Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
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Supporting Information for

Stereodivergent Synthesis of 2-Oxo-oligopyrrolidines by Iterative Coupling Strategy

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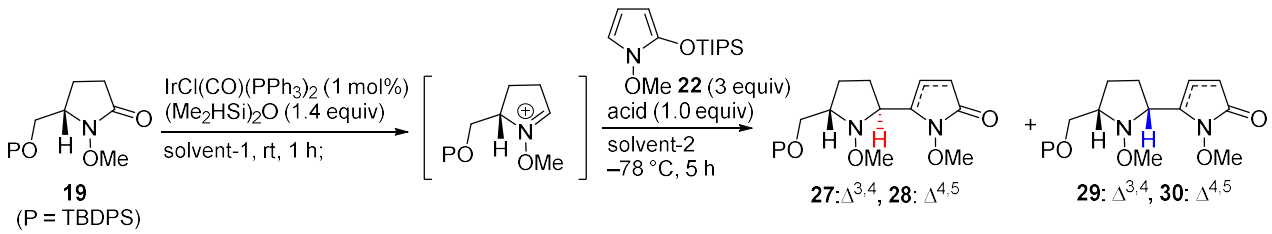
1. Optimization of Reaction Conditions

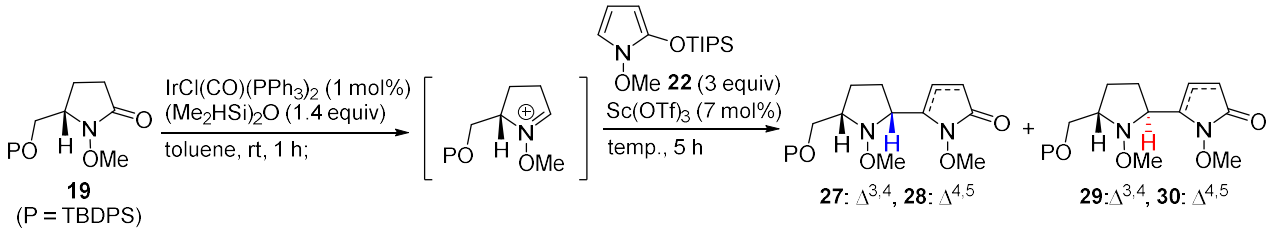
1-1. Optimization of *trans*-selective reductive nucleophilic addition



entry	acid	solvent-1	solvent-2	combined yield (%)[a]	*trans*-(**27**+**28**):*cis*-(**29**+**30**)[b]
1	MsOH	toluene	toluene	20	1.0:1.8
2	$BF_3{\cdot}OEt_2$	toluene	toluene	67	1.0:1.6
3	$SnCl_4$	toluene	toluene	43	1.0:1.9
4	TMSOTf	toluene	toluene	93	1.3:1.0
5	$Sc(OTf)_3$	toluene	toluene	88	1.6:1.0
6	$Sc(OTf)_3$	toluene	Et_2O	94	1.0:1.0
7	$Sc(OTf)_3$	toluene	CH_2Cl_2	100	2.8:1.0
8	$Sc(OTf)_3$	toluene	$CHCl_3$	100	3.0:1.0
9	$Sc(OTf)_3$	$CHCl_3$	$CHCl_3$	100	**4.0**:1.0

[a] Yields were determined by ^{1}H NMR using pyridine as an internal standard. [b] The ratio was determined by ^{1}H NMR.

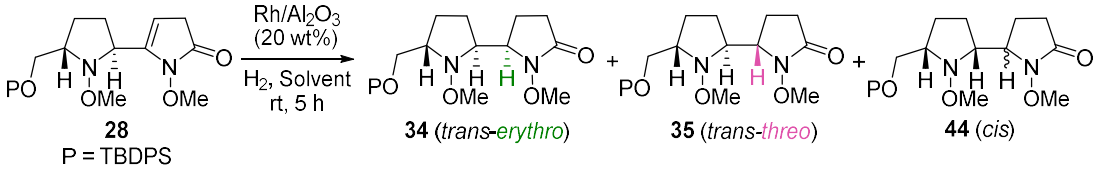
1-2. Optimization of *cis*-selective reductive nucleophilic addition



entry	temp. (°C)	combined yield (%)[a]	*cis*-(**27**+**28**)/*trans*-(**29**+**30**)[b]
1	–78	99	1:1.7
2	–40	89	1:1.7
3	–20	68	1:1.2
4	0	50	1.4:1
5	rt	31	3.1:1
6[c]	rt	62	**5.5**:1

[a] Yields were determined by ^{1}H NMR using pyridine as an internal standard. [b] The ratio was determined by ^{1}H NMR. [c] MeCN was added in the nucleophilic addition.

1-3. Rh/Al_2O_3-catalyzed hydrogenation of *trans*-enamide 28

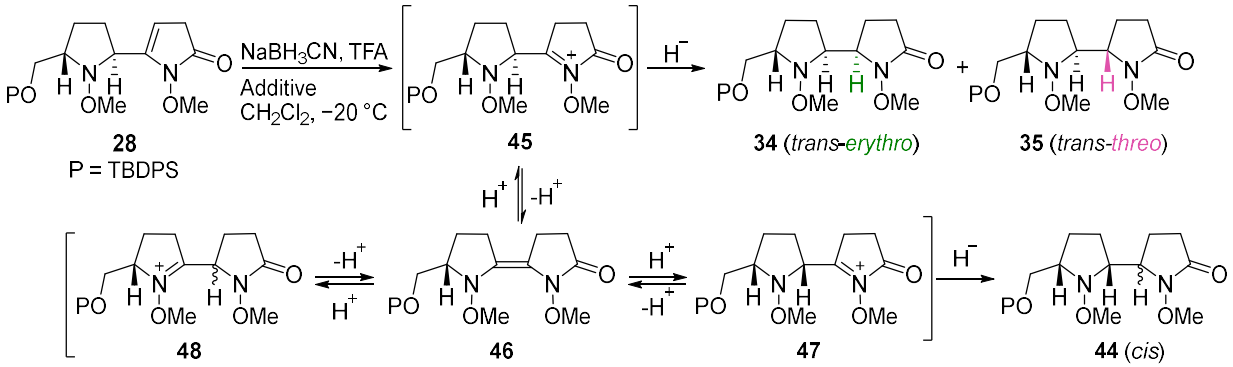


entry	solvent	yield of **34**+**35** (%)[a]	*erythro*-(**34**):*threo*-(**35**)	yield of **44** (%)[a]	recovery of **28**(%)
1	EtOH	87	2.1:1	12	0
2	MeOH	55	1.6:1	14	0
3	EtOAc	89	3.0:1	0	5
4[c]	EtOAc	100	3.1:1	0	0
5[d]	EtOAc	**34**: 58, **35**: 18	3.2:1	0	0

[a] Yields were determined by ^{1}H NMR using pyridine as an internal standard. [b] The ratio was determined by ^{1}H NMR. [c] Reaction time was extended to 10 h. [d] Isolated yield after reversed-phase HPLC.

1-4. Hydride reduction of *trans*-enamide 28

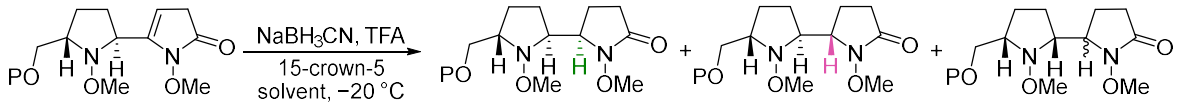
1-4-1. Screening of additives



entry	additive	yield of **34**+**35** (%)[a]	*erythro*-(**34**):*threo*-(**35**)[b]	yield of **44** (%)[a]
1	None	50	2.3:1	13
2	DMPU	30	2.3:1	23
3	HMPA	26	1.8:1	14
4	15-crown-5	60	1.4:1	trace

[a] Yields were determined by ^{1}H NMR using pyridine as an internal standard. [b] The ratio was determined by ^{1}H NMR.

1-4-2. Screening of solvents



28
P = TBDPS

34 (*trans-erythro*) **35** (*trans-threo*) **44** (*cis*)

entry	solvent	yield of **34**+**35** (%)[a]	*erythro*-(**34**):*threo*-(**35**)[b]	yield of **44** (%)[a]
1	CH_2Cl_2	50	2.3:1	0
2	Toluene	30	2.3:1	0
3	Et_2O	26	1.8:1	0
4	$CHCl_3$	60	1:**1.8**	0
5	$CHCl_3$ (no additive)	59	2.0:1	14
6[c]	$CHCl_3$ (TFA → HCl)	**34**: 28, **35**: 50	1:**1.8**	0

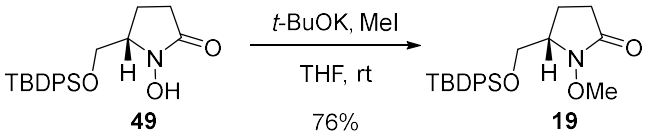
[a] Yields were determined by ^{1}H NMR using pyridine as an internal standard. [b] The ratio was determined by ^{1}H NMR. [c] Isolated yield after reversed-phase HPLC.

2. Experimental Procedure

General Details

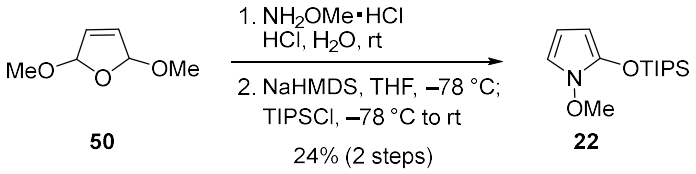
Reactions were performed in oven-dried glassware fitted with rubber septa under an argon atmosphere. Toluene was distilled from CaH_2. MeOH was distilled from $CaSO_4$. EtOAc was single distilled. EtOH, MeCN, and CH_2Cl_2 were single distilled and dried over activated 3A molecular sieves. THF (dehydrated, stabilizer free) and Et_2O (dehydrated, stabilizer free) were purchased from KANTO CHEMICAL CO., INC. All deoxidized solvents, toluene and $CHCl_3$ were purchased from FUJIFILM Wako Pure Chemical Corp. Other commercial reagents were used without further purification. Thin-layer chromatography was performed on Merck TLC silica gel 60 F_{254}, which were visualized by exposure to UV (254 nm) or stained by submersion in ethanolic ninhydrin or ethanolic phosphomolybdic acid solution followed by heating on a hot plate. Flash column chromatography was performed on silica gel (Silica Gel 60 N; 63–210 or 40–50 mesh, KANTO CHEMICAL CO., INC.). Preparative layer chromatography was performed on Merck PLC silica gel 60 F_{254}. ^{1}H NMR spectra were recorded at 500 MHz with JEOL ECA-500 spectrometer, 400 MHz with JEOL ECS-400 spectrometer or 400 MHz with JEOL ECZ-400 spectrometer. ^{13}C NMR spectra at 125 MHz with JEOL ECA-500 spectrometer, 100 MHz with JEOL ECS-400 spectrometer or 100 MHz with JEOL ECS-400 spectrometer. Chemical shifts are reported in ppm with reference to solvent signals [^{1}H NMR: $CDCl_3$ (7.26), C_6D_6 (7.16); ^{13}C NMR: $CDCl_3$ (77.16), C_6D_6 (128.06).]. Signal patterns are indicated as brs, broad peak; s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet. HPLC and GPC were performed on SSC-3462, 5410 (Senshu Scientific Co., Ltd.) with the recycle unit (SSC-1322). Infrared spectra were recorded using a BRUKER ALPHA FT-IR spectrometer. Mass spectra were measured with Waters, LCT Premier XE (ESI-TOF) and Burker, timsTOF Pro 2 (ESI-TOF).

2-1. Synthesis of 2-oxo-pyrrolidine 19 and siloxypyrrole 22



2-Oxo-pyrrolidine 19

Potassium *tert*-butoxide (1.60 g, 14.3 mmol, 1.5 equiv) was added to a solution of *N*-hydroxylactam **49**[1] (3.51 g, 9.50 mmol, 1.0 equiv) and THF (150 mL) at 0 °C. The resulting mixture was stirred for 15 min at 0 °C. Iodomethane (5.9 mL, 94.8 mmol, 10 equiv) was added dropwise to the mixture at 0 °C. The resulting suspension was allowed to warm to room temperature. After stirring for 1 h at room temperature, H_2O (50 mL) was added to the resulting suspension. After stirring for 10 min, the solution was quenched with aqueous saturated $Na_2S_2O_3$ (50 mL), aqueous saturated NH_4Cl (50 mL), and extracted with $CHCl_3$ (4x 100 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc/hexane 1:3 to 1:1) to give 2.75 mg of 2-oxo-pyrrolidine **19** (76%): a colorless oil; $[\alpha]^{24}_D$ −3.5 (*c* 1.0, $CHCl_3$); IR (film) 2932, 2858, 1716, 1472, 1428, 1113, 1054, 773, 742, 704, 505 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.68–7.62 (m, 4H), 7.45–7.35 (m, 6H), 3.90 (dd, *J* = 10.9, 3.4 Hz), 3.80–3.75 (m, 1H), 3.77 (s, 3H), 3.61 (dd, *J* = 10.9, 2.6 Hz, 1H), 2.45 (ddd, *J* = 17.2, 10.0, 6.6 Hz, 1H), 2.29 (ddd, *J* = 17.2, 10.0, 5.2 Hz, 1H), 2.14–1.97 (m, 2H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.6 (C), 135.8 (CH), 135.7 (CH), 133.2 (C), 132.7 (C), 130.0 (CH), 127.91 (CH), 127.88 (CH), 62.8 (CH_2), 62.7 (CH_3), 57.8 (CH), 27.4 (CH_2), 26.9 (CH_3), 19.3 (C), 18.9 (CH_2) ; HRMS (ESI), Calcd for $C_{22}H_{30}NO_3Si$ $(M+H)^+$ 384.1995, found 384.2001.



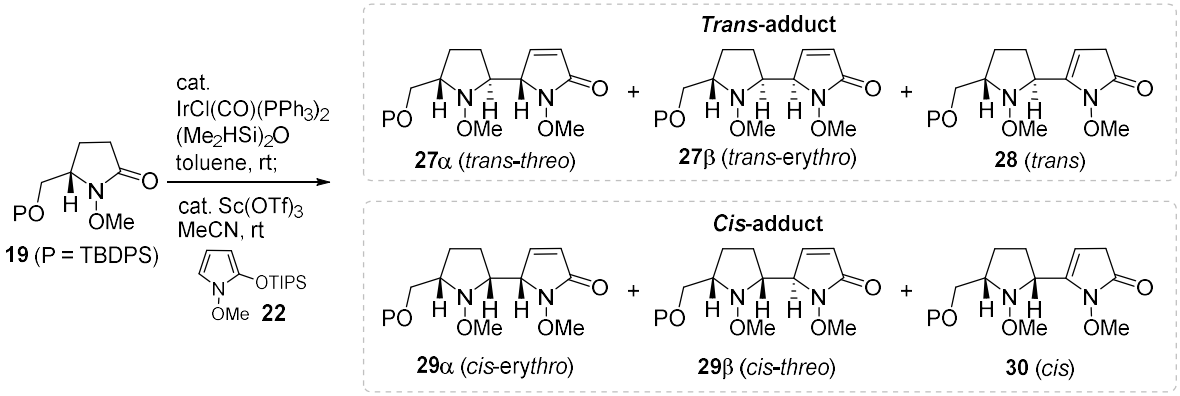
Siloxypyrrole 22[2]

A solution of methoxyamine hydrochloride (3.78 g, 45.3 mmol, 1.1 equiv) and H_2O (23 mL) was added dropwise over 2 h to a solution of 2,5-dihydro-2,5-dimethoxyfuran **50** (5.0 mL, 41 mmol, 1.0 equiv) and aqueous 1.0 M HCl (8.2 mL, 8.2 mmol, 0.2 equiv) at room temperature. Then, solid $NaHCO_3$ was added to the mixture until the mixture was neutralized. The resulting mixture was extracted with $CHCl_3$ (5x 150 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue wa filtrated through a pad of silica gel (EtOAc/hexane 1:1 to 2:1) to give a crude mixture, which was used in the next reaction without further purification.

Sodium bis(trimethylsilyl)amide (1.0 M in THF, 19.3 mL, 19.3 mmol, 1.1 equiv) was added to a solution of a crude mixture (1.98 g, 17.5 mmol, 1.0 equiv) and THF (70 mL) at –78 °C. After maintaining for 10 min at –78 °C, triisopropylsilyl chloride (3.5 mL, 16.5 mmol, 0.9 equiv) was added to the solution at –78 °C. The solution was allowed to warm to room temperature, stirred for 12 h, and diluted with hexane (500 mL). The resulting mixture was filtered through a pad of Celite® and concentrated. The residue was filtered through a pad

of activated aluminum oxide and washed with hexane. The filtrate was concentrated to give 3.28 g of siloxypyrrole **22** (36% over 2 steps): a pale yellow oil; IR (film) 2945, 2869, 1569, 1477, 1439, 1156, 1058, 902, 843, 659 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.34 (dd, *J* = 3.7, 2.3 Hz, 1H), 5.74 (dd, *J* = 4.0, 3.7 Hz, 1H), 5.12 (dd, *J* = 4.0, 2.3 Hz, 1H), 1.29 (sep, *J* = 7.0 Hz, 3H), 1.11 (d, *J* = 7.0 Hz, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.2 (C), 107.1 (CH), 100.4 (CH), 85.5 (CH), 66.3 (CH_3), 17.8 (CH_3), 12.4 (CH); HRMS (ESI), Calcd for $C_{14}H_{28}NO_2Si$ $(M+H)^+$ 270.1884, found 270.1886.

2-2. Synthesis of *trans*-enamide 28 and *cis*-enamide 30

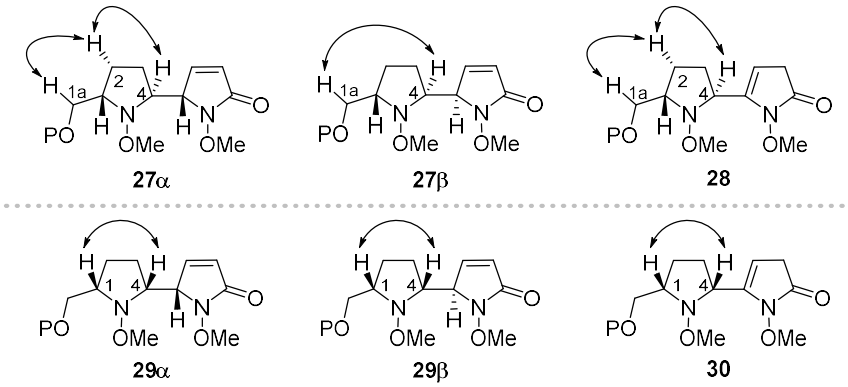


2-Oxo-bispyrrolidines 27–30

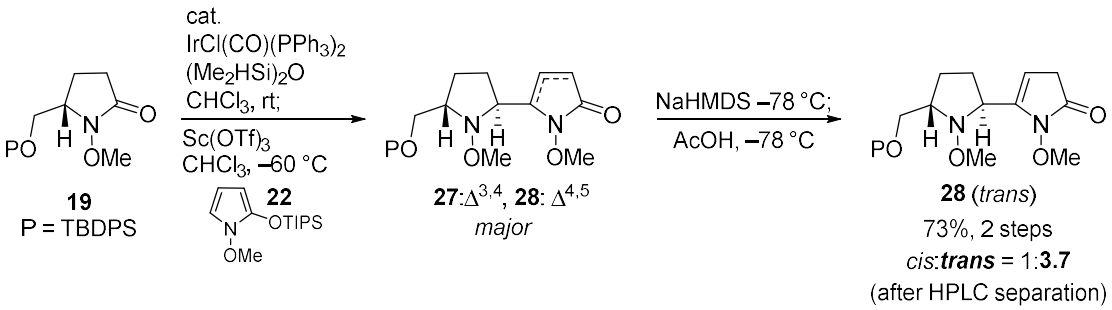
In a glove box, 1,1,3,3-tetramethyldisiloxane (160 μL, 910 μmol, 1.2 equiv) was added to a mixture of 2-oxo-pyrrolidine **19** (291 mg, 759 μmol, 1.0 equiv), $IrCl(CO)(PPh_3)_2$ (5.9 mg, 7.6 μmol, 1 mol %) and toluene (51 mL) at room temperature. After maintaining for 1 h at room temperature, toluene (51 mL) and siloxypyrrole **22** (613 mg, 2.27 mmol, 3.0 equiv) were added to the solution. After the flask was removed from the glove box, scandium trifluoromethanesulfonate (112 mg, 24.4 μmol, 32.1 mol %) was added to the solution at –40 °C. After stirring for 12 h at –40 °C, the solution was quenched with aqueous saturated $NaHCO_3$ (100 mL) and extracted with $CHCl_3$ (3x 100mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was filtrated through a pad of basified silica gel (EtOAc/hexane 1:5 to 1:3) to give a mixture of bicyclic compounds (**27**–**30**, 356 mg, 98% combined yield, **27α**:**27β**:**28**:**29α**:**29β**:**30** = 1.8:1.2:2.0:1.3:1.2:1, The ration was determined by ^{1}H NMR). For analytical samples, a mixture of bicyclic compounds (**27**–**30**) were separated by HPLC with recycle unit (PEGASIL Silica 120-5, 250×10 mm, EtOAc/hexane 1:1, 10 mL/min, **27α**: 12 cycles, T_R = 181.3 min, **27β**: 8 cycles, T_R = 116.5 min, **28**: 3 cycles, T_R = 35.9 min, **29α**: 7 cycles, T_R = 98.5 min, **29β**: 4 cycles, T_R = 53.4 min, **30**: 2 cycles, T_R = 21.9 min). ***Trans-threo-α,β* 27α**: a colorless oil; $[\alpha]^{23}_D$ −112.8 (*c* 1.0, $CHCl_3$); IR (film) 2934, 2858, 1723, 1462, 1428, 1190, 1112, 1049, 824, 742, 704, 505 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73–7.65 (m, 4H), 7.46–7.37 (m, 6H), 7.02 (d, *J* = 6.3 Hz, 1H), 6.17 (d, *J* = 6.3 Hz, 1H), 4.65 (d, *J* = 4.9 Hz, 1H), 3.85 (s, 3H), 3.78 (dd, *J* = 10.3, 5.2 Hz, 1H), 3.74–3.66 (m, 1H), 3.69 (dd, *J* = 10.3, 4.9 Hz, 1H), 3.51 (s, 3H), 3.52–3.46 (m, 1H), 1.88–1.78 (m, 1H), 1.78–1.68 (m, 2H), 1.40–1.29 (m, 1H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.5 (C), 145.0 (CH), 135.80 (CH), 135.78 (CH), 133.5 (C), 129.9 (CH), 129.8 (CH), 127.8 (CH), 127.2 (CH), 65.9 (CH), 65.2 (CH), 64.2 (CH_3), 63.7 (CH), 63.6 (CH_2), 60.8 (CH_3), 26.9 (CH_3), 24.3 (CH_2), 22.4 (CH_2), 19.3 (C); HRMS (ESI), Calcd for $C_{27}H_{37}N_2O_4Si$ $(M+H)^+$ 481.2523, found 481.2520. ***Trans-erythro-α,β* 27β**: a colorless oil; $[\alpha]^{22}_D$ +35.6 (*c* 1.0, $CHCl_3$); IR (film) 2934, 2857, 1725, 1472, 1428, 1193, 1112, 1052, 823, 742, 704, 505 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71–7.64 (m, 4H), 7.45–7.35 (m, 6H), 7.45–7.35 (m, 6H), 7.04 (d, *J* = 6.0, 1H), 6.12 (dd, *J* = 6.0, 1.2 Hz, 1H), 4.46 (brd, *J* = 5.7 Hz, 1H), 3.88 (s, 3H), 3.74 (dd, *J* = 10.3, 5.2 Hz, 1H), 3.63 (dd, *J* = 10.3, 5.2 Hz, 1H), 3.55–3.49 (m, 1H), 3.47 (s, 3H), 3.33 (brs, 1H), 2.04–1.86 (m, 2H), 1.80–1.66 (m, 2H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0 (C), 145.8 (CH), 135.8 (CH), 133.6 (C), 133.5 (C), 129.85 (CH), 129.82 (CH), 127.82 (CH), 127.80 (CH), 125.9 (CH), 66.7 (CH), 65.9 (CH), 64.7 (CH), 63.8 (CH_3), 63.5 (CH_2), 60.2 (CH), 26.9 (CH_3),

24.6 (CH_2), 24.5 (CH_2), 19.3 (C); HRMS (ESI), Calcd for $C_{27}H_{37}N_2O_4Si$ $(M+H)^+$ 481.2523, found 481.2520. ***Trans*-enamide 28**: a colorless oil; $[\alpha]^{22}_D$ −3.9 (*c* 1.0, $CHCl_3$); IR (film) 2936, 2858, 1726, 1472, 1428, 1220, 1112, 1035, 824, 772, 743, 704, 613, 505 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71–7.67 (m, 4H), 7.45–7.36 (m, 6H), 5.10–5.07 (m, 1H), 4.13 (dd, *J* = 7.7, 7.7 Hz, 1H), 3.99 (s, 3H), 3.81 (dd, *J* = 10.6, 5.2 Hz, 1H), 3.78 (dd, *J* = 10.6, 5.7 Hz, 1H), 3.48 (s, 3H), 3.52–3.45 (m, 1H), 3.00 (dd, *J* = 2.0, 2.0 Hz, 1H), 2.99 (dd, *J* = 2.0, 2.0 Hz, 1H), 2.16–2.06 (m, 1H), 2.02–1.94 (m, 1H), 1.94–1.85 (m, 1H), 1.80–1.71 (m, 1H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.6 (C), 144.4 (C), 135.7 (CH), 133.62 (C), 133.56 (C), 129.85 (CH), 129.82 (CH), 127.83 (CH), 127.79 (CH), 98.2 (CH), 67.0 (CH), 64.7 (CH_2), 64.1 (CH), 61.9 (CH_3), 60.9 (CH_3), 34.8 (CH_2), 26.9 (CH_3), 26.4 (CH_2), 24.8 (CH_2), 19.3 (C); HRMS (ESI), Calcd for $C_{27}H_{37}N_2O_4Si$ $(M+H)^+$ 481.2523, found 481.2521. ***Cis-erythro-α,β* 29α**: a colorless oil; $[\alpha]^{25}_D$ −39.4 (*c* 1.0, $CHCl_3$); IR (film) 2933, 2858, 1725, 1472, 1428, 1193, 1112, 1053, 821, 740, 704, 505 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70–7.64 (m, 4H), 7.46–7.35 (m, 6H), 6.85 (dd, *J* = 6.6, 1.2 Hz, 1H), 6.11 (dd, *J* = 6.6, 1.4 Hz, 1H), 4.48 (ddd, *J* = 3.2, 1.4, 1.2 Hz, 1H), 3.93 (s, 3H), 3.84 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.70 (dd, *J* = 10.3, 6.0 Hz, 1H), 3.57 (s, 3H), 3.22 (ddd, *J* = 8.6, 8.6, 3.2 Hz, 1H), 3.11–3.04 (m, 1H), 1.97–1.87 (m, 1H), 1.73–1.60 (m, 2H), 1.55–1.45 (m, 1H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.3 (C), 145.4 (CH), 135.74 (CH), 135.72 (CH), 133.7 (C), 133.6 (C), 129.8 (CH), 127.8 (CH), 126.5 (CH), 69.4 (CH), 67.8 (CH), 65.3 (CH_2), 65.2 (CH), 64.3 (CH_3), 62.5 (CH_3), 27.0 (CH_3), 23.2 (CH_2), 20.5 (CH_2), 19.4 (C); HRMS (ESI), Calcd for $C_{27}H_{37}N_2O_4Si$ $(M+H)^+$ 481.2523, found 481.2515. ***Cis-threo-α,β* 29β**: $[\alpha]^{25}_D$ +132.6 (*c* 1.0, $CHCl_3$) ; IR (film) 2934, 2859, 1725, 1471, 1428, 1188, 1112, 1049, 824, 741, 704, 506 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71–7.65 (m, 4H), 7.46–7.37 (m, 6H), 7.10 (dd, *J* = 6.6, 1.7 Hz, 1H), 6.18 (dd, *J* = 6.6, 1.7 Hz, 1H), 4.57 (ddd, *J* = 4.6, 1.7, 1.7 Hz, 1H), 3.86 (s, 3H), 3.83 (dd, *J* = 10.3, 4.3 Hz, 1H), 3.66 (dd, *J* = 10.3, 6.0 Hz, 1H), 3.61 (ddd, *J* = 8.6, 8.6, 4.6 Hz, 1H), 3.52 (s, 3H), 3.20–3.12 (m, 1H), 1.94–1.85 (m, 1H), 1.76–1.67 (m, 1H), 1.55–1.40 (m, 1H), 1.24–1.15 (m, 1H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7 (C), 144.4 (CH), 135.8 (CH), 135.7 (CH), 133.73 (C), 133.69 (C), 129.8 (CH), 127.8 (CH), 127.7 (CH), 69.5 (CH), 66.9 (CH), 65.5 (CH_2), 64.2 (CH_3), 64.0 (CH), 63.3 (CH_3), 27.0 (CH_3), 24.0 (CH_2), 20.5 (CH_2), 19.4 (C); HRMS (ESI), Calcd for $C_{27}H_{37}N_2O_4Si$ $(M+H)^+$ 481.2523, found 481.2519. ***Cis*-enamide 30**: a colorless oil; $[\alpha]^{24}_D$ +46.1 (*c* 1.0, $CHCl_3$); IR (film) 2934, 2859, 1723, 1472, 1428, 1190, 1113, 1058, 824, 743, 705, 506 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71–7.65 (m, 4H), 7.46–7.37 (m, 6H), 5.18 (ddd, *J* = 2.6, 2.6, 0.6 Hz, 1H), 3.95 (s, 3H), 3.88 (dd, *J* = 10.3, 4.6 Hz, 1H), 3.78 (ddd, *J* = 8.6, 8.6, 0.6 Hz, 1H), 3.67 (dd, *J* = 10.3, 6.6 Hz, 1H), 3.47 (s, 3H), 3.23–3.16 (m, 1H), 2.96 (dd, *J* = 2.6, 1.2 Hz, 2H), 2.15–2.05 (m, 1H), 2.05–1.96 (m, 1H), 1.87–1.78 (m, 1H), 1.76–1.68 (m, 1H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8 (C), 145.9 (C), 135.8 (CH), 135.7 (CH), 133.78 (C), 133.76 (C), 129.8 (CH), 127.8 (CH), 97.6 (CH), 69.4 (CH), 65.9 (CH_2), 65.9 (CH), 64.6 (CH_3), 62.9 (CH_3), 34.7 (CH_2), 27.0 (CH_3), 26.9 (CH_2), 24.8 (CH_2), 19.4 (C); HRMS (ESI), Calcd for $C_{27}H_{37}N_2O_4Si$ $(M+H)^+$ 481.2523, found 481.2526.

Determination of *cis*- and *trans*-configuration of dimeric compounds 27-30



NOESY experiments for bicyclic compounds (**27**–**30**) (500 MHz, $CDCl_3$)

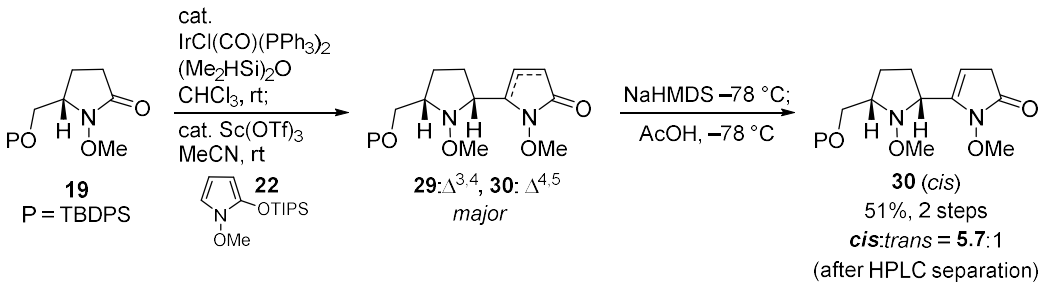


***Trans*-selective nucleophilic addition to afford 28**

Preparation of a stock solution of $IrCl(CO)(PPh_3)_2$ in $CHCl_3$ (0.14 mM): In a glove box, $CHCl_3$ (27 mL) was added to $IrCl(CO)(PPh_3)_2$ (3.0 mg, 3.9 μmol) at room temperature.

In a glove box, 1,1,3,3-tetramethyldisiloxane (66 μL, 380 μmol, 1.4 equiv) was added to a mixture of *N*-methoxylactam **19** (103 mg, 269μmol, 1.0 equiv) and $IrCl(CO)(PPh_3)_2$ (0.14 mM in $CHCl_3$, 18 mL, 2.5 μmol, 1.0 mol %) at room temperature. After maintaining for 1 h at room temperature, $CHCl_3$ (45 mL) and 1-methoxy-2-((triisopropylsilyl)oxy)-1*H*-pyrrole **22** (217 mg, 805 μmol, 3.0 equiv) were added to the solution. After the flask was removed from the glove box, scandium trifluoromethanesulfonate (132 mg, 268 μmol, 1.0 equiv) was added to the solution at –60 °C. After stirring for 12 h at –60 °C, the solution was quenched with aqueous saturated $NaHCO_3$ (60 mL) and extracted with $CHCl_3$ (3x 60mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was filtrated through a pad of basified silica gel (EtOAc/hexane 1:5 to 1:3) to give a mixture of a mixture of *trans*-adducts **27**, **28**, and *cis*-adducts **29**, **30**.

Sodium bis(trimethylsilyl)amide (1.0 M in THF, 740 μL, 740 μmol, 2.8 equiv) was added to a solution of a mixture of *trans*-adducts **27**, **28**, and *cis*-adducts **29**, **30** (127 mg, 264 μmol, 1.0 equiv) and THF (4.0 mL) at –78 °C. After maintaining for 10 min at –78 °C, acetic acid (44 μL, 763 μmol, 2.9 equiv) was added to the solution at –78 °C. After maintaining for 10 min at –78 °C, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (3x 10 mL). The residue was filtrated through a pad of silica gel (EtOAc) and concentrated. The mixture of *trans*-enamide **28** and *cis*-enamide **30** was purified by HPLC with recycle unit (PEGASIL Silica 120-5, 250×10 mm, EtOAc/hexane 1:1, 10 mL/min, 4 cycles, **28**: T_R = 49.2 min, **30**: T_R = 45.8 min) to afford of 91.5 mg of *trans*-enamide (**28**, 57%) and 2.7 mg *cis*-enamide (**30**, 16%).



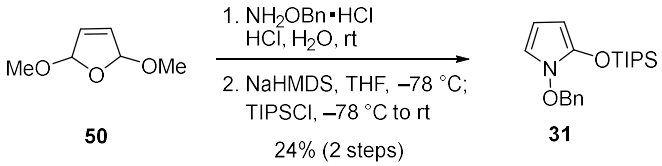
***Cis*-selective nucleophilic addition to afford 30**

Preparation of a stock solution of $IrCl(CO)(PPh_3)_2$ in toluene (0.14 mM): In a glove box, toluene (18 mL) was added to $IrCl(CO)(PPh_3)_2$ (2.0 mg, 2.6 μmol) at room temperature.

In a glove box, 1,1,3,3-tetramethyldisiloxane (23 μL, 130 μmol, 1.4 equiv) was added to a mixture of *N*-methoxylactam **19** (34.8 mg, 90.7 μmol, 1.0 equiv) and $IrCl(CO)(PPh_3)_2$ (0.14 mM in toluene, 5.9 mL, 0.83 μmol, 1.0 mol %) at room temperature. After maintaining for 1 h at room temperature, MeCN (30 mL) was added to the solution. Then, 1-methoxy-2-((triisopropylsilyl)oxy)-1*H*-pyrrole **22** (73.3 mg, 272 μmol, 3.0 equiv) and $Sc(OTf)_3$ (3.4 mg, 6.9 μmol, 7.6 mol %) were added to the solution at room temperature. The flask was removed from the glove box. After maintaining for 5 h at room temperature, the solution was filtrated through a pad of activated aluminum oxide (10 cc), washed with EtOAc/Et_3N (1:0.01), and concentrated. The residue was filtrated through a pad of basified silica gel (EtOAc/hexane 1:5 to 1:3) to give a mixture of *cis*-adducts **29**, **30** and *trans*-adducts **27**, **28** (26.9 mg, 62% combined yield, *cis*-adducts **29**, **30**:*trans*-adducts **27**, **28** = 5.5:1, The ration was determined by ^1H NMR).

Sodium bis(trimethylsilyl)amide (1.0 M in THF, 100 μL, 100 μmol, 1.8 equiv) was added to a solution of a mixture of *cis*-adducts **29**, **30** and *trans*-adducts **27**, **28** (26.9 mg, *cis*-(**29**, **30**):*trans*-(**27**, **28**) = 5.5:1, 56.0 μmol, 1.0 equiv) and THF (1.5 mL) at –78 °C. After maintaining for 10 min at –78 °C, acetic acid (6.4 μL, 110 μmol, 2.0 equiv) was added to the solution at –78 °C. After maintaining for 10 min at –78 °C, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (3x 10 mL). The residue was filtrated through a pad of silica gel (EtOAc) and concentrated. The mixture of *cis*-enamide **30** and *trans*-enamide **28** was purified by HPLC with recycle unit (PEGASIL Silica 120-5, 250×10 mm, EtOAc/hexane 1:1, 10 mL/min, 2 cycles, **30**: T_R = 26.4 min, **28**: T_R = 31.2 min) to afford 18.9 mg of *cis*-enamide (**30**, 43%) and 3.3 mg of *trans*-enamide (**28**, 8%).

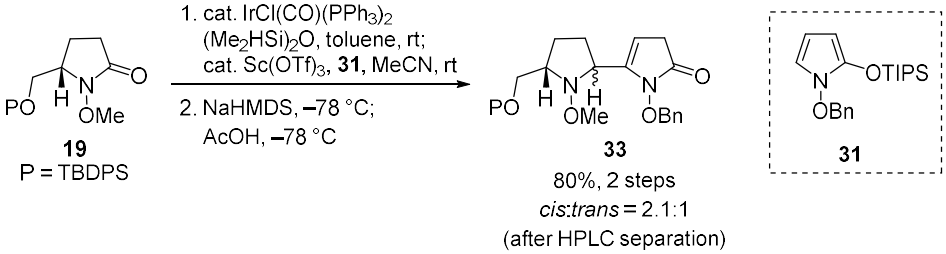
2-3. Elucidation of the retro-vinylogous Mannich reaction



N-Benzyloxysiloxypyrrole (31)

A solution of benzyloxyamine hydrochloride (200 mg, 1.25 mmol, 1.1 equiv) and H_2O (6.0 mL) was added dropwise over 3 h to a solution of 2,5-dihydro-2,5-dimethoxyfuran **50** (140 µL, 1.1 mmol, 1.0 equiv), aqueous 1.0 M HCl (230 µL, 230 µmol, 0.2 equiv) and H_2O (1.2 mL) at room temperature. Then, solid $NaHCO_3$ was added to the mixture until the mixture was neutralized. The resulting mixture was extracted with $CHCl_3$ (4x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was filtrated through a pad of silica gel (EtOAc/hexane 1:4 to 2:3) to give crude mixture, which was used in the next reaction without further purification.

Sodium bis(trimethylsilyl)amide (1.0 M in THF, 620 µL, 620 µmol, 1.1 equiv) was added to a solution of crude mixture (107 mg, 566 µmol, 1.0 equiv) and THF (2.0 mL) at –78 °C. After maintaining for 10 min at –78 °C, triisopropylsilyl chloride (120 µL, 570 mmol, 1.0 equiv) was added to the solution at –78 °C. The solution was allowed to warm to room temperature, stirred for 12 h, and diluted with hexane (20 mL). The resulting mixture was filtered through a pad of activated aluminum oxide and washed with hexane. The filtrate was concentrated to give 155 mg of *N*-benzyloxy-2-siloxypyrrole **31** (47% over 2 steps): a pale yellow oil; IR (film) 2945, 2868, 1567, 1476, 1432, 1157, 1056, 903, 842, 660 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45–7.33 (m, 5H), 6.17 (dd, J = 3.7, 2.3 Hz, 1H), 5.69 (dd, J = 4.1, 3.7 Hz, 1H), 5.15 (dd, J = 4.1, 2.3 Hz, 1H), 5.10 (s, 2H), 1.32 (sep, J = 7.3, 3H), 1.13 (d, J = 7.3 Hz, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.5 (C), 134.9 (C), 129.6 (CH), 129.0 (CH), 128.6 (CH), 108.5 (CH), 100.0 (CH), 85.4 (CH), 80.7 (CH_2), 17.9 (CH_3), 12.4 (CH) ; HRMS (ESI), Calcd for $C_{20}H_{32}NO_2Si$ $(M+H)^+$ 346.2197, found 346.2190.



N-OMe-*N*'-OBn-Enamide (33)

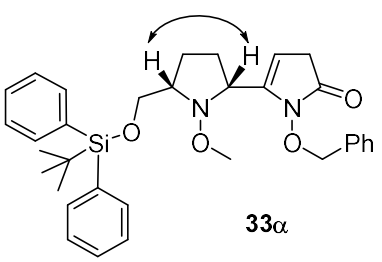
Preparation of a stock solution of $IrCl(CO)(PPh_3)_2$ in toluene (0.14 mM): In a glove box, toluene (18 mL) was added to $IrCl(CO)(PPh_3)_2$ (2.0 mg, 2.6 µmol) at room temperature.

In a glove box, 1,1,3,3-tetramethyldisiloxane (28 µL, 160 µmol, 1.5 equiv) was added to a mixture of *N*-methoxylactam **19** (40.0 mg, 104 µmol, 1.0 equiv) and $IrCl(CO)(PPh_3)_2$ (0.14 mM in toluene, 7.0 mL, 0.98 µmol, 1.0 mol %) at room temperature. After maintaining for 1 h at room temperature, MeCN (14 mL) and 1-benzyloxy-2-((triisopropylsilyl)oxy)-1*H*-pyrrole **35** (108 mg, 313 µmol, 3.0 equiv) were added to the solution.

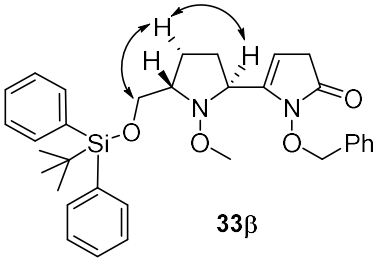
After the flask was removed from the glove box, scandium trifluoromethanesulfonate (15.4 mg, 31.1 μmol, 0.3 equiv) was added to the solution at –25 °C. After maintaining for 16 h at –25 °C, the solution was filtrated through a pad of activated aluminum oxide (10 cc), washed with EtOAc/Et_3N (1:0.01), and concentrated. The residue was filtrated through a pad of basified silica gel (EtOAc/hexane 1:5 to 1:3) to give a mixture of bicyclic compounds.

Sodium bis(trimethylsilyl)amide (1.0 M in THF, 310 μL, 310 μmol, 3.0 equiv) was added to a solution of a mixture of bicyclic compounds (57.7 mg, 104 μmol , 1.0 equiv) and THF (3.0 mL) at –78 °C. After maintaining for 10 min at –78 °C, acetic acid (18 μL, 310 μmol, 3.0 equiv) was added to the solution at –78 °C. After maintaining for 10 min at –78 °C, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (3x 10 mL). The residue was filtrated through a pad of silica gel (EtOAc) to give a mixture of bicyclic *cis*-enamide **33α** and *trans*-enamide **37β** (56.5mg, 97 % over 2 steps, **33α**:**33β** = 2.1:1, The ration was determined by ^{1}H NMR). For analytical samples, a mixture of *cis*-enamide **33α** and *trans*-enamide **33β** was purified by HPLC with recycle unit (PEGASIL Silica 120-5, 250×10 mm, EtOAc/hexane 1:1, 10 mL/min, 2 cycles, **33α**: T_R = 30.6 min, **33β**: T_R = 36.6 min). ***Cis*-enamide 33α**: a colorless oil; $[\alpha]^{24}_D$ +30.5 (*c* 1.0, $CHCl_3$); IR (film) 2932, 2858, 1722, 1470, 1428, 1113, 998, 824, 743, 700, 505 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72–7.66 (m, 4H), 7.47–7.33 (m, 6H), 5.20 (d, *J* = 9.6 Hz, 1H), 5.21–5.17 (m, 1H), 5.13 (d, *J* = 9.6 Hz, 1H), 3.90 (dd, *J* = 10.1, 5.0 Hz, 1H), 3.70 (dd, *J* = 7.8, 7.8 Hz, 1H), 3.65 (dd, *J* = 10.1, 6.9 Hz, 1H), 3.45 (s, 3H), 3.23–3.14 (m, 1H), 3.00 (dd, *J* = 1.6, 0.9 Hz, 2H), 2.06–1.89 (m, 2H), 1.79–1.69 (m, 1H), 1.66–1.57 (m, 1H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1 (C), 146.5 (C), 135.7 (CH), 135.7 (CH), 134.7 (C), 133.8 (C), 129.8 (CH), 129.6 (CH), 127.8 (CH), 97.2 (CH), 78.6 (CH), 69.5 (CH), 66.2 (CH_2), 64.4 (CH), 62.9 (CH_3), 34.8 (CH_2), 27.1 (CH_2), 27.0 (CH_3), 24.9 (CH_2), 19.4 (C); HRMS (ESI), Calcd for $C_{33}H_{41}N_2O_4Si$ $(M+H)^+$ 557.2836, found 557.2827. ***Trans*-enamide 33β**: a colorless oil; $[\alpha]^{24}_D$ −0.146 (*c* 1.0, $CHCl_3$); IR (film) 2934, 2858, 1781, 1457, 1428, 1113, 999, 824, 742, 703, 506 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.65 (m, 4H), 7.46–7.35 (m, 8H), 7.35–7.27 (m, 3H), 5.23 (d, *J* = 9.6 Hz, 1H), 5.17 (d, *J* = 9.6 Hz, 1H), 5.06 (ddd, *J* = 2.7, 2.7, 0.7 Hz, 1H), 3.87 (dd, *J* = 7.3, 7.3 Hz, 1H), 3.86 (dd, *J* = 10.1, 5.5 Hz, 1H), 3.67 (dd, *J* = 10.1, 6.4 Hz), 3.51–3.42 (m, 1H), 3.42 (s, 3H), 3.02 (d, *J* = 2.7 Hz, 1H), 3.01 (d, *J* = 2.7 Hz, 1H), 2.03–1.87 (m, 2H), 1.87–1.75 (m, 1H), 1.73–1.60 (m, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6 (C), 144.7 (C), 135.79 (CH), 135.77 (CH), 134.8 (C), 133.7 (C), 129.8 (CH), 129.7 (CH), 129.0 (CH), 128.6 (CH), 127.8 (CH), 127.8 (CH), 98.1 (CH), 78.6 (CH), 67.1 (CH), 64.2 (CH_2), 61.8 (CH), 61.1 (CH_3), 34.8 (CH_2), 27.0 (CH_3), 26.4 (CH_2), 25.2 (CH_2), 19.4 (C); HRMS (ESI), Calcd for $C_{33}H_{41}N_2O_4Si$ $(M+H)^+$ 557.2836, found 557.2831.

NOESY experiments for **33α** (500 MHz, $CDCl_3$) and **33β** (400 MHz, $CDCl_3$)

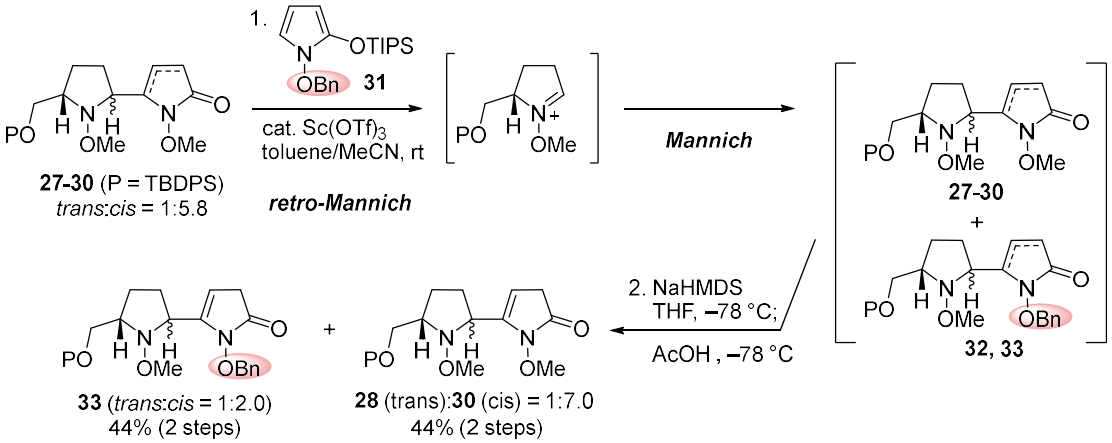


33α



33β

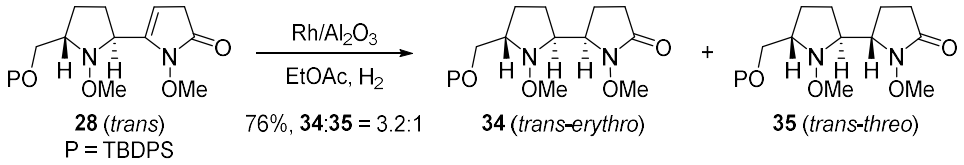
Confirmation of the retro-Mannich reaction



Scandium trifluoromethanesulfonate (2.3 mg, 4.7 μmol, 5 mol %) was added to the solution of bicyclic compounds (44.5 mg, *trans*-[**27**+**28**]:*cis*-[**29**+**30**] = 1:5.8, 92.6 μmol, 1.0 equiv), 1-benzyloxy-2-((triisopropylsilyl)oxy)-1*H*-pyrrole **31** (96.0 mg, 278 μmol, 3.0 equiv), toluene (6.2 mL) and MeCN (31 mL) at room temperature. After maintaining for 16 h at room temperature, the solution was filtrated through a pad of activated aluminum oxide (10 cc), washed with EtOAc/Et_3N (1:0.01), and concentrated. The residue was filtrated through a pad of basified silica gel (EtOAc/hexane 1:5 to 1:3) to give a mixture of bicyclic compounds.

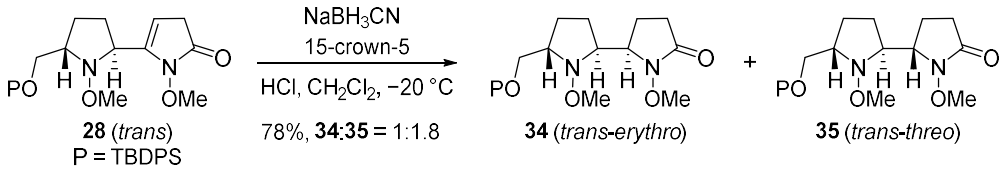
Sodium bis(trimethylsilyl)amide (1.0 M in THF, 238 μL, 238 μmol, 2.6 equiv) was added to a solution of a mixture of bicyclic compounds (44.1 mg) and THF (3.0 mL) at –78 °C. After maintaining for 10 min at –78 °C, acetic acid (14 μL, 250 μmol, 2.6 equiv) was added to the solution at –78 °C. After maintaining for 10 min at –78 °C, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (3x 10 mL). The residue was filtrated through a pad of silica gel (EtOAc) to give 42.3 mg of a mixture of *N*-OMe-*N'*-OMe-enamides (**28**, **30**) and *N*-OMe-*N'*-OBn-enamide (**33**) [*N*-OMe-*N'*-OMe-enamide (**28**, **30**): 44% combined yield, **28** (*trans*):**30** (*cis*) = 1:7.0, *N*-OMe-*N'*-OBn-enamide (**33**): 44% combined yield, *trans*:*cis* = 1:2.0, The ratios were determined by ^{1}H NMR].

2-4. Synthesis of 2-oxo-bispyrrolidine



***Erythro*-selective hydrogenation to afford 34**

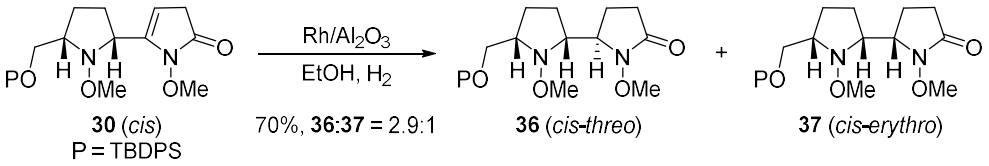
Rhodium on alumina (10.4 mg, 20 wt%) was added to a solution of *trans*-enamide **28** (51.8 mg, 10.8 μmol, 1.0 equiv) and EtOAc (10 mL). The flask was purged with hydrogen. The mixture was stirred under hydrogen atmosphere (1 atm) at room temperature for 10 h. Ethyl acetate was removed under reduced pressure. The residue was filtrated through basified silica gel (1 cc), washed with EtOAc. The mixture of *trans-erythro* lactam **34** and *trans-threo* lactam **35** was purified by reversed-phase HPLC with recycle unit (PEGASIL ODS SP100, 250×10 mm, MeCN/H_2O/TFA 94.9:5:0.1, 5 mL/min, **34**: 5 cycles, T_R = 178.7 min, **35**: 4 cycles, T_R = 134.2 min) to afford 30.1 mg of *trans-erythro*-lactam (**34**, 58%) and 9.4 mg of *trans-threo*-lactam (**35**, 18%). ***Trans-erythro*-lactam 34**: a colorless oil; $[\alpha]^{25}_D$ −6.4 (*c* 1.0, $CHCl_3$); IR (film) 2933, 2858, 1720, 1463, 1428, 1192, 1112, 1053, 825, 742, 704, 504 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71–7.64 (m, 4H), 7.46–7.33 (m, 6H), 3.90–3.83 (m, 1H), 3.78 (s, 3H), 3.70 (d, *J* = 5.3 Hz, 2H), 3.47–3.38 (m, 1H), 3.41 (s, 3H), 3.28 (brs, 1H), 2.38 (ddd, *J* = 17.2, 9.2, 6.9 Hz, 1H), 2.25 (ddd, *J* = 17.2, 8.9, 6.2 Hz, 1H), 2.17–1.99 (m, 3H), 1.99–1.87 (m, 1H), 1.76–1.53 (m, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6 (C), 135.77 (CH), 135.75 (CH), 133.69 (C), 133.67 (C), 129.82 (CH), 129.81 (CH), 127.8 (CH), 68.3 (CH), 67.4 (CH), 63.8 (CH_2), 62.2 (CH_3), 60.2 (CH_3), 58.5 (CH), 27.1 (CH_2), 27.0 (CH_3), 26.3 (CH_2), 25.7 (CH_2), 19.4 (CH_2), 19.3 (C); HRMS (ESI), Calcd for $C_{27}H_{38}N_2NaO_4Si$ $(M+Na)^+$ 505.2493, found 505.2490. ***Trans-threo*-lactam 35**: a colorless oil; $[\alpha]^{25}_D$ −27.0 (*c* 1.0, $CHCl_3$); IR (film) 2934, 2858, 1720, 1471, 1428, 1186, 1112, 1054, 824, 742, 704, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72–7.65 (m, 4H), 7.45–7.35 (m, 6H), 4.13 (ddd, *J* = 6.9, 6.4, 6.4 Hz, 1H), 3.79 (s, 3H), 3.74 (dd, *J* = 10.5, 5.5 Hz, 1H), 3.67 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.55–3.45 (m, 2H), 3.45 (s, 3H), 2.40–2.22 (m, 2H), 2.12–2.00 (m, 1H), 1.96–1.82 (m, 2H), 1.85–1.65 (m, 2H), 1.62–1.51 (m, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9 (C), 135.8 (CH), 133.6 (C), 129.82 (CH), 129.79 (CH), 127.80 (CH), 127.79 (CH), 67.02 (CH), 67.01 (CH), 64.0 (CH_2), 62.7 (CH_3), 60.3 (CH_3), 57.1 (CH), 27.4 (CH_2), 27.0 (CH_3), 24.5 (CH_2), 23.2 (CH_2), 19.3 (C), 18.6 (CH_2); HRMS (ESI), Calcd for $C_{27}H_{38}N_2NaO_4Si$ $(M+Na)^+$ 505.2493, found 505.2489.



***Threo*-selective hydride reduction to afford 35**

Hydrochloric acid (1.0 M, 2.3 mL, 2.3 mmol, 20 equiv) was added to a mixture of *trans*-enamide **28** (55.3 mg, 115 μmol, 1.0 equiv), $NaBH_3CN$ (217 mg, 3.45 mmol, 30 equiv), 15-crown-5 (670 μL, 3.44 mmol, 30 equiv) and CH_2Cl_2 (18 mL) at −20 °C. After stirring for 3 h, the mixture was quenched with aqueous saturated $NaHCO_3$

(20 mL) and brine (10 mL) and extracted with EtOAc/hexane = 1:1 (5x 30 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was filtrated through silica gel (1 cc), washed with EtOAc. The mixture of *trans-erythro*-lactam **34** and *trans-threo*-lactam **35** was purified by reversed-phase HPLC with recycle unit (PEGASIL ODS SP100, 250×10 mm, MeCN/H_2O/TFA 94.9:5:0.1, 10 mL/min, 5 cycles, **34**: T_R =83.6 min, **35**: T_R = 77.6 min) to afford 15.6 mg of *trans-erythro*-lactam (**34**, 28%) and 27.6 mg of *trans-threo*-lactam (**35**, 50%).



30 (*cis*)
P = TBDPS

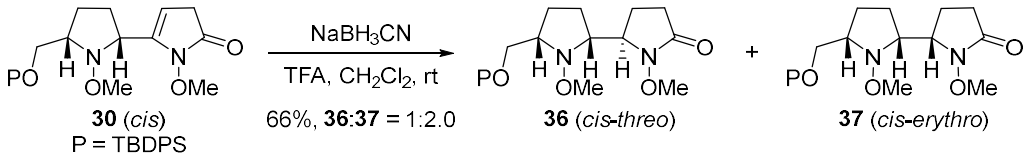
70%, **36**:**37** = 2.9:1

36 (*cis-threo*)

37 (*cis-erythro*)

***Threo*-selective hydrogenation to afford 36**

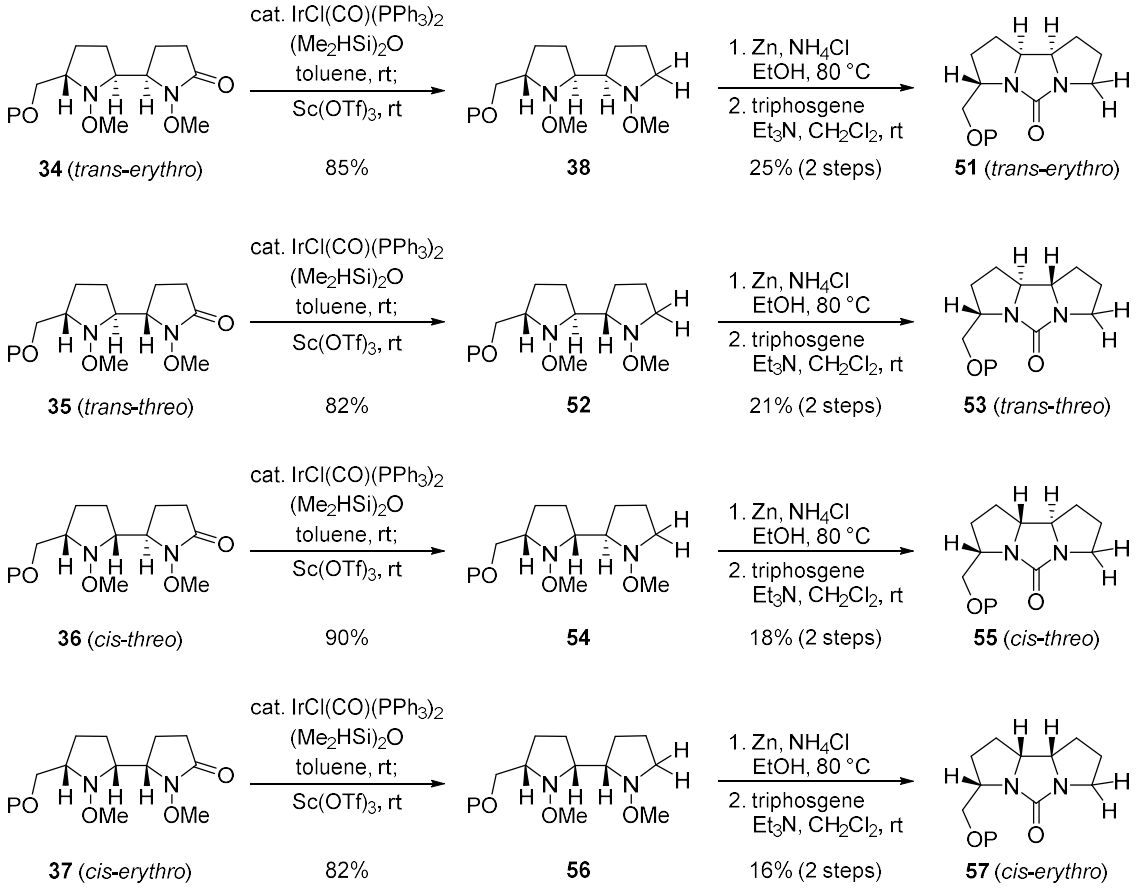
Rhodium on alumina (9.7 mg, 30 wt%) was added to a solution of *cis*-enamide **30** (32.3 mg, 67.2 μmol, 1.0 equiv) and EtOH (4.0 mL). The flask was purged with hydrogen. The mixture was stirred under hydrogen atmosphere (1 atm) at room temperature for 2.5 h. Ethanol was removed under reduced pressure. The residue was filtrated through a pad of silica gel (EtOAc) and concentrated. The mixture of *cis-threo*-lactam **36** and *cis-erythro*-lactam **37** was purified by HPLC with recycle unit (PEGASIL Silica 120-5, 250×10 mm, EtOAc/hexane 2:1, 10 mL/min, 7 cycles, **36**: T_R =157.7 min, **37**: T_R = 168.6 min) to afford 16.8 mg of *cis-threo*-lactam (**36**, 52%) and 5.8 mg of *cis-erythro*-lactam (**37**, 18%). ***Cis-threo*-lactam 36**: a colorless oil; $[\alpha]^{25}_D$ +25.0 (*c* 1.0, $CHCl_3$); IR (film) 2933, 2858, 1719, 1472, 1428, 1113, 1056, 940, 860, 824, 704, 506 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72–7.64 (m, 4H), 7.46–7.35 (m, 6H), 4.14 (ddd, *J* = 8.0, 5.3, 4.1 Hz, 1H), 3.82 (dd, *J* = 10.3, 4.4 Hz, 1H), 3.79 (s, 3H), 3.66 (dd, *J* = 10.3, 6.0 Hz, 1H), 3.45 (s, 3H), 3.48–3.41 (m, 1H), 3.18–3.10 (m, 1H), 2.30 (dd, *J* = 8.2, 8.2 Hz, 2H), 2.13–1.99 (m, 2H), 1.99–1.89 (m, 1H), 1.80–1.69 (m, 1H), 1.66–1.55 (m, 1H), 1.46–1.35 (m, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0 (C), 135.8 (CH), 135.7 (CH), 133.79 (C), 133.76 (C), 129.8 (CH), 127.79 (CH), 127.77 (CH), 69.2 (CH), 67.2 (CH), 65.7 (CH_2), 63.1 (CH_3), 62.4 (CH_3), 56.4 (CH), 27.3 (CH_2), 27.0 (CH_3), 23.9 (CH_2), 20.6 (CH_2), 19.4 (C), 16.4 (CH_2); HRMS (ESI), Calcd for $C_{27}H_{38}KN_2O_4Si$ $(M+K)^+$ 521.2232, found 521.2208. ***Cis-erythro*-lactam 37**: a colorless oil; $[\alpha]^{25}_D$ −7.4 (*c* 1.0, $CHCl_3$); IR (film) 2932, 2858, 1718, 1472, 1428, 1188, 1112, 1055, 824, 742, 704, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71–7.64 (m, 4H), 7.46–7.35 (m, 6H), 3.83 (s, 3H), 3.86–3.81 (m, 1H), 3.80 (dd, *J* = 10.3, 4.6 Hz, 1H), 3.65 (dd, *J* = 10.3, 6.2 Hz, 1H), 3.45 (s, 3H), 3.33 (ddd, *J* = 8.7, 8.7, 3.0 Hz, 1H), 3.24–3.15 (m, 1H), 2.47–2.36 (m, 1H), 2.31–2.21 (m, 1H), 2.07–1.98 (m, 2H), 1.98–1.84 (m, 2H), 1.72–1.60 (m, 1H), 1.55–1.42 (m, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3 (C), 135.75 (CH), 135.72 (CH), 133.71 (C), 133.65 (C), 129.8 (CH), 127.8 (CH), 70.2 (CH), 68.0 (CH), 65.6 (CH_2), 62.3 (CH_3), 62.2 (CH_3), 58.9 (CH), 27.2 (CH_2), 27.0 (CH_3), 24.1 (CH_2), 23.4 (CH_2), 19.4 (C), 17.7 (CH_2); HRMS (ESI), Calcd for $C_{27}H_{39}N_2O_4Si$ $(M+H)^+$ 483.2674, found 483.2673.

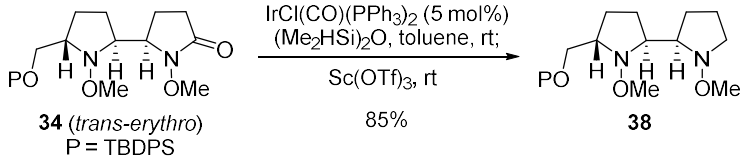


***Erythro*-selective hydride reduction to afford 36**

Trifluoroacetic acid (77 μL, 100 mmol, 15 equiv) was added to a mixture of *cis*-enamide **30** (32.1 mg, 66.8 μmol, 1.0 equiv), $NaBH_3CN$ (126 mg, 2.01 mmol, 30 equiv) and CH_2Cl_2 (5.0 mL) at room temperature. After stirring for 15 h, the mixture was quenched with aqueous saturated $NaHCO_3$ (5.0 mL) and extracted with $CHCl_3$ (4x 10mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by silica gel column chromatography (EtOAc/hexane 1:4 to 1:1) to give a mixture of *cis*-*threo*-lactam **36** and *cis*-*erythro*-lactam **37** (21.1 mg, 66% combined yield, **36**:**37** = 1:2.0, The ratio was determined by ^1H NMR).

Determination of *threo*- and *erythro*-configuration of dimeric compounds 51, 53, 55, and 57

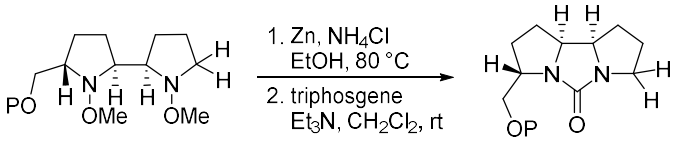




***Trans-erythro*-bispyrrolidine 38**

In a glove box, 1,1,3,3-tetramethyldisiloxane (66 μL, 370 μmol, 6.0 equiv) was added to a mixture of *trans-erythro*-lactam **34** (29.8 mg, 61.7 μmol, 1.0 equiv), $IrCl(CO)(PPh_3)_2$ (2.4 mg, 3.1 μmol, 5 mol %) and toluene (4.1 mL) at room temperature. After maintaining for 1 h at room temperature, $Sc(OTf)_3$ (15.3 mg, 31.1 μmol, 0.5 equiv) was added to the solution at room temperature. The flask was removed from the glove box. After maintaining for 12 h at room temperature, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (3x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by preparative layer chromatography (EtOAc/hexane 1:7) to give 24.6 mg of *trans-erythro*-bispyrrolidine (**38**: 85%): a colorless oil; $[\alpha]^{23}_D$ +11.3 (*c* 1.0, $CHCl_3$); IR (film) 2935, 2806, 1465, 1428, 1113, 1051, 1008, 938, 824, 740, 703, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74–7.68 (m, 4H), 7.46–7.35 (m, 6H), 3.73–3.63 (m, 1H), 3.60 (dd, *J* = 10.5, 5.5 Hz, 1H), 3.48 (s, 3H), 3.51–3.40 (m, 1H), 3.44 (s, 3H), 3.15 (brs, 2H), 2.92 (ddd, *J* = 11.4, 7.3, 7.3 Hz, 1H), 2.90 (brs, 1H), 2.14–2.05 (m, 1H), 2.05–1.95 (m, 2H), 1.92–

1.70 (m, 4H), 1.59–1.48 (m, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.84 (CH), 135.79 (CH), 133.95 (C), 133.86 (C), 129.7 (CH), 127.7 (CH), 70.4 (CH), 69.9 (CH), 69.2 (CH), 65.1 (CH_2), 60.0 (CH_3), 59.9 (CH_3), 56.1 (CH_2), 28.0 (CH_2), 27.8 (CH_2), 26.9 (CH_3), 26.2 (CH_2), 22.3 (CH_2), 19.3 (C); HRMS (ESI), Calcd for $C_{27}H_{41}N_2O_3Si$ $(M+H)^+$ 469.2881, found 469.2877.



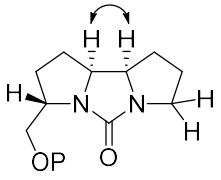
38 (P = TBDPS) 25% (2 steps) **51** (*trans-erythro*)

***Trans-erythro*-urea (51)**

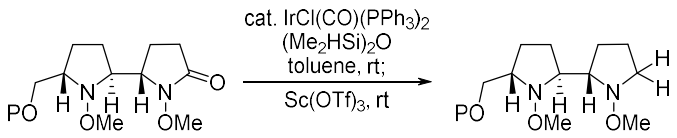
A mixture of *trans-erythro*-bispyrrolidine **38** (20.4 mg, 43.5 μmol, 1.0 equiv), activated zinc (powder, 1.71 g, 26.2 mmol, 600 equiv), NH_4Cl (1.40 g, 26.2 mmol, 600 equiv) and EtOH (5.0 mL) was warmed to 80 °C, stirred at 80 °C for 12 h, and cooled to room temperature. The mixture was quenched with aqueous saturated $NaHCO_3$ (5 mL), and extracted with $CHCl_3$ (10x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was filtrated through a pad of silica gel (1 cc), washed with MeOH, to give mixture of reductants, which was immediately used in the next reaction without further purification.

Bis(trichloromethyl) Carbonate (194 mg, 654 μmol, 15 equiv) was added to a solution of the above mixture of reductants, triethylamine (360 μL, 2.60 mmol, 60 equiv) and CH_2Cl_2 (4.0 mL) at room temperature. After maintaining for 12 h at room temperature, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL), and extracted with $CHCl_3$ (5x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by preparative layer chromatography (EtOAc/hexane 1:2) to give 4.8 mg of *trans-erythro*-urea (**51**: 25% over 2 steps): a colorless oil; $[\alpha]^{23}_D$ −24.0 (*c* 1.0, $CHCl_3$); IR (film) 2956, 2858, 1702, 1399, 1326, 1279, 1112, 773, 704, 506 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6) δ 7.87–7.76 (m, 4H), 7.29–7.19 (m, 6H), 4.24–4.17 (m, 1H), 3.79–3.69 (m, 3H), 3.53 (ddd, *J* = 9.5, 8.0, 5.7 Hz, 1H), 3.41 (ddd, *J* = 15.2, 8.0, 8.0 Hz, 1H), 2.72 (ddd, *J* = 10.9, 7.7, 5.4 Hz, 1H), 1.76–1.66 (m, 1H), 1.66–1.54 (m, 1H), 1.36–1.16 (m, 1H), 1.20 (s, 9H), 1.07 (ddd, *J* = 12.2, 10.9, 6.6 Hz, 1H), 0.96–0.84 (m, 2H); ^{13}C NMR (125 MHz, C_6D_6) δ 165.2 (C), 136.13 (CH), 136.11 (CH), 134.23 (C), 134.19 (C), 130.0 (CH), 128.1 (CH), 67.1 (CH_2), 61.1 (CH), 59.8 (CH), 58.6 (CH), 45.0 (CH_2), 28.7 (CH_2), 27.3 (CH_2), 27.2 (CH_3), 26.9 (CH_2), 26.2 (CH_2), 19.6 (C); HRMS (ESI), Calcd for $C_{26}H_{34}KN_2O_2Si$ $(M+K)^+$ 473.2021, found 473.1998.

NOESY experiment for *trans-erythro*-urea **51** (500 MHz, C_6D_6)



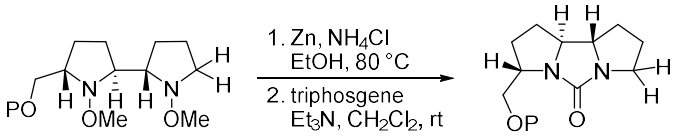
51 (P = TBDPS)



35 (*trans-threo*) P = TBDPS — 82% — **52**

***Trans-threo*-bispyrrolidine (52)**

In a glove box, 1,1,3,3-tetramethyldisiloxane (49 μL, 280 μmol, 6.0 equiv) was added to a mixture of *trans-threo*-lactam **35** (22.3 mg, 46.2 μmol, 1.0 equiv), $IrCl(CO)(PPh_3)_2$ (1.8 mg, 2.3 μmol, 5 mol %) and toluene (3.1 mL) at room temperature. After maintaining for 1 h at room temperature, $Sc(OTf)_3$ (11.4 mg, 23.2 μmol, 0.5 equiv) was added to the solution at room temperature. The flask was removed from the glove box. After maintaining for 12 h at room temperature, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (3x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by preparative layer chromatography (EtOAc/hexane 1:7) to give 17.8 mg of *trans-threo*-bipyrrolidine (**52**: 82%): a colorless oil**;** $[\alpha]^{23}_D$ −25.5 (*c* 1.0, $CHCl_3$); IR (film) 2934, 2858, 1471, 1426, 1113, 1058, 1008, 938, 824, 741, 703, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74–7.67 (m, 4H), 7.46–7.34 (m, 6H), 3.80 (dd, *J* = 10.1, 6.0 Hz, 1H), 3.65 (dd, *J* = 10.1, 6.4 Hz, 1H), 3.55 (s, 3H), 3.51–3.43 (m, 1H), 3.47 (s, 3H), 3.38 (m, 3H), 2.82 (ddd, *J* = 10.5, 8.2, 8.2 Hz, 1H), 2.00–1.73 (m, 4H), 1.73–1.56 (m, 3H), 1.56–1.45 (m, 1H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8 (CH), 133.92 (C), 133.89 (C), 129.7 (CH), 127.7 (CH), 68.3 (CH), 68.03 (CH), 67.95 (CH), 64.5 (CH_2), 60.8 (CH_3), 60.5 (CH_3), 55.8 (CH_2), 27.0 (CH_3), 25.5 (CH_2), 25.1 (CH_2), 24.9 (CH_2), 21.3 (CH_2), 19.3 (C); HRMS (ESI), Calcd for $C_{27}H_{41}N_2O_3Si$ $(M+H)^+$ 469.2881, found 469.2877.



52 (P = TBDPS) — 21% (2 steps) — **53** (*trans-threo*)

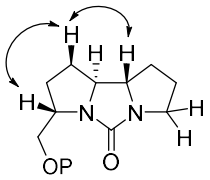
***Trans-threo*-urea (53)**

A mixture of *trans-threo*-bipyrrolidine **52** (21.1 mg, 45.0 μmol, 1.0 equiv), activated zinc (powder, 1.77 g, 27.1 mmol, 600 equiv), NH_4Cl (1.44 g, 26.9 mmol, 600 equiv) and EtOH (5.0 mL) was warmed to 80 °C, stirred at 80 °C for 12 h, and cooled to room temperature. The mixture was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (10x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was filtrated through a pad of silica gel (1 cc), washed with MeOH, to give mixture of reductants, which was immediately used in the next reaction without further purification.

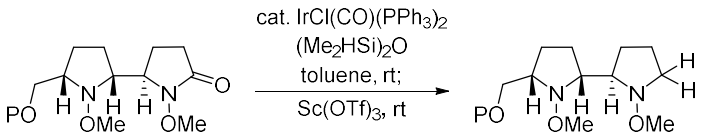
Bis(trichloromethyl) Carbonate (200 mg, 674 μmol, 15 equiv) was added to a solution of the above mixture of reductants, triethylamine (374 μL, 2.70 mmol, 60 equiv) and CH_2Cl_2 (4.0 mL) at room temperature. After maintaining for 12 h at room temperature, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (5x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by preparative layer chromatography (EtOAc/hexane 1:2) to give 4.1 mg of *trans-*

threo-urea (**53**: 21% over 2 steps): a colorless oil; $[\alpha]^{23}_{D}$ −73.3 (*c* 1.0, $CHCl_3$); IR (film) 2961, 2858, 1705, 1380, 1324, 1262, 1112, 770, 704, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69–7.59 (m, 4H), 7.47–7.29 (m, 6H), 3.91 (dddd, *J* = 11.9, 11.9, 4.6, 4.6 Hz, 1H), 3.77–3.68 (m, 2H), 3.65 (ddd, *J* = 1.8, 5.3, 0.7 Hz, 1H), 3.56 (ddd, *J* = 14.6, 9.9, 6.0 Hz, 1H), 3.08 (ddd, *J* = 11.5, 9.2, 4.4 Hz, 1H), 2.22–2.10 (m, 1H), 2.10–1.91 (m, 4H), 1.91–1.77 (m, 1H), 1.59–1.47 (m, 1H), 1.47–1.36 (m, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4 (C), 135.7 (CH), 133.8 (C), 133.7 (C), 129.8 (CH), 129.7 (CH), 127.78 (CH), 127.76 (CH), 67.1 (CH_2), 62.4 (CH), 62.1 (CH), 59.1 (CH), 45.6 (CH_2), 31.6 (CH_2), 30.7 (CH_2), 28.9 (CH_2), 27.0 (CH_3), 25.9 (CH_2), 19.5 (C); HRMS (ESI), Calcd for $C_{26}H_{34}KN_2O_2Si$ $(M+K)^+$ 473.2021, found 473.2002.

NOESY experimen for *trans-threo*-urea **53** (400 MHz, $CDCl_3$)



53 (P = TBDPS)



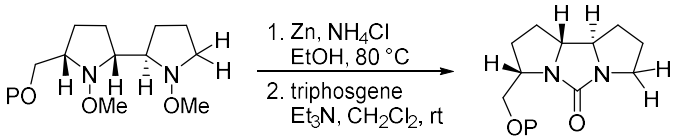
36 (*cis-threo*)
P = TBDPS

90%

54

***Cis-threo*-bispyrrolidine (54)**

In a glove box, 1,1,3,3-tetramethyldisiloxane (60 µL, 340 µmol, 6.0 equiv) was added to a mixture of *cis-threo*-lactam **36** (27.3 mg, 56.6 µmol, 1.0 equiv), $IrCl(CO)(PPh_3)_2$ (2.2 mg, 2.8 µmol, 5 mol %) and toluene (3.8 mL) at room temperature. After maintaining for 1 h at room temperature, $Sc(OTf)_3$ (14.6 mg, 26.7 µmol, 0.5 equiv) was added to the solution at room temperature. The flask was removed from the glove box. After maintaining for 12 h at room temperature, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (3x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by preparative layer chromatography (EtOAc/hexane 1:7) to give 23.9 mg of *cis-threo*-bispyrrolidine (**54**: 90%): a colorless oil; $[\alpha]^{23}_{D}$ +21.7 (*c* 1.0, $CHCl_3$); IR (film) 2934, 2807, 1471, 1428, 1112, 1059, 1007, 938, 824, 741, 703, 506 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72–7.65 (m, 4H), 7.46–7.35 (m, 6H), 3.86 (dd, *J* = 10.1, 4.4 Hz, 1H), 3.62 (dd, *J* = 10.1, 6.6 Hz, 1H), 3.54 (s, 3H), 3.45 (s, 3H), 3.35–3.18 (m, 3H), 3.16–3.07 (m, 1H), 2.76 (ddd, *J* = 8.0, 8.0, 8.0 Hz, 1H), 2.01–1.90 (m, 1H), 1.90–1.72 (m, 3H), 1.72–1.43 (m, 4H), 3.79 (s, 3H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8 (CH), 135.7 (CH), 134.02 (C), 134.01 (C), 129.7 (CH), 127.74 (CH), 127.72 (CH), 69.3 (CH), 68.4 (CH), 68.4 (CH), 66.1 (CH_2), 62.9 (CH_3), 61.0 (CH_3), 55.8 (CH_2) 55.8 (CH_2), 27.0 (CH_3), 24.4 (CH_2), 22.9 (CH_2), 21.8 (CH_2), 21.1 (CH_2), 19.5 (C); HRMS (ESI), Calcd for $C_{27}H_{41}N_2O_3Si$ $(M+H)^+$ 469.2881, found 469.2875.



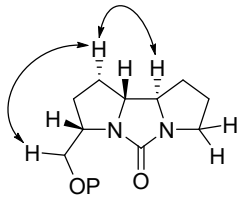
54 (P = TBDPS) 18% (2 steps) **55** (*cis-threo*)

***Cis-threo*-urea (55)**

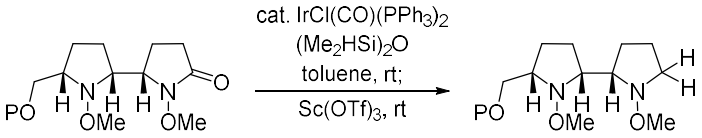
A mixture of *cis-threo*-bipyrrolidine **54** (10.0 mg, 21.3 μmol, 1.0 equiv), activated zinc (powder, 818 mg, 12.5 mmol, 600 equiv), NH_4Cl (685 mg, 12.5 mmol, 600 equiv) and EtOH (3.0 mL) was warmed to 80 °C, stirred at 80 °C for 12 h, and cooled to room temperature. The mixture was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (10x 5 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was filtrated through a pad of silica gel (1 cc), washed with MeOH, to give mixture of reductants, which was immediately used in the next reaction without further purification.

Bis(trichloromethyl) Carbonate (94.9 mg, 320 μmol, 15 equiv) was added to a solution of the above mixture of reductants, triethylamine (180 μL, 1.30 mmol, 60 equiv) and CH_2Cl_2 (3.0 mL) at room temperature. After maintaining for 12 h at room temperature, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (5x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by preparative layer chromatography (EtOAc/hexane 1:2) to give 1.7 mg of *cis-threo*-urea (**55**: 18% over 2 steps): a colorless oil; $[\alpha]^{23}_D$ +62.5 (*c* 1.0, $CHCl_3$); IR (film) 2958, 2889, 1697, 1395, 1317, 1267, 1112, 1052, 766, 703, 505 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.74–7.63 (m, 4H), 7.45–7.33 (m, 6H), 4.25 (dd, *J* = 10.3, 5.4 Hz, 1H), 3.93 (dd, *J* = 10.3, 2.6 Hz, 1H), 3.70 (ddd, *J* = 10.6, 5.7, 4.0 Hz, 1H), 3.65 (ddd, *J* = 8.6, 6.3, 4.0 Hz, 1H), 3.59 (dddd, *J* = 10.9, 5.4, 2.6, 2.6 Hz, 1H), 3.49 (ddd, *J* = 10.9, 7.7, 7.7 Hz, 1H), 3.03 (ddd, *J* = 10.9, 8.6, 4.3 Hz), 2.15–2.08 (m, 1H), 2.07–1.93 (m, 3H), 1.93–1.82 (m, 2H), 1.76 (dddd, *J* = 11.3, 11.2, 11.0, 7.7 Hz, 1H), 1.53–1.43 (m, 1H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6 (C), 136.0 (CH), 135.8 (CH), 134.0 (C), 133.4 (C), 129.72 (CH), 129.68 (CH), 127.74 (CH), 127.73 (CH), 65.7 (CH), 62.2 (CH_2), 62.0 (CH), 57.7 (CH), 45.2 (CH_2), 32.1 (CH_2), 32.0 (CH_2), 30.2 (CH_2), 27.0 (CH_3), 26.3 (CH_2), 19.5 (C); HRMS (ESI), Calcd for $C_{26}H_{34}N_2NaO_2Si$ $(M+Na)^+$ 457.2282, found 457.2265.

NOESY experiment for *cis-threo*-urea **55** (500 MHz, $CDCl_3$)



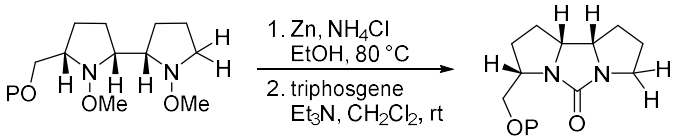
55 (P = TBDPS)



37 (*cis*-*erythro*) P = TBDPS — 82% — **56**

***Cis*-*erythro*-bipyrrolidine (56)**

In a glove box, 1,1,3,3-tetramethyldisiloxane (65 μL, 370 μmol, 6.0 equiv) was added to a mixture of *cis*-*erythro*-lactam **37** (29.6 mg, 61.3 μmol, 1.0 equiv), $IrCl(CO)(PPh_3)_2$ (2.4 mg, 3.1 μmol, 5 mol %) and toluene (4.1 mL) at room temperature. After maintaining for 1 h at room temperature, $Sc(OTf)_3$ (15.2 mg, 30.9 μmol, 0.5 equiv) was added to the solution at room temperature. The flask was removed from the glove box. After maintaining for 12 h at room temperature, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (3x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by preparative layer chromatography (EtOAc/hexane 1:7) to give 23.5 mg of *cis*-*erythro*-bispyrrolidine (**56**: 82%). $[\alpha]^{24}_D$ −16.0 (*c* 1.0, $CHCl_3$); IR (film) 2933, 2805, 1471, 1428, 1112, 1056, 1007, 939, 823, 740, 702, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75–7.66 (m, 4H), 7.45–7.35 (m, 6H), 3.84 (dd, *J* = 10.1, 4.8 Hz, 1H), 3.62 (dd, *J* = 10.1, 6.9 Hz, 1H), 3.52 (s, 3H), 3.49 (s, 3H), 3.28–3.15 (m, 1H), 3.19 (m, 1H), 3.05 (ddd, *J* = 7.3, 7.3, 7.3 Hz, 1H), 2.96 (ddd, *J* = 7.3, 7.3, 7.3 Hz, 1H), 2.79 (ddd, *J* = 10.3, 8.0. 8.0 Hz, 1H), 2.00–1.83 (m, 3H), 1.83–1.54 (m, 5H), 1.06 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.80 (CH), 135.76 (CH), 133.98 (C), 133.95 (C), 129.7 (CH), 127.7 (CH), 70.4 (CH), 70.0 (CH), 70.0 (CH), 66.3 (CH_2), 62.1 (CH_2), 60.4 (CH_3), 56.1 (CH_2), 55.8 (CH_2), 27.0 (CH_3), 25.7 (CH_2), 24.7 (CH_2), 24.5 (CH_2), 21.3 (CH_2), 19.4 (C); HRMS (ESI), Calcd for $C_{27}H_{41}N_2O_3Si$ $(M+H)^+$ 469.2881, found 469.2876.



56 (P = TBDPS) — 16% (2 steps) — **57** (*cis*-*erythro*)

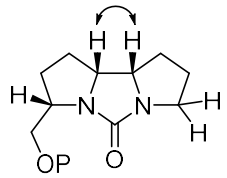
***Cis*-*erythro*-urea (57)**

A mixture of *cis*-*erythro*-bipyrrolidine **56** (8.8 mg, 18.8 μmol, 1.0 equiv), activated zinc (powder, 720 mg, 11.0 mmol, 600 equiv), NH_4Cl (603 mg, 11.3 mmol, 600 equiv) and EtOH (3.0 mL) was warmed to 80 °C, stirred at 80 °C for 12 h, and cooled to room temperature. The mixture was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (10x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was filtrated through a pad of silica gel (1 cc), washed with MeOH, to give mixture of reductants, which was immediately used in the next reaction without further purification.

Bis(trichloromethyl) Carbonate (84.0 mg, 283 μmol, 15 equiv) was added to a solution of the above mixture of reductants, triethylamine (160 μL, 1.20 mmol, 60 equiv) and CH_2Cl_2 (3.0 mL) at room temperature. After maintaining for 12 h at room temperature, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (5x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by preparative layer chromatography (EtOAc/hexane 1:2) to give 1.3 mg of *cis*-

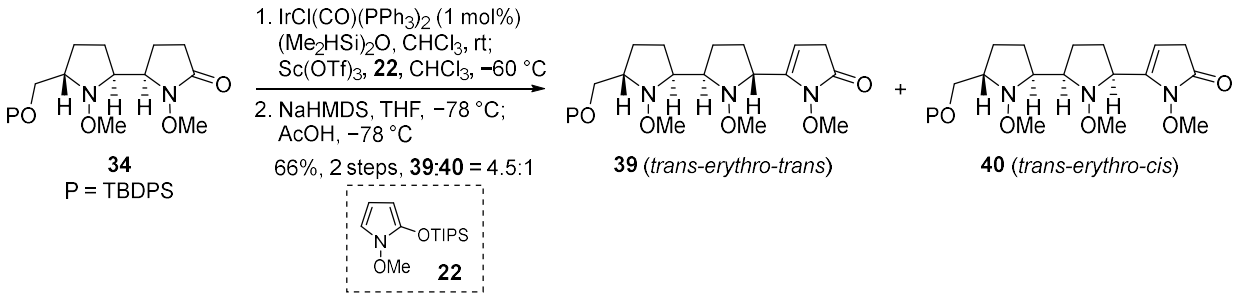
erythro-urea (**57**: 16% over 2 steps): a colorless oil; $[\alpha]^{23}_{D}$ −21.1 (*c* 1.0, $CHCl_3$); IR (film) 2960, 2892, 1699, 1407, 1317, 1261, 1112, 1069, 788, 704, 506 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.69–7.61 (m, 4H), 7.45–7.33 (m, 6H), 4.16 (dd, *J* = 10.6, 5.2 Hz, 1H), 4.12 (ddd, *J* = 9.2, 7.5, 7.5 Hz, 1H), 3.85 (dd, *J* = 10.6, 2.9 Hz, 1H), 3.70 (ddd, *J* = 11.5, 8.3, 8.3 Hz, 1H), 3.68–3.61 (m ,1H), 3.54 (ddd, *J* = 10.9, 7.5, 5.2 Hz, 1H), 2.98 (ddd, *J* = 11.5, 9.7, 3.2 Hz, 1H), 2.29–2.22 (m, 1H), 2.22–2.13 (m, 1H), 1.89–1.79 (m, 1H), 1.78–1.60 (m, 3H), 1.55–1.46 (m, 1H), 1.38 (dddd, *J* = 11.5, 11.2, 10.9, 8.9 Hz, 1H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1 (C), 135.79 (CH), 135.77 (CH), 133.5 (C), 129.8 (CH), 129.7 (CH), 127.82 (CH), 127.78 (CH), 62.4 (CH_2), 62.3 (CH), 59.8 (CH), 55.4 (CH), 45.5 (CH_2), 32.3 (CH_2), 27.1 (CH_3), 25.5 (CH_2), 24.8 (CH_2), 24.5 (CH_2), 19.4 (C); HRMS (ESI), Calcd for $C_{26}H_{35}N_2NaO_2Si$ $(M+H)^+$ 435.2462, found 435.2450.

NOESY experiment for *cis-erythro*-urea **57** (500 MHz, $CDCl_3$)



57 (P = TBDPS)

2-5. Synthesis of 2-oxo-trispyrrolidine



***Trans-erythro-trans*-enamide (39)**

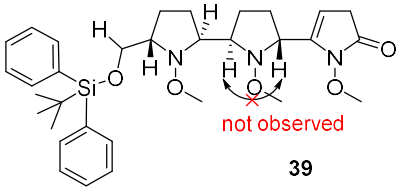
Preparation of a stock solution of $IrCl(CO)(PPh_3)_2$ in $CHCl_3$ (0.14 mM): In a glove box, $CHCl_3$ (18 mL) was added to $IrCl(CO)(PPh_3)_2$ (2.0 mg, 2.6 μmol) at room temperature.

In a glove box, 1,1,3,3-tetramethyldisiloxane (13 μL, 73.0 μmol, 1.5 equiv) was added to a mixture of *trans-erythro*-lactam **34** (23.5 mg, 48.7 μmol, 1.0 equiv) and $IrCl(CO)(PPh_3)_2$ (0.14 mM in $CHCl_3$, 5.1 mL, 0.71 μmol, 1.5 mol %) at room temperature. After maintaining for 1 h at room temperature, $CHCl_3$ (8.1 mL) and 1-methoxy-2-((triisopropylsilyl)oxy)-1H-pyrrole **22** (39.4 mg, 146 μmol, 3.0 equiv) were added to the solution. After the flask was removed from the glove box, scandium trifluoromethanesulfonate (24.0 mg, 48.8 μmol, 1.0 equiv) was added to the solution at –60 °C. After stirring for 12 h at –60 °C, the solution was quenched with aqueous saturated $NaHCO_3$ (15 mL) and extracted with $CHCl_3$ (3x 15mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was filtrated through a pad of basified silica gel (EtOAc/hexane 1:5 to 1:3) to give a mixture of tricyclic compounds.

Sodium bis(trimethylsilyl)amide (1.0 M in THF, 99 μL, 99 μmol, 2.3 equiv) was added to a solution of a mixture of tricyclic compounds (24.9 mg, 42.9 μmol , 1.0 equiv) and THF (2.0 mL) at –78 °C. After maintaining for 10 min at –78 °C, acetic acid (6.1 μL, 110 μmol, 2.5 equiv) was added to the solution at –78 °C. After maintaining for 10 min at –78 °C, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (3x 5mL). The residue was filtrated through a pad of silica gel (EtOAc) and concentrated. The mixture of *trans-erythro-trans*-enamide **39** and *trans-erythro-cis*-enamide **40** was purified by HPLC with recycle unit (PEGASIL Silica 120-5, 250×10 mm, EtOAc/hexane 1:1, 10 mL/min, 2 cycles, **39** T_R = 29.5 min, **40**: T_R = 25.4 min) to afford 3.4 mg of 15.2 mg of *trans-erythro-trans*-enamide (**39**, 54%) and *trans-erythro-cis*-enamide (**40**, 12%). ***Trans-erythro-trans*-enamide 39**: a colorless oil; $[\alpha]^{23}_D$ −48.9 (*c* 1.0, $CHCl_3$) (*c* 1.0, $CHCl_3$); IR (film) 2938, 2858, 1726, 1464, 1428, 1189, 1112, 1043, 824, 772, 704, 505 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73–7.68 (m, 4H), 7.45–7.35 (m, 6H), 5.08 (brs, 1H), 4.02 (s, 3H), 4.10–3.95 (m, 1H), 3.67 (d, *J* = 4.1 Hz, 2H), 3.52–3.06 (m, 3H), 3.47 (s, 3H), 3.44 (s, 3H), 2.98 (dd, *J* = 5.5, 2.7 Hz, 2H), 2.25–2.06 (m, 2H), 2.06–1.91 (m, 4H), 1.87–1.73 (m, 1H), 1.70–1.53 (m, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6 (C), 143.7 (C), 135.84 (CH), 135.79 (CH), 133.8 (C), 133.7 (C), 129.8 (CH), 127.8 (CH), 99.0 (CH), 69.3 (CH), 69.2 (CH), 69.1 (CH), 65.1 (CH), 64.8 (CH_3), 62.3 (CH_2), 60.02 (CH_3), 60.00 (CH_3), 34.8 (CH_2), 28.7 (CH_2), 27.9 (CH_2), 26.9 (CH_3), 26.1 (CH_2), 25.8 (CH_2), 19.3 (C); HRMS (ESI), Calcd for $C_{32}H_{46}N_3O_5Si$ $(M+H)^+$ 580.3201, found 580.3198. ***Trans-erythro-cis*-enamide 40**: a colorless oil; $[\alpha]^{22}_D$ −31.2 (*c* 1.0, $CHCl_3$); IR (film) 2937, 2858, 1727, 1471, 1428, 1188, 1113, 1050, 824, 743, 705, 505 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.72–

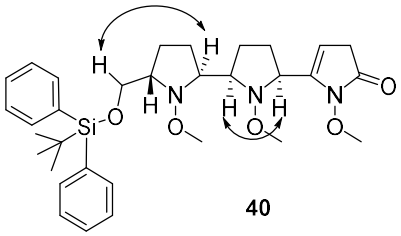
7.68 (m, 4H), 7.44–7.35 (m, 6H), 5.18 (m, 1H), 3.95 (s, 3H), 3.84 (dd, J = 7.7, 7.7 Hz, 1H), 3.67 (brs, 2H), 3.52 (s, 3H), 3.48-3.40 (m, 1H), 3.44 (s, 3H), 3.17 (brs, 1H), 3.09 (brs, 1H), 2.96 (brs, 2H), 2.15–2.03 (m, 2H), 2.03–1.95 (m, 2H), 1.95–1.77 (m, 3H), 1.63 (brs, 1H), 1.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8 (C), 146.1 (C), 135.82 (CH), 135.77 (CH), 133.9 (C), 133.8 (C), 129.8 (CH), 127.8 (CH), 97.9 (CH), 70.2 (CH), 69.8 (CH), 68.1 (CH), 65.2 (CH), 64.7 (CH_2), 64.6 (CH_3), 62.1 (CH_3), 59.9 (CH_3), 34.7 (CH_2), 27.3 (CH_2), 27.04 (CH_2), 26.95 (CH_3), 26.3 (CH_2), 25.7 (CH_2), 19.4 (C); HRMS (ESI), Calcd for $C_{32}H_{46}N_3O_5Si$ $(M+H)^+$ 580.3201, found 580.3195.

NOESY experiment for *trans-erythro-trans*-enamide **39** (500 MHz, $CDCl_3$)



39

NOESY experiment for *trans-erythro-cis*-enamide **40** (400 MHz, $CDCl_3$)



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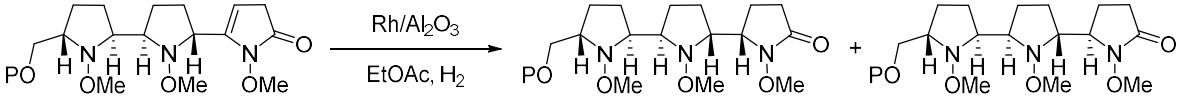


39 (*trans-erythro-trans*) P = TBDPS

75%, **41**:**42** = 4.9:1

41 (*trans-erythro-trans-erythro*)

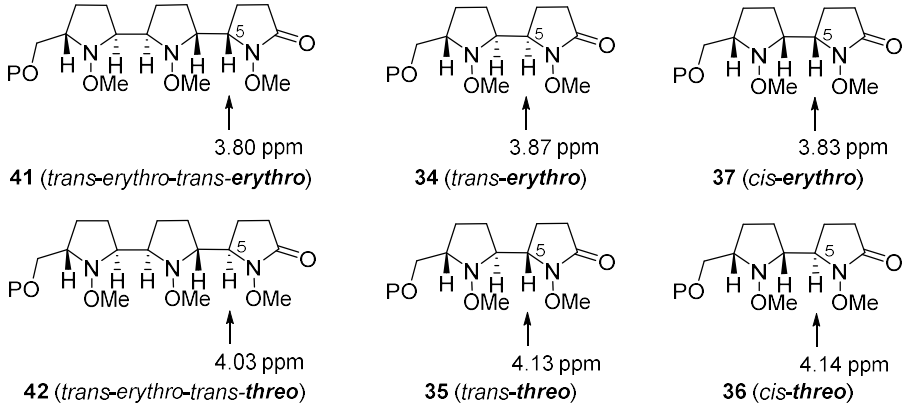
42 (*trans-erythro-trans-threo*)

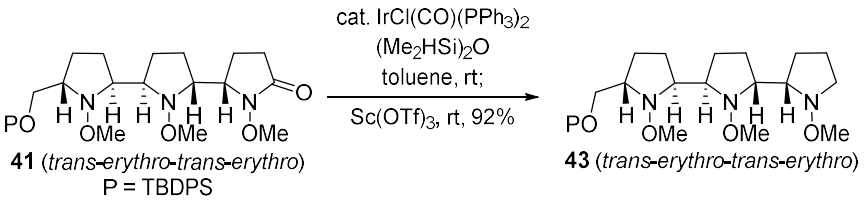
***Erythro*-selective hydrogenation to afford 41**

Rhodium on alumina (12.0 mg, 24 wt%) was added to a solution of *trans*-enamide **39** (51.0 mg, 88.0 μmol, 1.0 equiv) and EtOAc (2.5 mL). The flask was purged with hydrogen. The mixture was stirred under hydrogen atmosphere (1 atm) at room temperature for 3 h. Ethanol was removed under reduced pressure. The residue was filtrated through a pad of silica gel (EtOAc) and concentrated. The mixture of *erythro* lactam (**41**) and t*hreo* lactam (**42**) was purified by HPLC with recycle unit (PEGASIL Silica 120-5, 250×10 mm, EtOAc noly, 10 mL/min, 3 cycles, **41**: T_R =31.5 min, **42**: T_R = 30.0 min) to afford 33.1 mg of *trans-erythro-trans-erythro*-lactam (**41**, 64%) and 5.5 mg of *trans-erythro-trans-threo*-lactam (**42**, 11%). ***Trans-erythro-trans-erythro*-lactam 41**; a colorless oil; $[\alpha]^{23}_D$ −5.8 (*c* 0.6, $CHCl_3$); IR (film) 2935, 2892, 2859, 1720, 1463, 1428, 1112, 1047, 824, 704, 565, 488 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73–7.67 (m, 4H), 7.44–7.32 (m, 6H), 3.90–3.76 (m, 1H), 3.78 (s, 3H), 3.64 (brd, J = 3.4 Hz, 2H), 3.50–3.37 (m, 2H), 3.43 (s, 3H), 3.39 (s, 3H), 3.12 (brs, 1H), 3.02 (brs, 1H), 2.37 (ddd, J = 16.9, 9.7, 6.9 Hz, 1H), 2.23 (ddd, J = 16.9, 10.0, 5.2, 1H), 2.19–2.05 (m, 3H), 2.05–1.90 (m, 4H),

1.80–1.69 (m, 1H), 1.66 (brs, 1H), 1.64–1.51 (m, 1H), 1.04 (s, 9H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.5 (C), 135.8 (CH), 135.7 (CH), 133.8 (C), 133.7 (C), 129.72 (CH), 129.69 (CH), 127.7 (CH), 70.3 (CH), 70.0 (CH), 69.2 (CH), 68.8 (CH), 65.2 (CH_2), 62.1 (CH_3), 59.8 (CH_3), 59.7 (CH_3), 58.4 (CH), 29.1 (CH_2), 28.6 (CH_2), 27.8 (CH_2), 27.2 (CH_2), 26.9 (CH_3), 25.8 (CH_2), 19.7 (CH_2), 19.3 (C) ; HRMS (ESI), calcd for $C_{32}H_{48}N_3O_5Si$ $(M+H)^+$ 582.3358, found 582.3357. ***Trans-erythro-trans-threo*-lactam 42**: a colorless oil; $[\alpha]^{24}_D$ +3.8 (*c* 0.6, $CHCl_3$); IR (film) 2934, 2892, 2807, 1721, 1463, 1428, 1112, 1052, 800, 704, 505 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72–7.68 (m, 4H), 7.45–7.35 (m, 6H), 4.03 (brd, *J* = 4.6 Hz, 1H), 3.82 (s, 3H), 3.65 (brd, *J* = 4.6 Hz, 2H), 3.56–3.30 (m, 2H), 3.46 (s, 3H), 3.44 (s, 3H), 3.13 (brs, 1H), 2.86 (brs, 1H), 2.35 (ddd, *J* = 17.2, 9.7, 4.0 Hz, 1H), 2.25 (ddd, *J* = 17.2, 9.7, 8.0 Hz, 1H), 2.20–1.93 (m, 5H), 1.89–1.76 (m, 2H), 1.76–1.54 (m, 3H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.8 (C), 135.8 (CH), 135.7 (CH), 133.9 (C), 133.7 (C), 129.77 (CH), 129.74 (CH), 127.8 (CH), 70.8 (CH), 69.9 (CH), 69.6 (CH), 69.3 (CH), 65.4 (CH_2), 63.2 (CH_3), 59.9 (CH_3), 59.3 (CH_3), 57.8 (CH), 29.1 (CH_2), 27.5 (CH_2), 27.4 (CH_2), 27.0 (CH_3), 25.9 (CH_2), 25.5 (CH_2), 20.5 (CH_2), 19.4 (C) ; HRMS (ESI), calcd for $C_{32}H_{48}N_3O_5Si$ $(M+H)^+$ 582.3358, found 582.3374.

*Stereochemistry of the C5 carbon center in 2-oxo-trispyrrolidines **41** and **42** was empirically determined by comparison of ^{1}H-NMR. The chemical shift of the C5 proton of *erythro*-isomers (c.a. 3.8 ppm) tends to be located at higher field than that of the C5 proton of *threo*-isomers (c.a. 4.1 ppm).





***Trans-erythro-trans-erythro*-trispyrrolidine (43)**

In a glove box, 1,1,3,3-tetramethyldisiloxane (41 μL, 232 μmol, 6.0 equiv) was added to a mixture of *trans-erythro*-lactam **41** (22.4 mg, 38.5 μmol, 1.0 equiv), $IrCl(CO)(PPh_3)_2$ (1.5 mg, 1.9 μmol, 5 mol %) and toluene (2.6 mL) at room temperature. After maintaining for 1 h at room temperature, $Sc(OTf)_3$ (9.5 mg, 19.3 μmol, 0.5

equiv) was added to the solution at room temperature. The flask was removed from the glove box. After maintaining for 12 h at room temperature, the solution was quenched with aqueous saturated $NaHCO_3$ (5 mL) and extracted with $CHCl_3$ (3x 5mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The residue was purified by preparative layer chromatography (EtOAc/hexane 1:3) to give 20.1 mg of *trans-erythro-trans-erythro* trispyrrolidine (**43**: 92%): a colorless oil; $[\alpha]^{23}_D$ −19.7 (*c* 0.6, $CHCl_3$); IR (film) 2935, 2891, 2858, 1464, 1428, 1112, 1050, 775, 740, 673, 504, 489 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.75–7.69 (m, 4H), 7.47–7.35 (m, 6H), 3.79–3.57 (m, 1H), 3.62 (brd, *J* = 4.6 Hz, 1H), 3.50 (s, 3H), 3.47 (brs, 1H), 3.44 (s, 3H), 3.41 (s, 3H), 3.38–2.59 (m, 3H), 3.18 (brs, 1H), 2.92 (ddd, *J* = 11.7, 7.6, 7.6 Hz, 1H), 2.26–2.06 (m, 2H), 2.06–1.87 (m, 5H), 1.87–1.70 (m, 4H), 1.54 (brs, 1H), 1.05 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.85 (CH), 135.78 (CH), 133.9 (C), 133.8 (C), 129.7 (CH),127.7 (CH), 70.9 (CH), 70.5 (CH), 70.2 (CH), 69.9 (CH), 69.6 (CH), 65.3 (CH_2), 60.0 (CH_3), 59.9 (CH_3), 59.4 (CH_3), 56.1 (CH_2), 28.8 (CH_2), 28.6 (CH_2), 25.8 (CH_2), 28.0 (CH_2), 26.9 (CH_3), 26.0 (CH_2), 22.2 (CH_2), 19.3 (C); HRMS (ESI), calcd for $C_{32}H_{50}N_3O_4Si$ $(M+H)^+$ 568.3565, found 568.3569.

3. Biological Experiment

Cell culture

Human cervical cancer HeLa cells and human colon carcinoma HCT116 cells were cultured in Dulbecco's modified Eagle's medium (Nissui Pharmaceutical Co., Ltd.) that was supplemented with 10% (v/v) fetal bovine serum, 100 units/mL penicillin G, 100 mg/L kanamycin, 600 mg/L L-glutamine and 2.5 g/L $NaHCO_3$ at 37°C in 5% CO_2.

Human T cell leukemia Jurkat cells were cultured in Roswell Park Memorial Institute 1640 medium (Nissui Pharmaceutical Co., Ltd.) that was supplemented with 10% (v/v) fetal bovine serum, 100 units/mL penicillin G, 100 mg/L kanamycin, 150 mg/L L-glutamine and 2.5 g/L $NaHCO_3$ at 37 °C in 5% CO_2.

MTT assay

HeLa, HCT116 and Jurkat cells were treated with various concentrations of compounds for 72 h. Cells were treated with 0.5 mg/mL thiazolyl blue tetrazolium bromide (MTT; Merck KGaA) and were incubated for 4 h at 37°C. After incubation, the medium was removed, and the MTT formazan product was dissolved by 200 μL of DMSO. The amount of the product was determined by measuring absorbance at 570 nm using a microplate reader (Infinite M200 PRO).

4. References

1. S. Hiraoka, T. Matsumoto, K. Matsuzaka, T. Sato, N. Chida, *Angew. Chem. Int. Ed.*, **2019**, *58*, 4381–4385.
2. J. C. F. Alves, *J. Braz. Chem. Soc.*, **2007**, *18*, 855–859.

TBDPSO
N
H
OMe
O
19
X : parts per Million : 1H
abundance
9.12
6.13
4.04
4.00
2.01
1.02
1.03
1.02
1.00
1.02
1.050
7.673
7.671
7.658
7.655
7.642
7.640
7.442
7.436
7.424
7.411
7.387
7.383
7.260
3.915
3.908
3.893
3.886
3.781
3.771
3.628
3.623
3.606
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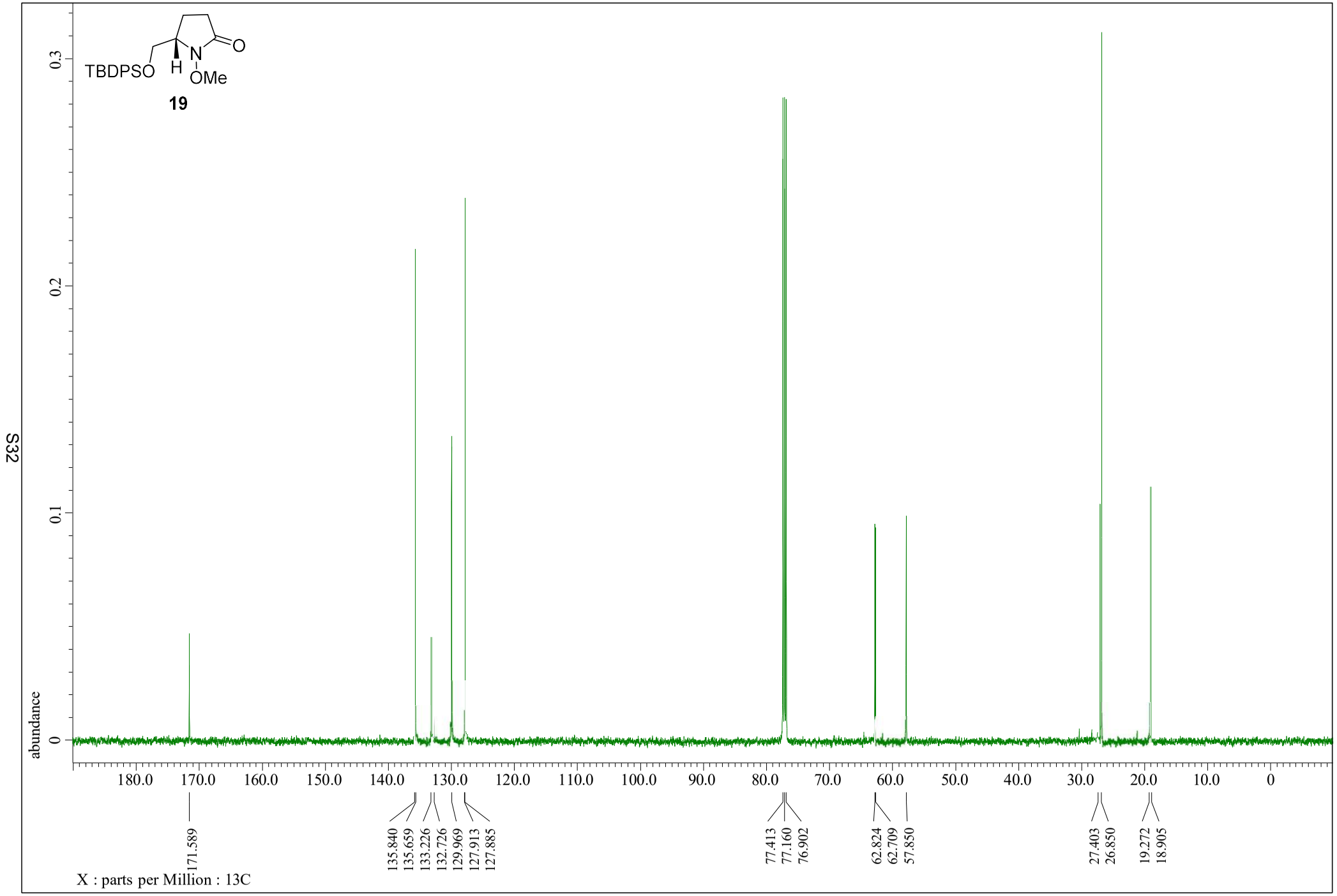
2.029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H
N
OMe
O
19
abundance
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150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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135.840
135.659
133.226
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129.969
127.913
127.885
77.413
77.160
76.902
62.824
62.709
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27.403
26.850
19.272
18.905
X : parts per Million : 13C

OTIPS
OMe
22
abundance
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3.0
4.0
X : parts per Million : 1H
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6.0
5.0
4.0
3.0
2.0
1.0
0
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6.343
6.340
6.336
5.749
5.742
5.741
5.734
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5.126
5.122
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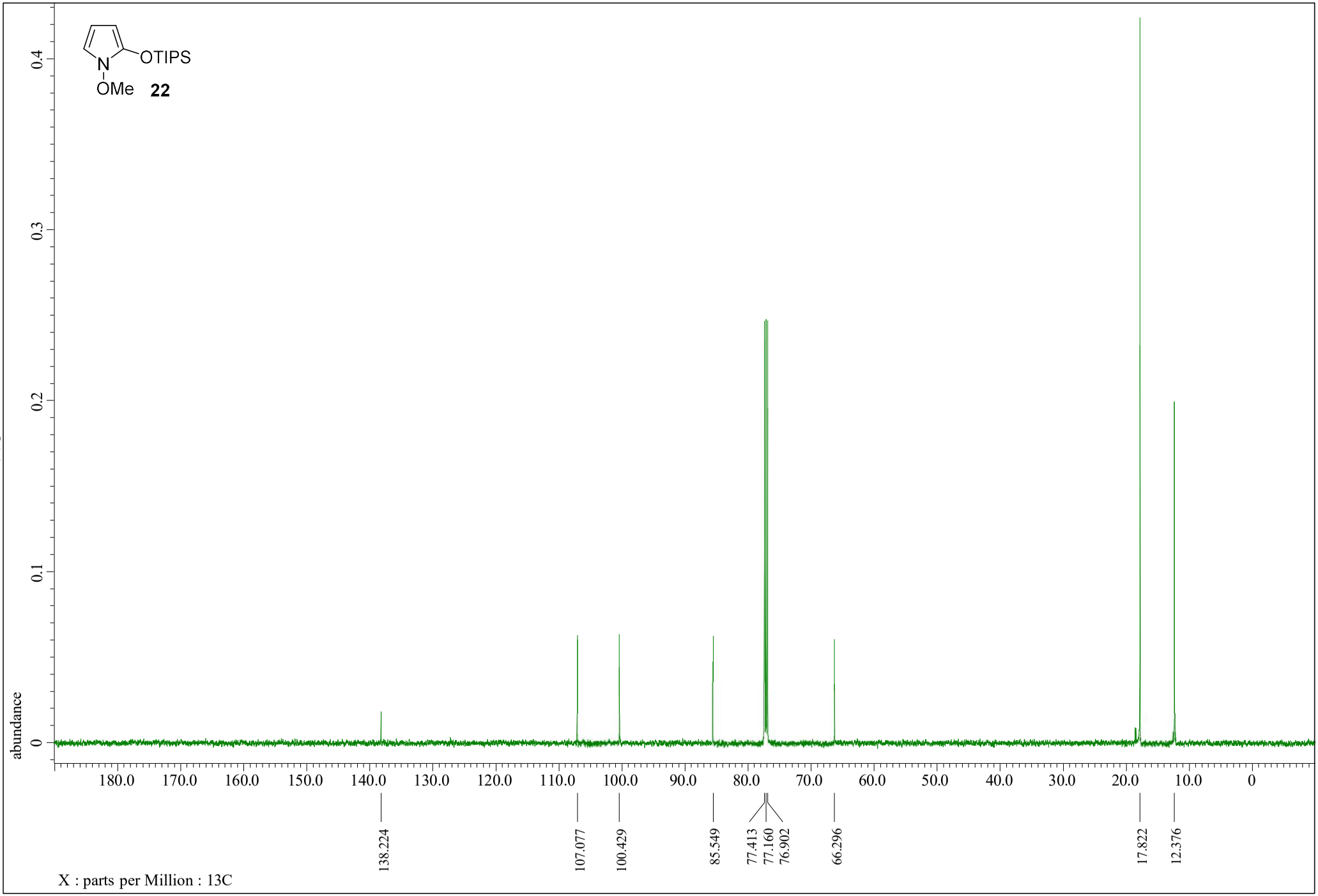
3.05
3.09
20.45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OMe
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130.0
120.0
110.0
100.0
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80.0
70.0
60.0
50.0
40.0
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20.0
10.0
0
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77.160
76.902
66.296
17.822
12.376
X : parts per Million : 13C

TBDPSO
OMe
OMe
27α (trans-threo)
abundance
X : parts per Million : 1H
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6.12
4.07
3.08
2.99
2.01
1.00
1.02
0.97
7.712
7.696
7.687
7.684
7.673
7.671
7.402
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7.024
7.011
6.175
6.162
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4.645
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3.768
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3.663
3.653
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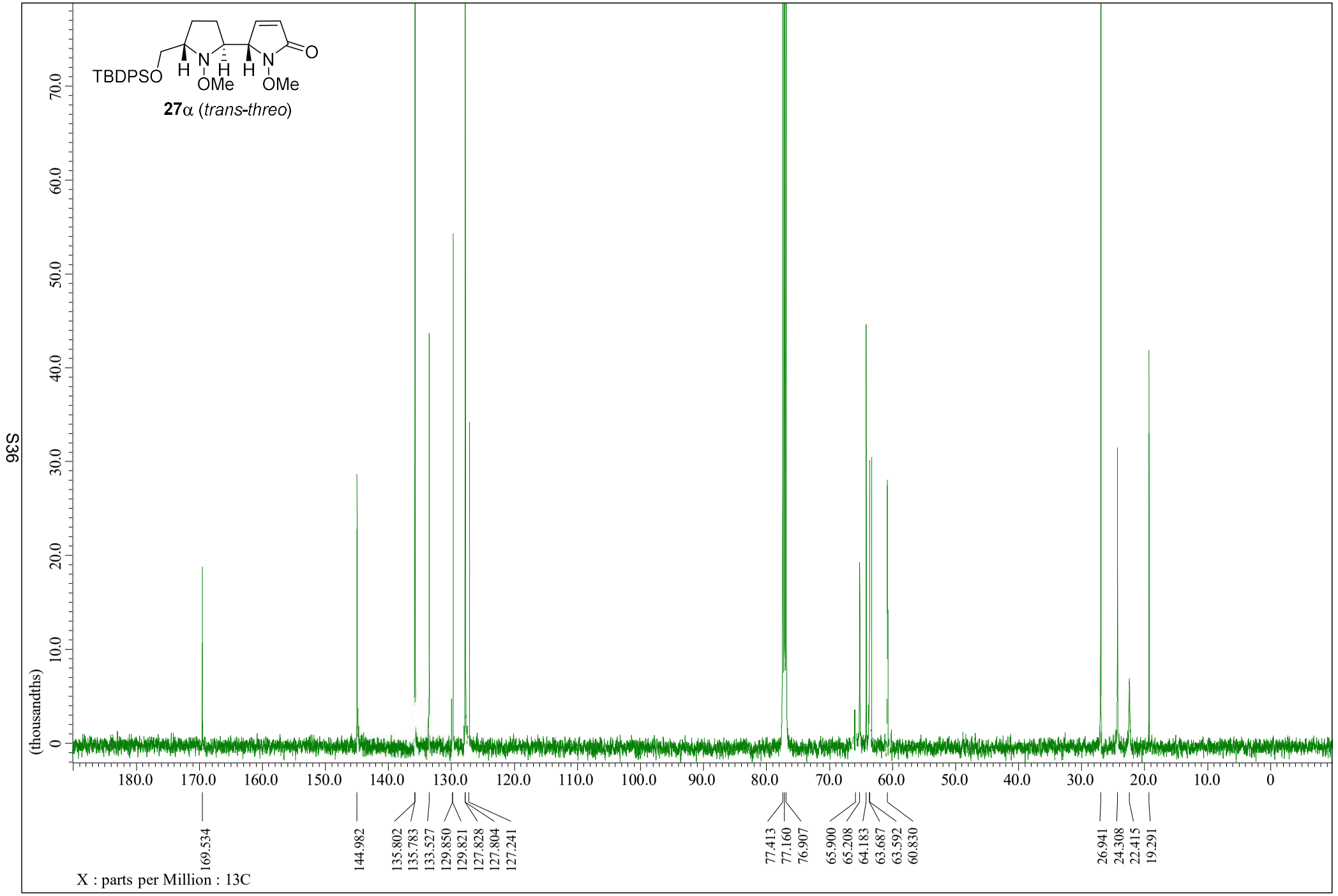
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OMe
H
H
N
OMe
O
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20.0
10.0
0
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135.783
133.527
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127.828
127.804
127.241
77.413
77.160
76.907
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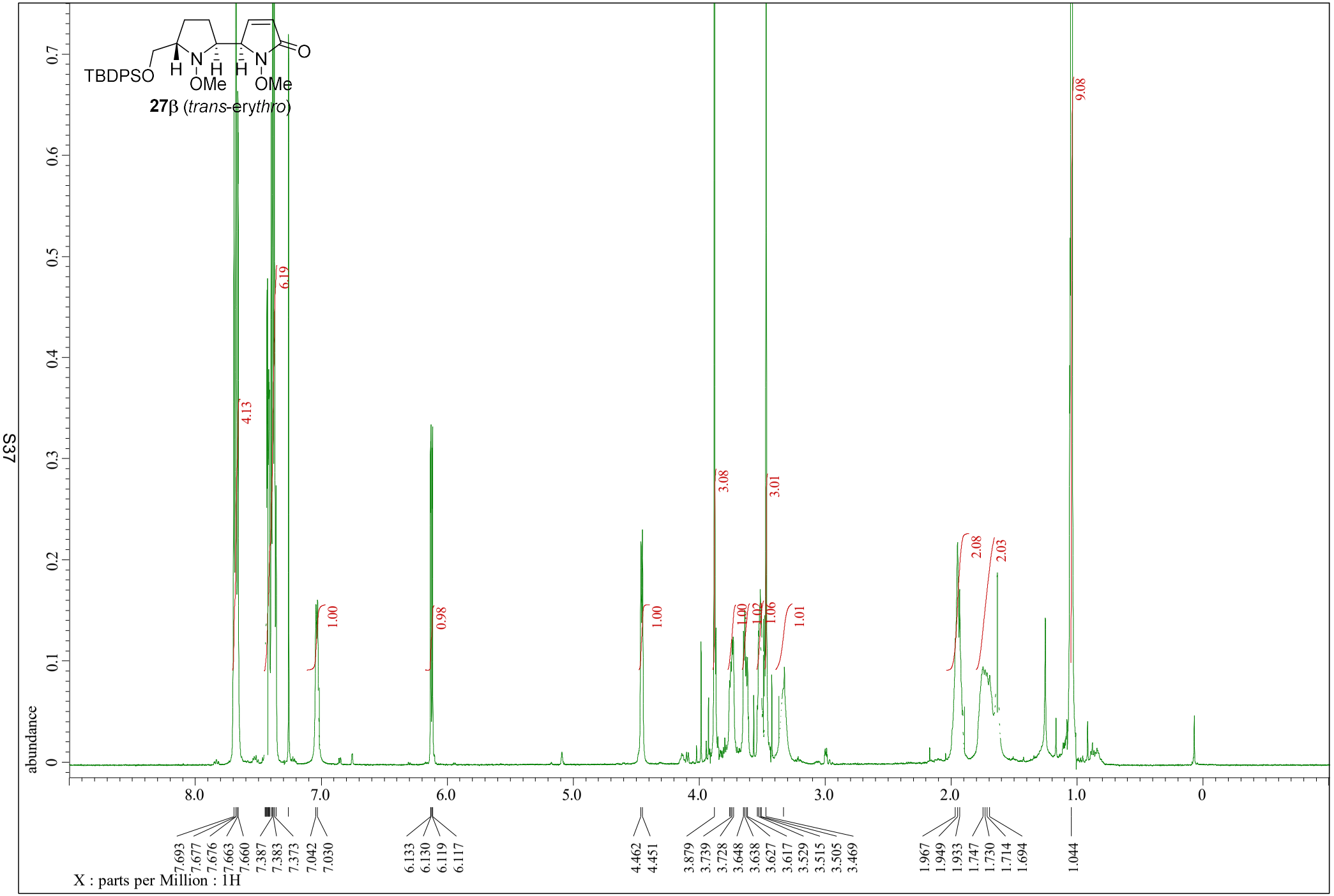
TBDPSO
H
N
H
OMe
H
N
H
OMe
O
27β (trans-erythro)
abundance
X : parts per Million : 1H
4.13
6.19
1.00
0.98
1.00
3.08
3.01
1.00
1.02
1.06
1.01
2.08
2.03
9.08
7.693
7.677
7.676
7.663
7.660
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4.451
3.879
3.739
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3.627
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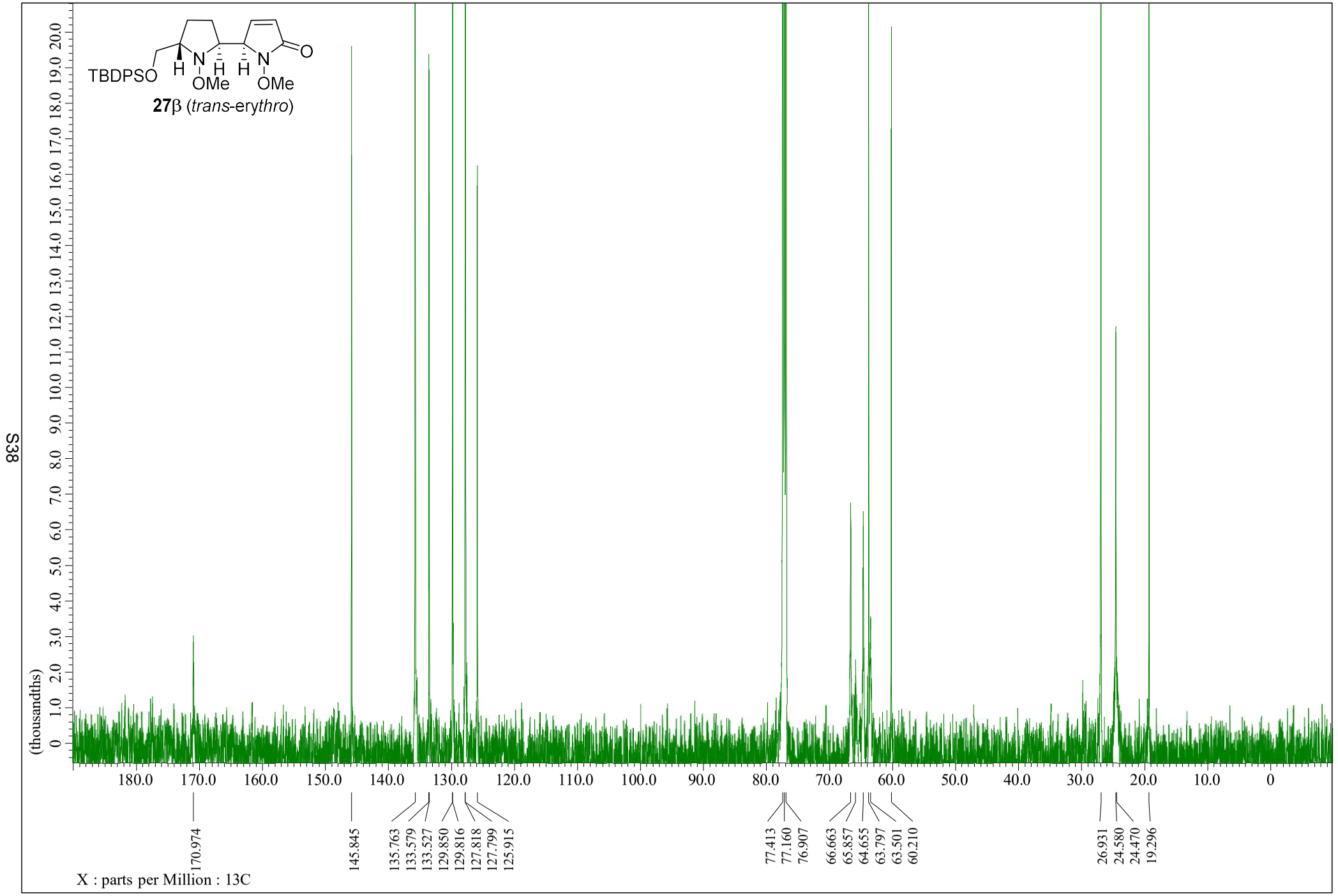
TBDPSO
H
N
H
OMe
H
N
OMe
O
27β (trans-erythro)
(thousandths)
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3.0
4.0
5.0
6.0
7.0
8.0
9.0
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127.818
127.799
125.915
77.413
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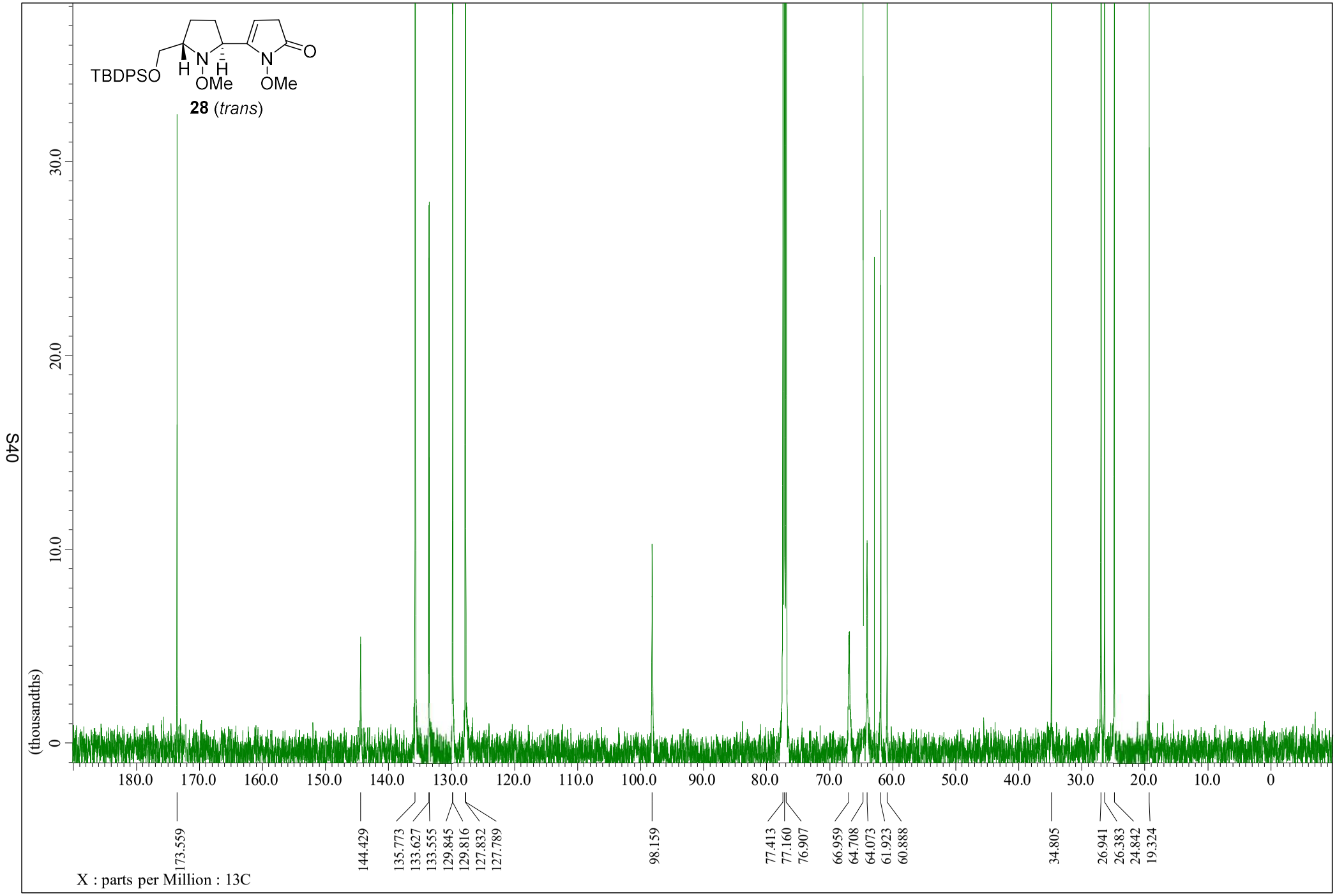
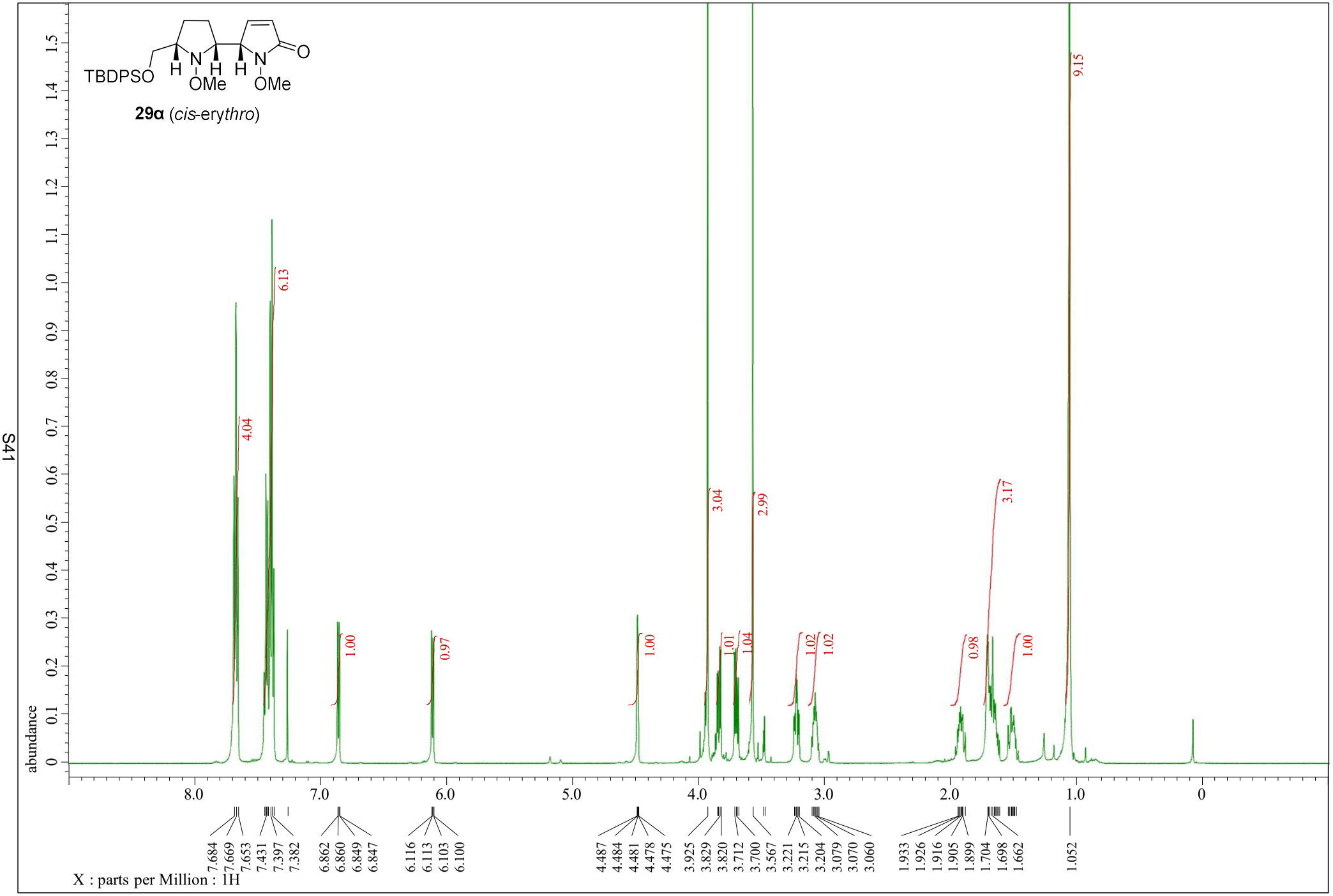
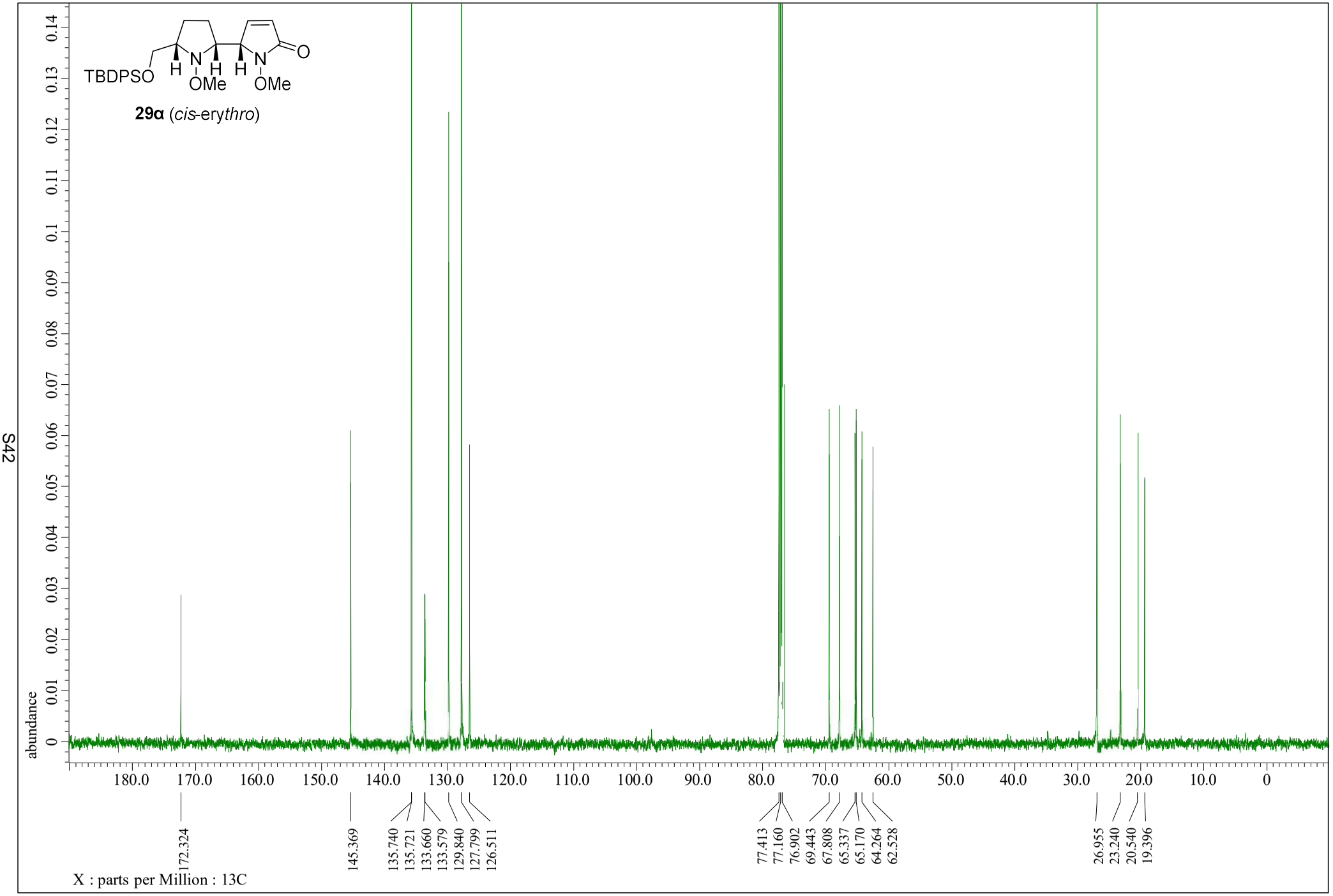
65.857
64.655
63.797
63.501
60.210
26.931
24.580
24.470
19.296
X : parts per Million : 13C

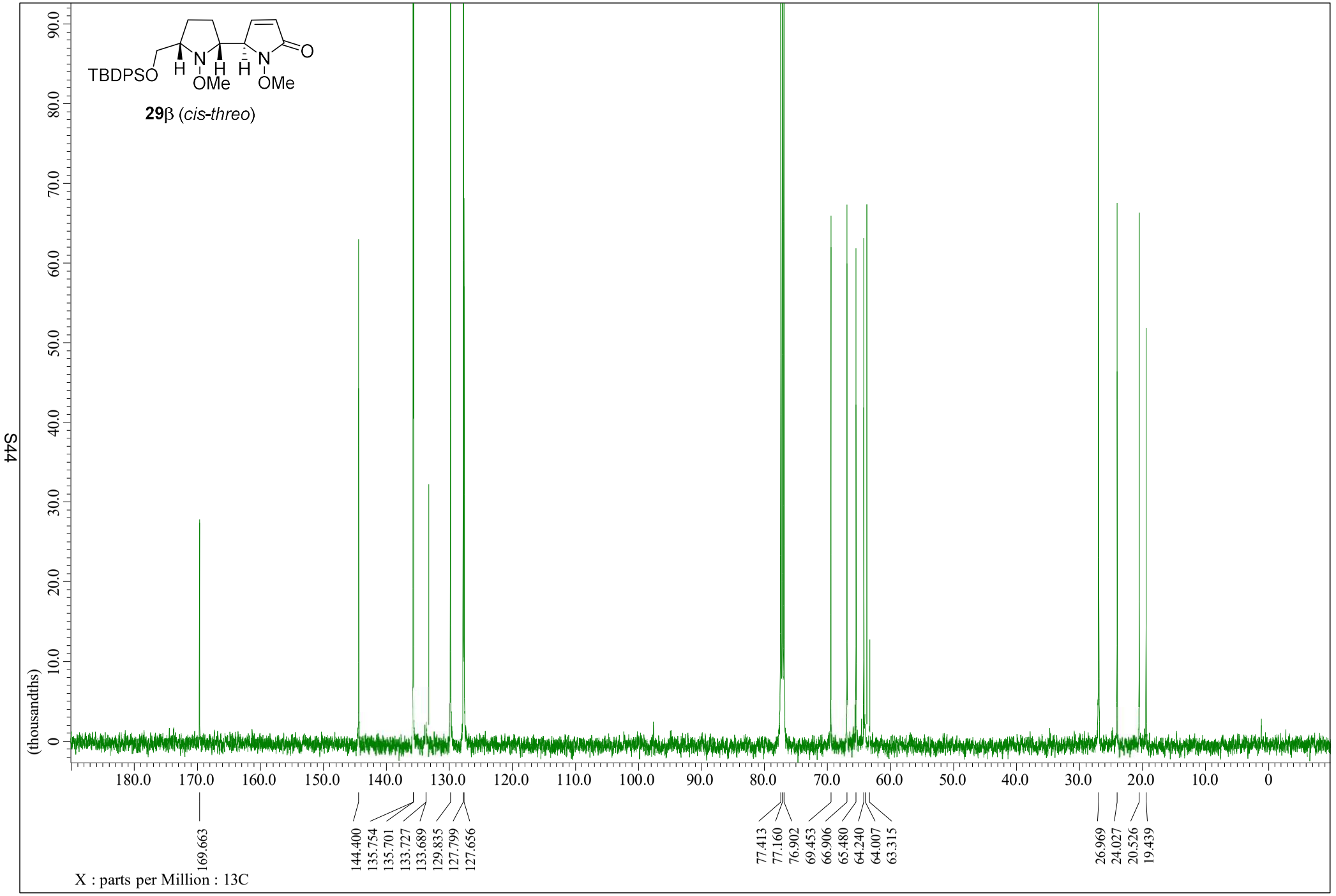
TBDPSO
OMe
OMe
28 (trans)
abundance
X : parts per Million : 1H
9.33
6.11
4.01
4.05
2.96
2.02
1.00
0.98
1.02
1.01
1.02
1.02
2.02
1.057
7.732
7.707
7.704
7.691
7.679
7.676
7.627
7.611
7.433
7.428
7.419
7.401
7.387
7.373
7.371
7.260
5.093
5.090
4.150
4.134
4.119
3.987
3.799
3.787
3.493
3.483
3.006
3.002
2.998
2.995
2.991
2.126
2.106
1.988
1.969
1.892
1.774
1.762
1.753
1.742


TBDPSO
H
N
H
OMe
N
OMe
O
28 (trans)
(thousandths)
30.0
20.0
10.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.559
144.429
135.773
133.627
133.555
129.845
129.816
127.832
127.789
98.159
77.413
77.160
76.907
66.959
64.708
64.073
61.923
60.888
34.805
26.941
26.383
24.842
19.324
X : parts per Million : 13C

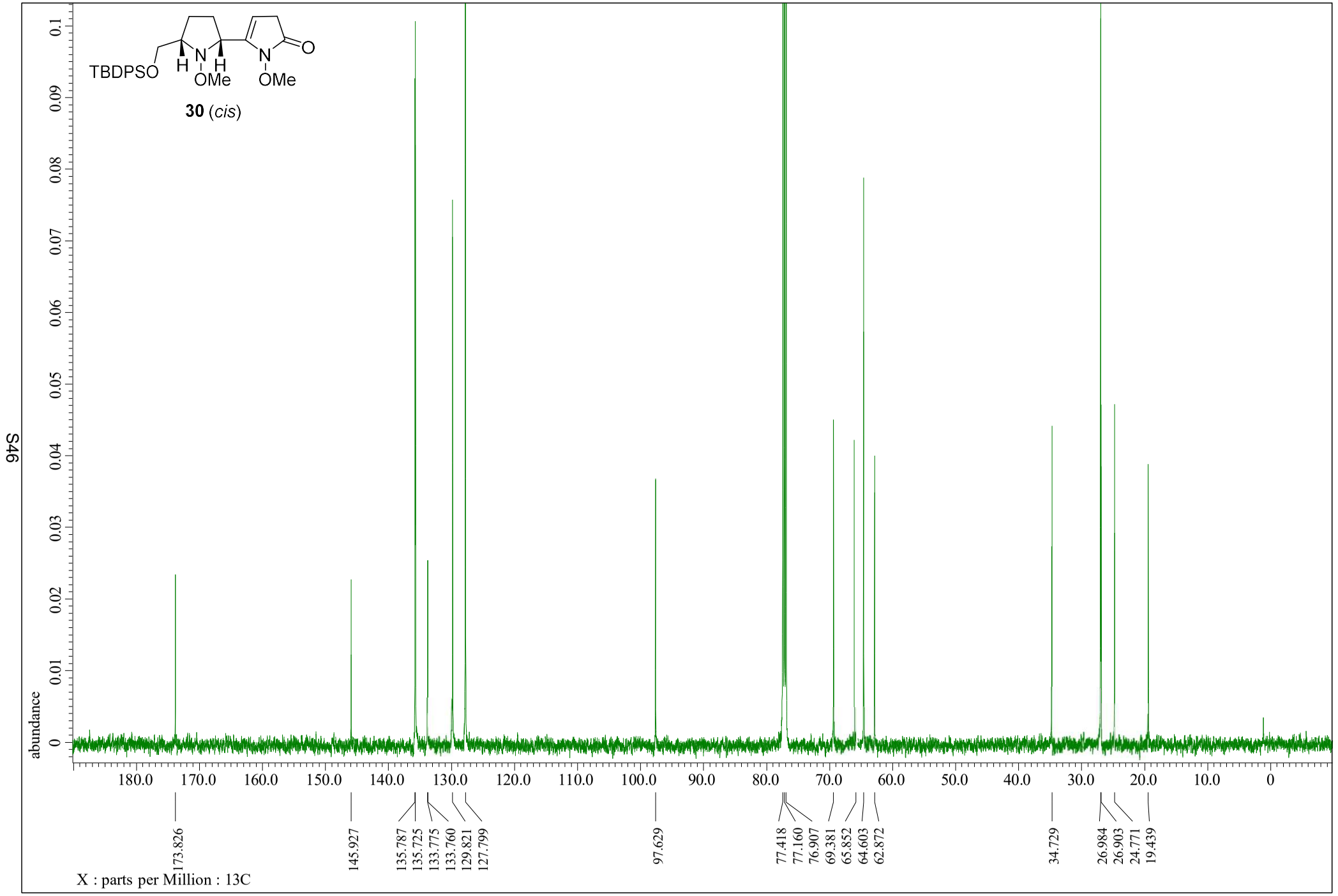

TBDPSO
H
N
H
OMe
H
N
OMe
O
29α (cis-erythro)
abundance
X : parts per Million : 1H
4.04
6.13
1.00
0.97
1.00
3.04
1.01
1.04
2.99
1.02
1.02
0.98
3.17
1.00
9.15
7.684
7.669
7.653
7.431
7.397
7.382
6.862
6.860
6.849
6.847
6.116
6.113
6.103
6.100
4.487
4.484
4.481
4.478
4.475
3.925
3.829
3.820
3.712
3.700
3.567
3.221
3.215
3.204
3.079
3.070
3.060
1.933
1.926
1.916
1.905
1.899
1.704
1.698
1.662
1.052


TBDPSO
H
N
H
OMe
H
N
OMe
O
29α (cis-erythro)
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
0.14
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
172.324
145.369
135.740
135.721
133.660
133.579
129.840
127.799
126.511
77.413
77.160
76.902
69.443
67.808
65.337
65.170
64.264
62.528
26.955
23.240
20.540
19.396
X : parts per Million : 13C

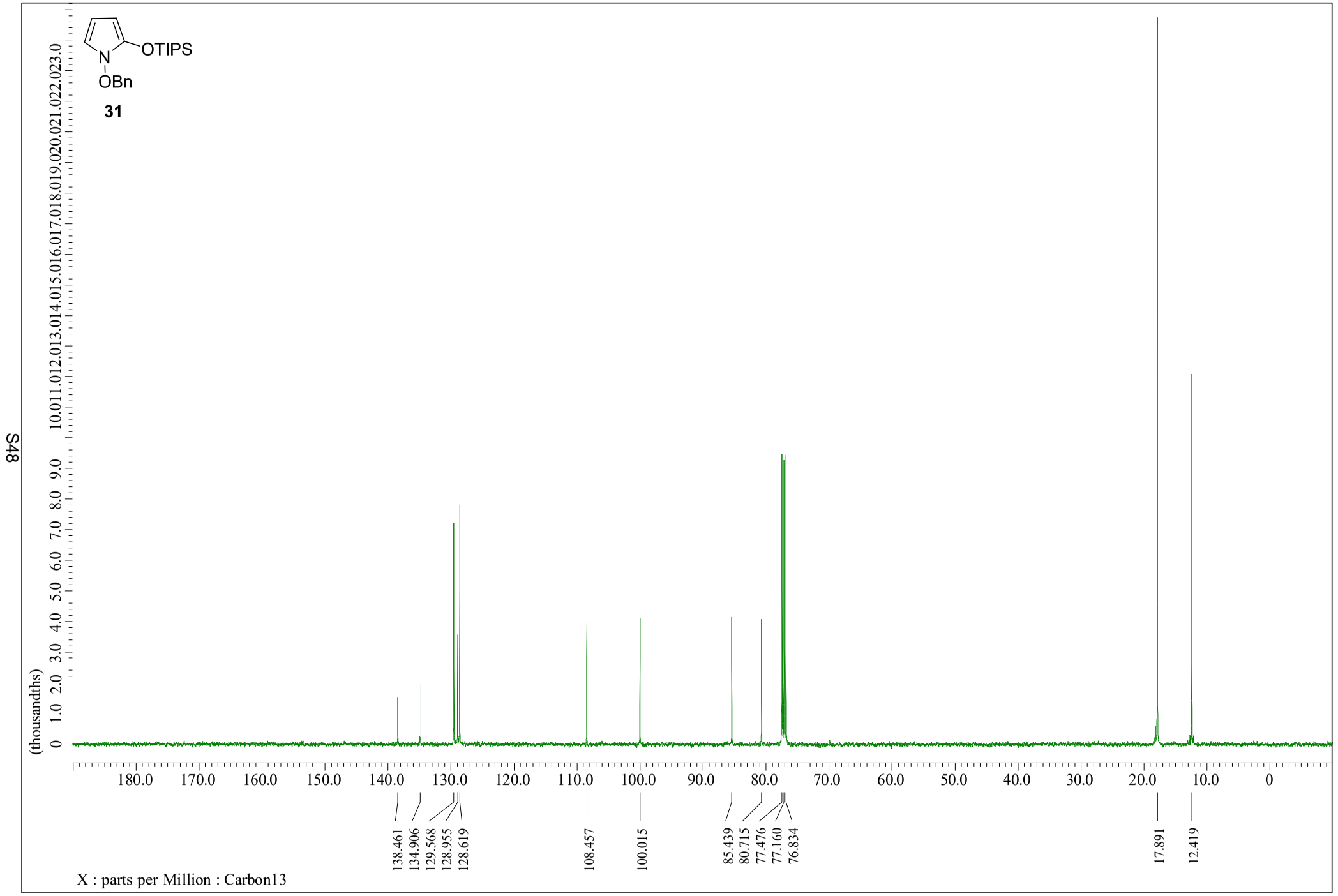
TBDPSO
OMe
OMe
O
29β (cis-threo)
abundance
X : parts per Million : 1H
9.15
6.05
4.09
3.03
3.02
2.13
1.04
1.02
1.01
1.00
0.99
0.97


TBDPSO
H
N
H
OMe
H
N
OMe
O
29β (cis-threo)
(thousandths)
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
169.663
144.400
135.754
135.701
133.727
133.689
129.835
127.799
127.656
77.413
77.160
76.902
69.453
66.906
65.480
64.240
64.007
63.315
26.969
24.027
20.526
19.439
X : parts per Million : 13C

X : parts per Million : 1H
abundance
TBDPSO
OMe
OMe
30 (cis)
9.12
6.14
4.18
3.00
3.00
1.98
1.01
0.99
0.98
0.98
0.96
0.96
0.98
1.00
1.02
7.703
7.700
7.687
7.684
7.675
7.671
7.668
7.387
7.260
5.181
5.180
5.176
5.175
5.171
5.169
3.945
3.883
3.872
3.863
3.782
3.688
3.675
3.473
3.201
3.189
2.968
2.966
2.963
2.093
2.087
2.016
2.006
1.662
1.657
1.650
1.646
1.063


TBDPSO
H
N
H
N
O
OMe
OMe
30 (cis)
abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.826
145.927
135.787
135.725
133.775
133.760
129.821
127.799
97.629
77.418
77.160
76.907
69.381
65.852
64.603
62.872
34.729
26.984
26.903
24.771
19.439
X : parts per Million : 13C

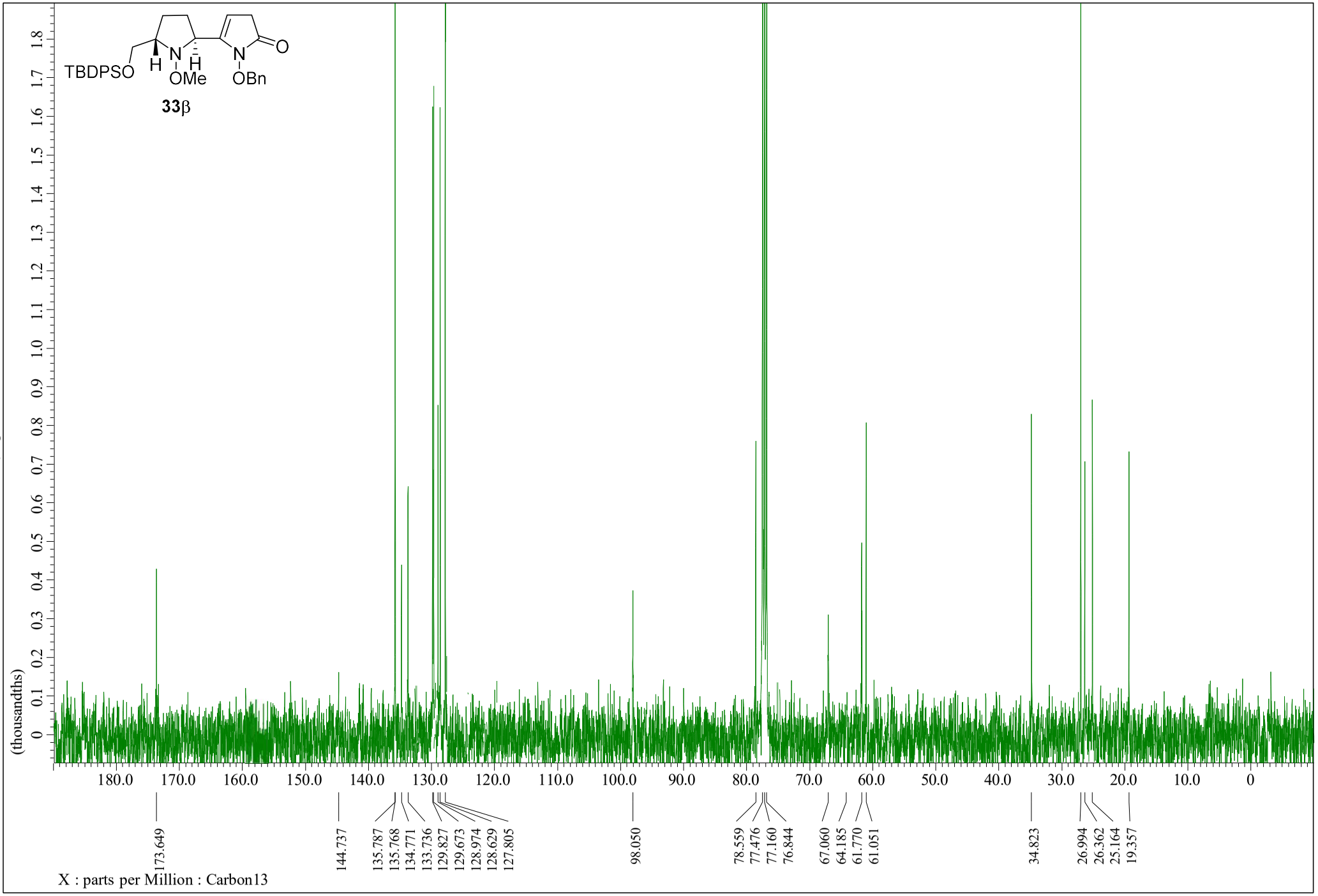
OTIPS
N
OBn
31
abundance
X : parts per Million : Proton
7.402
7.384
7.372
7.364
7.260
6.175
6.170
6.166
6.161
5.690
5.689
5.680
5.162
5.156
5.151
5.146
5.095
1.376
1.356
1.337
1.319
1.299
1.282
1.265
1.144
1.125
5.03
0.99
1.00
1.02
2.03
3.04
18.13

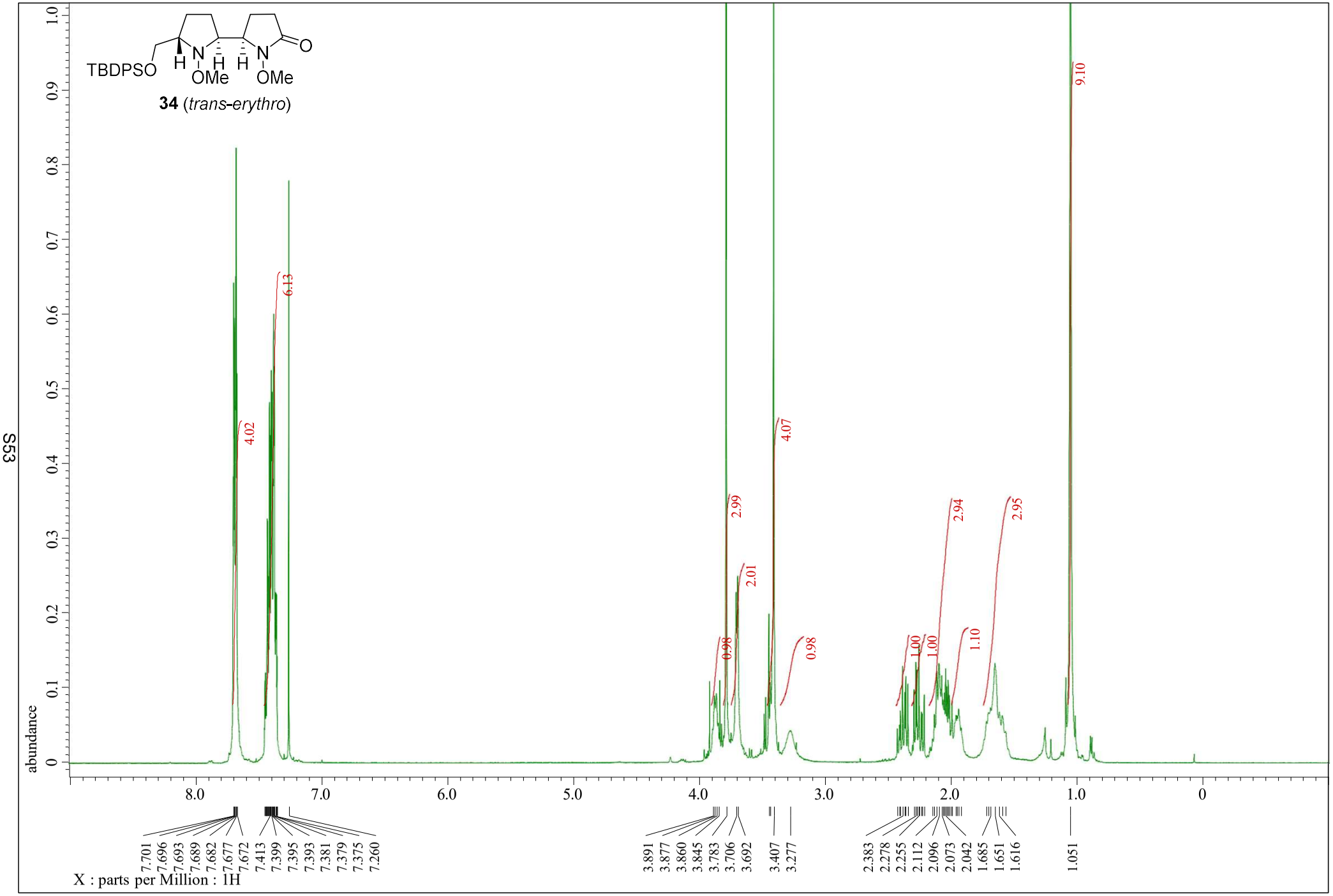

OTIPS
N
OBn
31
(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0 22.0 23.0
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
138.461
134.906
129.568
128.955
128.619
108.457
100.015
85.439
80.715
77.476
77.160
76.834
17.891
12.419
X : parts per Million : Carbon13

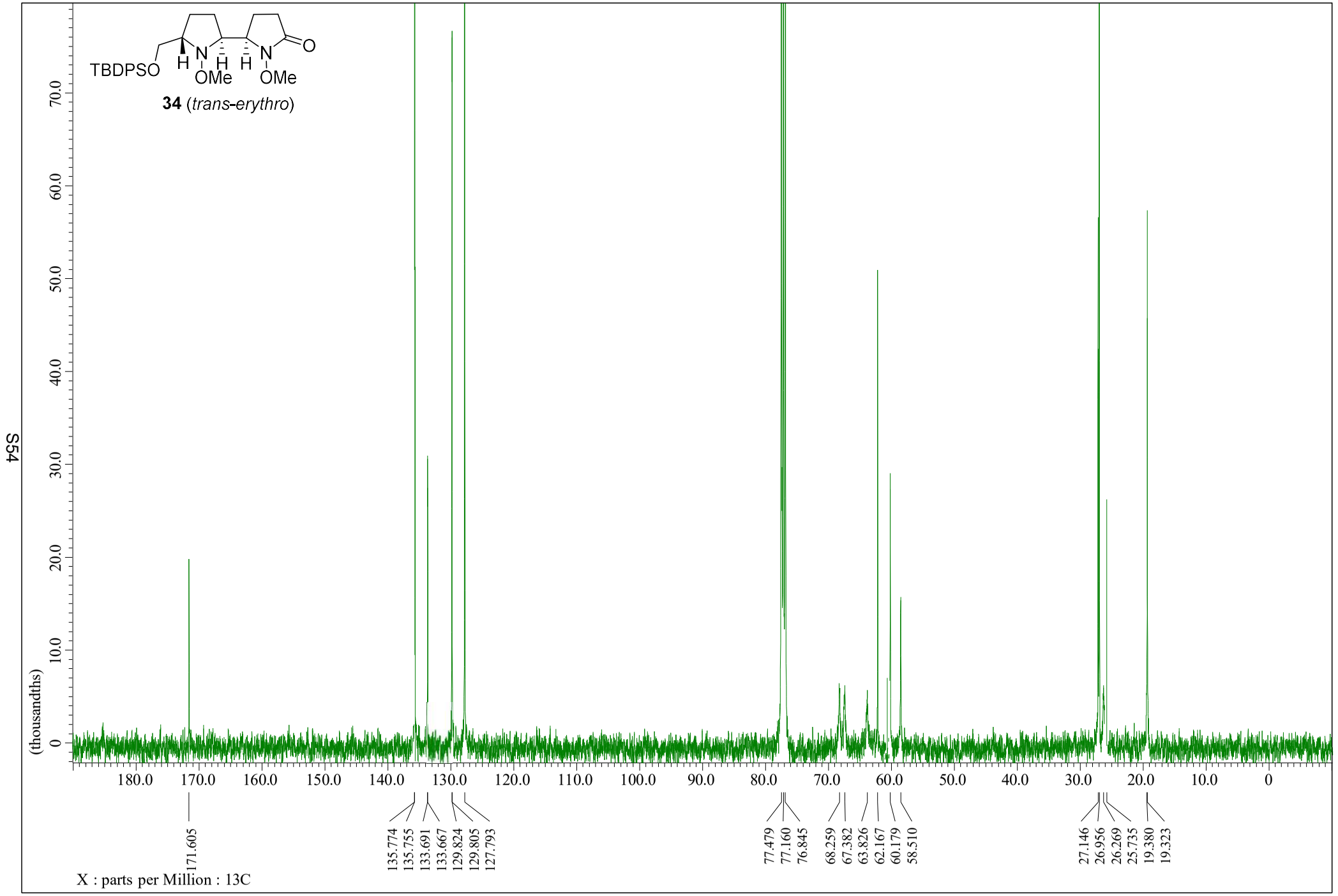
TBDPSO
H
N
H
N
OMe
OBn
O
33α
11.36
4.07
9.68
2.64
0.97
2.00
2.00
1.01
3.00
2.04
1.00
2.00
1.01
abundance
X : parts per Million : Proton
7.699
7.691
7.688
7.683
7.680
7.672
7.668
7.437
7.418
7.403
7.386
7.366
7.360
7.350
7.260
5.213
5.196
5.189
5.146
5.122
3.917
3.904
3.892
3.879
3.651
3.452
3.184
3.169
3.006
3.004
3.002
2.999
1.999
1.992
1.984
1.975
1.968
1.647
1.628
1.622
1.610
1.059

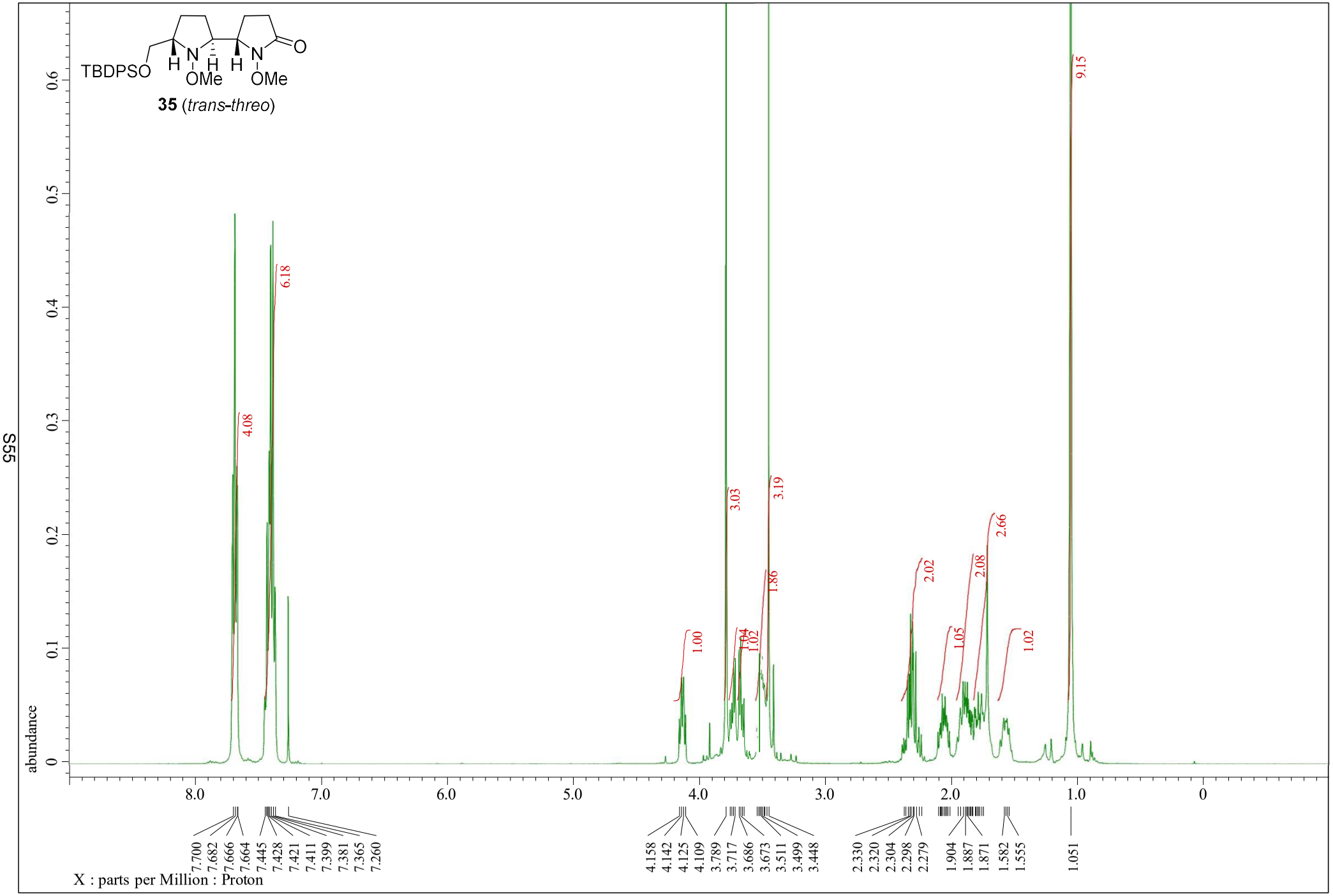
TBDPSO
OMe
OBn
33α
(thousandths)
X : parts per Million : Carbon13
174.061
146.453
135.768
135.720
134.656
133.804
129.808
129.645
129.060
128.696
127.805
97.207
78.559
77.476
77.160
76.844
69.455
66.178
64.425
62.882
34.776
27.138
26.975
24.944
19.434

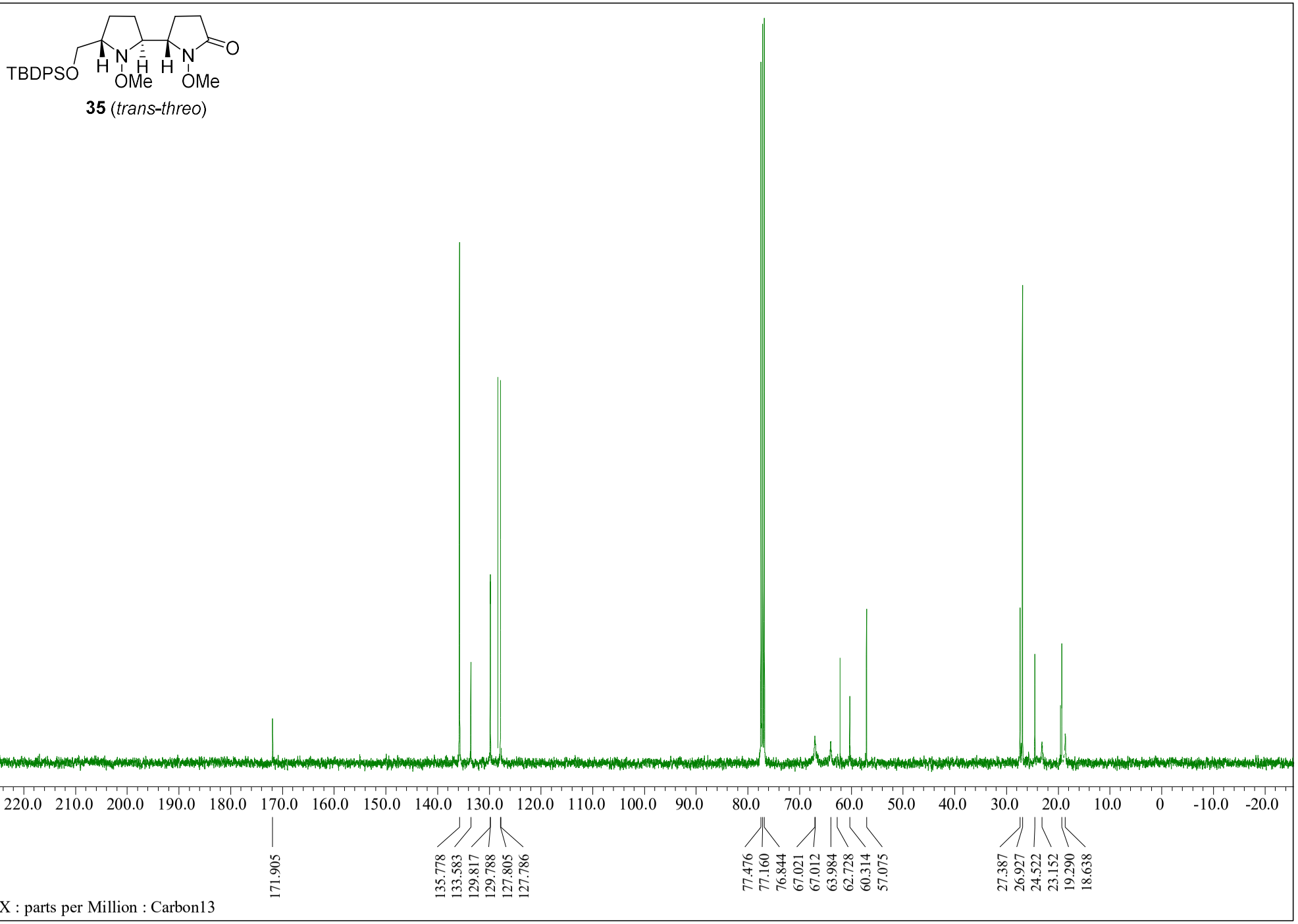
abundance
X : parts per Million : Proton
TBDPSO
OMe
OBn
33β
9.37
3.38
1.99
0.98
2.02
4.02
1.03
2.01
1.00
4.08
8.11
3.08
1.052
1.964
1.949
1.940
1.931
1.919
1.655
1.649
3.027
3.020
3.015
3.008
3.875
3.869
3.861
3.849
3.836
3.678
3.465
3.423
5.239
5.215
5.179
5.155
5.071
5.069
5.064
5.062
5.059
5.055
7.692
7.675
7.673
7.658
7.432
7.419
7.412
7.393
7.381
7.373
7.306
7.260


TBDPSO
H
N
H
OMe
N
O
OBn
33β
(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.649
144.737
135.787
135.768
134.771
133.736
129.827
129.673
128.974
128.629
127.805
98.050
78.559
77.476
77.160
76.844
67.060
64.185
61.770
61.051
34.823
26.994
26.362
25.164
19.357
X : parts per Million : Carbon13

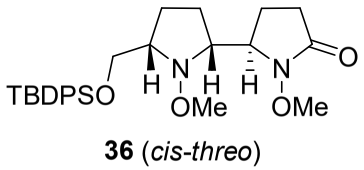

TBDPSO
H
N
OMe
H
H
N
OMe
O
34 (trans-erythro)
abundance
X : parts per Million : 1H
4.02
6.13
2.99
2.01
0.98
4.07
0.98
1.00
1.00
2.94
1.10
2.95
9.10
7.701
7.696
7.693
7.689
7.682
7.677
7.672
7.413
7.399
7.395
7.393
7.381
7.379
7.375
7.260
3.891
3.877
3.860
3.845
3.783
3.706
3.692
3.407
3.277
2.383
2.278
2.255
2.112
2.096
2.073
2.042
1.685
1.651
1.616
1.051


TBDPSO
H
N
OMe
H
H
N
OMe
O
34 (trans-erythro)
(thousandths)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.605
135.774
135.755
133.691
133.667
129.824
129.805
127.793
77.479
77.160
76.845
68.259
67.382
63.826
62.167
60.179
58.510
27.146
26.956
26.269
25.735
19.380
19.323
X : parts per Million : 13C


TBDPSO
H
N
H
H
N
O
OMe
OMe
35 (trans-threo)
abundance
0
0.1
0.2
0.3
0.4
0.5
0.6
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
4.08
6.18
1.00
3.03
1.04
1.02
3.19
1.86
2.02
1.05
2.08
2.66
1.02
9.15
7.700
7.682
7.666
7.664
7.445
7.428
7.421
7.411
7.399
7.381
7.365
7.260
4.158
4.142
4.125
4.109
3.789
3.717
3.686
3.673
3.511
3.499
3.448
2.330
2.320
2.304
2.298
2.279
1.904
1.887
1.871
1.582
1.555
1.051
X : parts per Million : Proton


TBDPSO
H
N
H
OMe
H
N
O
OMe
35 (trans-threo)
(thousandths)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
171.905
135.778
133.583
129.817
129.788
127.805
127.786
77.476
77.160
76.844
67.021
67.012
63.984
62.728
60.314
57.075
27.387
26.927
24.522
23.152
19.290
18.638
X : parts per Million : Carbon13

TBDPSO
OMe
OMe
36 (cis-threo)
abundance
X : parts per Million : Proton
9.23
6.07
4.13
4.03
3.95
1.98
1.94
1.03
1.03
1.00
1.01
0.99
1.00
1.00
1.058
1.415
1.430
1.680
1.745
2.034
2.054
2.284
2.325
3.128
3.139
3.142
3.153
3.447
3.661
3.792
4.122
4.132
4.135
4.142
4.145
4.152
4.155
7.260
7.384
7.659
7.663
7.679
7.682
7.686
7.702
7.706



36 (*cis-threo*)

(thousandths)

10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0

180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

170.994

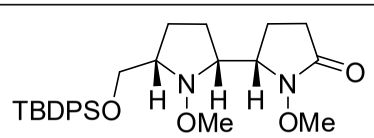
135.778 135.711 133.794 133.756 129.788 127.786 127.766

77.476 77.160 76.844 69.187 67.175 65.718 63.073 62.364 56.433

27.320 26.956 23.937 20.593 19.443 16.358

X : parts per Million : Carbon13

TBDPSO
OMe
OMe
37 (cis-erythro)
abundance
X : parts per Million : 1H
9.17
6.15
4.06
3.69
2.96
1.31
1.04
1.00
1.00
0.97
1.04
2.04
2.04
1.41
1.00
7.693
7.692
7.676
7.674
7.672
7.658
7.653
7.380
7.260
3.833
3.821
3.817
3.813
3.805
3.791
3.779
3.656
3.446
3.333
3.326
3.196
3.193
2.393
2.303
2.283
2.280
2.261
2.038
2.020
1.668
1.494
1.486
1.054



37 (*cis-erythro*)

abundance

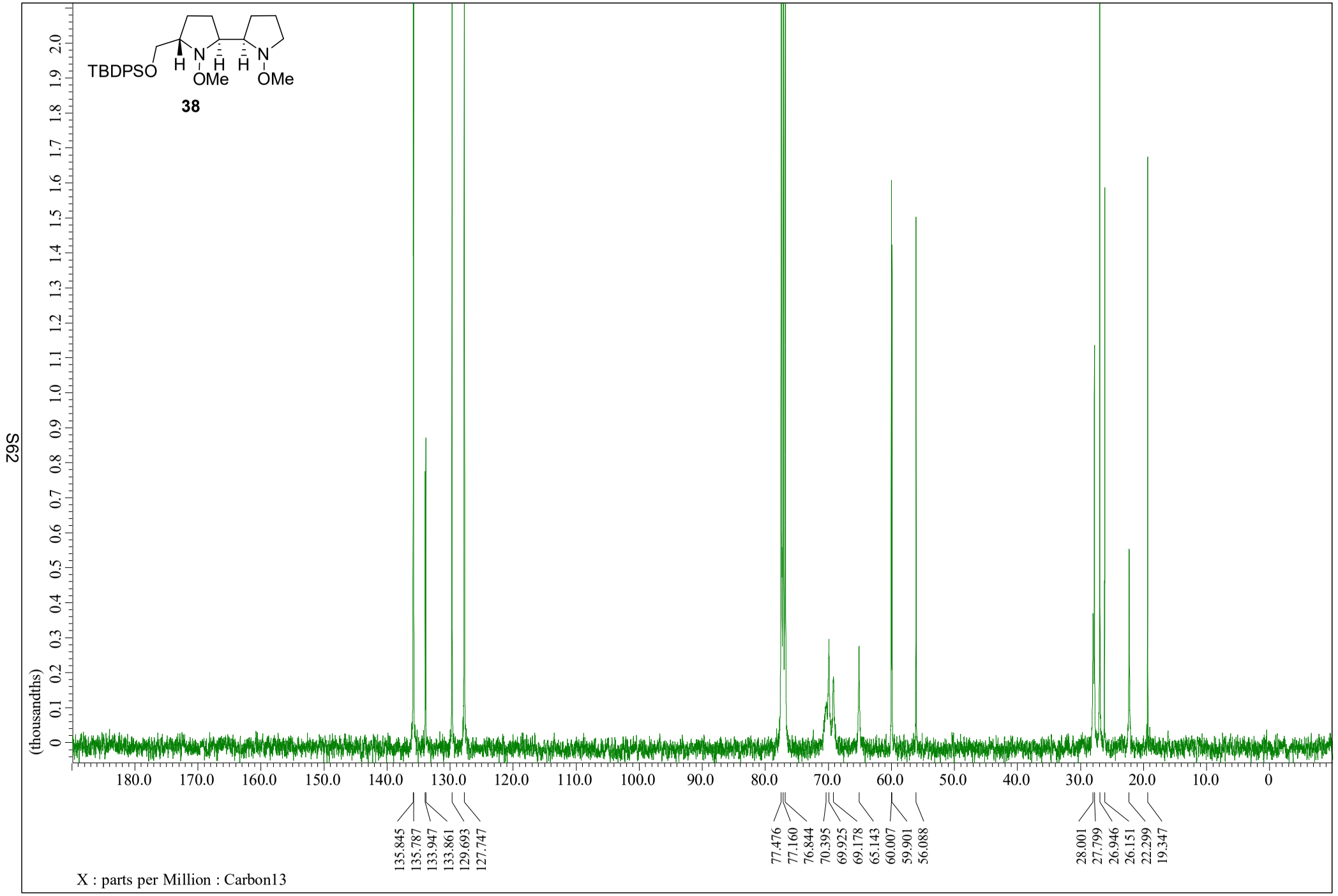
0 0.02 0.04 0.06 0.08 0.1 0.12 0.14 0.16 0.18 0.2 0.22 0.24 0.26

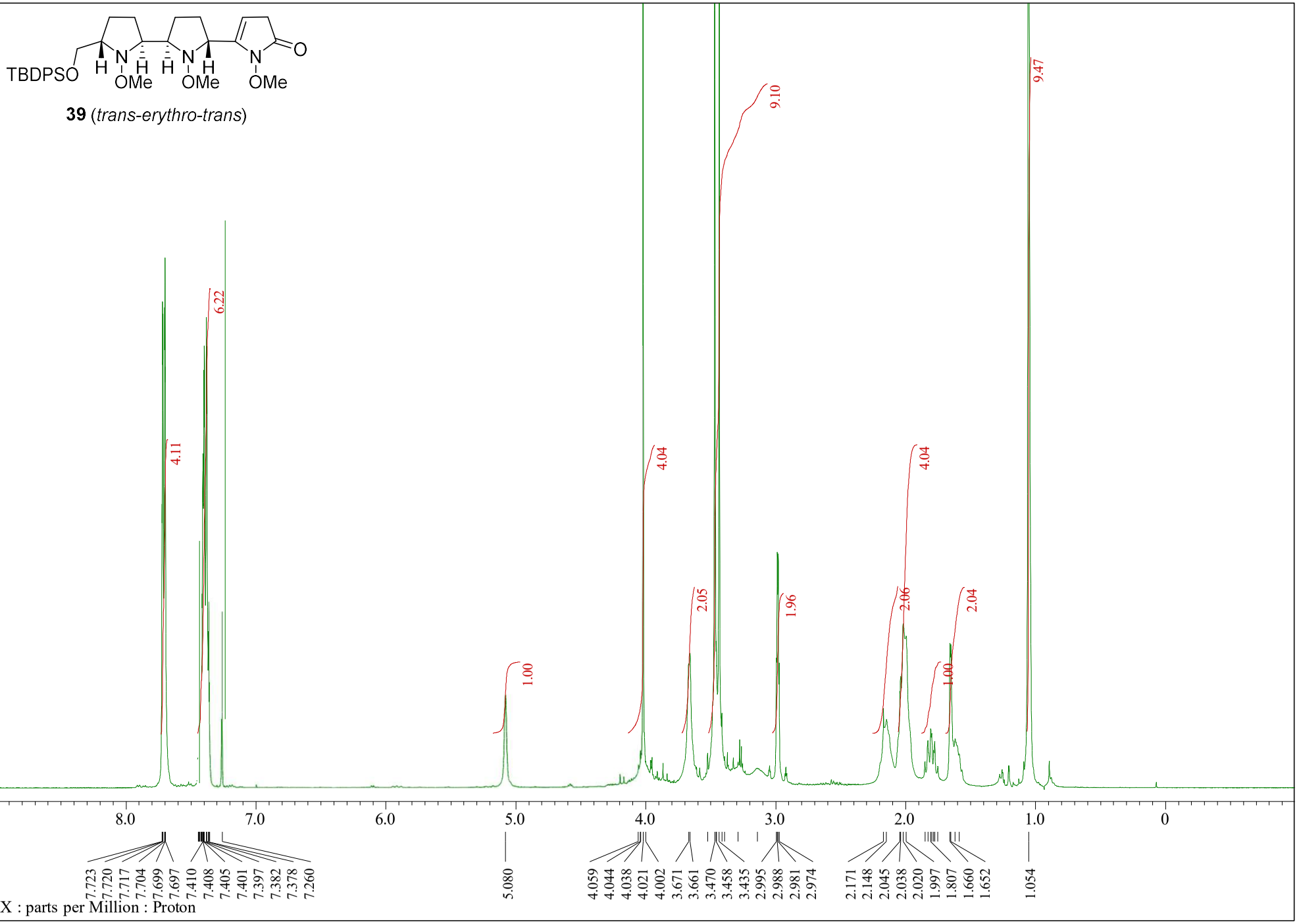
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

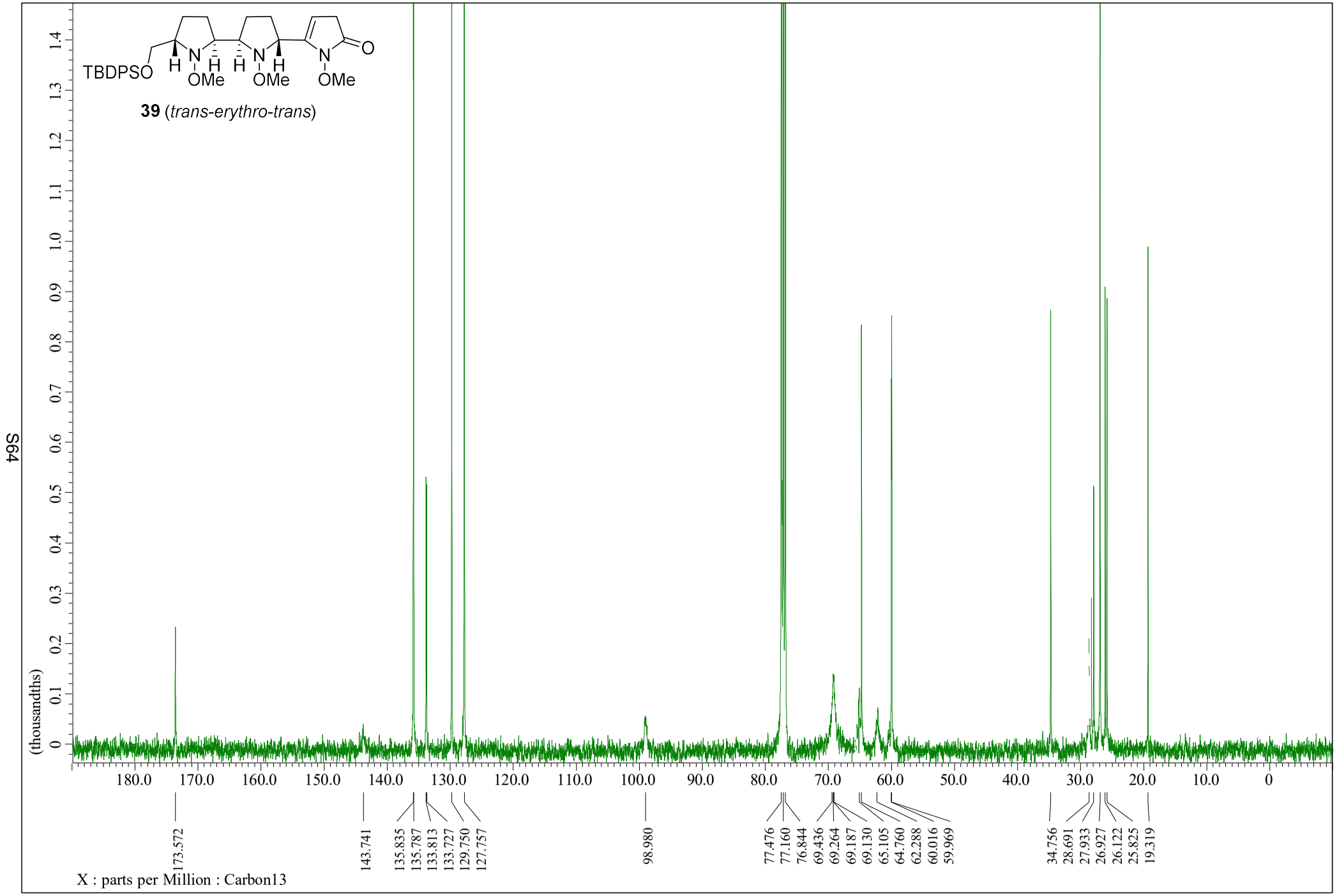
172.258
135.745
135.721
133.714
133.652
129.824
127.793
77.479
77.160
76.841
70.228
68.012
65.628
62.338
62.238
58.939
27.165
26.965
24.114
23.356
19.404
17.698

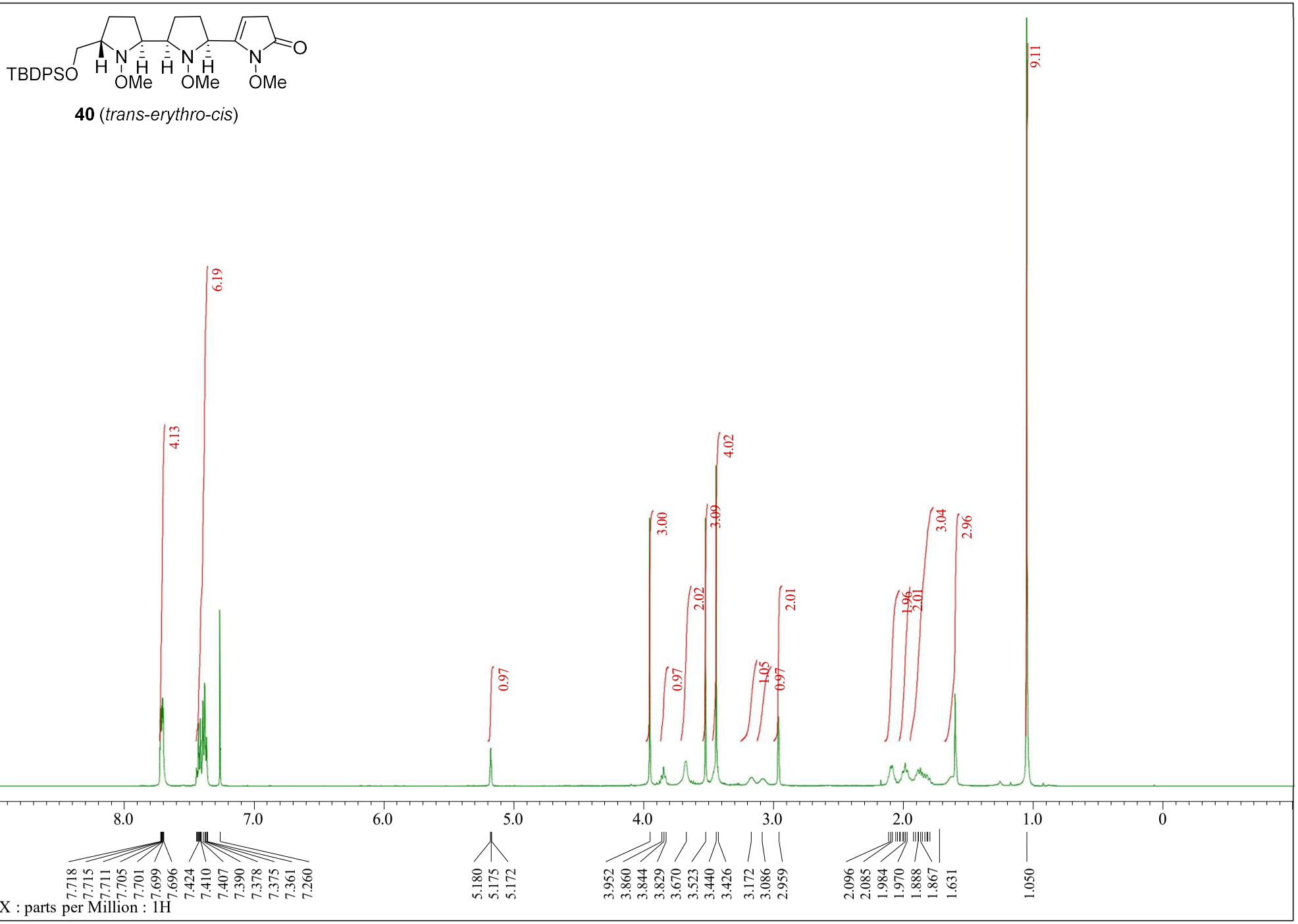
X : parts per Million : 13C

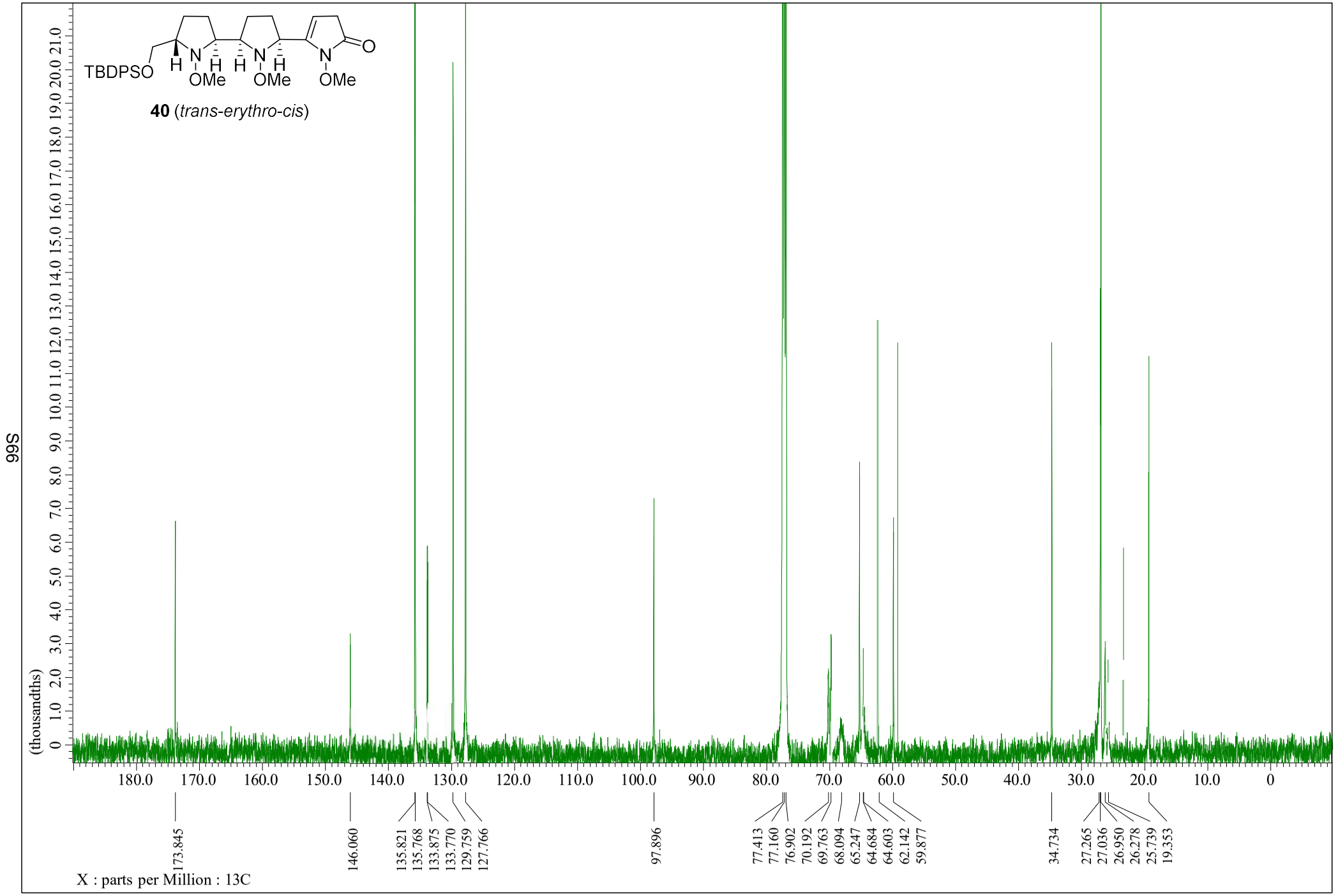
TBDPSO
OMe
OMe
38
abundance
X : parts per Million : Proton
9.14
6.14
4.05
4.02
3.73
2.04
2.00
2.00
1.04
1.01
1.01
1.04
7.727
7.721
7.717
7.712
7.707
7.702
7.697
7.422
7.410
7.405
7.401
7.395
7.381
7.376
7.260
3.671
3.658
3.617
3.603
3.591
3.577
3.484
3.467
3.438
3.148
2.935
2.924
2.917
2.907
1.990
1.849
1.843
1.827
1.804
1.797
1.546
1.539
1.533
1.054

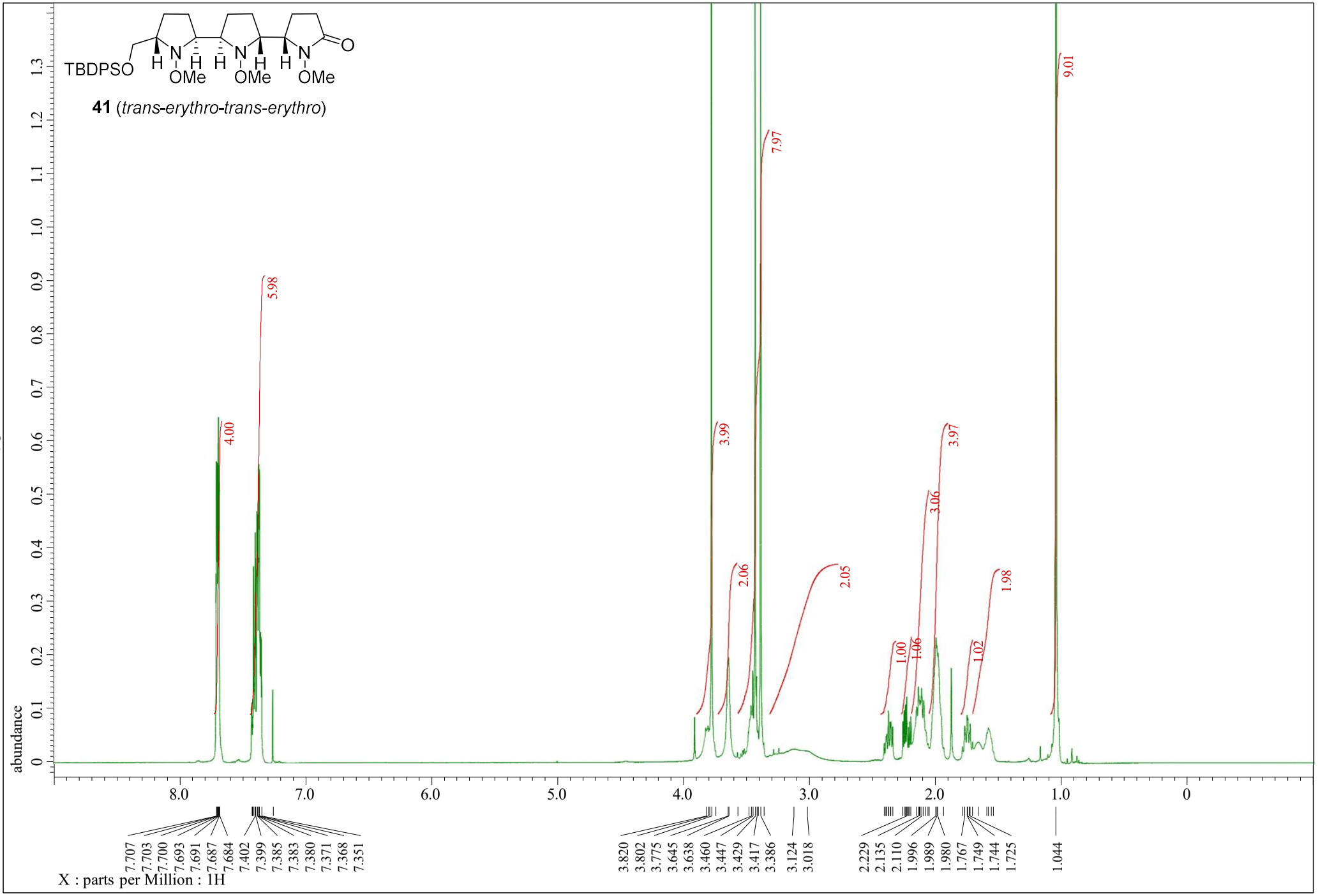

TBDPSO
H
N
H
OMe
H
N
OMe
38
(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
135.845
135.787
133.947
133.861
129.693
127.747
77.476
77.160
76.844
70.395
69.925
69.178
65.143
60.007
59.901
56.088
28.001
27.799
26.946
26.151
22.299
19.347
X : parts per Million : Carbon13

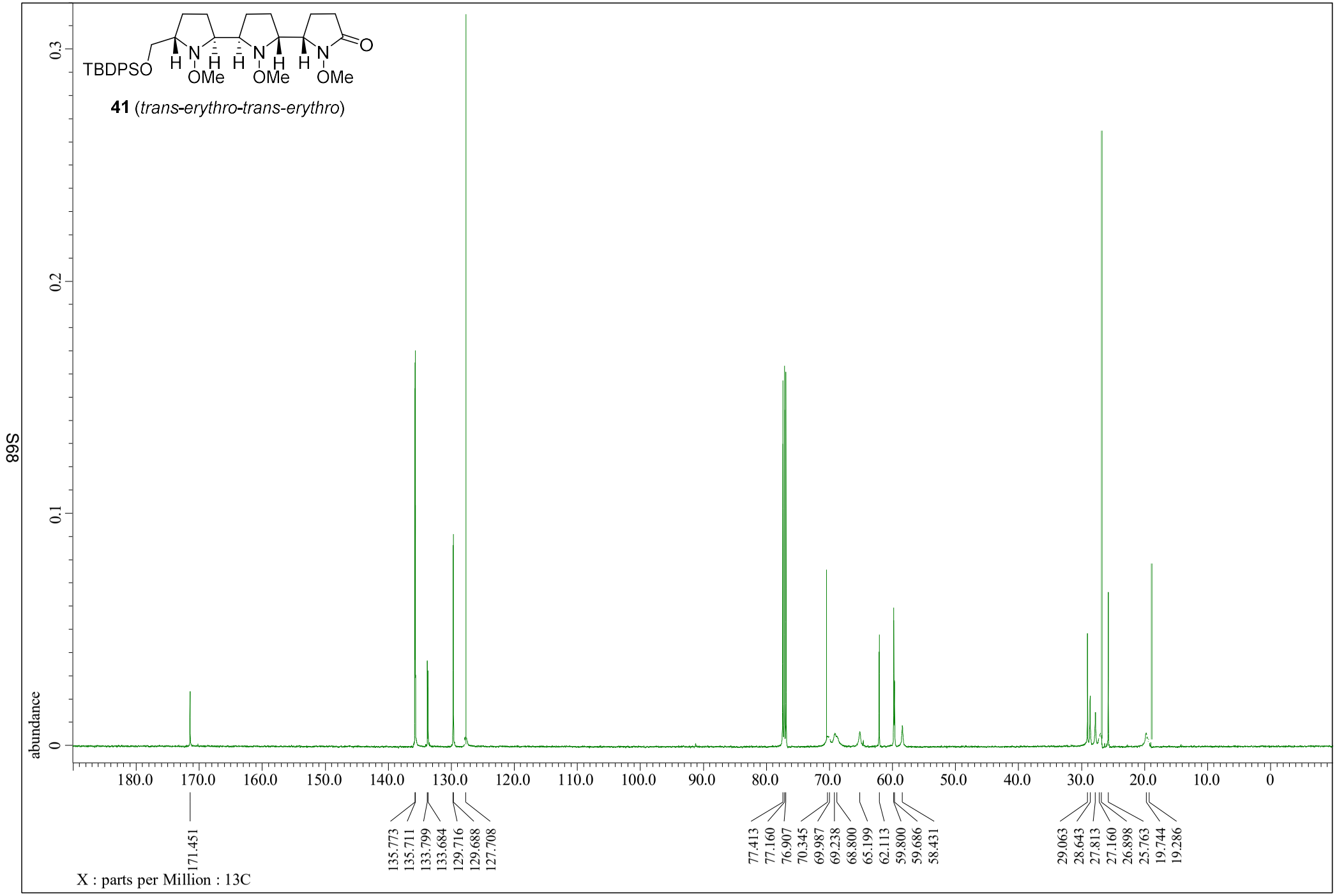

TBDPSO
H
N
OMe
H
H
N
OMe
H
N
OMe
O
39 (trans-erythro-trans)
abundance
0
0.1
0.2
0.3
0.4
4.11
6.22
1.00
4.04
2.05
9.10
1.96
2.06
4.04
1.00
2.04
9.47
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.723
7.720
7.717
7.704
7.699
7.697
7.410
7.408
7.405
7.401
7.397
7.382
7.378
7.260
5.080
4.059
4.044
4.038
4.021
4.002
3.671
3.661
3.470
3.458
3.435
2.995
2.988
2.981
2.974
2.171
2.148
2.045
2.038
2.020
1.997
1.807
1.660
1.652
1.054
X : parts per Million : Proton

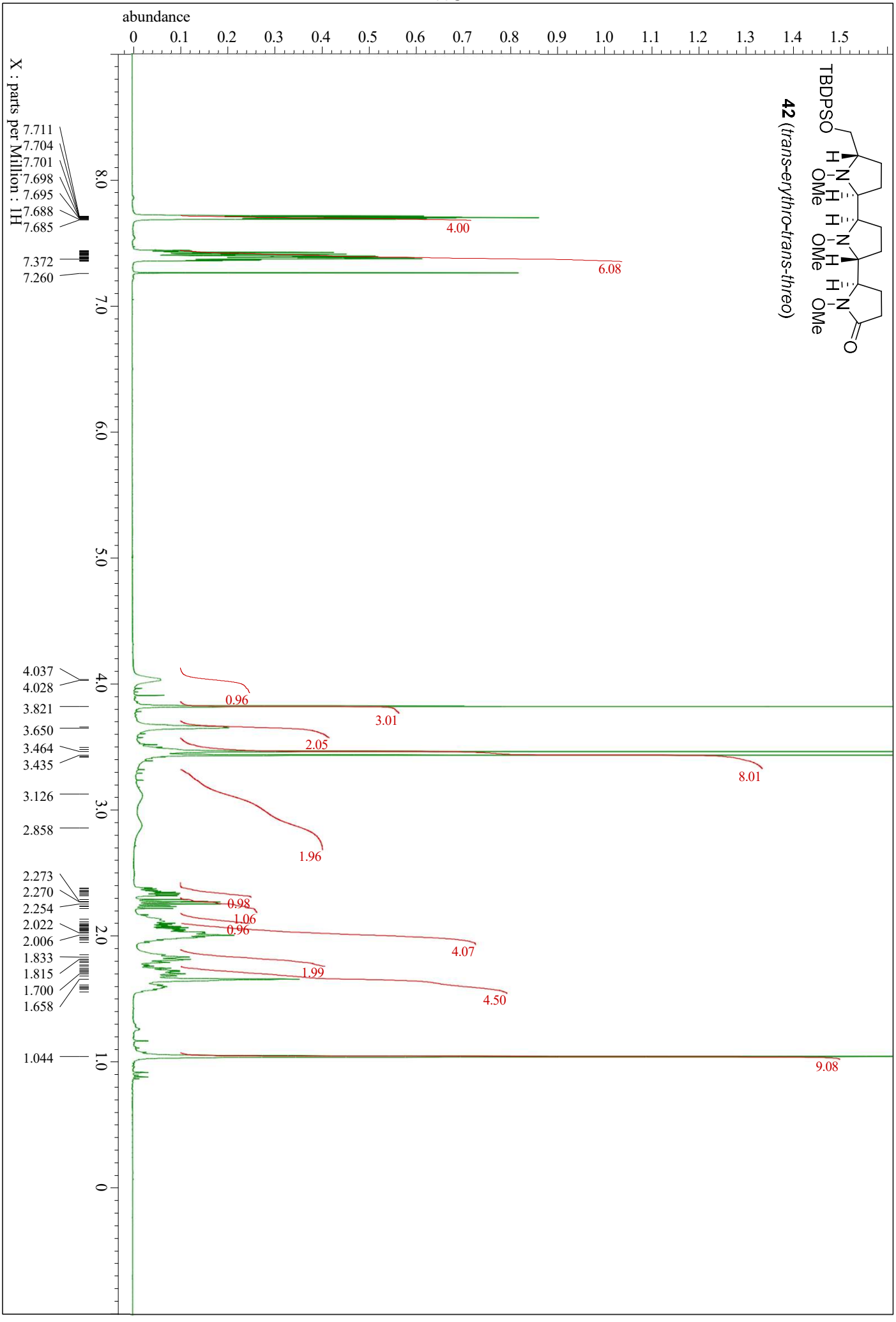

TBDPSO
H
N
OMe
H
H
N
OMe
H
N
OMe
O
39 (trans-erythro-trans)
(thousandths)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1.4
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.572
143.741
135.835
135.787
133.813
133.727
129.750
127.757
98.980
77.476
77.160
76.844
69.436
69.264
69.187
69.130
65.105
64.760
62.288
60.016
59.969
34.756
28.691
27.933
26.927
26.122
25.825
19.319
X : parts per Million : Carbon13

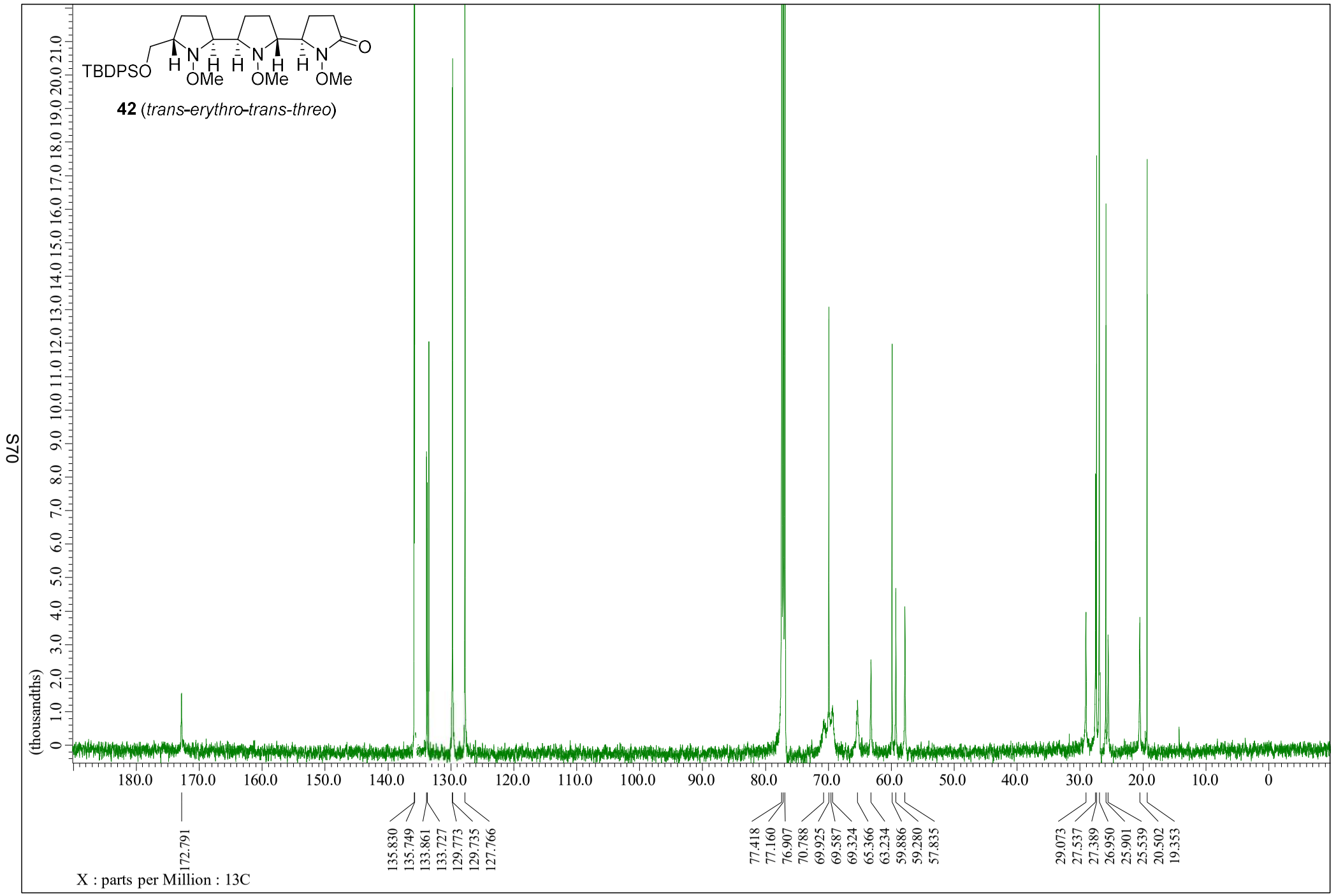

TBDPSO
OMe
OMe
OMe
40 (trans-erythro-cis)
abundance
X : parts per Million : 1H
9.11
6.19
4.13
4.02
3.09
3.00
2.96
3.04
2.02
2.01
2.01
1.96
1.05
0.97
0.97
0.97
7.718
7.715
7.711
7.705
7.701
7.699
7.696
7.424
7.410
7.407
7.390
7.378
7.375
7.361
7.260
5.180
5.175
5.172
3.952
3.860
3.844
3.829
3.670
3.523
3.440
3.426
3.172
3.086
2.959
2.096
2.085
1.984
1.970
1.888
1.867
1.631
1.050


TBDPSO
OMe
OMe
OMe
40 (trans-erythro-cis)
99S
(thousandths)
X : parts per Million : 13C
173.845
146.060
135.821
135.768
133.875
133.770
129.759
127.766
97.896
77.413
77.160
76.902
70.192
69.763
68.094
65.247
64.684
64.603
62.142
59.877
34.734
27.265
27.036
26.950
26.278
25.739
19.353

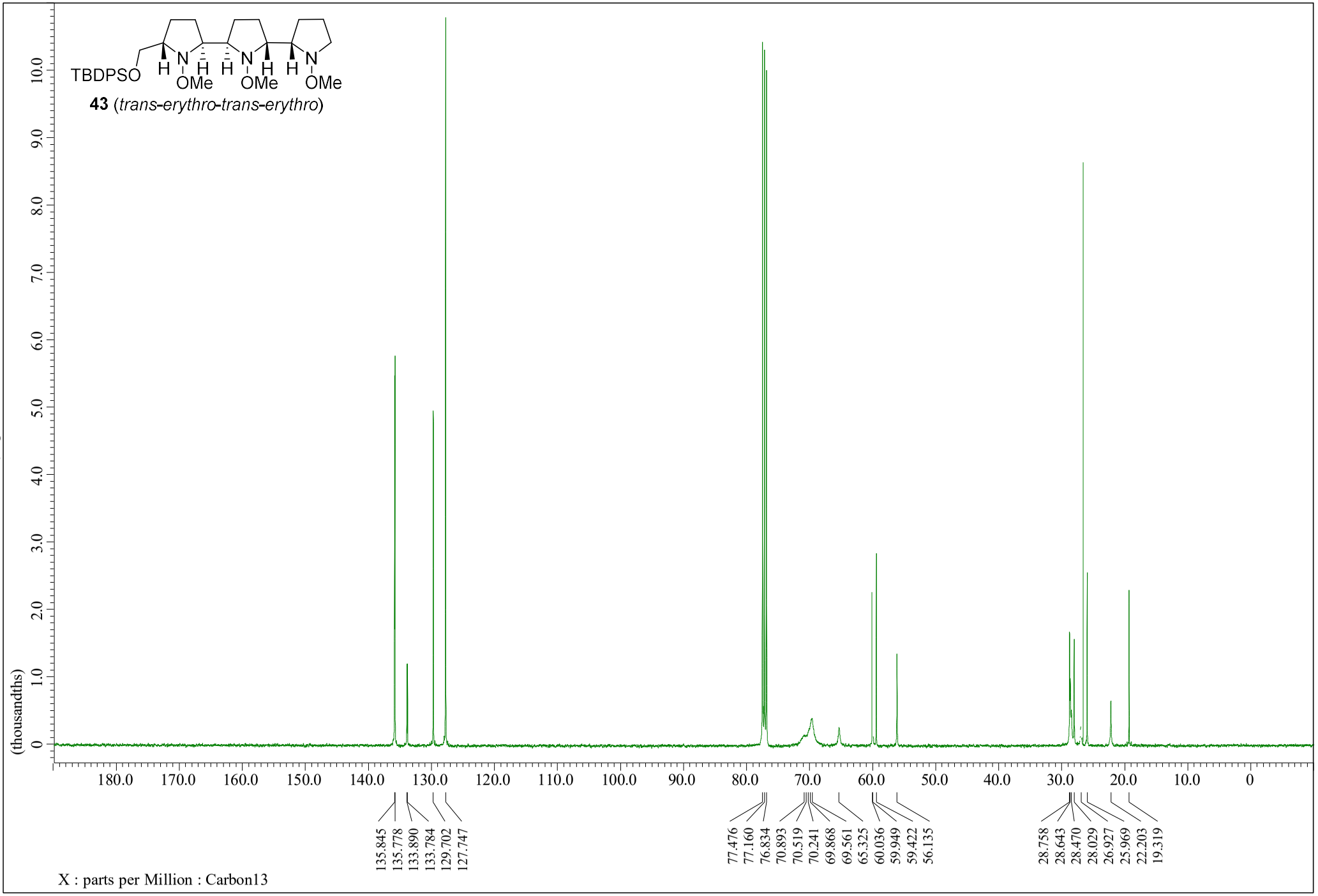

TBDPSO
OMe
OMe
OMe
41 (trans-erythro-trans-erythro)
abundance
X : parts per Million : 1H
9.01
7.97
5.98
4.00
3.99
3.97
3.06
2.06
2.05
1.98
1.00
1.06
1.02
7.707
7.703
7.700
7.693
7.691
7.687
7.684
7.402
7.399
7.385
7.383
7.380
7.371
7.368
7.351
3.820
3.802
3.775
3.645
3.638
3.460
3.447
3.429
3.417
3.386
3.124
3.018
2.229
2.135
2.110
1.996
1.989
1.980
1.767
1.749
1.744
1.725
1.044


TBDPSO
OMe
OMe
OMe
O
41 (trans-erythro-trans-erythro)
S68
abundance
0
0.1
0.2
0.3
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.451
135.773
135.711
133.799
133.684
129.716
129.688
127.708
77.413
77.160
76.907
70.345
69.987
69.238
68.800
65.199
62.113
59.800
59.686
58.431
29.063
28.643
27.813
27.160
26.898
25.763
19.744
19.286
X : parts per Million : 13C

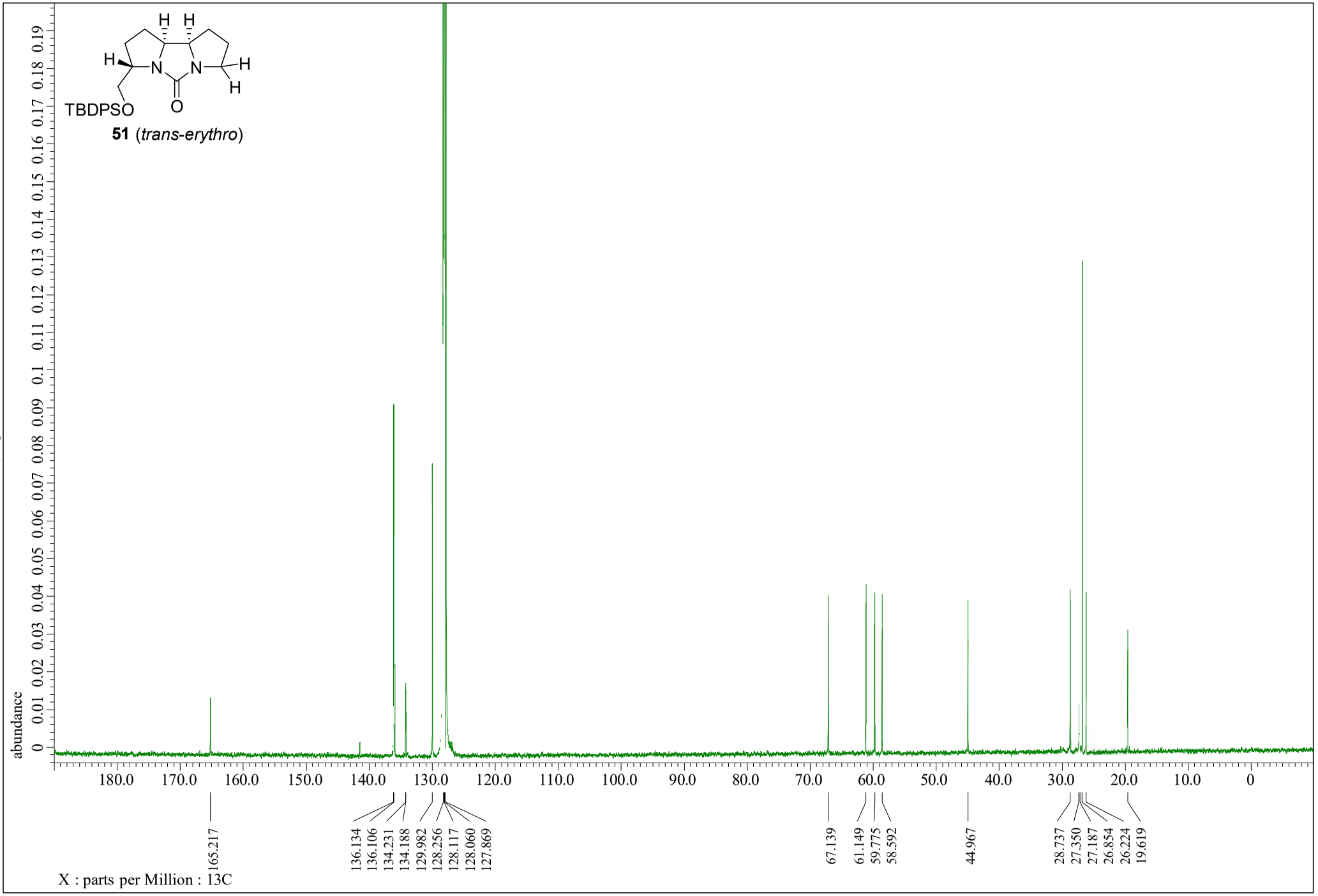

abundance
X : parts per Million : 1H
7.711
7.704
7.701
7.698
7.695
7.688
7.685
7.372
7.260
4.037
4.028
3.821
3.650
3.464
3.435
3.126
2.858
2.273
2.270
2.254
2.022
2.006
1.833
1.815
1.700
1.658
1.044
4.00
6.08
0.96
3.01
2.05
8.01
1.96
0.98
1.06
0.96
4.07
1.99
4.50
9.08
TBDPSO
OMe
OMe
OMe
O
42 (trans-erythro-trans-threo)


TBDPSO
OMe
OMe
OMe
42 (trans-erythro-trans-threo)
(thousandths)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0 16.0 17.0 18.0 19.0 20.0 21.0
180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
172.791
135.830 135.749 133.861 133.727 129.773 129.735 127.766
77.418 77.160 76.907 70.788 69.925 69.587 69.324 65.366 63.234 59.886 59.280 57.835
29.073 27.537 27.389 26.950 25.901 25.539 20.502 19.353
X : parts per Million : 13C

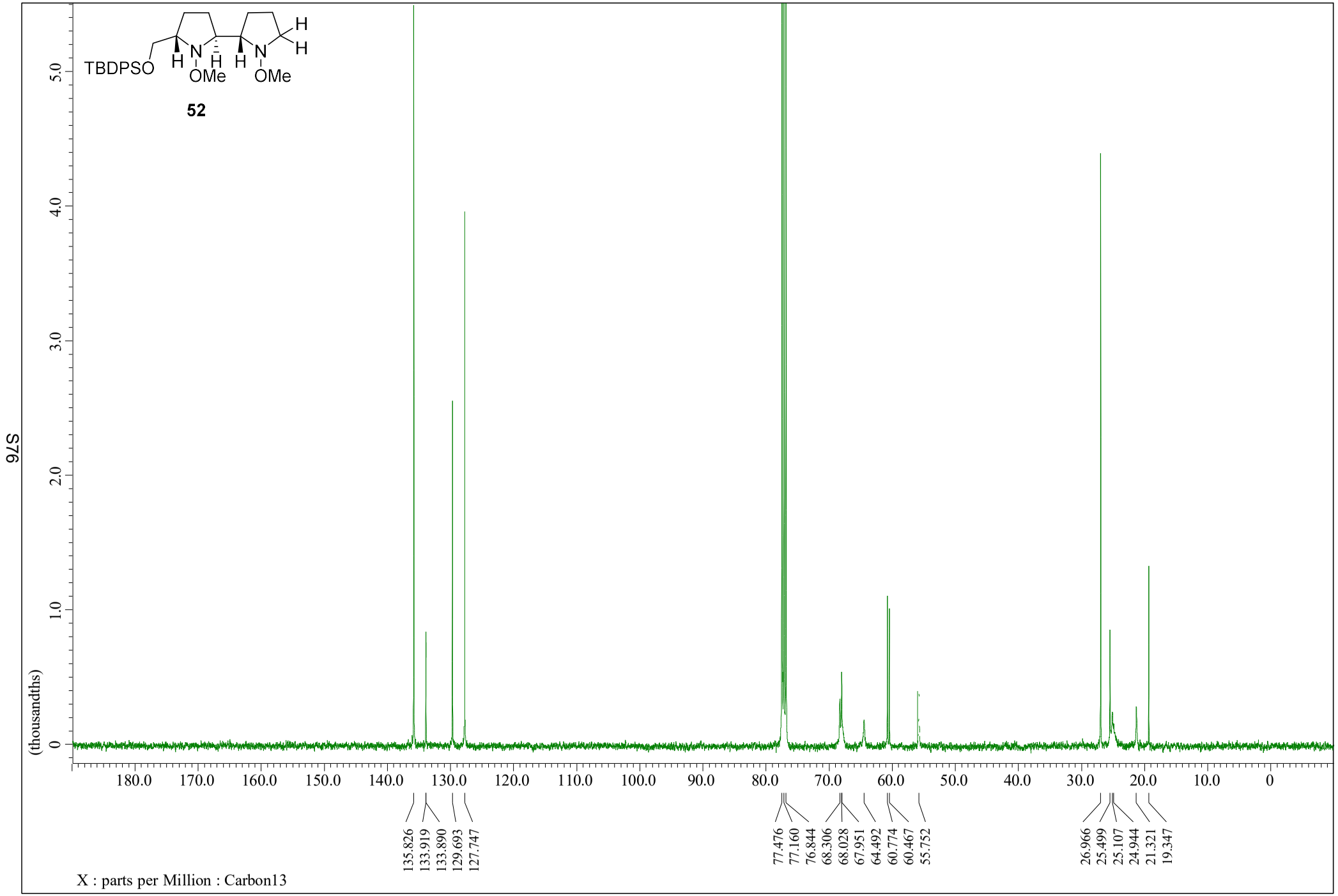
TBDPSO
OMe
OMe
OMe
43 (trans-erythro-trans-erythro)
abundance
X : parts per Million : Proton
9.04
6.03
4.00
10.06
2.03
2.97
3.03
4.99
4.08
1.98
1.00
1.055
1.537
1.695
1.760
1.767
1.783
1.790
1.985
2.909
2.919
2.928
2.938
3.176
3.407
3.443
3.469
3.502
3.593
3.615
3.627
3.651
3.676
7.381
7.388
7.391
7.394
7.396
7.401
7.406
7.412
7.702
7.707
7.712
7.722
7.726
7.727
7.732


TBDPSO
H N OMe H N OMe H N OMe
43 (trans-erythro-trans-erythro)
(thousandths)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
135.845
135.778
133.890
133.784
129.702
127.747
77.476
77.160
76.834
70.893
70.519
70.241
69.868
69.561
65.325
60.036
59.949
59.422
56.135
28.758
28.643
28.470
28.029
26.927
25.969
22.203
19.319
X : parts per Million : Carbon13

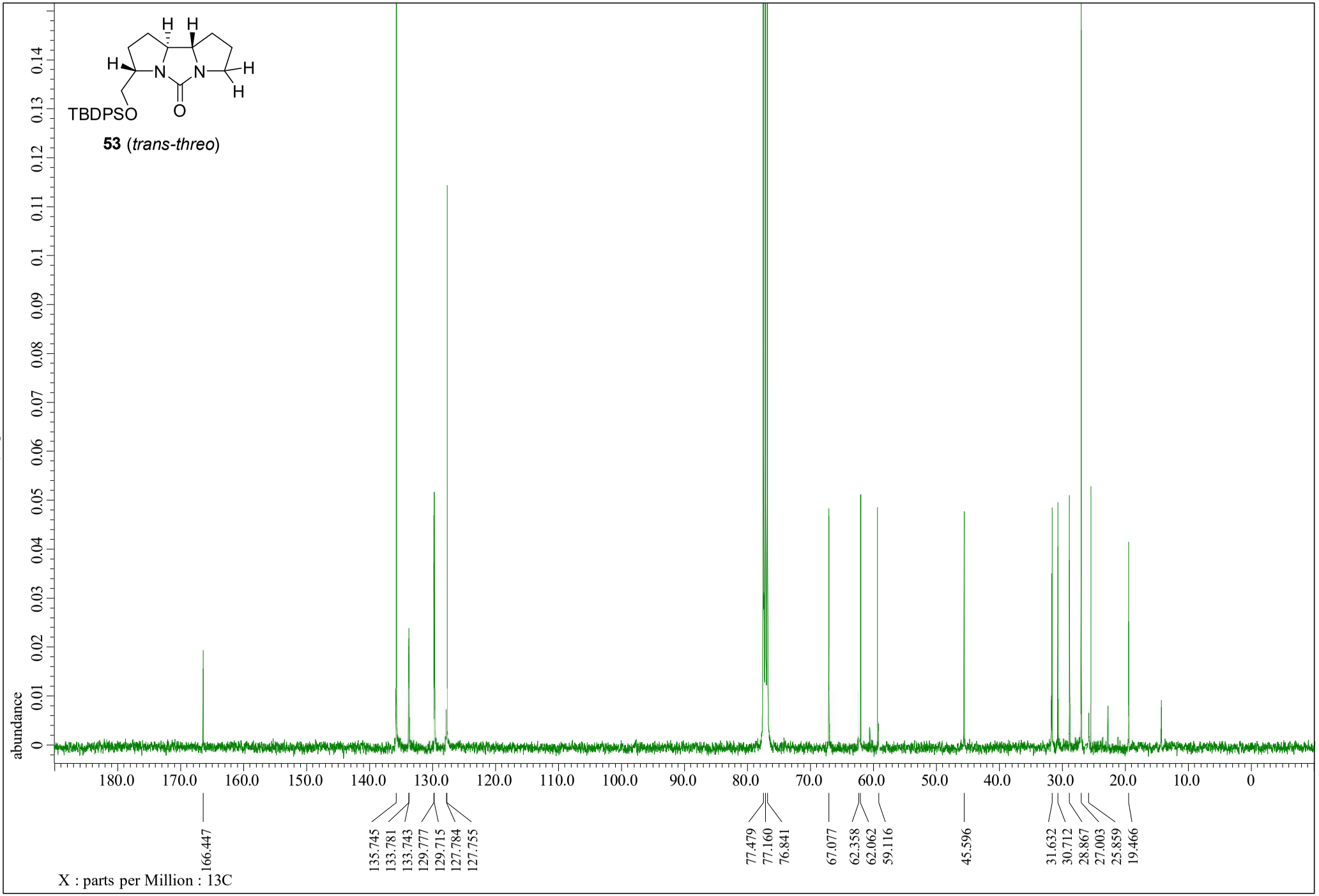
TBDPSO
51 (trans-erythro)
X : parts per Million : 1H
abundance
4.08
6.04
3.03
1.00
0.99
0.99
1.00
2.08
1.06
1.19
11.07
1.01
1.05


TBDPSO
51 (trans-erythro)
abundance
X : parts per Million : 13C
165.217
136.134
136.106
134.231
134.188
129.982
128.256
128.117
128.060
127.869
67.139
61.149
59.775
58.592
44.967
28.737
27.350
27.187
26.854
26.224
19.619

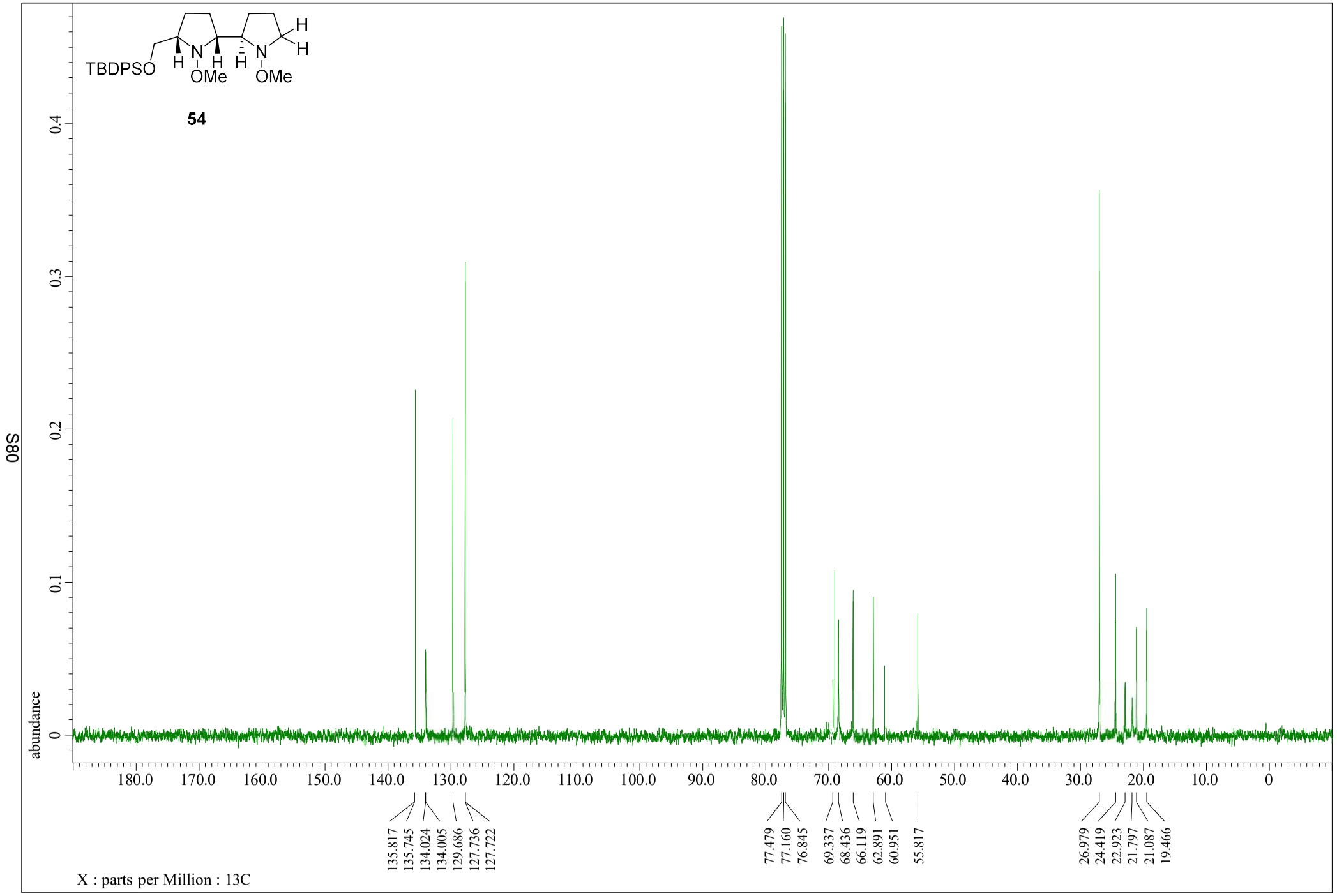
TBDPSO
OMe
OMe
52
9.14
6.09
4.00
4.46
3.93
1.04
1.02
2.03
0.96
4.04
3.03
1.01
1.00
abundance
X : parts per Million : Proton

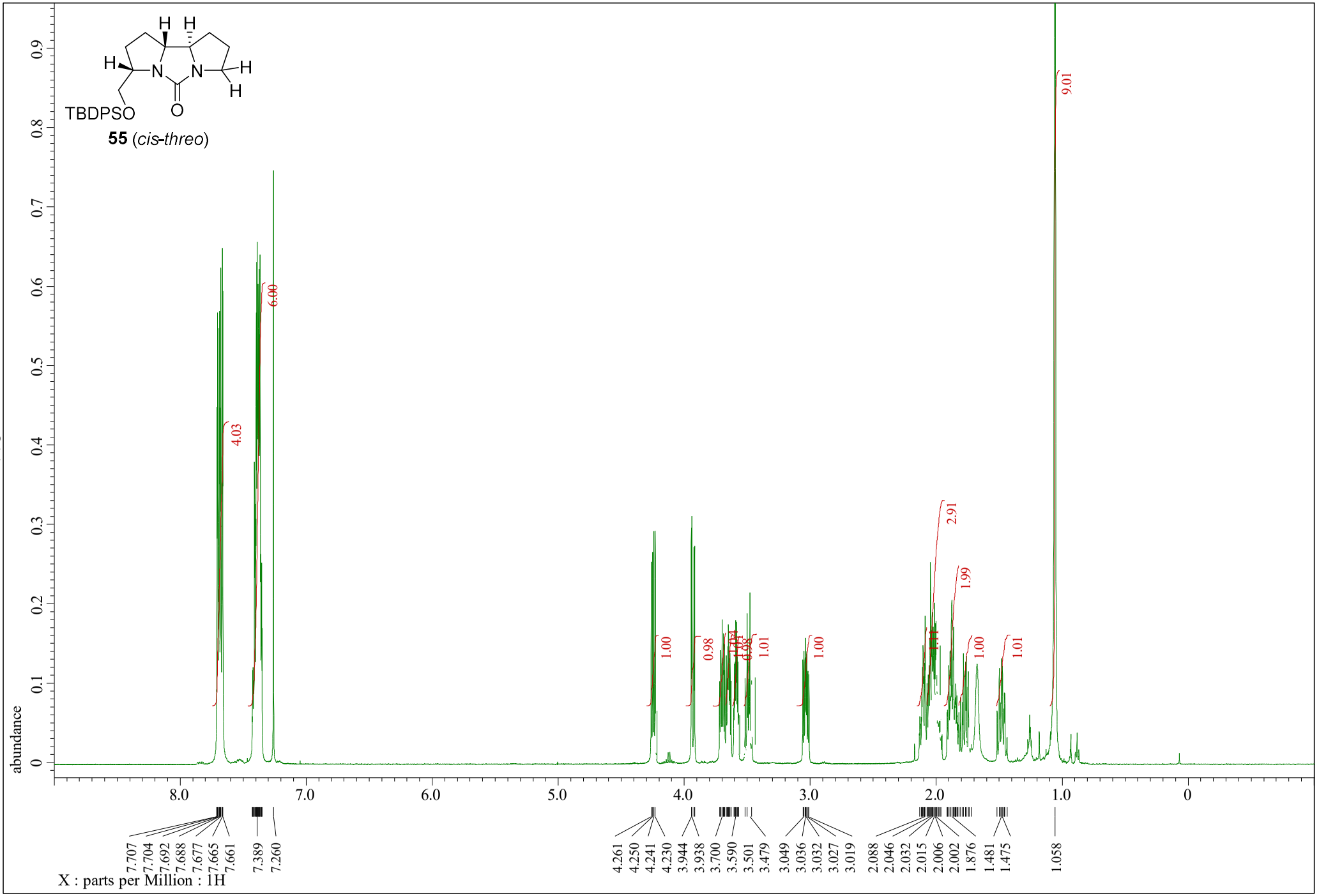

TBDPSO
H
N
H
OMe
H
N
H
OMe
H
H
52
(thousandths)
5.0
4.0
3.0
2.0
1.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
135.826
133.919
133.890
129.693
127.747
77.476
77.160
76.844
68.306
68.028
67.951
64.492
60.774
60.467
55.752
26.966
25.499
25.107
24.944
21.321
19.347
X : parts per Million : Carbon13

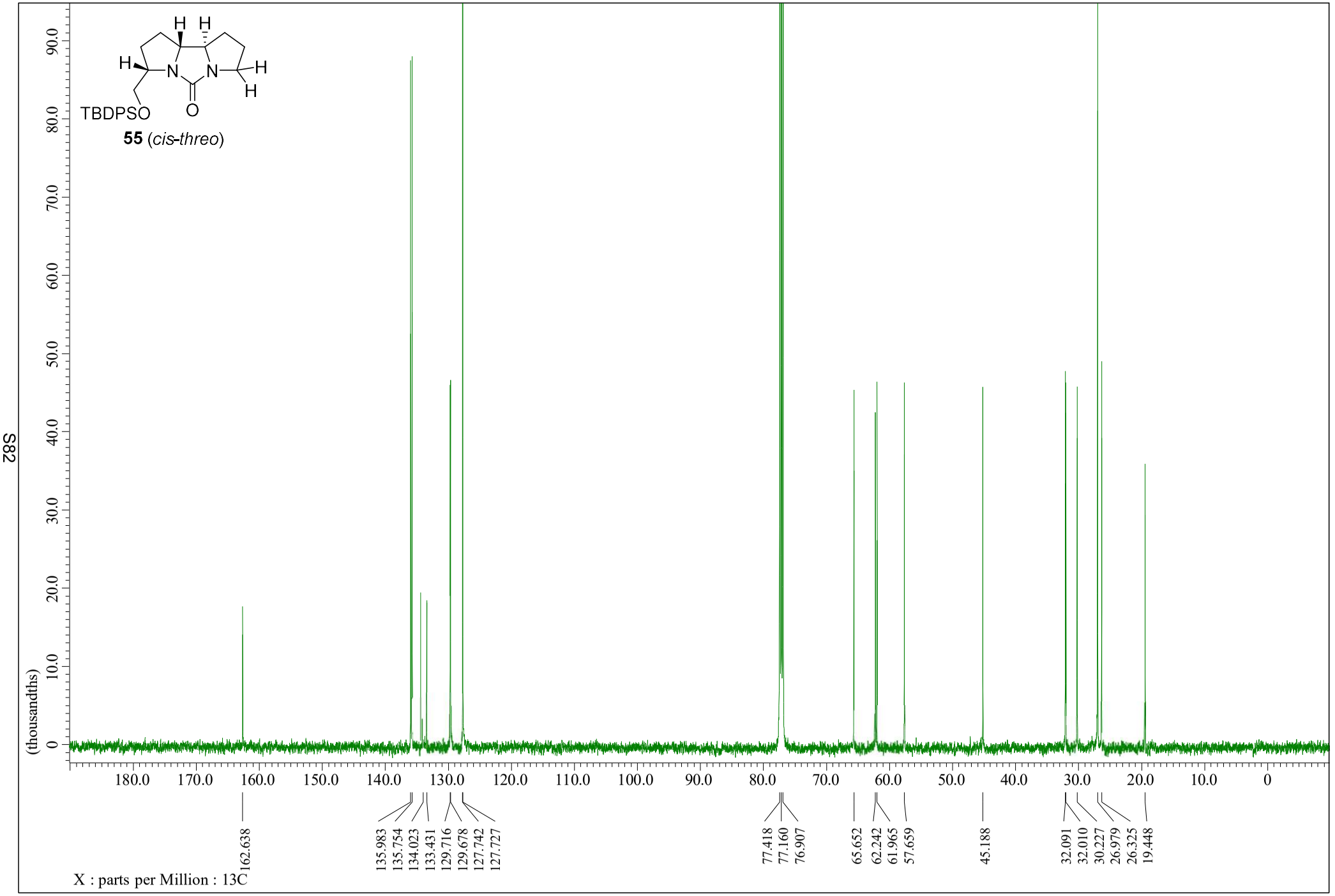
abundance
X : parts per Million : 1H
53 (trans-threo)
TBDPSO
9.02
5.97
4.35
4.03
2.04
2.03
1.04
1.03
1.01
1.00
0.98
1.054
1.423
1.551
1.632
1.962
1.990
2.019
2.025
2.037
2.046
3.057
3.074
3.080
3.085
3.097
3.715
3.718
3.727
3.884
3.895
3.903
3.913
3.921
3.931
3.943
7.260
7.357
7.361
7.367
7.377
7.381
7.392
7.396
7.635
7.639
7.646
7.650
7.655
7.658
7.666


TBDPSO
53 (trans-threo)
abundance
X : parts per Million : 13C
166.447
135.745
133.781
133.743
129.777
129.715
127.784
127.755
77.479
77.160
76.841
67.077
62.358
62.062
59.116
45.596
31.632
30.712
28.867
27.003
25.859
19.466

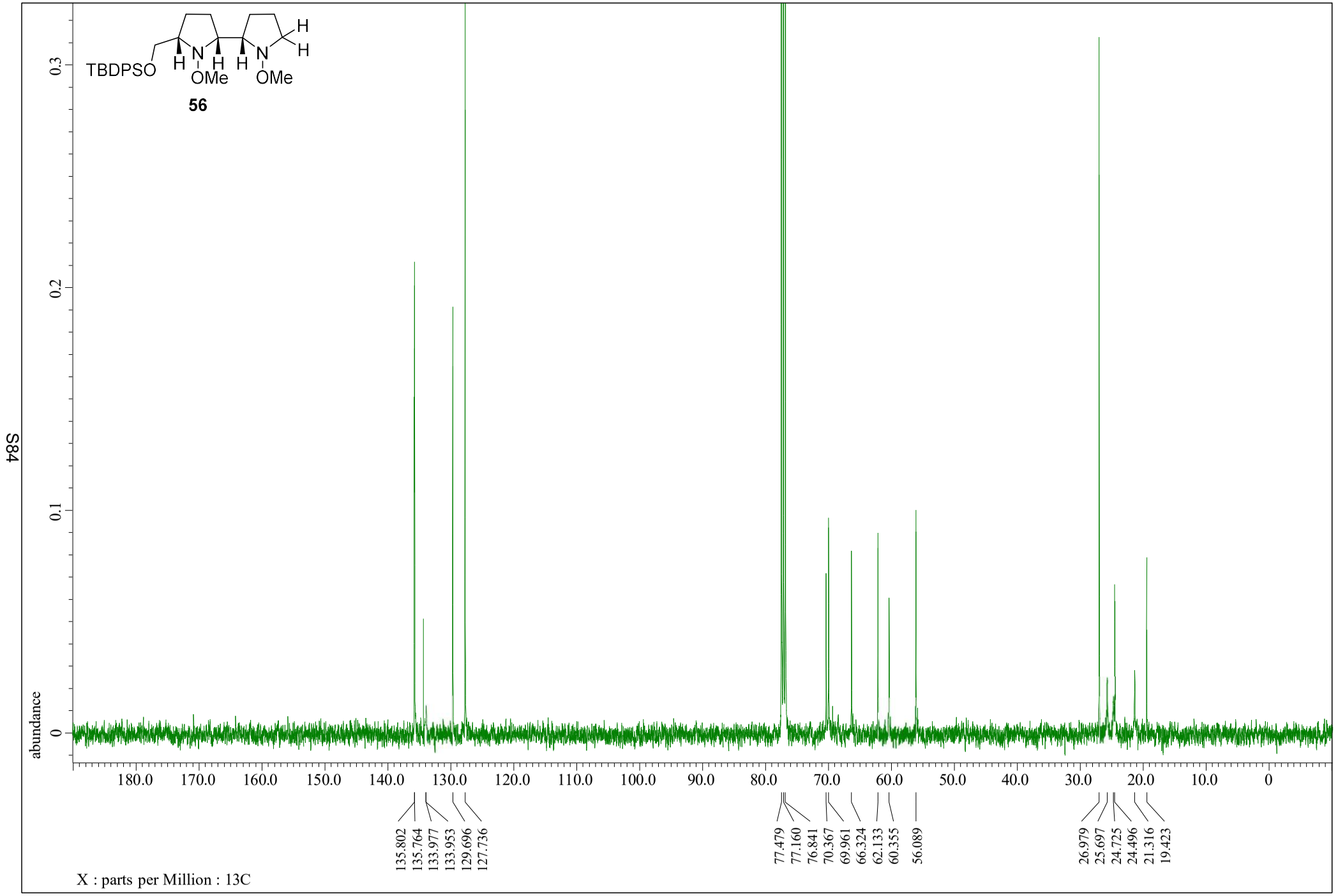
TBDPSO
OMe
OMe
54
X : parts per Million : 1H
abundance
9.07
6.06
4.05
4.79
2.98
1.05
1.01
1.00
3.03
2.98
3.01
1.02
1.00
1.00
1.056
1.523
1.572
1.596
1.640
1.778
1.798
1.807
1.830
2.726
2.748
2.772
2.792
3.252
3.270
3.309
3.455
3.536
3.839
3.850
3.864
3.875
7.260
7.360
7.363
7.379
7.397
7.407
7.417
7.424
7.671
7.674
7.691
7.692
7.695
7.711
7.714


TBDPSO
H
N
H
OMe
H
N
H
H
OMe
54
S80
abundance
0
0.1
0.2
0.3
0.4
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
135.817
135.745
134.024
134.005
129.686
127.736
127.722
77.479
77.160
76.845
69.337
68.436
66.119
62.891
60.951
55.817
26.979
24.419
22.923
21.797
21.087
19.466
X : parts per Million : 13C

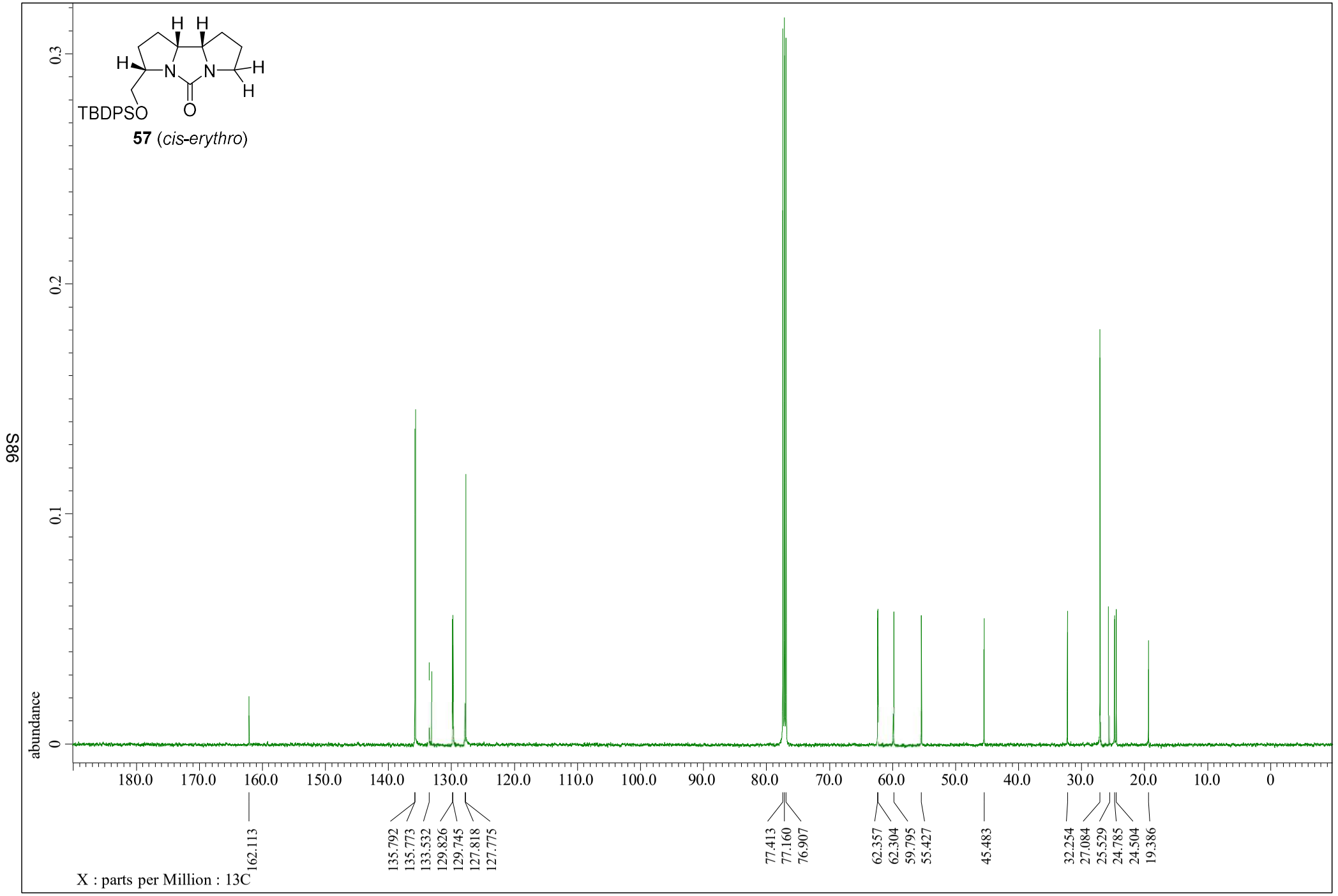

TBDPSO
55 (cis-threo)
abundance
X : parts per Million : 1H
7.707
7.704
7.692
7.688
7.677
7.665
7.661
7.389
7.260
4.261
4.250
4.241
4.230
3.944
3.938
3.700
3.590
3.501
3.479
3.049
3.036
3.032
3.027
3.019
2.088
2.046
2.032
2.015
2.006
2.002
1.876
1.481
1.475
1.058
4.03
6.00
1.00
0.98
1.01
1.00
2.91
1.99
1.00
1.01
9.01


TBDPSO
55 (cis-threo)
(thousandths)
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.638
135.983
135.754
134.023
133.431
129.716
129.678
127.742
127.727
77.418
77.160
76.907
65.652
62.242
61.965
57.659
45.188
32.091
32.010
30.227
26.979
26.325
19.448
X : parts per Million : 13C

TBDPSO
OMe
OMe
56
X : parts per Million : 1H
abundance
9.10
6.14
6.07
4.03
3.09
3.00
1.00
1.05
1.04
0.99
1.00
1.03
1.01
1.057
1.933
1.917
1.900
1.697
1.679
1.632
1.617
2.798
2.779
2.773
3.858
3.846
3.833
3.821
3.525
3.486
3.243
3.226
3.188
7.713
7.705
7.701
7.698
7.693
7.686
7.681
7.425
7.412
7.408
7.403
7.398
7.380
7.364
7.260


TBDPSO
H
N
H
OMe
H
N
H
OMe
H
H
56
abundance
0.3
0.2
0.1
0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
135.802
135.764
133.977
133.953
129.696
127.736
77.479
77.160
76.841
70.367
69.961
66.324
62.133
60.355
56.089
26.979
25.697
24.725
24.496
21.316
19.423
X : parts per Million : 13C

TBDPSO
57 (cis-erythro)
X : parts per Million : 1H
abundance
9.04
5.99
3.96
3.95
2.04
2.01
1.03
1.02
1.01
1.00
1.00
0.95
1.054
1.682
1.688
1.695
1.702
1.716
1.734
2.187
2.210
2.241
2.248
2.978
2.982
2.984
2.988
3.672
3.688
3.711
3.858
4.092
4.107
4.125
4.140
4.146
4.156
4.167
4.177
7.260
7.358
7.361
7.375
7.389
7.404
7.414
7.420
7.643
7.646
7.656
7.659
7.671
7.674


98S
abundance
0
0.1
0.2
0.3
TBDPSO
57 (cis-erythro)
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
162.113
135.792
135.773
133.532
129.826
129.745
127.818
127.775
77.413
77.160
76.907
62.357
62.304
59.795
55.427
45.483
32.254
27.084
25.529
24.785
24.504
19.386
X : parts per Million : 13C