

## **$\alpha$ - vs ortho-Lithiation of *N*-Alkylarylaziridines: Probing the Role of the Nitrogen Inversion Process**

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**General.** Tetrahydrofuran (THF) and diethylether were freshly distilled under a nitrogen over sodium/benzophenone ketyl. Toluene, hexanes and *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) were distilled over finely powdered calcium hydride. For the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra ( $^1\text{H}$  NMR 300, 400, 500, 600 MHz;  $^{13}\text{C}$  NMR 75.4, 100, 125, 150 MHz),  $\text{CDCl}_3$ ,  $\text{CD}_3\text{OD}$ ,  $\text{THF-}d_8$  or  $\text{toluene-}d_8$  were used as the solvents. MS-ESI analyses were performed on LC/MSD trap system VL. Melting points were uncorrected. Analytical thin layer chromatography (TLC) was carried out on precoated 0.25 mm thick plates of Kieselgel 60 F254; visualization was accomplished by UV light (254 nm) or by spraying a solution of 5 % (w/v) ammonium molybdate and 0.2 % (w/v) cerium(III) sulfate in 100 ml 17.6 % (w/v) aq. sulphuric acid and heating to 200 °C for some time until blue spots appear. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using syringe-septum cap technique.

The *trans-N*-propyl-2,3-diphenylaziridine **1** is commercially available, aziridine **4** was prepared starting from the corresponding *o*-bromo stilbene oxide<sup>1</sup> as reported<sup>2</sup>; aziridines *trans*-**1-D**, *trans*-**1-D**<sub>2</sub>, *trans*-**9a,b** and *cis*-**9a** were prepared according to a reported procedure.<sup>2a,3</sup> *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were distilled over finely powdered  $\text{CaH}_2$ , *s*-BuLi was purchased as cyclohexane solution and was filtered on celite before using and title established by titration method.<sup>4</sup>

<sup>1</sup> Akguen, E.; Glinski, M. B.; Dhawan, K. L.; Durst, T. *J. Org. Chem.* **1981**, *46*, 2730–2734.

<sup>2</sup> (a) Luisi, R.; Capriati, V.; Florio, S.; Musio, B. *Org. Lett.* **2007**, *9*, 1263-1266. (b) Anderson, W. K.; Milowsky, A. S. *J. Med. Chem.* **1986**, *29*, 2241-2249.

<sup>3</sup> Poelert, M. A.; Hof, R. P.; Peper, N. C. M.; Kellogg, R. M. *Heterocycles* **1994**, *37*, 461-475.

<sup>4</sup> R. Dieter, K.; Topping, C. M.; Nice, L. E. *J. Org. Chem.* **2001**, *66*, 2302-2311.

**General Procedure for lithium-bromine exchange on aziridine 4.** A solution of *n*-BuLi (1.05 mmol) was added to a precooled (-78 °C, dry ice/acetone bath) solution of aziridine **4** (1.0 mmol) in THF (5 mL) under N<sub>2</sub> and with stirring. After 1 h (20 min in the case of **6c**) at this temperature, the electrophile (D<sub>2</sub>O, MeI or Bu<sub>3</sub>SnCl; 10 mmol) was added dropwise. The resulting mixture was stirred for 20 min at -78 °C; after this time, it was allowed to warm to rt, quenched with satd aq NH<sub>4</sub>Cl, and extracted with Et<sub>2</sub>O (3 × 20 mL). The solvent was removed under reduced pressure and the crude, containing compounds **6a-c** and *trans*-**1a** analyzed by NMR spectroscopy and GC-MS and the products purified by flash chromatography.

**General procedure for the lithiation-trapping sequence of aziridines *trans*-1-D in THF.**

To a solution of aziridine *trans*-**1-D** (1 mmol) in 10 mL of dry THF, at -78 °C and under N<sub>2</sub>, *s*-BuLi (1.5 mmol of a 1.4 M cyclohexane solution) was added dropwise. The resulting brown mixture was stirred for 4 h at this temperature before quenching with D<sub>2</sub>O. Then, a solution of sat. aq. NH<sub>4</sub>Cl (3 mL) was added and the mixture poured in 20 mL of water and extracted with Et<sub>2</sub>O (3 × 10 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent evaporated in *vacuo*. The crude was purified by flash chromatography on silica gel (AcOEt/Petroleum Ether).

**General procedure for the lithiation-trapping sequence of aziridines *trans*-9a,b and *cis*-9a.**

The reaction conditions used for the lithiation are reported in Table 1. To a solution of aziridine (1 mmol) in 10 mL of the dry solvent and TMEDA, at the temperature indicated in table 1 and under N<sub>2</sub>, *s*-BuLi (a 1.4 M cyclohexane solution) was added dropwise. The resulting brown mixture was stirred at this temperature for the time indicated before quenching with the electrophile. Then, a solution of sat. aq. NH<sub>4</sub>Cl (3 mL) was added and the mixture poured in 20 mL of water and extracted with Et<sub>2</sub>O (3 × 10 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent evaporated in *vacuo*. The crude was purified by flash chromatography on silica gel (AcOEt/Petroleum Ether) or by distillation.

**Table 1.** Conditions for the lithiation-trapping sequence of aziridines *trans*-**9a,b** and *cis*-**9a**.

| Aziridine<br><i>trans</i> - <b>9</b> | Solvent           | T °C | <i>sec</i> -BuLi<br>equiv | TMEDA<br>equiv | Lithiation<br>time (h) | Electrophile     |
|--------------------------------------|-------------------|------|---------------------------|----------------|------------------------|------------------|
| <i>trans</i> - <b>9a</b>             | THF               | -78  | 2.0                       | 2.0            | 4                      | D <sub>2</sub> O |
| “                                    | “                 | “    | “                         | “              | “                      | MeI              |
| “                                    | Toluene           | “    | “                         | “              | “                      | D <sub>2</sub> O |
| “                                    | “                 | “    | “                         | “              | “                      | MeI              |
| “                                    | Et <sub>2</sub> O | “    | “                         | “              | “                      | D <sub>2</sub> O |
| “                                    | “                 | “    | “                         | “              | “                      | MeI              |
| “                                    | “                 | 0    | “                         | “              | 3.5                    | D <sub>2</sub> O |
| “                                    | “                 | “    | “                         | “              | “                      | MeI              |
| “                                    | “                 | -40  | “                         | “              | 4                      | “                |
| <i>trans</i> - <b>9b</b>             | THF               | -70  | “                         | “              | 6                      | D <sub>2</sub> O |
| “                                    | “                 | “    | “                         | “              | “                      | MeI              |
| “                                    | Et <sub>2</sub> O | “    | “                         | “              | “                      | “                |
| “                                    | “                 | 0    | “                         | “              | 4                      | D <sub>2</sub> O |
| “                                    | “                 | “    | “                         | “              | “                      | MeI              |
| <i>cis</i> - <b>9a</b>               | THF               | -78  | 3.0                       | 3.0            | 6                      | D <sub>2</sub> O |
| “                                    | “                 | “    | “                         | “              | “                      | MeI              |
| “                                    | “                 | 0    | “                         | “              | 5                      | “                |

**(2*R*\*,3*R*\*)-2-(2-Bromophenyl)-3-phenyl-1-propylaziridine 4.** Inseparable mixture of invertomers (dr: 70/30, CDCl<sub>3</sub>, 263 K). Colorless oil, 52%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, 263 K) δ: 0.86 (t, *J* = 6.9 Hz, 3 H, minor), 0.88 (t, *J* = 7.3 Hz, 3 H, major), 1.55-1.62 (m, 2 H, major), 1.62-1.71 (m, 2 H, minor), 1.90-1.99 (m, 1 H major + 1 H minor), 2.44-2.49 (m, 1 H, major), 2.72-2.76 (m, 1 H, minor), 2.98 (d, *J* = 3.5 Hz, 1 H, minor), 3.17 (d, *J* = 3.3 Hz, 1 H, major), 3.30 (d, *J* = 3.3 Hz, 1 H, major), 3.38 (d, *J* = 3.5 Hz, 1 H, minor), 7.14-7.66 (m, 9 H minor + 9 H major). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz, 263 K) δ: 12.1 (major + minor), 23.3 (major + minor), 45.8 (major), 46.5 (minor), 49.8 (major), 50.9 (minor), 54.6 (major), 55.0 (minor), 123.4, 126.4, 126.7, 127.1, 127.5, 127.8, 127.9, 128.1, 128.3, 129.4, 130.1, 131.6, 132.0, 132.8, 133.7, 134.5, 139.2, 139.5. EI-MS (70 eV) *m/z* (%): 317 (M<sup>+</sup> + 2, 25), 316 (77), 315 (M<sup>+</sup>, 26), 314 (75), 274 (93), 273 (18), 165 (80), 89 (55). FT-IR (Film) cm<sup>-1</sup>: 3061, 2959, 2931, 1470, 1024, 753, 698.

**(2*R*\*,3*R*\*)-2-(2-Methylphenyl)-3-phenyl-1-propylaziridine 6b.** Inseparable mixture of invertomers (dr: 58/42, toluene-*d*<sub>8</sub>, 233 K). Colorless oil, 57%. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 600 MHz, 233 K) δ: 0.87 (t, *J* = 7.3 Hz, 3 H, major), 0.95 (t, *J* = 7.3 Hz, 3 H, minor), 1.44-1.65 (m, 2 H major + 2 H minor), 1.66-1.73 (m, 1 H, major), 1.99-2.09 (m, 1 H, minor), 2.27 (s, 3 H, minor), 2.30 (s, 3 H, major), 2.33-2.41 (m, 1 H, minor), 2.42-2.50 (m, 1 H, major), 2.75 (d, *J* = 2.8 Hz, 1 H, major), 2.89 (d, *J* = 3 Hz, 1 H, minor), 2.96 (d, *J* = 3 Hz, 1 H, minor), 3.02 (d, *J* = 2.8 Hz, 1 H, major), 7.05-7.33 (m, 7 H major + 8 H minor), 7.50 (d, 2 H, major), 7.90 (d, 1 H, minor). <sup>13</sup>C NMR (toluene-*d*<sub>8</sub>, 150 MHz) δ: 13.0, 13.1, 20.4, 24.4, 24.5, 44.2, 46.2, 50.1, 55.1, 55.5, 127.2, 127.3, 127.8, 127.7, 130.3, 134.4, 135.5, 136.5, 140.0, 142.0. EI-MS (70 eV) *m/z* (%): 251 (M<sup>+</sup>, 34), 250 (100), 236 (85), 208 (75), 117 (34), 91 (40). FT-IR (Film) cm<sup>-1</sup>: 3029, 2959, 2930, 2872, 1603, 1496, 1458, 698.

**(2*R*\*,3*R*\*)-3-Phenyl-1-propyl-2-(2-tributylstannylphenyl)aziridine 6c.** Inseparable mixture of invertomers (dr: 50/50, CDCl<sub>3</sub>, 298 K). Colorless oil, 56%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, 298 K) δ: 0.80 (t, overlapping t at 0.85, *J* = 7.4 Hz, 3 H), 0.85 (t, *J* = 7.4 Hz, 9 H), 1.04-1.18 (m broad, 5 H), 1.23-1.36 (m, 6 H), 1.40-1.61 (m, 8 H), 2.30-2.40 (m, 1 H), 3.03 (s, broad, 1 H), 3.18 (s, broad, 1H), 7.17-7.52 (m, 9 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz, 220K) δ: 11.0, 11.6, 13.2, 13.3, 15.1, 15.2, 24.1, 24.4, 28.9, 30.4, 46.7, 48.4, 52.5, 54.0, 54.7, 55.5, 126.1, 127.3, 127.5, 128.0, 128.8, 129.1, 129.6, 129.8,

130.8, 134.4, 137.7, 137.9, 140.7, 141.3, 141.4, 147.0, 147.3. EI-MS (70 eV)  $m/z$  (%): 470 ( $M^+$ -56, 20), 468 (15), 237 (20), 236 (100). FT-IR (Film)  $cm^{-1}$ : 2959, 2927, 2856, 1459, 1072, 752, 698.

**(2*R*\*,3*S*\*)-2,3-Dideuterio-2,3-diphenyl-1-propylaziridine *cis*-1-D<sub>2</sub>.** Colorless oil, 32 %, 87% D. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K)  $\delta$ : 1.08 (t,  $J$  = 7.4 Hz, 3 H), 1.77 (sept.,  $J$  = 7.0 Hz, 2 H), 2.64 (t,  $J$  = 7.0 Hz, 2 H), 2.88 (s, 0.13 H), 7.08-7.11 (m, 2 H), 7.14-7.21 (m, 8 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$ : 11.9, 22.9, 48.8 (t,  $^1J_{C-D}$  = 23.0 Hz), 63.1, 126.2, 127.4, 127.7, 136.7. ESI-MS  $m/z$  (%): 240 [ $M+H$ ]<sup>+</sup> (100). EI-MS (70 eV)  $m/z$  (%): 239 ( $M^+$ , 28), 238 (77), 196 (100), 166 (18), 118 (17), 92 (13). FT-IR (Film)  $cm^{-1}$ : 2960, 2931, 1604, 1496, 1448, 735, 697.

**(2*R*\*,3*R*\*)-2-Deuterio-2-phenyl-3-(*o*-deuteriophenyl)-1-propylaziridine 6a-D<sub>2</sub>.** Inseparable mixture of invertomers (dr: 50/50, CDCl<sub>3</sub>, 263 K). Colorless oil, 50%, 80% D. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, 263 K)  $\delta$ : 0.86 (t,  $J$  = 7.4 Hz, 3 H), 1.50-1.60 (m, 2 H), 2.01-2.06 (m, 1 H), 2.47-2.50 (m, 1 H), 3.01 (br s, 0.38 H), 3.30 (br s, 0.38 H), 7.28-7.42 (m, 9 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz, 263 K)  $\delta$ : 12.2, 23.3, 45.2 (t,  $^1J_{C-D}$  = 23.0 Hz), 45.6, 50.0 (t,  $^1J_{C-D}$  = 23.0 Hz), 50.3, 54.7, 126.0 (t,  $^1J_{C-D}$  = 23.0 Hz), 126.3, 127.1, 127.8, 128.1, 128.2, 128.4, 128.5, 129.8 (t,  $^1J_{C-D}$  = 23.0 Hz), 130.1, 134.0, 140.0. ESI-MS  $m/z$ : 240 [ $M+H$ ]<sup>+</sup> (100). EI-MS (70 eV)  $m/z$  (%): 239 ( $M^+$ , 24), 238 (65), 196 (100), 166 (17), 118 (13), 91 (21). FT-IR (Film)  $cm^{-1}$ : 2959, 2930, 1602, 1446, 1181, 698.

**(2*R*\*,3*R*\*)-2,3-Dideuterio-2,3-diphenyl-1-propylaziridine *trans*-1-D<sub>2</sub>.** Colorless oil, 98 %, 80% D. <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$ : 0.88 (t,  $J$  = 7.4 Hz, 3 H); 1.54-1.61 (m, 2 H), 2.06 (td,  $J$  = 11.4, 7.3 Hz, 1 H); 2.48 (td,  $J$  = 11.8, 6.9 Hz, 1 H); 7.30-7.44 (m, 10 H). <sup>13</sup>C-NMR (150 MHz, CDCl<sub>3</sub>, 233 K)  $\delta$ : 13.2, 24.2, 45.9, (t,  $^1J_{C-D}$  = 28 Hz), 46.4 (residual C-H), 50.8 (t,  $^1J_{C-D}$  = 28 Hz), 51.2 (residual C-H), 55.6, 127.2, 128.1, 128.8, 129.2, 129.5, 131.1, 134.8, 140.9. ESI-MS  $m/z$  (%): 240 [ $M+H$ ]<sup>+</sup> (100). EI-MS (70 eV)  $m/z$  (%): 239 ( $M^+$ , 25), 238 (76), 197 (17), 196 (100), 195 (21), 168 (18), 166 (18), 118 (17). FT-IR (Film)  $cm^{-1}$ : 3026, 2958, 2929, 2872, 2850, 1601, 1495, 1446, 1376, 1180, 1079, 1029, 784, 697.

**(2*R*\*,3*R*\*)-2-Deuterio-3-methyl-2,3-diphenyl-1-propylaziridine *trans*-7-D.** Yellowish oil, 70%, 83% D. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ: 0.86 (t, *J* = 7.3 Hz, 3 H); 1.20 (s, 3 H); 1.47-1.60 (m, 2 H); 1.65-1.74 (m, 1 H); 2.68-2.73 (m, 1 H); 3.05 (s, residual protonated 0.19 H); 7.23-7.50 (m, 10 H). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ: 12.2, 23.0, 23.6, 51.1 (t, <sup>1</sup>*J*<sub>C-D</sub> = 22 Hz, overlapping residual C-H), 51.6, 57.7, 126.9, 127.6, 128.0, 128.3, 128.5, 129.8, 138.5, 140.7. EI-MS (70 eV) *m/z* (%): 252, (M<sup>+</sup>, 24), 251 (100), 209 (63), 168 (24), 91 (16), 92 (10). FT-IR (Film) cm<sup>-1</sup>: 2958, 2930, 1603, 1494, 1445, 695.

**(2*R*\*,3*S*\*)-2-Deuterio-3-methyl-2,3-diphenyl-1-propylaziridine *cis*-7-D.** Yellow oil, 20%, 96% D. <sup>1</sup>H-NMR (600 MHz, CDCl<sub>3</sub>, 298 K) δ: 1.08 (t, *J* = 7.3 Hz, 3 H); 1.68 (s, 3 H); 1.73-1.78 (m, 2 H); 2.69-2.73 (m, 1 H); 2.77 (s, 1 H); 2.85-2.90 (m, 1 H); 7.03-7.26 (m, 10 H). <sup>13</sup>C-NMR (125 MHz, CDCl<sub>3</sub>) δ: 13.0; 19.8; 24.9; 51.4; 54.6 (t, <sup>1</sup>*J*<sub>C-D</sub> = 22 Hz); 55.6; 126.8; 126.9; 128.0; 128.2; 128.4; 129.2; 139.4; 143.2. ESI-MS *m/z* (%): 253 [M+H]<sup>+</sup> (100). EI-MS (70 eV), *m/z* (%): 251 [M-1]<sup>+</sup> (100); 209 (61); 168 (25); 91 (16). FT-IR (Film) cm<sup>-1</sup>: 2959; 2930; 1445; 698.

**(2*R*\*,3*R*\*)-2,3-Dideuterio-2-(2-methylphenyl)-3-phenyl-1-propylaziridine 6b-D<sub>2</sub>.** Inseparable mixture of invertomers (dr ~ 50/50, CDCl<sub>3</sub>, 223 K). Colorless oil, 80%, 92% D. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, 223 K) δ: 0.84 (t, *J* = 7.3 Hz, 3 H), 0.89 (t, *J* = 7.3 Hz, 3 H), 1.50-1.70 (m, 4 H), 1.85-1.96 (m, 1 H), 2.49 (s, 3 H), 2.53 (s, 3 H), 2.42-2.61 (m, 3 H, overlapping singlet at 2.49 and 2.53), 7.05-7.33 (m, 18 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz, 223 K) δ: 15.2, 15.3, 22.9, 23.0, 48.0 (C-D), 51.5 (C-D), 57.5, 57.6, 128.3, 128.9, 129.2, 129.3, 129.9, 130.0, 130.9, 131.0, 131.2, 131.3, 132.5, 132.9, 133.0, 135.9, 139.1, 141.0, 142.4, 142.9. ESI-MS *m/z* (%): 254 [M+H]<sup>+</sup> (100). EI-MS (70 eV) *m/z* (%): 251 (M<sup>+</sup>, 34), 250 (100), 236 (85), 208 (75), 117 (34), 91 (40). FT-IR (Film) cm<sup>-1</sup>: 3029, 2959, 2930, 2872, 1603, 1496, 1458, 698.

**(2*R*\*,3*R*\*)-1,2-Dimethyl-3-phenylaziridine *trans*-9a.** Inseparable mixture of invertomers (dr~ 88/12, toluene-*d*<sub>8</sub>, 220 K). Colorless oil, 81%. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 600 MHz, 223 K) δ: 0.98 (d, *J* = 6.5 Hz, 3 H major), 1.24 (d, *J* = 6 Hz, 3 H minor), 1.58-1.64 (m, 1 H minor), 1.74 (d, *J* = 2.8 Hz, 1 H major), 1.85-1.92 (m, 1 H major), 2.05 (s, 3 H minor), 2.33 (s, 3 H major), 2.77 (d, *J* = 3 Hz, 1 H minor), 7.03-

7.35 (m, 5 H major + 5 H minor).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz, 220 K)  $\delta$ : 12.2, 19.5, 39.6, 40.2, 40.4, 44.1, 47.7, 50.1, 126.7, 127.8, 128.6, 129.1, 129.4, 131.3, 135.1, 141.6. EI-MS (70 eV)  $m/z$  (%): 147 ( $\text{M}^+$ , 14), 146 (100), 132(21), 1117(11), 105(38), 91 (14). FT-IR (Film)  $\text{cm}^{-1}$ : 2944, 2855, 1604, 1495, 1454, 1398, 1207, 1177, 1121, 1028, 733, 700.

**(2*R*\*,3*R*\*)-2-Methyl-3-phenyl-1-propylaziridine *trans*-9b.** Inseparable mixture of invertomers (dr~ 75/25,  $\text{CDCl}_3$ , 220 K). Colorless oil, 81%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz, 220 K)  $\delta$ : 0.79 (t,  $J = 7.3$  Hz, 3 H minor), 0.93 (t,  $J = 7.3$  Hz, 3 H major), 1.35 (d,  $J = 5.5$  Hz, 3 H minor), 1.39 (d,  $J = 5.5$  Hz, 3 H major), 1.40-1.53 (m, 2 H minor), 1.58-1.68 (m, 2 H major), 1.76-1.84 (m, 1 H minor), 2.05-2.12 (m, 1 H minor), 2.16 (d,  $J = 3$  Hz, 1 H major), 2.16-2.20 (m, overlapping d at 2.16, 1 H major), 2.35-2.43 (m, 1 H major), 2.72-2.80 (m, 1 H major), 2.92 (d,  $J = 2.8$  Hz, 1 H minor), 7.21-7.40 (m, 5 H major + 5 H minor).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz, 220 K)  $\delta$ : 12.5, 13.2, 13.3, 19.8, 24.3, 24.7, 39.4, 43.8, 47.7, 49.2, 54.9, 55.1, 126.8, 127.7, 128.5, 129.0, 129.4, 131.2, 135.4, 141.8. EI-MS (70 eV)  $m/z$  (%): 175 ( $\text{M}^+$ , 21), 174 (100), 160 (20), 146 (10), 132 (89), 117 (24), 105 (84), 91 (52). ESI-MS  $m/z$  (%): 176 [ $\text{M}+\text{H}$ ] $^+$  (100). FT-IR (Film)  $\text{cm}^{-1}$ : 2958, 2929, 2873, 1603, 1497, 1457, 1411, 1380, 1087, 1029, 739, 698.

**(2*R*\*,3*R*\*)-3-Deuterio-1,2-dimethyl-3-phenylaziridine 10a.** Inseparable mixture of invertomers (dr~ 75/25,  $\text{CDCl}_3$ , 298 K). Colorless oil, 90%, 97% D.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz, 298 K)  $\delta$ : 1.30 (d,  $J = 6$  Hz, 3 H minor), 1.34 (d,  $J = 6$  Hz, 3 H major), 1.94 (q,  $J = 6$  Hz, 1 H minor), 2.04 (s, 3 H minor), 2.10 (q,  $J = 6$  Hz, 1 H major), 2.52 (s, 3 H major), 2.84 (d,  $J = 3$  Hz, 1 H minor), 7.13-7.34 (m, 5 H major + 5 H minor).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz, 233 K)  $\delta$ : 12.1, 19.3, 39.5, 43.8, 49.9 (t,  $J_{\text{C-D}} = 24$  Hz), 126.7, 127.8, 129.0, 129.4, 131.3, 141.4. EI-MS (70 eV)  $m/z$  (%): 148 ( $\text{M}^+$ , 14), 147 (100), 133 (21), 118 (17), 106 (9), 105 (37). ESI-MS  $m/z$  (%): 149 [ $\text{M}+\text{H}$ ] $^+$  (100). FT-IR (Film)  $\text{cm}^{-1}$ : 2961, 2928, 2871, 1764, 1694, 1601, 1496, 1447, 1120, 1078, 732, 699.

**(2*R*\*,3*R*\*)-1,2-Dimethyl-3-(2-deuteriophenyl)aziridine 11a.** Inseparable mixture of invertomers (dr~ 75/25,  $\text{CDCl}_3$ , 298 K). Colorless oil, 92% D.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz, 298 K)  $\delta$ : 1.30 (d,  $J = 6$  Hz, 3 H minor), 1.34 (d,  $J = 6$  Hz, 3 H major), 1.90-1.98 (m, 1 H minor), 2.03 (d,  $J = 3$  Hz, 1 H major), 2.05 (s, overlapping d at 2.03, 3 H minor), 2.06-2.14 (m, 1 H major), 2.52 (s, 3 H major), 2.84 (d,  $J = 3$  Hz, 1 H minor), 7.13-7.34 (m, 4 H major + 4 H minor).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz, 220 K)  $\delta$ : 10.7, 18.3, 38.3, 39.1, 39.8, 42.5, 47.2, 49.5, 125.5 (t,  $J_{\text{C-D}} = 24$  Hz), 125.8, 126.6, 127.4, 127.8, 128.0, 128.1, 128.2, 130.2, 134.3, 140.7. EI-MS (70 eV)  $m/z$  (%): 148 ( $\text{M}^+$ , 15), 147 (100), 146 (34), 133 (27), 118



(15), 106 (42), 105 (14), 92 (16). ESI-MS  $m/z$  (%): 149  $[M+H]^+$  (100). FT-IR (Film)  $\text{cm}^{-1}$ : 2962, 2928, 2869, 1762, 1696, 1445, 1119, 1079, 1032, 774, 631.

**(2*R*\*,3*R*\*)-2-Methyl-3-deuterio-3-phenyl-1-propylaziridine 10c** Inseparable mixture of invertomers (dr ~ 80/20,  $\text{CDCl}_3$ , 220 K). Colorless oil, 93%, 97% D.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz, 220 K)  $\delta$ : 0.80 (t,  $J = 7$  Hz, 3 H minor), 0.94 (t,  $J = 7$  Hz, 3 H major), 1.36 (d,  $J = 5.5$  Hz, 3 H minor), 1.40 (d,  $J = 5.5$  Hz, 3 H major), 1.42-1.50 (m, 2 H minor), 1.60-1.68 (m, 2 H major), 1.78-1.84 (m, 1 H minor), 2.08 (q,  $J = 5.5$  Hz, 1 H minor), 2.20 (q,  $J = 5.5$  Hz, 1 H major), 2.17-2.23 (m, overlapping q at 2.20, 1 H minor), 2.36-2.43 (m, 1 H major), 2.74-2.80 (m, 1 H major), 7.22-7.40 (m, 5 H major + 5 H minor).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz, 220 K)  $\delta$ : 12.4, 13.1, 13.2, 19.6, 24.2, 24.6, 39.4, 43.5, 47.3 (t,  $J_{\text{C-D}} = 24$  Hz, minor), 48.9 (t,  $J_{\text{C-D}} = 24$  Hz, major), 54.8, 55.0, 126.8, 127.6, 128.5, 128.9, 129.3, 131.1, 135.2, 141.7. EI-MS (70 eV)  $m/z$  (%): 176 ( $M^+$ , 21), 175 (100), 161 (20), 133 (89), 119 (16), 118 (24), 105 (80), 92 (46), 91 (21). ESI-MS  $m/z$  (%): 177  $[M+H]^+$  (100). FT-IR (Film)  $\text{cm}^{-1}$ : 2958, 2929, 2873, 1497, 1449, 1378, 1081, 738, 697.

**(2*R*\*,3*R*\*)-2-Methyl-3-(2-deuteriophenyl)-1-propylaziridine 11c.** Inseparable mixture of invertomers (dr ~ 75/25,  $\text{CDCl}_3$ , 220 K). Colorless oil, 75%, 97% D.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz, 220 K)  $\delta$ : 0.79 (t,  $J = 7.3$  Hz, 3 H minor), 0.93 (t,  $J = 7.3$  Hz, 3 H major), 1.35 (d,  $J = 5.5$  Hz, 3 H minor), 1.39 (d,  $J = 5.5$  Hz, 3 H major), 1.40-1.53 (m, 2 H minor), 1.58-1.68 (m, 2 H major), 1.76-1.84 (m, 1 H minor), 2.05-2.12 (m, 1 H minor), 2.16 (d,  $J = 3$  Hz, 1 H major), 2.16-2.20 (m, overlapping d at 2.16, 1 H major), 2.35-2.43 (m, 1 H major), 2.72-2.80 (m, 1 H major), 2.92 (d,  $J = 2.8$  Hz, 1 H minor), 7.21-7.40 (m, 5 H major + 5 H minor).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 150 MHz, 220 K)  $\delta$ : 12.4, 13.2, 13.2, 19.7, 24.2, 24.6, 39.5, 43.6, 47.7, 49.2, 54.8, 55.1, 126.4, 126.5 (t,  $J_{\text{C-D}} = 24$  Hz), 126.8, 127.6, 128.4, 128.9, 129.2, 129.3, 129.9 (t,  $J_{\text{C-D}} = 24$  Hz), 131.1, 135.2, 141.7. EI-MS (70 eV)  $m/z$  (%): 176 ( $M^+$ , 21), 175 (84), 161 (24), 133 (100), 118 (24), 106 (86), 105 (22), 92 (57), 91 (16). ESI-MS  $m/z$  (%): 177  $[M+H]^+$  (100). FT-IR (Film)  $\text{cm}^{-1}$ : 2927, 1762, 1458, 1378, 1082, 774, 734, 631.

**(2*R*\*,3*R*\*)-1,2,3-Trimethyl-3-phenylaziridine 10b.** Colorless oil, 30%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 600 MHz, 298 K)  $\delta$ : 1.28 (d,  $J = 5.5$  Hz, 3 H), 1.38 (s, 3 H), 1.82 (q,  $J = 5.5$  Hz, 1 H), 1.98 (s, 3 H), 7.10-7.30 (m, 5H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, proton coupled, 298 K)  $\delta$ : 14.1 (qd,  $J = 129$ , 4.5 Hz,  $\text{CHCH}_3$ ), 22.6 (q,  $J = 128$  Hz,  $\text{CCH}_3$ ), 42.2 (qd,  $J = 135$ , 7 Hz,  $\text{NCH}_3$ ), 44.6 (d,  $J = 158$  Hz,  $\text{CHCH}_3$ ), 47.9 (s, CPh), 127.4 (dt,  $J = 161$ , 6.5 Hz,  $C_p$ ), 128.3 (dd,  $J = 161$ , 7.4 Hz,  $C_o$ ), 130.0 (dt,  $J = 159$ , 6 Hz,  $C_m$ ), 140.9 (s, S9

*C<sub>i</sub>*). EI-MS (70 eV) *m/z* (%): 161 (*M*<sup>+</sup>, 12), 160 (100), 145 (17), 105 (38), 103 (12), 77 (12). FT-IR (Film) cm<sup>-1</sup>: 2957, 2864, 1603, 1494, 1444, 1400, 1380, 1135, 1070, 1026, 768, 701.

**(2*R*\*,3*R*\*)-1,2-Dimethyl-3-(2-methylphenyl)aziridine 11b.** Inseparable mixture of invertomers (dr~ 60/40, CDCl<sub>3</sub>, 298 K). Colorless oil, 87 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, 298 K) δ: 1.37 (d, *J* = 5.5 Hz, 3 H minor), 1.42 (d, *J* = 5.8 Hz, 3 H major), 1.92-1.97 (m, 1 H minor), 2.01 (s, 3 H minor), 2.02-2.08 (m, 1 H major), 2.17 (d, *J* = 3 Hz, 1 H major), 2.40 (s, 3 H major), 2.45 (s, 3 H minor), 2.59 (s, 3 H major), 2.83 (d, *J* = 3.5 Hz, 1 H minor), 7.10-7.40 (m, 4 H major + 4 H minor). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 150 MHz, 298 K) δ: 18.1, 18.4, 19.1, 19.4, 38.4, 39.0, 39.8, 40.7, 46.4, 47.7, 125.1, 125.4, 125.8, 126.3, 127.5, 127.9, 129.4, 129.8, 130.0, 133.2, 136.0, 138.5, 139.4. EI-MS (70 eV) *m/z* (%): 161 (*M*<sup>+</sup>, 15), 160 (100), 146 (49), 145 (13), 131 (20), 117 (29), 105 (12), 104 (13), 103 (14), 91 (15). FT-IR (Film) cm<sup>-1</sup>: 2957, 2870, 1763, 1458, 1401, 1376, 755, 738.

**(2*R*\*,3*R*\*)-2,3-Dimethyl-3-phenyl-1-propylaziridine 10d.** Colorless oil, 87%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, 220 K) δ: 0.76 (t, *J* = 7 Hz, 3 H), 1.06-1.16 (m, 1 H), 1.33 (d, *J* = 6 Hz, 3 H), 1.42 (s, 3 H), 1.40-1.65 (m, 2 H), 1.89 (q, *J* = 6 Hz, 1 H), 2.45-2.55 (m, 1 H), 7.31-7.50 (m, 5 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 220 K) δ: 13.2, 15.7, 23.6, 24.4, 44.7, 46.8, 48.4, 58.6, 127.3, 128.2, 129.1, 130.7, 140.0. EI-MS (70 eV) *m/z* (%): 189 (*M*<sup>+</sup>, 15), 188 (100), 146 (23), 105 (67), 103 (12), 91 (10), 77 (11). FT-IR (Film) cm<sup>-1</sup>: 2958, 2928, 2873, 1494, 1458, 1444, 1378, 1140, 1074, 1026, 765, 701.

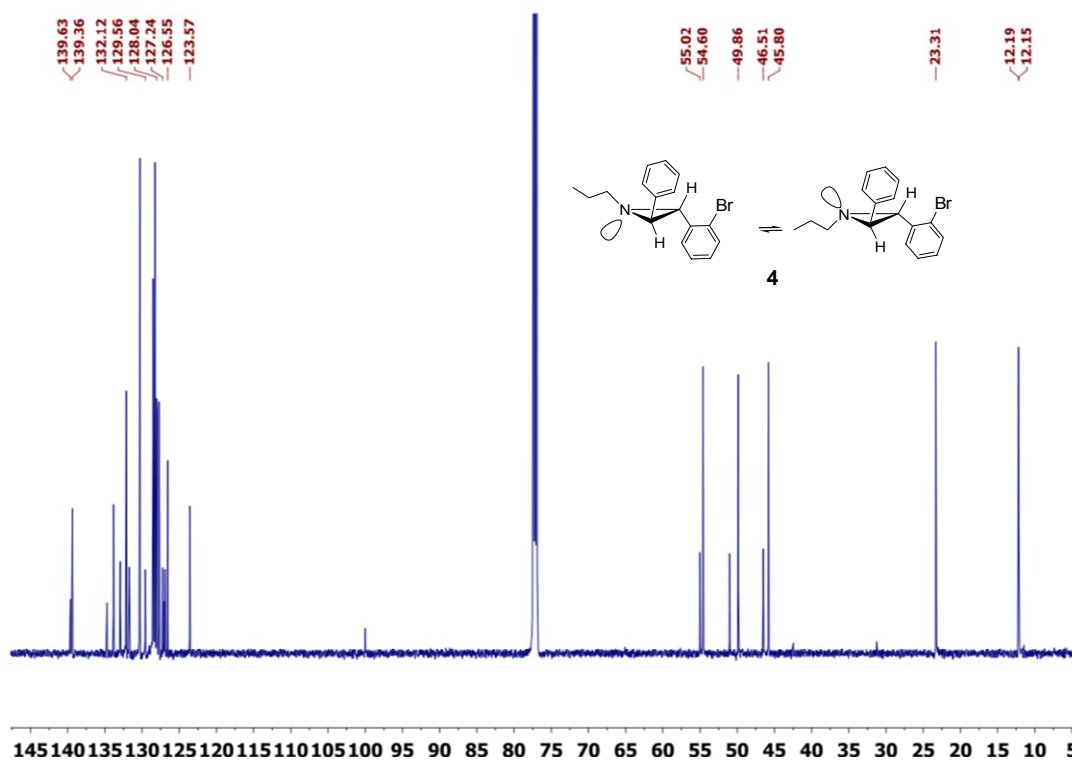
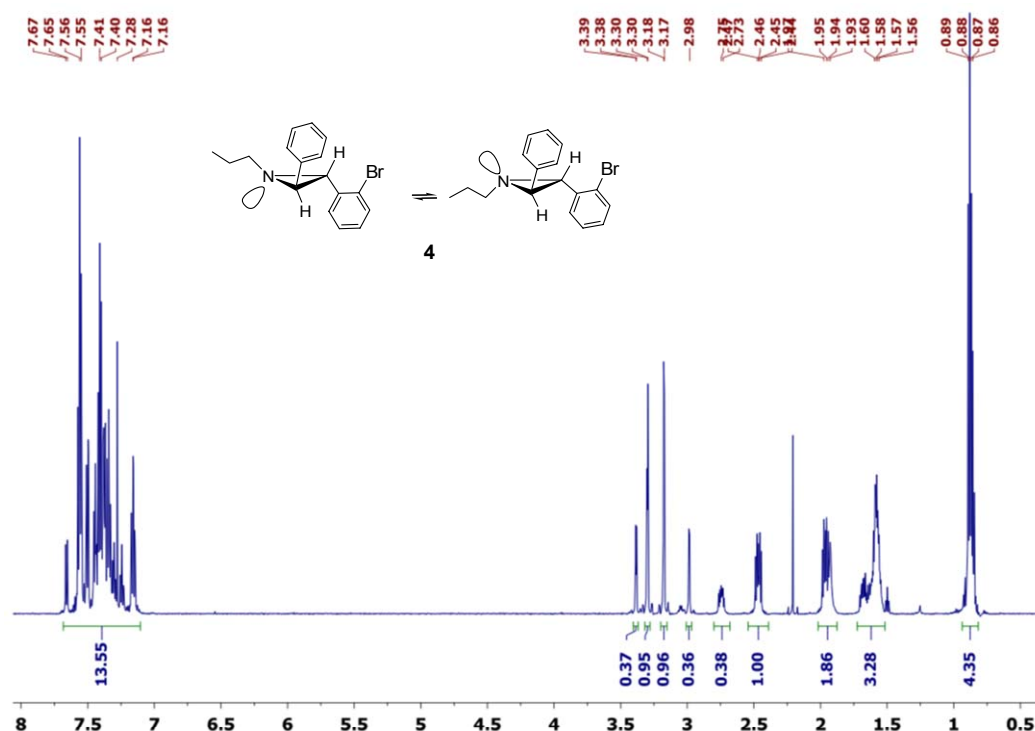
**(2*R*\*,3*R*\*)-2-Methyl-3-(2-methylphenyl)-1-propylaziridine 11d.** Inseparable mixture of invertomers (dr~ 62/38, CDCl<sub>3</sub>, 220 K). Colorless oil, 84%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, 220 K) δ: 0.83 (t, *J* = 7 Hz, 3 H minor), 0.98 (t, *J* = 7 Hz, 3 H major), 1.38 (d, *J* = 5.5 Hz, 3 H minor), 1.36-1.43 (m, overlapping d at 1.38, 1 H minor), 1.45 (d, *J* = 5.5 Hz, 3 H major), 1.44-1.58 (m, 2 H minor), 1.60-1.77 (m, 2 H major), 1.98-2.06 (m, 1 H major + 1 H minor), 2.23 (d, *J* = 3 Hz, 1 H major), 2.26-2.33 (m, 1 H minor), 2.35-2.42 (m, overlapping s at 2.39, 1 H major), 2.39 (s, 3 H major), 2.46 (s, 3 H minor), 2.78-2.85 (m, 1 H minor), 2.86 (d, *J* = 3 Hz, 1 H minor), 7.10-7.40 (m, 4 H major + 4 H minor). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 220 K) δ: 12.7, 13.2, 13.4, 19.8, 20.7, 24.3, 24.8, 39.7, 42.1, 46.8, 47.5, 54.8, 55.3, 126.1, 126.4, 127.0, 127.4, 128.6, 130.4, 130.6, 130.9, 134.5, 137.1, 139.8, 140.6. EI-MS (70 eV) *m/z* (%): 189 (*M*<sup>+</sup>, 21), 188 (100), 174 (35), 160 (11), 146 (44), 132 (17), 131 (18), 130 (19), 129 (21), 119 (24), 118 (17), 117 (26), 105 (20), 104 (14), 103 (15), 91 (17). FT-IR (Film) cm<sup>-1</sup>: 2958, 2930, 2873, 1459, 1380, 1107, 1082, 748.

**(2*R*\*,3*S*\*)-1,2-Dimethyl-3-phenylaziridine cis-9a** Colorless oil, 85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, 298 K) δ: 0.94 (d, *J* = 5.5 Hz, 3 H), 1.72 (quintet, *J* = 5.5 Hz, 1 H), 2.46 (d, *J* = 6 Hz, 1 H), 2.53 (s, 3 H), 7.20-7.35 (m, 5 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 298 K) δ: 12.6, 42.9, 47.5, 47.6, 126.4, 127.7, 127.8, 137.5. EI-MS (70 eV) *m/z* (%): 147 (M<sup>+</sup>, 14), 146 (100), 132 (22), 131 (9), 91 (13.). ESI-MS *m/z* (%): 148 [M+H]<sup>+</sup> (100). FT-IR (Film) cm<sup>-1</sup>: 2961, 2870, 1603, 1496, 1455, 1402, 1376, 1253, 1164, 1125, 1087, 1067, 1029, 733, 698.

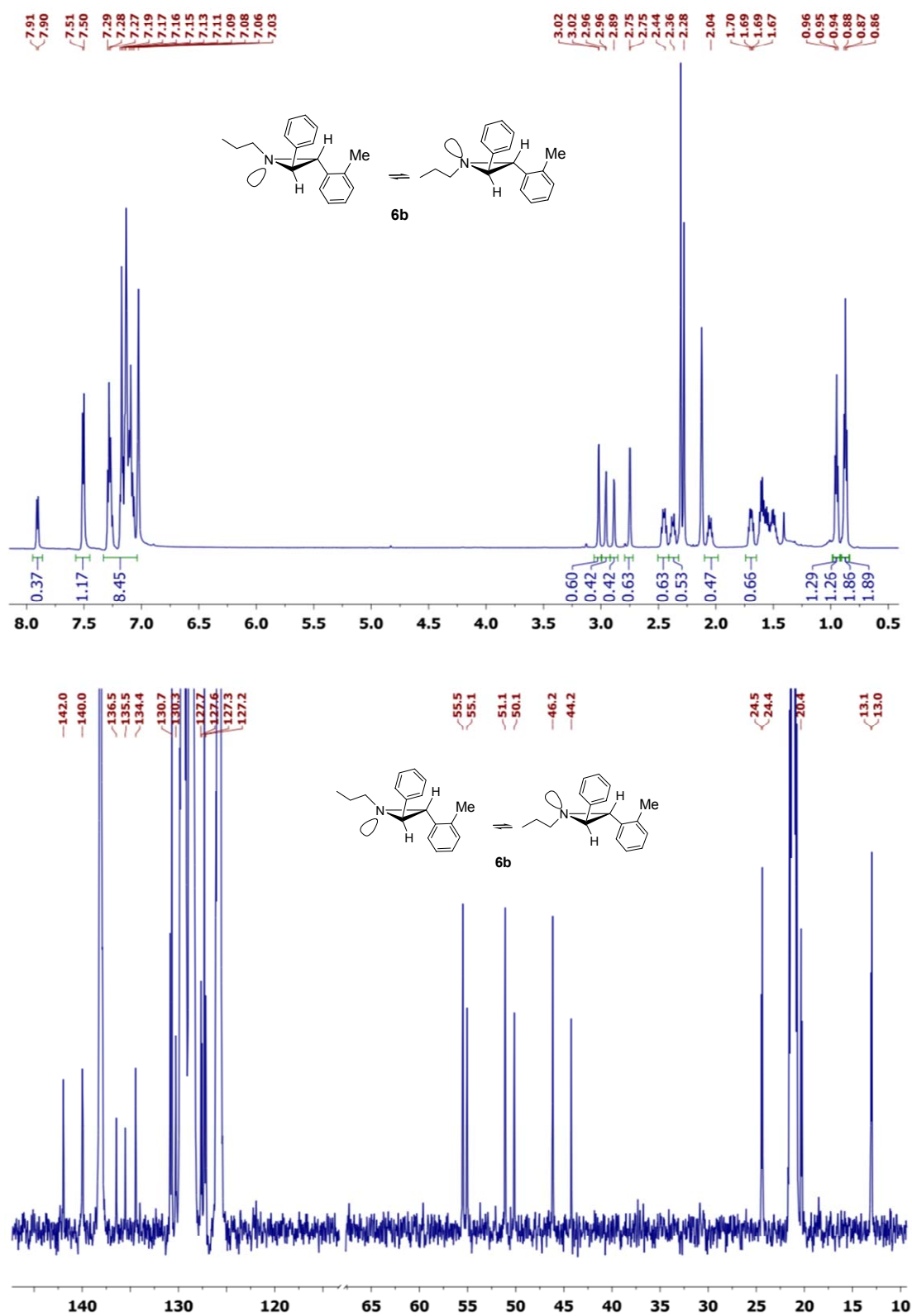
**(2*R*\*,3*S*\*)-1,2-Dimethyl-3-(2-deuteriophenyl)aziridine 13a** Colorless oil, 75%, 87% D. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 600 MHz, 298 K) δ: 0.94 (d, *J* = 5.5 Hz, 3 H), 1.72 (quintet, *J* = 5.5 Hz, 1 H), 2.46 (d, *J* = 6 Hz, 1 H), 2.53 (s, 3 H), 7.20-7.35 (m, 4 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 298 K) δ: 13.5, 43.8, 48.4, 48.5, 127.3, 128.3 (t, *J*<sub>C-D</sub> = 24 Hz), 128.6, 128.7, 138.3. EI-MS (70 eV) *m/z* (%): 148 (M<sup>+</sup>, 19), 147 (100), 146 (45), 133 (29), 118 (14), 106 (51), 105 (13), 92 (17). ESI-MS *m/z* (%): 149 [M+H]<sup>+</sup> (100). FT-IR (Film) cm<sup>-1</sup>: 2959, 2858, 1690, 1598, 1455, 1398, 1176, 1120, 777, 731.

**(2*R*\*,3*S*\*)-1,2-Dimethyl-3-(2-methylphenyl)aziridine 13b** Colorless oil, 51%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 298 K) δ: 0.83 (d, *J* = 6 Hz, 3 H), 1.75 (quintet, *J* = 6 Hz, 1 H), 2.29 (s, 3 H), 2.37 (d, *J* = 6 Hz, 1 H), 2.51 (s, 3 H), 7.10-7.40 (m, 4 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, 298 K) δ: 13.2, 19.3, 42.3, 46.6, 47.8, 125.6, 126.6, 127.9, 128.1, 128.3, 129.6, 135.8, 136.5. EI-MS (70 eV) *m/z* (%): 161 (M<sup>+</sup>, 16), 160 (100), 146 (48), 131 (17), 117 (17), 105 (10), 104 (11), 103 (12). FT-IR (Film) cm<sup>-1</sup>: 2944, 2859, 1605, 1491, 1456, 1399, 1176, 1122, 770, 741.

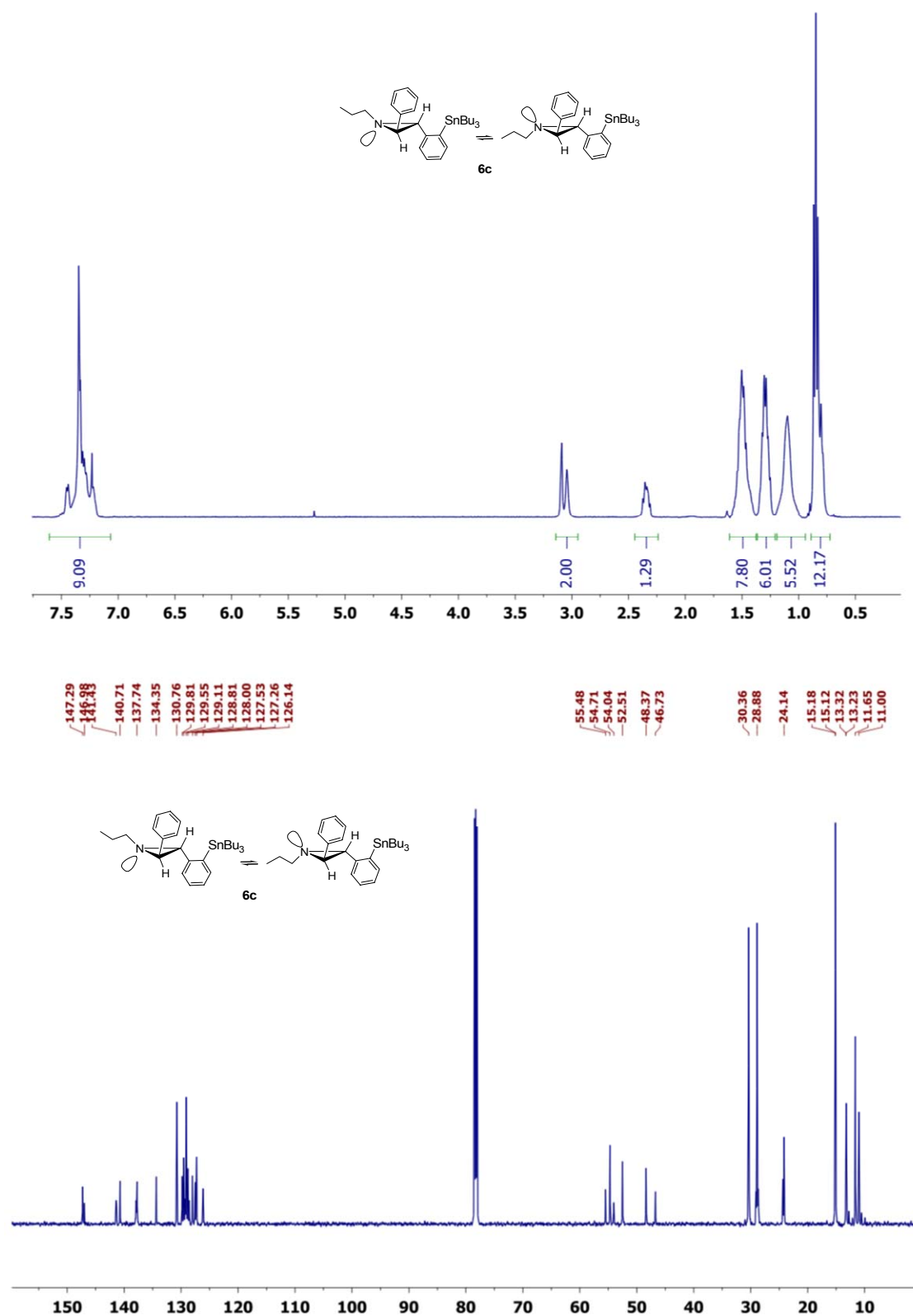
$^1\text{H}$  and  $^{13}\text{C}$  NMR of two slowly equilibrating invertomers of aziridine **4** in  $\text{CDCl}_3$  at 263 K.



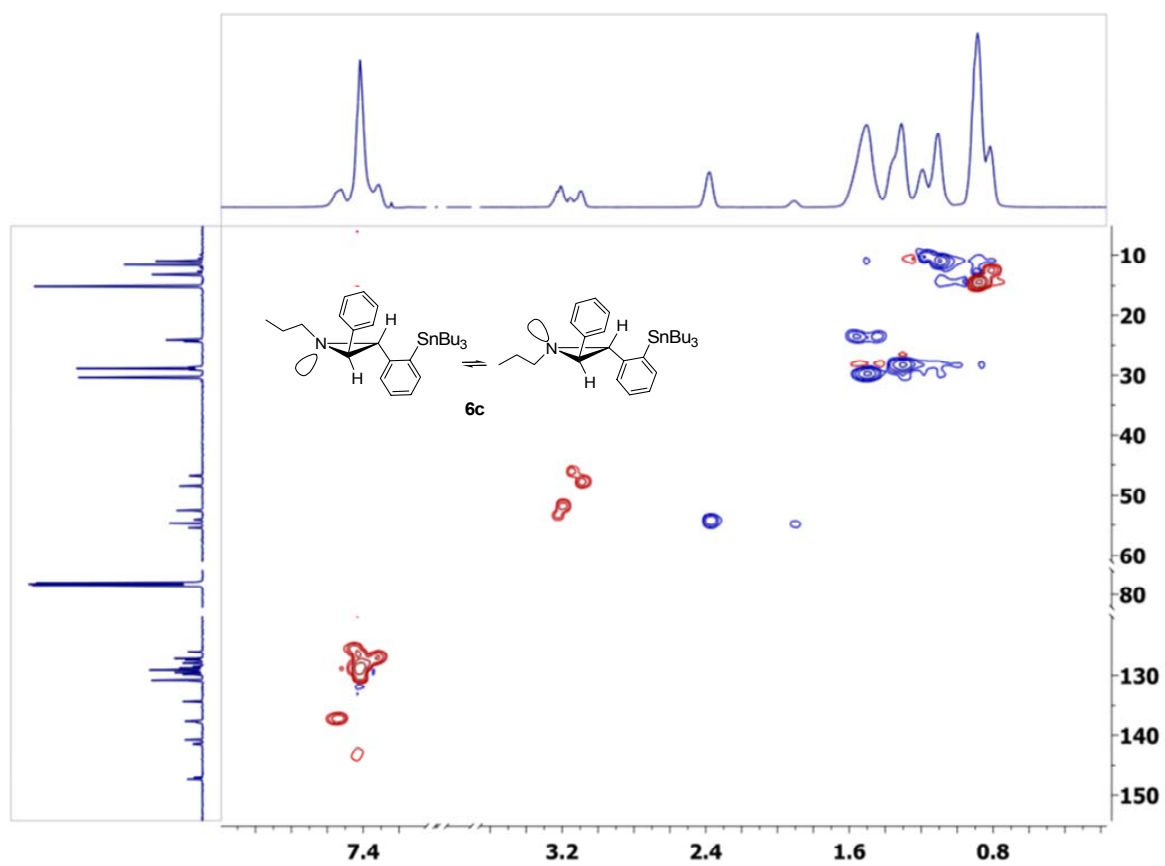
$^1\text{H}$  and  $^{13}\text{C}$  NMR of the mixture of slowly equilibrating invertomers of aziridine **6b** in toluene- $d_8$  at 233 K.



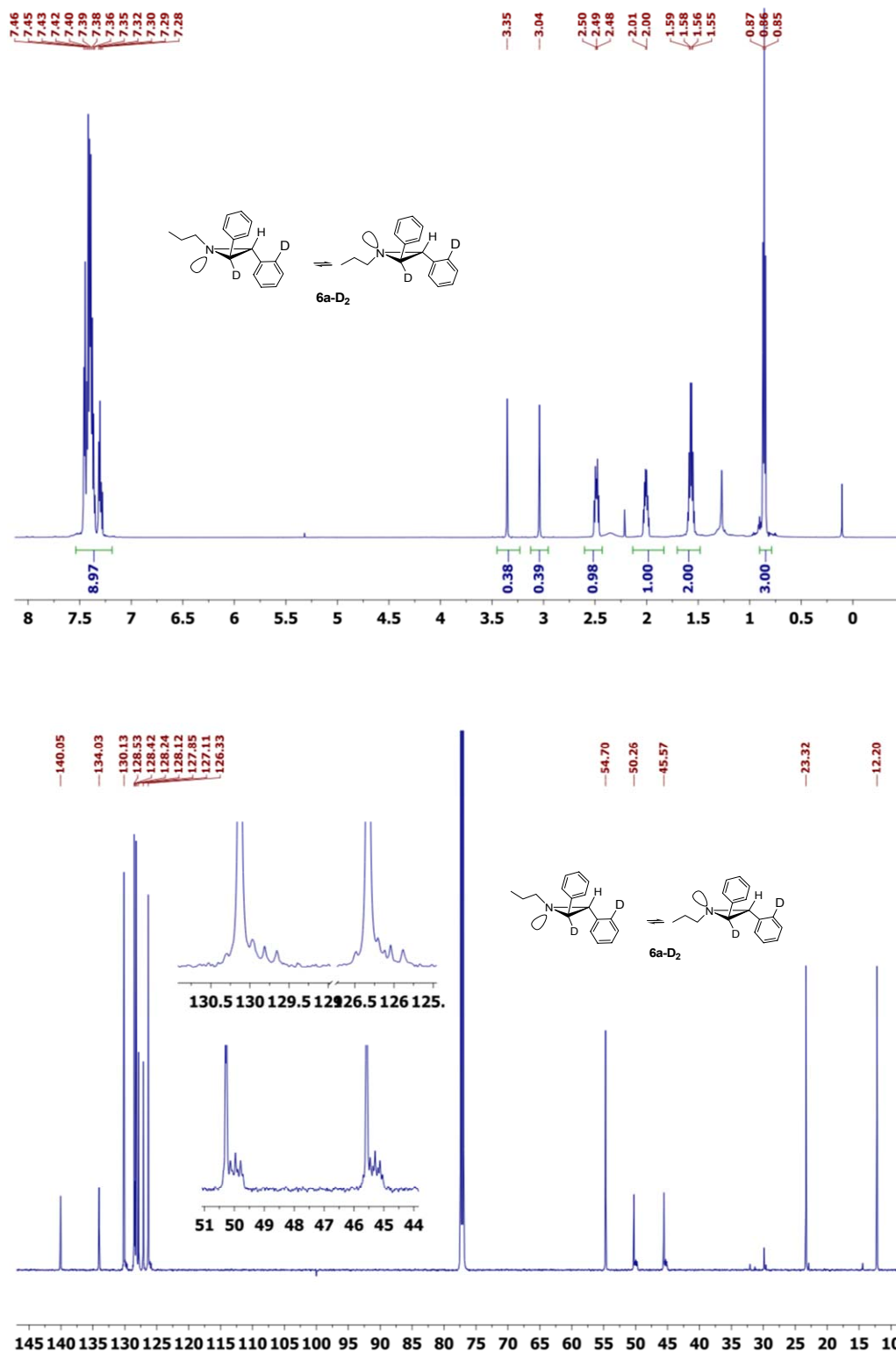
$^1\text{H}$  (298 K) and  $^{13}\text{C}$  NMR (220 K) of two slowly equilibrating invertomers of aziridine **6c**.



HSQC-DEPT of aziridine **6c** in CDCl<sub>3</sub> at 220 K (CH<sub>2</sub> in blue and CH and CH<sub>3</sub> in red)

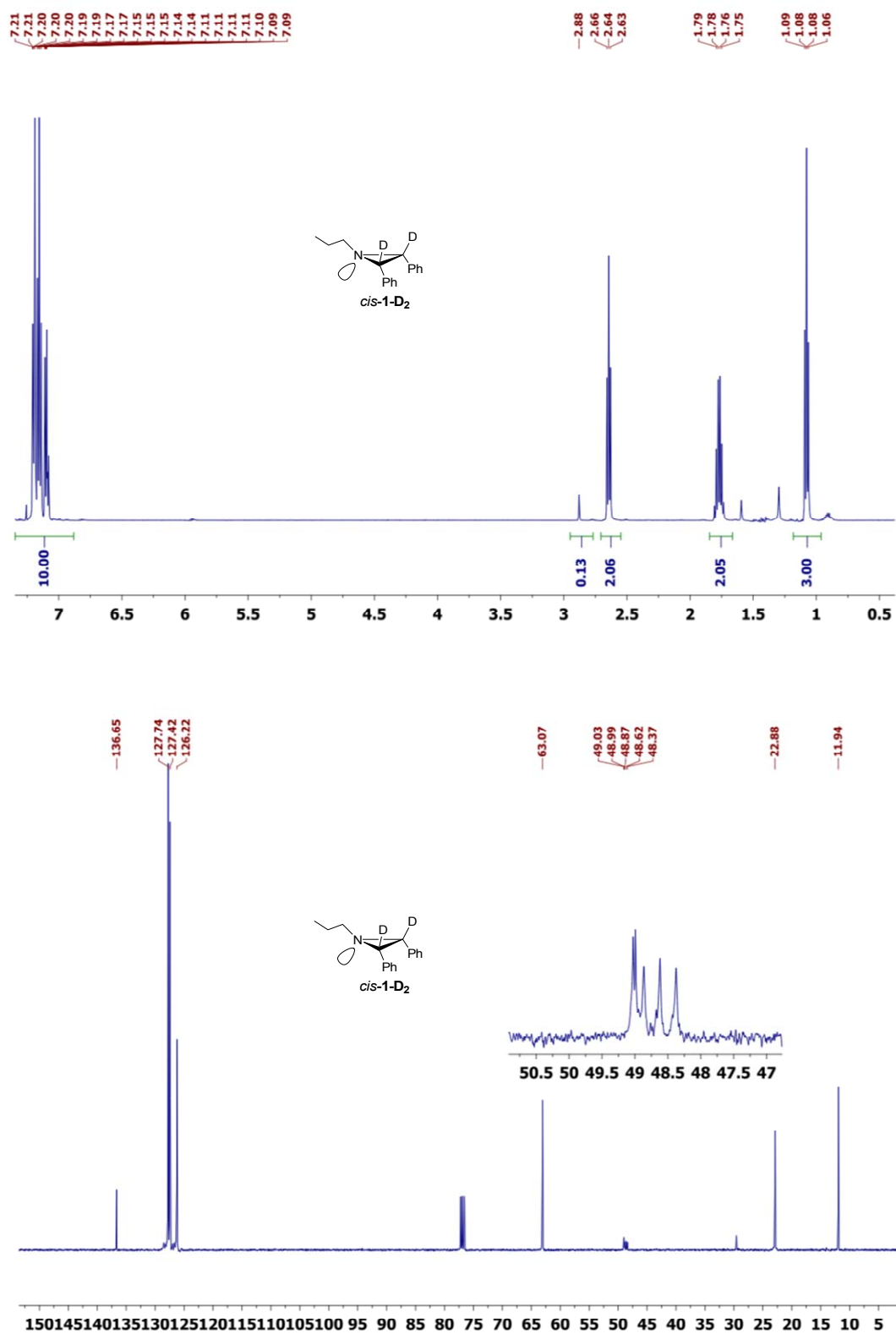


$^1\text{H}$  and  $^{13}\text{C}$  NMR of two slowly equilibrating invertomers of aziridine **6a-D<sub>2</sub>** in  $\text{CDCl}_3$  at 263 K.

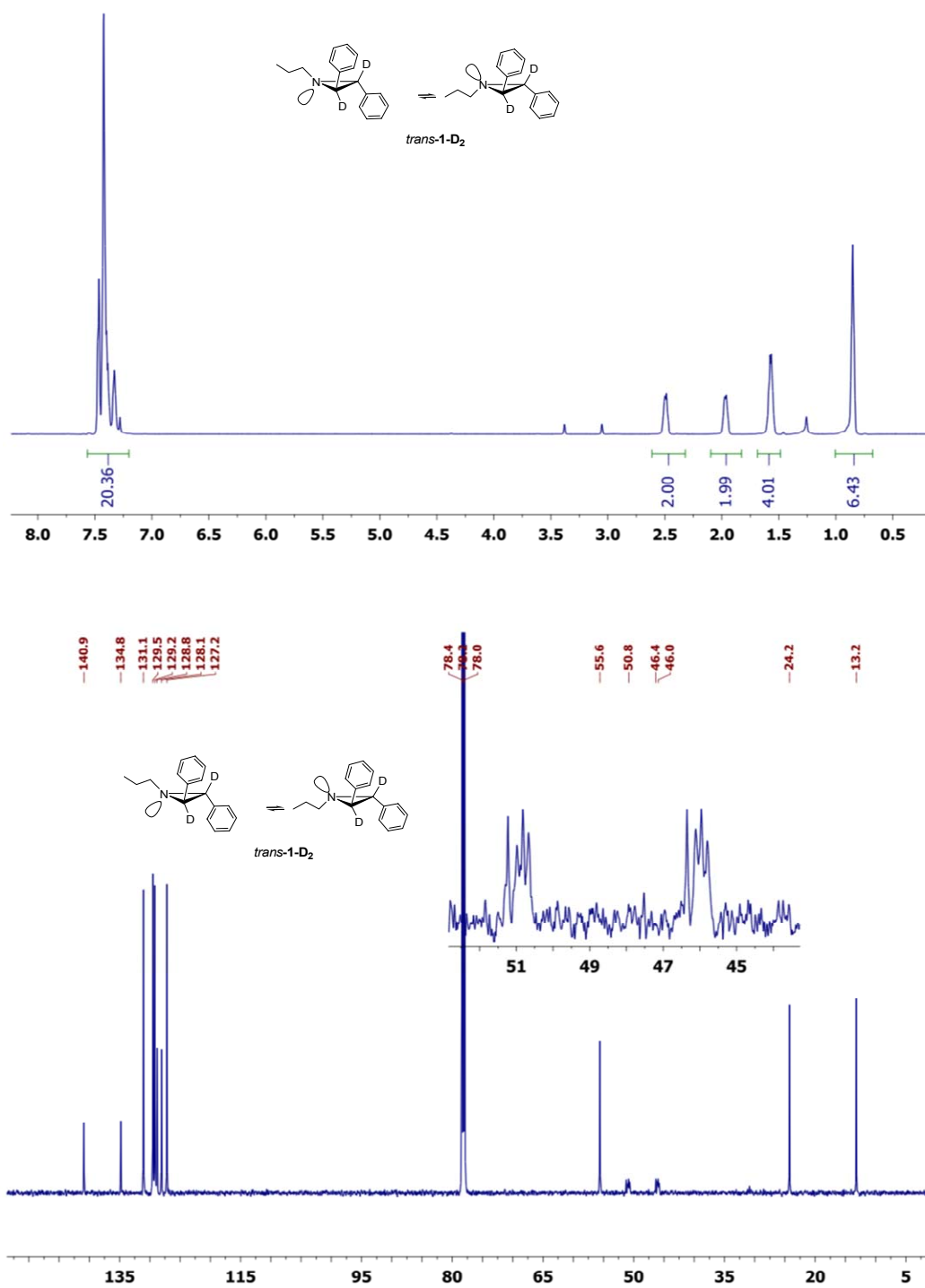




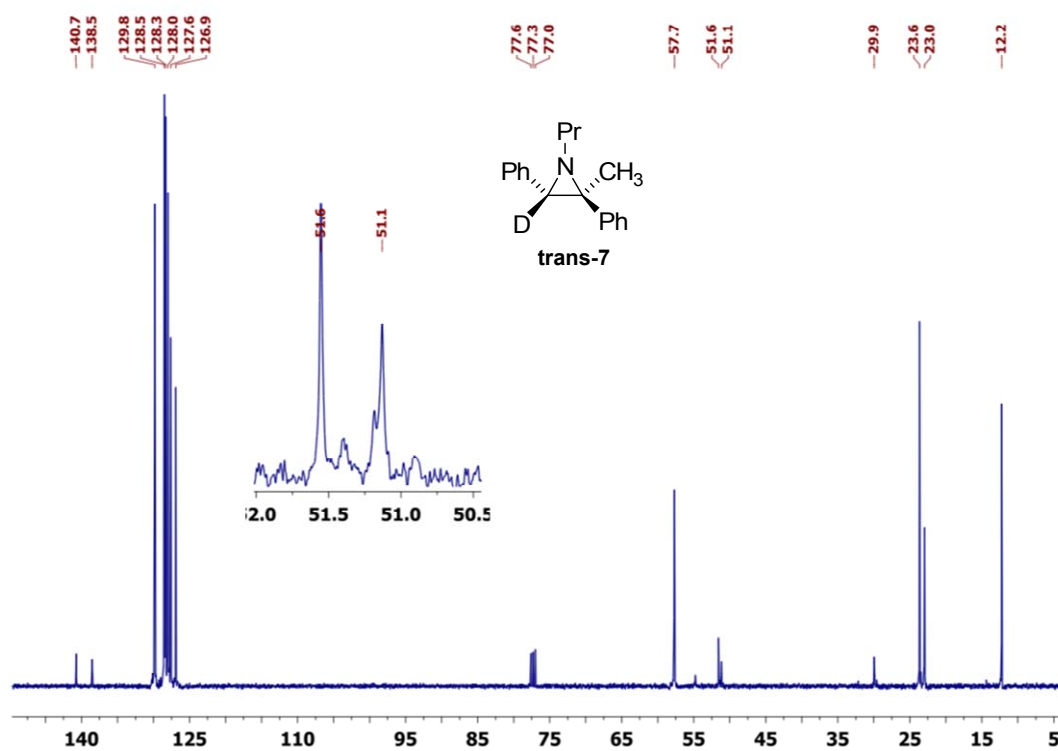
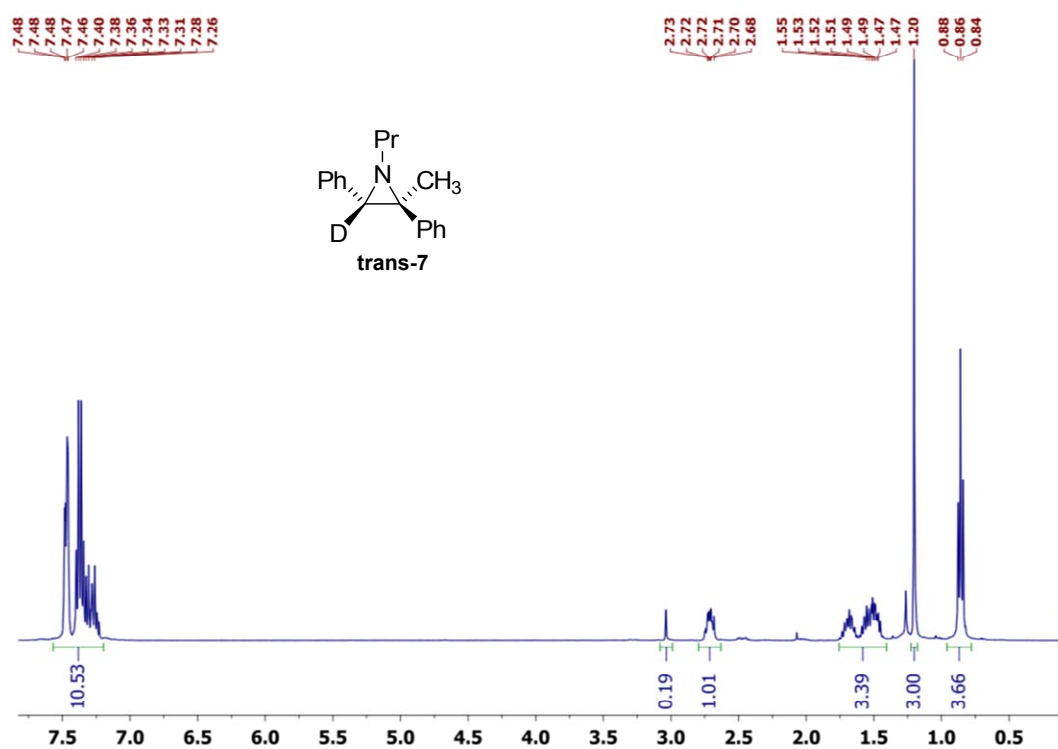
$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine *cis*-**1-D<sub>2</sub>** in  $\text{CDCl}_3$  at 298 K.



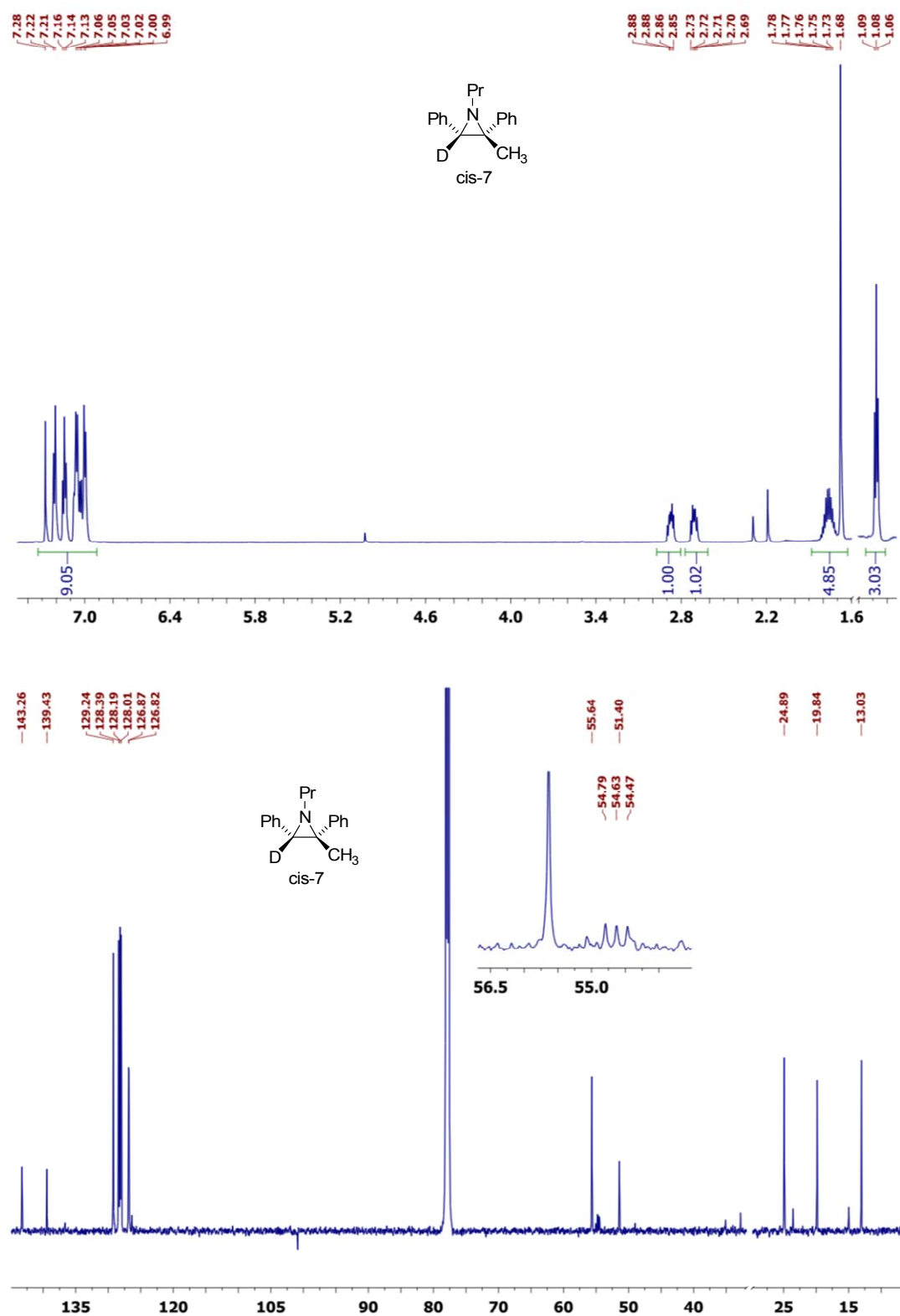
$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine *trans*-**1-D<sub>2</sub>** in  $\text{CDCl}_3$  at 223 K.



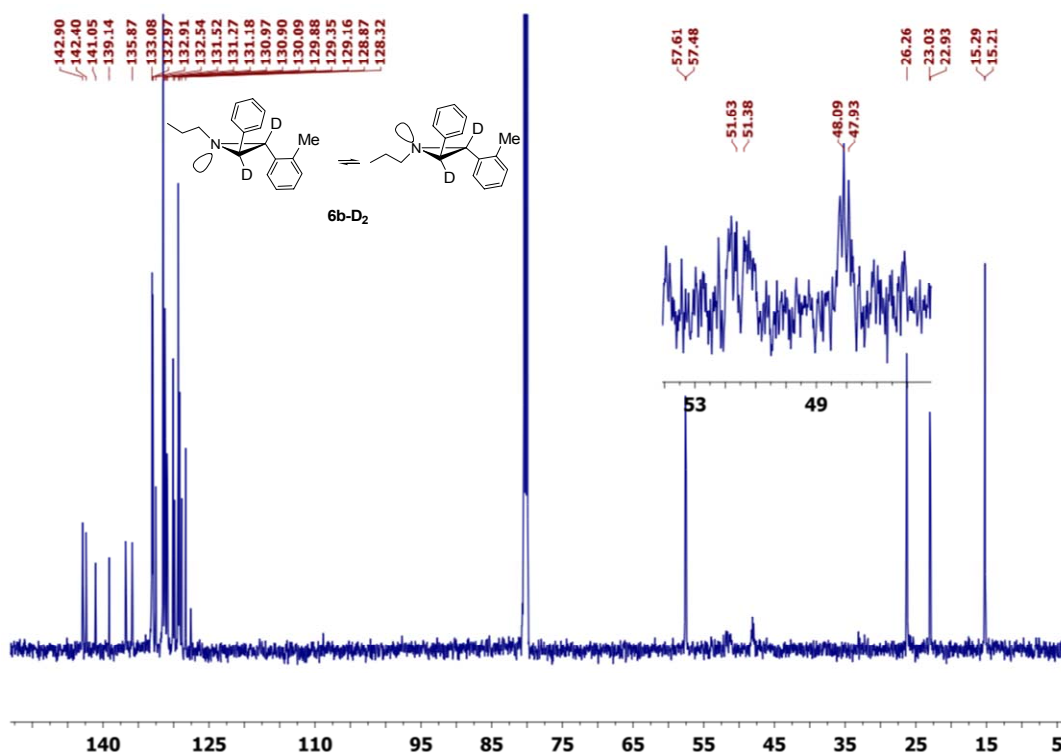
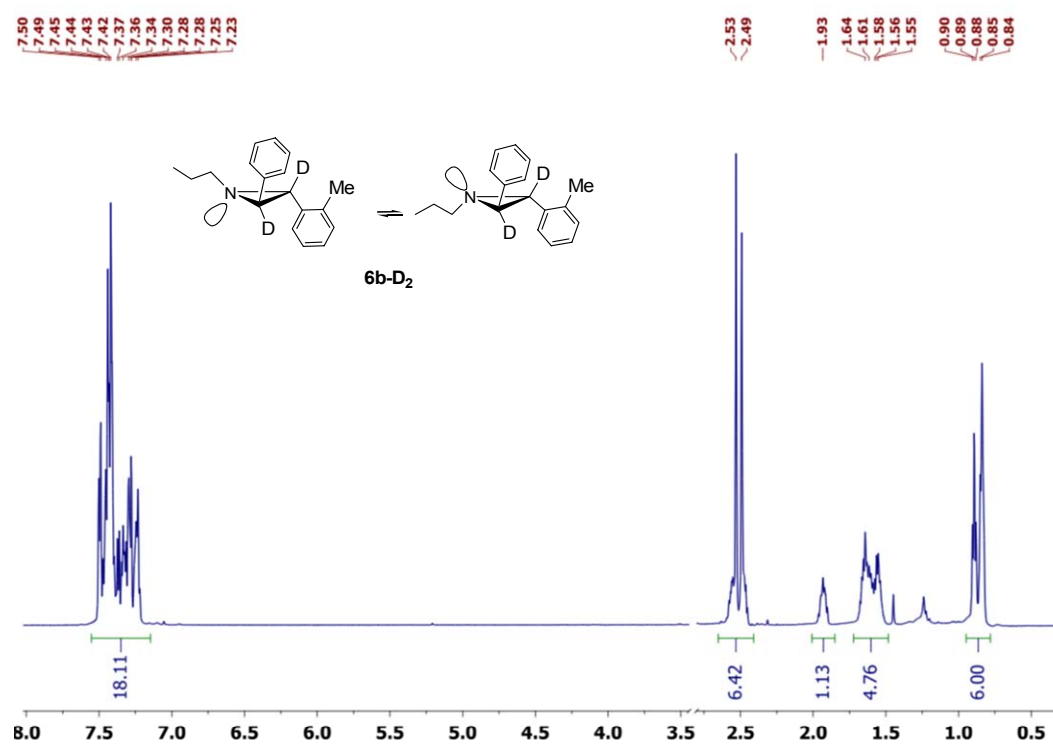
$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine *trans*-7-**D** in  $\text{CDCl}_3$  at 223 K.



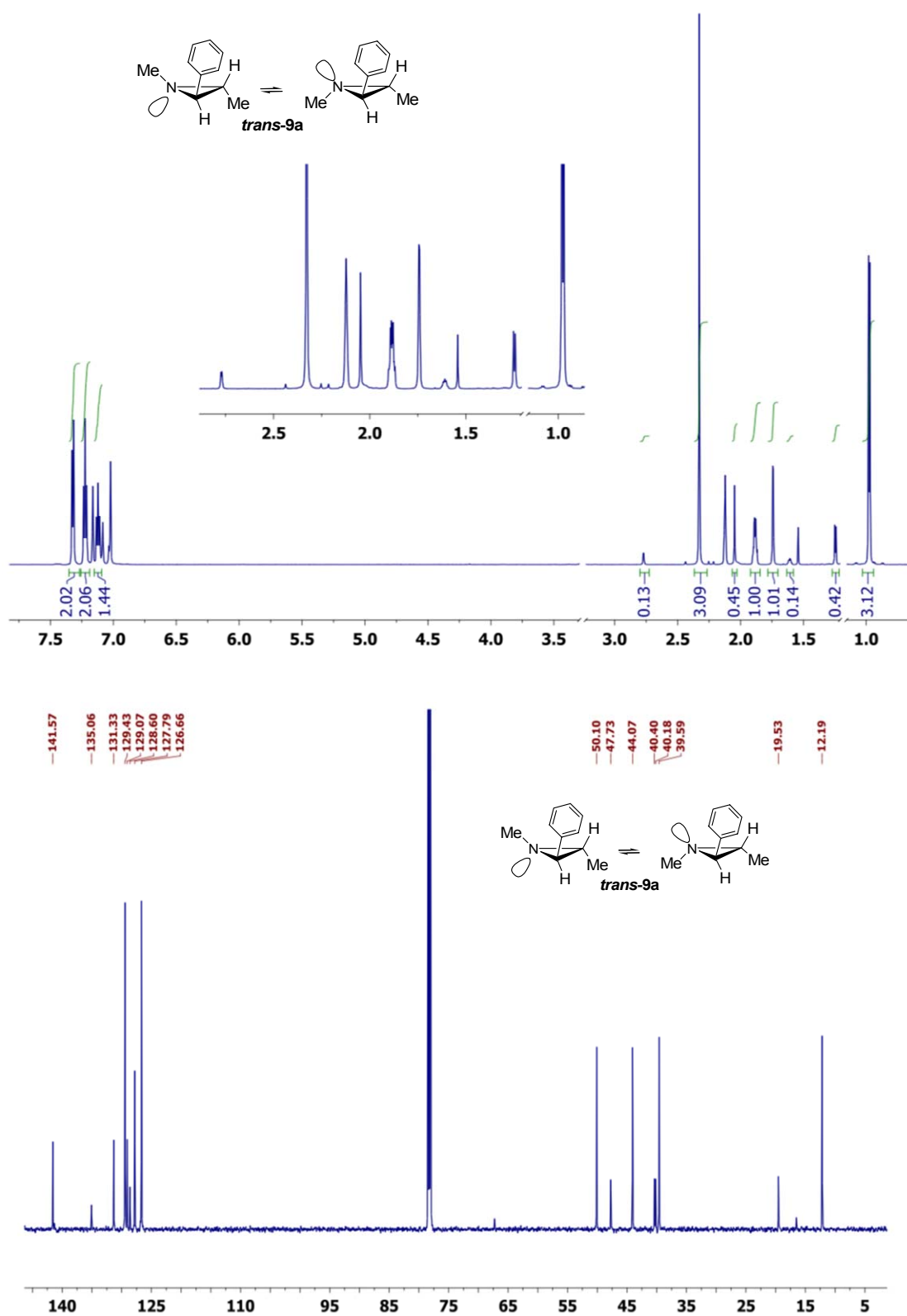
$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine *cis*-7-**D** in  $\text{CDCl}_3$  at 223 K.



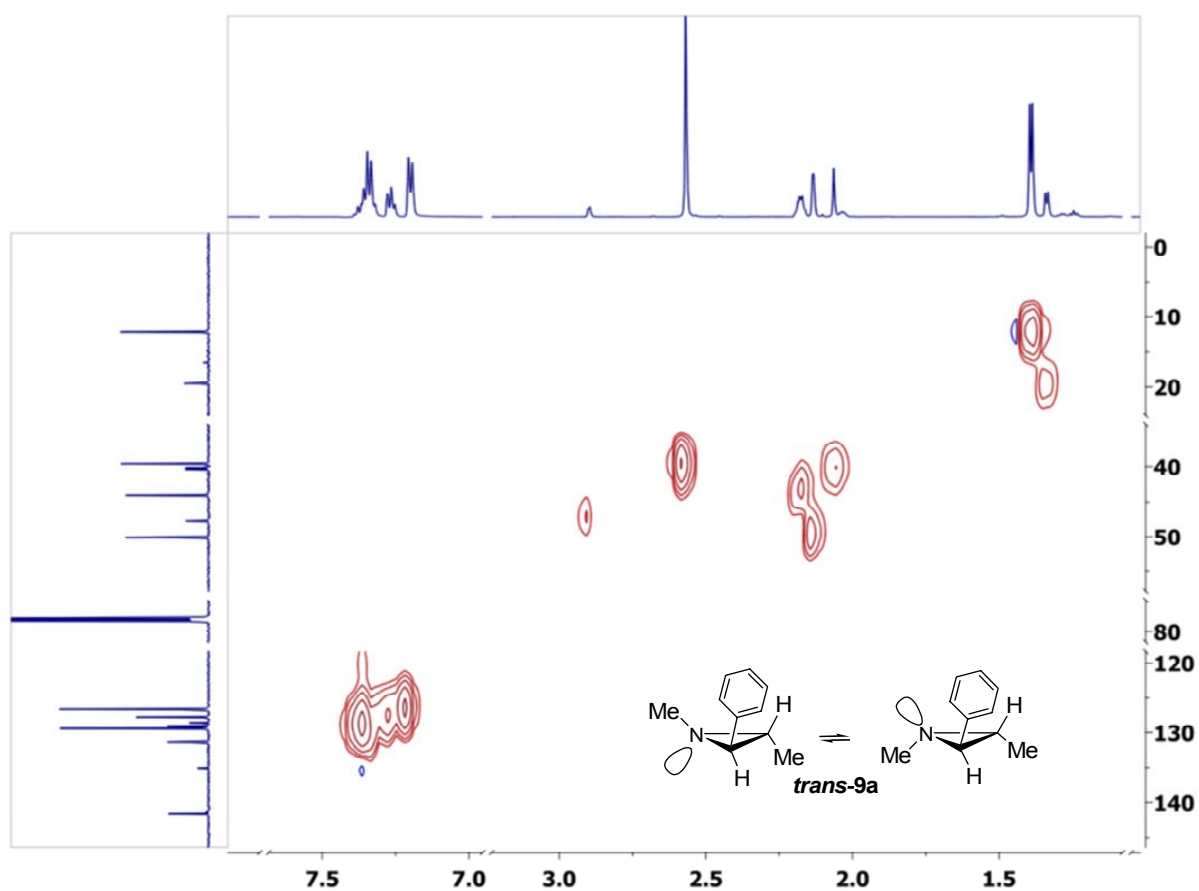
$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **6b-D<sub>2</sub>** in  $\text{CDCl}_3$  at 223 K.



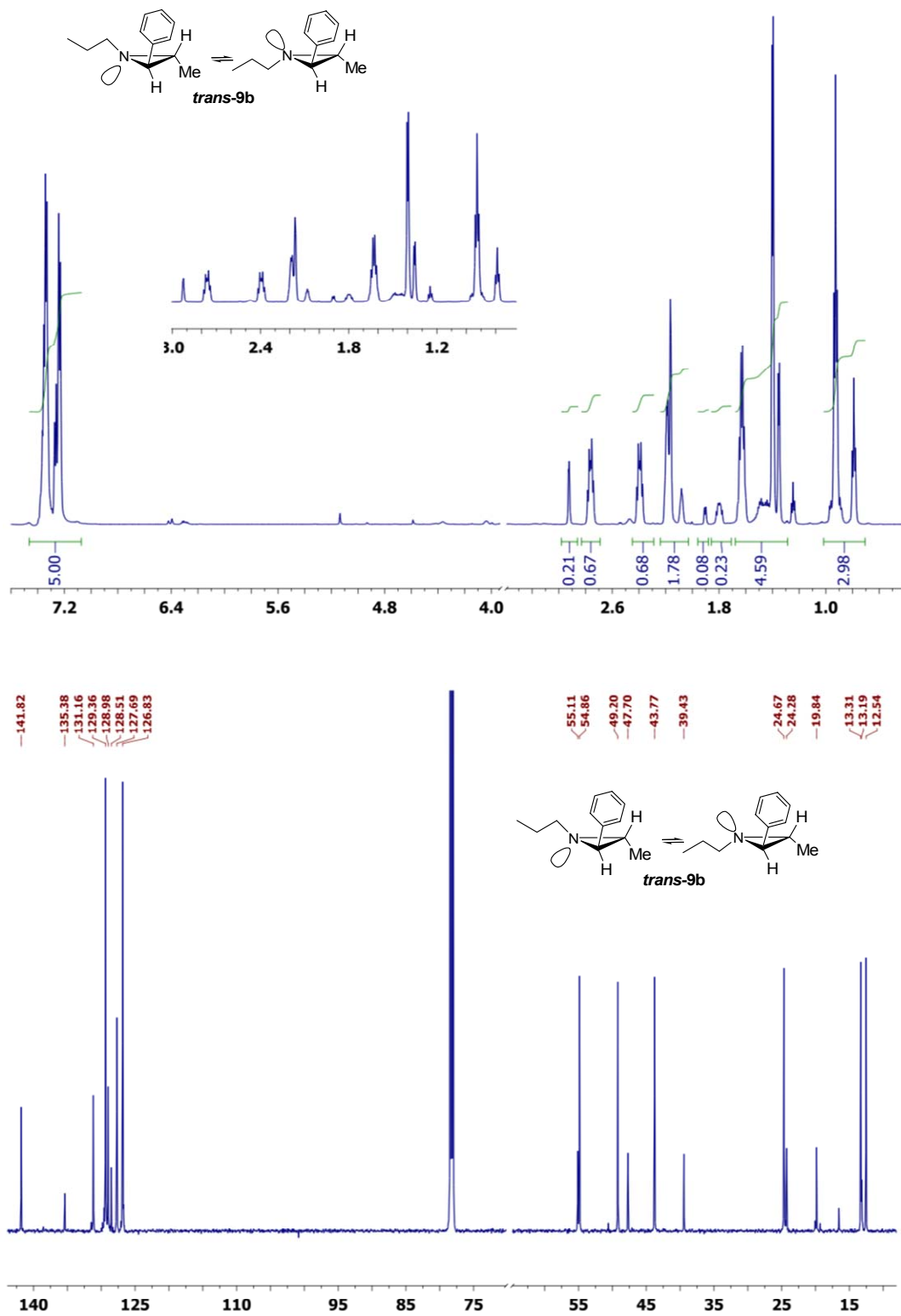
$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine *trans*-**9a** at 223 K.



HSQC-DEPT of aziridine *trans*-**9a** in CDCl<sub>3</sub> at 220 K, (CH<sub>2</sub> in blue and CH and CH<sub>3</sub> in red)

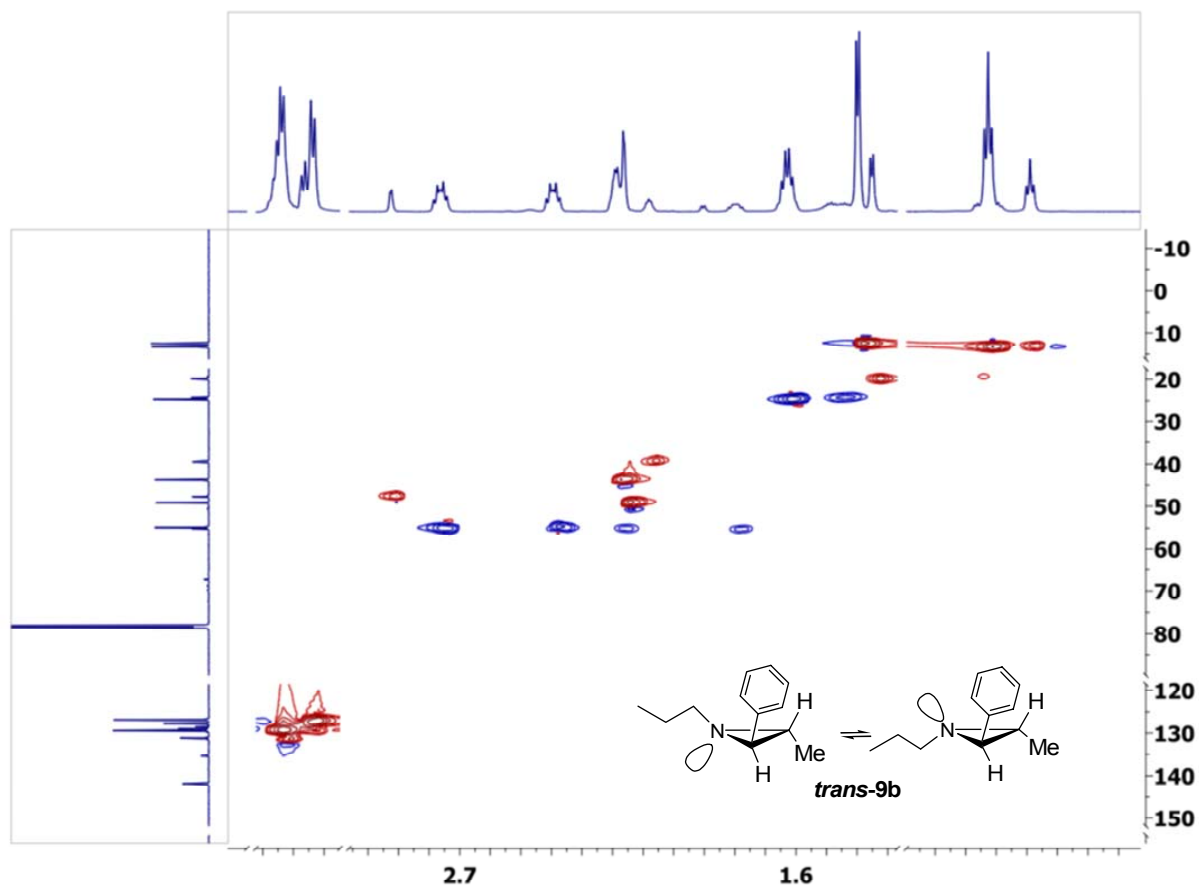


$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine *trans*-**9b** at 223 K.

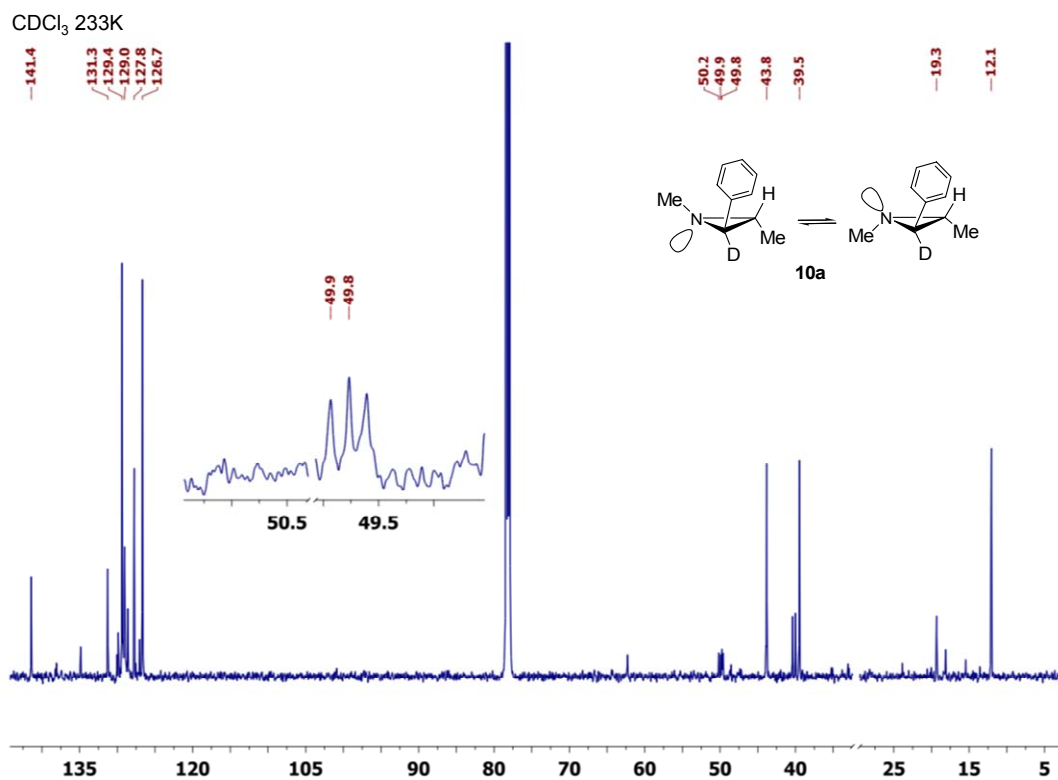
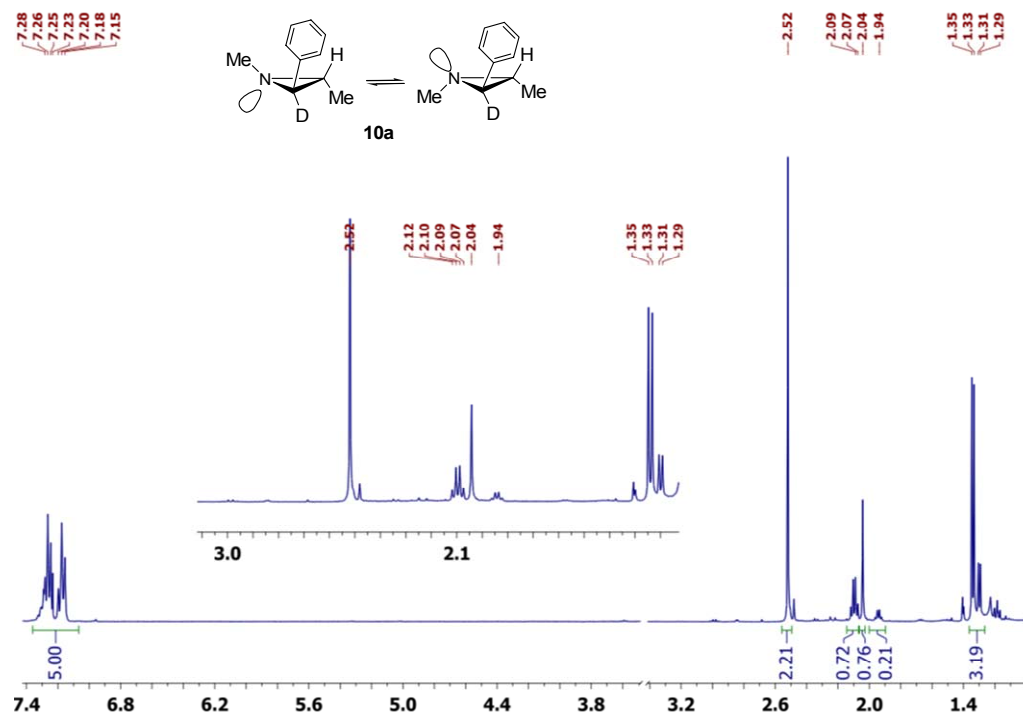




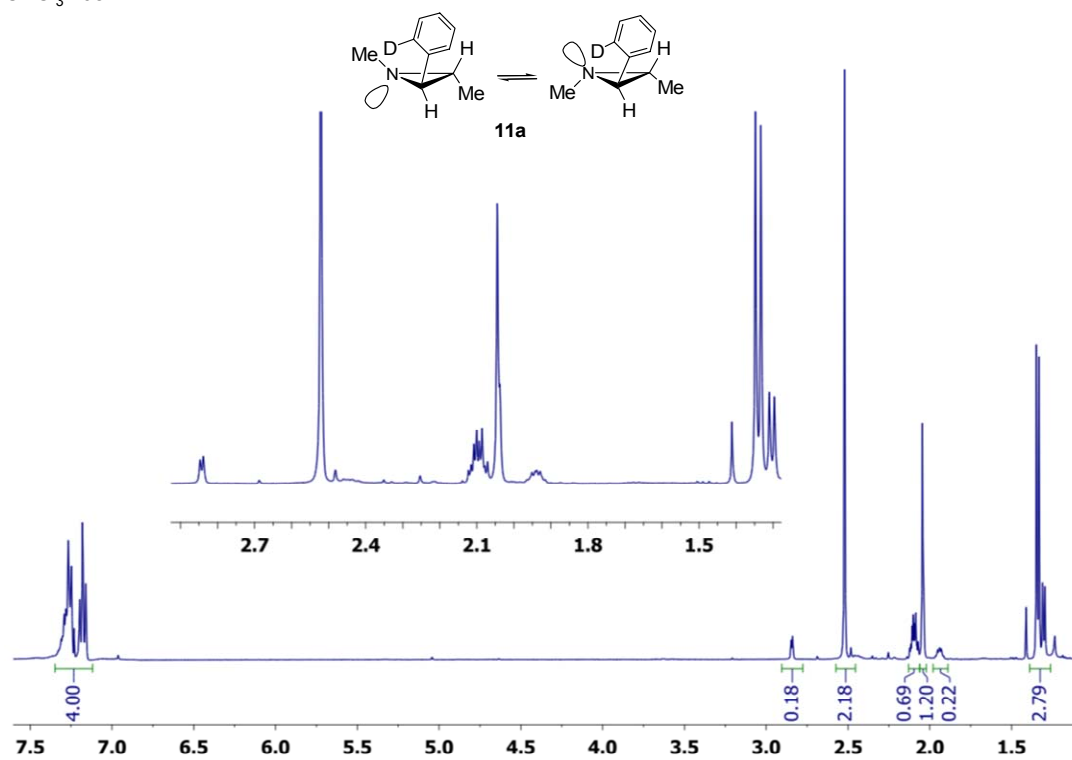
HSQC-DEPT of aziridine **trans-9b** in  $\text{CDCl}_3$  at 220 K, ( $\text{CH}_2$  in blue and  $\text{CH}$  and  $\text{CH}_3$  in red).



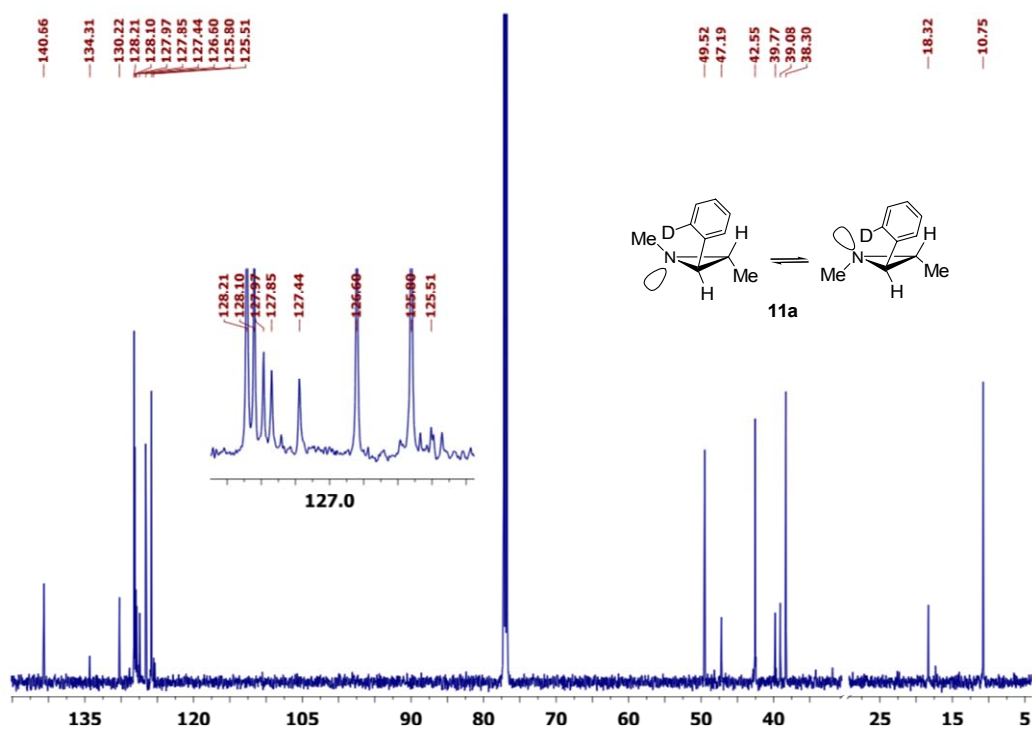
$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **10a**  
 $\text{CDCl}_3$  298K



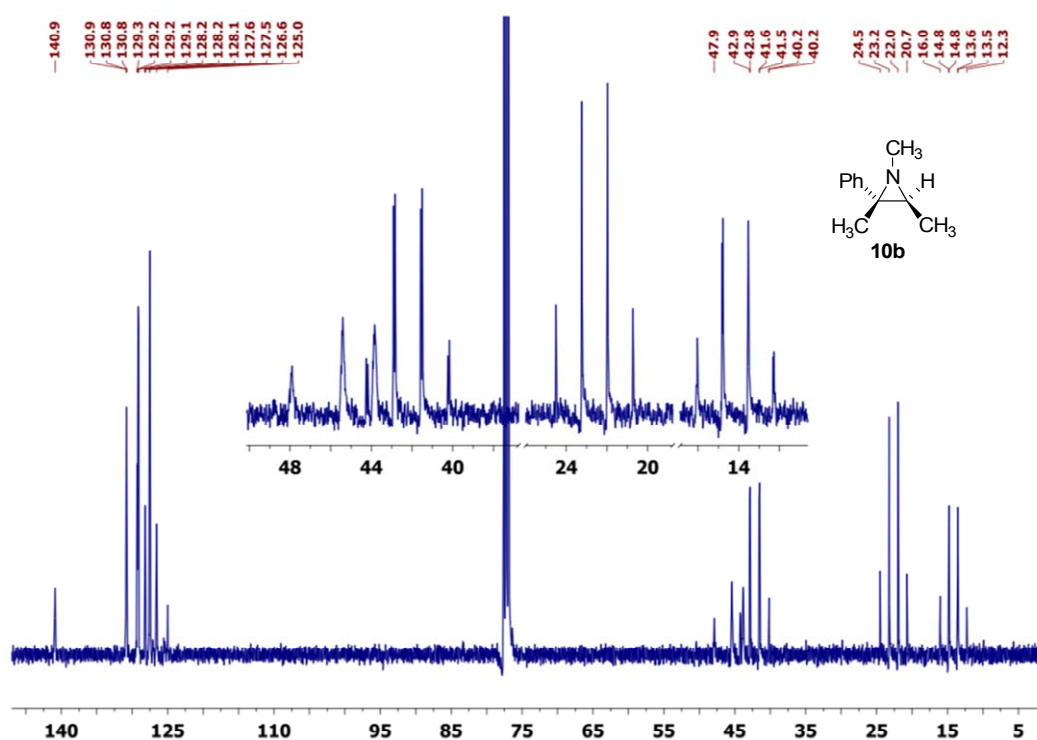
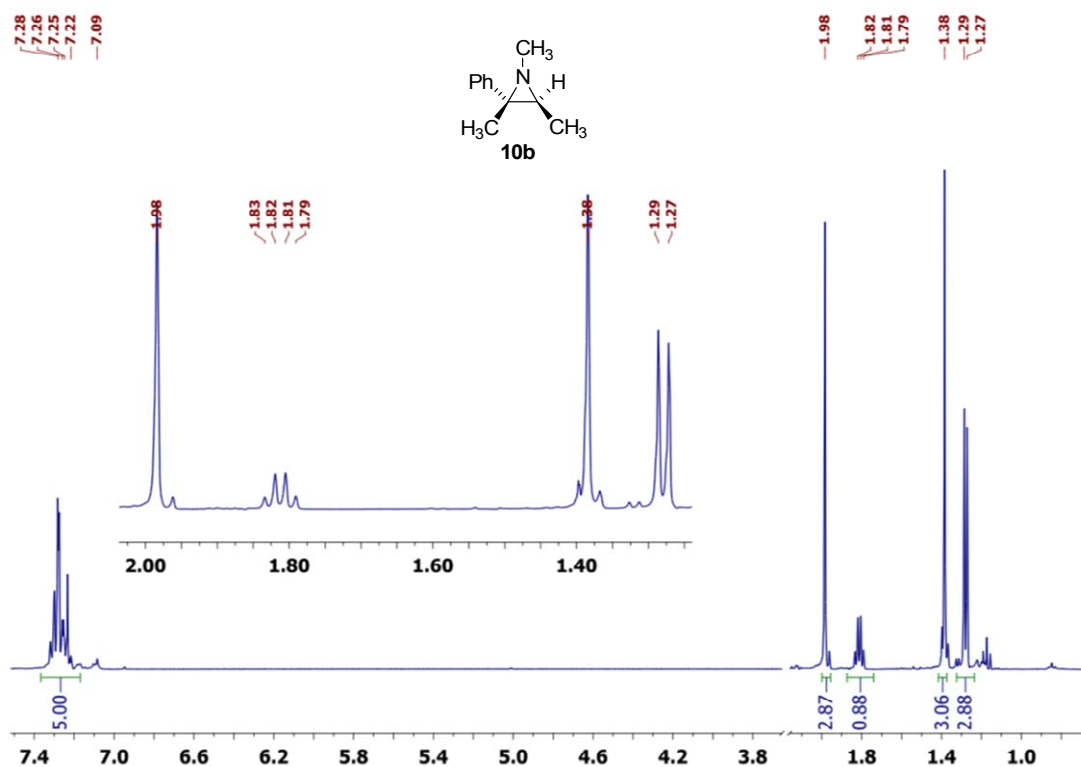
$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **11a**.  
 $\text{CDCl}_3$  298K



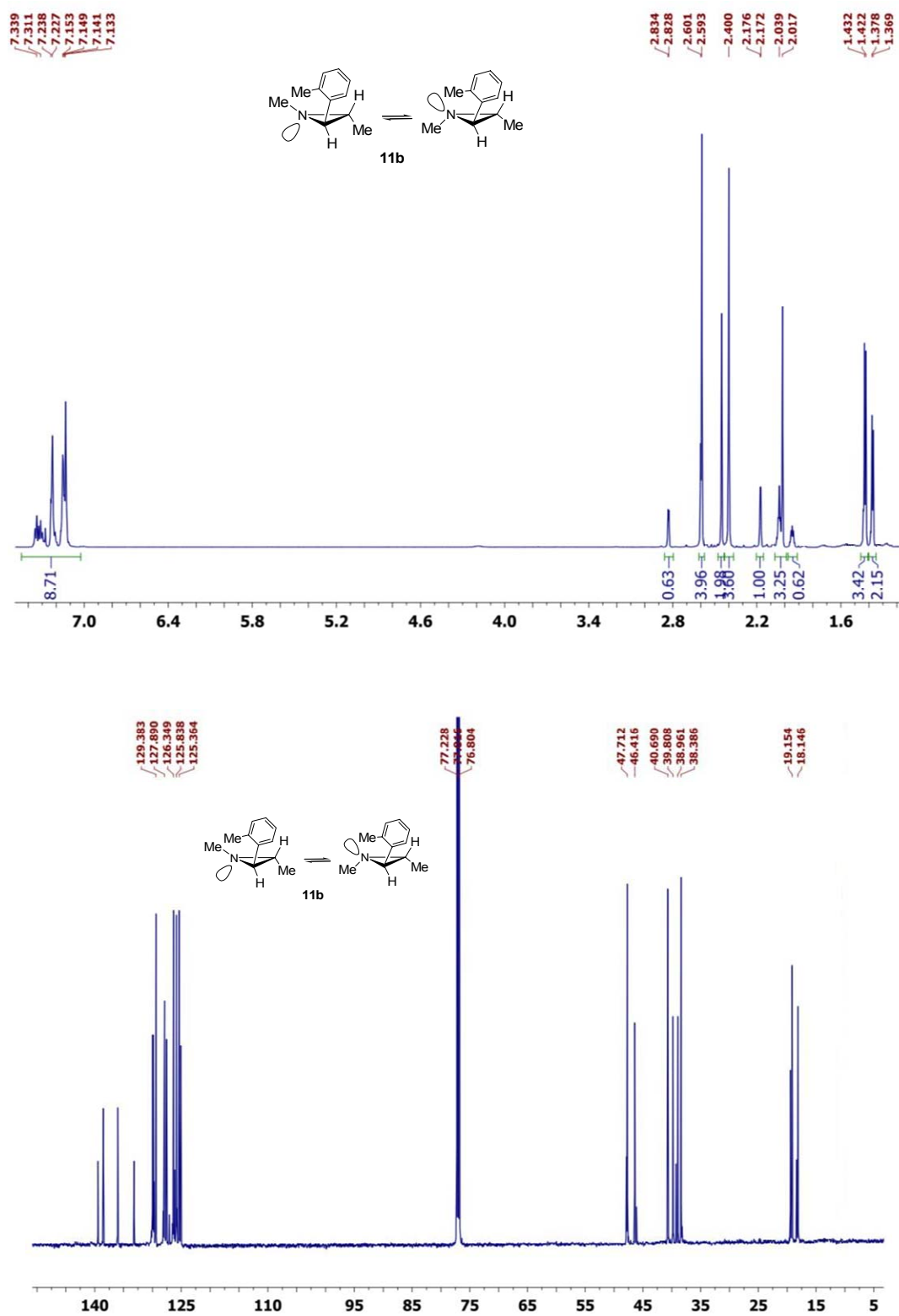
$\text{CDCl}_3$  298K



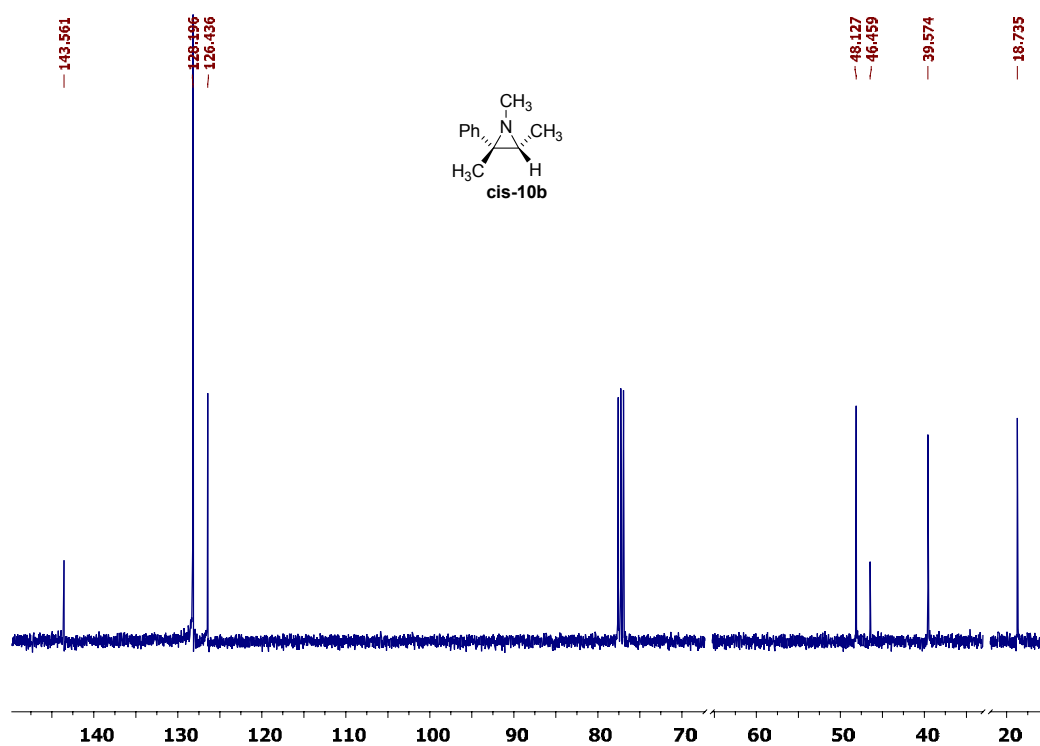
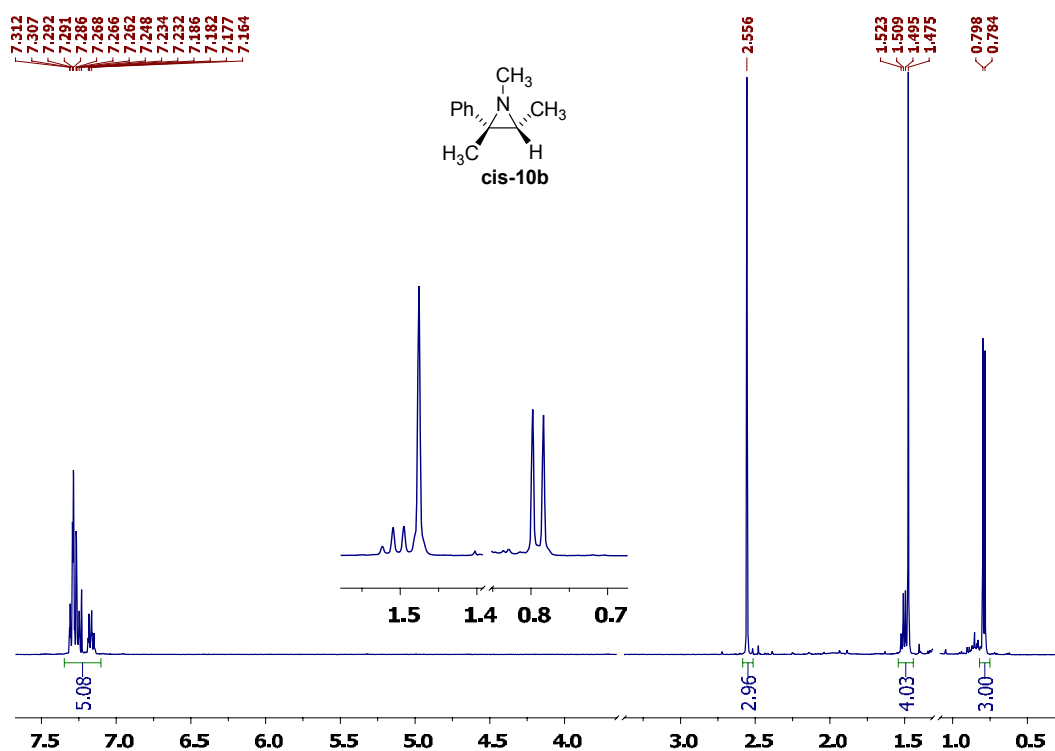
$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **10b**.

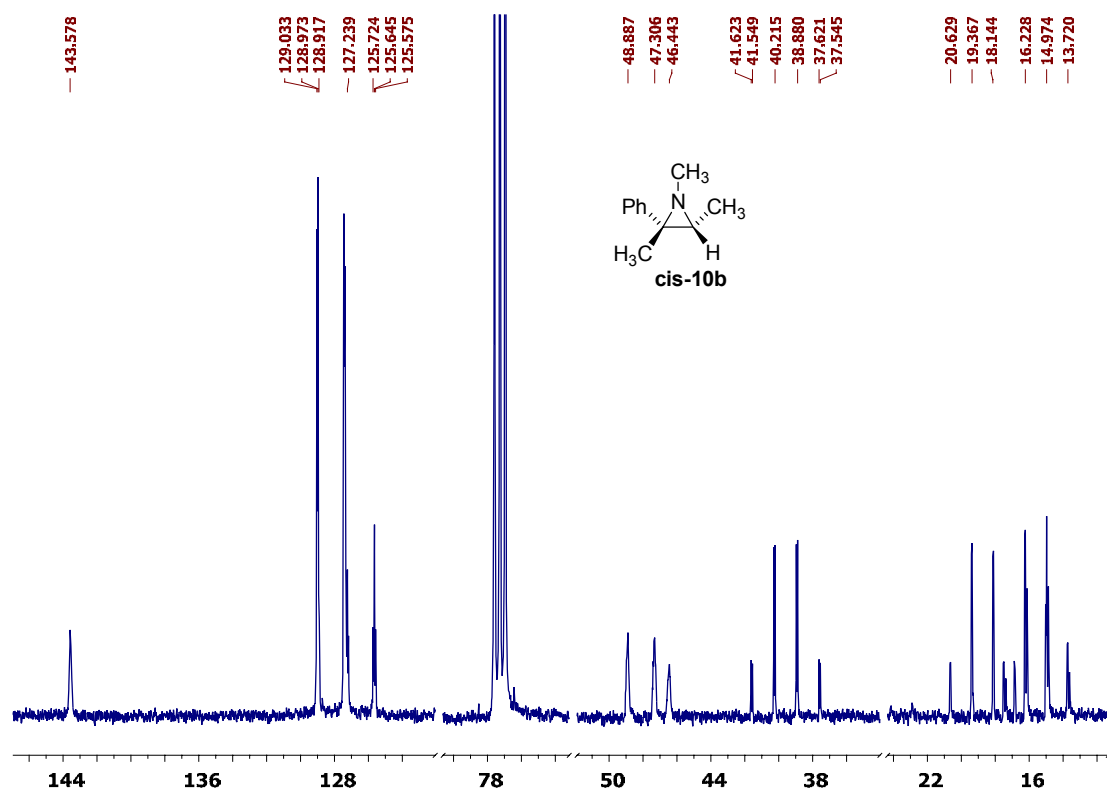


$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **11b**.



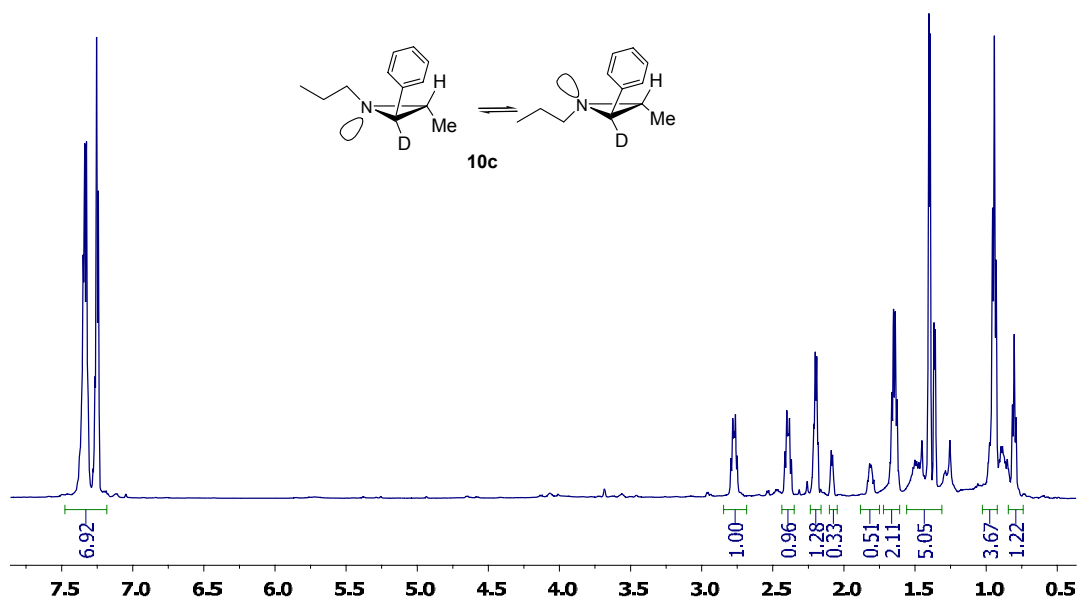
$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **cis-10b**.



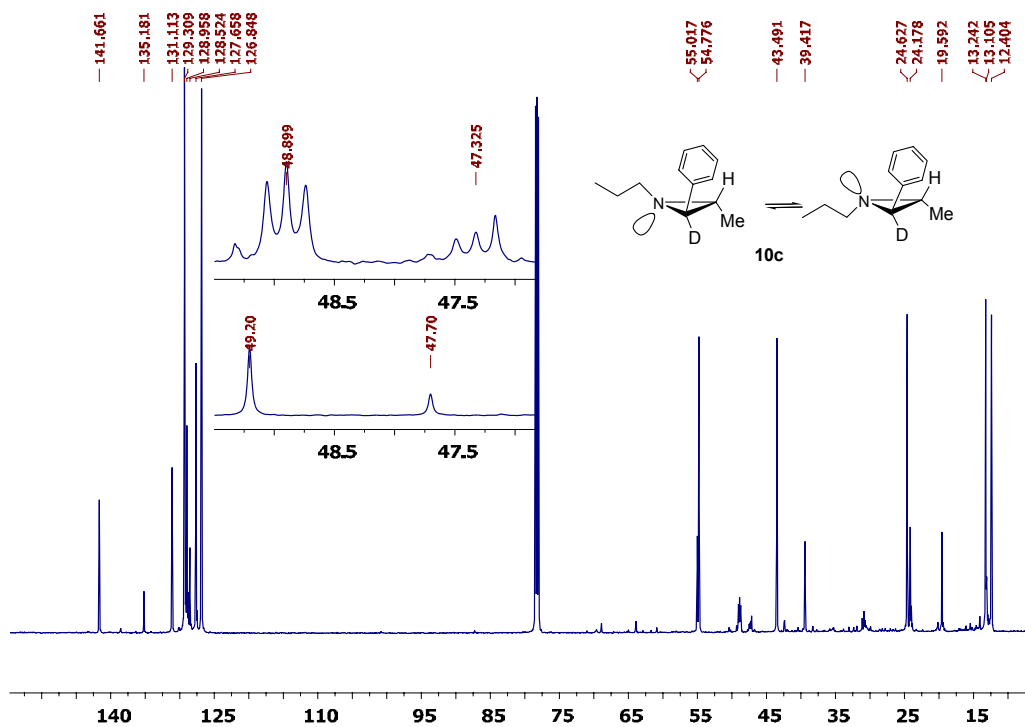


$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **10c** (in the inset of the  $^{13}\text{C}$  NMR there is a comparison between deuterated and undeuterated aziridines **10c** and *trans*-**9b**)

$\text{CDCl}_3$  220K



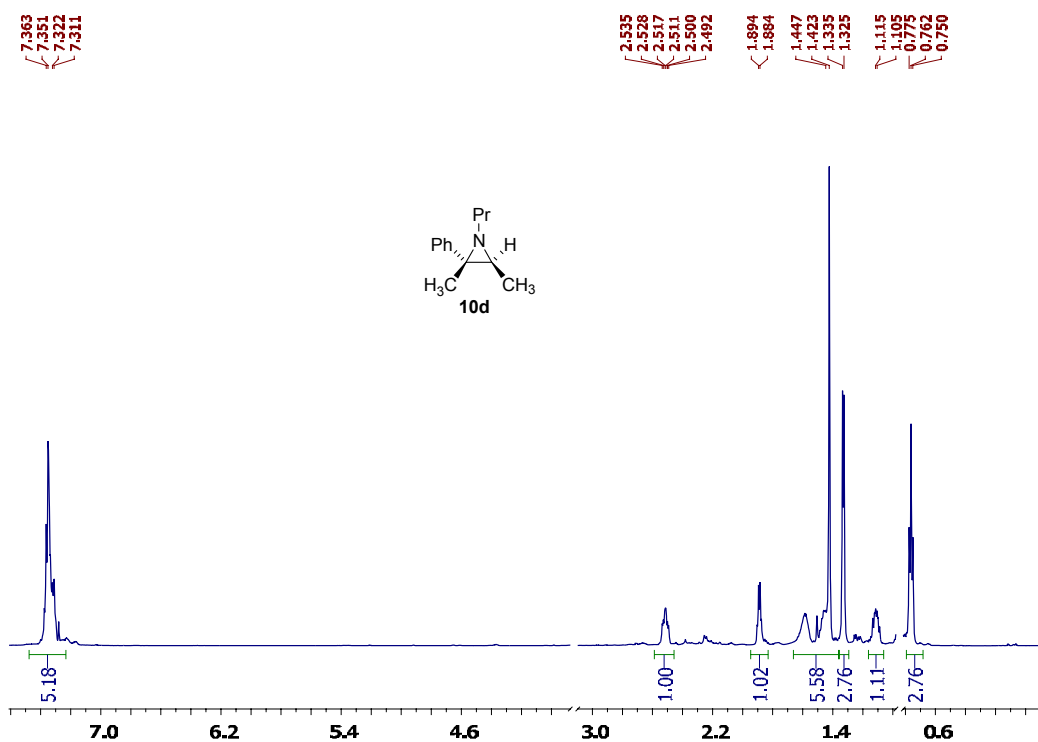
$\text{CDCl}_3$  220K



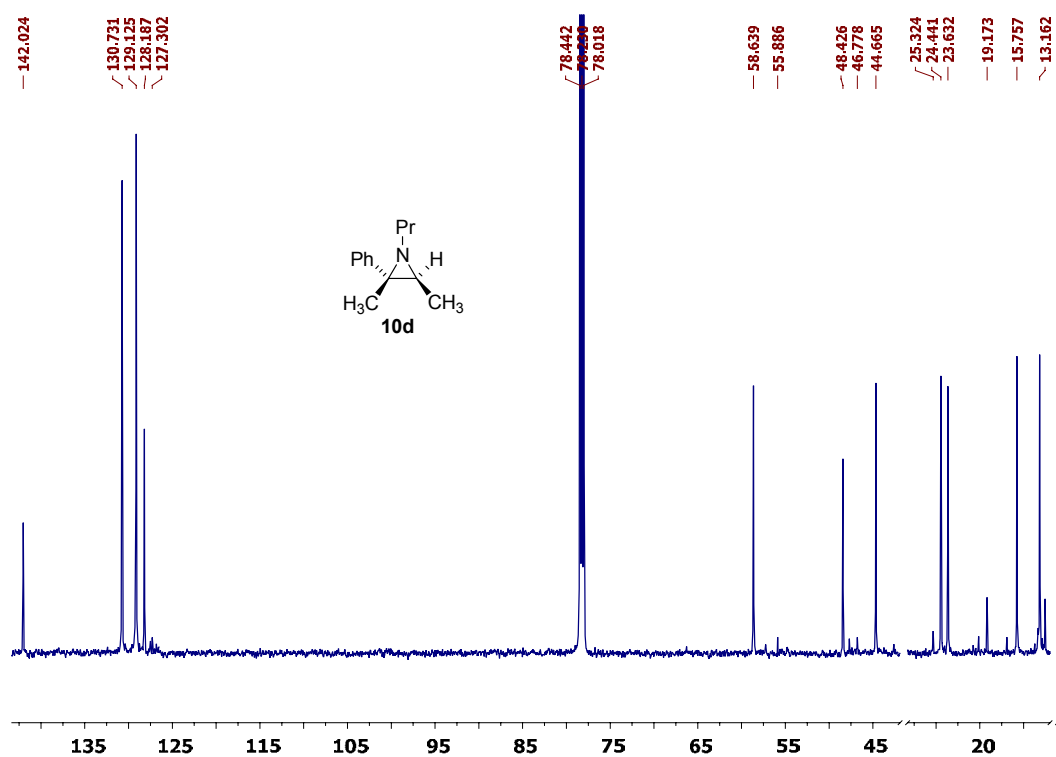


$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **10d**.

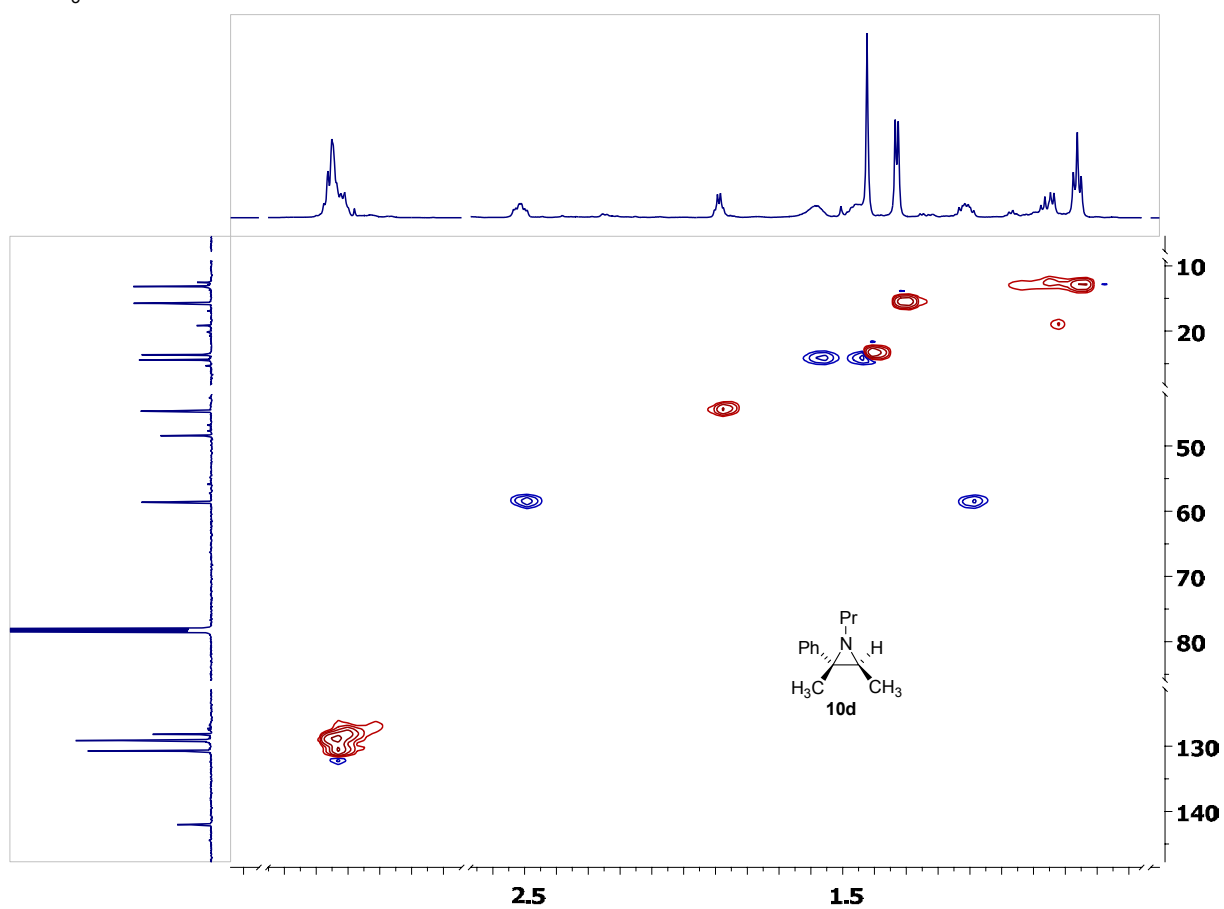
$\text{CDCl}_3$  220 K



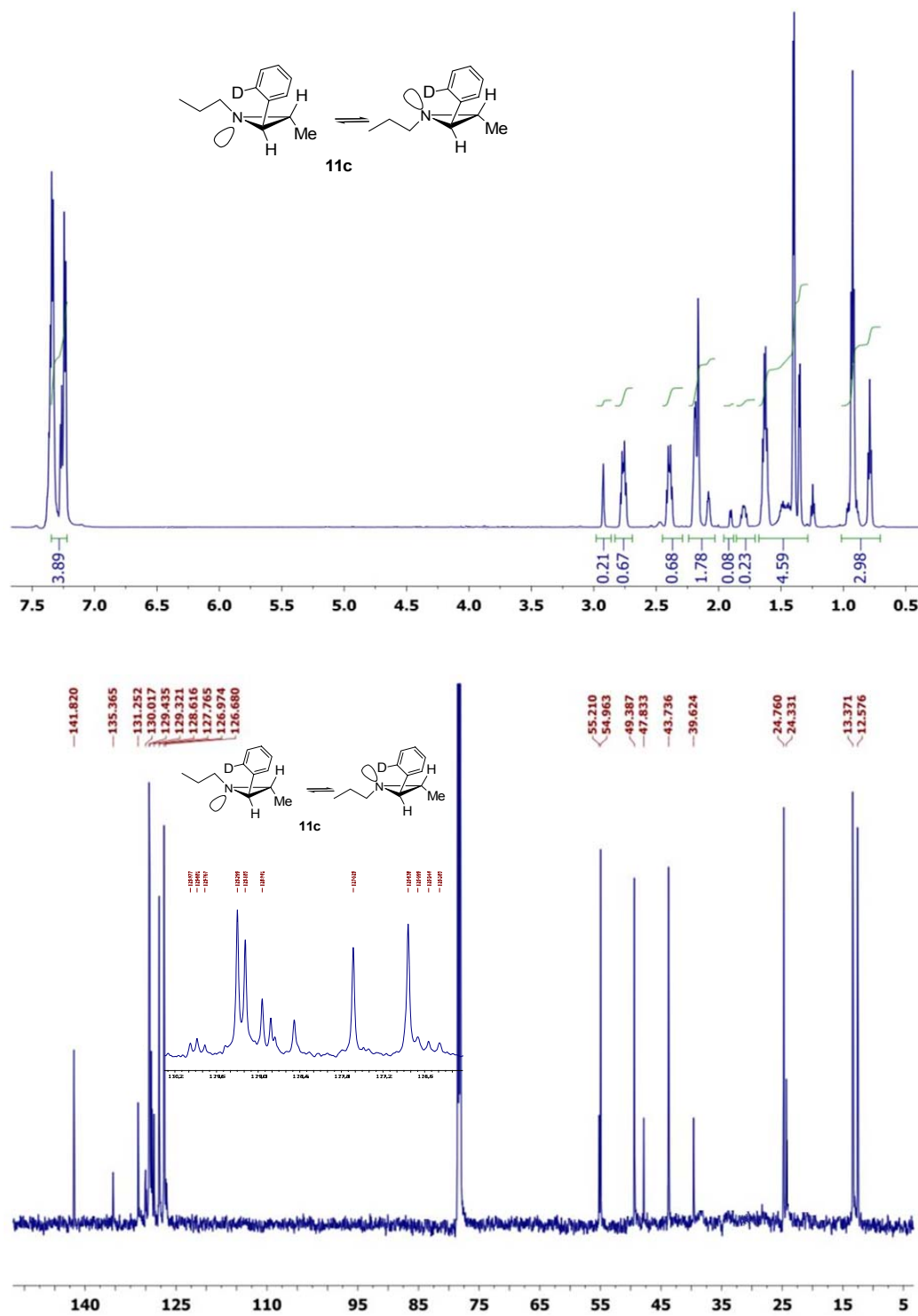
$\text{CDCl}_3$  220 K



HSQC-DEPT of aziridine **10d** in  $\text{CDCl}_3$  at 220 K, ( $\text{CH}_2$  in blue and  $\text{CH}$  and  $\text{CH}_3$  in red).  
 $\text{CDCl}_3$  220 K

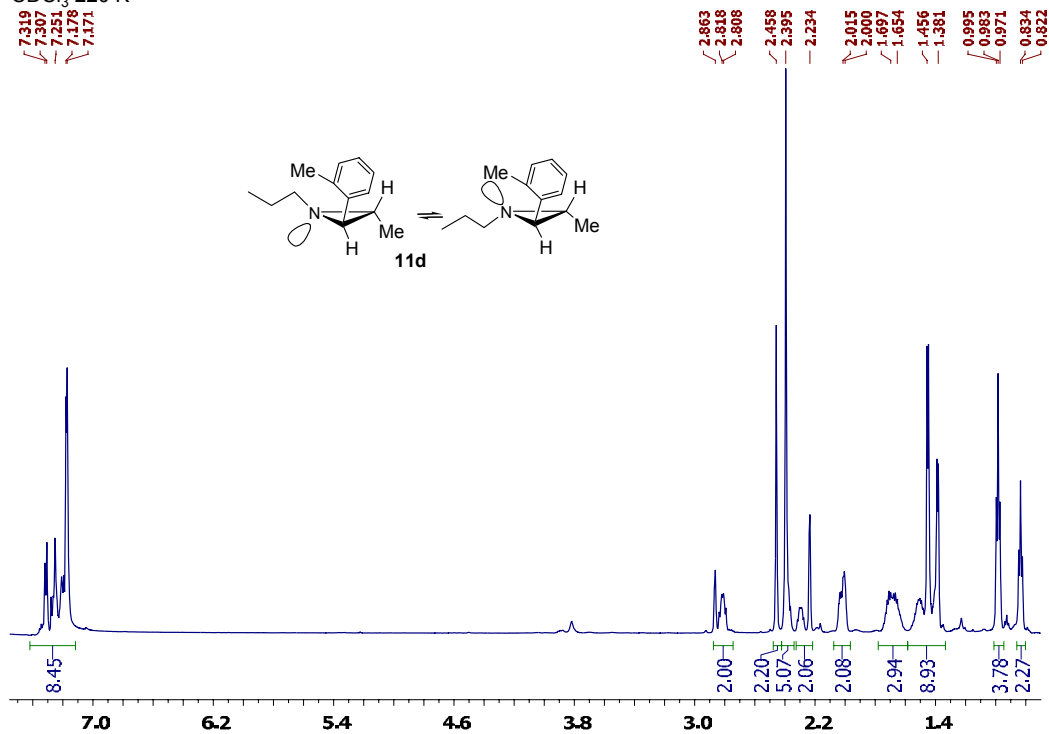


$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **11c**.

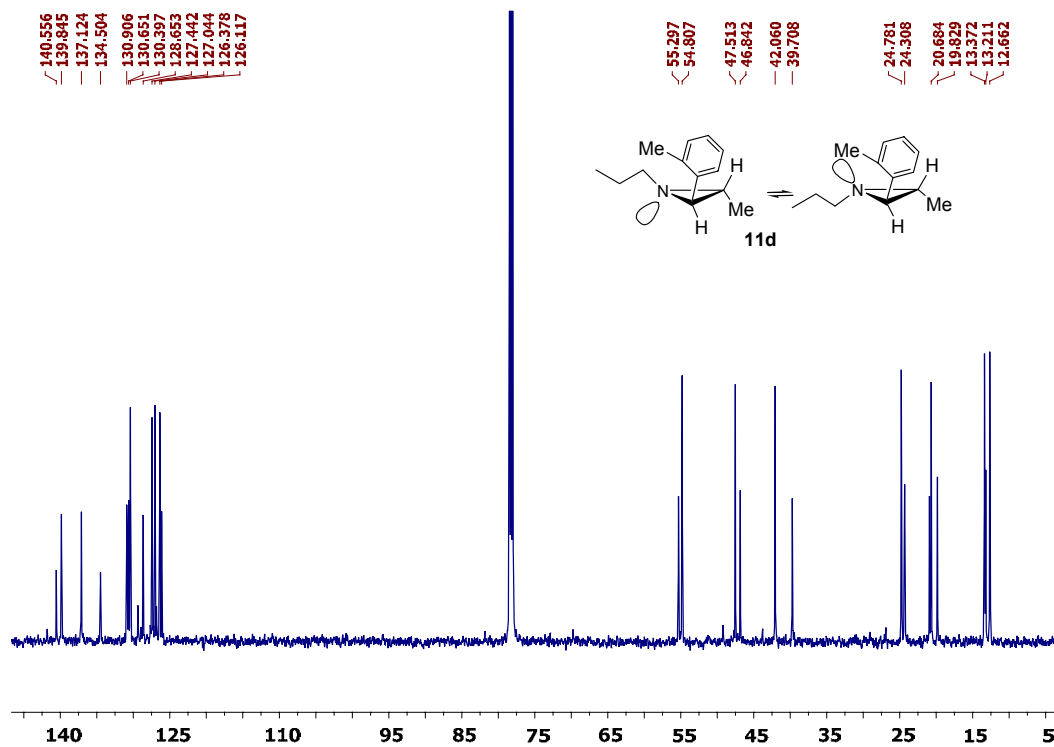


$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **11d**.

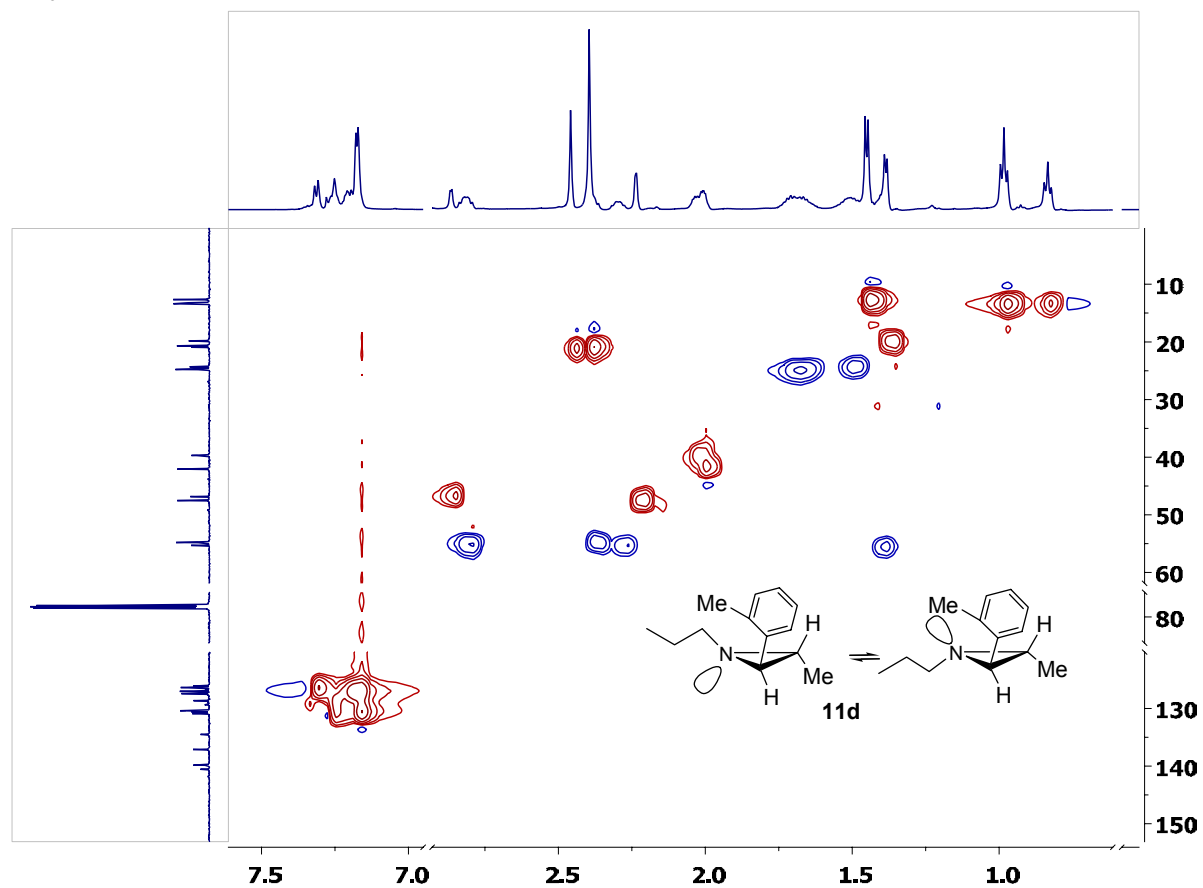
$\text{CDCl}_3$  220 K



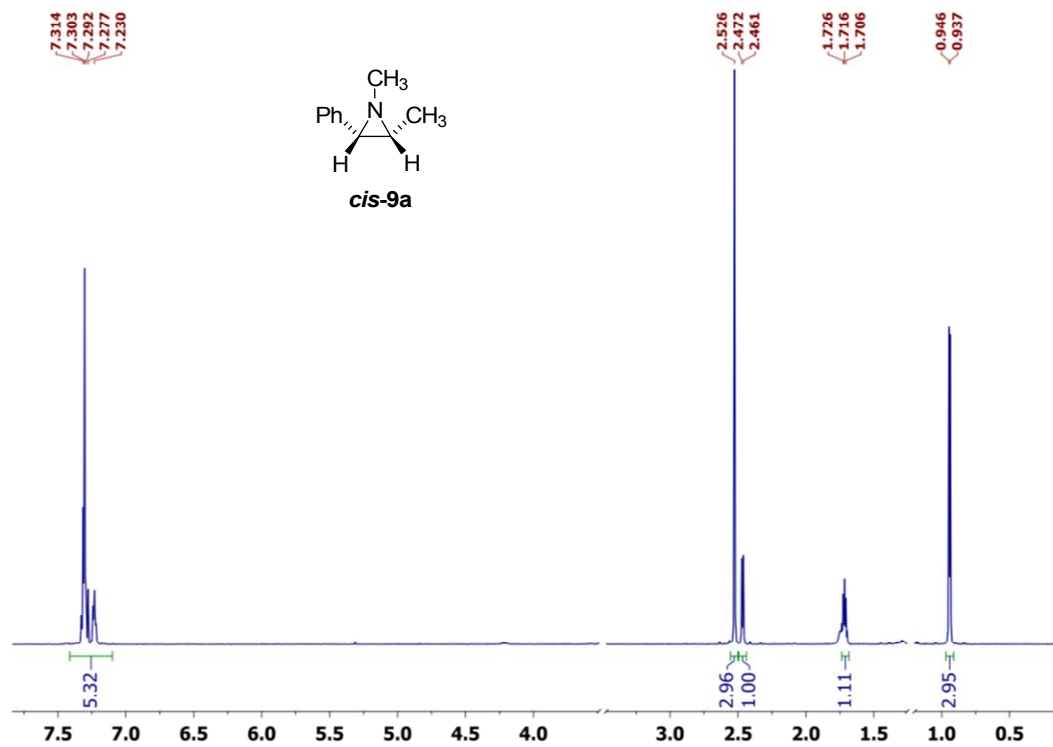
$\text{CDCl}_3$  220 K



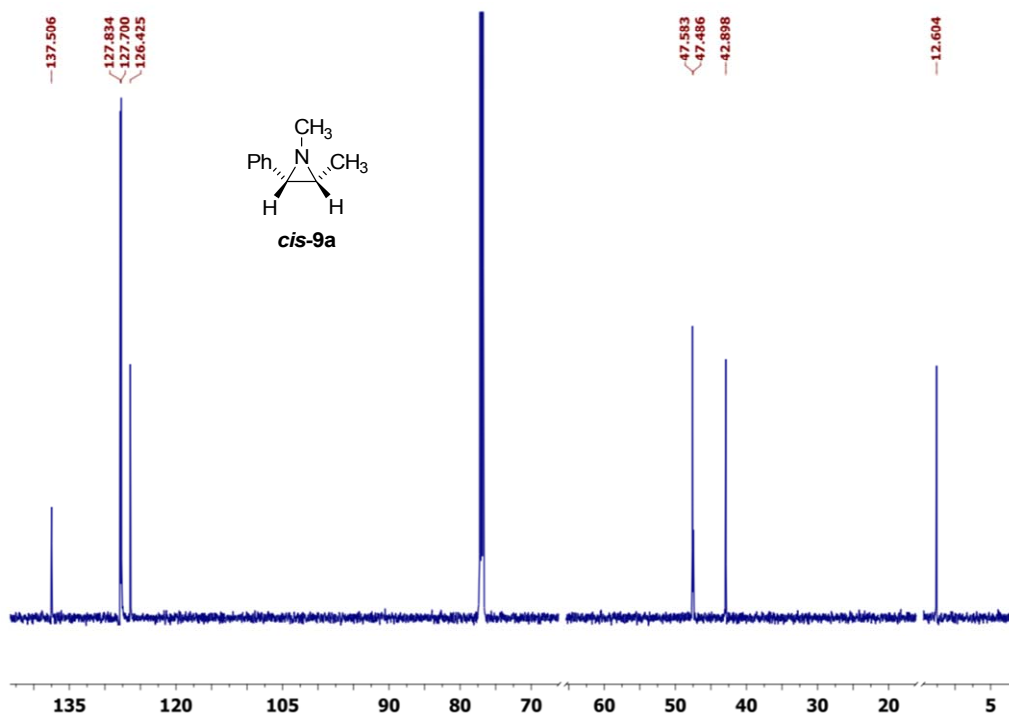
HSQC-DEPT of aziridine **11d** in CDCl<sub>3</sub> at 220 K, (CH<sub>2</sub> in blue and CH and CH<sub>3</sub> in red).  
CDCl<sub>3</sub> 220 K



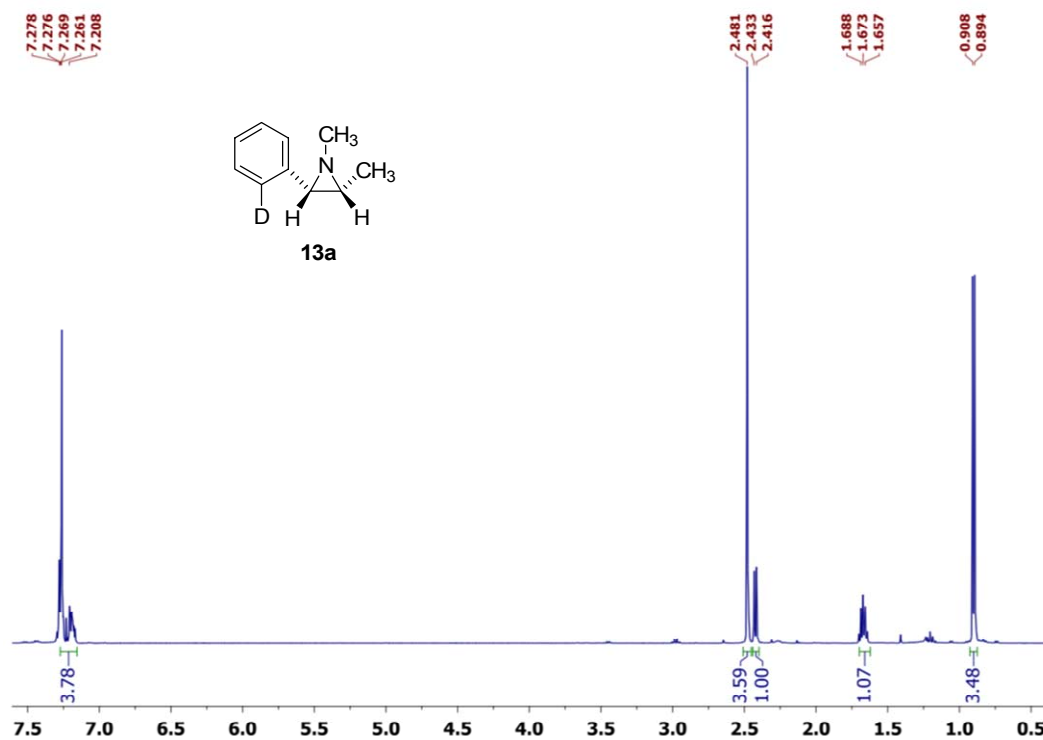
$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine *cis*-**9a**.



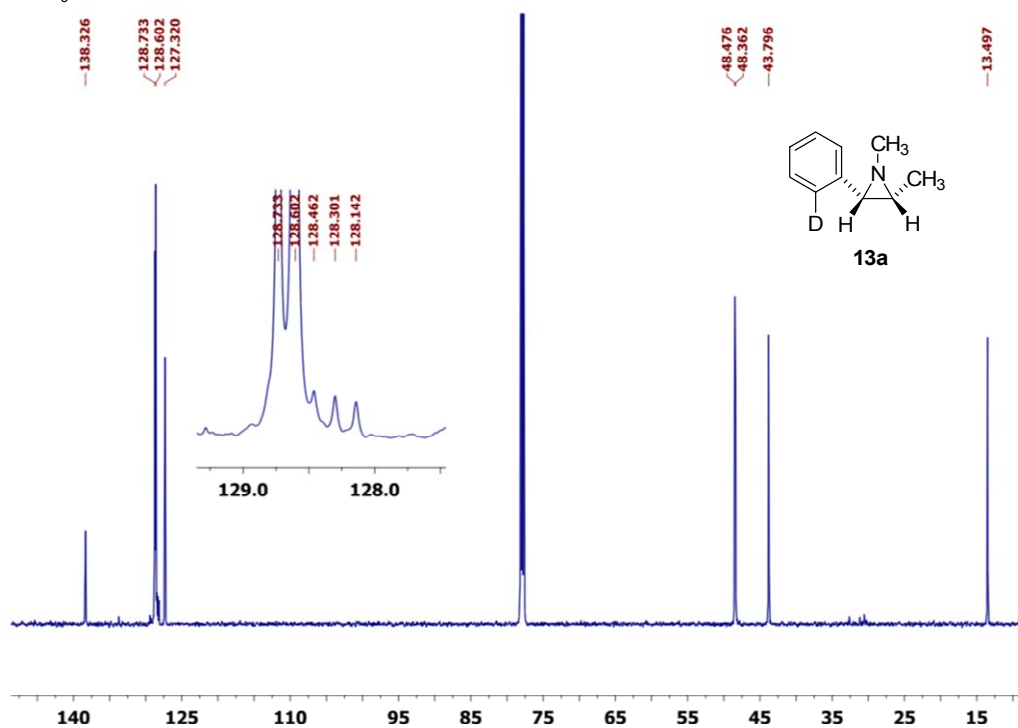
$\text{CDCl}_3$  298 K



$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **13a**.  
 $\text{CDCl}_3$  298 K

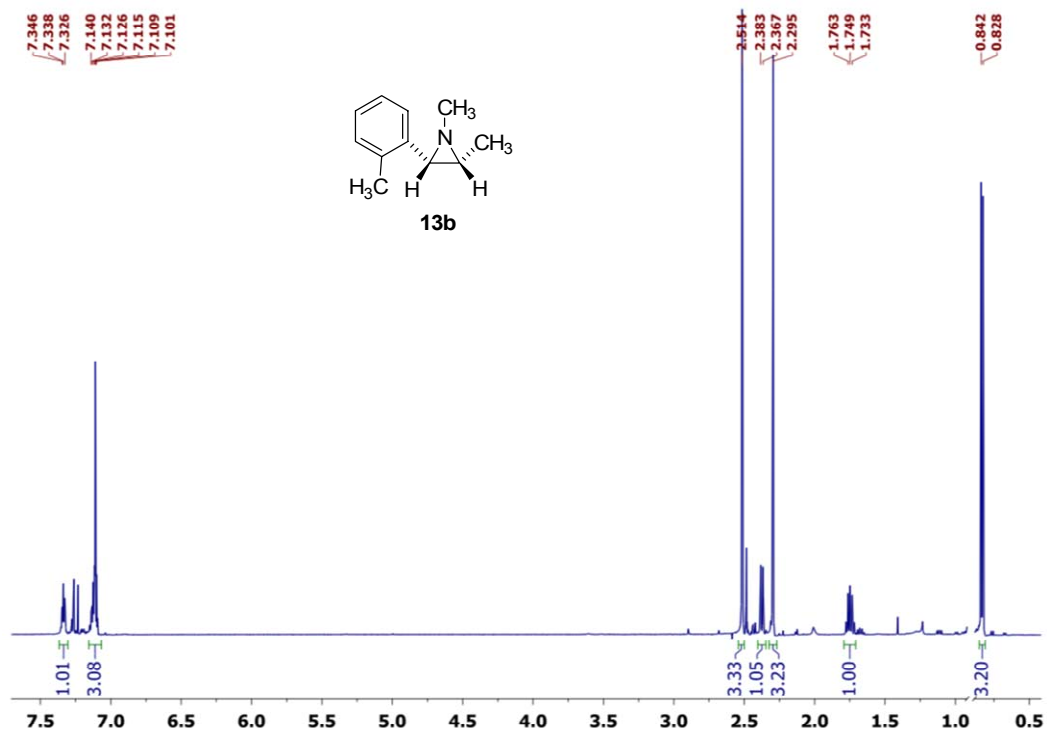


$\text{CDCl}_3$  298 K

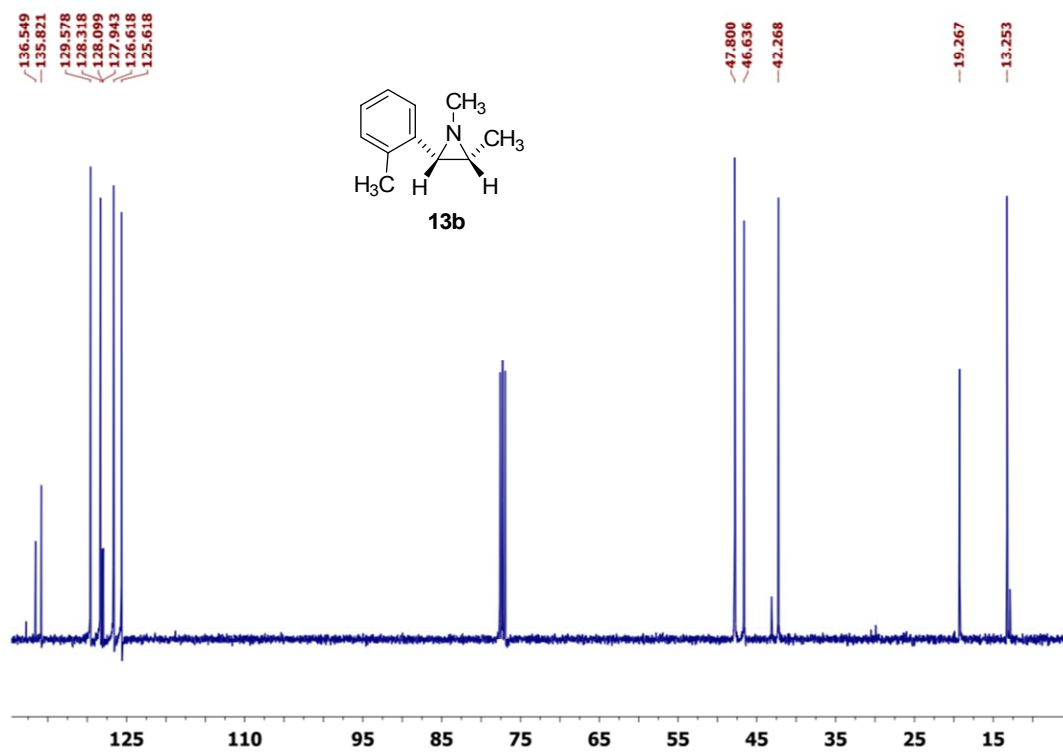


$^1\text{H}$  and  $^{13}\text{C}$  NMR of aziridine **13b**.

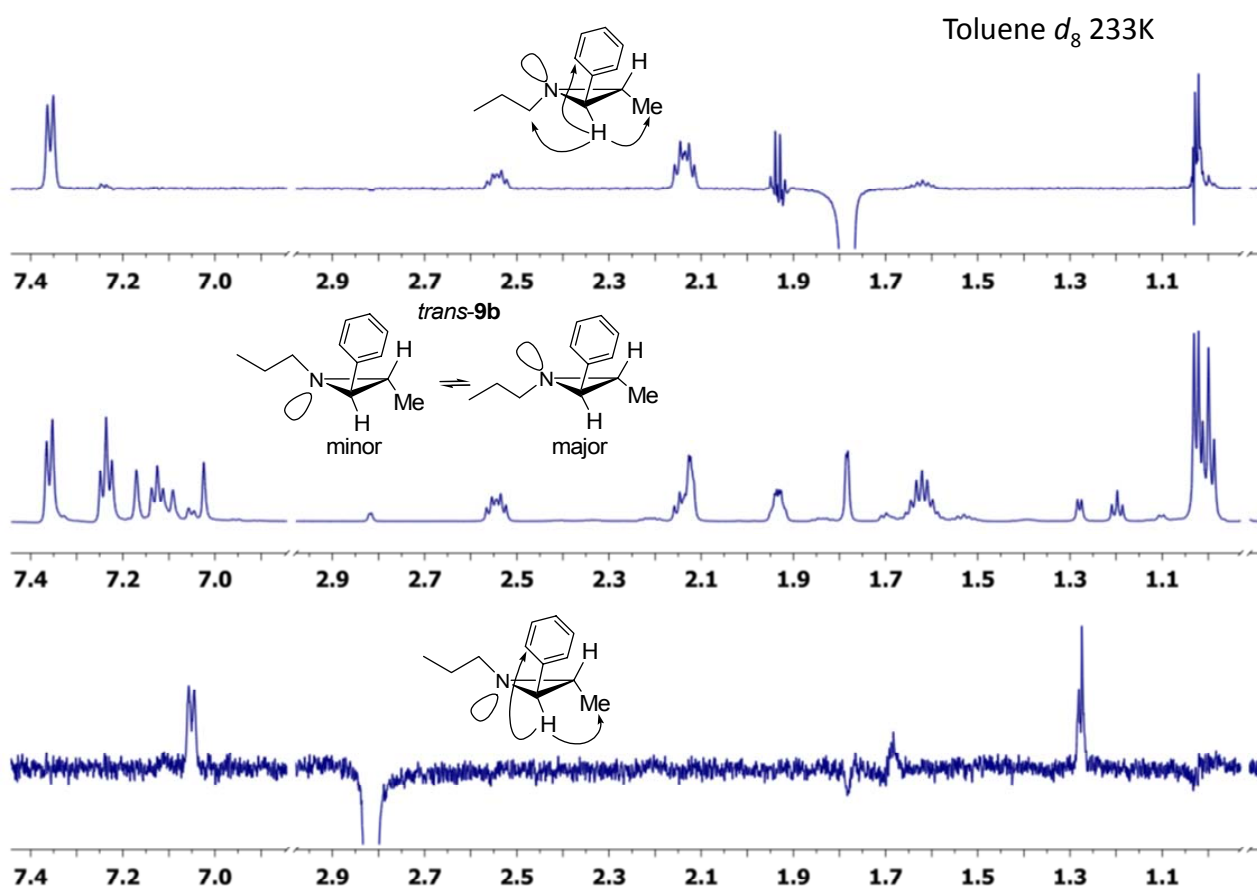
$\text{CDCl}_3$  298 K



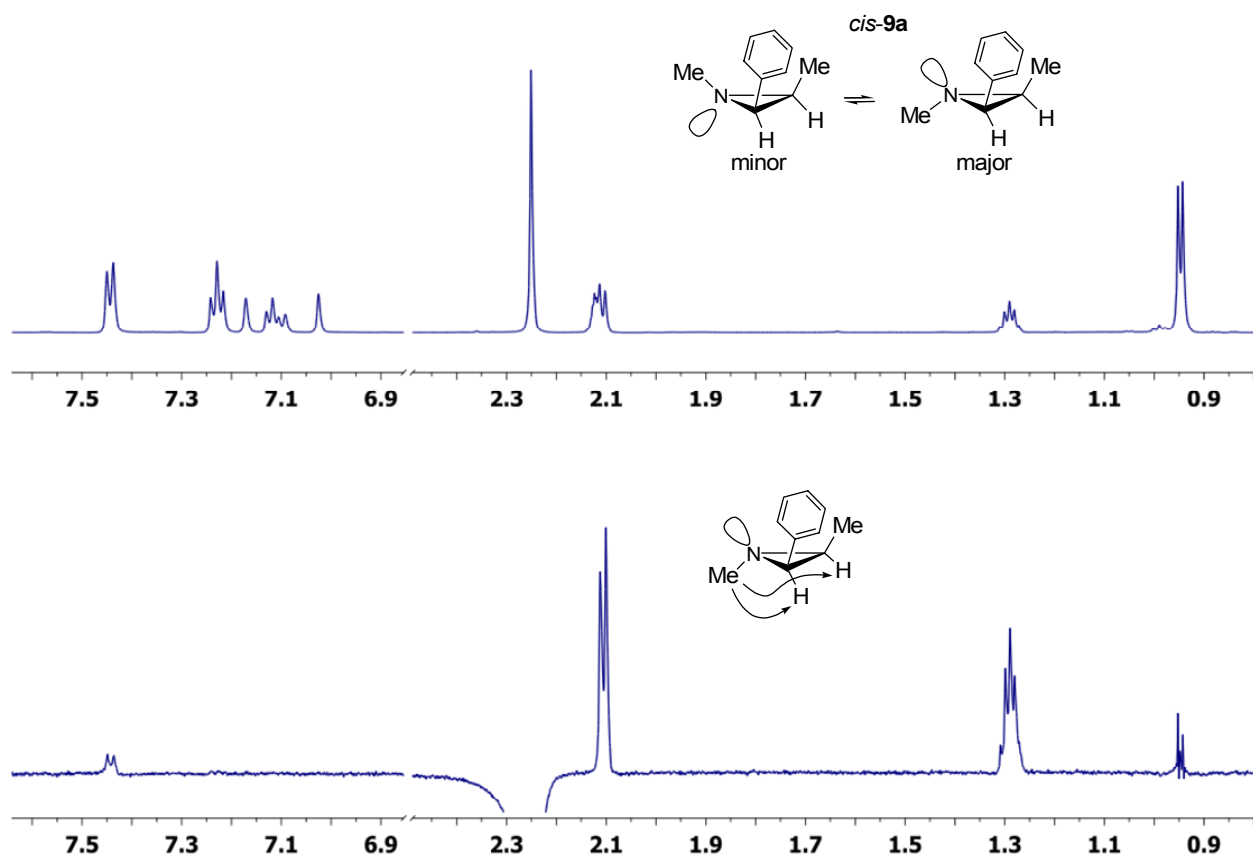
$\text{CDCl}_3$  298 K



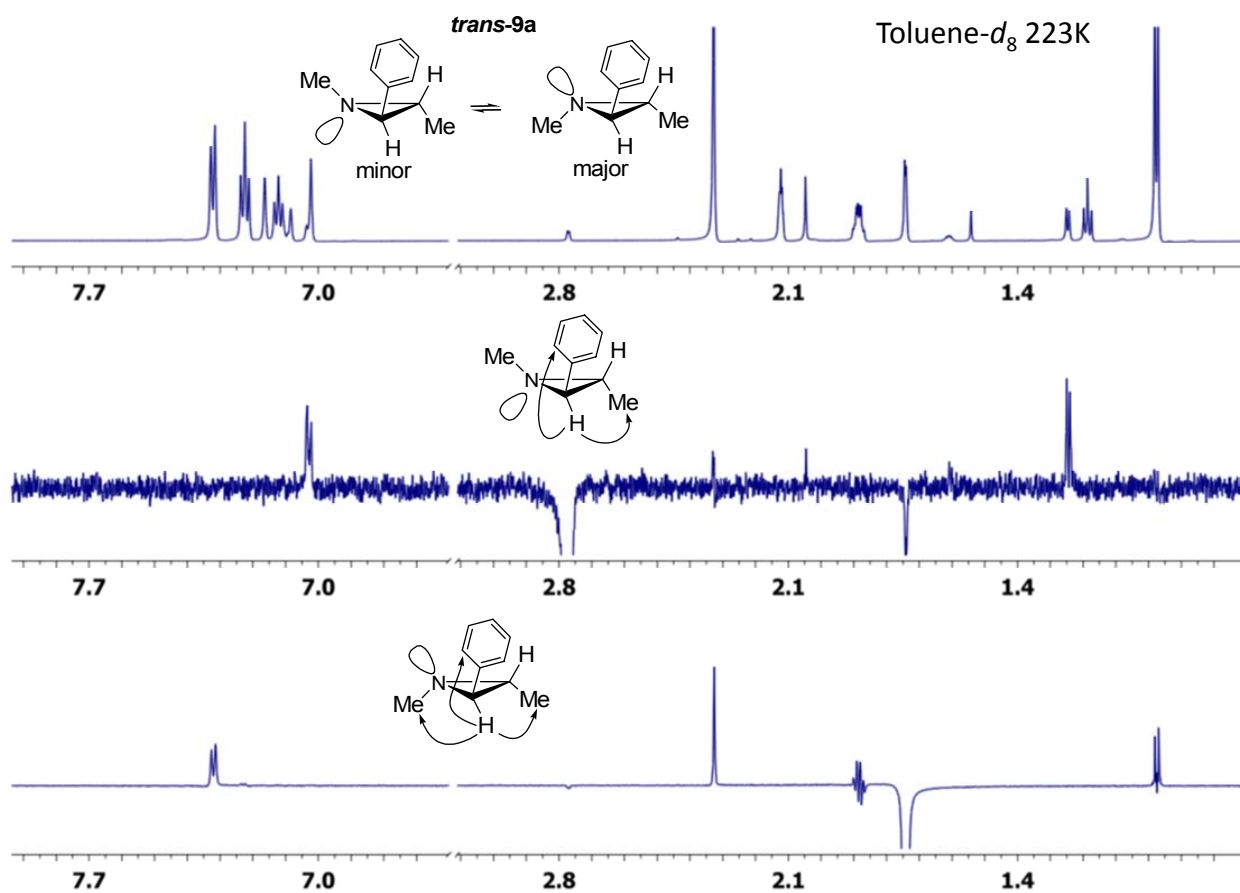




NOESY-1D spectra of aziridines *trans*-**9b** in toluene- $d_8$  at 233 K under slow exchange conditions.



NOESY-1D spectra of aziridines *cis-9* in toluene- $d_8$  at 223 K under slow exchange conditions.



NOESY-1D spectra of aziridines *trans*-9a in toluene-*d*<sub>8</sub> at 223 K under slow exchange conditions.

The deuterium incorporation was determined by ESI-MS on the protonated molecular ion and after correction of the amount of the non deuterated aziridine eventually present in the sample.

Sample preparation:

The crude (1 mg) was dissolved in 1 mL of MeOH and 10  $\mu$ L of formic acid were added. The resulting solution was directly injected into the ESI-MS analyzer.

