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## **Synthesis of vicinal (alkylamino)alkynylcyclopropanes from geminal alkynyl(chloro)cyclopropanes**

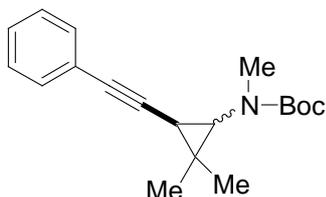
**Valentin D. Gvozdev, Konstantin N. Shavrin, Mikhail P. Egorov and Oleg M. Nefedov**

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-300 spectrometer in  $\text{CDCl}_3$ . Residual signal of the solvent was used as a reference. High resolution mass spectra were recorded on a Bruker micrOTOF II instrument with electrospray ionization (ESI). The measurements were performed on the positive ions (capillary voltage 4500 V). Masses were scanned in the range of  $m/z$  from 50 to 3000 Da, using an external or an internal calibration (Electrospray Calibrant Solution, Fluka). Sample solutions in MeCN were syringed, the flow rate  $3 \text{ dm}^3 \text{ min}^{-1}$ . Nebulizer gas was nitrogen ( $4 \text{ dm}^3 \text{ min}^{-1}$ ), the interface temperature was  $180 \text{ }^\circ\text{C}$ .

DMSO was distilled in vacuum over  $\text{CaH}_2$  prior use. THF was dried over  $\text{LiAlH}_4$  at room temperature followed by distillation in argon atmosphere. Starting alkynylchlorocyclopropanes **1a,b** were prepared as described [K. N. Shavrin, I. V. Krylova, I. B. Shvedova, G. P. Okonnishnikova, I. E. Dolgy, O. M. Nefedov, *J. Chem. Soc., Perkin Trans. 2*, 1991, 1875]. *tert*-Butyl alkylcarbamates were prepared by the room-temperature reaction of equimolar amounts of corresponding amine (methylamine, propylamine, isobutylamine, 2-methoxyethylamine, benzylamine and isopropylamine) and di-*tert*-butyl dicarbonate in  $\text{CH}_2\text{Cl}_2$  followed by distillation *in vacuo*.

*Synthesis of tert-butyl [2,2-dimethyl-3-alkynylcyclopropyl]alkylcarbamates 3a-g (general procedure)*. To a solution of the corresponding *tert*-butyl alkyl carbamate (1.83 mmol) in DMSO (4 ml),  $\text{Bu}^t\text{OK}$  (548 mg, 4.89 mmol) was added. After vigorous stirring for 5 min, a solution of the corresponding chlorocyclopropane **1a,b** (1.22 mmol) in anhydrous DMSO (1 ml) was added. The mixture was stirred for 2 h at  $60\text{--}70 \text{ }^\circ\text{C}$ , cooled to the room temperature, and thereafter diluted with water (15 ml) and  $\text{Et}_2\text{O}$  (20 ml). The organic layer was separated, and aqueous one was additionally extracted by  $\text{Et}_2\text{O}$  ( $2 \times 10$  ml). Then combined organic phases were washed with water three times, dried over anhydrous  $\text{K}_2\text{CO}_3$ , and the solvent was evaporated. The residue was subjected to column chromatography on basic  $\text{Al}_2\text{O}_3$  (gradient 20:1  $\rightarrow$  5:1 hexane– $\text{Et}_2\text{O}$ ) giving products **3a-g** as viscous liquids, which did not solidify on prolonged storing at  $-20 \text{ }^\circ\text{C}$ , except for compound **3c**. In case of products **3a-e**, the first fractions contained {[3-*tert*-butoxy-2,2-dimethylcyclopropyl]ethynyl}benzene **4** as  $\sim 3.5:1$  ( $1S^*,3R^*/1R^*,3R^*$ )-diastereomer mixtures.

Characterization data for compounds **3a-g**.

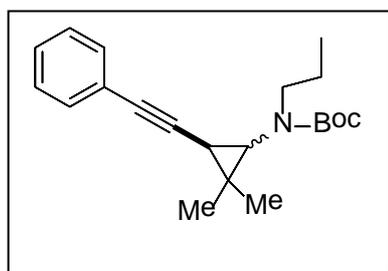


*tert*-Butyl [2,2-dimethyl-3-(2-phenylethynyl)cyclopropyl]-methylcarbamate **3a** was prepared from cyclopropane **1a** and *tert*-butyl methylcarbamate as mixture of (1*R*\*,3*S*\*)- and (1*S*\*,3*S*\*)-isomers (4.9:1) and isolated in 54% yield. HRMS,  $m/z$  300.1955, 317.2222, 322.1776, 338.1510, calculated for C<sub>19</sub>H<sub>25</sub>NO<sub>2</sub>, [M+H]<sup>+</sup>:  $m/z$  300.1958,

[M+NH<sub>4</sub>]<sup>+</sup>:  $m/z$  317.2224, [M+Na]<sup>+</sup>:  $m/z$  322.1778, [M+K]<sup>+</sup>:  $m/z$  338.1517.

**(1*R*\*, 3*S*\*)-3a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.15 (s, 3H, Me), 1.29 (s, 3H, Me), 1.43 (d, 1H, *CHC*≡C, <sup>3</sup>*J* 4.2 Hz), 1.50 (s, 9H, OBU<sup>t</sup>), 2.56 (d, 1H, *CHN*, <sup>3</sup>*J* 4.2 Hz), 2.90 (s, 3H, NMe), 7.25-7.32 (m, 3H, *m*, *p*-H, Ph), 7.35-7.43 (m, 2H, *o*-H, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$ : 19.9, 21.0, 21.1 (2Me, *CHC*≡C), 28.1 (CMe<sub>2</sub>), 28.4 (OC(CH<sub>3</sub>)<sub>3</sub>), 34.9 (br, NMe<sub>3</sub>), 50.8 (CHN), 79.6 (OC(CH<sub>3</sub>)<sub>3</sub>), 79.7, 88.6 (C≡C), 123.8 (C<sup>1</sup>, Ph), 127.5 (C<sup>4</sup>, Ph), 128.2, 131.5 (C<sup>2</sup>, C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>, Ph), 156.8 (C=O).

**(1*R*\*, 3*R*\*)-3a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>),  $\delta$ : 1.24 (s, 3H, Me), 1.28 (s, 3H, CH<sub>3</sub>), 1.50 (s, 9H, OBU<sup>t</sup>), 1.54 (d, 1H, *CHC*≡C, <sup>3</sup>*J* 7.2 Hz), 2.52 (d, 1H, *CHN*, <sup>3</sup>*J* 7.2 Hz), 3.05 (s, 3H, NMe), 7.25-7.32 (m, 3H, *m*, *p*-H, Ph), 7.35-7.43 (m, 2H, *o*-H, Ph). <sup>13</sup>C NMR (CDCl<sub>3</sub>),  $\delta$ : 16.7, 20.0, 25.3 (2Me, *CHC*≡C), 26.0 (C(CH<sub>3</sub>)<sub>2</sub>), 28.3 (OC(CH<sub>3</sub>)<sub>3</sub>), 35.2 (br, NMe), 57.4 (CHN), 79.5 (OC(CH<sub>3</sub>)<sub>3</sub>), 81.7, 87.6 (C≡C), 124.0 (C<sup>1</sup>, Ph), 127.5 (C<sup>4</sup>, Ph), 128.2, 131.4 (C<sup>2</sup>, C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>, Ph), 157.7 (C=O).

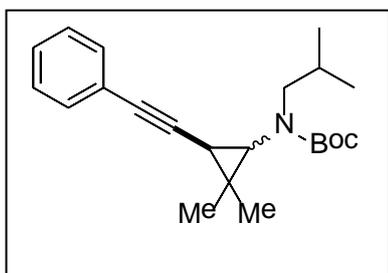


*tert*-Butyl [2,2-dimethyl-3-(2-phenylethynyl)cyclopropyl]-propylcarbamate **3b** was prepared from cyclopropane **1a** and *tert*-butyl propylcarbamate as mixture of (1*R*\*,3*S*\*)- and (1*R*\*,3*R*\*)-isomers (7.4:1) and isolated in 57% yield. HRMS,  $m/z$  328.2266, 345.2532, 350.2086, 366.1832, calculated for C<sub>21</sub>H<sub>29</sub>NO<sub>2</sub>, [M+H]<sup>+</sup>:  $m/z$  328.2271, [M+NH<sub>4</sub>]<sup>+</sup>:  $m/z$  345.2537, [M+Na]<sup>+</sup>:  $m/z$  350.2091, [M+K]<sup>+</sup>:  $m/z$

366.1830.

**(1*R*\*, 3*S*\*)-3b**: <sup>1</sup>H NMR,  $\delta$ : 0.94 (t, 3H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J* 7.4 Hz), 1.14 (s, 3H, CH<sub>3</sub>), 1.31 (s, 3H, CH<sub>3</sub>), 1.41 (d, 1H, *CHC*≡C, <sup>3</sup>*J* 4.3 Hz), 1.50 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 1.51-1.74 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.57 (d, 1H, *CHN*, <sup>3</sup>*J* 4.3 Hz), 2.99 (ddd, 1H, NCHHCH<sub>2</sub>CH<sub>3</sub>, <sup>2</sup>*J* 13.8 Hz, <sup>3</sup>*J* 8.5 Hz, <sup>3</sup>*J* 5.2 Hz), 3.43-3.58 (m, 1H, NCHHCH<sub>2</sub>CH<sub>3</sub>), 7.25-7.33 (m, 3H, *m*, *p*-H, Ph), 7.37-7.44 (m, 2H, *o*-H, Ph). <sup>13</sup>C NMR,  $\delta$ : 11.3 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.7, 21.0, 21.4 (2CH<sub>3</sub>, *CHC*≡C), 20.4 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 28.4 (C(CH<sub>3</sub>)<sub>2</sub>, (OC(CH<sub>3</sub>)<sub>3</sub>), 49.0 (br, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 49.3 (CHN), 79.3 (OC(CH<sub>3</sub>)<sub>3</sub>), 79.6, 88.7 (C≡C), 123.8 (C<sup>1</sup>, Ph), 127.5 (C<sup>4</sup>, Ph), 128.1, 131.5 (C<sup>2</sup>, C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>, Ph), 156.6 (C=O).

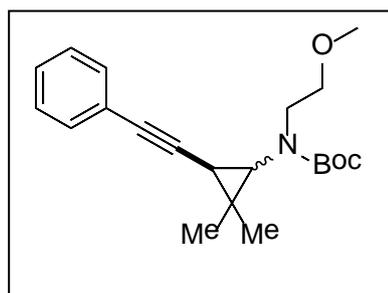
**(1*R*\*, 1*R*\*)-3b**:  $^1\text{H}$  NMR,  $\delta$ : 0.91 (t, 3H,  $\text{NCH}_2\text{CH}_2\text{CH}_3$ ,  $^3J$  7.4 Hz), 1.14 (s, 3H,  $\text{CH}_3$ ), 1.24 (s, 3H,  $\text{CH}_3$ ), 1.50 (s, 9H,  $\text{OC}(\text{CH}_3)_3$ ), 1.51-1.75 (m, 3H,  $\text{NCH}_2\text{CH}_2\text{CH}_3$ ,  $\text{CHC}\equiv\text{C}$ ), 2.52 (d, 1H,  $\text{CHN}$ ,  $^3J$  7.1 Hz), 3.43-3.58 (m, 2H,  $\text{NCH}_2\text{CH}_2\text{CH}_3$ ), 7.25-7.33 (m, 3H, *m*, *p*-H, Ph), 7.37-7.44 (m, 2H, *o*-H, Ph).  $^{13}\text{C}$  NMR,  $\delta$ : 11.4 ( $\text{NCH}_2\text{CH}_2\text{CH}_3$ ), 16.5, 19.8, 25.4 (2 $\text{CH}_3$ ,  $\text{CHC}\equiv\text{C}$ ), 21.1 ( $\text{NCH}_2\text{CH}_2\text{CH}_3$ ), 25.9 ( $\text{C}(\text{CH}_3)_2$ ), 28.3 ( $\text{OC}(\text{CH}_3)_3$ ), 45.1 ( $\text{CHN}$ ), 48.5 (br,  $\text{NCH}_2\text{CH}_2\text{CH}_3$ ), 79.3 ( $\text{OC}(\text{CH}_3)_3$ ), 81.7, 87.6 ( $\text{C}\equiv\text{C}$ ), 124.0 ( $\text{C}^1$ , Ph), 127.4 ( $\text{C}^4$ , Ph), 128.1, 131.4 ( $\text{C}^2$ ,  $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^6$ , Ph), 157.4 ( $\text{C}=\text{O}$ ).



*tert*-Butyl [2,2-dimethyl-3-(2-phenylethynyl)cyclopropyl]-isobutylcarbamate **3c** was prepared from cyclopropane **1a** and *tert*-butyl isobutylcarbamate as mixture of (1*R*\*,3*S*\*)- and (1*R*\*,3*R*\*)-isomers (6.5:1) and isolated in 52% yield. HRMS,  $m/z$  342.2433, 359.2695, 364.2243, calculated for  $\text{C}_{22}\text{H}_{31}\text{NO}_2$ ,  $[\text{M}+\text{H}]^+$ :  $m/z$  342.2428,  $[\text{M}+\text{NH}_4]^+$ :  $m/z$  359.2693,  $[\text{M}+\text{Na}]^+$ :  $m/z$  364.2247.

**(1*R*\*, 3*S*\*)-3c**:  $^1\text{H}$  NMR,  $\delta$ : 0.93 (d, 3H,  $\text{CH}_3$  in *i*-Bu,  $^3J$  6.7 Hz), 0.97 (d, 3H,  $\text{CH}_3$  in *i*-Bu,  $^3J$  6.7 Hz), 1.14 (s, 3H,  $\text{CH}_3$ ), 1.32 (s, 3H,  $\text{CH}_3$ ), 1.41 (d, 1H,  $\text{CHC}\equiv\text{C}$ ,  $^3J$  4.4 Hz), 1.51 (s, 9H,  $\text{OC}(\text{CH}_3)_3$ ), 1.99-2.16 (m, 1H,  $\text{NCH}_2\text{CH}(\text{CH}_3)_2$ ), 2.56 (d, 1H,  $\text{CHN}$ ,  $^3J$  4.4 Hz), 2.80 (dd, 1H,  $\text{NCHHCH}(\text{CH}_3)_2$ ,  $^2J$  13.8 Hz,  $^3J$  6.0 Hz), 3.35-3.49 (m, 1H,  $\text{NCHHCH}(\text{CH}_3)_2$ ), 7.25-7.33 (m, 3H, *m*, *p*-H, Ph), 7.36-7.44 (m, 2H, *o*-H, Ph).  $^{13}\text{C}$  NMR, 19.8, 20.0, 20.5, 20.6, 21.1 (2 $\text{CH}_3$ ,  $\text{NCH}_2\text{CH}(\text{CH}_3)_2$ ,  $\text{CHC}\equiv\text{C}$ ), 27.4 ( $\text{NCH}_2\text{CH}(\text{CH}_3)_2$ ), 28.4 ( $\text{OC}(\text{CH}_3)_3$ ), 28.7 ( $\text{C}(\text{CH}_3)_2$ ), 49.4 ( $\text{CHN}$ ), 54.3 (br,  $\text{NCH}_2\text{CH}(\text{CH}_3)_2$ ), 79.4 ( $\text{OC}(\text{CH}_3)_3$ ), 79.6, 88.7 ( $\text{C}\equiv\text{C}$ ), 123.9 ( $\text{C}^1$ , Ph), 127.6 ( $\text{C}^4$ , Ph), 128.2, 131.6 ( $\text{C}^2$ ,  $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^6$ , Ph), 156.9 ( $\text{C}=\text{O}$ ).

**(1*R*\*, 1*R*\*)-3c**:  $^1\text{H}$  NMR,  $\delta$ : 0.88 (d, 3H,  $\text{CH}_3$  in *i*-Bu,  $^3J$  6.7 Hz), 0.92 (d, 3H,  $\text{CH}_3$  in *i*-Bu,  $^3J$  6.7 Hz), 1.21 (s, 3H,  $\text{CH}_3$ ), 1.23 (s, 3H,  $\text{CH}_3$ ), 1.51 (s, 9H,  $\text{OC}(\text{CH}_3)_3$ ), 1.58 (d, 1H,  $\text{CHC}\equiv\text{C}$ ,  $^3J$  7.2 Hz), 1.99-2.16 (m, 1H,  $\text{NCH}_2\text{CH}(\text{CH}_3)_2$ ), 2.53 (d, 1H,  $\text{CHN}$ ,  $^3J$  7.2 Hz), 3.36-3.48 (m, 1H,  $\text{NCHHCH}(\text{CH}_3)_2$ ), 3.51 (dd, 1H,  $\text{NCHHCH}(\text{CH}_3)_2$ ,  $^2J$  14.0 Hz,  $^3J$  6.1 Hz), 7.25-7.33 (m, 3H, *m*, *p*-H, Ph), 7.36-7.44 (m, 2H, *o*-H, Ph).  $^{13}\text{C}$  NMR,  $\delta$ : 16.6, 19.9, 20.1, 20.5, 25.6 (2 $\text{CH}_3$ ,  $\text{NCH}_2\text{CH}(\text{CH}_3)_2$ ,  $\text{CHC}\equiv\text{C}$ ), 26.0 ( $\text{C}(\text{CH}_3)_2$ ), 28.3 ( $\text{OC}(\text{CH}_3)_3$ ), 45.0 ( $\text{CHN}$ ), 53.2 (br,  $\text{NCH}_2\text{CH}(\text{CH}_3)_2$ ), 79.3 ( $\text{OC}(\text{CH}_3)_3$ ), 81.9, 87.7 ( $\text{C}\equiv\text{C}$ ), 124.0 ( $\text{C}^1$ , Ph), 127.6 ( $\text{C}^4$ , Ph), 128.2, 131.5 ( $\text{C}^2$ ,  $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^6$ , Ph), 157.5 ( $\text{C}=\text{O}$ ).

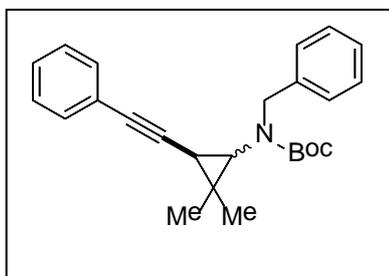


*tert*-Butyl [2,2-dimethyl-3-(phenylethynyl)cyclopropyl]-(2-methoxyethyl)carbamate **3d** was prepared from cyclopropane **1a** and *tert*-butyl 2-methoxyethylcarbamate as mixture of (1*R*\*,3*S*\*)- and (1*R*\*,3*R*\*)-isomers (6.5:1) and isolated in 48% yield. HRMS,  $m/z$  344.2223, 361.2482, 366.2036, 382.1778, calculated for  $\text{C}_{21}\text{H}_{29}\text{NO}_3$ ,  $[\text{M}+\text{H}]^+$ :  $m/z$  344.2220,  $[\text{M}+\text{NH}_4]^+$ :  $m/z$  361.2486,  $[\text{M}+\text{Na}]^+$ :  $m/z$

366.2040,  $[\text{M}+\text{K}]^+$ :  $m/z$  382.1779.

**(1*R*\*, 3*S*\*)-3d**:  $^1\text{H NMR}$ ,  $\delta$ : 1.16 (s, 3H,  $\text{CH}_3$ ), 1.30 (s, 3H,  $\text{CH}_3$ ), 1.51 (s, 9H,  $\text{OC}(\text{CH}_3)_3$ ), 1.60 (d, 1H,  $\text{CHC}\equiv\text{C}$ ,  $^3J$  4.5 Hz), 2.63 (d, 1H,  $\text{CHN}$ ,  $^3J$  4.5 Hz), 3.28-3.38 (m, 1H,  $\text{NCHHCH}_2\text{O}$ ), 3.38 (s, 3H,  $\text{OCH}_3$ ), 3.42-3.61 (m, 3H,  $\text{NCHHCH}_2\text{O}$ ), 7.25-7.33 (m, 3H, *m*, *p*-H, Ph), 7.37-7.44 (m, 2H, *o*-H, Ph).  $^{13}\text{C NMR}$ ,  $\delta$ : 19.6, 20.8, 21.1 ( $2\text{CH}_3$ ,  $\text{CHC}\equiv\text{C}$ ), 28.4 ( $\text{OC}(\text{CH}_3)_3$ ), 28.6 ( $\text{C}(\text{CH}_3)_2$ ), 47.6 (br,  $\text{NCH}_2\text{CH}_2\text{OCH}_3$ ), 50.2 ( $\text{CHN}$ ), 58.6 ( $\text{OCH}_3$ ), 70.5 ( $\text{NCH}_2\text{CH}_2\text{OCH}_3$ ), 79.6, 88.9 ( $\text{C}\equiv\text{C}$ ), 79.8 ( $\text{OC}(\text{CH}_3)_3$ ), 124.0 ( $\text{C}^1$ , Ph), 127.5 ( $\text{C}^4$ , Ph), 128.2, 131.6 ( $\text{C}^2$ ,  $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^6$ , Ph), 156.8 ( $\text{C}=\text{O}$ ).

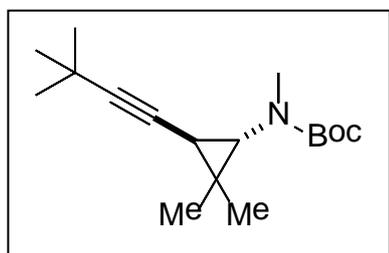
**(1*R*\*, 1*R*\*)-3d**:  $^1\text{H NMR}$ ,  $\delta$ : 1.20 (s, 3H,  $\text{CH}_3$ ), 1.24 (s, 3H,  $\text{CH}_3$ ), 1.51 (s, 9H,  $\text{OC}(\text{CH}_3)_3$ ), 1.53 (d, 1H,  $\text{CHC}\equiv\text{C}$ ,  $^3J$  7.2 Hz), 2.65 (d, 1H,  $\text{CHN}$ ,  $^3J$  7.2 Hz), 3.28-3.38 (m, 1H,  $\text{NCHHCH}_2\text{O}$ ), 3.36 (s, 3H,  $\text{OCH}_3$ ), 3.42-3.61 (m, 3H,  $\text{NCHHCH}_2\text{O}$ ), 7.25-7.33 (m, 3H, *m*, *p*-H, Ph), 7.37-7.44 (m, 2H, *o*-H, Ph).  $^{13}\text{C NMR}$ ,  $\delta$ : 16.6, 19.8, 25.4 ( $2\text{CH}_3$ ,  $\text{CHC}\equiv\text{C}$ ), 26.2 ( $\text{C}(\text{CH}_3)_2$ ), 28.3 ( $\text{OC}(\text{CH}_3)_3$ ), 46.2 (br,  $\text{NCH}_2\text{CH}_2\text{OCH}_3$ ), 50.2 ( $\text{CHN}$ ), 58.6 ( $\text{OCH}_3$ ), 70.5 ( $\text{NCH}_2\text{CH}_2\text{OCH}_3$ ), 79.8 ( $\text{OC}(\text{CH}_3)_3$ ), 80.7, 87.4 ( $\text{C}\equiv\text{C}$ ), 124.0 ( $\text{C}^1$ , Ph), 127.6 ( $\text{C}^4$ , Ph), 128.2, 131.5 ( $\text{C}^2$ ,  $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^6$ , Ph), 157.5 ( $\text{C}=\text{O}$ ).



*tert*-Butyl [2,2-dimethyl-3-(phenylethynyl)cyclopropyl]benzylcarbamate **3e** was prepared from cyclopropane **1a** and *tert*-butyl benzylcarbamate as mixture of (1*R*\*,3*S*\*)- and (1*R*\*,3*R*\*)-isomers (5.5:1) and isolated in 32% yield. HRMS,  $m/z$  376.2284, 398.2085, 414.1826, calculated for  $\text{C}_{25}\text{H}_{29}\text{NO}_2$ ,  $[\text{M}+\text{H}]^+$ :  $m/z$  376.2271,  $[\text{M}+\text{Na}]^+$ :  $m/z$  398.2091,  $[\text{M}+\text{K}]^+$ :  $m/z$  414.1830.

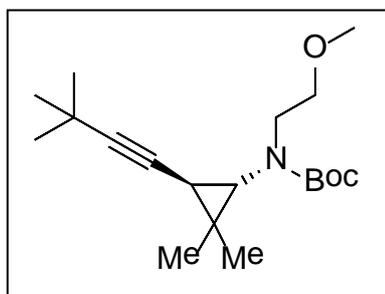
**(1*R*\*, 3*S*\*)-3e**:  $^1\text{H NMR}$ ,  $\delta$ : 1.19 (s, 3H,  $\text{CH}_3$ ), 1.26 (s, 3H,  $\text{CH}_3$ ), 1.46 (d, 1H,  $\text{CHC}\equiv\text{C}$ ,  $^3J$  4.3 Hz), 1.52 (s, 9H,  $\text{OC}(\text{CH}_3)_3$ ), 2.45 (d, 1H,  $\text{CHN}$ ,  $^3J$  4.3 Hz), 4.26 (d, 1H,  $\text{PhCHH}$ ,  $^2J$  14.8 Hz), 4.72 (br. d, 1H,  $\text{PhCHH}$ ,  $^2J$  14.8 Hz), 7.24-7.46 (m, 10H, 2Ph).  $^{13}\text{C NMR}$ ,  $\delta$ : 20.1, 21.0, 21.1 ( $2\text{CH}_3$ ,  $\text{CHC}\equiv\text{C}$ ), 28.4 ( $\text{OC}(\text{CH}_3)_3$ ), 28.8 ( $\text{C}(\text{CH}_3)_2$ ), 49.6 ( $\text{CHN}$ ), 51.6 (br,  $\text{NCH}_2\text{Ph}$ ), 79.8, 88.6 ( $\text{C}\equiv\text{C}$ ), 80.0 ( $\text{OC}(\text{CH}_3)_3$ ), 123.9 ( $\text{C}^1$ ,  $\text{PhC}\equiv\text{C}$ ), 127.3 ( $\text{C}^4$ ,  $\text{PhCH}_2$ ), 127.6 ( $\text{C}^4$ ,  $\text{PhC}\equiv\text{C}$ ), 128.2, 131.7 ( $\text{C}^2$ ,  $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^6$ ,  $\text{PhC}\equiv\text{C}$ ), 128.5 (two overlapped signals,  $\text{C}^2$ ,  $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^6$ ,  $\text{PhCH}_2$ ), 138.2 ( $\text{C}^1$ ,  $\text{PhCH}_2$ ), 156.9 ( $\text{C}=\text{O}$ ).

**(1*R*\*, 1*R*\*)-3e**:  $^1\text{H NMR}$ ,  $\delta$ : 1.28 (s, 3H,  $\text{CH}_3$ ), 1.30 (s, 3H,  $\text{CH}_3$ ), 1.52 (s, 9H,  $\text{OC}(\text{CH}_3)_3$ ), 1.55 (d, 1H,  $\text{CHC}\equiv\text{C}$ ,  $^3J$  7.2 Hz), 2.36 (br. d, 1H,  $\text{CHN}$ ,  $^3J$  7.2 Hz), 4.69 (d, 1H,  $\text{PhCHH}$ ,  $^2J$  15.0 Hz), 4.95 (br. d, 1H,  $\text{PhCHH}$ ,  $^2J$  15.0 Hz), 7.24-7.46 (m, 10H, 2Ph).  $^{13}\text{C NMR}$ ,  $\delta$ : 16.8, 19.9, 25.4 ( $2\text{CH}_3$ ,  $\text{CHC}\equiv\text{C}$ ), 26.3 ( $\text{C}(\text{CH}_3)_2$ ), 28.3 ( $\text{OC}(\text{CH}_3)_3$ ), 44.9 ( $\text{CHN}$ ), 48.8 (br,  $\text{NCH}_2\text{Ph}$ ), 80.0 ( $\text{OC}(\text{CH}_3)_3$ ), 82.2, 87.8 ( $\text{C}\equiv\text{C}$ ), 124.0 ( $\text{C}^1$ ,  $\text{PhC}\equiv\text{C}$ ), 127.1 ( $\text{C}^4$ ,  $\text{PhCH}_2$ ), 127.7 ( $\text{C}^4$ ,  $\text{PhC}\equiv\text{C}$ ), 128.3, 131.6 ( $\text{C}^2$ ,  $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^6$ ,  $\text{PhC}\equiv\text{C}$ ), 128.4, 128.5 ( $\text{C}^2$ ,  $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^6$ ,  $\text{PhCH}_2$ ), 138.6 ( $\text{C}^1$ ,  $\text{PhCH}_2$ ), 157.6 ( $\text{C}=\text{O}$ ).



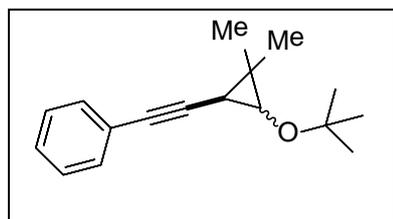
*tert*-Butyl [(1*R*\*,3*S*\*)-3-(3,3-dimethylbut-1-yn-1-yl)-2,2-dimethylcyclopropyl]methylcarbamate **3f** was prepared from cyclopropane **1b** and *tert*-butyl methylcarbamate and isolated in 36%

yield. HRMS,  $m/z$  280.2275, 297.2536, 302.2088, 318.1826, calculated for  $C_{17}H_{29}NO_2$ ,  $[M+H]^+$ :  $m/z$  280.2275,  $[M+NH_4]^+$ :  $m/z$  297.2537,  $[M+Na]^+$ :  $m/z$  302.2091,  $[M+K]^+$ :  $m/z$  318.1830.  $^1H$  NMR,  $\delta$ : 1.04 (s, 3H,  $CH_3$ ), 1.15 (d, 1H,  $CHC\equiv C$ ,  $^3J$  4.2 Hz), 1.16 (s, 3H,  $CH_3$ ), 1.18 (s, 9H,  $C(CH_3)_3$ ), 1.46 (s, 9H,  $OC(CH_3)_3$ ), 2.33 (d, 1H,  $CHN$ ,  $^3J$  4.2 Hz), 2.83 (s, 3H,  $NCH_3$ ).  $^{13}C$  NMR,  $\delta$ : 19.9, 20.5, 20.7 ( $2CH_3$ ,  $CHC\equiv C$ ), 26.8 ( $C(CH_3)_2$ ), 27.5 ( $C(CH_3)_3$ ), 28.5 ( $OC(CH_3)_3$ ), 31.2 ( $C(CH_3)_3$ ), 34.9 (br,  $NCH_3$ ), 50.5 ( $CHN$ ), 76.9, 88.3 ( $C\equiv C$ ), 79.5 ( $OC(CH_3)_3$ ), 157.1 ( $C=O$ ).



*tert*-Butyl [(1*R*\*,3*S*\*)-3-(3,3-dimethylbut-1-yn-1-yl)-2,2-dimethylcyclopropyl](2-methoxyethyl)carbamate **3g** was prepared from cyclopropane **1b** and *tert*-butyl 2-methoxyethylcarbamate and isolated in 19% yield. HRMS,  $m/z$  324.2531, calculated for  $C_{19}H_{33}NO_3$ ,  $[M+H]^+$ :  $m/z$  324.2533.  $^1H$  NMR,  $\delta$ : 1.04 (s, 3H,  $CH_3$ ), 1.15 (s, 3H,  $CH_3$ ), 1.17 (s, 9H,  $C(CH_3)_3$ ), 1.26 (d, 1H,  $CHC\equiv C$ ,  $^3J$  4.3 Hz), 1.46 (s, 9H,  $OC(CH_3)_3$ ), 2.36 (d, 1H,  $CHN$ ,  $^3J$  4.3 Hz), 3.18-3.30 (m, 1H,  $NCHHCH_2O$ ), 3.33 (s, 3H,  $OCH_3$ ), 3.18-3.30 (m, 1H,  $NCHHCH_2O$ ), 3.42-3.61 (m, 3H,  $NCHHCH_2O$ ).  $^{13}C$  NMR,  $\delta$ : 19.6, 20.3, 20.8 ( $2CH_3$ ,  $CHC\equiv C$ ), 27.2 ( $C(CH_3)_2$ ), 27.5 ( $C(CH_3)_3$ ), 28.5 ( $OC(CH_3)_3$ ), 31.4 ( $C(CH_3)_3$ ), 47.2 (br,  $NCH_2CH_2OCH_3$ ), 49.8 ( $CHN$ ), 58.5 ( $OCH_3$ ), 70.4 ( $NCH_2CH_2OCH_3$ ), 77.0, 88.2 ( $C\equiv C$ ), 79.6 ( $OC(CH_3)_3$ ), 156.9 ( $C=O$ ).

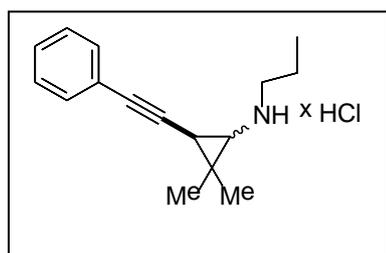
Characterization data for {[3-*tert*-butoxy-2,2-dimethylcyclopropyl]ethynyl}benzene **4**.



(1*S*\*,3*R*\*)-**4**:  $^1H$  NMR,  $\delta$ : 1.20 (s, 3H,  $CH_3$ ), 1.22 (s, 3H,  $CH_3$ ), 1.25 (d, 1H,  $CHC\equiv C$ ,  $^3J$  3.2 Hz), 1.28 (s, 9H,  $OC(CH_3)_3$ ), 3.10 (d, 1H,  $CHO$ ,  $^3J$  3.2 Hz), 7.25-7.33 (m, 3H, *m*, *p*-H, Ph), 7.34-7.42 (m, 2H, *o*-H, Ph).  $^{13}C$  NMR,  $\delta$ : 19.0, 20.9, 22.1 ( $2CH_3$ ,  $CHC\equiv C$ ), 24.2 ( $C(CH_3)_2$ ), 28.1 ( $OC(CH_3)_3$ ), 64.7 ( $CHO$ ), 75.0 ( $OC(CH_3)_3$ ), 79.1, 89.4 ( $C\equiv C$ ), 124.2 ( $C^1$ , Ph), 127.1 ( $C^4$ , Ph), 128.2, 131.6 ( $C^2$ ,  $C^3$ ,  $C^5$ ,  $C^6$ , Ph).

(1*R*\*,3*R*\*)-**4**:  $^1H$  NMR,  $\delta$ : 1.10 (s, 3H,  $CH_3$ ), 1.23 (s, 3H,  $CH_3$ ), 1.27 (d, 1H,  $CHC\equiv C$ ,  $^3J$  6.0 Hz), 1.31 (s, 9H,  $OC(CH_3)_3$ ), 3.14 (d, 1H,  $CHO$ ,  $^3J$  6.0 Hz), 7.25-7.33 (m, 3H, *m*, *p*-H, Ph), 7.34-7.42 (m, 2H, *o*-H, Ph).  $^{13}C$  NMR,  $\delta$ : 15.5, 20.3, 25.2 ( $2CH_3$ ,  $CHC\equiv C$ ), 28.0 ( $OC(CH_3)_3$ ), 28.7 ( $C(CH_3)_2$ ), 60.6 ( $CHO$ ), 74.7 ( $OC(CH_3)_3$ ), 81.3, 88.7 ( $C\equiv C$ ), 124.1 ( $C^1$ , Ph), 127.3 ( $C^4$ , Ph), 128.2, 131.6 ( $C^2$ ,  $C^3$ ,  $C^5$ ,  $C^6$ , Ph).

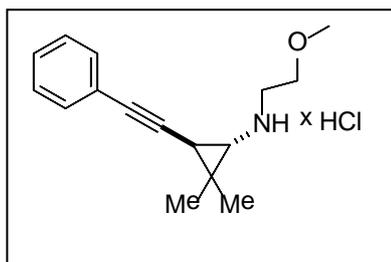
**Synthesis of *N*-alkyl-2,2-dimethyl-3-(2-phenylethynyl)cyclopropanamines 6a-c from carbamates 3b-d.** To carbamate **3** (1 mmol), a solution of HCl in dry isopropyl alcohol (9 M, 0.5 ml) was added. After the gas evolution ceased (*ca* 30 min), a clear solution was formed, which has been evaporated *in vacuo* (1 mbar, 30-40 °C) giving rise to viscous residues. In case of starting compounds **3b,c** these residues were additionally recrystallized from diethyl ether, giving pure corresponding chlorides **5a,c**. To these salts, a K<sub>2</sub>CO<sub>3</sub> (300 mg, 2.17 mmol) solution in water (1 ml) and CH<sub>2</sub>Cl<sub>2</sub> (2 ml) were added followed by vigorous stirring for 5 min. The organic layer was separated, the aqueous phase was additionally extracted with CH<sub>2</sub>Cl<sub>2</sub> (2x3 ml). The combined organic phases were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, the solvent was evaporated to leave ~95% pure amines **6a-c**.



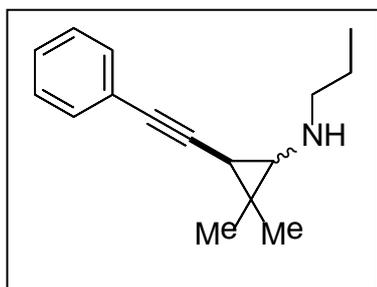
*2,2-Dimethyl-3-(2-phenylethynyl)-N-propylcyclopropanaminium chloride 5a* was prepared from carbamate **3b** as mixture of (1*R*\*,3*S*\*)- and (1*R*\*,1*R*\*)-isomers (7.2:1) and isolated in 93 % yield.

**(1*R*\*,3*S*\*)-5a:** <sup>1</sup>H NMR, δ: 1.04 (t, 3H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J* 7.4 Hz), 1.33 (s, 3H, CH<sub>3</sub>), 1.61 (s, 3H, CH<sub>3</sub>), 1.94-2.14 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.34 (d, 1H, CHC≡C, <sup>3</sup>*J* 4.0 Hz), 2.38-2.47 (m, 1H, CHN), 2.95-3.16 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.25-7.33 (m, 3H, *m*, *p*-H, Ph), 7.34-7.42 (m, 2H, *o*-H, Ph), 9.78 (br. s., 1H, NHH), 9.90 (br. s., 1H, NHH). <sup>13</sup>C NMR, δ: 11.3 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 18.9, 19.0, 19.4 (2CH<sub>3</sub>, CHC≡C), 21.5 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 24.3 (C(CH<sub>3</sub>)<sub>2</sub>), 47.4, 50.6 (CHN, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 80.6, 85.6 (C≡C), 122.9 (C<sup>1</sup>, Ph), 127.8 (C<sup>4</sup>, Ph), 128.1, 131.5 (C<sup>2</sup>, C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>, Ph).

**(1*R*\*,3*R*\*)-5a:** <sup>1</sup>H NMR, δ: 1.02 (t, 3H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J* 7.4 Hz), 1.25 (s, 3H, CH<sub>3</sub>), 1.61 (s, 3H, CH<sub>3</sub>), 1.85 (d, 1H, CHC≡C, <sup>3</sup>*J* 7.3 Hz), 1.94-2.14 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 2.51-2.61 (m, 1H, CHN), 3.13-3.35 (m, 2H, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 7.25-7.33 (m, 3H, *m*, *p*-H, Ph), 7.65-7.72 (m, 2H, *o*-H, Ph), 8.28 (br. s., 1H, NHH), 10.49 (br. s., 1H, NHH). <sup>13</sup>C NMR, δ: 11.3 (NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 16.5, 18.1, 18.8 (2CH<sub>3</sub>, CHC≡C) 23.6 (C(CH<sub>3</sub>)<sub>2</sub>), 25.3 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 43.9, 50.3 (CHN, NCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 82.2, 84.4 (C≡C), 122.5 (C<sup>1</sup>, Ph), 127.8 (C<sup>4</sup>, Ph), 128.1, 131.9 (C<sup>2</sup>, C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>, Ph).



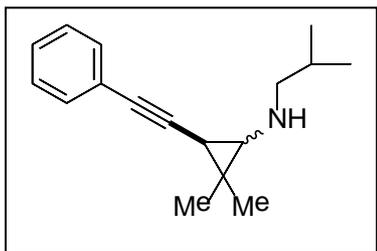
(*1R*\*,*3S*\*)-*N*-(2-Methoxyethyl)-2,2-dimethyl-3-(2-phenylethynyl)-cyclopropanaminium chloride **5c** was prepared from carbamate **3d** as single (*1R*\*,*3S*\*)-isomer and isolated in 74% yield. <sup>1</sup>H NMR,  $\delta$ : 1.32 (s, 3H, CH<sub>3</sub>), 1.60 (s, 3H, CH<sub>3</sub>), 2.32 (d, 1H, *CHC*≡C, <sup>3</sup>*J* 3.9 Hz), 2.61-2.70 (m, 1H, *CHN*), 3.31-3.40 (m, 2H, *NCH*<sub>2</sub>CH<sub>2</sub>O), 3.43 (s, 3H, OCH<sub>3</sub>), 3.86-3.92 (m, 2H, *NCH*<sub>2</sub>CH<sub>2</sub>O), 7.25-7.33 (m, 3H, *m*, *p*-H, Ph), 7.35-7.41 (m, 2H, *o*-H, Ph), 9.79 (br. s., 1H, *NHH*), 9.92 (br. s., 1H, *NHH*). <sup>13</sup>C NMR,  $\delta$ : 19.5, 19.6, 21.6 (2CH<sub>3</sub>, *CHC*≡C), 24.8 (*C*(CH<sub>3</sub>)<sub>2</sub>), 48.0, 48.1 (*CHN*, *NCH*<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 59.1 (OCH<sub>3</sub>), 67.4 (*NCH*<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 80.8, 85.8 (*C*≡C), 123.2 (*C*<sup>1</sup>, Ph), 128.0 (*C*<sup>4</sup>, Ph), 128.2, 131.7 (*C*<sup>2</sup>, *C*<sup>3</sup>, *C*<sup>5</sup>, *C*<sup>6</sup>, Ph).



2,2-Dimethyl-3-(2-phenylethynyl)-*N*-propylcyclopropanamine **6a** was prepared from hydrochloride **5a** as mixture of (*1R*\*,*3S*\*)- and (*1R*\*,*1R*\*)-isomers (8:1) and isolated in 84% yield. HRMS, *m/z* 228.1750, calculated for C<sub>16</sub>H<sub>21</sub>N, [*M*+*H*]<sup>+</sup>: *m/z* 228.1747.

(*1R*\*,*3S*\*)-**6a**: <sup>1</sup>H NMR,  $\delta$ : 0.95 (t, 3H, *NCH*<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J* 7.4 Hz), 1.20 (d, 1H, *CHC*≡C, <sup>3</sup>*J* 3.6 Hz), 1.24 (s, 3H, CH<sub>3</sub>), 1.26 (s, 3H, CH<sub>3</sub>), 1.50 (br. s, 1H, NH), 1.53 (tq, 2H, *NCH*<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J* 7.4 Hz, <sup>3</sup>*J* 7.2 Hz), 2.21 (d, 1H, *CHN*, <sup>3</sup>*J* 3.6 Hz), 2.64 (dt, 1H, *NCHH*CH<sub>2</sub>CH<sub>3</sub>, <sup>2</sup>*J* 11.8 Hz, <sup>3</sup>*J* 7.2 Hz), 2.70 (dt, 1H, *NCHH*CH<sub>2</sub>CH<sub>3</sub>, <sup>2</sup>*J* 11.8 Hz, <sup>3</sup>*J* 7.2 Hz), 7.23-7.34 (m, 3H, *m*, *p*-H, Ph), 7.36-7.46 (m, 2H, *o*-H, Ph). <sup>13</sup>C NMR,  $\delta$ : 11.9 (*NCH*<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 19.1, 21.9, 22.2 (2CH<sub>3</sub>, *CHC*≡C), 23.2 (*NCH*<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 25.9 (*C*(CH<sub>3</sub>)<sub>2</sub>), 51.6, 52.1 (*CHN*, *NCH*<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 78.9, 90.5 (*C*≡C), 124.3 (*C*<sup>1</sup>, Ph), 127.3 (*C*<sup>4</sup>, Ph), 128.2, 131.6 (*C*<sup>2</sup>, *C*<sup>3</sup>, *C*<sup>5</sup>, *C*<sup>6</sup>, Ph).

(*1R*\*,*3R*\*)-**6a**: <sup>1</sup>H NMR,  $\delta$ : 0.97 (t, 3H, *NCH*<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, <sup>3</sup>*J* 7.4 Hz), 1.13 (s, 3H, CH<sub>3</sub>), 1.24 (s, 3H, CH<sub>3</sub>), 1.41 (d, 1H, *CHC*≡C, <sup>3</sup>*J* 6.7 Hz), 1.46-1.69 (m, 2H, *NCH*<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.50 (br. s, 1H, NH), 2.23 (d, 1H, *CHN*, <sup>3</sup>*J* 6.7 Hz), 2.56-2.67 (m, 1H, *NCHH*CH<sub>2</sub>CH<sub>3</sub>, overlapped with signals from major isomer), 2.80 (dt, 1H, *NCHH*CH<sub>2</sub>CH<sub>3</sub>, <sup>2</sup>*J* 11.4 Hz, <sup>3</sup>*J* 7.2 Hz), 7.23-7.34 (m, 3H, *m*, *p*-H, Ph), 7.36-7.46 (m, 2H, *o*-H, Ph). <sup>13</sup>C NMR,  $\delta$ : 11.6 (*NCH*<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 15.3, 19.4, 23.4, 23.9 (2CH<sub>3</sub>, *CHC*≡C, *NCH*<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 26.2 (*C*(CH<sub>3</sub>)<sub>2</sub>), 47.9, 51.0 (*CHN*, *NCH*<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 82.6, 87.5 (*C*≡C), 124.3 (*C*<sup>1</sup>, Ph), 127.4 (*C*<sup>4</sup>, Ph), 128.2, 131.7 (*C*<sup>2</sup>, *C*<sup>3</sup>, *C*<sup>5</sup>, *C*<sup>6</sup>, Ph).

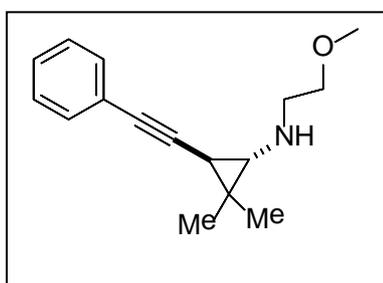


*N*-Isobutyl-2,2-dimethyl-3-(2-phenylethynyl)cyclopropanamine **6b** was prepared from carbamate **3d** as mixture of (*1R*\*,*3S*\*)- and (*1R*\*,*1R*\*)-isomers (8:1) and isolated in 74% yield. HRMS, *m/z* 242.1906, calculated for C<sub>17</sub>H<sub>23</sub>N, [*M*+*H*]<sup>+</sup>: *m/z* 242.1903.

(*1R*\*,*3S*\*)-**6b**: <sup>1</sup>H NMR,  $\delta$ : 0.94 (d, 3H, CH<sub>3</sub> in *i*-Bu, <sup>3</sup>*J* 6.7 Hz), 0.95 (d, 3H, CH<sub>3</sub> in *i*-Bu, <sup>3</sup>*J* 6.7 Hz), 1.19 (d, 1H, *CHC*≡C, <sup>3</sup>*J* 3.7 Hz), 1.25 (s, 3H, CH<sub>3</sub>), 1.26 (s, 3H, CH<sub>3</sub>), 1.51 (yш. c, 1H, NH), 1.69-1.83 (m, 1H, *NCH*<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.20 (d, 1H, *CHN*, <sup>3</sup>*J* 3.7 Hz), 2.47

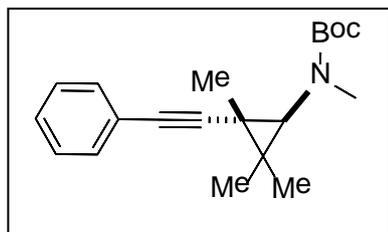
(dd, 1H, NCHHCH(CH<sub>3</sub>)<sub>2</sub>, <sup>2</sup>J 11.6 Hz, <sup>3</sup>J 6.8 Hz), 2.54 (dd, 1H, NCHHCH(CH<sub>3</sub>)<sub>2</sub>, <sup>2</sup>J 11.6 Hz, <sup>3</sup>J 6.8 Hz), 7.23-7.34 (m, 3H, *m*, *p*-H, Ph), 7.37-7.45 (m, 2H, *o*-H, Ph). <sup>13</sup>C NMR, 19.0, 20.4, 20.6, 21.8, 22.1 (2CH<sub>3</sub>, NCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>, CHC≡C), 26.0 (C(CH<sub>3</sub>)<sub>2</sub>), 28.4 (NCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 52.1 (CHN), 57.7 (NCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 78.8, 90.5 (C≡C), 124.3 (C<sup>1</sup>, Ph), 127.2 (C<sup>4</sup>, Ph), 128.2, 131.5 (C<sup>2</sup>, C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>, Ph).

**(1*R*\*,3*R*\*)-6b**: <sup>1</sup>H NMR, δ: 0.96 (d, 3H, CH<sub>3</sub> in *i*-Bu, <sup>3</sup>J 6.7 Hz), 0.97 (d, 3H, CH<sub>3</sub> in *i*-Bu, <sup>3</sup>J 6.7 Hz), 1.14 (s, 3H, CH<sub>3</sub>), 1.26 (s, 3H, CH<sub>3</sub>), 1.40 (d, 1H, CHC≡C, <sup>3</sup>J 7.0 Hz), 1.51 (yml. c, 1H, NH), 1.73-1.85 (m, 1H, NCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.23 (d, 1H, CHN, <sup>3</sup>J 7.0 Hz), 2.55 (dd, 1H, NCHHCH(CH<sub>3</sub>)<sub>2</sub>, <sup>2</sup>J 11.5 Hz, <sup>3</sup>J 6.8 Hz), 2.66 (dd, 1H, NCHHCH(CH<sub>3</sub>)<sub>2</sub>, <sup>2</sup>J 11.5 Hz, <sup>3</sup>J 6.8 Hz), 7.23-7.34 (m, 3H, *m*, *p*-H, Ph), 7.37-7.45 (m, 2H, *o*-H, Ph). <sup>13</sup>C NMR, 15.3, 19.4, 20.8, 20.9, 23.4 (2CH<sub>3</sub>, NCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>, CHC≡C), 26.2 (C(CH<sub>3</sub>)<sub>2</sub>), 28.7 (NCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 48.0 (CHN), 57.1 (NCH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 80.8, 88.1 (C≡C), 124.3 (C<sup>1</sup>, Ph), 127.2 (C<sup>4</sup>, Ph), 128.2, 131.5 (C<sup>2</sup>, C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>, Ph).

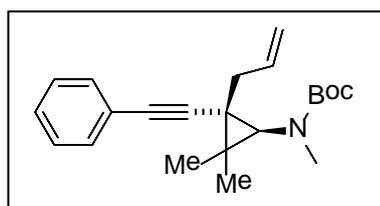


**(1*R*\*,3*S*\*)-N-(2-methoxyethyl)-2,2-dimethyl-3-(2-phenylethynyl)-cyclopropanamine 6c** was prepared from hydrochloride **5c** and isolated in 89% yield. HRMS, *m/z* 244.1691, calculated for C<sub>16</sub>H<sub>21</sub>NO, [M+H]<sup>+</sup>: *m/z* 244.1696. <sup>1</sup>H NMR, δ: 1.21 (d, 1H, CHC≡C, <sup>3</sup>J 3.7 Hz), 1.24 (s, 6H, 2CH<sub>3</sub>), 2.10 (br. s, 1H, NH), 2.23 (d, 1H, CHN, <sup>3</sup>J 3.7 Hz), 2.85 (dt, 1H, NCHHCH<sub>2</sub>O, <sup>2</sup>J 12.7 Hz, <sup>3</sup>J 5.1 Hz), 2.91 (dt, 1H, NCHHCH<sub>2</sub>O, <sup>2</sup>J 12.7 Hz, <sup>3</sup>J 5.1 Hz), 3.38 (s, 3H, OCH<sub>3</sub>), 3.52 (t, 2H, NCH<sub>2</sub>CH<sub>2</sub>O, <sup>3</sup>J 5.1 Hz), 7.22-7.35 (m, 3H, *m*, *p*-H, Ph), 7.35-7.42 (m, 2H, *o*-H, Ph). <sup>13</sup>C NMR, δ: 19.1, 21.9, 22.2 (2CH<sub>3</sub>, CHC≡C), 25.9 (C(CH<sub>3</sub>)<sub>2</sub>), 48.9, 51.8 (CHN, NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 58.8 (OCH<sub>3</sub>), 71.8 (NCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>), 79.0, 90.3 (C≡C), 124.3 (C<sup>1</sup>, Ph), 127.3 (C<sup>4</sup>, Ph), 128.2, 131.6 (C<sup>2</sup>, C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>, Ph).

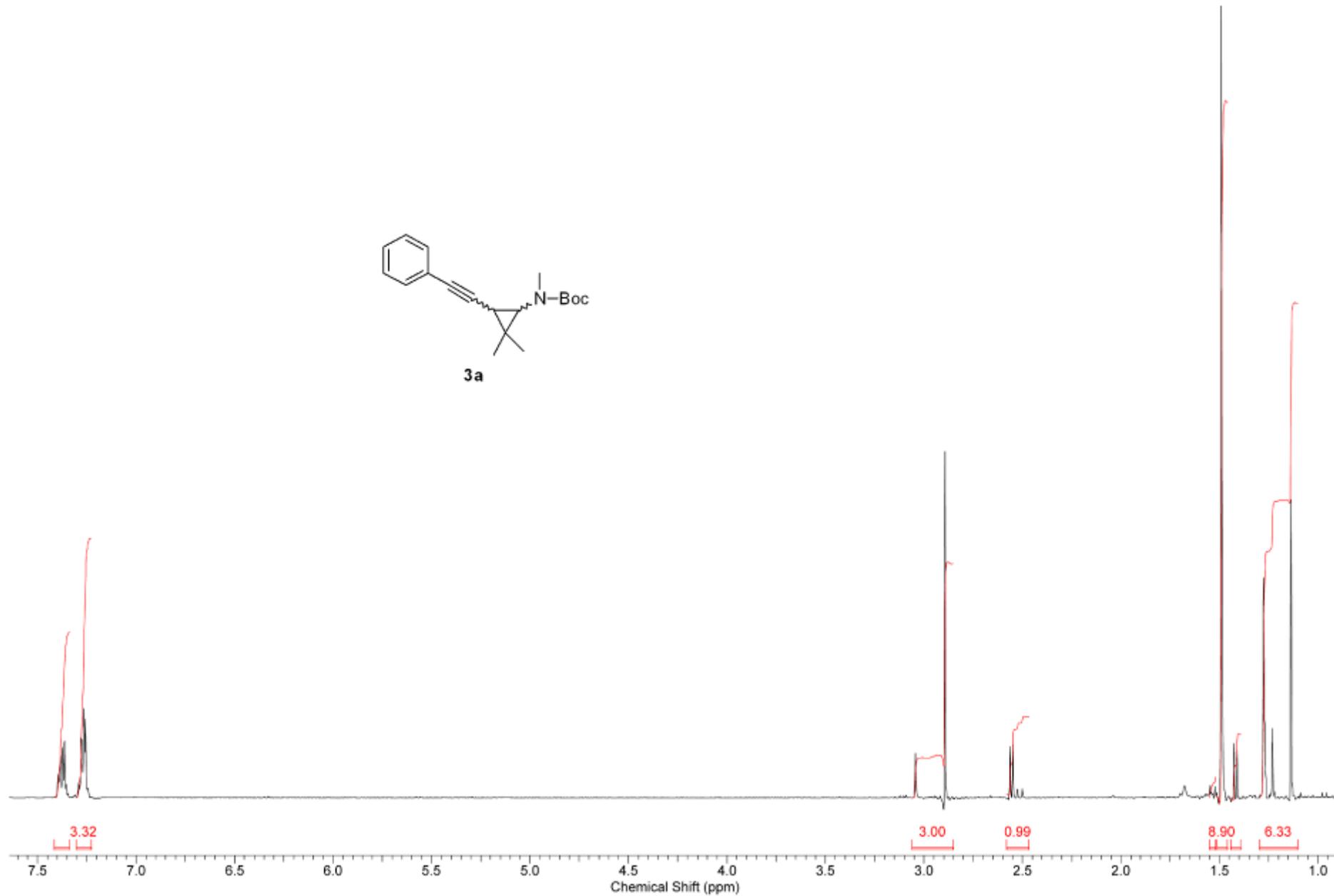
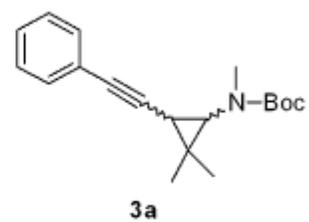
**Synthesis of compounds 7,8 from *tert*-butyl [2,2-dimethyl-3-(2-phenylethynyl)-cyclopropyl]methylcarbamate 3a.** To the solution of compound **3a** (1*R*\*,3*S*\*/1*R*\*,1*R*\* = 4.9:1, 150 mg, 0.5 mmol) of in anhydrous THF (2 ml) cooled to -65÷-70°C, a solution of *n*-BuLi in hexanes (2.5 M, 0.3 ml, 0.75 mmol) was syringed under argon. The resulting mixture was stirred at this temperature for 1 h. Thereafter a solution of iodomethane or allyl bromide (0.75 mmol) in THF (0.5 ml) was added in one portion. The mixture was allowed to warm up to the room temperature, then water (5 ml) and Et<sub>2</sub>O (10 ml) were added, the organic layer was separated and the aqueous phase was additionally extracted with Et<sub>2</sub>O (2x5 ml). The combined organic phases were dried over anhydrous K<sub>2</sub>CO<sub>3</sub>, the solvent was evaporated, and the residue was dissolved in hexane-Et<sub>2</sub>O (10:1) mixture, passed through thin layer of basic Al<sub>2</sub>O<sub>3</sub> and evaporated again to leave products **7,8**.

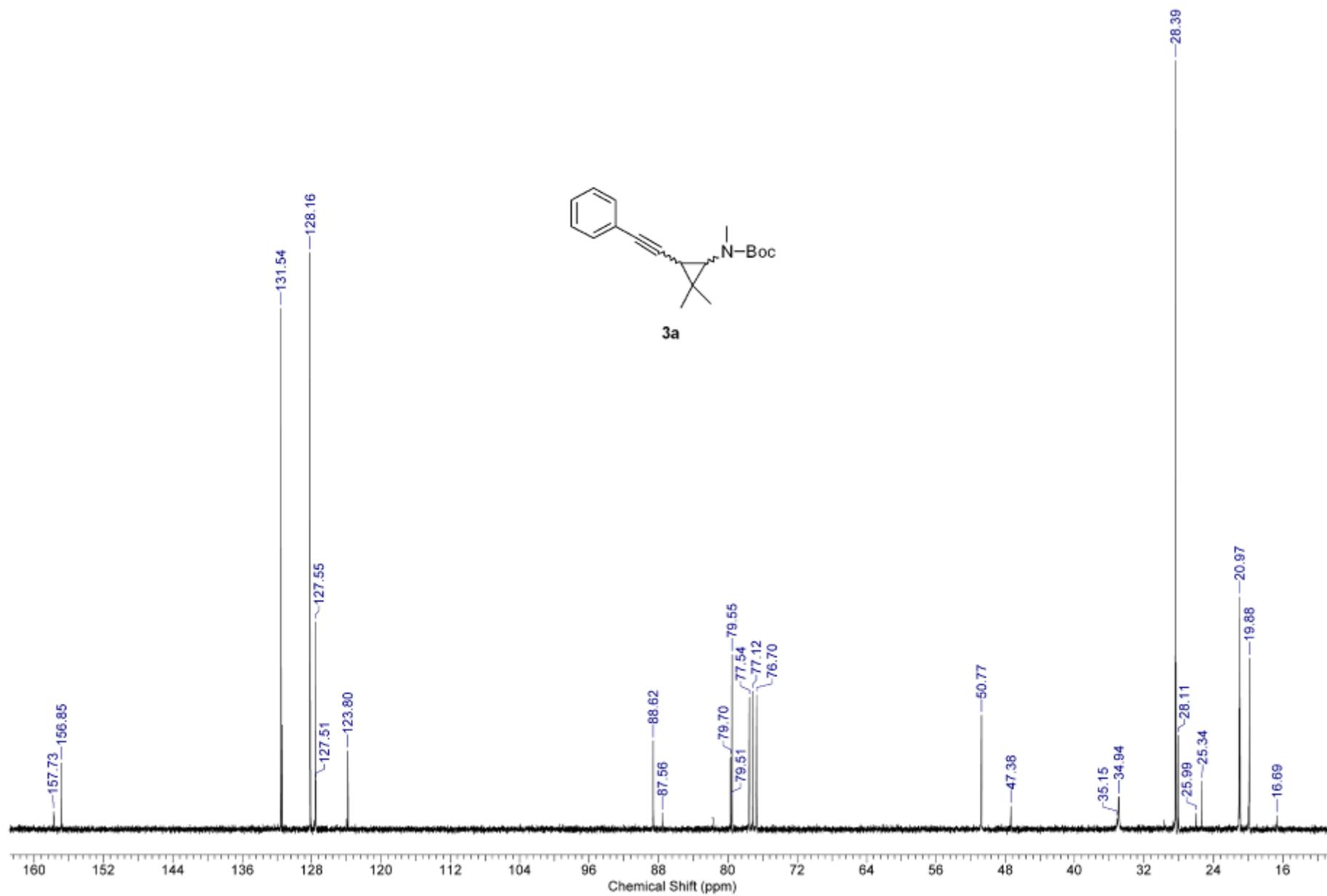


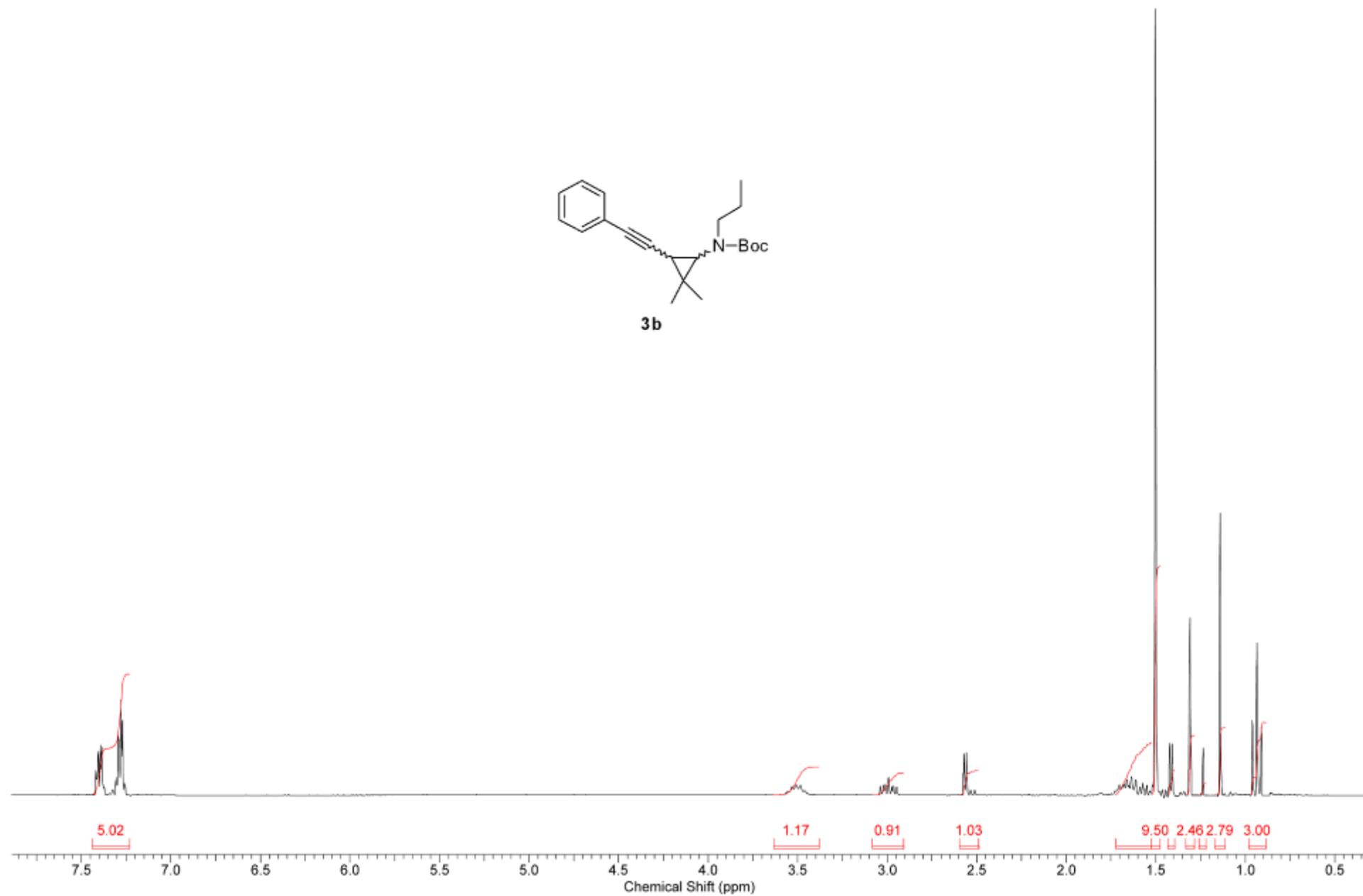
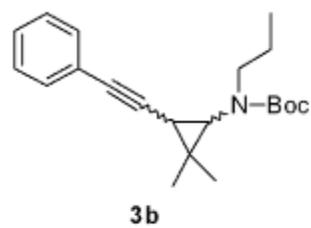
*tert*-Butyl methyl[(1*R*\*,3*R*\*)-2,2,3-trimethyl-3-(2-phenylethynyl)-cyclopropyl]carbamate **7** was obtained in 93% yield. HRMS,  $m/z$  314.2119, calculated for  $C_{20}H_{27}NO_2$ ,  $[M+H]^+$ :  $m/z$  314.2115.  $^1H$  NMR,  $\delta$ : 1.11 (s, 2H, CH<sub>3</sub>), 1.31 (s, 2H, CH<sub>3</sub>), 1.33 (s, 2H, CH<sub>3</sub>), 1.52 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 2.49 (s, 1H, CHN), 2.89 (s, 3H, NCH<sub>3</sub>), 7.23-7.35 (m, 3H, *m*, *p*-H, Ph), 7.34-7.42 (m, 2H, *o*-H, Ph).  $^{13}C$  NMR,  $\delta$ : 15.2, 16.3, 24.0 (3CH<sub>3</sub>), 22.0 (C $\equiv$ CCCH<sub>3</sub>), 27.4 (C(CH<sub>3</sub>)<sub>2</sub>), 28.3 (OC(CH<sub>3</sub>)<sub>3</sub>), 36.0 (NCH<sub>3</sub>), 52.5 (CHN), 78.4, 94.1 (C $\equiv$ C), 79.7 (OC(CH<sub>3</sub>)<sub>3</sub>), 124.1 (C<sup>1</sup>, Ph), 127.4 (C<sup>4</sup>, Ph), 128.1, 131.5 (C<sup>2</sup>, C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>, Ph), 157.9 (C=O).

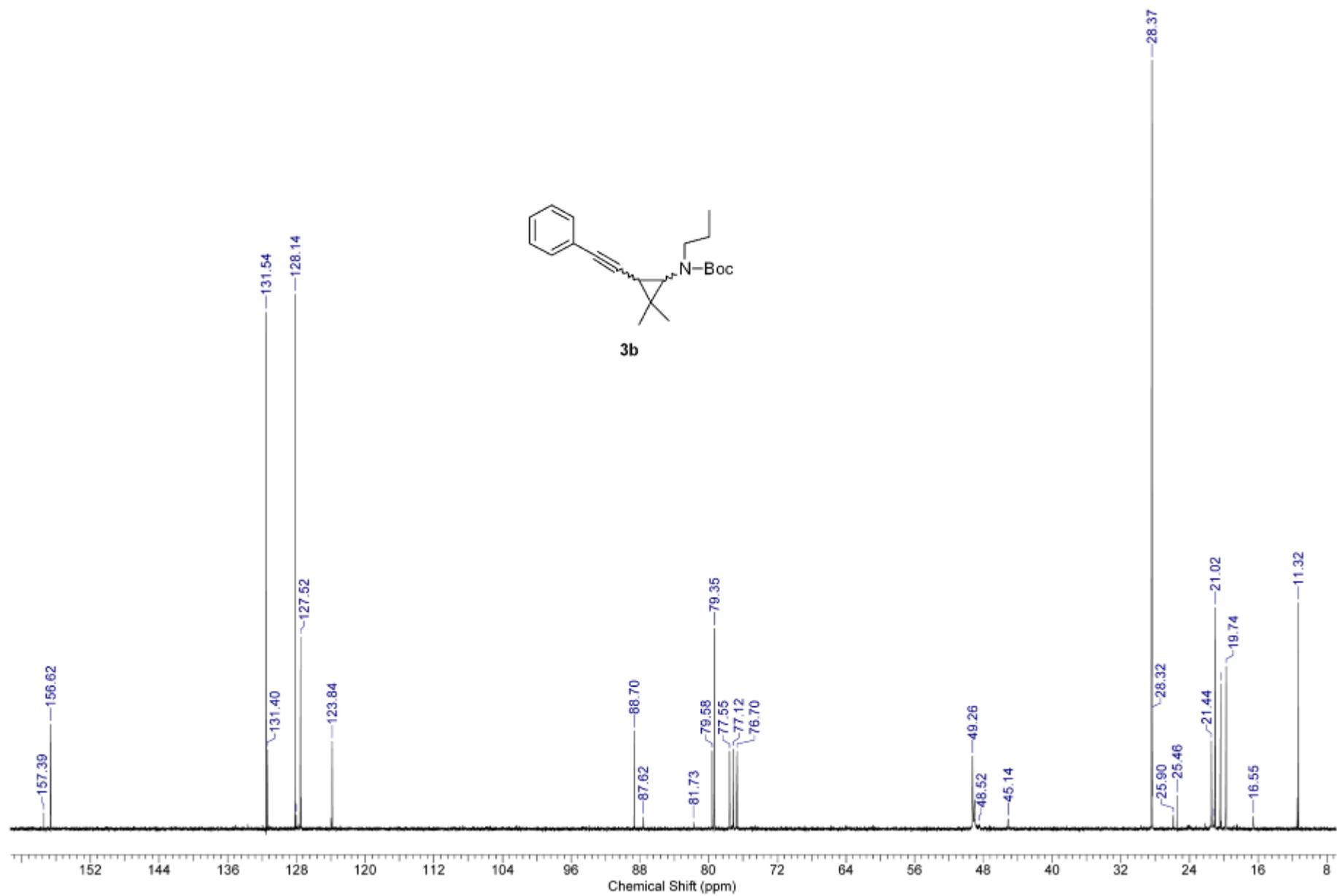
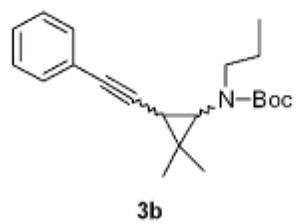


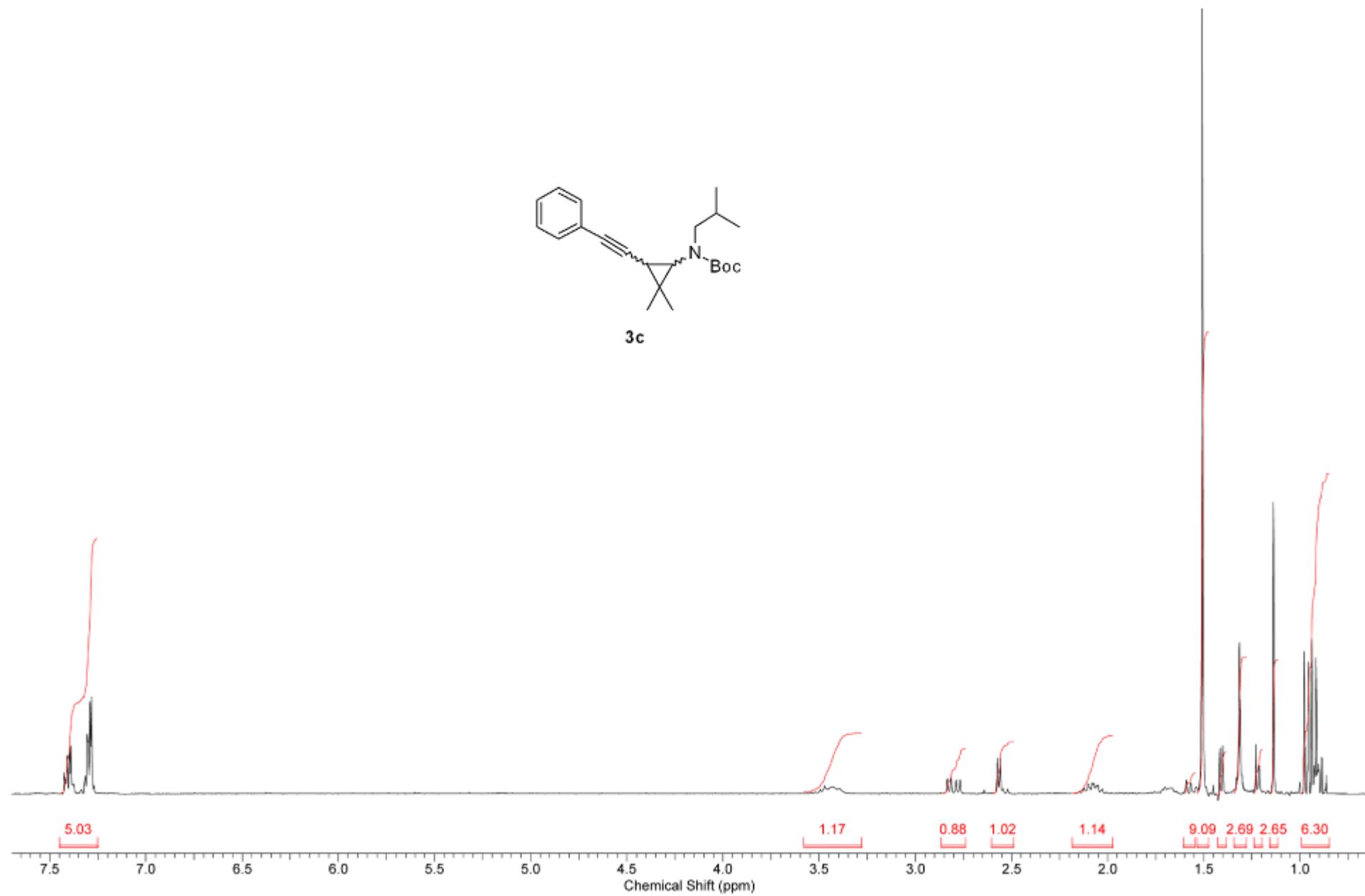
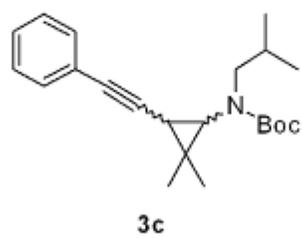
*tert*-Butyl [(1*R*\*,2*R*\*)-2-allyl-3,3-dimethyl-2-(2-phenylethynyl)-cyclopropyl]methylcarbamate **8** was obtained in 86% yield. HRMS,  $m/z$  340.2265, calculated for  $C_{22}H_{29}NO_2$ ,  $[M+H]^+$ :  $m/z$  340.2271.  $^1H$  NMR,  $\delta$ : 1.20 (s, 2H, CH<sub>3</sub>), 1.36 (s, 2H, CH<sub>3</sub>), 1.52 (s, 9H, OC(CH<sub>3</sub>)<sub>3</sub>), 2.24 (dddd, 1H, CHHCH=CH<sub>2</sub>,  $^2J$  15.4 Hz,  $^3J$  6.5 Hz,  $^4J$  1.5 Hz,  $^4J$  1.5 Hz), 2.56 (s, 1H, CHN), 2.59 (dddd, 1H, CHHCH=CH<sub>2</sub>,  $^2J$  15.4 Hz,  $^3J$  6.3 Hz,  $^4J$  1.5 Hz,  $^4J$  1.5 Hz), 2.91 (s, 3H, NCH<sub>3</sub>), 5.14 (dddd, 1H, CH<sub>2</sub>CH=CHH,  $^3J$  10.3 Hz,  $^2J$  1.8 Hz,  $^4J$  1.5 Hz,  $^4J$  1.5 Hz), 5.20 (dddd, 1H, CH<sub>2</sub>CH=CHH,  $^3J$  17.1 Hz,  $^2J$  1.8 Hz,  $^4J$  1.5 Hz,  $^4J$  1.5 Hz), 6.04 (dddd, 1H, CH<sub>2</sub>CH=CH<sub>2</sub>,  $^3J$  17.1 Hz,  $^3J$  10.3 Hz,  $^3J$  6.5 Hz,  $^3J$  6.3 Hz), 7.23-7.35 (m, 3H, *m*, *p*-H, Ph), 7.34-7.42 (m, 2H, *o*-H, Ph).  $^{13}C$  NMR,  $\delta$ : 16.4, 24.5 (2CH<sub>3</sub>), 26.2 (C $\equiv$ CCCH<sub>3</sub>), 28.2 (C(CH<sub>3</sub>)<sub>2</sub>), 28.4 (OC(CH<sub>3</sub>)<sub>3</sub>), 33.8 (CH<sub>2</sub>CH=CH<sub>2</sub>), 36.5 (NCH<sub>3</sub>), 53.0 (CHN), 79.9, 92.8 (C $\equiv$ C), 80.0 (OC(CH<sub>3</sub>)<sub>3</sub>), 116.4 (=CH<sub>2</sub>), 124.1 (C<sup>1</sup>, Ph), 127.4 (C<sup>4</sup>, Ph), 128.2, 131.6 (C<sup>2</sup>, C<sup>3</sup>, C<sup>5</sup>, C<sup>6</sup>, Ph), 135.6 (-CH=), 158.0 (C=O).

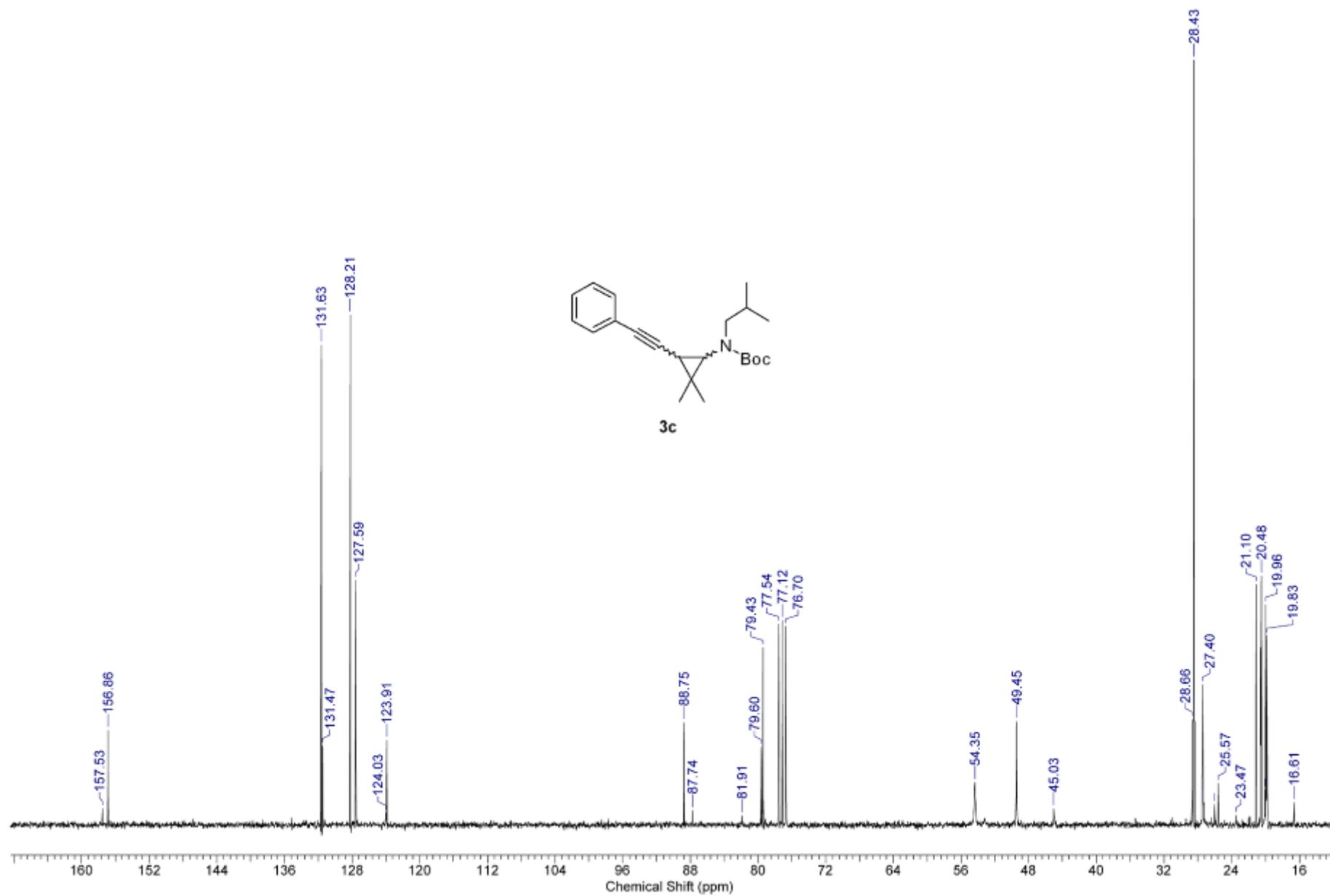
*Copies of NMR-spectra for compounds 3a-f, 5a,c, 6a-c, 7 and 8*

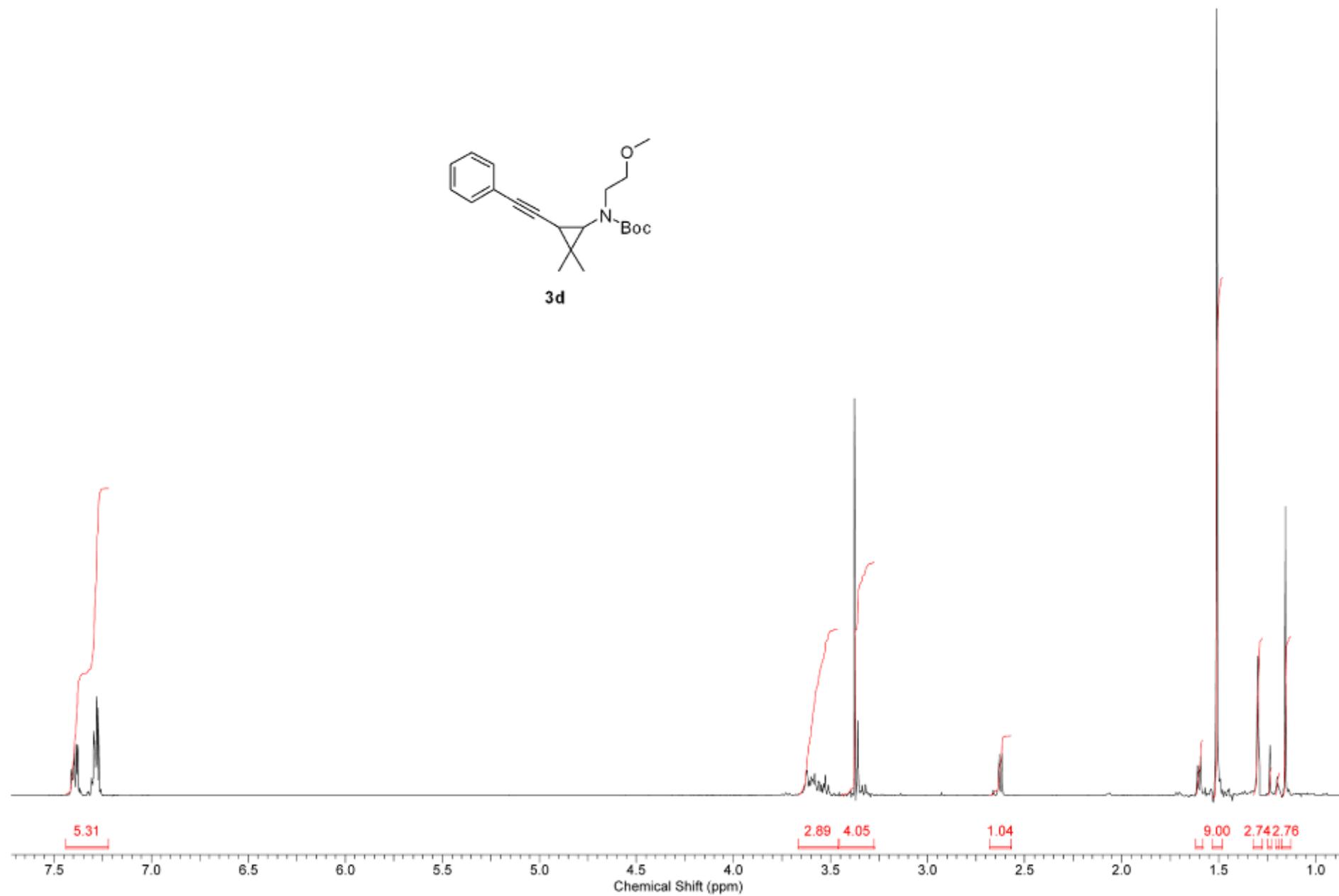
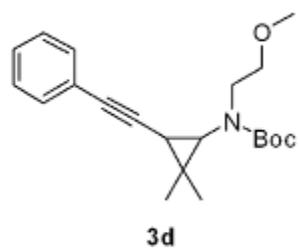


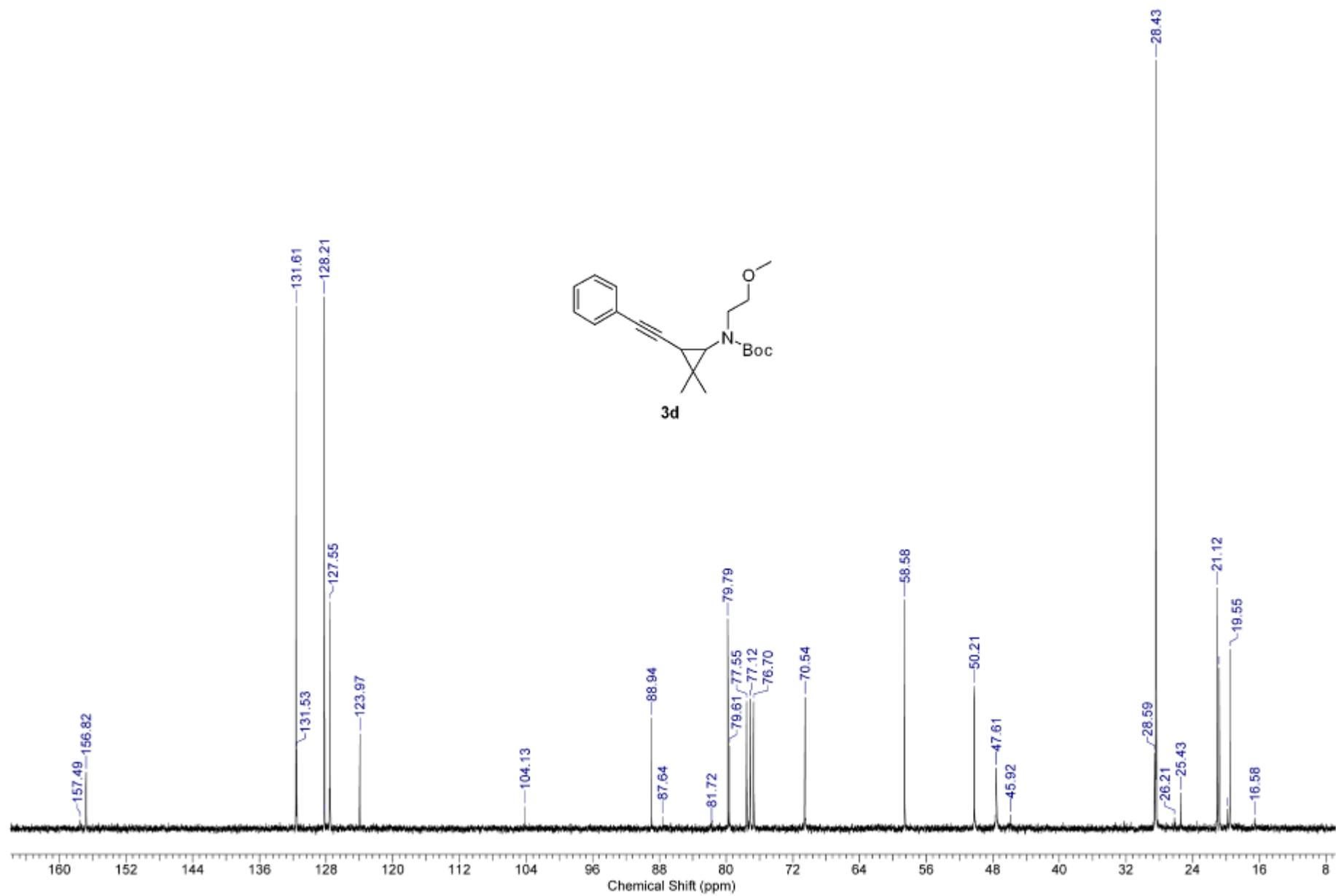


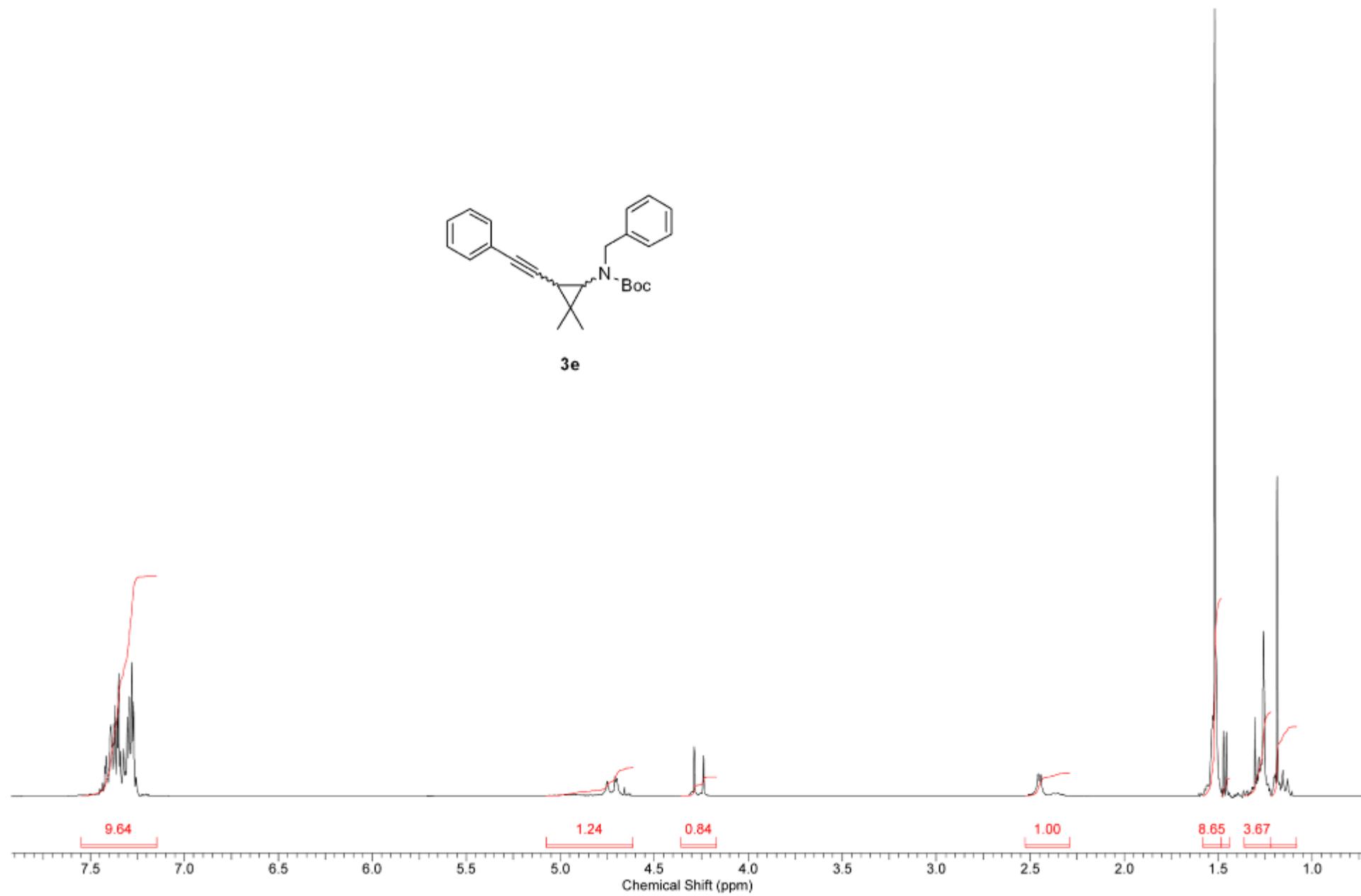
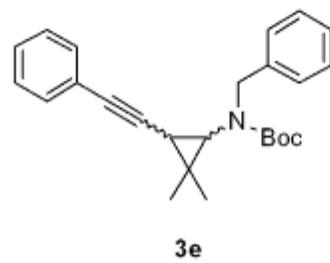


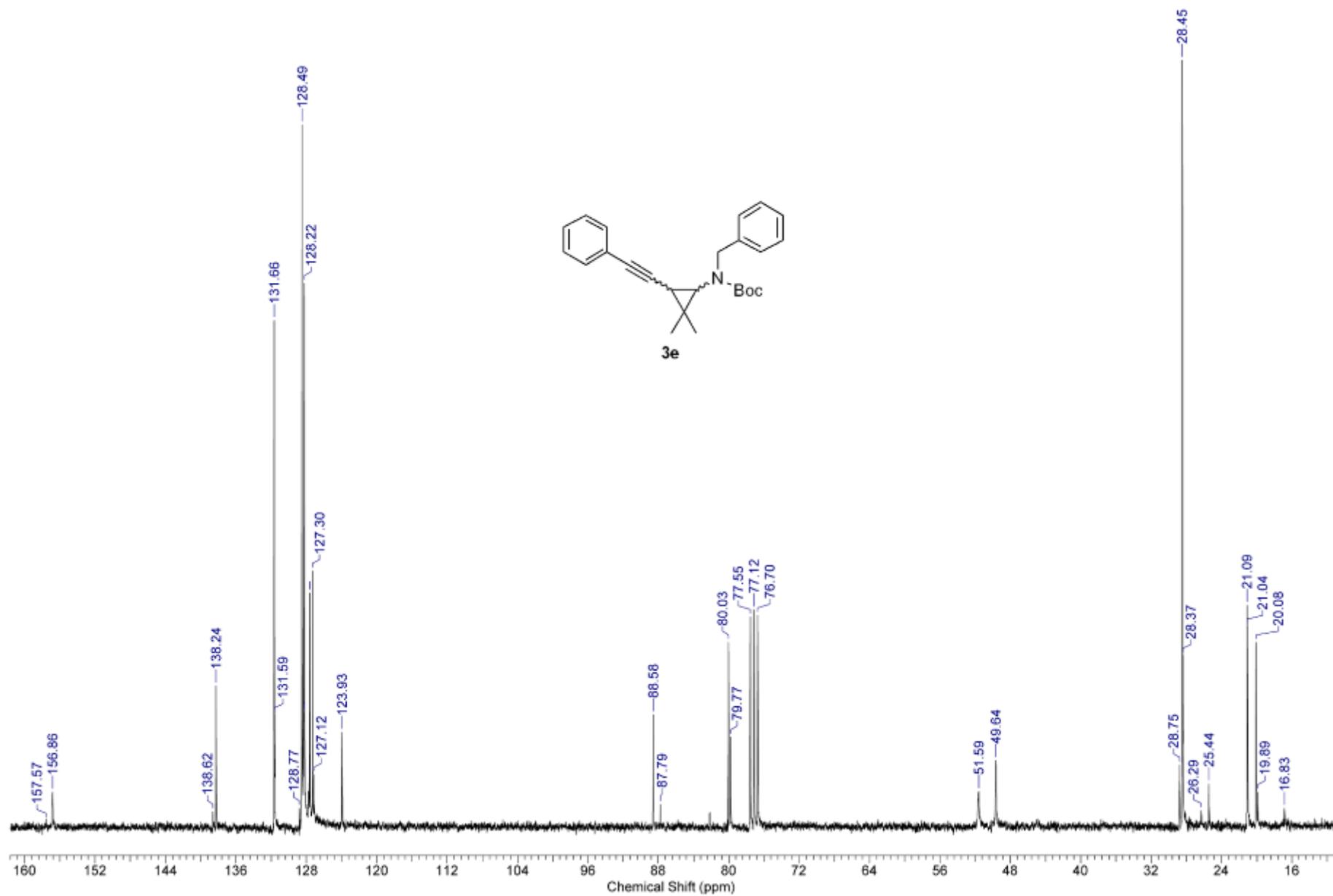


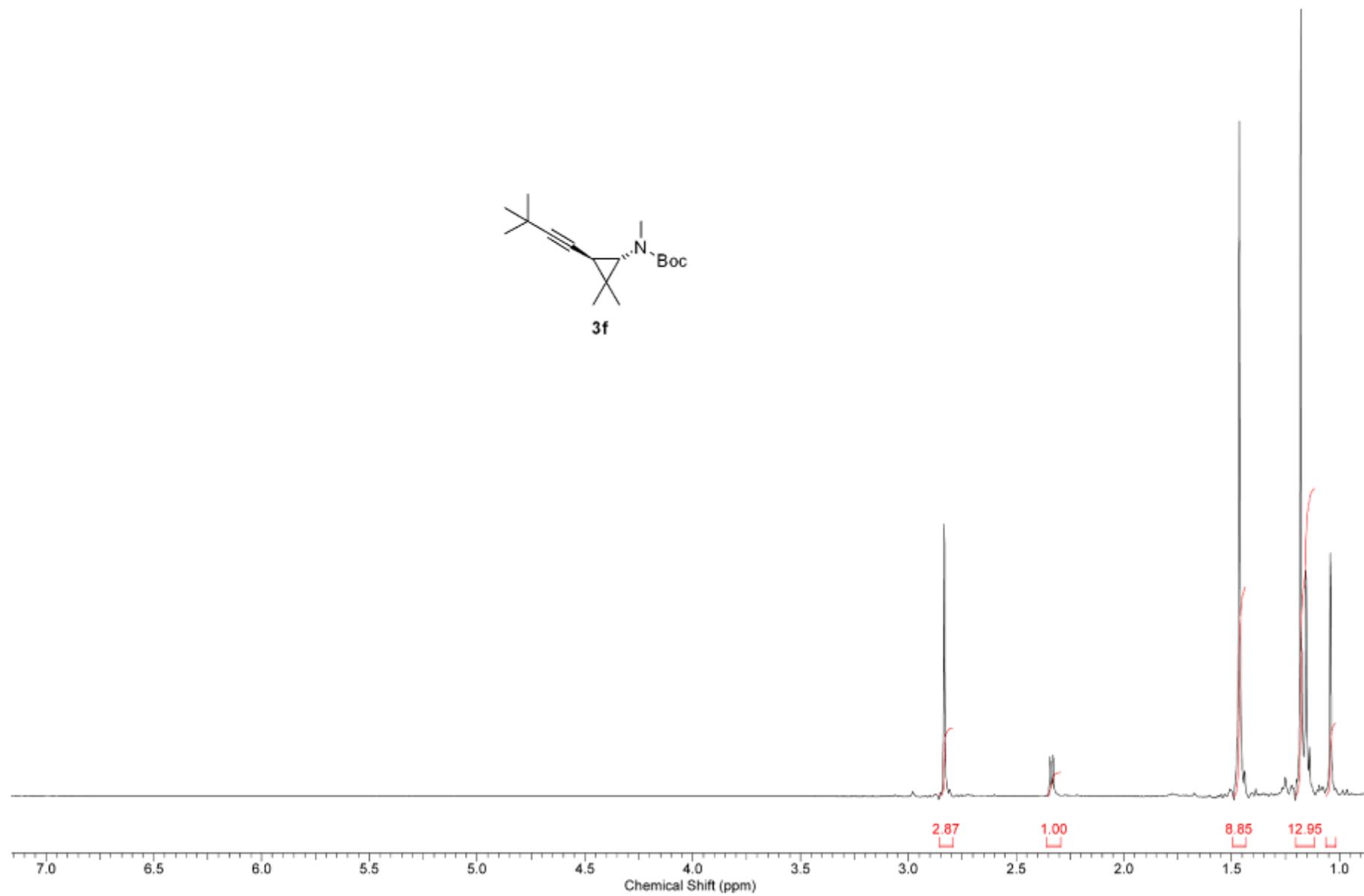
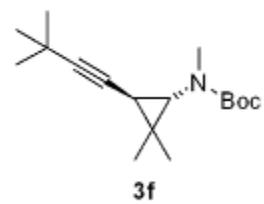


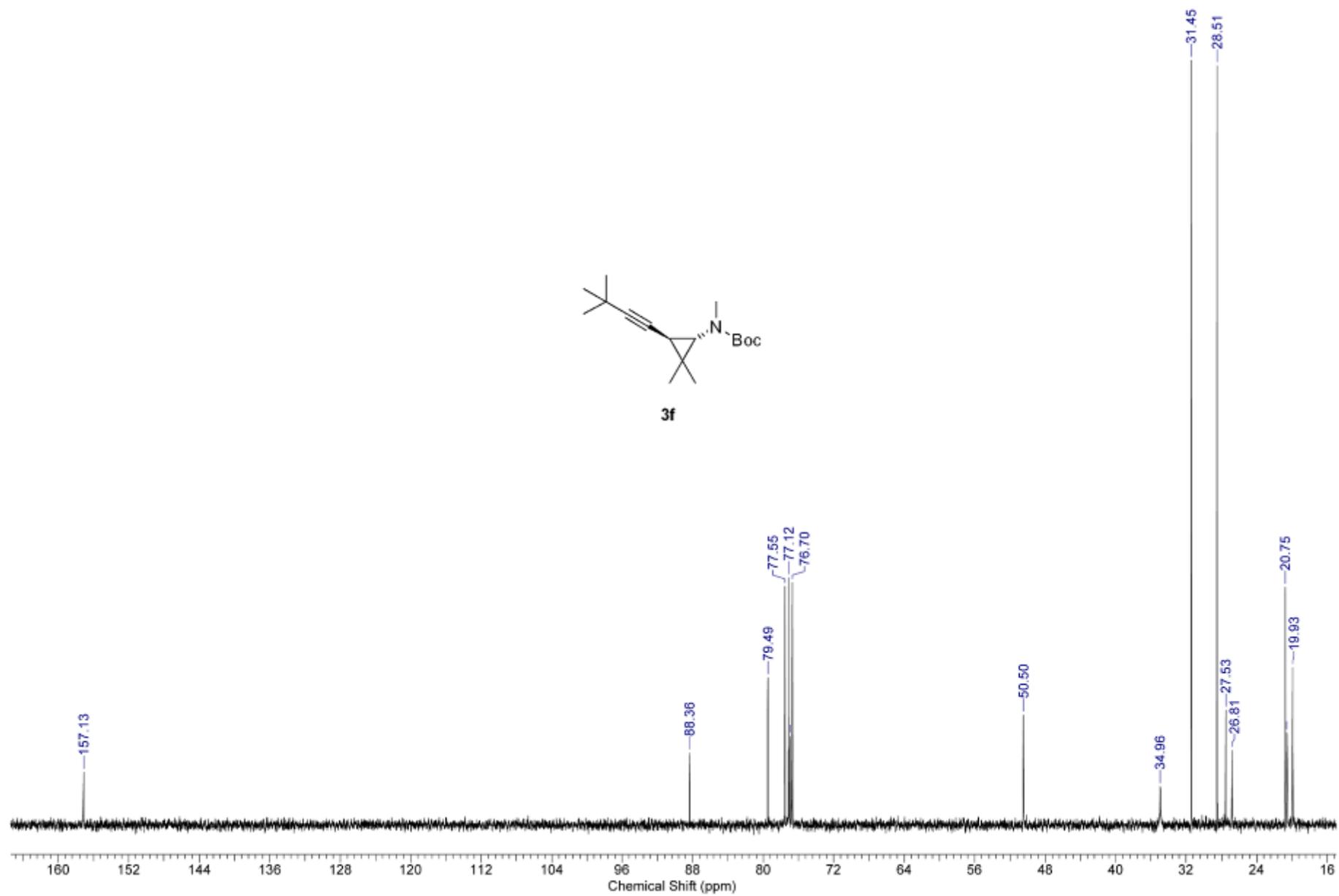
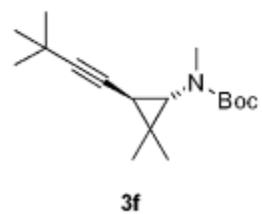


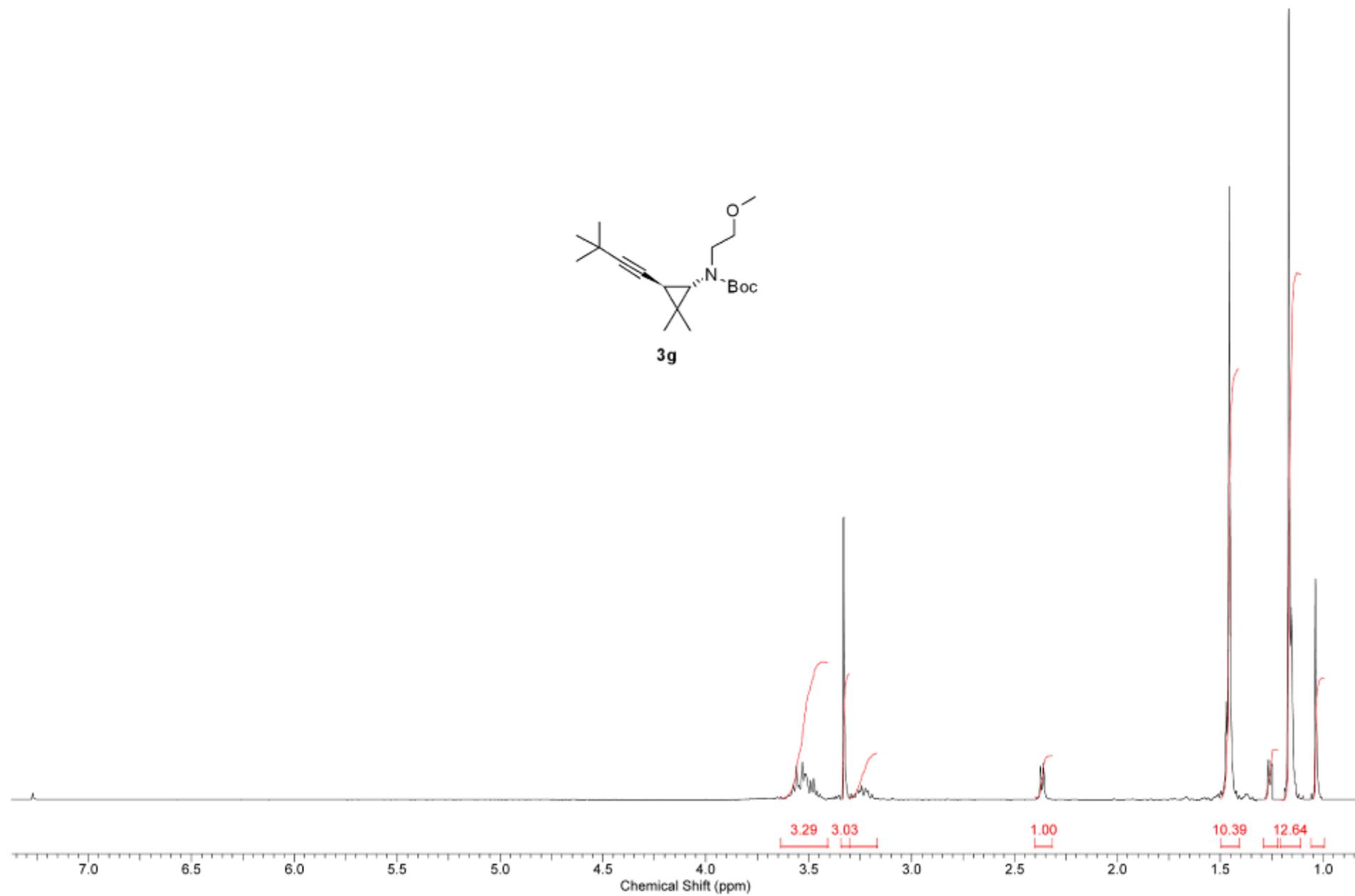
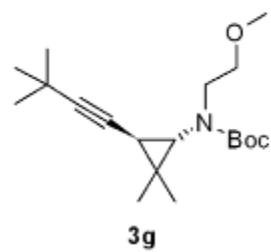


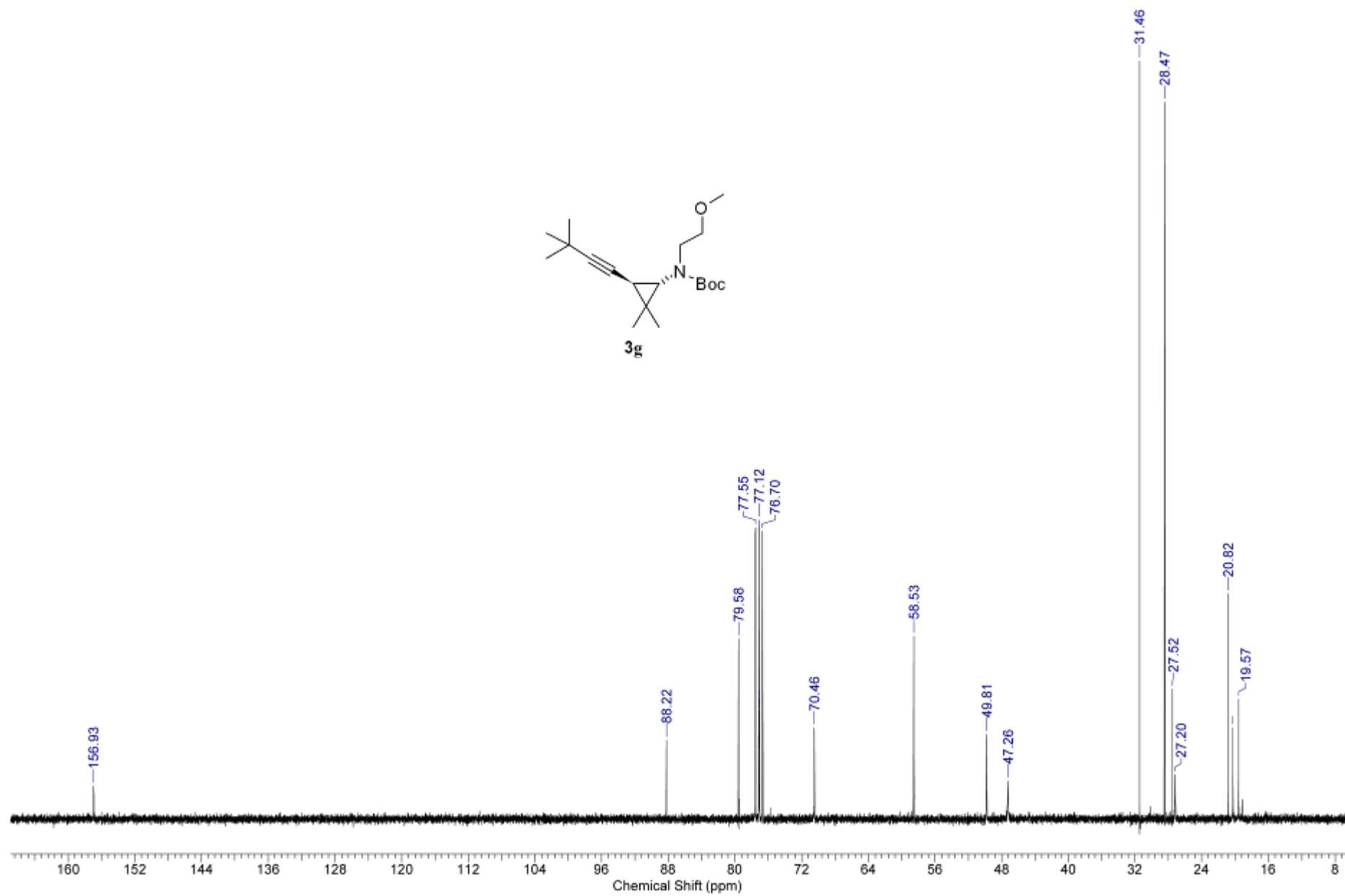
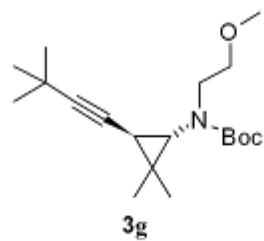


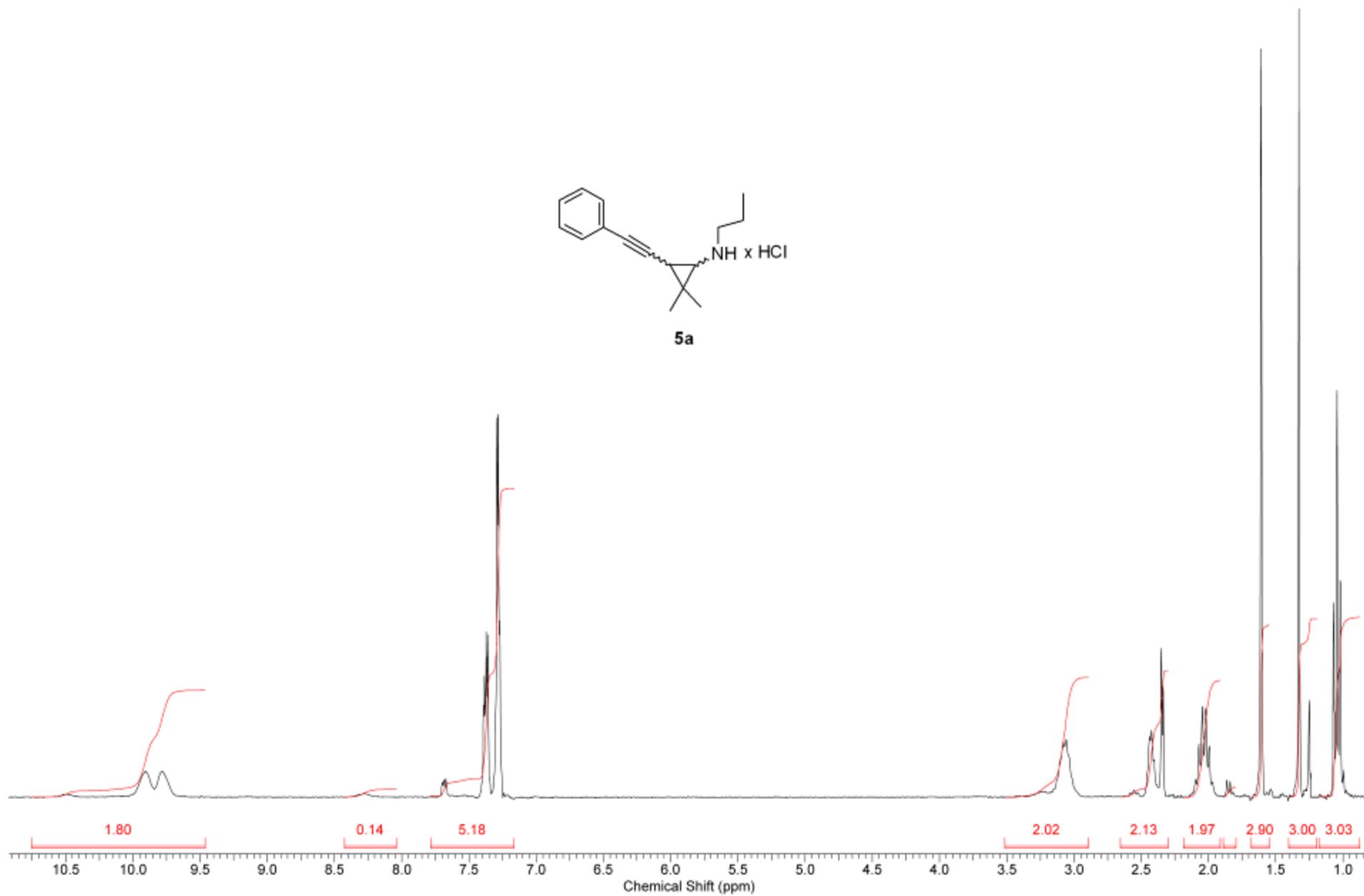
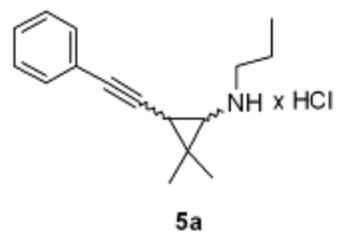


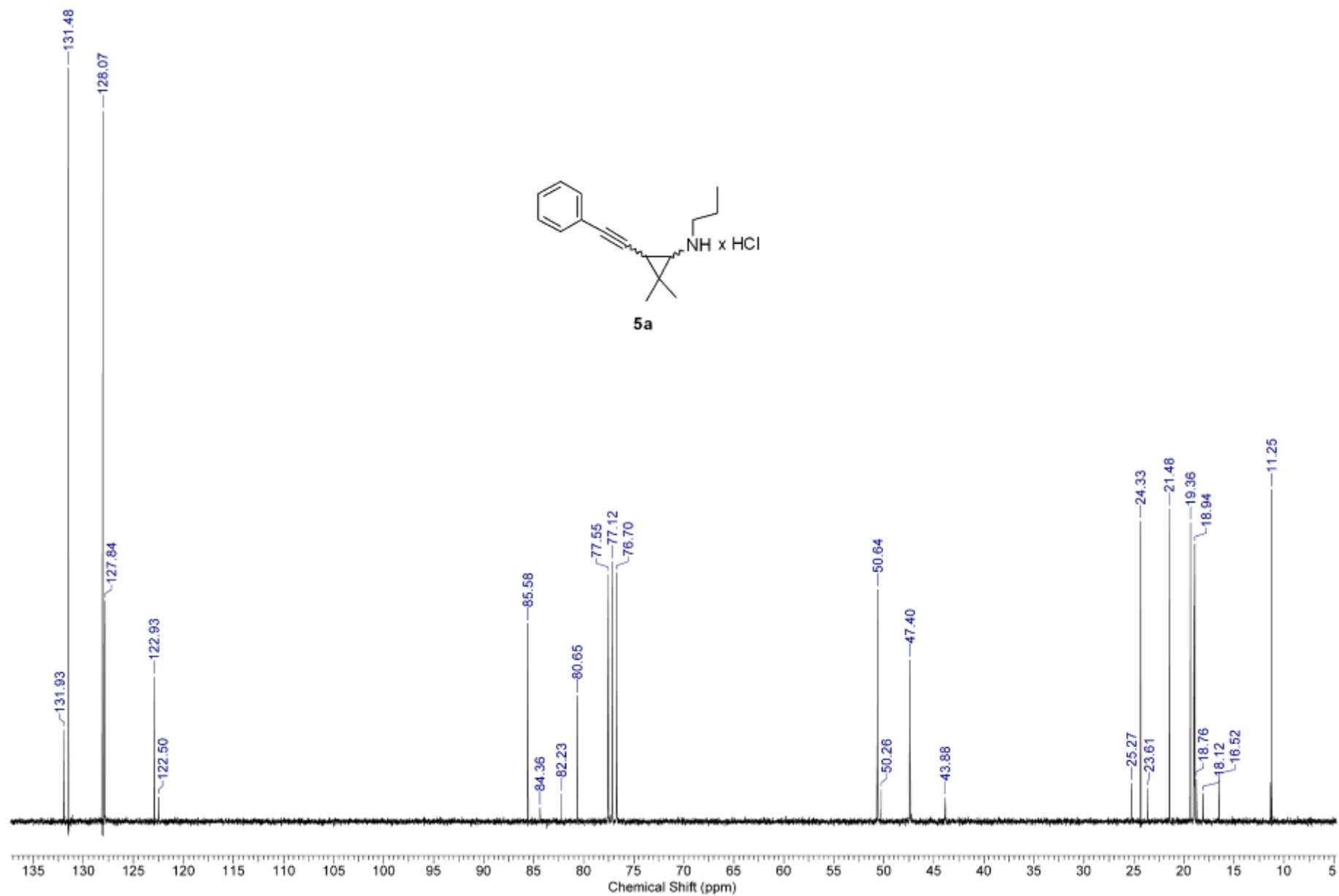


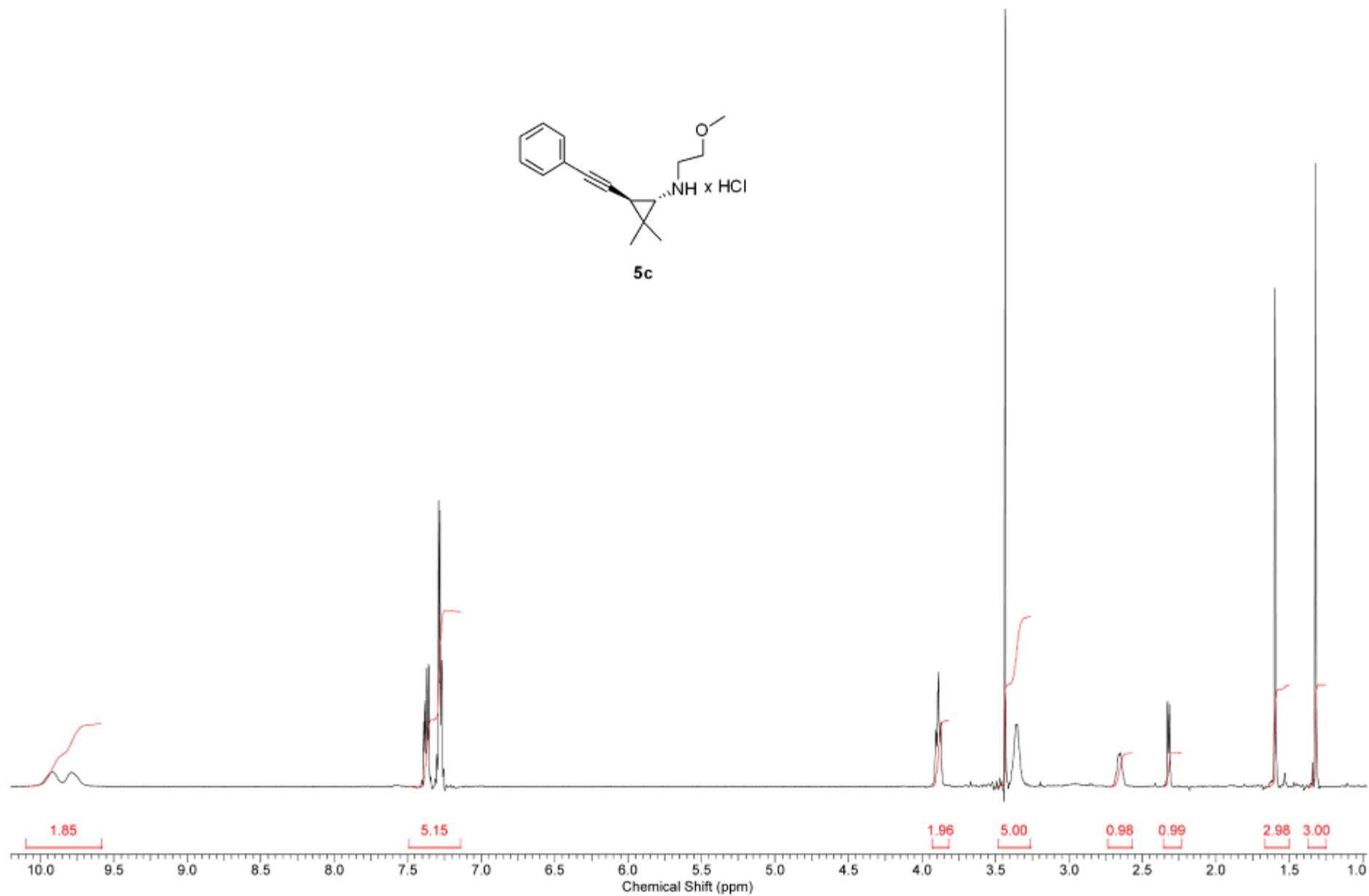
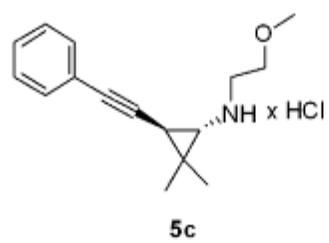


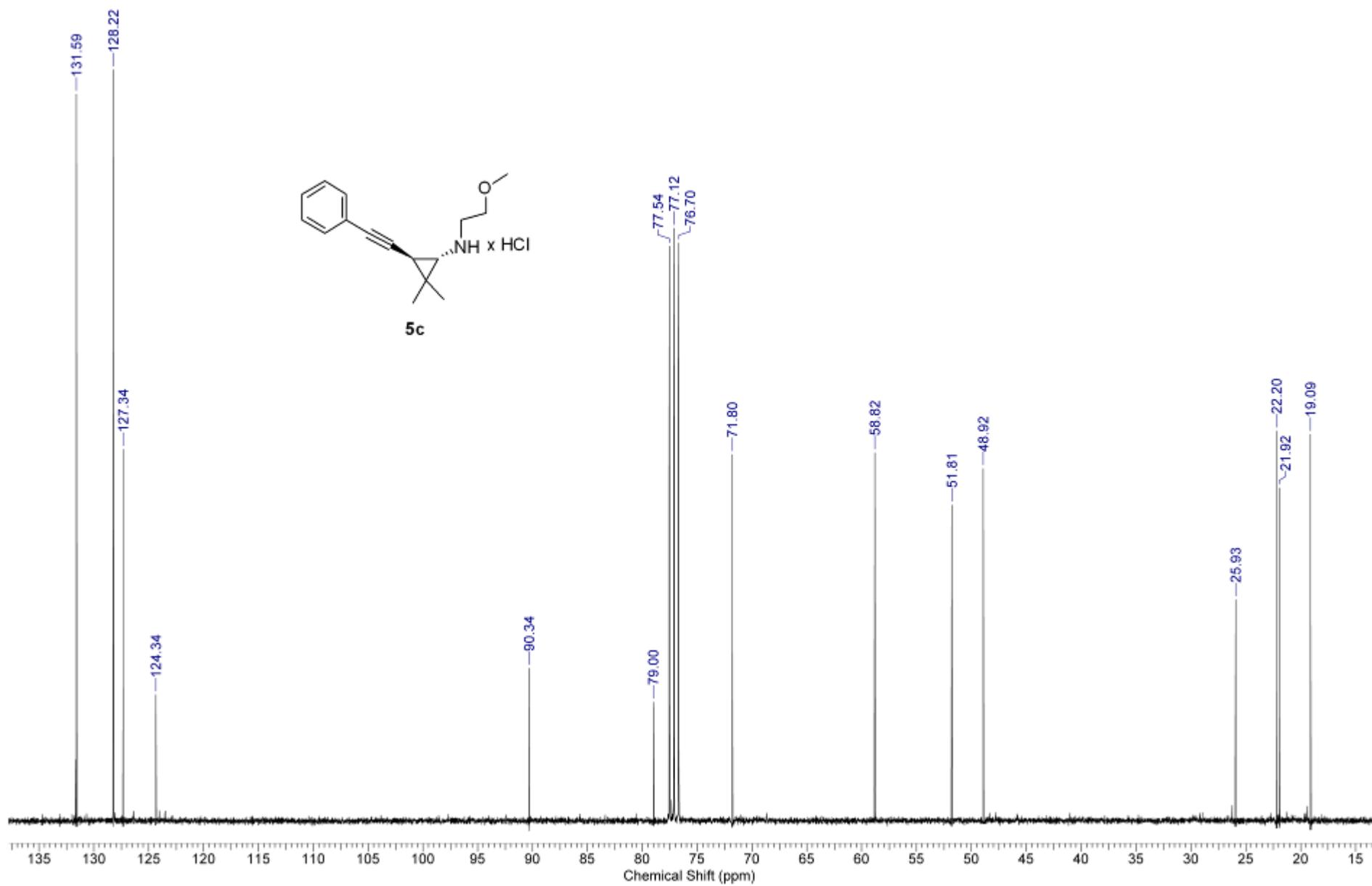


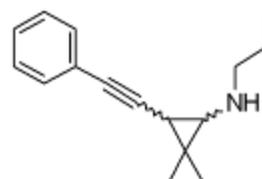






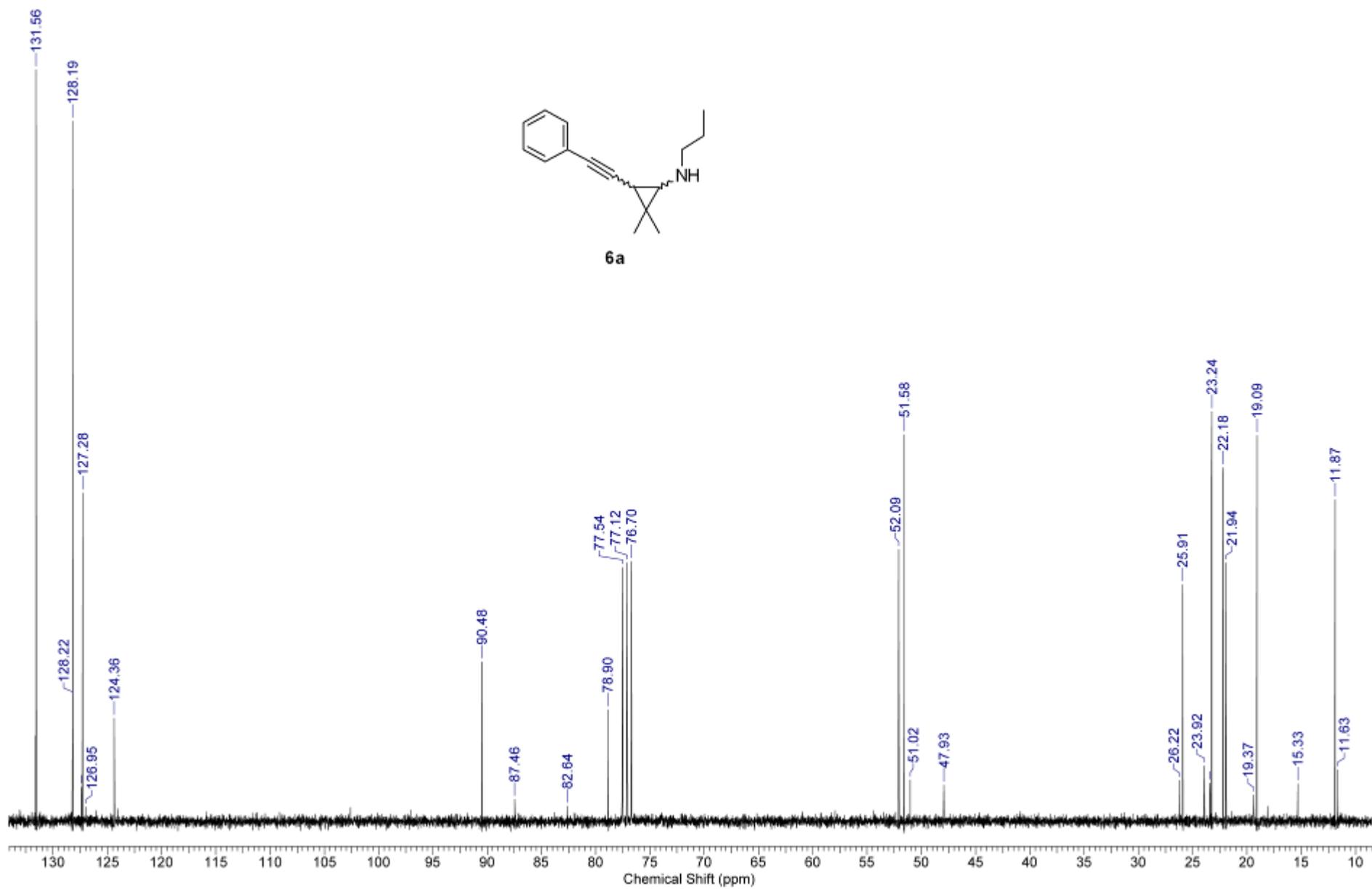
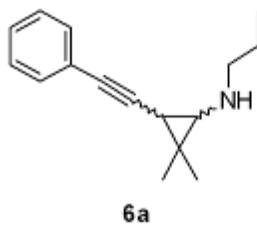


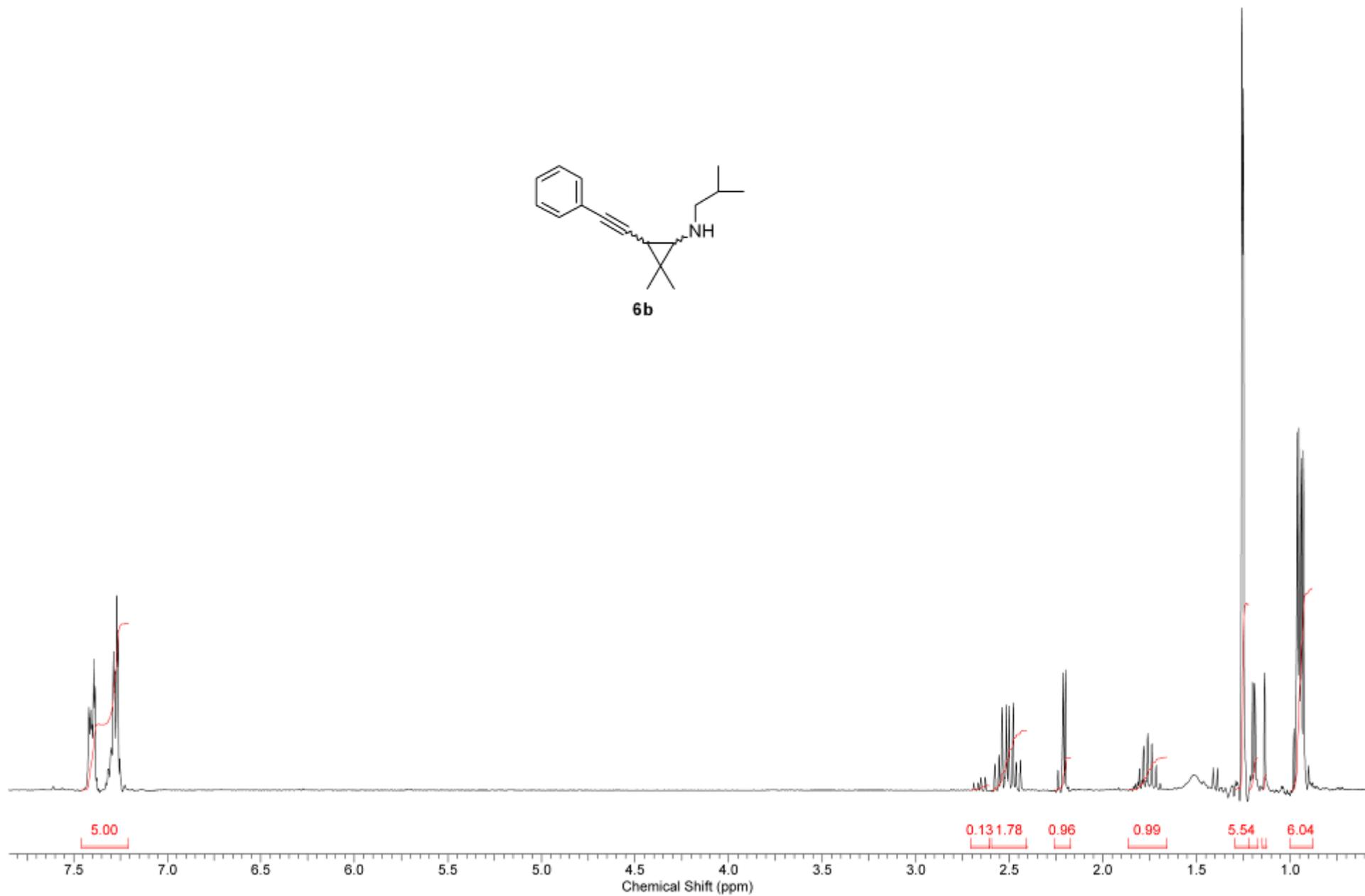
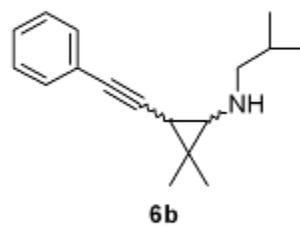


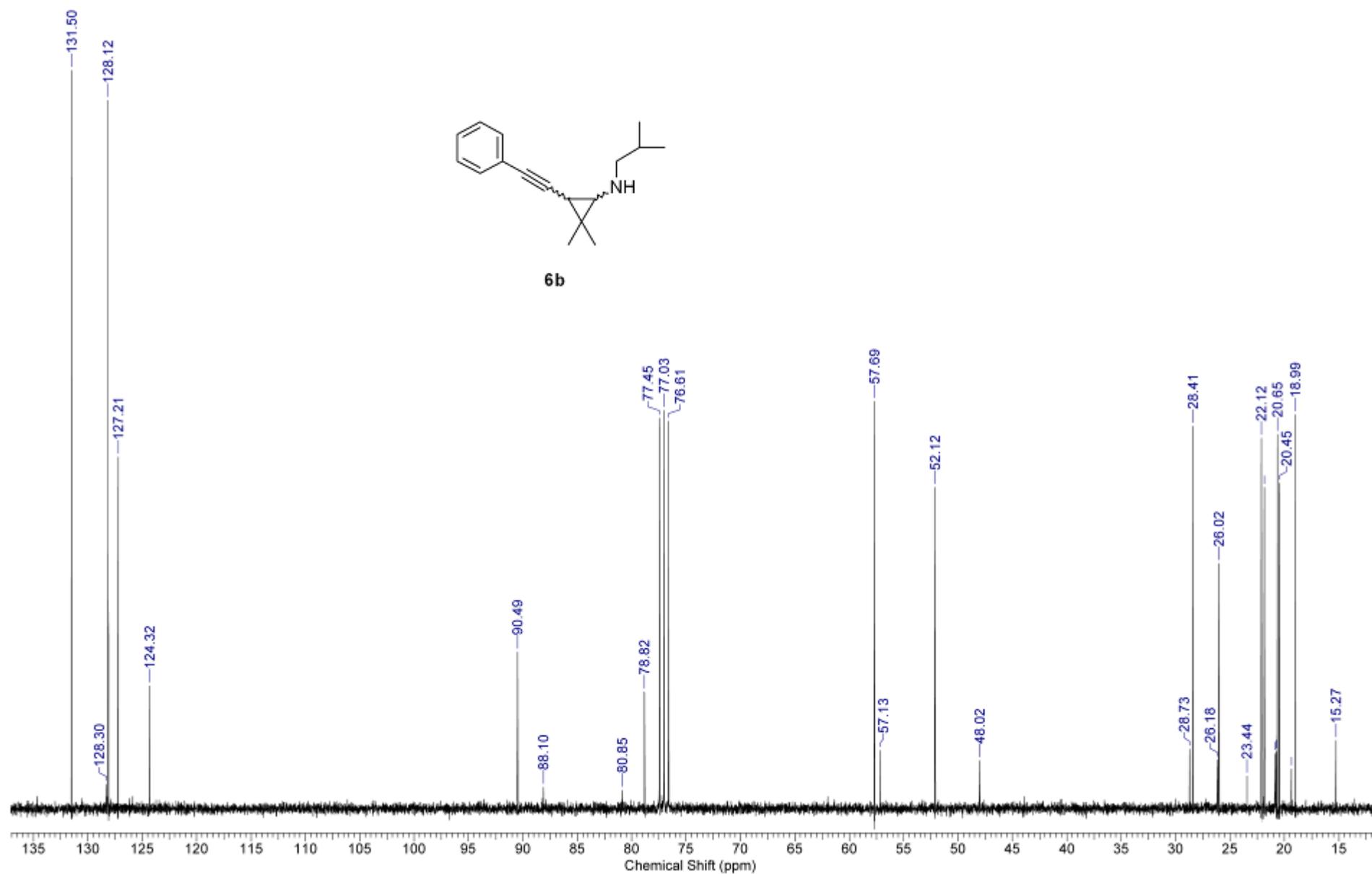


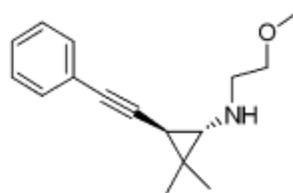
6a











6c

