Total Synthesis of (–)-Salinosporamide A via a Late Stage C-H Insertion

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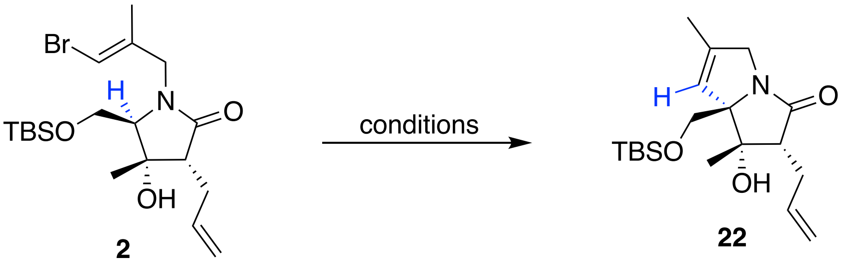
Supporting Information

Table of contents

General remarks

Molecular sieves (4Å) were dried at 160 °C under 0.25 mtorr pressure prior to use. Unless otherwise mentioned, solvents were purified as follows. Toluene and CH_2Cl_2 were dried over CaH_2 whereas THF and Et_2O were dried over sodium (dryness was monitored by color of benzophenone ketyl radical); they were freshly distilled prior to use. NMR spectra were obtained using 500 MHz Varian NMR spectrometers and referenced using the residual ^1H peak from the deuterated solvent. Waters 2795 (Alliance HT) instrument was used for HRMS analysis with polyethylene glycol (PEG-400-600) as a reference. Optical rotations were measured using a Jasco P-2000 polarimeter. Column chromatography was performed using Silicycle 60Å, 35-75 μm silica gel. Pre-coated 0.25 mm thick silica gel 60 F254 plates were used for analytical TLC and visualized using UV light, iodine, potassium permanganate stain, *p*-anisaldehyde stain or phosphomolybdic acid in EtOH stain. Enantiomeric excess determination of the chiral samples was performed using Agilent HPLC instruments (model 1260 or 1100).

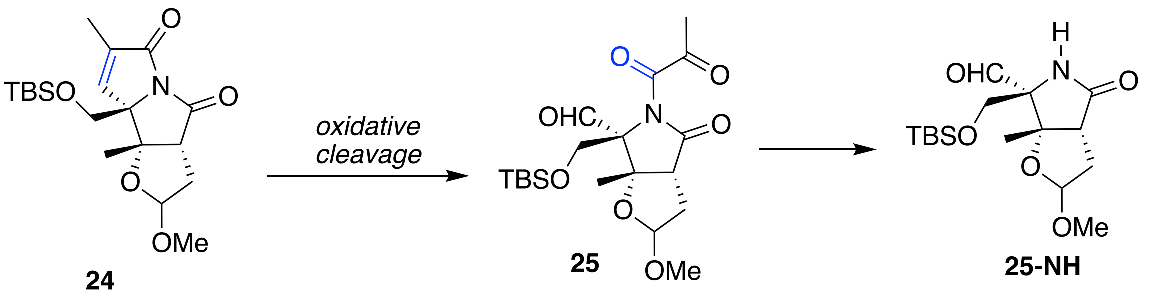
Table S1: Optimization of the C-H insertion reaction at the C5 center.



entry[a]	solvent	KHMDS (equiv)[b]	temp. (°C)[c]	time (h)	conversion (%)[d]	yield (%) **22**/**2**
1	THF	3.0	–40 to 4	12	40	25/53
2[f]	THF	6.0	–40 to rt	12	100	25/–
3	THF	5.0	–40 to rt	12	100	30/–
4	THF	2.0	–78 to –30	14	0	–/90
5[g]	THF	5.0	–78 to rt	6	0	–/85
6	toluene	3.0	–78 to 0	12	60	27/30
7[h]	toluene	3.0	–78 to 0	12	10	–/80
8	toluene	3.0	–40 to 0	12	100	33/–
9	toluene	2.0	–78 to 0	20	25	14/74
10	toluene	5.0	–40 to 0	4	100	43/–
11[i]	toluene	5.0	–40 to 0	6	80	10/36
12	toluene	5.0	0 to rt	6	90	15/9
13	toluene	3.0	–78	15	85	53/13
14	toluene	3.0	–40 to –20	12	70	60/17
15	toluene	3.0	–40 to –20	3.5	87	58/14
16	**toluene**	**5.0**	**–40 to –20**	**3.5**	**90**	**75/10**
17	toluene	6.0	–40 to –20	3.5	90	71/10
18	toluene	3.0	–40 to –20	12	70	51/20
19	toluene	3.0	–40 to –20	1	75	50/25[j]
20	toluene	3.0	–40 to –20	2	80	53/30[j]
21[k]	**toluene**	**5.0**	**–40 to –20**	**3.5**	**90**	**75/10**

[a] Reactions were performed on a 0.1 mmol scale. [b] KHMDS (0.5 M in toluene) was used. [c] The base was added at the first temperature and the reaction was stirred at the second temperature. [d] Conversions are estimated from ^{1}H-NMR using triphenylmethane as an internal standard. [e] Isolated yield unless otherwise noted. [f] KHMDS was added in two portions with 6 h interval. [g] KHMDS (0.5 M in THF) was used. [h] LiHMDS (1.0 M in hexane) was used. [i] KHMDS was added over 45 min at –40 °C. [j] Yields are estimated from ^{1}H-NMR using triphenylmethane as internal standard. [k] Reaction was performed on a 1 mmol scale.

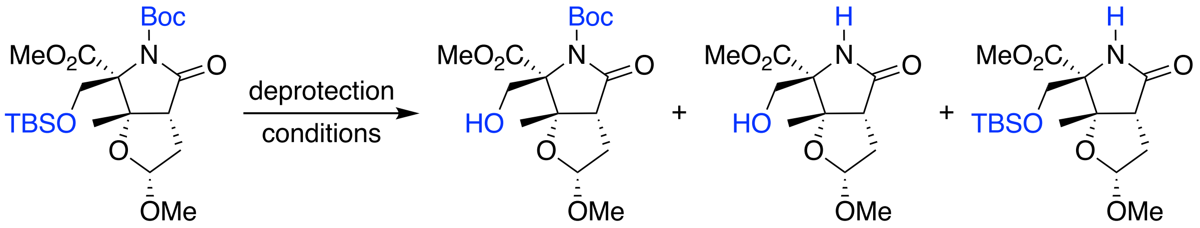
Table S2: Cleavage of the olefin to reveal the C5 carbonyl; Optimization studies.



entry	conditions	results (notes)
1	$KMnO_4$, 18-crown-6 then $NaIO_4$, LiOH	complex mixture of products
2	OsO_4, Oxone, DMF, r.t.	**24** was recovered (>98%)
3	OsO_4, Oxone, DMF, 65 °C	**24** was recovered (>98%)
4	$RuCl_3$, $NaClO_4$	**24** was recovered (>98%)
5	RuO_2, $NaIO_4$, EtOH/H_2O/TFA, r.t.	**24** was recovered (>98%)
6	O_3, DCM, –78 °C, 30 min	**24** was recovered (>98%)
7	O_3, acetone/H_2O (95:5), 0 °C	complex mixture of products
8	O_3, DCM, –78 °C, 90 min then DMS*	40% conv. (**25**:**25-NH** ~3:1) basic workup
9	O_3, DCM, –78 °C, 3-5 h then DMS*	>90% conv. (isolated yield **25**: 85%, **25-NH**: 8%) acidic workup
10	O_3, MeOH, $NaHCO_3$, –78 °C, 3-5 h then Ac_2O, Et_3N	Complex mixture of products

*DMS: Dimethyl sulfide.

Table S3: Selective deprotection of the TBS ether in the presence of Boc protecting group on **26**

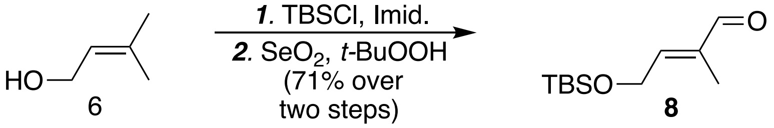


26 **27** **27-NH** **26-NH**

entry	solvent	reagent	conditions	results (notes)[a]
1	MeOH	CSA (1.1 equiv)	0 °C, 3 h	**26** was recovered (>98%)
2	THF	HCl (2N)	0 °C to rt, 3 h	**26** was recovered (>98%)
3	MeOH	PTSA (1.1 equiv)	rt, 3 h	**27-NH** was the major product (>80%)
4	MeOH	PTSA (1.1 equiv)	0 °C	~20 % conversion, **26-NH** as the major product
5	THF	HF•Pyr	0 °C to rt, 3 h	complex mixture of products
6	MeOH	AcCl	4 °C, 12 h	~30% conversion, **27-NH** as the major product
7	AcOH:THF:H_2O (3:1:1)		0 °C	**26** was recovered (>98%)
8	AcOH:THF:H_2O (3:1:1)		45 °C, 12 h	**26** was recovered (>98%)
9	HCO_2H:THF:H_2O (3:6:1)		rt	**26** was recovered (>98%)
10	DCM	BF_3•Et_2O	rt	**27-NH** and **26-NH** (~2:1) as products
11	THF	TBAF (5.0 equiv)	0 °C to rt, 5 h	complex mixture of products
12	MeOH	CCl_4, ultra-sonication	40 °C, 2 h	**26** was recovered (>98%)
13	MeOH	PPTS (1.1 equiv)	rt, 2 h	**26** was recovered (>98%)
14	MeOH	H_2SO_4 (con.) 1%	0 °C to rt, 2 h	**26** was recovered (>98%)
15	ACN	HF (aq.)	0 °C to rt, 3 h	~ 50% conv., **26-NH** as the major product
16	EtOH	HCl (con.) 1%	0 °C to rt, 3 h	**26** was recovered (>98%)
17	DCM	Quinolinium fluorochromate	rt, 5 h	**26** was recovered (>98%)
18	THF	TBAF (5.0 equiv), CSA (5.0 equiv)	0 °C to rt, 3 h	~ 20% conv., **27** as major product
19	THF	TBAF (2.5 equiv), AcOH (7.5 equiv)	rt, 72 h	~75% con., 60% **27** was isolated
20	THF	TBAF (5.0 equiv), AcOH (10.0 equiv)	45 °C, 48 h	>95% con., 85% **27** was isolated

[a] Unless otherwise stated, yield and the ratio of products were estimated based on ^{1}H-NMR analysis of the crude mixture using triphenylmethane as internal standard.

Synthetic procedures for the total synthesis of (–)-salinosporamide A



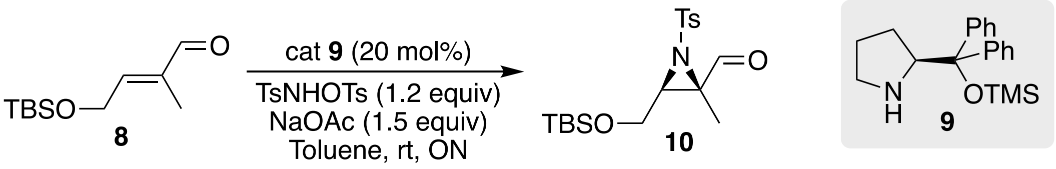
Synthesis of aldehyde 8: Commercially available 3-methyl-2-butenol **6** (12.0 g, 139 mmol) was dissolved in DMF (70 mL). To this solution imidazole (23.7 g, 348 mmol) and TBSCl (23.1 g, 153 mmol) were added at 0 °C. The mixture was stirred at room temperature for 5 h before it was quenched by addition of water (100 mL). The aqueous layer was extracted with ethyl acetate (3 x 100 mL). Combined organic layers were washed with brine (100 mL) and dried over sodium sulfate. Volatiles were removed under vacuum and the residue was used in the following step without purification.

SeO_2 (9.0 g, 82 mmol, 1.0 equiv) was dissolved in DCM (200 mL) at room temperature. To this mixture, *t*-BuOOH (70 wt.% in water, 30.0 mL, 217 mmol) was added dropwise at 0 °C. The reaction was stirred at this temperature for 30 min. To this mixture at 0 °C was added the crude TBS protected alcohol from **6** in DCM (100 mL) dropwise. The reaction mixture was stirred at room temperature for 15 h before it was quenched by addition of water (50 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 x100 mL). The combined organic extract was washed with 10% KOH (4 x 50 mL), sat. $NaHCO_3$ (1 X 100 mL) and water (1 x 50 mL). The organic solvent was evaporated under reduced pressure. Crude aldehyde was purified on column chromatography (silica, ethyl acetate/hexane = 5%) to yield the pure aldehyde **8** as a light yellow oil (15.2 g, 71.0 mmol, 71% yield).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.40 (s, 1H), 6.50 (m, 1H), 4.48 (dq, J = 5.3, 1.2 Hz, 2H), 1.71 (q, J = 1.3 Hz, 3H), 0.90 (s, 9H), 0.08 (s, 6H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 194.6, 153.2, 137.7, 60.5, 25.8, 18.3, 9.4, -5.3.

TOF MS ES$^+$ ($C_{11}H_{23}O_2Si$): Calc. $[M + H]^+$: 215.1467, Found $[M + H]^+$: 215.1463.



Synthesis of Aziridine 10:[1] To a stirred solution of aldehyde **8** (3.2 g, 15 mmol, 1.0 equiv) in toluene (30 mL), (*S*)-(–)-*α*,*α*-diphenyl-2-pyrrolidinemethanol trimethylsilyl ether **9** (1.0 g, 3.0 mmol, 0.2 equiv), 4-methyl-N-(tosyloxy)benzenesulfonamide (6.1 g, 18 mmol, 1.2 equiv) and NaOAc (1.8 g, 22 mmol, 1.5 equiv) were added at room temperature. The resulting mixture was vigorously stirred at room temperature for 12 h. After completion of the reaction, the insoluble salts were removed by filtration and the cake was washed with ethyl acetate. After removal of the volatiles the crude product was purified on silica column chromatography (ethyl acetate/hexane = 10%) yielding the aziridine product **10** as a light yellow oil (5.1 g, 13.3 mmol, 88%). The enantiomeric excess of **10** was determined by HPLC analysis in comparison with the racemic material (OJ-H column, hexanes/*i*-PrOH = 99/1, 0.5 mL/min, 250 nm); R_T (minor enantiomer) = 21.0 min, R_T (major enantiomer) = 25.0 min.

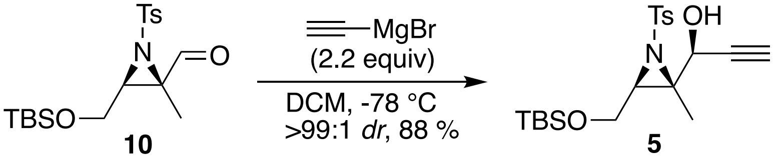
ee = >98%

$[\alpha]_D^{23}$ = +31.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, CDCl$_3$) δ 9.51 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 3.73 – 3.63 (m, 3H), 2.43 (s, 3H), 1.40 (s, 3H), 0.82 (s, 9H), -0.02 (s, 3H), -0.04 (s, 3H).

^{13}C-NMR (125 MHz, CDCl$_3$) δ 194.5, 144.6, 136.2, 129.7, 127.5, 60.3, 56.8, 51.0, 25.7, 21.6, 18.2, 11.9, -5.5, -5.6.

TOF MS ES$^+$ ($C_{18}H_{30}NO_4SSi$): Calc. [M + H]$^+$: 384.1665, Found [M + H]$^+$: 384.1667.



Synthesis of aziridine alcohol 5: To a solution of aldehyde **10** (5.0 g, 13 mmol, >98% *ee*) in dry DCM (100 mL) at –78 °C, ethynylmagnesium bromide (0.5 M in THF, 2.1 equiv, 27 mmol, 55 mL) was added dropwise under argon. The reaction mixture was stirred at this temperature and the reaction progress was monitored by TLC. After 30 min, TLC indicated complete consumption of the starting material. The reaction was quenched by addition of sat. ammonium chloride (50 mL) at –78 °C. The mixture was allowed to warm to room temperature. The organic layer was isolated and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic extract was washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The crude was purified by column chromatography (silica gel, ethyl acetate/hexane = 10%). Alcohol **5** was obtained as a white crystalline solid (4.7 g, 11.5 mmol, 88%, *dr* >99:1).

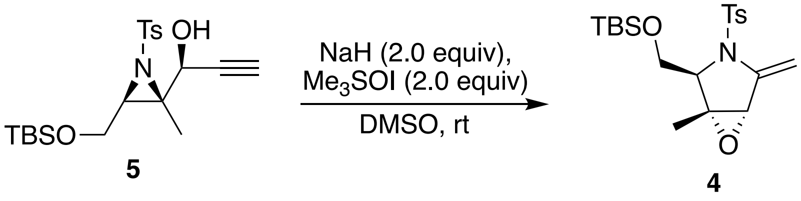
mp = 82–84 °C

$[\alpha]_D^{23} = -11.0$ (*c* 1.0, CHCl$_3$).

^{1}H-NMR (500 MHz, CDCl$_3$) δ 7.81 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.85 (dd, J = 3.6, 2.3 Hz, 1H), 3.67 (dd, *J* = 11.2, 5.3 Hz, 1H), 3.60 – 3.50 (m, 2H), 3.22 (dd, J = 6.8, 5.3 Hz, 1H), 2.50 (d, J = 2.3 Hz, 1H), 2.41 (s, 3H), 1.52 (s, 3H), 0.81 (s, 9H), -0.04 (s, 3H), -0.06 (s, 3H).

^{13}C-NMR (125 MHz, CDCl$_3$) δ 144.3, 137.1, 129.6, 127.3, 80.3, 74.4, 65.3, 60.4, 58.2, 50.9, 25.7, 21.6, 18.1, 12.9, -5.5, -5.6.

TOF MS ES$^+$ ($C_{20}H_{32}NO_4SSi$): Calc. [M + H]$^+$: 410.1821, Found [M + H]$^+$: 410.1819.



Synthesis of enamide 4: To trimethylsulfoxonium iodide (Me$_3$SOI, 9.5 g, 43 mmol, 2.0 equiv, dried under vacuum for 12 h) in dry DMSO (100 mL) was added sodium hydride (1.8 g, 43 mmol, 2.0 equiv, 60% in mineral oil) portion-wise at room temperature under argon. The reaction mixture was stirred under argon for 30 min. To this mixture was added alcohol **5** (8.8 g, 21 mmol) in dry DMSO (50 mL) drop-wise. The reaction was stirred for 12 h at room temperature before it was quenched with sat. NH$_4$Cl (100 mL). The aqueous layer was extracted with ethyl acetate (3 x 100 mL). The combined organic extract was washed with brine (100 mL), dried over sodium sulfate and concentrated under reduced pressure. Crude product was pure enough and utilized in the following step without further purification. An analytical sample of the crude was passed through a plug of silica (ethyl acetate/hexane = 20%) to give pure **4** as a white solid.

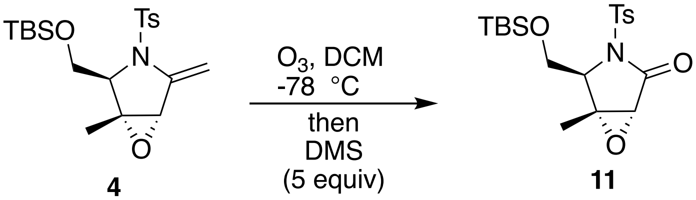
mp = 74–76 °C

$[\alpha]_D^{23}$ = +81.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H), 7.24 (d, J = 8.2 Hz, 2H), 5.36 (d, J = 1.0 Hz, 1H), 4.74 (d, J = 1.0 Hz, 1H), 4.03 (dd, J = 11.1, 3.4 Hz, 1H), 3.95 – 3.86 (m, 2H), 3.39 (d, J = 0.9 Hz, 1H), 2.38 (s, 3H), 1.47 (s, 3H), 0.85 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 143.9, 142.7, 134.6, 129.2, 127.7, 98.5, 66.9, 63.9, 62.7, 62.4, 25.7, 21.6, 18.0, 14.3, -5.6, -5.7.

TOF MS ES$^+$ ($C_{20}H_{32}NO_4SSi$): Calc. [M + H]$^+$: 410.1821, Found [M + H]$^+$: 410.1837.



Synthesis of pyrrolidinone 11: The crude enamide **4** (9.0 g, from the above reaction) was dissolved in anhydrous DCM (250 mL). Ozone gas (generated from an ozonizer) was bubbled through this solution at –78 °C, until the reaction mixture retained a persistent dark blue color (this process takes approximately 30 min). At this point the, bubbling of ozone was ceased and the excess ozone was removed by bubbling nitrogen through the reaction –78 °C until the blue color disappeared. Dimethyl sulfide (DMS, 7 mL) was added to the mixture and the reaction was allowed to warm to room temperature. Evaporation of the volatiles gave the crude product **11**, which was used in the next step without purification. An analytical sample of the crude was passed through a plug of silica (ethyl acetate/hexane = 10% to 20%) to afford pure **4** as a white solid.

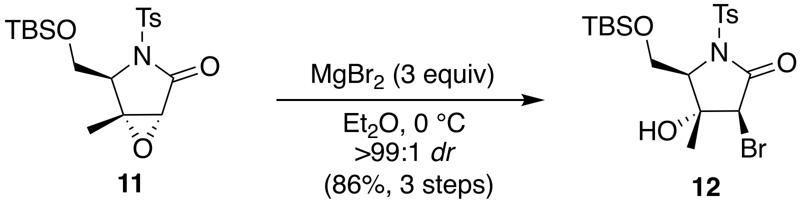
mp = 109–111 °C

$[\alpha]_D^{23}$ = –62.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.36 – 4.29 (m, 1H), 4.13 (dd, J = 11.5, 2.5 Hz, 1H), 3.88 (dt, J = 11.5, 1.2 Hz, 1H), 3.33 (s, 1H), 2.40 (s, 3H), 1.58 (s, 3H), 0.78 (s, 7H), 0.05 (s, 3H), -0.02 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 169.1, 145.1, 135.2, 129.6, 128.1, 64.5, 61.4, 59.4, 57.4, 25.5, 21.7, 17.8, 13.5, -5.8, -5.9.

TOF MS ES$^+$ ($C_{19}H_{30}NO_5SSi$): Calc. $[M + H]^+$: 412.1614, Found $[M + H]^+$: 412.1624.



Synthesis of bromo alcohol 12: To the crude epoxide **11** from the above reaction (dried under vacuum overnight) under argon was added dry diethyl ether (300 mL) and the reaction flask was place at 0 °C. Anhydrous $MgBr_2$ (dried overnight under vacuum, 3.0 equiv, 17 g) was added to the reaction in portions. The mixture was stirred at this temperature for 3 h, after which TLC showed complete consumption of the epoxide **11**. The reaction was quenched by very slow addition of saturated ammonium chloride (100 mL) at 0 °C. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 x 100 mL). The combined organic extract was washed with water and brine, then dried over sodium sulfate. Volatiles were evaporated and the crude product was purified with column chromatography (silica gel, ethyl acetate/hexane = 10% to 20%). Pure product **14** was isolated as a white solid (9.0 g, 18 mmol, 86% yield over 3 steps).

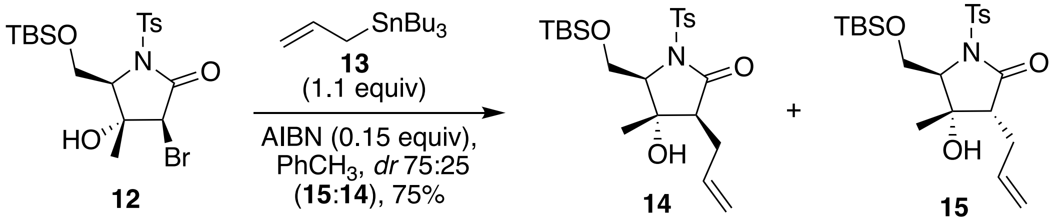
mp = 143–145 °C

$[\alpha]_D^{23}$ = +31.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 8.3 Hz, 1H), 7.31 (d, J = 8.1 Hz, 1H), 4.20 – 4.11 (m, 1H), 3.96 (s, 0H), 2.41 (s, 1H), 1.61 (s, 1H), 0.90 (s, 3H), 0.13 (s, 1H), 0.10 (s, 1H).

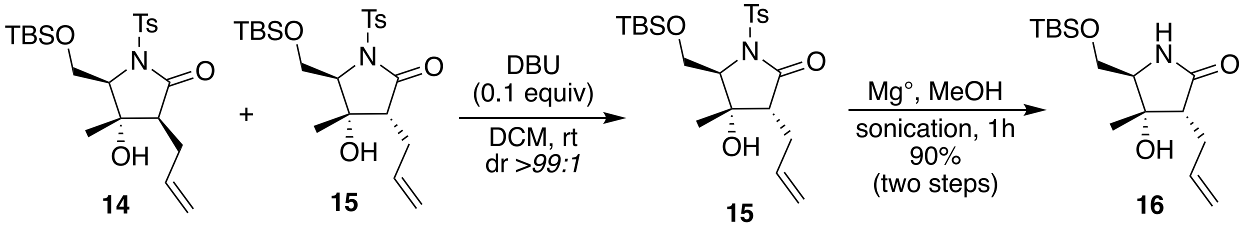
^{13}C-NMR (125 MHz, $CDCl_3$) δ 169.1, 145.1, 135.2, 129.6, 128.1, 64.5, 61.4, 59.4, 57.4, 25.5, 21.7, 17.8, 13.5, -5.8, -5.9.

TOF MS ES$^+$ ($C_{19}H_{31}BrNO_5SSi$): Calc. [M + H]$^+$: 492.0876, Found [M + H]$^+$: 492.0872.



Synthesis of 14 and 15: Bromo pyrrolidinone **12** (5.5 g, 11 mmol, 1.0 equiv) was dissolved in toluene (100 mL). The solution was degassed for 10 min at 100 °C under argon. AIBN (0.15 mmol, 1.65 mmol, 270 mg) was added to this mixture followed by addition of alllyltributyl stannane (1.1 equiv, 12 mmol, 4.0 mL). The reaction mixture was heated to reflux for 3 h (TLC confirmed completion of the reaction). The solvent was removed though a short path distillation apparatus (in a well ventilated hood) and the crude was purified via column chromatography (ethyl acetate/hexanes = 10 to 20%)

yielding an inseparable mixture of diastereomers as a 1:3 ratio of **14** and **15** (3.8 g, 8.3 mmol, 75% combined yield). The diastereomeric mixture was utilized in the following steps.



The diastereomeric mixture of **14** and **15** (5.9 g, 13 mmol) was dissolved in dry DCM (150 mL) at room temperature and DBU (0.20 mL, 1.3 mmol, 0.10 equiv) was added. The reaction was stirred at room temperature for 5 h. The solvent was evaporated and the residue was used in the following step without further purification. An analytical sample of the crude was passed through a plug of silica (ethyl acetate/hexane = 20%) to give pure diastereomer **15** as a white solid.

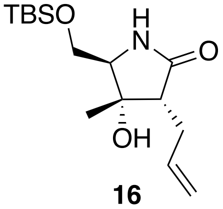
mp = 128–130 °C

$[\alpha]_D^{23}$ = –16.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.28 (d, J = 8.1 Hz, 2H), 5.88 – 5.76 (m, 1H), 5.07 (dp, J = 16.9, 1.5 Hz, 1H), 5.00 (dq, J = 10.1, 1.3 Hz, 1H), 4.10 (ddd, J = 11.7, 2.9, 1.0 Hz, 1H), 4.00 (dd, J = 2.9, 1.5 Hz, 1H), 3.89 (dt, J = 11.7, 1.3 Hz, 1H), 2.84 (ddd, J = 6.8, 5.7, 1.0 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.40 (s, 3H), 2.21 (dtd, J = 15.2, 8.2, 1.2 Hz, 1H), 1.62 (br, 1H), 1.45 (d, J = 1.1 Hz, 3H), 0.79 (d, J = 1.1 Hz, 9H), 0.06 (d, J = 1.0 Hz, 3H), 0.01 (d, J = 1.0 Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 174.0, 144.7, 136.6, 135.9, 129.5, 128.1, 116.7, 77.1, 70.7, 62.1, 52.1, 28.0, 25.7, 22.4, 21.7, 17.9, -5.7, -5.9.

TOF MS ES$^+$ ($C_{22}H_{36}NO_5SSi$): Calc. [M + H]$^+$: 454.2083, Found [M + H]$^+$: 454.2087.



16

Synthesis of amide 16: To the crude lactam **15** (5.8 g) in methanol (100 mL) was added magnesium powder (5.0 equiv, 1.6 g, 65 mmol). The solution was sonicated in an ultra-sonicator bath at room temperature for 1 h to afford the detosylated compound **16** (3.50 g, 11.7 mmol, 90% over two steps) as a white solid.

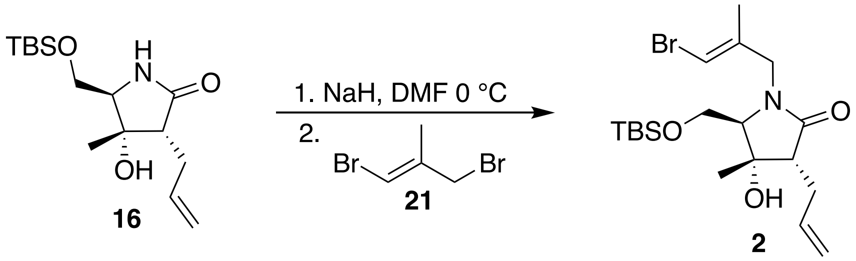
mp = 102–104 °C

$[\alpha]_D^{23}$ = +65.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.04 – 5.90 (m, 1H), 5.80 (br, 1H), 5.22 – 5.11 (d, J = 17.5 Hz, 1H), 5.09 – 5.03 (d, J = 11.5 Hz, 1H), 3.63 (dd, J = 10.6, 3.8 Hz, 1H), 3.59 (dd, J = 10.6, 5.4 Hz, 1H), 3.38 (ddd, J = 5.1, 3.8, 1.2 Hz, 1H), 2.57 (dddd, J = 11.8, 9.5, 7.9, 4.4 Hz, 1H), 2.47 – 2.35 (m, 2H), 1.37 (s, 3H), 0.86 (s, 10H), 0.03 (s, 3H), 0.03 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 177.3, 137.3, 116.5, 77.6, 65.0, 62.8, 50.8, 28.8, 25.8, 23.1, 18.1, -5.57, -5.63.

TOF MS ES$^+$ ($C_{15}H_{30}NO_3Si$): Calc. [M + H]$^+$: 300.1995, Found [M + H]$^+$: 300.1999.



Synthesis of vinyl bromide 2: To a solution of lactam **16** (2.4 g, 8.0 mmol, 1.0 equiv) in dry DMF (50 mL) at 0 °C was added sodium hydride (0.68 g, 17 mmol, 2.1 equiv). The reaction mixture was stirred at this temperature for 30 min before a solution of allyl bromide **21**[2] (1.79 g, 8.40 mmol, 1.05 equiv) in dry DMF (10 mL) was added dropwise. The reaction was stirred at 0 °C for 2 h, quenched by the addition of saturated NH_4Cl (50 mL) and the aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic extract was washed with brine (50 mL), dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography (ethyl acetate/hexane = 20%), yielding pure product **2** as an off white solid (2.9 g, 85%).

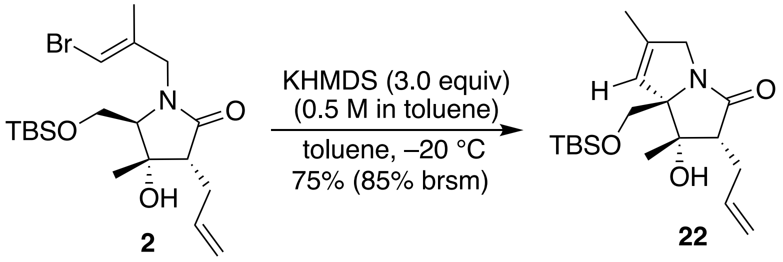
mp = 64–66 °C

$[\alpha]_D^{23}$ = +59.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.12 (q, J = 1.3 Hz, 1H), 5.96 (dddd, J = 17.1, 10.0, 8.5, 5.5 Hz, 1H), 5.15 (dq, J = 17.1, 1.7 Hz, 1H), 5.04 (dtd, J = 10.1, 1.8, 0.8 Hz, 1H), 4.45 – 4.38 (m, 1H), 3.73 – 3.63 (m, 2H), 3.42 (dt, J = 15.2, 1.0 Hz, 1H), 3.14 (t, J = 2.7 Hz, 1H), 2.63 (dddd, J = 14.7, 7.2, 3.6, 1.8 Hz, 1H), 2.59 – 2.54 (m, 1H), 2.41 – 2.31 (m, 1H), 1.76 – 1.73 (m, 3H), 1.62 (br, 1H), 1.43 (s, 3H), 0.84 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H).

^{13}C-NMR (125 MHz, CDCl$_3$) δ 174.7, 137.7, 137.3, 116.3, 104.7, 76.7, 67.9, 59.1, 50.9, 46.3, 29.0, 25.7, 23.3, 18.0, 17.3, -5.6, -5.6.

TOF MS ES$^+$ ($C_{19}H_{35}BrNO_3Si$): Calc. [M + H]$^+$: 432.1570, Found [M + H]$^+$: 432.1574.



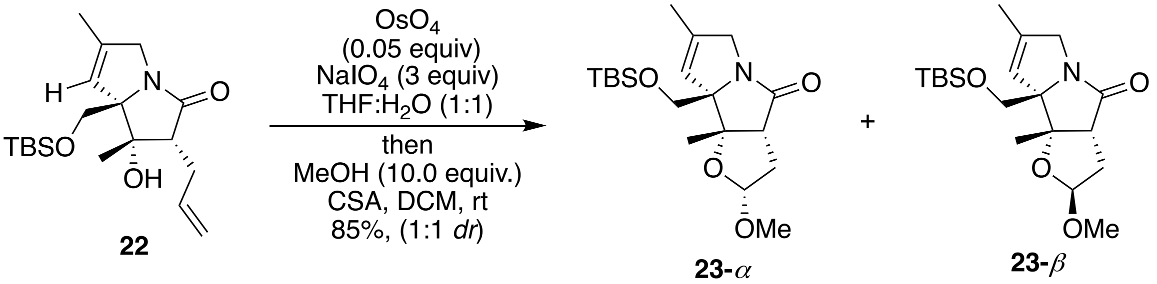
Synthesis of bicyclic 22: To a solution of vinyl bromide **2** (0.43 g, 1.0 mmol, 1.0 equiv) in dry toluene (20 mL) at 40 °C was added KHMDS (0.5 M in toluene, 10 mL, 5.0 mmol, 5.0 equiv) dropwise. The reaction mixture was cooled to–20 °C and was stirred at this temperature for 3.5 h. The reaction was then quenched at this temperature with sat. NH$_4$Cl (20 mL). The reaction mixture was brought to room temperature and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine (20 mL), dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified on column chromatography (ethyl acetate/hexane = 20% to 40%). Pure product **22** was isolated as a light yellow oil (263 mg, 0.75 mmol, 75% yield). The remaining vinyl bromide **2** was eluted from the column as the second fraction (41 mg, 0.1 mmol).

$[\alpha]_D^{23}$ = +76.0 (*c* 1.0, CHCl$_3$).

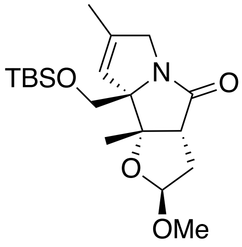
^{1}H-NMR (500 MHz, CDCl$_3$) δ 5.97 (ddd, J = 24.2, 9.4, 5.6 Hz, 1H), 5.33 (s, 1H), 5.14 – 5.06 (m, 1H), 4.99 (d, J = 10.1 Hz, 1H), 4.27 (d, J = 15.5 Hz, 1H), 3.70 (d, J = 10.7 Hz, 1H), 3.66 – 3.59 (m, 1H), 3.49 (d, J = 10.7 Hz, 1H), 2.94 (t, J = 6.7 Hz, 1H), 2.57 – 2.48 (m, 1H), 2.34 – 2.24 (m, 1H), 1.81 (d, J = 1.6 Hz, 3H), 1.43 (s, 3H), 1.42 (br, 1H), 0.85 (d, J = 0.9 Hz, 9H), 0.01 (s, 3H), 0.00 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 177.7, 142.5, 137.9, 120.3, 115.6, 83.3, 80.8, 65.2, 53.4, 53.3, 27.5, 25.7, 21.4, 18.1, 14.7, -5.6, -5.7.

TOF MS ES$^+$ ($C_{19}H_{34}NO_3Si$): Calc. [M + H]$^+$: 352.2308, Found [M + H]$^+$: 352.2325.



Synthesis of 23: To a solution of **22** (3.0 mmol, 1.0 g, 1.0 equiv) in THF:H_2O (1:1, 60 mL) at room temperature was added OsO_4 (0.05 M solution in water, 3.0 mL, 0.15 mmol, 0.05 equiv). After 5 min, sodium periodate (1.9 g, 9.0 mmol, 3.0 equiv) was added to the reaction mixture (during which the reaction turns dark). The reaction mixture was stirred at room temperature for 1 h (reaction turns to a milky suspension), at which time TLC indicated complete consumption of starting material. The reaction was quenched by addition of saturated sodium thiosulfate (10 mL), transferred to a separatory funnel and extracted with ethyl acetate (4 x 20 mL). The organic layers were combined, washed with brine (20 mL), dried over sodium sulfate, and concentrated under reduced pressure. To the resulting diastereomeric hemiacetal mixture in DCM (150 mL) were added methanol (2.0 equiv, 6.0 mmol, 0.25 mL) and CSA (0.15 mmol, 35 mg, 0.05 equiv) at room temperature. The reaction mixture was stirred at this temperature for 12 h after which the solvent was evaporated and the crude product was purified via column chromatography (silica, ethyl acetate/hexane = 20% to 40%). Two diastereomers were separated in a ~1:1 ratio with a combined yield of 85%.



23-*β*

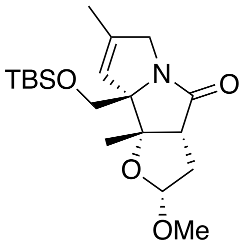
Data for the less polar diastereomer; 23-*β*: 450 mg, 1.22 mmol, 41% yield as a clear oil.

$[\alpha]_D^{23}$ = +48.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.38 (q, J = 1.5 Hz, 1H), 4.90 (dd, J = 6.3, 3.9 Hz, 1H), 4.12 (d, J = 15.3 Hz, 1H), 3.70 (d, J = 10.8 Hz, 1H), 3.56 (ddt, J = 15.3, 2.5, 1.2 Hz, 1H), 3.36 (d, J = 10.8 Hz, 1H), 3.30 (s, 3H), 3.11 (d, J = 8.6 Hz, 1H), 2.71 (ddd, J = 14.0, 6.2, 1.2 Hz, 1H), 2.00 (ddd, J = 14.0, 8.6, 3.9 Hz, 1H), 1.77 (d, J = 1.5 Hz, 3H), 1.51 (s, 3H), 0.85 (s, 9H), 0.01 (s, 3H), -0.00 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 177.7, 138.6, 121.3, 105.2, 89.6, 82.2, 65.3, 55.5, 54.6, 52.8, 34.3, 25.8, 19.6, 18.2, 14.8, -5.5, -5.8.

TOF MS ES$^+$ ($C_{19}H_{34}NO_4Si$): Calc. $[M + H]^+$: 368.2257, Found $[M + H]^+$: 368.2267.



23-α

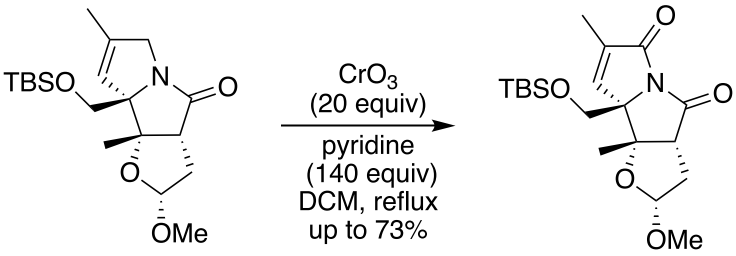
Data for the more polar diastereomer 23-α: 480 mg, 1.30 mmol, 44% yield as a clear oil.

$[\alpha]_D^{23}$ = –77.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 5.47 (q, J = 1.8 Hz, 1H), 4.88 (d, J = 5.0 Hz, 1H), 4.09 – 4.04 (m, 1H), 3.70 (d, J = 10.7 Hz, 1H), 3.68 – 3.63 (m, 1H), 3.37 (d, J = 10.7 Hz, 1H), 3.10 (s, 3H), 2.92 (d, J = 8.0 Hz, 1H), 2.43 (d, J = 13.2 Hz, 1H), 2.07 (ddd, J = 13.2, 8.1, 5.0 Hz, 1H), 1.77 (d, J = 1.5 Hz, 3H), 1.44 (s, 3H), 0.84 (s, 9H), 0.01 (s, 3H), 0.00 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 177.2, 138.6, 122.4, 104.2, 90.7, 83.2, 65.5, 54.3, 53.8, 53.7, 34.7, 25.7, 20.9, 18.1, 14.5, -5.5, -5.8.

TOF MS ES$^+$ ($C_{19}H_{34}NO_4Si$): Calc. $[M + H]^+$: 368.2257, Found $[M + H]^+$: 368.2267.



23 **24**

Synthesis of enone 24: To CrO_3 (22 mmol, 2.2 g, 20 equiv) in dry DCM (30 mL) at 0 °C was added pyridine (154 mmol, 12.4 mL, 140 equiv) dropwise under argon.[3] The reaction mixture was stirred at this temperature for 10 min followed by stirring at room temperature for 30 min. To this mixture at 0 °C was added **23** (1.1 mmol, 0.40 g, 1.0 equiv) in DCM (30 mL) and the reaction was heated to reflux. After 24 h, the mixture was cooled to room temperature and volatiles were removed under pressure. The residue was re-dissolved in ethyl acetate (100 mL) and the precipitates were removed by filtration through a pad of celite. The product was purified via column chromatography (silica, ethyl acetate/hexane = 20%), yielding **24** as a white solid (305 mg, 0.8 mmol, 73%).

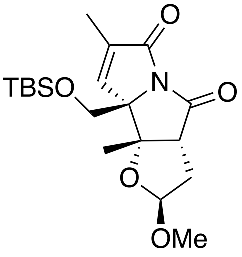
mp = 161–164 °C

$[\alpha]_D^{25} = -210.0$ (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.78 (q, J = 1.7 Hz, 1H), 4.87 (d, J = 4.8 Hz, 1H), 3.92 (d, J = 10.5 Hz, 1H), 3.39 (d, J = 10.5 Hz, 1H), 3.12 (d, J = 8.1 Hz, 1H), 3.05 (s, 2H), 2.46 (d, J = 13.2 Hz, 1H), 2.16 (ddd, J = 13.2, 8.1, 4.8 Hz, 1H), 1.89 (d, J = 1.7 Hz, 4H), 1.47 (s, 3H), 0.85 (s, 7H), 0.03 (s, 3H), 0.03 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 172.5, 168.7, 141.3, 136.1, 104.0, 88.7, 76.4, 66.8, 56.7, 54.7, 35.6, 25.8, 20.4, 18.1, 11.1, -5.6, -5.9.

TOF MS ES$^+$ ($C_{19}H_{32}NO_7Si$): Calc. $[M + H]^+$: 382.2050, Found $[M + H]^+$: 382.2060.


24-*β*

24-*β* (282 mg, 0.74 mmol, 74% yield) was synthesized as an off white solid from **23-*β*** (386 mg, 1.0 mmol), according to the procedure described above for the synthesis of **24**.

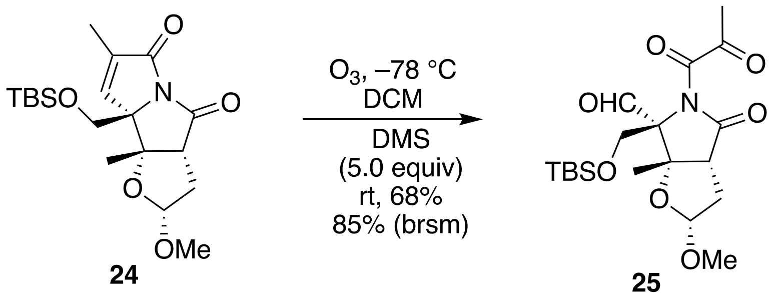
mp = 75–78 °C

$[\alpha]_D^{23}$ = –12.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.74 (q, J = 1.6 Hz, 1H), 4.89 (dd, J = 6.3, 4.0 Hz, 1H), 3.92 (d, J = 10.7 Hz, 1H), 3.39 (d, J = 10.7 Hz, 1H), 3.33 (d, J = 9.2 Hz, 1H), 3.29 (s, 3H), 2.71 (ddd, J = 14.3, 6.3, 1.1 Hz, 1H), 2.14 (ddd, J = 14.2, 9.0, 4.0 Hz, 1H), 1.88 (d, J = 1.6 Hz, 3H), 1.53 (s, 3H), 0.85 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.4, 169.1, 141.7, 136.2, 105.2, 87.2, 75.7, 66.5, 57.9, 55.7, 35.4, 25.7, 19.1, 18.1, 11.2, -5.6, -5.9.

TOF MS ES$^+$ ($C_{19}H_{32}NO_5Si$): Calc. $[M + H]^+$: 382.2050, Found $[M + H]^+$: 382.2051.



Synthesis of dicarbonyl 25: Enone **24** (0.25 g, 0.65 mmol) was dissolved in DCM (50 mL). To this mixture at –78 °C was bubbled ozone for 3 h. The excess ozone was removed via bubbling nitrogen at the same temperature. To the reaction mixture was added dimethyl sulfide (0.25 mL, 3.3 mmol, 5.0 equiv) at –78 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. Saturated aqueous ammonium chloride (20 mL) was added to the reaction mixture and the organic layer was separated. The aqueous layer was extracted with DCM (3 x 20 mL). The combined organics were washed with brine (20 mL), dried over sodium sulfate, and concentrated under reduced pressure. The crude product was purified via column chromatography (ethyl acetate/hexane = 10% to 20%) to give the pure product **25** as an off white solid (180 mg, 0.44 mmol, 68% yield). Starting material **24** (64 mg, 17%) was recovered as well.

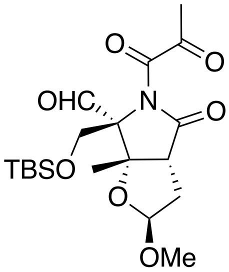
mp = 79–81 °C

$[\alpha]_D^{23}$ = –96.0 (*c* 1.0, CHCl$_3$).

^{1}H-NMR (500 MHz, CDCl$_3$) δ 9.50 (s, 1H), 4.99 (d, J = 4.7 Hz, 1H), 4.18 (d, J = 11.3 Hz, 1H), 4.11 (d, J = 11.4 Hz, 1H), 3.31 (s, 3H), 2.93 (dd, J = 8.2, 0.7 Hz, 1H), 2.45 (dd, J = 13.4, 0.7 Hz, 1H), 2.39 (s, 3H), 2.21 (ddd, J = 13.2, 8.2, 4.8 Hz, 1H),1.42 (s, 3H), 0.83 (s, 9H), 0.04 (s, 3H), 0.02 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 196.3, 193.8, 176.4, 168.2, 104.0, 89.8, 75.1, 60.1, 55.0, 51.3, 35.1, 26.2, 25.7, 25.6, 20.0, 17.9, -5.8, -5.9.

TOF MS ES$^+$ ($C_{19}H_{32}NO_7Si$): Calc. [M + H]$^+$: 414.1948, Found [M + H]$^+$: 414.1950.



25-*β*

25-*β* (170 mg, 0.41 mmol, 82%) was synthesized from **24-*β*** (191 mg, 0.50 mmol), as a white solid according to the procedure described above for the synthesis of **25**.

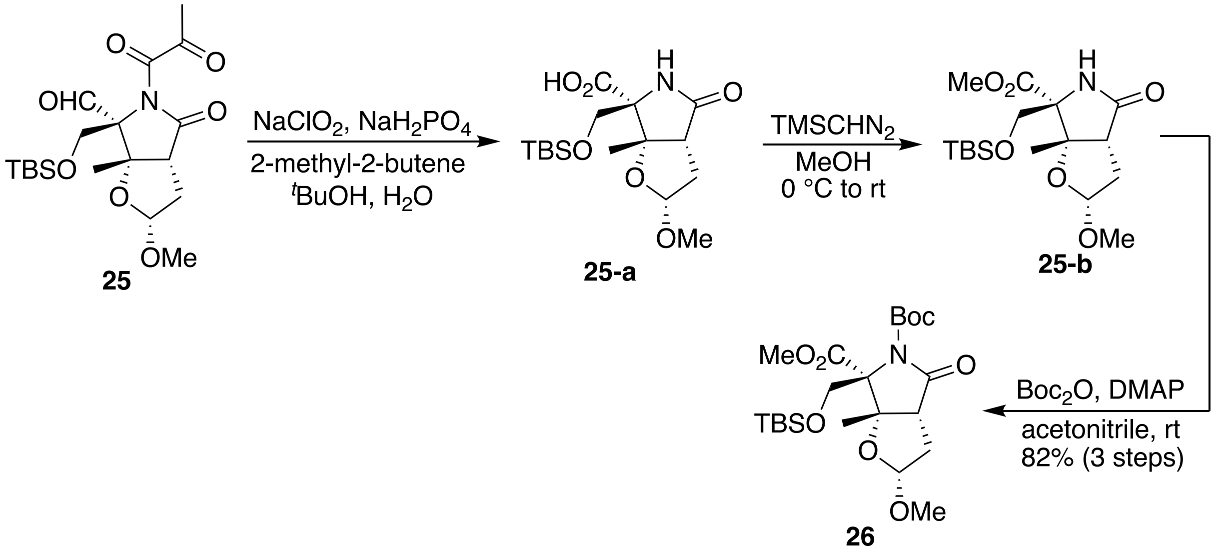
mp = 71–74 °C

$[\alpha]_D^{23}$ =+80.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 9.47 (s, 1H), 5.10 – 5.03 (m, 2H), 4.18 (d, J = 11.4 Hz, 1H), 4.06 (d, J = 11.4 Hz, 1H), 3.30 (s, 3H), 3.09 (ddd, J = 9.5, 1.5, 0.8 Hz, 1H), 2.64 (ddd, J = 14.4, 6.2, 1.6 Hz, 1H), 2.40 (s, 3H), 2.25 (ddd, J = 14.4, 9.4, 3.8 Hz, 1H), 1.53 (s, 3H), 0.84 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 196.8, 193.9, 177.5, 168.4, 105.2, 89.8, 75.0, 59.4, 55.8, 52.7, 35.4, 26.3, 25.6, 19.0, 17.9, -5.8.

TOF MS ES$^+$ ($C_{19}H_{32}NO_7Si$): Calc. [M + H]$^+$: 414.1948, Found [M + H]$^+$: 414.1936.



Synthesis of 26: Dicarbonyl **25** (0.17 g, 0.41 mmol, 1.0 equiv) was dissolved in *tert*-butyl alcohol (7 mL). To this solution at room temperature was added 2-methyl 2-butene (0.1 mL, 1.0 mmol) followed by addition of sodium chlorite (1.7 mmol, 3.5 mL of 0.5 M aqueous solution) and sodium phosphate mono basic (3.5 mmol, 3.5 mL of 1.0 M aqueous solution). The reaction was stirred at room temperature for 24 h, at which point aqueous saturated NH_4Cl (10 mL) was added to the reaction mixture and the solution was transferred to a separatory funnel. The aqueous layer was extracted with ethyl acetate (5 x 20 mL). The combined organic extracts were dried over sodium sulfate, filtered, and concentrated under reduced pressure. Crude acid **25-a** was used in the following step without further purification.

The crude carboxylic acid **25-a** was dissolved in methanol (10 mL). To this solution at 0 °C trimethylsilyl diazomethane (2.0 M in diethyl ether, 10 equiv, 4.0 mmol, 2.0 mL) was added dropwise under nitrogen. The reaction mixture was stirred for 12 h, during which the reaction mixture was allowed to warm up to room temperature. Aqueous saturated $NaHCO_3$ (20 mL) was added to the reaction mixture and the aqueous layer was extracted with ethyl acetate (4 x 10 mL). The combined organic extracts were washed with brine (20 mL), dried over sodium sulfate, and concentrated under reduced pressure. The resulting methyl ester **25-b** was used in the next step without further purification.

The crude methyl ester **25-b** was dissolved in dried acetonitrile (10 mL). To this mixture under nitrogen at 0 °C were added Boc-anhydride (0.72 g, 3.2 mmol, 8.0 equiv) and DMAP (49 mg, 0.4 mmol, 1.0 equiv). The reaction was stirred at 0 °C for another 5 h upon which, ^{1}H-NMR confirmed complete consumption of the starting material. It should be noted that monitoring with TLC was not fruitful and thus small aliquots of the reaction were removed, concentrated, and the crude was analyzed by NMR. Volatiles were removed under pressure and the residue was directly loaded onto a column (basified silica with Et_3N, ethyl acetate/hexane = 10% to 20% as eluent) to yield the Boc protected product **26** as a light yellow oil (160 mg, 0.34 mmol, 82% yield from **25**).

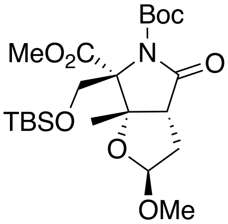
Data for 26:

$[\alpha]_D^{23} = -95.0$ (*c* 0.5, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.89 (d, J = 5.0, 1H), 4.37 (d, J = 10.8 Hz, 1H), 4.12 (d, J = 10.8 Hz, 1H), 3.74 (s, 3H), 3.21 (s, 3H), 2.76 (d, J = 8.1 Hz, 1H), 2.43 (d, J = 13.3 Hz, 1H), 2.16 (ddd, J = 13.3, 8.1, 5.0 Hz, 1H), 1.48 (s, 9H), 1.44 (s, 3H), 0.82 (s, 9H), 0.02 (s, 3H), -0.01 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.6, 167.6, 150.0, 103.9, 86.9, 82.9, 62.2, 55.0, 52.1, 51.6, 35.5, 28.2, 28.0, 25.7, 20.5, 18.0, -5.6, -5.8.

TOF MS ES^{+} ($C_{22}H_{40}NO_8Si$): Calc. $[M + H]^{+}$: 474.2523, Found $[M + H]^{+}$: 474.2519.



26-*β*

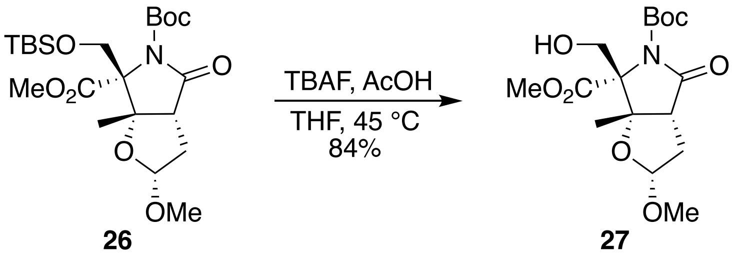
26-*β* (120 mg, 0.25 mmol, 77%, a light red colored oil) was synthesized from the corresponding dicarbonyl **25-*β*** (140 mg, 0.33 mmol) according to the procedure described above for the synthesis of **26**.

$[\alpha]_D^{23}$ = +28.0 (*c* 0.5, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 4.97 (dd, J = 6.0, 4.3 Hz, 1H), 4.30 (d, J = 10.8 Hz, 1H), 4.14 (d, J = 10.8 Hz, 1H), 3.71 (s, 3H), 3.26 (s, 3H), 2.90 (dd, J = 9.3, 1.5 Hz, 1H), 2.65 (ddd, J = 14.0, 6.0, 1.5 Hz, 1H), 2.15 (ddd, J = 14.0, 9.3, 4.3 Hz, 1H), 1.55 (s, 3H), 1.47 (s, 9H), 0.82 (s, 9H), 0.02 (s, 3H), 0.01 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 174.8, 167.8, 149.7, 105.1, 85.9, 83.5, 61.6, 55.6, 52.7, 52.0, 35.9, 28.0, 27.8, 25.7, 19.9, 17.9, -5.7, -5.7.

TOF MS ES$^+$ ($C_{22}H_{40}NO_8Si$): Calc. $[M + H]^+$: 474.2523, Found $[M + H]^+$: 474.2522.



26 **27**

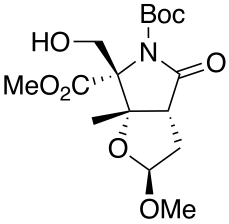
Synthesis of 27: To the silyl protected alcohol **26** (1.0 equiv, 0.30 mmol, 0.14 g) in dry THF (10 mL) under argon at 0 °C were added acetic acid (20.0 equiv, 6.00 mmol, 0.33 mL) and TBAF (1.0 M in THF, 10 equiv, 3.0 mmol, 3.0 mL) dropwise. The reaction mixture was placed in a pre-heated oil bath at 45 °C. The mixture was stirred at this temperature for 48 h, upon which TLC showed completion of the reaction. The reaction mixture was cooled to room temperature and was quenched by the addition of sat. $NaHCO_3$ (10 mL). The aqueous layer was extracted with ethyl acetate (4 x 10 mL). The combined organic extract was washed with brine (10 mL), dried over sodium sulfate, and concentrated under reduced pressure. The resulting crude product was purified on column chromatography (ethyl acetate/hexane = 50%) to yield the pure alcohol **27** as a white sticky solid (90 mg, 0.25 mmol, 84%).

$[\alpha]_D^{23} = -115.0$ (*c* 1.0, $CHCl_3$).

^1H-NMR (500 MHz, $CDCl_3$) δ 4.89 (d, J = 4.9 Hz, 1H), 4.41 (d, J = 12.2 Hz, 1H), 4.11 (d, J = 12.2 Hz, 1H), 3.75 (s, 3H), 3.20 (s, 3H), 2.96 (d, J = 8.0 Hz, 1H), 2.40 (d, J = 13.2 Hz, 1H), 2.13 (ddd, J = 13.2, 8.0, 4.9 Hz, 1H), 1.98 (br, 1H), 1.48 (s, 12H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 173.9, 162.1, 150.6, 103.9, 86.9, 83.6, 62.3, 55.0, 52.3, 51.2, 35.5, 28.0, 22.7, 20.7.

TOF MS ES$^+$ ($C_{16}H_{26}NO_8$): Calc. $[M + H]^+$: 360.1658, Found $[M + H]^+$: 360.1671.



27-*β*

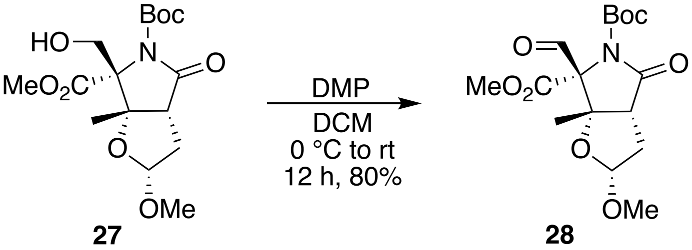
27-*β* (61 mg, 0.17 mmol, 81%, as a white sticky solid) was synthesized according to the procedure described above for the synthesis of **27**.

$[\alpha]_D^{23} = +65.0$ (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, CDCl$_3$) δ 5.03 – 4.96 (m, 1H), 4.38 (dd, J = 11.9, 5.3 Hz, 1H), 4.18 (dd, J = 11.9, 6.3 Hz, 1H), 3.74 (s, 3H), 3.28 (s, 3H), 3.01 (ddd, J = 9.3, 1.6, 0.7 Hz, 1H), 2.68 (ddd, J = 14.1, 6.0, 1.6 Hz, 1H), 2.18 (ddd, J = 14.1, 9.3, 4.1 Hz, 1H), 1.89 (br, 1H), 1.61 (s, 3H), 1.50 (s, 9H).

^{13}C-NMR (125 MHz, CDCl$_3$) δ 174.9, 167.5, 150.0, 105.1, 86.0, 84.0, 61.5, 55.6, 52.5, 52.2, 35.8, 27.9, 27.6, 20.1.

TOF MS ES$^+$ ($C_{16}H_{26}NO_8$): Calc. [M + H]$^+$: 360.1658, Found [M + H]$^+$: 360.1671.



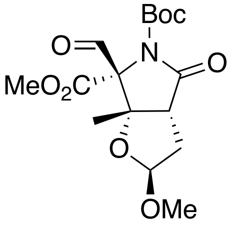
Synthesis of aldehyde 28: Alcohol **27** (1.0 equiv, 0.24 mmol, 85 mg) was dissolved in dry DCM (5 mL). To this solution at 0 °C were added Dess-Martin periodinane (5.0 equiv, 1.1 mmol, 400 mg) and sodium bicarbonate (5.0 equiv, 1.1 mmol, 85 mg). The reaction mixture was allowed to warm up to room temperature and stirred for 12 h. The reaction was quenched by addition of saturated sodium thiosulfate (5 mL), saturated sodium bicarbonate (5 mL) and water (5 mL). The mixture was extracted with DCM (4 x 10 mL). The combined organic extract was washed with brine, dried over sodium sulfate, and concentrated under reduced pressure. The crude aldehyde was purified by column chromatography (silica, ethyl acetate/hexane = 20% to 50%) to yield pure aldehyde **28** (68 mg, 0.19 mmol, 80%) as a white sticky gel.

$[\alpha]_D^{23} = -122.0$ (*c* 1.0, CHCl$_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 10.08 (s, 1H), 4.96 (d, J = 5.0 Hz, 1H), 3.89 (s, 3H), 3.23 (s, 3H), 2.82 (dd, J = 8.2, 0.7 Hz, 1H), 2.49 (dd, J = 13.4, 0.7 Hz, 1H), 2.16 (ddd, J = 13.4, 8.2, 5.0 Hz, 1H), 1.43 (s, 9H), 1.37 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 196.8, 172.1, 166.7, 105.0, 84.4, 55.5, 52.8, 50.7, 34.8, 27.8, 21.5.

TOF MS ES$^+$ ($C_{16}H_{24}NO_8$): Calc. $[M + H]^+$: 358.1502, Found $[M + H]^+$: 358.1504.



28-*β*

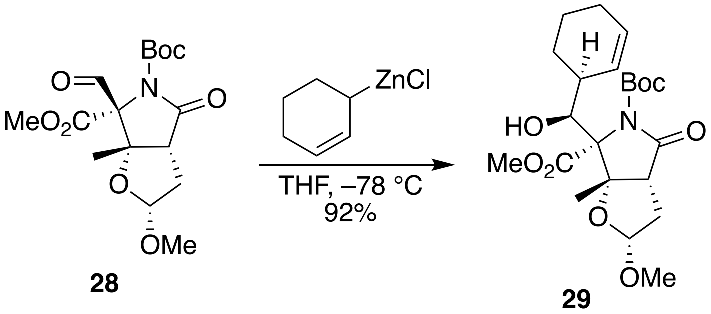
28-*β* was synthesis according to the procedure described above for the synthesis of **28**. 50 mg pure aldehyde was isolated (0.14 mmol, 85%) as a white sticky solid.

$[\alpha]_D^{23}$ = +48.0 (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$) δ 10.11 (s, 1H), 5.03 (dd, J = 5.8, 3.9 Hz, 1H), 3.87 (s, 3H), 3.32 (s, 3H), 2.99 (dd, J = 9.5, 2.6 Hz, 1H), 2.66 (ddd, J = 14.0, 5.8, 2.6 Hz, 1H), 2.20 (ddd, J = 14.0, 9.5, 3.9 Hz, 1H), 1.51 (s, 3H), 1.43 (s, 9H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 196.3, 172.8, 166.4, 166.2, 106.1, 85.4, 84.7, 55.8, 52.7, 51.9, 35.4, 27.7, 21.6.

TOF MS ES$^+$ ($C_{16}H_{23}NO_8$): Calc. $[M + H]^+$: 358.1502, Found $[M + H]^+$: 358.1502.



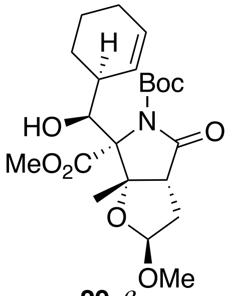
Synthesis of 29: Following reported procedures,[4] tributyl(2-cyclohexenyl) stannane (10 equiv, 1.8 mmol, 0.72 g) was dissolved in dry THF (2 mL). To this mixture at –78 °C under argon was added *n*-butyl lithium (10 equiv, 1.8 mmol, 1.0 mL of 1.8 M sol. in hexane) dropwise. After stirring for 1 h at the same temperature, $ZnCl_2$ (10 equiv, 1.8 mmol, 1.8 mL of 1.0 M sol. in diethyl ether) was added. The reaction mixture was stirred at –78 °C for another 30 min, after which aldehyde **28** (1.0 equiv, 0.18 mmol, 65 mg) in dry THF (2 mL) was added dropwise. The reaction mixture was further stirred at this temperature for 5 h. Aqueous NH_4Cl (10 mL, sat.) was added at –78 °C, the reaction mixture was warmed to room temperature and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (3 x 10 mL). The combined organic extracts were washed with brine (10 mL), dried over sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, ethyl acetate/hexane = 50%) yielding the pure product **29** as a white foam (72 mg, 0.16 mmol, 92% yield).

$[\alpha]_D^{25} = -149.0$ (*c* 1.0, $CHCl_3$).

^{1}H-NMR (500 MHz, $CDCl_3$). δ 5.98 (dq, J = 10.7, 3.3, 2.6 Hz, 1H), 5.49 (dd, J = 10.7, 2.9 Hz, 1H), 4.90 (d, J = 4.8 Hz, 1H), 4.25 – 4.17 (m, 1H), 3.78 (s, 3H), 3.25 (s, 2H), 2.99 (d, J = 7.9 Hz, 1H), 2.93 (s, 1H), 2.44 (d, J = 13.1 Hz, 1H), 2.16 (ddd, J = 13.1, 7.9, 4.9 Hz, 1H), 1.98 (m, 2H), 1.84 (d, J = 6.9 Hz, 1H), 1.79 (td, J = 10.1, 9.5, 6.0 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.56 (d, J = 8.8 Hz, 3H), 1.51 (s, 9H), 1.47 (s, 3H).

^{13}C-NMR (125 MHz, CDCl$_3$)175.5, 167.1, 150.4, 134.8, 125.2, 103.6, 89.2, 83.1, 76.0, 54.9, 51.9, 51.0, 37.8, 35.8, 30.2, 27.8, 25.1, 20.8, 20.7.

TOF MS ES$^+$ ($C_{22}H_{34}NO_8$): Calc. [M + H]$^+$: 440.2284, Found [M + H]$^+$: 440.2286.



29-*β*

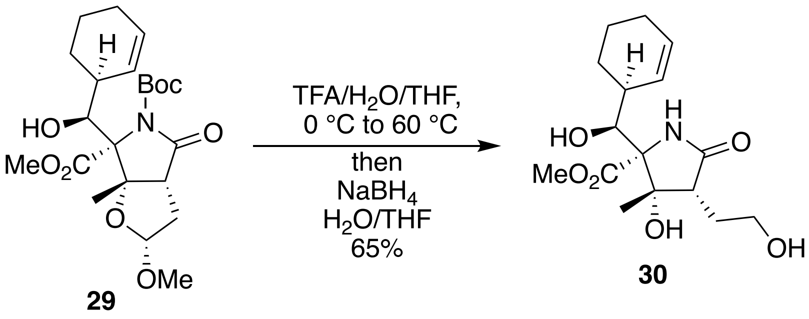
29-*β* was synthesized according to the procedure described above for the synthesis of **29**. **29-*β*** (51 mg, 0.12 mmol, 92% yield) was isolated as a white foam.

$[\alpha]_D^{23}$ = –10.0 (*c* 1.0, CHCl$_3$).

^{1}H-NMR (500 MHz, CDCl$_3$) δ 5.98 (ddt, J = 10.0, 3.9, 1.9 Hz, 1H), 5.44 (dd, J = 10.0, 2.9 Hz, 1H), 4.99 (dd, J = 6.0, 4.5 Hz, 1H), 4.25 (d, J = 6.4 Hz, 1H), 3.75 (s, 3H), 3.28 (s, 3H), 3.12 (d, J = 9.1 Hz, 1H), 2.90 (br, 1H), 2.65 (ddd, J = 14.0, 6.0, 1.4 Hz, 1H), 2.16 (ddd, J = 14.0, 9.1, 4.5 Hz, 1H), 1.98 (m, 2H), 1.88 – 1.68 (m, 4H), 1.60 (s, 3H), 1.57 – 1.53 (m, 2H), 1.49 (s, 9H).

^{13}C-NMR (125 MHz, CDCl$_3$) δ 176.3, 167.2, 150.2, 134.6, 125.3, 104.9, 88.0, 83.9, 75.3, 55.6, 52.3, 51.9, 37.8, 36.1, 30.3, 27.8, 25.1, 20.8, 20.2.

TOF MS ES$^+$ ($C_{22}H_{34}NO_8$): Calc. [M + H]$^+$: 440.2284, Found [M + H]$^+$: 440.2282.



Synthesis of diol 30: Following the reported procedure,[4b] to a solution of **29** (1.0 equiv, 0.13 mmol, 60 mg) in distilled THF (0.5 mL) at 0 °C was added a mixture of trifluoroacetic acid and water (1:1, v:v, 2 mL) dropwise. The reaction flask was placed in a preheated oil bath at 60 °C and stirring was continued at this temperature for 2 h. To the mixture at 0 °C was added ice (1.0 g) and toluene (3 mL), and the volatiles were removed under vacuum at room temperature. During the concentration period, toluene was added to the mixture to keep the concentration of TFA low. The resulting residue was dissolved in distilled THF (1 mL) and water (1 mL). To this mixture at 0 °C was added sodium borohydride (25 mg, 0.65 mmol, 5.0 equiv) and the mixture was stirred for 1 h. The reaction was quenched with saturated solution of ammonium chloride (5 mL) and the mixture was extracted with ethyl acetate (5 x 10 mL). The combined organic extracts were washed with brine, dried over sodium sulfate, and concentrated under reduced pressure to give the crude product as a white solid. The crude product was purified on silica column chromatography (silica, ethyl acetate/hexane = 20% then methanol/ethyl acetate = 5%) to give pure **30** as a white foam (28 mg, 0.08 mmol, 65%).

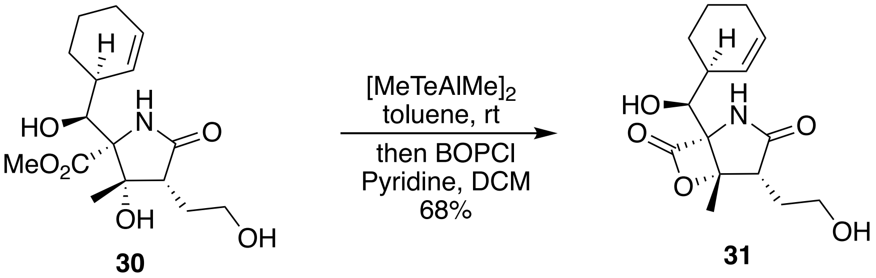
Similar procedure was utilized to convert **29-**β(50 mg, 0.11 mmol) to **30** (25 mg, 0.07 mmol, 69%).

$[\alpha]_D^{23} = -55.0$ (*c* 1.0, $CHCl_3$)

^{1}H-NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 6.10 – 6.02 (m, 1H), 5.74 (ddd, J = 10.3, 3.8, 2.1 Hz, 1H), 5.31 (s, 1H), 4.11 (m, 1H), 3.81 (s, 3H), 3.79 – 3.76 (m, 1H), 3.75 – 3.61 (m, 1H), 2.89 – 2.74 (m, 1H), 2.22 – 2.15 (m, 1H), 2.11 – 2.01 (m, 1H), 2.02 – 1.88 (m, 3H), 1.82 – 1.65 (m, 3H), 1.61 – 1.54 (m, 2H), 1.53 (s, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ 180.6, 172.6, 135.1, 123.4, 81.7, 79.9, 77.3, 77.0, 76.7, 75.3, 62.2, 52.9, 38.7, 28.6, 26.2, 24.8, 20.4, 19.8.

TOF MS ES$^+$ ($C_{16}H_{26}NO_6$): Calc. [M + H]$^+$: 328.1760, Found [M + H]$^+$: 328.1760.



Synthesis of *β*-lactone 31:[5] To a suspension of tellurium (0.72 g, 5.60 mmol) in toluene (2.5 mL) was added Me_3Al (2.0 M in toluene, 2.5 mL, 5.0 mmol). The mixture was refluxed for 6 h and cooled to room temperature. The resulting $[MeAlTeMe]_2$ (ca 0.8 M in toluene, 2.0 mL, 8.0 mmol, 10 equiv) was added to **30** (25.0 mg, 0.08 mmol). After stirring at room temperature for 12 h, the reaction mixture was diluted with ethyl acetate (5 mL). HCl (1.0 M, 3 mL) was added slowly to the mixture at 0 °C. The reaction mixture was further stirred at room temperature for 2 h. The acidified aqueous layer (pH = 1) was extracted with ethyl acetate/ethanol (20:1 v:v, 20 mL). The combined organic extracts were dried over sodium sulfate, and concentrated under reduced pressure to yield the crude carboxylic acid as an off white solid, which was used in the following step without purification.

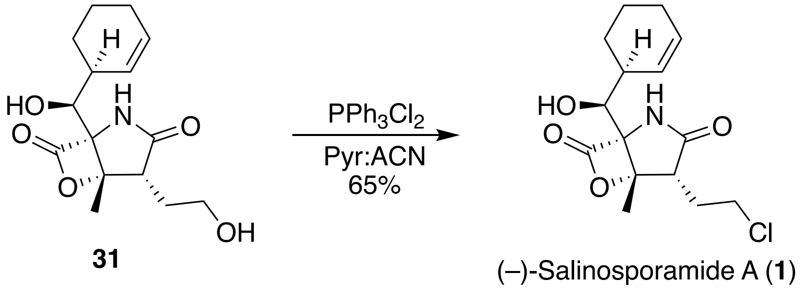
To a solution of the carboxylic acid (20 mg) in dichloromethane (2 mL) were added pyridine (0.3 mL) and BOPCl (100 mg, 0.25 mmol), and the mixture was stirred at room temperature for 3.5 h. The reaction mixture was diluted with ethyl acetate (5 mL) and saturated NH_4Cl (5 mL). The organic layer was separated and the aqueous layer was extracted with ethyl acetate (4 x 5 mL). The combined organic extracts were washed with brine (5 mL), dried over sodium sulfate, and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, ethyl acetate/hexane = 20% to 50%) to give the *β*-lactone **31** (12.0 mg, 0.04 mmol, 68%) as a colorless gel:

$[\alpha]_D^{23}$ = –72.0 (*c* 0.5, MeOH)

^{1}H-NMR (500 MHz, pyridine-*d*$_5$) δ 10.60 (s, 1H), 6.46 (d, J = 10.3 Hz, 1H), 5.91 (ddd, J = 10.3, 4.9, 2.5 Hz, 1H), 5.08 (br, 2H), 4.30 (m, 2H), 4.20 (dt, J = 8.8, 6.4 Hz, 1H), 3.41 (t, J = 7.0 Hz, 1H), 2.90 (m, 1H), 2.56 (m, 1H), 2.34 (m, 3H), 2.19 (s, 3H), 1.99 – 1.90 (m, 2H), 1.74 (m, 2H), 1.40 (m, 1H).

^{13}C-NMR (125 MHz, pyridine-*d*$_5$) δ 178.7, 170.3, 129.4, 129.2, 87.5, 80.6, 71.5, 60.3, 46.7, 39.8, 29.6, 26.9, 25.8, 22.2, 20.7.

TOF MS ES$^+$ ($C_{15}H_{22}NO_5$): Calc. $[M + H]^+$: 296.1498, Found $[M + H]^+$: 296.1497.



Synthesis of (–)-Salinosporamide A (1): *β*-lactone **31** (8.0 mg, 0.03 mmol) was dissolved in acetonitrile (0.5 mL) and anhydrous pyridine (0.5 mL) at room temperature under argon. To this solution was added Ph_3PCl_2 (5.00 equiv, 0.16 mmol, 55.0 mg), and stirring was continued for 3.5 h. The reaction was quenched by addition of water (5 mL) followed by addition of ethyl acetate (5 mL). The aqueous layer was extracted with ethyl acetate (4 x 5 mL), combined extracts were washed with brine (5 mL), dried over sodium sulfate and concentrated under reduced pressure. The crude product was purified by column chromatography (silica, ethyl acetate = 20% to 40%) to yield (–)-salinosporamide (**1**) A as a white solid (6.0 mg, 0.02 mmol, 64%).

$[\alpha]_D^{23} = -69.0$ (*c* 0.4, MeOH)

^{1}H-NMR (500 MHz, pyridine-*d*$_5$) δ 10.67 (s, 1H), 6.45 (d, J = 10.3 Hz, 1H), 5.91 (d, J = 10.3 Hz, 1H), 5.02 (br, 1H), 4.28 (t, J = 9.1 Hz, 1H), 4.21 – 4.11 (m, 1H), 4.05 (m, 1H), 3.21 (t, J = 7.2 Hz, 1H), 2.94 – 2.82 (m, 1H), 2.56 – 2.47 (m, 1H), 2.41 – 2.30 (m, 2H), 2.10 (d, J = 2.3 Hz, 3H), 1.99 – 1.90 (m, 2H), 1.72 (t, J = 11.0 Hz, 2H), 1.42 – 1.36 (m, 1H).

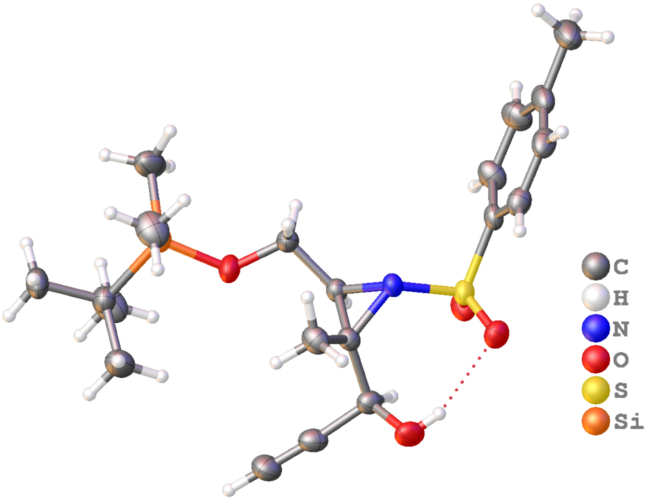
^{13}C-NMR (125 MHz, pyridine-*d*$_5$) δ 176.8, 169.3, 128.9, 128.6, 86.2, 80.2, 70.8, 46.0, 43.2, 39.2, 28.9, 26.3, 25.2, 21.6, 19.9.

TOF MS ES$^+$ ($C_{15}H_{21}ClNO_4$): Calc. $[M + H]^+$: 314.1159, Found $[M + H]^+$: 314.1165

Crystallographic analysis

Crystal data for 5 (enantio-pure);

CCDC 1879957



Experimental. Single colorless plate-shaped crystals of **5** were used as received. A suitable crystal (0.46×0.32×0.05) mm^3 was selected and mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 173(2) K during data collection. Using **Olex2**,[6] the structure was solved with the XT structure solution program, using the Intrinsic

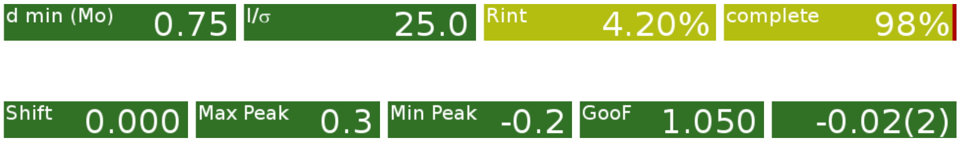
Compound	**5**
Formula	$C_{20}H_{31}NO_4SSi$
$D_{calc.}$/ g cm^{-3}	1.194
μ/mm^{-1}	0.218
Formula Weight	409.61
Color	colorless
Shape	plate
Size/mm^3	0.46×0.32×0.05
T/K	173(2)
Crystal System	orthorhombic
Flack Parameter	-0.02(2)
Hooft Parameter	-0.02(2)
Space Group	$P2_12_12_1$
a/Å	10.307(2)
b/Å	12.283(3)
c/Å	17.991(4)
α/°	90

Phasing solution method. The model was refined with version of **XL** using Least Squares minimisation.

Crystal Data. $C_{20}H_{31}NO_4SSi$, M_r = 409.61, orthorhombic, $P2_12_12_1$ (No. 19), a = 10.307(2) Å, b = 12.283(3) Å, c = 17.991(4) Å, $\alpha = \beta = \gamma = 90^\circ$, V = 2277.7(8) Å^3, T = 173(2) K, Z = 4, Z' = 1, μ(MoK$_\alpha$) = 0.218, 43882 reflections measured, 5640 unique (R_{int} = 0.0420) which were used in all calculations. The final wR_2 was 0.0993 (all data) and R_1 was 0.0372 (I > 2(I)).

$\beta/^\circ$	90
$\gamma/^\circ$	90
V/Å^3	2277.7(8)
Z	4
Z'	1
Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
$\Theta_{\mu in}/^\circ$	2.007
$\Theta_{\mu ax}/^\circ$	28.441
Measured Refl.	43882
Independent Refl.	5640
Reflections Used	5095
R_{int}	0.0420
Parameters	255
Restraints	0
Largest Peak	0.310
Deepest Hole	-0.217
GooF	1.050
wR_2 (all data)	0.0993

Structure Quality Indicators



Reflection:	d min (Mo) 0.75	I/σ 25.0	Rint 4.20%	complete 98%	
Refinemen:	Shift 0.000	Max Peak 0.3	Min Peak -0.2	GooF 1.050	-0.02(2)

A colorless plate-shaped crystal with dimensions 0.46×0.32×0.05 mm^3 was mounted on a nylon loop with paratone oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 173(2) K.

Data were measured using ω of -0.50° per frame for 200.84 s using MoK$_\alpha$ radiation (sealed tube, 50 kV, 40 mA). The total number of runs and images was based on the strategy calculation from the program **COSMO**.[7] The actually achieved resolution was Θ = 28.441.

Cell parameters were retrieved using the **SAINT**[8] software and refined using **SAINT**[8] on 9967 reflections, 23 % of the observed reflections. Data reduction was performed using the **SAINT**[8] software which corrects for Lorentz polarisation. The final completeness is 100.00 out to 28.441 in Θ. A multi-scan absorption correction was performed using SADABS-2014/5 (Bruker,2014/5) was used for absorption correction. wR_2 was 0.0660 before and 0.0554 after correction. The Ratio of minimum to maximum transmission is 0.9136. The λ/2 correction factor is 0.00150. The absorption coefficient μ of this material is 0.218 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.6813 and 0.7457. SADABS-2014/5 (Bruker,2014/5) was used for absorption correction. wR_2 was 0.0660 before and 0.0554 after correction. The Ratio of minimum to maximum transmission is 0.9136. The $\lambda/2$ correction factor is 0.00150.

The structure was solved in the space group $P2_12_12_1$ (# 19) by Intrinsic Phasing using the **XT**[9] structure solution program. The structure was refined by Least Squares using version 2014/6 of **XL**[9] incorporated in **Olex2**.[6] All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model, except for the Hydrogen atom on the oxygen atom which was found by difference Fourier methods and refined isotropically.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 4 and Z' is 1.

The Flack parameter was refined to -0.02(2). Determination of absolute structure using Bayesian statistics on Bijvoet differences using the Olex2 results in -0.02(2). Note: The Flack parameter is used to determine chirality of the crystal studied, the value should be near 0, a value of 1 means that the stereochemistry is wrong and the model should be inverted. A value of 0.5 means that the crystal consists of a racemic mixture of the two enantiomers.

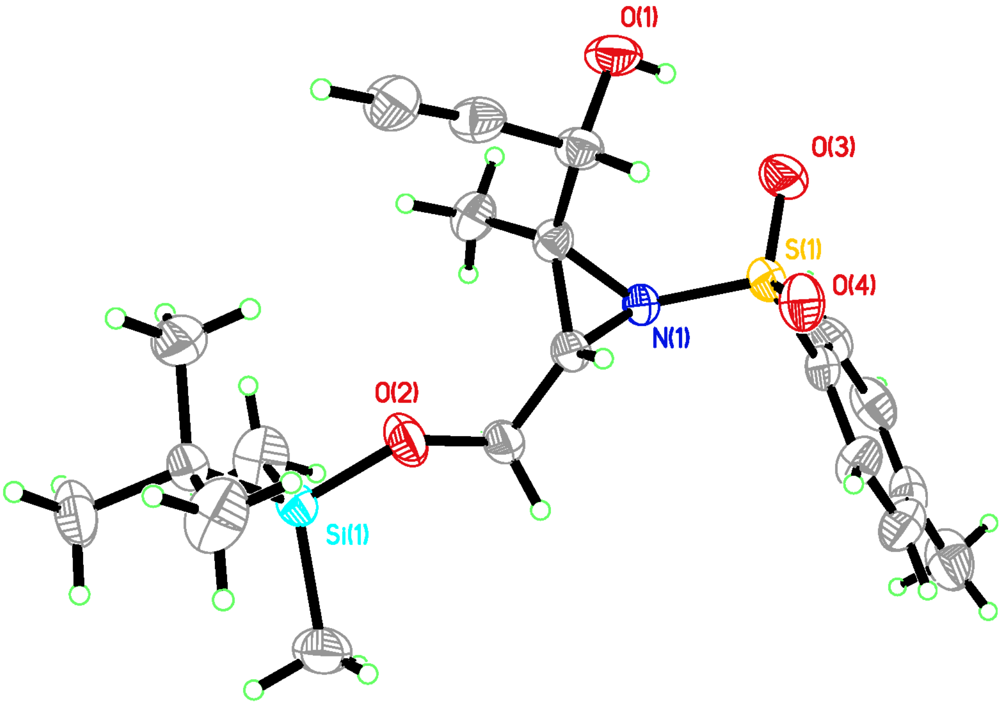


Figure S1. X-ray structure of **5** (view 1).

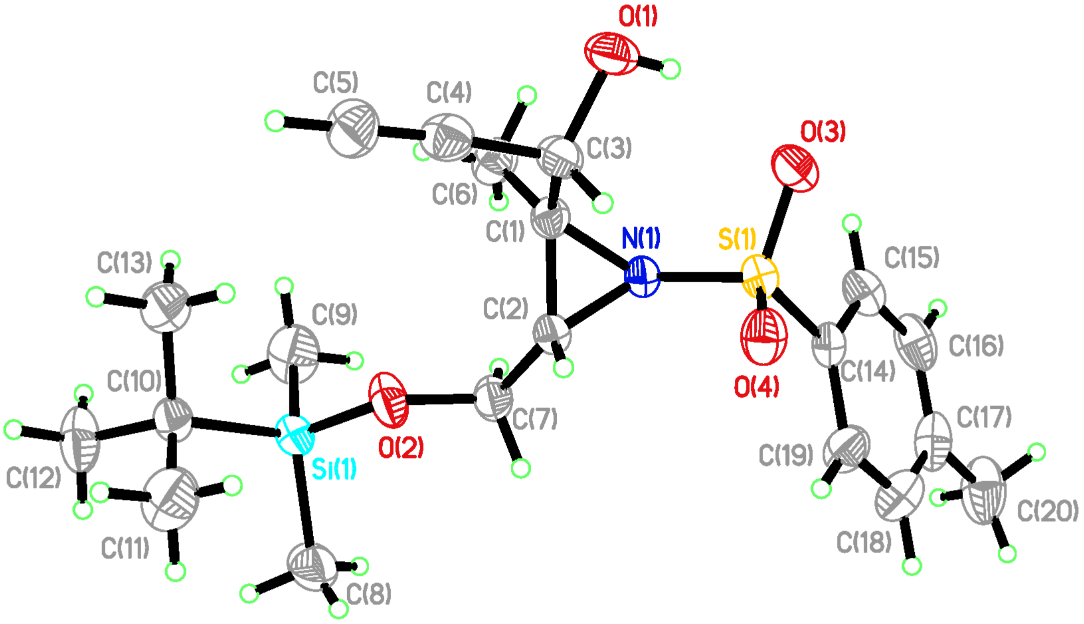


Figure S2. The model has chirality at C1 (Chiral SPGR) S verify; The model has chirality at C2 (Chiral SPGR) S verify; The model has chirality at C3 (Chiral SPGR) S verify.

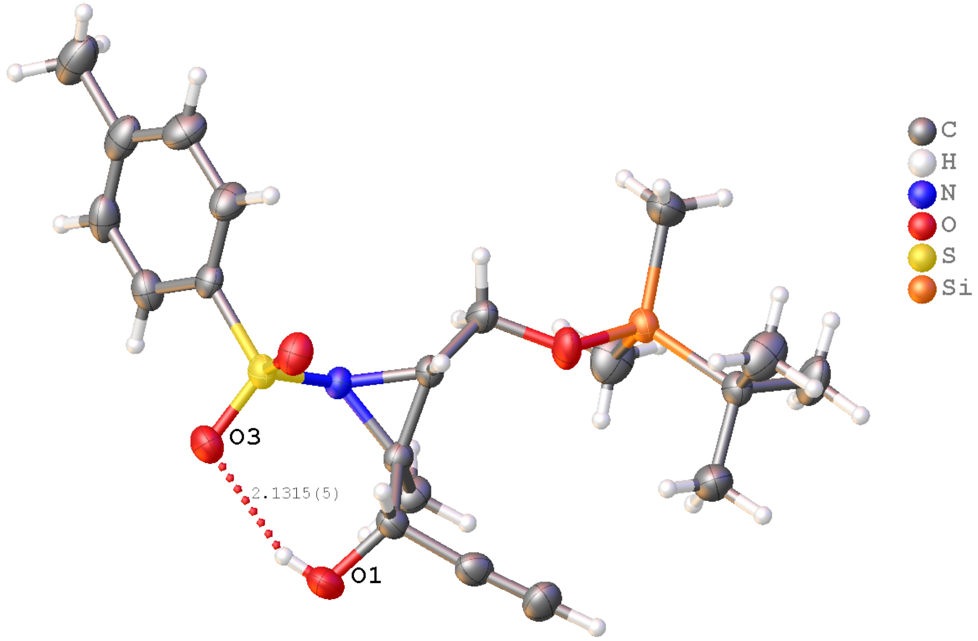


Figure S3. The following hydrogen bonding interactions with a maximum D-D distance of 2.9 Å and a minimum angle of 120 ° are present in **5**: O1–O3: 2.865 Å.

Table S4: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	**x**	**y**	**z**	U_{eq}
S1	828.6(5)	6886.9(5)	4781.5(3)	29.27(14)
Si1	5881.5(7)	5337.9(5)	2770.5(4)	30.61(16)
O1	429.0(18)	4081.6(17)	4822.9(13)	44.0(5)
O2	4872.6(17)	5517.8(16)	3472.8(11)	41.2(4)
O3	-385.9(17)	6311.0(15)	4848.5(11)	41.4(4)
O4	1622.2(18)	6996.9(16)	5431.6(10)	38.5(4)
N1	1616.0(18)	6305.4(15)	4079.7(11)	27.4(4)
C1	2001(2)	5125.6(18)	4083.4(13)	27.8(5)

C2	3003(2)	5993.0(19)	4150.1(13)	28.3(5)
C3	1748(2)	4458(2)	4789.7(15)	32.6(5)
C4	2615(3)	3501(2)	4781.9(15)	37.8(5)
C5	3375(3)	2779(2)	4767.9(18)	47.0(7)
C6	1730(3)	4554(2)	3359.2(14)	38.3(6)
C7	3886(2)	6318(2)	3517.2(15)	35.2(5)
C8	6873(3)	6589(2)	2629(2)	55.2(8)
C9	4948(4)	5015(3)	1911.7(18)	56.2(8)
C10	6914(2)	4152(2)	3075.2(14)	33.1(5)
C11	7723(4)	4472(3)	3752.3(19)	58.3(9)
C12	7836(3)	3807(3)	2447.9(18)	53.8(8)
C13	6056(3)	3185(2)	3284(2)	53.9(8)
C14	521(2)	8191.0(19)	4413.2(12)	29.4(5)
C15	-561(2)	8341(2)	3964.5(14)	37.1(6)
C16	-817(3)	9376(2)	3693.2(15)	43.3(6)
C17	-11(3)	10251(2)	3855.4(15)	44.2(7)
C18	1065(3)	10074(2)	4305.9(16)	47.4(7)
C19	1340(3)	9046(2)	4588.7(16)	39.7(6)
C20	-280(4)	11368(3)	3534(2)	62.0(9)

Table S5: Anisotropic Displacement Parameters (×10^4) **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	25.2(3)	31.9(3)	30.8(3)	-1.1(2)	3.4(2)	3.6(2)
Si1	25.7(3)	33.6(3)	32.6(3)	-0.5(2)	3.0(3)	1.5(3)
O1	31.3(9)	36.6(10)	64.1(13)	9.2(10)	4.3(9)	-7.0(8)
O2	33.2(9)	45.3(11)	45.2(10)	5.9(9)	13.2(8)	11.4(8)
O3	29.4(8)	42.2(10)	52.7(11)	2.3(9)	8.7(8)	-0.5(8)
O4	40.7(9)	43.3(10)	31.4(8)	-2.6(7)	-1.6(7)	8.9(8)
N1	24.6(9)	26.0(9)	31.5(9)	-1.1(8)	2.6(8)	3.5(7)
C1	26.1(10)	26.4(11)	31.1(11)	0.1(9)	-1.9(9)	2.9(9)
C2	23.9(10)	27.3(11)	33.7(11)	-0.3(9)	1.8(9)	2.5(9)
C3	27.0(11)	32.2(12)	38.5(12)	4.5(10)	0.3(10)	-1.5(9)
C4	37.1(12)	34.5(12)	41.6(13)	9.8(11)	-3.5(11)	-2.6(11)
C5	46.8(15)	39.4(14)	54.9(16)	11.9(12)	1.4(14)	7.6(12)
C6	42.7(14)	34.4(13)	38.0(13)	-5.3(10)	-5.8(11)	2.2(11)
C7	33.5(12)	29.4(12)	42.8(13)	3.9(10)	10.8(10)	3.8(10)
C8	39.4(15)	40.2(16)	86(2)	13.1(15)	7.9(16)	-2.0(13)
C9	58.7(19)	64(2)	46.4(16)	-4.5(15)	-16.0(14)	11.4(16)
C10	29.3(11)	33.0(12)	36.8(12)	-1(1)	5.1(10)	2.9(10)
C11	64(2)	55.6(19)	55.5(19)	-5.2(15)	-21.7(16)	12.4(16)
C12	54.7(18)	53.3(18)	53.3(17)	6.8(14)	20.5(15)	23.5(15)

C13	46.3(16)	37.7(15)	78(2)	7.0(14)	10.0(15)	1.2(13)
C14	27.8(11)	30.0(11)	30.3(11)	-3.5(9)	3.6(8)	6.8(9)
C15	28.3(12)	48.1(15)	34.8(12)	1.3(11)	0.9(9)	3.6(10)
C16	34.0(13)	59.1(17)	36.9(13)	10.8(12)	2.8(11)	16.1(13)
C17	53.8(17)	42.8(15)	36.0(13)	2.3(12)	11.1(12)	18.6(13)
C18	59.6(18)	33.2(13)	49.4(15)	-6.1(11)	-0.9(14)	2.3(13)
C19	41.8(14)	34.1(13)	43.2(14)	-7.4(11)	-9.0(11)	3.7(11)
C20	75(2)	52.0(18)	58.9(19)	15.3(16)	17.9(18)	25.6(17)

Table S6: Bond Lengths in Å for **5**

Atom	Atom	Length/Å
S1	O3	1.4428(19)
S1	O4	1.4336(19)
S1	N1	1.6622(19)
S1	C14	1.762(2)
Si1	O2	1.6512(18)
Si1	C8	1.864(3)
Si1	C9	1.863(3)
Si1	C10	1.886(3)
O1	C3	1.437(3)
O2	C7	1.417(3)
N1	C1	1.503(3)
N1	C2	1.486(3)
C1	C2	1.489(3)
C1	C3	1.535(3)
C1	C6	1.506(3)
C2	C7	1.511(3)
C3	C4	1.477(3)
C4	C5	1.183(4)
C10	C11	1.528(4)
C10	C12	1.535(4)

C10	C13	1.528(4)
C14	C15	1.388(3)
C14	C19	1.384(4)
C15	C16	1.387(4)
C16	C17	1.390(4)
C17	C18	1.391(4)
C17	C20	1.514(4)
C18	C19	1.390(4)

Table S7: Bond angles in ° for **5**.

Atom	Atom	Atom	Angle/°
O3	S1	N1	106.05(11)
O3	S1	C14	108.71(11)
O4	S1	O3	118.23(12)
O4	S1	N1	112.43(10)
O4	S1	C14	108.89(12)
N1	S1	C14	101.13(10)
O2	Si1	C8	109.85(14)
O2	Si1	C9	109.75(14)
O2	Si1	C10	103.68(10)
C8	Si1	C10	111.55(13)
C9	Si1	C8	110.21(17)
C9	Si1	C10	111.62(14)
C7	O2	Si1	126.02(16)
C1	N1	S1	122.69(15)
C2	N1	S1	121.07(16)
C2	N1	C1	59.75(14)
N1	C1	C3	118.29(19)
N1	C1	C6	113.37(19)
C2	C1	N1	59.57(14)
C2	C1	C3	115.71(19)

C2	C1	C6	122.1(2)
C6	C1	C3	115.8(2)
N1	C2	C1	60.68(14)
N1	C2	C7	116.53(19)
C1	C2	C7	123.1(2)
O1	C3	C1	111.6(2)
O1	C3	C4	108.4(2)
C4	C3	C1	108.3(2)
C5	C4	C3	175.7(3)
O2	C7	C2	106.93(19)
C11	C10	Si1	109.93(19)
C11	C10	C12	108.6(2)
C11	C10	C13	108.6(3)
C12	C10	Si1	110.44(18)
C13	C10	Si1	110.21(18)
C13	C10	C12	108.9(2)
C15	C14	S1	118.95(19)
C19	C14	S1	119.61(18)
C19	C14	C15	121.4(2)
C16	C15	C14	118.6(3)
C16	C17	C18	118.5(3)
C16	C17	C20	120.7(3)

C18	C17	C20	120.8(3)
C19	C18	C17	121.2(3)
C14	C19	C18	118.8(3)

Table S8: Hydrogen fractional atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) for **5**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H1	20(30)	4610(30)	4850(20)	51(10)
H2	3382	6084	4658	34
H3	1939	4914	5237	39
H5	3985	2200	4757	56
H6A	831	4295	3355	58
H6B	2320	3933	3305	58
H6C	1863	5062	2946	58
H7A	3393	6350	3045	42
H7B	4270	7044	3613	42
H8A	7671	6402	2361	83
H8B	7096	6905	3113	83
H8C	6375	7120	2339	83
H9A	4432	4356	1992	84
H9B	5551	4897	1498	84
H9C	4369	5624	1793	84
H11A	8274	5096	3627	87
H11B	8269	3857	3902	87
H11C	7145	4669	4163	87
H12A	7330	3613	2006	81

H12B	8346	3176	2609	81
H12C	8421	4411	2328	81
H13A	5508	3382	3709	81
H13B	6604	2563	3418	81
H13C	5506	2989	2860	81
H15	-1114	7747	3846	45
H16	-1560	9489	3390	52
H18	1622	10665	4423	57
H19	2077	8933	4897	48
H20A	-6	11385	3012	93
H20B	203,hh	11918	3815	93
H20C	-1211	11523	3565	93

Table S9: Hydrogen bond information for **5**.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1	H1	O3	0.78(4)	2.13(4)	2.865(3)	158(3)

Crystal data for 12 (racemic); CCDC 1881929

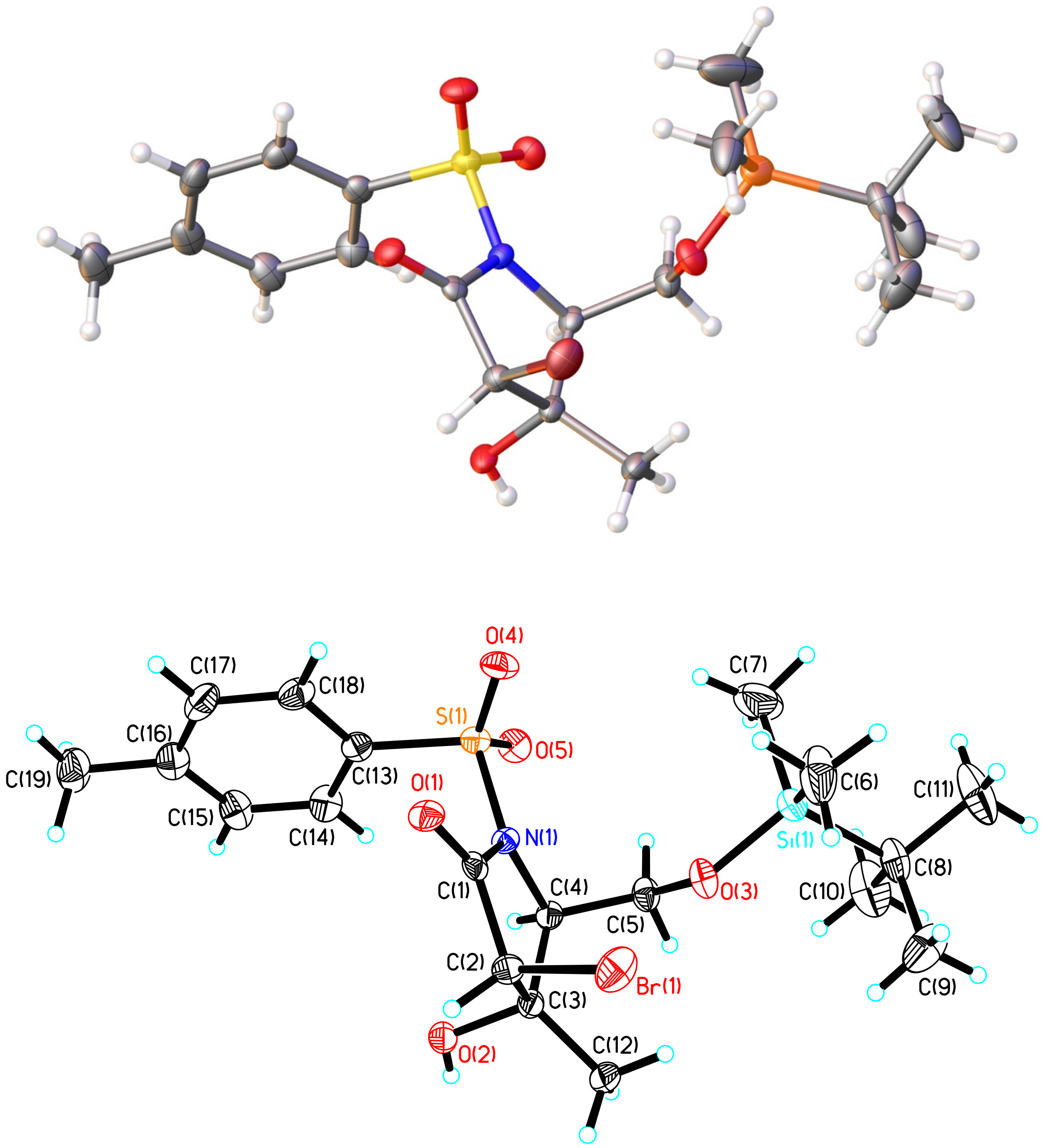


Figure S4. Perspective views of **12** showing 50% probability displacement.

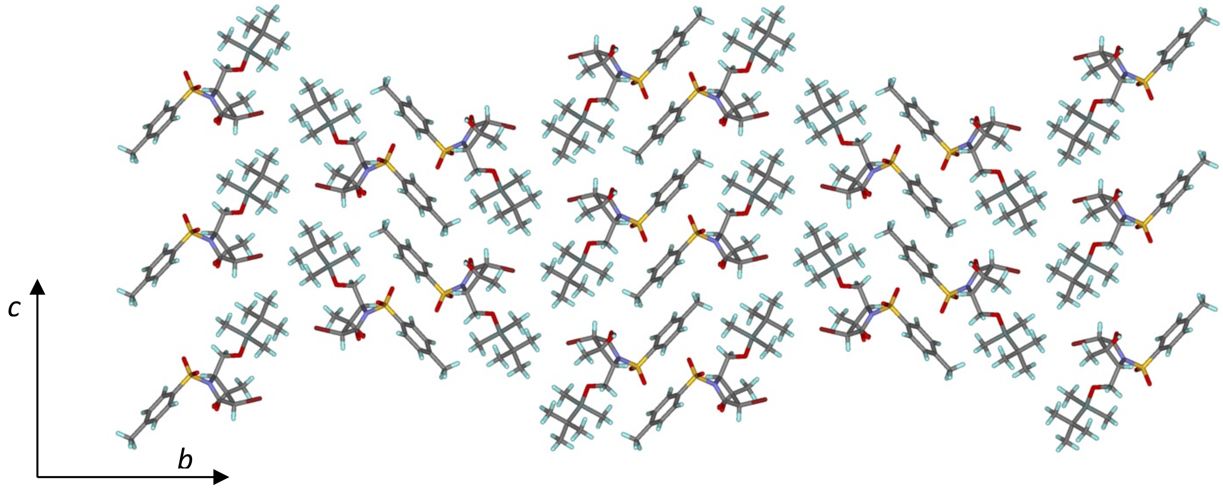


Figure S5. Three-dimensional supramolecular architecture of **12** viewed along the *a*-axis direction.

X-Ray Crystallography:

A crystal mounted on a diffractometer was collected data at 95 K. The intensities of the reflections were collected by means of a Bruker APEX II CCD along with the D8 Diffractometer (30 KeV, $\lambda = 0.41328$ Å), and equipped with an Oxford Cryosystems nitrogen open flow apparatus. The collection method involved 0.5° scans in Phi at -5° in 2θ. Data integration down to 0.82 Å resolution was carried out using SAINT V7.46 A (Bruker diffractometer, 2009) with reflection spot size optimisation. Absorption corrections were made with the program SADABS (Bruker diffractometer, 2009). The structure was solved by the direct methods procedure and refined by least-squares methods again F^2 using SHELXS-97 and SHELXL-97 (Sheldrick, 2008). Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were allowed to ride on the respective atoms. Crystal data as well as details of data collection and refinement are summarized in Table 1, while geometric parameters and Hydrogen-bond parameters are shown in Tables 2 and 3. The Ortep plots produced with SHELXL-97 program, and the other drawings were produced with Accelrys DS Visualizer 2.0 (Accelrys, 2007).

Table S10. Experimental details for **12**.

Crystal data	
Identification code	**12** (**CCDC 1881929**)
Chemical formula	$C_{19}H_{30}BrNO_5SSi$
M_r	492.50
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	95
a, b, c (Å)	6.7083 (6), 34.703 (3), 10.1768 (9)
β (°)	106.087 (2)
V (Å^3)	2276.4 (4)
Z	4
Radiation type	Synchrotron, λ = 0.41328 Å
μ (mm^{-1})	1.06
Crystal size (mm)	0.12 × 0.07 × 0.03
Data collection	
Diffractometer	Bruker D8 goniometer with CCD area detector diffractometer
Absorption correction	Multi-scan *SADABS* (Sheldrick, 2009)
T_{min}, T_{max}	0.883, 0.969
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	37474, 4171, 3825
R_{int}	0.063
Refinement	

$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.036, 0.083, 1.05
No. of reflections	4171
No. of parameters	257
No. of restraints	0
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, -0.47

Computer programs: *APEX2* v2009.3.0 (Bruker-AXS, 2009), *SAINT* 7.46A (Bruker-AXS, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), Bruker *SHELXTL*.

Table S11. Selected geometric parameters (Å°) for **12**.

Br1—C2	1.940 (3)	C8—C9	1.5292
S1—O4	1.425 (2)	C8—C10	1.532 (4)
S1—O5	1.427 (2)	C8—C11	1.534 (4)
S1—N1	1.679 (2)	C9—H9A	0.9594
S1—C13	1.752 (3)	C9—H9B	0.9720
Si1—O3	1.652 (2)	C9—H9C	0.9511
Si1—C7	1.857 (2)	C10—H10A	0.9800
Si1—C6	1.860 (4)	C10—H10B	0.9800
Si1—C8	1.875 (2)	C10—H10C	0.9800
O1—C1	1.212 (3)	C11—H11A	0.9800
O2—C3	1.430 (3)	C11—H11B	0.9800
O2—H2O	0.74 (3)	C11—H11C	0.9800

O3—C5	1.415 (3)	C12—H12A	0.9800
N1—C1	1.375 (3)	C12—H12B	0.9800
N1—C4	1.490 (3)	C12—H12C	0.9800
C1—C2	1.510 (3)	C13—C18	1.385 (4)
C2—C3	1.541 (4)	C13—C14	1.390 (4)
C2—H2A	1.0000	C14—C15	1.377 (4)
C3—C12	1.515 (4)	C14—H14A	0.9500
C3—C4	1.551 (4)	C15—C16	1.385 (5)
C4—C5	1.514 (4)	C15—H15A	0.9500
C4—H4A	1.0000	C16—C17	1.382 (4)
C5—H5A	0.9900	C16—C19	1.506 (4)
C5—H5B	0.9900	C17—C18	1.383 (4)
C6—H6A	0.9800	C17—H17A	0.9500
C6—H6B	0.9800	C18—H18A	0.9500
C6—H6C	0.9800	C19—H19C	0.9800
C7—H7A	0.9800	C19—H19D	0.9800
C7—H7B	0.9800	C19—H19A	0.9800
C7—H7C	0.9800		
O4—S1—O5	120.31 (12)	H7B—C7—H7C	109.5
O4—S1—N1	107.70 (11)	C9—C8—C10	108.19 (19)
O5—S1—N1	104.14 (11)	C9—C8—C11	108.7 (2)
O4—S1—C13	109.84 (13)	C10—C8—C11	108.9 (3)

O5—S1—C13	109.25 (12)	C9—C8—Si1	109.54 (7)
N1—S1—C13	104.29 (12)	C10—C8—Si1	111.0 (2)
O3—Si1—C7	109.26 (14)	C11—C8—Si1	110.4 (2)
O3—Si1—C6	104.58 (16)	C8—C9—H9A	109.5
C7—Si1—C6	111.52 (19)	C8—C9—H9B	109.3
O3—Si1—C8	110.11 (11)	H9A—C9—H9B	111.7
C7—Si1—C8	110.97 (12)	C8—C9—H9C	109.6
C6—Si1—C8	110.22 (14)	H9A—C9—H9C	107.2
C3—O2—H2O	109 (3)	H9B—C9—H9C	109.5
C5—O3—Si1	125.87 (18)	C8—C10—H10A	109.5
C1—N1—C4	114.4 (2)	C8—C10—H10B	109.5
C1—N1—S1	121.17 (17)	H10A—C10—H10B	109.5
C4—N1—S1	123.58 (17)	C8—C10—H10C	109.5
O1—C1—N1	125.9 (2)	H10A—C10—H10C	109.5
O1—C1—C2	126.2 (2)	H10B—C10—H10C	109.5
N1—C1—C2	107.8 (2)	C8—C11—H11A	109.5
C1—C2—C3	104.8 (2)	C8—C11—H11B	109.5
C1—C2—Br1	107.83 (16)	H11A—C11—H11B	109.5
C3—C2—Br1	117.73 (18)	C8—C11—H11C	109.5
C1—C2—H2A	108.7	H11A—C11—H11C	109.5
C3—C2—H2A	108.7	H11B—C11—H11C	109.5
Br1—C2—H2A	108.7	C3—C12—H12A	109.5

O2—C3—C12	111.5 (2)	C3—C12—H12B	109.5
O2—C3—C2	101.3 (2)	H12A—C12—H12B	109.5
C12—C3—C2	115.8 (2)	C3—C12—H12C	109.5
O2—C3—C4	107.2 (2)	H12A—C12—H12C	109.5
C12—C3—C4	114.6 (2)	H12B—C12—H12C	109.5
C2—C3—C4	105.2 (2)	C18—C13—C14	121.0 (3)
N1—C4—C5	112.6 (2)	C18—C13—S1	120.8 (2)
N1—C4—C3	102.5 (2)	C14—C13—S1	118.2 (2)
C5—C4—C3	117.8 (2)	C15—C14—C13	119.1 (3)
N1—C4—H4A	107.8	C15—C14—H14A	120.5
C5—C4—H4A	107.8	C13—C14—H14A	120.5
C3—C4—H4A	107.8	C14—C15—C16	121.1 (3)
O3—C5—C4	111.3 (2)	C14—C15—H15A	119.4
O3—C5—H5A	109.4	C16—C15—H15A	119.4
C4—C5—H5A	109.4	C17—C16—C15	118.8 (3)
O3—C5—H5B	109.4	C17—C16—C19	121.4 (3)
C4—C5—H5B	109.4	C15—C16—C19	119.8 (3)
H5A—C5—H5B	108.0	C16—C17—C18	121.5 (3)
Si1—C6—H6A	109.5	C16—C17—H17A	119.2
Si1—C6—H6B	109.5	C18—C17—H17A	119.2
H6A—C6—H6B	109.5	C17—C18—C13	118.6 (3)
Si1—C6—H6C	109.5	C17—C18—H18A	120.7

H6A—C6—H6C	109.5	C13—C18—H18A	120.7
H6B—C6—H6C	109.5	C16—C19—H19C	109.5
Si1—C7—H7A	109.5	C16—C19—H19D	109.5
Si1—C7—H7B	109.5	H19C—C19—H19D	109.5
H7A—C7—H7B	109.5	C16—C19—H19A	109.5
Si1—C7—H7C	109.5	H19C—C19—H19A	109.5
H7A—C7—H7C	109.5	H19D—C19—H19A	109.5
C7—Si1—O3—C5	39.3 (3)	C12—C3—C4—C5	-23.8 (3)
C6—Si1—O3—C5	158.8 (2)	C2—C3—C4—C5	104.5 (2)
C8—Si1—O3—C5	-82.8 (2)	Si1—O3—C5—C4	-146.18 (19)
O4—S1—N1—C1	53.5 (2)	N1—C4—C5—O3	57.6 (3)
O5—S1—N1—C1	-177.68 (19)	C3—C4—C5—O3	-61.3 (3)
C13—S1—N1—C1	-63.2 (2)	O3—Si1—C8—C9	-59.79 (10)
O4—S1—N1—C4	-138.0 (2)	C7—Si1—C8—C9	179.12 (14)
O5—S1—N1—C4	-9.1 (2)	C6—Si1—C8—C9	55.08 (16)
C13—S1—N1—C4	105.4 (2)	O3—Si1—C8—C10	59.6 (2)
C4—N1—C1—O1	-173.4 (2)	C7—Si1—C8—C10	-61.5 (3)
S1—N1—C1—O1	-3.9 (3)	C6—Si1—C8—C10	174.5 (2)
C4—N1—C1—C2	5.2 (3)	O3—Si1—C8—C11	-179.5 (2)
S1—N1—C1—C2	174.76 (17)	C7—Si1—C8—C11	59.5 (3)
O1—C1—C2—C3	160.9 (2)	C6—Si1—C8—C11	-64.6 (3)
N1—C1—C2—C3	-17.8 (3)	O4—S1—C13—C18	-8.2 (3)

O1—C1—C2—Br1	-72.9 (3)	O5—S1—C13—C18	-142.2 (2)
N1—C1—C2—Br1	108.43 (19)	N1—S1—C13—C18	106.9 (2)
C1—C2—C3—O2	-88.5 (2)	O4—S1—C13—C14	171.2 (2)
Br1—C2—C3—O2	151.72 (17)	O5—S1—C13—C14	37.2 (3)
C1—C2—C3—C12	150.7 (2)	N1—S1—C13—C14	-73.6 (2)
Br1—C2—C3—C12	30.9 (3)	C18—C13—C14—C15	-1.1 (4)
C1—C2—C3—C4	23.1 (3)	S1—C13—C14—C15	179.4 (2)
Br1—C2—C3—C4	-96.7 (2)	C13—C14—C15—C16	0.7 (4)
C1—N1—C4—C5	-118.1 (2)	C14—C15—C16—C17	0.2 (4)
S1—N1—C4—C5	72.6 (3)	C14—C15—C16—C19	-179.8 (3)
C1—N1—C4—C3	9.4 (3)	C15—C16—C17—C18	-0.7 (4)
S1—N1—C4—C3	-159.82 (17)	C19—C16—C17—C18	179.3 (3)
O2—C3—C4—N1	87.6 (2)	C16—C17—C18—C13	0.3 (4)
C12—C3—C4—N1	-148.0 (2)	C14—C13—C18—C17	0.7 (4)
C2—C3—C4—N1	-19.6 (2)	S1—C13—C18—C17	-179.9 (2)
O2—C3—C4—C5	-148.2 (2)		

Table S12. Hydrogen bond parameters for **12**.

D—H···*A*	*D*—H (Å)	H···*A* (Å)	*D*···*A* (Å)	*D*—H···*A* (°)
O2—H2O···O1^{i}	0.74 (3)	2.07 (3)	2.795 (3)	167 (4)

Symmetry code(s): (i) *x*-1, *y*, *z*.

Crystal data for 16 (racemic); CCDC 1881767

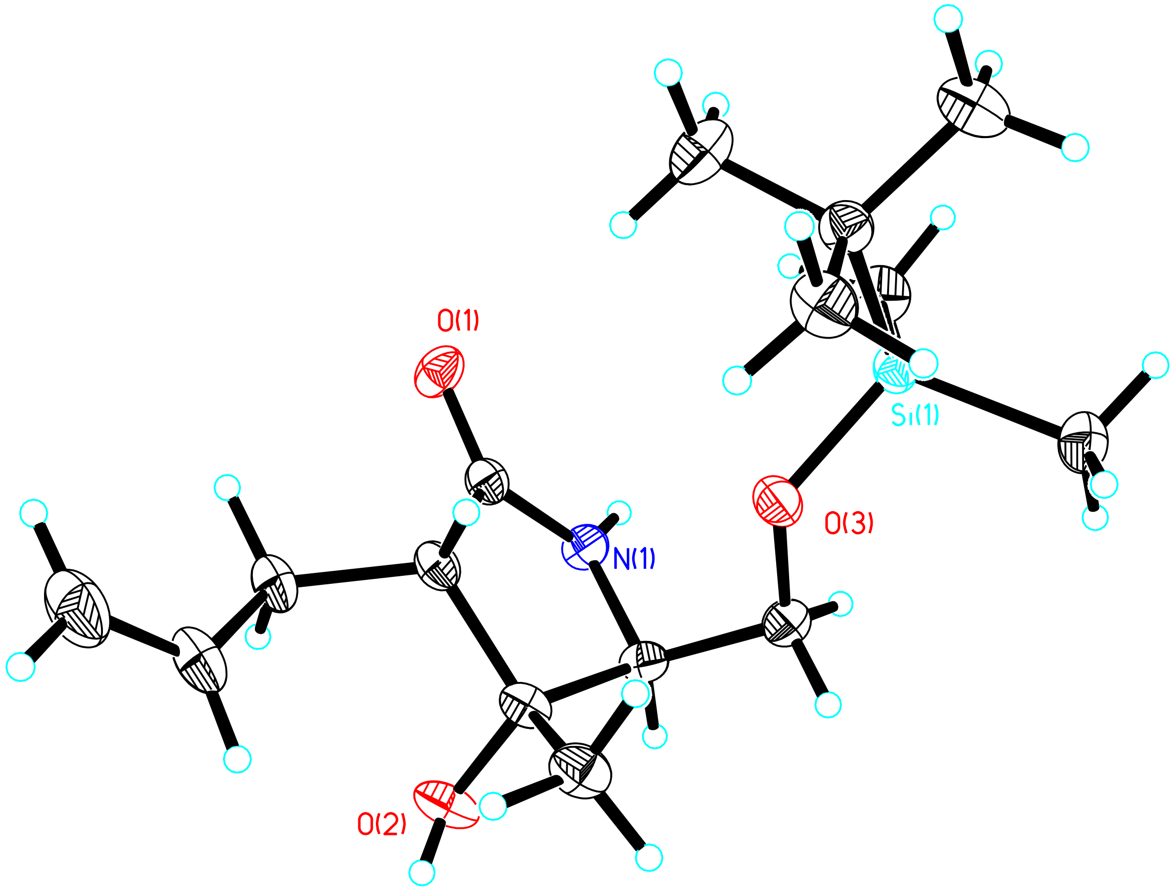


Figure S6. Perspective views of **12**

Experimental Section:

A colorless block crystal with dimensions 0.39 x 0.18 x 0.12 mm was mounted on a Nylon loop using very small amount of paratone oil.

Data were collected using a Bruker CCD (charge coupled device) based diffractometer equipped with an Oxford Cryostream low-temperature apparatus operating at 100 K. Data were measured using omega and phi scans of 0.5° per frame for 30 s. The total number of images was based on results from the program COSMO where redundancy was expected to be 4.0 and completeness of 100% out to 0.83 Å. Cell parameters were retrieved using APEX II software and refined using SAINT on all observed reflections.

Data reduction was performed using the SAINT software which corrects for Lp. Scaling and absorption corrections were applied using SADABS multi-scan technique, supplied by George Sheldrick. The structures are solved by the direct method using the SHELXS-97 program and refined by least squares method on F^2, SHELXL- 97, which are incorporated in SHELXTL-PC V 6.10.

The structure was solved in the space group $P2_1/c$ (# 14). All non-hydrogen atoms are refined anisotropically. Hydrogen atoms were found by difference Fourier methods and refined isotropically. The crystal used for the diffraction study showed no decomposition during data collection. All drawings are done at 50% ellipsoids.

Table S13. Crystal data and structure refinement for **16**.

Identification code	**16** (**CCDC 1881767**)	
Empirical formula	C15 H29 N O3 Si	
Formula weight	299.48	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.2284(3) Å	α= 90°.
	b = 12.1847(3) Å	β=116.5650(10)°
	c = 12.2126(3) Å	γ = 90°.
Volume	1760.66(7) Å^3	

Z	4
Density (calculated)	1.130 Mg/m^3
Absorption coefficient	0.140 mm^{-1}
F(000)	656
Crystal size	0.39 x 0.18 x 0.12 mm^3
Theta range for data collection	1.72 to 30.58°.
Index ranges	-18<=h<=18, -17<=k<=17, -17<=l<=17
Reflections collected	26464
Independent reflections	5385 [R(int) = 0.0531]
Completeness to theta = 25.00°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9829 and 0.9469
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5385 / 0 / 297
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0420, wR2 = 0.0954
R indices (all data)	R1 = 0.0663, wR2 = 0.1064
Largest diff. peak and hole	0.416 and -0.262 e.Å^{-3}

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **16**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Si(1)	6649(1)	-1197(1)	7455(1)	21(1)
O(1)	9359(1)	1334(1)	9999(1)	25(1)
O(2)	9615(1)	2171(1)	6733(1)	29(1)
O(3)	7226(1)	-189(1)	7013(1)	25(1)
N(1)	9498(1)	444(1)	8428(1)	21(1)
C(1)	9171(1)	1270(1)	8909(1)	20(1)
C(2)	8555(1)	2124(1)	7932(1)	19(1)
C(3)	8658(1)	1686(1)	6788(1)	21(1)
C(4)	8988(1)	456(1)	7098(1)	20(1)
C(5)	9062(1)	3265(1)	8386(1)	24(1)
C(6)	8442(1)	4190(1)	7545(2)	30(1)
C(7)	8084(2)	5077(1)	7876(2)	42(1)
C(8)	7585(1)	1851(1)	5598(1)	27(1)
C(9)	8049(1)	-395(1)	6583(1)	24(1)
C(10)	7741(1)	-1918(1)	8812(2)	32(1)
C(11)	5990(1)	-2195(1)	6172(2)	32(1)
C(12)	5566(1)	-500(1)	7819(1)	24(1)
C(13)	6155(2)	159(2)	9009(2)	36(1)

C(14)	4796(1)	-1368(1)	7972(2)	34(1)
C(15)	4842(1)	283(1)	6775(2)	30(1)

Table 15. Bond lengths [Å] and angles [°] for **16**.

Si(1)-O(3)	1.6574(10)
Si(1)-C(10)	1.8611(15)
Si(1)-C(11)	1.8633(15)
Si(1)-C(12)	1.8821(14)
O(1)-C(1)	1.2426(15)
O(2)-C(3)	1.4256(15)
O(2)-H(2)	0.810(18)
O(3)-C(9)	1.4274(16)
N(1)-C(1)	1.3307(16)
N(1)-C(4)	1.4536(16)
N(1)-H(1)	0.833(16)
C(1)-C(2)	1.5165(17)
C(2)-C(5)	1.5353(18)
C(2)-C(3)	1.5569(18)
C(2)-H(2A)	0.981(14)
C(3)-C(8)	1.5244(18)
C(3)-C(4)	1.5585(18)
C(4)-C(9)	1.5216(19)

C(4)-H(4)	0.957(14)
C(5)-C(6)	1.4992(19)
C(5)-H(5A)	0.955(17)
C(5)-H(5B)	1.019(15)
C(6)-C(7)	1.313(2)
C(6)-H(6)	0.966(19)
C(7)-H(7A)	0.99(2)
C(7)-H(7B)	0.97(2)
C(8)-H(8A)	0.986(16)
C(8)-H(8B)	0.986(17)
C(8)-H(8C)	1.015(18)
C(9)-H(9A)	0.987(16)
C(9)-H(9B)	1.004(15)
C(10)-H(10A)	0.962(19)
C(10)-H(10B)	0.964(19)
C(10)-H(10C)	0.988(19)
C(11)-H(11A)	0.990(19)
C(11)-H(11B)	1.00(2)
C(11)-H(11C)	0.99(2)
C(12)-C(13)	1.534(2)
C(12)-C(15)	1.5362(19)
C(12)-C(14)	1.537(2)

C(13)-H(13A)	0.989(19)
C(13)-H(13B)	0.979(18)
C(13)-H(13C)	0.974(19)
C(14)-H(14A)	0.950(19)
C(14)-H(14B)	0.988(19)
C(14)-H(14C)	1.008(19)
C(15)-H(15A)	0.980(18)
C(15)-H(15B)	0.972(17)
C(15)-H(15C)	0.999(18)
O(3)-Si(1)-C(10)	110.66(7)
O(3)-Si(1)-C(11)	108.68(6)
C(10)-Si(1)-C(11)	109.03(8)
O(3)-Si(1)-C(12)	104.61(5)
C(10)-Si(1)-C(12)	111.84(7)
C(11)-Si(1)-C(12)	111.93(7)
C(3)-O(2)-H(2)	110.7(12)
C(9)-O(3)-Si(1)	121.84(8)
C(1)-N(1)-C(4)	113.94(10)
C(1)-N(1)-H(1)	119.8(10)
C(4)-N(1)-H(1)	124.5(11)
O(1)-C(1)-N(1)	124.83(12)
O(1)-C(1)-C(2)	125.43(11)

N(1)-C(1)-C(2)	109.74(11)
C(1)-C(2)-C(5)	110.04(10)
C(1)-C(2)-C(3)	103.80(10)
C(5)-C(2)-C(3)	115.82(11)
C(1)-C(2)-H(2A)	106.8(8)
C(5)-C(2)-H(2A)	110.8(8)
C(3)-C(2)-H(2A)	109.0(8)
O(2)-C(3)-C(8)	111.56(10)
O(2)-C(3)-C(2)	109.64(10)
C(8)-C(3)-C(2)	113.12(11)
O(2)-C(3)-C(4)	104.58(10)
C(8)-C(3)-C(4)	113.50(11)
C(2)-C(3)-C(4)	103.85(9)
N(1)-C(4)-C(9)	109.85(10)
N(1)-C(4)-C(3)	102.72(10)
C(9)-C(4)-C(3)	117.81(11)
N(1)-C(4)-H(4)	110.7(8)
C(9)-C(4)-H(4)	108.7(8)
C(3)-C(4)-H(4)	106.8(8)
C(6)-C(5)-C(2)	114.63(11)
C(6)-C(5)-H(5A)	108.9(10)
C(2)-C(5)-H(5A)	107.4(10)

C(6)-C(5)-H(5B)	109.1(9)
C(2)-C(5)-H(5B)	110.4(9)
H(5A)-C(5)-H(5B)	105.9(13)
C(7)-C(6)-C(5)	124.74(16)
C(7)-C(6)-H(6)	119.0(11)
C(5)-C(6)-H(6)	116.2(11)
C(6)-C(7)-H(7A)	122.6(11)
C(6)-C(7)-H(7B)	120.2(12)
H(7A)-C(7)-H(7B)	117.1(17)
C(3)-C(8)-H(8A)	110.3(9)
C(3)-C(8)-H(8B)	109.3(9)
H(8A)-C(8)-H(8B)	107.8(13)
C(3)-C(8)-H(8C)	110.3(10)
H(8A)-C(8)-H(8C)	109.2(13)
H(8B)-C(8)-H(8C)	109.9(13)
O(3)-C(9)-C(4)	110.17(10)
O(3)-C(9)-H(9A)	109.6(9)
C(4)-C(9)-H(9A)	108.8(9)
O(3)-C(9)-H(9B)	113.0(9)
C(4)-C(9)-H(9B)	105.0(9)
H(9A)-C(9)-H(9B)	110.1(13)
Si(1)-C(10)-H(10A)	111.7(11)

Si(1)-C(10)-H(10B)	112.6(11)
H(10A)-C(10)-H(10B)	105.8(15)
Si(1)-C(10)-H(10C)	111.6(10)
H(10A)-C(10)-H(10C)	108.4(15)
H(10B)-C(10)-H(10C)	106.3(15)
Si(1)-C(11)-H(11A)	109.4(11)
Si(1)-C(11)-H(11B)	111.1(12)
H(11A)-C(11)-H(11B)	110.1(16)
Si(1)-C(11)-H(11C)	110.2(12)
H(11A)-C(11)-H(11C)	108.2(16)
H(11B)-C(11)-H(11C)	107.9(16)
C(13)-C(12)-C(15)	109.00(12)
C(13)-C(12)-C(14)	109.17(13)
C(15)-C(12)-C(14)	109.15(12)
C(13)-C(12)-Si(1)	110.01(10)
C(15)-C(12)-Si(1)	109.99(9)
C(14)-C(12)-Si(1)	109.50(10)
C(12)-C(13)-H(13A)	110.9(10)
C(12)-C(13)-H(13B)	110.9(10)
H(13A)-C(13)-H(13B)	107.9(14)
C(12)-C(13)-H(13C)	110.3(11)
H(13A)-C(13)-H(13C)	107.4(15)

H(13B)-C(13)-H(13C)	109.4(15)
C(12)-C(14)-H(14A)	112.7(11)
C(12)-C(14)-H(14B)	113.6(10)
H(14A)-C(14)-H(14B)	106.7(15)
C(12)-C(14)-H(14C)	110.5(11)
H(14A)-C(14)-H(14C)	106.6(14)
H(14B)-C(14)-H(14C)	106.3(15)
C(12)-C(15)-H(15A)	111.6(10)
C(12)-C(15)-H(15B)	112.0(10)
H(15A)-C(15)-H(15B)	106.8(14)
C(12)-C(15)-H(15C)	110.3(10)
H(15A)-C(15)-H(15C)	107.8(14)
H(15B)-C(15)-H(15C)	108.2(14)

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2$x 10^3) for **16**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$[h^2 $a^{*2}U^{11}$ + ... + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Si(1)	23(1)	16(1)	21(1)	0(1)	10(1)	-1(1)
O(1)	34(1)	21(1)	20(1)	1(1)	10(1)	8(1)
O(2)	21(1)	36(1)	30(1)	13(1)	12(1)	-1(1)
O(3)	28(1)	19(1)	34(1)	-1(1)	19(1)	-2(1)
N(1)	25(1)	18(1)	19(1)	3(1)	9(1)	6(1)
C(1)	19(1)	18(1)	22(1)	1(1)	9(1)	0(1)
C(2)	18(1)	15(1)	24(1)	4(1)	9(1)	2(1)
C(3)	19(1)	22(1)	22(1)	5(1)	10(1)	0(1)
C(4)	22(1)	22(1)	19(1)	2(1)	11(1)	3(1)
C(5)	22(1)	17(1)	32(1)	2(1)	12(1)	0(1)
C(6)	26(1)	20(1)	42(1)	7(1)	15(1)	0(1)
C(7)	44(1)	24(1)	65(1)	10(1)	31(1)	7(1)
C(8)	22(1)	30(1)	24(1)	8(1)	7(1)	2(1)
C(9)	28(1)	23(1)	25(1)	-3(1)	15(1)	0(1)
C(10)	30(1)	31(1)	31(1)	6(1)	11(1)	6(1)
C(11)	40(1)	24(1)	32(1)	-5(1)	16(1)	-6(1)
C(12)	25(1)	23(1)	23(1)	2(1)	10(1)	1(1)
C(13)	39(1)	38(1)	32(1)	-9(1)	16(1)	4(1)
C(14)	30(1)	36(1)	39(1)	11(1)	18(1)	1(1)

C(15)	30(1)	26(1)	35(1)	6(1)	14(1)	6(1)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10 ^{3}) for **16**.

	x	y	z	U(eq)
H(2)	9419(14)	2591(15)	6161(16)	35(5)
H(1)	9828(13)	-94(13)	8861(14)	24(4)
H(2A)	7760(12)	2100(11)	7770(12)	13(3)
H(4)	9538(11)	292(11)	6815(12)	15(3)
H(5A)	9822(14)	3253(13)	8492(14)	31(4)
H(5B)	9114(13)	3415(13)	9231(14)	26(4)
H(6)	8341(16)	4132(15)	6713(18)	48(5)
H(7A)	7687(16)	5678(17)	7298(17)	52(5)
H(7B)	8229(17)	5176(17)	8720(20)	57(6)
H(8A)	6927(14)	1547(13)	5671(14)	29(4)
H(8B)	7453(13)	2644(14)	5430(14)	32(4)
H(8C)	7658(15)	1475(14)	4894(16)	39(5)
H(9A)	7690(13)	-352(13)	5681(15)	28(4)
H(9B)	8440(13)	-1121(13)	6864(14)	26(4)
H(10A)	8148(16)	-1417(15)	9475(17)	44(5)
H(10B)	8304(16)	-2274(16)	8639(16)	48(5)

H(10C)	7404(15)	-2497(16)	9112(16)	44(5)
H(11A)	6575(16)	-2484(16)	5952(17)	46(5)
H(11B)	5366(17)	-1844(17)	5441(18)	58(6)
H(11C)	5666(17)	-2819(18)	6425(18)	62(6)
H(13A)	6610(15)	-328(15)	9704(17)	43(5)
H(13B)	5601(15)	534(15)	9204(15)	41(5)
H(13C)	6667(16)	698(16)	8939(16)	45(5)
H(14A)	5204(15)	-1884(15)	8599(16)	39(5)
H(14B)	4353(15)	-1796(15)	7220(17)	42(5)
H(14C)	4231(16)	-1010(15)	8201(17)	48(5)
H(15A)	5298(15)	874(15)	6677(15)	38(5)
H(15B)	4251(14)	632(14)	6918(15)	35(4)
H(15C)	4477(14)	-124(15)	5983(16)	42(5)

Table S18. Torsion angles [°] for **16**.

C(10)-Si(1)-O(3)-C(9)	63.33(11)
C(11)-Si(1)-O(3)-C(9)	-56.36(12)
C(12)-Si(1)-O(3)-C(9)	-176.07(10)
C(4)-N(1)-C(1)-O(1)	168.56(12)
C(4)-N(1)-C(1)-C(2)	-12.37(14)
O(1)-C(1)-C(2)-C(5)	50.36(17)
N(1)-C(1)-C(2)-C(5)	-128.71(12)
O(1)-C(1)-C(2)-C(3)	174.89(12)
N(1)-C(1)-C(2)-C(3)	-4.17(13)
C(1)-C(2)-C(3)-O(2)	-94.11(11)
C(5)-C(2)-C(3)-O(2)	26.61(14)
C(1)-C(2)-C(3)-C(8)	140.68(11)
C(5)-C(2)-C(3)-C(8)	-98.60(13)
C(1)-C(2)-C(3)-C(4)	17.19(12)
C(5)-C(2)-C(3)-C(4)	137.91(11)
C(1)-N(1)-C(4)-C(9)	-103.02(13)
C(1)-N(1)-C(4)-C(3)	23.13(13)
O(2)-C(3)-C(4)-N(1)	91.45(11)
C(8)-C(3)-C(4)-N(1)	-146.74(11)
C(2)-C(3)-C(4)-N(1)	-23.49(12)

O(2)-C(3)-C(4)-C(9)	-147.71(11)
C(8)-C(3)-C(4)-C(9)	-25.90(16)
C(2)-C(3)-C(4)-C(9)	97.34(12)
C(1)-C(2)-C(5)-C(6)	-174.04(11)
C(3)-C(2)-C(5)-C(6)	68.67(15)
C(2)-C(5)-C(6)-C(7)	127.92(16)
Si(1)-O(3)-C(9)-C(4)	-138.58(9)
N(1)-C(4)-C(9)-O(3)	57.25(14)
C(3)-C(4)-C(9)-O(3)	-59.82(15)
O(3)-Si(1)-C(12)-C(13)	-72.18(11)
C(10)-Si(1)-C(12)-C(13)	47.63(13)
C(11)-Si(1)-C(12)-C(13)	170.32(11)
O(3)-Si(1)-C(12)-C(15)	47.90(11)
C(10)-Si(1)-C(12)-C(15)	167.71(10)
C(11)-Si(1)-C(12)-C(15)	-69.60(11)
O(3)-Si(1)-C(12)-C(14)	167.84(10)
C(10)-Si(1)-C(12)-C(14)	-72.34(11)
C(11)-Si(1)-C(12)-C(14)	50.34(12)

Symmetry transformations used to generate equivalent atoms:

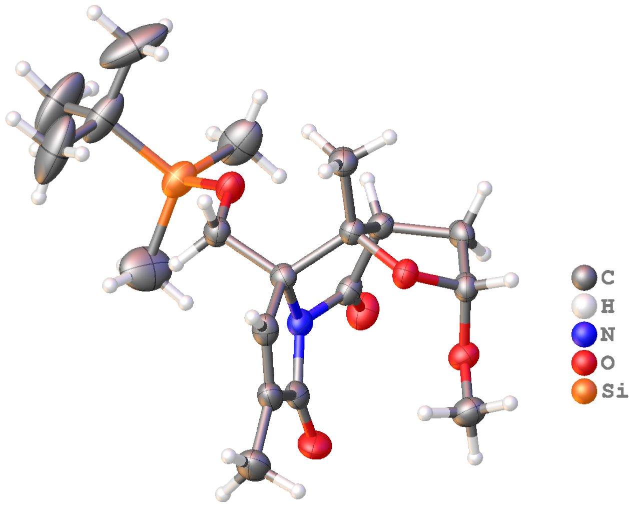
Table S19. Hydrogen bonds for **16** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2)...O(1)#1	0.810(18)	1.907(19)	2.6985(13)	165.3(17)
N(1)-H(1)...O(1)#2	0.833(16)	2.009(16)	2.8412(14)	176.3(15)

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z-1/2   #2 -x+2,-y,-z+2

Crystal data for 24 (racemic); CCDC 1879958



Experimental. Single colorless plate-shaped crystals of **24** were used as received. A suitable crystal (0.38×0.15×0.06) mm^3 was selected and mounted on a nylon loop with paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at T = 173(2) K during data collection. Using **Olex2**,[6] the structure was solved with the **ShelXT**[9] structure solution program, using the Intrinsic Phasing solution method. The model

Compound	24 (racemic)
Formula	$C_{19}H_{31}NO_5Si$
$D_{calc.}$/ g cm^{-3}	1.215
μ/mm^{-1}	0.140
Formula Weight	381.54
Color	colorless
Shape	plate
Size/mm^3	0.38×0.15×0.06
T/K	173(2)
Crystal System	triclinic
Space Group	P-1
a/Å	7.1927(8)
b/Å	7.5787(8)
c/Å	21.102(2)
α/°	83.7720(10)
β/°	82.5490(10)
γ/°	66.3970(10)
V/Å^3	1043.13(19)
Z	2
Z'	1

was refined with version of **XL**[9] using Least Squares minimisation.

Crystal Data. $C_{19}H_{31}NO_5Si$, M_r = 381.54, triclinic, P-1 (No. 2), a = 7.1927(8) Å, b = 7.5787(8) Å, c = 21.102(2) Å, α = 83.7720(10)°, β = 82.5490(10)°, γ = 66.3970(10)°, V = 1043.13(19) Å^3, T = 173(2) K, Z = 2, Z' = 1, μ(MoK$_\alpha$) = 0.140, 15883 reflections measured, 4145 unique (R_{int} = 0.0465) which were used in all calculations. The final wR_2 was 0.1580 (all data) and R_1 was 0.0547 (I > 2(I)).

Wavelength/Å	0.710730
Radiation type	MoK$_\alpha$
Θ_{min}/°	1.950
Θ_{max}/°	26.142
Measured Refl.	15883
Independent Refl.	4145
Reflections Used	2893
R_{int}	0.0465
Parameters	243
Restraints	0
Largest Peak	0.743
Deepest Hole	-0.271
GooF	1.063
wR_2 (all data)	0.1580
wR_2	0.1404
R_1 (all data)	0.0796
R_1	0.0547

Structure Quality Indicators

Reflection:	d min (Mo) 0.81	I/σ 12.0	Rint 4.65%	complete 100%
Refinement:	Shift 0.000	Max Peak 0.7	Min Peak -0.3	GooF 1.063

A colorless plate-shaped crystal with dimensions 0.38×0.15×0.06 mm^3 was mounted on a nylon loop with paratone oil. Data were collected using a Bruker APEX-II CCD diffractometer equipped with an Oxford Cryosystems low-temperature device, operating at T = 173(2) K.

Data were measured using ω of -0.50° per frame for 299.34 s using MoK$_\alpha$ radiation (sealed tube, 50 kV, 40 mA). The total number of runs and images was based on the strategy calculation from the program **COSMO**.[7] The actually achieved resolution was Θ = 26.142.

Cell parameters were retrieved using the **SAINT**[8] software and refined using **SAINT**[8] on 5215 reflections, 33% of the observed reflections. Data reduction was performed using the **SAINT**[8] software which corrects for Lorentz polarisation. The final completeness is 99.90 out to 26.142 in Θ. A multi-scan absorption correction was performed using SADABS-2014/5 (Bruker,2014/5) was used for absorption correction. wR_2 was 0.0606 before and 0.0512 after correction. The Ratio of minimum to maximum transmission is 0.9066. The λ/2 correction factor is 0.00150. The absorption coefficient μ of this material is 0.140 mm^{-1} at this wavelength (λ = 0.71073Å) and the minimum and maximum transmissions are 0.6757 and 0.7453. SADABS-2014/5 (Bruker,2014/5) was used for absorption correction. wR_2 was 0.0606 before and 0.0512 after correction. The Ratio of minimum to maximum transmission is 0.9066. The $\lambda/2$ correction factor is 0.00150.

The structure was solved in the space group *P*-1 (# 2) by Intrinsic Phasing using the **ShelXT**[9] structure solution program. The structure was refined by Least Squares using version 2014/6 of **XL**[9] incorporated in **Olex2**.[6] All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

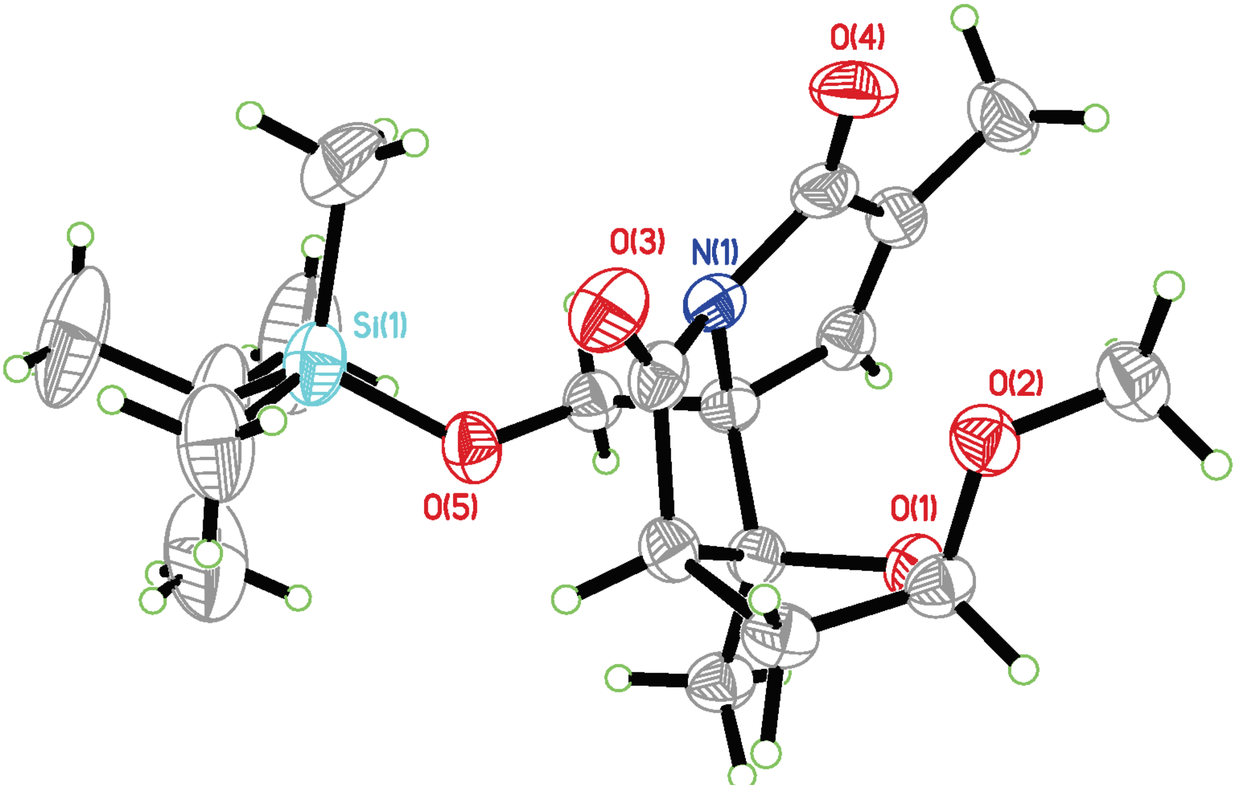


Figure S7. X-ray structure of **24** (view 1).

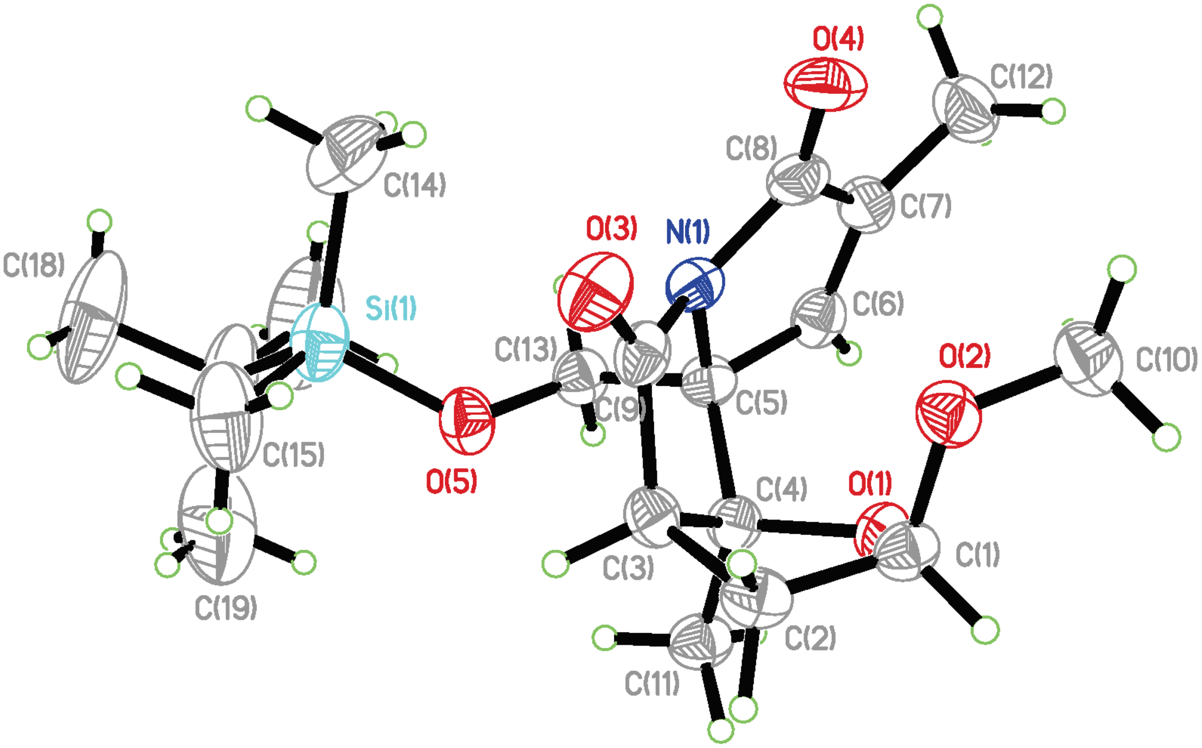


Figure S8. X-ray structure of **24** (view 2).

Table S20: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **24**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
Si1	5874.7(11)	7679.7(12)	3600.4(3)	45.6(2)
O1	9017(2)	4166(2)	1153.2(7)	30.7(4)
O2	12240(2)	4302(2)	1025.7(7)	34.8(4)
O3	11576(2)	5871(2)	2472.6(8)	42.2(4)
O4	10562(3)	9004(2)	1330.2(9)	46.7(5)
O5	6037(2)	6652(2)	2936.2(7)	37.8(4)
N1	8731(3)	7323(2)	1907.3(9)	29.0(4)
C1	11146(3)	3114(3)	1188.5(11)	31.6(5)
C2	11416(3)	2408(3)	1882.7(11)	33.6(5)
C3	9658(3)	4025(3)	2229.3(11)	30.1(5)
C4	7955(3)	4652(3)	1783(1)	29.2(5)
C5	6991(3)	6884(3)	1800.4(10)	28.2(5)
C6	6290(3)	8085(3)	1199.8(11)	33.0(5)
C7	7428(4)	9081(3)	990.3(11)	35.5(6)
C8	9118(4)	8541(3)	1406.3(12)	34.4(5)
C9	10180(3)	5781(3)	2236.8(10)	31.1(5)
C10	12161(4)	5057(4)	378.5(12)	43.5(6)
C11	6461(3)	3687(3)	1921.4(12)	36.3(6)
C12	7228(4)	10534(4)	440.4(13)	50.7(7)

C13	5312(3)	7603(3)	2348.5(10)	32.9(5)
C14	6444(7)	9874(6)	3406.9(18)	81.9(11)
C15	7853(5)	5821(5)	4060.5(15)	70(1)
C16	3272(4)	8301(6)	4033.4(14)	68.6(10)
C17	1671(5)	9814(8)	3628.5(19)	107.9(17)
C18	3191(6)	9092(8)	4680.3(17)	106.1(17)
C19	2843(7)	6460(8)	4149.4(19)	110.5(17)

Table S21: Anisotropic Displacement Parameters (×10^4) **24**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots +2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si1	39.2(4)	62.8(5)	35.3(4)	-9.3(3)	0.7(3)	-20.2(4)
O1	27.4(8)	32.2(8)	31.0(8)	-6.5(6)	-0.5(6)	-9.8(6)
O2	32.2(8)	39.4(9)	35.1(9)	-2.6(7)	-0.1(7)	-17.2(7)
O3	32.5(9)	51.5(11)	45.7(10)	-11.6(8)	-7.8(7)	-16.4(8)
O4	47.8(10)	36.7(9)	63.5(12)	-7.6(8)	6.6(9)	-27.3(8)
O5	37.0(9)	39.6(9)	30.4(9)	-2.1(7)	1.2(7)	-9.5(7)
N1	27.5(9)	28.1(9)	32.6(10)	-6.7(8)	-0.1(8)	-11.6(8)
C1	26.5(11)	27.4(11)	38.6(13)	-6.4(9)	-0.4(9)	-7.9(9)
C2	27.2(11)	27.6(11)	42.3(14)	0.3(10)	-3.5(10)	-7.5(9)
C3	27.4(11)	32.3(12)	29.0(12)	-0.4(9)	-0.6(9)	-11.1(9)
C4	28.1(11)	28.4(11)	29.9(12)	-3.2(9)	0.1(9)	-10.2(9)
C5	25.5(11)	28.0(11)	32.0(12)	-2.3(9)	-3.3(9)	-11.3(9)
C6	31.7(12)	31.5(12)	31.6(12)	-4.6(10)	-4.7(9)	-6.9(10)
C7	40.0(13)	25.5(11)	34.5(13)	-3.3(10)	3.9(10)	-7.9(10)
C8	36.4(13)	23.9(11)	41.6(14)	-10.5(10)	6.3(10)	-11.5(10)
C9	26.2(11)	37.8(13)	28.9(12)	-8.8(10)	2.0(9)	-11.9(10)
C10	42.3(14)	47.5(15)	39.8(14)	0.8(11)	2.9(11)	-19.7(12)
C11	32.9(12)	33.5(12)	44.6(14)	-5.6(10)	-0.1(10)	-15.4(10)
C12	59.6(17)	40.1(14)	45.2(16)	5.2(12)	2.4(13)	-16.2(13)

C13	30.8(12)	31.9(12)	32.5(12)	-3.1(10)	-1.3(10)	-8.8(10)
C14	113(3)	93(3)	68(2)	-23(2)	-6(2)	-67(2)
C15	53.0(18)	103(3)	46.4(18)	1.4(17)	-11.8(14)	-22.4(18)
C16	39.0(16)	125(3)	40.6(17)	-28.9(18)	6.0(13)	-28.1(18)
C17	42.7(19)	167(4)	76(3)	-39(3)	2.4(17)	4(2)
C18	65(2)	197(5)	58(2)	-65(3)	19.5(18)	-46(3)
C19	95(3)	215(6)	66(2)	-10(3)	15(2)	-114(4)

Table S22: Bond Lengths in Å for **24**.

Atom	Atom	Length/Å
Si1	O5	1.6449(17)
Si1	C14	1.859(4)
Si1	C15	1.846(3)
Si1	C16	1.872(3)
O1	C1	1.423(3)
O1	C4	1.450(3)
O2	C1	1.406(3)
O2	C10	1.422(3)
O3	C9	1.205(3)
O4	C8	1.210(3)
O5	C13	1.415(3)
N1	C5	1.466(3)
N1	C8	1.401(3)
N1	C9	1.404(3)
C1	C2	1.513(3)
C2	C3	1.533(3)
C3	C4	1.533(3)
C3	C9	1.523(3)
C4	C5	1.553(3)

C4	C11	1.509(3)
C5	C6	1.495(3)
C5	C13	1.530(3)
C6	C7	1.328(3)
C7	C8	1.488(3)
C7	C12	1.489(3)
C16	C17	1.535(5)
C16	C18	1.535(4)
C16	C19	1.534(6)

Table S23: Bond Angles in ° for **24**.

Atom	Atom	Atom	Angle/°
O5	Si1	C14	109.58(13)
O5	Si1	C15	103.70(13)
O5	Si1	C16	110.02(12)
C14	Si1	C16	110.77(18)
C15	Si1	C14	110.93(18)
C15	Si1	C16	111.60(15)
C1	O1	C4	111.33(16)
C1	O2	C10	113.84(18)
C13	O5	Si1	126.46(14)
C8	N1	C5	111.01(18)
C8	N1	C9	126.95(18)
C9	N1	C5	111.81(17)
O1	C1	C2	106.30(17)
O2	C1	O1	111.67(17)
O2	C1	C2	107.13(18)
C1	C2	C3	101.61(17)
C4	C3	C2	103.59(17)
C9	C3	C2	110.52(18)
C9	C3	C4	105.08(17)

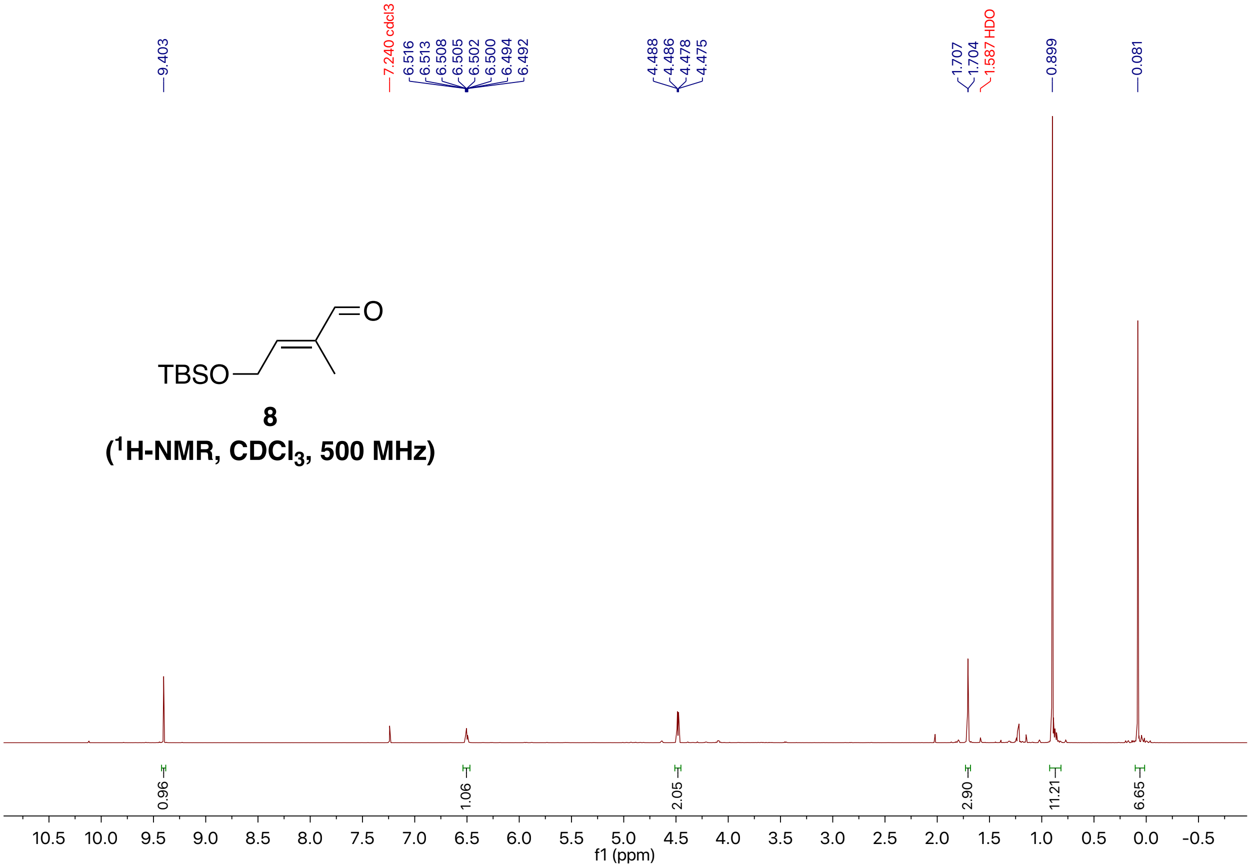
O1	C4	C3	104.42(16)
O1	C4	C5	108.23(17)
O1	C4	C11	108.55(18)
C3	C4	C5	103.74(17)
C11	C4	C3	116.22(19)
C11	C4	C5	114.95(18)
N1	C5	C4	102.37(16)
N1	C5	C6	102.37(17)
N1	C5	C13	109.52(17)
C6	C5	C4	119.14(18)
C6	C5	C13	109.09(17)
C13	C5	C4	113.21(18)
C7	C6	C5	111.5(2)
C6	C7	C8	109.1(2)
C6	C7	C12	130.3(2)
C8	C7	C12	120.6(2)
O4	C8	N1	126.2(2)
O4	C8	C7	128.1(2)
N1	C8	C7	105.71(19)
O3	C9	N1	125.0(2)
O3	C9	C3	127.6(2)
O5	C13	C5	110.00(17)

C17	C16	Si1	109.9(2)
C18	C16	Si1	109.7(2)
C18	C16	C17	109.8(3)
C19	C16	Si1	108.5(3)
C19	C16	C17	109.7(3)
C19	C16	C18	109.2(3)

Table S24: Hydrogen Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **24**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

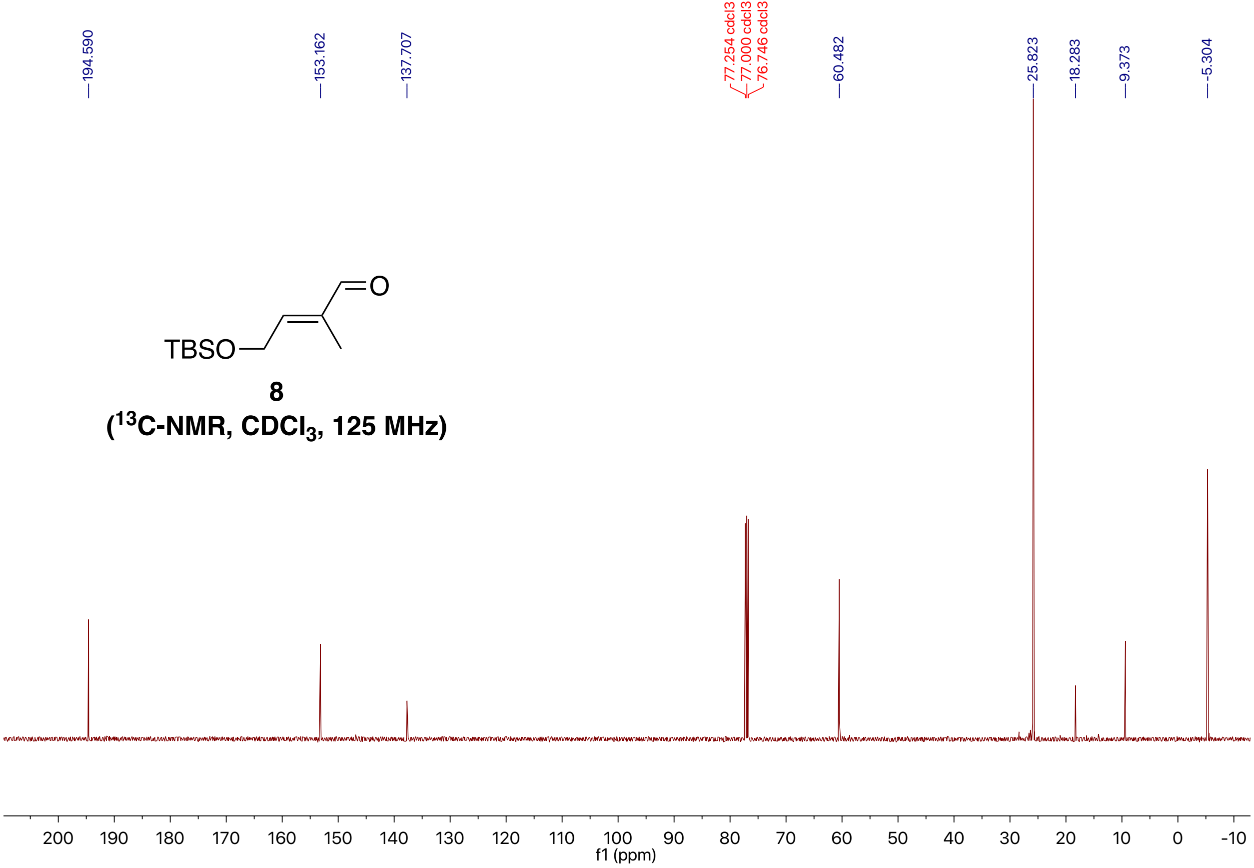
Atom	**x**	**y**	**z**	U_{eq}
H1	11670	2000	908	38
H2A	12753	2283	2001	40
H2B	11280	1154	1976	40
H3	9240	3581	2668	36
H6	5171	8129	994	40
H10A	12523	4004	94	65
H10B	13126	5688	279	65
H10C	10779	5999	316	65
H11A	5450	4184	1608	54
H11B	5772	3958	2353	54
H11C	7193	2290	1893	54
H12A	8335	9987	105	76
H12B	7303	11687	585	76
H12C	5914	10883	270	76
H13A	4877	9013	2370	39
H13B	4116	7350	2269	39
H14A	7693	9564	3115	123
H14B	6629	10330	3802	123
H14C	5308	10885	3202	123

H15A	7581	4644	4127	105
H15B	7834	6296	4476	105
H15C	9193	5539	3822	105
H17A	1649	9264	3232	162
H17B	2017	10946	3525	162
H17C	326	10200	3870	162
H18A	4295	8171	4921	159
H18B	1877	9285	4925	159
H18C	3348	10326	4608	159
H19B	1495	6756	4384	166
H19C	3883	5489	4401	166



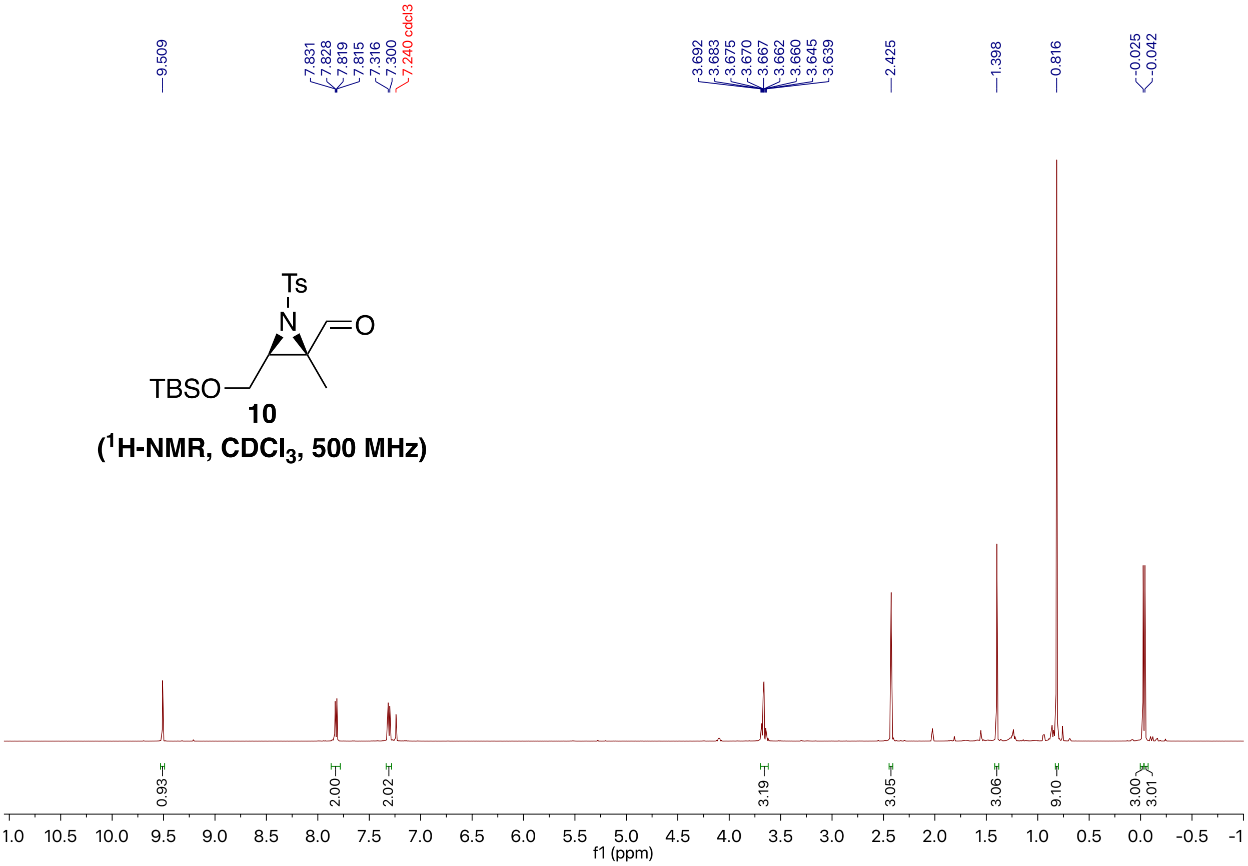
8

(^{1}H-NMR, CDCl$_3$, 500 MHz)



8

(^{13}C-NMR, CDCl$_3$, 125 MHz)



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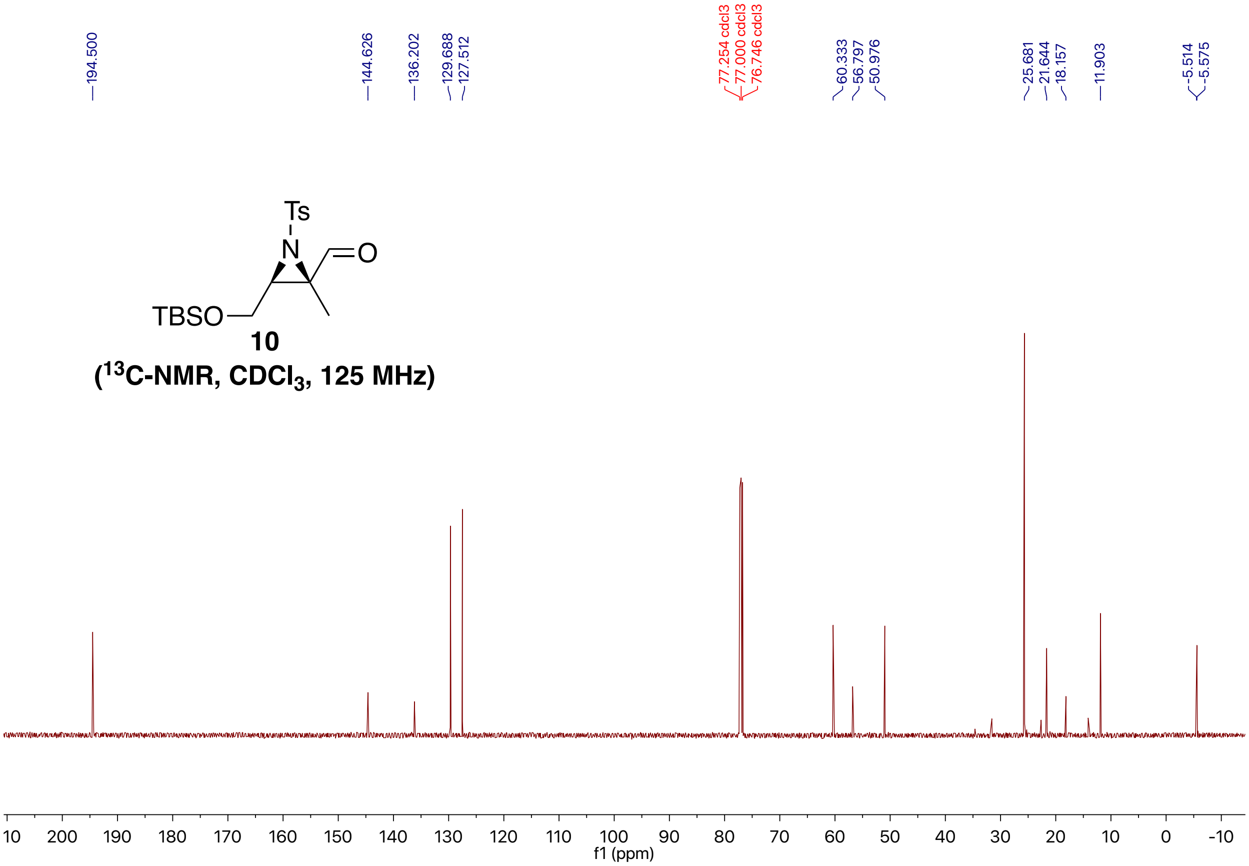

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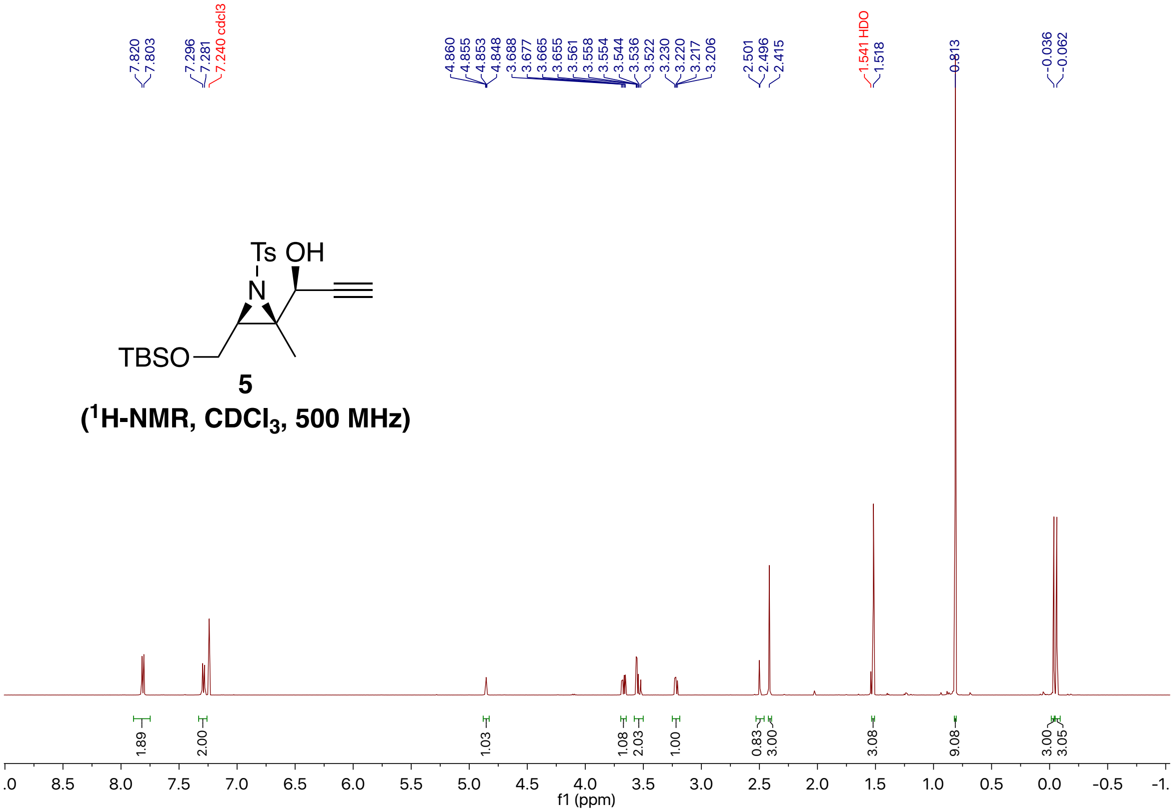

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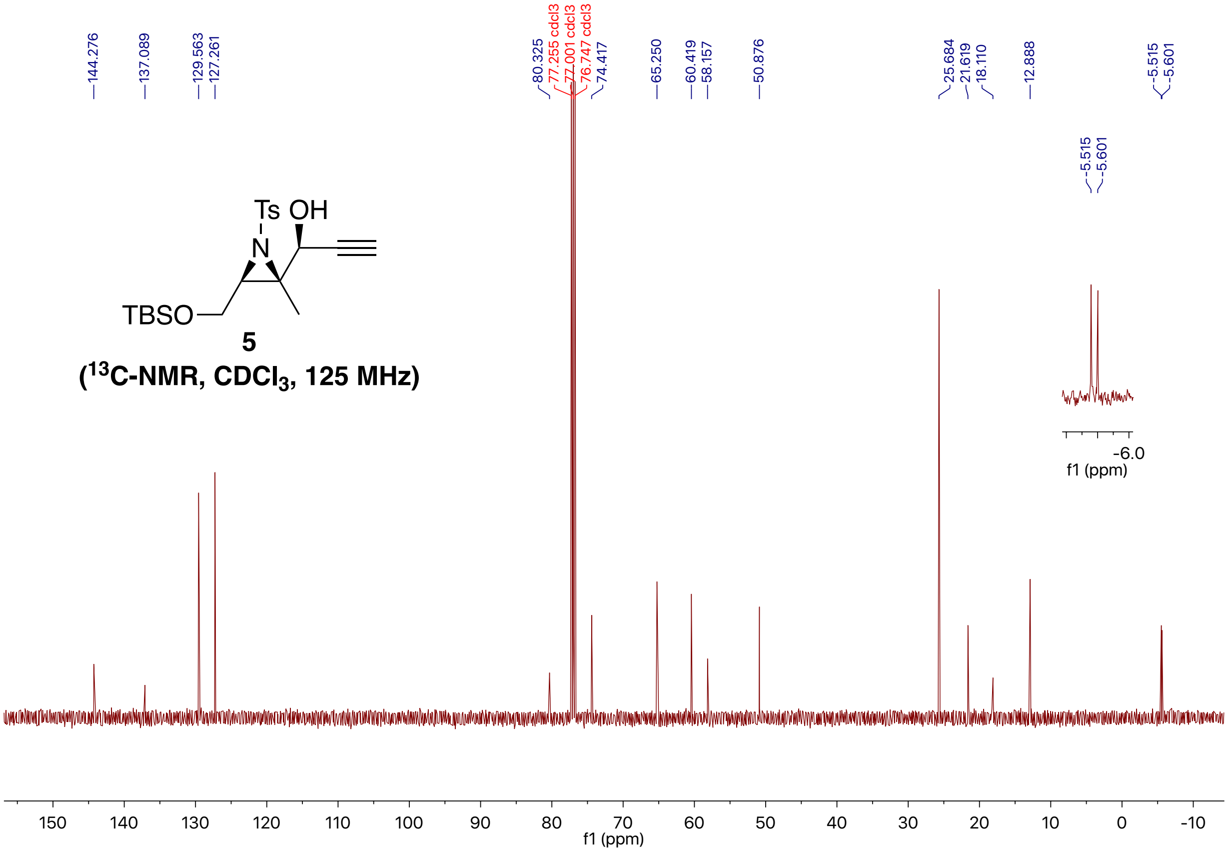

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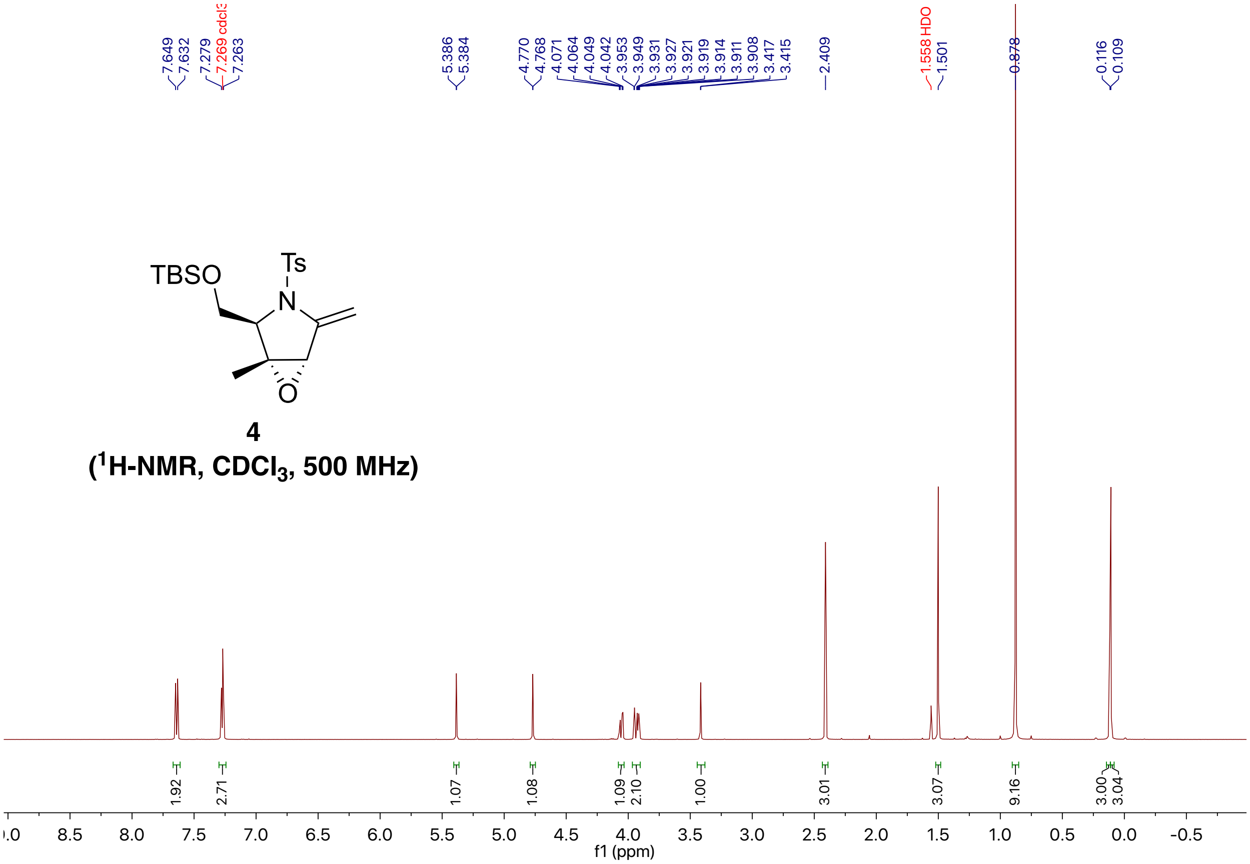

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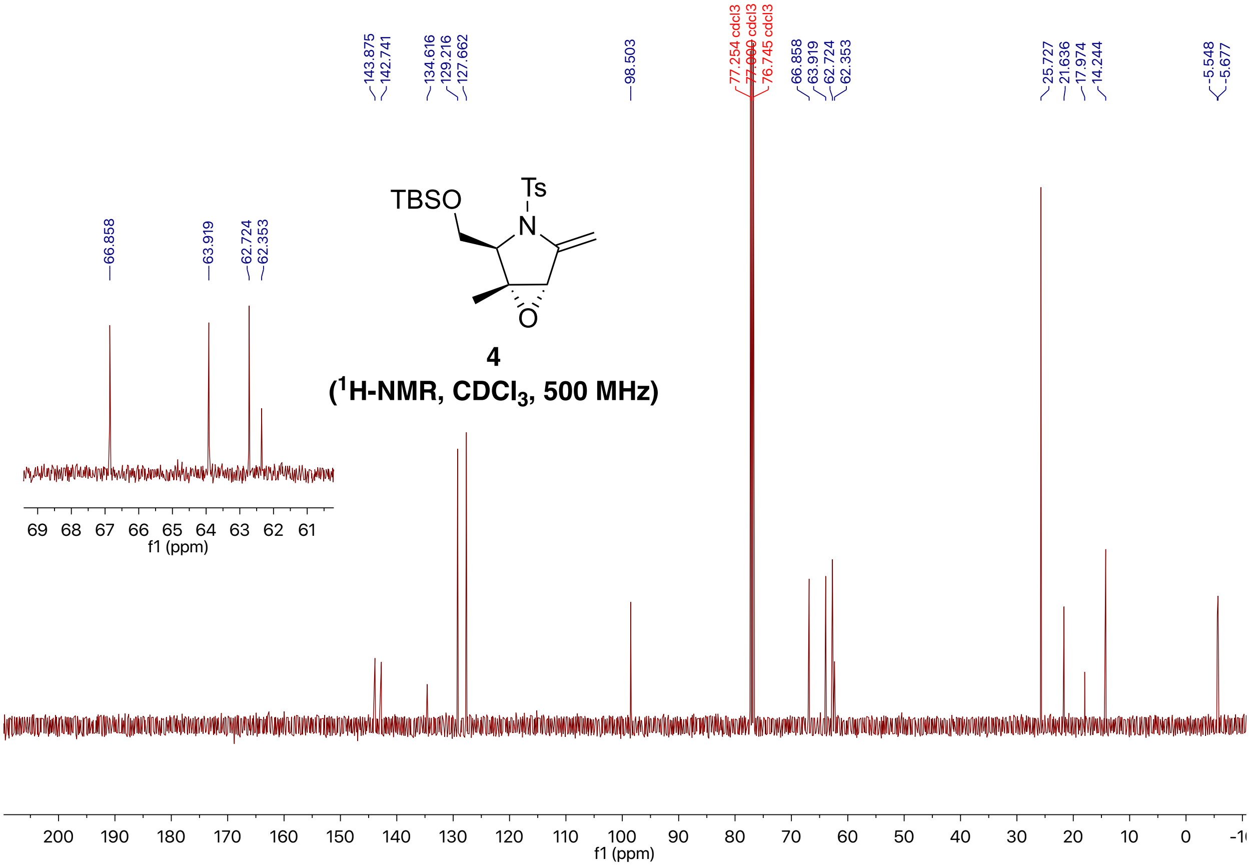

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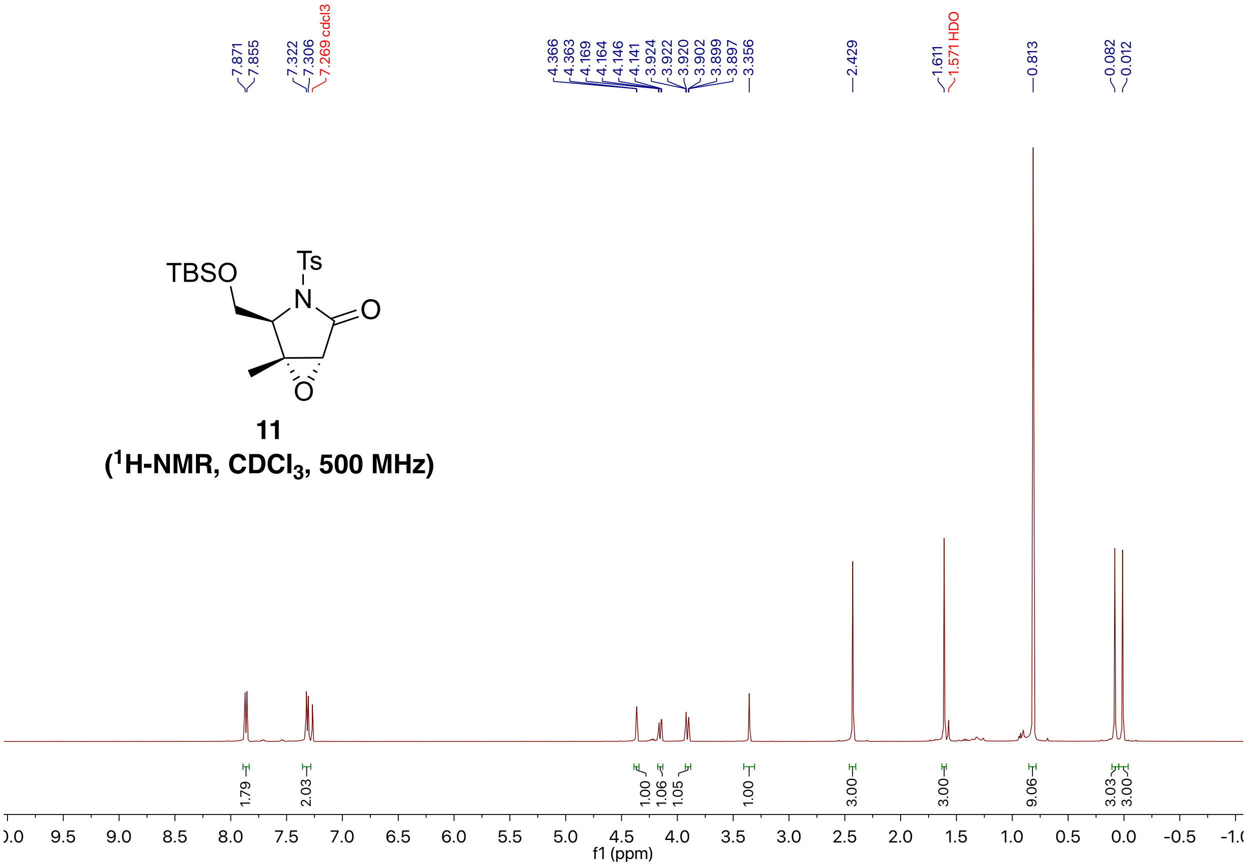
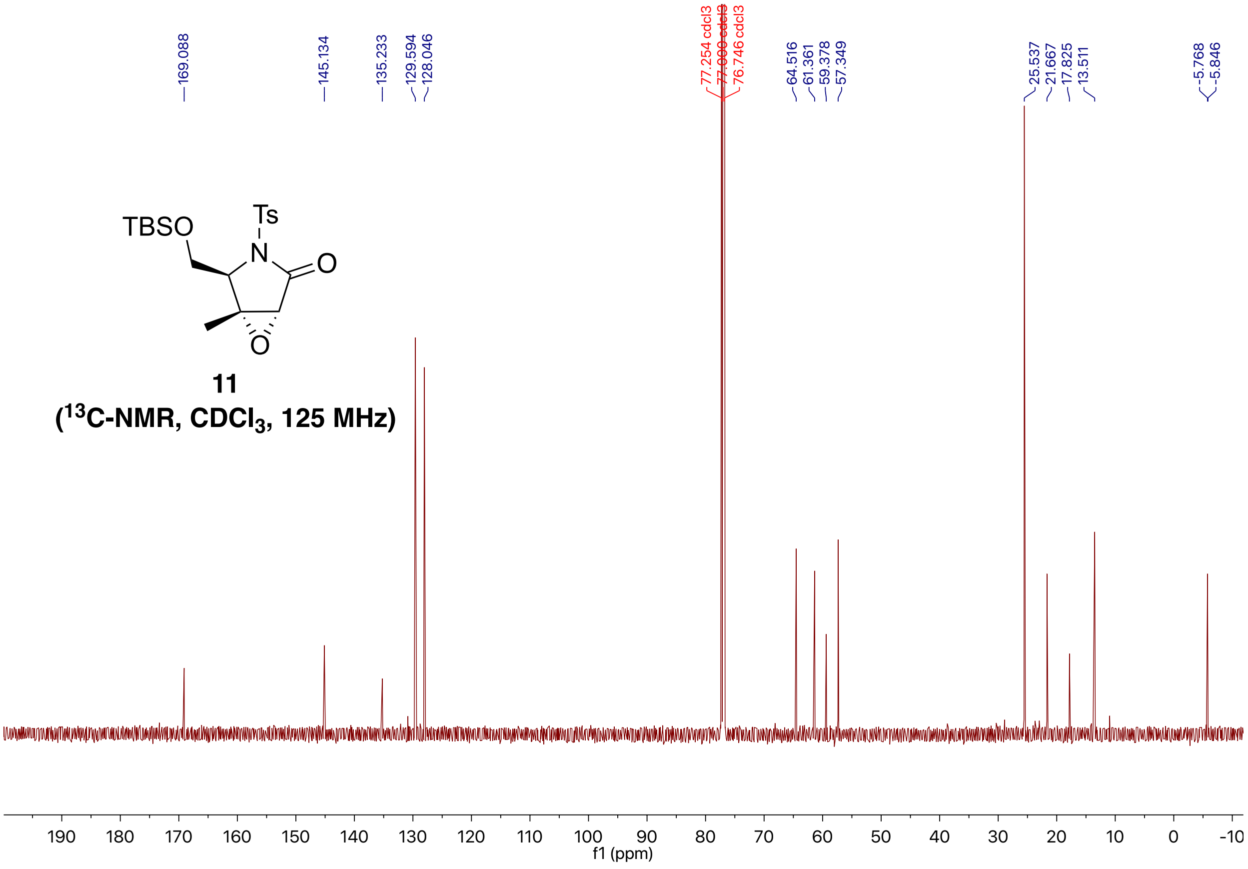


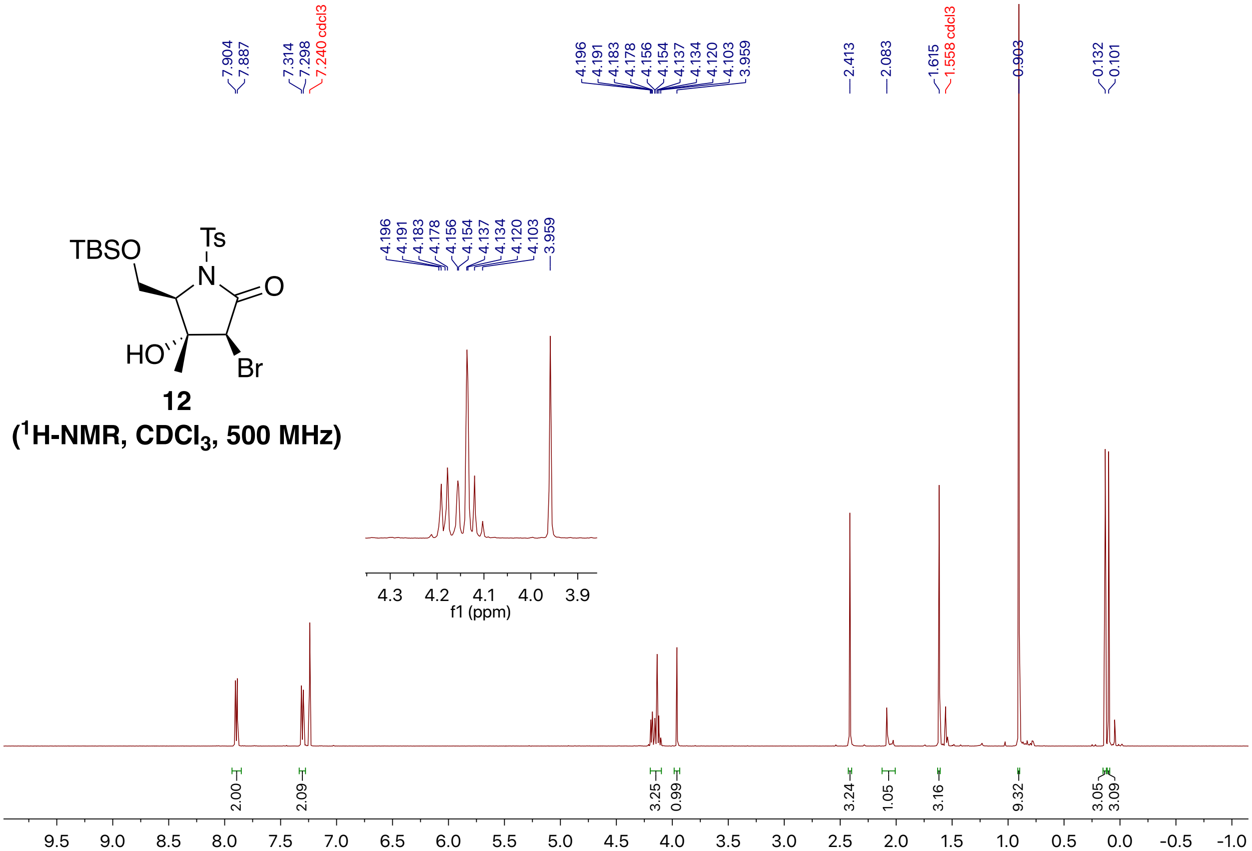
11

(^{1}H-NMR, CDCl$_3$, 500 MHz)



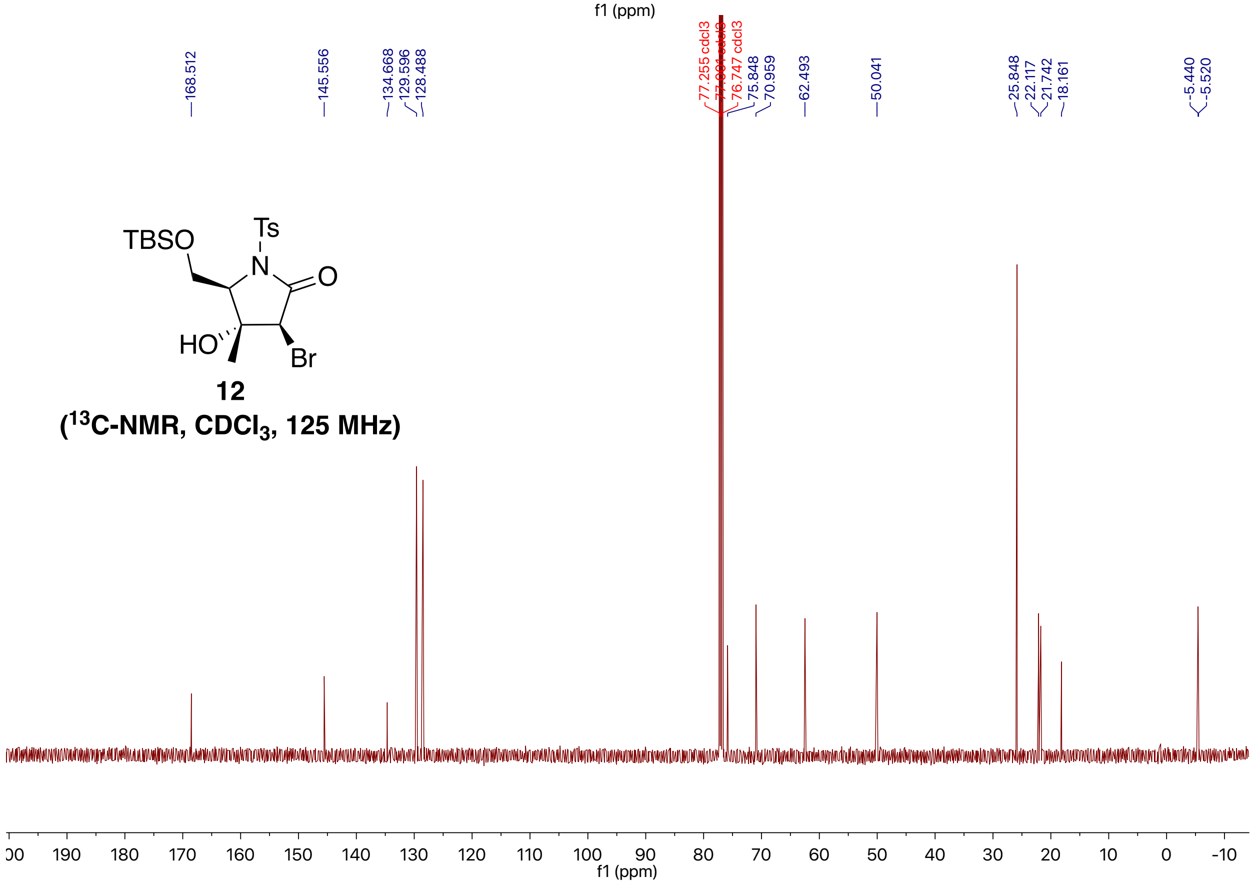
11

(^{13}C-NMR, CDCl$_3$, 125 MHz)



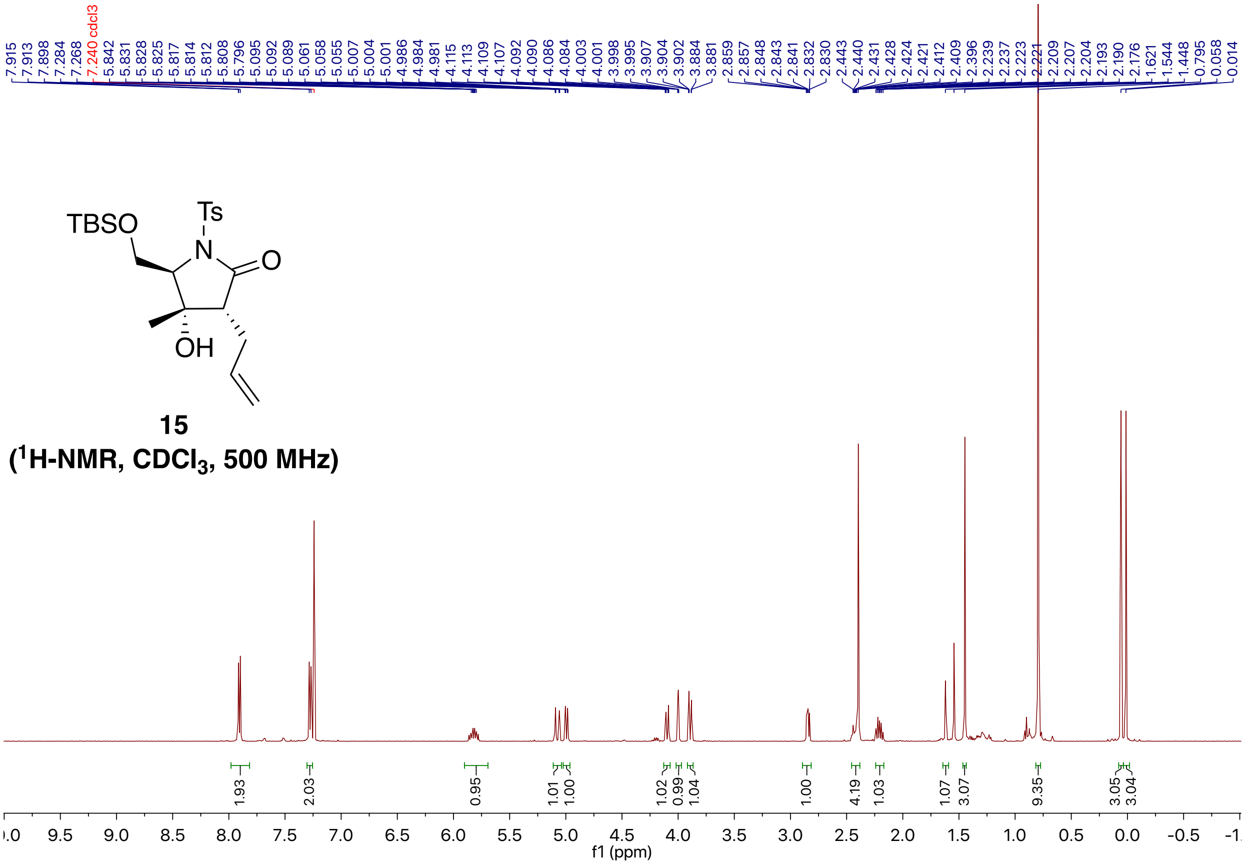
12

(^{1}H-NMR, CDCl$_3$, 500 MHz)



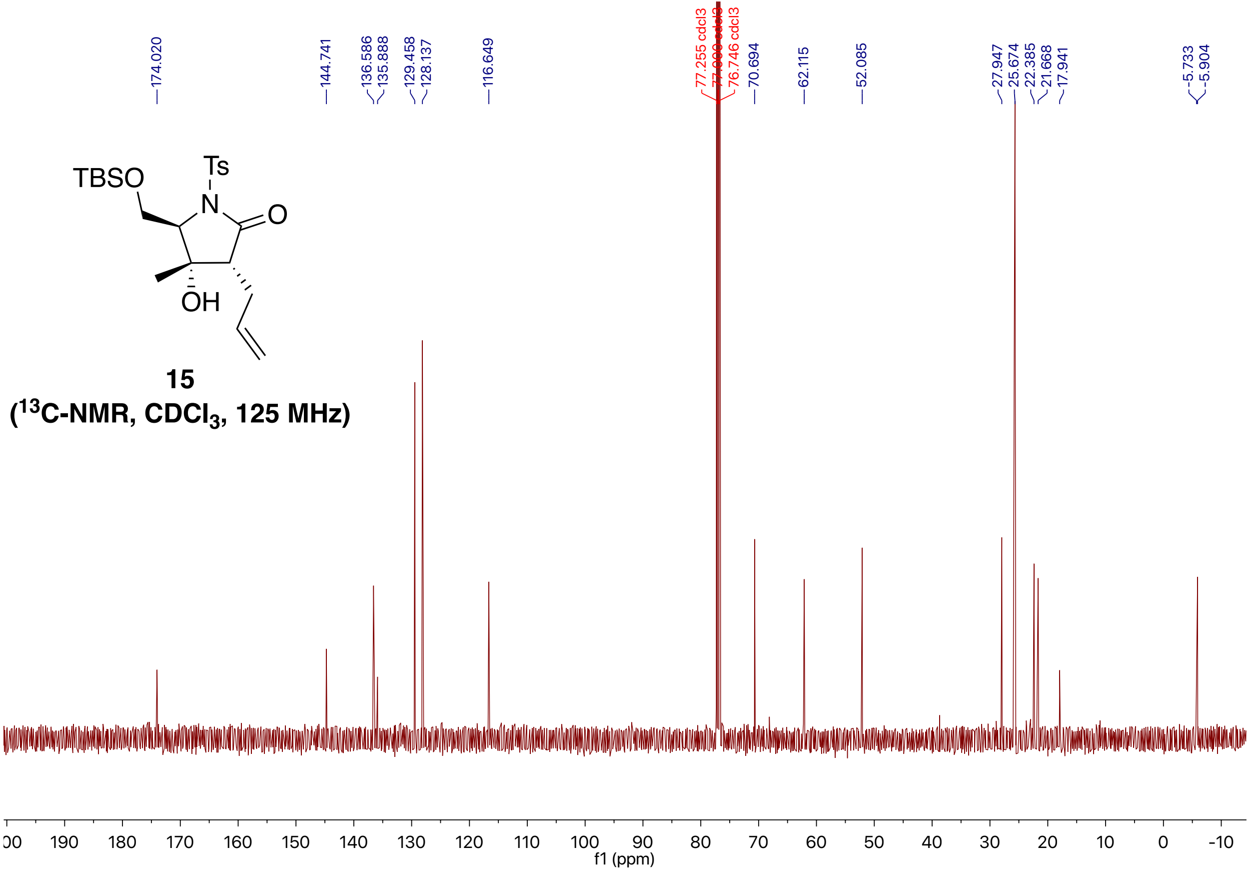
12

(^{13}C-NMR, CDCl$_3$, 125 MHz)



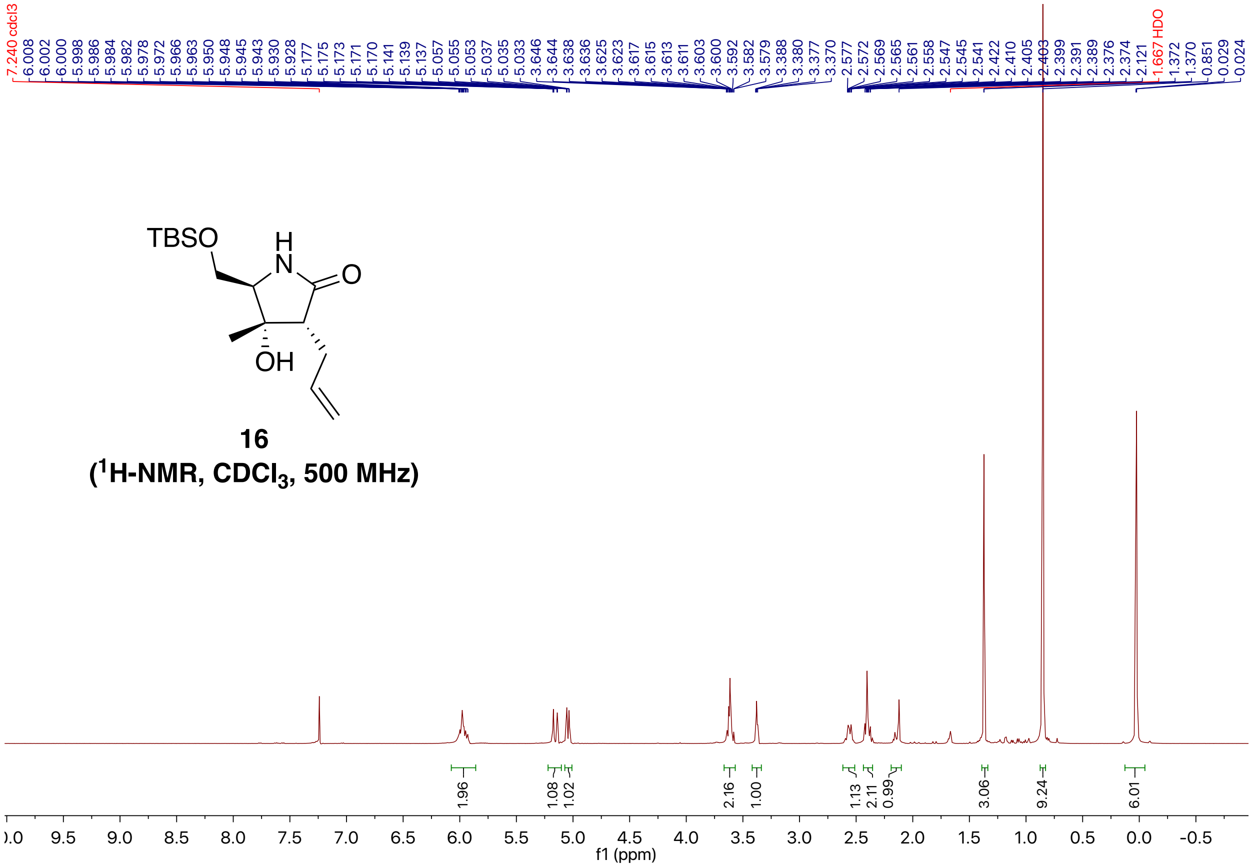
15

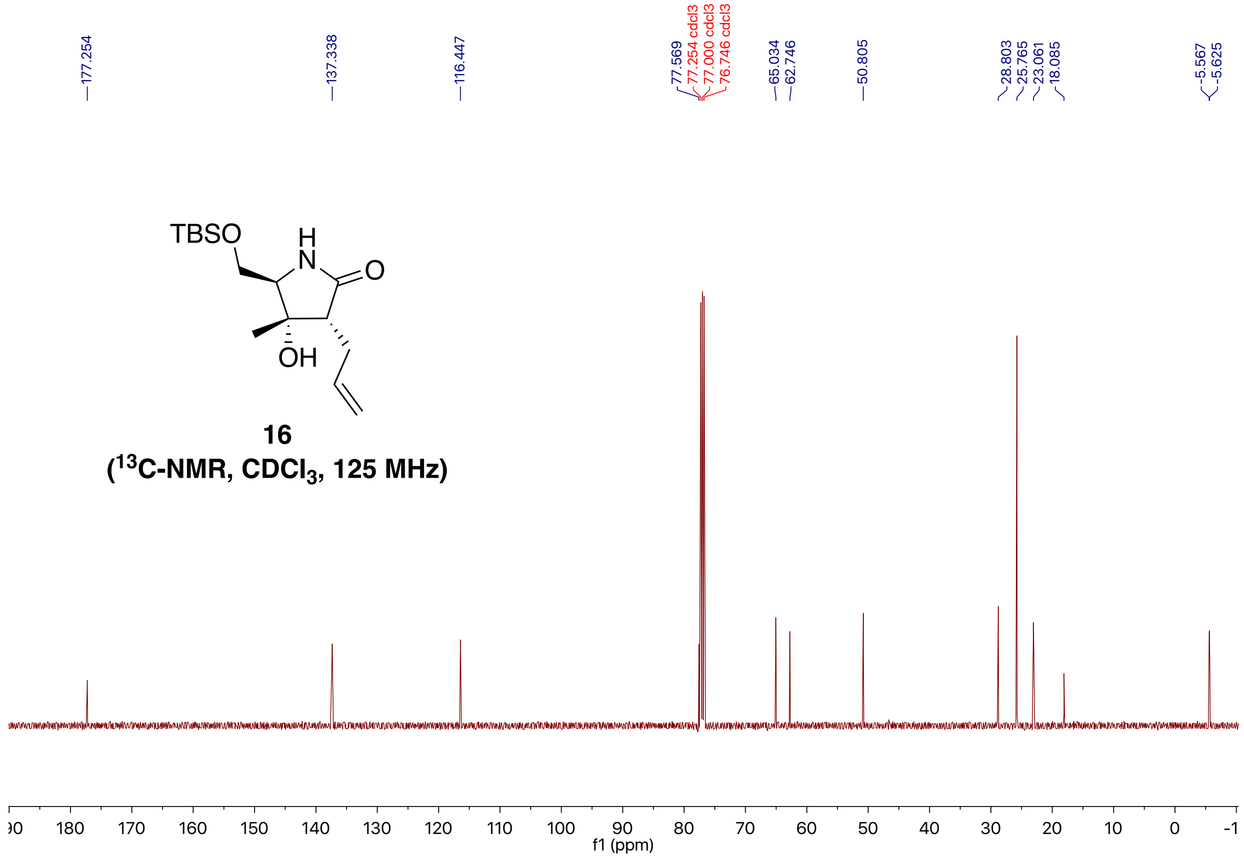
(^{1}H-NMR, CDCl$_3$, 500 MHz)

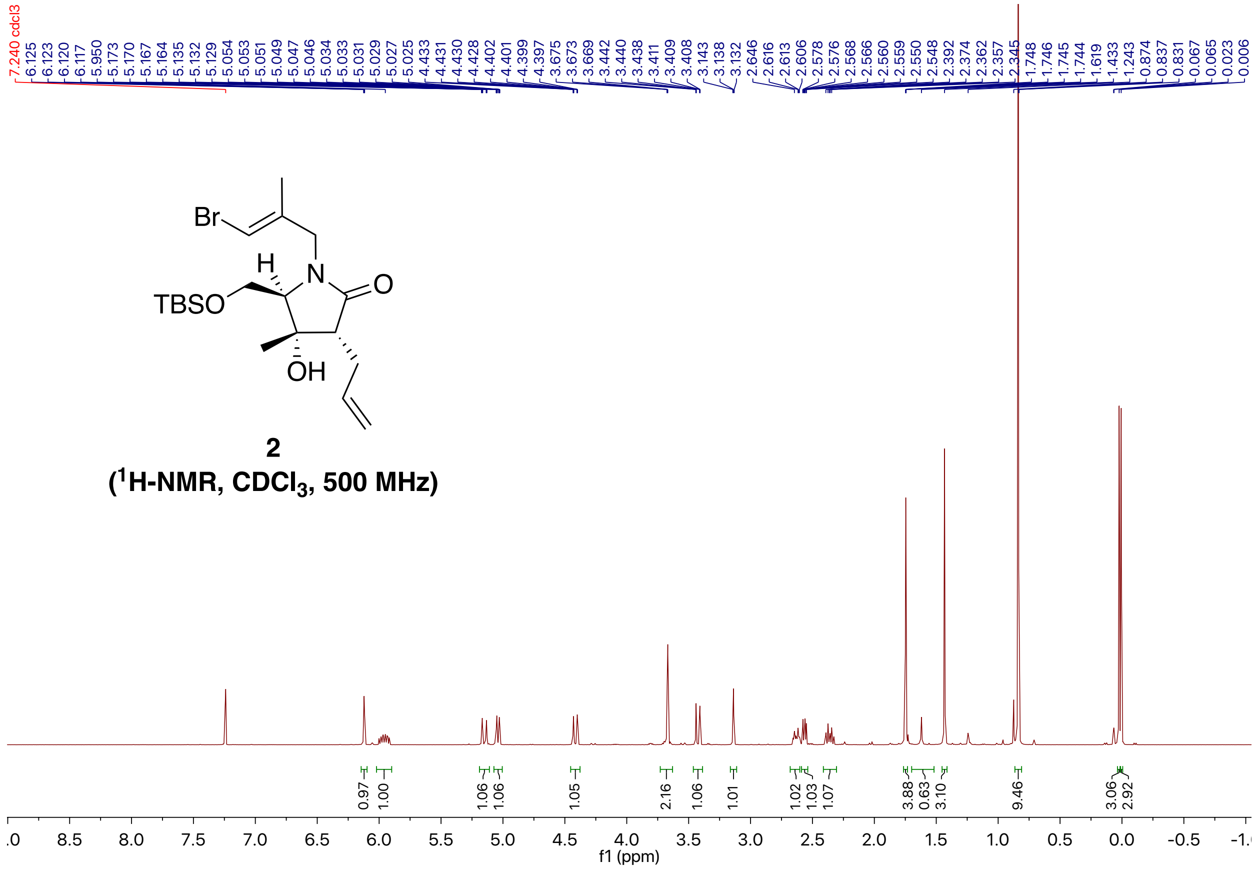


15

(^{13}C-NMR, CDCl$_3$, 125 MHz)

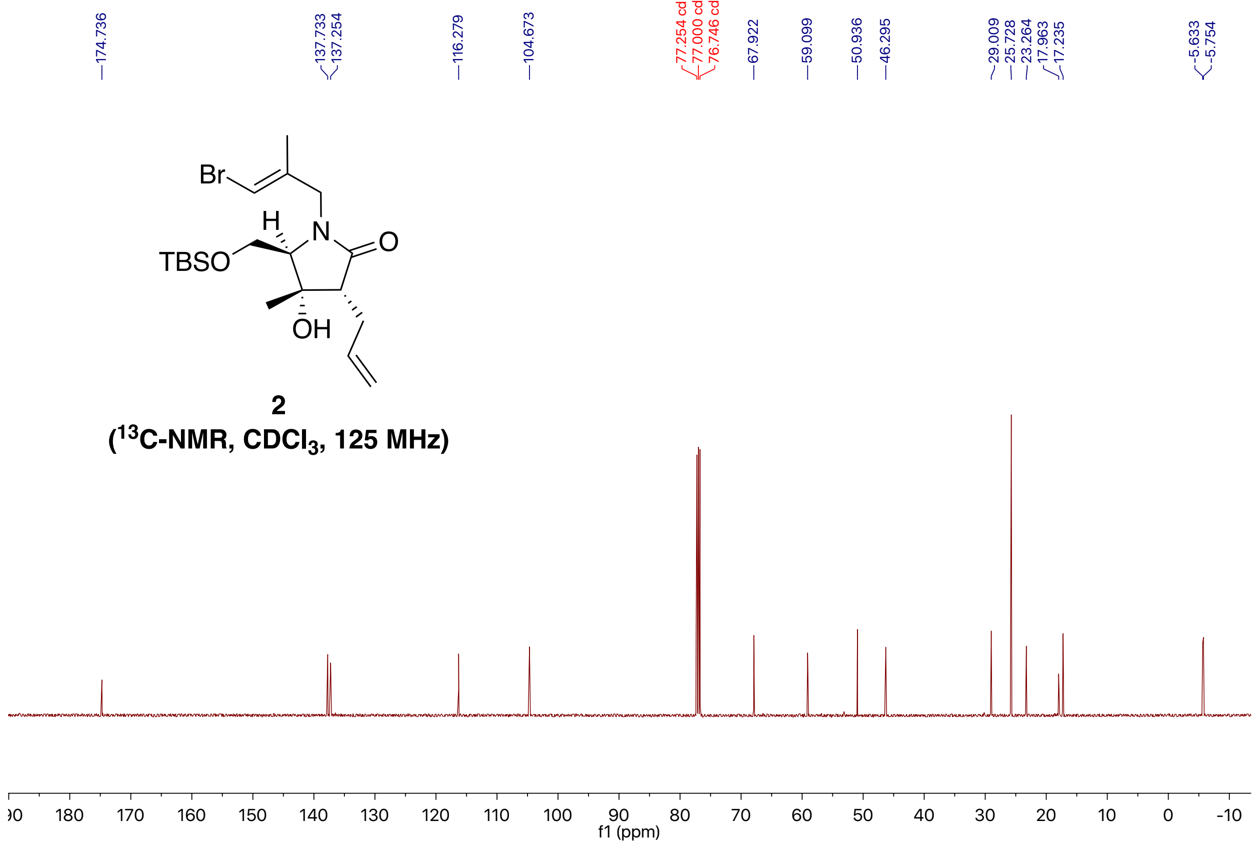

16
(^{1}H-NMR, CDCl$_3$, 500 MHz)


16
(^{13}C-NMR, CDCl$_3$, 125 MHz)



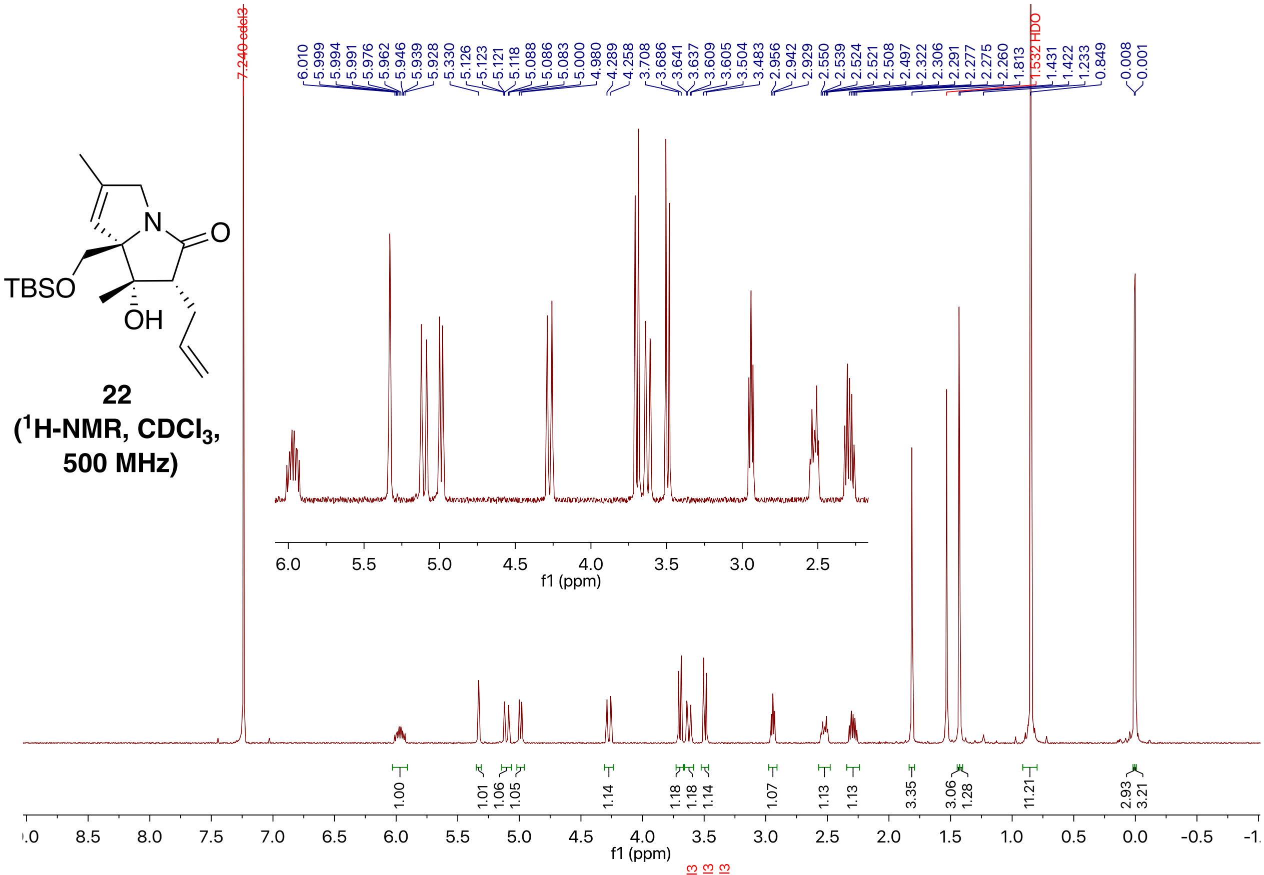
2

(^{1}H-NMR, CDCl$_3$, 500 MHz)



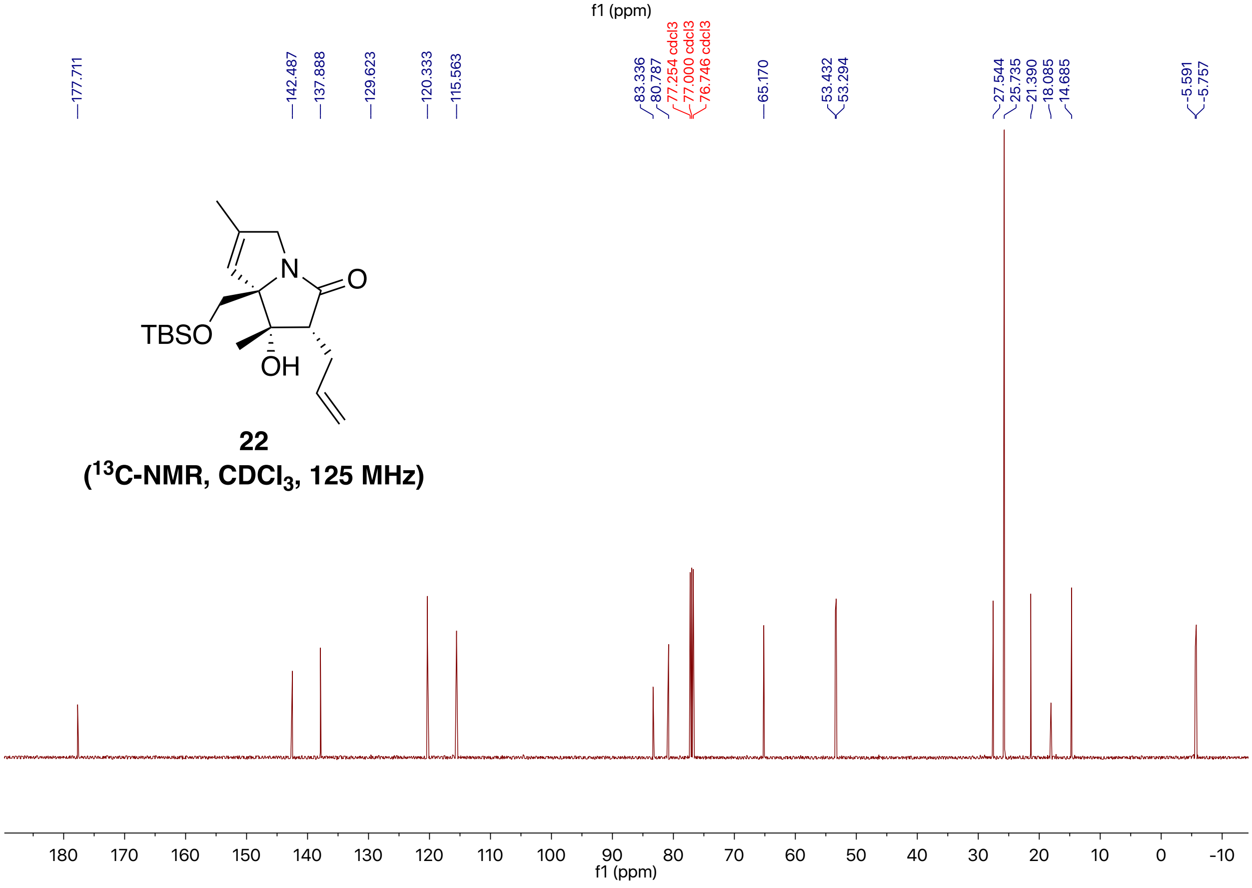
2

(^{13}C-NMR, CDCl$_3$, 125 MHz)



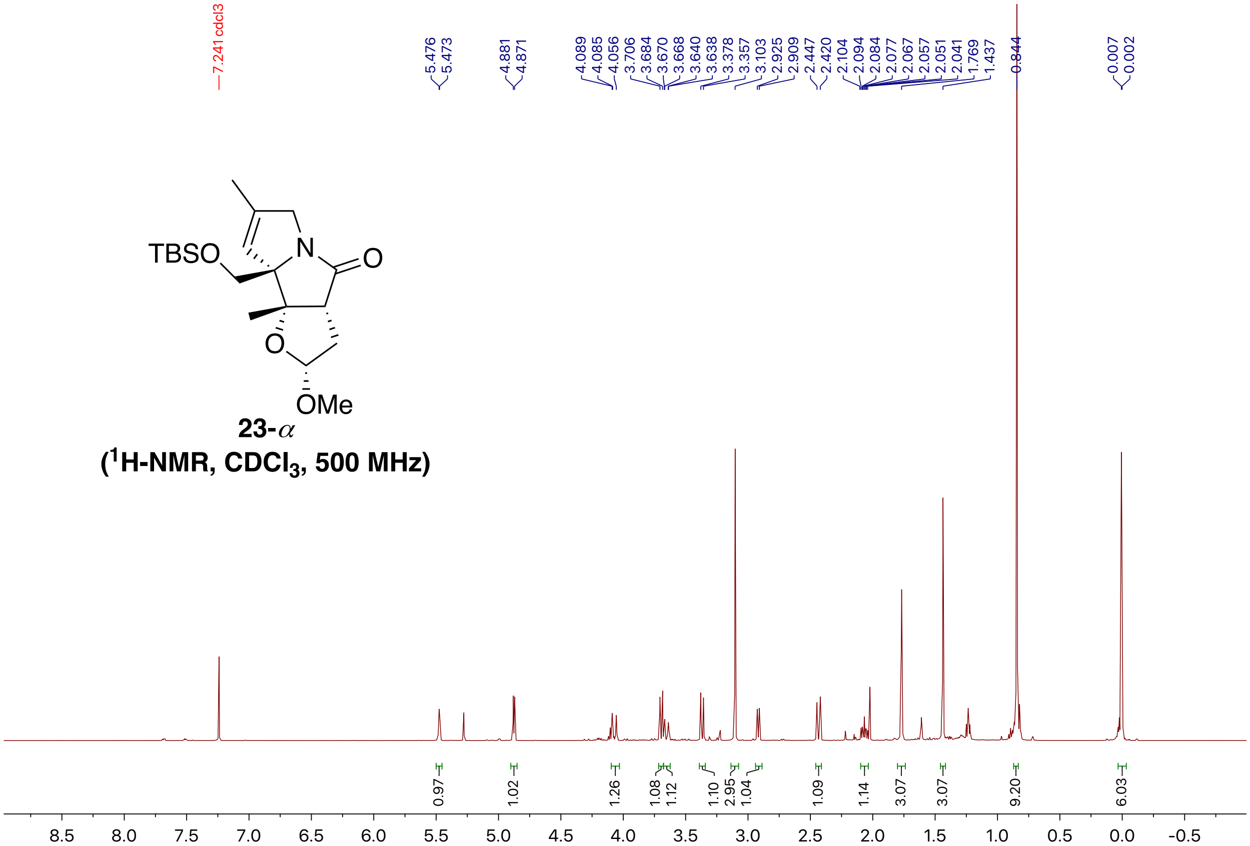
22

(^{1}H-NMR, CDCl$_3$, 500 MHz)



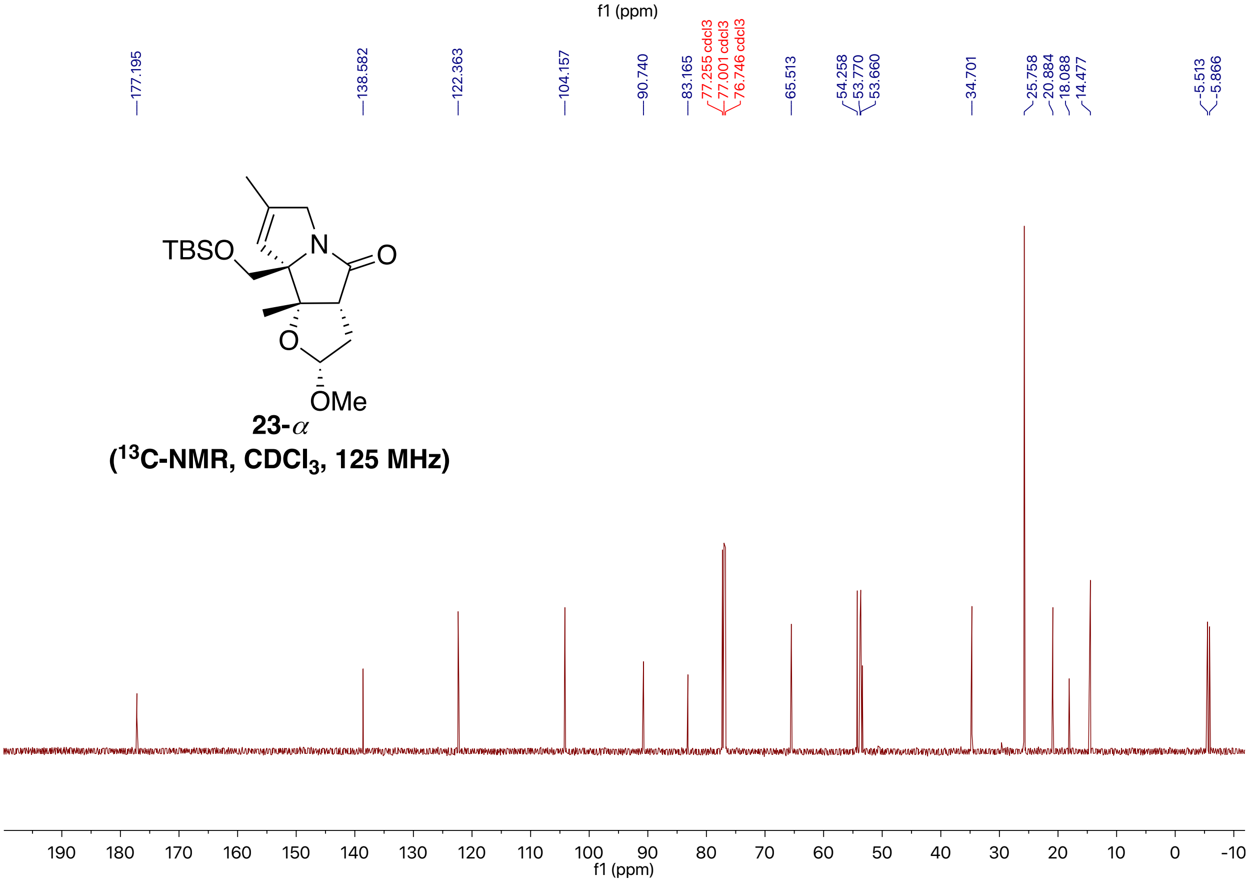
22

(^{13}C-NMR, CDCl$_3$, 125 MHz)



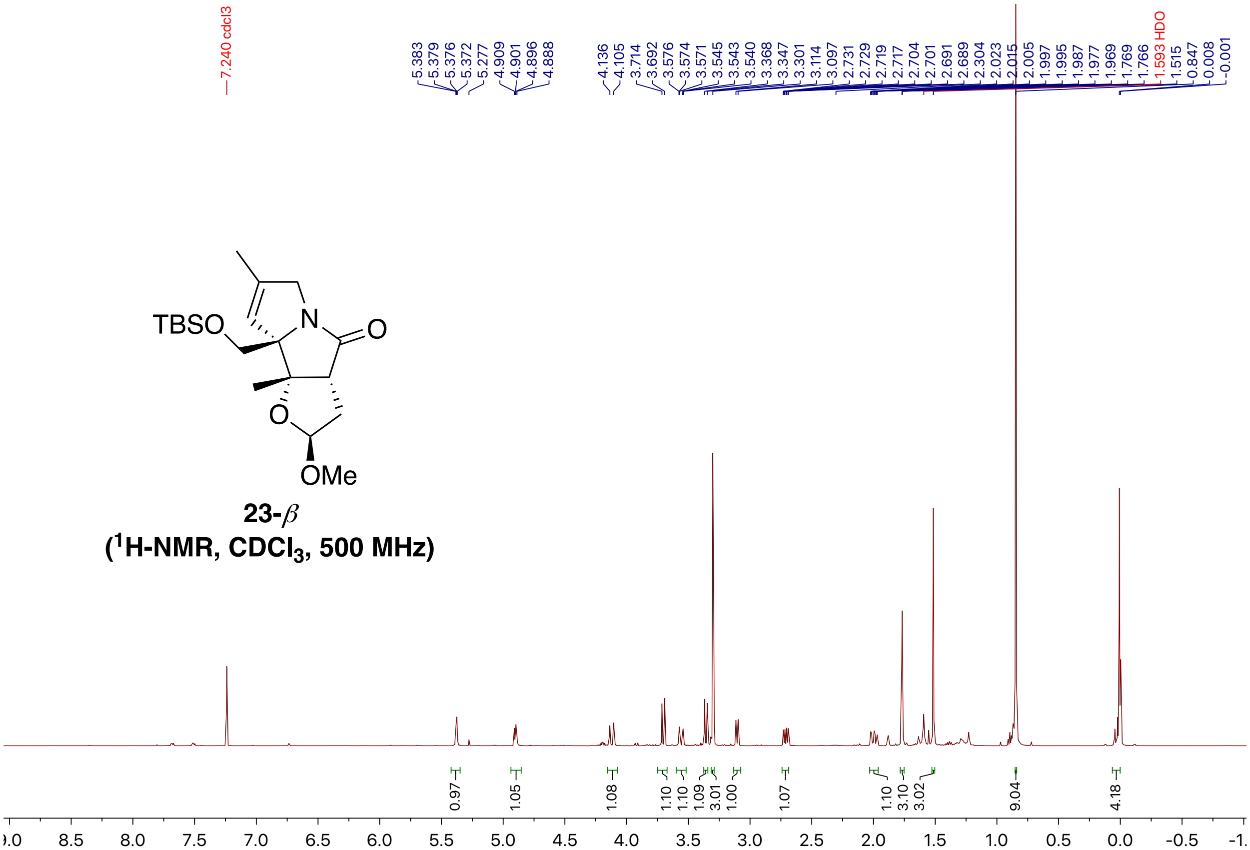
23-α

(^{1}H-NMR, CDCl$_3$, 500 MHz)

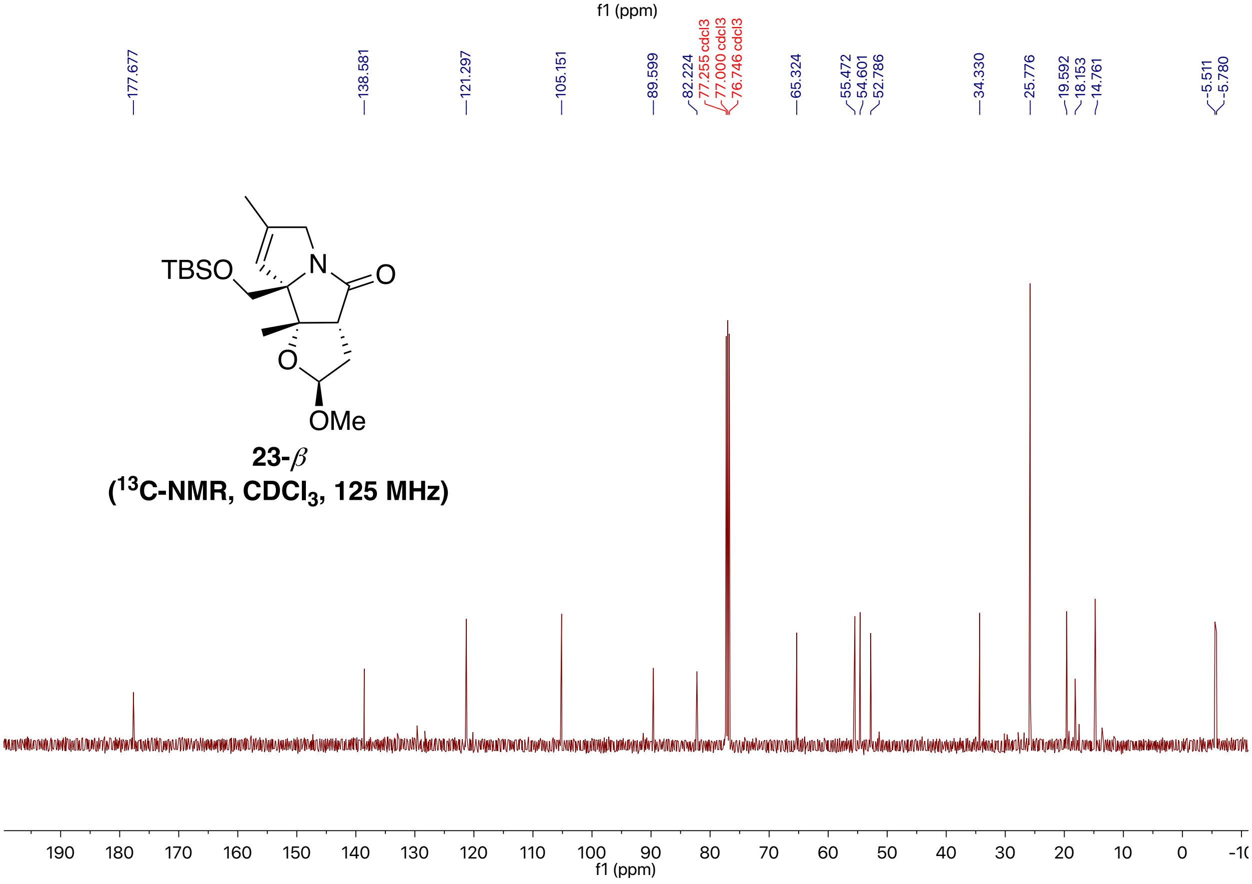


23-α

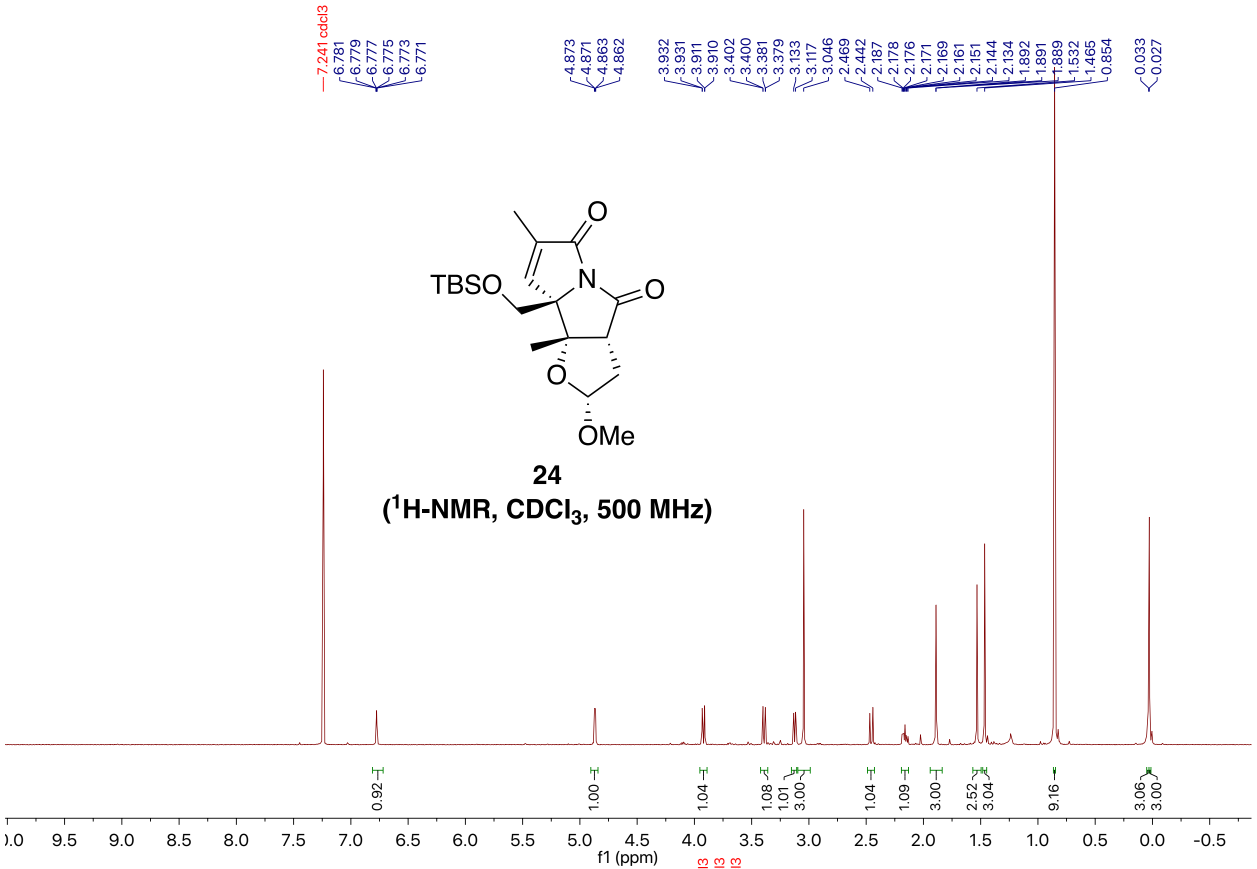
(^{13}C-NMR, CDCl$_3$, 125 MHz)



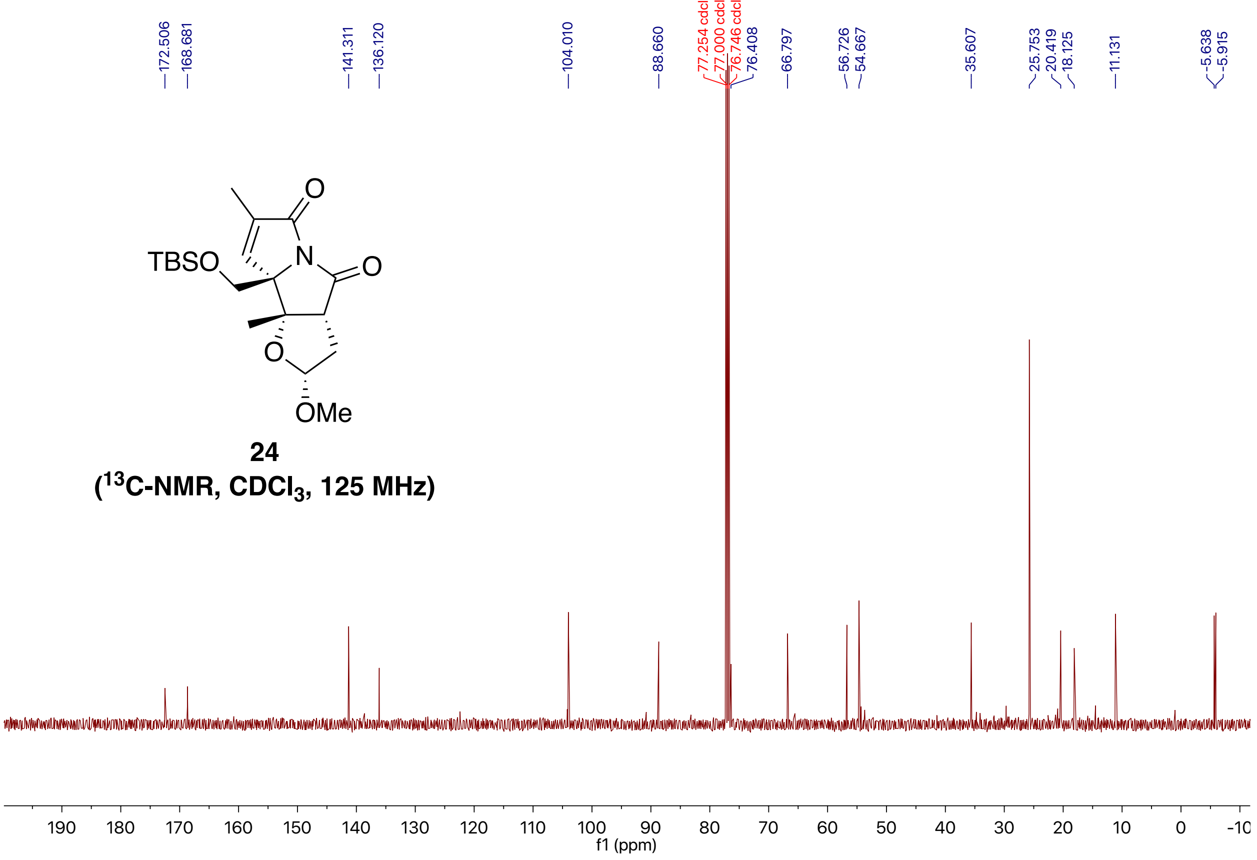
23-*β*
(^{1}H-NMR, CDCl$_3$, 500 MHz)



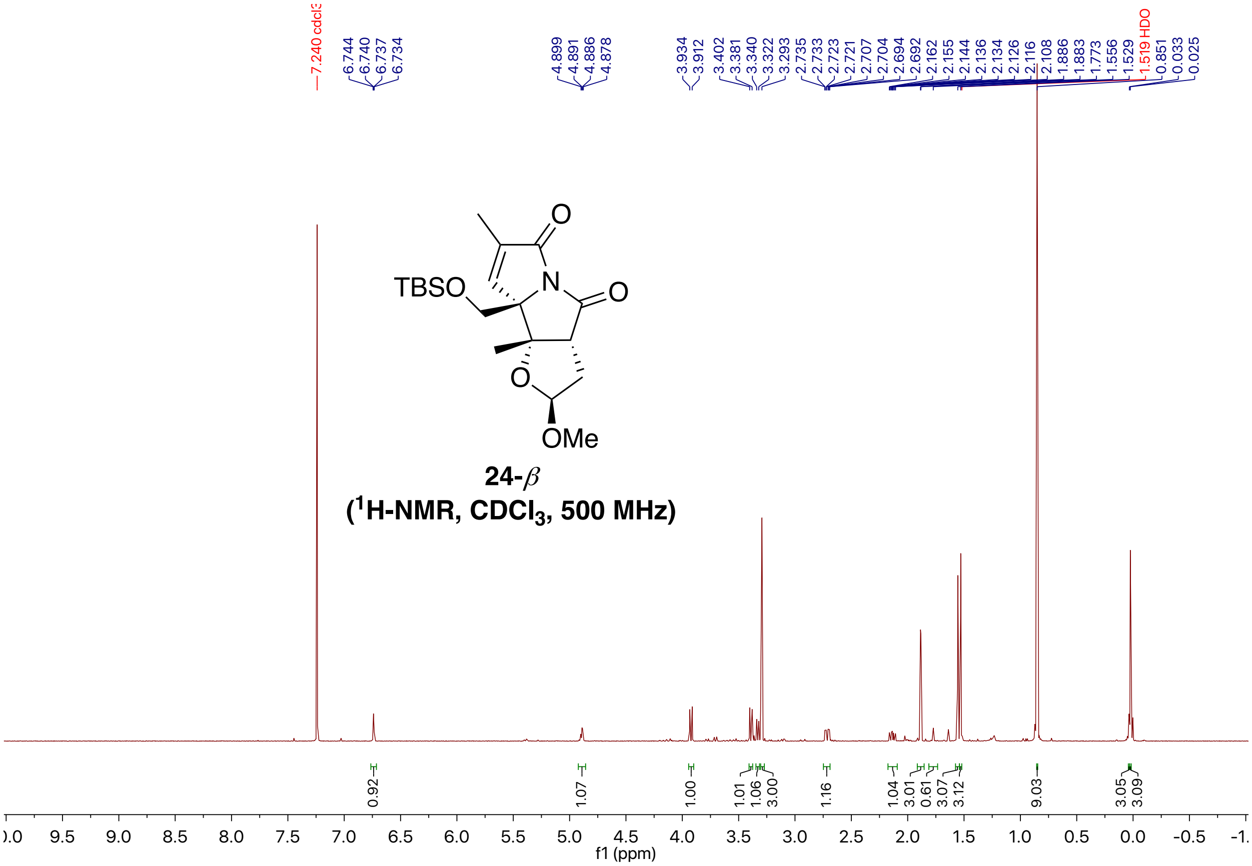
23-*β*
(^{13}C-NMR, CDCl$_3$, 125 MHz)



24
(^{1}H-NMR, CDCl$_3$, 500 MHz)



24
(^{13}C-NMR, CDCl$_3$, 125 MHz)



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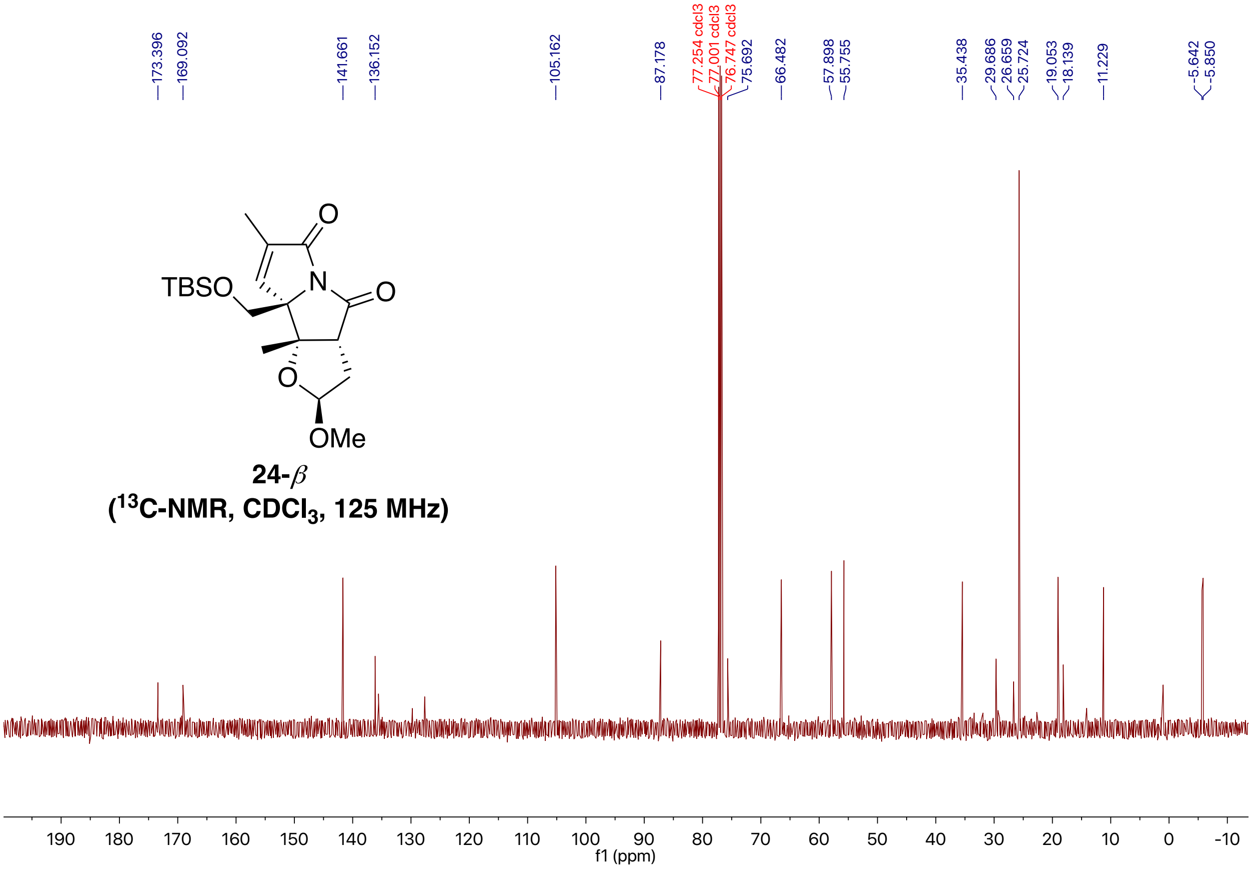
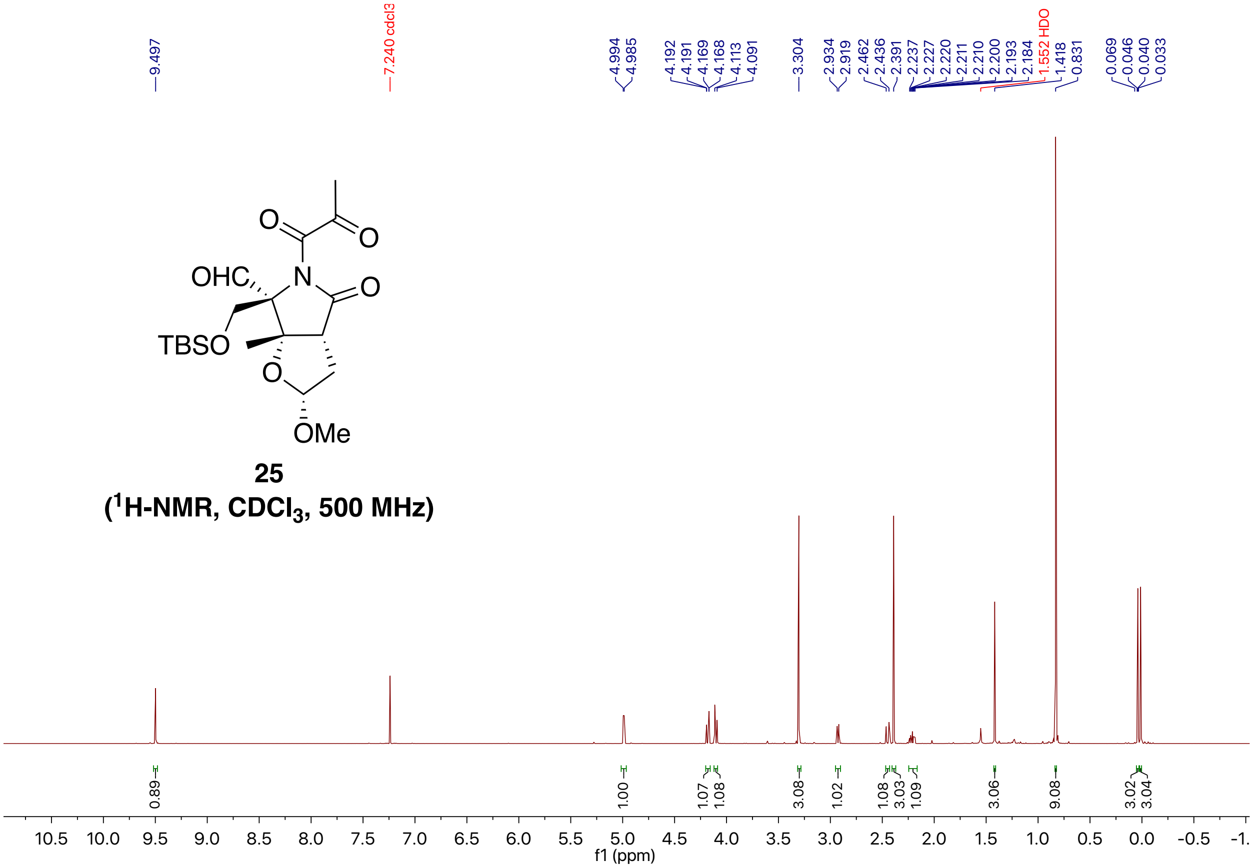
(^{1}H-NMR, CDCl$_3$, 500 MHz)



24-*β*
(^{13}C-NMR, CDCl$_3$, 125 MHz)



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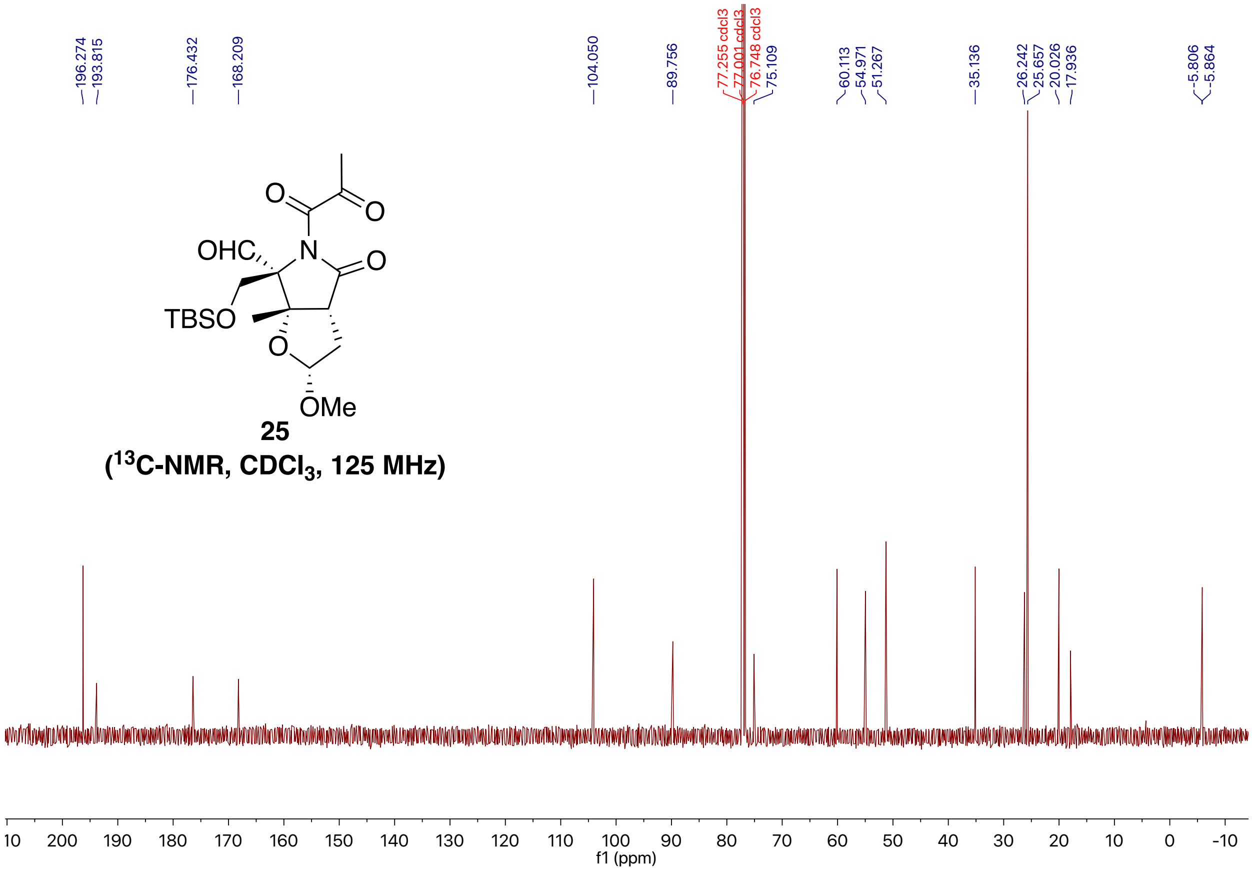
(^{1}H-NMR, CDCl$_3$, 500 MHz)



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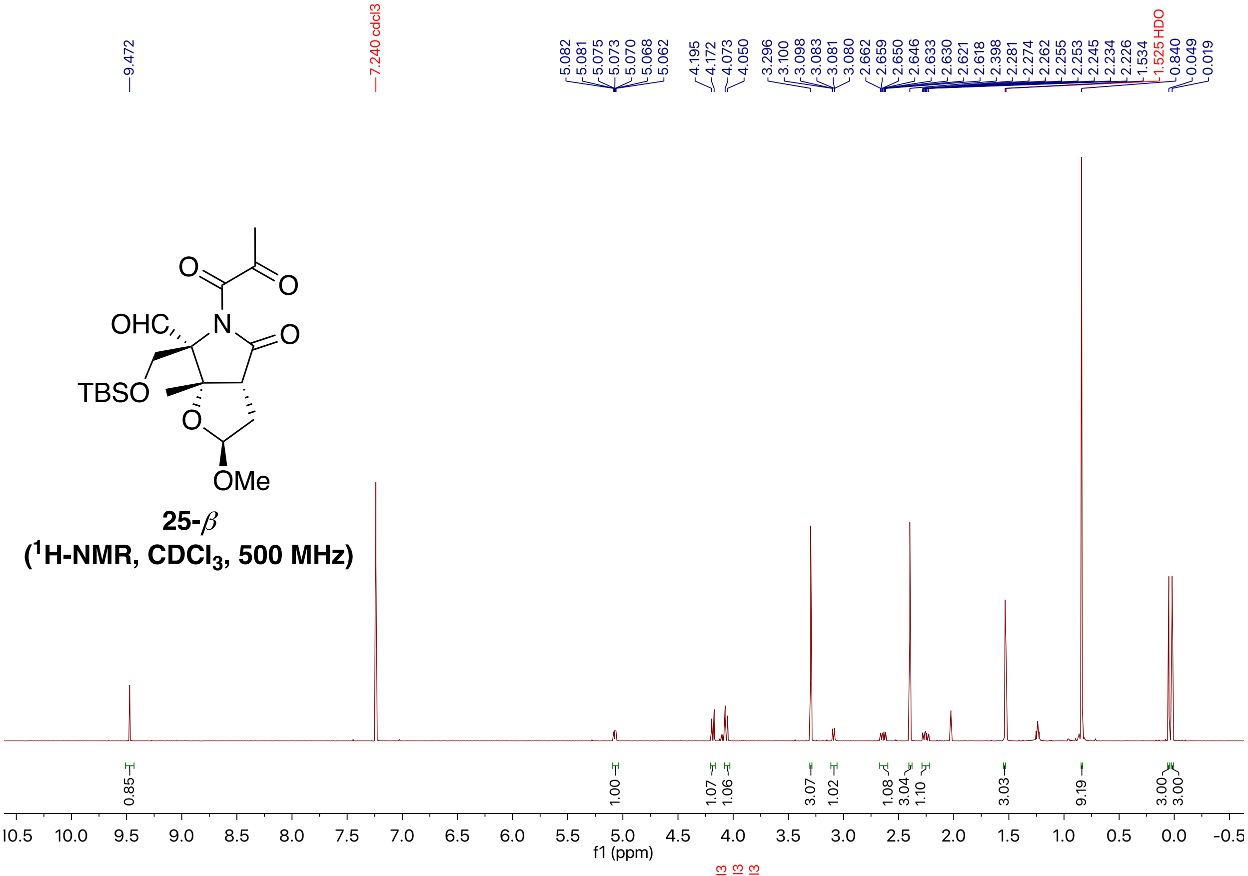
(^{13}C-NMR, CDCl$_3$, 125 MHz)



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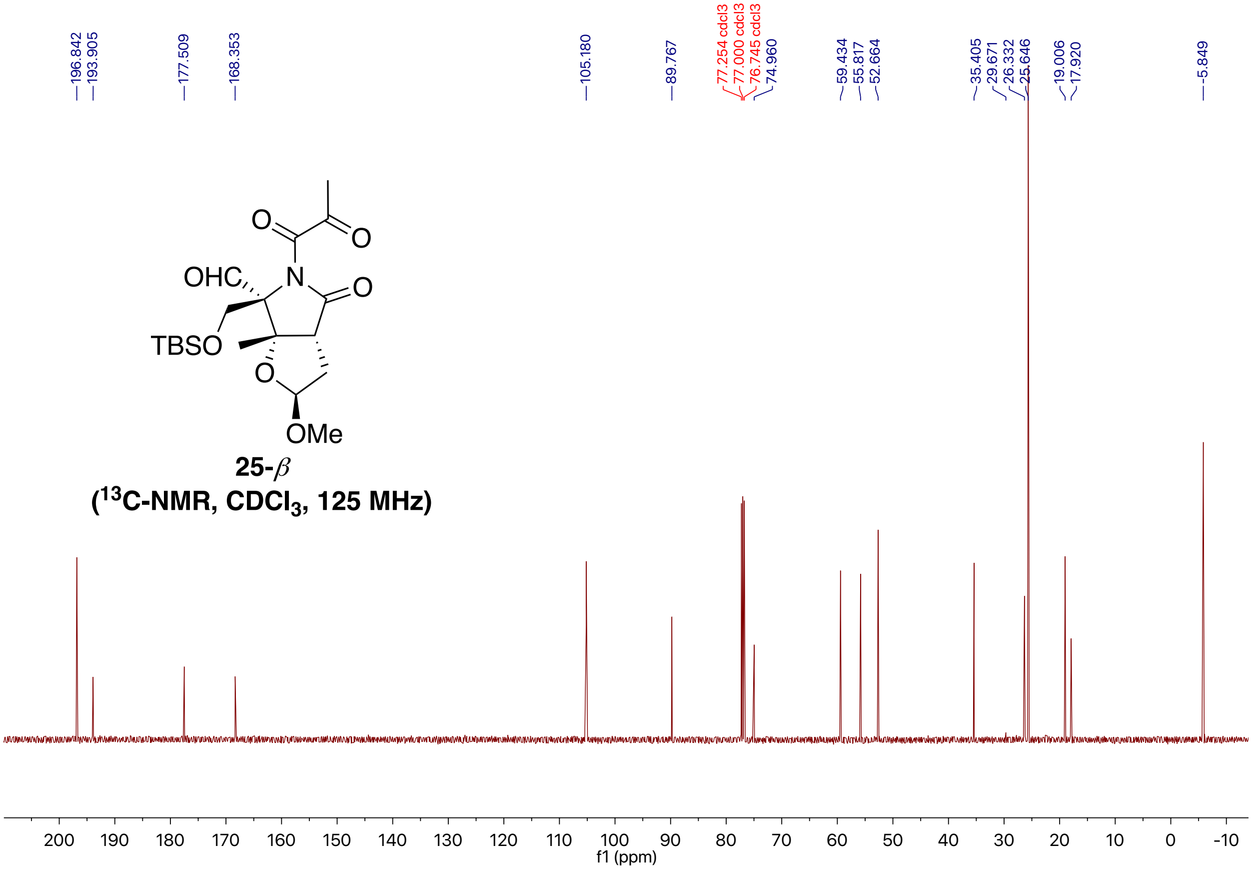
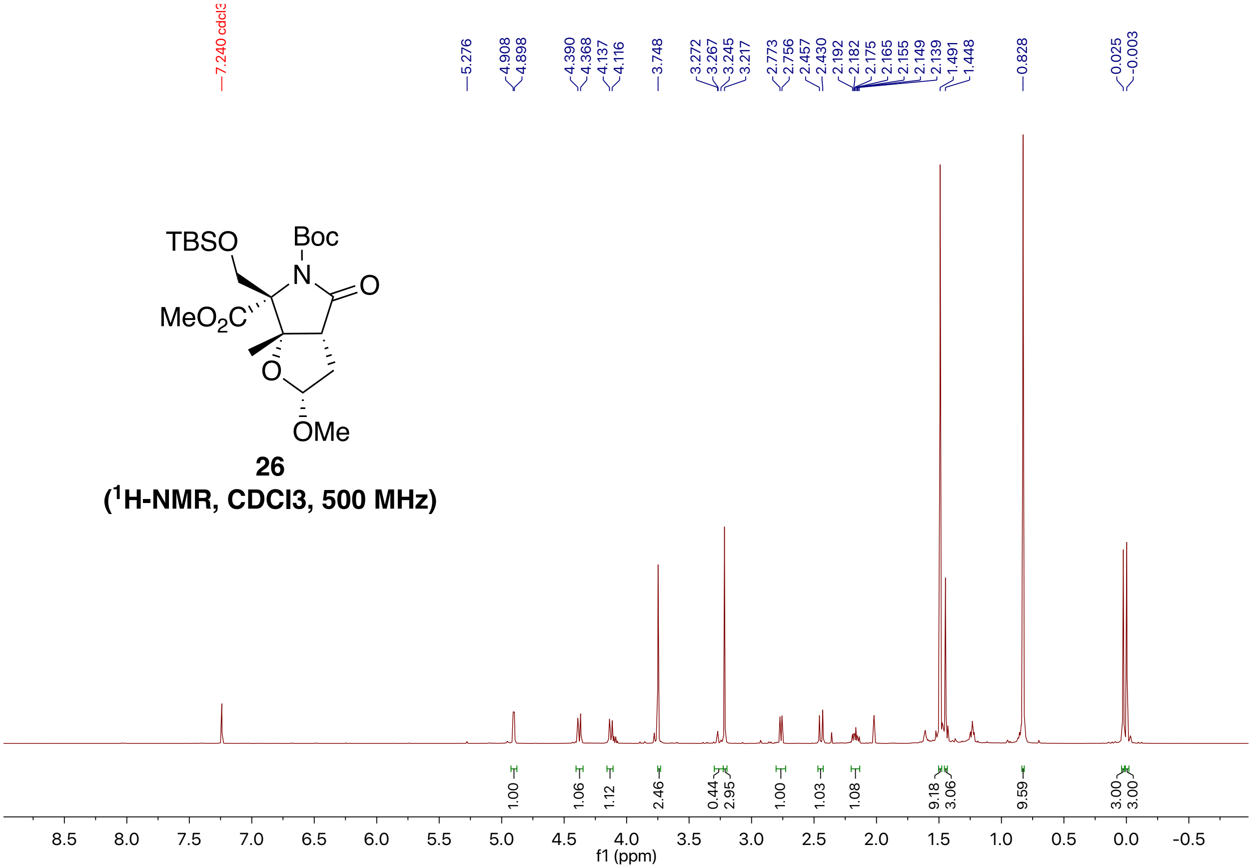
(^{1}H-NMR, CDCl$_3$, 500 MHz)

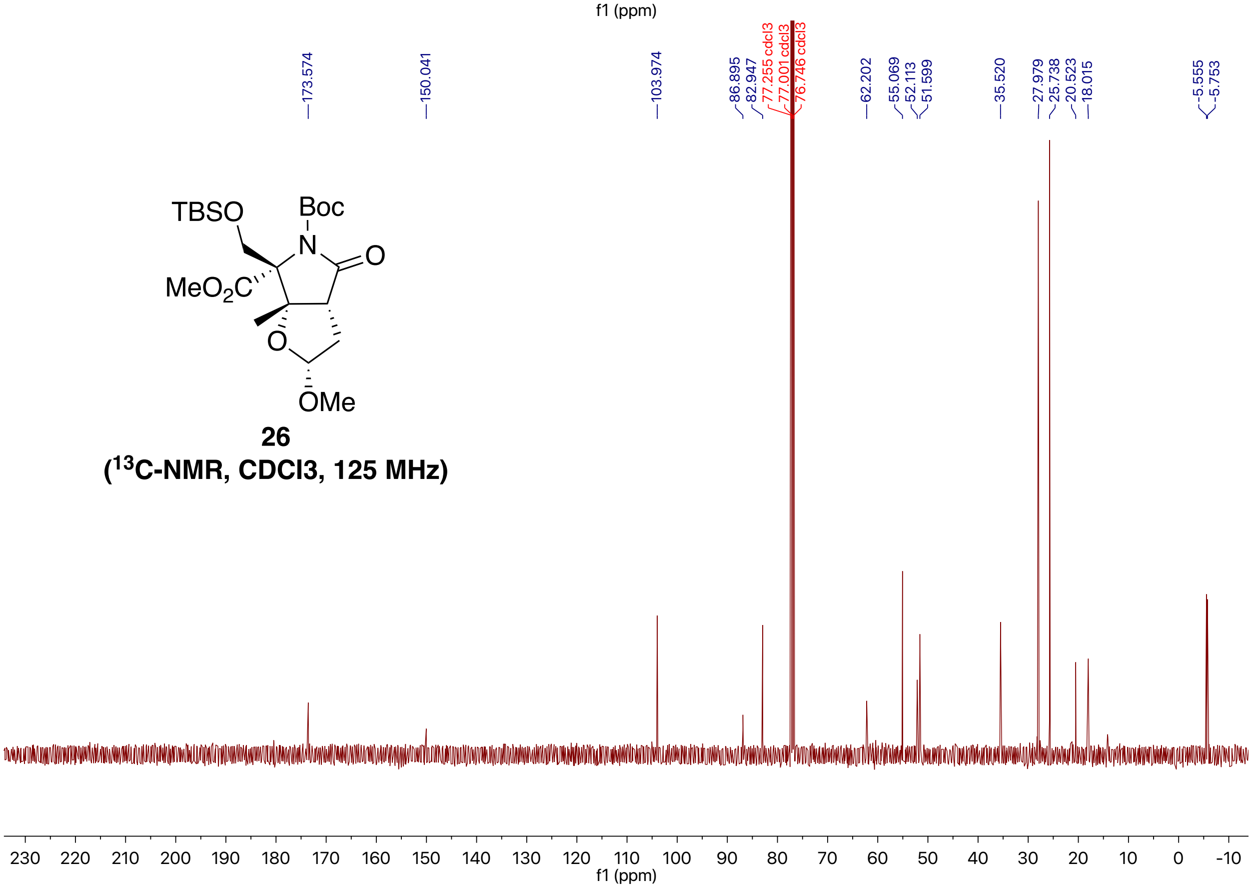


25-*β*
(^{13}C-NMR, CDCl$_3$, 125 MHz)



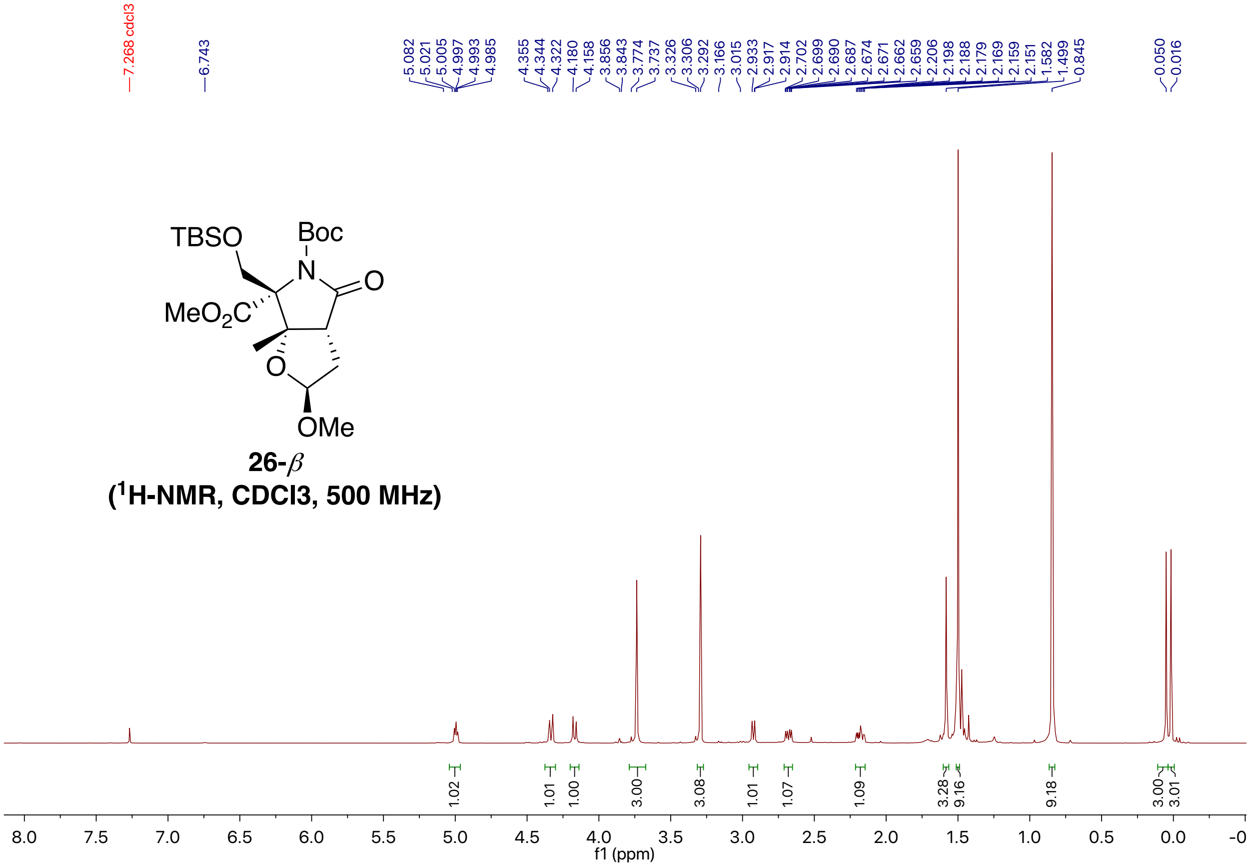
26

(^{1}H-NMR, CDCl3, 500 MHz)



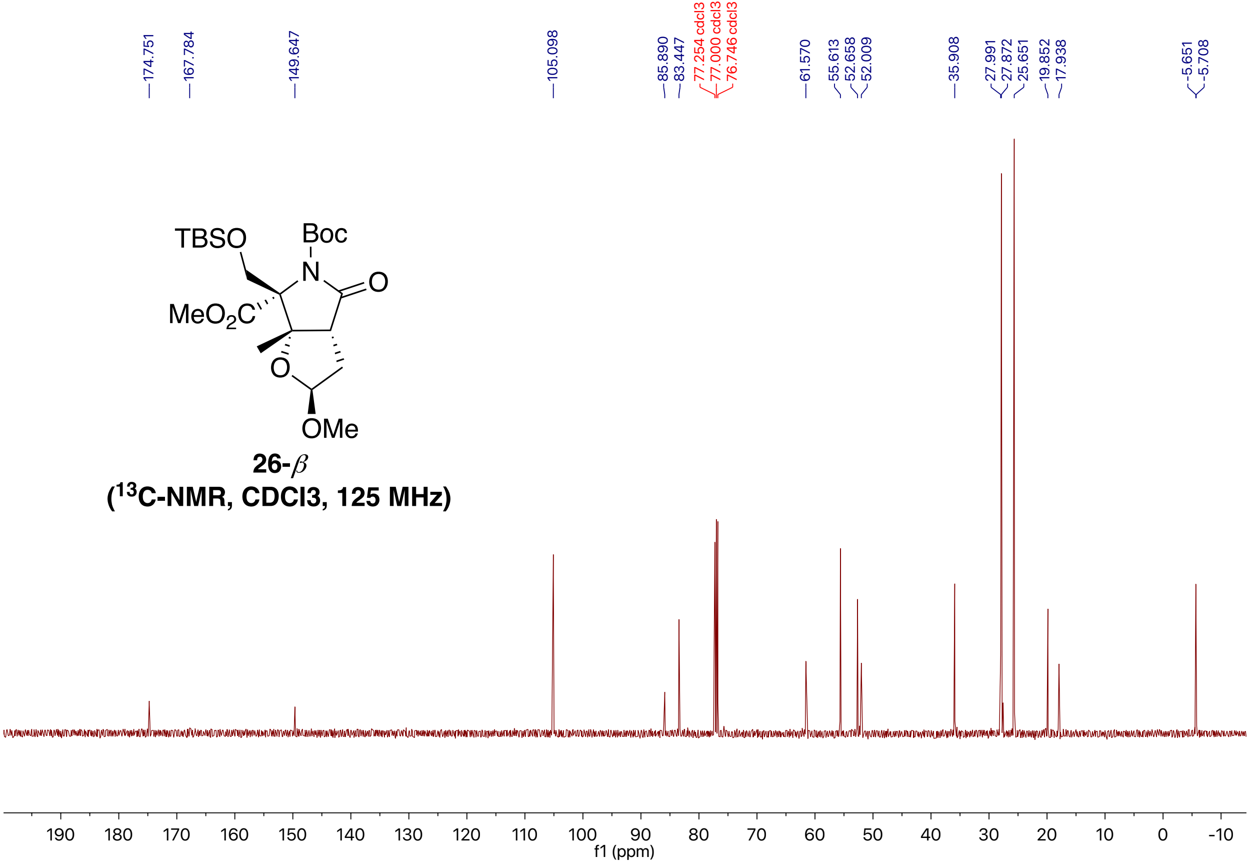
26

(^{13}C-NMR, CDCl3, 125 MHz)



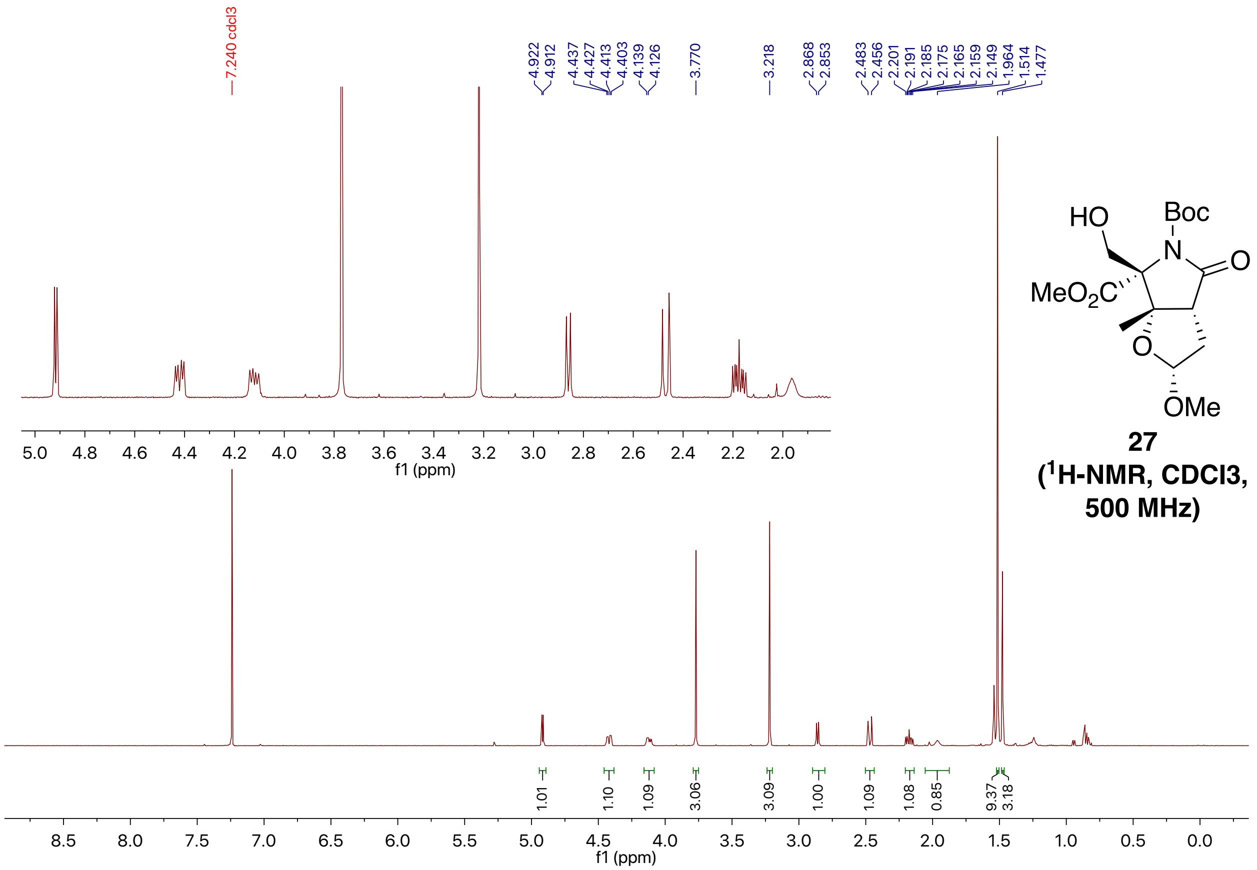
26-*β*

(^{1}H-NMR, CDCl3, 500 MHz)



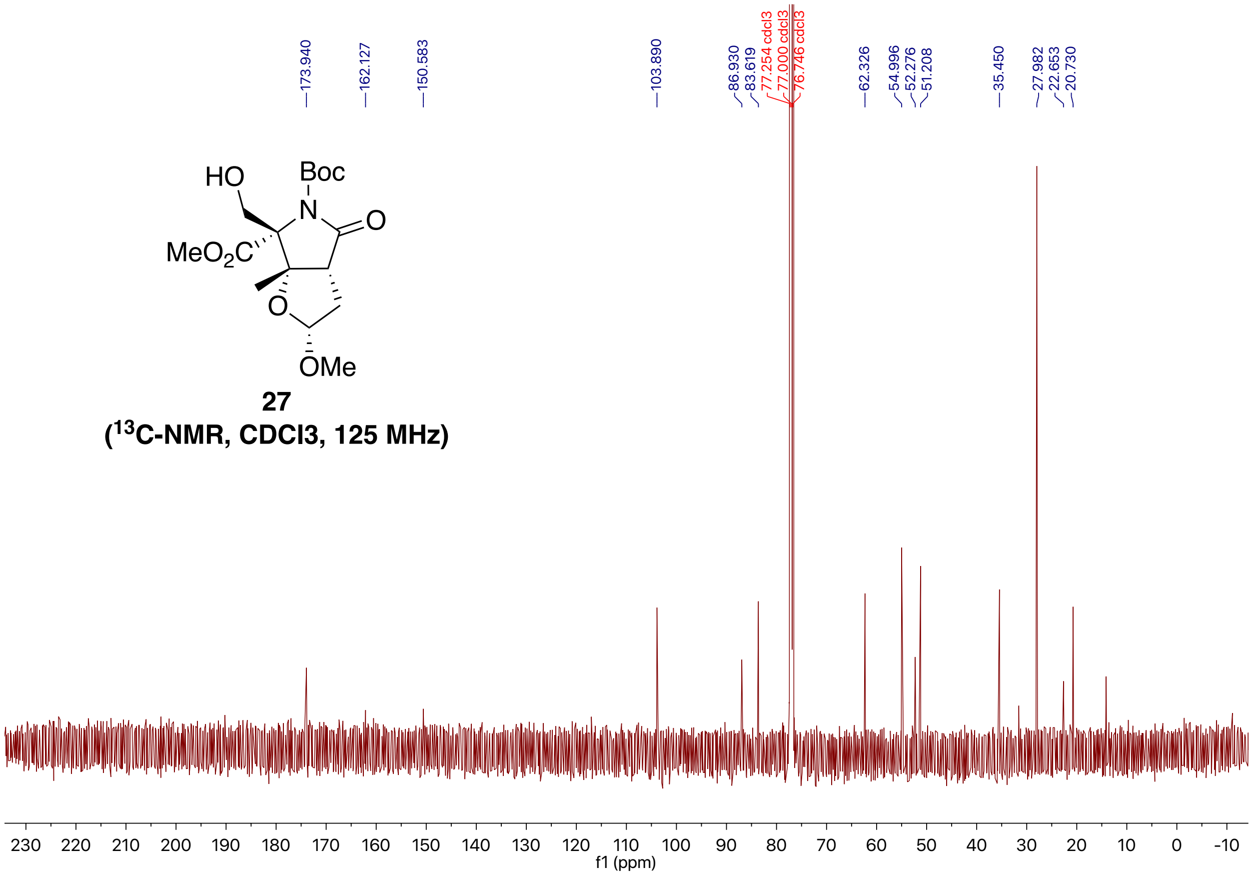
26-*β*

(^{13}C-NMR, CDCl3, 125 MHz)



27

(^{1}H-NMR, CDCl3, 500 MHz)



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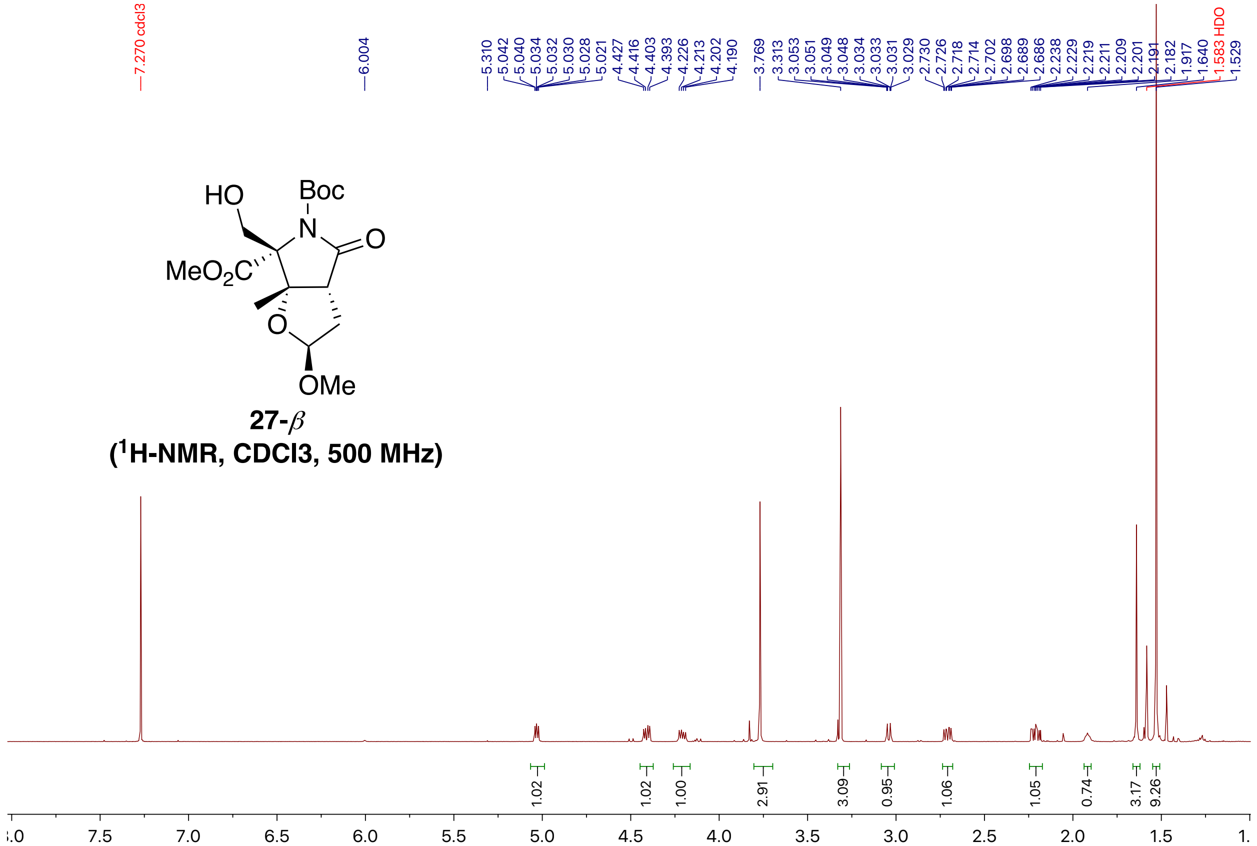
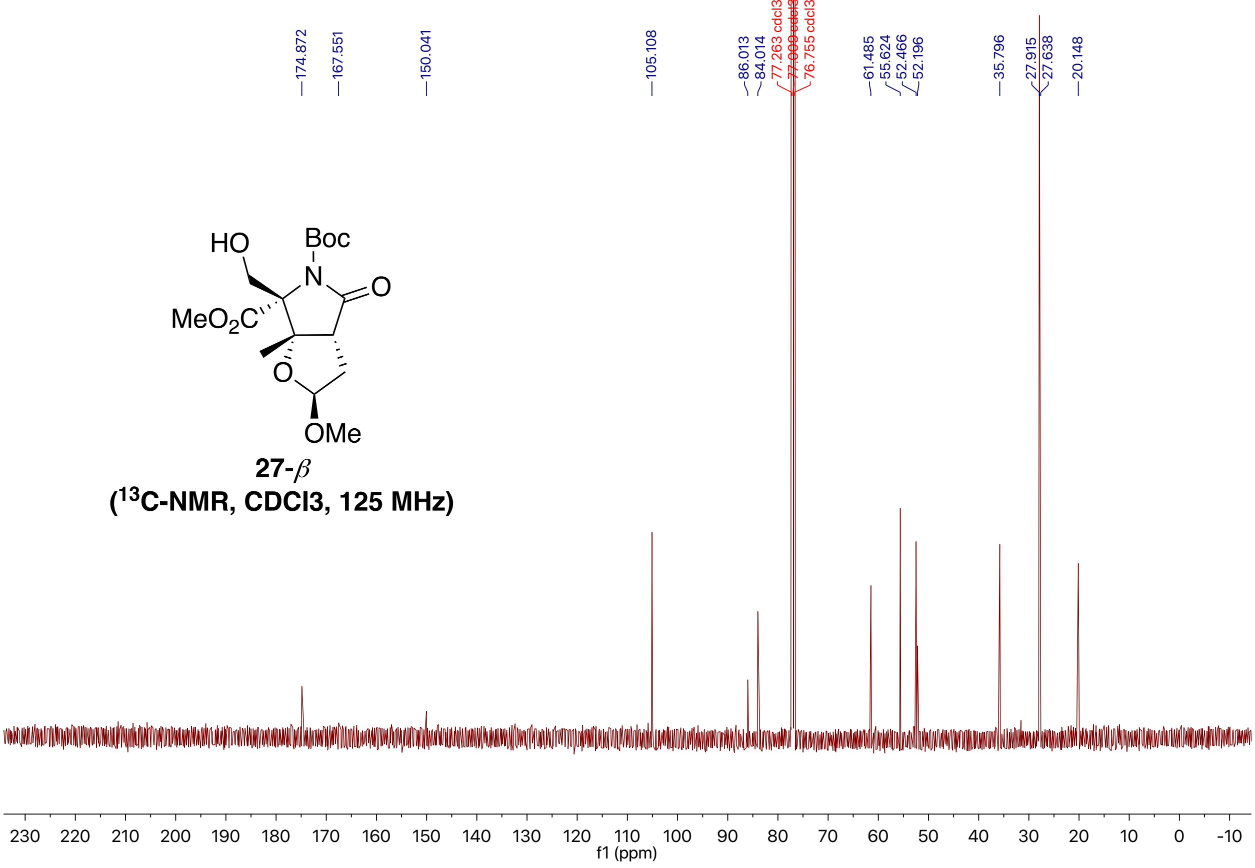
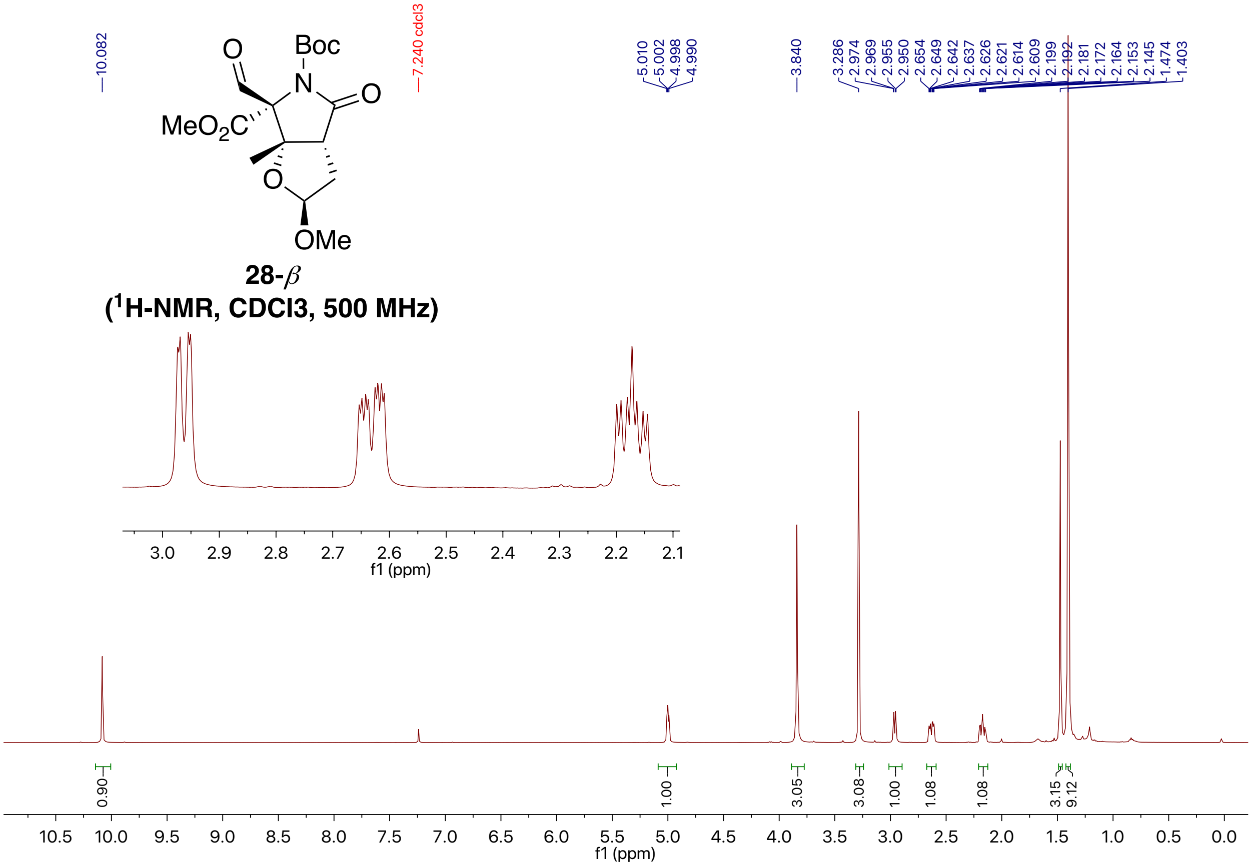
(^{13}C-NMR, CDCl3, 125 MHz)

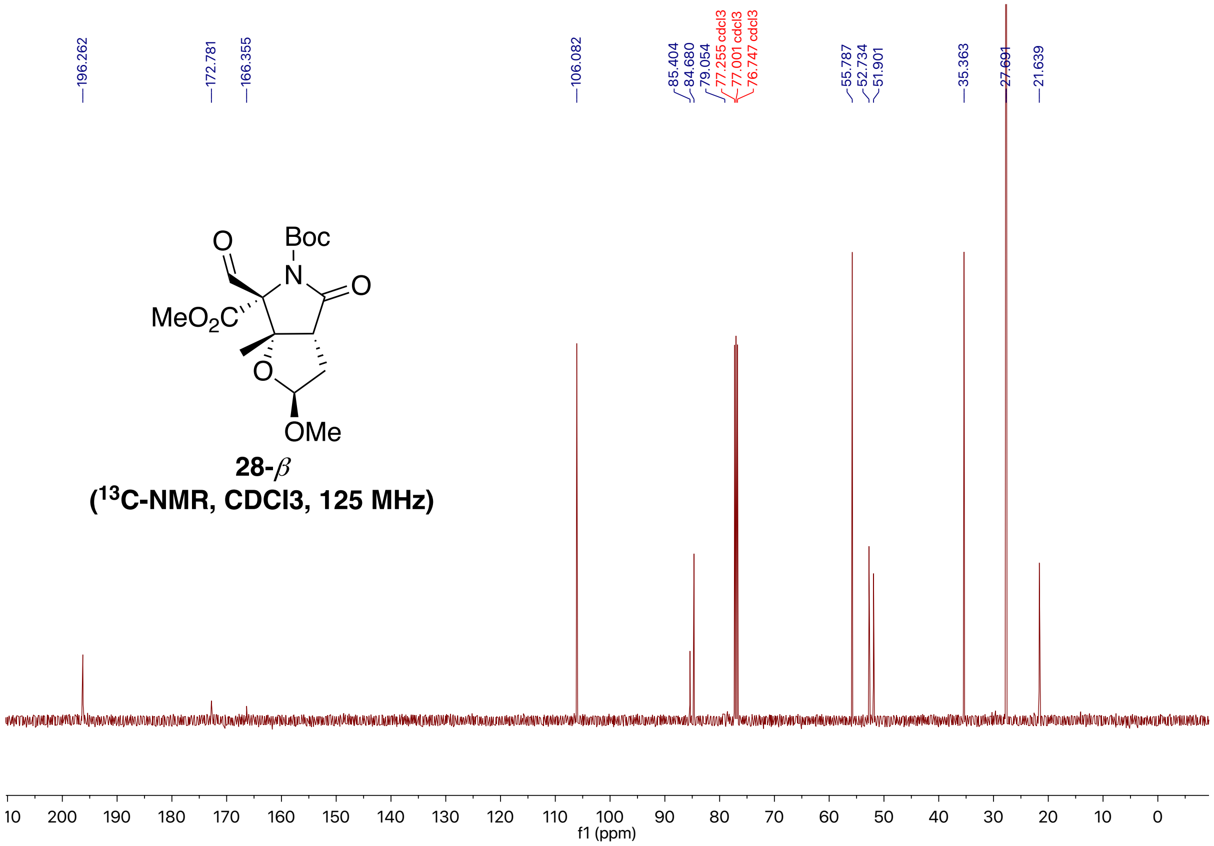

27-*β*

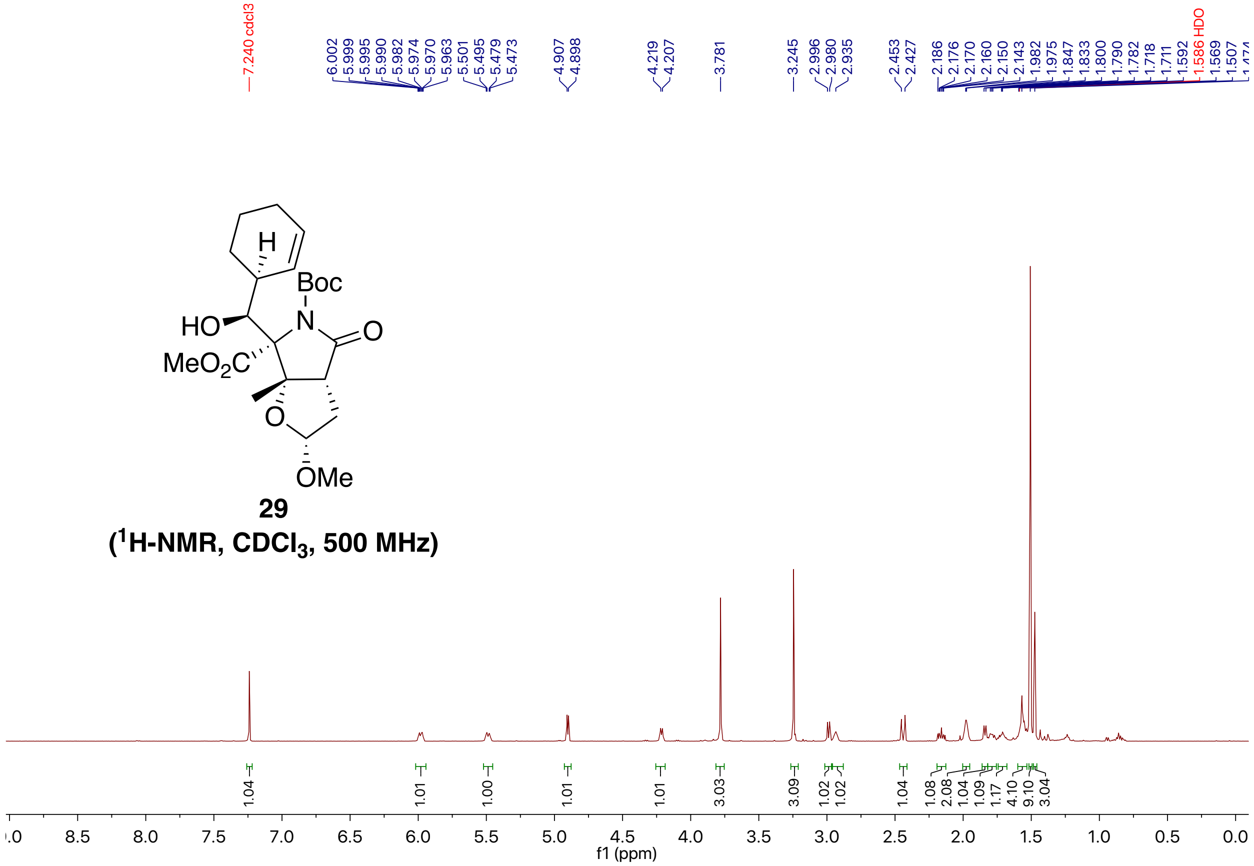
(^{1}H-NMR, CDCl3, 500 MHz)


27-*β*

(^{13}C-NMR, CDCl3, 125 MHz)

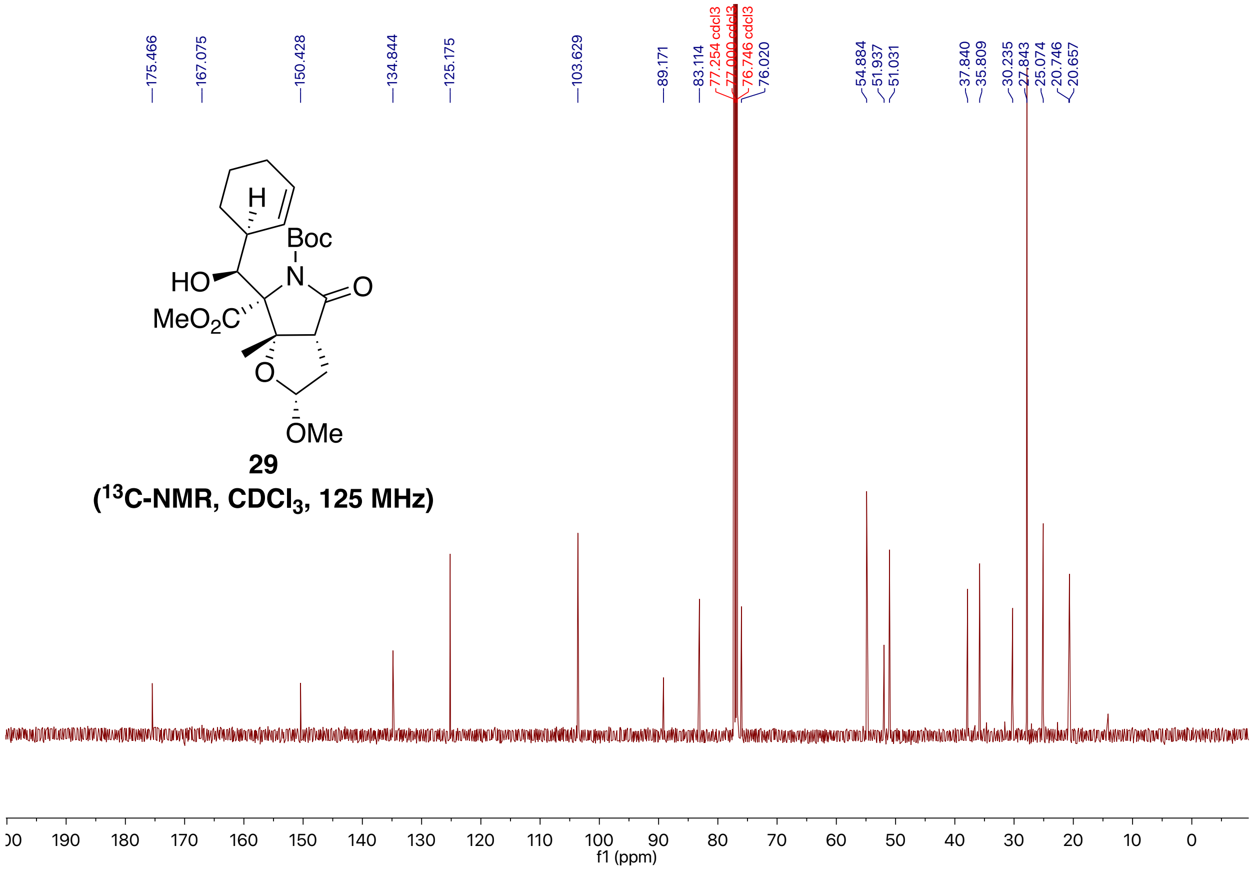

28-β
(^{1}H-NMR, CDCl3, 500 MHz)


28-β
(^{13}C-NMR, CDCl3, 125 MHz)



29

(^{1}H-NMR, CDCl$_3$, 500 MHz)



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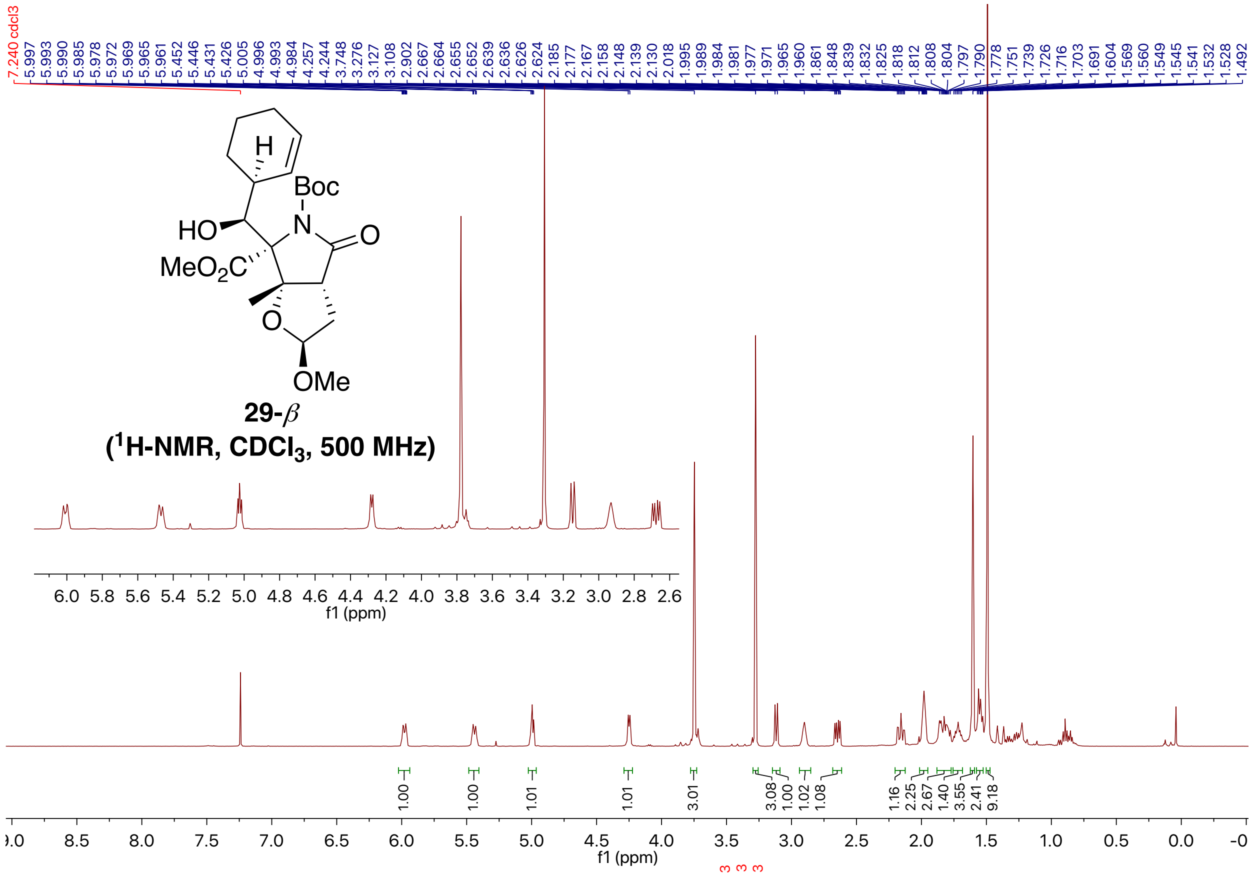
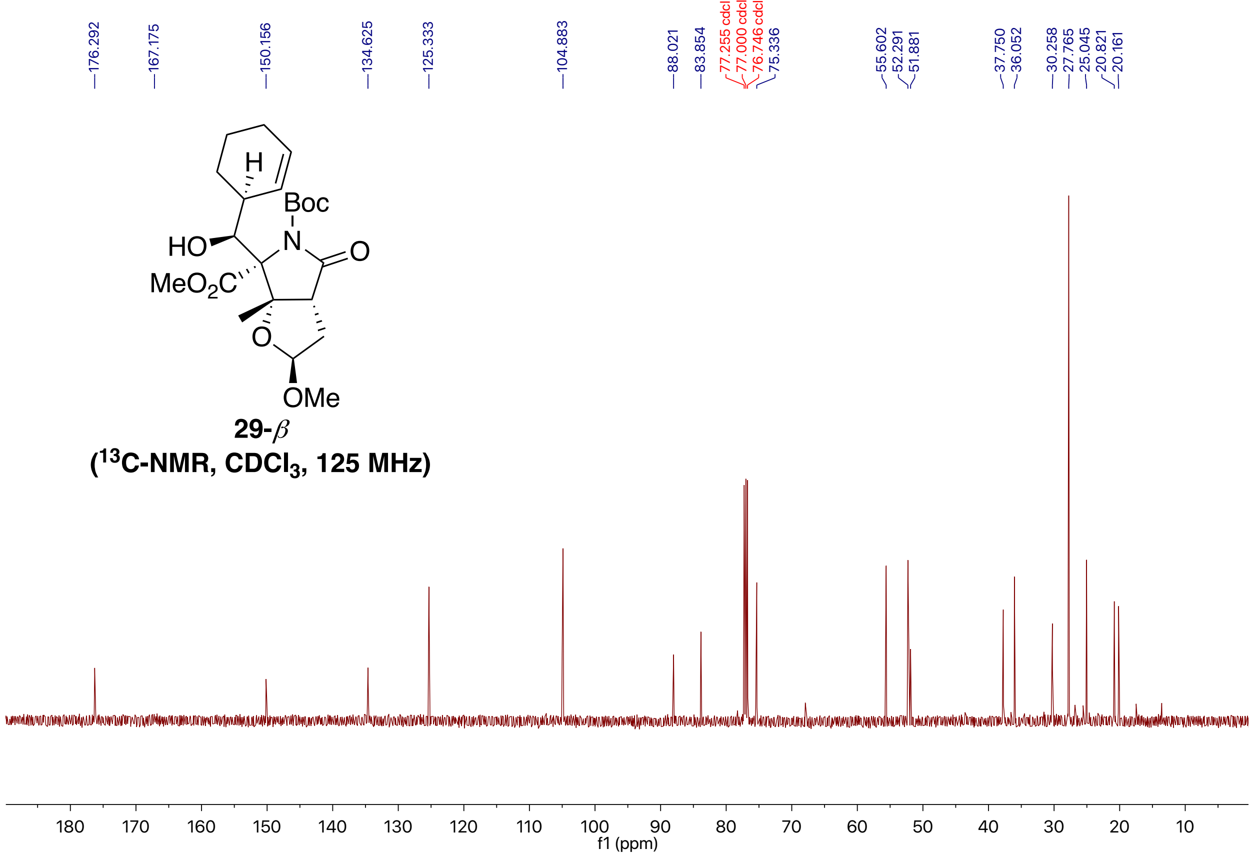
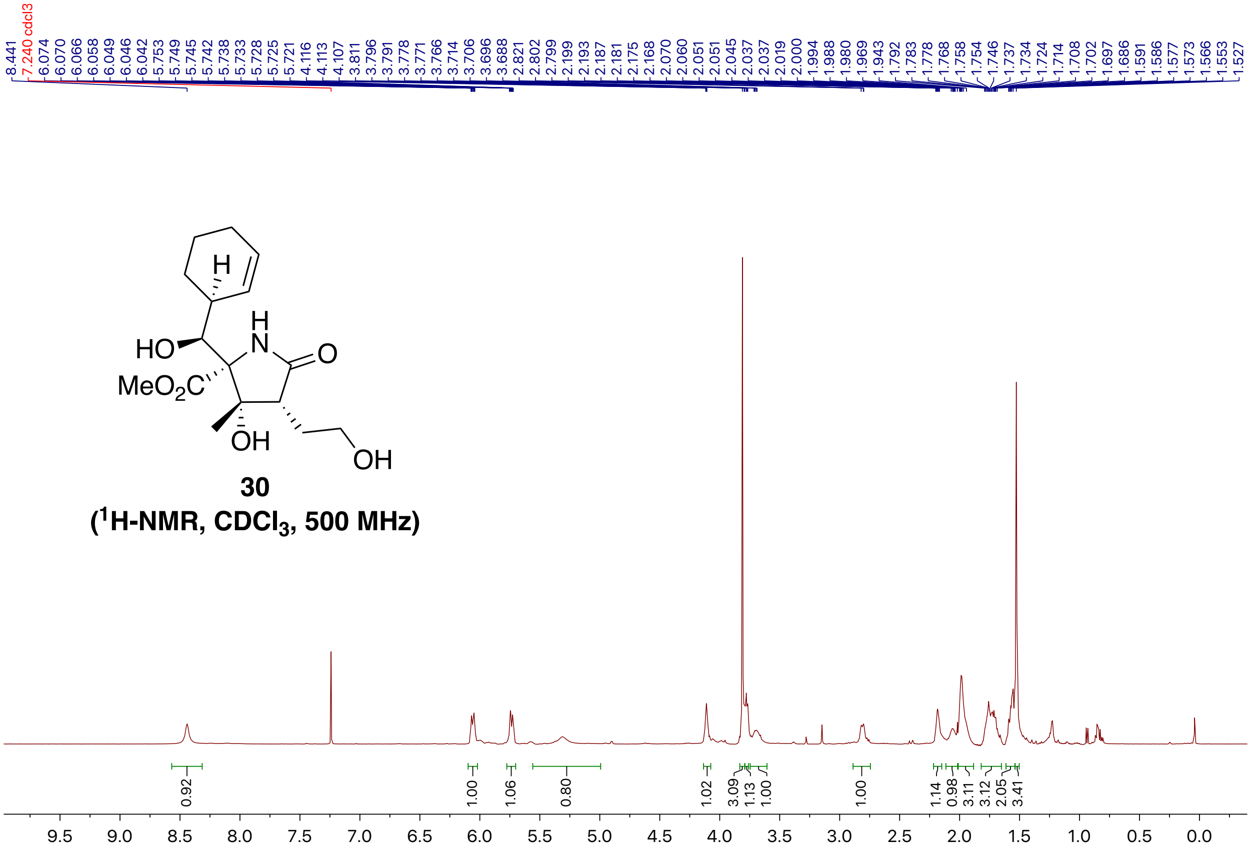
(^{13}C-NMR, CDCl$_3$, 125 MHz)



29-β
(^{1}H-NMR, CDCl$_3$, 500 MHz)

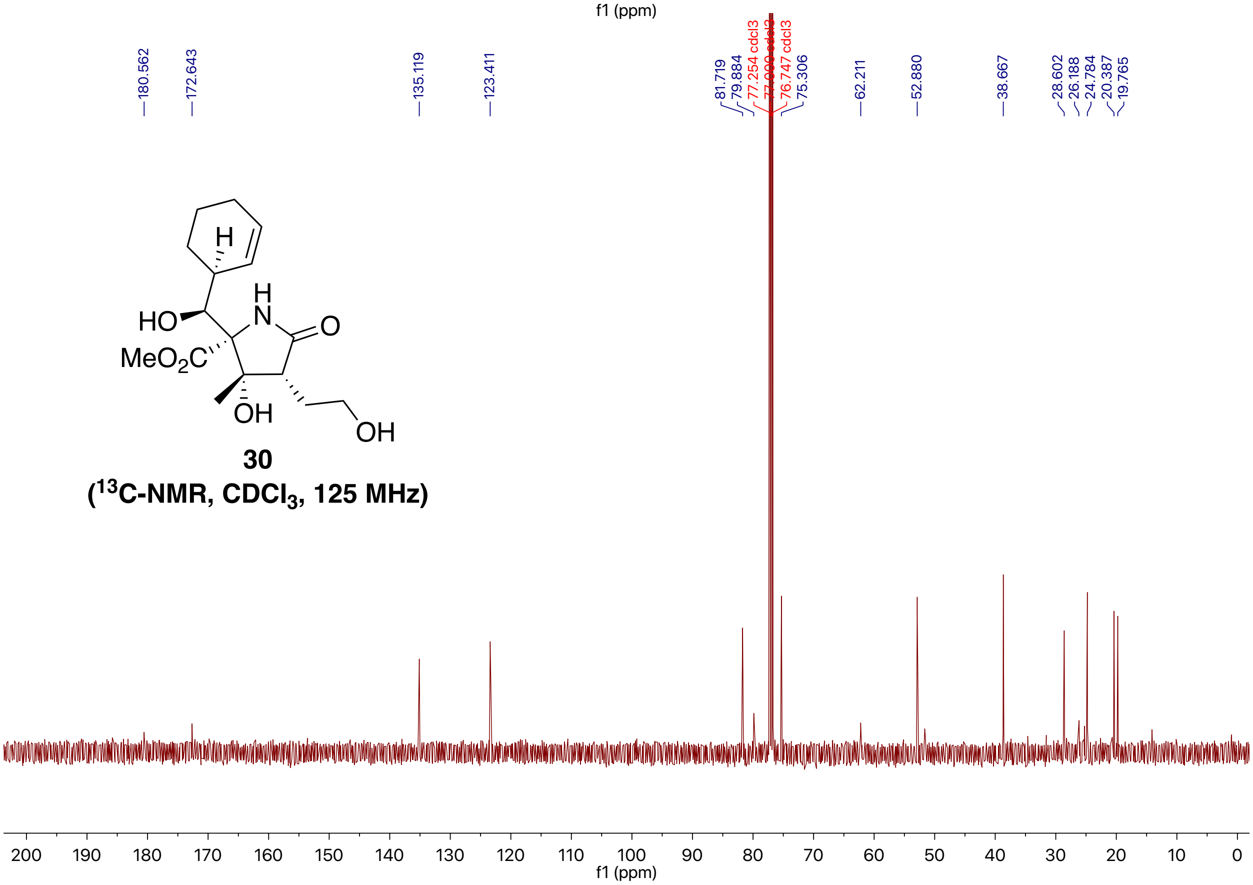


29-β
(^{13}C-NMR, CDCl$_3$, 125 MHz)



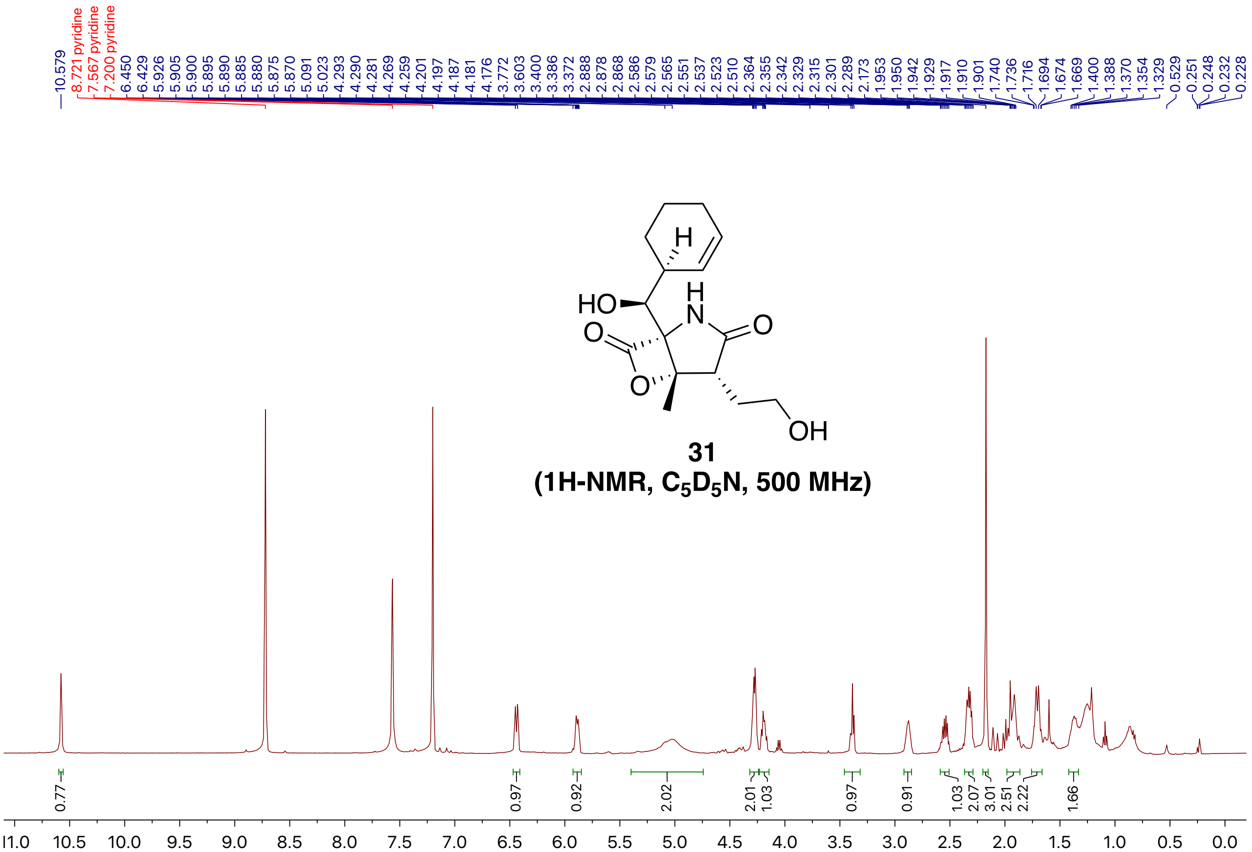
30

(^{1}H-NMR, CDCl$_3$, 500 MHz)

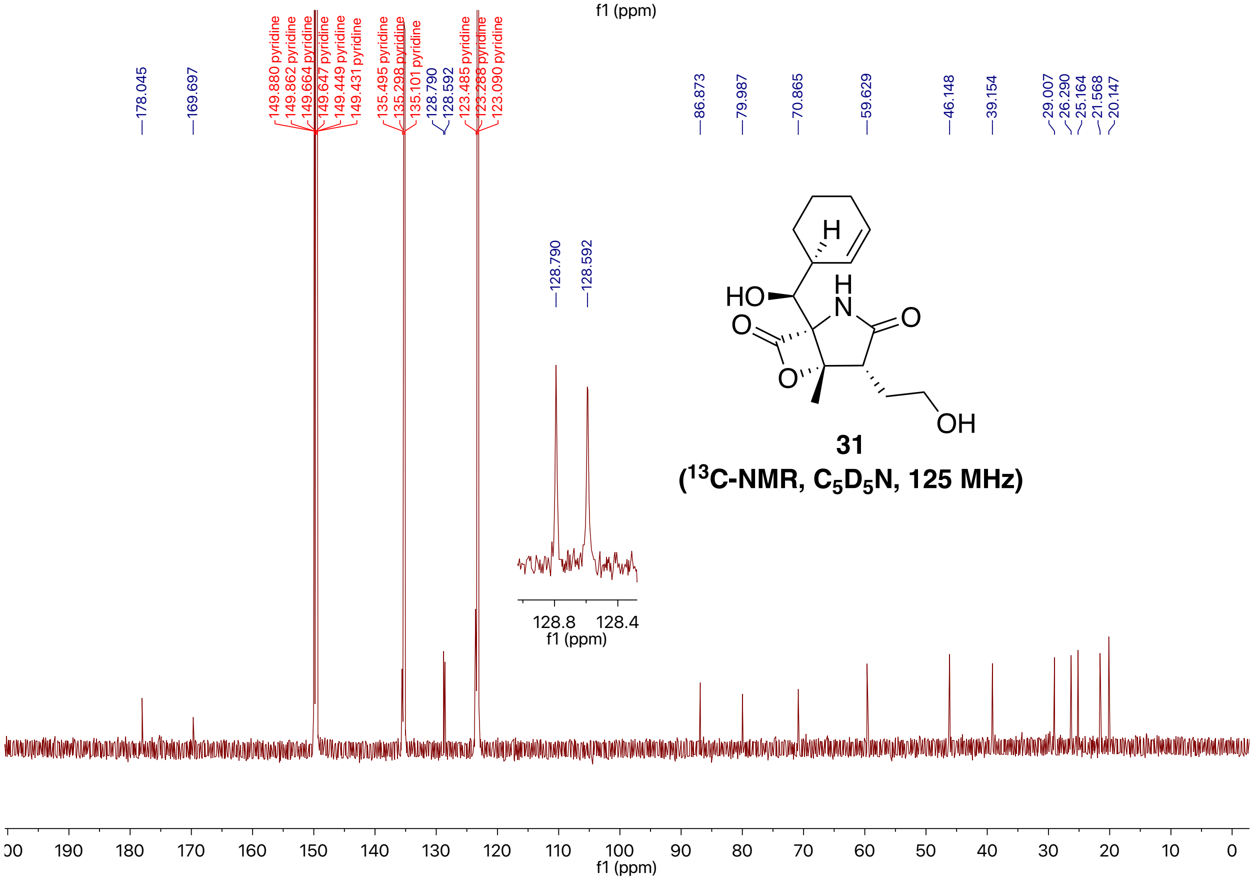


30

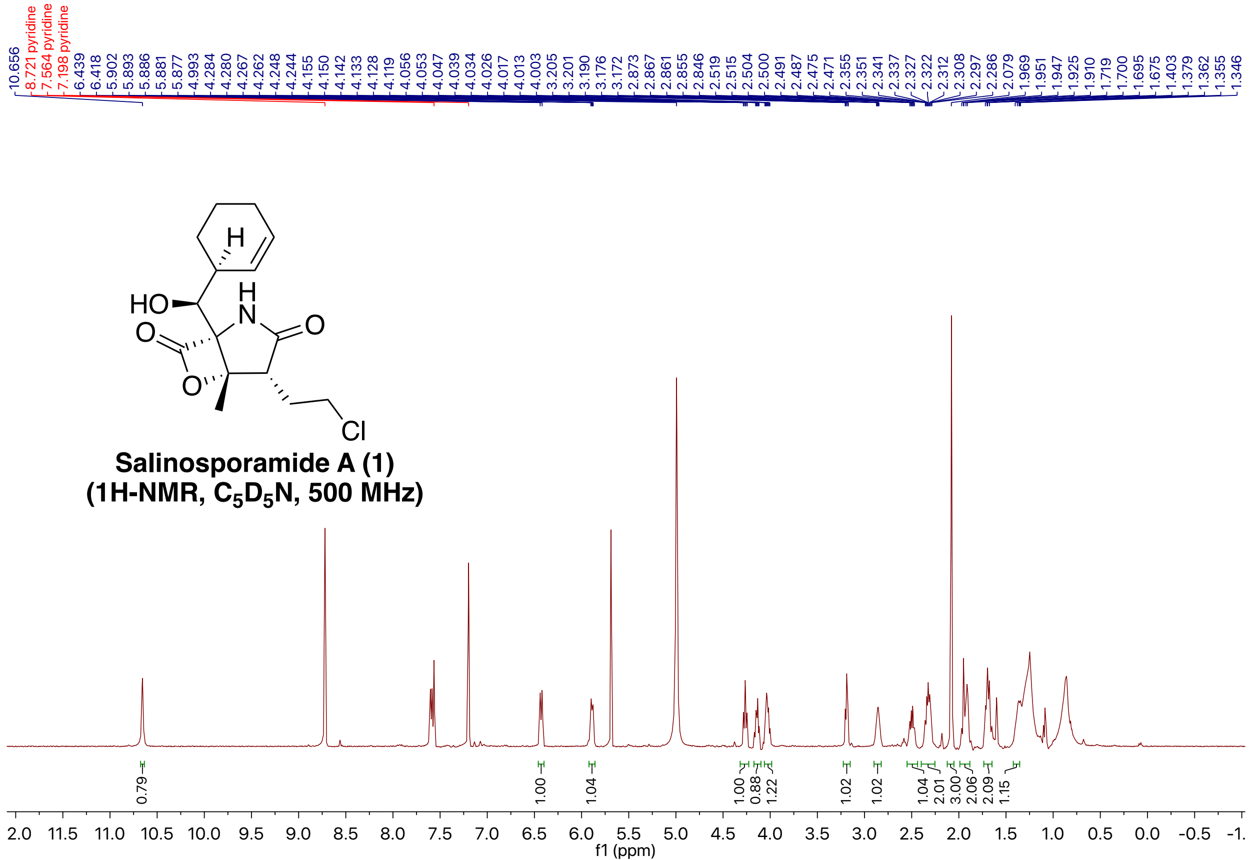
(^{13}C-NMR, CDCl$_3$, 125 MHz)

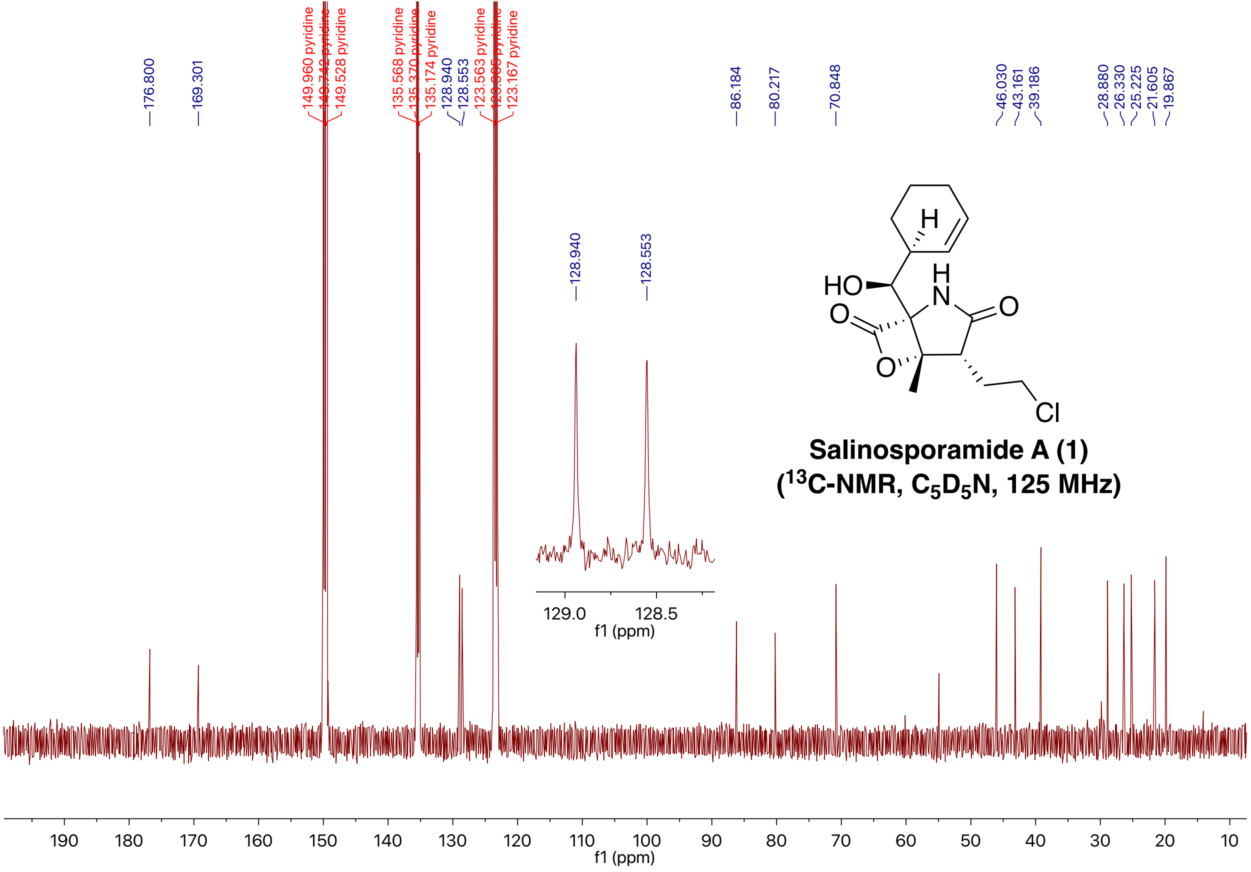


31
(1H-NMR, C_5D_5N, 500 MHz)



31
(^{13}C-NMR, C_5D_5N, 125 MHz)


Salinosporamide A (1)
(1H-NMR, C_5D_5N, 500 MHz)


Salinosporamide A (1)
(^{13}C-NMR, C_5D_5N, 125 MHz)

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