SUPPORTING INFORMATION

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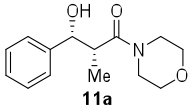
General Methods: Tetrahydrofuran, dimethylformamide, dichloromethane, and toluene were purified by passing through a solvent column of activated alumina (A-1). Anhydrous diethyl ether was used directly from a sealed, commercial bottle (Sigma-Aldrich, 296082). Commercially available reagents were used without further purification. Commercially available 4-acryloylmorpholine (TCI America, A0841) was stored under an inert atmosphere in a freezer and used without further purification. All commercially available aldehydes were purified by distillation under vacuum prior to use. Dicyclohexylborane[1] and diisopinocampheylborane[2] were prepared according to the procedures described by Brown. Unless otherwise indicated, all reactions were conducted under an atmosphere of argon using flamed-dried glassware. Standard handling techniques for air-sensitive compounds were also employed for all the operations. Removal of solvents was accomplished on a rotary evaporator at reduced pressure. Enantiomeric excess and absolute configurations were determined using the Mosher[3] method.

Physical Properties and Spectroscopic Measurements: ^{1}H NMR, COSY and NOESY spectra were recorded on a Bruker spectrometer at 400 MHz. ^{13}C NMR spectra were recorded on a Bruker spectrometer at 100 MHz. The proton signal for non-deuterated solvent (δ 7.26 ppm for $CHCl_3$ and δ 7.16 ppm for C_6H_6) was used as an internal reference for ^{1}H NMR spectra. For ^{13}C NMR spectra, chemical shifts are reported relative to the δ 77.00 ppm resonance of $CDCl_3$ and δ 128.06 ppm resonance of C_6D_6. Infrared (IR) spectra were recorded neat on a Perkin-Elmer Spectrum One FT-IR Spectrometer equipped with Universal ATR Sampling Accessory. Optical rotations were measured on a Rudolph Autopol IV polarimeter using a quartz cell with 1 mL capacity and a 1 dm path length. High-resolution mass spectra were recorded on a spectrometer at the University of Illinois Mass Spectrometry Laboratory.

Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. TLC plates were visualized with UV light and/or by staining with cerium molybdate (5g $Ce(SO_4)_2$, 25g $(NH_4)Mo_7O_{24}.4H_2O$, 450 mL H_2O, 50 mL H_2SO_4). Column chromatography was generally performed according to the method of Still[4] using Kieselgel 60 (230-400 mesh) silica gel.

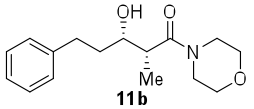
* *

General Procedure for the Reductive Aldol Reaction: To a 0 °C suspension of ($^{l \text{ or } d}$Ipc)$_2$BH (weighed in the glove box, 72 mg, 0.25 mmol) or Cy_2BH (weighed in the glove box, 45 mg, 0.25 mmol) in Et_2O (1.0 mL) was added 4-acryloylmorpholine **8** (35 μL, 0.275 mmol). The solution was stirred for 2 h at 0 °C at which time it became homogeneous. The resulting mixture was cooled to –78 °C, aldehyde (0.213 mmol) was added, and the solution was stirred overnight at -78 °C. An aqueous pH 7 buffer solution (0.5 mL), MeOH (0.5 mL) and THF (0.5 mL) were added and the reaction was stirred for 6 h at room temperature. The aqueous phase was extracted three times with CH_2Cl_2 (10 mL each). The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude product by flash chromatography (1/1 : CH_2Cl_2-ethyl acetate) provided the corresponding β–hydroxymorpholine amide **11** or **13**.



11a

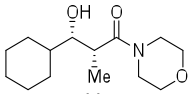
(1*R*,2*R*)-2-methyl-3-morpholin-4-yl-3-oxo-1-phenylpropan-1-ol (11a): 11a (48 mg, 90% yield, d.r. >20:1, 97 % ee, a white amorphous solid) was prepared using (^{l}Ipc)$_2$BH: $[\alpha]_D^{28.6}$ = +19.1 (c = 0.23, $CHCl_3$); ^{1}H (400 MHz, $CDCl_3$) δ 7.39-7.32 (m, 4H), 7.29-7.27 (m, 1H), 5.09 (dd, *J* = 1.3, 3.2 Hz, 1H), 4.55 (d, *J* = 1.6 Hz, 1H), 3.70-3.51 (m, 6H), 3.44-3.40 (m, 2H), 2.82 (dq, *J* = 3.1, 7.2 Hz, 1H), 1.08 (d, *J* = 7.2 Hz, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 175.5, 141.7, 128.2 (2C), 127.3, 126.0 (2C), 73.5, 66.7, 66.5, 46.1, 41.8, 41.6, 10.6; IR (neat) 3368, 2986, 2930, 2865, 1603, 1481, 1443, 1349, 1324, 1303, 1255, 1213, 1113, 1084, 1021, 950, 890, 843, 767, 704 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{19}NO_3$ $[M+H]^+$ 250.1443, found 250.1446.



11b

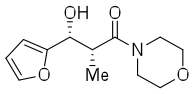
(2*R*,3*S*)-2-methyl-1-morpholin-4-yl-1-oxo-5-phenylpentan-3-ol (11b): 11b (41 mg, 70% yield, d.r.>20:1, 98% ee, a white amorphous solid) was prepared using (^{l}Ipc)$_2$BH: $[\alpha]_D^{28.4}$ = +20.4 (c = 0.25, $CHCl_3$); ^{1}H (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.24-7.16 (m, 3H), 4.38 (broad s, 1H), 3.93 (ddd, *J* = 2.1, 3.8, 9.3 Hz, 1H), 3.71-3.60 (m, 5H), 3.60-3.51 (m, 1H), 3.43 (t, *J* = 4.9 Hz, 2H), 2.88 (ddd, *J* = 5.2, 9.4, 13.6 Hz, 1H), 2.68 (ddd, *J* = 7.2, 9.2, 13.8 Hz, 1H), 2.52 (dq, *J* = 2.1, 7.2 Hz, 1H), 1.93 (dtd, *J* = 5.4, 9.3, 13.6 Hz, 1H), 1.56 (dddd, *J* = 3.8, 7.3, 9.5, 13.6 Hz, 1H), 1.15 (d, *J* = 7.2 Hz, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 176.2, 142.0, 128.5 (2C), 128.3 (2C), 125.8, 70.3, 66.8, 66.6, 46.0, 41.7, 38.8, 35.5, 32.3, 10.0;

IR (neat) 3436, 2923, 2857, 1616, 1455, 1435, 1225, 1113, 1027 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{23}NO_3$ $[M+H]^+$ 278.1756, found 278.1754.



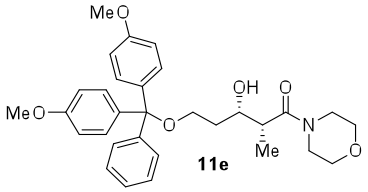
11c

(1*S*,2*R*)-1-cyclohexyl-2-methyl-3-morpholin-4-yl-3-oxopropan-1-ol (11c): 11c (48 mg, 88% yield, d.r. >20:1, 97% ee, a white amorphous solid) was prepared using $(^{l}Ipc)_2BH$: $[\alpha]_D^{28.4}$ = +17.2 (c = 0.43, $CHCl_3$); ^1H (400 MHz, $CDCl_3$) δ 4.44 (broad s, 1H), 3.74-3.63 (m, 5H), 3.60-3.48 (m, 4H), 2.79 (dq, *J* = 2.1, 7.2 Hz, 1H), 2.18-2.12 (m, 1H), 1.79-1.71 (m, 2H), 1.69-1.63 (m, 1H), 1.60-1.55 (m, 1H), 1.47-1.37 (m, 1H), 1.31-1.15 (m, 3H), 1.13 (d, *J* = 7.2 Hz, 3H), 1.01-0.85 (m, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 176.4, 75.4, 66.8, 66.6, 46.1, 41.8, 39.5, 35.1, 29.7, 28.9, 26.3, 26.0, 25.8, 9.9; IR (neat) 3350, 2954, 2923, 2852, 1614, 1472, 1445, 1427, 1373, 1315, 1302, 1273, 1235, 1210, 1114, 1070, 1027, 979, 955, 894, 869, 848, 771, 742 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{25}NO_3$ $[M+H]^+$ 256.1913, found 256.1916.



11d

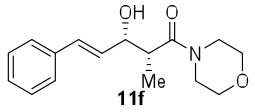
(1*R*,2*R*)-1-(2-furyl)-2-methyl-3-morpholin-4-yl-3-oxopropan-1-ol (11d): 11d (40 mg, 78% yield, d.r. >20:1, 96% ee, as a white amorphous solid) was prepared from $(^{l}Ipc)_2BH$: $[\alpha]_D^{27.9}$ = +6.8 (c = 0.22, $CHCl_3$); ^1H (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 1.0, 1.8 Hz, 1H), 6.33 (dd, *J* = 1.7, 3.3 Hz, 1H), 6.30 (td, *J* = 0.8, 3.5 Hz, 1H), 5.06 (d, *J* = 3.5 Hz, 1H), 4.48 (broad s, 1H), 3.68-3.53 (m, 6H), 3.51-3.44 (m, 2H), 3.05 (dq, *J* = 3.5, 7.2 Hz, 1H), 1.14 (d, *J* = 7.2 Hz, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 175.0, 154.3, 141.3, 110.3, 106.6, 68.9, 66.7, 66.6, 46.1, 41.8, 38.9, 11.2; IR (neat) 3365, 2970, 2855, 1607, 1467, 1441, 1229, 1107, 1009 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{17}NO_4$ $[M+H]^+$ 240.1236, found 240.1243.



11e

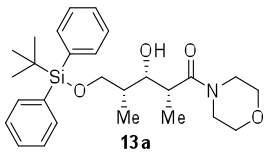
(2*R*,3S)-5-(bis(4-methoxyphenyl)(phenyl)methoxy)-3-hydroxy-2-methyl-1-morpholinopentan-1-one (11e): 11e (88 mg, 80% yield, d.r. >20:1, 97% ee, white amorphous solid) was prepared using $(^{l}Ipc)_2BH$: $[\alpha]_D^{28.0}$ = +3.8 (c = 0.21, $CHCl_3$); ^1H (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.31-7.25 (m, 6H), 7.22-7.18 (m, 1H), 6.84-6.80 (m, 4H), 4.27 (broad s, 1H), 4.06 (ddd, *J* = 3.1, 4.9, 8.0 Hz, 1H), 3.78 (s, 6H), 3.68-3.57 (m, 6H), 3.46-3.34 (m, 2H), 3.30-3.19 (m, 2H), 2.73 (dq, *J* = 3.4, 7.2 Hz, 1H), 1.85-1.68 (m, 2H), 1.16 (d, *J* = 7.1 Hz, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 175.6, 158.4 (2C), 144.9,

136.07, 136.06, 129.9 (4C), 128.0 (2C), 127.8 (2C), 126.7, 113.1 (4C), 86.3, 70.8, 66.9, 66.7, 61.4, 55.2 (2C), 46.1, 41.8, 38.9, 33.6, 11.2; IR (neat) 3457, 29.57, 2930, 2851, 2245, 1603, 1509, 1463, 1443, 1301, 1248, 1175, 1115, 1068, 1032, 908, 828, 726 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{37}NO_6$ $[M+Na]^+$ 542.2519, found 542.2524.



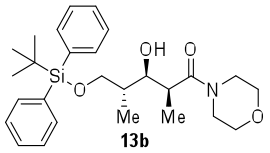
11f

(1*E*,3*S*,4*R*)-4-methyl-5-morpholin-4-yl-5-oxo-1-phenylpent-1-en-3-ol (11f): 11f (40 mg, 68% yield, d.r. >20:1, 97% ee, white amorphous solid) was prepared using (^{l}Ipc)$_2$BH: $[\alpha]_D^{28.5}$ = -15.2 (c = 0.25, $CHCl_3$); ^{1}H (400 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H), 7.34-7.29 (m, 2H), 7.25-7.21 (m, 1H), 6.72 (dd, *J* = 1.7, 16.0 Hz, 1H), 6.17 (dd, *J* = 5.5, 16.0 Hz, 1H), 4.69 (tdd, *J* = 1.6, 2.7, 5.4 Hz, 1H), 4.52 (d, *J* = 1.6 Hz, 1H), 3.77-3.48 (m, 8H), 2.76 (dq, *J* = 2.7, 7.3 Hz, 1H), 1.20 (d, *J* = 7.2 Hz, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 175.5, 136.7, 130.8, 128.9, 128.5 (2C), 127.5, 126.3 (2C), 72.1, 66.7, 66.6, 46.1, 41.8, 39.6, 10.8; IR (neat) 3406, 2971, 1901, 1858, 1615, 1436, 1228, 1114, 1026, 970 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{21}NO_3$ $[M+Na]^+$ 298.1419, found 298.1420.



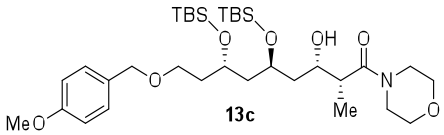
13a

(2*R*,3*S*,4*R*)-5-((tert-butyldiphenylsilyl)oxy)-3-hydroxy-2,4-dimethyl-1-morpholinopentan-1-one (13a): 13a was prepared from Cy_2BH (63 mg, 63% yield, d.r. **1.5**:1 **13a**:**3h**) and from (^{l}Ipc)$_2$BH (69 mg, 69% yield, d.r. >20:1), as a white amorphous solid: $[\alpha]_D^{28.7}$ = -1.8 (c = 0.63, $CHCl_3$); ^{1}H (400 MHz, $CDCl_3$) δ 7.64 (ddd, *J* = 1.6, 3.0, 7.8 Hz, 4H), 7.47-7.36 (m, 6H), 4.19 (d, *J* = 1.6 Hz, 1H), 3.94 (ddd, *J* = 1.5, 4.5, 6.3 Hz, 1H), 3.74 (dd, *J* = 3.7, 10.4 Hz, 1H), 3.66-3.52 (m, 6H), 3.59 (d, *J* = 4.9 Hz, 1H), 3.39-3.35 (m, 2H), 2.92 (dq, *J* = 4.6, 7.0 Hz, 1H), 1.82 (ddquint., *J* = 3.8, 4.5, 6.7 Hz, 1H), 1.18 (d, *J* = 7.1 Hz, 3H), 1.06 (s, 9H), 1.04 (d, *J* = 7.0 Hz, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 175.6, 135.6 (2C), 135.5 (2C), 133.1 (2C), 129.8 (2C), 127.8 (2C), 127.7 (2C), 75.0, 68.2, 66.9, 66.7, 46.0, 41.8, 37.3, 37.0, 26.9 (3C), 19.2, 12.8, 12.1; IR (neat) 3445, 2962, 2931, 2858, 2247, 1622, 1463, 1428, 1362, 1267, 1226, 1112, 1069, 1026, 984, 908, 823, 701 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{39}NO_4Si$ $[M+H]^+$ 470.2727, found 470.2725.



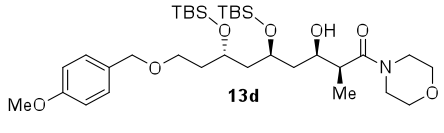
13b

(2*S*,3*R*,4*R*)-5-((tert-butyldiphenylsilyl)oxy)-3-hydroxy-2,4-dimethyl-1-morpholinopentan-1-one (13b): 13b was prepared from Cy_2BH (63 mg, 63% yield, d.r. 1.5:**1 13a**:**13b**) and from $(^{d}Ipc)_2BH$ (85 mg, 85% yield, d.r. >20:1), white amorphous solid: $[\alpha]_D^{28.6}$ = -12.0 (c = 0.25, $CHCl_3$); ^1H (400 MHz, $CDCl_3$) δ 7.72-7.65 (m, 4H), 7.45-7.34 (m, 6H), 4.35 (d, *J* = 2.9 Hz, 1H), 3.86-3.81 (m, 2H), 3.78 (dd, *J* = 3.6, 9.9 Hz, 1H), 3.71-3.60 (m, 5H), 3.57-3.48 (m, 1H), 3.47-3.35 (m, 2H), 2.75 (dq, *J* = 3.2, 7.2 Hz, 1H), 1.83-1.73 (m, 1H), 1.16 (d, *J* = 7.2 Hz, 3H), 1.06 (s, 9H), 1.01 (d, *J* = 7.0 Hz, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 175.8, 135.62 (2C), 135.60 (2C), 133.6, 133.5, 129.6 (2C), 127.6 (4C), 73.1, 66.8, 66.6, 66.0, 46.0, 41.8, 37.3, 36.4, 26.9 (3C), 19.3, 13.9, 10.6 cm^{-1}; IR (neat) 3436, 2961, 2931, 2857, 1619, 1462, 1428, 1227, 1110, 1067, 1027 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{39}NO_4Si$ $[M+H]^+$ 470.2727, found 470.2723.



13c

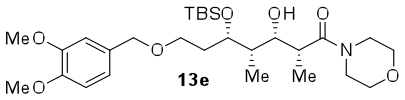
(2*R*,3*S*,5*S*,7*S*)-5,7-bis((tert-butyldimethylsilyl)oxy)-3-hydroxy-9-((4-methoxybenzyl)oxy)-2-methyl-1-morpholinononan-1-one (13c): 13c was prepared from $(^{l}Ipc)_2BH$ (114 mg, 82% yield, d.r. >20:1), white amorphous solid: $[\alpha]_D^{28.4}$ = -20.4 (c = 0.45, $CHCl_3$); ^1H (400 MHz, $CDCl_3$) δ 7.26-7.21 (m, 2H), 6.87-6.83 (m, 2H), 4.43-4.36 (m, 2H), 4.22 (broad s, 1H), 4.10 (ddd, *J* = 2.4, 4.0, 9.8 Hz, 1H), 4.04-3.96 (m, 1H), 3.87-3.79 (m, 1H), 3.78 (s, 3H), 3.68-3.40 (m, 10H), 2.66 (dq, *J* = 4.0, 7.1 Hz, 1H), 1.83-1.60 (m, 5H), 1.43 (ddd, *J* = 2.2, 6.3, 14.0 Hz, 1H), 1.13 (d, *J* = 7.1 Hz, 3H), 0.863 (s, 9H), 0.856 (s, 9H), 0.071 (s, 3H), 0.067 (s, 3H), 0.063 (s, 3H), 0.038 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 174.6, 159.0, 130.5, 129.2 (2C), 113.6 (2C), 72.6, 69.2, 68.5, 67.1, 66.9, 66.8, 66.5, 55.2, 46.2, 45.3, 41.8, 40.0, 39.5, 37.0, 25.84 (3C), 25.81 (3C), 18.0, 17.9, 12.1, -4.2, -4.4, -4.5, -4.6; IR (neat) 3461, 2954, 2929, 2856, 2245, 1622, 1514, 1463, 1436, 1361, 1248, 1115, 1032, 909, 834, 774, 729 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{63}NO_7Si_2$ $[M+H]^+$ 654.4221, found 654.4211.



13d

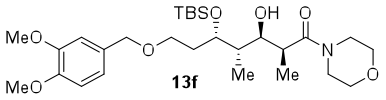
(2*S*,3*R*,5*S*,7*S*)-5,7-bis((*tert*-butyldimethylsilyl)oxy)-3-hydroxy-9-((4-methoxybenzyl)oxy)-2-methyl-1-morpholinononan-1-one (**13d**): **13d** was prepared from $(^{d}Ipc)_2BH$ (109 mg, 78% yield, d.r.

>20:1), white amorphous solid: $[\alpha]_D^{28.5}$ = -15.7 (c = 0.47, $CHCl_3$); ^1H (400 MHz, $CDCl_3$) δ 7.25-7.22 (m, 2H), 6.87-6.84 (m, 2H), 4.41 (d, *J* = 11.5 Hz, 1H), 4.37 (d, *J* = 11.5 Hz, 1H), 4.16 (d, *J* = 1.2 Hz, 1H), 4.03 (dddd, *J* = 1.2, 3.2, 4.5, 7.4 Hz, 1H), 3.95-3.83 (m, 2H), 3.79 (s, 3H), 3.70-3.37 (m, 10H), 2.66 (dq, *J* = 3.2, 7.2 Hz, 1H), 1.82-1.52 (m, 6H), 1.12 (d, *J* = 7.1 Hz, 3H), 0.86 (s, 9H), 0.85 (s, 9H), 0.07 (s, 3H), 0.053 (s, 3H), 0.051 (s, 3H), 0.03 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 175.4, 159.0, 130.5, 129.2 (2C), 113.7 (2C), 72.6, 69.3, 68.9, 67.3, 66.9, 66.7, 66.6, 55.2, 46.2, 46.0, 41.8, 40.7, 39.0, 37.5, 25.84 (3C), 25.81 (3C), 18.0, 17.9, 11.1, -4.0, -4.20, -4.23, -4.4; IR (neat) 3465, 2953, 2929, 2895, 2856, 1622, 1514, 1463, 1436, 1361, 1248, 1173, 1115, 1093, 1033, 938, 833, 808, 772 cm^{-1}; HRMS (ESI) calcd for $C_{34}H_{63}NO_7Si_2$ $[M+H]^+$ 654.4221, found 654.4222.



13e

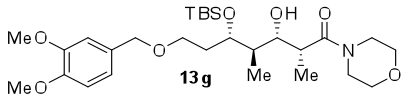
(2*R*,3*S*,4*S*,5*S*)-5-((tert-butyldimethylsilyl)oxy)-7-((3,4-dimethoxybenzyl)oxy)-3-hydroxy-2,4-dimethyl-1-morpholinoheptan-1-one (13e): 13e was prepared from Cy_2BH (62 mg, 54% yield, d.r. 3:1 **13e**:**13f**) and from $(^lIpc)_2BH$ (82 mg, 71% yield, d.r. >20:1), white amorphous solid: $[\alpha]_D^{28.5}$ = +6.8 (c = 0.47, $CHCl_3$); ^1H (400 MHz, $CDCl_3$) δ 6.89-6.81 (m, 3H), 4.40 (s, 2H), 4.16 (broad s, 1H), 3.92-3.87 (m, 2H), 3.89 (s, 3H), 3.88 (s, 3H), 3.67-3.61 (m, 5H), 3.59-3.52 (m, 1H), 3.46 (dd, *J* = 3.9, 6.0 Hz, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.91 (dq, *J* = 3.9, 7.1 Hz, 1H), 1.90-1.80 (m, 1H), 1.78-1.67 (m, 2H), 1.14 (d, *J* = 7.1 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.86 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 175.8, 148.9, 148.5, 130.8, 120.2, 111.0, 110.8, 73.4, 72.9, 72.5, 66.9, 66.8, 66.6, 55.9, 55.8, 46.1, 41.7, 38.9, 37.1, 34.1, 25.8 (3C), 17.9, 11.8, 9.6, -4.1, -4.4; IR (neat) 3466, 2955, 2931, 1622, 1516, 1464, 1437, 1260, 1232, 1115, 1027, 836 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{49}NO_7Si$ $[M+H]^+$ 540.3357, found 540.3354.



13f

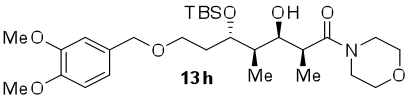
(2*S*,3*R*,4*S*,5*S*)-5-((tert-butyldimethylsilyl)oxy)-7-((3,4-dimethoxybenzyl)oxy)-3-hydroxy-2,4-dimethyl-1-morpholinoheptan-1-one (13f): 13f was prepared from Cy_2BH (62 mg, 54% yield, d.r. 3:1 **13e**:**13f**) and from $(^dIpc)_2BH$ (64 mg, 56% yield after 48 h at -78 °C or 71% yield brsm, d.r. >20:1), white amorphous solid: $[\alpha]_D^{28.4}$ = -9.1 (c = 0.22, $CHCl_3$); ^1H (400 MHz, $CDCl_3$) δ 6.91-6.79 (m, 3H), 4.53 (d, *J* = 1.6 Hz, 1H), 4.44 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 11.6 Hz, 1H), 4.28 (dt, *J* = 1.7, 6.8 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.75-3.61 (m, 6H), 3.60-3.39 (m, 5H), 2.72 (dq, *J* = 2.1, 7.1 Hz, 1H), 1.89-1.74 (m, 2H), 1.55 (dqd, *J* = 1.7, 7.0, 9.8 Hz, 1H), 1.09 (d, *J* = 7.1 Hz, 3H), 0.85 (s, 9H), 0.76 (d, *J* = 6.9 Hz, 3H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 176.0, 148.9, 148.4, 131.0, 120.1, 111.0, 110.8, 72.8, 71.7,

68.7, 67.3, 66.9, 66.7, 55.9, 55.8, 46.2, 41.9, 39.6, 35.9, 35.2, 25.9 (3C), 18.1, 9.6, 9.3, -4.49, -4.51; IR (neat) 3415, 2954, 2929, 2855, 1619, 1516, 1463, 1260, 1229, 1116, 1029 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{49}NO_7Si$ $[M+H]^+$ 540.3357, found 540.3351.



13g

(2*R*,3*S*,4*R*,5*S*)-5-((tert-butyldimethylsilyl)oxy)-7-((3,4-dimethoxybenzyl)oxy)-3-hydroxy-2,4-dimethyl-1-morpholinoheptan-1-one (13g): 13g was prepared from Cy_2BH (73 mg, 64% yield, d.r. **1.3**:1 **13g**:**13h**) and from $(^{l}Ipc)_2BH$ (85 mg, 74% yield, d.r. >20:1), white amorphous solid: $[\alpha]_D^{28.4}$ = -1.5 (c = 0.26, $CHCl_3$); ^1H (400 MHz, $CDCl_3$) δ 6.92-6.77 (m, 3H), 4.50 (broad s, 1H), 4.43 (d, *J* = 11.4 Hz, 1H), 4.39 (d, *J* = 11.4 Hz, 1H), 4.26 (ddd, *J* = 2.6, 3.8, 10.3 Hz, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.74-3.41 (m, 11H), 2.68 (dq, *J* = 1.7, 7.3 Hz, 1H), 1.86-1.75 (m, 2H), 1.56 (dddd, *J* = 4.6, 7.9, 10.0, 13.2 Hz, 1H), 1.10 (d, *J* = 7.2 Hz, 3H), 0.86 (s, 9H), 0.77 (d, *J* = 7.0 Hz, 3H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 176.4, 148.9, 148.3, 131.2, 120.1, 111.0, 110.8, 72.6, 72.5, 68.6, 68.1, 66.7, 66.6, 55.8, 55.7, 46.1, 41.7, 40.8, 35.4, 30.5, 25.8 (3C), 17.9, 9.3, 9.2, -4.4, -4.8; IR (neat) 3433, 2955, 2929, 2855, 1618, 1516, 1463, 1440, 1420, 1259, 1230, 1115, 1027 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{49}NO_7Si$ $[M+H]^+$ 540.3357, found 540.3351.



13h

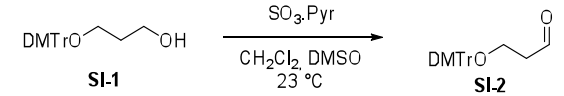
(2*S*,3*R*,4*R*,5*S*)-5-((tert-butyldimethylsilyl)oxy)-7-((3,4-dimethoxybenzyl)oxy)-3-hydroxy-2,4-dimethyl-1-morpholinoheptan-1-one (13h): 13h was prepared from Cy_2BH (73 mg, 64% yield, d.r. 1.3:**1 13g**:**13h**) and from $(^{d}Ipc)_2BH$ (82 mg, 72% yield, d.r. >20:1), white amorphous solid: $[\alpha]_D^{28.7}$ = +8.9 (c = 0.45, $CHCl_3$); ^1H (400 MHz, $CDCl_3$) δ 6.85-6.77 (m, 3H), 4.41 (d, *J* = 11.4 Hz, 1H), 4.33 (d, *J* = 11.4 Hz, 1H), 4.12 (broad s, 1H), 4.01 (dd, *J* = 4.3, 6.7 Hz, 1H), 3.95 (dt, *J* = 2.8, 6.7 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.62-3.43 (m, 8H), 3.43-3.30 (m, 2H), 2.74 (quint., *J* = 6.9 Hz, 1H), 1.83 (q, *J* = 6.3 Hz, 2H), 1.72 (ddq, *J* = 2.8, 4.0, 7.0 Hz, 1H), 1.18 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.87 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 174.3, 148.8, 148.4, 131.0, 120.0, 110.9, 110.7, 73.6, 72.8, 72.6, 66.8, 66.7, 66.5, 55.8, 55.7, 45.9, 41.7, 37.4, 37.3, 34.1, 25.7 (3C), 17.8, 13.5, 11.3, -4.60, -4.65; IR (neat) 3479, 2956, 2931, 2898, 2857, 1622, 1516, 1463, 1260, 1234, 1114, 1091, 1025 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{49}NO_7Si$ $[M+H]^+$ 540.3357, found 540.3349.

Synthesis of non-commercially available aldehydes

Aldehydes **12a**[5], **12b**[6] and**12c**[7] are known in the literature and were synthesized according to the published procedures. Characterization data for these aldehydes were in agreement with reported data.

Synthesis of aldehyde SI-2

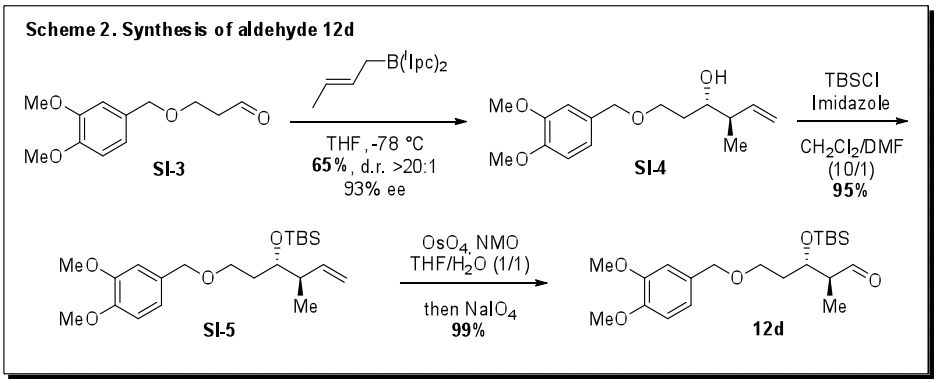
Scheme 1. Synthesis of aldehyde SI-2



3-(bis(4-methoxyphenyl)(phenyl)methoxy)propanal (SI-2): To a solution of known alcohol[8] **SI-1** (8.2 g, 21.75 mmol) in CH_2Cl_2 (87 mL) and DMSO (23 mL) was added SO_3.pyridine complex (10.4 g, 65.2 mmol) in several portions at room temperature. The resulting mixture was allowed to stir until the reaction was complete according to TLC analysis. The reaction mixture was diluted with Et_2O. The organic phase was washed five times with water and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude mixture was purified by flash chromatography on silica gel (7/3 : hexanes/ethyl acetate) providing aldehyde **SI-2** (5.73 g, 70% yield) as a colorless oil: ^{1}H (400 MHz, $CDCl_3$) δ 9.76 (t, *J* = 2.2 Hz, 1H), 7.43-7.39 (m, 2H), 7.33-7.26 (m, 6H), 7.25-7.21 (m, 1H), 6.85-6.80 (m, 4H), 3.79 (s, 6H), 3.46 (t, *J* = 6.1 Hz, 2H), 2.63 (dt, *J* = 2.2, 6.2 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 201.7, 158.5 (2C), 144.7, 135.9 (2C), 130.0 (4C), 128.1 (2C), 127.8 (2C), 126.8, 113.1 (4C), 86.3, 55.7, 55.2 (2C), 44.1; IR (neat) 2934, 2836, 1724, 1607, 1507, 1463, 1446, 1300, 1246, 1173, 1032, 827 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}O_4$ $[M+Na]^+$ 399.1567, found 399.1571.

Synthesis of aldehyde 12d

Scheme 2. Synthesis of aldehyde 12d



(3*S*,4*R*)-1-((3,4-dimethoxybenzyl)oxy)-4-methylhex-5-en-3-ol (SI-4): This compound was prepared using the known procedure.[9] To a stirred mixture of potassium *tert*-butoxide (95% purity, 934 mg, 7.91 mmol), THF (20 mL), and *trans*-2-butene (9 mL) at -78 °C was added (2.5 M) *n*-BuLi in THF

(3.19 mL, 7.97 mmol). After complete addition of *n*-BuLi, the mixture was stirred at -45 °C for 10 min. The resulting solution was recooled to -78 °C and to it was added (^{l}Ipc)$_2$BOMe (1M in Et_2O, 8.38 mmol). After the reaction mixture was stirred at -78 °C for 30 min, boron trifluoride etherate (1.4 mL, 11.3 mmol) was added dropwise. Then known aldehyde **SI-3**[10] (1.49 g, 6.64 mmol) in Et_2O (9.6 mL) was slowly added and the reaction was stirred at -78 °C for 4 h. The solution was then treated with 2M NaOH (12.6 mL, 25.2 mmol) and H_2O_2 (50% purity, 5 mL, 81.5 mmol) and was stirred overnight at room temperature. The aqueous phase was extracted twice with Et_2O and the combined organic layers were washed with brine, dried over Na_2SO_4, filtered and evaporated under reduced pressure. Purification of the crude product by flash chromatography (1/1 : hexanes/ethyl acetate) provided the corresponding alcohol **SI-4** (1.21g, 65% yield, d.r. >20:1, 93% ee) as a clear oil: $[\alpha]_D^{28.7}$ = +3.1 (c = 0.49, $CHCl_3$); ^{1}H (400 MHz, $CDCl_3$) δ 6.85-6.75 (m, 3H), 5.80-5.70 (m, 1H), 5.03 (broad s, 1H), 5.01-4.99 (m, 1H), 4.40 (s, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.67-3.53 (m, 3H), 2.23-2.13 (m, 1H), 1.72-1.61 (m, 2H), 0.99 (d, *J* = 6.9 Hz, 3H), OH not observed; ^{13}C (100 MHz, $CDCl_3$) δ 148.8, 148.4, 140.2, 130.4, 120.1, 115.2, 110.8, 110.7, 73.8, 72.9, 68.6, 55.7, 55.6, 43.7, 33.3, 15.6; IR (neat) 3489, 2923, 2855, 1594, 1516, 1464, 1419, 1261, 1236, 1157, 1138, 1086, 1027, 1002, 914, 854, 807, 766 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{24}O_4$ $[M+Na]^+$ 303.1572, found 303.1571.

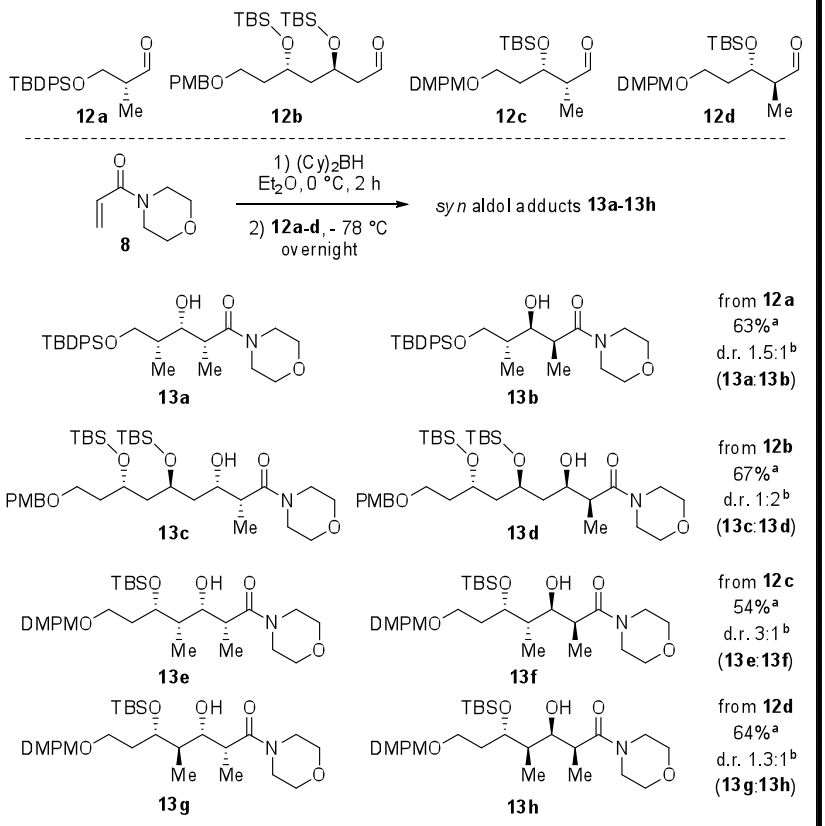
***tert*-butyl(((3*S*,4*R*)-1-((3,4-dimethoxybenzyl)oxy)-4-methylhex-5-en-3-yl)oxy)dimethylsilane (SI-5):** To a solution of alcohol **SI-4** (1.21 g, 4.31 mmol) in a mixture of CH_2Cl_2 (13 mL) and DMF (1.36 mL) was added imidazole (445 mg, 6.47 mmol) and TBSCl (822 mg, 5.18 mmol). The mixture was stirred overnight, then was diluted with water (10 mL). The organic layer was separated and the aqueous layer extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude product by flash chromatography (75/25 : hexanes/ethyl acetate) afforded **SI-5** (1.61 g, 95%) as a colorless oil: $[\alpha]_D^{28.6}$ = -2.1 (c = 0.52, $CHCl_3$); ^{1}H (400 MHz, $CDCl_3$) δ 6.90-6.81 (m, 3H), 5.82-5.72 (m, 1H), 5.01-4.99 (m, 1H), 4.99-4.95 (m, 1H), 4.44 (d, *J* = 11.4 Hz, 1H), 4.39 (d, *J* = 11.4 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.77 (ddd, *J* = 3.8, 4.7, 7.7 Hz, 1H), 3.53-3.44 (m, 2H), 2.34-2.25 (m, 1H), 1.76-1.61 (m, 2H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.88 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 148.9, 148.4, 140.6, 131.1, 120.2, 114.5, 111.0, 110.8, 72.8, 72.5, 67.2, 55.9, 55.8, 43.4, 33.2, 25.9 (3C), 18.1, 14.5, -4.4, -4.5; IR (neat) 2955, 2930, 2886, 2857, 1594, 1516, 1464, 1419, 1361, 1331, 1257, 1238, 1157, 1137, 1094, 1030, 1005, 913, 833, 805, 772 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{38}O_4Si$ $[M+H]^+$ 395.2618, found 395.2619.

(2*S*,3*S*)-3-((*tert*-butyldimethylsilyl)oxy)-5-((3,4-dimethoxybenzyl)oxy)-2-methylpentanal (12d): To a solution of alkene **SI-5** (1.61 g, 4.08 mmol) in THF and H_2O (1:1, 13.6 mL) were successively added OsO_4 (2.5% solution in *tert*-BuOH, 1 mL, 0.08 mmol) and *N*-methylmorpholine-*N*-oxide monohydrate (956 mg, 8.16 mmol). The brown solution was stirred at room temperature for 7 h. $NaIO_4$ (1.75 g, 8.16 mmol) was added and the resulting mixture was stirred for a further 2 h. The reaction was filtered through Celite and the organic phase was washed with water, brine, then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude product by flash chromatography (80/20 : hexanes/ethyl acetate) afforded **12d** (1.61 g, 99%) as a colorless oil: $[\alpha]_D^{28.0}$ = -2.1 (c = 0.38, $CHCl_3$); ^1H (400 MHz, $CDCl_3$) δ 9.71 (d, *J* = 2.2 Hz, 1H), 6.88-6.80 (m, 3H), 4.42 (d, *J* = 11.5 Hz, 1H), 4.39 (d, *J* = 11.5 Hz, 1H), 4.15 (td, *J* = 4.9, 6.7 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.53 (t, *J* = 6.4 Hz, 2H), 2.53 (ddq, *J* = 2.2, 4.6, 7.0 Hz, 1H), 1.90-1.72 (m, 2H), 1.10 (d, *J* = 7.0 Hz, 3H), 0.86 (s, 9H), 0.062 (s, 3H), 0.057 (s, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 204.4, 148.9, 148.5, 130.7, 120.1, 110.9, 110.8, 72.8, 70.4, 66.0, 55.8, 55.7, 51.5, 34.6, 25.7 (3C), 17.9, 10.0, -4.6, -4.8; IR (neat) 2956, 2930, 2901, 2857, 2323, 1594, 1517, 1464, 1419, 1361, 1258, 1240, 1158, 1128, 1097, 1033, 913, 836, 805, 775 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{36}O_5Si$ $[M+H]^+$ 397.2410, found 397.2411.

Determination of intrinsic diastereofacial selectivity of aldehydes 12a-d

The intrinsic diastereofacial selectivity of aldehydes **12a-d** as determined by reaction of each with the enolborane generated from N-acryloylmorpholine (**8**) with dicyclohexylborane, according to the general procedure described above (Scheme 3).

Scheme 3. Determination of intrinsic diastereofacial selectivity preferences of aldehydes **12a-12d** by reductive aldol reactions with N-acryloylmorpholine (**8**) and dicyclohexylborane.



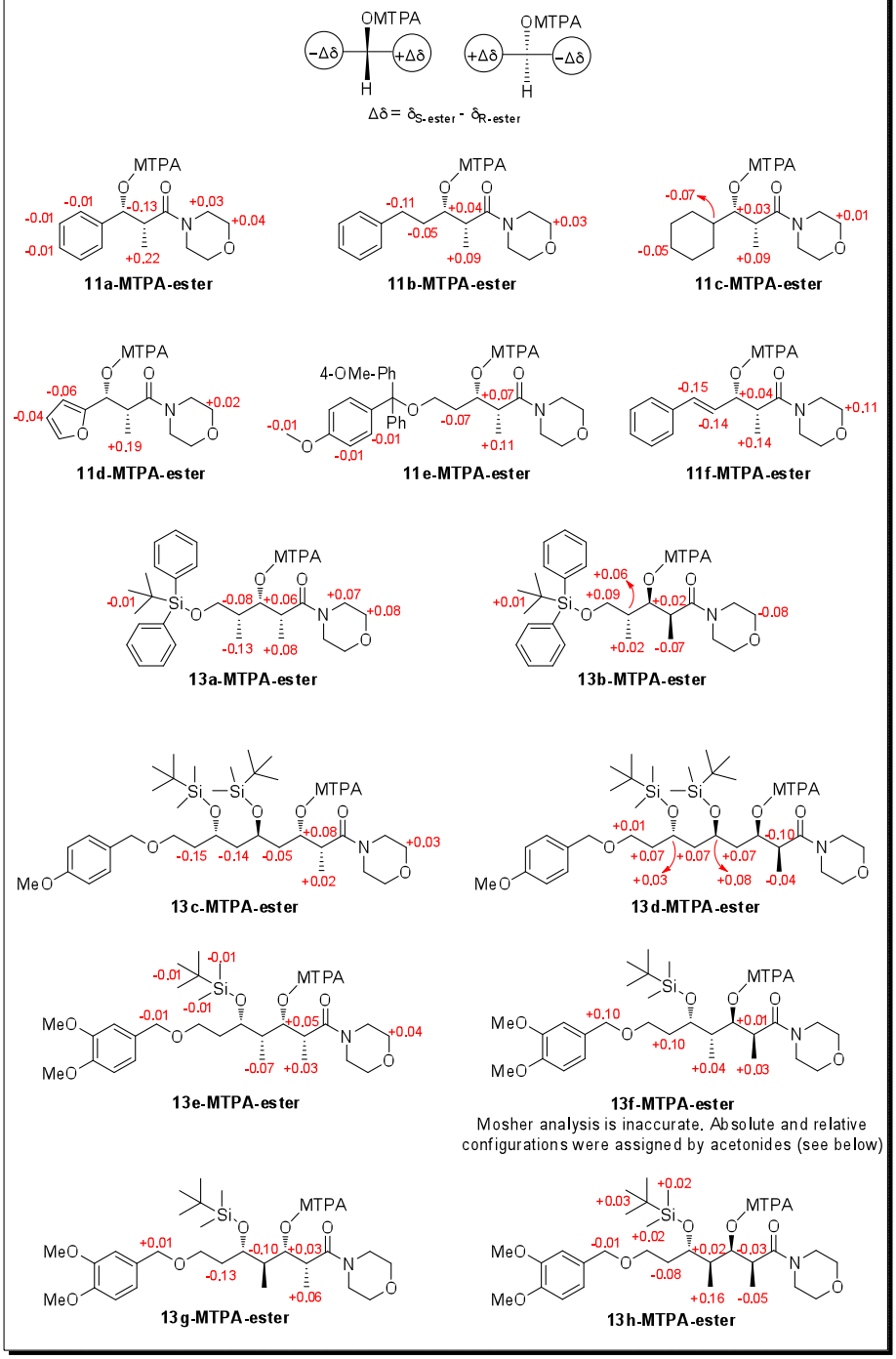
a) Isolated yields of product obtained by column chromatography

b) Diastereomer ratio (d.r.) determined by ^{1}H NMR analysis of crude reaction mixtures

Assignment of hydroxyl group absolute stereochemistry

The absolute stereochemistry of the hydroxyl-bearing carbon of aldol adducts was assigned by using the Mosher method. Key differential ^{1}H chemical shifts (ppm) in the pairs of diastereomeric MTPA esters are summarized below (Figure 1). ^{1}H NMR Mosher analysis of **11f** is provided as an example (see page S51).

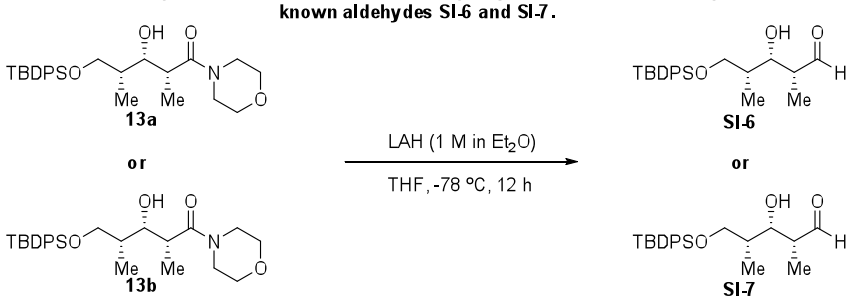
Figure 1. Mosher ester analysis of products 11a-f and 13a-h



Assignment of relative stereochemistry

The relative stereochemistry of aldol adducts **13a** and **13b** was determined by reduction of the morpholine amide moiety to the corresponding aldehydes **SI-6** and **SI-7,** respectively, and comparison with the literature data (Scheme 4).[11]

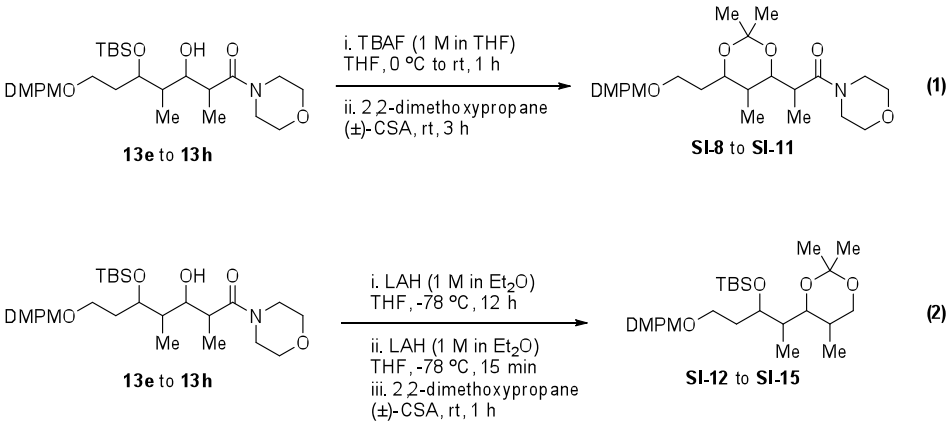
Scheme 4. Assignment of relative stereochemistry of products 13a and 13b: Synthesis of known aldehydes SI-6 and SI-7.



Synthesis of aldehydes **SI-6** and **SI-7**: To a solution of aldol adduct (9.8 mg, 0.021 mmol) in THF (210 µL) was slowly added at -78 °C under inert atmosphere a solution of lithium aluminum hydride (1 M in Et_2O, 104 µL, 0.104 mmol); the reaction mixture was stirred at this temperature for 12 h. A saturated aqueous solution of NH_4Cl (1.5 mL) was then added followed by CH_2Cl_2 (1.5 mL) and the mixture was allowed to warm up to room temperature. The aqueous layer was extracted two times with CH_2Cl_2 (1.5 mL), the combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduce pressure. Because of their instability, aldehydes **SI-6** and **SI-7** were analyzed as crude products and characterization data so obtained was in agreement with reported data.

The relative stereochemistry of aldol adducts **13e** to **13h** was determined by synthesis of both internal **SI-8** to **SI-11** and terminal **SI-12** to **SI-15** acetonides (Scheme 5). Coupling constants as well as nOe analyses allowed the unambiguous assignment of stereochemistry to these structures (Figure 2).

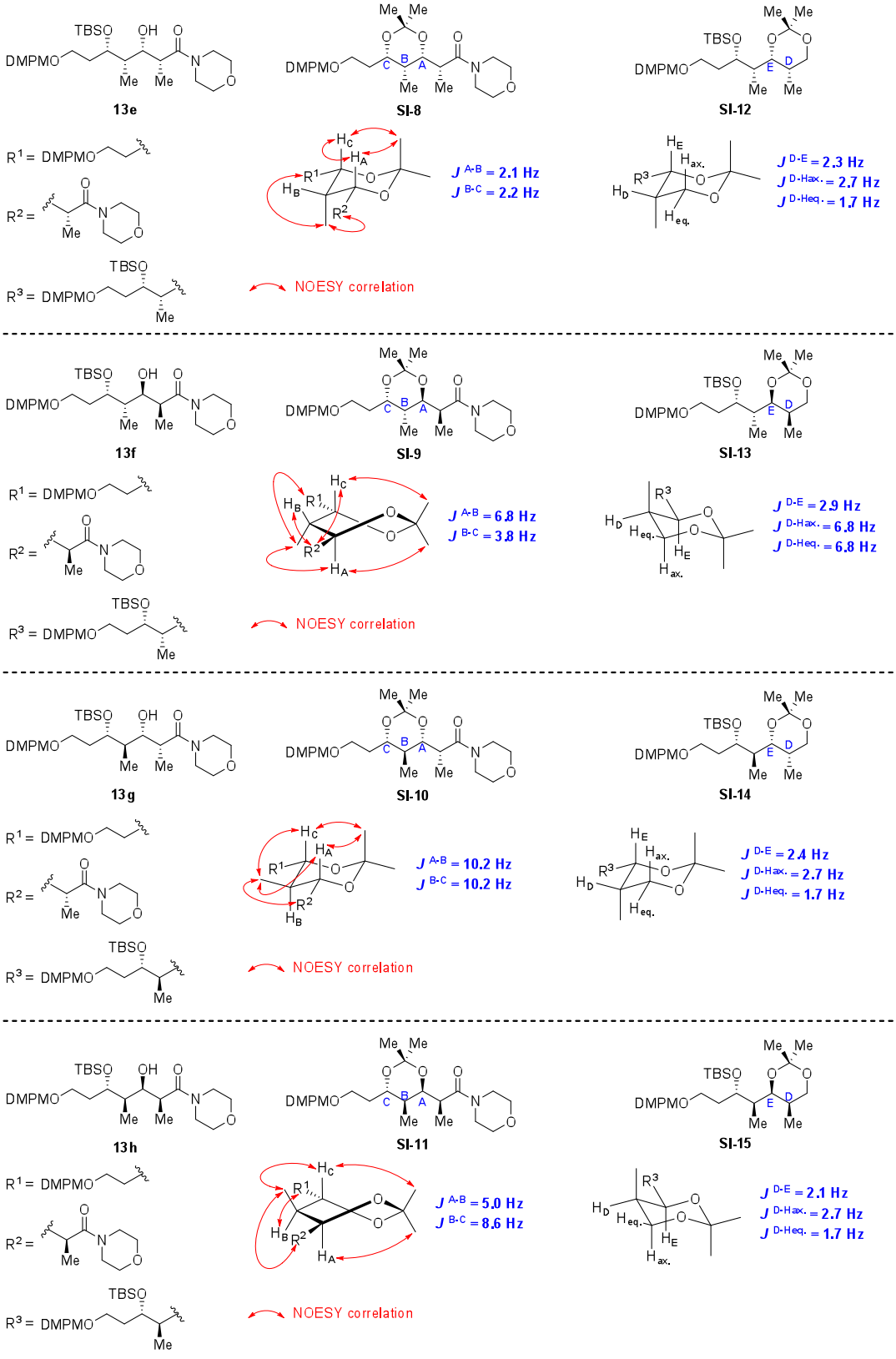
Scheme 5. Assignment of relative stereochemistry of products 13e-h: synthesis of internal (SI-8-11) and terminal (SI-12-15) acetonides.



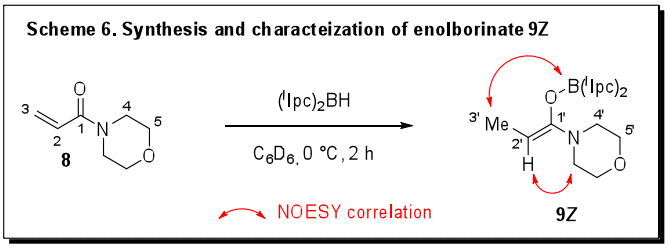
Synthesis of internal acetonides **SI-8** to **SI-11**, typical procedure given for **SI-8** : To a solution of aldol adduct **13e** (10 mg, 0.018 mmol) in THF (100 µL) was added at 0 °C under inert atmosphere a solution of tetrabutylammonium fluoride (1 M in THF, 39 µL, 0.039 mmol). The mixture was allowed to warm to room temperature and was stirred for 1 h at this temperature. An aqueous buffer solution (pH= 7.00, 1 mL) was added and the aqueous layer was extracted three times with CH_2Cl_2 (1 mL). The combined organic layers were dried over Na_2SO_4 and solvent was removed under reduce pressure. Crude diol was purified by flash chromatography (80/20 : CH_2Cl_2/ethyl acetate). Pure diol was dissolved in 2,2-dimethoxypropane (100 µL). A small amount of racemic camphor sulfonic acid (< 1 mg) was added to the solution at room temperature and the mixture was allowed to stir for 3 h. Freshly distilled triethylamine (25 µL) was added to the solution and the volatiles were then removed under reduced pressure, providing the desired clean internal acetonide **SI-8** as a colorless oil following filtration through a short silica gel column.

Synthesis of internal acetonides **SI-12** to **SI-15**, typical procedure given for **SI-12**: To a solution of aldol adduct **13e** (25 mg, 0.046 mmol) in THF (460 µL) was slowly added at -78 °C under inert atmosphere a solution of lithium aluminum hydride (1 M in Et_2O, 460 µL, 0.46 mmol); the reaction mixture was stirred at this temperature for 12 h. A saturated aqueous solution of NH_4Cl (3 mL) was then added followed by CH_2Cl_2 (3 mL) and the mixture was allowed to warm up to room temperature. The aqueous layer was extracted two times with CH_2Cl_2 (3 mL), the combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduce pressure. The crude aldehyde was dissolved in THF (460 µL) and the solution was cooled to -78 °C. A solution of lithium aluminum hydride (1M in Et_2O, 460 µL, 0.46 mmol) was added dropwise under inert atmosphere and the reaction mixture was allowed to stir for 15 minutes. At that time, a saturated aqueous solution of Rochelle's salt (3 mL) was added followed by CH_2Cl_2 (3 mL) and the mixture was stir at room temperature until complete separation of layers. The aqueous layer was extracted two times with CH_2Cl_2 (3 mL), the combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduce pressure. Flash chromatography (30/70 : hexanes/ethyl acetate) afforded pure diol which was dissolved in 2,2-dimethoxypropane (300 µL). A small amount of racemic camphor sulfonic acid (< 1 mg) was added to the solution at room temperature and the mixture was allowed to stir until completion (monitored by TLC), usually within 1 h. Freshly distilled triethylamine (50 µL) was added to the solution and the volatiles were then removed under reduced pressure, providing the desired clean terminal acetonide **SI-12** as a colorless oil after filtration through a short plug of silica gel.

Figure 2. Assignment of relative stereochemistry of products 13e-h: analysis of coupling constants and nOe correlations of acetonides SI-8 to SI-15.

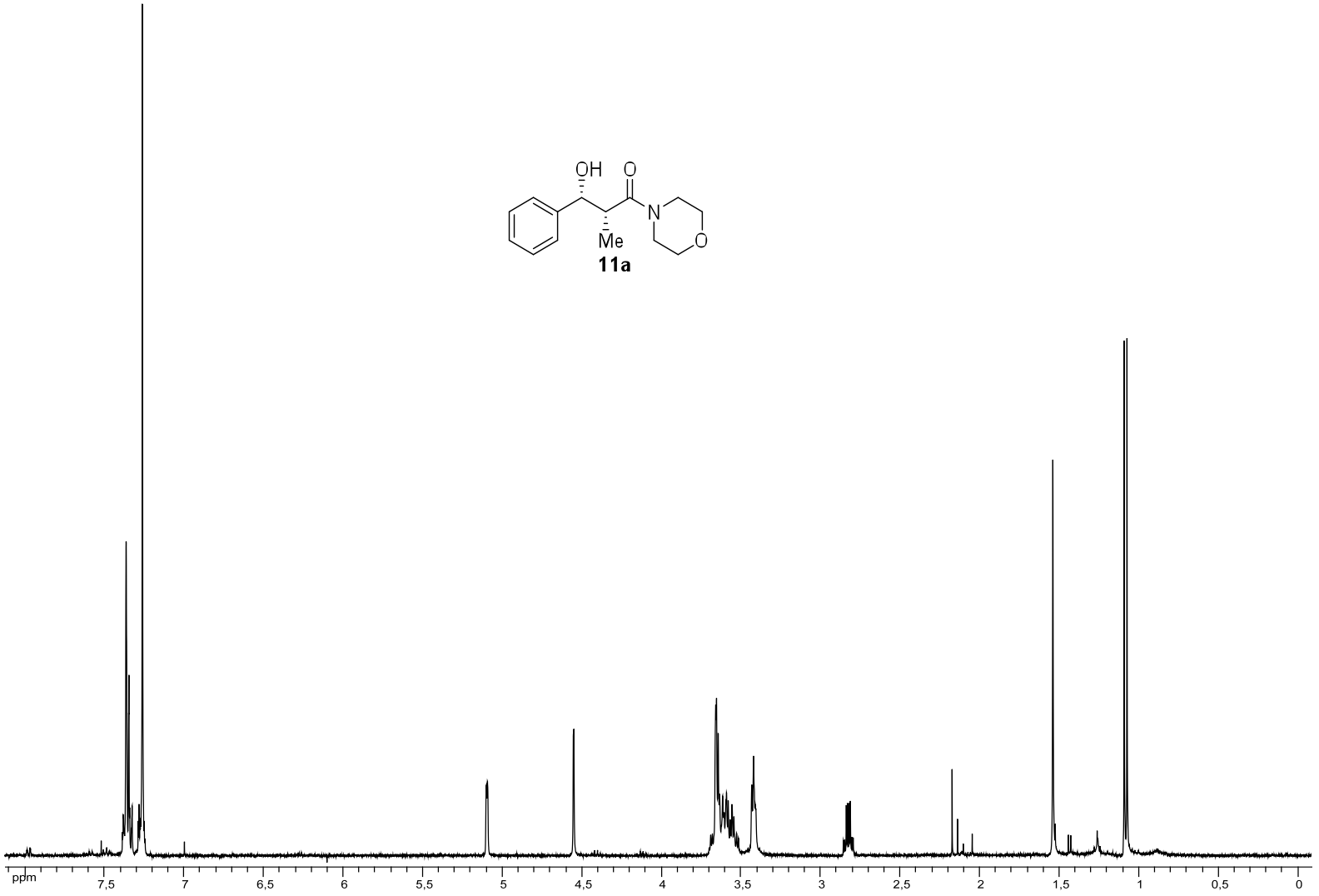


Synthesis and characterization of (diisopinocampheyl)enolborinate 9*Z*

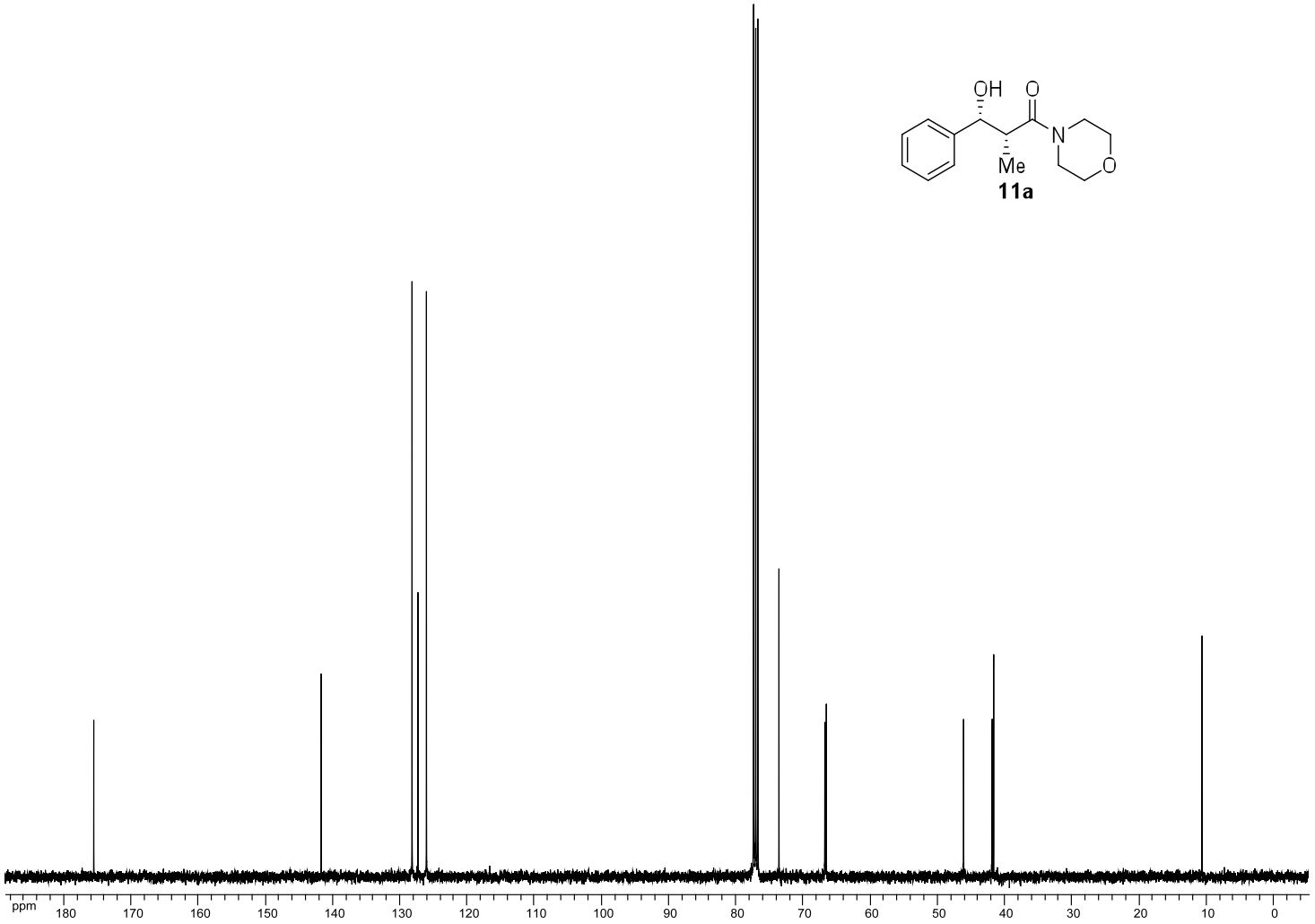


4-((*Z*)-1-((((1*S*,2*R*,3*S*,5*S*)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)((2*R*,3*S*)-2,6,6-trimethylbicyclo [3.1.1]heptan-3-yl)boryl)oxy)prop-1-en-1-yl)morpholine (9*Z*): To a 0 °C suspension of (^{t}Ipc)$_2$BH (weighed in the glove box, 72 mg, 0.25 mmol) in degassed C_6D_6 (1.0 mL) was added 4-acryloylmorpholine **8** (35 µL, 0.275 mmol). The solution was stirred 2 h at 0 °C at which time the content of the flask was transferred to an NMR tube for analysis. ^{1}H NMR, ^{13}C, COSY and NOESY NMR analysis showed that the reaction mixture consisted of **9*Z*** and **8** in an 11:1 ratio. Partial data ^{1}H (400 MHz, C_6D_6) δ 3.78 (q, *J* = 6.6 Hz, 1H$_{2'}$), 3.48 (t, *J* = 4.7 Hz, 4H$_{5'}$), 2.71-2.61 (m, 4H$_{4'}$), 1.60 (d, *J* = 6.6 Hz, 3H$_{3'}$); Partial data ^{13}C (100 MHz, C_6D_6) δ 154.9 ($C_{1'}$), 83.0 ($C_{2'}$), 66.6 (2$C_{5'}$), 48.9 (2$C_{4'}$), 11.0 ($C_{3'}$).

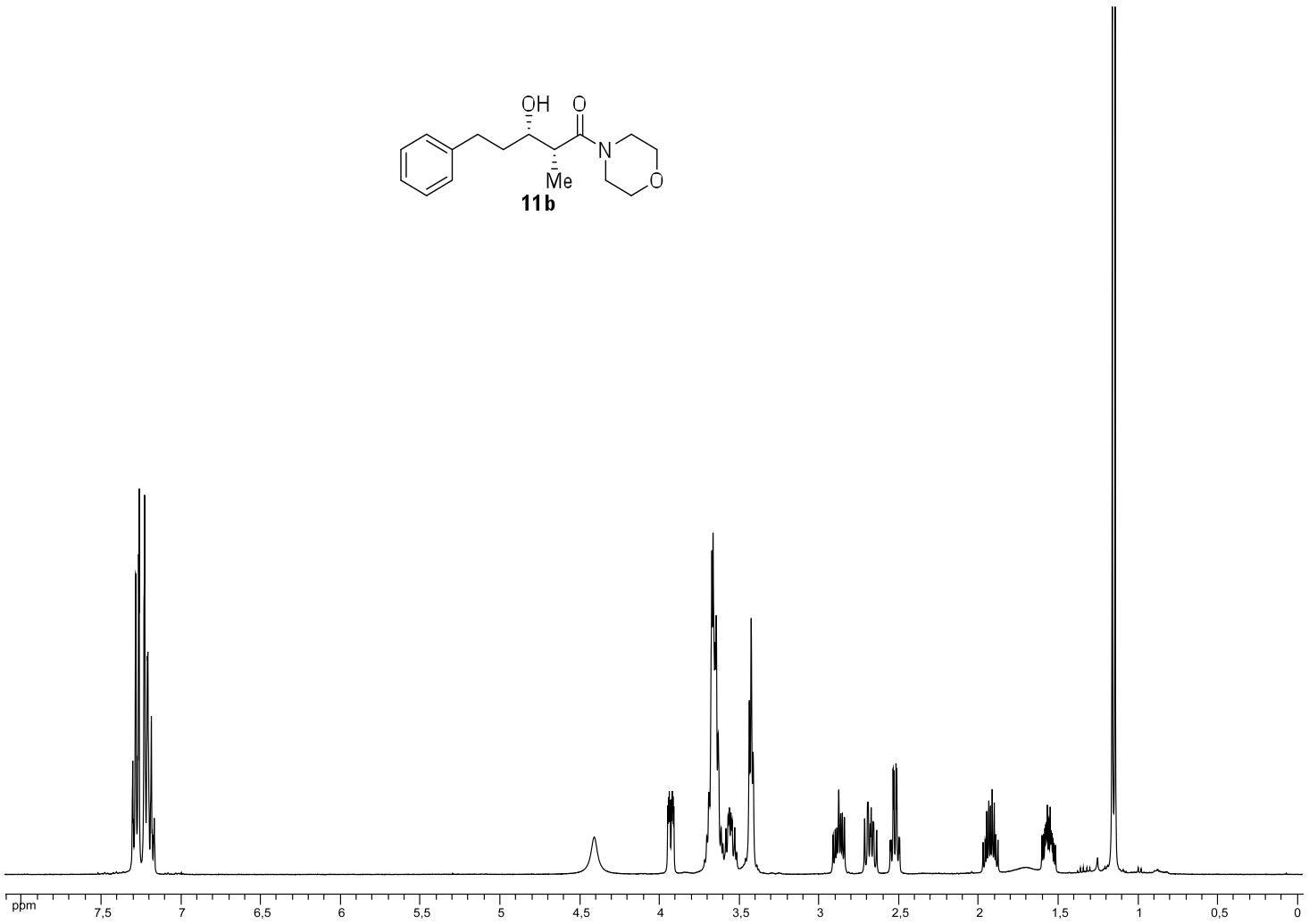
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11a**



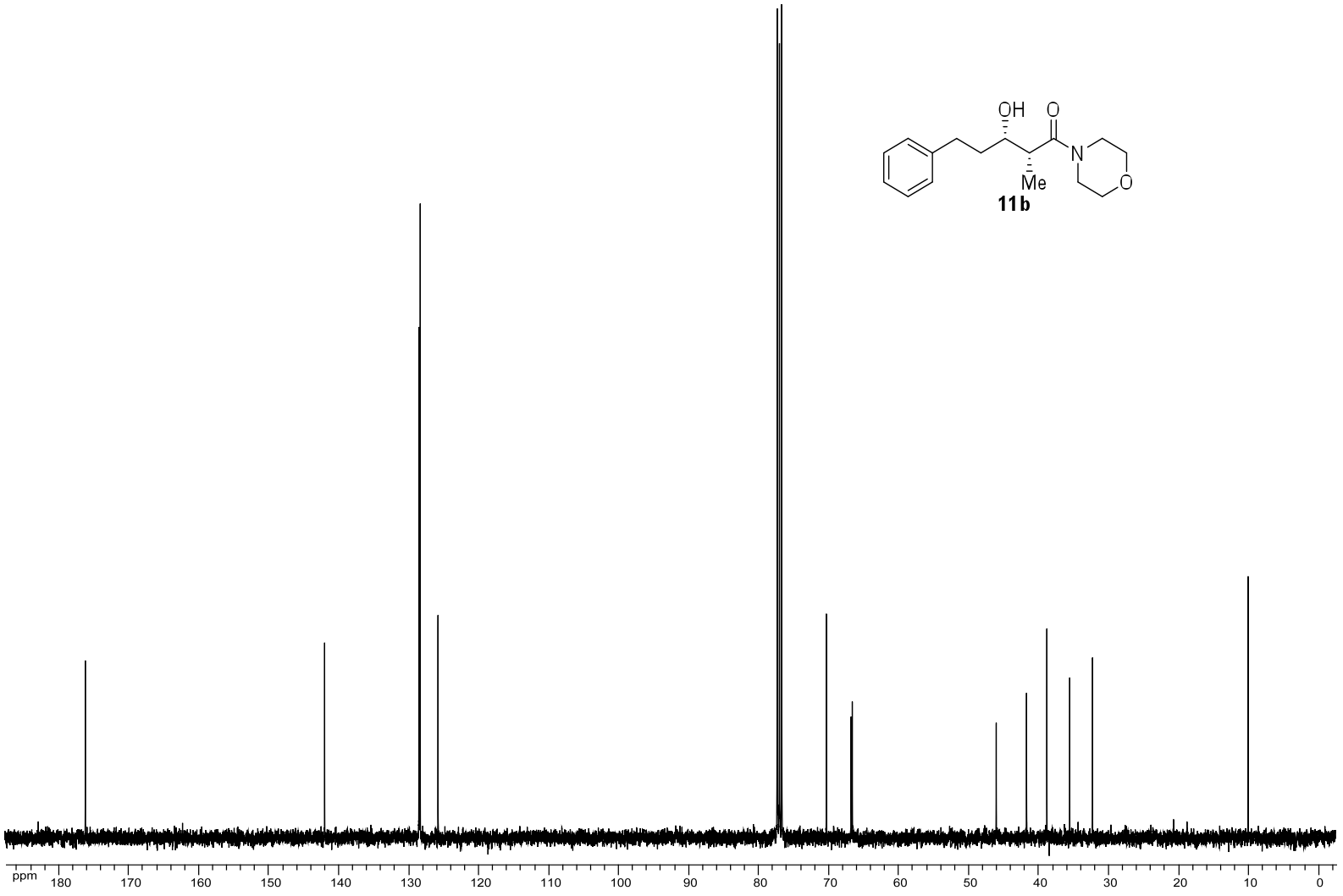
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11a**



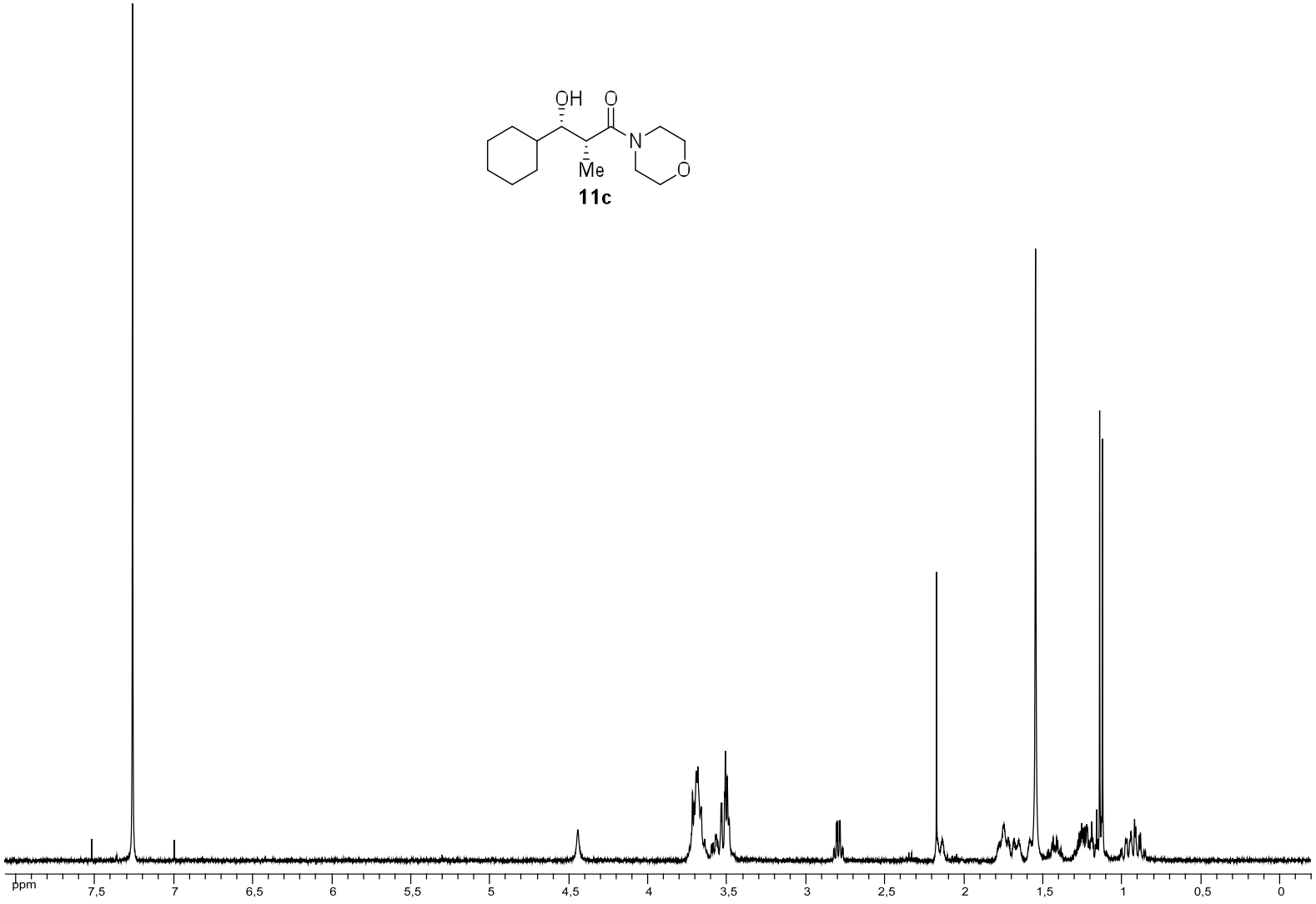
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11b**



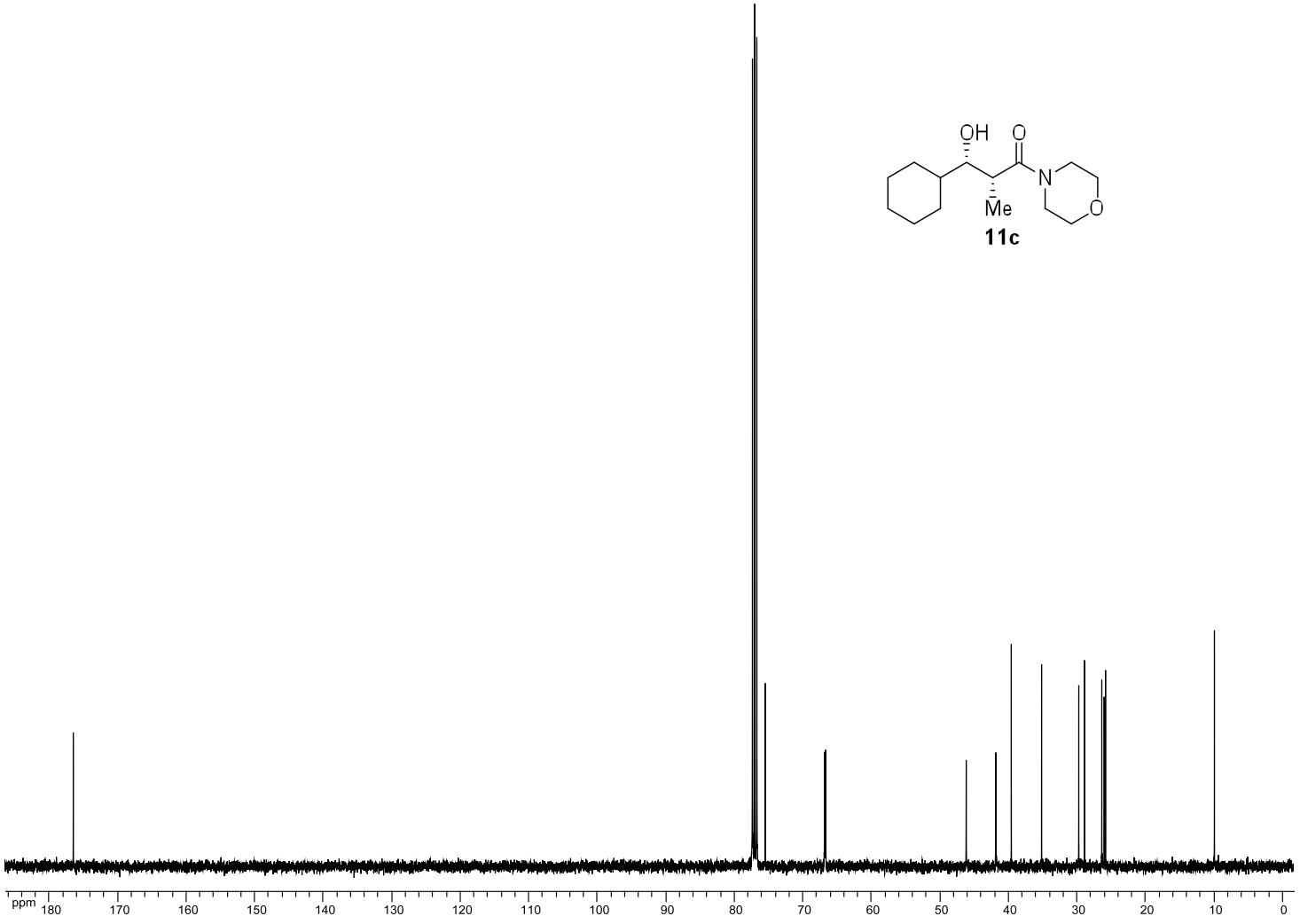
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11b**



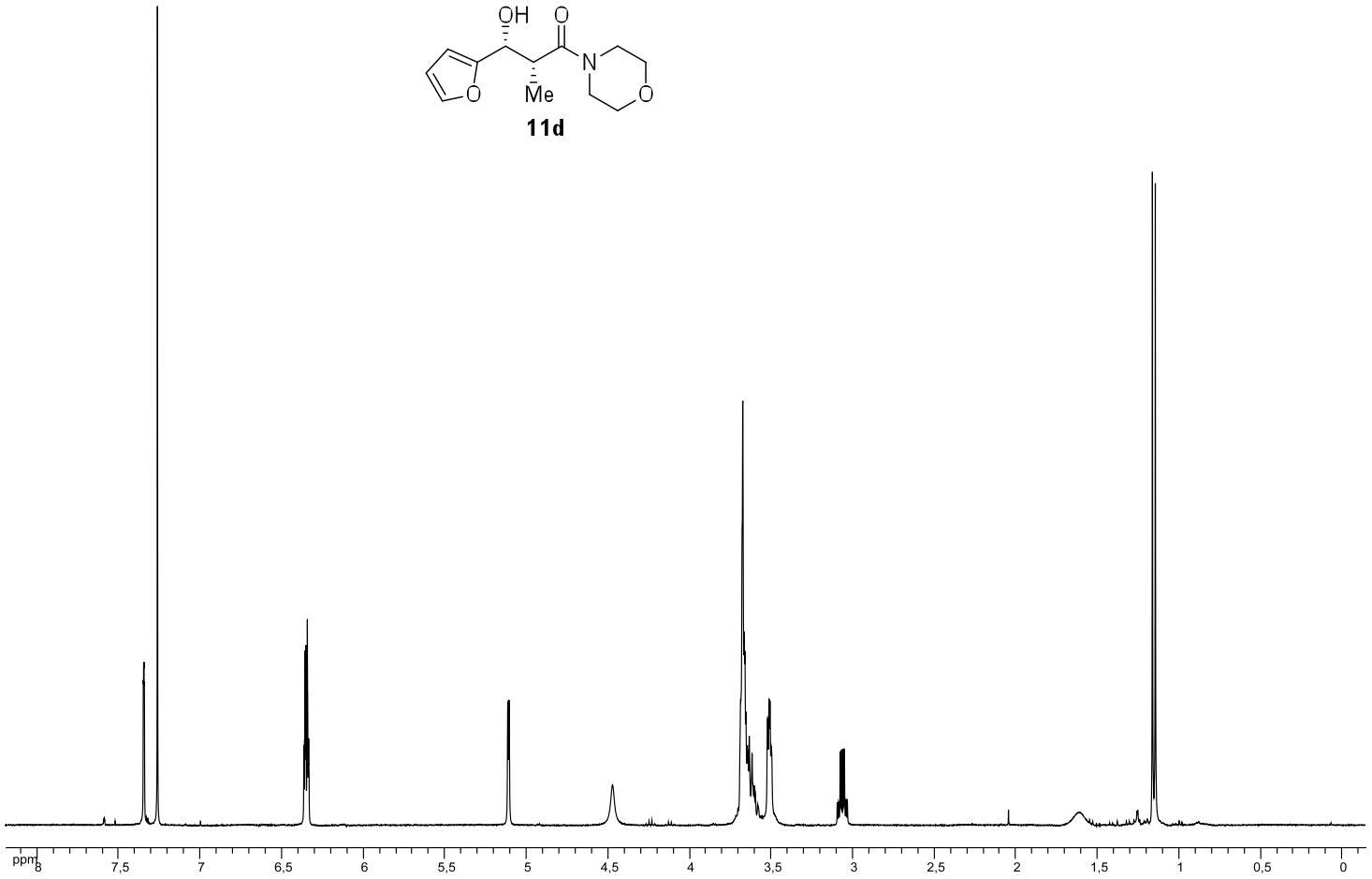
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11c**



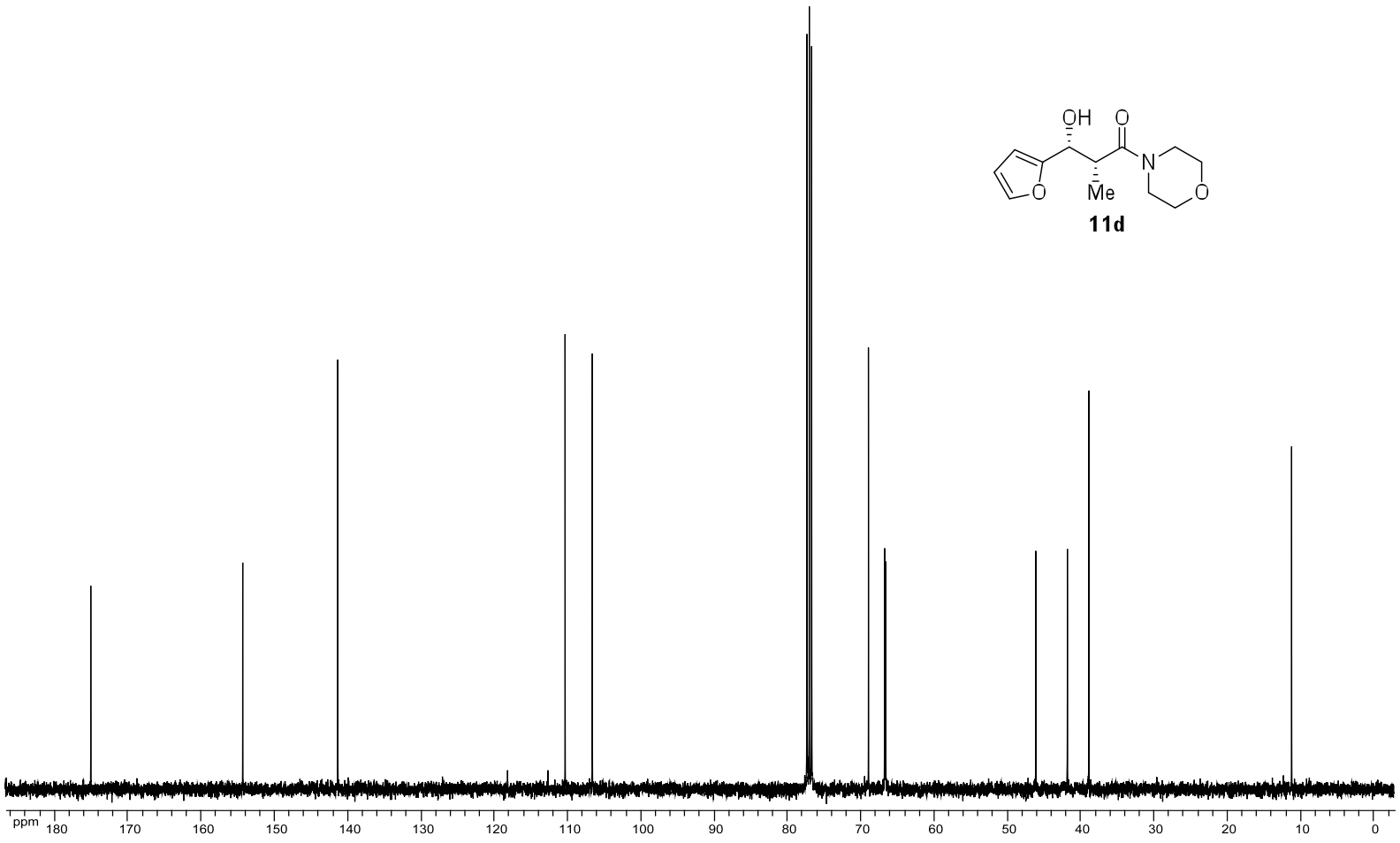
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11c**



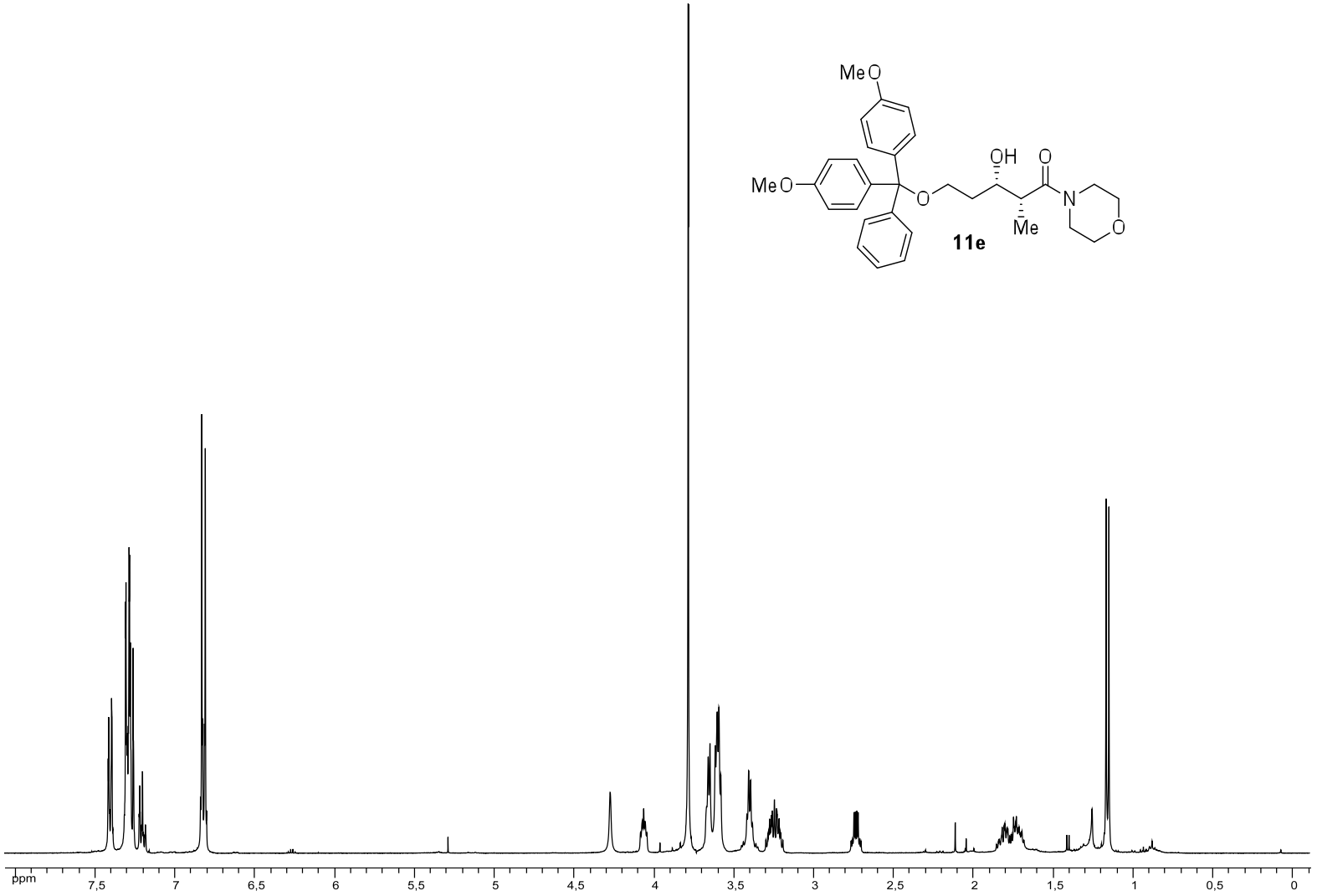
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11d**



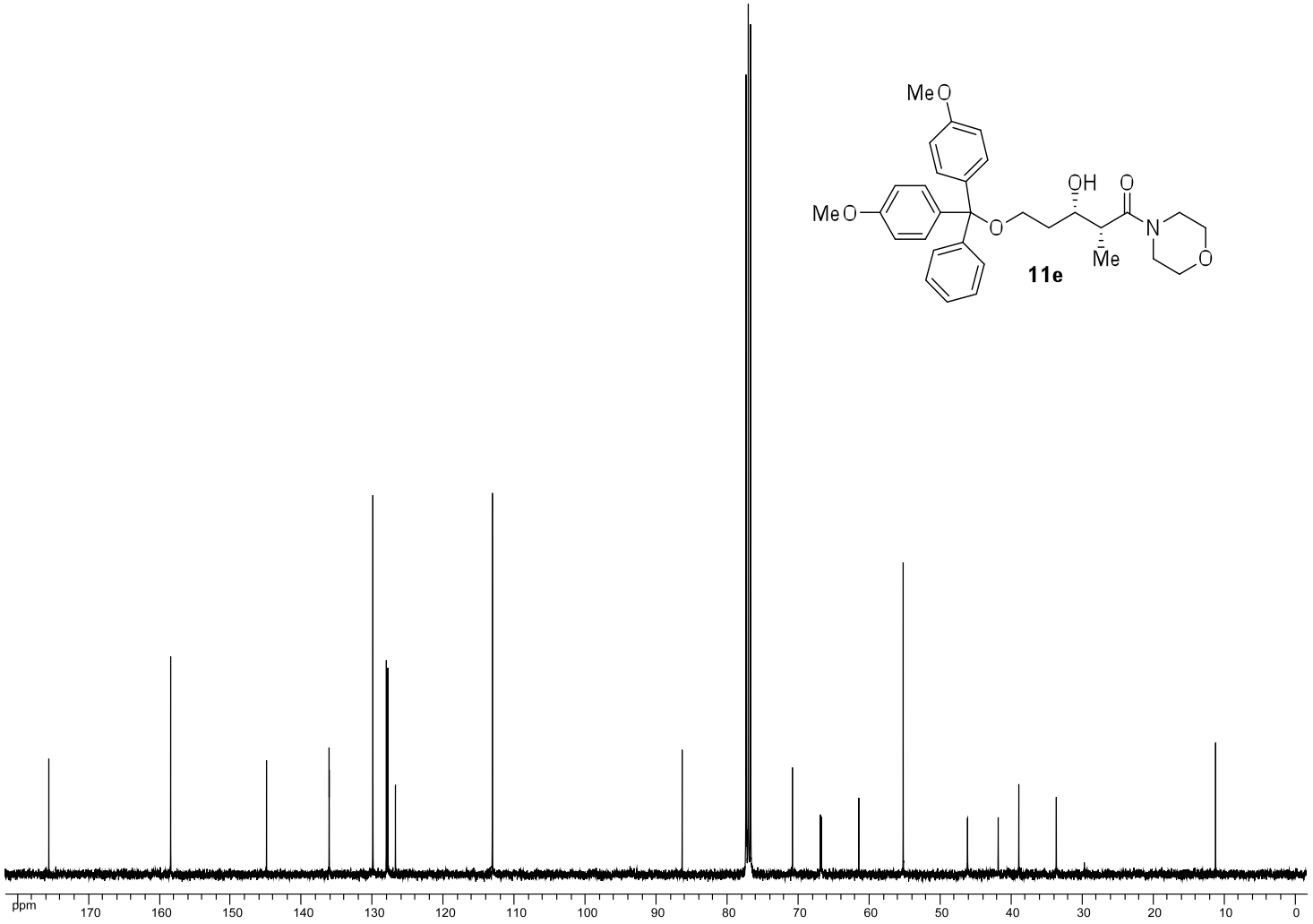
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11d**



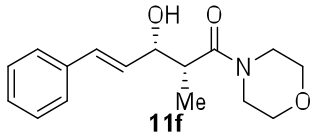
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11e**



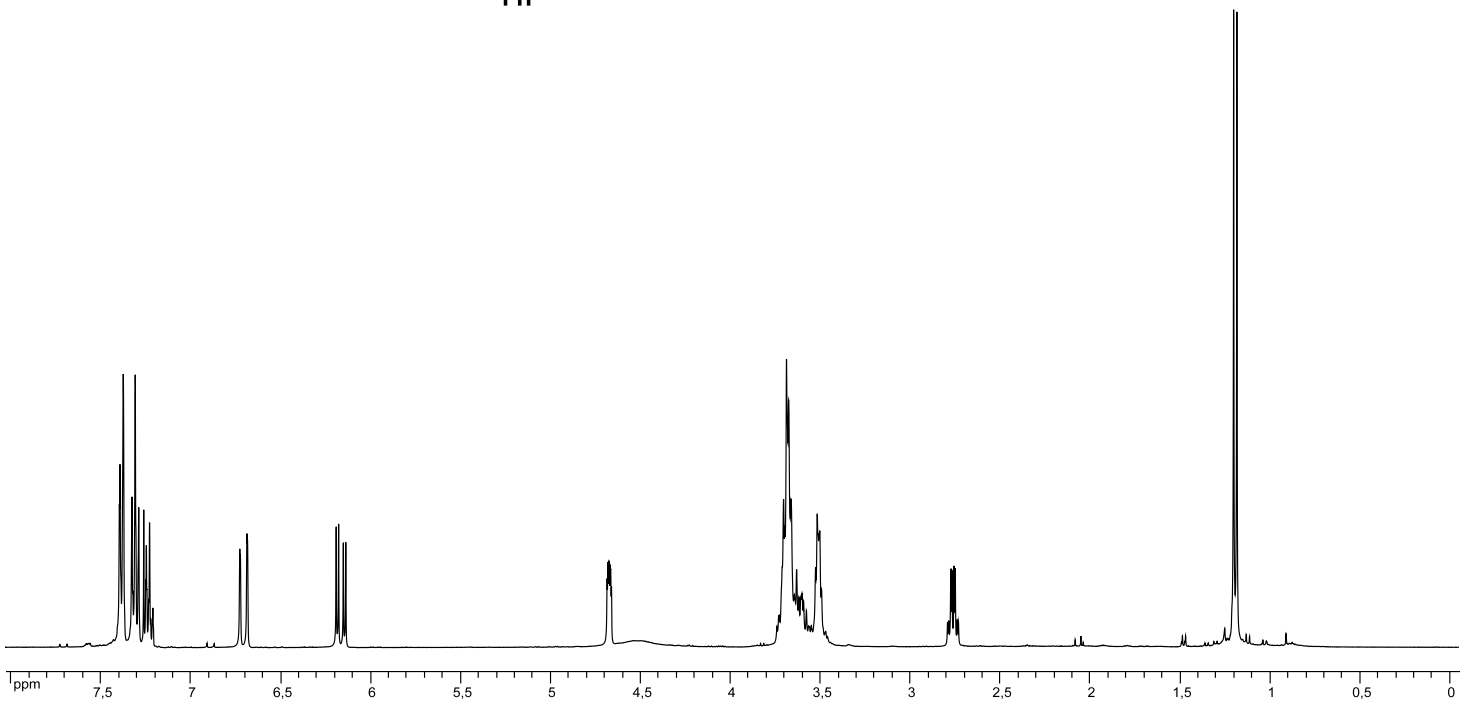
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11e**



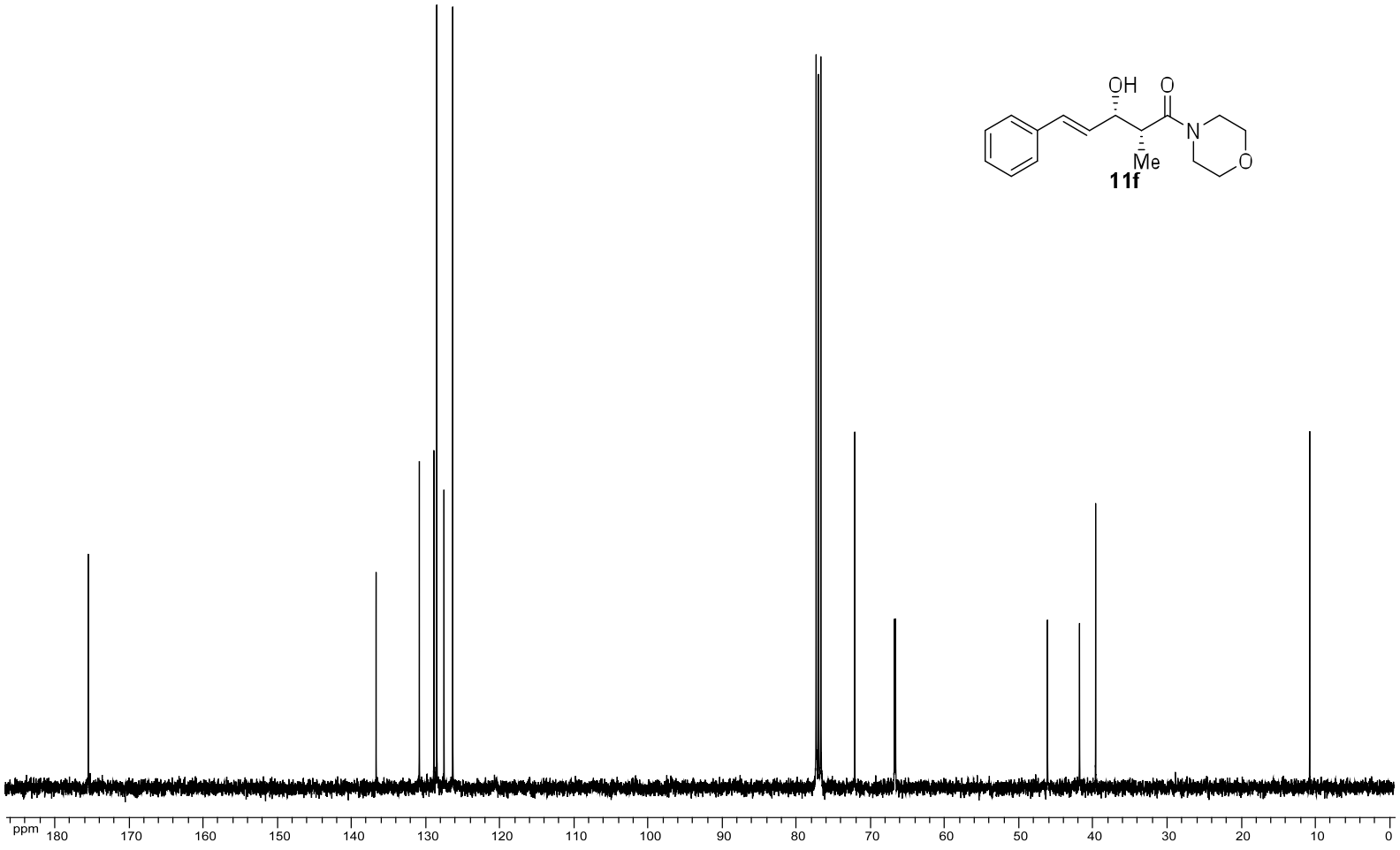
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **11f**



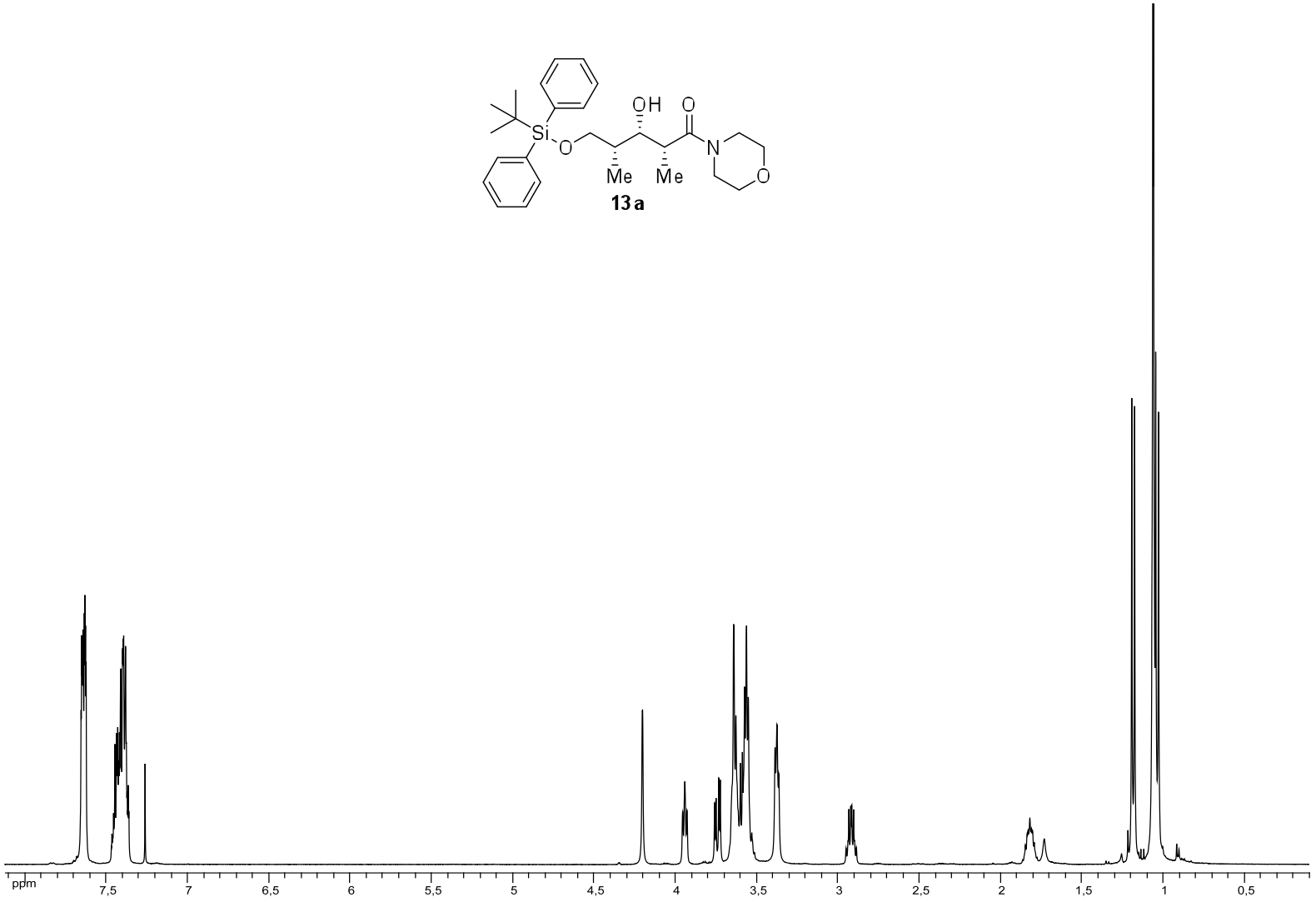
11f



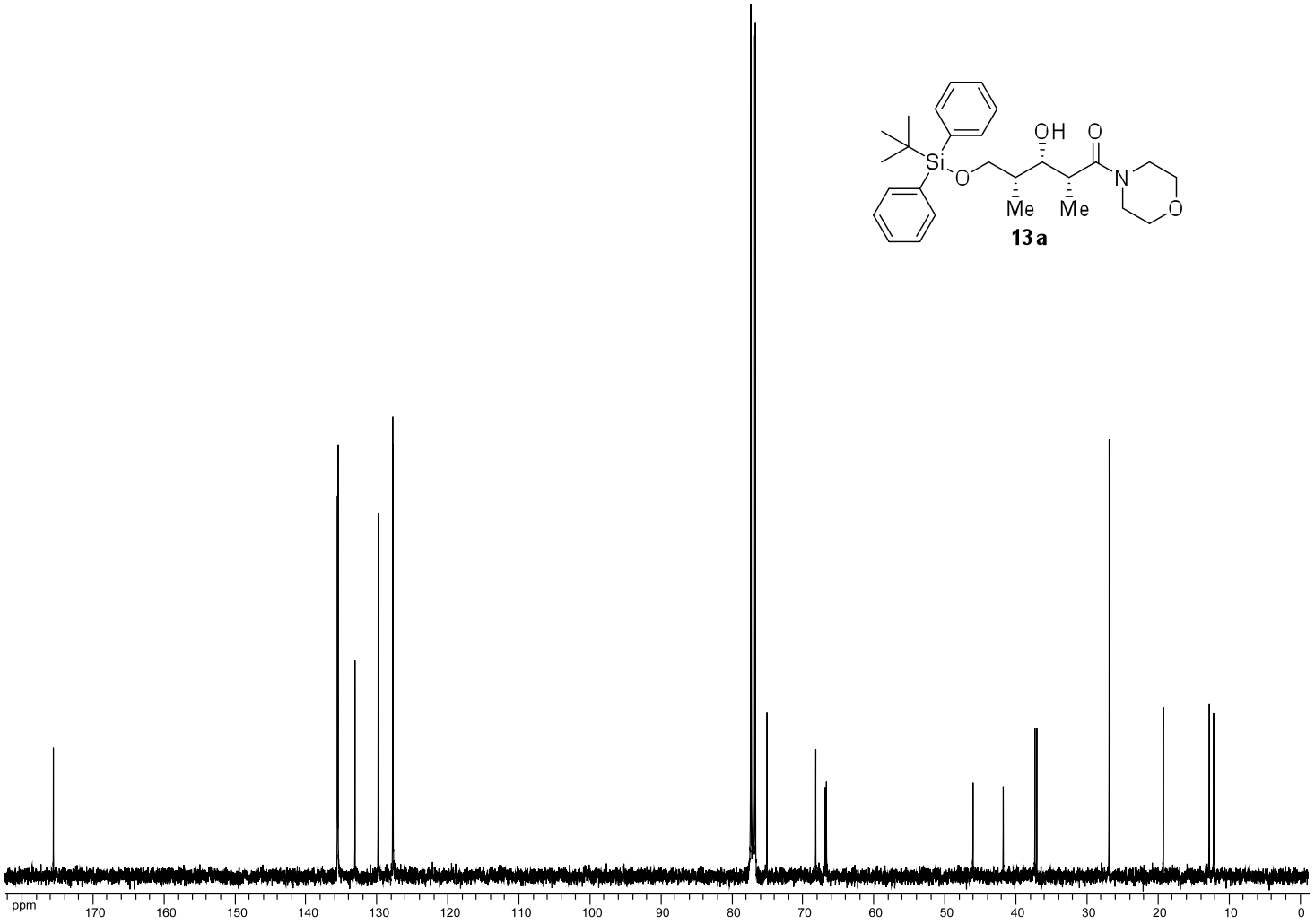
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **11f**



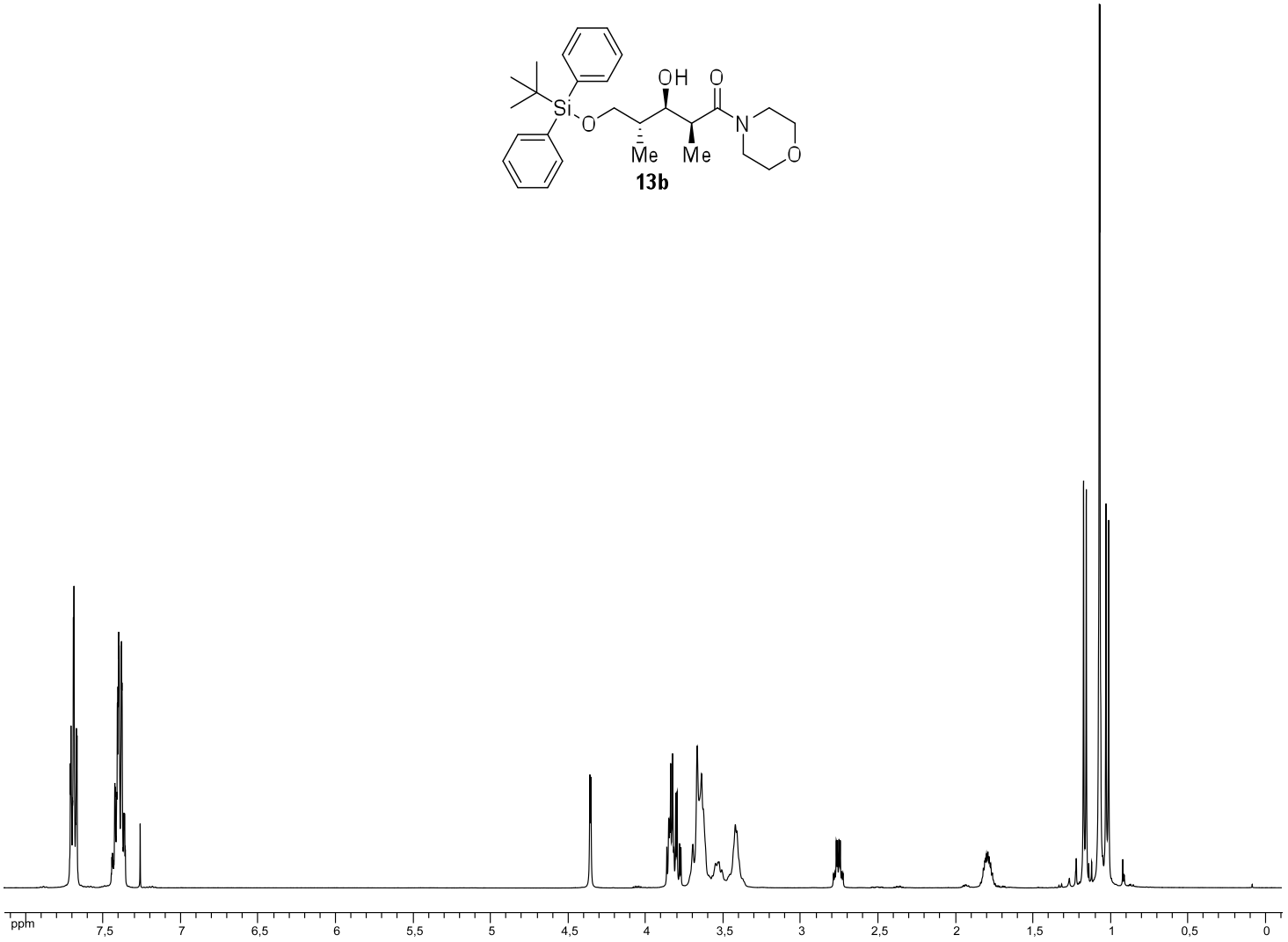
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13a**



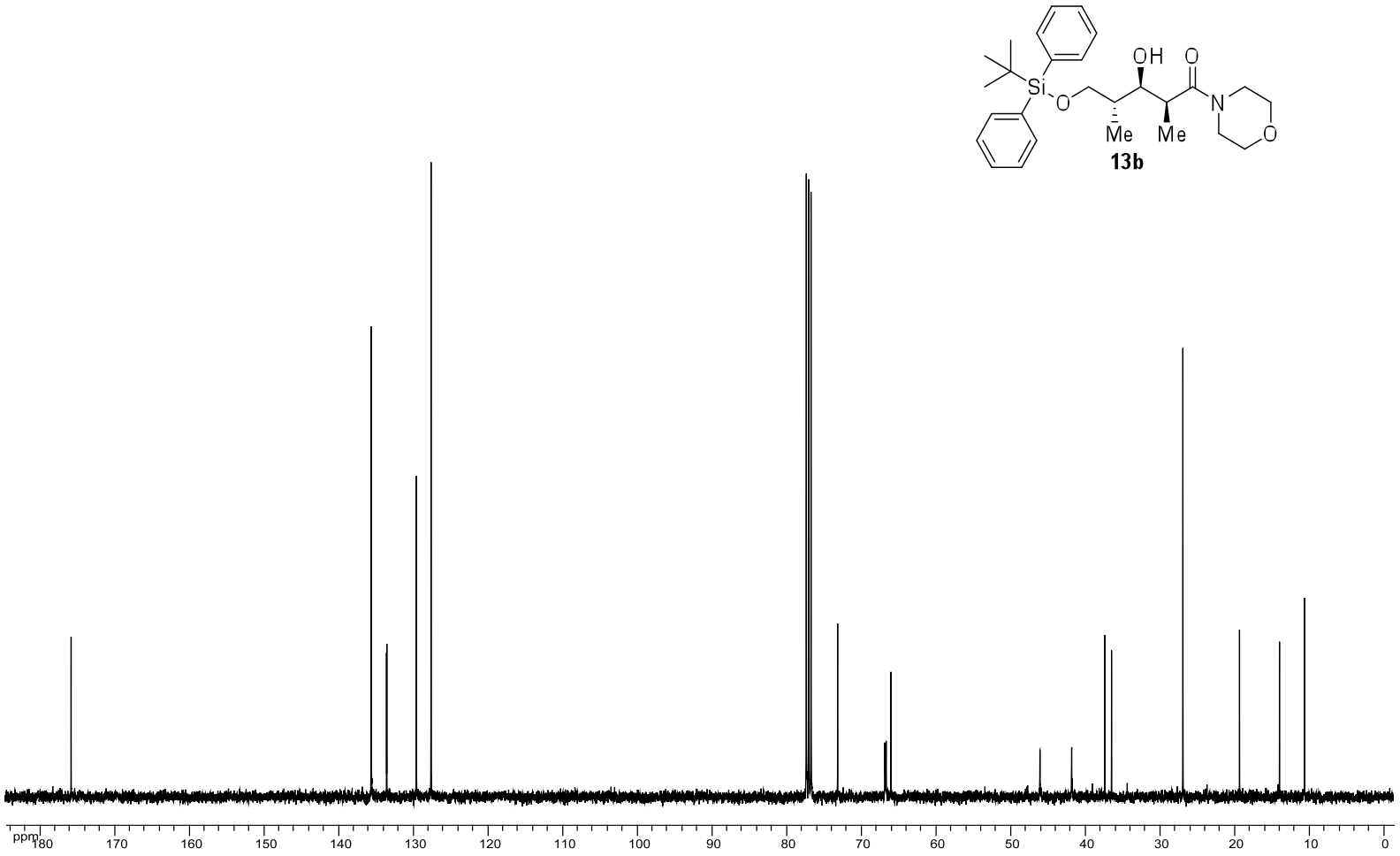
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13a**



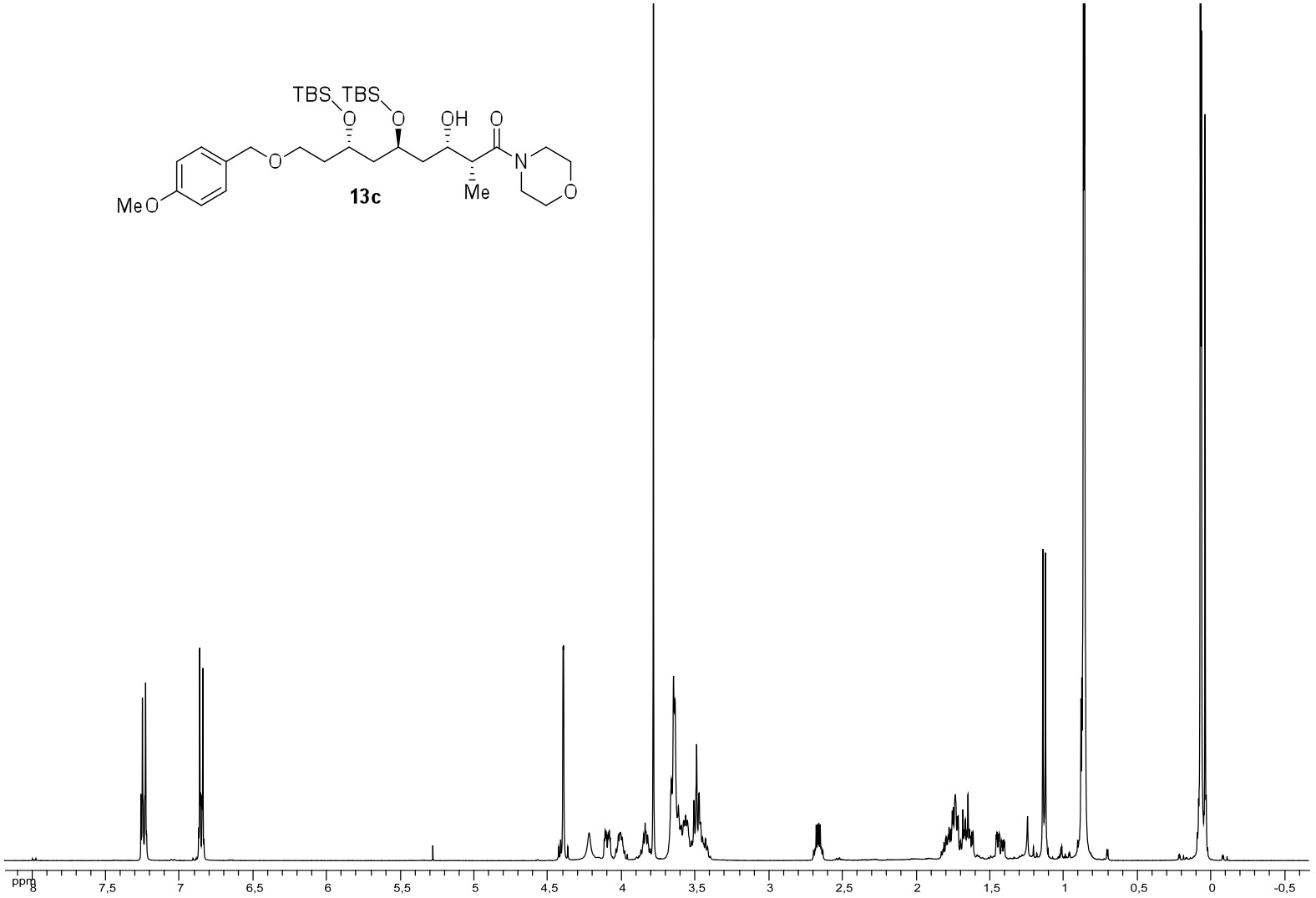
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13b**



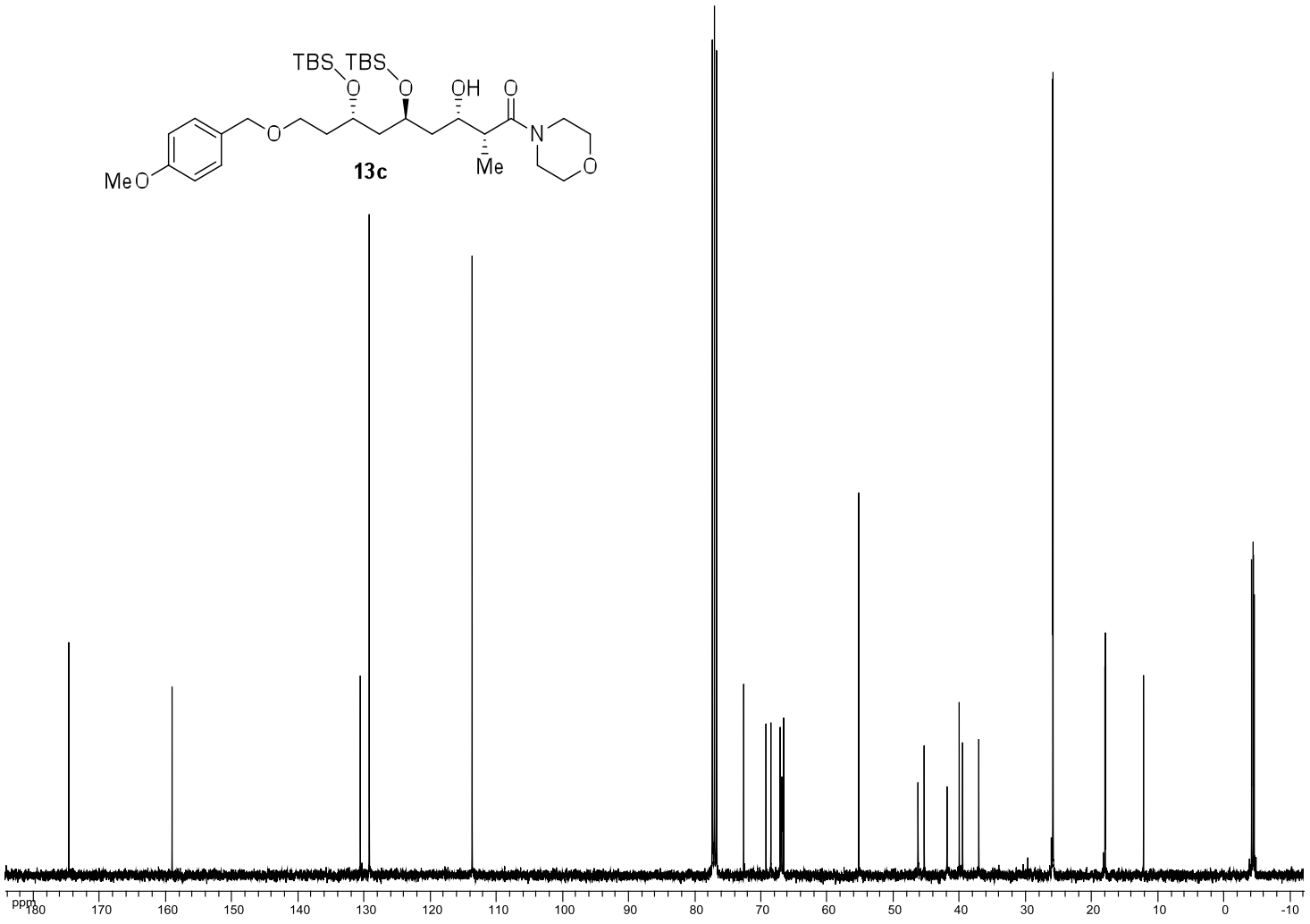
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13b**



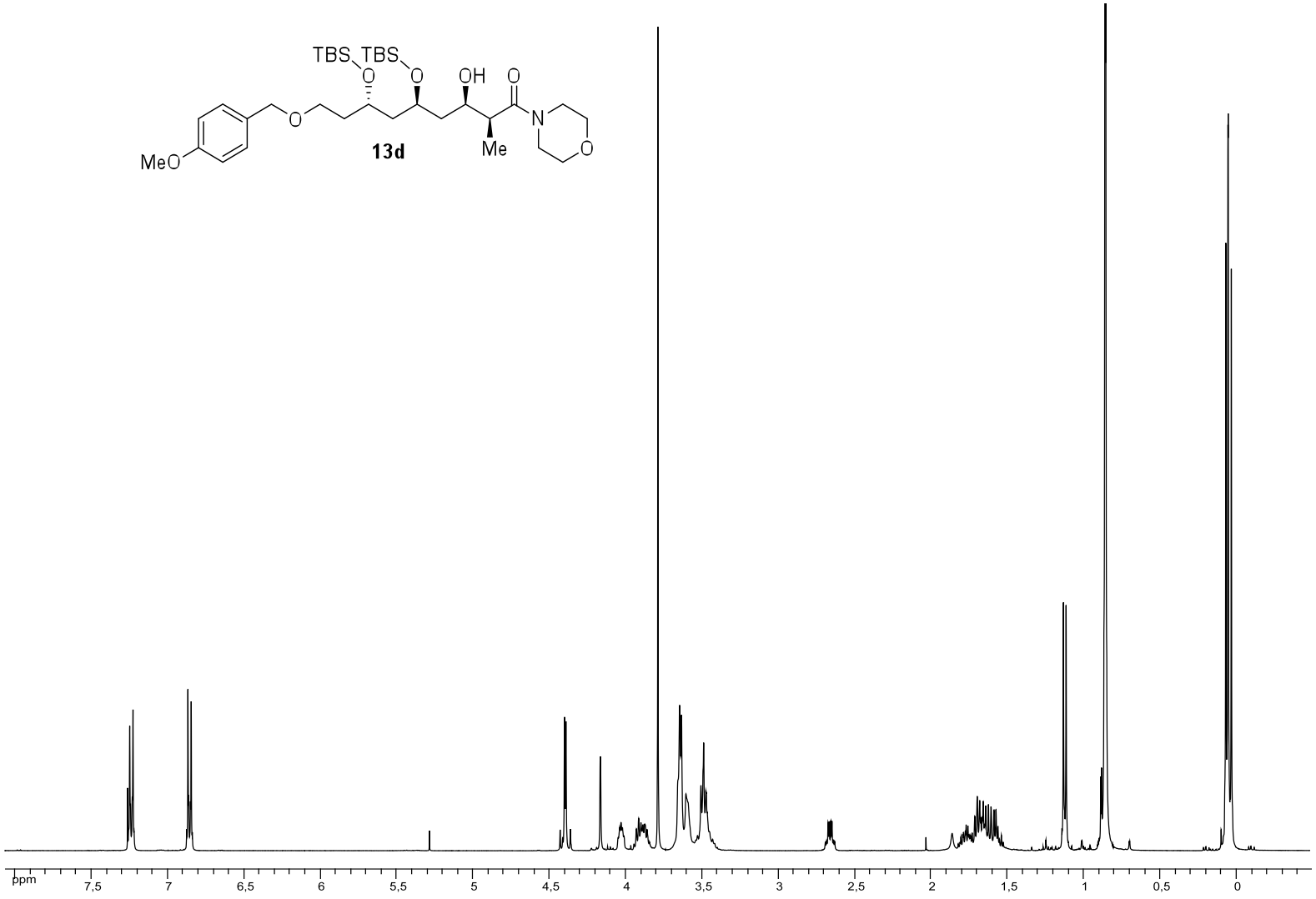
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13c**



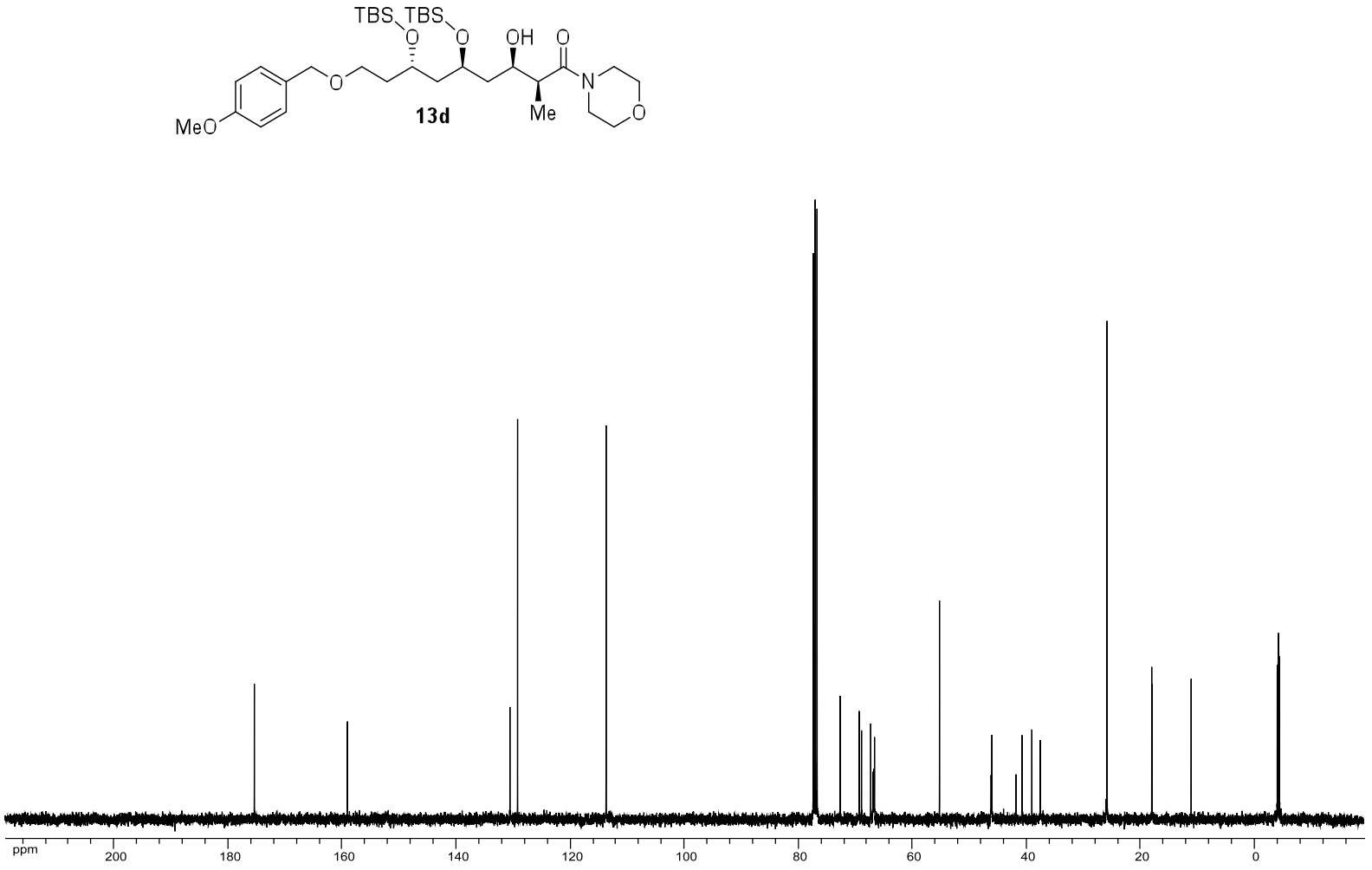
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13c**



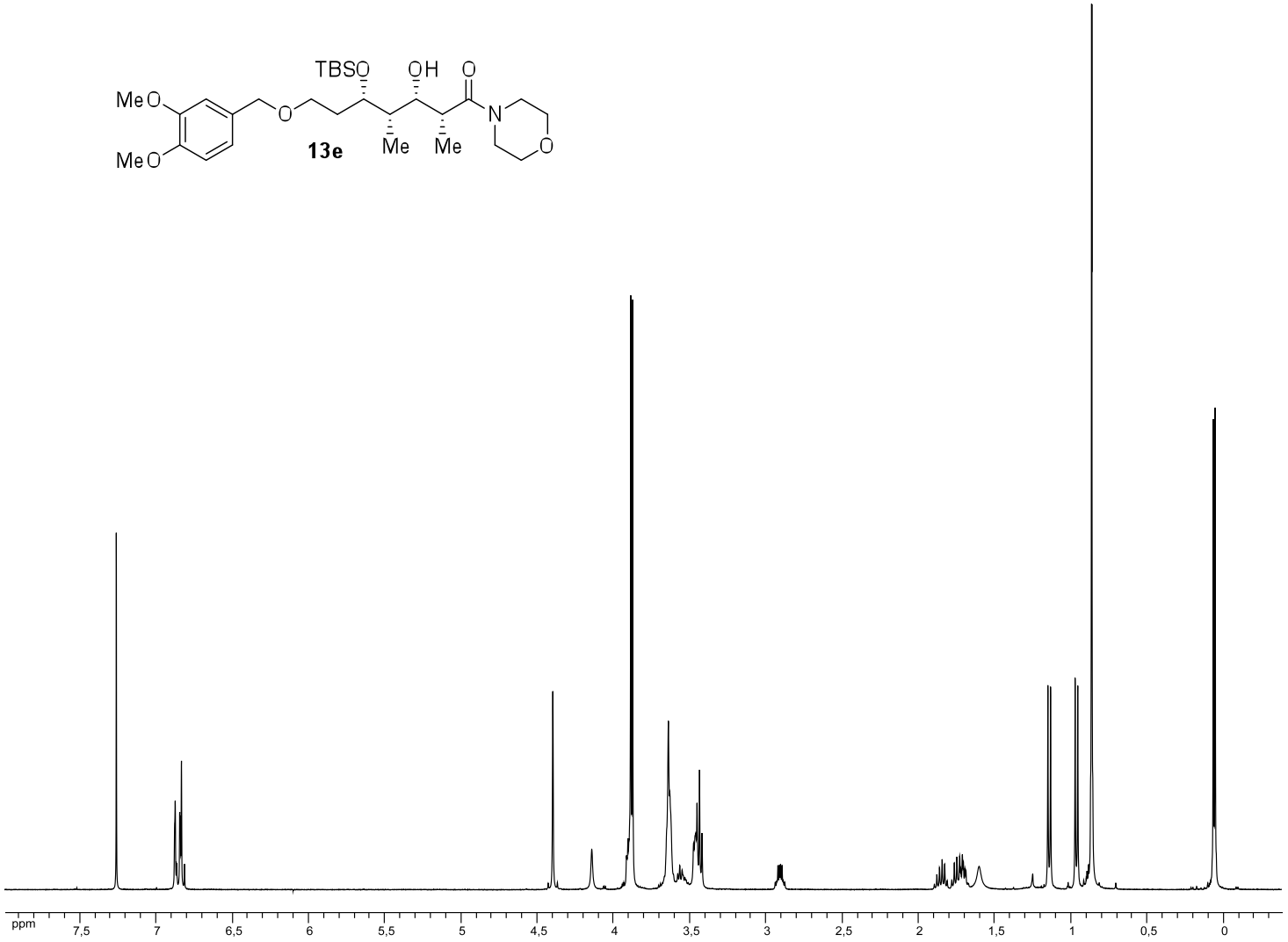
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13d**



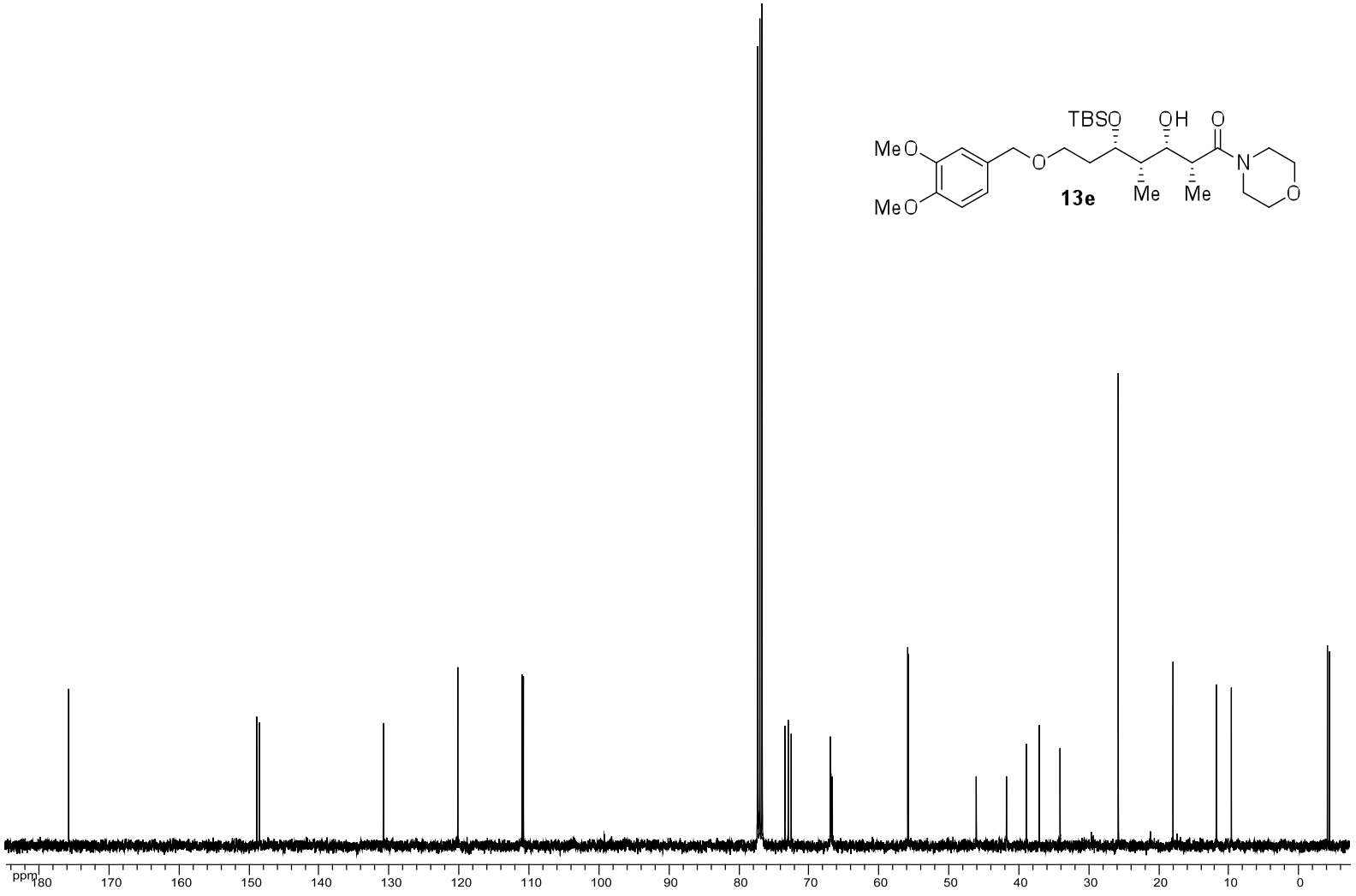
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13d**



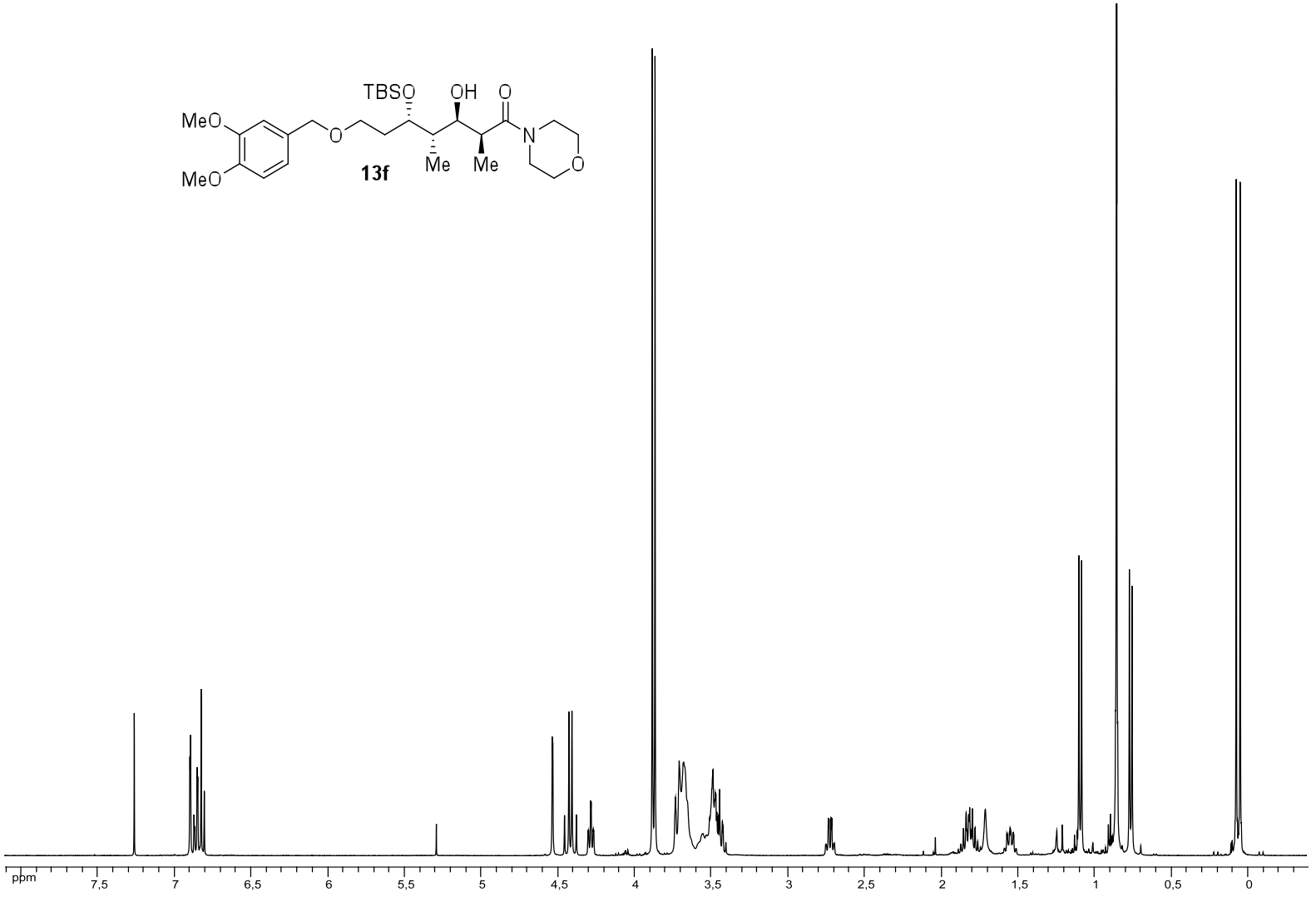
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13e**



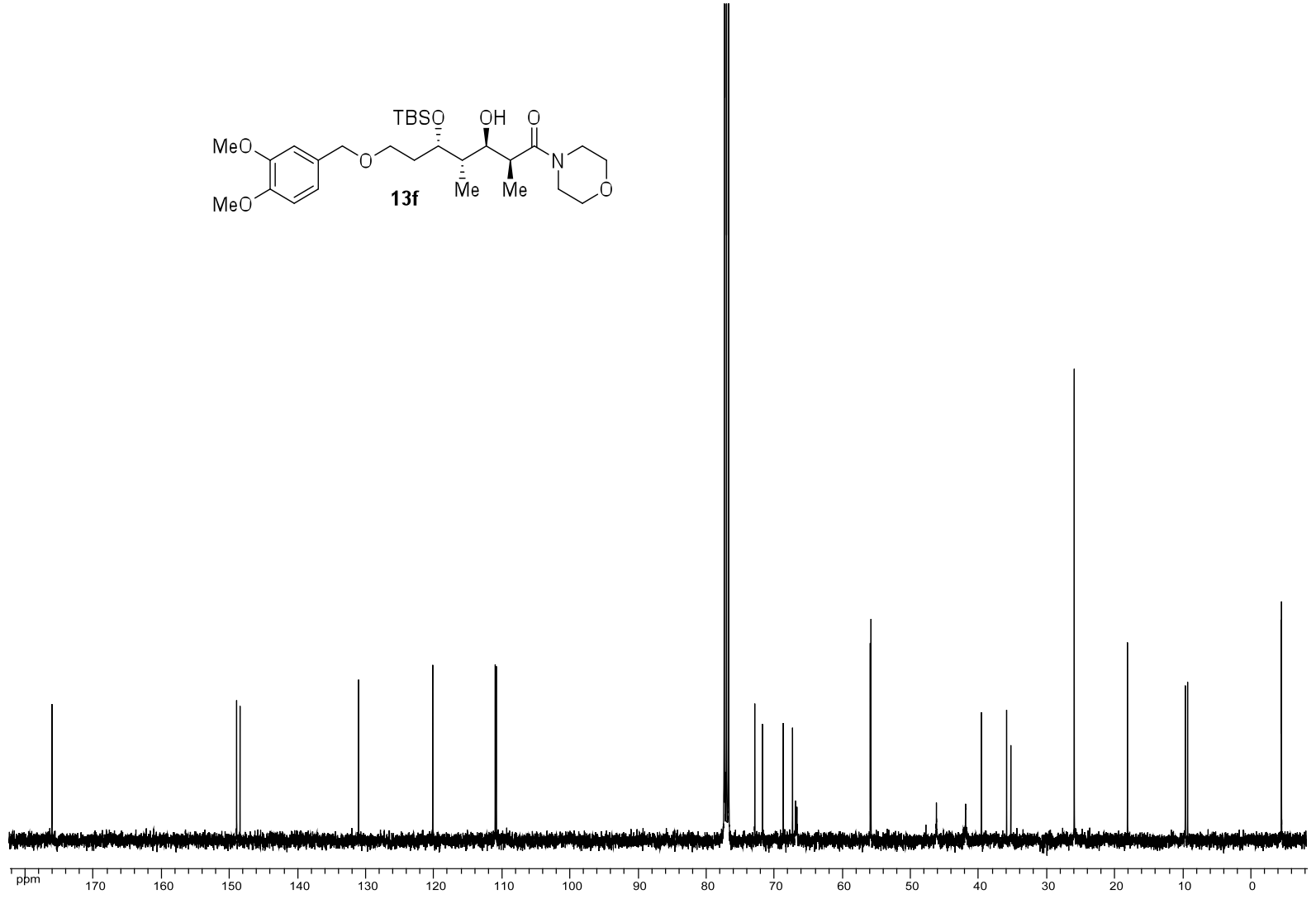
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13e**



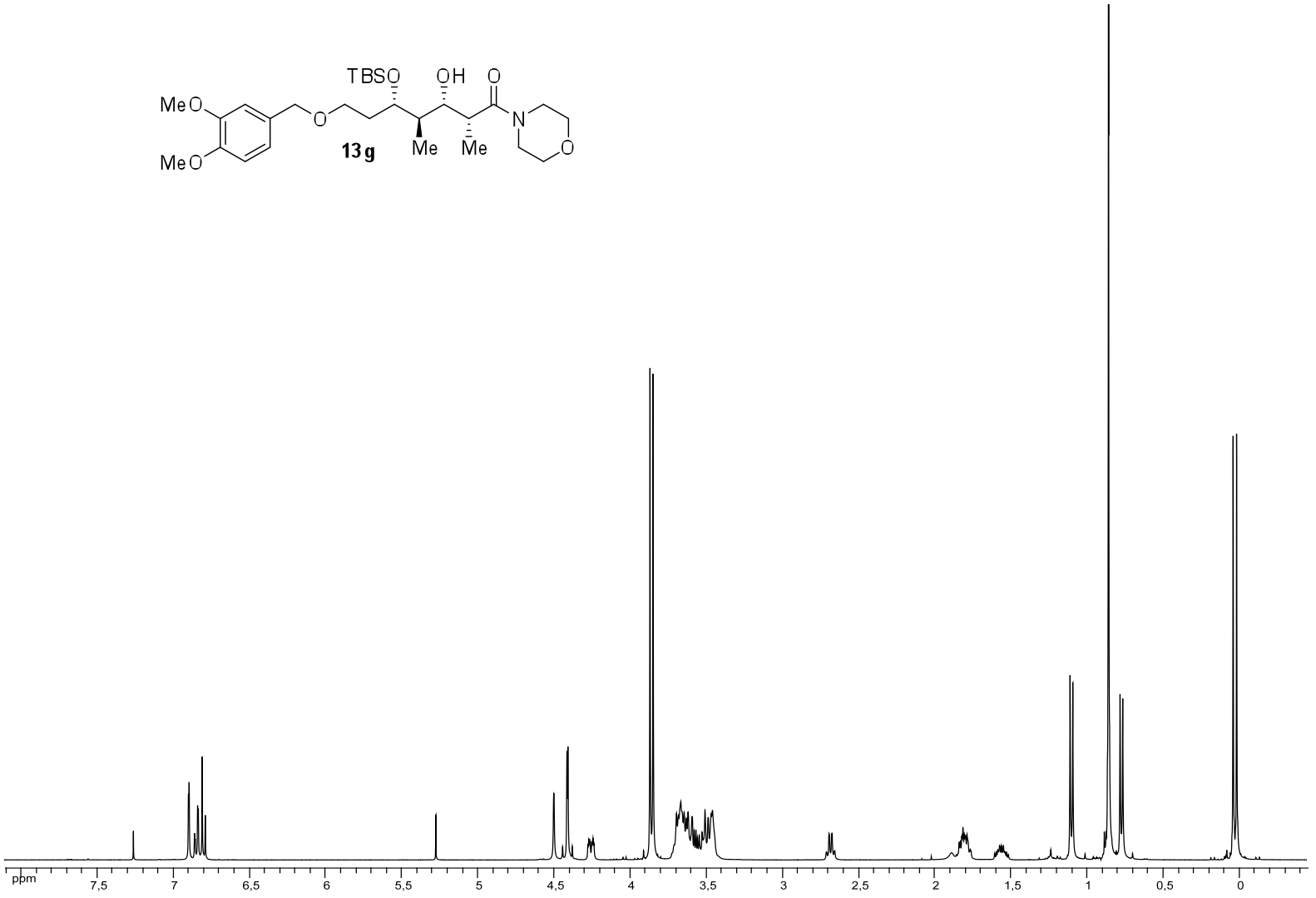
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13f**



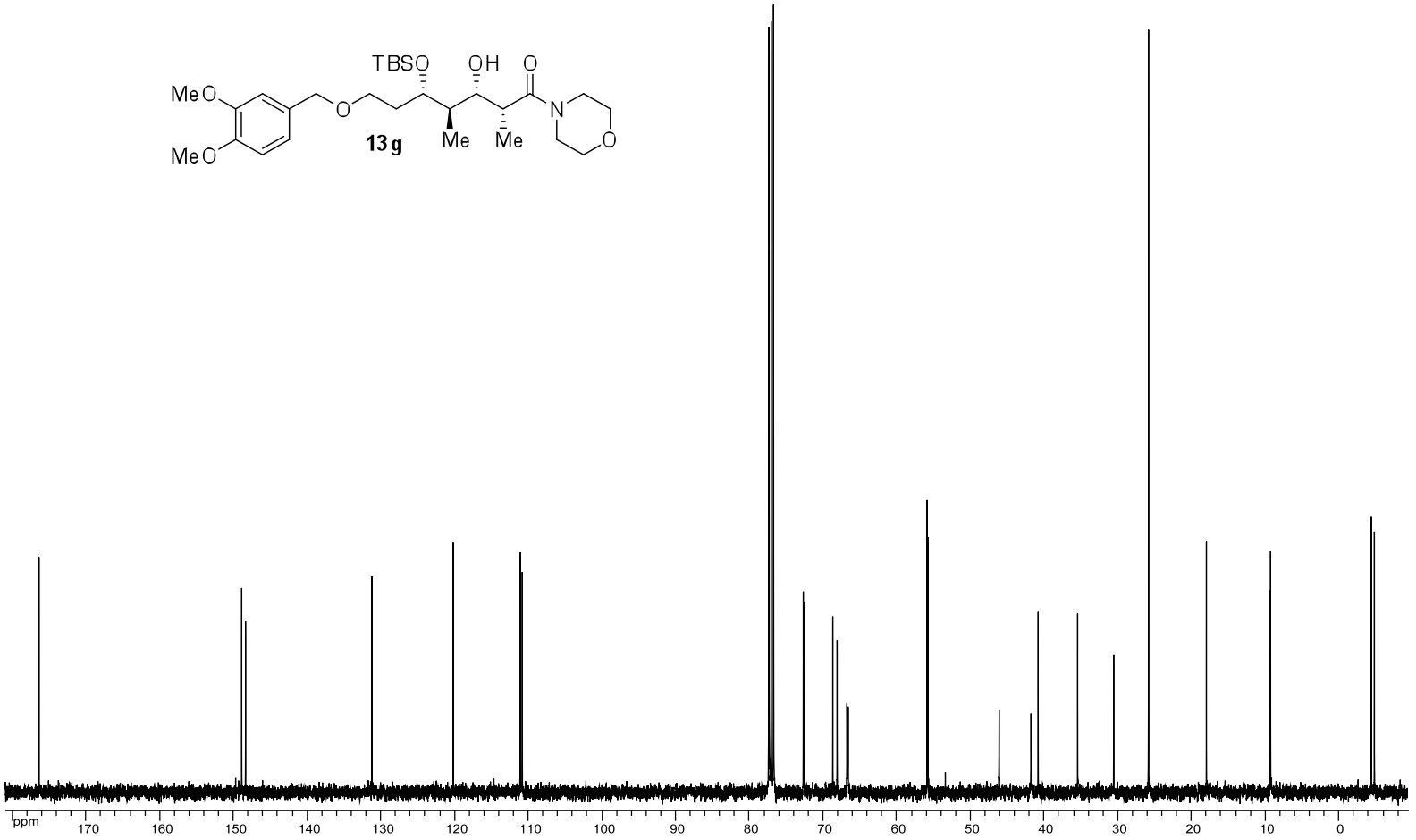
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13f**



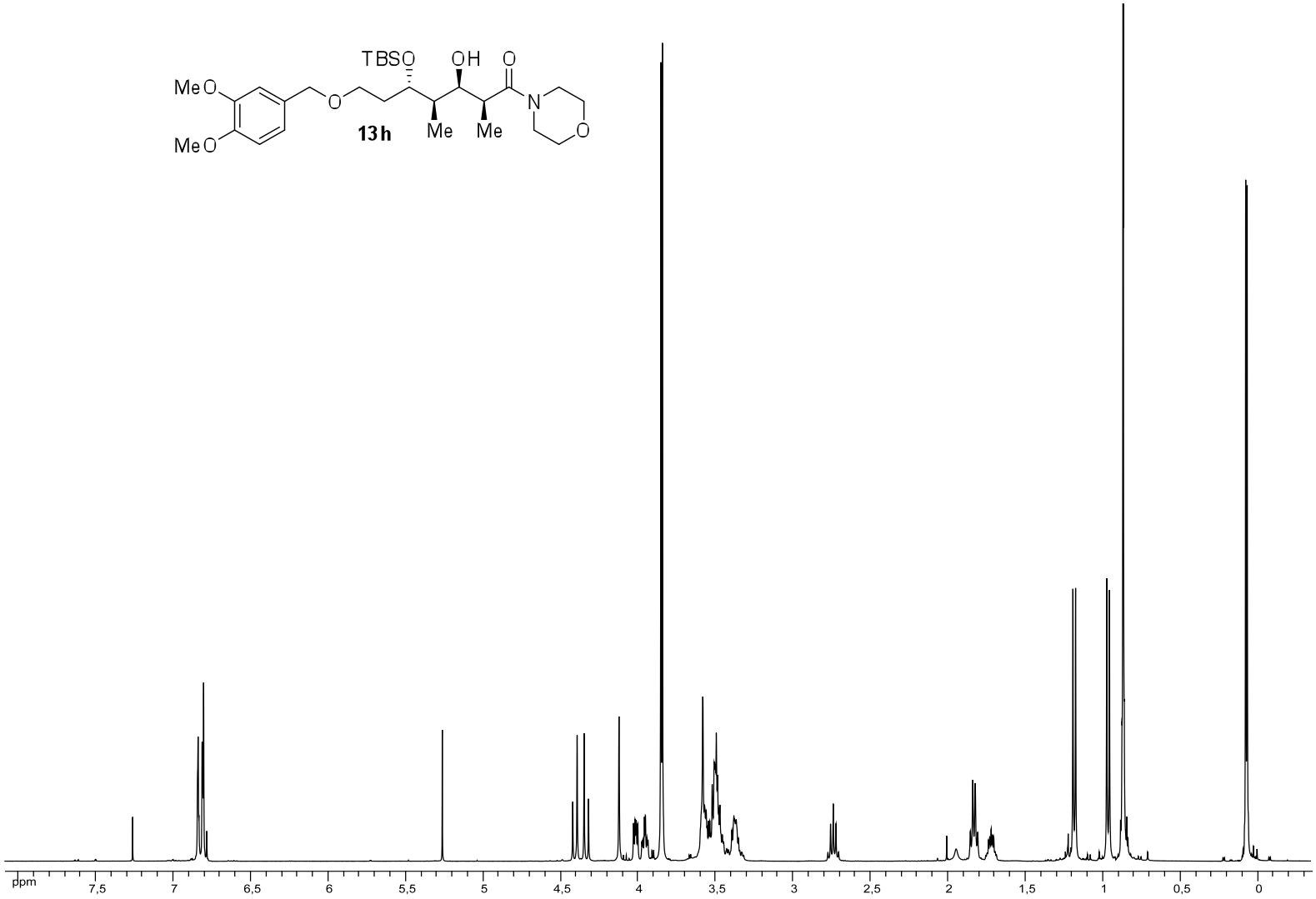
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13g**



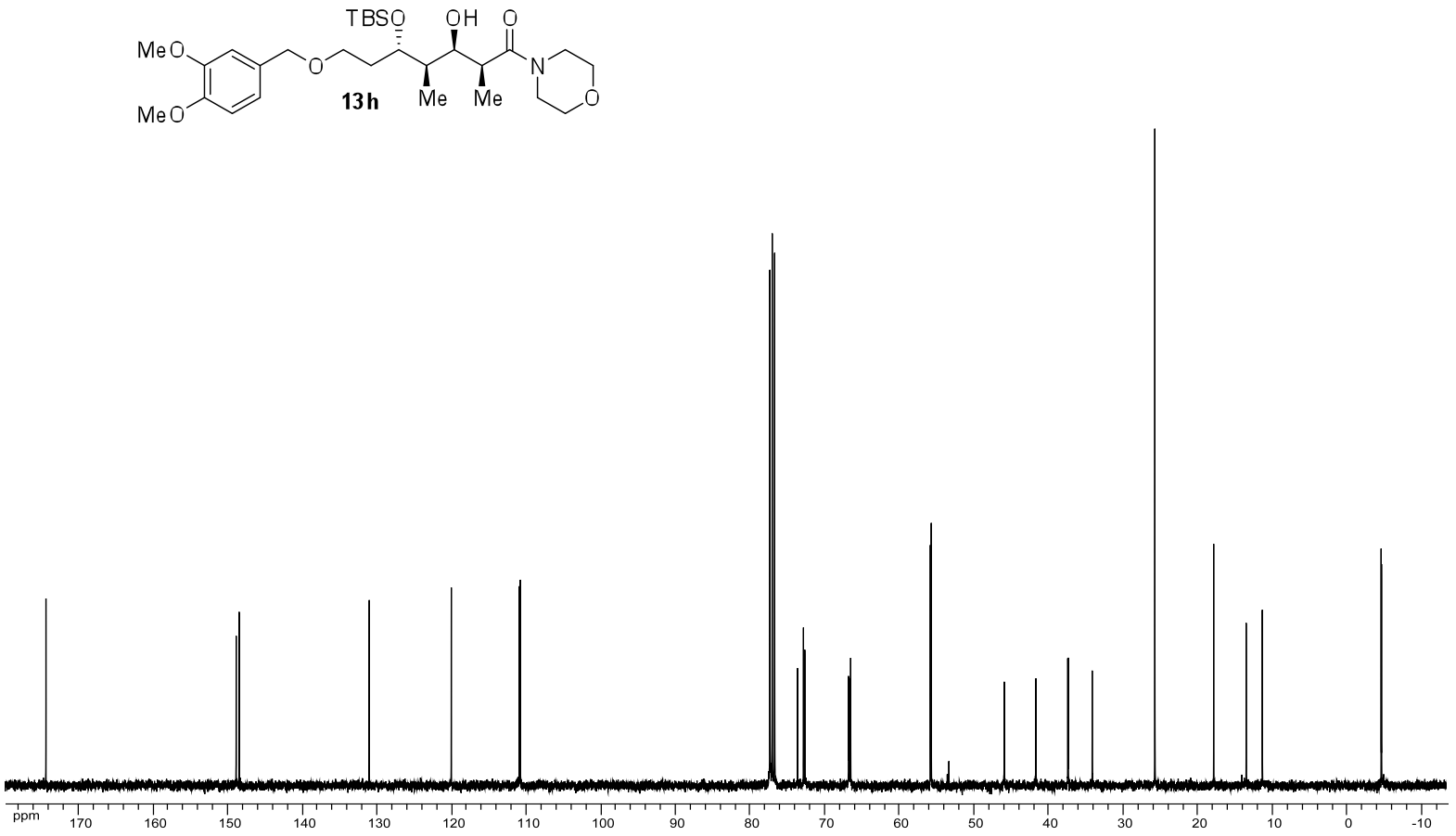
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13g**



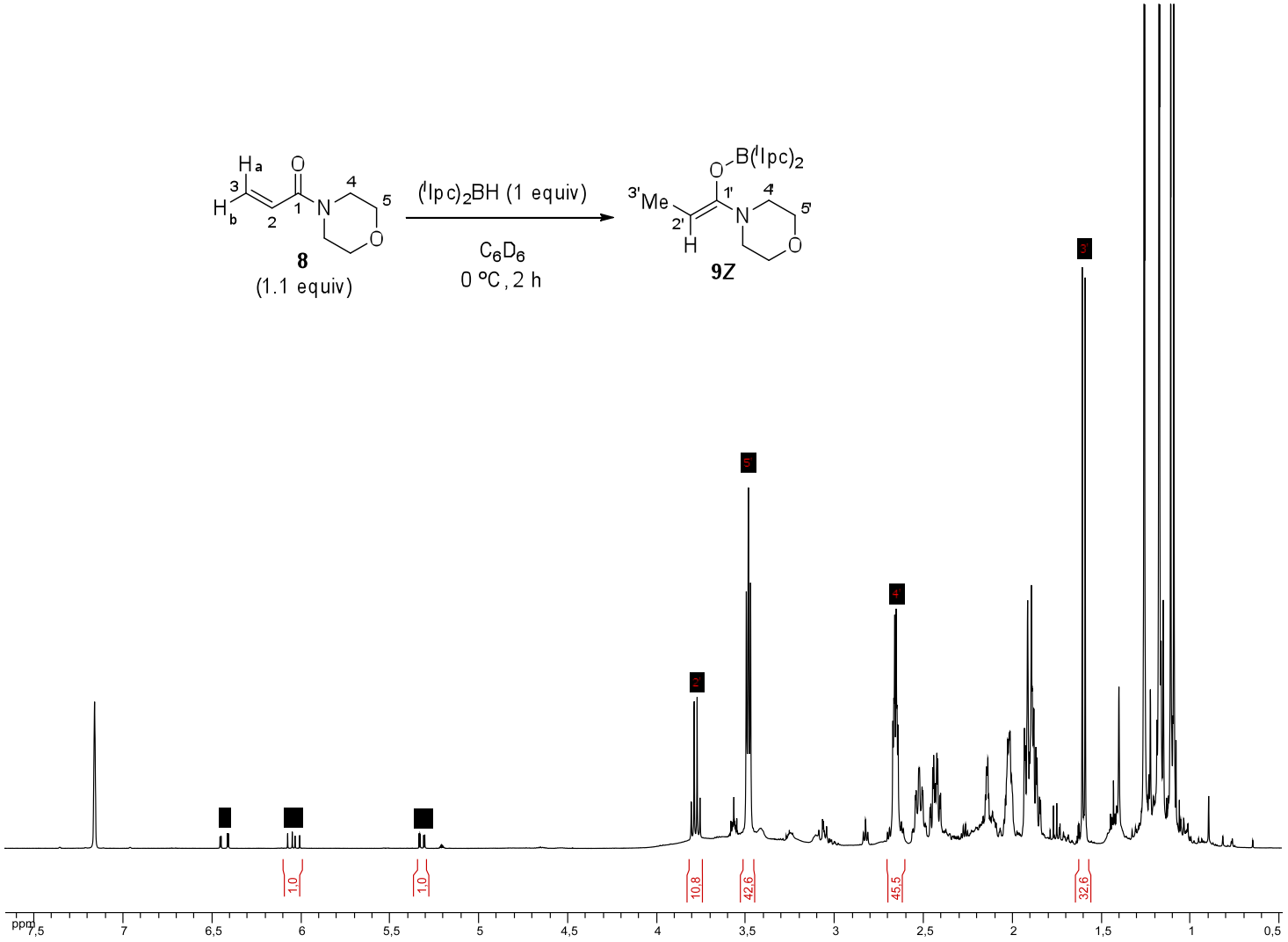
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **13h**



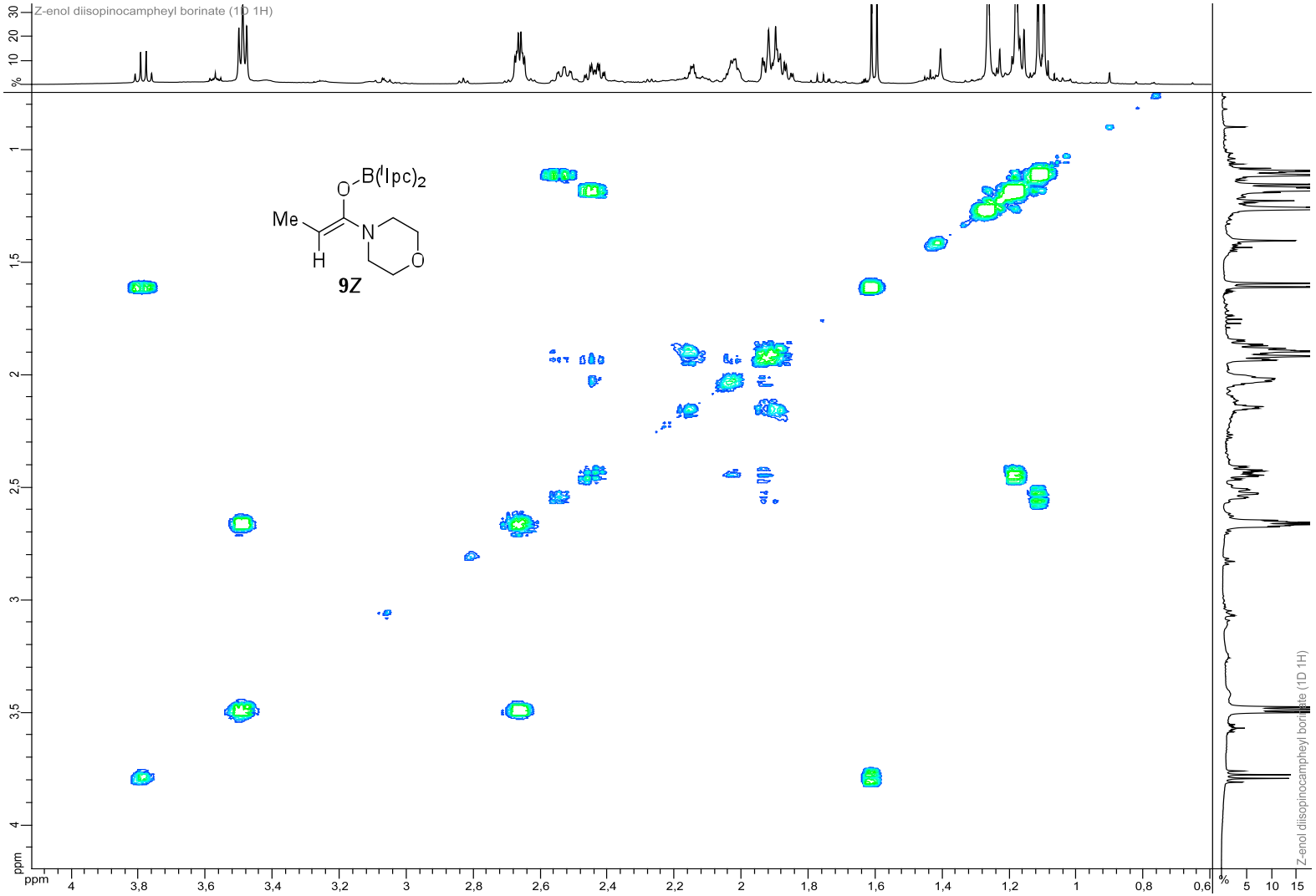
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound **13h**



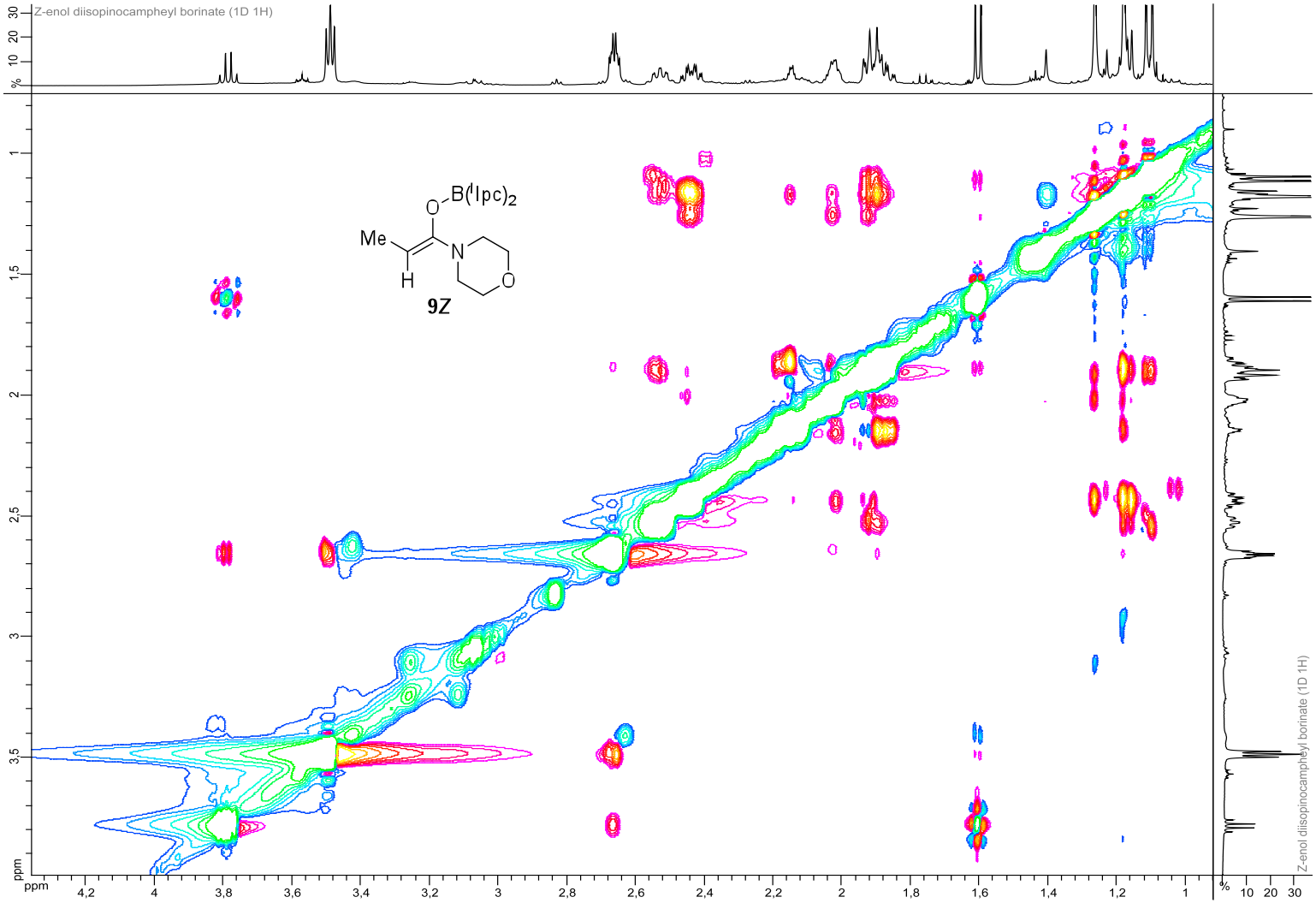
^{1}H NMR (400 MHz, C_6D_6) spectrum of **diisopinocampheyl enolborinate 9*Z*** (crude from hydroboration; mixture of **9*Z*** and **8** in a 11:1 ratio)



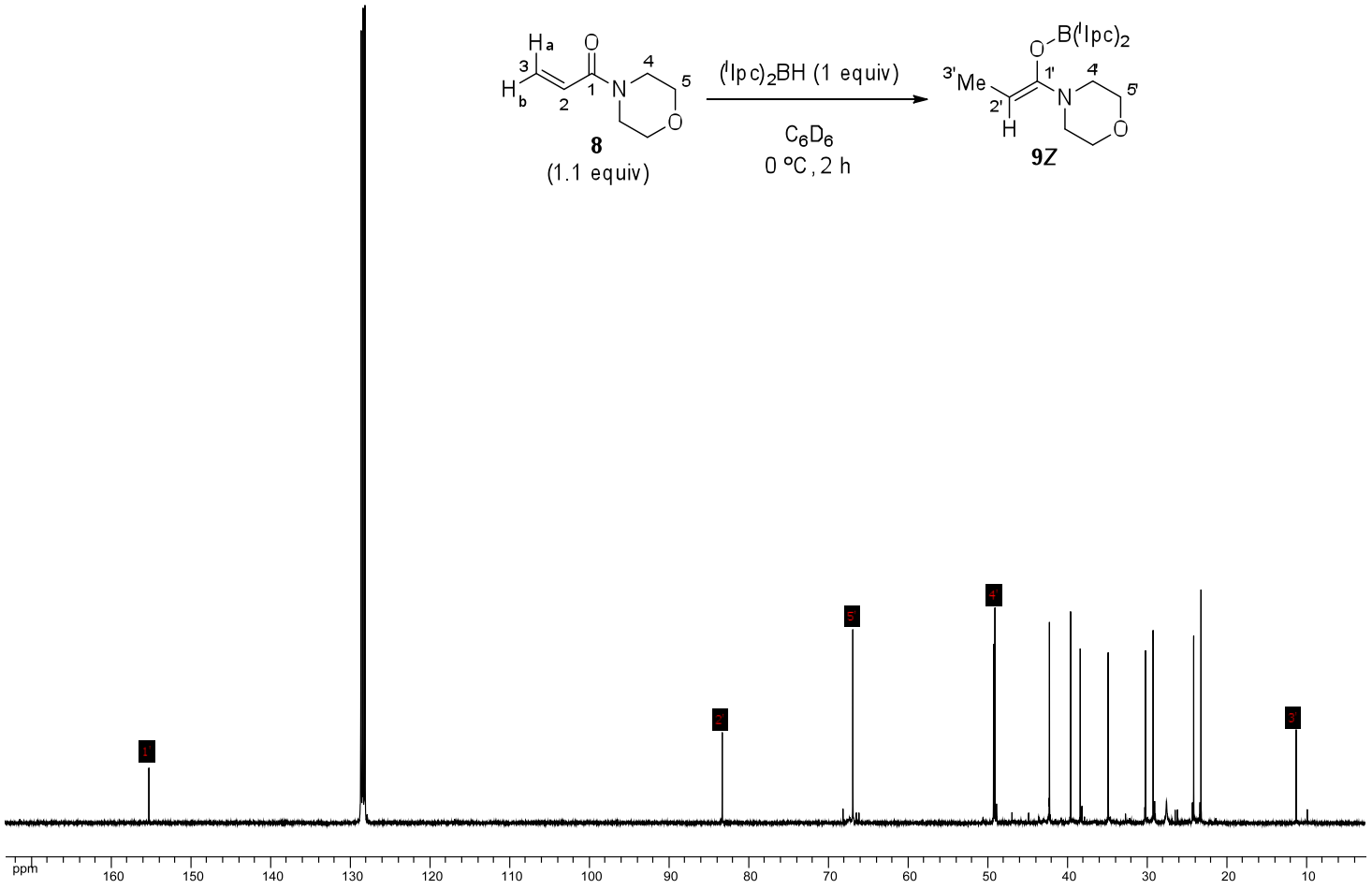
COSY (400 MHz, C_6D_6) spectrum of **diisopinocampheyl enolborinate 9*Z*** (crude from hydroboration; mixture of **9*Z*** and **8** in a 11:1 ratio)



NOESY (400 MHz, C_6D_6) spectrum of **diisopinocampheyl enolborinate 9*Z*** (crude from hydroboration; mixture of **9*Z*** and **8** in a 11:1 ratio)

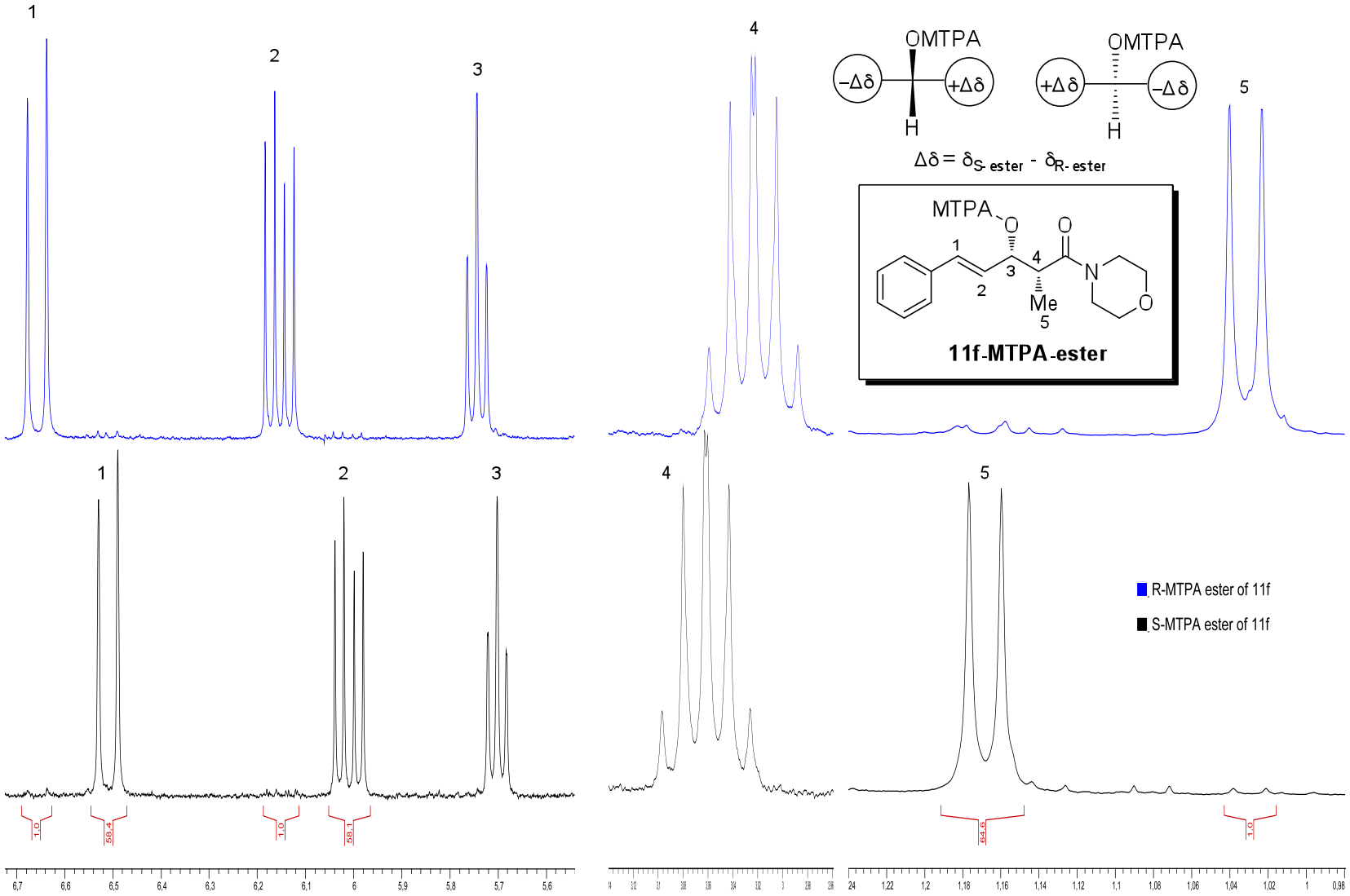


^{13}C NMR (100 MHz, C_6D_6) spectrum of **diisopinocampheyl enolborinate 9*Z*** (crude from hydroboration; mixture of **9*Z*** and **8** in a 11:1 ratio)



^{1}H NMR (400 MHz, $CDCl_3$) data for **11f-MTPA-ester**

Key portions of the ^{1}H NMR spectra of the Mosher ester derivatives of **11f** used for ee determination and absolute stereochemistry assignment are reproduced below.



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