Supporting Information for

Construction of Indole Structure on Pyrroloindolines via $AgNTf_2$-Mediated Amination/Cyclization Cascade: Application to Total Synthesis of (+)-Pestalazine B

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Contents

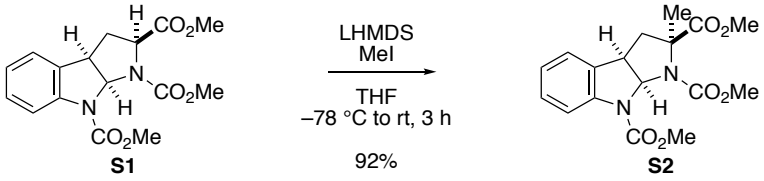
1. General Remarks

Materials were obtained from commercial suppliers and used without further purification unless otherwise mentioned. All reactions were carried out in oven-dried glassware under a slight positive pressure of argon unless otherwise noted. Anhydrous Et_2O, THF, MeCN, and CH_2Cl_2 were purchased from Kanto Chemical Co. Inc. Anhydrous toluene and DMF were purchased from Wako Pure Chemical Industries. Anhydrous MeOH and 1,2-dichloroethane were dried and distilled according to the standard protocols. Flash column chromatography was performed on Silica Gel 60N (Kanto, spherical neutral, 40–50 μm) using the indicated eluent. Preparative TLC was performed on Merck 60 F_{254} glass plates precoated with a 0.50 mm and a 0.25 mm thickness of silica gel. Analytical TLC was performed on Merck 60 F_{254} glass plates precoated with a 0.25 mm thickness of silica gel. IR spectra were measured on a JASCO FT/IR-4100 spectrometer. NMR spectra were recorded on a JNM-AL400 or JNM-AL600 spectrometer with tetramethylsilane (0 ppm), MeCN (1.93 ppm), acetone (2.04 ppm), methanol (3.31 ppm), and chloroform (7.26 ppm) as an internal standard. Chemical shifts were expressed in δ (ppm) values, and coupling constants were expressed in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. Mass spectra were recorded on a Brucker micrOTOF II (ESI).

2. Experimental Procedure for Construction of Indole Structure

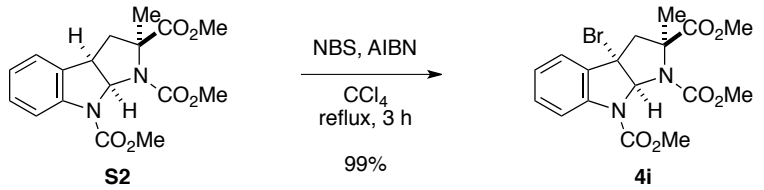
Preparation of Substrates

Pyrroloindoline S2



To a stirred solution of pyrroloindoline **S1** (1.53 g, 4.58 mmol) and DMPU (670 μL, 5.54 mmol) in THF (43 mL) was added LHMDS (8.54 mL, 11.1 mmol, 1.3 M in THF) at –78 °C. After 1 h, MeI was added to the reaction mixture and the resulting mixture was allowed to room temperature. After 2 h, the reaction mixture was concentrated under reduced pressure. The residue was diluted with EtOAc and washed with 1 M aqueous HCl and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 1/1) to afford pyrroloindoline **S2** (1.48 g, 4.23 mmol, 92%) as a white foam. R_f = 0.28 (hexanes/EtOAc = 1/1); $[\alpha]_D^{25}$ = –18.7 (*c* 0.715, $CHCl_3$); IR (film, cm^{-1}) 3015, 2952, 1714, 1483, 1446, 1064, 752; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (1H, d, *J* = 8.0 Hz), 7.21 (1H, dd, *J* = 8.0, 7.6 Hz), 7.08 (1H, d, *J* = 7.2 Hz), 7.01 (1H, dd, *J* = 7.6, 7.2 Hz), 6.43 (1H, d, *J* = 6.4 Hz), 3.91–3.85 (4H, m), 3.71 (3H, s), 3.05 (3H, s), 2.82 (1H, d, *J* = 13.6 Hz), 2.31 (1H, dd, *J* = 13.6, 7.2 Hz), 1.68 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 154.1, 154.0, 142.6, 131.7, 128.1, 123.4, 123.3, 116.8, 78.3, 66.0, 52.6, 52.0, 51.8, 42.8, 42.5, 25.2; HRMS (ESI) calcd. for $C_{17}H_{20}N_2NaO_6$ $[M+Na]^+$, 371.1214; found 371.1203.

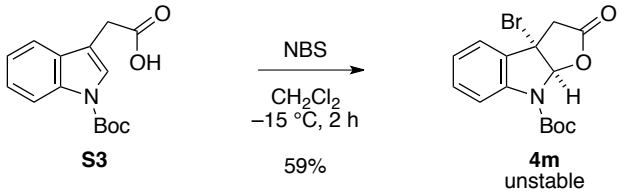
Bromopyrroloindoline 4i



To a stirred solution of pyrroloindoline **S2** (694 mg, 1.99 mmol) and NBS (354 mg, 1.99 mmol) in CCl_4 (40 mL) was AIBN (32.7 mg, 0.199 mmol) added at room temperature and the resulting mixture was heated to reflux. After 3 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 3/2) to afford bromopyrroloindoline **4i** (839 mg, 1.96 mmol, 99%) as a white foam. R_f = 0.40 (hexanes/EtOAc = 1/1); $[\alpha]_D^{25}$ = 121 (*c* 0.331, $CHCl_3$); IR (film, cm^{-1}) 3017, 2953, 1716, 1480, 1445, 754; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (1H, d, *J* = 7.6 Hz), 7.34–7.27 (2H, m), 7.08 (1H,

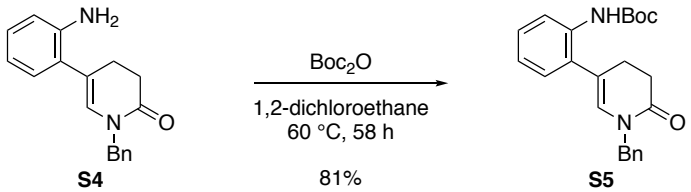
dd, J = 7.6, 7.2 Hz), 6.49 (1H, brs), 3.94 (3H, s), 3.71 (3H, s), 3.48 (1H, d, J = 13.2 Hz), 3.03 (3H, s), 2.88 (1H, d, J = 13.2 Hz), 1.73 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 153.8, 153.4, 141.9, 132.4, 130.5, 124.1, 123.5, 117.6, 85.5, 66.9, 58.2, 53.1, 52.1, 51.7, 25.3; HRMS (ESI) calcd. for $C_{17}H_{19}BrN_2NaO_6$ $[M+Na]^+$, 449.0319; found 449.0332.

Bromolactone 4m



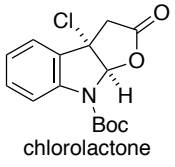
To a stirred solution of carboxylic acid **S3** (386 mg, 1.40 mmol) in CH_2Cl_2 (14 mL) was added NBS (274 mg, 1.54 mmol) at –15 °C. After 2 h, the reaction was quenched with saturated aqueous Na_2CO_3 at –15 °C. The resulting mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 7/1) to afford bromolactone **4m** (294 mg, 0.830 mmol, 59%) as a pale orange foam. R_f = 0.35 (hexanes/EtOAc = 7/1); IR (film, cm^{-1}) 3004, 2980, 2934, 2906, 1799, 1724, 1481, 1386, 1347, 1154, 974, 950, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.80 (1H, m), 7.42– 7.36 (2H, m), 7.16 (1H, dt, J = 7.6, 1.2 Hz), 6.60 (1H, s), 3.59 (1H, d, J = 18.0 Hz), 3.54 (1H, d, J = 18.0 Hz), 1.62 (9H, s). ^{1}H NMR of **4m** was almost identical with that of the known chlorolactone reported by Ishihara and co-workers*; ^{13}C NMR data could not be obtained due to the product instability; HRMS (ESI) calcd. for $C_{15}H_{16}BrNNaO_4$ $[M+Na]^+$, 376.0155; found 376.0143.

Boc-aniline S5



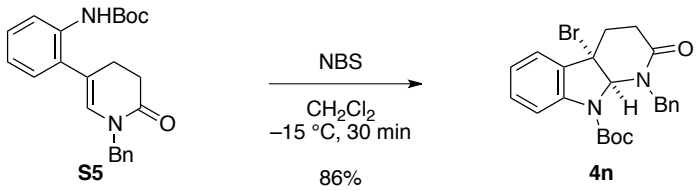
To a stirred solution of aniline **S4** (293 mg, 1.05 mmol) in 1,2-dichloroethane (11 mL) was added Boc_2O (344 mg, 1.58 mmol) at room temperature and the resulting mixture was heated at 60 °C.

* Reported ^{1}H NMR data of chrololacetone; 8.00–7.81 (1H, m), 7.42–7.38 (2H, m), 7.17 (1H, dt, J = 7.6, 1.0 Hz), 6.45 (1H, s), 3.52 (1H, d, J = 18.4 Hz), 3.47 (1H, d, J = 18.4 Hz), 1.62 (9H, s) Horibe, T.; Ohmura, S.; Ishihara, K. *Org. Lett.* **2017**, *19*, 5525.



After 17 h, to the reaction mixture was added additional Boc_2O (229 mg, 1.05 mmol). After 41 h, the reaction was quenched with H_2O at 0 °C. The resulting mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 3/1) to afford Boc-aniline **S5** (323 mg, 0.853 mmol, 81%) as a white foam. R_f = 0.62 (hexanes/EtOAc = 1/1); IR (film, cm^{-1}) 3420, 3300, 3063, 3030, 3006, 2978, 2932, 2902, 1723, 1669, 1514, 1158, 754; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (1H, d, J = 7.6 Hz), 7.33–7.19 (6H, m), 7.06–6.90 (2H, m), 6.40 (1H, brs), 6.17 (1H, s), 4.73 (2H, s), 2.75–2.59 (4H, m), 1.49 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 152.8, 136.8, 135.0, 130.1, 128.82, 128.76, 128.7, 128.0, 127.63, 127.57, 123.6, 121.3, 116.8, 70.5, 49.2, 31.5, 28.2, 25.6; HRMS (ESI) calcd. for $C_{23}H_{26}N_2NaO_3$ $[M+Na]^+$, 401.1836; found 401.1826.

α-Carboline 4n

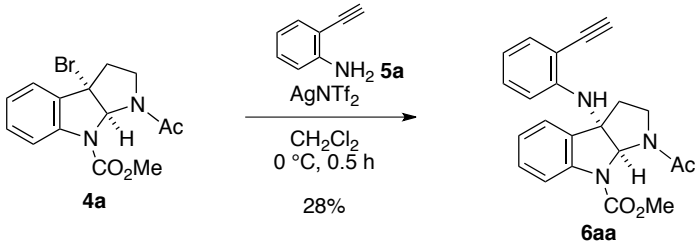


To a stirred solution of Boc-aniline **S5** (320 mg, 0.846 mmol) in CH_2Cl_2 (8.5 mL) was added NBS (166 mg, 0.930 mmol) at –15 °C. After 30 min, the reaction was quenched with saturated aqueous $NaHCO_3$ at –15 °C. The resulting mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 2/1) to afford α-carboline **4n** (331 mg, 0.724 mmol, 86%) as a white foam. R_f = 0.40 (hexanes/EtOAc = 2/1); IR (film, cm^{-1}) 3028, 3006, 2979, 2932, 1708, 1663, 1479, 1371, 1163, 1144, 754; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37–7.12 (9H, m), 6.21 (1H, brs), 4.83 (1H, d, J = 15.6 Hz), 4.76 (1H, d, J = 15.6 Hz), 3.06–2.89 (2H, m), 2.50–2.30 (2H, m), 1.47 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 152.1, 141.1, 137.3, 132.3, 130.6, 128.4, 128.1, 126.7, 124.6, 122.1, 119.0, 88.2, 83.6, 82.8, 47.7, 32.2, 30.3, 28.0; HRMS (ESI) calcd. for $C_{23}H_{26}BrN_2O_3$ $[M+H]^+$, 457.1121; found 457.1102.

Based on our working hypothesis, we initially tested the key reaction in a stepwise manner.

Initial Trial of $AgNTf_2$ Mediated Amination

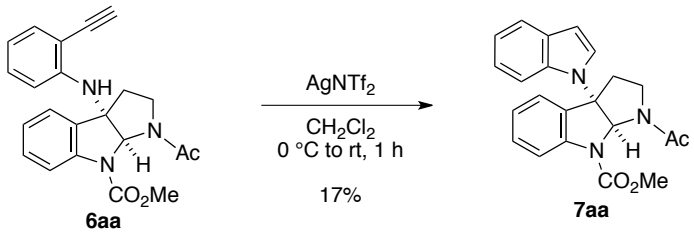
Aniline 6aa



To a stirred solution of bromopyrroloindoline **4a** (8.5 mg, 25 μmol) and 2-ethynylaniline **5a** (8.8 mg, 75 μmol) in CH_2Cl_2 (0.25 mL) was added $AgNTf_2$ (29.1 mg, 75.0 μmol) at 0 °C. After 0.5 h, the reaction was quenched with saturated aqueous $NaHCO_3$ at 0 °C. The mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified by preparative TLC (hexanes/EtOAc = 1/4) to afford aniline **6aa** (2.6 mg, 6.9 μmol, 28%) as a pale orange foam. R_f = 0.37 (hexanes/EtOAc = 1/4); IR (film, cm^{-1}) 3401, 3283, 3010, 2955, 1716, 1654, 1602, 1508, 1483, 1444, 1325, 1193, 750; ^1H NMR (400 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 7.77 (1H, brs), 7.35–7.24 (3H, m), 7.09–7.07 (1H, m), 7.01–6.97 (1H, m), 6.67–6.63 (1H, m), 6.20 (1H, brs), 6.07 (1H, brs), 5.12 (1H, brs), 4.51 (1H, brs), 3.87 (3H, s), 3.41 (1H, s), 2.81 (1H, brs), 2.31 (5H, brs); ^{13}C NMR (100 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 154.0, 146.3, 142.1, 133.2, 131.6, 130.8, 130.2, 130.0, 126.1, 124.9, 124.5, 123.5, 122.3, 118.2, 115.8, 111.9, 108.8, 102.4, 83.5, 80.4, 80.1, 53.0, 41.9, 41.6, 29.7, 21.4; HRMS (ESI) calcd. for $C_{22}H_{22}N_3O_3$ $[M+H]^+$, 376.1656; found 376.1642.

Initial Trial of $AgNTf_2$ Mediated Cyclization

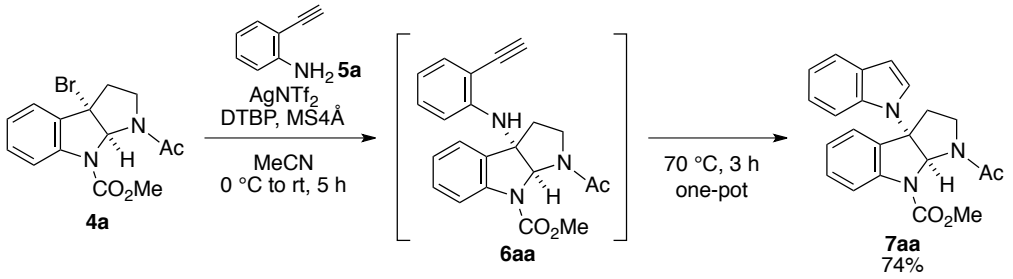
Indole 7aa



To a stirred solution of aniline **6aa** (9.4 mg, 25 μmol) in CH_2Cl_2 (0.25 mL) was added $AgNTf_2$ (29.1 mg, 75.0 μmol) at 0 °C. After 1 min, the resulting mixture was allowed to warm up to room temperature. After 1 h, the reaction was quenched with saturated aqueous $NaHCO_3$ at 0 °C. The mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified by preparative TLC (hexanes/EtOAc = 1/4) to afford indole **7aa** (1.6 mg, 4.3 μmol, 17%) as a pale orange foam. R_f = 0.34 (hexanes/EtOAc = 1/4); IR (film, cm^{-1}) 3009, 2954, 1718, 1484, 1443, 1401, 1325, 741; ^1H NMR (400 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 7.81 (1H, brs), 7.63–7.60 (1H, m), 7.41 (1H, dd, *J* = 8.0, 8.0 Hz), 7.29–7.24 (2H, m), 7.16–7.06 (4H, m), 6.52 (1H, brs), 6.48 (1H, d, *J* = 2.8 Hz), 4.63 (1H, brs), 3.85 (3H, s), 3.18 (1H, brs), 2.91 (1H, brs), 2.51 (1H, brs), 2.31 (3H, brs); ^{13}C NMR (100 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 170.2, 153.6, 142.4, 135.0, 130.7, 130.1, 129.9, 129.7, 126.0, 124.8, 124.4, 122.3, 121.7, 120.3, 116.7, 111.0, 102.4, 81.5, 75.4, 53.0, 52.8, 43.3, 37.2, 21.6; HRMS (ESI) calcd. for $C_{22}H_{22}N_3O_3$ $[M+H]^+$, 376.1656; found 376.1654.

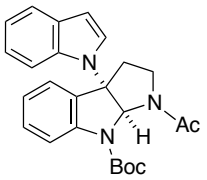
General Procedure for $AgNTf_2$ Mediated Amination/Cyclization Cascade

Indole 7aa



To a stirred solution of bromopyrroloindoline **4a** (49.2 mg, 0.145 mmol), pre-activated MS4Å (75 mg), DTBP (49 μL, 0.22 mmol), and 2-ethynylaniline **5a** (51.0 mg, 0.435 mmol) in MeCN (1.5 mL) was added $AgNTf_2$ (169 mg, 0.435 mmol) at 0 °C. After 5 min, the resulting mixture was allowed to warm up to room temperature and stirred for 5 h. After TLC indicated complete consumption of **4a**, the reaction mixture was allowed to 70 °C and stirred for 3 h. The reaction was quenched with saturated aqueous $NaHCO_3$ at 0 °C. The mixture was extracted with EtOAc three times and washed with brine. The combined organic extracts were filtered through a pad of Celite and concentrated under reduced pressure. The residue was diluted with CH_2Cl_2 and filtered through a pad of Celite and concentrated under reduced pressure again to remove polymer-like insoluble material. The residue was purified by flash column chromatography on silica gel (hexanes/CH_2Cl_2/EtOAc = 1/1/1) to afford indole **7aa** (40.2 mg, 0.107 mmol, 74%) as a pale orange foam. R_f = 0.34 (hexanes/EtOAc = 1/4); IR (film, cm^{-1}) 3009, 2954, 1718, 1484, 1443, 1401, 1325, 741; ^1H NMR (400 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 7.81 (1H, brs), 7.63–7.60 (1H, m), 7.41 (1H, dd, *J* = 8.0, 8.0 Hz), 7.29–7.24 (2H, m), 7.16–7.06 (4H, m), 6.52 (1H, brs), 6.48 (1H, d, *J* = 2.8 Hz), 4.63 (1H, brs), 3.85 (3H, s), 3.18 (1H, brs), 2.91 (1H, brs), 2.51 (1H, brs), 2.31 (3H, brs); ^{13}C NMR (100 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 170.2, 153.6, 142.4, 135.0, 130.7, 130.1, 129.9, 129.7, 126.0, 124.8, 124.4, 122.3, 121.7, 120.3, 116.7, 111.0, 102.4, 81.5, 75.4, 53.0, 52.8, 43.3, 37.2, 21.6; HRMS (ESI) calcd. for $C_{22}H_{22}N_3O_3$ $[M+H]^+$, 376.1656; found 376.1654.

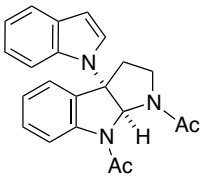
Indole 7ba



7ba

According to the general procedure described for **7aa**, indole **7ba** was obtained from bromopyrroloindoline **4b** (temp[1]: 0 °C to rt, time[1]: 6 h, temp[2]: 70 °C, time[2]: 3 h) in 0.100 mmol scale (32.0 mg, 76.6 μmol, 77%) as a pale orange foam. R_f = 0.75 (hexanes/EtOAc = 1/3); IR (film, cm^{-1}) 3006, 2979, 2932, 2889, 1709, 1661, 1482, 1404, 1153, 754, 742; ^1H NMR (600 MHz, $CDCl_3$, a mixture of rotamers) δ 7.64–7.62 (2H, m), 7.39 (1H, dd, *J* = 7.8, 7.8 Hz), 7.31 (1H, d, *J* = 7.2 Hz), 7.17–7.08 (5H, m), 6.55 (1H, brs), 6.48 (1H, d, *J* = 2.0 Hz), 4.60–4.56 (1H, m), 3.19–3.13 (1H, m), 2.87–2.84 (1H, m), 2.52–2.49 (1H, m), 2.41 (3H, brs), 1.59 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$, a mixture of rotamers) δ 170.9, 152.4, 142.6, 134.9, 130.6, 130.0, 126.1, 124.9, 124.3, 122.2, 121.7, 120.2, 117.5, 111.0, 102.1, 83.3, 80.8, 74.8, 43.6, 36.5, 28.2, 22.1 (one signal is missing due to overlap); HRMS (ESI) calcd. for $C_{25}H_{27}N_3NaO_3$ $[M+Na]^+$, 440.1945; found 440.1941.

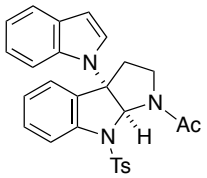
Indole 7ca



7ca

According to the general procedure described for **7aa**, indole **7ca** was obtained from bromopyrroloindoline **4c** (temp[1]: 0 °C to rt, time[1]: 6 h, temp[2]: 70 °C, time[2]: 3.5 h) in 0.100 mmol scale (27.6 mg, 76.8 μmol, 77%) as a pale orange foam. R_f = 0.34 (CH_2Cl_2/EtOAc = 3/1); IR (film, cm^{-1}) 3048, 3009, 2964, 2889, 1667, 1479, 1409, 754, 745; ^1H NMR (600 MHz, $CDCl_3$, 45 °C, a mixture of rotamers) δ 8.21 (1H, d, *J* = 7.2 Hz), 7.62 (1H, d, *J* = 9.0 Hz), 7.45 (1H, dd, *J* = 7.8, 7.2 Hz), 7.37 (1H, d, *J* = 7.2 Hz), 7.23–7.11 (4H, m), 6.96 (1H, d, *J* = 3.0 Hz), 6.73 (1H, brs), 6.44 (1H, d, *J* = 3.0 Hz), 3.90 (1H, brs), 3.31 (1H, brs), 3.23 (1H, brs), 2.58 (1H, brs), 2.43 (3H, s), 2.16 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$, 45 °C, a mixture of rotamers) δ 171.1, 170.0, 143.9, 134.8, 130.9, 130.7, 129.5, 126.3, 124.9, 124.5, 122.4, 121.8, 120.3, 120.0, 110.9, 102.3, 79.1, 73.6, 46.9, 35.8, 23.7, 22.7; HRMS (ESI) calcd. for $C_{22}H_{21}N_3NaO_2$ $[M+Na]^+$, 382.1526; found 382.1525.

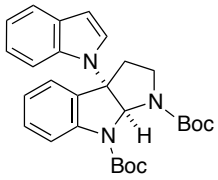
Indole 7da



7da

According to the general procedure described for **7aa**, indole **7da** was obtained from bromopyrroloindoline **4d** (temp[1]: 0 °C to rt, time[1]: 6 h, temp[2]: 70 °C, time[2]: 6 h) in 0.100 mmol scale (24.3 mg, 51.5 μmol, 52%) as a pale orange foam. R_f = 0.22 (toluene/EtOAc = 3/1); IR (film, cm^{-1}) 3048, 3009, 2962, 2929, 2888, 1666, 1456, 1399, 1356, 1171, 752, 655, 578; ^1H NMR (600 MHz, $CDCl_3$, 45 °C, a mixture of rotamers) δ 7.85 (1H, d, *J* = 7.8 Hz), 7.60 (1H, d, *J* = 6.6 Hz), 7.52–7.50 (1H, m), 7.37–7.34 (2H, m), 7.24–7.18 (6H, m), 6.90–6.88 (1H, m), 6.64 (1H, brs), 6.07 (1H, brs), 6.02 (1H, brs), 4.41 (1H, dd, *J* = 6.4, 5.6 Hz), 3.06–3.03 (1H, m), 2.79 (1H, brs), 2.60 (3H, brs), 2.25–2.22 (4H, m); ^{13}C NMR (150 MHz, $CDCl_3$, 45 °C, a mixture of rotamers) δ 171.1, 144.1, 142.7, 133.9, 133.7, 131.8, 131.3, 130.6, 129.5, 126.6, 126.5, 126.2, 125.6, 122.4, 121.8, 120.4, 120.3, 110.7, 101.8, 82.8, 75.7, 44.6, 34.3, 23.0, 21.4; HRMS (ESI) calcd. for $C_{27}H_{26}N_3O_3S$ $[M+H]^+$, 472.1689; found 472.1671.

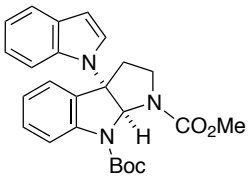
Indole 7ea



7ea

According to the general procedure described for **7aa**, indole **7ea** was obtained from bromopyrroloindoline **4e** (temp[1]: 0 °C to rt, time[1]: 6 h, temp[2]: 70 °C, time[2]: 3 h) in 0.100 mmol scale (32.1 mg, 67.5 μmol, 68%) as a pale yellow oil. R_f = 0.32 (hexanes/acetone = 10/1); the ^1H NMR spectrum of **7ea** was identical with those reported in the literature[2].

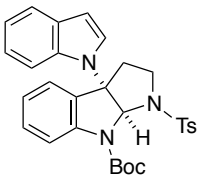
Indole 7fa



7fa

According to the general procedure described for **7aa**, indole **7fa** was obtained from bromopyrroloindoline **4f** (temp[1]: 0 °C to rt, time[1]: 5 h, temp[2]: 70 °C, time[2]: 3 h) in 0.100 mmol scale (35.6 mg, 82.1 μmol, 82%) as a pale orange oil. R_f = 0.23 (hexanes/EtOAc = 5/1); IR (neat, cm^{-1}) 3049, 3008, 2980, 2955, 2931, 2891, 1714, 1655, 1392, 1254, 754, 742; ^1H NMR (400 MHz, $CDCl_3$, 55 °C) δ 7.84 (1H, d, *J* = 7.6 Hz), 7.60–7.57 (1H, m), 7.35 (1H, ddd, *J* = 7.6, 7.6, 1.2 Hz), 7.24–7.21 (1H, m), 7.11–7.04 (5H, m), 6.72 (1H, brs), 6.45 (1H, d, *J* = 3.6 Hz), 4.17 (1H, dd, *J* = 11.6, 7.6 Hz), 3.75 (3H, s), 3.20–3.12 (1H, m), 3.07–3.00 (1H, m), 2.55 (1H, dd, *J* = 11.6, 5.2 Hz), 1.53 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$, 55 °C) δ 155.1, 152.2, 143.4, 135.3, 130.6, 129.8, 126.1, 124.4, 123.8, 122.1, 121.4, 120.1, 117.0, 111.4, 102.2, 82.2, 80.2, 74.4, 52.8, 45.4, 37.2, 28.3 (one signal is missing due to overlap); HRMS (ESI) calcd. for $C_{25}H_{27}N_3NaO_4$ $[M+Na]^+$, 456.1894; found 456.1884.

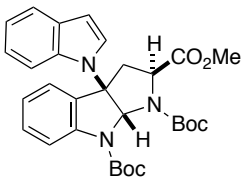
Indole 7ga



7ga

According to the general procedure described for **7aa**, indole **7ga** was obtained from bromopyrroloindoline **4g** (temp[1]: 0 °C to rt, time[1]: 6 h, temp[2]: 70 °C, time[2]: 3.5 h) in 0.100 mmol scale (38.5 mg, 72.7 μmol, 73%) as a pale yellow foam. R_f = 0.41 (hexanes/EtOAc = 3/1); IR (film, cm^{-1}) 3023, 3012, 2979, 2931, 1713, 1482, 1455, 1378, 1164, 768, 757, 664; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77–7.72 (3H, m), 7.58 (1H, d, *J* = 8.0 Hz), 7.35 (1H, dd, *J* = 7.2, 7.2 Hz), 7.28–7.24 (2H, m), 7.19 (1H, d, *J* = 7.6 Hz), 7.10–7.00 (3H, m), 6.92–6.90 (2H, m), 6.71 (1H, brs), 6.42 (1H, d, *J* = 3.6 Hz), 4.05 (1H, brs), 3.10–3.06 (2H, m), 2.48–2.43 (4H, m), 1.50 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 143.4, 142.8, 137.4, 134.9, 130.7, 130.4, 129.7, 129.4, 127.0, 126.0, 124.5, 123.9, 122.1, 121.4, 120.1, 116.9, 111.1, 102.0, 83.0, 81.2, 74.8, 47.6, 37.1, 28.1, 21.5; HRMS (ESI) calcd. for $C_{30}H_{31}N_3NaO_4S$ $[M+Na]^+$, 552.1927; found 552.1918.

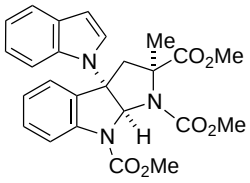
Indole 7ha



7ha

According to the general procedure described for **7aa**, indole **7ha** was obtained from bromopyrroloindoline **4h** (temp[1]: 0 °C to rt, time[1]: 6 h, temp[2]: 70 °C, time[2]: 3 h) in 0.100 mmol scale (44.0 mg, 82.5 μmol, 83%) as a white foam. R_f = 0.12 (hexanes/EtOAc = 10/1); the ^1H NMR spectrum of **7ha** was identical with those reported in the literature[3].

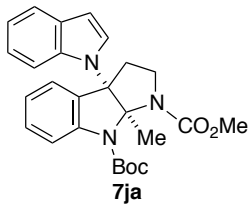
Indole 7ia



7ia

According to the general procedure described for **7aa**, indole **7ia** was obtained from above bromopyrroloindoline **4i** (temp[1]: 0 °C to rt, time[1]: 6 h, temp[2]: 70 °C, time[2]: 3 h) in 0.100 mmol scale (33.7 mg, 72.7 μmol, 73%) as an orange oil. R_f = 0.35 (hexanes/EtOAc = 1/1); $[\alpha]_D^{27}$ = –133 (*c* 0.290, $CHCl_3$); IR (neat, cm^{-1}) 3017, 2953, 1731, 1716, 752; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (1H, d, *J* = 7.6 Hz), 7.64 (1H, d, *J* = 7.6 Hz), 7.47–7.42 (2H, m), 7.38 (1H, dd, *J* = 7.6, 0.8 Hz), 7.31–7.27 (1H, m), 7.21–7.16 (2H, m), 6.88 (1H, brs), 6.77 (1H, d, *J* = 3.2 Hz), 6.38 (1H, d, *J* = 3.2 Hz), 3.78 (3H, s), 3.76 (3H, s), 3.40 (1H, d, *J* = 14.0 Hz), 3.17 (1H, d, *J* = 14.0 Hz), 3.12 (3H, s), 1.90 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.0, 154.3, 153.9, 143.6, 134.1, 131.2, 130.8, 129.5, 126.6, 125.6, 123.9, 122.1, 121.9, 120.2, 118.4, 111.2, 101.9, 80.9, 69.8, 66.9, 53.1, 52.6, 52.4, 46.3, 26.0; HRMS (ESI) calcd. for $C_{25}H_{25}N_3NaO_6$ $[M+Na]^+$, 486.1636; found 486.1631.

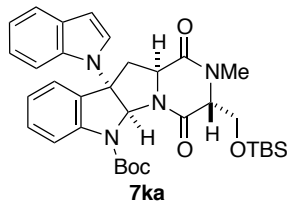
Indole 7ja



7ja

According to the general procedure described for **7aa**, indole **7ja** was obtained from bromopyrroloindoline **4j** (temp[1]: 0 °C to rt, time[1]: 4 h, temp[2]: 70 °C, time[2]: 6.5 h) in 0.100 mmol scale (36.9 mg, 82.4 μmol, 82%) as a pale orange foam. R_f = 0.22 (hexanes/EtOAc = 4/1); IR (film, cm^{-1}) 3048, 3006, 2979, 2954, 2934, 2889, 1698, 1451, 1374, 1353, 1148, 755, 741; ^1H NMR (600 MHz, $CDCl_3$, a mixture of rotamers) δ 7.91 (1H, brs), 7.53–7.48 (2H, m), 7.38 (1H, brs), 7.18–6.98 (3H, m), 6.83 (1H, brs), 6.60–6.44 (2H, m), 3.78–3.71 (4H, m), 3.09 (1H, brs), 2.95 (1H, brs), 2.64 (1H, brs), 1.55 (12H, brs); ^{13}C NMR (150 MHz, $CDCl_3$, a mixture of rotamers) δ 154.4, 151.9, 144.3, 136.3, 130.3, 130.2, 129.5, 125.4, 124.2, 123.9, 122.2, 120.9, 120.0, 118.5, 112.4, 102.6, 87.9, 81.8, 76.1, 52.3, 44.8, 33.3, 28.4, 19.8; HRMS (ESI) calcd. for $C_{26}H_{30}N_3O_4$ $[M+H]^+$, 448.2231; found 448.2216.

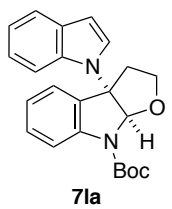
Indole 7ka



7ka

According to the general procedure described for **7aa**, indole **7ka** was obtained from bromopyrroloindoline **4k** (temp[1]: 0 °C, time[1]: 6.5 h, temp[2]: 70 °C, time[2]: 4 h) in 1.29 mmol scale (513 mg, 0.832 mmol, 64%) as a orange foam. R_f = 0.44 (CH_2Cl_2/EtOAc = 10/1); $[\alpha]_D^{25}$ = –179 (*c* 0.352, $CHCl_3$); IR (film, cm^{-1}) 3009, 2956, 2929, 2857, 1722, 1675, 1482, 1455, 1335, 1253, 1156, 837, 755; ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (1H, d, *J* = 8.4 Hz), 7.65–7.63 (1H, m), 7.48 (1H, d, *J* = 7.8 Hz), 7.41 (1H, ddd, *J* = 8.8, 8.4, 1.6 Hz), 7.20–7.15 (4H, m), 6.68 (1H, d, *J* = 3.2 Hz), 6.46 (1H, s), 6.38 (1H, d, *J* = 3.2 Hz), 5.08 (1H, dd, *J* = 10.4, 8.0 Hz), 4.19 (1H, dd, *J* = 10.8, 2.4 Hz), 3.95 (1H, dd, *J* = 10.8, 2.4 Hz), 3.76 (1H, dd, *J* = 2.4, 2.4 Hz), 3.49 (1H, dd, *J* = 14.4, 10.4 Hz), 3.27 (1H, dd, *J* = 14.4, 8.0 Hz), 2.90 (3H, s), 1.52 (9H, s), 0.95 (9H, s), 0.14 (3H, s), 0.12 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.3, 165.8, 151.8, 141.5, 134.3, 132.0, 130.9, 130.8, 126.8, 126.1, 124.2, 121.99, 121.95, 120.4, 117.6, 110.8, 102.0, 82.7, 80.1, 70.4, 67.0, 63.0, 56.5, 36.1, 32.1, 28.2, 25.9, 18.4, –5.35, –5.41; HRMS (ESI) calcd. for $C_{34}H_{44}N_4NaO_5Si$ $[M+Na]^+$, 639.2973; found 639.2956.

Indole 7la

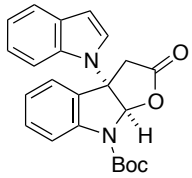


7la

According to the general procedure described for **7aa**, indole **7la** was obtained from bromofuroindoline **4l** (temp[1]: 0 °C to rt, time[1]: 6 h, temp[2]: 70 °C, time[2]: 3 h) in 0.100 mmol scale (24.3 mg, 64.5 μmol, 65%) as a white foam. R_f = 0.33 (hexanes/acetone = 9/1); IR (film, cm^{-1}) 3005, 2980, 2932, 2879, 1713, 1483, 1456, 1387, 1369, 1149, 754, 742; ^1H NMR (600 MHz, $CDCl_3$, a mixture of rotamers) δ 7.98 (1H, brs),

7.63 (1H, d, J = 8.4 Hz), 7.36 (1H, dd, J = 8.4, 7.2 Hz), 7.33–7.24 (2H, m), 7.16–7.10 (3H, m), 7.07 (1H, dd, J = 7.8, 7.8 Hz), 6.49 (1H, d, J = 3.0 Hz), 6.43 (1H, brs), 4.33 (1H, dd, J = 8.4, 7.8 Hz), 3.73–3.69 (1H, m), 3.42–3.35 (1H, m), 2.56 (1H, dd, J = 12.0, 4.2 Hz), 1.57 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$, a mixture of rotamers) δ 152.0, 143.4, 134.9, 130.6, 130.3, 128.9, 126.2, 125.0, 123.4, 122.1, 121.4, 120.1, 115.2, 111.4, 101.7, 96.3, 82.1, 74.3, 67.6, 39,6, 28.3; HRMS (ESI) calcd. for $C_{23}H_{24}N_2NaO_3$ $[M+Na]^+$, 399.1679; found 399.1668.

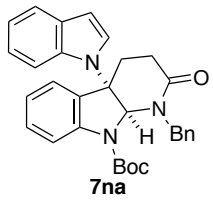
Indole 7ma



7ma

According to the general procedure described for **7aa**, indole **7ma** was obtained from above bromopyrroloindoline **4m** (temp^1: 0 °C to rt, time^1: 6 h, temp^2: 70 °C, time^2: 3 h) in 0.100 mmol scale (13.7 mg, 35.1 μmol, 35%) as a pale orange foam. R_f = 0.34 (hexanes/EtOAc = 8/1); IR (film, cm^{-1}) 3006, 2979, 2932, 1798, 1723, 1484, 1388, 1357, 1154, 984, 756, 742; ^{1}H NMR (600 MHz, $CDCl_3$, 55 °C) δ 7.92 (1H, brs), 7.66 (1H, d, J = 7.8 Hz), 7.47 (1H, dd, J = 8.4, 7.2 Hz), 7.45 (1H, d, J = 7.2 Hz), 7.29–7.18 (4H, m), 6.87 (1H, d, J = 3.0 Hz), 6.76 (1H, brs), 6.45 (1H, d, J = 3.0 Hz), 4.05 (1H, d, J = 18.6 Hz), 3.35 (1H, d, J = 18.6 Hz), 1.56 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$, 55 °C) δ 171.5, 150.8, 141.4, 134.1, 131.9, 131.0, 128.6, 126.2, 125.9, 124.4, 122.8, 122.3, 120.8, 116.9, 110.6, 102.7, 94.8, 83.7, 68.5, 40.0, 28.2; HRMS (ESI) calcd. for $C_{23}H_{23}N_2O_4$ $[M+H]^+$, 391.1652; found 391.1622.

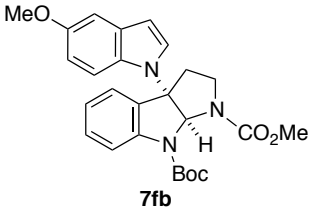
Indole 7na



7na

According to the general procedure described for **7aa**, indole **8na** was obtained from above α-carboline **4n** (temp^1: –15 °C, time^1: 2 h, temp^2: 70 °C, time^2: 3.5 h) in 0.100 mmol scale (37.5 mg, 76.0 μmol, 76%) as a pale yellow foam. R_f = 0.39 (hexanes/EtOAc = 2/1); IR (film, cm^{-1}) 3050, 3007, 2978, 2932, 1707, 1661, 1483, 1454, 1370, 1140, 753, 742; ^{1}H NMR (600 MHz, $CDCl_3$, 55 °C) δ 7.59 (1H, d, J = 8.4 Hz), 7.54 (1H, d, J = 8.4 Hz), 7.46 (1H, dd, J = 8.4, 7.8 Hz), 7.36–7.22 (7H, m), 7.03 (1H, dd, J = 7.8, 7.2 Hz), 6.89 (1H, dd, J = 8.4, 7.8 Hz), 6.81 (1H, d, J = 8.4 Hz), 6.63 (1H, d, J = 3.0 Hz), 6.43 (1H, brs), 6.29 (1H, d, J = 3.0 Hz), 5.27 (1H, d, J = 15.0 Hz), 4.54 (1H, d, J = 15.0 Hz), 3.20 (1H, ddd, J = 14.4, 13.8, 3.0 Hz), 2.55–2.50 (1H, m), 2.41–2.38 (1H, m), 2.28–2.22 (1H, m), 1.33 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$, 55 °C) δ 170.4, 152.8, 143.1, 137.9, 134.5, 131.0, 130.8, 129.8, 128.5, 128.3, 127.3, 125.9, 124.7, 124.5, 121.8, 121.6, 120.0, 119.3, 115.5, 101.7, 83.0, 79.6, 66.4, 47.9, 29.5, 28.3, 28.1; HRMS (ESI) calcd. for $C_{32}H_{32}N_3O_3$ $[M+Na]^+$, 494.2438; found 494.2423.

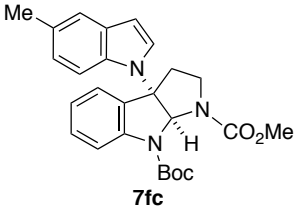
Indole 7fb



7fb

According to the general procedure described for **7aa**, indole **7fb** was obtained from 2-ethynyl-4-methoxyaniline (**5b**)[4] and bromopyrroloindoline **4f** (temp[1]: 0 °C to rt, time[1]: 1 h, temp[2]: 70 °C, time[2]: 1.5 h) in 0.100 mmol scale (40.4 mg, 87.2 μmol, 87%) as a white foam. R_f = 0.21 (hexanes/EtOAc = 3/1); IR (film, cm^{-1}) 3006, 2980, 2954, 2935, 2893, 1713, 1619, 1604, 1479, 1447, 1392, 1369, 1238, 1157, 753; ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 (1H, d, *J* = 7.6 Hz), 7.38–7.34 (1H, m), 7.22 (1H, d, *J* = 8.0 Hz), 7.10–7.05 (3H, m), 6.98 (1H, d, *J* = 9.2 Hz), 6.77 (1H, dd, *J* = 9.2, 2.4 Hz), 6.68 (1H, brs), 6.39 (1H, d, *J* = 3.6 Hz), 4.19–4.15 (1H, m), 3.82 (3H, s), 3.75 (3H, s), 3.11–2.99 (2H, m), 2.54 (1H, dd, 11.2, 4.4), 1.53 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 152.1, 143.1, 131.0, 130.6, 130.2, 129.6, 126.7, 124.4, 123.8, 116.8, 112.1, 111.9, 103.0, 101.6, 82.3, 79.9, 74.2, 55.7, 52.9, 45.4, 37.2, 28.3 (one signal is missing due to overlap); HRMS (ESI) calcd. for $C_{26}H_{29}N_3NaO_5$ $[M+Na]^+$, 486.1999; found 486.2016.

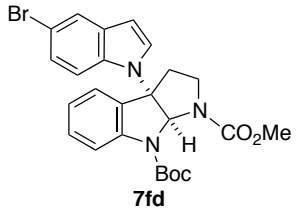
Indole 7fc



7fc

According to the general procedure described for **7aa**, indole **7fc** was obtained from 2-ethynyl-4-methylaniline (**5c**)[5] and bromopyrroloindoline **4f** (temp[1]: 0 °C to rt, time[1]: 2.5 h, temp[2]: 70 °C, time[2]: 2.5 h) in 0.100 mmol scale (41.4 mg, 92.5 μmol, 93%) as a pale yellow foam. R_f = 0.32 (hexanes/EtOAc = 3/1); IR (film, cm^{-1}) 3010, 2979, 2955, 2931, 2895, 1714, 1706, 1481, 1463, 1445, 1392, 1202, 1164, 1147, 786, 753; ^1H NMR (400 MHz, $CDCl_3$, a mixture of rotamers) δ 7.83 (1H, d, *J* = 7.6 Hz), 7.39–7.32 (2H, m), 7.24–7.20 (1H, m), 7.08–7.04 (2H, m), 6.98–6.93 (2H, m), 6.70 (1H, brs), 6.38 (1H, brs), 4.17–4.15 (1H, m), 3.75 (3H, s), 3.15–3.10 (1H, m), 3.06–2.99 (1H, m), 2.54–2.50 (1H, m), 2.40 (3H, s), 1.53 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of rotamers) δ 155.1, 152.1, 143.1, 133.4, 130.7, 130.5, 129.6, 129.3, 126.1, 124.4, 123.7, 121.1, 116.7, 110.9, 101.5, 82.2, 79.8, 74.2, 52.8, 45.4, 37.2, 28.3, 21.1; HRMS (ESI) calcd. for $C_{26}H_{29}N_3NaO_4$ $[M+Na]^+$, 470.2050; found 470.2072.

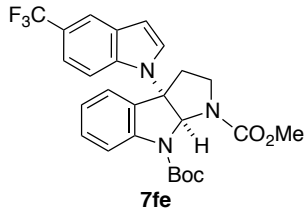
Indole 7fd



7fd

According to the general procedure described for **7aa**, indole **7fd** was obtained from 4-bromo-2-ethynylaniline (**5d**)[5] and bromopyrroloindoline **4f** (temp[1]: 0 °C to rt, time[1]: 5 h, temp[2]: 70 °C, time[2]: 3 h) in 0.100 mmol scale (43.6 mg, 85.1 μmol, 85%) as a pale orange foam. R_f = 0.35 (hexanes/EtOAc = 3/1); IR (film, cm^{-1}) 3008, 2979, 2955, 2932, 2892, 1714, 1446, 1392, 1146, 753; ^1H NMR (400 MHz, $CDCl_3$, a mixture of rotamers) δ 7.83 (1H, d, *J* = 7.6 Hz), 7.73 (1H, s), 7.37 (1H, dd, *J* = 7.2, 7.2 Hz), 7.22–7.13 (3H, m), 7.08 (1H, dd, *J* = 7.2, 7.2 Hz), 6.94 (1H, d, *J* = 8.8 Hz), 6.67 (1H, brs), 6.41 (1H, brs), 4.18 (1H, brs), 3.76 (3H, s), 3.11–3.03 (2H, m), 2.55 (1H, brs), 1.53 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of rotamers) δ 155.0, 152.0, 143.1, 133.7, 132.1, 130.8, 129.2, 127.3, 124.9, 124.3, 123.9, 116.9, 113.5, 112.5, 101.6, 82.4, 79.8, 74.3, 52.9, 45.3, 37.2, 28.2 (one signal is missing due to overlap); HRMS (ESI) calcd. for $C_{25}H_{26}BrN_3NaO_4$ $[M+Na]^+$, 534.0999; found 534.0980.

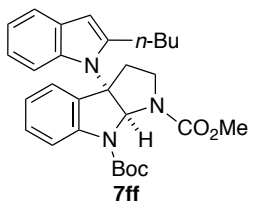
Indole 7fe



7fe

According to the general procedure described for **7aa**, indole **7fe** was obtained from 2-ethynyl-4-(trifluoromethyl)aniline (**5e**)[4] and bromopyrroloindoline **4f** (temp[1]: 0 °C to rt, time[1]: 6 h, temp[2]: 70 °C, time[2]: 24 h) in 0.100 mmol scale (33.6 mg, 67.0 μmol, 67%) as a pale yellow foam. R_f = 0.45 (hexanes/EtOAc = 3/1); IR (film, cm^{-1}) 3006, 2979, 2957, 2933, 2895, 1714, 1481, 1447, 1393, 1333, 1146, 1116, 754; ^1H NMR (600 MHz, $CDCl_3$) δ 7.90 (1H, s), 7.84 (1H, d, *J* = 7.2 Hz), 7.41–7.38 (1H, m), 7.35 (1H, d, *J* = 9.0 Hz), 7.26–7.22 (2H, m), 7.16 (1H, d, *J* = 9.0 Hz), 7.10 (1H, dd, *J* = 7.8, 7.2 Hz), 6.70 (1H, brs), 6.57 (1H, d, *J* = 3.6 Hz), 4.21–4.18 (1H, m), 3.77 (3H, s), 3.16–3.04 (2H, m), 2.60 (1H, dd, *J* = 12.0, 4.8 Hz), 1.54 (9H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 155.1, 152.0, 143.2, 136.3, 130.9, 129.8, 129.1, 127.8, 125.1(q, *J* = 271 Hz), 124.4, 123.9, 122.6 (q, *J* = 31.5 Hz), 119.1 (q, *J* = 4.2 Hz), 118.8 (q, *J* = 2.9 Hz), 117.0, 111.4, 103.0, 82.5, 79.9, 74.4, 53.0, 45.4, 37.3, 28.3; HRMS (ESI) calcd. for $C_{26}H_{26}F_3N_3NaO_4$ $[M+Na]^+$, 524.1768; found 524.1731.

Indole 7ff

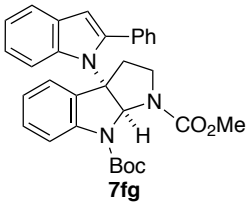


7ff

According to the general procedure described for **7aa**, indole **7ff** was obtained from 2-(hex-1-yn-1-yl)aniline (**5f**)[6] and bromopyrroloindoline **4f** (temp[1]: 0 °C to rt, time[1]: 6 h, temp[2]: 70 °C, time[2]: 6.5 h) in 0.100 mmol scale (30.5 mg, 62.2 μmol, 62%) as a pale yellow foam. R_f = 0.73 (toluene/EtOAc

= 20/1); IR (film, cm^{-1}) 3006, 2956, 2932, 2871, 1713, 1482, 1445, 1395, 1378, 1147, 754; ^1H NMR (400 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 7.84 (1H, d, *J* = 8.4 Hz), 7.48–7.46 (1H, m), 7.31–7.27 (2H, m), 7.15 (1H, d, *J* = 7.2 Hz), 7.04–7.02 (2H, m), 6.97 (1H, dd, *J* = 7.2, 7.2 Hz), 6.87 (1H, brs), 6.34 (1H, brs), 4.22 (1H, brs), 3.70 (3H, s), 3.37–3.29 (1H, m), 2.98–2.91 (1H, m), 2.81–2.78 (1H, m), 2.60–2.54 (1H, m), 2.47–2.40 (1H, m), 1.56–1.50 (11H, m), 1.30–1.24 (1H, m), 0.83 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 155.4, 152.3, 143.6, 143.2, 138.2, 131.1, 130.6, 129.6, 124.8, 124.0, 121.5, 120.5, 120.0, 116.2, 112.5, 104.2, 82.6, 82.3, 76.7, 53.2, 45.3, 41.6, 32.0, 29.4, 28.7, 22.9, 14.0; HRMS (ESI) calcd. for $C_{29}H_{35}N_3NaO_4$ $[M+Na]^+$, 512.2520; found 512.2523.

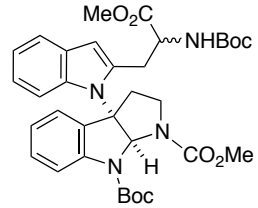
Indole 7fg



7fg

According to the general procedure described for **7aa**, indole **7fg** was obtained from 2-(phenylethynyl)aniline (**5g**)[6] and known bromopyrroloindoline **4f** (temp[1]: 0 °C to rt, time[1]: 4 h, temp[2]: 70 °C, time[2]: 6 h) in 0.100 mmol scale (33.0 mg, 64.8 μmol, 65%) as a white foam. R_f = 0.21 (hexanes/EtOAc = 6/1); IR (film, cm^{-1}) 3056, 3047, 3012, 2981, 2954, 2931, 2894, 1709, 1483, 1445, 1396, 1380, 1370, 1150, 750, 702; ^1H NMR (400 MHz, $CDCl_3$, a mixture of rotamers) δ 7.78 (1H, d, *J* = 7.6 Hz), 7.59 (1H, d, *J* = 8.0 Hz), 7.45 (1H, d, *J* = 6.8 Hz), 7.33–7.12 (9H, m), 6.91 (1H, dd, *J* = 7.6, 7.2 Hz), 6.74 (1H, brs), 6.42 (1H, s), 4.03 (1H, brs), 3.66 (3H, s), 3.04–2.96 (1H, m), 2.88–2.82 (1H, m), 2.56 (1H, brs), 1.46 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$, a mixture of rotamers) δ 155.0, 151.6, 142.8, 142.2, 137.8, 135.0, 131.5, 130.0, 129.5, 128.8, 128.1, 127.8, 124.2, 123.4, 122.1, 120.9, 120.3, 115.3, 112.8, 107.5, 81.8, 81.7, 76.4, 52.8, 44.7, 42.8, 28.4; HRMS (ESI) calcd. for $C_{31}H_{31}N_3NaO_4$ $[M+Na]^+$, 532.2207; found 532.2213.

Indole 7fh



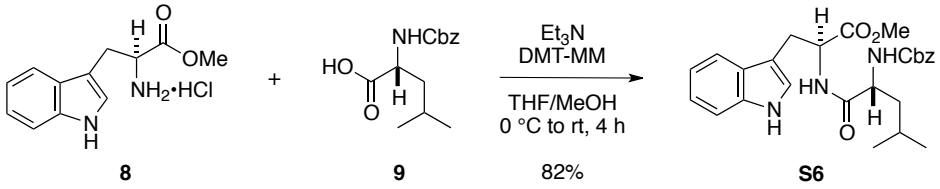
7fh
a mixture of diastereomers

According to the general procedure described for **7aa**, the indole **7fh** was obtained from methyl 5-(2-aminophenyl)-2-((*tert*-butoxycarbonyl)amino)pent-4-ynoate (**5h**)[7] and bromopyrroloindoline **4f** (temp[1]: 0 °C to rt, time[1]: 5 h, temp[2]: reflux, time[2]: 18 h) in 50.0 μmol scale (10.0 mg, 15.8 μmol, 32%, a mixture of diastereomers: the diastereomeric ratio could not be determined due to the romamers.) as a pale brown oil. R_f = 0.24 (hexanes/EtOAc = 2/1); IR (film, cm^{-1}) 3364, 3357, 3349, 3006, 2979, 2955, 2929, 1747, 1739, 1715, 1483, 1456, 1447, 1369, 1162, 750; ^1H NMR (600 MHz, $CDCl_3$, a mixture of rotamers) δ 7.87 (1H, brs), 7.51–7.50 (1H, m), 7.35–7.31 (1H, m), 7.23–7.18 (2H, m), 7.08–7.02 (3H, m), 6.83 (1H, brs), 6.40 (1H,

brs), 5.33 (0.22H, brs), 4.99 (0.46H, brs), 4.76 (0.32H, brs), 4.55 (0.32H, brs), 4.47 (0.18H, brs), 4.36–4.22 (1.5H, m), 3.81–3.61 (7H, m), 3.29–3.26 (1H, m), 3.05 (1H, brs), 2.98–2.96 (1H, m), 2.82–2.76 (1H, m), 1.60–1.36 (18H, m); ^{13}C NMR (150 MHz, $CDCl_3$, a mixture of rotamers) δ 172.3, 172.2, 170.8, 155.1, 151.9, 142.7, 137.8, 137.7, 136.7, 136.6, 131.0, 130.6, 130.5, 130.25, 130.18, 128.8,1 127.77, 128.5, 124.6, 123.9, 123.8, 121.9, 120.6, 120.0, 116.0, 112.1, 112.0, 105.1, 104.9, 82.5, 81.9, 80.4, 80.14, 80.06, 76.2, 53.0, 52.9, 52.8, 52.52, 52.45, 51.9, 45.0, 32.3, 31.6, 29.7, 29.4, 28.43, 28.4, 28.34, 28.30, 28.25, 28.21, 23.8, 22.7, 21.0, 14.2, 14.1; HRMS (ESI) calcd. for $C_{34}H_{43}N_4O_8$ $[M+H]^+$, 635.3075; found 635.3050.

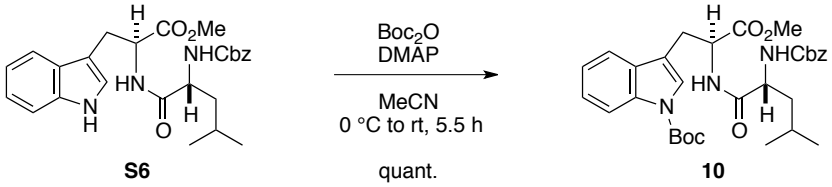
3. Total synthesis of (+)-pestalazine B

Amide S6



To a stirred solution of L-tryptophan methyl ester hydrochloride (**8**) (13.5 g, 53.1 mmol), *N*-Cbz-protected D-leucine (**9**) (15.5 g, 58.5 mmol) in THF (240 mL) and MeOH (26 mL) were added DMT-MM (17.6 g, 63.7 mmol) and Et_3N (8.14 mL, 58.4 mmol) at 0 °C. After 1 min, the resulting mixture was allowed to warm up to room temperature and stirred for 4 h. After the solvent was removed under reduce pressure, the residue was diluted with EtOAc. The resulting mixture was washed with saturated aqueous $NaHCO_3$, H_2O, aqueous 1 M HCl, H_2O, and brine respectively. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (eluent: CH_2Cl_2/EtOAc = 9/1→3/1) and recrystallization (EtOAc/hexanes) to afford amide **S6** (20.3 g, 43.5 mmol, 82%) as a white solid; mp 132-134 °C (EtOAc/hexanes); R_f = 0.34 (hexanes/CH_2Cl_2/EtOAc = 1/1/1); $[\alpha]_D^{29}$ = 47.6 (*c* 0.630, $CHCl_3$); IR (film, cm^{-1}) 3336, 3033, 2955, 1739, 1715, 1706, 1668, 1654, 1520, 1507, 1457, 1253, 1232, 1215, 742; ^1H NMR (400 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 7.87 (1H, brs), 7.50 (1H, d, *J* = 8.0 Hz), 7.32–7.24 (7H, m), 7.16 (1H, dd, *J* = 8.0, 6.8 Hz), 7.09 (1H, dd, *J* = 7.6, 7.2 Hz), 6.91 (1H, brs), 5.10 (1H, d, *J* = 12.0 Hz), 5.04 (1H, d, *J* = 12.0 Hz), 4.96 (1H, brs), 4.90–4.85 (1H, m), 4.14 (1H, brs), 3.65 (3H, s), 3.27 (2H, brs), 1.59–1.55 (2H, brs), 1.40 (1H, dd, *J* = 9.2, 8.0 Hz), 0.842 (6H, d, *J* = 5.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 172.2, 172.0, 156.1, 136.4, 136.3, 128.5, 128.1, 128.0, 127.6, 123.0, 122.2, 119.6, 118.5, 111.3, 109.8, 67.0, 53.9, 52.8, 52.2, 41.4, 27.6, 24.7, 22.8, 21.7; HRMS (ESI) calcd. for $C_{26}H_{31}N_3NaO_5$ $[M+Na]^+$, 488.2156; found 488.2141.

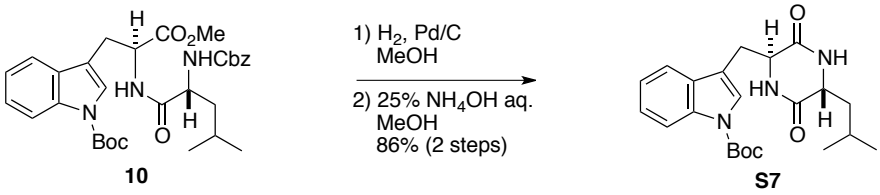
Boc-amide 10



To a stirred solution of amide **S6** (13.2 g, 28.5 mmol) and DMAP (347 mg, 2.84 mmol) in MeCN (360 mL) was added a solution of Boc_2O (7.44 g, 34.1 mmol) in MeCN (18 mL) at 0 °C via cannula. After 3 h, the resulting mixture was allowed to room temperature. After 2.5 h, the reaction mixture

was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 2/1) to afford Boc-amide **10** (16.1 g, 28.5 mmol, quant.) as a white foam. R_f = 0.28 (hexanes/EtOAc = 2/1); $[\alpha]_D^{27}$ = 36.8 (*c* 0.440, $CHCl_3$); IR (film, cm^{-1}) 3315, 2955, 1733, 1716, 1706, 1683, 1654, 1557, 1540, 1456, 1372, 1255, 747; ^1H NMR (400 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 8.10 (1H, d, *J* = 8.4 Hz), 7.47 (1H, d, *J* = 8.0 Hz), 7.39 (1H, s), 7.32–7.18 (7H, m), 6.52 (1H, brs), 5.10–5.02 (2H, m), 4.90 (1H, dd, *J* = 14.0, 6.4 Hz), 4.15 (1H, brs), 3.66 (3H, s), 3.22–3.14 (1H, m), 1.64 (9H, s), 1.58–1.40 (4H, m), 0.854 (6H, d, *J* = 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, 55 °C, a mixture of rotamers) δ 172.0, 171.8, 156.1, 149.5, 136.4, 135.5, 130.5, 128.5, 128.1, 128.0, 124.6, 124.2, 122.6, 118.8, 115.4, 114.9, 83.7, 67.1, 53.7, 52.5, 52.3, 41.6, 28.2, 27.6, 24.7, 22.8, 21.9; HRMS (ESI) calcd. for $C_{31}H_{40}N_3O_7$ $[M+H]^+$, 566.2861; found 566.2840.

Boc-diketopiperazine S7

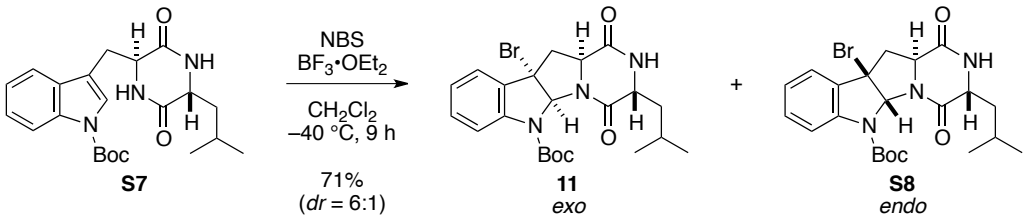


To a mixture of 10% Pd/C (2.63 g, 2.47 mmol) and Boc-protected amide **10** (14.0 g, 24.7 mmol) was added MeOH (247 mL) at room temperature. After stirring of the resulting suspension under hydrogen atmosphere for 1.5 h, the mixture was filtered through a pad of Celite and concentrated under reduced pressure to afford the corresponding amine. The residue was subjected to the next reaction without further purification.

To a stirred solution of the above amine in MeOH (2.06 L) was added 25% aqueous NH_4OH (86 mL) dropwise over 10 min at 0 °C. After 5 min, the resulting mixture was allowed to warm up to room temperature and stirred for 72 h. The reaction mixture was concentrated under reduced pressure to give a crude product as a white solid. The solid was washed with cold Et_2O three times to afford Boc-diketopiperazine **S7** (8.48 g, 21.2 mmol, 86%) as a white solid. R_f = 0.40 (hexanes/EtOAc = 1/1); mp 188-190 °C (CH_2Cl_2/hexanes); $[\alpha]_D^{29}$ = –11.5 (*c* 0.720, $CHCl_3$); IR (film, cm^{-1}) 3187, 3087, 3054, 2958, 2934, 2871, 1733, 1675, 1455, 1370, 1329, 1255, 1159, 1085, 758, 745; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (1H, d, *J* = 8.0 Hz), 7.57 (1H, d, *J* = 8.0 Hz), 7.52 (1H, s), 7.36 (1H, dd, *J* = 8.0, 7.2 Hz), 7.27 (1H, dd, *J* = 8.0, 7.2 Hz), 6.10 (1H, brs), 5.88 (1H, brs), 4.29 (1H, dd, *J* = 9.6, 3.2 Hz), 3.76 (1H, dd, *J* = 9.2, 2.4 Hz), 3.56 (1H, dd, *J* = 15.2, 3.2 Hz), 3.02 (1H, dd, *J* = 15.2, 9.6 Hz), 1.77–1.56 (12H, m), 0.95 (3H, d, *J* = 6.4 Hz), 0.87 (3H, d, *J* = 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 168.3, 149.4, 135.6, 129.6, 125.0, 124.8, 122.7, 118.8, 115.4,

114.3, 83.9, 54.0, 53.3, 42.3, 29.2, 28.1, 24.0, 23.0, 21.1; HRMS (ESI) calcd. for $C_{22}H_{29}N_3NaO_4$ $[M+Na]^+$, 422.2050; found 422.2030.

Bromopyrroloindoline 11 and S8

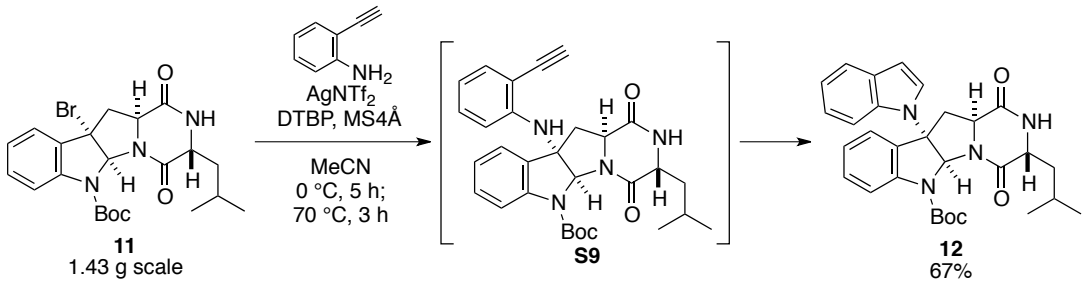


To a stirred solution of Boc-diketopiperazine **S7** (2.00 g, 5.00 mmol) in CH_2Cl_2 (96 mL) was added BF_3•OEt_2 (1.26 mL, 10.0 mmol) at –40 °C. After 25 min, to the reaction mixture was added a solution of NBS (979 mg, 5.50 mmol) in CH_2Cl_2 (144 mL) dropwise over 40 min. After 9 h, the reaction was quenched with saturated aqueous $NaHCO_3$. The resulting mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 2/1) to afford bromopyrroloindoline **11** (*exo*) (1.44 g, 3.01 mmol, 60%) as a white foam and **S8** (*endo*) (255 mg, 0.533 mmol, 11%) as a white foam, respectively.

Bromopyrroloindoline **11** (*exo*); R_f = 0.89 (hexanes/EtOAc = 1/1); $[\alpha]_D^{27}$ = 83.6 (*c* 0.525, $CHCl_3$); IR (film, cm^{-1}) 3253, 3008, 2960, 2932, 2871, 1716, 1684, 1478, 1369, 1157, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (1H, d, *J* = 8.0 Hz), 7.39 (1H, d, *J* = 8.0 Hz), 7.23 (1H, dd, *J* = 8.0, 7.6 Hz), 7.06 (1H, dd, *J* = 8.0, 7.6 Hz), 6.41 (1H, brs), 6.27 (1H, s), 4.37 (1H, dd, *J* = 10.4, 4.4 Hz), 3.76–3.71 (1H, m), 3.61 (1H, dd, *J* = 14.0, 4.4 Hz), 3.13 (1H, dd, *J* = 14.0, 10.4 Hz), 1.73–1.57 (12H, m), 0.97 (3H, d, *J* = 6.8 Hz), 0.89 (3H, d, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 166.3, 151.7, 139.9, 133.1, 130.6, 124.4, 124.3, 116.9, 85.3, 82.6, 59.6, 56.4, 55.9, 41.1, 39.0, 28.2, 24.5, 23.0, 21.0; HRMS (ESI) calcd. for $C_{22}H_{28}BrN_3NaO_4$ $[M+Na]^+$, 500.1155; found 500.1129.

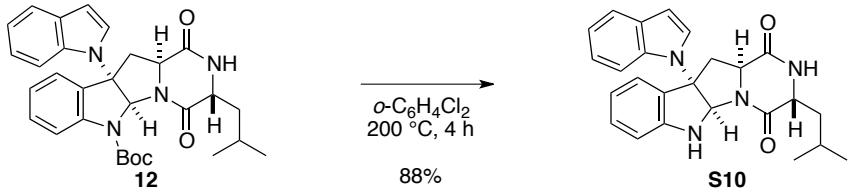
Bromopyrroloindoline **S8** (*endo*); R_f = 0.80 (hexanes/EtOAc = 1/1); $[\alpha]_D^{28}$ = –141 (*c* 0.490, $CHCl_3$); IR (film, cm^{-1}) 3005, 2960, 2933, 2904, 2871, 1716, 1685, 1479, 1416, 1154, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (1H, d, *J* = 8.4 Hz), 7.42 (1H, d, *J* = 7.6 Hz), 7.34 (1H, dd, *J* = 8.4, 7.2 Hz), 7.14 (1H, dd, *J* = 7.6, 7.2 Hz), 6.70 (1H, s), 6.18 (1H, brs), 3.97–3.92 (1H, m), 3.85 (1H, dd, *J* = 12.0, 5.2 Hz), 3.32 (1H, dd, *J* = 12.4, 5.2 Hz), 2.88 (1H, dd, *J* = 12.4, 12.0 Hz), 1.67–1.51 (12H, m), 0.93 (3H, d, *J* = 6.4 Hz), 0.90 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.9, 151.6, 142.1, 131.2, 130.9, 124.4, 124.1, 116.8, 83.5, 82.8, 58.3, 58.0, 56.0, 46.8, 43.8, 28.1, 24.2, 23.0, 21.3; HRMS (ESI) calcd. for $C_{22}H_{28}BrN_3NaO_4$ $[M+Na]^+$, 500.1155; found 500.1127.

Indole 12



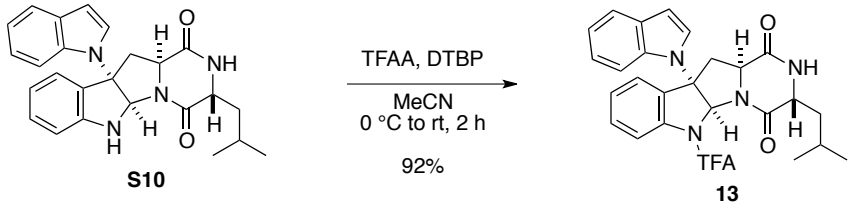
To a stirred solution bromopyrroloindoline **11** (1.43 g, 2.99 mmol), pre-activated MS4Å (1.50 g), DTBP (1.01 mL, 4.49 mmol), and 2-ethynylaniline (1.05 g, 8.96 mmol) in MeCN (30 mL) was added $AgNTf_2$ (3.48 g, 8.96 mmol) at 0 °C. After TLC indicated complete consumption of **S9**, the reaction mixture was stirred at 70 °C for 3 h. The reaction was quenched with saturated aqueous $NaHCO_3$ at 0 °C. The mixture was extracted with EtOAc three times and washed with brine. The combined organic extracts were dried over Na_2SO_4, filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (CH_2Cl_2/EtOAc = 9/1) to afford indole **12** (1.03 g, 2.00 mmol, 67%) as a pale orange foam. R_f = 0.37 (CH_2Cl_2/EtOAc = 9/1); $[\alpha]_D^{26}$ = –119 (*c* 1.07, $CHCl_3$); IR (film, cm^{-1}) 3283, 3276, 2961, 2931, 1715, 1694, 1684, 1481, 1370, 1337, 1157, 753; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (1H, d, *J* = 8.4 Hz), 7.64 (1H, d, *J* = 8.0 Hz), 7.51 (1H, d, *J* = 7.6 Hz), 7.40–7.36 (2H, m), 7.26–7.13 (3H, m), 6.69 (1H, d, *J* = 3.2 Hz), 6.62 (1H, s), 6.39 (1H, d, *J* = 3.2 Hz), 6.01 (1H, brs), 4.70 (1H, t, *J* = 8.0 Hz), 3.87–3.82 (1H, m), 3.50 (2H, d, *J* = 8.0 Hz), 1.76–1.74 (3H, m), 1.53 (9H, s), 1.00 (3H, d, *J* = 5.6 Hz), 0.93 (3H, d, *J* = 5.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.0, 166.9, 151.6, 141.1, 134.2, 130.9, 130.8, 130.7, 236.6, 235.9, 124.0, 122.0, 121.9, 120.3, 117.6, 111.0, 120.1, 82.7, 80.3, 70.1, 54.5, 55.9, 41.1, 33.6, 28.2, 24.6, 23.1, 21.0; HRMS (ESI) calcd. for $C_{30}H_{35}N_4O_4$ $[M+H]^+$, 515.2653; found 515.2635.

Indoline S10



A stirred solution of indole **12** (317 mg, 0.616 mmol) in *o*-$C_6H_4Cl_2$ (6.2 mL) was heated at 200 °C. After 4 h, the reaction mixture was cooled to room temperature. The residue was purified directly by flash column chromatography on silica gel (hexanes/EtOAc = 1/1) to afford indoline **S10** (225 mg, 0.543 mmol, 88%) as a pale yellow foam. R_f = 0.25 (hexanes/EtOAc = 1/1); $[\alpha]_D^{28}$ = 233 (*c* 0.135, $CHCl_3$); IR (film, cm^{-1}) 3324, 3261, 2957, 2930, 2871, 1683, 1675, 1655, 1613, 1456, 1436, 1320, 1215, 1145, 742; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (1H, d, *J* = 8.0 Hz), 7.45 (1H, d, *J* = 4.0 Hz), 7.21 (1H, dd, *J* = 8.0, 7.2 Hz), 7.08 (1H, dd, *J* = 8.0, 6.8 Hz), 7.00 (1H, dd, *J* = 8.0, 6.8 Hz), 6.90 (1H, d, *J* = 7.2 Hz), 6.76–6.70 (3H, m), 6.61 (1H, d, *J* = 3.6 Hz), 6.12 (1H, d, *J* = 3.6 Hz), 5.64 (1H, d, *J* = 4.0 Hz), 4.63 (1H, dd, *J* = 11.2, 6.0 Hz), 3.96–3.91 (1H, m), 3.65 (1H, dd, *J* = 15.2, 6.0 Hz), 2.73 (1H, dd, *J* = 15.2, 11.2 Hz), 1.79–1.73 (1H, m), 1.64–1.56 (2H, m), 0.96 (3H, d, *J* = 6.4 Hz), 0.92 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 167.5, 146.7, 135.2, 130.33, 130.32, 128.1, 124.1, 123.3, 122.1, 121.4, 120.3, 119.9, 112.1, 110.2, 102.8, 82.9, 73.3, 56.8, 56.3, 42.3, 40.1, 24.5, 22.9, 21.2; HRMS (ESI) calcd. for $C_{25}H_{27}N_4O_2$ $[M+H]^+$, 415.2134; found 415.2105.

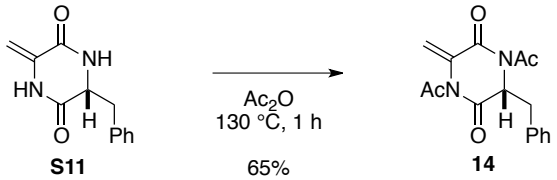
TFA-indoline 13



S10 13

To a stirred solution of indoline **S10** (54.4 mg, 0.131 mmol) and DTBP (147 μL, 0.655 mmol) in MeCN (2.6 mL) was added TFAA (55 μL, 0.39 mmol) at room temperature. After 2 h, the reaction was quenched with H_2O at 0 °C. The mixture was extracted with EtOAc twice. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 2/1→1/1) and preparative TLC (hexanes/EtOAc = 1/1) to afford TFA-indoline **13** (61.5 mg, 0.120 mmol, 92%) as a colorless oil; $[\alpha]_D^{25}$ = –189 (*c* 0.170, $CHCl_3$); IR (neat, cm^{-1}) 2959, 2919, 2851, 1714, 1696, 1685, 1456, 1254, 1221, 1188, 1147, 761, 741; ^1H NMR (600 MHz, $CDCl_3$) δ 8.21 (1H, d, *J* = 7.8 Hz), 7.67 (1H, d, *J* = 7.2 Hz), 7.65 (1H, d, *J* = 7.2 Hz), 7.52 (1H, dd, *J* = 8.4, 7.8 Hz), 7.40–7.37 (2H, m), 7.31 (1H, dd, *J* = 7.8, 7.2 Hz), 7.22 (1H, dd, *J* = 8.4, 7.2 Hz), 6.73 (1H, s), 6.53 (1H, d, *J* = 3.6 Hz), 6.40 (1H, d, *J* = 3.6 Hz), 6.02 (1H, brs), 4.76 (1H, dd, *J* = 10.8, 4.8 Hz), 3.84–3.80 (1H, m), 3.63 (1H, dd, *J* = 15.6, 11.4 Hz), 3.57 (1H, dd, *J* = 15.6, 3.6 Hz), 1.76–1.71 (3H, m), 1.00 (3H, d, *J* = 6.0 Hz), 0.93 (3H, d, *J* = 6.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.7, 167.5, 156.3 (q, *J* = 38.7 Hz), 140.6, 134.0, 131.8, 130.9, 130.4, 126.7, 126.6, 126.5, 122.4, 120.7, 119.2, 115.8 (q, *J* = 288 Hz), 110.3, 102.8, 79.4 (q, *J* = 4.2 Hz), 71.1, 56.3, 56.1, 41.2, 32.6, 24.6, 23.0, 21.1 (one signal is missing due to overlap); HRMS (ESI) calcd. for $C_{27}H_{26}F_3N_4O_3$ $[M+H]^+$, 511.1957; found 511.1929.

Ac-enamide 14

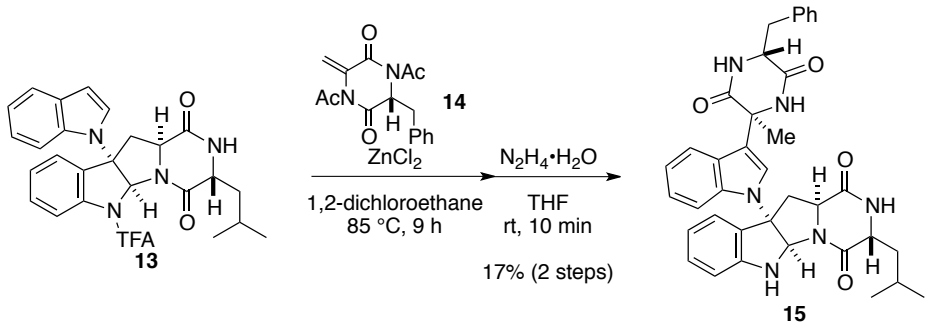


S11 14

A stirred solution of enamide **S11** (150 mg, 0.640 mmol) in Ac_2O (6.4 mL) was heated to 130 °C. After 1 h, the reaction mixture was cooled down to room temperature. The mixture was diluted with toluene and EtOAc and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 4/1→3/1) to afford Ac-enamide **14** (124 mg, 0.413 mmol, 65%) as a colorless oil. R_f = 0.46 (hexanes/EtOAc = 3/1); $[\alpha]_D^{27}$ = –121 (*c* 0.55, $CHCl_3$); IR (neat, cm^{-1}) 3063, 3029, 3007, 2939, 1730, 1715, 1623, 1338, 1369, 1226, 1194; ^1H

NMR (400 MHz, $CDCl_3$) δ 7.27–7.02 (3H, m), 7.03 (2H, dd, *J* = 7.2, 1.2 Hz), 6.02 (1H, s), 5.61 (1H, s), 5.52 (1H, dd, *J* = 6.4, 5.6 Hz), 3.23 (1H, dd, *J* = 14.0, 5.6 Hz), 3.14 (1H, dd, *J* = 14.0, 6.4 Hz), 2.55 (3H, s), 2.54 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.3, 167.3, 161.6, 134.1, 130.8, 129.9, 128.8, 127.8, 120.4, 58.4, 38.7, 27.5, 26.5; HRMS (ESI) calcd. for $C_{16}H_{16}N_2NaO_4$ $[M+Na]^+$, 323.1008; found 323.1002.

Indole adduct 15

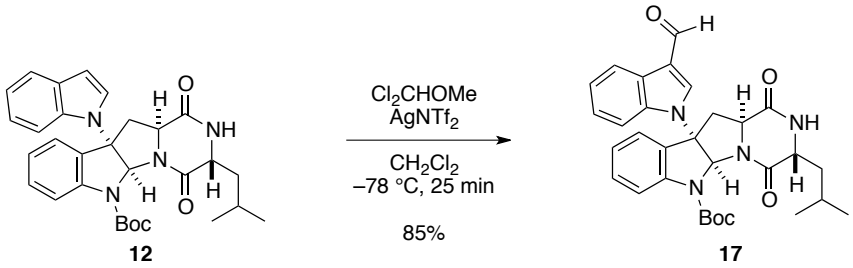


To a stirred solution of TFA-indoine **13** (14.7 mg, 28.8 μmol) and Ac-enamide **14** (17.0 mg, 56.6 μmol) in 1,2-dichloroethane (1.2 mL) was added a solution of $ZnCl_2$ (28.8 μL, 28.8 μmol, 1 M in Et_2O) at room temperature and the resulting mixture was heated at 85 °C. After 3.5 h, the additional solution of $ZnCl_2$ (57.6 μL, 57.6 μmol, 1 M in Et_2O) was added to the reaction mixture. After 5.5 h, the reaction was quenched with saturated aqueous $NaHCO_3$ at 0 °C. The resulting mixture was extracted with CH_2Cl_2 three times and washed with brine. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified roughly by preparative TLC (CH_2Cl_2/EtOAc = 3/1) to afford a mixture of inseparable compounds.

To a stirred solution of the mixture in THF (0.90 mL) was added N_2H_4•H_2O (4.4 μL, 90.5 μmol) at room temperature. After 10 min, the reaction was quenched with saturated aqueous NH_4Cl. The resulting mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by preparative TLC (CH_2Cl_2/EtOAc = 3/1) to afford indole adduct **15** (3.0 mg, 4.76 μmol, 17% in 2 steps) as a white foam. R_f = 0.29 (hexanes/EtOAc = 1/3); $[\alpha]_D^{28}$ = 18.2 (*c* 0.0700, $CHCl_3$); IR (film, cm^{-1}) 2952, 2924, 2851, 1733, 1716, 1698, 1684, 1671, 1653, 1558, 1541, 1507, 772; ^1H NMR (600 MHz, acetone-d_6) δ 7.82 (1H, d, *J* = 8.4 Hz), 7.71 (1H, s), 7.65 (1H, d, *J* = 4.8 Hz), 7.60 (1H, brs), 7.35–7.30 (4H, m), 7.34 (2H, d, *J* = 6.6 Hz), 7.31 (2H, dd, *J* = 7.8, 7.2 Hz), 6.87–6.83 (3H, m), 6.63 (1H, dd, *J* = 7.8, 6.6 Hz), 6.94 (1H, dd, *J* = 8.4, 7.2 Hz), 6.87–6.83 (3H, m), 6.63 (1H, dd, *J* = 7.8, 6.6 Hz), 6.58 (1H, d, *J* = 3.6 Hz), 6.08 (1H, d, *J* = 3.6 Hz), 4.83 (1H, dd, *J* = 11.4, 6.6 Hz), 4.48 (1H, dd, *J* = 6.0, 4.8 Hz), 3.92–3.88 (1H, m), 3.74 (1H, dd, *J* = 15.0, 6.0 Hz), 3.27 (1H, dd, *J* = 14.4,

5.4 Hz), 3.21 (1H, dd, *J* = 14.4, 4.8 Hz), 2.49 (1H, dd, *J* = 14.4, 11.4 Hz), 1.80–1.75 (1H, m), 1.68–1.63 (1H, m), 1.54–1.49 (1H, m), 1.44 (3H, s), 1.08 (1H, dd, *J* = 9.6, 6.6 Hz), 0.92 (3H, d, *J* = 7.2 Hz), 0.88 (3H, d, *J* = 6.6 Hz); ^{13}C NMR (150 MHz, acetone-*d*$_6$) δ 169.7, 168.7, 168.5, 168.0, 148.8, 137.5, 137.2, 131.1, 130.8, 129.7, 129.2, 128.3, 127.7, 124.0, 123.6, 122.5, 121.8, 120.6, 119.6, 118.7, 113.1, 111.0, 83.3, 74.5, 59.0, 57.1, 56.9, 56.7, 43.0, 40.9, 38.8, 27.0, 25.0, 23.1, 21.7; HRMS (ESI) calcd. for $C_{37}H_{38}N_6NaO_4$ $[M+Na]^+$, 653.2847; found 653.2815.

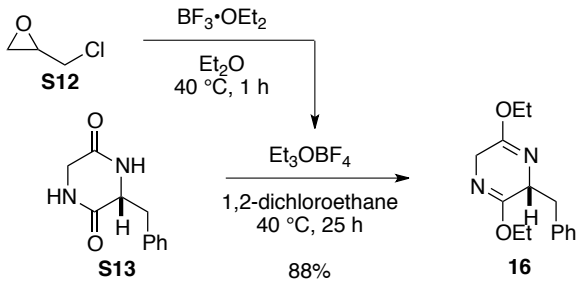
Aldehyde 17



12 **17**

To a stirred solution of indole **12** (300 mg, 1.99 mmol) and $AgNTf_2$ (679 mg, 1.75 mmol) in CH_2Cl_2 (12 mL) was added Cl_2CHOMe (158 μL, 1.75 mmol) at –78 °C. After 25 min, the reaction was quenched with saturated aqueous $NaHCO_3$. The resulting mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (CH_2Cl_2/EtOAc = 2/1) to afford aldehyde **17** (269 mg, 0.500 mmol, 85%) as a white solid. mp 233-235 °C (CH_2Cl_2/hexanes); R_f = 0.42 (CH_2Cl_2/EtOAc = 2/1); $[\alpha]_D^{28}$ = –138 (*c* 0.474, $CHCl_3$); IR (film, cm^{-1}) 3290, 3276, 3253, 3009, 2959, 2935, 2871, 1715, 1695, 1684, 1669, 1654, 1156, 750; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (1H, s), 8.40–8.38 (1H, m), 7.74 (1H, d, *J* = 8.4 Hz), 7.55 (1H, d, *J* = 7.6 Hz), 7.49–7.23 (6H, m), 6.67 (1H, s), 6.19 (1H, brs), 4.75 (1H, dd, *J* = 10.4, 5.6 Hz), 3.88–3.86 (1H, m), 3.58–3.50 (2H, m), 1.77–1.69 (3H, m), 1.53 (9H, s), 1.01 (3H, d, *J* = 5.2 Hz), 0.93 (3H, d, *J* = 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.7, 167.5, 166.9, 151.4, 141.3, 137.6, 135.1, 131.8, 129.1, 127.2, 126.2, 124.4, 123.6, 123.3, 118.2, 118.0, 111.4, 83.2, 80.0, 70.5, 56.5, 55.8, 41.1, 32.9, 28.1, 24.6, 23.1, 21.0 (one signal is missing due to overlap); HRMS (ESI) calcd. for $C_{31}H_{35}N_4O_5$ $[M+H]^+$, 543.2602; found 543.2562.

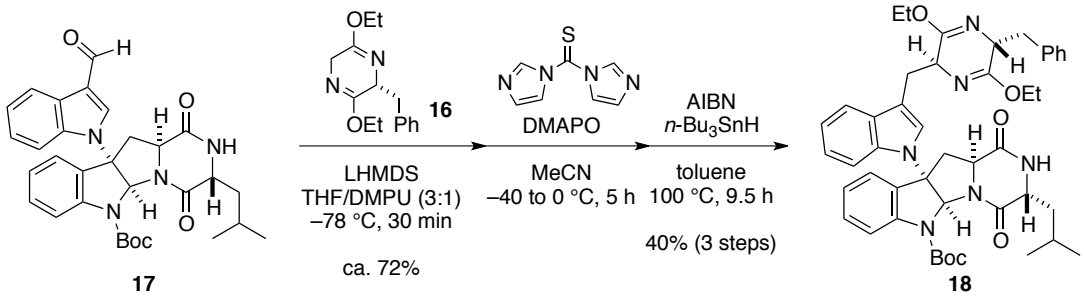
Imidate 16



To a stirred solution of epichlorohydrin **S12** (408 μL, 5.29 mmol) in Et_2O (10 mL) was added BF_3•OEt_2 (864 μL, 6.88 mmol) at room temperature and the resulting mixture was heated at 40 °C. After 1 h, the reaction mixture was cooled to room temperature and a white solid precipitated in situ. The solvent was removed via syringe and the solid was washed with Et_2O. This protocol was repeated three times and the resulting suspension was concentrated under reduced pressure. The resulting solid (Et_3OBF_4) was used in the next step without further purification.[9]

A stirred solution of the above solid (Et_3OBF_4) and diketopiperazine **S13** (270 mg, 1.32 mmol) in 1,2-dichloroethane (17 mL) was heated at 40 °C. After 25 h, the reaction mixture was cooled to room temperature and the reaction was quenched with saturated aqueous $NaHCO_3$ at 0 °C. The resulting mixture was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexanes/EtOAc = 4/1) to afford imidate **16** (301 mg, 1.16 mmol, 88%) as a colorless oil. R_f = 0.36 (hexanes/EtOAc = 4/1); $[\alpha]_D^{26}$ = –162 (*c* 0.407, $CHCl_3$); IR (neat, cm^{-1}) 3062, 3030, 2979, 2931, 2871, 1694, 1368, 1242, 1035, 702; ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.19 (3H, m), 7.07–7.04 (2H, m), 4.41–4.37 (1H, m), 4.20–4.06 (4H, m), 3.66 (1H, dd, *J* = 20.0, 3.2 Hz), 3.14 (1H, dd, *J* = 13.2, 4.4 Hz), 3.02 (1H, dd, *J* = 13.2, 4.4 Hz), 2.90 (1H, dd, *J* = 20.0, 3.2 Hz), 1.33 (3H, t, *J* = 7.2 Hz), 1.28 (3H, t, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 162.9, 136.8, 130.0, 127.8, 126.4, 60.8, 60.7, 57.0, 46.3, 39.7, 14.32, 14.28; HRMS (ESI) calcd. for $C_{15}H_{21}N_2O_2$ $[M+H]^+$, 261.1598; found 261.1589.

Imidate 18



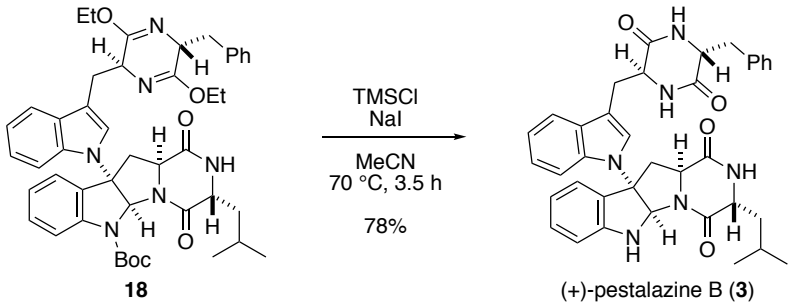
Imidate **16** (111 mg, 0.426 mmol) was dried azeotropically (concentration of a benzene solution) under reduced pressure and placed under an argon atmosphere. To the stirred solution of imidate **16** in THF (1.4 mL) was added LHMDS (655 μL, 0.852 mmol, 1.3 M in THF) dropwise at –78 °C. After 30 min, a solution of aldehyde **17** (77.1 mg, 0.142 mmol) in a mixture of DMPU (0.71 mL) and THF (0.71 mL) was added to the reaction mixture via cannula. After 30 min, the reaction was quenched with H_2O. The resulting mixture was extracted with EtOAc three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified roughly by flash column chromatography on silica gel (CH_2Cl_2/EtOAc = 2/1) to afford a mixture of inseparable diastereomers (81.6 mg, ca. 0.102 mmol, ca. 72%) This mixture was subjected to next reaction due to the difficulty of separation of the diastereomers.

The mixture (48.5 mg, ca. 60.4 μmol) was dried azeotropically (concentration of a benzene solution) under reduced pressure and placed under an argon atmosphere. To a stirred solution of the mixture of diastereomers and DMAPO (8.3 mg, 60 μmol) in MeCN (2.4 mL) was added 1,1'-thiocarbonyldiimidazole (21.5 mg, 0.121 mmol) at –40 °C. The additional DMAPO (24.9 mg, 0.180 mmol) was added to the reaction mixture and the reaction temperature was gradually raised to 0 °C before a consumption of the starting material. After 5 h, the reaction was quenched with H_2O. The resulting mixture was extracted with EtOAc three times. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified roughly by flash column chromatography on silica gel (CH_2Cl_2/EtOAc = 2/1→1/1) to afford a mixture of inseparable diastereomers. This mixture was subjected directly to the next reaction due to the difficulty of separation of diastereomers.

The mixture was dried azeotropically (concentration of a benzene solution) under reduced pressure and placed under an argon atmosphere. A stirred solution of the mixture in toluene (1.2 mL) was bubbled with Argon gas for 30 min. To the reaction mixture was added a solution of AIBN (7.5 mg, 46 mmol) and *n*-Bu_3SnH (183 μL, 0.693 mmol) in toluene (1.7 mL) dropwise over 9.5 h at 100 °C. The reaction mixture was cooled to room temperature and the resulting mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography on

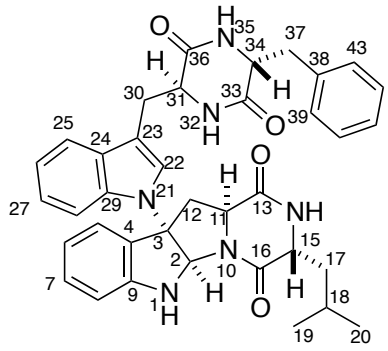
silica gel (hexanes/EtOAc = 1/0→1/1→1/3) to afford imidate **18** (26.7 mg, 33.9 μmol, 40% in 3 steps) as a white foam; R_f = 0.21 (hexanes/EtOAc = 1/1); $[\alpha]_D^{25}$ = –109 (*c* 0.778, $CHCl_3$); IR (film, cm^{-1}) 3281, 3250, 3210, 3028, 2976, 2961, 2931, 2900, 2871, 1715, 1691, 1369, 1240, 1157, 754; ^1H NMR (600 MHz, $CDCl_3$) δ 7.72 (1H, d, *J* = 8.4 Hz), 7.60 (1H, d, *J* = 8.4 Hz), 7.39 (1H, dd, *J* = 8.4, 7.8 Hz), 7.25 (1H, d, *J* = 8.4 Hz), 7.23–7.09 (6H, m), 7.00 (1H, d, *J* = 7.8 Hz), 6.52 (1H, s), 6.27 (1H, s), 6.05 (1H, d, *J* = 4.8 Hz), 4.69 (1H, dd, *J* = 10.4, 5.4 Hz), 4.07–4.03 (1H, m), 3.96–3.93 (1H, m), 3.90–3.86 (1H, m), 3.85–3.81 (1H, m), 3.79–3.76 (1H, m), 3.62–3.56 (2H, m), 3.45 (1H, dd, *J* = 14.4, 10.4 Hz), 3.34 (1H, dd, *J* = 14.4, 5.4 Hz), 2.96 (2H, d, *J* = 4.8 Hz), 2.93 (1H, dd, *J* = 13.2, 5.4 Hz), 2.88 (1H, dd, *J* = 13.2, 4.8 Hz), 1.78–1.74 (3H, m), 1.52 (9H, s), 1.22–1.16 (6H, m), 1.00 (3H, d, *J* = 5.4 Hz), 0.92 (3H, d, *J* = 6.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.9, 166.9, 162.8, 162.4, 151.6, 141.3, 137.5, 133.8, 131.1, 130.8, 130.0, 127.7, 126.3, 126.2, 125.7, 123.8, 121.7, 120.6, 119.5, 117.5, 110.8, 110.5, 82.5, 80.0, 69.9, 60.5, 60.4, 56.54, 56.52, 56.1, 55.9, 41.2, 39.6, 33.5, 28.8, 28.2, 24.6, 23.2, 21.0, 14.44, 14.37 (one signal is missing due to overlap); HRMS (ESI) calcd. for $C_{46}H_{55}N_6O_6$ $[M+H]^+$, 787.4178; found 787.4138.

(+)-Pestalazine B (3)



Imidate **18** (30.6 mg, 38.9 μmol) was dried azeotropically (concentration of a benzene solution) under reduced pressure and placed under an argon atmosphere. To the stirred solution of the imidate **18** and NaI (29.2 mg, 195 μl) in MeCN (1.9 mL) was added TMSCl (15 μl, 195 μmol) at room temperature and the mixture was heated at 70 °C. The additional NaI (40.9 mg, 272 μmol) and TMSCl (21 μL, 272 μmol) were added to the reaction mixture. After 3.5 h, the reaction was quenched with H_2O. The resulting mixture was extracted with EtOAc three times and washed with 10% aqueous $Na_2S_2O_3$ and H_2O. The combined organic extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by recrystallization (MeOH/hexanes) to afford (+)-pestalazine B (**3**) (19.1 mg, 30.3 μmol, 78%) as a white solid; R_f = 0.58 (hexanes/acetone = 1/3); $[\alpha]_D^{29}$ = +218 (*c* 0.1, MeOH), $[\alpha]_D^{23}$ = +199 (*c* 0.1, MeOH) (lit.[10]), $[\alpha]_D^{28}$ = +194 (*c* 0.1, MeOH) (lit.[11]), $[\alpha]_D^{25}$ = +204 (*c* 0.2, MeOH) (lit.[12]), $[\alpha]_D^{23}$ = +191 (*c* 0.1, MeOH) (lit.[13]); IR (film, cm^{-1}) 3320, 3265, 3255, 3159, 3084, 3062, 2956, 2921, 2871, 1682, 1456, 1445, 1321, 1218, 745; ^1H NMR (600 MHz, acetone-d_6) δ 7.67–7.61 (2H, m), 7.50 (1H, d, *J* = 8.4 Hz), 7.22–7.13 (4H, m), 7.10-7.09 (2H, m), 7.00–6.90 (4H, m), 6.84 (1H, d, *J* = 7.8 Hz), 6.79–6.75 (2H, m), 6.63 (1H, dd, *J* = 7.8, 7.2 Hz), 6.58 (1H, d, *J* = 3.0 Hz), 6.04 (1H, d, *J* = 3.6 Hz), 4.85 (1H, dd, *J* = 12.0, 5.4 Hz), 3.91–3.88 (1H, m), 3.69–3.64 (2H, m), 3.51 (1H, br t, *J* = 4.8 Hz), 3.23 (2H, d, *J* = 5.4 Hz), 3.05 (1H, dd, *J* = 13.8, 5.4 Hz), 2.99 (1H, dd, *J* = 14.4, 4.8 Hz), 2.46 (1H, dd, *J* = 14.4, 12.0 Hz), 1.82-1.77 (1H, m), 1.76–1.71 (1H, m), 1.55–1.49 (1H, m), 0.95 (3H, d, *J* = 6.8 Hz), 0.90 (3H, d, *J* = 6.8 Hz); ^{13}C NMR (150 MHz, acetone-d_6) δ 168.9, 168.5, 148.8, 137.0, 136.5, 130.8, 130.7, 130.69, 129.8, 129.1, 127.6, 126.5, 123.5, 122.4, 120.4, 120.3, 119.6, 112.9, 110.9, 111.0, 83.4, 74.3, 57.3, 56.8, 56.2, 55.8, 42.9, 41.2, 39.2, 30.3, 25.0, 23.2, 21.7 (two signals are missing due to overlap); HRMS (ESI) calcd. for $C_{37}H_{39}N_6O_4$ $[M+H]^+$, 631.3027; found 631.3000.

Comparison of ^{1}H NMR chemical shifts of natural and synthetic (+)-pestalazine B



(+)-pestalazine B (**3**)

position	Synthetic (This work) (600 MHz, acetone-d_6)	Natural[10] (600 MHz, acetone-d_6)	Synthetic (de Lera)[11] (600 MHz, acetone-d_6)	Synthetic (Deng/Liao)[12] (600 MHz, acetone-d_6)
C22, N35	7.67-7.61 (2H, m)	8.05 (1H, d, J = 3.5 Hz)	7.81 (1H, d, J = 4.3 Hz)	7.69–7.61 (2H, m)
	–	7.64 (1H, s)	7.66 (1H, s)	–
C25	7.50 (1H, d, J = 8.4 Hz)	7.38 (1H, brs)	7.52 (1H, d, J = 7.8 Hz)	7.53–7.48 (1H, m)
C7, C39, C40, C41, C42, C43	7.22–7.09 (6H, m)	7.32 (1H, brs)	7.2-7.1 (6H, m)	7.25–7.15 (4H, m)
	-	7.20–7.14 (6H, m)	–	7.12–7.06 (2H, m)
C5, N14, C26, C27	7.00–6.90 (4H, m)	7.0–6.9 (7H, m)	7.0–6.9 (4H, m)	7.00–6.90 (4H, m)
C8	6.84 (1H, d, J = 7.8 Hz)	6.83 (1H, d, J = 7.8 Hz)	6.85 (1H, d, J = 7.9 Hz)	6.85 (1H, dt, J = 5.2, 0.4 Hz)
C28, N32	6.79–6.75 (2H, m)	6.83 (1H, d, J = 3.0 Hz)	6.78 (1H, d, J = 8.2 Hz)	6.79 (1H, dt, J = 5.6, 0.8 Hz)
	–	6.75 (1H, d, J = 7.8 Hz)	-	6.76 (1H, s)
C6	6.63 (1H, dd, J = 7.8, 7.2 Hz)	6.62 (1H, t, J = 7.2 Hz)	6.64 (1H, t, J = 7.2 Hz)	6.64 (1H, td, J = 5.6, 0.8 Hz)

N1	6.58 (1H, d, *J* = 3.0 Hz)	–	6.65 (1H, d, *J* = 3.0 Hz)	6.58 (1H, d, *J* = 2.4 Hz)
C2	6.04 (1H, d, *J* = 3.6 Hz)	6.03 (1H, d, *J* = 3.0 Hz)	6.05 (1H, d, *J* = 3.3 Hz)	6.05 (1H, d, *J* = 4 Hz)
C11	4.85 (1H, dd, *J* = 12.0, 5.4 Hz)	4.82 (1H, dd, *J* = 12.0, 6.0 Hz)	4.84 (1H, dd, *J* = 11.7, 6.0 Hz)	4.85 (1H, dd, *J* = 7.6, 4.0 Hz)
C15	3.91–3.88 (1H, m)	3.85 (1H, m)	3.89 (1H, dt, *J* = 9.6, 4.8 Hz)	3.91 (1H, quint, *J* = 3.2 Hz)
C12, C31	3.69–3.64 (2H, m)	3.68 (1H, dd, *J* = 14.0, 6.0 Hz)	3.69 (1H, dd, *J* = 14.8, 6.0 Hz)	3.72–3.65 (2H, m)
	–	3.62 (1H, dd, *J* = 5.2, 4.8 Hz)	3.7–3.6 (1H, m)	–
C34	3.51 (1H, br t, *J* = 4.8 Hz)	3.47 (1H, br t, *J* = 4.8 Hz)	3.50 (1H, br t, *J* = 4.7 Hz)	3.51 (1H, t, *J* = 3.6 Hz)
C30	3.23 (2H, d, *J* = 5.4 Hz)	3.21 (2H, dd, *J* = 14.0, 5.4 Hz)	3.21 (2H, app. dd, *J* = 3.2 Hz)	3.23 (2H, d, *J* = 3.6 Hz)
	–	3.15 (2H, dd, *J* = 14.0, 4.8 Hz)	–	–
C37	3.05 (1H, dd, *J* = 13.8, 5.4 Hz)	3.06 (1H, dd, *J* = 14, 4.8 Hz)	3.06 (1H, dd, *J* = 13.9, 5.4 Hz)	3.05 (1H, dd, *J* = 9.2, 3.6 Hz)
C37	2.99 (1H, dd, *J* = 14.4, 4.8 Hz)	2.88 (overlapped)	2.96 (1H, dd, *J* = 13.9, 4.6 Hz)	2.99 (1H, dd, *J* = 9.2, 3.2 Hz)
C12	2.46 (1H, dd, *J* = 14.4, 12.0 Hz)	2.42 (1H, dd, *J* = 14.0, 12.0 Hz)	2.41 (1H, dd, *J* = 14.6, 11.7 Hz)	2.47 (1H, dd, *J* = 10.0, 8.0 Hz)
C18	1.82–1.77 (1H, m)	1.80 (1H, m)	1.9–1.8 (1H, m)	1.75–1.67 (1H, m)
C17	1.76–1.71 (1H, m)	1.73 (1H, m)	1.8–1.7 (1H, m)	1.58–1.47 (1H, m)
C17	1.55–1.49 (1H, m)	1.50 (1H, m)	1.52 (1H, ddd, *J* = 13.6, 8.5, 5.3 Hz)	–
C19	0.95 (3H, d, *J* = 6.8 Hz)	0.95 (3H, d, *J* = 6.6 Hz)	0.95 (3H, d, *J* = 6.5 Hz)	0.95 (3H, d, *J* = 4.4 Hz)
C20	0.90 (3H, d, *J* = 6.8 Hz)	0.90 (3H, d, *J* = 6.0 Hz)	0.90 (3H, d, *J* = 6.5 Hz)	0.90 (3H, d, *J* = 4.4 Hz)

Comparison of ^{13}C NMR chemical shifts of natural and synthetic (+)-pestalazine B

position	Synthetic (150 MHz, acetone-d_6)	Natural[10] (150 MHz, acetone-d_6)	Synthetic (de Lera)[11] (150 MHz, acetone-d_6)	Synthetic (Deng/Liao)[12] (150 MHz, acetone-d_6)
C13, C33	168.9	168.9	169.0	168.9
	Overlapped	168.8	169.0	–
C12, C36	168.6	168.6	168.6	168.52
	Overlapped	168.4	168.6	168.49
C9	148.8	148.9	148.9	148.8
C38	137.0	137.1	137.1	137.0
C29	136.6	136.3	136.6	136.6
C39, C43	130.8	130.9	131.0	130.8
C7, C24	130.71	130.9	131.0	130.7
	130.69	130.8	130.8	–
C4	129.8	130.5	130.8	129.8
C40, C42	129.1	129.8	129.1	129.1
C41	127.6	127.4	127.7	127.6
C22	126.5	126.4	126.6	126.48
	–	–	–	126.45
C5	123.5	123.3	123.6	123.5
C27	122.4	122.2	122.4	122.4
C26	120.4	120.3	120.5	120.5
C25	120.3	120.3	120.4	120.27
	–	–	–	120.26
C6	119.6	119.4	119.7	119.7
C28	112.9	112.8	113.0	112.9
C8	110.9	110.9	111.0	111.0
C23	110.0	109.9	110.0	–
C2	83.4	83.4	83.5	83.4
C3	74.3	74.2	74.4	76.4
C11	57.3	57.2	57.3	57.30

C15	56.8	56.7	56.9	57.26
C34	56.2	56.1	56.3	56.2
C31	55.8	55.8	55.8	55.8
C17	42.9	42.8	42.9	–
C12	41.2	41.2	41.3	–
C37	39.2	38.9	39.1	–
C30	30.3	30.2	30.3	–
C18	25.0	24.9	25.1	25.1
C19	23.2	23.2	23.3	23.2
	–	–	–	23.2
C20	21.7	21.7	21.8	21.8

4. References

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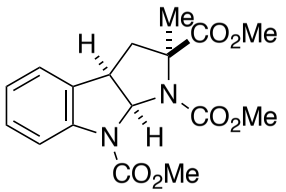
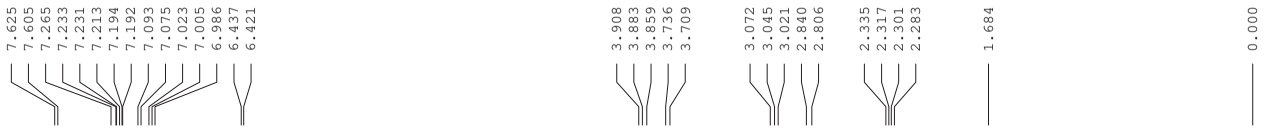
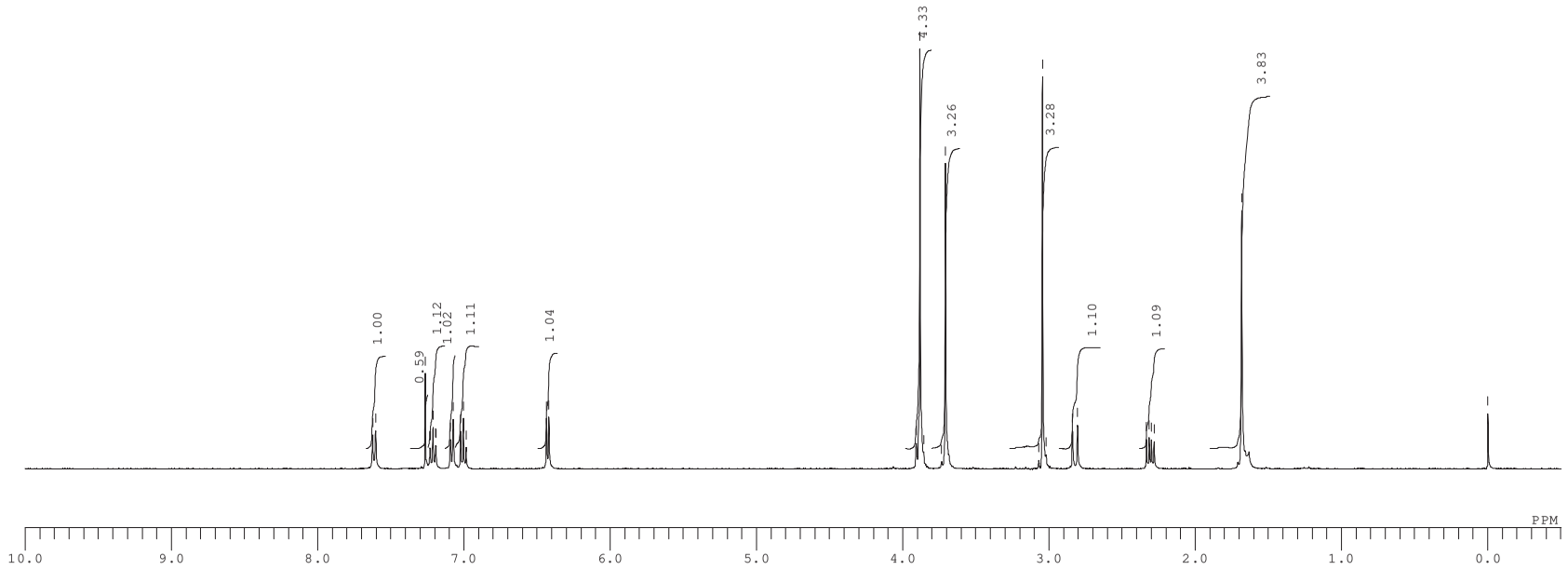
^{1}H-NMR (400 MHz, $CDCl_3$)

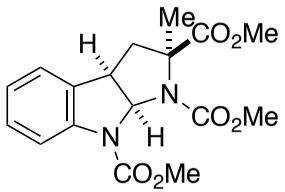


S2





^{13}C-NMR (100 MHz, $CDCl_3$)



S2

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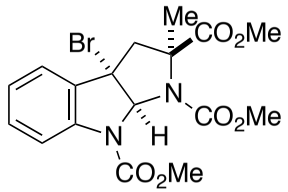
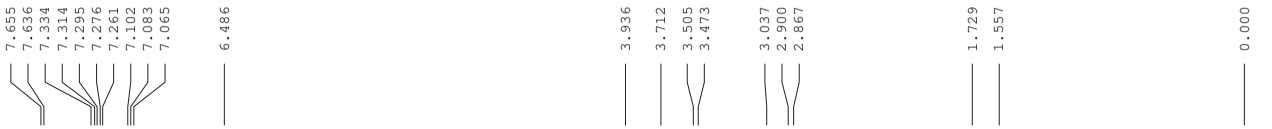
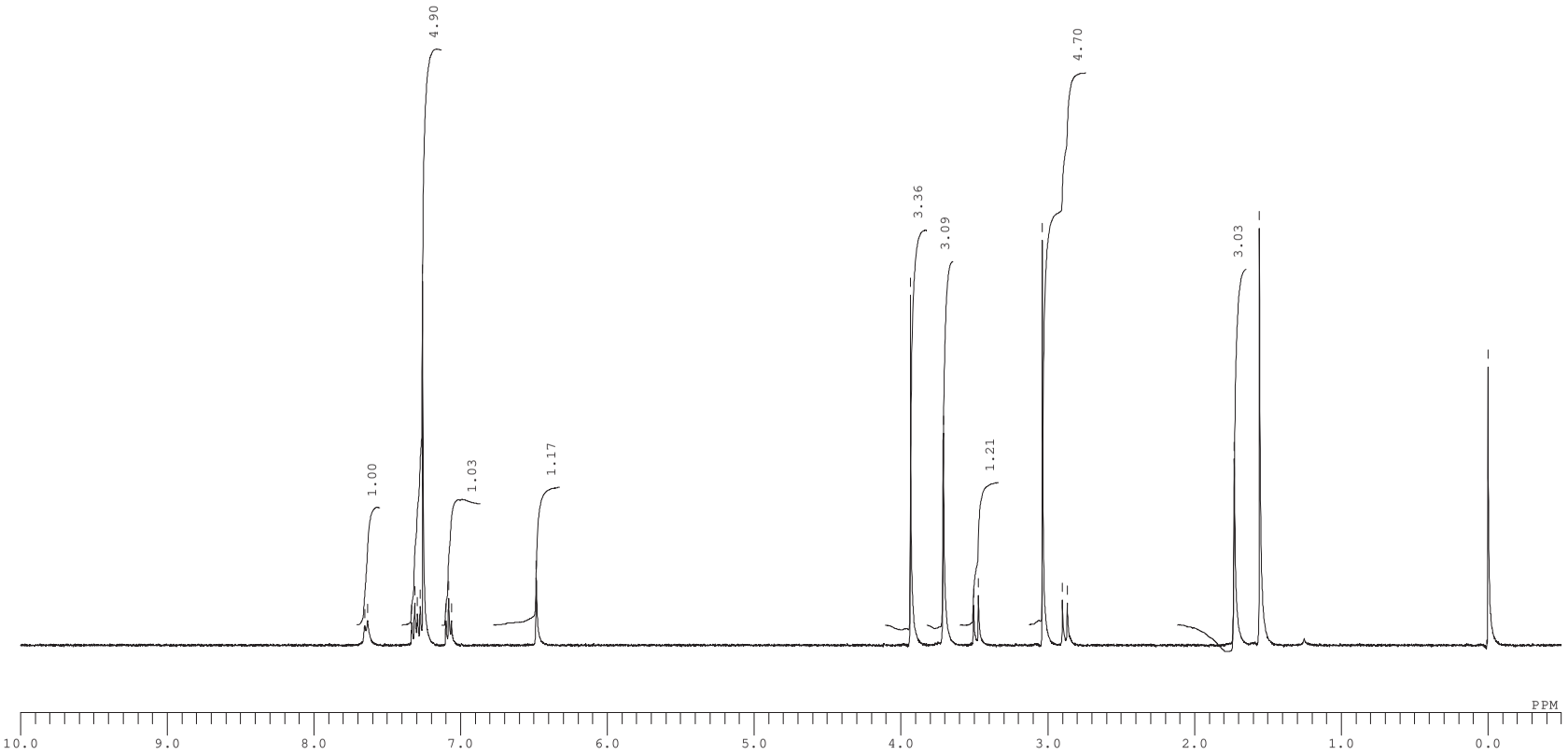
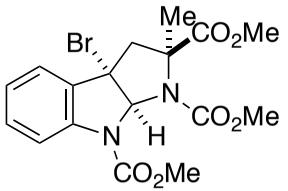


4i





^{13}C-NMR (100 MHz, $CDCl_3$)



4i

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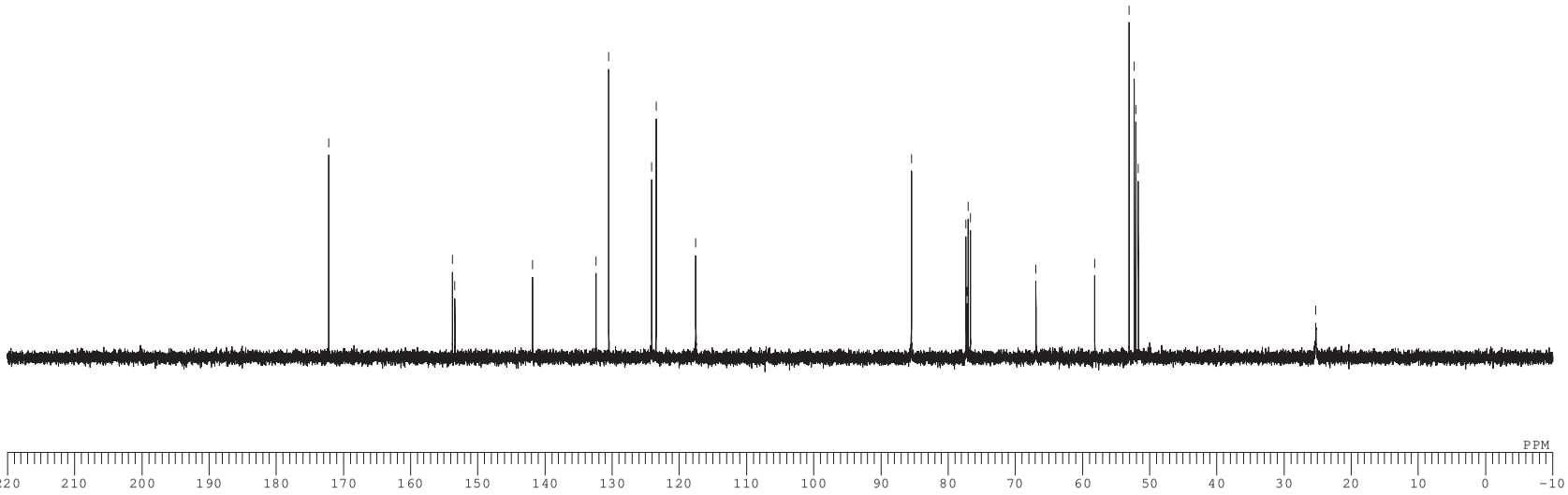

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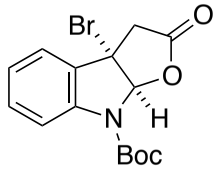
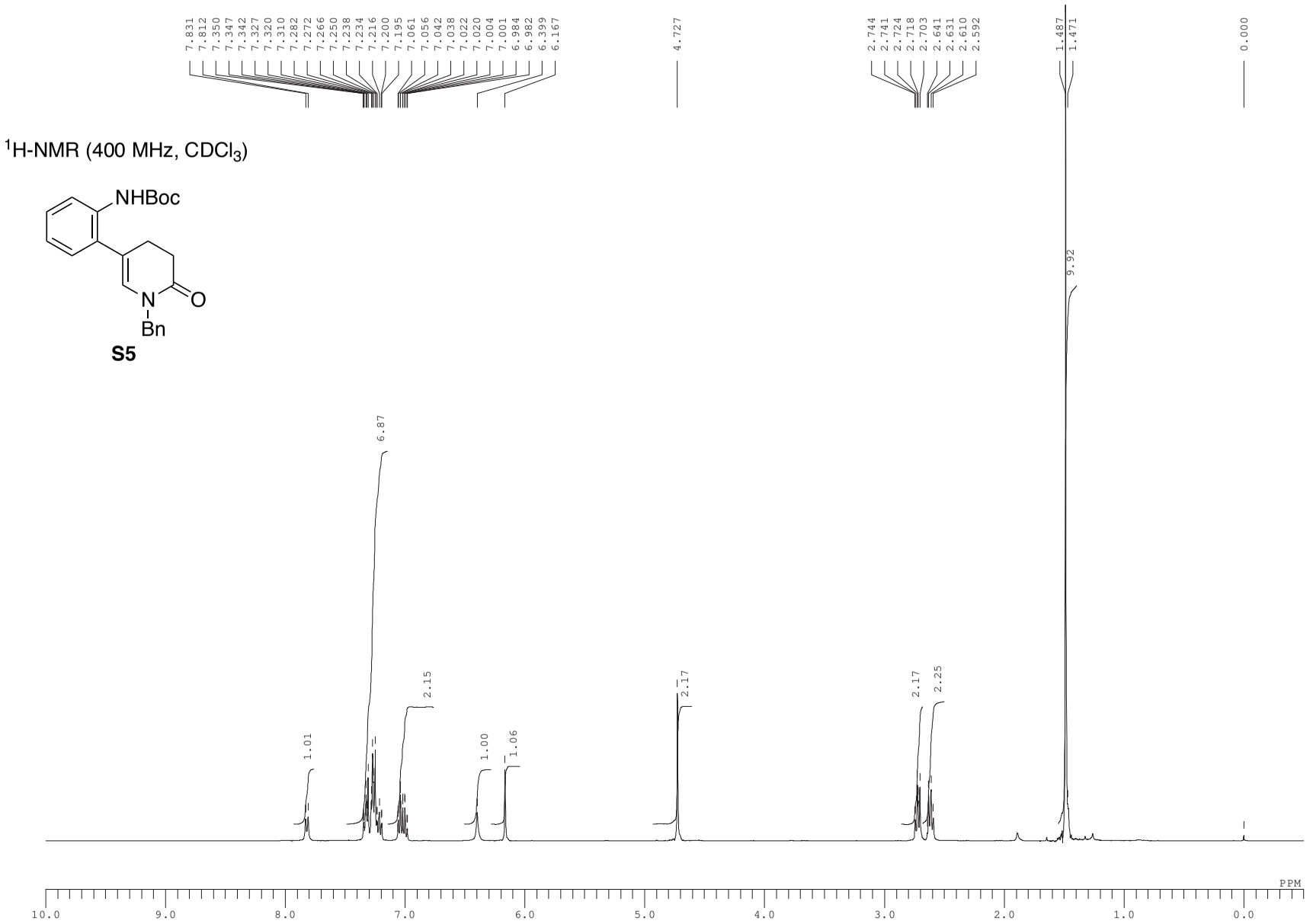


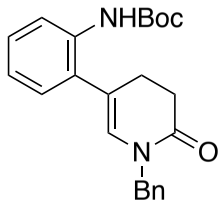
4m
unstable



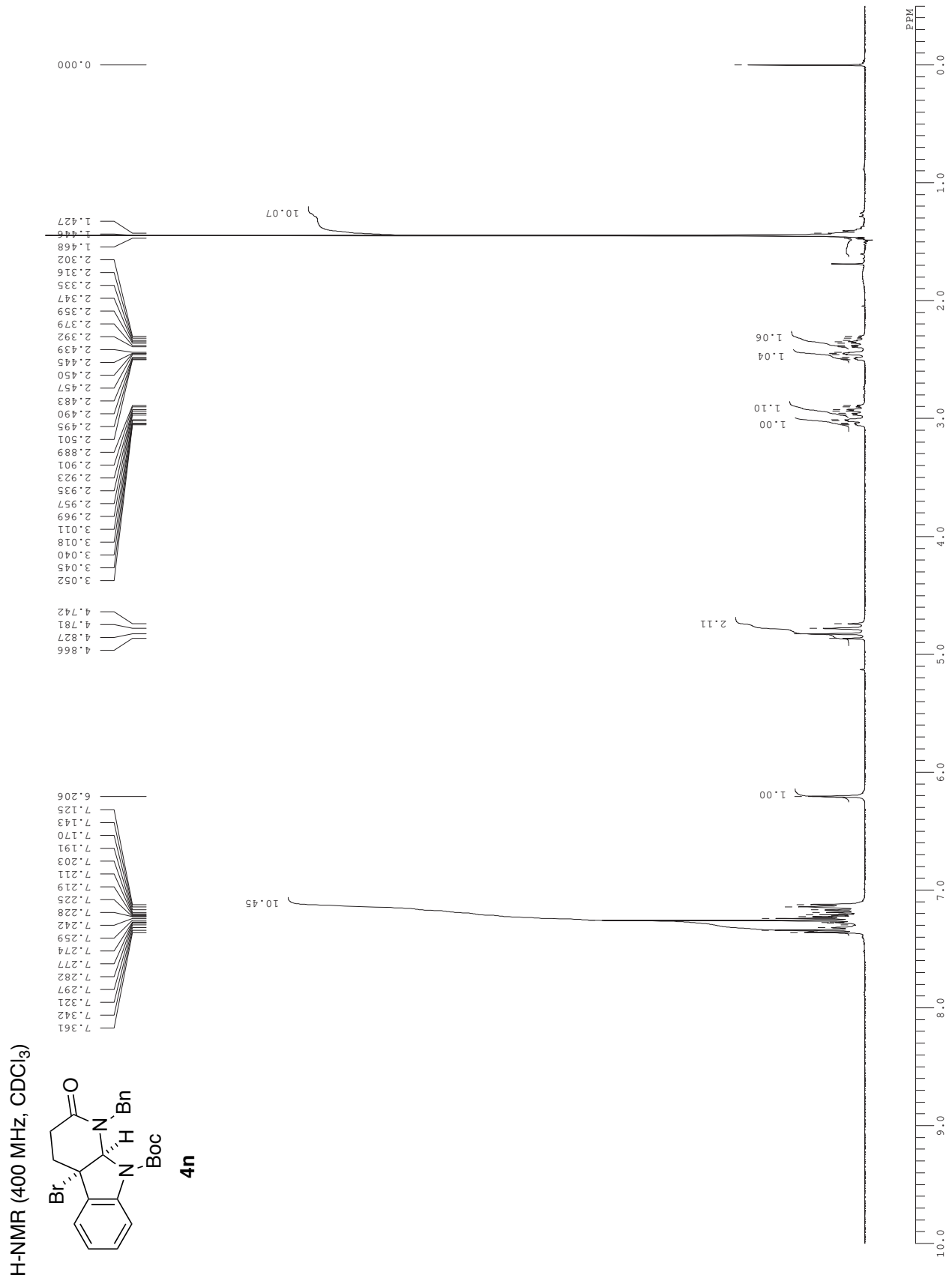
^{1}H-NMR (400 MHz, $CDCl_3$)

S5

^{13}C-NMR (100 MHz, $CDCl_3$)



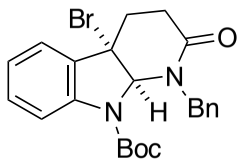
S5



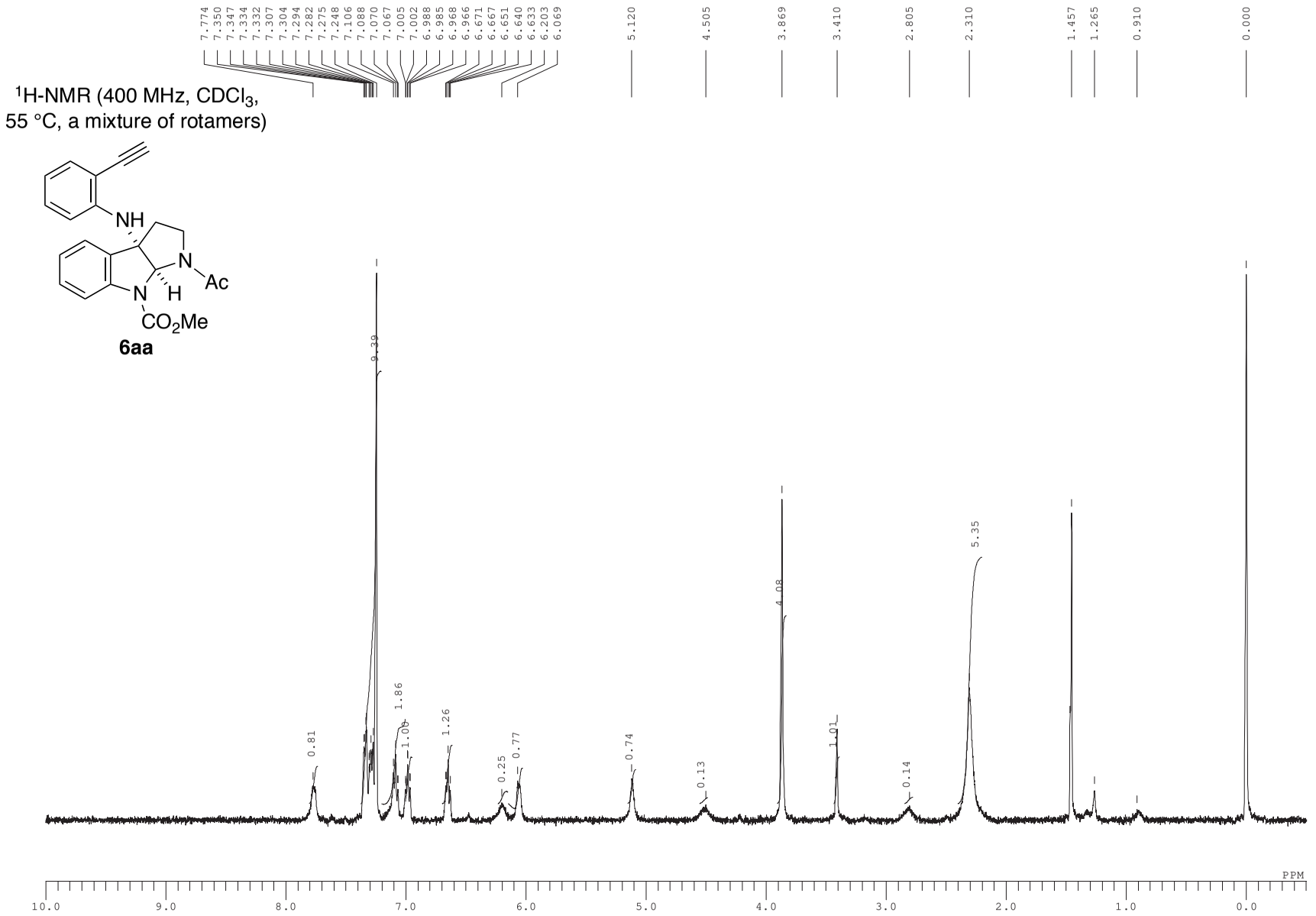
^{1}H-NMR (400 MHz, $CDCl_3$)

4n

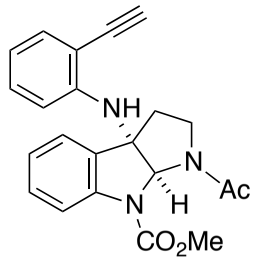
^{13}C-NMR (100 MHz, $CDCl_3$)



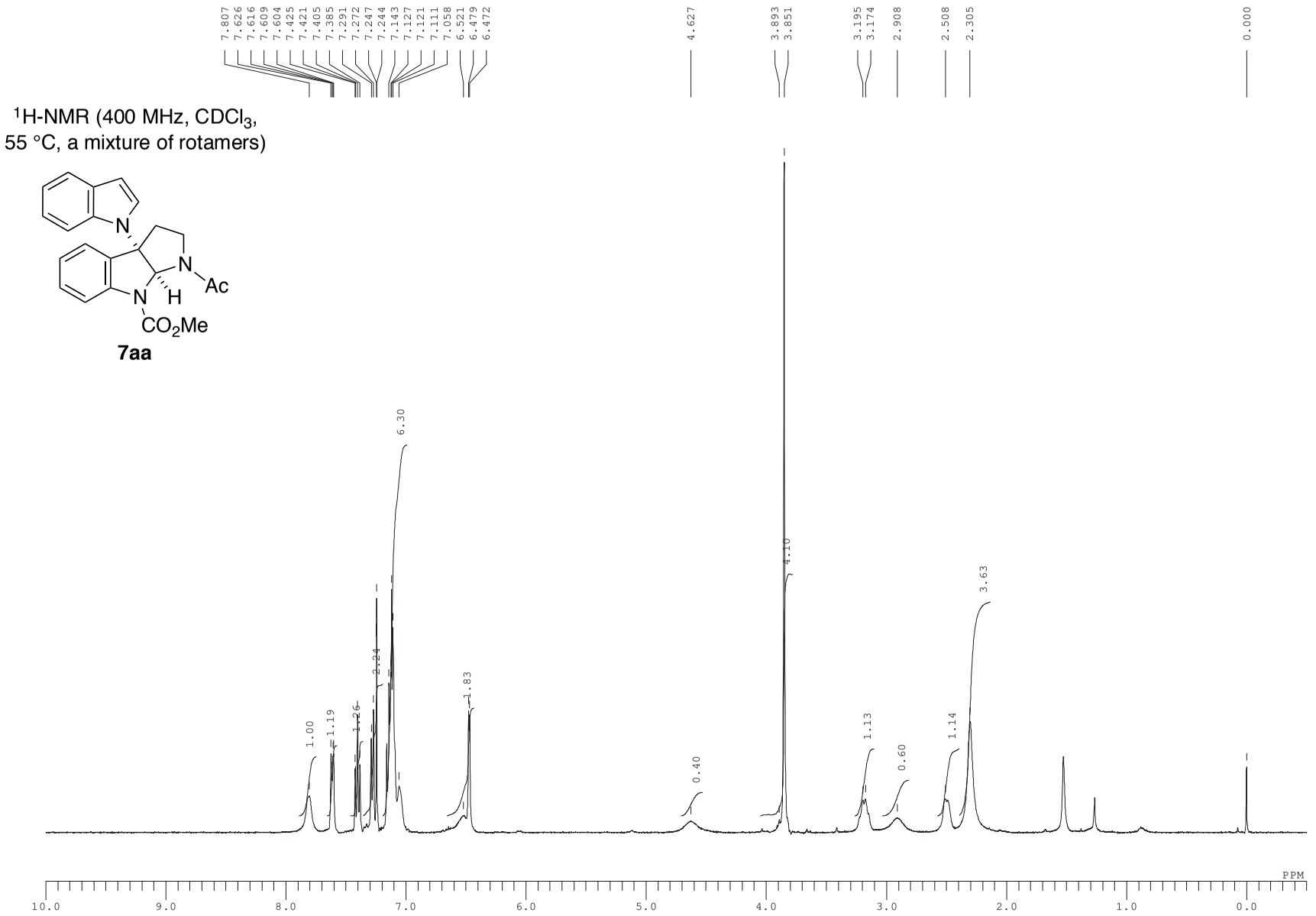
4n


7.774
7.350
7.347
7.334
7.332
7.307
7.304
7.294
7.282
7.275
7.248
7.106
7.088
7.070
7.067
7.005
7.002
6.988
6.985
6.968
6.966
6.671
6.667
6.651
6.640
6.633
6.203
6.069
5.120
4.505
3.869
3.410
2.805
2.310
1.457
1.265
0.910
0.000
^{1}H-NMR (400 MHz, $CDCl_3$,
55 °C, a mixture of rotamers)
NH
N
Ac
N
H
CO_2Me
6aa
9.39
1.86
1.05
1.26
0.81
0.25
0.77
0.74
0.13
4.08
1.01
0.14
5.35
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

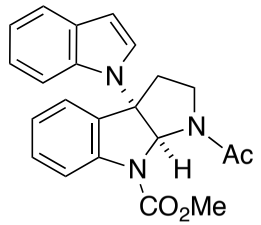
^{13}C-NMR (100 MHz, $CDCl_3$,
55 °C, a mixture of rotamers)



6aa

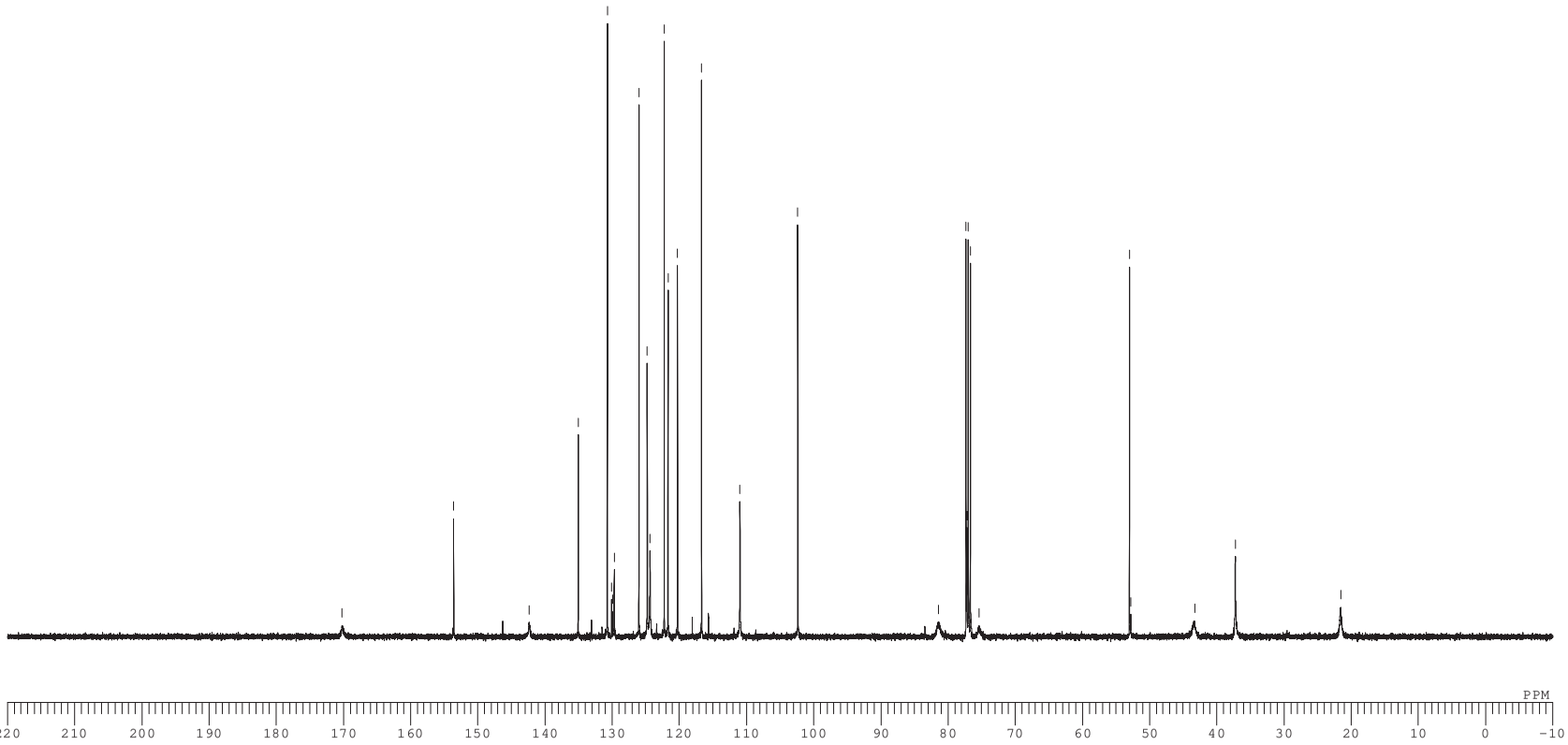

7.807
7.626
7.616
7.609
7.604
7.425
7.421
7.405
7.385
7.291
7.272
7.247
7.244
7.143
7.127
7.121
7.111
7.058
6.521
6.479
6.472
4.627
3.893
3.851
3.195
3.174
2.908
2.508
2.305
0.000
1H-NMR (400 MHz, CDCl3,
55 °C, a mixture of rotamers)
N
N
Ac
N
H
CO2Me
7aa
1.00
1.19
1.26
2.24
6.30
1.83
0.40
4.10
1.13
0.60
1.14
3.63
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

^{13}C-NMR (100 MHz, $CDCl_3$, 55 °C, a mixture of rotamers)

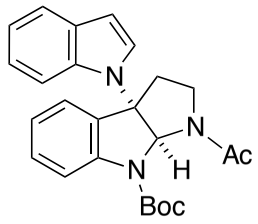


7aa

170.194
153.589
142.368
135.049
130.727
130.084
129.912
129.698
126.017
124.783
124.371
122.255
121.687
120.255
116.698
110.976
102.365
81.479
77.321
77.198
77.000
76.687
75.411
52.993
52.821
43.295
37.236
21.561

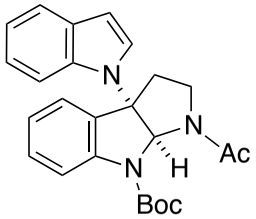


^{1}H-NMR (600 MHz, $CDCl_3$, a mixture of rotamers)

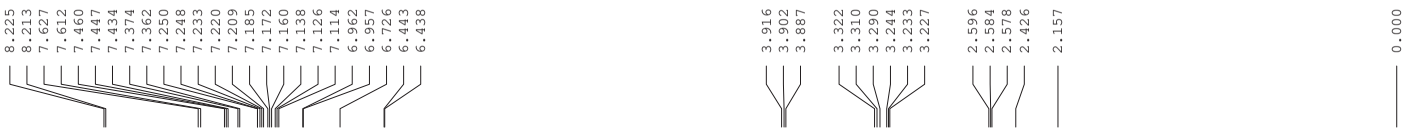


7ba

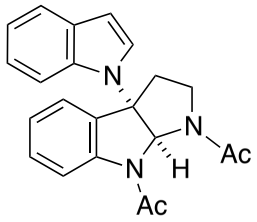
^{13}C-NMR (150 MHz, $CDCl_3$, a mixture of rotamers)



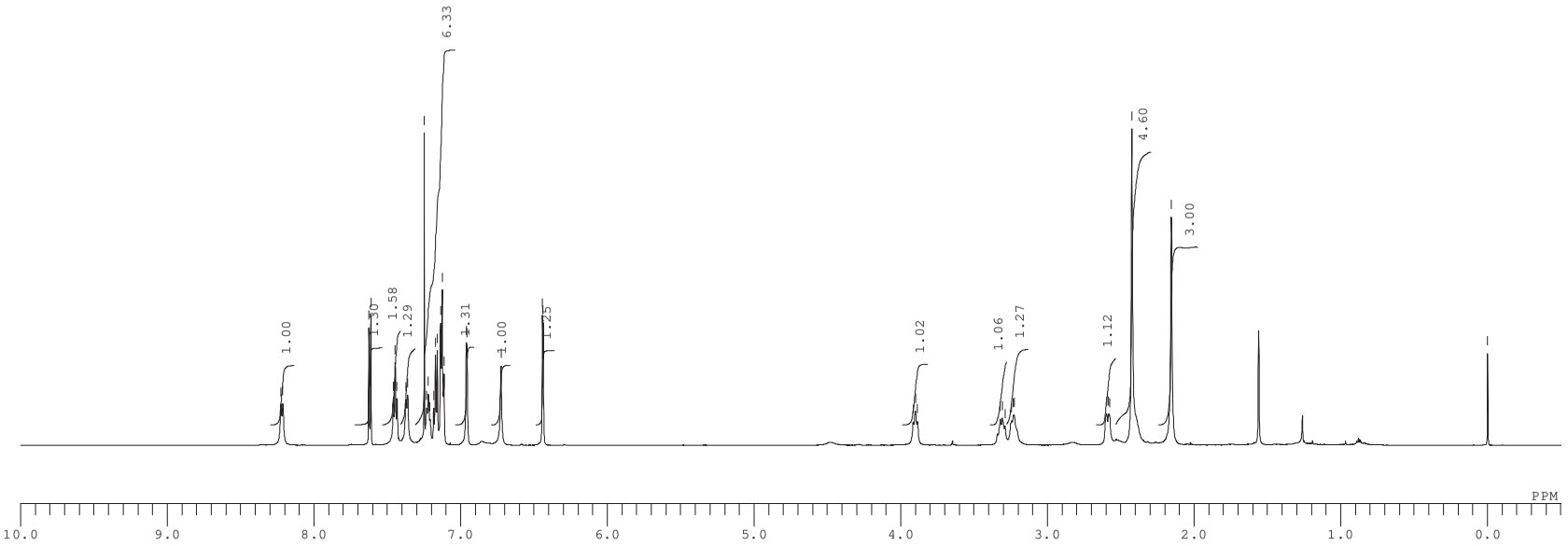
7ba



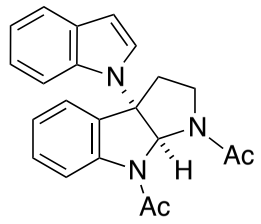
^{1}H-NMR (600 MHz, $CDCl_3$,
45 °C, a mixture of rotamers)



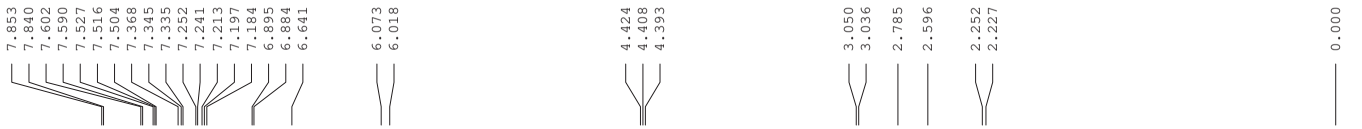
7ca



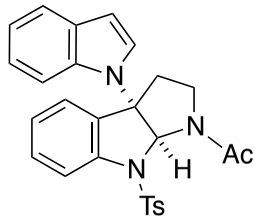
^{13}C-NMR (150 MHz, $CDCl_3$, 45 °C, a mixture of rotamers)



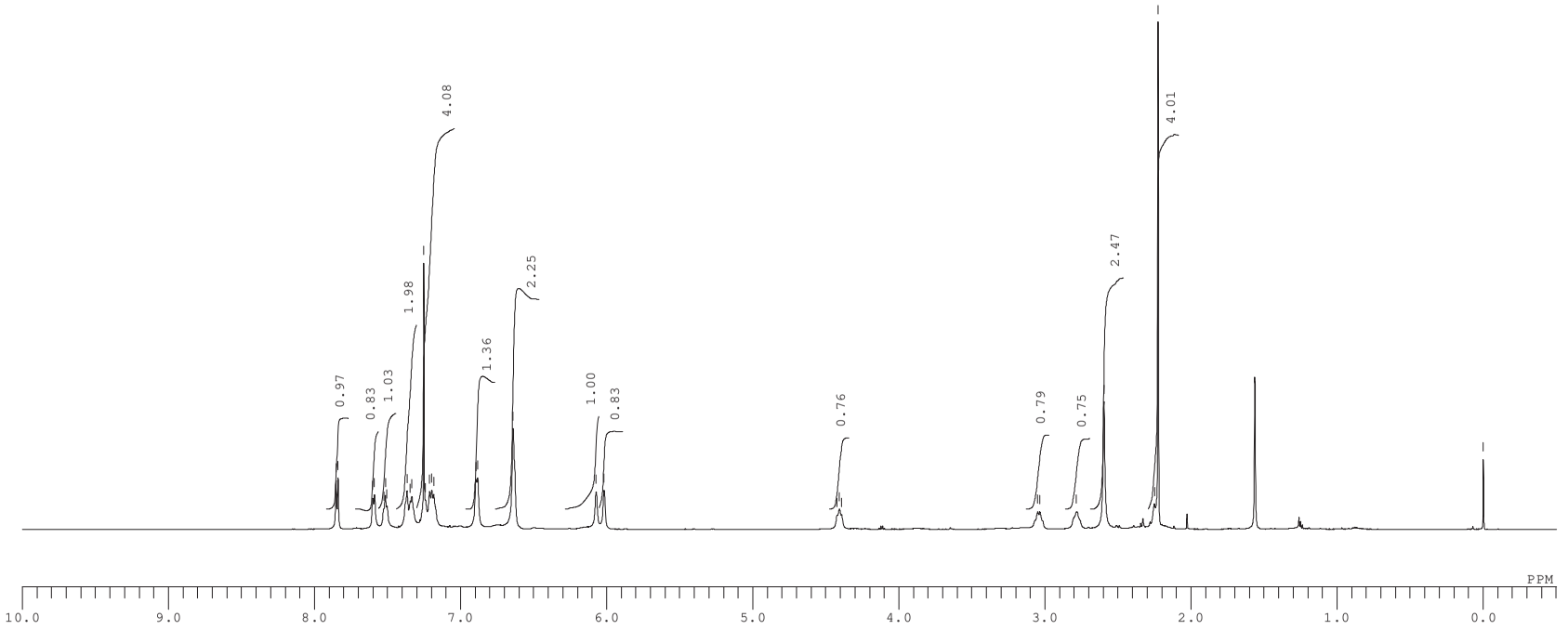
7ca



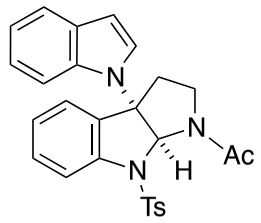
^{1}H-NMR (600 MHz, $CDCl_3$,
45 °C, a mixture of rotamers)



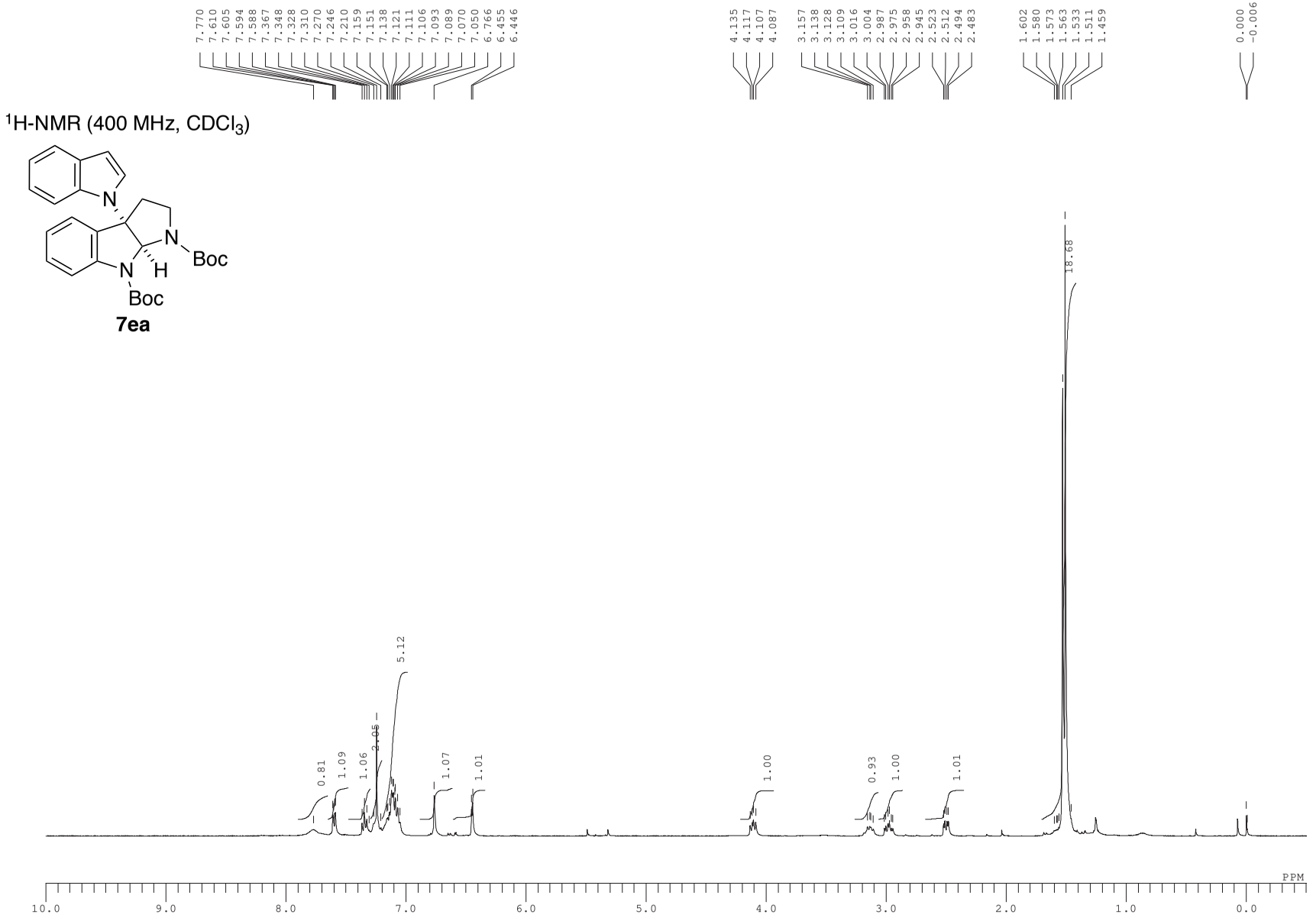
7da

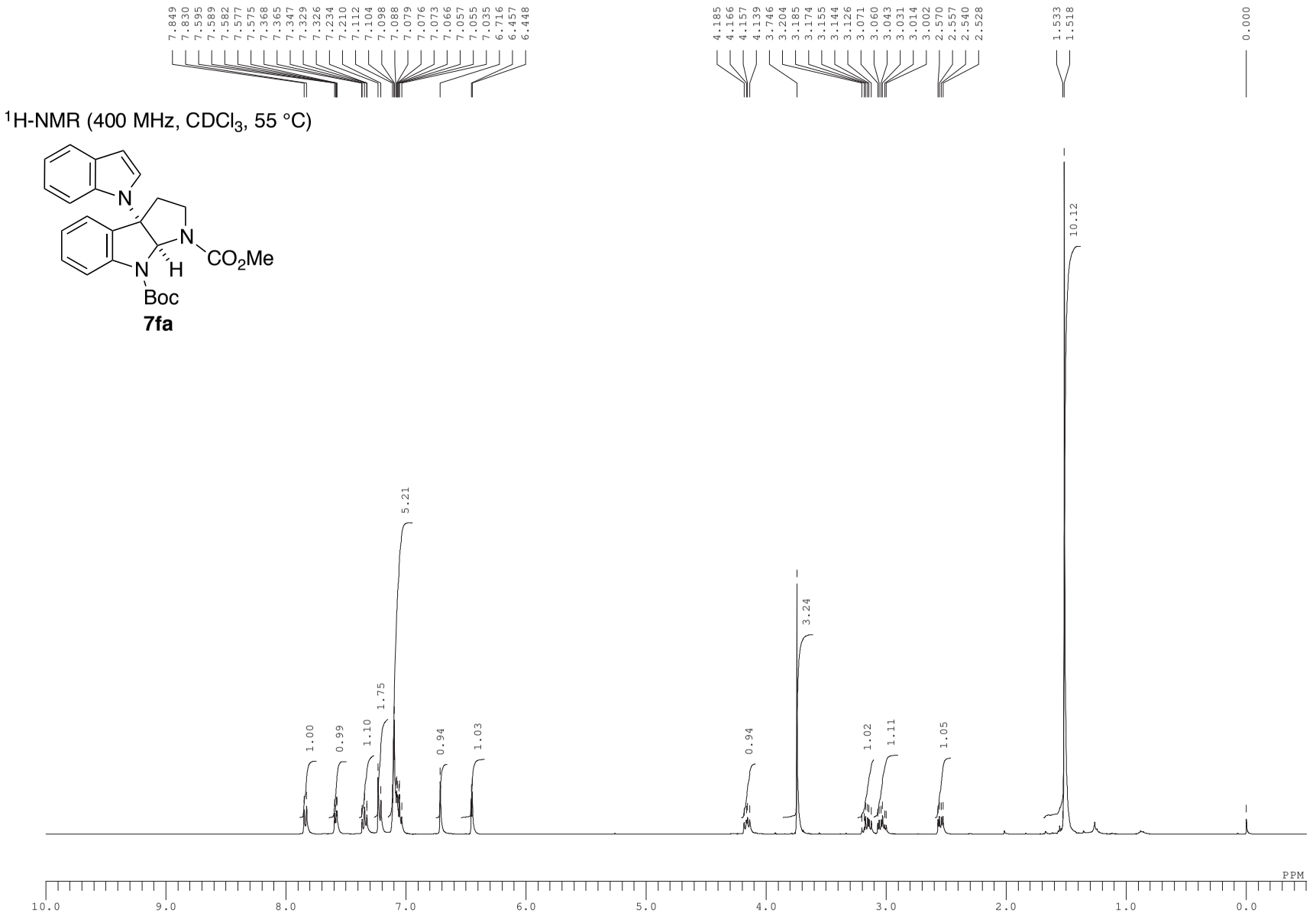


^{13}C-NMR (150 MHz, $CDCl_3$, 45 °C, a mixture of rotamers)

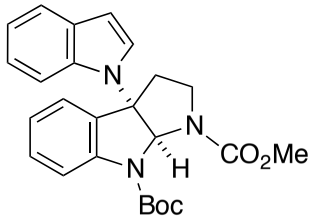


7da


7.770
7.610
7.605
7.594
7.588
7.367
7.348
7.328
7.310
7.270
7.246
7.210
7.159
7.151
7.138
7.121
7.111
7.106
7.093
7.089
7.070
7.050
6.766
6.455
6.446
4.135
4.117
4.107
4.087
3.157
3.138
3.128
3.109
3.016
3.004
2.987
2.975
2.958
2.945
2.523
2.512
2.494
2.483
1.602
1.580
1.573
1.563
1.533
1.511
1.459
0.000
-0.006
1H-NMR (400 MHz, CDCl3)
N
N
Boc
N
H
Boc
7ea
18.68
5.12
0.81
1.09
1.06
2.05
1.07
1.01
1.00
0.93
1.00
1.01
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

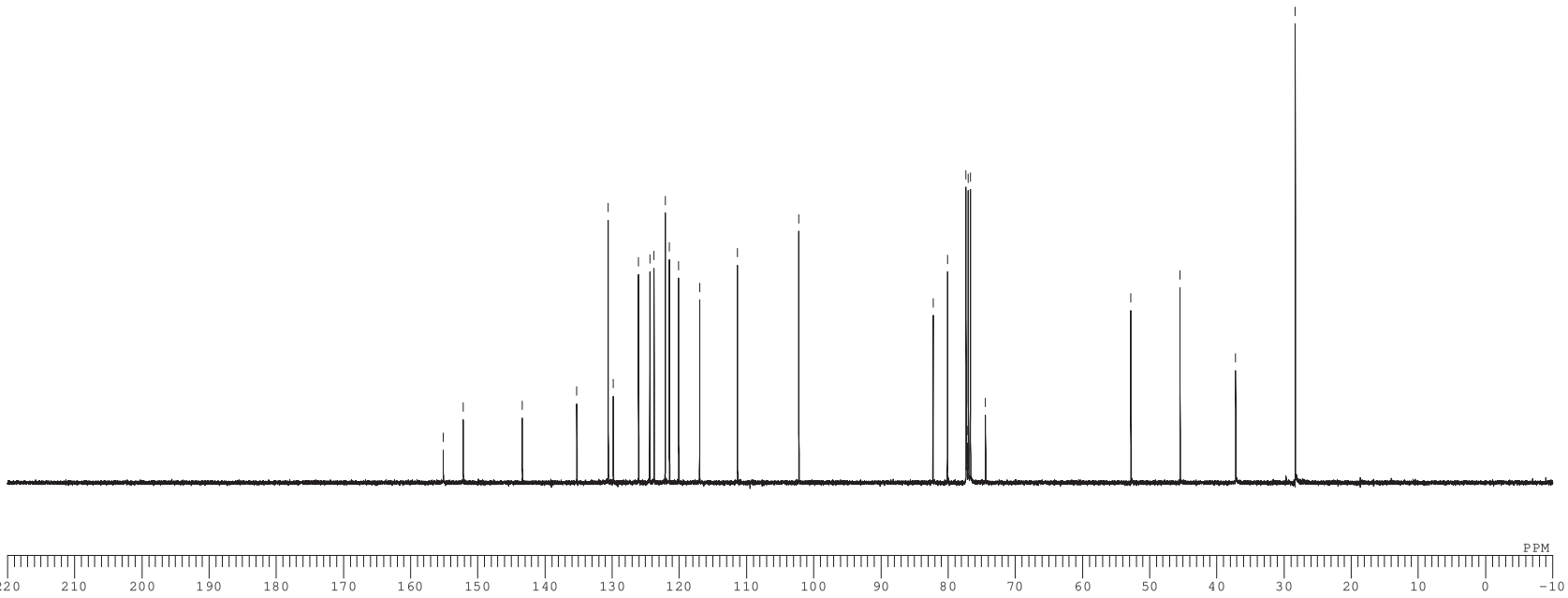

7.849
7.830
7.595
7.589
7.582
7.577
7.575
7.368
7.365
7.347
7.329
7.326
7.234
7.210
7.112
7.104
7.098
7.088
7.079
7.076
7.073
7.066
7.057
7.055
7.035
6.716
6.457
6.448
4.185
4.166
4.157
4.139
3.746
3.204
3.185
3.174
3.155
3.144
3.126
3.071
3.060
3.043
3.031
3.014
3.002
2.570
2.557
2.540
2.528
1.533
1.518
0.000
1H-NMR (400 MHz, CDCl3, 55 °C)
N
N
N
H
CO2Me
Boc
7fa
10.12
5.21
3.24
1.75
1.00
0.99
1.10
0.94
1.03
0.94
1.02
1.11
1.05
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

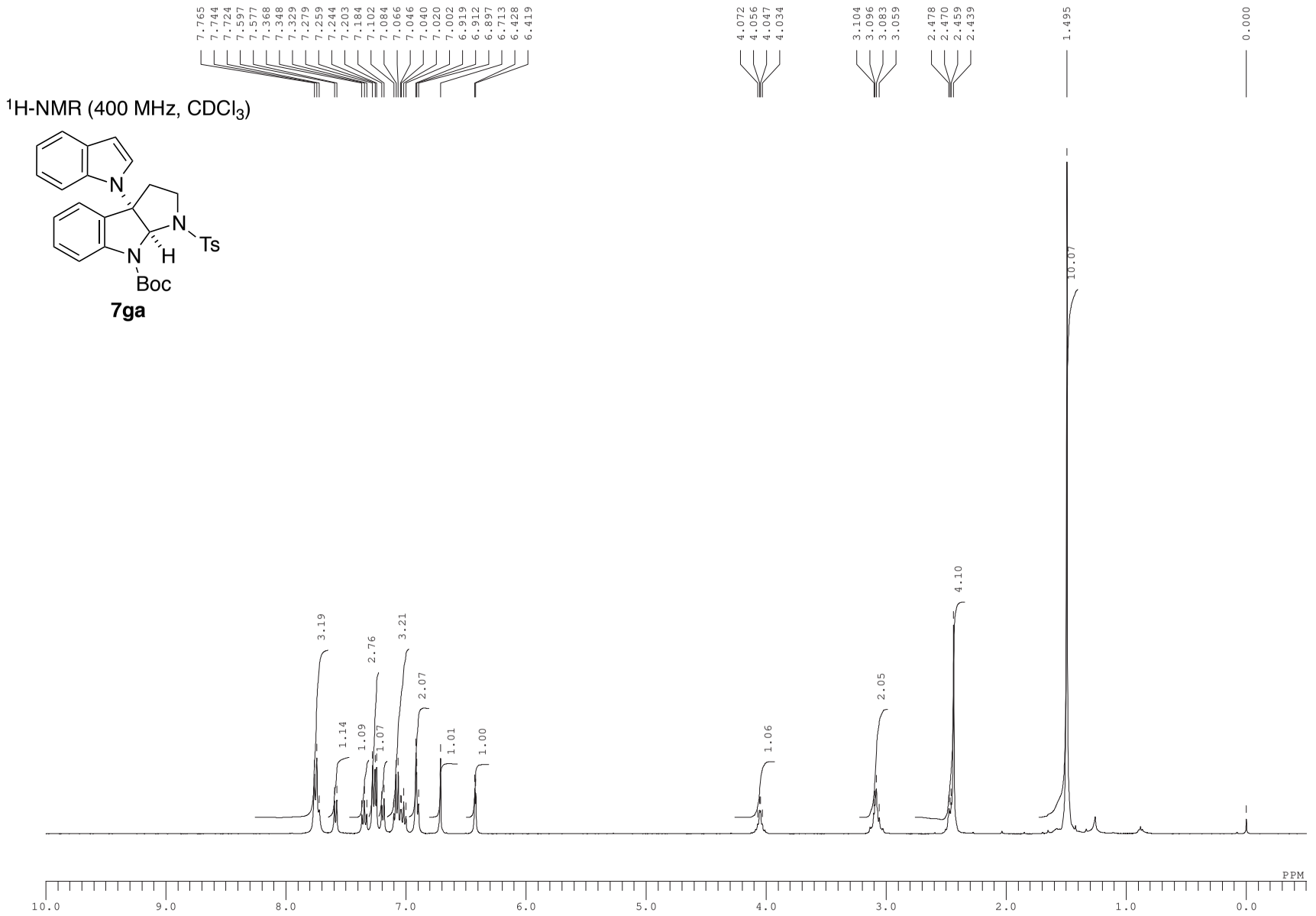
^{13}C-NMR (100 MHz, $CDCl_3$, 55 °C)



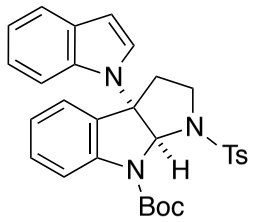
7fa

155.145
152.165
143.372
135.255
130.587
129.846
126.059
124.420
123.754
122.107
121.481
120.106
116.994
111.355
102.209
82.244
80.095
77.321
77.206
77.000
76.687
74.415
52.779
45.444
37.178
28.304



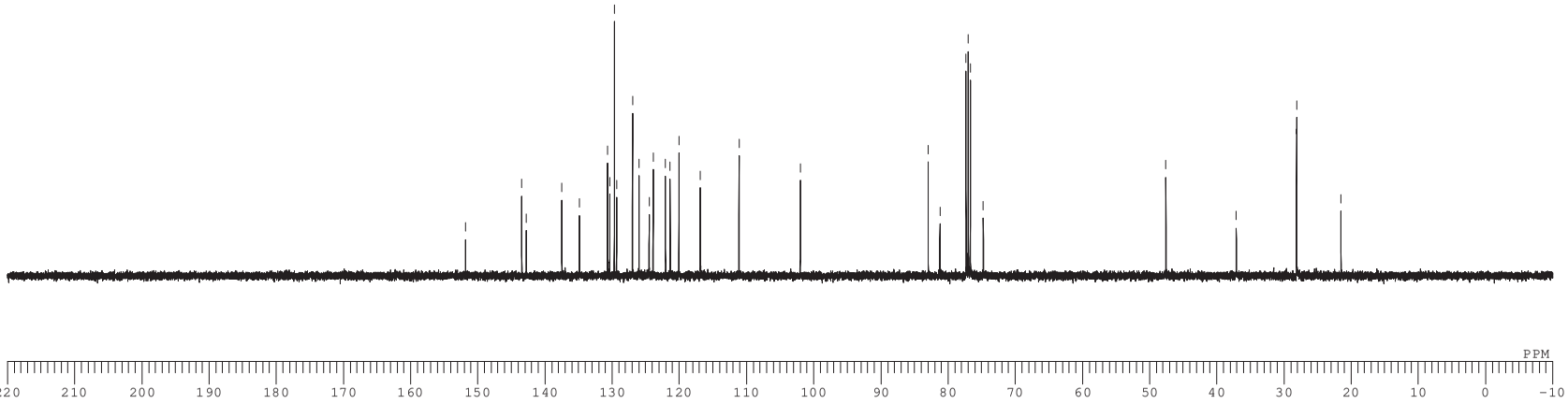

7.765
7.744
7.724
7.597
7.577
7.368
7.348
7.329
7.279
7.259
7.244
7.203
7.184
7.102
7.084
7.066
7.046
7.040
7.020
7.002
6.919
6.912
6.897
6.713
6.428
6.419
4.072
4.056
4.047
4.034
3.104
3.096
3.083
3.059
2.478
2.470
2.459
2.439
1.495
0.000
1H-NMR (400 MHz, CDCl3)
N
N
Ts
N
H
Boc
7ga
3.19
1.14
1.09
2.76
1.07
3.21
2.07
1.01
1.00
1.06
2.05
4.10
10.07
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

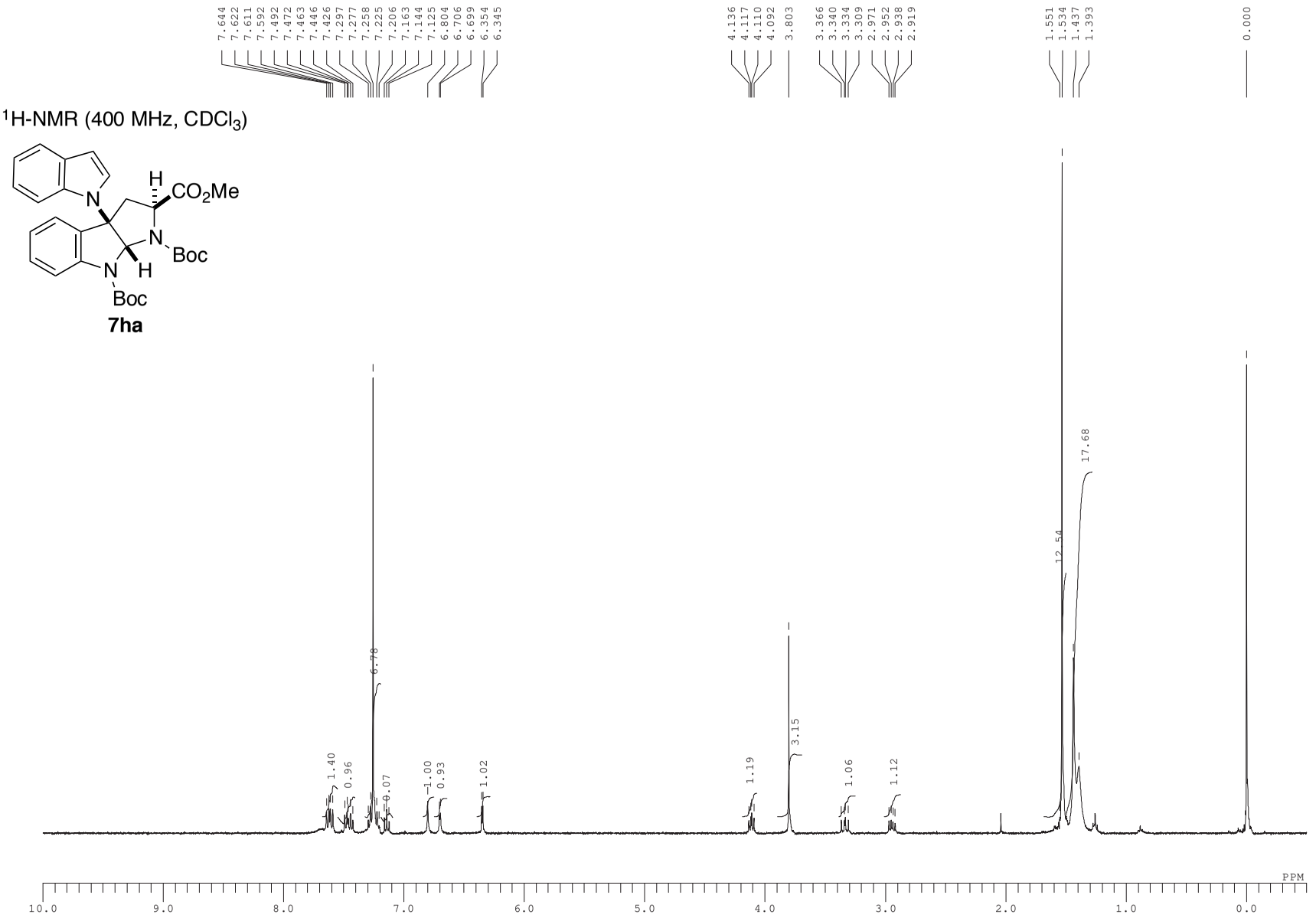
^{13}C-NMR (100 MHz, $CDCl_3$)

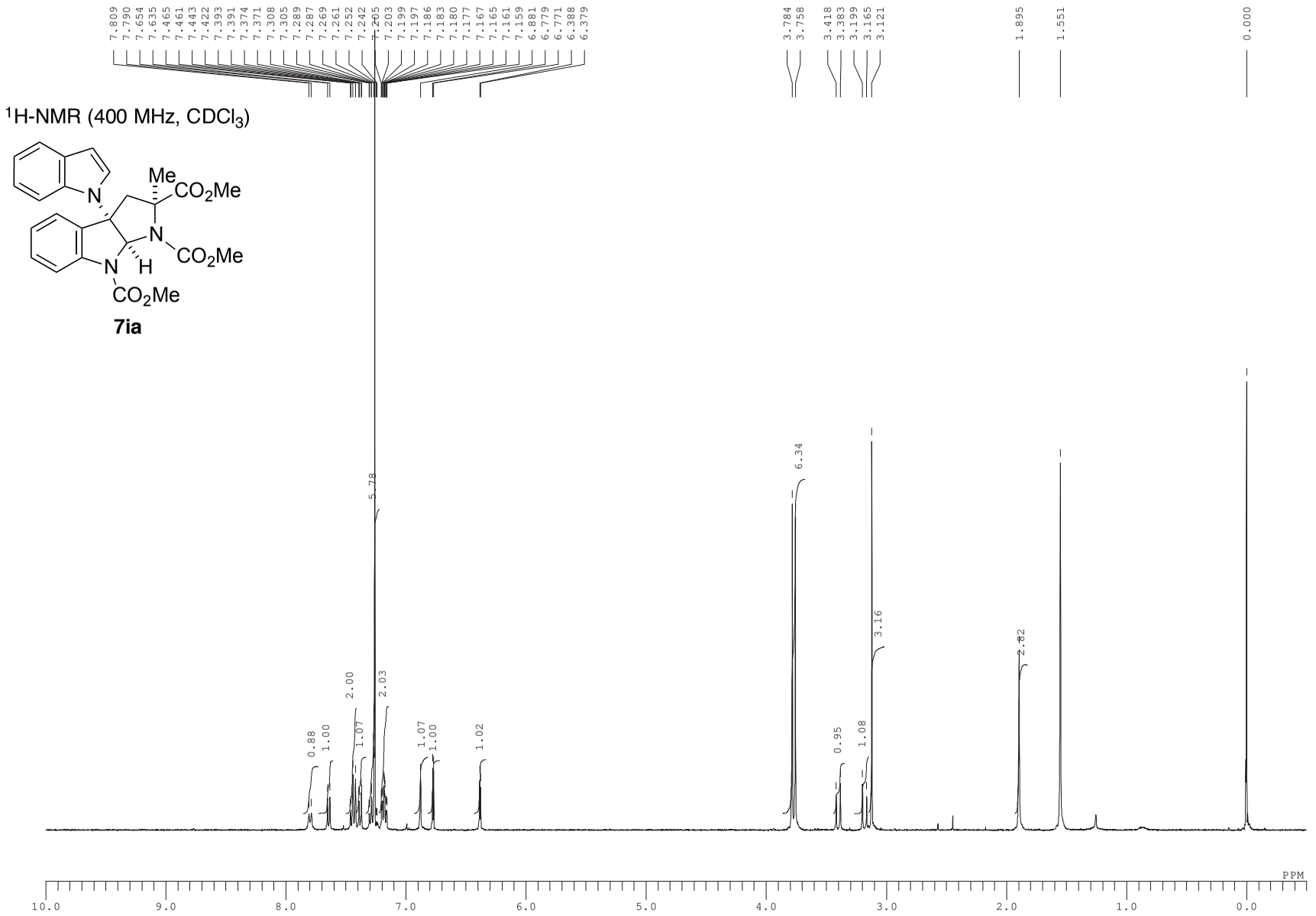


7ga

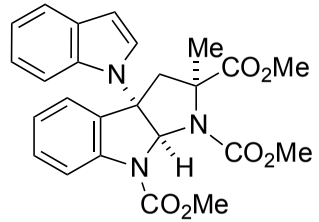
151.827
143.446
142.787
137.477
134.859
130.685
130.381
129.689
129.360
126.972
126.009
124.503
123.902
122.066
121.366
120.073
116.879
111.133
101.994
82.952
81.223
77.321
77.000
76.679
74.752
47.568
37.088
28.114
21.512




7.644
7.622
7.611
7.592
7.492
7.472
7.463
7.446
7.426
7.297
7.277
7.258
7.225
7.206
7.163
7.144
7.125
6.804
6.706
6.699
6.354
6.345
4.136
4.117
4.110
4.092
3.803
3.366
3.340
3.334
3.309
2.971
2.952
2.938
2.919
1.551
1.534
1.437
1.393
0.000
1H-NMR (400 MHz, CDCl3)
H
CO2Me
N
N
Boc
N
H
Boc
7ha
6.78
1.40
0.96
0.07
1.00
0.93
1.02
1.19
3.15
1.06
1.12
12.54
17.68
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

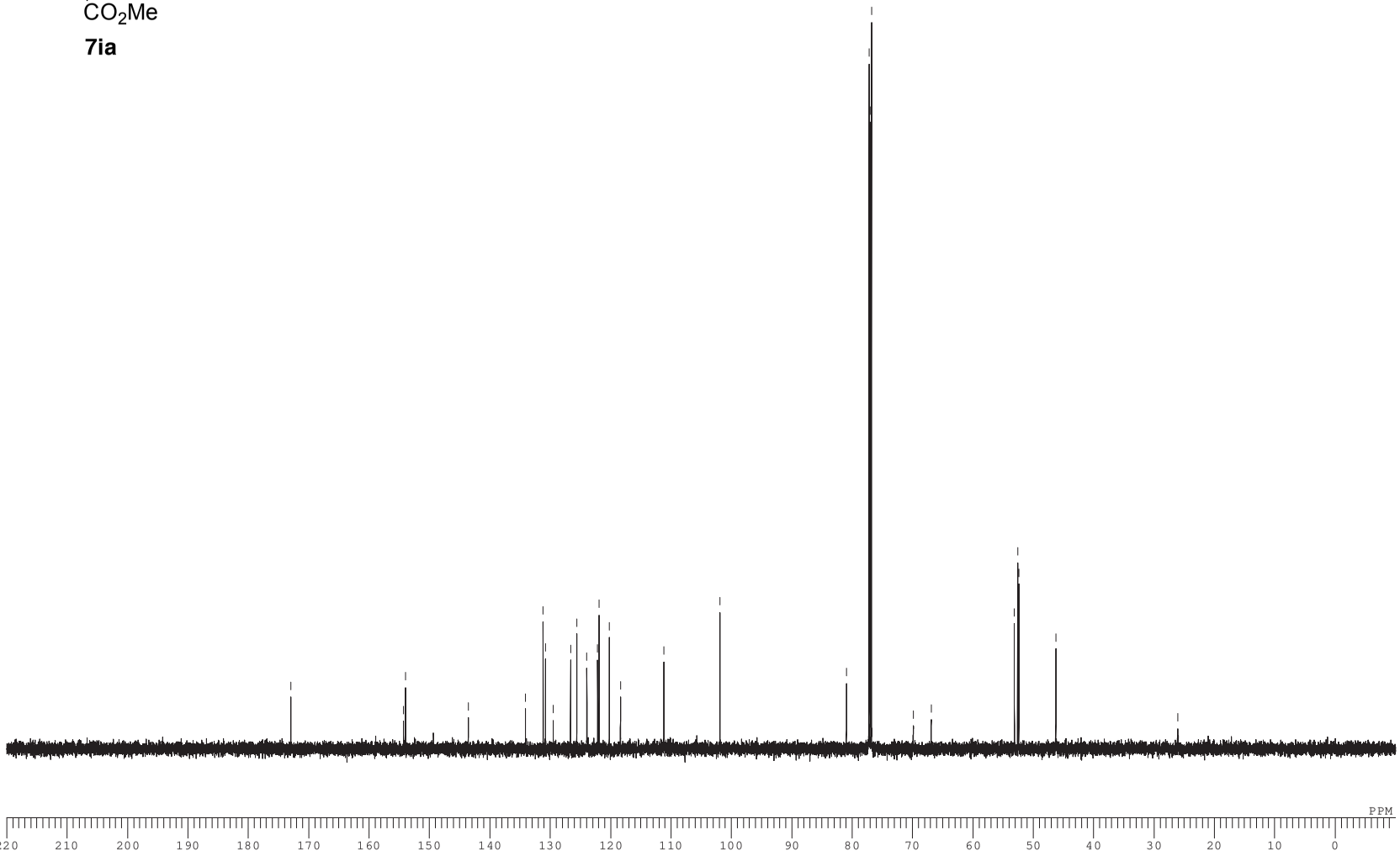

7.809
7.790
7.654
7.635
7.465
7.461
7.443
7.422
7.393
7.391
7.374
7.371
7.308
7.305
7.289
7.287
7.269
7.261
7.252
7.242
7.205
7.203
7.199
7.197
7.186
7.183
7.180
7.177
7.167
7.165
7.161
7.159
6.881
6.779
6.771
6.388
6.379
3.784
3.758
3.418
3.383
3.199
3.165
3.121
1.895
1.551
0.000
^{1}H-NMR (400 MHz, $CDCl_3$)
Me
CO_2Me
N
N
CO_2Me
N
H
CO_2Me
7ia
6.34
5.78
3.16
2.82
2.03
2.00
1.07
1.00
1.08
1.07
1.00
1.02
0.95
0.88
1.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

^{13}C-NMR (150 MHz, $CDCl_3$)

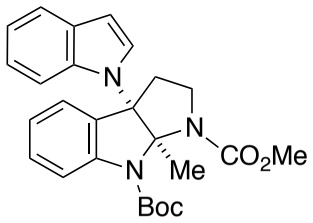


7ia

172.965
154.284
153.950
143.578
134.084
131.171
130.751
129.500
126.635
125.603
123.922
122.136
121.917
120.226
118.364
111.201
101.889
80.935
77.220
77.000
76.790
69.847
66.895
53.123
52.588
52.407
46.266
26.028

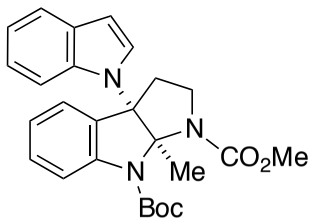


^{1}H-NMR (600 MHz, $CDCl_3$, a mixture of rotamers)

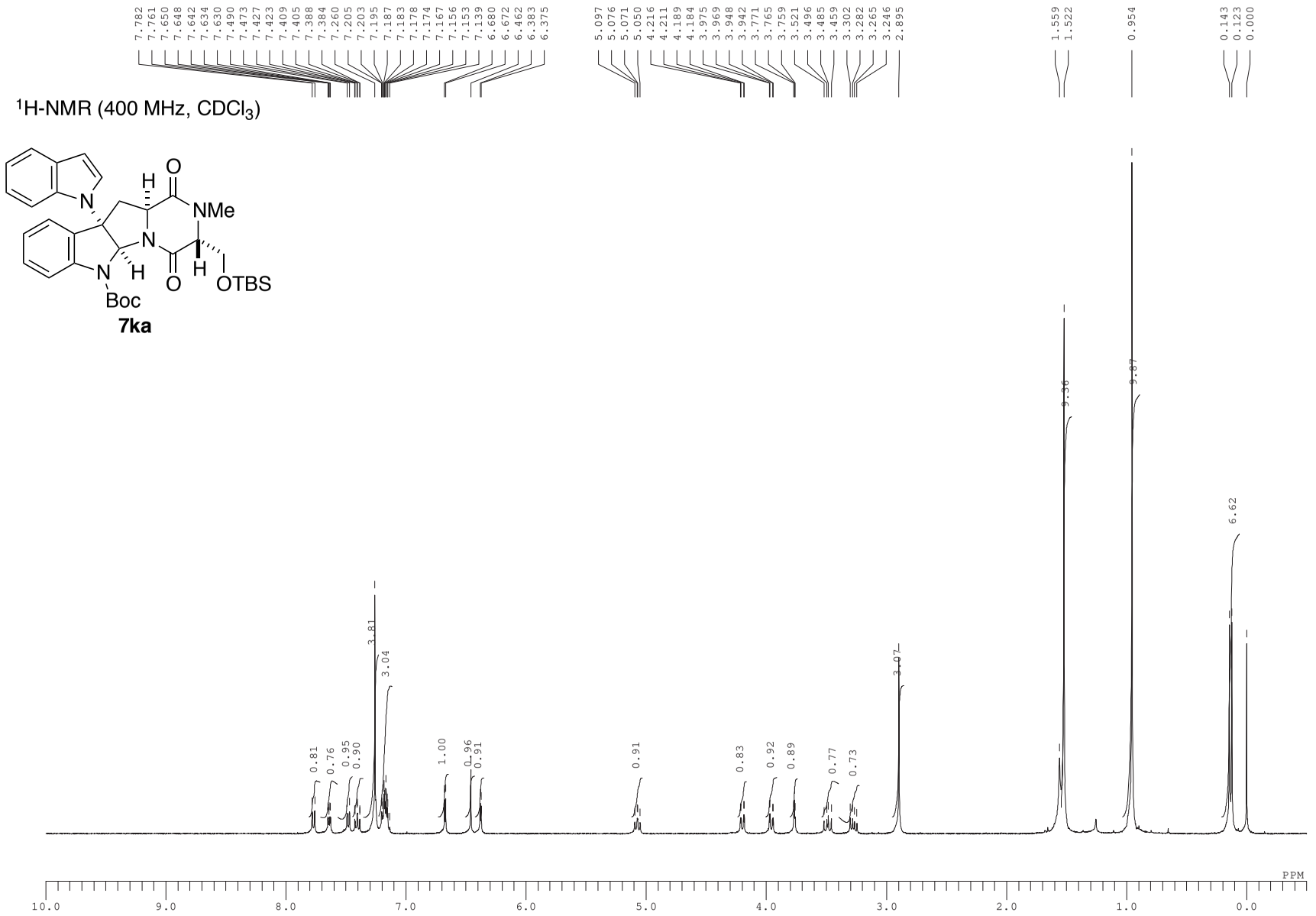


7ja

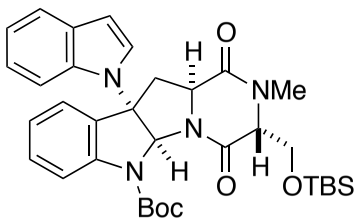
^{13}C-NMR (150 MHz, $CDCl_3$,
a mixture of rotamers)



7ja

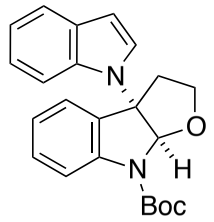

7.782
7.761
7.650
7.648
7.642
7.634
7.630
7.490
7.473
7.427
7.423
7.409
7.405
7.388
7.384
7.260
7.205
7.203
7.195
7.187
7.183
7.178
7.174
7.167
7.156
7.153
7.139
6.680
6.672
6.462
6.383
6.375
5.097
5.076
5.071
5.050
4.216
4.211
4.189
4.184
3.975
3.969
3.948
3.942
3.771
3.765
3.759
3.521
3.496
3.485
3.459
3.302
3.282
3.265
3.246
2.895
1.559
1.522
0.954
0.143
0.123
0.000
1H-NMR (400 MHz, CDCl3)
O
H
NMe
N
N
H
H
O
OTBS
Boc
7ka
9.36
9.87
6.62
3.81
3.04
3.07
0.81
0.76
0.95
0.90
1.00
0.96
0.91
0.91
0.83
0.92
0.89
0.77
0.73
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

^{13}C-NMR (150 MHz, $CDCl_3$)



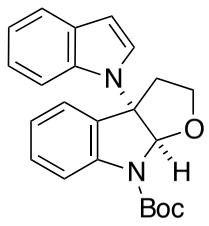
7ka

^{1}H-NMR (600 MHz, $CDCl_3$,
a mixture of rotamers)



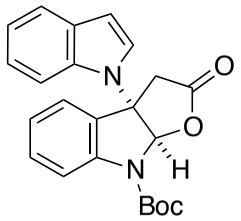
7la

^{13}C-NMR (150 MHz, $CDCl_3$, a mixture of rotamers)

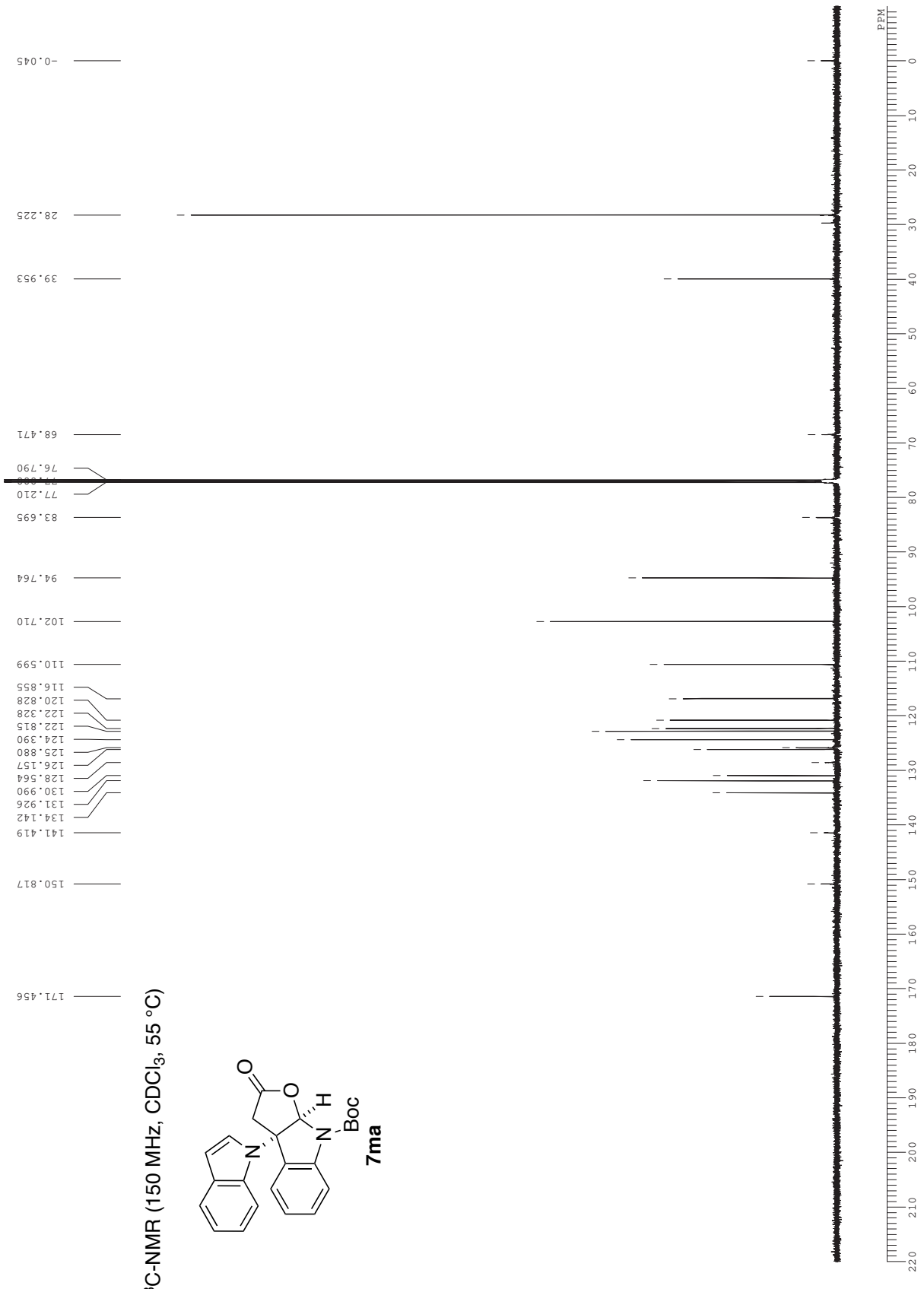


7la

^{1}H-NMR (600 MHz, $CDCl_3$, 55 °C)

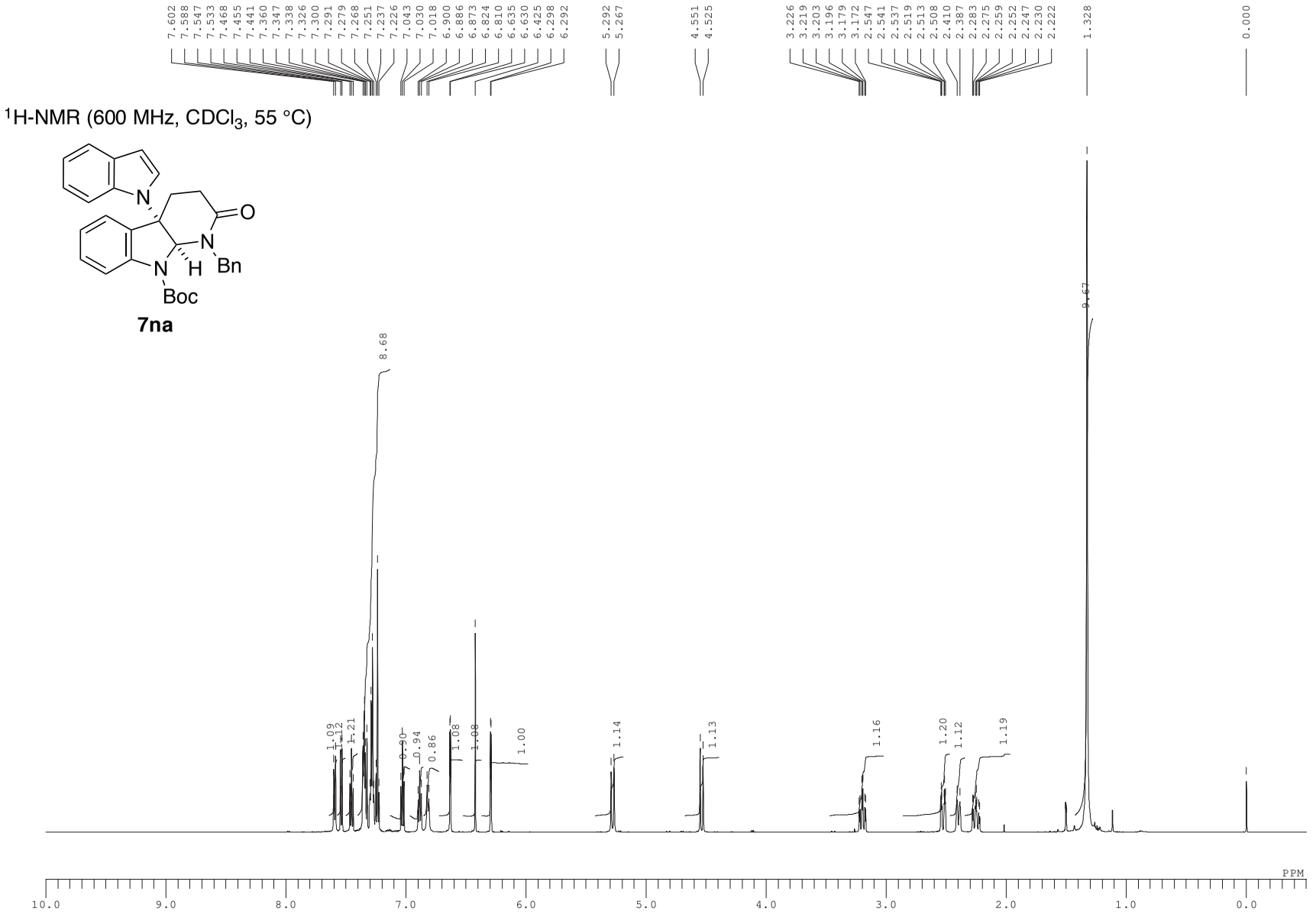


7ma

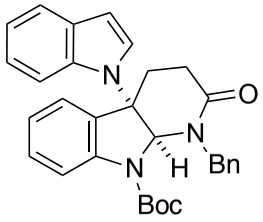


^{13}C-NMR (150 MHz, $CDCl_3$, 55 °C)

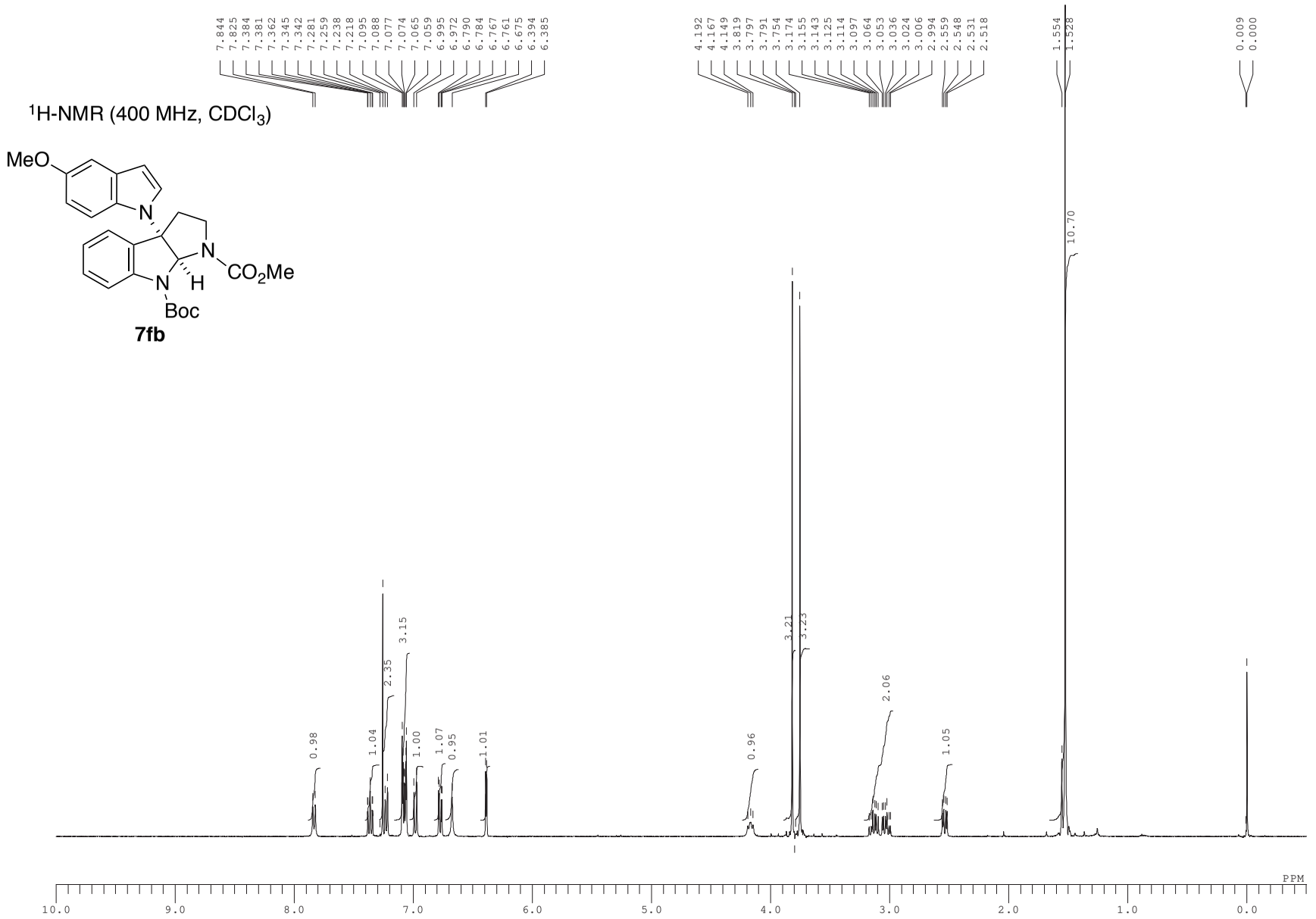
7ma


7.602
7.588
7.547
7.533
7.468
7.455
7.441
7.360
7.347
7.338
7.326
7.300
7.291
7.279
7.268
7.251
7.237
7.226
7.043
7.030
7.018
6.900
6.886
6.873
6.824
6.810
6.635
6.630
6.425
6.298
6.292
5.292
5.267
4.551
4.525
3.226
3.219
3.203
3.196
3.179
3.172
2.547
2.541
2.537
2.519
2.513
2.508
2.410
2.387
2.283
2.275
2.259
2.252
2.247
2.230
2.222
1.328
0.000
1H-NMR (600 MHz, CDCl3, 55 °C)
O
N
N
H
Bn
N
Boc
7na
8.68
9.67
1.09
1.12
1.21
0.90
0.94
0.86
1.08
1.08
1.00
1.14
1.13
1.16
1.20
1.12
1.19
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

^{13}C-NMR (150 MHz, $CDCl_3$, 55 °C)



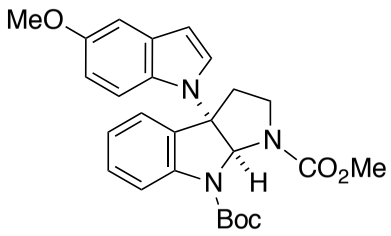
7na



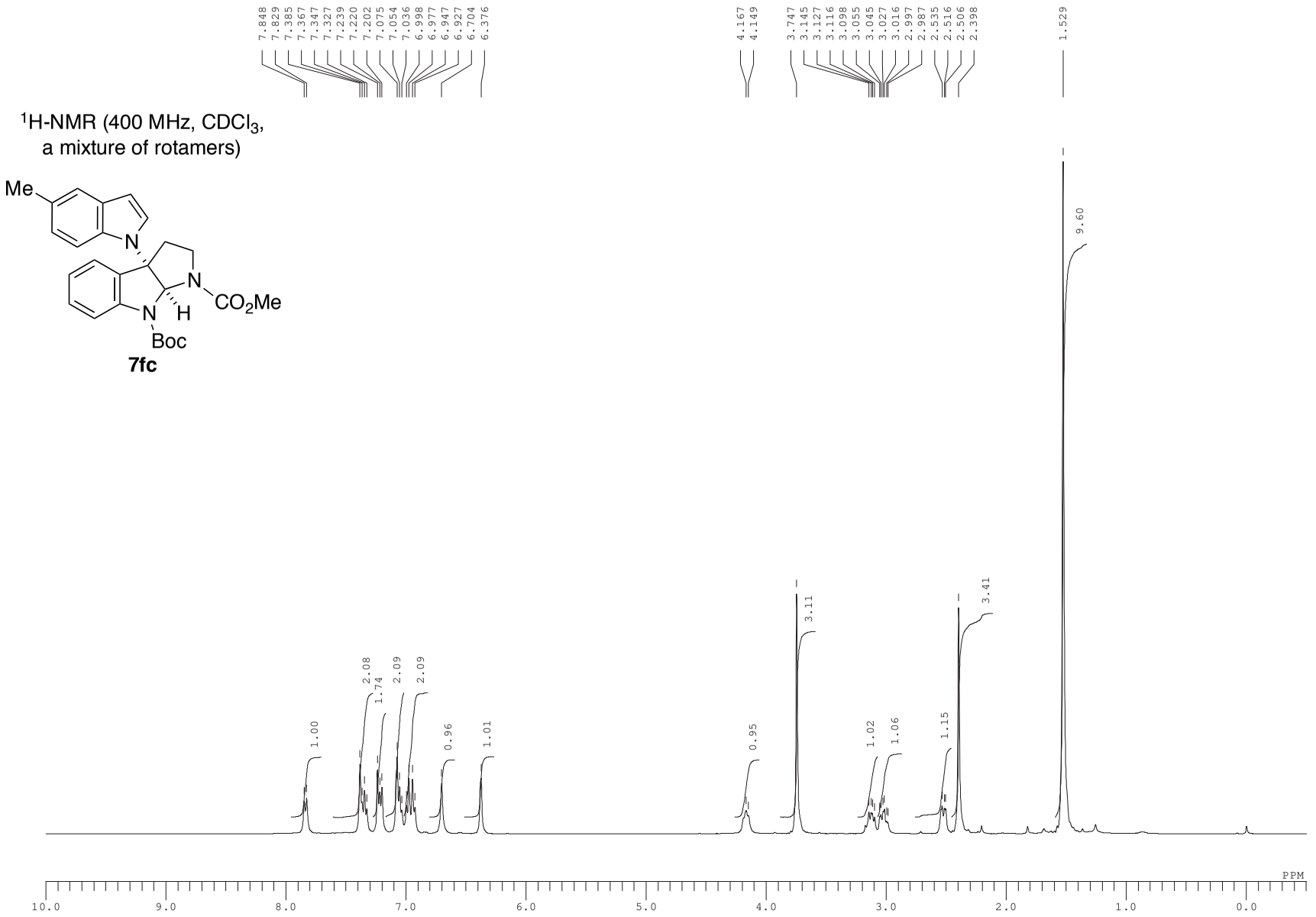
^{1}H-NMR (400 MHz, $CDCl_3$)

7fb

^{13}C-NMR (100 MHz, $CDCl_3$)



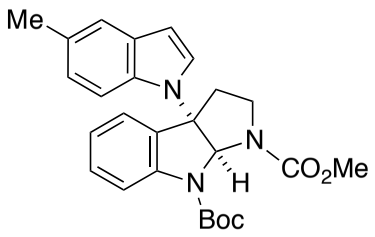
7fb



^{1}H-NMR (400 MHz, $CDCl_3$, a mixture of rotamers)

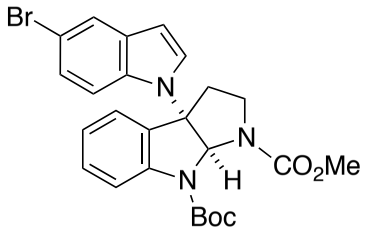
7fc

^{13}C-NMR (100 MHz, $CDCl_3$, a mixture of rotamers)



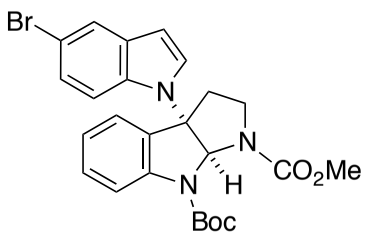
7fc

^{1}H-NMR (400 MHz, $CDCl_3$, a mixture of rotamers)



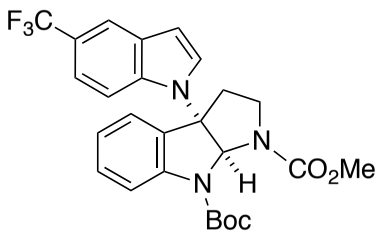
7fd

^{13}C-NMR (100 MHz, $CDCl_3$, a mixture of rotamers)



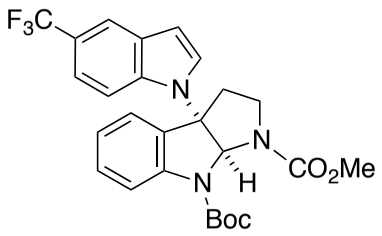
7fd

^{1}H-NMR (600 MHz, $CDCl_3$)



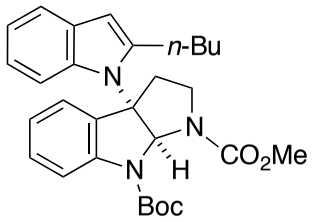
7fe

^{13}C-NMR (150 MHz, $CDCl_3$)



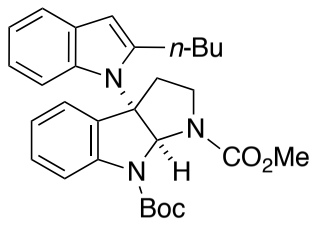
7fe

^{1}H-NMR (400 MHz, $CDCl_3$,
55 °C, a mixture of rotamers)



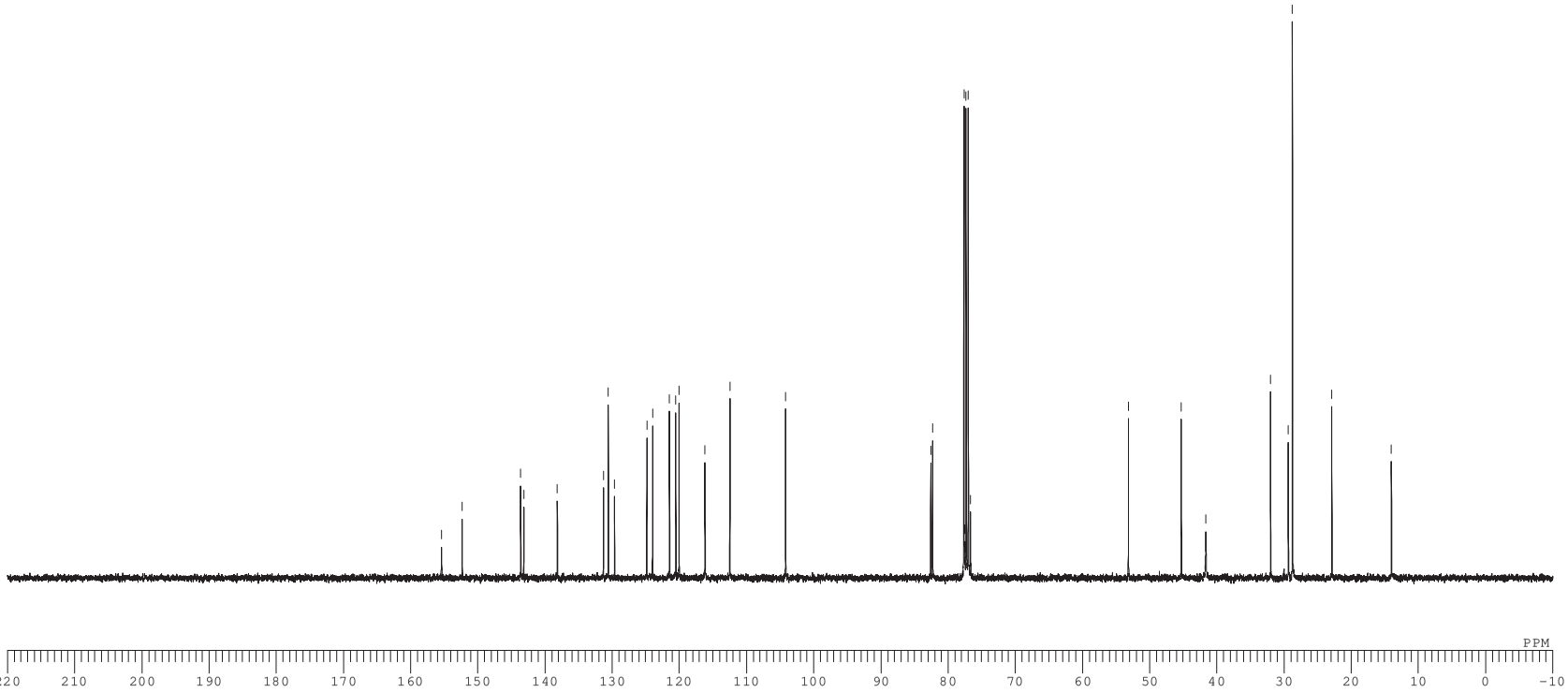
7ff

^{13}C-NMR (100 MHz, $CDCl_3$,
55 °C, a mixture of rotamers)

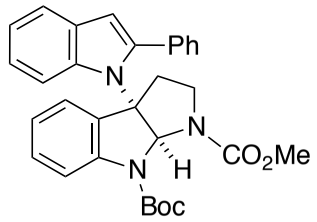


7ff

155.400
152.329
143.619
143.150
138.153
131.303
130.570
129.640
124.840
123.968
121.457
120.518
120.041
116.188
112.475
104.184
82.582
82.318
77.634
77.519
77.313
77.000
76.662
53.158
45.279
41.641
31.984
29.357
28.732
22.862
13.995

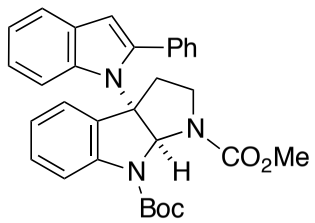


^{1}H-NMR (400 MHz, $CDCl_3$,
55 °C, a mixture of rotamers)



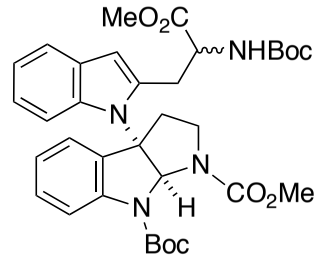
7fg

^{13}C-NMR (100 MHz, $CDCl_3$,
55 °C, a mixture of rotamers)



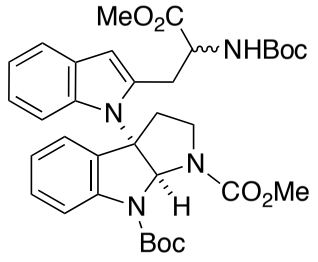
7fg

^{1}H-NMR (600 MHz, $CDCl_3$,
a mixture of rotamers)



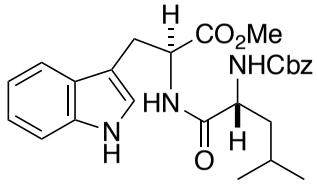
7fh
a mixture of diastereomers

^{13}C-NMR (150 MHz, $CDCl_3$,
a mixture of rotamers)



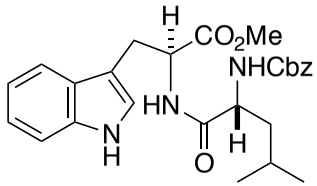
7fh
a mixture of diastereomers

^{1}H-NMR (400 MHz, $CDCl_3$, 55 °C, a mixture of rotamers)



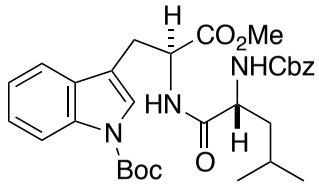
S6

^{13}C-NMR (100 MHz, $CDCl_3$,
55 °C, a mixture of rotamers)



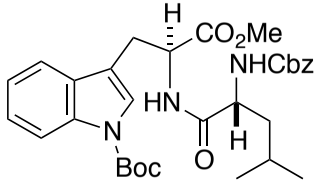
S6

^{1}H-NMR (400 MHz, $CDCl_3$, 55 °C, a mixture of rotamers)



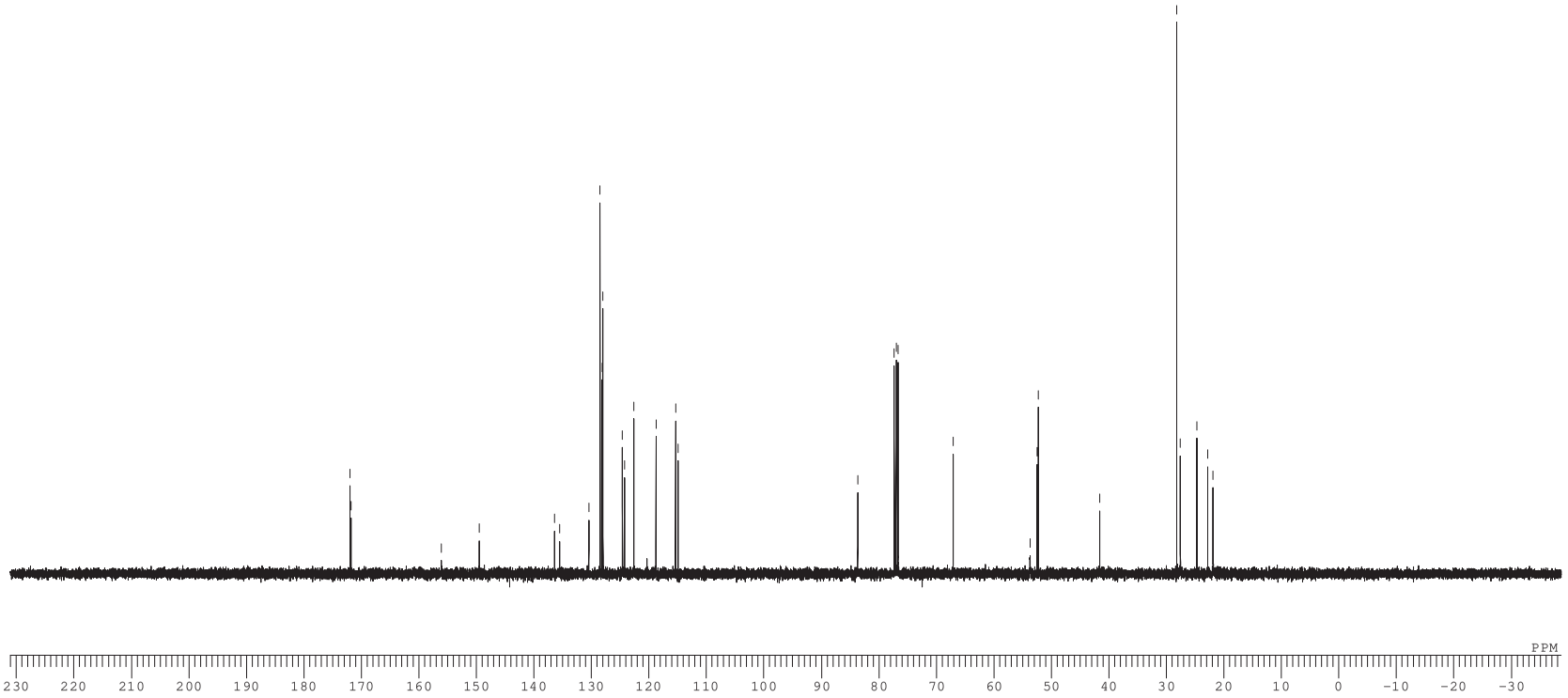
10

^{13}C-NMR (100 MHz, $CDCl_3$,
55 °C, a mixture of rotamers)

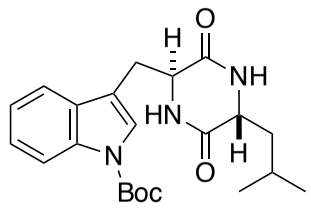


10

171.951
171.794
156.083
149.532
136.380
135.516
130.455
128.471
128.093
127.986
124.586
124.224
122.636
118.776
115.377
114.933
83.691
77.321
77.198
77.000
76.679
67.091
53.717
52.515
52.293
41.586
28.237
27.578
24.722
22.788
21.891



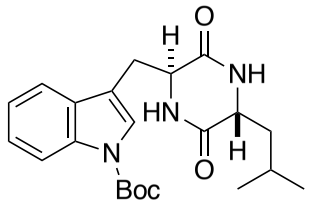
^{1}H-NMR (400 MHz, $CDCl_3$)



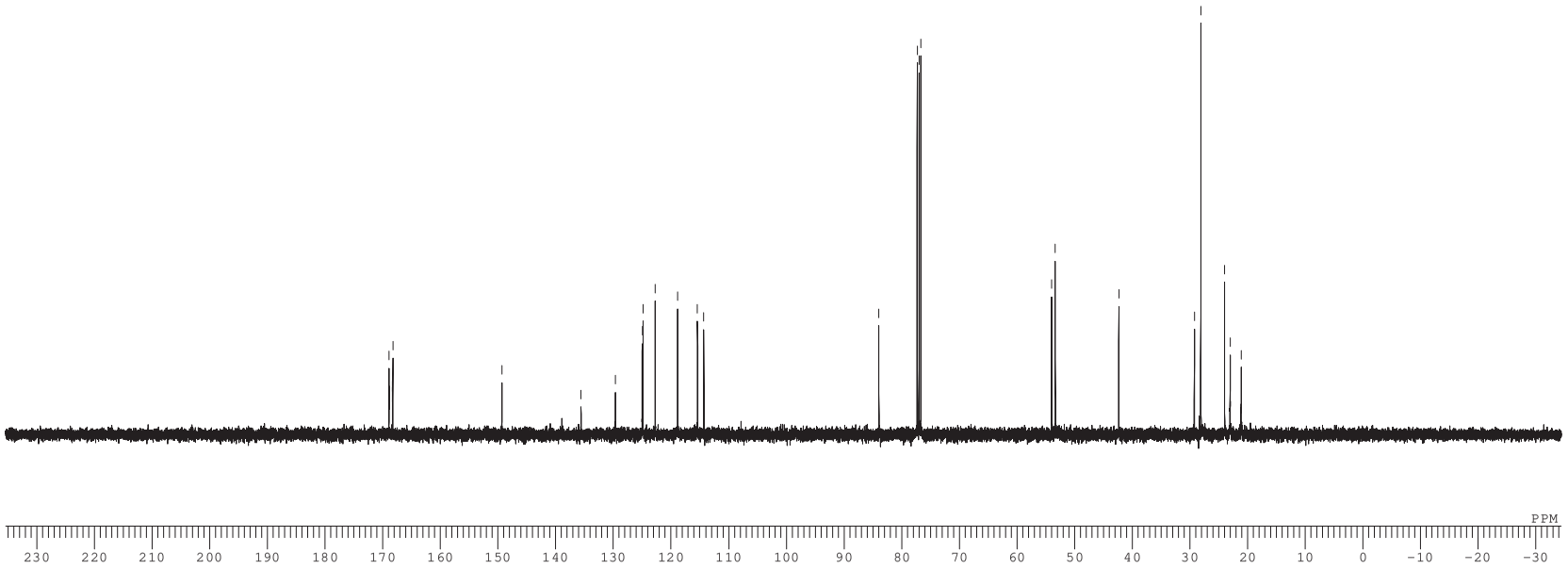
S7

168.910
168.268
149.357
135.609
129.640
124.988
124.840
122.741
118.839
115.406
114.302
83.940
77.313
77.000
76.679
53.973
53.347
42.332
29.226
28.114
23.981
23.035
21.108

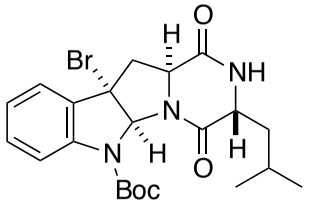
^{13}C-NMR (100 MHz, $CDCl_3$)



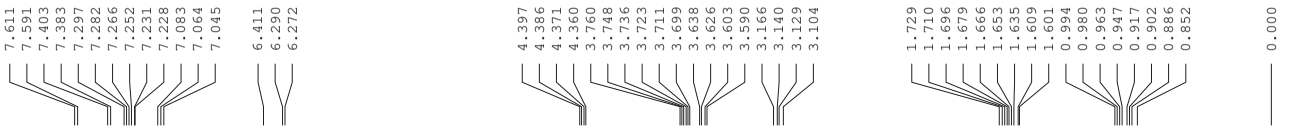
S7

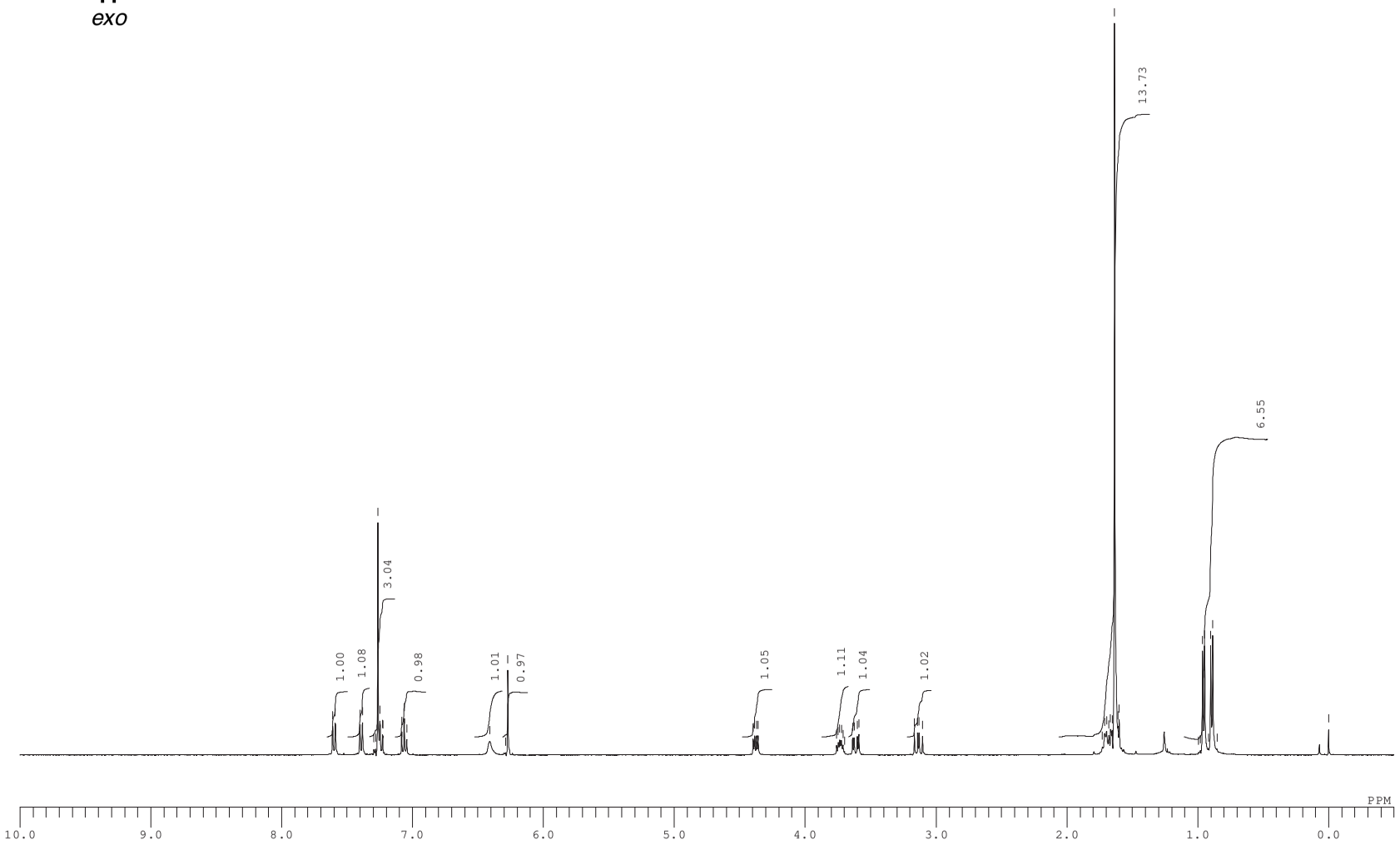


^{1}H-NMR (400 MHz, $CDCl_3$)

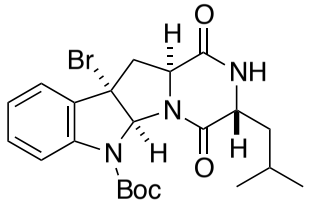


11
exo



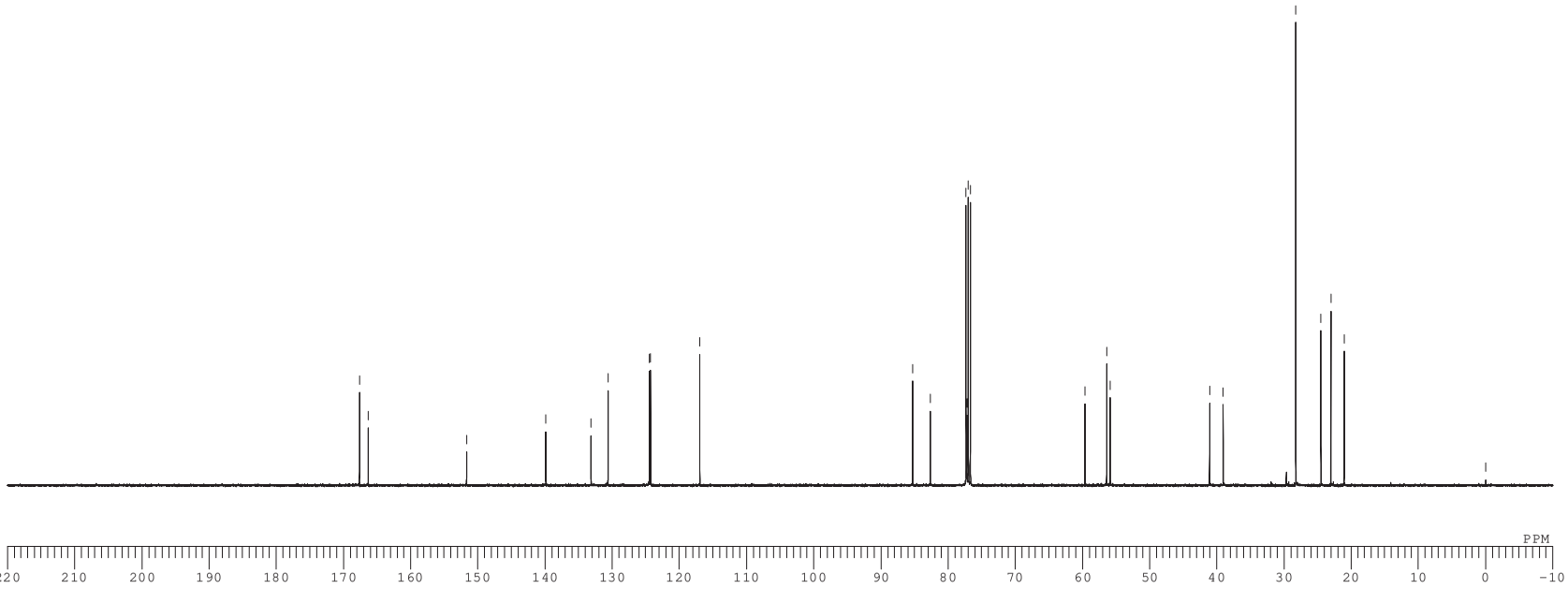


^{13}C-NMR (100 MHz, $CDCl_3$)

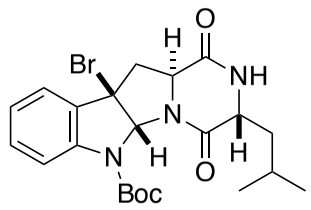


11
exo

167.622
166.297
151.688
139.870
133.138
130.611
124.438
124.266
116.949
85.271
82.629
77.321
77.206
77.000
76.679
59.634
56.408
55.873
41.076
39.043
28.245
24.484
23.019
21.044
-0.034



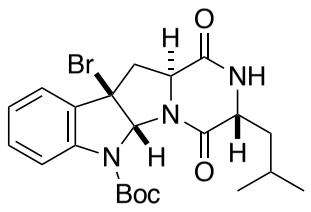
^{1}H-NMR (400 MHz, $CDCl_3$)



S8

endo

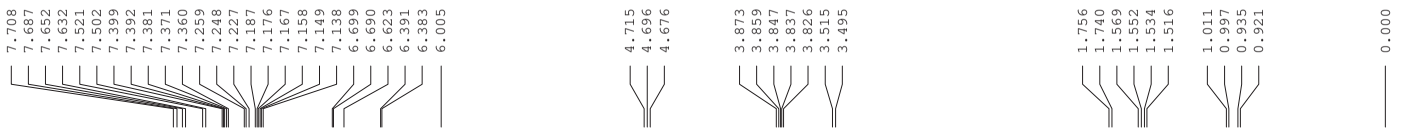
^{13}C-NMR (100 MHz, $CDCl_3$)



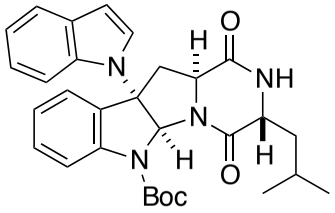
S8

endo

166.824
164.943
151.629
142.078
131.171
130.942
124.419
124.142
116.759
83.542
82.778
77.210
77.000
76.790
58.319
58.023
55.979
46.820
43.811
28.101
24.185
22.953
21.320

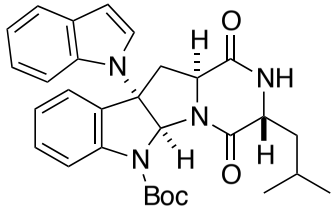


^{1}H-NMR (400 MHz, $CDCl_3$)



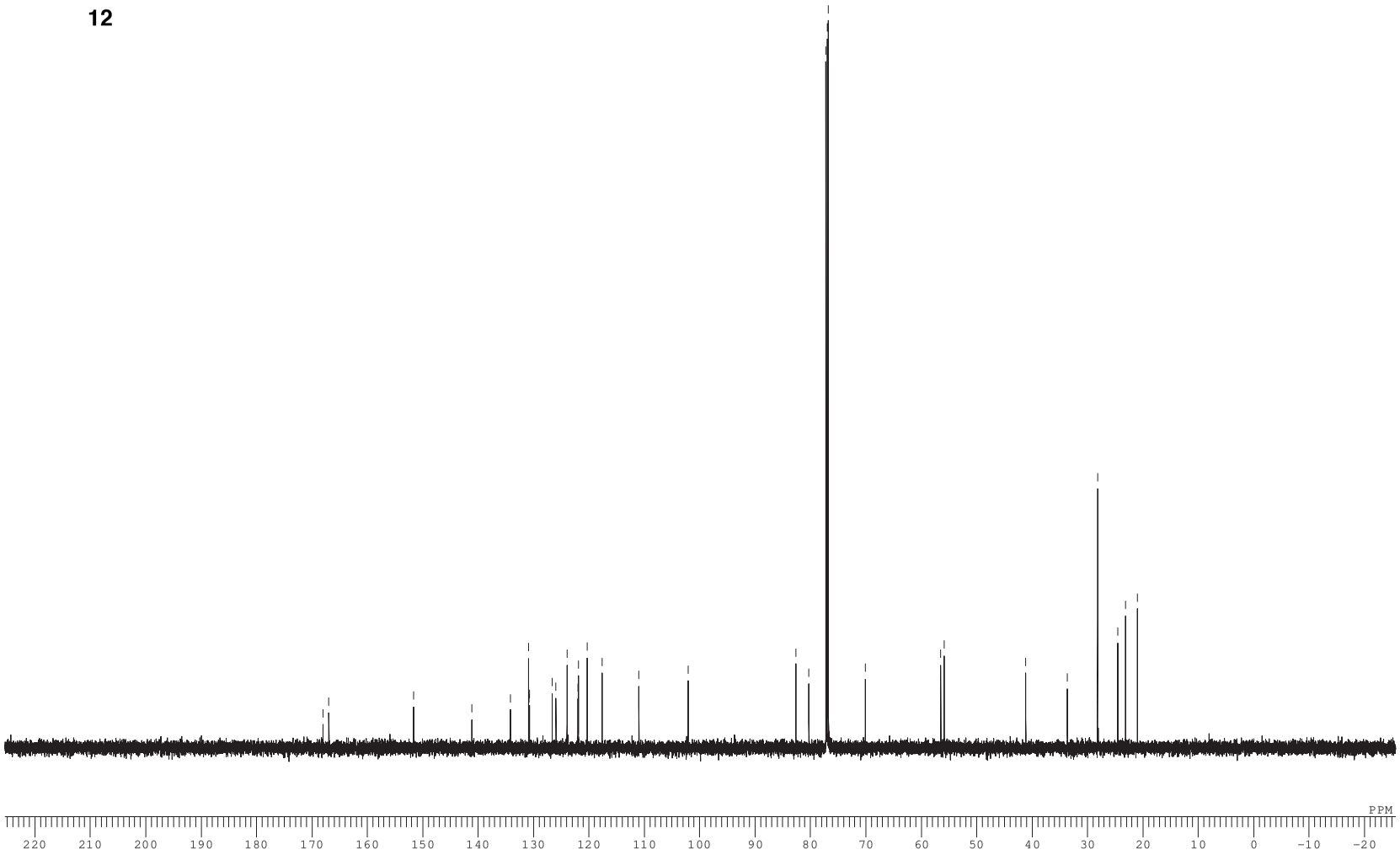
12

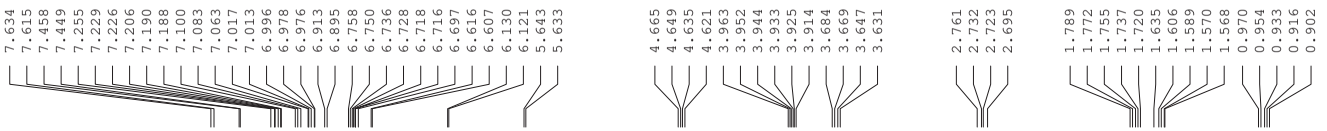
^{13}C-NMR (150 MHz, $CDCl_3$)



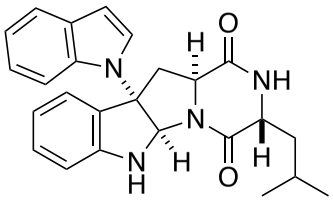
12

167.989
166.945
151.645
141.141
134.171
130.916
130.839
130.714
126.636
125.937
123.964
121.992
121.925
120.307
117.607
110.981
102.076
82.659
80.294
77.211
77.000
76.789
70.125
56.472
55.868
41.142
33.617
28.188
24.559
23.132
20.997

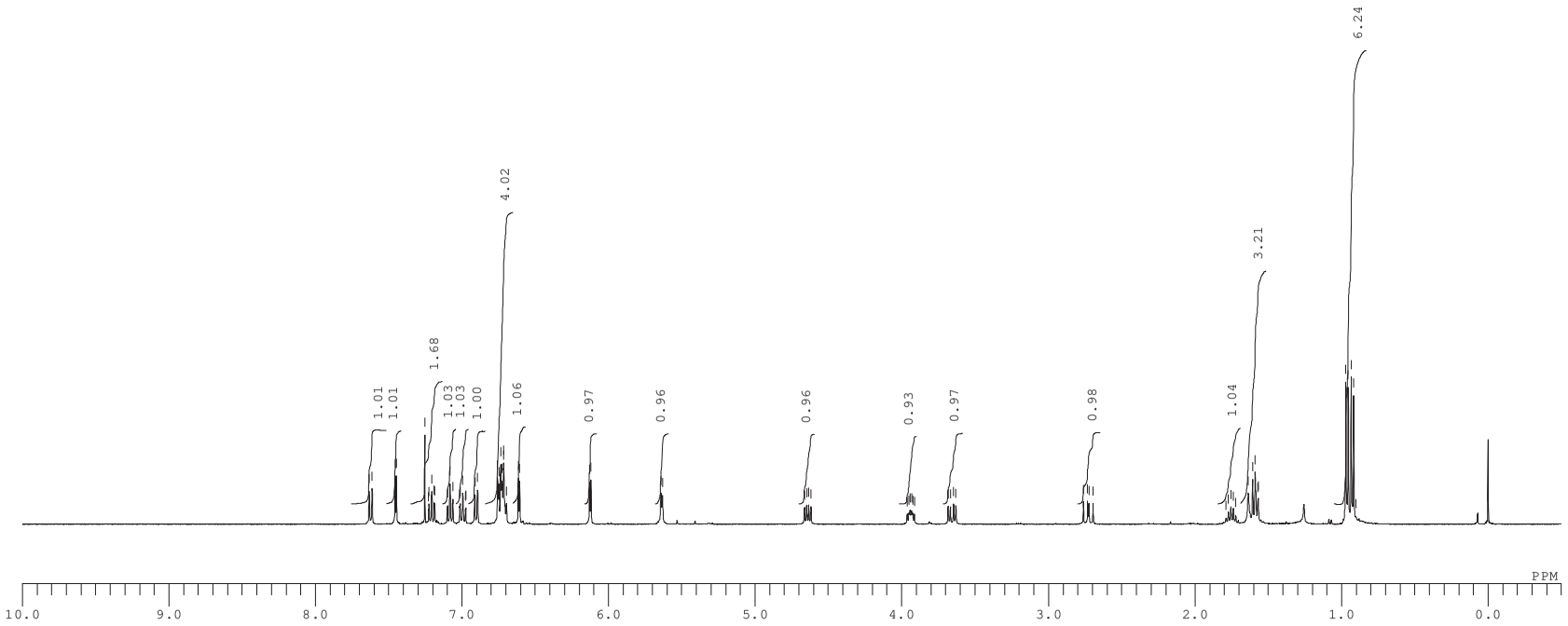




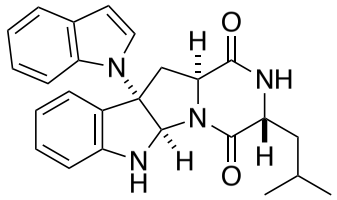
^{1}H-NMR (400 MHz, $CDCl_3$)



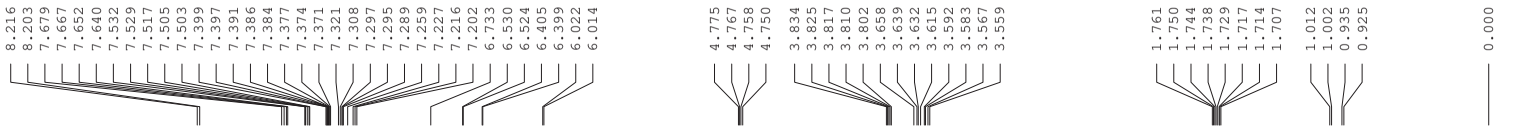
S10



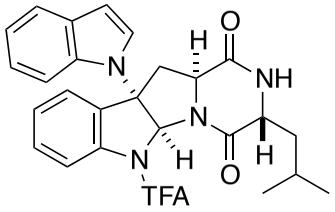
^{13}C-NMR (100 MHz, $CDCl_3$)



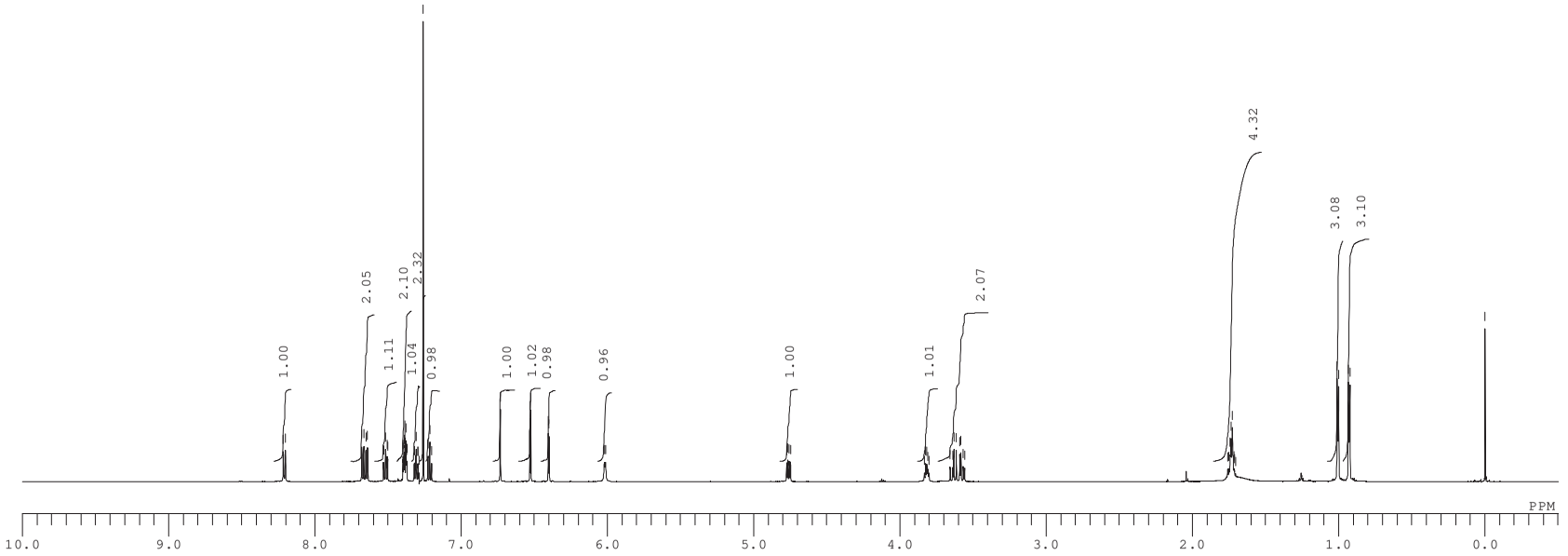
S10



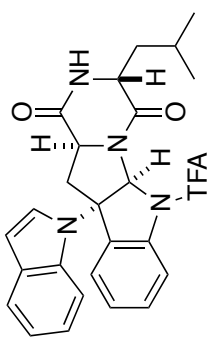
^{1}H-NMR (600 MHz, $CDCl_3$)



13

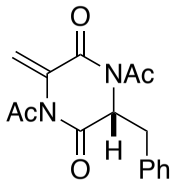


^{13}C-NMR (150 MHz, $CDCl_3$)



13

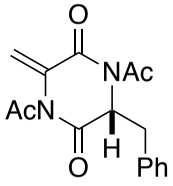
^{1}H-NMR (400 MHz, $CDCl_3$)



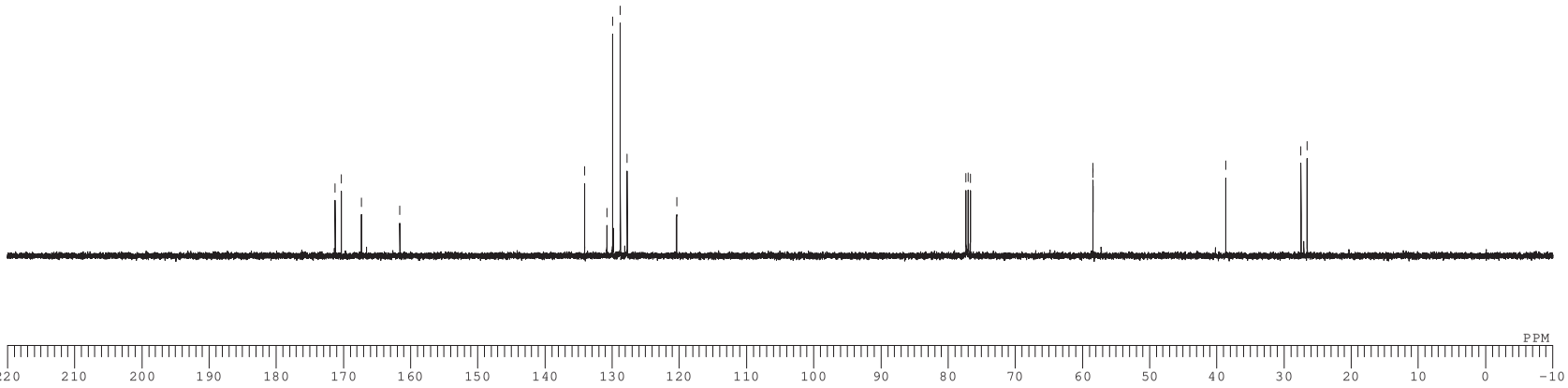
14

171.218
170.296
167.309
161.589
134.109
130.808
129.911
128.784
127.763
120.422
77.321
77.000
76.679
58.441
58.425
38.656
27.455
26.533

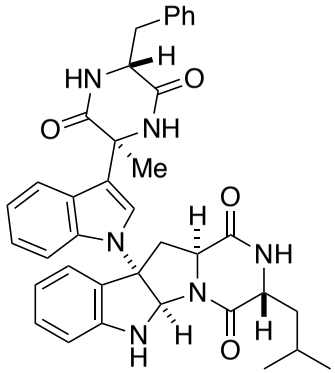
^{13}C-NMR (100 MHz, $CDCl_3$)



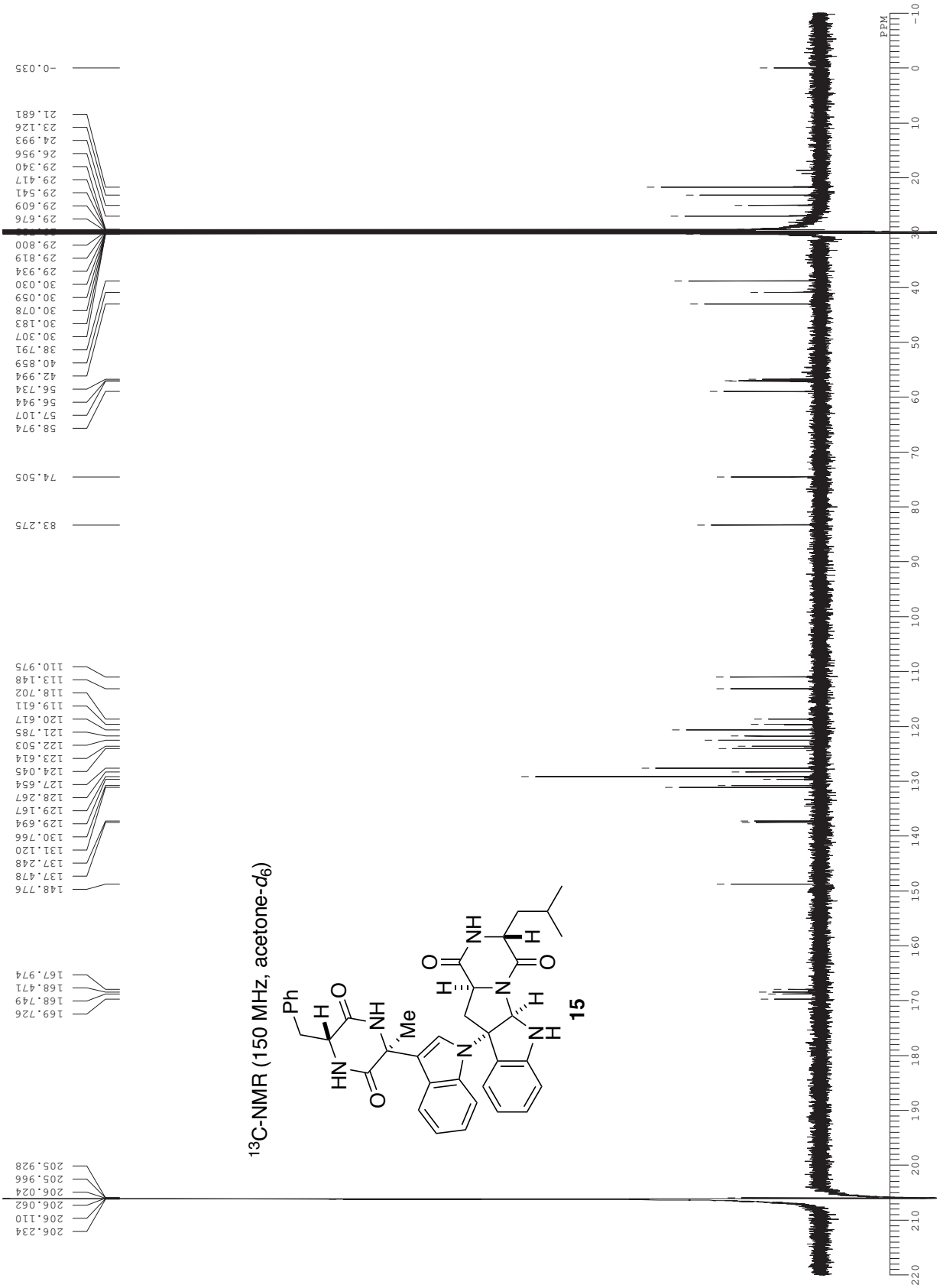
14



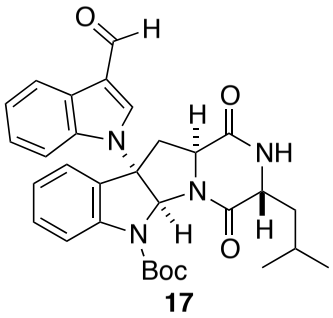
^{1}H-NMR (600 MHz, acetone-d_6)



15

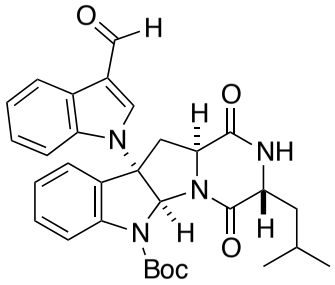

13C-NMR (150 MHz, acetone-d6)
15
PPM

^{1}H-NMR (400 MHz, $CDCl_3$)



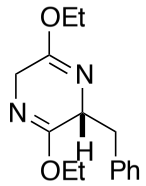
17

^{13}C-NMR (100 MHz, $CDCl_3$)



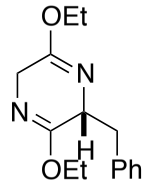
17

^{1}H-NMR (400 MHz, $CDCl_3$)



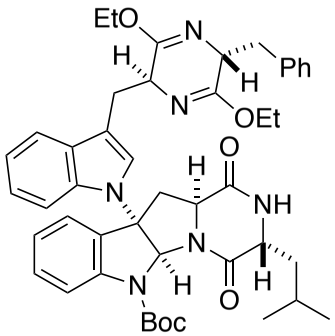
16

^{13}C-NMR (100 MHz, $CDCl_3$)

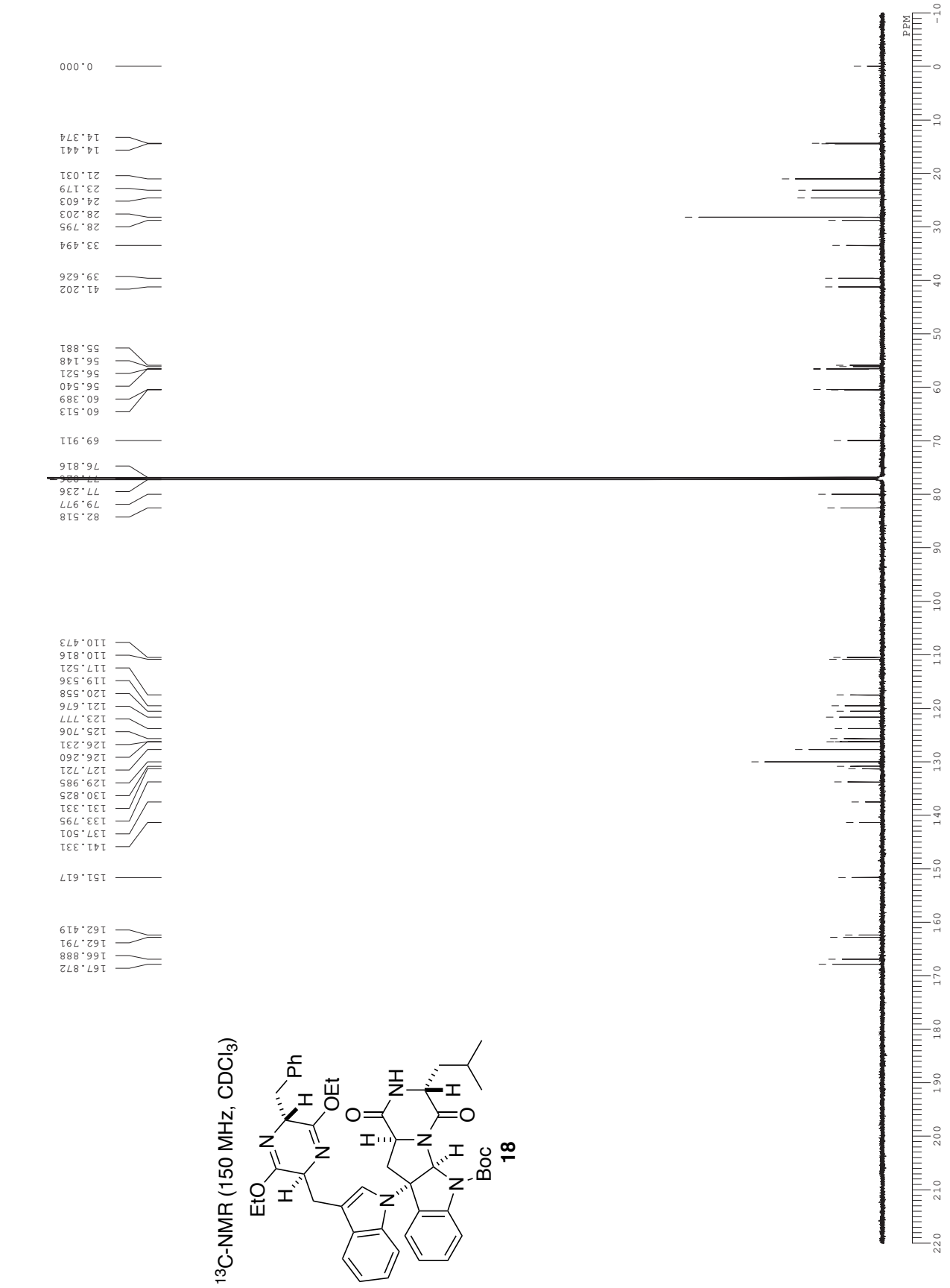


16

^{1}H-NMR (600 MHz, $CDCl_3$)

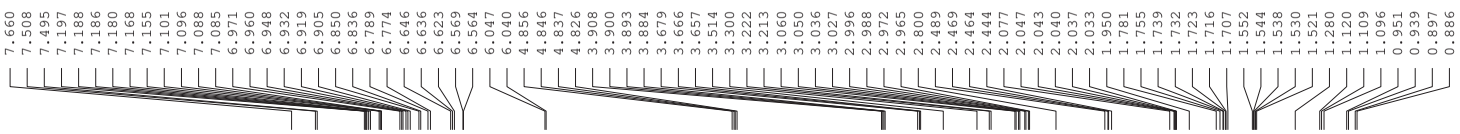


18

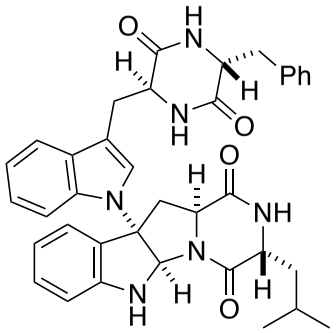


^{13}C-NMR (150 MHz, $CDCl_3$)

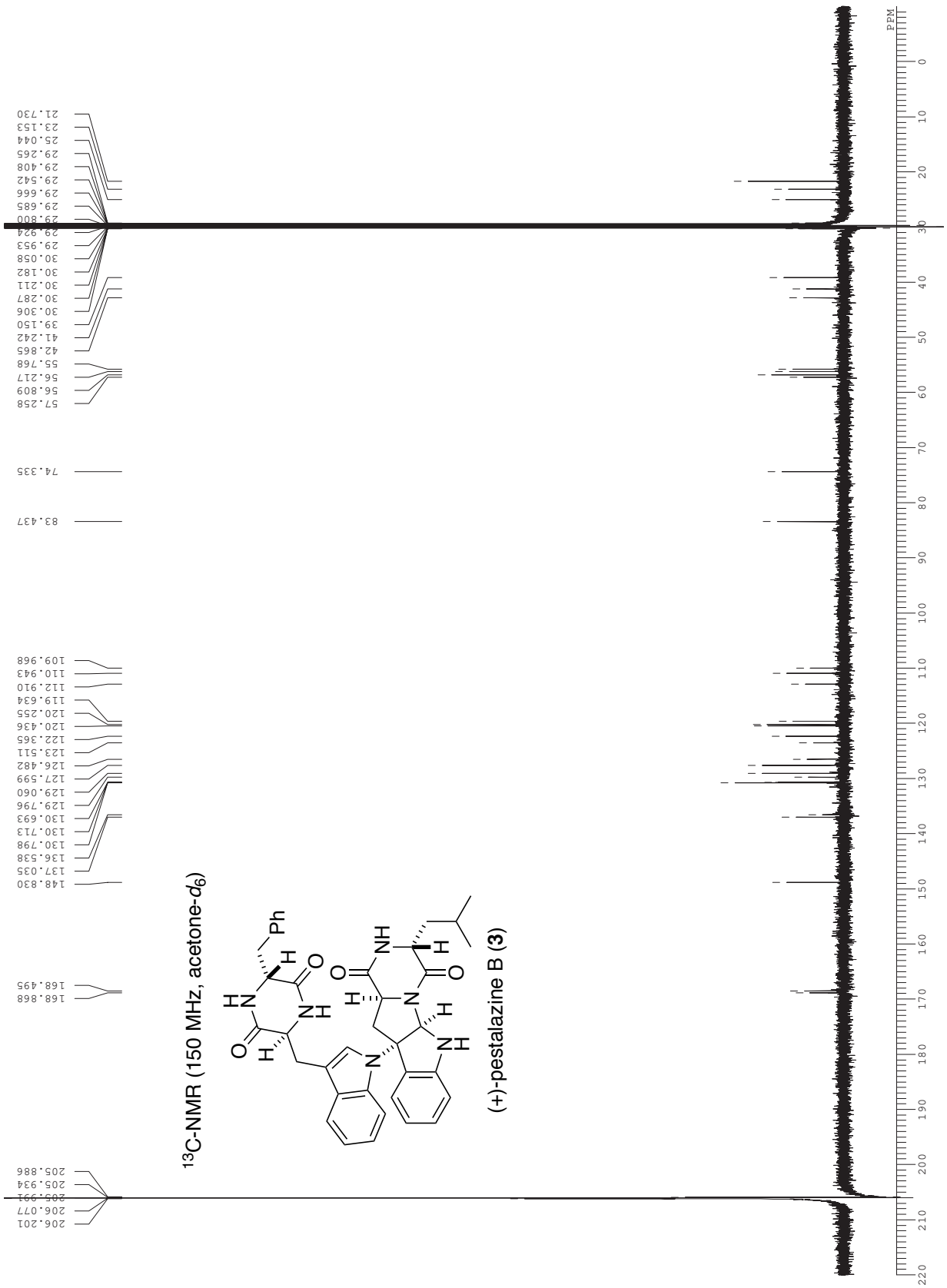
18



^{1}H-NMR (600 MHz, acetone-d_6)



(+)-pestalazine B (**3**)


21.730
23.153
25.044
29.265
29.408
29.542
29.666
29.685
29.800
29.924
29.953
30.058
30.182
30.211
30.287
30.306
39.150
41.242
42.865
55.768
56.217
56.809
57.258
74.335
83.437
109.968
110.943
112.910
119.634
120.255
120.436
122.365
123.511
126.482
127.599
129.060
129.796
130.693
130.713
130.798
136.538
137.035
148.830
168.495
168.868
205.886
205.934
205.991
206.077
206.201
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
^{13}C-NMR (150 MHz, acetone-d_6)
(+)-pestalazine B (**3**)