SUPPORTING INFORMATION

Stereocontrolled synthesis of some novel functionalized heterocyclic amino ester and amide derivatives with multiple stereocenters

Anas Semghouli,[1,2] Attila M. Remete,[1*] Loránd Kiss[2*]

[1]Institute of Pharmaceutical Chemistry, University of Szeged, H-6720 Szeged, Eötvös u. 6, Hungary

[2]Institute of Organic Chemistry, Stereochemistry Research Group, Research Centre for Natural Sciences, H-1117 Budapest, Magyar tudósok krt. 2, Hungary

E-mail: kiss.lorand@ttk.hu

remete.attila.mario@szte.hu

Tel: +36-30-1600354

Experimental part

General information

The chemicals were bought from Sigma-Aldrich. Solvents were used as received from the supplier. TLC plates (TLC Silica gel 60 F_{254}) and silica gel for column chromatography (technical grade, pore size 60 Å, 70-230 mesh) were purchased from Merck. Melting points were measured using a Kofler apparatus. NMR spectra were recorded at room temperature using a Bruker Avance Neo 500 spectrometer with an 11.75 T magnetic field (^{1}H frequency 500.20 MHz, ^{13}C frequency 125.78 MHz) in $CDCl_3$ solution, using deuterium signal of the solvent to lock the field. The chemical shifts of ^{1}H and ^{13}C are given relative to TMS. HRMS were acquired on either a Thermo Scientific Q-Exactive Plus Orbitrap mass spectrometer (Thermo Fisher Scientific Inc., Budapest, Hungary) equipped with an electrospray ionization ion source in the positive ionization mode, or a Q-TOF Premier mass spectrometer (Waters Corporation, Milford, MA, USA) in positive electrospray ionization mode.

Synthesis of new compounds

Compounds (±)-**17** and (±)-**22** were synthesized according to Ref. 17 of the article (M. Palkó, M. E. Haimer, Z. Kormányos, F. Fülöp, *Molecules* **2019**, *24*, 772.). Compound (±)-**27** was synthesized according to Ref. 19 of the article (P. Canonne, M. Akssira, A. Dahdouh, H. Kasmi, M. Boumzebra, *Tetrahedron* **1993**, *49*, 1985–1992.).

General procedure for *O*-alkylation

To a solution of *N*-Boc protected amino acid (3.95 mmol) in 50 mL THF, 1,8-diazabicyclo[5.4.0]undec-7-ene (1.5 equiv.) was added dropwise. The reaction mixture was stirred for 5 min at room temperature, and then allyl bromide or propargyl bromide (1.2 equiv.) was added. The solution was stirred vigorously for 2 h (monitored by TLC). After that, it was diluted with 25 mL EtOAc, then washed with 3×30 mL water. The organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel.

General procedure for amidation reaction

To an ice-cooled solution of *N*-Boc protected amino acid (3.70 mmol) in 50 mL CH_2Cl_2, dicyclohexyl carbodiimide (1.2 equiv.) and 4-dimethylaminopyridine (0.1 equiv.) were added under Ar atmosphere. The reaction mixture was stirred for 10 min, followed by addition of allylamine or propargylamine (2 equiv.). Stirring was then continued at room temperature overnight. Then, the organic layer was washed with 3×60 mL water, dried (Na_2SO_4) and concentrated under vacuum. The residue was purified by chromatography on silica gel.

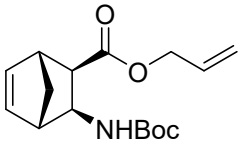
General procedure for the ring-rearrangement metathesis process

To a solution of 100 mg of substrate in 10 mL anhydrous CH_2Cl_2, ethylene and 3 mol% metathesis catalyst (G-1, G-2, HG-1 or HG-2) were added. The reaction mixture was stirred at room temperature for 4 h. Then, in order to decompose the catalyst, a mixture of water (12 mL), methanol (2 mL) and $NaHCO_3$ (0.1 g) was added, and the reaction mixture was stirred for an additional 2 hours. Afterwards, the phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel.

Attempts to trigger ring-closing metathesis of certain ROM products

To a solution of 100 mg of substrate in 10 mL anhydrous CH_2Cl_2, 3 mol% metathesis catalyst (G-1, G-2, HG-1 or HG-2) was added. The reaction mixture was stirred at room temperature or reflux. Even after a prolonged time, TLC only showed the spot of the substrate (and sometimes a spot on the baseline, which probably belongs to a substrate-derived oligomer/polymer). Because of this, the reaction was stopped and the mixture was discarded.

Characterization of the new synthetized compounds



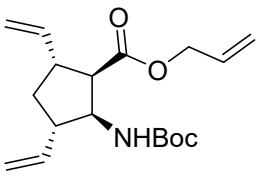
(1*R,2*R**,3*S**,4*S**)-allyl 3-((*tert*-butoxycarbonyl)amino)bicyclo[2.2.1]hept-5-ene-2-carboxylate,** (±)-**18**

Prepared from compound (±)-**17** with allyl bromide according to *General procedure for O-alkylation* (eluent of column chromatography: *n*-hexane/ethyl acetate 3:1). White solid, yield: 90%. Mp. 126-127 °C; R_f = 0.49 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.41-1.45 (s, 9H, CH_3), 1.55-1.59 (d, J = 9.40 Hz, 1H, H-7), 1.95-1.99 (d, J = 9.40 Hz, 1H, H-7), 2.63-2.67 (d, J = 8.30 Hz, 1H, H-2), 2.69-2.72 (s, 1H, H-4), 2.94-2.97 (s, 1H, H-1), 3.92-4.01 (s, 1H, H-3), 4.51-4.64 (m, 2H, O-CH_2-), 5.06-5.18 (brs, 1H, NH), 5.20-5.35 (m, 2H, =CH_2), 5.85-5.95 (m, 1H, -CH=), 6.15-6.23 (m, 2H, H-5 and H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.39, 44.44, 45.81, 46.56, 48.51, 52.78, 65.43, 79.36, 118.50, 132.03, 137.35, 138.32, 155.24, 173.99.

HRMS calcd. for $C_{16}H_{23}NNaO_4^+$ ([M+Na]$^+$): 316.1516. Found: 316.1519.



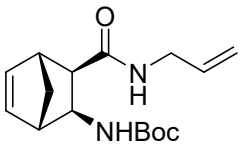
(1*R,2*S**,3*S**,5*R**)-allyl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)-**19**

Prepared from compound (±)-**18** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 8:1). White solid, yield: **73% (with G-1 catalyst)**, 65% (with G-2 catalyst), 70% (with HG-1 catalyst), 68% (with HG-2 catalyst). Mp. 61-62 °C; R_f = 0.54 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.32-1.37 (m, 1H, H-4), 1.39-1.44 (s, 9H, CH_3), 2.04-2.11 (m, 1H, H-4), 2.51-2.59 (m, 1H, H-3), 2.90-3.01 (m, 2H, H-1 and H-5), 4.01-4.10 (m, 1H, H-2), 4.53-4.65 (m, 2H, O-CH_2-), 4.79-4.91 (brs, 1H, NH), 4.95-5.12 (m, 4H, =CH_2), 5.19-5.33 (m, 2H, =CH_2), 5.70-5.82 (m, 2H, -CH=), 5.85-5.94 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.31, 36.52, 45.58, 50.12, 52.12, 57.18, 65.30, 79.33, 114.57, 115.80, 118.24, 132.08, 138.48, 140.08, 155.37, 173.53.

HRMS calcd. for $C_{18}H_{27}NNaO_4^+$ ([M+Na]$^+$): 344.1830. Found: 344.1832.



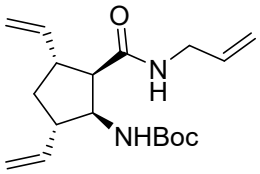
***tert*-Butyl ((1*S**,2*S**,3*R**,4*R**)-3-(allylcarbamoyl)bicyclo[2.2.1]hept-5-en-2-yl)carbamate,** (±)-**20**

Prepared from compound (±)-**17** with allylamine according to *General procedure for amidation reaction* (eluent of column chromatography: *n*-hexane/ethyl acetate 4:1). White solid, yield: 89%. Mp. 176-178 °C; R_f = 0.54 (*n*-hexane/EtOAc 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.40-1.45 (s, 9H, CH_3), 1.54-1.59 (d, J = 9.30 Hz, 1H, H-7), 2.08-2.14 (d, J = 9.30 Hz, 1H, H-7), 2.31-2.36 (d, J = 8.20 Hz, 1H, H-3), 2.67-2.71 (s, 1H, H-1), 2.92-2.97 (s, 1H, H-4), 3.74-3.82 (m, 1H, N-CH_2-), 3.86-3.96 (m, 2H, N-CH_2- and H-2), 5.09-5.21 (m, 2H, =CH_2), 5.23-5.32 (brs, 1H, NH), 5.75-5.86 (m, 2H, -CH= and NH), 6.61-6.23 (m, 2H, H-5 and H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.41, 42.11, 44.87, 45.83, 48.01, 48.20, 52.84, 79.34, 116.53, 134.08, 137.47, 138.82, 155.86, 172.96.

HRMS calcd. for $C_{16}H_{24}N_2NaO_3^+$ ([M+Na]$^+$): 315.1679. Found: 315.1684.



***tert*-Butyl ((1*S**,2*R**,3*R**,5*S**)-2-(allylcarbamoyl)-3,5-divinylcyclopentyl)carbamate,** (±)-**21**

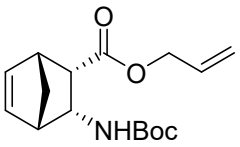
Prepared from compound (±)-**20** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 8:1). White solid, yield: 69% (with G-1 catalyst), 67% (with G-2 catalyst), **74% (with HG-1 catalyst)**, 65% (with HG-2 catalyst). Mp. 152-154 °C; R_f = 0.59 (*n*-hexane/EtOAc 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.28-1.36 (m, 1H, H-4), 1.37-1.43 (s, 9H, CH_3), 2.02-2.09 (m, 1H, H-4), 2.56-2.65 (m, 1H, H-3), 2.66-2.73 (m, 1H, H-5), 3.03-3.11 (m, 1H, H-2),

3.75-3.82 (m, 1H, N-CH_2-), 3.86-3.95 (m, 2H, N-CH_2- and H-1), 4.92-5.20 (m, 7H, =CH_2 and NH), 5.62-5.85 (m, 4H, -CH= and NH).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.33, 36.78, 42.06, 45.32, 49.94, 53.93, 57.62, 79.33, 114.41, 115.97, 116.41, 134.06, 138.57, 140.85, 156.11, 172.67.

HRMS calcd. for $C_{18}H_{28}N_2NaO_3^+$ ([M+Na]$^+$): 343.1992. Found: 343.1993.



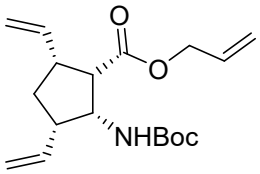
(1*R,2*S**,3*R**,4*S**)-allyl 3-((*tert*-butoxycarbonyl)amino)bicyclo[2.2.1]hept-5-ene-2-carboxylate,** (±)-**23**

Prepared from compound (±)-**22** with allyl bromide according to *General procedure for O-alkylation* (eluent of column chromatography: *n*-hexane/ethyl acetate 3:1). White solid, yield: 89%. Mp. 87-88 °C; R_f = 0.50 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.33-1.37 (d, J = 9.05 Hz, 1H, H-7), 1.38-1.44 (s, 9H, CH_3), 1.46-1.50 (d, J = 9.05 Hz, 1H, H-7), 3.04-3.12 (m, 2H, H-1 and H-4), 3.20-3.25 (m, 1H, H-2), 4.45-4.50 (m, 1H, O-CH_2-), 4.53-4.61 (m, 2H, H-3 and O-CH_2-), 4.88-4.99 (brs, 1H, NH), 5.19-5.33 (m, 2H, =CH_2), 5.83-5.92 (m, 1H, -CH=), 6.16-6.20 (m, 1H, H-5), 6.38-6.42 (m, 1H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.40, 46.59, 47.33, 47.62, 48.63, 53.80, 65.15, 79.12, 118.31, 132.12, 133.20, 138.20, 155.49, 172.51.

HRMS calcd. for $C_{16}H_{23}NNaO_4^+$ ([M+Na]$^+$): 316.1520. Found: 316.1523.



(1*S,2*R**,3*S**,5*R**)-allyl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)-**24**

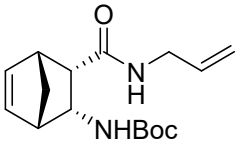
Prepared from compound (±)-**23** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 8:1). Colorless oil, yield:

69% (with G-1 catalyst), **79% (with G-2 catalyst)**, 71% (with HG-1 catalyst), 75% (with HG-2 catalyst). R_f = 0.56 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.38-1.42 (s, 9H, CH_3), 1.82-1.91 (m, 1H, H-4), 1.97-2.04 (m, 1H, H-4), 2.71-2.80 (m, 1H, H-5), 2.92-3.01 (m, 1H, H-3), 3.29 (t, J = 7.20 Hz, 1H, H-1), 4.39-4.46 (m, 1H, H-2), 4.53-4.57 (m, 2H, O-CH_2-), 4.91-4.98 (brs, 1H, NH), 5.01-5.12 (m, 4H, =CH_2), 5.20-5.33 (m, 2H, =CH_2), 5.74-5.94 (m, 3H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.34, 35.51, 44.66, 44.77, 52.78, 54.55, 64.97, 79.28, 115.94, 117.23, 118.39, 132.04, 137.21, 138.51, 155.53, 172.19.

HRMS calcd. for $C_{18}H_{27}NNaO_4^+$ ([M+Na]$^+$): 344.1836. Found: 344.1838.



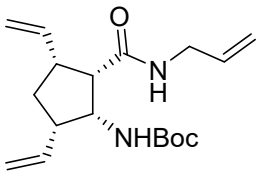
***tert*-Butyl ((1*S**,2*R**,3*S**,4*R**)-3-(allylcarbamoyl)bicyclo[2.2.1]hept-5-en-2-yl)carbamate,** (±)-**25**

Prepared from compound (±)-**22** with allylamine according to *General procedure for amidation reaction* (eluent of column chromatography: *n*-hexane/ethyl acetate 4:1). White solid, yield: 88%. Mp. 136-138 °C; R_f = 0.52 (*n*-hexane/EtOAc 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.32-1.35 (d, J = 8.60 Hz, 1H, H-7), 1.38-1.41 (s, 9H, CH_3), 1.45-1.48 (d, J = 8.60 Hz, 1H, H-7), 2.99-3.07 (m, 3H, H-1, H-3 and H-4), 3.61-3.68 (m, 1H, N-CH_2-), 3.89-3.97 (m, 1H, N-CH_2-), 4.52-4.58 (m, 1H, H-2), 4.77-4.87 (brs, 1H, NH), 5.08-5.18 (m, 2H, =CH_2), 5.73-5.83 (m, 2H, -CH= and NH), 6.07-6.11 (s, 1H, H-5), 6.59-6.63 (s, 1H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.38, 42.01, 46.43, 47.20, 47.65, 51.75, 54.15, 79.35, 116.42, 130.96, 134.20, 140.30, 156.23, 171.53.

HRMS calcd. for $C_{16}H_{24}N_2NaO_3^+$ ([M+Na]$^+$): 315.1679. Found: 315.1678.



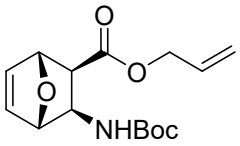
***tert*-Butyl ((1*R**,2*S**,3*R**,5*S**)-2-(allylcarbamoyl)-3,5-divinylcyclopentyl)carbamate,** (±)-**26**

Prepared from compound (±)-**25** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 8:1). White solid, yield: 72% (with G-1 catalyst), **85% (with G-2 catalyst)**, 73% (with HG-1 catalyst), 78% (with HG-2 catalyst). Mp. 118-120 °C; R_f = 0.57 (*n*-hexane/EtOAc 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.37-1.43 (s, 9H, CH_3), 1.93-2.07 (m, 2H, H-4), 2.64-2.74 (m, 1H, H-3), 2.89-2.99 (m, 2H, H-2 and H-5), 3.77-3.91 (m, 2H, N-CH_2-), 4.29-4.37 (m, 1H, H-1), 4.99-5.21 (m, 7H, =CH_2 and NH), 5.49-5.61 (brs, 1H, NH), 5.74-5.85 (m, 2H, -CH=), 5.94-6.04 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.35, 36.52, 41.67, 45.11, 45.58, 54.71, 54.89, 79.18, 116.18, 116.41, 117.07, 134.06, 138.17, 139.02, 155.96, 171.27.

HRMS calcd. for $C_{18}H_{28}N_2NaO_3^+$ ([M+Na]$^+$): 343.1992. Found: 343.1991.



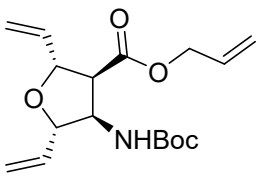
(1*R,2*S**,3*R**,4*S**)-allyl 3-((*tert*-butoxycarbonyl)amino)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylate,** (±)-**28**

Prepared from compound (±)-**27** with allyl bromide according to *General procedure for O-alkylation* (eluent of column chromatography: *n*-hexane/ethyl acetate 2:1). White solid, yield: 89%. Mp. 106-107 °C; R_f = 0.40 (*n*-hexane/EtOAc 2:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.40-1.45 (s, 9H, CH_3), 2.79-2.83 (d, J = 7.80 Hz, 1H, H-2), 4.22 (t, J = 8.80 Hz, 1H, H-3), 4.55-4.67 (m, 2H, O-CH_2-), 4.70-4.72 (s, 1H, H-1), 5.09-5.11 (s, 1H, H-4), 5.16-5.21 (brs, 1H, NH), 5.22-5.35 (m, 2H, =CH_2), 5.86-5.95 (m, 1H, -CH=), 6.40-6.45 (m, 2H, H-5 and H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.34, 47.14, 52.31, 65.72, 79.69, 80.09, 84.00, 118.75, 131.87, 135.34, 137.86, 155.38, 171.54.

HRMS calcd. for $C_{15}H_{21}NNaO_5^+$ ([M+Na]$^+$): 318.1310. Found: 318.1312.



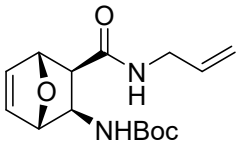
(2*R,3*S**,4*R**,5*S**)-allyl 4-((*tert*-butoxycarbonyl)amino)-2,5-divinyltetrahydrofuran-3-carboxylate,** (±)-**29**

Prepared from compound (±)-**28** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 6:1). White solid, yield: **77% (with G-1 catalyst)**, 71% (with G-2 catalyst), 72% (with HG-1 catalyst), 69% (with HG-2 catalyst). Mp. 45-47 °C; R_f = 0.50 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.40-1.44 (s, 9H, CH_3), 3.08 (t, J = 7.80 Hz, 1H, H-3), 4.21-4.31 (m, 2H, H-4 and H-5), 4.57-4.67 (m, 3H, H-2 and O-CH_2-), 5.07-5.16 (brs, 1H, NH), 5.18-5.41 (m, 6H, =CH_2), 5.84-5.94 (m, 3H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.25, 52.20, 57.26, 65.71, 79.86, 81.68, 84.71, 117.38, 117.63, 118.73, 131.65, 135.73, 136.49, 155.06, 170.69.

HRMS calcd. for $C_{17}H_{25}NNaO_5^+$ ([M+Na]$^+$): 346.1624. Found: 346.1625.



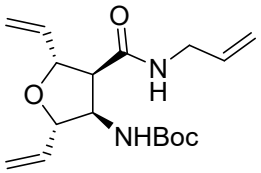
***tert*-Butyl ((1*S**,2*R**,3*S**,4*R**)-3-(allylcarbamoyl)-7-oxabicyclo[2.2.1]hept-5-en-2-yl)carbamate,** (±)-**30**

Prepared from compound (±)-**27** with allylamine according to *General procedure for amidation reaction* (eluent of column chromatography: *n*-hexane/ethyl acetate 2:1). White solid, yield: 87%. Mp. 138-140 °C; R_f = 0.39 (*n*-hexane/EtOAc 2:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.39-1.44 (s, 9H, CH_3), 2.58-2.62 (m, 1H, H-3), 3.75-3.84 (m, 1H, N-CH_2-), 3.94-4.02 (m, 1H, N-CH_2-), 4.08-4.16 (m, 1H, H-2), 4.71-4.75 (s, 1H, H-4), 5.07-5.22 (m, 4H, H-1 and NH and =CH_2), 5.77-5.87 (m, 1H, -CH=), 5.88-5.99 (brs, 1H, NH), 6.39-6.45 (s, 2H, H-5 and H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.35, 33.97, 42.14, 52.44, 79.87, 80.23, 83.69, 116.84, 134.02, 135.52, 137.66, 155.92, 170.50.

HRMS calcd. for $C_{15}H_{22}N_2NaO_4^+$ ([M+Na]$^+$): 317.1472. Found: 317.1476.



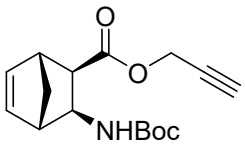
***tert*-Butyl ((2*S**,3*R**,4*S**,5*R**)-4-(allylcarbamoyl)-2,5-divinyltetrahydrofuran-3-yl)carbamate,** (±)-**31**

Prepared from compound (±)-**30** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 6:1). White solid, yield: **80% (with G-1 catalyst)**, 77% (with G-2 catalyst), 79% (with HG-1 catalyst), 72% (with HG-2 catalyst). Mp. 161-163 °C; R_f = 0.48 (*n*-hexane/ EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.39-1.44 (s, 9H, CH_3), 2.76-2.83 (t, J = 8.10 Hz, 1H, H-4), 3.80-3.95 (m, 2H, N-CH_2-), 4.09-4.16 (m, 1H, H-3), 4.20-4.25 (t, J = 6.90 Hz, 1H, H-5), 4.69-4.74 (t, J = 7.10 Hz, 1H, H-2), 5.11-5.42 (m, 7H, NH and =CH_2), 5.71-5.94 (m, 4H, NH and -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.29, 42.08, 54.02, 57.52, 79.87, 82.13, 84.51, 116.79, 117.35, 117.92, 133.65, 135.64, 136.85, 169.85, 176.95.

HRMS calcd. for $C_{17}H_{26}N_2NaO_4^+$ ([M+Na]$^+$): 345.1785. Found: 345.1786.



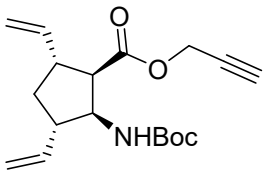
(1*R,2*R**,3*S**,4*S**)-prop-2-yn-1-yl 3-((*tert*-butoxycarbonyl)amino)bicyclo[2.2.1]hept-5-ene-2-carboxylate,** (±)-**32**

Prepared from compound (±)-**17** with propargyl bromide according to *General procedure for O-alkylation* (eluent of column chromatography: *n*-hexane/ethyl acetate 3:1). White solid, yield: 88%. Mp. 108-109 °C; R_f = 0.43 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.41-1.45 (s, 9H, CH_3), 1.57-1.61 (d, J = 9.40 Hz, 1H, H-7), 1.94-1.98 (d, J = 9.40 Hz, 1H, H-7), 2.43-2.46 (s, 1H, CH), 2.65-2.73 (m, 2H, H-2 and H-4), 2.96-2.99 (s, 1H, H-1), 3.93-4.03 (s, 1H, H-3), 4.55-4.61 (m, 1H, O-CH_2-), 4.71-4.77 (m, 1H, O-CH_2-), 4.99-5.14 (brs, 1H, NH), 6.15-6.23 (m, 2H, H-5 and H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.37, 44.42, 45.78, 46.45, 48.50, 52.11, 53.00, 74.95, 77.51, 79.41, 137.41, 138.20, 155.21, 173.41.

HRMS calcd. for $C_{16}H_{21}NNaO_4^+$ ([M+Na]$^+$): 314.1362. Found: 314.1364.



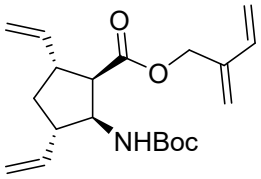
(1*R,2*S**,3*S**,5*R**)-prop-2-yn-1-yl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)-**33**

Prepared from compound (±)-**32** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 10:1). White solid, yield: 18% (with G-1 catalyst), **47% (with G-2 catalyst)**, 16% (with HG-1 catalyst), 38% (with HG-2 catalyst). Mp. 56-57 °C; R_f = 0.52 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.33-1.38 (m, 1H, H-4), 1.40-1.45 (s, 9H, CH_3), 2.05-2.12 (m, 1H, H-4), 2.44-2.47 (s, 1H, CH), 2.51-2.60 (m, 1H, H-3), 2.91-3.05 (m, 2H, H-1 and H-5), 4.02-4.10 (m, 1H, H-2), 4.60-4.76 (m, 2H, O-CH_2-), 4.79-4.89 (brs, 1H, NH), 4.97-5.14 (m, 4H, =CH_2), 5.69-5.81 (m, 2H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.31, 36.50, 45.43, 49.97, 51.84, 52.12, 57.27, 72.30, 74.95, 79.48, 114.83, 116.07, 138.32, 139.86, 155.41, 173.14.

HRMS calcd. for $C_{18}H_{25}NNaO_4^+$ ([M+Na]$^+$): 342.1677. Found: 342.1679.



(1*R,2*S**,3*S**,5*R**)-2-methylenebut-3-en-1-yl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)-**34**

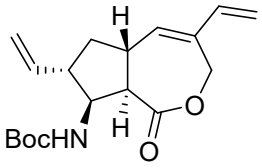
Prepared from compound (±)-**32** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 10:1). White solid, yield: 25% (with G-1 catalyst), 0% (with G-2 catalyst), **31% (with HG-1 catalyst)**, 0% (with HG-2 catalyst). Mp. 46-47 °C; R_f = 0.57 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.32-1.38 (m, 1H, H-4), 1.40-1.44 (s, 9H, CH_3), 2.03-2.11 (m, 1H, H-4), 2.52-2.61 (m, 1H, H-3), 2.89-3.03 (m, 2H, H-1 and H-5), 4.02-4.10 (m, 1H,

H-2), 4.67-4.73 (m, 1H, O-CH_2-), 4.83-4.93 (m, 2H, NH and O-CH_2-), 4.96-5.15 (m, 5H, =CH_2), 5.20-5.29 (m, 3H, =CH_2), 5.71-5.82 (m, 2H, -CH=), 6.33-6.40 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.29, 36.49, 45.68, 50.20, 52.15, 57.16, 63.75, 79.31, 114.61, 114.66, 115.79, 118.15, 136.03, 138.51, 140.05, 140.40, 155.38, 173.50.

HRMS calcd. for $C_{20}H_{29}NNaO_4^+$ ([M+Na]$^+$): 370.1978. Found: 370.1989.



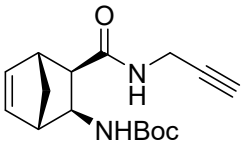
***tert*-Butyl ((5a*R**,7*S**,8*S**,8a*R**)-1-oxo-4,7-divinyl-3,5a,6,7,8,8a-hexahydro-1H-cyclopenta[*c*]oxepin-8-yl)carbamate,** (±)-**35**

Prepared from compound (±)-**32** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 10:1). White solid, yield: **12% (with G-1 catalyst)**, 0% (with G-2 catalyst), 10% (with HG-1 catalyst), 0% (with HG-2 catalyst). Mp. 73-74 °C; R_f = 0.45 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.39-1.44 (s, 9H, CH_3), 1.55-1.60 (d, J = 9.40 Hz, 1H, H-6), 1.95-2.00 (d, J = 9.40 Hz, 1H, H-6), 2.65-2.73 (m, 2H, H-7 and H-5a), 2.94-2.97 (s, 1H, H-8a), 3.93-4.01 (m, 1H, H-8), 4.67-4.72 (d, J = 13.09 Hz, 1H, H-3), 4.82-4.87 (d, J = 13.09 Hz, 1H, H-3), 5.11-5.31 (m, 5H, =CH_2 and NH), 6.15-6.23 (m, 2H, -CH=), 6.33-6.41 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.38, 29.66, 44.39, 45.95, 46.51, 48.60, 63.81, 79.26, 114.67, 118.20, 136.05, 137.40, 138.25, 140.43, 155.92, 173.10.

HRMS calcd. for $C_{18}H_{25}NNaO_4^+$ ([M+Na]$^+$): 342.1676. Found: 342.1684.



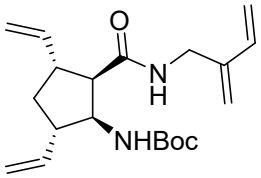
***tert*-Butyl ((1*S**,2*S**,3*R**,4*R**)-3-(prop-2-yn-1-ylcarbamoyl)bicyclo[2.2.1]hept-5-en-2-yl)carbamate,** (±)-**36**

Prepared from compound (±)-**17** with propargylamine according to *General procedure for amidation reaction* (eluent of column chromatography: *n*-hexane/ethyl acetate 4:1). White solid, yield: 87%. Mp. 161-163 °C; R_f = 0.51 (*n*-hexane/EtOAc 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.40-1.45 (s, 9H, CH_3), 1.55-1.60 (d, J = 8.90 Hz, 1H, H-7), 2.04-2.09 (d, J = 8.90 Hz, 1H, H-7), 2.19-2.23 (s, 1H, CH), 2.33-2.38 (d, J = 8.06 Hz, 1H, H-3), 2.67-2.70 (s, 1H, H-1), 2.95-2.99 (s, 1H, H-4), 3.83-3.93 (m, 2H, N-CH_2- and H-2), 4.09-4.17 (m, 1H, N-CH_2-), 5.10-5.19 (brs, 1H, NH), 5.88-5.97 (brs, 1H, NH), 6.15-6.22 (m, 2H, H-5 and H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.40, 29.40, 44.93, 45.62, 47.95, 48.10, 53.02, 71.71, 79.29, 79.49, 137.45, 138.78, 155.92, 172.83.

HRMS calcd. for $C_{16}H_{22}N_2NaO_3^+$ ([M+Na]$^+$): 313.1523. Found: 313.1526.



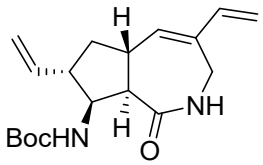
***tert*-Butyl ((1*S**,2*R**,3*R**,5*S**)-2-((2-methylenebut-3-en-1-yl)carbamoyl)-3,5-divinylcyclopentyl)carbamate,** (±)-**37**

Prepared from compound (±)-**36** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 10:1). Pale yellow solid, yield: 25% (with G-1 catalyst), 23% (with G-2 catalyst), **31% (with HG-1 catalyst)**, 19% (with HG-2 catalyst). Mp. 117-119 °C; R_f = 0.62 (*n*-hexane/EtOAc 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.29-1.36 (m, 1H, H-4), 1.38-1.43 (s, 9H, CH_3), 2.02-2.09 (m, 1H, H-4), 2.59-2.71 (m, 2H, H-3 and H-5), 3.00-3.09 (m, 1H, H-2), 3.87-3.97 (m, 2H, N-CH_2- and H-1), 4.14-4.21 (m, 1H, N-CH_2-), 4.93-5.15 (m, 8H, NH and =CH_2), 5.23-5.29 (m, 1H, =CH_2), 5.64-5.80 (m, 3H, -CH= and NH), 6.31-6.40 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.33, 36.77, 40.54, 45.69, 50.20, 53.91, 57.51, 79.31, 114.60, 114.66, 116.04, 116.96, 136.47, 138.58, 140.81, 142.15, 156.07, 172.79.

HRMS calcd. for $C_{20}H_{30}N_2NaO_3^+$ ([M+Na]$^+$): 369.2149. Found: 369.2154.



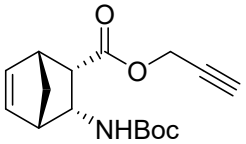
***tert*-Butyl ((5a*R**,7*S**,8*S**,8a*R**)-1-oxo-4,7-divinyl-1,2,3,5a,6,7,8,8a-octahydrocyclopenta[*c*]azepin-8-yl)carbamate,** (±)-**38**

Prepared from compound (±)-**36** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 10:1). White solid, yield: **45% (with G-1 catalyst)**, 18% (with G-2 catalyst), 41% (with HG-1 catalyst), 14% (with HG-2 catalyst). Mp. 135-137 °C; R_f = 0.55 (*n*-hexane/EtOAc 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.39-1.45 (s, 9H, CH_3), 1.55-1.62 (d, J = 9.20 Hz, 1H, H-6), 2.11-2.16 (d, J = 9.20 Hz, 1H, H-6), 2.30-2.34 (d, J = 8.50 Hz, 1H, H-7), 2.68-2.71 (s, 1H, H-5a), 2.91-2.95 (s, 1H, H-8a), 3.86-3.97 (m, 2H, H-3 and H-8), 4.14-4.21 (m, 1H, H-3), 5.10-5.16 (m, 3H, =CH_2), 5.24-5.30 (m, 1H, =CH_2), 5.32-5.40 (brs, 1H, NH), 5.66-5.73 (brs, 1H, NH), 6.15-6.23 (m, 2H, -CH=), 6.32-6.40 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.42, 40.58, 44.78, 46.02, 47.97, 48.33, 52.84, 79.32, 114.68, 117.14, 136.52, 137.58, 138.71, 142.21, 156.09, 172.96.

HRMS calcd. for $C_{18}H_{26}N_2NaO_3^+$ ([M+Na]$^+$): 341.1836. Found: 341.1838.



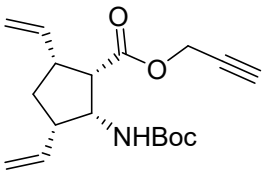
(1*R,2*S**,3*R**,4*S**)-prop-2-yn-1-yl 3-((*tert*-butoxycarbonyl)amino)bicyclo[2.2.1]hept-5-ene-2-carboxylate,** (±)-**39**

Prepared from compound (±)-**22** with propargyl bromide according to *General procedure for O-alkylation* (eluent of column chromatography: *n*-hexane/ethyl acetate 3:1). White solid, yield: 88%. Mp. 90-91 °C; R_f = 0.42 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.34-1.38 (d, J = 9.06 Hz, 1H, H-7), 1.39-1.43 (s, 9H, CH_3), 1.47-1.51 (d, J = 9.06 Hz, 1H, H-7), 2.43-2.45 (s, 1H, CH), 3.05-3.14 (m, 2H, H-1 and H-4), 3.22-3.26 (m, 1H, H-2), 4.50-4.55 (m, 1H, O-CH_2-), 4.56-4.63 (m, 1H, H-3), 4.65-4.70 (m, 1H, O-CH_2-), 4.85-4.92 (brs, 1H, NH), 6.17-6.20 (m, 1H, H-5), 6.39-6.42 (m, 1H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.38, 46.57, 47.33, 47.59, 48.42, 51.87, 53.90, 74.85, 77.57, 79.22, 133.36, 138.13, 155.49, 172.02.

HRMS calcd. for $C_{16}H_{21}NNaO_4^+$ ([M+Na]$^+$): 314.1360. Found: 314.1363.



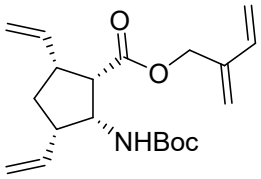
(1*S,2*R**,3*S**,5*R**)-prop-2-yn-1-yl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)-**40**

Prepared from compound (±)-**39** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 10:1). Colorless oil, yield: 30% (with G-1 catalyst), 26% (with G-2 catalyst), **35% (with HG-1 catalyst)**, 19% (with HG-2 catalyst). R_f = 0.51 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.37-1.45 (s, 9H, CH_3), 1.83-1.93 (m, 1H, H-4), 1.98-2.05 (m, 1H, H-4), 2.42-2.46 (s, 1H, CH), 2.72-2.81 (m, 1H, H-5), 2.91-3.01 (m, 1H, H-3), 3.31 (t, J = 7.25 Hz, 1H, H-1), 4.38-4.47 (m, 1H, H-2), 4.59-4.68 (m, 2H, O-CH_2-), 4.85-4.95 (brs, 1H, NH), 5.01-5.13 (m, 4H, =CH_2), 5.77-5.94 (m, 2H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.31, 35.55, 44.61, 44.79, 51.57, 52.57, 54.70, 74.84, 77.51, 79.31, 116.14, 117.32, 136.92, 138.32, 155.45, 171.66.

HRMS calcd. for $C_{18}H_{25}NNaO_4^+$ ([M+Na]$^+$): 342.1675. Found: 342.1676.



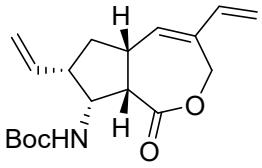
(1*S,2*R**,3*S**,5*R**)-2-methylenebut-3-en-1-yl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)-**41**

Prepared from compound (±)-**39** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 10:1). Pale yellow oil, yield: **22% (with G-1 catalyst)**, 0% (with G-2 catalyst), 18% (with HG-1 catalyst), 0% (with HG-2 catalyst). R_f = 0.56 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.37-1.44 (s, 9H, CH_3), 1.83-1.92 (m, 1H, H-4), 1.96-2.04 (m, 1H, H-4), 2.72-2.80 (m, 1H, H-5), 2.91-3.00 (m, 1H, H-3), 3.28-3.34 (m, 1H, H-1), 4.39-4.47 (m, 1H, H-2), 4.69-4.78 (m, 2H, O-CH_2-), 4.90-4.97 (brs, 1H, NH), 5.00-5.28 (m, 8H, =CH_2), 5.75-5.93 (m, 2H, -CH=), 6.32-6.40 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.33, 35.49, 44.66, 44.80, 52.97, 54.55, 63.38, 79.28, 114.76, 116.02, 117.22, 118.46, 136.01, 137.20, 138.50, 140.28, 155.52, 172.22.

HRMS calcd. for $C_{20}H_{29}NNaO_4^+$ ([M+Na]$^+$): 370.1969. Found: 370.1984.



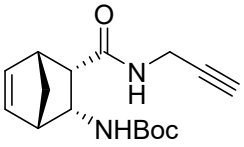
***tert*-Butyl ((5a*R**,7*S**,8*R**,8a*S**)-1-oxo-4,7-divinyl-3,5a,6,7,8,8a-hexahydro-1H-cyclopenta[*c*]oxepin-8-yl)carbamate,** (±)-**42**

Prepared from compound (±)-**39** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 10:1). White solid, yield: 8% (with G-1 catalyst), 0% (with G-2 catalyst), **10% (with HG-1 catalyst)**, 0% (with HG-2 catalyst). Mp. 83-85 °C; R_f = 0.46 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.33-1.37 (d, J = 8.80 Hz, 1H, H-6), 1.41-1.44 (s, 9H, CH_3), 1.47-1.51 (d, J = 8.80 Hz, 1H, H-6), 2.57-2.64 (m, 1H, H-5a), 3.01-3.12 (m, 2H, H-7 and H-8a), 4.05-4.11 (m, 1H, H-8), 4.41-4.46 (m, 1H, H-3), 4.58-4.63 (m, 1H, H-3), 5.09-5.19 (m, 3H, =CH_2), 5.21-5.25 (m, 1H, =CH_2), 5.37-5.55 (brs, 1H, NH), 6.12-6.21 (m, 2H, H-5 and -CH=), 6.45-6.55 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.22, 29.41, 43.21, 43.82, 45.58, 47.62, 64.93, 79.33, 113.55, 116.98, 134.36, 136.92, 138.55, 141.31, 154.12, 172.28.

HRMS calcd. for $C_{18}H_{25}NNaO_4^+$ ([M+Na]$^+$): 342.1676. Found: 342.1678.



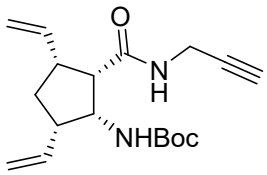
***tert*-Butyl ((1*S**,2*R**,3*S**,4*R**)-3-(prop-2-yn-1-ylcarbamoyl)bicyclo[2.2.1]hept-5-en-2-yl)carbamate,** (±)-**43**

Prepared from compound (±)-**22** with propargylamine according to *General procedure for amidation reaction* (eluent of column chromatography: *n*-hexane/ethyl acetate 4:1). White solid, yield: 87%. Mp. 145-147 °C; R_f = 0.49 (*n*-hexane/EtOAc 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.32-1.35 (d, J = 8.75 Hz, 1H, H-7), 1.39-1.42 (s, 9H, CH_3), 1.46-1.49 (d, J = 8.75 Hz, 1H, H-7), 2.16-2.18 (s, 1H, CH), 2.99-3.08 (m, 3H, H-1, H-3 and H-4), 3.74-3.81 (m, 1H, N-CH_2-), 4.06-4.12 (m, 1H, N-CH_2-), 4.51-4.58 (m, 1H, H-2), 4.68-4.79 (brs, 1H, NH), 5.85-5.96 (brs, 1H, NH), 6.07-6.11 (s, 1H, H-5), 6.58-6.62 (s, 1H, H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.36, 29.20, 46.33, 47.15, 47.62, 51.64, 54.27, 71.48, 79.44, 79.49, 131.00, 140.34, 154.66, 171.39.

HRMS calcd. for $C_{16}H_{22}N_2NaO_3^+$ ([M+Na]$^+$): 313.1523. Found: 313.1521.



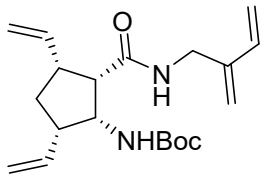
***tert*-Butyl ((1*R**,2*S**,3*R**,5*S**)-2-(prop-2-yn-1-ylcarbamoyl)-3,5-divinylcyclopentyl)carbamate,** (±)-**44**

Prepared from compound (±)-**43** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 10:1). Pale yellow solid, yield: 22% (with G-1 catalyst), **34% (with G-2 catalyst)**, 26% (with HG-1 catalyst), 31% (with HG-2 catalyst). Mp. 124-126 °C; R_f = 0.55 (*n*-hexane/EtOAc 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.38-1.43 (s, 9H, CH_3), 1.95-2.02 (m, 2H, H-4), 2.18-2.23 (s, 1H, CH), 2.65-2.74 (m, 1H, H-3),, 2.92-2.99 (m, 2H, H-2 and H-5), 3.91-4.07 (q, J = 17.40 Hz, 2H, N-CH_2-), 4.28-4.36 (m, 1H, H-1), 5.02-5.15 (m, 5H, =CH_2 and NH), 5.70-5.83 (m, 2H, -CH= and NH), 5.92-6.01 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.35, 28.94, 36.46, 44.98, 45.58, 54.25, 54.93, 71.63, 79.28, 80.26, 116.39, 117.21, 137.86, 138.90, 155.96, 171.31.

HRMS calcd. for $C_{18}H_{26}N_2NaO_3^+$ ([M+Na]$^+$): 341.1836. Found: 341.1841.



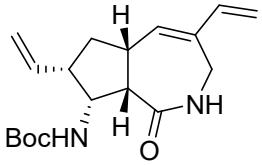
***tert*-Butyl ((1*R**,2*S**,3*R**,5*S**)-2-((2-methylenebut-3-en-1-yl)carbamoyl)-3,5-divinylcyclopentyl)carbamate,** (±)-**45**

Prepared from compound (±)-**43** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 10:1). Pale yellow solid, yield: **19% (with G-1 catalyst)**, 16% (with G-2 catalyst), 15% (with HG-1 catalyst), 13% (with HG-2 catalyst). Mp. 104-106 °C; R_f = 0.60 (*n*-hexane/EtOAc 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.37-1.42 (s, 9H, CH_3), 1.94-2.06 (m, 2H, H-4), 2.64-2.73 (m, 1H, H-3), 2.91-3.00 (m, 2H, H-2 and H-5), 3.98-4.08 (m, 2H, N-CH_2-), 4.31-4.38 (m, 1H, H-1), 4.99-5.16 (m, 8H, NH and =CH_2), 5.23-5.30 (m, 1H, =CH_2), 5.60-5.70 (brs, 1H, NH), 5.75-5.83 (m, 1H, -CH=), 5.95-6.04 (m, 1H, -CH=), 6.31-6.40 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.35, 36.51, 40.20, 45.13, 45.63, 54.77, 54.87, 79.15, 114.68, 116.21, 116.99, 117.03, 136.47, 138.18, 139.01, 142.15, 155.91, 171.29.

HRMS calcd. for $C_{20}H_{30}N_2NaO_3^+$ ([M+Na]$^+$): 369.2149. Found: 369.2150.



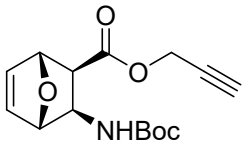
***tert*-Butyl ((5a*R**,7*S**,8*R**,8a*S**)-1-oxo-4,7-divinyl-1,2,3,5a,6,7,8,8a-octahydrocyclopenta[*c*]azepin-8-yl)carbamate,** (±)-**46**

Prepared from compound (±)-**43** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 10:1). White solid, yield: **15% (with G-1 catalyst)**, 11% (with G-2 catalyst), 12% (with HG-1 catalyst); 9% with HG-2 catalyst. Mp. 99-101 °C; R_f = 0.51 (*n*-hexane/EtOAc 4:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.31-1.35 (d, J = 9.10 Hz, 1H, H-6), 1.38-1.41 (s, 9H, CH_3), 1.44-1.48 (d, J = 9.10 Hz, 1H, H-6), 2.99-3.07 (m, 3H, H-7, H-5a and H-8a), 3.72-3.80 (m, 1H, H-3), 4.17-4.24 (m, 1H, H-3), 4.49-4.57 (m, 1H, H-8), 4.88-4.99 (brs, 1H, NH), 5.07-5.14 (m, 3H, =CH_2), 5.21-5.27 (m, 1H, =CH_2), 5.74-5.86 (brs, 1H, NH), 6.08-6.14 (s, 1H, -CH=), 6.30-6.39 (m, 1H, H-5), 6.53-6.60 (s, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.38, 40.38, 46.62, 47.26, 47.63, 51.38, 54.16, 79.31, 114.51, 116.93, 131.32, 136.59, 139.86, 142.31, 156.18, 171.58.

HRMS calcd. for $C_{18}H_{26}N_2NaO_3^+$ ([M+Na]$^+$): 341.1836. Found: 341.1839.



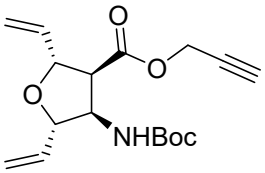
(1*R,2*S**,3*R**,4*S**)-prop-2-yn-1-yl 3-((*tert*-butoxycarbonyl)amino)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylate,** (±)-**47**

Prepared from compound (±)-**27** with propargyl bromide according to *General procedure for O-alkylation* (eluent of column chromatography: *n*-hexane/ethyl acetate 2:1). White solid, yield: 86%. Mp. 114-115 °C; R_f = 0.35 (*n*-hexane/EtOAc 2:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.41-1.45 (s, 9H, CH_3), 2.45-2.47 (s, 1H, CH), 2.82-2.86 (d, J = 7.80 Hz, 1H, H-2), 4.24 (t, J = 8.80 Hz, 1H, H-3), 4.59-4.64 (m, 1H, O-CH_2-), 4.71-4.73 (s, 1H, H-1), 4.76-4.81 (m, 1H, O-CH_2-), 5.11-5.13 (s, 1H, H-4), 5.14-5.21 (brs, 1H, NH), 6.42-6.45 (m, 2H, H-5 and H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.33, 47.05, 52.41, 52.51, 75.19, 77.30, 79.79, 80.02, 84.02, 135.46, 137.74, 155.39, 171.07.

HRMS calcd. for $C_{15}H_{19}NNaO_5^+$ ([M+Na]$^+$): 316.1153. Found: 316.1155.



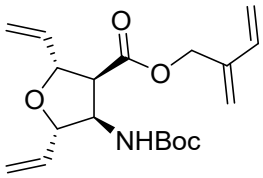
(2*R,3*S**,4*R**,5*S**)-prop-2-yn-1-yl 4-((*tert*-butoxycarbonyl)amino)-2,5-divinyltetrahydrofuran-3-carboxylate,** (±)-**48**

Prepared from compound (±)-**47** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 8:1). White solid, yield: **21% (with G-1 catalyst)**, 17% (with G-2 catalyst), 19% (with HG-1 catalyst), 15% (with HG-2 catalyst). Mp. 81-82 °C; R_f = 0.48 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.40-1.45 (s, 9H, CH_3), 2.46-2.49 (s, 1H, CH), 3.10 (t, J = 7.60 Hz, 1H, H-3), 4.20-4.32 (m, 2H, H-4 and H-5), 4.62-4.78 (m, 3H, H-2 and O-CH_2-), 4.95-5.12 (brs, 1H, NH), 5.18-5.27 (m, 2H, =CH_2), 5.33-5.42 (m, 2H, =CH_2), 5.83-5.93 (m, 2H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.26, 52.03, 52.50, 57.31, 75.30, 77.09, 80.01, 81.55, 84.59, 117.55, 117.88, 135.57, 136.32, 155.04, 170.30.

HRMS calcd. for $C_{17}H_{23}NNaO_5^+$ ([M+Na]$^+$): 344.1465. Found: 344.1468.



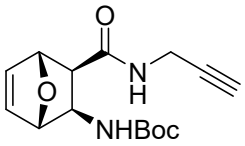
(2*R,3*S**,4*R**,5*S**)-2-methylenebut-3-en-1-yl 4-((*tert*-butoxycarbonyl)amino)-2,5-divinyltetrahydrofuran-3-carboxylate,** (±)-**49**

Prepared from compound (±)-**47** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 8:1). White solid, yield: 35% (with G-1 catalyst), 38% (with G-2 catalyst), 32% (with HG-1 catalyst), **40% (with HG-2 catalyst)**. Mp 103-104 °C; R_f = 0.52 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.40-1.44 (s, 9H, CH_3), 3.09 (t, J = 7.50 Hz, 1H, H-3), 4.21-4.30 (m, 2H, H-4 and H-5), 4.64 (t, J = 7.06 Hz, 1H, H-2), 4.72-4.89 (m, 2H, O-CH_2-), 5.10-5.41 (m, 9H, NH and =CH_2), 5.83-5.93 (m, 2H, -CH=), 6.32-6.40 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.26, 52.20, 57.23, 64.25, 79.89, 81.76, 84.82, 114.85, 117.44, 117.66, 118.63, 135.73, 135.89, 136.49, 140.12, 155.07, 170.71.

HRMS calcd. for $C_{19}H_{27}NNaO_5^+$ ([M+Na]$^+$): 372.1781. Found: 372.1781.



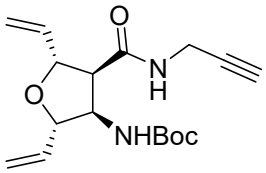
***tert*-Butyl ((1*S**,2*R**,3*S**,4*R**)-3-(prop-2-yn-1-ylcarbamoyl)-7-oxabicyclo[2.2.1]hept-5-en-2-yl)carbamate,** (±)-**50**

Prepared from compound (±)-**27** with propargylamine according to *General procedure for amidation reaction* (eluent of column chromatography: *n*-hexane/ethyl acetate 2:1). White solid, yield: 85%. Mp. 164-166 °C; R_f = 0.37 (*n*-hexane/EtOAc 2:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.41-1.45 (s, 9H, CH_3), 2.19-2.23 (s, 1H, CH), 2.62-2.66 (m, 1H, H-3), 3.84-3.93 (m, 1H, N-CH_2-), 4.10-4.14 (m, 1H, H-2), 4.17-4.24 (m, 1H, N-CH_2-), 4.74-4.77 (s, 1H, H-4), 5.09-5.19 (m, 2H, NH and H-1), 6.13-6.26 (brs, 1H, NH), 6.39-6.47 (m, 2H, H-5 and H-6).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.33, 33.97, 47.88, 52.74, 71.79, 79.31, 79.96, 80.12, 83.69, 135.62, 137.45, 155.97, 170.46.

HRMS calcd. for $C_{15}H_{20}N_2NaO_4^+$ ([M+Na]$^+$): 315.1315. Found: 315.1314.



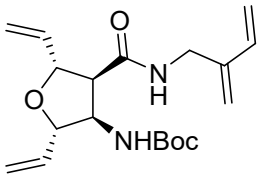
***tert*-Butyl ((2*S**,3*R**,4*S**,5*R**)-4-(prop-2-yn-1-ylcarbamoyl)-2,5-divinyltetrahydrofuran-3-yl)carbamate,** (±)-**51**

Prepared from compound (±)-**50** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 8:1). White solid, yield: 18% (with G-1 catalyst), **22% (with G-2 catalyst)**, 16% (with HG-1 catalyst), 20% (with HG-2 catalyst). Mp. 178-180 °C; R_f = 0.45 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.39-1.45 (s, 9H, CH_3), 2.20-2.25 (s, 1H, CH), 2.80-2.86 (t, J = 7.80 Hz, 1H, H-4), 3.94-4.15 (m, 3H, N-CH_2- and H-3), 4.18-4.23 (t, J = 6.95 Hz, 1H, H-5), 4.69-4.75 (t, J = 6.80 Hz, 1H, H-2), 5.17-5.43 (m, 5H, NH and =CH_2), 5.83-5.98 (m, 3H, NH and -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.29, 29.47, 53.67, 57.49, 72.07, 78.85, 80.06, 81.92, 84.28, 117.58, 118.37, 135.44, 136.67, 169.84, 177.19.

HRMS calcd. for $C_{17}H_{24}N_2NaO_4^+$ ([M+Na]$^+$): 343.1628. Found: 343.1634.



***tert*-Butyl ((2*S**,3*R**,4*S**,5*R**)-4-((2-methylenebut-3-en-1-yl)carbamoyl)-2,5-divinyltetrahydrofuran-3-yl)carbamate,** (±)-**52**

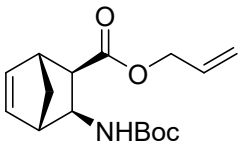
Prepared from compound (±)-**50** according to *General procedure for the ring-rearrangement metathesis process* (eluent of column chromatography: *n*-hexane/EtOAc 8:1). White solid, yield: **45% (with G-1 catalyst)**, 37% (with G-2 catalyst), 41% (with HG-1 catalyst), 39% (with HG-2 catalyst). Mp 118-120 °C; R_f = 0.53 (*n*-hexane/EtOAc 3:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.39-1.44 (s, 9H, CH_3), 2.74-2.80 (t, J = 7.80 Hz, 1H, H-4), 3.96-4.02 (m, 1H, N-CH_2-), 4.10-4.19 (m, 2H, N-CH_2- and H-3), 4.22-4.27 (t, J = 6.60 Hz, 1H, H-5), 4.67-4.72 (t, J = 7.14 Hz, 1H, H-2), 5.10-5.43 (m, 9H, NH and =CH_2), 5.66-5.76 (brs, 1H, NH), 5.83-5.94 (m, 2H, -CH=), 6.31-6.39 (m, 1H, -CH=).

^{13}C NMR (126 MHz, $CDCl_3$): δ (ppm) = 28.31, 40.64, 53.92, 57.40, 79.88, 82.37, 84.77, 114.84, 117.38, 117.65, 118.02, 135.61, 136.32, 136.74, 141.88, 169.87, 175.29.

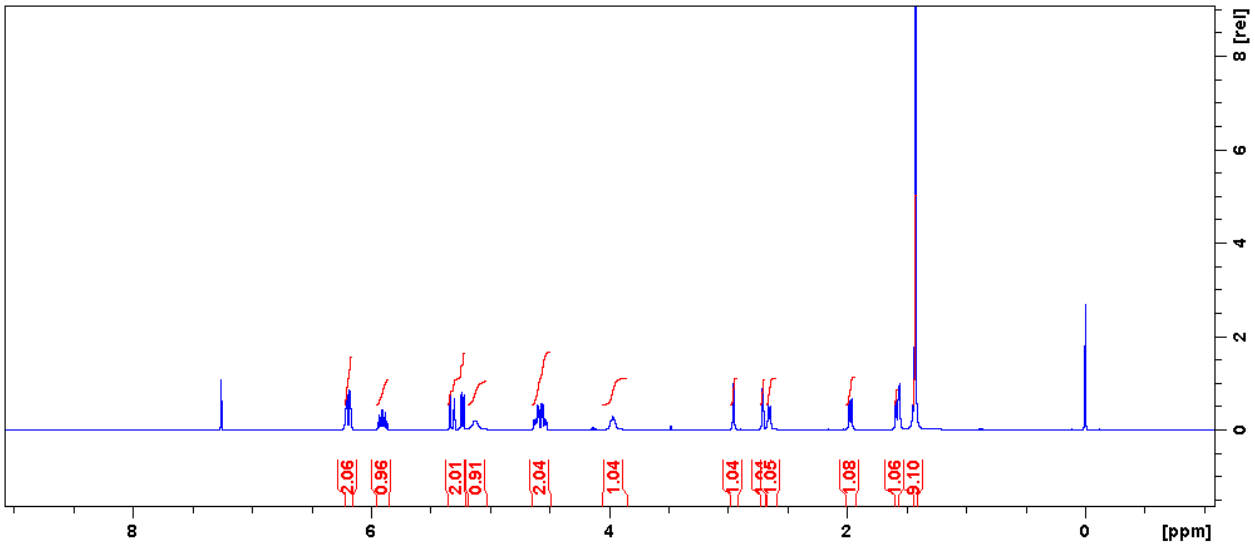
HRMS calcd. for $C_{19}H_{28}N_2NaO_4^+$ ($[M+Na]^+$): 371.1941. Found: 371.1944.

NMR spectra of the new synthesized compounds

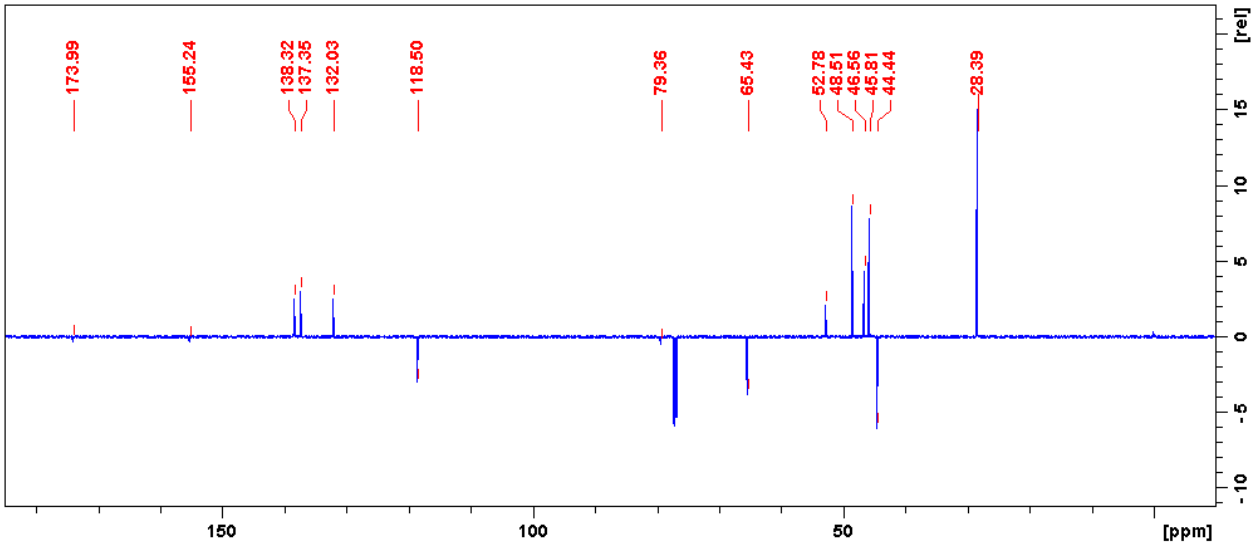


(1*R,2*R**,3*S**,4*S**)-allyl 3-((*tert*-butoxycarbonyl)amino)bicyclo[2.2.1]hept-5-ene-2-carboxylate,** (±)**-18**

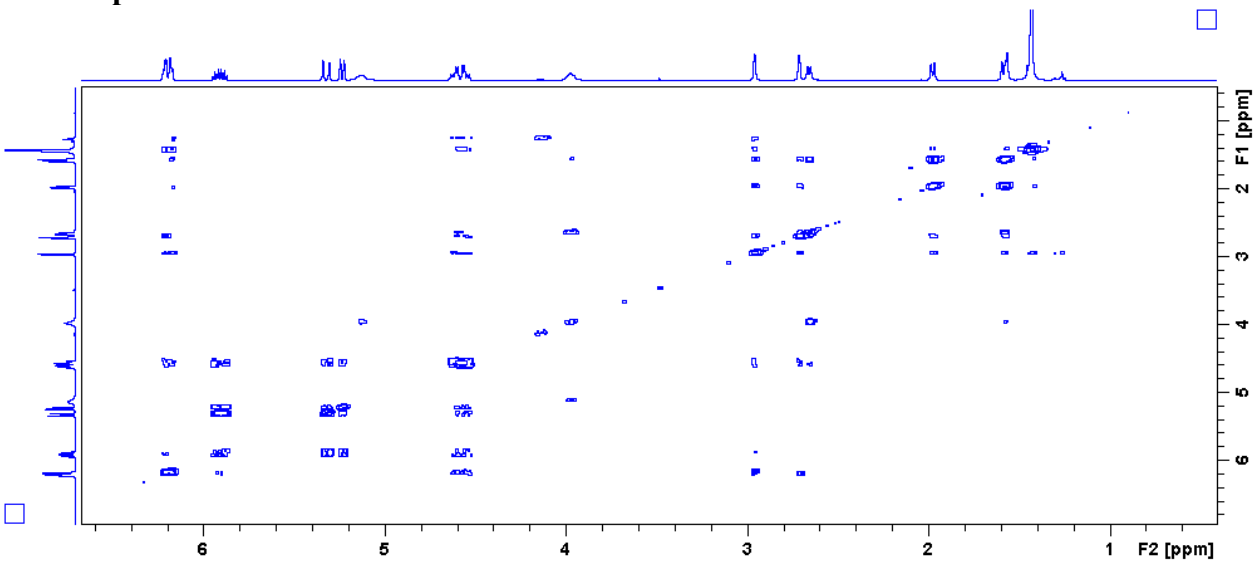
^{1}H NMR spectrum:



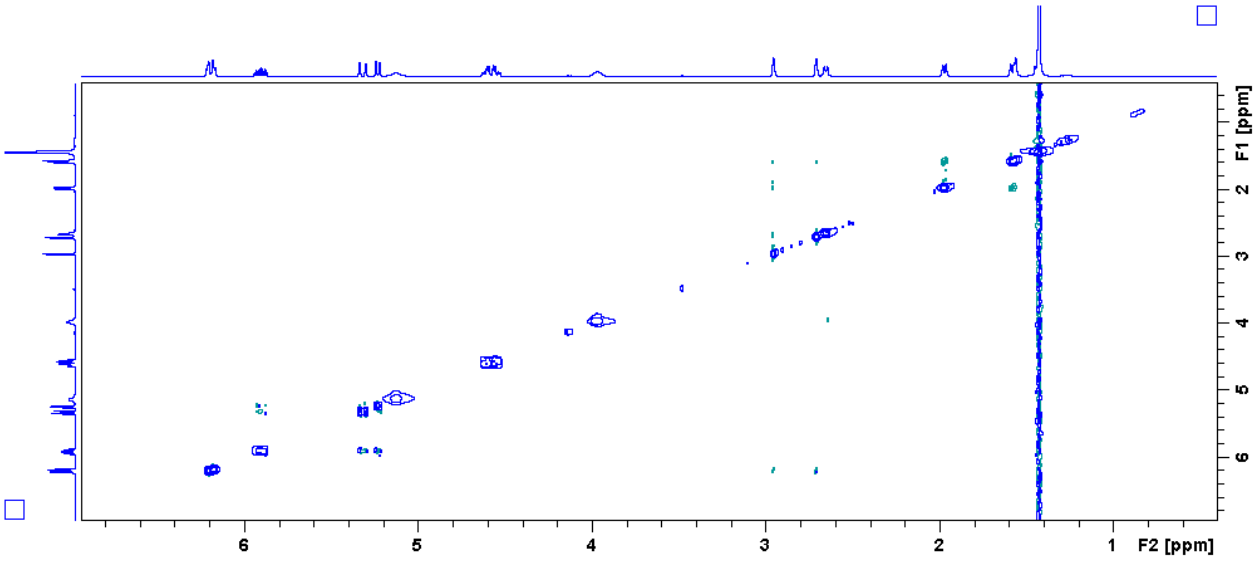
^{13}C (jmod) NMR spectrum:

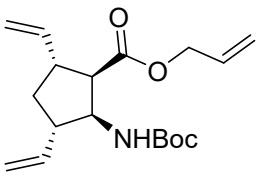


COSY spectrum:



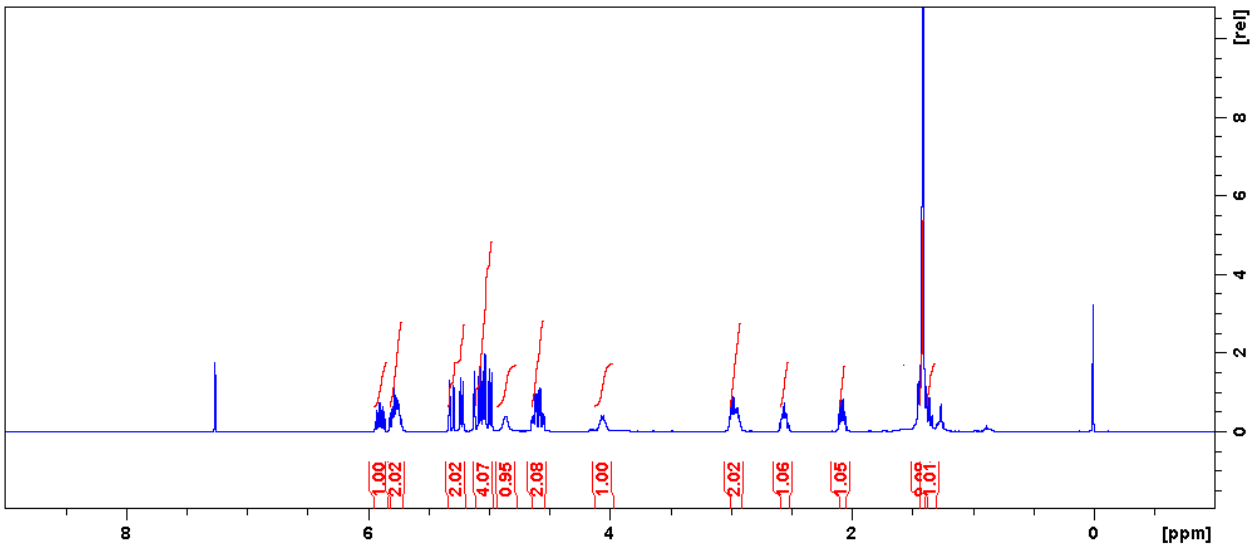
NOESY spectrum:



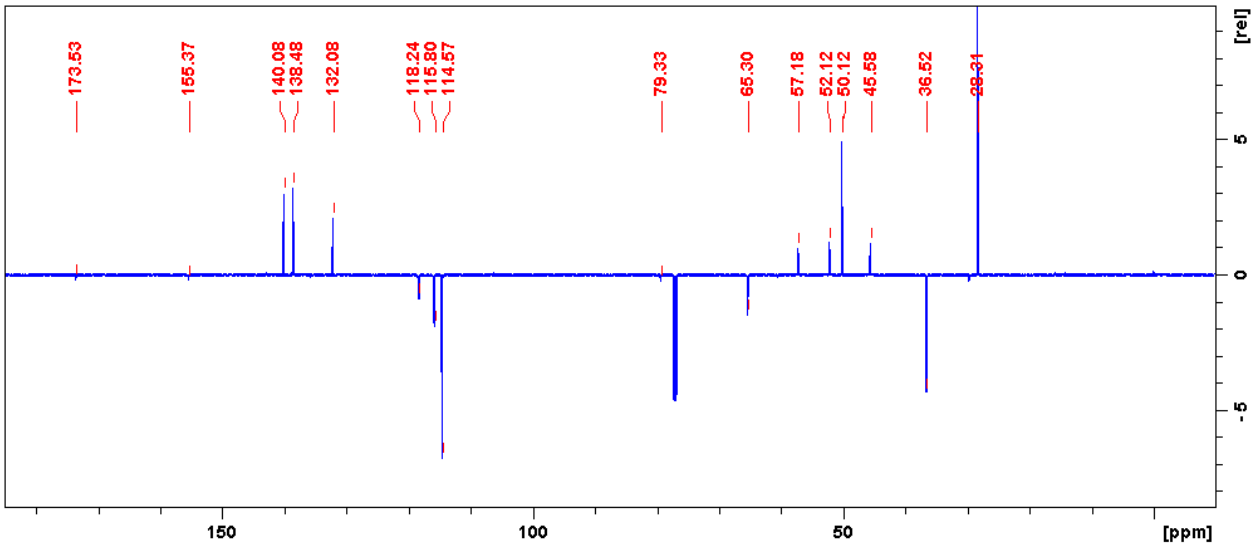


(1*R,2*S**,3*S**,5*R**)-allyl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)**-19**

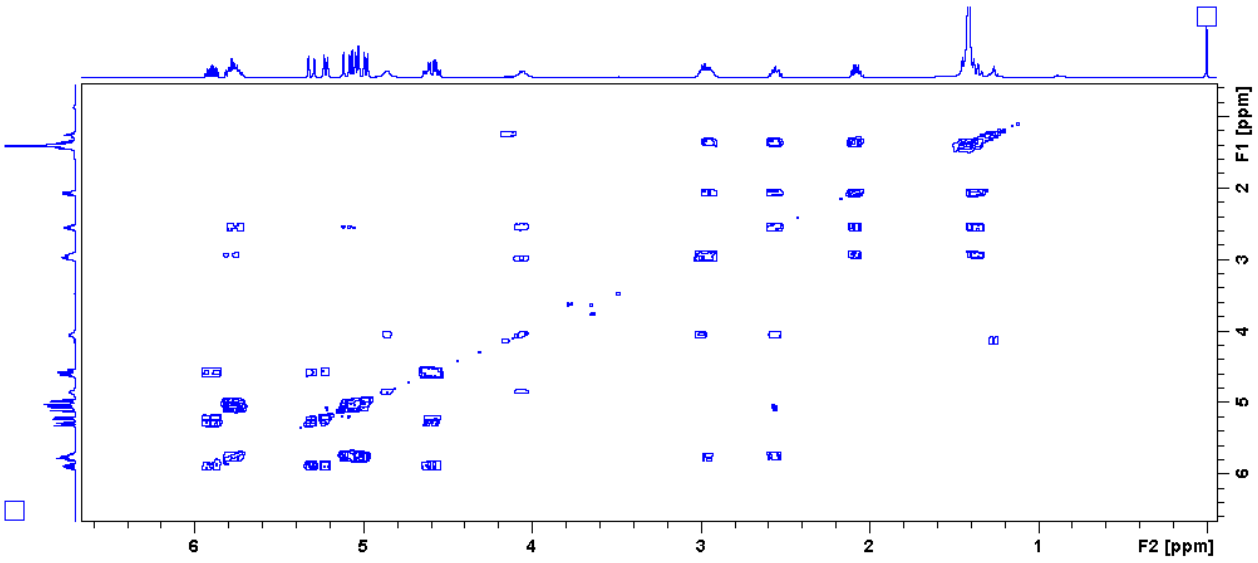
^{1}H NMR spectrum:



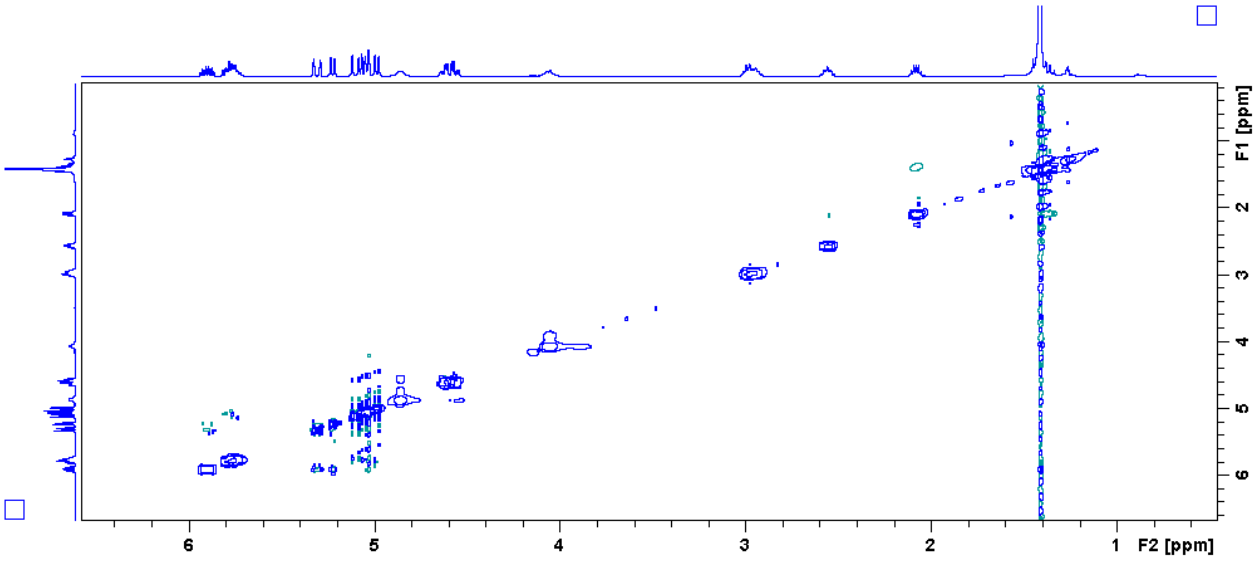
^{13}C (jmod) NMR spectrum:

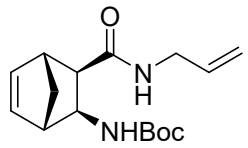


COSY spectrum:



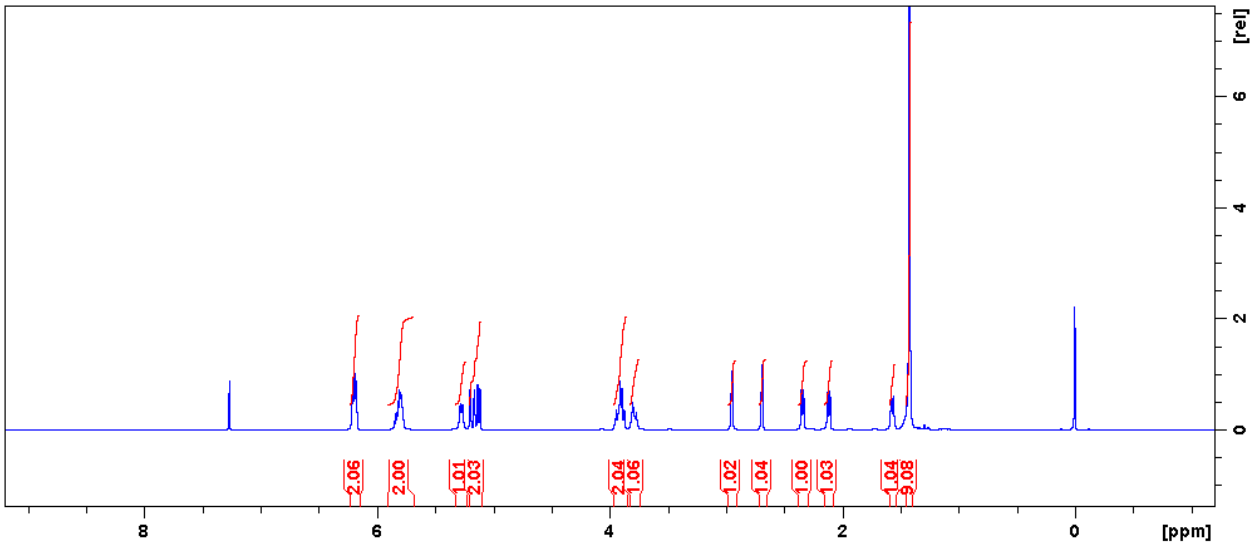
NOESY spectrum:



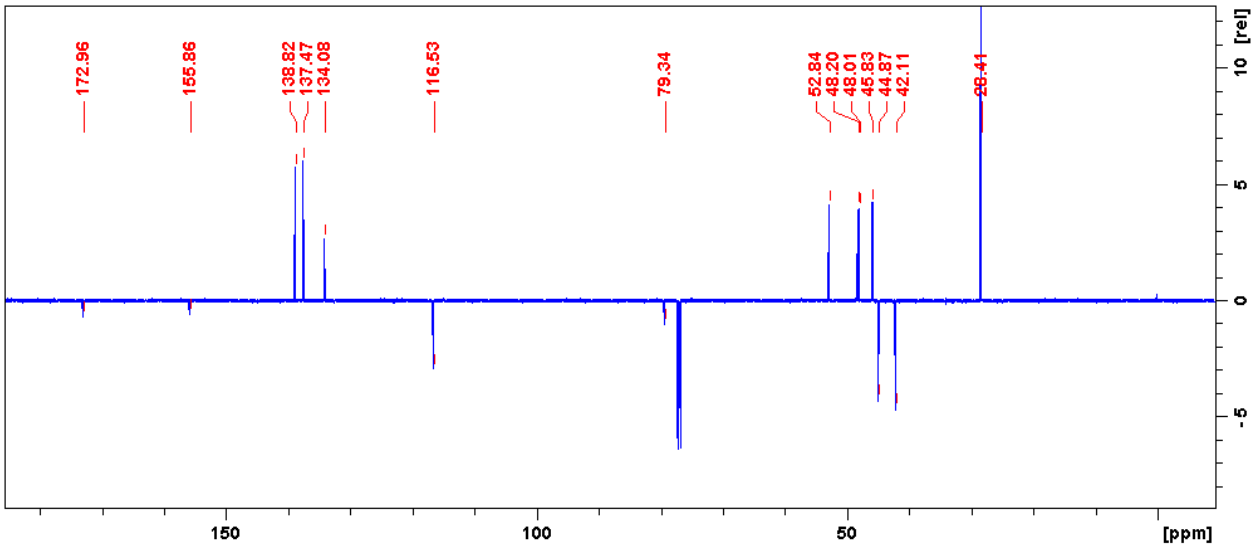


***tert*-Butyl ((1*S**,2*S**,3*R**,4*R**)-3-(allylcarbamoyl)bicyclo[2.2.1]hept-5-en-2-yl)carbamate, (±)-20**

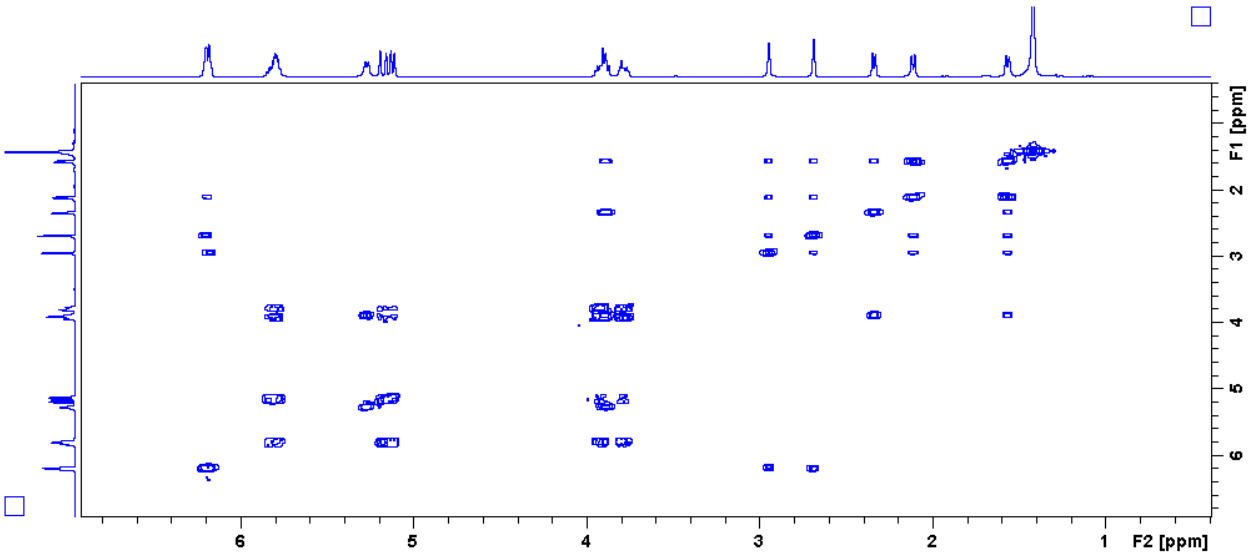
^{1}H NMR spectrum:



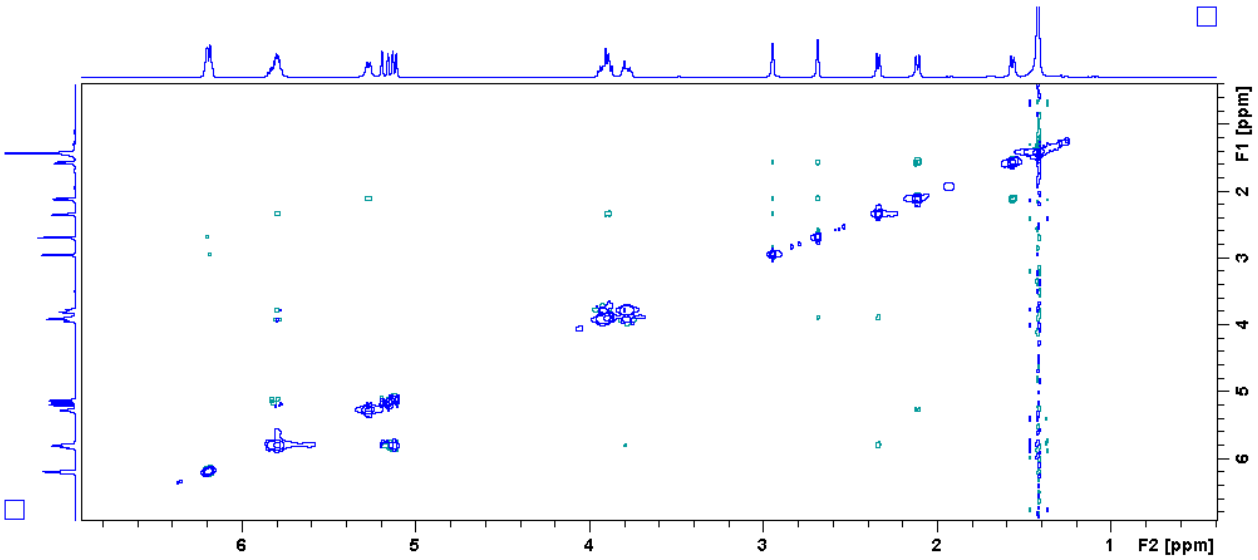
^{13}C (jmod) NMR spectrum:

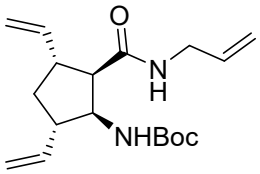


COSY spectrum:



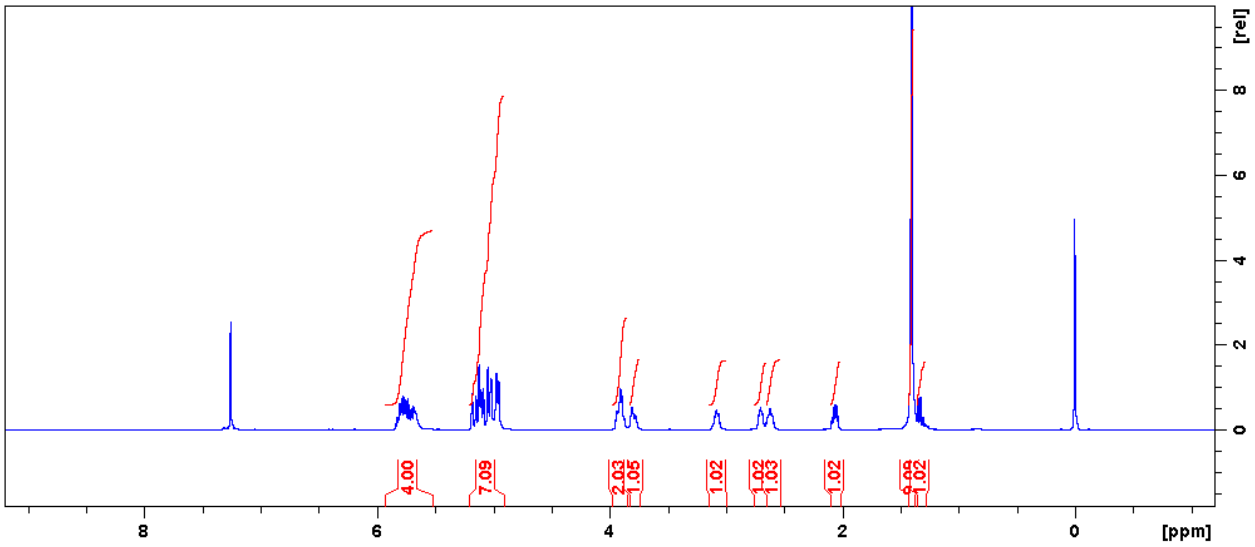
NOESY spectrum:



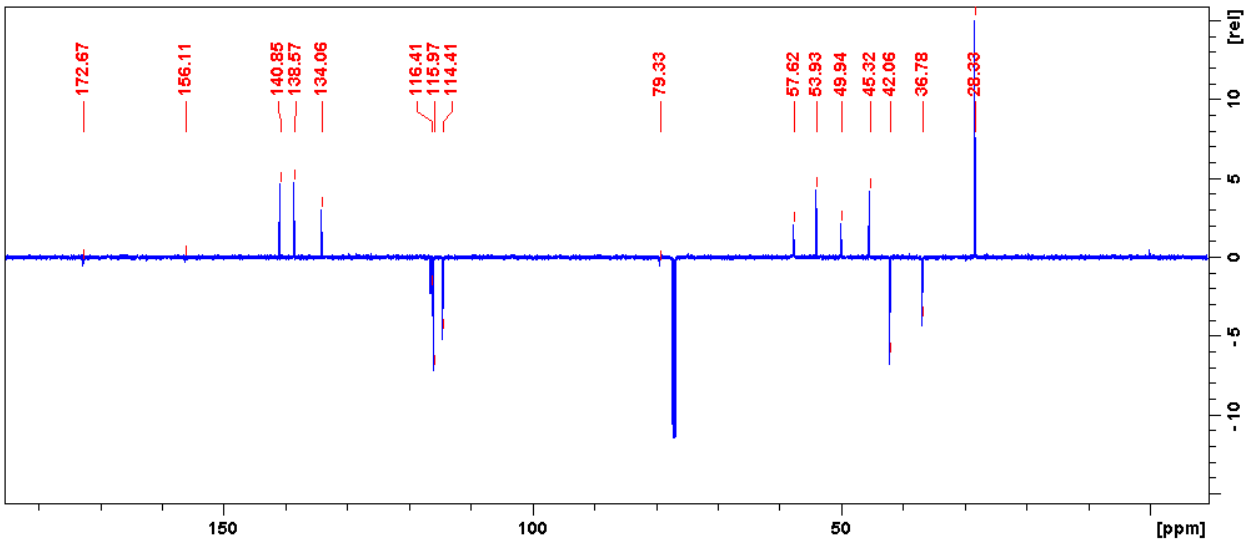


***tert*-Butyl ((1*S**,2*R**,3*R**,5*S**)-2-(allylcarbamoyl)-3,5-divinylcyclopentyl)carbamate, (±)-21**

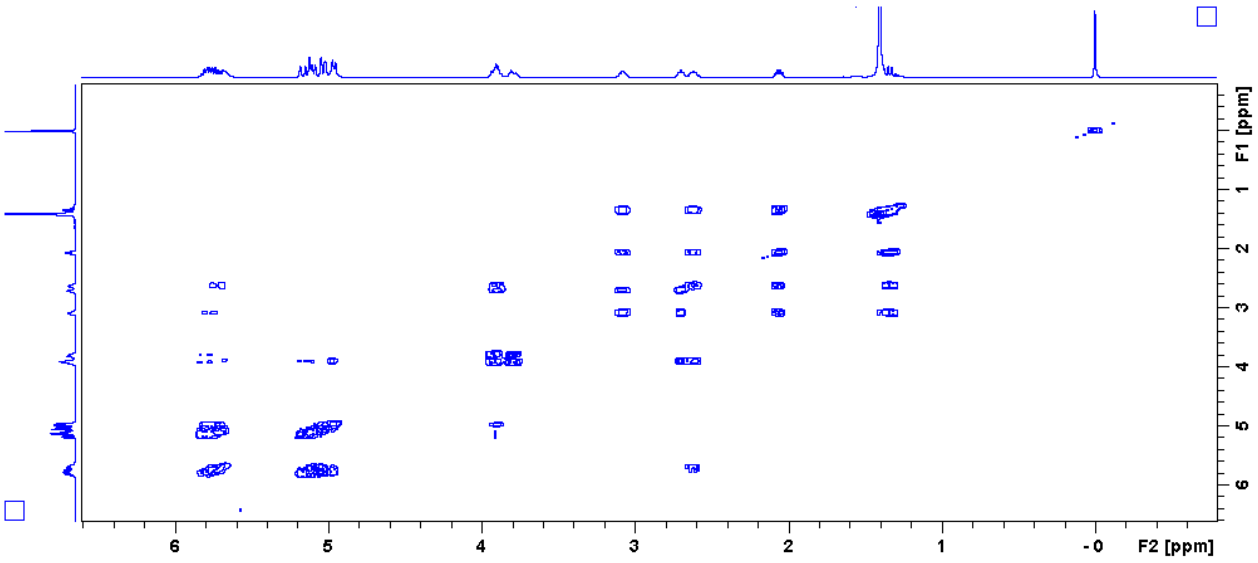
^{1}H NMR spectrum:



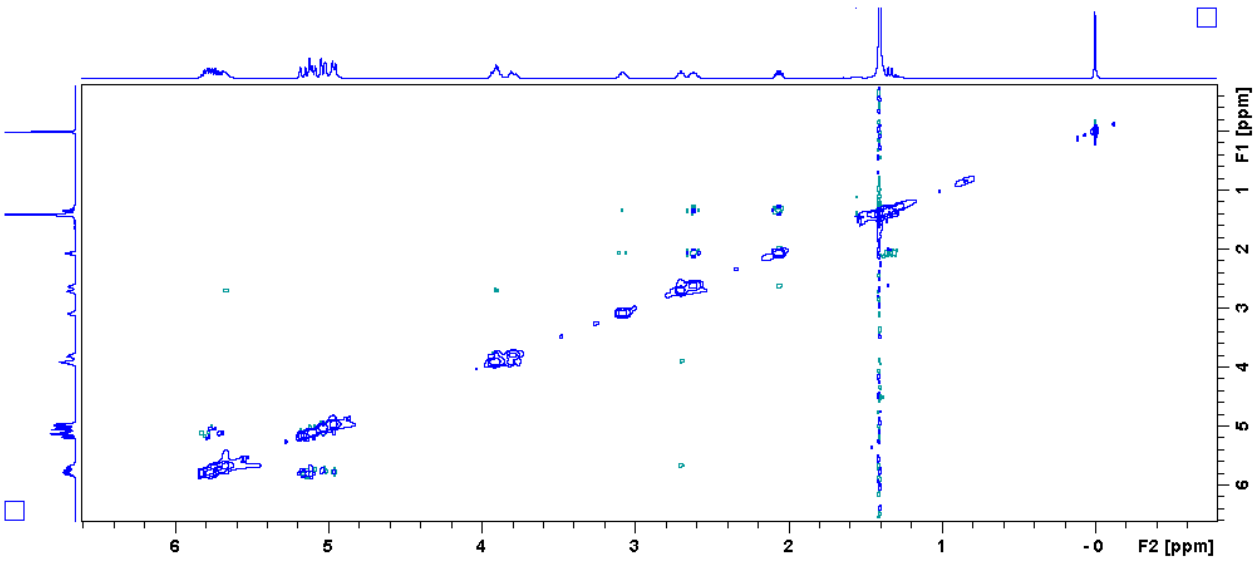
^{13}C (jmod) NMR spectrum:

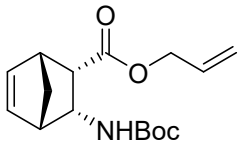


COSY spectrum:



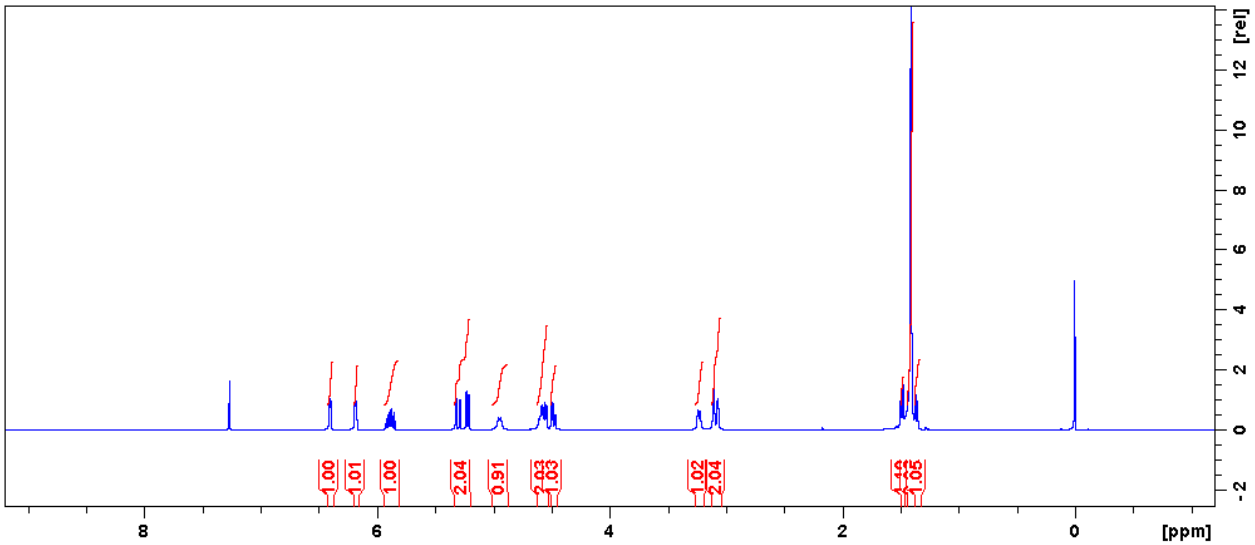
NOESY spectrum:



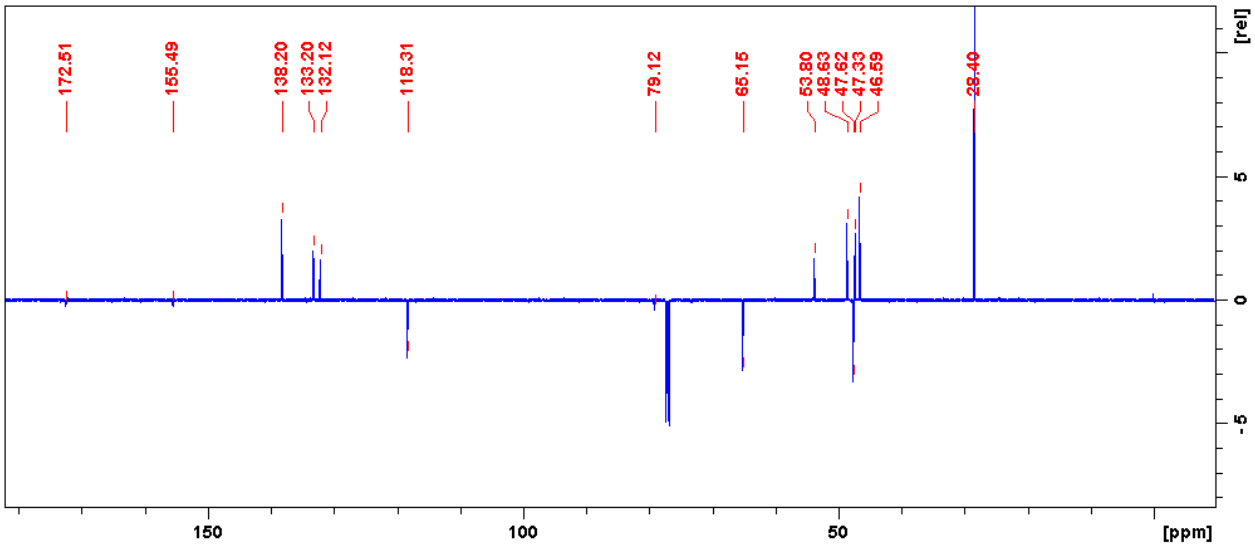


(1*R,2*S**,3*R**,4*S**)-allyl 3-((*tert*-butoxycarbonyl)amino)bicyclo[2.2.1]hept-5-ene-2-carboxylate,** (±)-**23**

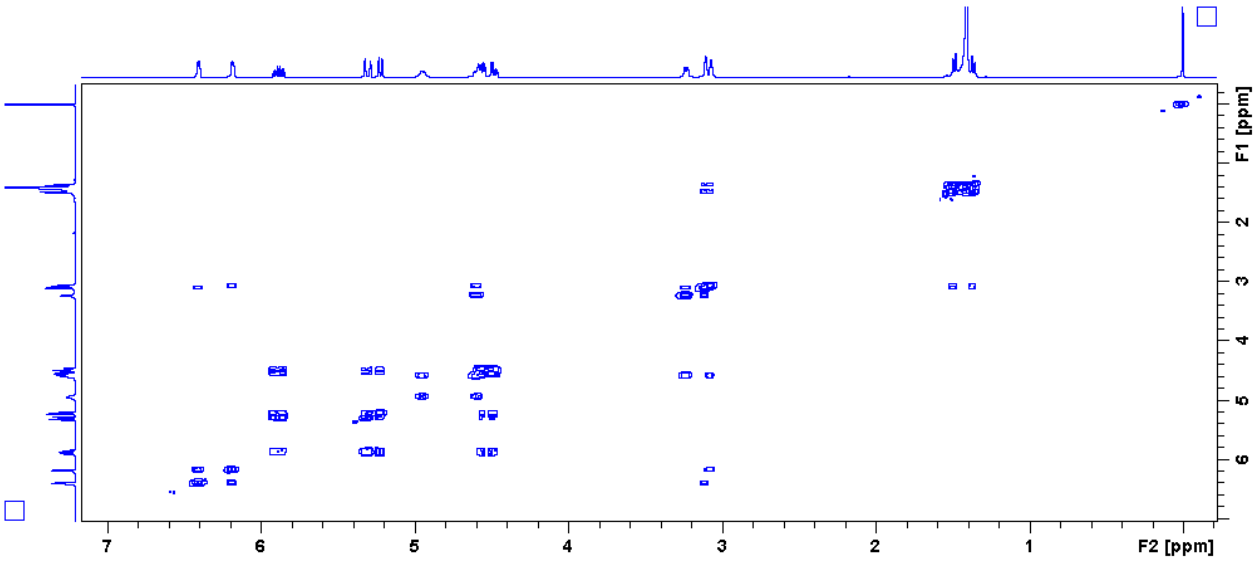
^{1}H NMR spectrum:



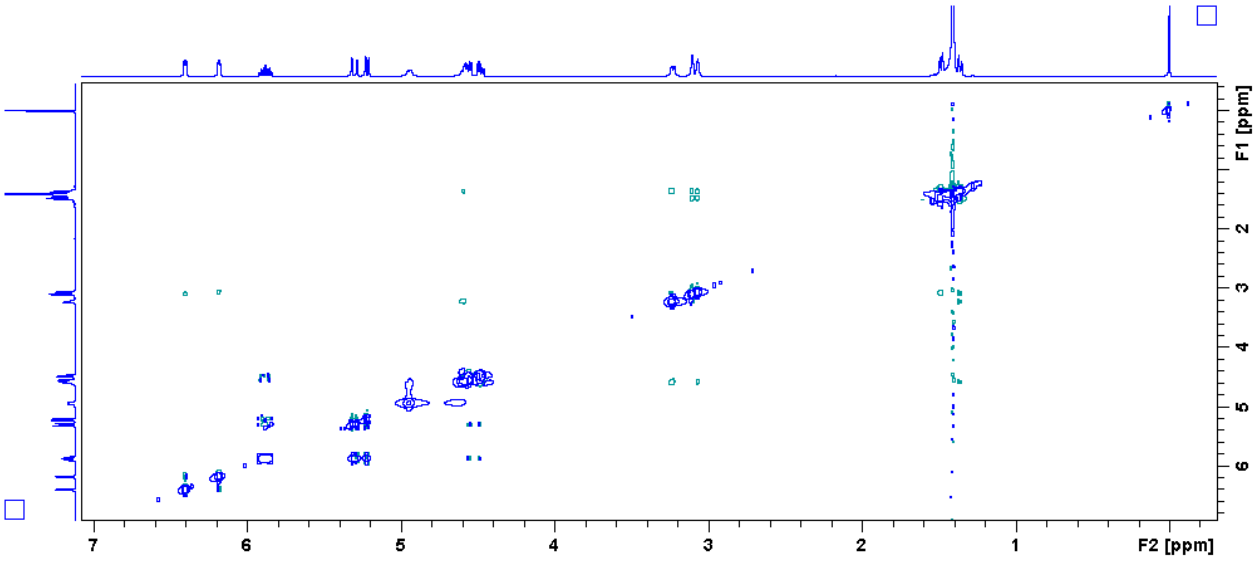
^{13}C (jmod) NMR spectrum:

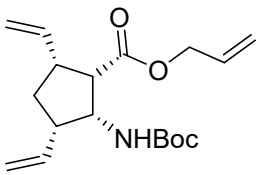


COSY spectrum:



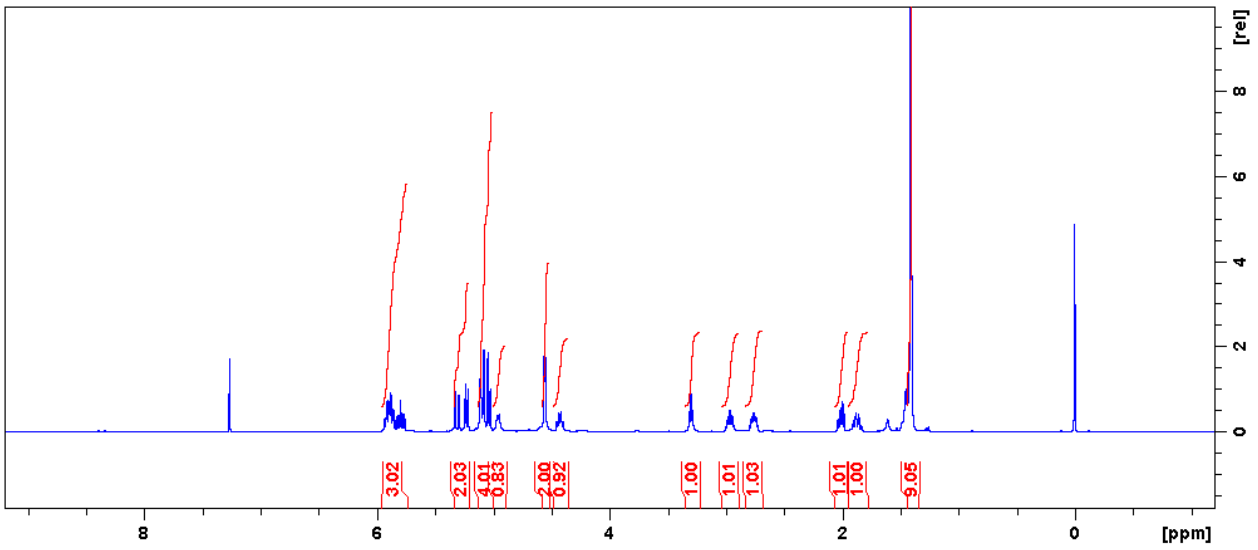
NOESY spectrum:



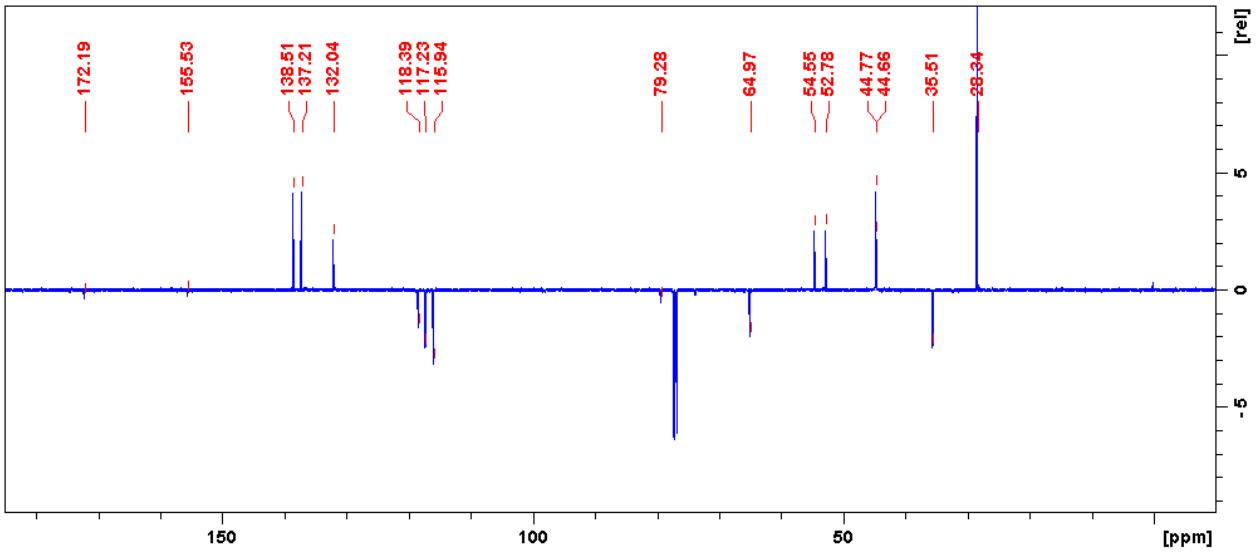


(1*S,2*R**,3*S**,5*R**)-allyl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)**-24**

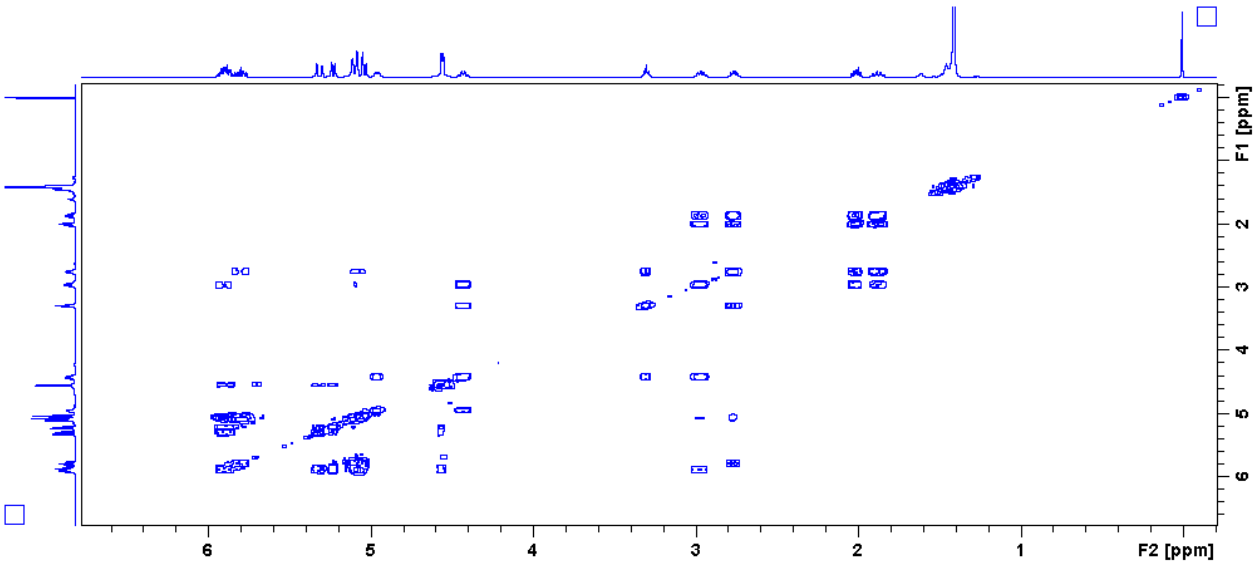
^{1}H NMR spectrum:



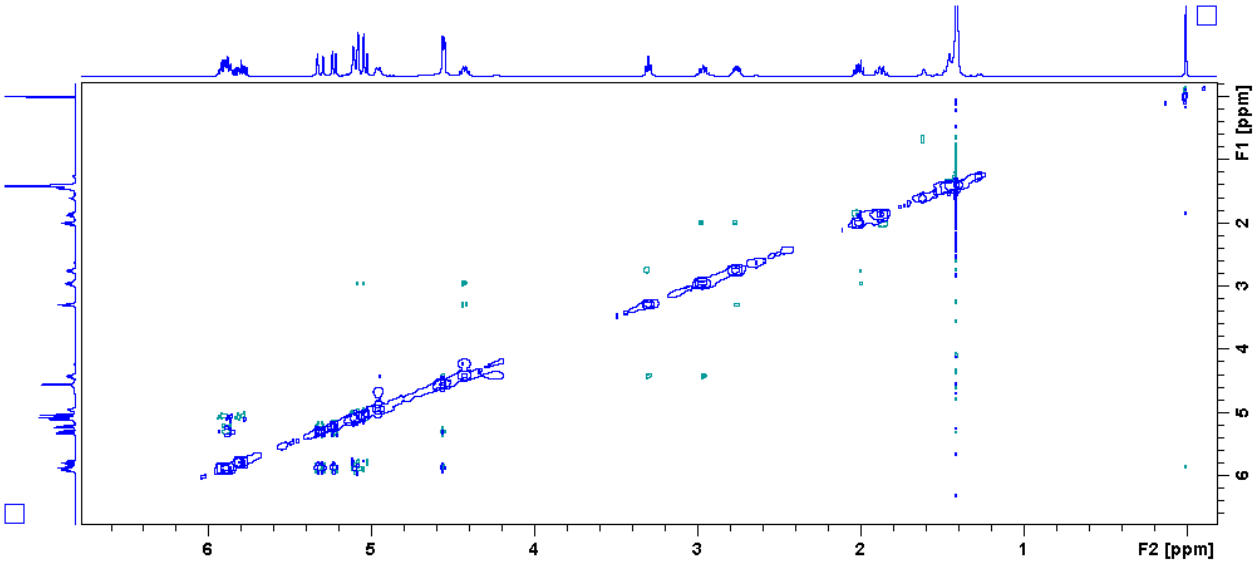
^{13}C (jmod) NMR spectrum:

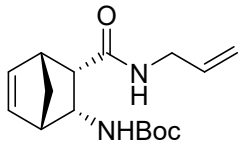


COSY spectrum:



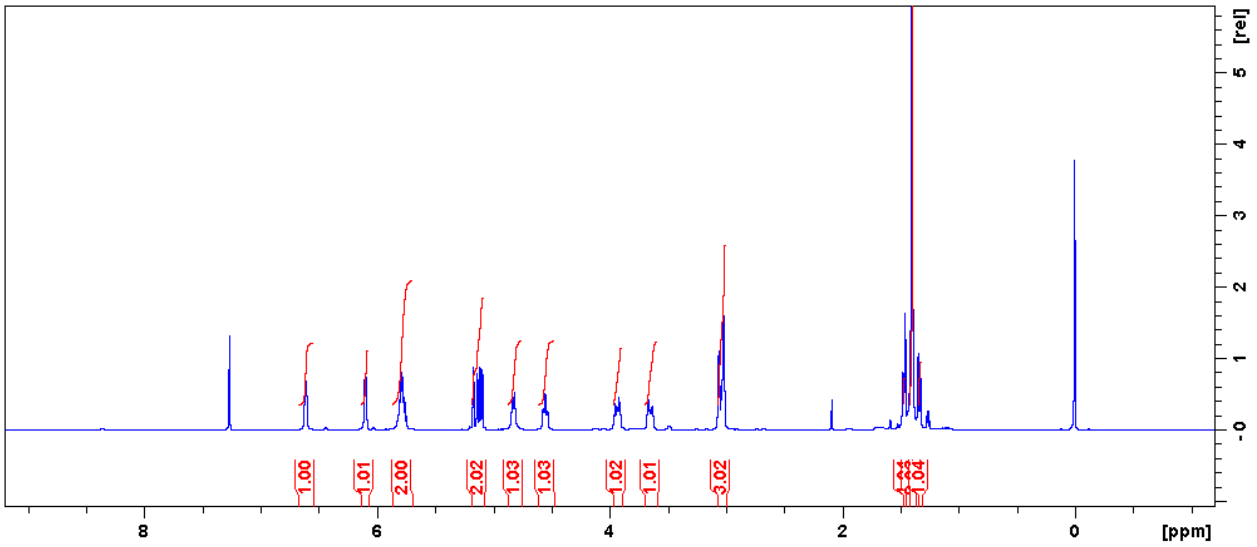
NOESY spectrum:



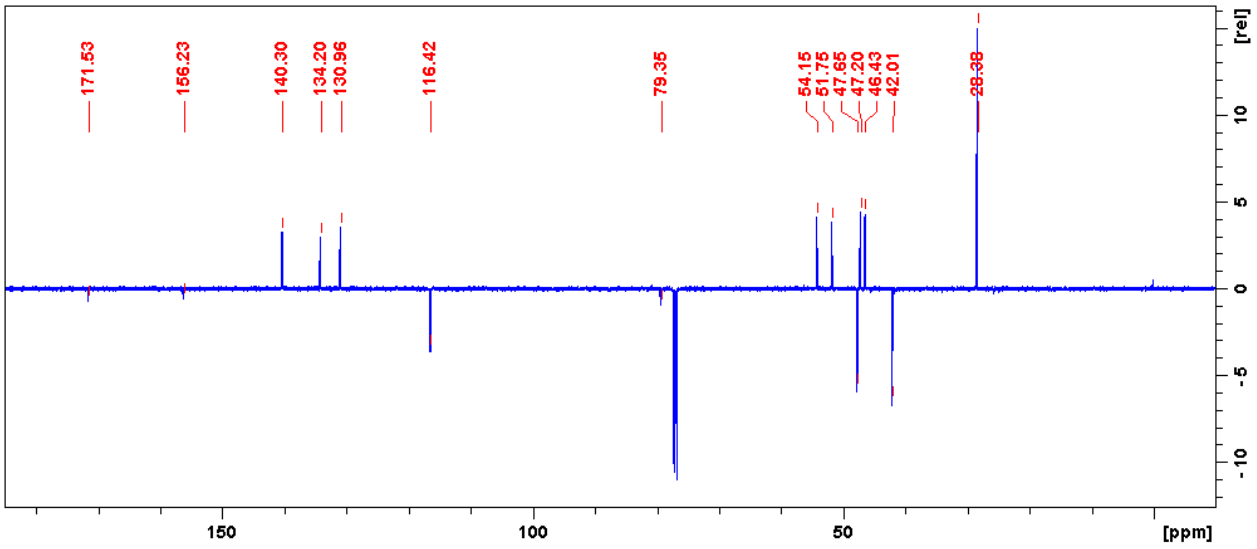


***tert*-Butyl ((1*S**,2*R**,3*S**,4*R**)-3-(allylcarbamoyl)bicyclo[2.2.1]hept-5-en-2-yl)carbamate, (±)-25**

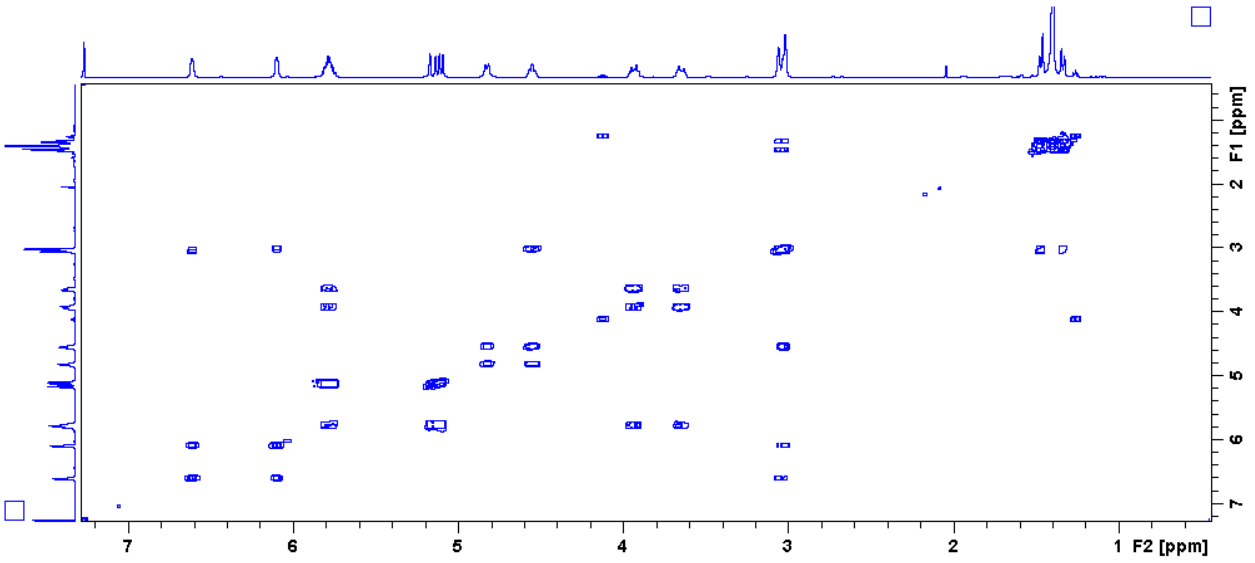
^{1}H NMR spectrum:



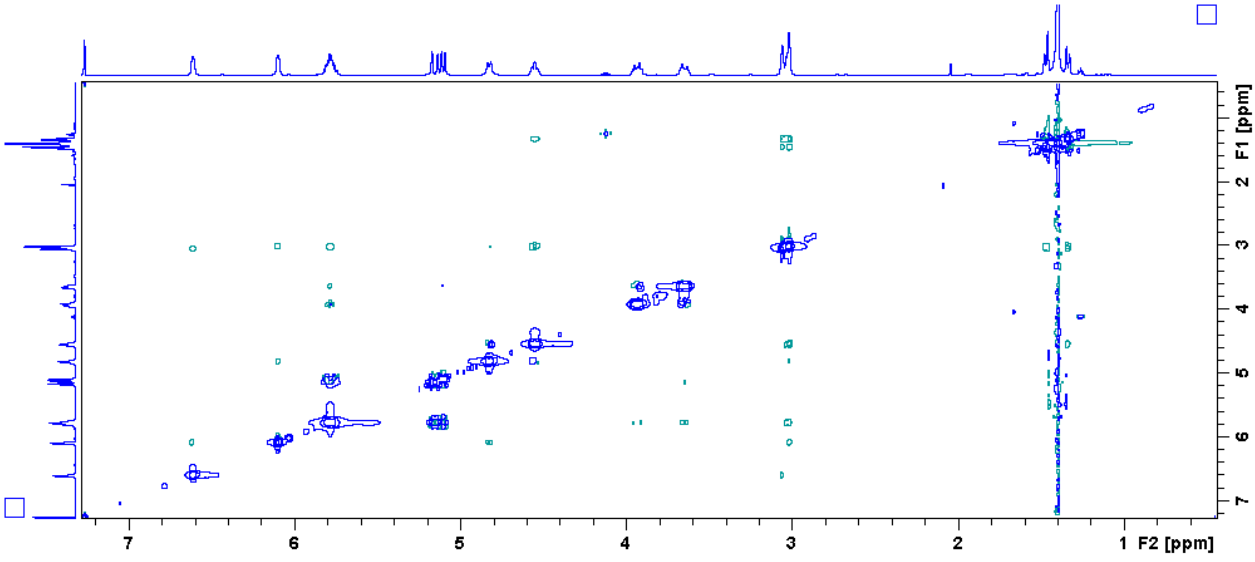
^{13}C (jmod) NMR spectrum:

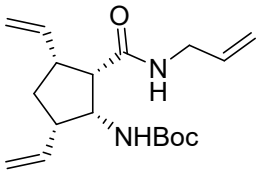


COSY spectrum:



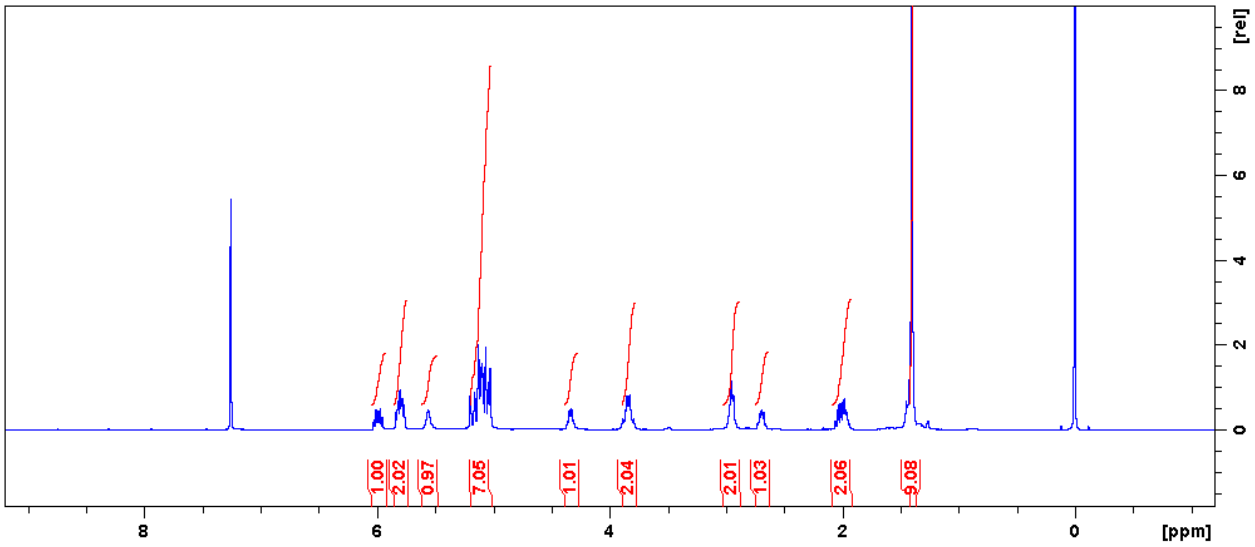
NOESY spectrum:



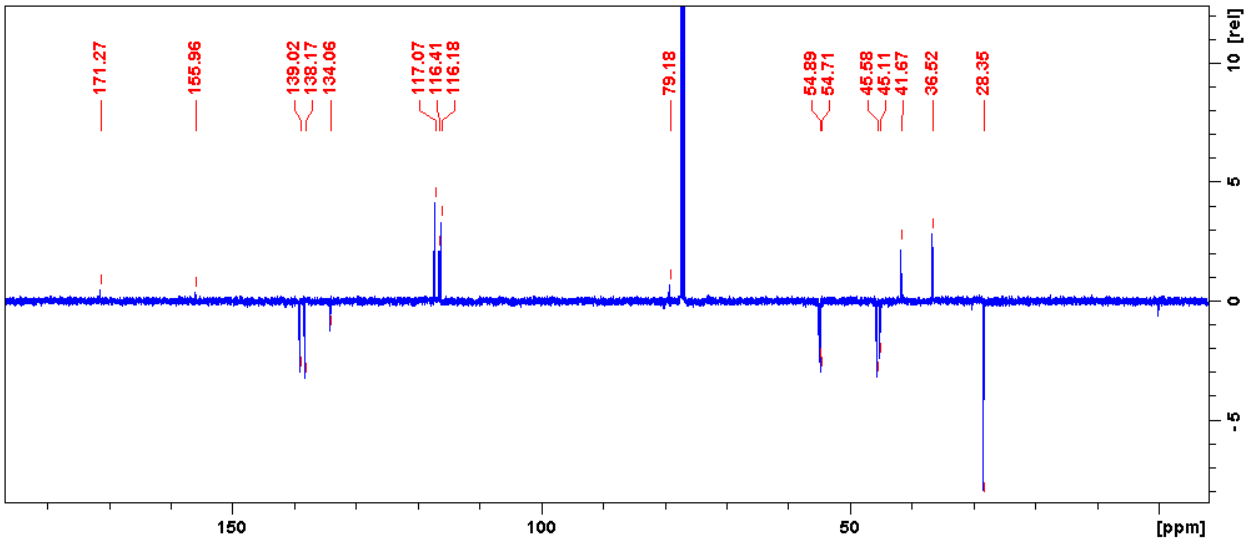


***tert*-Butyl ((1*R**,2*S**,3*R**,5*S**)-2-(allylcarbamoyl)-3,5-divinylcyclopentyl)carbamate, (±)-26**

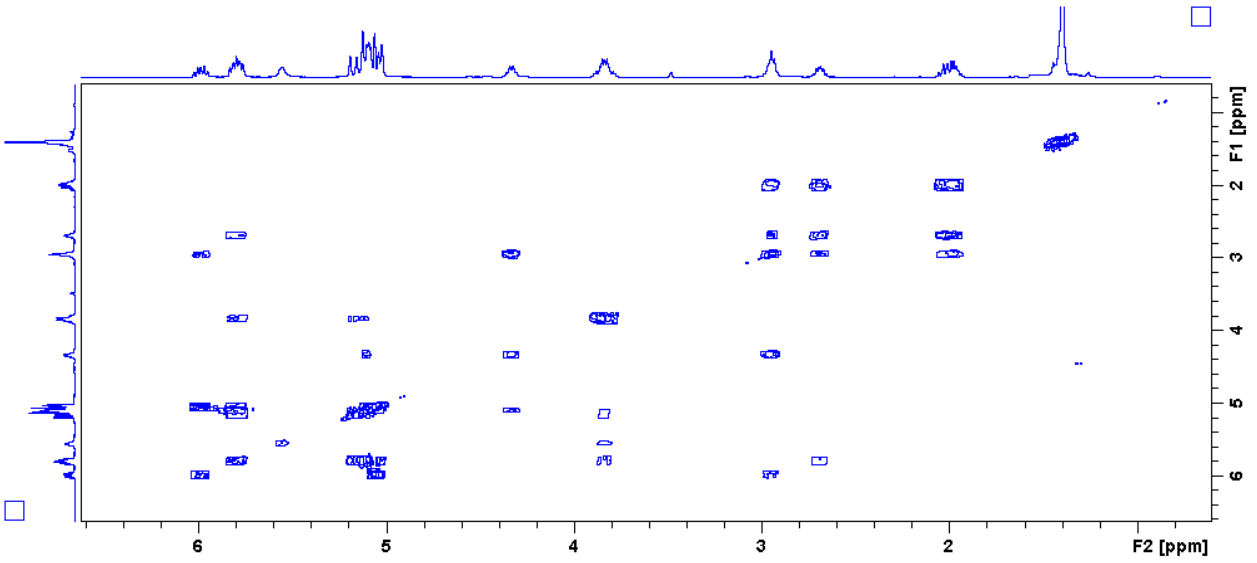
^{1}H NMR spectrum:



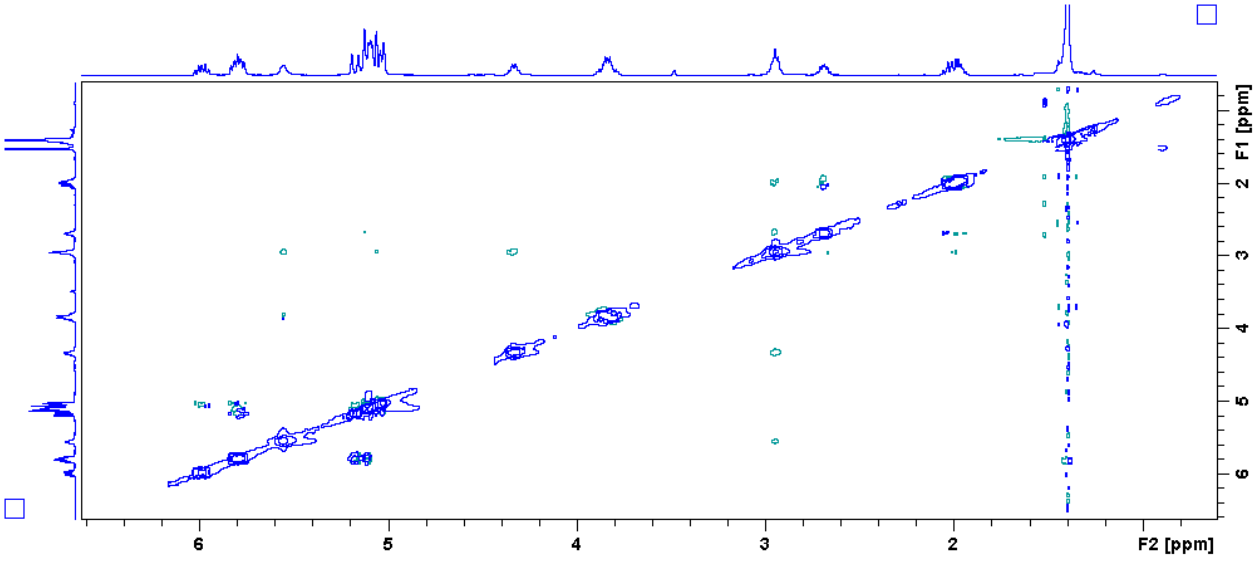
^{13}C (jmod) NMR spectrum:

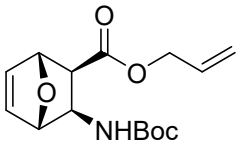


COSY spectrum:



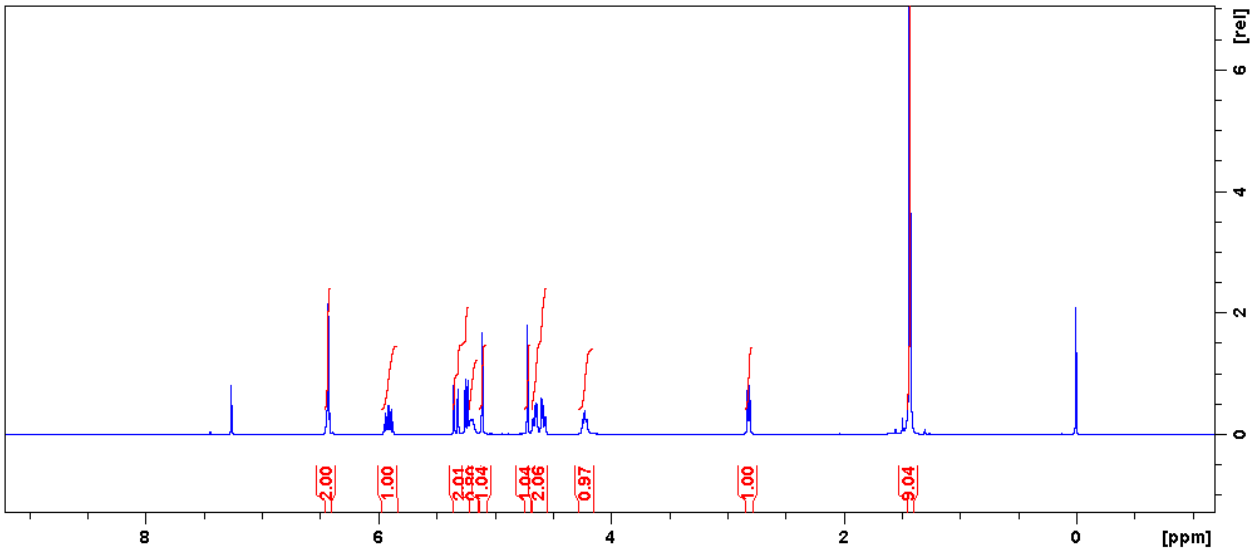
NOESY spectrum:



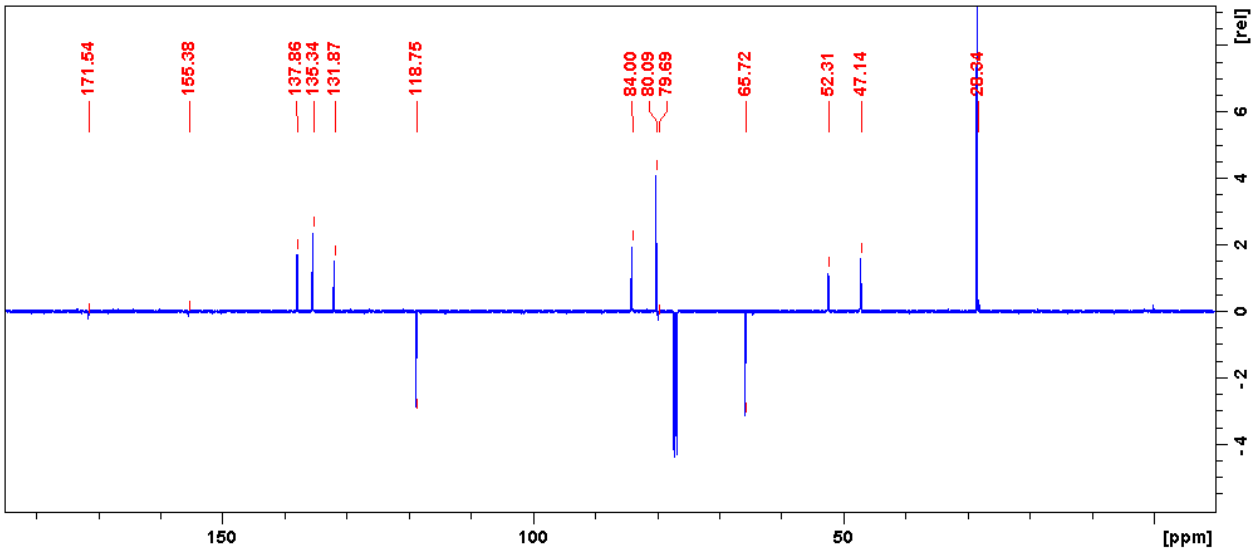


(1*R,2*S**,3*R**,4*S**)-allyl 3-((*tert*-butoxycarbonyl)amino)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylate,** (±)**-28**

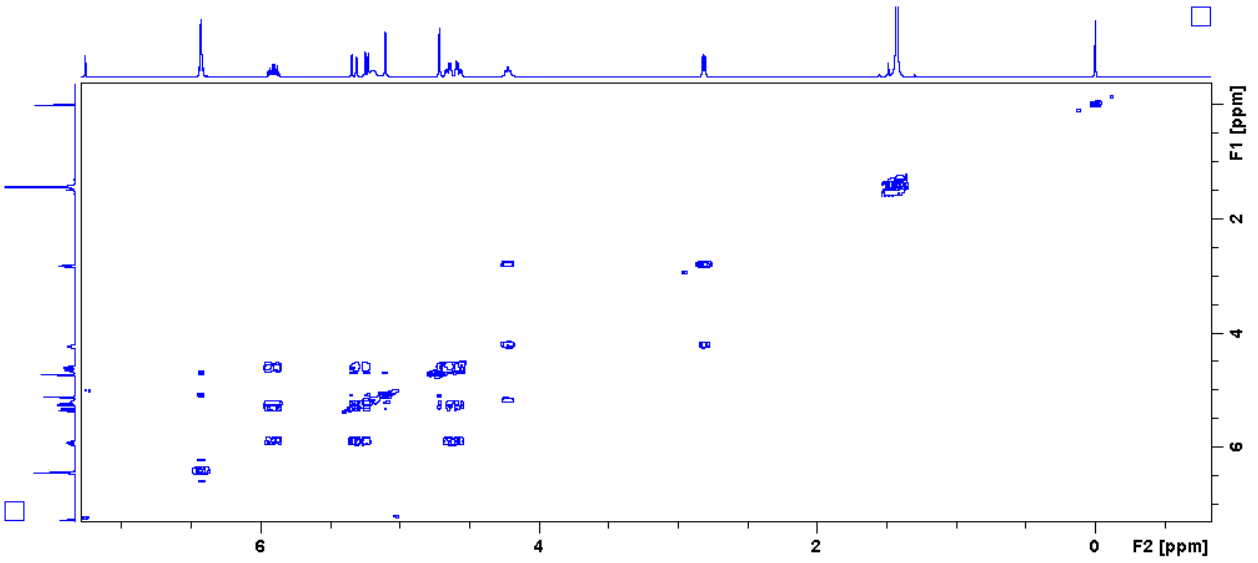
^{1}H NMR spectrum:



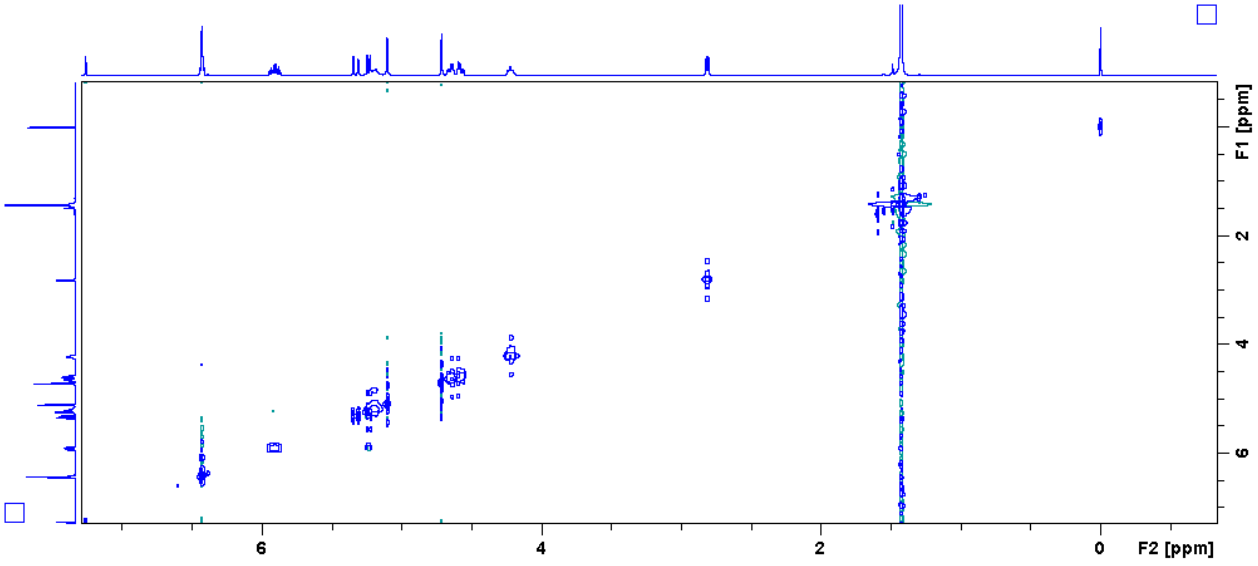
^{13}C (jmod) NMR spectrum:

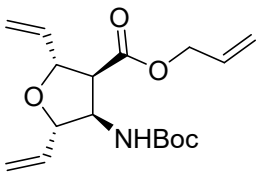


COSY spectrum:



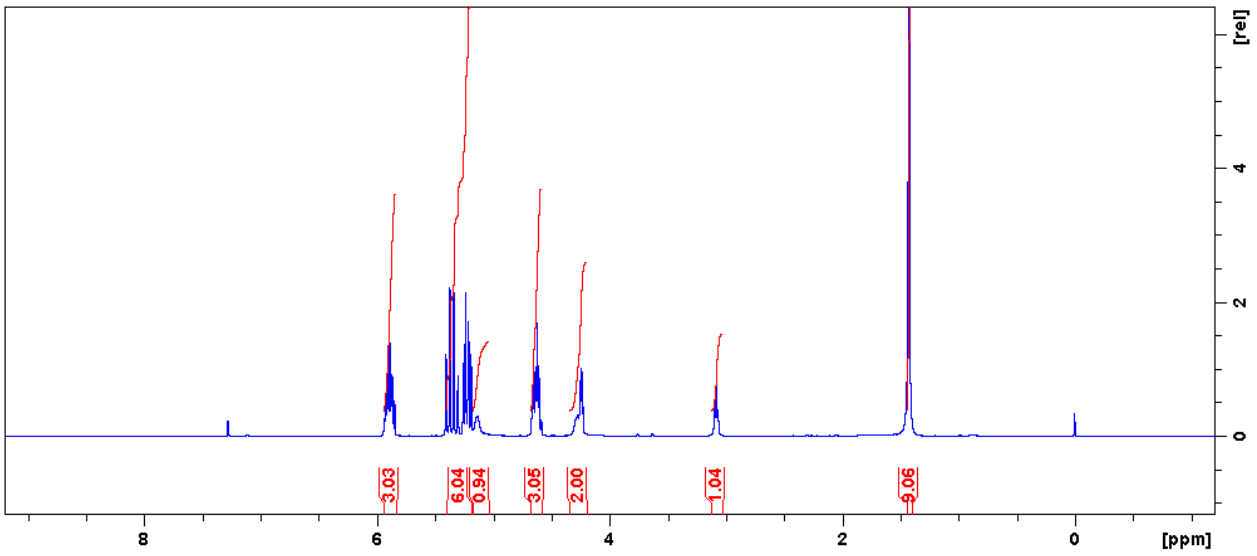
NOESY spectrum:



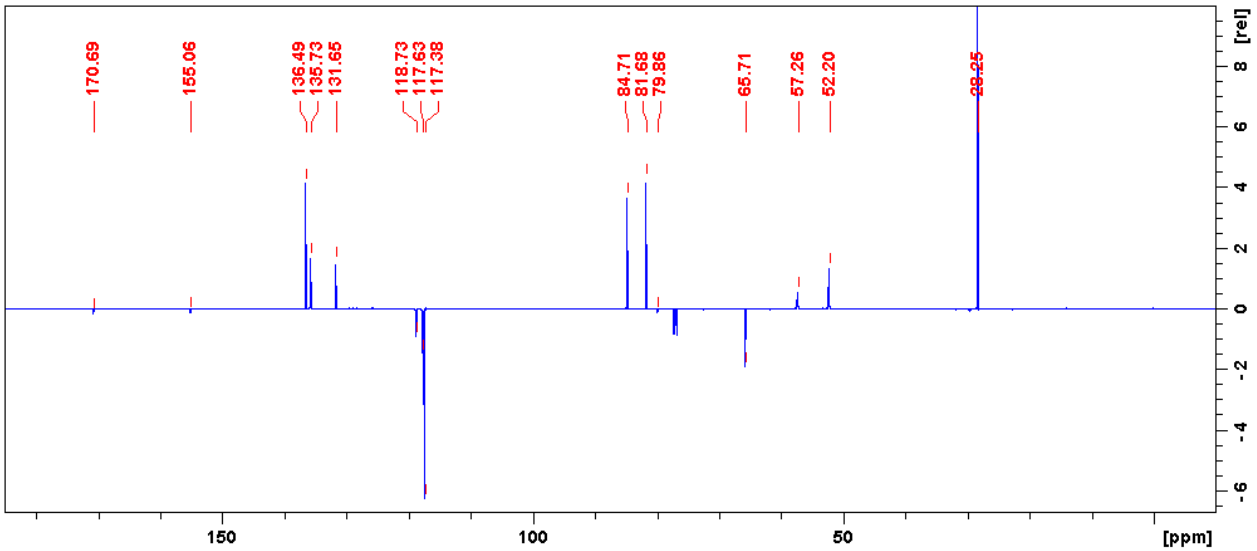


(2*R,3*S**,4*R**,5*S**)-allyl 4-((*tert*-butoxycarbonyl)amino)-2,5-divinyltetrahydrofuran-3-carboxylate,** (±)-**29**

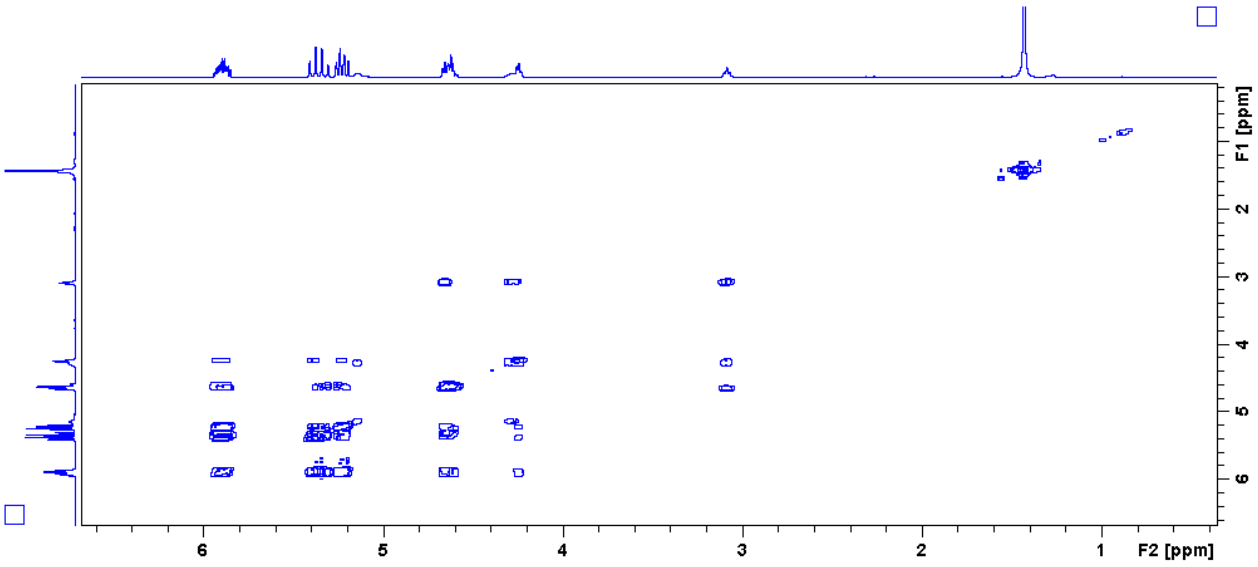
^{1}H NMR spectrum:



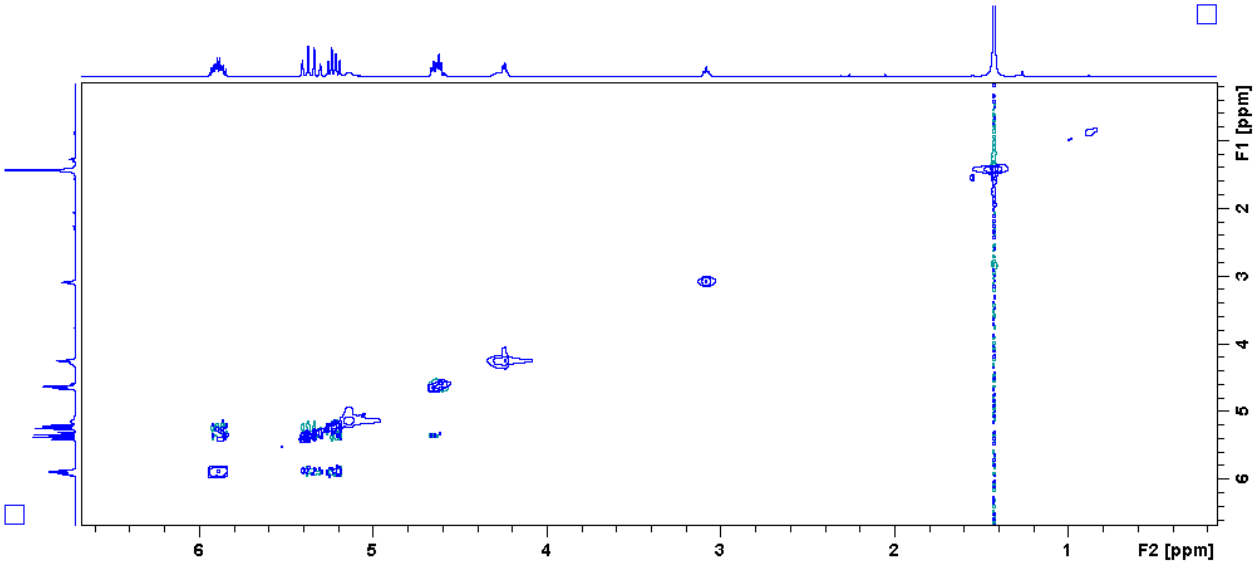
^{13}C (jmod) NMR spectrum:

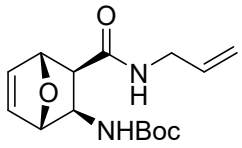


COSY spectrum:



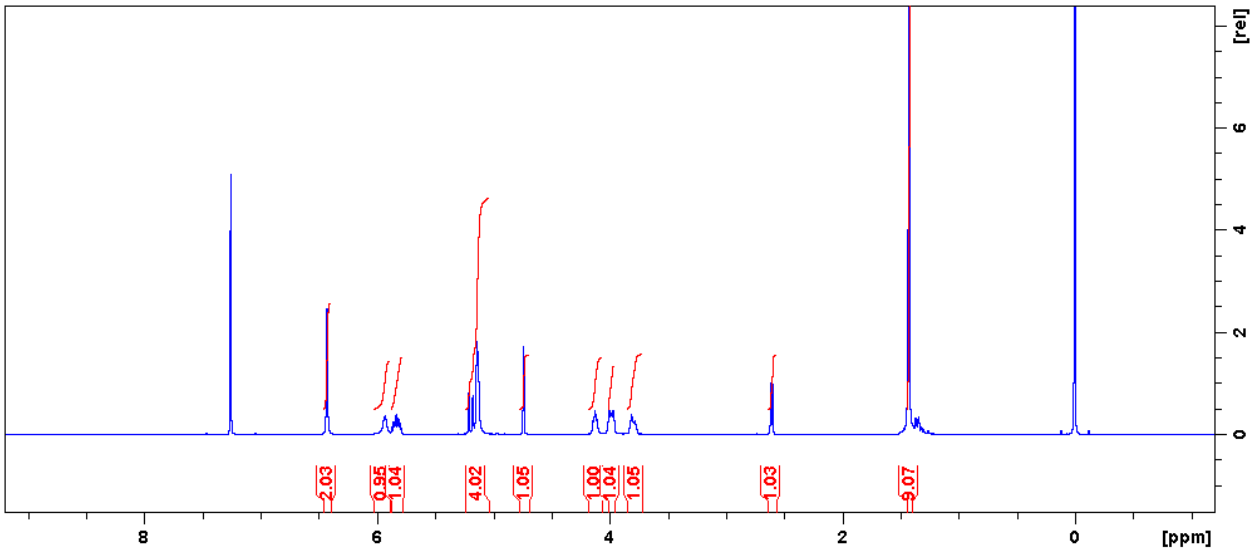
NOESY spectrum:



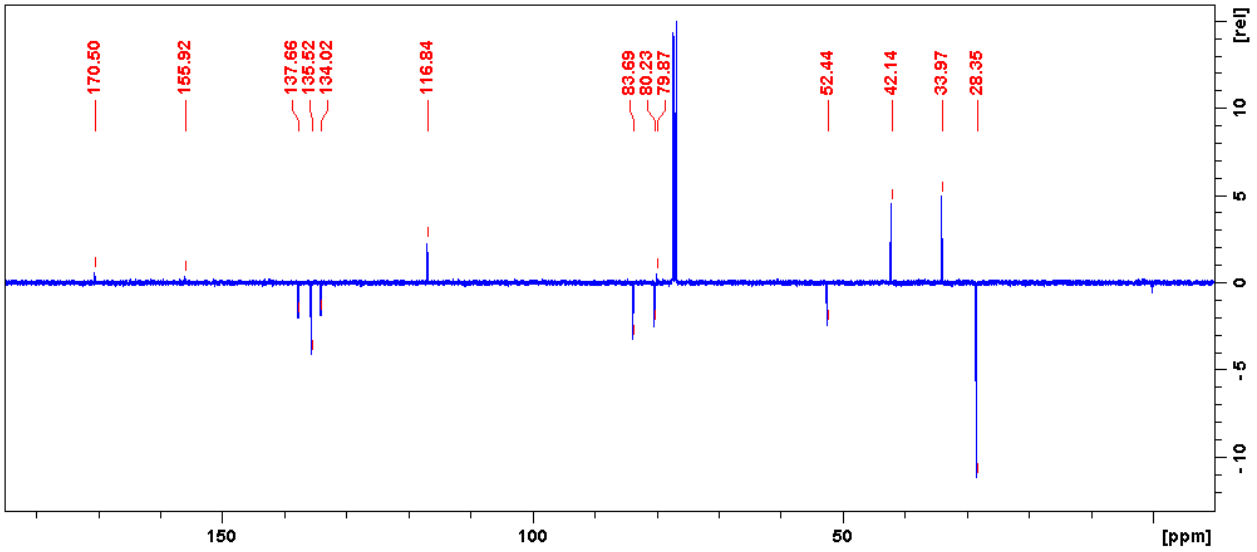


***tert*-Butyl ((1*S**,2*R**,3*S**,4*R**)-3-(allylcarbamoyl)-7-oxabicyclo[2.2.1]hept-5-en-2-yl)carbamate, (±)-30**

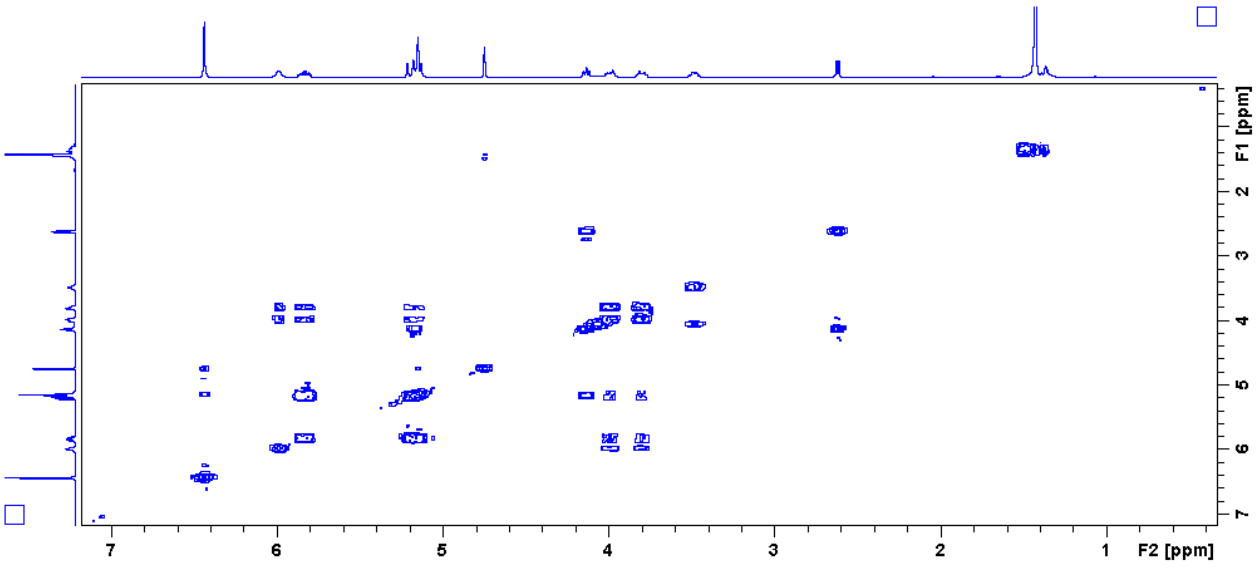
^{1}H NMR spectrum:



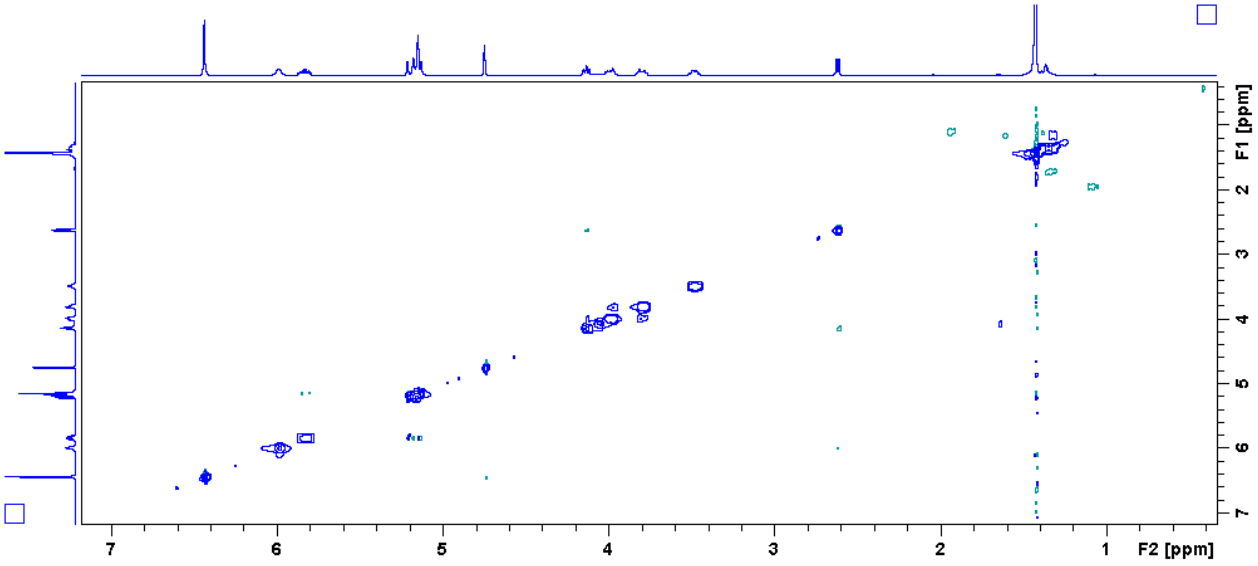
^{13}C (jmod) NMR spectrum:

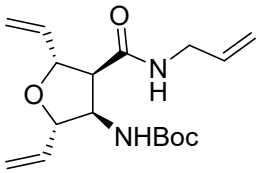


COSY spectrum:



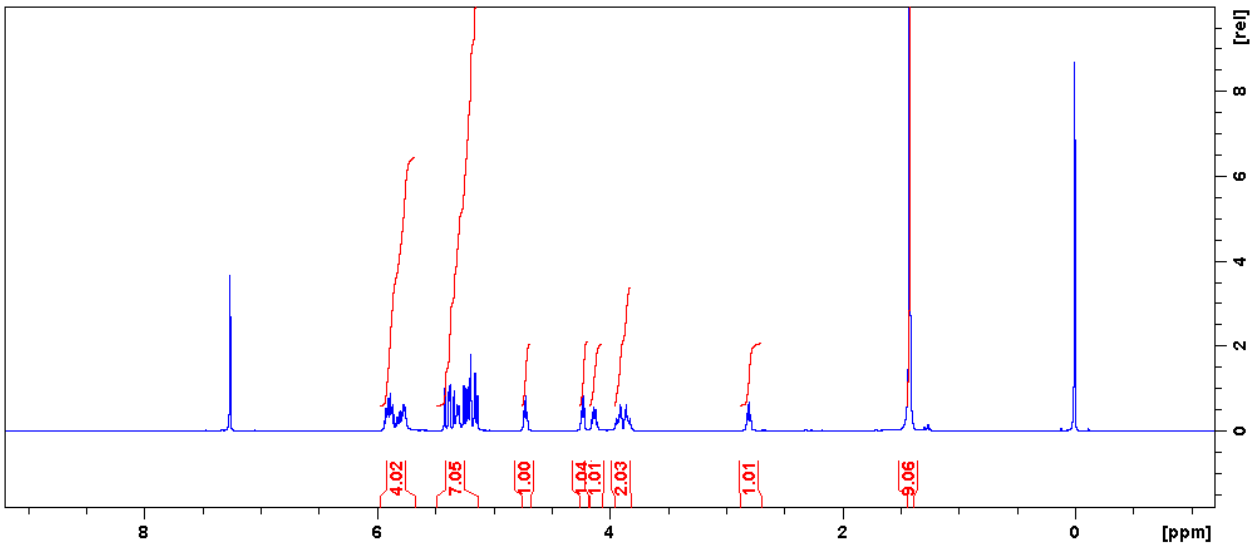
NOESY spectrum:



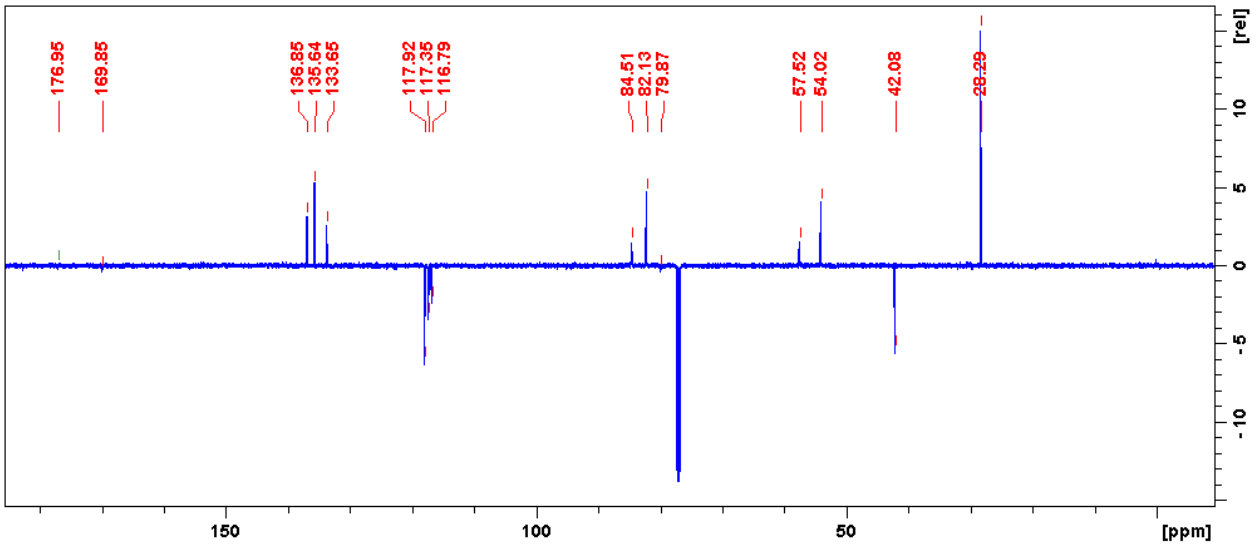


***tert*-Butyl ((2*S**,3*R**,4*S**,5*R**)-4-(allylcarbamoyl)-2,5-divinyltetrahydrofuran-3-yl)carbamate, (±)-31**

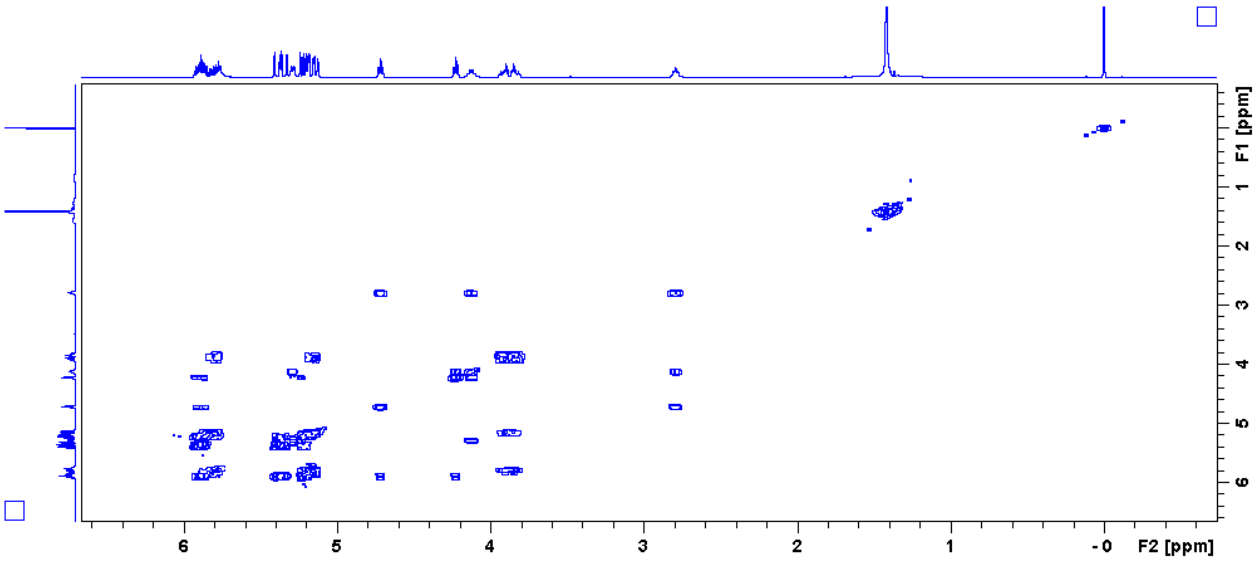
^{1}H NMR spectrum:



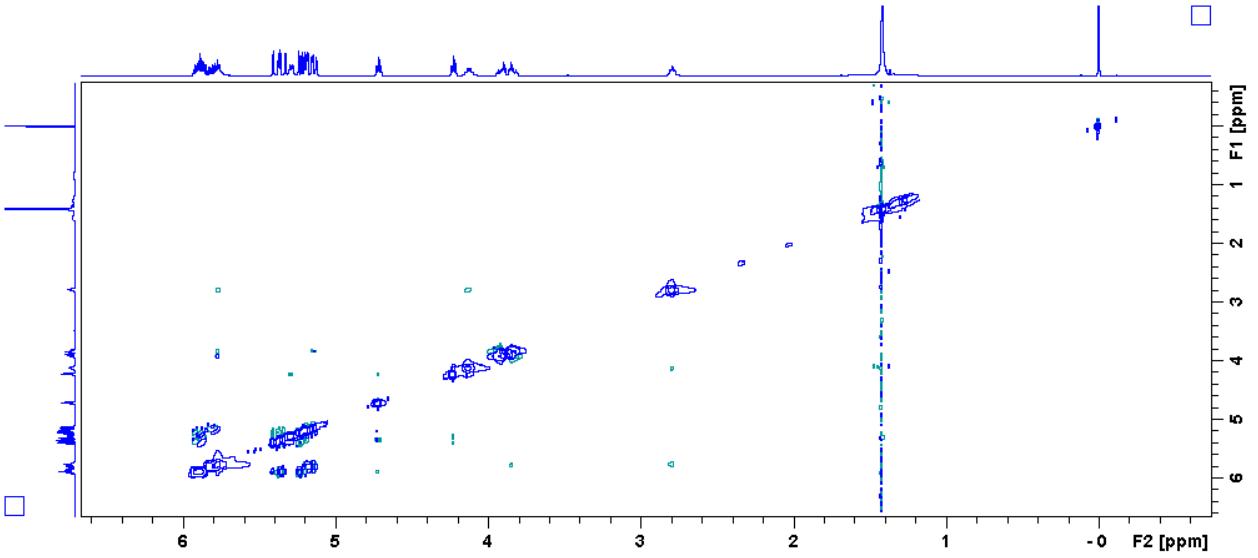
^{13}C (jmod) NMR spectrum:

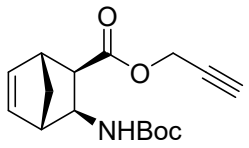


COSY spectrum:



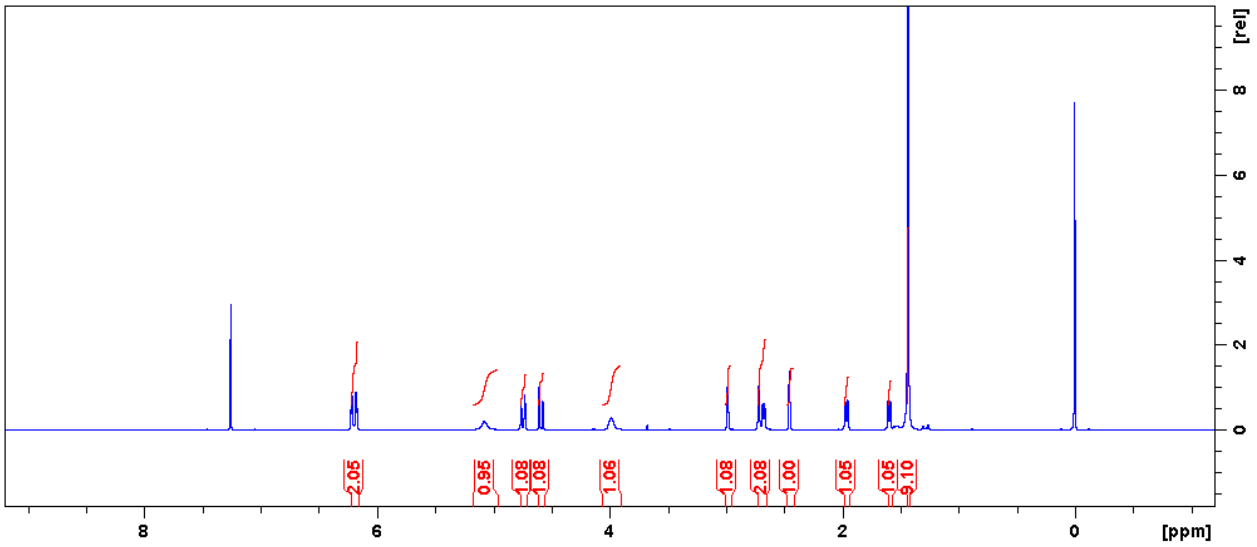
NOESY spectrum:



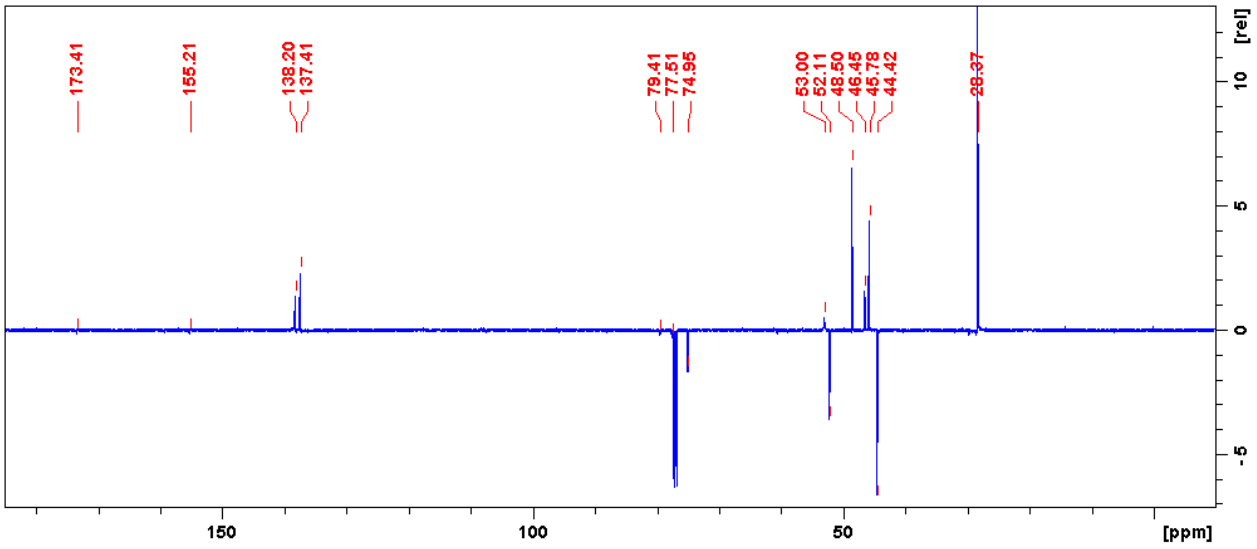


(1*R,2*R**,3*S**,4*S**)-prop-2-yn-1-yl 3-((*tert*-butoxycarbonyl)amino)bicyclo[2.2.1]hept-5-ene-2-carboxylate,** (±)**-32**

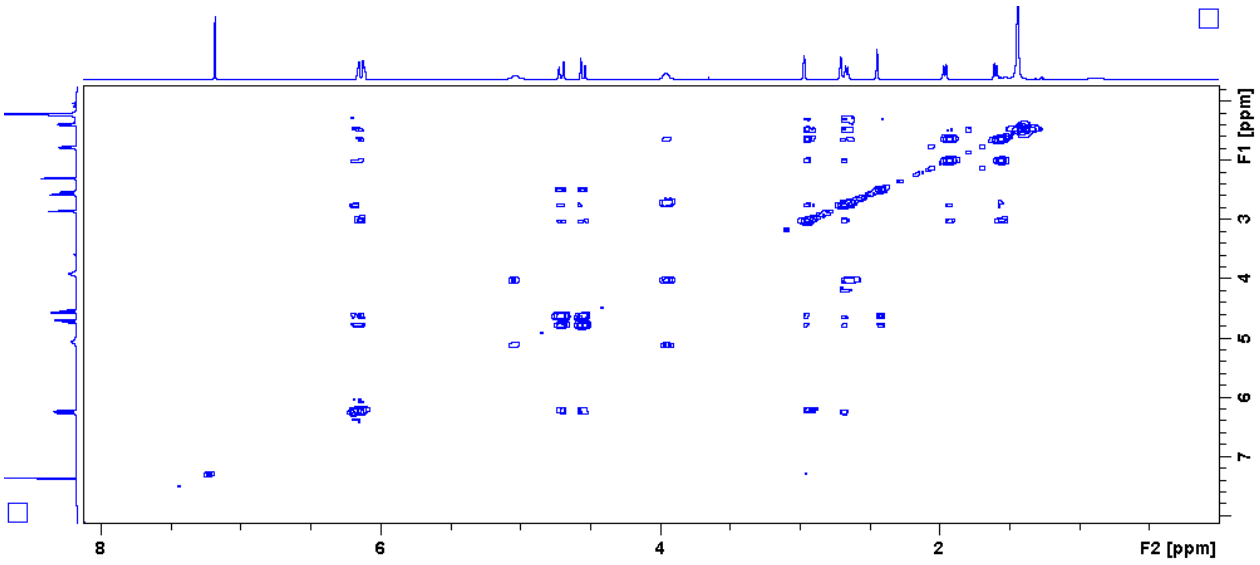
^{1}H NMR spectrum:



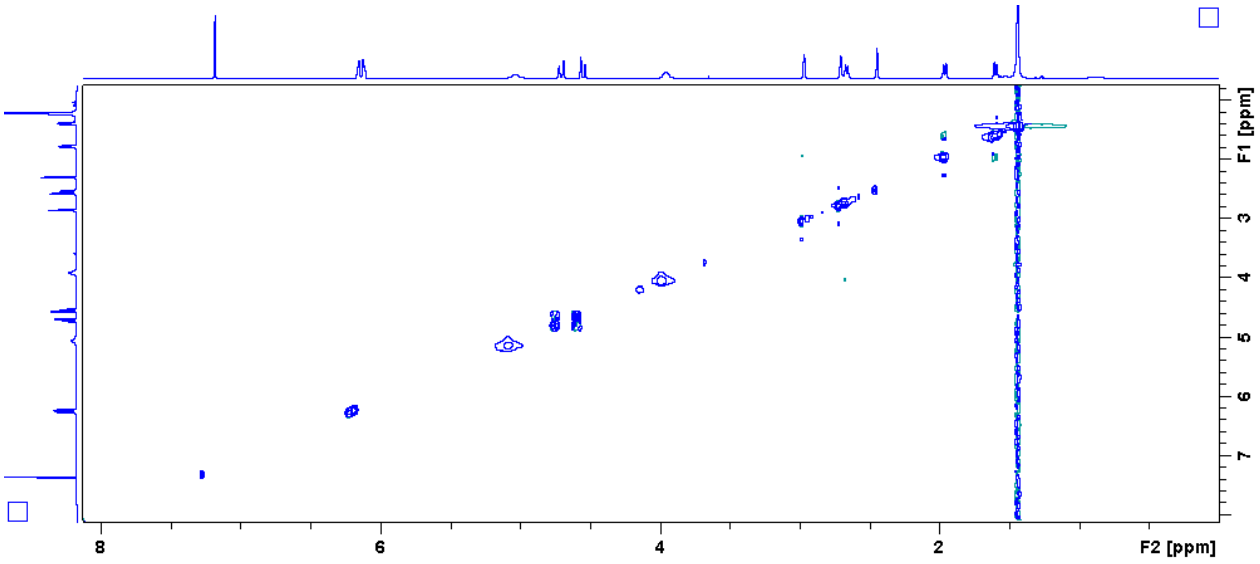
^{13}C (jmod) NMR spectrum:

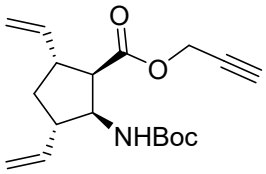


COSY spectrum:



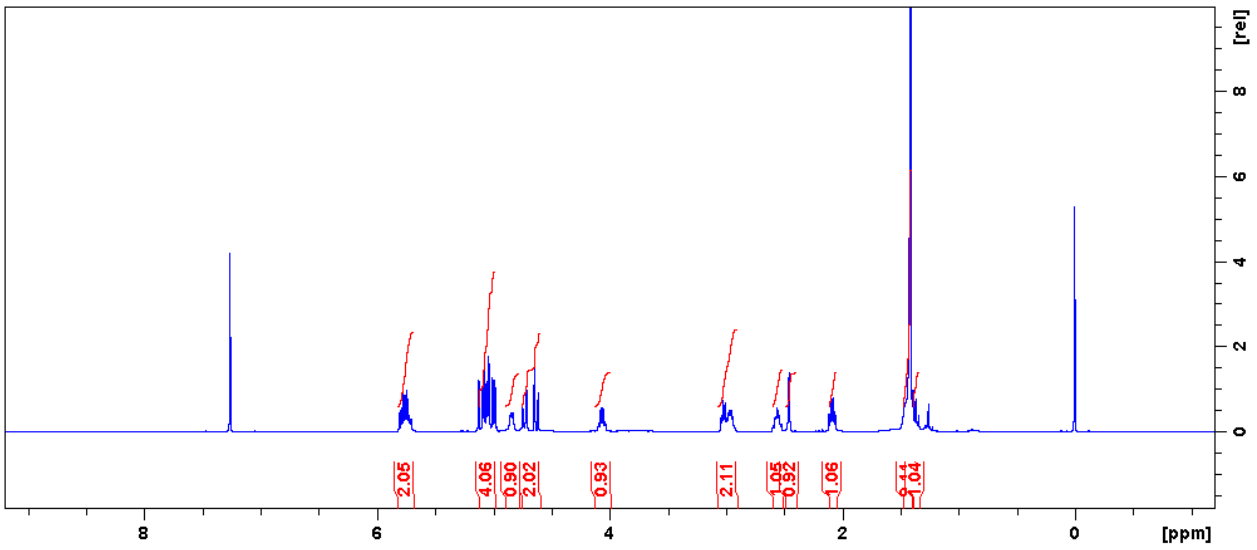
NOESY spectrum:



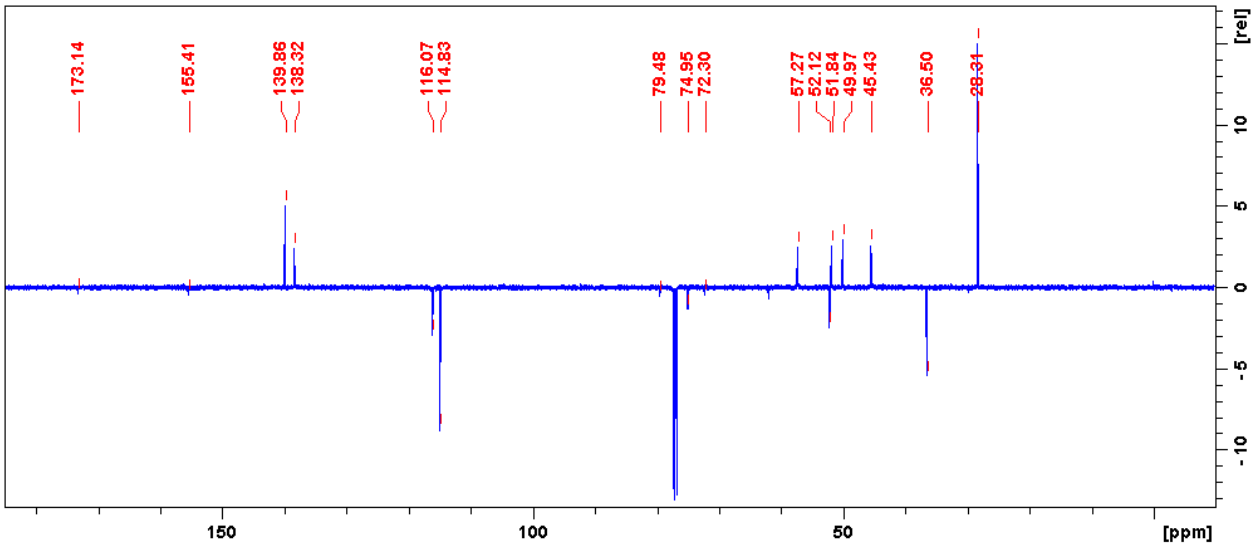


(1*R,2*S**,3*S**,5*R**)-prop-2-yn-1-yl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)**-33**

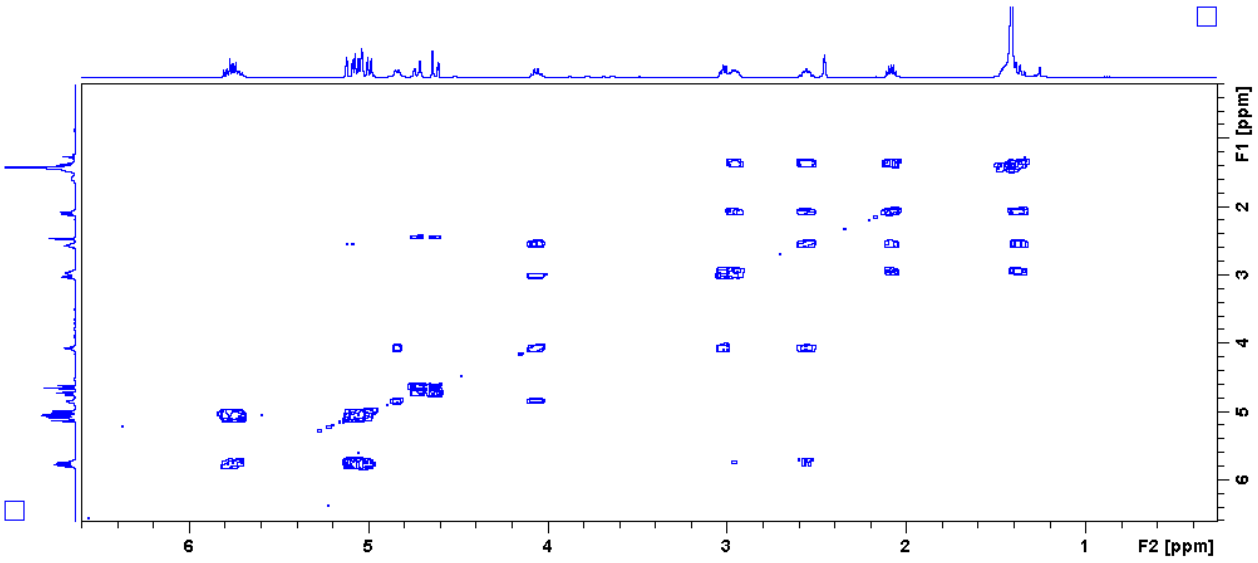
^{1}H NMR spectrum:



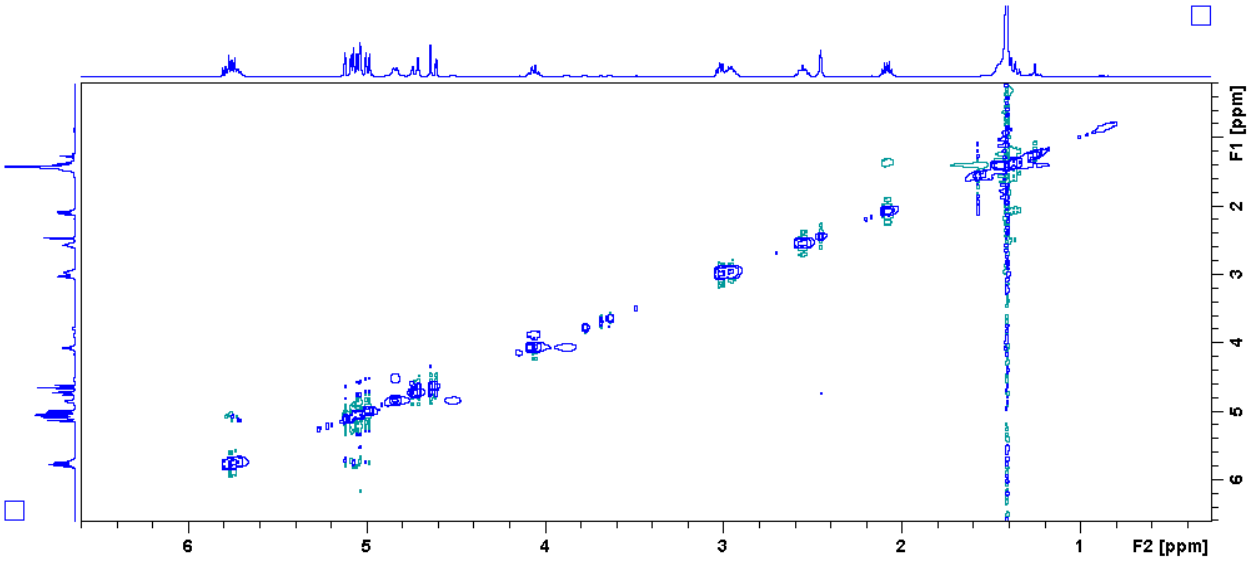
^{13}C (jmod) NMR spectrum:

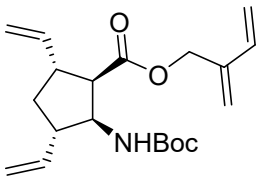


COSY spectrum:



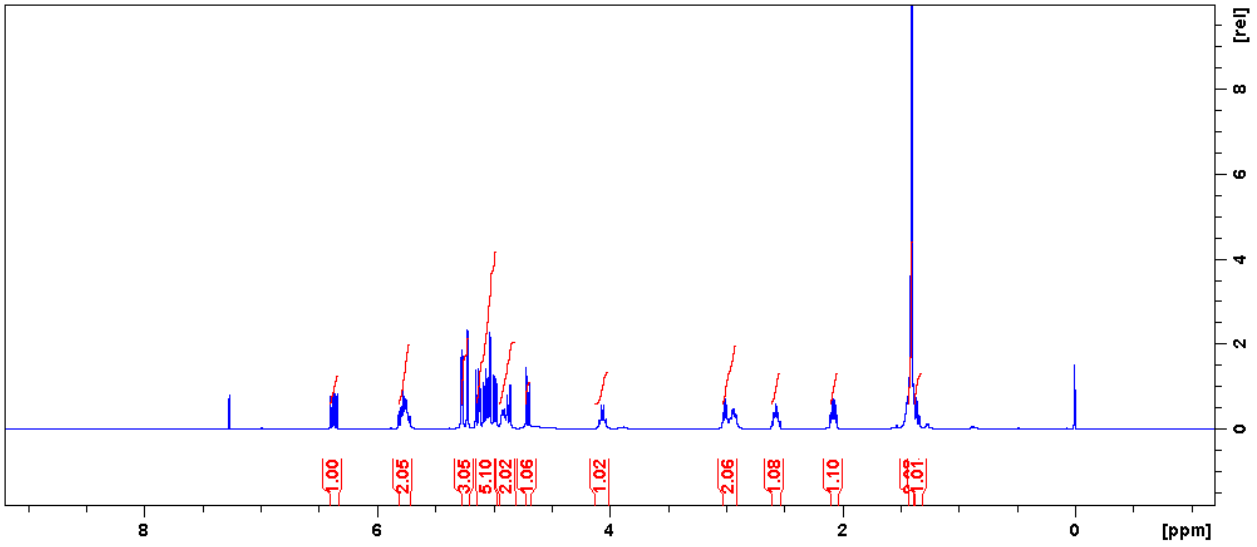
NOESY spectrum:



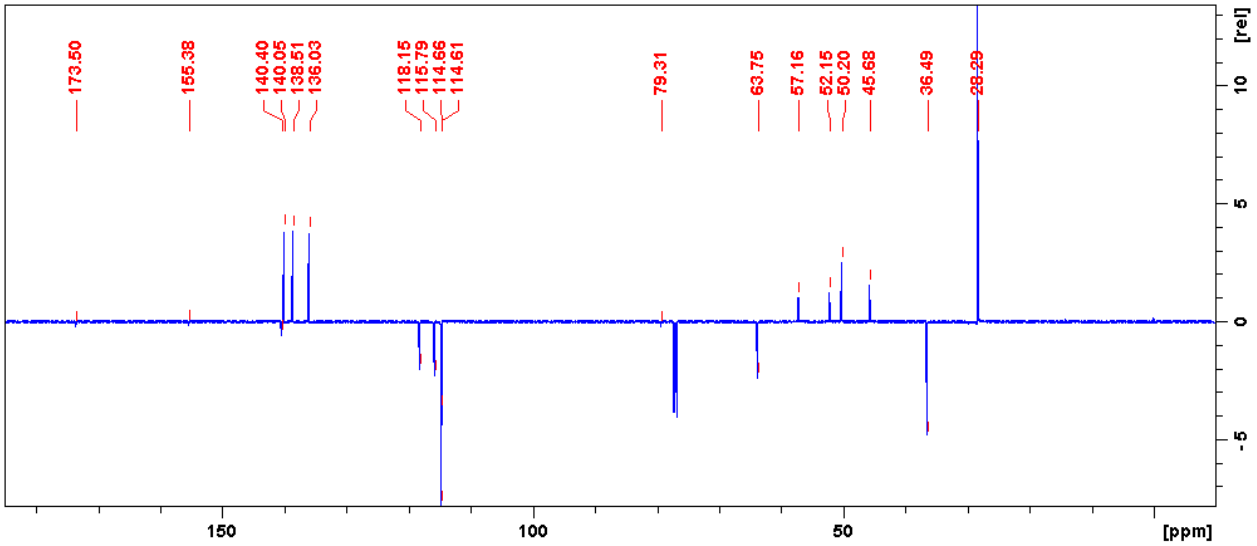


(1*R,2*S**,3*S**,5*R**)-2-methylenebut-3-en-1-yl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)**-34**

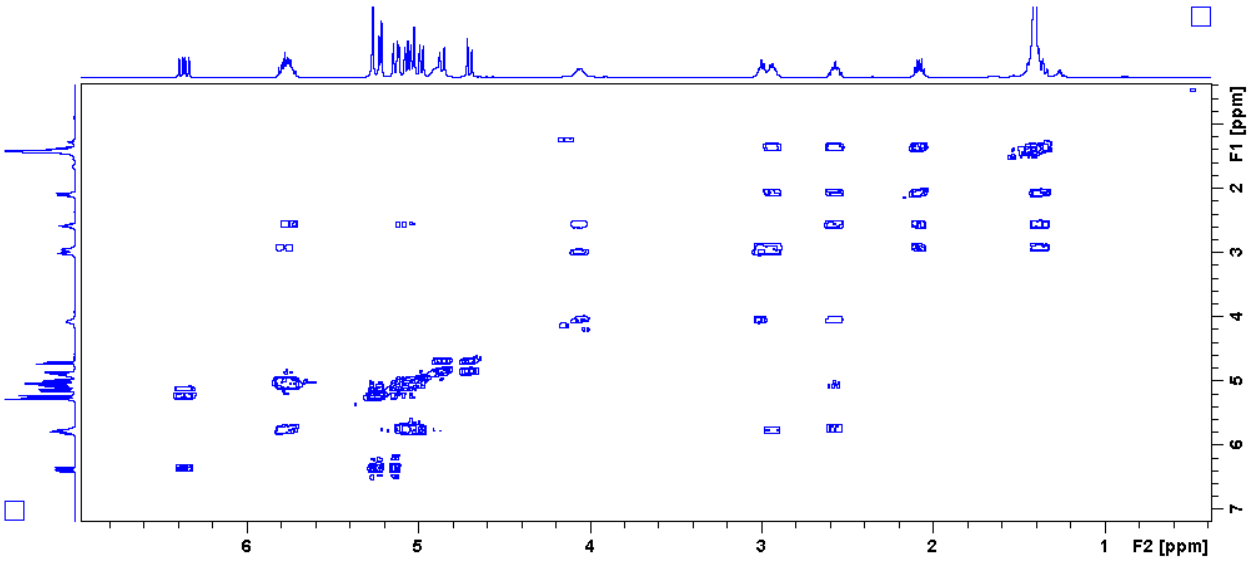
^{1}H NMR spectrum:



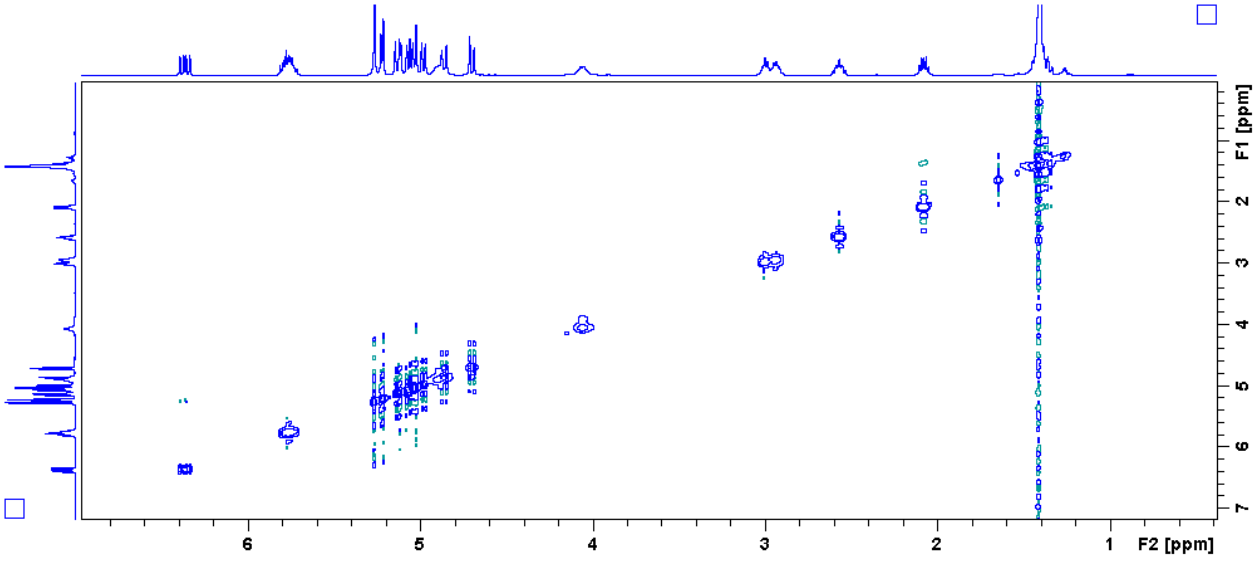
^{13}C (jmod) NMR spectrum:

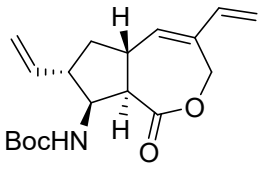


COSY spectrum:



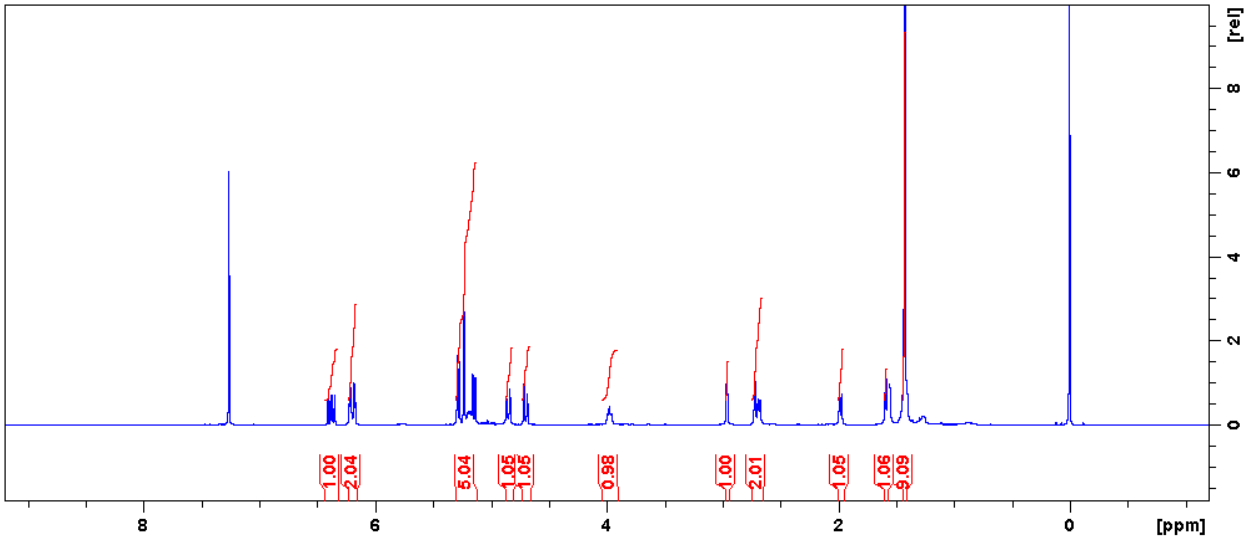
NOESY spectrum:



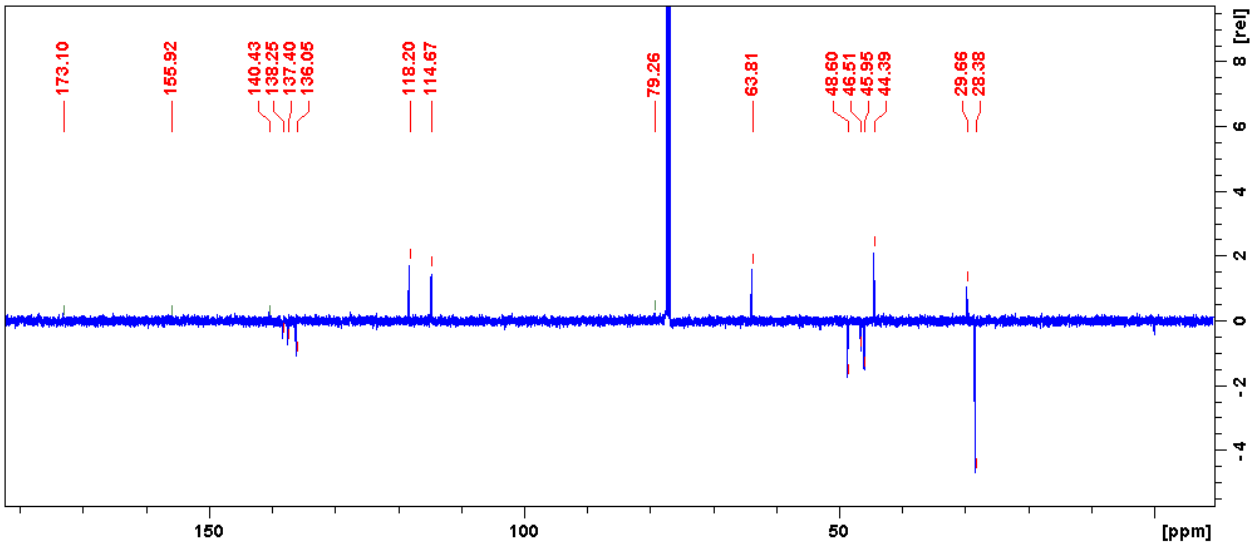


***tert*-Butyl ((5a*R**,7*S**,8*S**,8a*R**)-1-oxo-4,7-divinyl-3,5a,6,7,8,8a-hexahydro-1H-cyclopenta[*c*]oxepin-8-yl)carbamate, (±)-35**

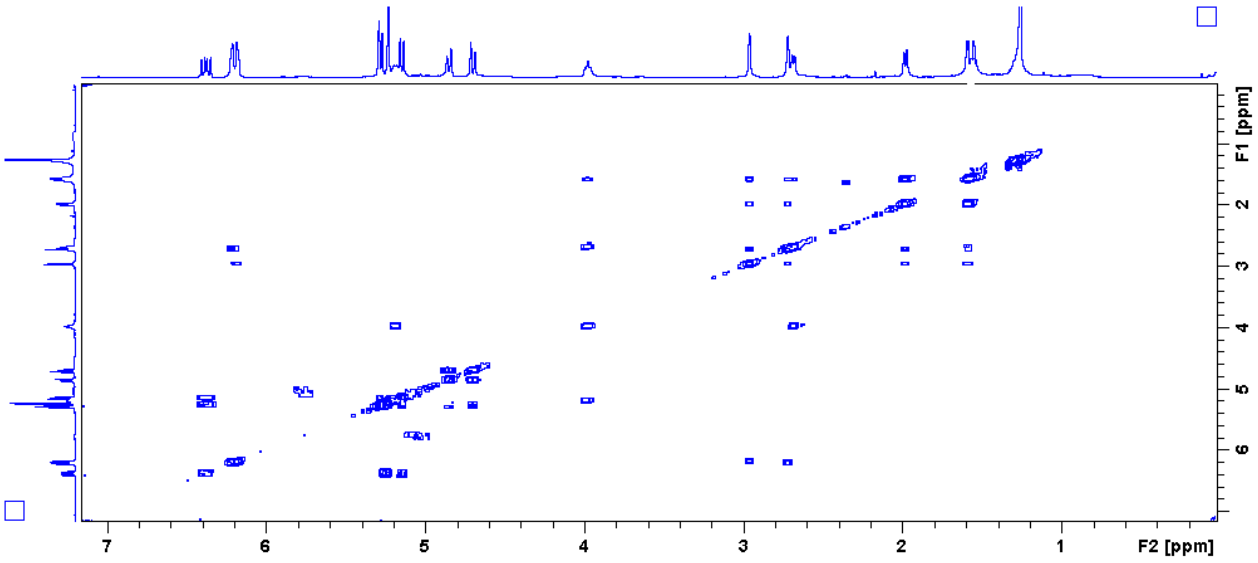
^{1}H NMR spectrum:



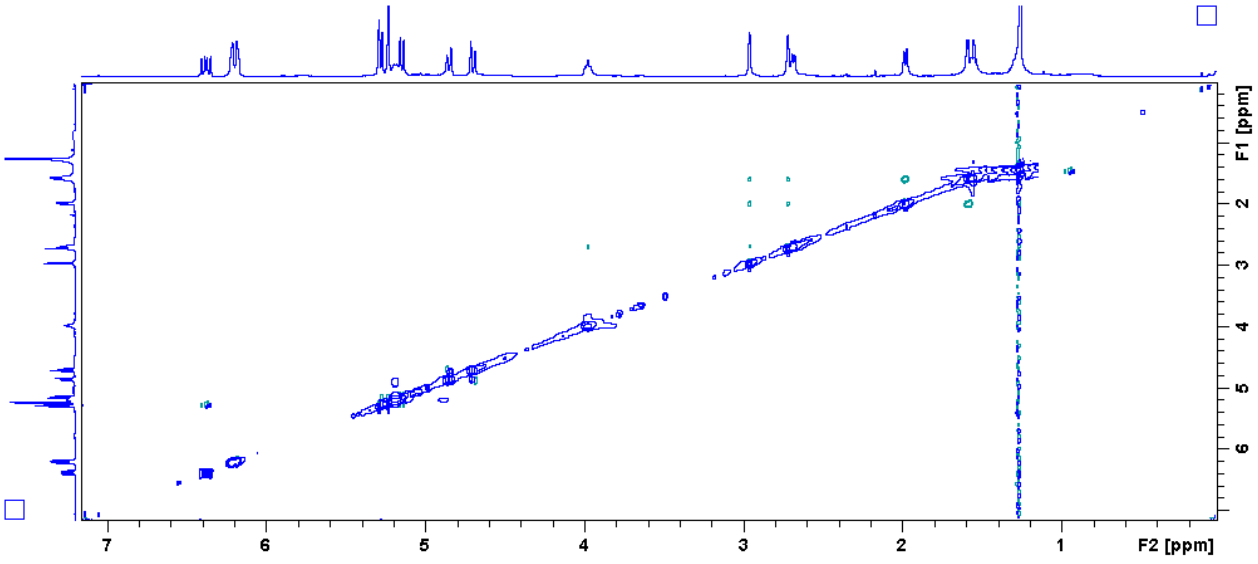
^{13}C (jmod) NMR spectrum:

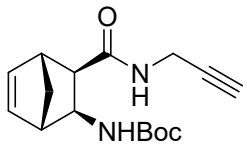


COSY spectrum:



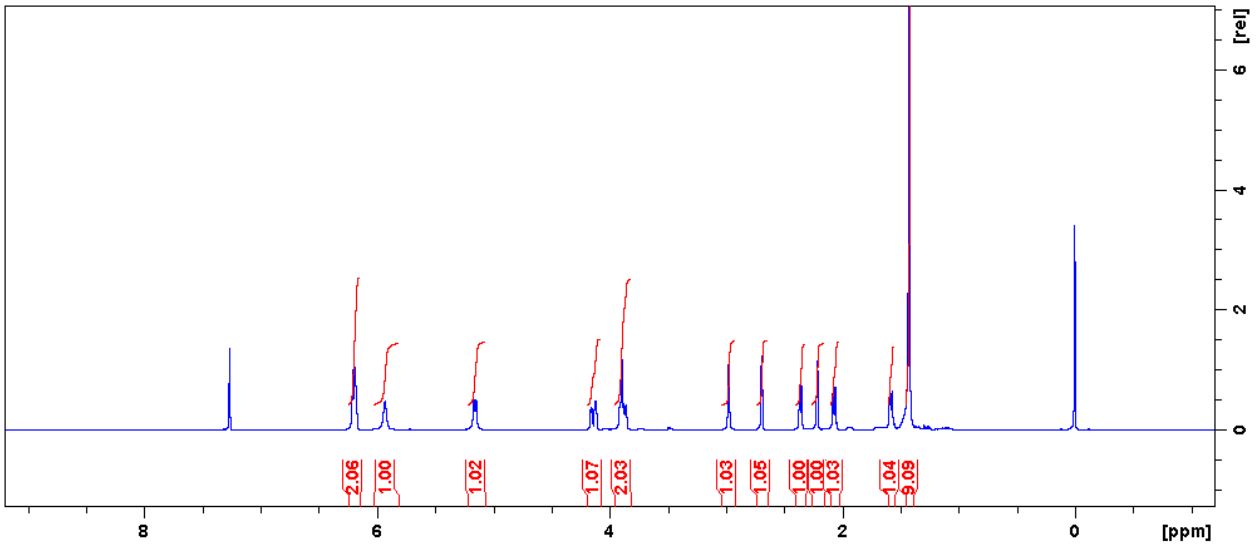
NOESY spectrum:



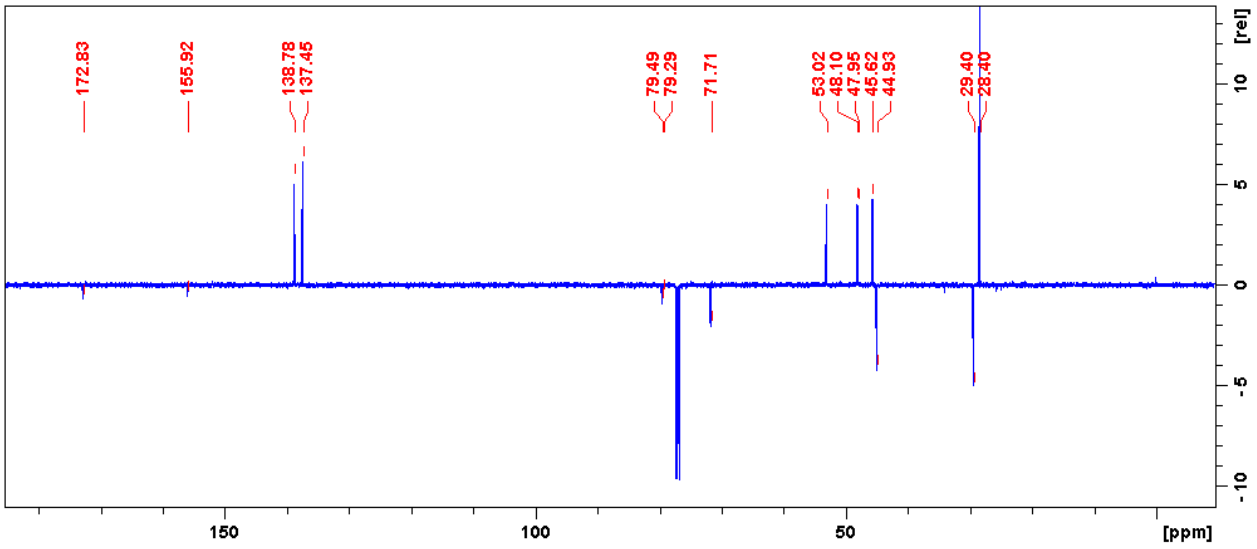


***tert*-Butyl ((1*S**,2*S**,3*R**,4*R**)-3-(prop-2-yn-1-ylcarbamoyl)bicyclo[2.2.1]hept-5-en-2-yl)carbamate, (±)-36**

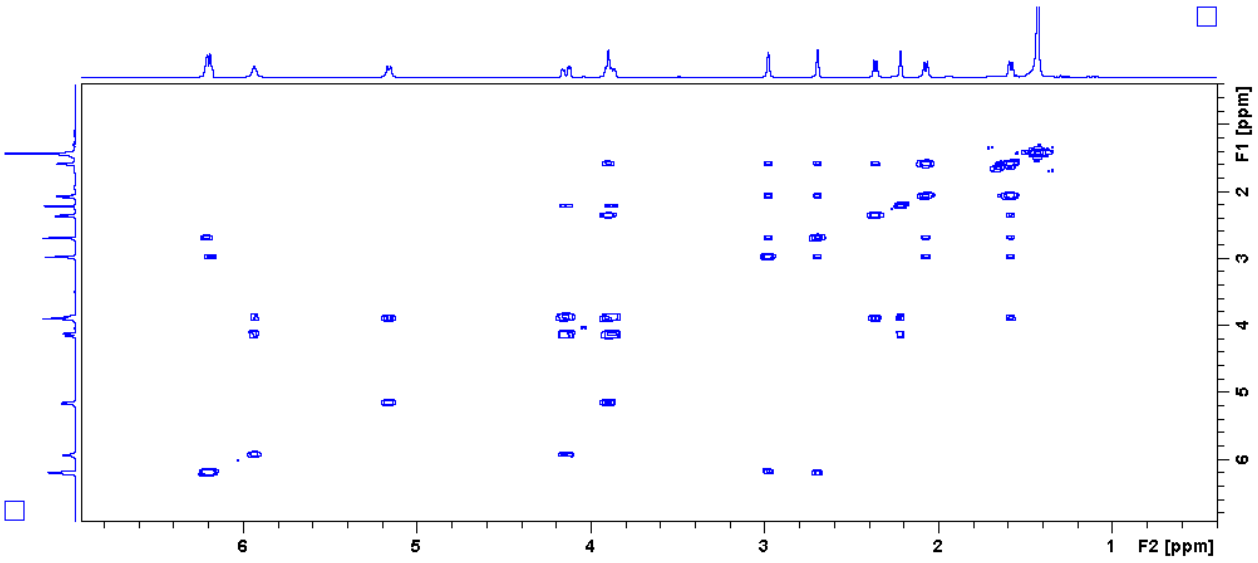
^{1}H NMR spectrum:



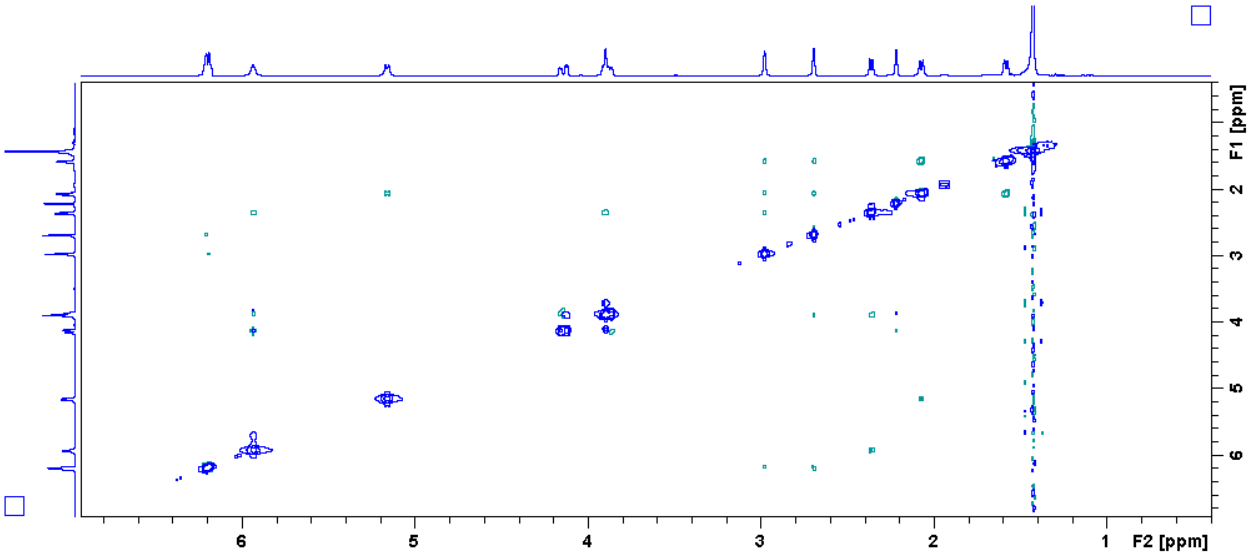
^{13}C (jmod) NMR spectrum:

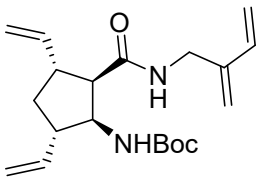


COSY spectrum:



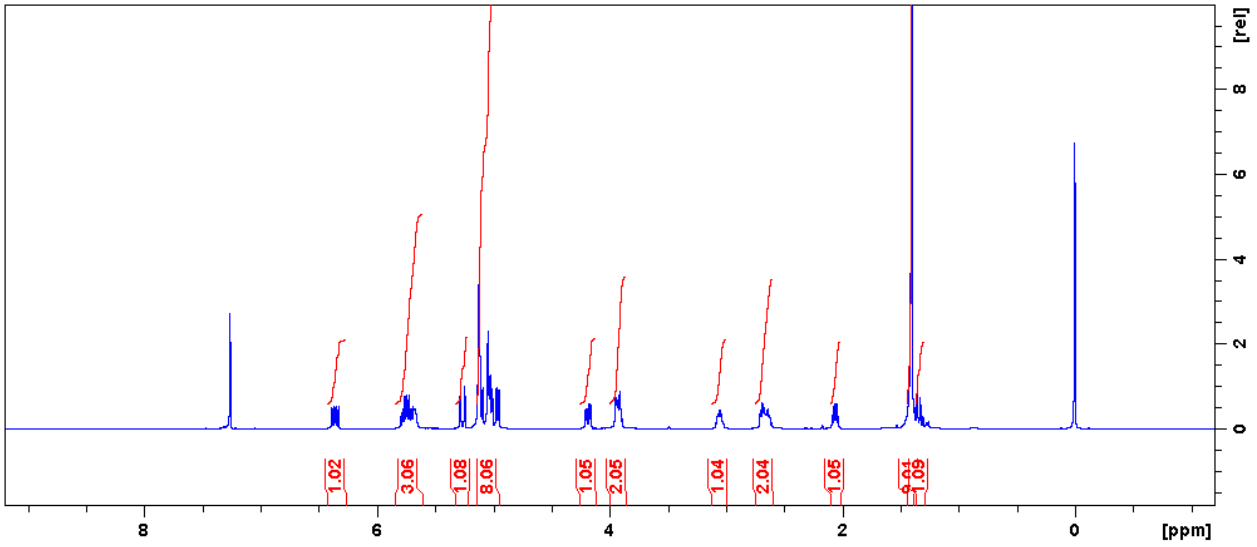
NOESY spectrum:



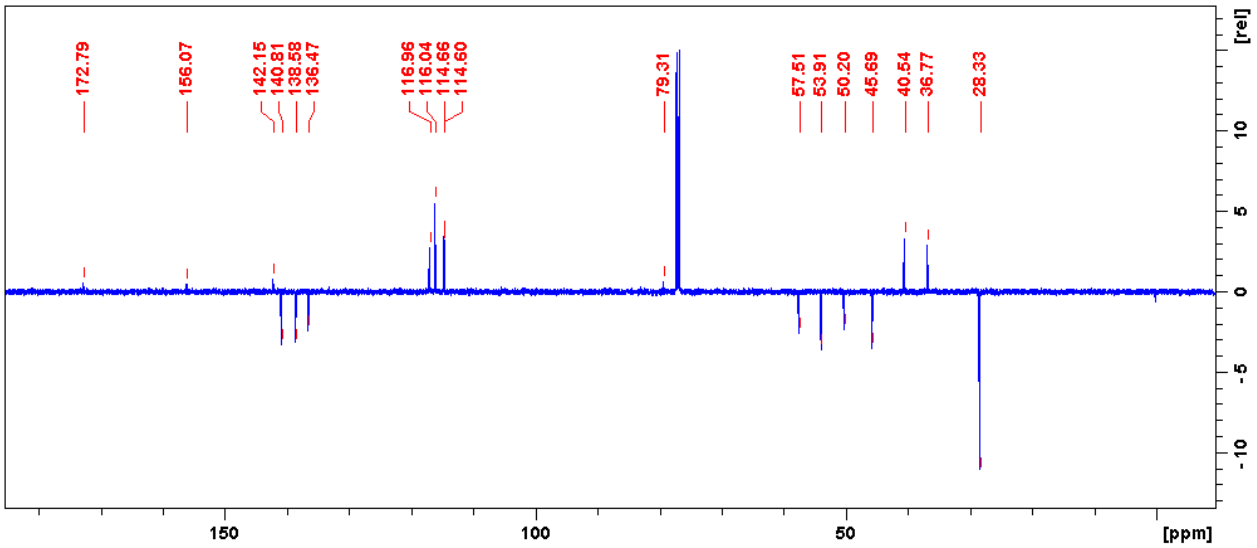


***tert*-Butyl ((1*S**,2*R**,3*R**,5*S**)-2-((2-methylenebut-3-en-1-yl)carbamoyl)-3,5-divinylcyclopentyl)carbamate,** (±)**-37**

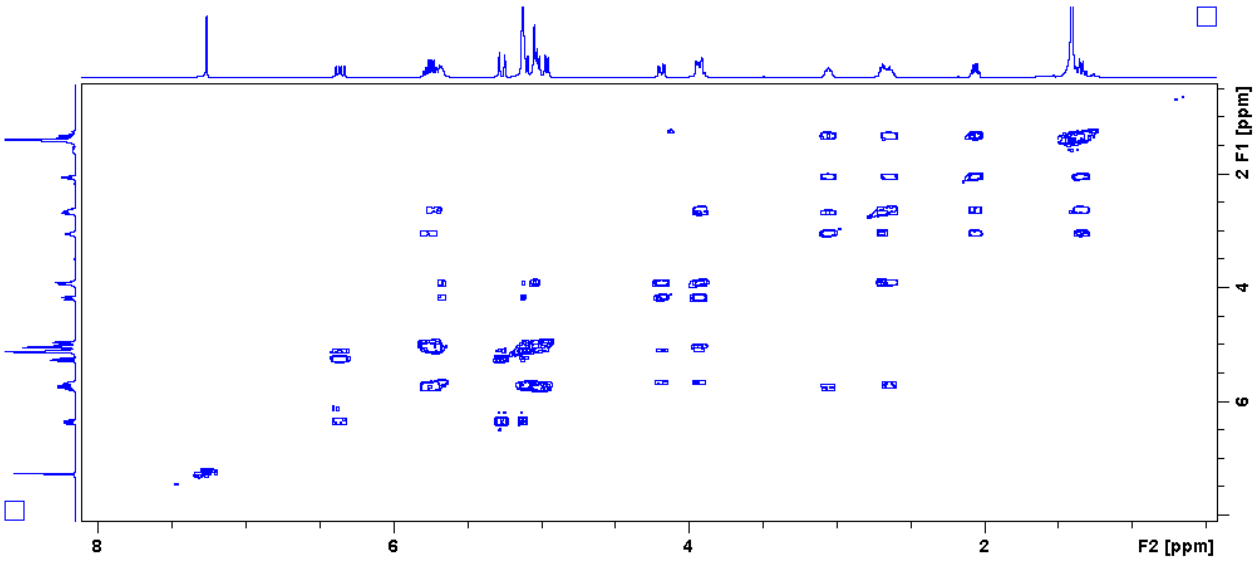
^{1}H NMR spectrum:



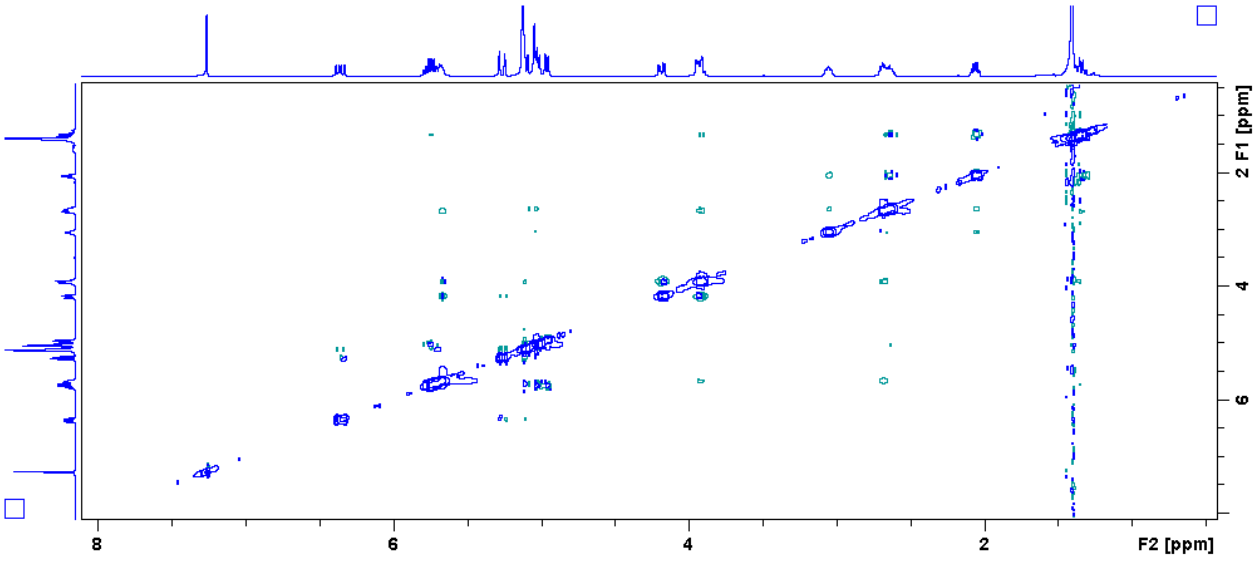
^{13}C (jmod) NMR spectrum:

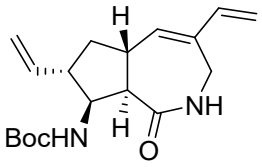


COSY spectrum:



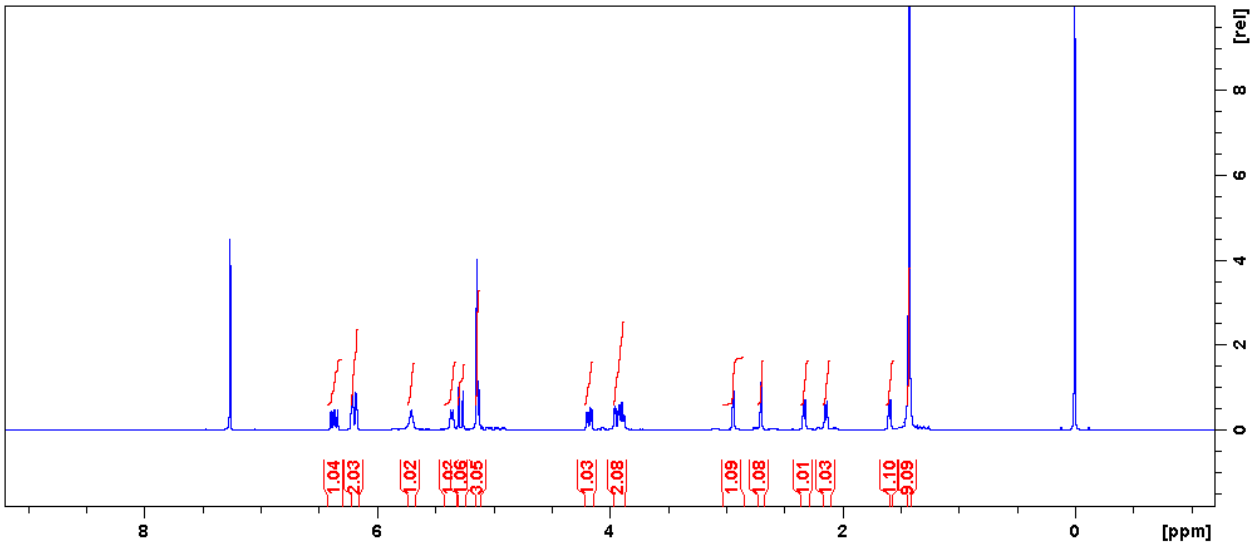
NOESY spectrum:



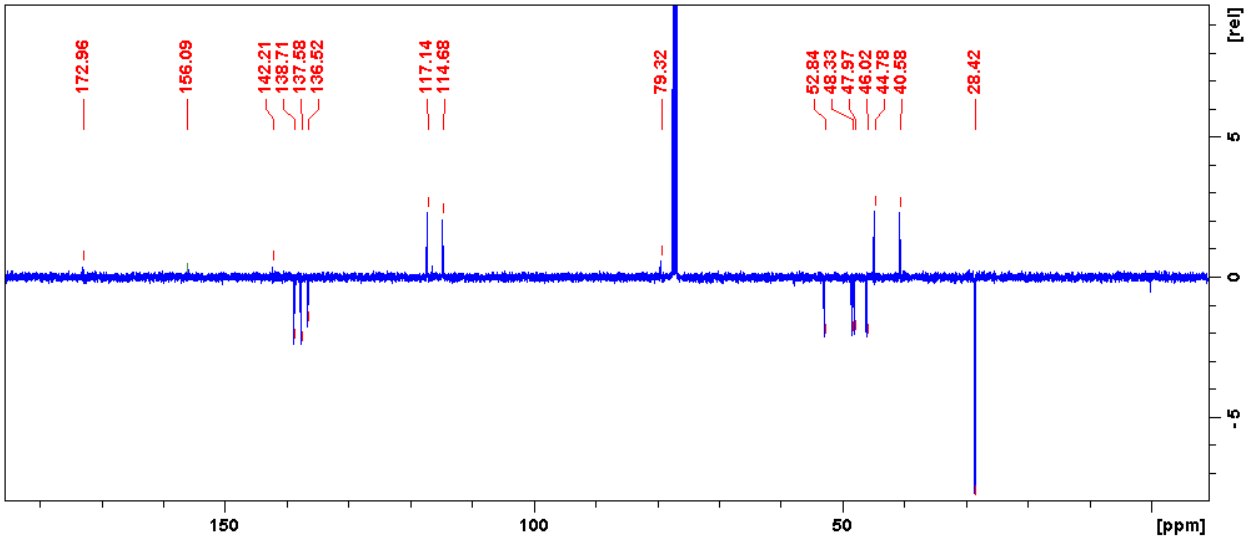


***tert*-Butyl ((5a*R**,7*S**,8*S**,8a*R**)-1-oxo-4,7-divinyl-1,2,3,5a,6,7,8,8a-octahydrocyclopenta[*c*]azepin-8-yl)carbamate, (±)-38**

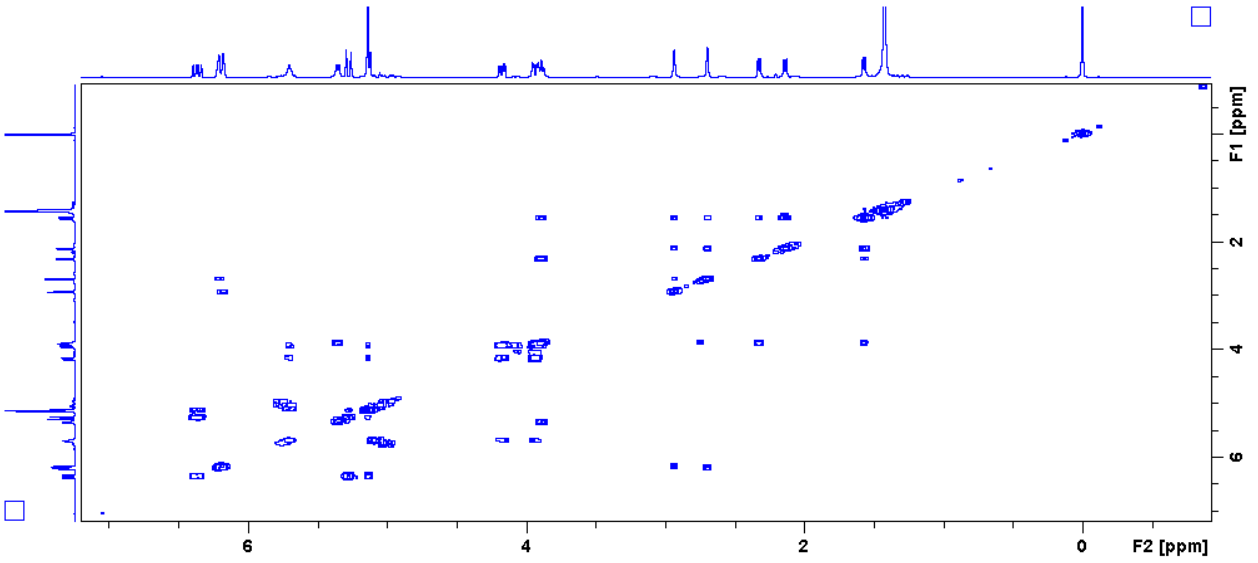
^{1}H NMR spectrum:



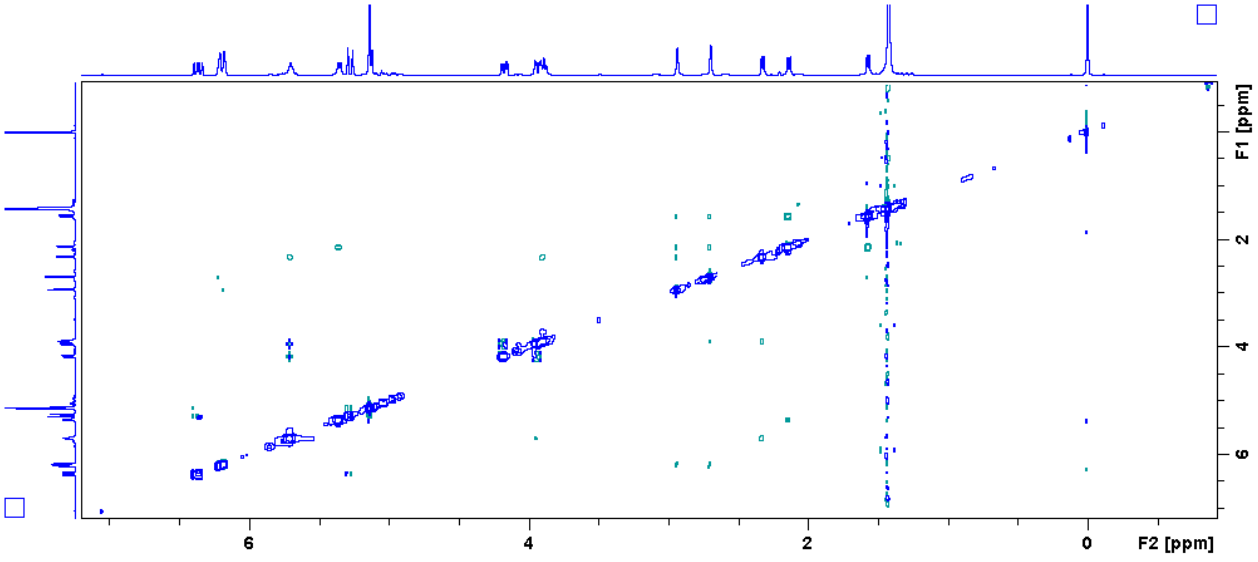
^{13}C (jmod) NMR spectrum:

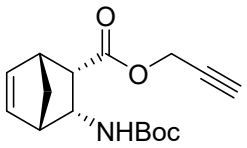


COSY spectrum:



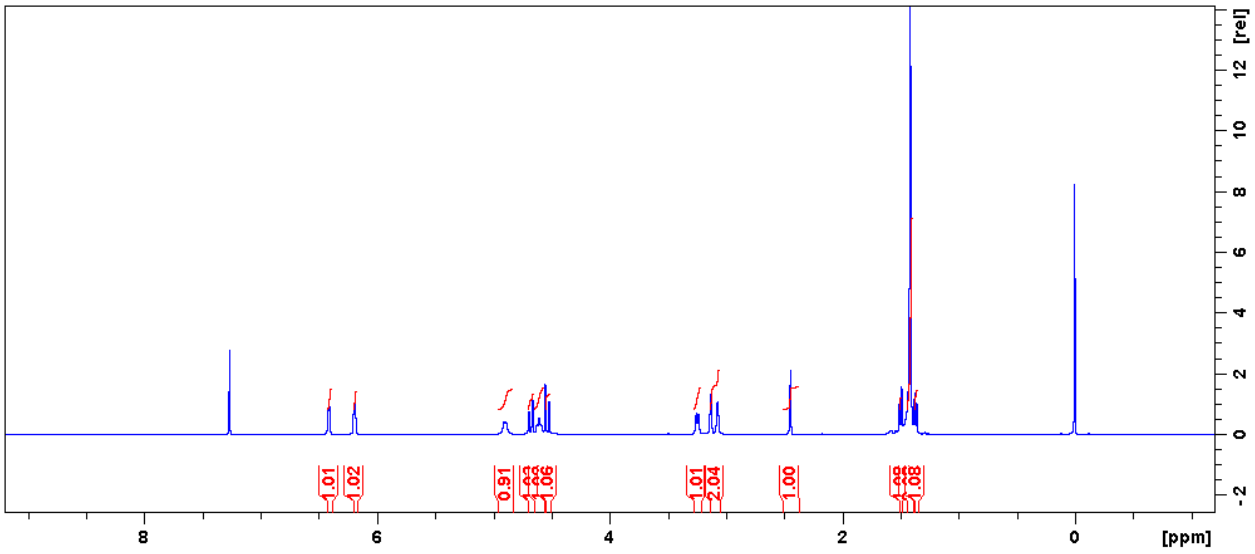
NOESY spectrum:



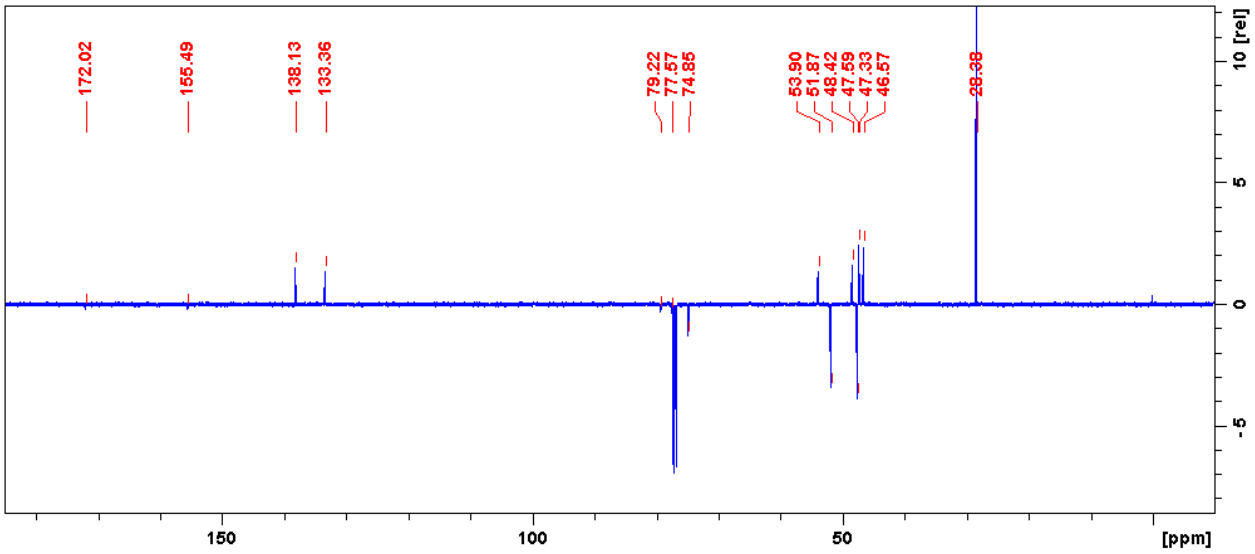


(1*R,2*S**,3*R**,4*S**)-prop-2-yn-1-yl 3-((*tert*-butoxycarbonyl)amino)bicyclo[2.2.1]hept-5-ene-2-carboxylate, (±)-39**

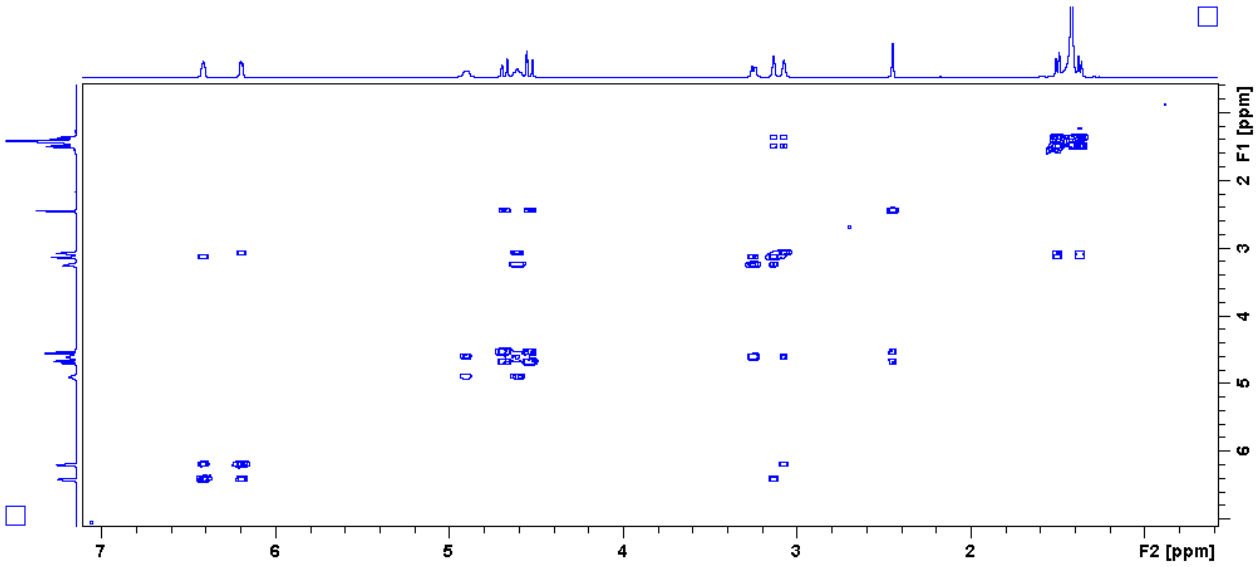
^{1}H NMR spectrum:



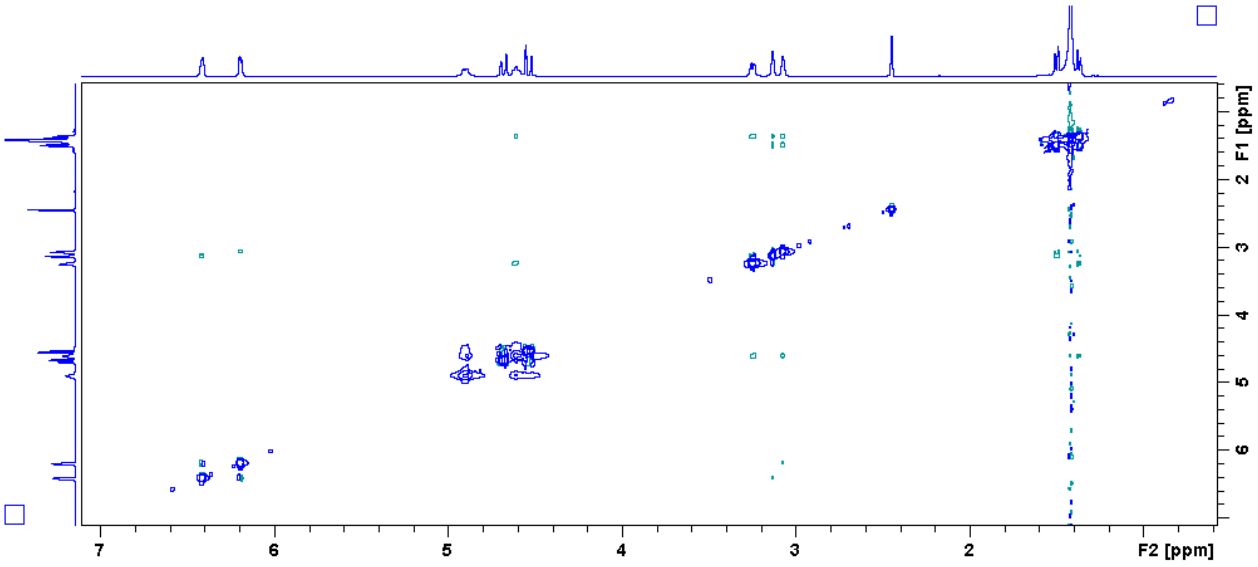
^{13}C (jmod) NMR spectrum:

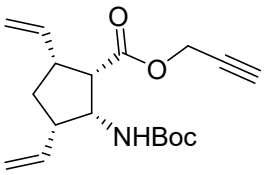


COSY spectrum:



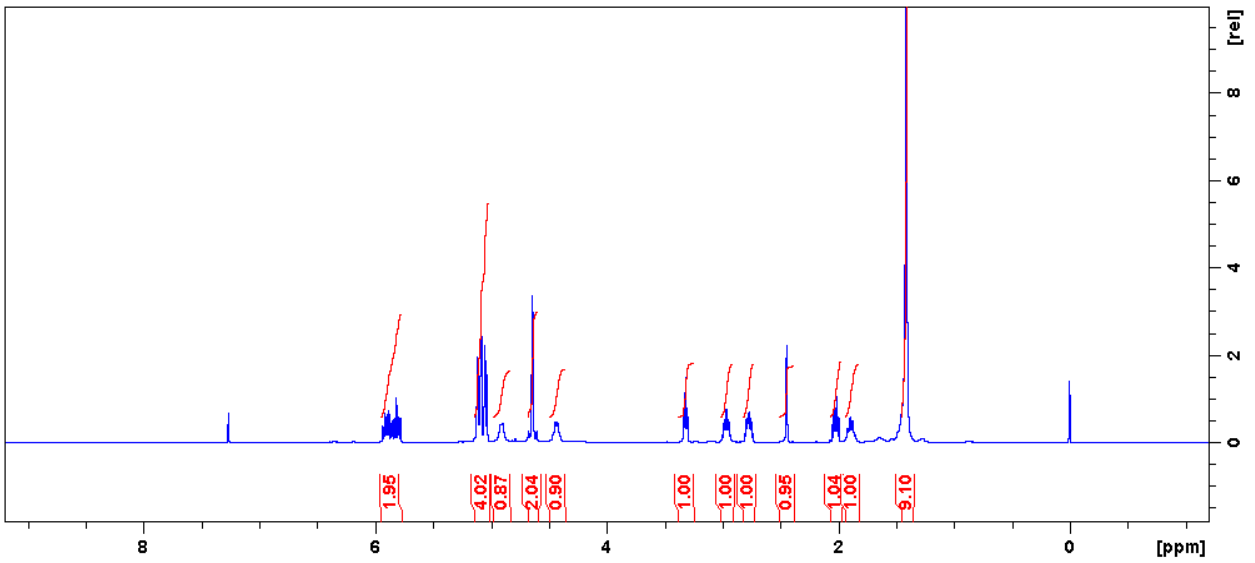
NOESY spectrum:



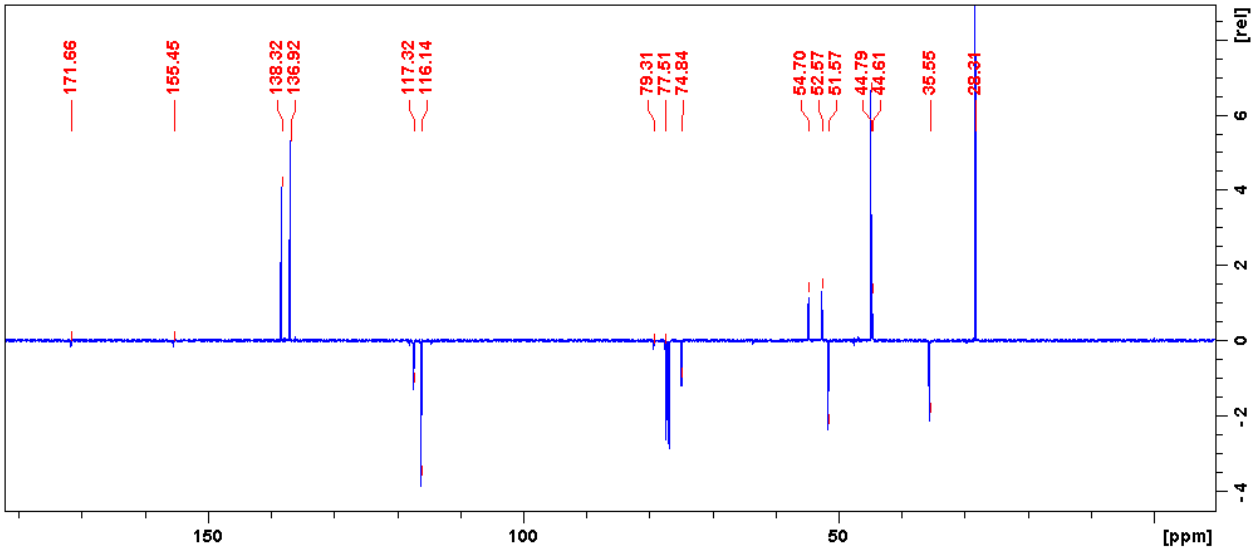


(1*S,2*R**,3*S**,5*R**)-prop-2-yn-1-yl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)**-40**

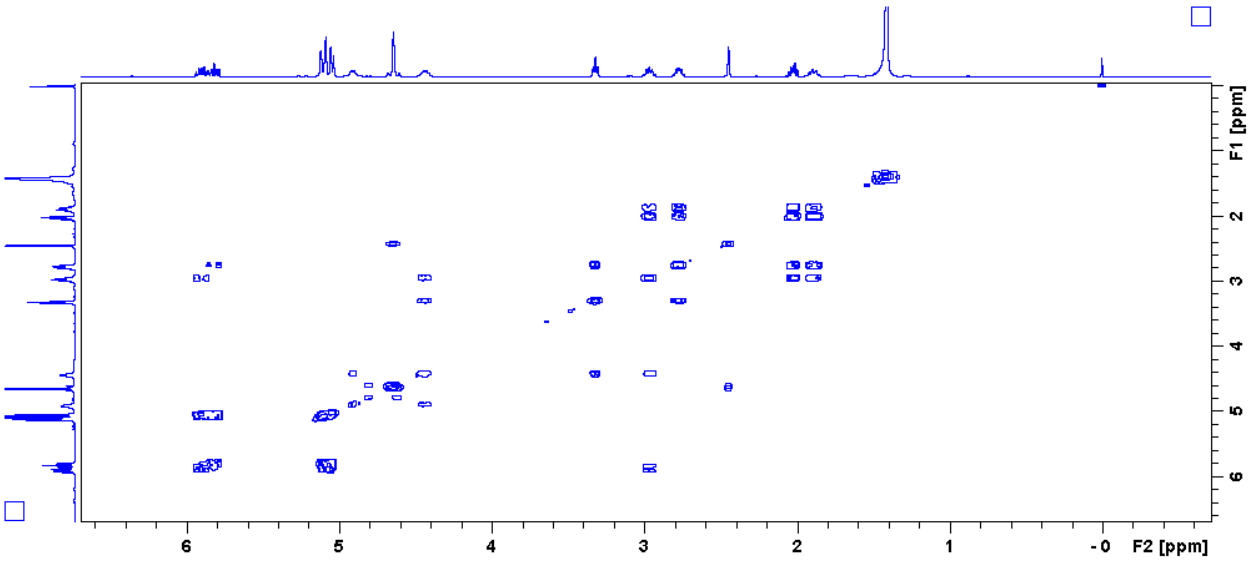
^{1}H NMR spectrum:



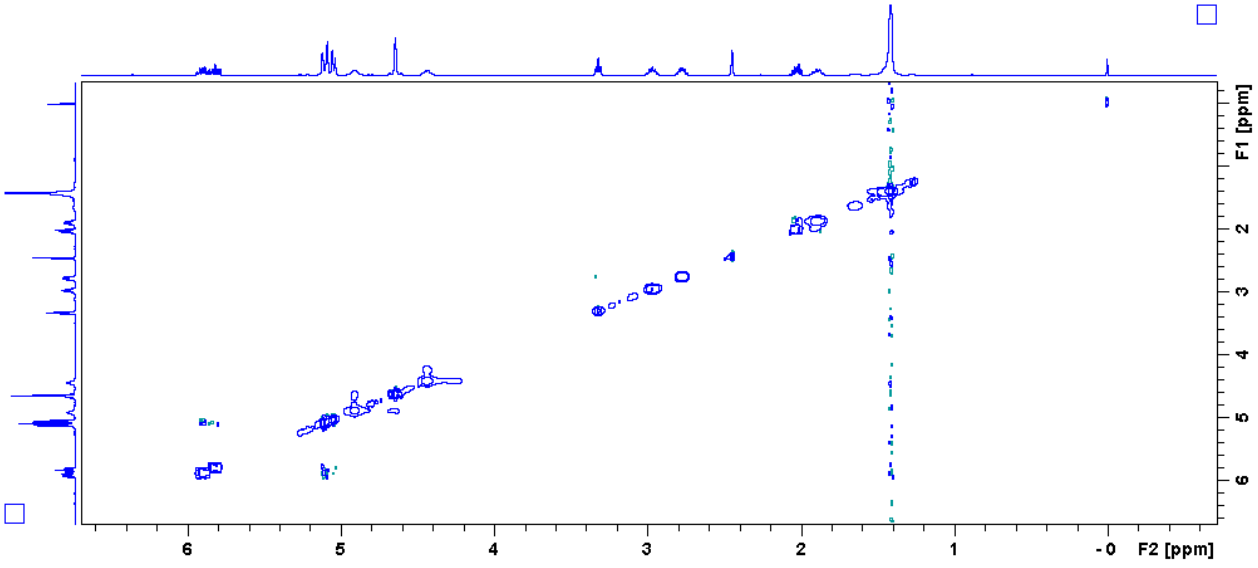
^{13}C (jmod) NMR spectrum:

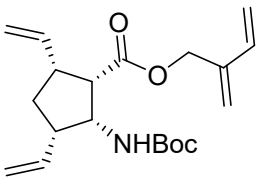


COSY spectrum:



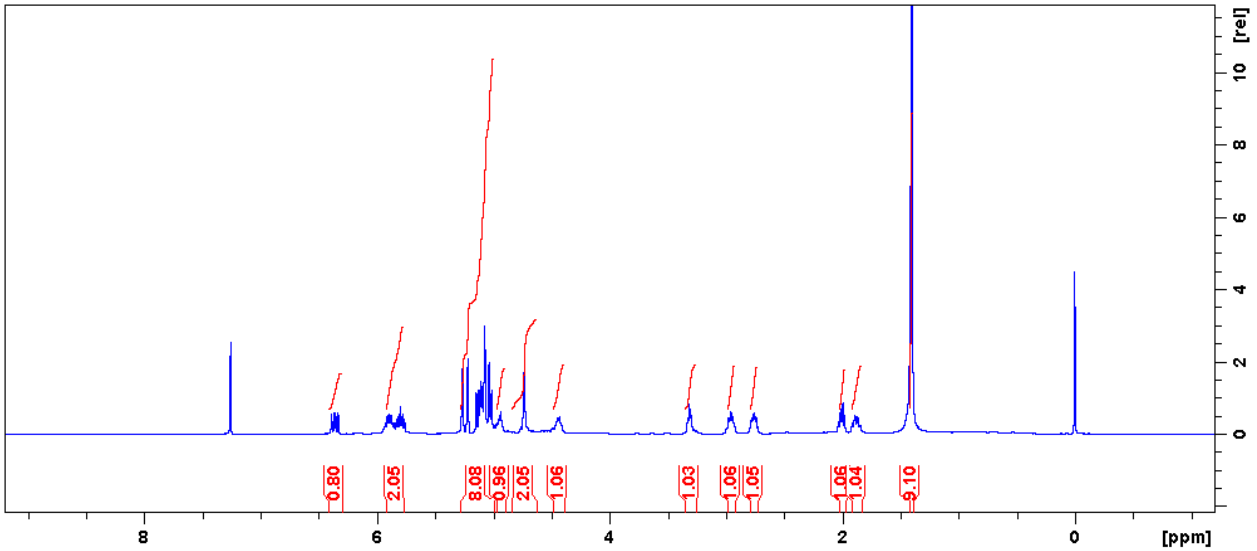
NOESY spectrum:



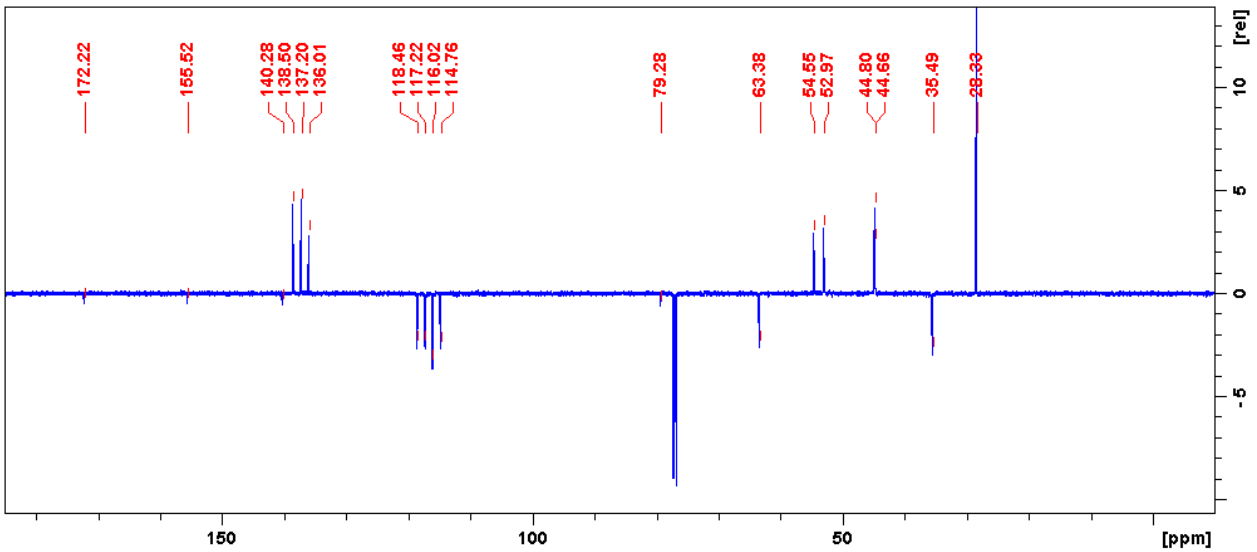


(1*S,2*R**,3*S**,5*R**)-2-methylenebut-3-en-1-yl 2-((*tert*-butoxycarbonyl)amino)-3,5-divinylcyclopentanecarboxylate,** (±)**-41**

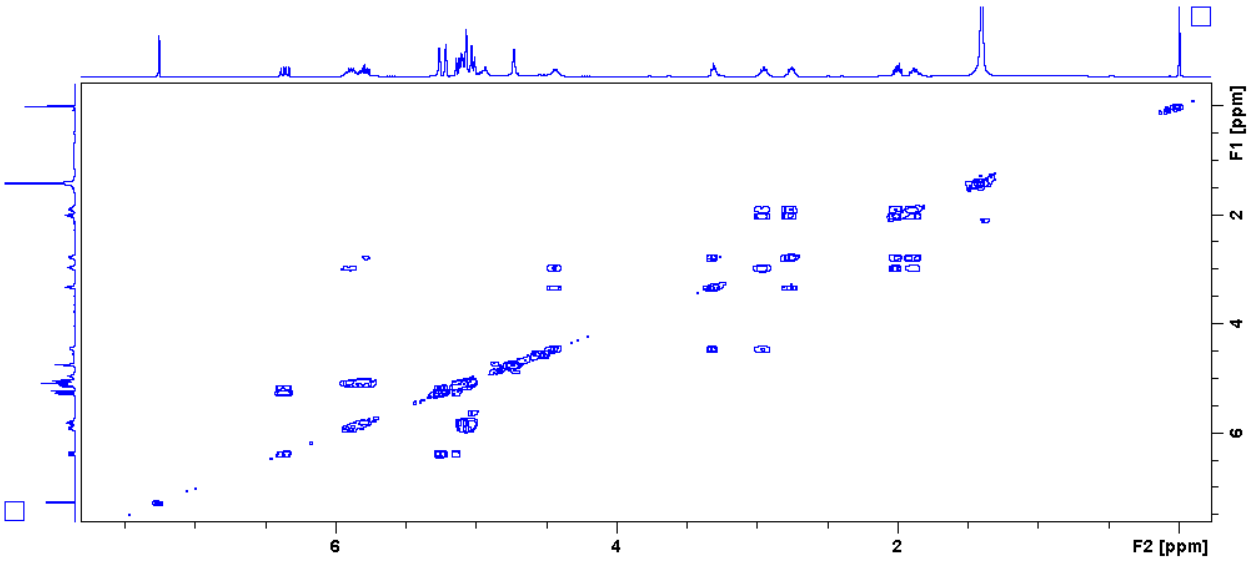
^{1}H NMR spectrum:



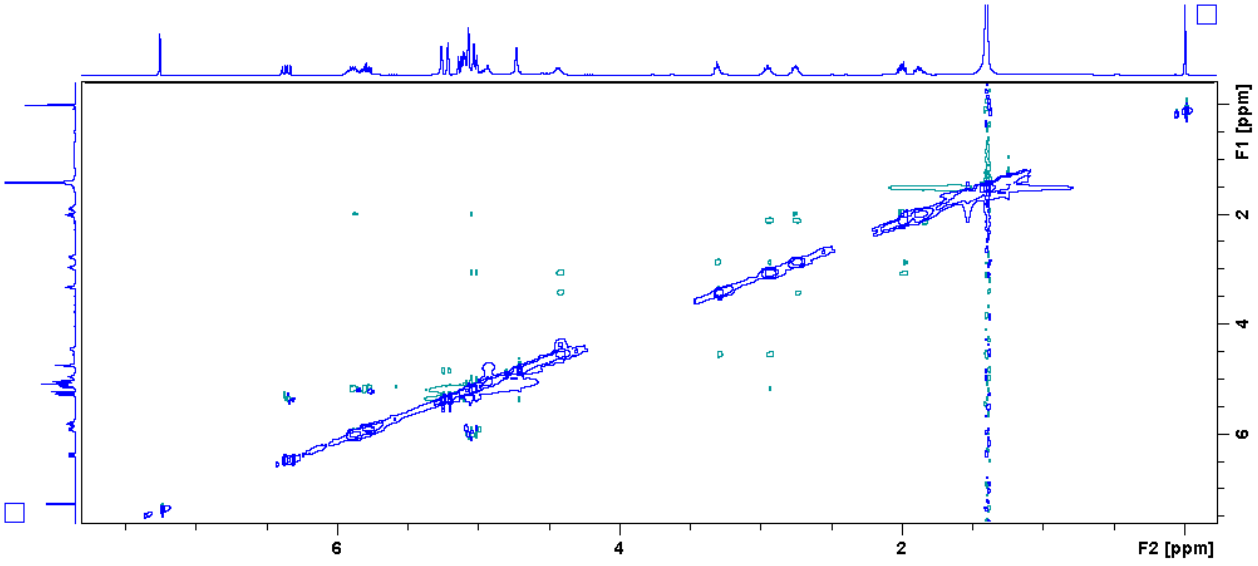
^{13}C (jmod) NMR spectrum:

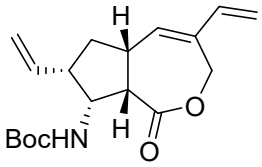


COSY spectrum:



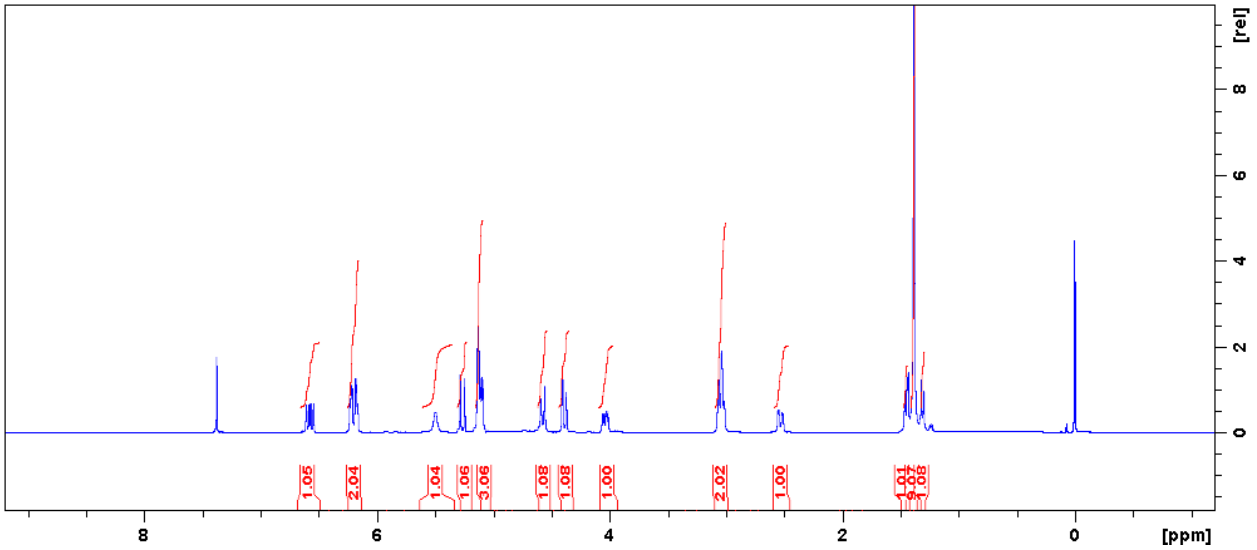
NOESY spectrum:



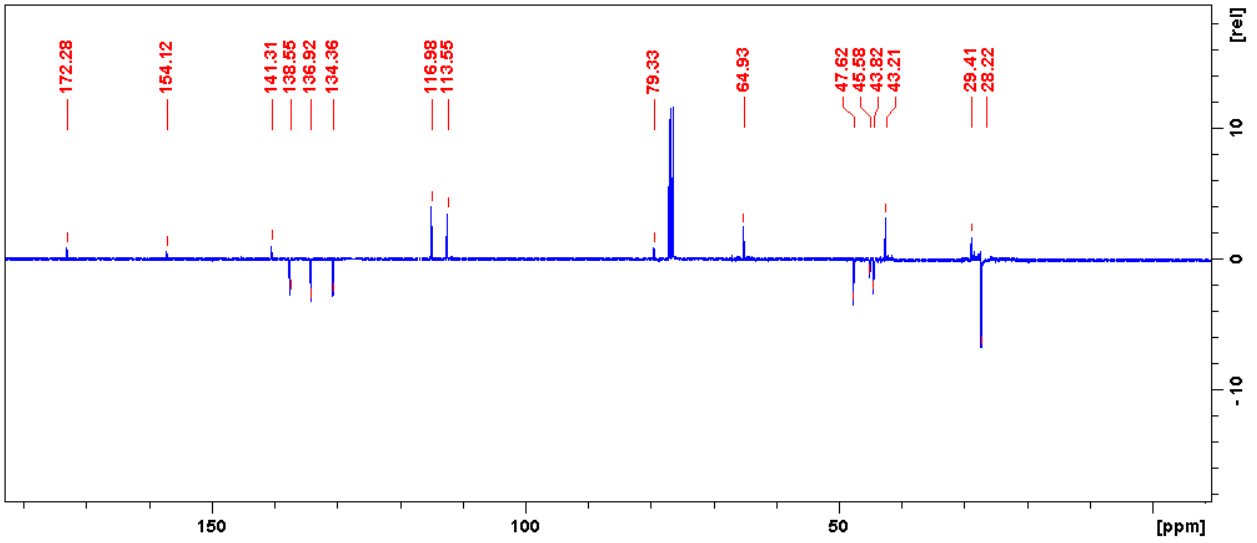


***tert*-Butyl ((5a*R**,7*S**,8*R**,8a*S**)-1-oxo-4,7-divinyl-3,5a,6,7,8,8a-hexahydro-1H-cyclopenta[*c*]oxepin-8-yl)carbamate, (±)-42**

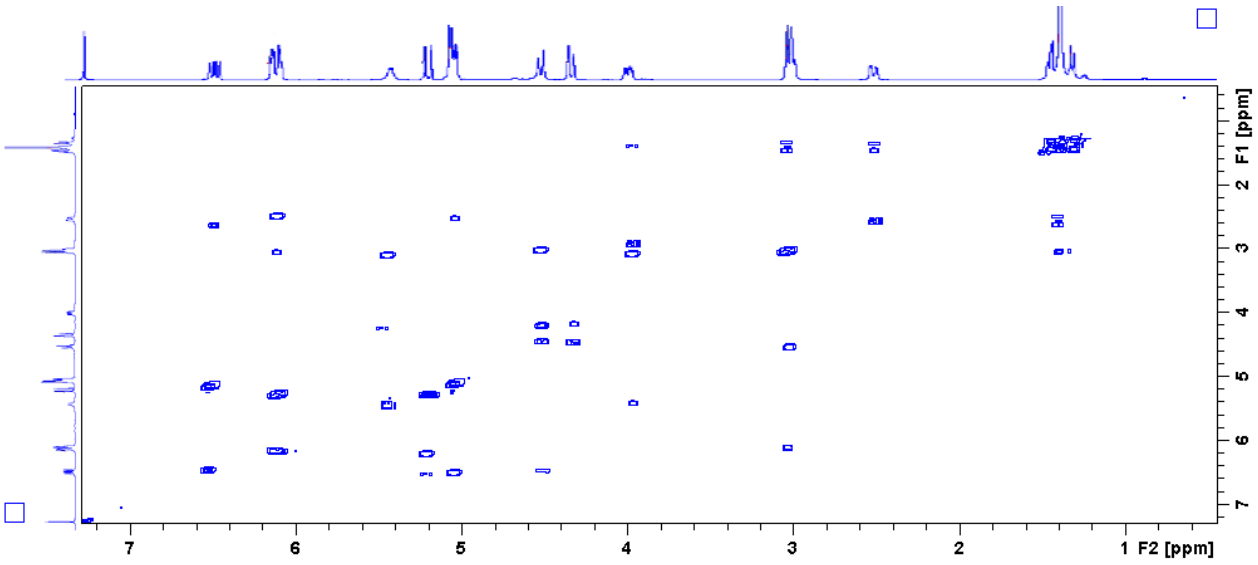
^{1}H NMR spectrum:



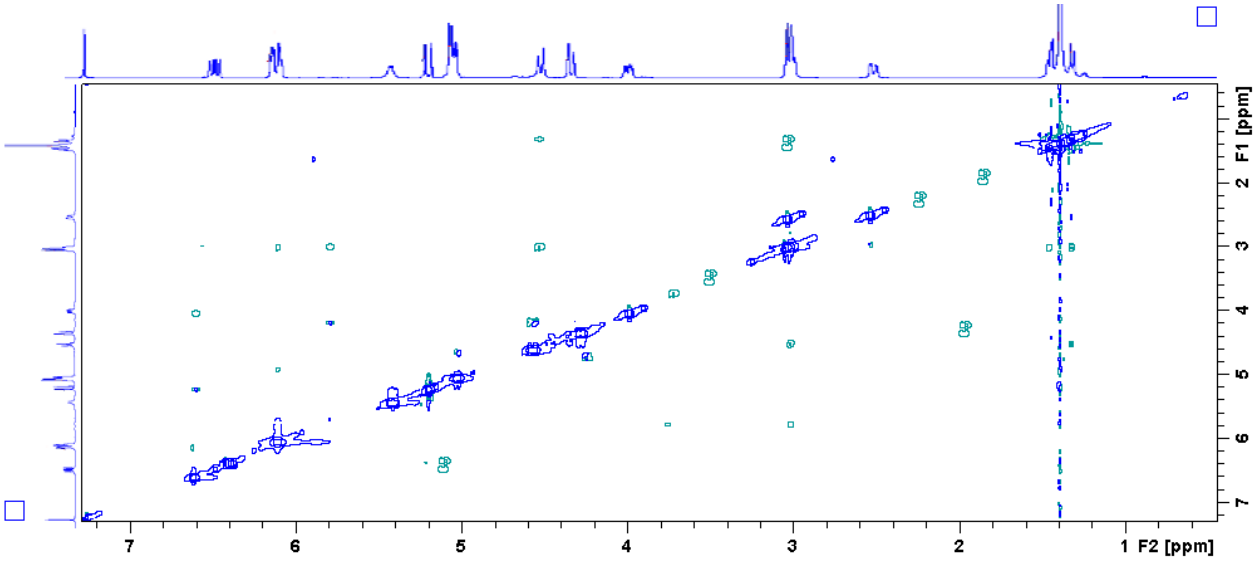
^{13}C (jmod) NMR spectrum:

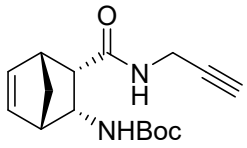


COSY spectrum:



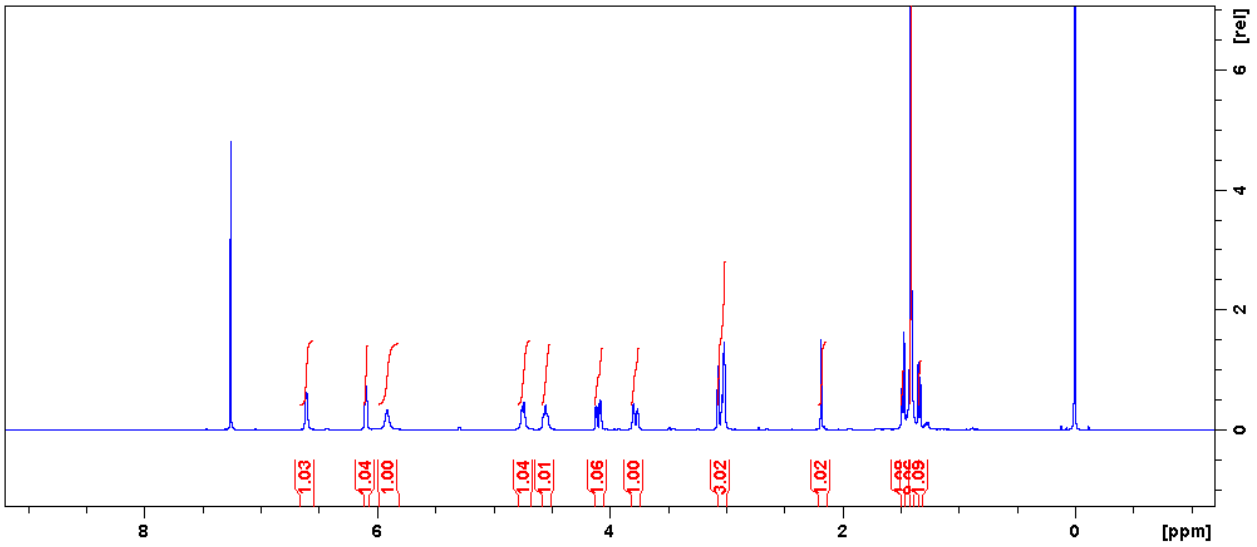
NOESY spectrum:



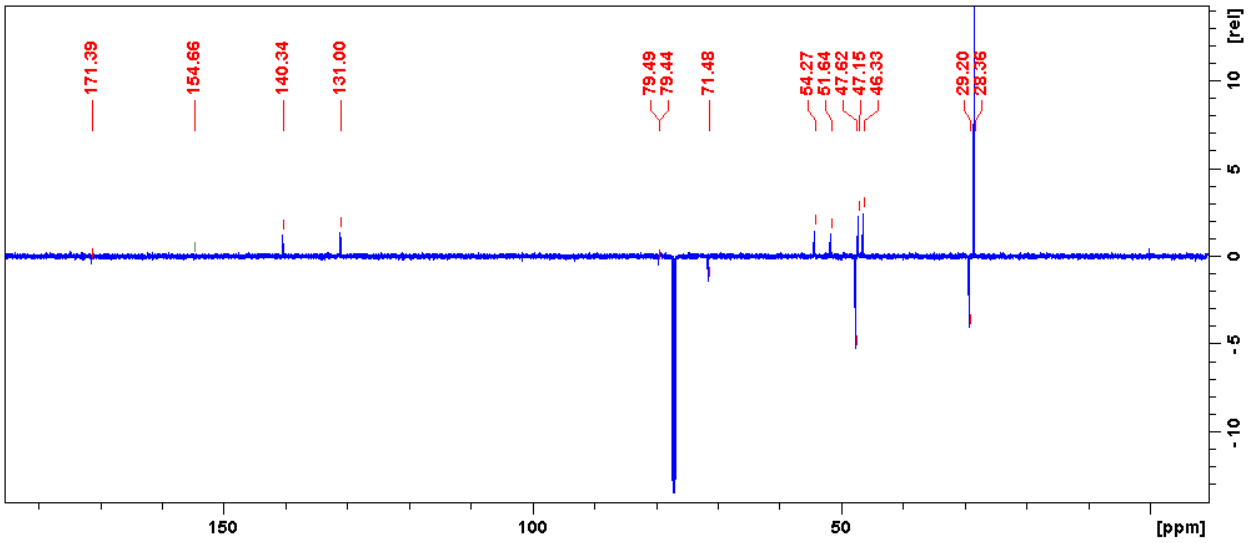


***tert*-Butyl ((1*S**,2*R**,3*S**,4*R**)-3-(prop-2-yn-1-ylcarbamoyl)bicyclo[2.2.1]hept-5-en-2-yl)carbamate, (±)-43**

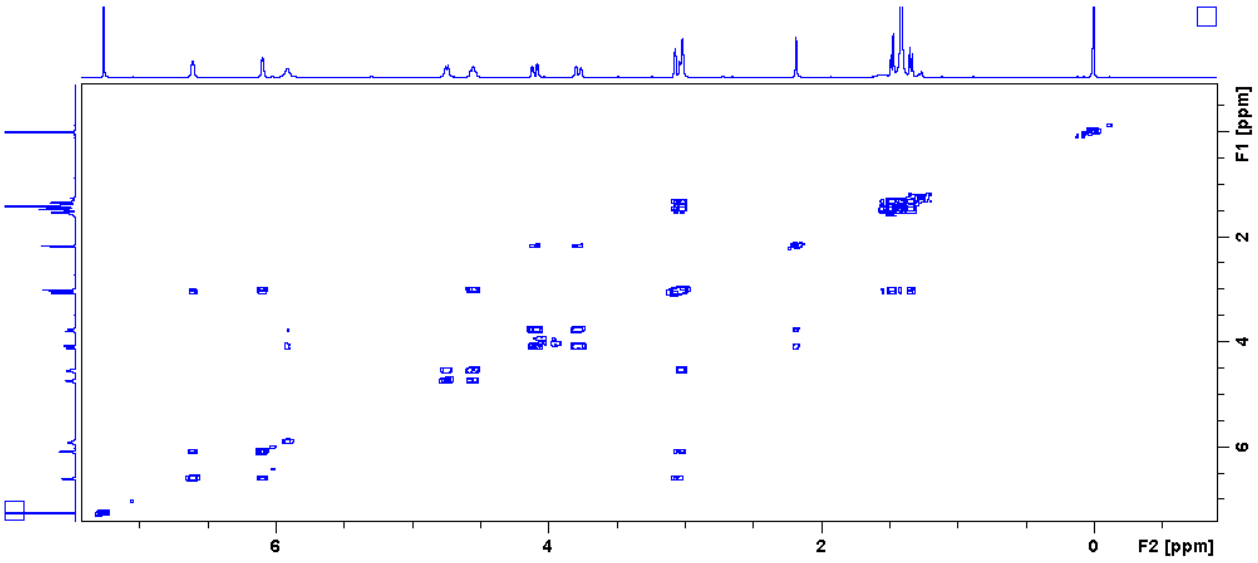
^{1}H NMR spectrum:



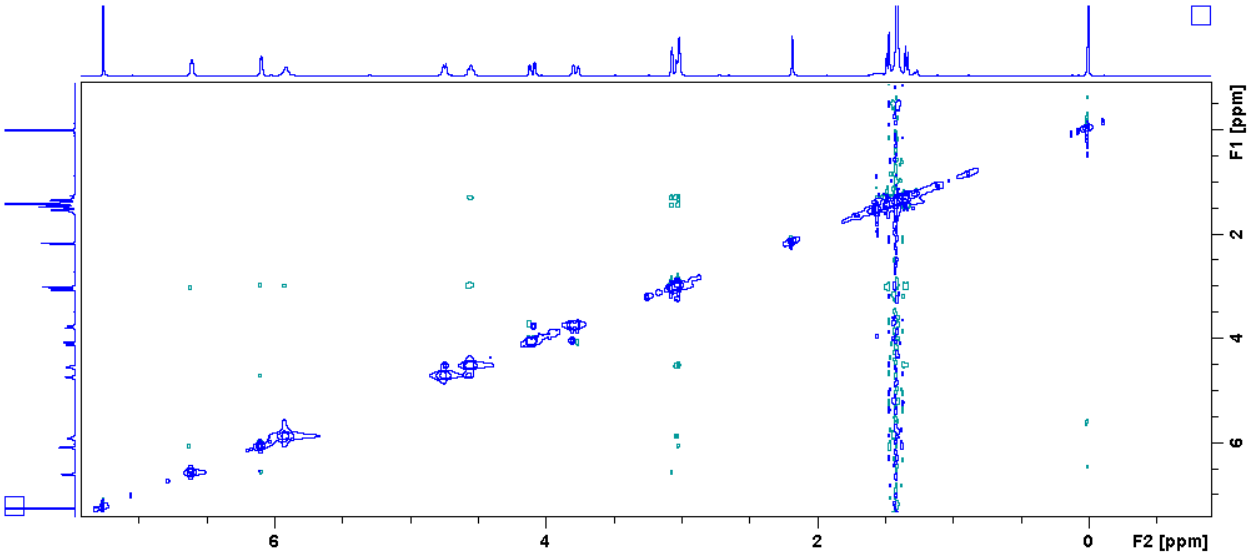
^{13}C (jmod) NMR spectrum:

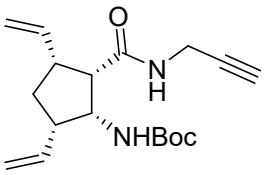


COSY spectrum:



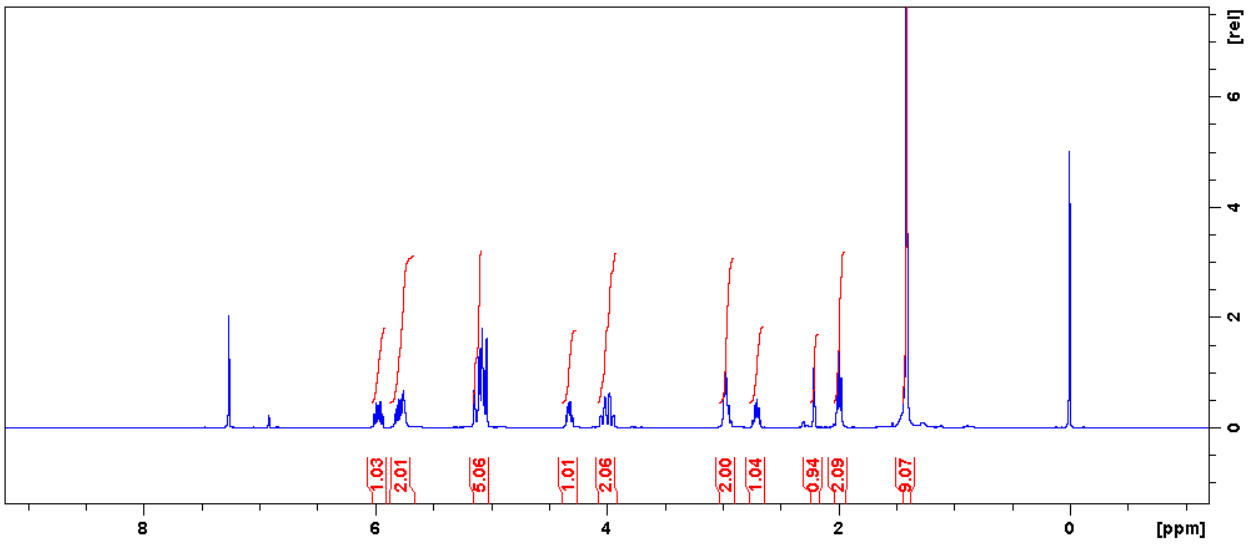
NOESY spectrum:



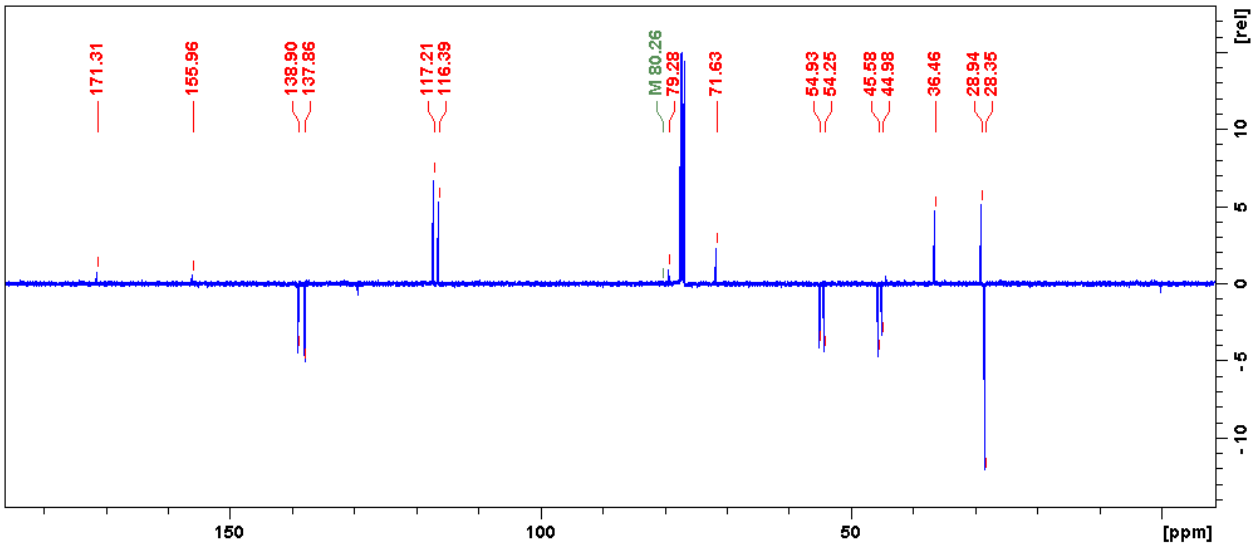


***tert*-Butyl ((1*R**,2*S**,3*R**,5*S**)-2-(prop-2-yn-1-ylcarbamoyl)-3,5-divinylcyclopentyl)carbamate, (±)-44**

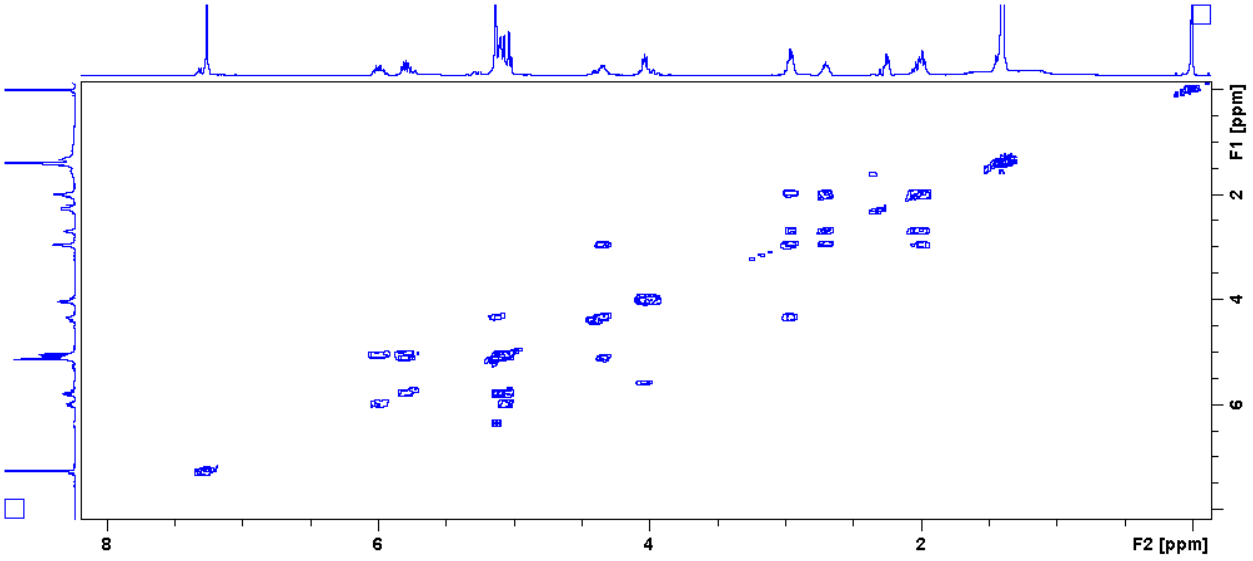
^{1}H NMR spectrum:



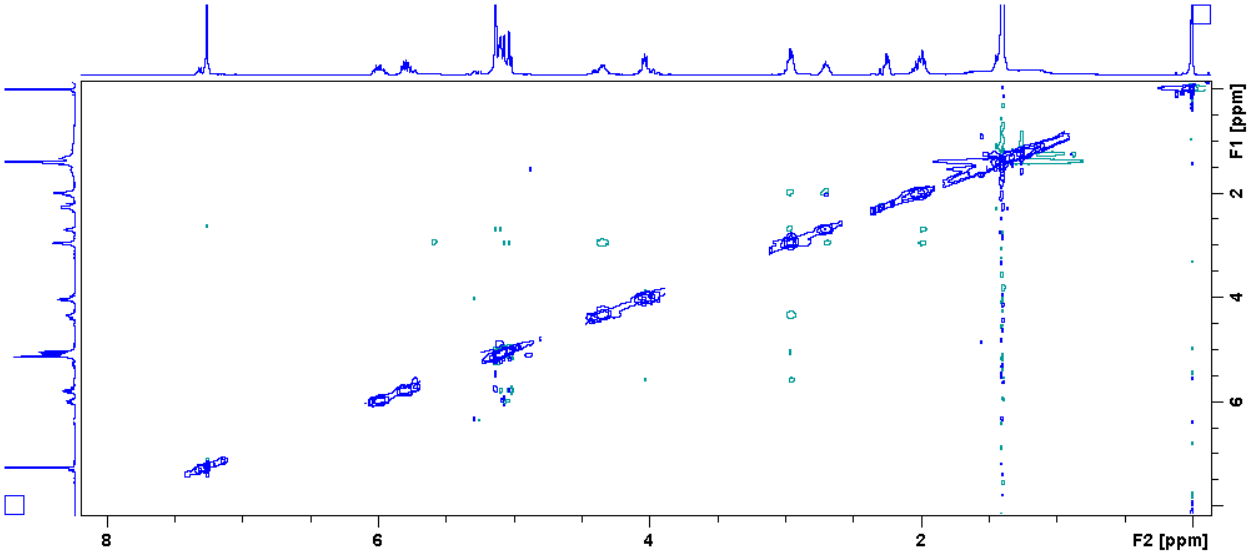
^{13}C (jmod) NMR spectrum:

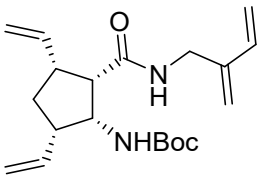


COSY spectrum:



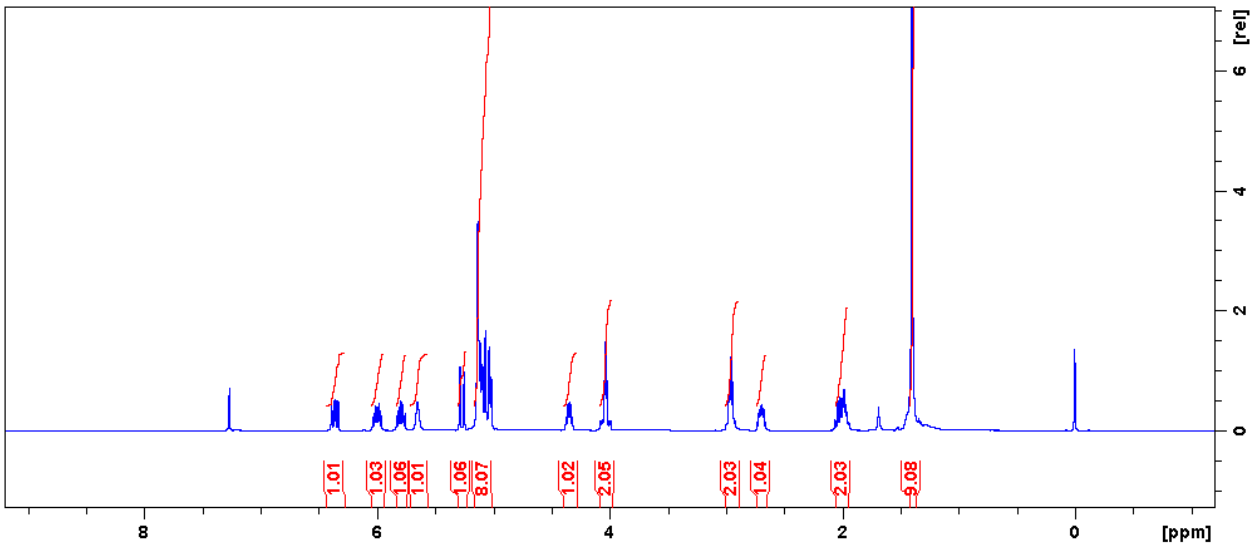
NOESY spectrum:



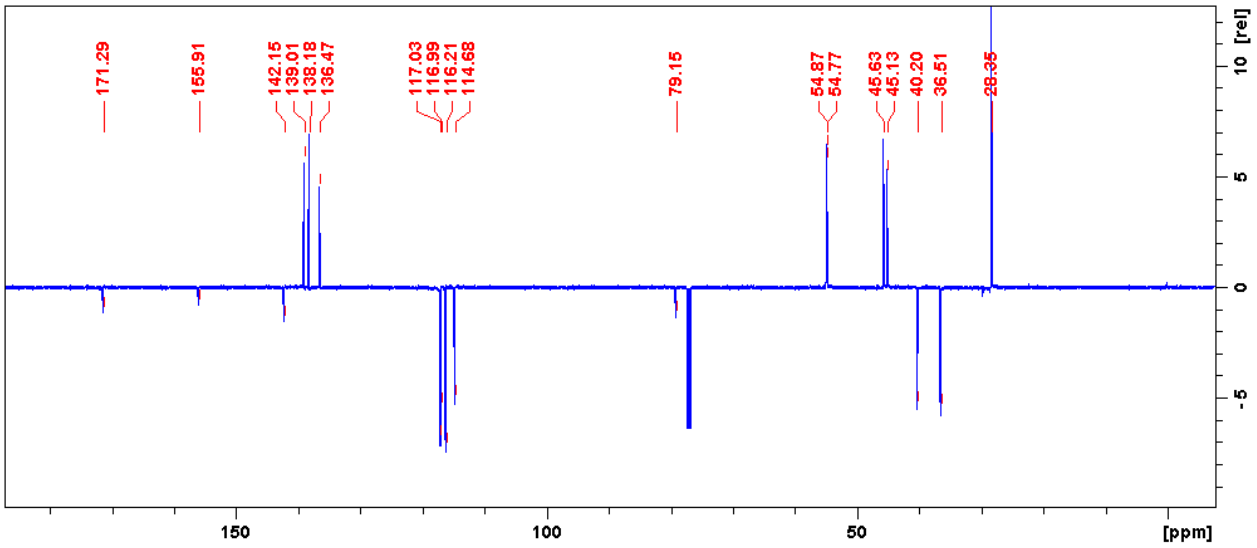


***tert*-Butyl ((1*R**,2*S**,3*R**,5*S**)-2-((2-methylenebut-3-en-1-yl)carbamoyl)-3,5-divinylcyclopentyl)carbamate, (±)-45**

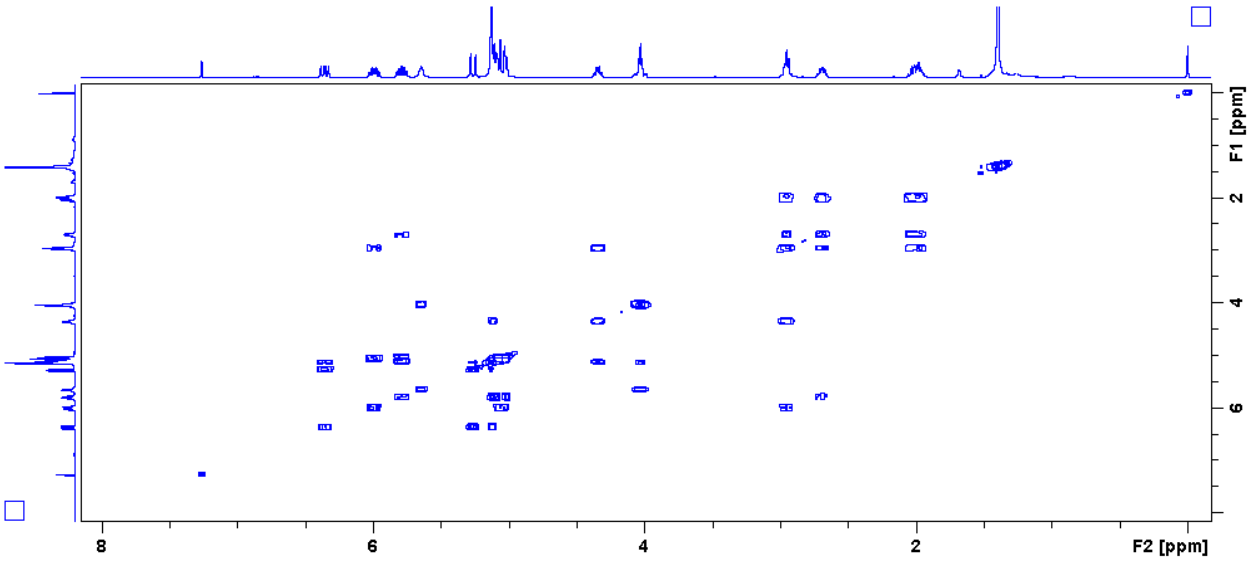
^{1}H NMR spectrum:



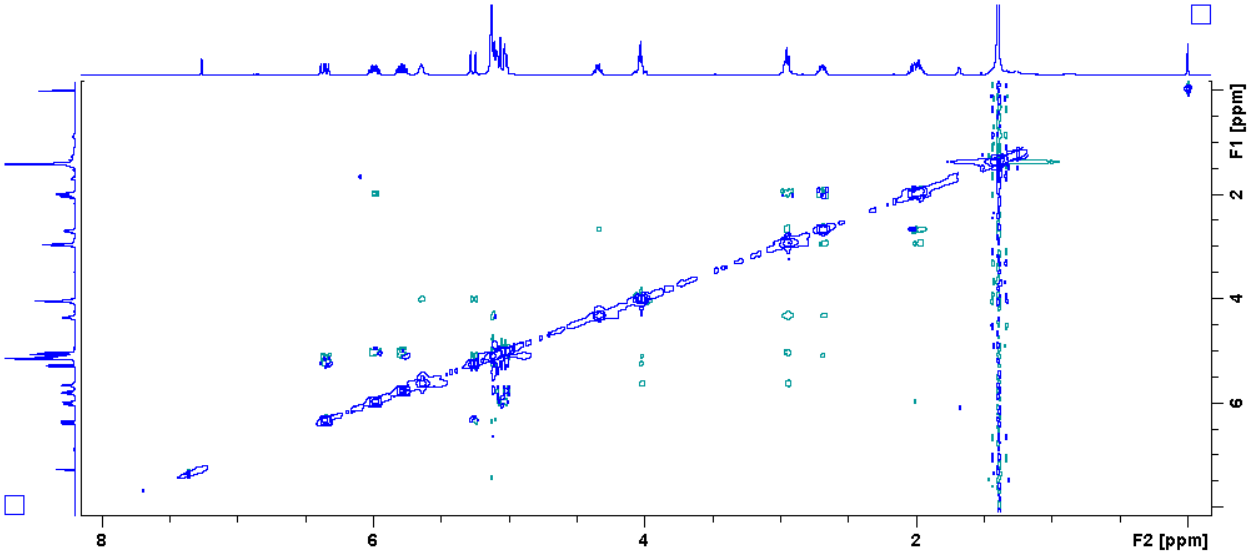
^{13}C (jmod) NMR spectrum:

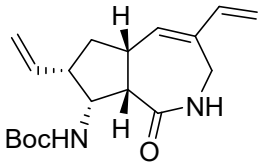


COSY spectrum:



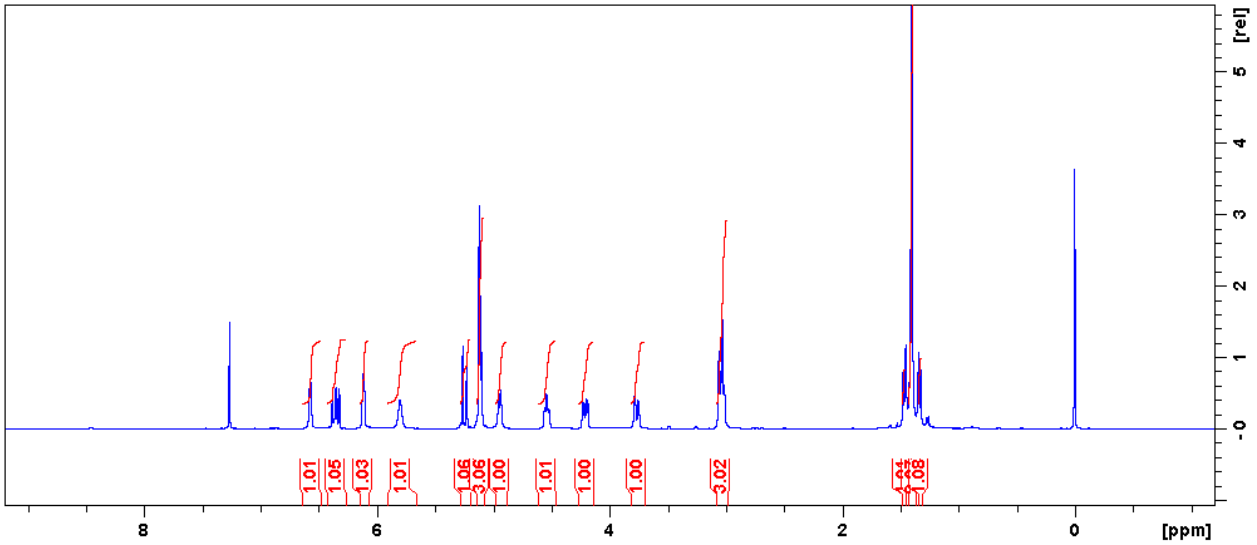
NOESY spectrum:



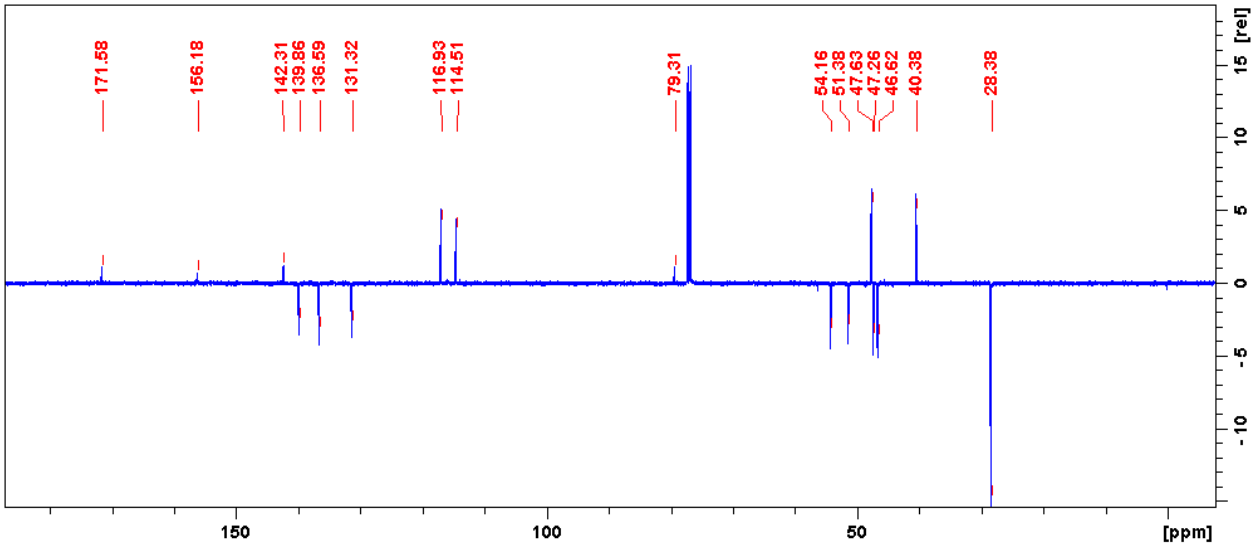


***tert*-Butyl ((5a*R**,7*S**,8*R**,8a*S**)-1-oxo-4,7-divinyl-1,2,3,5a,6,7,8,8a-octahydrocyclopenta[*c*]azepin-8-yl)carbamate, (±)-46**

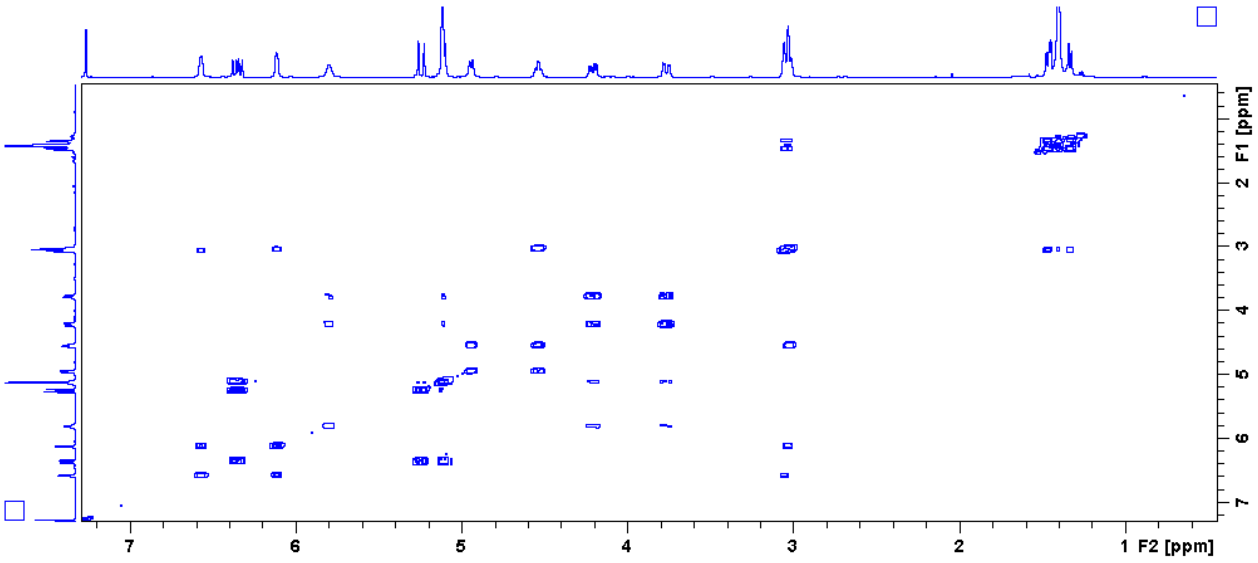
^{1}H NMR spectrum:



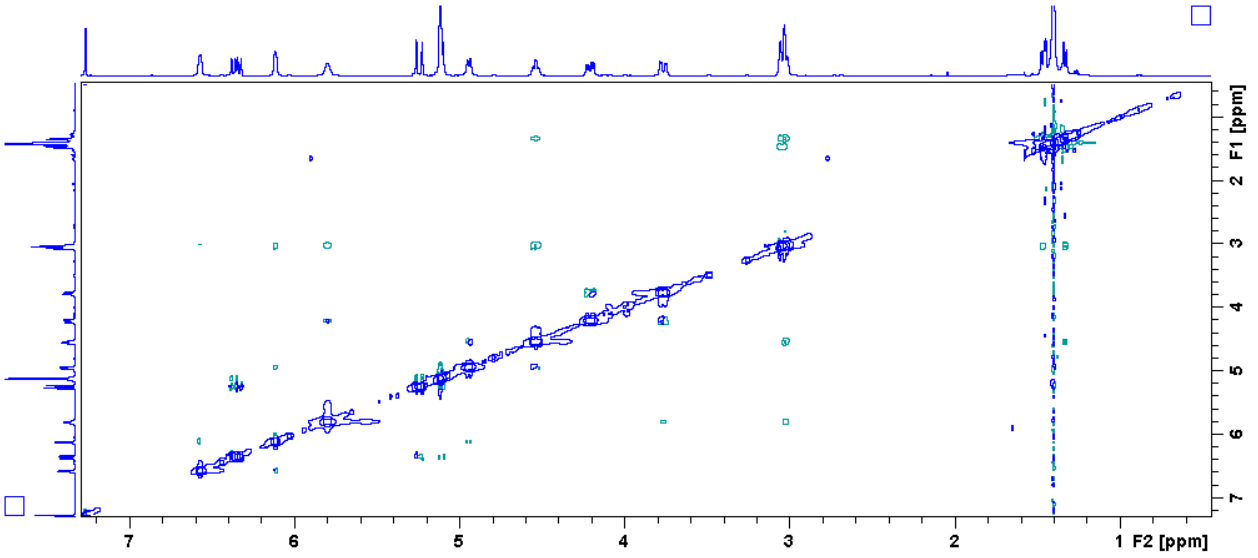
^{13}C (jmod) NMR spectrum:

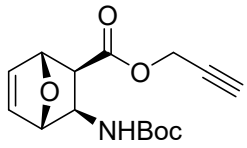


COSY spectrum:



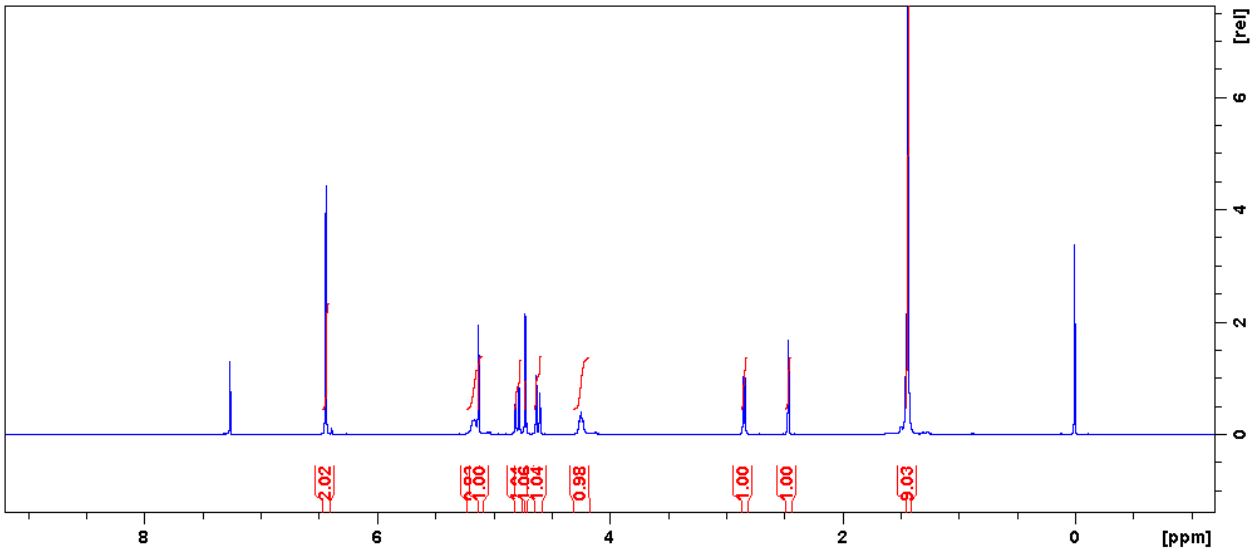
NOESY spectrum:



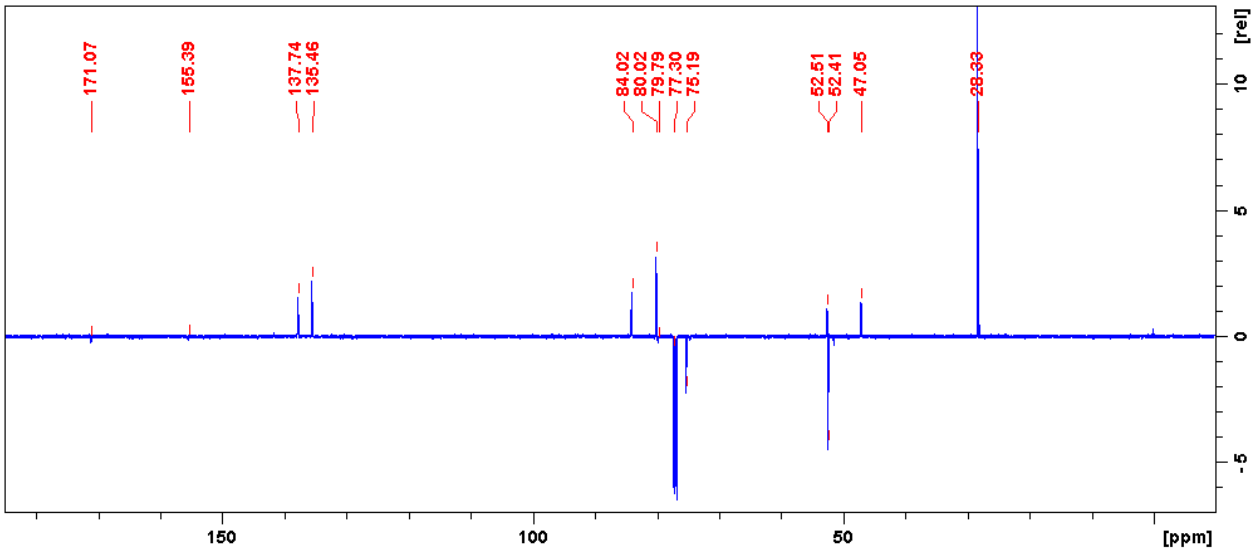


(1*R,2*S**,3*R**,4*S**)-prop-2-yn-1-yl 3-((*tert*-butoxycarbonyl)amino)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylate,** (±)**-47**

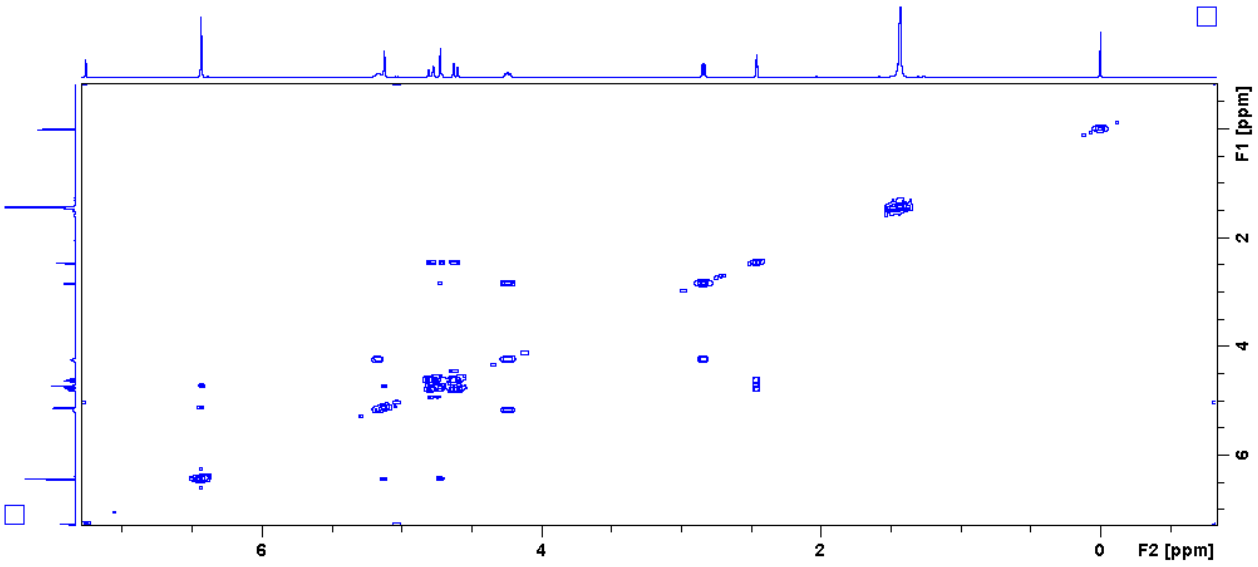
^{1}H NMR spectrum:



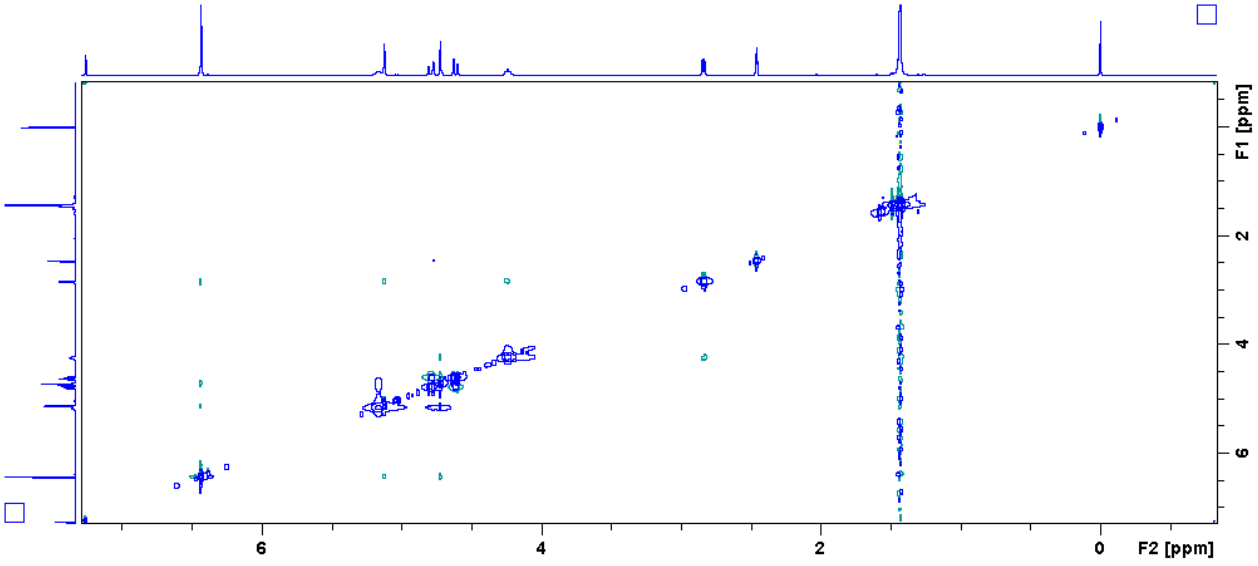
^{13}C (jmod) NMR spectrum:

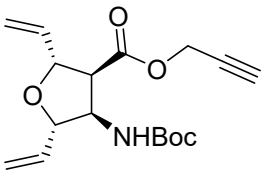


COSY spectrum:



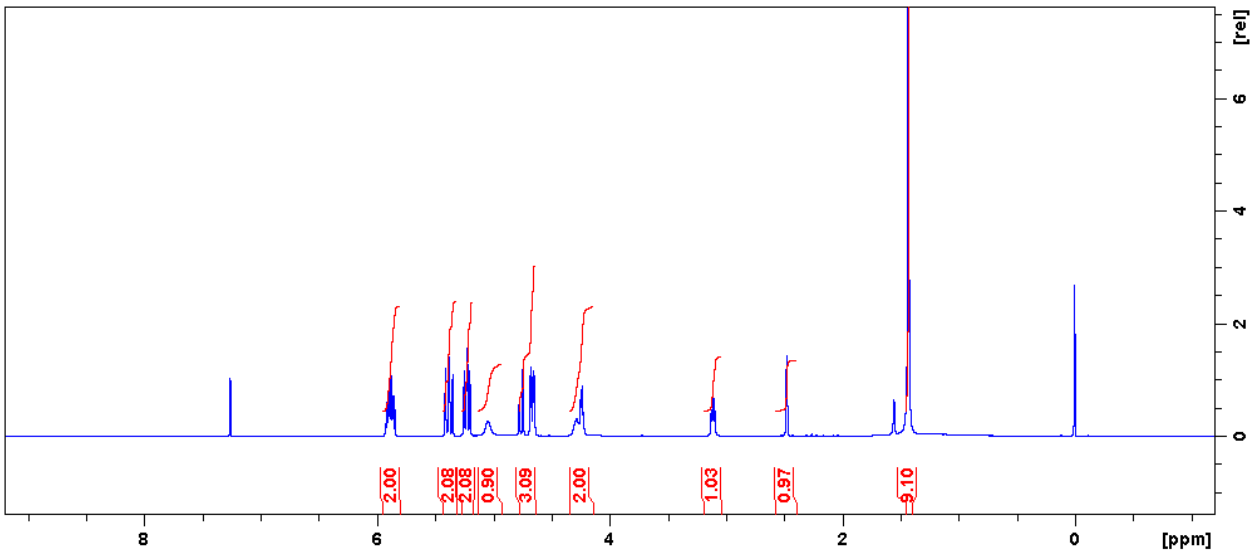
NOESY spectrum:



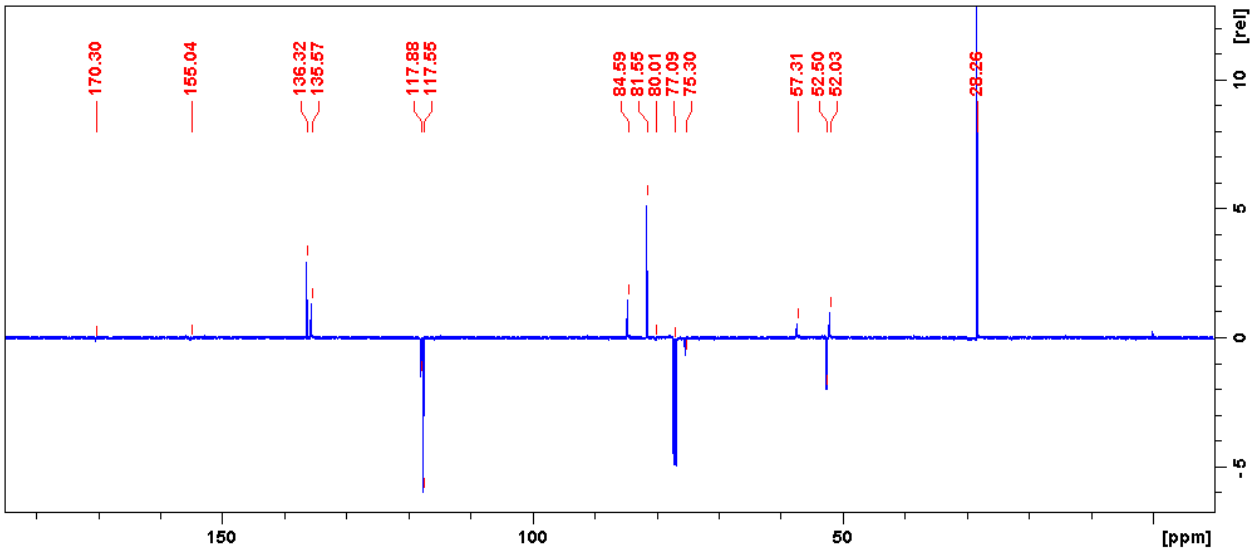


(2*R,3*S**,4*R**,5*S**)-prop-2-yn-1-yl 4-((*tert*-butoxycarbonyl)amino)-2,5-divinyltetrahydrofuran-3-carboxylate,** (±)**-48**

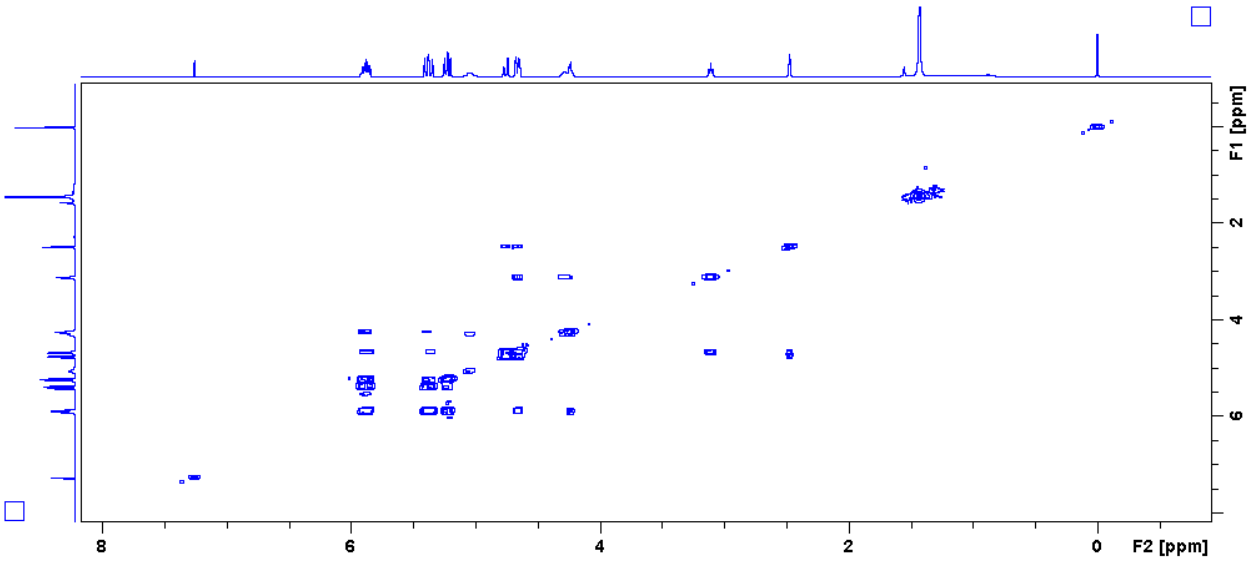
^{1}H NMR spectrum:



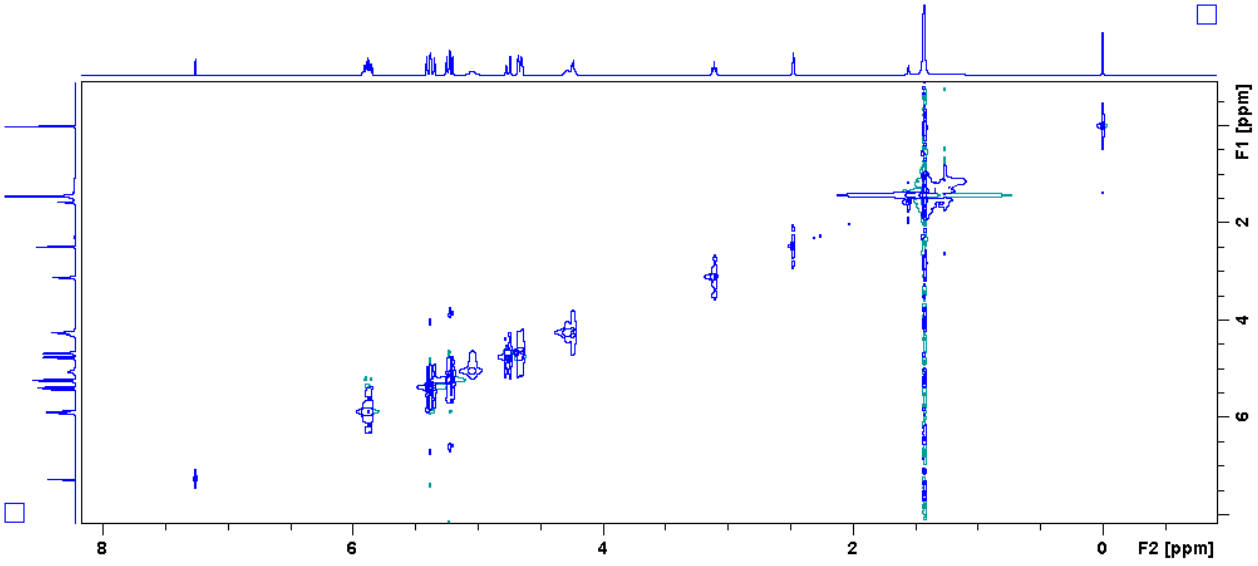
^{13}C (jmod) NMR spectrum:

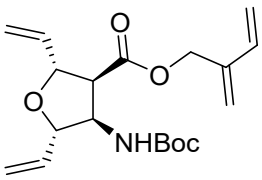


COSY spectrum:



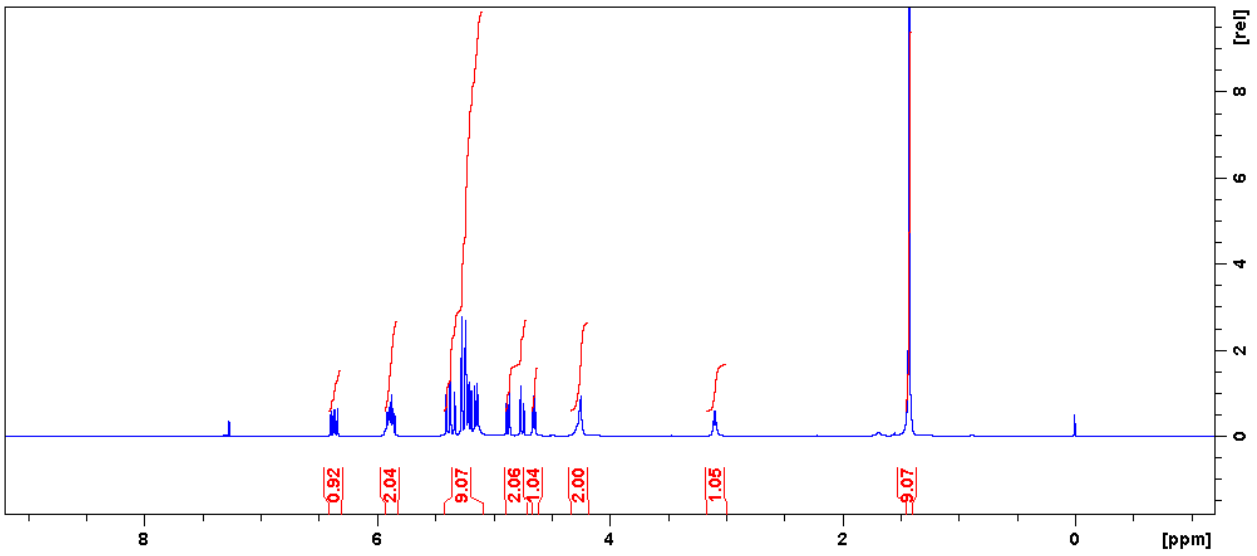
NOESY spectrum:



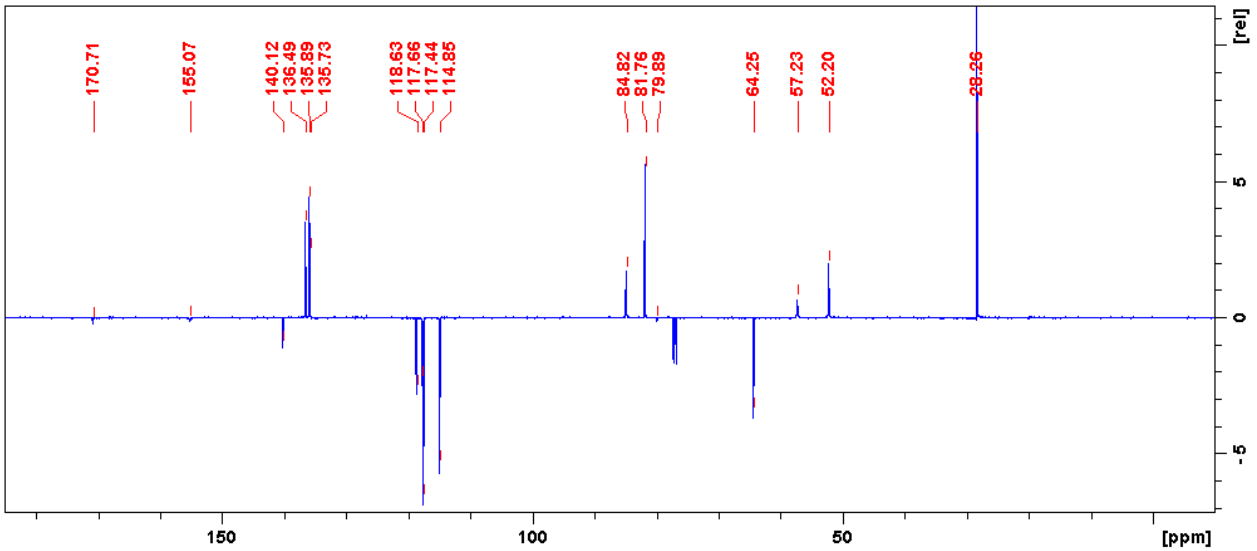


(2*R,3*S**,4*R**,5*S**)-2-methylenebut-3-en-1-yl 4-((*tert*-butoxycarbonyl)amino)-2,5-divinyltetrahydrofuran-3-carboxylate,** (±)**-49**

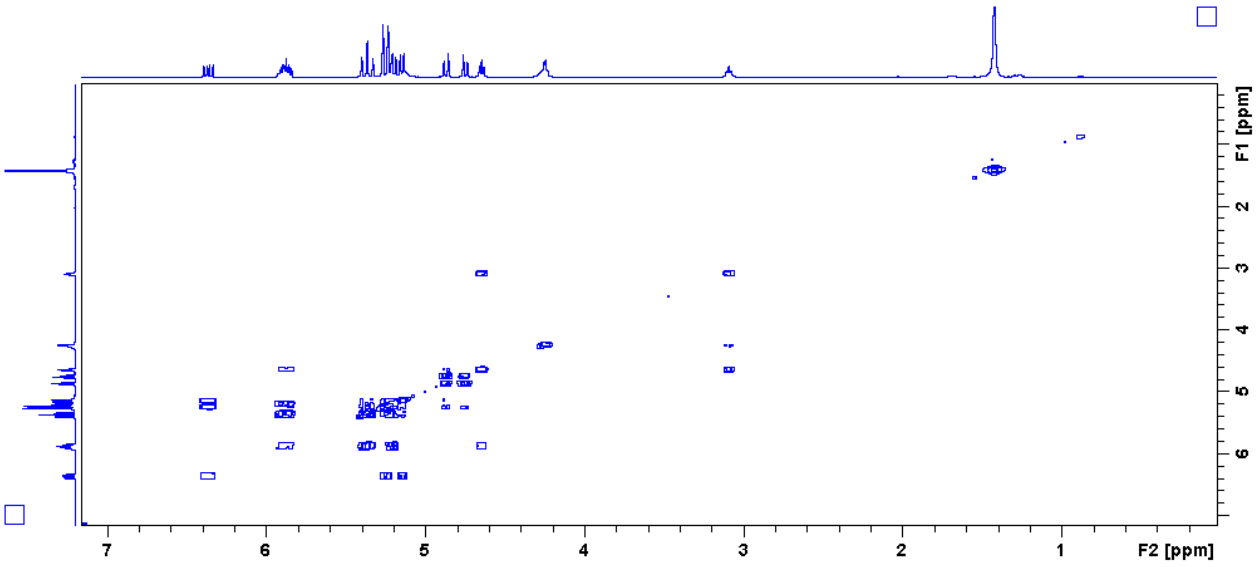
^{1}H NMR spectrum:



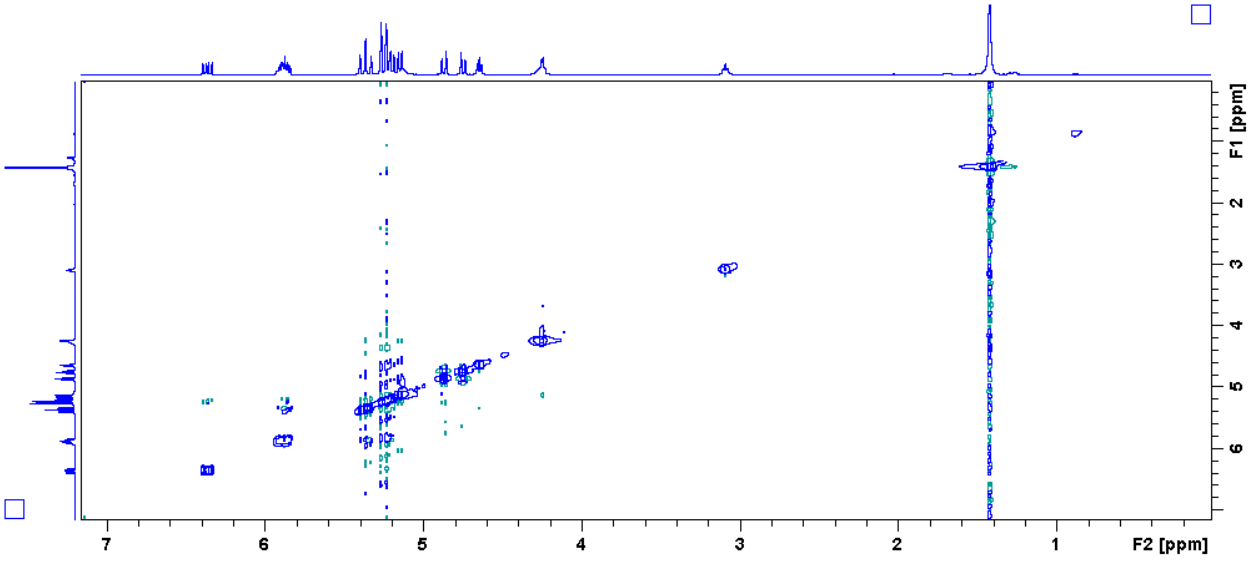
^{13}C (jmod) NMR spectrum:

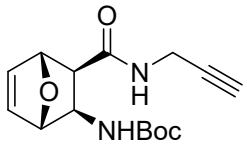


COSY spectrum:



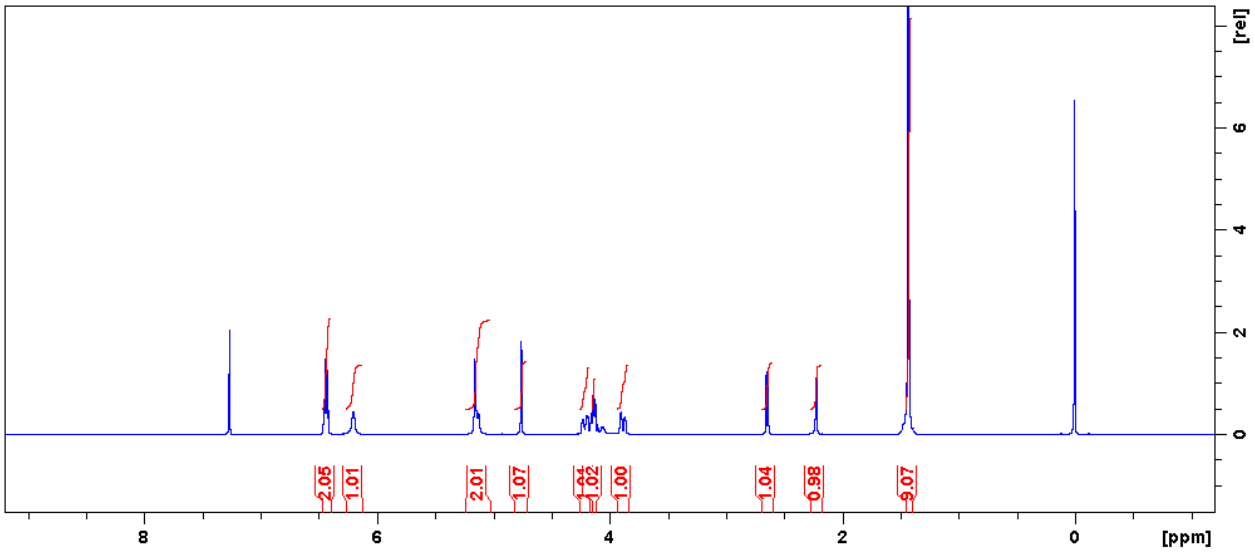
NOESY spectrum:



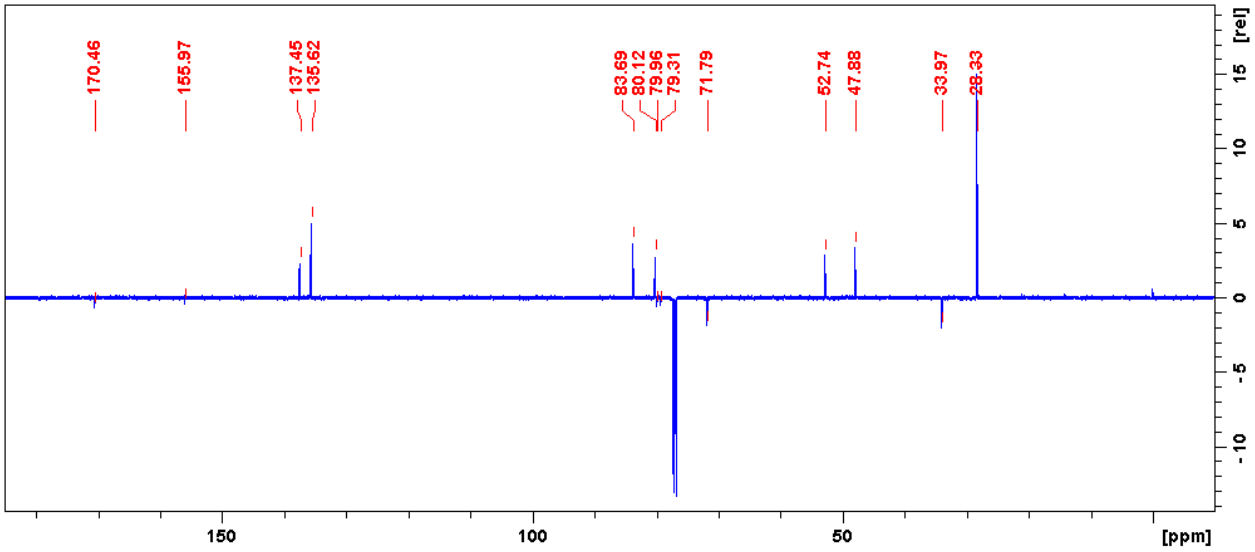


***tert*-Butyl ((1*S**,2*R**,3*S**,4*R**)-3-(prop-2-yn-1-ylcarbamoyl)-7-oxabicyclo[2.2.1]hept-5-en-2-yl)carbamate, (±)-50**

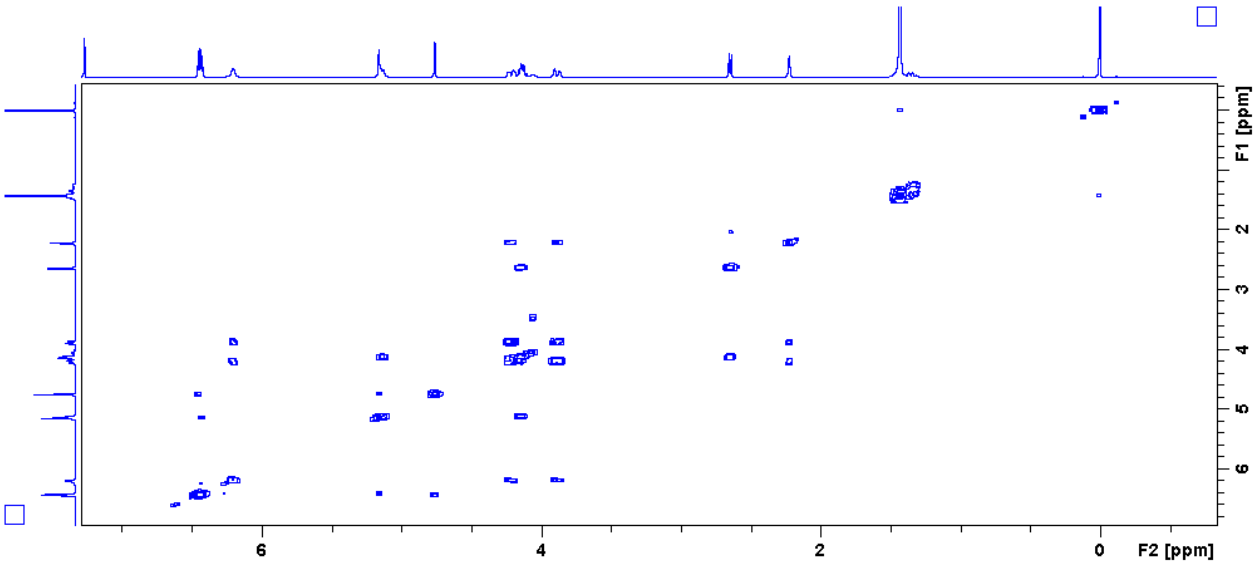
^{1}H NMR spectrum:



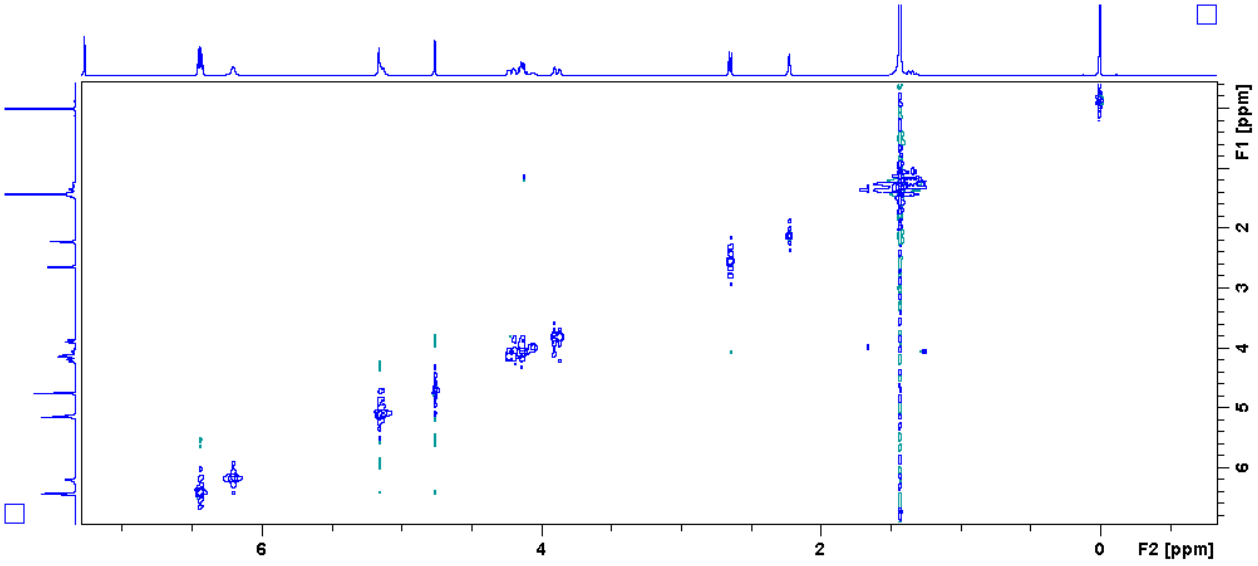
^{13}C (jmod) NMR spectrum:

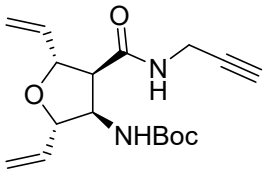


COSY spectrum:



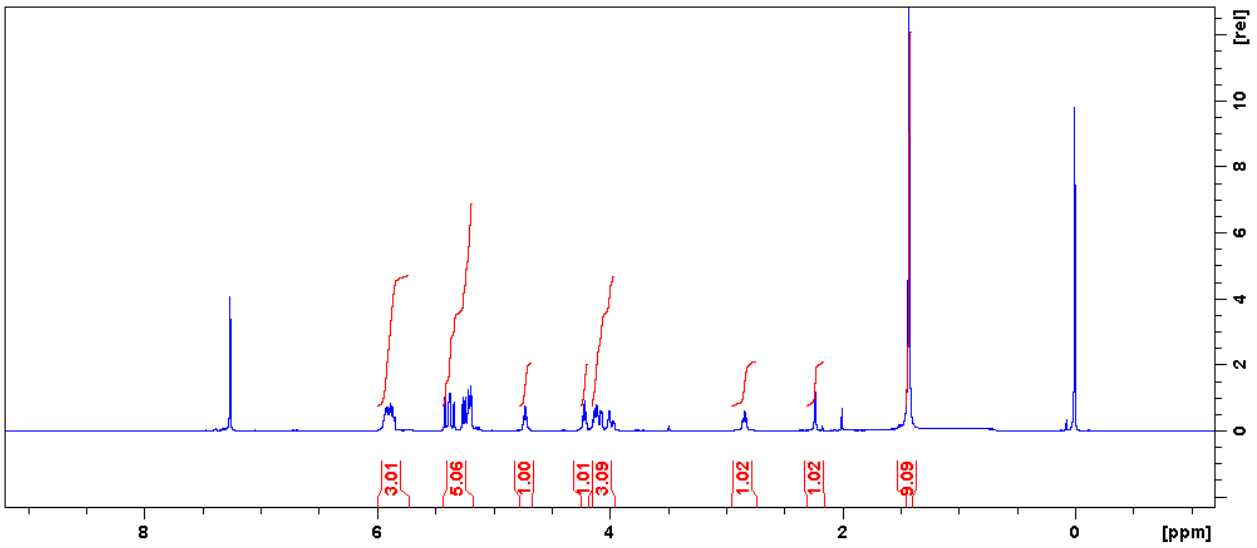
NOESY spectrum:



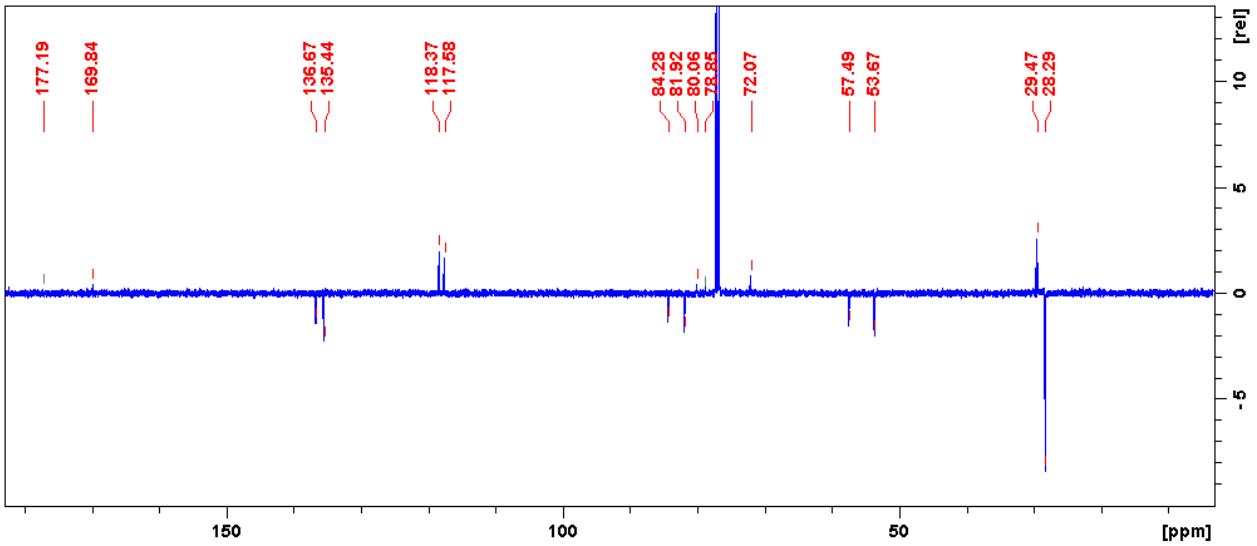


***tert*-Butyl ((2*S**,3*R**,4*S**,5*R**)-4-(prop-2-yn-1-ylcarbamoyl)-2,5-divinyltetrahydrofuran-3-yl)carbamate, (±)-51**

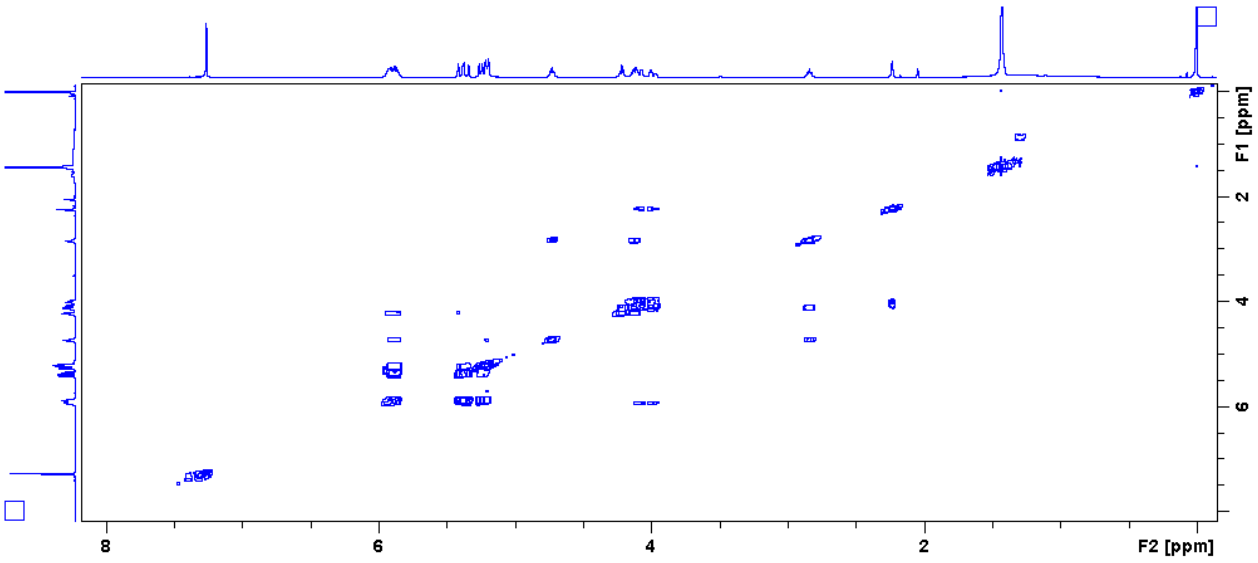
^{1}H NMR spectrum:



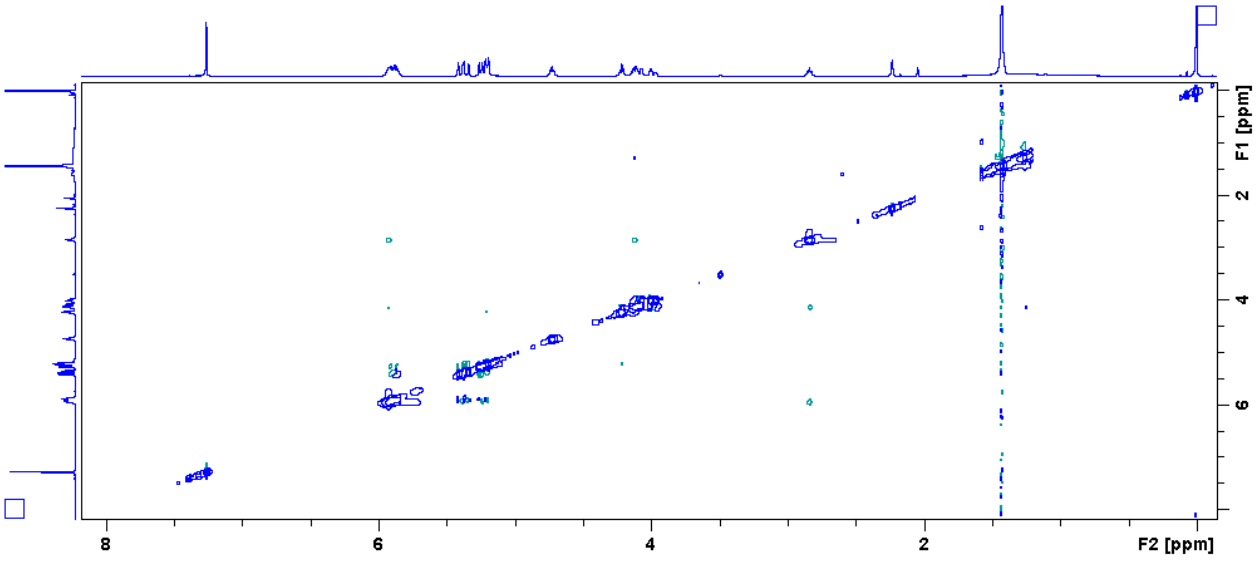
^{13}C (jmod) NMR spectrum:

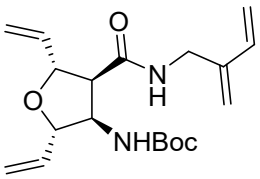


COSY spectrum:



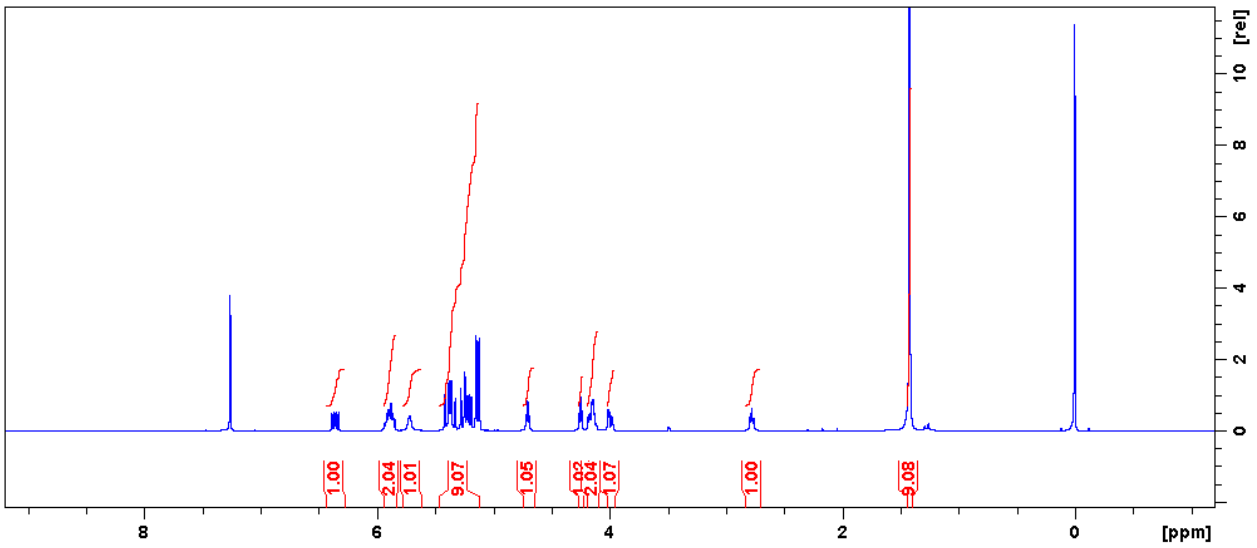
NOESY spectrum:



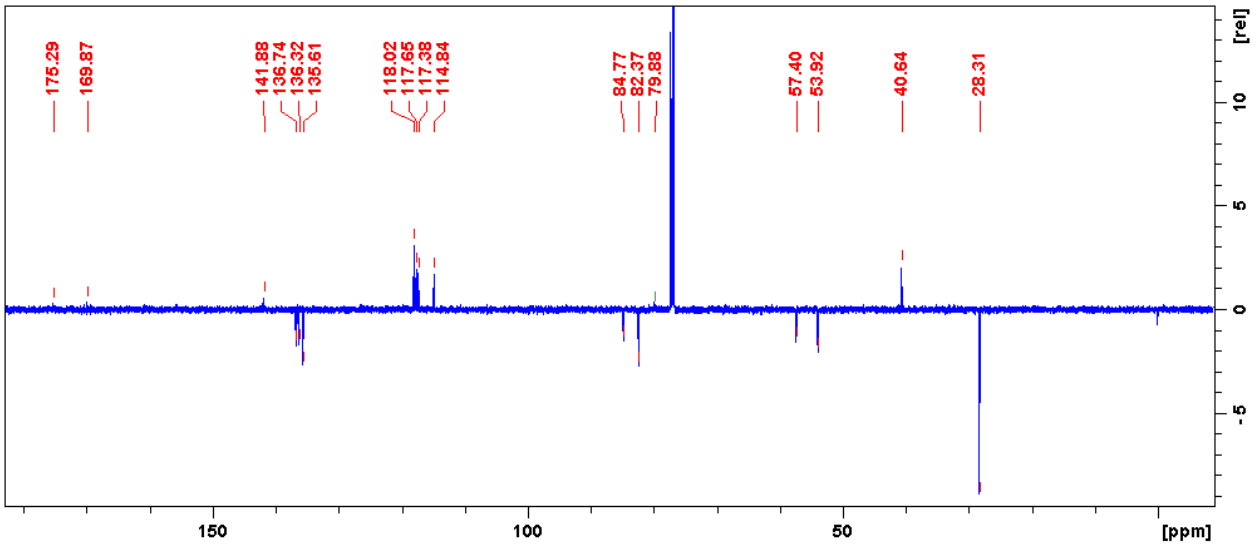


***tert*-Butyl ((2*S**,3*R**,4*S**,5*R**)-4-((2-methylenebut-3-en-1-yl)carbamoyl)-2,5-divinyltetrahydrofuran-3-yl)carbamate, (±)-52**

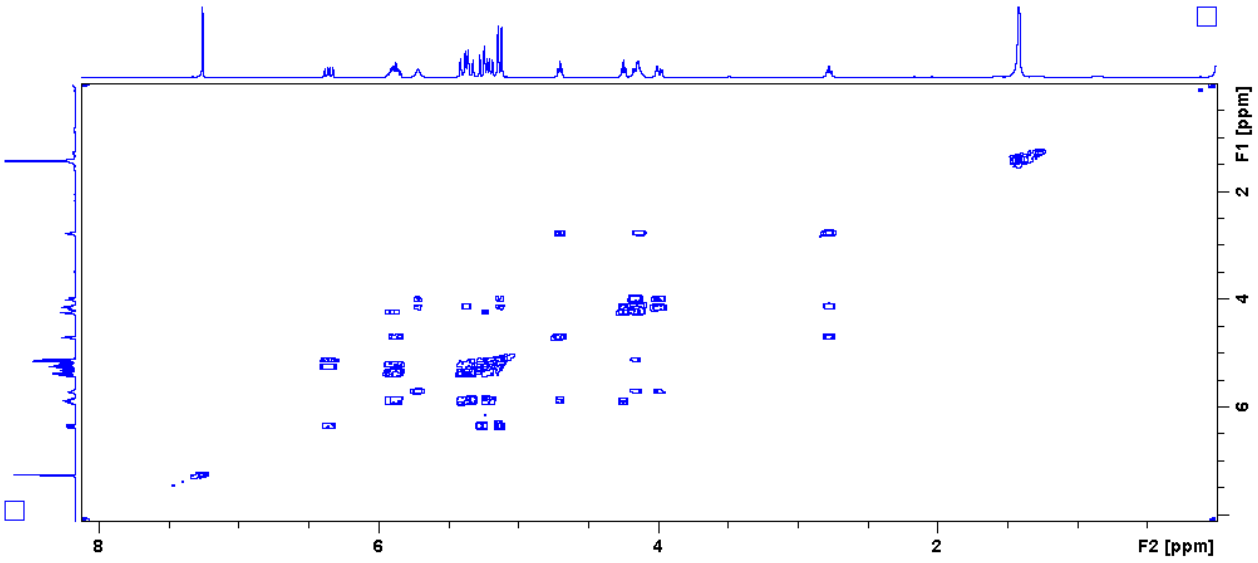
^{1}H NMR spectrum:



^{13}C (jmod) NMR spectrum:



COSY spectrum:



NOESY spectrum: