Supporting Information for the Paper

Investigation of the Passerini and Ugi Reactions in β-Lactam Aldehydes. Synthetic Applications

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PREPARATION AND CHARACTERIZATION OF COMPOUNDS 2b-h

Passerini adduct 2b. **Method A.** From 37 mg (0.10 mmol) of aldehyde (+)-**1b**, compound **2b** was obtained as a mixture of isomers in a *syn/anti* ratio (65:35). After flash chromatography using *n*-hexane/ethyl acetate (3:1) as eluent, the less polar compound *syn*-(+)-**2b** (31 mg, 56%) and the more polar compound *anti*-(+)-**2b** (17 mg, 32%) were obtained. ***syn*-(+)-2b**. White solid; mp 148–149°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ +110.2 (c 0.9, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.97-7.95 (m, 2H), 7.57 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.50 (AA'*XX'*, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.28-7.22 (m, 5H), 7.03-6.92 (m, 5H), 6.84 (*AA'*XX', 2H), 6.37 (t, *J* = 5.7 Hz, 1H), 5.95 (d, *J* = 2.0 Hz, 1H), 5.52 (d, *J* = 5.3 Hz, 1H), 5.40 (dd, *J* = 5.3, 2.2 Hz, 1H), 4.37 (dd, *J* = 14.9, 5.7 Hz, 1H), 4.26 (dd, *J* = 14.9, 5.8 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 168.1, 165.0, 163.2, 157.1, 156.9, 136.7, 133.8, 130.0, 129.6, 128.65, 128.61, 127.6, 122.6, 119.8, 115.5, 114.5, 79.5, 69.8, 58.0, 55.4, 43.5; IR (KBr, cm^{-1}) ν 3369, 1749, 1668; HRMS (ESI) calcd for $C_{32}H_{29}N_2O_6^+$ $[M+H]^+$: 537.2020; found: 537.2000. ***anti*-(+)-2b**. White solid; mp 147–148°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ +91.3 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 8.03-8.00 (m, 2H), 7.59 (tt, *J* = 7.5, 1.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.35 (AA'*XX'*, 2H), 7.35-7.30 (m, 2H), 7.24-7.22 (m, 3H), 7.09-7.00 (m, 5H), 6.85 (*AA'*XX', 2H), 6.47 (t, *J* = 5.7 Hz, 1H), 6.29 (d, *J* = 3.2 Hz, 1H), 5.54 (d, *J* = 5.1 Hz, 1H), 5.27 (dd, *J* = 5.0, 3.3 Hz, 1H), 4.36 (dd, *J* = 14.8, 6.4 Hz, 1H), 3.88 (dd, *J* = 14.8, 5.0 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 166.9,

164.8, 162.8, 157.7, 156.9, 136.9, 133.9, 130.0, 129.8, 129.5, 128.74, 128.69, 128.3, 127.7, 127.6, 122.8, 118.9, 115.7, 114.6, 80.1, 68.7, 58.6, 55.4, 43.3; IR (KBr, cm^{-1}) ν 3375, 1756, 1666; HRMS (ESI) calcd for $C_{32}H_{29}N_2O_6^+$ $[M+H]^+$: 537.2020; found: 537.2022.

Passerini adduct 2c. **Method A.** From 60 mg (0.26 mmol) of aldehyde (+)-**1c**, compound **2c** was obtained as a mixture of isomers in a *syn/anti* ratio (72:28). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, an inseparable mixture of isomers (80 mg, 65%) was obtained as a colorless oil. ***syn*-2c**. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 8.11-8.08 (m, 2H); 7.64-7.59 (m, 1H), 7.50-7.43 (m, 2H), 7.33-7.20 (m, 7H), 7.05-6.94 (m, 1H), 6.94-6.87 (m, 2H), 6.69 (t, *J* = 5.4 Hz, 1H), 5.81 (d, *J* = 5.1 Hz, 1H), 5.41 (d, *J* = 5.1 Hz, 1H), 4.91 (t, *J* = 5.0 Hz, 1H), 4.51-4.40 (m, 2H), 4.32 (dd, *J* =17.8, 2.6 Hz, 1H), 3.92 (dd, *J* = 17.7, 2.4 Hz, 1H), 2.30 (t, *J* = 2.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 166.9, 165.7, 165.2, 157.0, 137.2, 133.9, 130.0, 129.6, 128.74, 128.68, 128.6, 127.8, 127.7, 122.6, 115.6, 80.5, 76.3, 73.2, 71.6, 57.5, 43.6, 31.1; HRMS (ESI) calcd for $C_{28}H_{25}N_2O_5^+$ $[M+H]^+$: 469.1758; found: 469.1776. ***anti*-2c**. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 8.07-8.04 (m, 2H), 7.64-7.59 (m, 1H), 7.50-7.43 (m, 2H), 7.33-7.20 (m, 7H), 7.14-7.11 (m, 2H), 7.05-6.94 (m, 1H), 6.53 (t, *J* = 5.4 Hz, 1H), 6.09 (d, *J* = 4.0 Hz, 1H), 5.43 (d, *J* = 5.0 Hz, 1H), 4.93 (dd, *J* = 4.9, 3.9 Hz, 1H), 4.45-4.40 (m, 1H), 4.29 (dd, *J* = 17.8, 2.6 Hz, 1H), 4.02 (dd, *J* = 14.8, 5.3 Hz, 1H), 3.86 (dd, *J* = 17.8, 2.5 Hz, 1H), 2.31 (t, *J* = 2.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ: 166.7, 165.3, 165.2, 157.4, 137.0, 134.0, 130.0, 129.7, 128.74, 128.7, 128.68, 127.7, 127.6, 122.6, 115.5, 80.8, 75.8, 73.6, 69.7, 58.1, 43.3, 30.4.

Passerini adduct 2d. **Method A.** From 52 mg (0.22 mmol) of aldehyde (+)-**1a**, compound **2d** was obtained as a mixture of isomers in a *syn/anti* ratio (60:40). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, the less polar

compound *syn*-(+)-**2d** (46 mg, 51%) and the more polar compound *anti*-(+)-**2d** (30 mg, 33%) were obtained. ***syn*-(+)-2d**. Colorless oil; $[\alpha]_D$ +106.1 (c 0.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.39 (AA'*XX'*, 2H), 7.30-7.26 (m, 3H), 7.08-7.05 (m, 2H), 6.82 (*AA'*XX', 2H), 6.45 (bs, 1H), 5.56 (d, *J* = 4.5 Hz, 1H), 4.97 (t, *J* = 4.8 Hz, 1H), 4.66 (d, *J* = 5.3 Hz, 1H), 4.43 (dd, *J* = 14.8, 5.8 Hz, 1H), 4.25 (dd, *J* = 14.9, 5.6 Hz, 1H), 3.77 (s, 3H), 3.52 (s, 3H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 169.6, 167.7, 164.4, 156.7, 137.0, 130.1, 128.6, 127.62, 127.56, 119.7, 114.1, 82.7, 70.5, 59.8, 57.3, 55.4, 43.4, 20.7; IR ($CHCl_3$, cm^{-1}) ν 3347, 1750, 1668; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_6^+$ $[M+H]^+$: 413.1707; found: 413.1713. ***anti*-(+)-2d**. White solid; mp 179–181°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ +31.3 (c 0.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.37 (AA'*XX'*, 2H), 7.34-7.27 (m, 3H), 7.20-7.18 (m, 2H), 6.87 (*AA'*XX', 2H), 6.61 (t, *J* = 5.3 Hz, 1H), 5.78 (d, *J* = 3.7 Hz, 1H), 4.80 (dd, *J* = 5.1, 3.8 Hz, 1H), 4.67 (d, *J* = 5.1 Hz, 1H), 4.64 (dd, *J* = 14.7, 5.9 Hz, 1H), 4.27 (dd, *J* = 14.8, 5.4 Hz, 1H), 3.78 (s, 3H), 3.48 (s, 3H), 2.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ: 169.2, 166.9, 164.4, 156.6, 137.3, 130.0, 128.7, 127.8, 127.6, 118.6, 114.4, 83.0, 69.0, 60.0, 58.1, 55.4, 43.4, 20.6. IR (KBr, cm^{-1}) ν 3330, 1752, 1666; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_6^+$ $[M+H]^+$: 413.1707; found: 413.1709.

Passerini adduct 2e. **Method A.** From 59 mg (0.25 mmol) of aldehyde (+)-**1a**, compound **2e** was obtained as a mixture of isomers in a *syn/anti* ratio (60:40). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, the less polar compound *syn*-(+)-**2e** (50 mg, 53%) and the more polar compound *anti*-(+)-**2e** (33 mg, 35%) were obtained. ***syn*-(+)-2e**. Colorless oil; $[\alpha]_D$ +77.9 (c 0.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.42 (AA'*XX'*, 2H), 6.85 (*AA'*XX', 2H), 5.94 (bs, 1H), 5.39 (d, *J* = 5.1 Hz, 1H), 4.92 (t, *J* = 5.1 Hz, 1H), 4.67 (d, *J* = 5.1 Hz, 1H), 3.79 (s, 3H), 3.59 (s, 3H), 1.99 (s, 3H), 1.29 (s, 9H,); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 169.6, 166.5, 164.5,

156.7, 130.3, 119.9, 114.1, 82.7, 71.3, 59.8, 57.2, 55.4, 51.5, 28.4, 20.6. IR ($CHCl_3$, cm^{-1}) ν 3360, 1753, 1677; HRMS (ESI) calcd for $C_{19}H_{27}N_2O_6^+$ $[M+H]^+$: 379.1864; found: 379.1875. ***anti*-(+)-2e**. Colorless oil; $[\alpha]_D$ +86.3 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.41 (AA'*XX'*, 2H), 6.86 (*AA'*XX', 2H), 6.23 (bs, 1H), 5.55 (d, *J* = 2.3 Hz, 1H), 4.71 (d, *J* = 5.4 Hz, 1H), 4.66 (dd, *J* = 5.4, 2.3 Hz, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 2.17 (s, 3H), 1.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 169.4, 164.8, 164.2, 156.6, 130.3, 118.7, 114.3, 82.6, 69.8, 60.0, 58.7, 55.4, 51.4, 28.4, 20.7; IR ($CHCl_3$, cm^{-1}) ν = 3355, 1752, 1695; HRMS (ESI) calcd for $C_{19}H_{27}N_2O_6^+$ $[M+H]^+$: 379.1864; found: 379.1868.

Passerini adduct 2f. **Method A.** From 46 mg (0.20 mmol) of aldehyde (–)-**1d**, compound **2f** was obtained as a mixture of isomers in a *syn/anti* ratio (73:27). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, an inseparable mixture of isomers (68 mg, 61%) was obtained as a colorless oil. ***syn*-2f**. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.98 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.77 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.41 (td, *J* = 7.6, 1.1 Hz, 1H), 7.29-7.23 (m, 2H), 7.19 (td, *J* = 7.7, 1.6 Hz, 1H), 7.08-6.97 (m, 3H), 6.23 (bs, 1H), 5.85-5.70 (m, 1H), 5.70 (d, *J* = 3.2 Hz, 1H), 5.39 (d, *J* = 5.1 Hz, 1H), 5.23-5.16 (m, 2H), 4.78 (dd, *J* = 5.0, 3.2 Hz, 1H), 4.21-4.11 (m, 1H), 3.68 (dd, *J* = 15.7, 6.5 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 166.0, 165.8, 165.7, 157.1, 140.9, 134.7, 133.1, 130.9, 130.8, 129.6, 128.4, 122.6, 118.9, 115.5, 93.8, 80.1, 71.5, 57.3, 51.9, 44.0, 28.5; HRMS (ESI) calcd for $C_{25}H_{28}IN_2O_5^+$ $[M+H]^+$: 563.1037; found: 563.1017. ***anti*-2f**. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 8.00 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.40 (td, *J* = 7.6, 1.1 Hz, 1H), 7.29-7.23 (m, 3H), 7.08-6.97 (m, 3H), 6.30 (bs, 1H), 5.85-5.70 (m, 1H), 5.73 (d, *J* = 3.9 Hz, 1H), 5.42 (d, *J* = 5.0 Hz, 1H), 5.34-5.25 (m, 2H), 4.66 (dd, *J* = 4.8, 4.1 Hz, 1H), 4.21-4.11 (m, 1H), 3.68 (dd, *J* = 15.7, 6.5 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ: 166.0, 165.7,

165.1, 157.1, 141.4, 134.7, 133.3, 131.5, 130.6, 129.7, 128.2, 122.6, 119.7, 115.5, 94.4, 80.2, 71.3, 57.7, 51.8, 43.6, 28.4.

Passerini adduct 2g. **Method A.** From 35 mg (0.15 mmol) of aldehyde (–)-**1d**, compound **2g** was obtained as a mixture of isomers in a *syn/anti* ratio (77:23). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, the less polar compound *anti*-(–)-**2g** (14 mg, 17%) and the more polar compound *syn*-(–)-**2g** (46 mg, 55%) were obtained. ***syn*-(–)-2g**. White solid; mp 165–166°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ −4.6 (c 1.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.92 (AA'*BB'*, 2H), 7.78 (*AA'*BB', 2H), 7.33-7.28 (m, 2H), 7.10 (t, *J* = 5.5 Hz, 1H), 7.06-7.01 (m, 3H), 5.74-5.61 (m, 1H), 5.64 (d, *J* = 2.3 Hz, 1H), 5.28 (d, *J* = 5.0 Hz, 1H), 5.18-5.12 (m, 2H), 4.66 (dd, *J* = 5.0, 2.3 Hz, 1H), 4.60 (d, *J* = 17.4 Hz, 1H), 4.54 (d, *J* = 17.2 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 4.23 (dd, *J* = 18.0, 6.4 Hz, 1H), 3.91 (dd, *J* = 17.8, 4.9 Hz, 1H), 3.94-3.87 (m, 1H), 3.63 (dd, *J* = 15.6, 6.9 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 168.9, 167.4, 167.2, 165.9, 165.3, 157.1, 134.4, 131.8, 130.8, 129.6, 123.8, 122.6, 119.0, 115.5, 80.2, 70.3, 61.6, 57.2, 43.3, 41.2, 39.2, 14.1; IR (KBr, cm^{-1}) ν 3372, 1760, 1721, 1684; HRMS (ESI) calcd for $C_{28}H_{28}N_3O_9^+$ $[M+H]^+$: 550.1820; found: 550.1810. ***anti*-(–)-2g**. White solid; mp 159–161°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ −16.2 (c 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.69 (AA'*BB'*, 2H), 7.54 (*AA'*BB', 2H), 7.19-7.14 (m, 2H), 6.98-6.93 (m, 2H), 6.76-6.73 (m, 2H), 5.79 (d, *J* = 3.5 Hz, 1H), 5.82-5.68 (m, 1H), 5.31-5.25 (m, 2H), 5.09 (d, *J* = 5.0 Hz, 1H), 4.66 (d, *J* = 17.5 Hz, 1H), 4.53 (dd, *J* = 4.9, 3.7 Hz, 1H), 4.52 (d, *J* = 17.7 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.08 (ddt, *J* = 15.4, 5.8, 1.4 Hz, 1H), 4.02 (dd, *J* = 18.3, 5.8 Hz, 1H), 3.68 (dd, *J* = 18.1, 4.7 Hz, 1H), 3.58 (dd, *J* = 15.4, 7.1 Hz, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 168.7, 167.5, 166.3, 165.9, 165.2, 157.3, 134.0, 131.5, 130.6, 129.3, 123.6, 122.3, 120.1, 115.6, 80.7, 69.7, 61.6, 57.3, 43.4, 41.2, 38.9, 14.1; IR (KBr,

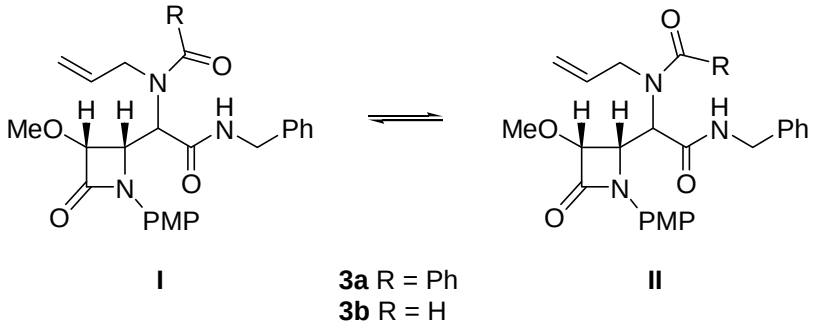
cm^{-1}) ν 3384, 1760, 1721, 1682; HRMS (ESI) calcd for $C_{28}H_{28}N_3O_9^+$ [*M*+*H*]$^+$: 550.1820; found: 550.1845.

Passerini adduct 2h. **Method A.** From 56 mg (0.24 mmol) of aldehyde (+)-**1a**, compound **2h** was obtained as a mixture of isomers in a *syn/anti* ratio (68:32). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, the less polar compound *syn*-(+)-**2h** (69 mg, 58%) and the more polar compound *anti*-(+)-**2h** (32 mg, 28%) were obtained. **Method B.** From 30 mg (0.13 mmol) of aldehyde (+)-**1a**, compound **2h** was obtained as a mixture of isomers in a *syn/anti* ratio (63:37). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, the less polar compound *syn*-(+)-**2h** (36 mg, 56%) and the more polar compound *anti*-(+)-**2h** (21 mg, 33%) were obtained. ***syn*-(+)-2h**. Colorless oil; $[\alpha]_D$ +65.6 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.71 (AA'*BB'*, *2H*,), 7.36 (*AA'*BB', 2H), 7.29 (AA'*XX'*, 2H), 7.16 (dd, *J* = 8.2, 5.1 Hz, 1H), 6.82 (*AA'*XX', 2H), 5.41 (d, *J* = 5.0 Hz, 1H), 4.88 (dd, *J* = 14.0, 8.5 Hz, 1H), 4.65 (d, *J* = 5.1 Hz, 1H), 4.62 (t, *J* = 5.1 Hz, 1H), 4.17 (dd, *J* = 14.0, 5.1 Hz, 1H), 3.77 (s, 3H), 3.61 (s, 3H), 2.45 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 169.3, 167.5, 164.0, 156.8, 145.6, 133.6, 130.0, 129.9, 128.7, 119.8, 114.1, 82.3, 70.3, 59.8, 59.7, 56.8, 55.4, 21.7, 20.4; IR ($CHCl_3$, cm^{-1}) ν 3333, 1752, 1696; HRMS (ESI) calcd for $C_{23}H_{26}N_2NaO_8S^+$ [*M*+*Na*]$^+$: 513.1302; found: 513.1306. ***anti*-(+)-2h**. Colorless oil; $[\alpha]_D$ +31.3 (c 3.1, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ: 7.73 (AA'*BB'*, 2H), 7.39 (bs, 1H), 7.32 (*AA'*BB', 2H), 7.28 (AA'*XX'*, 2H), 6.84 (*AA'*XX', 2H), 5.66 (d, *J* = 3.2 Hz, 1H), 4.66 (d, *J* = 5.3 Hz, 1H), 4.62-4.48 (m, 2H), 4.60 (dd, *J* = 5.3, 3.4 Hz, 1H), 3.77 (s, 3H), 3.62 (s, 3H), 2.43 (s, 3H), 2.11 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ: 169.0, 166.9, 164.1, 156.8, 145.4, 133.8, 129.9, 129.7, 128.7, 118.7, 114.4, 82.8, 68.7, 60.1, 59.8, 57.9, 55.4, 21.7, 20.5; IR ($CHCl_3$, cm^{-1}) ν 3331, 1753, 1700; HRMS (ESI) calcd for $C_{23}H_{27}N_2O_8S^+$ [*M*+*H*]$^+$: 419.1483; found: 491.1467.

PREPARATION AND CHARACTERIZATION OF COMPOUNDS 3a-h and 3j-m

Ugi adduct 3a. **Method A.** From 100 mg (0.43 mmol) of aldehyde (+)-**1a**, compound **3a** was obtained as a mixture of isomers in a *syn/anti* ratio (65:35). After flash chromatography using *n*-hexane/ethyl acetate (2:1) as eluent, the less polar compound *syn*-(+)-**3a** (110 mg, 50%) and the more polar compound *anti*-(+)-**3a** (60 mg, 28%) were obtained.

Compounds **3a** and **3b** are a mixture of the corresponding rotamers, as shown in Scheme S1. Thus, the ^{1}H and ^{13}C NMR characterization has been achieved as is explained bellow.



Scheme S1. Rotamers of compounds **3a** and **3b**

^{1}H NMR spectra of both *syn*-(+)-**3a** and *anti*-(+)-**3a** at room temperature using $CDCl_3$ showed a collection of broad signals. In addition, some signals of the ^{13}C NMR spectra ($CDCl_3$, 25°C) for both isomers were missed. Then, the multiplicity of the corresponding signals of ^{1}H NMR was achieved at 100°C using 1,1,2,2-tetrachloroethane as deuterated solvent. See: ^{1}H NMR in $(CDCl_2)_2$ of compound *syn*-(+)-**3a** at different temperatures in page 22.

***syn*-(+)-3a**. White solid; mp 77–79°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ +125.0 (c 0.3, $CHCl_3$). ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 100°C) δ 7.41-7.24 (m, 10H), 7.06-7.04 (m, 2H,), 6.85-6.82 (m, 1H), 6.83 (*AA*′XX', 2H), 5.88-5.75 (m, 1H), 5.19 (dd, *J* = 9.1, 5.3 Hz, 1H), 5.13-5.04 (m, 2H), 4.83 (d, *J* = 8.8 Hz, 1H), 4.68 (d, *J* = 5.1 Hz, 1H), 4.19 (dd, *J* =

15.0, 5.7 Hz, 1H), 4.18-4.02 (m, 3H), 3.78 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 100°C) δ 174.6, 170.2, 166.5, 159.0, 139.2, 137.7, 135.7, 131.5, 131.1, 130.1, 129.9, 129.1, 129.0, 128.2, 123.0, 119.4, 116.0, 85.7, 62.6, 60.8, 58.1, 57.2, 45.2; IR (KBr, cm^{-1}) ν 3305, 1752, 1675, 1632; HRMS (ESI) calcd for $C_{30}H_{32}N_3O_5^+$ $[M+H]^+$: 514.2337; found: 514.2345. ***anti*-(+)-3a**. Colorless oil; $[\alpha]_D$ +6.2 (c 1.4, $CHCl_3$); ^{1}H NMR (300 MHz, $C_2D_2Cl_4$, 100°C) δ 7.35-7.18 (m, 10H), 6.89 (*AA'*XX', 2H), 6.75 (d, *J* = 7.1 Hz, 2H), 6.44 (t, *J* = 5.5 Hz, 1H), 5.58-5.45 (m, 1H), 5.26 (dd, *J* = 9.4, 5.2 Hz, 1H), 4.89 (d, *J* = 9.3 Hz, 1H), 5.02-4.87 (m, 2H), 4.72 (d, *J* = 5.1 Hz, 1H), 4.47 (dd, *J* = 14.7, 5.5 Hz, 1H), 4.40 (dd, *J* = 14.7, 5.6 Hz, 1H), 3.85-3.66 (m, 2H), 3.79 (s, 3H), 3.54 (s, 3H); ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 100°C) δ: 174.5, 169.6, 166.9, 159.4, 139.7, 137.0, 134.1, 131.5, 131.4, 130.2, 129.6, 129.2, 129.0, 128.2, 123.8, 120.8, 116.5, 85.8, 61.6, 61.0, 58.0, 57.3, 53.5, 45.1; IR ($CHCl_3$, cm^{-1}) ν 3327, 1751, 1674, 1630; HRMS (ESI) calcd for $C_{30}H_{32}N_3O_5^+$ $[M+H]^+$: 514.2337; found: 514.2337.

Ugi adduct 3b. **Method A.** From 71 mg (0.30 mmol) of aldehyde (+)-**1a**, compound **3b** was obtained as a mixture of isomers in a *syn/anti* ratio (55:45). After flash chromatography using *n*-hexane/ethyl acetate (2:1) as eluent, the less polar compound *syn*-(+)-**3b** (50 mg, 38%) and the more polar compound *anti*-(+)-**3b** (41 mg, 31%) were obtained.[1] ***syn*-(+)-3b**. Colorless oil; $[\alpha]_D$ +27.0 (c 0.3, $CHCl_3$). ^{1}H NMR[2] (300 MHz, $C_2D_2Cl_4$, 25°C) δ 7.97 (s, 0.3H), 7.65 (s, 0.7H), 7.31-7.09 (m, 7H), 6.81 (*AA'*XX', 2H), 6.22 (bs, 0.3H), 6.17 (t, *J* = 5.9 Hz, 0.7H), 5.65-5.43 (m, 1H), 5.17-5.04 (m, 2H), 5.06 (dd, *J* = 9.7, 5.2 Hz, 0.7H), 4.94 (dd, *J* = 8.6, 5.2 Hz, 0.3H), 4.69-4.13 (m, 4H), 3.83-3.55 (m, 2H), 3.74 (s, 2.1H), 3.72 (s, 0.9H), 3.45 (s, 2.1H), 3.44 (s, 0.9H); ^{13}C NMR (75

[1] ^{1}H NMR spectra of both isomers of compound **3b** at room temperature in $CDCl_3$ and $(CDCl_2)_2$ showed two collections of well resolved signals of the corresponding rotamers **I** and **II**. However, it was not possible to achieve the coalescence temperature. Then, *syn*-(+)-**3b** and *anti*-(+)-**3b** are described as a mixture of rotamers at room temperature.

[2] Compound *syn*-(+)-**3b** is observed as a mixture of rotamers 37:63 in $CDCl_3$ and 30:70 in $C_2D_2Cl_4$ at 25°C.

MHz, $CDCl_3$, 25°C) (m, rotamer) δ 167.33, 165.1, 162.8, 157.1, 137.4, 132.0, 129.3, 128.63, 127.8, 127.6, 120.3, 118.7, 114.5, 83.3, 60.9, 57.0, 56.1, 55.4, 45.7, 43.5; (M, rotamer) δ 167.27, 165.2, 163.7, 157.4, 137.7, 132.5, 128.8, 128.57, 127.7, 127.5, 122.0, 119.9, 114.1, 83.6, 60.1, 55.5, 55.3, 55.4, 49.6, 43.4; IR (KBr, cm^{-1}) ν 3307, 1752, 1662; HRMS (ESI) calcd for $C_{24}H_{28}N_3O_5^+$ $[M+H]^+$: 438.2024; found: 438.2034. ***anti*-(+)-3b**. White solid; mp 130–132°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ +70.3 (c 0.5, $CHCl_3$); ^{1}H NMR[3] (300 MHz, $C_2D_2Cl_4$, 25°C) δ 8.30 (s, 0.5H), 8.00 (s, 0.5H), 7.27-7.14 (m, 5H), 6.86-6.76 (m, 4H), 6.76 (bs, 0.5H), 6.33 (bs, 0.5H), 5.84-5.64 (m, 1H), 5.28-5.08 (m, 2H), 5.07 (dd, *J* = 9.4, 5.1 Hz, 0.5H), 4.80 (dd, *J* = 9.2, 5.1 Hz, 0.5H), 4.74 (d, *J* = 9.5 Hz, 0.5H), 4.58 (d, *J* = 4.9 Hz, 0.5H), 4.56 (d, *J* = 4.9 Hz, 0.5H), 4.43 (dd, *J* = 15.8, 4.2 Hz, 0.5H), 4.16-3.98 (m, 2.5H), 3.83 (dd, *J* = 15.7, 7.8 Hz, 0.5H), 3.74 (s, 1.5H), 3.72 (s, 1.5H), 3.73-3.65 (m, 0.5H), 3.48-3.42 (m, 0.5H), 3.52 (s, 1.5H), 3.46 (s, 1.5H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): (m, rotamer) δ 168.11, 164.9, 163.8, 157.10, 137.0, 133.3, 129.0, 128.47, 127.6, 127.4, 120.9, 118.0, 114.1, 83.6, 60.3, 56.8, 55.6, 55.37, 46.1, 43.8; (M, rotamer) δ 168.09, 165.1, 163.5, 157.13, 136.7, 134.0, 129.1, 128.49, 127.8, 127.5, 120.2, 118.6, 114.2, 84.0, 60.0, 59.4, 57.0, 55.43, 49.8, 43.5; IR ($CHCl_3$, cm^{-1}) ν 3308, 1752, 1663; HRMS (ESI) calcd for $C_{24}H_{28}N_3O_5^+$ $[M+H]^+$: 438.2024; found: 438.2034.

Ugi adduct 3c. **Method A.** From 82 mg (0.35 mmol) of aldehyde (+)-**1a**, compound **3c** was obtained as a mixture of isomers in a *syn/anti* ratio (57:43). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, an inseparable mixture of isomers (85 mg, 54%) was obtained as a colorless oil. ***syn*-3c** ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.35-7.18 (m, 5H), 6.91-6.80 (m, 4H), 6.76 (t, *J* = 5.6 Hz, 1H), 5.91-5.78

[3] Compound *anti*-(+)-**3b** is observed as a mixture of rotamers 47:53 in $CDCl_3$ and 50:50 in $C_2D_2Cl_4$ at 25°C.

(m, 1H), 5.29-5.09 (m, 3H), 5.01-4.96 (m, 1H), 4.60 (d, *J* = 5.0 Hz, 1H), 4.36-4.27 (m, 1H), 4.14 (dd, *J* = 14.6 Hz, 6.3 Hz, 1H), 4.02 (dd, *J* = 14.8, 5.1 Hz, 1H), 3.78 (s, 3H), 3.60 (s, 3H), 3.56-3.48 (m, 1H), 2.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 172.1, 168.7, 165.1, 157.1, 137.2, 134.0, 128.9, 128.4, 127.6, 127.2, 121.3, 116.9, 114.0, 83.7, 59.2, 56.1, 55.43, 55.35, 49.5, 43.4, 21.7; HRMS (ESI) calcd for $C_{25}H_{30}N_3O_5^+$ $[M+H]^+$: 452.2180; found: 452.2199. ***anti*-3c** ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.35-7.18 (m, 5H), 6.91-6.80 (m, 4H), 6.25 (t, *J* = 5.5 Hz, 1H), 5.66-5.53 (1H, m), 5.29-5.09 (m, 3H), 5.01-4.96 (m, 1H), 4.73 (d, *J* = 5.0 Hz, 1H), 4.50 (dd, *J* = 14.9, 6.2 Hz, 1H), 4.36-4.27 (m, 1H), 4.13-4.06 (m, 1H), 3.84-3.78 (m, 1H), 3.78 (s, 3H), 3.59 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 172.0, 168.0, 165.2, 157.1, 137.8, 132.5, 129.0, 128.5, 127.7, 127.4, 121.7, 118.2, 114.2, 83.6, 60.1, 57.3, 55.7, 55.4, 49.5, 43.3, 21.2.

Ugi adduct 3d. **Method A.** From 56 mg (0.24 mmol) of aldehyde (+)-**1a**, compound **3d** was obtained as a mixture of isomers in a *syn/anti* ratio (60:40). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, the less polar compound *syn*-(+)-**3d** (56 mg, 44%) and the more polar compound *anti*-(+)-**3d** (37 mg, 30%) were obtained. ***syn*-(+)-3d**. Colorless oil; $[\alpha]_D$ +85.3 (c 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.31 (AA'*XX'*, 2H), 7.22-7.19 (m, 3H), 6.92-6.88 (m, 2H), 6.84 (*AA'*XX', 2H), 6.64 (t, *J* = 5.4 Hz, 1H), 5.96-5.81 (m, 1H), 5.31-5.21 (m, 2H), 5.16 (d, *J* = 9.2 Hz, 1H), 4.98 (dd, *J* = 9.1, 5.1 Hz, 1H), 4.61 (d, *J* = 5.0 Hz, 1H), 4.46-4.33 (m, 2H), 4.17 (dd, *J* = 14.8, 5.9 Hz, 1H), 4.06 (dd, *J* = 14.8, 5.4 Hz, 1H), 3.85 (s, 2H), 3.78 (s, 3H), 3.62 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 168.2, 167.9, 165.0, 157.2, 137.0, 133.8, 128.8, 128.4, 127.5, 127.3, 121.4, 117.3, 114.0, 83.6, 59.2, 57.9, 55.8, 55.4, 49.3, 43.4, 26.2; IR ($CHCl_3$, cm^{-1}) ν 3313, 1752, 1659; HRMS (ESI) calcd for $C_{25}H_{28}BrN_3NaO_5^+$ $[M+Na]^+$: 552.1105; found: 552.1127. ***anti*-(+)-3d**. Colorless oil; $[\alpha]_D$ +16.1 (c 1.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.36-7.26 (m, 5H), 7.19 (AA'*XX'*, 2H), 6.85 (*AA'*XX',

2H), 6.17 (t, *J* = 5.0 Hz, 1H), 5.73-5.60 (m, 1H), 5.27-5.17 (m, 3H), 4.80 (d, *J* = 9.2 Hz, 1H), 4.75 (d, *J* = 5.1 Hz, 1H), 4.42 (d, *J* = 5.7 Hz, 2H), 3.91 (dd, *J* = 16.3, 4.9 Hz, 1H), 3.78 (s, 3H), 3.62-3.54 (m, 1H), 3.56 (s, 3H), 3.50 (d, *J* = 11.7 Hz, 1H), 3.32 (d, *J* = 11.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 167.7, 167.5, 165.3, 157.4, 137.6, 131.7, 129.0, 128.6, 127.7, 127.5, 121.8, 120.0, 114.4, 83.8, 60.2, 58.5, 55.8, 55.5, 51.3, 43.5, 26.5; IR ($CHCl_3$, cm^{-1}) ν 3307, 1751, 1654; HRMS (ESI) calcd for $C_{25}H_{29}BrN_3O_5^+$ $[M+H]^+$: 530.1285; found: 530.1271.

Ugi adduct 3e. **Method A.** From 66 mg (0.28 mmol) of aldehyde (+)-**1a**, compound **3e** was obtained as a mixture of isomers in a *syn/anti* ratio (57:43). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, the less polar compound *syn*-(+)-**3e** (88 mg, 52%) and the more polar compound *anti*-(–)-**3e** (66 mg, 39%) were obtained. ***syn*-(+)-3e**. Colorless oil; $[\alpha]_D$ +89.9 (c 1.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.88 (AA'*BB'*, 2H), 7.74 (*AA'*BB', 2H), 7.29 (AA'*XX'*, 2H), 7.21-7.19 (m, 3H), 6.89-6.86 (m, 2H), 6.81 (*AA'*XX', 2H), 6.62 (t, *J* = 5.7 Hz, 1H), 6.00-5.87 (m, 1H), 5.46-5.36 (m, 2H), 5.12 (d, *J* = 9.1 Hz, 1H), 5.01 (dd, *J* = 9.1, 5.0 Hz, 1H), 4.64 (d, *J* = 5.0 Hz, 1H), 4.60-4.42 (m, 1H), 4.57 (d, *J* = 16.5 Hz, 1H), 4.45 (d, *J* = 16.5 Hz, 1H), 4.23-4.16 (m, 1H), 4.20 (dd, *J* = 14.9, 6.3 Hz, 1H), 4.02 (dd, *J* = 14.8, 4.8 Hz, 1H), 3.77 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 168.1, 167.8, 167.6, 165.0, 157.1, 137.0, 134.1, 133.1, 132.1, 128.9, 128.5, 127.6, 127.3, 123.5, 121.2, 118.0, 114.0, 83.8, 59.5, 58.3, 55.7, 55.4, 48.5, 43.5, 39.5; IR ($CHCl_3$, cm^{-1}) ν 3336, 1752, 1718, 1667; HRMS (ESI) calcd for $C_{33}H_{33}N_4O_7^+$ $[M+H]^+$: 597.2344; found: 597.2339. ***anti*-(–)-3e**. White solid; mp 157–158°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ –15.2 (c 1.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.84 (AA'*BB'*, 2H), 7.75 (*AA'*BB', 2H), 7.33-7.22 (m, 7H), 7.06 (*AA'*XX', 2H), 6.24 (t, *J* = 5.3 Hz, 1H), 5.84-5.71 (m, 1H), 5.38-5.28 (m, 2H), 5.21 (dd, *J* = 9.5, 5.0 Hz, 1H), 4.74 (d, *J* = 5.0 Hz, 1H), 4.66-4.52 (m, 1H), 4.46

(dd, *J* = 15.0, 6.1 Hz, 1H), 4.34 (dd, *J* = 14.9, 5.6 Hz, 1H), 4.00 (AB, *J* = 16.3 Hz, 2H), 3.88 (s, 3H), 3.83-3.74 (m, 1H), 3.54 (s, 3H), 3.50 (dd, *J* = 11.8, 6.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 167.6, 167.5, 167.4, 165.3, 157.3, 137.8, 134.1, 132.1, 131.3, 129.0, 128.5, 127.6, 127.2, 123.4, 121.4, 120.1, 114.8, 83.9, 60.3, 59.8, 55.6, 55.5, 50.7, 43.4, 39.3; IR (KBr, cm^{-1}) ν 3329, 1751, 1719, 1664; HRMS (ESI) calcd for $C_{33}H_{33}N_4O_7^+$ $[M+H]^+$: 597.2344; found: 597.2362.

Ugi adduct 3f. **Method A.** From 53 mg (0.23 mmol) of aldehyde (+)-**1a**, compound **3f** was obtained as a mixture of isomers in a *syn/anti* ratio (60:40). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, the less polar compound *anti*-(+)-**3f** (31 mg, 36%) and the more polar compound *syn*-(+)-**3f** (46 mg, 54%) were obtained. ***syn*-(+)-3f**. White solid; mp 176–178°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ +79.6 (c 1.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.30 (AA'*XX'*, 2H), 6.82 (*AA'*XX', 2H), 6.22 (bs, 1H), 5.90-5.78 (m, 1H), 5.27-5.21 (m, 2H), 5.11 (d, *J* = 8.6 Hz, 1H), 4.89 (dd, *J* = 8.6, 5.1 Hz, 1H), 4.60 (d, *J* = 5.0 Hz, 1H), 4.24 (dd, *J* = 18.2, 5.6 Hz, 1H), 4.13-4.04 (m, 1H), 3.76 (s, 3H), 3.62 (s, 3H), 2.10 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 172.1, 167.6, 165.3, 157.4, 134.2, 128.9, 122.2, 116.7, 114.0, 83.6, 59.3, 57.9, 56.5, 55.5, 51.3, 49.3, 28.2, 21.8; IR (KBr, cm^{-1}) ν 3310, 1753, 1675, 1634; HRMS (ESI) calcd for $C_{22}H_{32}N_3O_5^+$ $[M+H]^+$: 418.2337; found: 418.2358; ***anti*-(+)-3f**. White solid; mp 134–135°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ +10.8 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.19 (AA'*XX'*, 2H), 6.87 (*AA'*XX', 2H), 5.77-5.63 (m, 1H), 5.63 (bs, 1H), 5.22-5.15 (m, 2H), 5.00 (dd, *J* = 9.5, 4.8 Hz, 1H), 4.93 (d, *J* = 8.8 Hz, 1H), 4.71 (d, *J* = 4.7 Hz, 1H), 3.91 (dd, *J* = 16.7, 4.7 Hz, 1H), 3.79 (s, 3H), 3.58 (s, 3H), 3.52 (dd, *J* = 17.0, 6.9 Hz, 1H), 1.60 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 171.9, 167.5, 165.3, 157.3, 132.9, 129.4, 122.0, 118.3, 114.3, 83.8, 60.3, 58.0,

56.1, 55.5, 51.4, 50.0, 28.6, 21.4; IR (KBr, cm^{-1}) ν 3312, 1753, 1642; HRMS (ESI) calcd for $C_{22}H_{32}N_3O_5^+$ $[M+H]^+$: 418.2337; found: 418.2334.

Ugi adduct 3g. **Method A.** From 66 mg (0.23 mmol) of aldehyde (+)-**1b**, compound **3g** was obtained as a mixture of isomers in a *syn/anti* ratio (65:35). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, the less polar compound *anti*-(+)-**3g** (22 mg, 20%) and the more polar compound *syn*-(+)-**3g** (42 mg, 37%) were obtained. ***syn*-(+)-3g**. White solid; mp 137−138°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ +28.5 (c 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.31-7.25 (m, 5H), 7.24 (AA'*XX'*, 2H), 7.17-7.14 (m, 2H), 7.05-7.01 (m, 3H), 6.90 (*AA'*XX', 2H), 6.26 (t, *J* = 5.5 Hz, 1H), 5.65-5.52 (m, 1H), 5.49 (d, *J* = 4.8 Hz, 1H), 5.34 (d, *J* = 9.9 Hz, 1H), 5.27 (dd, *J* = 9.4, 5.1 Hz, 1H), 5.18-5.09 (m, 2H), 4.30 (dd, *J* = 14.6, 6.0 Hz, 1H), 4.20 (dd, *J* = 14.6, 5.3 Hz, 1H), 4.02-3.94 (m, 1H), 3.80 (s, 3H), 3.56 (dd, *J* = 17.0, 6.3 Hz, 1H), 1.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 172.2, 167.6, 163.8, 157.7, 157.5, 137.4, 132.6, 129.5, 128.9, 128.6, 128.0, 127.5, 122.6, 122.1, 118.0, 116.4, 114.3, 80.8, 57.1, 55.7, 55.5, 49.8, 43.5, 21.4; IR (KBr, cm^{-1}) ν 3324, 1756, 1641; HRMS (ESI) calcd for $C_{30}H_{32}N_3O_5^+$ $[M+H]^+$: 514.2336; found: 514.2317. ***anti*-(+)-3g**. White solid; mp 158−159°C (*n*-hexane/ethyl acetate); $[\alpha]_D$ +95.5 (c 0.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.39 (AA'*XX'*, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.22-7.19 (m, 3H), 7.06-7.02 (m, 3H), 6.89-6.84 (m, 3H), 6.85 (*AA'*XX', 2H), 5.77-5.64 (m, 1H), 5.44 (d, *J* = 4.5 Hz, 1H), 5.30 (dd, *J* = 9.9, 4.4 Hz, 1H), 5.23 (d, *J* = 9.8 Hz, 1H), 5.18-5.10 (m, 2H), 4.22-4.10 (m, 1H), 4.19 (dd, *J* = 15.0, 6.6 Hz, 1H), 4.01-3.95 (m, 1H), 4.00 (dd, *J* = 14.7, 4.9 Hz, 1H), 3.79 (s, 3H), 1.94 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 172.2, 168.6, 164.4, 157.3, 157.2, 137.1, 133.6, 129.6, 128.8, 128.5, 127.6, 127.3, 122.3, 121.5, 117.3, 115.3, 114.0, 80.1, 58.5, 56.1, 55.4, 50.0, 43.4, 21.8; IR (KBr, cm^{-1}) ν 3286, 1757, 1642; HRMS (ESI) calcd for $C_{30}H_{32}N_3O_5^+$ $[M+H]^+$: 514.2336; found: 514.2355.

Ugi adduct 3h. **Method A.** From 77 mg (0.35 mmol) of aldehyde (+)-**1e**, compound **3h** was obtained as a mixture of isomers in a *syn/anti* ratio (76:24). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as an eluent, the less polar compound *syn*-(–)-**3h** (20 mg) and an inseparable mixture of isomers (68 mg) in a *syn/anti* ratio (69:31), (62% yield considering both fractions). ***syn*-(–)-3h**. Colorless oil; $[\alpha]_D$ –29.0 (c 1.4, $CHCl_3$);^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.38-7.13 (m, 10H), 6.45 (t, *J* = 5.6 Hz, 1H), 5.50-5.38 (m, 1H), 5.25 (d, *J* = 10.0 Hz, 1H), 4.98-5.04 (m, 2H), 4.66 (d, *J* = 5.0 Hz, 1H), 4.60 (d, *J* = 15.9 Hz, 1H), 4.47 (dd, *J* = 10.0, 4.9 Hz, 1H), 4.46 (dd, *J* = 14.9, 5.1 Hz, 1H), 4.18 (dd, *J* = 14.9, 5.3 Hz, 1H), 4.16 (d, *J* = 16.2 Hz, 1H), 3.71 (dd, *J* = 17.1, 4.8 Hz, 1H), 3.48 (s, 3H), 3.47 (dd, *J* = 16.9, 6.9 Hz, 1H), 1.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 172.6, 168.6, 168.3, 137.8, 135.7, 132.7, 128.8, 128.5, 127.8, 127.7, 127.4, 127.1, 117.8, 84.4, 59.8, 56.5, 55.4, 48.3, 44.8, 43.1, 21.9; IR ($CHCl_3$, cm^{-1}) ν 3318, 1755, 1645; HRMS (ESI) calcd for $C_{25}H_{30}N_3O_4^+$ $[M+H]^+$: 436.2231; found: 436.2229.

Ugi adduct 3j. **Method A.** From 78 mg (0.34 mmol) of aldehyde (–)-**1d**, compound **3j** was obtained as a mixture of isomers in a *syn/anti* ratio (68:32). After flash chromatography using *n*-hexane/ethyl acetate (2:1) as eluent, the less polar compound *anti*-(+)-**3j** (49 mg, 28%) and the more polar compound *syn*-(–)-**3j** (103 mg, 58%) were obtained. ***syn*-(–)-3j**. Colorless oil; $[\alpha]_D$ –39.0 (c 1.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.28-7.23 (m, 5H), 7.18-7.15 (m, 2H), 7.07-6.92 (m, 3H), 6.37 (t, *J* = 5.6 Hz, 1H), 5.85-5.62 (m, 2H), 5.42 (d, *J* = 10.2 Hz, 1H), 5.40 (d, *J* = 5.0 Hz, 1H), 5.31-5.11 (m, 4H), 4.73 (dd, *J* = 9.9, 4.9 Hz, 1H), 4.26-4.04 (m, 5H), 3.99 (d, *J* = 10.8 Hz, 1H), 3.85 (d, *J* = 11.0 Hz, 1H), 3.64 (dd, *J* = 16.2, 6.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 168.7, 167.4, 166.1, 157.4, 137.2, 132.8, 131.8, 129.4, 128.7, 128.1, 127.6, 122.6, 118.35, 118.27, 116.2, 81.4, 57.5, 54.6, 48.3, 43.6, 43.5, 26.2; IR ($CHCl_3$,

cm^{-1}) ν 3323, 1760, 1660; HRMS (ESI) calcd for $C_{26}H_{29}BrN_3O_4^+$ $[M+H]^+$: 526.1336; found: 526.1357. ***anti*-(+)-3j**. Colorless oil; $[\alpha]_D$ +105.3 (c 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.35-7.24 (m, 7H), 7.12-6.95 (m, 3H), 5.91-5.62 (m, 2H), 5.29 (d, *J* = 10.4 Hz, 1H), 5.26 (d, *J* = 5.0 Hz, 1H), 5.32-5.12 (m, 4H), 4.61 (dd, *J* = 9.9, 4.8 Hz, 1H), 4.44 (dd, *J* = 14.7, 6.1 Hz, 1H), 4.36 (dd, *J* = 14.9, 6.0 Hz, 1H), 4.16-3.87 (m, 3H), 3.71 (d, *J* = 11.1 Hz, 1H), 3.64 (d, *J* = 11.0 Hz, 1H), 3.65-3.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 168.3, 168.2, 166.0, 157.0, 137.4, 132.9, 131.6, 129.6, 128.6, 127.7, 127.6, 122.3, 118.4, 117.9, 115.4, 80.6, 58.0, 55.4, 48.8, 43.8, 43.6, 26.1; IR ($CHCl_3$, cm^{-1}) ν 3321, 1759, 1652; HRMS (ESI) calcd for $C_{26}H_{29}BrN_3O_4^+$ $[M+H]^+$: 526.1336; found: 526.1356.

Ugi adduct 3k. **Method B.** From 76 mg (0.32 mmol) of aldehyde (+)-**1a**, compound **3k** was obtained as a mixture of isomers in a *syn/anti* ratio (60:40). After flash chromatography using *n*-hexane/ethyl acetate (2:1) as eluent, the less polar compound *syn*-(+)-**3k** (58 mg, 34%), and the more polar compound *anti*-(+)-**3k** (38 mg, 23%) were obtained. ***syn*-(+)-3k**. Colorless oil; $[\alpha]_D$ +35.4 (c 0.8, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.23-7.19 (m, 5H), 7.22 (AA'*XX'*, 2H), 6.94 (*AA'*XX', 2H), 6.86-6.83 (m, 2H), 6.82 (*AA'*XX', 2H), 6.50 (t, *J* = 5.5 Hz, 1H), 5.21 (d, *J* = 9.8 Hz, 1H), 4.39 (dd, *J* = 9.8, 5.1 Hz, 1H), 4.34 (d, *J* = 5.0 Hz, 1H), 4.13 (dd, *J* = 14.6, 5.1 Hz, 1H), 3.98 (dd, *J* = 14.6, 6.1 Hz, 1H), 3.87 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 171.5, 169.2, 165.0, 159.6, 157.0, 137.1, 132.1, 128.9, 128.4, 127.6, 127.2, 121.2, 114.5, 113.8, 82.6, 58.8, 58.1, 56.1, 55.4, 55.3, 43.6, 22.7; IR ($CHCl_3$, cm^{-1}) ν 3301, 1751, 1654; HRMS (ESI) calcd for $C_{29}H_{32}N_3O_6^+$ $[M+H]^+$: 518.2286; found: 518.2293. ***anti*-(+)-3j**. Colorless oil; $[\alpha]_D$ +29.1 (c 0.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.38-7.19 (m, 7H), 6.91 (*AA'*XX', 2H), 6.71-6.67 (m, 1H), 6.69 (AA'*XX'*, 2H), 6.51 (*AA'*XX', 2H), 5.12 (dd, *J* = 9.3, 5.2 Hz, 1H), 4.95 (d, *J* =

9.2 Hz, 1H), 4.68 (d, *J* = 5.0 Hz, 1H), 4.51 (d, *J* = 5.7 Hz, 2H), 3.82 (s, 3H), 3.76 (s, 3H), 3.50 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 173.0, 168.2, 166.0, 159.0, 158.0, 138.1, 129.1, 128.7, 128.6, 127.7, 127.5, 123.7, 114.6, 114.2, 83.6, 60.0, 56.8, 55.5, 55.4, 43.5, 23.1; IR ($CHCl_3$, cm^{-1}) ν 3366, 1751, 1660; HRMS (ESI) calcd for $C_{29}H_{32}N_3O_6^+$ $[M+H]^+$: 518.2286; found: 518.2295.

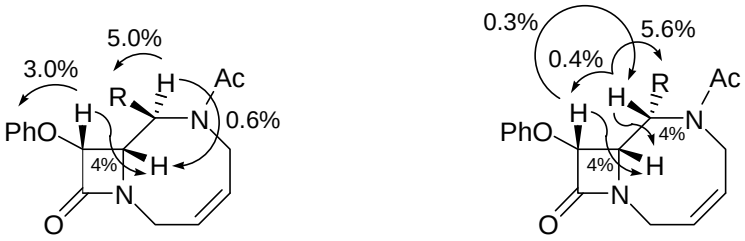
Ugi adduct 3l. **Method B.** From 112 mg (0.48 mmol) of aldehyde (–)-**1d**, compound **3l** was obtained as a mixture of isomers in a *syn/anti* ratio (70:30). After flash chromatography using *n*-hexane/ethyl acetate (1:1), the less polar compound *anti*-(+)-**3l** (34 mg, 19%) and the more polar compound *syn*-(+)-**3l** (80 mg, 46%) were obtained. ***syn*-(+)-3l**. Colorless oil; $[\alpha]_D$ +36.7 (c 1.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.33-7.21 (m, 7H), 7.02-6.97 (m, 5H), 6.84 (*AA'*BB', 2H), 6.74 (t, *J* = 5.9 Hz, 1H), 5.89-5.76 (m, 1H), 5.71 (d, *J* = 8.9 Hz, 1H), 5.31 (d, *J* = 4.4 Hz, 1H), 5.26-5.19 (m, 2H), 4.46 (dd, *J* = 8.9, 5.0 Hz, 1H), 4.41 (dd, *J* = 14.5, 5.8 Hz, 1H), 4.32 (dd, *J* = 14.7, 5.9 Hz, 1H), 3.96 (ddt, *J* = 16.7, 5.3, 1.5 Hz, 1H), 3.82 (s, 3H), 3.81 (ddt, *J* = 16.5, 5.4, 1.5 Hz, 1H), 1.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 172.7, 168.2, 166.5, 159.5, 157.6, 137.8, 132.2, 131.7, 130.0, 129.3, 128.6, 128.1, 127.4, 122.3, 117.5, 116.2, 114.7, 81.9, 58.9, 56.4, 55.4, 43.5, 43.3, 23.1; IR ($CHCl_3$, cm^{-1}) ν 3336, 1758, 1653; HRMS (ESI) calcd for $C_{30}H_{32}N_3O_5^+$ $[M+H]^+$: 514.2336; found: 514.2339. ***anti*-(+)-3l**. Colorless oil; $[\alpha]_D$ +50.7 (c 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.40-7.29 (m, 7H), 7.15-7.12 (m, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 6.83 (AA'*BB'*, 2H), 6.79 (*AA'*BB', 2H), 5.76-5.63 (m, 1H), 5.62 (d, *J* = 10.8 Hz, 1H), 5.17-5.05 (m, 2H), 5.11 (d, *J* = 4.8 Hz, 1H), 4.51 (dd, *J* = 14.6, 6.0 Hz, 1H), 4.44 (dd, *J* = 14.4, 5.6 Hz, 1H), 4.00 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.84 (ddt, *J* = 15.6, 6.2, 1.2 Hz, 1H), 3.78 (s, 3H), 3.63 (ddt, *J* = 15.6, 5.6, 1.4 Hz, 1H), 1.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 171.9, 169.4, 165.9, 159.7, 157.3, 137.9, 131.9, 131.3, 129.9, 129.7, 128.6, 127.8, 127.5, 122.3, 117.8, 115.7, 114.9, 80.5,

57.1, 55.6, 55.4, 43.9, 43.6, 22.5; IR ($CHCl_3$, cm^{-1}) ν 3345, 1760, 1676, 1651; HRMS (ESI) calcd for $C_{30}H_{32}N_3O_5^+$ $[M]^+$: 514.2336; found: 514.2358.

Ugi adduct 3m. **Method B.** From 76 mg (0.33 mmol) of aldehyde (–)-**1d**, compound **3m** was obtained as a mixture of isomers in a *syn/anti* ratio (70:30). After flash chromatography using *n*-hexane/ethyl acetate (1:1) as eluent, the less polar compound *anti*-(+)-**3m** (44 mg, 20%) and the more polar compound *syn*-(+)-**3m** (103 mg, 48%) were obtained. ***syn*-(+)-3m**. Colorless oil; $[\alpha]_D$ +26.4 (c 0.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.87 (AA'*BB'*, 2H), 7.74 (*AA'*BB', 2H), 7.44 (AA'*XX'*, 2H), 7.24-7.21 (m, 2H), 7.02-6.96 (m, 5H), 6.76 (t, *J* = 5.6 Hz, 1H), 5.97-5.84 (m, 1H), 5.64 (d, *J* = 8.6 Hz, 1H), 5.37-5.31 (m, 2H), 5.32 (d, *J* = 5.1 Hz, 1H), 4.59 (dd, *J* = 8.6, 5.0 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 4.22 (d, *J* = 17.2 Hz, 1H), 4.14-4.03 (m, 2H), 4.13 (d, *J* = 17.1 Hz, 1H), 3.84 (s, 3H), 3.82-3.75 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 169.3, 168.3, 167.8, 167.7, 166.4, 160.1, 157.3, 134.1, 132.1, 132.0, 130.4, 129.8, 129.3, 123.5, 122.3, 118.0, 115.9, 115.2, 81.4, 61.4, 59.8, 56.0, 55.5, 43.4, 40.9, 40.3, 14.1; IR ($CHCl_3$, cm^{-1}) ν 3340, 1759, 1718, 1669; HRMS (ESI) calcd for $C_{35}H_{34}N_4NaO_9^+$ $[M+Na]^+$: 677.2218; found: 677.2237. ***anti*-(+)-3m**. Colorless oil; $[\alpha]_D$ +134.7 (c 0.3, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$, 25°C) δ 7.93 (AA'*BB'*, 2H), 7.75 (*AA'*BB', 2H), 7.47-7.41 (m, 2H), 7.38-7.35 (m, 2H), 7.20 (t, *J* = 6.1 Hz, 1H), 7.11 (tt, *J* = 7.1, 1.2 Hz, 1H), 7.04-6.82 (m, 4H), 5.78-5.65 (m, 1H), 5.59 (d, *J* = 10.2 Hz, 1H), 5.18-5.07 (m, 2H), 5.15 (d, *J* = 5.0 Hz, 1H), 4.31 (d, *J* = 16.8 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.16 (dd, *J* = 17.8, 6.6 Hz, 1H), 4.06 (d, *J* = 16.8 Hz, 1H), 4.04 (dd, *J* = 10.4, 4.8 Hz, 1H), 3.93-3.86 (m, 1H), 3.91 (dd, *J* = 17.8, 5.5 Hz, 1H), 3.82 (s, 3H), 3.68 (ddt, *J* = 15.6, 5.7, 1.3 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C) δ 169.6, 169.0, 167.7, 167.6, 166.0, 160.2, 157.3, 134.0, 132.1, 131.8, 130.8, 129.8, 129.0, 123.5, 122.4, 117.9, 116.1, 115.3, 80.6, 61.5, 57.5, 55.5, 54.9, 43.8, 41.3, 40.0, 14.2; IR

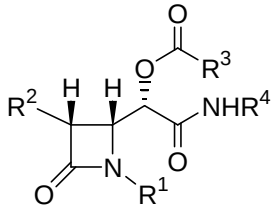
($CHCl_3$, cm^{-1}): ν 3364, 1760, 1721, 1682; HRMS (ES): calcd for $C_{35}H_{34}N_4O_9^+$ $[M+H]^+$: 655.2399; found: 655.2410.

Figure S1. Observed NOE for compounds **5**

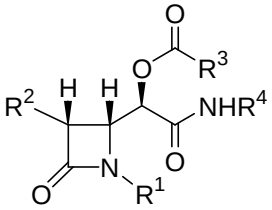


(–)-**5a** R = CONHBn (+)-**5b**

Table S1. Representative chemical shifts (δ, ppm) and vicinal coupling constants (^3J, Hz) of ^{1}H and ^{13}C NMR of compounds **2**[a]



syn-**2**

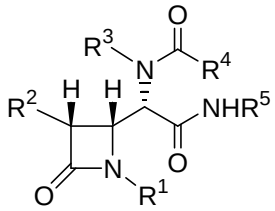


anti-**2**

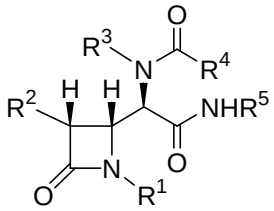
Comp.	R^1	R^2	R^3	R^4	*syn*				*anti*			
					δ		^3J		δ		^3J	
					H4'	C4'	H3-H4	H4-H4'	H4'	C4'	H3-H4	H4-H4'
2a	PMP[b]	MeO	Ph	Bn	5.80	70.4	5.3	3.2	6.10	69.1	5.3	3.4
2b	PMP[b]	PhO	Ph	Bn	5.95	69.8	5.3	2.1	6.29	68.7	5.1	3.2
2c	2-propynyl	PhO	Ph	Bn	5.81	71.6	5.1	5.1	6.09	69.7	5.0	4.0
2d	PMP[b]	MeO	Me	Bn	5.56	70.5	5.3	4.6	5.78	69.0	5.1	3.8
2e	PMP[b]	MeO	Me	*t*-Bu	5.39	71.3	5.1	5.1	5.55	69.8	5.4	2.3
2f	2-propenyl	PhO	2-IC_6H_4	*t*-Bu	5.70	71.5	5.1	3.2	5.73	71.3	5.0	4.0
2g	2-propenyl	PhO	CH_2Phth	CH_2CO_2Et	5.64	70.3	5.0	2.3	5.79	69.7	5.0	3.6
2h	PMP[b]	MeO	Me	CH_2Ts	5.41	70.3	5.1	5.0	5.66	68.7	5.3	3.3

[a]Chemical shifts and vicinal coupling constants from ^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75 MHz) recorded at 300 MHz using $CDCl_3$ as solvent. [b]PMP =- 4-MeO-C_6H_4. [C]Phth = Phtalimido.

Table S2. Representative chemical shifts (δ, ppm) and vicinal coupling constants (^3J, Hz) of ^{1}H and ^{13}C NMR of compounds **3**[a]



syn-**3**

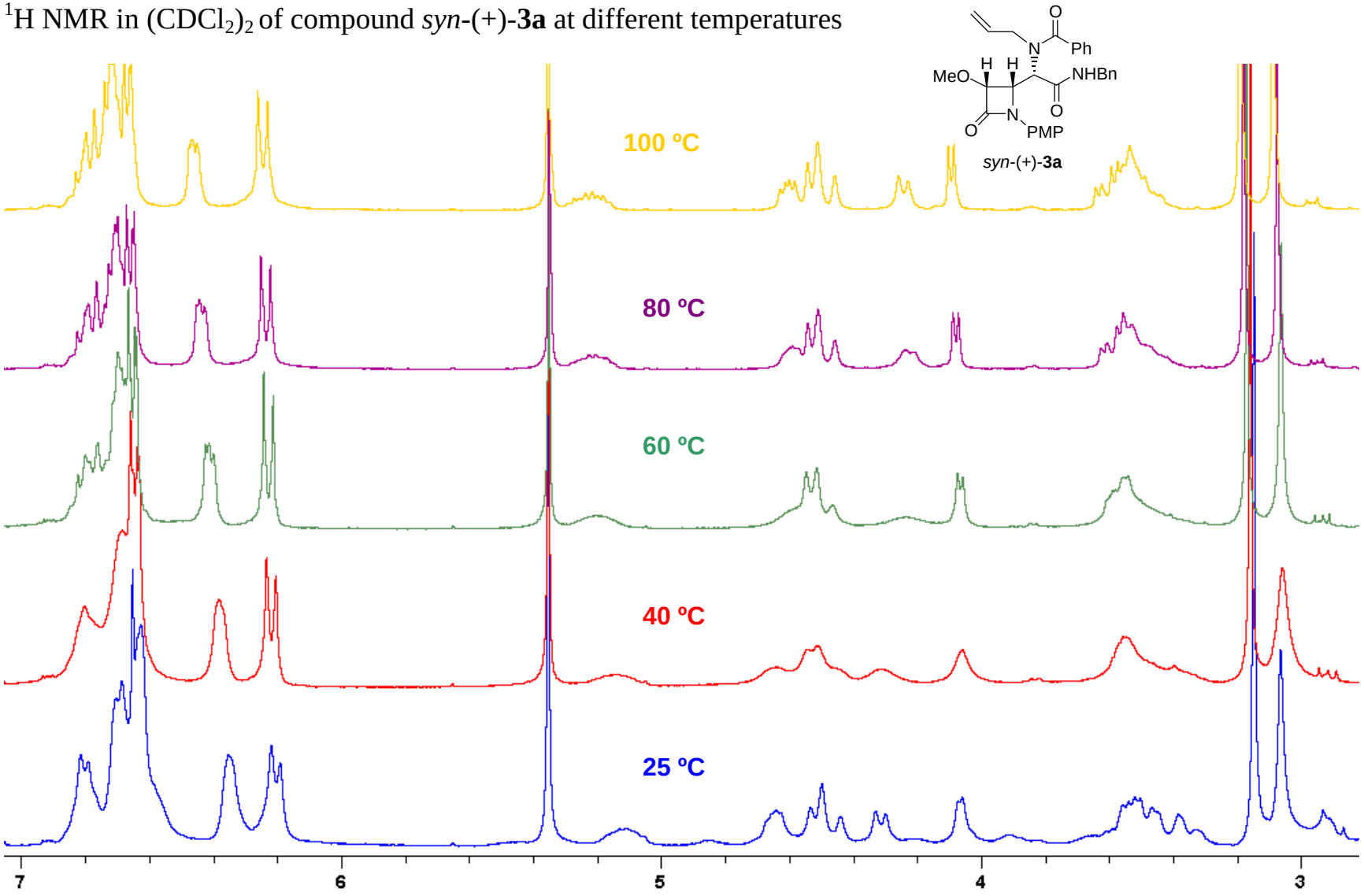


anti-**3**

Comp.	R^1	R^2	R^3	R^4	R^5	*syn* δ	*syn* ^3J			*anti* δ	*anti* ^3J		
						H4'	C4'	H3-H4	H4-H4'	H4'	C4'	H3-H4	H4-H4'
3c	PMP[b]	MeO	2-propenyl	Me	Bn	–[d]	56.1	5.0	–[d]	–[d]	57.3	5.0	–[d]
3d	PMP[b]	MeO	2-propenyl	CH_2Br	Bn	5.16	57.9	5.0	9.2	4.80	58.5	5.1	9.2
3e	PMP[b]	MeO	2-propenyl	CH_2Phth[c]	Bn	5.12	58.3	5.0	9.1	4.59	59.8	5.0	9.5
3f	PMP[b]	MeO	2-propenyl	Me	*t*-Bu	5.11	57.9	5.0	8.6	4.93	58.0	4.7	9.2
3g	Bn	MeO	2-propenyl	Me	Bn	5.25	56.5	5.0	10.0	–	–	–	–
3h	PMP[b]	PhO	2-propenyl	Me	Bn	5.34	57.1	4.8	9.6	5.23	58.5	4.5	9.8
3i	2-propenyl	PhO	2-propenyl	Me	Bn	5.53	56.2	4.9	10.0	5.09	58.1	4.7	10.2
3j	2-propenyl	PhO	2-propenyl	CH_2Br	Bn	5.42	57.5	5.0	10.1	5.29	58.0	5.0	10.2
3k	PMP[b]	MeO	PMP[b]	Me	Bn	5.21	58.1	5.0	9.8	4.95	56.8	5.0	9.2
3l	2-propenyl	PhO	PMP[b]	Me	Bn	5.71	58.9	4.4	8.9	5.62	57.1	4.8	10.6
3m	2-propenyl	PhO	PMP[b]	CH_2Phth[c]	CH_2CO_2Et	5.64	59.8	5.1	8.6	5.59	57.5	5.0	10.3

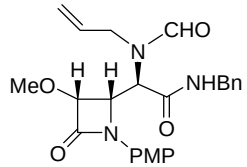
[a]Chemical shifts and vicinal coupling constants from ^{1}H NMR spectra (300 MHz) and ^{13}C NMR spectra (75 MHz) recorded at 300 MHz using $CDCl_3$ as solvent. [b]PMP =- 4-MeO-C_6H_4.[c] Phth = Phtalimido. [d] It could not be measured because the corresponding signals are observed as a complex multiplet.

^{1}H NMR in $(CDCl_2)_2$ of compound *syn*-(+)-**3a** at different temperatures

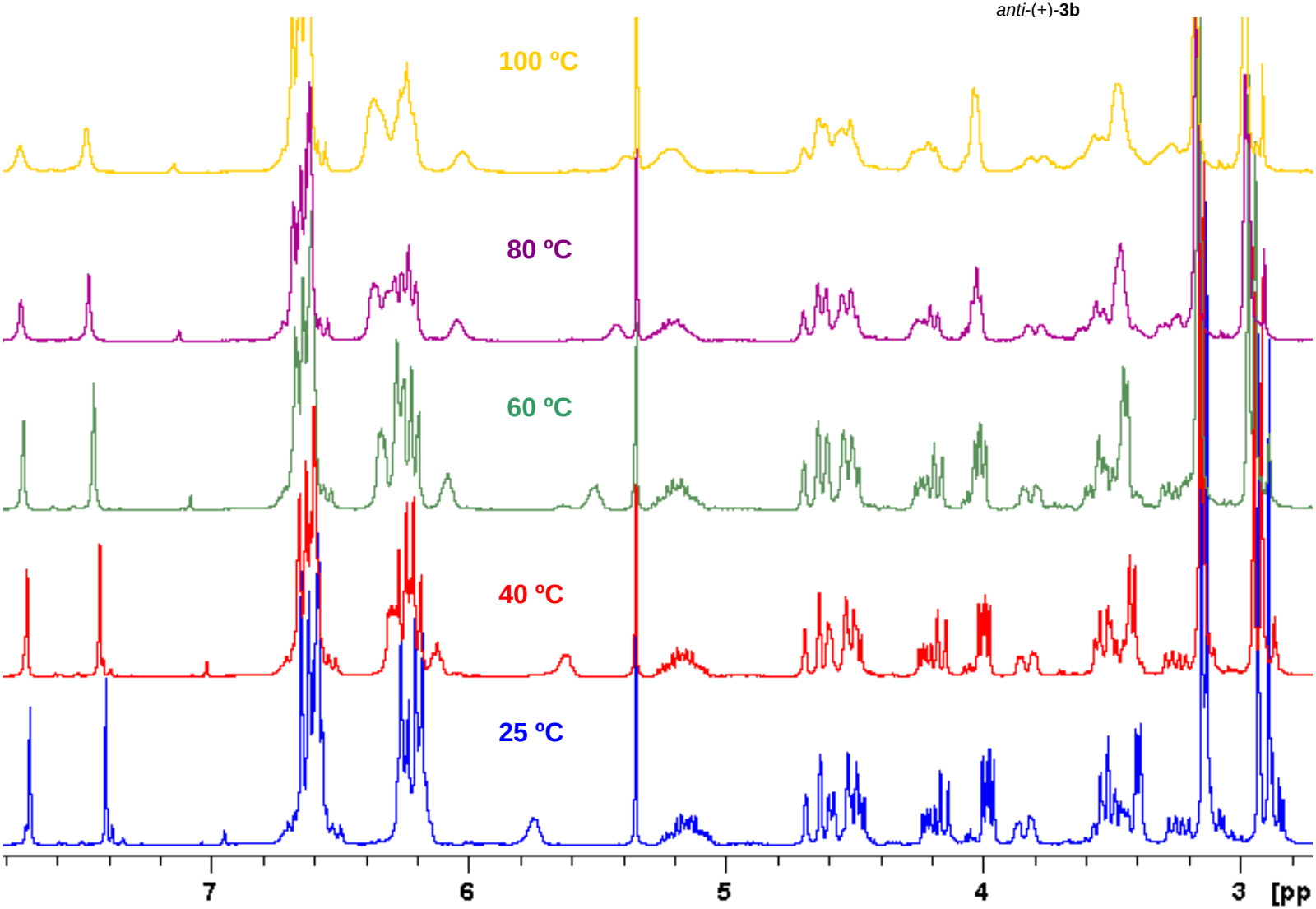


syn-(+)-**3a**

^{1}H NMR in $(CDCl_2)_2$ of compound *anti*-(+)-**3b** at different temperatures

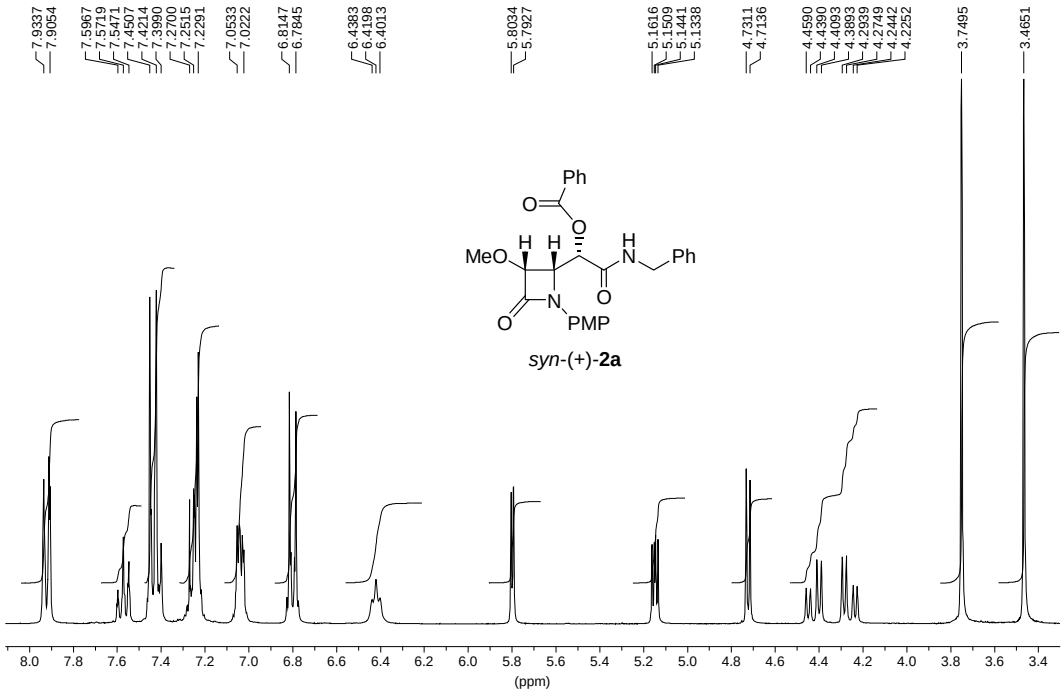


anti-(+)-**3b**

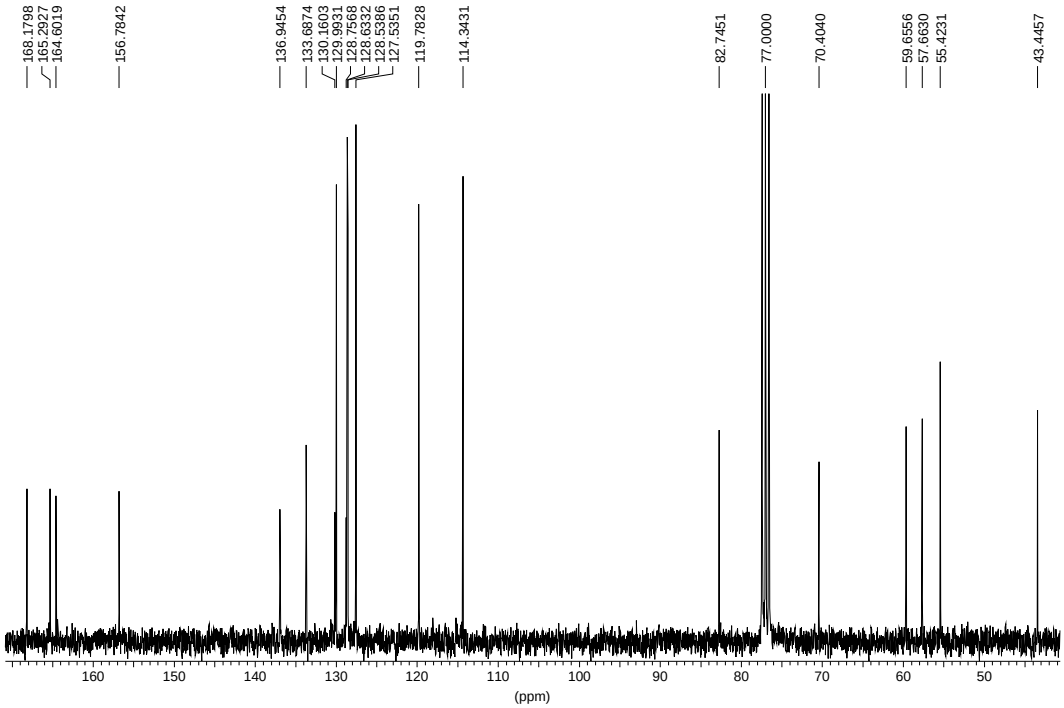


^{1}H and ^{13}C NMR spectra for all new compounds

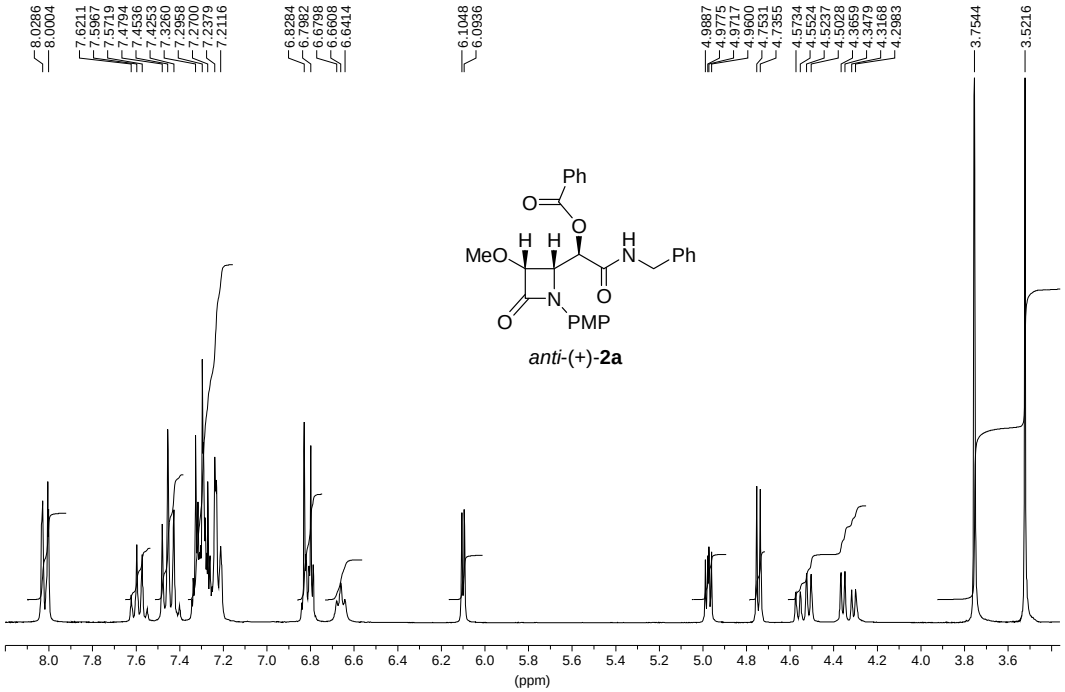
300 MHz ($CDCl_3$, 25ºC)



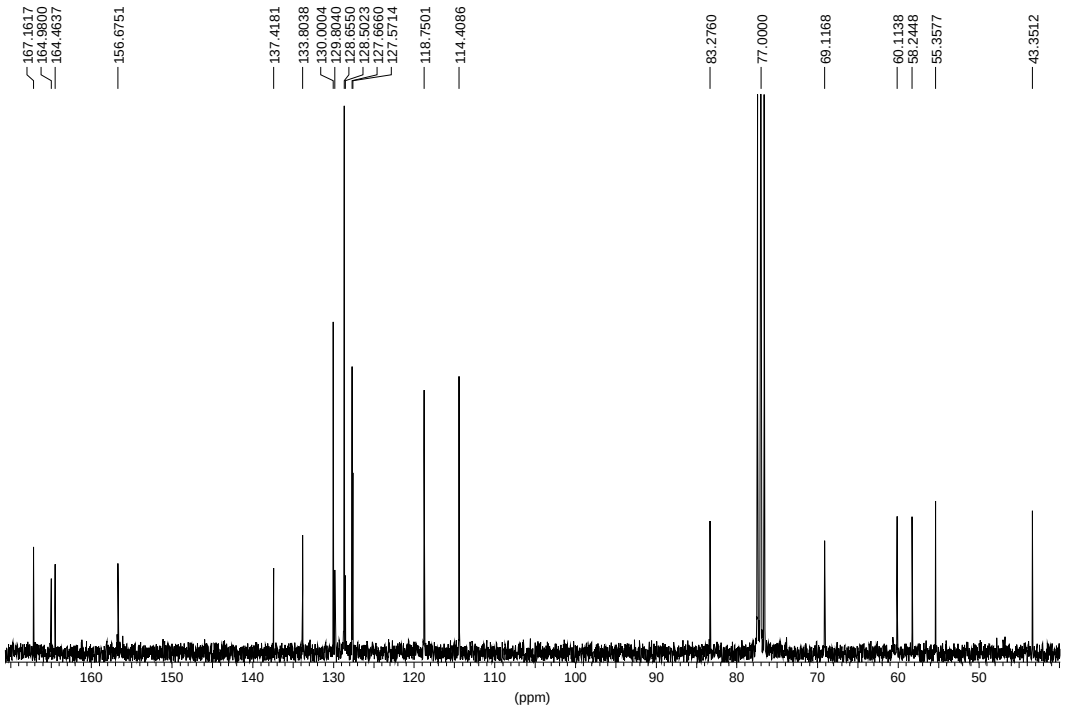
75 MHz ($CDCl_3$, 25ºC)



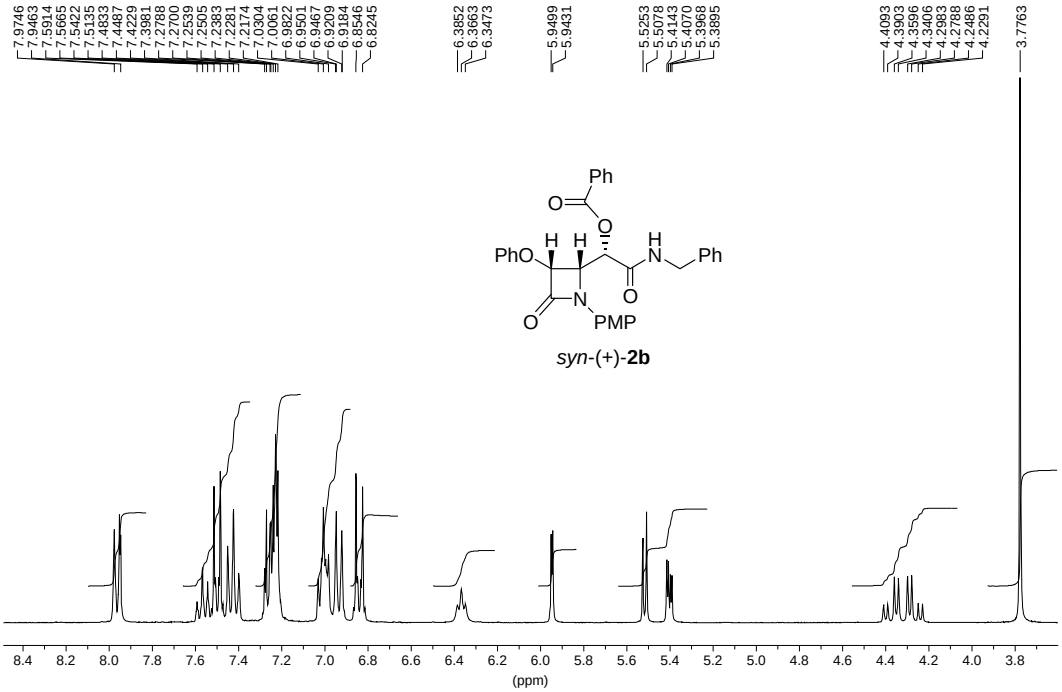
300 MHz ($CDCl_3$, 25ºC)



75 MHz ($CDCl_3$, 25ºC)

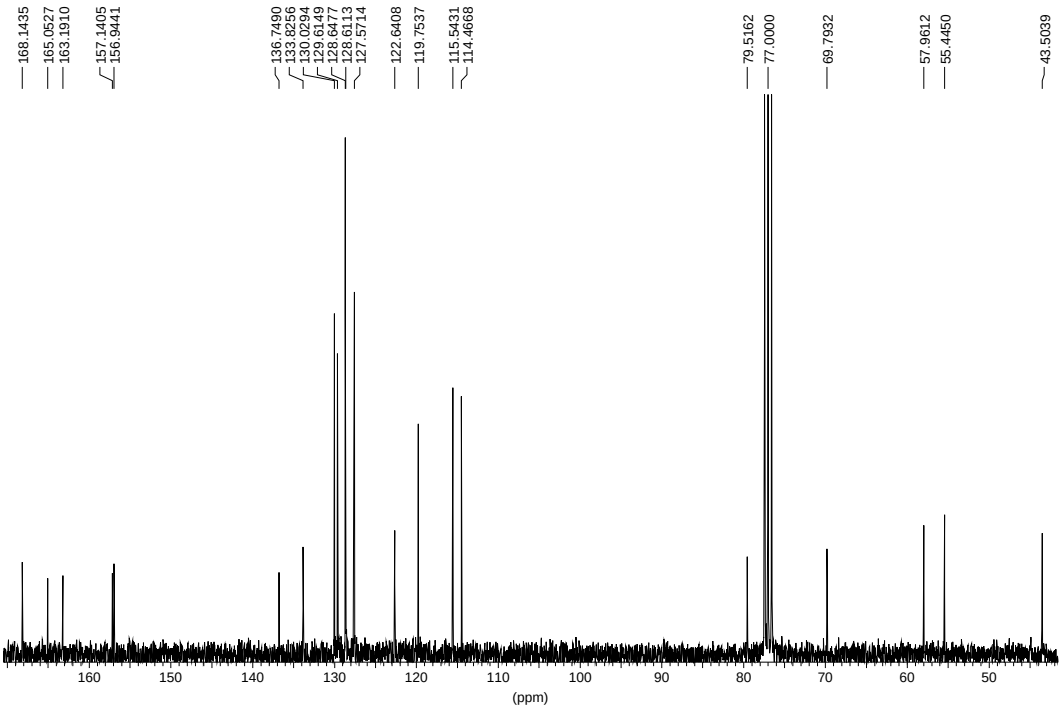


300 MHz ($CDCl_3$, 25ºC)

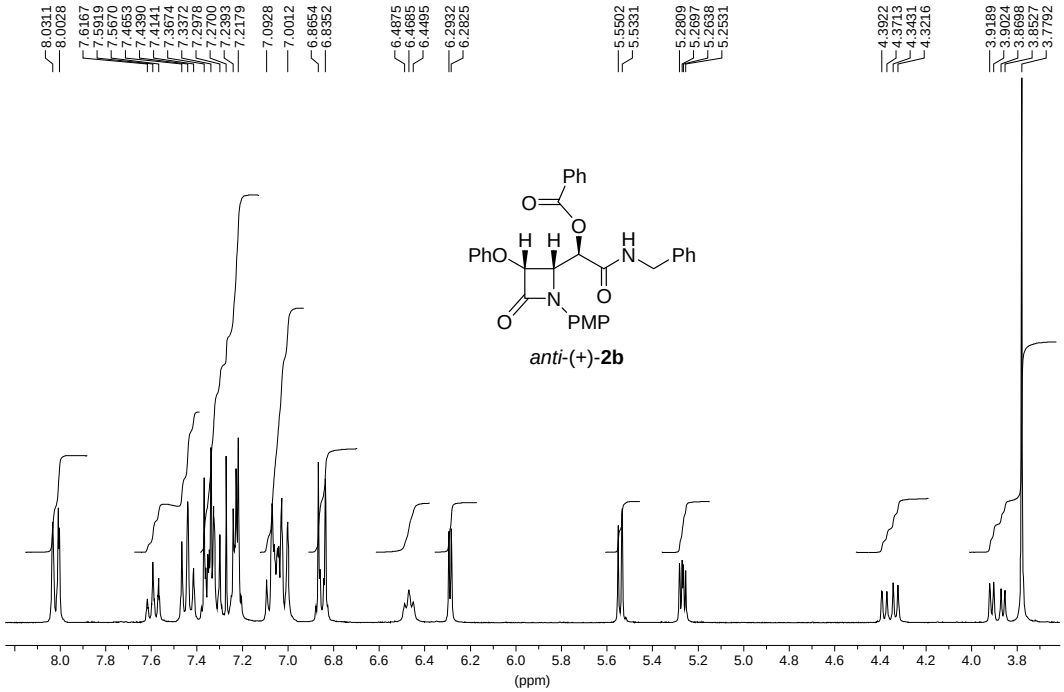


syn-(+)-**2b**

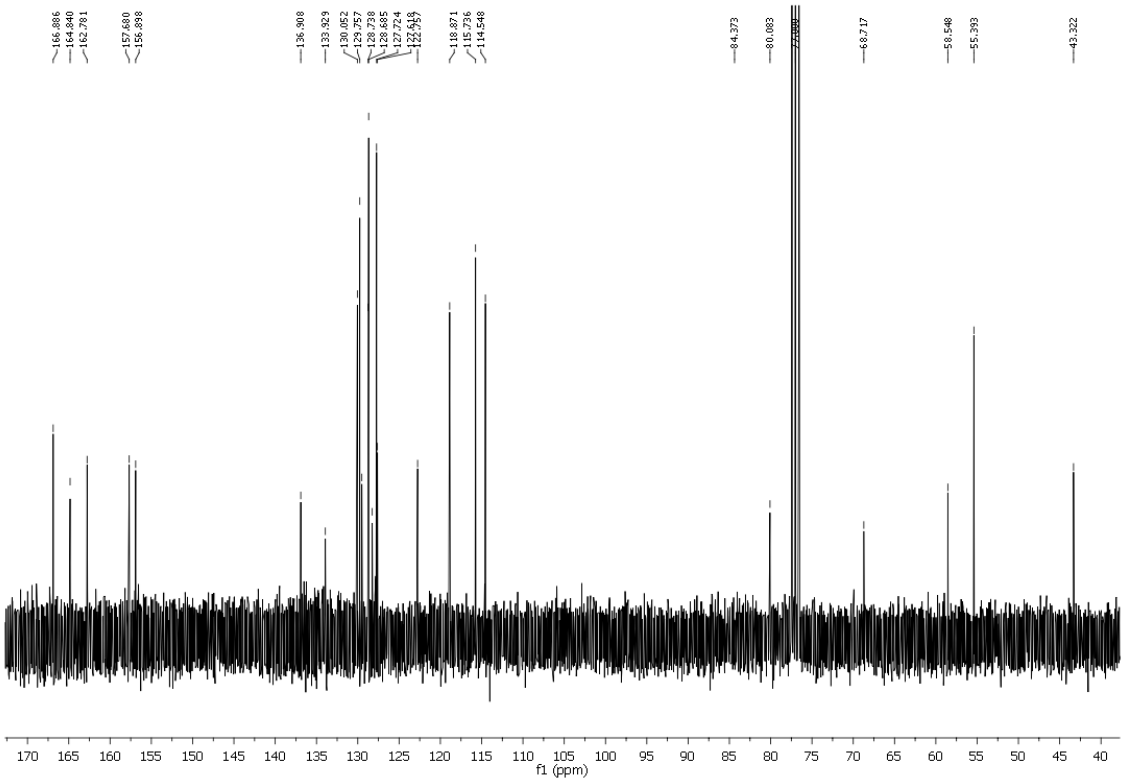
75 MHz ($CDCl_3$, 25ºC)



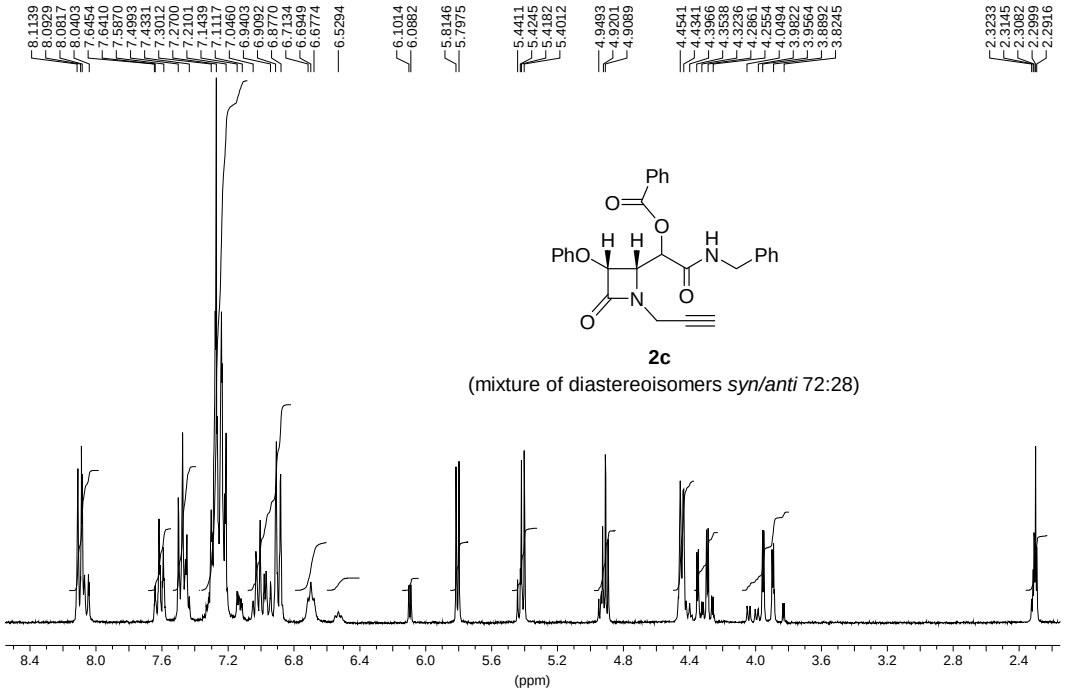
300 MHz ($CDCl_3$, 25ºC)



75 MHz ($CDCl_3$, 25ºC)



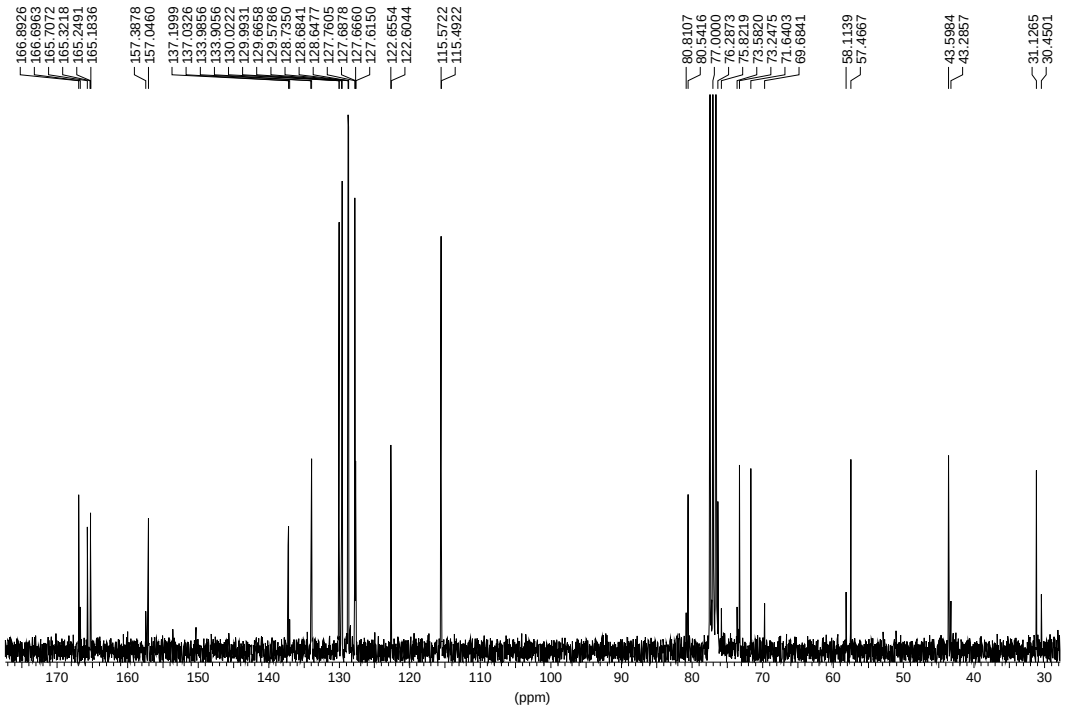
300 MHz ($CDCl_3$, 25ºC)



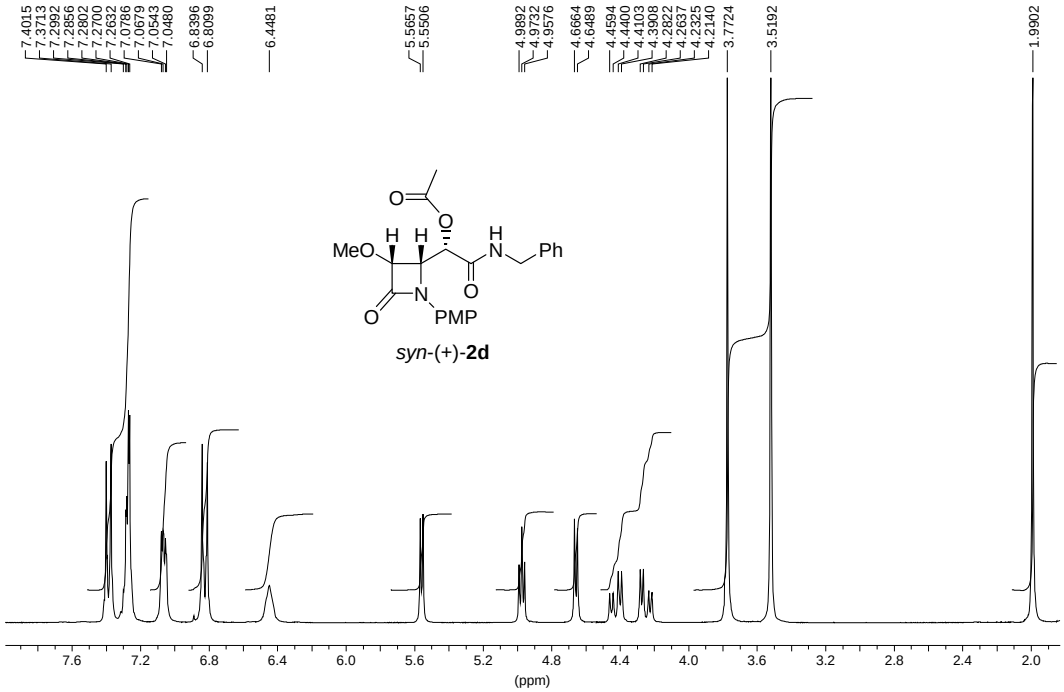
2c

(mixture of diastereoisomers *syn/anti* 72:28)

75 MHz ($CDCl_3$, 25ºC)

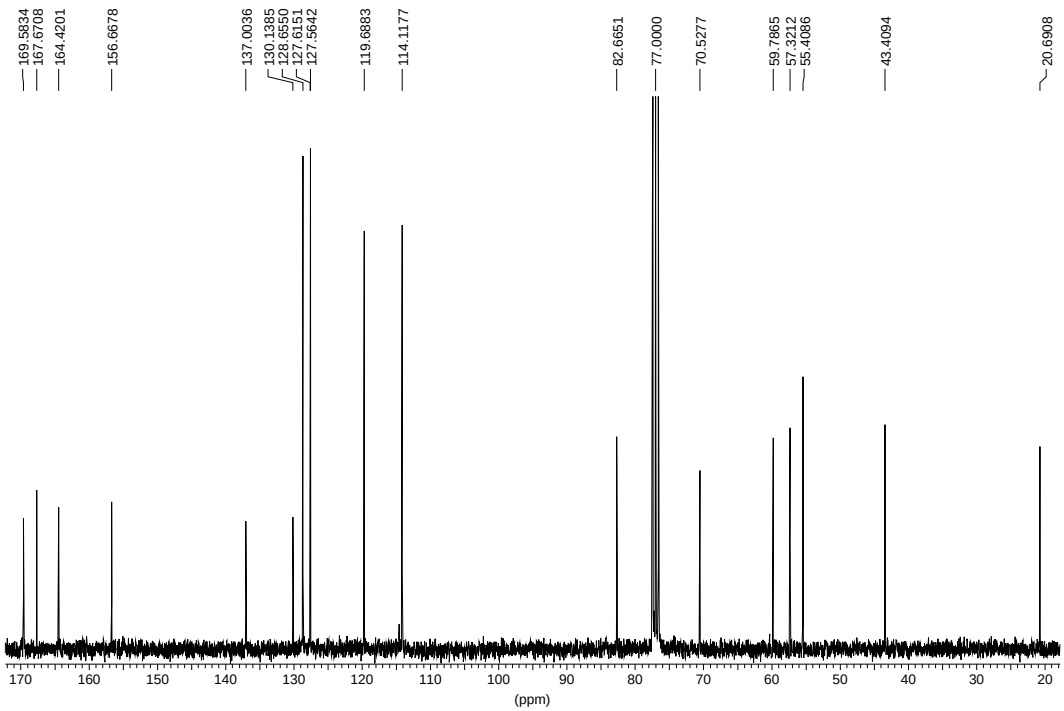


300 MHz ($CDCl_3$, 25ºC)

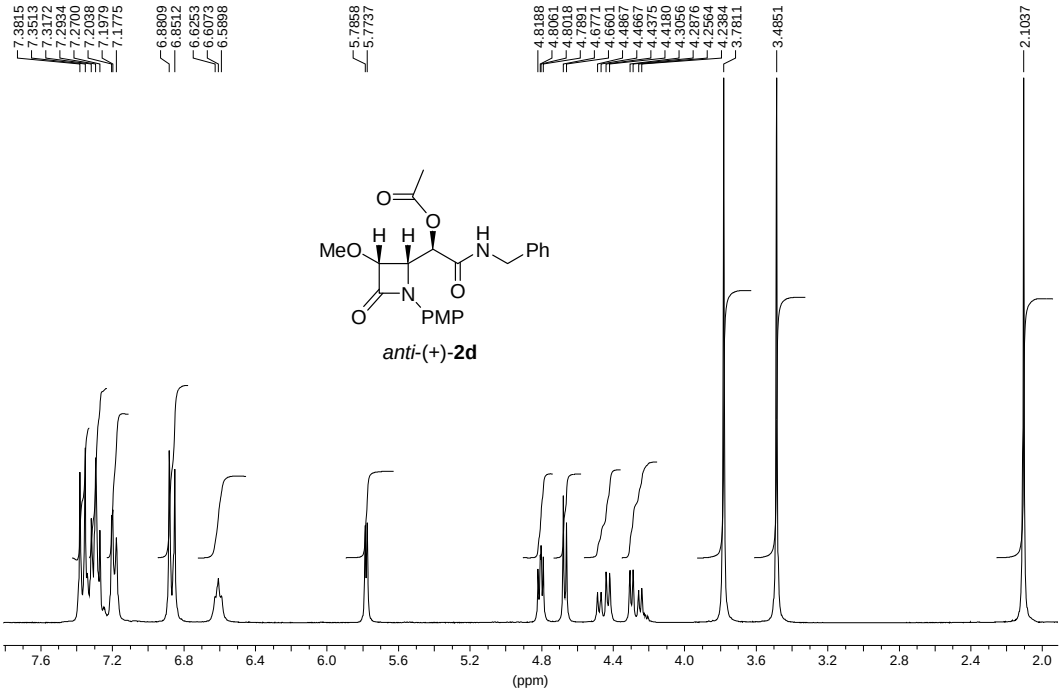


syn-(+)-**2d**

75 MHz ($CDCl_3$, 25ºC)

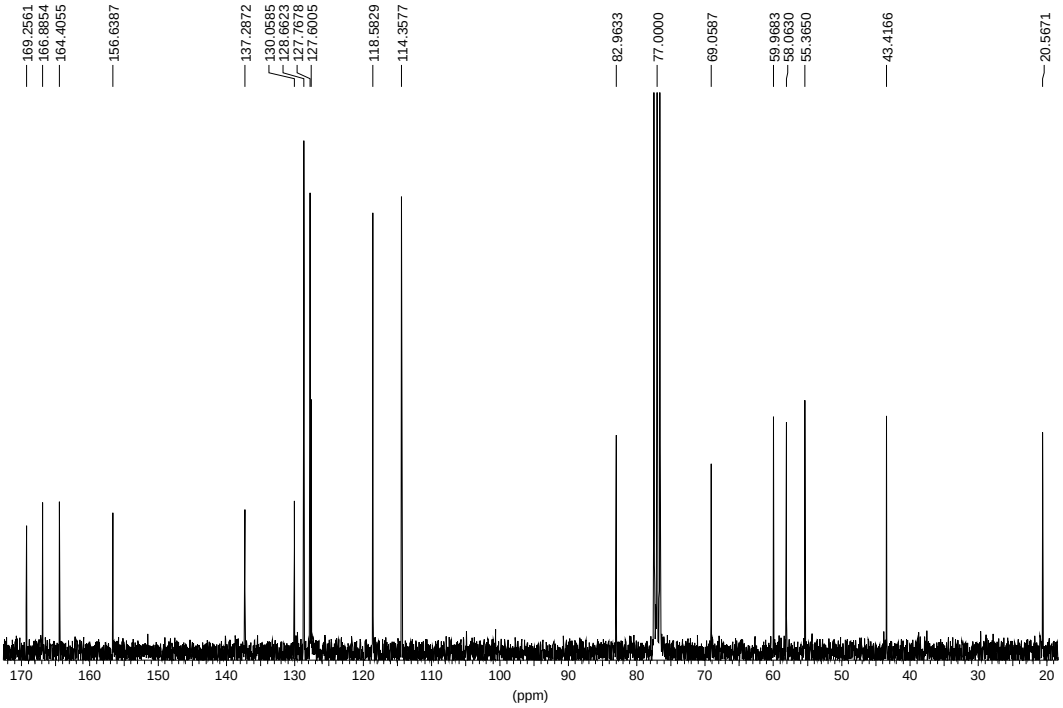


300 MHz ($CDCl_3$, 25ºC)

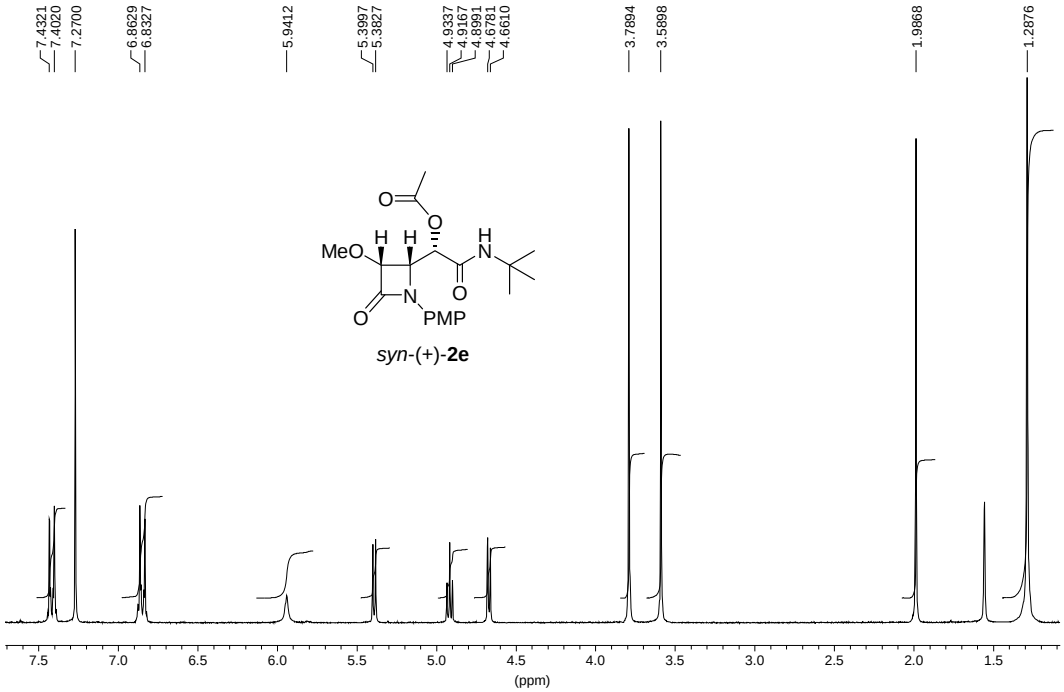


anti-(+)-**2d**

75 MHz ($CDCl_3$, 25ºC)

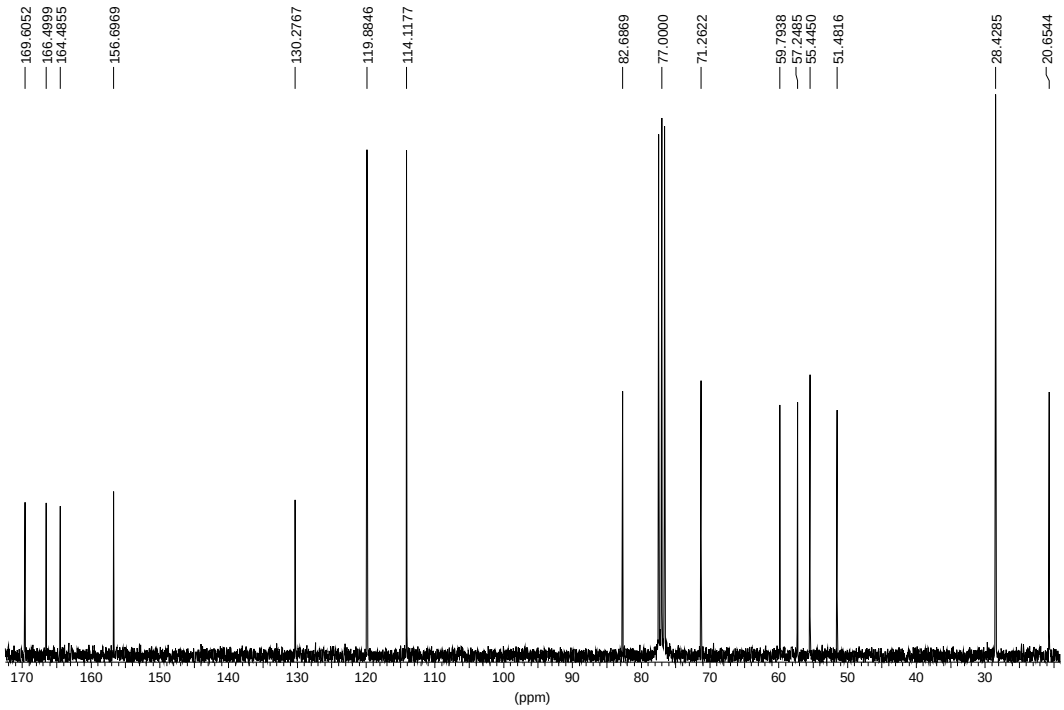


300 MHz ($CDCl_3$, 25ºC)

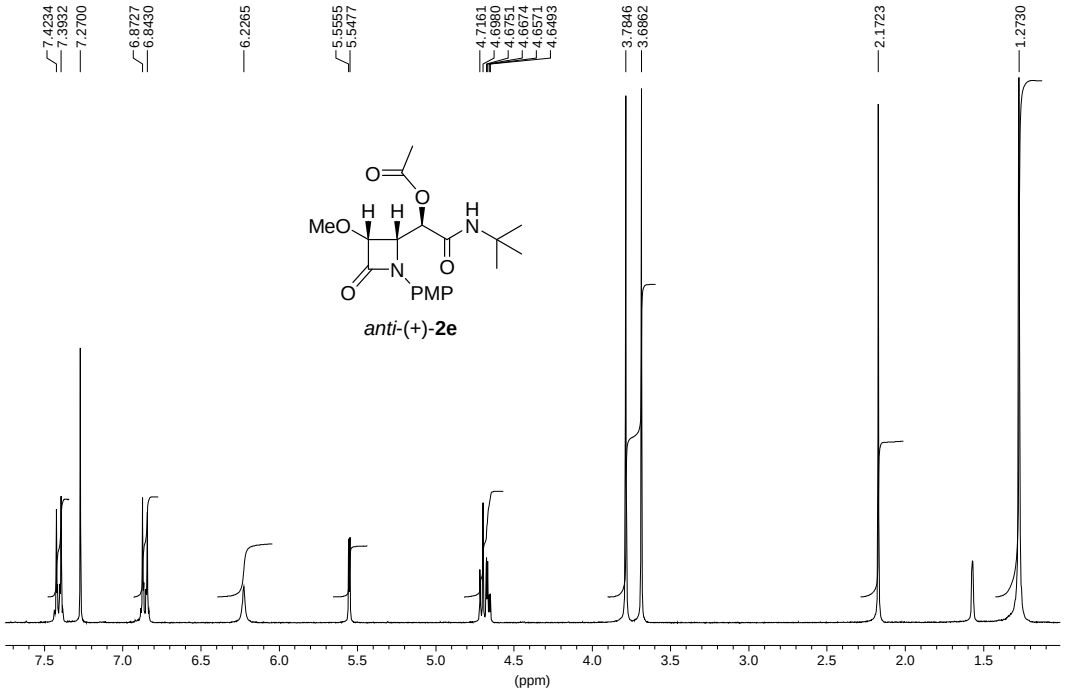


syn-(+)-**2e**

75 MHz ($CDCl_3$, 25ºC)

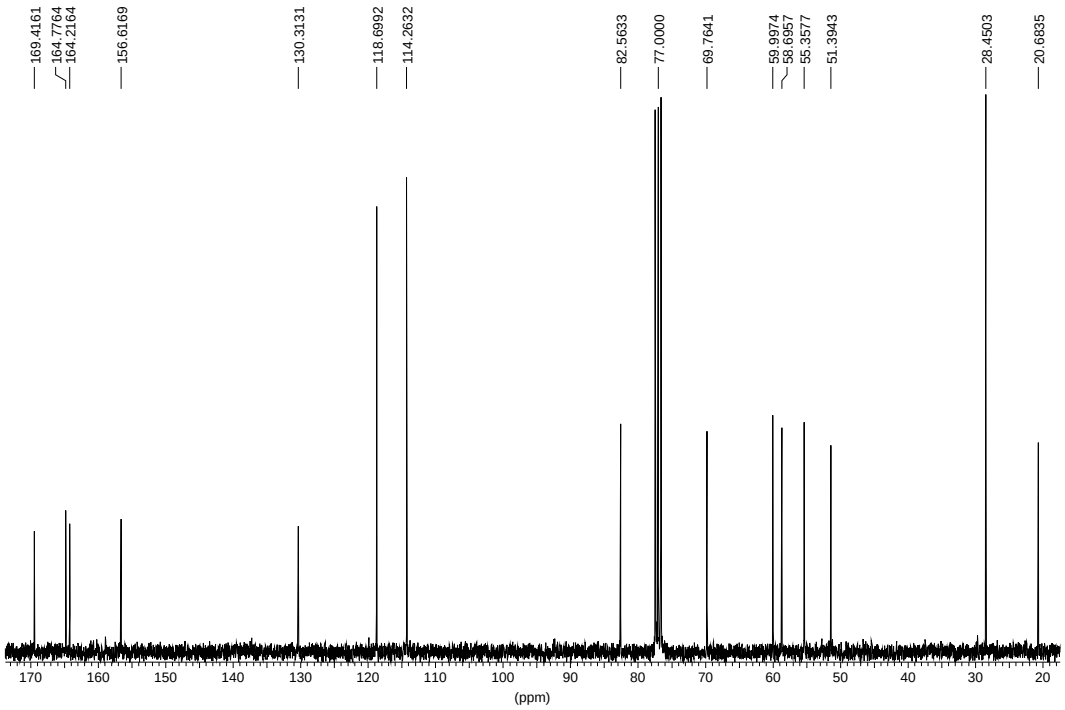


300 MHz ($CDCl_3$, 25ºC)

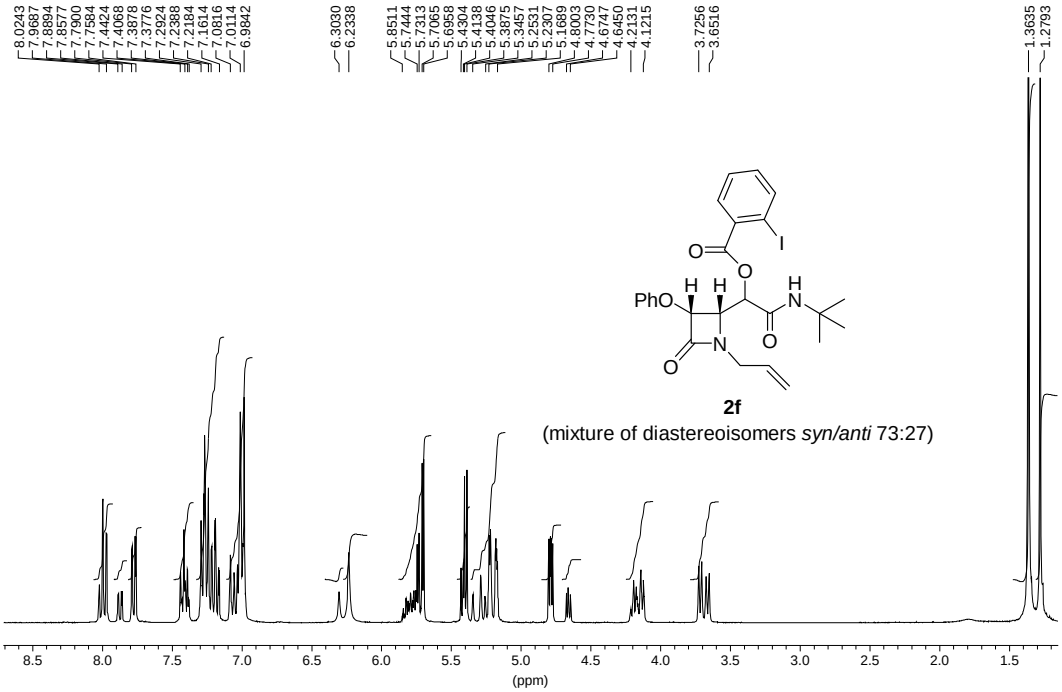


anti-(+)-**2e**

75 MHz ($CDCl_3$, 25ºC)



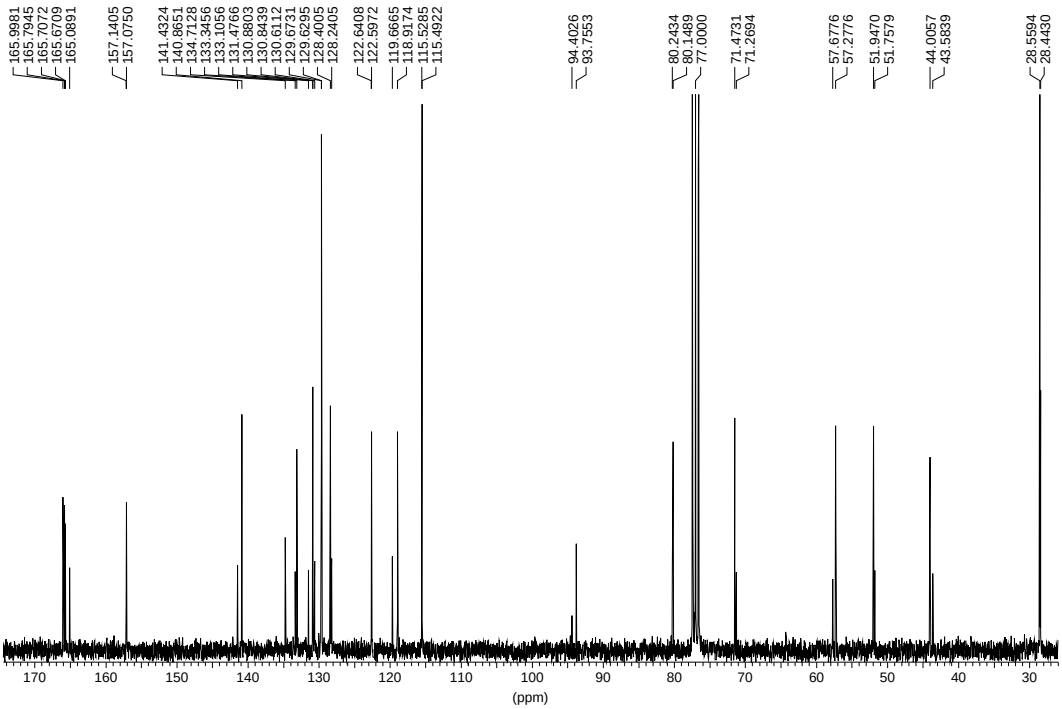
300 MHz ($CDCl_3$, 25ºC)



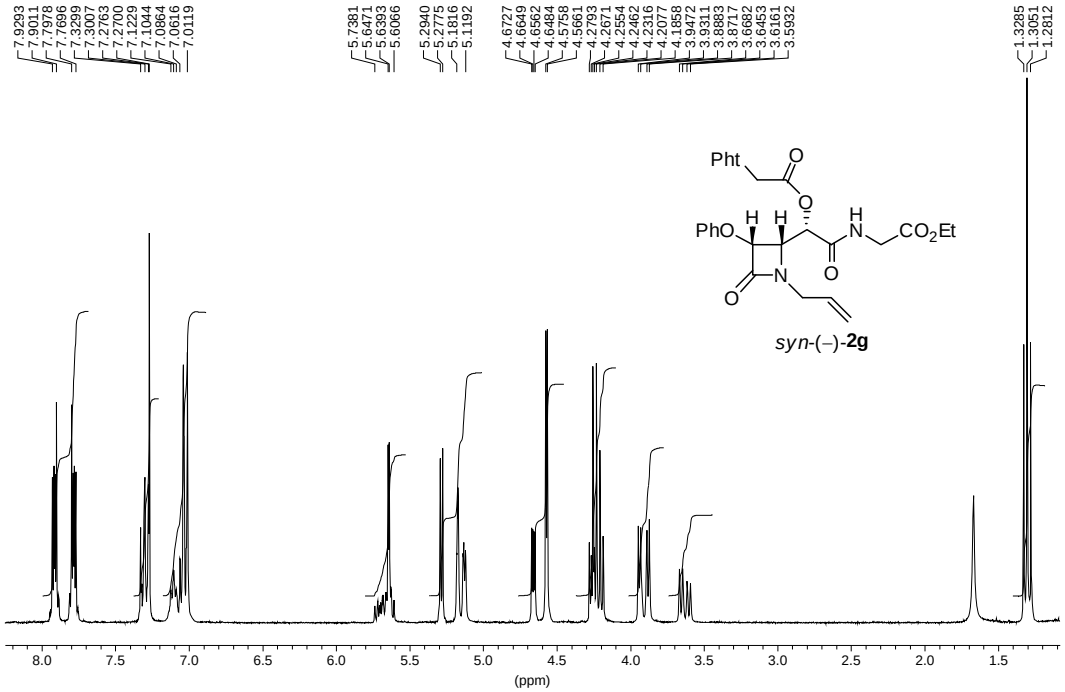
2f

(mixture of diastereoisomers *syn/anti* 73:27)

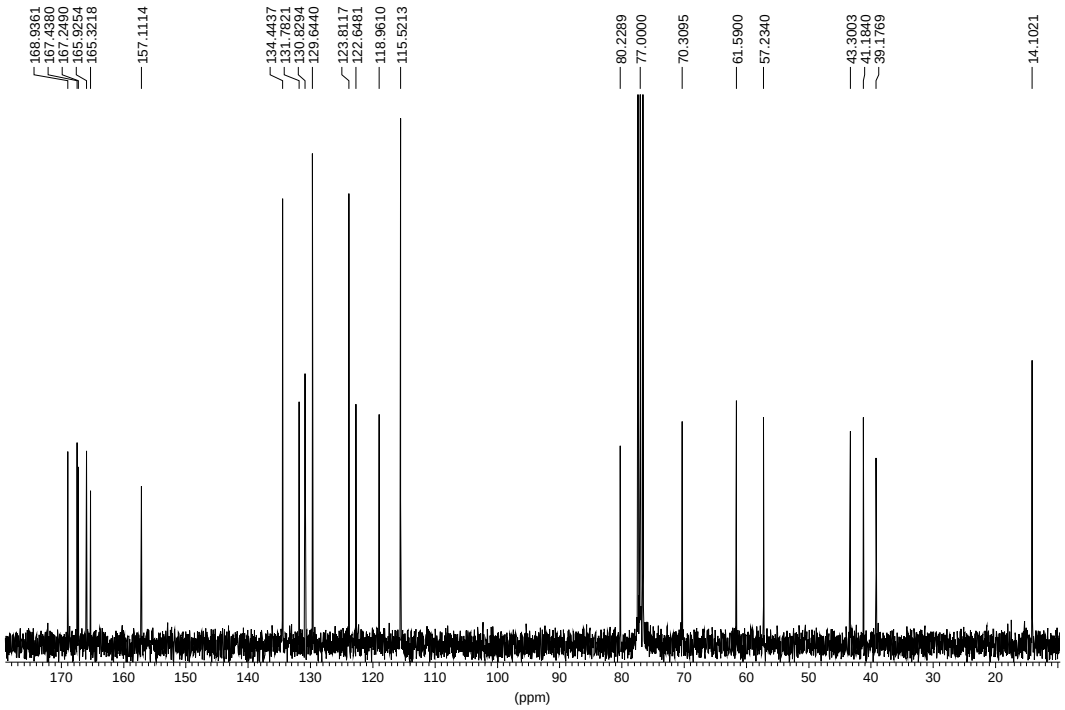
75 MHz ($CDCl_3$, 25ºC)



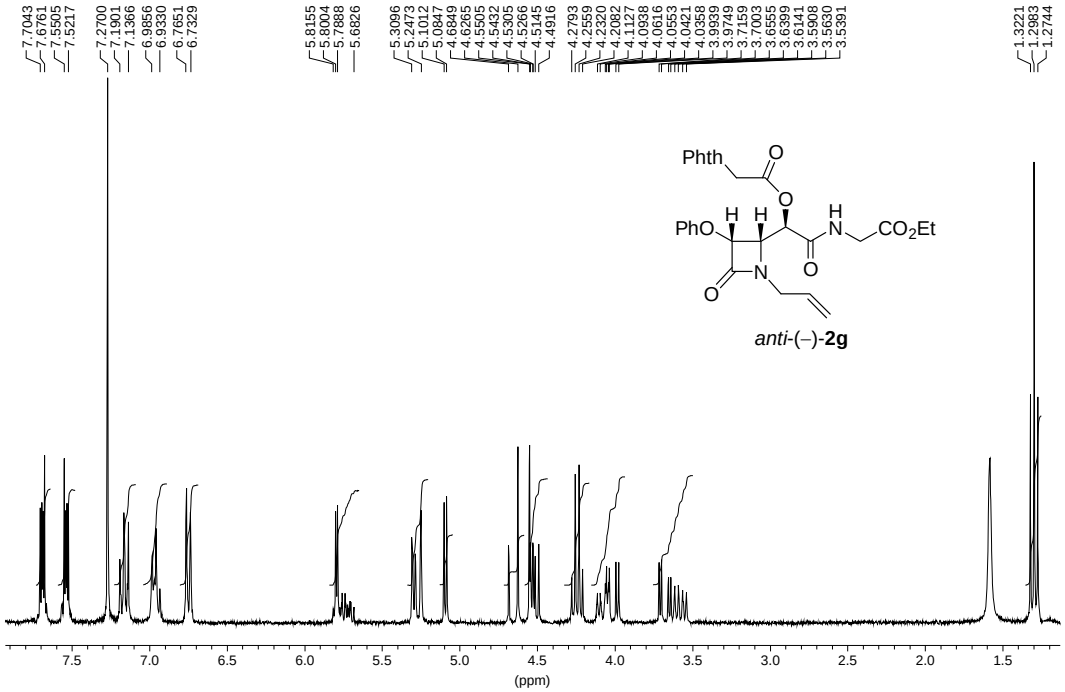
300 MHz ($CDCl_3$, 25ºC)



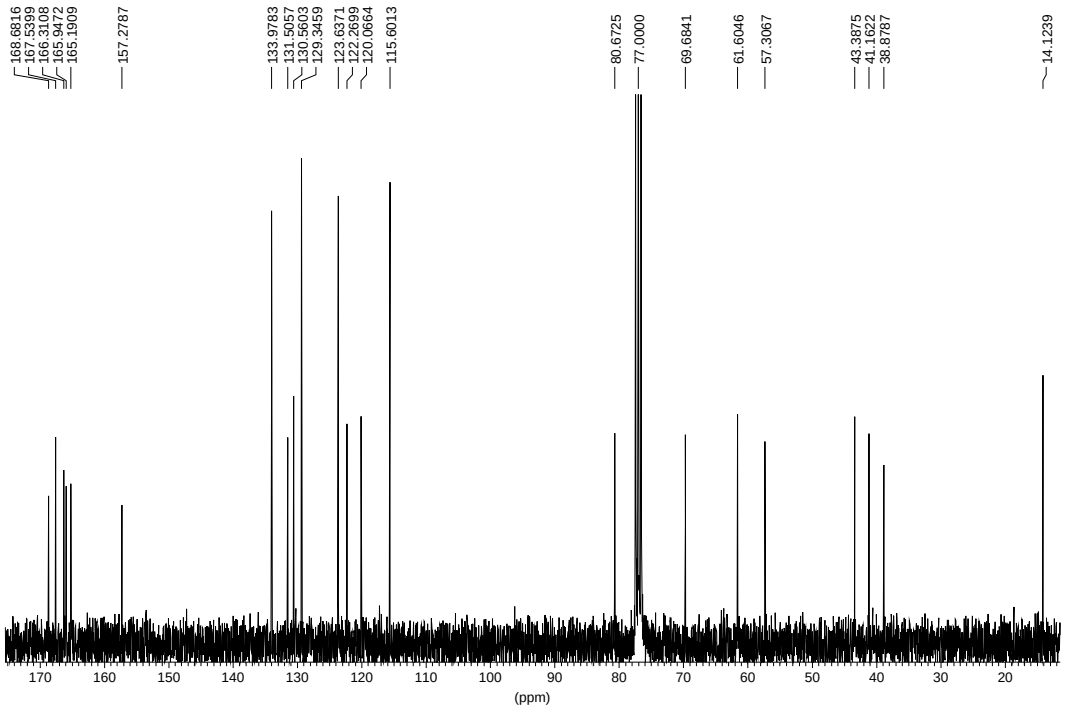
75 MHz ($CDCl_3$, 25ºC)



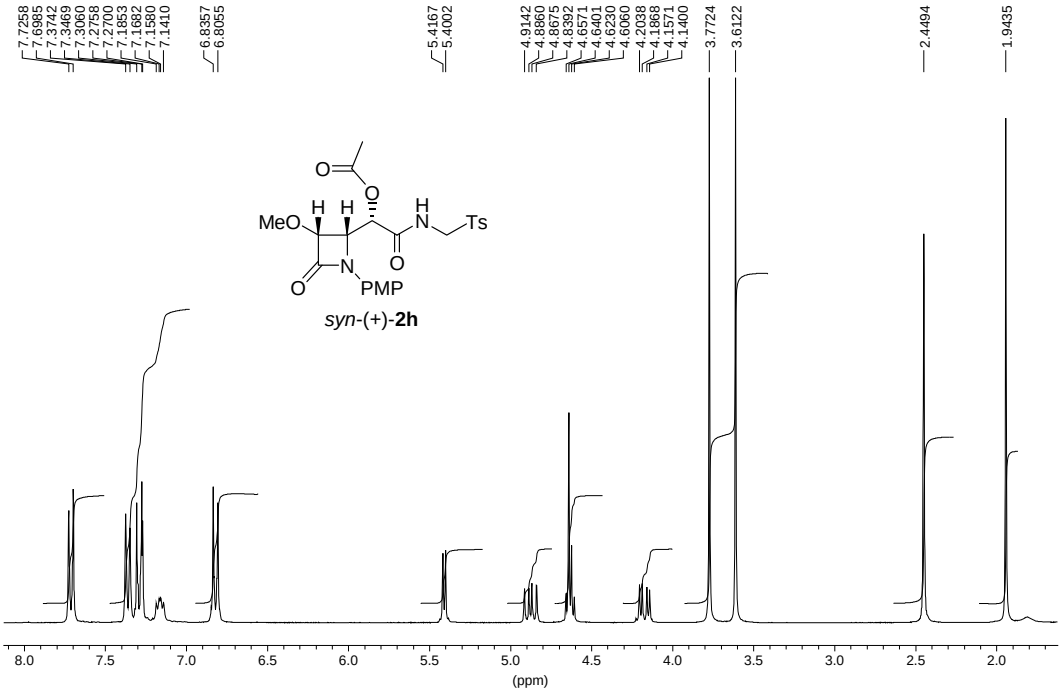
300 MHz ($CDCl_3$, 25ºC)



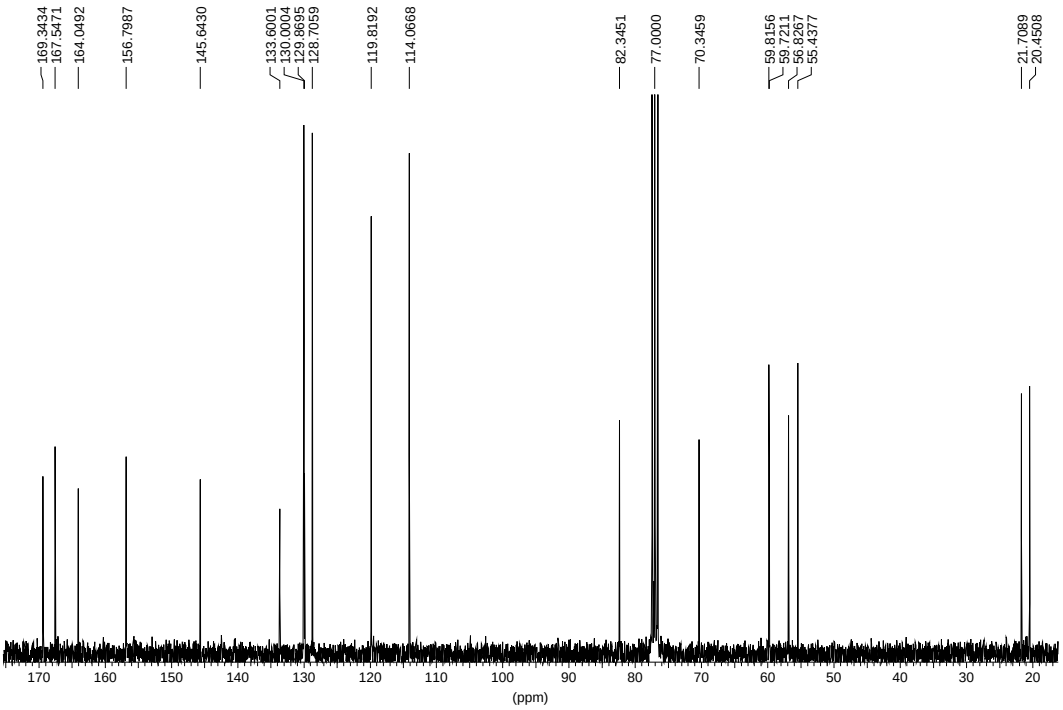
75 MHz ($CDCl_3$, 25ºC)



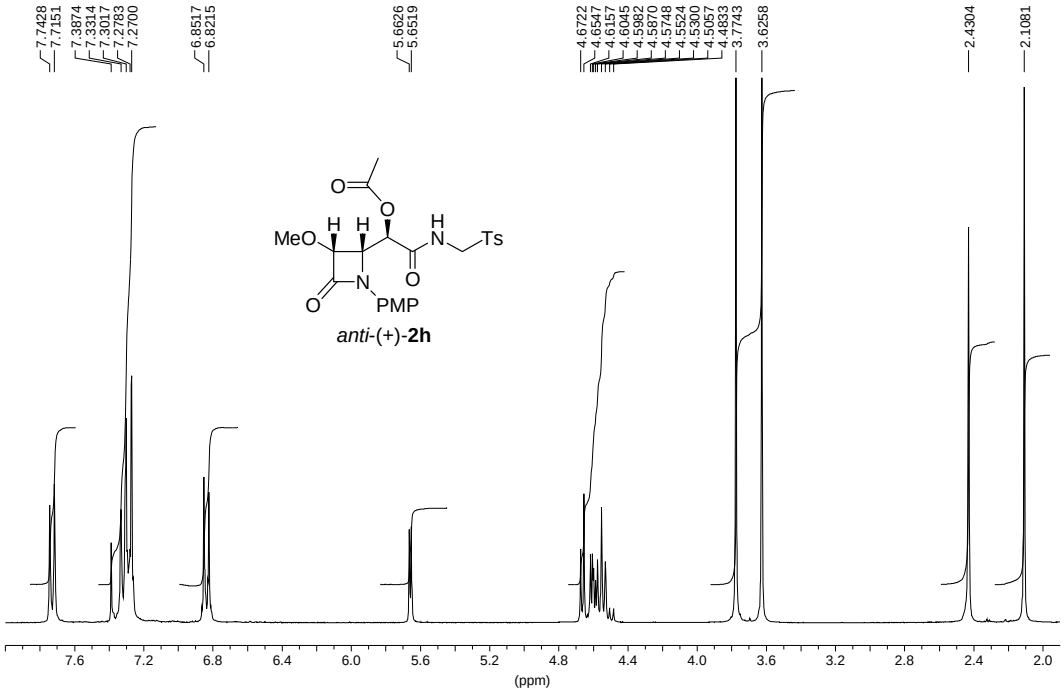
300 MHz ($CDCl_3$, 25ºC)



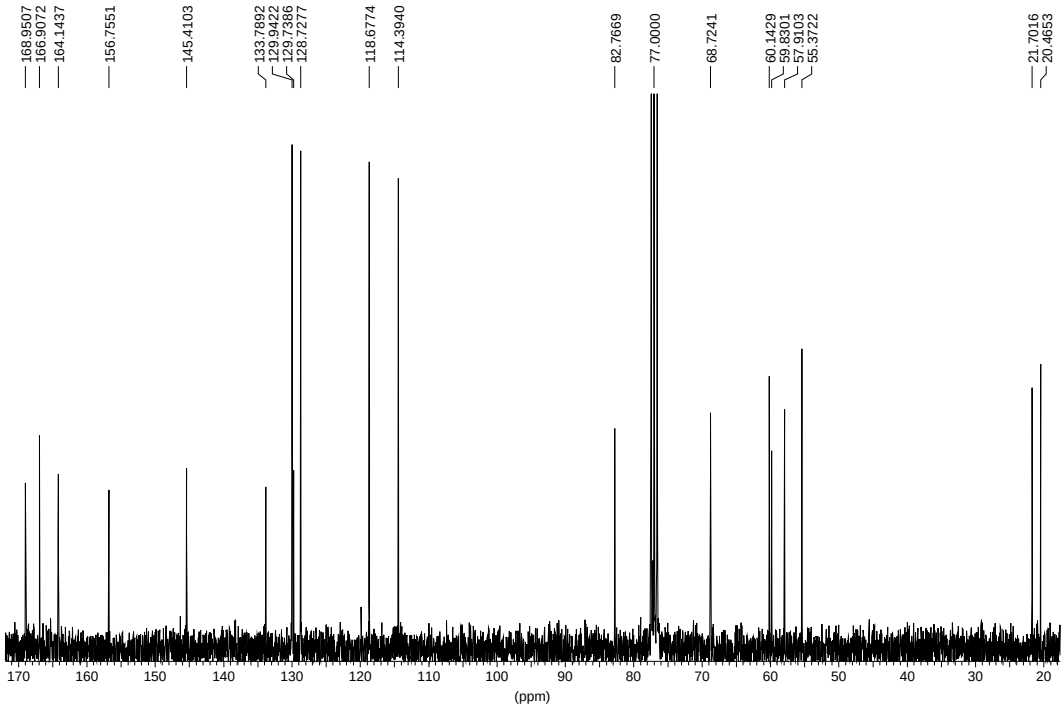
75 MHz ($CDCl_3$, 25ºC)



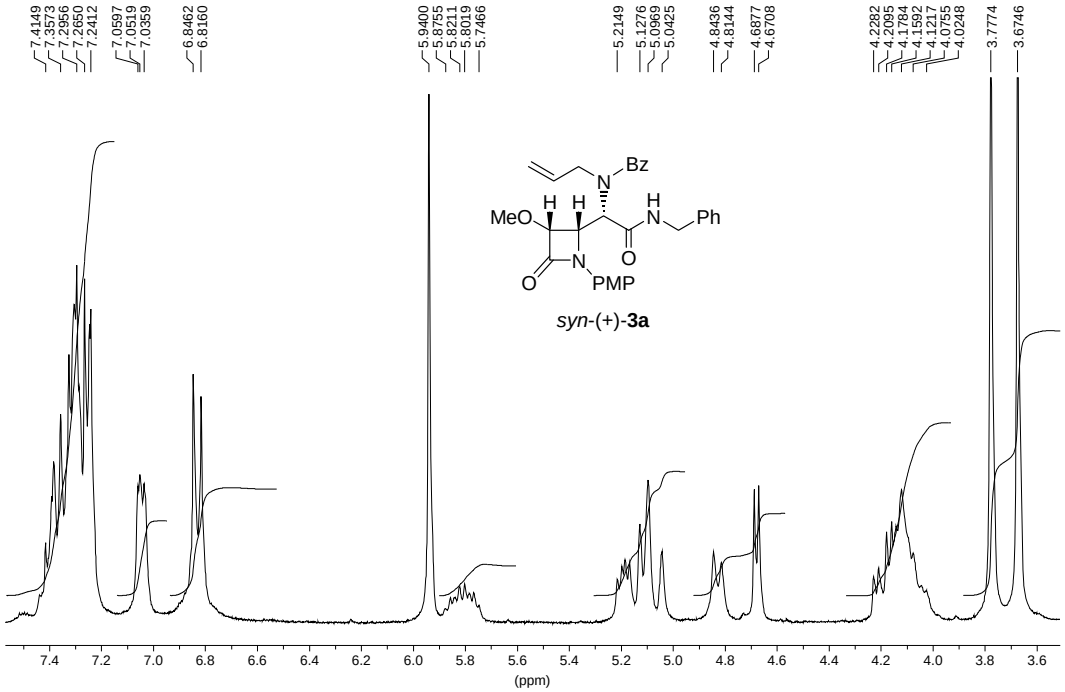
300 MHz ($CDCl_3$, 25ºC)



75 MHz ($CDCl_3$, 25ºC)

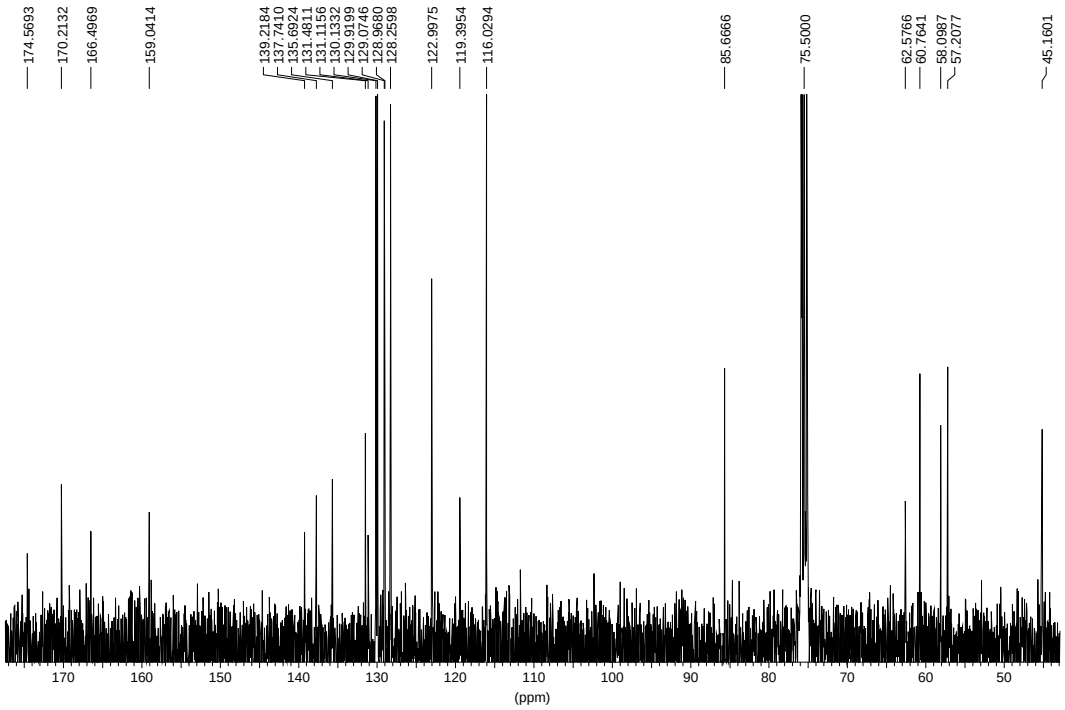


300 MHz ($C_2D_2Cl_4$, 100ºC)

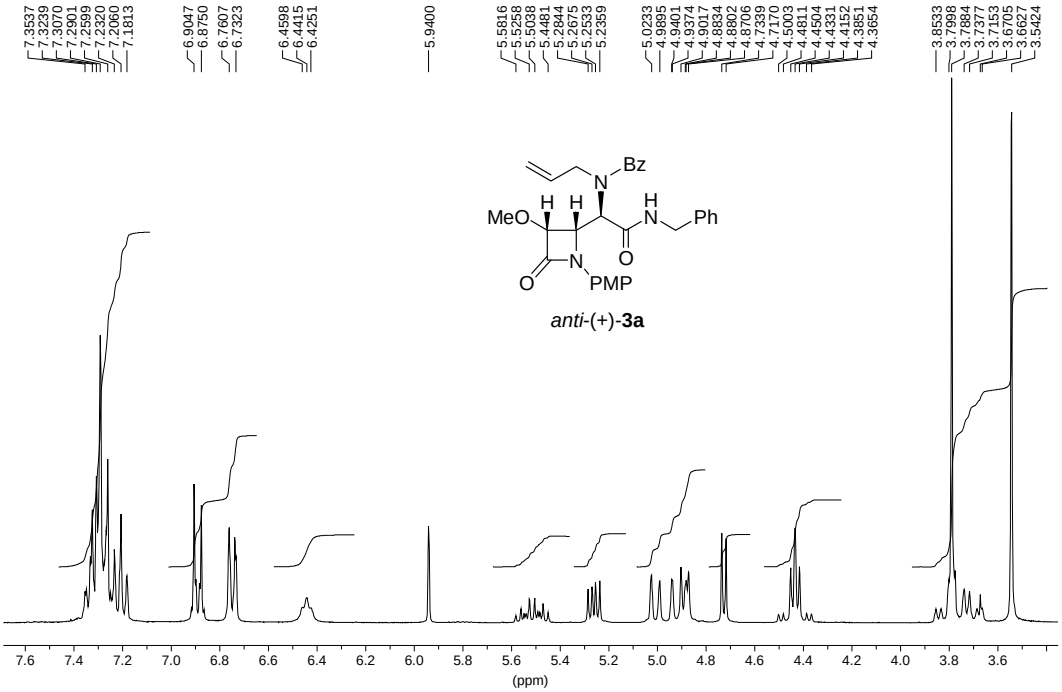


syn-(+)-**3a**

75 MHz ($C_2D_2Cl_4$, 100ºC)

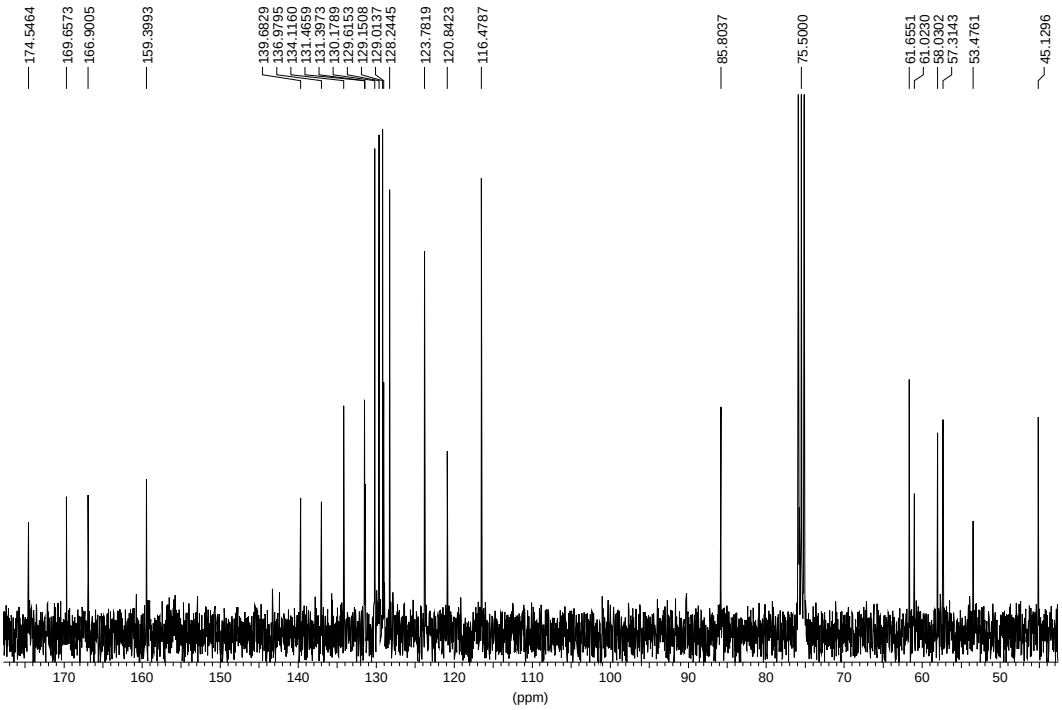


300 MHz ($C_2D_2Cl_4$, 100ºC)

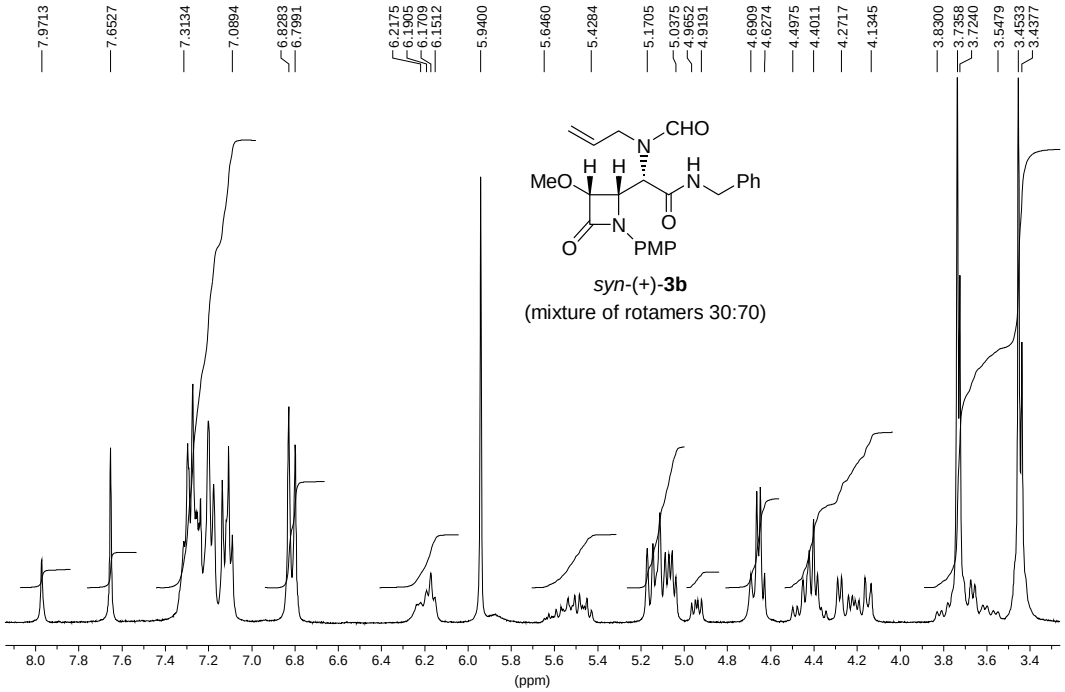


anti-(+)-**3a**

75 MHz ($C_2D_2Cl_4$, 100ºC)

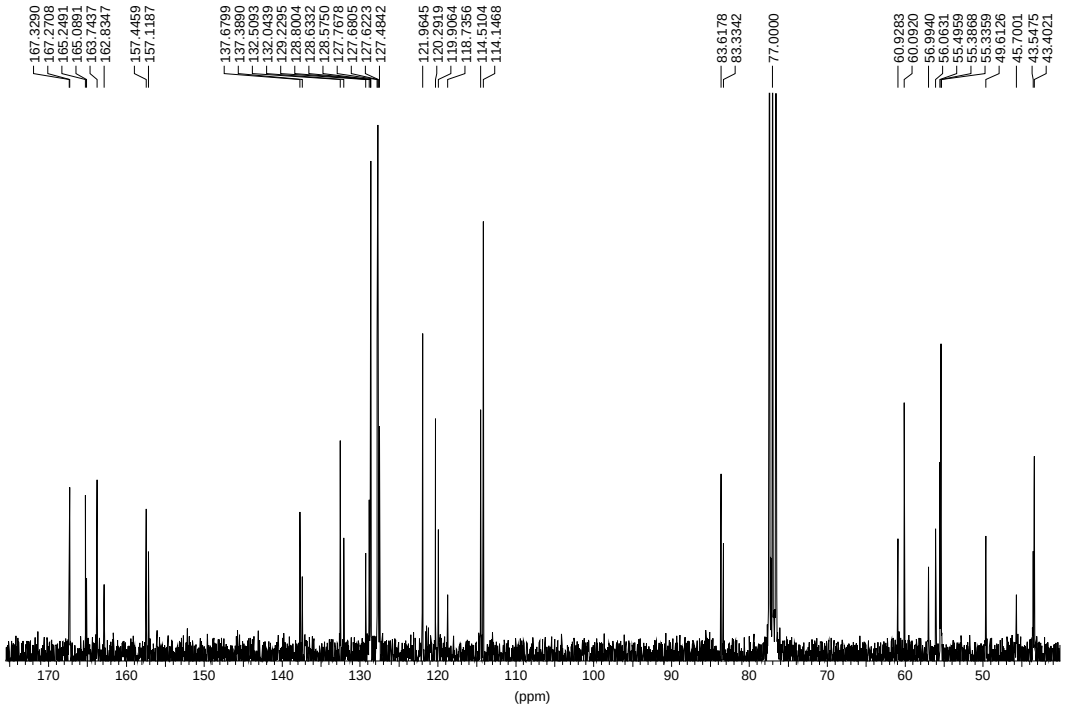


300 MHz ($C_2D_2Cl_4$, 25ºC)

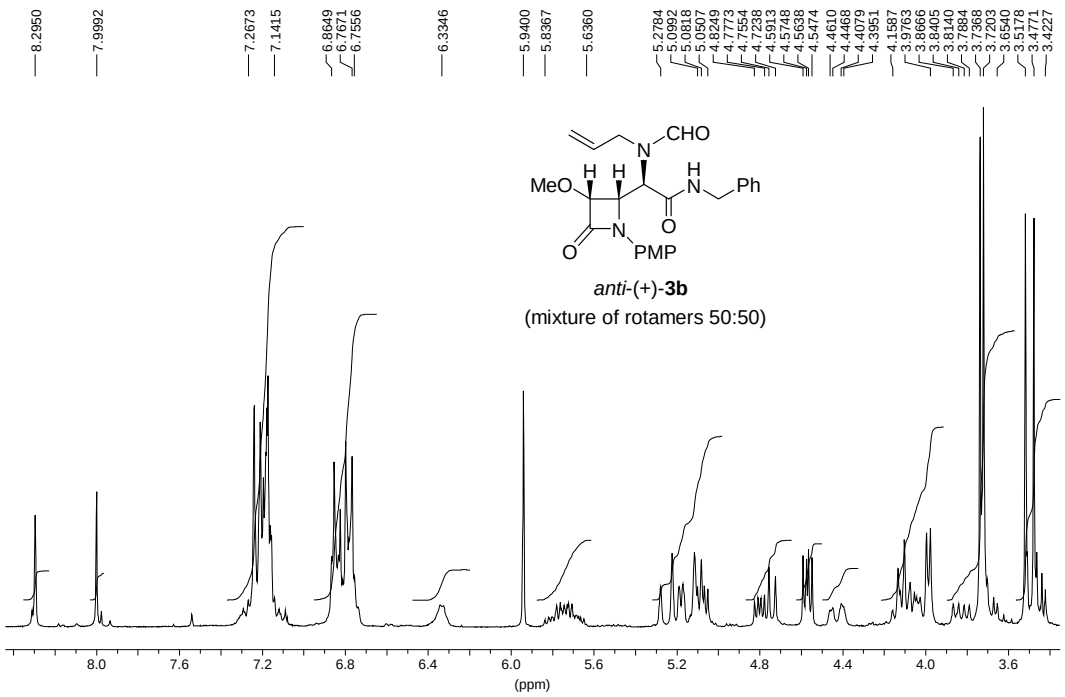


syn-(+)-**3b**
(mixture of rotamers 30:70)

75 MHz ($CDCl_3$, 25ºC)

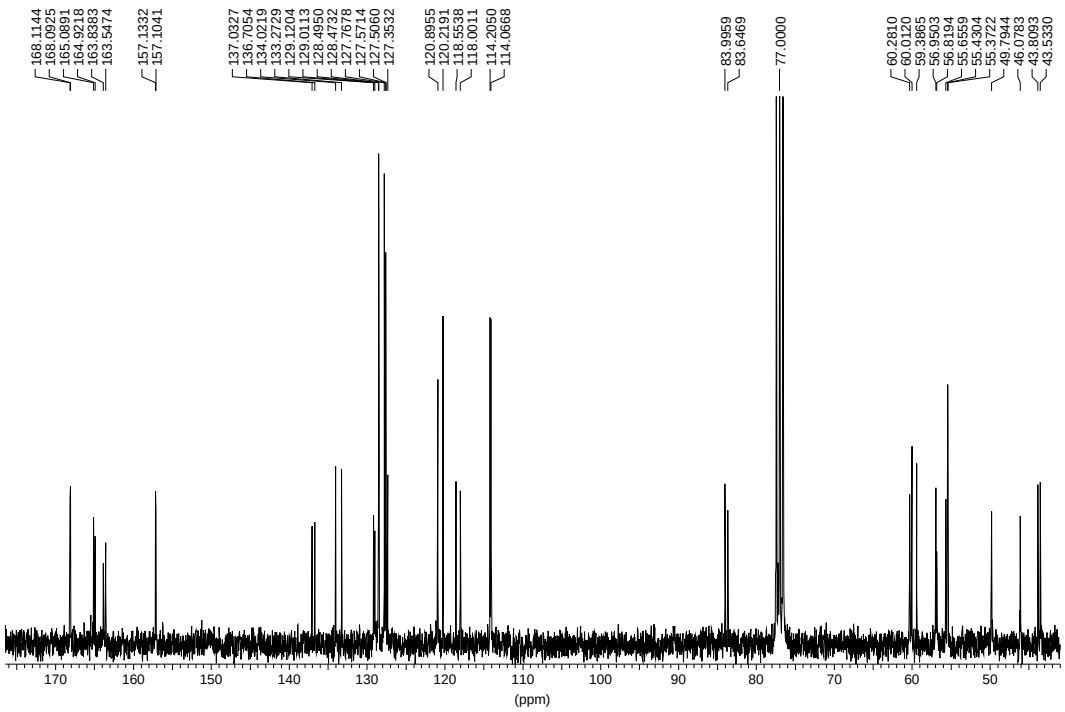


300 MHz ($C_2D_2Cl_4$, 25ºC)

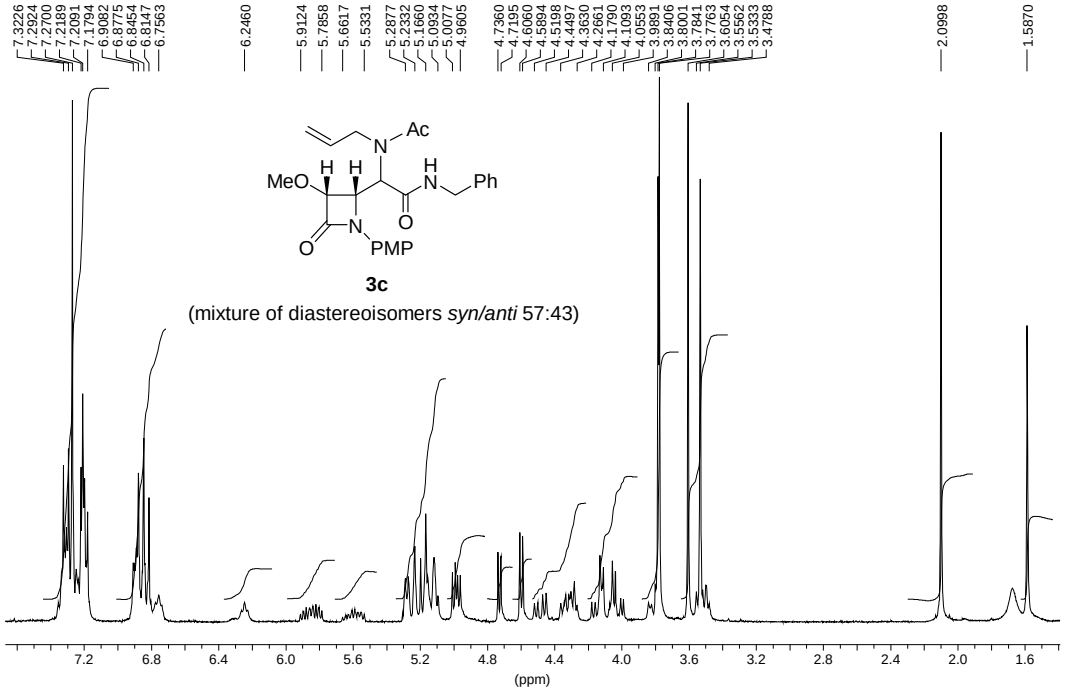


anti-(+)-**3b**
(mixture of rotamers 50:50)

75 MHz ($CDCl_3$, 25ºC)



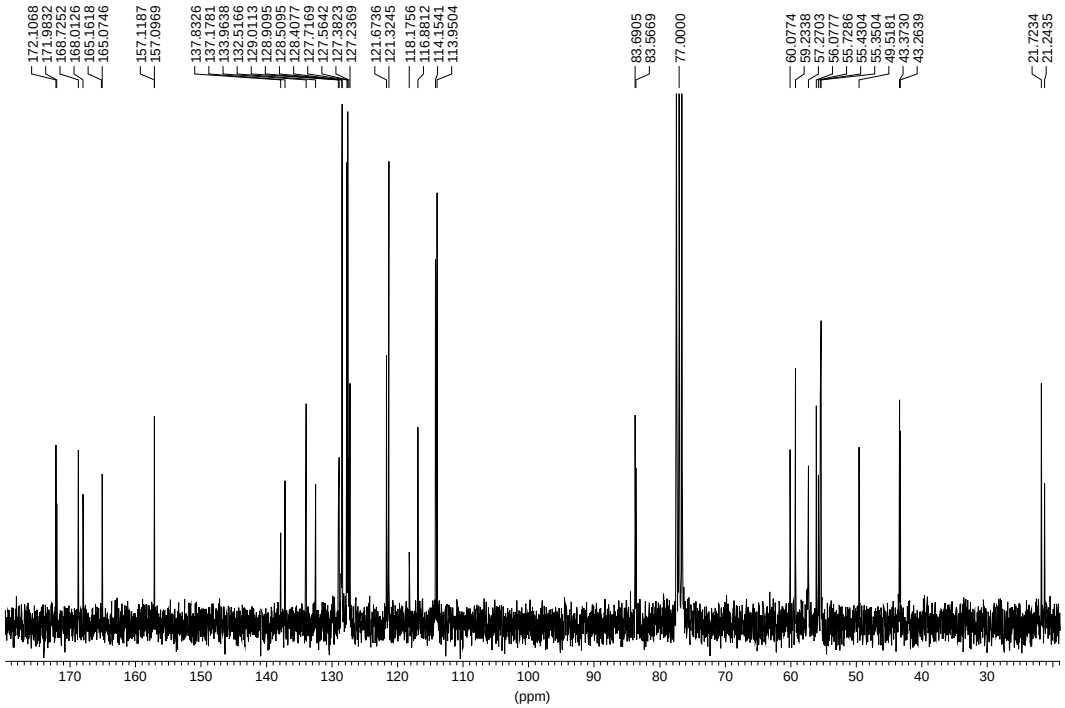
300 MHz ($CDCl_3$, 25ºC)



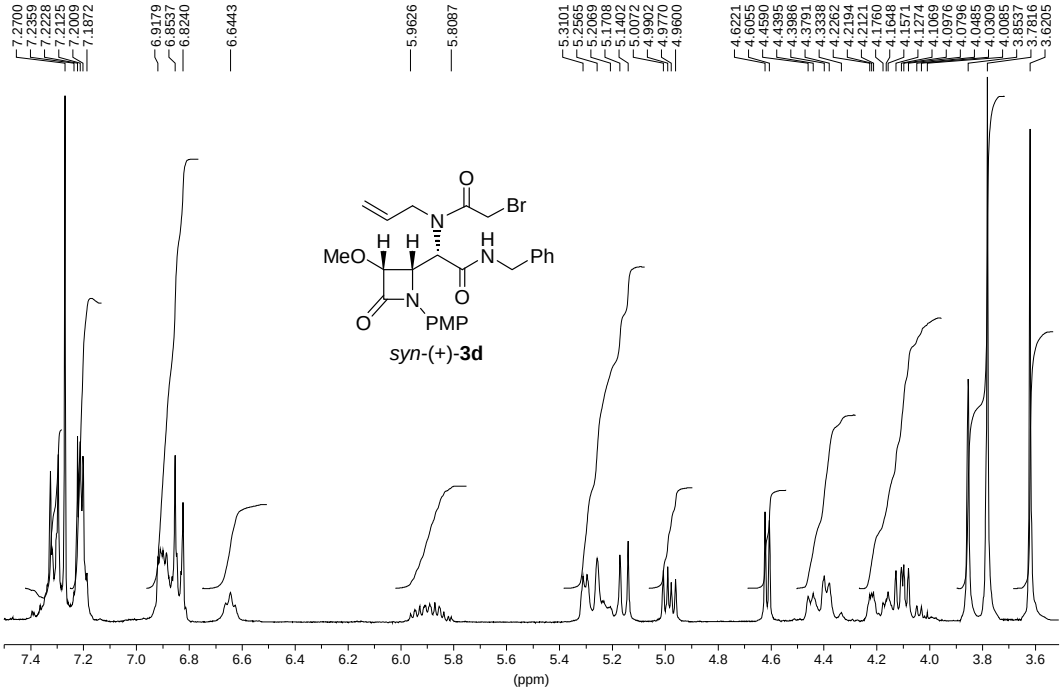
3c

(mixture of diastereoisomers *syn/anti* 57:43)

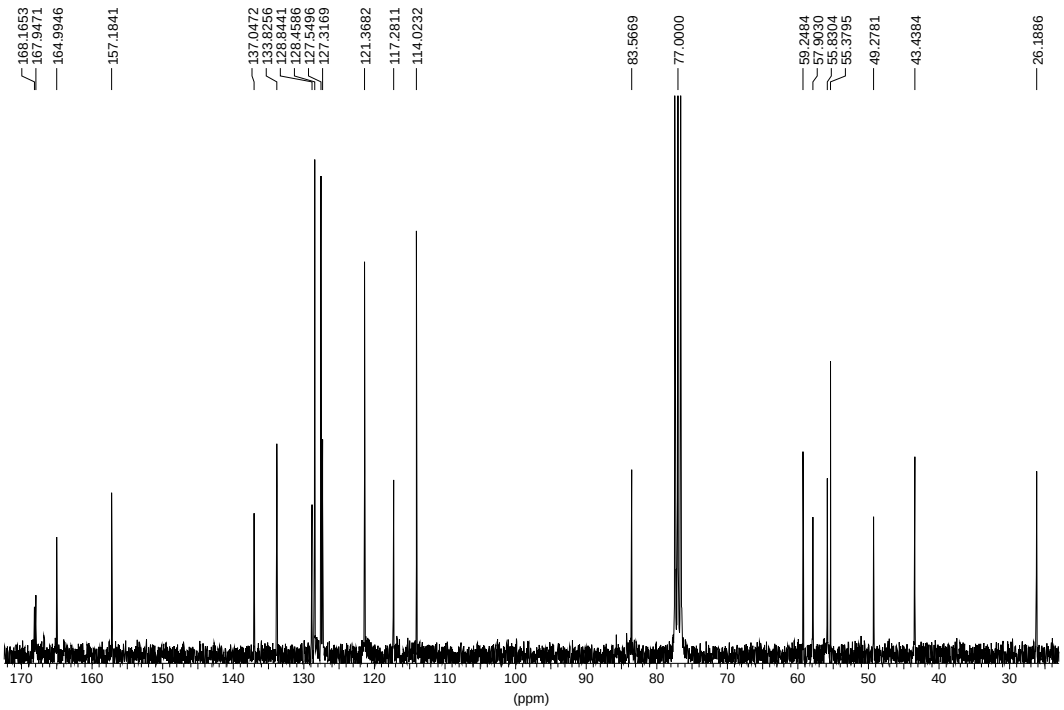
75 MHz ($CDCl_3$, 25ºC)



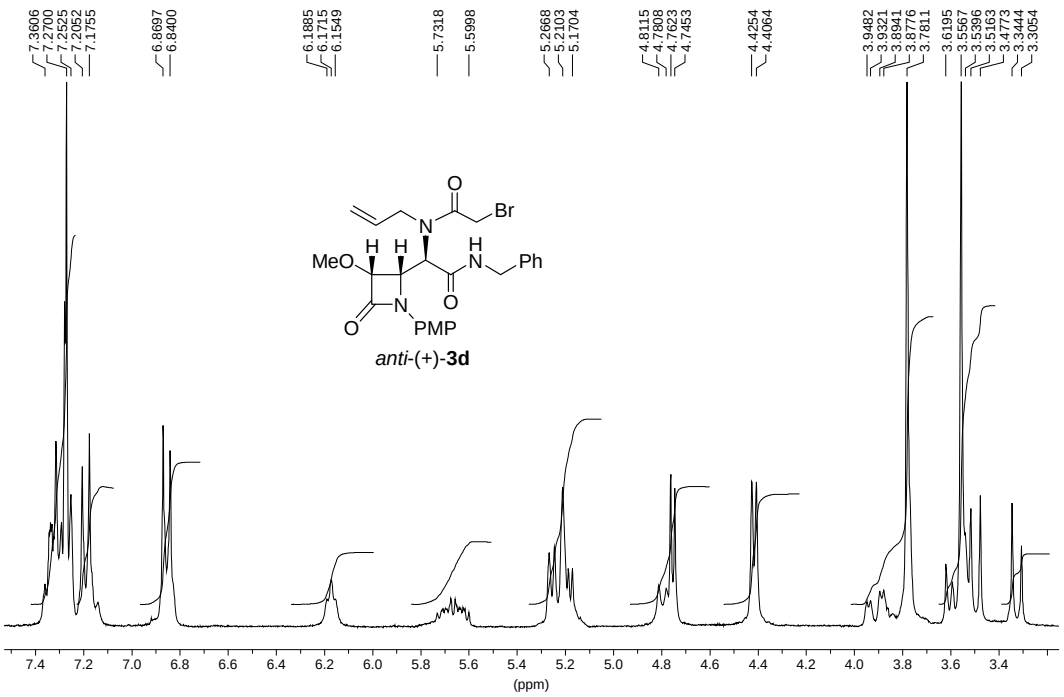
300 MHz ($CDCl_3$, 25ºC)



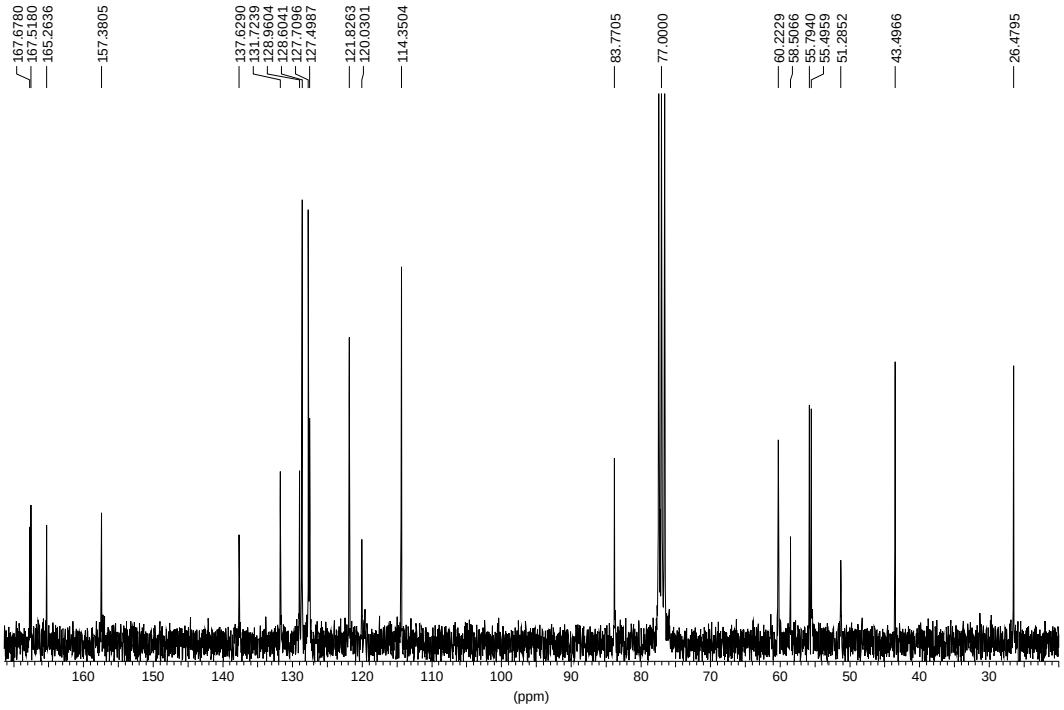
75 MHz ($CDCl_3$, 25ºC)



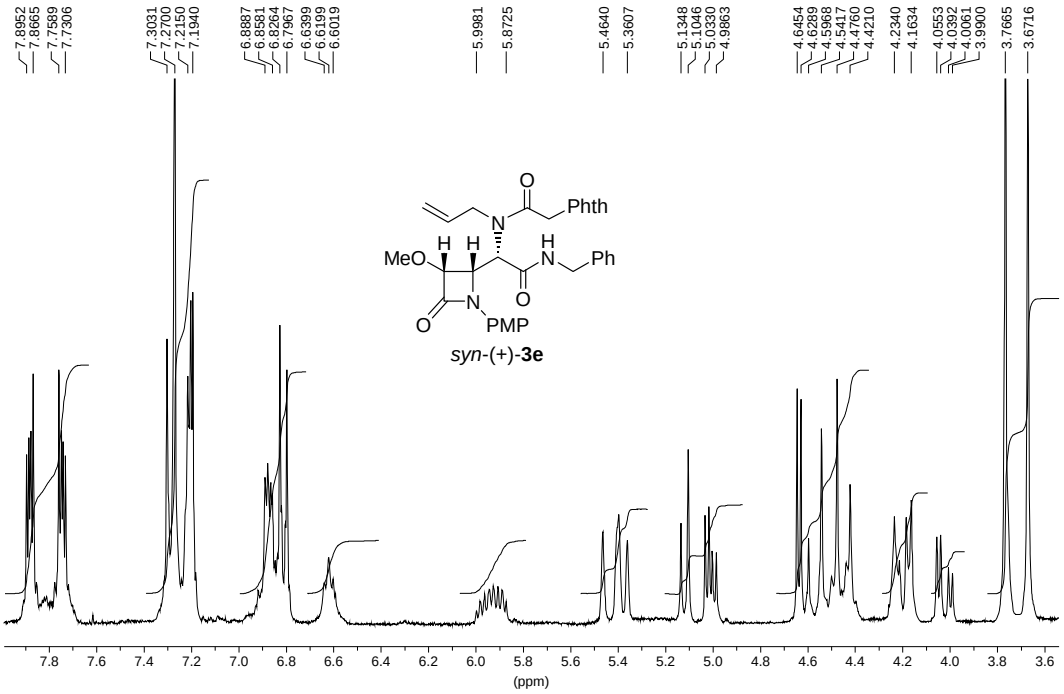
300 MHz ($CDCl_3$, 25ºC)



75 MHz ($CDCl_3$, 25ºC)

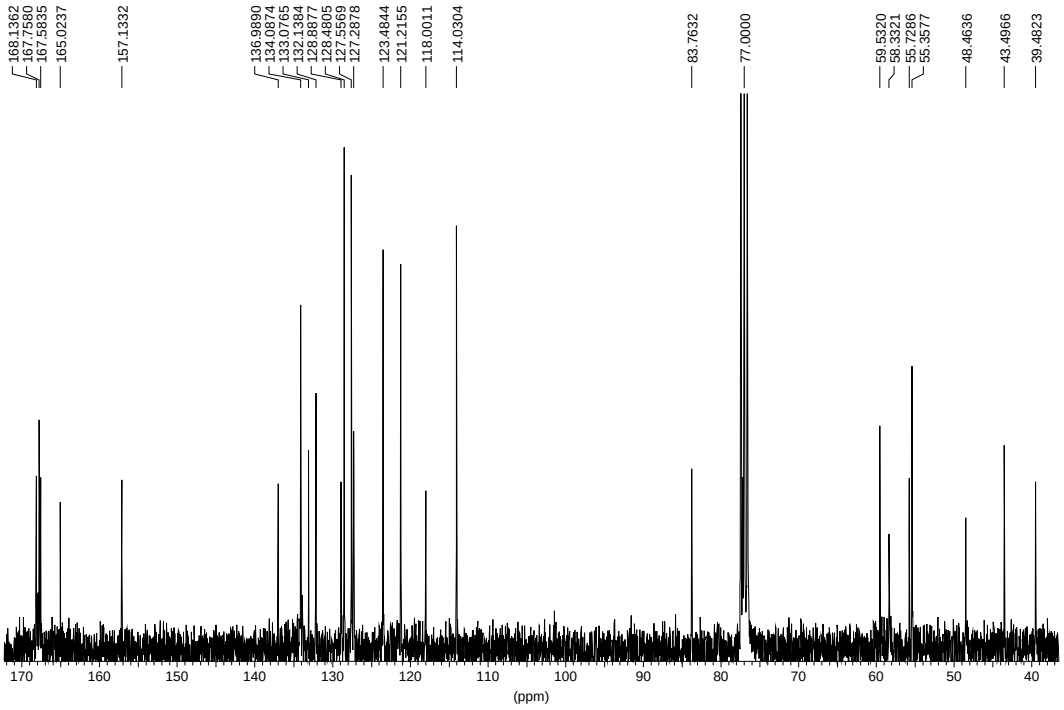


300 MHz ($CDCl_3$, 25ºC)

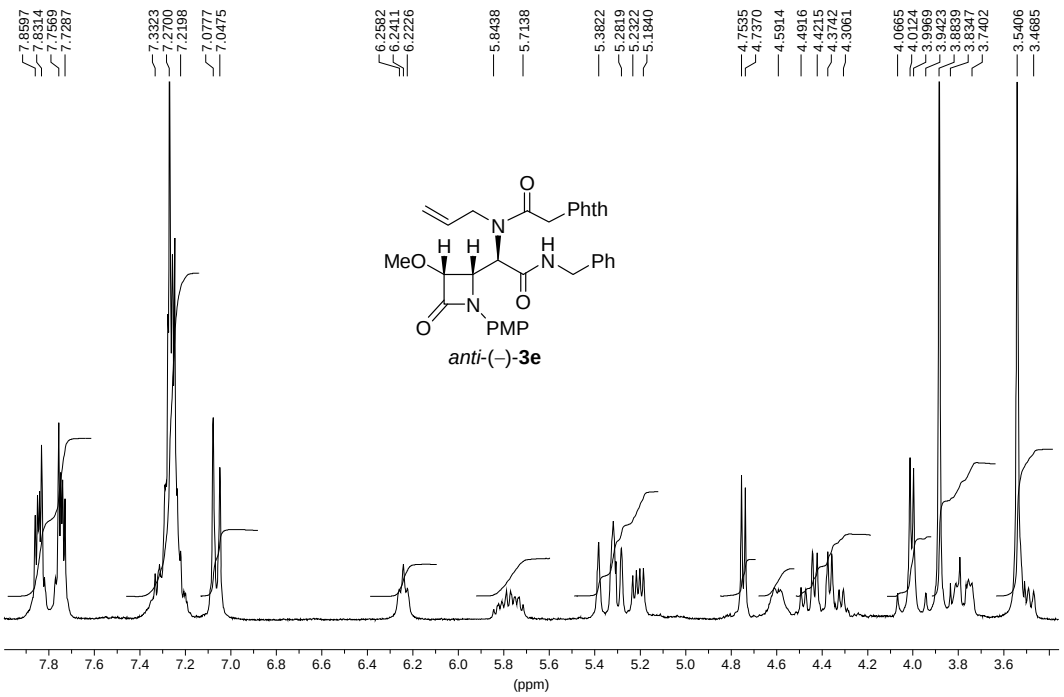


syn-(+)-**3e**

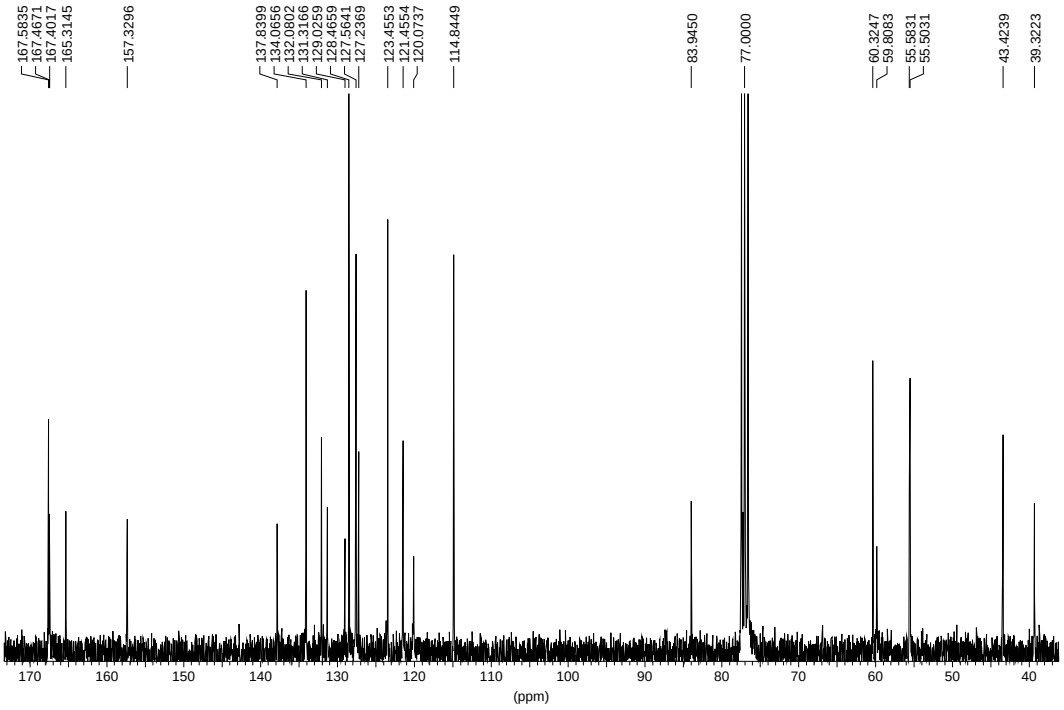
75 MHz ($CDCl_3$, 25ºC)



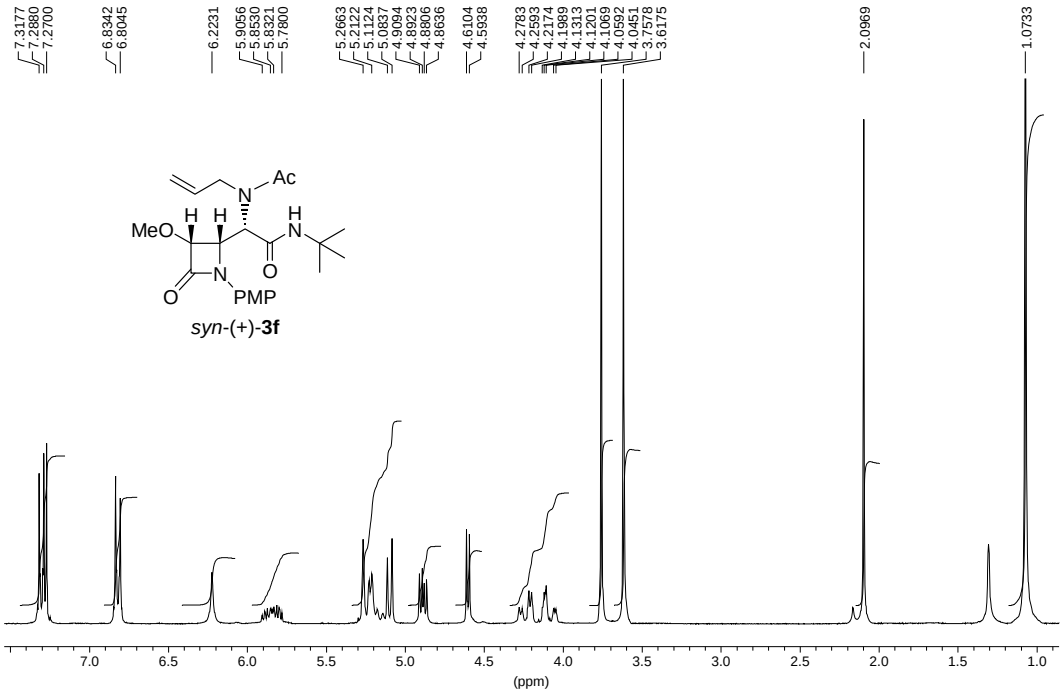
300 MHz ($CDCl_3$, 25ºC)



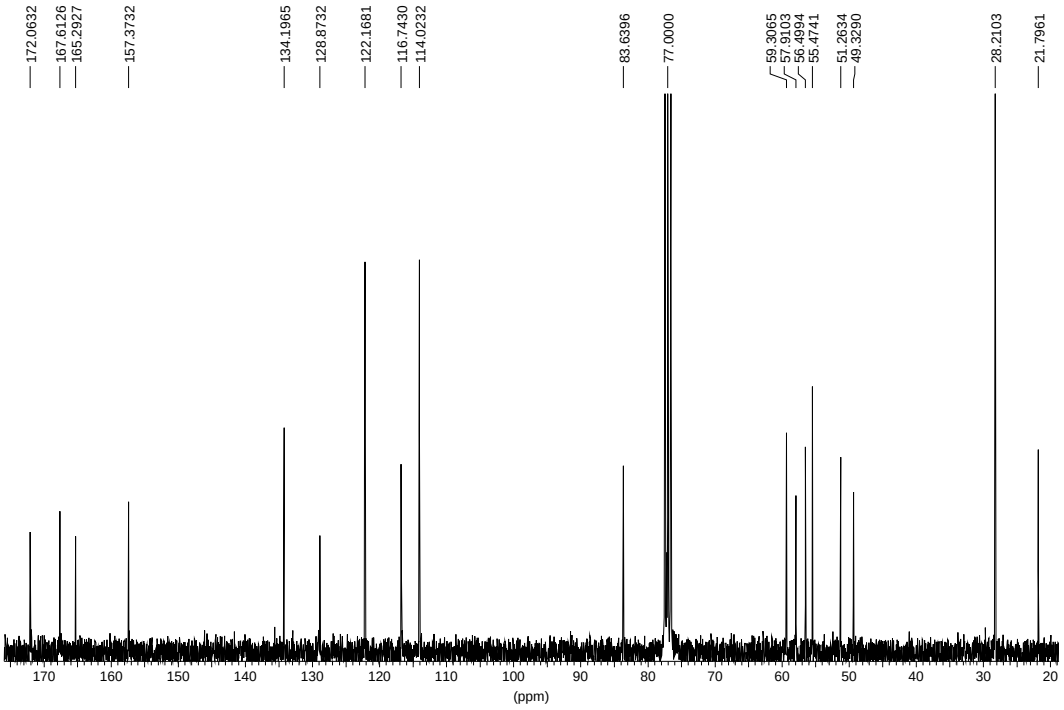
75 MHz ($CDCl_3$, 25ºC)



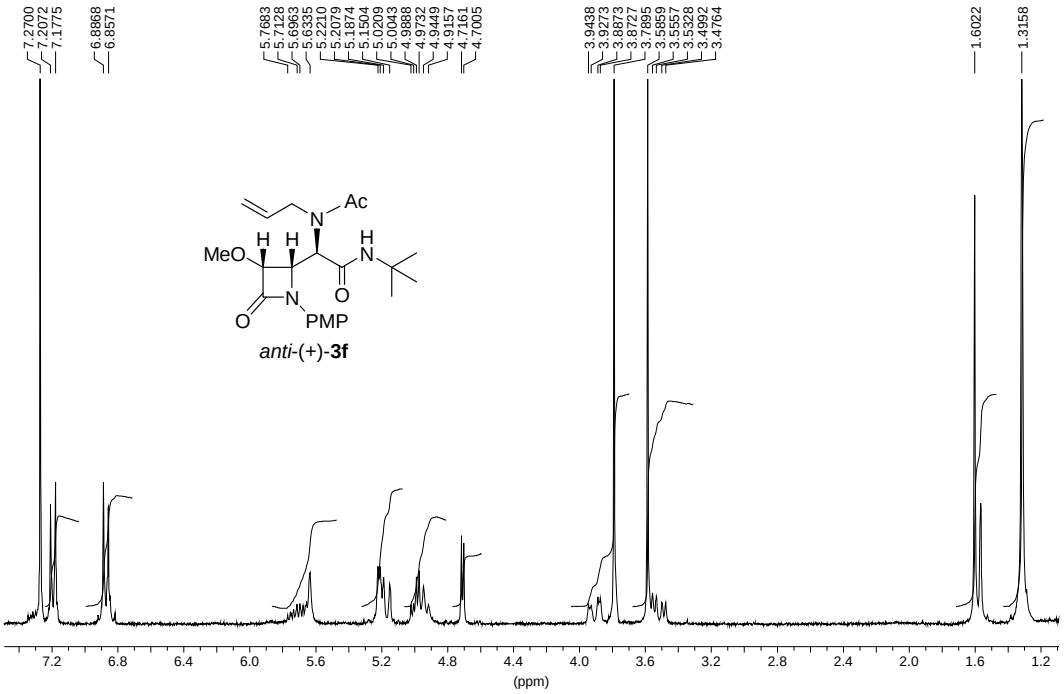
300 MHz ($CDCl_3$, 25ºC)



75 MHz ($CDCl_3$, 25ºC)

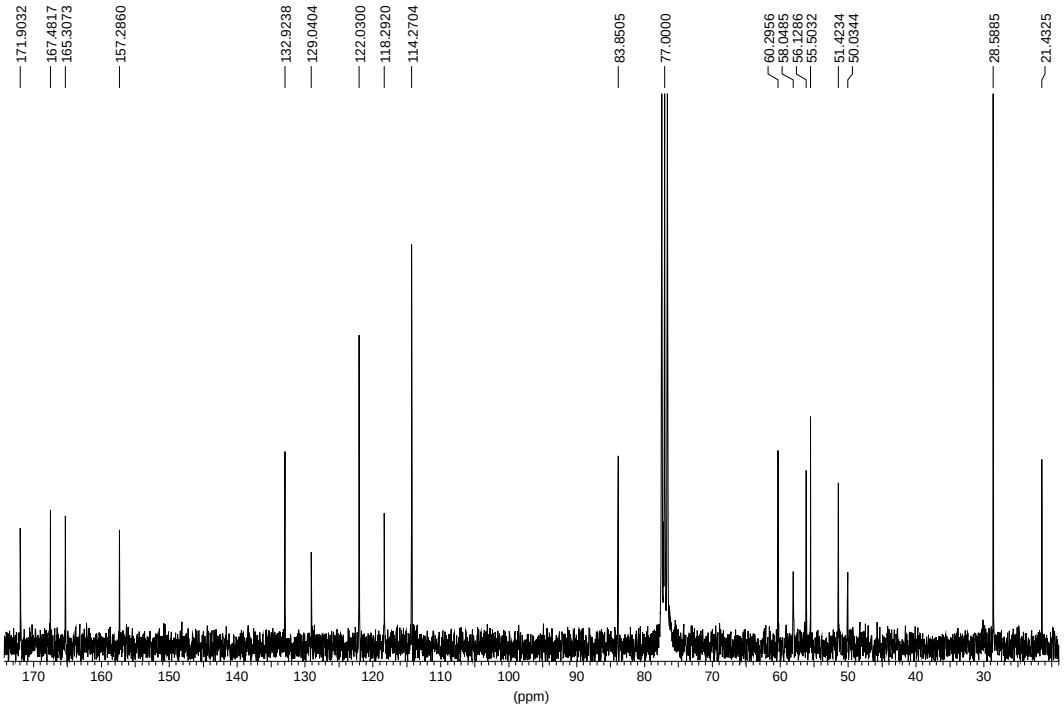


300 MHz ($CDCl_3$, 25ºC)



anti-(+)-**3f**

75 MHz ($CDCl_3$, 25ºC)



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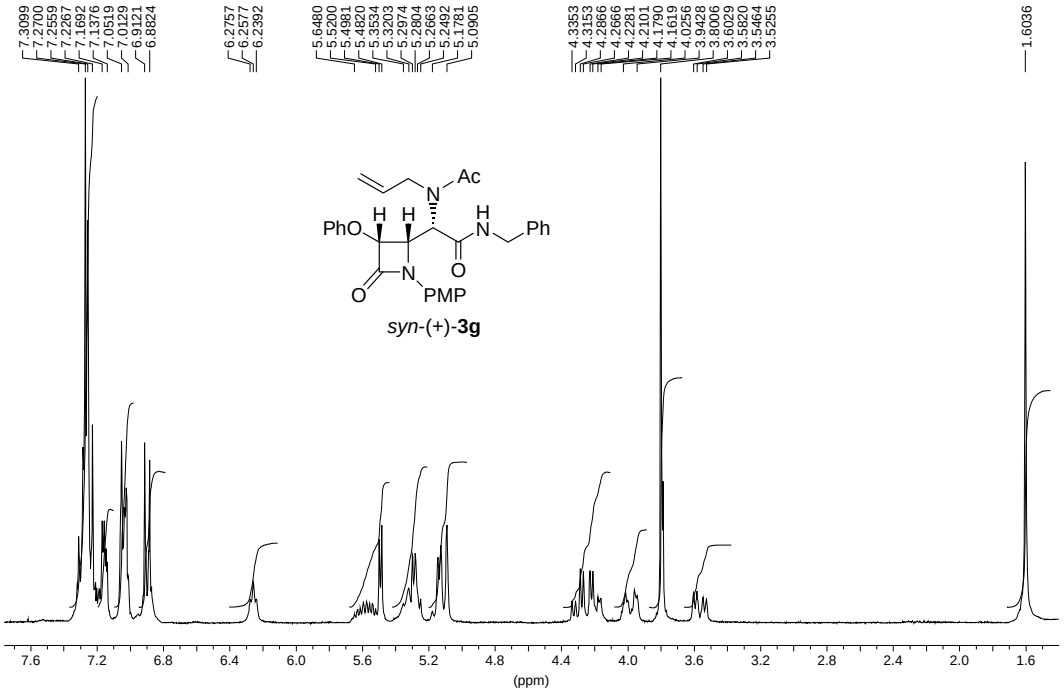
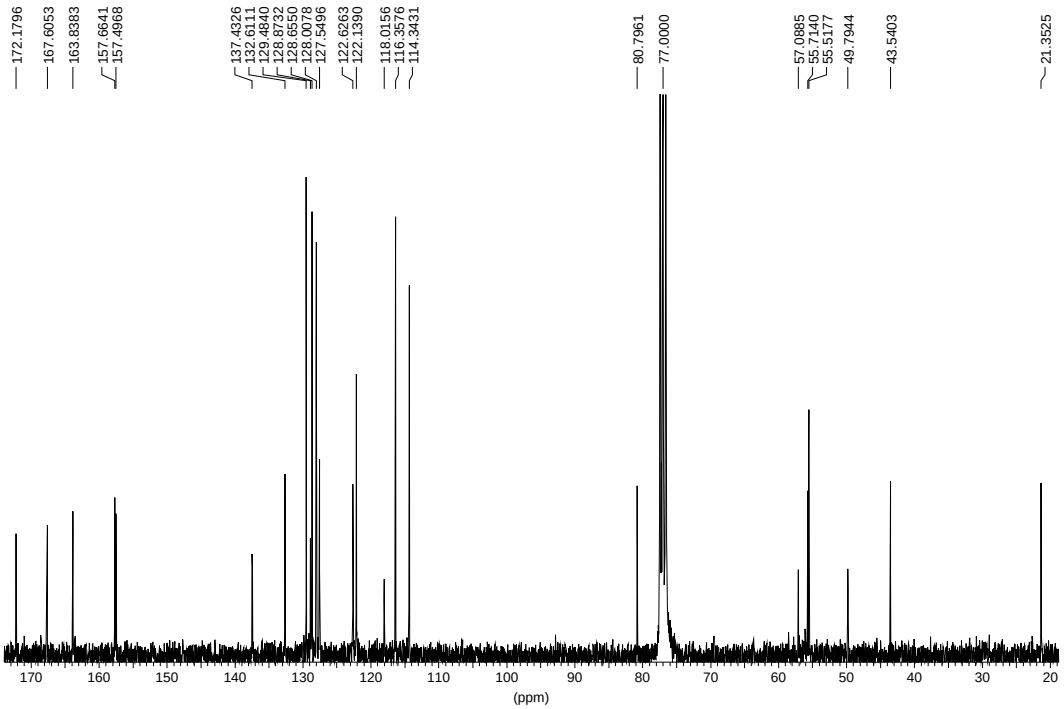


75 MHz ($CDCl_3$, 25ºC)



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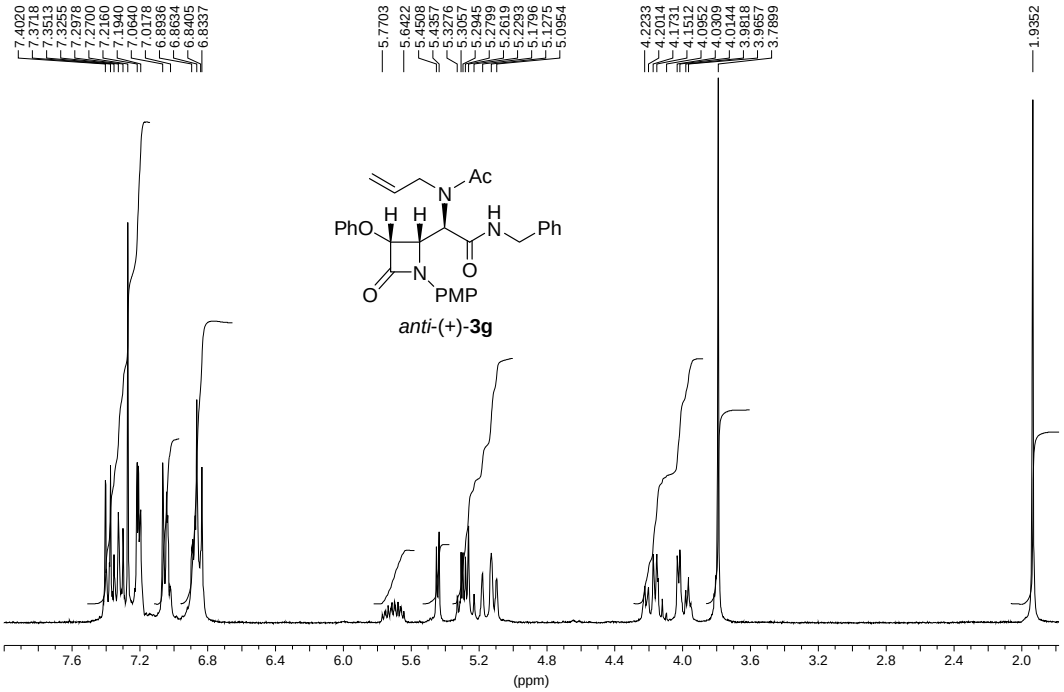

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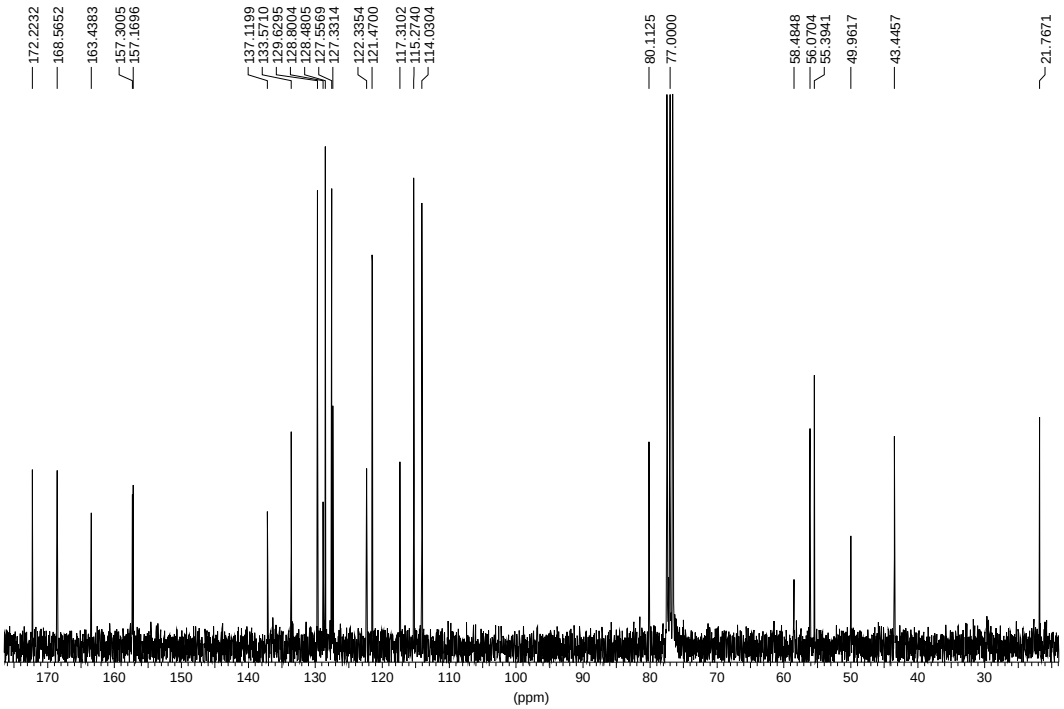

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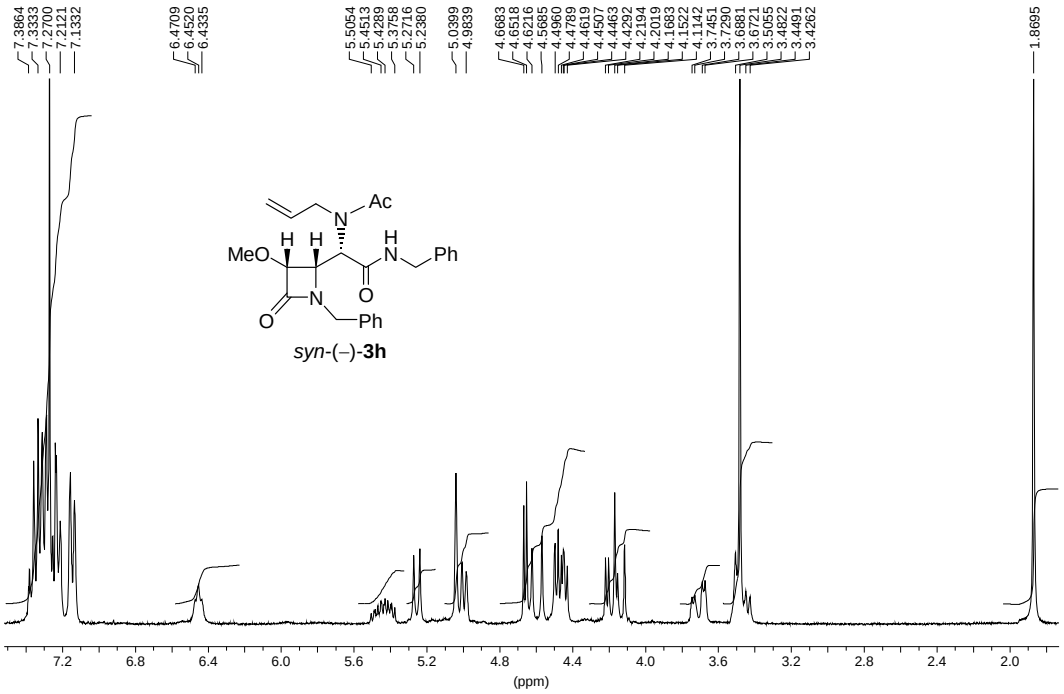
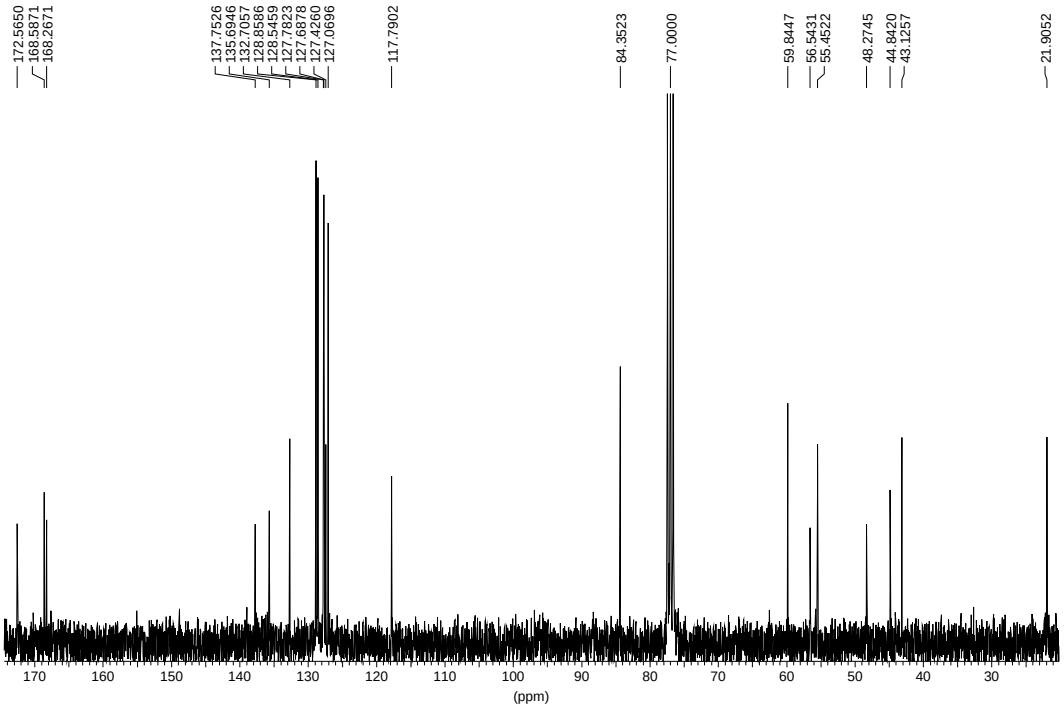
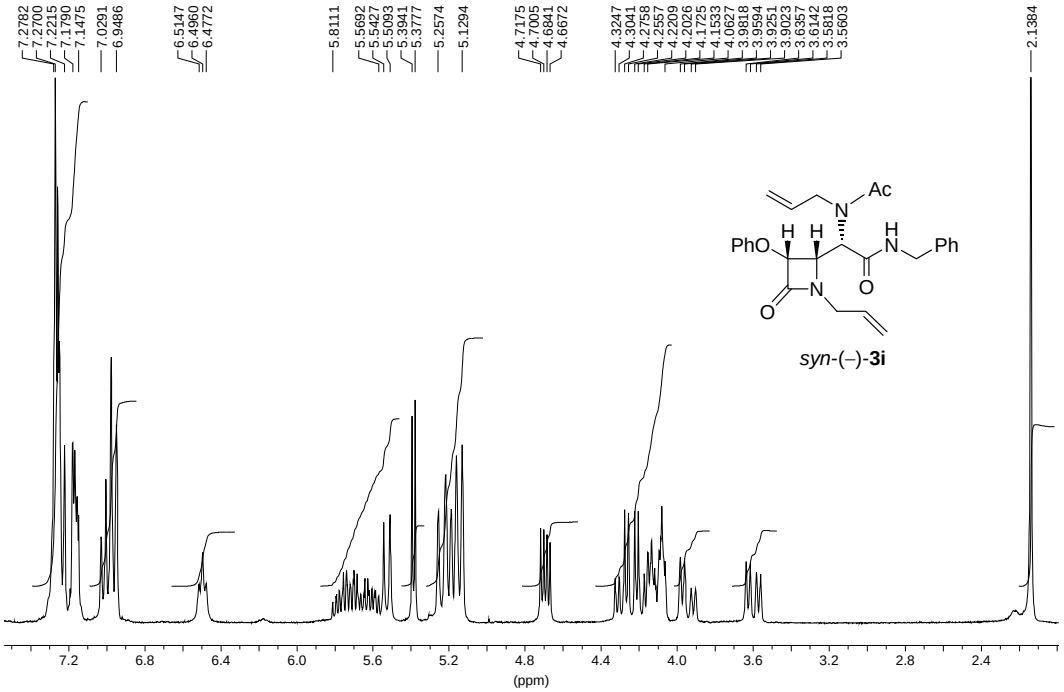


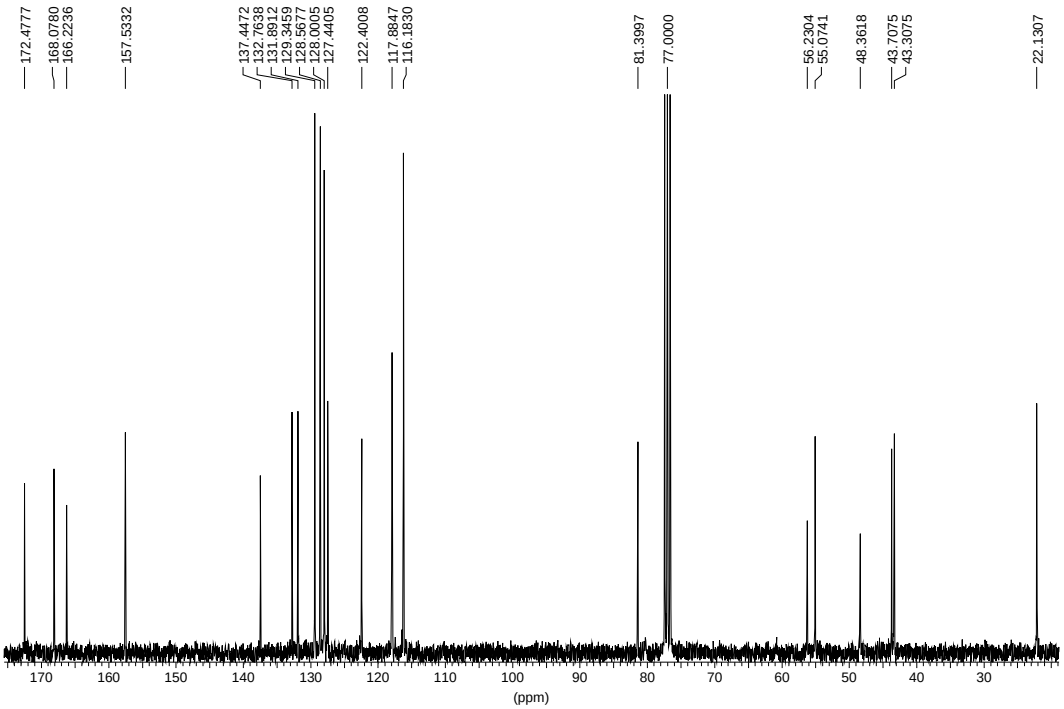
75 MHz ($CDCl_3$, 25ºC)



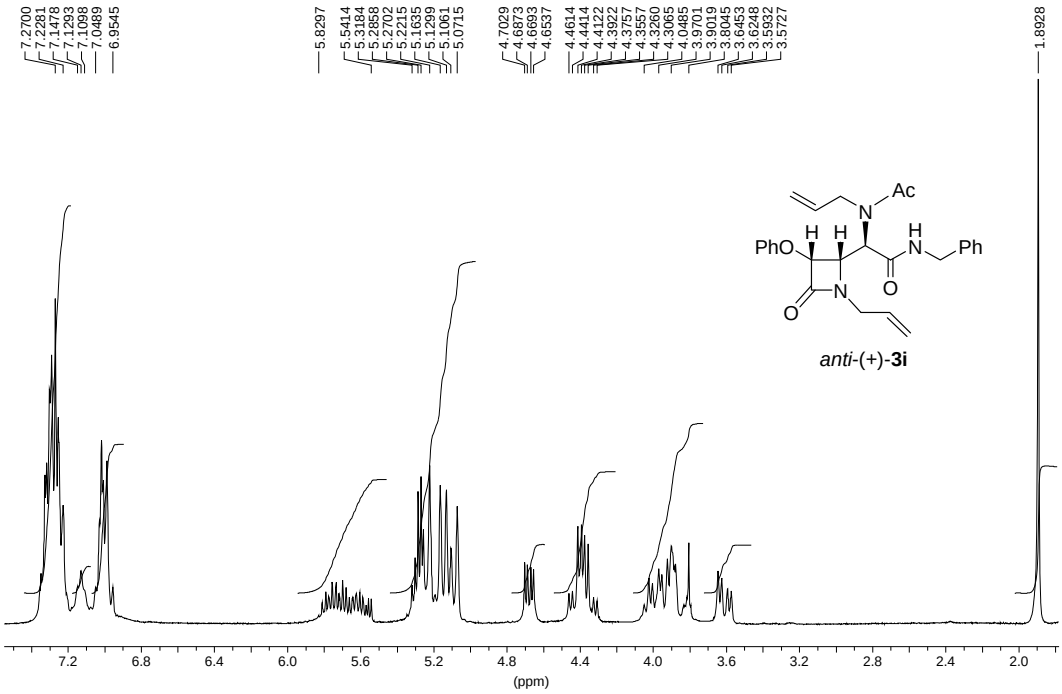
300 MHz ($CDCl_3$, 25ºC)



75 MHz ($CDCl_3$, 25ºC)

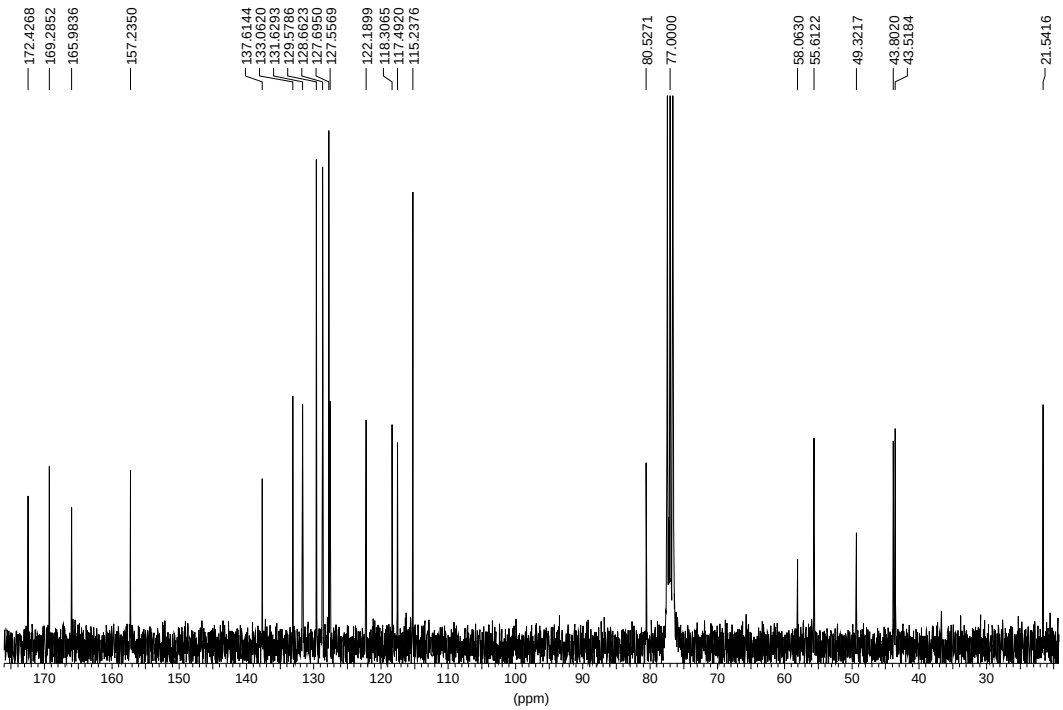


300 MHz ($CDCl_3$, 25ºC)

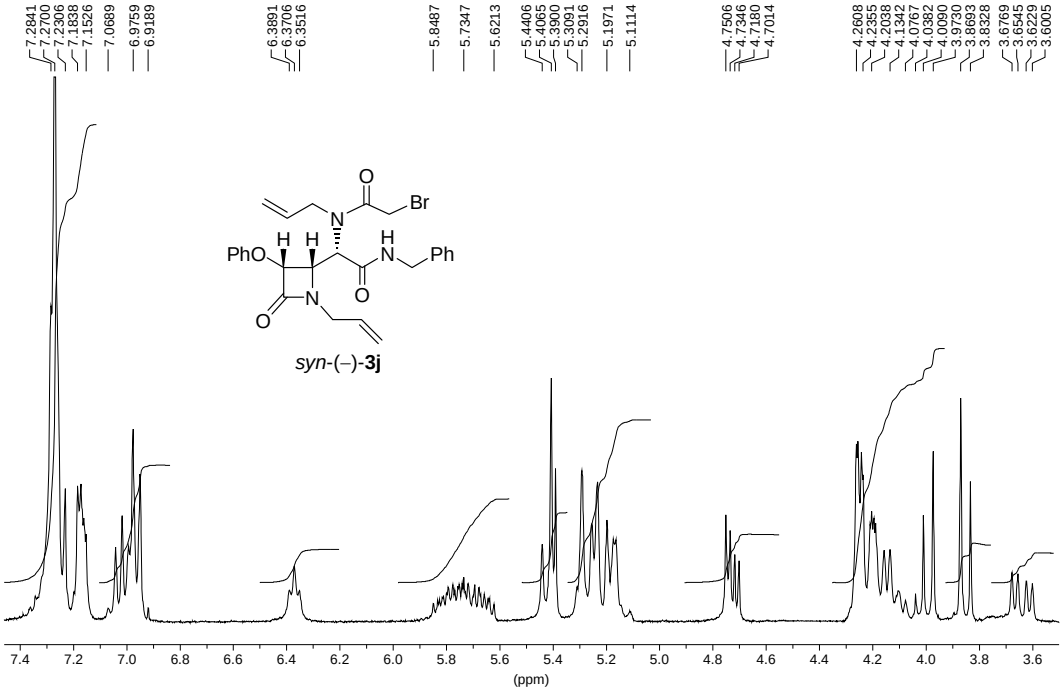


anti-(+)-**3i**

75 MHz ($CDCl_3$, 25ºC)



300 MHz ($CDCl_3$, 25ºC)



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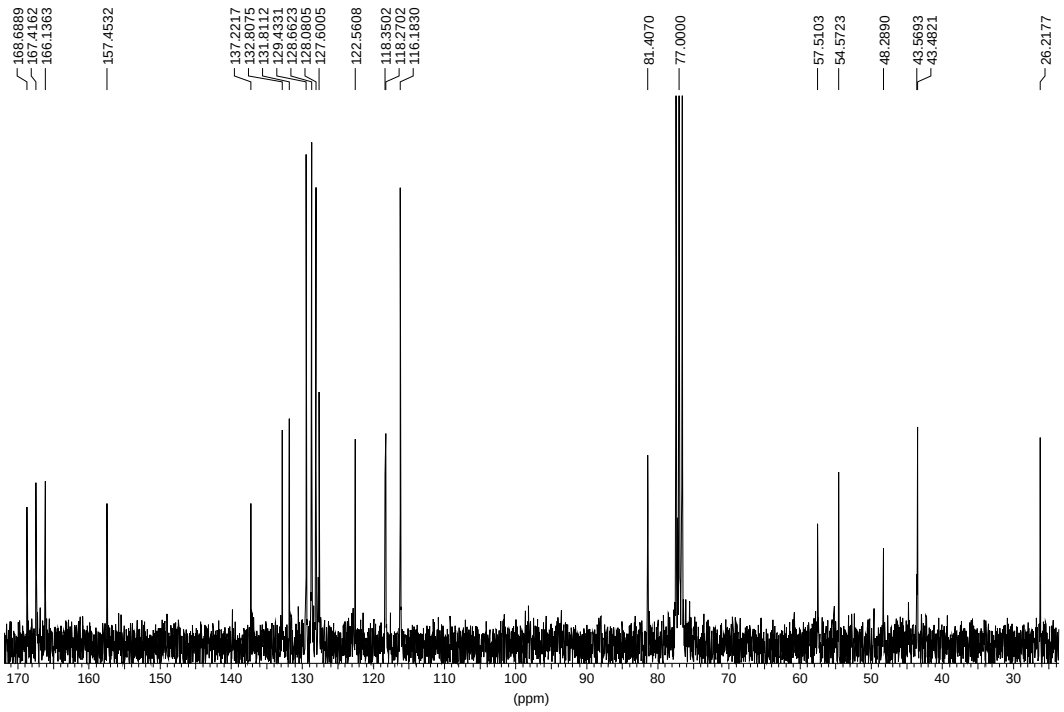
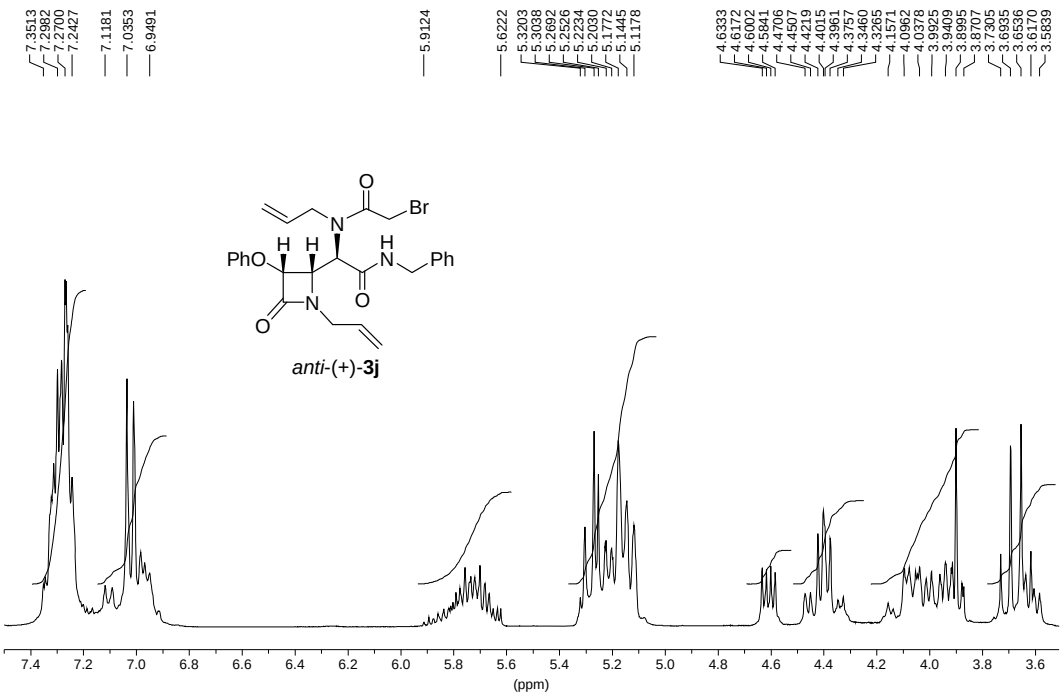
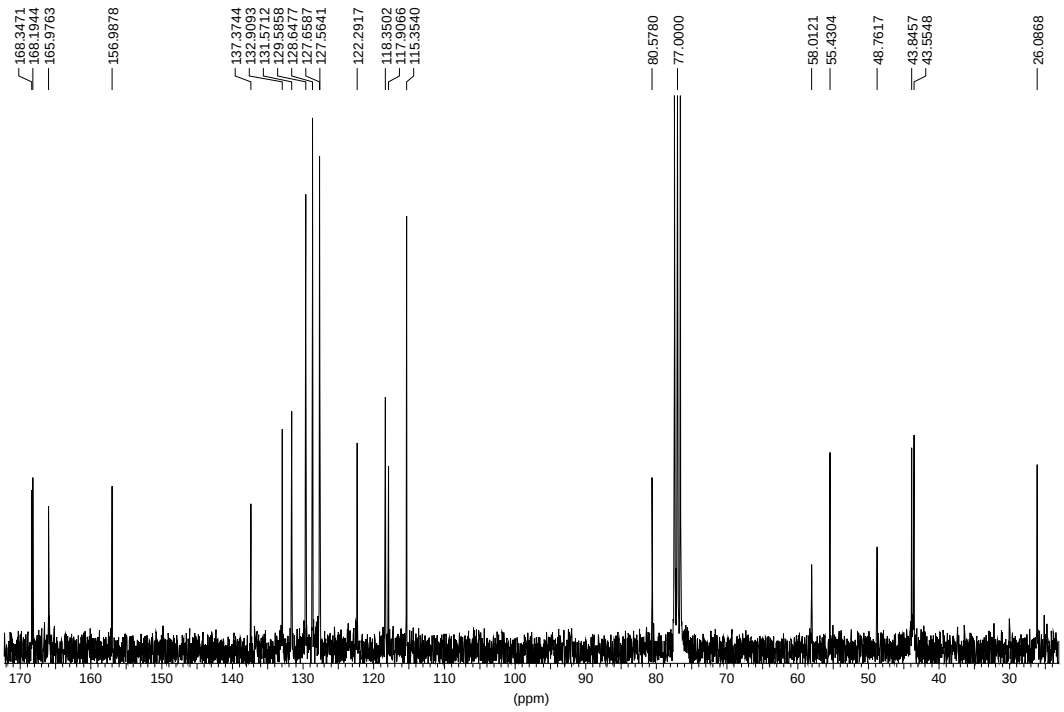


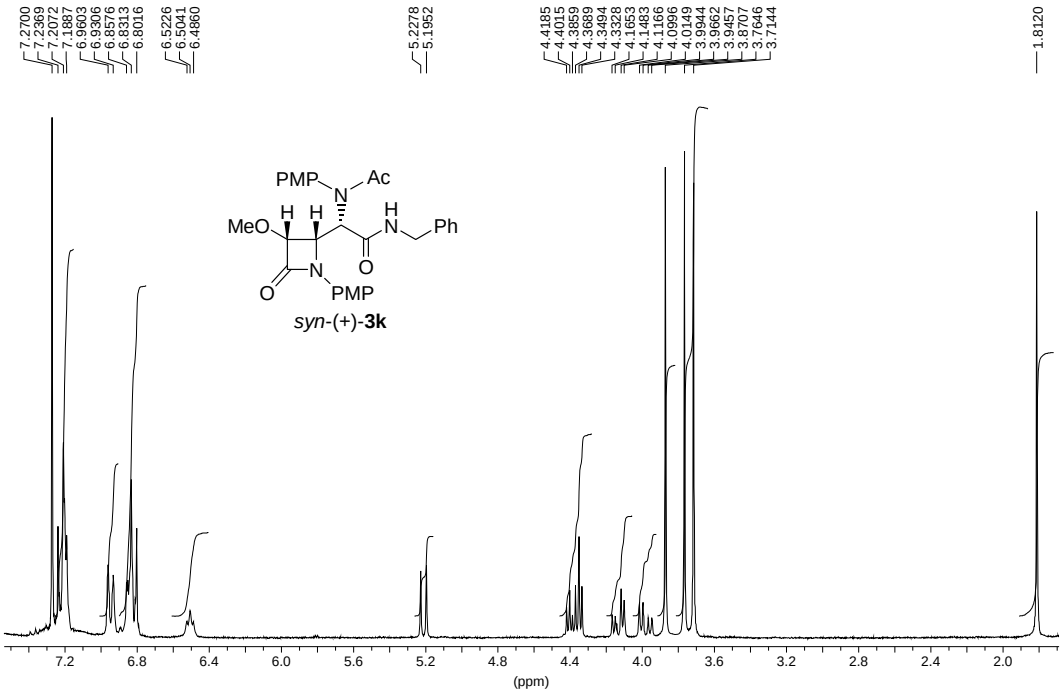
300 MHz ($CDCl_3$, 25ºC)



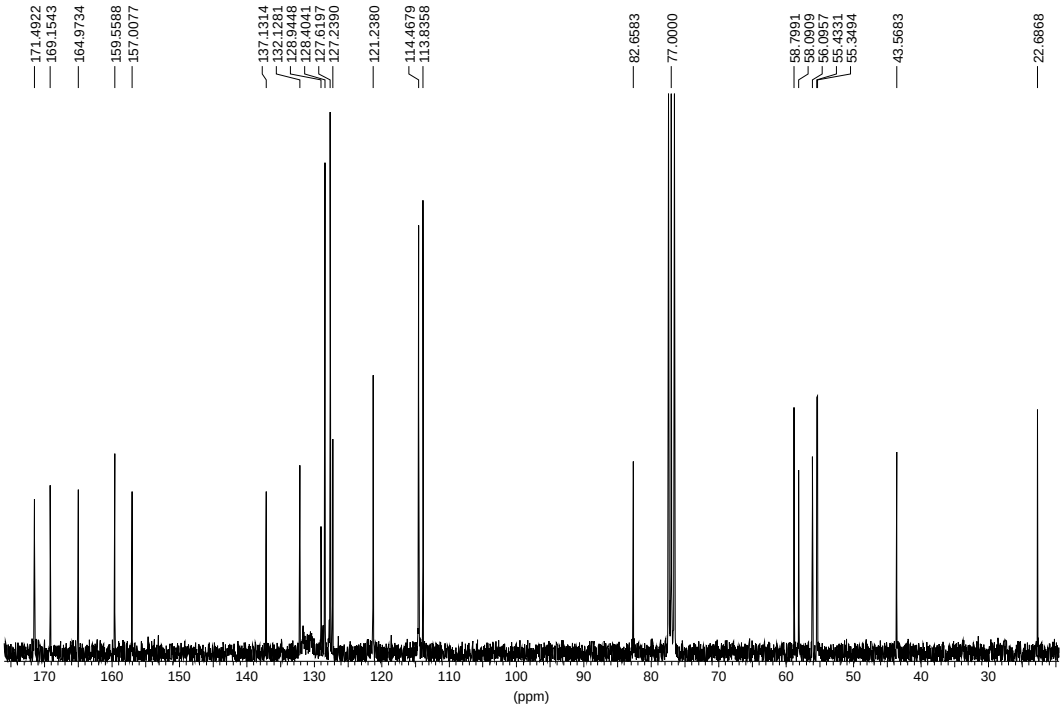
75 MHz ($CDCl_3$, 25ºC)



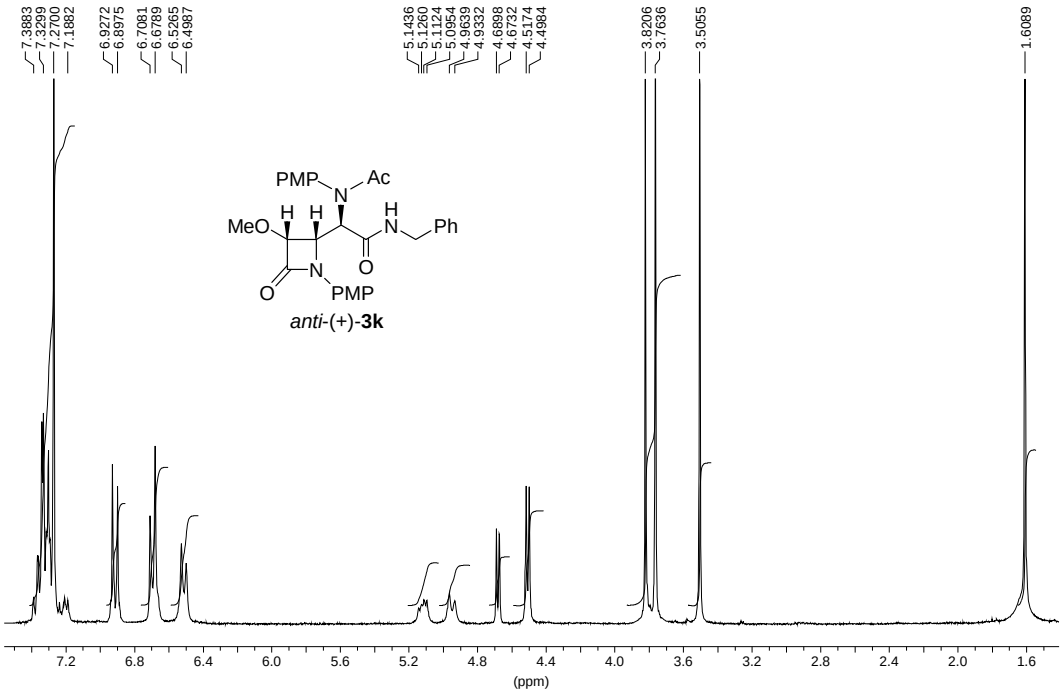
300 MHz ($CDCl_3$, 25ºC)



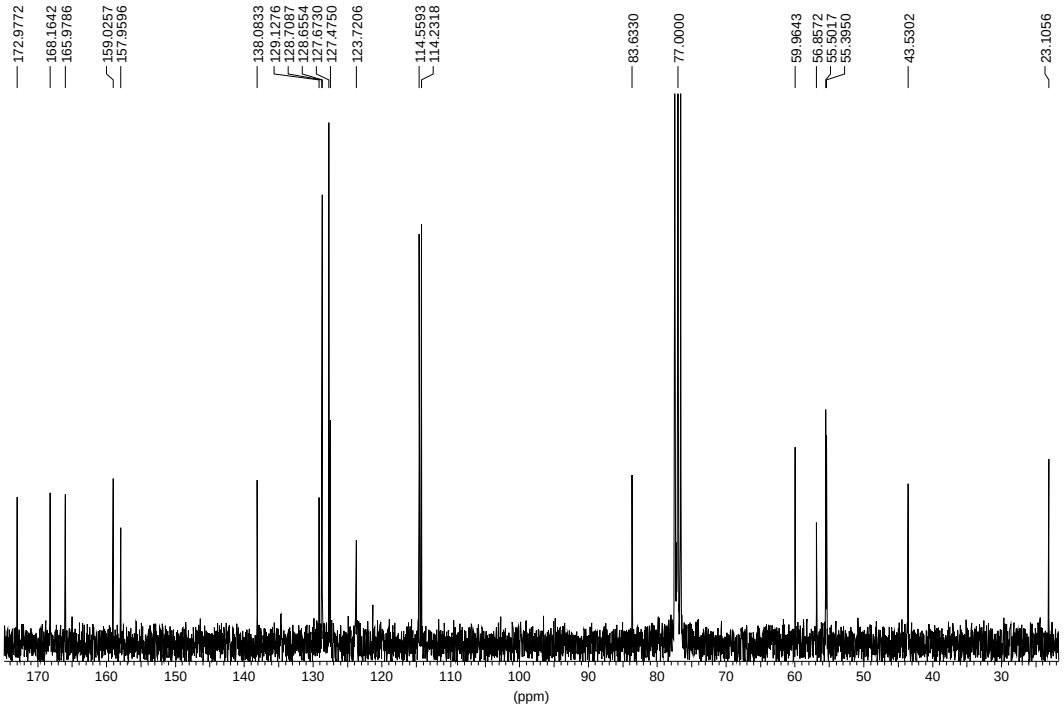
75 MHz ($CDCl_3$, 25ºC)



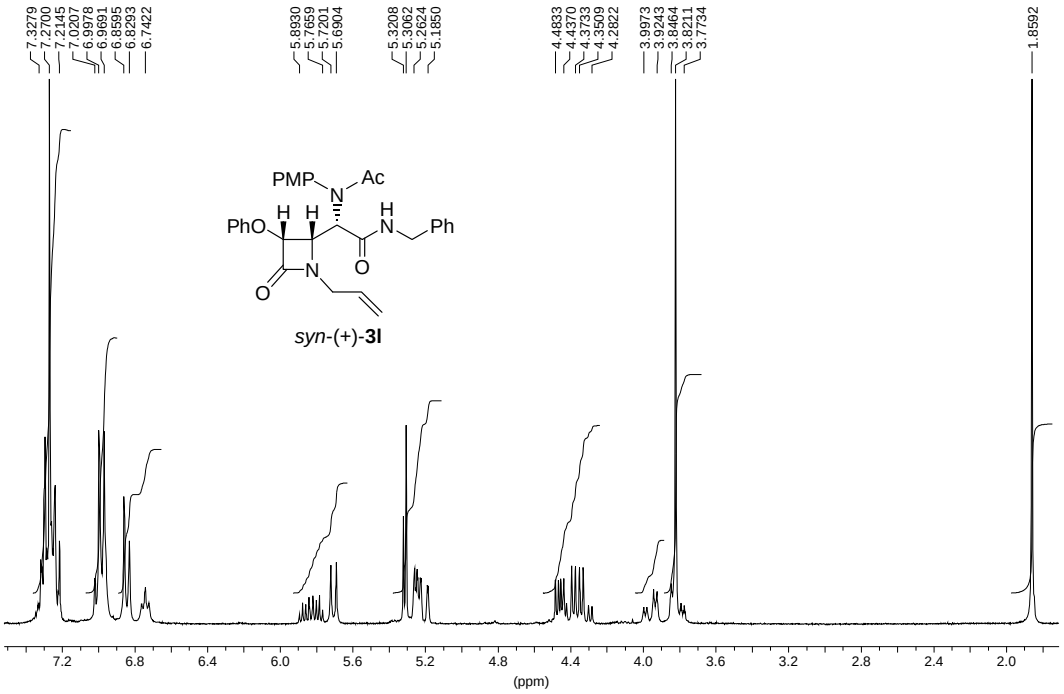
300 MHz ($CDCl_3$, 25ºC)



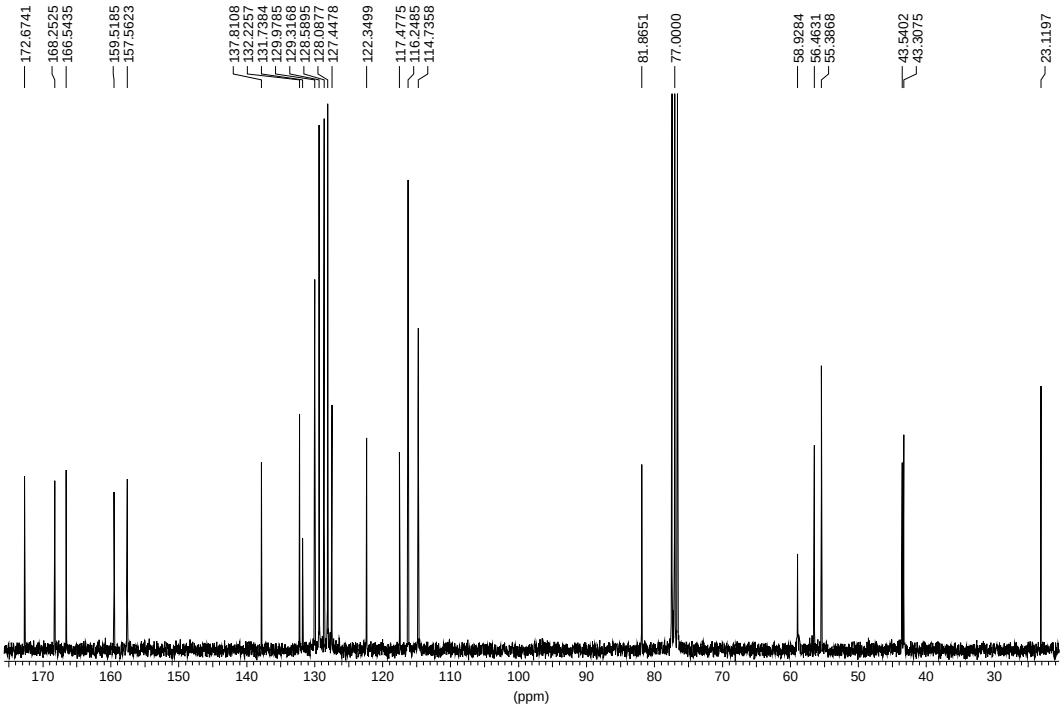
75 MHz ($CDCl_3$, 25ºC)



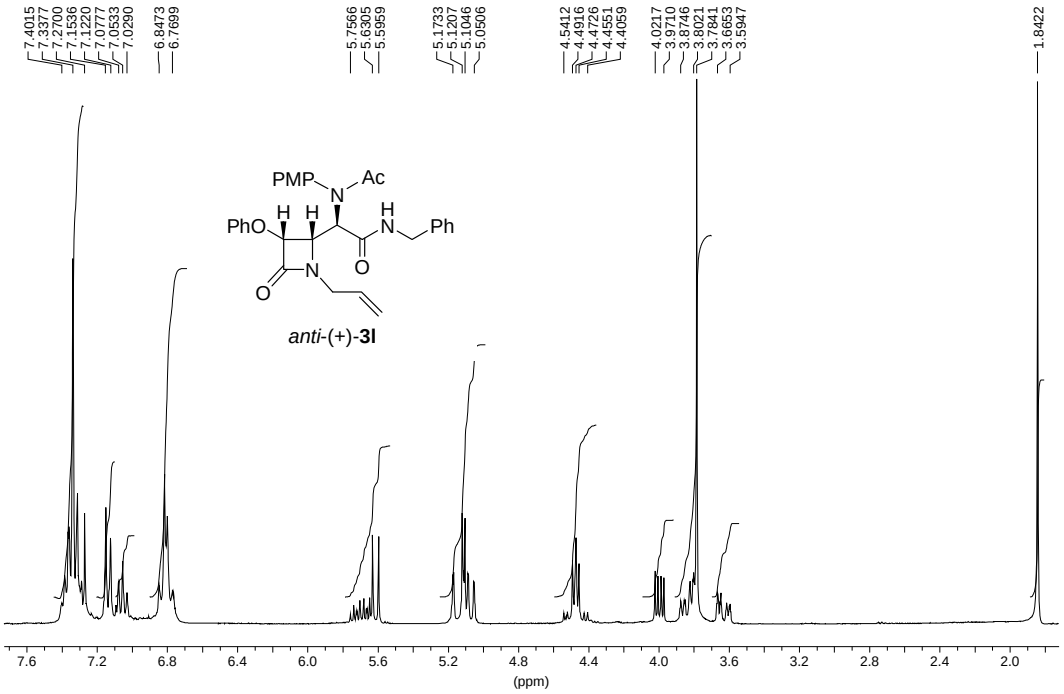
300 MHz ($CDCl_3$, 25ºC)



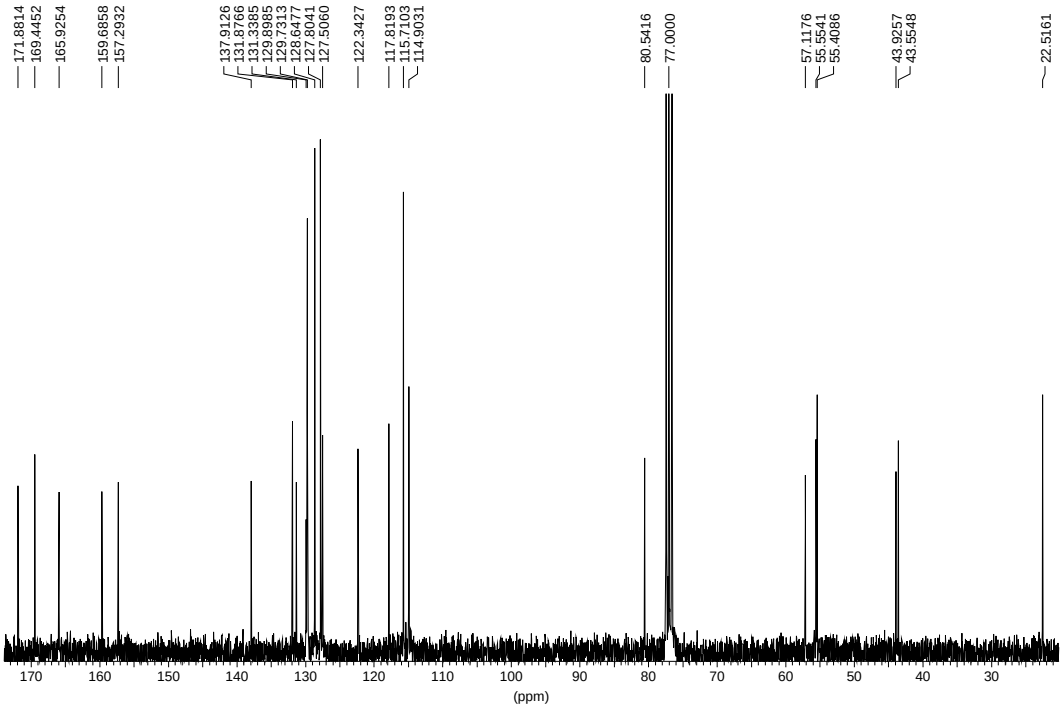
75 MHz ($CDCl_3$, 25ºC)



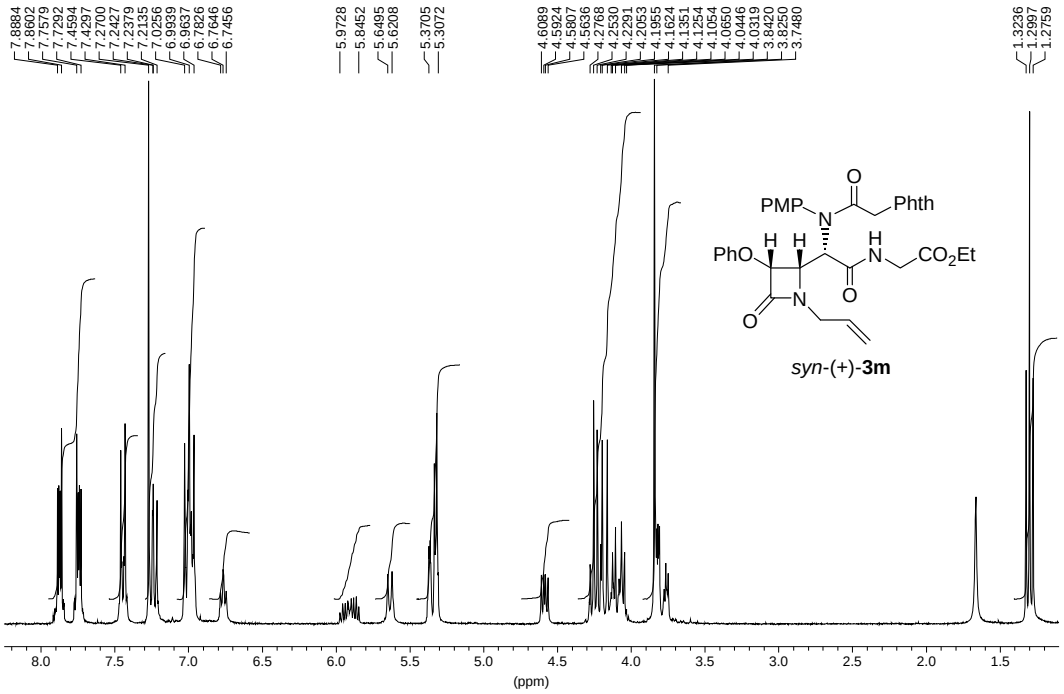
300 MHz ($CDCl_3$, 25ºC)



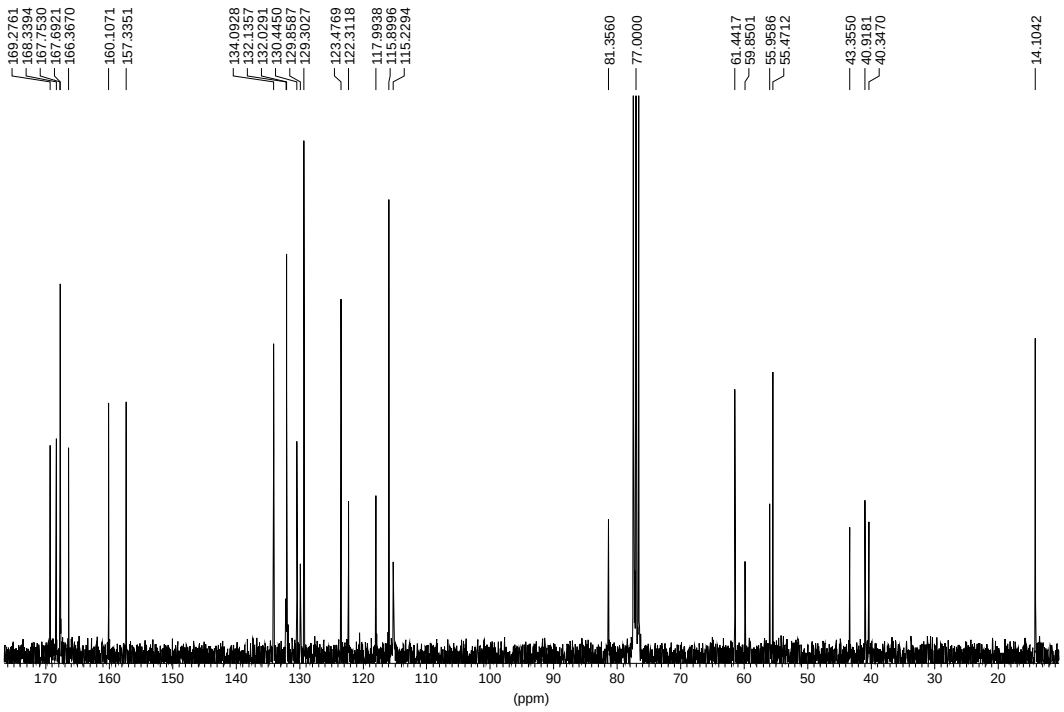
75 MHz ($CDCl_3$, 25ºC)



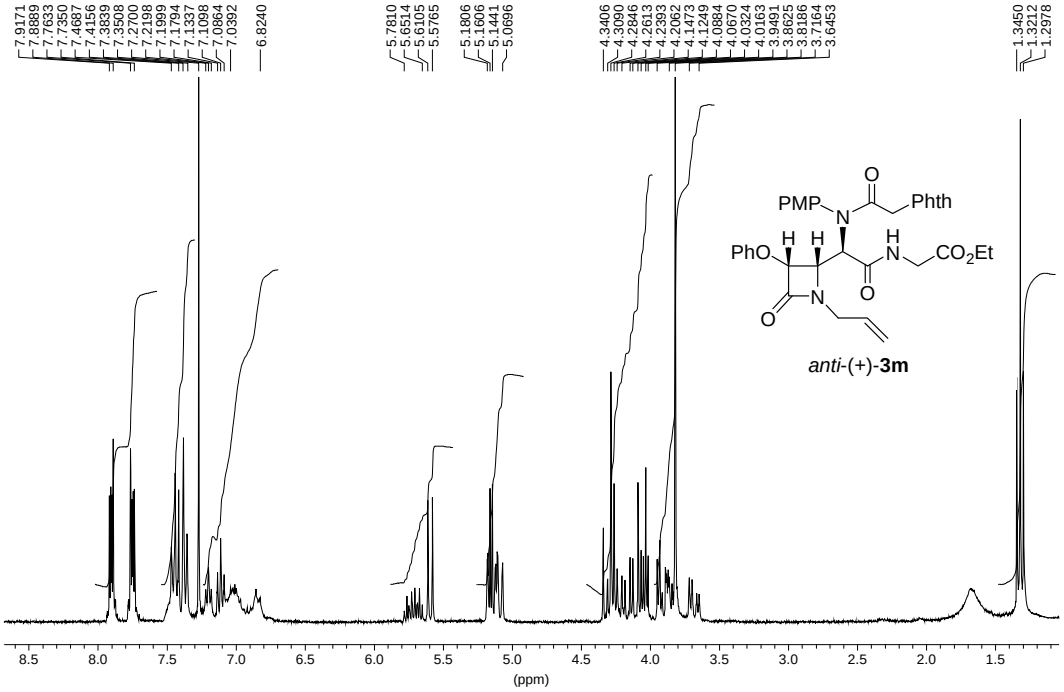
300 MHz ($CDCl_3$, 25ºC)



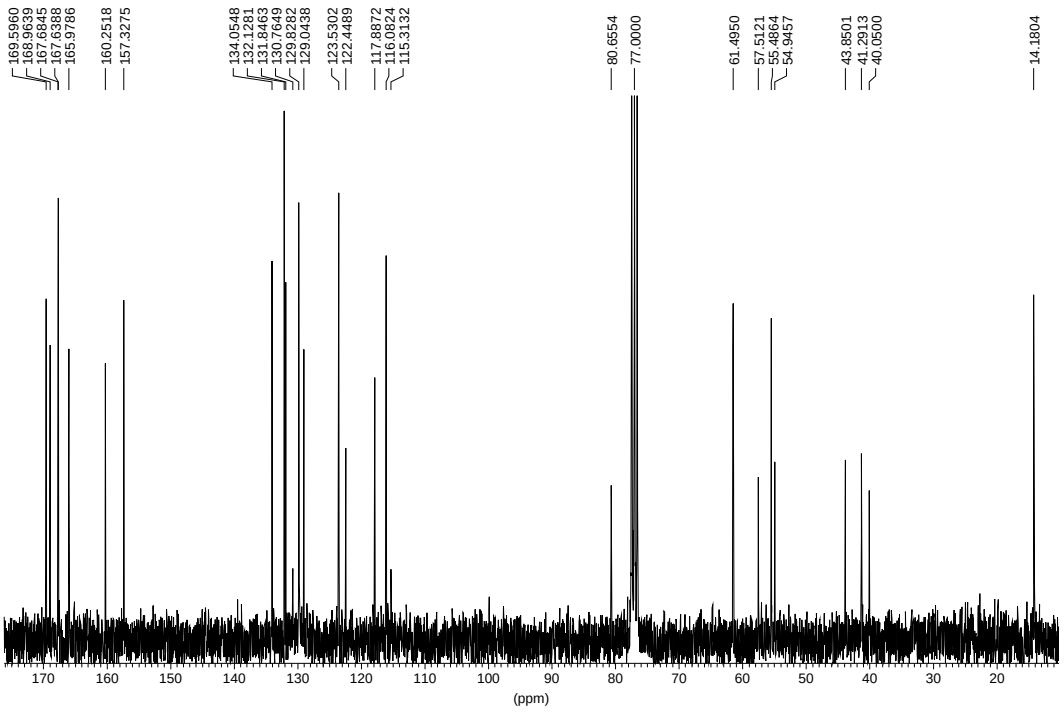
75 MHz ($CDCl_3$, 25ºC)



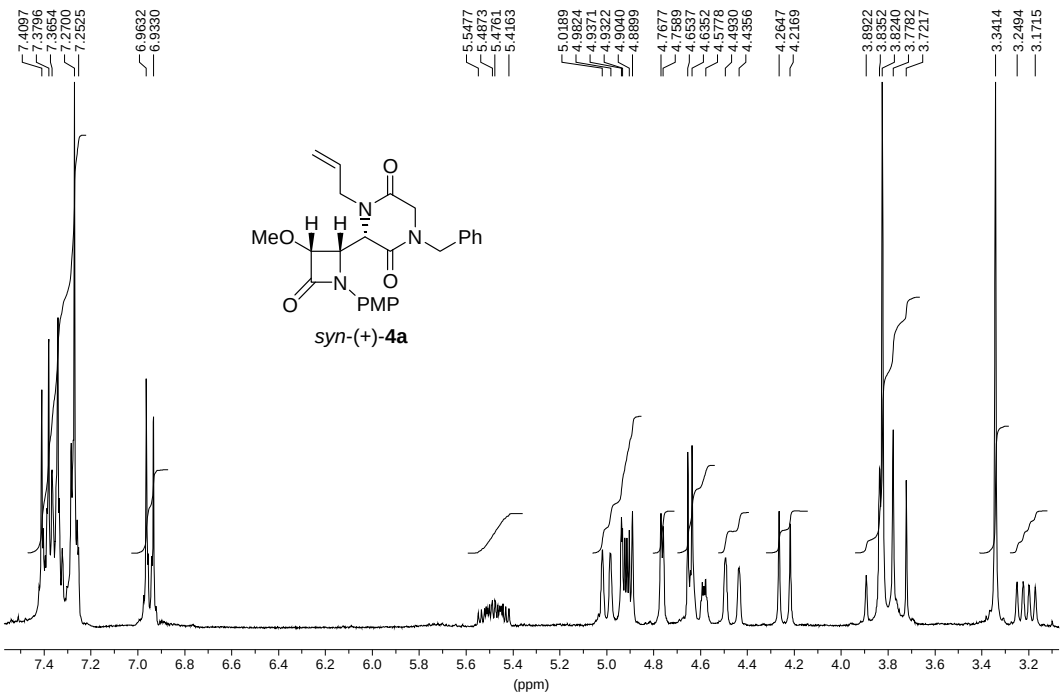
300 MHz ($CDCl_3$, 25ºC)



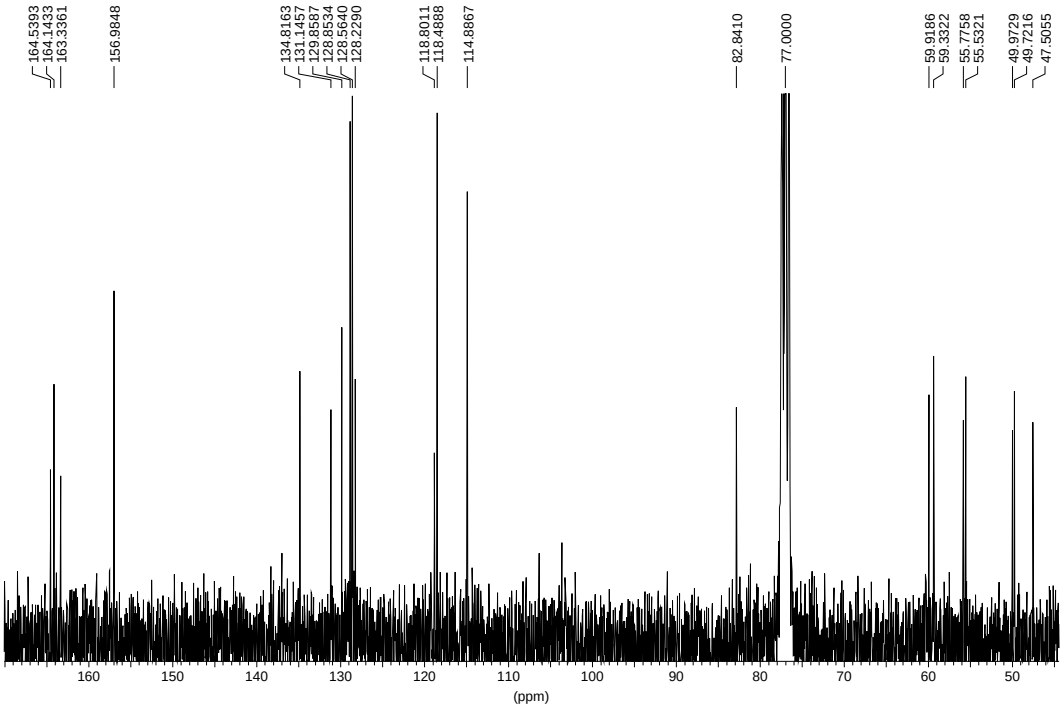
75 MHz ($CDCl_3$, 25ºC)



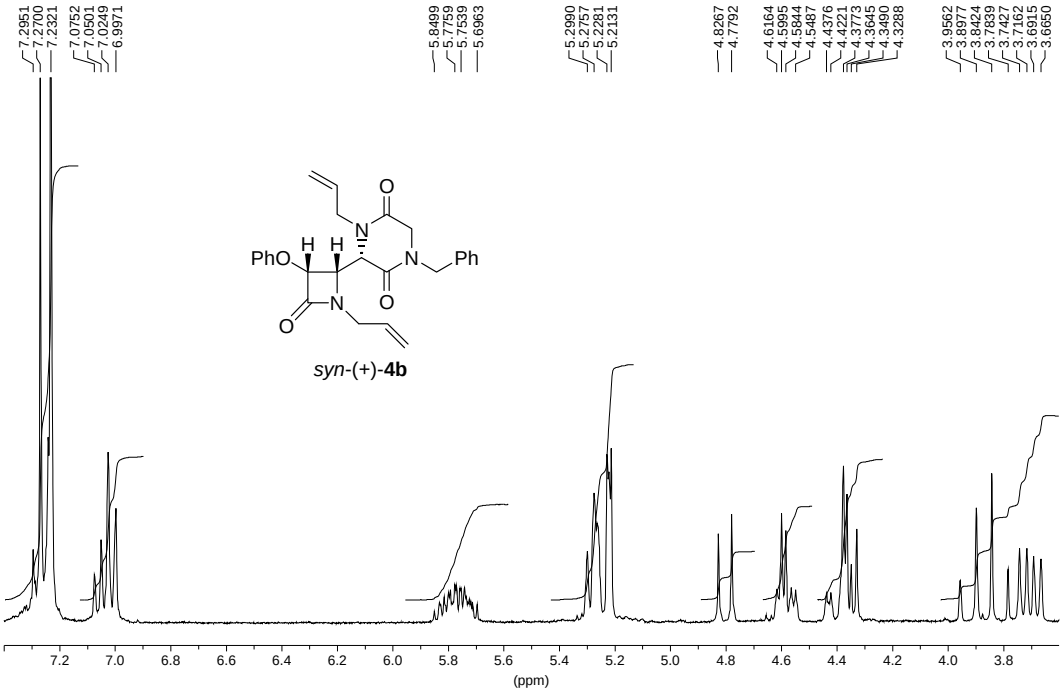
300 MHz ($CDCl_3$, 25ºC)



75 MHz ($CDCl_3$, 25ºC)

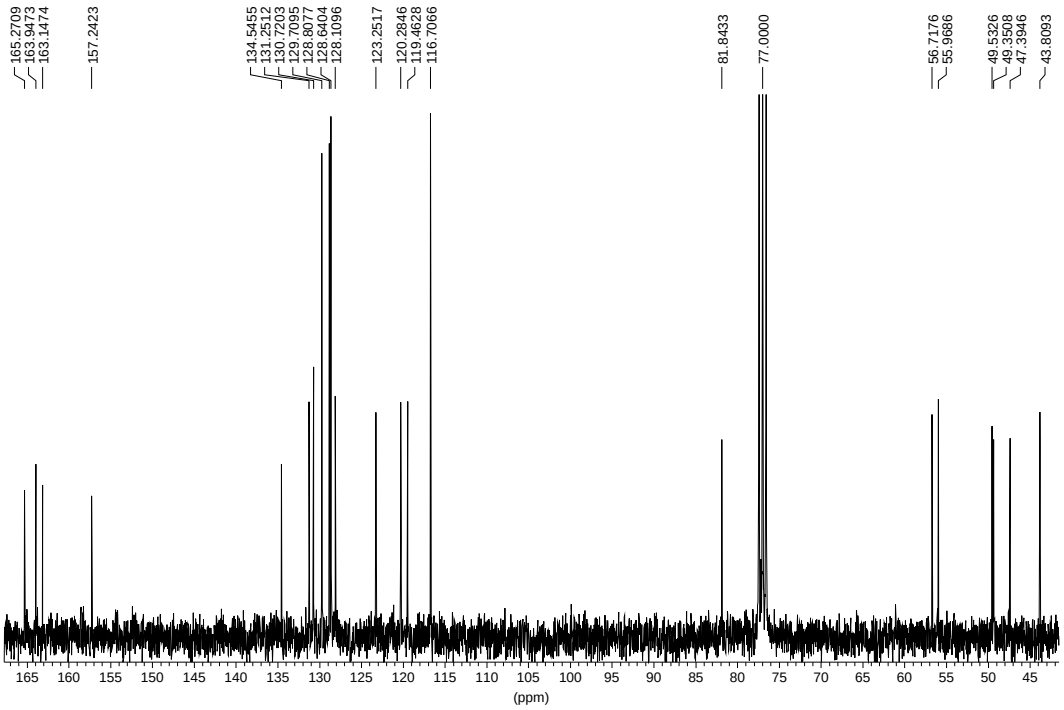


300 MHz ($CDCl_3$, 25ºC)

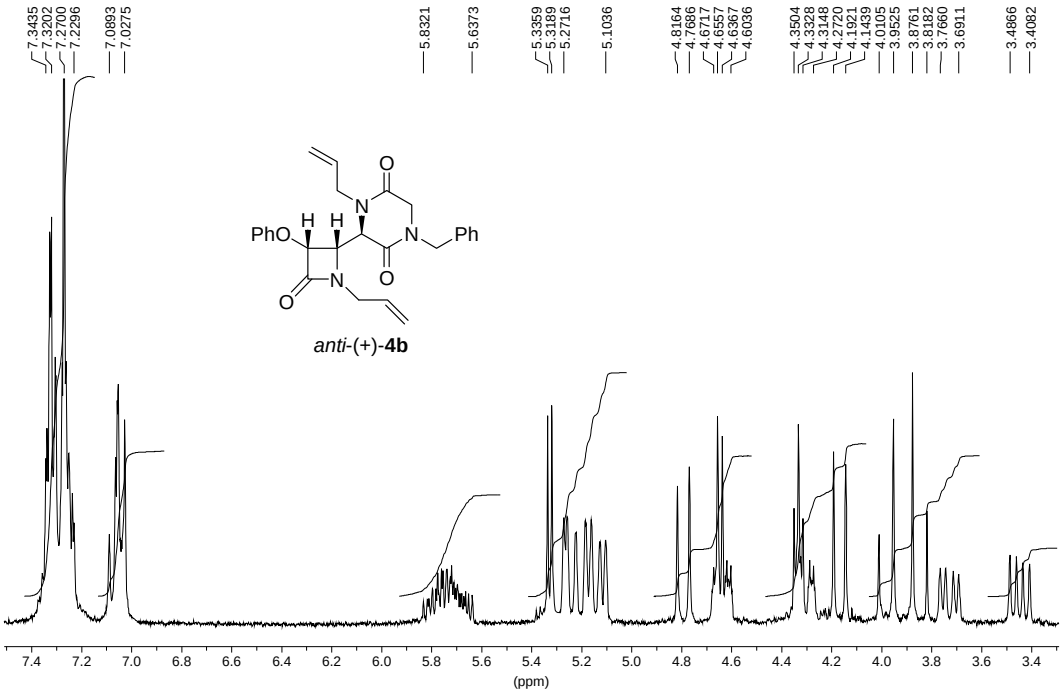


syn-(+)-**4b**

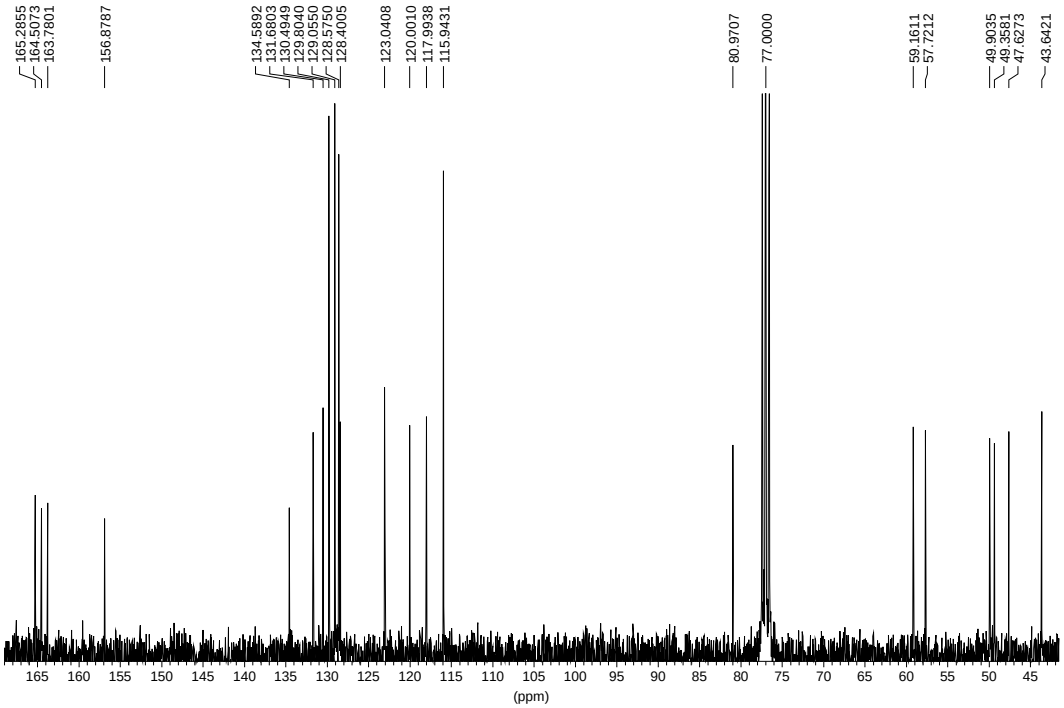
75 MHz ($CDCl_3$, 25ºC)



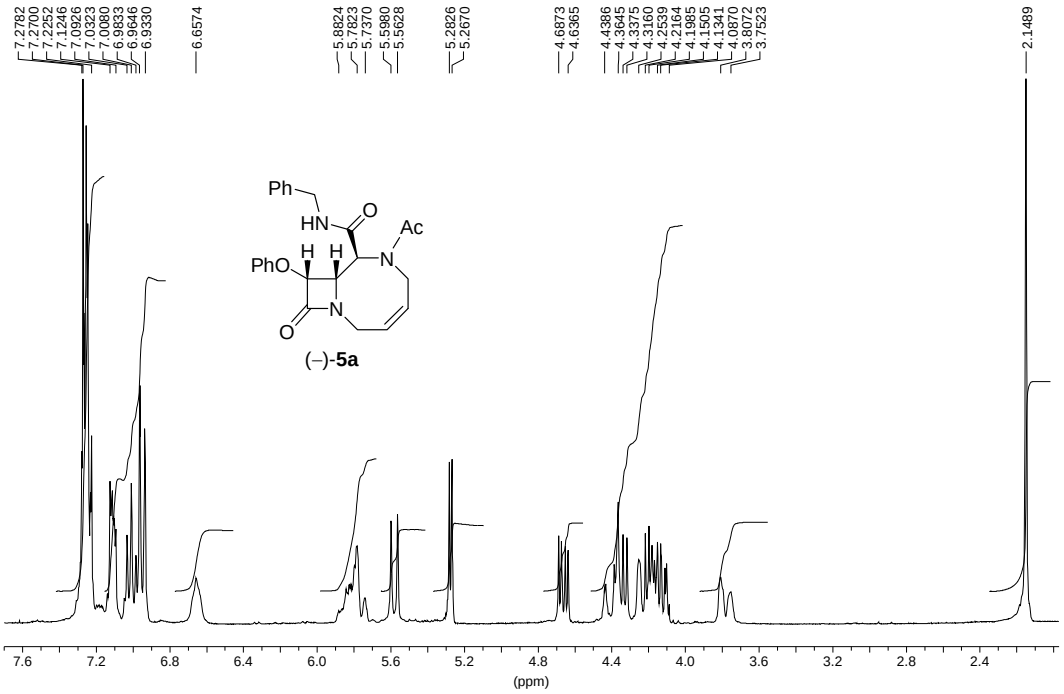
300 MHz ($CDCl_3$, 25ºC)



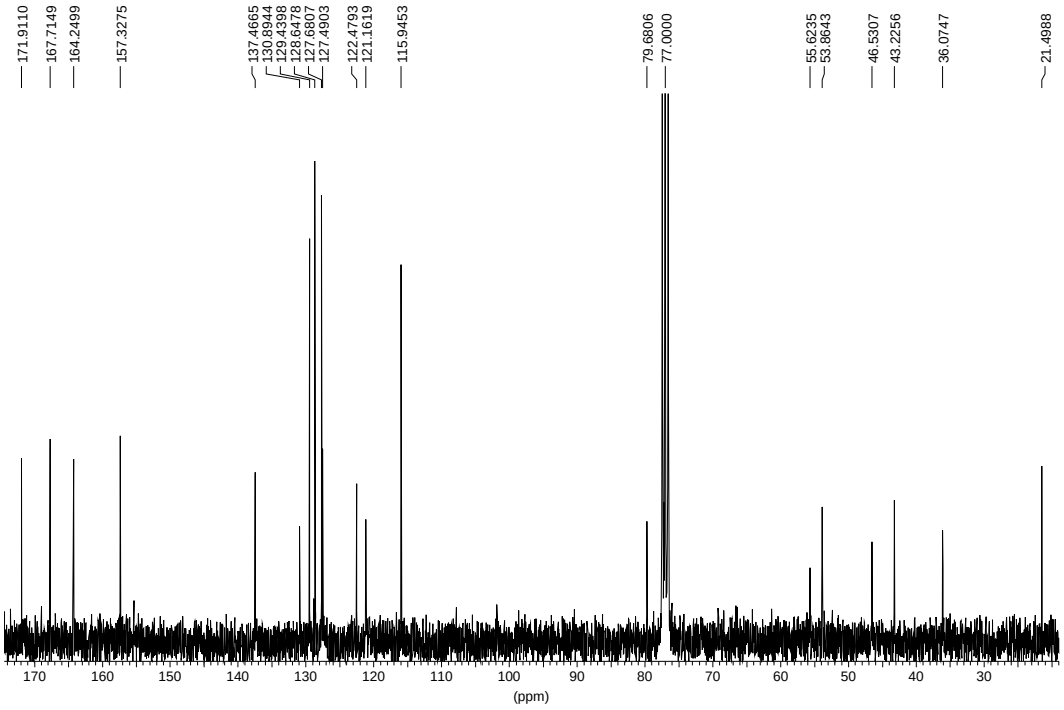
75 MHz ($CDCl_3$, 25ºC)



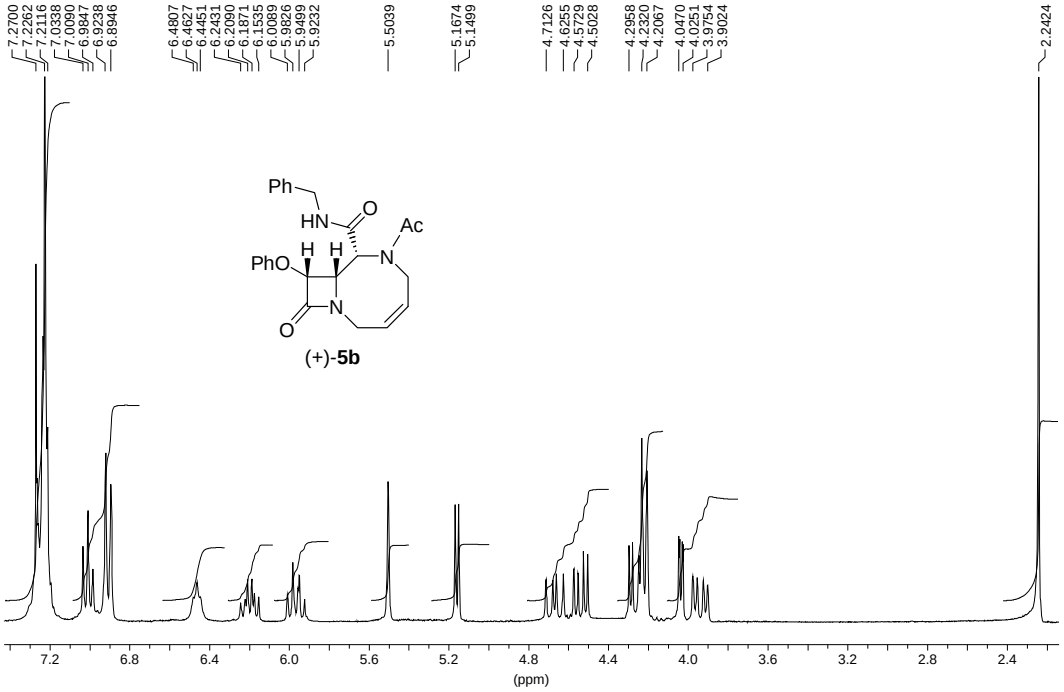
300 MHz ($CDCl_3$, 25ºC)



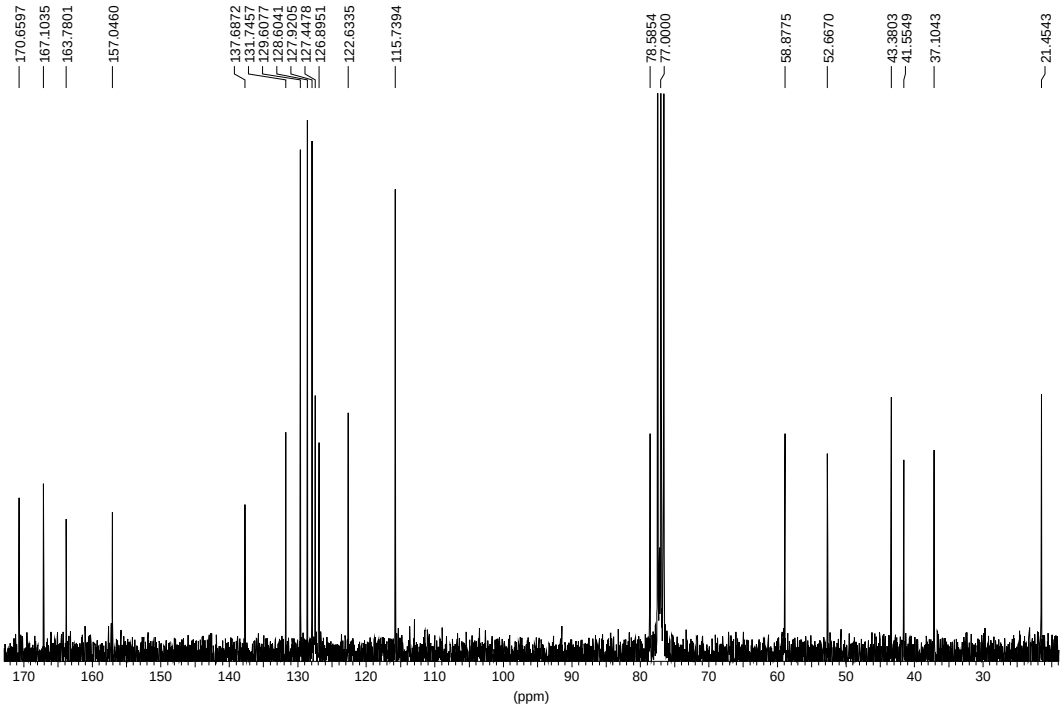
75 MHz ($CDCl_3$, 25ºC)



300 MHz ($CDCl_3$, 25ºC)



75 MHz ($CDCl_3$, 25ºC)



X-Ray data for compound *anti*-(+)-2d

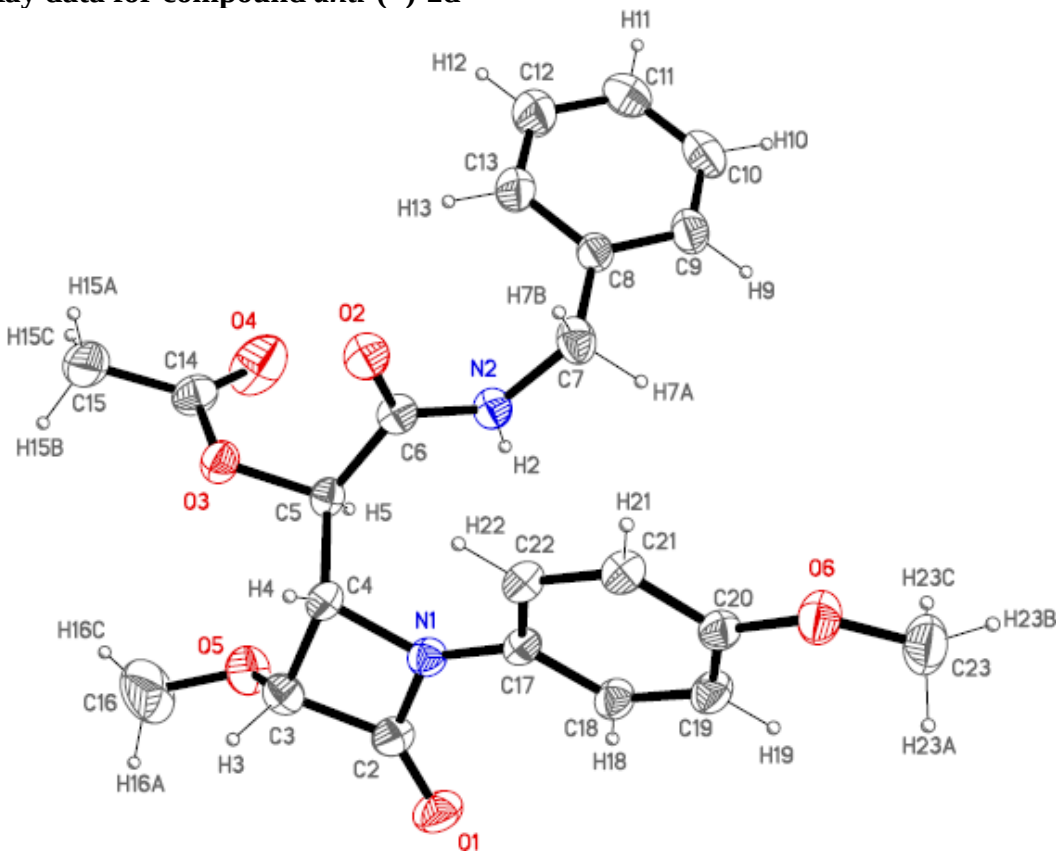


Table 1. Crystal data and structure refinement for C22H24N2O6.

Empirical formula	C22 H24 N2 O6	
Formula weight	412.43	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 9.4466(14) Å	α= 90°.
	b = 12.1860(18) Å	β= 90°.
	c = 18.704(3) Å	γ = 90°.
Volume	2153.2(6) $Å^3$	
Z	4	
Density (calculated)	1.272 Mg/m^3	
Absorption coefficient	0.093 mm^{-1}	
F(000)	872	
Crystal size	0.56 x 0.18 x 0.09 mm^3	
Theta range for data collection	1.99 to 26.00°.	
Index ranges	-11<=h<=11, -15<=k<=14, -21<=l<=23	
Reflections collected	17599	

Independent reflections	4213 [R(int) = 0.0822]
Completeness to theta = 26.00°	99.8 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4213 / 0 / 272
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0526, wR2 = 0.1280
R indices (all data)	R1 = 0.1557, wR2 = 0.1747
Absolute structure parameter	0(2)
Extinction coefficient	0.0094(18)
Largest diff. peak and hole	0.278 and -0.155 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for C22H24N2O6. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(2)	5484(4)	2866(3)	-417(2)	60(1)
C(2)	6255(6)	4044(4)	1765(3)	67(1)
C(3)	5537(5)	3007(4)	2004(2)	68(1)
C(4)	4695(5)	3073(3)	1295(2)	56(1)
C(5)	5008(4)	2175(3)	762(2)	54(1)
C(6)	4514(4)	2448(3)	11(2)	56(1)
C(7)	5187(5)	3278(4)	-1129(2)	74(1)
C(8)	5723(5)	2554(4)	-1709(2)	64(1)
C(9)	6550(5)	2947(5)	-2254(3)	79(2)
C(10)	7033(6)	2277(6)	-2793(3)	90(2)
C(11)	6674(7)	1195(6)	-2805(3)	109(2)
C(12)	5855(8)	794(5)	-2263(3)	118(2)
C(13)	5390(6)	1443(4)	-1723(3)	91(2)
C(14)	4586(6)	264(4)	803(3)	76(1)
C(15)	3709(7)	-621(4)	1097(3)	102(2)
C(16)	6002(9)	1442(6)	2677(3)	162(3)
C(17)	5173(5)	4990(3)	690(2)	55(1)
C(18)	6169(5)	5799(3)	594(2)	63(1)
C(19)	5906(5)	6669(4)	148(2)	70(1)
C(20)	4639(5)	6750(3)	-203(2)	60(1)
C(21)	3632(5)	5936(4)	-116(2)	60(1)
C(22)	3894(5)	5062(3)	331(2)	59(1)
C(23)	5347(7)	8267(5)	-926(3)	107(2)
N(1)	5446(4)	4109(3)	1163(2)	59(1)
O(6)	4255(4)	7595(2)	-647(2)	81(1)
O(1)	7165(4)	4656(3)	2002(2)	93(1)
O(2)	3265(3)	2330(3)	-170(2)	73(1)
O(3)	4196(3)	1255(2)	1026(2)	68(1)
O(4)	5537(5)	165(3)	377(3)	137(2)
O(5)	6391(4)	2095(3)	2113(2)	86(1)

Table 3. Bond lengths [Å] and angles [°] for C22H24N2O6.

N(2)-C(6)	1.319(5)
N(2)-C(7)	1.452(5)
N(2)-H(2)	0.8600
C(2)-O(1)	1.221(5)
C(2)-N(1)	1.362(6)
C(2)-C(3)	1.502(6)
C(3)-O(5)	1.388(5)
C(3)-C(4)	1.549(6)
C(3)-H(3)	0.9800
C(4)-N(1)	1.468(5)
C(4)-C(5)	1.510(5)
C(4)-H(4)	0.9800
C(5)-O(3)	1.445(4)
C(5)-C(6)	1.517(6)
C(5)-H(5)	0.9800
C(6)-O(2)	1.236(5)
C(7)-C(8)	1.486(6)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(13)	1.391(6)
C(8)-C(9)	1.371(6)
C(9)-C(10)	1.374(7)
C(9)-H(9)	0.9300
C(10)-C(11)	1.362(7)
C(10)-H(10)	0.9300
C(11)-C(12)	1.365(8)
C(11)-H(11)	0.9300
C(12)-C(13)	1.357(7)
C(12)-H(12)	0.9300
C(13)-H(13)	0.9300
C(14)-O(4)	1.207(6)
C(14)-O(3)	1.330(5)
C(14)-C(15)	1.467(7)
C(15)-H(15A)	0.9600
C(15)-H(15B)	0.9600
C(15)-H(15C)	0.9600

C(16)-O(5)	1.372(6)
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
C(17)-C(18)	1.375(5)
C(17)-C(22)	1.385(6)
C(17)-N(1)	1.415(5)
C(18)-C(19)	1.371(6)
C(18)-H(18)	0.9300
C(19)-C(20)	1.369(6)
C(19)-H(19)	0.9300
C(20)-O(6)	1.372(5)
C(20)-C(21)	1.384(6)
C(21)-C(22)	1.377(5)
C(21)-H(21)	0.9300
C(22)-H(22)	0.9300
C(23)-O(6)	1.417(6)
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600

C(6)-N(2)-C(7)	123.8(4)
C(6)-N(2)-H(2)	118.1
C(7)-N(2)-H(2)	118.1
O(1)-C(2)-N(1)	131.2(5)
O(1)-C(2)-C(3)	136.3(5)
N(1)-C(2)-C(3)	92.4(4)
O(5)-C(3)-C(2)	117.0(4)
O(5)-C(3)-C(4)	117.7(4)
C(2)-C(3)-C(4)	86.1(3)
O(5)-C(3)-H(3)	111.2
C(2)-C(3)-H(3)	111.2
C(4)-C(3)-H(3)	111.2
N(1)-C(4)-C(5)	114.7(3)
N(1)-C(4)-C(3)	86.6(3)
C(5)-C(4)-C(3)	115.3(3)
N(1)-C(4)-H(4)	112.6
C(5)-C(4)-H(4)	112.6

C(3)-C(4)-H(4)	112.6
O(3)-C(5)-C(6)	108.8(3)
O(3)-C(5)-C(4)	103.5(3)
C(6)-C(5)-C(4)	113.1(3)
O(3)-C(5)-H(5)	110.4
C(6)-C(5)-H(5)	110.4
C(4)-C(5)-H(5)	110.4
O(2)-C(6)-N(2)	122.8(4)
O(2)-C(6)-C(5)	121.4(4)
N(2)-C(6)-C(5)	115.7(4)
N(2)-C(7)-C(8)	113.4(4)
N(2)-C(7)-H(7A)	108.9
C(8)-C(7)-H(7A)	108.9
N(2)-C(7)-H(7B)	108.9
C(8)-C(7)-H(7B)	108.9
H(7A)-C(7)-H(7B)	107.7
C(13)-C(8)-C(9)	117.0(5)
C(13)-C(8)-C(7)	121.0(4)
C(9)-C(8)-C(7)	122.0(5)
C(10)-C(9)-C(8)	121.8(5)
C(10)-C(9)-H(9)	119.1
C(8)-C(9)-H(9)	119.1
C(9)-C(10)-C(11)	120.3(6)
C(9)-C(10)-H(10)	119.9
C(11)-C(10)-H(10)	119.9
C(12)-C(11)-C(10)	118.4(6)
C(12)-C(11)-H(11)	120.8
C(10)-C(11)-H(11)	120.8
C(11)-C(12)-C(13)	121.8(6)
C(11)-C(12)-H(12)	119.1
C(13)-C(12)-H(12)	119.1
C(12)-C(13)-C(8)	120.6(5)
C(12)-C(13)-H(13)	119.7
C(8)-C(13)-H(13)	119.7
O(4)-C(14)-O(3)	120.3(5)
O(4)-C(14)-C(15)	126.5(5)
O(3)-C(14)-C(15)	113.2(5)
C(14)-C(15)-H(15A)	109.5

C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
O(5)-C(16)-H(16A)	109.5
O(5)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
O(5)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(18)-C(17)-C(22)	119.2(4)
C(18)-C(17)-N(1)	120.1(4)
C(22)-C(17)-N(1)	120.7(4)
C(17)-C(18)-C(19)	120.7(4)
C(17)-C(18)-H(18)	119.6
C(19)-C(18)-H(18)	119.6
C(20)-C(19)-C(18)	120.4(4)
C(20)-C(19)-H(19)	119.8
C(18)-C(19)-H(19)	119.8
C(19)-C(20)-O(6)	125.2(4)
C(19)-C(20)-C(21)	119.5(4)
O(6)-C(20)-C(21)	115.3(4)
C(22)-C(21)-C(20)	120.2(4)
C(22)-C(21)-H(21)	119.9
C(20)-C(21)-H(21)	119.9
C(21)-C(22)-C(17)	120.0(4)
C(21)-C(22)-H(22)	120.0
C(17)-C(22)-H(22)	120.0
O(6)-C(23)-H(23A)	109.5
O(6)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
O(6)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(2)-N(1)-C(17)	131.5(4)
C(2)-N(1)-C(4)	94.7(3)
C(17)-N(1)-C(4)	132.0(4)

C(20)-O(6)-C(23)	117.7(4)
C(14)-O(3)-C(5)	116.7(4)
C(3)-O(5)-C(16)	114.9(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for C22H24N2O6. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(2)	43(2)	71(2)	65(2)	4(2)	0(2)	-1(2)
C(2)	68(3)	61(3)	72(3)	-3(3)	-9(3)	-1(3)
C(3)	70(3)	71(3)	63(3)	1(2)	1(3)	8(3)
C(4)	50(3)	52(2)	67(3)	1(2)	-1(2)	-7(2)
C(5)	50(2)	50(2)	61(3)	3(2)	6(2)	-1(2)
C(6)	38(3)	62(3)	68(3)	-4(2)	4(2)	6(2)
C(7)	66(3)	83(3)	72(3)	22(3)	-5(3)	0(3)
C(8)	56(3)	78(3)	59(3)	10(2)	-6(2)	-14(3)
C(9)	70(3)	94(4)	73(3)	24(3)	-8(3)	-13(3)
C(10)	75(4)	130(6)	65(4)	19(4)	3(3)	3(4)
C(11)	135(6)	122(6)	69(4)	-14(4)	11(4)	-7(5)
C(12)	164(7)	100(4)	89(4)	-6(4)	22(5)	-29(5)
C(13)	114(5)	83(4)	76(4)	-1(3)	17(3)	-21(4)
C(14)	85(4)	56(3)	88(4)	-11(3)	-4(3)	5(3)
C(15)	149(6)	62(3)	95(4)	10(3)	-15(4)	-12(4)
C(16)	254(10)	121(5)	111(5)	54(4)	-2(6)	29(7)
C(17)	54(3)	47(2)	62(3)	-5(2)	1(2)	-4(2)
C(18)	56(3)	64(3)	69(3)	4(2)	-9(2)	-11(3)
C(19)	63(3)	65(3)	80(3)	-2(3)	-1(3)	-17(3)
C(20)	65(3)	52(3)	62(3)	-5(2)	2(3)	1(3)
C(21)	49(3)	59(3)	72(3)	-2(2)	-3(2)	2(2)
C(22)	55(3)	51(3)	72(3)	-2(2)	-2(2)	-4(2)
C(23)	113(5)	99(4)	108(4)	31(3)	-8(4)	-33(4)
N(1)	55(2)	60(2)	62(2)	1(2)	-5(2)	-4(2)
O(6)	81(2)	71(2)	90(2)	18(2)	-7(2)	-8(2)
O(1)	96(3)	85(3)	98(3)	-7(2)	-33(2)	-21(2)
O(2)	42(2)	95(2)	82(2)	6(2)	-5(2)	-3(2)
O(3)	71(2)	56(2)	77(2)	1(2)	9(2)	-3(2)
O(4)	114(3)	88(3)	208(5)	-41(3)	54(4)	10(3)
O(5)	86(2)	81(2)	91(2)	16(2)	-5(2)	13(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for C22H24N2O6.

	x	y	z	U(eq)
H(2)	6342	2895	-265	72
H(3)	4922	3141	2417	81
H(4)	3678	3180	1372	68
H(5)	6020	1999	763	64
H(7A)	5613	3998	-1180	89
H(7B)	4172	3363	-1183	89
H(9)	6790	3687	-2260	95
H(10)	7609	2564	-3150	108
H(11)	6978	741	-3173	130
H(12)	5608	55	-2265	141
H(13)	4844	1142	-1358	109
H(15A)	2818	-641	851	153
H(15B)	3550	-491	1597	153
H(15C)	4187	-1310	1036	153
H(16A)	6019	1864	3110	243
H(16B)	6652	839	2717	243
H(16C)	5064	1165	2598	243
H(18)	7030	5756	833	76
H(19)	6593	7207	84	83
H(21)	2776	5979	-360	72
H(22)	3212	4519	392	71
H(23A)	5783	8670	-544	160
H(23B)	4955	8771	-1267	160
H(23C)	6044	7816	-1157	160

Table 6. Torsion angles [°] for C22H24N2O6.

O(1)-C(2)-C(3)-O(5)	-60.6(7)
N(1)-C(2)-C(3)-O(5)	122.2(4)
O(1)-C(2)-C(3)-C(4)	-179.8(6)
N(1)-C(2)-C(3)-C(4)	2.9(3)
O(5)-C(3)-C(4)-N(1)	-121.3(4)
C(2)-C(3)-C(4)-N(1)	-2.7(3)
O(5)-C(3)-C(4)-C(5)	-5.5(6)
C(2)-C(3)-C(4)-C(5)	113.1(4)
N(1)-C(4)-C(5)-O(3)	177.9(3)
C(3)-C(4)-C(5)-O(3)	79.5(4)
N(1)-C(4)-C(5)-C(6)	-64.5(5)
C(3)-C(4)-C(5)-C(6)	-162.9(4)
C(7)-N(2)-C(6)-O(2)	3.0(6)
C(7)-N(2)-C(6)-C(5)	-173.7(4)
O(3)-C(5)-C(6)-O(2)	33.7(5)
C(4)-C(5)-C(6)-O(2)	-80.7(5)
O(3)-C(5)-C(6)-N(2)	-149.6(3)
C(4)-C(5)-C(6)-N(2)	96.0(4)
C(6)-N(2)-C(7)-C(8)	-107.4(5)
N(2)-C(7)-C(8)-C(13)	52.3(6)
N(2)-C(7)-C(8)-C(9)	-128.4(5)
C(13)-C(8)-C(9)-C(10)	-0.1(7)
C(7)-C(8)-C(9)-C(10)	-179.4(4)
C(8)-C(9)-C(10)-C(11)	1.3(8)
C(9)-C(10)-C(11)-C(12)	-1.5(9)
C(10)-C(11)-C(12)-C(13)	0.4(10)
C(11)-C(12)-C(13)-C(8)	0.9(10)
C(9)-C(8)-C(13)-C(12)	-1.0(8)
C(7)-C(8)-C(13)-C(12)	178.3(5)
C(22)-C(17)-C(18)-C(19)	0.0(6)
N(1)-C(17)-C(18)-C(19)	-178.7(4)
C(17)-C(18)-C(19)-C(20)	0.7(7)
C(18)-C(19)-C(20)-O(6)	178.4(4)
C(18)-C(19)-C(20)-C(21)	-1.3(7)
C(19)-C(20)-C(21)-C(22)	1.2(6)
O(6)-C(20)-C(21)-C(22)	-178.5(4)

C(20)-C(21)-C(22)-C(17)	-0.6(6)
C(18)-C(17)-C(22)-C(21)	0.0(6)
N(1)-C(17)-C(22)-C(21)	178.6(4)
O(1)-C(2)-N(1)-C(17)	-14.7(8)
C(3)-C(2)-N(1)-C(17)	162.8(4)
O(1)-C(2)-N(1)-C(4)	179.4(5)
C(3)-C(2)-N(1)-C(4)	-3.1(3)
C(18)-C(17)-N(1)-C(2)	29.1(7)
C(22)-C(17)-N(1)-C(2)	-149.6(5)
C(18)-C(17)-N(1)-C(4)	-170.0(4)
C(22)-C(17)-N(1)-C(4)	11.3(7)
C(5)-C(4)-N(1)-C(2)	-113.3(4)
C(3)-C(4)-N(1)-C(2)	3.0(3)
C(5)-C(4)-N(1)-C(17)	80.9(5)
C(3)-C(4)-N(1)-C(17)	-162.8(4)
C(19)-C(20)-O(6)-C(23)	18.8(6)
C(21)-C(20)-O(6)-C(23)	-161.6(4)
O(4)-C(14)-O(3)-C(5)	-3.1(7)
C(15)-C(14)-O(3)-C(5)	179.9(4)
C(6)-C(5)-O(3)-C(14)	79.7(4)
C(4)-C(5)-O(3)-C(14)	-159.8(4)
C(2)-C(3)-O(5)-C(16)	143.2(5)
C(4)-C(3)-O(5)-C(16)	-116.3(5)

Symmetry transformations used to generate equivalent atoms: