Supporting Information

Synthesis of labionin and avionin precursors via nitrogen-centred-radical-triggered 1,5-HAT reaction of Tris derivatives

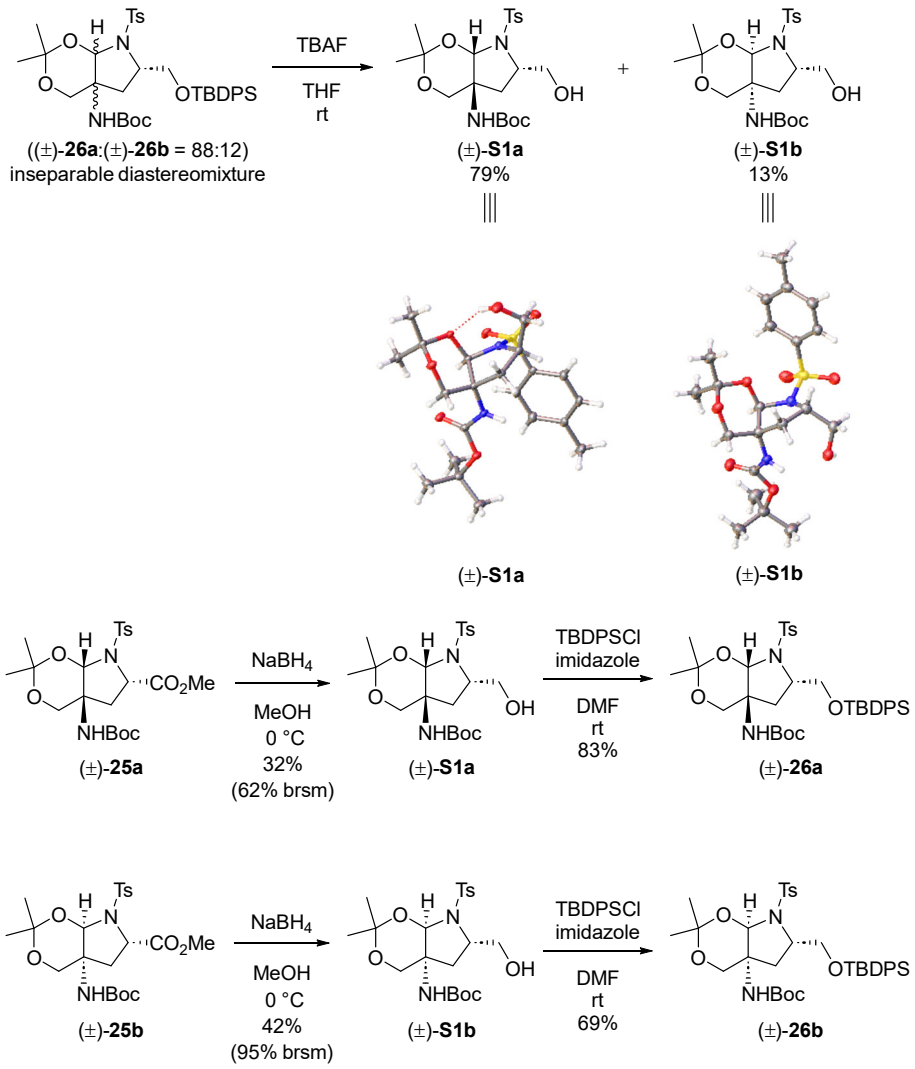
Ayuta Yamaguchi, Naoki Obiya, Norihito Arichi, Shinya Oishi, Hiroaki Ohno* and Shinsuke Inuki*

Graduate School of Pharmaceutical Sciences, Kyoto University,
Sakyo-ku, Kyoto 606-8501 (*Japan*)

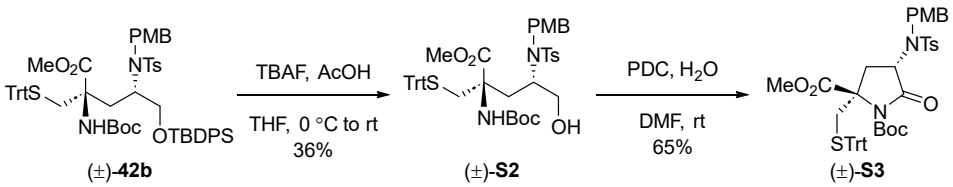
E-mail: hohno@pharm.kyoto-u.ac.jp
sinuki@pharm.kyoto-u.ac.jp

Table of Contents

Synthetic Schemes



Scheme S1. Synthesis of (±)-**S1a** and (±)-**S1b** and determination of relative configuration of (±)-**25a,** (±)-**25b**, (±)-**26a** and (±)-**26b**

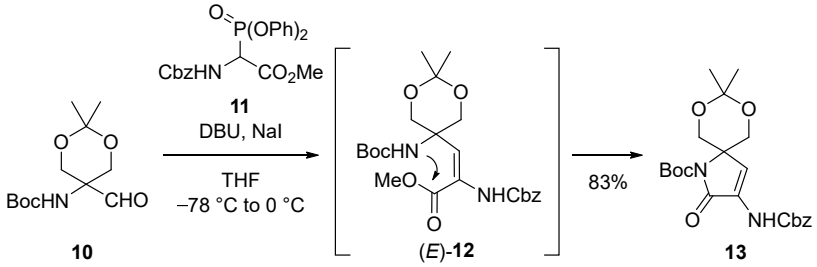


Scheme S2. Oxidation of compound (±)-**S2** from (±)-**42b**.

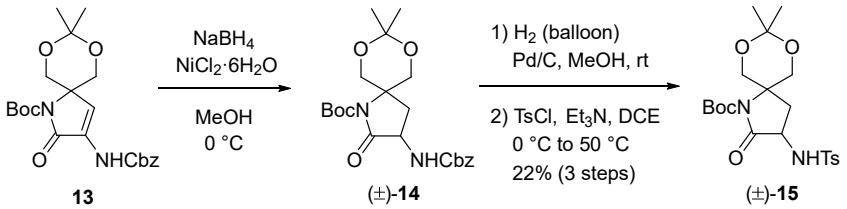
Experimental Procedures

General Methods. ^{1}H NMR spectra were recorded using a JEOL ECA-500. Chemical shifts are reported in δ (ppm) relative to Me_4Si [in $CDCl_3$ or DMSO-d_6] as the internal standard. ^{13}C NMR spectra were recorded using a JEOL ECA-500 or a JEOL ECZ600R, and referenced to the residual solvent signal. IR spectra were obtained on a JASCO FT/IR-4100 spectrometer. Exact mass (HRMS) spectra were recorded on a Shimadzu LC-ESI-IT-TOF-MS equipment (ESI). Optical rotations were measured with a JASCO P-1020 polarimeter. Column chromatography was performed using a forced flow (flash chromatography) of the indicated solvent system on Wakogel C-300E (Wako) or Biotage Isolera flash purification system on Presep® Silica Gel Type M (Wako), Presep® Silica Gel Type L (Wako) or Biotage® Sfär Silica D. All the heating experiments were performed in an oil bath. X-ray crystallography was recorded on XtaLAB P200 deffractometer (Rigaku, Tokyo, Japan). The compounds **19** is commercially available. The known compounds **10**[1] and **11**[2] were synthesized according to the literatures.

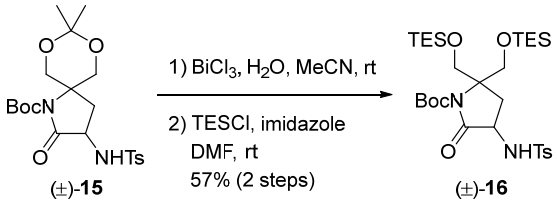
1. J. W. Lane, R. L. Halcomb, *Tetrahedron* 2001, **57**, 6531–6538.
2. M. Hamada, T. Shinada, Y. Ohfune, *Org. Lett.* 2009, **11**, 4664–4667.



Compound 13. To a mixture of **10** (379 mg, 1.14 mmol) and NaI (197 mg, 1.31 mmol) in THF (10 mL) was added DBU (179 μL, 1.20 mmol) at 0 °C under Ar. The mixture was stirred for 10 min at 0 °C and cooled to –78 °C. To the mixture was added a solution of **11** (148 mg, 0.572 mmol) in THF (4.3 mL). The mixture was gradually warmed to 0 °C and stirred for 8.5 h. The reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 4 to 40% EtOAc in hexane) to give **13** (205 mg, 83%) as a white solid; mp 163–165 °C; IR (neat cm^{-1}): 3327 (NH), 1738 (C=O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.39–7.34 (m, 5H), 6.99 (s, 1H), 5.21 (s, 2H), 4.82 (d, J = 10.9 Hz, 2H), 3.43 (d, J = 10.9 Hz, 2H), 1.59–1.58 (m, 12H), 1.46 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 164.7, 152.8, 149.1, 135.5, 128.7 (2C), 128.5, 128.2 (2C), 126.2, 98.9, 84.4, 67.7, 63.9 (2C), 61.8, 28.3, 28.1 (3C), 19.3 (one peak of olefin was not observed); HRMS (ESI-TOF) *m/z*: [M + Na]$^{+}$ calcd for $C_{22}H_{28}N_2NaO_7$, 455.1789; found 455.1784.

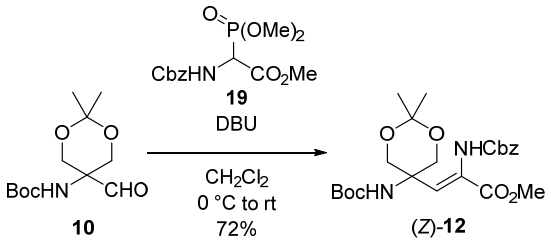


Compound (±)-15. To a stirred mixture of **13** (440 mg, 1.02 mmol) and $NiCl_2·6H_2O$ (506 mg, 2.13 mmol) in MeOH (11 mL) was added $NaBH_4$ (164 mg, 4.34 mmol) at 0 °C under Ar. After being stirred at 0 °C for 2.5 h, the reaction mixture was filtered through a short pad of celite and diluted with H_2O. The resulting mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 7 to 20% EtOAc in hexane twice) to give (±)-**14** (185 mg) including inseparable impurities, as a colorless amorphous solid. To a solution of (±)-**14** (185 mg) including impurities in MeOH (6.0 mL) was added Pd/C (90.4 mg, 0.850 mmol) at room temperature, and the mixture was flushed with H_2 gas (1 atm). After being stirred at this temperature for 1 h, the reaction mixture was filtered through celite with MeOH. The filtrate was concentrated *in vacuo* to give a crude amine, which was used without further purification. To a solution of crude amine in DCE (7.0 mL) were added TsCl (183 mg, 9.60 mmol) and Et_3N (0.180 mL, 1.25 mmol) at 0 °C under Ar. After being stirred at 50 °C for 17 h, the reaction mixture was diluted with H_2O and the whole was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 10 to 30% EtOAc in hexane) to give (±)-**15** (100 mg, 22%, 3 steps) as a white solid; mp 169–172 °C; IR (neat cm^{-1}): 3294 (NH), 1788 (C=O), 1723 (C=O), 1255 (S=O), 1159 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.79 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 5.13 (s, 1H), 4.73 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 10.9 Hz, 1H), 3.75–3.70 (m, 1H), 3.45 (d, J = 11.5 Hz, 1H), 3.34 (d, J = 10.9 Hz, 1H), 3.27 (dd, J = 12.6, 8.9 Hz, 1H), 2.43 (s, 3H), 1.88–1.81 (m, 1H), 1.53–1.51 (m, 12H), 1.41 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.1, 149.4, 144.1, 135.6, 129.9 (2C), 127.3 (2C), 98.9, 84.9, 66.5, 61.8, 58.8, 52.3, 36.7, 27.9 (3C), 27.8, 21.6, 19.7; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{30}N_2NaO_7S$, 477.1666; found 477.1661.

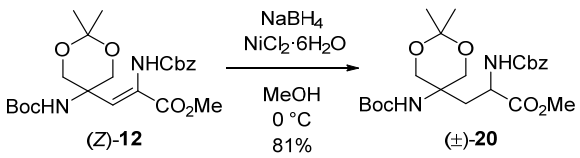


Compound (±)-16. To a solution of (±)-**15** (24.6 mg, 0.0541 mmol) in MeCN/H_2O (2.0/0.1 mL) was added $BiCl_3$ (64.5 mg, 0.205 mmol) at room temperature. After being stirred at this temperature for 30 min, the mixture was diluted with saturated aqueous NH_4Cl. The resulting mixture was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give a crude diol, which was used without further purification. To a stirred mixture of the crude diol and imidazole (46.7 mg, 0.686 mmol) in DMF (0.7 mL) was added TESCl (91.0 μL, 0.540 mmol) at room temperature. After being stirred at this temperature for 1 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted

with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 2 to 15% EtOAc in hexane) to give (±)-**16** (20.0 mg, 57%, 2 steps) as colorless oil; IR (neat cm^{-1}): 3424 (NH), 1724 (C=O), 1297 (S=O), 1164 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2H) 7.30 (d, J = 8.0 Hz, 2H), 5.24 (d, J = 2.9 Hz, 1H), 4.03 (d, J = 10.3 Hz, 1H), 4.00 (ddd, J = 10.0, 9.2, 2.9 Hz, 1H), 3.95 (d, J = 9.7 Hz, 1H), 3.50 (d, J = 9.7 Hz, 1H), 3.47 (d, J = 10.3 Hz, 1H), 2.49 (dd, J = 13.2, 9.2 Hz, 1H), 2.42 (s, 3H), 2.19 (dd, J = 13.2, 10.0 Hz, 1H), 1.49 (s, 9H), 0.93–0.92 (m, 9H), 0.84–0.82 (m, 9H), 0.58–0.56 (m, 6H), 0.46–0.45 (m, 6H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.3, 149.7, 143.6, 135.9, 129.7 (2C), 127.4 (2C), 83.5, 68.2, 64.0, 62.9, 53.4, 35.5, 27.9 (3C), 21.5, 6.68 (3C), 6.59 (3C), 4.19 (3C), 4.03 (3C); HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{30}H_{54}N_2NaO_7SSi_2$, 665.3082; found 665.3082.

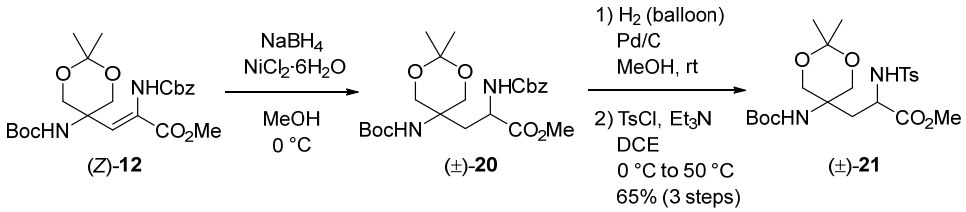


Compound (*Z*)-**12.** To a stirred solution of **10** (4.78 g, 14.4 mmol) in CH_2Cl_2 (10.0 mL) was added DBU (2.15 mL, 14.4 mmol) at 0 °C under Ar. After the mixture was stirred for 30 min at this temperature, **19** (2.88 g, 11.1 mmol) in CH_2Cl_2 (17.7 mL) was added to the mixture. After being stirred at room temperature for 15 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 4 to 25% EtOAc in hexane and gradient 5 to 40% EtOAc in hexane) to give (*Z*)-**12** (3.69 g, 72%) as a white solid; mp 125–127 °C; IR (neat cm^{-1}): 3320 (NH), 1725 (C=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.37–7.32 (m, 5H), 5.97 (s, 1H), 5.22 (s, 1H), 5.15 (s, 2H), 4.05 (d, J = 12.0 Hz, 2H), 3.91 (d, J = 12.0 Hz, 2H), 3.78–3.68 (m, 3H), 1.42–1.41 (m, 15H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 164.9, 155.2, 154.3, 135.9, 129.2, 128.5 (2C), 128.2, 128.1 (2C), 127.9, 98.7, 80.4, 67.4, 64.9 (2C), 52.6, 51.7, 28.2 (3C), 27.4, 19.4; HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd for $C_{23}H_{33}N_2O_8$, 465.2231; found 465.2230.

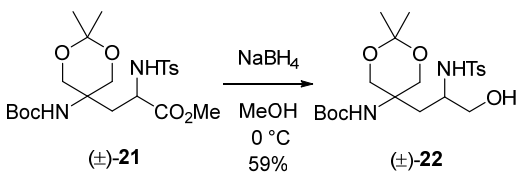


Compound (±)-20. According to the procedure described for the preparation of (±)-**14**, compound (*Z*)-**12** (72.0 mg, 0.155 mmol) was converted into compound (±)-**20** (58.4 mg, 81%) by the reaction with $NiCl_2·6H_2O$ (36.8 mg, 0.155 mmol) and $NaBH_4$ (12.9 mg, 0.341 mmol) in MeOH (5.2 mL) at 0 °C for 2 h. Column chromatography: silica gel (gradient 10 to 20% EtOAc in hexane); a colorless amorphous solid; IR (neat cm^{-1}): 3362 (NH), 1720 (C=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.37–7.29 (m, 5H), 5.55–5.42 (m, 1H), 5.12 (d, J = 12.0 Hz, 1H), 5.07 (d, J = 12.0 Hz,

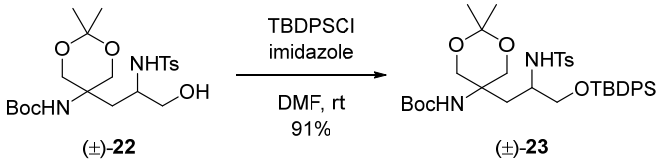
1H), 5.02–4.92 (m, 1H), 4.37–4.36 (m, 1H), 3.96 (d, J = 11.5 Hz, 1H), 3.91 (d, J = 11.5 Hz, 1H), 3.76–3.72 (m, 5H), 2.22–2.19 (m, 2H), 1.42–1.41 (m, 15H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.9, 155.9, 155.1, 136.1, 128.5 (2C), 128.1, 128.0 (2C), 98.5, 79.8, 67.1, 65.9, 65.8, 52.6, 51.1, 50.1, 33.6, 28.3 (3C), 26.1, 21.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{23}H_{34}N_2NaO_8$, 489.2207; found 489.2203.



Compound (±)-21. To a stirred mixture of (*Z*)-**12** (1.86 g, 4.00 mmol) and $NiCl_2·6H_2O$ (955 mg, 4.02 mmol) in MeOH (40 mL) was added $NaBH_4$ (333 mg, 8.79 mmol) at 0 °C under Ar. After the reaction mixture was stirred at this temperature for 3.5 h, a second portion of $NaBH_4$ (333 mg, 8.79 mmol) was added to the reaction mixture at 0 °C. After being stirred at this temperature for additional 2.5 h, the reaction mixture was filtered through a short pad of celite and diluted with H_2O. The resulting mixture was extracted with CH_2Cl_2 twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give a crude (±)-**20**, which was used without further purification. To a solution of crude (±)-**20** in MeOH (20 mL) was added Pd/C (891 mg, 8.38 mmol) at room temperature, and the mixture was flushed with H_2 gas (1 atm). After being stirred at room temperature for 50 min, the reaction mixture was filtered through celite with MeOH. The filtrate was concentrated *in vacuo* to give a crude amine as a colorless amorphous solid, which was used without further purification. To a solution of crude amine in DCE (20 mL) were added TsCl (916 mg, 4.81 mmol) and Et_3N (1.4 mL, 9.59 mmol) at 0 °C under Ar. After the reaction mixture was stirred at 50 °C for 28.5 h, a second portion of TsCl (980 mg, 5.14 mmol) was added to the reaction mixture. After being stirred at 50 °C for additional 19.5 h, the reaction mixture was diluted with H_2O at 0 °C and the whole was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (gradient 7 to 40% EtOAc in hexane) to give (±)-**21** (1.26 g, 65%, 3 steps) as a white solid; mp 142–144 °C; IR (neat cm^{-1}): 3266 (NH), 1743 (C=O), 1708 (C=O), 1338 (S=O), 1160 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 5.14 (d, J = 10.3 Hz, 1H), 5.00 (s, 1H), 4.01–3.99 (m, 3H), 3.84 (d, J = 12.0 Hz, 1H), 3.74 (d, J = 12.0 Hz, 1H), 3.40 (s, 3H), 2.42 (s, 3H), 2.34–2.31 (m, 1H), 1.88 (dd, J = 14.6, 9.5 Hz, 1H), 1.47 (s, 9H), 1.42 (s, 3H), 1.40 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 172.2, 155.0, 143.9, 136.0, 129.6 (2C), 127.5 (2C), 98.5, 79.7, 66.5, 65.1, 52.6, 52.2, 51.4, 34.4, 28.3 (3C), 25.8, 21.6, 21.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{34}N_2NaO_8S$, 509.1928; found 509.1921.

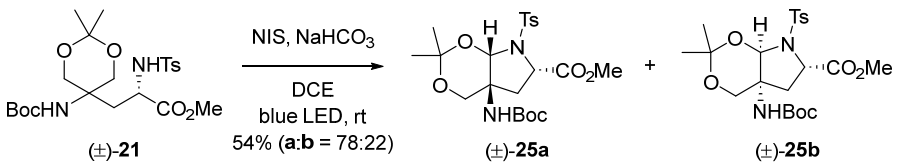


Compound (±)-22. To a solution of (±)-**21** (2.81 g, 5.77 mmol) in MeOH (58 mL) was added $NaBH_4$ (4.62 g, 122 mmol) at 0 °C under Ar. After being stirred at this temperature for 3 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 12 to 65% EtOAc in hexane) to give (±)-**22** (1.57 g, 59%) as a colorless amorphous solid; IR (neat cm^{-1}): 3428 (NH and OH), 1696 (C=O), 1250 (S=O), 1160 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.25 (d, J = 8.0 Hz, 1H), 5.07 (s, 1H), 3.81–3.80 (m, 2H), 3.67 (d, J = 12.0 Hz, 1H), 3.57 (d, J = 12.0 Hz, 1H), 3.50–3.48 (m, 1H), 3.35–3.34 (m, 2H), 2.43–2.41 (m, 4H), 2.21–2.12 (m, 1H), 1.45 (s, 9H), 1.40 (s, 3H), 1.37 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 156.0, 143.7, 137.5, 129.8 (2C), 127.1 (2C), 98.4, 80.1, 66.7, 65.5, 64.9, 51.1, 50.9, 33.4, 28.3 (3C), 26.8, 21.5, 20.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{34}N_2NaO_7S$, 481.1979; found 481.1979.



(±)-**22** (±)-**23**

Compound (±)-23. To a stirred mixture of (±)-**22** (1.57 g, 3.43 mmol) and imidazole (746 mg, 11.0 mmol) in DMF (11 mL) was added TBDPSCl (1.8 mL, 7.0 mmol) at room temperature. After being stirred at this temperature for 3 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc/hexane (10:1) twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 6 to 40% EtOAc in hexane) to give (±)-**23** (2.14 g, 91%) as a white solid; mp 147–149 °C; IR (neat cm^{-1}): 3432 (NH), 1705 (C=O), 1249 (S=O), 1162 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 8.6 Hz, 2H), 7.51–7.42 (m, 6H), 7.38–7.35 (m, 4H), 7.16 (d, J = 8.6 Hz, 2H), 5.05 (s, 1H), 4.99 (d, J = 7.4 Hz, 1H), 3.99 (d, J = 12.0 Hz, 1H), 3.89 (d, J = 11.5 Hz, 1H), 3.71 (d, J = 12.0 Hz, 1H), 3.56 (d, J = 11.5 Hz, 1H), 3.45 (dd, J = 10.0, 3.2 Hz, 1H), 3.34–3.30 (m, 1H), 3.26 (dd, J = 10.0, 4.6 Hz, 1H), 2.38 (s, 3H), 2.01–1.98 (m, 2H), 1.42–1.41 (m, 12H), 1.38 (s, 3H), 1.02 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 155.2, 143.4, 137.3, 135.5 (4C), 132.7, 132.6, 129.9 (2C), 129.6 (2C), 127.8 (2C), 127.7 (2C), 127.1 (2C), 98.3, 79.4, 66.7, 65.9, 65.1, 51.1 (2C), 34.2, 28.3 (3C), 26.9 (3C), 25.5, 21.6, 21.5, 19.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{37}H_{53}N_2O_7SSi$, 697.3337; found 697.3338.



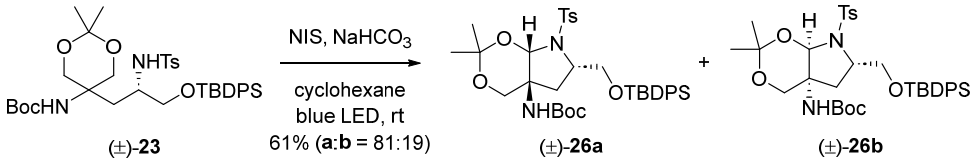
(±)-**21** (±)-**25a** (±)-**25b**

1,5-HAT reaction of (±)-21 (Table 1, entry 2). A mixture of (±)-**21** (42.8 mg, 0.0880 mmol), NIS (79.2 mg, 0.352 mmol) and $NaHCO_3$ (29.6 mg, 0.352 mmol) in DCE was stirred at room temperature under Ar and irradiated with 40W blue LED lamp using EvoluChem™ PhotoRedOx Box. After being stirred for 12 h at this temperature, the reaction mixture was diluted with saturated aqueous $Na_2S_2O_3$ and the whole was extracted with EtOAc twice. The

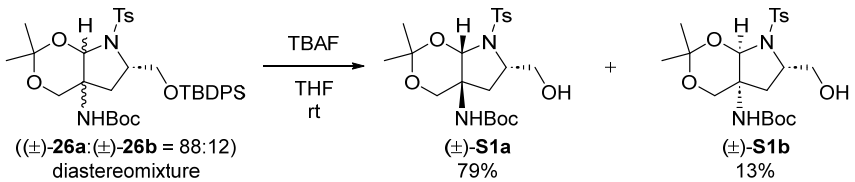
combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (gradient 0 to 25% EtOAc in hexane) and PTLC (hexane/EtOAc = 3/1) to give (±)-**25a** (17.9 mg, 42%) and (±)-**25b** (5.0 mg, 12%).

Compound (±)-**25a**: colorless amorphous solid; IR (neat cm^{-1}): 3347 (NH), 1713 (C=O), 1251 (S=O), 1164 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.55 (s, 1H), 4.60 (dd, J = 9.7, 8.0 Hz, 1H), 4.42 (s, 1H), 4.25 (d, J = 12.0 Hz, 1H), 3.91 (d, J = 12.0 Hz, 1H), 3.62 (s, 3H), 2.67 (dd, J = 13.2, 9.7 Hz, 1H), 2.51 (dd, J = 13.2, 8.0 Hz, 1H), 2.43 (s, 3H), 1.53 (s, 3H), 1.42 (s, 9H), 1.35 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 171.2, 154.2, 143.6, 137.0, 129.4 (2C), 127.6 (2C), 99.9, 85.8, 80.6, 63.4, 59.1, 58.1, 52.4, 35.6, 28.3 (3C), 28.1, 21.6, 20.5; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{32}N_2NaO_8S$, 507.1772; found 507.1777.

Compound (±)-**25b**: colorless amorphous solid; IR (neat cm^{-1}): 3314 (NH), 1739 (C=O), 1709 (C=O), 1276 (S=O), 1170 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.78 (d, J = 8.6 Hz, 2H), 7.28 (d, J = 8.6 Hz, 2H), 5.71 (s, 1H), 5.60 (s, 1H), 4.51 (d, J = 12.0 Hz, 1H), 4.03 (dd, J = 10.3, 1.7 Hz, 1H), 3.81–3.78 (m, 4H), 2.85 (dd, J = 13.7, 10.3 Hz, 1H), 2.43 (s, 3H), 2.03–2.00 (m, 1H), 1.60 (s, 3H), 1.45 (s, 9H), 1.15 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 173.0, 155.0, 143.9, 135.6, 129.0 (2C), 128.8 (2C), 99.2, 86.3, 80.2, 62.4, 57.8, 57.0, 53.0, 35.8, 28.3 (3C), 28.2, 21.6, 20.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{22}H_{32}N_2NaO_8S$, 507.1772; found 507.1774.



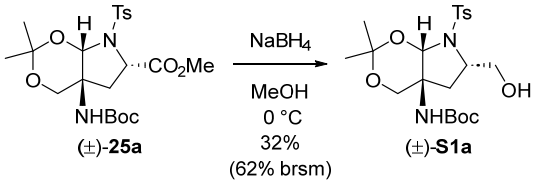
1,5-HAT reaction of (±)-23 (Table 1, entry 6). A mixture of (±)-**23** (782 mg, 1.12 mmol), NIS (1.01 g, 4.49 mmol) and $NaHCO_3$ (377 mg, 4.49 mmol) in cyclohexane was stirred at room temperature under Ar and irradiated with two 40W blue LED lamps (approximately 5 cm away from the light source). After being stirred for 12 h, the reaction mixture was diluted with saturated aqueous $Na_2S_2O_3$ and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude mixture was purified by column chromatography on silica gel (gradient 4 to 15% EtOAc in hexane) to give diastereomeric mixture of (±)-**26** (474 mg, 61%, **a**:**b** = 81:19).



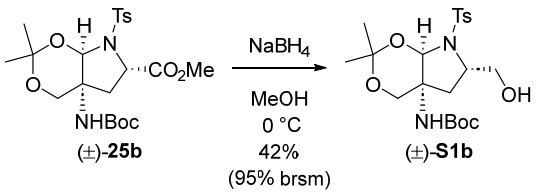
Compound (±)-S1a and (±)-S1b. To a solution of the 88:12 diastereomeric mixture of (±)-**26** (18.2 mg, 0.0262 mmol) in THF (1.5 mL) was added a 1 M solution of TBAF in THF (53 μL, 0.053 mmol) at 0 °C under Ar. After being stirred at room temperature for 13 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC (hexane/EtOAc = 3/1) to give (±)-**S1a** (9.4 mg, 79%) and (±)-**S1b** (1.6 mg, 13%).

Compound (±)-**S1a**: white solid; mp: 173–175 °C; IR (neat cm^{-1}): 3401 (NH and OH), 1709 (C=O), 1252 (S=O), 1164 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.79 (s, 1H), 4.38 (d, J = 12.0 Hz, 1H), 4.27 (s, 1H), 4.15–4.14 (m, 1H), 3.82–3.80 (m, 1H), 3.77 (d, J = 12.0 Hz, 1H), 3.50–3.45 (m, 1H), 2.76 (dd, J = 13.7, 9.2 Hz, 1H), 2.56–2.55 (m, 1H), 2.43 (s, 3H), 1.93 (dd, J = 13.7, 7.4 Hz, 1H), 1.64 (s, 3H), 1.43 (s, 9H), 1.38 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 154.2, 143.8, 137.0, 129.8 (2C), 127.1 (2C), 100.0, 85.1, 80.5, 62.8, 62.6, 60.1, 57.1, 33.7, 28.5, 28.3 (3C), 21.6, 20.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{32}N_2NaO_7S$, 479.1822; found 479.1819.

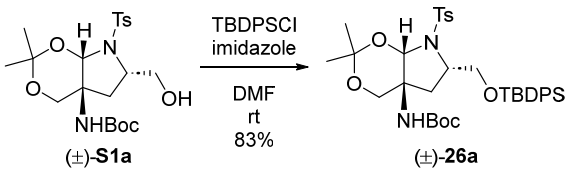
Compound (±)-**S1b**: white solid; mp: 171–173 °C; IR (neat cm^{-1}): 3482 (NH and OH), 1710 (C=O), 1275 (S=O), 1157 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.93 (s, 1H), 5.61 (s, 1H), 4.68 (d, J = 11.5 Hz, 1H), 4.16 (d, J = 12.0 Hz, 1H), 3.55 (d, J = 11.5 Hz, 1H), 3.46–3.43 (m, 2H), 2.87 (dd, J = 13.5, 10.6 Hz, 1H), 2.64–2.53 (m, 1H), 2.43 (s, 3H), 1.71–1.69 (m, 4H), 1.45 (s, 9H), 1.24 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 154.8, 143.9, 135.2, 129.2 (2C), 128.8 (2C), 99.1, 86.9, 80.1, 63.5, 61.8, 58.4, 54.7, 36.8, 28.4 (4C), 21.6, 20.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{21}H_{32}N_2NaO_7S$, 479.1822; found 479.1828.



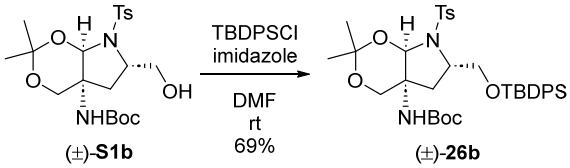
Synthesis of (±)-S1a from (±)-25a. To a solution of (±)-**25a** (14.1 mg, 0.0291 mmol) in MeOH (0.6 mL) was added $NaBH_4$ (22.5 mg, 0.0464 mmol) at 0 °C under Ar. After the reaction mixture was stirred at this temperature for 40 min, a second portion of $NaBH_4$ (52.3 mg, 1.38 mmol) was added to the reaction mixture at 0 °C. After being stirred at this temperature for additional 20 min, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC (hexane/EtOAc = 2/1) to give (±)-**S1a** (4.2 mg, 32%) and (±)-**25a** (6.9 mg, 48%) was recovered. All the spectral data were in agreement with those described above.



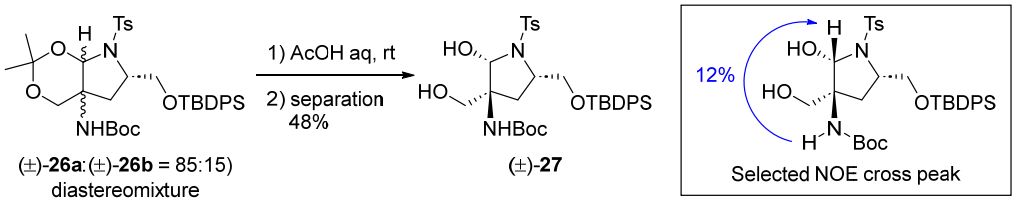
Synthesis of (±)-S1b from (±)-25b. According to the procedure described for the preparation of (±)-**S1a** from (±)-**25a**, (±)-**25b** (4.12 mg, 0.0850 mmol) was converted into compound (±)-**S1b** (1.6 mg, 42%) with a recovery of (±)-**25b** (2.3 mg, 56%) by the reaction with $NaBH_4$ (7.42 mg, 0.196 mmol) at 0 °C for 40 min, and additional 20 min after addition of a second portion of $NaBH_4$ (22.5 mg, 0.619 mmol) at 0 °C. PTLC: (hexane/EtOAc = 2/1). All the spectral data were in agreement with those described above.



Synthesis of (±)-26a from (±)-S1a. According to the procedure described for the preparation of (±)-**23**, compound (±)-**S1a** (4.67 mg, 0.0102 mmol) was converted into compound (±)-**26a** (5.59 mg, 83%) by the reaction with TBDPSCl (30 µL, 0.12 mmol) and imidazole (7.59 mg, 0.111 mmol) in DMF (200 µL) at room temperature for 17 h. PTLC (hexane/EtOAc = 4/1 and 6/1); white solid; mp: 168–169 °C; IR (neat cm^{-1}): 3482 (NH), 1712 (C=O), 1250 (S=O), 1163 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.60–7.55 (m, 6H), 7.47–7.34 (m, 6H), 7.14 (d, J = 8.0 Hz, 2H), 5.67 (s, 1H), 4.37–4.35 (m, 1H), 4.27 (br s, 1H), 3.97–3.96 (m, 1H), 3.92 (dd, J = 9.7, 4.0 Hz, 1H), 3.80 (d, J = 12.0 Hz, 1H), 3.55 (dd, J = 9.7, 8.6 Hz, 1H), 2.62 (dd, J = 13.7, 8.6 Hz, 1H), 2.36 (s, 3H), 2.17 (dd, J = 13.7, 6.9 Hz, 1H), 1.59 (s, 3H), 1.42 (s, 9H), 1.33 (s, 3H), 1.02 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): 154.3, 143.1, 137.5, 135.6 (4C), 133.4, 133.3, 129.7 (2C), 129.5 (2C), 127.7 (2C), 127.6 (2C), 127.1 (2C), 99.7, 85.7, 80.2, 66.5, 63.2, 58.9, 57.1, 36.7, 28.5, 28.3 (3C), 26.8 (3C), 21.6, 20.5, 19.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{37}H_{50}N_2NaO_7SSi$, 717.3000; found 717.2999.

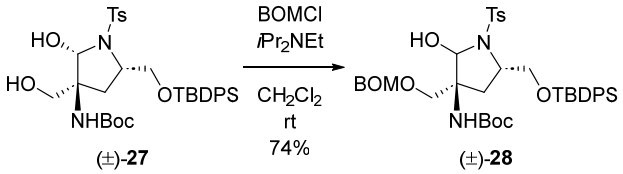


Synthesis of (±)-26b from (±)-S1b. According to the procedure described for the preparation of (±)-**23**, compound (±)-**S1b** (1.74 mg, 0.00381 mmol) was converted into compound (±)-**26b** (1.82 mg, 69%) by the reaction with TBDPSCl (10.0 µL, 0.0381 mmol) and imidazole (3.68 mg, 0.0541 mmol) in DMF (80 µL) at room temperature for 17 h. PTLC: (hexane/EtOAc = 4/1 and 6/1); white solid; mp: 143–145 °C; IR (neat cm^{-1}): 3344 (NH), 1712 (C=O), 1251 (S=O), 1162 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.68–7.66 (m, 4H), 7.58–7.57 (m, 2H), 7.46–7.41 (m, 6H), 7.19–7.17 (m, 2H), 5.81 (s, 1H), 5.11 (s, 1H), 4.50–4.48 (m, 1H), 3.98–3.96 (m, 2H), 3.69 (d, J = 11.5 Hz, 1H), 3.49–3.47 (m, 1H), 2.66 (dd, J = 13.2, 10.3 Hz, 1H), 2.40 (s, 3H), 2.23–2.13 (m, 1H), 1.62 (s, 3H), 1.38 (s, 9H), 1.16 (s, 3H), 1.08 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 154.6, 143.3, 136.0, 135.7 (2C), 135.6 (2C), 133.1, 133.0, 129.9, 129.8, 128.8 (4C), 127.8 (4C), 98.9, 86.9, 80.2, 65.4, 62.4, 57.9, 55.5, 33.5, 28.3 (4C), 27.1 (3C), 21.5, 20.3, 19.3; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{37}H_{50}N_2NaO_7SSi$, 717.3000; found 717.2996.



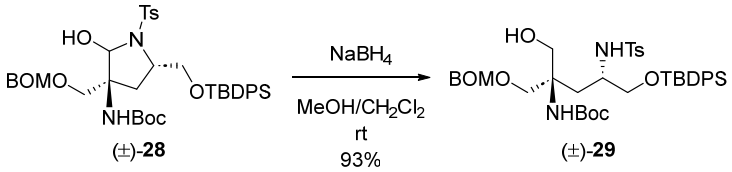
Compound (±)-27 A solution of 85:15 diastereomeric mixture of (±)-**26** (159 mg, 0.229 mmol) in AcOH (18 mL) and H_2O (2.08 mL) was stirred for 7 h at room temperature. The reaction mixture was diluted with saturated aqueous

$NaHCO_3$ and the whole was extracted with EtOAc twice. The combined organic layer was washed with saturated aqueous $NaHCO_3$ three times, brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 10 to 85% EtOAc in hexane) to give (±)-**27** (71.8 mg, 48%) as a colorless amorphous solid; IR (neat cm^{-1}): 3341 (NH and OH), 1696 (C=O), 1250 (S=O), 1164 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, J = 8.0 Hz, 2H), 7.59–7.55 (m, 4H), 7.46–7.44 (m, 2H), 7.39–7.37 (m, 4H), 7.24 (d, J = 8.0 Hz, 2H), 5.33 (d, J = 5.7 Hz, 1H), 4.38 (s, 1H), 4.01–3.99 (m, 2H), 3.87 (dd, J = 10.3, 4.9 Hz, 1H), 3.82 (dd, J = 11.7, 6.6 Hz, 1H), 3.72 (dd, J = 10.3, 2.3 Hz, 1H), 3.65–3.63 (m, 1H), 2.42–2.41 (m, 4H), 2.26–2.24 (m, 1H), 1.38 (s, 9H), 1.03 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 155.2, 143.5, 136.7, 135.6 (4C), 132.5, 132.3, 130.01, 129.96, 129.8 (2C), 127.8 (4C), 127.1 (2C), 87.8, 80.3, 66.5, 64.8, 64.2, 59.6, 32.9, 28.2 (3C), 26.8 (3C), 21.6, 19.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{34}H_{46}N_2NaO_7SSi$, 677.2687; found 677.2688.



(±)-**27** (±)-**28**

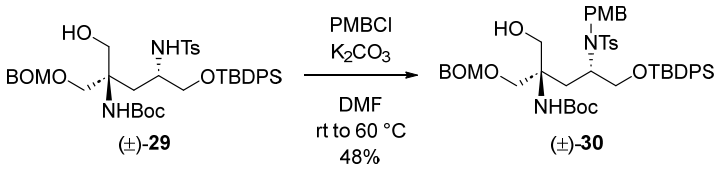
Compound (±)-28. To a solution of (±)-**27** (120 mg, 0.183 mmol) in CH_2Cl_2 (4.0 mL) were added iPr$_2$NEt (114 μL, 0.655 mmol) and BOMCl (90 μL, 0.66 mmol) in CH_2Cl_2 (0.5 mL) at room temperature under Ar. After the reaction mixture was stirred at this temperature for 10 h, a second portion of iPr$_2$NEt (114 μL, 0.655 mmol) and BOMCl (90 μL, 0.66 mmol) was added to the reaction mixture at room temperature. After being stirred at this temperature for additional 4 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 7 to 20% EtOAc in hexane) to give (±)-**28** (104 mg, 74%) as a colorless amorphous solid; IR (neat cm^{-1}): 3387 (NH and OH), 1716 (C=O), 1249 (S=O), 1163 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8.0 Hz, 2H), 7.58–7.55 (m, 4H), 7.46–7.42 (m, 2H), 7.39–7.31 (m, 8H), 7.31–7.27 (m, 1H), 7.25 (d, J = 8.6 Hz, 2H), 5.25 (d, J = 6.9 Hz, 1H), 4.77–4.71 (m, 2H), 4.60 (d, J = 11.5 Hz, 1H), 4.55 (d, J = 11.5 Hz, 1H), 4.19 (s, 1H), 4.05–4.03 (m, 1H), 4.00 (d, J = 9.7 Hz, 1H), 3.94 (dd, J = 10.6, 4.0 Hz, 1H), 3.88 (d, J = 9.7 Hz, 1H), 3.64 (dd, J = 10.6, 1.4 Hz, 1H), 3.38 (d, J = 6.9 Hz, 1H), 2.65–2.63 (m, 1H), 2.41 (s, 3H), 2.08 (dd, J = 13.5, 8.9 Hz, 1H), 1.36 (s, 9H), 1.02 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 154.6, 143.4, 137.7, 137.1, 135.7 (2C), 135.6 (2C), 132.5, 132.3, 130.1, 130.0, 129.8 (2C), 128.4 (2C), 128.1 (2C), 127.9 (2C), 127.8 (2C), 127.7, 127.1 (2C), 94.7, 87.5, 79.6, 69.2, 66.7, 65.6, 64.4, 59.7, 32.1, 28.3 (3C), 26.8 (3C), 21.6, 19.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{42}H_{54}N_2NaO_8SSi$, 797.3262; found 797.3266.



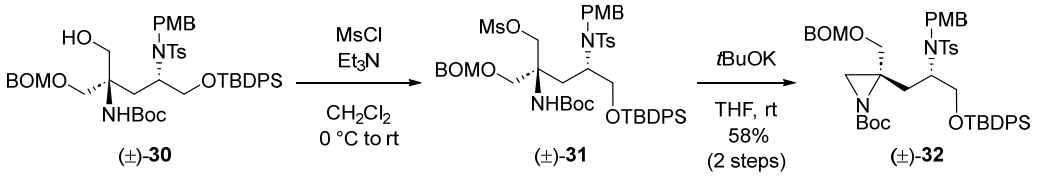
(±)-**28** (±)-**29**

Compound (±)-29. To a solution of (±)-**28** (128 mg, 0.165 mmol) in MeOH/CH_2Cl_2 (1.6/1.6 mL) was added $NaBH_4$ (21.5 mg, 0.567 mmol) at room temperature under Ar. After the reaction mixture was stirred at rt for 40 min, a

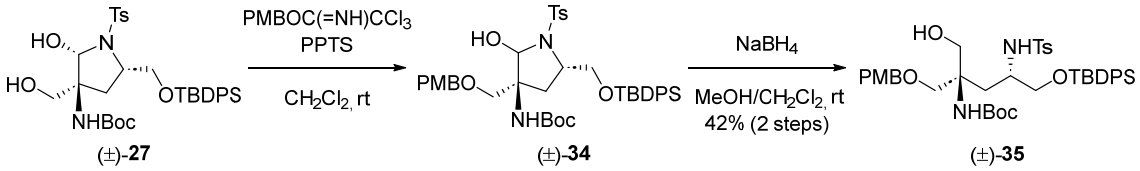
second portion of $NaBH_4$ (28.1 mg, 0.743 mmol) was added to the reaction mixture at room temperature. After the reaction mixture was stirred at this temperature for additional 1 h, a third portion of $NaBH_4$ (62.1 mg, 1.64 mmol) was added to the reaction mixture at room temperature. After being stirred at this temperature for additional 1 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 7 to 35% EtOAc in hexane) to give (±)-**29** (119 mg, 93%) as a colorless amorphous solid; IR (neat cm^{-1}): 3393 (NH and OH), 1695 (C=O), 1247 (S=O), 1160 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, J = 8.0 Hz, 2H), 7.52–7.50 (m, 2H), 7.48 (dd, J = 8.0, 1.7 Hz, 2H), 7.46–7.41 (m, 2H), 7.36–7.32 (m, 8H), 7.31–7.27 (m, 1H), 7.14 (d, J = 8.0 Hz, 2H), 5.32–5.22 (m, 1H), 5.01 (d, J = 8.0 Hz, 1H), 4.72 (s, 2H), 4.58 (s, 2H), 4.18–4.02 (m, 1H), 3.80 (d, J = 9.7 Hz, 1H), 3.70 (dd, J = 12.0, 8.0 Hz, 1H), 3.62 (dd, J = 11.5, 5.2 Hz, 1H), 3.49–3.47 (m, 2H), 3.44 (dd, J = 10.0, 3.2 Hz, 1H), 3.23 (dd, J = 9.7, 4.6 Hz, 1H), 2.36 (s, 3H), 1.97–1.96 (m, 2H), 1.41 (s, 9H), 1.02 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 156.2, 143.4, 137.6, 137.5, 135.55 (2C), 135.50 (2C), 132.8, 132.6, 129.92, 129.89, 129.7 (2C), 128.5 (2C), 127.8 (5C), 127.7 (2C), 127.0 (2C), 95.1, 80.0, 69.9, 69.7, 66.3, 66.1, 58.3, 51.3, 34.6, 28.3 (3C), 26.9 (3C), 21.5, 19.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{42}H_{56}N_2NaO_8SSi$, 799.3419; found 799.3414.



Compound (±)-30. To a suspension of K_2CO_3 (12.9 mg, 0.0936 mmol) in DMF (1.0 mL) were added PMBCl (12.0 μL, 0.0885 mmol) and (±)-**29** (57.5 mg, 0.0740 mmol) in DMF (2.0 mL) at room temperature under Ar. After being stirred at this temperature for 2 h, the mixture was warmed to 60 °C. After being stirred at 60 °C for additional 18 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 7 to 30% and 7 to 20% EtOAc in hexane) and PTLC (hexane/acetone = 3/1 and hexane/EtOAc = 2/1) to give (±)-**30** (32.5 mg, 48%) as a colorless oil; IR (neat cm^{-1}): 3387 (NH and OH), 1714 (C=O), 1247 (S=O), 1156 (S=O); ^1H NMR (500 MHz, $CDCl_3$, 55 °C): δ 7.64 (d, J = 8.0 Hz, 2H), 7.50–7.48 (m, 4H), 7.41–7.40 (m, 2H), 7.35–7.25 (m, 9H), 7.15 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.71 (d, J = 8.0 Hz, 2H), 5.15–5.04 (m, 1H), 4.61–4.56 (m, 2H), 4.51–4.48 (m, 2H), 4.40 (s, 2H), 4.11–4.02 (m, 1H), 3.83–3.73 (m, 1H), 3.74 (s, 3H), 3.67 (d, J = 9.7 Hz, 1H), 3.56–3.45 (m, 4H), 3.37 (d, J = 9.7 Hz, 1H), 2.32 (s, 3H), 1.91 (dd, J = 15.2, 5.4 Hz, 1H), 1.84 (dd, J = 15.2, 5.4 Hz, 1H), 1.33 (s, 9H), 0.97 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, 55 °C): δ 159.3, 156.0, 143.0, 138.3, 137.9, 135.7 (4C), 133.3, 133.1, 130.1 (2C), 129.8 (2C), 129.7, 129.6 (2C), 128.4 (2C), 127.9 (2C), 127.8 (2C), 127.7 (3C), 127.6 (2C), 114.0 (2C), 94.9, 79.7, 69.7, 69.4, 66.1, 65.4, 58.5, 56.2, 55.3, 48.5, 33.7, 28.3 (3C), 27.0 (3C), 21.4, 19.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{50}H_{64}N_2NaO_9SSi$, 919.3994; found 919.3992.

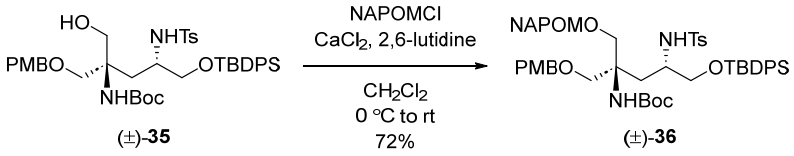


Compound (±)-32. To a mixture of (±)-**30** (30.0 mg, 0.0334 mmol) in CH_2Cl_2 (0.7 mL) and Et_3N (48 μL, 0.33 mmol) was added MsCl (26 μL, 0.34 mmol) at 0 °C under Ar. After being stirred at this temperature for 10 min, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give a crude (±)-**31**, which was used without further purification. To a solution of crude (±)-**31** in THF (0.7 mL) was added *t*BuOK (4.73 mg, 0.0422 mmol) at room temperature under Ar. After the reaction mixture was stirred at this temperature for 45 min, a second portion of *t*BuOK (7.68 mg, 0.0684 mmol) was added to the reaction mixture at room temperature. After being stirred at this temperature for additional 45 min, the reaction mixture was diluted with H_2O and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC (hexane/EtOAc = 3/1) to give (±)-**32** (17.1 mg, 58%, 2 steps) as a colorless amorphous solid; IR (neat cm^{-1}): 1717 (C=O), 1247 (S=O), 1158 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.71 (d, J = 8.6 Hz, 2H), 7.50–7.48 (m, 4H), 7.45–7.39 (m, 2H), 7.36–7.28 (m, 9H), 7.14–7.12 (m, 4H), 6.73 (d, J = 8.6 Hz, 2H), 4.64–4.56 (m, 2H), 4.54 (d, J = 11.5 Hz, 1H), 4.50 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 15.5 Hz, 1H), 4.33 (d, J = 15.5 Hz, 1H), 3.92–3.90 (m, 1H), 3.73 (s, 3H), 3.64 (dd, J = 11.2, 4.9 Hz, 1H), 3.57–3.55 (m, 1H), 3.43 (d, J = 10.9 Hz, 1H), 3.31 (d, J = 10.9 Hz, 1H), 2.33 (s, 3H), 2.11 (dd, J = 14.6, 3.7 Hz, 1H), 2.04–2.02 (m, 1H), 1.88–1.86 (m, 1H), 1.30–1.28 (m, 10H), 0.96 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 159.9, 159.0, 142.9, 138.3, 137.7, 135.6 (2C), 135.5 (2C), 133.0 (2C), 129.8, 129.7, 129.6 (5C), 128.4 (2C), 127.9 (2C), 127.7 (5C), 127.3 (2C), 113.8 (2C), 94.3, 80.7, 69.4, 68.0, 64.4, 56.8, 55.2, 48.6, 42.3, 34.1, 31.9, 27.9 (3C), 26.8 (3C), 21.5, 19.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{50}H_{62}N_2NaO_8SSi$, 901.3888; found 901.3881.

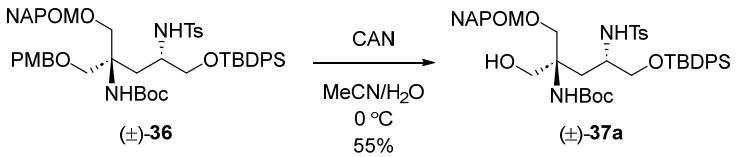


Compound (±)-35. To a stirred mixture of (±)-**27** (209 mg, 0.319 mmol) and PPTS (9.4 mg, 0.0374 mmol) in CH_2Cl_2 (1.6 mL) was added PMBOC(=NH)CCl_3 (0.400 mL, 1.93 mmol) at room temperature under Ar. After being stirred at this temperature for 10 min, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 20 to 30% EtOAc in hexane and gradient 2 to 25% EtOAc in hexane) to give (±)-**34** (162 mg), including inseparable impurities, as a white solid. According to the procedure described for the preparation of (±)-**29**, the compound (±)-**34** (72.0 mg) including inseparable impurities was converted into compound (±)-**35** (58.4 mg, 42%, 2 steps) by the reaction with $NaBH_4$ (36.8 mg, 0.155 mmol) in MeOH/CH_2Cl_2 (1.6/1.6 mL) at room temperature for 40 min.

Column chromatography: silica gel (gradient 2 to 25% EtOAc in hexane and 2 to 22% EtOAc in hexane); colorless oil; IR (neat cm^{-1}): 3419 (NH and OH), 1698 (C=O), 1250 (S=O), 1163 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, J = 8.6 Hz, 2H), 7.51–7.50 (m, 2H), 7.47–7.41 (m, 4H), 7.35–7.33 (m, 4H), 7.22 (d, J = 8.6 Hz, 2H), 7.14 (d, J = 8.6 Hz, 2H), 6.87–6.86 (m, 2H), 5.36–5.28 (m, 1H), 5.08 (d, J = 8.0 Hz, 1H), 4.47 (d, J = 11.5 Hz, 1H), 4.36 (d, J = 11.5 Hz, 1H), 4.24–4.14 (m, 1H), 3.81 (s, 3H), 3.70–3.66 (m, 2H), 3.60 (dd, J = 11.7, 4.9 Hz, 1H), 3.45–3.40 (m, 2H), 3.32 (d, J = 9.2 Hz, 1H), 3.22 (dd, J = 9.7, 4.6 Hz, 1H), 2.37 (s, 3H), 1.96–1.95 (m, 2H), 1.42 (s, 9H), 1.00 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 159.4, 156.3, 143.3, 137.8, 135.6 (2C), 135.5 (2C), 132.9, 132.7, 129.9 (2C), 129.8, 129.7 (2C), 129.5 (2C), 127.8 (2C), 127.7 (2C), 127.0 (2C), 113.9 (2C), 80.0, 73.1, 71.4, 66.6, 66.1, 58.6, 55.3, 51.4, 34.6, 28.3 (3C), 26.9 (3C), 21.6, 19.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{42}H_{57}N_2O_8SSi$, 777.3599; found 777.3594.

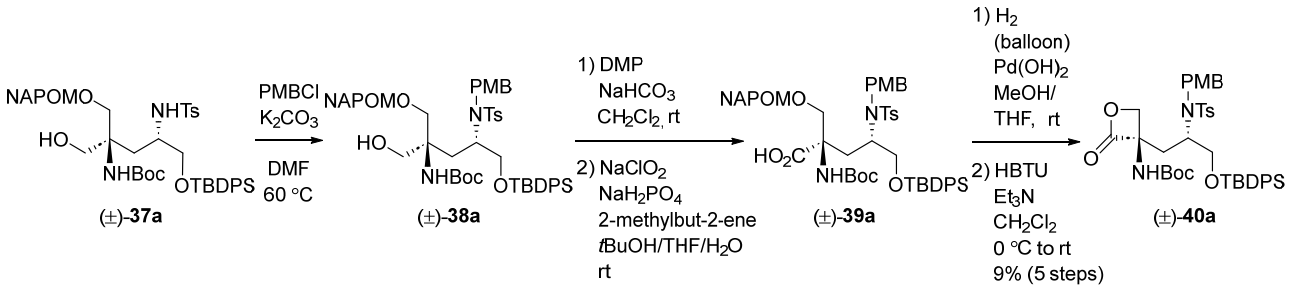


Compound (±)-36. To a mixture of (±)-**35** (61.6 mg, 0.0793 mmol) and $CaCl_2$ (18.5 mg, 0.167 mmol) in CH_2Cl_2 (0.8 mL) were added 2,6-lutidine (110 μL, 0.950 mmol) and NAPOMCl (109 mg, 0.527 mmol) at 0 °C under Ar. After being stirred at room temperature for 16 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 2 to 15% EtOAc in hexane) and PTLC (hexane/EtOAc = 3/1) to give (±)-**36** (54.1 mg, 72%) as a colorless oil; IR (neat cm^{-1}): 3369 (NH), 1716 (C=O), 1247 (S=O), 1161 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.81–7.80 (m, 3H), 7.76 (s, 1H), 7.54–7.52 (m, 6H), 7.45–7.43 (m, 5H), 7.35–7.33 (m, 4H), 7.14 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 5.30 (d, J = 6.9 Hz, 1H), 5.12–5.03 (m, 1H), 4.72 (s, 2H), 4.70 (s, 2H), 4.34 (d, J = 11.5 Hz, 1H), 4.29 (d, J = 11.5 Hz, 1H), 3.75–3.74 (m, 5H), 3.53–3.49 (m, 3H), 3.46–3.44 (m, 1H), 3.36 (dd, J = 10.0, 6.0 Hz, 1H), 2.34 (s, 3H), 2.21 (dd, J = 15.2, 8.3 Hz, 1H), 2.05 (dd, J = 15.2, 3.4 Hz, 1H), 1.42 (s, 9H), 1.01 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 159.2, 155.1, 143.0, 137.8, 135.6, 135.5, 135.1, 133.3, 133.0, 132.9, 129.9, 129.8, 129.4, 129.3, 128.1, 127.9, 127.7, 127.6, 127.1, 126.7, 126.0, 125.9, 113.8, 94.7, 79.5, 73.0, 70.4, 69.3, 69.1, 66.1, 57.2, 55.2, 51.4, 34.2, 28.4 (3C), 26.9 (3C), 21.5, 19.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{54}H_{67}N_2O_9SSi$, 947.4331; found 947.4326.



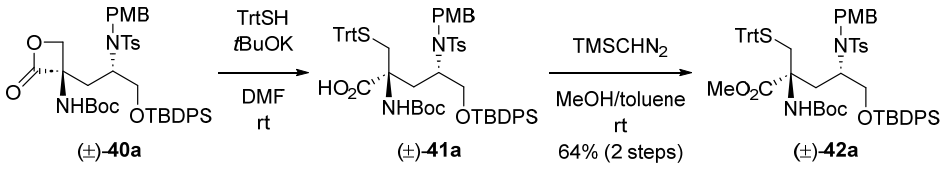
Compound (±)-37a. To a solution of (±)-**36** (49.3 mg, 0.0520 mmol) in MeCN/H_2O (0.8/0.2 mL) was added CAN (116 mg, 0.212 mmol) at 0 °C. After being stirred at this temperature for 1 h, the reaction mixture was diluted with brine and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried

over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 2 to 30% EtOAc in hexane) to give (±)-**37a** (23.8 mg, 55%) as a colorless oil; IR (neat cm^{-1}): 3413 (NH and OH), 1689 (C=O), 1251 (S=O), 1160 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.86–7.80 (m, 3H), 7.78 (s, 1H), 7.60 (d, J = 8.6 Hz, 2H), 7.55–7.40 (m, 9H), 7.36–7.32 (m, 4H), 7.10 (d, J = 8.0 Hz, 2H), 6.06–5.93 (m, 1H), 5.47–5.37 (m, 1H), 4.85–4.74 (m, 1H), 4.75–4.70 (m, 4H), 3.61–3.59 (m, 3H), 3.39–3.37 (m, 1H), 3.33–3.31 (m, 3H), 2.34 (s, 3H), 2.17 (dd, J = 14.9, 9.7 Hz, 1H), 2.01 (dd, J = 14.9, 2.9 Hz, 1H), 1.43 (s, 9H), 1.02 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 156.6, 143.1, 137.8, 135.55, 135.51, 134.8, 133.2, 133.04, 133.00, 132.95, 129.83, 129.80, 129.5, 128.3, 127.9, 127.73, 127.68, 127.0, 126.6, 126.2, 126.0, 125.7, 95.0, 80.3, 69.9, 69.7, 66.3, 65.6, 58.6, 51.5, 33.5, 28.3 (3C), 26.9 (3C), 21.5, 19.2; HRMS (ESI-TOF) *m/z*: $[M + Na]^+$ calcd for $C_{46}H_{58}N_2NaO_8SSi$, 849.3575; found 849.3569.



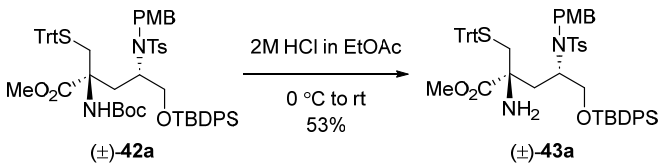
Compound (±)-40a. To a suspension of (±)-**37a** (13.5 mg, 0.0163 mmol) and K_2CO_3 (7.1 mg, 0.051 mmol) in DMF (350 μL) was added PMBCl (5.0 μL, 0.037 mmol) at room temperature under Ar. After being stirred at 60 °C for 17.5 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC (hexane/EtOAc = 4/1 and hexane/EtOAc = 2/1) to give (±)-**38a** (9.0 mg), including inseparable impurities, as a colorless amorphous solid. To a mixture of (±)-**38a** (9.0 mg) including inseparable impurities and $NaHCO_3$ (9.35 mg, 0.111 mmol) in CH_2Cl_2 (0.4 mL) was added DMP (17.9 mg, 0.0422 mmol) at room temperature under Ar. After the reaction mixture was stirred at this temperature for 1.5 h, the additional CH_2Cl_2 (0.4 mL) was added to the reaction mixture at room temperature. After being stirred at this temperature for additional 1 h, the reaction mixture was diluted with saturated aqueous $Na_2S_2O_3$ and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was filtered through a short silica gel column eluting with EtOAc to give the corresponding aldehyde. To a mixture of crude aldehyde and 2-methylbut-2-ene (61.0 μL, 0.574 mmol) in *t*BuOH (0.6 mL) were added $NaClO_4$ (9.5 mg, 0.105 mmol) and NaH_2PO_4 (16.0 mg, 0.133 mmol) at room temperature. After being stirred at this temperature for 1.5 h, the reaction mixture was diluted with brine and the whole was extracted with EtOAc twice. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was filtered through a short silica gel column eluting with $CHCl_3$/MeOH = 20/1 to give a crude (±)-**39a**. To a solution of crude (±)-**39a** in MeOH/THF (0.25/0.25 mL) was added $Pd(OH)_2$ (13.1 mg, 0.0933 mmol) at room temperature, and the mixture was flushed with H_2 gas (1 atm). After the reaction mixture was stirred at this temperature for 1 h, a second portion of $Pd(OH)_2$ (28.6 mg, 0.204 mmol) was added to the reaction mixture at room

temperature. After being stirred at this temperature for additional 1.5 h, the reaction mixture was filtered through celite with MeOH. The filtrate was concentrated *in vacuo* to give the corresponding carboxylic acid as a colorless amorphous solid. To a stirred solution of crude carboxylic acid in CH_2Cl_2 (380 μL) were added HBTU (18.5 mg, 0.0488 mmol) and Et_3N (14 μL, 0.097 mmol) at 0 °C under Ar. After the reaction mixture was stirred at room temperature for 17.5 h, the additional CH_2Cl_2 (0.6 mL) was added to the reaction mixture at room temperature. After being stirred at this temperature for additional 3.5 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with CH_2Cl_2 twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on PTLC (hexane/EtOAc = 3/3) to give (±)-**40a** (1.1 mg, 9%, 5 steps) as a colorless amorphous solid; IR (neat cm^{-1}): 3363 (NH), 1833 (C=O), 1716 (C=O), 1248 (S=O), 1155 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.69 (d, J = 8.0 Hz, 2H), 7.51–7.42 (m, 6H), 7.39–7.36 (m, 4H), 7.18 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.70 (d, J = 8.6 Hz, 2H), 6.18–6.08 (m, 1H), 4.50–4.47 (m, 2H), 4.04–4.01 (m, 2H), 3.85–3.83 (m, 1H), 3.75 (s, 3H), 3.67–3.65 (m, 1H), 3.44 (dd, J = 10.6, 7.7 Hz, 1H), 2.37 (s, 3H), 2.21–2.19 (m, 1H), 1.72–1.69 (m, 1H), 1.46 (s, 9H), 0.95 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.0, 159.2, 154.5, 143.6, 137.1, 135.7 (2C), 135.5 (2C), 132.4, 132.1, 130.0, 129.9, 129.8 (4C), 128.6, 127.8 (4C), 127.2 (2C), 113.9 (2C), 80.9, 70.5, 69.0, 63.7, 55.5, 55.1, 48.1, 36.9, 28.2 (3C), 26.8 (3C), 21.4, 18.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{42}H_{52}N_2NaO_8SSi$, 795.3106; found, 795.3110.



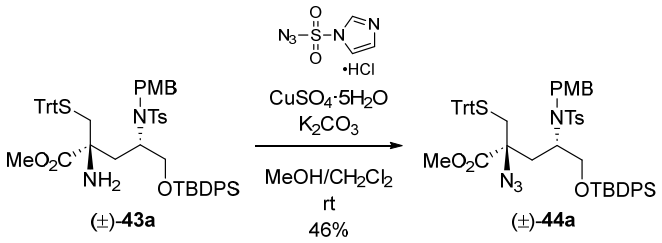
Compound (±)-42a. To a mixture of TrtSH (75.5 mg, 0.273 mmol) and *t*BuOK (38.0 mg, 0.287 mmol) in DMF (0.4 mL) was added (±)-**40a** (69.0 mg, 0.0893 mmol) in DMF (0.5 mL) at 0 °C under Ar. After being stirred at room temperature for 1 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc/hexane twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 0 to 4% MeOH in $CHCl_3$) to give (±)-**41a** (79.2 mg, *ca.* 85%), including impurities as a colorless amorphous solid. To a stirred solution of (±)-**41a** (79.2 mg, *ca.* 0.0755 mmol) in MeOH/toluene (0.9/0.9 mL) was added $TMSCHN_2$ (0.70 mL, 0.42 mmol) at room temperature under Ar. After being stirred at this temperature for 3.5 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 0% to 15% EtOAc in hexane) and PTLC (hexane/EtOAc = 4/1) to give (±)-**42a** (61.2 mg, 64%, 2 steps) as a colorless amorphous solid; IR (neat cm^{-1}): 3444 (NH), 1741 (C=O), 1708 (C=O), 1251 (S=O), 1157 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.72–7.70 (m, 2H), 7.38–7.31 (m, 17H), 7.24–7.22 (m, 5H), 7.18–7.17 (m, 5H), 7.09–7.08 (m, 2H), 6.61–6.60 (m, 2H), 5.55–5.48 (m, 1H), 4.27–4.23 (m, 2H), 3.86–3.84 (m, 1H), 3.66 (s, 3H), 3.39–3.37 (m, 1H), 3.32 (s, 3H), 3.16 (d, J = 10.9 Hz, 1H), 2.86–2.84 (m, 1H), 2.51–2.49 (m, 1H), 2.38 (s, 3H), 2.33 (d, J = 10.9 Hz, 1H), 1.67–1.65 (m, 1H), 1.48 (s, 9H), 0.91 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.0, 159.0, 154.2, 144.6, 142.8, 138.2, 135.5, 133.01, 132.98, 130.1, 129.7, 129.6, 129.49, 129.46, 127.8, 127.7, 127.60, 127.57, 126.6, 113.7,

79.4, 65.7, 65.0, 61.8, 56.9, 55.1, 52.7, 47.3, 37.9, 35.7, 28.4 (3C), 26.7 (3C), 21.5, 19.0; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{62}H_{70}N_2NaO_8S_2Si$, 1085.4235; found 1085.4234.



(±)-**42a** (±)-**43a**

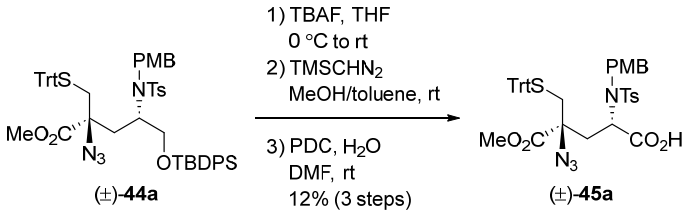
Compound (±)-43a. To a solution of (±)-**42a** (1.91 g, 1.80 mmol) in EtOAc (20 mL) was added 4M HCl in EtOAc (20 mL) at 0 °C. After being stirred at room temperature for 1.5 h, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 2 to 25% EtOAc in hexane) to give (±)-**43a** (917 mg, 53%) as a colorless amorphous solid; IR (neat cm^{-1}): 3383 (NH), 1736 (C=O), 1248 (S=O), 1177 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, J = 8.6 Hz, 2H), 7.46–7.31 (m, 16H), 7.29–7.22 (m, 6H), 7.21–7.17 (m, 3H), 7.12 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.6 Hz, 2H), 4.31 (d, J = 15.5 Hz, 1H), 4.25 (d, J = 15.5 Hz, 1H), 3.96–3.94 (m, 1H), 3.72 (s, 3H), 3.43–3.41 (m, 1H), 3.36 (s, 3H), 3.21–3.19 (m, 1H), 2.42 (d, J = 11.5 Hz, 1H), 2.33 (s, 3H), 2.25 (d, J = 11.5 Hz, 1H), 1.79–1.71 (m, 2H), 0.93 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 175.1, 159.0, 144.5, 142.8, 138.2, 135.6, 133.1, 133.0, 130.0, 129.70, 129.66, 129.5, 129.3, 127.9, 127.7, 127.4, 126.7, 113.7, 66.5, 64.8, 60.4, 56.8, 55.2, 52.2, 48.7, 42.7, 39.9, 26.7 (3C), 21.5, 19.0; HRMS (ESI-TOF) *m*/*z*: $[M + H]^+$ calcd for $C_{57}H_{63}N_2O_6S_2Si$, 963.3891; found 963.3888.



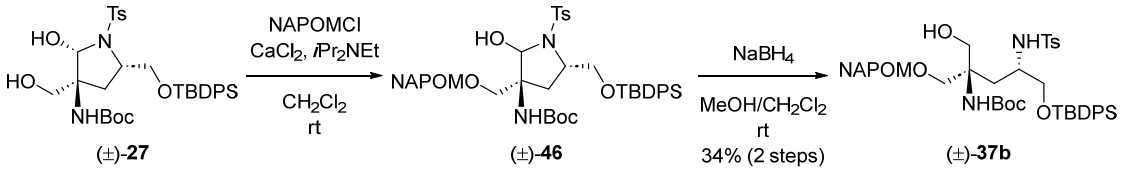
(±)-**43a** (±)-**44a**

Compound (±)-44a. To a mixture of (±)-**43a** (281 mg, 0.292 mmol), K_2CO_3 (366 mg, 2.65 mmol) and $CuSO_4 \cdot 5H_2O$ (38.0 mg, 0.0877 mmol) in MeOH (3.0 mL) and CH_2Cl_2 (3.0 mL) was added 1*H*-imidazole-1-sulfonyl azide hydrochloride salt (373 mg, 1.78 mmol). After being stirred at room temperature for 19.5 h, the reaction mixture was diluted with H_2O and acidified with saturated aqueous $KHSO_4$, and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 2 to 25% EtOAc in hexane) to give (±)-**44a** (134 mg, 46%) as a colorless amorphous solid; IR (neat cm^{-1}): 2116 (N=N=N), 1742 (C=O), 1247 (S=O), 1155 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, J = 8.0 Hz, 2H), 7.47–7.45 (m, 4H), 7.42–7.37 (m, 8H), 7.33–7.31 (m, 4H), 7.28–7.24 (m, 6H), 7.21–7.15 (m, 5H), 7.10 (d, J = 8.6 Hz, 2H), 6.65 (d, J = 8.6 Hz, 2H), 4.34 (d, J = 15.5 Hz, 1H), 4.21 (d, J = 15.5 Hz, 1H), 3.91–3.87 (m, 1H), 3.72 (s, 3H), 3.47–3.44 (m, 1H), 3.42 (s, 3H), 3.15–3.13 (m, 1H), 2.58 (d, J = 12.0 Hz, 1H), 2.43 (d, J = 12.0 Hz, 1H), 2.33 (s, 3H), 2.01–1.99 (m, 1H), 1.84–1.82 (m, 1H), 0.95

(s, 9H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 170.7, 159.0, 144.0, 142.7, 138.1, 135.5, 133.1, 132.9, 130.0, 129.64, 129.62, 129.4, 129.3, 128.0, 127.6, 127.3, 126.9, 113.6, 67.9, 66.9, 64.9, 56.8, 55.2, 52.8, 47.9, 39.4, 35.7, 26.7 (3C), 21.4, 19.0; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{57}H_{60}N_4NaO_6S_2Si$, 1011.3616; found 1011.3607.

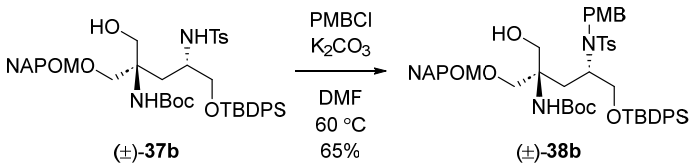


Compound (±)-45a. To a solution of (±)-**44a** (34.8 mg, 0.0352 mmol) in THF (0.4 mL) was added a 1 M solution of TBAF in THF (0.7 mL, 0.7 mmol) at 0 °C under Ar. After being stirred at room temperature for 2 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and acidified with saturated aqueous $KHSO_4$. The whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give the corresponding carboxylic acid. To a solution of the crude carboxylic acid in MeOH/toluene (0.4/0.4 mL) was added $TMSCHN_2$ (290 μL, 0.176 mmol) at room temperature under Ar. After being stirred at this temperature for 30 min, the reaction mixture was filtered through a short silica gel column eluting with EtOAc and concentrated *in vacuo* to give the corresponding alcohol. To a solution of crude alcohol in H_2O/DMF (0.04/0.9 mL) was added PDC (399 mg, 1.06 mmol) at room temperature. After being stirred at this temperature for 12.5 h, the reaction mixture was diluted with saturated aqueous $KHSO_4$ and the whole was extracted with EtOAc twice. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC ($CHCl_3$/MeOH = 20/1) to give (±)-**45a** (3.2 mg, 12%, 3 steps) as a white amorphous solid; IR (neat cm^{-1}): 2120 (N=N=N), 1745 (C=O), 1249 (S=O), 1158 (S=O); ^1H NMR ($CDCl_3$): δ 7.72 (d, J = 8.6 Hz, 2H), 7.40–7.38 (m, 7H), 7.29–7.24 (m, 10H), 7.11 (d, J = 8.6 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 4.35–4.34 (m, 1H), 4.26 (d, J = 15.5 Hz, 1H), 4.20 (d, J = 15.5 Hz, 1H), 3.73 (s, 3H), 3.62 (s, 3H), 2.70 (d, J = 12.6 Hz, 1H), 2.45 (d, J = 12.6 Hz, 1H), 2.39 (dd, J = 14.3, 7.4 Hz, 1H), 2.34 (s, 3H), 1.88–1.85 (m, 1H); $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): δ 173.1, 170.1, 159.4, 144.0, 143.9, 136.4, 130.1, 129.6, 129.5, 128.1, 127.9, 127.2, 126.9, 113.8, 67.8, 67.0, 55.2, 55.1, 53.1, 49.6, 39.5, 37.2, 21.5; HRMS (ESI-TOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{41}H_{40}N_4NaO_7S_2$,787.2231; found 787.2231.

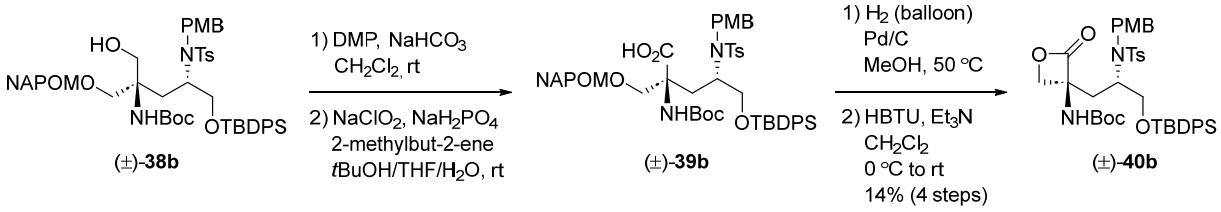


Compound (±)-37b. To a mixture of (±)-**27** (103 mg, 0.156 mmol) and $CaCl_2$ (86.9 mg, 0.783 mmol) in CH_2Cl_2 (1.6 mL) were added *i*Pr_2NEt (270 μL, 1.59 mmol) and NAPOMCl (165 mg, 0.796 mmol) at 0 °C under Ar. After being stirred at room temperature for 16 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 0

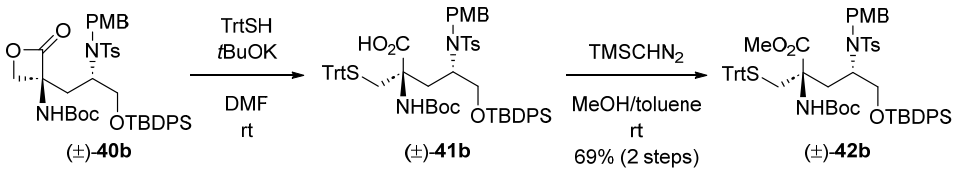
to 25% EtOAc in hexane) to give (±)-**46** (60.1 mg) including inseparable impurities, as a colorless amorphous solid. According to the procedure described for the preparation of (±)-**29**, compound (±)-**46** (60.1 mg) including inseparable impurities was converted into compound (±)-**37b** (43.7 mg, 34%, 2 steps) by the reaction with $NaBH_4$ (62.5 mg, 1.65 mmol) in $MeOH/CH_2Cl_2$ (0.7/0.7 mL) at room temperature for 40 min. Column chromatography: silica gel (gradient 0 to 25% EtOAc in hexane); colorless oil; IR (neat cm^{-1}): 3392 (NH and OH), 1690 (C=O), 1250 (S=O), 1162 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.82–7.80 (m, 4H), 7.60–7.58 (m, 2H), 7.52–7.40 (m, 9H), 7.35–7.34 (m, 4H), 7.12–7.10 (m, 2H), 5.38–5.27 (m, 1H), 5.01 (d, J = 8.0 Hz, 1H), 4.78–4.74 (m, 4H), 4.18–4.07 (m, 1H), 3.85 (d, J = 9.7 Hz, 1H), 3.72 (dd, J = 12.0, 8.0 Hz, 1H), 3.64 (dd, J = 12.0, 5.2 Hz, 1H), 3.52 (d, J = 9.7 Hz, 1H), 3.50–3.49 (m, 1H), 3.44 (dd, J = 10.0, 3.2 Hz, 1H), 3.23 (dd, J = 10.0, 4.9 Hz, 1H), 2.34 (s, 3H), 1.98–1.97 (m, 2H), 1.41 (s, 9H), 1.01 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 156.2, 143.4, 137.6, 135.55, 135.50, 135.0, 133.2, 133.0, 132.8, 132.6, 129.9, 129.7, 128.2, 127.9, 127.78, 127.75, 127.7, 127.0, 126.6, 126.2, 126.0, 125.8, 95.0, 80.0, 69.9, 69.6, 66.3, 66.1, 58.4, 51.3, 34.6, 28.3 (3C), 26.9 (3C), 21.5, 19.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{46}H_{59}N_2O_8SSi$, 827.3756; found 827.3755.



Compound (±)-38b. According to the procedure described for the preparation of (±)-**38a**, (±)-**37b** (29.2 mg, 0.0353 mmol) was converted into (±)-**38b** (21.9 mg, 65%) by the reaction with PMBCl (10.0 μL, 0.0738 mmol) and K_2CO_3 (19.6 mg, 0.142 mmol) in DMF (1.0 mL) at 60 °C for 7.5 h. Column chromatography: silica gel (gradient 6 to 25% EtOAc in hexane) and PTLC (hexane/EtOAc = 2/1): colorless amorphous solid; IR (neat cm^{-1}): 3418 (NH and OH), 1698 (C=O), 1247 (S=O), 1158 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.83–7.80 (m, 3H), 7.76 (s, 1H), 7.65 (d, J = 8.0 Hz, 2H), 7.50–7.45 (m, 6H), 7.42–7.41 (m, 3H), 7.35–7.33 (m, 4H), 7.17 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.73 (d, J = 8.6 Hz, 2H), 5.26–5.16 (m, 1H), 4.67–4.59 (m, 4H), 4.43 (d, J = 15.5 Hz, 1H), 4.37 (d, J = 15.5 Hz, 1H), 4.11–4.09 (m, 1H), 4.05–4.03 (m, 1H), 3.75–3.73 (m, 4H), 3.53–3.47 (m, 4H), 3.35 (d, J = 9.7 Hz, 1H), 2.31 (s, 3H), 1.86–1.84 (m, 1H), 1.81–1.79 (m, 1H), 1.33 (s, 9H), 0.96 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 159.1, 156.0, 143.1, 137.8, 135.6, 135.1, 133.3, 133.1, 133.0, 132.8, 130.0, 129.9, 129.8, 129.6, 129.5, 128.2, 127.9, 127.8, 127.72, 127.66, 127.4, 126.7, 126.1, 125.9, 113.8, 94.6, 79.7, 69.4, 68.7, 66.2, 64.9, 58.4, 55.9, 55.2, 48.2, 33.5, 28.2 (3C), 26.8 (3C), 21.5, 19.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{54}H_{66}N_2NaO_9SSi$, 969.4151; found 969.4155.

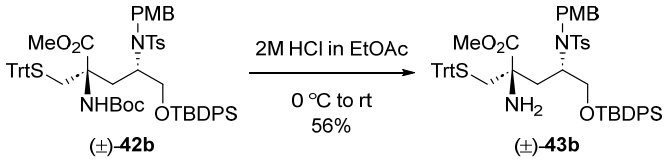


Compound (±)-40b. To a mixture of (±)-**38b** (19.7 mg, 0.0208 mmol) and $NaHCO_3$ (10.0 mg, 0.119 mmol) in CH_2Cl_2 (1.0 mL) was added DMP (18.2 mg, 0.0429 mmol) at room temperature under Ar. After being stirred at this temperature for 3 h, the reaction mixture was diluted with saturated aqueous $Na_2S_2O_3$ and the whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 2 to 15% EtOAc in hexane) to give the corresponding aldehyde (15.9 mg) including inseparable impurities, as a colorless amorphous solid. To a mixture of the crude aldehyde (15.9 mg) including inseparable impurities and 2-methylbut-2-ene (107 μL, 1.53 mmol) in *t*BuOH (0.8 mL) were added $NaClO_4$ (19.3 mg, 0.213 mmol) and NaH_2PO_4 (16.0 mg, 0.168 mmol) at room temperature. After being stirred at this temperature for 3.5 h, the reaction mixture was diluted with brine and the whole was extracted with EtOAc twice. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 1 to 10% MeOH in $CHCl_3$) to give (±)-**39b** (16.6 mg) including inseparable impurities, as a colorless amorphous solid. To a solution of (±)-**39b** (16.6 mg) including inseparable impurities in MeOH (0.8 mL) was added Pd/C (20.1 mg, 0.189 mmol) at room temperature, and the mixture was flushed with H_2 gas (1 atm). After being stirred at 50 °C for 3.5 h, the reaction mixture was filtered through celite with MeOH and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 7 to 17% MeOH in $CHCl_3$) to give the corresponding carboxylic acid (9.96 mg) including inseparable impurities, as a colorless amorphous solid. According to the procedure described for the preparation of (±)-**40a**, the carboxylic acid (9.96 mg) including inseparable impurities was converted into (±)-**40b** (2.2 mg, 14%, 4 steps) by the reaction with HBTU (11.8 mg, 0.0311 mmol) and Et_3N (20.0 μL, 0.138 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C to room temperature for 14 h, and the additional 13.5 h after addition of a second portion of HBTU (21.8 mg, 0.0575 mmol) and Et_3N (20.0 μL, 0.138 mmol) at room temperature. PTLC (hexane/EtOAc = 3/1): colorless amorphous solid; IR (neat cm^{-1}): 3343 (NH), 1834 (C=O), 1716 (C=O), 1249 (S=O), 1155 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, J = 8.0 Hz, 2H), 7.49–7.46 (m, 6H), 7.39–7.38 (m, 4H), 7.20 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.6 Hz, 2H), 6.74 (d, J = 8.6 Hz, 2H), 5.79–5.68 (m, 1H), 4.42–4.32 (m, 1H), 4.27 (d, J = 14.9 Hz, 1H), 4.19 (d, J = 14.9 Hz, 1H), 3.85–3.84 (m, 1H), 3.78–3.75 (m, 4H), 3.61–3.59 (m, 1H), 3.51–3.49 (m, 1H), 2.38 (s, 3H), 2.27–2.23 (m, 1H), 2.07–2.05 (m, 1H), 1.43 (s, 9H), 0.97 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.3, 159.4, 154.3, 143.6, 137.4, 135.5 (2C), 135.4 (2C), 132.3, 132.2, 130.1 (3C), 130.0, 129.8 (2C), 128.0, 127.9 (4C), 127.2 (2C), 114.1 (2C), 80.9, 69.8, 69.2, 64.5, 56.8, 55.1, 50.0, 35.5, 28.2 (3C), 26.8 (3C), 21.5, 18.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{42}H_{52}N_2NaO_8SSi$, 795.3106; found 795.3103.



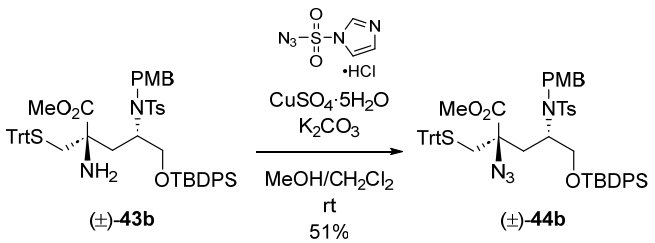
Compound (±)-42b. According to the procedure described for the preparation of (±)-**41a**, (±)-**40b** (75.4 mg, 0.0975 mmol) was converted into crude (±)-**41b** (88.9 mg) including impurities, by the reaction with TrtSH (85.0 mg, 0.308 mmol) and *t*BuOK (41.5 mg, 0.314 mmol) in DMF (1.0 mL) at 0 °C to room temperature for 1 h. Column chromatography: silica gel (gradient 0 to 4% MeOH in $CHCl_3$); colorless amorphous solid. According to the

procedure described for the preparation of (±)-**42a**, (±)-**41b** (88.9 mg) including impurities was converted into (±)-**42b** (72.0 mg, 69%, 2 steps) by the reaction with $TMSCHN_2$ (0.8 mL, 0.48 mmol) in MeOH/toluene (1.0/1.0 mL) at room temperature for 3.5 h. Column chromatography: silica gel (gradient 0 to 15% EtOAc in hexane twice) and PTLC (hexane/EtOAc = 5/1); colorless amorphous solid; IR (neat cm^{-1}): 3411 (NH), 1715 (C=O), 1682 (C=O), 1251 (S=O), 1158 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.51–7.50 (m, 4H), 7.40–7.32 (m, 14H), 7.25–7.23 (m, 6H), 7.19–7.18 (m, 3H), 7.02–7.01 (m, 4H), 6.63 (d, J = 8.6 Hz, 2H), 5.55 (s, 1H), 4.21 (d, J = 15.5 Hz, 1H), 4.09 (d, J = 15.5 Hz, 1H), 3.89–3.86 (m, 1H), 3.72–3.70 (m, 6H), 3.50–3.48 (m, 1H), 3.37–3.35 (m, 1H), 3.00 (d, J = 10.9 Hz, 1H), 2.42–2.40 (m, 1H), 2.31–2.29 (m, 4H), 1.88–1.86 (m, 1H), 1.22 (s, 9H), 0.90 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 172.1, 158.9, 153.7, 144.5, 142.6, 138.4, 135.5, 132.9, 132.8, 129.9, 129.7, 129.6, 129.5, 129.3, 127.8, 127.7, 127.6, 127.4, 126.6, 113.6, 79.4, 65.6, 64.4, 61.3, 56.7, 55.1, 53.1, 47.8, 37.8, 37.5, 28.1 (3C), 26.7 (3C), 21.4, 18.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{62}H_{70}N_2NaO_8S_2Si$, 1085.4235; found 1085.4238.



(±)-**42b** (±)-**43b**

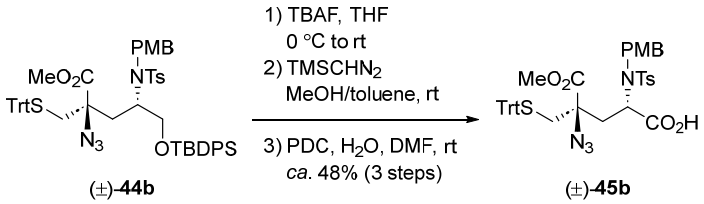
Compound (±)-43b. According to the procedure described for the preparation of (±)-**43a**, (±)-**42b** (1.10 g, 1.03 mmol) was converted into (±)-**43b** (557 mg, 56%) by the reaction with 4M HCl in EtOAc (10 mL) and EtOAc (10 mL) at room temperature for 15.5 h. Column chromatography: silica gel (gradient 2 to 25% EtOAc in hexane): colorless amorphous solid; IR (neat cm^{-1}): 3382 (NH), 1736 (C=O), 1249 (S=O), 1156 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.50–7.43 (m, 6H), 7.43–7.33 (m, 8H), 7.34–7.28 (m, 4H), 7.28–7.23 (m, 6H), 7.22–7.18 (m, 3H), 7.05 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.6 Hz, 2H), 6.63 (d, J = 8.6 Hz, 2H), 4.27 (d, J = 15.5 Hz, 1H), 4.21 (d, J = 15.5 Hz, 1H), 3.93–3.91 (m, 1H), 3.73–3.72 (m, 6H), 3.53–3.51 (m, 1H), 3.39–3.37 (m, 1H), 2.54 (d, J = 11.5 Hz, 1H), 2.33 (s, 3H), 2.19 (d, J = 11.5 Hz, 1H), 2.05–2.04 (m, 1H), 1.67–1.65 (m, 1H), 0.92 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): 175.1, 158.9, 144.5, 142.6, 138.5, 135.6, 133.0, 130.1, 129.7, 129.6, 129.3, 129.1, 127.9, 127.7, 127.3, 126.7, 113.6, 66.5, 65.7, 59.8, 56.8, 55.2, 52.6, 48.6, 42.7, 40.7, 26.8 (3C), 21.5, 19.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{57}H_{63}N_2NaO_8S_2Si$, 963.3891; found 963.3889.



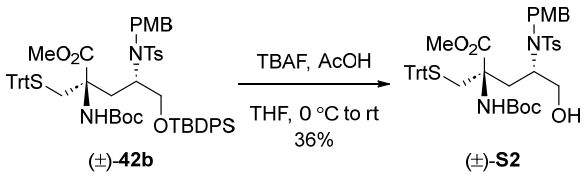
(±)-**43b** (±)-**44b**

Compound (±)-44b. According to the procedure described for the preparation of (±)-**44a**, (±)-**43b** (85.4 mg, 0.0887 mmol) was converted into (±)-**44b** (44.3 mg, 51%) by the reaction with K_2CO_3 (110 mg, 0.532 mmol), $CuSO_4 \cdot 5H_2O$ (2.9 mg, 0.0182 mmol) and 1*H*-imidazole-1-sulfonyl azide hydrochloride salt (130 mg, 0.619 mmol) in $MeOH/CH_2Cl_2$ (900/360 μL). Column chromatography: silica gel (gradient 2 to 15% EtOAc in hexane): colorless

amorphous solid; IR (neat cm^{-1}): 2119 (N=N=N), 1745 (C=O), 1248 (S=O), 1158 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, J = 8.6 Hz, 2H), 7.50–7.49 (m, 4H), 7.44–7.39 (m, 3H), 7.36–7.33 (m, 11H), 7.28–7.25 (m, 4H), 7.22–7.19 (m, 3H), 7.08 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.6 Hz, 2H), 4.38 (d, J = 15.5 Hz, 1H), 4.22 (d, J = 15.5 Hz, 1H), 3.90–3.88 (m, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.61 (dd, J = 10.9, 5.2 Hz, 1H), 3.42 (dd, J = 10.9, 8.0 Hz, 1H), 2.53 (d, J = 11.5 Hz, 1H), 2.34–2.33 (m, 4H), 1.97–1.95 (m, 1H), 1.82–1.80 (m, 1H), 0.92 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): 170.5, 159.0, 144.0, 142.8, 138.3, 135.63, 135.55, 133.0, 132.9, 129.8, 129.73, 129.67, 129.5, 129.4, 128.0, 127.7, 127.6, 127.3, 126.8, 113.7, 67.8, 66.7, 64.5, 56.6, 55.2, 53.2, 39.5, 38.0, 26.7 (3C), 21.5, 19.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{57}H_{60}N_4NaO_6S_2Si$, 1011.3616; found 1011.3612.

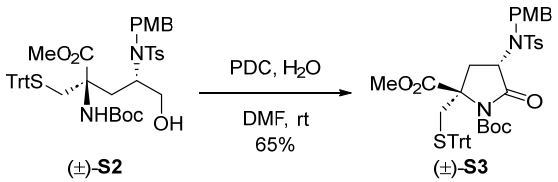


Compound (±)-45b. To a solution of (±)-**44b** (19.3 mg, 0.0199 mmol) in THF (0.2 mL) was added a 1 M solution of TBAF in THF (0.2 mL, 0.2 mmol) at 0 °C under Ar. After being stirred at room temperature for 4 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and saturated aqueous $KHSO_4$ and the whole was extracted with EtOAc/hexane twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give the corresponding carboxylic acid. To a solution of crude carboxylic acid in MeOH/toluene (0.3/0.3 mL) was added $TMSCHN_2$ (160 μL, 0.0975 mmol) at room temperature under Ar. After being stirred at this temperature for 4 h, the reaction mixture was filtered through a short silica gel column eluting with EtOAc and concentrated *in vacuo* to give the corresponding alcohol. To a solution of crude alcohol in H_2O/DMF (0.02/0.5 mL) was added PDC (222 mg, 0.591 mmol) at room temperature. After being stirred at this temperature for 12.5 h, the reaction mixture was diluted with saturated aqueous $KHSO_4$ and the whole was extracted with EtOAc twice. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by PTLC ($CHCl_3$/MeOH = 20/1) to give (±)-**45b** (*ca*. 7.1 mg containing a small amount of impurities, *ca*. 48%, 3 steps) as a white amorphous solid; IR (neat cm^{-1}): 2119 (N=N=N), 1745 (C=O), 1248 (S=O), 1159 (S=O); ^1H NMR (600 MHz, $CDCl_3$): δ 7.65 (d, J = 8.0 Hz, 2H), 7.37–7.36 (m, 7H), 7.29–7.28 (m, 5H), 7.22–7.21 (m, 5H), 7.11 (d, J = 8.6 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 4.42 (d, J = 15.5 Hz, 1H), 4.30–4.29 (m, 1H), 4.12 (d, J = 15.5 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 2.57 (d, J = 12.0 Hz, 1H), 2.46–2.43 (m, 1H), 2.39 (s, 3H), 2.28 (d, J = 12.0 Hz, 1H), 2.00–1.98 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.8, 170.1, 159.4, 143.9, 143.8, 136.5, 130.1, 130.0, 129.5, 129.4, 128.0, 127.8, 127.4, 126.9, 113.8, 67.6, 66.9, 55.3, 55.2, 53.3, 49.4, 38.7, 37.8, 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{41}H_{40}N_4NaO_7S_2$, 787.2231; found 787.2237.



(±)-**42b** (±)-**S2**

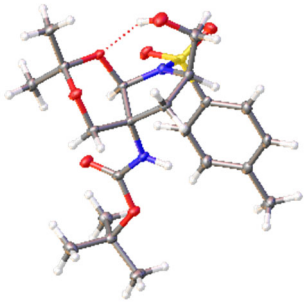
Compound (±)-S2. To a solution of (±)-**42b** (1.08 g, 1.02 mmol) in AcOH/THF (5.8/10 mL) was added a 1 M solution of TBAF in THF (20 mL, 20 mmol) at 0 °C under Ar. After the reaction mixture was stirred at room temperature for 19 h, a second portion of AcOH (5.8 mL) and TBAF in THF (20 mL, 20 mmol) was added to the reaction mixture at 0 °C. After being stirred at room temperature for additional 20 h, the reaction mixture was diluted with saturated aqueous NH_4Cl and acidified with saturated aqueous $KHSO_4$. The whole was extracted with EtOAc twice. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (gradient 2 to 35% EtOAc in hexane) to give (±)-**S2** (300 mg, 36%) as a colorless amorphous solid; IR (neat cm^{-1}): 3420 (NH), 1739 (C=O), 1713 (C=O), 1248 (S=O), 1158 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 2H), 7.37–7.36 (m, 6H), 7.28–7.25 (m, 6H), 7.23–7.19 (m, 5H), 7.12 (d, J = 8.6 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H), 5.82–5.79 (m, 1H), 4.25–4.22 (m, 2H), 3.77–3.76 (m, 6H), 3.63–3.61 (m, 1H), 3.38–3.35 (m, 2H), 3.08 (d, J = 10.9 Hz, 1H), 2.51 (dd, J = 14.3, 8.6 Hz, 1H), 2.39 (s, 3H), 2.24 (d, J = 10.9 Hz, 1H), 1.78–1.76 (m, 1H), 1.46 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.9, 159.2, 154.4, 144.4, 143.2, 138.0, 129.9, 129.6, 129.4, 129.0, 127.9, 127.2, 126.7, 113.9, 80.1, 65.7, 63.8, 61.5, 56.9, 55.2, 53.3, 48.1, 37.9, 36.0, 28.3 (3C), 21.5; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{46}H_{52}N_2NaO_8S_2$, 847.3057; found 847.3052.



(±)-**S2** (±)-**S3**

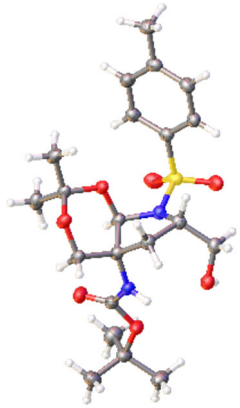
Compound (±)-S3. According to the procedure described for the preparation of (±)-**45a**, (±)-**S2** (36.3 mg, 0.0440 mmol) was converted into (±)-**S3** (22.3 mg, 65%) by the reaction with PDC (341 mg, 0.907 mmol) in H_2O/DMF (0.02/0.9 mL). Column chromatography: silica gel (gradient 2 to 25% EtOAc in hexane): colorless amorphous solid; IR (neat cm^{-1}): 1794 (C=O), 1749 (C=O), 1250 (S=O), 1159 (S=O); ^1H NMR (500 MHz, $CDCl_3$): δ 7.77 (d, J = 8.6 Hz, 2H), 7.28–7.24 (m, 3H), 7.22–7.20 (m, 10H), 7.15–7.13 (m, 6H), 6.56 (d, J = 8.6 Hz, 2H), 5.01 (dd, J = 12.0, 9.7 Hz, 1H), 4.60 (d, J = 17.2 Hz, 1H), 4.01 (d, J = 17.2 Hz, 1H), 3.67 (s, 3H), 3.59 (s, 3H), 3.32 (d, J = 12.0 Hz, 1H), 2.41 (s, 3H), 2.33–2.30 (m, 1H), 1.99–1.97 (m, 2H), 1.41 (s, 9H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 171.5, 169.9, 158.8, 148.2, 144.2, 143.5, 136.7, 129.5, 129.4, 129.3, 128.6, 127.9, 127.8, 126.8, 113.8, 84.6, 66.1, 63.9, 58.4, 55.1, 53.2, 48.7, 36.5, 31.0, 27.7 (3C), 21.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{46}H_{48}N_2NaO_8S_2$, 843.2744; found 843.2740.

Crystallographic Data



(±)-S1a

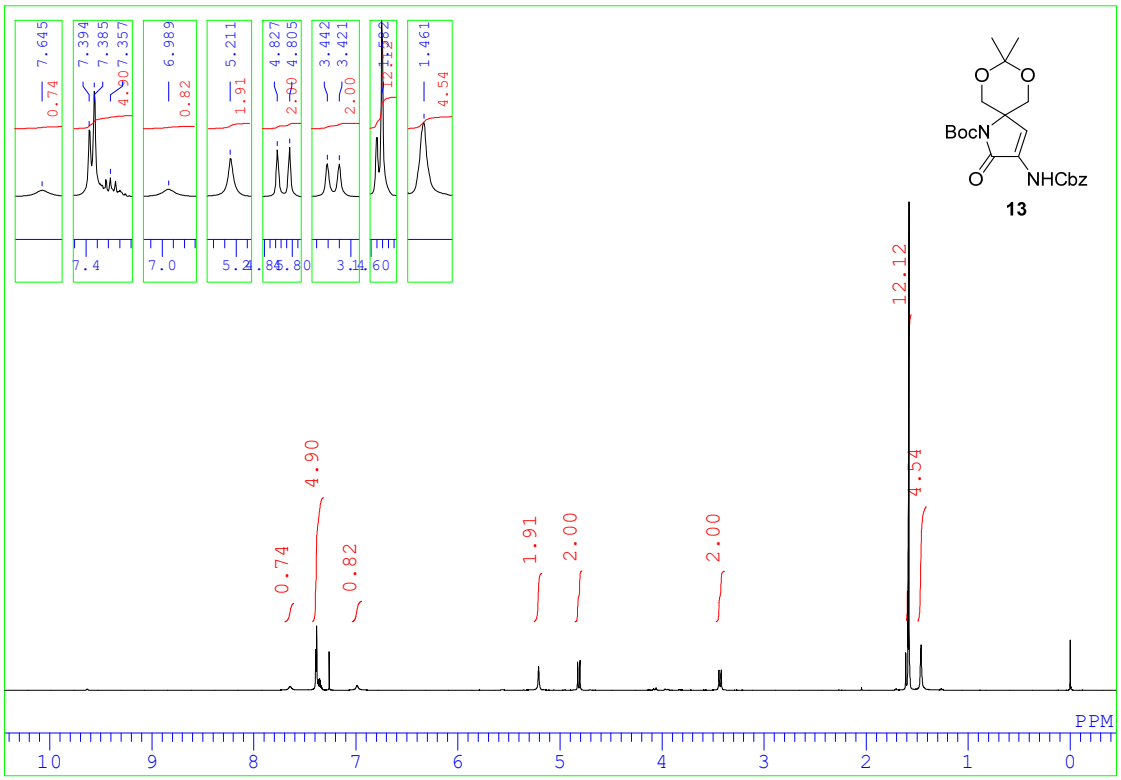
The data of the compound **(±)-S1a** ($C_{21}H_{32}N_2O_7S$) was collected with a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation at 93 K. The substance was crystallized from EtOAc-hexane as clear block crystals and solved in primitive orthorhombic space group $P2_1/c$ with $Z = 4$. The unit cell dimensions are a = 16.8319(2), b = 10.57530(10), c = 12.59590(10), V = 2236.56(4) Å^3, Dcalc = 1.356 g/cm^3, Mw: 456.54. R_1 = 0.0386, wR_2 = 0.1026, GOF = 1.090. The CCDC deposition number: CCDC 2314065.



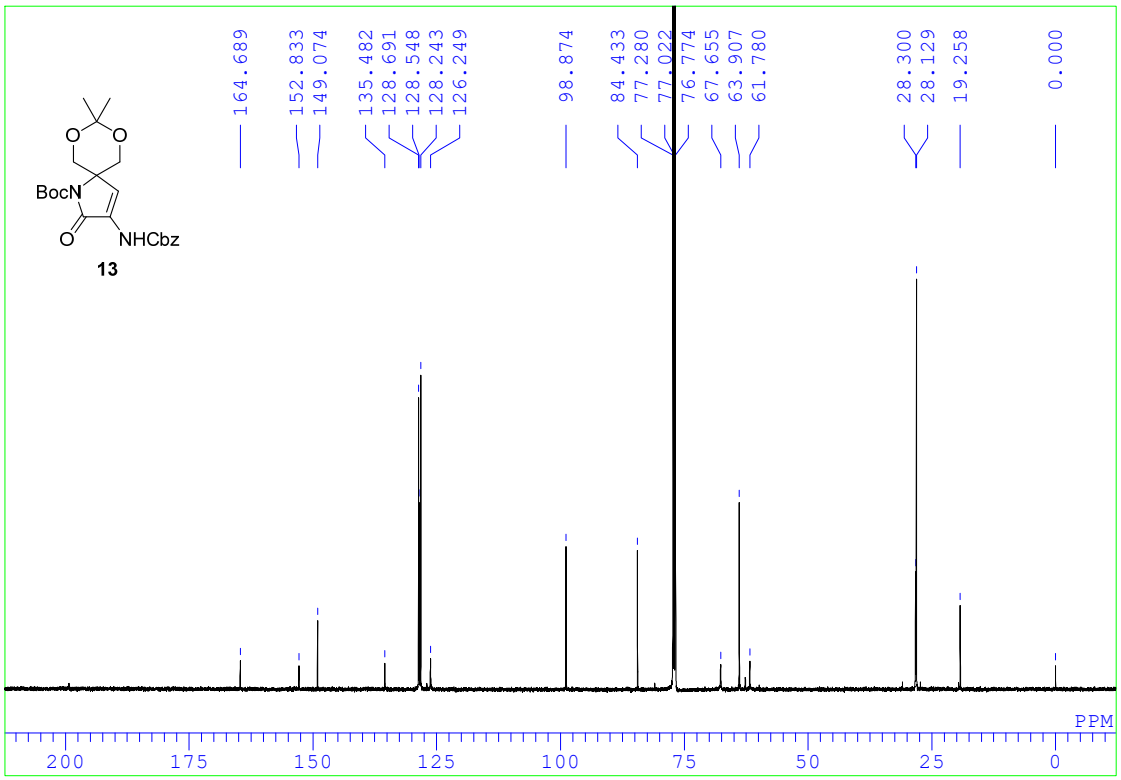
(±)-S1b

The data of the compound **(±)-S1b** ($C_{21}H_{32}N_2O_7S$) was collected with a Rigaku XtaLAB P200 diffractometer using multi-layer mirror monochromated Cu-Kα radiation at 93 K. The substance was crystallized from EtOAc-hexane as clear block crystals and solved in primitive orthorhombic space group $P2_1/c$ with $Z = 4$. The unit cell dimensions are a = 10.5663(2), b = 16.3098(3), c = 13.8053(2), V = 2344.35(7) Å^3, Dcalc = 1.294 g/cm^3, Mw: 456.54. R_1 = 0.0372, wR_2 = 0.1027, GOF = 1.059. The CCDC deposition number: CCDC 2314066.

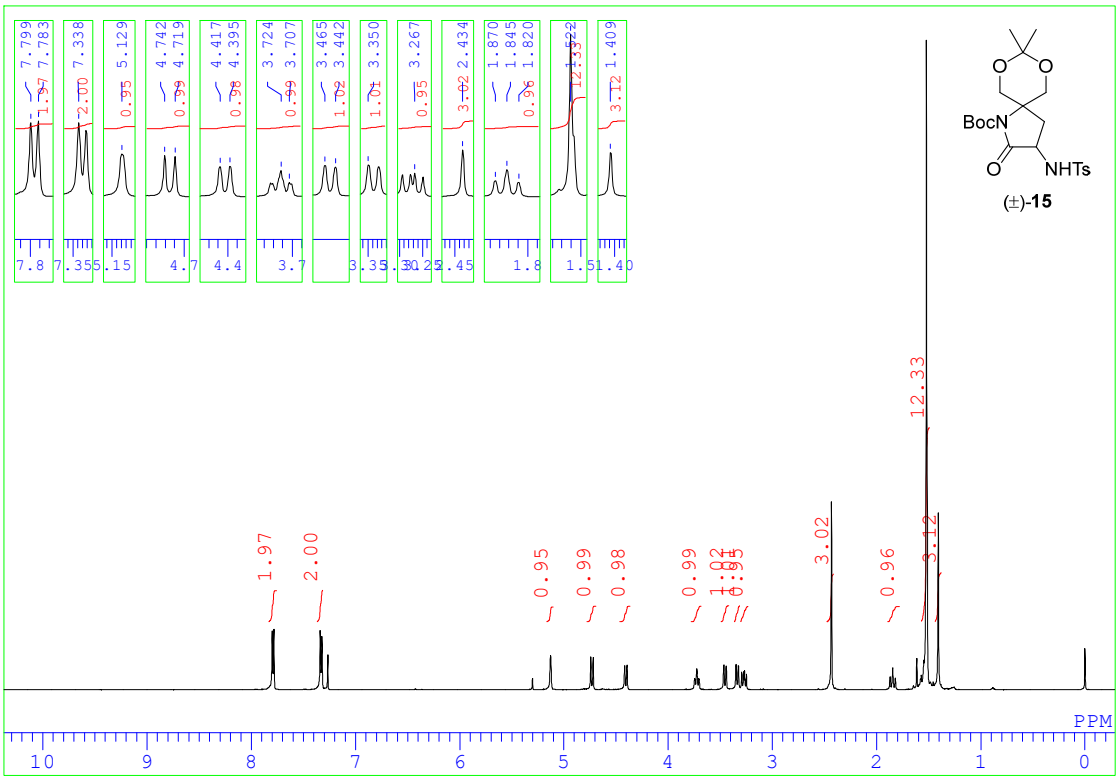
^{1}H NMR spectrum for compound 13



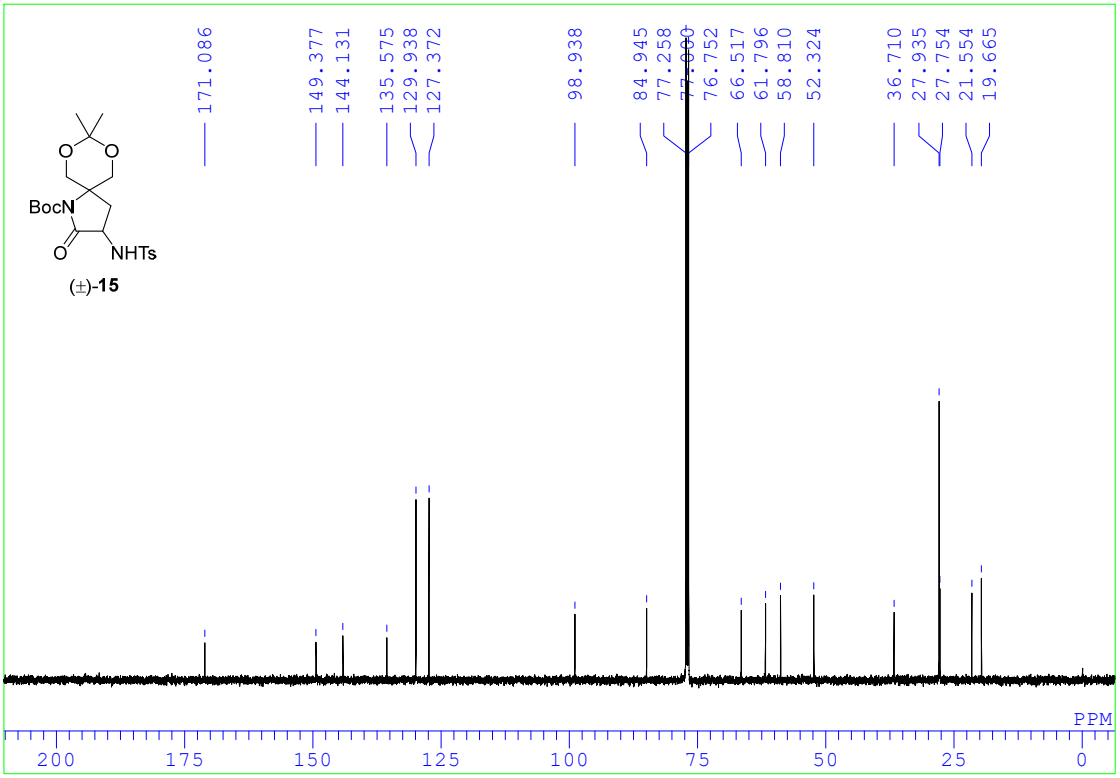
^{13}C NMR spectrum for compound 13



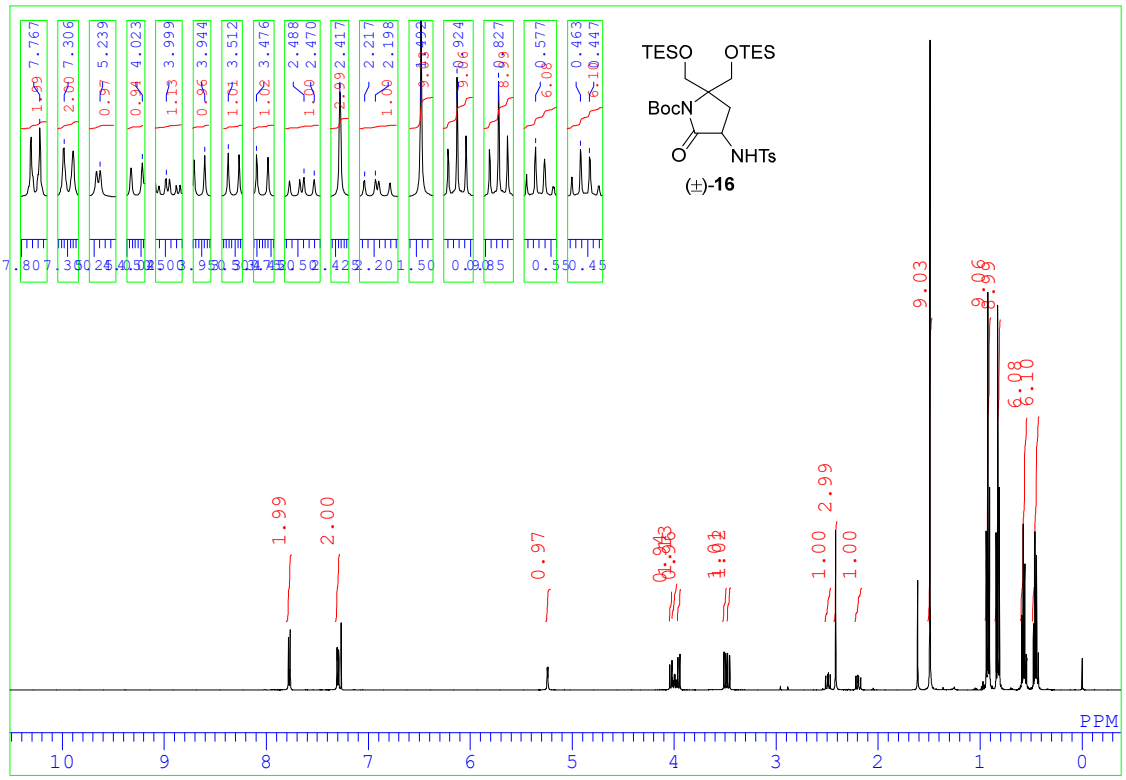
^{1}H NMR spectrum for compound 15



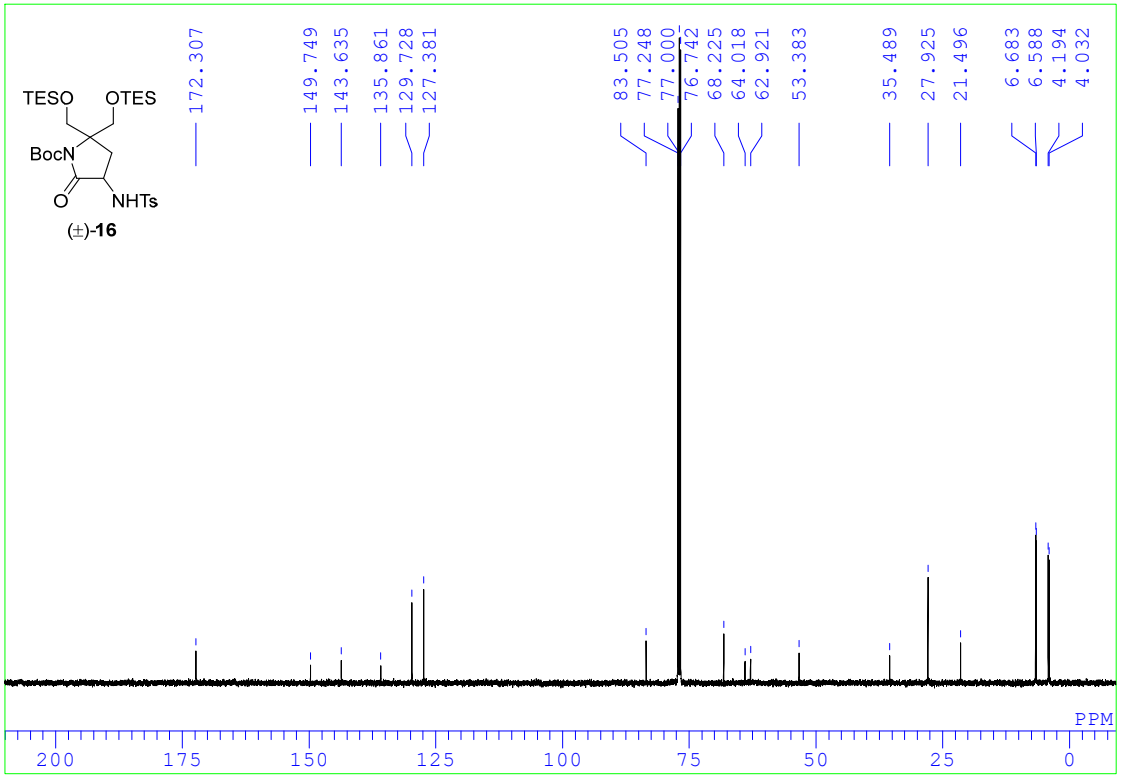
^{13}C NMR spectrum for compound 15



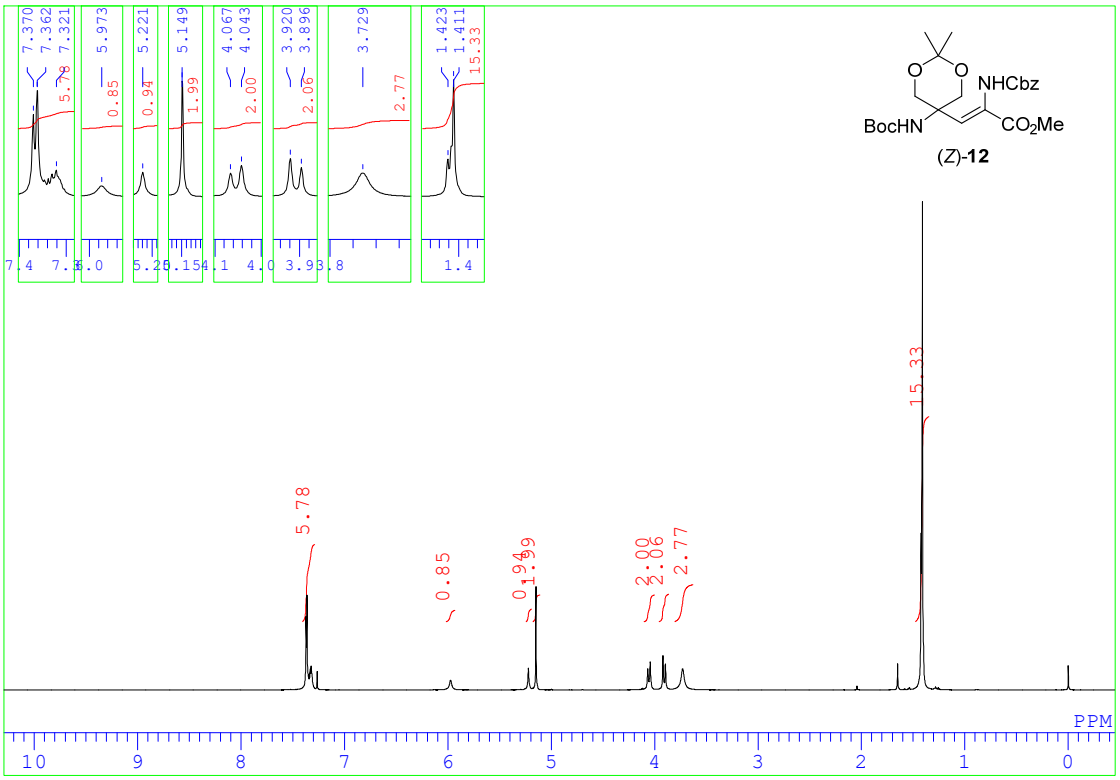
^{1}H NMR spectrum for compound 16



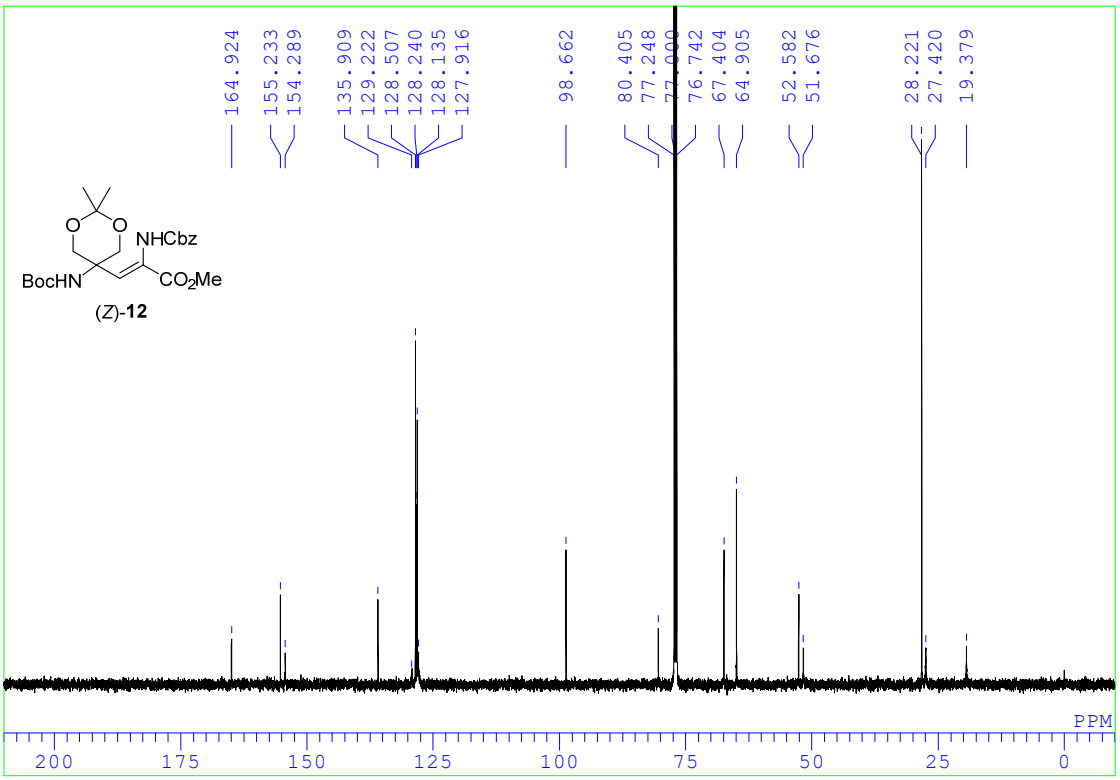
^{13}C NMR spectrum for compound 16



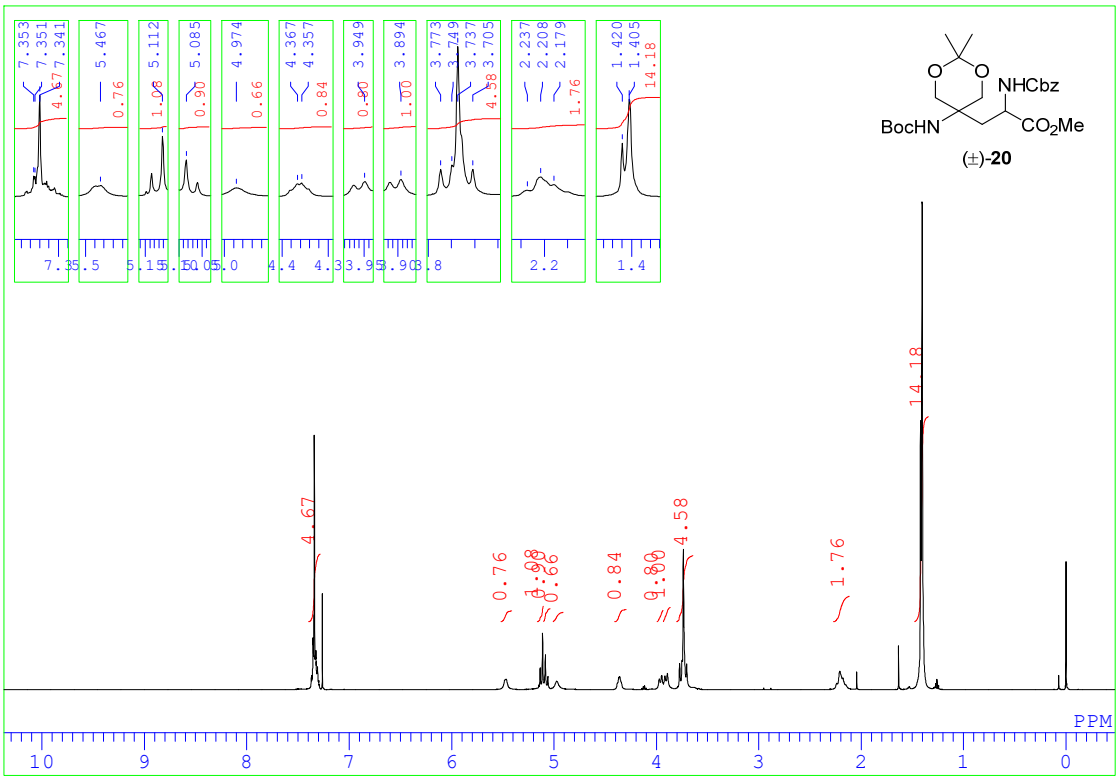
^{1}H NMR spectrum for compound 12



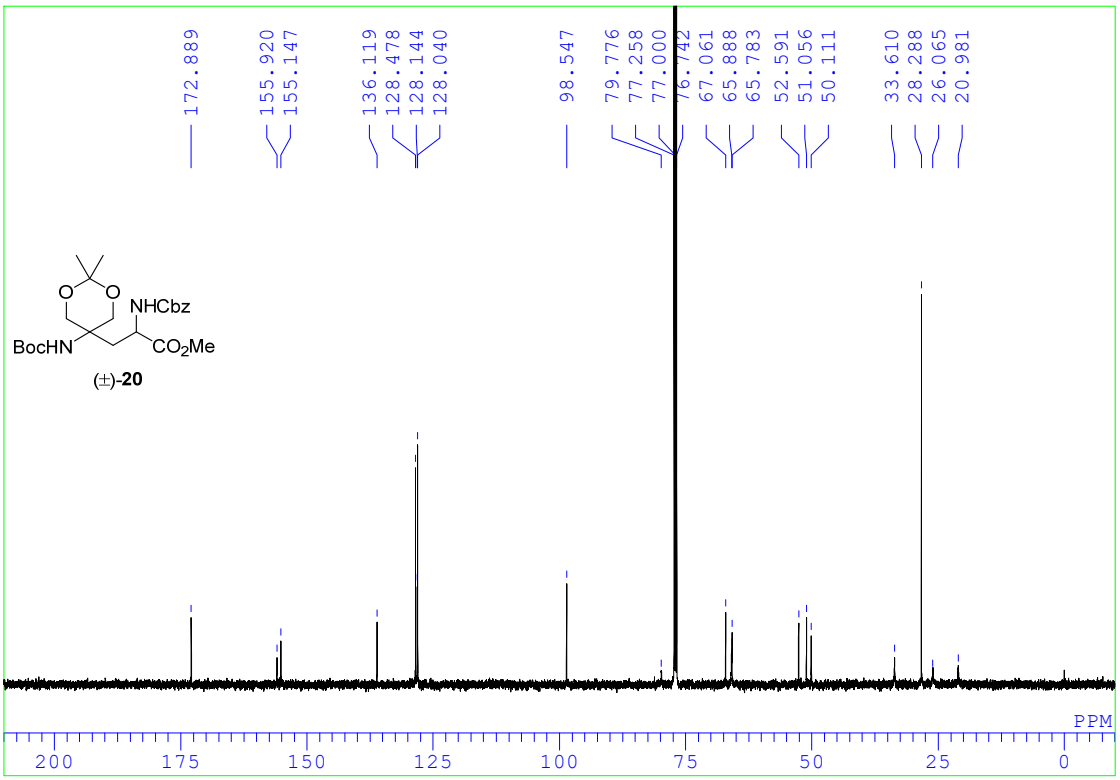
^{13}C NMR spectrum for compound 12



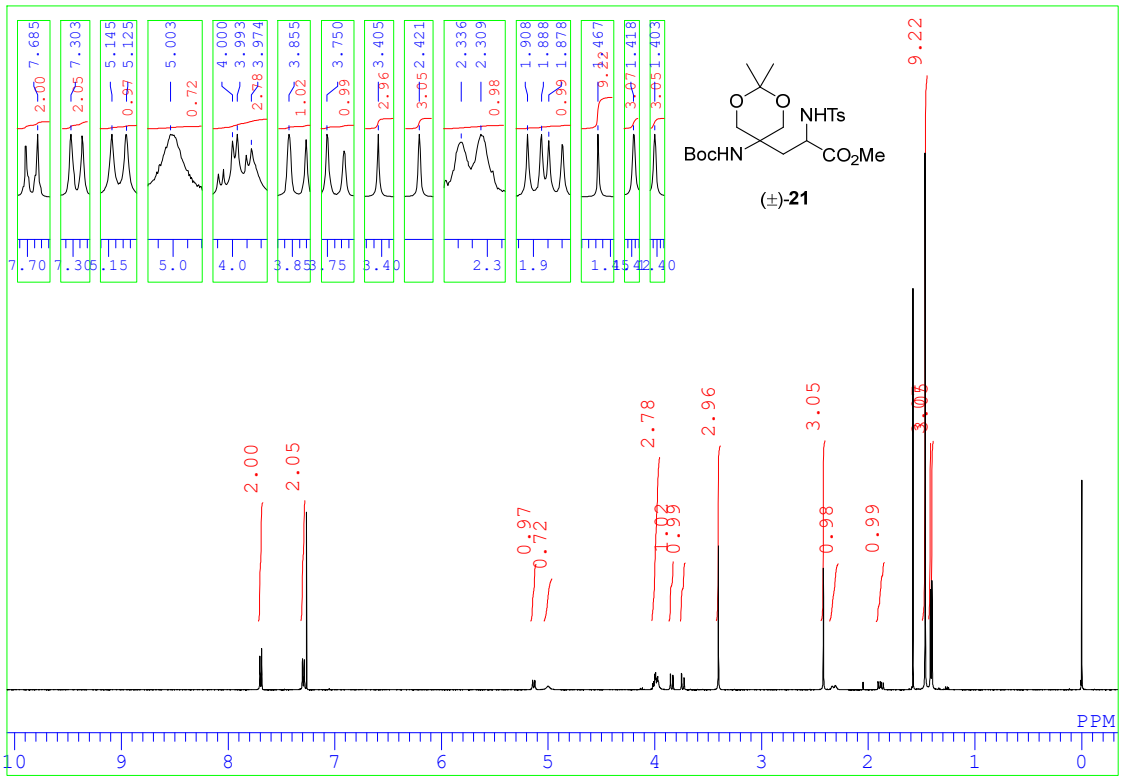
^{1}H NMR spectrum for compound 20



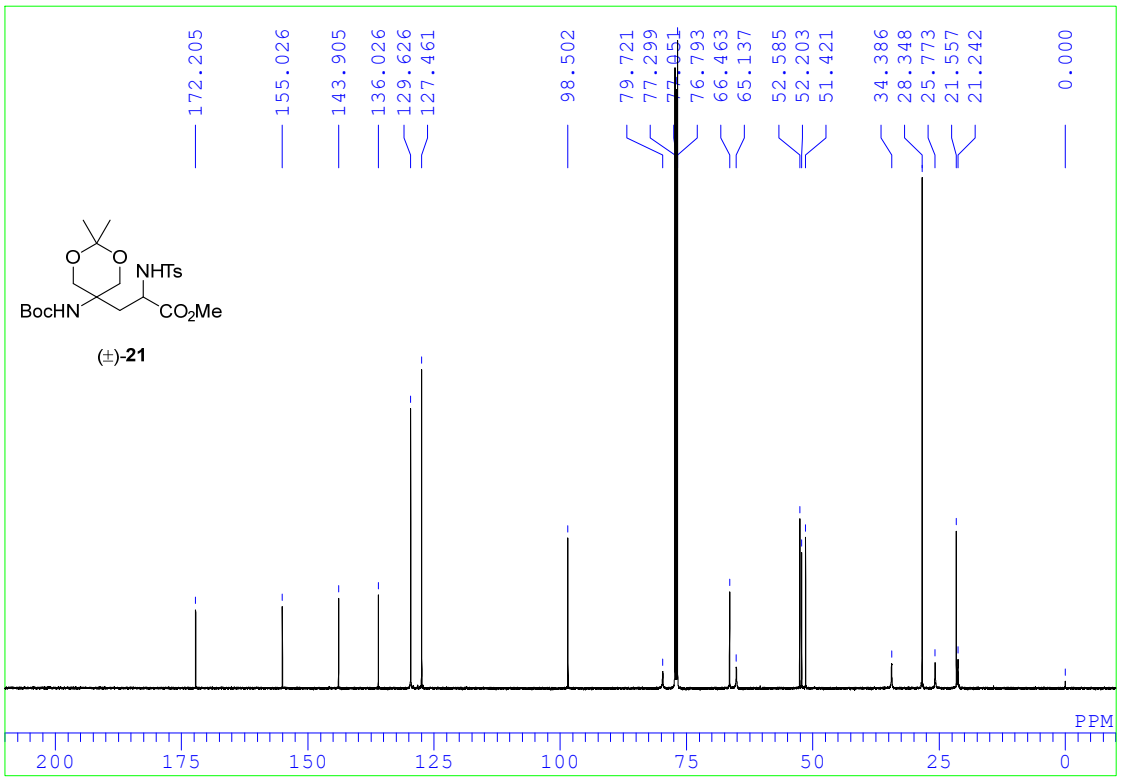
^{13}C NMR spectrum for compound 20



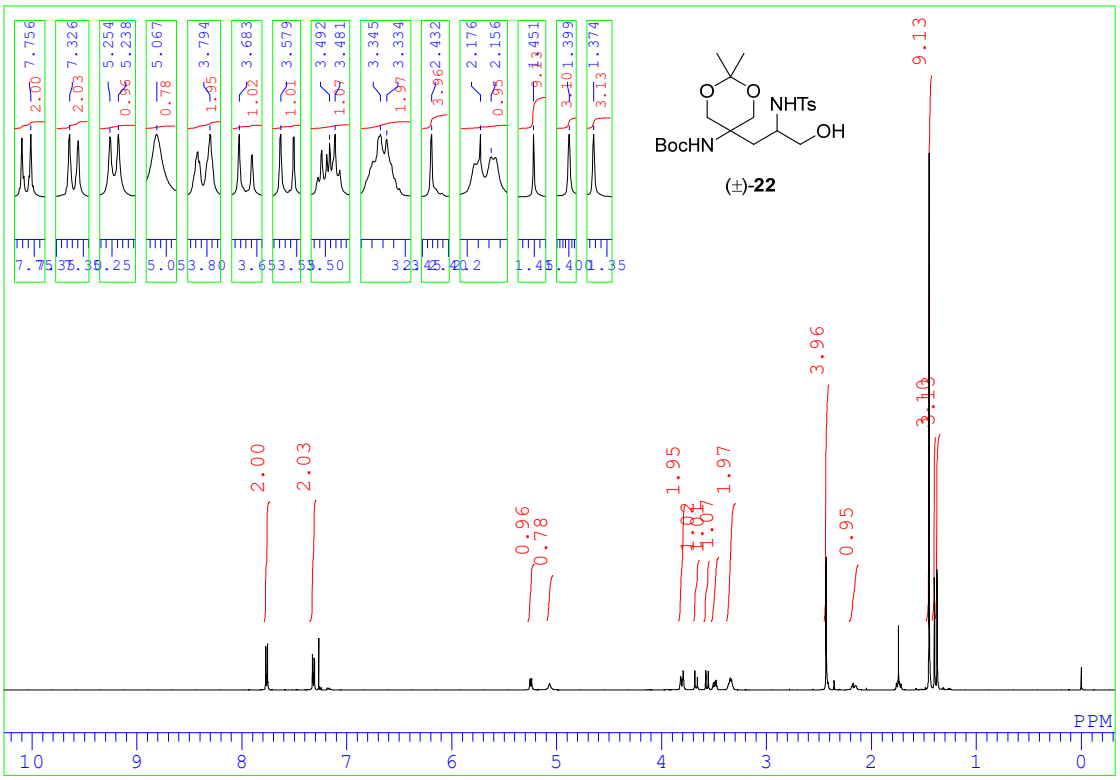
^{1}H NMR spectrum for compound 21



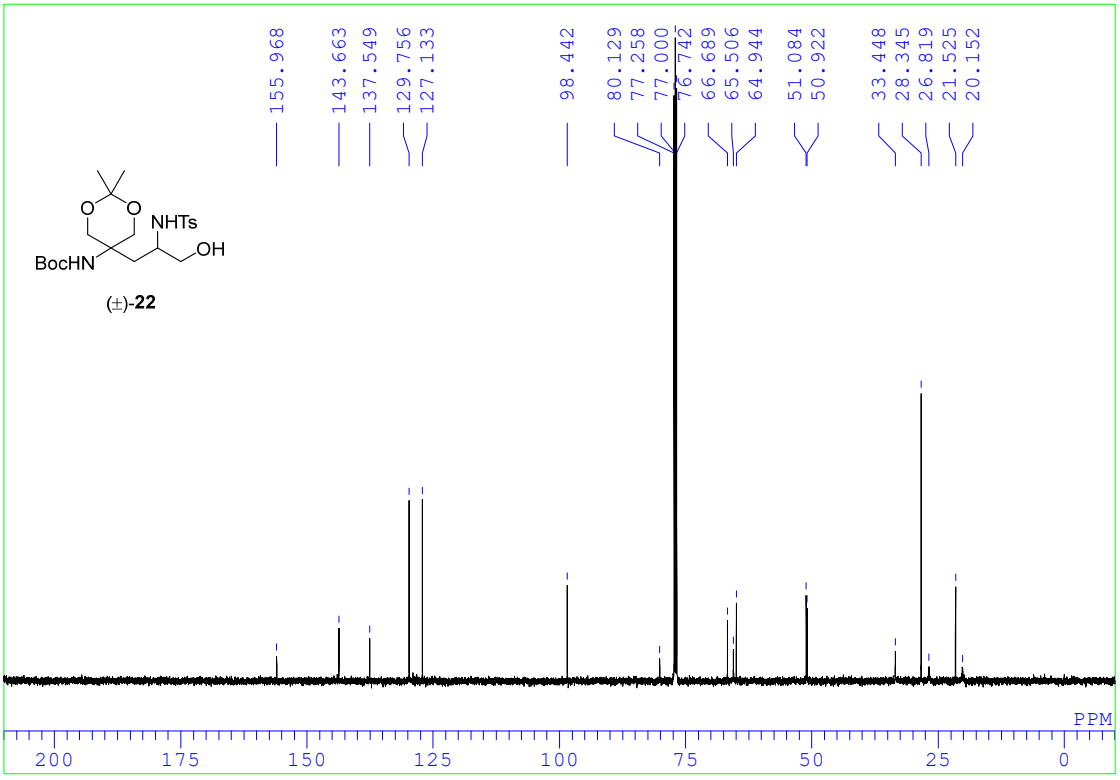
^{13}C NMR spectrum for compound 21



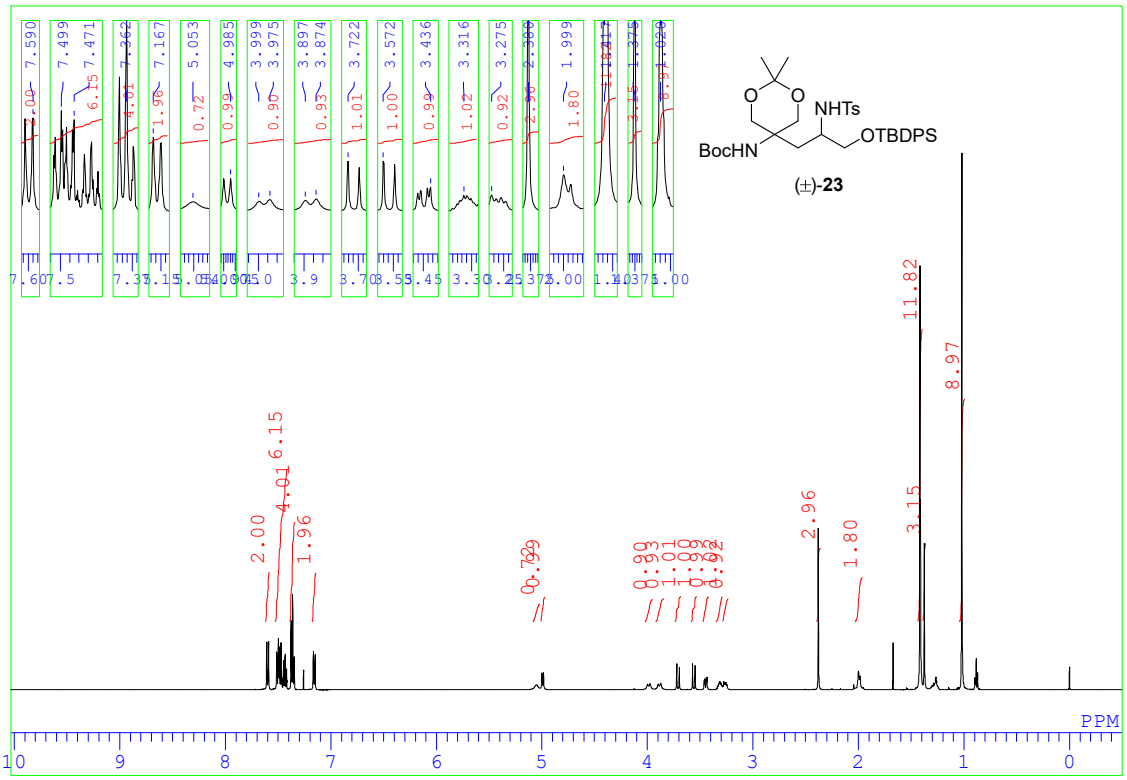
^{1}H NMR spectrum for compound 22



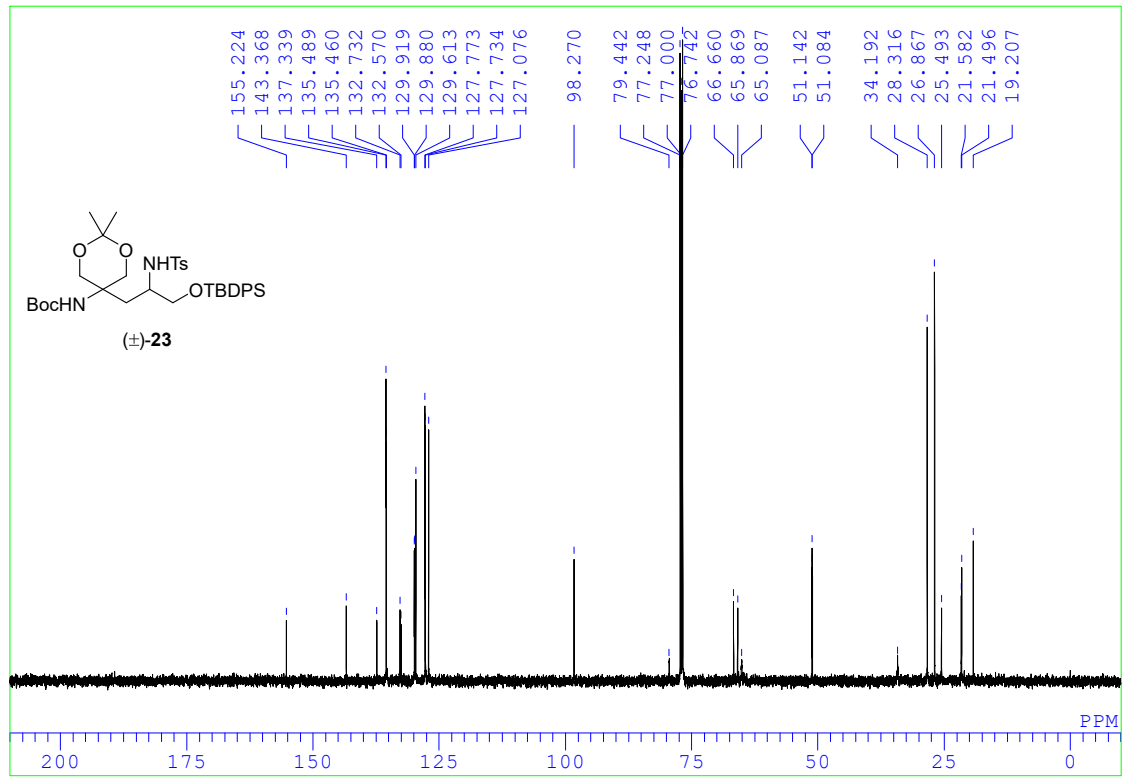
^{13}C NMR spectrum for compound 22



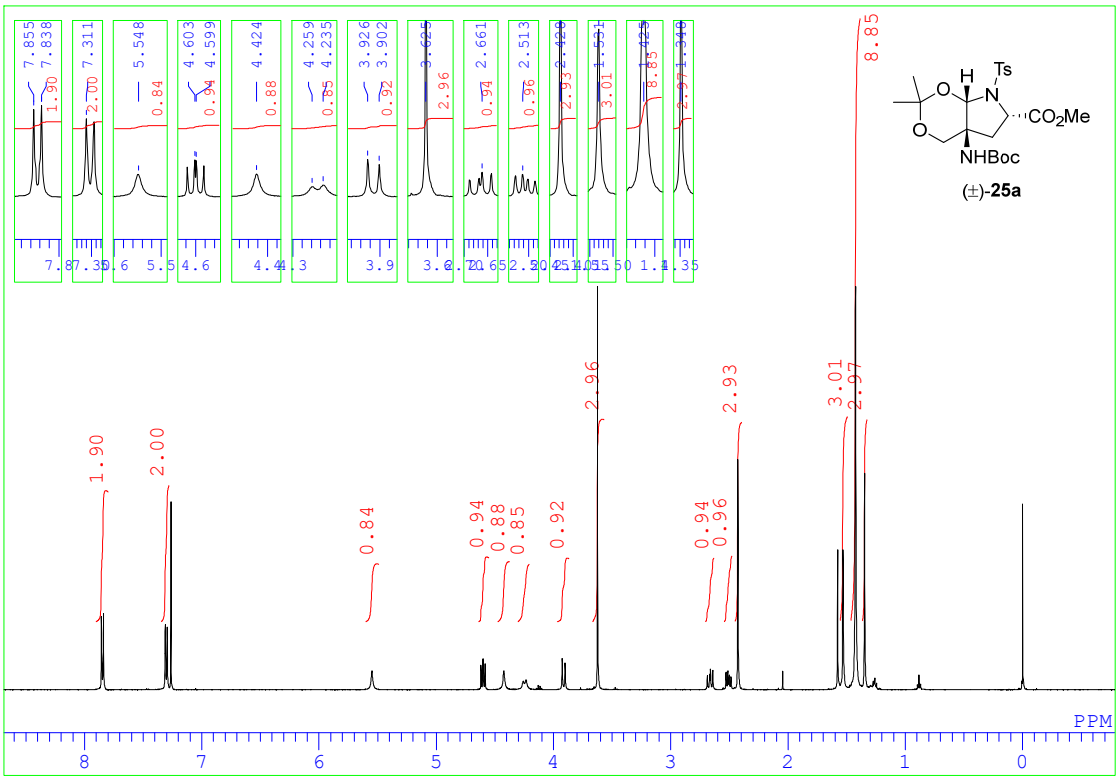
^{1}H NMR spectrum for compound 23



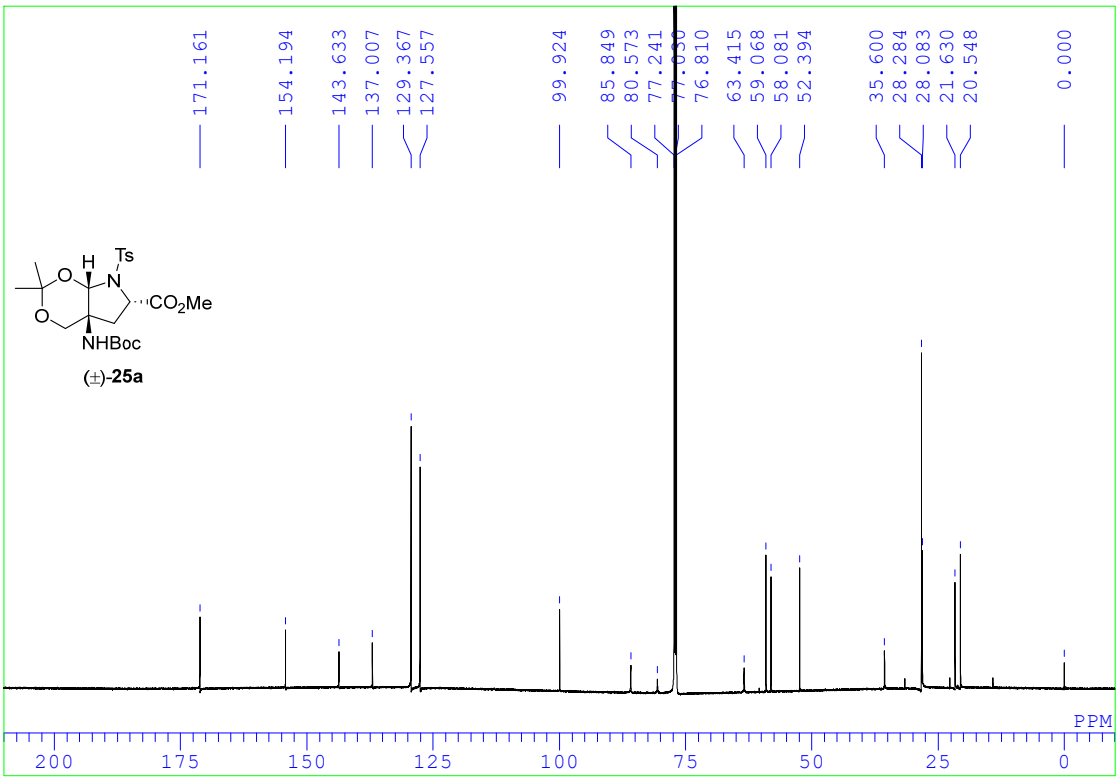
^{13}C NMR spectrum for compound 23



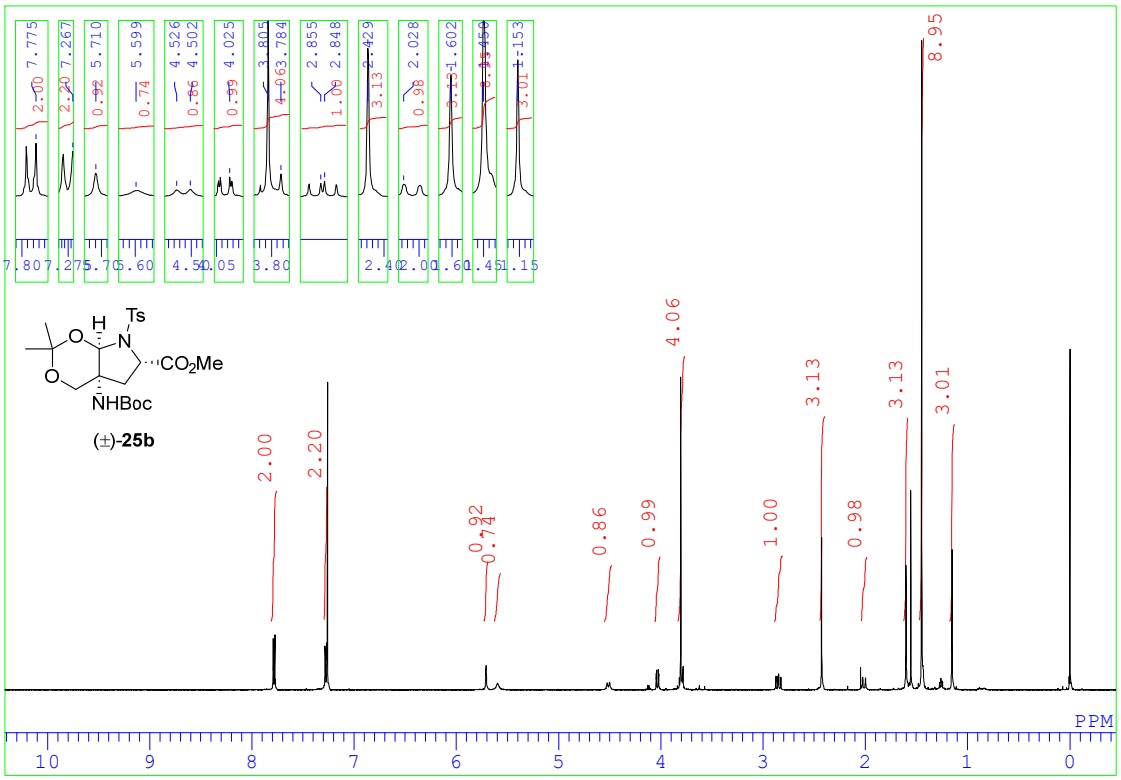
^{1}H NMR spectrum for compound 25a



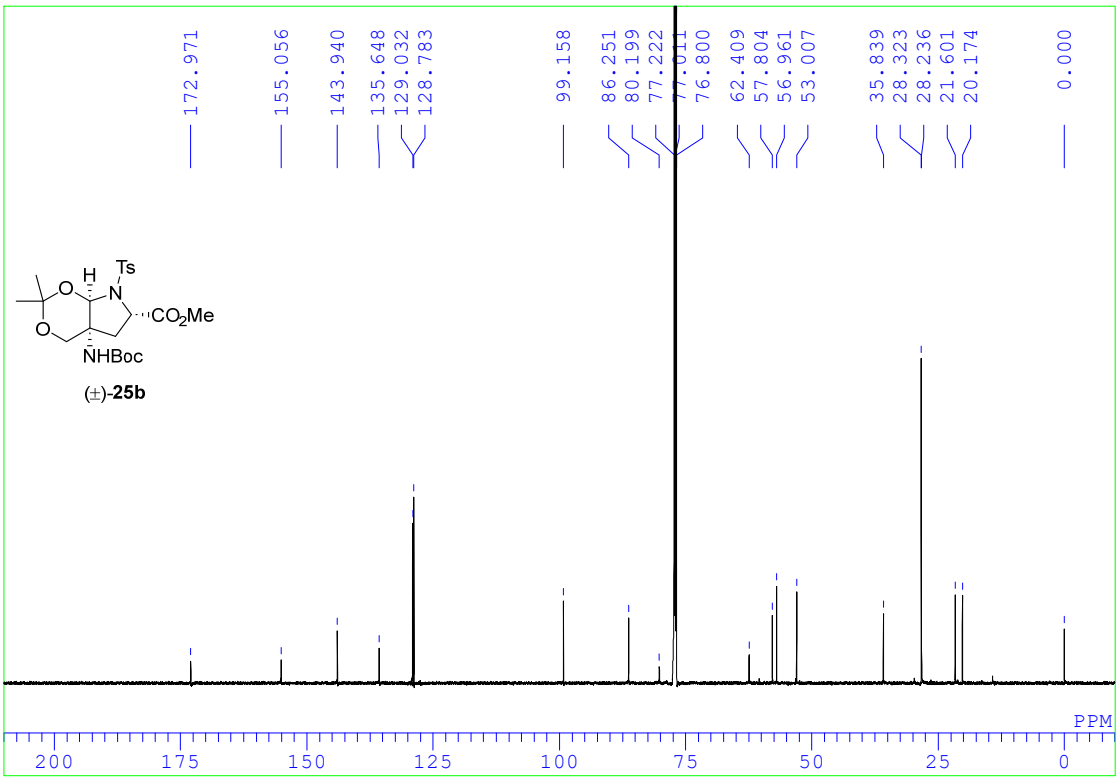
^{13}C NMR spectrum for compound 25a



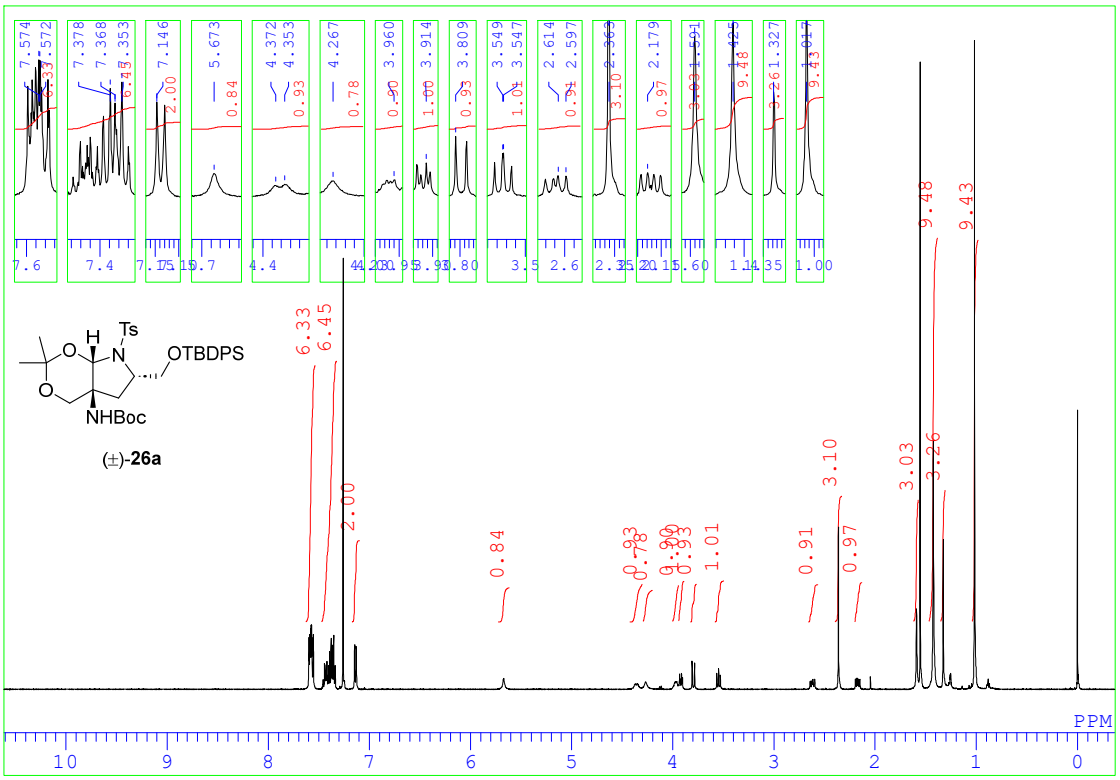
^{1}H NMR spectrum for compound 25b



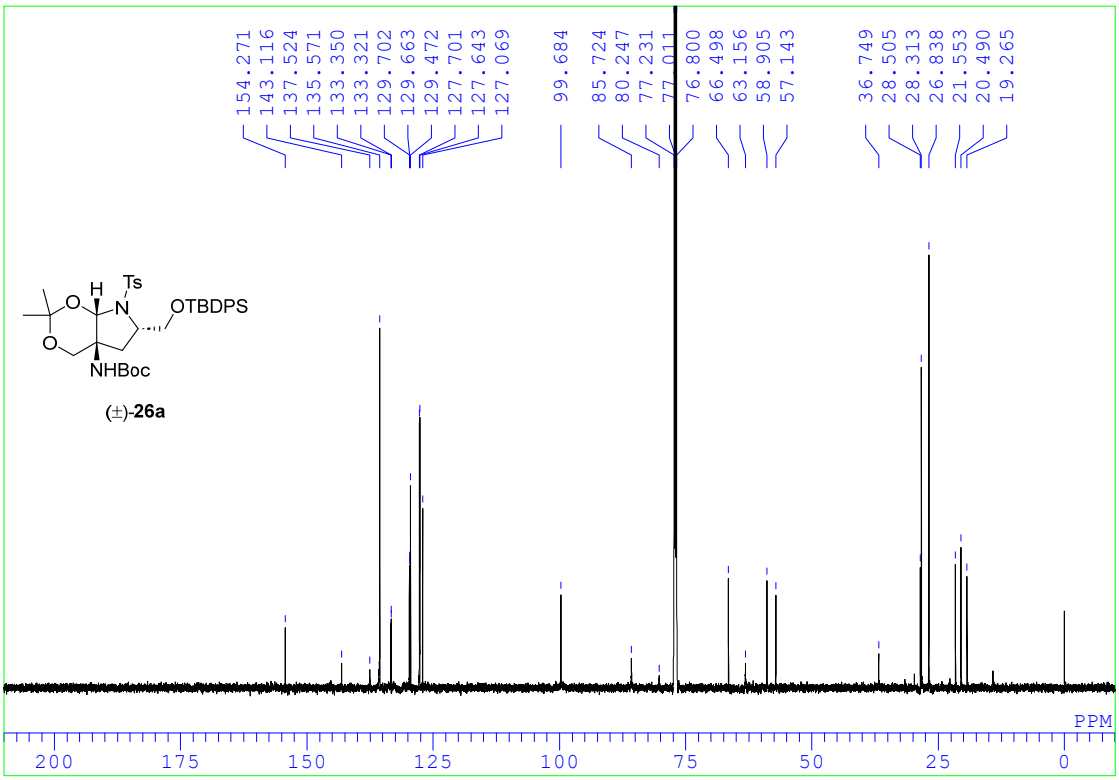
^{13}C NMR spectrum for compound 25b



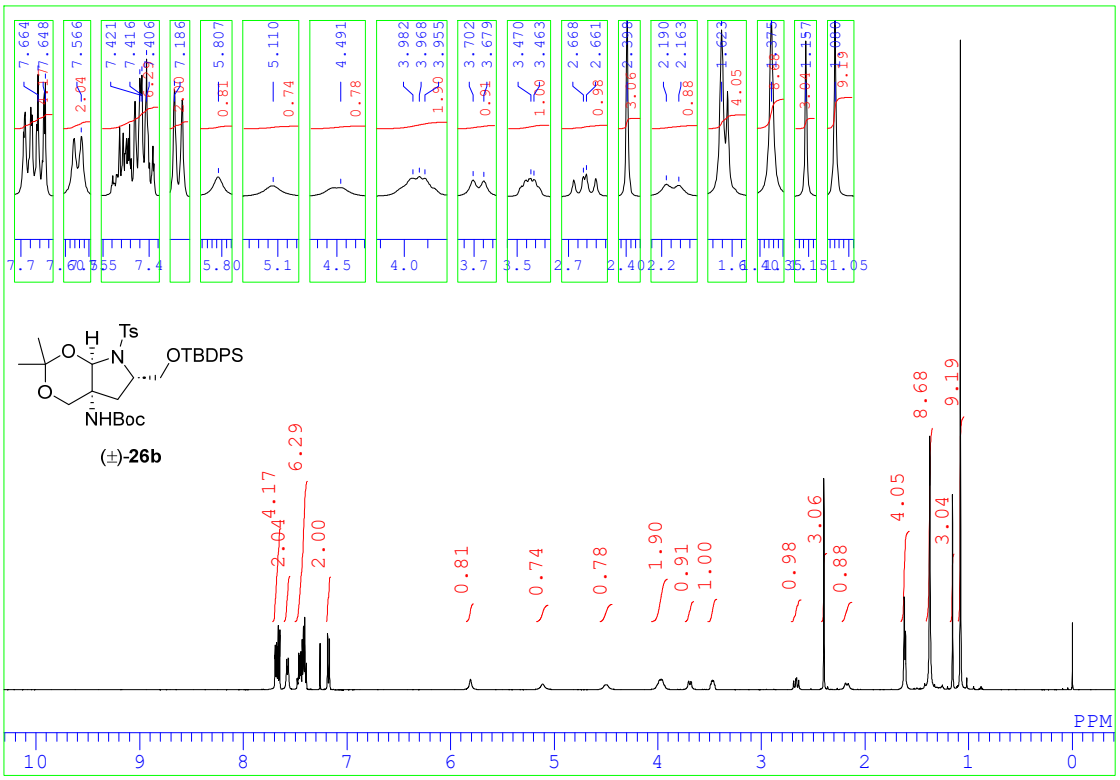
^{1}H NMR spectrum for compound 26a



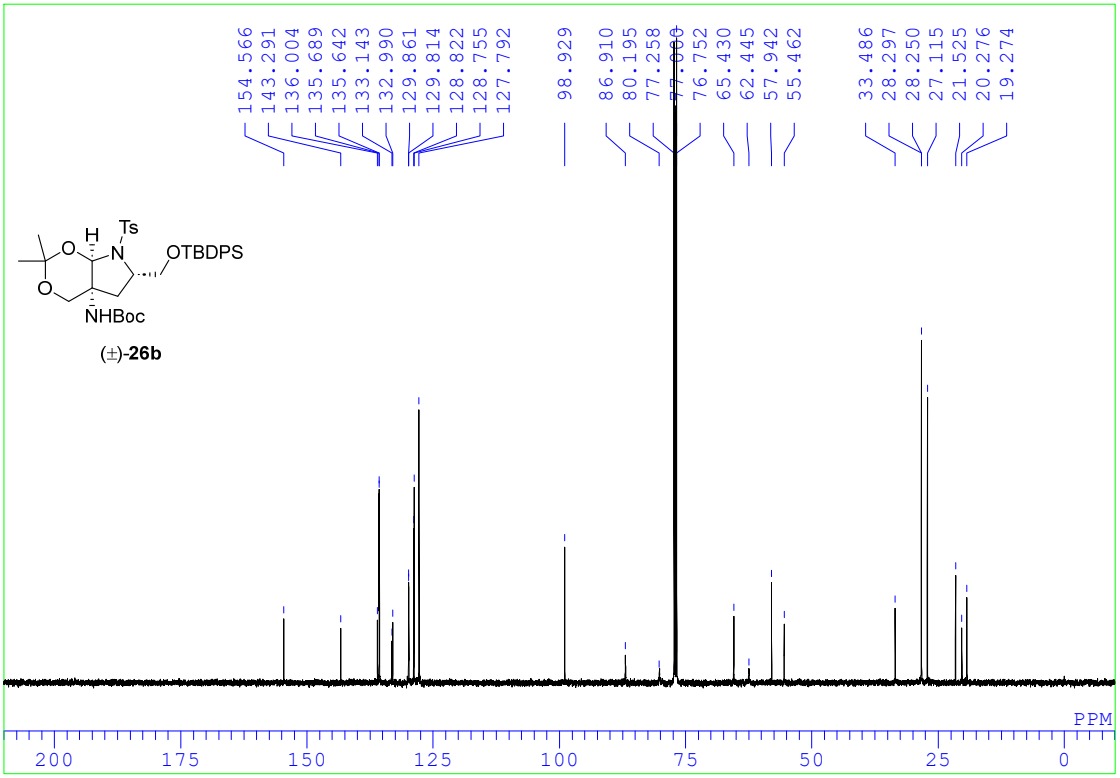
^{13}C NMR spectrum for compound 26a



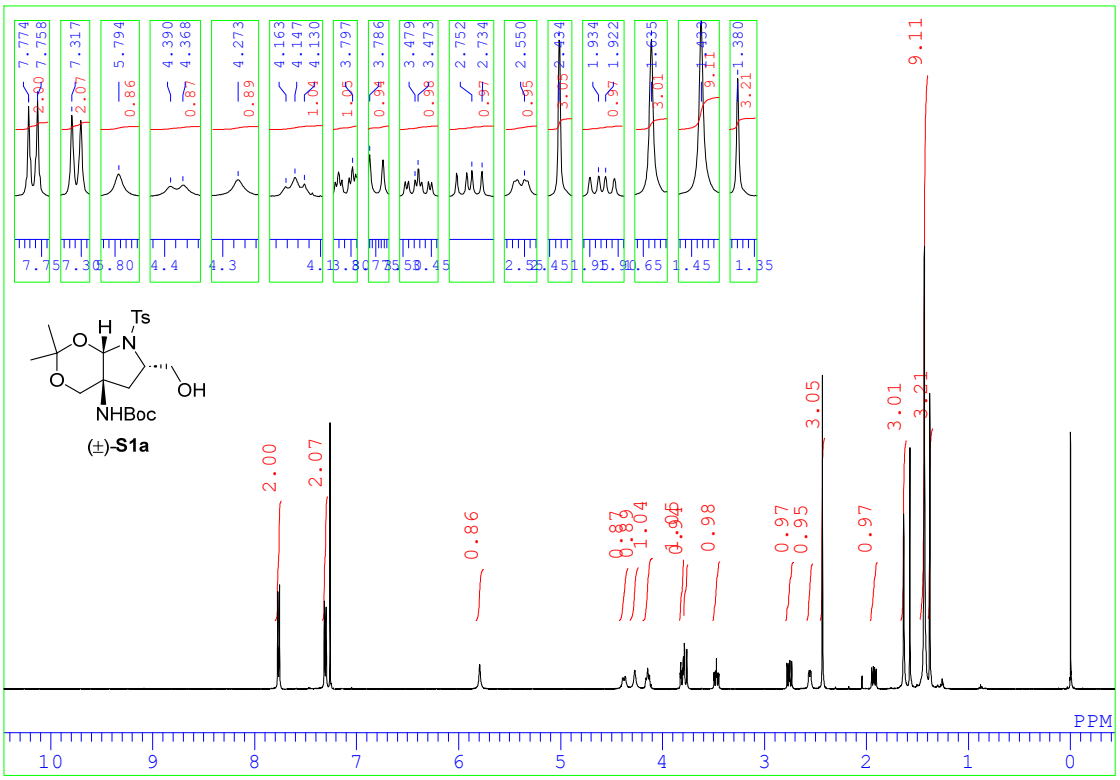
^{1}H NMR spectrum for compound 26b



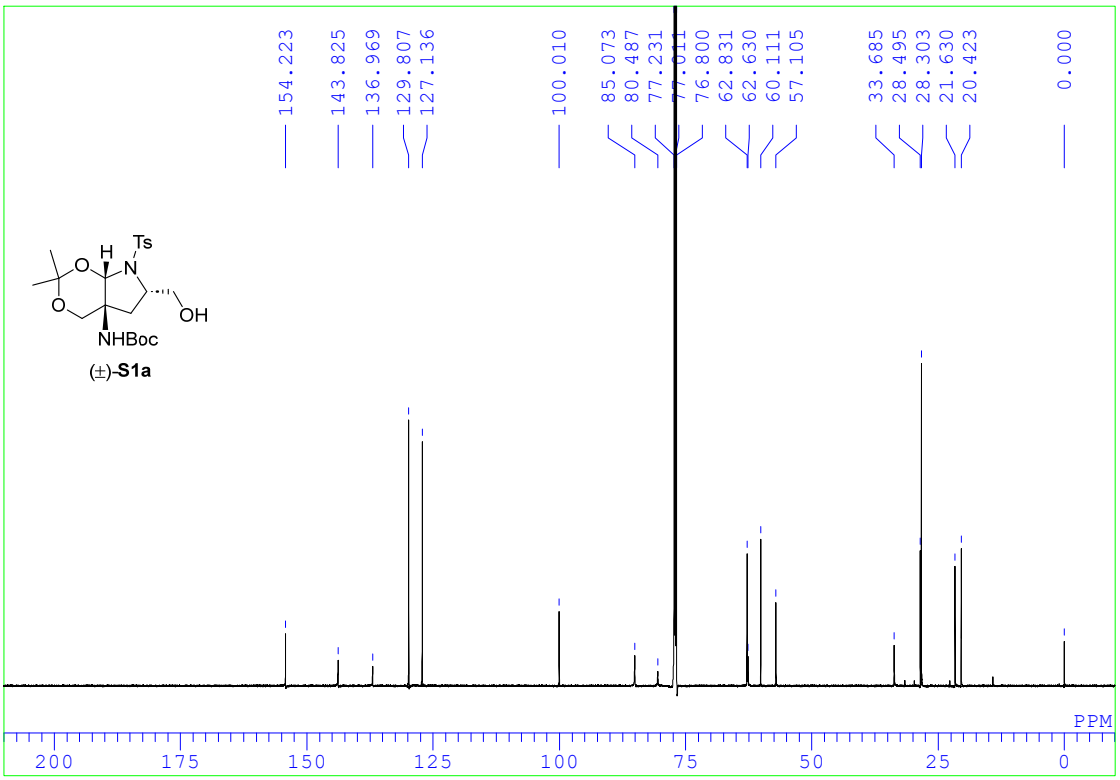
^{13}H NMR spectrum for compound 26b



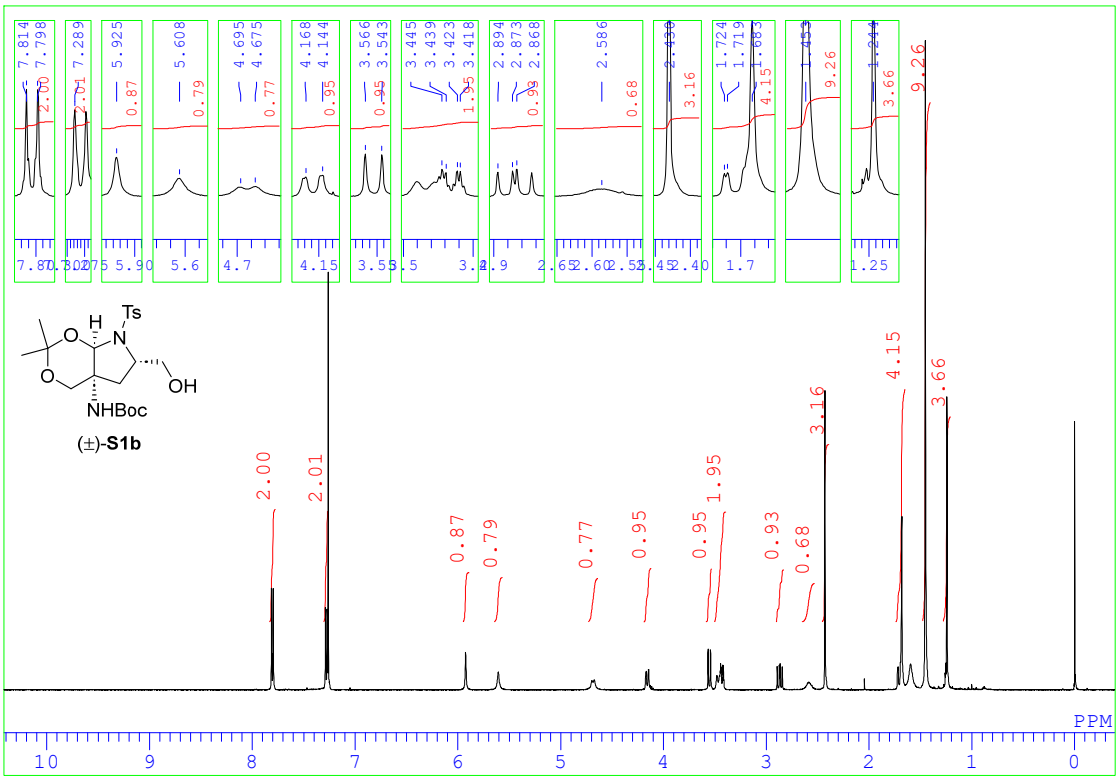
^{1}H NMR spectrum for compound S1a



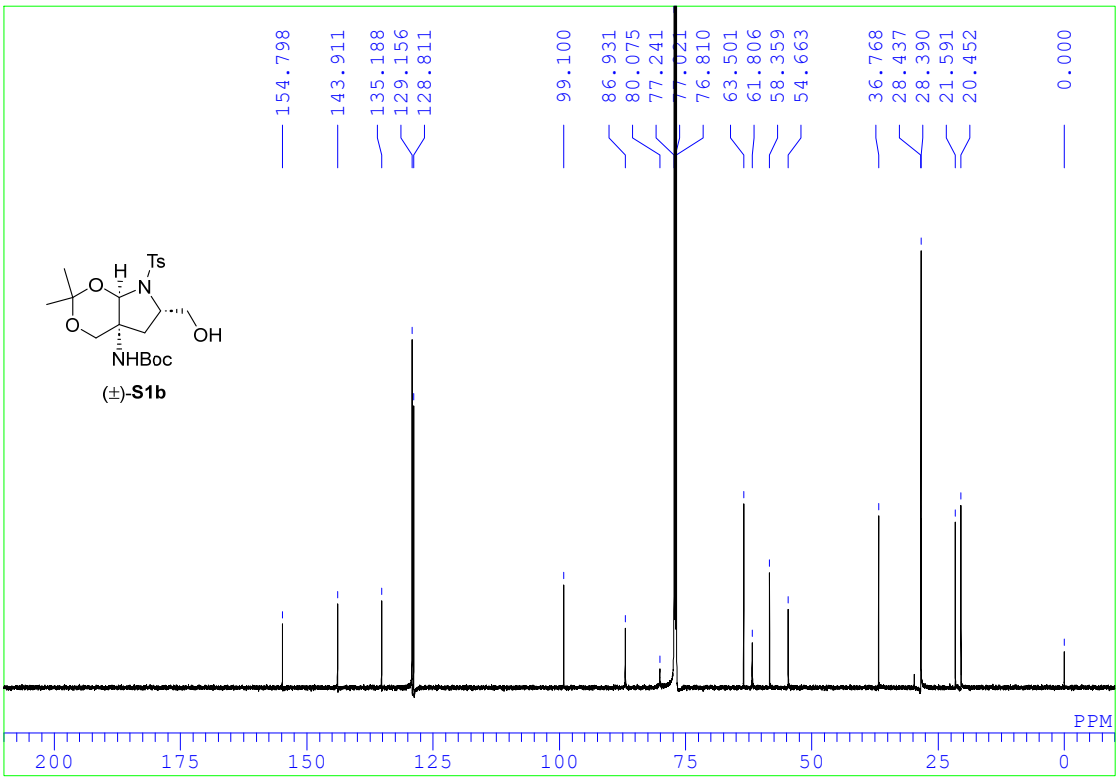
^{13}C NMR spectrum for compound S1a



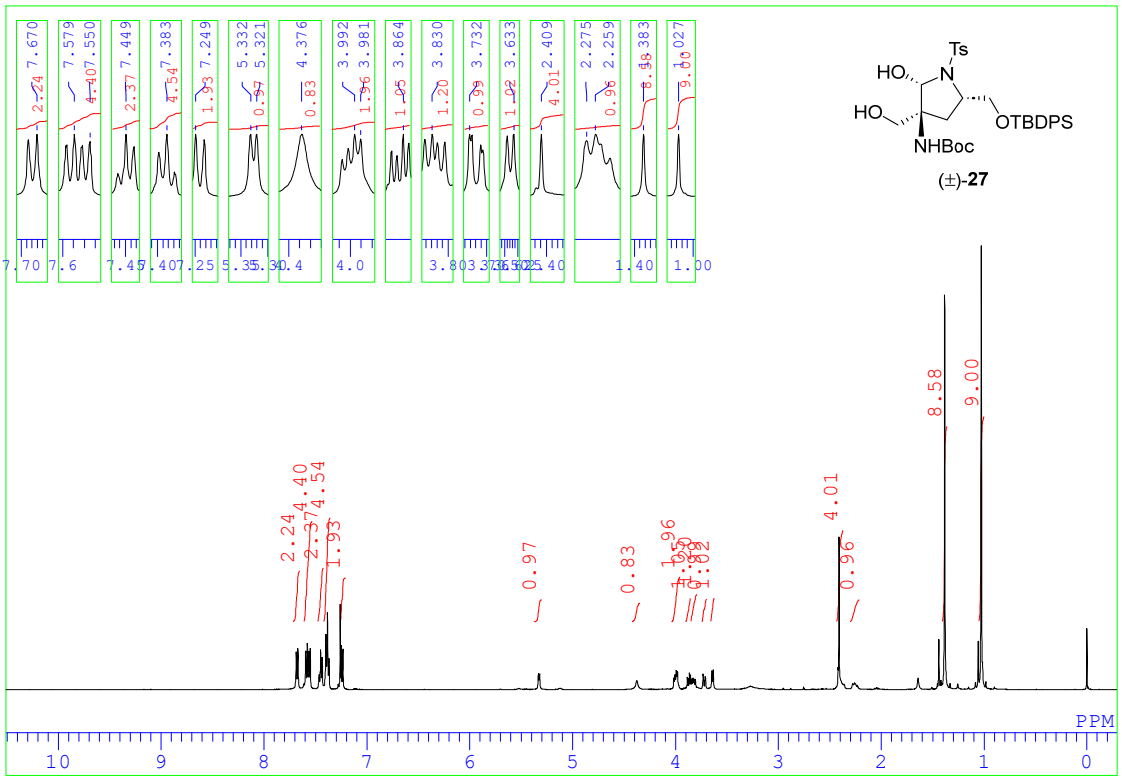
^{1}H NMR spectrum for compound S1b



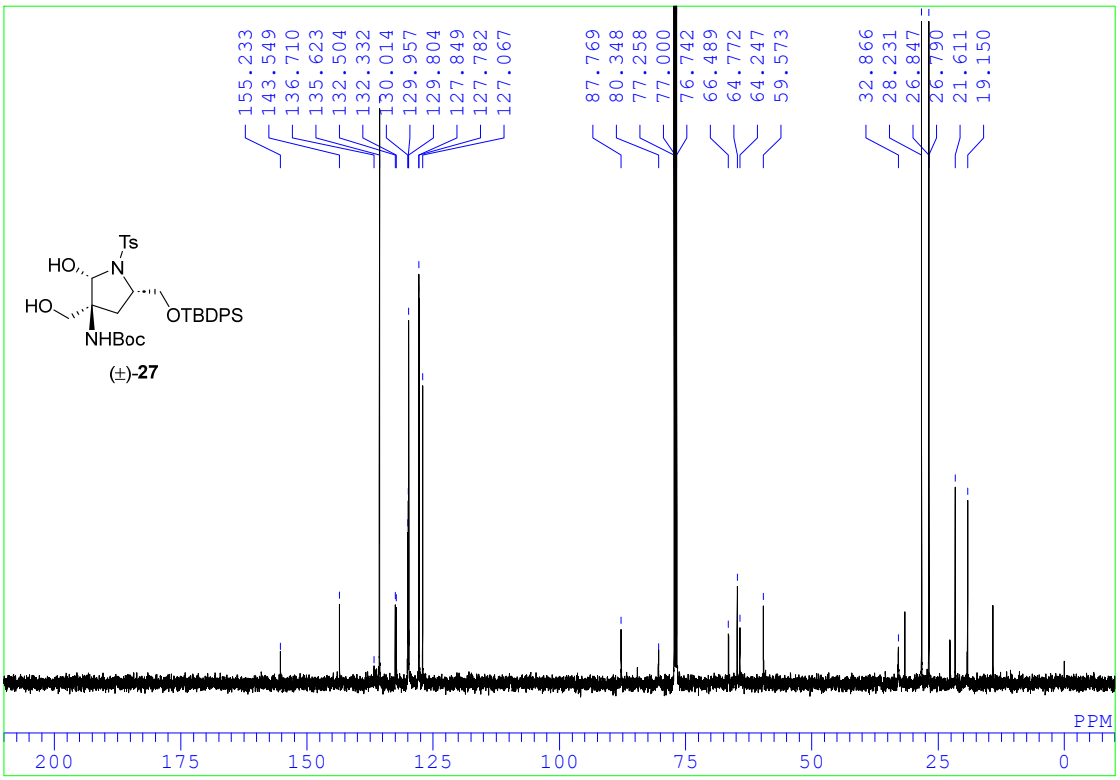
^{13}C NMR spectrum for compound S1b



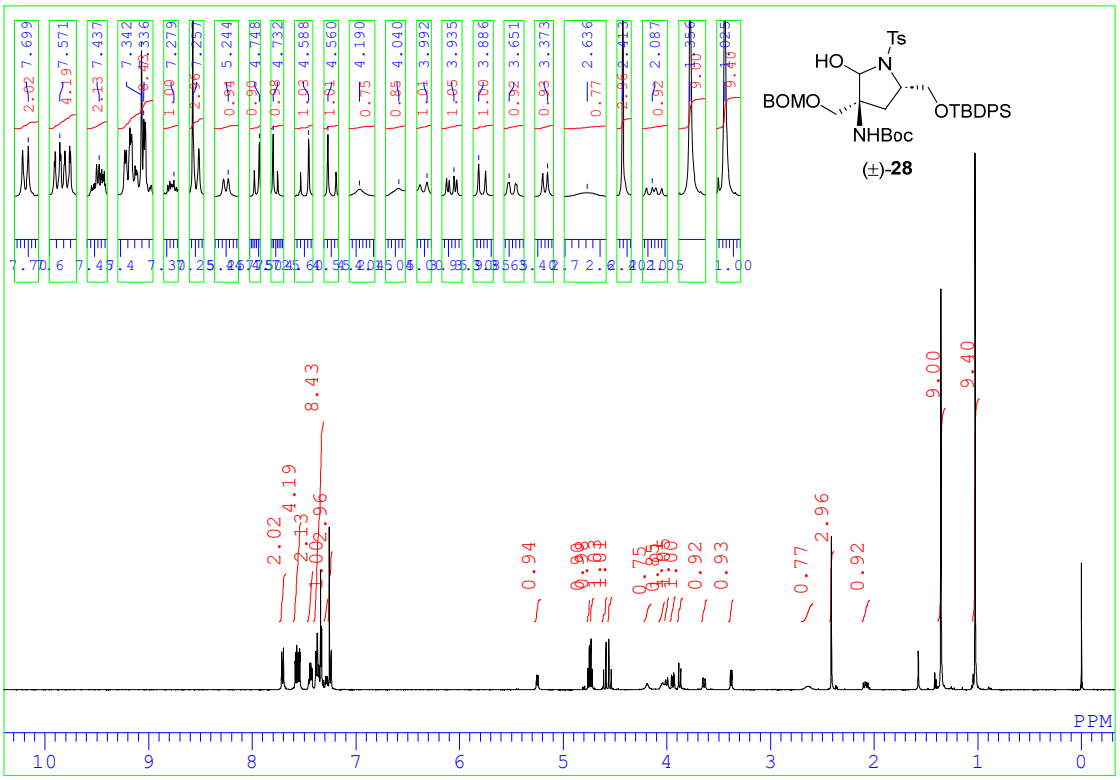
^{1}H NMR spectrum for compound 27



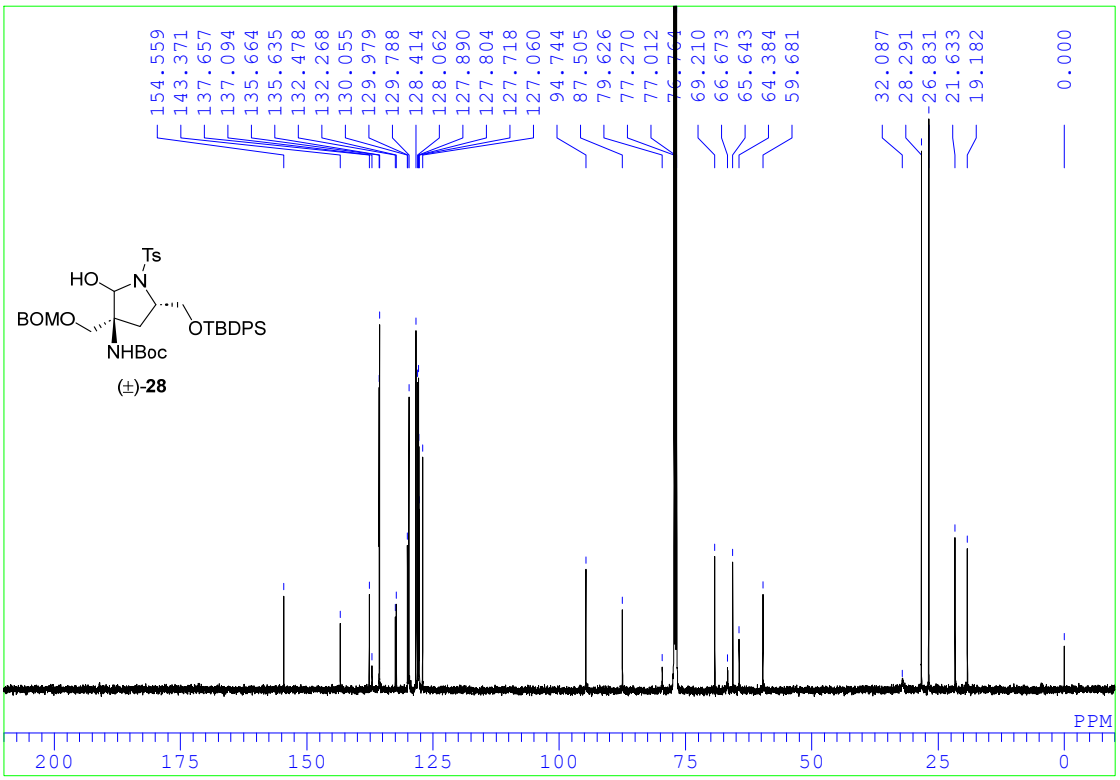
^{13}C NMR spectrum for compound 27



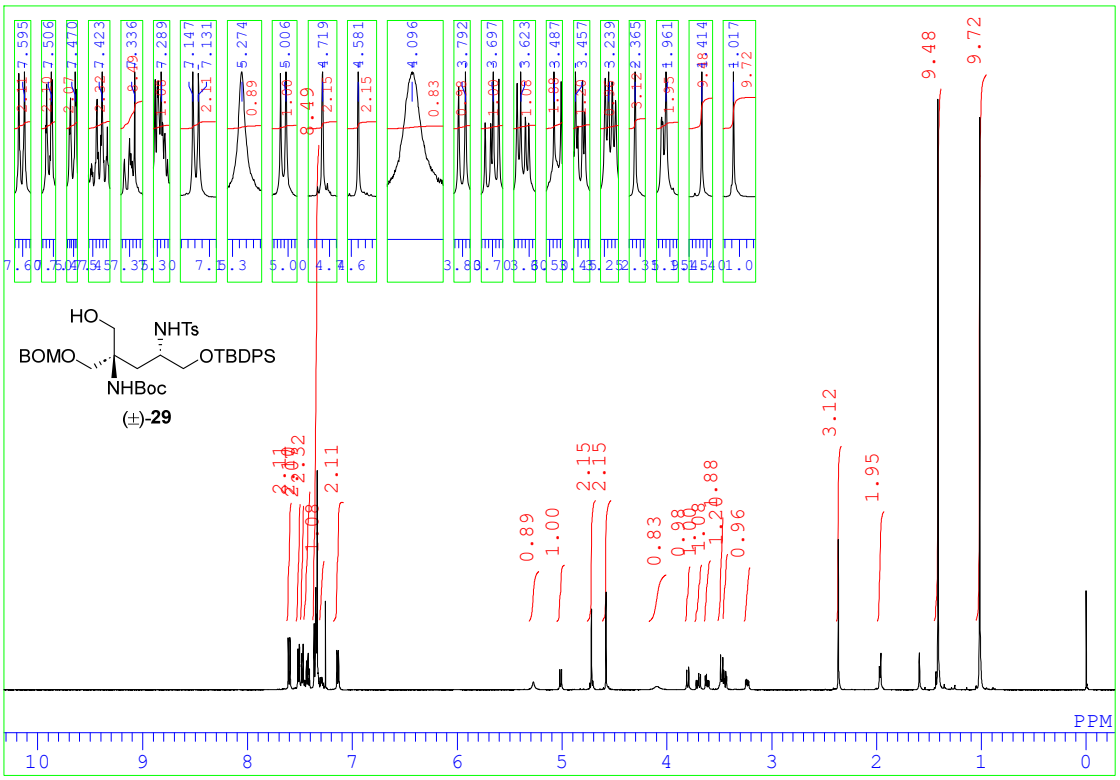
^{1}H NMR spectrum for compound 28



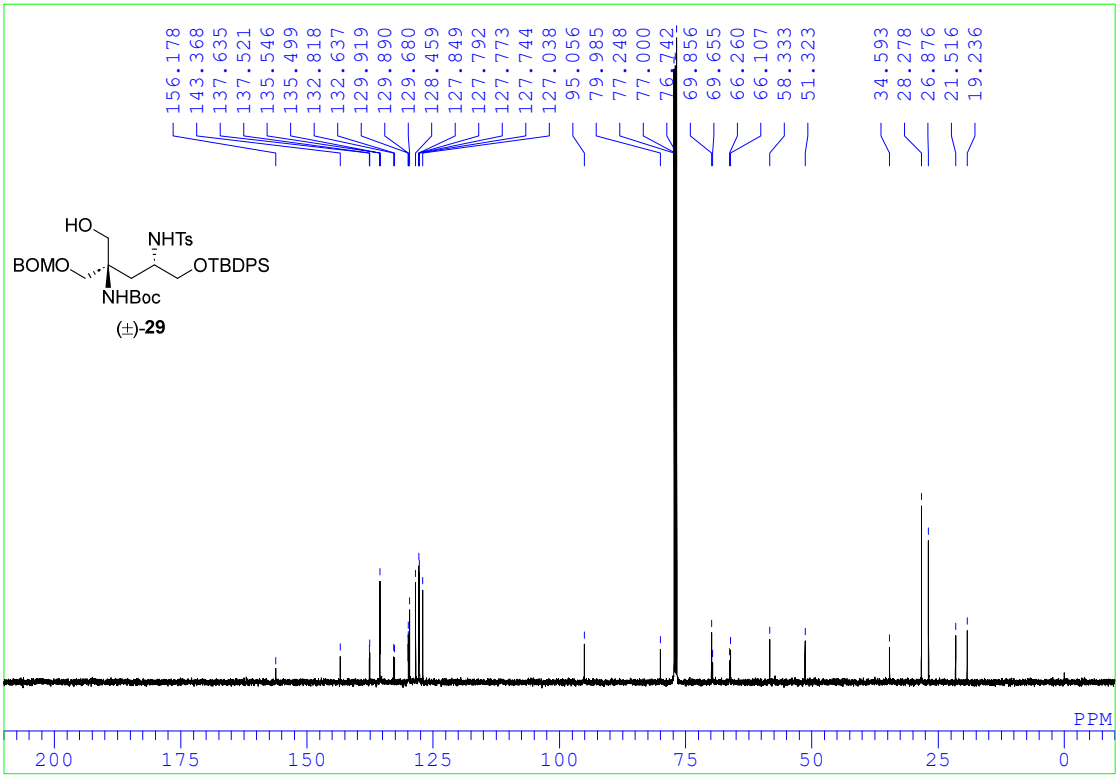
^{13}C NMR spectrum for compound 28



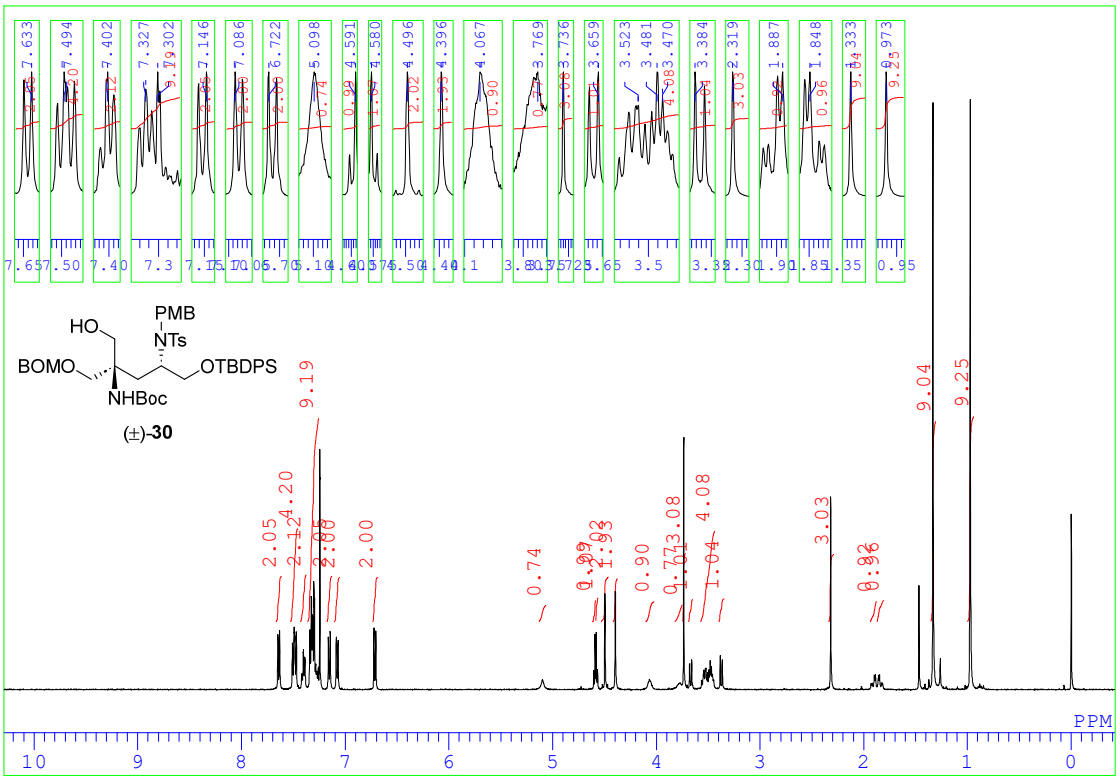
^{1}H NMR spectrum for compound 29



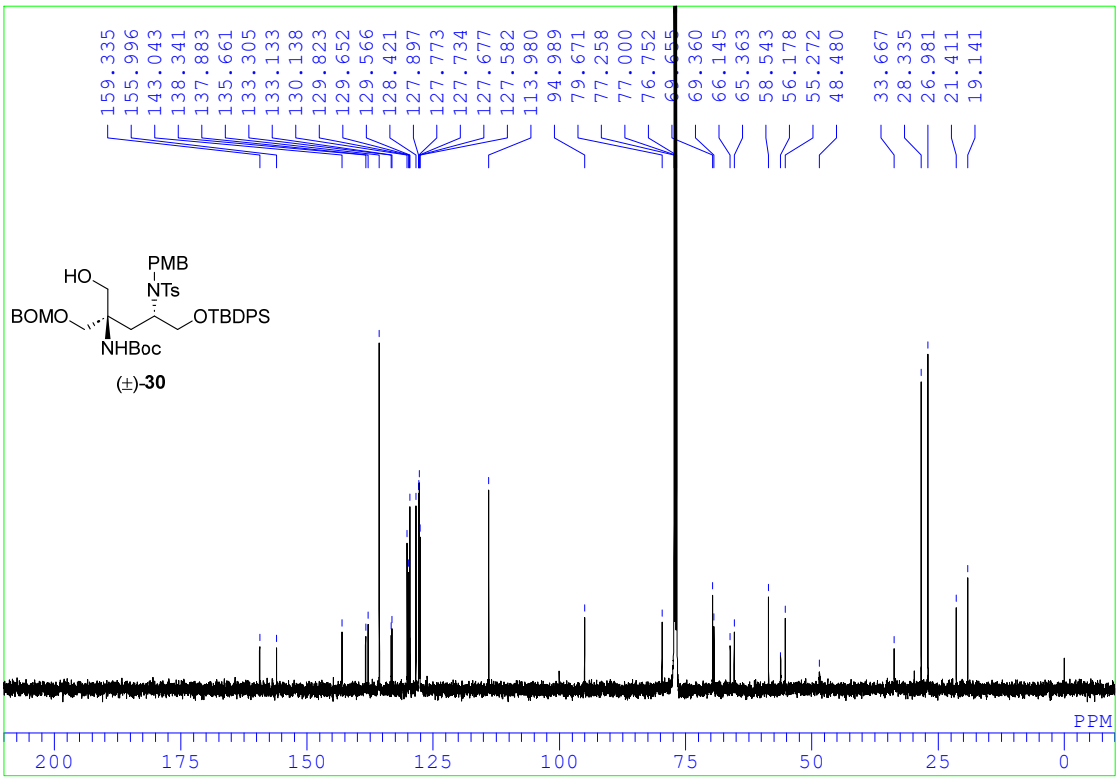
^{13}C NMR spectrum for compound 29



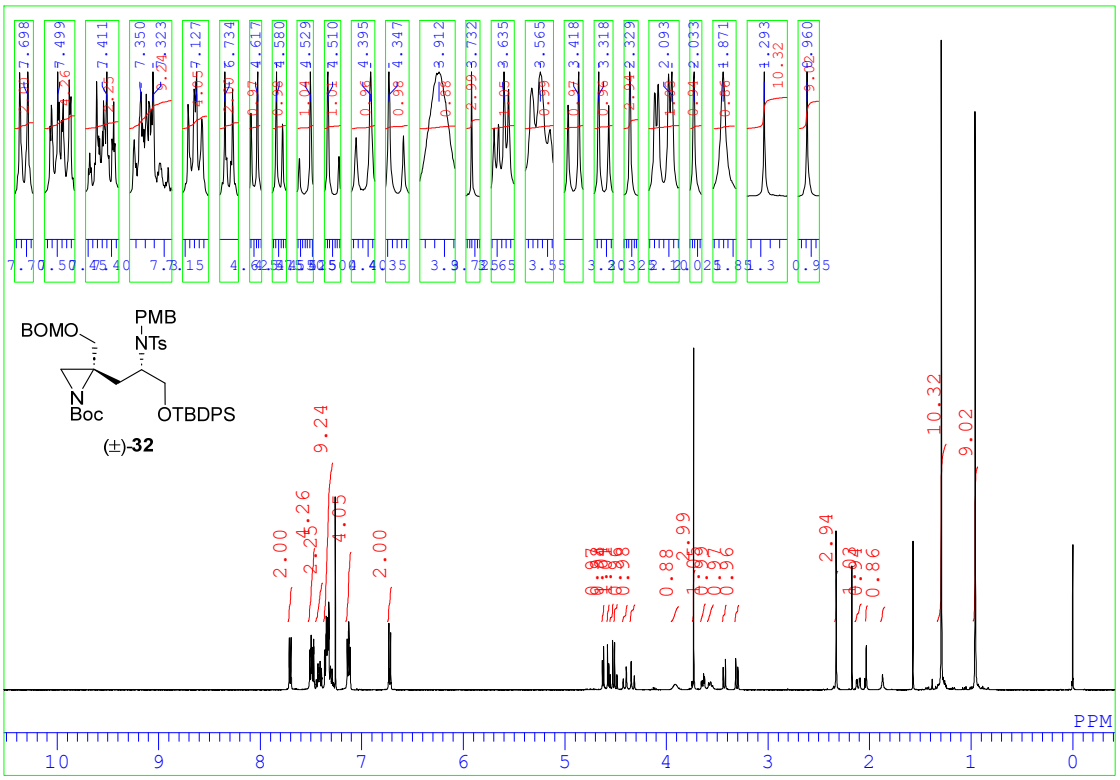
^{1}H NMR spectrum for compound 30



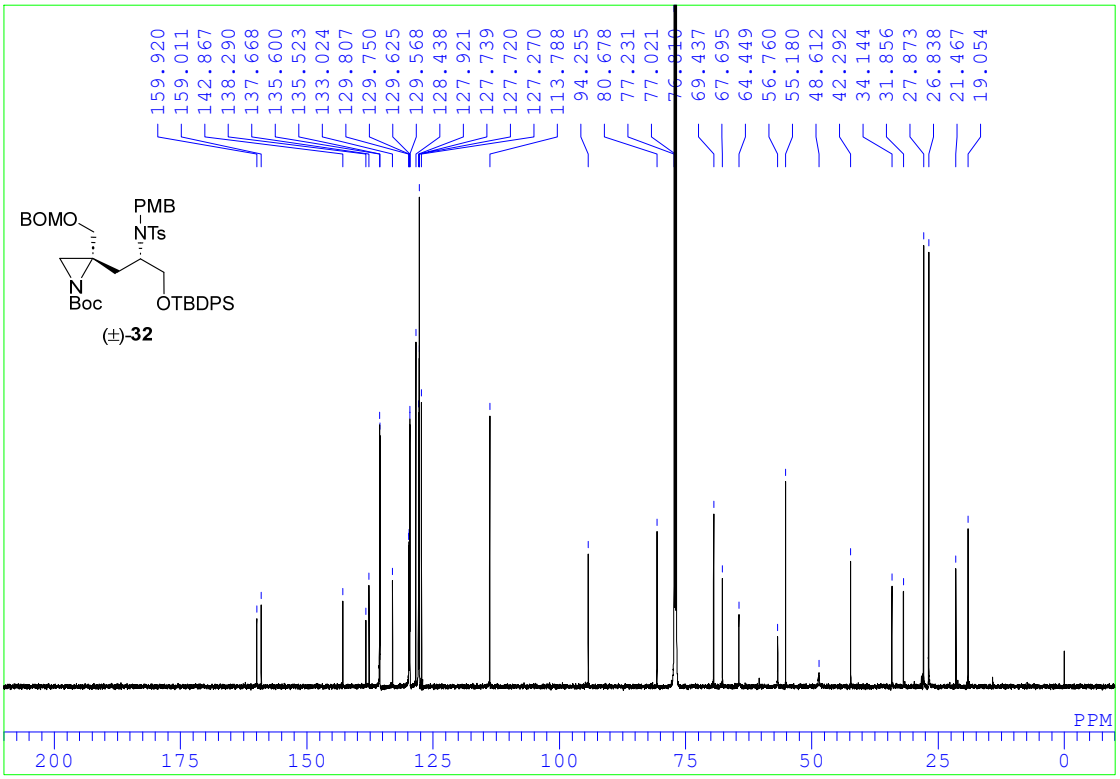
^{13}C NMR spectrum for compound 30



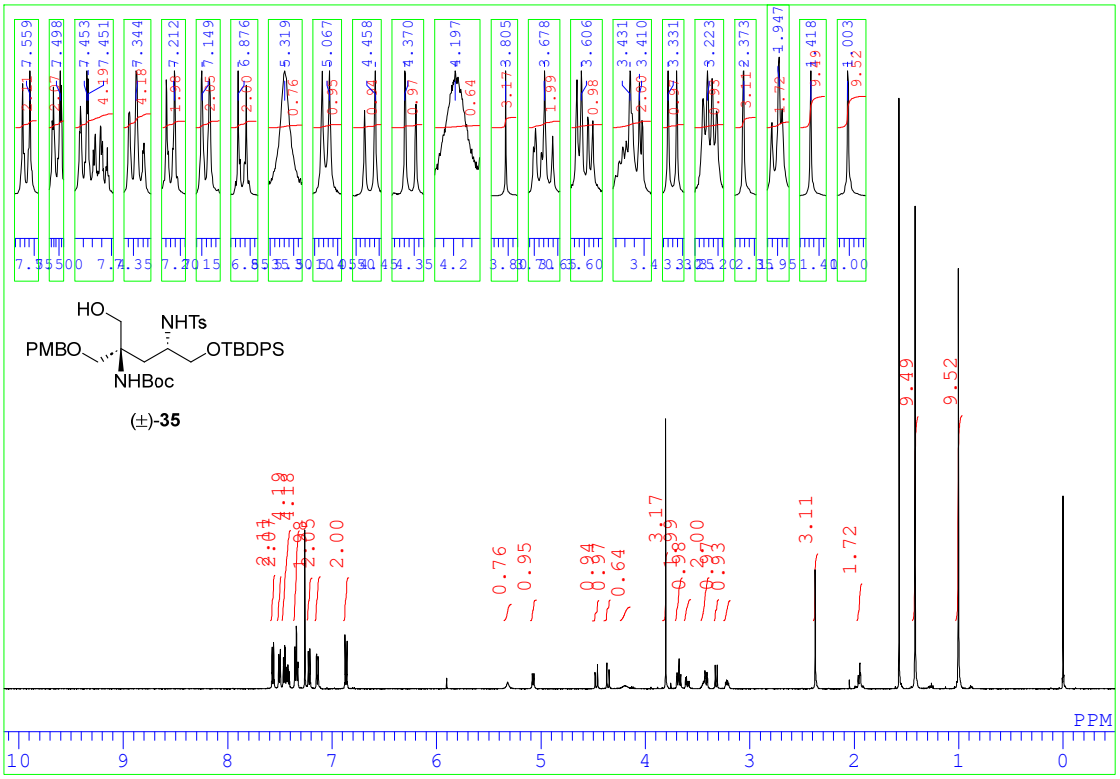
^{1}H NMR spectrum for compound 32



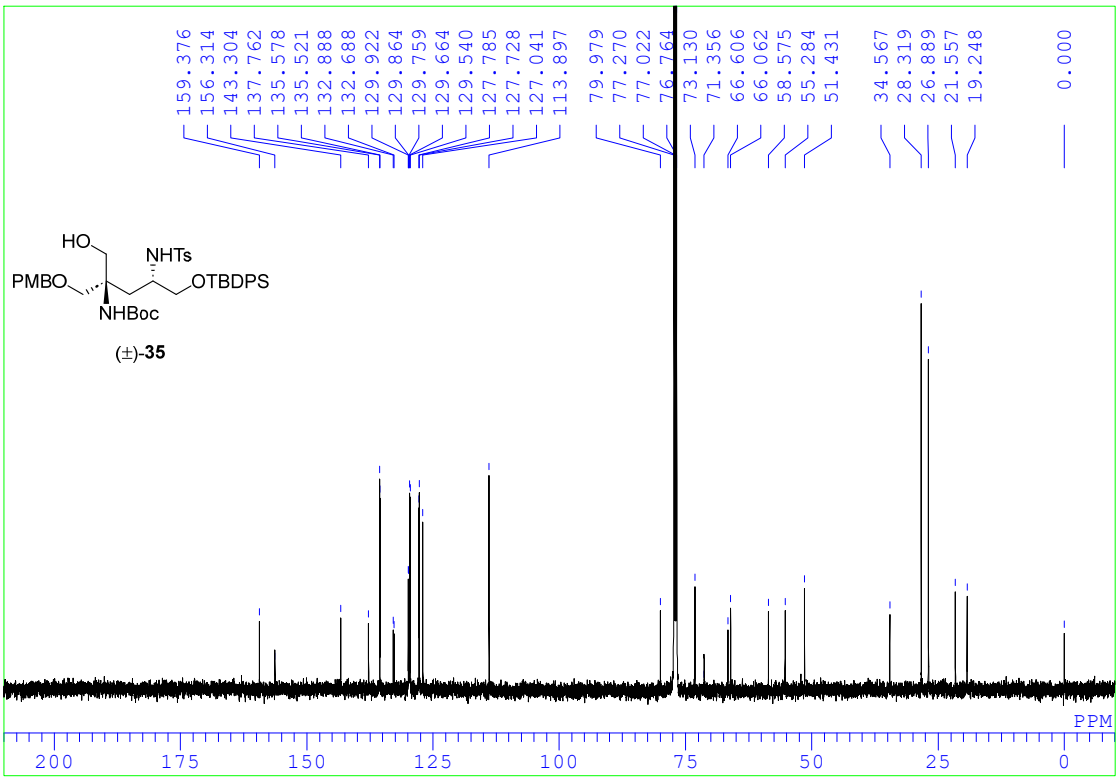
^{13}C NMR spectrum for compound 32



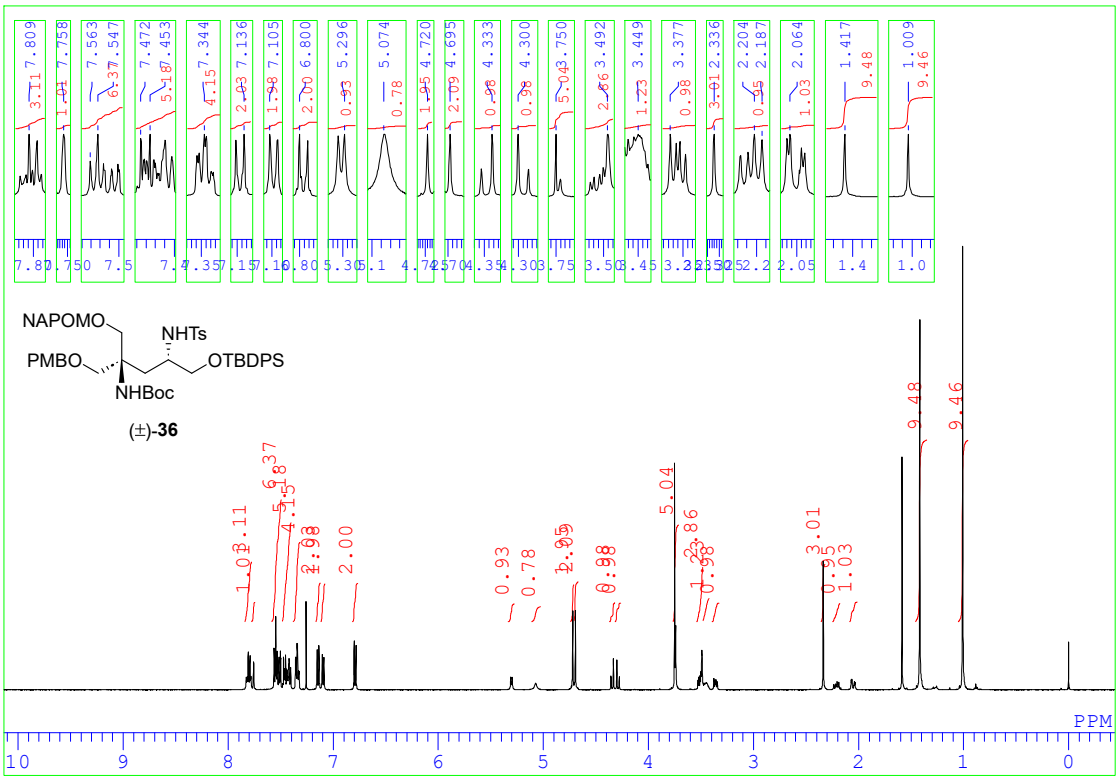
^{1}H NMR spectrum for compound 35



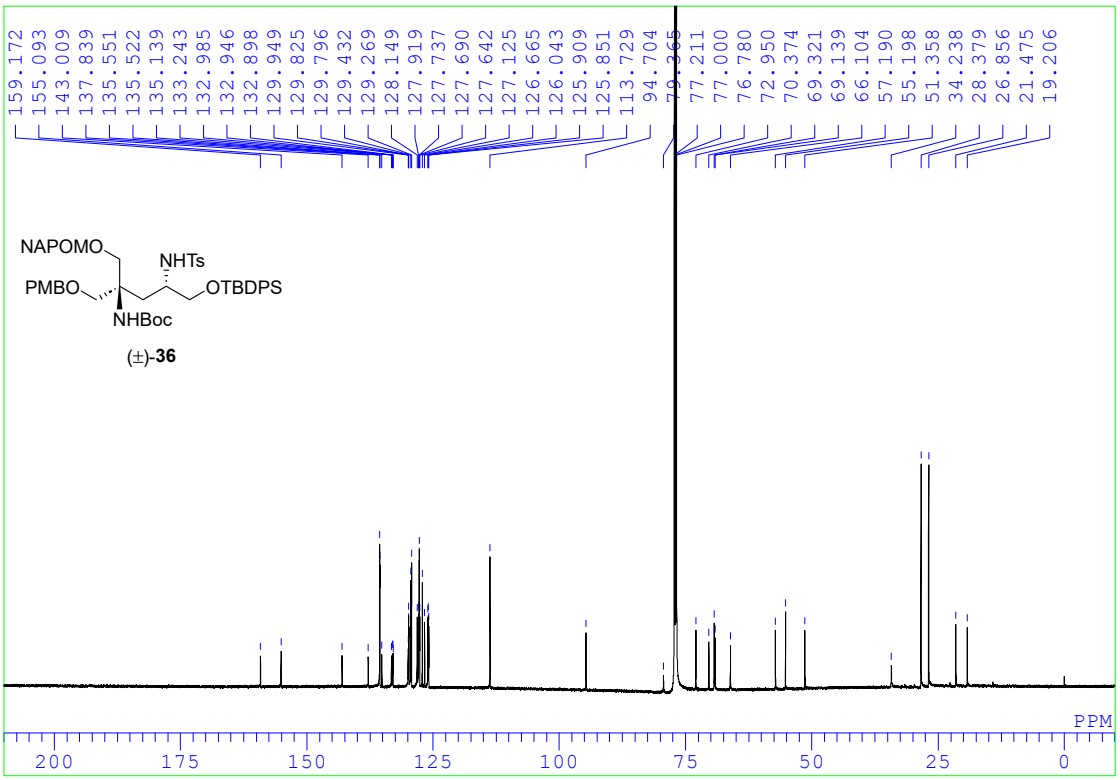
^{13}C NMR spectrum for compound 35



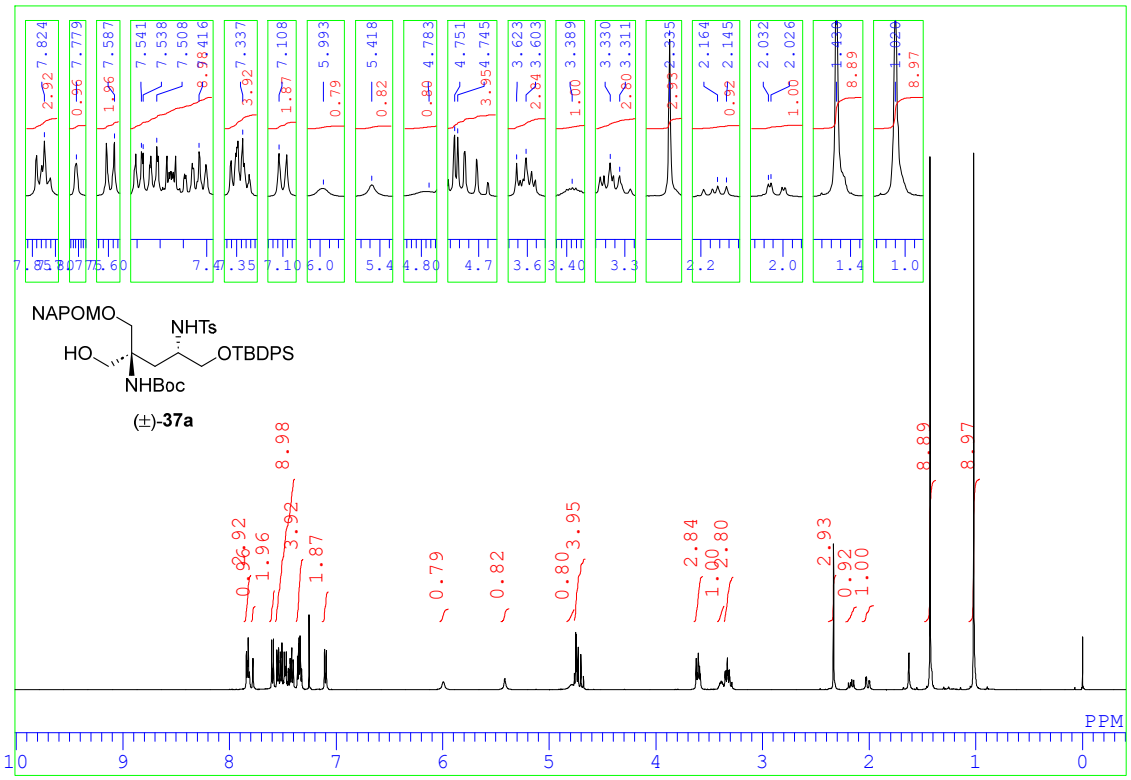
^{1}H NMR spectrum for compound 36



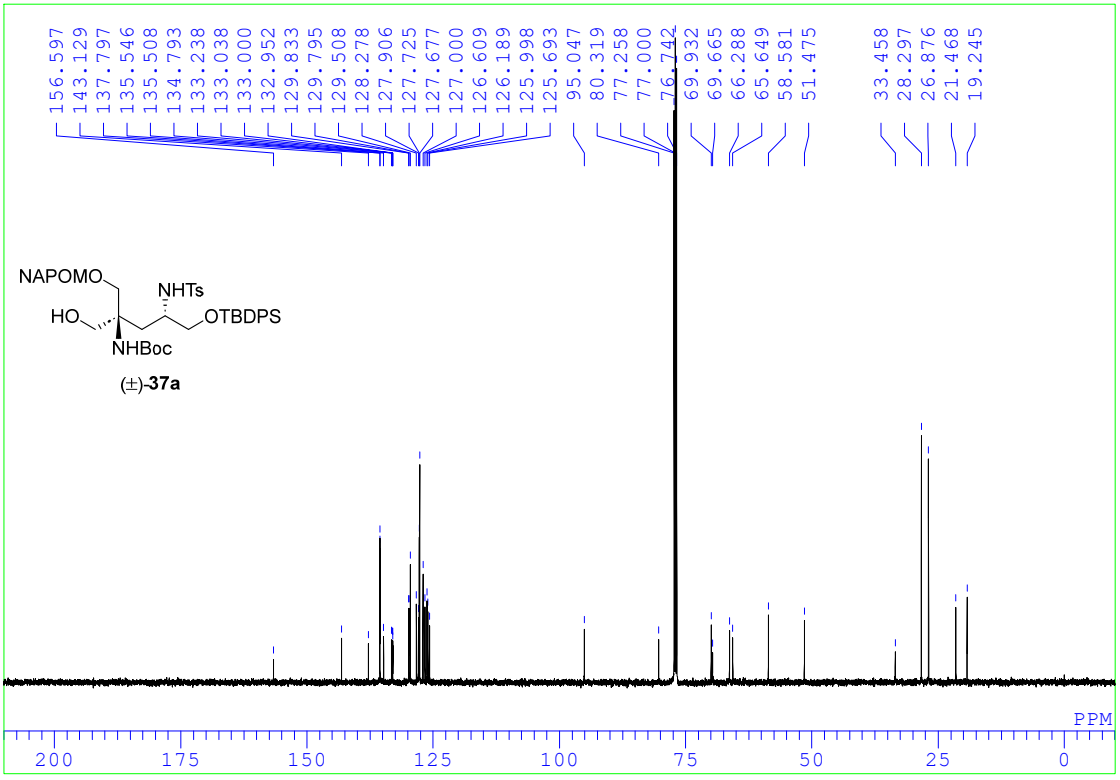
^{13}C NMR spectrum for compound 36



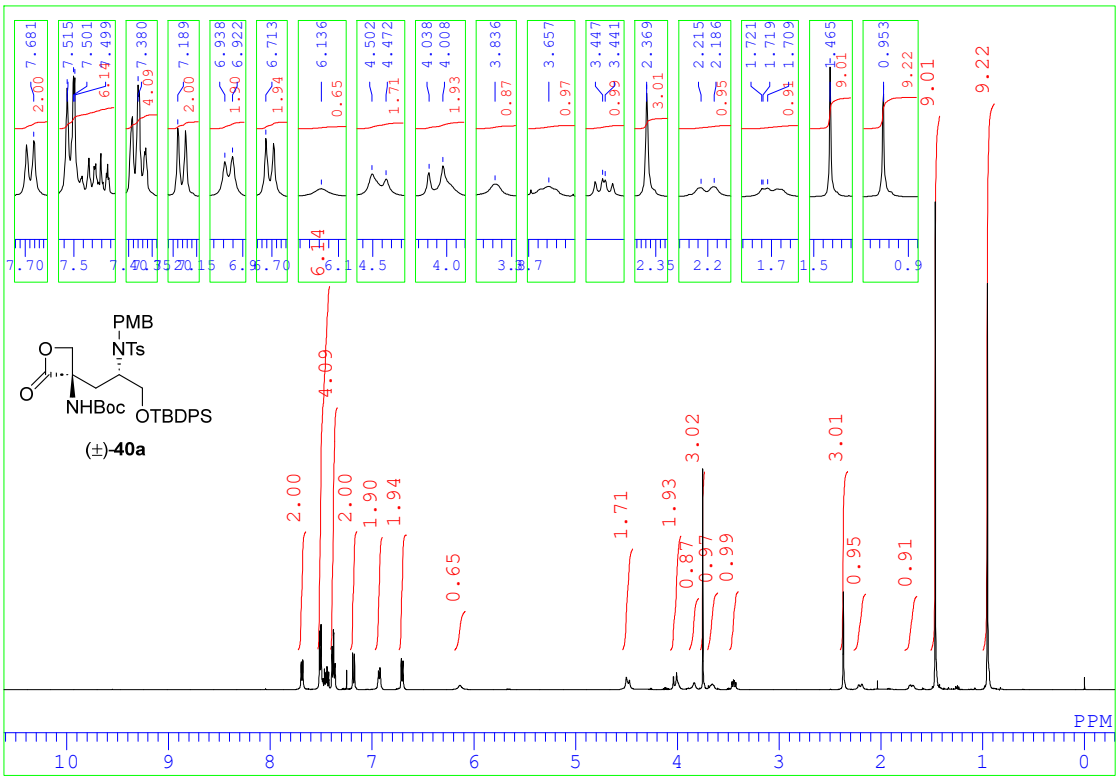
^{1}H NMR spectrum for compound 37a



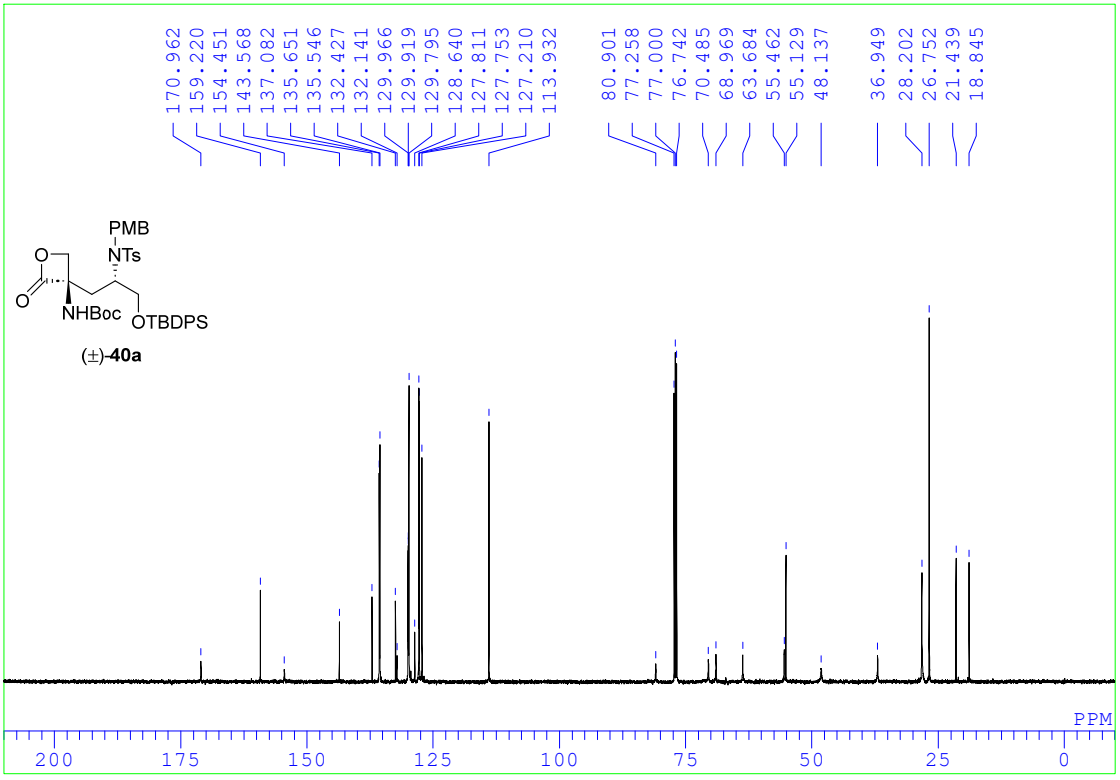
^{13}C NMR spectrum for compound 37a



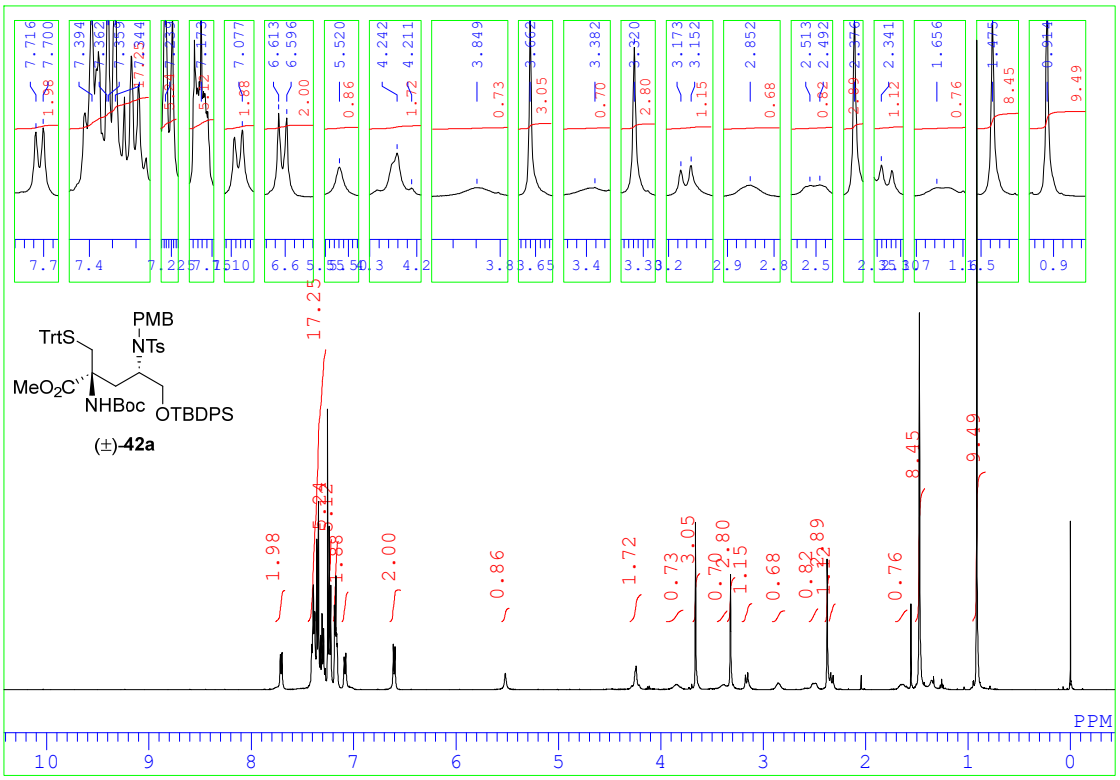
^{1}H NMR spectrum for compound 40a



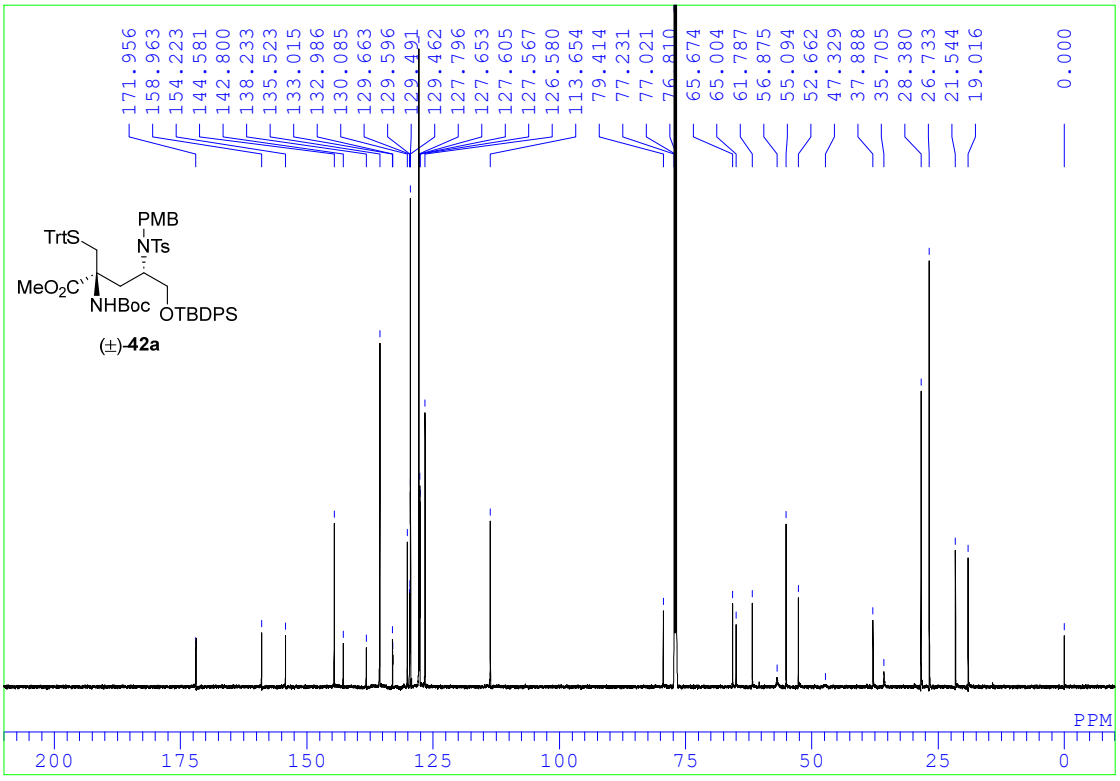
^{13}C NMR spectrum for compound 40a



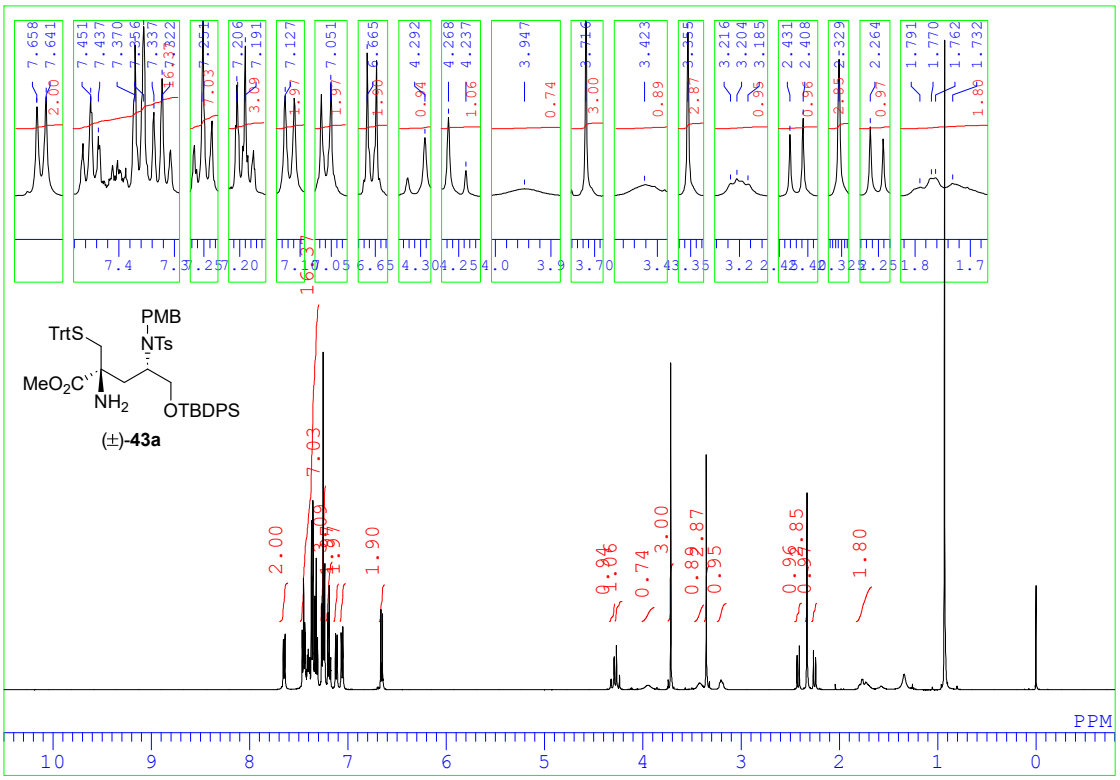
^{1}H NMR spectrum for compound 42a



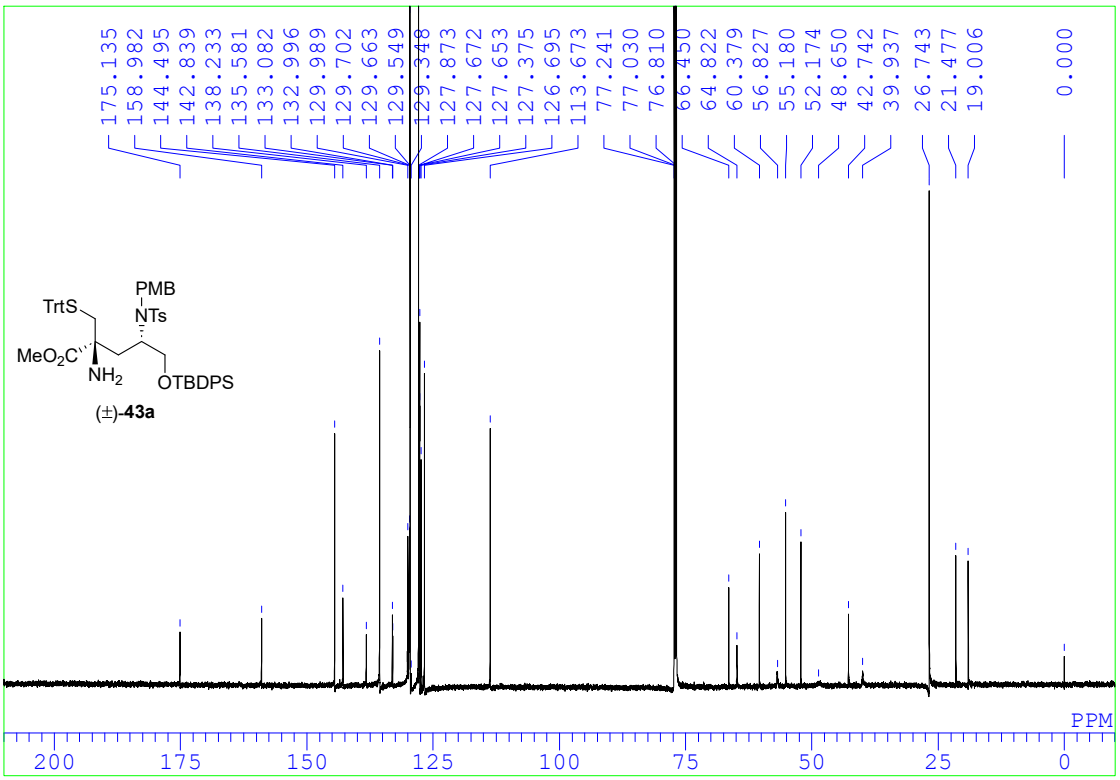
^{13}C NMR spectrum for compound 42a



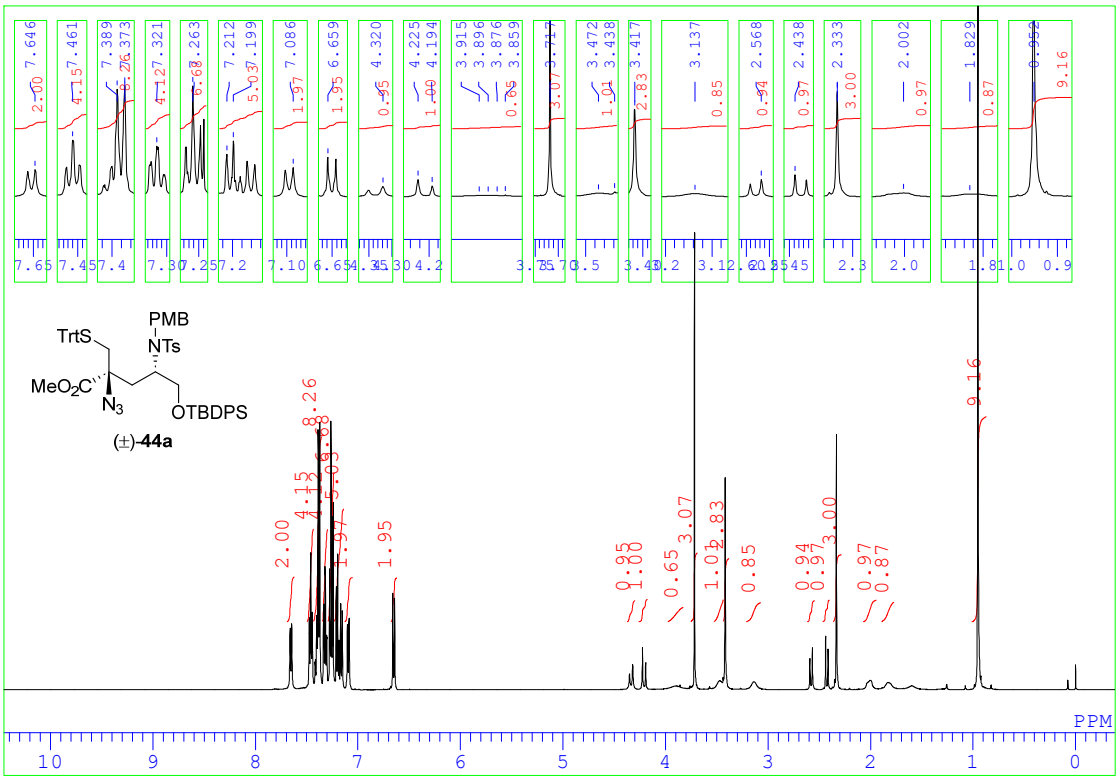
^{1}H NMR spectrum for compound 43a



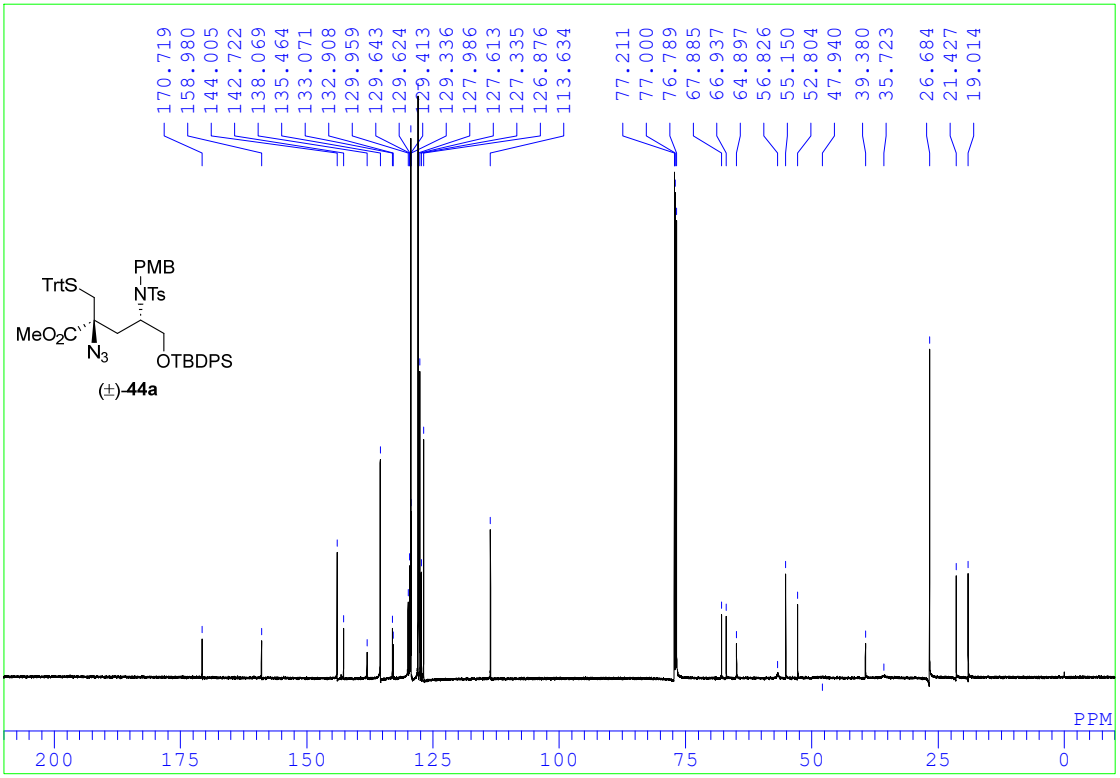
^{13}C NMR spectrum for compound 43a



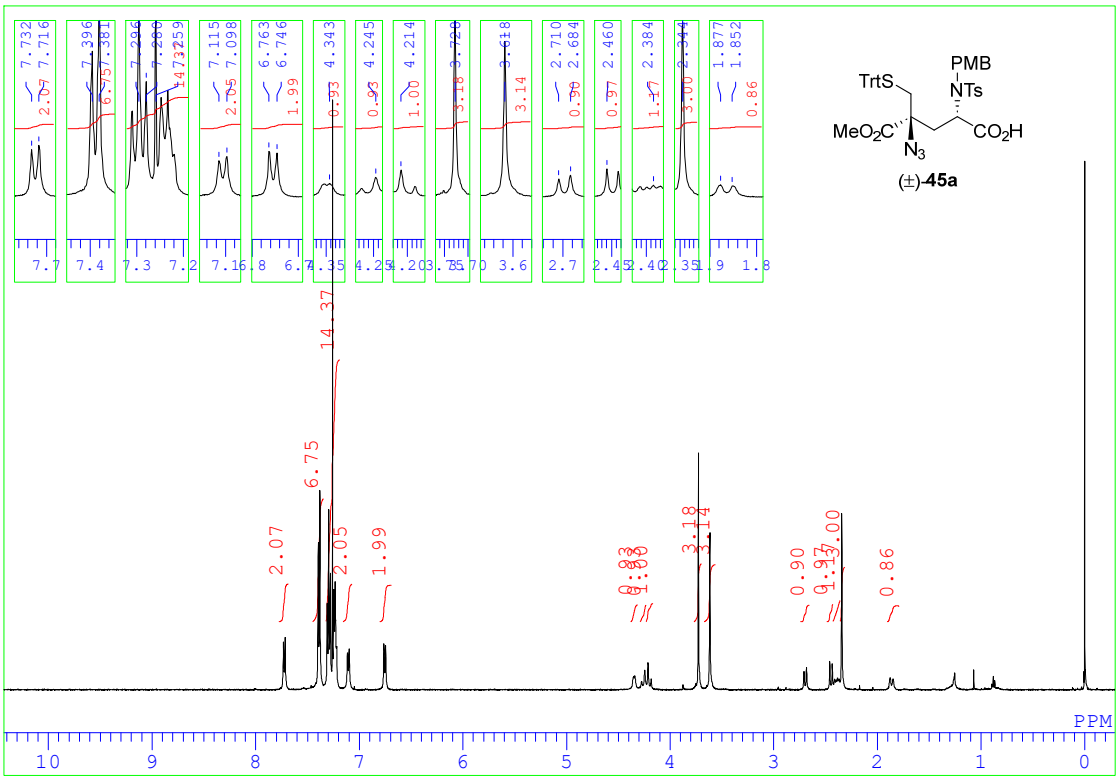
^{1}H NMR spectrum for compound 44a



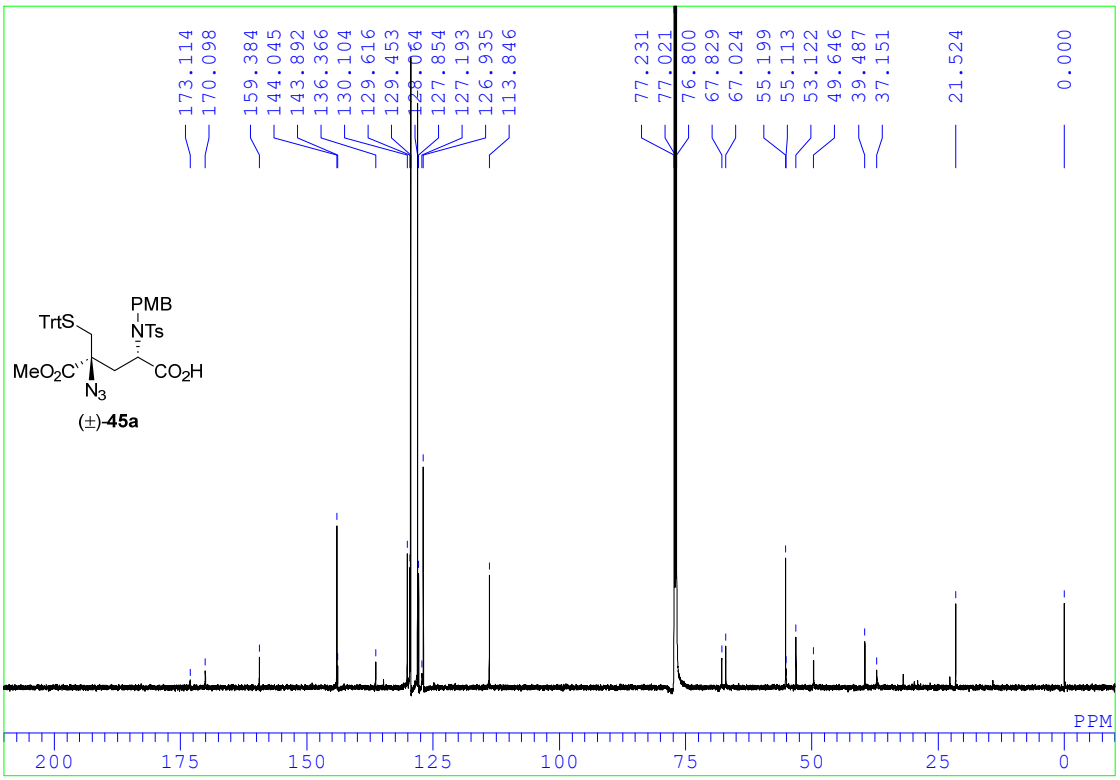
^{13}C NMR spectrum for compound 44a



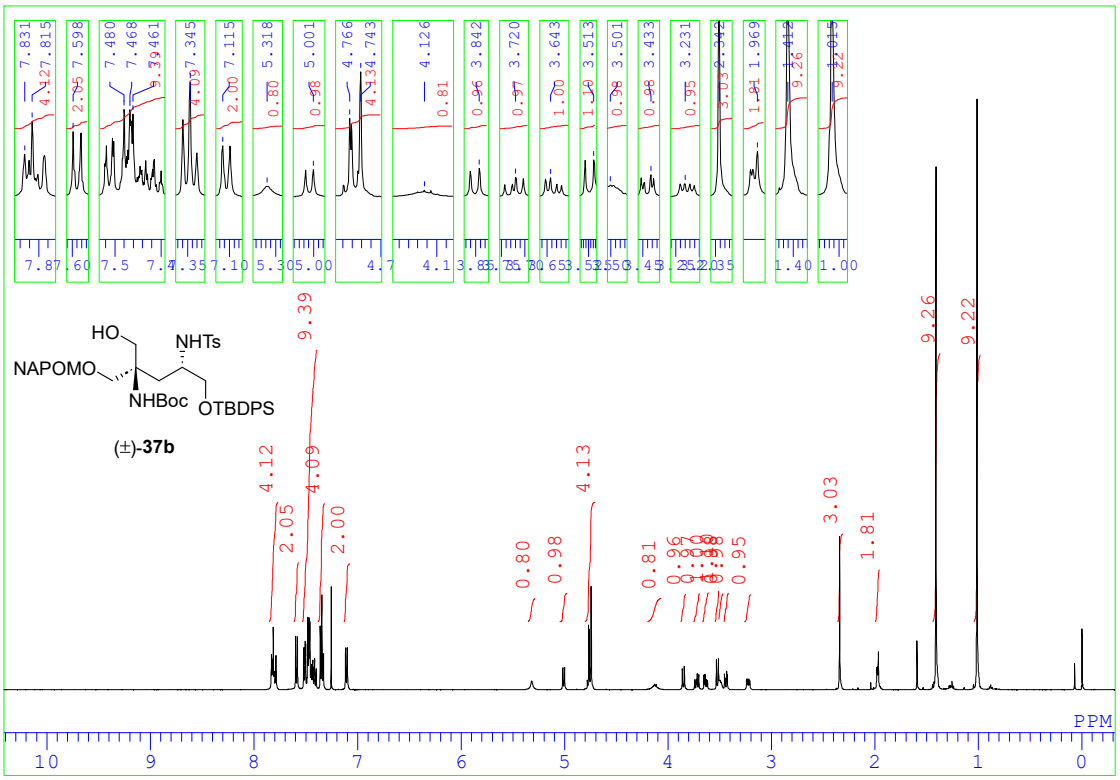
^{1}H NMR spectrum for compound 45a



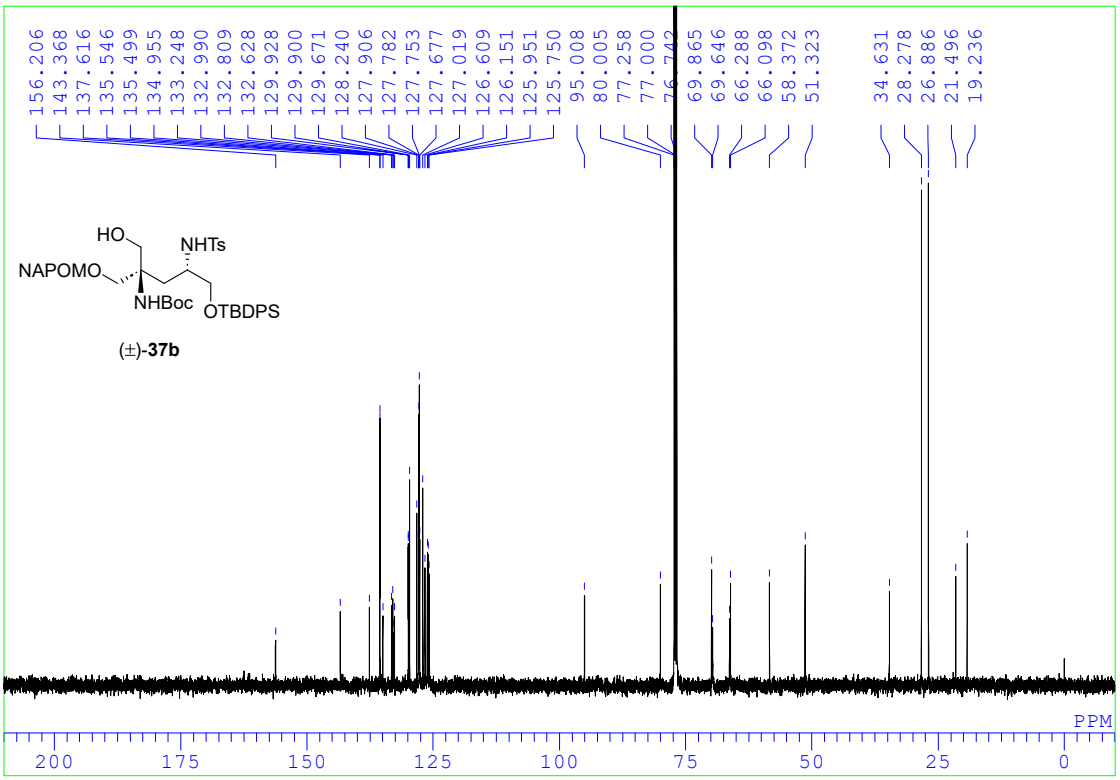
^{13}C NMR spectrum for compound 45a



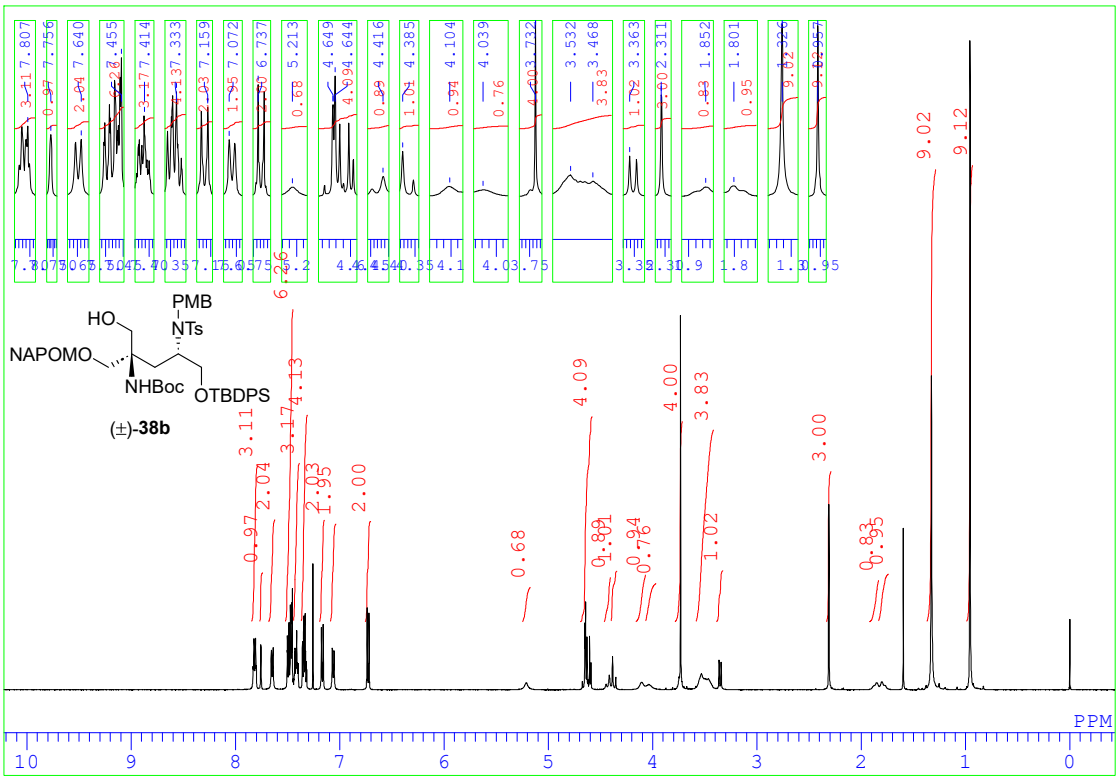
^{1}H NMR spectrum for compound 37b



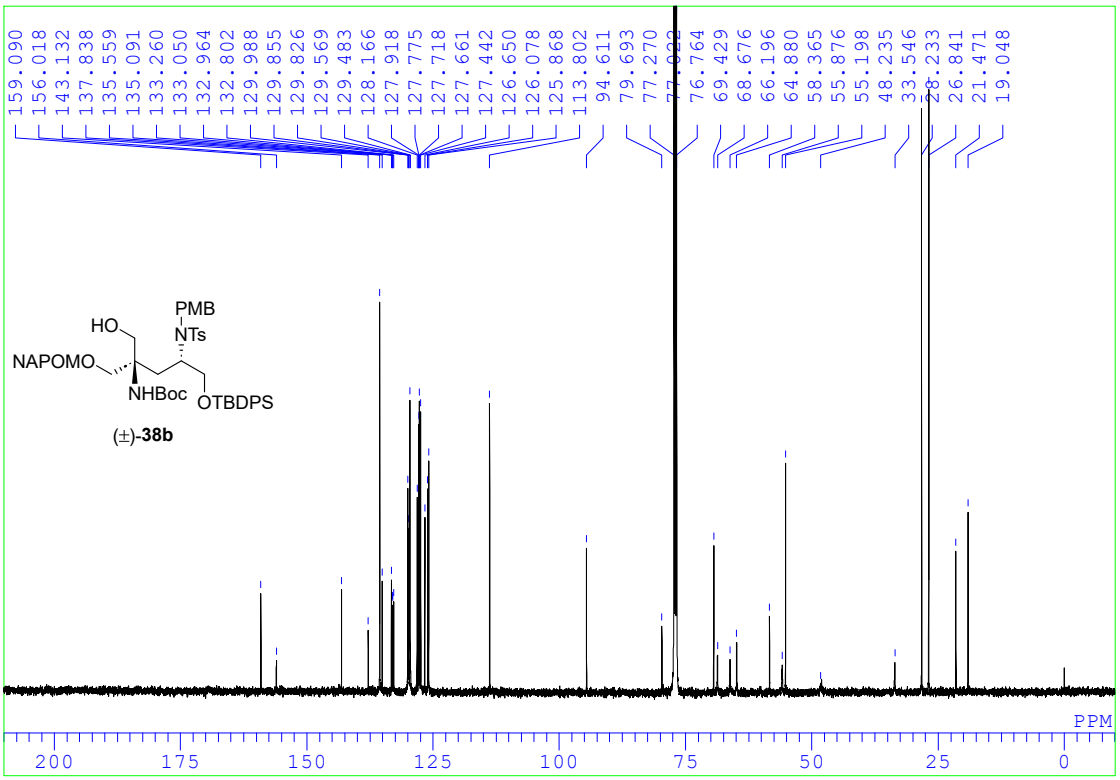
^{13}C NMR spectrum for compound 37b



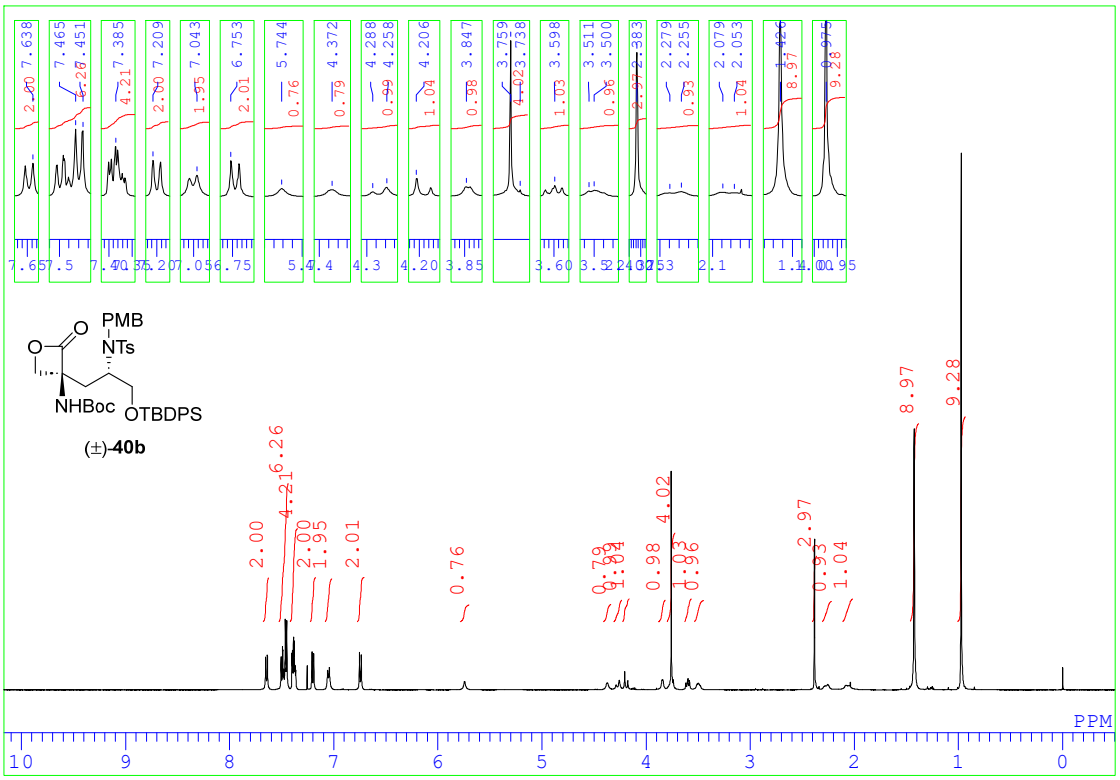
^{1}H NMR spectrum for compound 38b



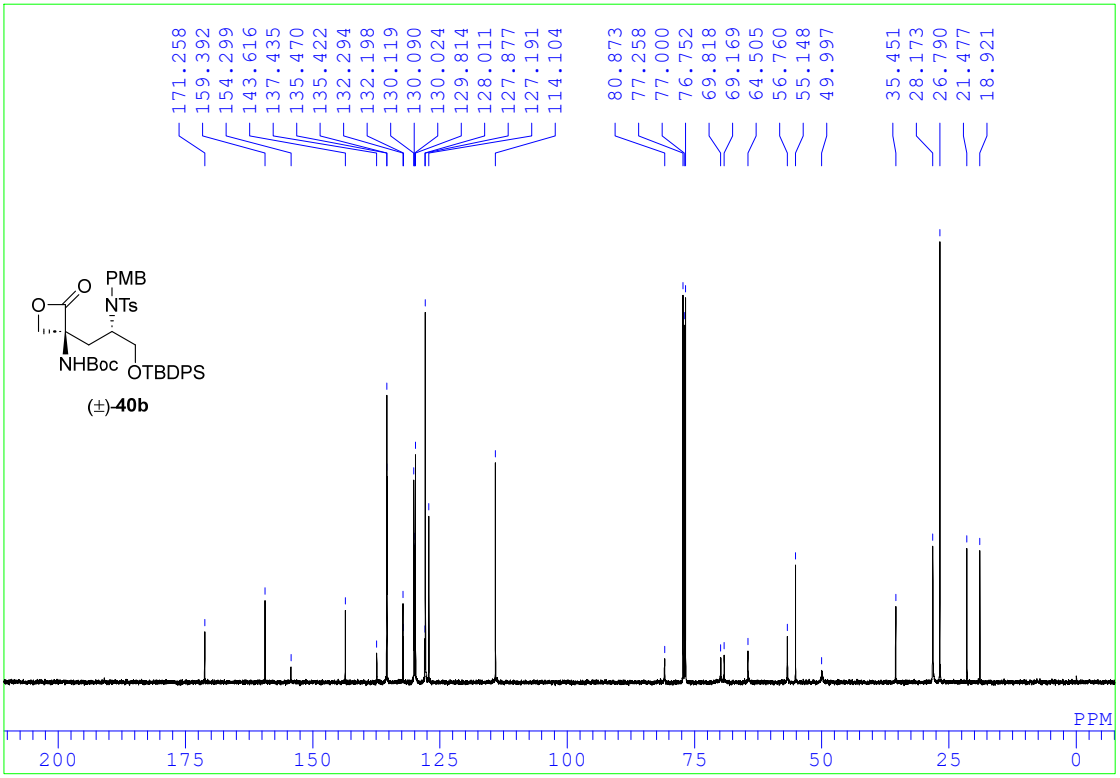
^{13}C NMR spectrum for compound 38b



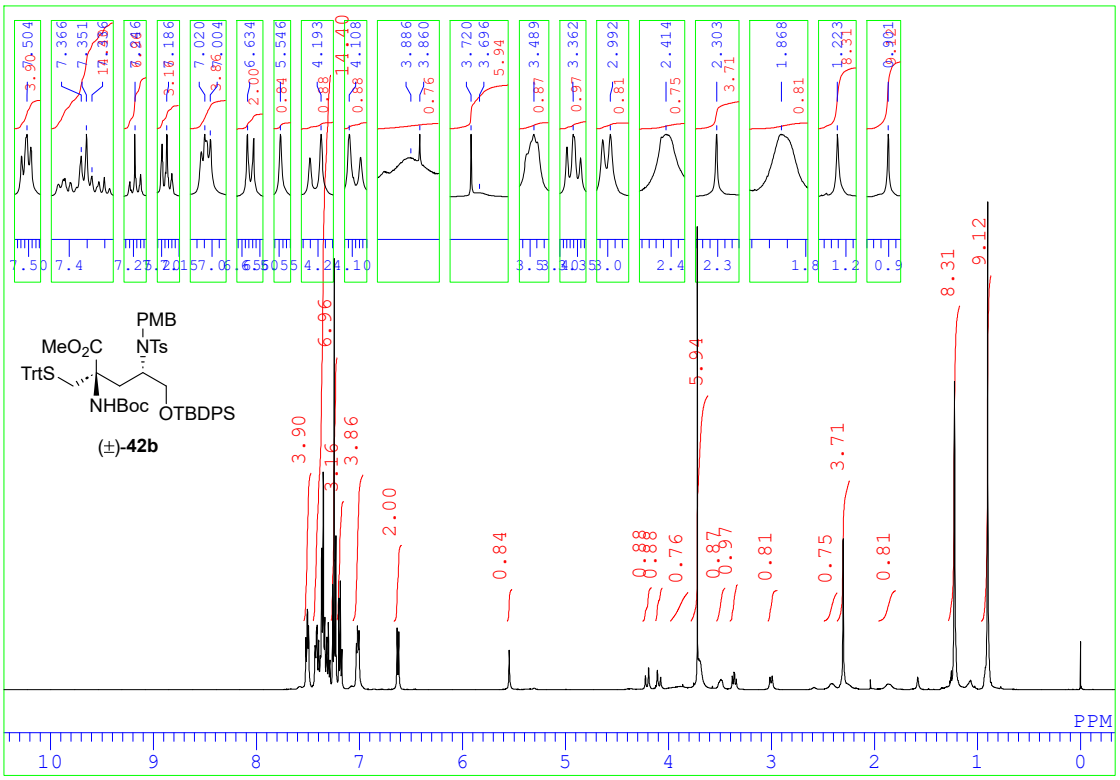
^{1}H NMR spectrum for compound 40b



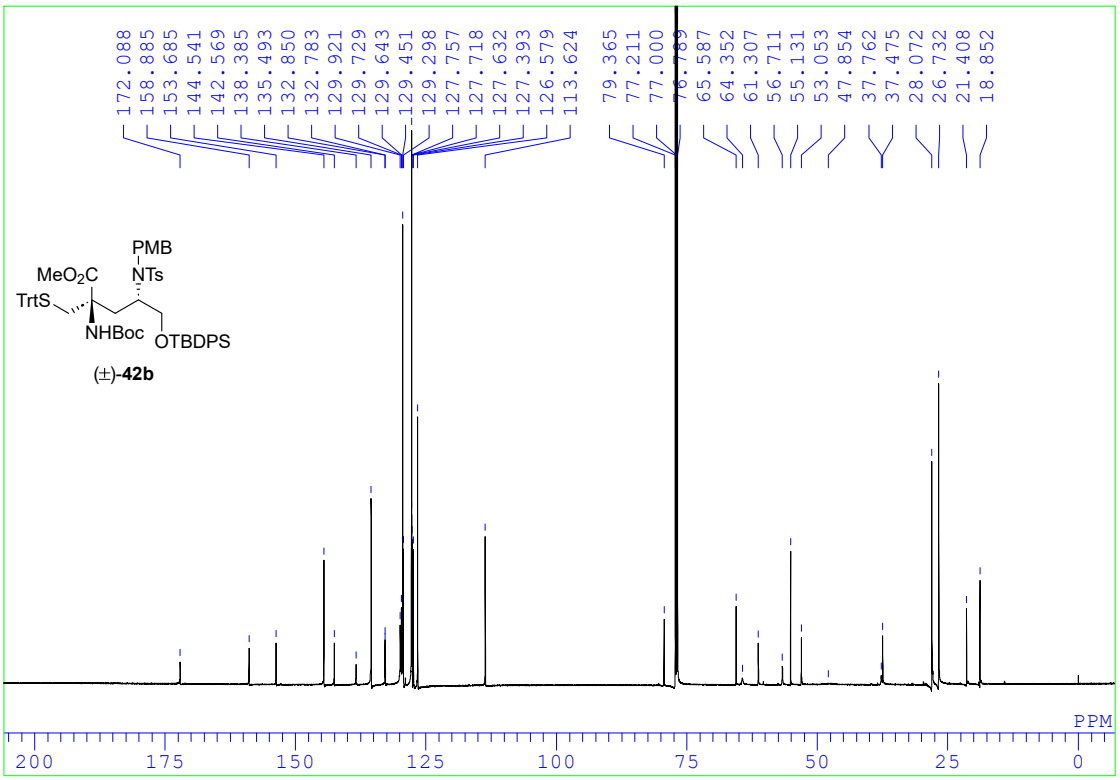
^{13}C NMR spectrum for compound 40b



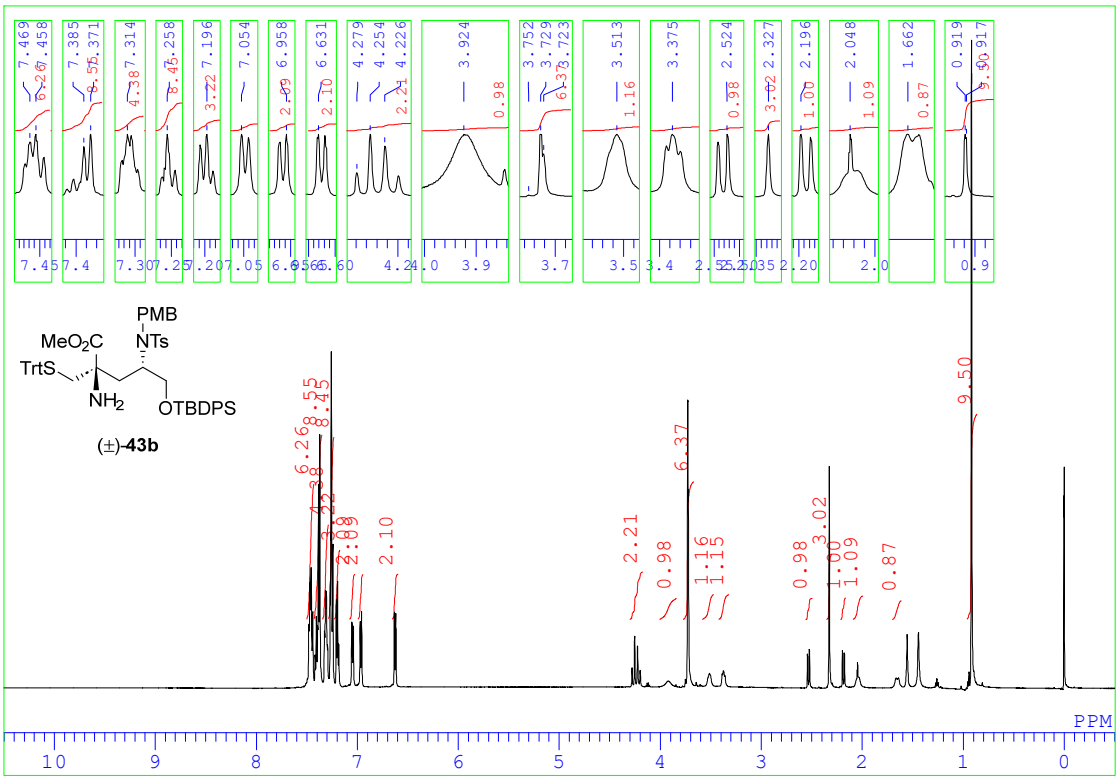
^{1}H NMR spectrum for compound 42b



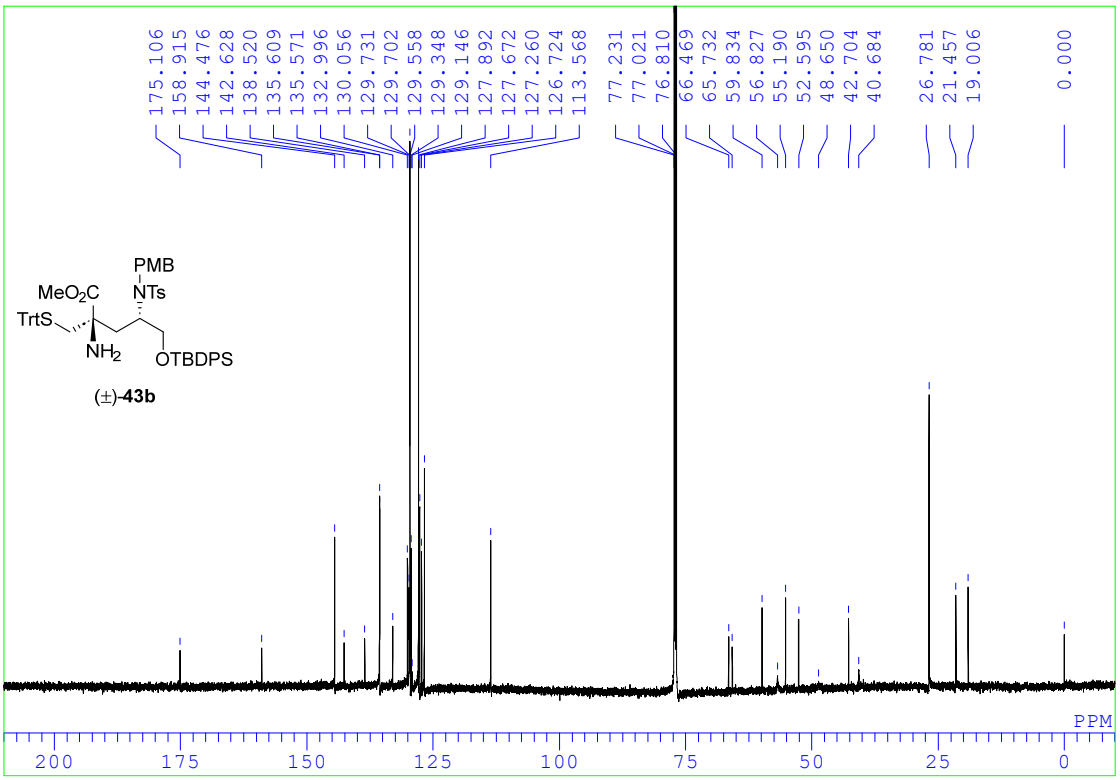
^{13}C NMR spectrum for compound 42b



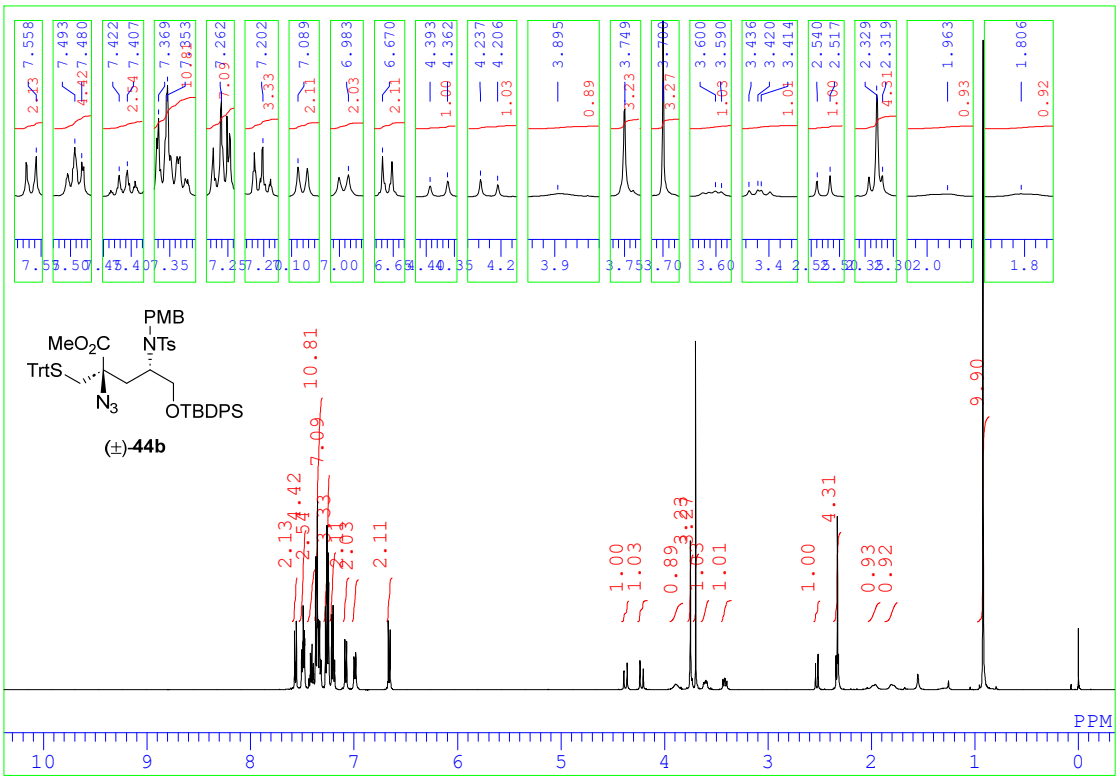
^{1}H NMR spectrum for compound 43b



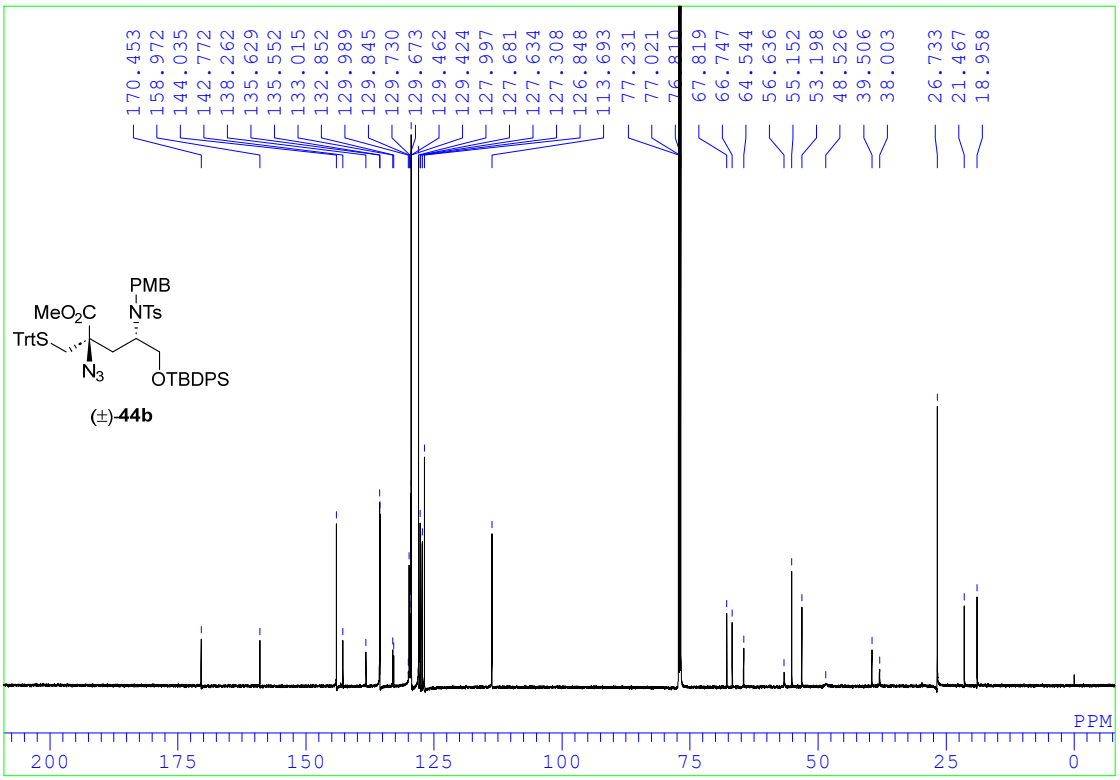
^{13}C NMR spectrum for compound 43b



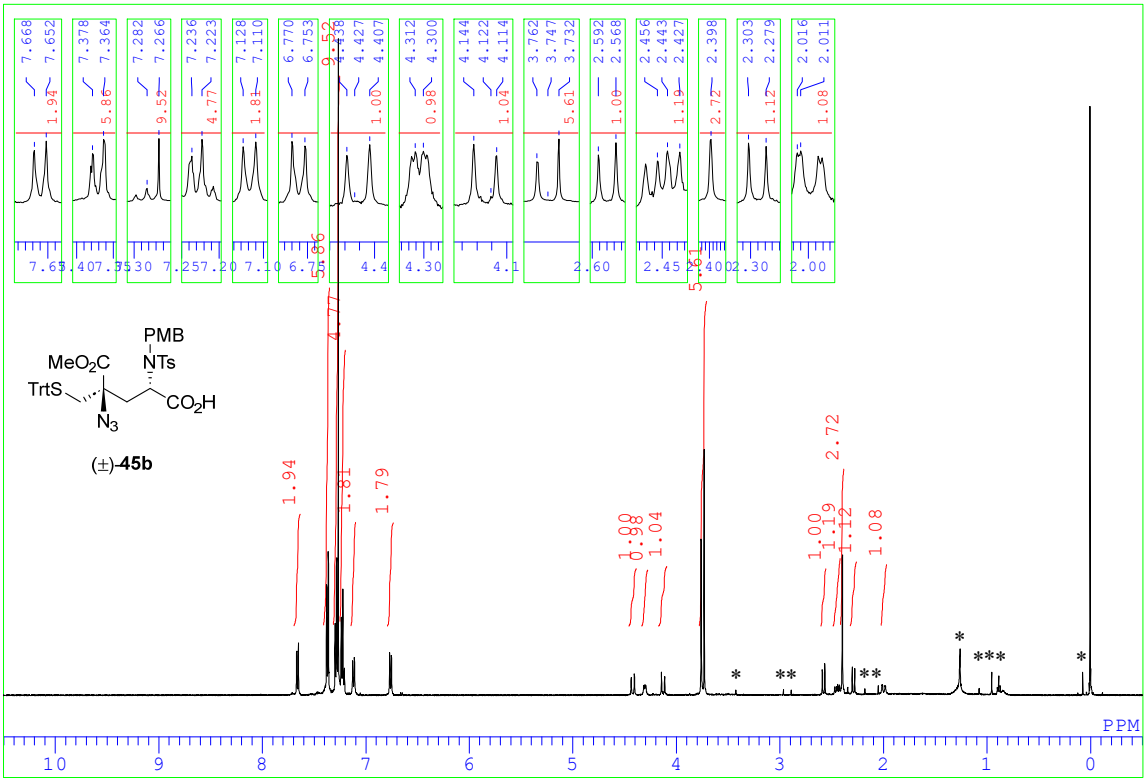
^{1}H NMR spectrum for compound 44b



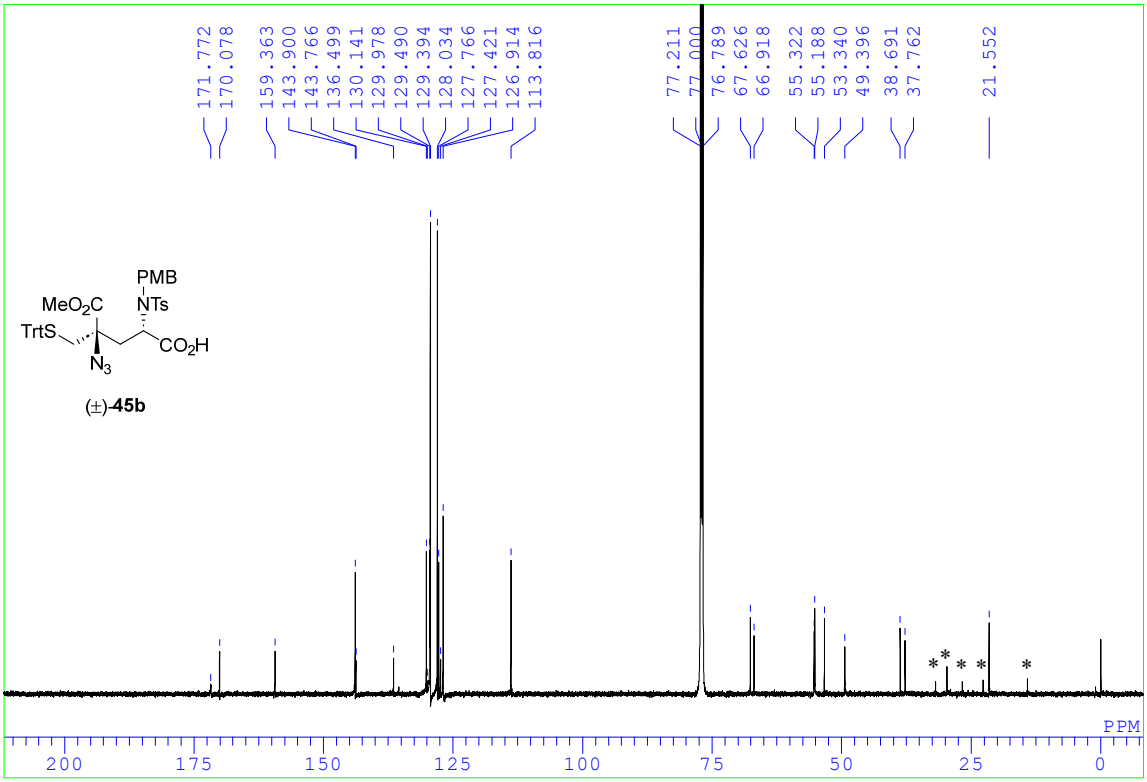
^{13}C NMR spectrum for compound 44b



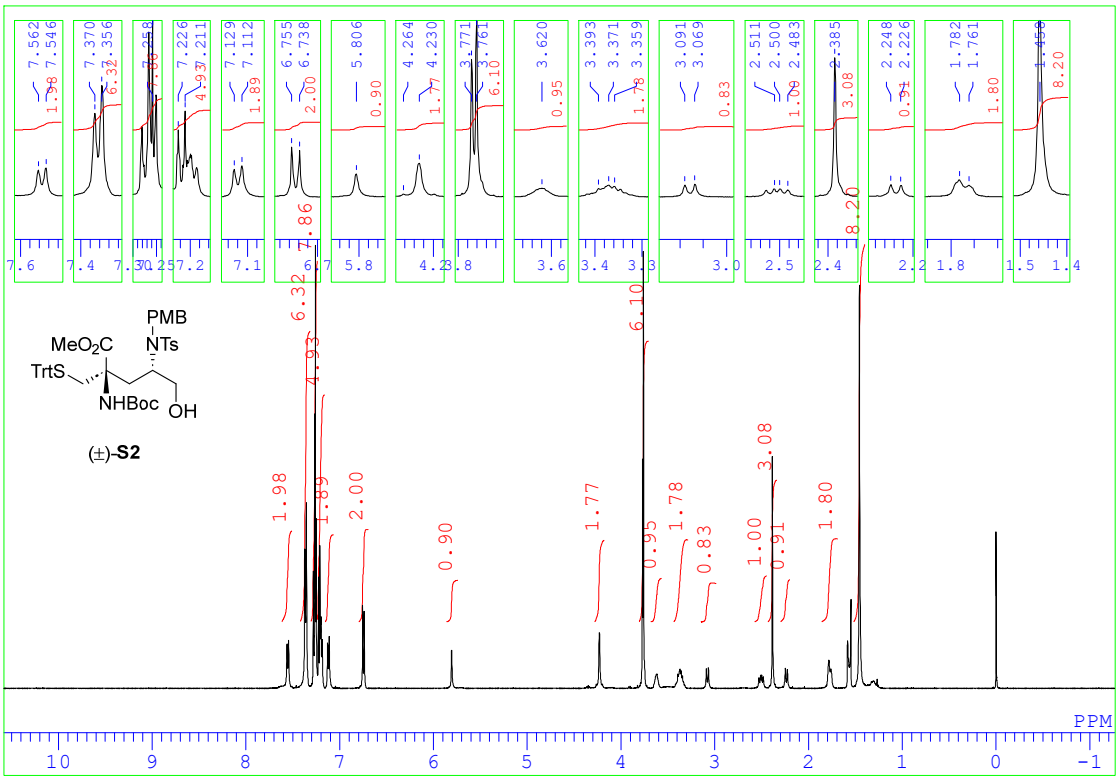
^{1}H NMR spectrum for compound 45b (* indicates peaks derived from the minor impurities)



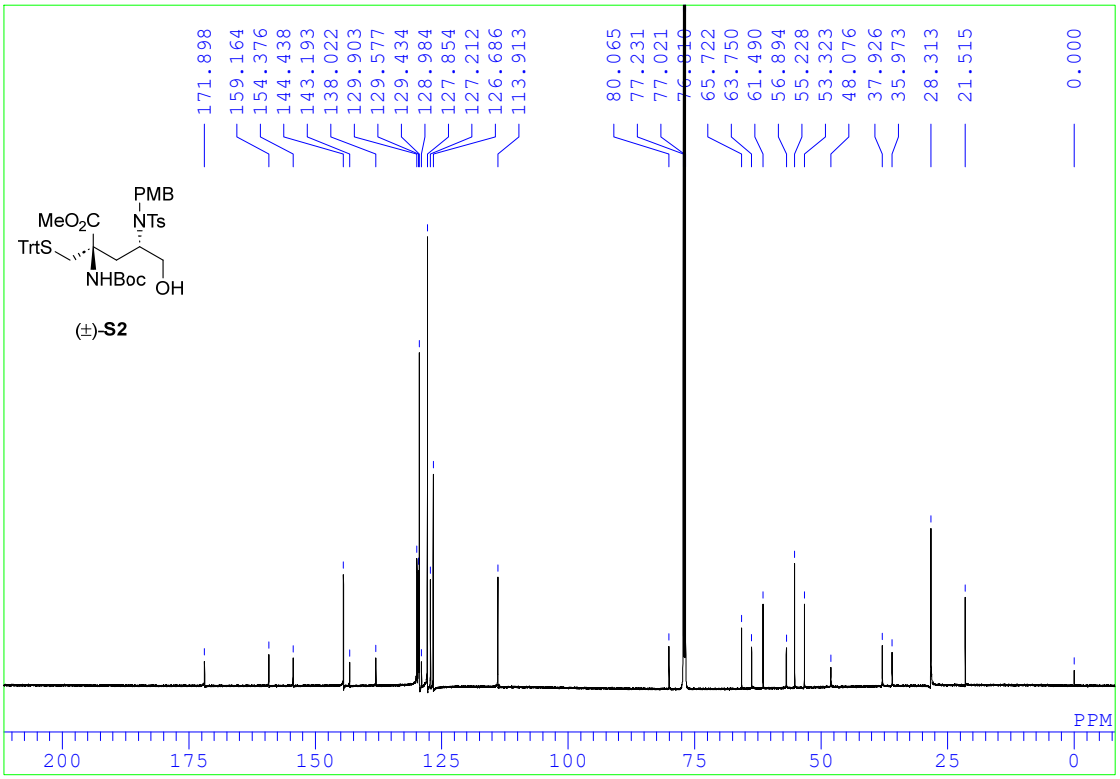
^{13}C NMR spectrum for compound 45b (* indicates peaks derived from the minor impurities)



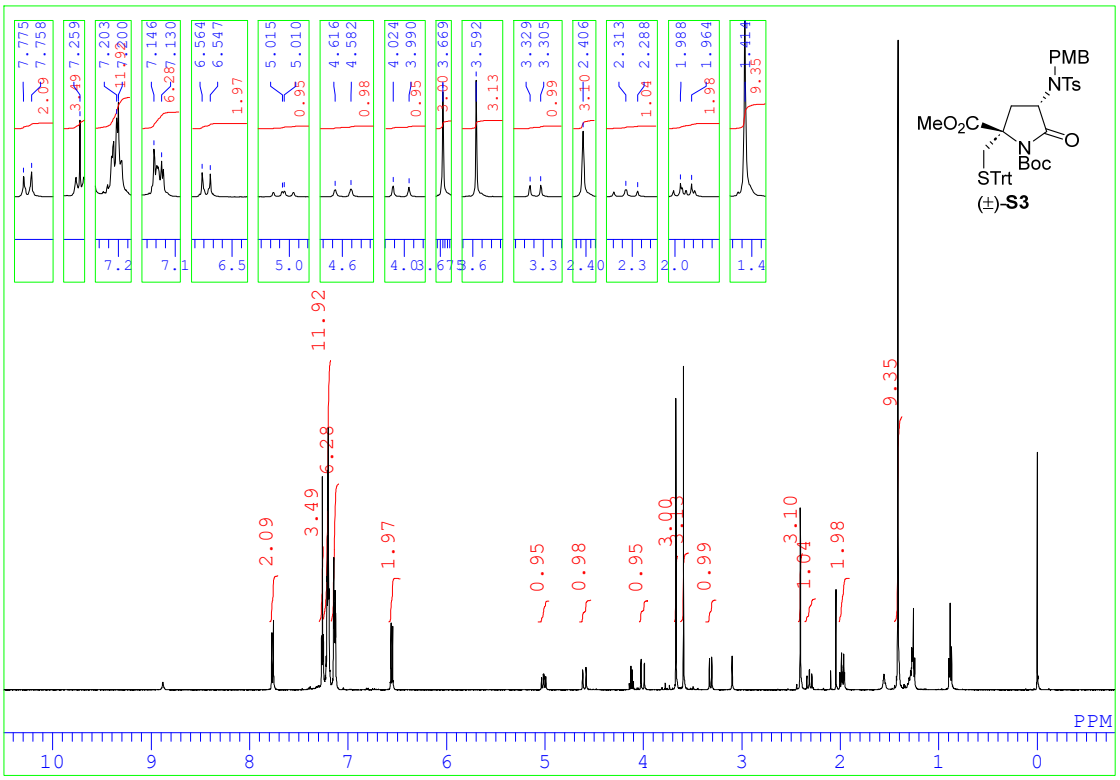
^{1}H NMR spectrum for compound S2



^{13}C NMR spectrum for compound S2



^{1}H NMR spectrum for compound S3



^{13}C NMR spectrum for compound S3