Total Synthesis of (–)-Flueggenine A and (–)-15′-*epi*-Flueggenine D

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Supplementary Information

1. General Information

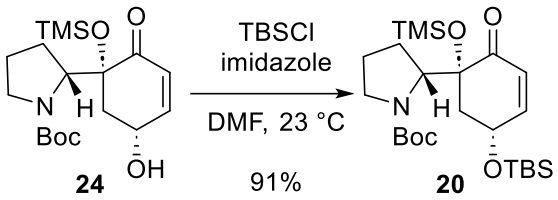
All reactions were performed in oven-dried or flame-dried round-bottomed flasks and vials. Unless otherwise noted, the flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon, and vials were tightly sealed with plastic septa, Teflon tape, and parafilm. Stainless steel syringes were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 40–63 μm, 4-6% H_2O content, Merck).[1] Analytical thin–layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light, an aqueous ammonium cerium nitrate/ammonium molybdate (Seebach's staining),[2] and/or a basic aqueous potassium permanganate ($KMnO_4$).

Unless otherwise stated, all commercial reagents and solvents were used without additional purification with the following exceptions as indicated below. Dichloromethane and tetrahydrofuran were purchased from Merck and Daejung Inc., respectively and were purified by the method of Grubbs et al. under positive argon pressure.[3]

^1H and ^{13}C nuclear magnetic resonance spectra were recorded with Bruker Avance NEO (500 MHz) and calibrated by using the residual undeuterated chloroform (δ_H= 7.24 ppm) and $CDCl_3$ (δ_C= 77.2 ppm) or undeuterated CD_3OD (δ_H= 3.31 ppm) and CD_3OD (δ_C= 49.2 ppm) as internal references. Data are reported in the following manners: chemical shift in ppm [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, app = apparent, br = broad), coupling constant(s) in Hertz, integration]. High resolution mass spectra were obtained from KAIST Analysis Center for Research (Daejeon) by using ESI method. Specific rotation $[\alpha]_D^T$ was obtained by JASCO P-2000 polarimeter.

All DFT calculations were conducted by Gaussian 09 package.[4] Molecular geometries were optimized using B3LYP[5] functional with Grimme's D3 dispersion correction[6] and 6-31G* basis set. Single point energies were calculated with B3LYP-D3 functional and 6-311+G** basis set, including solvation effect under SMD[7] solvation model with the dielectric constant of ε = 4.7113 for chloroform. Frequency calculations were carried out at the same level of geometry optimization to confirm the stationary points as local minima (no imaginary and to obtain thermal corrections to the Gibbs free energies at 298.15 K unless otherwise stated.

2. Experimental Procedures and Physical Data for Synthesized Compounds



(+)-Enone 20:

Imidazole (785 mg , 11.5 mmol, 6.0 equiv.) and *tert*-butyldimethylchlorosilane (869 mg, 5.77 mmol, 3.0 equiv.) were added to a stirred solution of **24**[8] (710.3 mg, 1.92 mmol, 1.0 equiv.) in dimethylformamide (19 mL) at 23 °C. After 2.5 h, saturated aqueous ammonium chloride solution (100 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water (3 × 100 mL) followed by brine (100 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 10 cm; eluent: ethyl acetate : hexanes = 1 : 20) to afford **20** (845 mg, 91%) as a white crystalline solid.

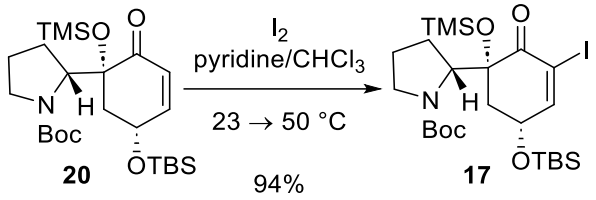
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.69 (dt, *J* = 10.4, 2.0 Hz, 1H), 5.88 (dd, *J* = 10.1, 2.3 Hz, 1H), 5.38 (dd, *J* = 9.3, 5.8 Hz, 1H), 4.05 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.59 (td, *J* = 9.6, 5.6 Hz, 1H), 3.20 (ddd, *J* = 10.4, 8.8, 5.9 Hz, 1H), 2.53 (ddd, *J* = 12.7, 5.8, 1.9 Hz, 1H), 1.99 – 1.90 (m, 1H), 1.87 – 1.74 (m, 2H), 1.68 – 1.58 (m, 1H), 1.54 – 1.46 (m, 1H), 1.44 (s, 9H), 0.86 (s, 9H), 0.14 (s, 3H), 0.10 (s, 3H), 0.07 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.5, 156.4, 153.8, 127.0, 84.0, 79.6, 67.0, 60.5, 48.2, 45.5, 28.7 (3C), 26.0 (3C), 25.5, 24.8, 18.1, 2.4 (3C), -4.1, -4.6.

HRMS (ESI): Calculated for $C_{24}H_{45}NO_5Si_2$ $[M+Na]^+$: 506.2729, found: 506.2734.

TLC (ethyl acetate : hexanes = 1 : 8) R*f*: 0.58 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: +67.32 (c 1.0, CH_2Cl_2);



(+)-*α*-Iodoenone (17):

Iodine (2.54 g, 10.0 mmol, 3.0 equiv.) was added to a stirred solution of **20** (1.62 g, 3.34 mmol, 1 equiv.) in anhydrous chloroform (17 mL) and pyridine (17 mL) co-solvent at 23 °C. The reaction temperature was raised to 50 °C. After 3.5 h, saturated aqueous sodium thiosulfate solution (100 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting residue was purified by flash column chromatography (silica gel: diam. 4 cm, ht. 12 cm; eluent: ethyl acetate : hexanes = 1 : 15) to afford **17** (1.95 g, 96%) as a pale yellow oil.

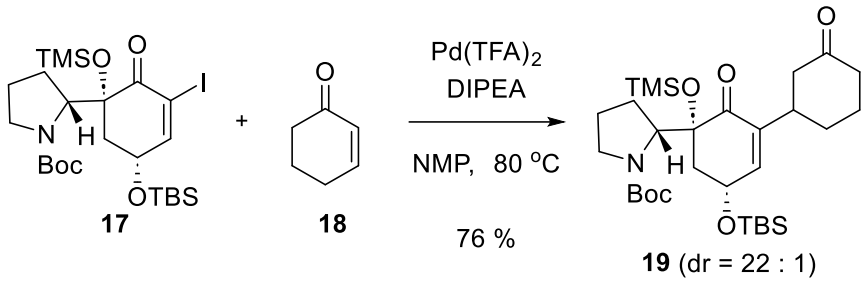
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (s, 1H), 5.38 (ddd, *J* = 9.2, 6.1, 2.6 Hz, 1H), 4.05 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.61 (td, *J* = 9.5, 5.6 Hz, 1H), 3.19 (ddd, *J* = 10.5, 8.6, 6.0 Hz, 1H), 2.60 (ddd, *J* = 12.8, 5.9, 1.7 Hz, 1H), 1.99 – 1.89 (m, 1H), 1.86 (dd, *J* = 12.7, 8.9 Hz, 1H), 1.76 (tt, *J* = 9.1, 4.1 Hz, 1H), 1.69 – 1.59 (m, 1H), 1.58 – 1.48 (m, 1H), 1.45 (s, 9H), 0.88 (s, 9H), 0.16 (s, 3H), 0.11 (s, 3H), 0.09 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 195.0, 162.2, 156.4, 101.0, 83.2, 79.9, 68.8, 60.6, 48.2, 45.3, 28.7 (3C), 26.0 (3C), 25.8, 24.8, 18.1, 2.3 (3C), -4.1, -4.6.

HRMS (ESI): Calculated for $C_{24}H_{44}INO_5Si_2$ $[M+H]^+$: 610.1876, found: 610.1879.

TLC (ethyl acetate : hexanes = 1 : 15) R*f*: 0.44 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: +35.43 (c 1.0, CH_2Cl_2);



(+)-Cyclohexanone 19:

Compound 19 was synthesized following a modified protocol of the procedure described in a previous report.[9]

N,*N*-diisopropylethyl amine (0.13 mL, 0.744 mmol, 6.0 equiv.) and $Pd(TFA)_2$ as a 0.2 M stock solution in *N*-Methyl-2-pyrrolidone (40 μL, 6.20 μmol, 5.0 mol%) were added to a stirred solution of cyclohexenone **18** (12 μL, 0.124 mmol, 1.0 equiv.) and iodide **17** (153 mg, 0.251 mmol, 2.0 equiv.) in *N*-Methyl-2-pyrrolidone (0.11 mL) at 23 °C. The reaction temperature was raised to 80 °C. After 24 h, saturated aqueous ammonium chloride solution (10 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were washed with water (3 × 30 mL) followed by brine (30 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 2 cm, ht. 14 cm; eluent: ethyl acetate : hexanes = 1 : 15) to afford **19** (54 mg, 76%) as a white foam.

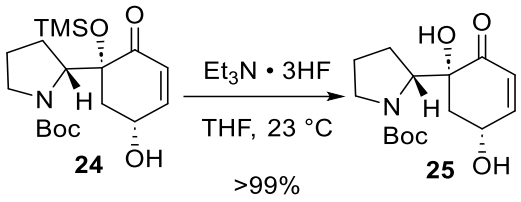
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.40 (s, 1H), 5.38 (t, *J* = 7.8 Hz, 1H), 4.01 (dd, *J* = 8.5, 2.4 Hz, 1H), 3.60 (td, *J* = 9.6, 5.3 Hz, 1H), 3.20 (ddd, *J* = 10.6, 8.8, 6.2 Hz, 1H), 2.89 (tt, *J* = 12.2, 3.7 Hz, 1H), 2.54 (dd, *J* = 12.7, 5.9 Hz, 1H), 2.38 (d, *J* = 14.0 Hz, 1H), 2.32 (ddd, *J* = 14.0, 4.2, 2.0 Hz, 1H), 2.25 (td, *J* = 13.6, 6.3 Hz, 1H), 2.17 (t, *J* = 13.4 Hz, 1H), 2.08 (ddq, *J* = 12.4, 5.9, 3.1 Hz, 1H), 1.98 – 1.91 (m, 1H), 1.91 – 1.85 (m, 1H), 1.77 (dd, *J* = 12.6, 9.1 Hz, 1H), 1.73 – 1.56 (m, 4H), 1.48 – 1.43 (m, 1H) 1.45 (s, 9H), 0.88 (s, 9H), 0.15 (s, 3H), 0.11 (s, 3H), 0.08 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 210.5, 200.2, 156.5, 147.0, 139.6, 84.6, 79.7, 66.2, 60.4, 48.1, 46.8, 45.3, 41.3, 38.0, 29.8, 28.7 (3C), 26.1 (3C), 25.4, 25.2, 24.8, 18.2, 2.5 (3C), -4.0, -4.5.

HRMS (ESI): Calculated for $C_{30}H_{53}NO_6Si_2$ $[M+Na]^+$: 602.3304, found: 602.3307.

TLC (ethyl acetate : hexanes = 1 : 5) R*f*: 0.46 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$: +54.60 (c 1.0, CH_2Cl_2);

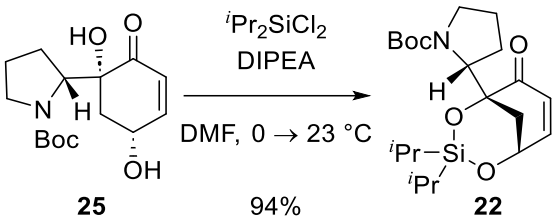


(+)-Diol 25:

*Compound **25** was synthesized via a modified procedure of our previous report.*[8]

To a stirred solution of **24**[8] (702 mg, 1.90 mmol, 1.0 equiv.) in THF (19 mL) at 23 °C was added triethylamine trihydrofluoride (9.30 mL, 57.0 mmol, 30.0 equiv.) under argon. After 3 h, saturated aqueous sodium bicarbonate solution (250 mL) was added to the reaction mixture, and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 30 mL), and the combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 16 cm; eluent: ethyl acetate : hexanes = 1 : 1) to afford **25** (565 mg, >99%) as a colorless oil.

The spectral data matches those of our previous report.[8]



25 94% **22**

(+)-Tethered enone 22:

N,*N*-diisopropylethyl amine (1.45 mL , 8.32 mmol, 5.0 equiv.) were added to a stirred solution of **25** (495 mg, 1.66 mmol, 1.0 equiv.) in dimethylformamide (33 mL) at 0 °C. Dichlorodiisopropylsilane (0.60 mL , 3.33 mmol, 2.0 equiv.) was added to the reaction mixture dropwise over 10 min at 0 °C. At the same temperature, the reaction mixture was stirred for 10 min and ice-water bath was then removed. The reaction mixture was further stirred 23 °C. After 17 h, saturated aqueous ammonium chloride solution (150 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water (3 × 100 mL) followed by brine (100 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 12 cm; eluent: ethyl acetate : hexanes = 1 : 5) to afford **22** (643 mg, 94%) as a pale yellow oil.

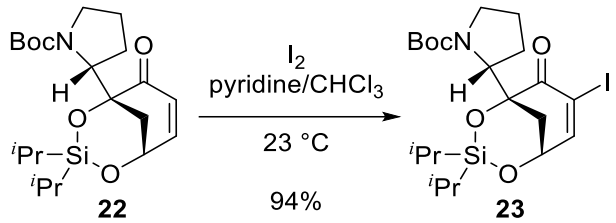
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (dd, *J* = 10.3, 5.5 Hz, 1H), 5.94 (d, *J* = 10.0 Hz, 1H), 4.55 (s, 1H), 4.12 (dd, *J* = 8.6, 2.7 Hz, 1H), 3.64 – 3.36 (br, 1H), 3.24 (ddd, *J* = 10.6, 8.3, 4.3 Hz, 1H), 2.43 (d, *J* = 15.3 Hz, 1H), 2.38 – 2.14 (m, 2H), 2.06 (dq, *J* = 12.9, 8.7 Hz, 1H), 1.92 (dp, *J* = 10.9, 8.2 Hz, 1H), 1.77 – 1.68 (m, 1H), 1.41 (s, 9H), 1.01 (dd, *J* = 7.5, 4.5 Hz, 6H), 0.94 – 0.86 (m, 8H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 196.7, 156.4, 146.1, 128.2, 79.4, 78.4, 64.0, 61.0, 48.2, 38.9, 28.6 (3C), 28.1, 25.0, 17.2, 16.9, 16.8, 16.6, 14.4, 14.0.

HRMS (ESI): Calculated for $C_{21}H_{35}NO_5Si$ $[M+Na]^+$: 432.2177, found: 432.2181.

TLC (ethyl acetate : hexanes = 1 : 5) R*f*: 0.44 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$: +215.55 (c 1.0, CH_2Cl_2);



(+)-α-Iodo-tethered-enone 23:

Iodine (100 mg, 0.397 mmol, 3.0 equiv.) was added to a stirred solution of **22** (54 mg, 0.132 mmol, 1 equiv.) in anhydrous chloroform (0.66 mL) and pyridine (0.66 mL) co-solvent at 23 °C. After 2.5 h, saturated aqueous sodium thiosulfate solution (20 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting residue was purified by flash column chromatography (silica gel: diam. 2 cm, ht. 14 cm; eluent: ethyl acetate : hexanes = 1 : 15) to afford **23** (61 mg, 85%) as a white crystalline solid.

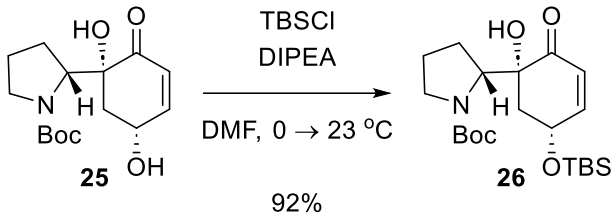
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, *J* = 5.9 Hz, 1H), 4.45 (dt, *J* = 6.2, 2.9 Hz, 1H), 4.15 (dd, *J* = 8.7, 2.8 Hz, 1H), 3.46 (brs, 1H), 3.24 (ddd, *J* = 10.8, 8.2, 4.4 Hz, 1H), 2.48 (d, *J* = 15.3 Hz, 1H), 2.39 (brs, 1H), 2.22 (ddt, *J* = 11.1, 7.3, 3.5 Hz, 1H), 2.09 (dq, *J* = 13.2, 8.7 Hz, 1H), 1.96 – 1.85 (m, 1H), 1.73 (dtt, *J* = 12.2, 8.2, 4.2 Hz, 1H), 1.42 (s, 9H), 1.01 (dd, *J* = 7.3, 4.5 Hz, 6H), 0.95 – 0.88 (m, 8H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 190.4, 156.5, 155.0, 106.3, 79.7, 78.9, 66.8, 61.7, 48.3, 39.1, 28.6 (3C), 28.2, 25.0, 17.2, 17.0, 16.8, 16.6, 14.4, 14.0.

HRMS (ESI): Calculated for $C_{21}H_{34}INO_5Si$ $[M+H]^+$: 536.1324, found: 536.1328.

TLC (ethyl acetate : hexanes = 1 : 6) R*f*: 0.49 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: +119.52 (c 1.0, CH_2Cl_2);



(+)-Enone 26:

N,*N*-diisopropylethyl amine (7.35 mL , 42.2 mmol, 10.0 equiv.) and *tert*-butyldimethylchlorosilane (2.55 g, 16.9 mmol, 4.0 equiv.) were added to a stirred solution of **25** (1.26 g, 4.22 mmol, 1.0 equiv.) in dimethylformamide (42 mL) at 0 °C. At the same temperature, the reaction mixture was stirred for 10 min and ice-water bath was then removed. The reaction mixture was further stirred 23 °C. After 2 hours, saturated aqueous ammonium chloride solution (150 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water (3 × 100 mL) followed by brine (100 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 4 cm, ht. 25 cm; eluent: ethyl acetate : hexanes = 1 : 15) to afford **26** (1.60 g, 92%) as a white solid.

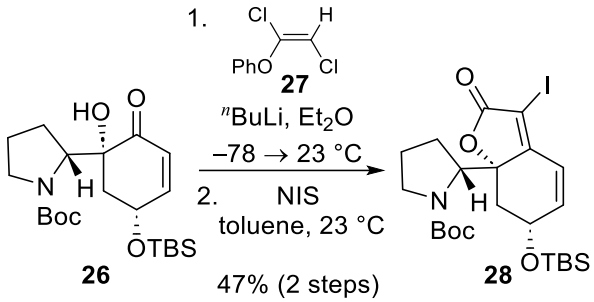
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.79 (d, *J* = 9.8 Hz, 1H), 6.01 (dd, *J* = 10.2, 2.2 Hz, 1H), 5.43 – 5.28 (m, 1H), 4.07 (dd, *J* = 7.7, 3.6 Hz, 1H), 3.77 (s, 1H), 3.58 (ddd, *J* = 10.9, 8.2, 6.1 Hz, 1H), 3.29 (ddd, *J* = 10.8, 8.4, 5.6 Hz, 1H), 2.75 – 2.60z (m, 1H), 1.92 (dtd, *J* = 16.2, 8.2, 6.1 Hz, 1H), 1.75 (dd, *J* = 13.0, 9.1 Hz, 1H), 1.71 – 1.54 (m, 3H), 1.43 (s, 9H), 0.85 (s, 9H), 0.14 (s, 3H), 0.10 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 202.0, 156.5, 155.9, 125.5, 80.3, 79.8, 66.5, 60.0, 48.2, 44.3, 28.7 (3C), 25.9 (3C), 25.6, 25.0, 18.1, -4.1, -4.7.

HRMS (ESI): Calculated for $C_{21}H_{37}NO_5Si$ $[M+Na]^+$: 434.2334, found: 434.2339.

TLC (ethyl acetate : hexanes = 1 : 6) R*f*: 0.46 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: +81.98 (c 1.0, CH_2Cl_2);



(+)-*α*-Iodobutenolide 28:

*n*BuLi (2.5 M in hexane, 4.0 mL, 9.97 mmol, 4.6 equiv.) was added to a stirred solution of 1,2-dichlorovinyl ether[10] **27** (983 mg, 5.20 mmol, 2.4 equiv.) in anhydrous diethyl ether (10 mL) at –78 °C under an atmosphere of argon. After 10 min, the resulting mixture was warmed to –20 °C. After 2 h, the reaction mixture was cooled to –78 °C and a solution of **26** (892 mg, 2.17 mmol, 1 equiv.) in anhydrous diethyl ether (23 mL) was added. The resulting mixture was slowly warmed to 23 °C. After 1 h, saturated sodium bicarbonate solution (30 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated.

The resulting crude residue was dissolved in anhydrous toluene (22 mL). *N*-iodosuccinimide (1.46 g, 6.50 mmol, 3.0 equiv.) was added at 23 °C while stirring. After 1.5 h, saturated aqueous sodium thiosulfate solution (50 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting residue was purified by flash column chromatography (silica gel, dry loading: diam. 4 cm, ht. 23 cm; eluent: ethyl acetate : hexanes = 1 : 20) to afford **28** as a white solid (571 mg, 47%, 2 steps).

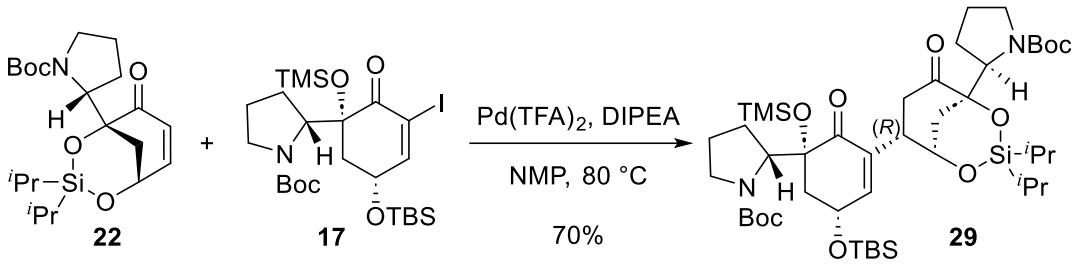
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.31 (dd, *J* = 9.9, 2.1 Hz, 1H), 6.24 (dd, *J* = 9.9, 2.4 Hz, 1H), 5.33 (dt, *J* = 8.0, 3.3 Hz, 1H), 4.12 (dd, *J* = 8.5, 2.1 Hz, 1H), 3.58 (ddd, *J* = 11.0, 8.6, 6.6 Hz, 1H), 3.36 (ddd, *J* = 11.0, 8.8, 5.1 Hz, 1H), 2.79 (dd, *J* = 12.2, 6.1 Hz, 1H), 1.90 – 1.80 (m, 1H), 1.77 – 1.67 (m, 1H), 1.63 – 1.54 (m, 2H), 1.46 (s, 9H), 1.35 – 1.27 (m, 1H), 0.86 (s, 9H), 0.15 (s, 3H), 0.10 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 169.6, 167.7, 156.5, 145.4, 120.4, 92.8, 80.3, 78.3, 67.5, 59.5, 47.6, 41.9, 28.7 (3C), 26.0 (3C), 25.3, 24.9, 18.1, -4.2, -4.7.

HRMS (ESI): Calculated for $C_{23}H_{36}INO_5Si$ $[M+Na]^+$: 584.1300, found: 584.1305.

TLC (ethyl acetate : hexanes = 1 : 5) R*f*: 0.54 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: +19.65 (c 1.0, CH_2Cl_2);



(+)-Diketo-dimer 29:

*Compound **29** was synthesized following a modified protocol of the procedure described in a previous report.*[9]

N,*N*-diisopropylethyl amine (0.50 mL, 2.89 mmol, 6.0 equiv.) and $Pd(TFA)_2$ as a 0.2 M stock solution in *N*-Methyl-2-pyrrolidone (0.12 mL, 2.41×10^{-2} mmol, 5.0 mol%) were added to a stirred solution of enone **22** (198 mg, 0.482 mmol, 1.0 equiv.) and iodide **17** (588 mg, 0.964 mmol, 2.0 equiv.) in *N*-Methyl-2-pyrrolidone (0.44 mL) at 23 °C. The reaction temperature was raised to 80 °C. After 24 h, saturated aqueous ammonium chloride solution (20 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with water (3 × 30 mL) followed by brine (30 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 12 cm; eluent: ethyl acetate : hexanes = 1 : 20) to afford **29** (302 mg, 70%) as a white foam.

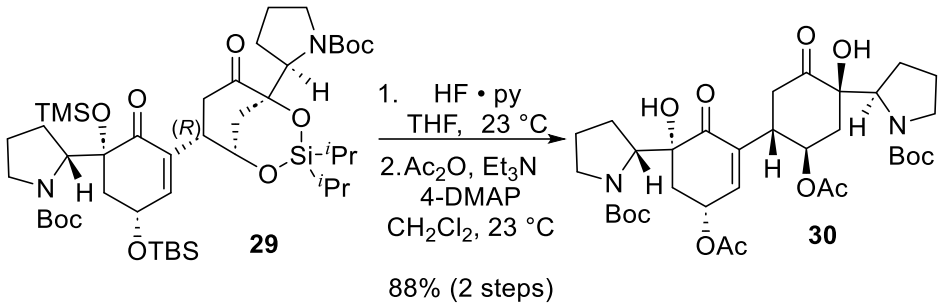
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.56 (s, 1H), 5.42 (t, J = 7.5 Hz, 1H), 4.15 (d, J = 8.0 Hz, 1H), 4.03 (s, 1H), 3.92 (brs, 1H), 3.73 (brs, 1H), 3.64 – 3.37 (br, 1H), 3.58 (brs, 1H), 3.44 (dd, *J* = 14.9, 8.0 Hz, 1H), 3.22 (ddd, J = 11.7, 7.9, 4.1 Hz, 1H), 3.16 (q, J = 8.6 Hz, 1H), 2.55 (brs, 1H), 2.34 (d, J = 14.7 Hz, 1H), 2.25 (d, J = 15.4 Hz, 1H), 2.07 – 1.82 (m, 5H), 1.80 – 1.54 (m, 5H), 1.43 (s, 9H), 1.35 (s, 10H), 1.06 – 1.00 (m, 13H), 0.97 – 0.92 (m, 1H), 0.89 (s, 9H), 0.17 (s, 3H), 0.11 (s, 3H), 0.08 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): 210.6, 200.0, 156.2, 155.8, 149.6, 137.2, 84.8, 82.5 ,81.8, 79.8, 79.4, 69.5, 66.4, 61.0, 60.0, 48.4, 48.0, 45.5, 44.3, 36.9, 36.1, 28.6 (7C), 26.1 (3C), 25.6, 24.9, 24.2, 18.1, 17.4, 17.3, 17.3, 17.3, 15.9, 15.6, 14.2, 2.5 (3C), -4.2, -4.5. (mixture of rotamers)

HRMS (ESI): Calculated for $C_{45}H_{80}N_2O_{10}Si_3$ $[M+H]^+$: 893.5194, found: 893.5208.

TLC (ethyl acetate : hexanes = 1 : 8) R*f*: 0.5 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$: +69.61 (c 1.0, CH_2Cl_2);



(–)-Dihydroxy diacetate 30:

To a stirred solution of **29** (261 mg, 0.292 mmol, 1 equiv) in THF (4.9 mL) at 23 °C was added hydrogen fluoride pyridine complex (0.39 mL, 4.37 mmol, 15.0 equiv). After 4 h, saturated sodium bicarbonate solution (50 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated.

The resulting crude residue was dissolved in anhydrous dichloromethane (2.9 mL) and triethylamine (0.33 mL, 2.36 mmol, 8.1 equiv.), 4-(dimethylamino)pyridine (36 mg, 0.292 mmol, 1.0 equiv.) and acetic anhydride (0.11 mL, 1.17 mmol, 4.0 equiv.) was added at 23 C. After 1 h, saturated aqueous ammonium chloride solution (50 mL) was added to the mixture and the resultant mixture was extracted with dichloromethane (3 × 20 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 18 cm; eluent: ethyl acetate : hexanes = 2 : 3) to afford **30** as a white foam (175 mg, 88%, 2 steps).

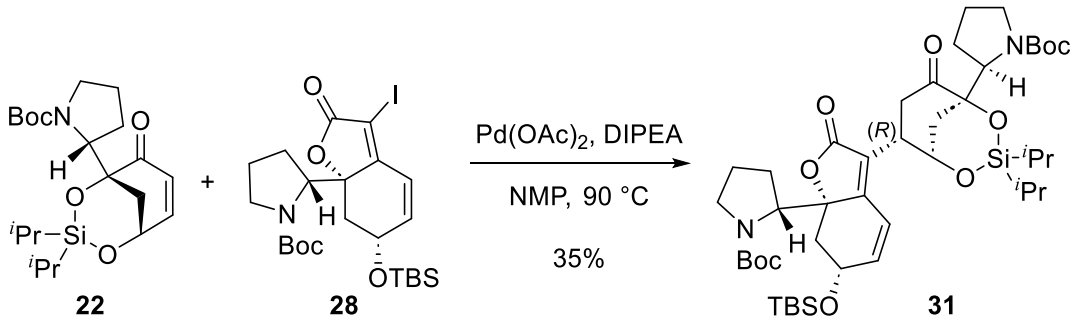
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.71 – 6.43 (br, 1H), 6.11 (s, 1H), 5.98 – 5.49 (br, 1H), 4.42 (s, 1H), 4.04 – 3.81 (br, 1H), 3.96 (d, *J* = 7.6 Hz, 1H), 3.90 (brs, 1H) 3.79 – 3.47 (br, 1H), 3.53 (s, 1H), 3.41 (brs, 1H), 3.36 – 3.17 (m, 2H), 2.80 – 2.55 (m, 4H), 2.06 – 1.97 (m, 2H), 2.03 (s, 3H), 1.93 (s, 3H), 1.86 – 1.67 (m, 6H), 1.64 – 1.53 (m, 2H), 1.42 (s, *J* = 2.7 Hz, 18H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 210.6, 200.4, 169.7, 169.5, 156.2, 156.0, 146.3, 136.3, 81.2, 79.9, 79.8, 79.4, 70.0, 67.4, 61.1, 60.7, 48.1, 47.9 (2C), 41.3, 39.0, 38.8, 28.5 (3C), 28.4 (3C), 25.9 (2C), 24.7 (2C), 21.0, 20.9.

HRMS (ESI): Calculated for $C_{34}H_{50}N_2O_{12}$ $[M+Na]^+$: 701.3256, found: 701.3265.

TLC (ethyl acetate : hexanes = 1 : 1) R*f*: 0.42 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: -26.55 (c 1.0, CH_2Cl_2);



(+)-Monoketo-dimer 31:

*Compound **31** was synthesized following a modified protocol of the procedure described in a previous report.*[9]

N,*N*-diisopropylethyl amine (78 μL, 0.448 mmol, 6.0 equiv.) and $Pd(OAc)_2$ as a 0.2 M stock solution in *N*-Methyl-2-pyrrolidone (19 μL, 3.73 μmol, 5.0 mol%) were added to a stirred solution of enone **22** (31 mg, 7.47×10^{-2} mmol, 1.0 equiv.) and iodide **28** (126 mg, 0.224 mmol, 3.0 equiv.) in *N*-Methyl-2-pyrrolidone (52 μL) at 23 °C. The reaction temperature was raised to 90 °C. After 48 h, saturated aqueous ammonium chloride solution (10 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were washed with water (3 × 10 mL) followed by brine (10 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 3 cm, ht. 19 cm; eluent: ethyl acetate : hexanes = 1 : 15) to afford **31** (22 mg, 35%) as a pale yellow foam.

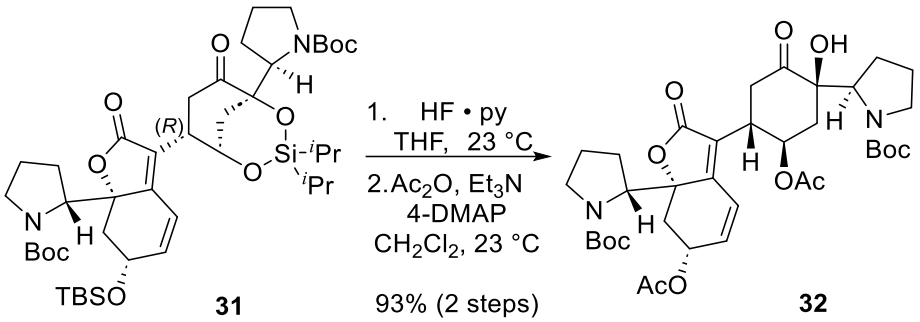
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.55 (dd, *J* = 10.1, 2.2 Hz, 1H), 6.15 (d, *J* = 8.9 Hz, 1H), 5.28 (s, 1H), 4.58 – 4.32 (br 1H), 4.15 (dd, *J* = 8.4, 2.7 Hz, 1H), 4.06 (dd, *J* = 8.3, 2.5 Hz, 1H), 3.67 – 3.35 (br, 1H), 3.57 (dd, *J* = 12.8, 6.2 Hz, 1H), 3.44 (s, 1H), 3.33 – 3.26 (m, 1H), 3.23 (ddd, *J* = 11.6, 7.5, 4.4 Hz, 1H), 3.10 (brs, 1H), 2.84 (dd, *J* = 12.1, 6.2 Hz, 1H), 2.68 (brs, 1H), 2.39 (d, *J* = 15.3 Hz, 1H), 2.31 (brs, 1H), 2.17 (brs, 1H), 1.99 (dq, *J* = 11.7, 8.1, 7.4 Hz, 1H), 1.91 (dq, *J* = 17.0, 8.1 Hz, 1H), 1.77 (brs, 1H), 1.73 – 1.70 (m, 1H), 1.69 – 1.61 (brs, 1H), 1.58 – 1.47 (m, 2H), 1.44 (s, 9H), 1.37 (s, 9H), 1.17 (brs, 1H), 1.05 – 0.97 (m, 13H), 0.97 – 0.91 (m, 1H), 0.86 (s, 9H), 0.14 (s, 3H), 0.09 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 208.9, 207.4, 172.2, 159.7, 158.4, 156.5, 156.0, 143.8, 123.5, 118.2, 88.7, 80.1, 80.0, 79.4, 70.2, 66.7, 61.5, 59.5, 48.1, 47.6, 42.8, 41.9, 37.3, 36.5, 36.0, 28.6 (3C), 28.6 (3C), 27.8, 26.0 (3C), 25.3, 24.9, 24.3, 18.1, 17.4, 17.3, 17.2, 17.2, 15.4, 14.0, -4.3, -4.6. (mixture of rotamers)

HRMS (ESI): Calculated for $C_{44}H_{72}N_2O_{10}Si_2$ $[M+H]^+$: 845.4799, found: 845.4800.

TLC (ethyl acetate : hexanes = 1 : 4) R*f*: 0.53 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: +38.00 (c 1.0, CH_2Cl_2);



(–)-Monohydroxy diacetate 32:

To a stirred solution of **31** (86 mg, 0.101 mmol, 1 equiv) in THF (1.7 mL) at 23 °C was added hydrogen fluoride pyridine complex (0.14 mL, 1.52 mmol, 15.0 equiv). After 5 h, saturated sodium bicarbonate solution (30 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated.

The resulting crude residue was dissolved in anhydrous dichloromethane (1.0 mL) and triethylamine (57 μL, 0.405 mmol, 4.0 equiv.), 4-(dimethylamino)pyridine (12 mg, 0.101 mmol, 1.0 equiv.) and acetic anhydride (19 μL, 0.203 mmol, 2.0 equiv.) was added at 23 °C. After 1 h, saturated aqueous ammonium chloride solution (30 mL) was added to the mixture and the resultant mixture was extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting residue was purified by flash column chromatography (silica gel: diam. 2 cm, ht. 12 cm; eluent: ethyl acetate : hexanes = 2 : 3) to afford **32** as a white foam (66 mg, 93%, 2 steps).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.71 – 6.51 (brs, 1H), 6.09 (dd, *J* = 10.3, 2.4 Hz, 1H) 6.18 – 5.98 (br, 1H), 5.96 – 5.46 (br, 1H), 4.41 (dd, *J* = 8.3, 2.5 Hz, 1H), 4.03 (d, *J* = 8.2 Hz, 1H), 3.94 (brs, 1H, OH), 3.80 – 3.56 (br, 1H), 3.62 (t, *J* = 14.1 Hz, 1H), 3.56 – 3.47 (m, 1H), 3.42 – 3.30 (m, 2H), 3.02 (ddd, *J* = 14.4, 10.4, 4.4 Hz, 1H), 2.93 (dd, *J* = 12.5, 6.5 Hz, 1H), 2.72 (d, *J* = 11.4 Hz, 1H), 2.56 (d, *J* = 14.4 Hz, 1H), 2.06 – 1.96 (m, 1H), 2.01 (s, 3H), 1.93 – 1.87 (m, 1H), 1.88 (s, 3H), 1.86 – 1.81 (m, 1H), 1.81 – 1.73 (m, 2H), 1.70 – 1.64 (m, 2H), 1.62 – 1.54 (m, 2H), 1.46 – 1.36 (m, 1H), 1.44 (s, 9H), 1.42 (s, 9H).

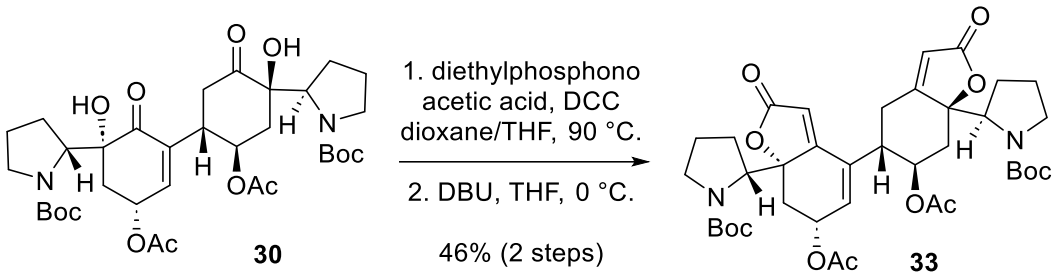
^{13}C NMR (126 MHz, $CDCl_3$): δ 210.2, 171.0, 169.8, 169.6, 159.2, 156.1, 136.6, 122.5, 121.1, 87.3, 81.3, 80.2, 69.4, 68.5, 60.7, 60.4, 47.9, 47.5, 41.6, 41.0, 38.7, 36.6, 28.5 (3C), 28.4 (3C), 26.3, 25.6, 24.7 (2C), 21.1, 21.0.

Note: Two carbons were missing in ^{13}C NMR. X-ray crystallography assigned the structure.

HRMS (ESI): Calculated for $C_{36}H_{50}N_2O_{12}$ $[M+Na]^+$: 725.3256, found: 725.3265.

TLC (ethyl acetate : hexanes = 1 : 1) R*f*: 0.42 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$: -65.28 (c 1.0, CH_2Cl_2);



(+)-Dibutenolide 33:

To a stirred solution of **30** (164 mg, 0.241 mmol, 1 equiv.) in dioxane (2.4 mL) at 23 °C was added *N,N′*-dicyclohexylcarbodiimide (1.99 g, 9.65 mmol, 40.0 equiv.) under argon, and the reaction mixture was heated to 90 °C. After 30 min, a solution of diethylphosphonoacetic acid (0.78 mL, 4.82 mmol, 20.0 equiv.) in THF (1.2 mL) was added slowly via syringe pump over 3 h. After 1 h, the reaction mixture was filtered and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography (silica gel: diam. 3 cm, ht. 12 cm; eluent: acetone : hexanes = 1 : 1) to afford an inseparable mixture.

To a stirred solution of the inseparable mixture in THF (2.1 mL) at 0 °C was added 1,8-diazabicyclo[5.4.0]undec-7-ene (0.31 mL, 2.07 mmol, 10 equiv.) under argon. After 3 h, a saturated aqueous ammonium chloride solution (20 mL) was added and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography (silica gel: diam. 3 cm, ht. 21 cm; eluent: ethyl acetate : hexanes = 1 : 2) to afford **33** (80.4 mg, 46%, 2 steps) as a white foam:

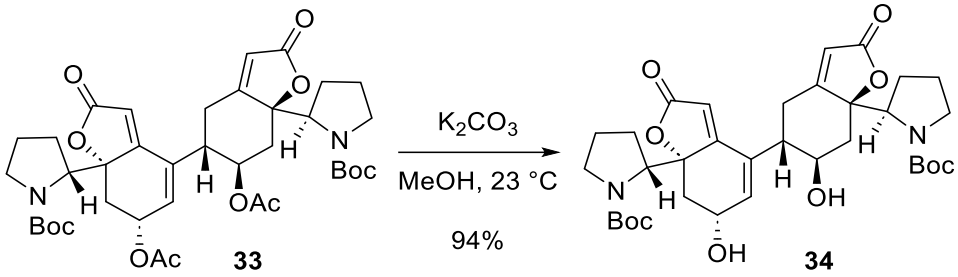
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.37 (s, 1H), 6.21 (s, 1H), 6.02 (s, 1H), 5.92 (s, 1H), 5.77 (s, 1H), 4.32 (d, *J* = 7.6 Hz, 1H), 4.14 (d, *J* = 8.3 Hz, 1H), 3.62 (s, 2H), 3.52 – 3.34 (m, 2H), 3.03 (dd, *J* = 12.9, 7.1 Hz, 1H), 2.86 (dd, *J* = 12.8, 6.5 Hz, 2H), 2.64 (t, *J* = 13.5 Hz, 1H), 2.53 (t, *J* = 10.2 Hz, 1H), 2.13 – 2.01 (m, 1H), 2.04 (s, 3H), 2.01 – 1.93 (m, 1H), 1.97 (s, 3H), 1.92 – 1.84 (m, 2H), 1.82 – 1.75 (m, 1H), 1.71 – 1.59 (m, 3H), 1.55 – 1.41 (m, 2H), 1.50 (s, 9H), 1.49 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 171.8, 171.7, 170.6, 169.6, 168.9, 163.3, 156.4, 156.1, 136.0, 133.0, 116.1, 114.1, 90.6, 89.4, 80.8, 80.3, 69.2, 68.3, 60.4, 59.5, 50.1, 47.6, 47.3, 40.0, 37.4, 28.9, 28.4 (3C), 28.3 (3C), 25.6, 25.3, 24.9, 24.8, 21.0, 20.7.

HRMS (ESI): Calculated for $C_{38}H_{50}N_2O_{12}$ $[M+Na]^+$: 749.3256, found: 749.3259.

TLC (ethyl acetate : hexanes = 1 : 1) R*f*: 0.40 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: +39.66 (c 1.0, CH_2Cl_2);



(+)-Dibutenolide 34:

Potassium carbonate (45 mg, 0.325 mmol, 3.0 equiv.) was added to a stirred solution of **33** (79 mg, 0.108 mmol, 1 equiv.) in methanol (2.2 mL) at 23 °C. After 1 h, saturated aqueous ammonium chloride solution (20 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting residue was purified by flash column chromatography (silica gel: diam. 2 cm, ht. 13 cm; eluent: ethyl acetate : hexanes = 2 : 1) to afford **34** as a white solid (65 mg, 94%).

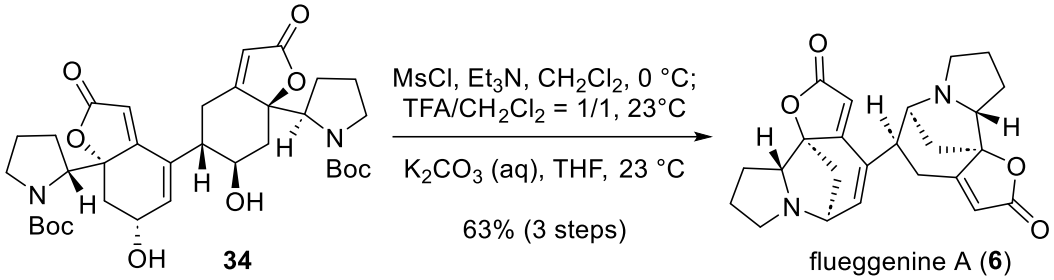
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.42 (d, *J* = 2.4 Hz, 1H), 5.93 (s, 1H), 5.88 (s, 1H), 5.23 (s, 1H), 4.47 – 4.37 (m, 1H), 4.35 (d, *J* = 6.6 Hz, 1H), 4.01 (d, *J* = 7.8 Hz, 1H), 3.59 – 3.48 (m, 2H), 3.46 – 3.34 (m, 2H), 3.09 (dd, *J* = 11.7, 5.7 Hz, 1H), 2.88 (d, *J* = 9.4 Hz, 1H), 2.80 (dd, *J* = 12.8, 4.3 Hz, 1H), 2.53 – 2.38 (m, 2H), 1.96 – 1.84 (m, 1H), 1.80 – 1.68 (m, 3H), 1.64 – 1.50 (m, 3H), 1.49 – 1.40 (m, 2H), 1.42 (s, 9H), 1.40 – 1.32 (m, 1H), 1.36 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.2, 172.1, 171.1, 168.1, 157.3, 156.2, 135.9, 135.6, 115.7, 111.5, 91.0, 90.5, 81.3, 80.7, 71.0, 66.2, 58.7, 58.2, 48.8, 47.8, 47.6, 44.7, 42.1, 30.7, 28.6 (3C), 28.5 (3C), 26.5, 25.0, 24.7, 24.3.

HRMS (ESI): Calculated for $C_{34}H_{46}N_2O_{10}$ $[M+Na]^+$: 665.3045, found: 665.3044.

TLC (ethyl acetate : hexanes = 3 : 1) R*f*: 0.40 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: +89.05 (c 1.0, CH_2Cl_2);



(–)-Flueggenine A (6):

Triethylamine (0.16 mL, 1.15 mmol, 12.0 equiv.) and methanesulfonyl chloride (37 μL, 0.478 mmol, 5.0 equiv.) were added to a stirred solution of **34** (62 mg, 9.57×10^{-2} mmol, 1 equiv.) in anhydrous dichloromethane (4.8 mL) at 0 °C. After 30 min, brine (20 mL) was added and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulfate and the resulting filtrate concentrated under reduced pressure. The resulting crude mixture was dissolved in anhydrous dichloromethane (2.2 mL) and trifluoroacetic acid (2.2 mL) cosolvent and the mixture was stirred at 23 °C. After 30 min, the reaction mixture was concentrated under reduced pressure.

The resulting crude mixture was dissolved in a mixture of tetrahydrofuran (2.2 mL) and saturated aqueous potassium carbonate solution (2.2 mL). After 30 min, brine (20 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting crude residue was purified by flash purified by flash column chromatography (silica gel: diam. 2 cm, ht. 14 cm; eluent: dichloromethane : methanol : ammonium hydroxide = 10 : 0.5 : 0.1) to afford flueggenine A (**6**) (24 mg, 63%, 3 steps) as a white amorphous solid.

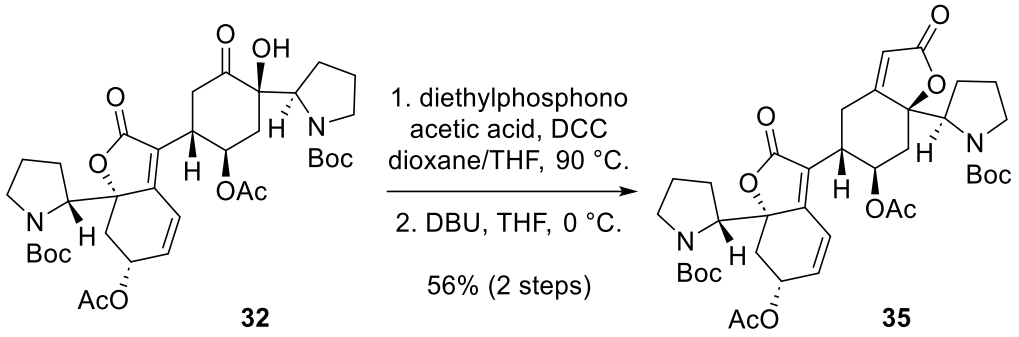
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.94 (d, *J* = 6.7 Hz, 1H), 6.01 (s, 1H), 5.74 (d, *J* = 1.9 Hz, 1H), 3.80 (dd, *J* = 6.8, 4.5 Hz, 1H), 3.30 – 3.27 (m, 1H), 3.23 (dd, *J* = 9.5, 6.3 Hz, 1H), 3.19 (d, *J* = 5.9 Hz, 1H), 3.16 (dd, *J* = 8.2, 6.9 Hz, 1H), 3.13 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.01 (dd, *J* = 13.4, 3.6 Hz, 1H), 2.78 – 2.70 (m, 2H), 2.70 – 2.61 (m, 4H), 2.07 – 2.00 (m, 1H), 2.00 – 1.94 (m, 2H), 1.92 – 1.82 (m, 2H), 1.81 – 1.77 (m, 1H), 1.77 – 1.71 (m, 1H), 1.75 (d, *J* = 10.5 Hz, 1H), 1.71 – 1.64 (m, 1H), 1.58 (d, *J* = 11.0 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 176.3, 175.4, 174.7, 171.8, 140.6, 135.8, 110.8, 108.2, 94.0, 93.5, 68.4, 66.4, 66.1, 60.7, 58.3, 56.1, 44.1, 37.0, 36.5, 30.3, 30.2, 29.2, 27.8, 27.8.

HRMS (ESI): Calculated for $C_{24}H_{26}N_2O_4$ $[M+H]^+$: 407.1966, found: 407.1983.

TLC (dichloromethane : methanol : ammonium hydroxide =10 : 1 : 0.1) R*f*: 0.35 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: –27.64 (c 0.5, MeOH);



(+)-Dibutenolide 35:

To a stirred solution of **32** (56 mg, 8.25 ×10^{-2} mmol, 1 equiv.) in dioxane (0.83 mL) at 23 °C was added *N,N′*-dicyclohexylcarbodiimide (341 mg, 1.65 mmol, 20.0 equiv.) under argon, and the reaction mixture was heated to 90 °C. After 30 min, a solution of diethylphosphonoacetic acid (0.13 mL, 0.825 mmol, 10.0 equiv.) in THF (0.20 mL) was added slowly via syringe pump over 3 h. After 1 h, the reaction mixture was filtered and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography (silica gel: diam. 2 cm, ht. 11 cm; eluent: acetone : hexanes = 2 : 5) to afford an inseparable mixture.

To a stirred solution of the inseparable mixture in THF (0.83 mL) at 0 °C was added 1,8-diazabicyclo[5.4.0]undec-7-ene (62.0 μL, 0.413 mmol, 5.0 equiv.) under argon. After 3 h, a saturated aqueous ammonium chloride solution (10 mL) was added and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 5 mL), and the combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography (silica gel: diam. 2 cm, ht. 14 cm; eluent: ethyl acetate : hexanes = 1 : 1) to afford **35** (34 mg, 56%) as a white foam:

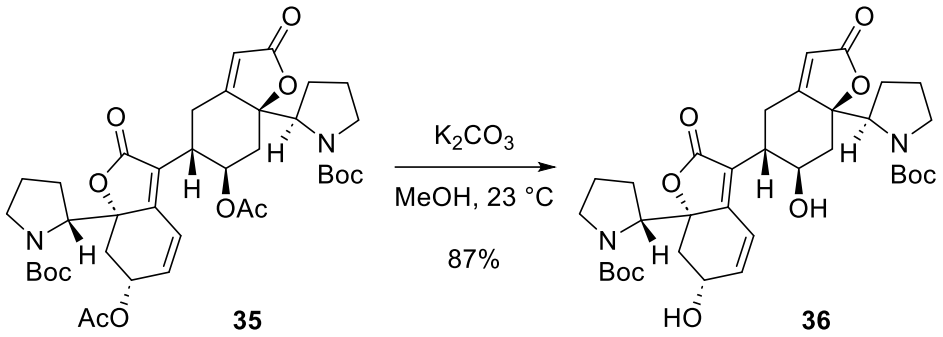
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.60 (s, 1H), 6.07 (d, *J* = 9.9 Hz, 2H), 5.93 – 5.57 (br, 1H) 5.86 (s, 1H), 4.42 (d, *J* = 7.1 Hz, 1H), 4.01 (d, *J* = 8.1 Hz, 1H), 3.79 – 3.46 (br, 1H), 3.51 (brs, 1H), 3.41 – 3.26 (m, 3H), 2.90 (dd, *J* = 12.4, 6.5 Hz, 1H), 2.86 – 2.68 (m, 3H), 1.98 (s, 3H), 1.94 – 1.87 (brs, 2H), 1.84 (s, 3H), 1.81 – 1.73 (m, 3H), 1.72 – 1.64 (m, 1H), 1.61 – 1.54 (m, 1H), 1.51 – 1.44 (m, 3H), 1.41 (s, 9H), 1.39 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.1, 171.0, 169.9 (2C), 169.4, 159.6 (2C), 156.1, 136.5, 123.0, 121.2, 115.7, 90.3, 87.3, 81.6, 80.3, 69.6, 68.4, 60.5, 59.2, 47.6 (2C), 41.6, 40.3, 36.6, 28.5 (3C), 28.4 (3C), 27.5, 25.7, 25.5, 24.7, 23.7, 21.1, 21.0.

HRMS (ESI): Calculated for $C_{38}H_{50}N_2O_{12}$ $[M+Na]^+$: 749.3256, found: 749.3264.

TLC (ethyl acetate : hexanes = 1 : 1) R*f*: 0.39 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: +39.68 (c 1.0, CH_2Cl_2);



(+)-Dibutenolide 36:

Potassium carbonate (29 mg, 0.209 mmol, 3.0 equiv.) was added to a stirred solution of **33** (51 mg, 6.96×10^{-2} mmol, 1 equiv.) in methanol (1.4 mL) at 23 °C. After 1 h, saturated aqueous ammonium chloride solution (10 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting residue was purified by flash column chromatography (silica gel: diam. 2 cm, ht. 13 cm; eluent: dichloromethane : acetone = 3 : 1) to afford **36** as a white solid (39 mg, 87%).

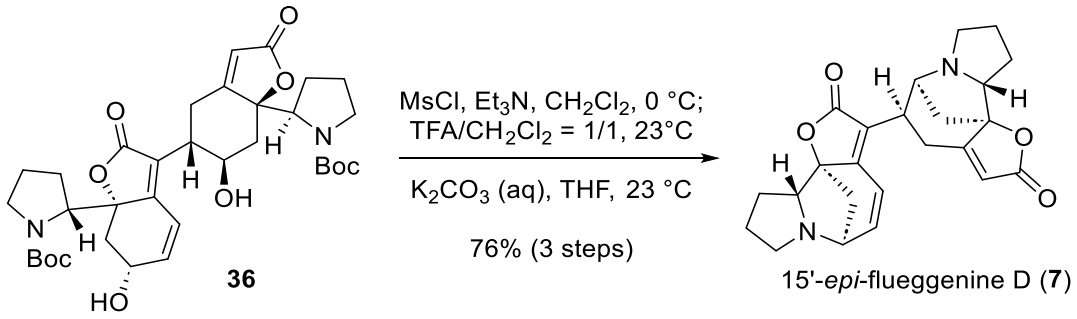
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.53 (d, *J* = 10.0 Hz, 1H), 6.17 (d, *J* = 10.2 Hz, 1H), 5.81 (s, 1H), 5.14 (s, 1H), 4.63 (s, 1H), 4.41 (d, *J* = 7.6 Hz, 1H), 3.97 (d, *J* = 7.9 Hz, 1H), 3.53 (t, *J* = 10.2 Hz, 2H), 3.36 (brs, 2H), 3.02 – 2.92 (m, 1H), 2.86 (s, 1H), 2.72 (t, *J* = 12.5 Hz, 2H), 2.58 (brs, 1H), 1.92 – 1.79 (m, 2H), 1.79 – 1.61 (m, 4H), 1.57 – 1.49 (m, 2H), 1.44 (s, 9H), 1.43 (s, 9H), 1.37 – 1.28 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 172.6, 172.2, 171.5, 161.4, 156.3 (2C), 141.7, 122.9, 119.5, 115.3, 91.4, 88.2, 80.5, 80.3, 66.6, 65.9, 60.7, 58.2, 47.6, 47.5, 43.9, 43.2, 41.1, 28.6 (3C), 28.5 (3C), 28.2, 25.7, 25.1, 24.8 (2C).

HRMS (ESI): Calculated for $C_{34}H_{46}N_2O_{10}$ $[M+Na]^+$: 665.3045, found: 665.3047.

TLC (ethyl acetate : hexanes = 4 : 1) R*f*: 0.43 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\boldsymbol{23}}$: +67.49 (c 1.0, CH_2Cl_2);



(−)-15′-*epi*-Flueggenine D (7):

Triethylamine (84 μL, 0.605 mmol, 12.0 equiv.) and methanesulfonyl chloride (20 μL, 0.252 mmol, 5.0 equiv.) were added to a stirred solution of **36** (32 mg, 5.04×10^{-2} mmol, 1 equiv.) in anhydrous dichloromethane (2.5 mL) at 0 °C. After 30 min, brine (20 mL) was added and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The combined organic layer was dried over anhydrous sodium sulfate and the resulting filtrate concentrated under reduced pressure. The resulting crude mixture was dissolved in anhydrous dichloromethane (1.2 mL) and trifluoroacetic acid (1.2 mL) cosolvent and the mixture was stirred at 23 °C. After 30 min, the reaction mixture was concentrated under reduced pressure.

The resulting crude mixture was dissolved in a mixture of tetrahydrofuran (1.2 mL) and saturated aqueous potassium carbonate solution (1.2 mL). After 30 min, brine (20 mL) was added to the mixture and the resultant mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated. The resulting crude residue was purified by flash purified by flash column chromatography (silica gel: diam. 2 cm, ht. 14 cm; eluent: dichloromethane : methanol : ammonium hydroxide = 10 : 0.5 : 0.1) to afford 15′-*epi*-flueggenine D (**7**, 16 mg, 76%, 3 steps) as a white crystalline solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (d, *J* = 9.4 Hz, 1H), 6.66 (dd, *J* = 9.2, 6.3 Hz, 1H), 5.62 (d, *J* = 2.2 Hz, 1H), 3.69 – 3.54 (m, 1H), 3.29 (s, 1H), 3.25 – 3.10 (m, 3H), 3.00 – 2.88 (m, 3H), 2.80 (ddd, *J* = 13.9, 11.1, 2.4 Hz, 1H), 2.59 – 2.49 (m, 4H), 2.01 – 1.94 (m, 2H), 1.94 – 1.84 (m, 2H), 1.83 – 1.72 (m, 3H), 1.69 (d, *J* = 10.5 Hz, 1H), 1.66 – 1.60 (m, 1H), 1.51 (d, *J* = 11.1 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.9, 173.1, 172.9, 163.2, 142.6, 122.4, 120.4, 110.3, 92.0, 90.7, 67.3, 65.9, 65.8, 59.9, 57.4, 55.3, 39.4, 36.0, 35.7, 29.6, 29.1, 28.7, 27.0, 26.9.

HRMS (ESI): Calculated for $C_{24}H_{26}N_2O_4$ $[M+H]^+$: 407.1966, found: 407.1965.

TLC (dichloromethane : methanol : ammonium hydroxide =10 : 1 : 0.1) R*f*: 0.31 (UV, $KMnO_4$).

$[\boldsymbol{\alpha}]_{\boldsymbol{D}}^{\mathbf{23}}$: –26.96 (c 0.25, CH_2Cl_2);

3. Comparison of Spectroscopic Data of Natural and Synthetic Flueggenine A (6)

Table S1. Comparison of ^{1}H NMR spectroscopic data between synthetic and isolated flueggenine A (6).

Position	Isolation report (ppm ; multi, *J* in Hz) [11, a]	This work (ppm ; multi, *J* in Hz)[b]	Difference (ppm)
2	3.17 (dd, 8.2, 6.3)	3.16 (dd, 8.2, 6.9)	–0.01
3	a 1.88 (m)	a 1.86 (m)	–0.02
	b 1.97 (m)	b 1.98 (m)	0.01
4	a 2.03 (m)	a 2.04 (m)	0.01
	b 1.73 (m)	b 1.75 (m)	0.02
5	a 2.65 (m)	a 2.65 (m)	-
	b 3.24 (dd, 8.6, 7.2)	b 3.23 (dd, 9.5, 6.3)	–0.01
7	3.81 (dd, 1.8, 4.7)	3.80 (dd, 6.8, 4.5)	–0.01
8	a 1.75 (d, 10.7)	a 1.75 (d, 10.5)	-
	b 2.67 (m)	b 2.65 (m)	–0.02
12	6.00 (s)	6.01 (s)	0.01
15	6.93 (d, 6.7)	6.94 (d, 6.7)	0.01
2′	3.13 (dd, 9.2, 7.1)	3.13 (dd, 8.8, 6.4)	-
3′	a 1.84 (m)	a 1.86 (m)	0.02
	b 1.75 (m)	b 1.79 (m)	0.04
4′	a 1.96 (m)	a 1.98 (m)	0.02
	b 1.68 (m)	b 1.68 (m)	-
5′	a 2.63 (m)	a 2.65 (m)	0.02
	b 3.29 (m)	b 3.29 (m)	-
7′	3.19 (m)	3.19 (d, 5.9)	-
8′	a 1.57 (d, 11.0)	a 1.58 (d, 11.0)	0.01
	b 2.64 (m)	b 2.65 (m)	0.01
12′	5.73 (d, 1.9)	5.74 (d, 1.9)	0.01
14′	a 2.73 (m)	a 2.73 (m)	-
	b 3.00 (m)	b 3.01 (dd, 13.4, 3.6)	0.01
15′	2.71 (m)	2.73 (m)	0.02

[a] Reference: residual methanol δ = 3.30 ppm.

[b] Reference: residual methanol δ = 3.31 ppm.

Table S2. Comparison of ^{13}C NMR spectroscopic data between synthetic and isolated flueggenine A (6).

Position	Isolation report (ppm) [11, a]	This work (ppm)[b]	Difference (ppm)
2	66.6	66.4	–0.2
3	30.4	30.3	–0.1
4	27.9	27.8	–0.1
5	56.3	56.1	–0.2
7	61.0	60.7	–0.3
8	37.2	37.0	–0.2
9	93.5	93.5	-
11	174.8	174.7	–0.1
12	108.4	108.2	–0.2
13	171.8	171.8	-
14	136.1	135.8	–0.3
15	140.6	140.6	-
2′	68.6	68.4	–0.2
3′	30.3	30.2	–0.1
4′	27.9	27.8	–0.1
5′	58.5	58.3	–0.2
7′	66.3	66.1	–0.2
8′	36.6	36.5	–0.1
9′	94.1	94.0	–0.1
11′	175.6	175.4	–0.2
12′	110.9	110.8	–0.1
13′	176.4	176.3	–0.1
14′	29.3	29.2	–0.1
15′	44.3	44.1	–0.2

[a] Reference: residual chloroform δ = 49.2 ppm.

[b] Reference: residual chloroform δ = 49.2 ppm.

4. Single Crystal X-Ray Diffraction Analysis of Compounds 20, 23, 28, 32, and 7

4.1 X-ray Crystal Structure of Compound 20

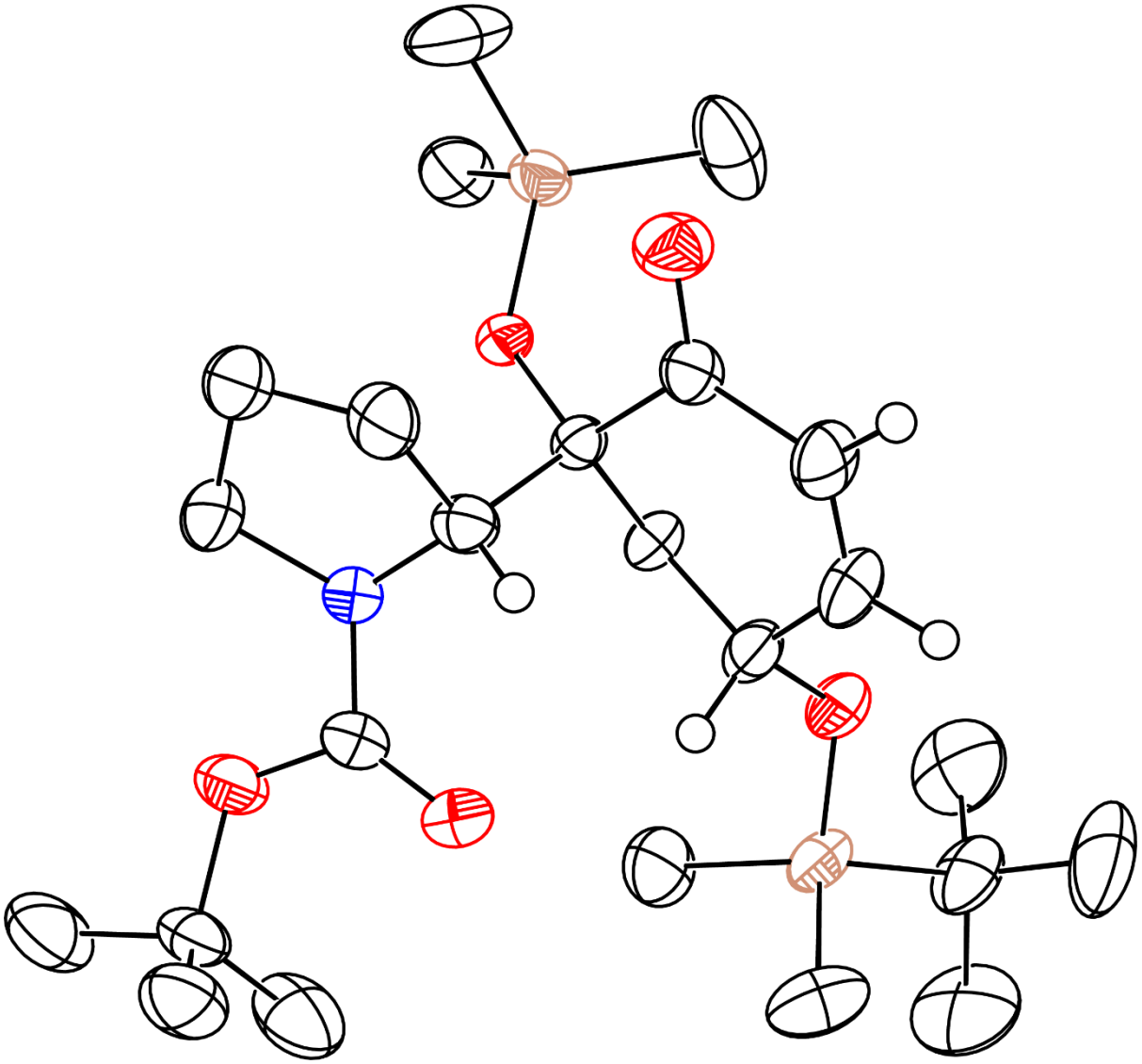


Figure S1. Thermal ellipsoid representation of **20**

Table S3. Crystal data and structure refinement for **20**.

Empirical formula	C_{24} H_{45} N O_5 Si_2	
Formula weight	483.79	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.8112(3) Å	α = 90°
	b = 9.0531(4) Å	β = 95.8682(16)°
	c = 23.2935(10) Å	γ = 90°
Volume	1428.81(11) $Å^3$	
Z	2	
Density (calculated)	1.125 Mg/m^3	
Absorption coefficient	0.155 mm^{-1}	
F(000)	528	
Crystal size	0.212 x 0.162 x 0.042 mm^3	
Theta range for data collection	2.637 to 28.983°.	
Index ranges	–9<=h<=9, –12<=k<=12, –31<=l<=30	
Reflections collected	28483	
Independent reflections	7574 [R(int) = 0.0602]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7458 and 0.7152	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7574 / 97 / 334	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0372, wR2 = 0.0882	
R indices (all data)	R1 = 0.0423, wR2 = 0.0902	
Absolute structure parameter	0.08(4)	
Largest diff. peak and hole	0.262 and –0.162 $e \cdot Å^{-3}$	

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **20**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2522(3)	6777(2)	2299(1)	26(1)
C(2)	1210(3)	6269(2)	2752(1)	30(1)
C(3)	-930(3)	6363(3)	2534(1)	38(1)
C(4)	-1604(3)	6432(3)	1977(1)	36(1)
C(5)	-274(3)	6430(2)	1518(1)	28(1)
C(6)	1934(3)	6155(2)	1693(1)	22(1)
C(7)	2228(3)	4451(2)	1656(1)	28(1)
C(8)	1647(10)	3853(10)	1059(3)	38(1)
C(9)	3652(7)	3774(6)	785(2)	49(1)
C(10)	5192(17)	3517(9)	1283(5)	40(2)
C(8B)	2020(30)	3860(30)	987(8)	37(2)
C(9B)	3793(15)	3108(12)	896(4)	42(2)
C(10B)	5390(30)	3852(19)	1308(11)	31(3)
N(11)	4281(3)	3981(2)	1811(1)	31(1)
O(12)	1545(3)	7181(2)	3252(1)	38(1)
Si(13)	2722(1)	6630(1)	3872(1)	33(1)
C(14)	1678(5)	4856(3)	4104(1)	54(1)
C(15)	5367(4)	6328(3)	3783(1)	51(1)
C(16)	2344(4)	8182(4)	4384(1)	46(1)
C(17)	3298(7)	7794(5)	4992(1)	81(1)
C(18)	138(5)	8448(5)	4407(2)	77(1)
C(19)	3260(7)	9603(4)	4177(2)	73(1)
O(20)	-900(2)	6609(2)	1015(1)	40(1)
O(21)	3130(2)	6821(1)	1306(1)	24(1)
Si(22)	2841(1)	8240(1)	858(1)	29(1)
C(23)	5362(4)	9032(3)	863(1)	42(1)
C(24)	1994(5)	7634(4)	111(1)	58(1)
C(25)	1199(5)	9697(3)	1112(2)	61(1)
C(26)	4769(3)	3296(2)	2325(1)	31(1)
O(27)	3746(3)	3293(2)	2724(1)	41(1)
O(28)	6560(3)	2656(2)	2334(1)	39(1)
C(29)	7215(3)	1560(2)	2782(1)	36(1)
C(30)	7424(6)	2242(3)	3378(1)	63(1)

C(31)	5766(5)	285(3)	2745(1)	48(1)
C(32)	9179(5)	1062(4)	2596(2)	59(1)

Table S5. Bond lengths [Å] and angles [°] for **20**.

C(1)-C(2)	1.523(3)
C(1)-C(6)	1.534(2)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(2)-O(12)	1.427(2)
C(2)-C(3)	1.496(3)
C(2)-H(2)	1.01(3)
C(3)-C(4)	1.334(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.469(3)
C(4)-H(4)	0.9500
C(5)-O(20)	1.216(2)
C(5)-C(6)	1.538(3)
C(6)-O(21)	1.411(2)
C(6)-C(7)	1.559(2)
C(7)-N(11)	1.471(3)
C(7)-C(8)	1.507(8)
C(7)-C(8B)	1.640(19)
C(7)-H(7)	0.89(3)
C(8)-C(9)	1.567(8)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.501(12)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-N(11)	1.493(13)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(8B)-C(9B)	1.42(2)
C(8B)-H(8C)	0.9900
C(8B)-H(8D)	0.9900
C(9B)-C(10B)	1.53(2)
C(9B)-H(9C)	0.9900
C(9B)-H(9D)	0.9900
C(10B)-N(11)	1.46(3)
C(10B)-H(10C)	0.9900

C(10B)-H(10D)	0.9900
N(11)-C(26)	1.360(2)
O(12)-Si(13)	1.6542(17)
Si(13)-C(15)	1.854(3)
Si(13)-C(14)	1.859(3)
Si(13)-C(16)	1.879(3)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-C(18)	1.528(4)
C(16)-C(19)	1.529(5)
C(16)-C(17)	1.536(4)
C(17)-H(17A)	0.9800
C(17)-H(17B)	0.9800
C(17)-H(17C)	0.9800
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
O(21)-Si(22)	1.6548(13)
Si(22)-C(24)	1.859(3)
Si(22)-C(23)	1.859(3)
Si(22)-C(25)	1.864(3)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(26)-O(27)	1.216(3)

C(26)-O(28)	1.349(3)
O(28)-C(29)	1.474(2)
C(29)-C(30)	1.513(3)
C(29)-C(32)	1.516(4)
C(29)-C(31)	1.516(3)
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800

C(2)-C(1)-C(6)	114.25(16)
C(2)-C(1)-H(1A)	108.7
C(6)-C(1)-H(1A)	108.7
C(2)-C(1)-H(1B)	108.7
C(6)-C(1)-H(1B)	108.7
H(1A)-C(1)-H(1B)	107.6
O(12)-C(2)-C(3)	108.26(17)
O(12)-C(2)-C(1)	109.63(17)
C(3)-C(2)-C(1)	111.61(17)
O(12)-C(2)-H(2)	107.8(17)
C(3)-C(2)-H(2)	109.6(18)
C(1)-C(2)-H(2)	109.8(18)
C(4)-C(3)-C(2)	124.00(18)
C(4)-C(3)-H(3)	118.0
C(2)-C(3)-H(3)	118.0
C(3)-C(4)-C(5)	122.10(19)
C(3)-C(4)-H(4)	118.9
C(5)-C(4)-H(4)	118.9
O(20)-C(5)-C(4)	121.24(19)
O(20)-C(5)-C(6)	120.90(17)
C(4)-C(5)-C(6)	117.85(17)
O(21)-C(6)-C(1)	108.51(14)
O(21)-C(6)-C(5)	112.02(15)

C(1)-C(6)-C(5)	109.88(15)
O(21)-C(6)-C(7)	107.59(15)
C(1)-C(6)-C(7)	113.02(15)
C(5)-C(6)-C(7)	105.84(15)
N(11)-C(7)-C(8)	106.0(3)
N(11)-C(7)-C(6)	113.37(16)
C(8)-C(7)-C(6)	112.6(4)
N(11)-C(7)-C(8B)	97.2(7)
C(6)-C(7)-C(8B)	112.1(8)
N(11)-C(7)-H(7)	109(2)
C(8)-C(7)-H(7)	108.9(19)
C(6)-C(7)-H(7)	106.9(19)
C(8B)-C(7)-H(7)	118(2)
C(7)-C(8)-C(9)	103.6(5)
C(7)-C(8)-H(8A)	111.0
C(9)-C(8)-H(8A)	111.0
C(7)-C(8)-H(8B)	111.0
C(9)-C(8)-H(8B)	111.0
H(8A)-C(8)-H(8B)	109.0
C(10)-C(9)-C(8)	105.1(6)
C(10)-C(9)-H(9A)	110.7
C(8)-C(9)-H(9A)	110.7
C(10)-C(9)-H(9B)	110.7
C(8)-C(9)-H(9B)	110.7
H(9A)-C(9)-H(9B)	108.8
N(11)-C(10)-C(9)	106.1(7)
N(11)-C(10)-H(10A)	110.5
C(9)-C(10)-H(10A)	110.5
N(11)-C(10)-H(10B)	110.5
C(9)-C(10)-H(10B)	110.5
H(10A)-C(10)-H(10B)	108.7
C(9B)-C(8B)-C(7)	107.8(13)
C(9B)-C(8B)-H(8C)	110.1
C(7)-C(8B)-H(8C)	110.1
C(9B)-C(8B)-H(8D)	110.1
C(7)-C(8B)-H(8D)	110.1
H(8C)-C(8B)-H(8D)	108.5
C(8B)-C(9B)-C(10B)	104.9(13)

C(8B)-C(9B)-H(9C)	110.8
C(10B)-C(9B)-H(9C)	110.8
C(8B)-C(9B)-H(9D)	110.8
C(10B)-C(9B)-H(9D)	110.8
H(9C)-C(9B)-H(9D)	108.8
N(11)-C(10B)-C(9B)	98.2(13)
N(11)-C(10B)-H(10C)	112.1
C(9B)-C(10B)-H(10C)	112.1
N(11)-C(10B)-H(10D)	112.1
C(9B)-C(10B)-H(10D)	112.1
H(10C)-C(10B)-H(10D)	109.8
C(26)-N(11)-C(10B)	124.7(9)
C(26)-N(11)-C(7)	119.21(17)
C(10B)-N(11)-C(7)	112.6(9)
C(26)-N(11)-C(10)	120.8(4)
C(7)-N(11)-C(10)	110.2(4)
C(2)-O(12)-Si(13)	124.12(14)
O(12)-Si(13)-C(15)	109.72(12)
O(12)-Si(13)-C(14)	110.38(12)
C(15)-Si(13)-C(14)	108.05(14)
O(12)-Si(13)-C(16)	104.08(11)
C(15)-Si(13)-C(16)	112.26(13)
C(14)-Si(13)-C(16)	112.32(14)
Si(13)-C(14)-H(14A)	109.5
Si(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
Si(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
Si(13)-C(15)-H(15A)	109.5
Si(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
Si(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(18)-C(16)-C(19)	108.2(3)
C(18)-C(16)-C(17)	109.2(3)
C(19)-C(16)-C(17)	109.6(3)

C(18)-C(16)-Si(13)	109.8(2)
C(19)-C(16)-Si(13)	110.00(18)
C(17)-C(16)-Si(13)	110.0(2)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(6)-O(21)-Si(22)	134.11(12)
O(21)-Si(22)-C(24)	111.52(12)
O(21)-Si(22)-C(23)	104.18(9)
C(24)-Si(22)-C(23)	108.56(14)
O(21)-Si(22)-C(25)	112.67(11)
C(24)-Si(22)-C(25)	111.54(17)
C(23)-Si(22)-C(25)	107.98(13)
Si(22)-C(23)-H(23A)	109.5
Si(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
Si(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
Si(22)-C(24)-H(24A)	109.5
Si(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
Si(22)-C(24)-H(24C)	109.5

H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
Si(22)-C(25)-H(25A)	109.5
Si(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
Si(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
O(27)-C(26)-O(28)	125.10(19)
O(27)-C(26)-N(11)	124.5(2)
O(28)-C(26)-N(11)	110.39(17)
C(26)-O(28)-C(29)	120.51(17)
O(28)-C(29)-C(30)	111.58(19)
O(28)-C(29)-C(32)	102.18(19)
C(30)-C(29)-C(32)	112.4(2)
O(28)-C(29)-C(31)	108.92(19)
C(30)-C(29)-C(31)	111.2(2)
C(32)-C(29)-C(31)	110.2(2)
C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(29)-C(32)-H(32A)	109.5
C(29)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(29)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters ($Å^2$ x 10^3) for **20**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	27(1)	30(1)	20(1)	-3(1)	5(1)	-3(1)
C(2)	35(1)	35(1)	23(1)	-2(1)	10(1)	0(1)
C(3)	32(1)	50(1)	36(1)	-2(1)	17(1)	-3(1)
C(4)	23(1)	46(1)	40(1)	1(1)	10(1)	-3(1)
C(5)	23(1)	29(1)	31(1)	3(1)	4(1)	-1(1)
C(6)	22(1)	24(1)	21(1)	2(1)	4(1)	-1(1)
C(7)	33(1)	24(1)	26(1)	2(1)	1(1)	0(1)
C(8)	49(3)	30(1)	32(2)	-10(2)	-3(2)	6(2)
C(9)	74(2)	42(2)	31(2)	-5(1)	5(2)	20(2)
C(10)	56(3)	35(3)	31(2)	-4(2)	12(2)	8(2)
C(8B)	49(3)	31(3)	29(3)	-8(3)	-1(3)	3(3)
C(9B)	54(3)	36(3)	37(3)	-10(2)	9(2)	4(3)
C(10B)	32(5)	33(7)	29(5)	-7(5)	8(4)	2(5)
N(11)	37(1)	31(1)	26(1)	5(1)	7(1)	9(1)
O(12)	51(1)	43(1)	21(1)	-5(1)	8(1)	7(1)
Si(13)	32(1)	45(1)	24(1)	1(1)	8(1)	-4(1)
C(14)	59(2)	64(2)	40(1)	12(1)	6(1)	-22(1)
C(15)	37(1)	55(1)	62(2)	7(1)	14(1)	2(1)
C(16)	49(1)	65(1)	26(1)	-13(1)	5(1)	-3(1)
C(17)	108(3)	101(3)	32(1)	-15(2)	-11(2)	-6(2)
C(18)	62(2)	115(3)	58(2)	-34(2)	19(2)	18(2)
C(19)	99(3)	57(2)	62(2)	-20(2)	13(2)	-10(2)
O(20)	29(1)	57(1)	32(1)	7(1)	-2(1)	3(1)
O(21)	24(1)	27(1)	23(1)	6(1)	6(1)	2(1)
Si(22)	28(1)	29(1)	32(1)	10(1)	6(1)	4(1)
C(23)	36(1)	41(1)	52(1)	15(1)	13(1)	-2(1)
C(24)	60(2)	85(2)	28(1)	18(1)	-4(1)	-6(2)
C(25)	49(2)	32(1)	107(3)	12(1)	26(2)	11(1)
C(26)	35(1)	26(1)	31(1)	6(1)	2(1)	3(1)
O(27)	47(1)	47(1)	30(1)	12(1)	10(1)	12(1)
O(28)	35(1)	39(1)	43(1)	17(1)	7(1)	8(1)
C(29)	40(1)	31(1)	35(1)	9(1)	-3(1)	7(1)
C(30)	80(2)	56(1)	48(2)	-6(1)	-23(2)	20(2)

C(31)	57(2)	33(1)	56(2)	9(1)	6(1)	-1(1)
C(32)	44(2)	57(2)	76(2)	23(1)	7(1)	16(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **20**.

	x	y	z	U(eq)
H(1A)	3899	6480	2423	31
H(1B)	2487	7869	2279	31
H(2)	1550(50)	5220(30)	2872(13)	46
H(3)	-1867	6374	2810	46
H(4)	-2987	6485	1873	43
H(7)	1470(50)	4040(30)	1899(12)	42
H(8A)	705	4521	836	45
H(8B)	1043	2861	1077	45
H(9A)	3638	2953	504	59
H(9B)	3906	4710	585	59
H(10A)	5566	2460	1308	48
H(10B)	6387	4110	1238	48
H(8C)	878	3184	919	44
H(8D)	1810	4705	717	44
H(9C)	4088	3214	490	51
H(9D)	3691	2044	986	51
H(10C)	6579	3221	1387	37
H(10D)	5781	4828	1164	37
H(14A)	2325	4580	4484	82
H(14B)	1901	4083	3824	82
H(14C)	257	4971	4127	82
H(15A)	6066	6028	4154	76
H(15B)	5942	7245	3653	76
H(15C)	5490	5550	3497	76
H(17A)	3076	8601	5258	122
H(17B)	4720	7648	4981	122
H(17C)	2708	6884	5124	122
H(18A)	-51	9270	4670	116
H(18B)	-472	7554	4547	116
H(18C)	-479	8689	4020	116
H(19A)	2995	10418	4436	109
H(19B)	2683	9830	3785	109
H(19C)	4689	9471	4180	109

H(23A)	5344	9833	580	64
H(23B)	6278	8261	764	64
H(23C)	5791	9421	1248	64
H(24A)	2097	8460	-156	87
H(24B)	618	7307	93	87
H(24C)	2821	6815	2	87
H(25A)	1180	10551	853	92
H(25B)	1695	10001	1504	92
H(25C)	-142	9304	1112	92
H(30A)	7965	1509	3660	95
H(30B)	6126	2567	3475	95
H(30C)	8315	3093	3383	95
H(31A)	6284	-510	3003	73
H(31B)	5579	-84	2348	73
H(31C)	4497	624	2861	73
H(32A)	9708	256	2847	88
H(32B)	10107	1892	2625	88
H(32C)	8990	714	2196	88

4.2 X-ray Crystal Structure of Compound 23

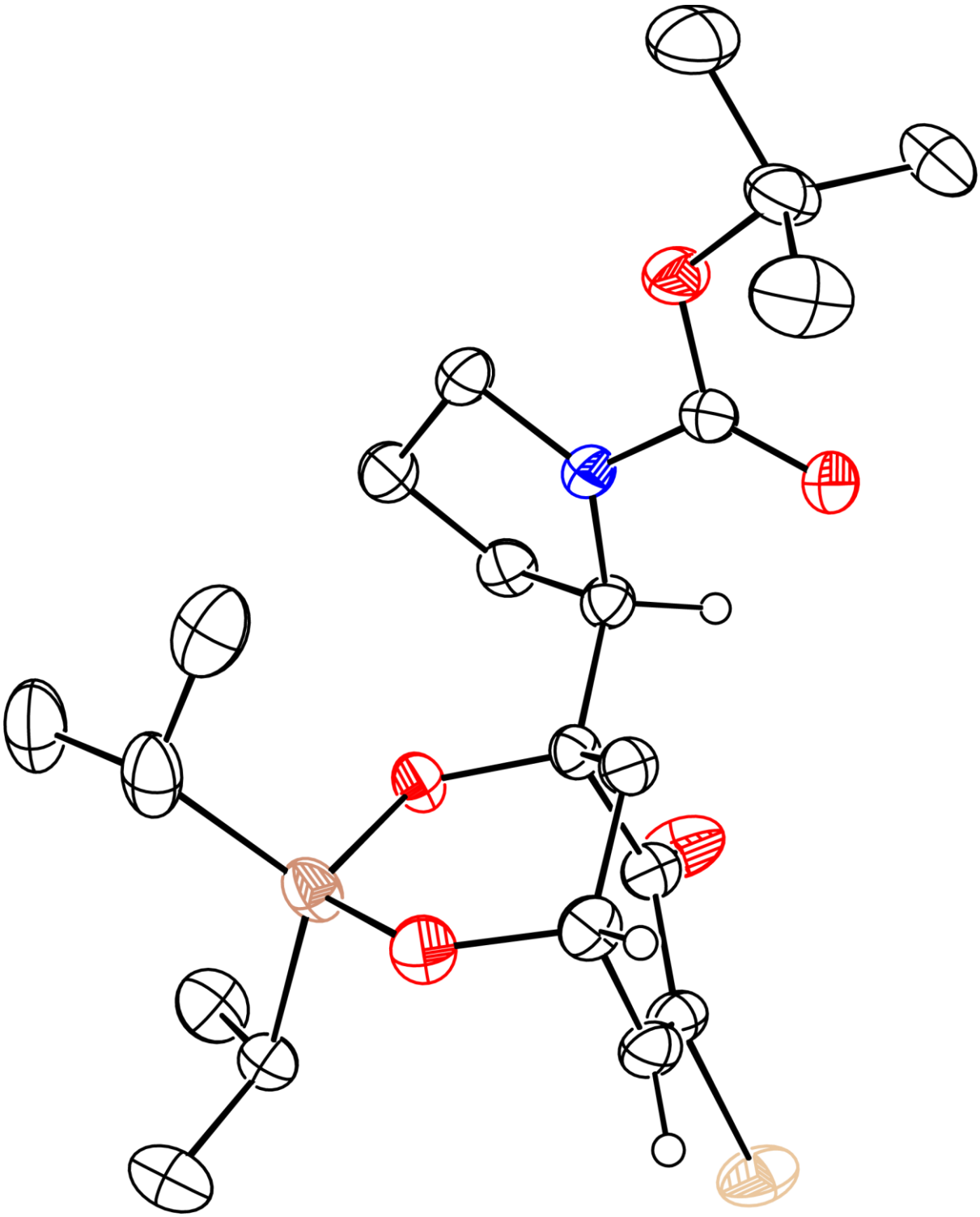


Figure S2. Thermal ellipsoid representation of **23**

Table S8. Crystal data and structure refinement for **23**.

Empirical formula	C_{21} H_{34} I N O_5 Si	
Formula weight	535.48	
Temperature	2035(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 8.9672(4) Å	α = 90°
	b = 14.2728(6) Å	β = 90°
	c = 19.4271(9) Å	γ = 90°
Volume	2486.42(19) $Å^3$	
Z	4	
Density (calculated)	1.430 Mg/m^3	
Absorption coefficient	1.365 mm^{-1}	
F(000)	1096	
Crystal size	0.283 x 0.269 x 0.117 mm^3	
Theta range for data collection	2.536 to 27.591°.	
Index ranges	–11<=h<=10, –18<=k<=18, –25<=l<=21	
Reflections collected	34500	
Independent reflections	5717 [R(int) = 0.0548]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5621	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5717 / 0 / 302	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0256, wR2 = 0.0530	
R indices (all data)	R1 = 0.0333, wR2 = 0.0569	
Absolute structure parameter	-0.020(8)	
Largest diff. peak and hole	0.178 and –0.476 e·$Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **23**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	7339(3)	6752(2)	6771(2)	56(1)
C(2)	6404(4)	6904(2)	6337(2)	35(1)
C(3)	5912(4)	7867(2)	6158(2)	36(1)
I(4)	6850(1)	8950(1)	6745(1)	56(1)
C(5)	4946(4)	8049(2)	5658(2)	37(1)
C(6)	4289(4)	7285(2)	5224(2)	36(1)
C(7)	5263(4)	6413(2)	5219(2)	33(1)
C(8)	5602(3)	6101(2)	5949(1)	29(1)
O(9)	4234(2)	5941(2)	6320(1)	33(1)
O(10)	2809(2)	7082(2)	5470(1)	40(1)
Si(11)	2598(1)	6431(1)	6168(1)	39(1)
C(12)	2259(12)	7268(7)	6937(3)	41(2)
C(13)	2480(20)	6732(18)	7606(7)	53(3)
C(14)	810(13)	7789(7)	6863(4)	61(3)
C(12B)	1722(19)	6951(10)	6904(6)	36(3)
C(13B)	2540(50)	6890(40)	7620(20)	90(16)
C(14B)	1720(30)	8047(9)	6821(7)	58(5)
C(15)	1191(4)	5523(3)	5949(2)	54(1)
C(16)	1676(5)	4923(3)	5334(2)	61(1)
C(17)	738(5)	4900(3)	6558(3)	68(1)
C(18)	6594(3)	5217(2)	6001(2)	32(1)
C(19)	6398(3)	4664(2)	6670(2)	37(1)
C(20)	5264(4)	3900(2)	6490(2)	39(1)
C(21)	5634(4)	3641(2)	5753(2)	39(1)
N(22)	6259(3)	4513(2)	5468(1)	33(1)
C(23)	7005(4)	4531(2)	4862(2)	36(1)
O(24)	7796(3)	5177(2)	4672(1)	46(1)
O(25)	6736(3)	3745(1)	4503(1)	44(1)
C(26)	7180(5)	3668(2)	3772(2)	48(1)
C(27)	6416(6)	4429(3)	3359(2)	70(1)
C(28)	8869(5)	3697(3)	3706(3)	68(1)
C(29)	6596(6)	2705(3)	3588(2)	64(1)

Table S10. Bond lengths [Å] and angles [°] for **23**.

O(1)-C(2)	1.208(4)
C(2)-C(3)	1.485(4)
C(2)-C(8)	1.549(4)
C(3)-C(5)	1.328(5)
C(3)-I(4)	2.097(3)
C(5)-C(6)	1.499(5)
C(5)-H(5)	0.9300
C(6)-O(10)	1.440(4)
C(6)-C(7)	1.520(4)
C(6)-H(6)	0.9800
C(7)-C(8)	1.518(4)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-O(9)	1.441(3)
C(8)-C(18)	1.548(4)
O(9)-Si(11)	1.651(2)
O(10)-Si(11)	1.655(2)
Si(11)-C(12B)	1.793(12)
Si(11)-C(15)	1.858(4)
Si(11)-C(12)	1.937(7)
C(12)-C(14)	1.504(12)
C(12)-C(13)	1.521(19)
C(12)-H(12)	0.9800
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-H(14A)	0.9600
C(14)-H(14B)	0.9600
C(14)-H(14C)	0.9600
C(12B)-C(14B)	1.57(2)
C(12B)-C(13B)	1.58(4)
C(12B)-H(12B)	0.9800
C(13B)-H(13D)	0.9600
C(13B)-H(13E)	0.9600
C(13B)-H(13F)	0.9600
C(14B)-H(14D)	0.9600

C(14B)-H(14E)	0.9600
C(14B)-H(14F)	0.9600
C(15)-C(16)	1.533(6)
C(15)-C(17)	1.535(6)
C(15)-H(15)	0.9800
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-H(17A)	0.9600
C(17)-H(17B)	0.9600
C(17)-H(17C)	0.9600
C(18)-N(22)	1.472(4)
C(18)-C(19)	1.532(4)
C(18)-H(18)	1.04(4)
C(19)-C(20)	1.531(5)
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(20)-C(21)	1.515(5)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(21)-N(22)	1.473(4)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
N(22)-C(23)	1.355(4)
C(23)-O(24)	1.219(4)
C(23)-O(25)	1.344(4)
O(25)-C(26)	1.478(4)
C(26)-C(29)	1.514(5)
C(26)-C(27)	1.514(6)
C(26)-C(28)	1.521(6)
C(27)-H(27A)	0.9600
C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600
C(28)-H(28A)	0.9600
C(28)-H(28B)	0.9600
C(28)-H(28C)	0.9600
C(29)-H(29A)	0.9600
C(29)-H(29B)	0.9600

C(29)-H(29C)	0.9600
O(1)-C(2)-C(3)	122.4(3)
O(1)-C(2)-C(8)	121.9(3)
C(3)-C(2)-C(8)	115.6(3)
C(5)-C(3)-C(2)	123.1(3)
C(5)-C(3)-I(4)	121.0(2)
C(2)-C(3)-I(4)	115.8(2)
C(3)-C(5)-C(6)	121.7(3)
C(3)-C(5)-H(5)	119.1
C(6)-C(5)-H(5)	119.1
O(10)-C(6)-C(5)	108.8(3)
O(10)-C(6)-C(7)	111.6(2)
C(5)-C(6)-C(7)	111.9(3)
O(10)-C(6)-H(6)	108.1
C(5)-C(6)-H(6)	108.1
C(7)-C(6)-H(6)	108.1
C(8)-C(7)-C(6)	110.4(3)
C(8)-C(7)-H(7A)	109.6
C(6)-C(7)-H(7A)	109.6
C(8)-C(7)-H(7B)	109.6
C(6)-C(7)-H(7B)	109.6
H(7A)-C(7)-H(7B)	108.1
O(9)-C(8)-C(7)	110.1(2)
O(9)-C(8)-C(18)	109.1(2)
C(7)-C(8)-C(18)	114.5(2)
O(9)-C(8)-C(2)	105.6(2)
C(7)-C(8)-C(2)	109.3(2)
C(18)-C(8)-C(2)	107.8(2)
C(8)-O(9)-Si(11)	126.85(17)
C(6)-O(10)-Si(11)	119.29(18)
O(9)-Si(11)-O(10)	106.45(11)
O(9)-Si(11)-C(12B)	115.0(5)
O(10)-Si(11)-C(12B)	118.1(4)
O(9)-Si(11)-C(15)	110.44(15)
O(10)-Si(11)-C(15)	106.36(16)
C(12B)-Si(11)-C(15)	100.0(6)
O(9)-Si(11)-C(12)	105.2(3)

O(10)-Si(11)-C(12)	107.7(3)
C(15)-Si(11)-C(12)	120.0(4)
C(14)-C(12)-C(13)	116.4(10)
C(14)-C(12)-Si(11)	111.5(7)
C(13)-C(12)-Si(11)	109.2(10)
C(14)-C(12)-H(12)	106.4
C(13)-C(12)-H(12)	106.4
Si(11)-C(12)-H(12)	106.4
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(14B)-C(12B)-C(13B)	98(3)
C(14B)-C(12B)-Si(11)	109.3(12)
C(13B)-C(12B)-Si(11)	118.7(19)
C(14B)-C(12B)-H(12B)	109.9
C(13B)-C(12B)-H(12B)	109.9
Si(11)-C(12B)-H(12B)	109.9
C(12B)-C(13B)-H(13D)	109.5
C(12B)-C(13B)-H(13E)	109.5
H(13D)-C(13B)-H(13E)	109.5
C(12B)-C(13B)-H(13F)	109.5
H(13D)-C(13B)-H(13F)	109.5
H(13E)-C(13B)-H(13F)	109.5
C(12B)-C(14B)-H(14D)	109.5
C(12B)-C(14B)-H(14E)	109.5
H(14D)-C(14B)-H(14E)	109.5
C(12B)-C(14B)-H(14F)	109.5
H(14D)-C(14B)-H(14F)	109.5
H(14E)-C(14B)-H(14F)	109.5

C(16)-C(15)-C(17)	110.6(4)
C(16)-C(15)-Si(11)	112.1(3)
C(17)-C(15)-Si(11)	114.1(3)
C(16)-C(15)-H(15)	106.6
C(17)-C(15)-H(15)	106.6
Si(11)-C(15)-H(15)	106.6
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(15)-C(17)-H(17A)	109.5
C(15)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(15)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
N(22)-C(18)-C(19)	102.8(2)
N(22)-C(18)-C(8)	113.2(2)
C(19)-C(18)-C(8)	114.1(2)
N(22)-C(18)-H(18)	110(2)
C(19)-C(18)-H(18)	112(2)
C(8)-C(18)-H(18)	105(2)
C(20)-C(19)-C(18)	104.4(3)
C(20)-C(19)-H(19A)	110.9
C(18)-C(19)-H(19A)	110.9
C(20)-C(19)-H(19B)	110.9
C(18)-C(19)-H(19B)	110.9
H(19A)-C(19)-H(19B)	108.9
C(21)-C(20)-C(19)	104.1(3)
C(21)-C(20)-H(20A)	110.9
C(19)-C(20)-H(20A)	110.9
C(21)-C(20)-H(20B)	110.9
C(19)-C(20)-H(20B)	110.9
H(20A)-C(20)-H(20B)	108.9
N(22)-C(21)-C(20)	103.4(2)
N(22)-C(21)-H(21A)	111.1

C(20)-C(21)-H(21A)	111.1
N(22)-C(21)-H(21B)	111.1
C(20)-C(21)-H(21B)	111.1
H(21A)-C(21)-H(21B)	109.0
C(23)-N(22)-C(18)	119.8(3)
C(23)-N(22)-C(21)	122.1(2)
C(18)-N(22)-C(21)	112.9(2)
O(24)-C(23)-O(25)	125.3(3)
O(24)-C(23)-N(22)	124.4(3)
O(25)-C(23)-N(22)	110.3(3)
C(23)-O(25)-C(26)	120.8(2)
O(25)-C(26)-C(29)	101.6(3)
O(25)-C(26)-C(27)	109.6(3)
C(29)-C(26)-C(27)	111.7(4)
O(25)-C(26)-C(28)	110.3(4)
C(29)-C(26)-C(28)	110.4(3)
C(27)-C(26)-C(28)	112.7(4)
C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(26)-C(29)-H(29A)	109.5
C(26)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(26)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2$ x 10^3) for **23**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	72(2)	40(1)	57(2)	-1(1)	-31(2)	-2(1)
C(2)	43(2)	34(2)	27(2)	0(1)	0(1)	-1(1)
C(3)	48(2)	29(1)	31(2)	-2(1)	3(1)	-2(1)
I(4)	84(1)	37(1)	46(1)	-10(1)	-5(1)	-5(1)
C(5)	49(2)	29(1)	34(2)	7(1)	6(1)	2(1)
C(6)	43(2)	36(2)	29(2)	10(1)	-1(1)	2(1)
C(7)	38(2)	33(1)	28(2)	0(1)	2(1)	0(1)
C(8)	30(1)	31(1)	25(1)	3(1)	2(1)	2(1)
O(9)	30(1)	37(1)	31(1)	10(1)	4(1)	6(1)
O(10)	39(1)	42(1)	40(1)	12(1)	-3(1)	6(1)
Si(11)	36(1)	43(1)	37(1)	11(1)	5(1)	12(1)
C(12)	41(4)	37(4)	44(3)	-4(3)	8(3)	1(3)
C(13)	61(8)	66(7)	33(5)	0(4)	2(5)	5(5)
C(14)	59(6)	59(4)	65(5)	-10(4)	3(4)	19(4)
C(12B)	37(7)	21(5)	49(6)	-3(4)	2(5)	-11(5)
C(13B)	80(20)	80(20)	110(30)	-9(15)	-34(17)	20(15)
C(14B)	79(13)	43(6)	50(7)	-10(5)	5(9)	4(7)
C(15)	31(2)	62(2)	68(3)	26(2)	-1(2)	4(2)
C(16)	57(2)	65(2)	60(2)	13(2)	-16(2)	-13(2)
C(17)	44(2)	76(3)	83(3)	30(2)	11(2)	-2(2)
C(18)	31(2)	30(1)	34(2)	0(1)	-2(1)	-1(1)
C(19)	37(2)	37(2)	38(2)	6(1)	-4(1)	6(1)
C(20)	45(2)	36(2)	37(2)	10(1)	4(1)	3(2)
C(21)	45(2)	30(1)	41(2)	4(1)	6(2)	-4(1)
N(22)	38(1)	26(1)	35(1)	2(1)	6(1)	-2(1)
C(23)	40(2)	29(1)	40(2)	0(1)	9(2)	3(1)
O(24)	52(2)	37(1)	49(1)	0(1)	20(1)	-5(1)
O(25)	64(2)	33(1)	35(1)	-4(1)	14(1)	-4(1)
C(26)	65(3)	41(2)	39(2)	-2(1)	14(2)	11(2)
C(27)	103(4)	60(2)	46(2)	7(2)	0(2)	18(2)
C(28)	66(3)	62(3)	76(3)	-10(2)	32(2)	13(2)
C(29)	94(3)	53(2)	46(2)	-14(2)	7(2)	-2(2)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **23**.

	x	y	z	U(eq)
H(5)	4670	8667	5574	45
H(6)	4209	7516	4751	43
H(7A)	4755	5914	4975	40
H(7B)	6188	6546	4979	40
H(12)	3051	7740	6919	49
H(13A)	2351	7150	7989	80
H(13B)	3469	6473	7617	80
H(13C)	1763	6234	7634	80
H(14A)	722	8241	7226	92
H(14B)	-5	7354	6888	92
H(14C)	789	8103	6426	92
H(12B)	696	6722	6947	43
H(13D)	1982	7239	7959	135
H(13E)	3522	7144	7583	135
H(13F)	2597	6245	7764	135
H(14D)	1257	8327	7216	86
H(14E)	1173	8214	6414	86
H(14F)	2727	8267	6782	86
H(15)	290	5859	5805	64
H(16A)	893	4492	5218	92
H(16B)	2560	4579	5453	92
H(16C)	1880	5320	4947	92
H(17A)	49	4430	6403	102
H(17B)	273	5277	6906	102
H(17C)	1608	4603	6745	102
H(18)	7680(40)	5460(30)	5940(20)	47
H(19A)	7336	4390	6816	45
H(19B)	6022	5064	7035	45
H(20A)	5373	3363	6792	47
H(20B)	4253	4136	6526	47
H(21A)	6359	3137	5736	46
H(21B)	4746	3452	5504	46

H(27A)	6609	4333	2878	105
H(27B)	6793	5030	3496	105
H(27C)	5360	4405	3440	105
H(28A)	9152	3508	3250	103
H(28B)	9306	3278	4036	103
H(28C)	9216	4323	3790	103
H(29A)	6824	2571	3115	96
H(29B)	5535	2689	3654	96
H(29C)	7059	2245	3878	96

4.3 X-ray Crystal Structure of Compound 28

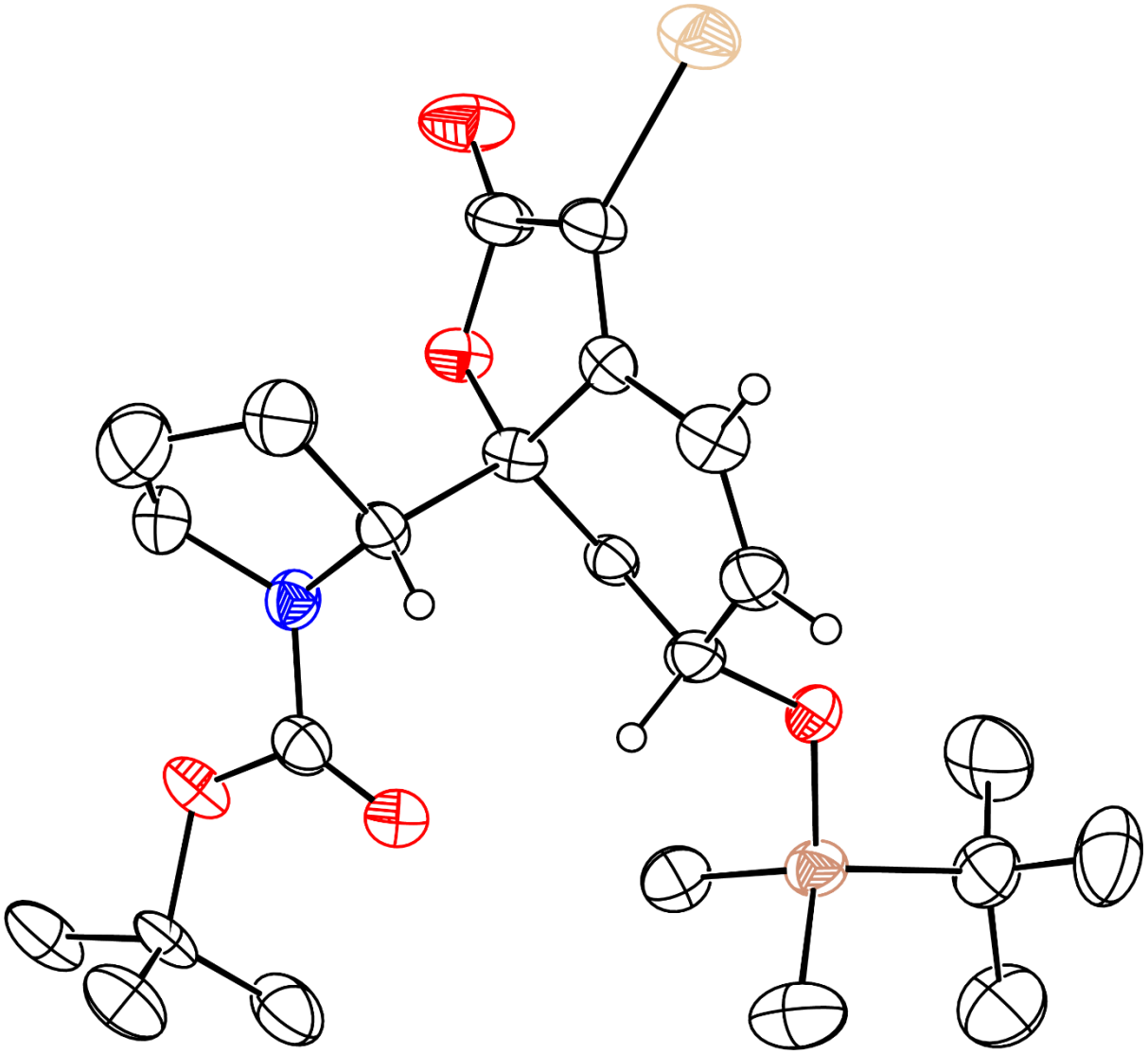


Figure S3. Thermal ellipsoid representation of **28**

Table S13. Crystal data and structure refinement for **28**.

Empirical formula	$C_{23}H_{35}INO_5Si$	
Formula weight	560.51	
Temperature	253(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12$	
Unit cell dimensions	a = 8.5047(19) Å	α = 90°
	b = 46.069(10) Å	β = 90°
	c = 6.8117(16) Å	γ = 90°
Volume	2668.9(10) $Å^3$	
Z	4	
Density (calculated)	1.395 Mg/m^3	
Absorption coefficient	1.275 mm^{-1}	
F(000)	1148	
Crystal size	0.221 x 0.041 x 0.038 mm^3	
Theta range for data collection	2.435 to 26.070°.	
Index ranges	–10<=h<=9, –53<=k<=56, –8<=l<=8	
Reflections collected	33699	
Independent reflections	5114 [R(int) = 0.1109]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7453 and 0.5410	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5114 / 437 / 288	
Goodness-of-fit on F^2	1.198	
Final R indices [I>2sigma(I)]	R1 = 0.0849, wR2 = 0.1419	
R indices (all data)	R1 = 0.1205, wR2 = 0.1550	
Absolute structure parameter	0.24(6)	
Largest diff. peak and hole	0.974 and –0.710 $e \cdot Å^{-3}$	

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **28**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4832(9)	5624(2)	5498(11)	46(2)
O(2)	3184(12)	5246(2)	5823(16)	80(3)
C(3)	3946(15)	5429(3)	6569(19)	54(3)
C(4)	4149(14)	5504(3)	8653(18)	51(3)
I(5)	2944(1)	5289(1)	10836(2)	79(1)
C(6)	5062(12)	5735(2)	8797(16)	38(2)
C(7)	5393(13)	5925(3)	10444(17)	48(3)
C(8)	5722(14)	6205(3)	10082(19)	50(3)
C(9)	5796(13)	6334(2)	8061(19)	46(3)
C(10)	5167(12)	6132(2)	6487(16)	38(2)
C(11)	5644(12)	5818(2)	6814(16)	38(2)
O(12)	4892(9)	6598(2)	8068(13)	52(2)
Si(13)	5429(4)	6905(1)	7004(6)	50(1)
C(14)	5729(18)	6850(3)	4340(30)	72(4)
C(15)	7290(18)	7037(3)	8100(30)	87(5)
C(16)	3763(18)	7156(3)	7530(20)	71(4)
C(17)	4100(20)	7460(4)	6620(30)	111(7)
C(18)	2253(19)	7039(4)	6540(30)	108(6)
C(19)	3500(20)	7187(4)	9700(30)	104(6)
C(20)	7460(12)	5769(2)	6546(17)	43(3)
C(21)	7943(17)	5452(3)	6970(20)	65(3)
C(22)	8790(20)	5357(4)	5200(30)	102(6)
C(23)	8317(17)	5550(3)	3570(20)	68(4)
N(24)	7955(11)	5823(2)	4547(12)	43(2)
C(25)	8729(12)	6081(3)	4140(20)	46(2)
O(26)	8749(10)	6285(2)	5234(14)	59(2)
O(27)	9370(9)	6068(2)	2342(13)	57(2)
C(28)	10554(13)	6292(3)	1760(19)	52(3)
C(29)	11909(16)	6277(3)	3150(20)	73(4)
C(30)	9783(18)	6589(3)	1670(30)	80(5)
C(31)	11018(17)	6189(4)	-280(20)	79(4)

Table S15. Bond lengths [Å] and angles [°] for **28**.

O(1)-C(3)	1.382(14)
O(1)-C(11)	1.443(13)
O(2)-C(3)	1.177(14)
C(3)-C(4)	1.472(18)
C(4)-C(6)	1.319(16)
C(4)-I(5)	2.061(11)
C(6)-C(7)	1.453(16)
C(6)-C(11)	1.489(16)
C(7)-C(8)	1.340(17)
C(7)-H(7)	0.9400
C(8)-C(9)	1.502(17)
C(8)-H(8)	0.9400
C(9)-O(12)	1.440(13)
C(9)-C(10)	1.518(16)
C(9)-H(9)	0.9900
C(10)-C(11)	1.518(15)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(11)-C(20)	1.572(15)
O(12)-Si(13)	1.652(8)
Si(13)-C(14)	1.850(17)
Si(13)-C(15)	1.853(15)
Si(13)-C(16)	1.864(15)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(14)-H(14C)	0.9700
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(15)-H(15C)	0.9700
C(16)-C(19)	1.50(2)
C(16)-C(18)	1.55(2)
C(16)-C(17)	1.56(2)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(17)-H(17C)	0.9700

C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(18)-H(18C)	0.9700
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(19)-H(19C)	0.9700
C(20)-N(24)	1.447(14)
C(20)-C(21)	1.544(16)
C(20)-H(20)	0.9900
C(21)-C(22)	1.47(2)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(22)-C(23)	1.48(2)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(23)-N(24)	1.457(15)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
N(24)-C(25)	1.387(14)
C(25)-O(26)	1.202(14)
C(25)-O(27)	1.340(16)
O(27)-C(28)	1.497(14)
C(28)-C(29)	1.493(18)
C(28)-C(30)	1.52(2)
C(28)-C(31)	1.520(19)
C(29)-H(29A)	0.9400
C(29)-H(29B)	0.9400
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(30)-H(30C)	0.9700
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(31)-H(31C)	0.9700

C(3)-O(1)-C(11)	109.7(8)
O(2)-C(3)-O(1)	122.5(12)
O(2)-C(3)-C(4)	130.5(12)
O(1)-C(3)-C(4)	107.0(10)

C(6)-C(4)-C(3)	109.3(10)
C(6)-C(4)-I(5)	128.8(9)
C(3)-C(4)-I(5)	121.6(8)
C(4)-C(6)-C(7)	131.2(11)
C(4)-C(6)-C(11)	109.7(10)
C(7)-C(6)-C(11)	118.7(9)
C(8)-C(7)-C(6)	118.7(11)
C(8)-C(7)-H(7)	120.7
C(6)-C(7)-H(7)	120.7
C(7)-C(8)-C(9)	124.0(11)
C(7)-C(8)-H(8)	118.0
C(9)-C(8)-H(8)	118.0
O(12)-C(9)-C(8)	108.1(10)
O(12)-C(9)-C(10)	109.5(9)
C(8)-C(9)-C(10)	112.9(9)
O(12)-C(9)-H(9)	108.8
C(8)-C(9)-H(9)	108.8
C(10)-C(9)-H(9)	108.8
C(11)-C(10)-C(9)	112.8(9)
C(11)-C(10)-H(10A)	109.0
C(9)-C(10)-H(10A)	109.0
C(11)-C(10)-H(10B)	109.0
C(9)-C(10)-H(10B)	109.0
H(10A)-C(10)-H(10B)	107.8
O(1)-C(11)-C(6)	104.1(8)
O(1)-C(11)-C(10)	111.8(8)
C(6)-C(11)-C(10)	106.9(9)
O(1)-C(11)-C(20)	107.9(9)
C(6)-C(11)-C(20)	113.2(9)
C(10)-C(11)-C(20)	112.6(9)
C(9)-O(12)-Si(13)	125.0(7)
O(12)-Si(13)-C(14)	110.6(6)
O(12)-Si(13)-C(15)	109.8(6)
C(14)-Si(13)-C(15)	108.9(8)
O(12)-Si(13)-C(16)	103.6(6)
C(14)-Si(13)-C(16)	112.2(7)
C(15)-Si(13)-C(16)	111.6(7)
Si(13)-C(14)-H(14A)	109.5

Si(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
Si(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
Si(13)-C(15)-H(15A)	109.5
Si(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
Si(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(19)-C(16)-C(18)	109.7(15)
C(19)-C(16)-C(17)	109.6(15)
C(18)-C(16)-C(17)	106.9(14)
C(19)-C(16)-Si(13)	111.2(11)
C(18)-C(16)-Si(13)	109.4(11)
C(17)-C(16)-Si(13)	109.9(12)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
N(24)-C(20)-C(21)	105.1(9)
N(24)-C(20)-C(11)	111.7(9)
C(21)-C(20)-C(11)	112.2(9)

N(24)-C(20)-H(20)	109.2
C(21)-C(20)-H(20)	109.2
C(11)-C(20)-H(20)	109.2
C(22)-C(21)-C(20)	105.0(11)
C(22)-C(21)-H(21A)	110.7
C(20)-C(21)-H(21A)	110.7
C(22)-C(21)-H(21B)	110.7
C(20)-C(21)-H(21B)	110.7
H(21A)-C(21)-H(21B)	108.8
C(21)-C(22)-C(23)	107.6(12)
C(21)-C(22)-H(22A)	110.2
C(23)-C(22)-H(22A)	110.2
C(21)-C(22)-H(22B)	110.2
C(23)-C(22)-H(22B)	110.2
H(22A)-C(22)-H(22B)	108.5
N(24)-C(23)-C(22)	103.4(12)
N(24)-C(23)-H(23A)	111.1
C(22)-C(23)-H(23A)	111.1
N(24)-C(23)-H(23B)	111.1
C(22)-C(23)-H(23B)	111.1
H(23A)-C(23)-H(23B)	109.0
C(25)-N(24)-C(20)	118.5(10)
C(25)-N(24)-C(23)	123.1(10)
C(20)-N(24)-C(23)	110.0(9)
O(26)-C(25)-O(27)	126.7(11)
O(26)-C(25)-N(24)	123.5(12)
O(27)-C(25)-N(24)	109.7(11)
C(25)-O(27)-C(28)	118.9(10)
C(29)-C(28)-O(27)	108.6(10)
C(29)-C(28)-C(30)	113.5(13)
O(27)-C(28)-C(30)	110.0(9)
C(29)-C(28)-C(31)	111.5(11)
O(27)-C(28)-C(31)	101.6(11)
C(30)-C(28)-C(31)	111.0(13)
C(28)-C(29)-H(29A)	120.0
C(28)-C(29)-H(29B)	120.0
H(29A)-C(29)-H(29B)	120.0
C(28)-C(30)-H(30A)	109.5

C(28)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(28)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(28)-C(31)-H(31A)	109.5
C(28)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(28)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2$ x 10^3) for **28**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	54(4)	50(4)	35(4)	2(3)	-3(4)	-14(3)
O(2)	89(7)	77(6)	73(5)	4(6)	-14(6)	-45(5)
C(3)	61(7)	51(6)	51(6)	4(5)	9(5)	-16(5)
C(4)	52(6)	48(6)	53(6)	10(5)	9(5)	-8(5)
I(5)	102(1)	66(1)	70(1)	10(1)	28(1)	-20(1)
C(6)	33(5)	43(5)	37(5)	6(4)	-2(4)	3(4)
C(7)	45(6)	62(6)	36(6)	2(5)	-15(5)	-5(5)
C(8)	44(6)	57(6)	50(6)	-6(5)	-5(5)	-8(5)
C(9)	33(6)	38(5)	68(6)	0(5)	2(5)	-3(4)
C(10)	29(5)	39(5)	47(6)	6(4)	3(5)	0(4)
C(11)	31(5)	45(5)	40(5)	8(4)	-11(4)	-4(4)
O(12)	51(5)	33(4)	71(5)	0(4)	13(4)	6(3)
Si(13)	46(2)	39(2)	65(2)	4(2)	-2(2)	2(2)
C(14)	77(9)	58(8)	82(9)	4(8)	5(8)	0(7)
C(15)	77(9)	67(9)	116(12)	11(9)	-24(9)	-16(7)
C(16)	76(8)	54(7)	84(9)	6(7)	6(7)	14(6)
C(17)	125(14)	60(9)	147(18)	25(10)	8(13)	20(9)
C(18)	61(9)	117(13)	145(16)	14(11)	-9(10)	15(8)
C(19)	141(15)	76(10)	96(10)	1(9)	28(10)	42(10)
C(20)	35(5)	43(5)	52(6)	3(5)	10(4)	2(4)
C(21)	49(7)	62(7)	85(8)	13(6)	-9(7)	14(6)
C(22)	119(12)	65(9)	123(11)	15(8)	43(9)	19(8)
C(23)	65(8)	58(6)	81(8)	-17(6)	23(7)	0(6)
N(24)	48(5)	43(4)	38(5)	-2(4)	3(4)	3(4)
C(25)	36(6)	53(5)	51(6)	5(5)	1(5)	1(4)
O(26)	57(5)	47(4)	74(6)	-2(4)	15(4)	-7(4)
O(27)	38(4)	76(5)	56(5)	6(4)	10(4)	-10(4)
C(28)	26(5)	78(7)	53(6)	2(6)	9(4)	-14(5)
C(29)	40(6)	108(11)	70(8)	15(8)	-5(6)	-9(7)
C(30)	65(9)	82(8)	94(12)	29(8)	24(8)	3(7)
C(31)	51(8)	123(12)	62(8)	1(8)	16(6)	-25(8)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **28**.

	x	y	z	U(eq)
H(7)	5376	5854	11738	57
H(8)	5919	6327	11158	60
H(9)	6904	6382	7753	56
H(10A)	4017	6145	6463	46
H(10B)	5558	6196	5204	46
H(14A)	6017	7033	3734	108
H(14B)	4764	6779	3754	108
H(14C)	6564	6710	4134	108
H(15A)	7556	7224	7550	130
H(15B)	8125	6899	7824	130
H(15C)	7162	7055	9513	130
H(17A)	3226	7589	6889	166
H(17B)	4229	7441	5207	166
H(17C)	5054	7539	7182	166
H(18A)	1380	7168	6841	161
H(18B)	2025	6846	7039	161
H(18C)	2405	7031	5135	161
H(19A)	2644	7322	9932	157
H(19B)	4451	7260	10313	157
H(19C)	3237	6999	10254	157
H(20)	8040	5900	7443	52
H(21A)	8624	5441	8125	78
H(21B)	7014	5330	7189	78
H(22A)	8530	5155	4886	123
H(22B)	9931	5370	5412	123
H(23A)	9175	5575	2620	82
H(23B)	7393	5473	2883	82
H(29A)	11903	6141	4179	87
H(29B)	12766	6404	3000	87
H(30A)	10436	6720	913	120
H(30B)	9662	6664	2995	120
H(30C)	8758	6572	1061	120
H(31A)	11849	6312	-789	118
H(31B)	10113	6199	-1144	118

H(31C)	11388	5990	-209	118

4.4 X-ray Crystal Structure of Compound 32

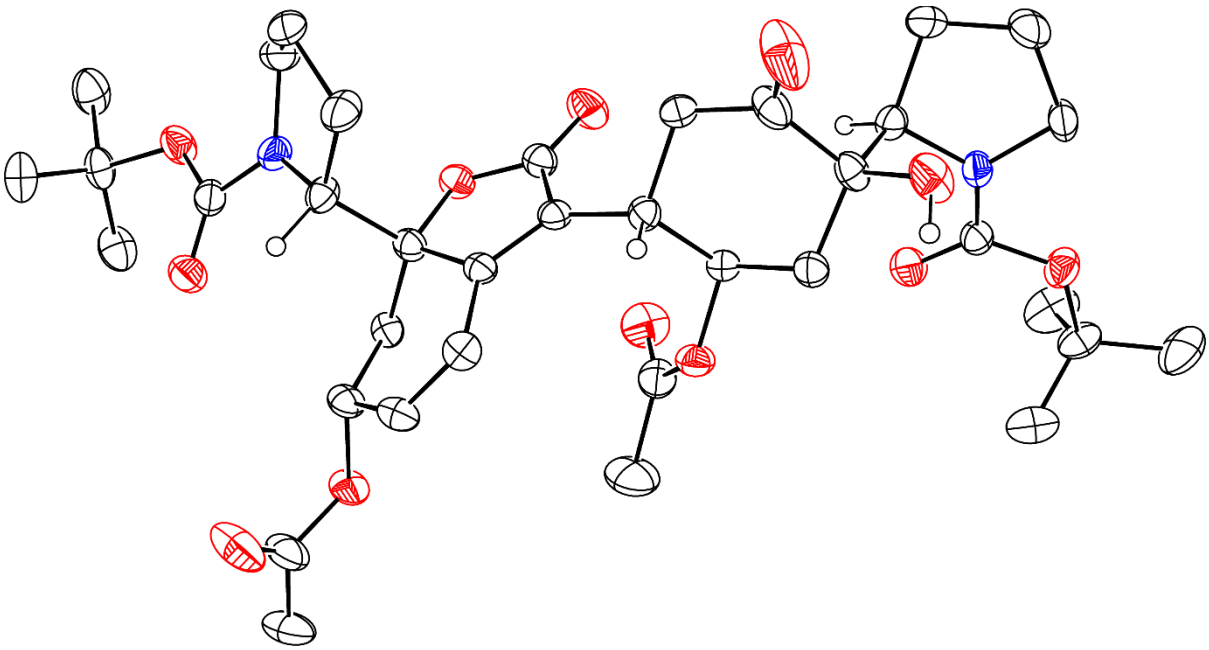


Figure S4. Thermal ellipsoid representation of **32**

Table S18. Crystal data and structure refinement for **32**.

Empirical formula	$C_{23}H_{35}INO_5Si$	
Formula weight	560.51	
Temperature	253(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12$	
Unit cell dimensions	a = 8.5047(19) Å	α = 90°
	b = 46.069(10) Å	β = 90°
	c = 6.8117(16) Å	γ = 90°
Volume	2668.9(10) $Å^3$	
Z	4	
Density (calculated)	1.395 Mg/m^3	
Absorption coefficient	1.275 mm^{-1}	
F(000)	1148	
Crystal size	0.221 x 0.041 x 0.038 mm^3	
Theta range for data collection	2.435 to 26.070°.	
Index ranges	–10<=h<=9, –53<=k<=56, –8<=l<=8	
Reflections collected	33699	
Independent reflections	5114 [R(int) = 0.1109]	
Completeness to theta = 25.242°	99.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7453 and 0.5410	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5114 / 437 / 288	
Goodness-of-fit on F^2	1.198	
Final R indices [I>2sigma(I)]	R1 = 0.0849, wR2 = 0.1419	
R indices (all data)	R1 = 0.1205, wR2 = 0.1550	
Absolute structure parameter	0.24(6)	
Largest diff. peak and hole	0.974 and –0.710 $e \cdot Å^{-3}$	

Table S19. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **32**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4832(9)	5624(2)	5498(11)	46(2)
O(2)	3184(12)	5246(2)	5823(16)	80(3)
C(3)	3946(15)	5429(3)	6569(19)	54(3)
C(4)	4149(14)	5504(3)	8653(18)	51(3)
I(5)	2944(1)	5289(1)	10836(2)	79(1)
C(6)	5062(12)	5735(2)	8797(16)	38(2)
C(7)	5393(13)	5925(3)	10444(17)	48(3)
C(8)	5722(14)	6205(3)	10082(19)	50(3)
C(9)	5796(13)	6334(2)	8061(19)	46(3)
C(10)	5167(12)	6132(2)	6487(16)	38(2)
C(11)	5644(12)	5818(2)	6814(16)	38(2)
O(12)	4892(9)	6598(2)	8068(13)	52(2)
Si(13)	5429(4)	6905(1)	7004(6)	50(1)
C(14)	5729(18)	6850(3)	4340(30)	72(4)
C(15)	7290(18)	7037(3)	8100(30)	87(5)
C(16)	3763(18)	7156(3)	7530(20)	71(4)
C(17)	4100(20)	7460(4)	6620(30)	111(7)
C(18)	2253(19)	7039(4)	6540(30)	108(6)
C(19)	3500(20)	7187(4)	9700(30)	104(6)
C(20)	7460(12)	5769(2)	6546(17)	43(3)
C(21)	7943(17)	5452(3)	6970(20)	65(3)
C(22)	8790(20)	5357(4)	5200(30)	102(6)
C(23)	8317(17)	5550(3)	3570(20)	68(4)
N(24)	7955(11)	5823(2)	4547(12)	43(2)
C(25)	8729(12)	6081(3)	4140(20)	46(2)
O(26)	8749(10)	6285(2)	5234(14)	59(2)
O(27)	9370(9)	6068(2)	2342(13)	57(2)
C(28)	10554(13)	6292(3)	1760(19)	52(3)
C(29)	11909(16)	6277(3)	3150(20)	73(4)
C(30)	9783(18)	6589(3)	1670(30)	80(5)
C(31)	11018(17)	6189(4)	-280(20)	79(4)

Table S20. Bond lengths [Å] and angles [°] for **32**.

O(1)-C(3)	1.382(14)
O(1)-C(11)	1.443(13)
O(2)-C(3)	1.177(14)
C(3)-C(4)	1.472(18)
C(4)-C(6)	1.319(16)
C(4)-I(5)	2.061(11)
C(6)-C(7)	1.453(16)
C(6)-C(11)	1.489(16)
C(7)-C(8)	1.340(17)
C(7)-H(7)	0.9400
C(8)-C(9)	1.502(17)
C(8)-H(8)	0.9400
C(9)-O(12)	1.440(13)
C(9)-C(10)	1.518(16)
C(9)-H(9)	0.9900
C(10)-C(11)	1.518(15)
C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(11)-C(20)	1.572(15)
O(12)-Si(13)	1.652(8)
Si(13)-C(14)	1.850(17)
Si(13)-C(15)	1.853(15)
Si(13)-C(16)	1.864(15)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(14)-H(14C)	0.9700
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(15)-H(15C)	0.9700
C(16)-C(19)	1.50(2)
C(16)-C(18)	1.55(2)
C(16)-C(17)	1.56(2)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(17)-H(17C)	0.9700

C(18)-H(18A)	0.9700
C(18)-H(18B)	0.9700
C(18)-H(18C)	0.9700
C(19)-H(19A)	0.9700
C(19)-H(19B)	0.9700
C(19)-H(19C)	0.9700
C(20)-N(24)	1.447(14)
C(20)-C(21)	1.544(16)
C(20)-H(20)	0.9900
C(21)-C(22)	1.47(2)
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(22)-C(23)	1.48(2)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(23)-N(24)	1.457(15)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
N(24)-C(25)	1.387(14)
C(25)-O(26)	1.202(14)
C(25)-O(27)	1.340(16)
O(27)-C(28)	1.497(14)
C(28)-C(29)	1.493(18)
C(28)-C(30)	1.52(2)
C(28)-C(31)	1.520(19)
C(29)-H(29A)	0.9400
C(29)-H(29B)	0.9400
C(30)-H(30A)	0.9700
C(30)-H(30B)	0.9700
C(30)-H(30C)	0.9700
C(31)-H(31A)	0.9700
C(31)-H(31B)	0.9700
C(31)-H(31C)	0.9700

C(3)-O(1)-C(11)	109.7(8)
O(2)-C(3)-O(1)	122.5(12)
O(2)-C(3)-C(4)	130.5(12)
O(1)-C(3)-C(4)	107.0(10)

C(6)-C(4)-C(3)	109.3(10)
C(6)-C(4)-I(5)	128.8(9)
C(3)-C(4)-I(5)	121.6(8)
C(4)-C(6)-C(7)	131.2(11)
C(4)-C(6)-C(11)	109.7(10)
C(7)-C(6)-C(11)	118.7(9)
C(8)-C(7)-C(6)	118.7(11)
C(8)-C(7)-H(7)	120.7
C(6)-C(7)-H(7)	120.7
C(7)-C(8)-C(9)	124.0(11)
C(7)-C(8)-H(8)	118.0
C(9)-C(8)-H(8)	118.0
O(12)-C(9)-C(8)	108.1(10)
O(12)-C(9)-C(10)	109.5(9)
C(8)-C(9)-C(10)	112.9(9)
O(12)-C(9)-H(9)	108.8
C(8)-C(9)-H(9)	108.8
C(10)-C(9)-H(9)	108.8
C(11)-C(10)-C(9)	112.8(9)
C(11)-C(10)-H(10A)	109.0
C(9)-C(10)-H(10A)	109.0
C(11)-C(10)-H(10B)	109.0
C(9)-C(10)-H(10B)	109.0
H(10A)-C(10)-H(10B)	107.8
O(1)-C(11)-C(6)	104.1(8)
O(1)-C(11)-C(10)	111.8(8)
C(6)-C(11)-C(10)	106.9(9)
O(1)-C(11)-C(20)	107.9(9)
C(6)-C(11)-C(20)	113.2(9)
C(10)-C(11)-C(20)	112.6(9)
C(9)-O(12)-Si(13)	125.0(7)
O(12)-Si(13)-C(14)	110.6(6)
O(12)-Si(13)-C(15)	109.8(6)
C(14)-Si(13)-C(15)	108.9(8)
O(12)-Si(13)-C(16)	103.6(6)
C(14)-Si(13)-C(16)	112.2(7)
C(15)-Si(13)-C(16)	111.6(7)
Si(13)-C(14)-H(14A)	109.5

Si(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
Si(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
Si(13)-C(15)-H(15A)	109.5
Si(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
Si(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(19)-C(16)-C(18)	109.7(15)
C(19)-C(16)-C(17)	109.6(15)
C(18)-C(16)-C(17)	106.9(14)
C(19)-C(16)-Si(13)	111.2(11)
C(18)-C(16)-Si(13)	109.4(11)
C(17)-C(16)-Si(13)	109.9(12)
C(16)-C(17)-H(17A)	109.5
C(16)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(16)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
N(24)-C(20)-C(21)	105.1(9)
N(24)-C(20)-C(11)	111.7(9)
C(21)-C(20)-C(11)	112.2(9)

N(24)-C(20)-H(20)	109.2
C(21)-C(20)-H(20)	109.2
C(11)-C(20)-H(20)	109.2
C(22)-C(21)-C(20)	105.0(11)
C(22)-C(21)-H(21A)	110.7
C(20)-C(21)-H(21A)	110.7
C(22)-C(21)-H(21B)	110.7
C(20)-C(21)-H(21B)	110.7
H(21A)-C(21)-H(21B)	108.8
C(21)-C(22)-C(23)	107.6(12)
C(21)-C(22)-H(22A)	110.2
C(23)-C(22)-H(22A)	110.2
C(21)-C(22)-H(22B)	110.2
C(23)-C(22)-H(22B)	110.2
H(22A)-C(22)-H(22B)	108.5
N(24)-C(23)-C(22)	103.4(12)
N(24)-C(23)-H(23A)	111.1
C(22)-C(23)-H(23A)	111.1
N(24)-C(23)-H(23B)	111.1
C(22)-C(23)-H(23B)	111.1
H(23A)-C(23)-H(23B)	109.0
C(25)-N(24)-C(20)	118.5(10)
C(25)-N(24)-C(23)	123.1(10)
C(20)-N(24)-C(23)	110.0(9)
O(26)-C(25)-O(27)	126.7(11)
O(26)-C(25)-N(24)	123.5(12)
O(27)-C(25)-N(24)	109.7(11)
C(25)-O(27)-C(28)	118.9(10)
C(29)-C(28)-O(27)	108.6(10)
C(29)-C(28)-C(30)	113.5(13)
O(27)-C(28)-C(30)	110.0(9)
C(29)-C(28)-C(31)	111.5(11)
O(27)-C(28)-C(31)	101.6(11)
C(30)-C(28)-C(31)	111.0(13)
C(28)-C(29)-H(29A)	120.0
C(28)-C(29)-H(29B)	120.0
H(29A)-C(29)-H(29B)	120.0
C(28)-C(30)-H(30A)	109.5

C(28)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(28)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(28)-C(31)-H(31A)	109.5
C(28)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(28)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S21. Anisotropic displacement parameters ($Å^2$ x 10^3) for **32**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	54(4)	50(4)	35(4)	2(3)	-3(4)	-14(3)
O(2)	89(7)	77(6)	73(5)	4(6)	-14(6)	-45(5)
C(3)	61(7)	51(6)	51(6)	4(5)	9(5)	-16(5)
C(4)	52(6)	48(6)	53(6)	10(5)	9(5)	-8(5)
I(5)	102(1)	66(1)	70(1)	10(1)	28(1)	-20(1)
C(6)	33(5)	43(5)	37(5)	6(4)	-2(4)	3(4)
C(7)	45(6)	62(6)	36(6)	2(5)	-15(5)	-5(5)
C(8)	44(6)	57(6)	50(6)	-6(5)	-5(5)	-8(5)
C(9)	33(6)	38(5)	68(6)	0(5)	2(5)	-3(4)
C(10)	29(5)	39(5)	47(6)	6(4)	3(5)	0(4)
C(11)	31(5)	45(5)	40(5)	8(4)	-11(4)	-4(4)
O(12)	51(5)	33(4)	71(5)	0(4)	13(4)	6(3)
Si(13)	46(2)	39(2)	65(2)	4(2)	-2(2)	2(2)
C(14)	77(9)	58(8)	82(9)	4(8)	5(8)	0(7)
C(15)	77(9)	67(9)	116(12)	11(9)	-24(9)	-16(7)
C(16)	76(8)	54(7)	84(9)	6(7)	6(7)	14(6)
C(17)	125(14)	60(9)	147(18)	25(10)	8(13)	20(9)
C(18)	61(9)	117(13)	145(16)	14(11)	-9(10)	15(8)
C(19)	141(15)	76(10)	96(10)	1(9)	28(10)	42(10)
C(20)	35(5)	43(5)	52(6)	3(5)	10(4)	2(4)
C(21)	49(7)	62(7)	85(8)	13(6)	-9(7)	14(6)
C(22)	119(12)	65(9)	123(11)	15(8)	43(9)	19(8)
C(23)	65(8)	58(6)	81(8)	-17(6)	23(7)	0(6)
N(24)	48(5)	43(4)	38(5)	-2(4)	3(4)	3(4)
C(25)	36(6)	53(5)	51(6)	5(5)	1(5)	1(4)
O(26)	57(5)	47(4)	74(6)	-2(4)	15(4)	-7(4)
O(27)	38(4)	76(5)	56(5)	6(4)	10(4)	-10(4)
C(28)	26(5)	78(7)	53(6)	2(6)	9(4)	-14(5)
C(29)	40(6)	108(11)	70(8)	15(8)	-5(6)	-9(7)
C(30)	65(9)	82(8)	94(12)	29(8)	24(8)	3(7)
C(31)	51(8)	123(12)	62(8)	1(8)	16(6)	-25(8)

Table S22. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **32**.

	x	y	z	U(eq)
H(7)	5376	5854	11738	57
H(8)	5919	6327	11158	60
H(9)	6904	6382	7753	56
H(10A)	4017	6145	6463	46
H(10B)	5558	6196	5204	46
H(14A)	6017	7033	3734	108
H(14B)	4764	6779	3754	108
H(14C)	6564	6710	4134	108
H(15A)	7556	7224	7550	130
H(15B)	8125	6899	7824	130
H(15C)	7162	7055	9513	130
H(17A)	3226	7589	6889	166
H(17B)	4229	7441	5207	166
H(17C)	5054	7539	7182	166
H(18A)	1380	7168	6841	161
H(18B)	2025	6846	7039	161
H(18C)	2405	7031	5135	161
H(19A)	2644	7322	9932	157
H(19B)	4451	7260	10313	157
H(19C)	3237	6999	10254	157
H(20)	8040	5900	7443	52
H(21A)	8624	5441	8125	78
H(21B)	7014	5330	7189	78
H(22A)	8530	5155	4886	123
H(22B)	9931	5370	5412	123
H(23A)	9175	5575	2620	82
H(23B)	7393	5473	2883	82
H(29A)	11903	6141	4179	87
H(29B)	12766	6404	3000	87
H(30A)	10436	6720	913	120
H(30B)	9662	6664	2995	120
H(30C)	8758	6572	1061	120
H(31A)	11849	6312	-789	118
H(31B)	10113	6199	-1144	118

H(31C)	11388	5990	-209	118

4.5 X-ray Crystal Structure of Compound 7

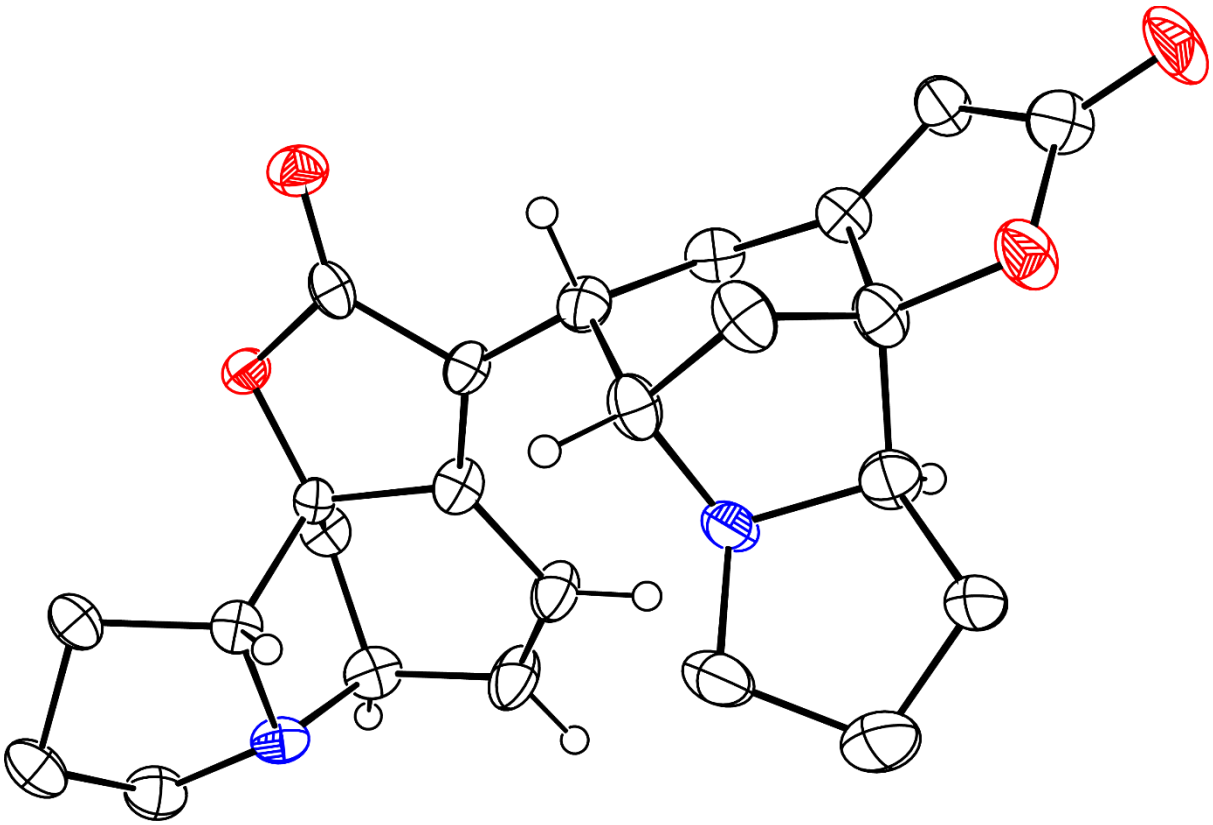


Figure S5. Thermal ellipsoid representation of **7**

Table S23. Crystal data and structure refinement for **7.**

Empirical formula	$C_{24}H_{26}N_2O_4$	
Formula weight	406.47	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.950(2) Å	α = 90°
	b = 6.4623(13) Å	β = 103.465(5)°
	c = 13.674(2) Å	γ = 90°
Volume	1026.9(3) $Å^3$	
Z	2	
Density (calculated)	1.315 Mg/m^3	
Absorption coefficient	0.090 mm^{-1}	
F(000)	432	
Crystal size	0.072 x 0.043 x 0.017 mm^3	
Theta range for data collection	2.582 to 27.195°.	
Index ranges	–14<=h<=15, –8<=k<=8, –16<=l<=16	
Reflections collected	14906	
Independent reflections	4183 [R(int) = 0.1161]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6756	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4183 / 106 / 299	
Goodness-of-fit on F^2	1.130	
Final R indices [I>2sigma(I)]	R1 = 0.0932, wR2 = 0.1118	
R indices (all data)	R1 = 0.1784, wR2 = 0.1343	
Absolute structure parameter	-0.4(10)	
Largest diff. peak and hole	0.232 and –0.286 $e \cdot Å^{-3}$	

Table S24. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **7**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3006(4)	4831(8)	18(3)	45(1)
O(2)	3848(5)	6819(9)	-964(4)	57(2)
C(3)	3662(6)	6525(12)	-147(6)	39(2)
C(4)	4010(6)	7692(12)	790(5)	36(2)
C(5)	3596(6)	6736(11)	1500(5)	29(2)
C(6)	2971(6)	4816(12)	1074(5)	34(2)
C(7)	1747(6)	4744(12)	1245(5)	39(2)
C(8)	848(10)	3287(19)	606(8)	48(3)
C(9)	155(10)	2670(20)	1355(7)	63(4)
C(10)	1100(30)	2300(70)	2303(15)	53(4)
C(8B)	1270(60)	2740(60)	670(40)	51(9)
C(9B)	850(50)	1230(90)	1380(30)	55(7)
C(10B)	1150(190)	2300(400)	2430(90)	56(10)
N(11)	1940(5)	3988(9)	2305(4)	34(2)
C(12)	3162(6)	3401(11)	2654(5)	34(2)
C(13)	3554(7)	2973(11)	1666(5)	39(2)
C(14)	3637(6)	7201(11)	2580(5)	33(2)
C(15)	3865(5)	5186(12)	3215(4)	32(2)
O(16)	4375(3)	5495(8)	6015(3)	29(1)
O(17)	5732(4)	5293(8)	5123(3)	37(1)
C(18)	4731(6)	5368(12)	5127(5)	31(2)
C(19)	3713(5)	5454(12)	4272(4)	27(2)
C(20)	2785(5)	5777(11)	4655(5)	31(2)
C(21)	3129(5)	5608(12)	5791(4)	26(2)
C(22)	2595(6)	3703(10)	6164(5)	28(2)
C(23)	3224(6)	2859(12)	7197(5)	35(2)
C(24)	2248(6)	2298(12)	7709(5)	39(2)
C(25)	1417(6)	4111(12)	7365(5)	42(2)
N(26)	1440(5)	4453(9)	6296(4)	30(2)
C(27)	1383(6)	6692(12)	5994(5)	37(2)
C(28)	2636(6)	7424(10)	6262(5)	31(2)
C(29)	908(6)	6776(13)	4859(5)	45(2)
C(30)	1580(6)	6293(11)	4234(5)	38(2)

Table S25. Bond lengths [Å] and angles [°] for **7**.

O(1)-C(3)	1.395(8)
O(1)-C(6)	1.454(8)
O(2)-C(3)	1.203(8)
C(3)-C(4)	1.461(9)
C(4)-C(5)	1.339(9)
C(4)-H(4)	0.9500
C(5)-C(6)	1.494(9)
C(5)-C(14)	1.498(9)
C(6)-C(13)	1.516(10)
C(6)-C(7)	1.535(9)
C(7)-N(11)	1.495(8)
C(7)-C(8)	1.539(12)
C(7)-C(8B)	1.55(3)
C(7)-H(7)	1.0000
C(8)-C(9)	1.513(13)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.53(3)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-N(11)	1.48(4)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(8B)-C(9B)	1.55(3)
C(8B)-H(8BA)	0.9900
C(8B)-H(8BB)	0.9900
C(9B)-C(10B)	1.54(3)
C(9B)-H(9BA)	0.9900
C(9B)-H(9BB)	0.9900
C(10B)-N(11)	1.5(2)
C(10B)-H(10C)	0.9900
C(10B)-H(10D)	0.9900
N(11)-C(12)	1.477(8)
C(12)-C(15)	1.524(9)
C(12)-C(13)	1.554(10)
C(12)-H(12)	1.0000

C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.553(10)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(19)	1.507(8)
C(15)-H(15)	1.0000
O(16)-C(18)	1.379(7)
O(16)-C(21)	1.451(7)
O(17)-C(18)	1.199(7)
C(18)-C(19)	1.479(8)
C(19)-C(20)	1.349(8)
C(20)-C(30)	1.460(9)
C(20)-C(21)	1.515(8)
C(21)-C(28)	1.521(9)
C(21)-C(22)	1.528(9)
C(22)-N(26)	1.512(8)
C(22)-C(23)	1.538(9)
C(22)-H(22)	1.0000
C(23)-C(24)	1.536(9)
C(23)-H(23A)	0.9900
C(23)-H(23B)	0.9900
C(24)-C(25)	1.537(10)
C(24)-H(24A)	0.9900
C(24)-H(24B)	0.9900
C(25)-N(26)	1.485(9)
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900
N(26)-C(27)	1.502(9)
C(27)-C(29)	1.524(9)
C(27)-C(28)	1.532(9)
C(27)-H(27)	1.0000
C(28)-H(28A)	0.9900
C(28)-H(28B)	0.9900
C(29)-C(30)	1.339(9)
C(29)-H(29)	0.9500
C(30)-H(30)	0.9500

C(3)-O(1)-C(6)	108.2(5)
O(2)-C(3)-O(1)	120.4(7)
O(2)-C(3)-C(4)	131.0(7)
O(1)-C(3)-C(4)	108.6(6)
C(5)-C(4)-C(3)	108.7(7)
C(5)-C(4)-H(4)	125.7
C(3)-C(4)-H(4)	125.7
C(4)-C(5)-C(6)	109.6(6)
C(4)-C(5)-C(14)	133.7(7)
C(6)-C(5)-C(14)	116.7(6)
O(1)-C(6)-C(5)	104.7(6)
O(1)-C(6)-C(13)	114.8(6)
C(5)-C(6)-C(13)	108.6(6)
O(1)-C(6)-C(7)	113.6(5)
C(5)-C(6)-C(7)	111.9(6)
C(13)-C(6)-C(7)	103.3(6)
N(11)-C(7)-C(6)	102.7(5)
N(11)-C(7)-C(8)	106.3(6)
C(6)-C(7)-C(8)	119.8(7)
N(11)-C(7)-C(8B)	100.0(19)
C(6)-C(7)-C(8B)	102(2)
N(11)-C(7)-H(7)	109.2
C(6)-C(7)-H(7)	109.2
C(8)-C(7)-H(7)	109.2
C(9)-C(8)-C(7)	101.3(8)
C(9)-C(8)-H(8A)	111.5
C(7)-C(8)-H(8A)	111.5
C(9)-C(8)-H(8B)	111.5
C(7)-C(8)-H(8B)	111.5
H(8A)-C(8)-H(8B)	109.3
C(8)-C(9)-C(10)	101.6(16)
C(8)-C(9)-H(9A)	111.5
C(10)-C(9)-H(9A)	111.5
C(8)-C(9)-H(9B)	111.5
C(10)-C(9)-H(9B)	111.5
H(9A)-C(9)-H(9B)	109.3
N(11)-C(10)-C(9)	105(3)
N(11)-C(10)-H(10A)	110.8

C(9)-C(10)-H(10A)	110.8
N(11)-C(10)-H(10B)	110.8
C(9)-C(10)-H(10B)	110.8
H(10A)-C(10)-H(10B)	108.9
C(9B)-C(8B)-C(7)	110(3)
C(9B)-C(8B)-H(8BA)	109.7
C(7)-C(8B)-H(8BA)	109.7
C(9B)-C(8B)-H(8BB)	109.7
C(7)-C(8B)-H(8BB)	109.7
H(8BA)-C(8B)-H(8BB)	108.2
C(10B)-C(9B)-C(8B)	106(9)
C(10B)-C(9B)-H(9BA)	110.6
C(8B)-C(9B)-H(9BA)	110.6
C(10B)-C(9B)-H(9BB)	110.6
C(8B)-C(9B)-H(9BB)	110.6
H(9BA)-C(9B)-H(9BB)	108.8
N(11)-C(10B)-C(9B)	104(10)
N(11)-C(10B)-H(10C)	111.0
C(9B)-C(10B)-H(10C)	111.0
N(11)-C(10B)-H(10D)	111.0
C(9B)-C(10B)-H(10D)	111.0
H(10C)-C(10B)-H(10D)	109.0
C(12)-N(11)-C(10)	115.5(19)
C(12)-N(11)-C(10B)	112(10)
C(12)-N(11)-C(7)	108.4(5)
C(10)-N(11)-C(7)	106.7(11)
C(10B)-N(11)-C(7)	113(5)
N(11)-C(12)-C(15)	110.8(6)
N(11)-C(12)-C(13)	103.9(6)
C(15)-C(12)-C(13)	109.3(6)
N(11)-C(12)-H(12)	110.9
C(15)-C(12)-H(12)	110.9
C(13)-C(12)-H(12)	110.9
C(6)-C(13)-C(12)	97.5(5)
C(6)-C(13)-H(13A)	112.3
C(12)-C(13)-H(13A)	112.3
C(6)-C(13)-H(13B)	112.3
C(12)-C(13)-H(13B)	112.3

H(13A)-C(13)-H(13B)	109.9
C(5)-C(14)-C(15)	110.1(6)
C(5)-C(14)-H(14A)	109.6
C(15)-C(14)-H(14A)	109.6
C(5)-C(14)-H(14B)	109.6
C(15)-C(14)-H(14B)	109.6
H(14A)-C(14)-H(14B)	108.1
C(19)-C(15)-C(12)	113.2(6)
C(19)-C(15)-C(14)	113.2(6)
C(12)-C(15)-C(14)	110.4(5)
C(19)-C(15)-H(15)	106.5
C(12)-C(15)-H(15)	106.5
C(14)-C(15)-H(15)	106.5
C(18)-O(16)-C(21)	109.2(5)
O(17)-C(18)-O(16)	121.2(6)
O(17)-C(18)-C(19)	129.5(6)
O(16)-C(18)-C(19)	109.2(5)
C(20)-C(19)-C(18)	107.3(5)
C(20)-C(19)-C(15)	133.2(6)
C(18)-C(19)-C(15)	119.5(5)
C(19)-C(20)-C(30)	134.9(6)
C(19)-C(20)-C(21)	109.7(5)
C(30)-C(20)-C(21)	115.4(5)
O(16)-C(21)-C(20)	103.9(5)
O(16)-C(21)-C(28)	115.4(6)
C(20)-C(21)-C(28)	109.8(6)
O(16)-C(21)-C(22)	112.2(6)
C(20)-C(21)-C(22)	111.4(6)
C(28)-C(21)-C(22)	104.3(5)
N(26)-C(22)-C(21)	104.2(5)
N(26)-C(22)-C(23)	105.6(5)
C(21)-C(22)-C(23)	116.1(6)
N(26)-C(22)-H(22)	110.2
C(21)-C(22)-H(22)	110.2
C(23)-C(22)-H(22)	110.2
C(24)-C(23)-C(22)	104.0(6)
C(24)-C(23)-H(23A)	111.0
C(22)-C(23)-H(23A)	111.0

C(24)-C(23)-H(23B)	111.0
C(22)-C(23)-H(23B)	111.0
H(23A)-C(23)-H(23B)	109.0
C(23)-C(24)-C(25)	100.8(6)
C(23)-C(24)-H(24A)	111.6
C(25)-C(24)-H(24A)	111.6
C(23)-C(24)-H(24B)	111.6
C(25)-C(24)-H(24B)	111.6
H(24A)-C(24)-H(24B)	109.4
N(26)-C(25)-C(24)	104.8(6)
N(26)-C(25)-H(25A)	110.8
C(24)-C(25)-H(25A)	110.8
N(26)-C(25)-H(25B)	110.8
C(24)-C(25)-H(25B)	110.8
H(25A)-C(25)-H(25B)	108.9
C(25)-N(26)-C(27)	113.8(6)
C(25)-N(26)-C(22)	107.3(5)
C(27)-N(26)-C(22)	105.1(6)
N(26)-C(27)-C(29)	107.3(6)
N(26)-C(27)-C(28)	104.6(6)
C(29)-C(27)-C(28)	110.1(6)
N(26)-C(27)-H(27)	111.5
C(29)-C(27)-H(27)	111.5
C(28)-C(27)-H(27)	111.5
C(21)-C(28)-C(27)	96.6(5)
C(21)-C(28)-H(28A)	112.4
C(27)-C(28)-H(28A)	112.4
C(21)-C(28)-H(28B)	112.4
C(27)-C(28)-H(28B)	112.4
H(28A)-C(28)-H(28B)	110.0
C(30)-C(29)-C(27)	120.4(6)
C(30)-C(29)-H(29)	119.8
C(27)-C(29)-H(29)	119.8
C(29)-C(30)-C(20)	119.0(6)
C(29)-C(30)-H(30)	120.5
C(20)-C(30)-H(30)	120.5

Symmetry transformations used to generate equivalent atoms:

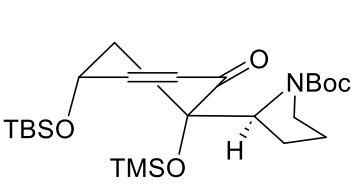
Table S26. Anisotropic displacement parameters ($Å^2$ x 10^3) for **7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	63(3)	45(4)	28(3)	-8(3)	14(3)	-19(3)
O(2)	82(4)	71(4)	24(3)	-11(3)	26(3)	-22(4)
C(3)	46(5)	37(5)	37(5)	-14(4)	14(4)	-7(4)
C(4)	46(5)	33(5)	30(4)	-3(4)	10(4)	-10(4)
C(5)	34(4)	23(4)	30(4)	-4(4)	11(3)	2(3)
C(6)	47(4)	31(5)	25(4)	-6(3)	12(3)	-3(4)
C(7)	44(5)	33(5)	39(5)	-3(4)	7(4)	-11(4)
C(8)	42(7)	66(7)	36(6)	2(5)	7(5)	-22(6)
C(9)	53(7)	71(8)	61(6)	-6(6)	8(5)	-29(6)
C(10)	52(7)	61(7)	48(8)	5(8)	20(7)	-21(6)
C(8B)	51(15)	63(15)	36(14)	0(13)	5(13)	-24(14)
C(9B)	54(12)	65(12)	49(12)	3(11)	15(11)	-27(11)
C(10B)	53(15)	63(15)	53(15)	2(14)	12(14)	-21(14)
N(11)	38(4)	39(4)	29(4)	-1(3)	13(3)	-12(3)
C(12)	48(5)	25(5)	30(4)	2(3)	10(4)	2(4)
C(13)	54(5)	28(5)	40(5)	4(4)	19(4)	7(4)
C(14)	34(4)	27(5)	39(5)	-5(4)	10(4)	-1(4)
C(15)	29(4)	36(5)	31(4)	-2(4)	8(3)	7(4)
O(16)	23(2)	38(3)	26(2)	-1(3)	4(2)	-2(3)
O(17)	29(3)	40(3)	43(3)	0(3)	13(2)	3(3)
C(18)	42(4)	22(4)	29(4)	7(4)	10(4)	2(4)
C(19)	26(3)	28(4)	27(4)	-1(4)	2(3)	5(4)
C(20)	33(4)	30(5)	28(4)	-7(3)	5(3)	5(4)
C(21)	24(4)	30(4)	24(4)	5(4)	4(3)	2(4)
C(22)	31(4)	27(4)	28(4)	-5(3)	10(3)	5(3)
C(23)	44(5)	26(4)	37(5)	4(4)	13(4)	-1(4)
C(24)	56(5)	33(5)	36(4)	-2(4)	24(4)	-4(4)
C(25)	41(5)	44(5)	43(5)	-5(4)	18(4)	-2(4)
N(26)	27(3)	31(4)	36(4)	-9(3)	14(3)	0(3)
C(27)	36(4)	36(5)	39(5)	-9(4)	12(4)	1(4)
C(28)	38(5)	25(4)	32(4)	-4(3)	11(4)	2(4)
C(29)	32(4)	63(6)	38(5)	1(4)	2(4)	18(4)
C(30)	31(4)	52(6)	30(4)	0(4)	3(3)	13(4)

Table S27. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for **7**.

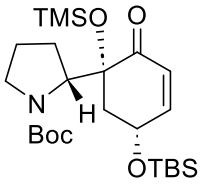
	x	y	z	U(eq)
H(4)	4456	8925	880	43
H(7)	1427	6180	1204	47
H(8A)	366	4015	20	58
H(8B)	1215	2071	370	58
H(9A)	-297	1399	1142	75
H(9B)	-371	3796	1455	75
H(10A)	788	2373	2912	63
H(10B)	1466	935	2279	63
H(8BA)	620	3093	97	61
H(8BB)	1876	2071	398	61
H(9BA)	6	1007	1163	66
H(9BB)	1238	-128	1402	66
H(10C)	456	2795	2616	68
H(10D)	1547	1272	2949	68
H(12)	3246	2133	3084	41
H(13A)	4401	3018	1767	47
H(13B)	3256	1640	1354	47
H(14A)	2896	7817	2638	39
H(14B)	4255	8216	2839	39
H(15)	4692	4826	3276	38
H(22)	2486	2579	5648	34
H(23A)	3687	1623	7123	42
H(23B)	3736	3922	7588	42
H(24A)	2521	2257	8450	47
H(24B)	1891	954	7467	47
H(25A)	630	3753	7427	50
H(25B)	1677	5363	7772	50
H(27)	896	7510	6358	44
H(28A)	2742	8758	5939	37
H(28B)	2952	7516	6997	37
H(29)	132	7175	4594	55
H(30)	1277	6285	3527	46

5. Computational Details on the Conformation of Enone 20

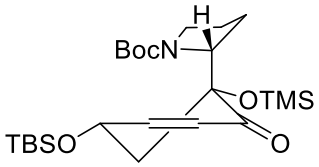


20-ax

0.00 kcal/mol



20



20-eq

–14.35 kcal/mol

The following is absolute energies and coordinates of **20**-ax and **20**-eq

20-ax

E [B3LYP-D3/6-311+G**, SMD (chloroform)]: -1952.22603834 Hartree
Thermal Correction to Gibbs free energy [B3LYP-D3/6-31G*]: 0.595190 Hartree

O	-1.537875	2.732642	4.774156
C	-1.462113	1.563016	5.106793
C	-2.326678	1.035221	6.191719
C	-1.924971	0.009005	6.952771
C	-0.569888	-0.622098	6.708980
O	0.468104	0.152714	7.302395
Si	0.616769	0.755691	8.868828
C	2.289457	1.610748	8.871600
C	-0.721344	2.027979	9.264119
C	0.579475	-0.686910	10.130127
C	-0.830164	-1.305449	10.246924
C	0.994845	-0.154227	11.519389
C	1.576179	-1.777963	9.686218
C	-0.304714	-0.736977	5.205877
C	-0.499356	0.577011	4.388354
O	0.690473	1.287631	4.176061
Si	2.293602	0.874111	3.881951
C	3.014998	2.381726	3.030354
C	3.204881	0.586700	5.509711
C	2.473867	-0.669028	2.806516
C	-1.138062	0.202281	2.993511
H	-0.395814	-0.423052	2.489856
C	-2.521361	-0.514727	3.093586
C	-3.444001	0.229713	2.109549
C	-2.844567	1.640797	2.064753

N	-1.404034	1.369149	2.147488
C	-0.496311	1.782479	1.213364
O	-0.991316	2.820234	0.495744
C	-0.273299	3.350276	-0.666884
C	-0.123827	2.258730	-1.731528
C	-1.212905	4.458077	-1.150345
C	1.078143	3.935868	-0.245766
O	0.607348	1.277210	1.044834
H	-3.229691	1.603618	6.400724
H	-2.509383	-0.320699	7.809185
H	-0.550943	-1.634258	7.137502
H	2.508502	2.045570	9.853729
H	3.099733	0.923182	8.609439
H	2.293513	2.422813	8.136284
H	-0.471731	2.560499	10.190532
H	-0.785447	2.767207	8.457355
H	-1.715910	1.588509	9.388652
H	-0.834180	-2.106472	11.000653
H	-1.166850	-1.754069	9.304747
H	-1.579559	-0.566172	10.555089
H	0.974027	-0.965611	12.261640
H	2.011582	0.256017	11.514146
H	0.316742	0.631066	11.877413
H	1.583992	-2.610257	10.405289
H	2.600217	-1.390539	9.621882
H	1.318193	-2.189837	8.703157
H	0.713679	-1.100859	5.059331
H	-0.971854	-1.517640	4.825357
H	2.527700	2.523016	2.062909
H	4.094971	2.272471	2.870478
H	2.849957	3.280870	3.635187
H	2.724996	-0.173802	6.132533
H	3.235798	1.510081	6.097423
H	4.240117	0.277531	5.313456
H	1.970869	-0.517304	1.848196
H	2.073092	-1.575096	3.277114
H	3.539022	-0.852410	2.612198
H	-2.924314	-0.444638	4.108610
H	-2.435887	-1.579419	2.858184
H	-4.493009	0.219391	2.422770
H	-3.383027	-0.221735	1.112409
H	-3.161247	2.244699	2.921586
H	-3.073844	2.189928	1.153489
H	0.315242	2.686055	-2.640016
H	-1.105147	1.843384	-1.987486
H	0.519906	1.454034	-1.372630
H	-0.798182	4.943363	-2.040079

H	-2.195101	4.045257	-1.403786
H	-1.346823	5.213129	-0.369096
H	1.502075	4.512606	-1.075849
H	1.777677	3.147338	0.030429
H	0.946618	4.606117	0.610005

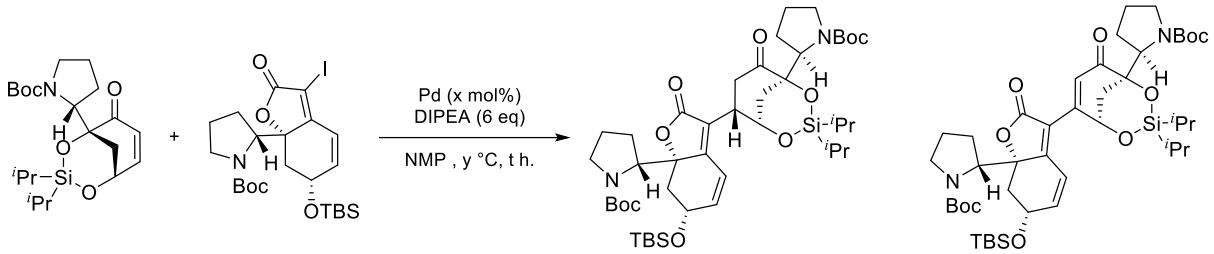
20-eq

E [B3LYP-D3/6-311+G**, SMD (chloroform)]: -1952.24984409 Hartree
Thermal Correction to Gibbs free energy [B3LYP-D3/6-31G*]: 0.594555 Hartree

C	1.031777	6.059483	5.299150
H	2.026992	5.746404	5.620995
H	1.019301	7.154946	5.273968
C	-0.033865	5.605723	6.304953
H	0.108530	4.536161	6.506835
C	-1.418352	5.786352	5.751769
H	-2.220232	5.802915	6.487328
C	-1.685235	5.912682	4.440715
H	-2.697638	6.046606	4.068975
C	-0.624875	5.950961	3.418821
C	0.794495	5.544262	3.866363
C	0.889083	3.982261	3.764187
H	0.173976	3.533809	4.457242
C	0.671730	3.493960	2.301588
H	0.611853	4.352595	1.631091
H	-0.265374	2.937873	2.208599
N	2.236443	3.502800	4.111048
O	0.065101	6.348091	7.515713
Si	1.017605	5.916747	8.838362
C	0.636456	4.147512	9.364934
H	1.226409	3.870564	10.247670
H	0.886590	3.445718	8.562139
H	-0.422592	4.019404	9.616933
C	2.848744	6.067410	8.406608
H	3.480118	5.882440	9.284533
H	3.089017	7.064373	8.020756
H	3.123420	5.331751	7.644118
C	0.514432	7.186197	10.166807
C	1.306286	6.931913	11.466399
H	1.018682	7.660517	12.238352
H	2.388559	7.030483	11.313931
H	1.113903	5.931727	11.875172
C	-0.995837	7.059431	10.455880
H	-1.306440	7.801574	11.206080

H	-1.253909	6.068624	10.850562
H	-1.590749	7.227765	9.551115
C	0.811455	8.611895	9.656484
H	0.502906	9.358530	10.403141
H	0.272252	8.823787	8.726346
H	1.881764	8.762383	9.467601
O	-0.863659	6.282944	2.263607
O	1.800971	6.051433	3.026612
Si	1.999178	7.425848	2.074772
C	3.843330	7.786606	2.233013
H	4.139996	8.636848	1.606175
H	4.439671	6.919614	1.923757
H	4.111402	8.020767	3.269998
C	1.585417	7.034586	0.281295
H	1.845982	7.871329	-0.379315
H	0.518028	6.822625	0.176092
H	2.145294	6.155059	-0.060622
C	1.005624	8.895598	2.714001
H	1.275497	9.800133	2.153832
H	1.211871	9.094016	3.772829
H	-0.070082	8.735327	2.596195
C	2.502024	2.990073	5.345658
O	1.720211	3.041534	6.294259
O	3.735597	2.437008	5.393501
C	4.194990	1.695898	6.576052
C	4.298350	2.627668	7.786859
H	4.805416	2.106471	8.606722
H	3.312446	2.944031	8.126814
H	4.885627	3.515780	7.530645
C	3.270028	0.503778	6.839332
H	3.686101	-0.113689	7.643074
H	3.186997	-0.115513	5.939301
H	2.274119	0.839669	7.131895
C	5.583407	1.221794	6.139809
H	6.051519	0.639875	6.940478
H	6.225212	2.077971	5.908373
H	5.511437	0.592143	5.246925
C	1.904013	2.631921	1.964377
H	1.720582	1.579194	2.210800
C	2.993233	3.185180	2.891357
H	2.180703	2.688804	0.906905
H	3.790376	2.477760	3.112949
H	3.427739	4.106471	2.491246

6. Attempted Optimization of Reductive Heck Reaction Between 22 and 28.



22 (1 eq) + **28** → P (**31**, desired) + H

Entry	Pd	**28**	x	y	t	Note	Crude ratio (**31** : H)	Yield of P
1	$Pd(TFA)_2$	3eq	5	80	24		1 : 0.2	13%
2	$Pd(TFA)_2$	2eq	2	90	19	AgTFA as an additive	-	0%
3	$Pd(TFA)_2$	3eq	5	90	49+37	2 cycles	1 : 0.5	37%
4	$Pd(TFA)_2$	3eq	10	90	48	2.5 mol%/12h stepwise Pdaddition	1 : 0.7	35%
5	$Pd(TFA)_2$	3eq	10	90	37		1 : 0.4	30%
6	$Pd(TFA)_2$	3eq	5	110	24		1 : 0.8	30%
7	BrettPhos Pd G3	3eq	5	90	48		1 : 1.2	17%
8	$Pd(OAc)_2$	3eq	5	90	48		1 : 0.2	35 %
9	$Pd(OAc)_2$	3eq	5	80	24		1 : 0.7	16 %

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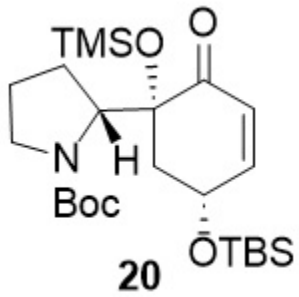
8. Copies of NMR Spectra of Newly Synthesized Compounds

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



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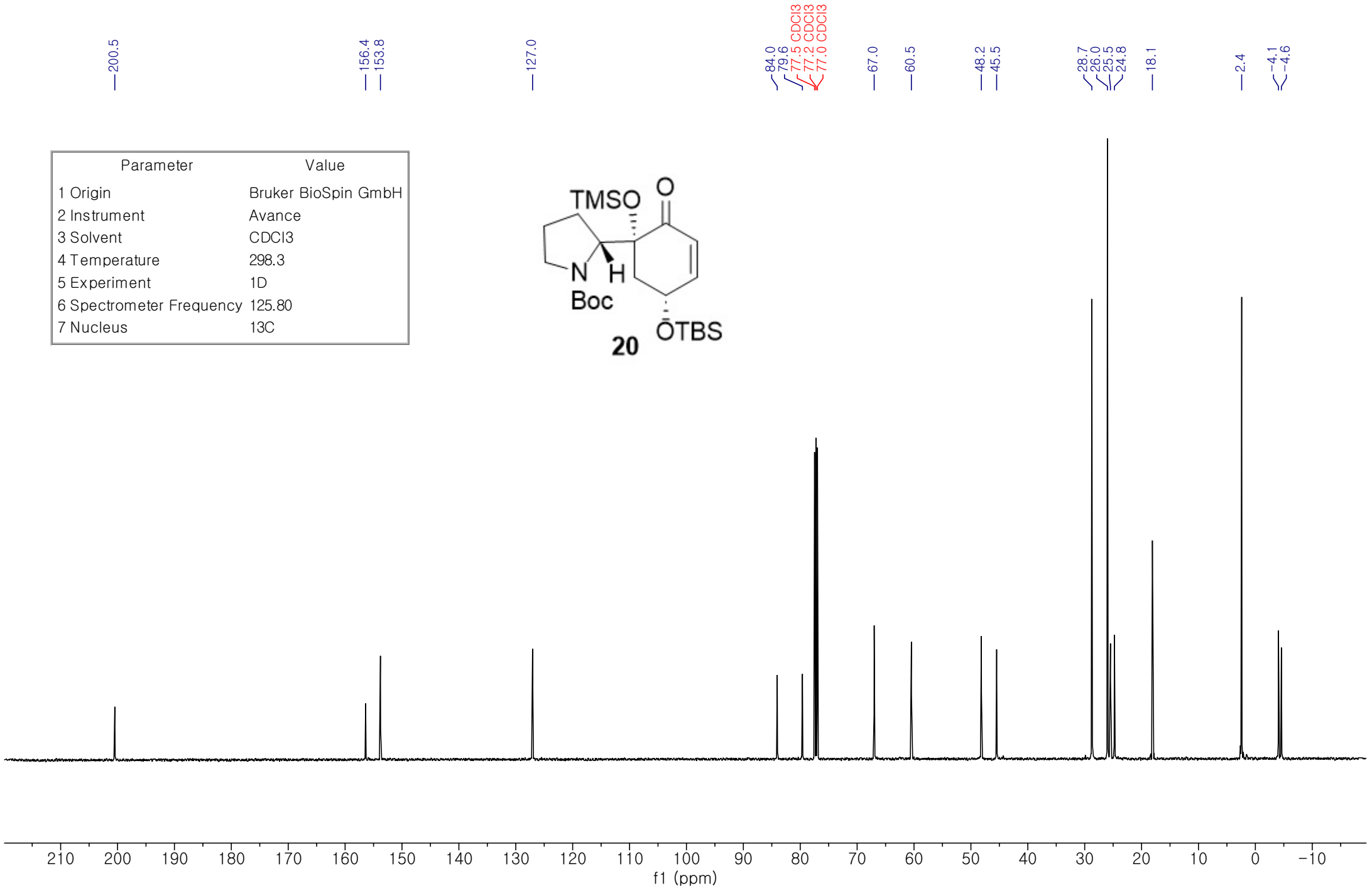
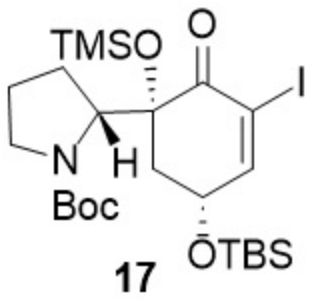

200.5
156.4
153.8
127.0
84.0
79.6
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
67.0
60.5
48.2
45.5
28.7
26.0
25.5
24.8
18.1
2.4
-4.1
-4.6
Parameter
Value
1 Origin
Bruker BioSpin GmbH
2 Instrument
Avance
3 Solvent
CDCl3
4 Temperature
298.3
5 Experiment
1D
6 Spectrometer Frequency
125.80
7 Nucleus
13C
TMSO
O
N
H
Boc
OTBS
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

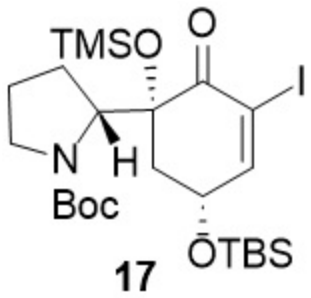
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



17

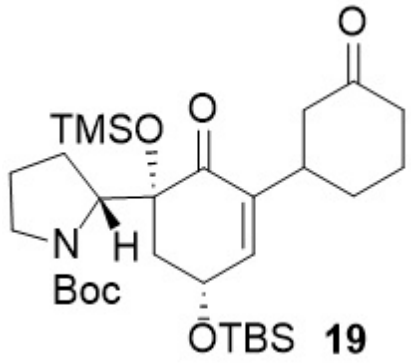
195.0
162.2
156.4
101.0
83.2
79.9
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
68.8
60.6
48.2
45.3
28.7
26.0
25.8
24.8
18.1
2.3
-4.1
-4.6

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.2
5 Experiment	1D
6 Spectrometer Frequency	125.80
7 Nucleus	13C

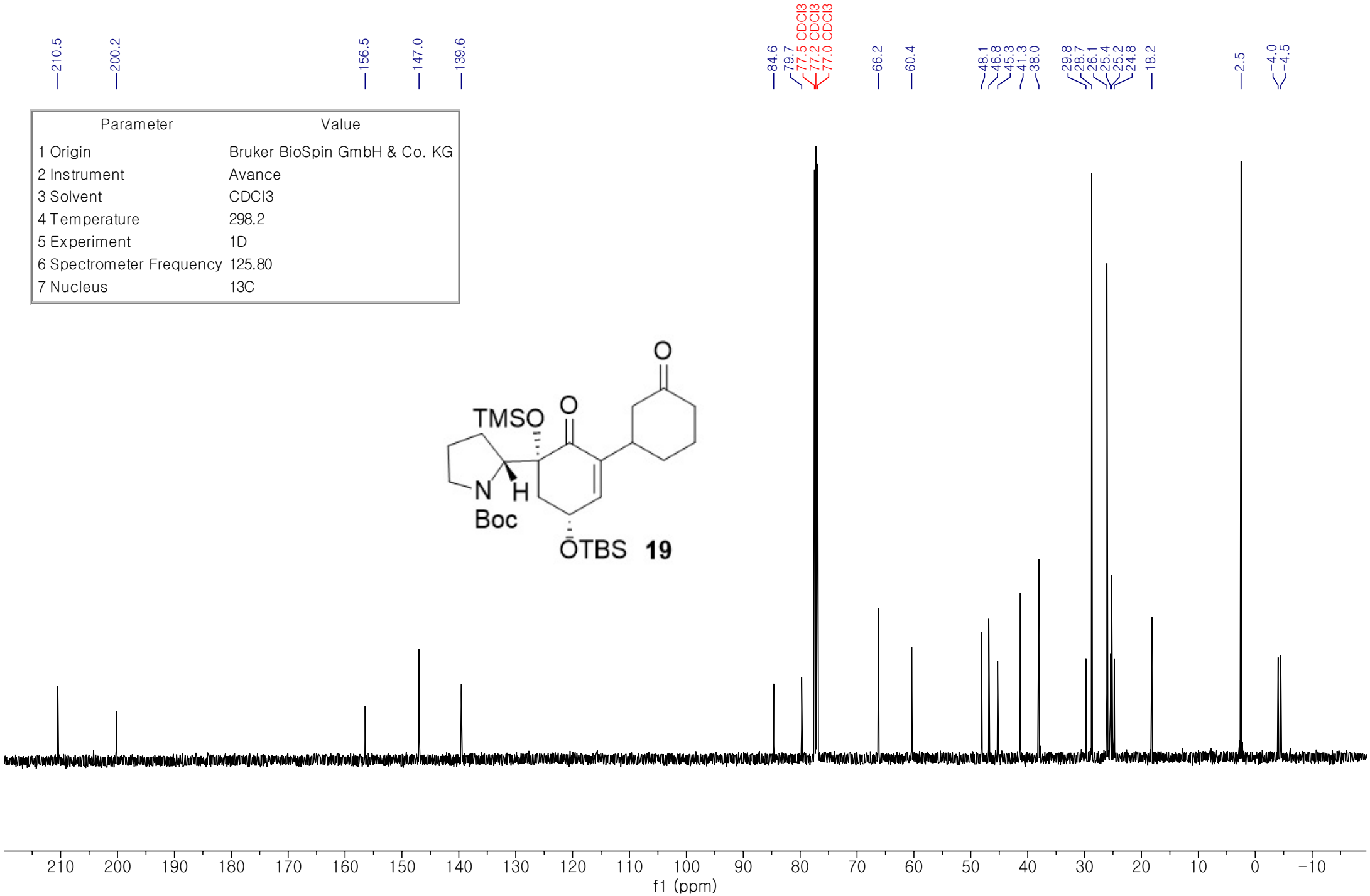


17

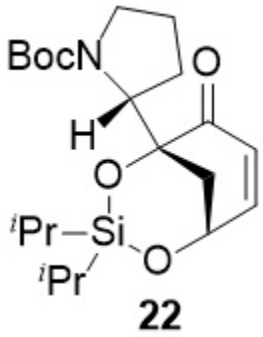
Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



19


210.5
200.2
156.5
147.0
139.6
84.6
79.7
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
66.2
60.4
48.1
46.8
45.3
41.3
38.0
29.8
28.7
26.1
25.4
25.2
24.8
18.2
2.5
-4.0
-4.5
Parameter
Value
1 Origin
Bruker BioSpin GmbH & Co. KG
2 Instrument
Avance
3 Solvent
CDCl3
4 Temperature
298.2
5 Experiment
1D
6 Spectrometer Frequency
125.80
7 Nucleus
13C
TMSO
O
O
N
H
Boc
OTBS
19
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

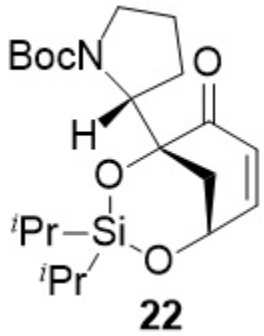
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



22

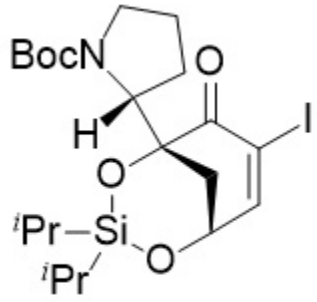
196.7 156.4 146.1 128.2 79.4 78.4 77.5 CDCl3 77.2 CDCl3 77.0 CDCl3 64.0 61.0 48.2 38.9 28.6 28.1 25.0 17.2 16.9 16.8 16.6 14.4 14.0

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	125.80
7 Nucleus	13C



22

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



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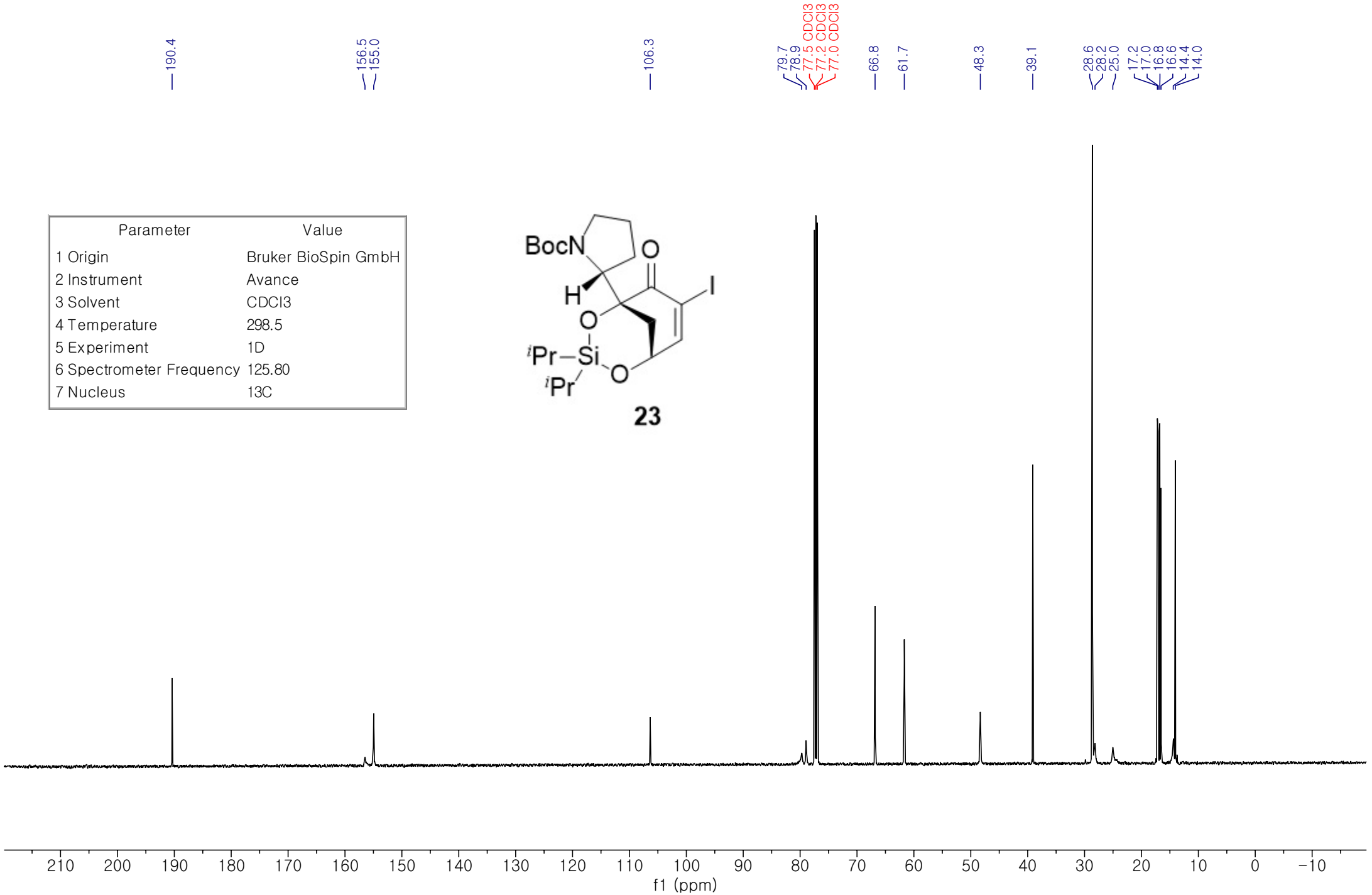
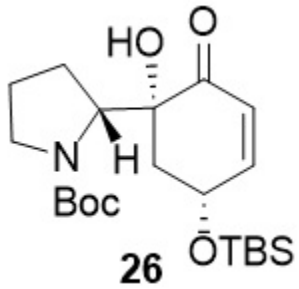

190.4
156.5
155.0
106.3
79.7
78.9
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
66.8
61.7
48.3
39.1
28.6
28.2
25.0
17.2
17.0
16.8
16.6
14.4
14.0
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Instrument Avance
3 Solvent CDCl3
4 Temperature 298.5
5 Experiment 1D
6 Spectrometer Frequency 125.80
7 Nucleus 13C
BocN
O
H
O
I
iPr–Si
O
iPr
23
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

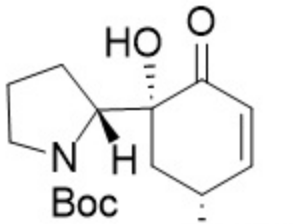
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



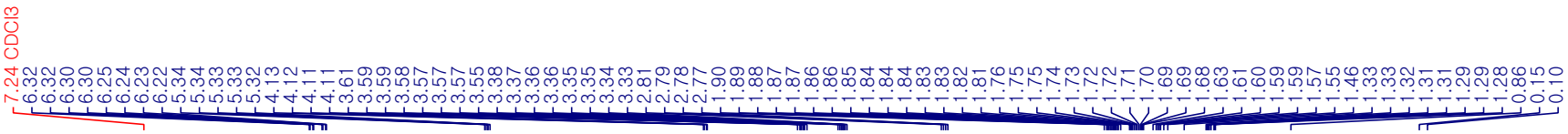
26

202.0
156.5
155.9
125.5
80.3
79.8
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
66.5
60.0
48.2
44.3
28.7
25.9
25.6
25.0
18.1
-4.1
-4.7

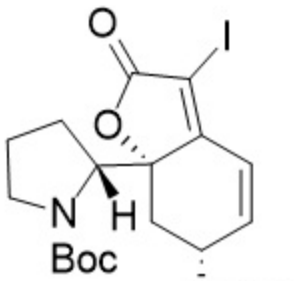
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	125.80
7 Nucleus	13C



26



Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



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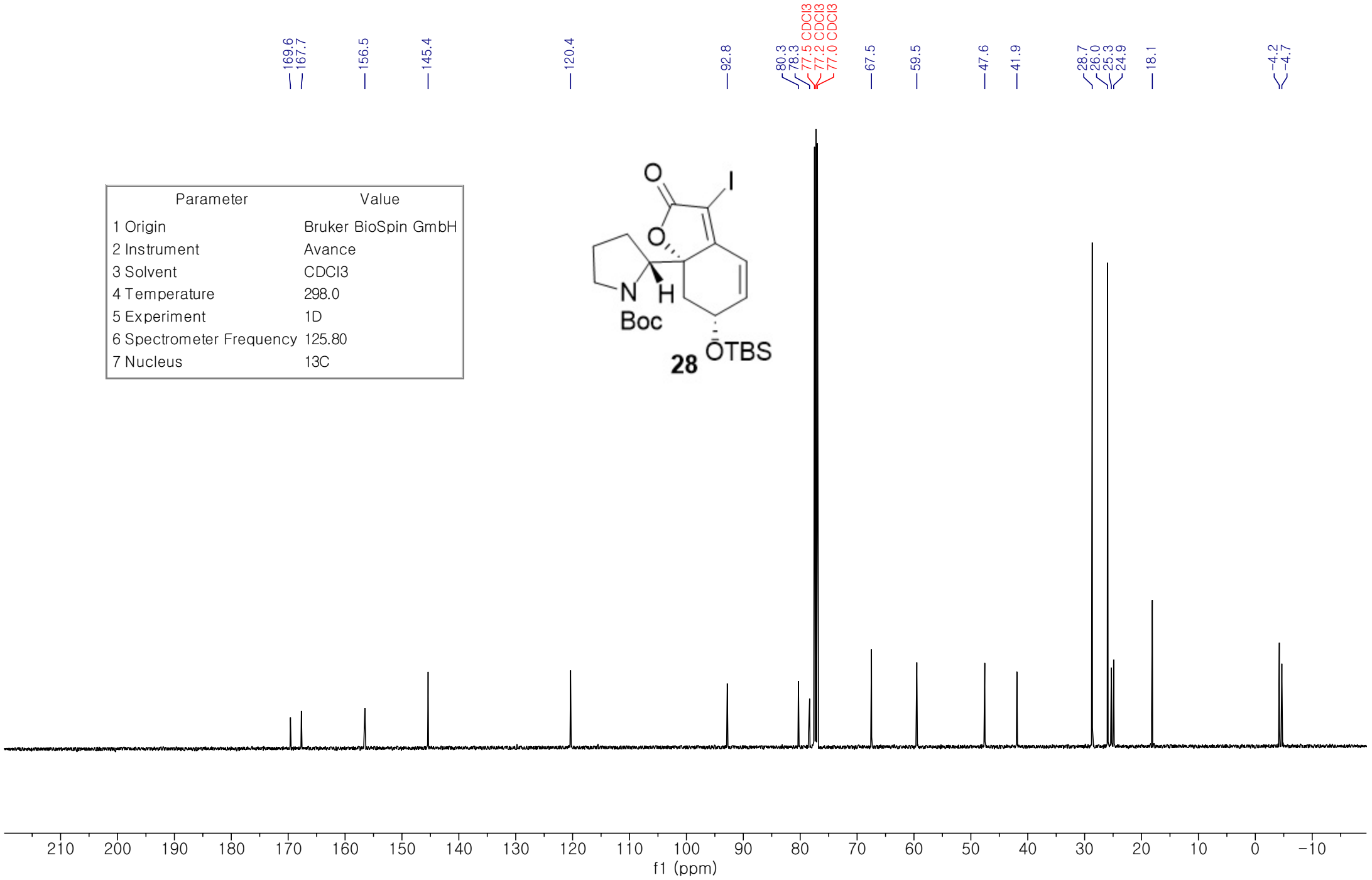
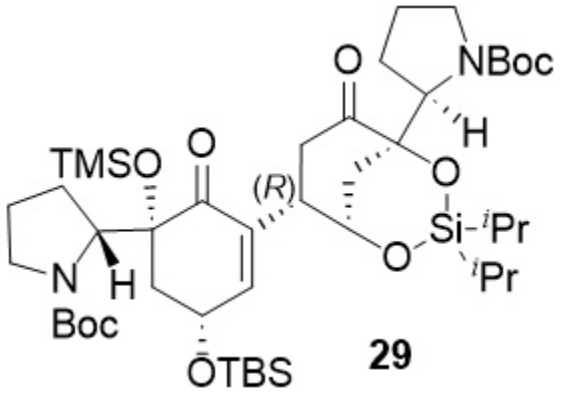

169.6
167.7
156.5
145.4
120.4
92.8
80.3
78.3
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
67.5
59.5
47.6
41.9
28.7
26.0
25.3
24.9
18.1
-4.2
-4.7
Parameter
Value
1 Origin
Bruker BioSpin GmbH
2 Instrument
Avance
3 Solvent
CDCl3
4 Temperature
298.0
5 Experiment
1D
6 Spectrometer Frequency
125.80
7 Nucleus
13C
O
I
O
N H
Boc
OTBS
28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

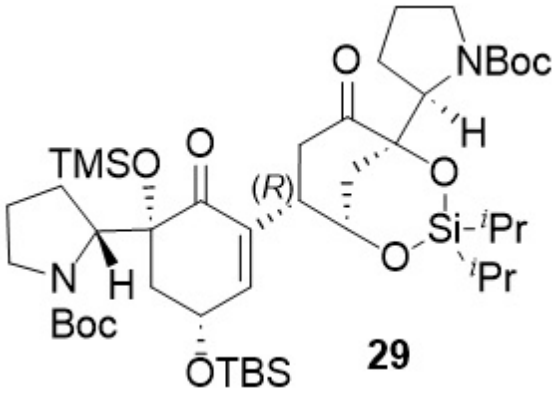
Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



29

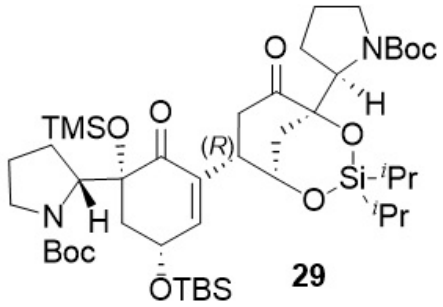
210.6
200.0
156.2
155.8
149.6
137.2
84.8
82.5
81.8
79.8
79.4
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
69.5
66.4
61.0
60.0
48.4
48.0
45.5
44.3
36.9
36.1
28.6
26.1
25.6
24.9
24.2
18.1
17.4
17.3
17.3
17.3
15.9
15.6
14.2
2.5
-4.2
-4.5

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.3
5 Experiment	1D
6 Spectrometer Frequency	125.80
7 Nucleus	13C



29

^{13}C NMR (126 MHz) spectrum of **29** in $CDCl_3$ at 298 K

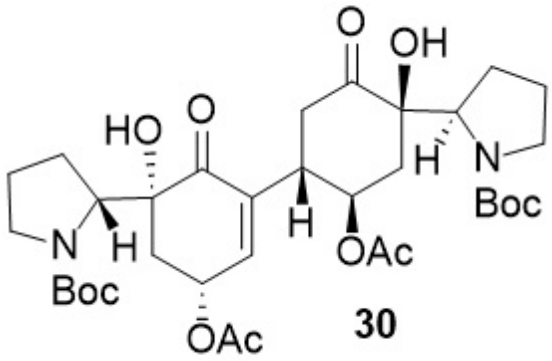


29

^{13}C NMR (126 MHz) spectrum of **29** in $CDCl_3$ at 273 K

^{13}C NMR (126 MHz) spectrum of **29** in $CDCl_3$ at 253 K

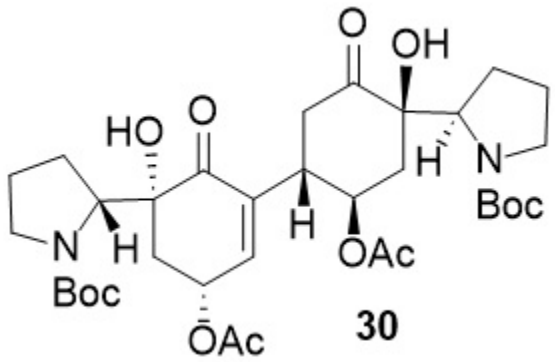
Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



30

210.6 200.4 169.7 169.5 156.2 156.0 146.3 136.3 81.2 79.9 79.8 79.4 77.5 CDCl3 77.2 CDCl3 77.0 CDCl3 70.0 67.4 61.1 60.7 48.1 47.9 41.3 39.0 38.8 28.5 28.4 25.9 24.7 21.0 20.9

Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.1
5 Experiment	1D
6 Spectrometer Frequency	125.80
7 Nucleus	13C



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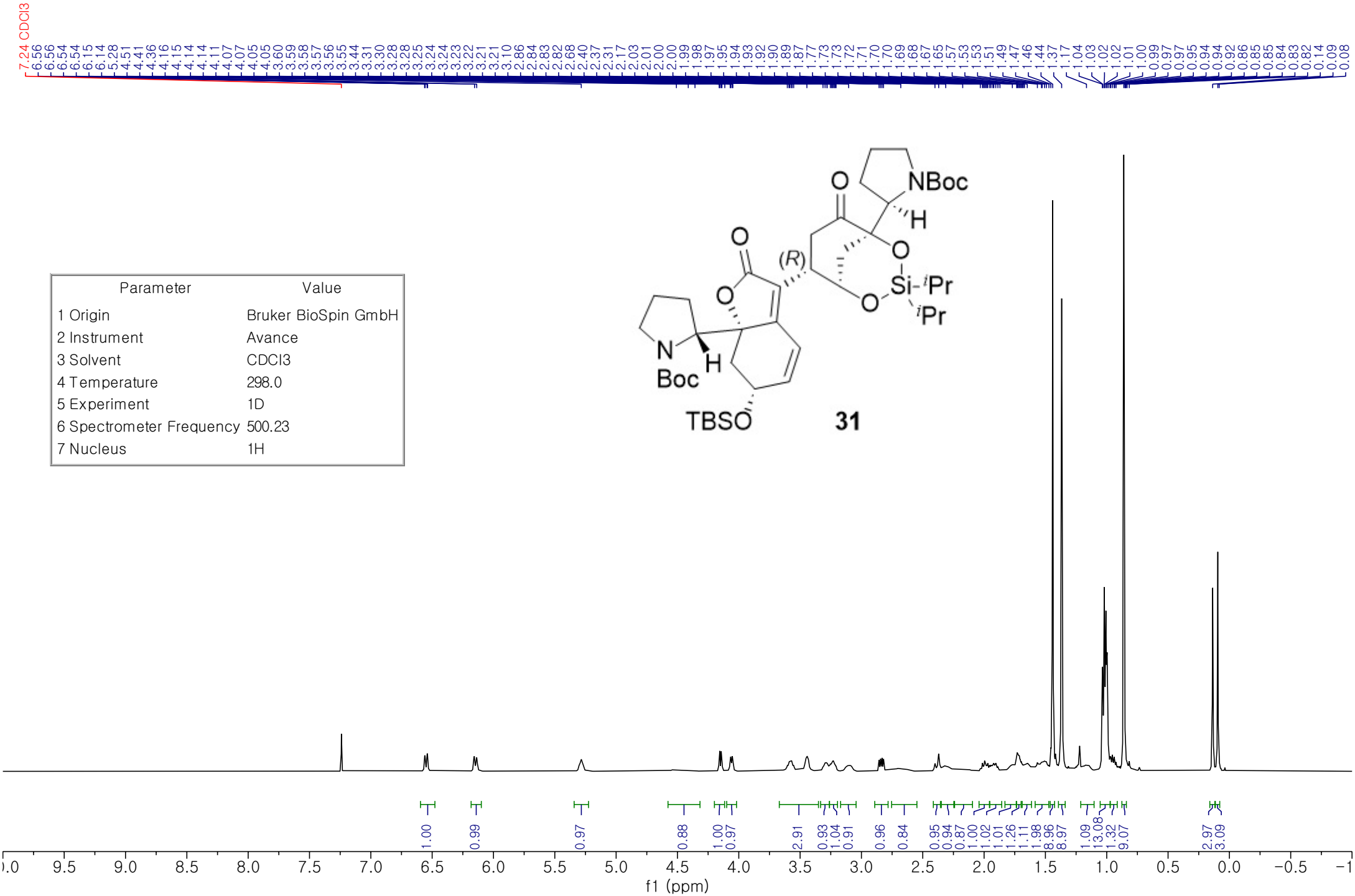
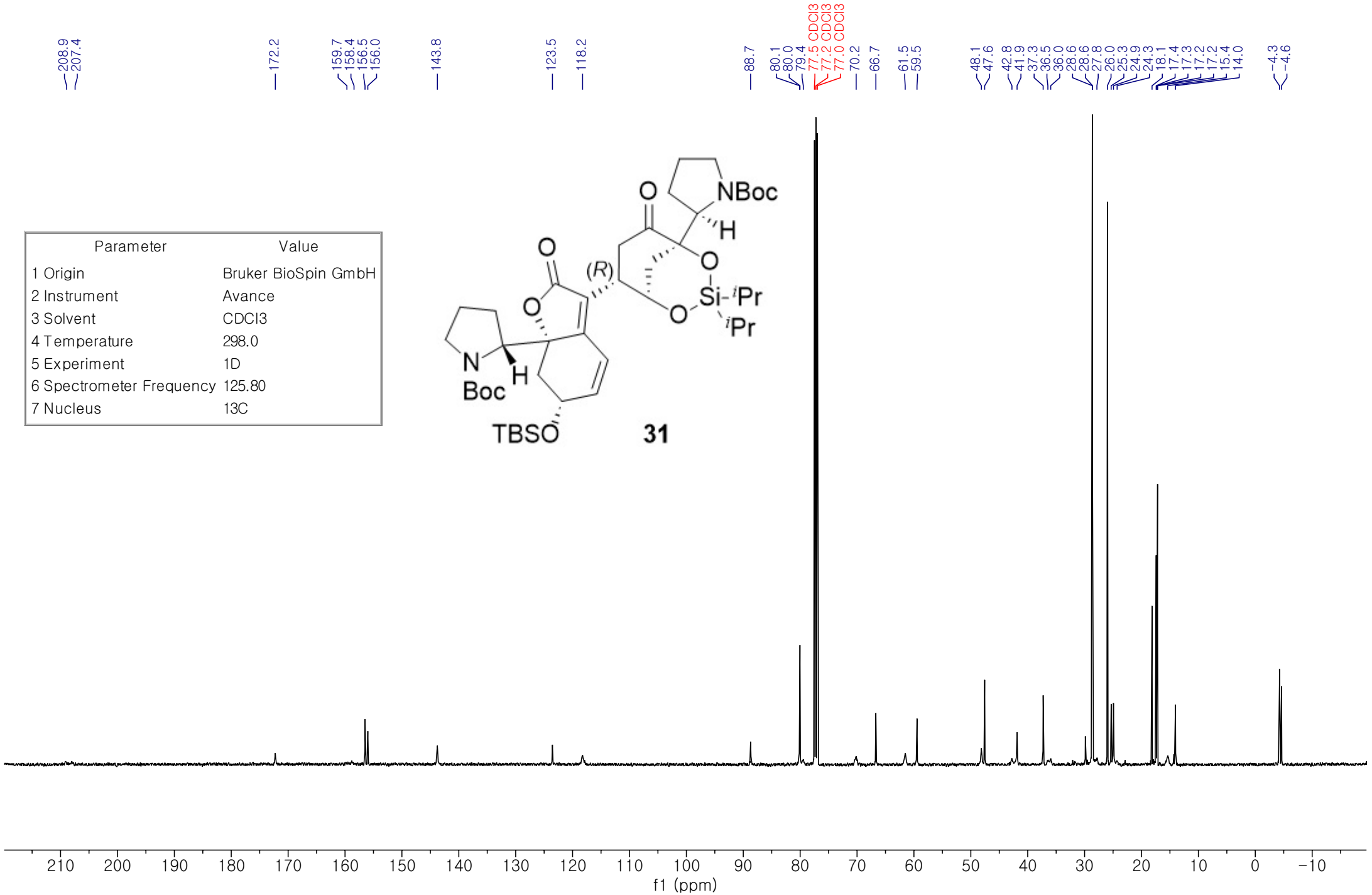
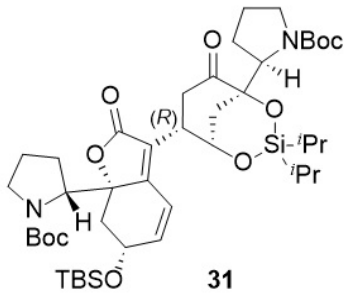

7.24 CDCl3
6.56 6.54 6.54 6.15 6.14 5.28 4.51 4.41 4.36 4.16 4.15 4.14 4.14 4.11 4.07 4.07 4.05 4.05 3.60 3.59 3.58 3.57 3.56 3.55 3.44 3.31 3.30 3.28 3.28 3.25 3.24 3.24 3.23 3.22 3.21 3.21 3.10 2.86 2.84 2.83 2.82 2.68 2.40 2.37 2.31 2.17 2.03 2.01 2.00 2.00 1.99 1.98 1.97 1.95 1.94 1.93 1.92 1.90 1.89 1.87 1.77 1.73 1.72 1.71 1.70 1.69 1.68 1.67 1.65 1.57 1.53 1.53 1.51 1.49 1.47 1.46 1.44 1.37 1.17 1.04 1.03 1.02 1.02 1.01 1.00 0.99 0.97 0.97 0.95 0.94 0.94 0.92 0.86 0.85 0.84 0.83 0.82 0.14 0.09 0.08
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Instrument Avance
3 Solvent CDCl3
4 Temperature 298.0
5 Experiment 1D
6 Spectrometer Frequency 500.23
7 Nucleus 1H
NBoc
H
O
O
(R)
O
Si-iPr
iPr
O
O
N
H
Boc
TBSO
31
1.00 0.99 0.97 0.88 1.00 0.97 2.91 0.93 1.04 0.91 0.96 0.84 0.95 0.94 0.87 1.00 1.02 1.01 1.26 1.11 1.98 8.96 8.97 1.09 13.08 1.32 9.07 2.97 3.09
f1 (ppm)


208.9
207.4
172.2
159.7
158.4
156.5
156.0
143.8
123.5
118.2
88.7
80.1
80.0
79.4
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
70.2
66.7
61.5
59.5
48.1
47.6
42.8
41.9
37.3
36.5
36.0
28.6
28.6
27.8
26.0
25.3
24.9
24.3
18.1
17.4
17.3
17.2
17.2
15.4
14.0
-4.3
-4.6
Parameter
Value
1 Origin
Bruker BioSpin GmbH
2 Instrument
Avance
3 Solvent
CDCl3
4 Temperature
298.0
5 Experiment
1D
6 Spectrometer Frequency
125.80
7 Nucleus
13C
NBoc
H
O
O
(R)
O
Si-iPr
iPr
O
O
N
H
Boc
TBSO
31
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

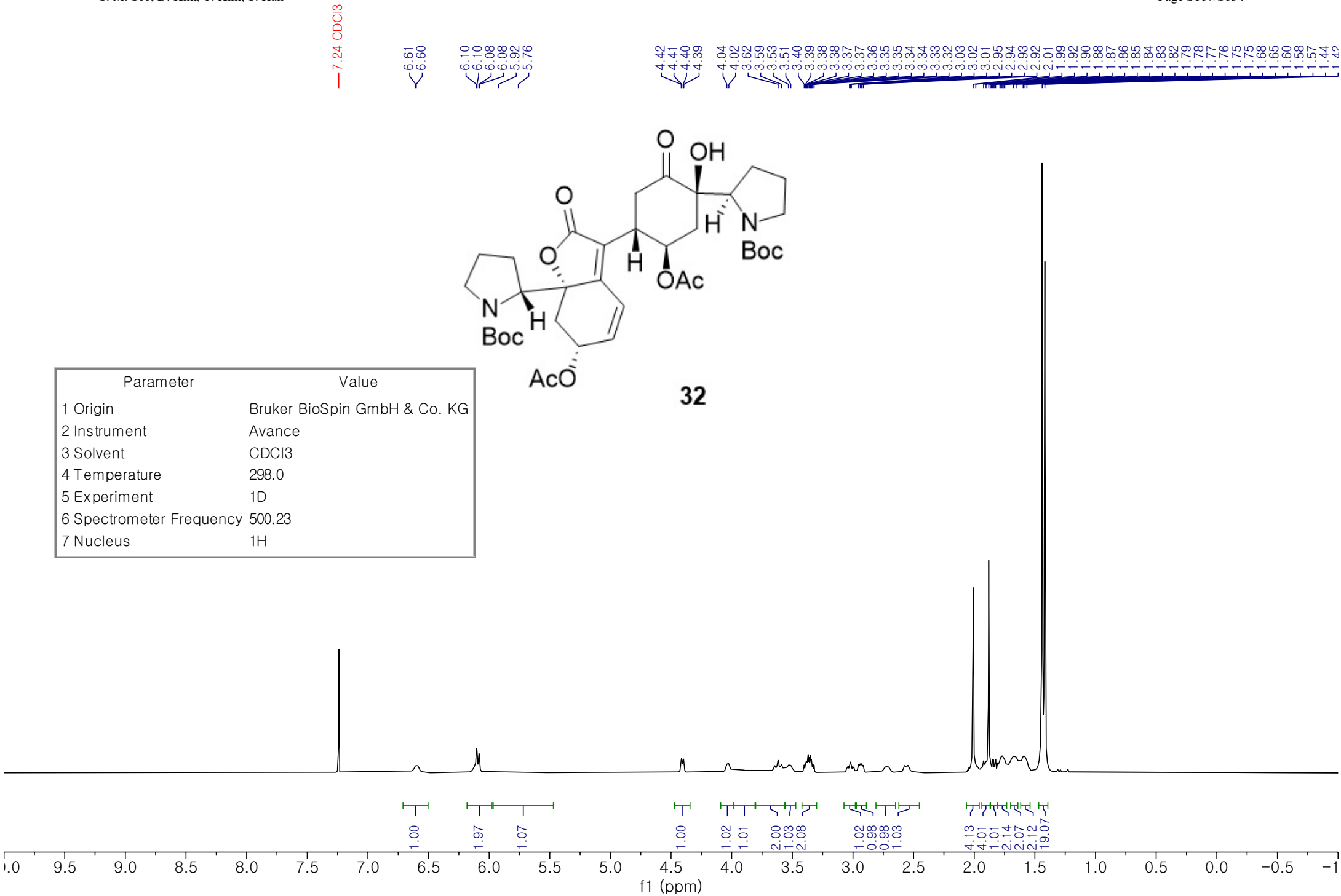
^{13}C NMR (126 MHz) spectrum of **31** in $CDCl_3$ at 298 K



31

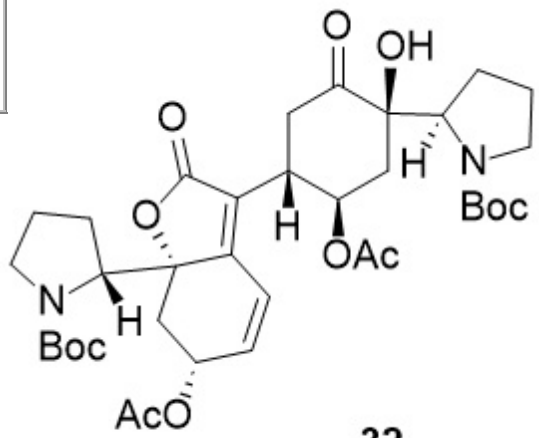
^{13}C NMR (126 MHz) spectrum of **31** in $CDCl_3$ at 273 K

^{13}C NMR (126 MHz) spectrum of **31** in $CDCl_3$ at 253 K


7.24 CDCl3
6.61
6.60
6.10
6.10
6.08
6.08
5.92
5.76
4.42
4.41
4.40
4.39
4.04
4.02
3.62
3.59
3.53
3.51
3.40
3.39
3.38
3.38
3.37
3.37
3.36
3.35
3.35
3.34
3.34
3.33
3.32
3.03
3.02
3.01
2.95
2.94
2.93
2.92
2.01
1.99
1.92
1.90
1.88
1.87
1.86
1.85
1.84
1.83
1.82
1.79
1.78
1.77
1.76
1.75
1.75
1.68
1.65
1.60
1.58
1.57
1.44
O
OH
O
O
H
N
Boc
H
OAc
N
H
Boc
AcO
32
Parameter
Value
1 Origin
Bruker BioSpin GmbH & Co. KG
2 Instrument
Avance
3 Solvent
CDCl3
4 Temperature
298.0
5 Experiment
1D
6 Spectrometer Frequency
500.23
7 Nucleus
1H
1.00
1.97
1.07
1.00
1.02
1.01
2.00
1.03
2.08
1.02
0.98
0.98
1.03
4.13
4.01
1.01
2.14
2.07
2.12
19.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)

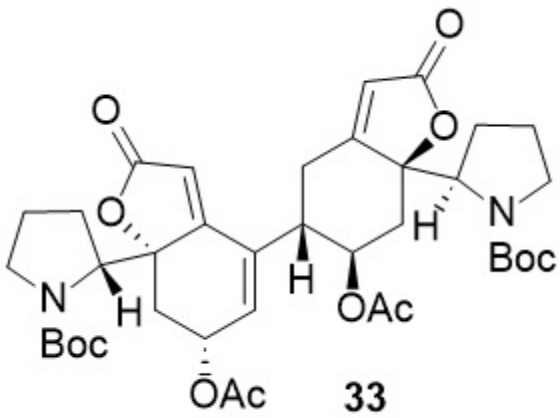
210.2
171.0
169.8
169.6
159.2
156.1
136.6
122.5
121.1
87.3
81.3
80.2
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
69.4
68.5
60.7
60.4
47.9
47.5
41.6
41.0
38.7
36.6
28.5
28.4
26.3
25.6
24.7
21.1
21.0

Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.4
5 Experiment	1D
6 Spectrometer Frequency	125.80
7 Nucleus	13C



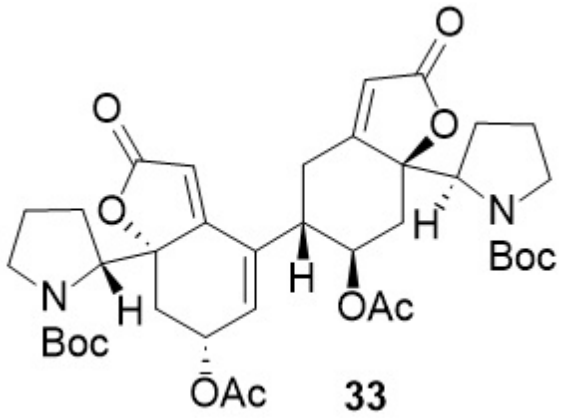
32

Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



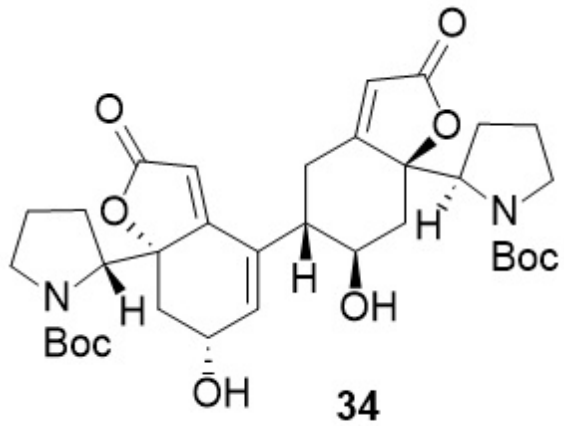
33

Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.3
5 Experiment	1D
6 Spectrometer Frequency	125.80
7 Nucleus	13C



33

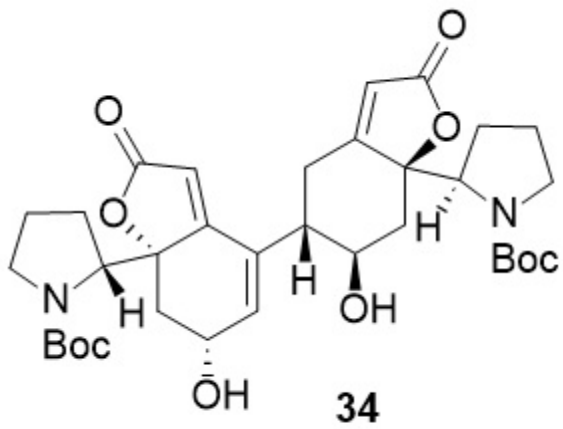
Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



34

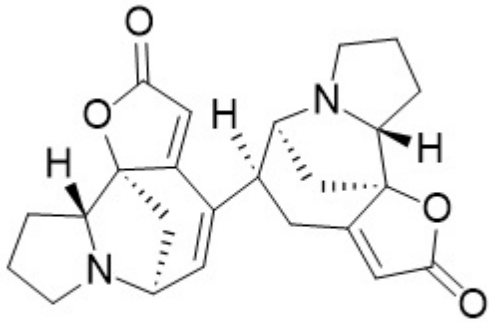
172.2
172.1
171.1
168.1
157.3
156.2
135.9
135.6
115.7
111.5
91.0
90.5
81.3
80.7
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
71.0
66.2
58.7
58.2
48.8
47.8
47.6
44.7
42.1
30.7
28.6
28.5
26.5
25.0
24.7
24.3

Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.3
5 Experiment	1D
6 Spectrometer Frequency	125.80
7 Nucleus	13C

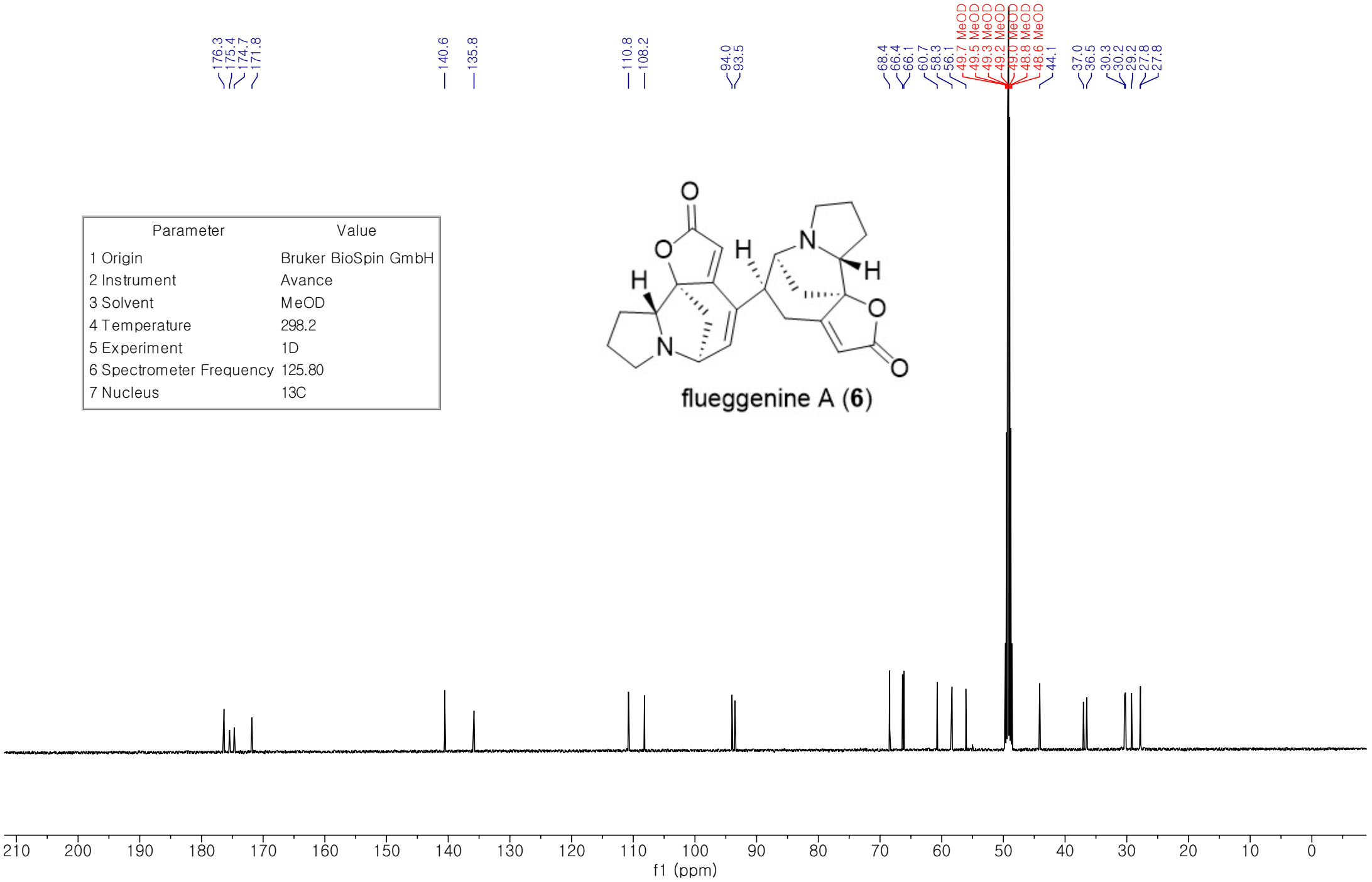


34

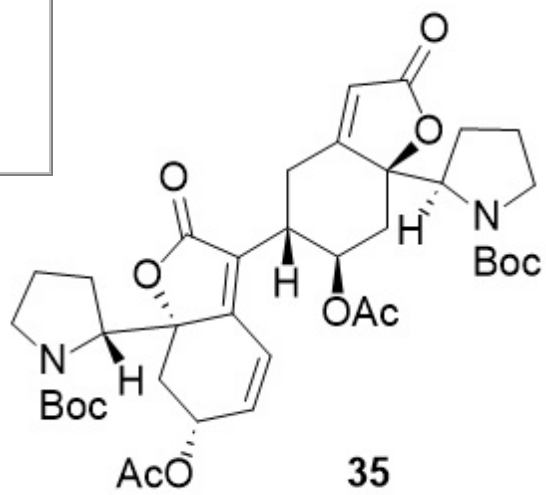
Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	MeOD
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



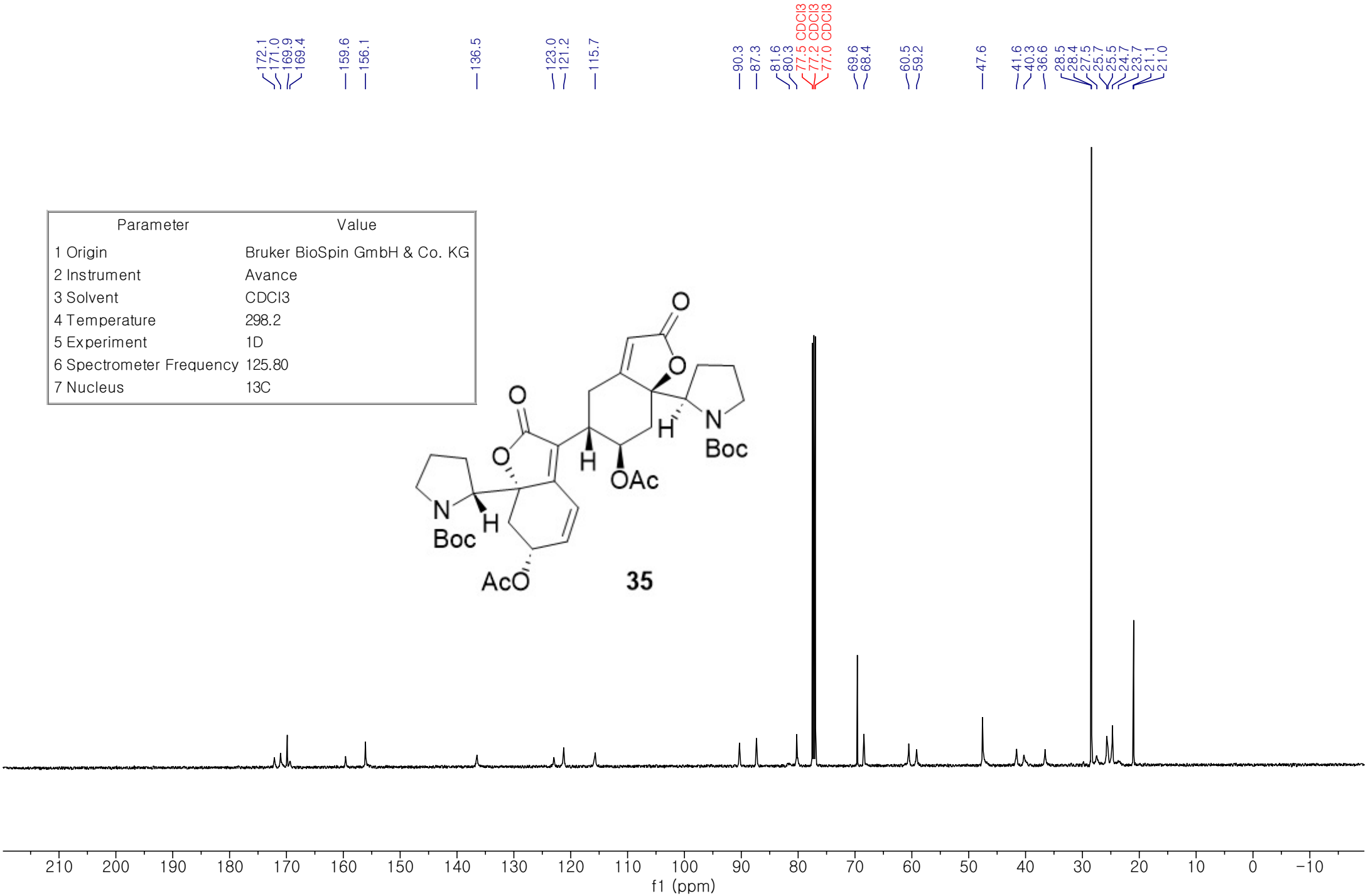
flueggenine A (**6**)


176.3
175.4
174.7
171.8
140.6
135.8
110.8
108.2
94.0
93.5
68.4
66.4
66.1
60.7
58.3
56.1
49.7 MeOD
49.5 MeOD
49.3 MeOD
49.2 MeOD
49.0 MeOD
48.8 MeOD
48.6 MeOD
44.1
37.0
36.5
30.3
30.2
29.2
27.8
27.8
Parameter | Value
1 Origin | Bruker BioSpin GmbH
2 Instrument | Avance
3 Solvent | MeOD
4 Temperature | 298.2
5 Experiment | 1D
6 Spectrometer Frequency | 125.80
7 Nucleus | 13C
flueggenine A (6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

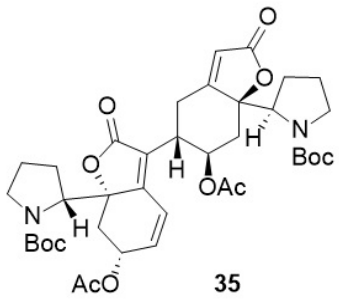
Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



35


172.1
171.0
169.9
169.4
159.6
156.1
136.5
123.0
121.2
115.7
90.3
87.3
81.6
80.3
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
69.6
68.4
60.5
59.2
47.6
41.6
40.3
36.6
28.5
28.4
27.5
25.7
25.5
24.7
23.7
21.1
21.0
Parameter
Value
1 Origin
Bruker BioSpin GmbH & Co. KG
2 Instrument
Avance
3 Solvent
CDCl3
4 Temperature
298.2
5 Experiment
1D
6 Spectrometer Frequency
125.80
7 Nucleus
13C
O
O
O
H
N
Boc
H
OAc
N
H
Boc
AcO
35
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

^{13}C NMR (126 MHz) spectrum of **35** in $CDCl_3$ at 298 K

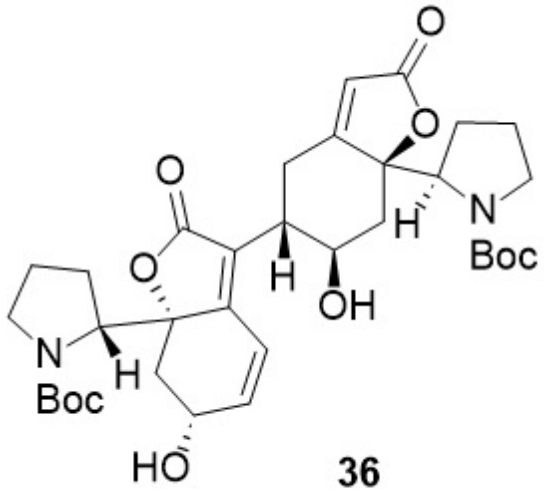


35

^{13}C NMR (126 MHz) spectrum of **35** in $CDCl_3$ at 273 K

^{13}C NMR (126 MHz) spectrum of **35** in $CDCl_3$ at 253 K

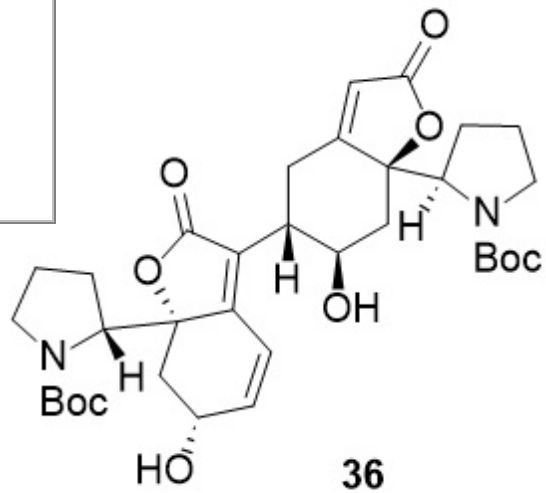
Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.0
5 Experiment	1D
6 Spectrometer Frequency	500.23
7 Nucleus	1H



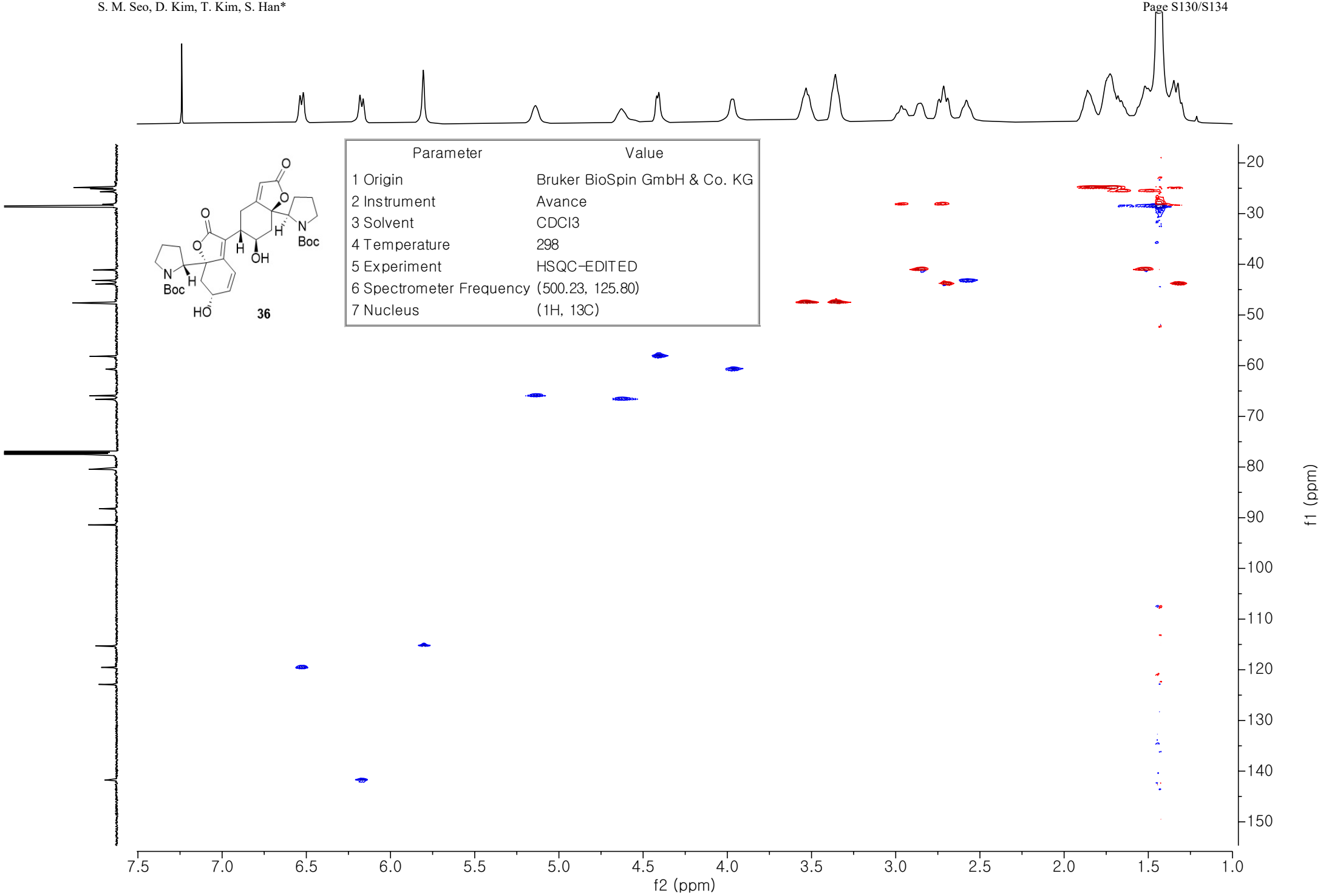
36

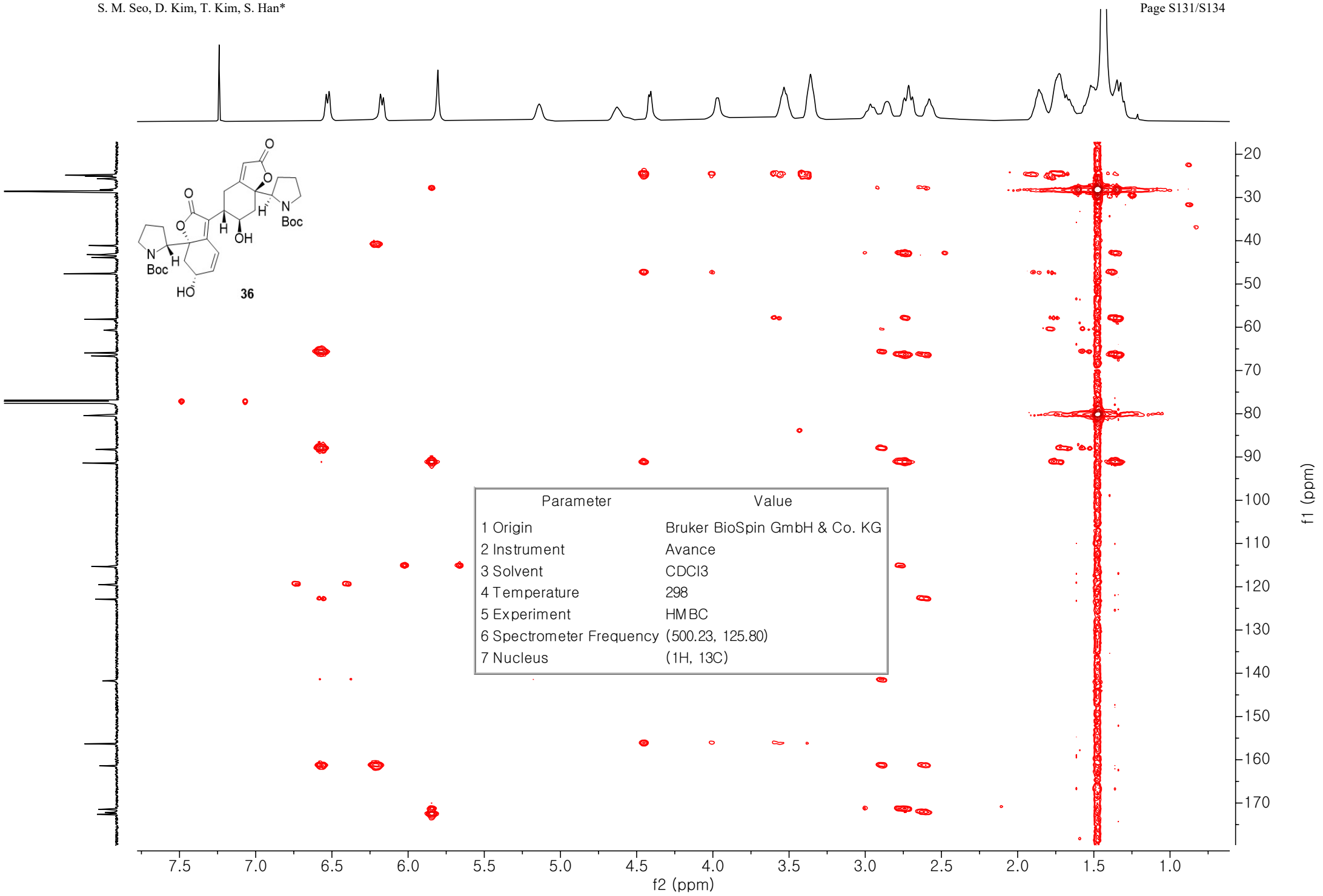
172.6
172.2
171.5
161.4
156.3
141.7
122.9
119.5
115.3
91.4
88.2
80.5
80.3
77.5 CDCl3
77.2 CDCl3
77.0 CDCl3
66.6
65.9
60.7
58.2
47.6
47.5
43.9
43.2
41.1
28.6
28.5
28.2
25.7
25.1
24.8

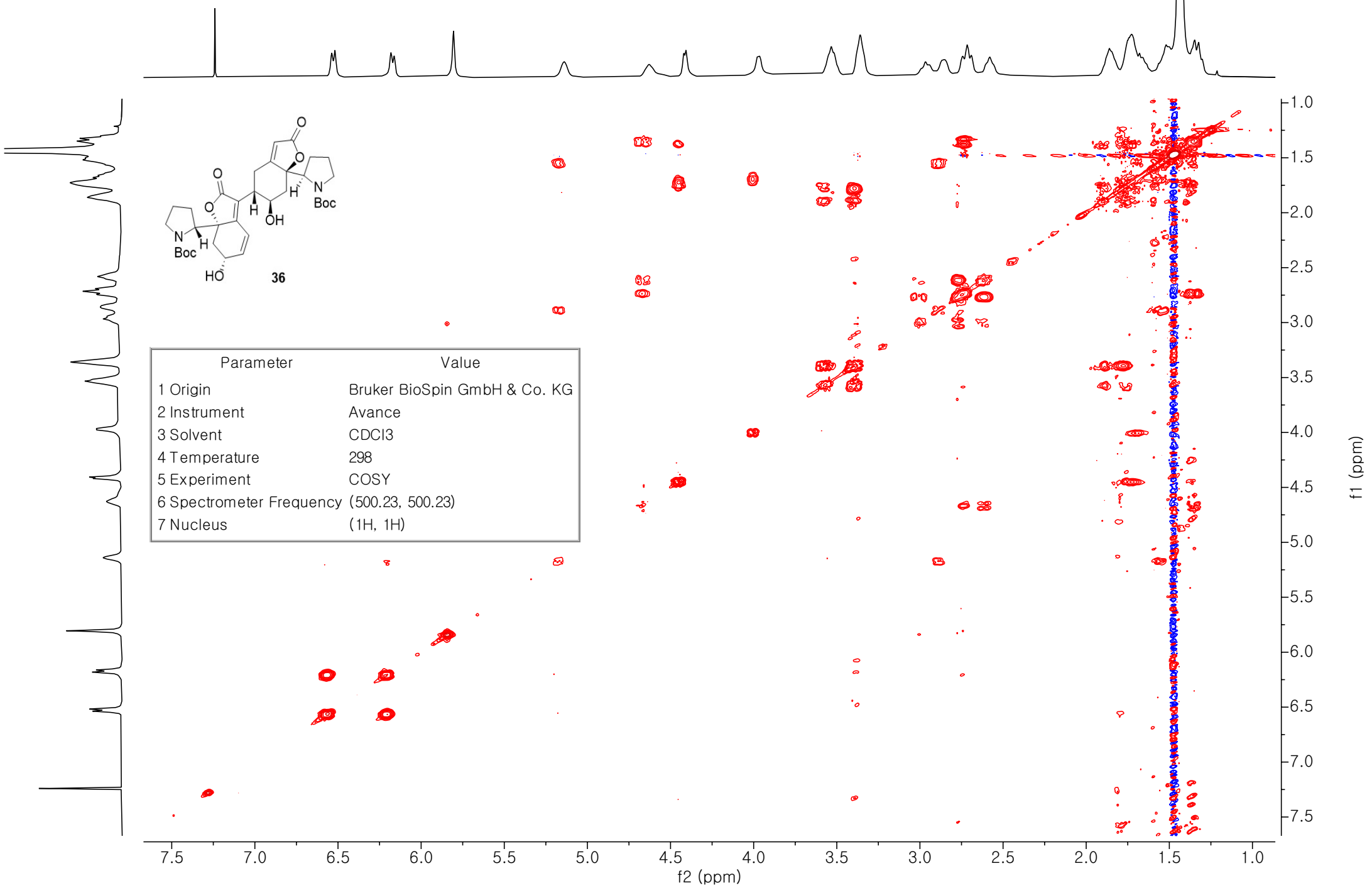
Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.5
5 Experiment	1D
6 Spectrometer Frequency	125.80
7 Nucleus	13C

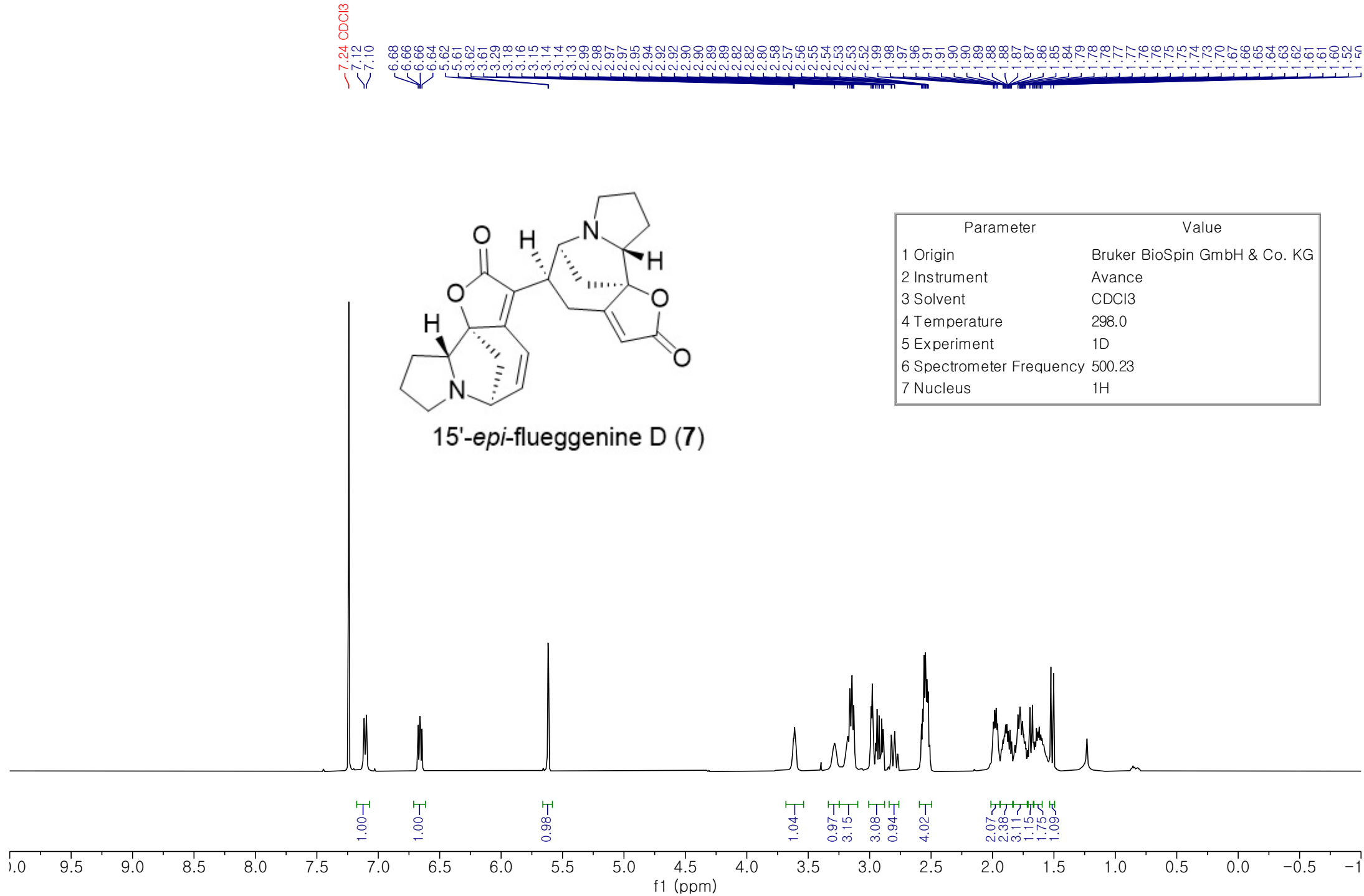


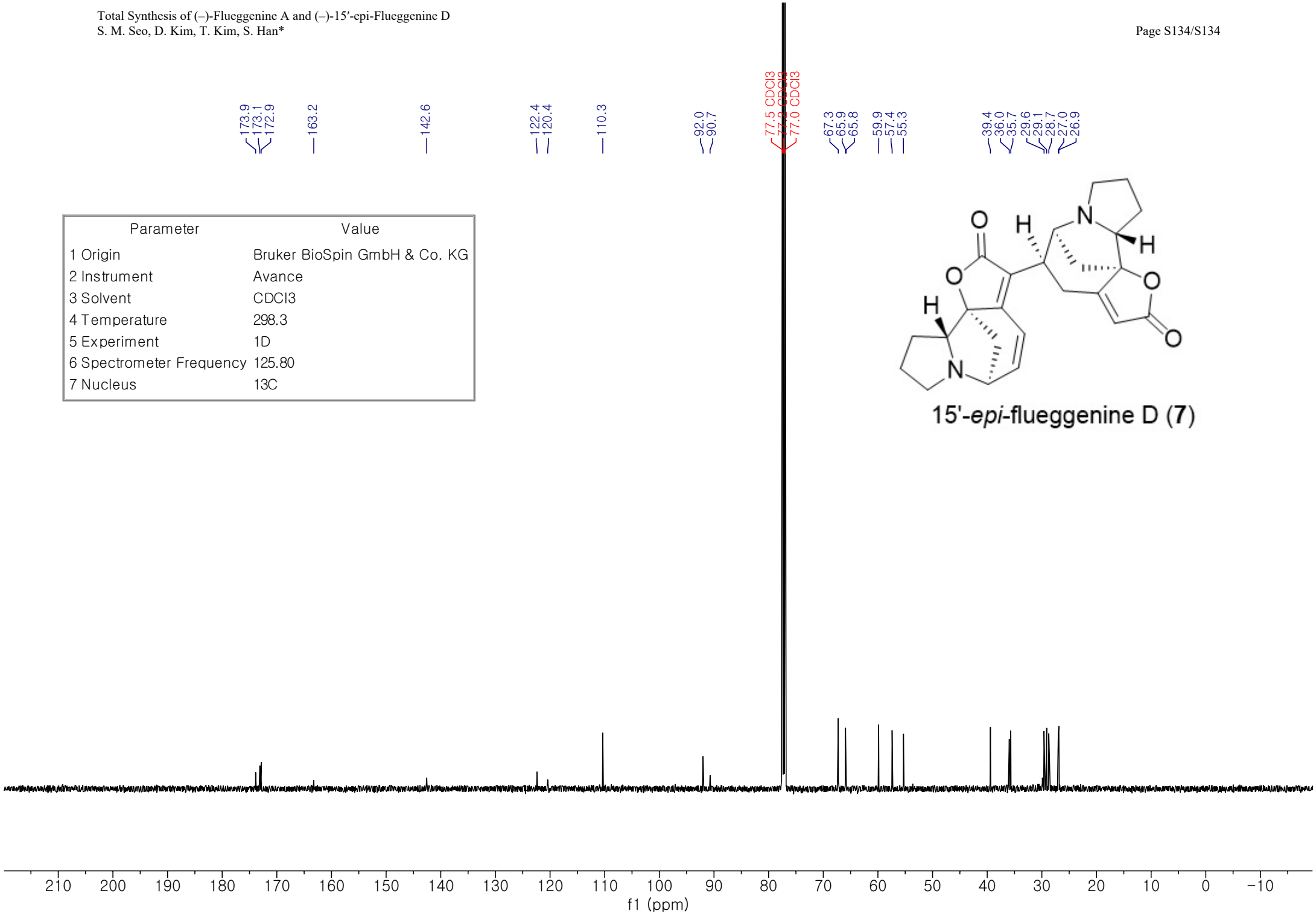
36


Parameter
Value
1 Origin
Bruker BioSpin GmbH & Co. KG
2 Instrument
Avance
3 Solvent
CDCl3
4 Temperature
298
5 Experiment
HSQC-EDITED
6 Spectrometer Frequency
(500.23, 125.80)
7 Nucleus
(1H, 13C)
36
f2 (ppm)
f1 (ppm)


O
O
O
H
OH
N
Boc
N
H
Boc
HO
36
Parameter Value
1 Origin Bruker BioSpin GmbH & Co. KG
2 Instrument Avance
3 Solvent CDCl3
4 Temperature 298
5 Experiment HMBC
6 Spectrometer Frequency (500.23, 125.80)
7 Nucleus (1H, 13C)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f2 (ppm)
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170
f1 (ppm)


O
O
O
H
N
Boc
O
H
OH
N
H
Boc
HO
36
Parameter Value
1 Origin Bruker BioSpin GmbH & Co. KG
2 Instrument Avance
3 Solvent CDCl3
4 Temperature 298
5 Experiment COSY
6 Spectrometer Frequency (500.23, 500.23)
7 Nucleus (1H, 1H)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f2 (ppm)
1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5
f1 (ppm)


7.24 CDCl3
7.12
7.10
6.68
6.66
6.66
6.64
5.62
5.61
3.62
3.61
3.29
3.18
3.16
3.15
3.14
3.14
3.13
2.99
2.98
2.97
2.97
2.95
2.94
2.92
2.92
2.90
2.90
2.89
2.89
2.82
2.82
2.80
2.58
2.57
2.56
2.55
2.54
2.53
2.53
2.52
1.99
1.98
1.97
1.96
1.91
1.91
1.90
1.90
1.89
1.88
1.88
1.87
1.87
1.86
1.85
1.84
1.79
1.78
1.77
1.77
1.76
1.76
1.75
1.75
1.74
1.73
1.70
1.67
1.66
1.65
1.64
1.63
1.62
1.61
1.61
1.60
1.52
O
H
N
H
O
O
H
N
O
15'-epi-flueggenine D (7)
Parameter
Value
1 Origin
Bruker BioSpin GmbH & Co. KG
2 Instrument
Avance
3 Solvent
CDCl3
4 Temperature
298.0
5 Experiment
1D
6 Spectrometer Frequency
500.23
7 Nucleus
1H
1.00
1.00
0.98
1.04
0.97
3.15
3.08
0.94
4.02
2.07
2.38
3.11
1.15
1.75
1.09
f1 (ppm)



Parameter	Value
1 Origin	Bruker BioSpin GmbH & Co. KG
2 Instrument	Avance
3 Solvent	CDCl3
4 Temperature	298.3
5 Experiment	1D
6 Spectrometer Frequency	125.80
7 Nucleus	13C