Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Selective Synthesis of *exo*-Spiro[oxirane-3,2'-tropanes]

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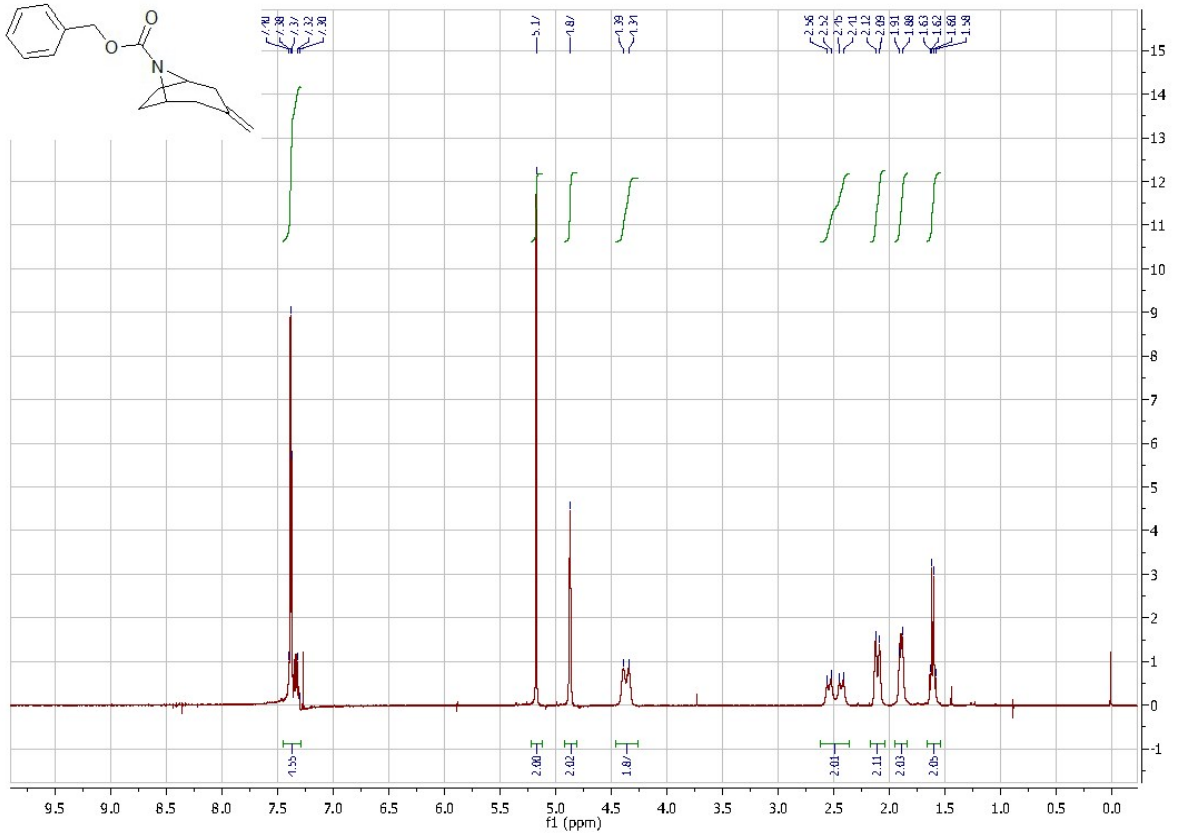
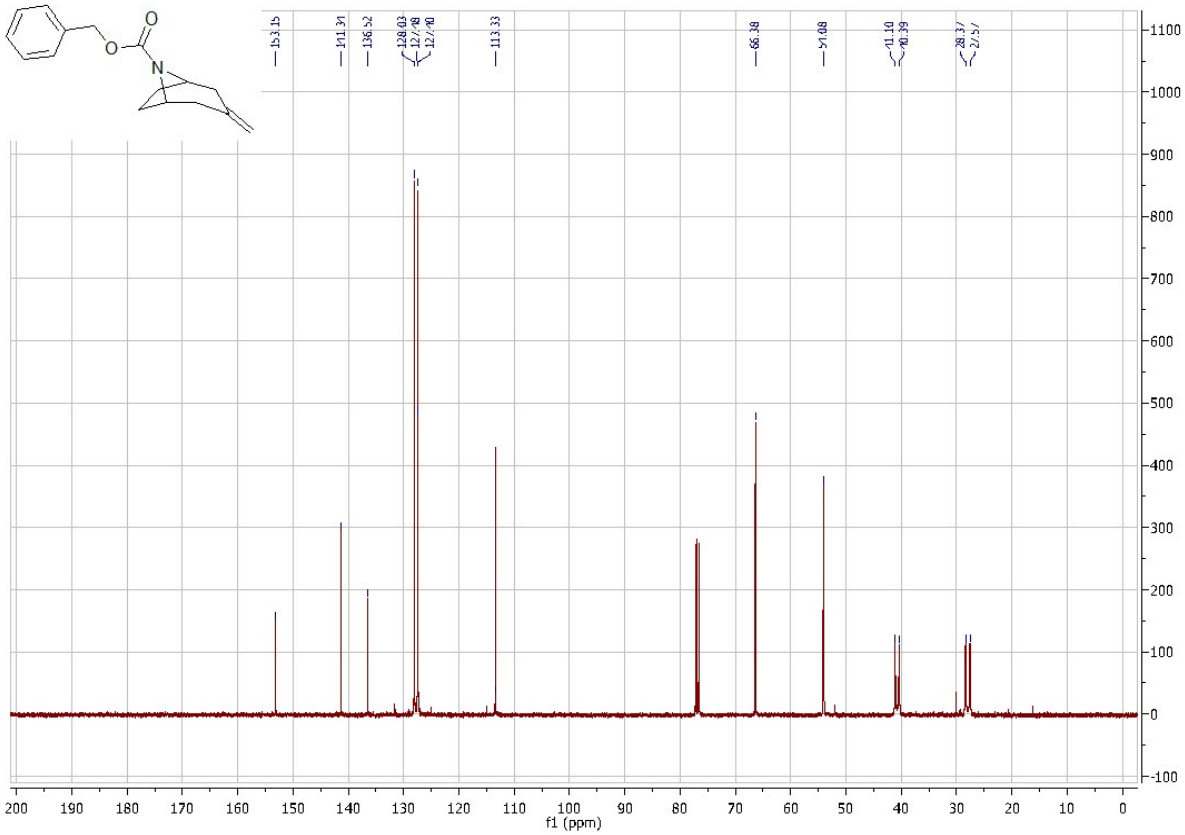
Supporting information

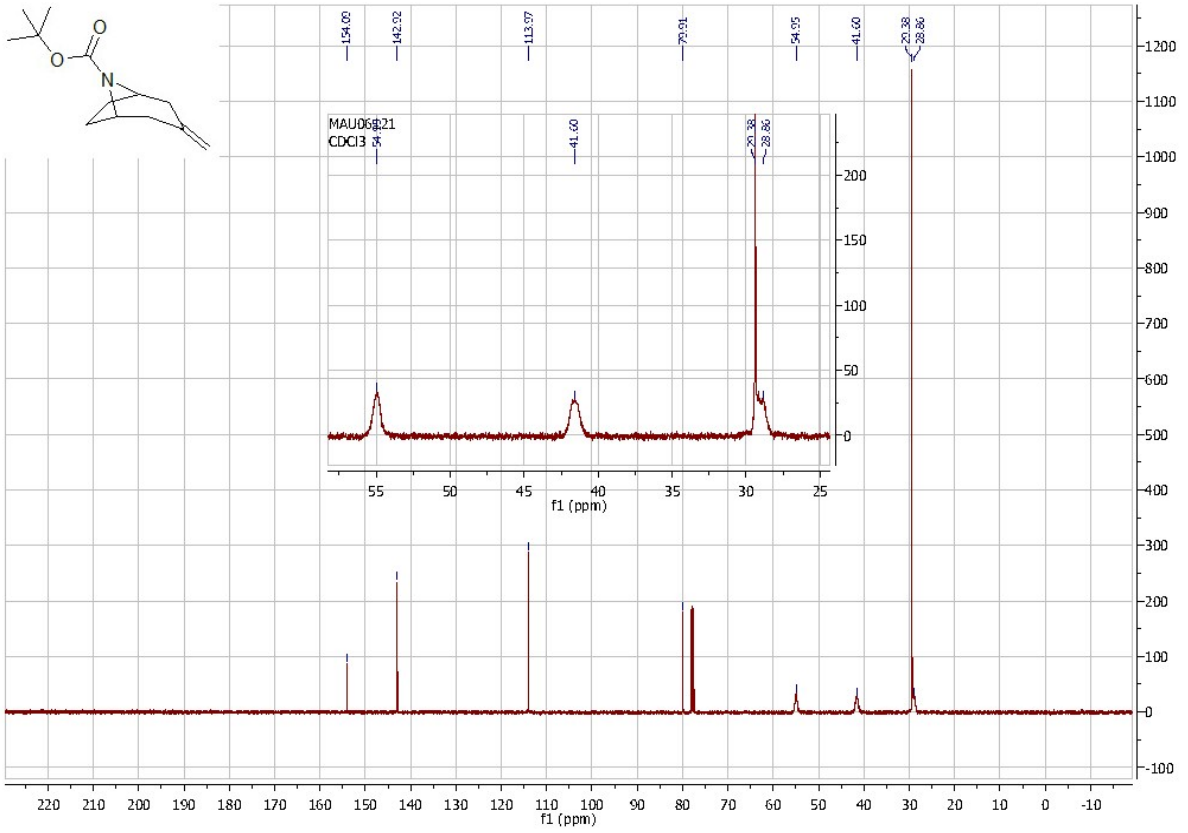
Contents

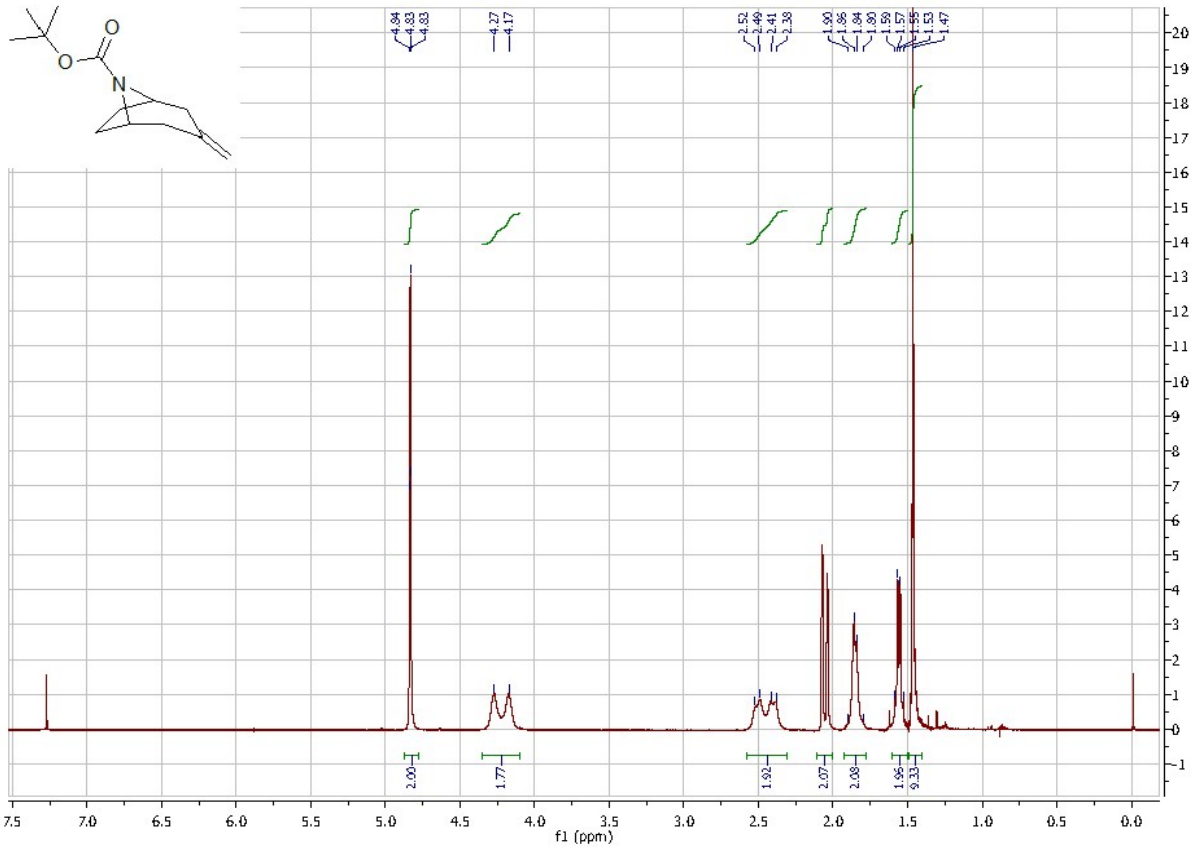
^{1}H (top) and ^{13}C (bottom) NMR spectra of **5b**



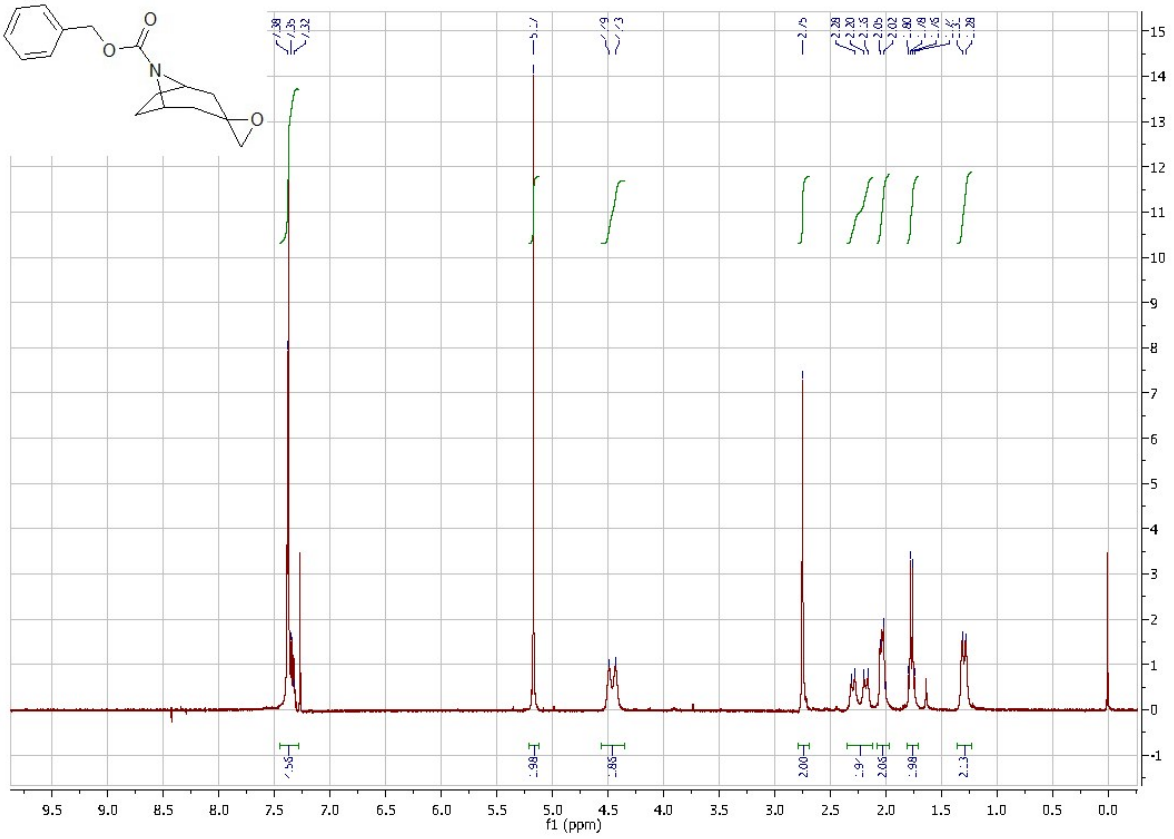


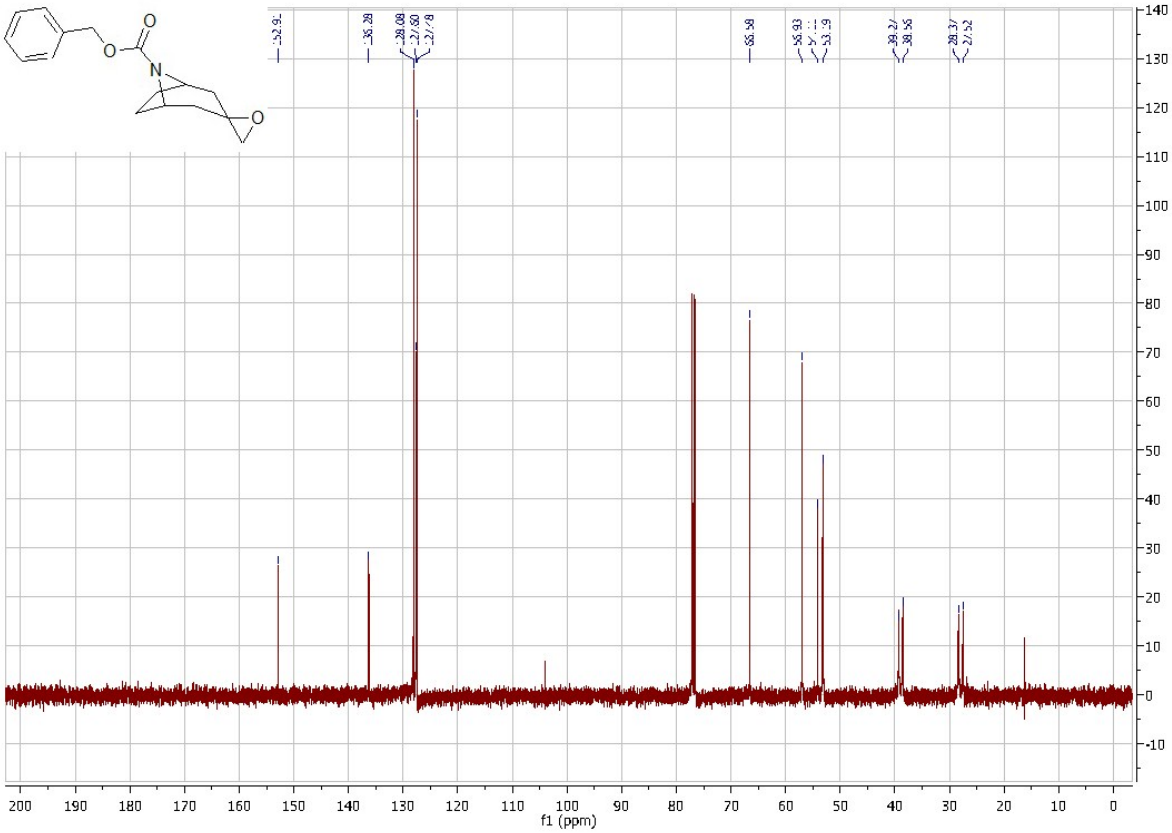
^{1}H (bottom) and ^{13} C (top) NMR spectra of **5a**



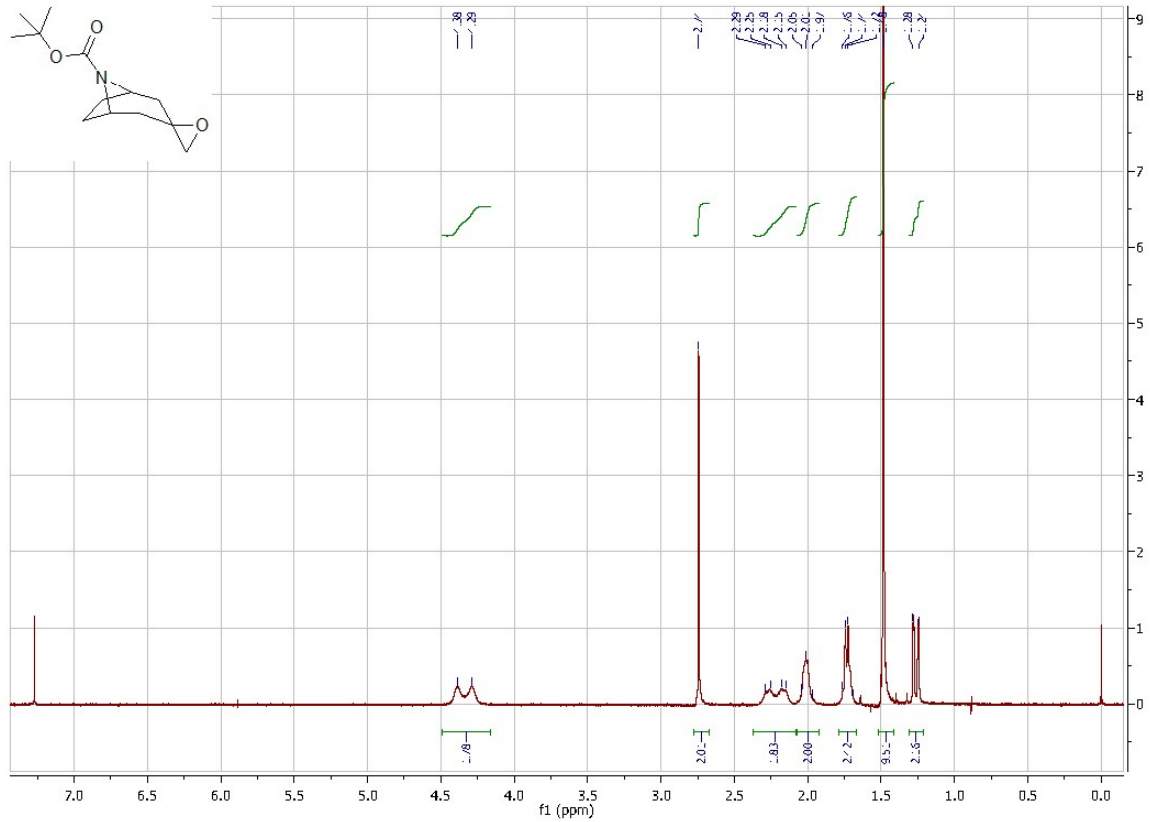


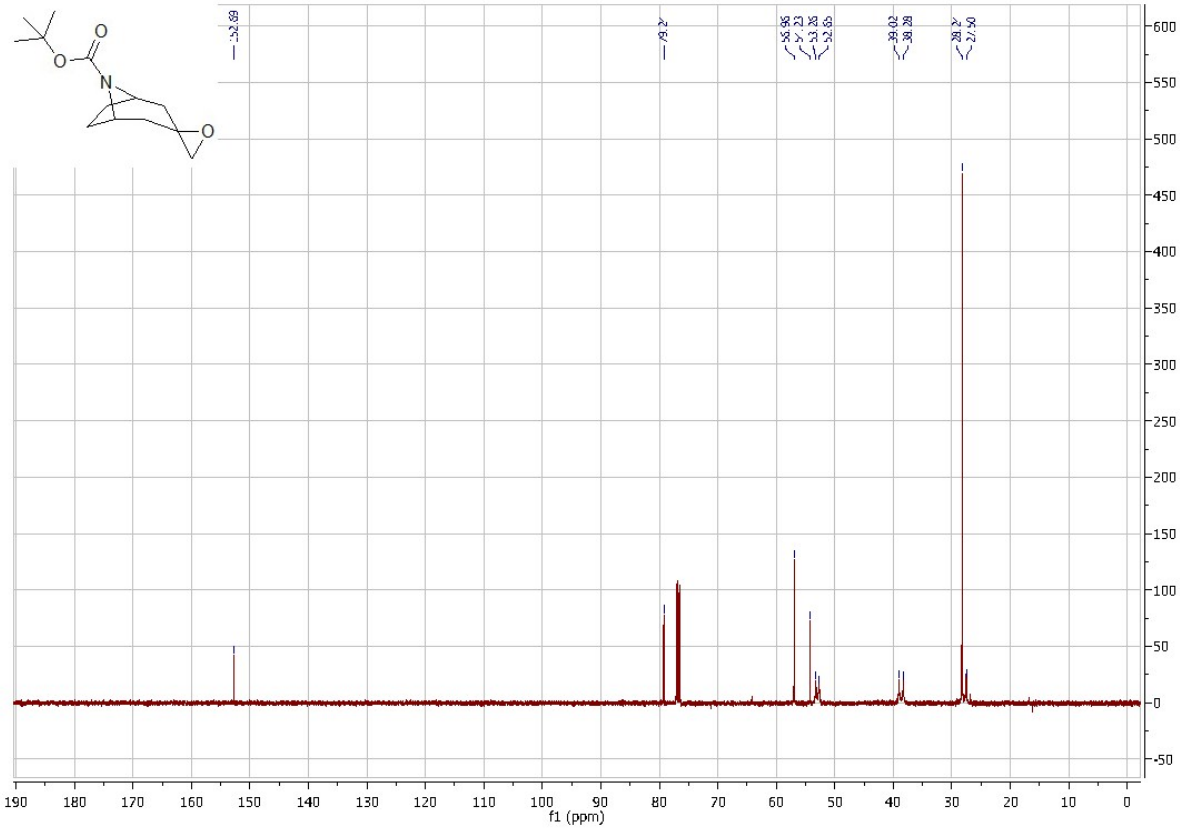
^{1}H (top) and ^{13}C (bottom) NMR spectra of **6b**



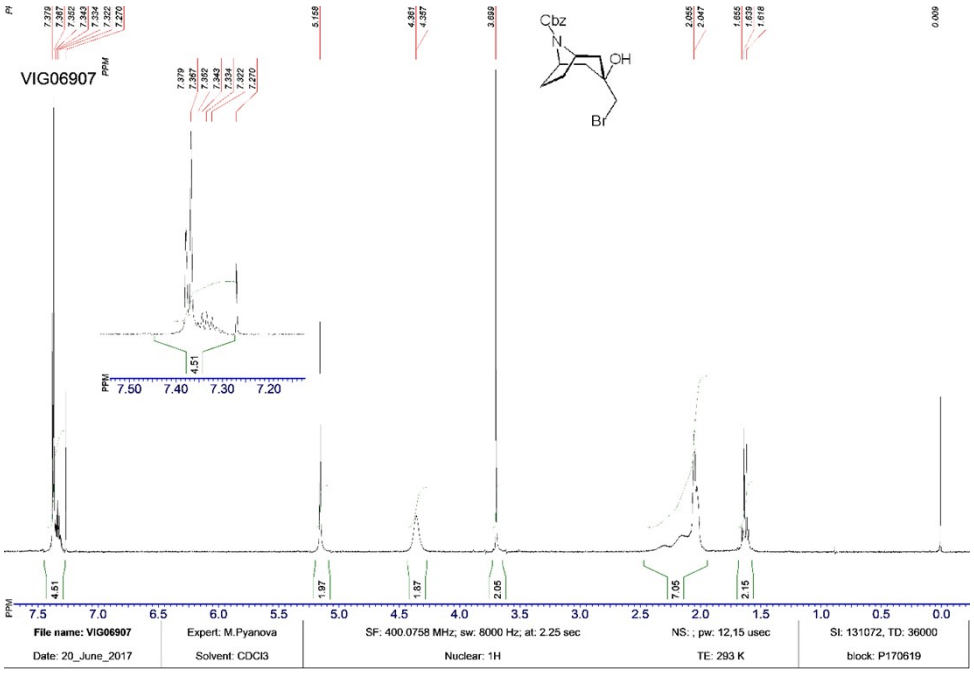


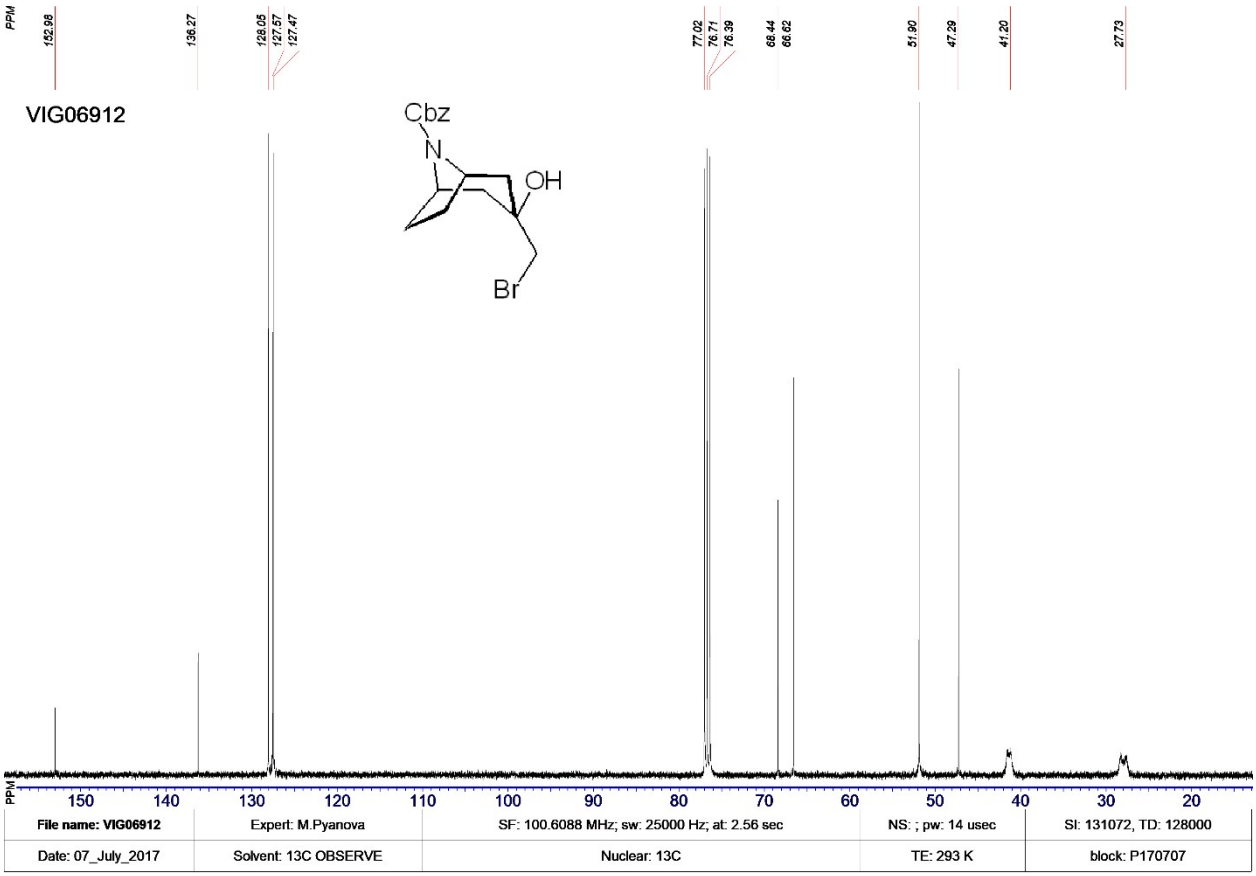
^{1}H (top) and ^{13}C (bottom) NMR spectra of **6a**



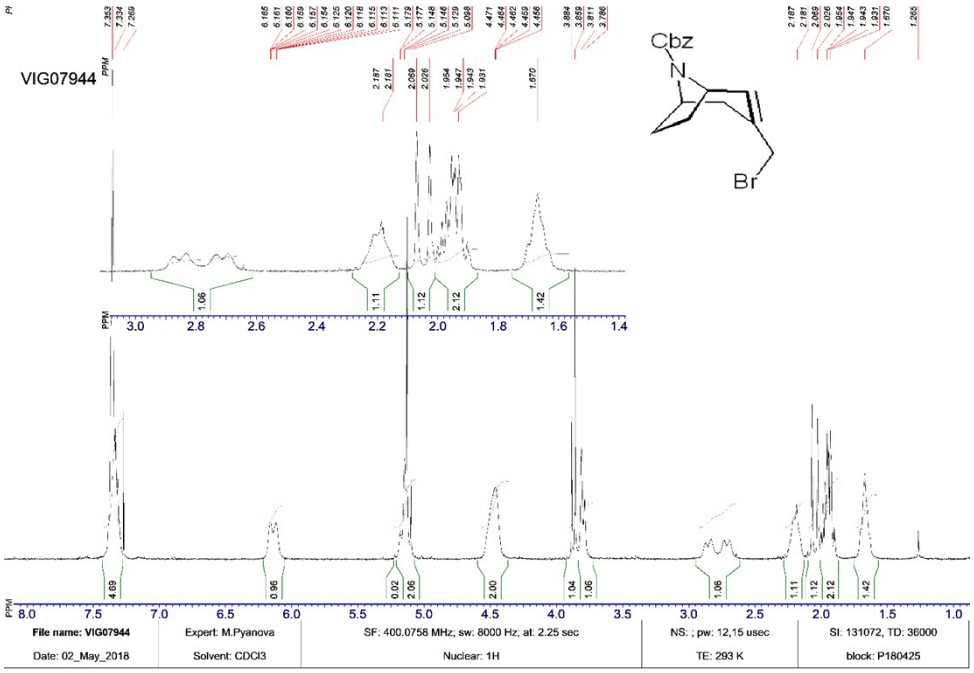


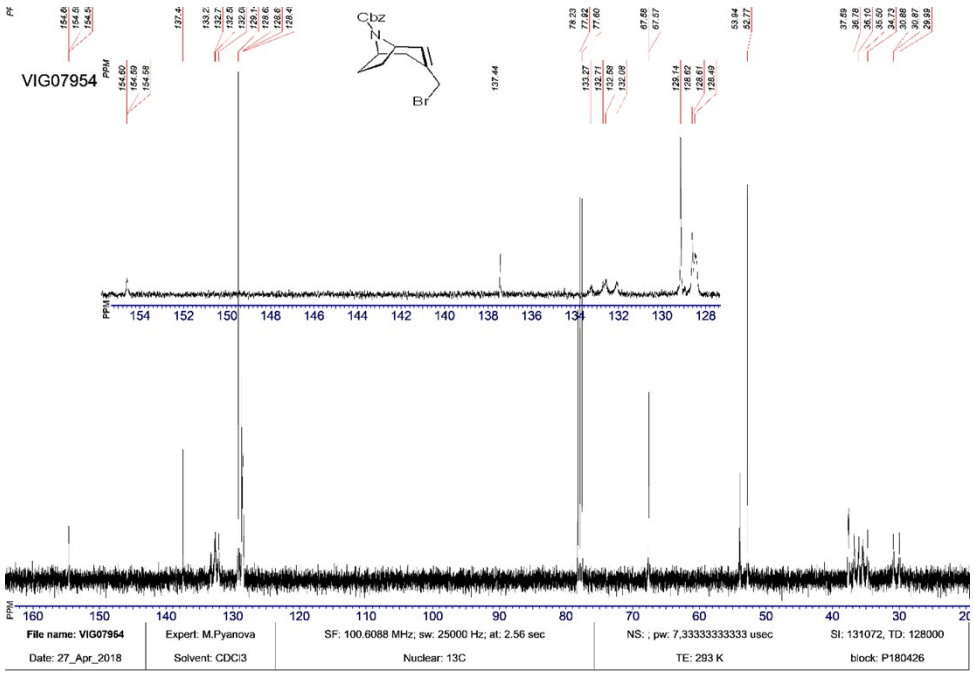
^{1}H (top) and ^{13} C (bottom) NMR spectra of **9**



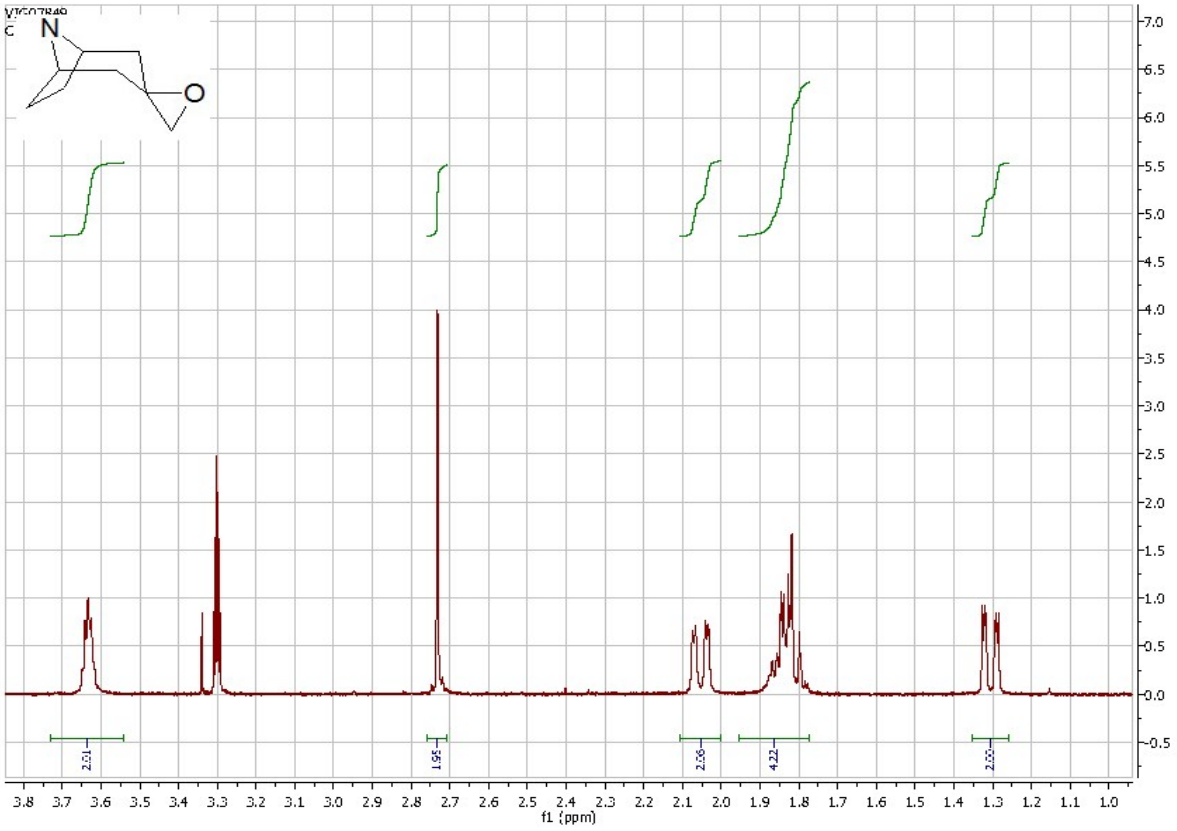


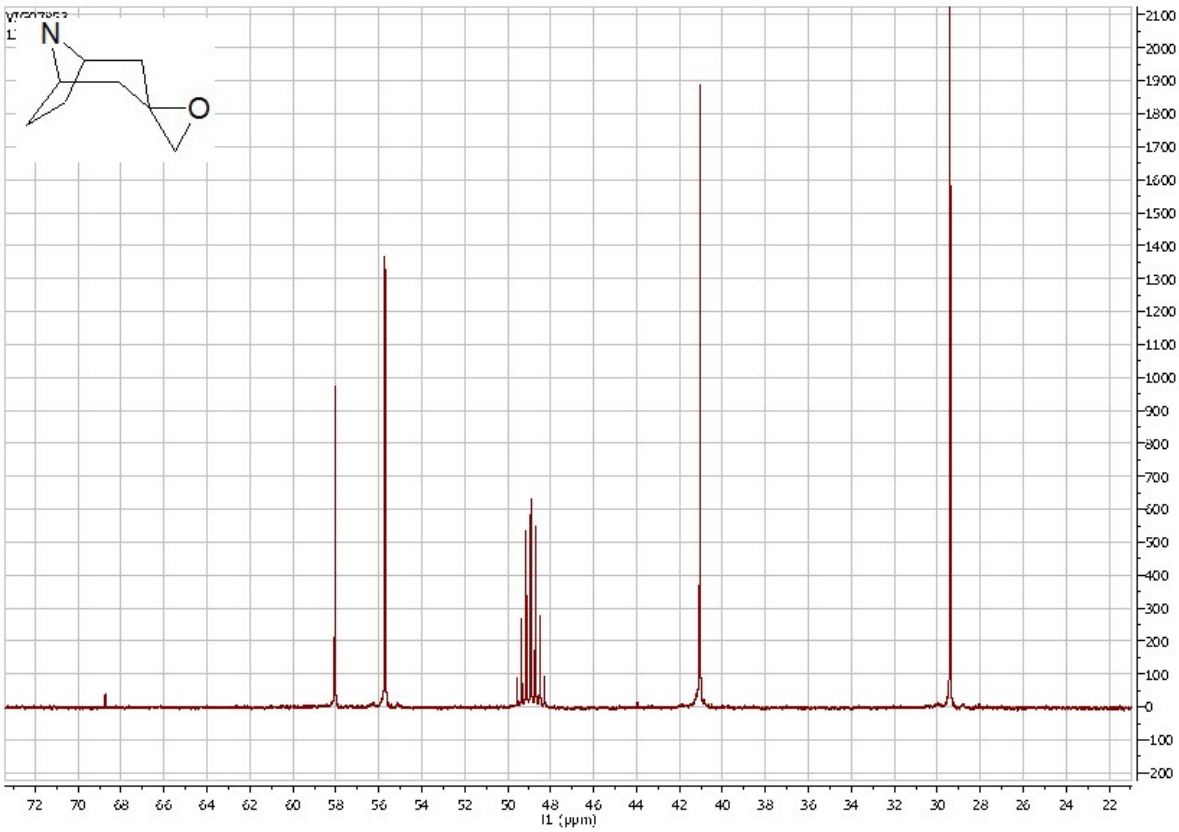
^{1}H (top) and ^{13}C (bottom) NMR spectra of **10**





^{1}H (top) and ^{13} C (bottom) NMR spectra of **11**





X-ray Structure determination

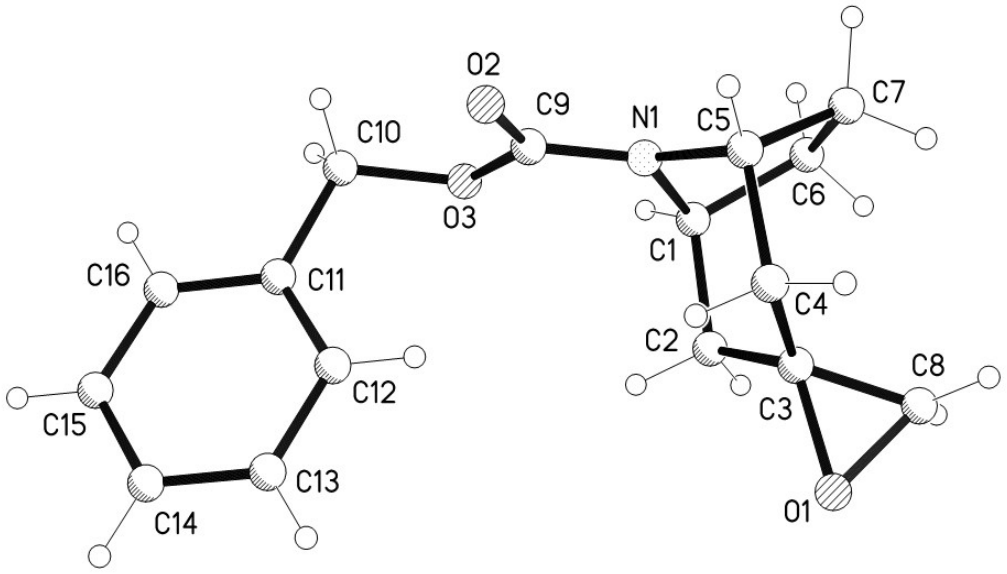


Figure 1S. Molecular structure of **6b** and selected bond lengths and angles: C1 N1 1.472(2), C5 N1 1.465(2), C9 N1 1.339(2), C3 C8 1.463(3), C3 O1 1.443(2), C8 O1 1.443(3), Å; C9 N1 C5 122.74(16), C9 N1 C1 127.95(16), C5 N1 C1 105.57(14), O1 C3 C8 59.52(13), C8 O1 C3 60.92(12), O1 C8 C3 59.56(13)°.

In structure **6b** (Figure 1S) central bicyclical system consist of six- and five-membered cycles. Six membered cycle N1C1-C5 has chair conformation with dihedral angles between planes C1C2C4C5, N1C1C5, C2C3C4 of 64.5(2) and 44.0(4)º respectively. Five membered cycle N1C1C5-C7 has an envelope conformation with dihedral angle 47.7(2)º between N1C1C5 and C1C5-C7 planes. The N1-C9 bond lengths is significantly shorter (1.339(2)Å) comparison with standard C-N bond lengths value in amines(1.45Å) and N1 atom has almost planar arrangement (sum bond angles around N1 atom is 356.26(16)º) due to conjugation of LP N1 atoms with π-system C9=O2 carbonyl group. Geometric parameters of epoxy ring are standard.