), 1.43 (s, 9H). ^{13}C NMR (125 MHz, CD_3OD): δ 178.9, 174.0, 173.3, 160.0, 157.8, 156.0, 139.4, 134.2, 133.6, 132.7, 129.6, 126.1, 118.5, 87.8, 80.6, 79.9, 75.6, 64.3, 61.9, 60.4, 53.1, 52.8, 48.3, 43.9, 42.0, 40.0, 37.5, 30.0, 29.8, 29.4, 28.7, 26.2, 26.0, 19.7, 18.5, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{47}H_{70}N_5O_{12}S$ 928.4736; Found 928.4744. $[\alpha]_D^{20}$: − 5.5˚ (*c* 0.51, CH_3OH).

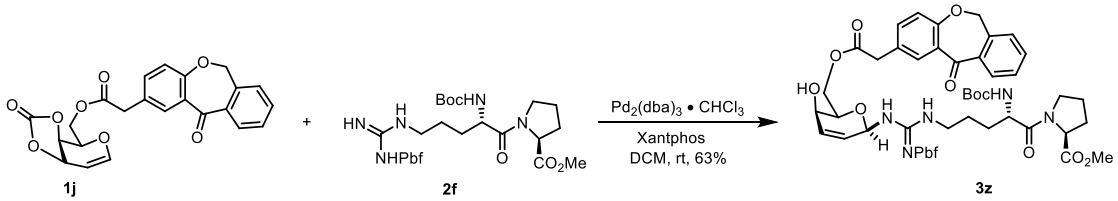
Product (3y)



To a solution of **1i**[4] (65.7 mg, 0.15 mmol), **2f** (31.9 mg, 0.05 mmol), $Pd_2(dba)_3 \bullet CHCl_3$ (2.7 mg, 0.0026 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 2 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:2, 1:3) afforded the **3y** (23.6 mg, 46%) as a yellow solid.

3y: Mp = 48−53 ℃. TLC R_f (EA) = 0.37. ^{1}H NMR (500 MHz, CD_3OD): δ 6.19 (s, 1H), 5.71 (s, 1H), 4.45 (dd, J = 8.5, 5.0 Hz, 1H), 4.35-4.15 (m, 3H), 3.93 (d, J = 3.5 Hz, 1H), 3.89 (dd, J = 6.5, 6.5 Hz, 1H), 3.75 (s, 1H), 3.68 (s, 3H), 3.63-3.53 (m,1H), 3.26 (s, 2H), 3.04 (d, J = 15.5 Hz, 1H), 3.00 (d, J = 15.5 Hz, 1H), 2.59 (s, 3H), 2.52 (s, 3H), 2.33 (t, J = 7.5 Hz, 2H), 2.29-2.20 (m, 1H), 2.09 (s, 3H), 2.05-1.89 (m, 3H), 1.79-1.69 (m, 1H), 1.68-1.54 (m, 5H), 1.46 (s, 6H), 1.43 (s, 9H), 1.33-1.26 (m, 28H), 0.90 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, CD_3OD): δ 175.2, 174.0, 173.3, 160.0, 157.8, 155.9, 139.5, 134.23, 134.20, 133.6, 132.5, 129.8, 126.1, 118.5, 87.8, 80.6, 78.8, 75.8, 64.7, 62.0, 60.4, 53.1, 52.8, 48.3, 43.9, 42.1, 34.9, 33.1, 30.81, 30.79, 30.75, 30.63, 30.62, 30.50, 30.48, 30.44, 30.42, 30.2, 30.0, 29.8, 28.8, 26.1, 26.00, 25.98, 23.8, 19.71, 19.68, 18.5, 14.50, 14.46, 12.62, 12.58. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{54}H_{90}N_5O_{12}S$ 1032.6301; Found 1032.6352. $[\alpha]_D^{20}$: − 13.4° (c 0.42, CH_3OH).

Product (3z)

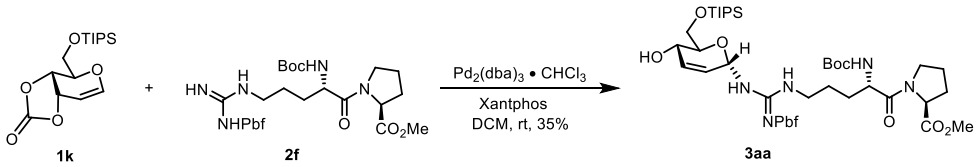


To a solution of **1j**[4] (63.3 mg, 0.15 mmol), **2f** (31.8 mg, 0.05 mmol), $Pd_2(dba)_3 \bullet CHCl_3$ (2.7 mg, 0.0026 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 1 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:3 then EA), concentration and then further purification by a big TLC (EA) afforded the **3z** (31.8 mg, 63%) as a white solid.

3z: Mp = 110−113 ℃. TLC R_f (EA) = 0.33. ^{1}H NMR (500 MHz, CD_3OD): δ 8.06 (s, 1H), 7.83 (dd, J = 7.5, 1.0 Hz, 1H), 7,61 (td, J = 7.5, 1.0 Hz, 1H), 7.49 (dd, J = 7.5, 1.0 Hz, 1H), 7.48-7.35 (m, 2H), 7.01 (d, J = 8.5 Hz, 1H), 6.17 (s, 1H), 5.69 (s, 1H), 5.38 (brs, 1H), 5.21 (s, 2H), 4.43 (dd, J = 8.5, 4.5 Hz, 1H), 4.38-4.18 (m, 3H), 3.91 (s, 2H), 3.78-3.62 (m, 3H), 3.65

(s, 3H), 3.55 (brs, 1H), 3.24 (t, *J* = 6.5 Hz, 1H), 2.96 (s, 2H), 2.58 (s, 3H), 2.50 (s, 3H), 2.28-2.15 (m, 1H), 2.07 (s, 3H), 2.02-1.82 (m, 3H), 1.78-1.52 (m, 4H), 1.40 (s, 15H). ^{13}C NMR (125 MHz, CD_3OD): δ 192.3, 174.0, 173.3, 173.0, 162.0, 160.0, 157.8, 155.9, 141.6, 139.5, 137.9, 137.6, 134.21, 134.17, 133.6, 133.2, 130.3, 130.2, 129.5, 129.2, 126.3, 126.1, 122.1, 118.5, 87.8, 80.6, 78.9, 75.8, 74.6, 65.3, 62.0, 60.4, 53.1, 52.8, 48.3, 43.9, 42.1, 40.7, 29.9, 29.8, 28.72, 28.69, 26.2, 26.0, 19.7, 18.5, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{52}H_{66}N_5O_{14}S$ 1016.4321; Found 1016.4360. $[\alpha]_D^{20}$: − 11.4° (*c* 0.34, CH_3OH).

Product (3aa)

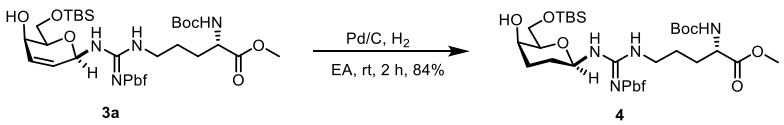


To a solution of **1k**[1] (49.3 mg, 0.15 mmol), **2f** (31.9 mg, 0.05 mmol), $Pd_2(dba)_3$ • $CHCl_3$ (2.6 mg, 0.0025 mmol) and Xantphos (2.9 mg, 0.005 mmol) was added anhydrous DCM (4 mL) under an argon atmosphere. The mixture was stirred at room temperature for 24 h and then concentrated in vacuo. Purification of the residue through column chromatography on silica gel (Hexane/EA 1:1, 1:2) afforded the **3aa** (16.2 mg, 35%) as a yellow solid.

3aa: Mp = 68−70 ℃. TLC R_f (EA) = 0.70. ^{1}H NMR (500 MHz, CD_3OD): δ 6.07 (d, *J* = 10.0 Hz, 1H), 5.76 (d, *J* = 10.0 Hz, 1H), 5.44 (brs, 1H), 4.47 (dd, *J* = 9.0, 4.5 Hz, 1H), 4.29 (t, *J* = 6.5 Hz, 1H), 4.03 (d, *J* = 8.5 Hz, 1H), 3.90 (dd, *J* = 11.5, 1.5 Hz, 1H), 3.86-3.75 (m, 2H), 3.69 (s, 3H), 3.66-3.57 (m, 1H), 3.47-3.35 (m, 2H), 3.19-3.09 (m, 1H), 3.04 (d, *J* = 15.5 Hz, 1H), 3.00 (d, *J* = 15.5 Hz, 1H), 2.59 (s, 3H), 2.51 (s, 3H), 2.33-2.21 (m, 1H), 2.09 (s, 3H), 2.06-1.99 (m, 2H), 1.97-1.91 (m, 1H), 1.76-1.68 (m, 1H), 1.68-1.55 (m, 3H), 1.47 (s, 3H), 1.45 (s, 3H), 1.43 (s, 9H), 1.12-1.07 (m, 5H), 1.06 (s, 9H), 1.06-1.02 (m, 7H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.1, 173.4, 160.0, 157.9, 156.1, 139.4, 137.1, 134.1, 133.5, 126.2, 125.2, 118.6, 87.8, 80.6, 75.9, 74.7, 64.4, 63.5, 60.4, 53.3, 52.8, 48.3, 43.9, 42.1, 30.0, 29.9, 28.7, 26.5, 26.0, 19.8, 18.6, 18.5, 13.2, 12.6. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{45}H_{76}N_5O_{11}SSi$ 922.5026; Found 922.5038. $[\alpha]_D^{20}$: − 26.1° (*c* 0.29, CH_3OH).

2.3 Derivation

Product (4)

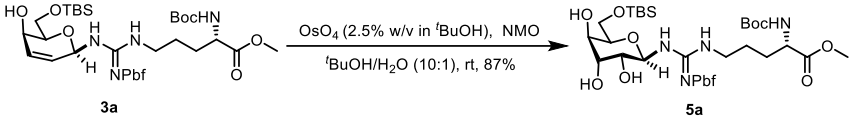


To a solution of **3a** (39.1 mg, 0.05 mmol) in EA (2 mL) was added Pd/C (10.6 mg, 10% on dry basis, 0.01 mmol) and bubbled by H_2 (1.0 atm) for 5 min. The reaction mixture was stirred at room temperature under balloon pressure gas of H_2

(1.0 atm) for 2 h. The mixture was filtered through celite by washing with EA, concentrated and purified by column chromatography (Hexane/EA 1:1.5, 1:2) to give **4** (33.0 mg, 84% yield) as a white solid.

4: Mp = 65−68 ℃. TLC R_f (Hexane/EA 1:1) = 0.16. ^{1}H NMR (500 MHz, CD_3OD): δ 4.71 (brs, 1H), 4.04 (d, J = 7.5 Hz, 1H), 3.78 (dd, J = 10.0, 6.0 Hz, 1H), 3.74 (s, 2H), 3.68 (s, 3H), 3.60 (s, 1H), 3.29-3.15 (m, 2H), 3.00 (s, 2H), 2.58 (s, 3H), 2.51 (s, 3H), 2.08 (s, 3H), 2.00-1.84 (m, 2H), 1.83-1.68 (m, 2H), 1.65-1.51 (m, 4H), 1.46 (s, 3H), 1.45 (s, 3H), 1.44 (s, 9H), 0.90 (s, 9H), 0.083 (s, 3H), 0.076 (s, 3H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.6, 159.9, 158.0, 156.0, 139.4, 134.1, 133.4, 126.1, 118.5, 87.7, 81.3, 80.6, 79.8, 64.5, 63.9, 54.8, 52.6, 43.9, 41.8, 31.0, 29.9, 28.7, 27.2, 26.43, 26.39, 26.0, 19.7, 19.2, 18.5, 12.6, -5.1, -5.2. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{37}H_{65}N_4O_{10}SSi$ 785.4185; Found 785.4220. $[\alpha]_D^{20}$: − 32.0° (*c* 0.60, CH_3OH).

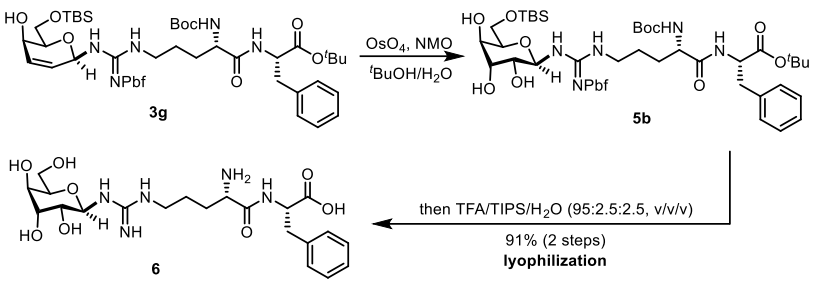
Product (5a)



To a reaction tube was added **3a** (156.4 mg, 0.2 mmol), NMO (23.3 mg, 0.2 mmol), ^{t}BuOH (880 μL) and water (88 μL). Put the tube to an ice bath, then add the OsO_4 (2.5% *w*/*v* in ^{t}BuOH, 14 μL). The mixture was stirred at 0 ℃ for 1 h and then warmed to room temperature for overnight. It was quenched with Na_2SO_3 aqueous and extracted with EA for 3 times, combined organic phase and sequentially wash with water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated and purified by column chromatography (Hexane/EA 1:3, 1:5 then EA) to give **5a** (142.2 mg, 87% yield) as a white solid.

5a: Mp = 94−96 ℃. TLC R_f (EA) = 0.46. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (brs, 1H), 6.10 (brs, 1H), 5.24 (d, J = 5.5 Hz, 1H), 4.82 (brs, 1H), 4.38 (brs, 1H), 4.21 (d, J = 4.0 Hz, 1H), 4.15 (s, 1H), 4.01 (d, J = 7.0 Hz, 1H), 3.96 (s, 2H), 3.84 (s, 3H), 3.69 (s, 3H), 3.22 (s, 2H), 2.95 (s, 2H), 2.55 (s, 3H), 2.48 (s, 3H), 2.08 (s, 3H), 1.82-1.68 (m, 1H), 1.66-1.50 (m, 3H), 1.45 (s, 6H), 1.42 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 173.3, 171.3, 159.0, 155.7, 138.7, 132.7, 132.5, 124.7, 117.6, 86.6, 81.0, 80.2, 73.3, 70.7, 67.3, 64.2, 60.5, 53.3, 52.5, 43.3, 41.1, 30.0, 28.7, 28.5, 26.0, 25.7, 19.4, 18.4, 18.1, 14.3, 12.6, -5.31, -5.33. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{37}H_{65}N_4O_{12}SSi$ 817.4083; Found 817.4112. $[\alpha]_D^{20}$: − 27.3° (*c* 0.18, CH_3OH).

Product (6)



To a reaction tube was added **3g** (44.8 mg, 0.046 mmol), NMO (5.7 mg, 0.048 mmol), ^{t}BuOH (406 μL) and water (40.6 μL). Put the tube to an ice bath, then add the OsO_4 (2.5% *w*/*v* in ^{t}BuOH, 3.2 μL). The mixture was stirred at 0 ℃ for 1 h and then warmed to room temperature for overnight. It was quenched with Na_2SO_3 aqueous and extracted with EA for 3 times, combined organic phase and sequentially wash with water and brine, then dried over anhydrous sodium sulphate, filtered, concentrated. The crude product was not purified and directly used in next step.

To the vial with crude **5b** was added water (50 μL), TFA (1.9 mL) and TIPS (50 μL). The mixture was stirred at room temperature for 30 min. The TFA was blown away with air. The residue was dissolved with CH_3CN/H_2O (1/8, *v*/*v*) and then filtered. The filtrate was purified by HPLC and then lyophilized to give **6** (20.3 mg, 91% yield over 2 steps) as a white foam. HPLC for separation: retention time = 5.0 min (4.5 mL/min, 15% to 40% CH_3CN over 20 min, Higgins Analytical Proto, 250 × 10 mm, C18 5 μm column). Analytic HPLC: retention time = 8.1 min (0.6 mL/min, 15% to 45% CH_3CN over 20 min, Higgins Clipeus C18 5 μm column, 250 × 4 mm).

Compound **6** completely dissolves in CD_3OD, however, the peak of anomeric proton (H_{C1}) of compound **6** was partially overlapped by water peak, and the coupling constant could not be determined. We removed the CD_3OD and partially re-dissolved **6** in CD_3CN due to the solubility issue. ^{1}H NMR and COSY (see Page S78-S80) were used to determine and assign H_{C1} and H_{C2} peaks. The observed large coupling constant of J_{aa} = 9.0 Hz indicates that H_{C1} and H_{C2} are in anti-geometry on the pyranose where adapts near 180 degree dihedral angle.[5] Overall, the stereochemistry of dihydroxylation can be determined as OsO_4 approaches from less sterically demanding convex face.

6: ^{1}H NMR (500 MHz, CD_3OD): δ 7.35-7.15 (m, 5H), 4.85 (s, 1H), 4.73 (dd, *J* = 9.5, 5.0 Hz, 1H), 4.04 (dd, *J* = 7.5, 4.5 Hz, 1H), 3.97 (t, *J* = 3.5 Hz, 1H), 3.89 (t, *J* = 6.0 Hz, 1H), 3.83-3.77 (m, 1H), 3.77-3.72 (m, 2H), 3.69 (dd, *J* = 11.5, 4.0 Hz, 1H), 3.30-3.23 (m, 3H), 3.01 (dd, *J* = 14.0, 9.5 Hz, 1H), 1.93 (dd, *J* = 15.5, 8.0 Hz, 2H), 1.82-1.63 (m, 2H). ^{13}C NMR (125 MHz, CD_3OD): δ 174.5, 170.0, 158.4, 138.3, 130.2, 129.6, 128.0, 80.9, 75.6, 72.4, 71.1, 68.4, 62.9, 55.5, 53.7, 42.1, 38.0, 29.7, 24.5. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{34}N_5O_8$ 484.2402; Found 484.2439. $[\alpha]_D^{20}$: − 15.8° (*c* 0.095, CH_3OH).

3 References

(1) Dai, Y.; Zheng, J.; Zhang, Q. *Org. Lett.* **2018**, *20*, 3923.

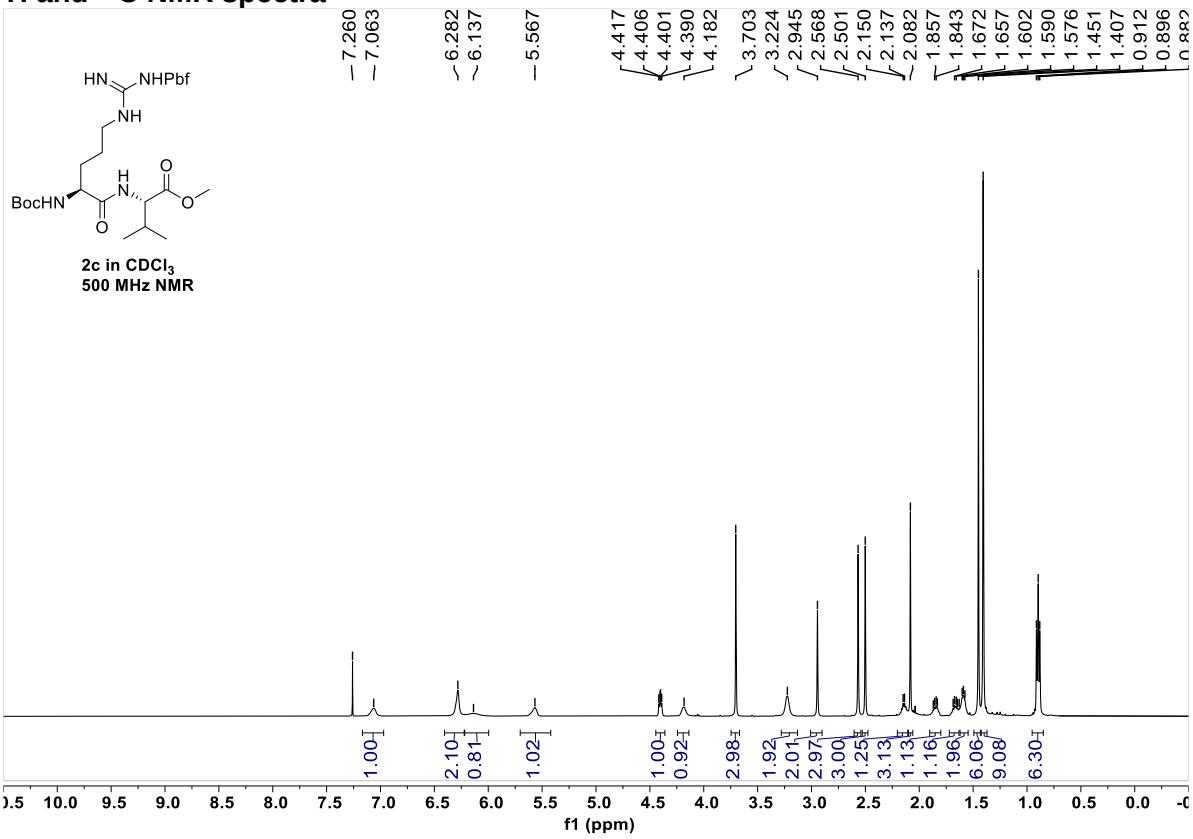
(2) Ward, D. J.; Van de Langemheen, H.; Koehne, E.; Kreidenweiss, A.; Liskamp, R. M. J. *Bioorg. Med. Chem.* **2019**, *27*, 2857.

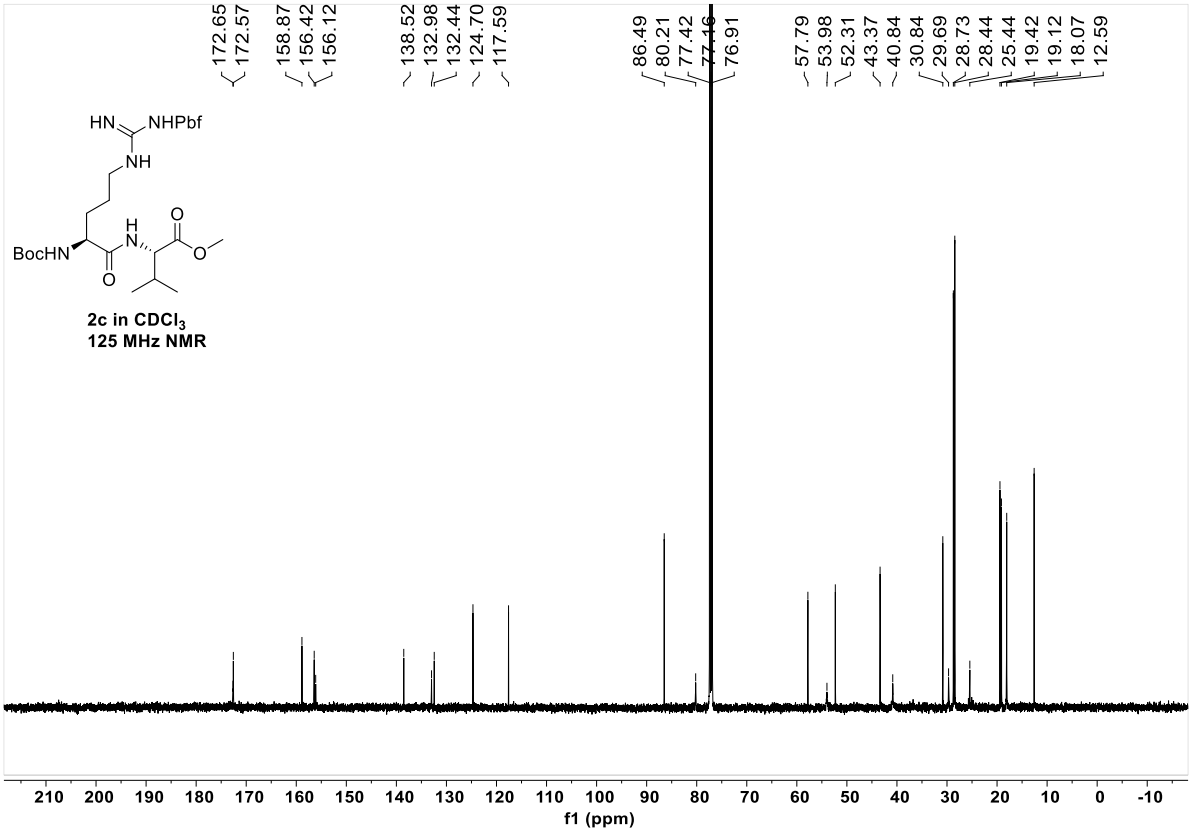
(3) Grogg, M.; Hilvert, D.; Beck, A. K.; Seebach, D. *Synthesis* **2019**, *51*, 31.

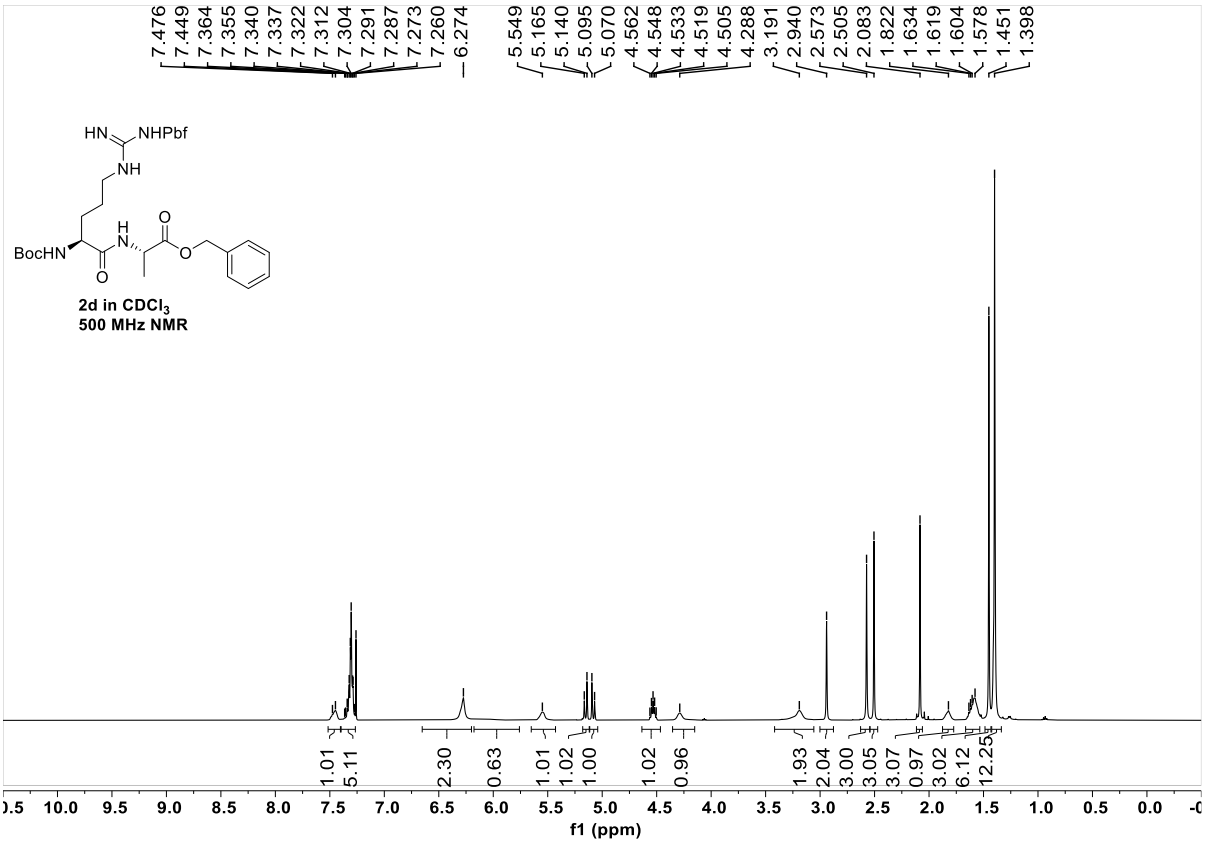
(4) Dai, Y.; Tian, B.; Chen, H.; Zhang, Q. *ACS Catal.* **2019**, *9*, 2909.

(5) Altona, C.; Haasnoot, C. A. G. *Org. Magn. Reson*. **1980**, *13*, 417.

4 ^{1}H and ^{13}C NMR spectra



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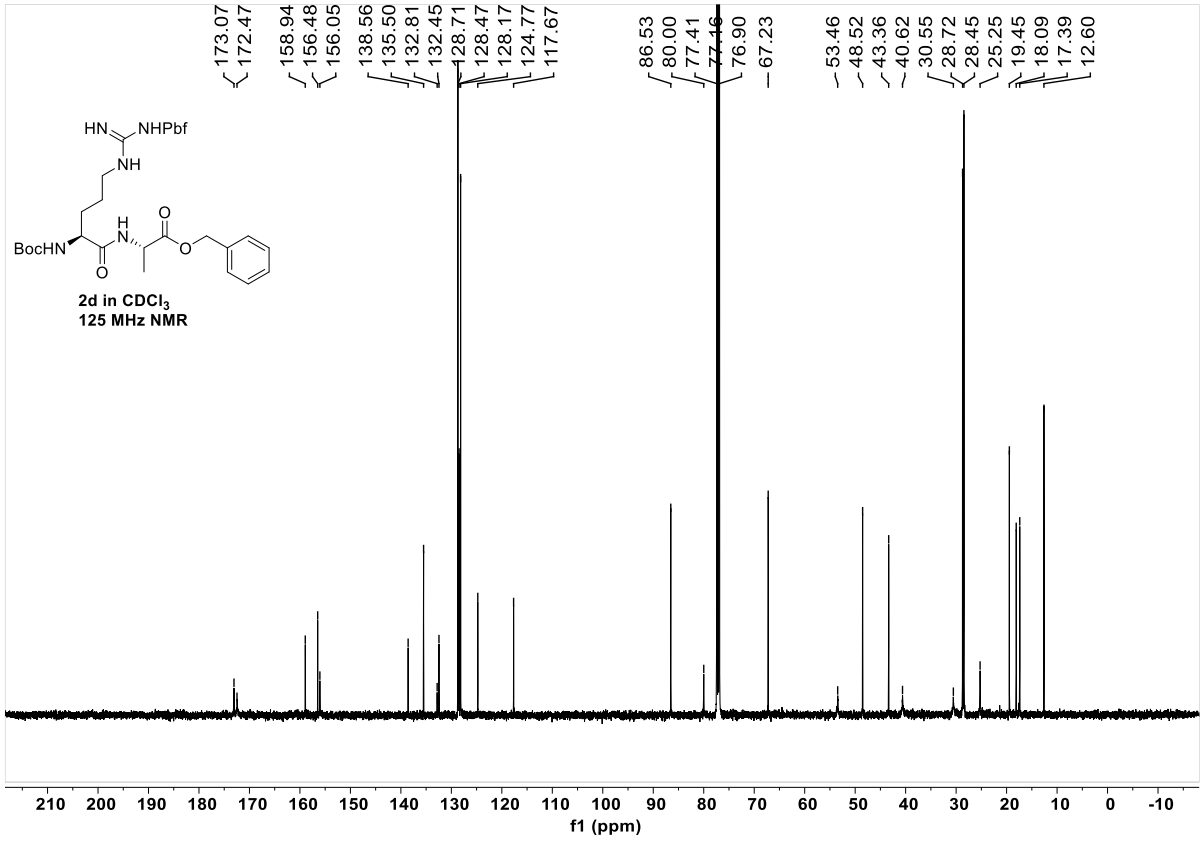
7.260
6.274
5.549
5.165
5.140
5.095
5.070
4.562
4.548
4.533
4.519
4.505
4.288
3.191
2.940
2.573
2.505
2.083
1.822
1.634
1.619
1.604
1.578
1.451
1.398
HN
NHPbf
NH
BocHN
H
N
O
O
O
2d in CDCl3
500 MHz NMR
1.01
5.11
2.30
0.63
1.01
1.02
1.00
1.02
0.96
1.93
2.04
3.00
3.05
3.07
0.97
3.02
6.12
12.25
f1 (ppm)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80.00
77.41
77.16
76.90
67.23
53.46
48.52
43.36
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30.55
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28.45
25.25
19.45
18.09
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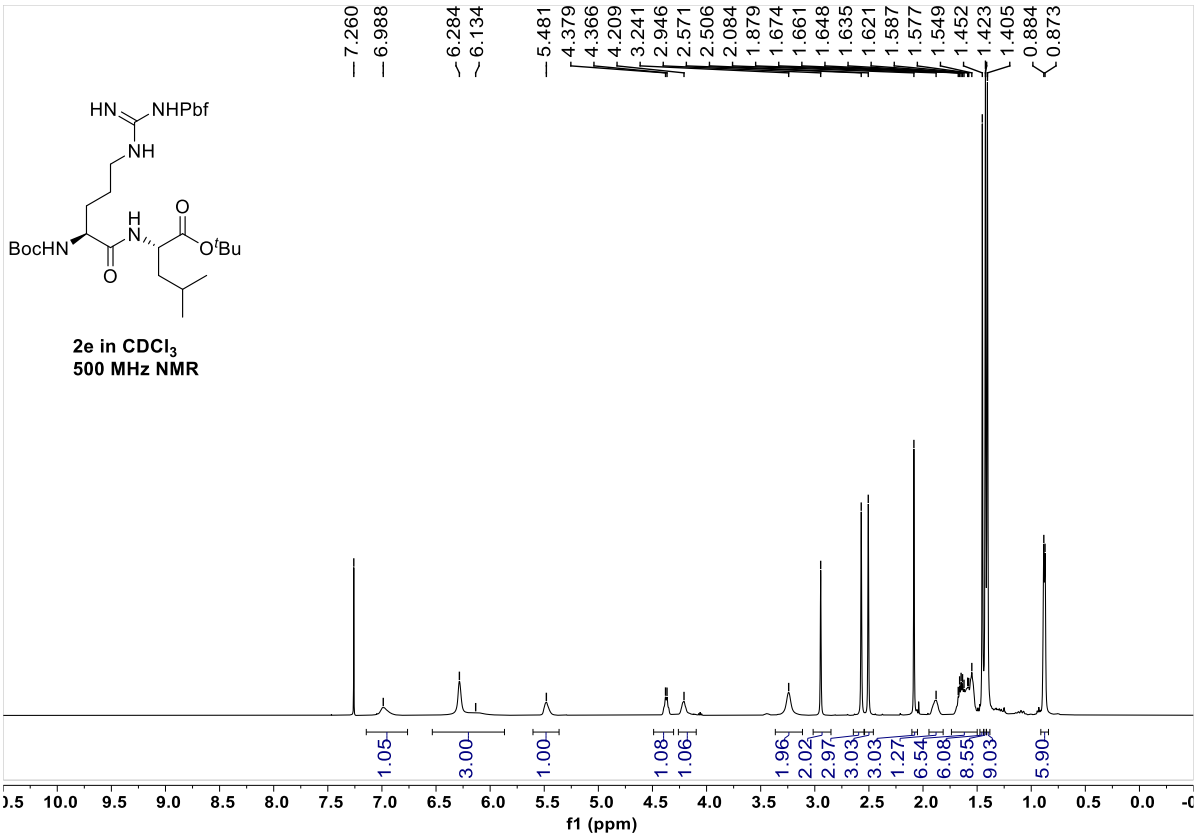
O
O
O
2d in CDCl3
125 MHz NMR
f1 (ppm)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2.084
1.879
1.674
1.661
1.648
1.635
1.621
1.587
1.577
1.549
1.452
1.423
1.405
0.884
0.873
1.05
3.00
1.00
1.08
1.06
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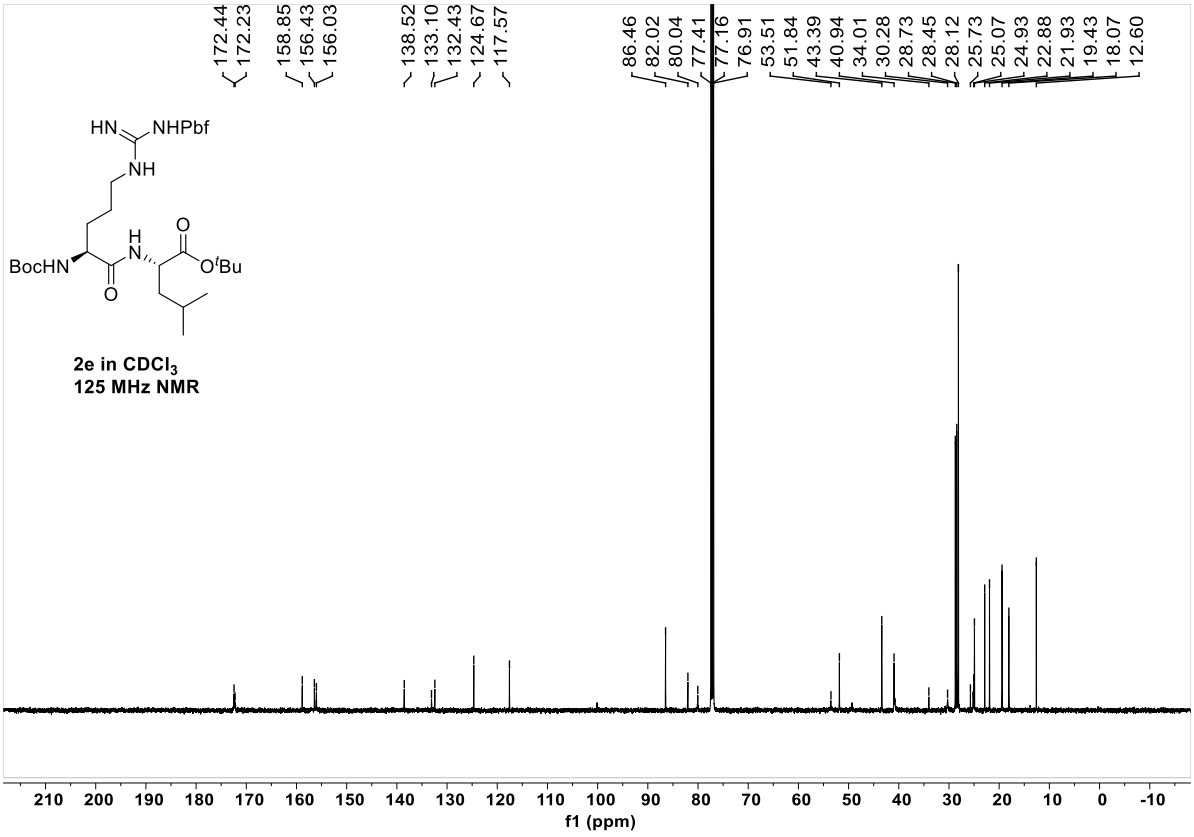
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77.16
76.91
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51.84
43.39
40.94
34.01
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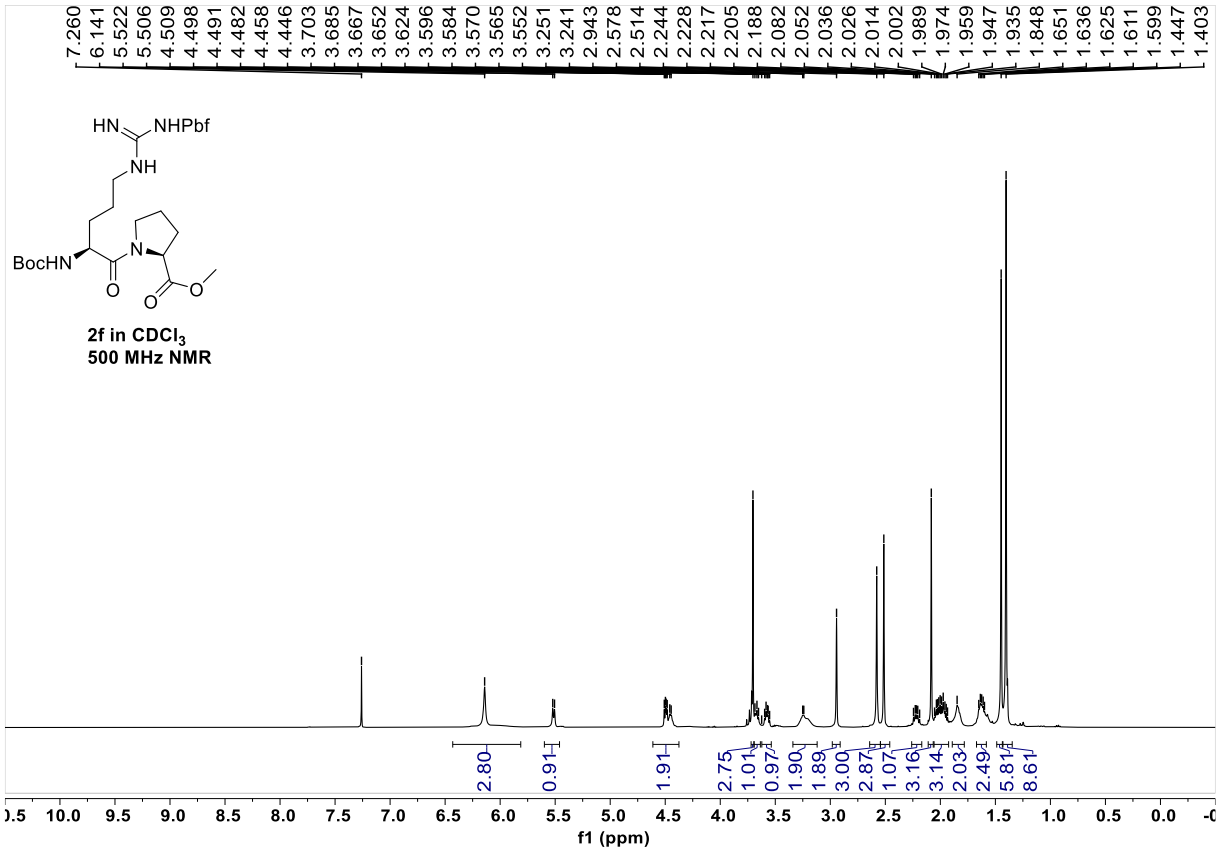
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O
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500 MHz NMR
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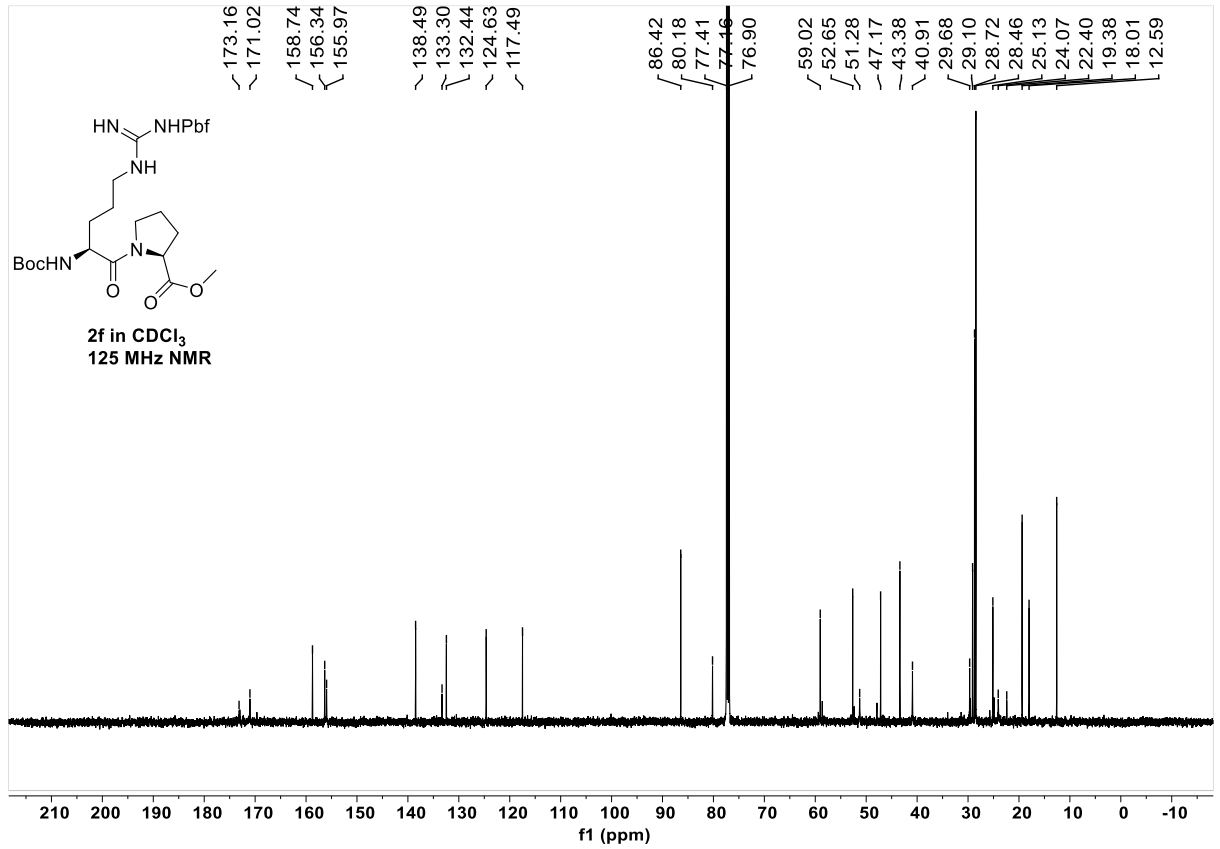
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O
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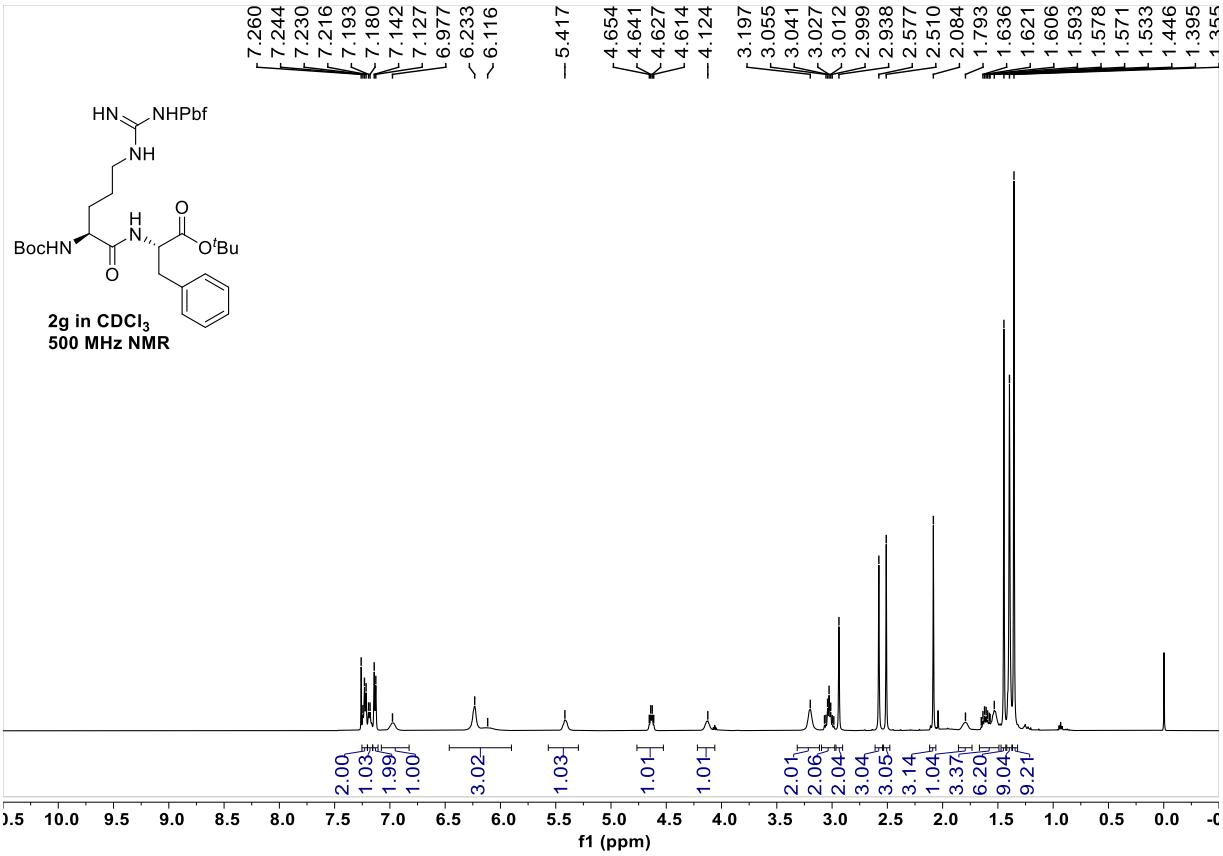
f1 (ppm)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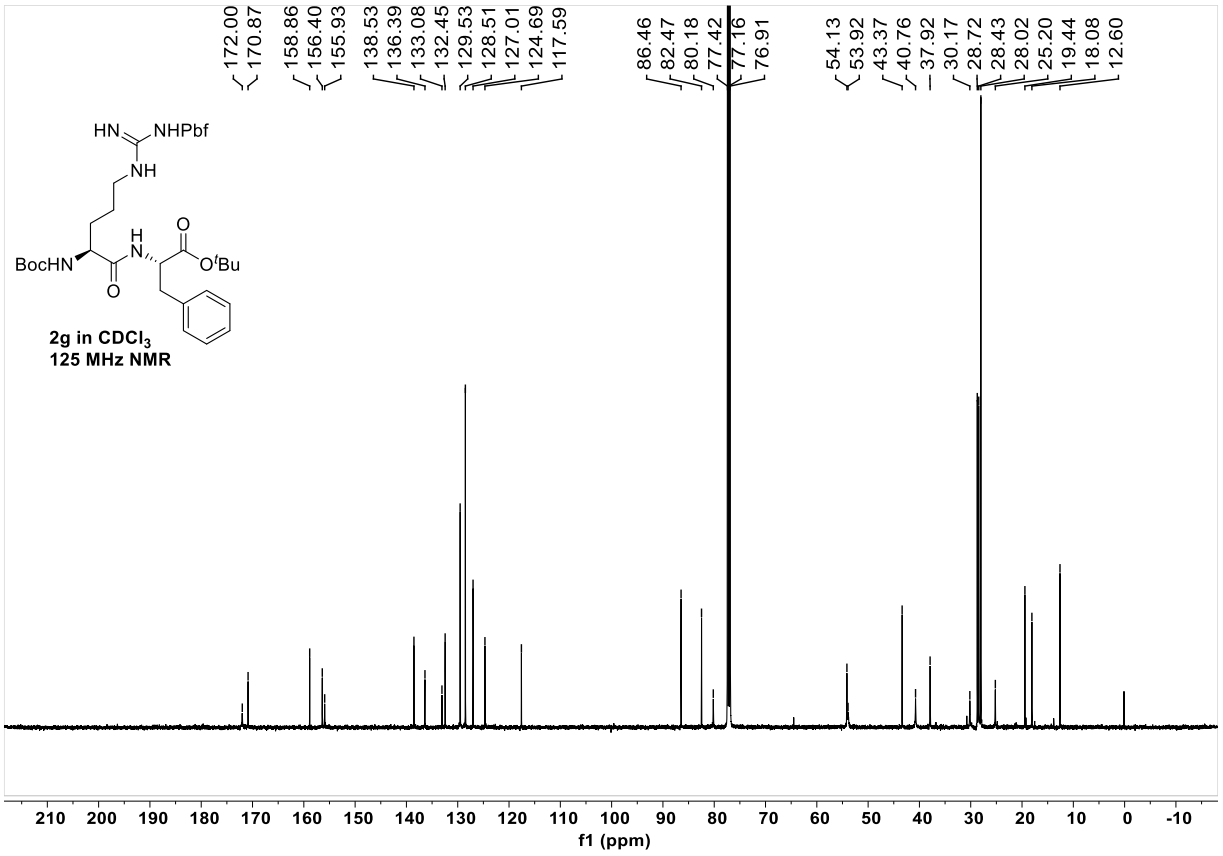
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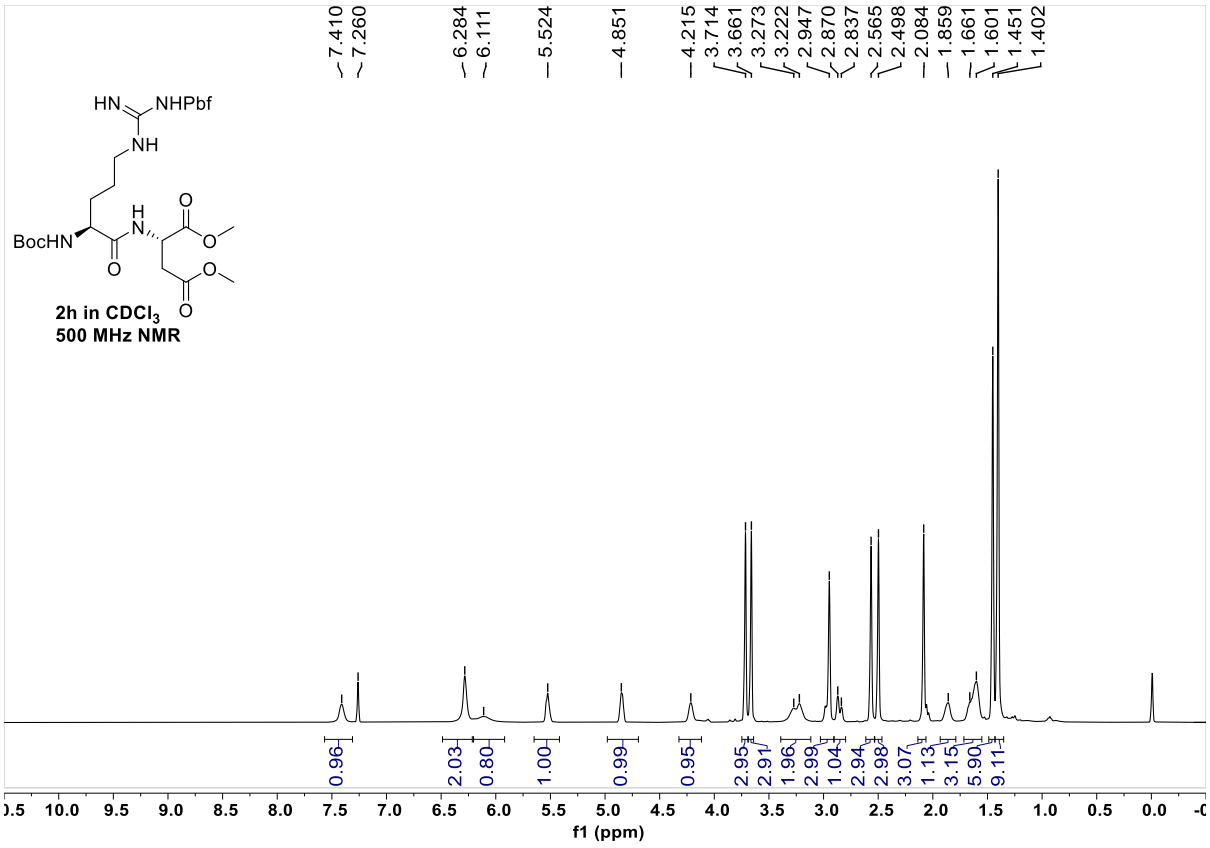
125 MHz NMR
f1 (ppm)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1.601
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NHPbf
NH
BocHN
H
N
O
O
O
O
O
O
2h in CDCl3
500 MHz NMR
0.96
2.03
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1.00
0.99
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2.95
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3.15
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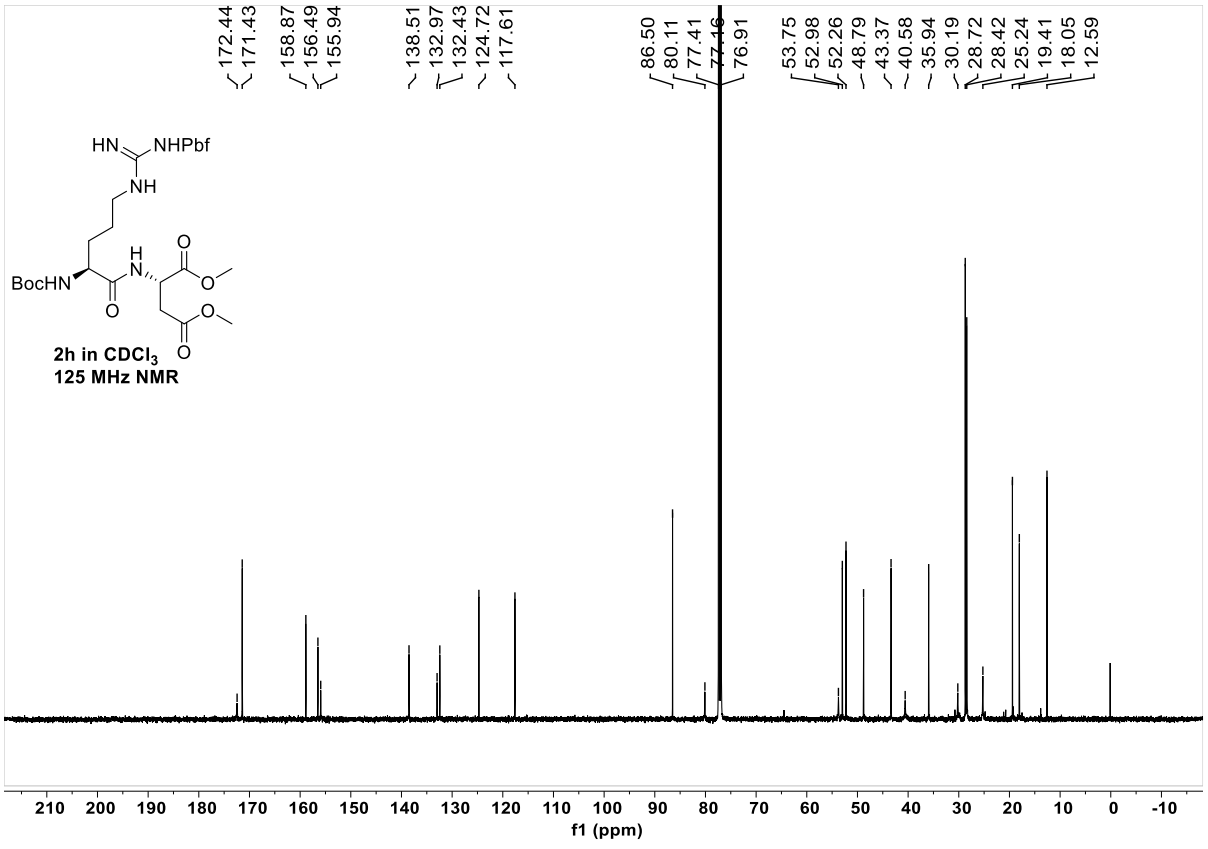
f1 (ppm)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35.94
30.19
28.72
28.42
25.24
19.41
18.05
12.59
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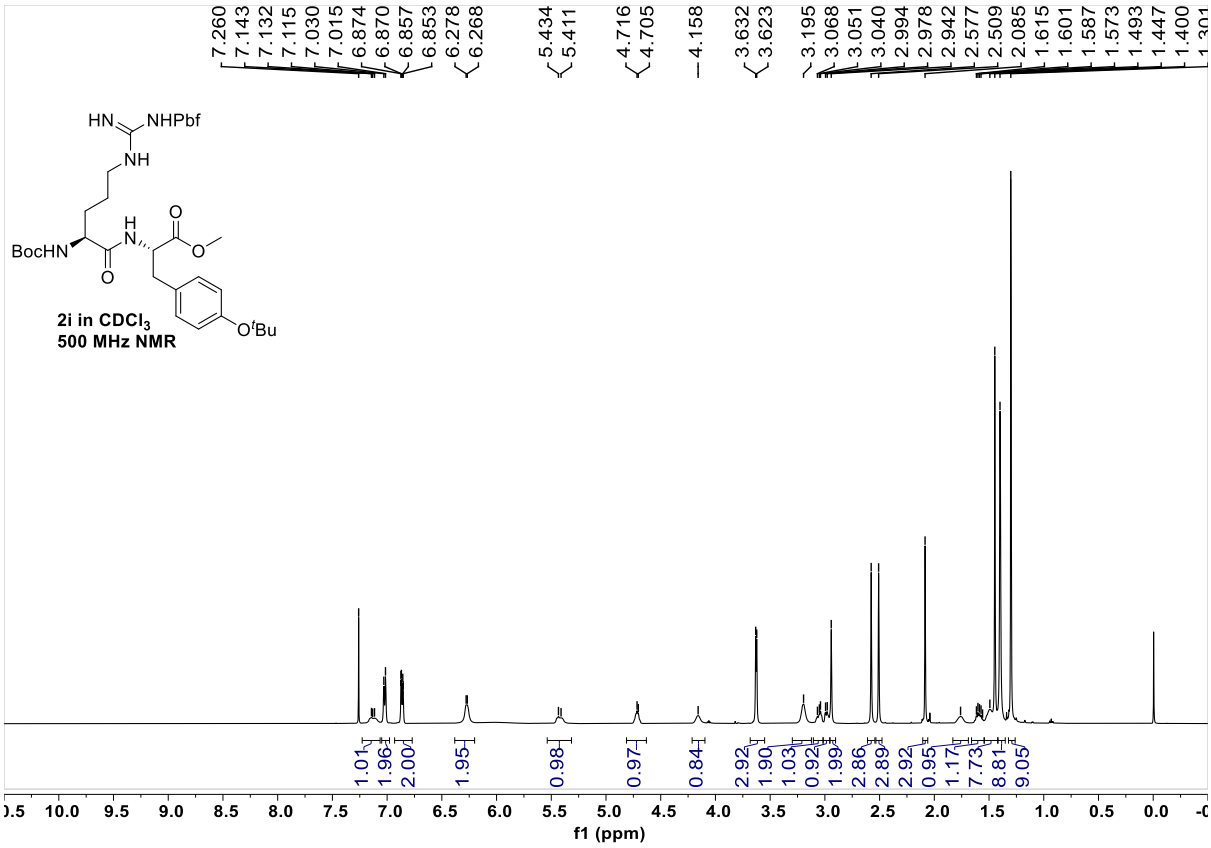
H
N
O
O
O
O
O
O
2h in CDCl3
125 MHz NMR
f1 (ppm)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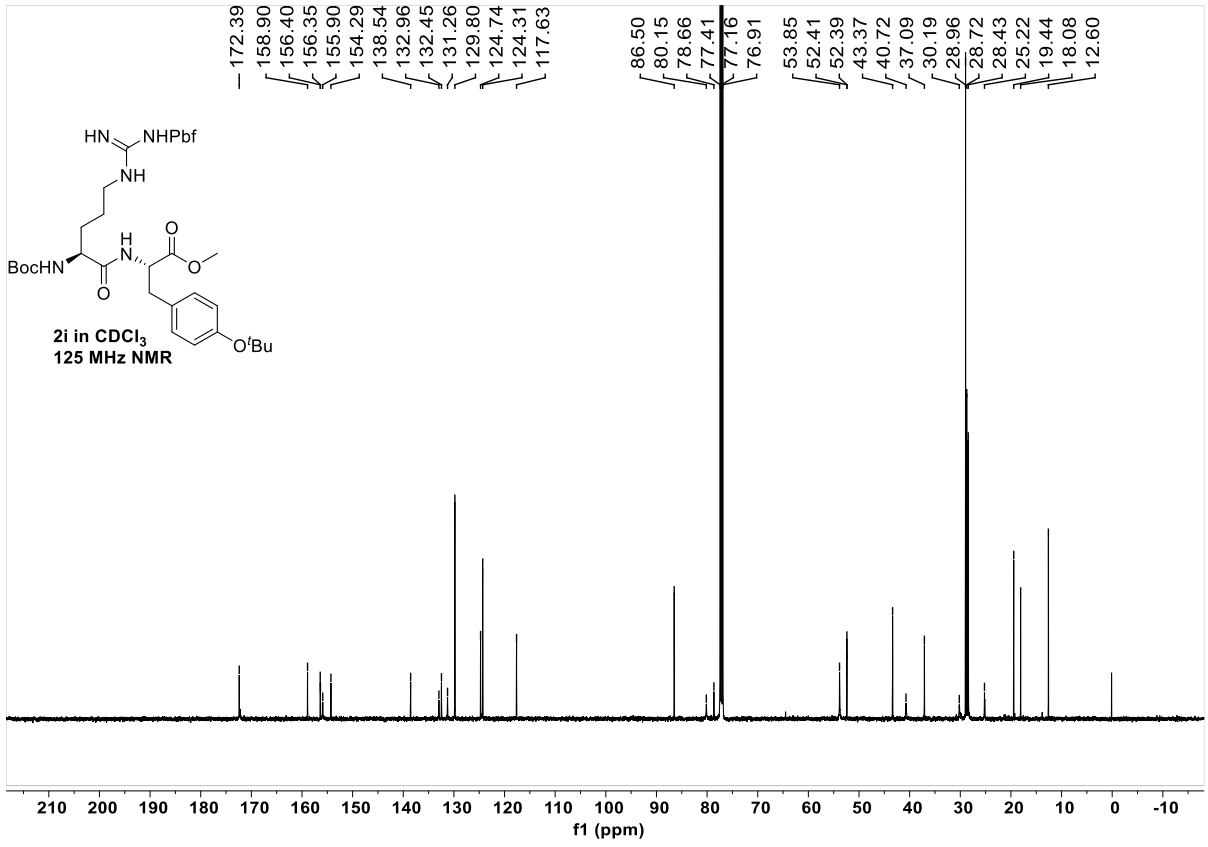
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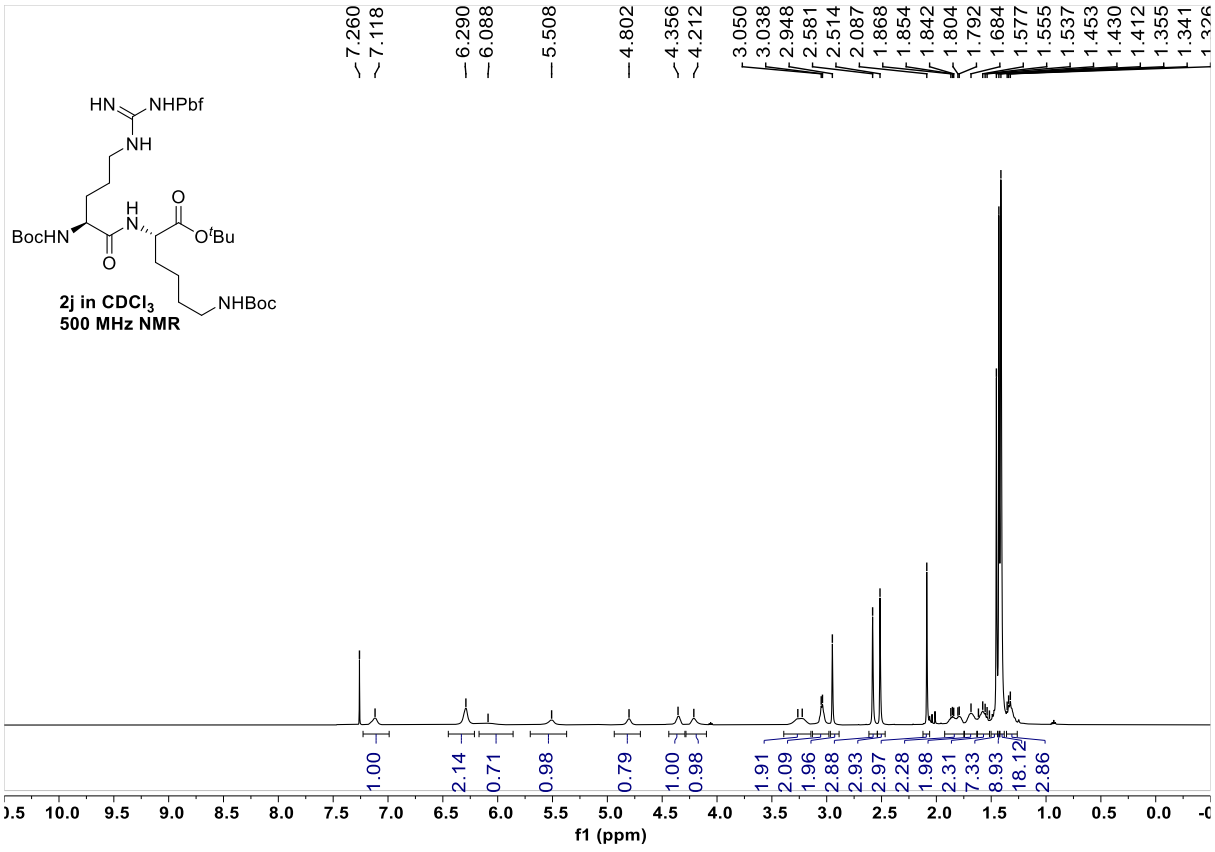
f1 (ppm)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1.453
1.430
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1.355
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1.00
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0.79
1.00
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2.09
1.96
2.88
2.93
2.97
2.28
1.98
2.31
7.33
8.93
18.12
2.86
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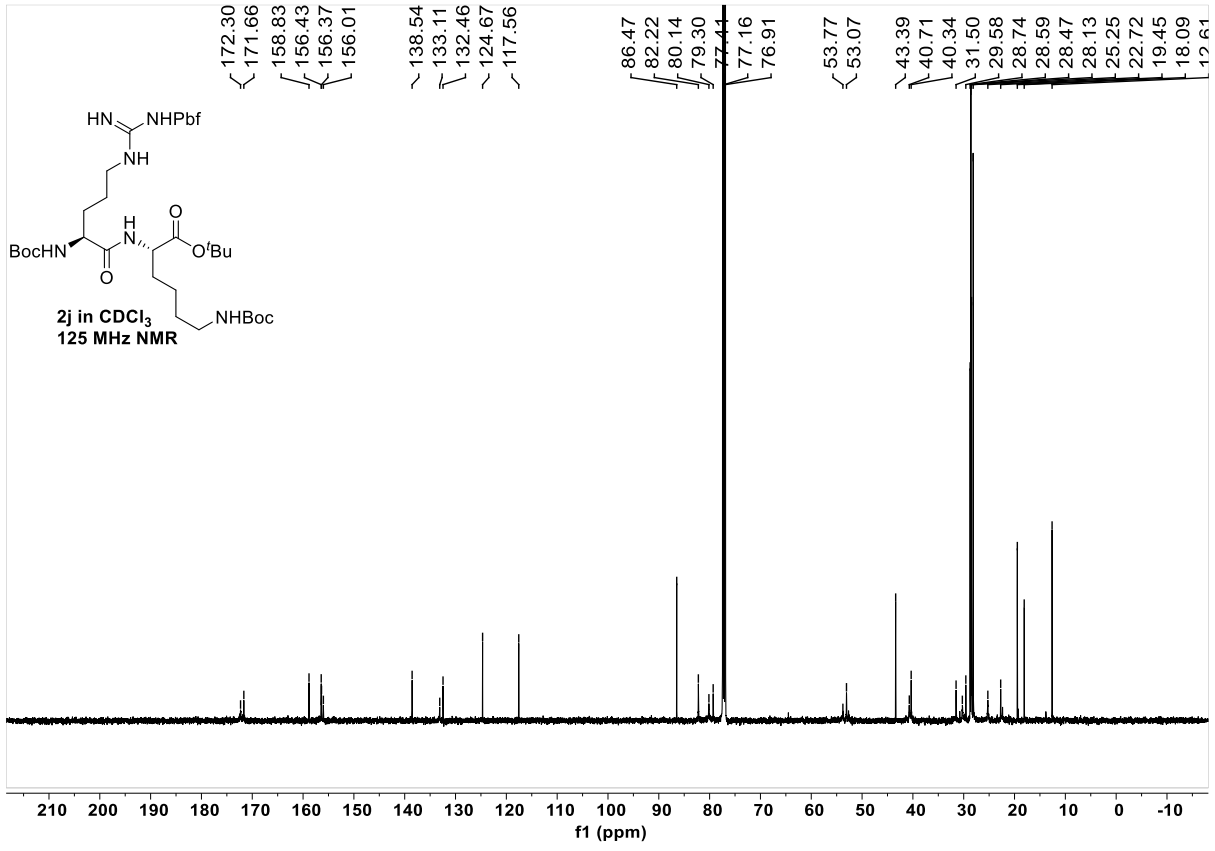
N
O
O'Bu
NHBoc
2j in CDCl3
500 MHz NMR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31.50
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28.47
28.13
25.25
22.72
19.45
18.09
f1 (ppm)
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O
O
H
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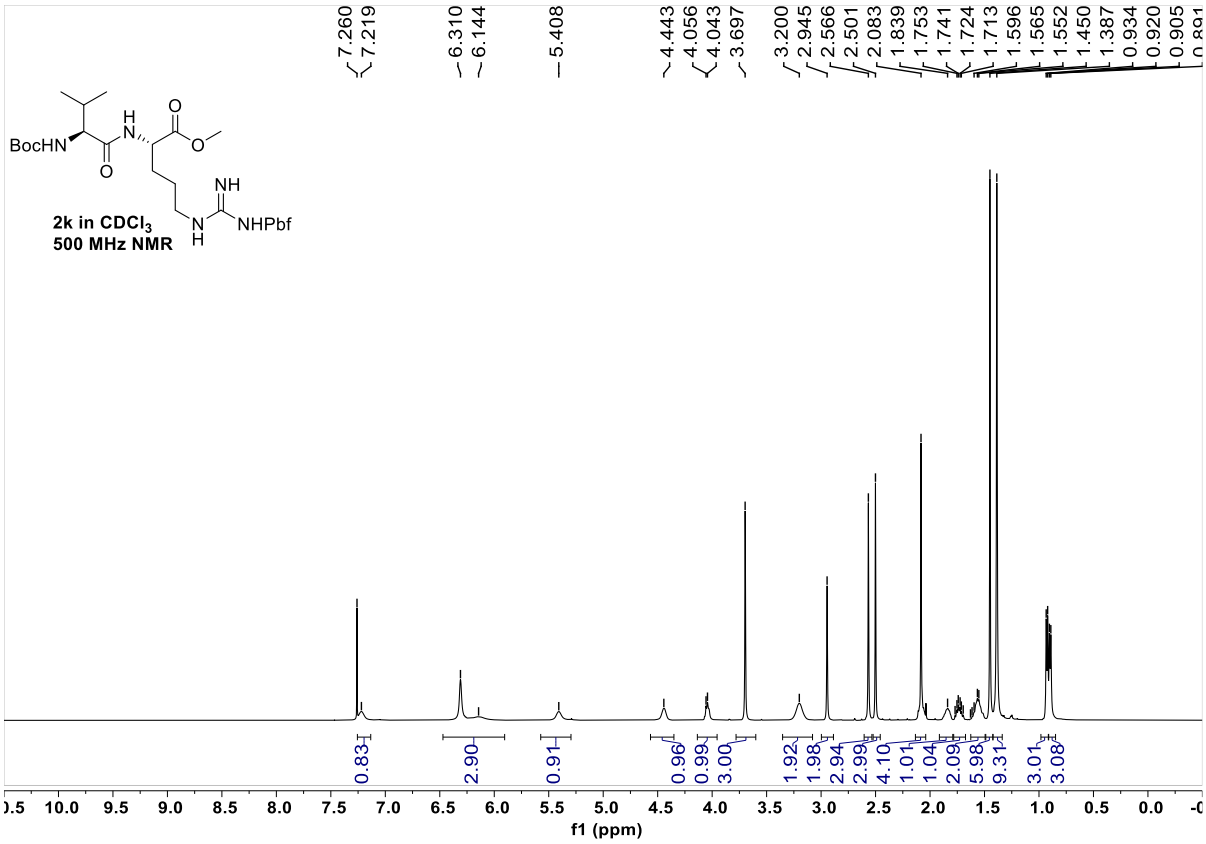
O'Bu
NHBoc
2j in CDCl3
125 MHz NMR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2.083
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1.753
1.741
1.724
1.713
1.596
1.565
1.552
1.450
1.387
0.934
0.920
0.905
BocHN
NH
NHPbf
2k in CDCl3
500 MHz NMR
0.83
2.90
0.91
0.96
0.99
3.00
1.92
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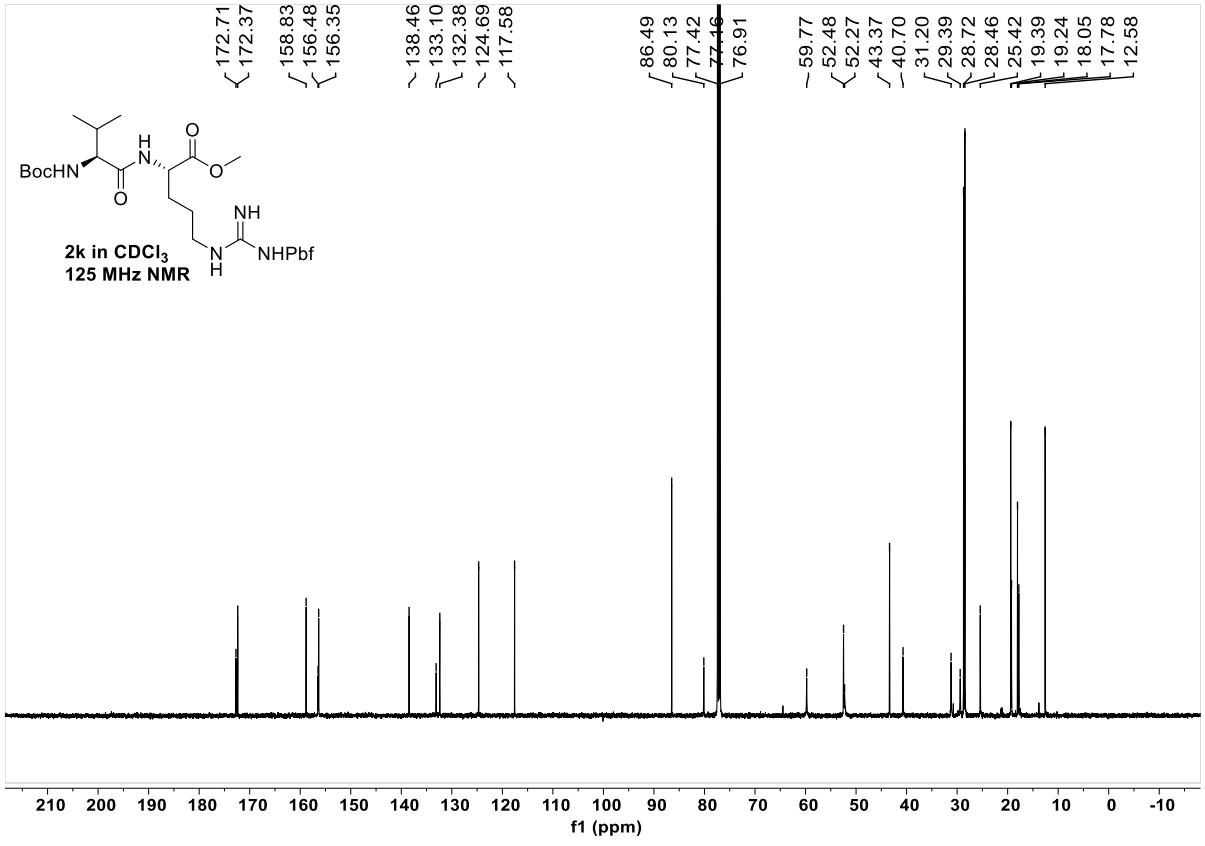
f1 (ppm)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59.77
52.48
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31.20
29.39
28.72
28.46
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NH
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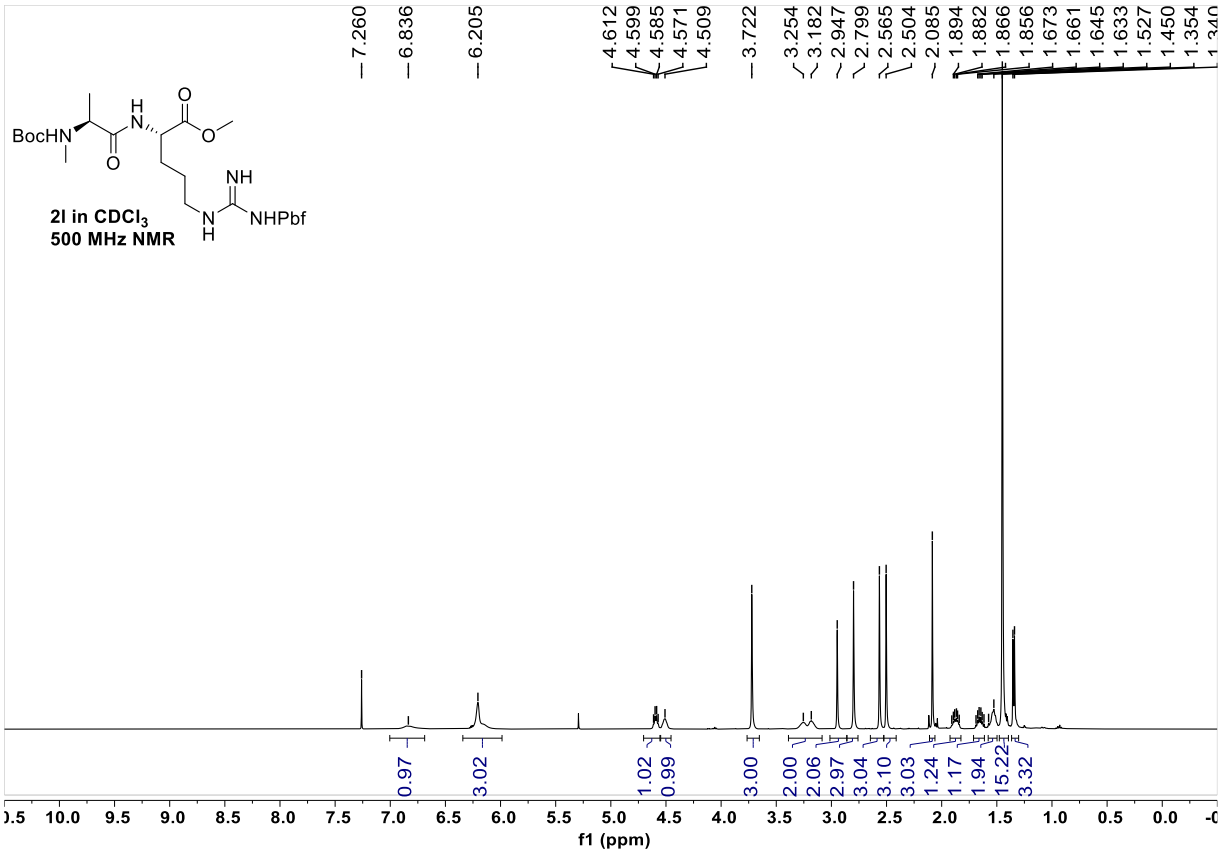
2k in CDCl3
125 MHz NMR
f1 (ppm)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1.02
0.99
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2.00
2.06
2.97
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3.32
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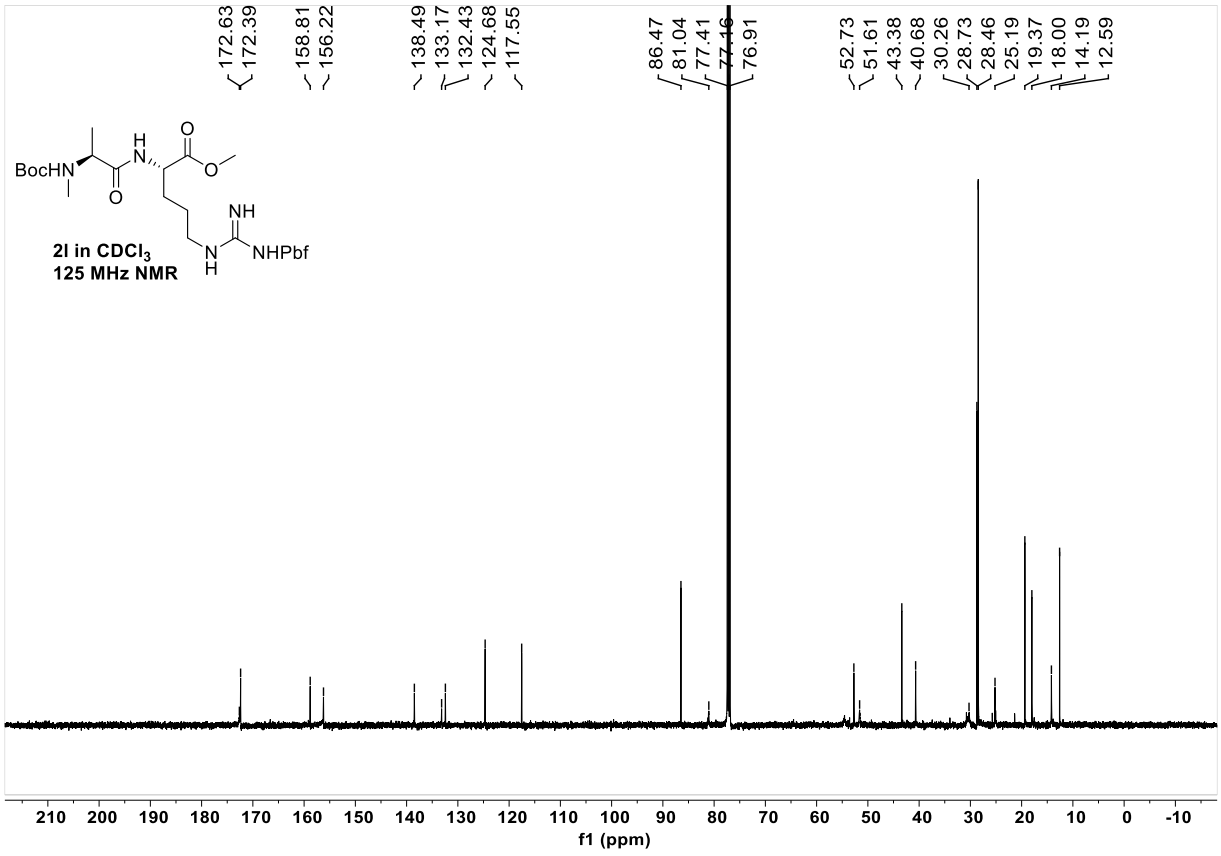
2l in CDCl3
500 MHz NMR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52.73
51.61
43.38
40.68
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25.19
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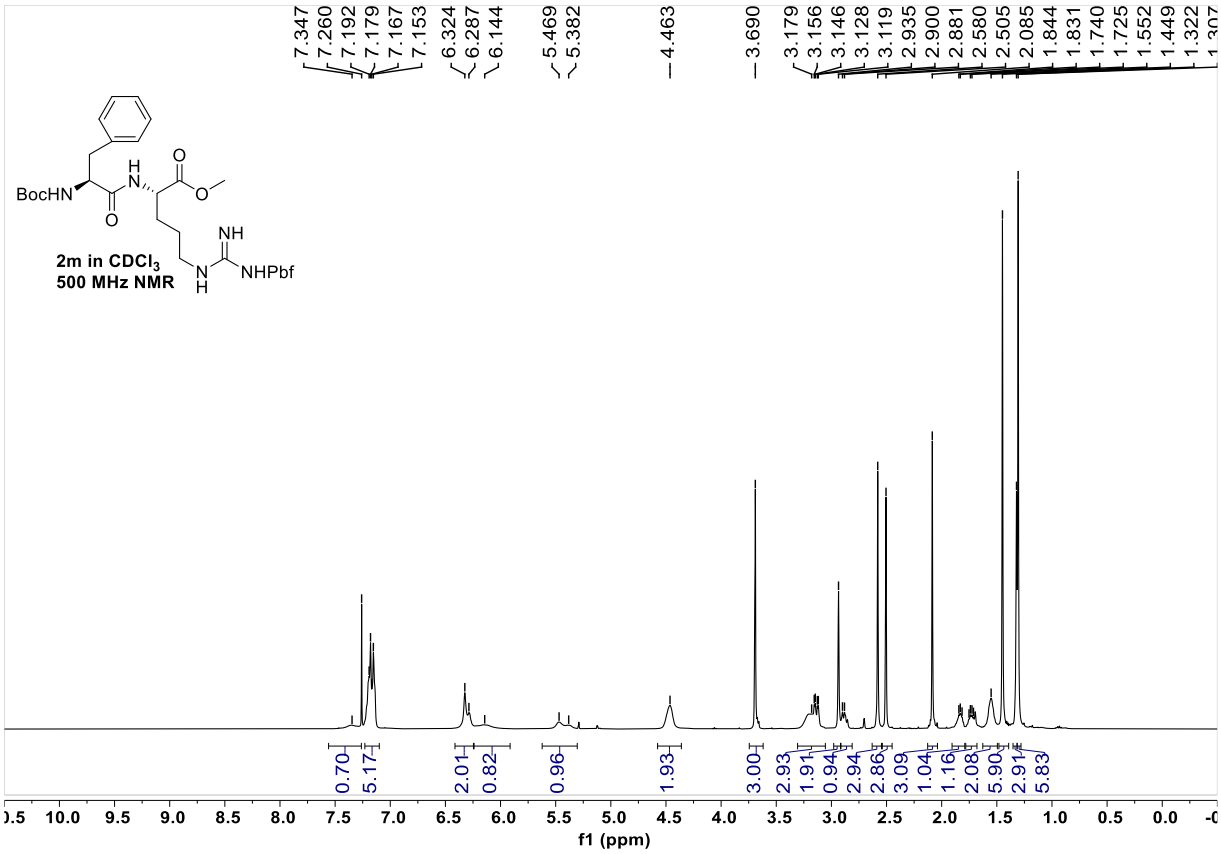
12.59
f1 (ppm)
2l in CDCl3
125 MHz NMR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1.322
BocHN
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NHPbf
2m in CDCl3
500 MHz NMR
0.70
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0.82
0.96
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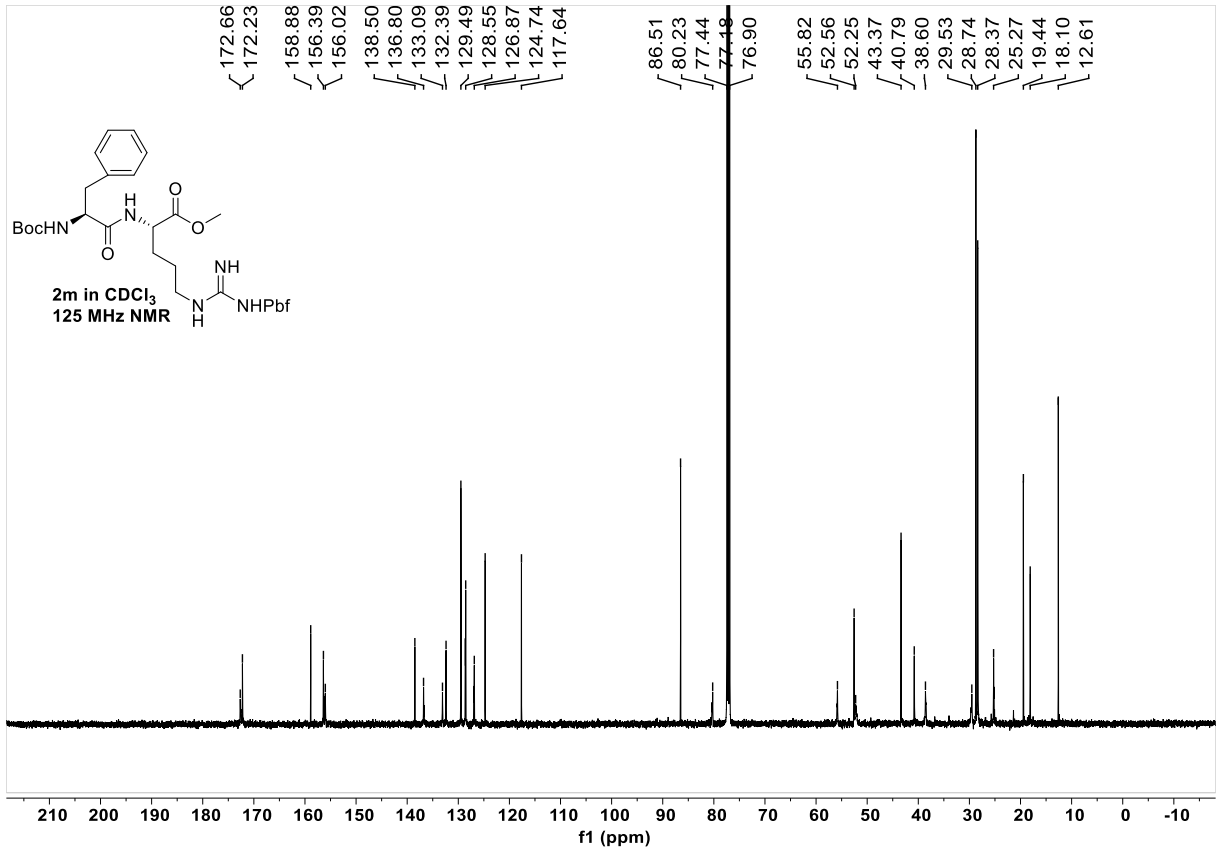
5.83
f1 (ppm)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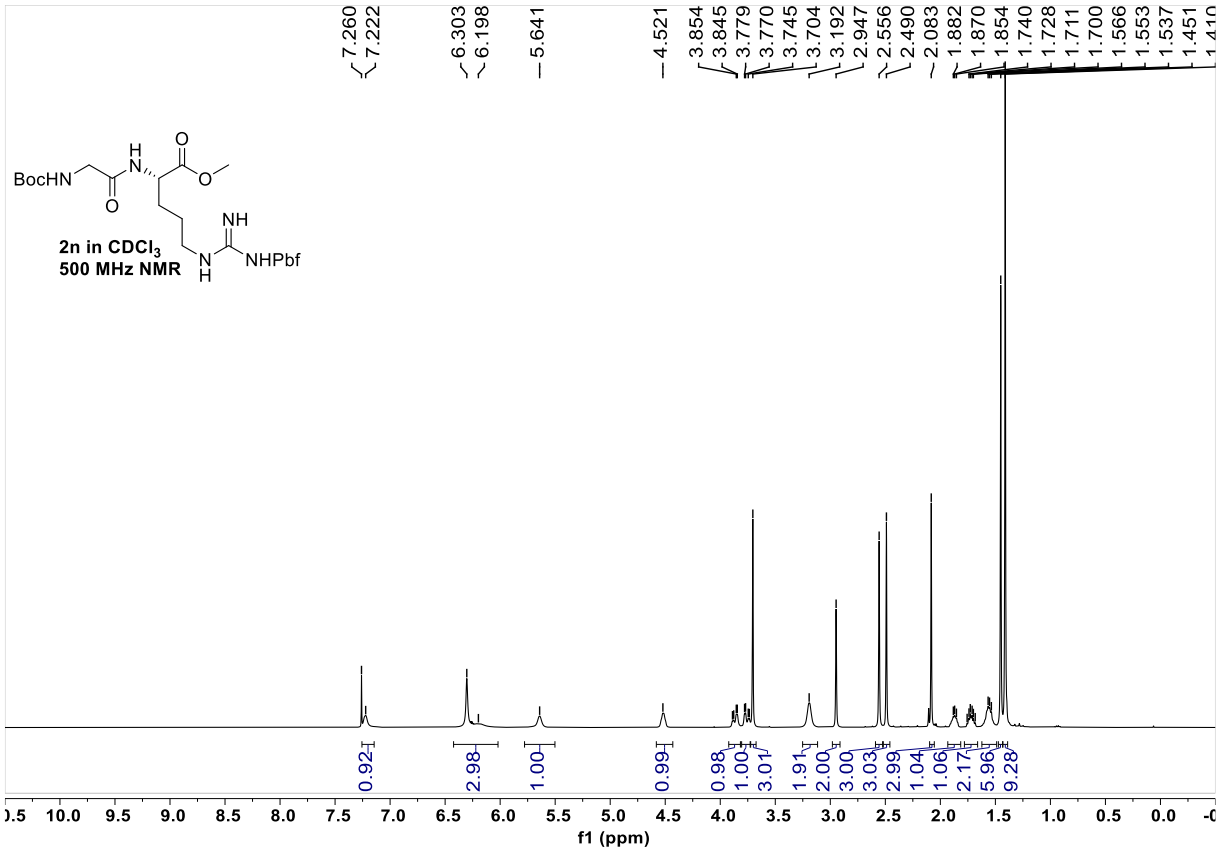
2m in CDCl3
125 MHz NMR
f1 (ppm)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1.700
1.566
1.553
1.537
1.451
BocHN
NH
NHPbf
2n in CDCl3
500 MHz NMR
0.92
2.98
1.00
0.99
0.98
1.00
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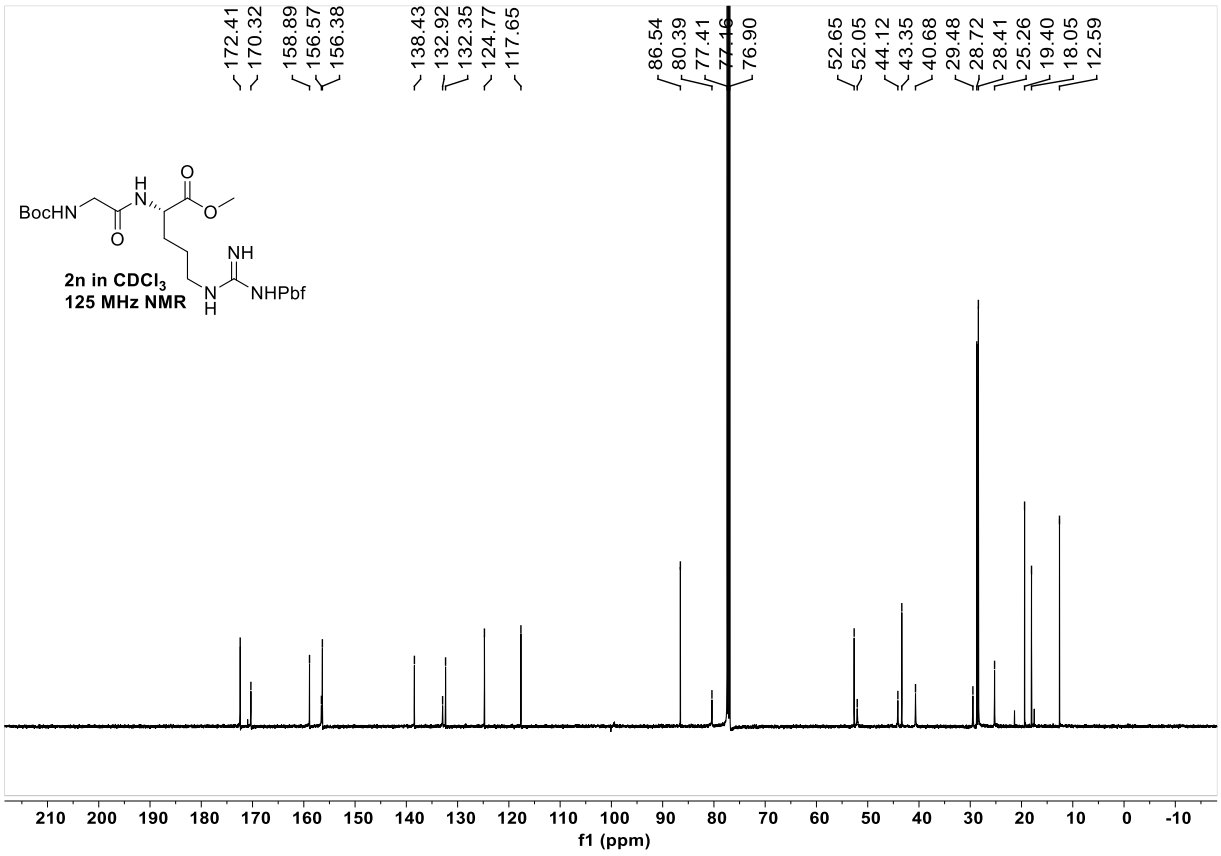
f1 (ppm)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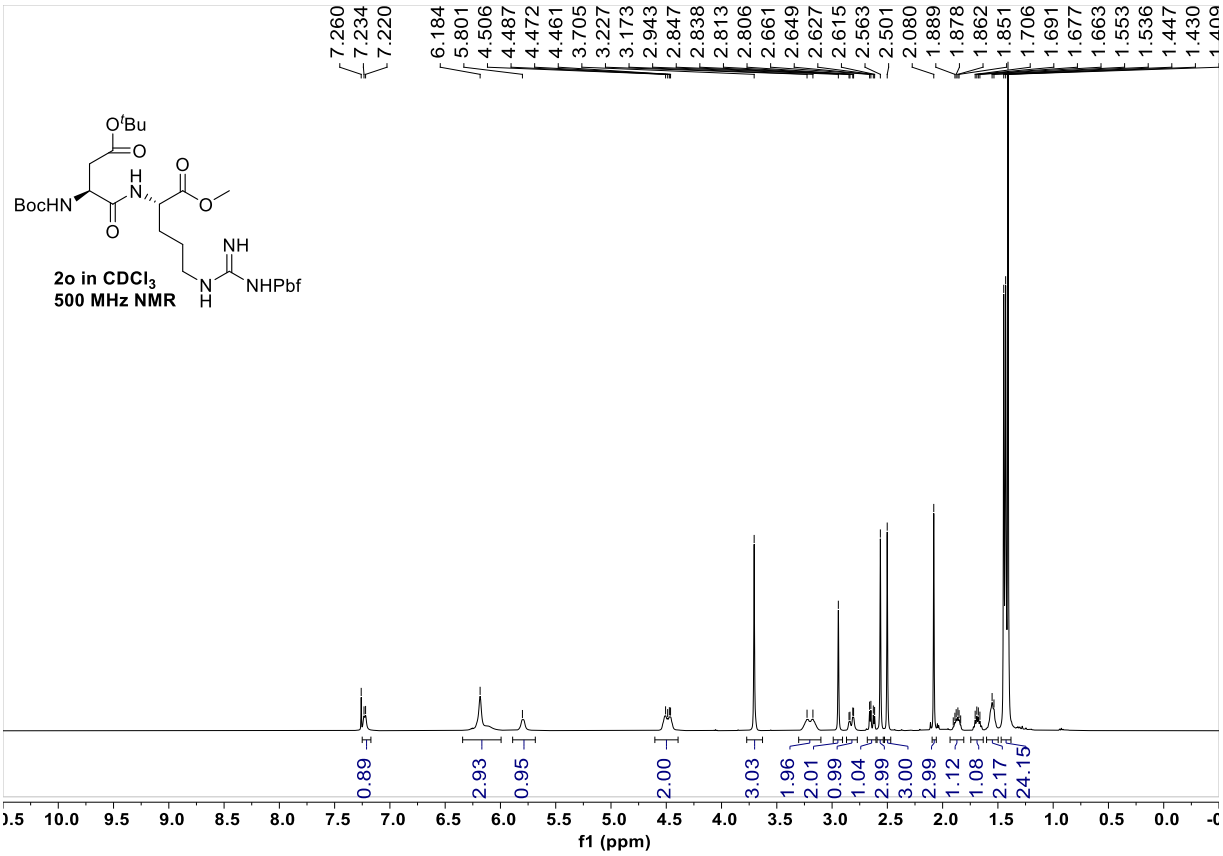
2n in CDCl3
125 MHz NMR
f1 (ppm)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O^{t}Bu
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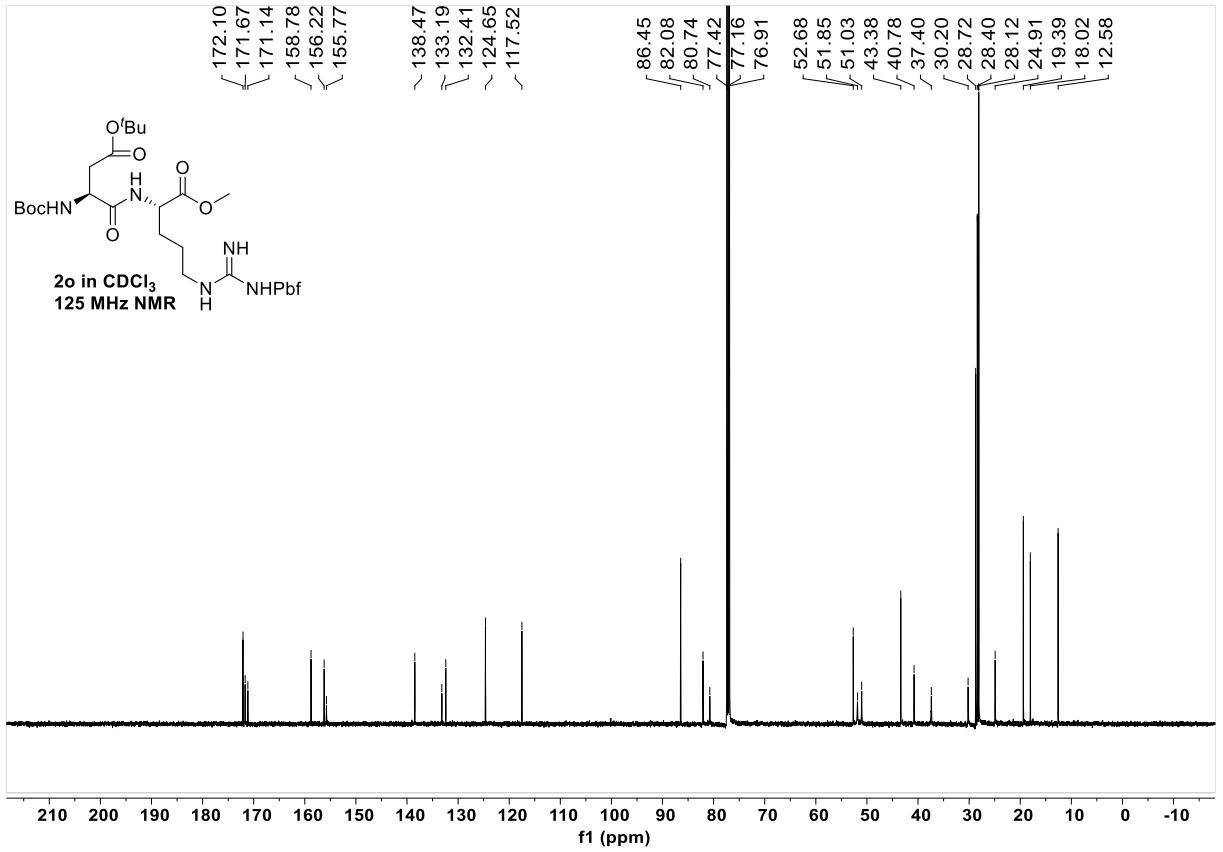
NH
NHPbf
2o in CDCl$_3$
500 MHz NMR
0.89
2.93
0.95
2.00
3.03
1.96
2.01
0.99
1.04
2.99
3.00
2.99
1.12
1.08
2.17
24.15
f1 (ppm)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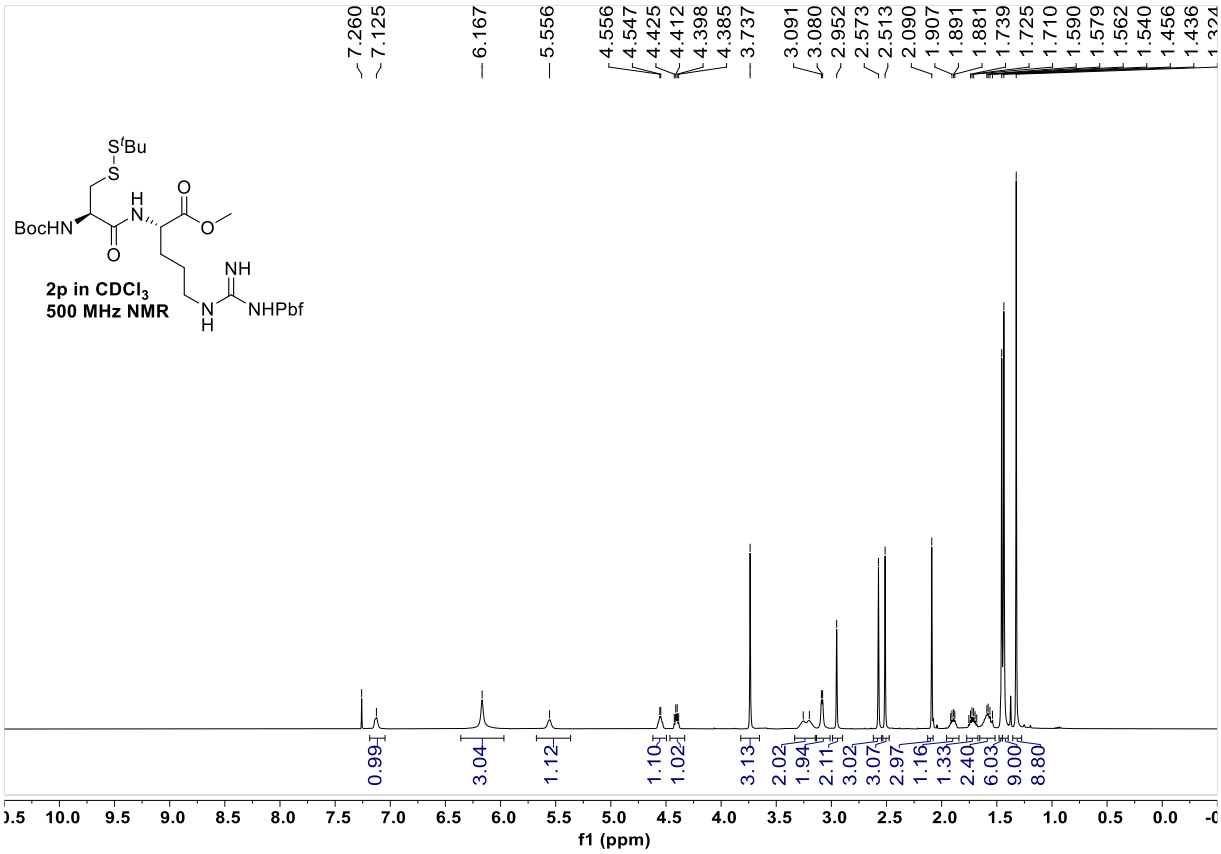
171.67
171.14
158.78
156.22
155.77
138.47
133.19
132.41
124.65
117.52
86.45
82.08
80.74
77.42
77.16
76.91
52.68
51.85
51.03
43.38
40.78
37.40
30.20
28.72
28.40
28.12
24.91
19.39
18.02
12.58
O^{t}Bu
BocHN
NH
NHPbf
2o in CDCl$_3$
125 MHz NMR
f1 (ppm)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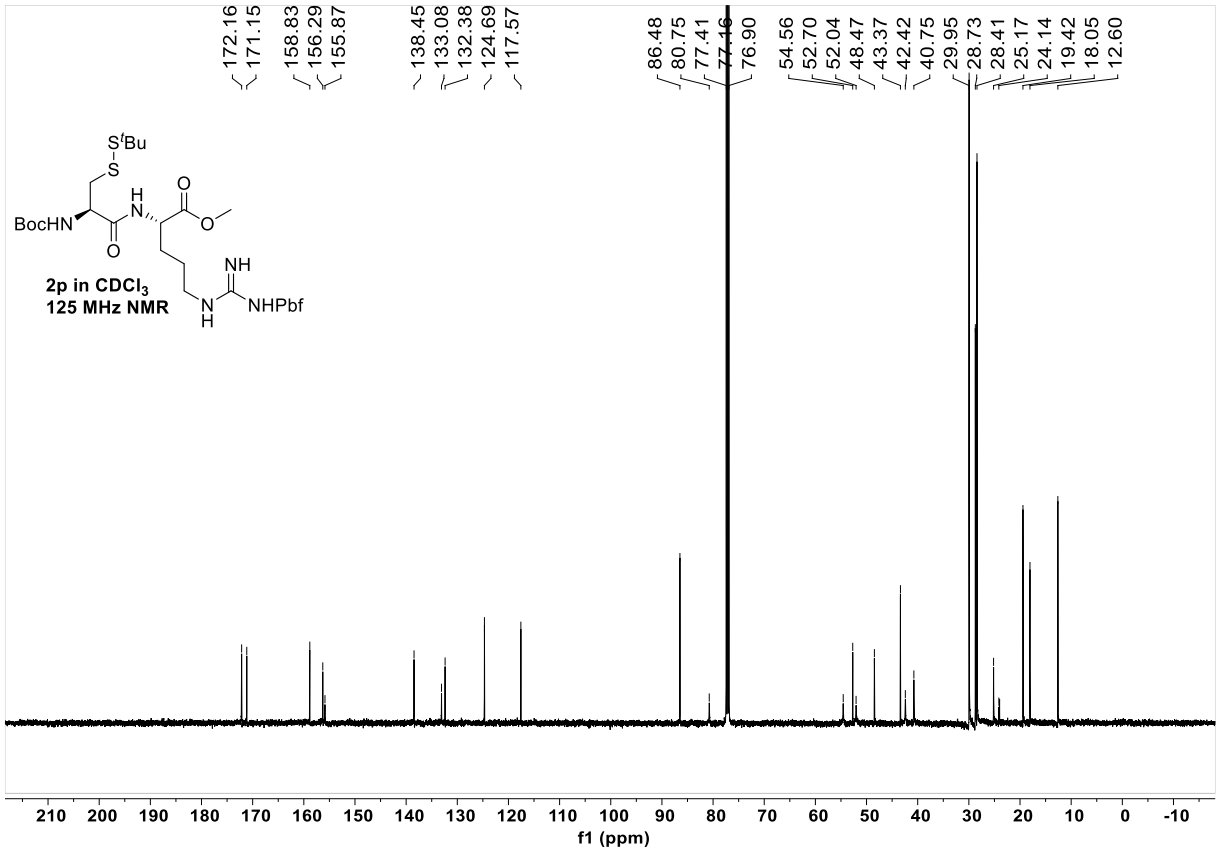
7.125
6.167
5.556
4.556
4.547
4.425
4.412
4.398
4.385
3.737
3.091
3.080
2.952
2.573
2.513
2.090
1.907
1.891
1.881
1.739
1.725
1.710
1.590
1.579
1.562
1.540
1.456
1.436
0.99
3.04
1.12
1.10
1.02
3.13
2.02
1.94
2.11
3.02
3.07
2.97
1.16
1.33
2.40
6.03
9.00
8.80
f1 (ppm)
2p in CDCl3
500 MHz NMR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158.83
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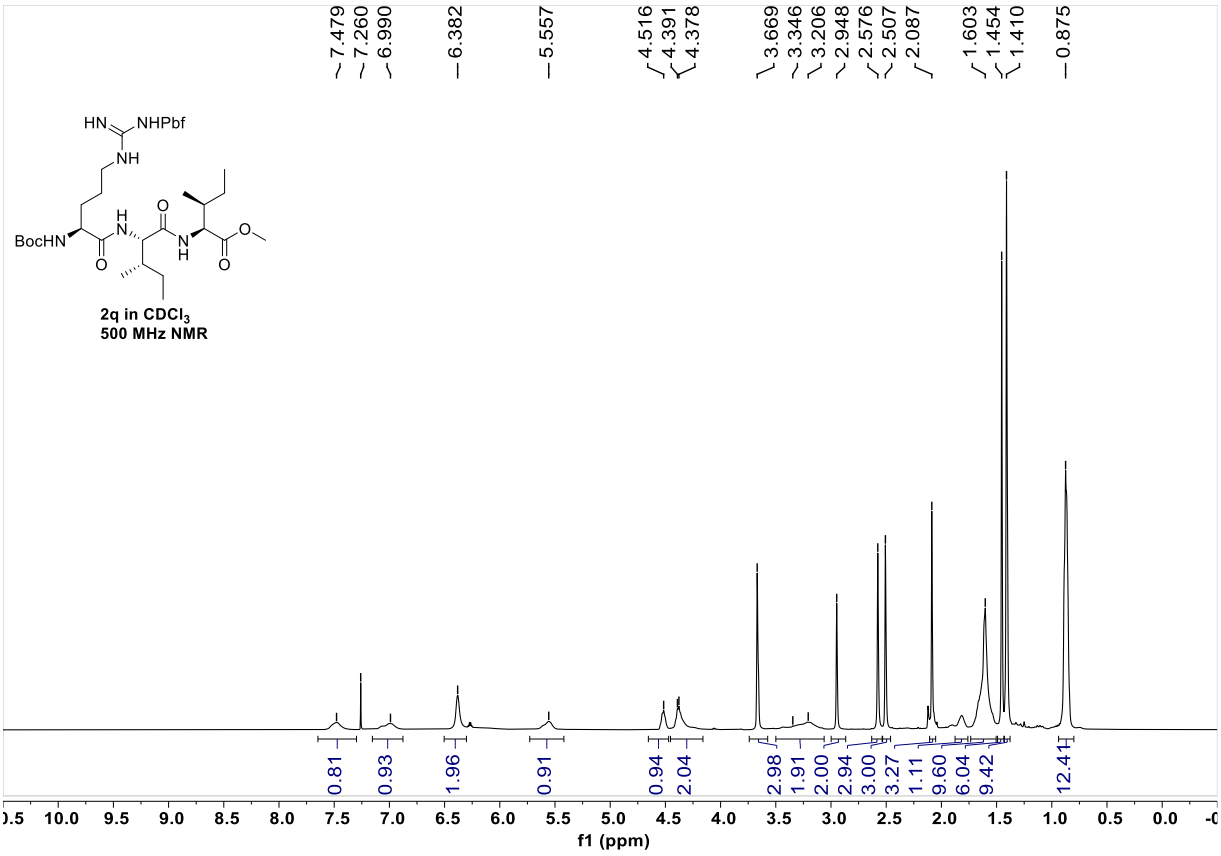
133.08
132.38
124.69
117.57
86.48
80.75
77.41
77.16
76.90
54.56
52.70
52.04
48.47
43.37
42.42
40.75
29.95
28.73
28.41
25.17
24.14
19.42
18.05
12.60
f1 (ppm)
2p in CDCl3
125 MHz NMR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4.378
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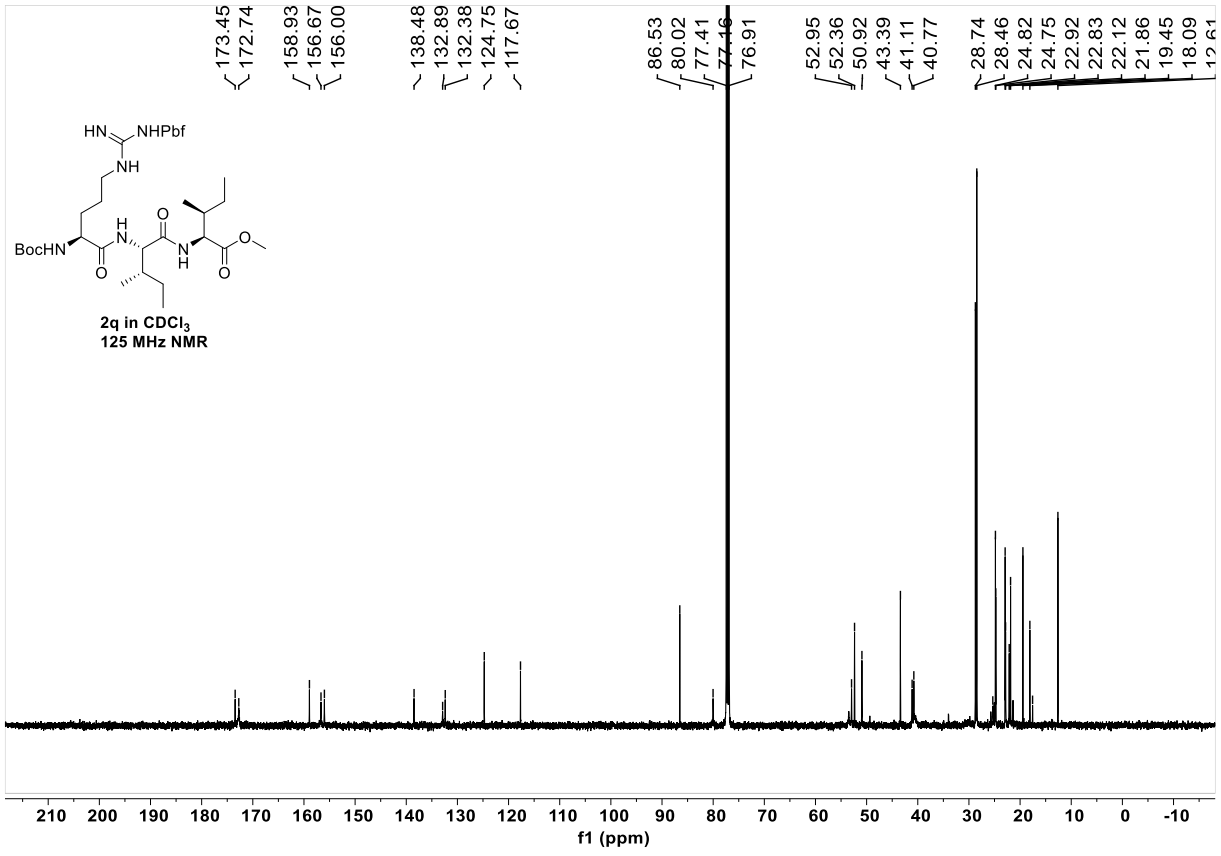
3.206
2.948
2.576
2.507
2.087
1.603
1.454
1.410
0.875
0.81
0.93
1.96
0.91
0.94
2.04
2.98
1.91
2.00
2.94
3.00
3.27
1.11
9.60
6.04
9.42
12.41
f1 (ppm)
2q in CDCl3
500 MHz NMR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158.93
156.67
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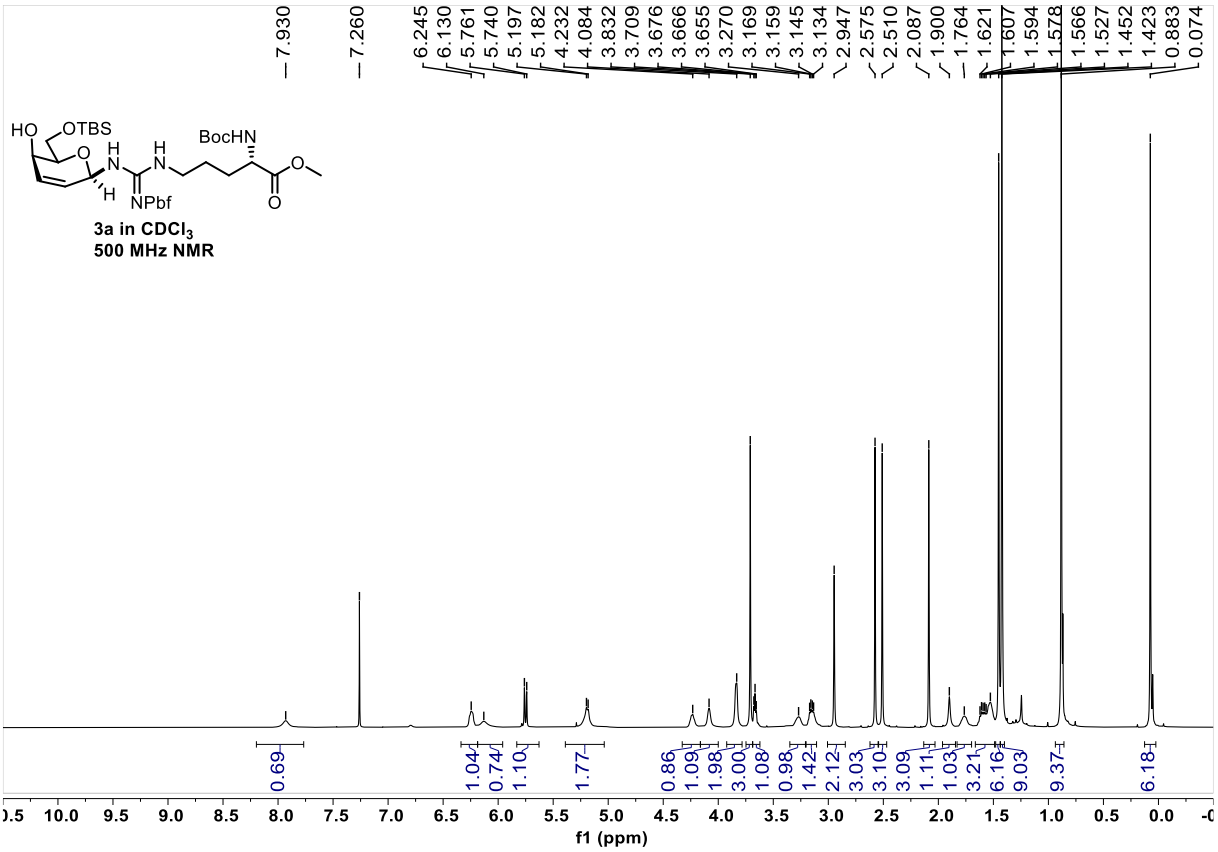
132.89
132.38
124.75
117.67
86.53
80.02
77.41
77.16
76.91
52.95
52.36
50.92
43.39
41.11
40.77
28.74
28.46
24.82
24.75
22.92
22.83
22.12
21.86
19.45
18.09
f1 (ppm)
2q in CDCl3
125 MHz NMR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6.245
6.130
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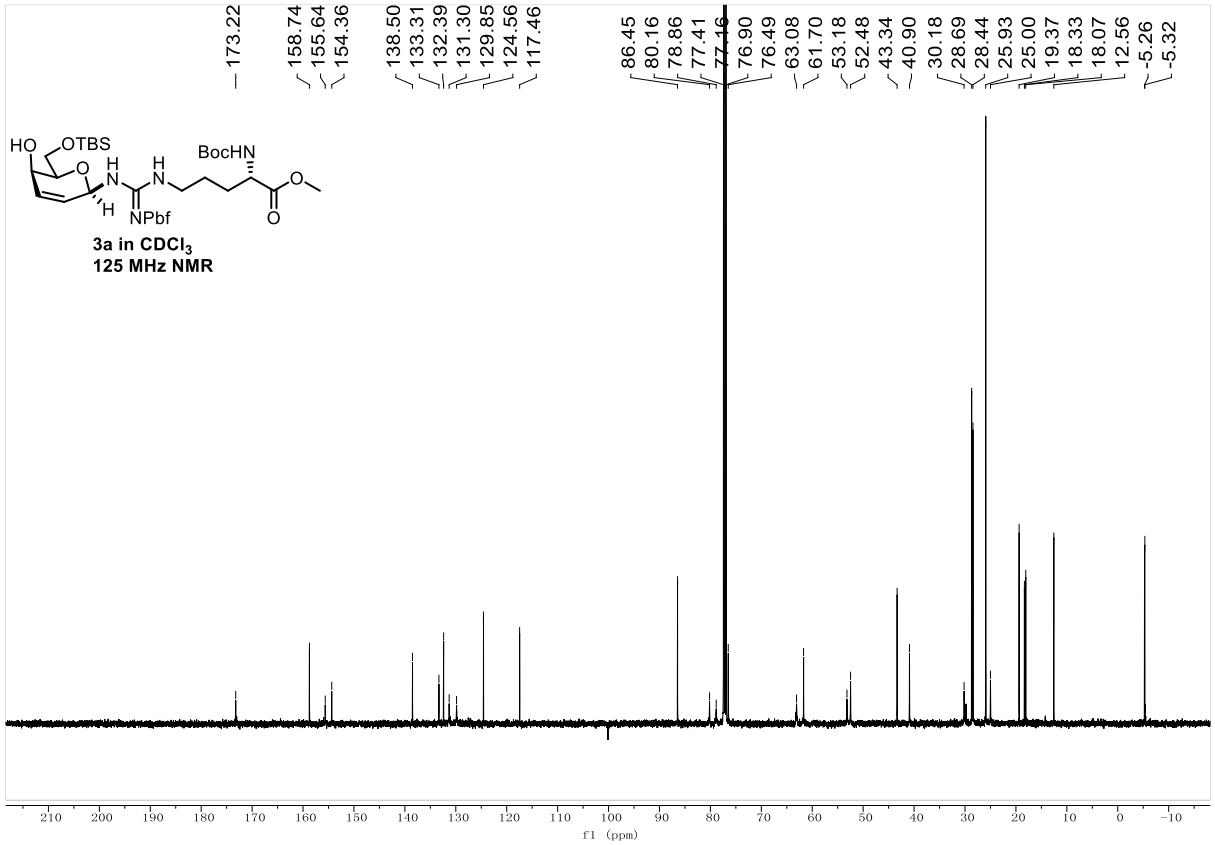
5.740
5.197
5.182
4.232
4.084
3.832
3.709
3.676
3.666
3.655
3.270
3.169
3.159
3.145
3.134
2.947
2.575
2.510
2.087
1.900
1.764
1.621
1.607
1.594
1.578
1.566
1.527
1.452
1.423
0.883
0.074
HO
OTBS
BocHN
NPbf
3a in CDCl3
500 MHz NMR
0.69
1.04
0.74
1.10
1.77
0.86
1.09
1.98
3.00
1.08
0.98
1.42
2.12
3.03
3.10
3.09
1.11
1.03
3.21
6.16
9.03
9.37
6.18
f1 (ppm)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158.74
155.64
154.36
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133.31
132.39
131.30
129.85
124.56
117.46
86.45
80.16
78.86
77.41
77.16
76.90
76.49
63.08
61.70
53.18
52.48
43.34
40.90
30.18
28.69
28.44
25.93
25.00
19.37
18.33
18.07
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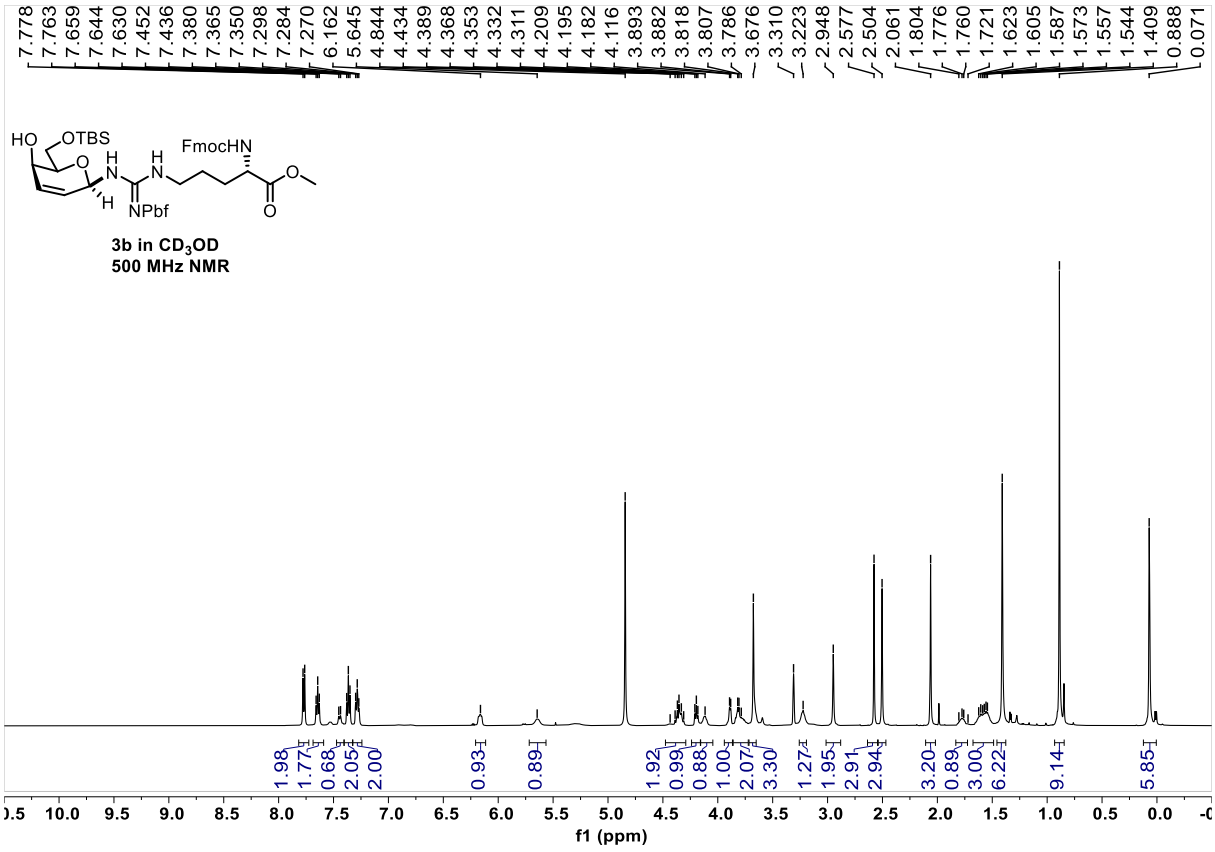
-5.26
-5.32
HO
OTBS
BocHN
NPbf
3a in CDCl3
125 MHz NMR
f1 (ppm)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7.630
7.452
7.436
7.380
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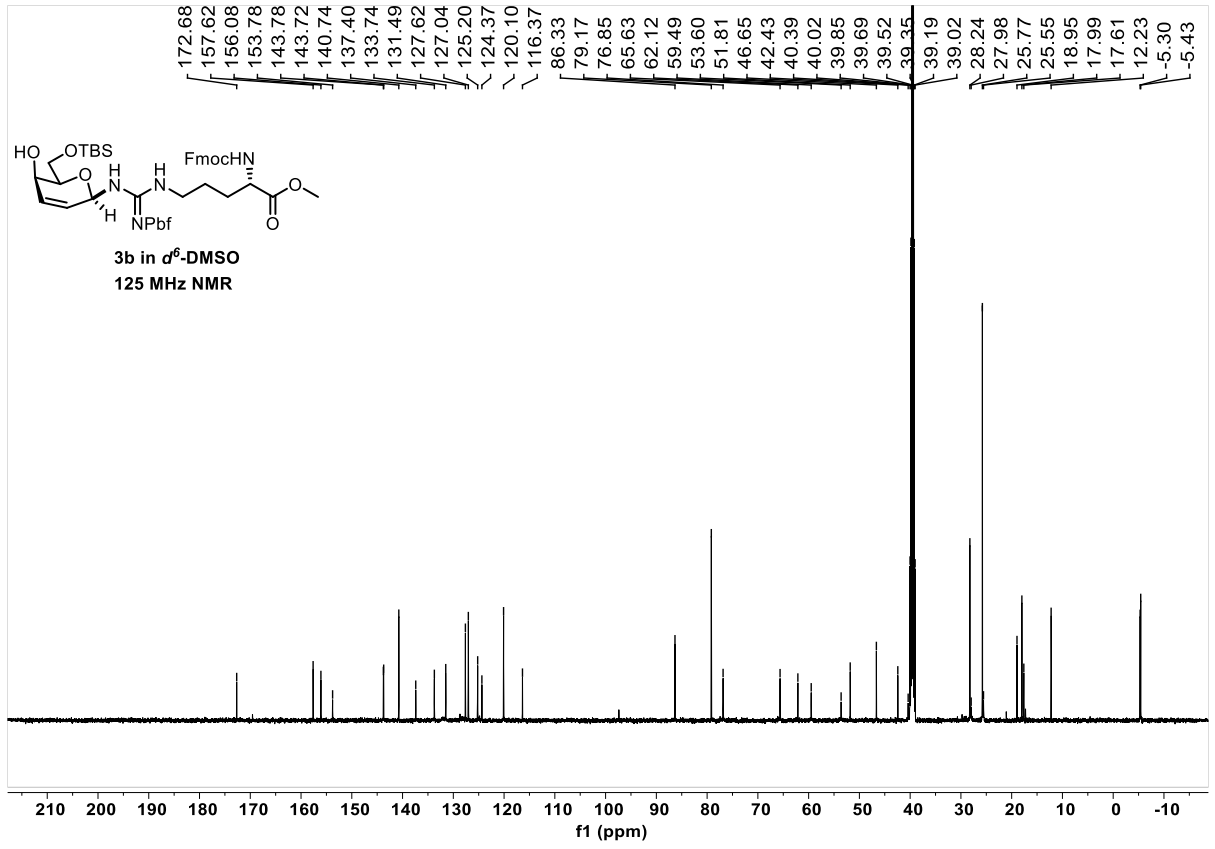
7.350
7.298
7.284
7.270
6.162
5.645
4.844
4.434
4.389
4.368
4.353
4.332
4.311
4.209
4.195
4.182
4.116
3.893
3.882
3.818
3.807
3.786
3.676
3.310
3.223
2.948
2.577
2.504
2.061
1.804
1.776
1.760
1.721
1.623
1.605
1.587
1.573
1.557
1.544
1.409
0.888
0.071
HO
OTBS
O
H
N
H
N
FmocHN
O
O
H
NPbf
3b in CD3OD
500 MHz NMR
1.98
1.77
0.68
2.05
2.00
0.93
0.89
1.92
0.99
0.88
1.00
2.07
3.30
1.27
1.95
2.91
2.94
3.20
0.89
3.00
6.22
9.14
5.85
f1 (ppm)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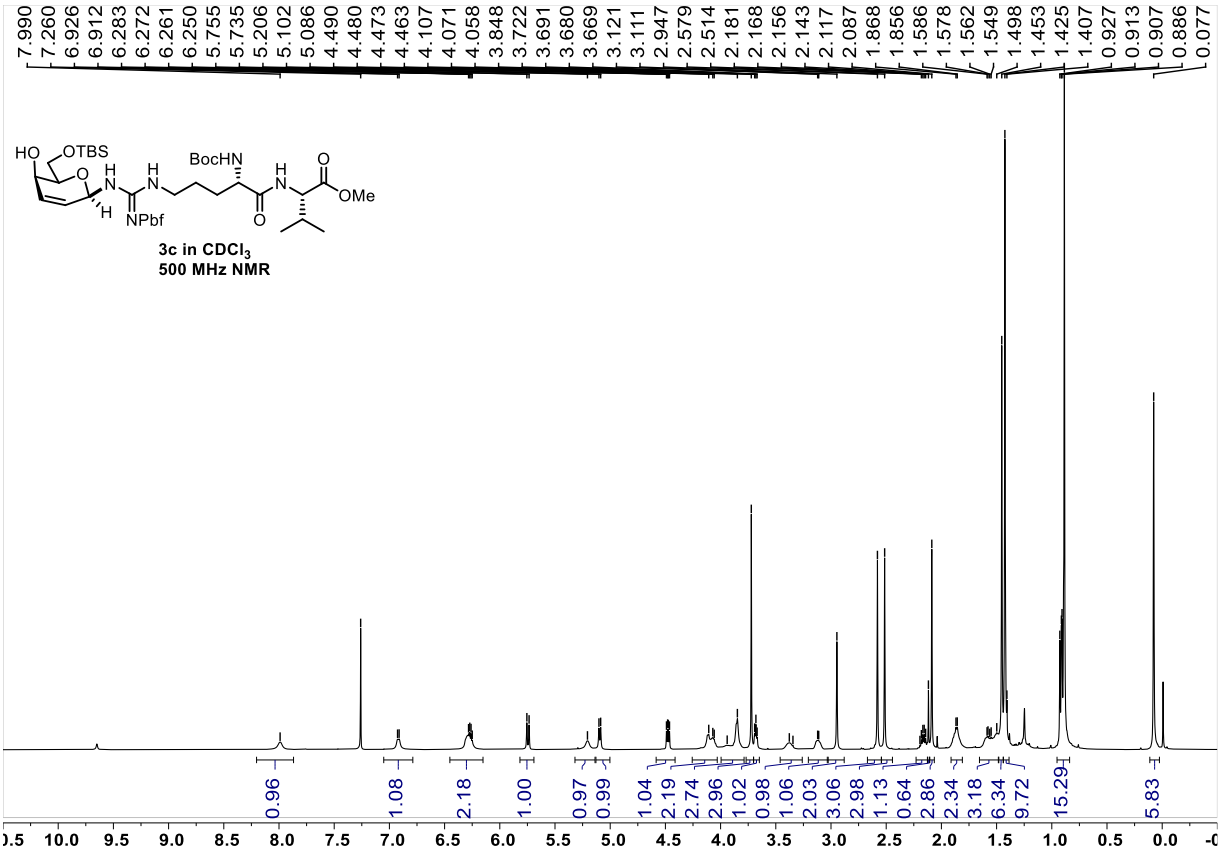
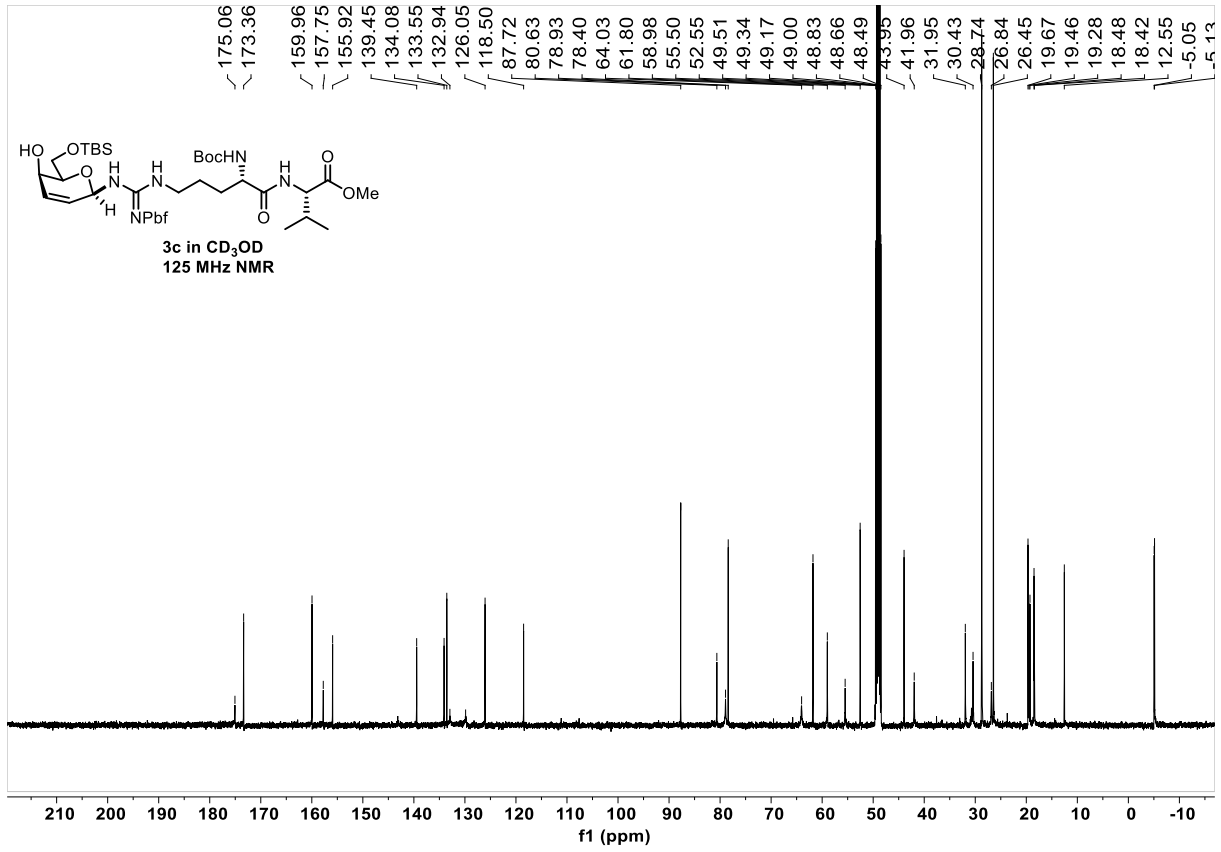
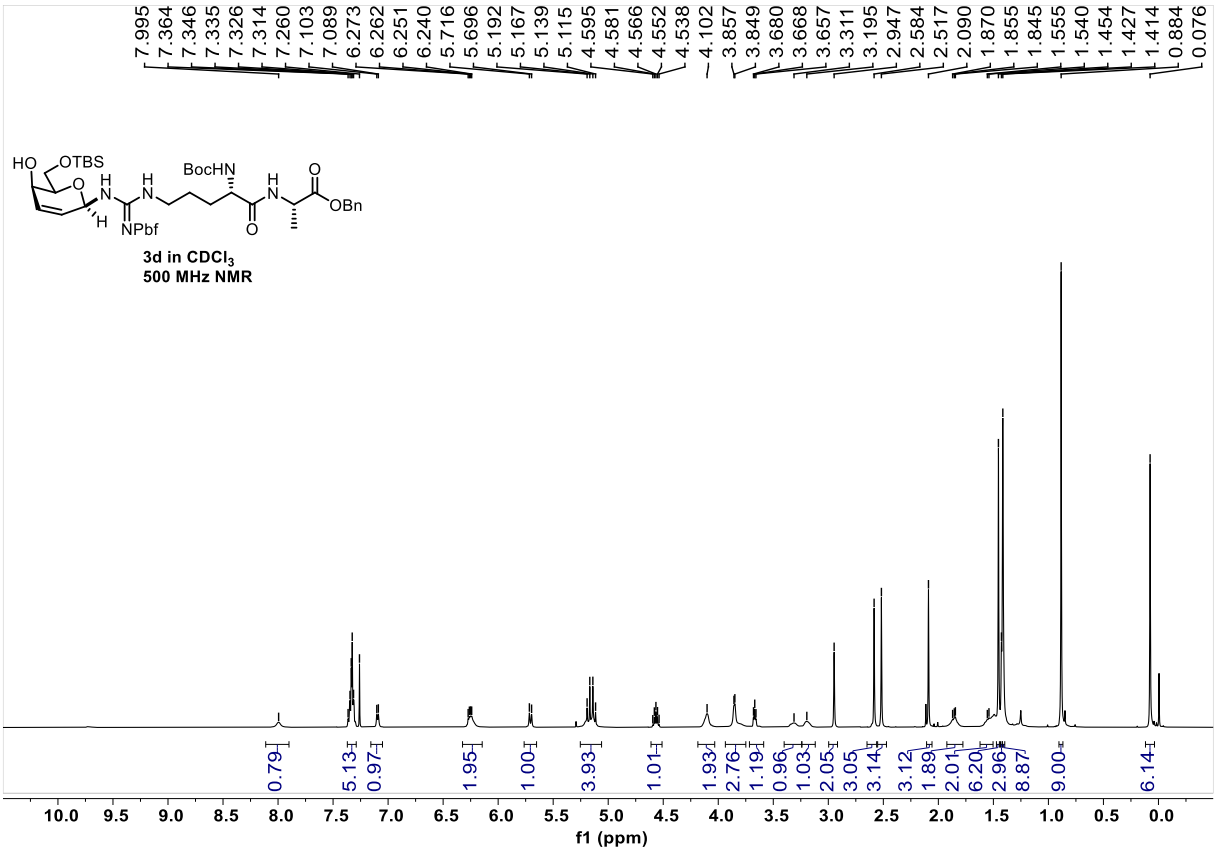
157.62
156.08
153.78
143.78
143.72
140.74
137.40
133.74
131.49
127.62
127.04
125.20
124.37
120.10
116.37
86.33
79.17
76.85
65.63
62.12
59.49
53.60
51.81
46.65
42.43
40.39
40.02
39.85
39.69
39.52
39.35
39.19
39.02
28.24
27.98
25.77
25.55
18.95
17.99
17.61
12.23
-5.30
-5.43
HO
OTBS
O
H
N
H
N
FmocHN
O
O
H
NPbf
3b in d6-DMSO
125 MHz NMR
f1 (ppm)


3c in CDCl3
500 MHz NMR


3c in CD3OD
125 MHz NMR
f1 (ppm)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7.364
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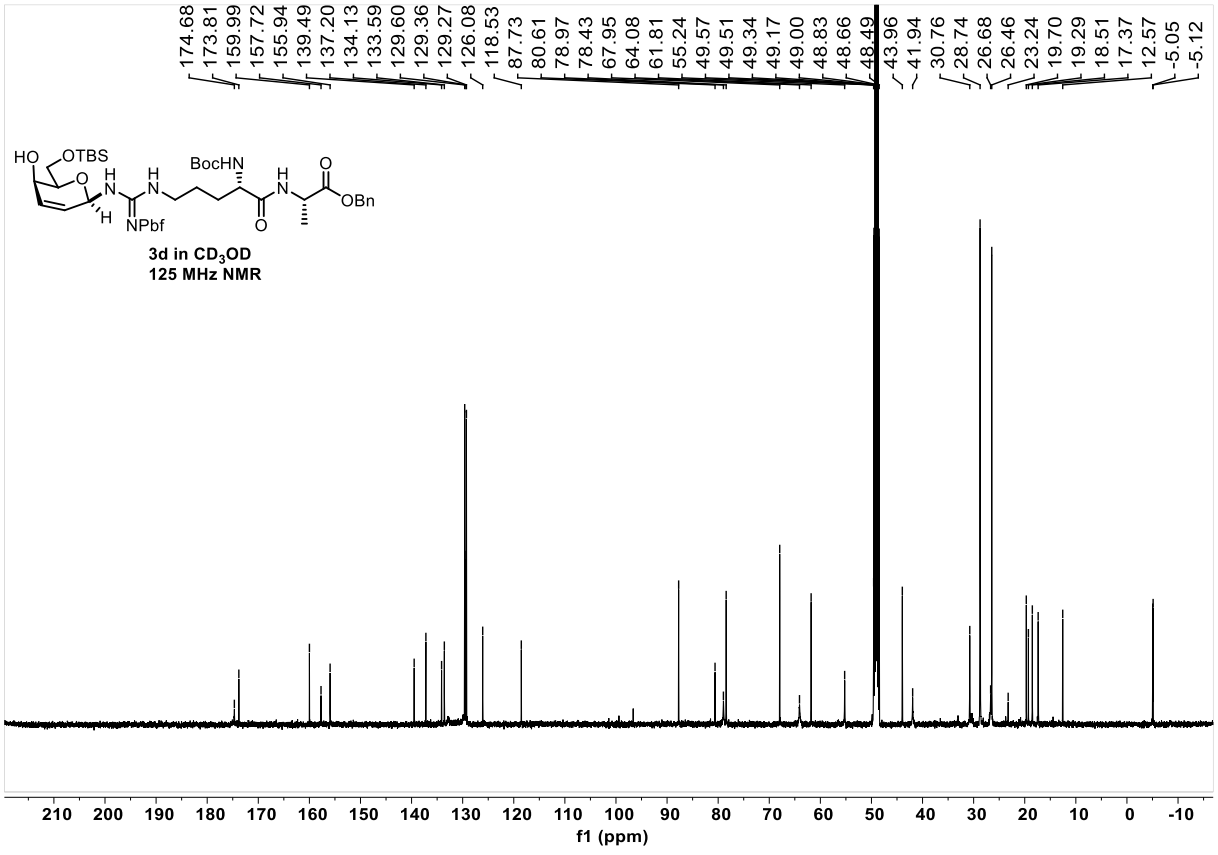
7.335
7.326
7.314
7.260
7.103
7.089
6.273
6.262
6.251
6.240
5.716
5.696
5.192
5.167
5.139
5.115
4.595
4.581
4.566
4.552
4.538
4.102
3.857
3.849
3.680
3.668
3.657
3.311
3.195
2.947
2.584
2.517
2.090
1.870
1.855
1.845
1.555
1.540
1.454
1.427
1.414
0.884
0.076
HO
OTBS
BocHN
OBn
NPbf
3d in CDCl3
500 MHz NMR
0.79
5.13
0.97
1.95
1.00
3.93
1.01
1.93
2.76
1.19
0.96
1.03
2.05
3.05
3.14
3.12
1.89
2.01
6.20
2.96
8.87
9.00
6.14
f1 (ppm)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173.81
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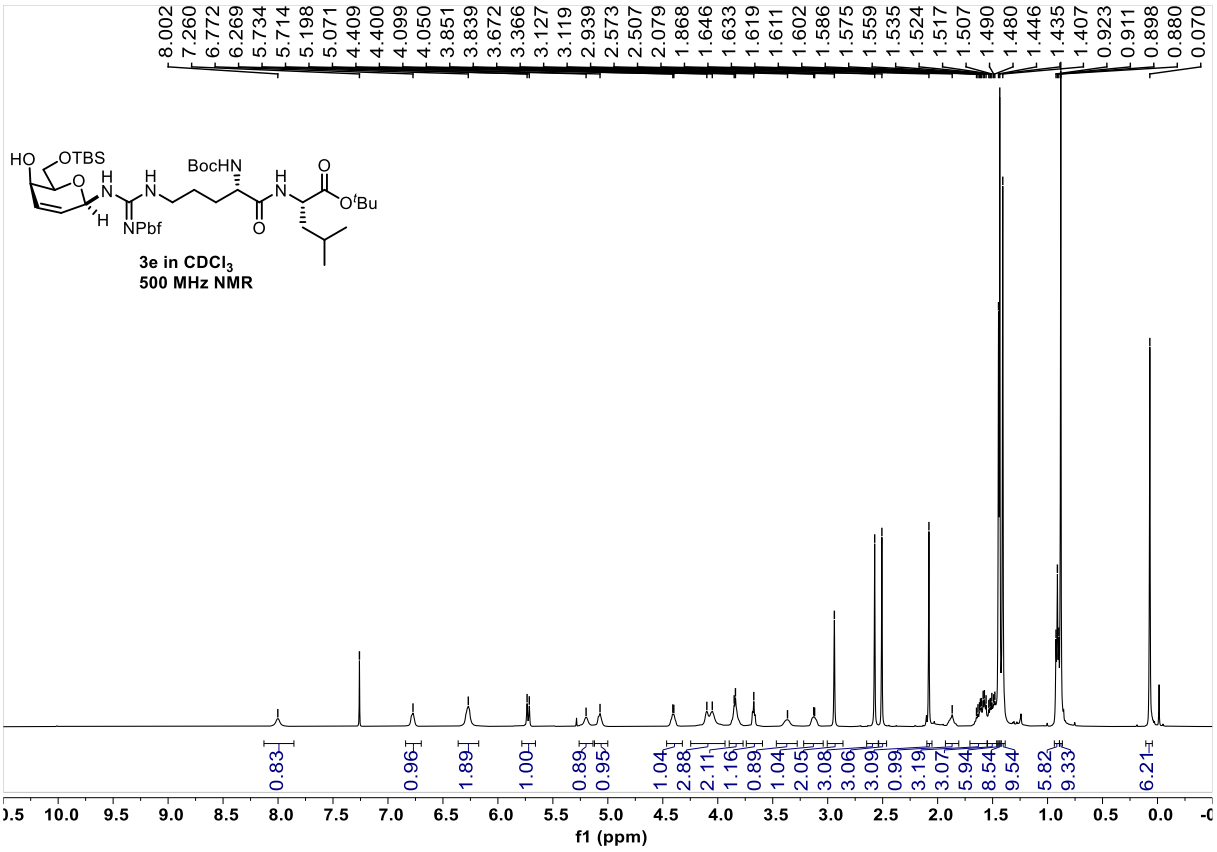
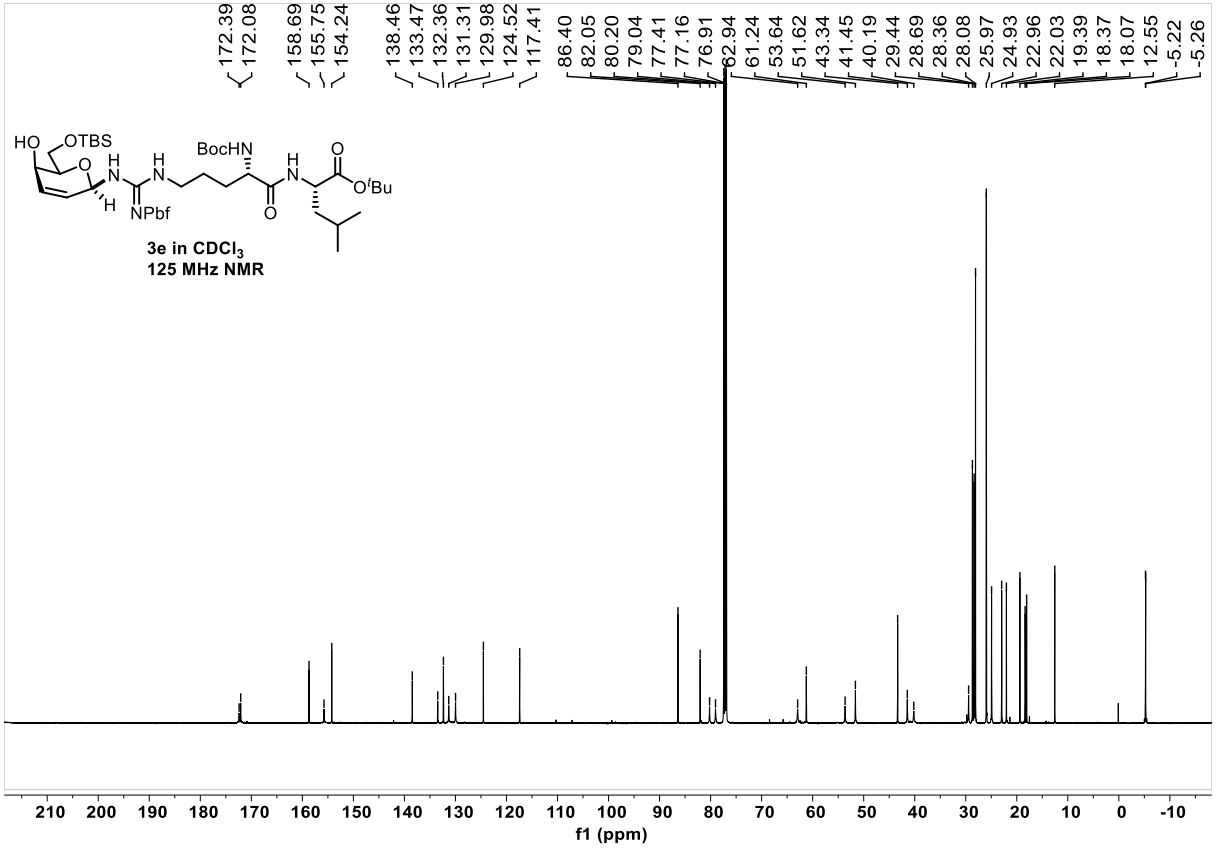
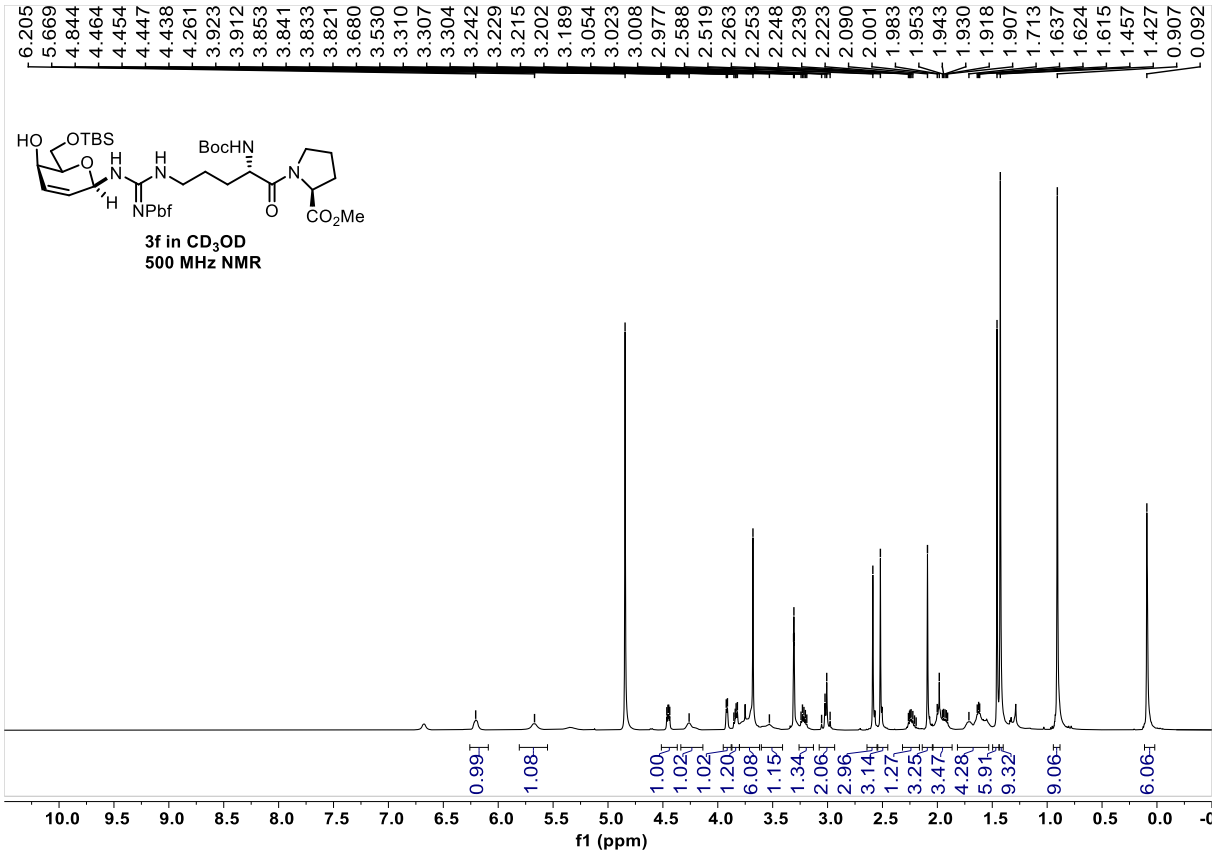
157.72
155.94
139.49
137.20
134.13
133.59
129.60
129.36
129.27
126.08
118.53
87.73
80.61
78.97
78.43
67.95
64.08
61.81
55.24
49.57
49.51
49.34
49.17
49.00
48.83
48.66
48.49
43.96
41.94
30.76
28.74
26.68
26.46
23.24
19.70
19.29
18.51
17.37
12.57
-5.05
-5.12
HO
OTBS
BocHN
OBn
NPbf
3d in CD3OD
125 MHz NMR
f1 (ppm)


3e in CDCl3
500 MHz NMR
f1 (ppm)


3e in CDCl3
125 MHz NMR
f1 (ppm)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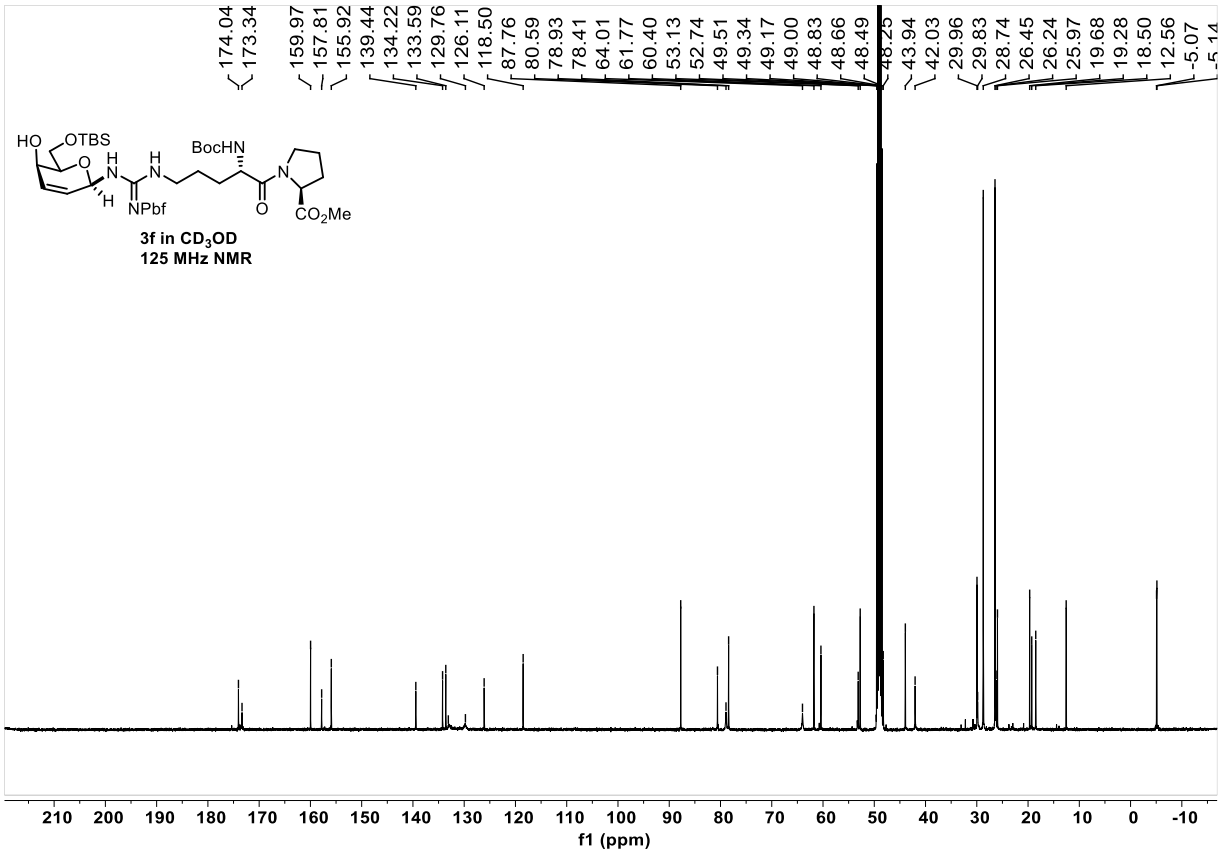
4.464
4.454
4.447
4.438
4.261
3.923
3.912
3.853
3.841
3.833
3.821
3.680
3.530
3.310
3.307
3.304
3.242
3.229
3.215
3.202
3.189
3.054
3.023
3.008
2.977
2.588
2.519
2.263
2.253
2.248
2.239
2.223
2.090
2.001
1.983
1.953
1.943
1.930
1.918
1.907
1.713
1.637
1.624
1.615
1.457
1.427
0.907
0.092
HO
OTBS
O
H
N
H
N
H
NPbf
BocHN
O
N
CO2Me
3f in CD3OD
500 MHz NMR
0.99
1.08
1.00
1.02
1.02
1.20
6.08
1.15
1.34
2.06
2.96
3.14
1.27
3.25
3.47
4.28
5.91
9.32
9.06
6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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173.34
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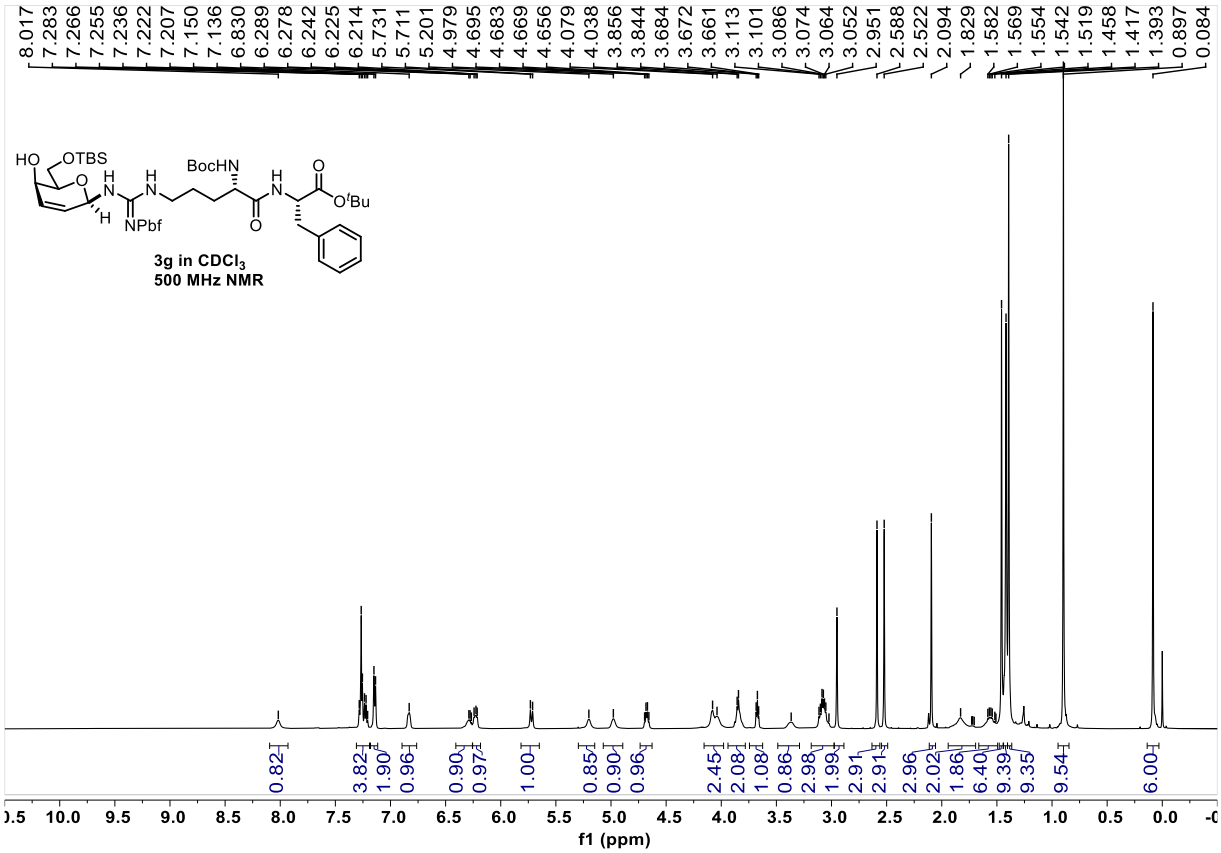
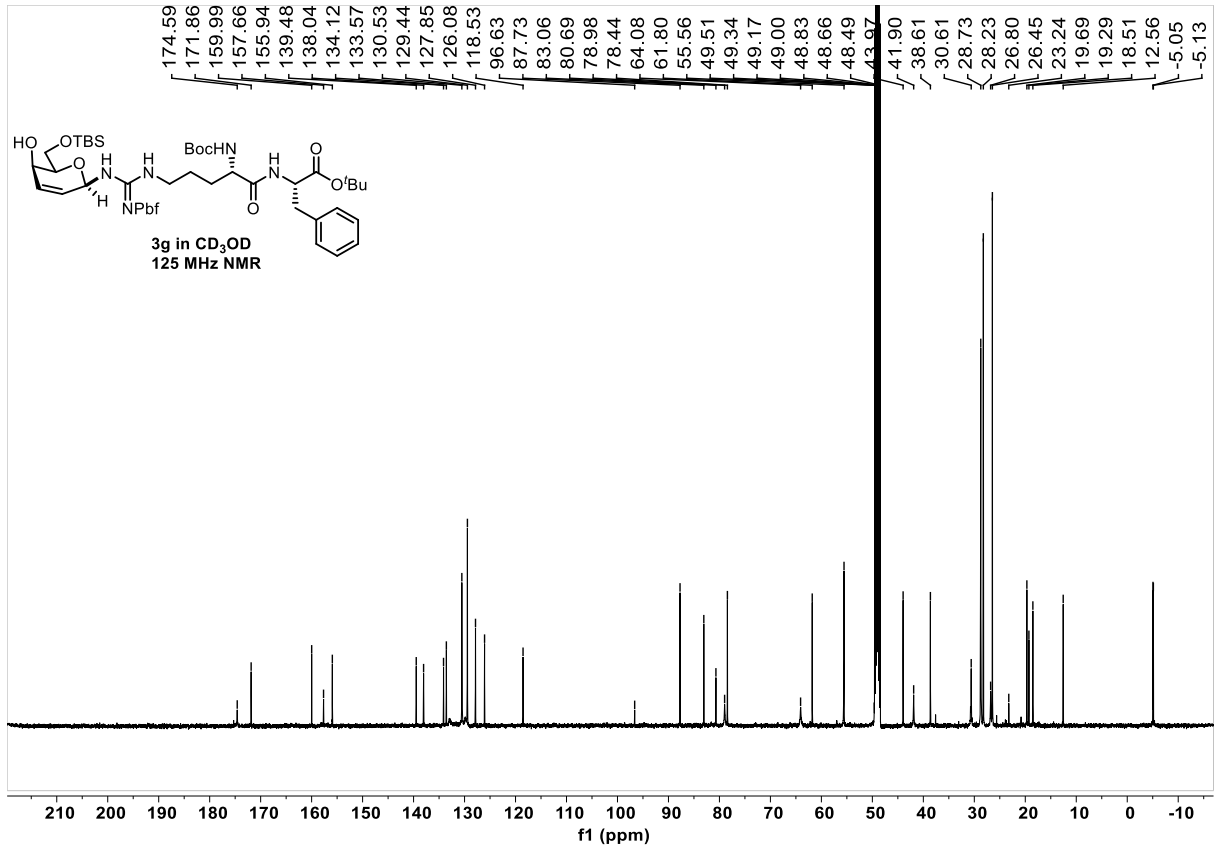
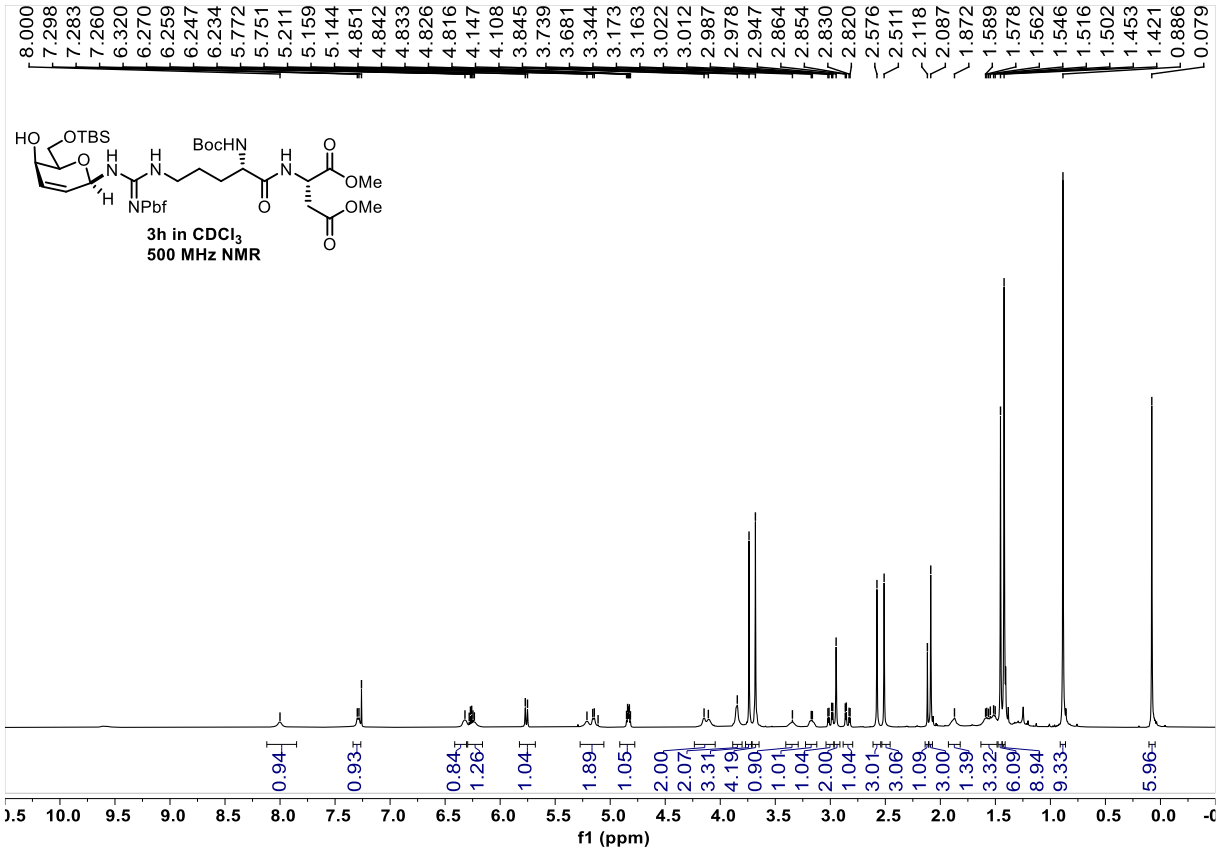
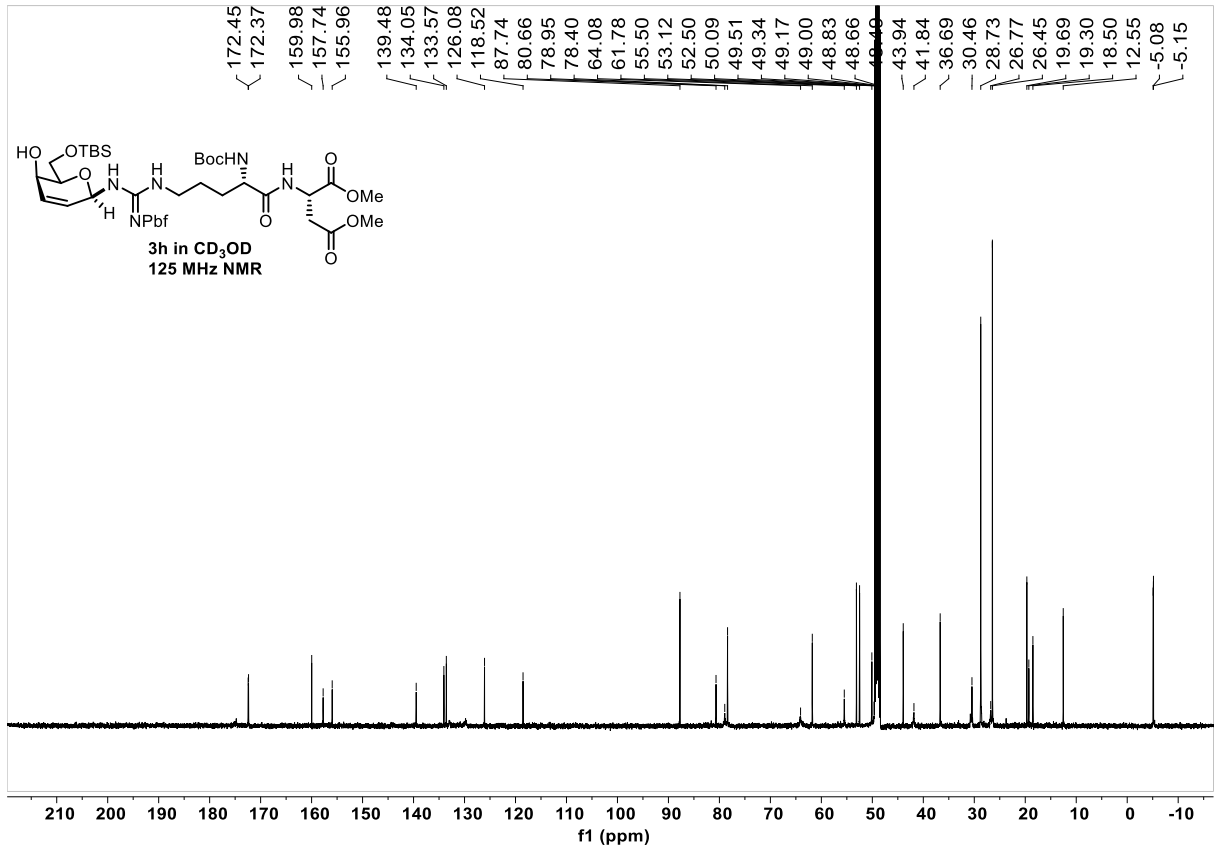
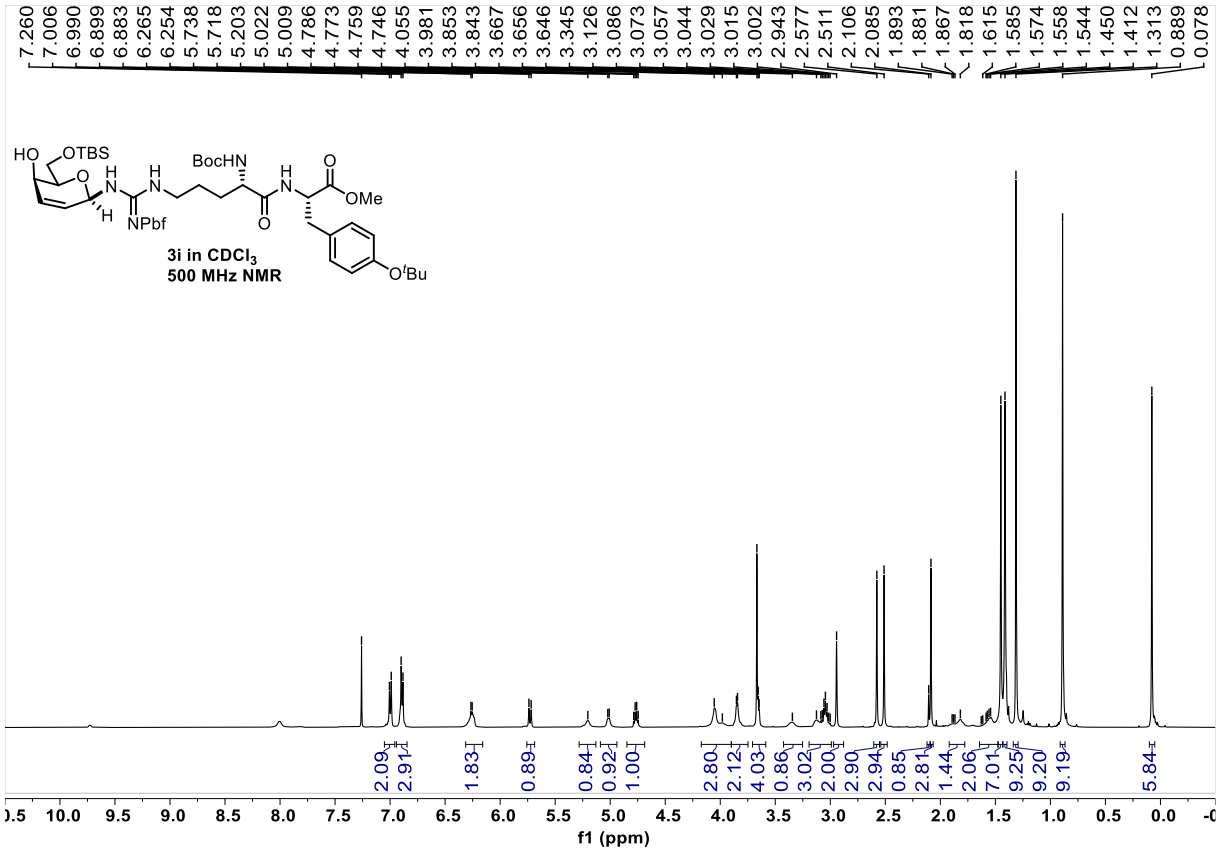
157.81
155.92
139.44
134.22
133.59
129.76
126.11
118.50
87.76
80.59
78.93
78.41
64.01
61.77
60.40
53.13
52.74
49.51
49.34
49.17
49.00
48.83
48.66
48.49
48.25
43.94
42.03
29.96
29.83
28.74
26.45
26.24
25.97
19.68
19.28
18.50
12.56
-5.07
HO
OTBS
O
H
N
H
N
H
NPbf
BocHN
O
N
CO2Me
3f in CD3OD
125 MHz NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


3g in CDCl3
500 MHz NMR
f1 (ppm)


3g in CD3OD
125 MHz NMR
f1 (ppm)


3h in CDCl3
500 MHz NMR
f1 (ppm)


3h in CD3OD
125 MHz NMR
f1 (ppm)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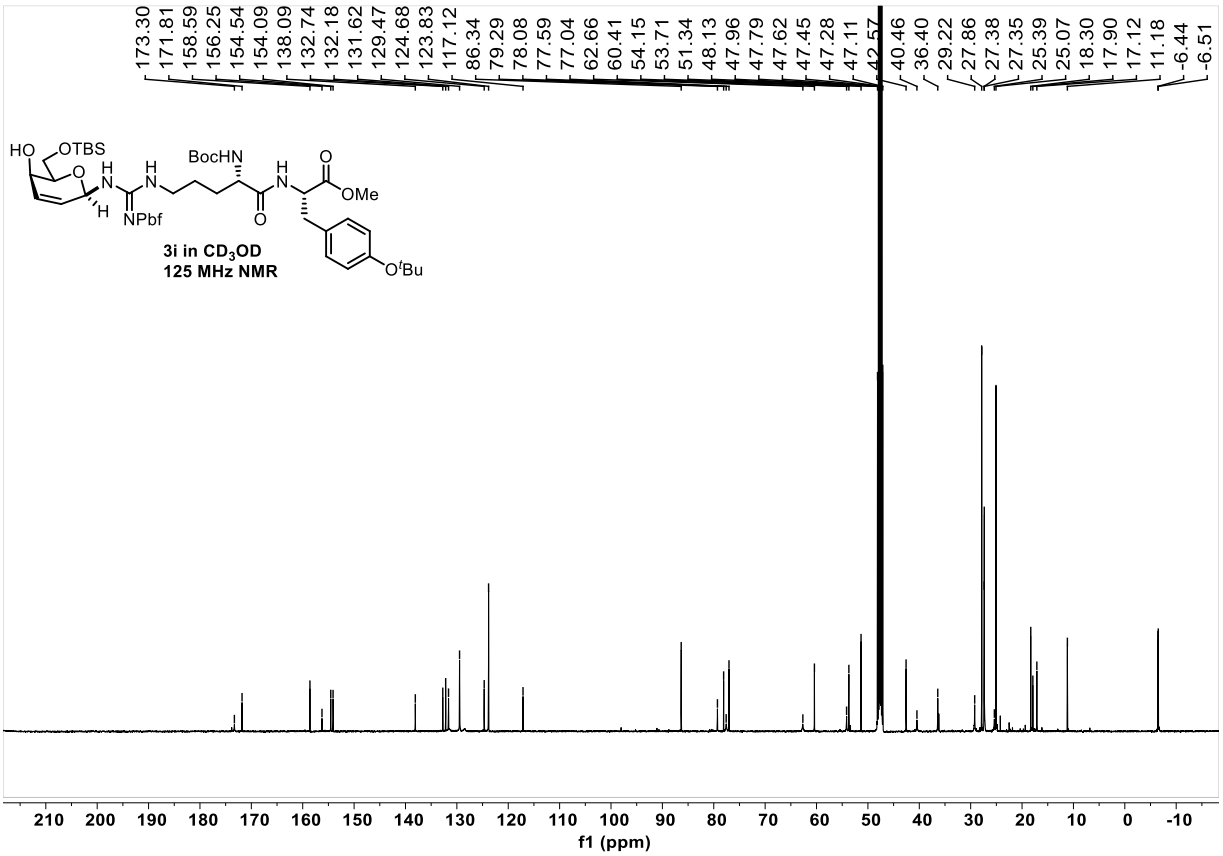
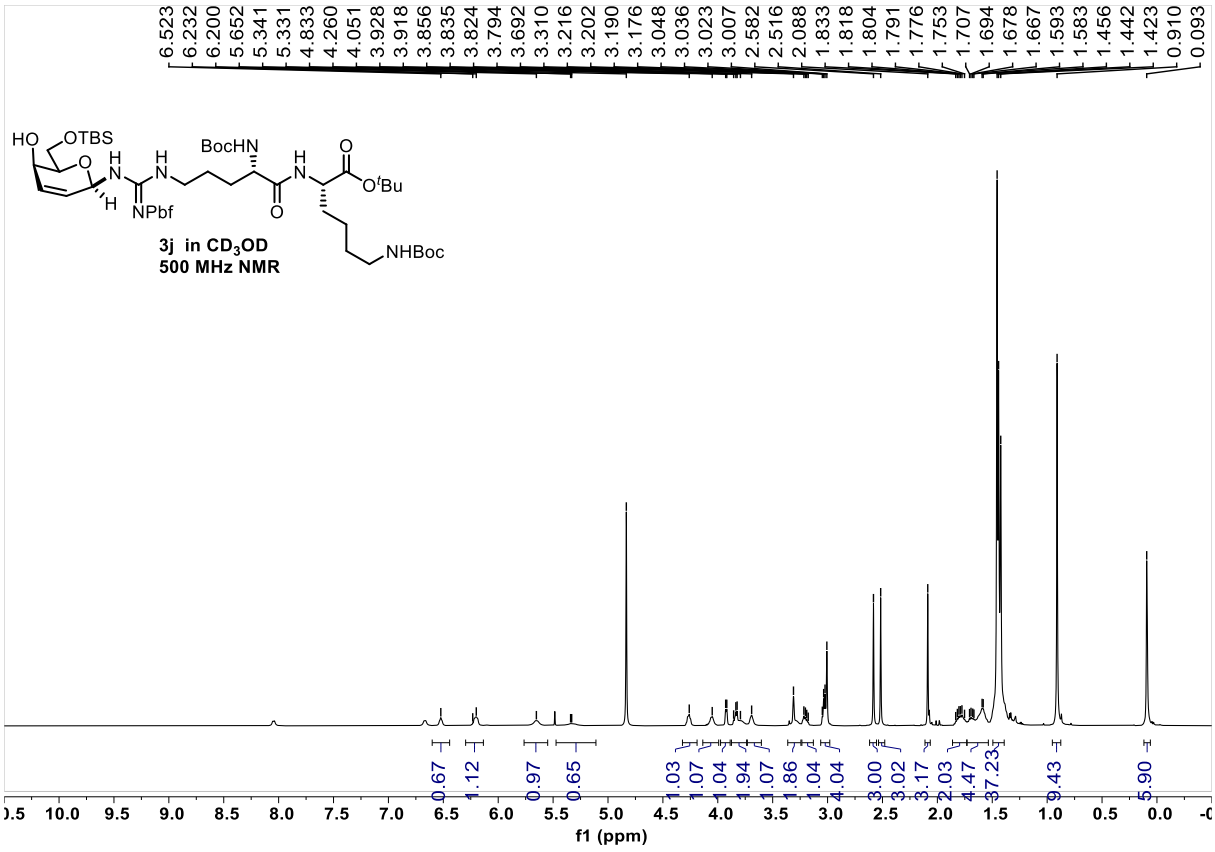
500 MHz NMR
f1 (ppm)


3i in CD3OD
125 MHz NMR
f1 (ppm)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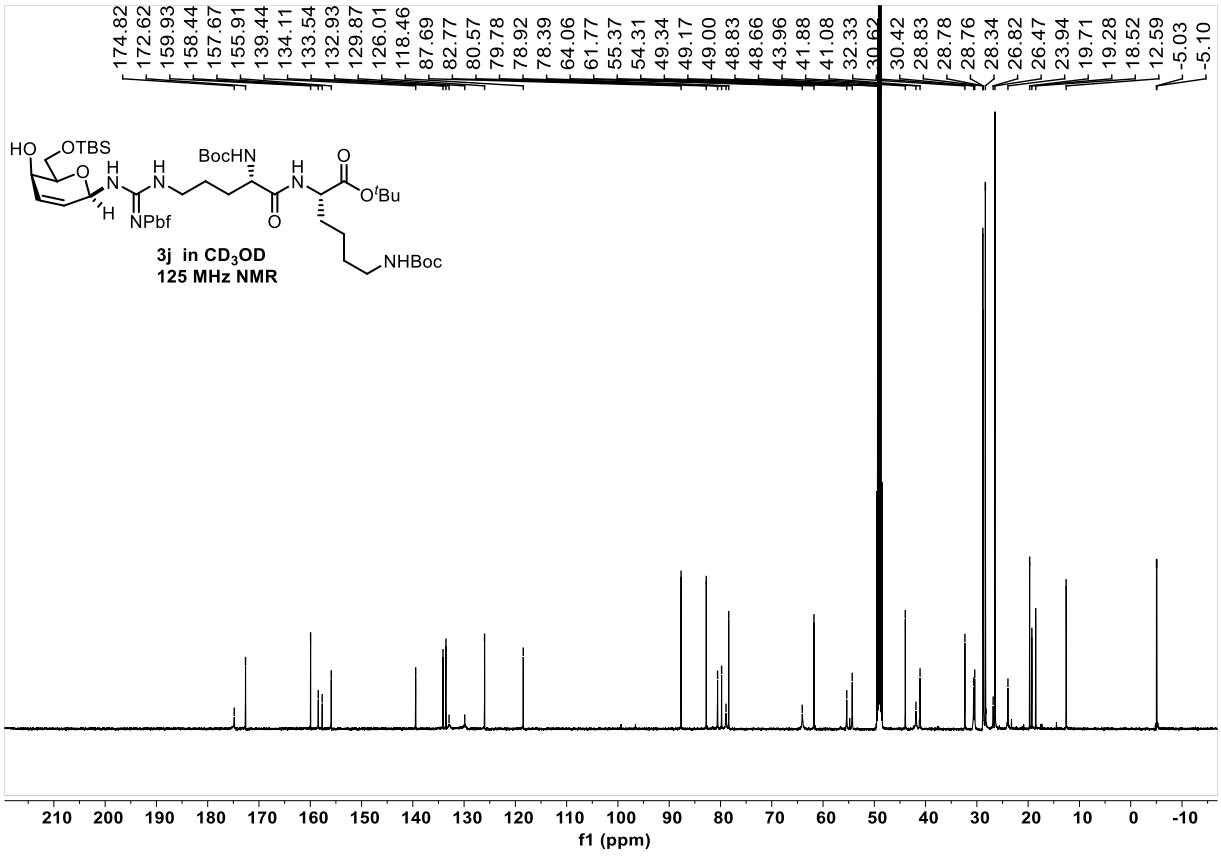
6.200
5.652
5.341
5.331
4.833
4.260
4.051
3.928
3.918
3.856
3.835
3.824
3.794
3.692
3.310
3.216
3.202
3.190
3.176
3.048
3.036
3.023
3.007
2.582
2.516
2.088
1.833
1.818
1.804
1.791
1.776
1.753
1.707
1.694
1.678
1.667
1.593
1.583
1.456
1.442
1.423
0.910
0.093
HO
OTBS
BocHN
O
O
O
tBu
NPbf
NHBoc
3j in CD3OD
500 MHz NMR
0.67
1.12
0.97
0.65
1.03
1.07
1.04
1.94
1.07
1.86
1.04
4.04
3.00
3.02
3.17
2.03
4.47
37.23
9.43
5.90
f1 (ppm)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155.91
139.44
134.11
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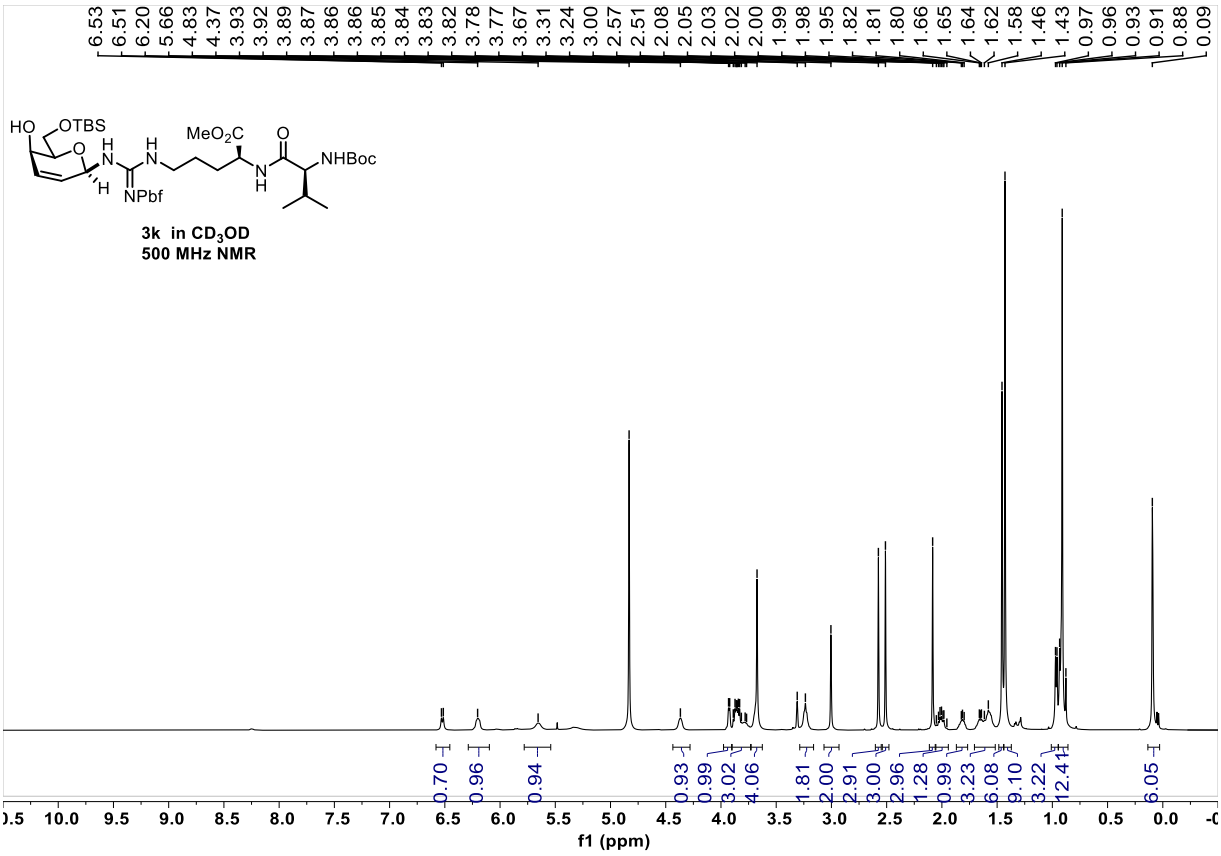
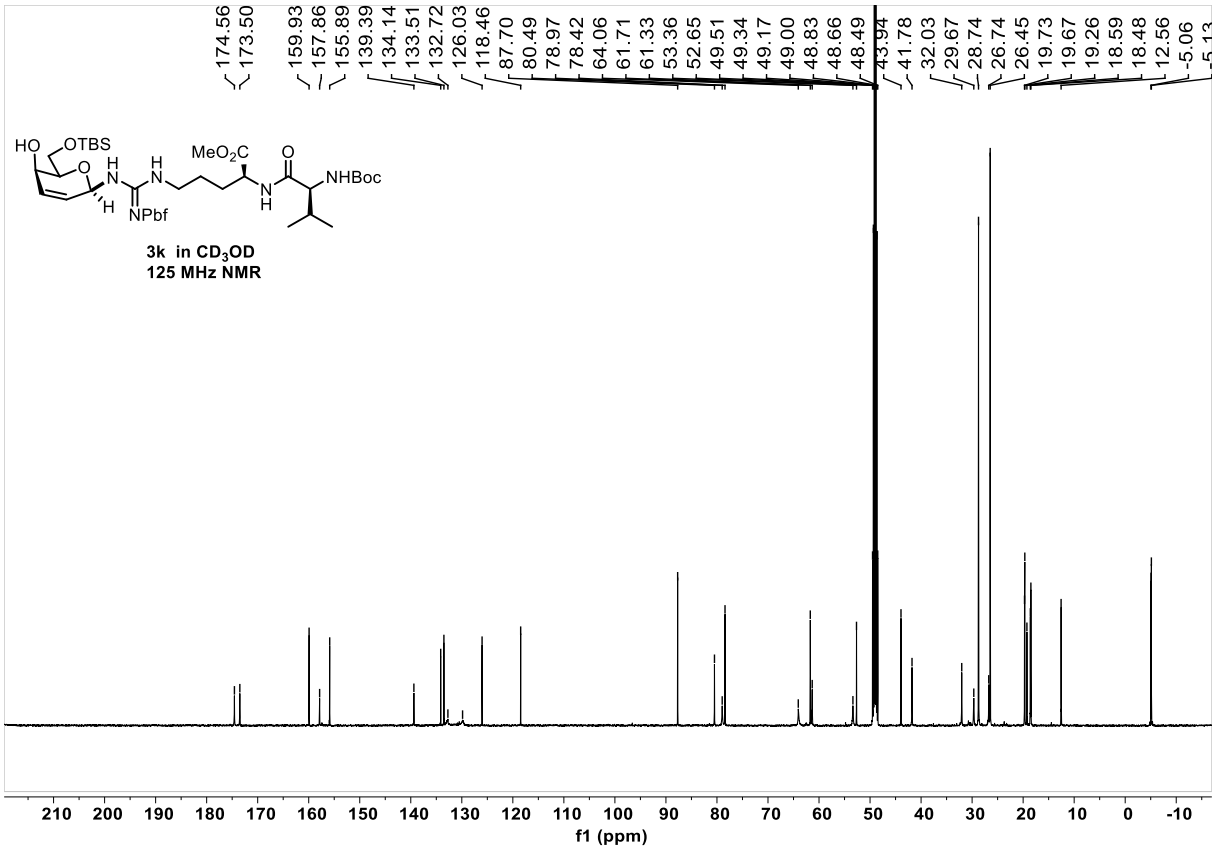
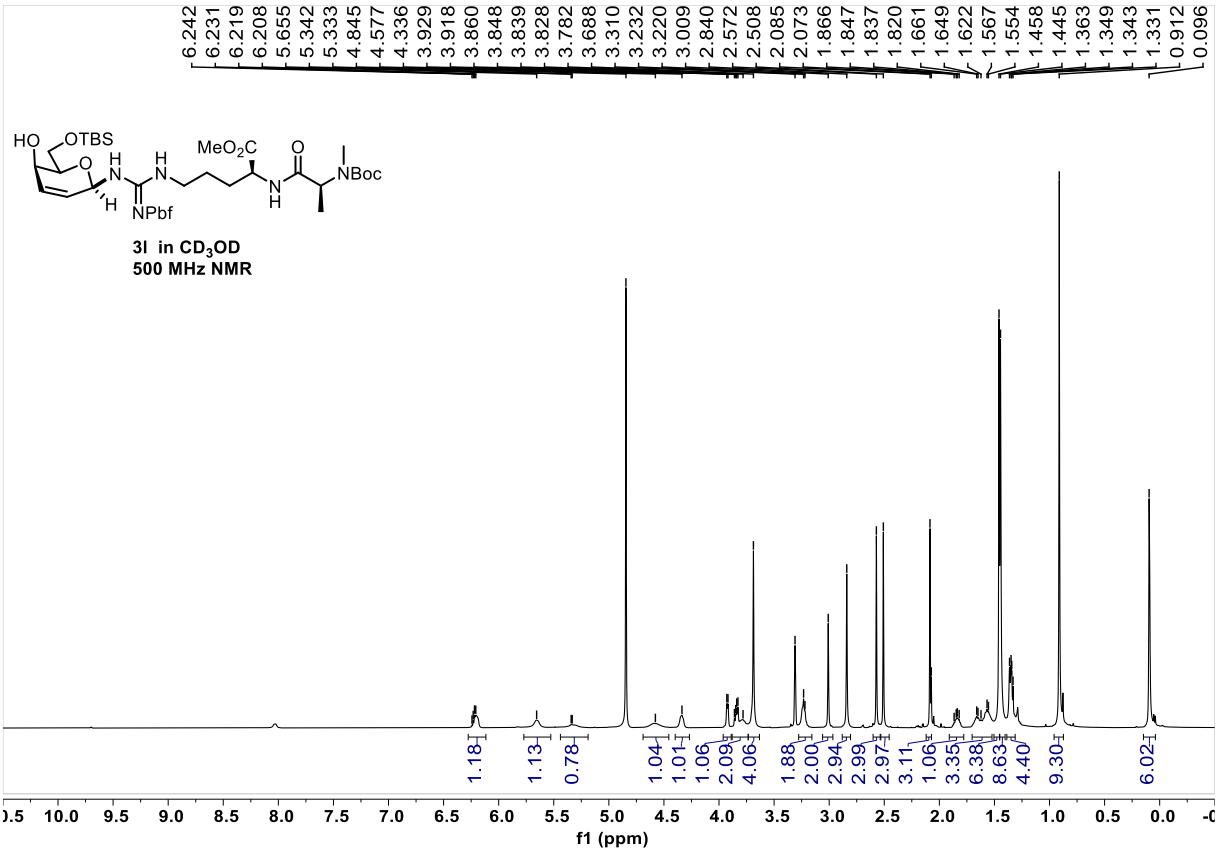
132.93
129.87
126.01
118.46
87.69
82.77
80.57
79.78
78.92
78.39
64.06
61.77
55.37
54.31
49.34
49.17
49.00
48.83
48.66
43.96
41.88
41.08
32.33
30.62
30.42
28.83
28.78
28.76
28.34
26.82
26.47
23.94
19.71
19.28
18.52
12.59
-5.03
-5.10
HO
OTBS
BocHN
O
O
O
tBu
NPbf
NHBoc
3j in CD3OD
125 MHz NMR
f1 (ppm)


3k in CD3OD
500 MHz NMR
f1 (ppm)


3k in CD3OD
125 MHz NMR
f1 (ppm)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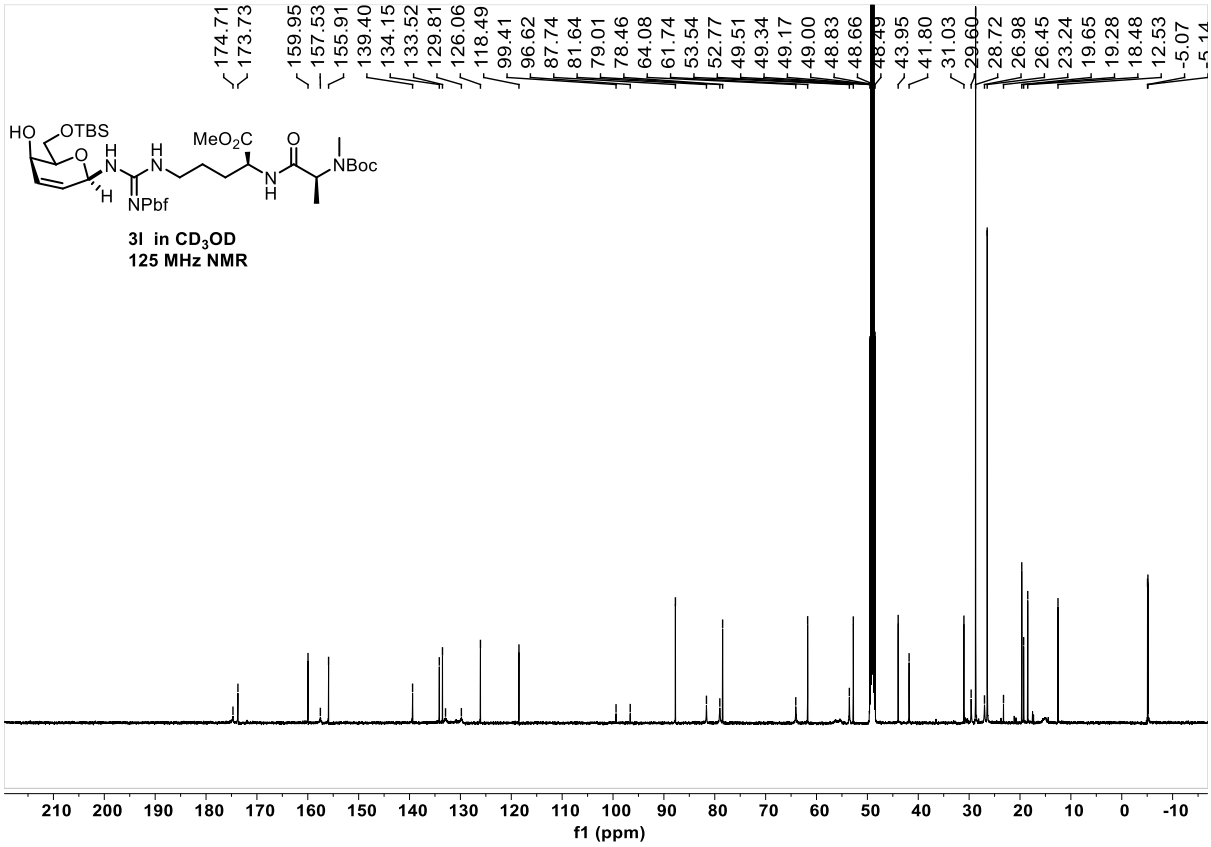
3.918
3.860
3.848
3.839
3.828
3.782
3.688
3.310
3.232
3.220
3.009
2.840
2.572
2.508
2.085
2.073
1.866
1.847
1.837
1.820
1.661
1.649
1.622
1.567
1.554
1.458
1.445
1.363
1.349
1.343
1.331
0.912
0.096
HO
OTBS
MeO2C
NBoc
NPbf
3l in CD3OD
500 MHz NMR
1.18
1.13
0.78
1.04
1.01
1.06
2.09
4.06
1.88
2.00
2.94
2.99
2.97
3.11
1.06
3.35
6.38
8.63
4.40
9.30
6.02
f1 (ppm)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96.62
87.74
81.64
79.01
78.46
64.08
61.74
53.54
52.77
49.51
49.34
49.17
49.00
48.83
48.66
48.49
43.95
41.80
31.03
29.60
28.72
26.98
26.45
23.24
19.65
19.28
18.48
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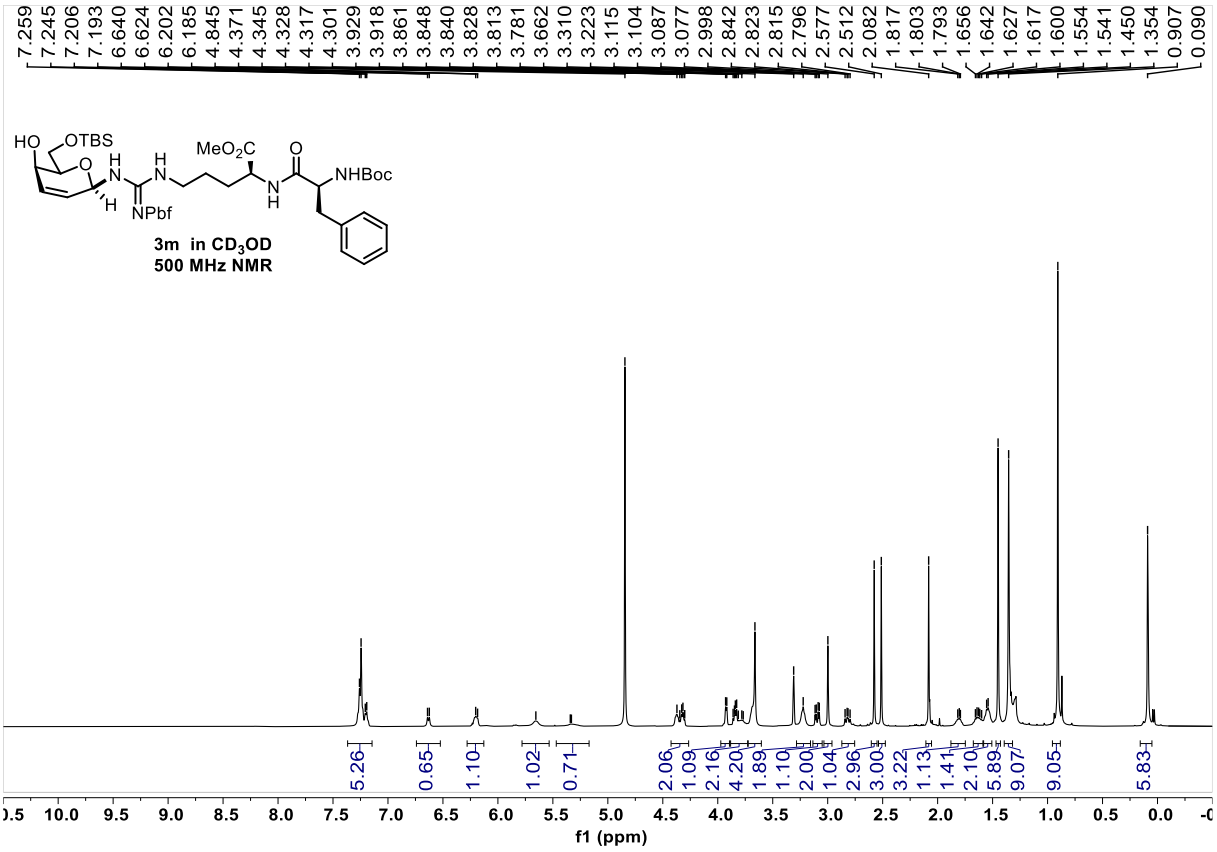
HO
OTBS
MeO2C
NBoc
NPbf
3l in CD3OD
125 MHz NMR
f1 (ppm)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6.185
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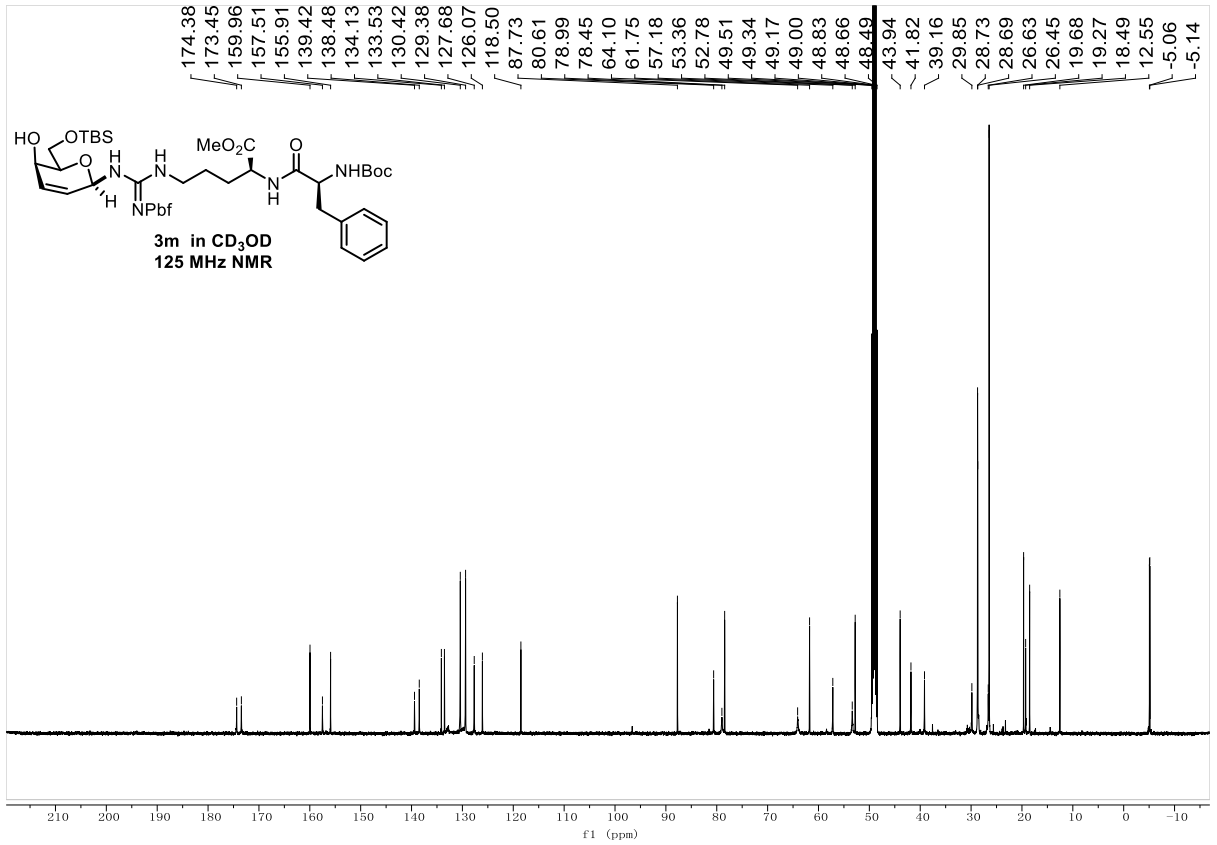
4.328
4.317
4.301
3.929
3.918
3.861
3.848
3.840
3.828
3.813
3.781
3.662
3.310
3.223
3.115
3.104
3.087
3.077
2.998
2.842
2.823
2.815
2.796
2.577
2.512
2.082
1.817
1.803
1.793
1.656
1.642
1.627
1.617
1.600
1.554
1.541
1.450
1.354
0.907
0.090
HO
OTBS
MeO2C
O
NHBoc
NPbf
3m in CD3OD
500 MHz NMR
5.26
0.65
1.10
1.02
0.71
2.06
1.09
2.16
4.20
1.89
1.10
2.00
1.04
2.96
3.00
3.22
1.13
1.41
2.10
5.89
9.07
9.05
5.83
f1 (ppm)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118.50
87.73
80.61
78.99
78.45
64.10
61.75
57.18
53.36
52.78
49.51
49.34
49.17
49.00
48.83
48.66
48.49
43.94
41.82
39.16
29.85
28.73
28.69
26.63
26.45
19.68
19.27
18.49
12.55
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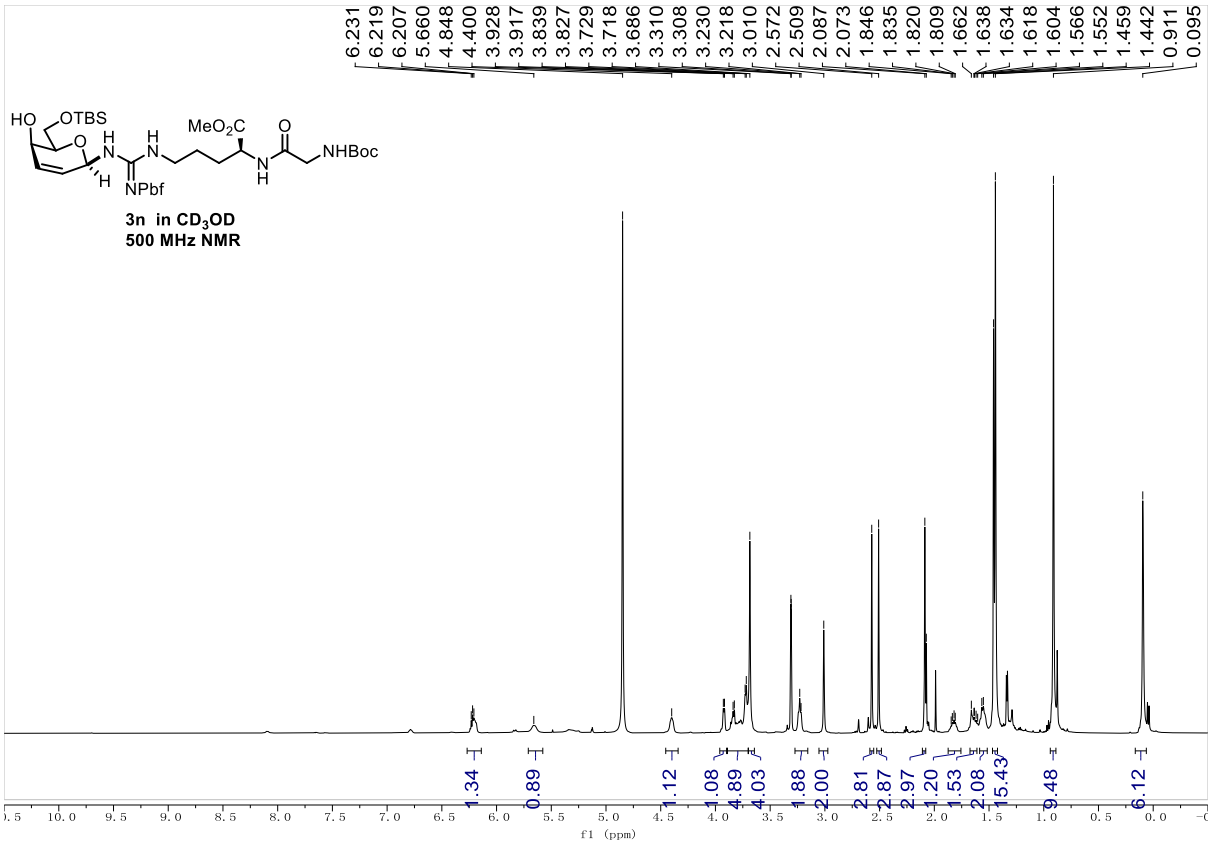
HO
OTBS
MeO2C
O
NHBoc
NPbf
3m in CD3OD
125 MHz NMR
f1 (ppm)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5.660
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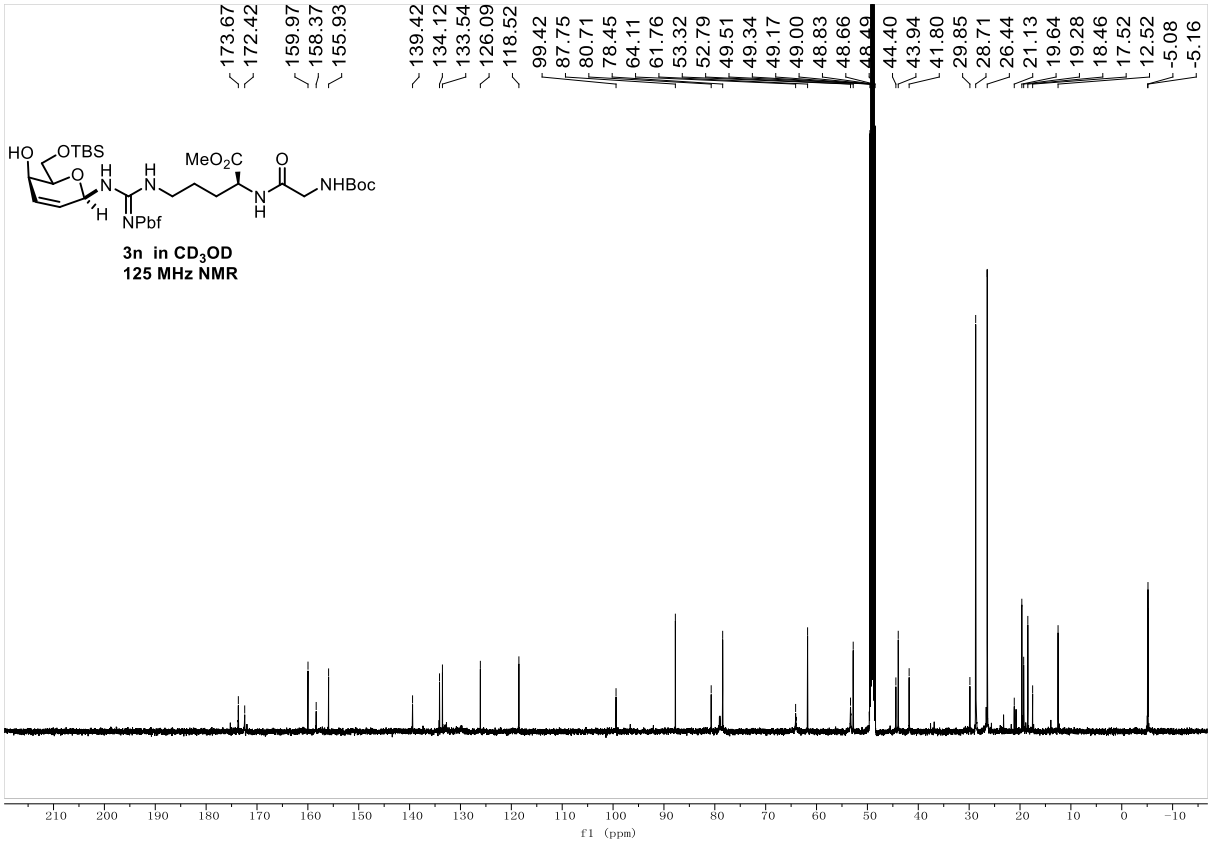
4.400
3.928
3.917
3.839
3.827
3.729
3.718
3.686
3.310
3.308
3.230
3.218
3.010
2.572
2.509
2.087
2.073
1.846
1.835
1.820
1.809
1.662
1.638
1.634
1.618
1.604
1.566
1.552
1.459
1.442
0.911
0.095
HO
OTBS
MeO2C
NHBoc
NPbf
3n in CD3OD
500 MHz NMR
1.34
0.89
1.12
1.08
4.89
4.03
1.88
2.00
2.81
2.87
2.97
1.20
1.53
2.08
15.43
9.48
6.12
f1 (ppm)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155.93
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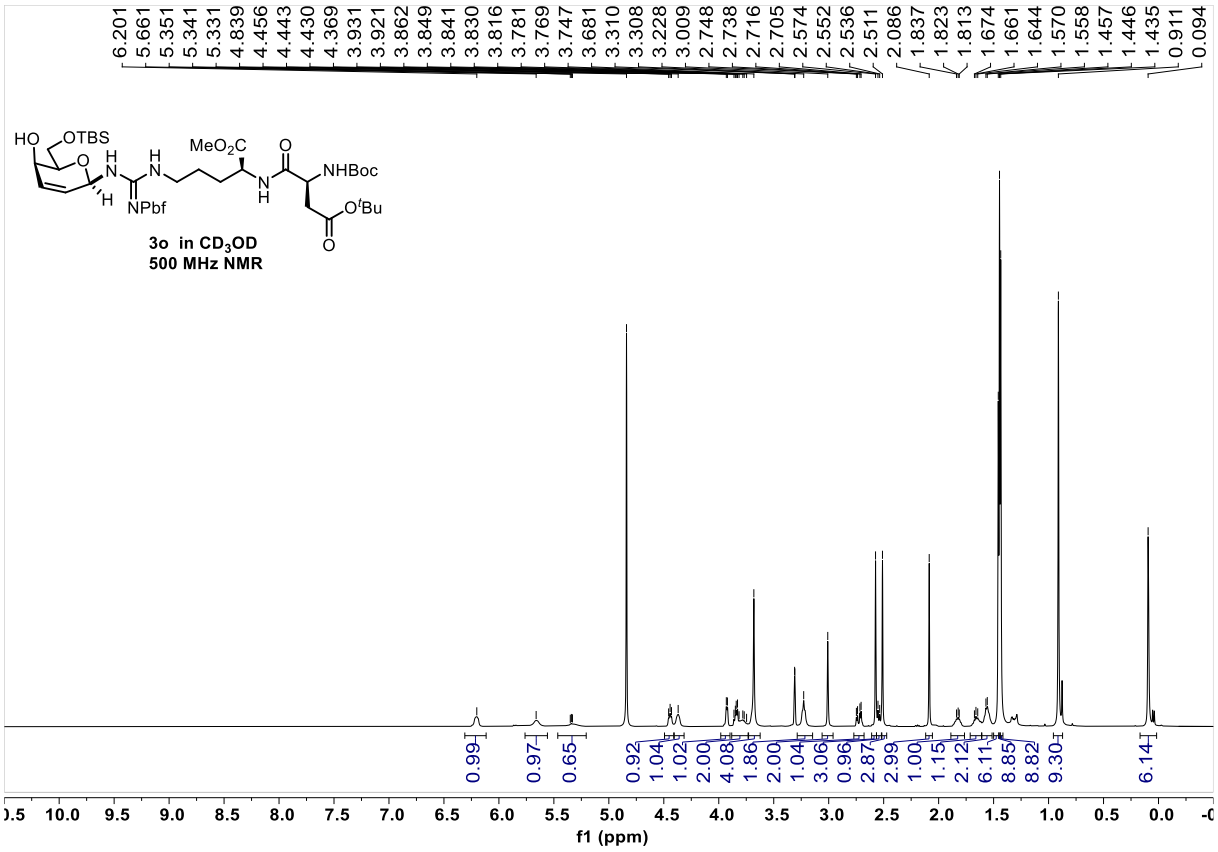
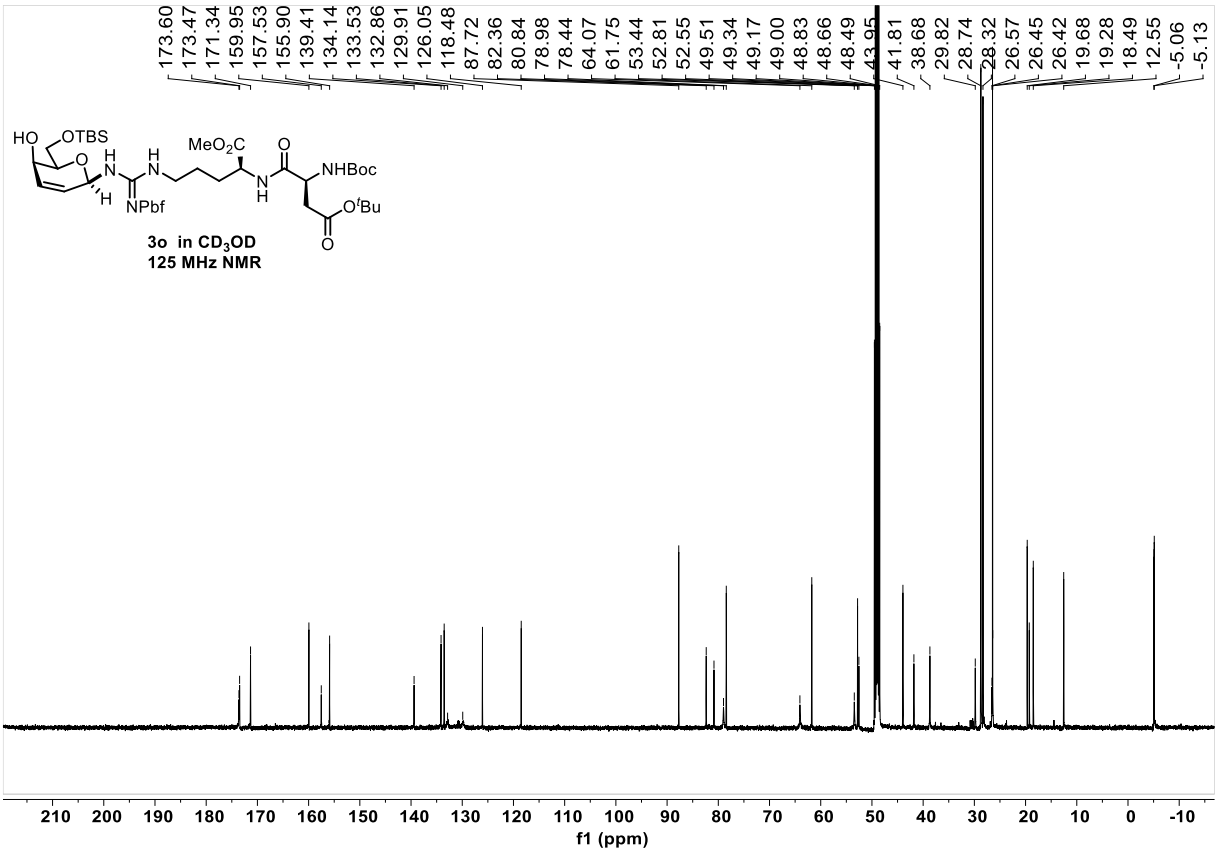
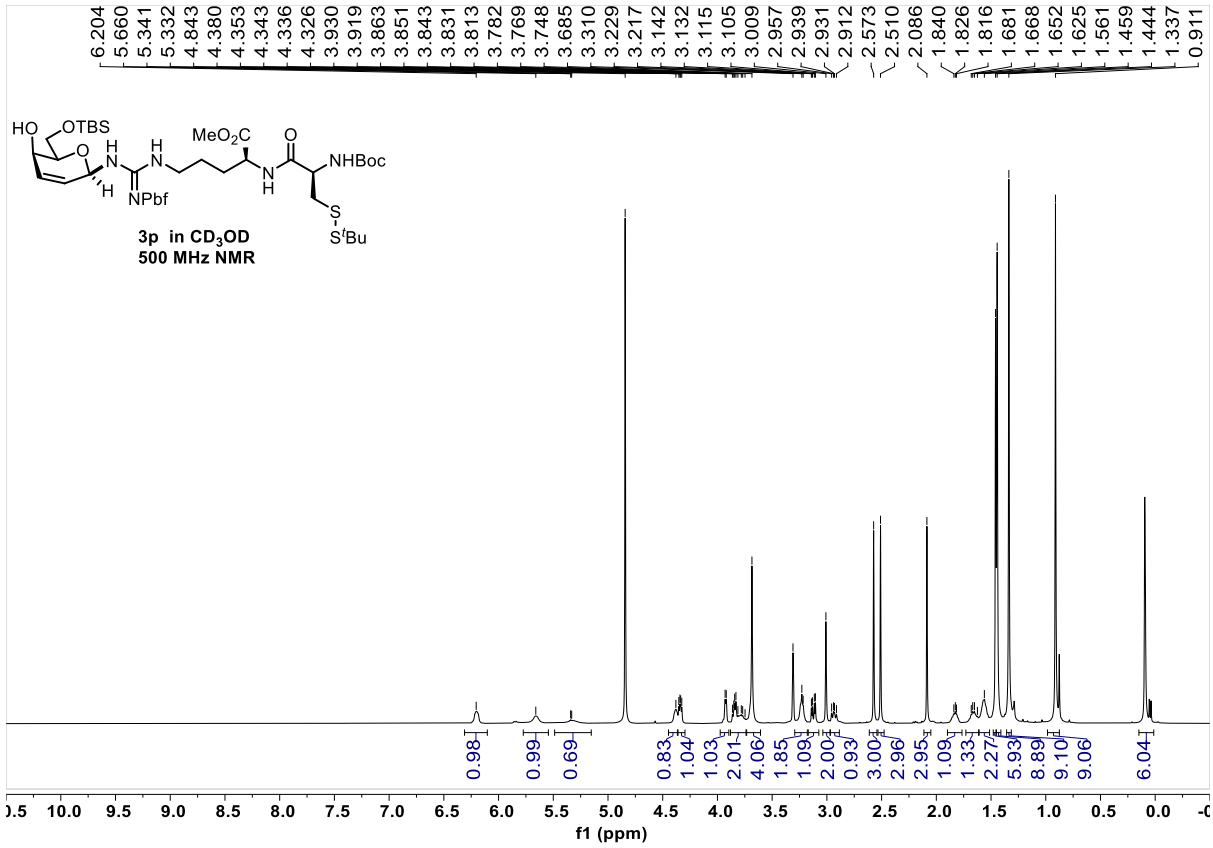
134.12
133.54
126.09
118.52
99.42
87.75
80.71
78.45
64.11
61.76
53.32
52.79
49.51
49.34
49.17
49.00
48.83
48.66
48.49
44.40
43.94
41.80
29.85
28.71
26.44
21.13
19.64
19.28
18.46
17.52
12.52
-5.08
-5.16
HO
OTBS
MeO2C
NHBoc
NPbf
3n in CD3OD
125 MHz NMR
f1 (ppm)


3o in CD3OD
500 MHz NMR
f1 (ppm)


3o in CD3OD
125 MHz NMR
f1 (ppm)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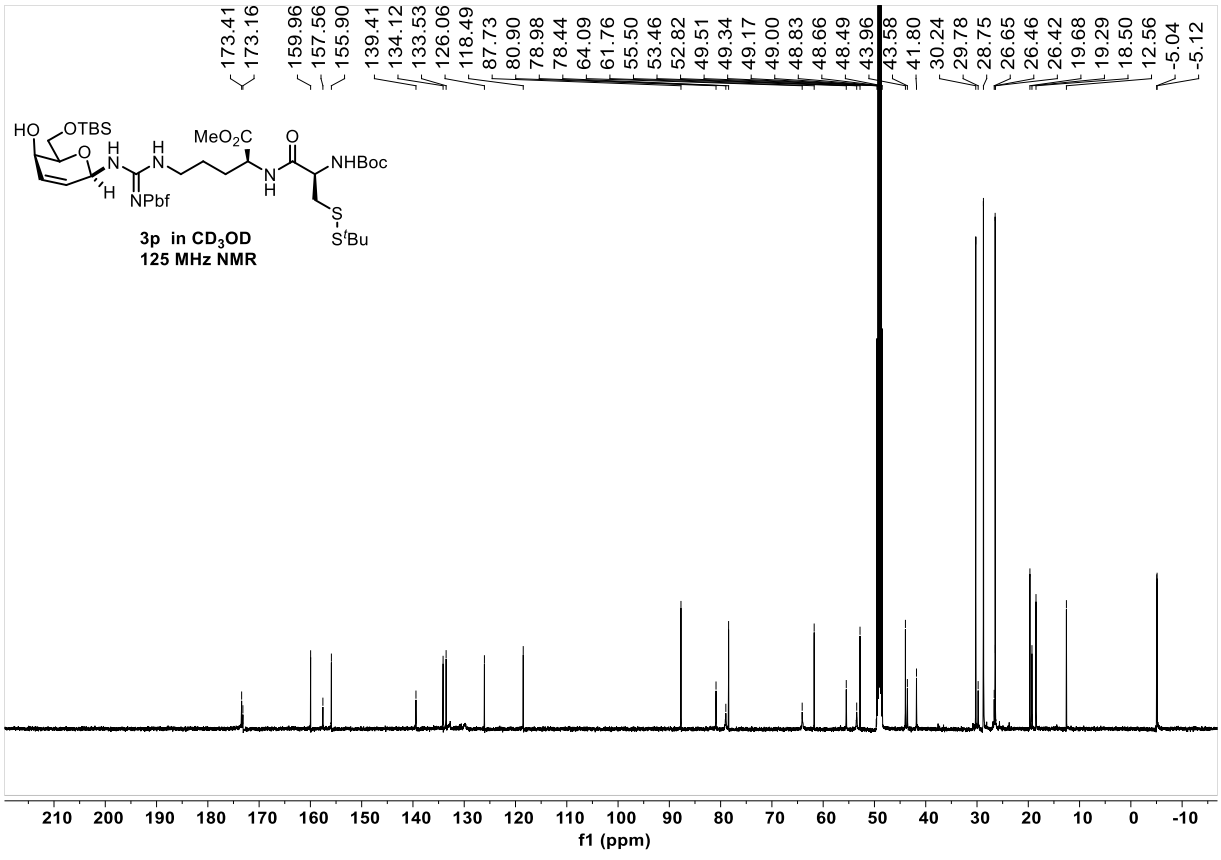
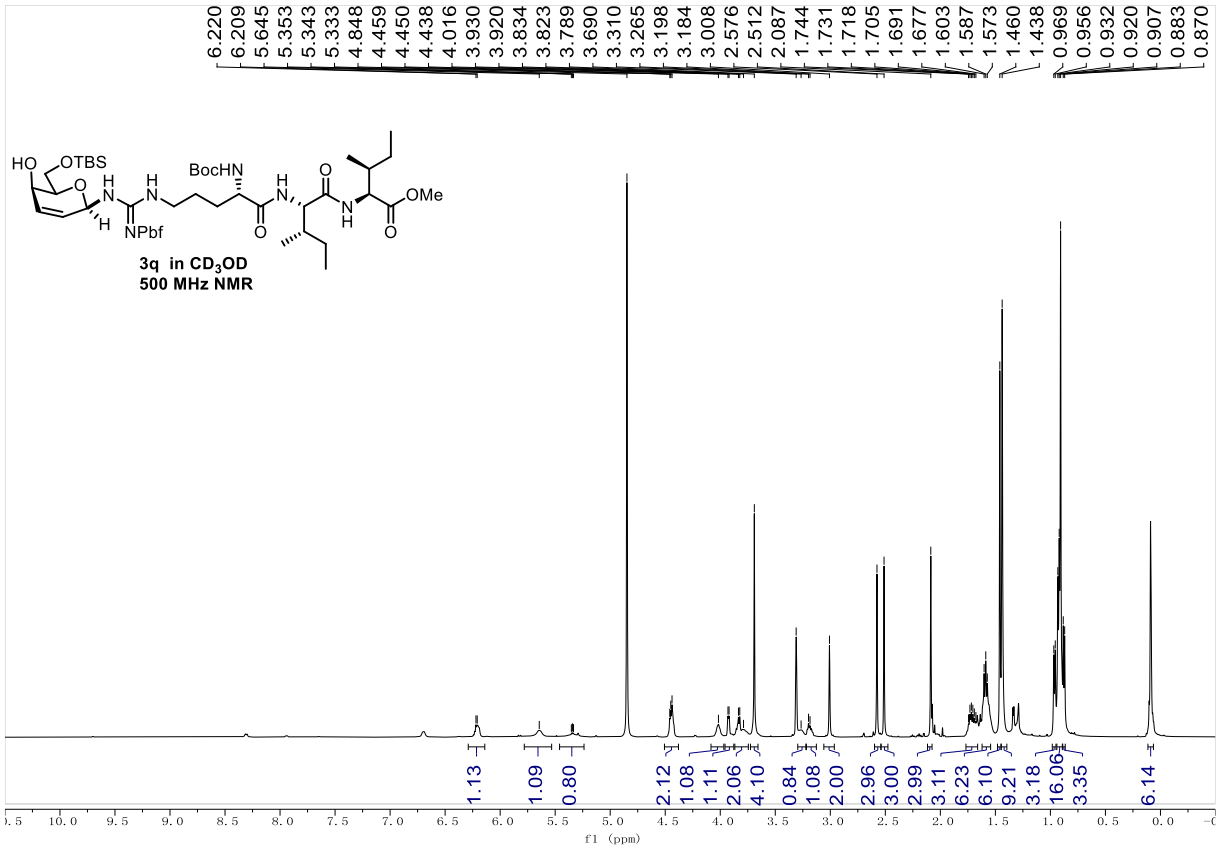
500 MHz NMR
f1 (ppm)


3p in CD3OD
125 MHz NMR
f1 (ppm)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5.333
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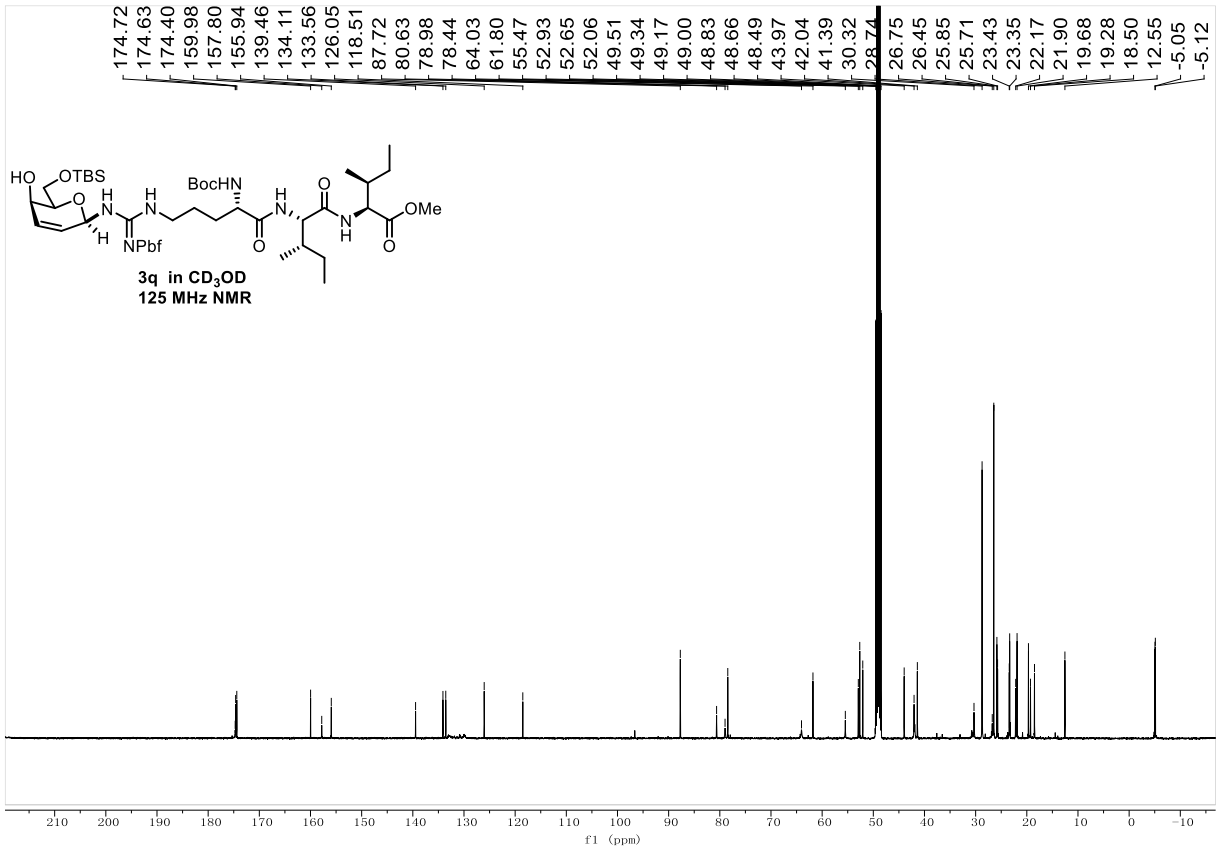
4.459
4.450
4.438
4.016
3.930
3.920
3.834
3.823
3.789
3.690
3.310
3.265
3.198
3.184
3.008
2.576
2.512
2.087
1.744
1.731
1.718
1.705
1.691
1.677
1.603
1.587
1.573
1.460
1.438
0.969
0.956
0.932
0.920
0.907
0.883
0.870
HO
OTBS
BocHN
OMe
NPbf
3q in CD3OD
500 MHz NMR
1.13
1.09
0.80
2.12
1.08
1.11
2.06
4.10
0.84
1.08
2.00
2.96
3.00
2.99
3.11
6.23
6.10
9.21
3.18
16.06
3.35
6.14
f1 (ppm)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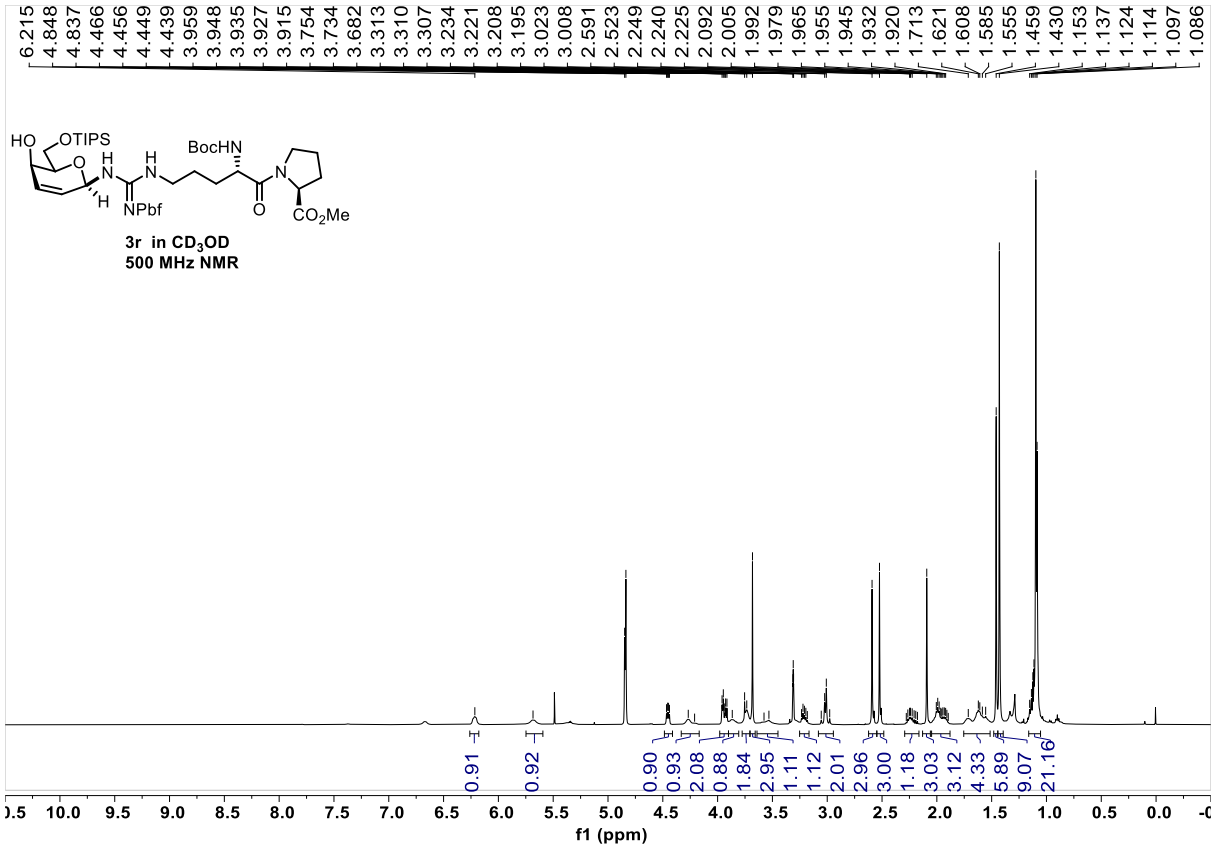
78.98
78.44
64.03
61.80
55.47
52.93
52.65
52.06
49.51
49.34
49.17
49.00
48.83
48.66
48.49
43.97
42.04
41.39
30.32
28.74
26.75
26.45
25.85
25.71
23.43
23.35
22.17
21.90
19.68
19.28
18.50
12.55
-5.05
-5.12
HO
OTBS
BocHN
OMe
NPbf
3q in CD3OD
125 MHz NMR
f1 (ppm)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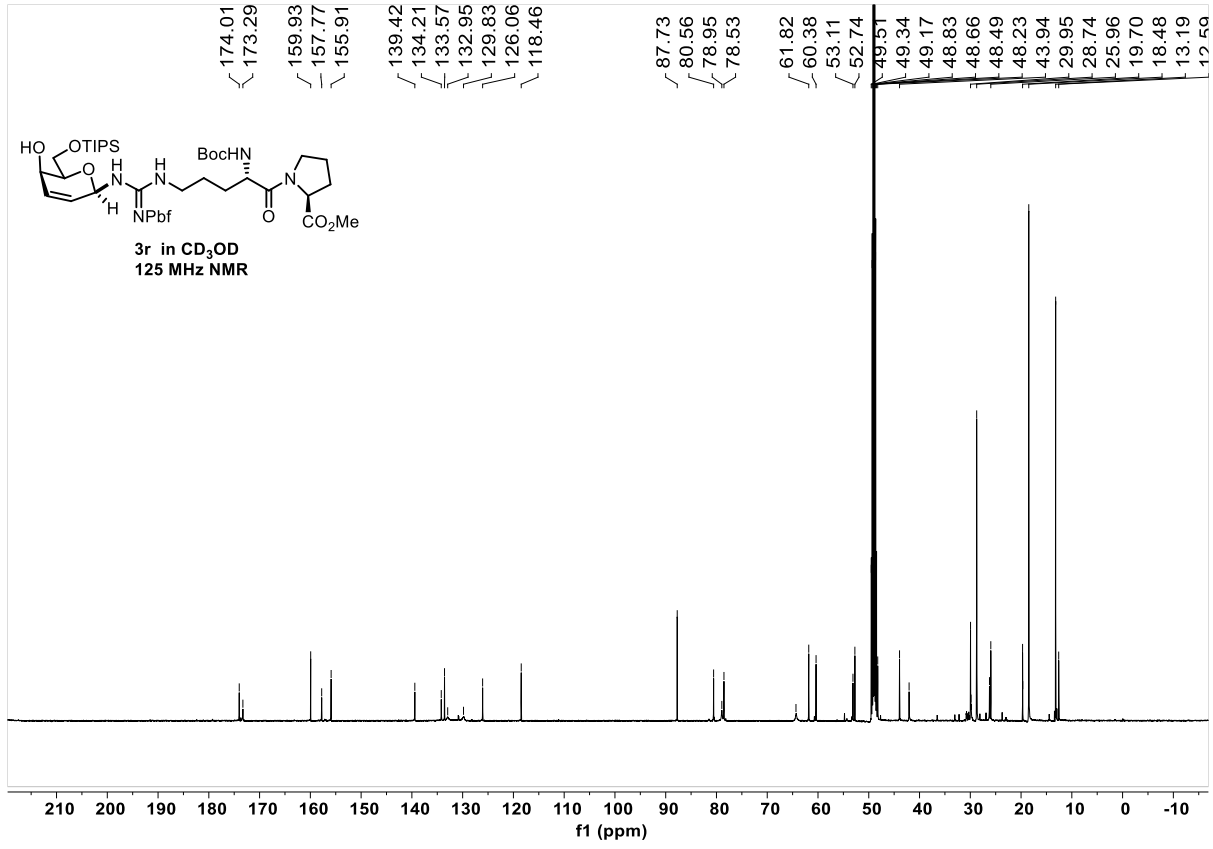
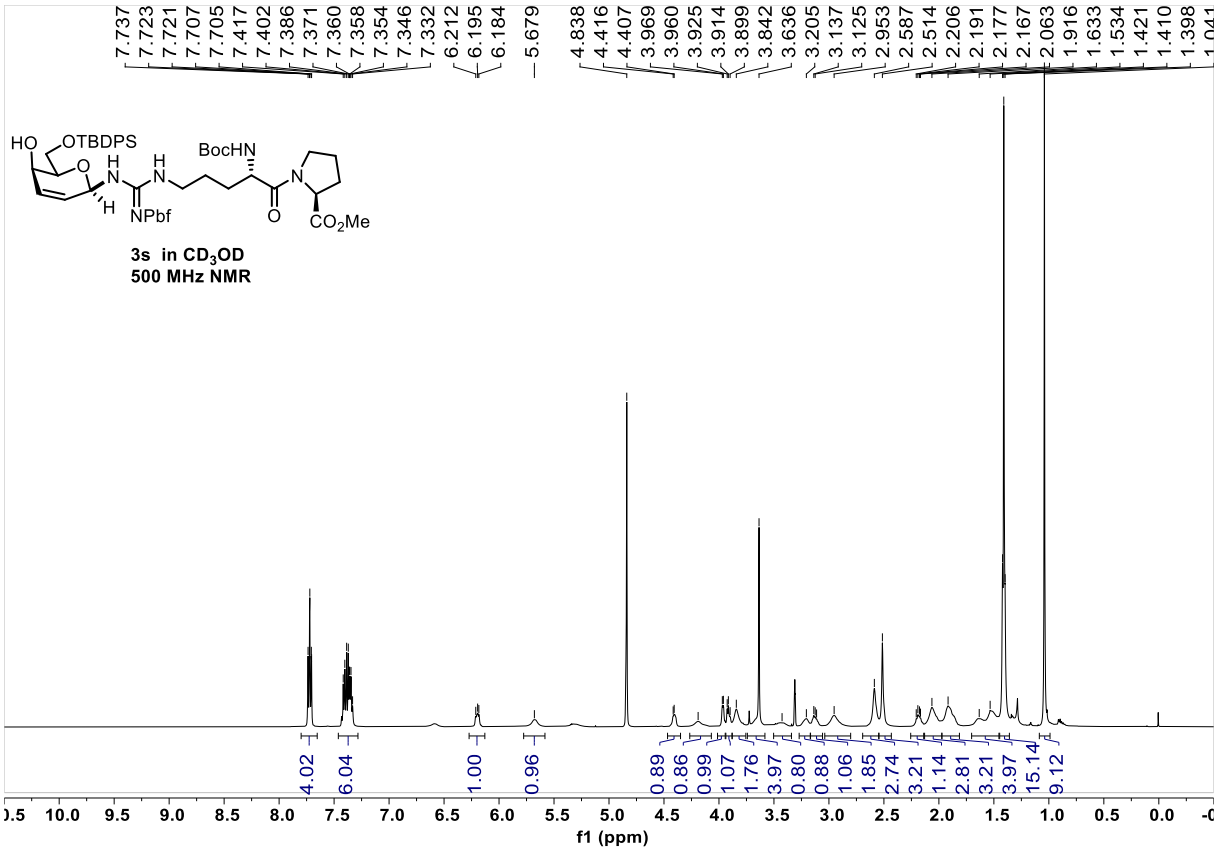
HO
OTIPS
O
H
N
H
N
NPbf
H
BocHN
N
O
CO2Me
3r in CD3OD
500 MHz NMR
0.91 0.92 0.90 0.93 2.08 0.88 1.84 2.95 1.11 1.12 2.01 2.96 3.00 1.18 3.03 3.12 4.33 5.89 9.07 21.16
f1 (ppm)


174.01 173.29 159.93 157.77 155.91 139.42 134.21 133.57 132.95 129.83 126.06 118.46 87.73 80.56 78.95 78.53 61.82 60.38 53.11 52.74 49.51 49.34 49.17 48.83 48.66 48.49 48.23 43.94 29.95 28.74 25.96 19.70 18.48 13.19
HO
OTIPS
O
H
N
H
N
NPbf
H
BocHN
N
O
CO2Me
3r in CD3OD
125 MHz NMR
f1 (ppm)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7.346
7.332
6.212
6.195
6.184
5.679
4.838
4.416
4.407
3.969
3.960
3.925
3.914
3.899
3.842
3.636
3.205
3.137
3.125
2.953
2.587
2.514
2.206
2.191
2.177
2.167
2.063
1.916
1.633
1.534
1.421
1.410
1.398
HO
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O
H
N
H
N
H
NPbf
BocHN
O
N
CO2Me
3s in CD3OD
500 MHz NMR
4.02
6.04
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0.96
0.89
0.86
0.99
1.07
1.76
3.97
0.80
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1.14
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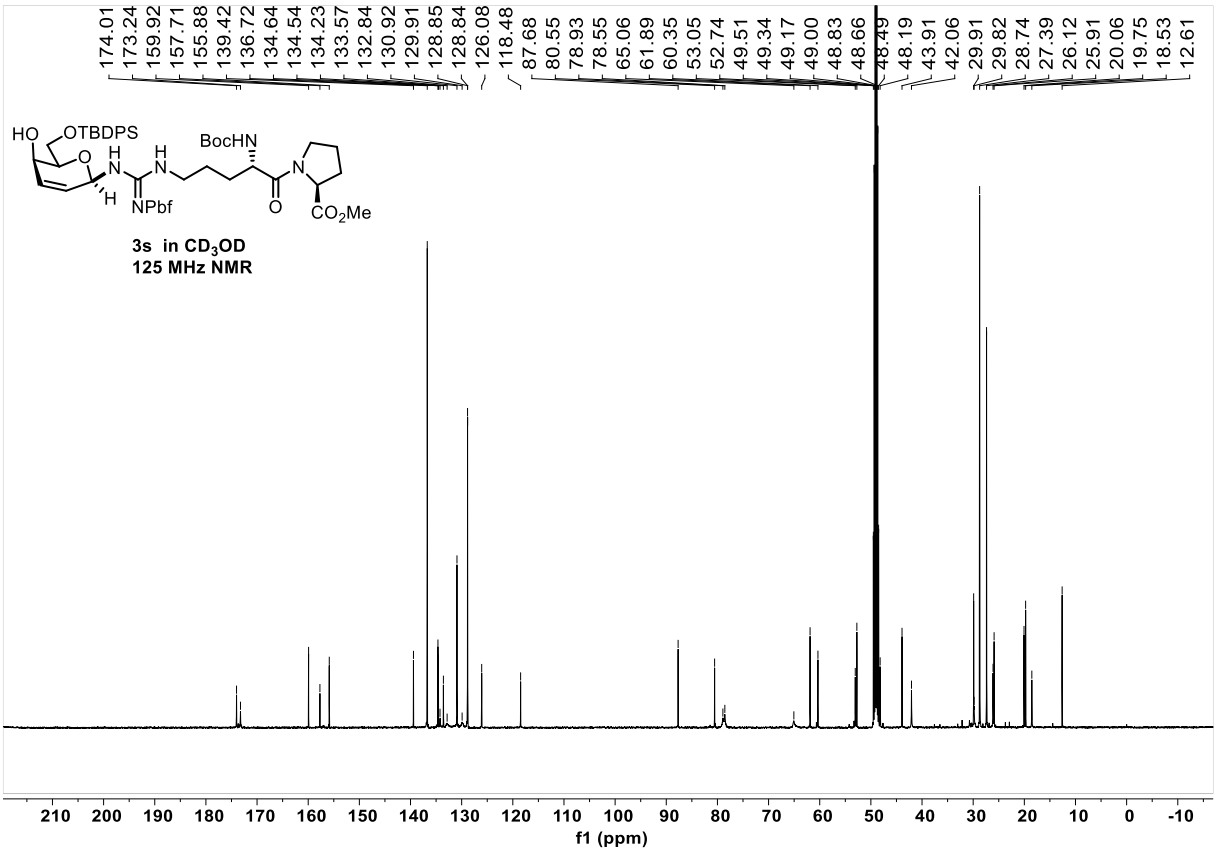
3.97
15.14
9.12
f1 (ppm)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128.85
128.84
126.08
118.48
87.68
80.55
78.93
78.55
65.06
61.89
60.35
53.05
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49.51
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48.19
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29.82
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18.53
12.61
HO
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O
H
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H
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H
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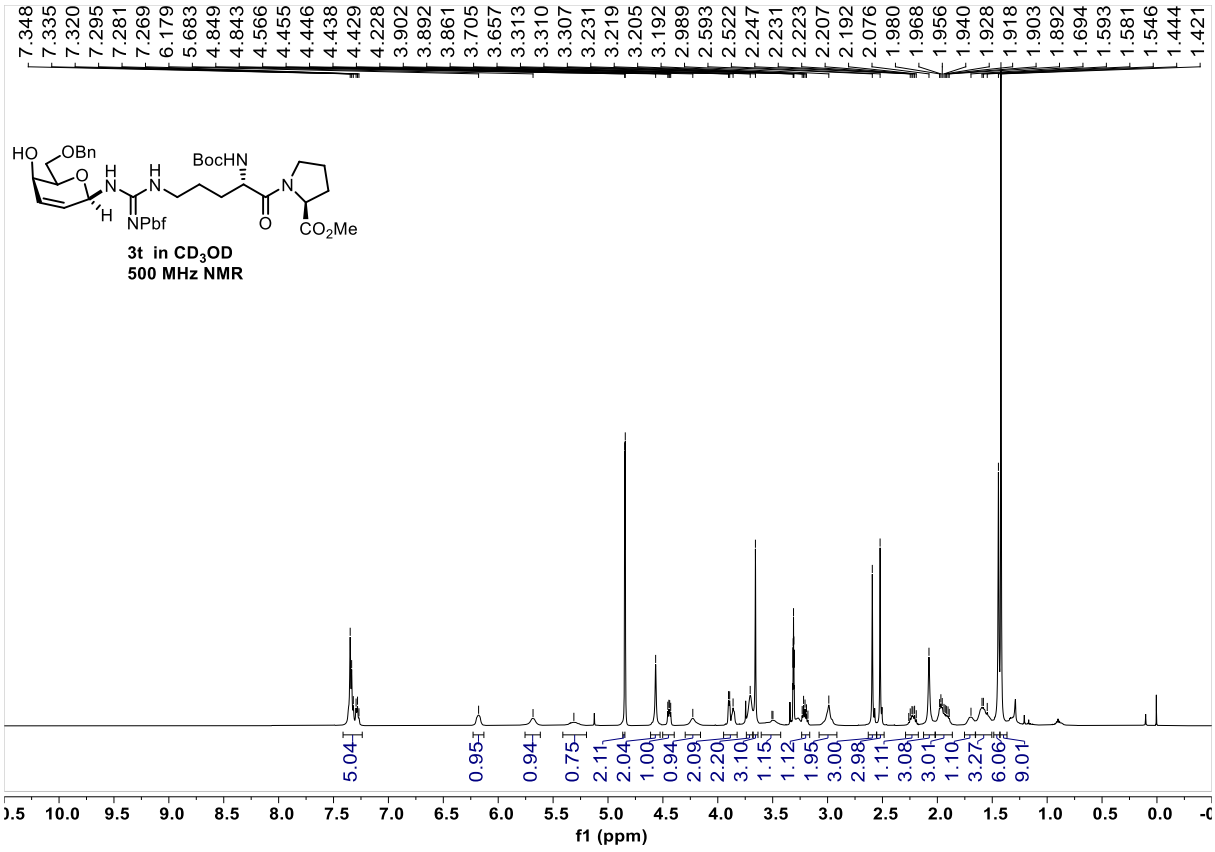
BocHN
O
N
CO2Me
3s in CD3OD
125 MHz NMR
f1 (ppm)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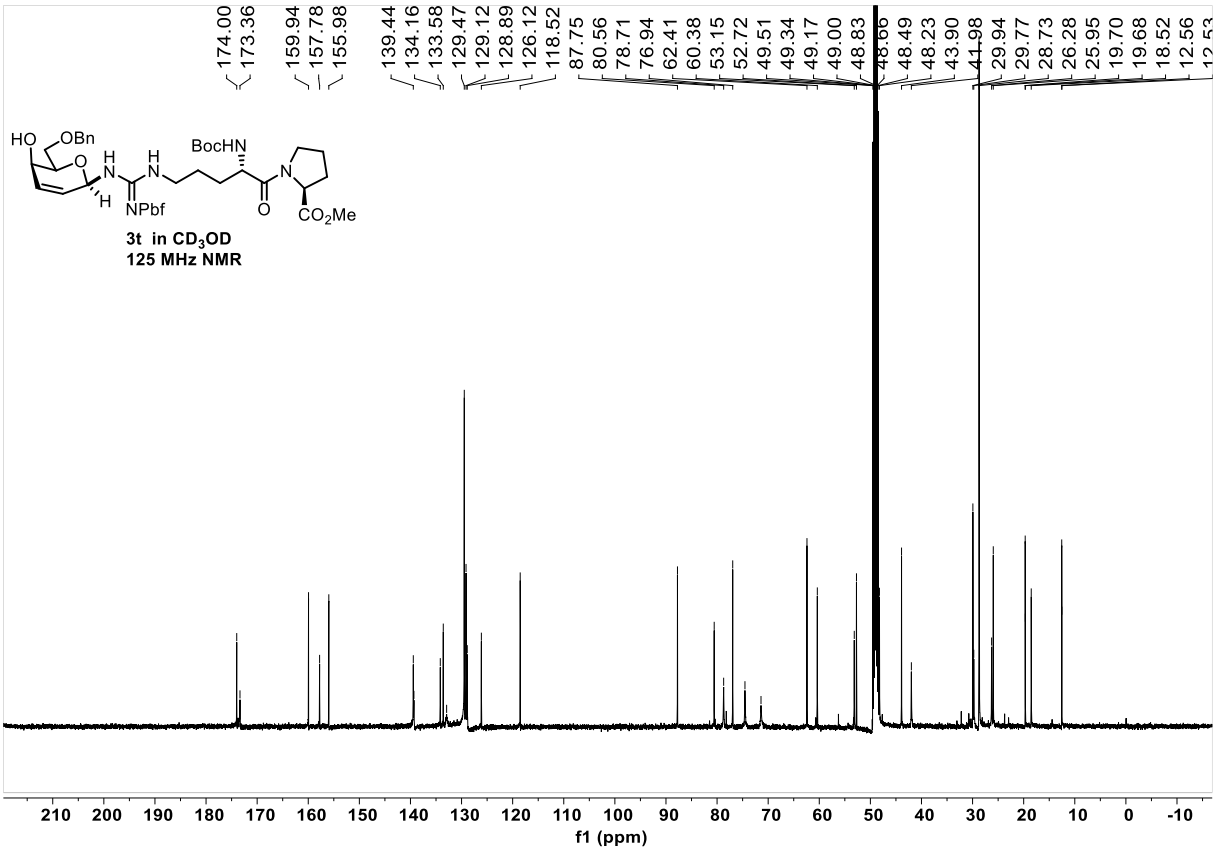
500 MHz NMR
f1 (ppm)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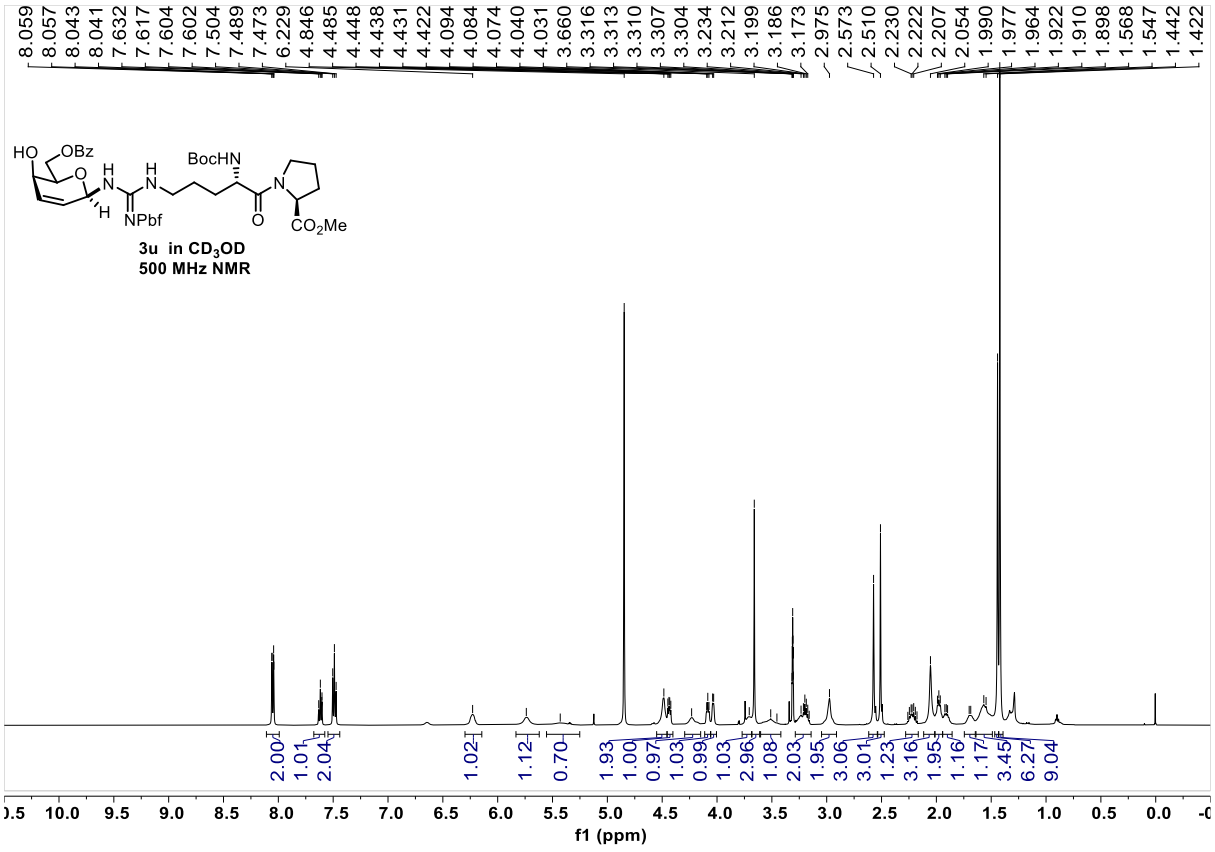
125 MHz NMR
f1 (ppm)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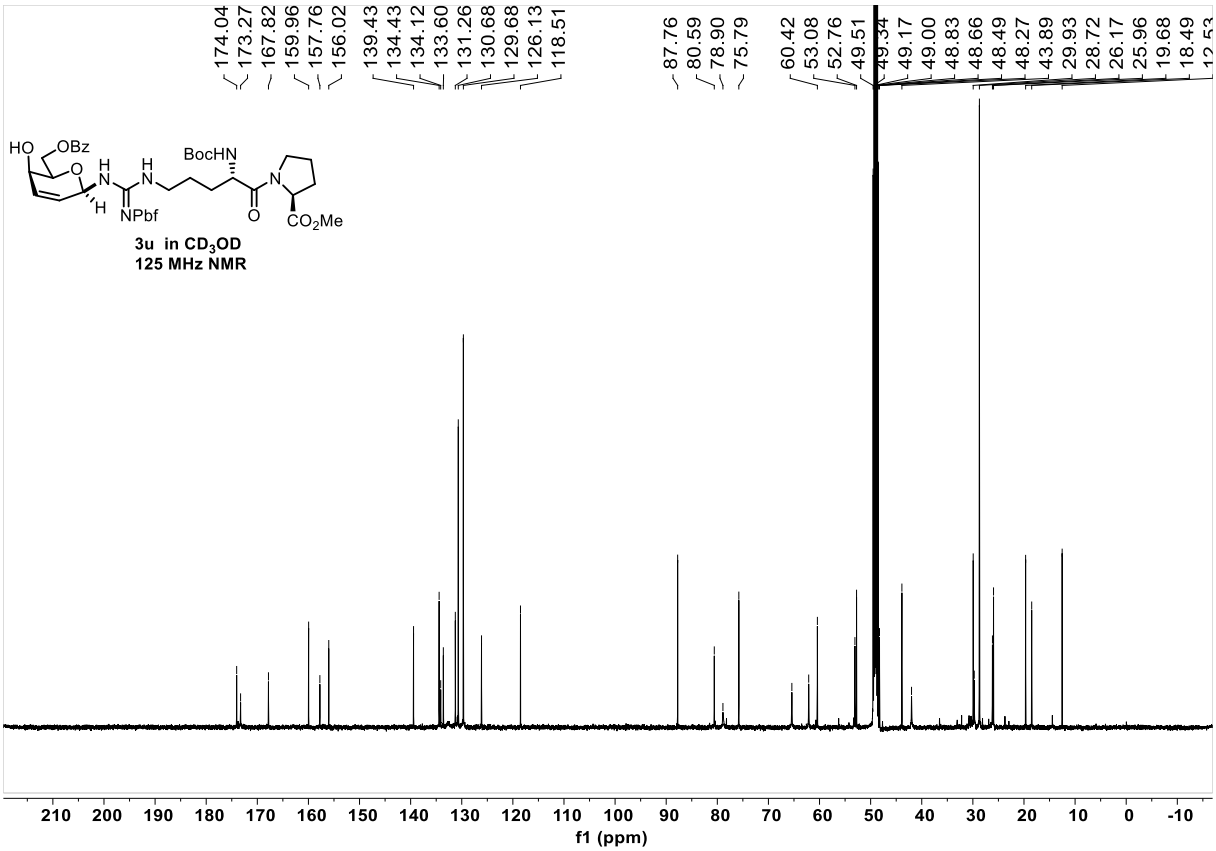
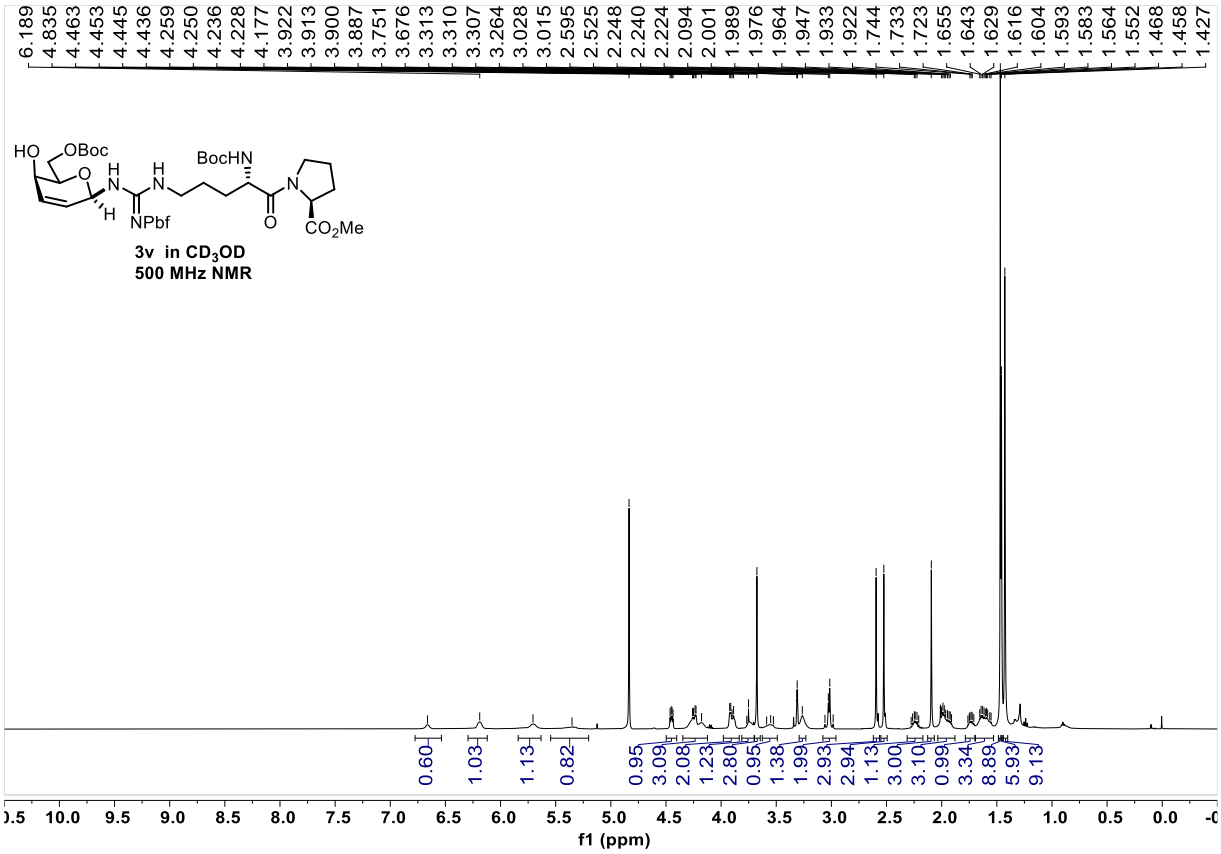

3u in CD3OD
125 MHz NMR
f1 (ppm)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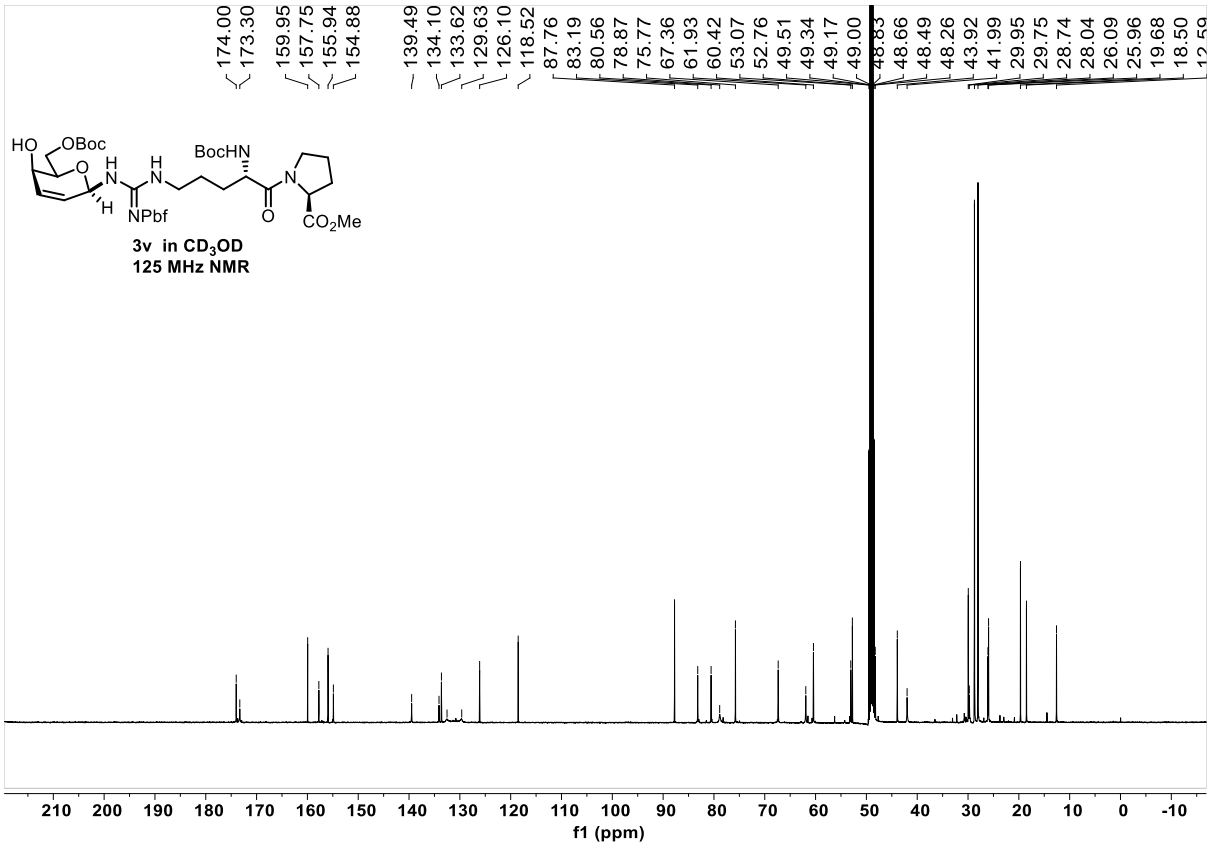
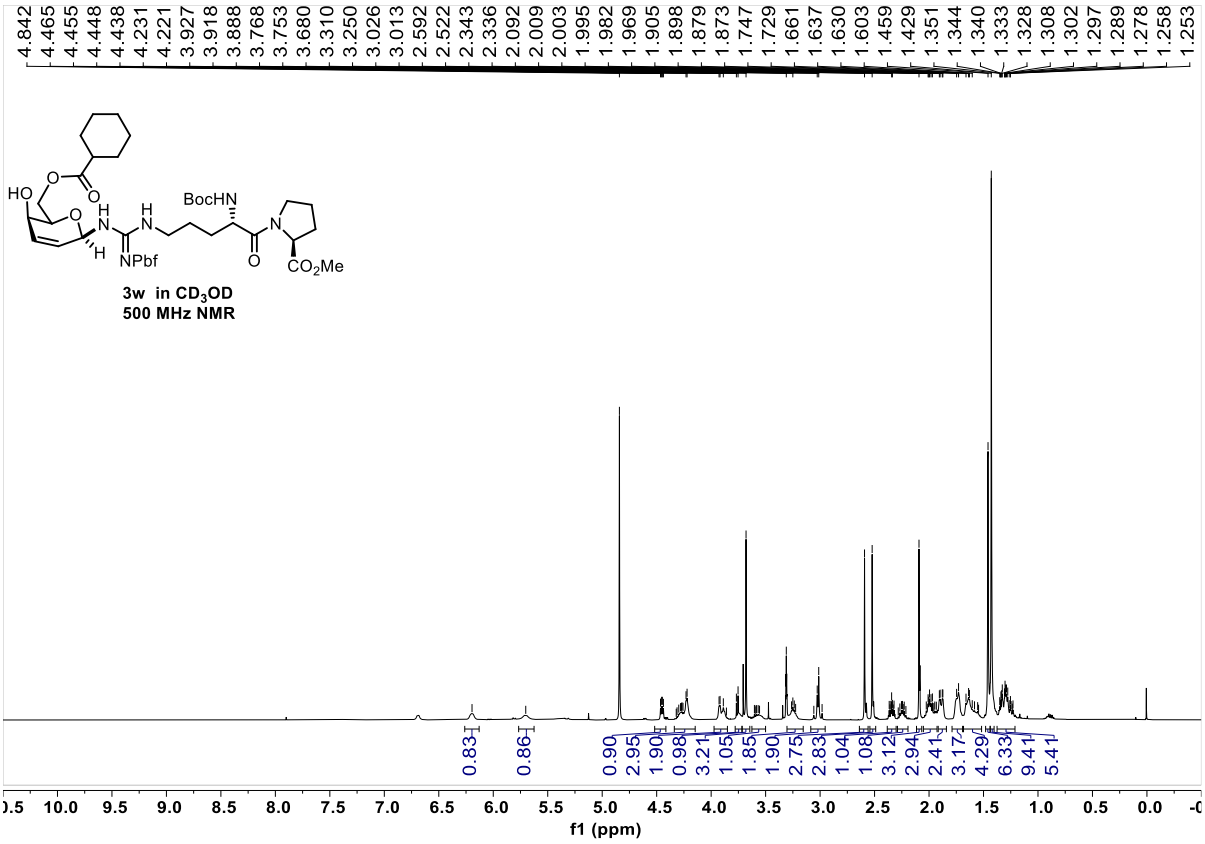
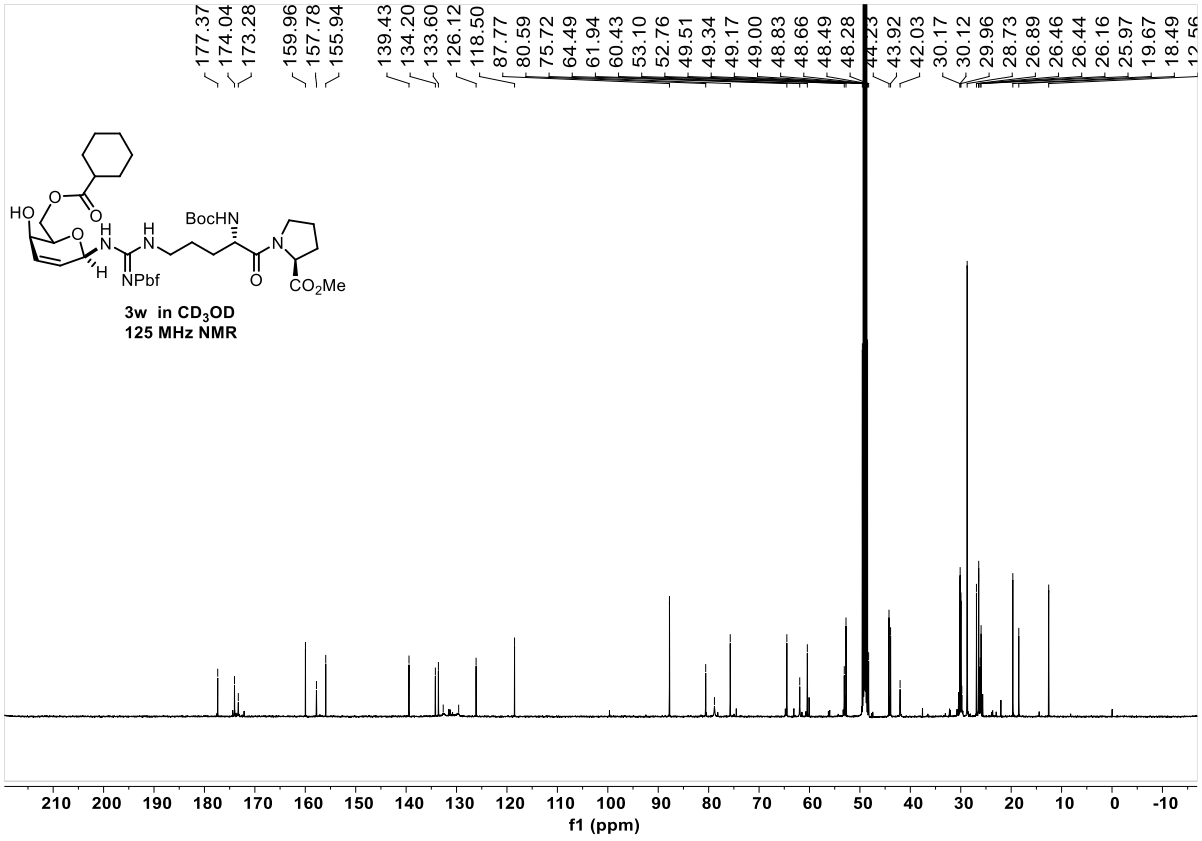
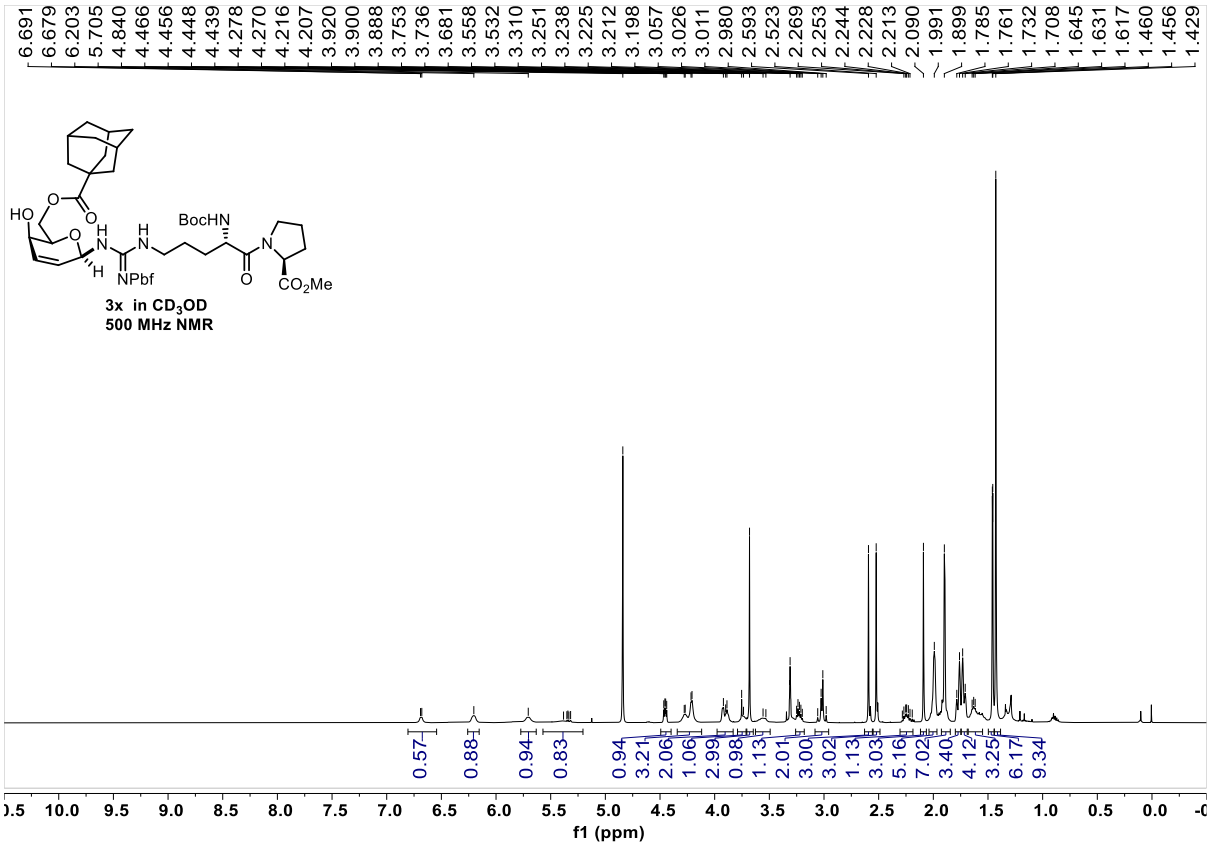
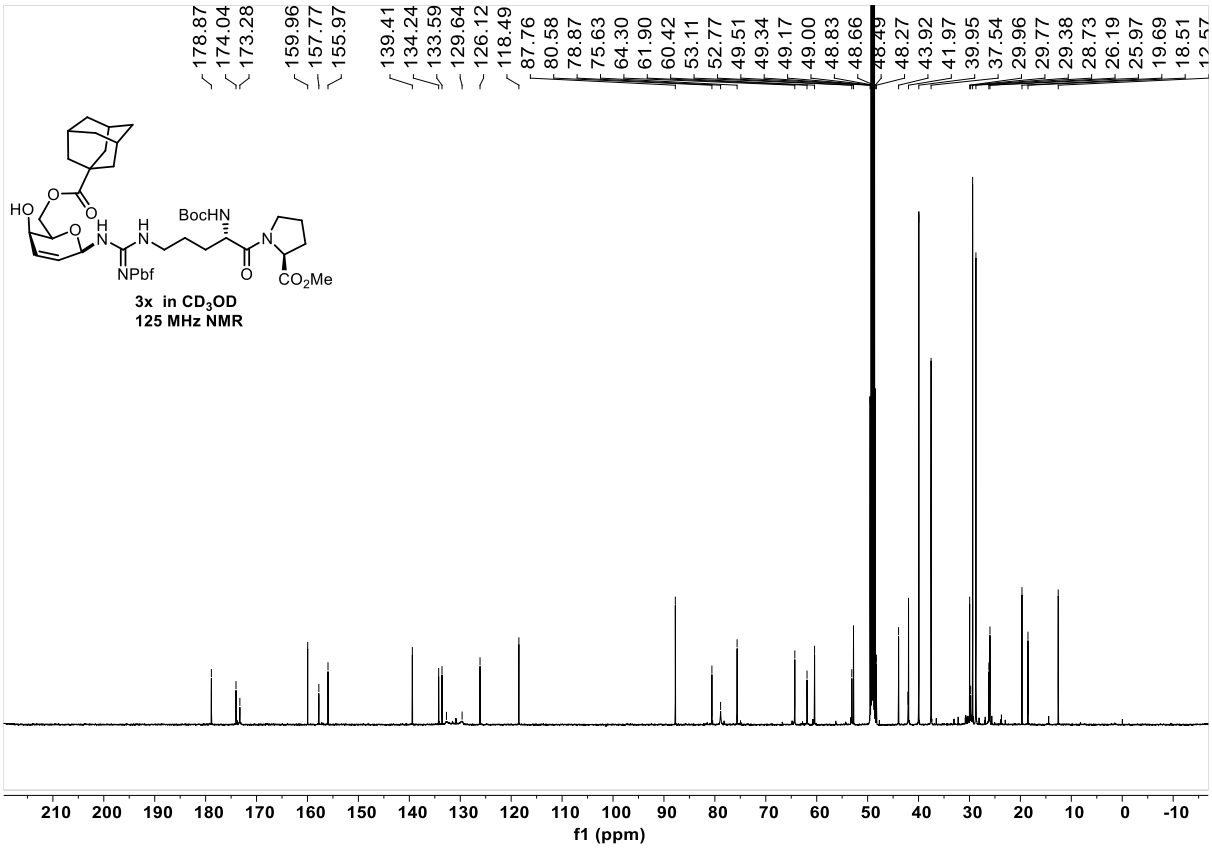
f1 (ppm)

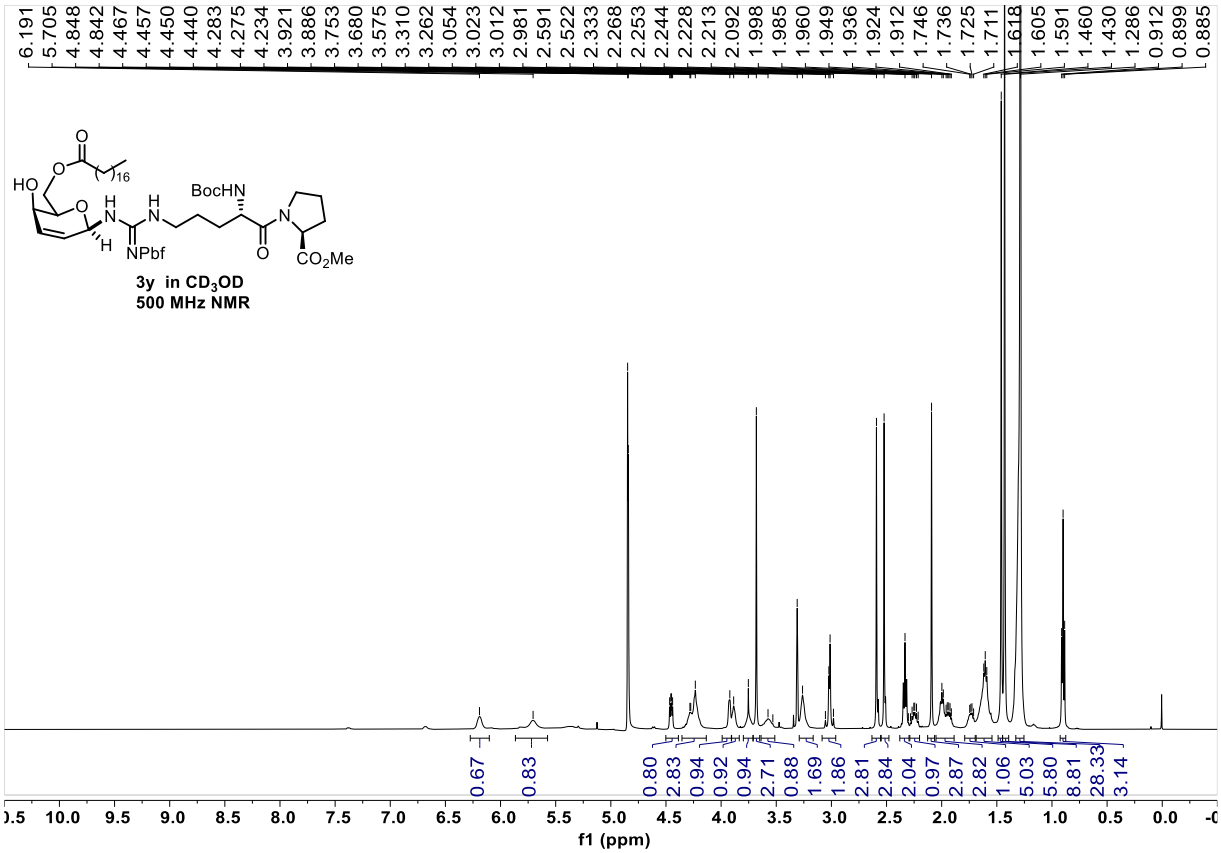

3v in CD3OD
125 MHz NMR
f1 (ppm)

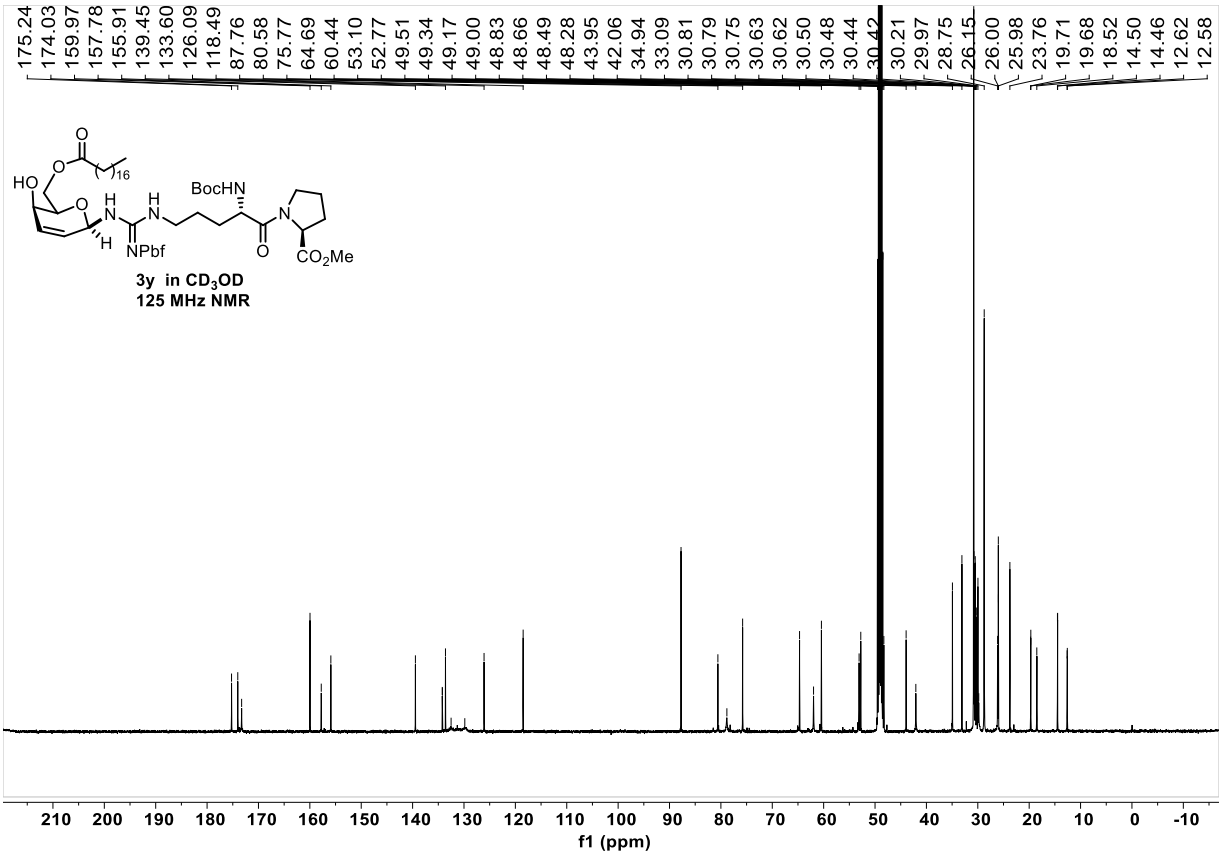

3w in CD3OD
500 MHz NMR
f1 (ppm)

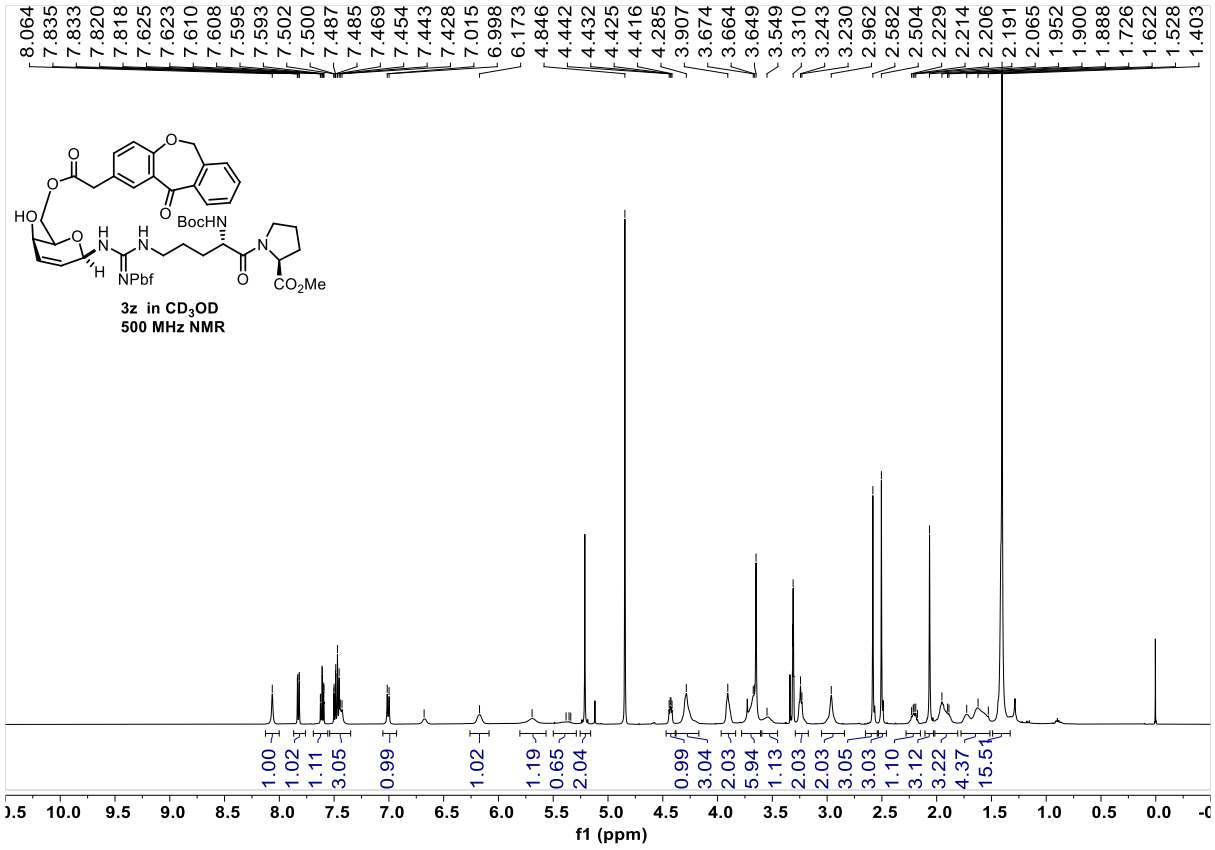

3w in CD3OD
125 MHz NMR
f1 (ppm)

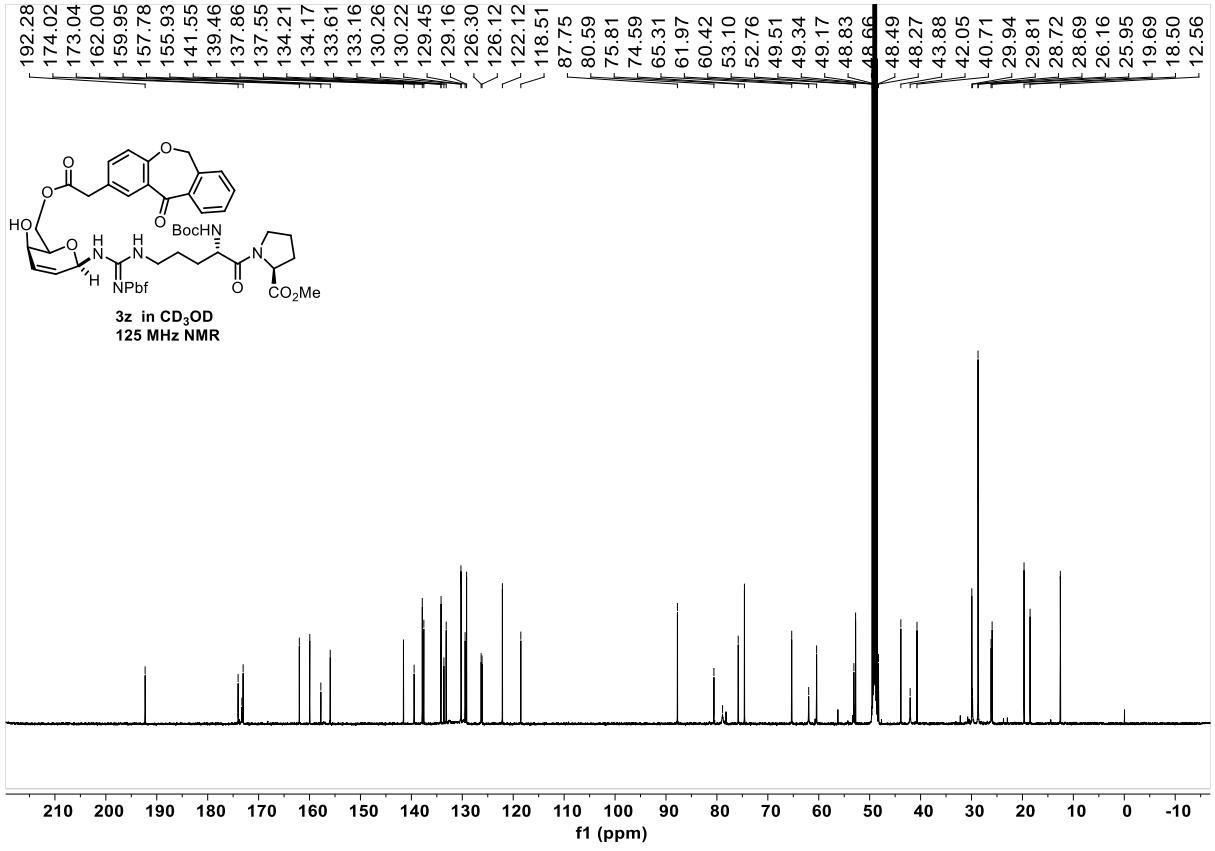

3x in CD3OD
500 MHz NMR
f1 (ppm)

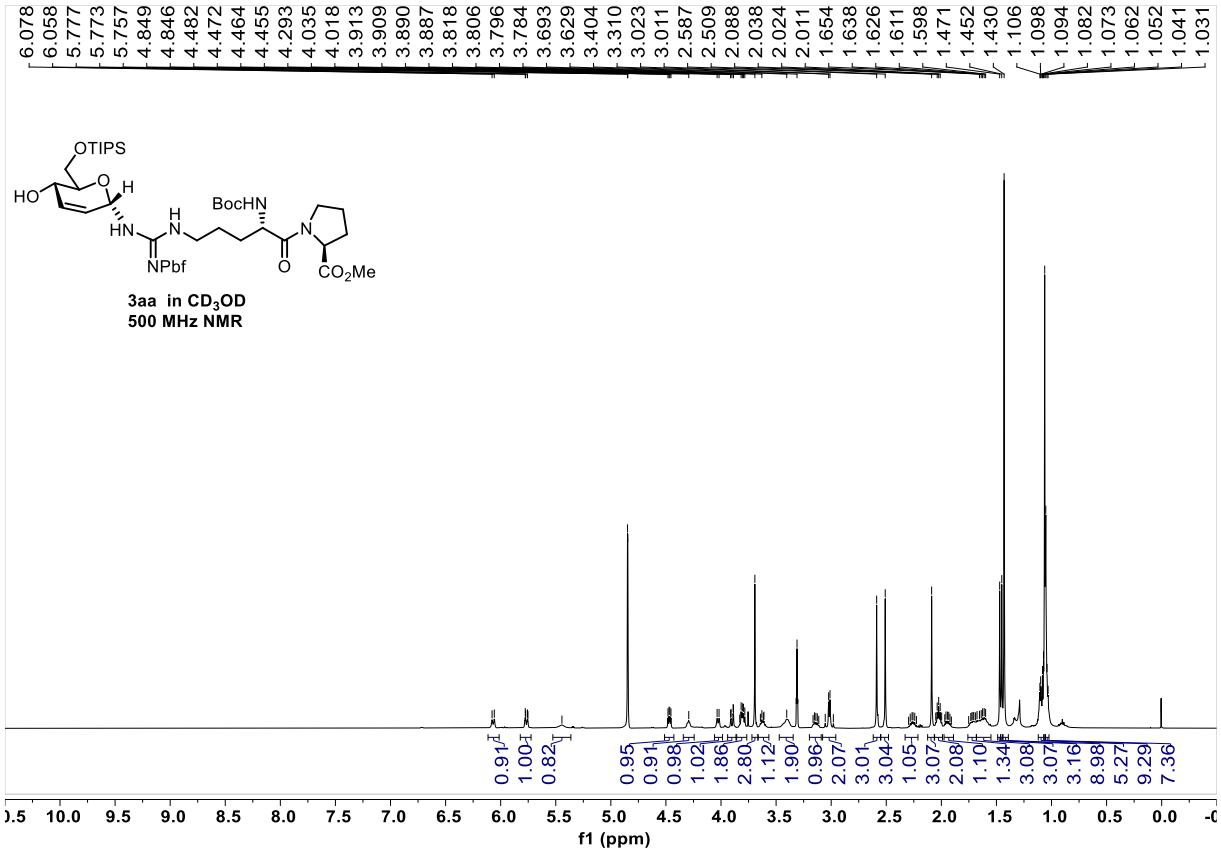

3x in CD3OD
125 MHz NMR
f1 (ppm)

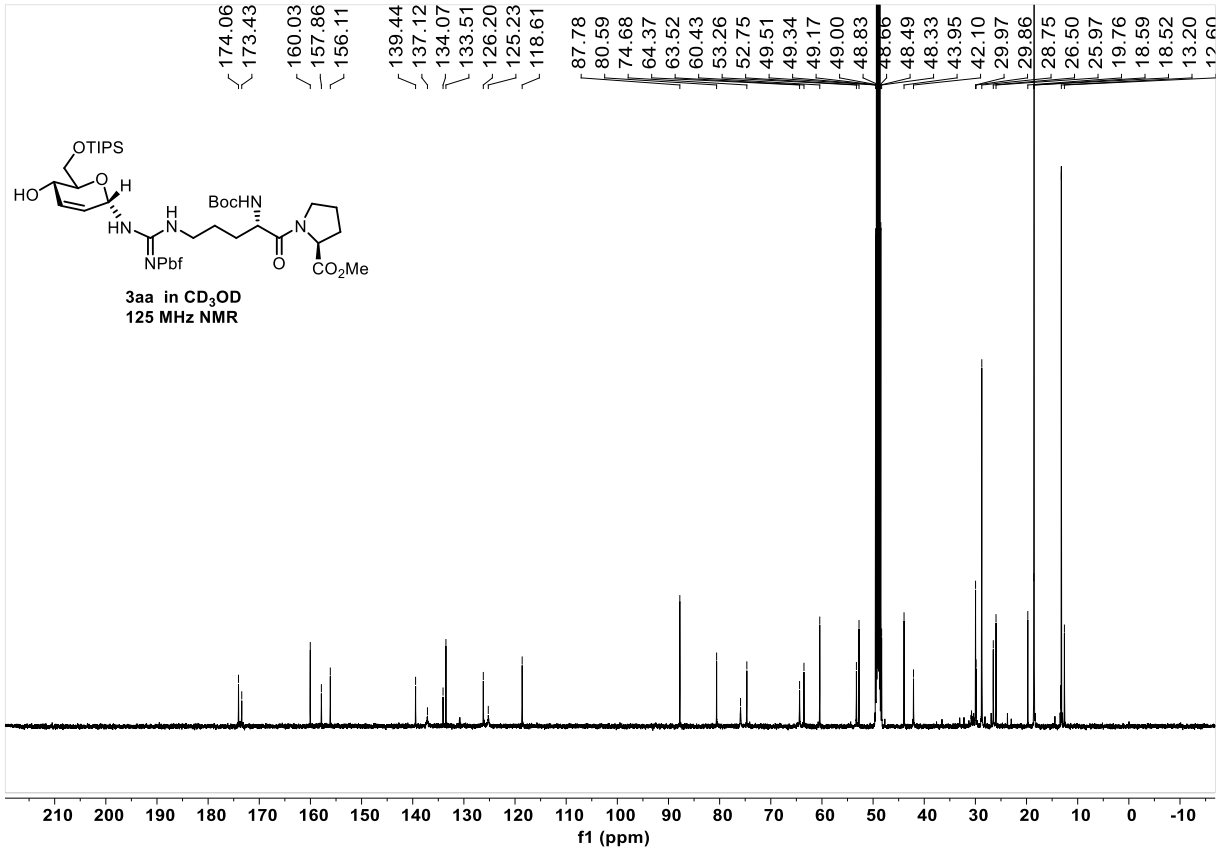

3y in CD3OD
500 MHz NMR
f1 (ppm)

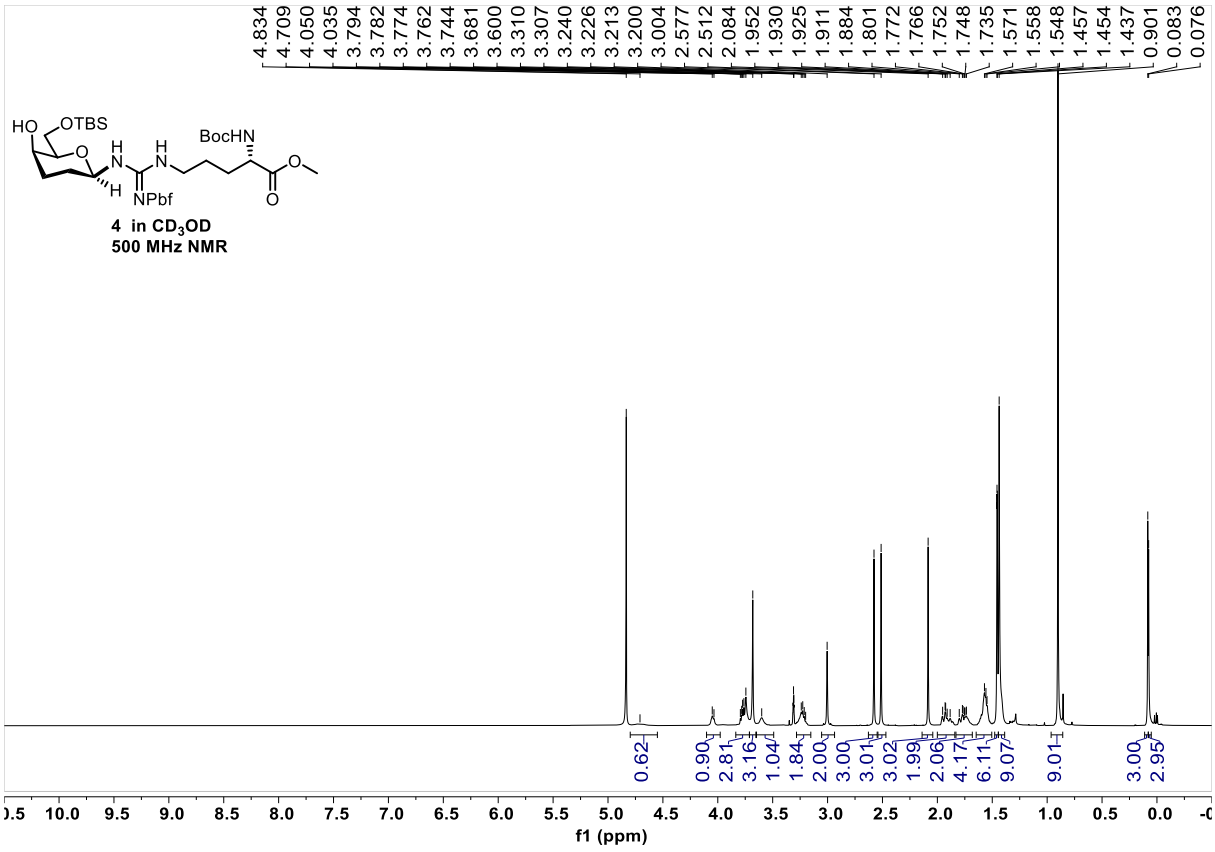

3y in CD3OD
125 MHz NMR
f1 (ppm)

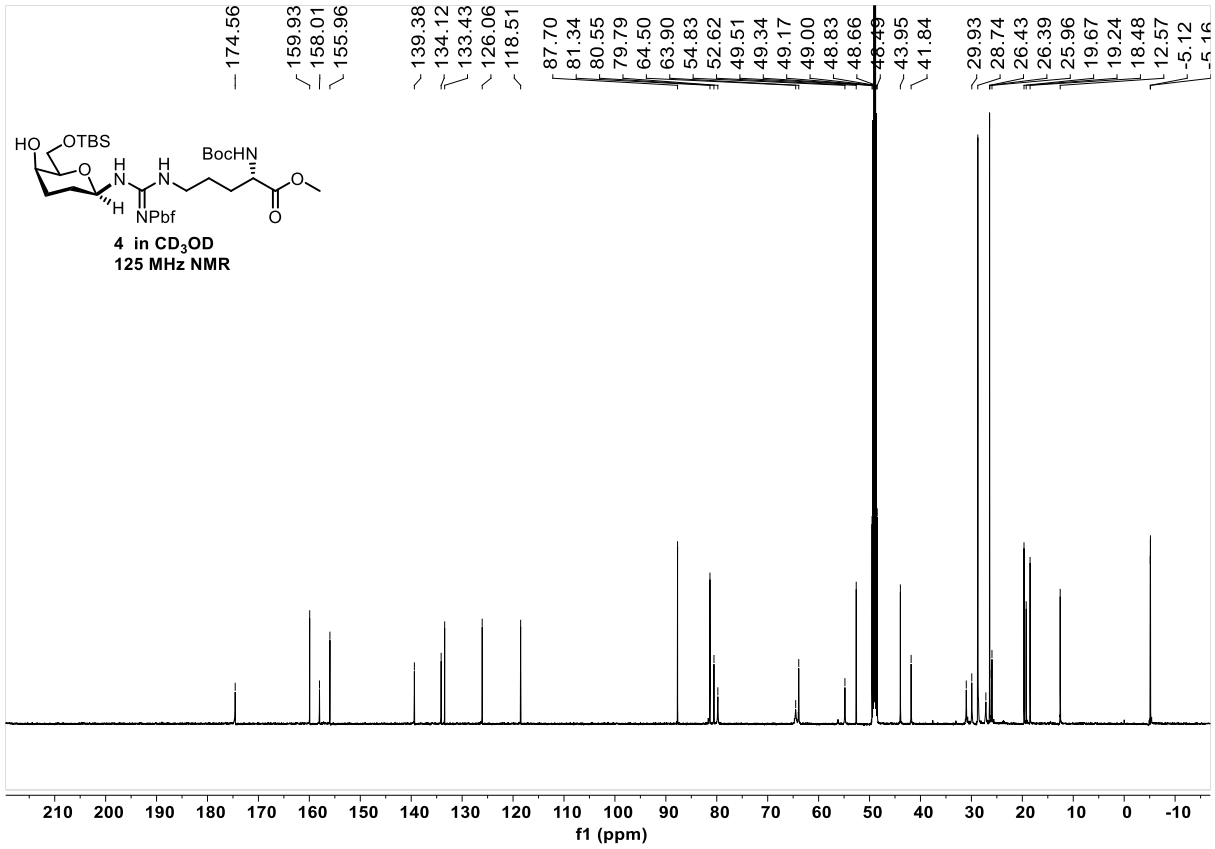

3z in CD3OD
500 MHz NMR
f1 (ppm)

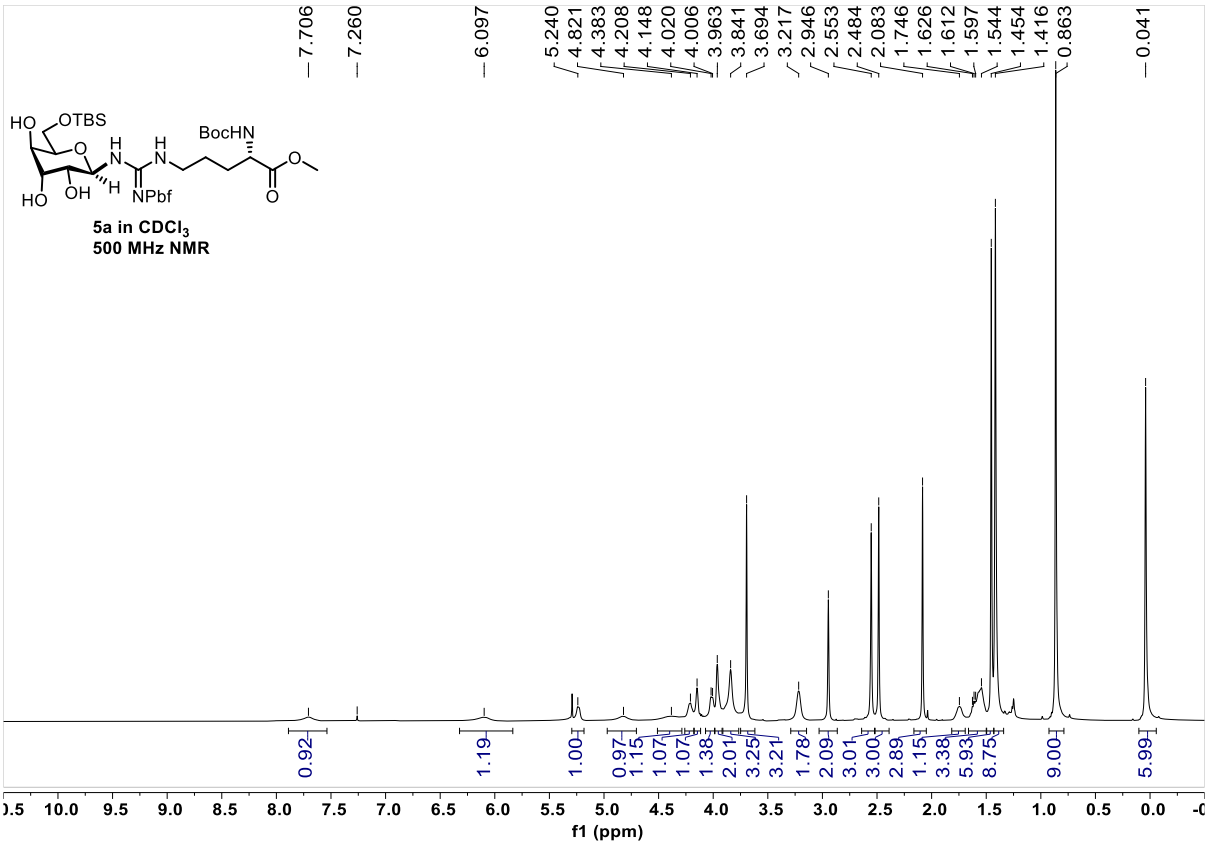

3z in CD3OD
125 MHz NMR
f1 (ppm)

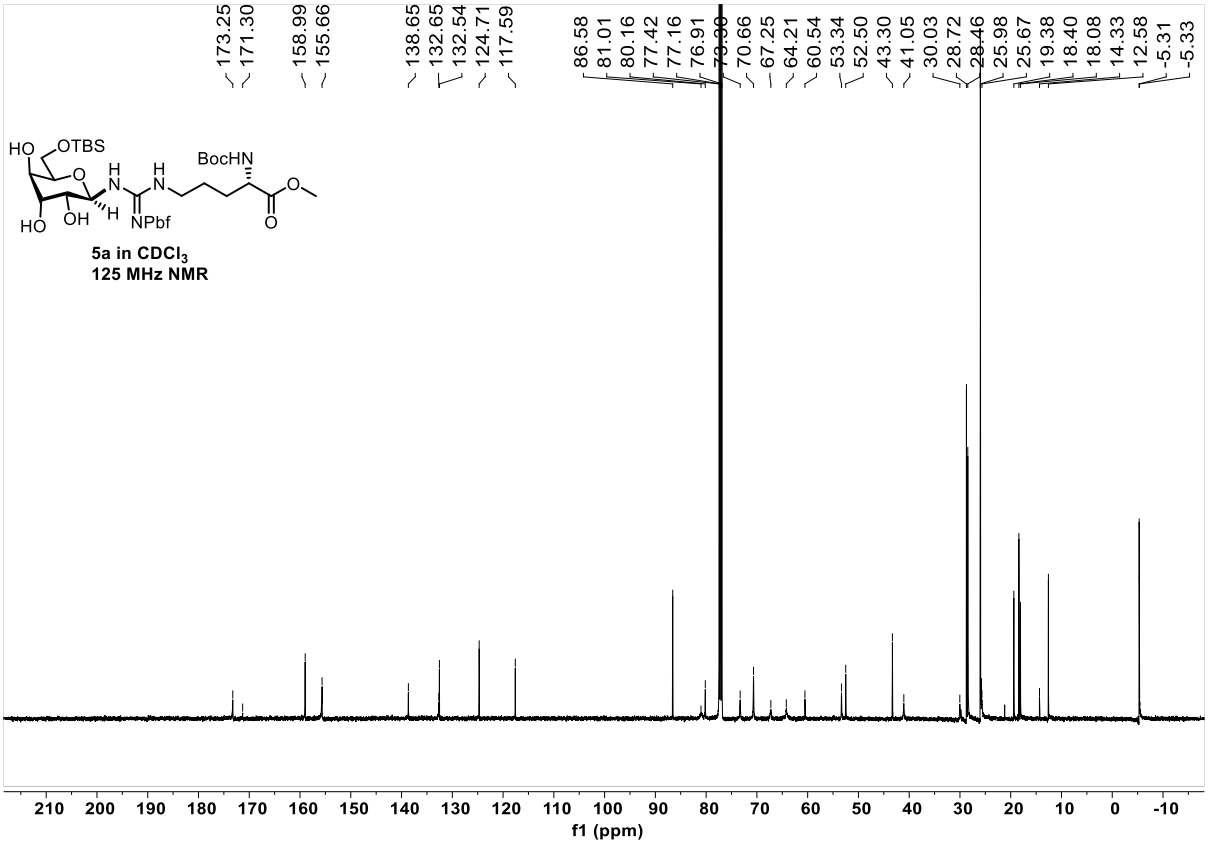

OTIPS
HO
O
H
HN
H
N
BocHN
NPbf
O
N
CO2Me
3aa in CD3OD
500 MHz NMR
f1 (ppm)

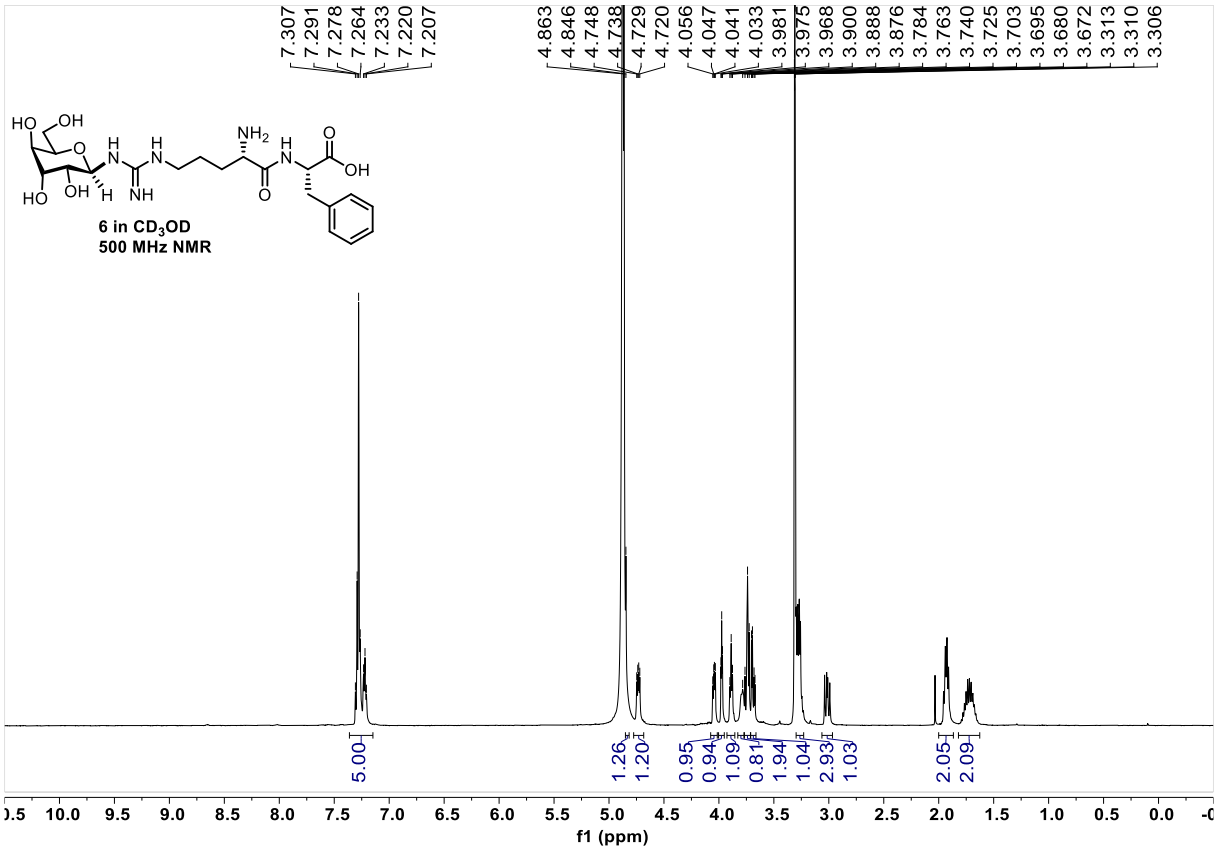

OTIPS
HO
O
H
HN
H
N
BocHN
NPbf
O
N
CO2Me
3aa in CD3OD
125 MHz NMR
f1 (ppm)

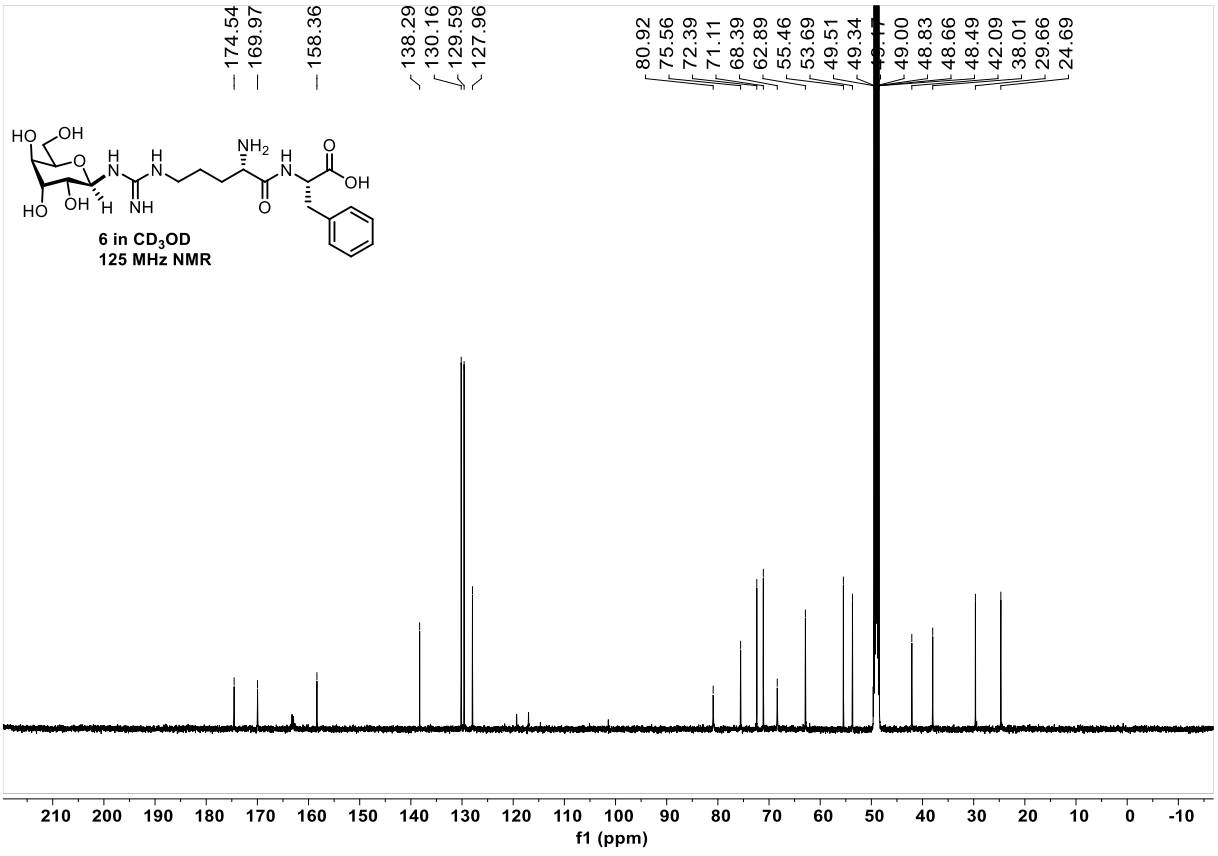

4.834
4.709
4.050
4.035
3.794
3.782
3.774
3.762
3.744
3.681
3.600
3.310
3.307
3.240
3.226
3.213
3.200
3.004
2.577
2.512
2.084
1.952
1.930
1.925
1.911
1.884
1.801
1.772
1.766
1.752
1.748
1.735
1.571
1.558
1.548
1.457
1.454
1.437
0.901
0.083
0.076
HO
OTBS
O
H
N
H
N
H
NPbf
BocHN
O
O
4 in CD3OD
500 MHz NMR
0.62
0.90
2.81
3.16
1.04
1.84
2.00
3.00
3.01
3.02
1.99
2.06
4.17
6.11
9.07
9.01
3.00
2.95
f1 (ppm)

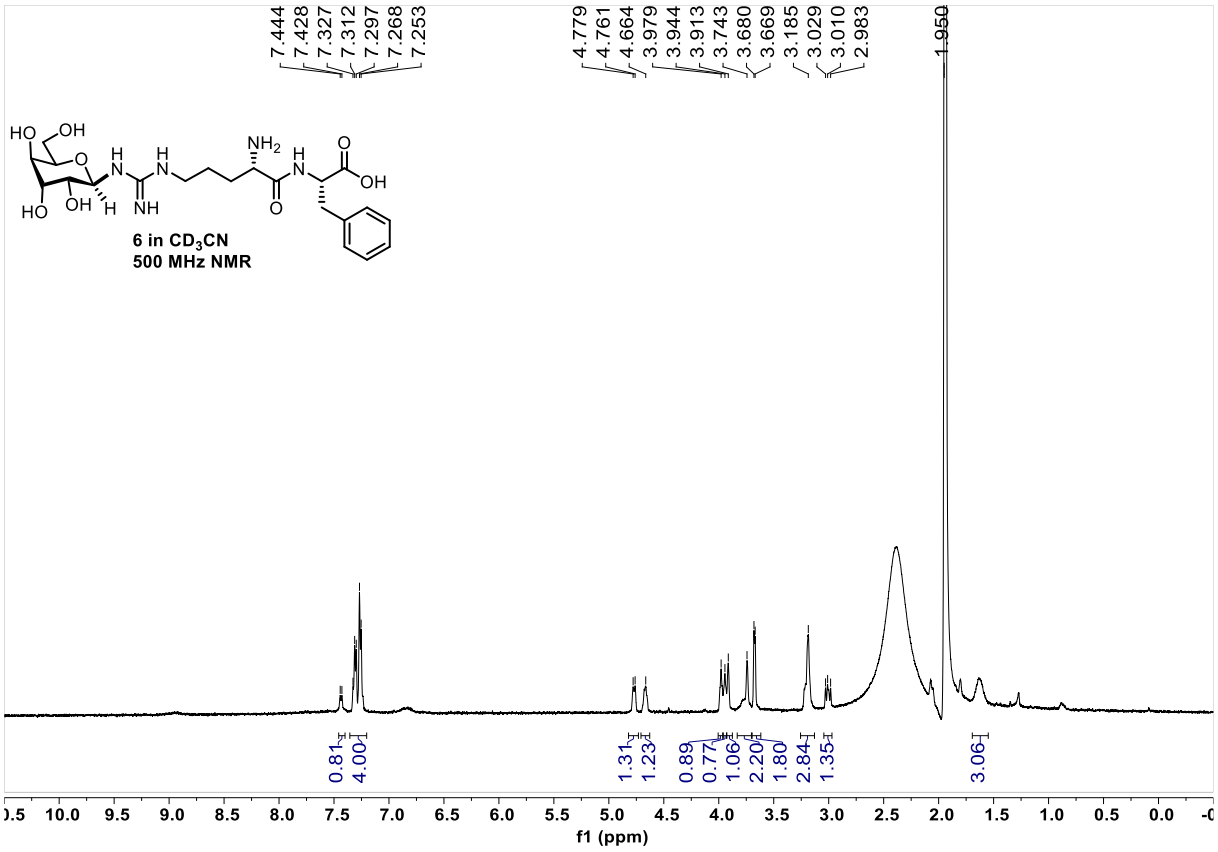

174.56
159.93
158.01
155.96
139.38
134.12
133.43
126.06
118.51
87.70
81.34
80.55
79.79
64.50
63.90
54.83
52.62
49.51
49.34
49.17
49.00
48.83
48.66
48.49
43.95
41.84
29.93
28.74
26.43
26.39
25.96
19.67
19.24
18.48
12.57
-5.12
HO
OTBS
O
H
N
H
N
H
NPbf
BocHN
O
O
4 in CD3OD
125 MHz NMR
f1 (ppm)

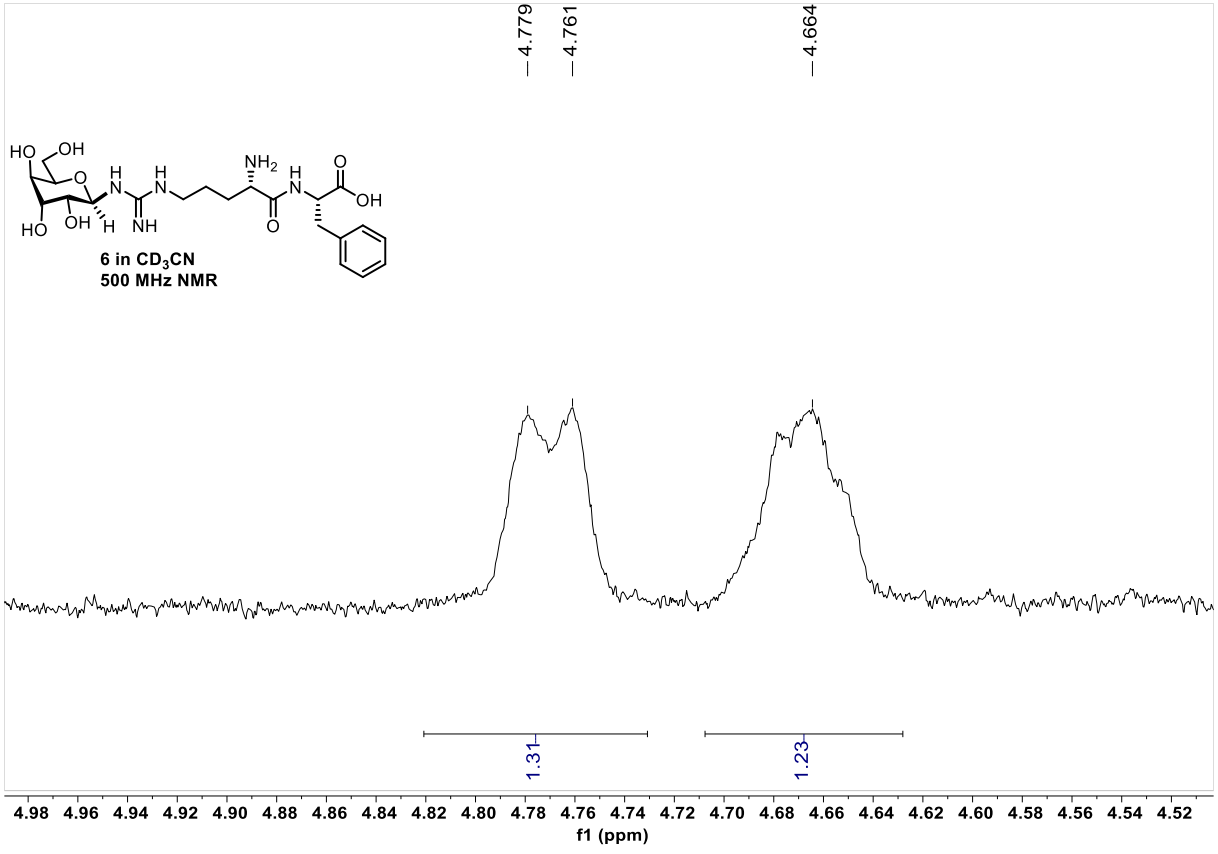

7.706
7.260
6.097
5.240
4.821
4.383
4.208
4.148
4.020
4.006
3.963
3.841
3.694
3.217
2.946
2.553
2.484
2.083
1.746
1.626
1.612
1.597
1.544
1.454
1.416
0.863
0.041
HO
OTBS
O
H
N
H
N
BocHN
O
O
HO
OH
H
NPbf
5a in CDCl3
500 MHz NMR
0.92
1.19
1.00
0.97
1.15
1.07
1.07
1.38
2.01
3.25
3.21
1.78
2.09
3.01
3.00
2.89
1.15
3.38
5.93
8.75
9.00
5.99
f1 (ppm)


173.25
171.30
158.99
155.66
138.65
132.65
132.54
124.71
117.59
86.58
81.01
80.16
77.42
77.16
76.91
70.66
67.25
64.21
60.54
53.34
52.50
43.30
41.05
30.03
28.72
28.46
25.98
25.67
19.38
18.40
18.08
14.33
12.58
-5.31
-5.33
HO
OTBS
O
H
N
H
N
BocHN
O
O
HO
OH
H
NPbf
5a in CDCl3
125 MHz NMR
f1 (ppm)

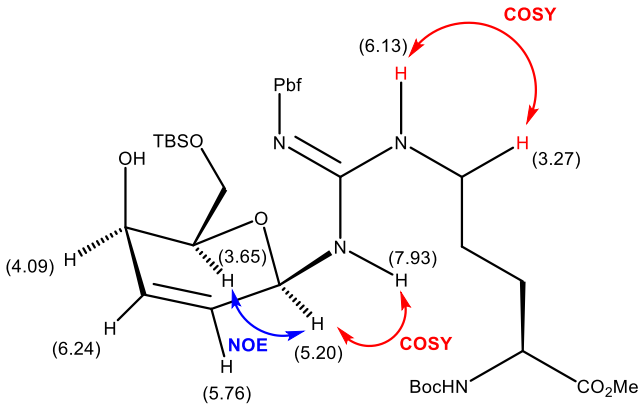

7.307
7.291
7.278
7.264
7.233
7.220
7.207
4.863
4.846
4.748
4.738
4.729
4.720
4.056
4.047
4.041
4.033
3.981
3.975
3.968
3.900
3.888
3.876
3.784
3.763
3.740
3.725
3.703
3.695
3.680
3.672
3.313
3.310
3.306
6 in CD3OD
500 MHz NMR
5.00
1.26
1.20
0.95
0.94
1.09
0.81
1.94
1.04
2.93
1.03
2.05
2.09
f1 (ppm)

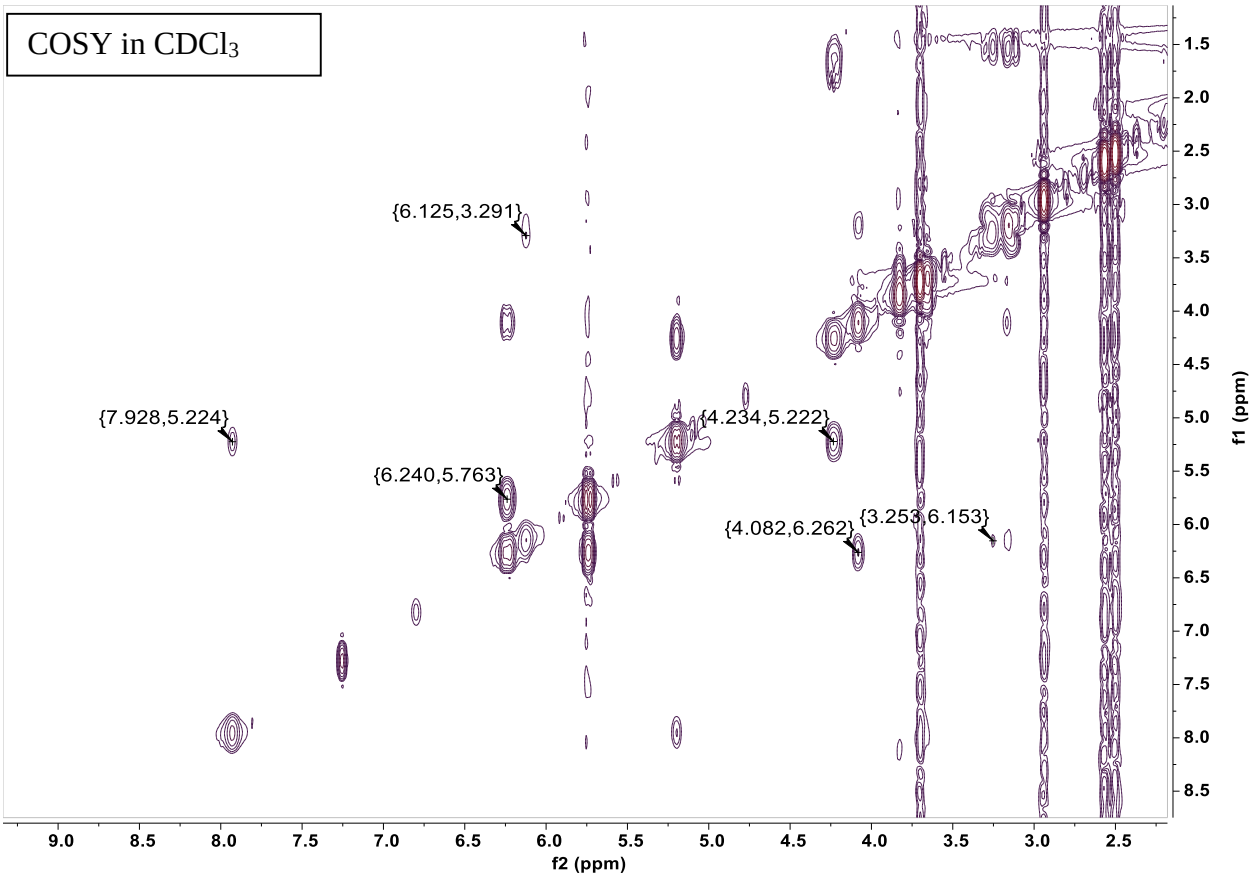

174.54
169.97
158.36
138.29
130.16
129.59
127.96
80.92
75.56
72.39
71.11
68.39
62.89
55.46
53.69
49.51
49.34
49.00
48.83
48.66
48.49
42.09
38.01
29.66
24.69
6 in CD3OD
125 MHz NMR
f1 (ppm)

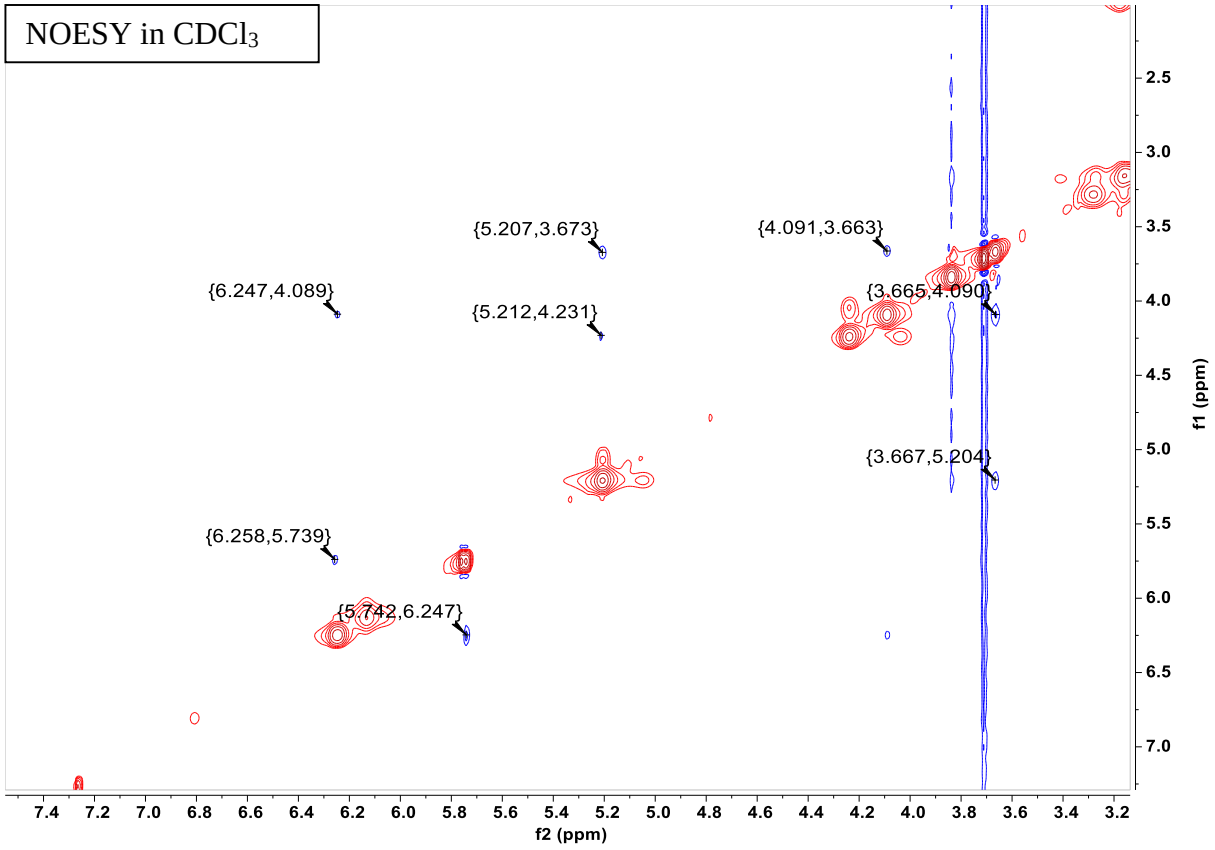

7.444
7.428
7.327
7.312
7.297
7.268
7.253
4.779
4.761
4.664
3.979
3.944
3.913
3.743
3.680
3.669
3.185
3.029
3.010
2.983
1.950
6 in CD3CN
500 MHz NMR
0.81
4.00
1.31
1.23
0.89
0.77
1.06
2.20
1.80
2.84
1.35
3.06
f1 (ppm)

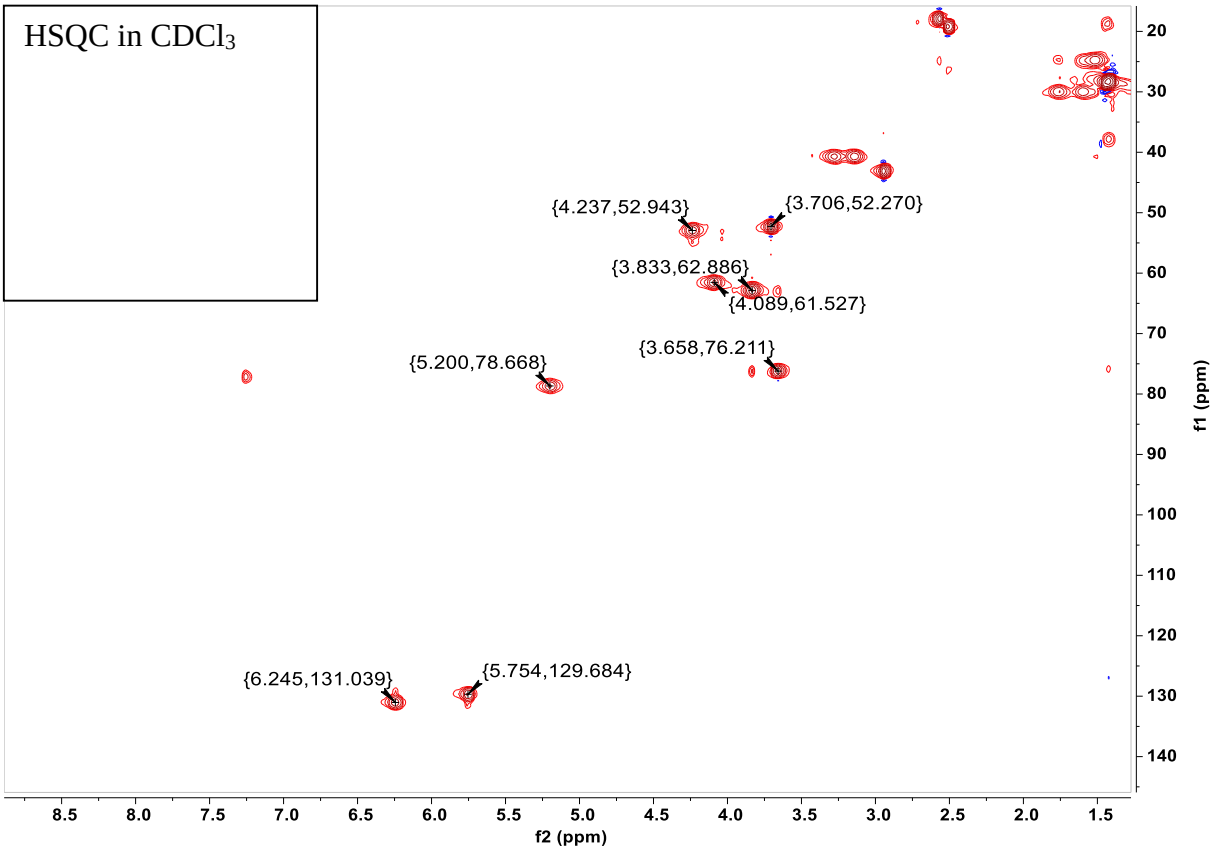

4.779
4.761
4.664
6 in CD3CN
500 MHz NMR
1.31
1.23
f1 (ppm)

5 2D NMR Spectra for compound 3a

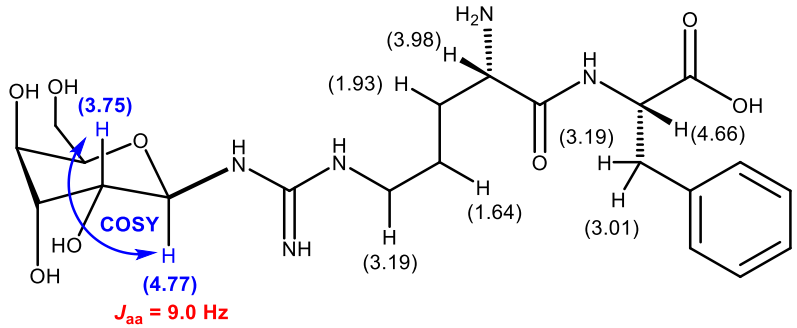


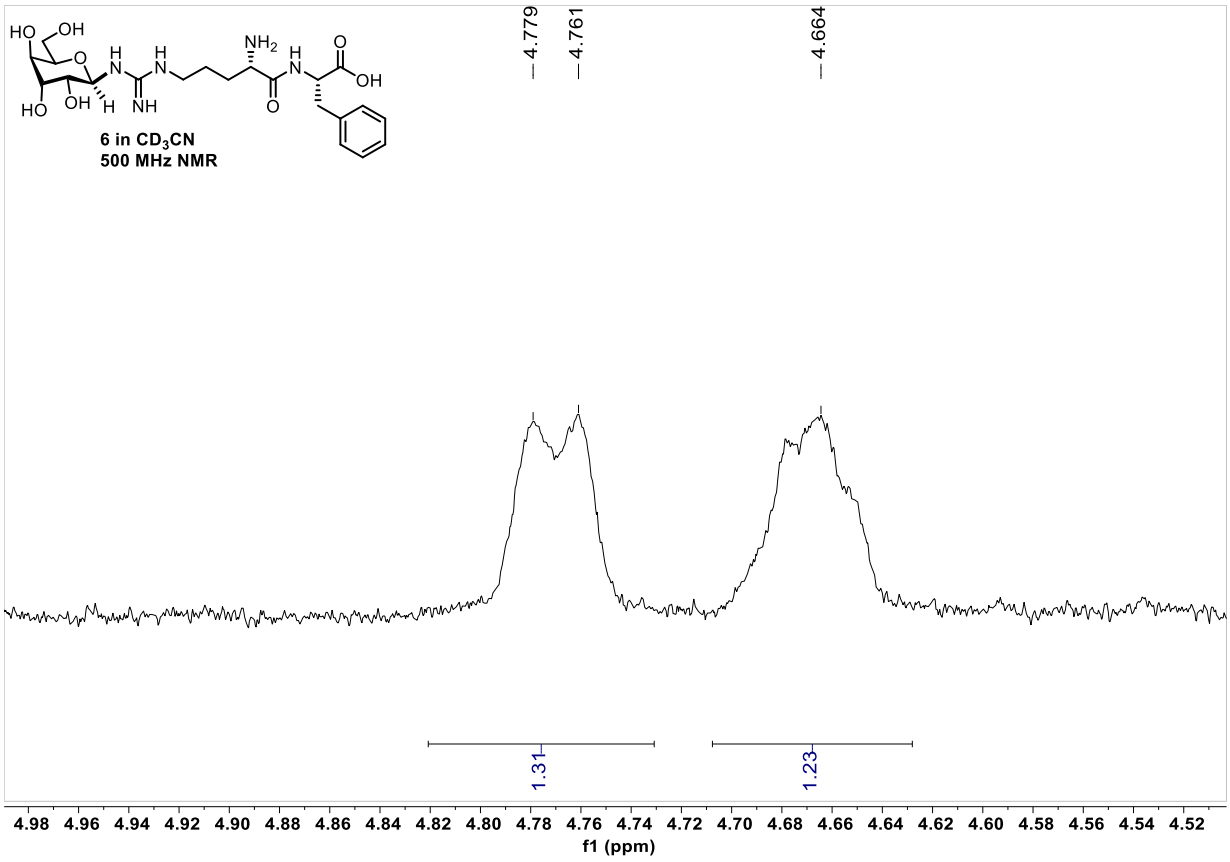


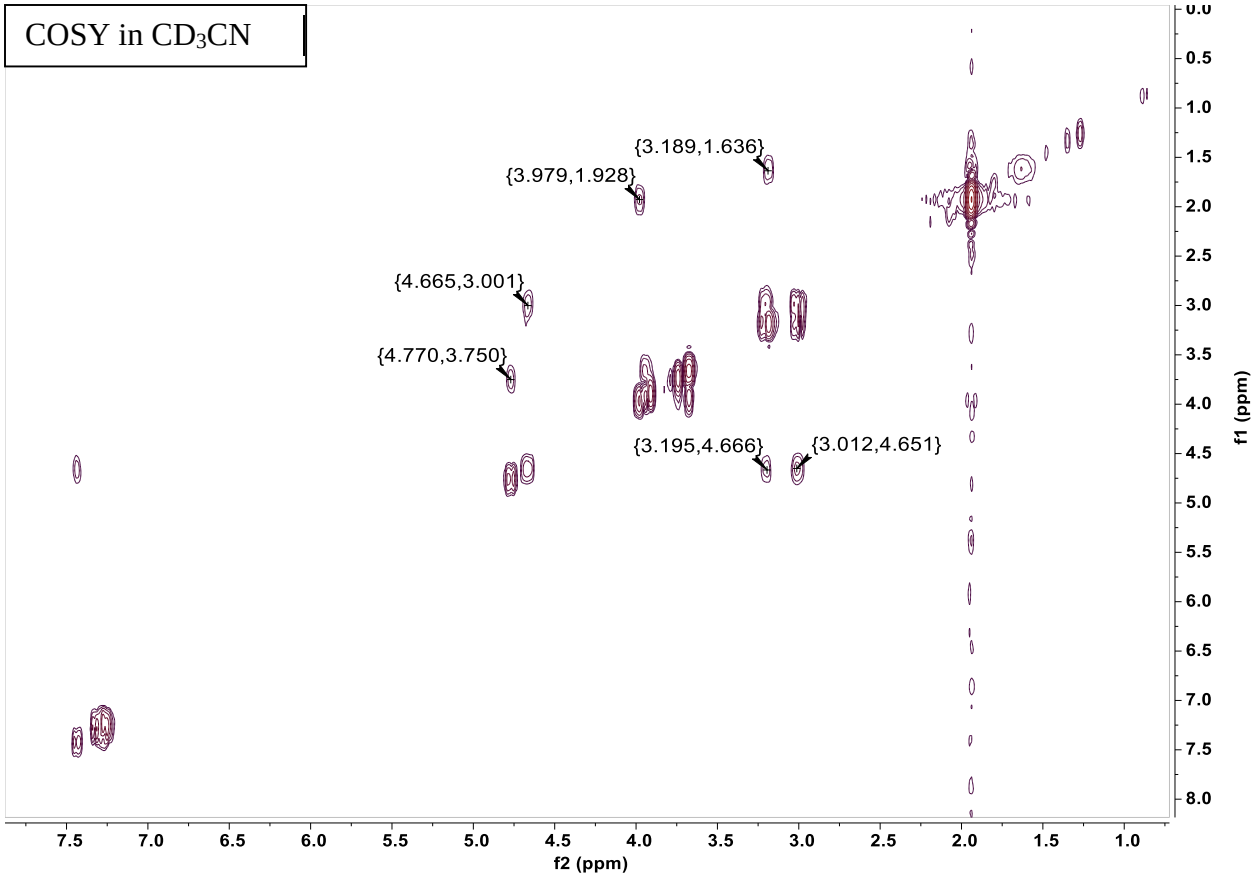

NOESY in CDCl3
{5.207,3.673}
{4.091,3.663}
{6.247,4.089}
{3.665,4.090}
{5.212,4.231}
{3.667,5.204}
{6.258,5.739}
{5.742,6.247}
f2 (ppm)
f1 (ppm)

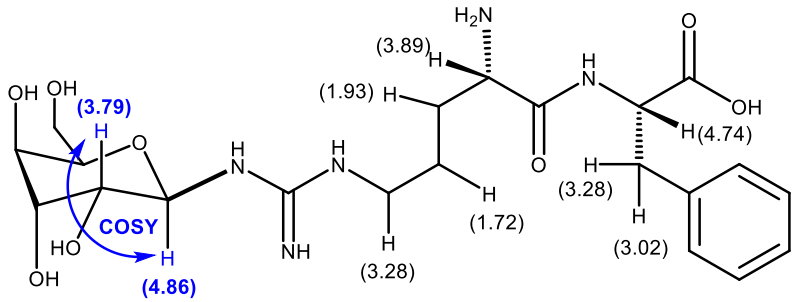

HSQC in CDCl3
{4.237,52.943}
{3.706,52.270}
{3.833,62.886}
{4.089,61.527}
{3.658,76.211}
{5.200,78.668}
{6.245,131.039}
{5.754,129.684}
f2 (ppm)
f1 (ppm)

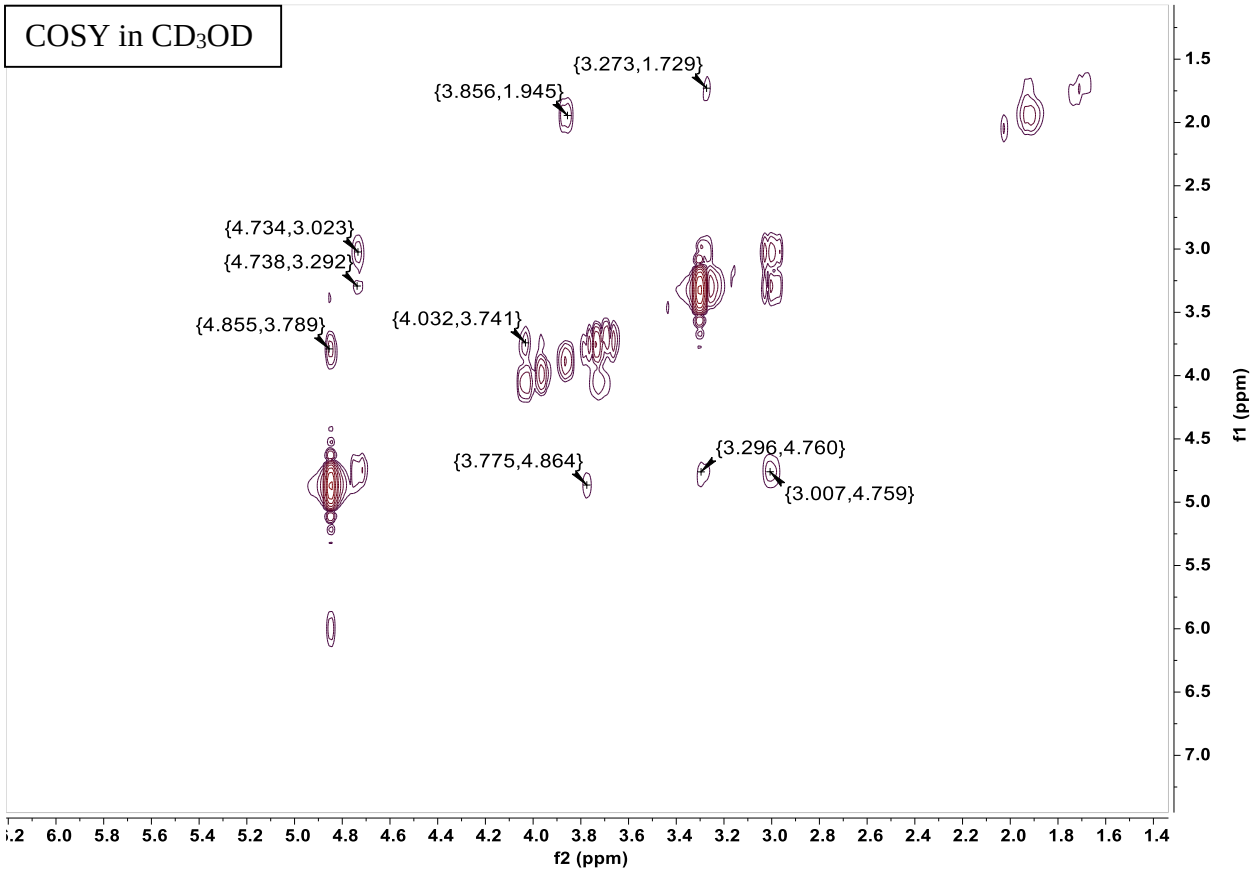
6 2D NMR Spectra for compound 6






COSY in CD3CN
{3.189,1.636}
{3.979,1.928}
{4.665,3.001}
{4.770,3.750}
{3.195,4.666}
{3.012,4.651}
f2 (ppm)
f1 (ppm)


OH
OH
(3.79)
H
O
COSY
HO
H
(4.86)
OH
H
N
NH
H
N
H
(3.28)
(1.93)
H
(3.89)
H
H_2N
O
H
N
O
H
(1.72)
H
(3.28)
H
(3.02)
OH
H(4.74)


COSY in CD_3OD
{3.273,1.729}
{3.856,1.945}
{4.734,3.023}
{4.738,3.292}
{4.855,3.789}
{4.032,3.741}
{3.775,4.864}
{3.296,4.760}
{3.007,4.759}
f2 (ppm)
f1 (ppm)

7 HPLC for compound 6