Supporting Information

A Flexible Route to Chiral 2-*Endo*-Substituted 9-Oxabispidines and their Application in the Enantioselective Oxidation of Secondary Alcohols

Matthias Breuning,* Melanie Steiner, Christian Mehler, Alexander Paasche, and David Hein

Institute of Organic Chemistry, University of Würzburg, Am Hubland, 97074 Würzburg, Germany
breuning@chemie.uni-wuerzburg.de

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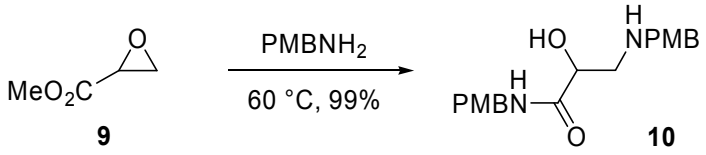
1. General information

Reactions with anhydrous solvents, prepared by standard procedures, were performed under an argon atmosphere. All reactions were monitored by thin layer chromatography (TLC) on precoated silica gel; spots were visualized by UV light (254 nm) or by staining with aqueous $KMnO_4$ solution or I_2. The peak assignments in the ^1H and ^{13}C NMR data were made on basis of 2D NMR methods (COSY, HMQC, HMBC). The enantiomeric excess (ee) of the alcohols **27** and **28** was determined by chiral HPLC.

(*R*)-Epichlorohydrin (**11**, 97% ee), (*R*)-3-aminopropane-1,2-diol (**17**, 98% ee), phenyl magnesium bromide (1.0 M in THF), ethyl magnesium bromide (3.0 M in Et_2O), 1-indanol (**27**), 1-(4-methoxyphenyl)ethanol (**28a**), 1-phenylethanol (**28c**), 1-phenylpropan-1-ol (**28d**), $Pd(nbd)Cl_2$ and $PdBr_2$ are commercially available and were used as received. Methyl glycidate (**9**),[1] 3-benzyloxy-2-bromopropionic acid (**16**),[2] 4-(*tert*-butyldimethylsilyloxy)butylmagnesiumbromide,[3] and 1-(3,4-dimethoxyphenyl)ethanol (**28b**)[4] were prepared according to literature procedures.

2. Synthesis of the *N*-Boc-9-oxabispidin-2-one 8 starting from 9

2.1 2-Hydroxy-*N*-(4-methoxybenzyl)-3-(4-methoxybenzylamino)propionamide (10)



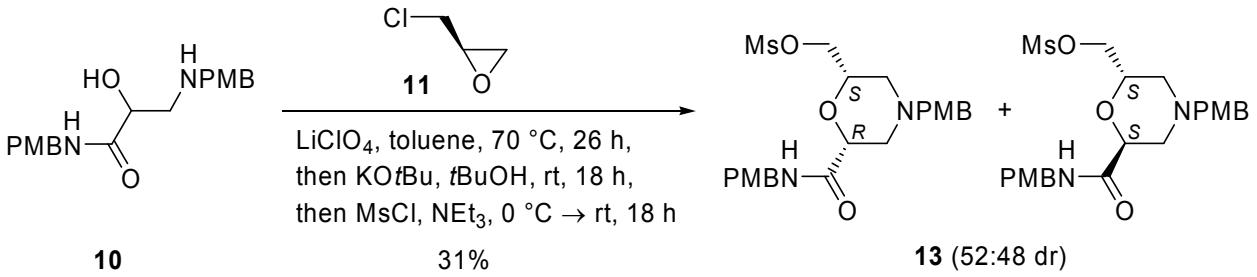
9 **10**

PMB: *para*-methoxybenzyl

A solution of 4-methoxybenzylamine (5.12 mL, 5.38 g, 39.2 mmol) and methyl glycidate (**9**, 858 µL, 1.00 g, 9.80 mmol) was stirred for 6 h at 60 °C. The precipitate formed was collected by suction through a sintered glass funnel and washed with CH_2Cl_2 (3 mL) and MeOH (3 mL). A second crop was obtained after addition of *n*-pentane (30 mL) to the mother liquor. The two precipitates were combined and dried under reduced pressure to give **10** (3.34 g, 9.69 mmol, 99%) as a white solid. Mp. 119–121 °C. ^1H NMR (400 MHz, $CDCl_3$): δ 2.50–3.50 (br s, 2H, NH, OH), 2.96 (dd, J = 12.3, 6.2 Hz, 1H, 3-H), 3.01 (dd, J = 12.3, 5.9 Hz, 1H, 3-H), 3.67 (d, J = 13.0 Hz, 1H, C*H*HAr), 3.72 (d, J = 12.9 Hz, 1H, CH*H*Ar), 3.79 (s, 6H, OMe), 4.03 (t, J = 6.1 Hz, 1H, 2-H), 4.38 (pseudo-t, J = 5.8 Hz, 2H, CH_2Ar), 6.83 (d, J = 7.1 Hz, 2H, Ar-H), 6.85 (d, J = 7.0 Hz, 2H, Ar-H), 7.13 (d, J = 8.6 Hz, 2H, Ar-H), 7.19 (d, J = 8.7 Hz, 2H, Ar-H), 7.50 (br s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 42.6 (CH_2Ar), 51.1 (C-3), 52.8 (CH_2Ar), 55.2 (OMe), 55.3 (OMe), 69.1 (C-2), 113.9, 114.1, 129.1, 129.4, 130.1, 131.3, 158.9, 159.0 (Ar-C), 172.8 (C=O). IR (KBr): 3280, 2833, 1646, 1514, 1306, 1247, 1179, 1131, 1033, 820 cm^{-1}. HRMS (ESI) calcd for $[C_{19}H_{24}N_2O_4 + H]^+$ 345.1809, found 345.1815. Anal. calcd for $C_{19}H_{24}N_2O_4$: C, 66.26; H, 7.02; N, 8.13. Found C, 65.92; H, 6.90; N, 8.04.

(1) Nemes, A.; Czibula, L.; Visky, G.; Farkas, M.; Kreidl, J. *Heterocycles* **1991**, *32*, 2329.
(2) Ward, R. S.; Pelter, A.; Goubet, D.; Pritchard, M. C. *Tetrahedron: Asymmetry* **1995**, 6, 469.
(3) (a) Tauh, P.; Fallis, A. G. *J. Org. Chem.* **1999**, *64*, 6960. (b) Fürstner, A.; Mlynarski, J.; Albert, M. *J. Am. Chem. Soc.* **2002**, *124*, 10274. (c) E. Vedejs, M. J. Arnost, J. P. Hagen, *J. Org. Chem.* **1979**, *44*, 3230.
(4) Koul, S.; Koup, J. L.; Taneja, S. C.; Dhar, K. L.; Jamwal, D. S.; Singh, K.; Reen, R. K.; Singh, J.; *Bioorg. Med. Chem.* **2000**, *8*, 251.

2.2 (6*S*)-6-(Methanesulfonyloxymethyl)-4-(4-methoxybenzyl)morpholine-2-carboxylic acid 4-methoxybenzylamide (13)



10 31% **13** (52:48 dr)

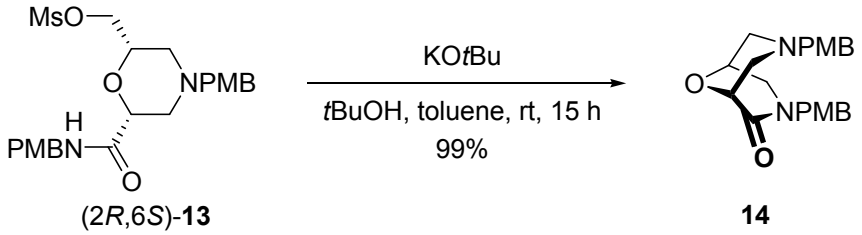
A suspension of **10** (2.00 g, 5.81 mmol), $LiClO_4$ (744 mg, 6.99 mmol) and (*R*)-epichlorohydrin (**11**, 548 µL, 647 mg, 6.99 mmol) in toluene (100 mL) was stirred for 26 h at 70 °C. *t*BuOH (100 mL) and KO*t*Bu (1.63 g, 14.5 mmol) were added at rt and stirring was continued for 18 h. NEt_3 (2.43 mL, 1.75 g, 17.3 mmol) and MsCl (906 µL, 1.34 g, 11.7 mmol) were introduced at 0 °C. After 1 h at rt, the reaction mixture was diluted with water (250 mL) and extracted with Et_2O (3 × 250 mL). The combined organic layers were washed with brine (250 mL), dried over $MgSO_4$, and concentrated in vacuo. Column chromatographic purification (silica gel, Et_2O/MeOH 100:0 → 95:5) afforded in the order of elution (2*S*,6*S*)-**13** (417 mg, 871 µmol, 15%, yellowish oil) and (2*R*,6*S*)-**13** (445 mg, 930 µmol, 16%, colorless solid).

(2*R*,6*S*)-**13**: $[\alpha]^{22}_D$ = –0.8 (*c* 0.12 in MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ 1.93 (t, *J* = 11.2 Hz, 1H, 3-H_{ax}), 1.99 (t, *J* = 11.1 Hz, 1H, 5-H_{ax}), 2.83 (dt, *J* = 11.3, 1.9 Hz, 1H, 5-H_{eq}), 3.05 (s, 3H, $MeSO_2$), 3.12 (ddd, *J* = 11.5, 2.5, 1.6 Hz, 1H, 3-H_{eq}), 3.45 (d, *J* = 12.8 Hz, 1H, 4-C*H*HAr), 3.54 (d, *J* = 12.7 Hz, 1H, 4-CH*H*Ar), 3.77 (s, 3H, OMe), 3.78 (s, 3H, OMe), 3.93 (m, 1H, 6-H), 4.14 (dd, *J* = 10.9, 2.7 Hz, 1H, 2-H), 4.29 (m, 2H, 6-CH_2), 4.31 (s, 2H, NHCH_2Ar), 6.86 (d, *J* = 8.8 Hz, 2H, Ar-H), 6.88 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.18 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.24 (d, *J* = 8.7 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, CD_3OD): δ 37.5 ($MeSO_2$), 43.0 (NCH_2Ar), 54.3 (C-5), 55.67 (C-3), 55.75 (2 × OMe), 63.2 (NCH_2Ar), 71.2 (6-CH_2), 74.9 (C-6), 76.9 (C-2), 114.9, 115.0, 129.9 (2 ×), 131.8 (2 ×), 160.5, 160.7 (Ar-C), 171.7 (C=O). IR (ATR): 3376, 2934, 2835, 1666, 1611, 1511, 1352, 1244, 1173, 1030, 814 cm^{-1}. HRMS (ESI) calcd for $[C_{23}H_{30}N_2O_7S + Na]^+$ 501.1666, found 501.1666.

(2*S*,6*S*)-**13**: Mp. 124–125 °C. $[\alpha]^{21}_D$ = +46.9 (*c* = 0.09, MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ 2.40 (dd, *J* = 11.7, 5.7 Hz, 1H, 5-H), 2.51 (dd, *J* = 11.7, 3.5 Hz, 1H, 5-H), 2.65 (dd, *J* = 11.7, 6.2 Hz, 1H, 3-H), 2.72 (dd, *J* = 11.6, 3.7 Hz, 1H, 3-H), 3.04 (s, 3H, $MeSO_2$), 3.44 (s, 2H, 4-CH_2Ar), 3.77 (s, 6H, 2 × OMe), 4.15 (m, 1H, 6-H), 4.29 (dd, *J* = 11.1, 4.4 Hz, 1H, 6-C*H*H), 4.30–4.39 (m, 3H, 2-H, NHCH_2Ar), 4.51 (dd, *J* = 11.1, 6.9 Hz, 1H, 6-CH*H*), 6.86 (d, *J* = 8.7 Hz, 2H, ArH), 6.87 (d, *J* = 8.8 Hz, 2H, ArH), 7.20 (d, *J* = 8.7 Hz, 2H, ArH), 7.21 (d, *J* = 8.8 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.5 ($MeSO_2$), 43.2 (NCH_2Ar), 53.9 (C-5), 54.9 (C-3), 55.7 (OMe), 55.8 (OMe), 63.2 (NCH_2Ar), 70.1 (6-CH_2), 72.4 (C-6), 73.3 (C-2), 114.8, 115.0, 129.9, 130.5, 131.4, 132.0, 160.5, 160.6. (C-Ar), 172.4 (C=O). IR (ATR): 2939, 2812, 1655, 1612, 1510, 1330, 1248, 1167, 1031, 965, 831, 815 cm^{-1}. HRMS (ESI) calcd for $[C_{23}H_{30}N_2O_7S + H]^+$ 479.1847, found 479.1847.

2.3 (1*R*,5*S*)-3,7-Bis(4-methoxybenzyl)-9-oxa-3,7-diazabicyclo[3.3.1]nonan-2-one (14)

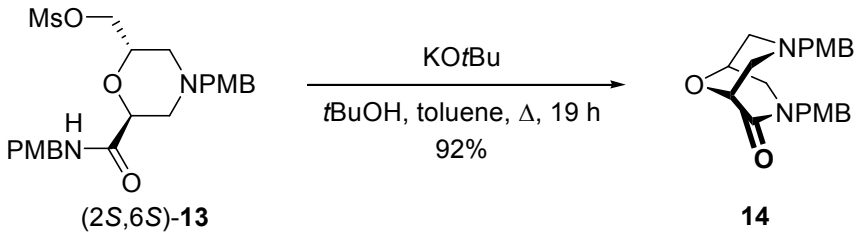
2.3.1 From (2*R*,6*S*)-13



(2*R*,6*S*)-**13** **14**

The morpholine (2*R*,6*S*)-**13** (200 mg, 418 µmol) was dissolved in anhydrous toluene (20 mL) and *t*BuOH (30 mL), and KO*t*Bu (188 mg, 1.67 mmol) was added. After 15 h at rt, the reaction mixture was quenched with sat aq. NH_4Cl (30 mL) and extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with brine (50 mL) and dried over $MgSO_4$. Removal of all volatiles under reduced pressure delivered **14** (158 mg, 413 µmol, 99%) as a colorless oil. $[\alpha]^{22}_D = -107.2$ (*c* 1.01 in MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.32 (dd, *J* = 11.4, 2.9 Hz, 1H, 6-H_{exo}), 2.43 (dd, *J* = 11.2, 3.1 Hz, 1H, 8-H_{exo}), 2.53 (d, *J* = 11.8 Hz, 1H, 6-H_{endo}), 2.98 (d, *J* = 11.8 Hz, 1H, 4-H_{endo}), 3.13 (d, *J* = 11.4 Hz, 1H, 8-H_{endo}), 3.19 (d, *J* = 12.7 Hz, 1H, C*H*HAr), 3.53 (d, *J* = 12.9 Hz, 1H, CH*H*Ar), 3.56 (ddd, *J* = 11.8, 7.1, 0.7 Hz, 1H, 4-H_{exo}), 3.78 (s, 3H, OMe), 3.83 (s, 3H, OMe), 4.00 (d, *J* = 14.6 Hz, 1H, C*H*HAr), 4.11 (m, 1H, 5-H), 4.30 (br s, 1H, 1-H), 5.16 (d, *J* = 14.6 Hz, 1H, CH*H*Ar), 6.75 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.91 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.99 (dd, *J* = 8.3 Hz, 2H, Ar-H), 7.32 (d, *J* = 8.7 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.3 (C-4), 48.6 (CH_2Ar), 55.0 (C-8), 55.2 (OMe), 55.3 (OMe), 57.0 (C-6), 61.9 (CH_2Ar), 66.7 (C-5), 72.8 (C-1), 113.7, 114.0, 128.6, 129.3, 129.87, 129.93, 158.8, 159.1 (Ar-C), 169.0 (C-2). IR (ATR): 2933, 2798, 1651, 1510, 1241, 1174, 1100, 1030, 818 cm^{-1}. HRMS (ESI) calcd for $[C_{22}H_{26}N_2O_4 + Na]^+$ 405.1785, found 405.1794.

2.3.2 From (2*S*,6*S*)-13

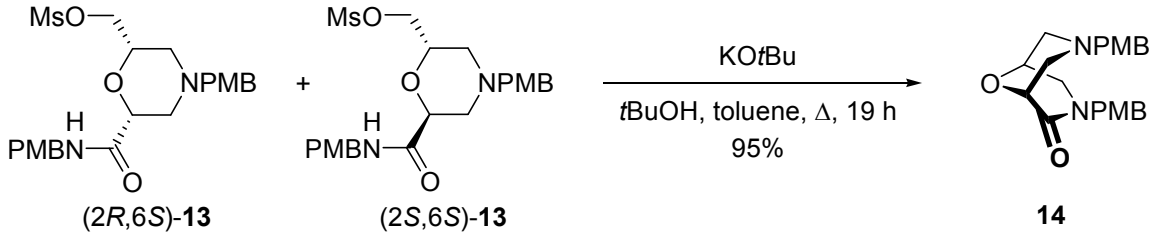


(2*S*,6*S*)-**13** **14**

A solution of (2*S*,6*S*)-**13** (200 mg, 418 µmol) in anhydrous toluene (20 mL) and *t*BuOH (25 mL) was treated with KO*t*Bu (282 mg, 2.51 mmol) and refluxed for 19 h. Work up as described in experiment 2.3.1 delivered **14** (147 mg, 384 µmol, 92%) as a colorless oil.

The spectroscopic and analytical data were in agreement with those of **14** from experiment 2.3.1.

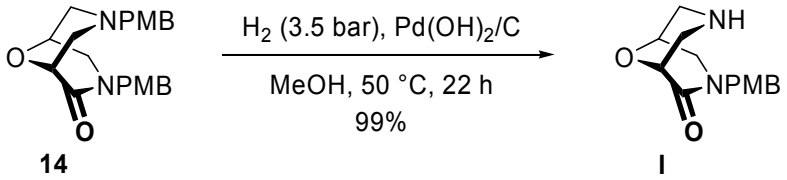
2.3.3 From (2*R*,6*S*)-13 and (2*S*,6*S*)-13



A solution of **13** [50:50 mixture of (2*R*,6*S*)-**13** and (2*S*,6*S*)-**13**, 400 mg, 836 µmol] in anhydrous toluene (40 mL) and *t*BuOH (80 mL) was treated with KO*t*Bu (564 mg, 5.02 mmol) and refluxed for 19 h. Work up as described in experiment 2.3.1 gave **14** (303 mg, 792 µmol, 95%) as a colorless oil. $[\alpha]^{22}_{D}$ = –105.6 (*c* 2.09 in MeOH).

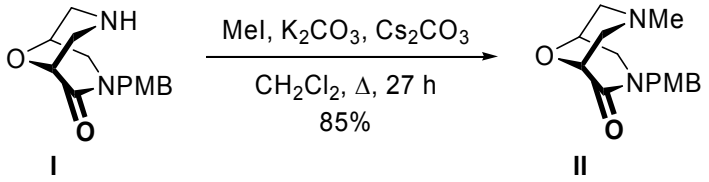
The further spectroscopic data were in agreement with those of **14** from experiment 2.3.1.

2.4 (1*R*,5*S*)-3-(4-Methoxybenzyl)-9-oxa-3,7-diazabicyclo[3.3.1]nonan-2-one (I)



$Pd(OH)_2$/C (20 w/w%, 200 mg) was added to a solution of **14** (593 mg, 1.46 mmol) in MeOH (40 mL). The reaction mixture was hydrogenated for 22 h at 50 °C under 3.5 bar H_2 pressure. The reaction mixture was filtered through a pad of Celite™, washed with CH_2Cl_2 (150 mL), and concentrated under reduced pressure to afford **I** (300 mg, 1.45 mmol, 99%) as a colorless oil. $[\alpha]^{22}_{D}$ = –134.0 (*c* 0.12 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (br s, 1H, NH), 2.81 (d, *J* = 12.8 Hz, 1H, 6-H_{endo}), 3.10 (d, *J* = 12.1 Hz, 1H, 4-H_{endo}), 3.13 (dd, *J* = 12.4, 3.2 Hz, 1H, 8-H_{exo}), 3.18 (br d, *J* = 12.2 Hz, 1H, 8-H_{endo}), 3.24 (dd, *J* = 12.7, 2.8 Hz, 1H, 6-H_{exo}), 3.66 (ddd, *J* = 12.0, 6.8, 1.0 Hz, 1H, 4-H_{exo}), 3.80 (s, 3H, OMe), 3.99 (dd, *J* = 6.7, 3.2 Hz, 1H, 5-H), 4.24 (br s, 1H, 1-H), 4.45 (d, *J* = 14.6 Hz, 1H, C*H*HAr), 4.81 (d, *J* = 14.5 Hz, 1H, CH*H*Ar), 6.87 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.27 (d, *J* = 8.1 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 47.8 (C-8), 48.6 (C-4), 48.7 (CH_2Ar), 50.6 (C-6), 55.3 (OMe), 66.3 (C-5), 72.8 (C-1), 114.1, 128.4, 129.5, 159.1 (Ar-C), 168.8 (C-2). IR (film): 3357, 2923, 2851, 1643, 1513, 1344, 1247, 1177, 1096, 1032 cm^{-1}. HRMS (ESI) calcd for $[C_{14}H_{18}N_2O_3 + Na]^+$ 285.1210, found 285.1210.

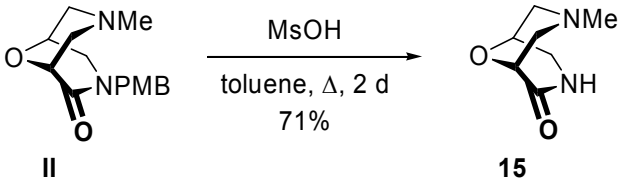
2.5 (1*R*,5*S*)-3-(4-Methoxybenzyl)-7-methyl-9-oxa-3,7-diazabicyclo[3.3.1]nonan-2-one (II)



I II

K_2CO_3 (276 mg, 2.00 mmol), Cs_2CO_3 (43.4 mg, 133 µmol), and MeI (125 µL, 284 mg, 2.00 mmol) were added at rt to a solution of **I** (350 mg, 1.33 mmol) in anhydrous CH_2Cl_2 (15 mL). After 27 h at reflux, the reaction mixture was diluted with sat aq. NH_4Cl (20 mL) and extracted with Et_2O (3 × 30 mL). The combined organic layers were washed with brine (20 mL) and dried over Na_2SO_4. Removal of the solvent in vacuo afforded **II** (313 mg, 1.13 mmol, 85%) as a yellowish oil. $[\alpha]^{22}_D = -37.9$ (*c* 0.22 in MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.23 (s, 3H, NMe), 2.32 (dd, *J* = 11.3, 3.1 Hz, 1H, 8-H_{exo}), 2.44 (dd, *J* = 11.6, 3.2 Hz, 1H, 6-H_{exo}), 2.63 (br d, *J* = 11.6 Hz, 1H, 6-H_{endo}), 3.04 (d, *J* = 11.9 Hz, 2H, 4-H_{endo}, 8-H_{endo}), 3.61 (ddd, *J* = 11.8, 7.0, 0.8 Hz, 1H, 4-H_{exo}), 3.80 (s, 3H, OMe), 4.10 (dd, *J* = 6.8, 2.7 Hz, 1H, 5-H), 4.29 (br s, 1H, 1-H), 4.44 (d, *J* = 14.9 Hz, 1H, C*H*HAr), 4.77 (d, *J* = 14.9 Hz, 1H, CH*H*Ar), 6.85 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.25 (d, *J* = 8.7 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 45.8 (NMe), 48.4 (CH_2Ar), 48.6 (C-4), 55.2 (OMe), 56.4 (C-8), 59.5 (C-6), 66.5 (C-5), 72.7 (C-1), 113.9, 128.3, 129.2, 158.9 (Ar-C), 169.0 (C-2). IR (ATR): 2935, 2792, 1650, 1512, 1243, 1176, 1153, 1097, 1031, 817 cm^{-1}. HRMS (ESI) calcd for $[C_{15}H_{20}N_2O_3 + Na]^+$ 299.1366, found 299.1366.

2.6 (1*R*,5*R*)-7-Methyl-9-oxa-3,7-diazabicyclo[3.3.1]nonan-2-one (15)



II 15

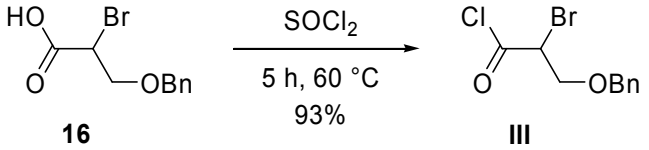
A solution of **II** (280 mg, 1.01 mmol) and MsOH (328 µL, 485 mg, 5.05 mmol) in anhydrous toluene (25 mL) was refluxed for 2 d. EtOAc (40 mL), water (20 mL), and 1N NaOH (20 mL) were successively added at rt. The aqueous layer was extracted with EtOAc (3 × 60 mL) and concentrated in vacuo. Soxhlet extraction of the residue with $CHCl_3$ (500 mL) gave **15** (112 mg, 717 µmol, 71%) as a white solid. Mp. 123–125 °C. $[\alpha]^{22}_D = -28.4$ (*c* 0.10 in MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.25 (s, 3H, NMe), 2.31 (dd, *J* = 11.4, 3.3 Hz, 1H, 8-H_{exo}), 2.48 (dd, *J* = 11.6, 3.4 Hz, 1H, 6-H_{exo}), 2.77 (d, *J* = 11.7 Hz, 1H, 6-H_{endo}), 2.98 (dt, *J* = 11.4, 1.7 Hz, 1H, 8-H_{endo}), 3.33 (dd, *J* = 11.8, 3.1 Hz, 1H, 4-H_{endo}), 3.82 (ddt, *J* = 11.8, 6.9, 1.0 Hz, 1H, 4-H_{exo}), 4.14 (dd, *J* = 6.9, 3.5 Hz, 1H, 5-H), 4.24 (dd, *J* = 2.7, 2.0 Hz, 1H, 1-H), 6.62 (br s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 44.8 (C-4), 46.1 (NMe), 56.1 (C-8), 59.7 (C-6), 65.3 (C-5), 72.7 (C-1), 170.8 (C-2). IR (film): 3341, 2925, 2852, 2798, 1673, 1460, 1356, 1259, 1156, 1103, 1046, 735 cm^{-1}. HRMS (ESI) calcd for $[C_7H_{12}N_2O_2 + Na]^+$ 179.0791, found 179.0793.

2.7 (1*R*,5*S*)-7-Methyl-2-oxo-9-oxa-3,7-diazabicyclo[3.3.1]nonane-3-carboxylic acid *tert*-butyl ester (8)

For the preparation and characterization data of **8**, see experiment 3.6.

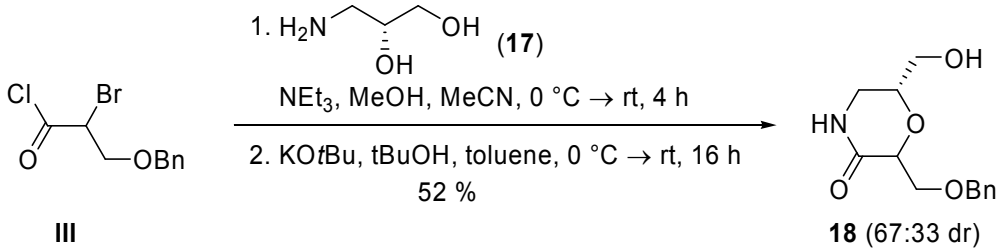
3. Synthesis of the *N*-Boc-9-oxabispidin-2-one 8 starting from 16

3.1 3-Benzyloxy-2-bromopropionyl chloride (III)



3-Benzyloxy-2-bromopropionic acid (**16**, 10.4 g, 40.1 mmol) was dissolved at 0 °C in $SOCl_2$ (20 mL). After 5 h at 60 °C, excess $SOCl_2$ was removed by bulb-to-bulb distillation (0.7 mbar, rt → 60 °C) to give **III** (10.4 g, 37.5 mmol, 93%) as a yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.86 (dd, J = 10.4, 5.1 Hz, 1H, 3-H), 3.99 (dd, J = 10.4, 8.4 Hz, 1H, 3-H), 4.61 (m, 3H, 2-H, CH_2Ph), 7.28–7.42 (m, 5H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 49.9 (C-2), 70.5 (C-3), 73.9 (CH_2Ph), 127.9, 128.2, 128.6, 136.8 (ArC), 169.0 (C=O). IR (ATR): 3031, 2867, 1778, 1454, 1361, 1104, 1075, 933, 913, 737, 697, 632 cm^{-1}. HRMS (ESI, MeOH as the solvent) calcd for [$C_{10}H_{10}BrClO_2$ – HCl + MeOH + Na = $C_{11}H_{13}BrO_3$ + Na]$^+$ 294.9946, found 294.9942.

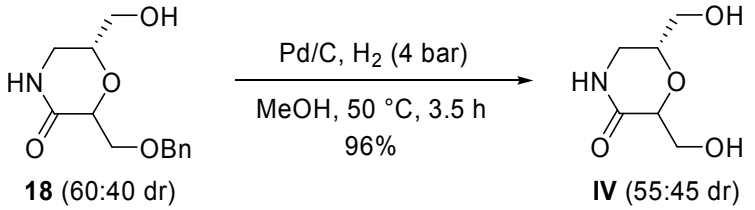
3.2 (6*R*)-2-Benzyloxymethyl-3-oxomorpholin-6-methanol (18)



(*R*)-3-Aminopropane-1,2-diol (**17**, 3.22 g, 35.3 mmol) was dissolved in warm anhydrous MeOH (100 mL) and diluted with MeCN (400 mL). NEt_3 (5.20 mL, 3.75 g, 37.1 mmol) and a solution of **III** (10.3 g, 37.1 mmol) in MeCN (100 mL) were added dropwise at 0 °C. The reaction mixture was stirred for 1 h at 0 °C and 3 h at rt. The solvent was removed in vacuo and the resulting brownish oil was dissolved in *t*BuOH (400 mL) and toluene (100 mL). KO*t*Bu (9.16 g, 81.6 mmol) was added at 0 °C and the suspension was warmed to rt overnight. Solid NH_4Cl (4.00 g, 74.8 mmol) was added and the reaction mixture was sucked through a pad of Celite^{TM}, washed with EtOAc (750 mL). Evaporation of the solvent under reduced pressure and column chromatographic purification (silica gel, EtOAc/MeOH 9:1 → 7:3) afforded **18** (4.61 g, 18.3 mmol, 52%, colorless oil) as a 67:33 mixture of epimers at C-2 (**A**: major epimer, **B**: minor epimer). $[\alpha]^{22}_D$ = +14.5 (*c* 0.20 in MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ 3.24–3.34 (m, 2H **A**, 2H **B**, 5-H), 3.59 (dd, J = 11.7, 5.0 Hz, 1H **B**, 6-C*H*H), 3.61 (dd, J = 11.7, 4.7 Hz, 1H **A**, 6-C*H*H), 3.62–3.67 (m, overlapped, 1H **B**, 6-CH*H*), 3.66 (dd, J = 11.6, 5.7 Hz, 1H **A**, 6-CH*H*), 3.80 (dd, J = 10.6, 2.4 Hz, 1H **B**, 2-C*H*H), 3.82–3.89 (m, 2H **A**, 6-H, 2-C*H*H), 3.92 (dd, J = 10.6, 4.5 Hz, 1H **A**, 2-CH*H*), 4.01 (dd, J = 10.6, 4.8 Hz, 1H **B**, 2-CH*H*), 4.29 (m, 1H **B**, 6-H), 4.33 (m, 1H **A**, 2-H), 4.36 (dd, J = 4.7, 2.3 Hz, 1H **B**, 2-H), 4.56 (s, 2H **B**, CH_2Ph), 4.59 (s, 2H **A**, CH_2Ph), 7.24–7.40 (m, 5H **A**, 5H **B**, Ph-H). ^{13}C NMR (100 MHz, CD_3OD): δ 44.17 (C-5, **B**), 44.23 (C-5, **A**), 63.3 (6-CH_2, **B**), 63.5 (6-CH_2, **A**), 71.3 (2-CH_2, **A**), 71.7 (C-6, **B**), 72.8 (2-CH_2, **B**), 74.6 (*C*H_2Ph, **B**), 74.7 (*C*H_2Ph, **A**), 75.0 (C-6, **A**), 76.5 (C-2, **B**), 78.6 (C-2, **A**), 128.7, 128.8, 128.9, 129.38, 129.41 (2 ×), 139.4, 139.5 (C-Ph, **A**, **B**), 171.0

(C=O, **A**), 171.1 (C=O, **B**). IR (film): 3329, 2927, 2871, 1666, 1494, 1453, 1362, 1115, 1040, 739, 699 cm^{-1}. HRMS (ESI) calcd for $[C_{13}H_{17}NO_4 + Na]^+$ 274.1050, found 274.1050.

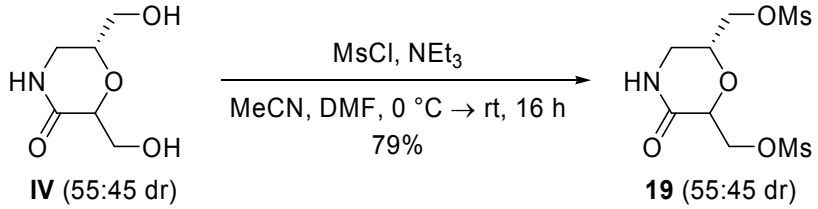
3.3 (6*R*)-3-Oxomorpholin-2,6-dimethanol (IV)



18 (60:40 dr) **IV** (55:45 dr)

A solution of **18** (4.55 g, 18.1 mmol) in MeOH (120 mL) was hydrogenated at 50 °C and 4 bar for 3.5 h in the presence of Pd/C (10 w/w%, 400 mg). The reaction mixture was filtered through a pad of Celite™, washed with MeOH (700 mL), and concentrated under reduced pressure to deliver **IV** (2.81 g, 17.4 mmol, 96%, colorless oil) as a 55:45 mixture of epimers at C-2 (**A**: major epimer, **B**: minor epimer). $[\alpha]^{22}_D$ = +18.9 (*c* 0.23 in MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ 3.23–3.38 (m, 2H **A**, 2H **B**, 5-H), 3.55–3.71 (m, 1H **A**, 6-C*H*H, 2H **B**, 6-CH_2), 3.80 (dd, *J* = 11.9, 3.0 Hz, 1H **B**, 2-C*H*H), 3.80–3.92 (m, 3H **A**, 6-H, 6-CH*H*, 2-C*H*H), 3.91 (dd, *J* = 11.8, 4.2 Hz, 1H **A**, 2-CH*H*), 4.01 (dd, *J* = 11.9, 6.3 Hz, 1H **B**, 2-CH*H*), 4.13–4.20 (m, 1H **A**, 2-H, 1H **B**, 6-H), 4.24 (dd, *J* = 6.3, 2.9 Hz, 1H **B**, 2-H). ^{13}C NMR (100 MHz, CD_3OD): δ 43.9 (C-5, **B**), 44.1 (C-5, **A**), 63.2 (CH_2OH, **B**), 63.3 (CH_2OH, **A**), 63.4 (CH_2OH, **B**), 63.5 (CH_2OH, **A**), 71.1 (C-6, **B**), 74.6 (C-6, **A**), 77.9 (C-2, **B**), 79.5 (C-2, **A**), 171.2 (C=O, **B**), 171.4 (C=O, **A**). IR (film): 3385, 2940, 2886, 1652, 1495, 1417, 1384, 1124, 1065, 1036 cm^{-1}. HRMS (ESI) calcd for $[C_6H_{11}NO_4 + Na]^+$ 184.0580, found 184.0581.

3.4 (6*R*)-2,6-Bis(methanesulfonyloxymethyl)morpholin-3-one (19)

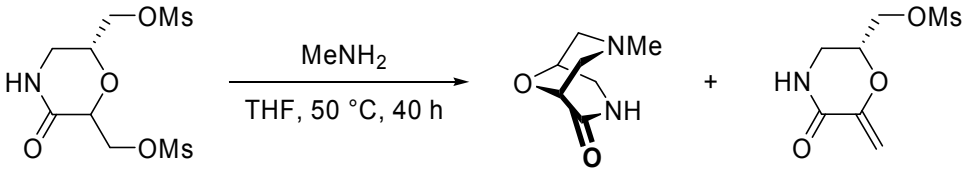


IV (55:45 dr) **19** (55:45 dr)

Diol **IV** (2.75 g, 17.1 mmol) was dissolved in DMF (35 mL) and diluted with MeCN (340 mL). NEt_3 (7.91 mL, 5.69 g, 56.3 mmol) and MsCl (3.91 mL, 5.78 g, 50.5 mmol) were added at 0 °C. The reaction mixture was warmed to rt overnight, quenched with sat aq. NH_4Cl (350 mL) and extracted with EtOAc (6 × 250 mL). The combined organic layers were washed with brine (400 mL), dried over $MgSO_4$, and concentrated under reduced pressure. Column chromatography (silica gel, EtOAc/MeOH 1:0 → 4:1) afforded a 1:2.1 mixture of **19** and DMF [6.40 g, containing **19**: 4.29 g, 13.5 mmol, 79%, 55:45 mixture of epimers at C-2 (**A**: major epimer, **B**: minor epimer)] as a yellowish oil. This mixture was used in the next step without any further purification. Analytically pure material for characterization was obtained by repeated chromatography. $[\alpha]^{22}_D$ = +18.0 (*c* 0.27 in MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ 3.10 (s, 3H **A**, $MeSO_2$), 3.13 (s, 3H **B**, $MeSO_2$), 3.14 (s, 3H **A**, $MeSO_2$, 3H **B**, $MeSO_2$), 3.32–3.45 (m, 2H **A**, 2H **B**, 5-CH_2), 4.23 (m, 1H **A**, 6-H), 4.32 (m, 1H **B**, 6-C*H*H), 4.33–4.43 (m, 2H **A**, 6-CH_2, 1H **B**, 6-H), 4.47 (dd, *J* = 11.1, 2.5 Hz, 1H **B**, 2-C*H*H), 4.51–4.65 (m, 3H **A**, 2-H, 2-CH_2, 2H **B**, 2-H, 6-CH*H*), 4.72 (dd, *J*

= 11.1, 5.3 Hz, 1H **B**, 2-CH*H*). ^{13}C NMR (100 MHz, CD_3OD): δ 37.5 ($MeSO_2$, **B**), 37.56 ($MeSO_2$, **B**), 37.59 ($MeSO_2$, **A**), 37.60 ($MeSO_2$, **A**), 43.2 (C-5, **B**), 43.3 (C-5, **A**), 69.6 (C-6, **B**), 70.1 (CH_2OMs, **B**), 70.4 (CH_2OMs, **A**), 70.8 (CH_2OMs, **A**), 71.5 (CH_2OMs, **B**), 72.2 (C-6, **A**), 74.9 (C-2, **B**), 76.8 (C-2, **A**), 168.6 (C=O, **B**), 168.7 (C=O, **A**). IR (ATR): 2936, 1673, 1339, 1168, 1138, 965, 906, 801 cm^{-1}. HRMS (ESI) calcd for $[C_8H_{15}NO_8S_2 + Na]^+$ 340.0131, found 340.0133.

3.5 (1*R*,5*R*)-7-Methyl-9-oxa-3,7-diazabicyclo[3.3.1]nonan-2-one (15) and (*R*)-6-Methanesulfonyloxymethyl-2-methylenmorpholin-3-one (20)



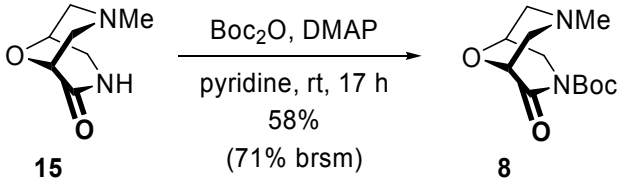
19 (55:45 dr) **15** (33%) **20** (34%)

The **19**/DMF mixture (6.34 g, containing **19**: 4.25 g, 13.4 mmol) from the experiment above was added to a solution of methylamine in anhydrous THF (2.0 M, 100 mL, 200 mmol) After 40 h at 50 °C, the solvent was removed in vacuo to give a 45:55 mixture of the unsaturated morpholin-2-one **20** and the bispidine-derived lactam **15**. Separation by column chromatography (silica gel, EtOAc/MeOH 1:0 → 4:1) afforded **20** (1.01 g, 4.57 mmol, 34%) as a yellowish oil and **15** (691 mg, 4.42 mmol, 33%) as a white solid.

The characterization data of **15** are given in experiment 2.6.

20: $[\alpha]^{22}_D$ = +8.2 (*c* 1.3 in MeOH). ^{1}H NMR (400 MHz, MeOD): δ 3.14 (s, 3H, $MeSO_2$), 3.50 (m, 2H, 5-H), 4.40 (m, 3H, 6-H, 6-CH_2), 4.89 (d, *J* = 1.0 Hz, 1H, C*H*H=C), 5.43 (d, *J* = 1.0 Hz, 1H, CH*H*=C). ^{13}C NMR (100 MHz, MeOD): δ 37.5 ($MeSO_2$), 42.7 (C-5), 69.7 (6-CH_2), 73.1 (C-6), 100.2 (CH_2=C), 151.7 (C=CH_2), 162.1 (C=O). IR (ATR): 3357, 3013, 2929, 1667, 1627, 1476, 1391, 1348, 1168, 1128, 1072, 974, 937, 835 cm^{-1}. HRMS (ESI) calcd for $[C_7H_{11}NO_5S+Na^+]$ 244.0250, found 244.0250.

3.6 (1*R*,5*S*)-7-Methyl-2-oxo-9-oxa-3,7-diazabicyclo[3.3.1]nonan-3-carboxylic acid *tert*-butyl ester (8)



15 **8**

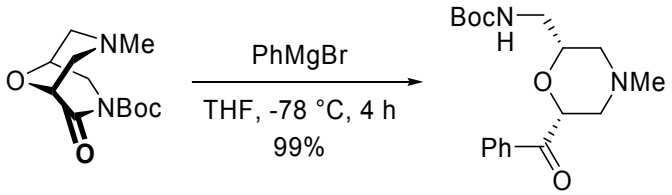
brsm: based on recovered starting material

To a solution of **15** (680 mg, 4.35 mmol) and DMAP (26.6 mg, 218 µmol) in anhydrous pyridine (35 mL), Boc_2O (4.76 g, 21.8 mmol) was portionwise added at rt. After 12 h of stirring, a second batch of Boc_2O (2.38 g, 10.9 mmol) was added and stirring was continued for 5 h. The solvent was distilled off under reduced pressure. Column chromatography of the residue (silica gel, *n*-pentane/Et_2O 2:1 → 0:1) delivered unreacted starting material **15** (122 mg, 781 µmol, 18%) and the target imide **8** [647 mg, 2.52

mmol, 58% (71% based on recovered starting material)] as a brownish oil. $[\alpha]^{22}_D$ = –3.9 (*c* 1.00 in MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53 (s, 9H, CMe_3), 2.19 (s, 3H, NMe), 2.27 (dd, *J* = 11.3, 3.0 Hz, 1H, 8-H_{exo}), 2.44 (dd, *J* = 11.7, 3.2 Hz, 1H, 6-H_{exo}), 2.71 (d, *J* = 11.6 Hz, 1H, 6-H_{endo}), 2.98 (dt, *J* = 11.3, 1.8 Hz, 1H, 8-H_{endo}), 3.59 (d, *J* = 12.5 Hz, 1H, 4-H_{endo}), 3.95 (ddd, *J* = 12.5, 7.6, 0.9 Hz, 1H, 4-H_{exo}), 4.23 (dd, *J* = 7.5, 2.8 Hz, 1H, 5-H), 4.27 (t, *J* = 2.4 Hz, 1H, 1-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.0 (C*Me*$_3$), 45.9 (NMe), 48.2 (C-4), 56.9 (C-8), 59.3 (C-6), 66.3 (C-5), 73.7 (C-1), 83.3 (*C*Me$_3$), 151.4 (CO_2), 170.5 (C-2). IR (film): 2922, 2851, 2796, 1773, 1720, 1460, 1369, 1284, 1252, 1151, 1113 cm^{-1}. HRMS (ESI) calcd for $[C_{12}H_{20}N_2O_4 + H]^+$ 257.1496, found 257.1496.

4. Synthesis of the bicyclic *2-endo*-phenyl-substituted 9-oxabispidine 7b

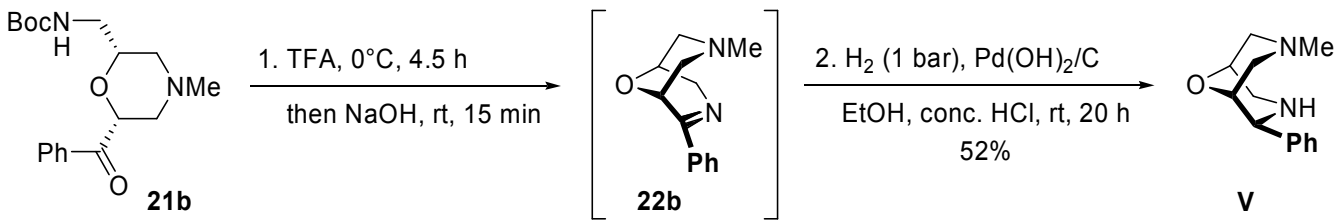
4.1 (2*R*,6*R*)-2-Benzoyl-6-*tert*-butoxycarbonylaminomethyl-4-methylmorpholine (21b)



8 **21b**

PhMgBr (1.40 mL, 1.40 mmol, 1.0 M in THF) was added at -78 °C to a solution of **8** (300 mg, 1.17 mmol) in abs. THF (10 mL). After 4 h at -78 °C, the reaction mixture was quenched with sat aq. NH_4Cl (50 mL), diluted with water (150 mL), and extracted with EtOAc (2 × 150 mL). The combined organic layers were dried over Na_2SO_4, and the solvent was removed in vacuo to give **21b** (387 mg, 1.16 mmol, 99%) as a colorless solid. Mp. 89–93 °C. $[\alpha]^{22}_D$ = +14.5 (*c* 0.32 in MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (s, 9H, CMe_3), 1.89 (t, *J* = 11.0 Hz, 1H, 5-H_{ax}), 2.10 (t, *J* = 11.2 Hz, 1H, 3-H_{ax}), 2.31 (s, 3H, NMe), 2.77 (d, *J* = 11.4 Hz, 1H, 3-H_{eq}), 3.02 (d, *J* = 11.6 Hz, 1H, 5-H_{eq}), 3.15 (ddd, *J* = 14.1, 7.1, 5.2 Hz, 1H, 6-C*H*H), 3.40 (m, 1H, 6-CH*H*), 3.84 (m, 1H, 6-H), 4.94 (dd, *J* = 10.5, 2.2 Hz, 1H, 2-H), 5.01 (br s, 1H, NH), 7.45 (t, *J* = 7.7 Hz, 2H, Ph-H), 7.57 (t, *J* = 7.4 Hz, 1H, Ph-H), 7.95 (d, *J* = 7.2 Hz, 2H, Ph-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.3 (C*Me*$_3$), 42.8 (6-CH_2), 46.0 (NMe), 56.0 (C-3), 56.7 (C-5), 75.7 (C-6), 77.8 (C-2), 79.3 (*C*Me$_3$), 128.6, 128.9, 133.5, 134.9 (C-Ph), 155.9 (CO_2), 196.0 (*C*OPh). IR (KBr): 3371, 2932, 2807, 1494, 1516, 1450, 1366, 1252, 1172, 1118, 698 cm^{-1}. HRMS (ESI) calcd for $[C_{18}H_{26}N_2O_4 + H]^+$ 335.1965, found 335.1966.

4.2 (1*R*,2*S*,5*R*)-7-Methyl-2-phenyl-9-oxa-3,7-diazabicyclo[3.3.1]nonane (V)



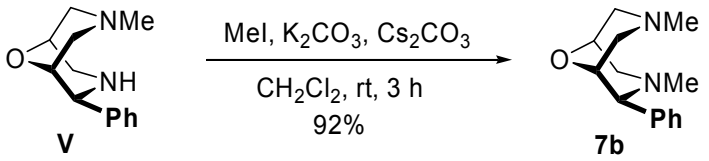
21b **22b** **V**

A solution of the morpholine **21b** (360 mg, 1.08 mmol) in TFA (3 mL) was stirred for 4.5 h at 0 °C. 11N NaOH (50 mL) was added and the reaction was warmed to rt within 15 min. After extraction with

Et_2O (3 × 100 mL), the combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, and evaporated. Conc. HCl (3 mL) and $Pd(OH)_2/C$ (20 w/w%, 120 mg) were added to the residue dissolved in EtOH (30 mL). The reaction mixture was hydrogenated for 20 h under 1 bar of H_2 pressure. The crude product was sucked through a pad of Celite™, washed with MeOH (150 mL), and concentrated under reduced pressure. The residue was dissolved in H_2O (30 mL) and the pH was adjusted to 11 with 1N NaOH (ca. 40 mL). After extraction with $CHCl_3$ (5 × 60 mL), the combined organic layers were dried over Na_2SO_4. Removal of the solvent in vacuo yielded **V** (122 mg, 559 µmol, 52%) as a low-melting colorless solid. Mp. 30–35 °C (ref. 5: mp. 35 °C). $[\alpha]^{22}_D$ = +42.0 (*c* 0.19 in MeOH) {ref. 5: $[\alpha]^{20}_D$ = +42.3 (*c* 0.17 in MeOH)}.

The further spectroscopic and analytical data of **V** were identical to those reported in ref. 5.

4.3 (1*R*,2*S*,5*S*)-3,7-Dimethyl-2-phenyl-9-oxa-3,7-diazabicyclo[3.3.1]nonane (7b)

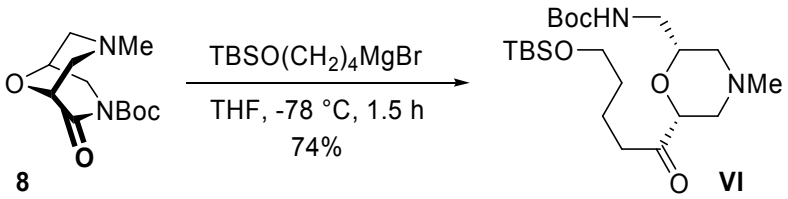


In analogy to ref. 5, K_2CO_3 (88.6 mg, 641 µmol) and MeI (39.9 µL, 91.0 mg, 641 µmol) were added to a solution of **V** (100 mg, 458 µmol) in CH_2Cl_2 (5 mL). After 3 h at rt, water (10 mL) was added and the reaction mixture was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated in vacuo to give **7b** (97.9 mg, 421 µmol, 92%) as white solid. Mp. 58–60 °C (ref. 5: mp. 65 °C). $[\alpha]^{21}_D$ = +149.0 (*c* 0.3 in MeOH) {ref. 5: $[\alpha]^{20}_D$ = +154.4 (*c* 1.15 in MeOH)}.

The further spectroscopic and analytical data of **7b** were in agreement with those reported in ref. 5.

5. Synthesis of the tricyclic 9-oxabispidine 6

5.1 (2*R*,6*R*)-6-*tert*-Butoxycarbonylaminomethyl-2-(5-*tert*-butyldimethylsilyloxypentanoyl)-4-methylmorpholine (VI)

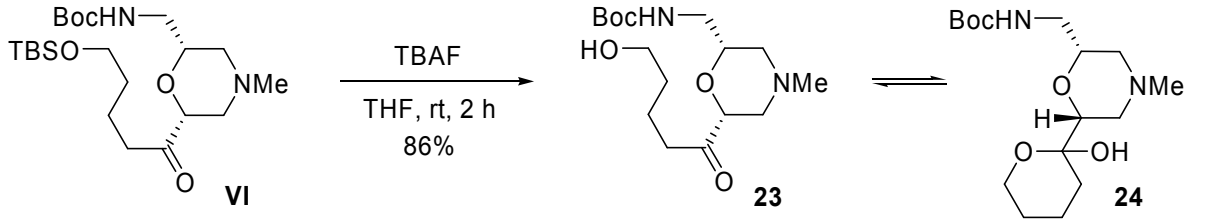


4-(*tert*-Butyldimethylsilyloxy)butylmagnesiumbromide, prepared from the corresponding bromobutane (4.25 g, 15.9 mmol) and Mg (773 mg, 31.8 mmol, activated with a small amount of I_2) in anhydrous THF (10 mL, reflux, 1.5 h),[3] was added at -78 °C to a solution of **8** (680 mg, 2.65 mmol) in anhydrous THF (20 mL). After 1.5 h at -78 °C, the reaction mixture was quenched with sat aq. NH_4Cl

(5) Breuning, M.; Steiner, M. *Synthesis* **2007**, 1702.

(25 mL) and extracted with EtOAc (4 × 100 mL). The combined organic layers were washed with brine (100 mL) and dried over Na_2SO_4. Removal of the solvent in vacuo and column chromatography (silica gel, Et_2O/MeOH 1:0 → 6:1) delivered **VI** (872 mg, 1.96 mmol, 74%) as a colorless oil. $[\alpha]^{22}_D$ = +18.3 (*c* 0.13 in MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.05 (s, 6H, $SiMe_2$), 0.89 (s, 9H, $SiCMe_3$), 1.46 (s, 9H, $OCMe_3$), 1.47–1.66 (m, 4H, 3'-H, 4'-H), 1.79 (t, *J* = 11.0 Hz, 1H, 5-H_{ax}), 1.80 (t, *J* = 11.2 Hz, 1H, 3-H_{ax}), 2.29 (s, 3H, NMe), 2.62 (t, *J* = 7.3 Hz, 2H, 2'-H), 2.71 (br d, *J* = 11.3 Hz, 1H, 5-H_{eq}), 2.98 (br d, *J* = 11.4 Hz, 1H, 3-H_{eq}), 3.18 (m, 1H, 6-C*H*H), 3.38 (m, 1H, 6-CH*H*), 3.62 (t, *J* = 6.3 Hz, 2H, 5'-H), 3.67 (m, 1H, 6-H), 4.04 (dd, *J* = 10.8, 2.7 Hz, 1H, 2-H), 4.84 (br s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ -5.3 ($SiMe_2$), 18.3 (Si*C*Me_3), 19.4 (3'-H), 26.0 (SiC*Me*$_3$), 28.4 (OC*Me*$_3$), 32.2 (C-4'), 38.2 (C-2'), 43.0 (6-CH_2), 46.0 (NMe), 55.6 (C-3), 56.9 (C-5), 62.9 (C-5'), 75.3 (C-6), 79.5 (O*C*Me_3), 80.9 (C-2), 155.9 (CO_2), 208.9 (1'-C). IR (film): 3375, 1717, 1512, 1460, 1365, 1254, 1173, 1109, 837, 776 cm^{-1}. HRMS (ESI) calcd for $[C_{22}H_{44}N_2O_5Si + H]^+$ 445.3092, found 445.3092.

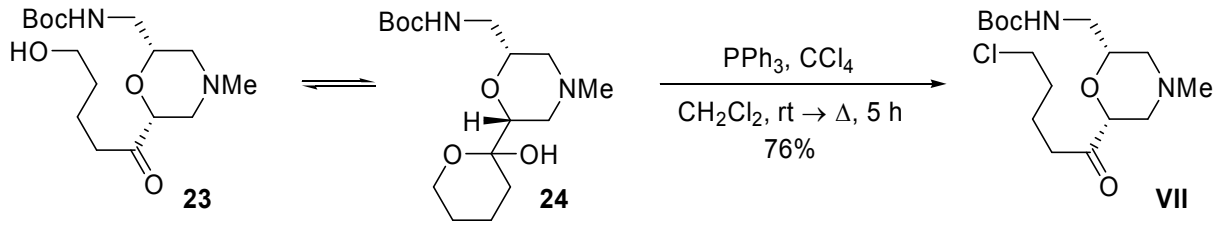
5.2 (2*R*,6*R*)-6-*tert*-Butoxycarbonylaminomethyl-2-(5-hydroxypentanoyl)-4-methylmorpholine (23) ⇆ (2*R*,6*R*)-6-*tert*-Butoxycarbonylaminomethyl-2-(2-hydroxytetrapyran-2-yl)-4-methylmorpholine (24)



23 : **24** (diastereomer 1) : **24** (diastereomer 2) = 20:40:40

A solution of **VI** (840 mg, 1.89 mmol) and TBAF·H_2O (987 mg, 3.78 mmol) in anhydrous THF (30 mL) was stirred for 2.5 h at rt. Removal of the solvent under reduced pressure and column chromatography (silica gel, EtOAc/MeOH 1:0 → 4:1) afforded **23** ⇆ **24** (537 mg, 1.63 mmol, 86%) as a colorless oil. According to ^{1}H NMR ($CDCl_3$ as the solvent), the ratio was **23** (**A**) : **24** (diastereomer 1, **B**) : **24** (diastereomer 2, **C**) = 20:40:40. $[\alpha]^{22}_D$ = –9.2 (*c* 1.2 in MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.40 (m, 1H **B**, 3'-H), 1.44 (s, 9H **B**, 9H **C**, CMe_3), 1.46 (s, 9H **A**, CMe_3), 1.48–1.70 (m, 4H **A**, 5H **B**, 6H **C**, CH_2), 1.72–1.92 (m, 2H **A**, 3-H_{ax}, 5-H_{ax}, 2H **B**, 3-H_{ax}, 5-H_{ax}, 1H **C**, 5-H_{ax}), 2.04 (t, *J* = 11.2, 10.7 Hz, 1H **C**, 3-H_{ax}), 2.26 (s, 3H **B**, NMe), 2.28 (s, 3H **A**, NMe), 2.29 (s, 3H **C**, NMe), 2.61 (m, 2H **A**, 2'-H), 2.69 (m, 1H **A**, 1H **B**, 1H **C**, 5-H_{eq}), 2.73 (d, *J* = 11.2 Hz, 1H **B**, 3-H_{eq}), 2.80 (d, *J* = 11.5 Hz, 1H **C**, 3-H_{eq}), 2.97 (br d, *J* = 11.4 Hz, 1H **A**, 3-H_{eq}), 3.17 (m, 1H **A**, 1H **B**, 1H **C**, 6-C*H*H), 3.32 (m, 1H **A**, 1H **B**, 1H **C**, 6-CH*H*), 3.42 (dd, *J* = 10.4, 2.2 Hz, 1H **C**, 2-H), 3.54 (dd, *J* = 10.7, 2.4 Hz, 1H **B**, 2-H), 3.60-3.73 (m, 3H **A**, 5'-H, 6-H, 2H **B**, 2H **C**, 6'-H, 6-H), 3.95 (m, 1H **B**, 1H **C**, 6'-H), 4.04 (dd, *J* = 10.8, 2.7 Hz, 1H **A**, 2-H), 4.85–5.18 (br m, 1H **A**, 1H **B**, 1H **C**, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 18.3, 19.1, 25.2, 25.3 (CH_2, **A**, **B**, **C**), 28.4 (3 × C*Me*$_3$, **A**, **B**, **C**), 29.6 (CH_2, **A**), 30.1 (CH_2, **B**), 31.0 (CH_2, **C**), 38.1 (C-2', **A**), 43.0 (3 × 6-CH_2, **A**, **B**, **C**), 46.0 (NMe, **A**), 46.2 (NMe, **C**), 46.3 (NMe, **B**), 54.5 (C-3, **B**), 54.3 (C-3, **C**), 54.2 (C-3, **A**), 56.8 (C-5, **A**), 56.96 (C-5, **B**), 57.03 (C-5, **C**), 61.0, 61.2 (C-6', **B**, **C**), 62.1 (C-5', **A**), 75.0 (C-6, **B**), 75.3 (C-6, **A**), 75.8 (C-6, **C**), 79.3, 79.4, 79.5 (*C*Me_3, **A**, **B**, **C**), 80.2 (C-2, **B**), 80.8 (C-2, **A**), 80.9 (C-2, **C**), 94.7 (C-2', **C**), 95.2 (C-2', **B**), 155.9 (2 ×), 156.0 (CO_2, **A**, **B**, **C**), 209.1 (C=O, **A**). IR (film): 3351, 2940, 2874, 1698, 1529, 1456, 1366, 1272, 1172, 1120, 1079 cm^{-1}. HRMS (ESI) calcd for $[C_{16}H_{30}N_2O_5 + H]^+$ 331.2228, found 331.2228.

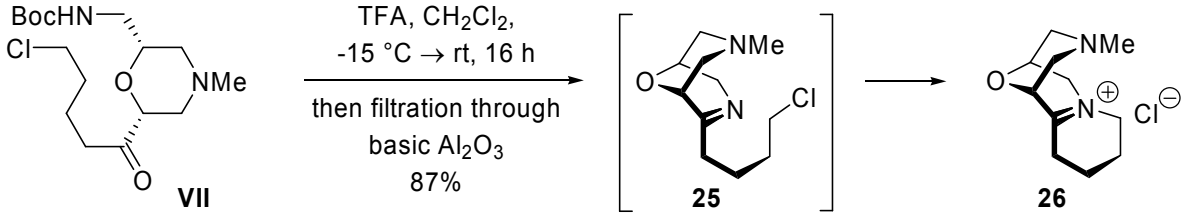
5.3 (2*R*,6*R*)-6-*tert*-Butoxycarbonylaminomethyl-2-(5-chloropentanoyl)-4-methylmorpholine (VII)



23 : **24** (diastereomer 1) : **24** (diastereomer 1) = 20:40:40

To a solution of **23** ⇆ **24** (510 mg, 1.54 mmol) in CH_2Cl_2 (40 mL), CCl_4 (968 µL, 1.54 g, 10.0 mmol) and PPh_3 (1.01 g, 3.85 mmol) were added at rt. After 30 min at rt and 4.5 h under reflux, the reaction mixture was concentrated. Column chromatography (silica gel, EtOAc/MeOH 1:0 → 4:1) yielded **VII** (410 mg, 1.18 mmol, 76%) as a colorless oil. $[\alpha]^{22}_D$ = +15.9 (*c* 0.25 in MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (s, 9H, CMe_3), 1.70–1.82 (m, 6H, 3-H_{ax}, 5-H_{ax}, 3'-H, 4'-H), 2.29 (s, 3H, NMe), 2.63 (t, *J* = 6.3 Hz, 2H, 2'-H), 2.71 (br d, *J* = 11.4 Hz, 1H, 5-H_{eq}), 2.99 (br d, *J* = 11.5 Hz, 1H, 3-H_{eq}), 3.19 (m, 1H, 6-C*H*H), 3.36 (m, 1H, 6-CH*H*), 3.54 (t, *J* = 6.3 Hz, 2H, 5'-H), 3.66 (m, 1H, 6-H), 4.04 (dd, *J* = 10.9, 2.8 Hz, 1H, 2-H), 4.83 (br s, 1H, NH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.2 (C-3'), 28.4 (C*Me*$_3$), 31.9 (C-4'), 37.5 (C-2'), 43.0 (6-CH_2), 44.6 (C-5'), 46.0 (NMe), 55.6 (C-3), 56.9 (C-5), 75.4 (C-6), 79.6 (*C*Me$_3$), 80.9 (C-2), 155.9 (CO_2), 208.5 (C-1'). IR (film): 3360, 2975, 2939, 2872, 2799, 1714, 1516, 1456, 1366, 1275, 1252, 1172, 1119 cm^{-1}. HRMS (ESI) calcd for $[C_{16}H_{29}ClN_2O_4 + H]^+$ 349.1889, found 349.1890.

5.4 (1*R*,9*S*)-11-Methyl-13-oxa-11-aza-7-azoniatricyclo[7.3.1.0^{2,7}]tridec-2(7)-ene chloride (6)



TFA (5 mL) was dropwise added to a solution of **VI** (390 mg, 1.12 mmol) in anhydrous CH_2Cl_2 (5 mL) at -15 °C. The reaction mixture was warmed to rt overnight and concentrated in vacuo. The residue was co-evaporated with CH_2Cl_2 (2 mL) for three times. The resulting yellow oil was chromatographed (basic Al_2O_3, activity V, EtOAc/MeOH 1:0 → 9:1) providing the cyclized iminium salt **26** (225 mg, 975 µmol, 87%) as a violet oil.

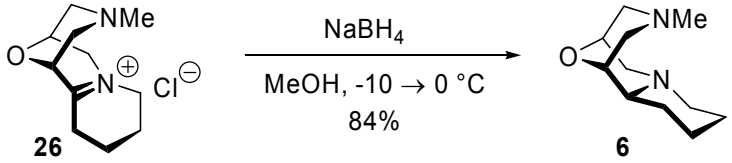
$[\alpha]^{21}_D$ = –55.7 (*c* 0.25 in MeOH). ^{1}H NMR (400 MHz, CD_3OD): δ 1.80 (m, 1H, 4-H), 1.90–2.15 (m, 3H, 4-H, 5-H), 2.27 (s, 3H, NMe), 2.51 (dd, *J* = 12.5, 3.5 Hz, 1H, 12-H_{exo}), 2.54 (dd, *J* = 12.5, 3.5 Hz, 1H, 10-H_{exo}), 2.94 (br d, *J* = 12.0 Hz, 1H, 10-H_{endo}), 3.09 (dt, *J* = 12.4, 1.7 Hz, 1H, 12-H_{endo}), 3.71 (d, *J* = 16.0 Hz, 1H, 8-H_{exo}), 3.76–3.93 (m, 2H, 6-H), 4.11 (dd, *J* = 16.0, 6.7 Hz, 1H, 8-H_{endo}), 4.40 (dd, *J* = 6.3, 3.0 Hz, 1H, 9-H), 4.78 (br s, 1H, 1-H). ^{13}C NMR (100 MHz, CD_3OD): δ 17.2 (C-4), 21.4 (C-5), 29.3 (quin, *J* = 20.1 Hz, C-3), 45.8 (NMe), 54.7 (C-6), 55.3 (C-8), 56.2 (C-12), 60.1 (C-10), 67.5 (C-9), 72.4 (C-1), 188.7 (C-2). IR (ATR): 2945, 2800, 1685, 1451, 1197, 1152, 1098, 818, 798, 716 cm^{-1}. HRMS (ESI) calcd for $[C_{11}H_{19}N_2O]^+$ 195.1492, found 195.1487.

Note: The two acidic protons at C-3 undergo in CD_3OD a fast H/D exchange and were not detected in the ^1H NMR spectra. The carbon atom C-3 of the resulting CD_2-group appears in the ^{13}C NMR spectra as a weak quintett.

TABLE S1. HMBC-interactions in **26** (400 MHz, $CDCl_3$).

proton	HMBC	proton	HMBC	proton	HMBC
1-H	9, 12	8-H_{endo}	2, 9, 10	10-H_{exo}	8, 9, NMe
4-H	2, 3, 5	8-H_{exo}	2, 6, 10	12-H_{endo}	10, NMe
4'-H, 5-H_2	2, 3, 4, 5, 6	9-H	1	12-H_{exo}	1, 2, 10, NMe
6-H_2	2, 4, 5, 8	10-H_{endo}	9, 12, NMe	NMe	10, 12

5.5 (1*R*,2*S*,9*S*)-11-Methyl-13-oxa-7,11-diazatricyclo[7.3.1.$0^{2,7}$]tridecane (6)



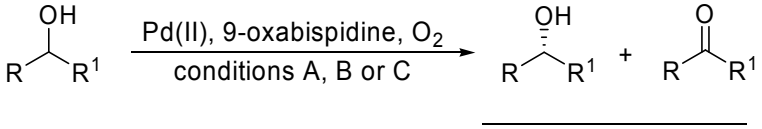
$NaBH_4$ (35.4 mg, 936 µmol) was added at -10 °C to a solution of **26** (200 mg, 867 µmol) in anhydrous MeOH (20 mL). After 4 h at 0 °C, the reaction mixture was evaporated. MeOH (2.5 mL) was added and all volatiles were removed in vacuo. 1 N HCl (25 mL) was added to the residue and the reaction mixture was extracted with CH_2Cl_2 (3 × 10 mL). The organic layers were discarded. The aqueous layer was basified (pH > 10) with 6 N NaOH (7 mL) and extracted with $CHCl_3$ (12 × 10 mL). The combined organic layers were washed with brine (30 mL), dried over $MgSO_4$, and concentrated in vacuo. Column chromatography delivered **6** (154 mg, 786 µmol, 84%) as a low-melting colorless solid. Mp. 35–37°C (ref. 6: mp. 36–38 °C). $[\alpha]^{21}_D$ = +18.7 (*c* 1.2 in MeOH) {ref. 6: $[\alpha]^{22}_D$ = +19.0 (*c* 1.2, MeOH)}.

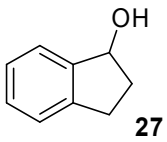
The further spectroscopic and analytical data of **6** were in agreement with those reported in ref. 6.

(6) Breuning, M.; Steiner, M. *Tetrahedron: Asymmetry* **2008**, *19*, 1978.

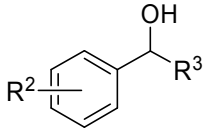
6. Pd(II)/9-oxabispidine-catalyzed oxidative kinetic resolutions

The selectivity factors s were calculated using the equation s = ln[(1–C)(1–ee)]/ln[(1–C)(1+ee)], where C is the conversion.





27



28	R^2	R^3
a	4-OMe	Me
b	3,4-$(OMe)_2$	Me
c	H	Me
d	H	Et

6.1 Conditions A, general procedure

In analogy to refs. 7 and 8, a flask was charged with powdered mol sieves 3Å (250 mg) and flame-dried under vacuum. Under an argon atmosphere, Pd(nbd)Cl_2 (6.7 mg, 25.0 µmol), toluene (5 mL), and the chiral diamine (100 µmol, **6**: 19.6 mg, **7a**: 18.4 mg, **7b**: 23.2 mg) were added. The flask was evacuated and filled with O_2 (3 ×, balloon). The mixture was heated (60 °C for **27**, 80 °C for **28a**) for 10 min and the racemic alcohol (500 µmol, **27**: 67.1 mg, **28a**: 76.1 mg) was introduced. Heating (60 °C for **27**, 80 °C for **28a**) under an oxygen atmosphere (balloon) was continued. The progress of the reaction was monitored by taking samples (ca. 200 µL) every 5–6 days. Each aliquot was filtered through a short pad of silica gel, washed with Et_2O (50 mL), and evaporated under reduced pressure. The conversion was determined by ^1H NMR and the enantiomeric excess was measured by chiral HPLC (see experiments 6.4.1 and 6.4.2). The results are summarized in Table S2, entries 1–6.

6.2 Conditions B, general procedure

In analogy to ref. 9, a flask was charged with powdered mol sieves 3Å (210 mg) and flame-dried under vacuum. Under an argon atmosphere, Pd(nbd)Cl_2 (5.7 mg, 21.3 µmol), $CHCl_3$ (850 µL), and the chiral 9-oxabispidine **6** (10.0 mg, 50.9 µmol) were added. The flask was cooled to -78 °C, evacuated and filled with O_2 (3 ×, balloon). At rt, Cs_2CO_3 (55.4 mg, 170 µmol) and a solution of the racemic alcohol (425 µmol, **27**: 57.0 mg, **28a**: 64.6 mg) in $CHCl_3$ (850 mL) were introduced. Stirring at rt under an oxygen atmosphere (balloon) was continued. The progress of the reaction was monitored by taking samples (ca. 200 µL) every day. Work up and analysis of the aliquots were done as described in experiment 6.1. The results are summarized in Table S2, entries 7 and 8.

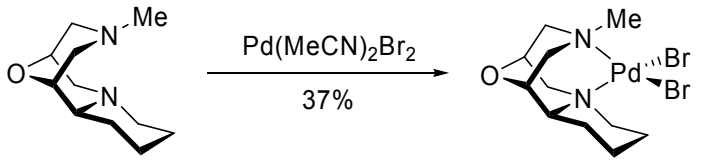
(7) Dearden, M. J.; McGrath, M. J.; O'Brien, P. *J. Org. Chem.* **2004**, *69*, 5789.
(8) Ferreira, E. M.; Stoltz, B. M. *J. Am. Chem. Soc.* **2001**, *123*, 7725.
(9) Bagdanoff, J. T.; Stoltz, B. M. *Angew. Chem. Int. Ed.* **2004**, *43*, 353.

TABLE S2. Results of the 9-oxabispidine/$PdCl_2$-catalyzed oxidative kinetic resolutions of the alcohols **27** and **28a** under conditions A and B.

entry	starting material	9-oxa-bispidine	conditions	t (d)	conversion[a] (%)	er[b] (*R*/*S*)	s
1	**27**	**7a**	A	17	31	50:50	0.0
2	**27**	**7b**	A	17	25	54:46	1.8
3	**27**	**6**	A	30	54	75:25	3.8
4	**28a**	**7a**	A	17	47	50:50	0.0
5	**28a**	**7b**	A	17	41	59:41	2.0
6	**28a**	**6**	A	17	61	89:11	6.7
7	**27**	**6**	B	4.5	62	80:20	3.7
8	**28a**	**6**	B	4.5	53	83:17	7.1

[a] Determined by ^{1}H NMR. [b] Determined by chiral HPLC.

6.3 Preparation of the catalyst 29



6 **29**

$PdBr_2$ (247 mg, 927 μmol) was refluxed for 1 h in anhydrous MeCN (5 mL) to give an orange solution. A solution of the 9-oxabispidine **6** (182 mg, 927 μmol) in MeCN (5 mL) was added at rt resulting in the formation of a brownish solution. The precipitate formed (265 mg) within 3 h was collected by filtration through a sintered glass funnel, suspended in $CHCl_3$ (35 mL), and refluxed for 1 h. Et_2O (15 mL) was added at rt and the precipitate was collected by filtration through a sintered glass funnel to give the catalyst **29** as a fine orange-brown solid (206 mg, 445 μmol, 48%). Mp. >230 °C. $[\alpha]^{21}_D$ = –53.4 (*c* 0.02 in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.50–1.70 (m, 3H, CH_2), 1.98–2.08 (m, 2H, CH_2), 2.29 (m, 1H, 2-H), 2.32 (dd, *J* = 13.2, 4.2 Hz, 1H, 12-H), 2.53 (dd, *J* = 13.2, 3.9 Hz, 1H, 8-H), 2.75 (dd, *J* = 13.0, 4.0 Hz, 1H, 10-H), 2.81 (m, 2H, CH_2), 2.90 (s, 3H, NMe), 3.19 (d, *J* = 13.1 Hz, 1H, 12-H), 3.73 (t, *J* = 3.7 Hz, 1H, 1-H), 3.92 (dd, *J* = 12.7, 1.1 Hz, 1H, 10-H), 4.15 (d, *J* = 13.2 Hz, 1H, 8-H), 4.20 (m, 1H, CH_2), 4.25 (t, *J* = 3.9 Hz, 1H, 9-H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9 (CH_2), 25.3 (CH_2), 27.4 (CH_2), 56.2 (C-12), 59.3 (NMe), 61.8 (C-10), 62.0 (C-8), 64.5 (CH_2), 67.0 (C-9), 67.5 (C-2), 69.8 (C-1). IR (ATR): 2952, 1453, 1362, 1283, 1090, 1071, 1030, 1016, 814, 757, 722 cm^{-1}.

6.4 Conditions C, general procedure

In analogy to ref. 10, a flask was charged with powdered mol sieves 3Å (500 mg) and flame-dried under vacuum. Under an argon atmosphere, complex **29** (23.1 mg, 50.0 µmol), $CHCl_3$ (2.0 mL), and the chiral 9-oxabispidine **6** (13.7 mg, 70.0 µmol) were added. The flask was cooled to -78 °C, evacuated and filled with O_2 (3 ×, balloon). At rt, Cs_2CO_3 (130 mg, 400 µmol) and a solution of the racemic alcohol **27** or **28** (1.00 mmol) in $CHCl_3$ (2.0 mL) was introduced. Stirring at rt under an oxygen atmosphere (balloon) was continued for 18–60 h. The progress of the reaction was daily monitored by taking samples (ca. 100 µL), the conversion of which was directly determined by ^{1}H NMR after addition of $CDCl_3$. For work up, the reaction mixture was filtered through a pad of silica gel and washed with Et_2O (50 mL). After evaporation of all volatile compounds, column chromatography (silica gel, *n*-pentane/EtOAc 6:1 → 2:1) delivered the enantioenriched alcohol **27** or **28** in analytically pure form.

The absolute configurations of the enantioenriched alcohols were assigned according to their known retention times on chiral HPLC.[9,11]

6.4.1 (*R*)-1-Indanol [(*R*)-27]

According to the general procedure, (*R*)-**27** (28.6 mg, 213 µmol, 21%, 93.0:7.0 er) was obtained from *rac*-**27** (134 mg, 1.00 mmol) after 18 h (conversion: 66.6%). Calculated selectivity factor: s = 6.4. HPLC analysis: Chiralcel OD-H, *n*-hexane/*i*PrOH 97:3, 0.8 mL/min, 256 nm, retention times: *S*-enantiomer: t_R = 21.8 min, *R*-enantiomer: t_R = 25.0 min.

6.4.2 (*R*)-1-(4-Methoxyphenyl)ethanol [(*R*)-28a]

According to the general procedure, (*R*)-**28a** (50.2 mg, 330 µmol, 33%, 99.6:0.4 er) was obtained from *rac*-**28a** (152 mg, 1.00 mmol) after 20 h (conversion: 63.0%). Calculated selectivity factor: s = 19.1. HPLC analysis: Chiralcel OD-H, *n*-hexane/*i*PrOH 99:1, 0.6 mL/min, 223 nm, retention times: *R*-enantiomer: t_R = 92.0 min, *S*-enantiomer: t_R = 102 min.

6.4.3 (*R*)-1-(3,4-Dimethoxyphenyl)ethanol [(*R*)-28b]

According to the general procedure, (*R*)-**28b** (64.0 mg, 351 µmol, 35%, 93.5:6.5 er) was obtained from *rac*-**28b** (182 mg, 1.00 mmol) after 42 h (conversion: 58.0%). Calculated selectivity factor: s = 12.0. HPLC analysis: Chiralcel OD-H, *n*-hexane/*i*PrOH 95:5, 1.0 mL/min, 226 nm, retention times: *S*-enantiomer: t_R = 64.7 min, *R*-enantiomer: t_R = 67.5 min.

6.4.4 (*R*)-1-Phenylethanol [(*R*)-28c]

According to the general procedure, (*R*)-**28c** (47.3 mg, 387 µmol, 39%, 82.7:17.3 er) was obtained from *rac*-**28c** (122 mg, 1.00 mmol) after 60 h (conversion: 47.6%). Calculated selectivity factor: s = 11.9. HPLC analysis: Chiralcel OD-H, *n*-hexane/*i*PrOH 98:2, 0.4 mL/min, 216 nm, retention times: *R*-enantiomer: t_R = 24.4 min, *S*-enantiomer: t_R = 30.9 min.

6.4.5 (*R*)-1-Phenylpropan-1-ol [(*R*)-28d]

According to the general procedure, (*R*)-**28d** (65.6 mg, 482 µmol, 48%, 76.1:23.9 er) was obtained from *rac*-**28d** (136 mg, 1.00 mmol) after 60 h (conversion: 42.0%). Calculated selectivity factor: s = 10.3. HPLC analysis: Chiralcel OD-H, *n*-hexane/*i*PrOH 99.5:0.5, 1.0 mL/min, 215 nm, retention times: *R*-enantiomer: t_R = 51.5 min, *S*-enantiomer: t_R = 64.1 min.

---

(10) Ebner, D. C.; Trend, R. M.; Genet, C.; McGrath, M. J.; O'Brien, P.; Stoltz, B. M. *Angew. Chem. Int. Ed.* **2008**, *47*, 6367.

(11) Bagdanoff, J. T.; Ferreira, E. M.; Stoltz, B. M. *Org. Lett.* **2003**, *5*, 835.

7 Quantum chemical calculations

7.1 Computational methods

All energies were computed on the DFT level, employing the TURBOMOLE program package,[12] with standard settings. The optimization of geometrical parameters was performed with the BLYP exchange correlation functional,[13] the resolution of identity approximation (RI),[14] and the triple zeta basis set TZVP,[15] which includes three sizes of contracted functions and further p-functions to take polarization into account. For palladium, the default core potential ecp-28-mwb was used in all calculations. Minimum energy structures were confirmed in their nature by frequency calculations. The electronic energies of all obtained geometries were recalculated by additional single point calculations, employing Becke's three parameter hybrid functional B3LYP,[13] and corrected by unscaled zero point energies (ZPE). For all geometry optimizations and single point calculations, solvent effects were taken into account within the conductor-like screening model (COSMO).[16] The dielectric constant of the polarizable environment was set to $\varepsilon = 36.64$, which corresponds to acetonitrile. For cavity radii, standard settings were used.

7.2 Calculation of the pKa values of 3 and 6

The pKa values of **3** and **6** were determined using a method established by Gogoll et al.[17]

The proton affinities (PA), given as energy differences between the protonated species and the free bases, were calculated for the bispidines **VIII**–**X**, **1**, and **3** and for the 9-oxabispidine **6** (Table S3). In the cases of the C_1-symmetric diamines **1**, **3** and **6**, the slightly more basic nitrogen atoms being part of the *endo*-anellated rings were used. Correlation of the known[17] pKa_{MeCN} values of **VIII**–**X** and **1** with the proton affinities delivered, as illustrated in Figure S1, the regression line $pKa = 0.1383 \times PA - 145.8$ ($r^2 = 0.9639$), from which the pKa values of **3** and **6** were taken.

(12) TURBOMOLE Vers. 5.9, Quantum Chem. Group, University of Karlsruhe, Germany, **2007**.

(13) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

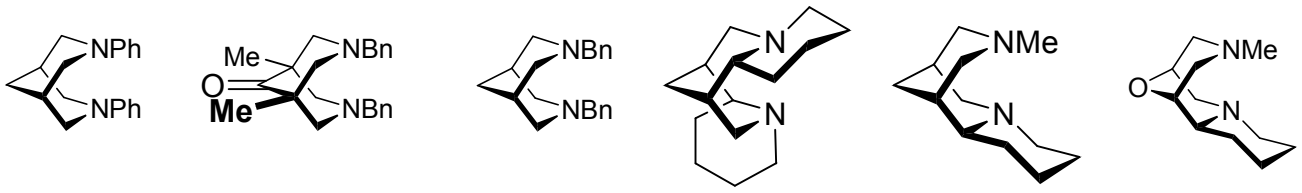
(14) Kendall,R. A.; Früchtl, H. A. *Theor. Chem. Acc*. **1997**, *97*, 158.

(15) Schäfer, A.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1997**, *100*, 5929.

(16) Klamt, A.; Schüürmann, G. *J. Chem. Soc. Perkin Trans. 2* **1993**, 799.

(17) Toom, L.; Kütt, A.; Kaljurand, I.; Leito, I.; Ottosson, H.; Grennberg, H.; Gogoll, A. *J. Org. Chem.* **2006**, *71*, 7155.

TABLE S3. Calculated proton affinities (PA) and pKa values of the bispidines **VIII**–**X**, **1**, **3**, and **6**.



VIII **IX** **X** (–)-sparteine (**1**) **3** **6**

entry	bispidine	H_f (base) [H]	H_f (base-H^+) [H]	proton affinity[a] (PA) [kJmol^{-1}]	pKa[b,17] (exp.)	pKa[b,c] (calc.)	ΔpKa
1	**VIII**	-846.12879	-846.56922	1156.42	13.97	14.14	0.16
2	**IX**	-1077.24029	-1077.69029	1181.54	17.48	17.61	0.13
3	**X**	-924.65729	-925.11467	1200.92	21.25	20.29	-0.96
4	**1**	-696.11673	-696.57972	1215.65	21.66	22.32	0.66
5	**3**	-579.49204	-579.95370	1212.16	---	21.84	---
6	**6**	-615.43108	-615.88629	1195.22	---	19.50	---

[a] PA = H_f (base) – H_f (base-H^+). [b] pKa Value of the protonated base. [c] Using the regression line pKa = 0.1383 × PA – 145.8.

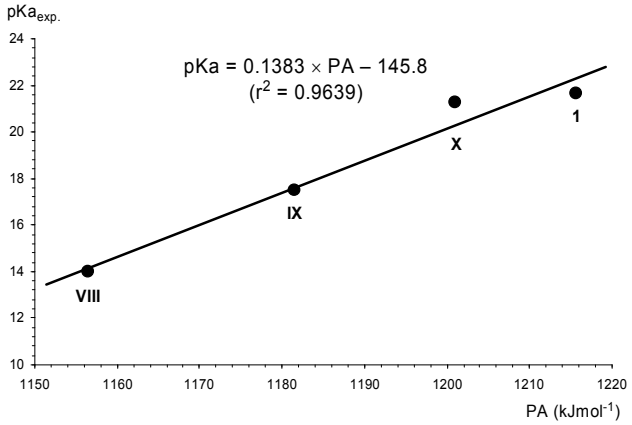


FIGURE S1. Correlation of the proton affinities (PA) with the known pKa values of the bispidines **VIII**–**X** and **1**.

7.3 Structures of the 9-oxabispidine (6)–$PdBr_2$ complexes 29 and 30

The optimized structures of **29** (H_f = -5891.5055 H) and **30** (H_f = -5891.4888 H) are shown in Figure S2. The calculated structure of **29** is in excellent agreement with the known[10] X-ray analysis of the related complex [(**3**)$PdBr_2$].

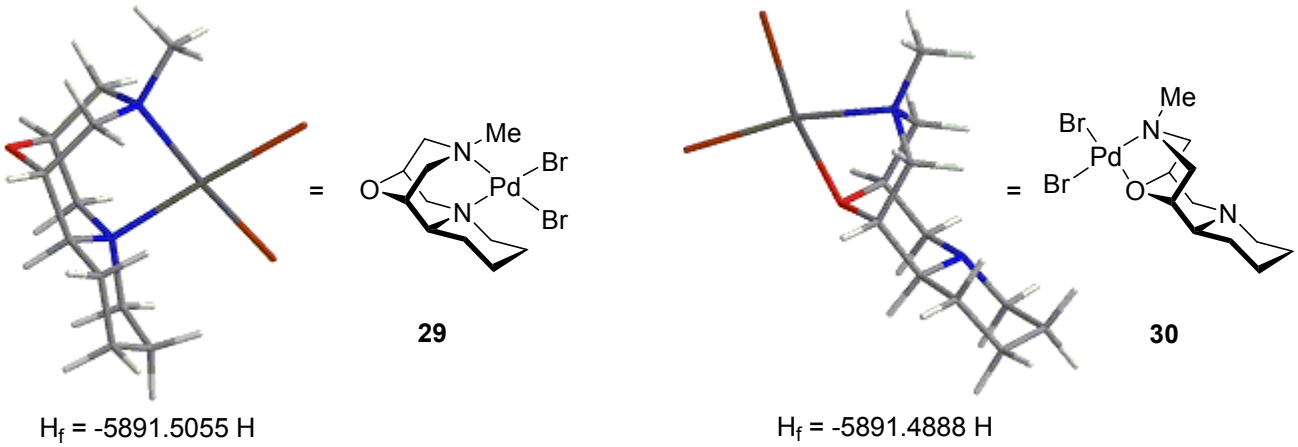
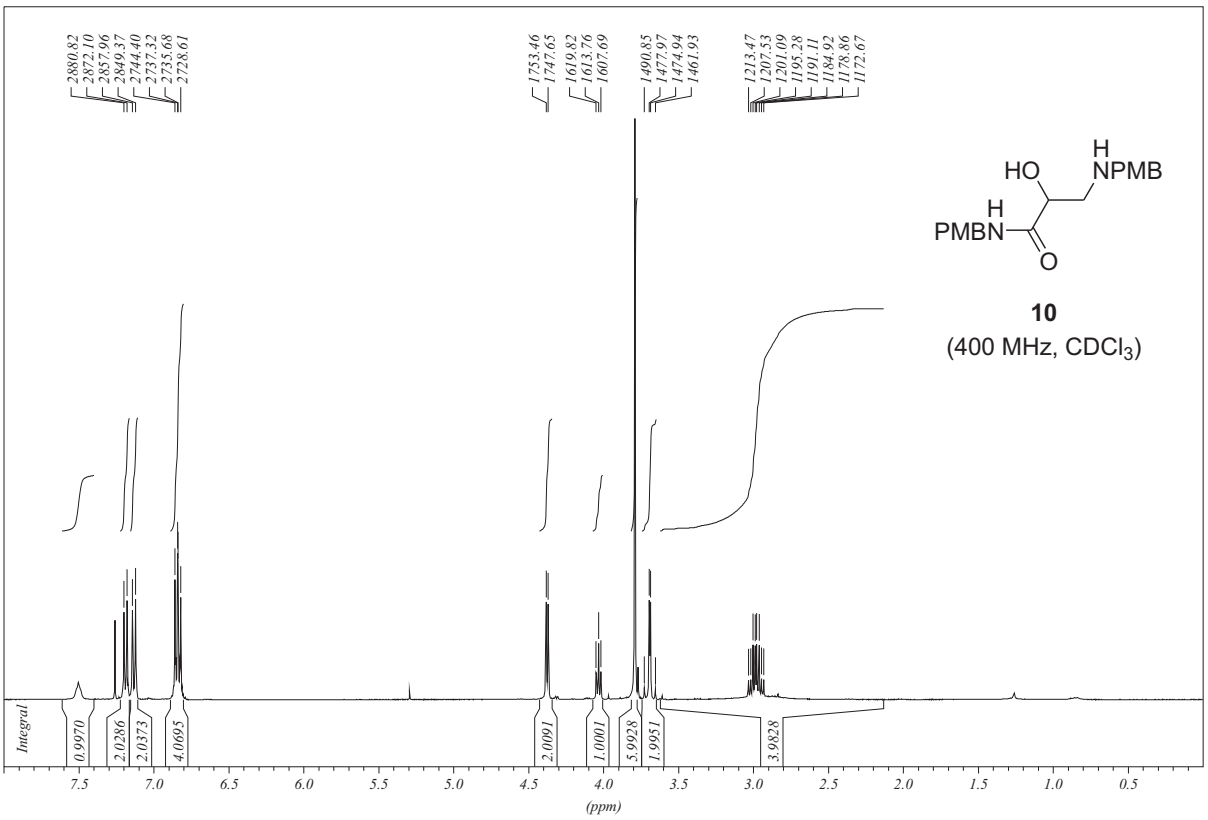
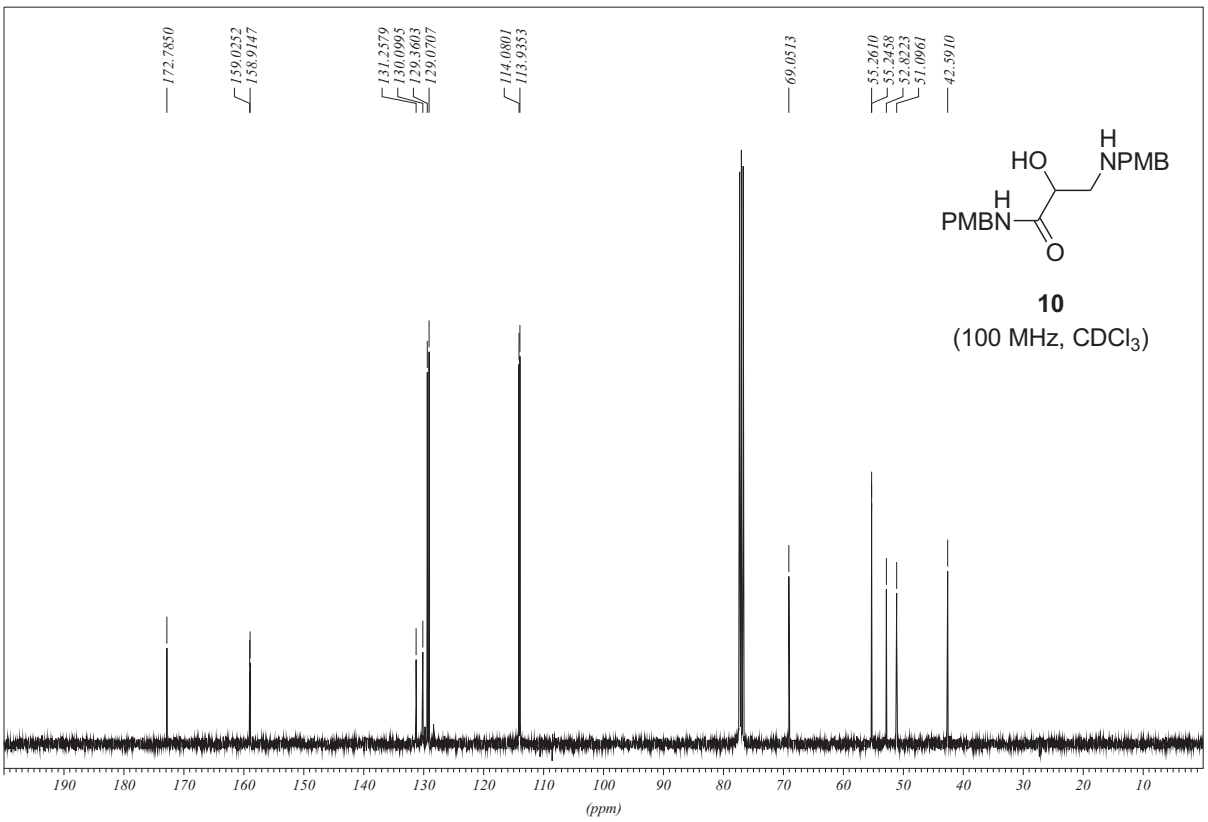
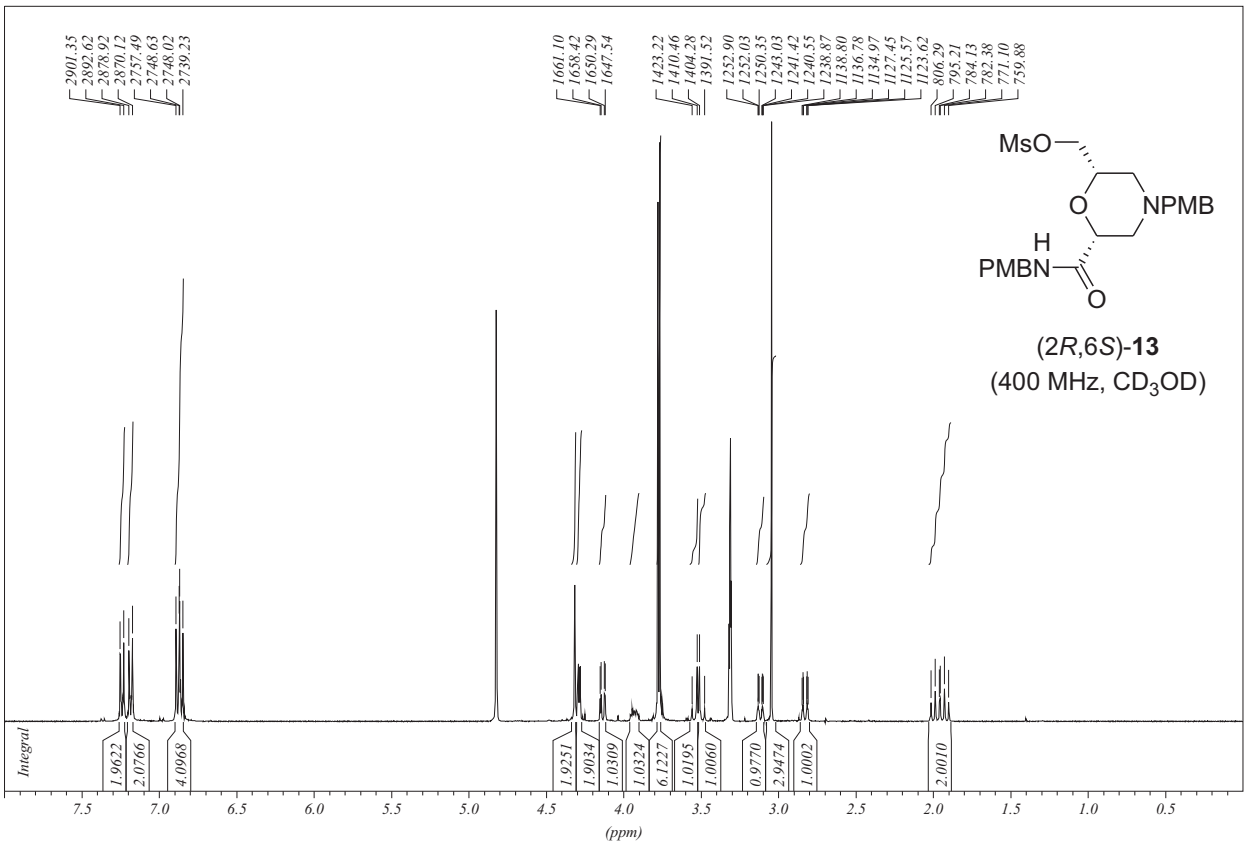


FIGURE S2. Calculated structures of the 9-oxabispidine (**6**)–$PdBr_2$ complexes **29** and **30**.

8. Copies of ^{1}H and ^{13}C NMR spectra



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2878.92
2870.12
2757.49
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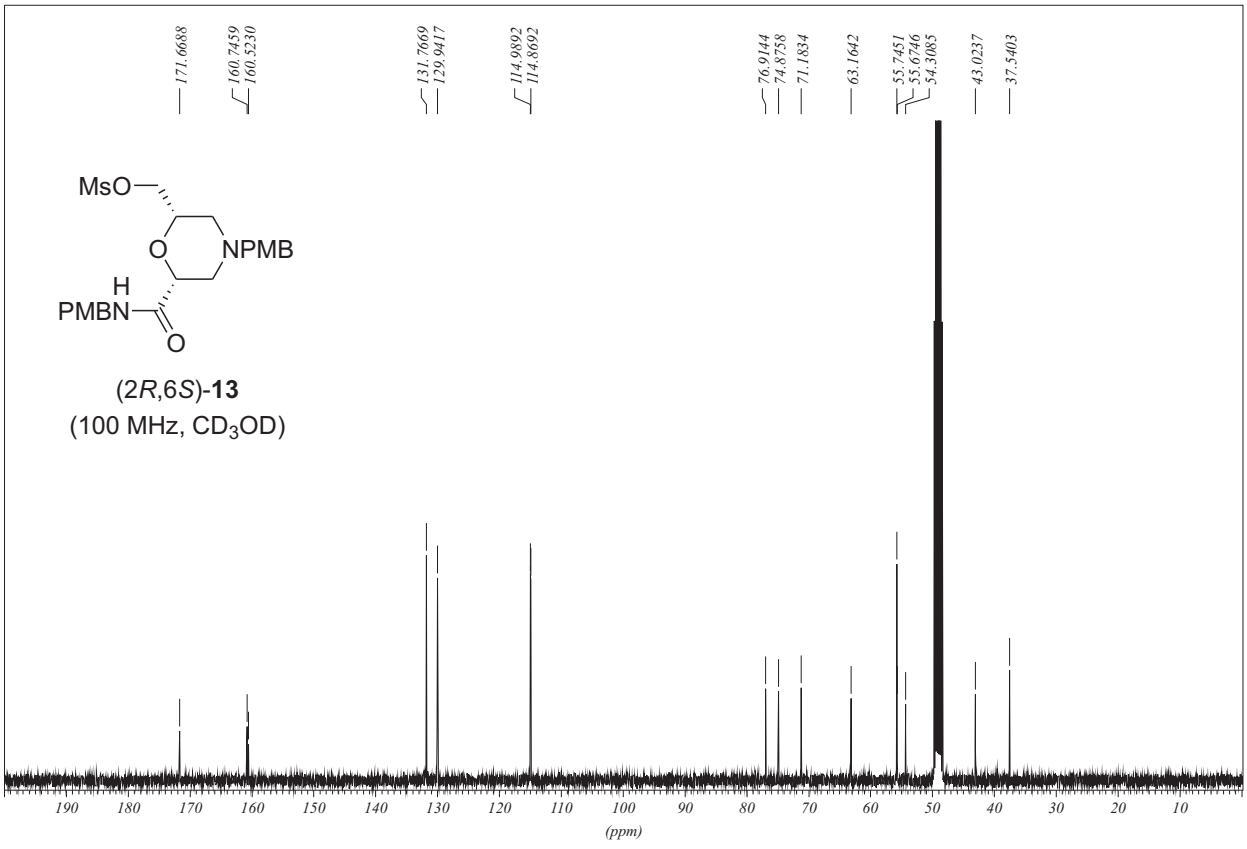
2748.02
2739.23
1661.10
1658.42
1650.29
1647.54
1423.22
1410.46
1404.28
1391.52
1252.90
1252.03
1250.35
1243.03
1241.42
1240.55
1238.87
1138.80
1136.78
1134.97
1127.45
1125.57
1123.62
806.29
795.21
784.13
782.38
771.10
759.88
MsO
O
NPMB
H
PMBN
O
(2R,6S)-13
(400 MHz, CD3OD)
Integral
1.9622
2.0766
4.0968
1.9251
1.9034
1.0309
1.0324
6.1227
1.0195
1.0060
0.9770
2.9474
1.0002
2.0010
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
(ppm)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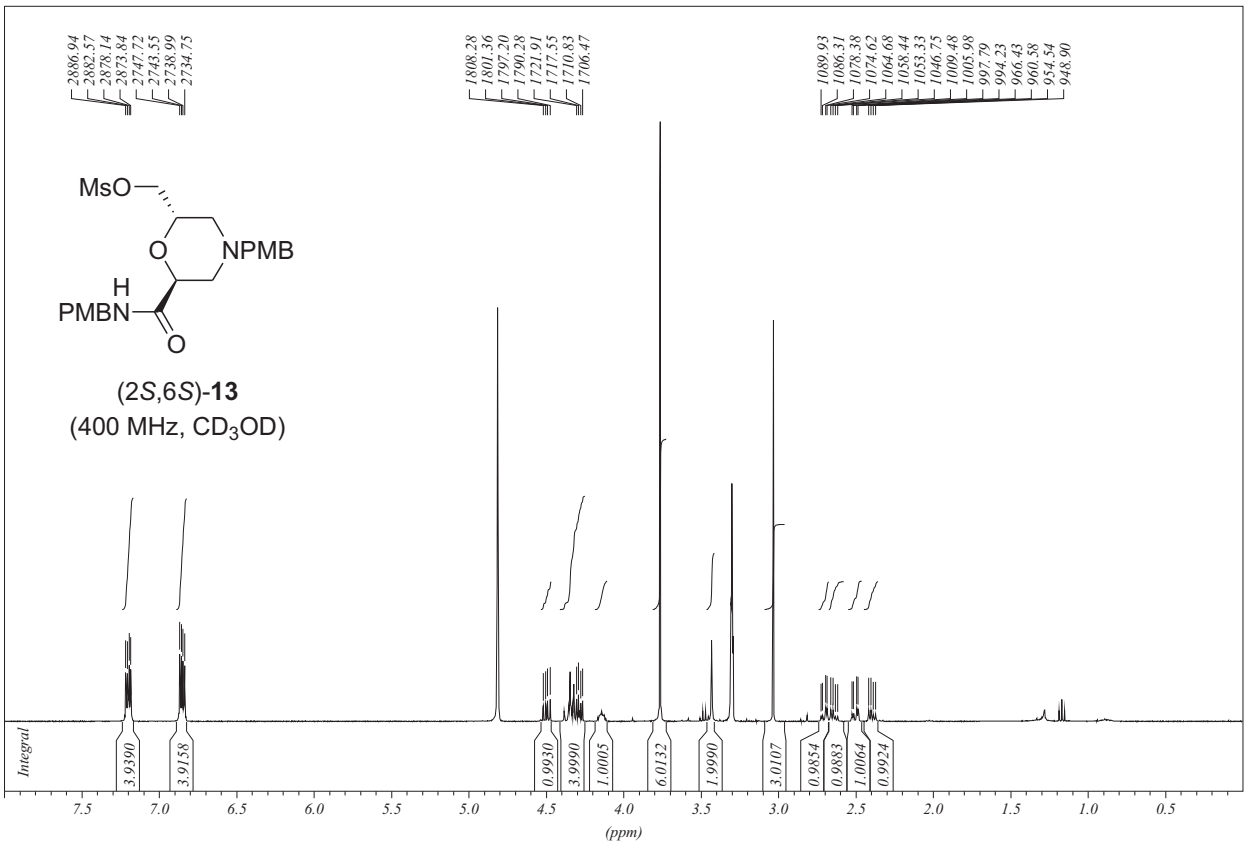
160.7459
160.5230
131.7669
129.9417
114.9892
114.8692
76.9144
74.8758
71.1834
63.1642
55.7451
55.6746
54.3085
43.0237
37.5403
MsO
O
NPMB
H
PMBN
O
(2R,6S)-13
(100 MHz, CD3OD)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)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2734.75
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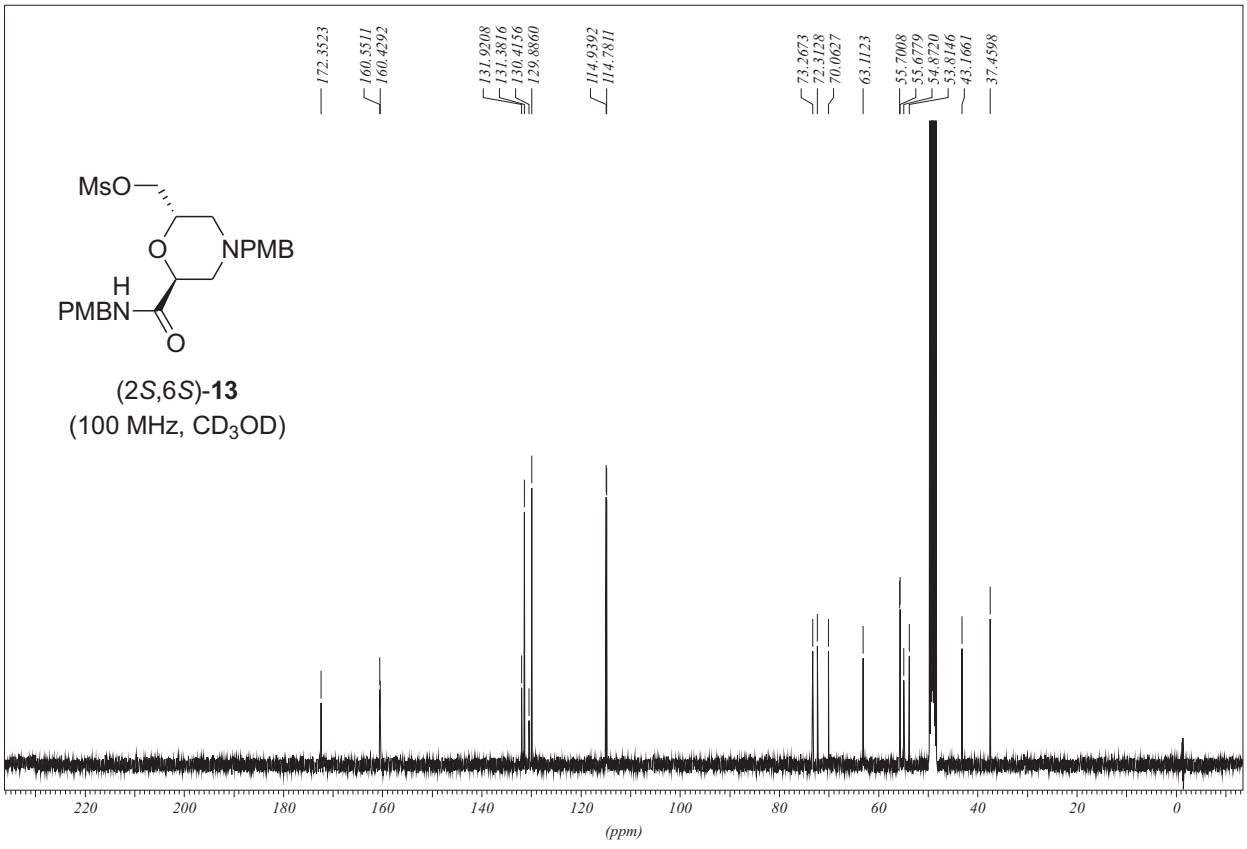
1797.20
1790.28
1721.91
1717.55
1710.83
1706.47
1089.93
1086.31
1078.38
1074.62
1064.68
1058.44
1053.33
1046.75
1009.48
1005.98
997.79
994.23
966.43
960.58
954.54
948.90
MsO
O
NPMB
H
PMBN
O
(2S,6S)-13
(400 MHz, CD3OD)
Integral
3.9390
3.9158
0.9930
3.9990
1.0005
6.0132
1.9990
3.0107
0.9854
0.9883
1.0064
0.9924
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
(ppm)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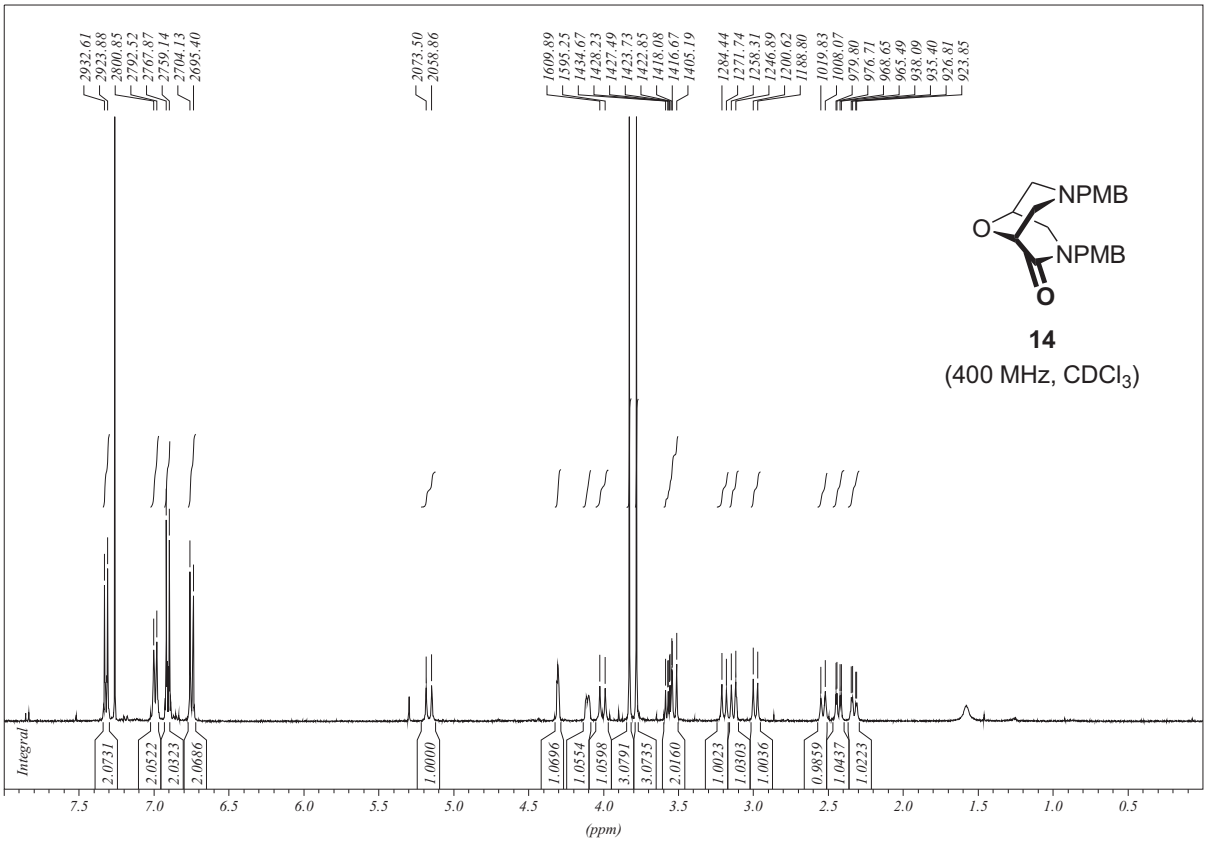
72.3128
70.0627
63.1123
55.7008
55.6779
54.8720
53.8146
43.1661
37.4598
MsO
O
NPMB
H
PMBN
O
(2S,6S)-13
(100 MHz, CD3OD)
220
200
180
160
140
120
100
80
60
40
20
0
(ppm)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2759.14
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2073.50
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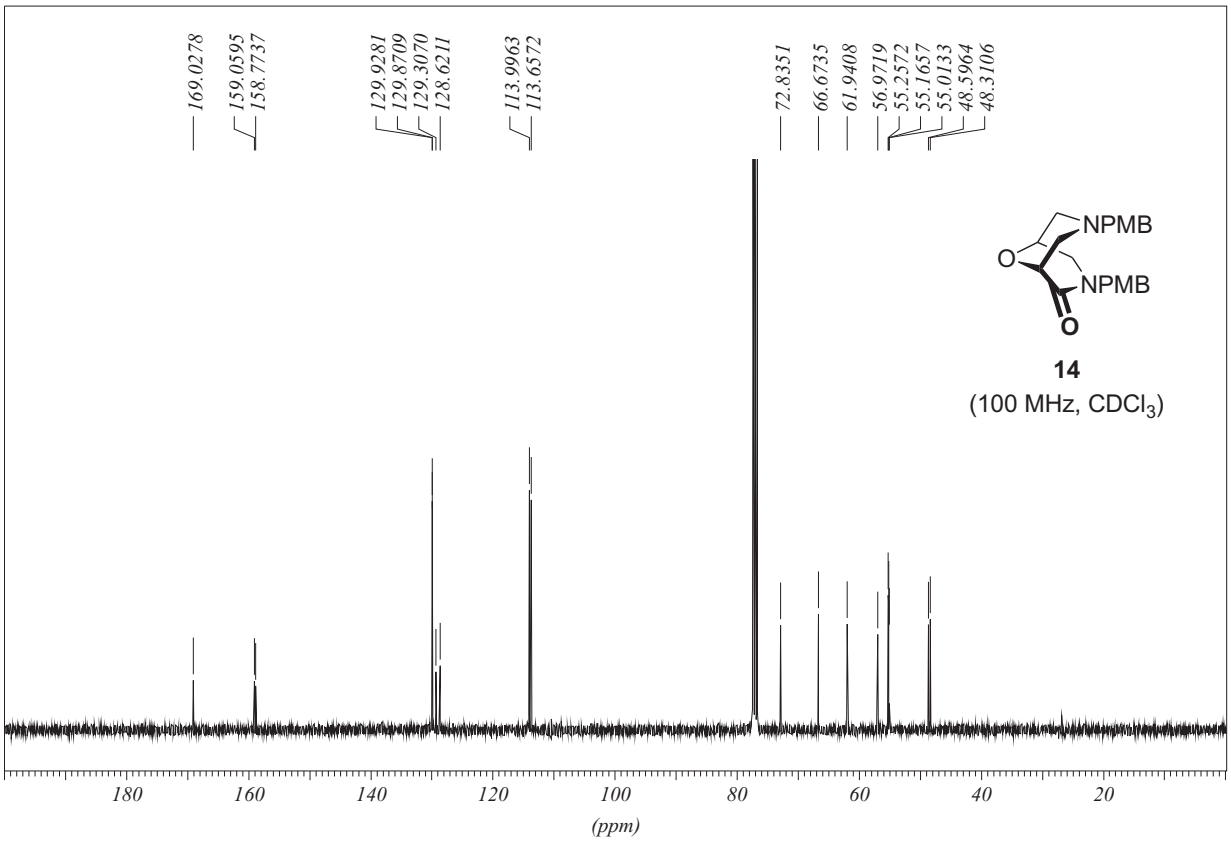
1609.89
1595.25
1434.67
1428.23
1427.49
1423.73
1422.85
1418.08
1416.67
1405.19
1284.44
1271.74
1238.31
1246.89
1200.62
1188.80
1019.83
1008.07
979.80
976.71
968.65
965.49
938.09
935.40
926.81
923.85
Integral
2.0731
2.0522
2.0323
2.0686
1.0000
1.0696
1.0554
1.0598
3.0791
3.0735
2.0160
1.0023
1.0303
1.0036
0.9859
1.0437
1.0223
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
(ppm)
NPMB
O
NPMB
O
14
(400 MHz, CDCl3)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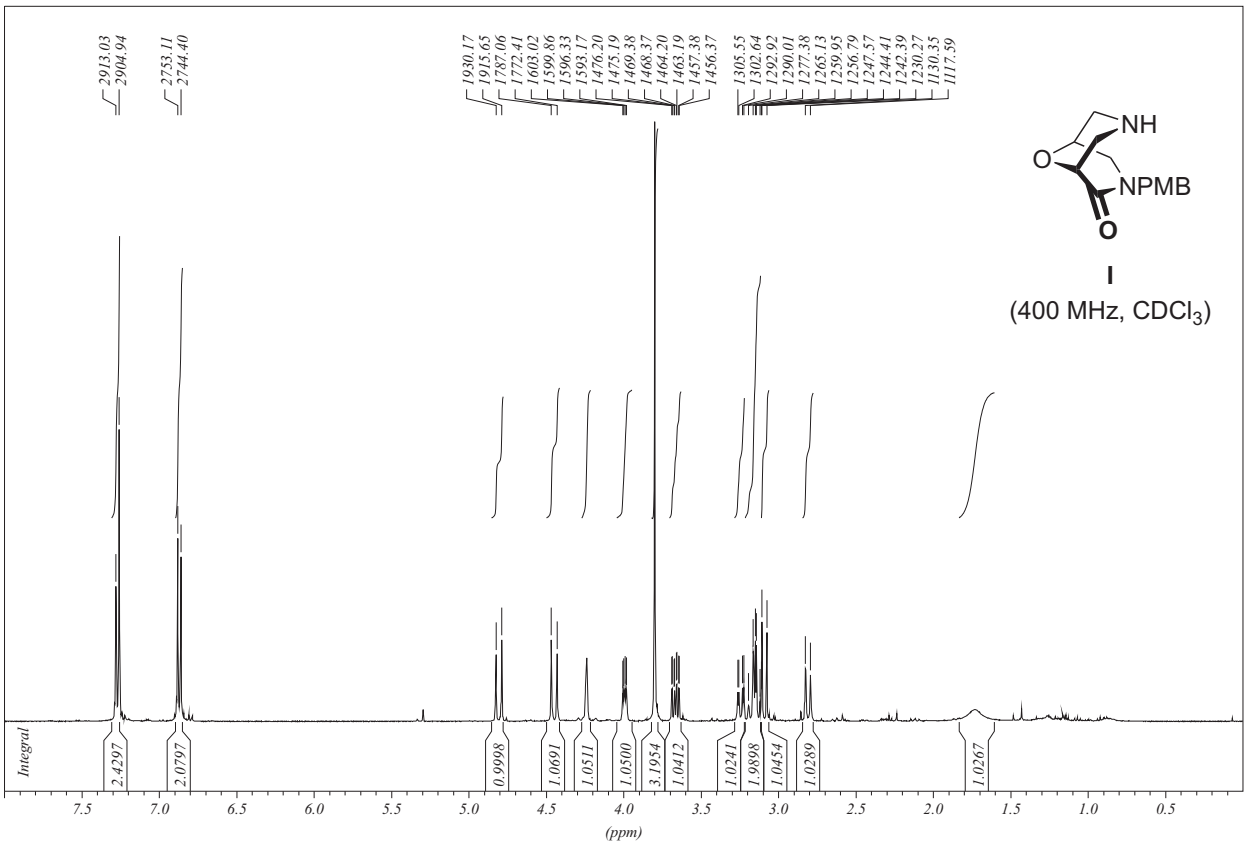
72.8351
66.6735
61.9408
56.9719
55.2572
55.1657
55.0133
48.5964
48.3106
180
160
140
120
100
80
60
40
20
(ppm)
NPMB
O
NPMB
O
14
(100 MHz, CDCl3)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2744.40
1930.17
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1603.02
1599.86
1596.33
1593.17
1476.20
1475.19
1469.38
1468.37
1464.20
1463.19
1457.38
1456.37
1305.55
1302.64
1292.92
1290.01
1277.38
1265.13
1259.95
1256.79
1247.57
1244.41
1242.39
1230.27
1130.35
1117.59
NH
O
NPMB
O
I
(400 MHz, CDCl3)
Integral
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2.0797
0.9998
1.0691
1.0511
1.0500
3.1954
1.0412
1.0241
1.9898
1.0454
1.0289
1.0267
7.5
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6.5
6.0
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4.0
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2.5
2.0
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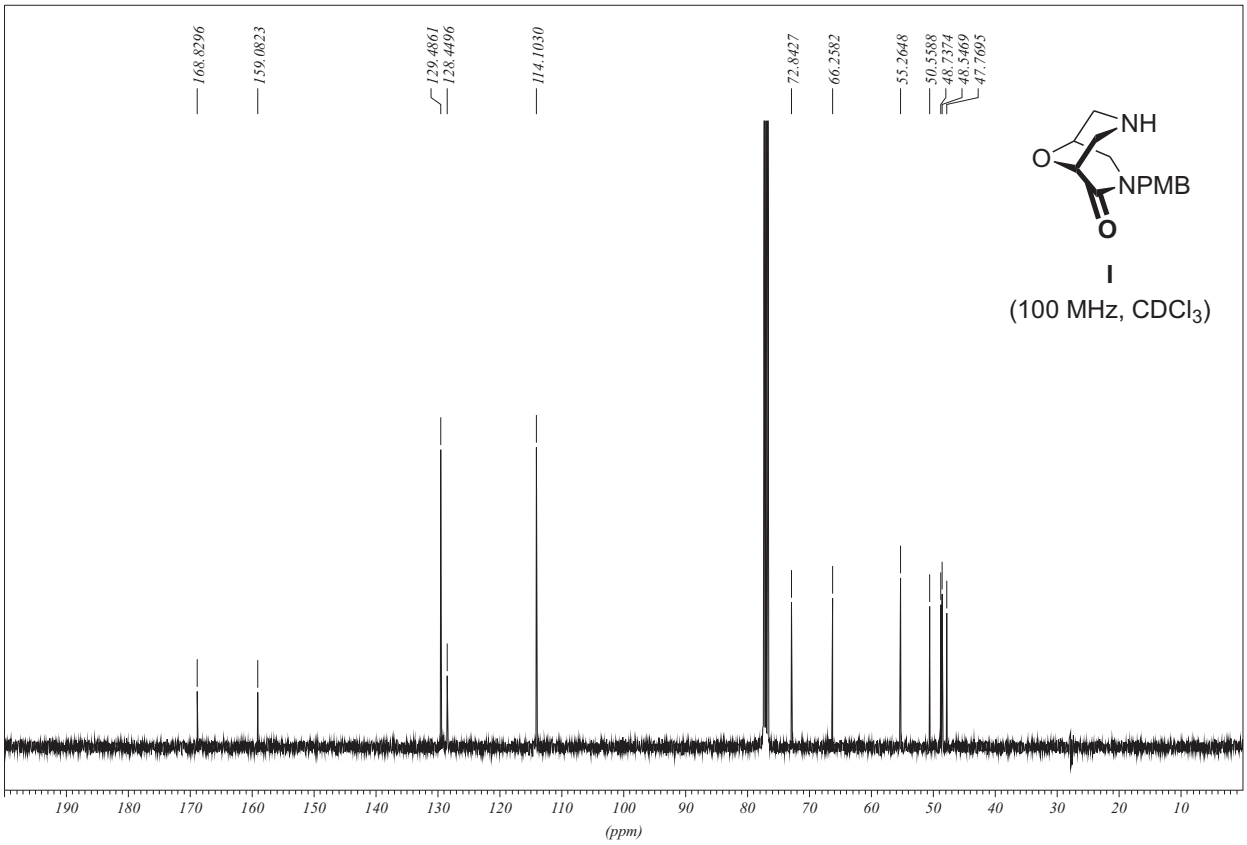
1.0
0.5
(ppm)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114.1030
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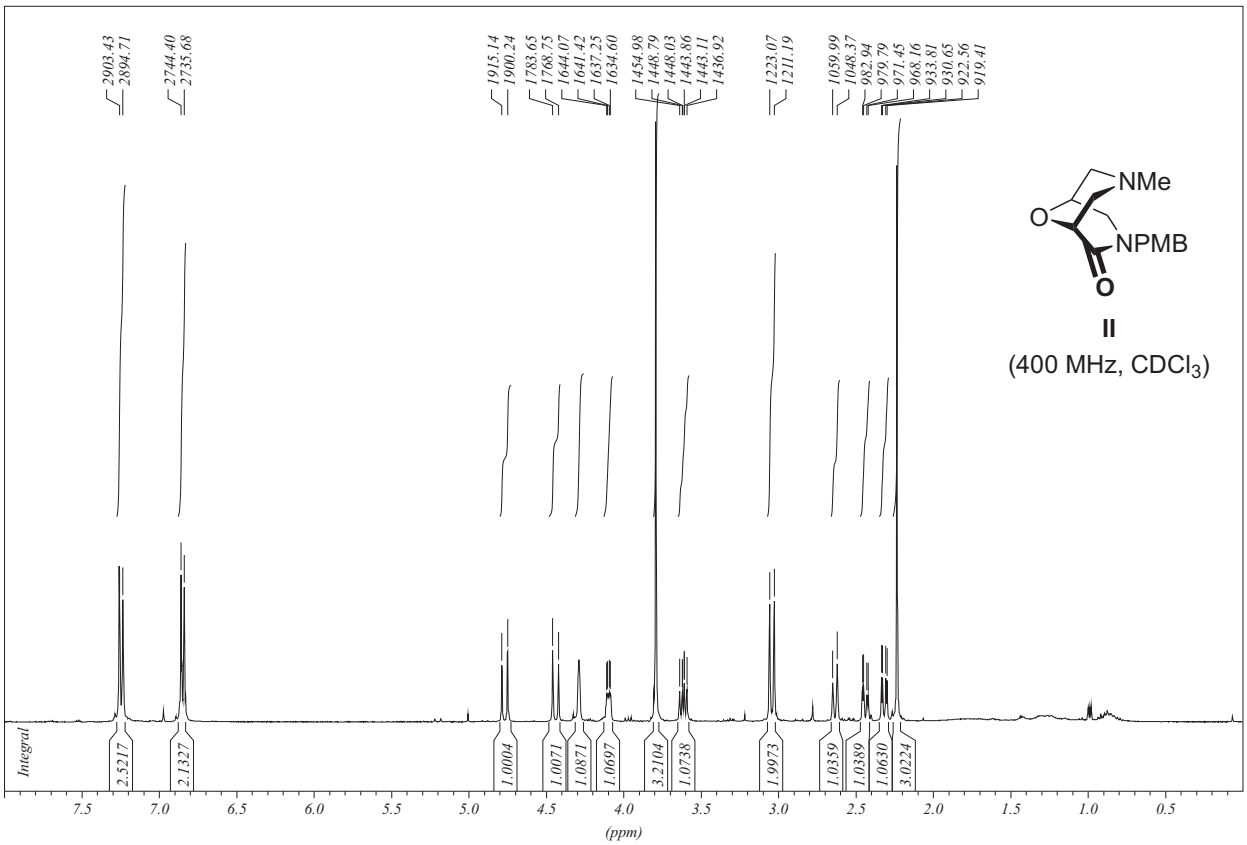
48.7374
48.5469
47.7695
NH
O
NPMB
O
I
(100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)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1637.25
1634.60
1454.98
1448.79
1448.03
1443.86
1443.11
1436.92
1223.07
1211.19
1059.99
1048.37
982.94
979.79
971.45
968.16
933.81
930.65
922.56
919.41
NMe
O
NPMB
O
II
(400 MHz, CDCl3)
Integral
2.5217
2.1327
1.0004
1.0071
1.0871
1.0697
3.2104
1.0738
1.9973
1.0359
1.0389
1.0630
3.0224
7.5
7.0
6.5
6.0
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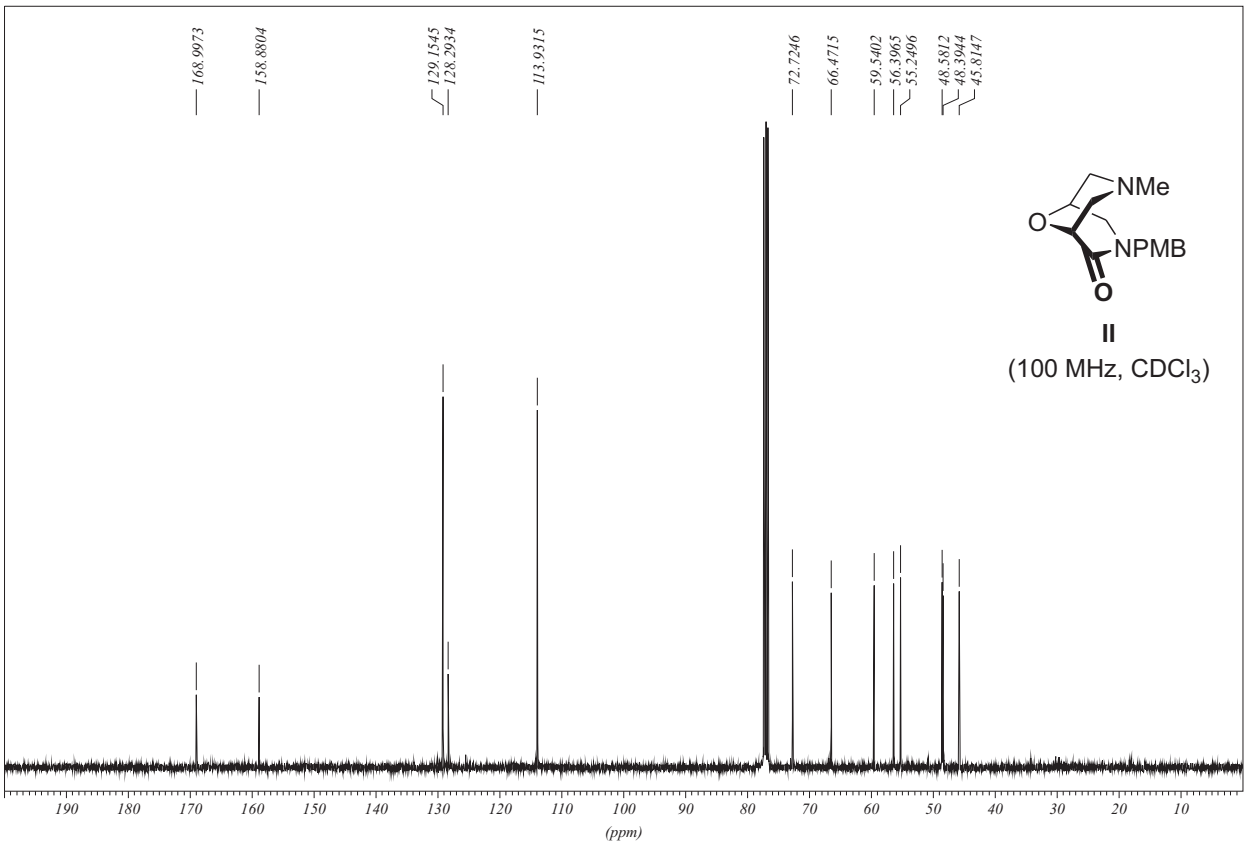
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)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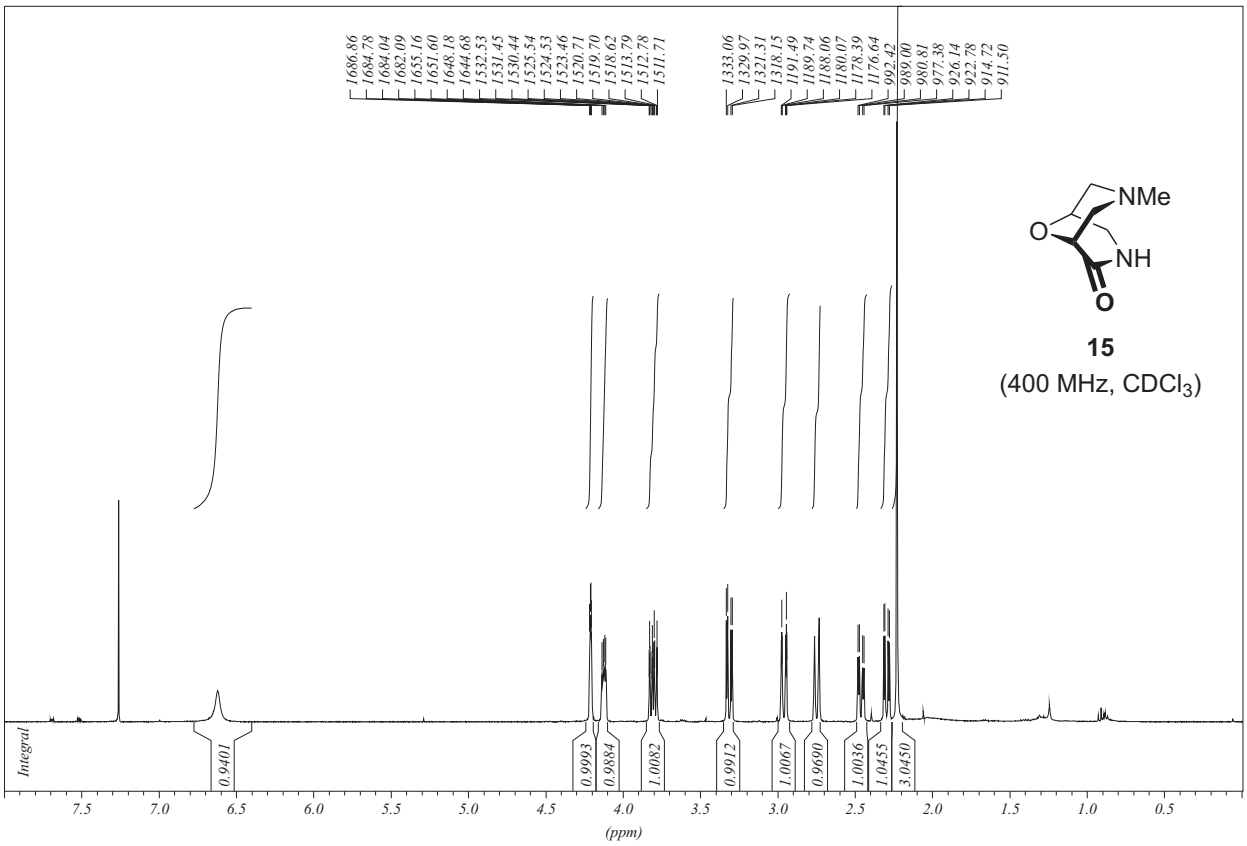
48.5812
48.3944
45.8147
NMe
O
NPMB
O
II
(100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)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1648.18
1644.68
1532.53
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1530.44
1525.54
1524.53
1523.46
1520.71
1519.70
1518.62
1513.79
1512.78
1511.71
1333.06
1329.97
1321.31
1318.15
1191.49
1189.74
1188.06
1180.07
1178.39
1176.64
992.42
989.00
980.81
977.38
926.14
922.78
914.72
911.50
NMe
O
NH
O
15
(400 MHz, CDCl3)
Integral
0.9401
0.9993
0.9884
1.0082
0.9912
1.0067
0.9690
1.0036
1.0455
3.0450
7.5
7.0
6.5
6.0
5.5
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4.5
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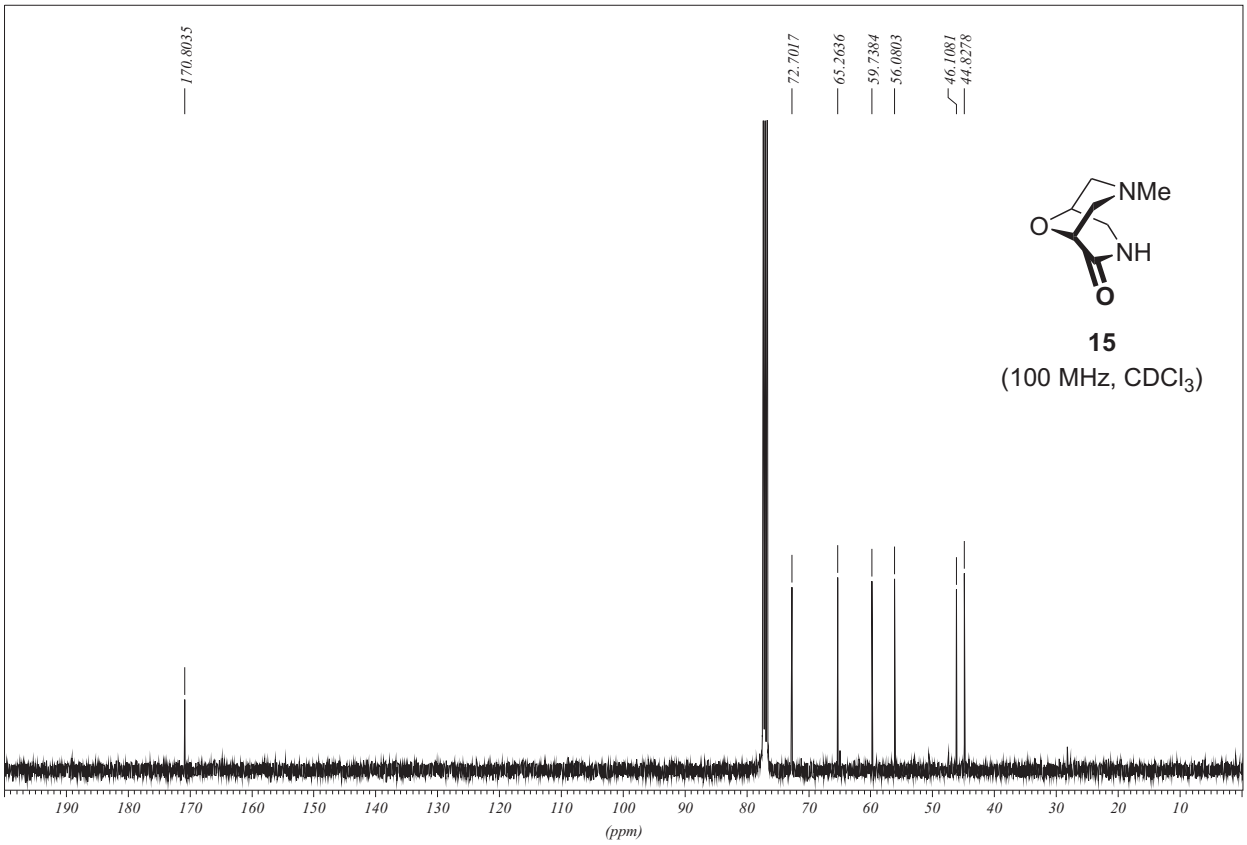
1.5
1.0
0.5
(ppm)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72.7017
65.2636
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56.0803
46.1081
44.8278
NMe
O
NH
O
15
(100 MHz, CDCl3)
190
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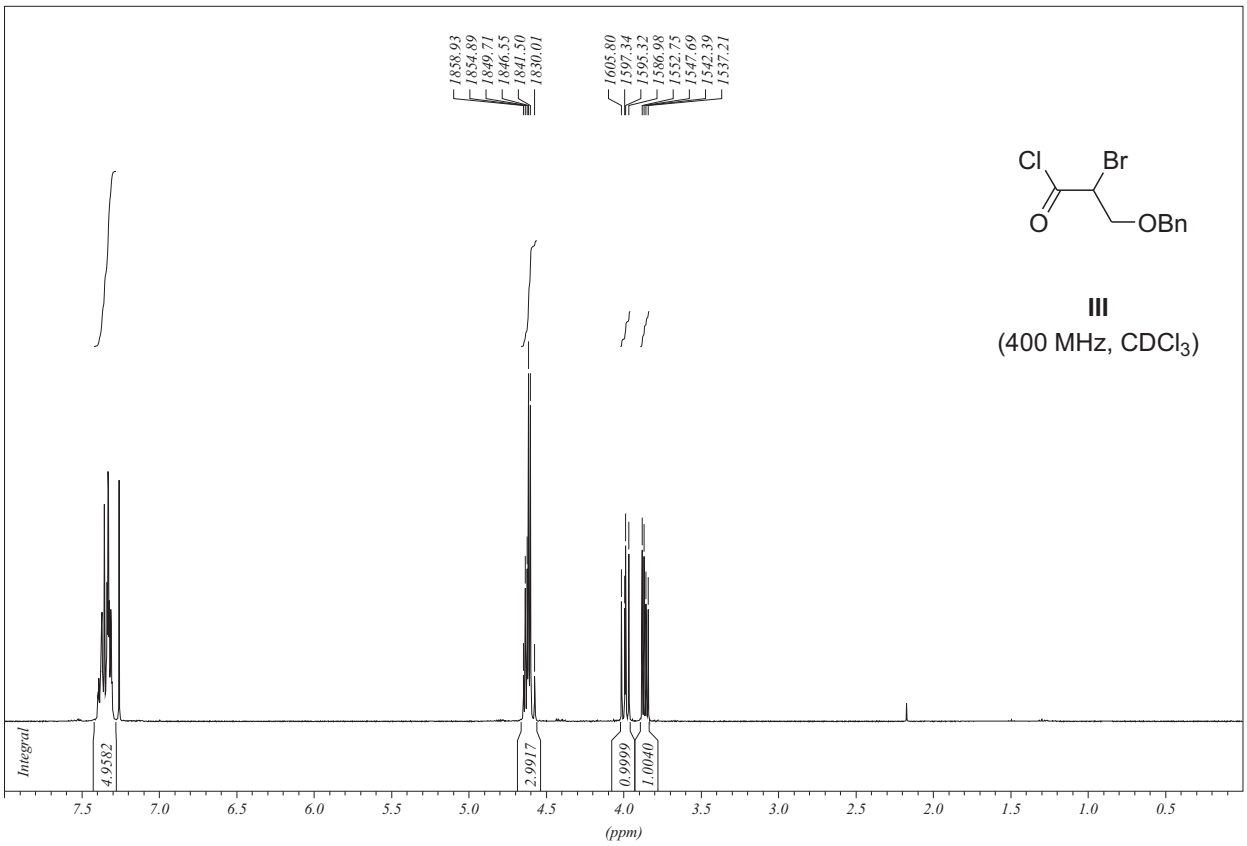
80
70
60
50
40
30
20
10
(ppm)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1854.89
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1846.55
1841.50
1830.01
1605.80
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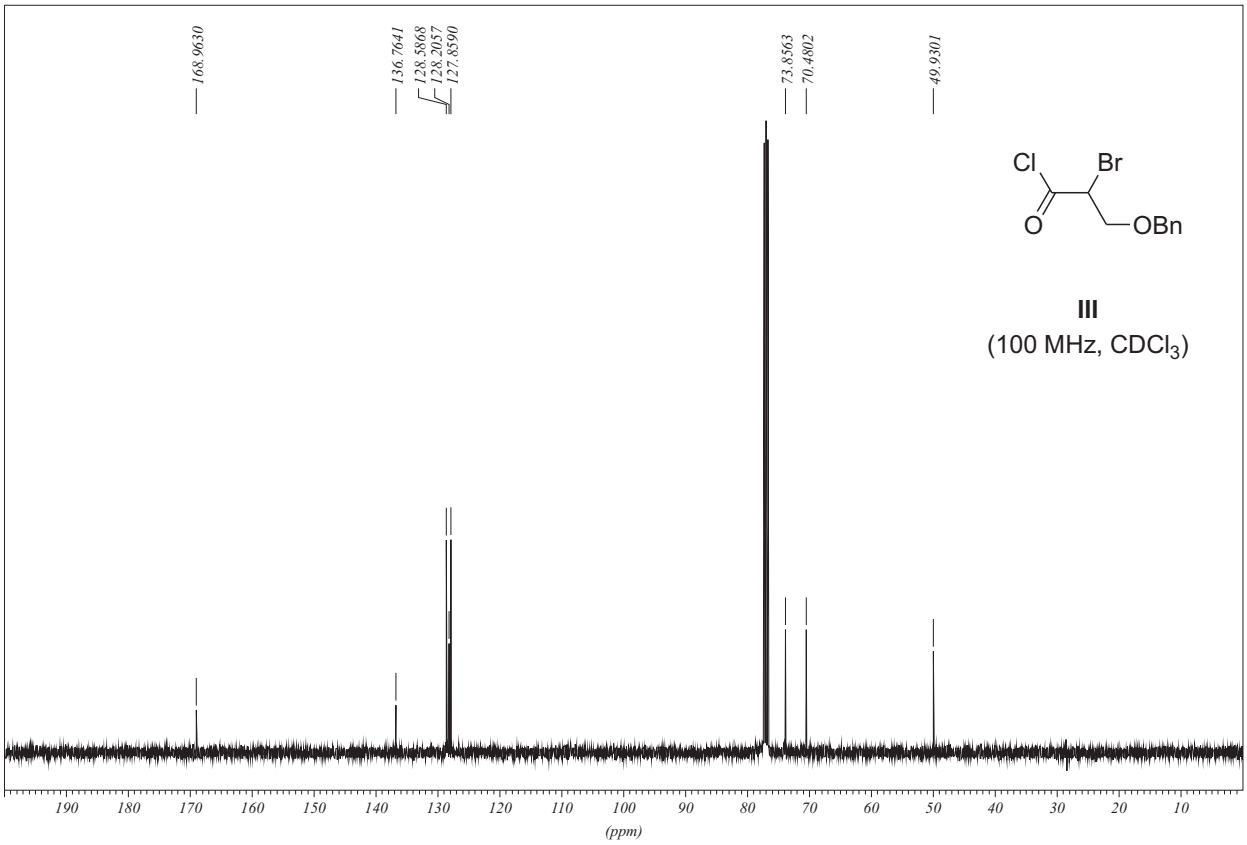
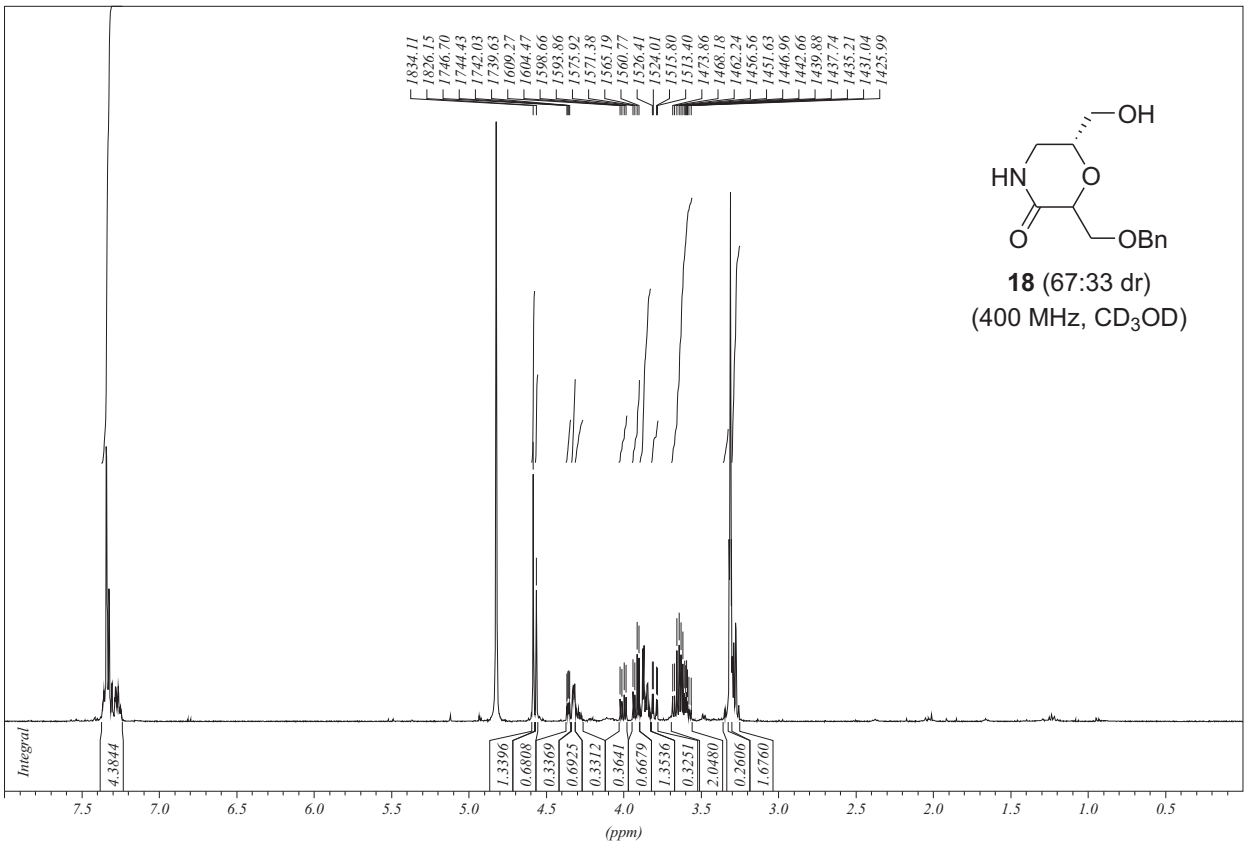
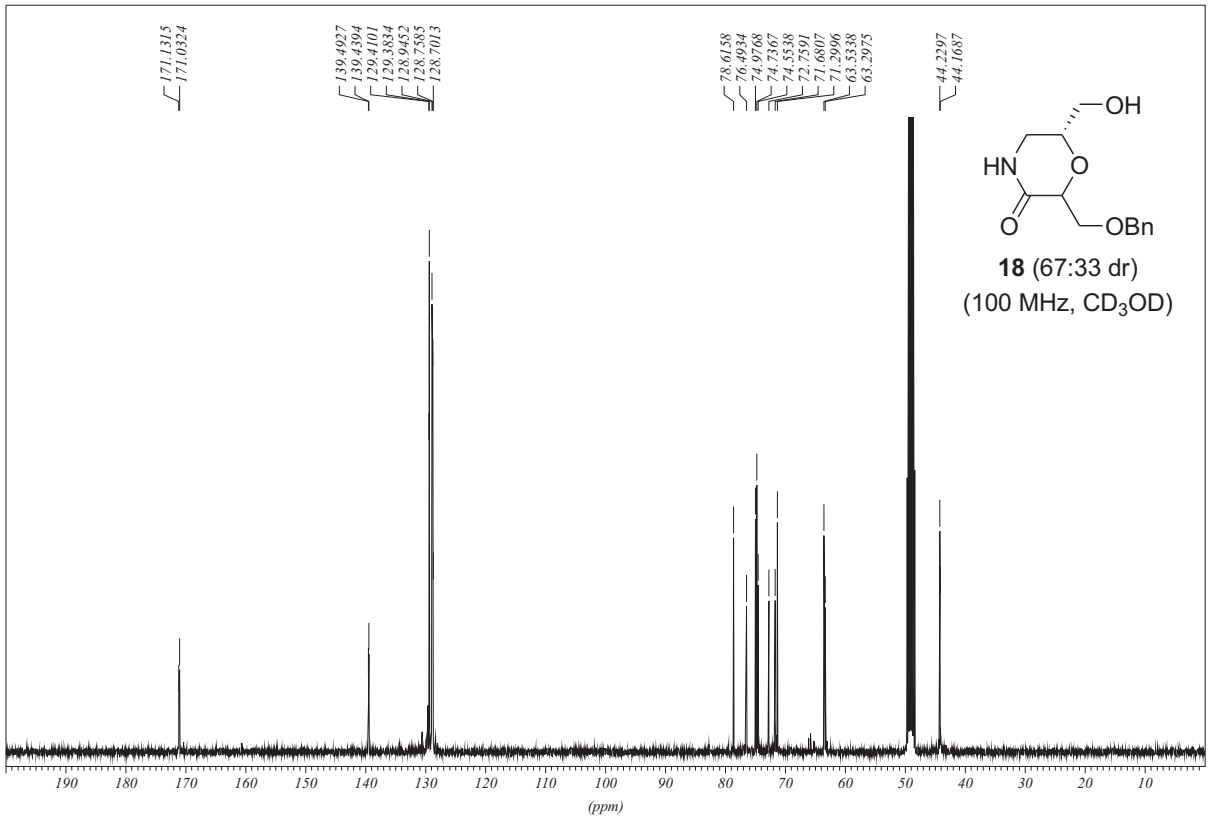
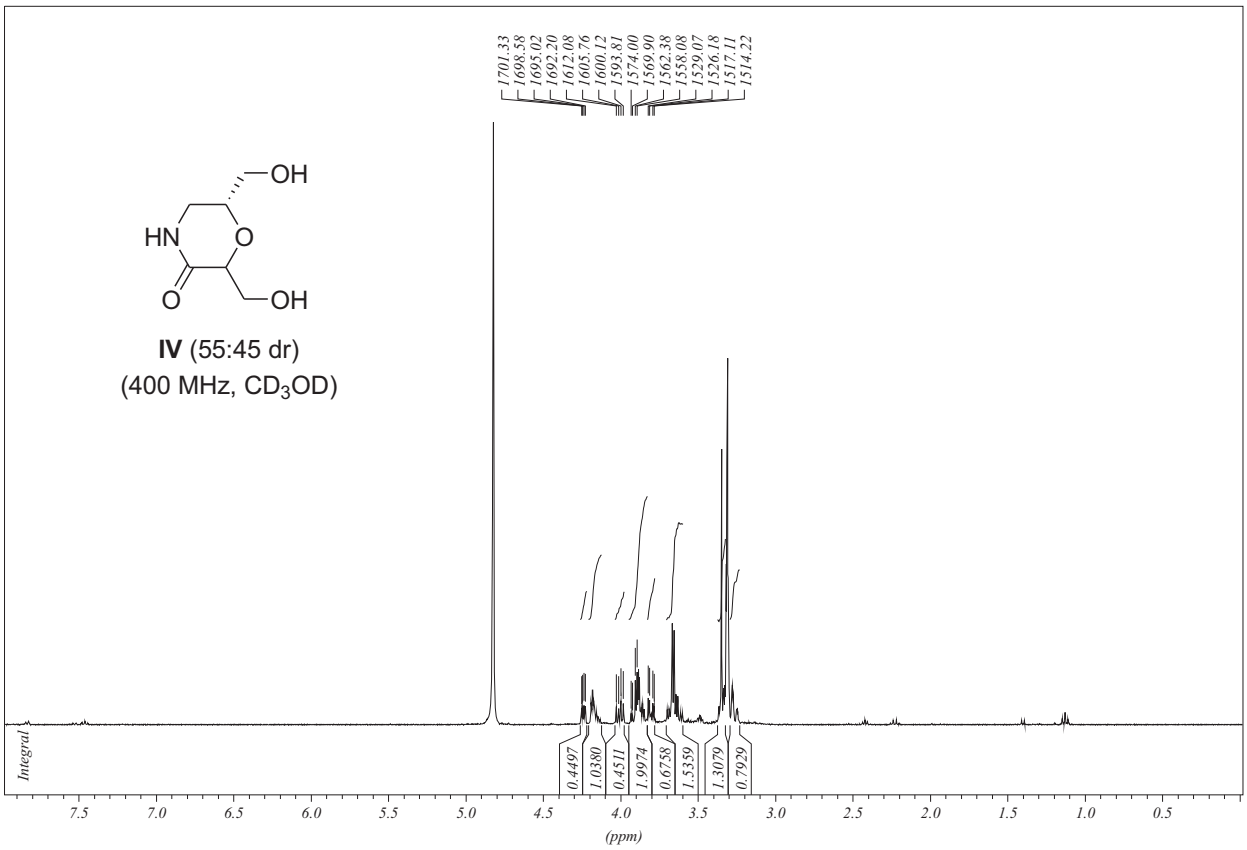
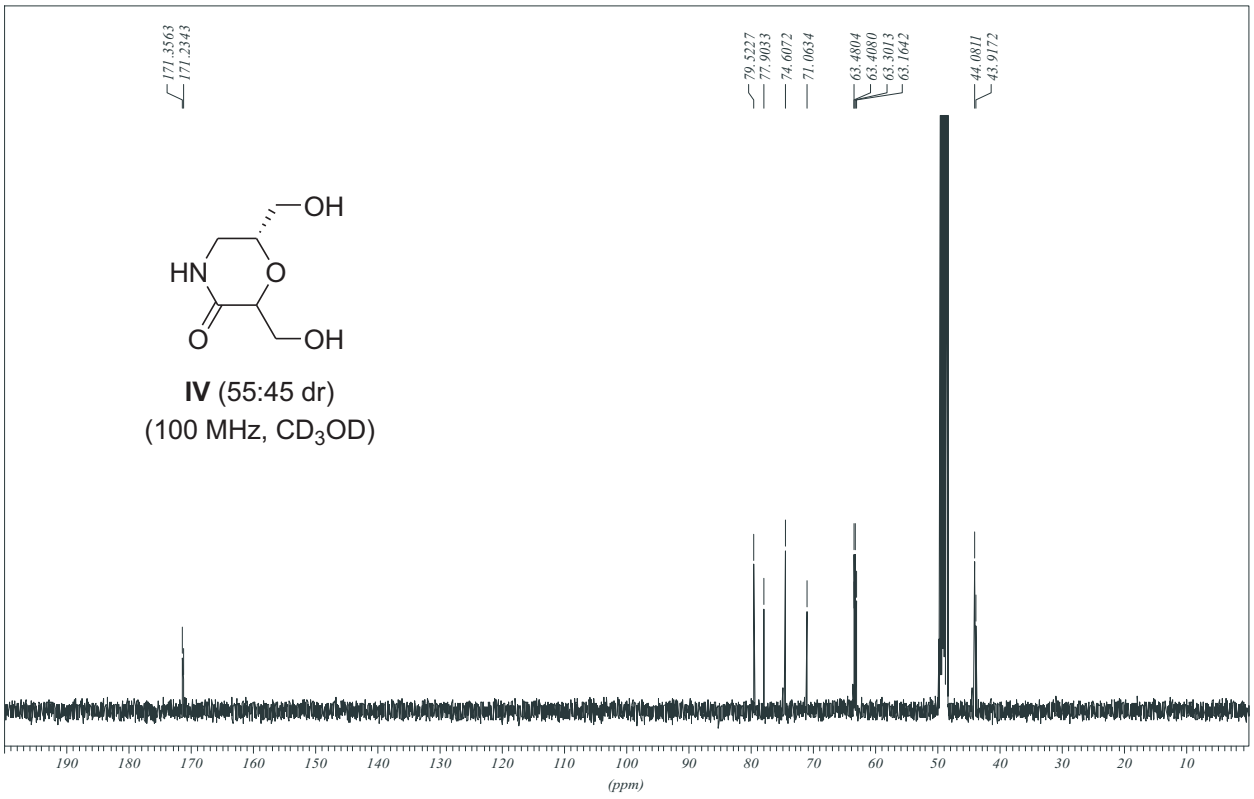
1595.32
1586.98
1552.75
1547.69
1542.39
1537.21
Cl
Br
O
OBn
III
(400 MHz, CDCl3)
Integral
4.9582
2.9917
0.9999
1.0040
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

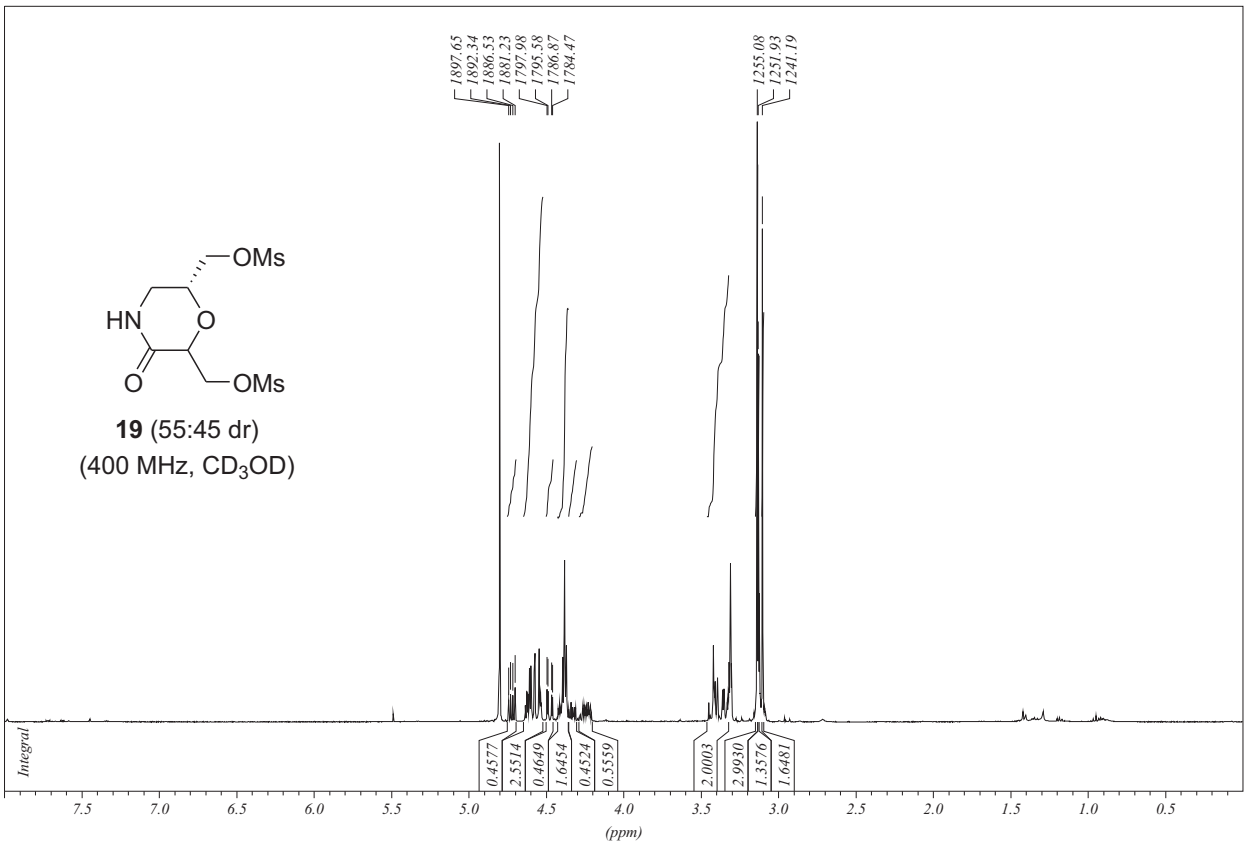

168.9630
136.7641
128.5868
128.2057
127.8590
73.8563
70.4802
49.9301
Cl
Br
O
OBn
III
(100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

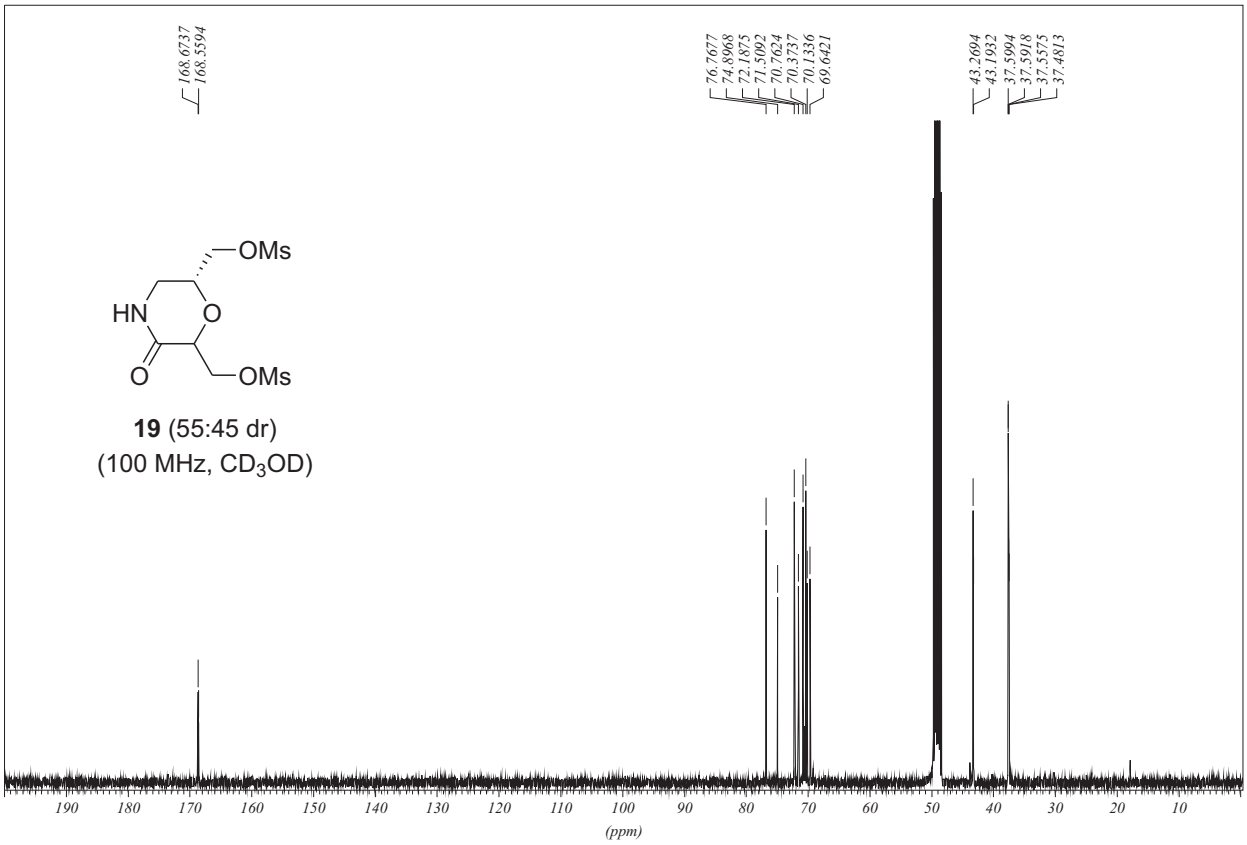

1834.11
1826.15
1746.70
1744.43
1742.03
1739.63
1609.27
1604.47
1598.66
1593.86
1575.92
1571.38
1565.19
1560.77
1526.41
1524.01
1515.80
1513.40
1473.86
1468.18
1462.24
1456.56
1451.63
1446.96
1442.66
1439.88
1437.74
1435.21
1431.04
1425.99
OH
HN
O
O
OBn
18 (67:33 dr)
(400 MHz, CD3OD)
Integral
4.3844
1.3396
0.6808
0.3369
0.6925
0.3312
0.3641
0.6679
1.3536
0.3251
2.0480
0.2606
1.6760
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
(ppm)

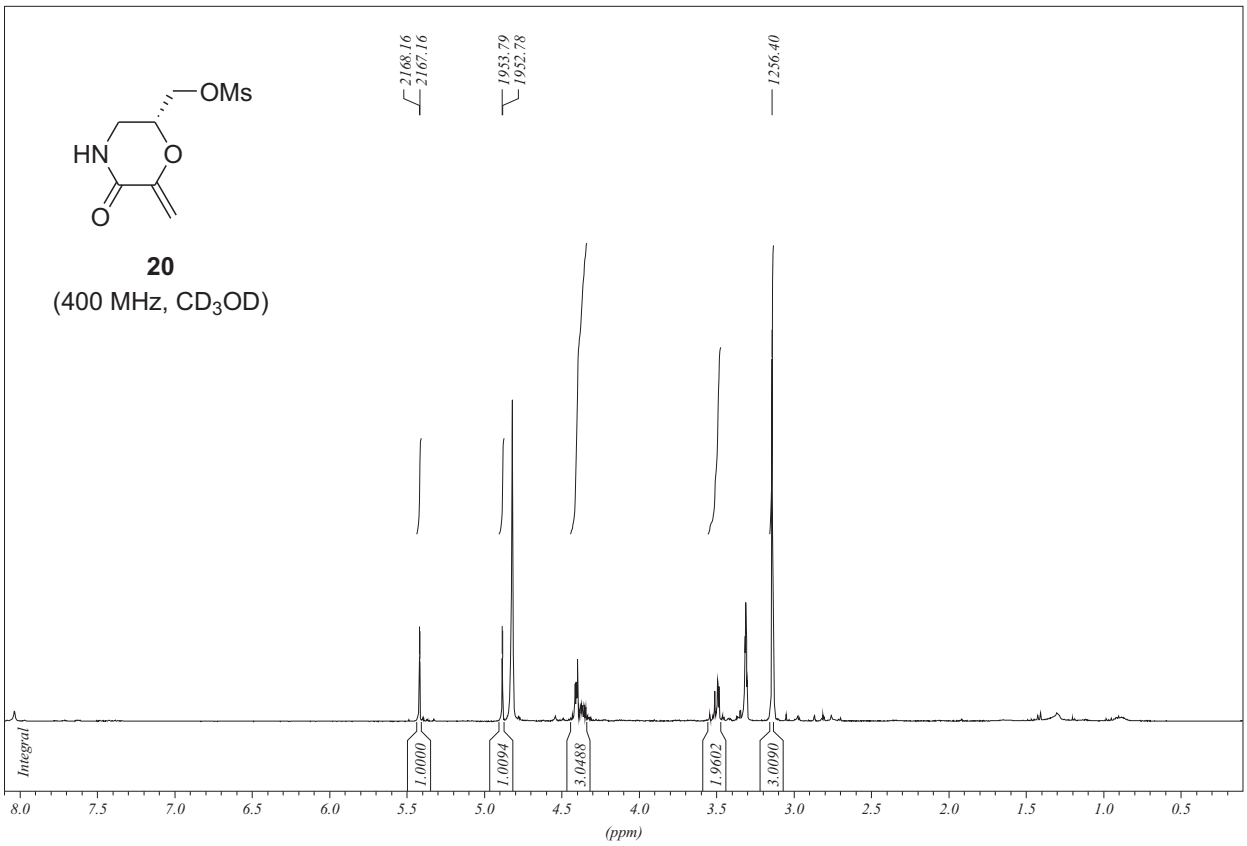

171.1315
171.0324
139.4927
139.4394
129.4101
129.3834
128.9452
128.7585
128.7013
78.6158
76.4934
74.9768
74.7367
74.5538
72.7591
71.6807
71.2996
63.5338
63.2975
44.2297
44.1687
OH
HN
O
O
OBn
18 (67:33 dr)
(100 MHz, CD3OD)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

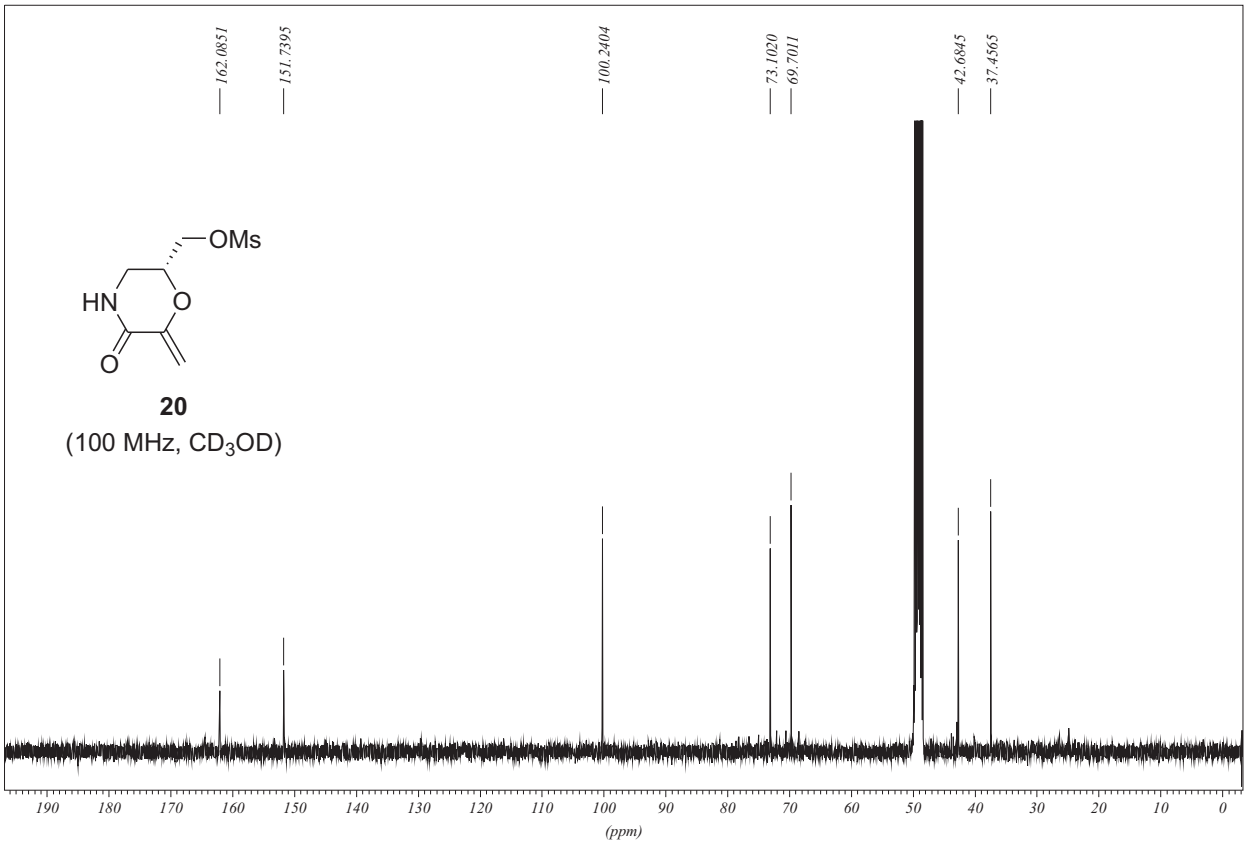

1701.33
1698.58
1695.02
1692.20
1612.08
1605.76
1600.12
1593.81
1574.00
1569.90
1562.38
1558.08
1529.07
1526.18
1517.11
1514.22
OH
HN
O
O
OH
IV (55:45 dr)
(400 MHz, CD3OD)
Integral
0.4497
1.0380
0.4511
1.9974
0.6758
1.5359
1.3079
0.7929
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

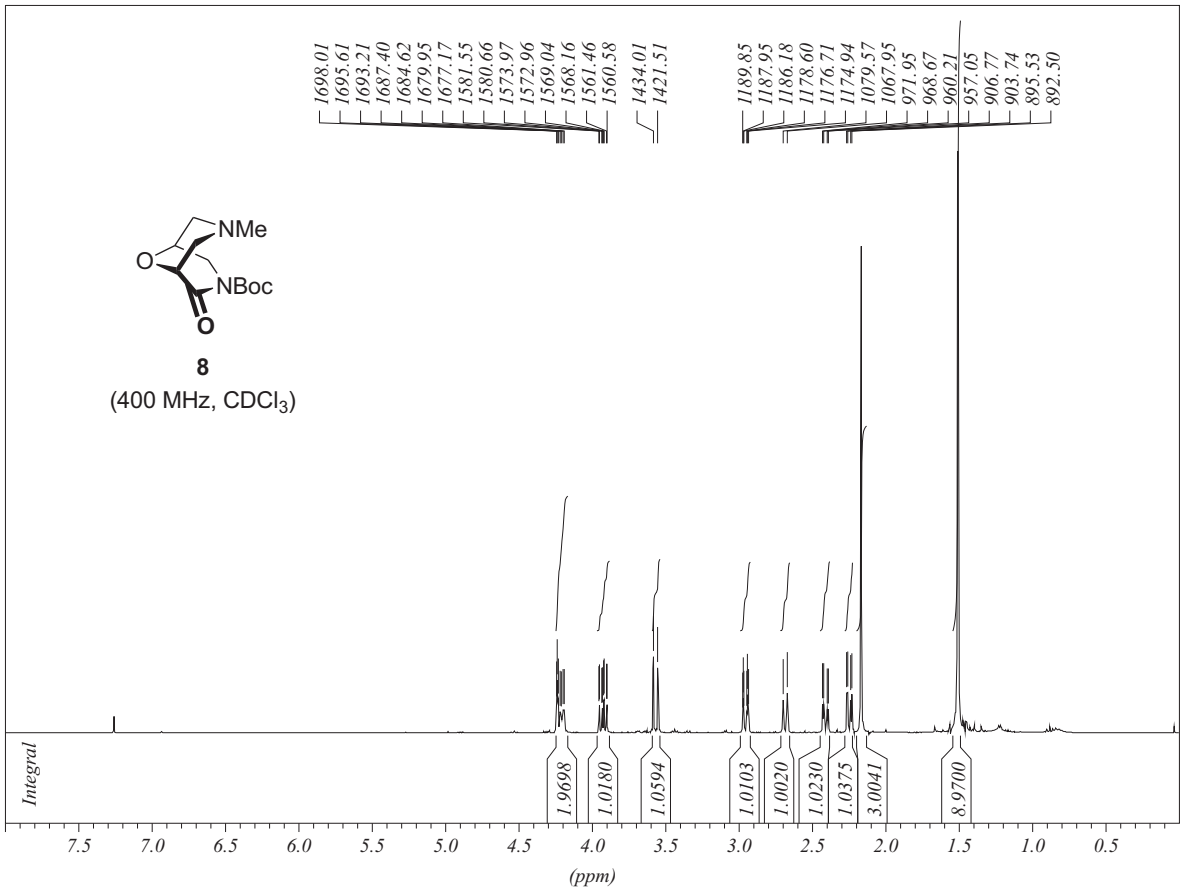

171.3563
171.2343
79.5227
77.9033
74.6072
71.0634
63.4804
63.4080
63.3013
63.1642
44.0811
43.9172
OH
HN
O
O
OH
IV (55:45 dr)
(100 MHz, CD3OD)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)


1897.65
1892.34
1886.53
1881.23
1797.98
1795.58
1786.87
1784.47
1255.08
1251.93
1241.19
OMs
HN
O
O
OMs
19 (55:45 dr)
(400 MHz, CD3OD)
Integral
0.4577
2.5514
0.4649
1.6454
0.4524
0.5559
2.0003
2.9930
1.3576
1.6481
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
(ppm)


168.6737
168.5594
76.7677
74.8968
72.1875
71.5092
70.7624
70.3737
70.1336
69.6421
43.2694
43.1932
37.5994
37.5918
37.5575
37.4813
OMs
HN
O
O
OMs
19 (55:45 dr)
(100 MHz, CD3OD)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

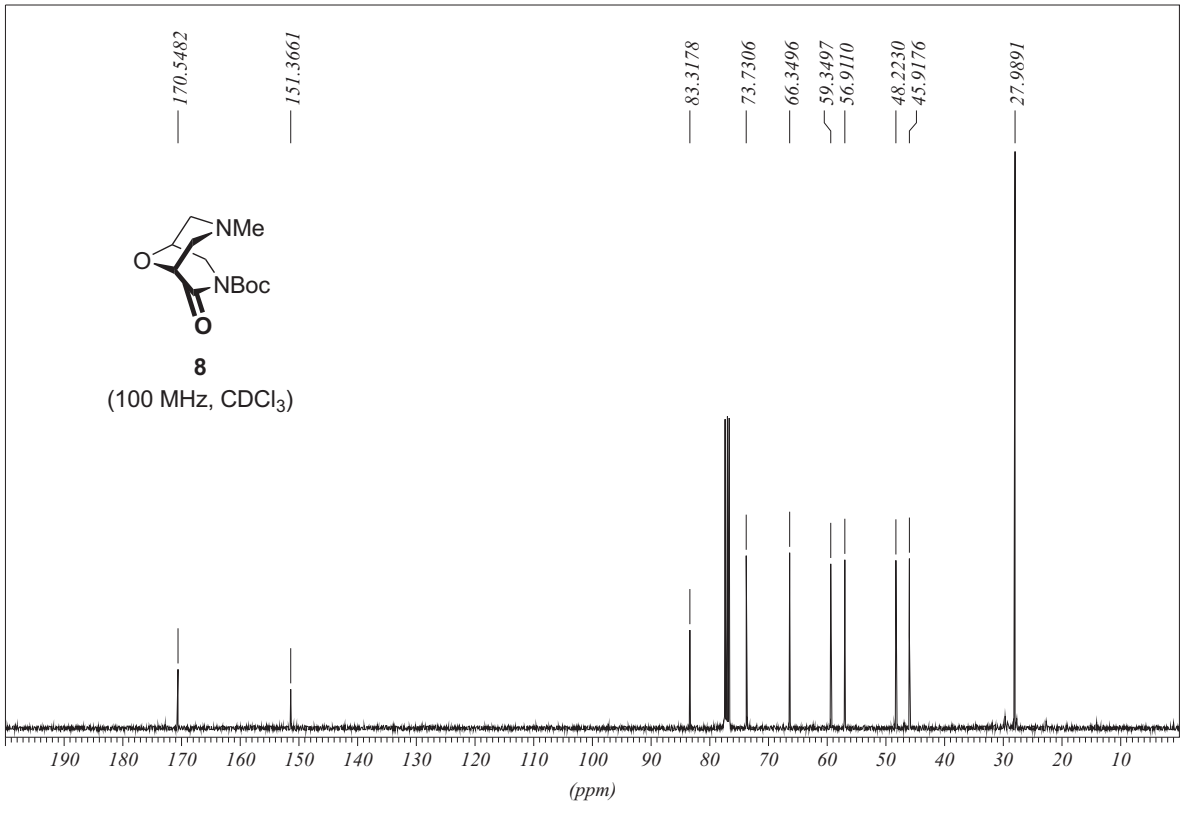

OMs
HN
O
O
20
(400 MHz, CD3OD)
2168.16
2167.16
1953.79
1952.78
1256.40
Integral
1.0000
1.0094
3.0488
1.9602
3.0090
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


OMs
HN
O
O
20
(100 MHz, CD3OD)
162.0851
151.7395
100.2404
73.1020
69.7011
42.6845
37.4565
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)



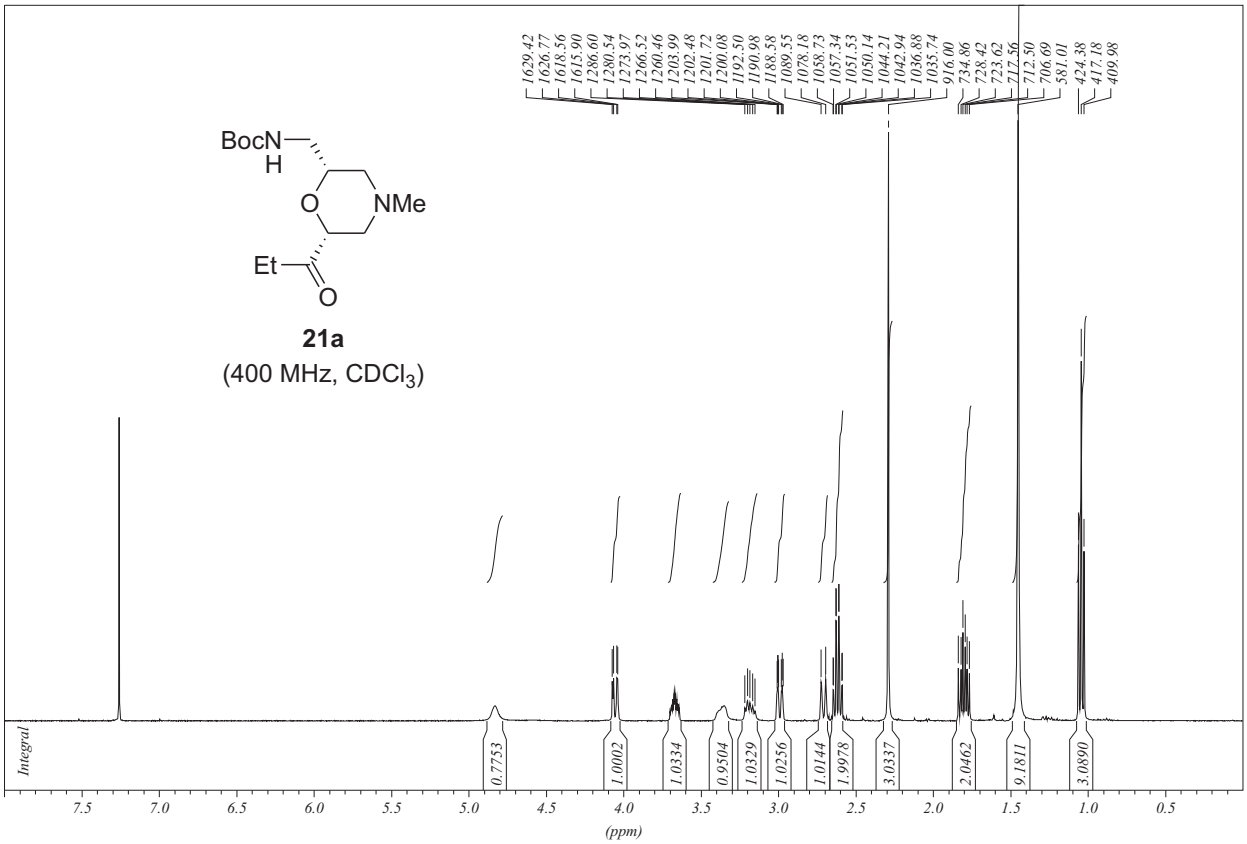
8

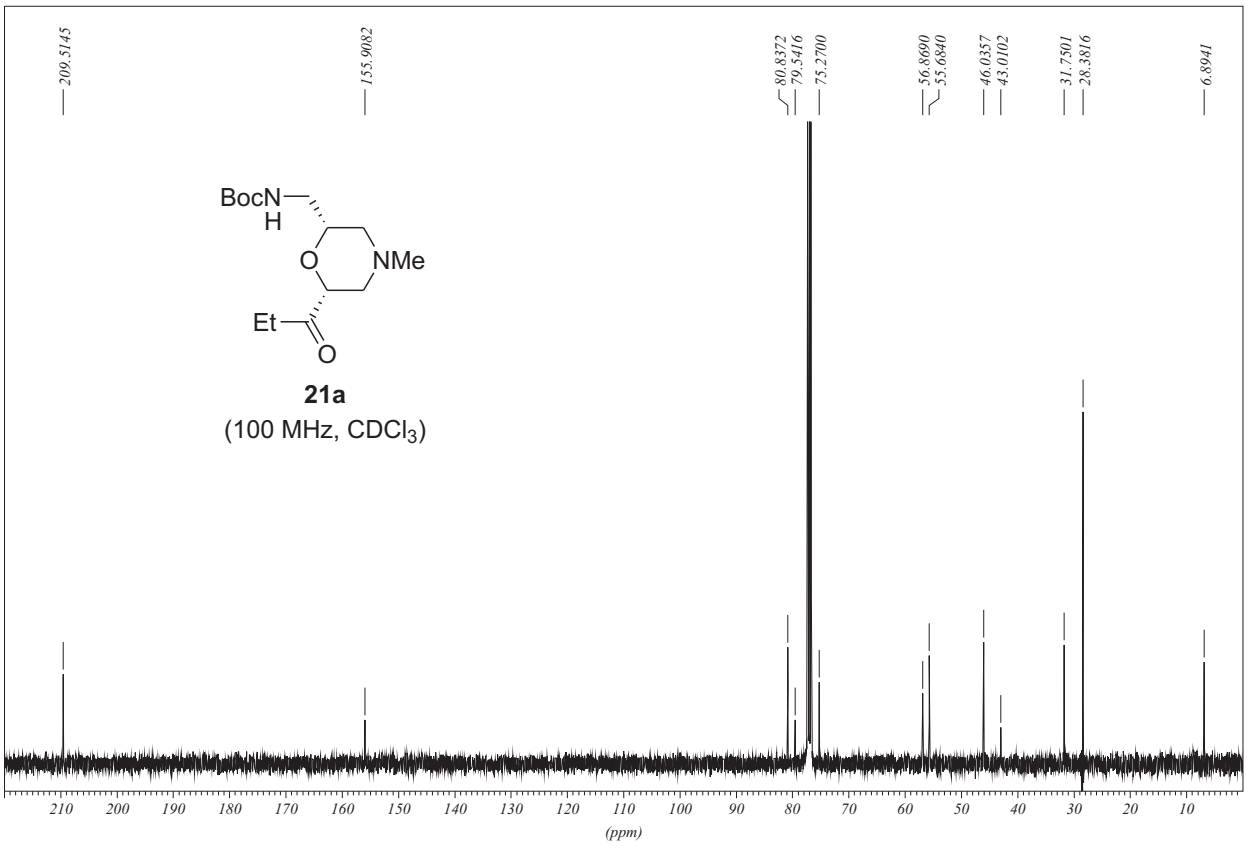
(400 MHz, $CDCl_3$)

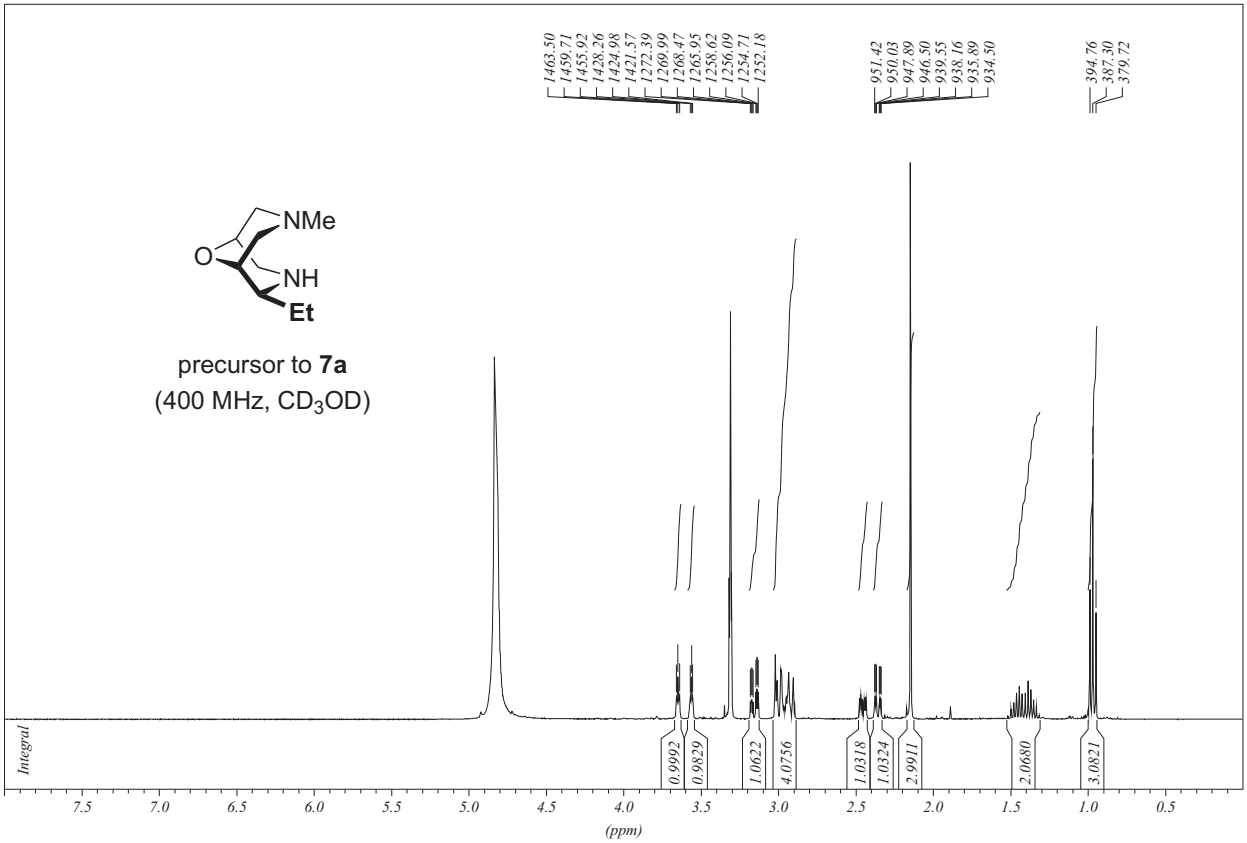


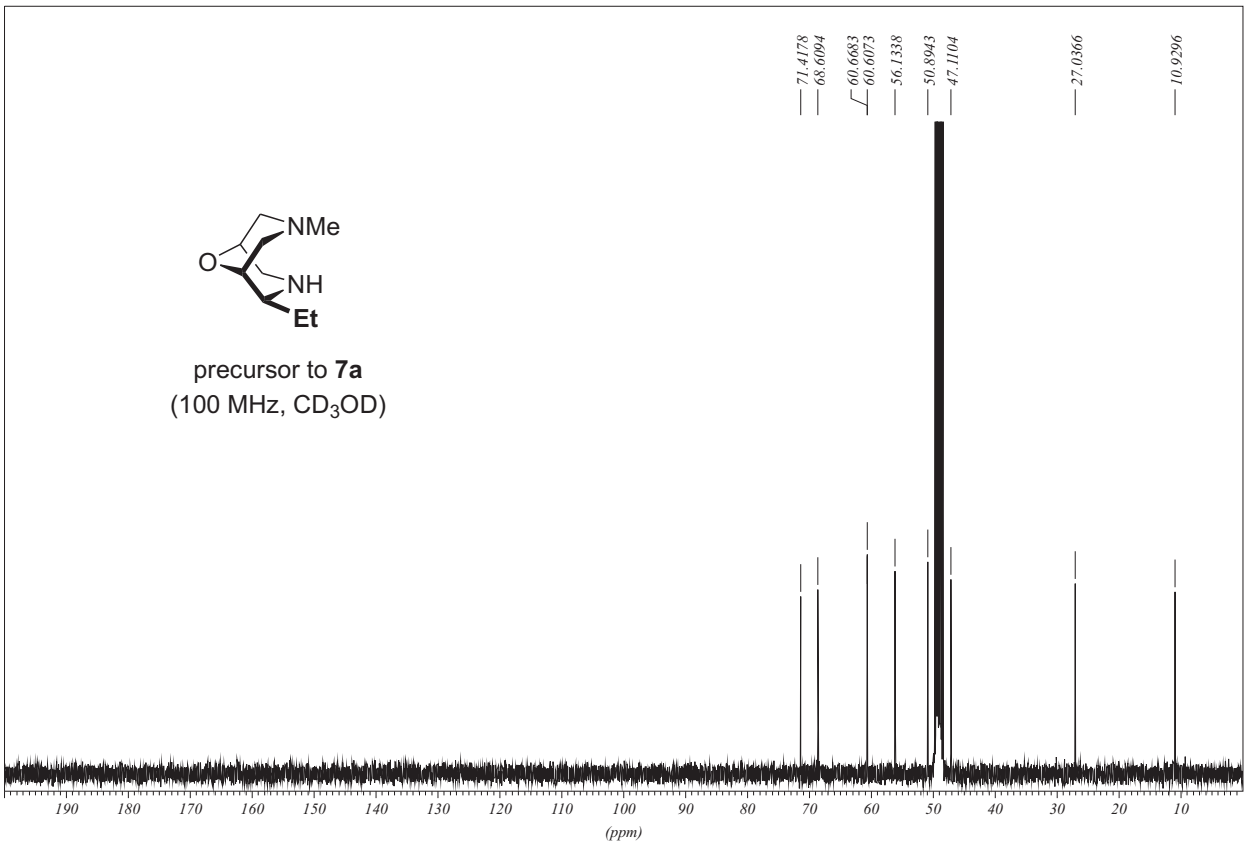
8

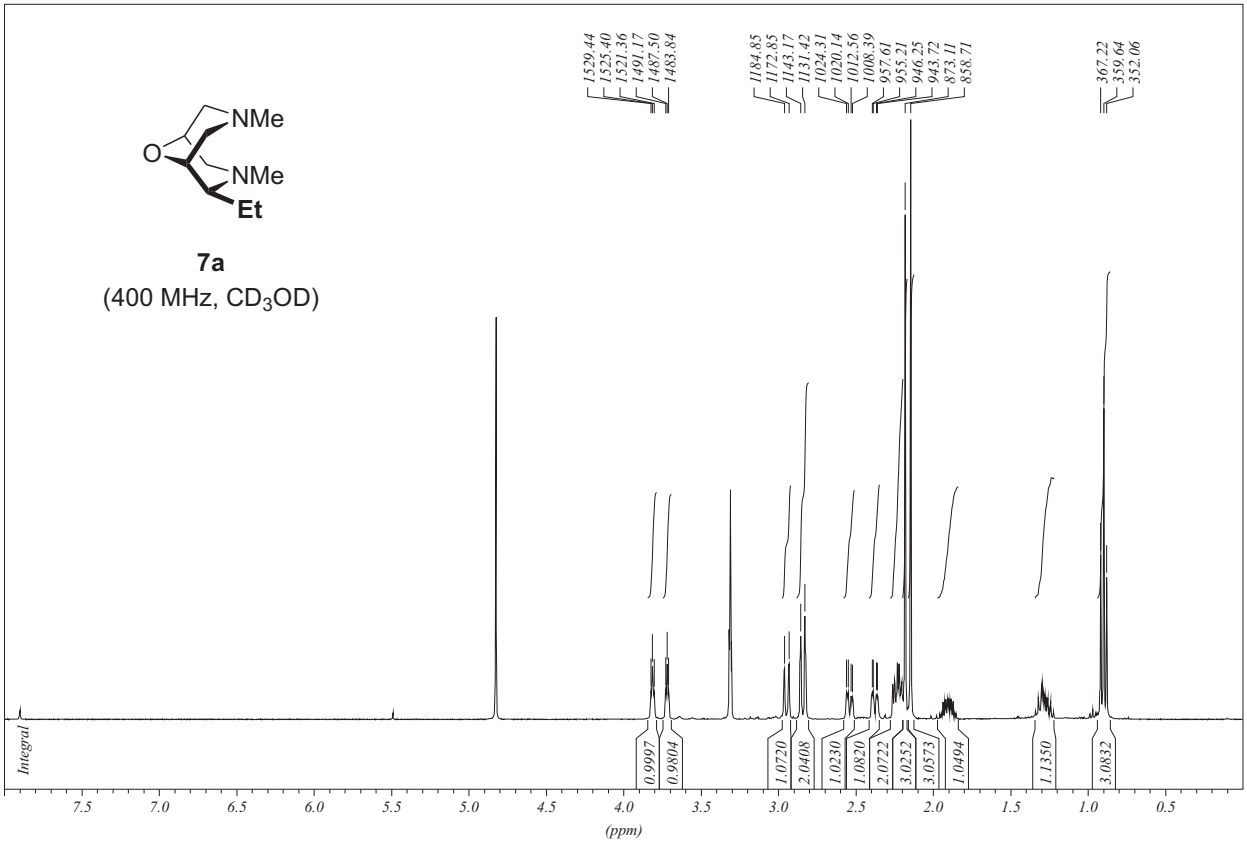
(100 MHz, $CDCl_3$)

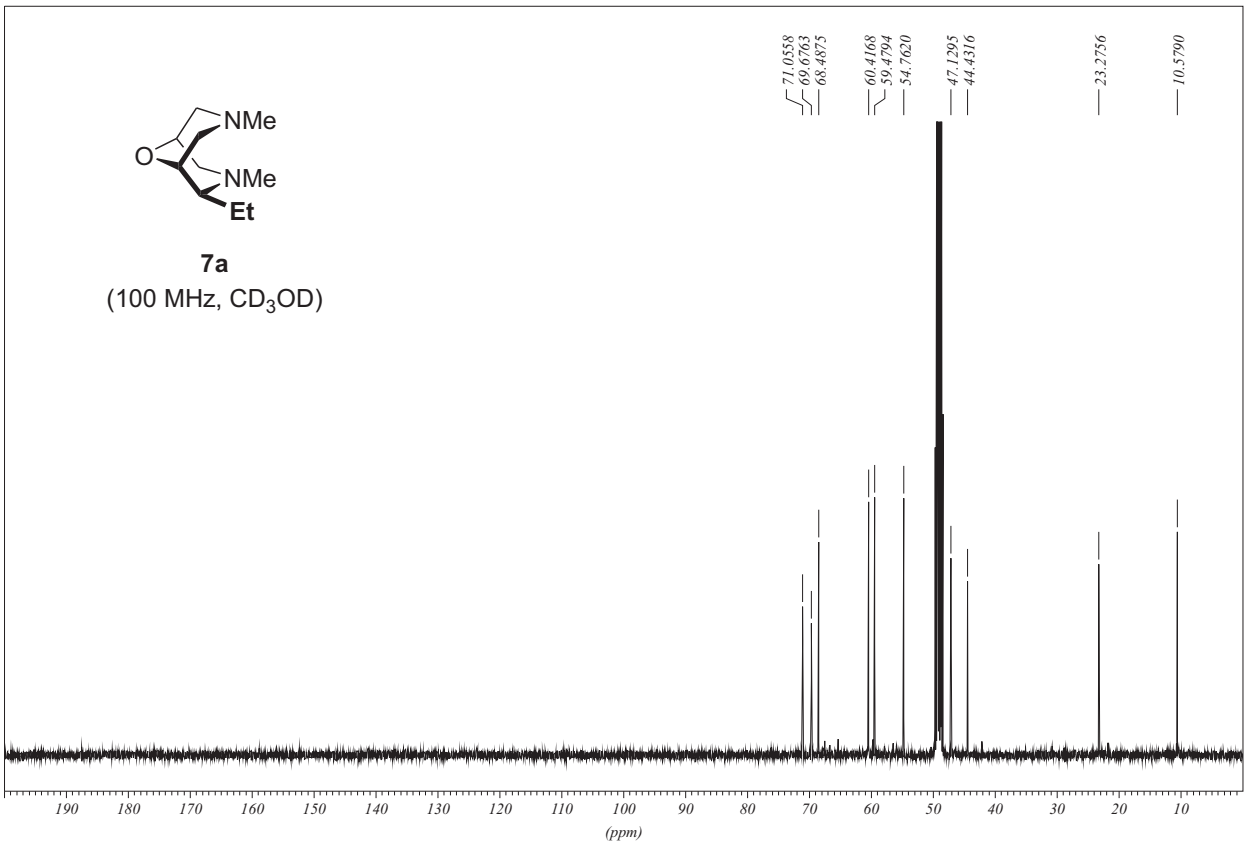

BocN
H
O
NMe
Et
O
21a
(400 MHz, CDCl3)
Integral
0.7753
1.0002
1.0334
0.9504
1.0329
1.0256
1.0144
1.9978
3.0337
2.0462
9.1811
3.0890
(ppm)

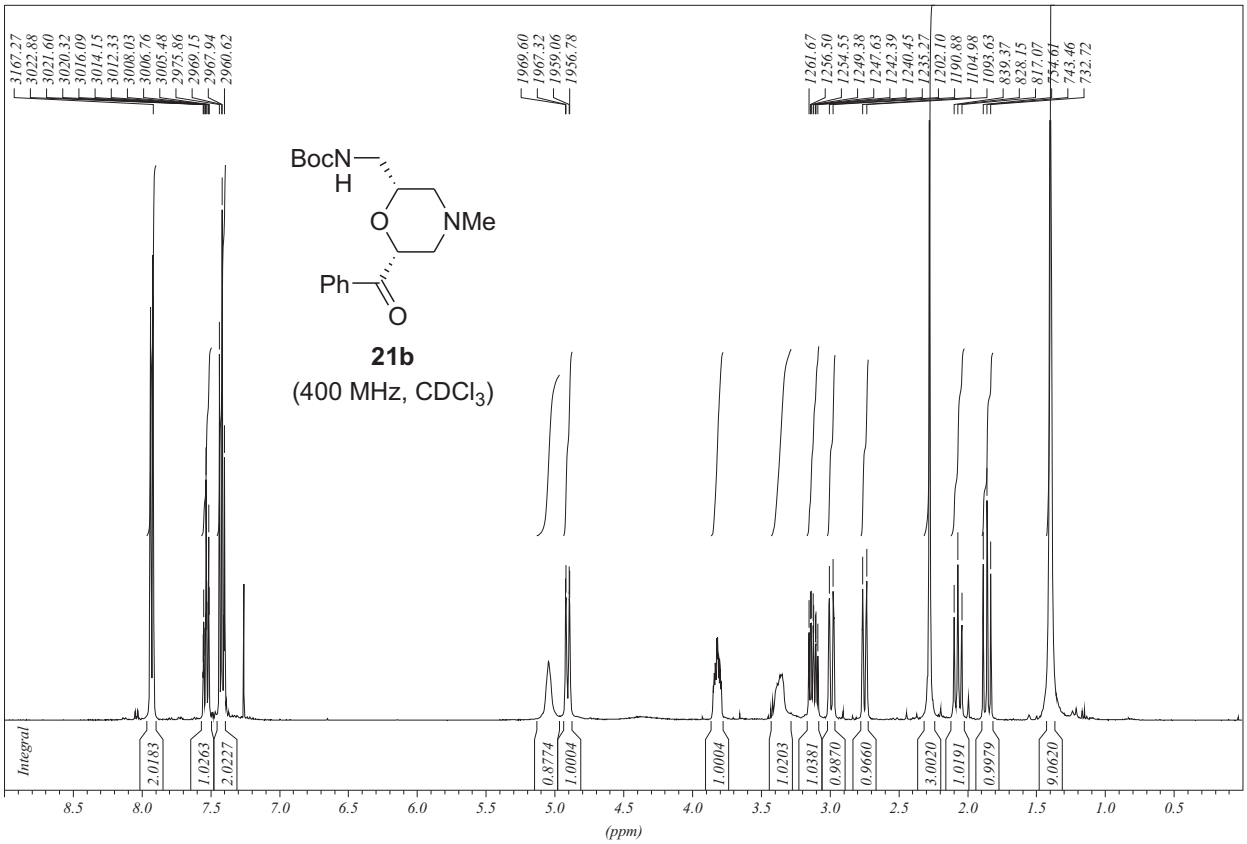

209.5145
155.9082
80.8372
79.5416
75.2700
56.8690
55.6840
46.0357
43.0102
31.7501
28.3816
6.8941
BocN
H
O
NMe
Et
O
21a
(100 MHz, CDCl3)
(ppm)

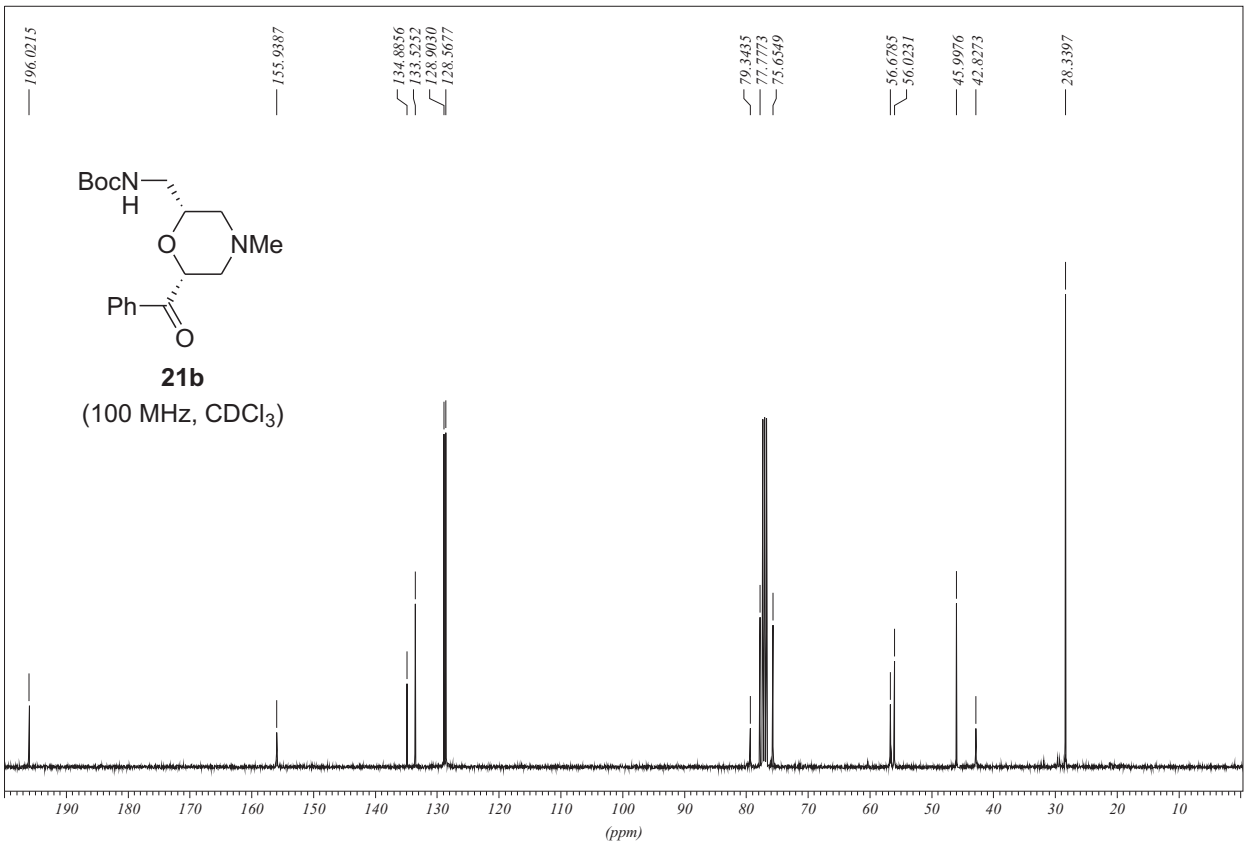

1463.50
1459.71
1455.92
1428.26
1424.98
1421.57
1272.39
1269.99
1268.47
1265.95
1258.62
1256.09
1254.71
1252.18
951.42
950.03
947.89
946.50
939.55
938.16
935.89
934.50
394.76
387.30
379.72
NMe
O
NH
Et
precursor to 7a
(400 MHz, CD3OD)
Integral
0.9992
0.9829
1.0622
4.0756
1.0318
1.0324
2.9911
2.0680
3.0821
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
(ppm)

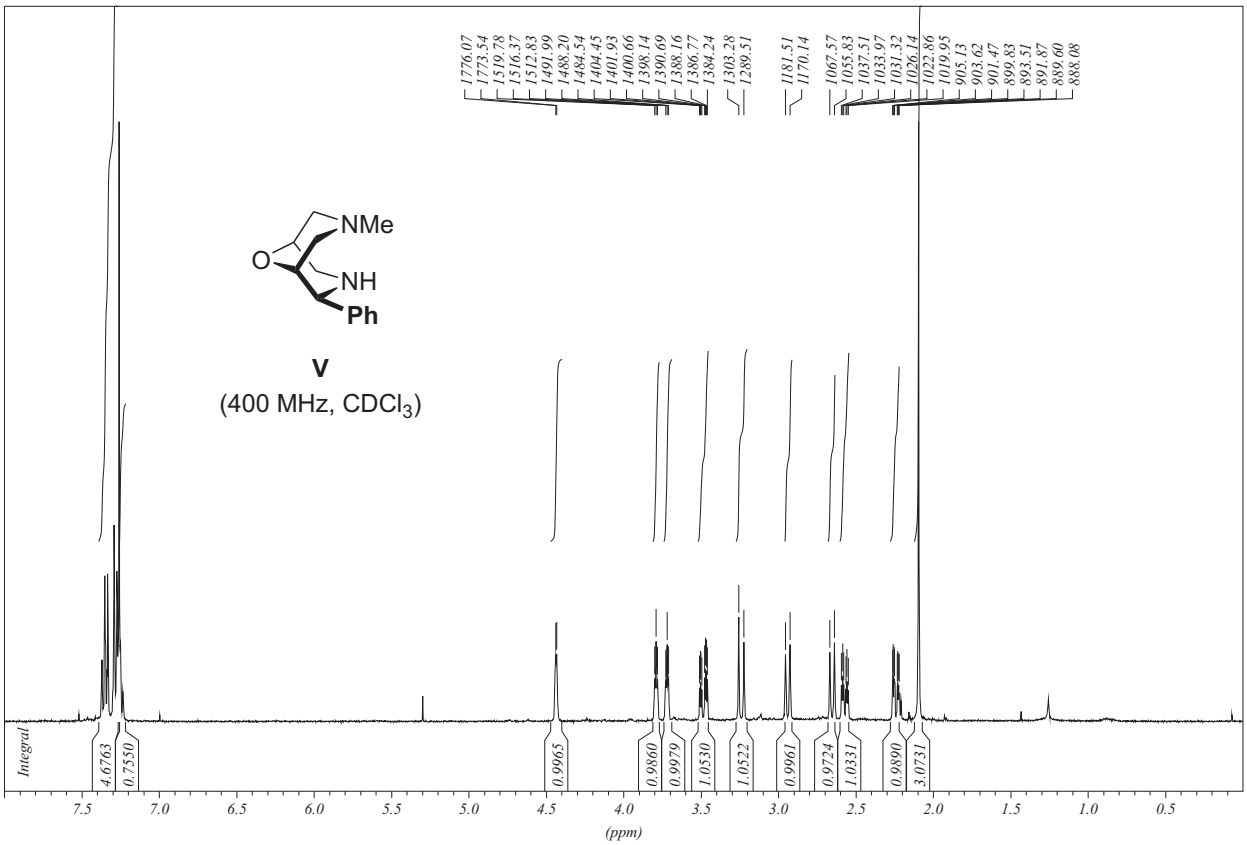

71.4178
68.6094
60.6683
60.6073
56.1338
50.8943
47.1104
27.0366
10.9296
NMe
O
NH
Et
precursor to 7a
(100 MHz, CD3OD)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

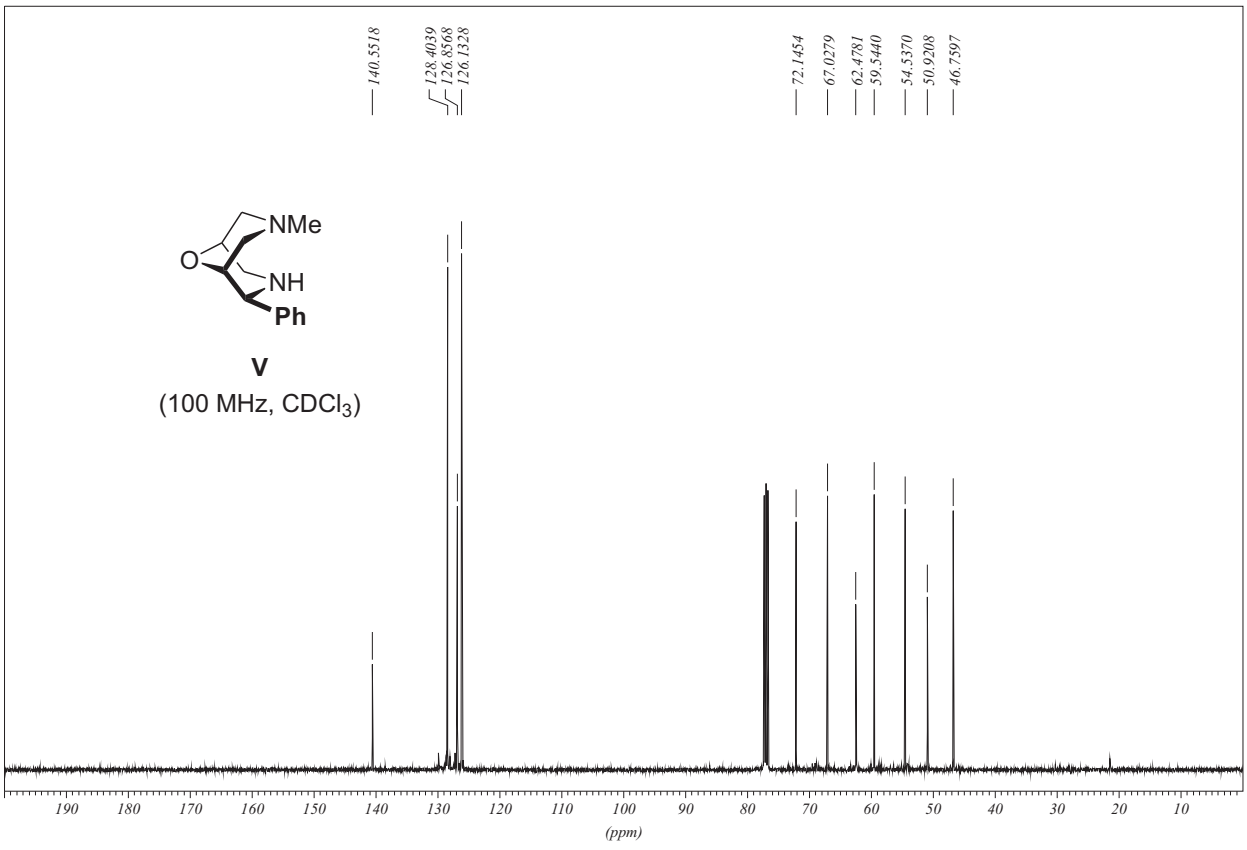

NMe
O
NMe
Et
7a
(400 MHz, CD3OD)
1529.44
1525.40
1521.36
1491.17
1487.50
1483.84
1184.85
1172.85
1143.17
1131.42
1024.31
1020.14
1012.56
1008.39
957.61
935.21
946.25
943.72
873.11
858.71
367.22
359.64
352.06
Integral
0.9997
0.9804
1.0720
2.0408
1.0230
1.0820
2.0722
3.0252
3.0573
1.0494
1.1350
3.0832
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
(ppm)

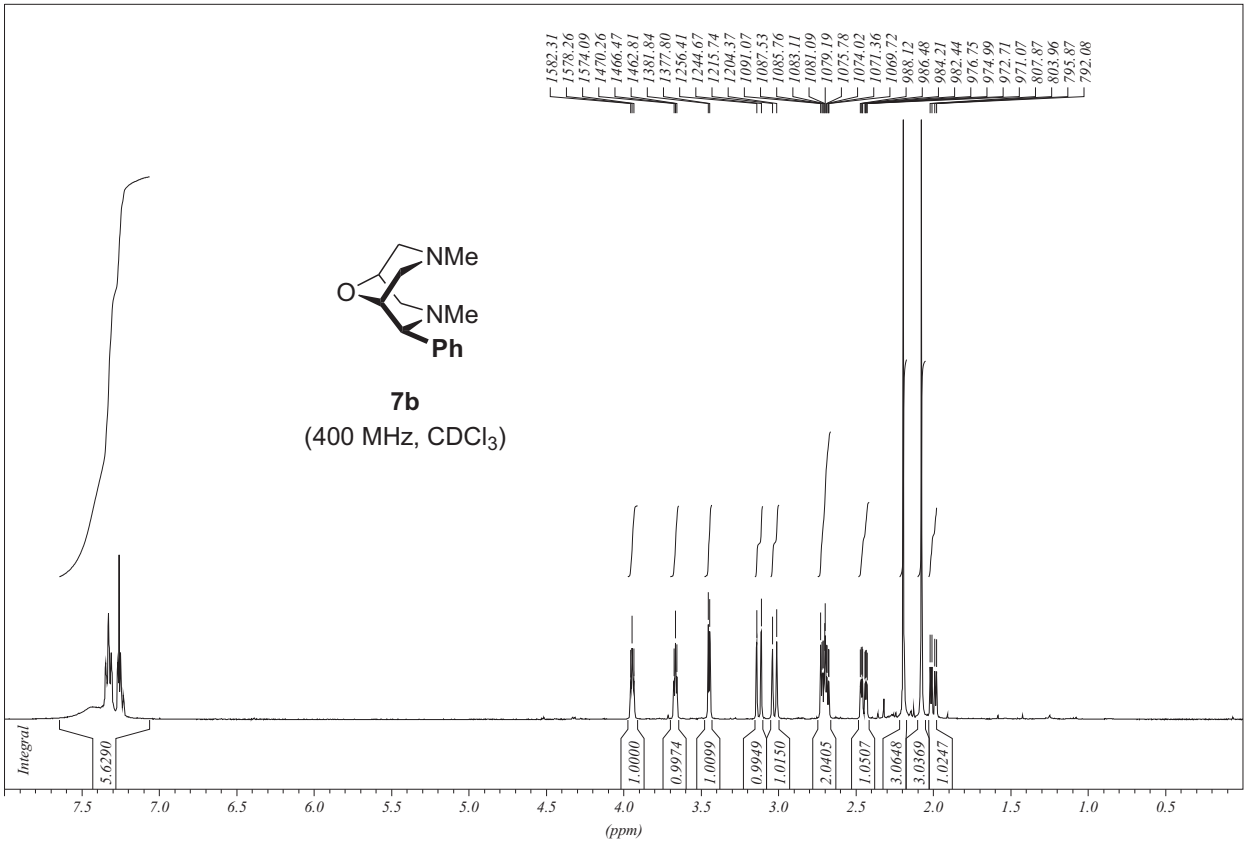

NMe
O
NMe
Et
7a
(100 MHz, CD3OD)
71.0558
69.6763
68.4875
60.4168
59.4794
54.7620
47.1295
44.4316
23.2756
10.5790
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

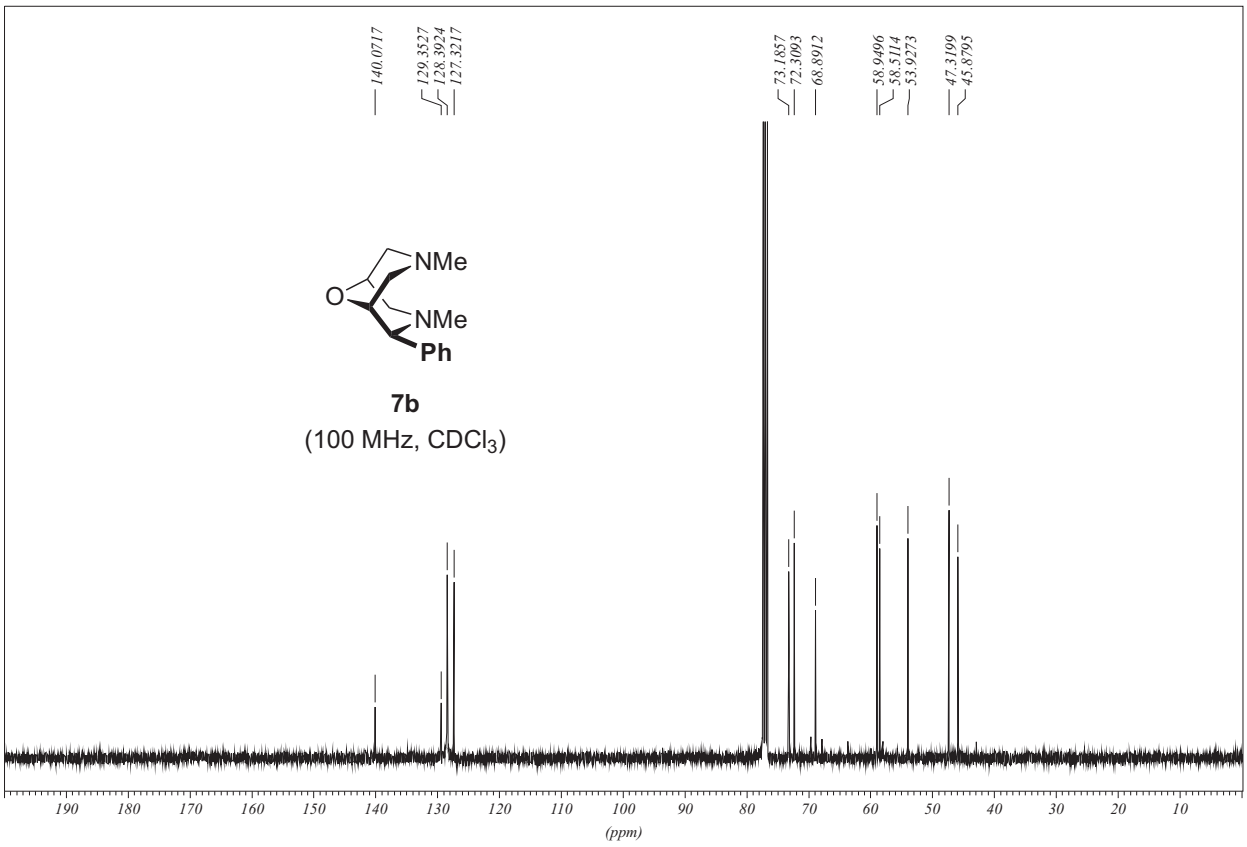

3167.27
3022.88
3021.60
3020.32
3016.09
3014.15
3012.33
3008.03
3006.76
3005.48
2975.86
2969.15
2967.94
2960.62
1969.60
1967.32
1959.06
1956.78
1261.67
1256.50
1254.55
1249.38
1247.63
1242.39
1240.45
1235.27
1202.10
1190.88
1104.98
1093.63
839.37
828.15
817.07
754.61
743.46
732.72
BocN
H
O
NMe
Ph
O
21b
(400 MHz, CDCl3)
Integral
2.0183
1.0263
2.0227
0.8774
1.0004
1.0004
1.0203
1.0381
0.9870
0.9660
3.0020
1.0191
0.9979
9.0620
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
(ppm)

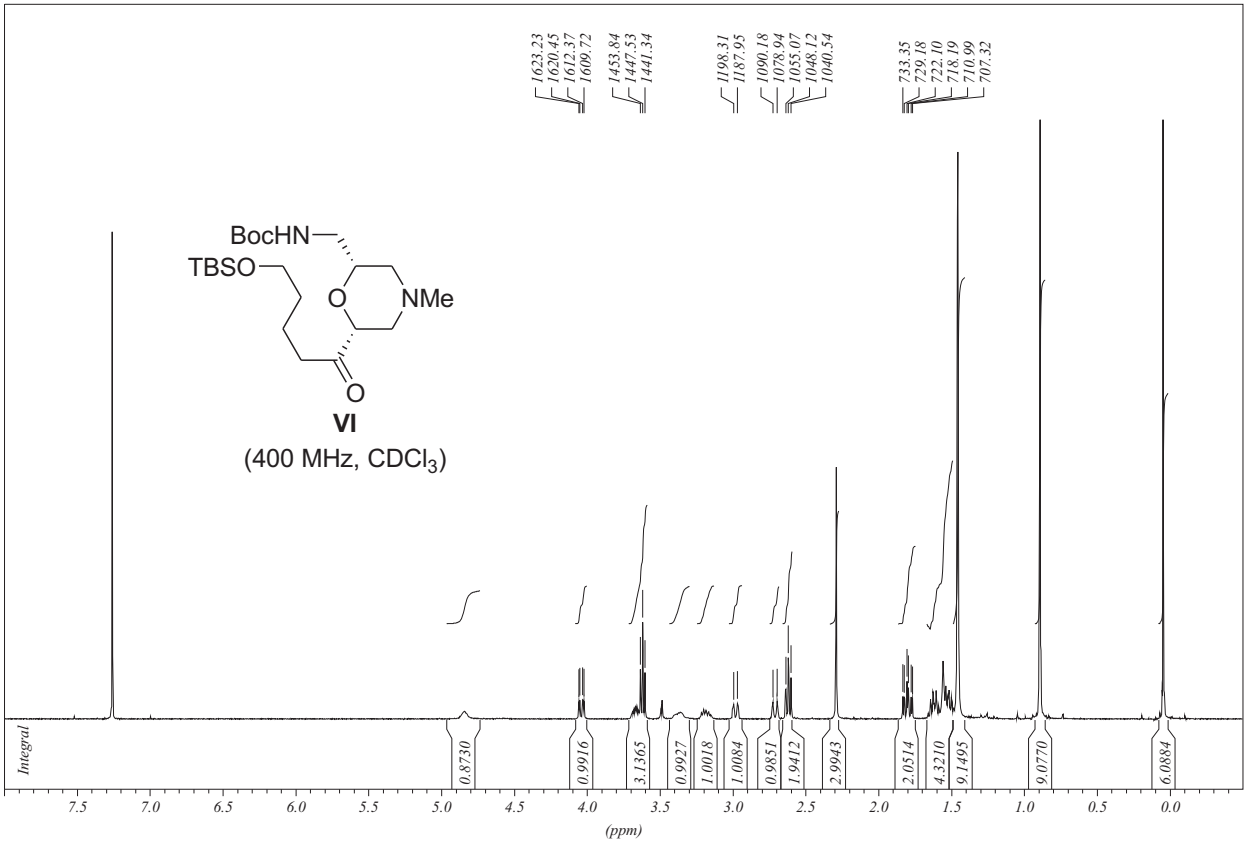

196.0215
155.9387
134.8856
133.5252
128.9030
128.5677
79.3435
77.7773
75.6549
56.6785
56.0231
45.9976
42.8273
28.3397
BocN
H
O
NMe
Ph
O
21b
(100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

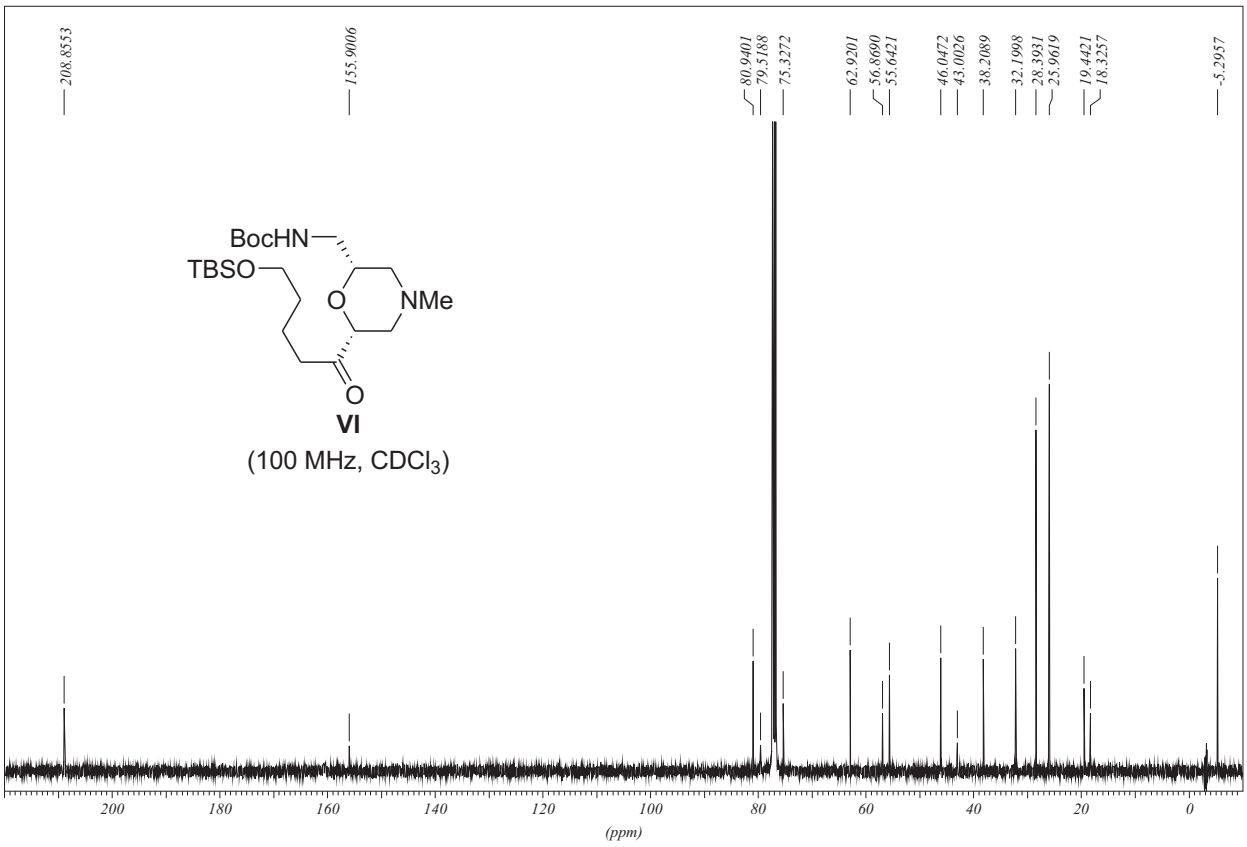

NMe
O
NH
Ph
V
(400 MHz, CDCl3)
Integral
4.6763
0.7550
0.9965
0.9860
0.9979
1.0530
1.0522
0.9961
0.9724
1.0331
0.9890
3.0731
(ppm)

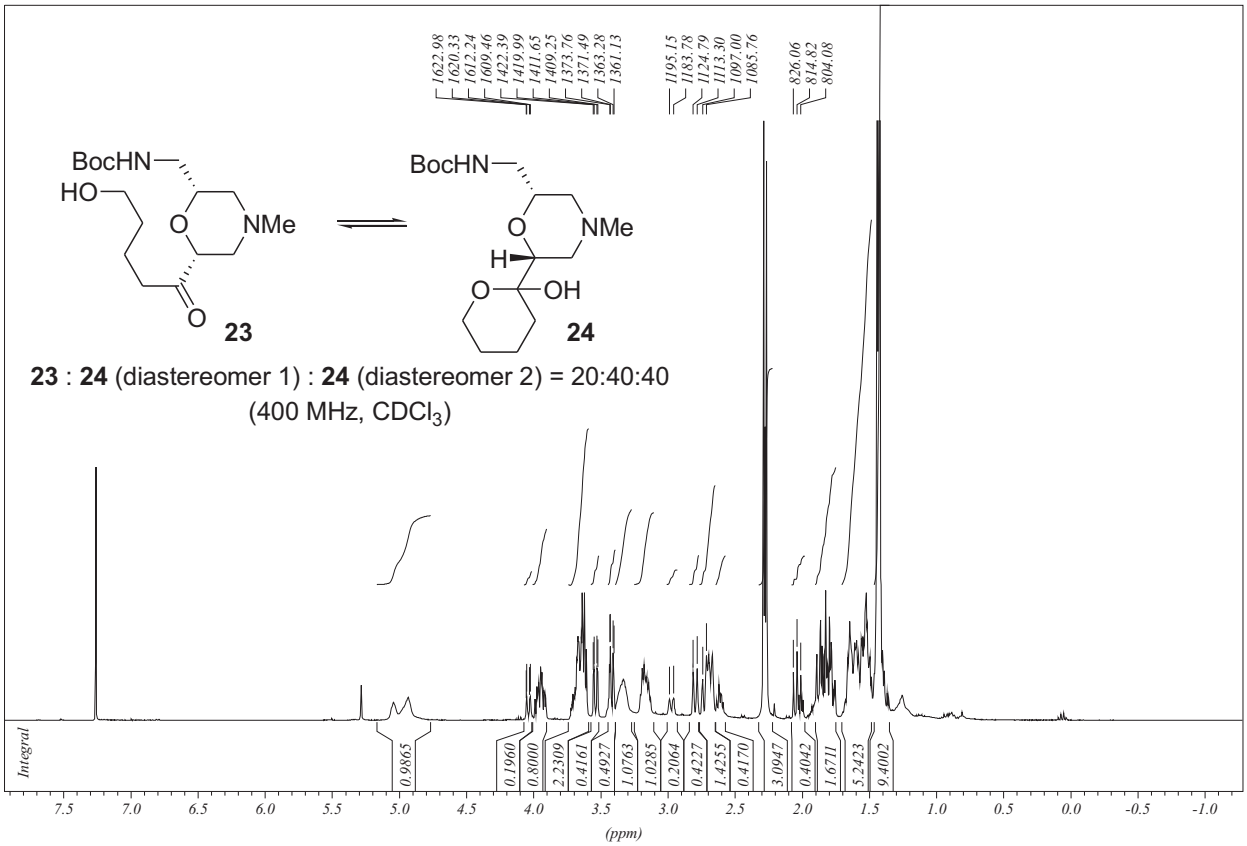

NMe
O
NH
Ph
V
(100 MHz, CDCl3)
140.5518
128.4039
126.8568
126.1328
72.1454
67.0279
62.4781
59.5440
54.5370
50.9208
46.7597
(ppm)

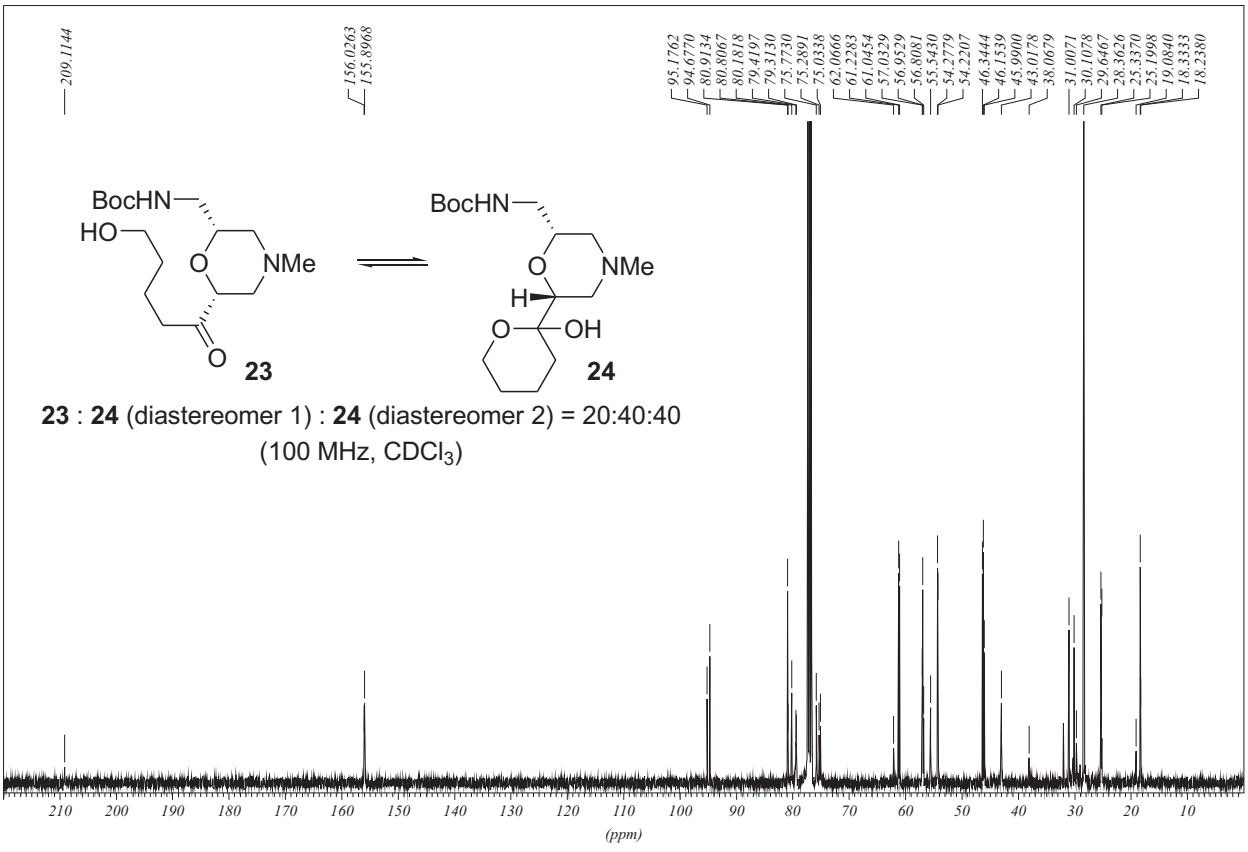

1582.31
1578.26
1574.09
1470.26
1466.47
1462.81
1381.84
1377.80
1256.41
1244.67
1215.74
1204.37
1091.07
1087.53
1085.76
1083.11
1081.09
1079.19
1075.78
1074.02
1071.36
1069.72
988.12
986.48
984.21
982.44
976.75
974.99
972.71
971.07
807.87
803.96
795.87
792.08
NMe
O
NMe
Ph
7b
(400 MHz, CDCl3)
Integral
5.6290
1.0000
0.9974
1.0099
0.9949
1.0150
2.0405
1.0507
3.0648
3.0369
1.0247
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
(ppm)

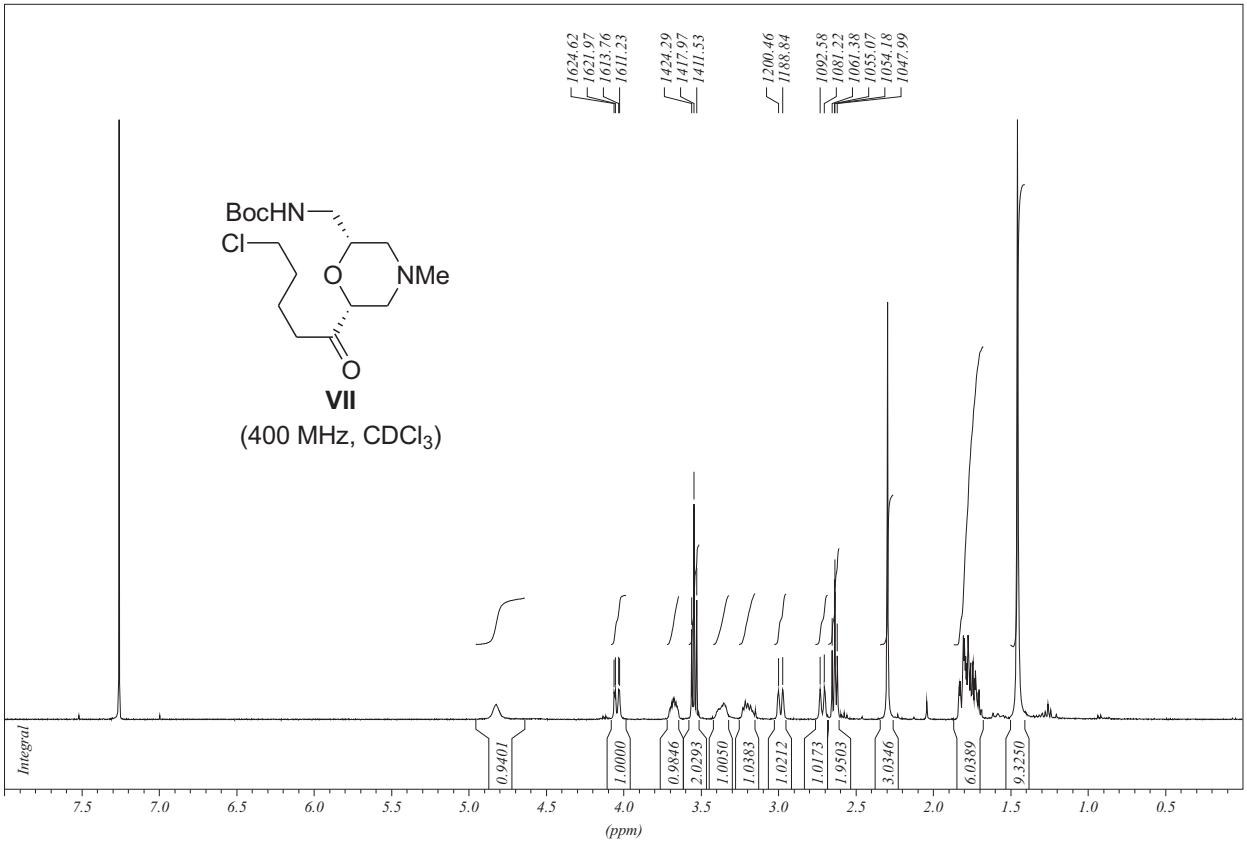

140.0717
129.3527
128.3924
127.3217
73.1857
72.3093
68.8912
58.9496
58.5114
53.9273
47.3199
45.8795
NMe
O
NMe
Ph
7b
(100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

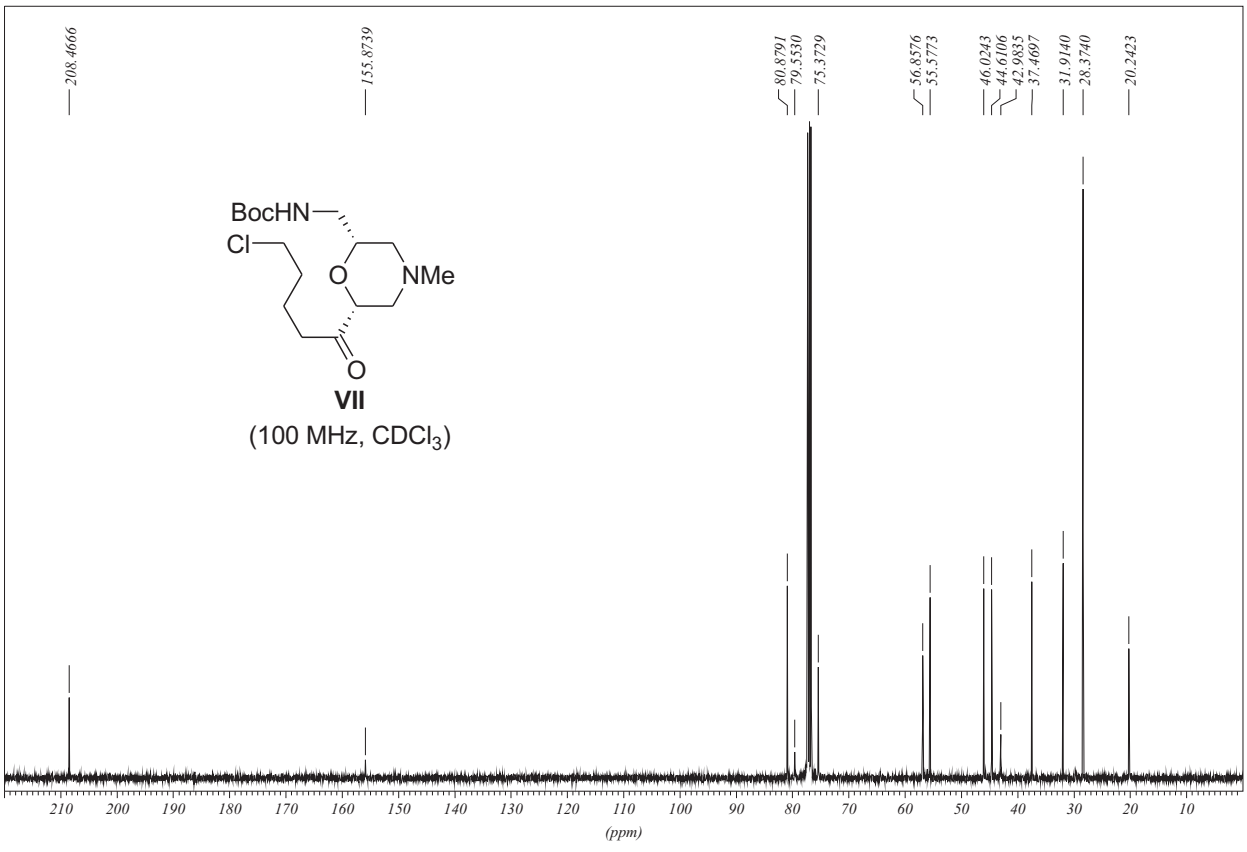

1623.23
1620.45
1612.37
1609.72
1453.84
1447.53
1441.34
1198.31
1187.95
1090.18
1078.94
1055.07
1048.12
1040.54
733.35
729.18
722.10
718.19
710.99
707.32
BocHN
TBSO
O
NMe
O
VI
(400 MHz, CDCl3)
Integral
0.8730
0.9916
3.1365
0.9927
1.0018
1.0084
0.9851
1.9412
2.9943
2.0514
4.3210
9.1495
9.0770
6.0884
7.5 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
(ppm)

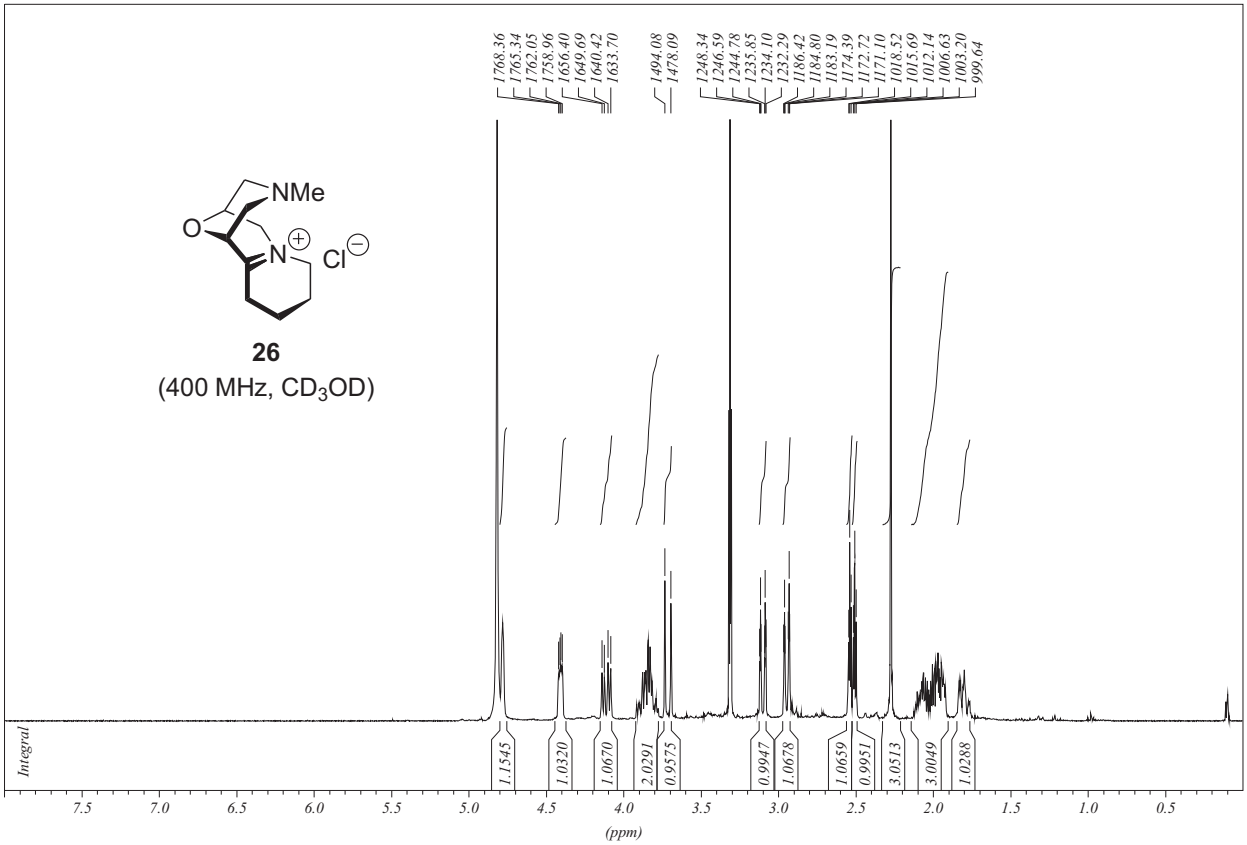

208.8553
155.9006
80.9401
79.5188
75.3272
62.9201
56.8690
55.6421
46.0472
43.0026
38.2089
32.1998
28.3931
25.9619
19.4421
18.3257
-5.2957
BocHN
TBSO
O
NMe
O
VI
(100 MHz, CDCl3)
200 180 160 140 120 100 80 60 40 20 0
(ppm)

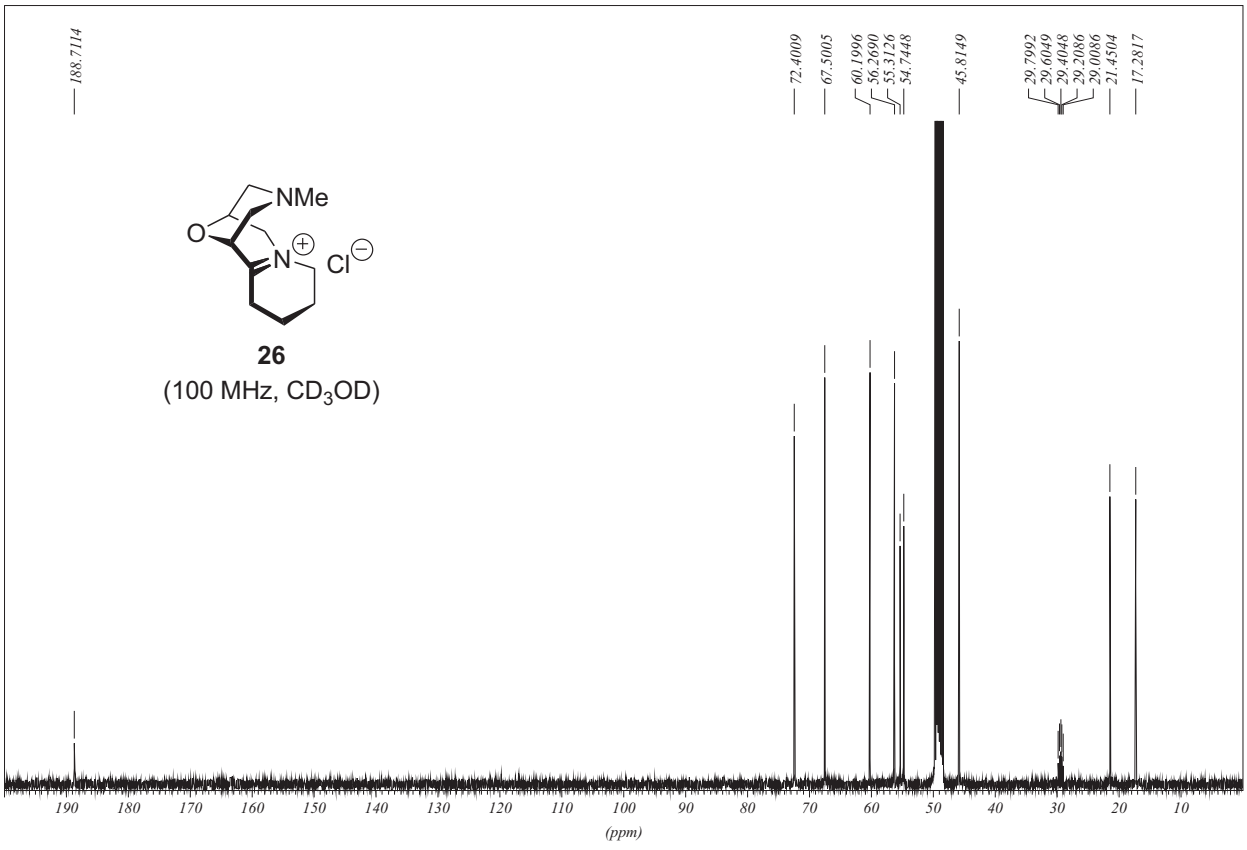

BocHN
HO
O
NMe
O
23
BocHN
O
NMe
H
O
OH
24
23 : 24 (diastereomer 1) : 24 (diastereomer 2) = 20:40:40
(400 MHz, CDCl3)
Integral
(ppm)

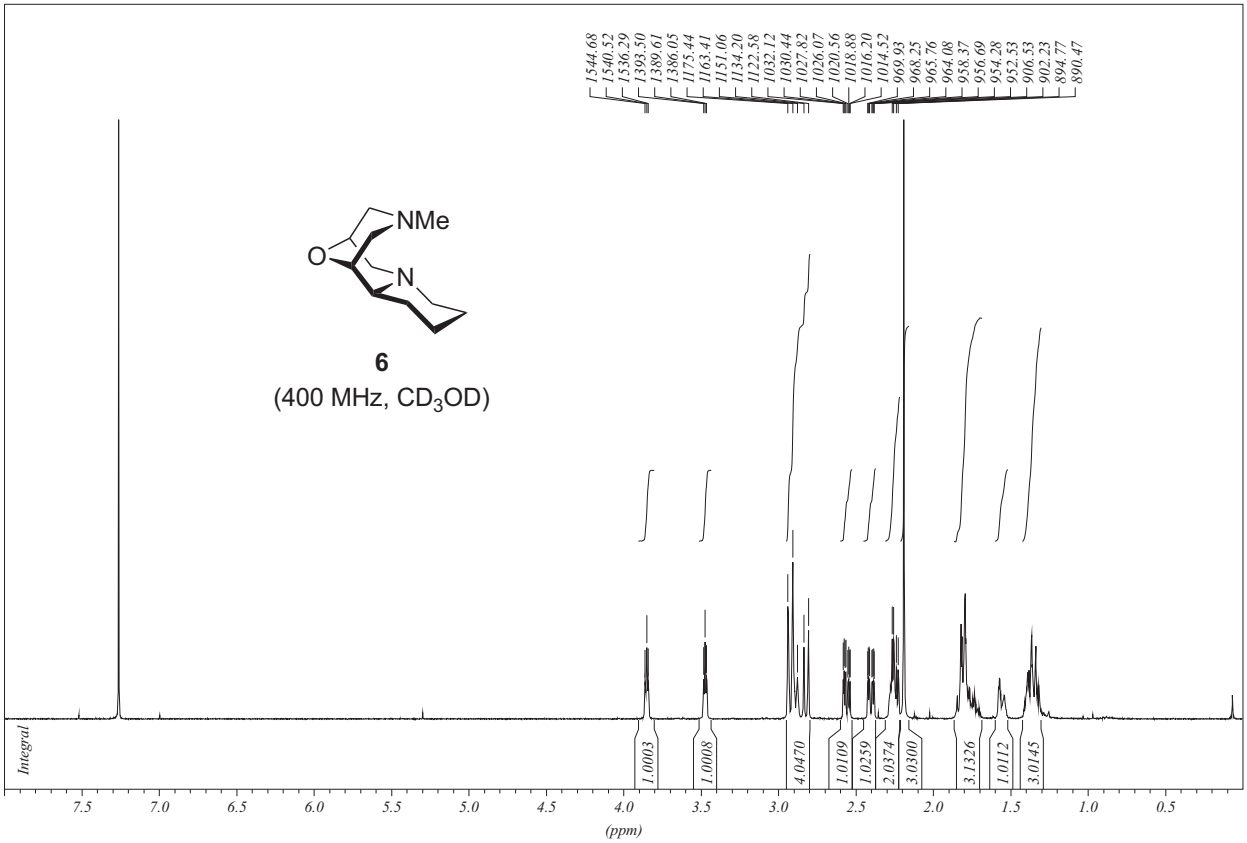

BocHN
HO
O
NMe
O
23
BocHN
O
NMe
H
O
OH
24
23 : 24 (diastereomer 1) : 24 (diastereomer 2) = 20:40:40
(100 MHz, CDCl3)
(ppm)

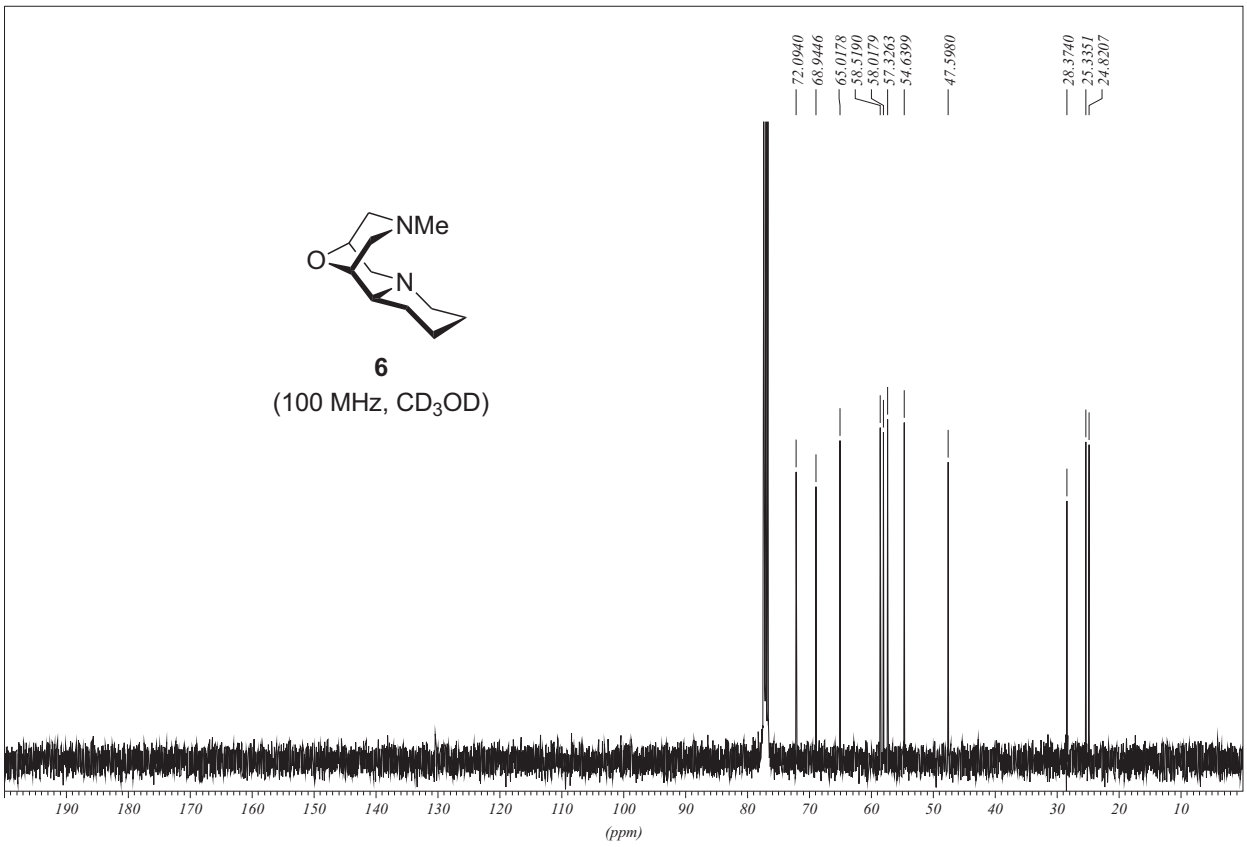

1624.62
1621.97
1613.76
1611.23
1424.29
1417.97
1411.53
1200.46
1188.84
1092.58
1081.22
1061.38
1055.07
1054.18
1047.99
BocHN
Cl
O
NMe
O
VII
(400 MHz, CDCl3)
Integral
0.9401
1.0000
0.9846
2.0293
1.0050
1.0383
1.0212
1.0173
1.9503
3.0346
6.0389
9.3250
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)

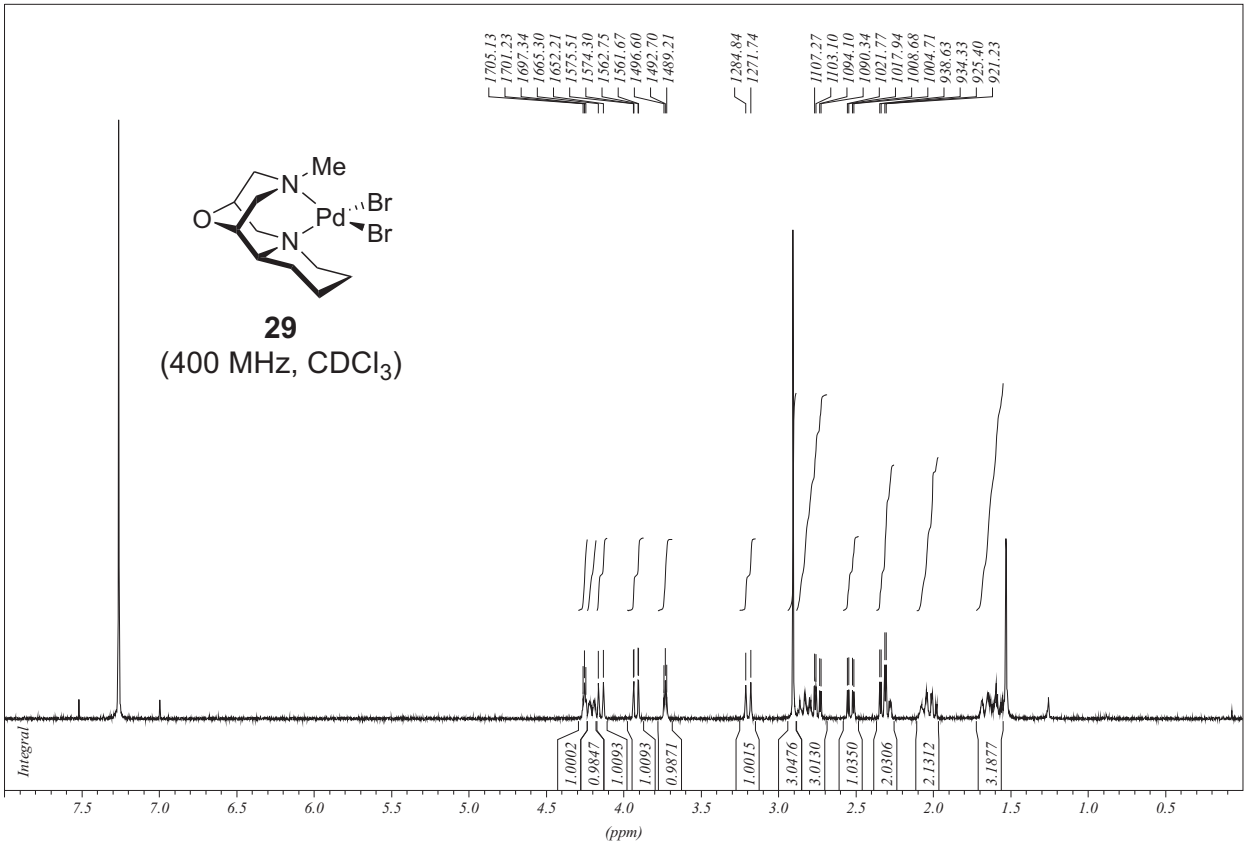

208.4666
155.8739
80.8791
79.5530
75.3729
56.8576
55.5773
46.0243
44.6106
42.9835
37.4697
31.9140
28.3740
20.2423
BocHN
Cl
O
NMe
O
VII
(100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

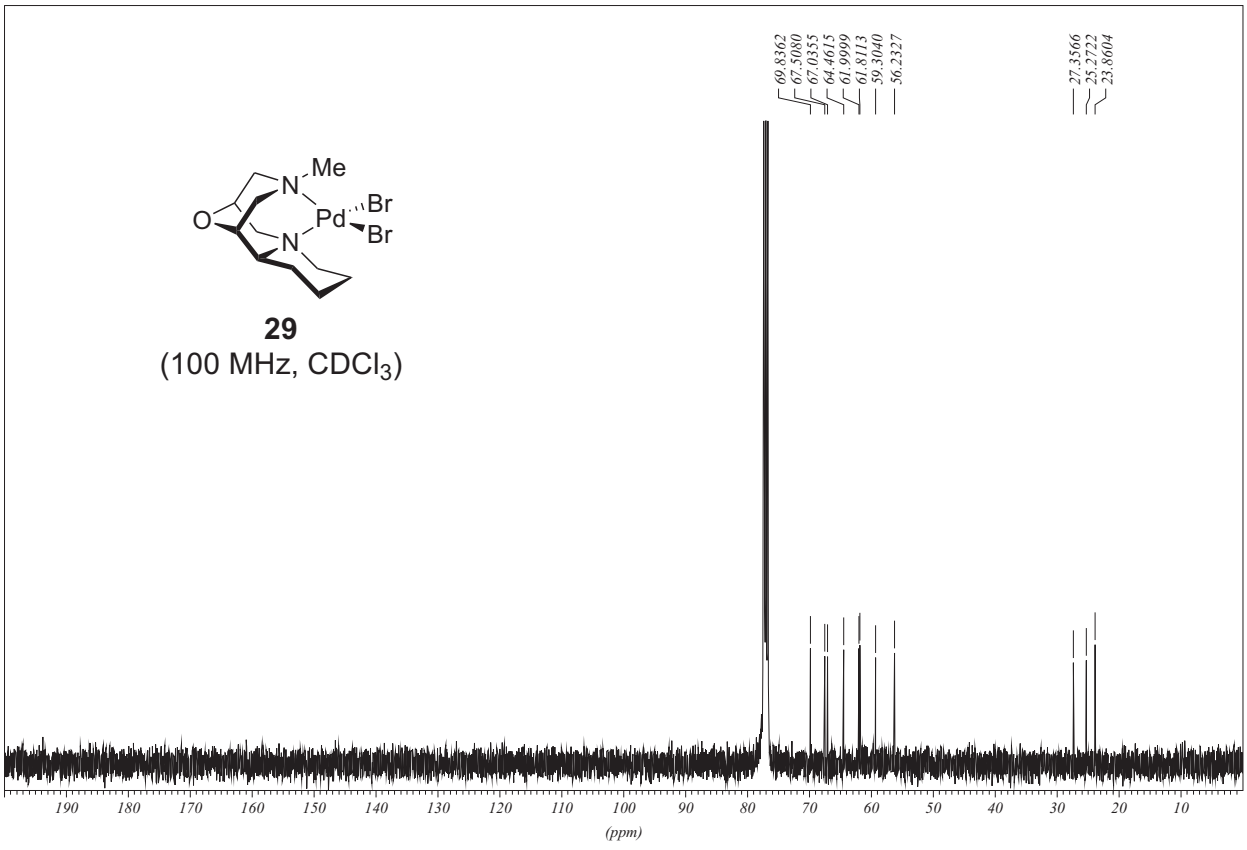

NMe
O
N
Cl
26
(400 MHz, CD3OD)
1768.36
1765.34
1762.05
1758.96
1656.40
1649.69
1640.42
1633.70
1494.08
1478.09
1248.34
1246.59
1244.78
1235.85
1234.10
1232.29
1186.42
1184.80
1183.19
1174.39
1172.72
1171.10
1018.52
1015.69
1012.14
1006.63
1003.20
999.64
Integral
1.1545
1.0320
1.0670
2.0291
0.9575
0.9947
1.0678
1.0659
0.9951
3.0513
3.0049
1.0288
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
(ppm)


188.7114
72.4009
67.5005
60.1996
56.2690
55.3126
54.7448
45.8149
29.7992
29.6049
29.4048
29.2086
29.0086
21.4504
17.2817
NMe
O
N
Cl
26
(100 MHz, CD3OD)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)


1544.68
1540.52
1536.29
1393.50
1389.61
1386.05
1175.44
1163.41
1151.06
1134.20
1122.58
1032.12
1030.44
1027.82
1026.07
1020.56
1018.88
1016.20
1014.52
969.93
968.25
965.76
964.08
958.37
956.69
954.28
952.53
906.53
902.23
894.77
890.47
NMe
O
N
6
(400 MHz, CD3OD)
Integral
1.0003
1.0008
4.0470
1.0109
1.0259
2.0374
3.0300
3.1326
1.0112
3.0145
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
(ppm)


72.0940
68.9446
65.0178
58.5190
58.0179
57.3263
54.6399
47.5980
28.3740
25.3351
24.8207
NMe
O
N
6
(100 MHz, CD3OD)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)


1705.13
1701.23
1697.34
1665.30
1652.21
1575.51
1574.30
1562.75
1561.67
1496.60
1492.70
1489.21
1284.84
1271.74
1107.27
1103.10
1094.10
1090.34
1021.77
1017.94
1008.68
1004.71
938.63
934.33
925.40
921.23
Me
N
O
Pd
Br
Br
N
29
(400 MHz, CDCl3)
Integral
1.0002
0.9847
1.0093
1.0093
0.9871
1.0015
3.0476
3.0130
1.0350
2.0306
2.1312
3.1877
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
(ppm)


69.8362
67.5080
67.0355
64.4615
61.9999
61.8113
59.3040
56.2327
27.3566
25.2722
23.8604
Me
N
O
Pd
Br
Br
N
29
(100 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

9. Cartesian coordinates of the calculated structures

All coordinates are given in Å.

compound **VIII**			
N	-1.568070	0.005248	0.695886
C	-1.282919	-1.246036	1.435689
C	0.006627	-1.197204	2.285026
C	-0.002172	0.036013	3.200156
C	-0.002465	1.250106	2.259886
C	-1.291695	1.272864	1.409492
C	1.292549	1.279088	1.417923
N	1.572248	0.014250	0.699072
C	1.302611	-1.234908	1.445340
C	2.580472	0.005317	-0.275347
H	2.149972	-1.473323	2.118017
H	1.218536	-2.057190	0.726209
H	2.140301	1.533501	2.083690
H	1.201388	2.087610	0.685679
H	-0.892326	0.039383	3.846491
H	0.882457	0.045765	3.854053
H	0.007915	-2.119614	2.884148
H	-0.006456	2.184723	2.839687
H	-2.143316	1.534183	2.067851
H	-1.195738	2.076176	0.671200
H	-2.131933	-1.500010	2.100176
H	-1.181910	-2.062745	0.712735
C	-2.578842	-0.008486	-0.274763
C	-3.105836	1.196276	-0.828659
C	-4.070473	1.171226	-1.841835
C	-4.573970	-0.039028	-2.340533
C	-4.088730	-1.233466	-1.788772
C	-3.124228	-1.228367	-0.774889
H	-2.762529	2.164170	-0.476621
H	-4.437064	2.119074	-2.237808
H	-5.327928	-0.050766	-3.126429
H	-4.470910	-2.192261	-2.141323
H	-2.796643	-2.184690	-0.379113
C	3.045454	1.207612	-0.886662
C	4.002289	1.183154	-1.906569
C	4.560111	-0.023367	-2.355282
C	4.140840	-1.212864	-1.742806
C	3.184489	-1.207763	-0.720658
H	2.653775	2.172432	-0.579191
H	4.318050	2.128298	-2.350008
H	5.307459	-0.034302	-3.147410
H	4.569119	-2.166862	-2.052941
H	2.909886	-2.158995	-0.275575

compound **VIII-H$^+$**			
N	-1.405688	0.024112	0.691192
C	-1.293371	-1.166602	1.586863
C	0.033379	-1.130415	2.385236
C	0.101239	0.155405	3.235279
C	0.048928	1.348267	2.257437
C	-1.276774	1.310831	1.462248
C	1.289259	1.329019	1.342332
N	1.346760	0.007959	0.548967
C	1.273851	-1.222053	1.475354
C	2.453367	-0.052320	-0.442581
H	2.198079	-1.246795	2.060331
H	1.243483	-2.095652	0.815614
H	2.214245	1.402599	1.921818
H	1.269747	2.129617	0.595489
H	-0.749118	0.197104	3.929050
H	1.020401	0.180327	3.836258
H	0.055559	-2.020405	3.028569
H	0.082496	2.299497	2.805587
H	-2.123799	1.417545	2.162516
H	-1.321207	2.145823	0.756792
H	-2.133826	-1.213042	2.302453
H	-1.331795	-2.067308	0.963251
C	-2.478715	0.004198	-0.271098
C	-2.494279	0.973455	-1.300404
C	-3.498238	0.967540	-2.272514
C	-4.505975	-0.010633	-2.251982
C	-4.493848	-0.977263	-1.240815
C	-3.495827	-0.971615	-0.253313
H	-1.709526	1.727095	-1.351424
H	-3.484982	1.722974	-3.057927
H	-5.283970	-0.017865	-3.014073
H	-5.268397	-1.743367	-1.206474
H	-3.526559	-1.729470	0.524892
C	2.120947	-0.137849	-1.797719
C	3.148562	-0.196454	-2.749117
C	4.488008	-0.171878	-2.338183
C	4.803513	-0.092217	-0.973880
C	3.784794	-0.029882	-0.013958
H	1.078904	-0.160670	-2.116249
H	2.897318	-0.261146	-3.806342
H	5.284906	-0.218451	-3.078514
H	5.843100	-0.073967	-0.651491
H	4.037736	0.033995	1.042321
H	0.420954	-0.014396	0.053022

compound **IX**			
C	2.039209	-2.224041	-0.197394
C	1.204964	-2.970631	0.656130
C	1.426868	-4.354943	0.770173
C	2.463513	-4.979372	0.059268
C	3.291100	-4.225207	-0.784791
C	3.071870	-2.844579	-0.913535
C	0.118994	-2.296578	1.490653
N	-0.625088	-1.237394	0.784419
C	-1.402341	-0.421208	1.733137
C	-2.273891	0.694624	1.063928
C	-3.134682	0.009203	0.001500
C	-2.282258	-0.683914	-1.063005
C	-1.445650	-1.772683	-0.312493
C	-1.401007	0.423388	-1.733269
N	-0.613340	1.231192	-0.785752
C	-1.427558	1.774965	0.311798
C	0.138194	2.283812	-1.495135
C	1.220877	2.960373	-0.658891
C	1.421122	4.349634	-0.750452
C	2.453989	4.977326	-0.036743
C	3.299840	4.221176	0.786969
C	3.102687	2.835195	0.893178
C	2.073760	2.211736	0.174487
H	-2.134288	2.553932	-0.054867
H	-0.760454	2.263591	1.034889
H	-2.086498	1.060277	-2.335929
H	-0.705995	-0.057283	-2.437439
C	-3.123198	1.385518	2.147717
C	-3.140023	-1.366061	-2.145633
H	-2.159317	-2.545181	0.054326
H	-0.784146	-2.267283	-1.036746
H	-2.093005	-1.050312	2.337981
H	-0.701002	0.053068	2.435381
H	0.592732	-1.825012	2.365547
H	-0.562851	-3.078962	1.890569
H	0.614542	1.804689	-2.364407
H	-0.539765	3.065497	-1.902918
H	0.762352	4.946946	-1.382617
H	2.592512	6.055368	-0.120070
H	4.100392	4.706387	1.344980
H	3.752420	2.240325	1.535472
H	1.910395	1.138959	0.266703
H	0.782125	-4.951084	1.417786
H	2.619038	-6.053594	0.160223
H	4.094167	-4.708153	-1.341131
H	3.706823	-2.251475	-1.572070
H	1.857710	-1.155768	-0.306296
O	-4.365059	0.014014	0.003192
H	-2.495048	-1.840709	-2.897283
H	-3.784870	-2.138318	-1.708392
H	-3.785398	-0.639326	-2.654312
H	-3.762283	2.162725	1.710836
H	-3.773860	0.665182	2.658760
H	-2.472599	1.855449	2.897503

compound **IX-H**$^+$			
C	2.570364	1.866085	-0.462601
C	1.436196	2.606450	-0.847171
C	1.362718	3.963448	-0.483537
C	2.390016	4.563958	0.259529
C	3.508881	3.813246	0.645721
C	3.598688	2.461248	0.279693
C	0.331808	1.954914	-1.663091
N	-0.583032	1.079528	-0.855104
C	-1.482933	0.309910	-1.762028
C	-2.417561	-0.670607	-0.975260
C	-3.220688	0.193459	0.015116
C	-2.308461	0.950503	0.998254
C	-1.380957	1.865020	0.126782
C	-1.590463	-1.698862	-0.150363
N	-0.686682	-1.019667	0.866140
C	-1.478670	-0.100501	1.788545
C	0.170293	-2.010820	1.678241
C	1.173476	-2.771314	0.839620
C	2.419010	-2.191413	0.529501
C	3.360620	-2.894055	-0.232619
C	3.071009	-4.190122	-0.684626
C	1.840441	-4.782024	-0.367100
C	0.897205	-4.077179	0.392618
C	-3.103385	1.807770	2.000399
O	-4.438678	0.300707	-0.005700
C	-3.322546	-1.436217	-1.957617
H	-2.011419	2.616386	-0.384622
H	-0.692097	2.402173	0.789090
H	-2.116499	0.987310	-2.364053
H	-0.860364	-0.269499	-2.455781
H	-2.249180	-2.378857	0.401406
H	-0.949395	-2.286267	-0.814828
H	-2.127835	-0.733628	2.403057
H	-0.753148	0.399359	2.440037
H	0.671486	-1.402819	2.437783
H	-0.537443	-2.680655	2.177592
H	0.773745	1.311337	-2.434184
H	-0.259986	2.731721	-2.179665
H	0.500245	4.557236	-0.788218
H	2.317180	5.616574	0.531899
H	4.309458	4.278671	1.219927
H	4.473809	1.876833	0.563057
H	2.657217	0.822370	-0.766419
H	-0.051896	-4.548940	0.647343
H	1.616276	-5.793371	-0.703930
H	3.805701	-4.739649	-1.271941
H	4.323036	-2.438234	-0.462019
H	2.663310	-1.197342	0.905823
H	-2.714587	-2.029764	-2.652188
H	-3.999524	-2.111779	-1.421241
H	-3.933723	-0.737936	-2.541035
H	-3.705114	2.555314	1.471232
H	-3.781968	1.186225	2.596552
H	-2.419749	2.330970	2.681291
H	-0.093805	-0.362538	0.292395

compound **X**			
N	-0.712967	1.333662	1.136192
C	-1.705810	0.555799	1.907409
C	-1.082749	-0.591696	2.738417
C	-0.003619	-0.008216	3.670795
C	1.079493	0.585767	2.749843
C	0.461402	1.743840	1.932086
C	1.705631	-0.551690	1.907737
N	0.716102	-1.320691	1.122639
C	-0.461045	-1.740240	1.909831
C	1.353147	-2.446398	0.424103
H	-0.194160	-2.559931	2.617440
H	-1.207625	-2.151000	1.216086
H	2.263483	-1.214073	2.610101
H	2.444706	-0.140369	1.203889
H	-0.427727	0.768416	4.325363
H	0.417709	-0.792188	4.318327
H	-1.899286	-1.032810	3.330290
H	1.893685	1.019793	3.350170
H	0.192245	2.555955	2.647510
H	1.210870	2.162065	1.245746
H	-2.266905	1.209057	2.615849
H	-2.441780	0.152819	1.195548
C	-1.342933	2.465913	0.443452
C	-0.507605	3.063698	-0.687920
H	-2.288053	2.096531	0.014677
H	-1.621039	3.279723	1.150369
H	2.289482	-2.065616	-0.013753
H	1.646779	-3.255789	1.129846
C	0.513200	-3.056275	-0.696711
C	0.523107	-4.445719	-0.916045
C	-0.192306	-5.012807	-1.982033
C	-0.935861	-4.194386	-2.844341
C	-0.959640	-2.807196	-2.629537
C	-0.239542	-2.244964	-1.566534
H	1.091930	-5.091057	-0.244650
H	-0.173291	-6.092212	-2.133601
H	-1.495057	-4.632091	-3.671136
H	-1.540923	-2.163817	-3.290706
H	-0.267403	-1.171157	-1.386814
C	-0.542415	4.447289	-0.939821
C	0.165311	5.002156	-2.017278
C	0.927355	4.177641	-2.857426
C	0.977333	2.796856	-2.608567
C	0.264424	2.246307	-1.534646
H	-1.125464	5.097930	-0.285900
H	0.125631	6.076940	-2.195522
H	1.481519	4.606074	-3.692410
H	1.572247	2.149032	-3.253113
H	0.312042	1.178175	-1.327480

compound **X-H**$^+$			
N	-0.790454	1.139035	1.132749
C	-1.744811	0.359886	1.982889
C	-1.000960	-0.687507	2.845216
C	0.019446	0.024020	3.758603
C	1.015053	0.755599	2.833579
C	0.257486	1.794738	1.972379
C	1.778027	-0.273602	1.976486
N	0.808682	-1.106766	1.131206
C	-0.280382	-1.749496	1.989768
C	1.565401	-2.108671	0.247167
H	0.208555	-2.502787	2.618482
H	-0.969344	-2.251191	1.303494
H	2.344380	-0.973580	2.601219
H	2.465209	0.209282	1.272585
H	-0.491917	0.743362	4.412292
H	0.540325	-0.697856	4.403255
H	-1.748649	-1.225057	3.443951
H	1.770560	1.291717	3.423776
H	-0.194855	2.552899	2.641837
H	0.953291	2.316779	1.304395
H	-2.316543	1.031486	2.652276
H	-2.464406	-0.132506	1.315179
C	-1.534606	2.129527	0.296829
H	0.293839	-0.392175	0.556494
C	-0.691086	2.775527	-0.790995
H	-2.369419	1.585008	-0.163679
H	-1.971918	2.914165	0.942587
H	2.364179	-1.530925	-0.229281
H	2.021012	-2.832041	0.931673
C	0.695405	-2.788045	-0.788104
C	0.195525	-4.085657	-0.572461
C	-0.595741	-4.713436	-1.544217
C	-0.893179	-4.051640	-2.743576
C	-0.389546	-2.762529	-2.973279
C	0.404085	-2.137742	-2.003282
H	0.432393	-4.611363	0.352645
H	-0.972452	-5.720109	-1.366704
H	-1.505521	-4.540825	-3.500253
H	-0.603832	-2.251548	-3.911277
H	0.818014	-1.148158	-2.201179
C	-0.267475	4.112233	-0.680770
C	0.498283	4.709659	-1.693696
C	0.848616	3.975748	-2.835057
C	0.419733	2.645203	-2.963585
C	-0.346006	2.054300	-1.950143
H	-0.539060	4.691561	0.202403
H	0.819102	5.746090	-1.590181
H	1.441141	4.438233	-3.624018
H	0.673607	2.074765	-3.856949
H	-0.694131	1.027114	-2.064658

compound **1** [(–)-sparteine]			
C	3.883950	-1.479850	0.573450
C	3.081450	-1.411950	-0.737150
N	1.771250	-0.757750	-0.547250
C	1.919150	0.630150	-0.035550
C	2.668950	0.611750	1.314250
C	4.043750	-0.076550	1.190850
C	0.957550	-0.857750	-1.776550
C	-0.389250	-0.100650	-1.702650
C	-0.088350	1.376750	-1.374550
C	0.560950	1.391250	0.023650
C	-1.406650	-0.699450	-0.689550
N	-0.971750	-0.480650	0.716650
C	-0.481350	0.870850	1.042950
C	-1.940650	-1.022050	1.689650
H	-1.938750	-2.122450	1.589650
H	-1.576150	-0.790450	2.700750
H	-1.291250	1.632850	1.086850
H	-0.049350	0.826550	2.052850
H	-1.411650	-1.796050	-0.832850
H	0.594750	1.799650	-2.127250
H	-1.000550	1.989350	-1.384750
H	0.800750	2.426250	0.313350
H	-0.846750	-0.179750	-2.700750
H	1.516150	-0.455750	-2.654950
H	0.782650	-1.926050	-1.976250
H	2.550750	1.214750	-0.749650
H	2.901750	-2.426250	-1.122750
H	3.683650	-0.875550	-1.508950
H	2.788250	1.646850	1.669250
H	2.060150	0.075650	2.056350
H	4.531550	-0.138850	2.174850
H	4.700550	0.532650	0.547950
H	4.866850	-1.932650	0.373950
H	3.357650	-2.138150	1.281750
C	-3.393850	-0.521450	1.501750
C	-2.861750	-0.211650	-0.965850
C	-3.860250	-0.798950	0.056850
H	-3.450950	0.558250	1.711850
H	-4.052850	-1.023850	2.226850
H	-4.866850	-0.388850	-0.114150
H	-3.934050	-1.889750	-0.093450
H	-3.148750	-0.505050	-1.987550
H	-2.907650	0.887450	-0.925350

compound **1-H**$^+$			
C	3.715900	-1.216850	0.988650
C	2.938000	-1.573050	-0.281050
N	1.682100	-0.728750	-0.428450
C	1.950300	0.792950	-0.351250
C	2.757200	1.120050	0.918350
C	4.047500	0.286150	1.036050
C	0.909500	-1.105150	-1.692150
C	-0.406900	-0.311050	-1.795150
C	-0.077300	1.198750	-1.817250
C	0.596100	1.546650	-0.471650
C	-1.375600	-0.666650	-0.631550
N	-0.778800	-0.204550	0.672950
C	-0.403200	1.240350	0.673050
C	-1.644400	-0.591050	1.822050
H	-1.621900	-1.690050	1.887550
H	-1.184000	-0.199050	2.738750
H	-1.271200	1.912350	0.552950
H	0.032600	1.463550	1.654650
H	-1.414000	-1.766050	-0.556850
H	0.589200	1.430550	-2.659850
H	-0.987000	1.797750	-1.950550
H	0.835200	2.618250	-0.435250
H	-0.881000	-0.614550	-2.738750
H	1.567200	-0.899550	-2.544350
H	0.731200	-2.184450	-1.634250
H	2.560700	1.018850	-1.236450
H	2.611300	-2.618250	-0.283550
H	3.540300	-1.391450	-1.179650
H	2.988300	2.193650	0.887250
H	2.138000	0.955350	1.811850
H	4.563100	0.530750	1.974050
H	4.734000	0.540850	0.213950
H	4.630400	-1.824450	1.001550
H	3.129900	-1.503750	1.875650
C	-3.110100	-0.118850	1.692150
C	-2.831400	-0.180750	-0.842250
C	-3.721500	-0.590150	0.354450
H	-3.160500	0.978750	1.760250
H	-3.688200	-0.513650	2.540550
H	-4.734000	-0.180550	0.229450
H	-3.823000	-1.687850	0.369250
H	-3.219000	-0.619250	-1.773550
H	-2.864000	0.911250	-0.968750
H	0.994900	-0.904550	0.351650

compound **3**			
C	-1.452577	-0.547103	-0.303160
C	-1.587185	-1.282861	1.045473
C	-0.154181	-1.450903	1.589409
C	-0.656337	-1.452906	-1.273853
C	0.654687	-2.341084	0.617240
N	0.678697	-1.825251	-0.766484
C	-0.872674	0.876371	-0.049194
C	0.442865	-0.049274	1.847511
N	0.431076	0.836814	0.663598
C	1.353687	-2.759078	-1.674163
C	0.894375	2.191030	1.027098
C	-0.739471	1.720514	-1.334793
C	-0.240277	3.146991	-1.028108
C	1.063671	3.090798	-0.208525
H	2.371704	-2.960702	-1.313573
H	0.823694	-3.734415	-1.765361
H	1.424933	-2.317765	-2.677774
H	-1.279110	-2.359811	-1.459891
H	-0.520950	-0.963801	-2.248600
H	0.212116	-3.364594	0.652672
H	1.696120	-2.434065	0.961660
H	-2.204511	-0.703105	1.747900
H	-2.071767	-2.261667	0.908847
H	-2.447618	-0.400376	-0.750963
H	-0.173008	-1.972888	2.558187
H	-0.131368	0.405833	2.687872
H	1.485813	-0.136603	2.188989
H	-1.626658	1.388580	0.598535
H	1.853394	2.091155	1.556153
H	0.183281	2.674339	1.739033
H	-1.716376	1.755805	-1.840406
H	-0.032284	1.228092	-2.018333
H	-0.088172	3.709326	-1.961267
H	-1.010283	3.687552	-0.453009
H	1.364836	4.098244	0.115374
H	1.877458	2.691960	-0.834194

compound **3-H**$^+$			
C	1.046708	2.976790	-0.352982
C	1.202762	2.034819	0.843683
N	0.522041	0.696425	0.599996
C	-0.966499	0.833122	0.194730
C	-1.097570	1.801994	-0.993807
C	-0.435951	3.167662	-0.723716
C	0.710421	-0.242077	1.792385
C	0.066204	-1.614956	1.526965
C	-1.439252	-1.427355	1.237462
C	-1.556163	-0.584495	-0.052523
C	0.736229	-2.354952	0.346137
N	0.564136	-1.592644	-0.923173
C	-0.877018	-1.353451	-1.214325
C	1.247975	-2.253689	-2.051354
H	2.314960	-2.360371	-1.820520
H	0.832301	-3.258324	-2.262037
H	1.145301	-1.638744	-2.953865
H	-1.416706	-2.310168	-1.364313
H	-0.943537	-0.796576	-2.156625
H	0.299798	-3.369890	0.259720
H	1.813525	-2.470898	0.526675
H	-1.939840	-0.927381	2.078295
H	-1.924418	-2.402875	1.096820
H	-2.612924	-0.438203	-0.314298
H	0.212412	-2.214598	2.435479
H	0.258758	0.248212	2.662245
H	1.791516	-0.321273	1.952113
H	-1.458128	1.270878	1.074210
H	2.253567	1.814058	1.058616
H	0.741106	2.456216	1.745073
H	-2.170418	1.922344	-1.196612
H	-0.652922	1.356404	-1.895353
H	-0.524732	3.804674	-1.613113
H	-0.960557	3.681617	0.096405
H	1.514085	3.934379	-0.086959
H	1.604322	2.577578	-1.214058
H	0.960737	0.178243	-0.202583

compound **6**			
C	-3.109899	1.061060	-0.239696
C	-2.216868	0.920377	1.004402
N	-0.856533	0.464241	0.648316
C	-0.886520	-0.846598	-0.044415
C	-1.720867	-0.750237	-1.338404
C	-3.151867	-0.257308	-1.038619
C	0.018411	0.440289	1.835682
C	1.403382	-0.164520	1.548035
O	1.226628	-1.512514	1.008673
C	0.542594	-1.398551	-0.279332
C	2.337447	0.632401	0.618383
N	1.836036	0.693585	-0.766973
C	1.462624	-0.644799	-1.258333
C	2.802585	1.343630	-1.661554
H	3.020683	2.356913	-1.298558
H	3.764056	0.788595	-1.733783
H	2.377287	1.422349	-2.671095
H	2.362413	-1.283031	-1.410256
H	0.974402	-0.539968	-2.236765
H	3.338474	0.146663	0.662127
H	2.454497	1.656945	1.000878
H	0.440454	-2.429779	-0.641056
H	1.918811	-0.300415	2.507384
H	-0.435871	-0.159654	2.655622
H	0.133892	1.468046	2.210507
H	-1.378138	-1.600841	0.615764
H	-2.125415	1.887362	1.519636
H	-2.693603	0.213531	1.723138
H	-1.747357	-1.736117	-1.825996
H	-1.233843	-0.050574	-2.033210
H	-3.712628	-0.124523	-1.975231
H	-3.686203	-1.023181	-0.452976
H	-4.121673	1.357952	0.073305
H	-2.714905	1.867813	-0.876495

compound **6-H$^+$**			
C	-2.085231	1.188807	0.844733
N	-0.729164	0.541849	0.593684
C	-0.839033	-0.938988	0.170614
C	-1.778188	-1.076089	-1.038837
C	-3.160438	-0.445191	-0.772945
C	-3.008289	1.033886	-0.367069
C	0.197616	0.689214	1.792998
C	1.556460	0.035950	1.498913
O	1.351522	-1.375125	1.191105
C	0.591059	-1.499012	-0.047756
C	2.345032	0.720062	0.368199
N	1.609487	0.584531	-0.916805
C	1.382405	-0.855904	-1.201551
C	2.309982	1.264334	-2.024928
H	2.419668	2.329176	-1.786640
H	3.314934	0.837686	-2.207337
H	1.717631	1.169511	-2.943075
H	2.338830	-1.402722	-1.312114
H	0.835257	-0.951401	-2.146883
H	3.350003	0.260412	0.306110
H	2.471358	1.786408	0.596299
H	0.497071	-2.575793	-0.227441
H	2.148348	0.057415	2.420509
H	-0.289597	0.202368	2.643702
H	0.301738	1.759903	1.996808
H	-1.272325	-1.451603	1.039017
H	-1.887022	2.238829	1.083531
H	-2.500767	0.696283	1.731947
H	-1.874873	-2.146905	-1.262791
H	-1.327714	-0.604628	-1.923874
H	-3.780948	-0.526870	-1.674275
H	-3.675296	-0.999272	0.026566
H	-3.980328	1.471191	-0.103240
H	-2.612871	1.620463	-1.210442
H	-0.223691	1.009610	-0.196192

compound **29**			
C	-1.999861	-1.950209	-0.967371
C	-3.070754	-0.923898	-0.591830
O	-3.595166	-1.230254	0.733787
C	-2.525564	-1.062691	1.708962
C	-1.435079	-2.104675	1.433427
N	-0.874098	-2.009351	0.032136
C	-2.668618	0.557857	-0.648160
N	-1.613059	0.899102	0.397183
C	-2.087121	0.408531	1.744073
C	-2.265361	1.065744	-2.042454
C	-2.139768	2.602059	-2.029790
C	-1.171509	3.044946	-0.916467
C	-1.508571	2.417097	0.442987
Pd	0.325872	-0.154976	0.050646
Br	1.801953	1.827482	0.655451
C	-0.083721	-3.256089	-0.241337
Br	2.508478	-1.295084	-0.570606
H	0.722806	-3.347022	0.487859
H	-0.755750	-4.123535	-0.165010
H	0.343123	-3.204365	-1.244805
H	-2.480824	-2.939362	-1.001380
H	-1.571671	-1.745334	-1.954344
H	-1.885028	-3.102153	1.554290
H	-0.604725	-2.012303	2.142486
H	-3.914604	-1.058086	-1.278319
H	-2.969016	-1.298428	2.683376
H	-2.955359	1.011868	2.051621
H	-1.283646	0.563615	2.472123
H	-3.573695	1.108664	-0.337445
H	-0.754120	2.672490	1.190597
H	-2.486520	2.783906	0.794330
H	-3.030228	0.744585	-2.763372
H	-1.312359	0.610410	-2.349958
H	-1.786797	2.963745	-3.004939
H	-3.135421	3.043466	-1.864158
H	-1.199155	4.136968	-0.790128
H	-0.142683	2.781428	-1.189461

compound **30**			
C	-0.278522	5.198109	0.942648
N	-0.025543	3.756137	0.689026
C	-0.609010	3.290158	-0.592754
C	-0.123920	4.142690	-1.787824
C	-0.372005	5.645091	-1.543837
C	0.246613	6.077438	-0.200513
C	-0.531488	2.936401	1.803699
C	-0.216612	1.455475	1.599735
O	-0.848762	1.003931	0.321703
C	-0.270825	1.800843	-0.803231
C	1.296267	1.104620	1.530349
N	1.590082	0.463562	0.196686
C	1.242878	1.450331	-0.891750
Pd	0.014682	-1.009345	0.037030
Br	1.358728	-3.068637	-0.228188
C	3.018487	0.047184	0.102493
Br	-2.134012	-2.284454	-0.071804
H	3.667915	0.927998	0.211227
H	3.235337	-0.672348	0.895638
H	3.191557	-0.421709	-0.869405
H	1.480201	0.989923	-1.854335
H	1.871139	2.341212	-0.756193
H	1.566343	0.394048	2.316196
H	1.919388	2.004779	1.629009
H	-0.804608	1.434657	-1.684089
H	-0.719395	0.863388	2.368194
H	-1.627695	3.046366	1.932335
H	-0.055448	3.262507	2.738940
H	-1.717940	3.355582	-0.551627
H	0.214267	5.457492	1.889516
H	-1.366029	5.382018	1.076900
H	-0.644630	3.805120	-2.694949
H	0.952190	3.980990	-1.948628
H	0.050400	6.230142	-2.372649
H	-1.455697	5.842934	-1.529849
H	0.006127	7.127509	0.018165
H	1.343443	5.996855	-0.249783