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Supplementary Materials

Enzyme-catalyzed kinetic resolution of spirocyclic secondary amines obtained by ring-closing metathesis, as well as synthesis of cyclopentane[c]pyrrole and -pyridines by the Pauson-Khand reaction

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[1] GENERAL

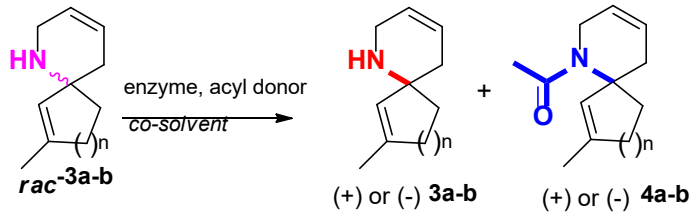
All experiments were carried out in pre-dried glassware (1 h, 150 ºC) under an inert atmosphere of Argon. The following reaction solvents were distilled from the indicated drying agents: dichloromethane (P_2O_5), tetrahydrofuran (sodium, benzophenone). ^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on JEOL ECS-400 spectrometer. ^{1}H (400 MHz) and ^{13}C-NMR were recorded in $CDCl_3$ and the chemical shift were expressed in ppm as the internal standard relative to $CDCl_3$ (δ 7.26 and 77.0 for ^{1}H and ^{13}C-NMR, respectively). Infrared spectra were recorded on a Thermo Nicolet IS10 ATR-FT-IR spectrophotometer**.** HRMS spectra were detected on an Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS at Central Laboratory in METU. Optical rotations were measured employing a Rudolph research analytical, autopol II automatic polarimeter.

Flash column chromatography was performed using thick-walled glass columns with a flash grade (Merck Silica Gel 60). Reactions were monitored appropriately by thin layer chromotography using precoated silica gel plates (Merck Silica Gel PF-254),visualized by UV-light and polymolybden phosphoric acid in ethanol. All extracts were dried over anhydrous magnesium sulphate and solutions were concentrated under vacuum using rotary evaporator.

Homoallylic **1a, 1b** and homopropargylic imines, **1c-3c** were prepared by reported procedure [1]. Also, *N*-homoallylic **5a, 5b** and *N*-homopropargylic carbamates **7a, 7b, 10b** were synthesized according to the modified literature procedure [2].
All reactions were monitored by thin layer chromatography (TLC).

[2] Enzymatic resolution of azaspirodecadiene *rac*-3a and azaspiroundecadiene *rac*-3b †

The most important part is the enantiomeric resolution of racemic azaspirodecadiene *rac*-**3a** and azaspiroundecadiene *rac*-3**b** substrates by the enzymes (Scheme S1) to produce the valuable enantiomerically enriched azaspirodecadiene and azaspiroundecadiene compounds respectively. Results are summarized in Table S1



rac-3a-b (+) or (-) **3a-b** (+) or (-) **4a-b**

a, n=1
b, n=2

[3] Scheme S1 Enzyme catalyzed acyl-transfer reaction. Reagents and conditions: *enzyme:* CAL-A *CLEA*, CAL-B Recombinant from *Aspergillus oryzae,* or (b) Candida *Rugosa Lipase acyl donor*: vinyl acetate, octyl acetate, or (b) isopropenyl acetate 40 °C, *co*-solvent: TBME or none.

[4] Table S1 The results of enzyme-catalyzed resolution of azaspirodecadiene *rac*-3**a**, and azaspiroundecadiene *rac-3**b***

Substrate	**Enzyme**	**Acyl donor**	**Co-solvent**	**Time(h)**	**c[a] (%)**	**ee$_p$[b](%)**	**ee$_s$ (%)**	***E*[c]**
rac-3a	CAL-A-*CLEA*	vinyl acetate	-	78	31	55	25	4
rac-3a	CAL-B recombinant from *Aspergillus oryzae*	vinyl acetate	-	78	44	75	60	13
rac-3a	CAL-B recombinant from *Aspergillus oryzae*	octyl acetate	TBME	78	60	52	77	7
rac-3b	CAL-A-*CLEA*	octyl acetate	TBME	85	6	30	2	2
rac-3b	CAL-B recombinant from *Aspergillus oryzae*	octyl acetate	TBME	85	27	55	20	4
rac-3b	Candida *Rugosa Lipase*	isopropenyl acetate	TBME	85	14	30	5	2

[a] $c = ee_s/ee_s+ee_{p,}$

[b] Enantiomeric excesses were determined by Daicel Chiralcel OD-H column HPLC analysis

[c] $E = \ln [(1-c)(1-ee_s)]/ \ln [(1-c)(1+ee_s)]$ [3].

[5] 1. General procedure for enzymatic resolution of *rac*-3a and *rac*- 3b

For 100 mg of substrate, *rac*-**3a** and *rac*-**3b** and 1 mL acyl donor with 50 mg of the enzyme was shaken at suitable temperature (38 ºC-40 °C) with or without co-solvent. The reaction was followed by TLC. When it came to the end, the mixture was filtered and the residue was concentrated under vacuo. Followed by flash-column chromatography, the crude mixture was purified using suitable ethylacetate/hexane and triethylamine as an eluent.

1.1. (+)-2-Methyl-6-azaspiro[4,5]deca-1,8-diene (+)-3a enzyme: CAL-B recombinant from *Aspergillus oryzae*, acyl donor: vinyl acetate Dark brown thick oil (40 mg, 40% yield). $[\alpha]^{26}_{D}$= + 15.55 (*c* 0.25, $CHCl_3$), 60% ee. The enantiomeric excess of the product was determined by HPLC analysis (Daicel Chiralcel OD-H, λ = 230 nm, n-hexane/2-propanol 98:2, 0.5 mL/min), t_1= 6.41 min (minor) and t_2= 6.91 min (major).

1.2. (-)-2-Methyl-6-azaspiro[4,5]deca-1,8-diene (-)-3a enzyme: CAL-A-*CLEA*, acyl donor: vinyl acetate (25 mg, 25% yield). $[\alpha]^{26}_{D}$= -6.94 (*c* 0.25, $CHCl_3$), 25% ee. The enantiomeric excess of the product was determined by HPLC analysis (Daicel Chiralcel OD-H, λ = 230 nm, n-hexane/2-propanol 98:2, 0.5 mL/min), t_1= 6.88 min (minor) and t_2= 7.08 min (major).

1.3. (+)-2-Methyl-6-azaspiro[4,5]deca-1,8-diene (+)-3a enzyme: CAL-B recombinant from *Aspergillus oryzae*, acyl donor: octyl acetate, *co*-solvent: TBME (42 mg, 42% yield). $[\alpha]^{26}_{D}$= + 17.84 (*c* 0.25, $CHCl_3$), 77% ee. The enantiomeric excess of the product was determined by HPLC analysis (Daicel Chiralcel OD-H, λ = 230 nm, n-hexane/2-propanol 98:2, 0.5 mL/min), t_1= 6.86 min (minor) and t_2= 7.06 min (major).

1.4. (-)-1-(2-Methyl-6-azaspiro[4,5]deca-1,8-dien-6-yl)ethanone (-)-4a enzyme: CAL-B recombinant from *Aspergillus oryzae*, acyl donor: vinyl acetate Yellow oil (26 mg, 20% yield). $[\alpha]^{26}_{D}$= -33.54 (*c* 0.25, $CHCl_3$), 75% ee. IR ν_{max} (neat, cm^{-1}): 3016, 2924, 2854, 1731, 1660, 1018, 1455. ^{1}H NMR ($CDCl_3$, 400 MHz): δ ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 5.73- 5.86 (m, 1H), 5.18 (s, 1H), 5.06 (d, *J* = 17.2 Hz, 1H), 3.30 (d, *J* =1.6 Hz, 2H), 2.19 (dd, *J* =7.2 and 12.0 Hz, 1H), 2.15 (d, *J* = 2.0 Hz, 1H), 1.78-1.93 (m, 2H), 1.64 (s, 3H), 1.60 (dd, *J* = 2.8 and 9.2 Hz, 1H), 1.43 (dd, *J* = 6.8 and 15.6 Hz, 1H), 1.22 (s, 3H), ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 170.2, 137.7, 134.0, 127.2, 118.0, 70.6, 44.6, 34.0, 31.8, 30.0, 23.6, 19.9. HRMS (ESI-TOF) m/z was calculated for $C_{12}H_{17}NO$ $[M]^+$: 191.1310 found 191.1115. HPLC conditions: (Daicel Chiralcel OD-H, λ = 230 nm, n-hexane/2-propanol 98:2, 0.5 mL/min), t_1= 6.93 min (major) and t_2= 7.06 min (minor).

1.5. (+)-1-(2-Methyl-6-azaspiro[4,5]deca-1,8-dien-6-yl)ethanone (+)-**4a** enzyme: CAL-A-*CLEA*, acyl donor: vinyl acetate (19 mg, 15 % yield). $[\alpha]^{26}_{D}$= +22.56 (*c* 0.25, $CHCl_3$), 55% ee. The enantiomeric excess of the product was determined by HPLC analysis (Daicel Chiralcel OD-H, λ = 230 nm, n-hexane/2-propanol 98:2, 0.5 mL/min), t_1= 6.38 min (minor) and t_2= 6.78 min (major).

1.6. (-)-1-(2-Methyl-6-azaspiro[4,5]deca-1,8-dien-6-yl)ethanone (-)-**4a** enzyme: CAL-B recombinant from *Aspergillus oryzae,* acyl donor: octyl acetate, *co*-solvent: TBME (13 mg, 10 % yield). $[\alpha]^{26}_{D}$= -18.50 (*c* 0.25, $CHCl_3$), 52% ee. The enantiomeric excess of the product was determined by HPLC analysis (Daicel Chiralcel OD-H, λ = 230 nm, n-hexane/2-propanol 98:2, 0.5 mL/min), t_1= 6.37 min (major) and t_2= 6.53 min (minor).

1.7. **(+)-8-Methyl-1-azaspiro[5,5]undeca-3,7-diene (+)-3b** enzyme: CAL-B recombinant from *Aspergillus oryzae*, acyl donor: octyl acetate, *co*-solvent: TBME Dark brown thick oil (25 mg, 25% yield). $[\alpha]^{26}_{D}$= +8.88 (*c* 0.25, $CHCl_3$), 20 % ee. The enantiomeric excess of the product was determined by HPLC analysis (Daicel Chiralcel OD-H, λ = 230 nm, n-hexane/2-propanol 98:2, 0.5 mL/min), t_1= 6.86 min (minor) and t_2= 7.06 min (major).

1.8. (-)-1-(8-Methyl-1-azaspiro[5,5]undeca-3,7-dien-1-yl)ethanone (-)-4b enzyme: CAL-B recombinant from *Aspergillus oryzae,* acyl donor: octyl acetate, *co*-solvent: TBME Dark brown liquid (15 mg, 12% yield). $[\alpha]^{26}_{D}$= -15.37 (*c* 0.25, $CHCl_3$), 55% ee. IR ν_{max} (neat, cm^{-1}): 3010, 2955, 2916, 1701, 1653, 1097, 1484 cm^{-1}, ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 5.80 (dd, *J* = 4.0 Hz, 2H), 5.47 (s, 1H), 4.23 (dd, *J* = 4.8 and 7.8. Hz, 1H), 3.82 (dd, *J* = 4.0 and 24.2 Hz, 1H), 2.27 (t, *J* = 3.3 Hz, 1H), 2.22 (d, *J* = 2.0 Hz, 1H), 2.17 (d, *J* = 2.0 Hz, 1H) 2.16 (d, *J* =3.6 Hz, 1H), 2.14 (s, 3H), 1.92-2.03 (m, 4H), 1.72 (s, 3H), ^{13}C NMR ($CDCl_3$, 100.6 MHz): δ 164.0, 132.3, 129.1, 127.0, 122.9, 57.0, 39.3, 39.2, 30.3, 29.5, 24.0, 21.2, 18.0, HRMS (ESI-TOF) m/z was calculated for $C_{13}H_{19}NO$ $[M]^+$: 205.1467, found 205.1409, HPLC conditions: (Daicel Chiralcel OD-H, λ = 230 nm, n-hexane/2-propanol 98:2, 0.5 L/min), t_1= 6.38 min (minor) and t_2= 7.03 min (major).

1.9. (+)-1-(8-Methyl-1-azaspiro[5,5]undeca-3,7-dien-1-yl)ethanone (+)-**4b** enzyme: *Candida Rugosa Lipase*, acyl donor: isopropenyl acetate, *co*-solvent: TBME Dark brown liquid (12 mg, 10% yield). $[\alpha]^{26}_{D}$= +5.20 (*c* 0.25, $CHCl_3$), 30 % ee. The enantiomeric excess of the product was determined by HPLC analysis (Daicel Chiralcel OD-H, λ = 230 nm, n-hexane/2-propanol 98:2, 0.5 mL/min), t_1= 6.64 min (minor) and t_2= 6.92 min (major).

2. Synthesis of homoallyl 1a, 1b and homopropargyl imines 1c- 3c

A sealable tube was charged with a 0.5 M solution of cyclic ketone; 3-methyl-2-cyclopentenone or -cyclohexenone; (10.2 mmol) in benzene (20 mL). Allylamine or propargylamine (20.4 mmol) and crushed molecular sieves (1/1 ratio, w/w) were then added, the tube sealed and the reaction mixture heated to 55-60 °C. After stirring overnight, the solution was diluted with ether and filtered. The ether was carefully removed by vacuum evaporation at low temperature. Benzene was removed by blowing nitrogen gas over the solution to give the pure imine product as an orange-yellow oil used directly in the next step [1].

3. Synthesis of *N*-homoallylic 2a, 2b and *N*-homopropargylic enamines 9b, 12b

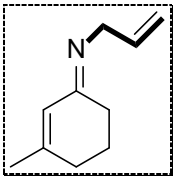
To a stirred solution of Mg turnings (15 mmol) and iodine (2 pieces) in dry diethyl ether (15 mL) at room temperature equipped with a reflux condenser, a mixture of allylbromide (11 mmol) in anhydrous diethyl ether (7 mL) was added dropwise. The mixture was allowed to reflux for 25 min. Then cooled down to 0 °C followed by the addition of the corresponding imine **1a, 1b** or **2c, 3c** (10 mmol) in dry diethylether (5 mL) was added dropwise. The resultant mixture was stirred for 4 h. The reaction mixture was hydrolyzed with saturated ammonium chloride solution (20 mL). The resultant mixture was extracted with diethyl ether (3x30 mL). The combined organic phase was washed with brine (20 mL) and dried over $MgSO_4$ and evaporated in vacuo. The crude products were purified by flash column chromatography with a mixture of ethylacetate/ hexane and triethylamine in suitable ratios.

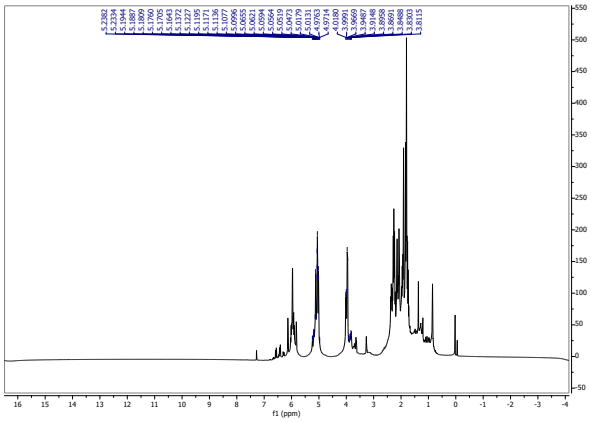
[6] ^{1}H- and ^{13}C-NMR spectra

(IMINE COMPOUNDS CAN NOT BE PURIFIED THEY ARE EASILY DECOMPOSED ON SILICA GEL SO THE CRUDE NMR HAD TAKEN IMMIDIATELY)

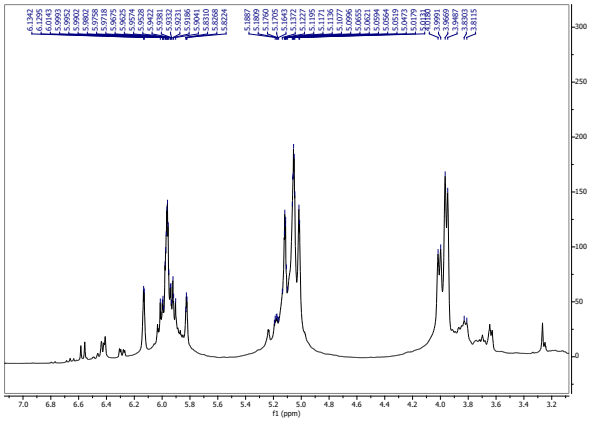
***E*-(*N*)-(3-methylcyclohex-2-en-1-ylidene)prop-2-en-1-amine: (CRUDE NMR) (1b) (new compound)**

Color: Orange yellow liquid (FT-IR KBr, *ν, cm^{-1})* 3015 (CH_2 (C sp^2-H), (cyclohexene ring), 2970 (CH_3(sp^3 -H), 2901(CH_3 (Csp^3-H), 1661 (imine C=N), 1504(-C=C- stretching, allyl + cyclohexene ring), 1193 (-CH_2-N), 1027 and 913 (C sp^2 -H).^{1}H-NMR (400 MHz, $CDCl_3$,.δppm): δ_H 6.11 (d, *J* = 1.2 Hz, 1H, 5.94 (d, *J* =1.2 Hz, 1H), 5.84-5.99 (m, 1H), 5.07 (dd, *J* = 1.6 and 17.2 Hz, 1H), 5.01 (dd, *J* =1.2 and 10.2 Hz,1H), 3.93 (d, *J* = 6.4 Hz, 1H), 3.98 (d, *J* = 5.6 Hz, 1H), 2.33 (t, *J* = 6.6 Hz, 1H), 2.11 (t, *J* = 5.2 Hz, 1H), 2.05 (t, *J* = 6.0 Hz, 1H), 2.24 (t, *J* = 6.45 Hz, 1H), 2.19-2.28 (m, 1H), 1.74 (t, *J* = 6.6 Hz, 1H), 1.78 (s, 3H), 1.81 (s, 3H) ^{13}C-NMR (100 MHz, $CDCl_3$, δppm): δ_C 167.0, 147.7, 135.6, 126.4, 114.3, 33.9, 29.4, 24.9, 23.0 21.1.

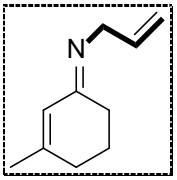


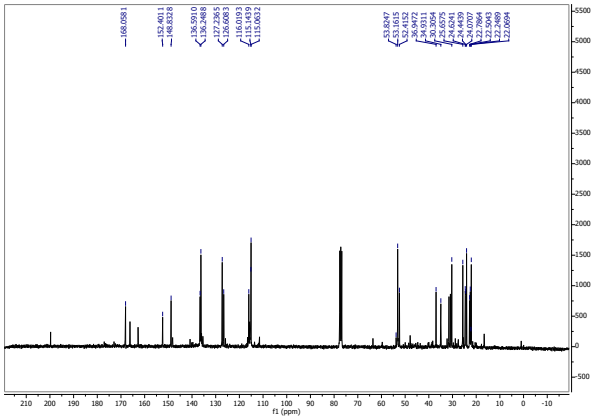


^{1}H-NMR spectrum of (*E*)-*N*-(3-methylcyclohex-2-en-1-ylidene)prop-2-en-1-amine (crude)

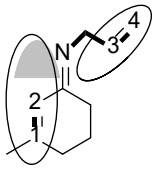


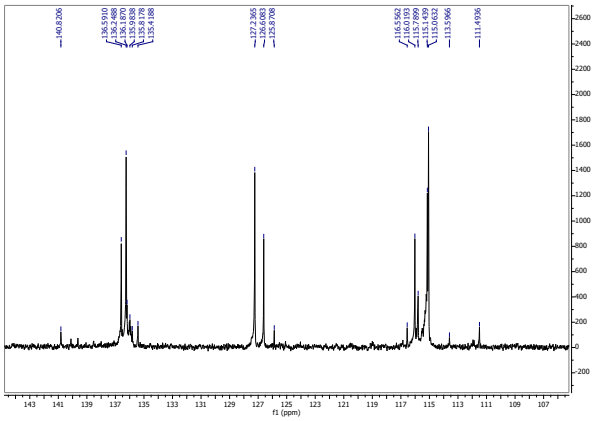
δ_H 6.11 (d, *J* = 1.2 Hz, 1H, 5.94 (d, *J* =1.2 Hz, 1H), 5.84-5.99 (m, 1H), 5.07 (dd, *J* = 1.6 and 17.2 Hz, 1H), 5.01 (dd, *J* =1.2 and 10.2 Hz,1H), (^{1}H-NMR signals of allyl part).





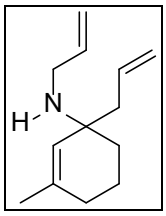
^{13}C-NMR spectrum of (*E*)-*N*-(3-methylcyclohex-2-en-1-ylidene)prop-2-en-1-amine (crude)



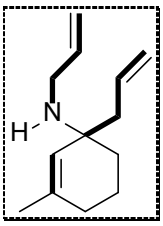


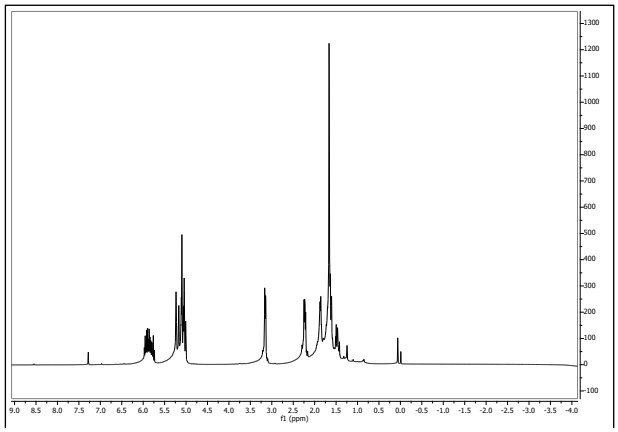
^{13}C-NMR spectrum of the signals of allyl side chain as well as olefinic part (*δc* 147.7(1), 135.6(2), 126.4 (3), 114.3(4). ^{13}CNMR signal at 167.0 ppm for imine carbon atom.

***N*,1-diallyl-3-methylcyclohex-2-enamine (2b) (new compound)**

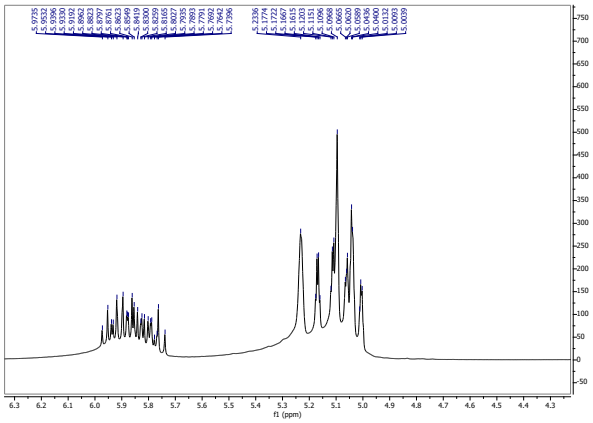


Color: Thick yellow oil Yield: 1.63 g, 75 % yield). FT-IR (KBr, *ν*, $cm^{-1)}$: 3305 (*N*-H), 3073 (C sp^2-H), 2971 (CH_3 (sp^3 -H), 2927 (CH_3 (Csp^3-H), 1668 (-C=C- stretching, cyclohexene ring), 1639 (-C=C- stretching, allyl grup, 1075 (-CH_2 -N-), 995 and 909 (C sp^2-H twisting,) Purified by Flash column chromatography (1:5:1 % EtOAc: Hexane: Et_3N) ^{1}H-NMR (400 MHz, $CDCl_3$,δ, ppm): δ_H 5.80-5.89 (m, 1H), 5.69-5.80 (m,1H), 5.16 (s, 1H), 5.07 (dd, *J* = 1.6 ve 17.0 Hz, 1H), 5.02 (s, 1H), 4.99 (dd, *J* =1.2 and 6.2 Hz, 1H), 4.95 (dd, *J* =1.6 and 10.4 Hz, 1H), 3.09 (dd, *J* = 1.2 and 2.8 Hz, 1H), 3.07(dd, *J* = 1.2 and 3.2 Hz, 1H), 2.20 (dd, 0.8 and 7.2 Hz, 1H), 2.15 (t, *J* = 7.2 Hz, 1H), 1.81-1.85 (m, 1H), 1.79 (broad singlet, N-*H*), 1.78 (d, *J*= 6.4 Hz, 1H), 1.60 (s, 3H), 1.58-1.60 (m, 2H), 1.57 (d, *J* =2.0 Hz, 1H), 1.53 (dd, *J*= 3.2 and 8.2 Hz, 1H), ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 137.7, 136.1, 134.6, 127.8, 117.7, 115.2, 69.7, 54.5, 45.3, 44.1, 30.0, 23.9, 19.7. $C_{13}H_{22}N$, HRMS-ESI, $[M+H]^+$ Calculated; 192.1752, found; 192.1757

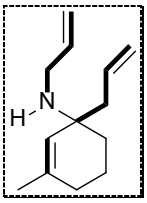


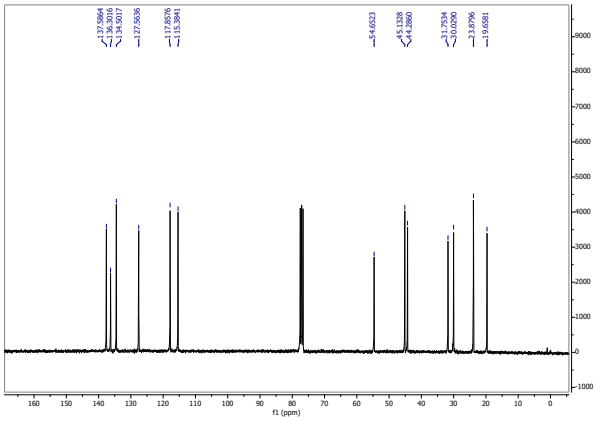


^{1}H-NMR spectrum of *N*,1-diallyl-3-methylcyclohex-2-enamine

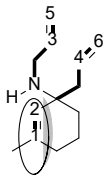


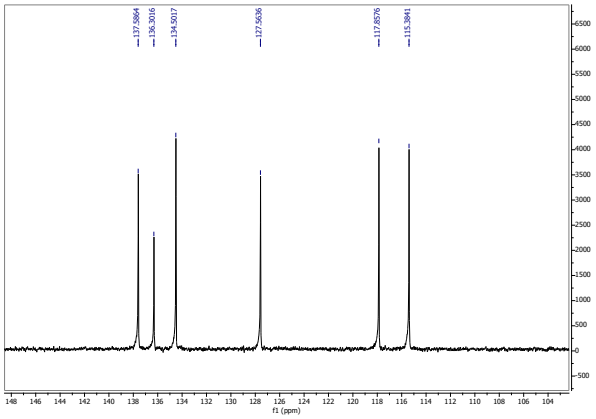
^{1}H-NMR spectrum of the signals of diene part and olefinic proton; δ_H 5.80-5.89 (m, 1H), 5.69-5.80 (m,1H), 5.16 (s, 1H), 5.07 (dd, *J* = 1.6 ve 17.0 Hz, 1H), 5.02 (s, 1H), 4.99 (dd, *J* =1.2 and 6.2 Hz, 1H), 4.95 (dd, *J* =1.6 and 10.4 Hz, 1H), 3.09 (dd, *J* = 1.2 and 2.8 Hz, 1H), 3.07(dd, *J* = 1.2 and 3.2 Hz, 1H), 2.20 (dd, 0.8 and 7.2 Hz, 1H).





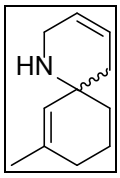
^{13}C-NMR spectrum of *N*,1-diallyl-3-methylcyclohex-2-enamine



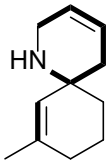


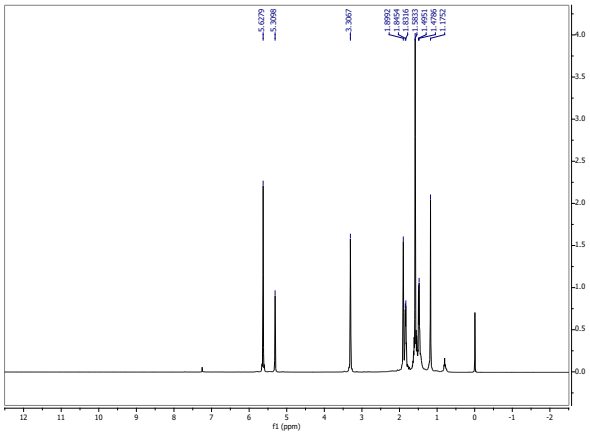
^{13}C-NMR spectrum of the signals of diene and olefin part; δ_C 137.7(1), 136.1(2), 134.6(3), 127.8(4), 117.7(5), 115.2 (6).

8-methyl-1-azaspiro[5.5]undeca-3,7-diene (3b) (new compound)

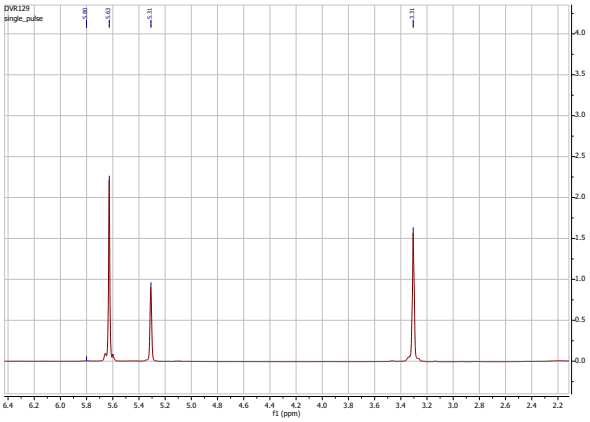


Color:Thick dark brown oil Yield: 560 mg, 82 % yield FT-IR (KBr, ν, cm^{-1}) : 3245 (N-H), 3016 (CH_2, Csp^2-H, cyclohexene ring), 2986 (CH_3(sp^3 -H), 2969 (CH_3 (Csp^3-H), 1660 (-C=C- stretching, cyclohexene ring), 1076 (-CH_2-N-), 1437 (-C=C- stretching, tetrahydropyridine ring). Purified by Flash column chromatography (1:1:1 % Et_3N; EtOAc:Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$,, δ, ppm): δ_H 5.64 (d, J = 11.6 Hz, 1H), 5.61 (d, J = 11.6 Hz, 1H), 5.31 (s, 1H), 3.32 (d, J = 10.4 Hz, 1H), 3.29 (d, J = 14.4 Hz, 1H), 1.87-1.93 (m, 2H), 1.85 (d, J = 5.2 Hz, 1H), 1.82 (d, J = 5.6 Hz, 1H), 1.63 (dd, J = 6.0 and 13.6 Hz, 1H), 1.58 (s, 3H), 1.54 (dd, J = 6.0 and 10..8 Hz, 1H), 1.50 (broad singlet, N-*H*), 1.49 (d, J = 6.4 Hz, 1H), 1.47 (d, J = 1.6 Hz, 1H), ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 135.6, 127.5, 125.5, 124.3, 49.4, 41.4, 37.1, 33.5, 29.7, 23.9, 19.3 $C_{11}H_{18}N$, HRMS-ESI, $[M+H]^+$ calculated mass; 164.1439, found mass; 164.1459.

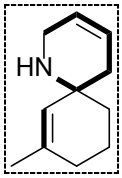


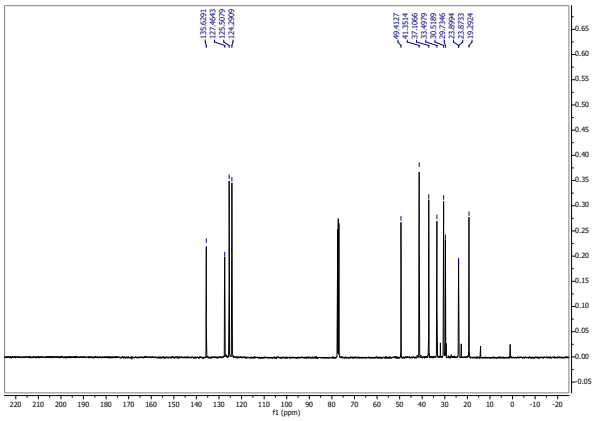


^{1}H-NMR spectrum of 8-methyl-1-azaspiro[5.5]undeca-3,7-diene

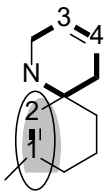


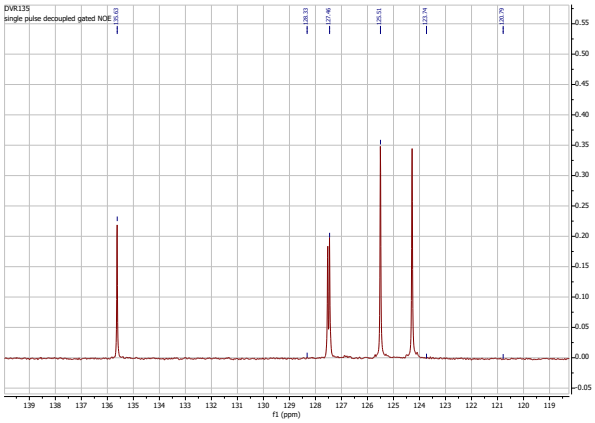
^{1}H-NMR spectrum signals of tetrahydropyridine part δ_H 5.64 (d, J = 11.6 Hz, 1H), 5.61 (d, J = 11.6 Hz, 1H), 5.31 (s, 1H), 3.32 (d, J = 10.4 Hz, 1H), 3.29 (d, J = 14.4 Hz, 1H).





^{13}C-NMR spectrum of 8-methyl-1-azaspiro[5.5]undeca-3,7-diene.

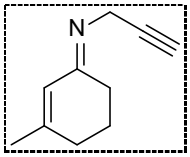




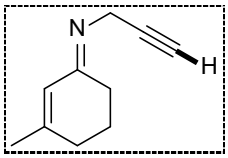
^{13}C-NMR spectrum of the signals of tetrahydropyridine and olefin part-δ_C 135.6 (1), 127.5(2), 125.5(3), 124.3(4).

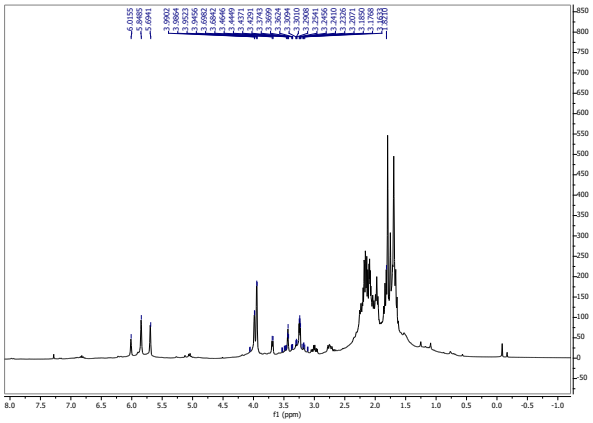
(IMINE COMPOUNDS CAN NOT BE PURIFIED THEY ARE EASILY DECOMPOSED ON SILICA GEL: SO THE CRUDE NMR HAD TAKEN IMMIDIATELY)

***(E)-N*-(3-methylcyclohex-2-en-1-ylidene)prop-2-yn-1-amine (2c) (crude nmr) (new compound)**

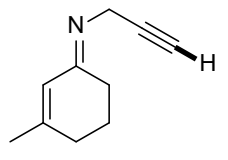


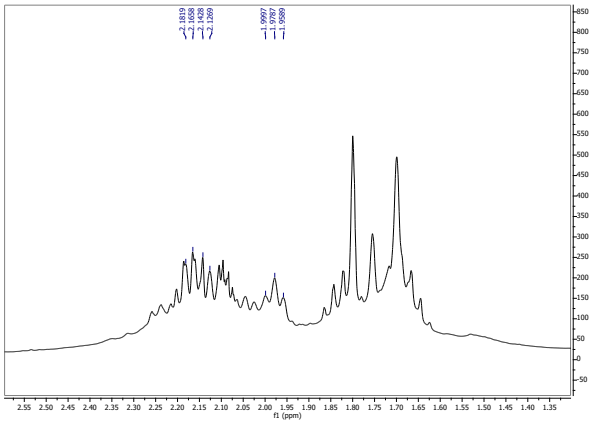
Color: Dark brown oil: FT-IR (KBr, ν, cm^{-1}) 3302 (C≡C-H, C sp-H stretching), 2986 (CH_3(sp^3-H), 2971 (CH_3 (Csp^3-H), 2125 (-C≡C- stretching), 1661 (imine, -C=N- stretching), 1625 (-C=C- stretching, cycohexene ring), 1264 and 733 (C≡C-H, (C sp -H twisting) 1194 (-CH_2-N) , ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 6.05 (q, *J* = 1.2 Hz, 1H, keton), 5.88 (q, *J* =1.2 Hz, 1H), 5.74 (q, *J* =1.2 Hz, 1H), 4.03 (t, *J* =1.2 Hz, 1H, N-*H*), 3.99 (d, *J*= 2.4 Hz, 2H), 2.28 (t, *J* = 6.4Hz, 2H), 2.23 (dd, *J* = 2.0 and 4.8 Hz, 1H), 2.20 (dd, *J*= 2.0 and 7.2 Hz, 1H), 2.16 (t, *J* = 5.6 Hz, 1H), 2.12 (dd, *J* = 0.8 and 2.4 Hz, 1H), 2.11 (dd, *J*= 0.4 and 2.8 Hz, 1H), 2.07 (d, *J*= 6.4 Hz, 1H), 2.01 (t, *J* = 6.0 Hz, 1H, C≡C-*H*), 1.87 (q, *J* = 6.4 Hz, 1H), 1.84 (d, *J* = 0.4 Hz, 3H, methyl of ketone), 1.70 (t, *J* = 6.0 Hz, 1H), 1.74 (s, 3H) ^{13}C-NMR (100 MHz, $CDCl_3$,δ, ppm): δ_C 199.5 (carbonyl of ketone), 168.1, 162.6 (ketone), 154.0, 149.9 (other izomer), 126.7 (ketone), 115.5, 81.9, 70.6, 39.3, 38.4, 37.0, 35.0, 31.5, 30.9, 30.2, 25.7, 24.2, 22.4, 21.7.



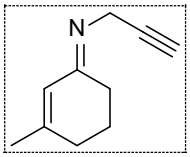


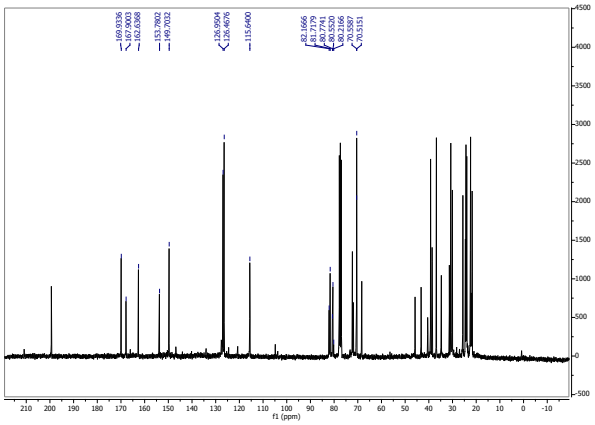
^{1}H-NMR spectrum of -(E)-N-(3-methylcyclohex-2-en-1-ylidene)prop-2-yn-1-amine (crude)



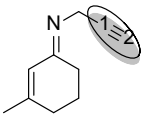


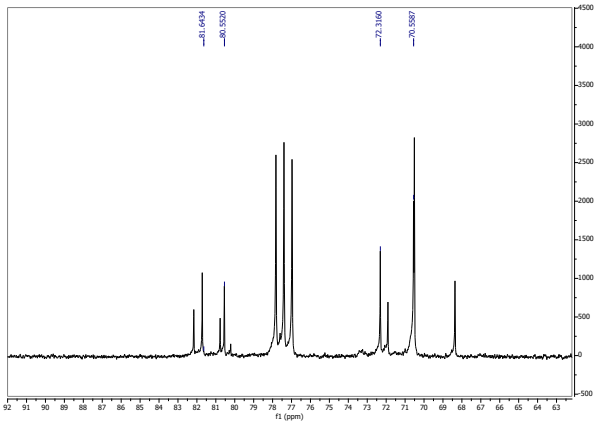
^{1}H-NMR spectrum of the signals of acetylenic proton and diasetereotopic methylene protons δ_H 2.11 (dd, J= 0.4 and 2.8 Hz, 1H), 2.07 (d, J= 6.4 Hz, 1H), 2.01 (t, J = 6.0 Hz, 1H, C≡C-*H*).



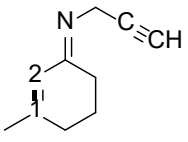


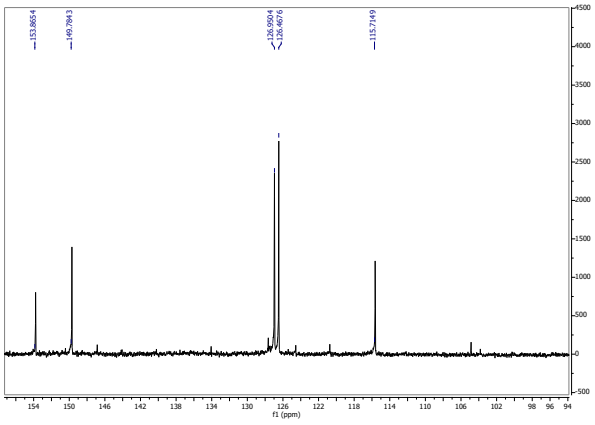
^{13}C-NMR spectrum of (E)-N-(3-methylcyclohex-2-en-1-ylidene)prop-2-yn-1-amine. (crude)





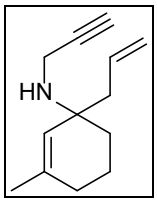
^{13}C-NMR spectrum of the signal of acetylenic part δ_C(C≡C-H 81.9(1), 70.6(2)).



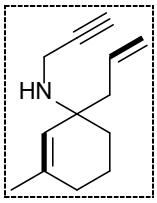


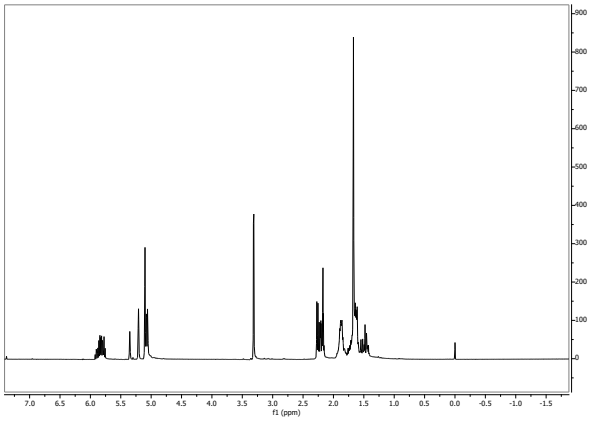
^{13}C-NMR spectrum of the signals of olefinic part δ_C 154.0(1), 115.5 (2) as well as ^{13}C-NMR signal at 168.1 ppm for imine carbon atom.

1-allyl-3-methyl-N-(prop-2-yn-1-yl)cyclohex-2-enamine (9b) (new compound)

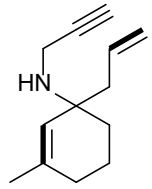


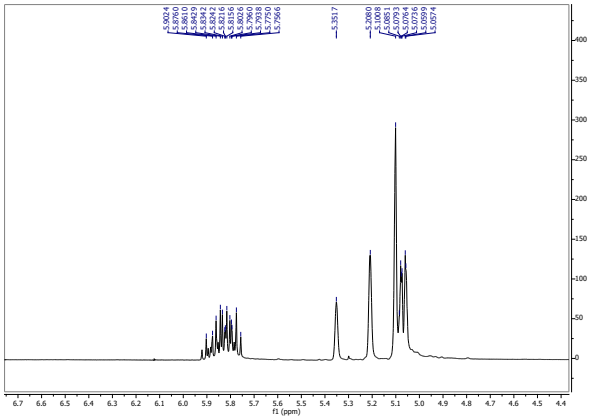
Color: Thick yellow oil Yield: 1.39 g, 83 % chemical yield .FT- IR (KBr, *ν*, cm^{-1}) : 3311 (C≡C-H (C sp-H), 3238 (N-H stretching), 3010 (C sp^2-H), 2971 (C sp ^{3}-H), 2901 ((CH_3), Csp^3-H), 2090 (-C≡C-, stretching), 1661 (-C=C- stretching, cyclohexene ring and -C=C- stretching of allyl group (matching)), 1102 (-CH_2-N-), 1249 and 647 (C≡C-H, (C sp -H twisting), 961 ve 885 (C sp^2-H twisting, specific for terminal alkenes) cm^{-1} Purified by Flash Column Chromatography (1:5:1 % Et_3N EtOAc:Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): δ_H 5.76-5.91 (m, 1H), 5.35 (s, 1H), 5.21 (broad singlet, N-*H*), 5.09 (dd, *J* = 1.2 and 12.1 Hz, 1H) 5.07 (dd, J= 2.0 and 7.2 Hz, 1H), 3.31 (d, *J* = 2.8 Hz, 2H), 2.26 (dd, *J*= 1.2 and 8.4 Hz, 1H), 2.21 (dd, *J* =7.2 and 11.8 Hz, 1H), 2.17 (t, *J* = 2.4 Hz, 1H, C≡C-*H)*, 1.84-1.91 (m, 2H), 1.67 (s, 3H), 1.64 (dd, *J* = 1.6 and 4.4 Hz Hz, 1H), 1.62 (dd, *J* =2.4 and 5.6 Hz, 1H), 1.55 (d, *J* = 2.4 Hz, 1H), 1.52 (d, *J* = 1.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 136.9, 134.0, 126.9, 117.9, 83.4, 70.5, 54.9, 44.7, 35.1, 31.6, 29.7, 23.8, 19.5 $C_{13}H_{20}N$, HRMS-ESI, $[M+H]^+$ Calculated mass ; 190.1596, Found mass; 190.1613.



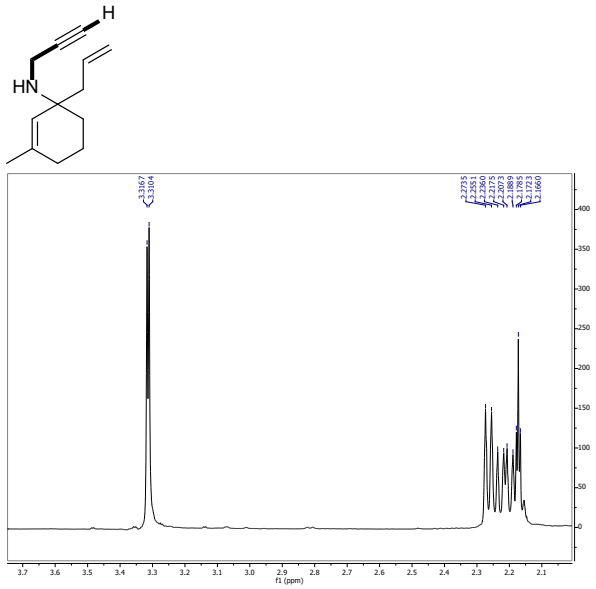


^{1}H-NMR spectrum of 1-allyl-3-methyl-N-(prop-2-yn-1-yl)cyclohex-2-enamine

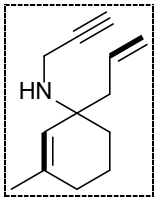


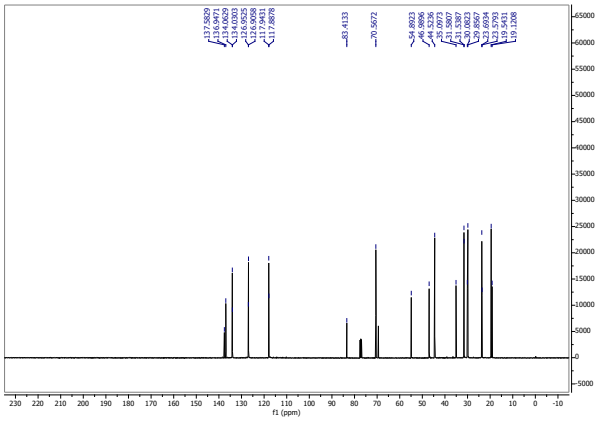


^{1}H-NMR spectrum of the signals of allyl side chain and olefin part δ_H 5.76-5.91 (m, 1H), 5.35 (s, 1H), 5.21 (broad singlet, N-*H*), 5.09 (dd, *J* = 1.2 and 12.1 Hz, 1H) 5.07 (dd, J= 2.0 and 7.2 Hz, 1H).

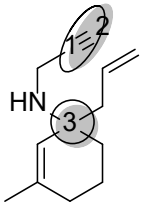


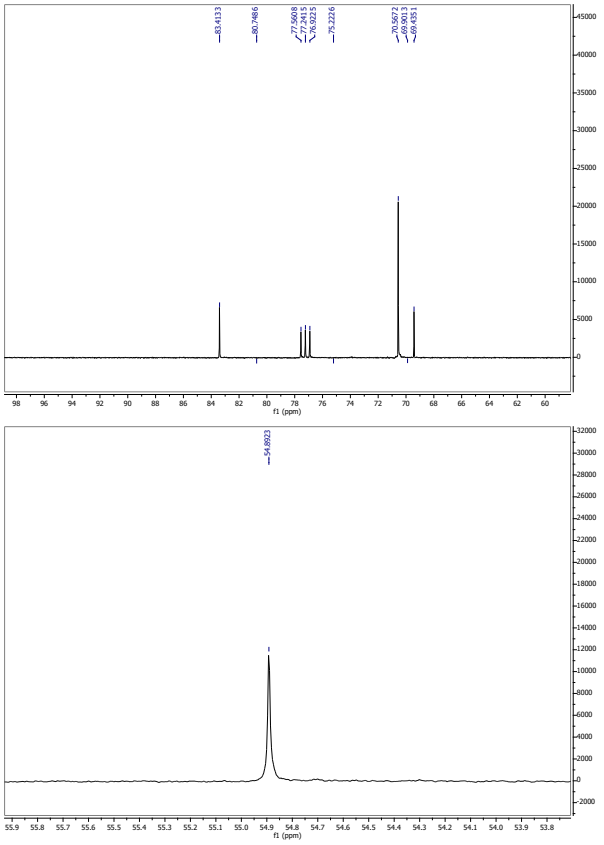
^{1}H-NMR spectrum of the signals of acetylenic proton and CH_2 protons directly attached to *Nitrogen* atom δ_H 3.31 (d, *J* = 2.8 Hz, 2H), 2.26 (dd, *J*= 1.2 and 8.4 Hz, 1H), 2.21 (dd, *J* =7.2 and 11.8 Hz, 1H), 2.17 (t, *J* = 2.4 Hz, 1H, C≡C-*H)*.



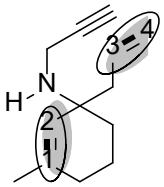


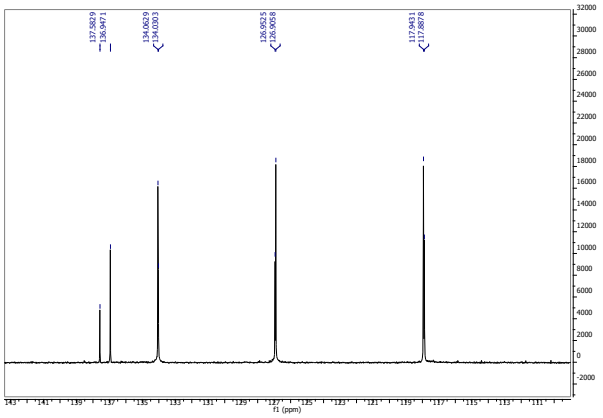
^{13} C-NMR spectrum of 1-allyl-3-methyl-N-(prop-2-yn-1-yl)cyclohex-2-enamine





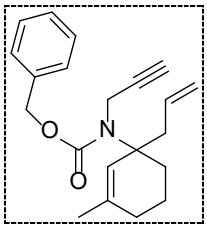
^{13}C-NMR spectrum of the signals of acetylenic part C≡C-H and CH_2 directly attached to *Nitrogen* atom δ_C 83.4 (1), 70.5 (2), 54.9 (3).



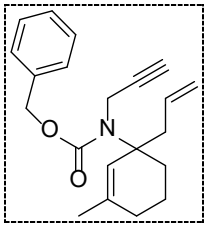


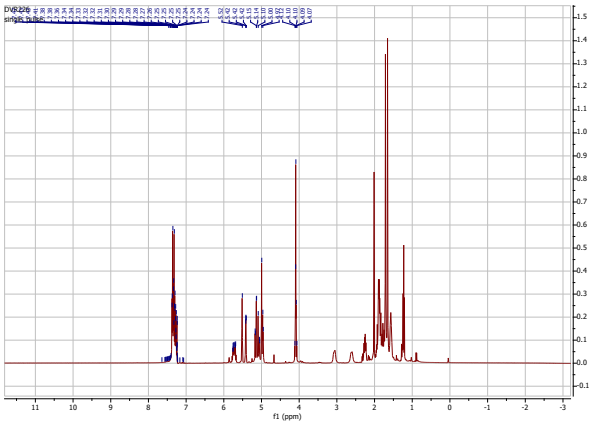
^{13}C-NMR spectrum of the signals of the olefinic and allylic part δ_C 136.9(1), 134.0(2), 126.9(3), 117.9(4).

Benzyl (1-allyl-3-methylcyclohex-2-en-1-yl)(prop-2-yn-1-yl)carbamate (10b) (new compound)

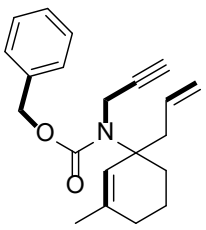


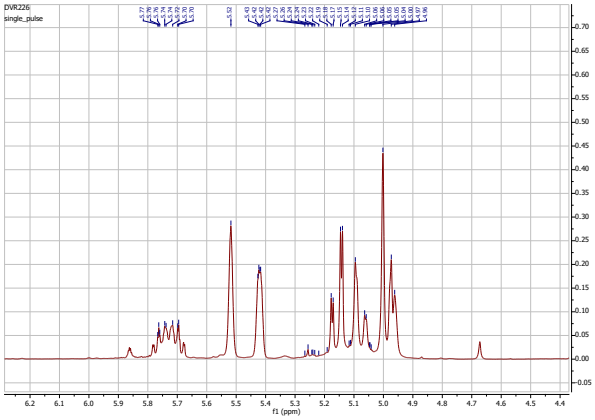
Color. Yellow oil. Yield. 910 mg, 72 % yield. FT-IR (KBr, ν, cm^{-1}) : 3072 (aromatic, (Csp^2-H)), 3310 (C≡C-H (C sp-H), 3025 (C sp^2-H), 2942 (C sp^3-H), 2911 ((CH_3), Csp^3-H), 2250 (-C≡C-, stretching), 1697 (C=O stretching), 1655 (-C=C- stretching, signals belong to the cyclohexene and aromatic ring are matched) 1606 (-C=C- stretching, allyl group), 1266 (-CH_2-N-), 1141 (-CH_2-***C-O***- stretching), 1241 and 696 (C≡C-H, (C sp -H twisting), 908 and 766 (C sp^2-H twisting, specific for terminal alkenes). Purified by Flash Column Chromatography (1:5:1 % Et_3N, EtOAc: Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 7.25-7.38 (m, 5H), 5.68-5.78 (m, 1H), 5.16 (dd, J= 2.4 and 12.6 Hz, 1H), 5.08 (dd, *J*= 2.0 and 12.6 Hz, 1H), 5.52 (s, 1H), 5.00 (s, 1H), 4.97 (d, J= 5Hz, 1H), 4.07-4.12 (m, 2H), 2.32-2.38 (m, 2H), 2.02 (s, 1H, C≡C-*H)*, 1.88-1.93 (m, 2H), 1.84-1.87 (m, 2H), 1.52-1.62 (m, 2H),^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 189.3 (ester carbonyl carbon), 137.8, 134.3, 128.4, 127.7, 127.5, 125.3, 123.5, 118.3, 117.8, 86.1,81.3, 65.8, 37.7, 30.4, 29.8, 24.0, 23.6, 19.5, 18.7. $C_{21}H_{26}NO_2$, HRMS-ESI, $[M+H]^+$ Calculated mass; 324.1964, Found mass; 324.1971.



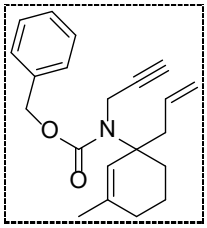


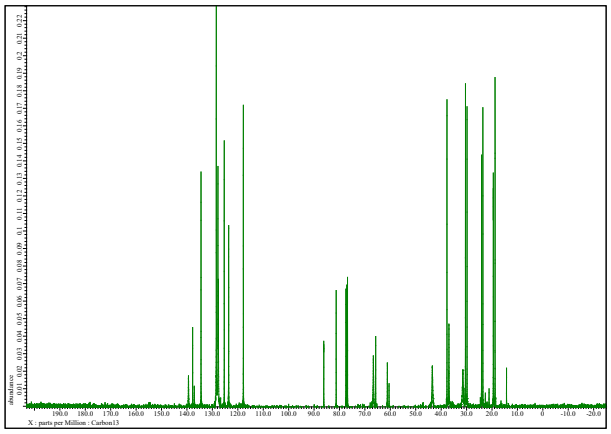
^{1}H-NMR spectrum of Benzyl (1-allyl-3-methylcyclohex-2-en-1-yl)(prop-2-yn-1-yl)carbamate



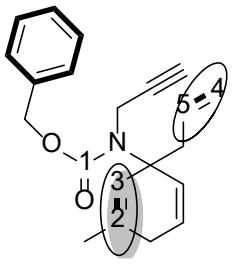


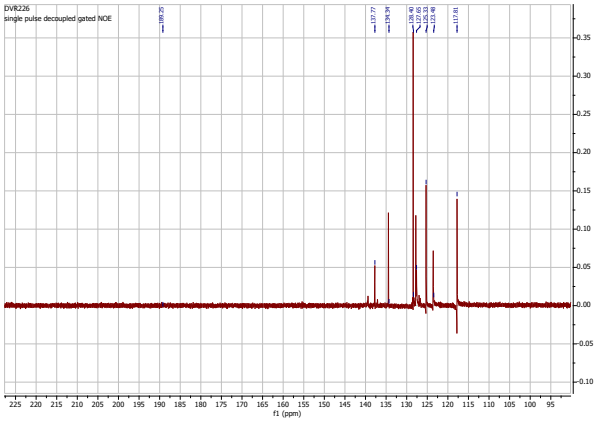
^{1}H-NMR spectrum of the signals of δ_H 5.68-5.78 (m, 1H), 5.16 (dd, J= 2.4 and 12.6 Hz, 1H), 5.08 (dd, J= 2.0 and 12.6 Hz, 1H), 5.52 (s, 1H), 5.00 (s, 1H), 4.97 (d, J= 5Hz, 1H), 4.07-4.12 (m, 2H).



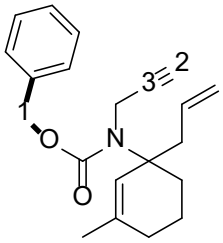


^{13}C-NMR spectrum of Benzyl (1-allyl-3-methylcyclohex-2-en-1-yl)(prop-2-yn-1-yl)carbamate (10b)



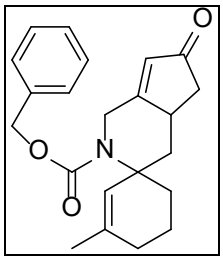


^{13}C-NMR spectrum of the signals of phenyl and olefinic carbon atoms as well as ester carbonyl carbon atom δ_C 189.3 (1) ester carbonyl carbon, 137.8 (2), 134.3, 128.4,(5) (high intensity belongs to the two carbon atoms 127.7, 127.5, 125.3, 123.5 (3) 118.3, 117.8 (4).

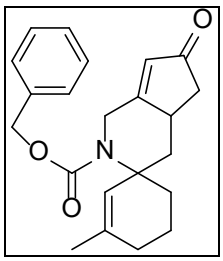


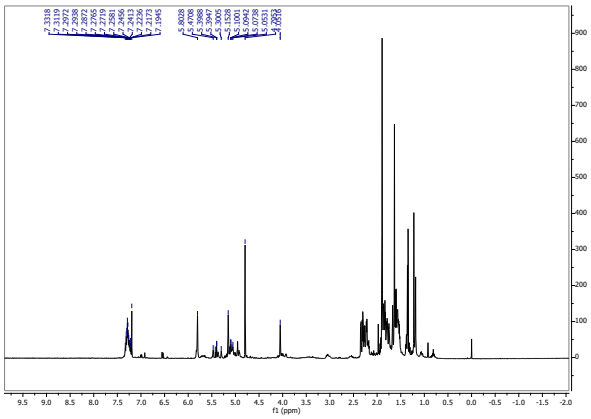
The signals at δ_C 86.1 (3), 81.3 (2), 65.8 (1) ppm are due to the methylene carbon atom directly attached to oxygen atom as well as acetylenic carbon atoms in the ^{13}C-NMR spectrum.

Benzyl 3-methyl-6'-oxo-4',4a',5',6'-tetrahydrospiro[cyclohex[2]ene-1,3'-cyclopenta[c]pyridine]-2'(1'H)-carboxylate (11b) (new compound)

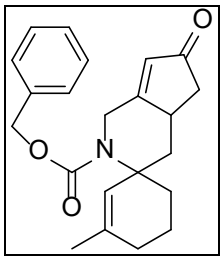


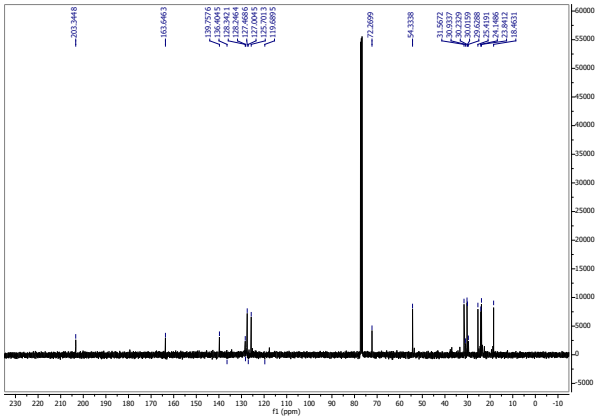
Color: Light yellow liquid, Yield.1.62 g 75 % chemical yield. FT-IR (KBr, ν, cm^{-1}): 1696 (C=O), 1672 (-C=C- stretching, cyclohexene ring), 1622 (-C=C- stretching, cyclopentenone ring). Purified by Flash Column Chromatography (2:1, EtOAc: Hexane).^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 7.21-7.34 (m, 5H), 5.80 (s, 1H), 5.15 (s, 1H), 4.80 (s, 2H), 4.05 (t, J= 0.8 Hz, 2H), 2.33 (dd, J =4.4 and 14.0 Hz, 1H), 2.28 (d, J=17.2 Hz, 1H), 2.23 (m, 1H), 2.17-2.21 (m, 1H), 1.85-1.88 (m, 1H), 1.82-1.84 (m, 1H), 1.60 (J=7.6 Hz, 1H), ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 203.4, 163.4, 139.6, 128.5, 128.3, 127.7 (belongs two carbon atoms), 127.5 (belongs two carbon atoms) 125.8, 125.2, 118.4 72.2, 54.3, 53.6, 31.6, 30.2, 30.0, 25.4, 24.1, 23.8, 18.5 $C_{22}H_{26}NO_3$, HRMS-ESI, $[M+H]^+$ Calculated mass; 352.1964, Found mass; 352.1913.



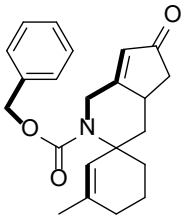


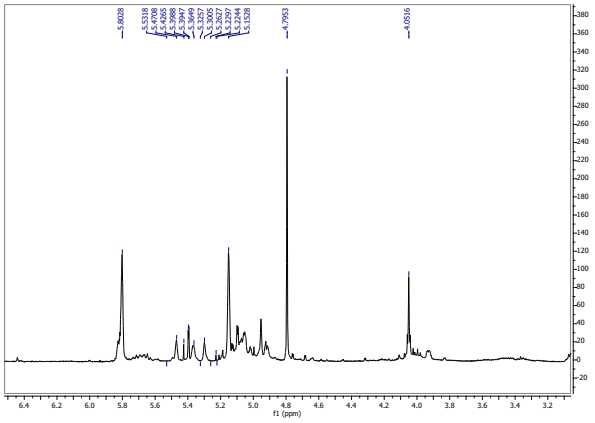
^{1}H-NMR spectrum of benzyl 3-methyl-6'-oxo-4',4a',5',6'-tetrahydrospiro[cyclohex[2]ene-1,3'-cyclopenta[c]pyridine]-2'(1'H)-carboxylate



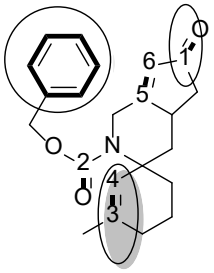


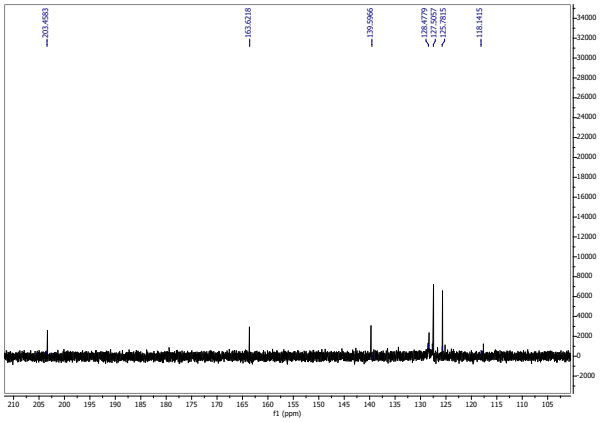
^{13}C-NMR spectrum of benzyl 3-methyl-6'-oxo-4',4a',5',6'-tetrahydrospiro[cyclohex[2]ene-1,3'-cyclopenta[c]pyridine]-2'(1'H)-carboxylate



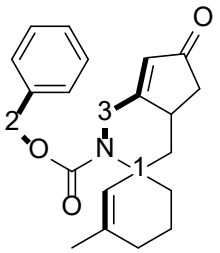


^{1}H-NMR spectrum of the signals of olefinic and methylene protons δ_H 5.80 (s, 1H), 5.15 (s, 1H), 4.80 (s, 2H), 4.05 (t, J= 0.8 Hz, 2H).



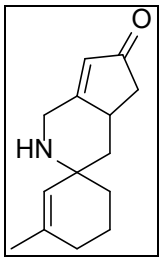


^{13}C-NMR spectrum of the signals of enone and ester carbonyl carbon with aromatic ring and olefin part δ_C 203.4, (carbonyl carbon of enone) (1) 163.4 (ester carbonyl carbon atom) (2), 139.6 (3), 128.5 (5), 128.3, 127.7 (belongs two carbon atoms), 127.5 (belongs two carbon atoms) 125.8, 125.2 (4), 118.4 (6).

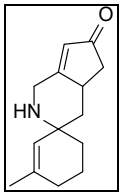


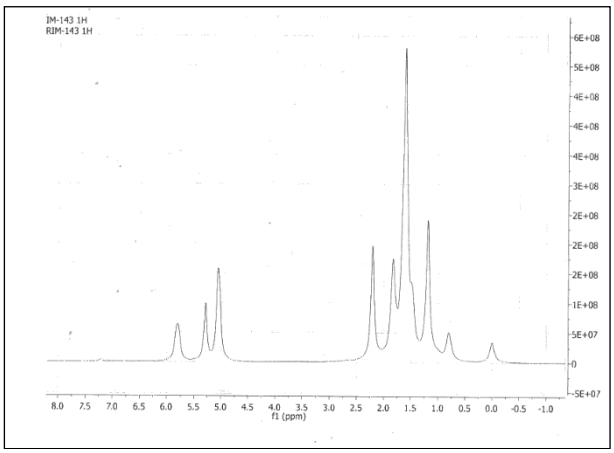
^{13}C-NMR signals at 74.2 (1) ppm are due to the quaternary carbon atom as well as methylene carbon atoms at 54.3(2), 53.6(3) ppm respectively.

3-methyl-1',2',4a',5'-tetrahydrospiro[cyclohex[2]ene-1,3'-cyclopenta[c]pyridin]-6'(4'H)-one (13b) (new compound).

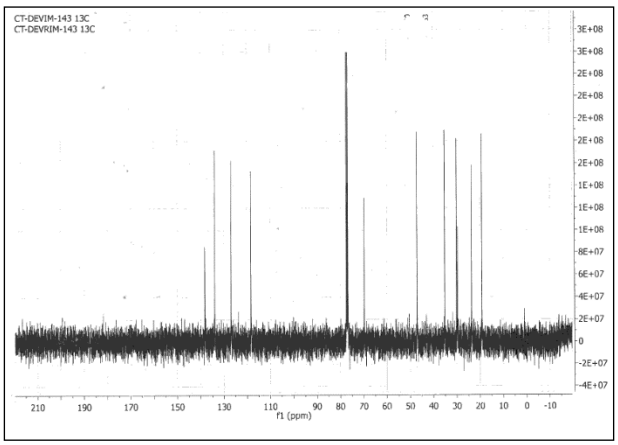


Color. Dark Red oil. Yield; 1.20 g, 65 % chemical yield. FT-IR (KBr, ν, cm^{-1}). 1696 (C=O), 1672 (-C=C- stretching, cyclohexene ring), 1622 (-C=C-stretching, cyclopentenone ring). Purified by Flash Column Chromatography (2:1, EtOAc: Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 5.81 (s,1H), 5.28 (s, 1H), 5.06 (s, 1H, N-*H*), 2.16-2.27 (m, 4H), 2.06-2.36 (m, 2H), 1.75-1.95 (m, 2H), 1.61 (s, 3H), 1.35-1.50 (m, 2H), 1.03-1.32 (m, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 198.3, 182.2, 138.3, 134.1, 118.3, 61.5, 50.6, 46.8, 42.6, 35.2, 30.1, 29.3, 23.4, 19.2 (198.3 ppm due to the carbonyl carbon).

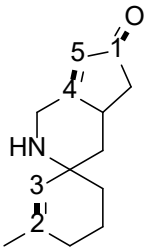




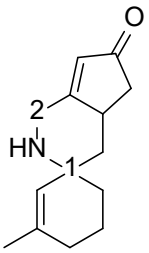
^{1}H-NMR spectrum of 3-methyl-1',2',4a',5'-tetrahydrospiro[cyclohex[2]ene-1,3'-cyclopenta[c]pyridin]-6'(4'H)-one



^{13}C-NMR spectrum of 3-methyl-1',2',4a',5'-tetrahydrospiro[cyclohex[2]ene-1,3'-cyclopenta[c]pyridin]-6'(4'H)-one

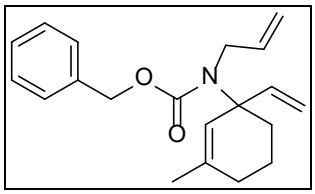


^{13}C-NMR signals at δ_C 198.3 (1) ppm (due to the carbonyl carbon of enone, as well as olefinic carbon atoms of cyclohexene ring and cyclopentenone ring system 182.2(2) 138.3 (3), 134.1(4), 118.3 (5) pppm.

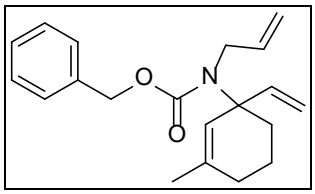


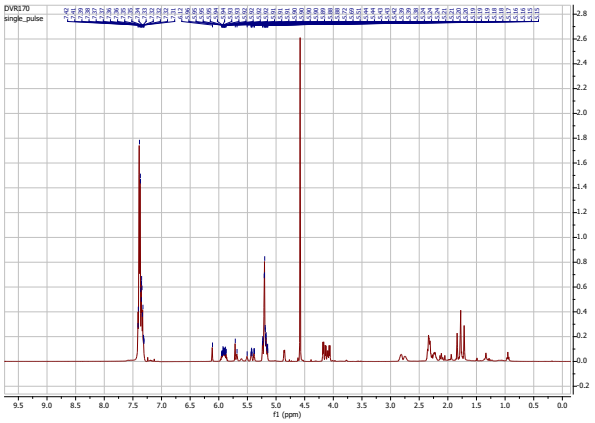
^{13}C-NMR signals for the quaternary and methylene carbon atoms 61.5, 50.6 ppm. respectively.

Benzyl allyl(3-methyl-1-vinylcyclohex-2-en-1-yl)carbamate (5b) (new compound)

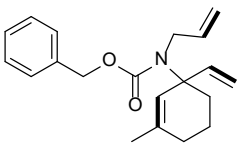


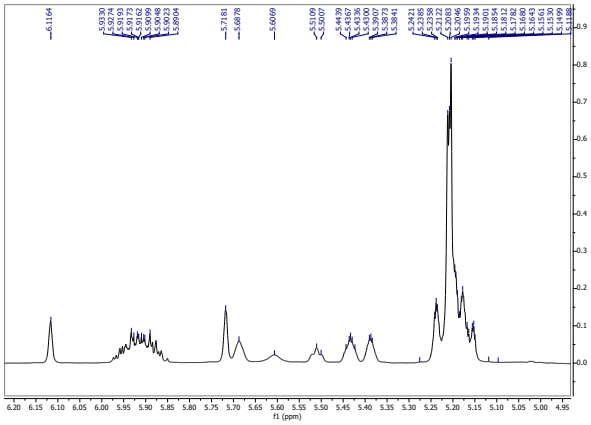
Color. Brown Liquid Yield: 2.45 g, 65 % chemical yield. FT-IR (KBr, $\nu_{max,}$ cm^{-1}) 3068 (aromatic, (Csp^2-H)), 3031 (Csp^2-H), 2930 (CH_3 (Csp^3-H)), 1703 (C=O),1670 (-C=C- stretching (signals from cyclohexene and aromatic ring are matched), 1496 (-C=CH_2 stretching, (allyl and vinyl group)), 1264 (-CH_2 -N-),1140 (-CH_2-***C-O***- stretching), 991, 921, 695 and 677 (C sp^2-H twisting, specific for terminal alkenes)**,** Purified by Flash Column Chromatography (1:5:1 % Et_3N, EtOAC,Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 7.41 (d, *J* =2.0 Hz, 1H), 7.38 (d, *J* = 6.4 Hz, 2H), 7.35 (d, *J*= 2.8 Hz, 1H), 7.34 (d, *J* =4 Hz, 1H), 5.91-5.97 (m, 1H), 5.85-5.91 (m, 1H), 5.72 (s, 1H), 5.22 (dd, *J* = 1.2 and 10.8 Hz, 2H), 5.21 (d, *J* =1.2 Hz, 2H), 4.58 (s, 2H), 4.16 (dd, *J*= 5.6 and 16.0 Hz, 1H), 4.09 (dd, *J* = 6.0 and 12.8 Hz, 1H), 2.79 (dd, *J* =3.6 and 28.2 Hz, 1H), 2.35 (dd, *J* =0.8 and 7.6 Hz, 1H), 2.32 (dd, *J* =1.2 and 9.0 Hz, 1H), 2.24 (dd, *J* = 2.0 and 6.6 Hz, 1H), 2.11 (t, *J* = 9.2 Hz, 1H), 1.84 (s, 1H), 1.78 (d, *J* = 1.6 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 155.1, 137.7, 134.5, 130.9, 128.9, 128.7, 128.6, 128.5, 128.0, 127.9, 119.0, 117.6, 117.1, 67.5, 67.1, 52.8, 46.4, 30.1, 27.7, 24.0. $C_{20}H_{25}NO_2$, HRMS-ESI, $[M]^+$ Calculated mass; 311.1885, Found mass; 311.1717.



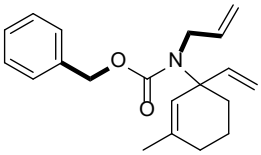


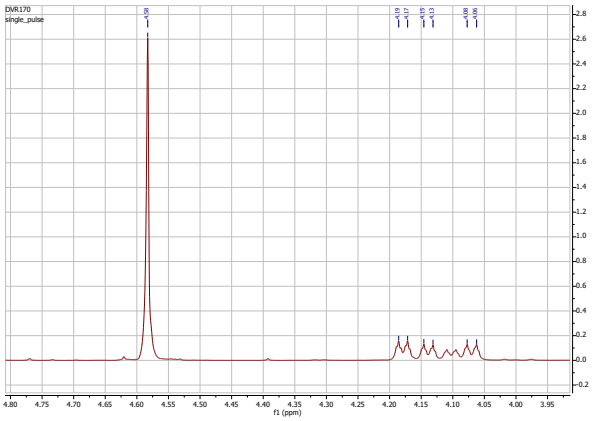
^{1}H-NMR spectrum of Benzyl allyl(3-methyl-1-vinylcyclohex-2-en-1-yl)carbamate



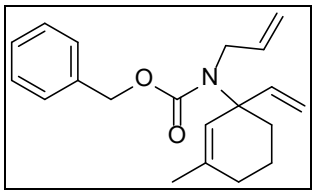


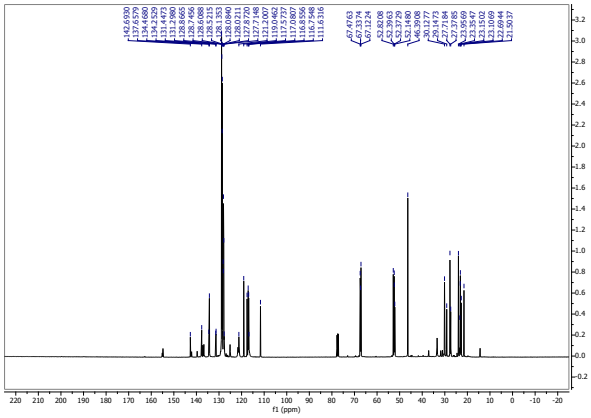
^{1}H-NMR spectrum of the signals of diene and olefin part δ_H 5.91-5.97 (m, 1H), 5.85-5.91 (m, 1H), 5.72 (s, 1H), 5.22 (dd, *J* = 1.2 and 10.8 Hz, 2H), 5.21 (d, *J* =1.2 Hz, 2H).



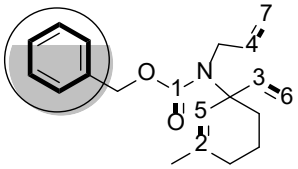


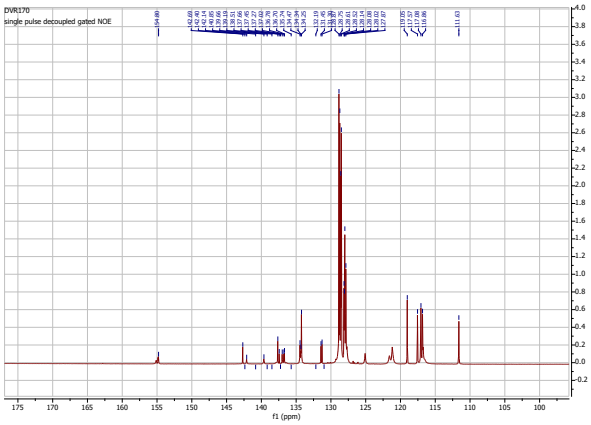
^{1}H-NMR spectrum of the signals of CH_2 protons directly attached to the O and N atoms 4.58 (s, 2H), 4.16 (dd, *J*= 5.6 and 16.0 Hz, 1H), 4.09 (dd, *J* = 6.0 and 12.8 Hz, 1H).



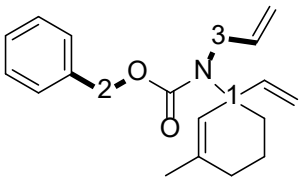


^{13}C-NMR spectrum of Benzyl allyl(3-methyl-1-vinylcyclohex-2-en-1-yl)carbamate



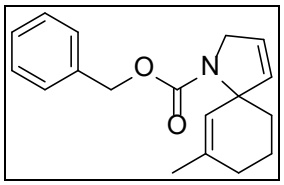


^{13}C-NMR spectrum of the signals of ester carbonyl carbon δ_C 155.1 (1) with aromatic ring and diene as well as olefin carbon atoms; δ_C 137.7, 134.5(2), 130.9 (3), 128.9(4), 128.7, 128.6, 128.5, 128.0, 127.9 (5), 119.0(6), 117.6, 117.1 (7). (others are for aromatic carbon atoms).

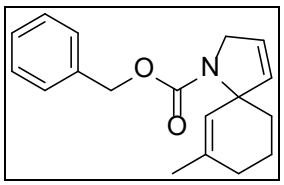


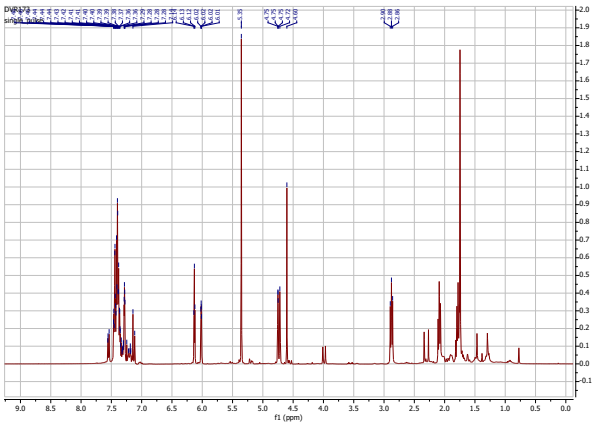
^{13}C-NMR signals at 67.5,(1) 67.1 (2), 52.8 (3) ppm for the quaternary carbon and methylene carbon atoms respectively.

Benzyl 7-methyl-1-azaspiro[4.5]deca-3,6-diene-1-carboxylate (6b) (new compound)

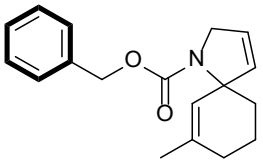


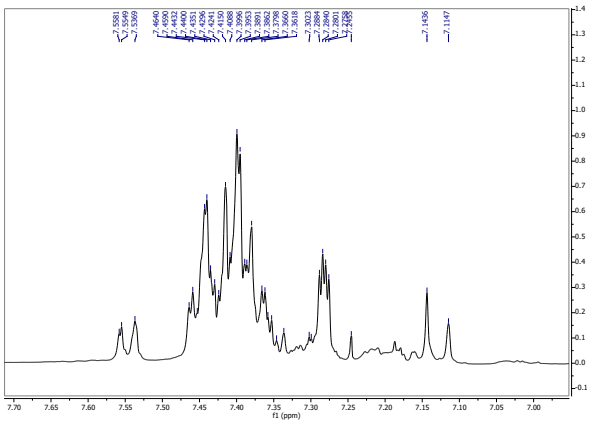
Color: Dark green oil. Yield: 509 mg, 70 % chemical yield FT-IR (KBr, ν, cm^{-1}) 3072 (Csp^2-H, aromatic), 3031 (C sp^2-H), 2932 (CH_3 (sp^3-H), 2850 (CH_3 (Csp^3-H), 1648 (-C=C- stretching, (signals from cyclohexene and aromatic ring are matched), 1495 (-C=C- stretching), 1122 (-CH_2-N-),1064 (-CH_2-*C*-*O*- stretching). Purified by Flash Column Chromatogaphy (1:1:1 % Et_3N, EtOAc: Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 7.46 (d, J = 2.0 Hz, 1H), 7.45 (dd, J = 1.2 and 8.0 Hz, 1H), 7.44 (dd, J = 1.2 and 3.6 Hz, 1H), 7.40 (d, J = 2.0 Hz, 1H), 7.38 (J = 2.4 Hz, 1H), 7.28 (dd, J =1.6 ve 3.2 Hz, 1H), 6.13 (t, J = 3.2 Hz, 1H), 6.02 (dd, J =1.2 and 2.6 Hz, 1H), 5.36 (s, 2H), 4.74 (d, J = 12.8 Hz, 2H), 2.88 (t, J =7.6 Hz, 2H), 1.79 (dd, J = 8.0 and 15.4 Hz, 2H), 2.09 (t, J =7.6 Hz, 2H) 1.75 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 150.9 145.8, 136.7, 135.2, 128.8, 128.8, 128.7, 128.6, 127.8, 126.6, 120.8, 68.7, 46.4, 37.5, 28.4, 26.8, 22.6.$C_{18}H_{22}NO_2$, HRMS-ESI, $[M+H]^+$ Calculated mass; 284.1651, Found mass; 284.1642.



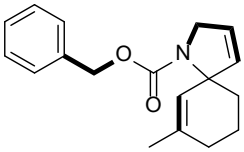


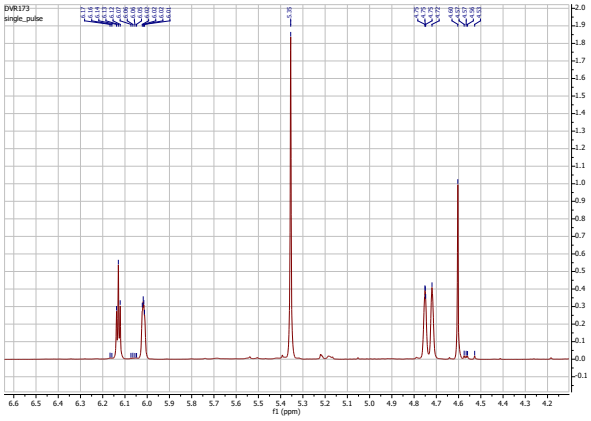
^{1}H-NMR spectrum of Benzyl 7-methyl-1-azaspiro[4.5]deca-3,6-diene-1-carboxylate



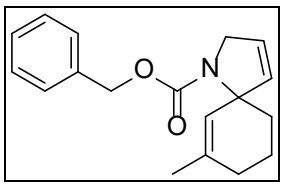


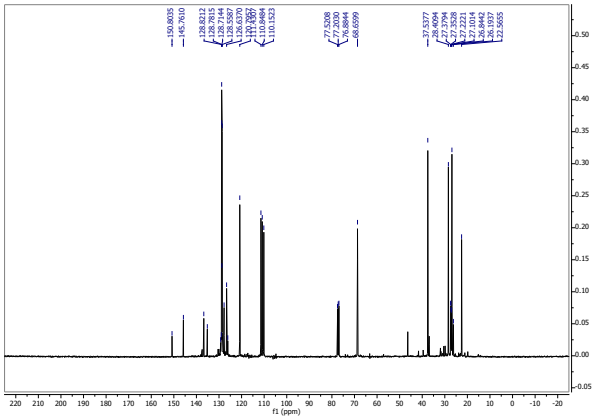
^{1}H-NMR spectrum of the signals at δ_H 7.46 (d, *J* = 2.0 Hz, 1H), 7.45 (dd, *J* = 1.2 and 8.0 Hz, 1H), 7.44 (dd, *J* = 1.2 and 3.6 Hz, 1H), 7.40 (d, *J* = 2.0 Hz, 1H), 7.38 (*J* = 2.4 Hz, 1H), 7.28 (dd, *J* =1.6 ve 3.2 Hz, 1H) are for the aromatic part.



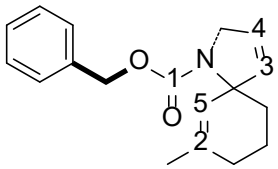


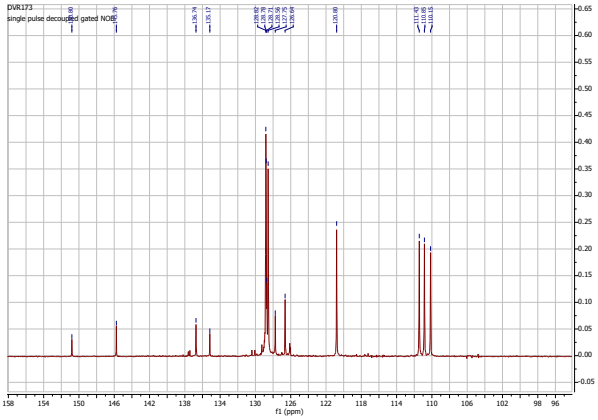
^{1}H-NMR spectrum of the signals due to CH_2 directly attached to the oxygen and nitrogen atom as well as olefinic protons; δ_H 6.13 (t, *J* = 3.2 Hz, 1H), 6.02 (dd, *J* =1.2 and 2.6 Hz, 1H), 5.36 (s, 2H), 4.74 (d, *J* = 12.8 Hz, 2H)



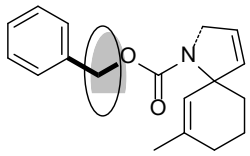


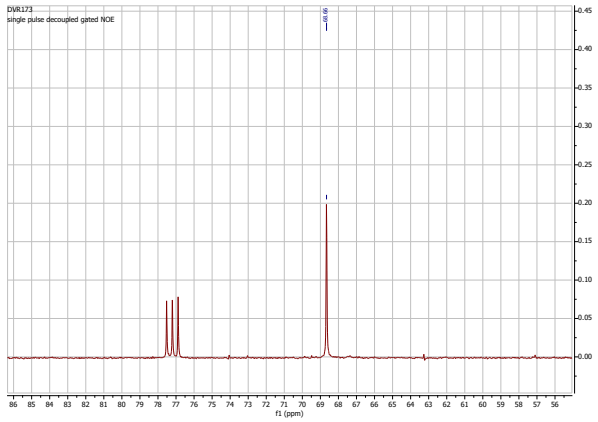
^{13}C-NMR spectrum of Benzyl 7-methyl-1-azaspiro[4.5]deca-3,6-diene-1-carboxylate





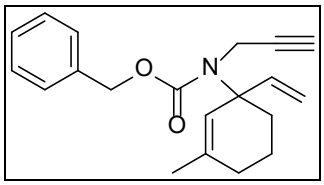
^{13}C-NMR spectrum of the signals due to the ester carbonyl carbon atom at δ_C 150.9 (1) as well as carbon atoms due to the phenyl ring and CH carbon atoms of the olefin part δ_C 145.8 (2), 136.7, 135.2(3), 128.8, 128.8, 128.7, 128.6, 127.8, 126.6(4), 120.8 (5).



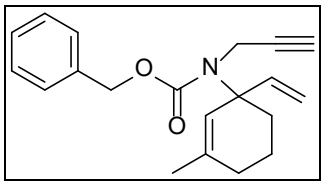


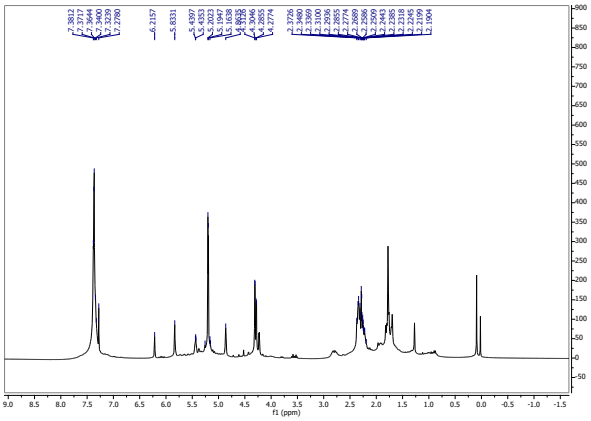
^{13}C-NMR spectrum of the signal of CH_2 directly attached to oxygen atom δ_C 68.7.

Benzyl (3-methyl-1-vinylcyclohex-2-en-1-yl)(prop-2-yn-1-yl)carbamate (7b) (new compound)

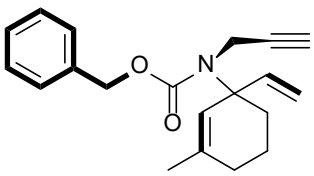


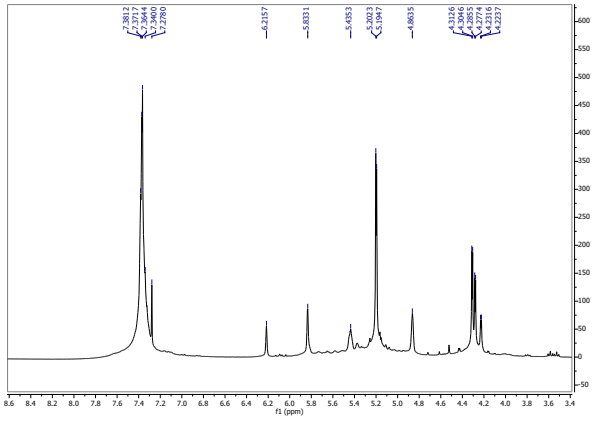
Color: Brown liquid. Yield: 2.84 g, 75 % chemical yield. FT-IR (KBr, *ν*, cm^{-1}) : 3292 (≡C-H, C sp-H), 3020 (Csp^2-H matching of aromatic and cyclohexene ring signals), 2930 (Csp^3-H), 2110 (C≡C-H (C sp-H)), 1703 (-N-***C=O***), 1660 (-C=C- stretching, matching of cylohexene and vinyl ring signals) 1496 (-C=CH_2 stretching, vinyl group), 1225 (-CH_2-N-), 1126 ve 695 (C≡C-H, (C sp -H twisting), 902 ve 735 (C sp^2-H twisting, specific for terminal alkynes), 1:5:1% Et_3N (EtOAc: Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 7.34 (dd, *J* =3.2 and 5.8 Hz, 2H), 7.32 (dd, *J* = 0.8 and 5.0 Hz, 2H), 7.29 (dd, *J* = 2.4 and 9.0 Hz, 1H), 5.82 (s, 1H), 5.63 (t, *J* = 3.6 Hz, 1H), 5.41 (dd, *J* =1.2 and 4.0 Hz, 1H), 5.40 (dd, *J* = 1.2 and 2.6 Hz, 1H), 5.17 (d, *J* = 4.8 Hz, 2H), 4.27 (d, *J* = 2.4 Hz, 1H), 4.24 (d, *J* = 2.0 Hz, 1H), 2.31 (dd, *J* = 3.2 and 11.4 Hz, 1H), 2.29 (d, J=2.4 Hz, 1H), 2.27 (d, *J* =2.0 Hz, 1H), 2.26 (dd, *J* = 2.0 and 4.4 Hz, 1H), 2.25 (d, *J* = 1.2 Hz, 1H), 2.16-2.23 (m, 1H). 2.08 (t, *J* = 9.2 Hz, 1H, C≡C-*H*), 1.75 (d, *J* =1.6 Hz, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 154.4, 142.2, 137.6, 131.2, 128.6, 128.5, 128.4, 128.1, 128.0, 127.8, 119.4, 79.9, 72.3, 67.7, 67.4, 39.6, 39.2, 30.0, 27.3, 23.9. $C_{20}H_{24}NO_2$, HRMS-ESI, $[M+H]^+$ Calculated mass; 310.1807, Found mass; 310.1821



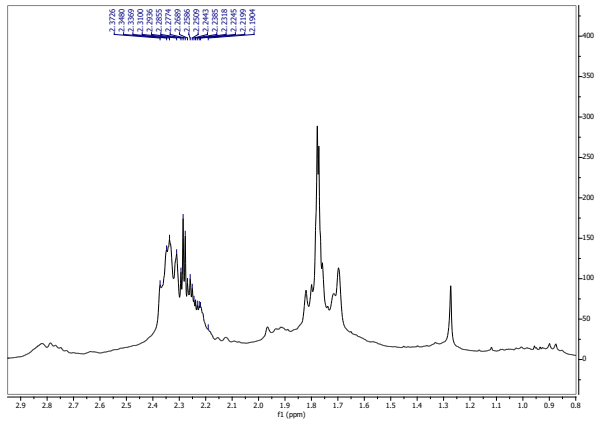


^{1}H-NMR spectrum of benzyl (3-methyl-1-vinylcyclohex-2-en-1-yl)(prop-2-yn-1-yl)carbamate

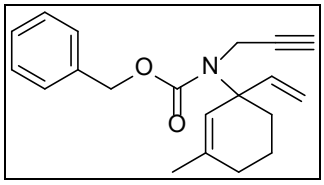


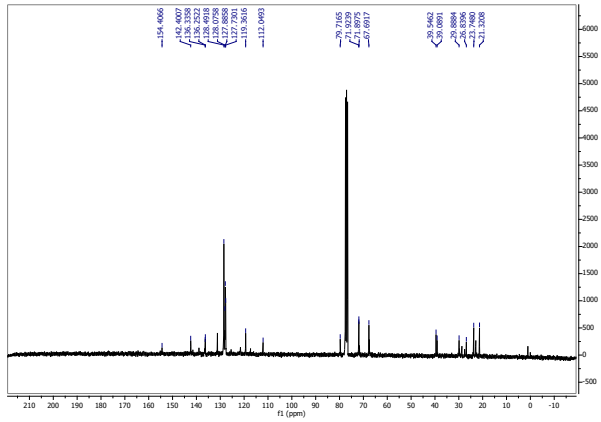


^{1}H-NMR spectrum of the signals of the phenyl ring δ_H 7.34 (dd, J =3.2 and 5.8 Hz, 2H), 7.32 (dd, J = 0.8 and 5.0 Hz, 2H), 7.29 (dd, J = 2.4 and 9.0 Hz, 1H), CH2 directly attached to oxygen and nitrogen atoms as well as olefinic protons 5.82 (s, 1H), 5.63 (t, J = 3.6 Hz, 1H), 5.41 (dd, J =1.2 and 4.0 Hz, 1H), 5.40 (dd, J = 1.2 and 2.6 Hz, 1H), 5.17 (d, J = 4.8 Hz, 2H), 4.27 (d, J = 2.4 Hz, 1H), 4.24 (d, J = 2.0 Hz, 1H).

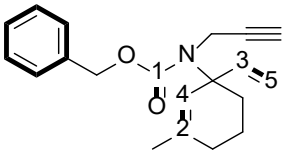


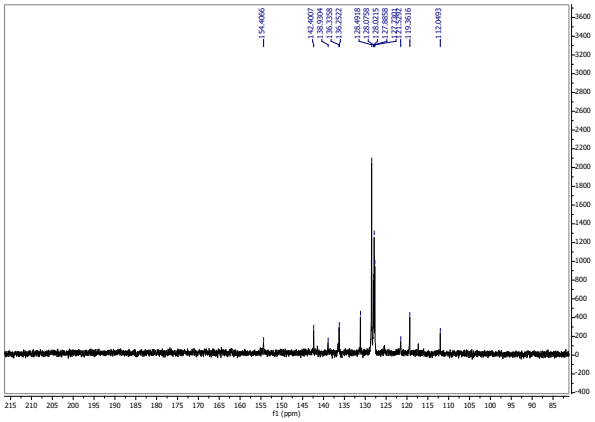
^{1}H-NMR spectrum of the signals of the acetylenic proton δ_H 2.08 (t, J = 9.2 Hz, 1H, C≡C-*H*).



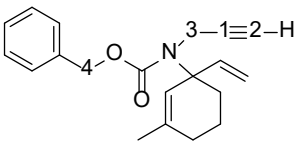


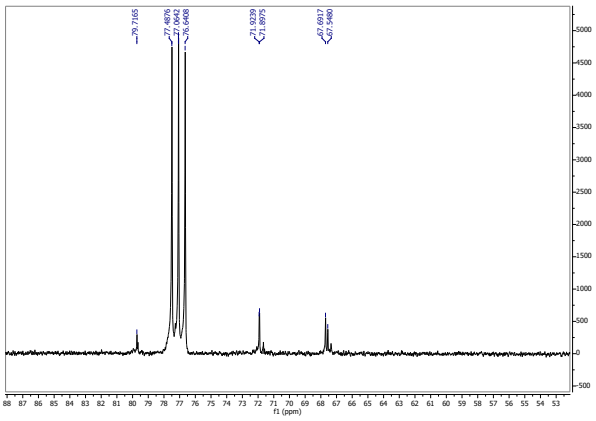
^{13}C-NMR spectrum of benzyl (3-methyl-1-vinylcyclohex-2-en-1-yl)(prop-2-yn-1-yl)carbamate





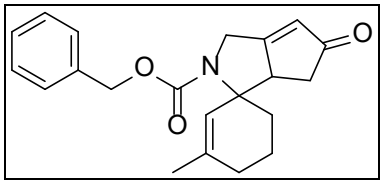
^{13}C-NMR spectrum of the signal due to the ester carbonyl carbon atom as well as aromatic and olefinic carbon atoms δ_C 154.4 (1) (ester carbonyl carbon), 142.2 (2), 137.6, 131.2(3), 128.6, 128.5, 128.4, 128.1, 128.0, 127.8(4), 119.4 (5). (others for the aromatic ring).



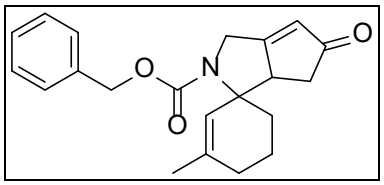


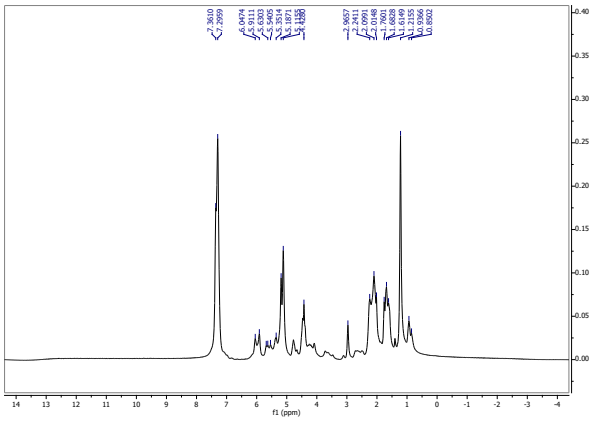
^{13}C-NMR spectrum of the signals of the acetylenic carbon atoms *C*≡*C*-H: δ_C 79.9(1), 72.3(2). And signals at 67.7(4), 39.6 (3) for the carbon atoms directly attached to oxygen and nitrogen atoms.

Benzyl 3-methyl-5'-oxo-3',5',6',6a'-tetrahydro-2'H-spiro[cyclohex[2]ene-1,1'-cyclopenta[c]pyrrole]-2'-carboxylate (8b) (new compound)

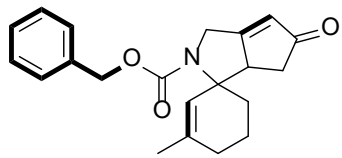


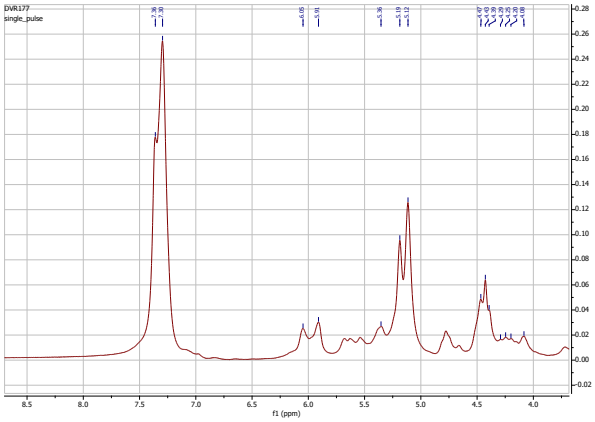
Color: Dark Brown Liquid. Yield: 1.25 g, 65 % chemical yield. FT-IR (KBr, *ν*, cm^{-1}) 3010 (Csp^2-H, aromatic), 2968 (CH_3 (sp^3-H), 2924 (CH_3 (Csp^3-H), 1697 (C=O), 1645 (-C=C- stretching), 1497 ve 1453 (aromatic -C=C- stretching), 1278 (-CH_2-N-), 1213 (-CH_2-*C-O-stretching*). Purified by Flash Column Chromatography (2:1 EtOAc: Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 7.18-7.45 (m, 4H), 7.33 (d, *J* = 25.6 Hz, 1H), 6.04 (s, 1H), 5.91 (s, 1H), 5.15 (d, *J* =28.8 Hz, 2H), 4.42 (d, *J* = 3.2 Hz, 1H), 4.41 (d, *J* =12.8 Hz, 1H), 2.97 (s, 1H), 2.18 (dd, *J* = 10.8 and 42 Hz, 1H), 2.17 (dd, *J* = 3.6 and 53.6 Hz, 1H), 2.07 (d, *J* = 18.0 Hz, 2H), 1.73 (dd, *J* = 3.6 and 26 Hz, 1H), 1.64 (dd, *J* = 6.0 and 36.8 Hz, 1H),1.59 (d, *J* =10 Hz, 1H), 1.22 (s, 3H), 0.90 (dd, *J*= 2.4 and 33.6 Hz, 1H), ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 213.4, 171.5, 152.6, 142.2, 136.6, 128.7, 128.6, 128.4, 128.3, 128.1, 127.0, 123.7, 67.4, 54.7, 49.1, 47.0, 31.1, 29.8, 27.6, 22.3, 21.2.$C_{21}H_{24}NO_3$, HRMS-ESI, $[M+H]^+$ Calculated mass; 338.1756, Found mass; 338.1784



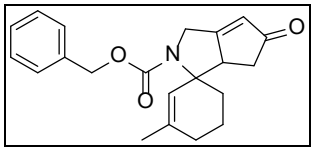


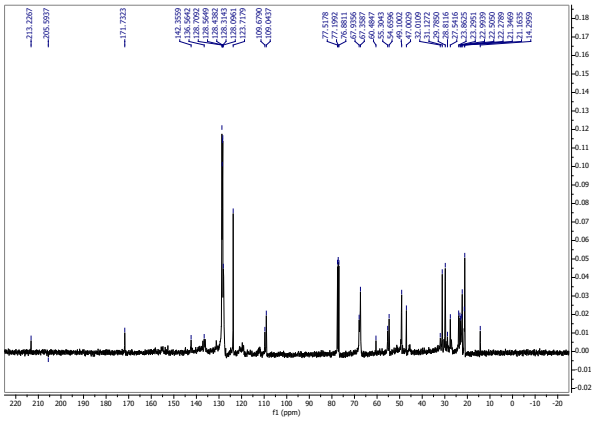
^{1}H-NMR spectrum of Benzyl 3-methyl-5'-oxo-3',5',6',6a'-tetrahydro-2'H-spiro[cyclohex[2]ene-1,1'-cyclopenta[c]pyrrole]-2'-carboxylate



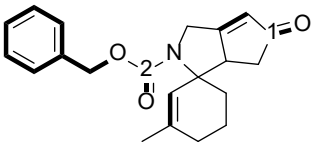


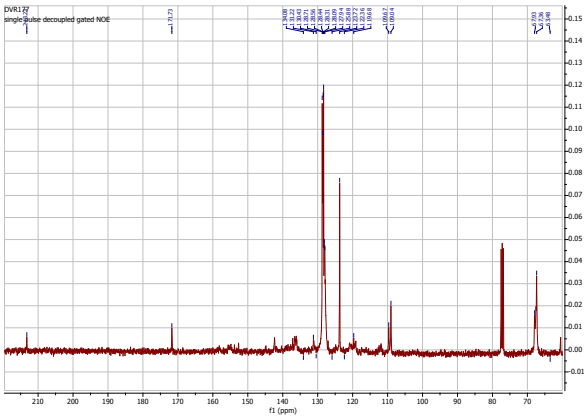
^{1}H-NMR spectrum of the signals of the aromatic and olefinic part as well as CH_2 protons attached to the oxygen atom. δ_H 7.18-7.45 (m, 4H), 7.33 (d, J = 25.6 Hz, 1H), 6.04 (s, 1H), 5.91 (s, 1H), 5.15 (d, J =28.8 Hz, 2H), 4.42 (d, J = 3.2 Hz, 1H), 4.41 (d, J =12.8 Hz, 1H).



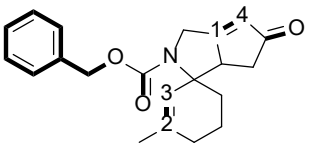


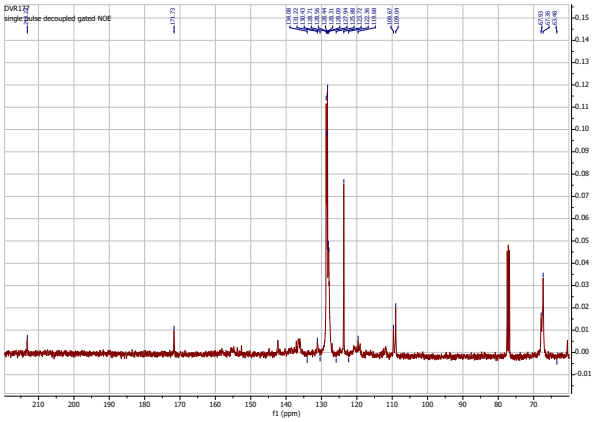
^{13}C-NMR spectrum of Benzyl 3-methyl-5'-oxo-3',5',6',6a'-tetrahydro-2'H-spiro[cyclohex[2]ene-1,1'-cyclopenta[c]pyrrole]-2'-carboxylate



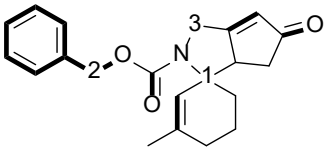


^{13}C-NMR spectrum of the signals at δ_C 213.4 (1), 171.5 (2) ppm are due to the ketone carbonyl and ester carbonyl carbon respectively.



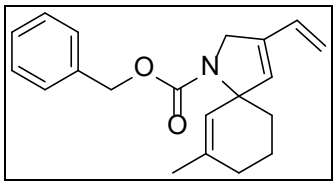


^{13}C-NMR spectrum of the signals at 142. 2 (1), 136.6, 128.7(2), 128.6, 128.4, 128.3(3), 128.1(4), 127.0, 123.7 ppm are for the olefinic and aromatic part carbon atoms.

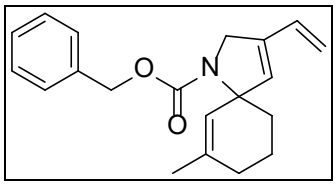


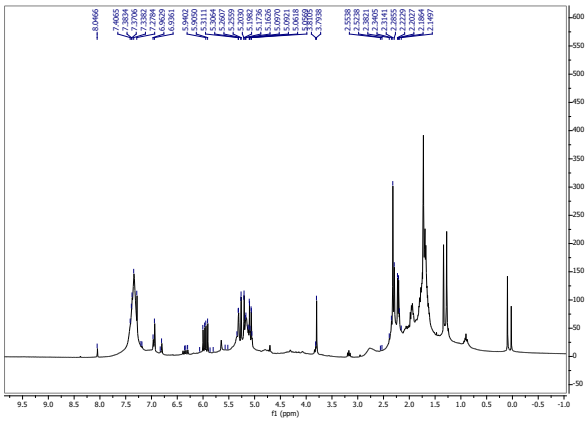
^{13}C-NMR signals due to quaternary and methylene carbon atoms δ_C 67.4 (1), 54.7(2), 49.1 (3) ppm respectively.

Benzyl 7-methyl-3-vinyl-1-azaspiro[4.5]deca-3,6-diene-1-carboxylate (14b) (new compound)

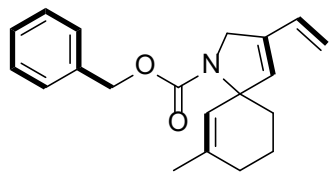


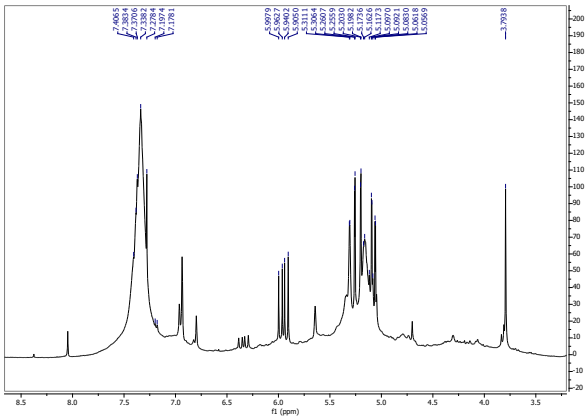
Color: Light Brown oil Yield: 50 % chemical yield. FT-IR (KBr, ν, cm^{-1}) 3011 (Csp^2-H, aromatic), 2970 (CH_3 (sp^3-H), 2920 (CH_3 (Csp^3-H), 1703 (-O-***C=O***),1520 and 1492 (aromatic -C=C- stretching), 1075 (-CH_2-N-), 1228 (-CH_2-*C*-*O*-stretching) cm^{-1} 892 ve 697 (C sp^2-H twisting, specific for terminal alkenes), Purified by Flash Column Chromatography (1:5:1 % Et_3N EtOAc: Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 7.38 (d, J=4.4 Hz, 1H), 7.34 (d, *J*= 5.6 Hz, 1H), 7.33 (d, *J*= 4.8 Hz, 2H), 7.29 (d, *J*= 3.6 Hz, 1H), 5.76-5.82 (m, 1H), 5.62 (t, *J*=4.4 Hz, 1H), 5.55 (s, 1H), 5.28 (d J=0.4 Hz, 1H), 5.27 (s, 1H), 5.16 (d, J= 3.6 Hz, 2H), 4.40 (d, J= 2.4 Hz, 1H), 4.19 (d, J=2.4 Hz, 1H), 2.31 (dd, J= 4.0 ve 11.6 Hz, 1H), 2.28 (dd, J=4.4 ve 9.4 Hz, 1H), 2.07 (dd, J= 9.6 and 21.2 Hz, 1H),1.76 (dd, J= 2.0 and 17.6 Hz, 1H), 1.19 (dd, J=6.4 and 22.6 Hz, 1H), 1.41 (d, J= 5.6 Hz, 1H), 1.24 (s, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 157.2, 142.5, 139.1, 137.8, 131.2, 128.9, 128.7, 128.6, 128.5, 128.0, 127.9, 119.4, 112.1, 71.5, 69.2, 67.5, 39.2, 31.6, 29.8, 27.5. $C_{20}H_{24}NO_2$, HRMS-ESI, $[M+H]^+$ Calculated mass; 310.1729, Found mass; 310.1807.



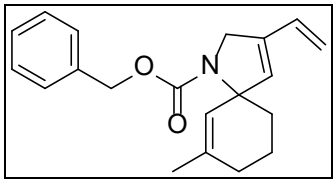


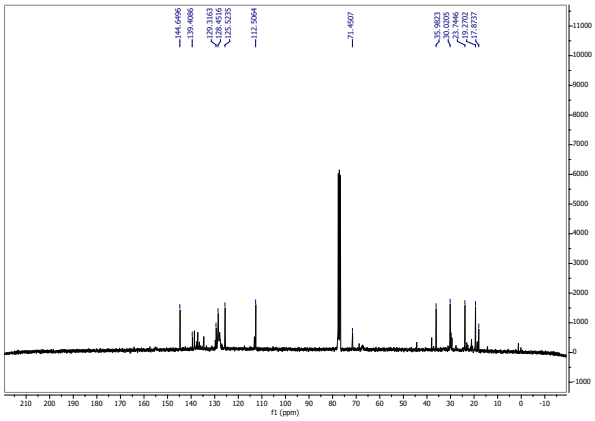
^{1}H-NMR spectrum of benzyl 7-methyl-3-vinyl-1-azaspiro[4.5]deca-3,6-diene-1-carboxylate



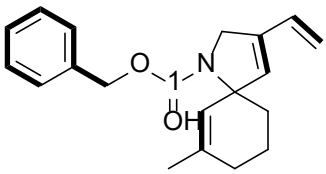


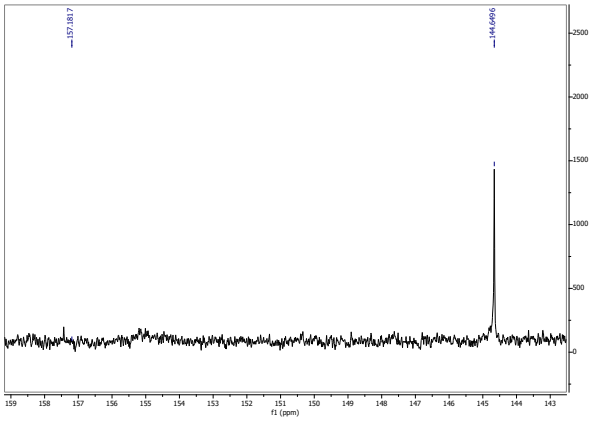
^{1}H-NMR spectrum of the signals are due to the aromatic and olefinic part protons δ_H 7.38 (d, J=4.4 Hz, 1H), 7.34 (d, *J*= 5.6 Hz, 1H), 7.33 (d, *J*= 4.8 Hz, 2H), 7.29 (d, *J*= 3.6 Hz, 1H), 5.76-5.82 (m, 1H), 5.62 (t, *J*=4.4 Hz, 1H), 5.55 (s, 1H), 5.28 (d J=0.4 Hz, 1H), 5.27 (s, 1H), 5.16 (d, J= 3.6 Hz, 2H), 4.40 (d, J= 2.4 Hz, 1H), 4.19 (d, J=2.4 Hz, 1H),



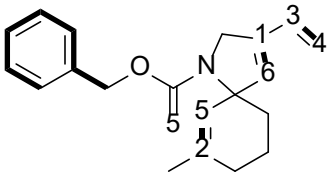


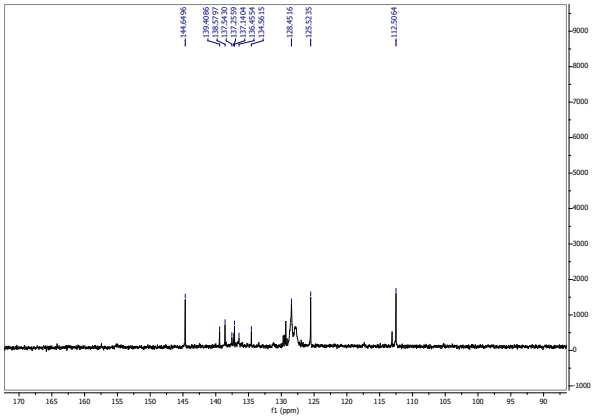
^{13}C-NMR spectrum of benzyl 7-methyl-3-vinyl-1-azaspiro[4.5]deca-3,6-diene-1-carboxylate



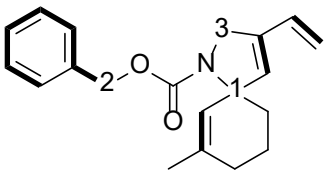


^{13}C-NMR spectrum of the signal of ester carbonyl carbon atom at 157.2 ppm.



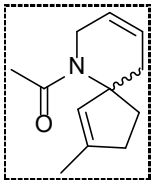


^{13}C-NMR spectrum of the signals of olefinic and aromatic carbon atoms respectively δ_C 142.5 (1), 139 (2).1, 137.8, 131.2(3), 128.9(4), 128.7, 128.6, 128.5, 128.0, 127.9(5), 119.4, 112.1 (6).

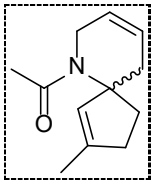


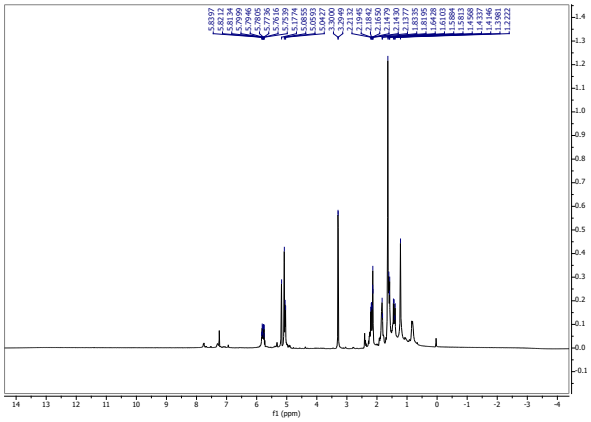
^{13}C-NMR Signals for quaternary and methylene carbon atoms at 71.5 (1), 69.2 (2), 67.5 (3) ppm respectively.

1-(2-methyl-6-azaspiro[4.5]deca-1,8-dien-6-yl)ethanone 4a (After enzymatic kinetic resolution reaction) (new compound)

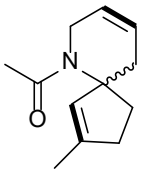


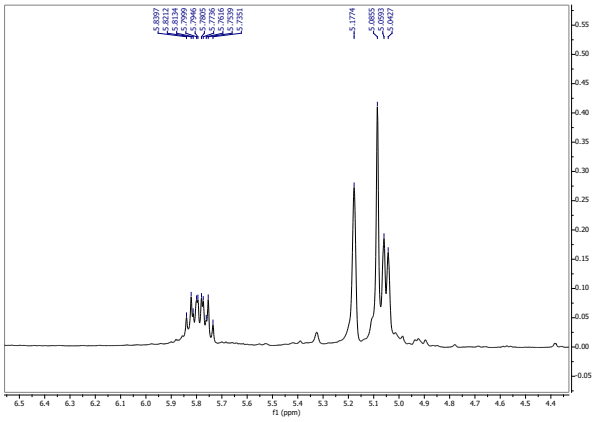
Color: Yellow oil. Yield: 26 mg, 20 % chemical yield. FT-IR (KBr, ν, cm^{-1}) : 3016 (CH_2, Csp^2-H, cyclohexene ring), 2924 (CH_3(sp^3 -H), 2854 (CH_3 (Csp^3-H), 1731 (C=O), 1660 (-C=C- stretching of cyclohexene ring) , 1018 (-CH_2-N-), 1455 (-C=C- stretching, tetrahydropyridine ring), Purified by Flash Column Chromatography (1:5:1 % Et_3N, EtOAc: Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 5.73- 5.86 (m, 1H), 5.18 (s, 1H), 5.06 (d, *J* = 17.2 Hz, 1H), 3.30 (d, *J* =1.6 Hz, 2H), 2.19 (dd, *J* =7.2 and 12.0 Hz, 1H), 2.15 (d, *J* = 2.0 Hz, 1H), 1.78-1.93 (m, 2H), 1.64 (s, 3H), 1.60 (dd, *J*= 2.8 and 9.2 Hz, 1H), 1.43 (dd, *J* = 6.8 and 15.6 Hz, 1H), 1.22 (s, 3H), ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 164.8, 137.2, 134.4, 126.9, 118.5, 70.8, 44.5, 31.8, 31.7, 30.0, 23.9, 19.7. $C_{12}H_{20}NO$, HRMS-ESI, $[M+H]^+$ Calculated mass; 194.1545, Found mass; 194.1543.



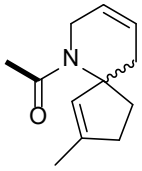


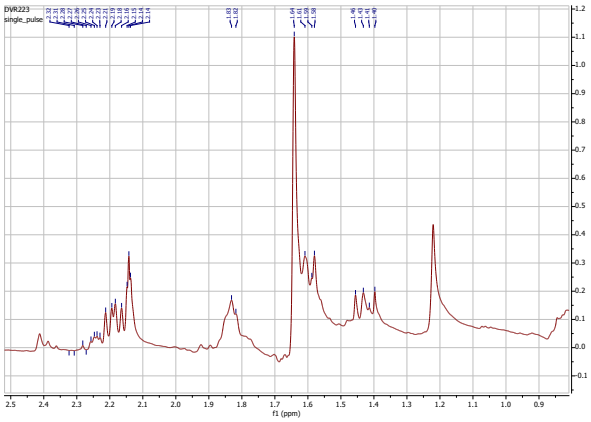
^{1}H-NMR spectrum of 1-(2-methyl-6-azaspiro[4.5]deca-1,8-dien-6-yl)ethanone



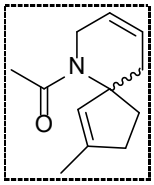


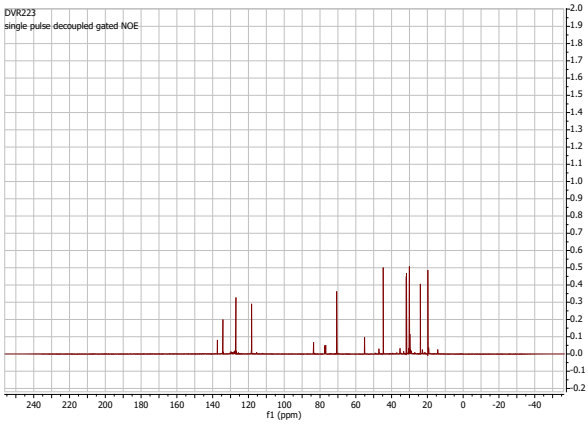
^{1}H-NMR spectrum of the signals of olefinic protons δ_H 5.73- 5.86 (m, 1H), 5.18 (s, 1H), 5.06 (d, *J* = 17.2 Hz, 1H).



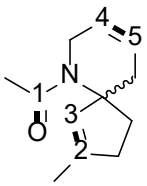


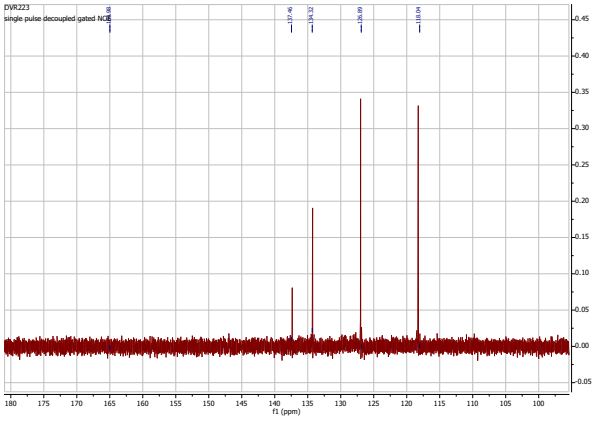
^{1}H-NMR spectrum of the signal; singlet at 1.22 ppm for methyl protons of the acetyl moiety.



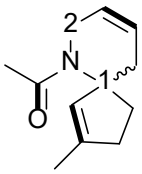


^{13}C-NMR spectrum of 1-(2-methyl-6-azaspiro[4.5]deca-1,8-dien-6-yl)ethanone



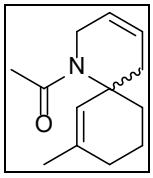


^{13}C-NMR spectrum of the signal at δ_C 164.8 (1), due to the carbonyl carbon as well as olefinic carbon atoms 137.2 (2), 134.4 (3), 126.9 (4), 118.5 (5).

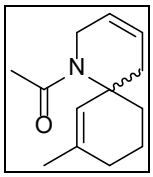


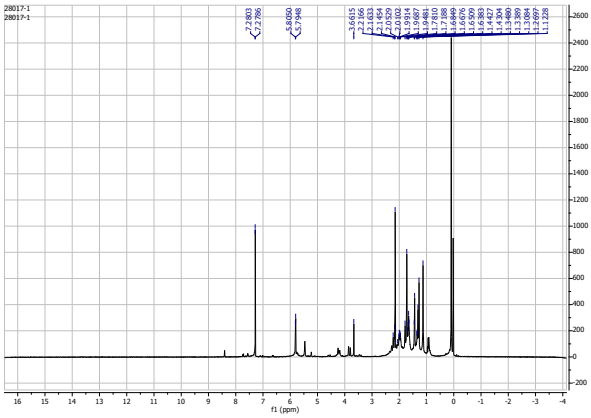
^{13}C-NMR signals for the quaternary and methylene carbon directly attached to nitrogen atom 70.8, 44.5 ppm respectively.

1-(8-methyl-1-azaspiro[5.5]undeca-3,7-dien-1-yl)ethanone 4b (After enzymatic kinetic resolution reaction) (new compound)

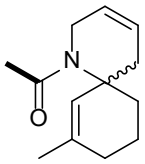


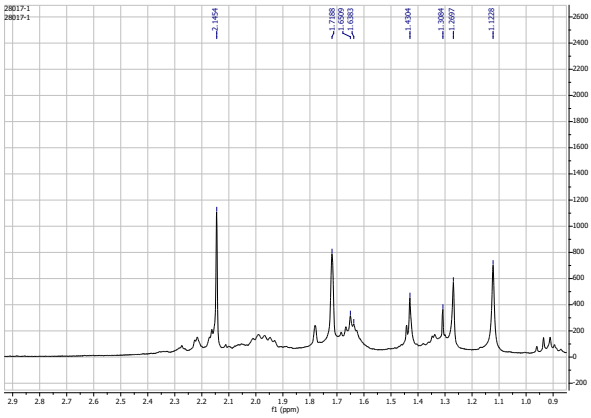
Color: Dark Brown Liquid. Yield: 10 mg, 12 % chemical yield FT-IR (KBr, ν, cm^{-1}) : 3016 (CH_2, Csp^2-H, cyclohexene ring), 2924 (CH_3(sp^3 -H), 2854 (CH_3 (Csp^3-H), 1731 (C=O), 1660 (-C=C- stretching, cyclohexene ring), 1018 (-CH_2-N-), 1455 (-C=C- stretching, tetrahydropyridine ring), (Purified by Flash Column Chromatography 1:5:1 % Et_3N, EtOAc: Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 5.80 (dd, J= 4.0 Hz, 2H), 5.47 (s, 1H), 4.23 (dd, *J* = 4.8 and 7.8 Hz, 1H), 3.82 (dd, *J* = 4.0 and 24.2 Hz, 1H), 2.27 (t, *J*= 3.3 Hz,1H), 2.22 (d, *J* = 2.0 Hz, 1H), (2.17 d, *J* = 2.0 Hz, 1H) (d, *J* =3.6 Hz, 1H), 2.14 (s, 3H), 1.92-2.03 (m, 4H), 1.72 (s, 3H) ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 170.0, 137.5, 135.0, 125.0, 118.5, 82.1, 70.4, 55.1, 44.9, 32.1, 30.0, 22.5, 19.9. $C_{13}H_{20}NO$, HRMS-ESI, $[M+H]^+$ Calculated mass; 206.2911, Found mass; 206.1545.



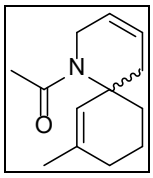


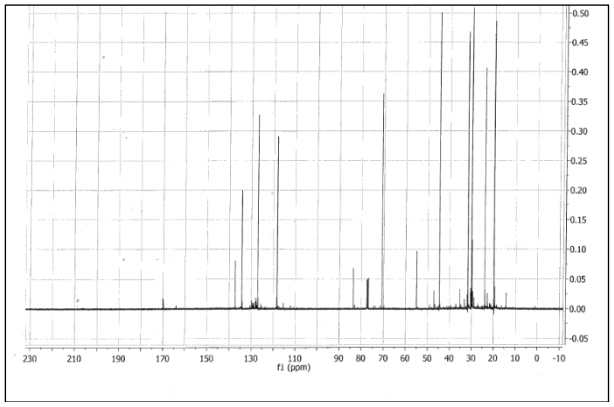
^{1}H-NMR spectrum of 1-(8-methyl-1-azaspiro[5.5]undeca-3,7-dien-1-yl)ethanone



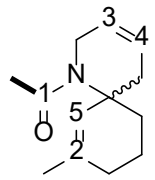


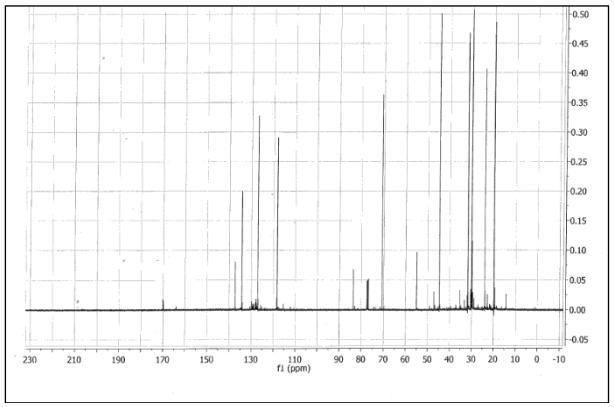
^{1}H-NMR spectrum signal at 2.14 ppm is due to the methyl protons of the acetyl moiety.



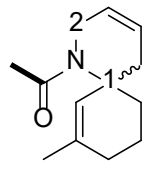


^{13}C-NMR spectrum of 1-(8-methyl-1-azaspiro[5.5]undeca-3,7-dien-1-yl)ethanone

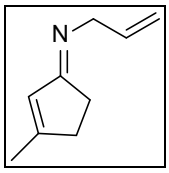




^{13}C-NMR spectrum exhibits a signal at δ_C 170.0 (1) ppm for the amide carbonyl carbon atom as well as the methine carbon atoms of tetrahydropyridine ring with cyclohexene ring 137.5 (2), 135.0 (3), 125.0 (4), 118.5 (5).

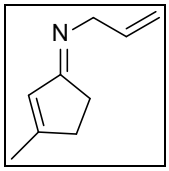


^{13}C-NMR signals at 82.1, 70.4 ppm for the quaternary and methylene carbon directly attached to nitrogen atom respectively.

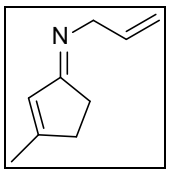


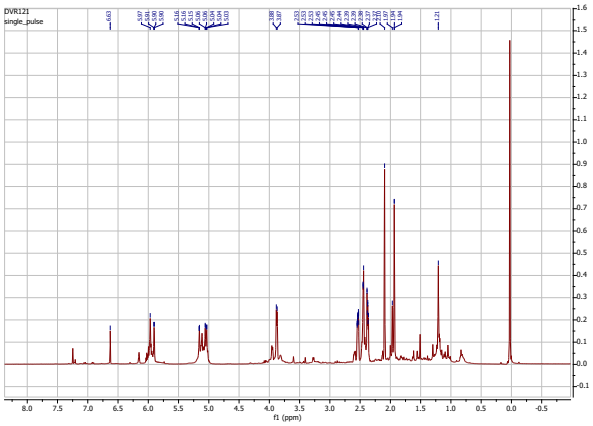
(IMINE COMPOUNDS CAN NOT BE PURIFIED SINCE THEY ARE EASILY DECOMPOSED ON SILICA GEL SO ^{1}H AND ^{13}C NMR SPECTRA ARE TAKEN IMMIDIATELY AND SUBJECTED TO FURTHER REACTION)

***(E)-N*-(3-methylcyclopent-2-en-1-ylidene)prop-2-en-1-amine (1a) (Crude NMR)**

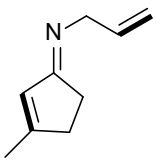


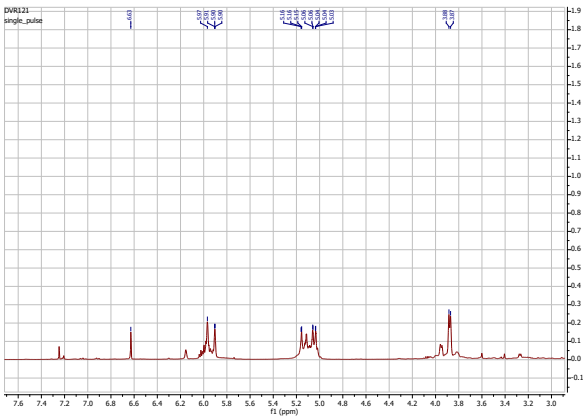
Color: Orange yellow oil; FT-IR (KBr, $\nu_{max,}$ cm^{-1}) : 3076 (CH_2 (C sp^2-H), (cyclopentene ring), 2913 (CH_3, C sp^3-H), 2865 (CH_3, C sp^3-H), 1640 (imine C=N), 1625 (-C=C- stretching, allyl group + cyclopentene ring), 1202 (-CH_2-N-,), 964 and 913 (C sp^2 -H twisting; specific for terminal alkenes), ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 5.93-6.04 (m, 1H), 5.91(d, *J* = 0.8 Hz, 1H), 5.14 (dd, *J* = 1.6 and 17.2 Hz, 1H), 5.05 (dd, *J*= 0.8 and 10 Hz, 1H), 3.95 (d, *J* = 5.2 Hz, 1H), 3.88 (d, *J* = 5.6 Hz, 1H), 2.54 (dd, *J* = 0.8 and 1.2 Hz, 1H), 2.52 (dd, *J* = 1.2 and 2.0 Hz, 1H), 2.43 (dd, *J* = 3.2 and 8.8 Hz, 1H), 2.37 (t, *J* = 4.4 Hz, 1H), 2.10 (s, 3H, methyl of ketone), 1.94 (s, 3H, methyl of imine). ^{13}C-NMR (100 MHz, $CDCl_3$,δ, ppm): δ_C 210.1 (carbonyl of ketone), 179.1, 163.0, 130.5, 116.3, 114.8, 55.7, 35.9, 19.5.



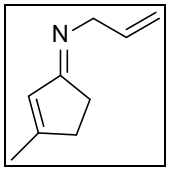


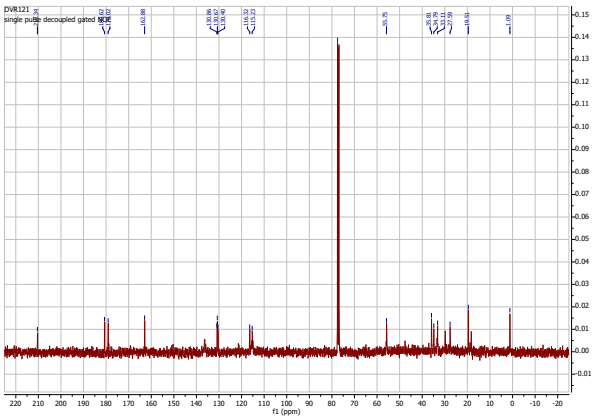
^{1}H-NMR spectrum of *(E)-N*-(3-methylcyclopent-2-en-1-ylidene)prop-2-en-1-amine (crude NMR)



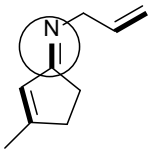


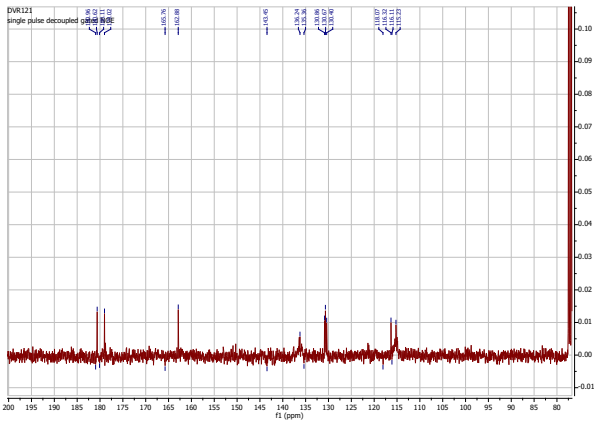
^{1}H-NMR spectrum of the signals of the protons due to the homoallyl and olefin part δ_H 5.93-6.04 (m, 1H), 5.91(d, J = 0.8 Hz, 1H), 5.14 (dd, J = 1.6 and 17.2 Hz, 1H), 5.05 (dd, J= 0.8 and 10 Hz, 1H), 3.95 (d, J = 5.2 Hz, 1H), 3.88 (d, J = 5.6 Hz, 1H).



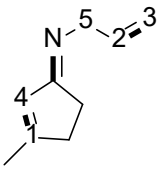


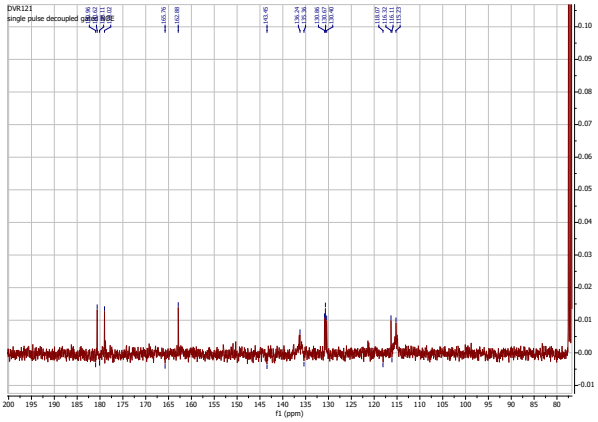
^{13}C-NMR spectrum of *(E)-N*-(3-methylcyclopent-2-en-1-ylidene)prop-2-en-1-amine (crude NMR)





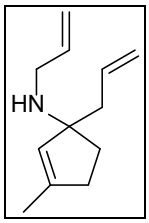
^{13}C-NMR spectrum of the signals due to the carbon atom of the imine at 163.0 ppm.



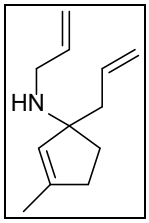


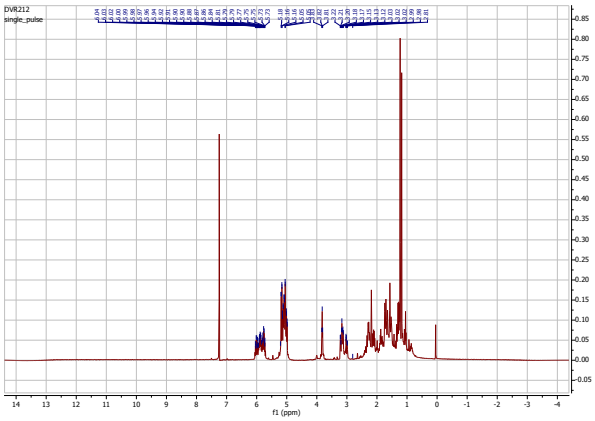
^{13}C-NMR spectrum of the signals due to the carbon atoms of the olefin part δ_C 179.1(1), 130.5 (2), 116.3 (3), 114.8 (4). Finally signal at 55.7 ppm (5) is due to the methylene carbon directly attached to nitrogen atom.

***N*,1-diallyl-3-methylcyclopent-2-enamine (2a) (new compound)**

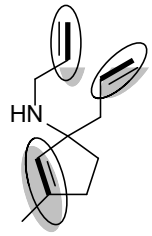


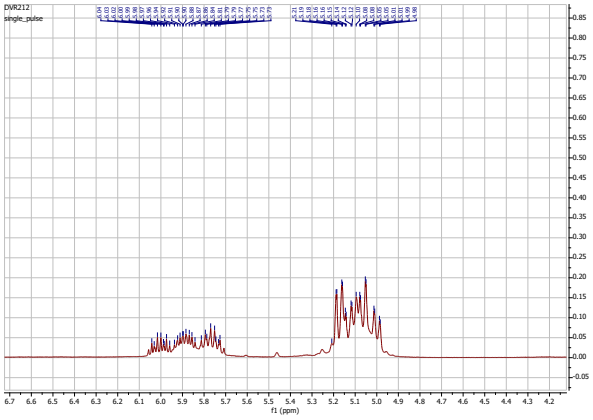
Color: Brownish Thick Yellow oil Yield: 2.81 g, 70 % chemical yield FT-IR (KBr, ν, cm^{-1}): 3290 (N-H), 3074 (C sp^2-H), 2949 (CH_3(sp^3-H), 2914 (CH_3 (Csp^3-H), 1679 (-C=C- stretching, cyclopentene ring), 1640 (-C=C- stretching, allyl group), 1100 (-CH_2-N-), 993 and 913 (C sp^2-H twisting, specific for terminal alkenes). Purified by Flash Column Chromatography (1:1:1 % Et_3N EtOAc: Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 5.71-6.06 (m, 2H), 5.28 (s, 1H), 5.17 (dd, *J* =1.2 and 10.6 Hz, 1H), 5.13 (dd, 1.6 and 10.6 Hz, 1H), 5.06 (dd, *J*= 1.2 9.8 Hz, 1H), 5.00 (dd, *J* = 1.2 and 10.4 Hz, 1H), 3.82 (t, *J* = 5.2 Hz, 1H), 3.19 (dd, *J*= 4.0 and 17.2 Hz, 1H), 3.14 (dd, *J* = 5.2 and 12.4 Hz, 1H), 2.28 (dd, *J*= 2.8 and 7.2 Hz, 1H), 2.24 (d, *J* = 8.8 Hz, 1H), 2.18 (broad singlet, N-*H*, 1H), 2.10 (dd, *J* = 6.8 and 14.0 Hz, 1H), 1.72 (td, *J*= 3.6 and 14.1 Hz, 1H), 1.56 (d, *J*= 7.6 Hz, 1H), 1.51 (dd, *J* = 2.4 and 7.8 Hz, 1H), 1.23 (s, 3H), 1.18 (belongs to H_2O). ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 137.9, 136.4, 134.3, 118.9, 115.4, 114.3, 65.7, 39.3, 38.1, 33.2, 30.6, 22.6 $C_{12}H_{20}N$, HRMS-ESI, $[M+H]^+$ Calculated mass; 178.1596, Found mass; 178.1589.



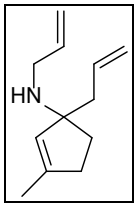


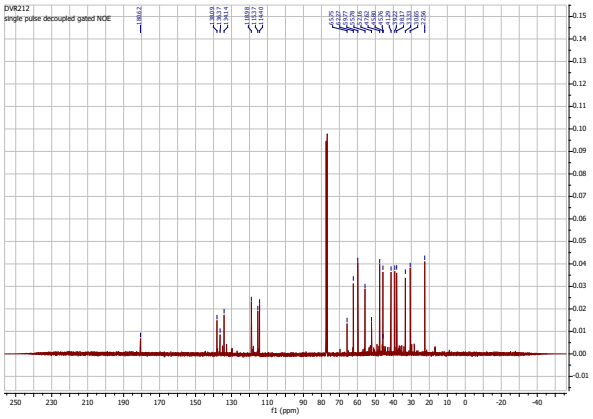
^{1}H-NMR spectrum of *N*,1-diallyl-3-methylcyclopent-2-enamine



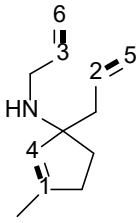


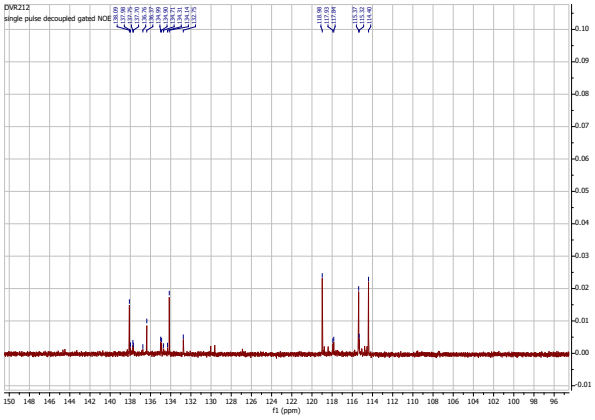
^{1}H-NMR spectrum of the signals due to the diene part δ_H 5.71-6.06 (m, 2H), 5.28 (s, 1H), 5.17 (dd, *J* =1.2 and 10.6 Hz, 1H), 5.13 (dd, 1.6 and 10.6 Hz, 1H), 5.06 (dd, *J*= 1.2 9.8 Hz, 1H), 5.00 (dd, *J* = 1.2 and 10.4 Hz, 1H).



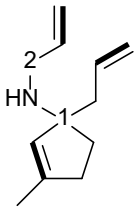


^{13}C-NMR spectrum of *N*,1-diallyl-3-methylcyclopent-2-enamine

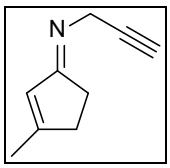




^{13}C-NMR spectrum of the signals due to the diene and carbon atoms of the cyclopentene ring δ_C 137.9 (1), 136.4 (2), 134.3 (3), 118.9 (4), 115.4 (5), 114.3 (6).

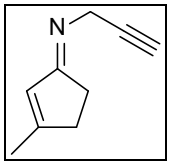


^{13}C-NMR signals at 65.7 and 39.3 ppm are due to the quaternary and methylene carbon atoms respectively.

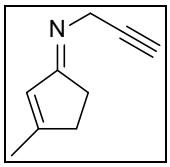


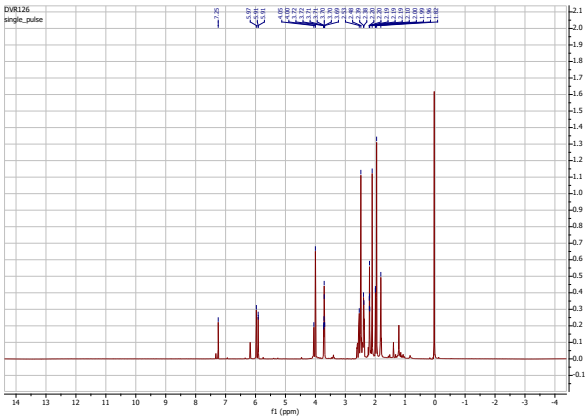
(IMINE COMPOUNDS CAN NOT BE PURIFIED THEY CAN EASILY DECOMPOSED ON SILICA GEL SO ^{1}H- AND ^{13}C-NMR SPECTRA TAKEN IMMIDIATELY AND SUBJECTED TO FURTHER REACTION)

***(E)-N*-(3-methylcyclopent-2-en-1-ylidene)prop-2-yn-1-amine 1c (Crude NMR)**

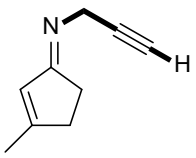


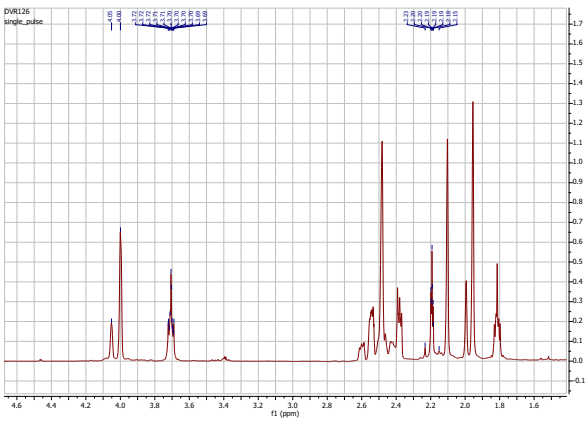
Color: Orange yellow oil FT-IR (KBr, ν, cm^{-1}): 3289 (C≡C-H, C sp-H stretching), 3020 (C sp^{2} -H), 2913 (CH_3, C sp^{3} -H), 2863 (CH_3, C sp^{3} -H), 2150 (-C≡C- stretching), 1635 (imine, -C=N-) 1622 (-C=C- stretching),1327 and 633 (C≡C-H, (C sp -H twisting)), 1202 (-CH_2-N), ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 5.97 (s, 1H, ketone), 5.91 (s, 1H,), 4.05 (d, *J* = 1.6 Hz, 1H), 3.99 (d, *J* = 4.0 Hz, 1H) 3.69 (t, *J* = 6.8 Hz,1H, N-*H*), 2.54 (dd, *J* = 0.8 and 2.0 Hz, 1H) (ketone), 2.53 (dd, *J*= 0.8 and 2.0 Hz, 1H), 2.48 (d, *J*= 1.2 Hz, 1H), 2.46 (d, *J*= 1.2 Hz, 1H), 2.38 (dd, *J* = 2.54 Hz, 1H), 2.19 (t, *J* = 2.4 Hz, C≡C-*H*), 2.10 (s, 3H, ketone methyl),1.96 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 210.9 (ketone carbonyl), 182.8, 163.8, 130,6, 82.4, 70.5, 67.9 (other isomer), 41.7, 35.0, 27.7, 18.2.



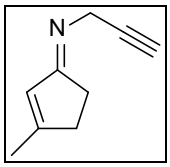


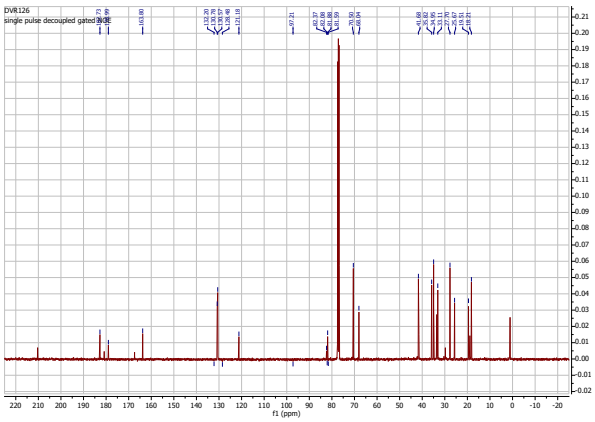
^{1}H-NMR spectrum of *(E)-N*-(3-methylcyclopent-2-en-1-ylidene)prop-2-yn-1-amine (crude NMR)



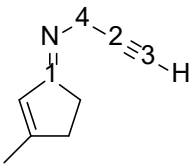


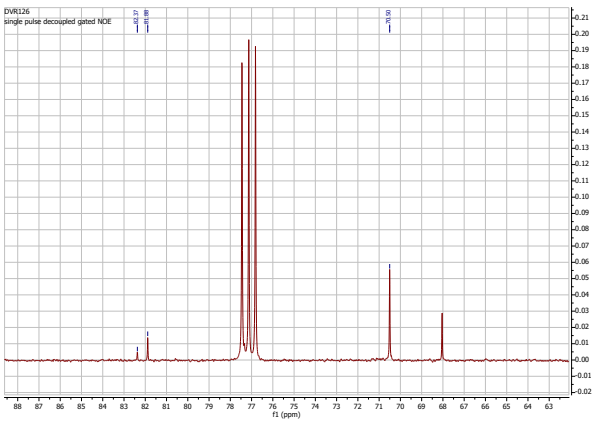
^{1}H-NMR spectrum of the signal due to the acetylenic proton δ_H 2.19 (t, J = 2.4 Hz, C≡C-*H*).



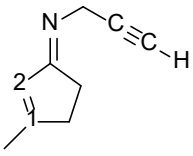


^{13}C-NMR spectrum of *(E)-N*-(3-methylcyclopent-2-en-1-ylidene)prop-2-yn-1-amine (crude NMR).



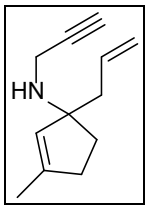


^{13}C-NMR spectrum of the signals at δ_C 70.5 (2), 67.9 (3) ppm due to the triple bond carbon atoms as well as imine carbon atom at 163.8 (1) ppm. The signal at 41.7 ppm (4) is due to the methylene carbon attached to nitrogen atom.

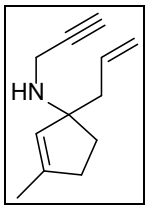


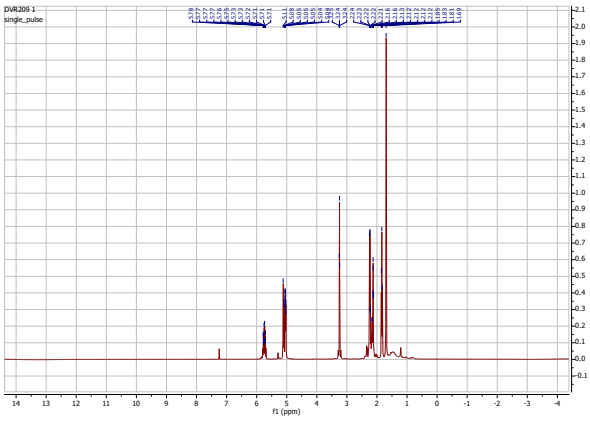
The signals at 182.8 (1), 130,6 (2) ppm in the ^{13}C-NMR spectrum are due to the olefinic carbon atoms in the cyclopentene ring.

1-allyl-3-methyl-*N*-(prop-2-yn-1-yl)cyclopent-2-enamine (new compound)

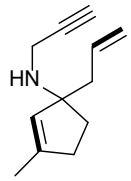


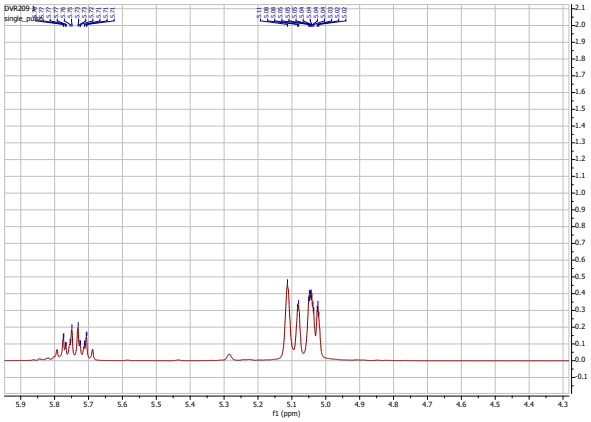
Color: Dark Brown oil: FT-IR (KBr, *ν, cm*$^{-1}$) : 3305 (C≡C-H (C sp-H ve N-H stretching (signals are matched)), 3074 (C sp^2-H), 2972 (C sp ^{3}-H), 2914 (C sp^3-H), 2125 (-C≡C-, stretching), 1659 (-C=C- stretching, cyclopentene ring),1638 (-C=C- stretching, allyl group), 1106 (-CH_2-N-), 1294 ve 643 (C≡C-H, (C sp -H twisting), 995 ve 912 (C sp^2-H twisting, specific for terminal alkynes) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 5.69-5.80 (m, 1H), 5.29 (broad singlet, N-*H*) 5.11 (s, 1H), 5.10 (dd, *J* =1.2 and 13.2 Hz, 1H), 5.04 (dd, J= 0.8 and 10 Hz, 1H), 3.24 (t, *J*= 2.4 Hz, 2H), 2.25 (d, *J*= 2.8 Hz, 1H), 2.22 (dd, *J*= 0.4 and 4.2 Hz, 1H), 2.19 (dd, *J* = 0.8 and 8.0 Hz, 1H), 2.15 (dd, *J*= 0.8 and 8.0 Hz, 1H), 2.12 (t, *J*=2.4 Hz, 1H, (C≡C-*H*) 1.83 (t, *J* = 7.0 Hz, 2H), 1.69 (s, 3H) ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 142.8, 134.5, 129.3, 118.1, 83.5, 70.7, 70.4, 45.2, 36.1, 33.8, 32.4, 16.9. $C_{12}H_{18}N$, HRMS-ESI, $[M+H]^+$ Calculated ; 176.1439, Found ; 176.1437.



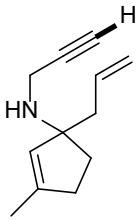


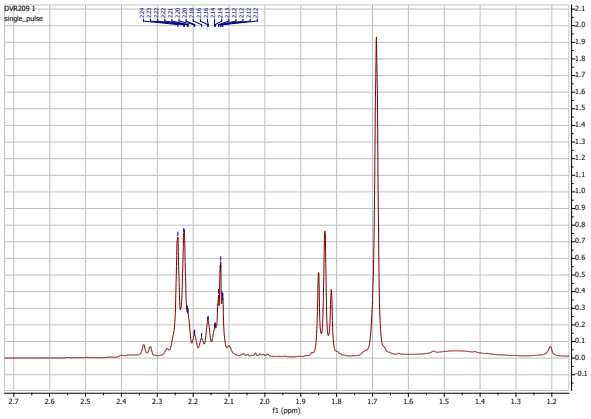
^{1}H-NMR spectrum of 1-allyl-3-methyl-N-(prop-2-yn-1-yl)cyclopent-2-enamine



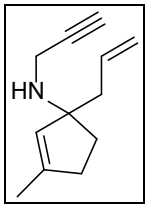


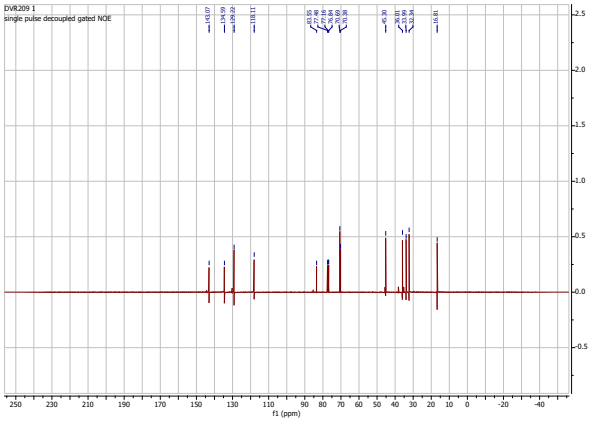
^{1}H-NMR spectrum of the signals of the allylic protons as well as olefinic proton δ_H 5.69-5.80 (m, 1H), 5.29 (broad singlet, N-*H*) 5.11 (s, 1H), 5.10 (dd, *J* =1.2 and 13.2 Hz, 1H), 5.04 (dd, J= 0.8 and 10 Hz, 1H).



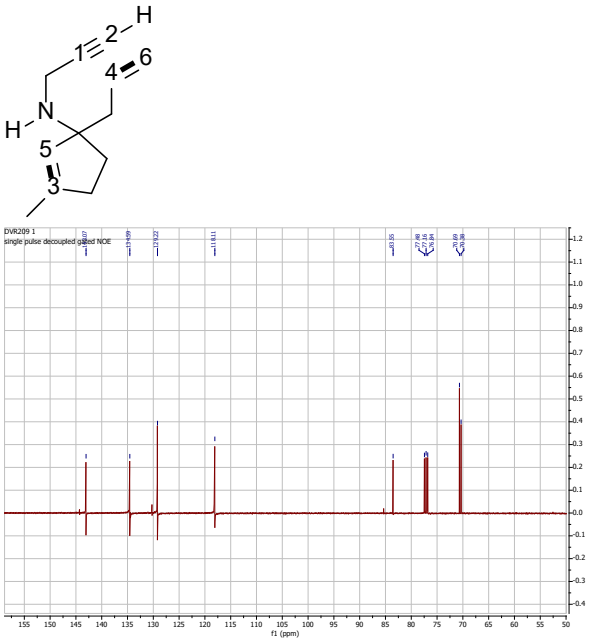


^{1}H-NMR spectrum of the signals of the acetylenic proton δ_H 2.12 (t, *J*=2.4 Hz, 1H, (C≡C-*H*).

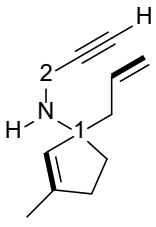




^{13}C-NMR spectrum of 1-allyl-3-methyl-N-(prop-2-yn-1-yl)cyclopent-2-enamine

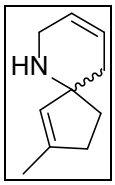


^{13}C-NMR spectrum of the signals of homoallylic part as well as triple bond carbon atoms (C≡C) and olefinic carbon atoms; δ_C 142.8 (3), 134.5 (4), 129.3 (5), 118.1 (6), (C≡C), 83.5 (1), 70.7 (2).

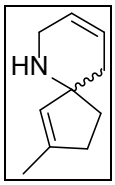


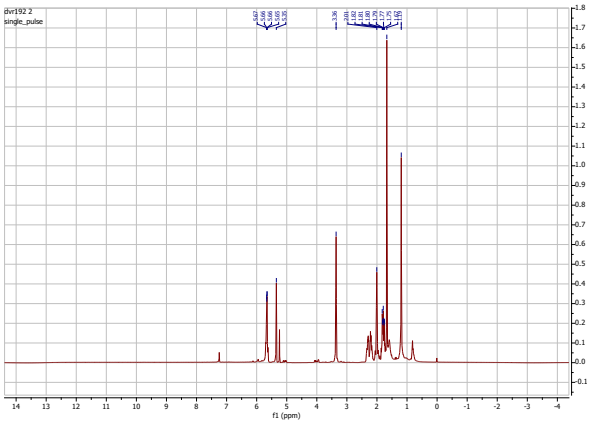
^{13}C-NMR signals at 70.4 (1) and 45.2 (2) ppm for the quaternary and mehylene carbon atoms respectively.

2-methyl-6-azaspiro[4.5]deca-1,8-diene (3a) (new compound)

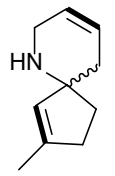


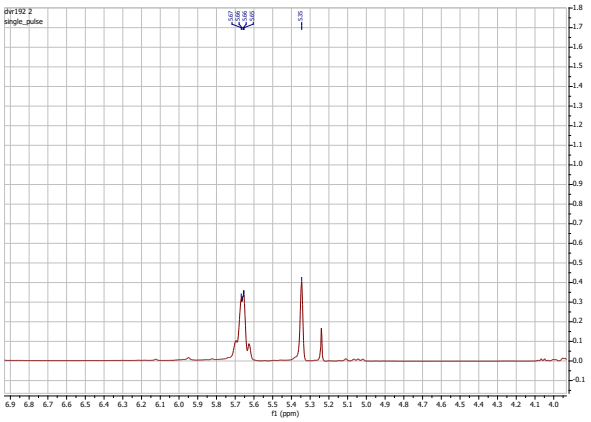
Color: Thick Brown oil Yield: 460 mg, 78 % chemical Yield) FT-IR (KBr, *ν, cm*$^{-1}$): 3421 (N-H), 3018 (CH_2, $Csp^{2a}H$), 2928 (Csp^3-H), 1653 (-C=C- stretching, cyclopentene ring), 1558 (-C=C- stretching, tetrahydropyridin ring), Prufied by Flash Column Chromatography (1:5:1 % Et_3N EtOAc: Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$,δ, ppm): δ_H 5.68 (d, *J* = 11.2 Hz, 1H), 5.64 (dd, *J* = 0.8 and 11.4 Hz, 1H), 5.34 (s, 1H), 3.36 (broad singlet, 2H), 2.31 (dd, *J*= 6.0 and 15.8 Hz, 1H), 2.19 (dd, *J* = 6.0 and 17.0 Hz, 1H), 2.02 (t, 1H, *J* = 18.0 Hz, 1H), 1.81 (dd, *J* = 5.2 and 8.8 Hz, 1H), 1.67 (s, 3H), 1.59 (broad singlet, N-*H*), 1.81 (dd, *J* = 5.2 and 8.8 Hz, 1H) 1.76 (dd, *J* = 2.4 and 9.4 Hz, 1H) ^{13}C-NMR (100 MHz, $CDCl_3$,δ, ppm): δ_C 141.8, 130.8, 125.9, 125.0, 65.0, 42.6, 37.2, 36.3, 35.0, 29.8.



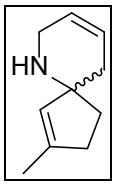


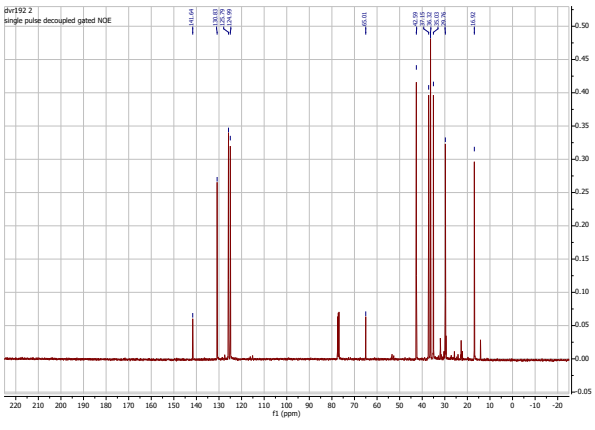
^{1}H-NMR spectrum of-2-methyl-6-azaspiro[4.5]deca-1,8-diene



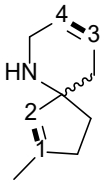


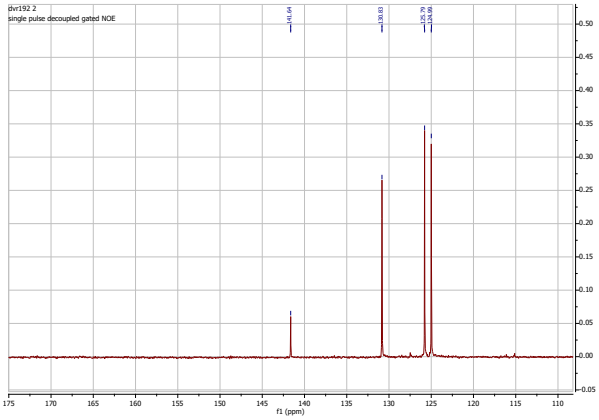
^{1}H-NMR spectrum of the signals of tetrahydropyridine and olefin part δ_H 5.68 (d, J = 11.2 Hz, 1H), 5.64 (dd, J = 0.8 and 11.4 Hz, 1H), 5.34 (s, 1H).



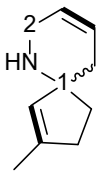


^{13}C-NMR spectrum of-2-methyl-6-azaspiro[4.5]deca-1,8-diene



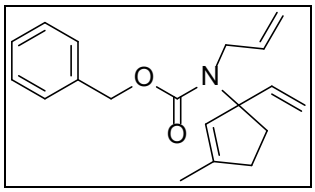


^{13}C-NMR specrum of the signals due to the tetrahydropyridine and olefinic carbon atoms δ_C 141.8(1), 130.8 (2), 125.9 (3), 125.0 (4).

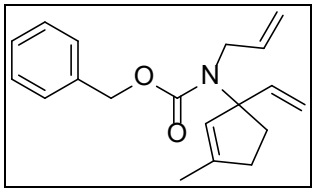


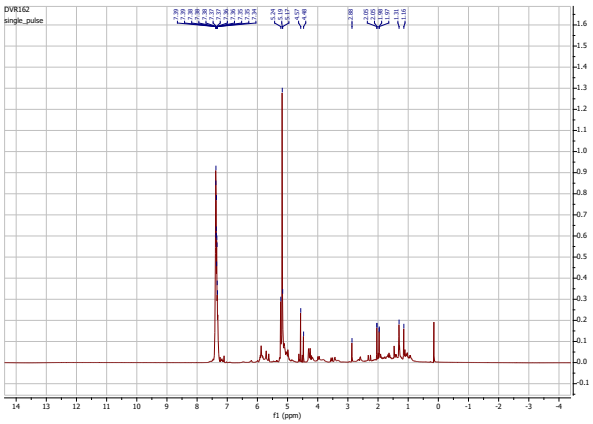
^{13}C-NMR signals due to the quaternary 65.0 (1) and methylene carbon atoms respectively 42.6 (2) ppm.

Benzyl allyl(3-methyl-1-vinylcyclopent-2-en-1-yl)carbamate (5a) (new compound)

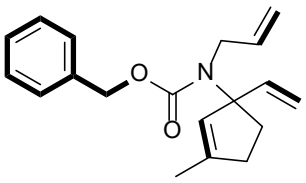


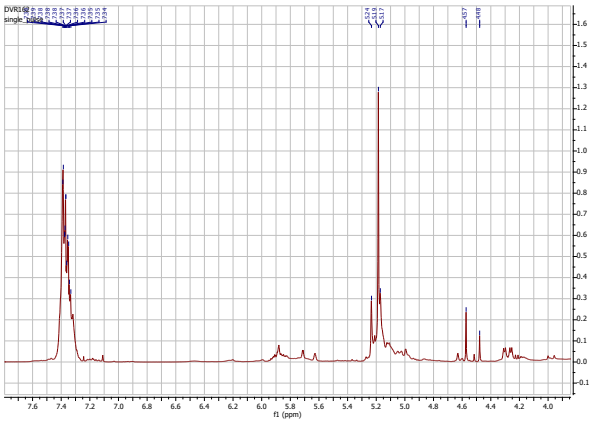
Color: Dark Brown oil Yield: 2.40 g, 62 % chemical yield FT- IR (KBr, *ν, cm*$^{-1}$) : 3015, 2875, 1725, 1600, 1205. Purified by Flash Column Chromatography (1:1:1 % Et_3N, EtOAc, Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 7.40 (dd, *J* =1.6 and 8.0 Hz, 1H), 7.39 (d, *J* =1.6 Hz, 1H), 7.37 (dd *J* = 0.8 and 2.6 Hz, 1H), 7.35 (dd, *J* = 2.0 and 5.2 Hz, 1H), 7.34 (d, *J* =4.0 Hz, 1H), 5.82-5.95 (m, 2H), 5.89 (d, *J* =4.2 Hz, 1H), 5.11 (dd, *J* = 4.4 and 9.8 Hz, 1H), 5.01 (dd, *J* =8.0 and 21.4 Hz, 1H), 5.19 (s, 2H), 5.22 (dd, *J* =2.0 and 7.2 Hz, 1H) 5.18 (dd, *J* =2 and 7.2 Hz, 1H), 4.31 (d, *J* =5.2 Hz, 1H), 4.26 (d, *J* =5.2 Hz, 1H), 2.62 (dd, *J* = 6.0 and 20.2 Hz, 1H), 2.05 (d, *J* =1.2 Hz, 2H), 1.97 (d, *J* = 0.6 Hz, 3H) 1.66 (dd, *J* =1.6 and 13.6 Hz, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 155.2, 140.9, 136.9, 136.5, 136.1, 135.4, 133.9, 133.7, 133.3, 128.7, 128.5, 128.2, 116.5, 69.8, 67.7, 53.0, 42.6, 29.7, 19.2. $C_{19}H_{23}NO_2$, HRMS-ESI, $[M]^+$ Calculated mass; 297.1729, Found mass; 297.2327.



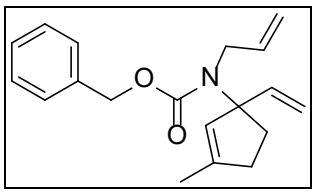


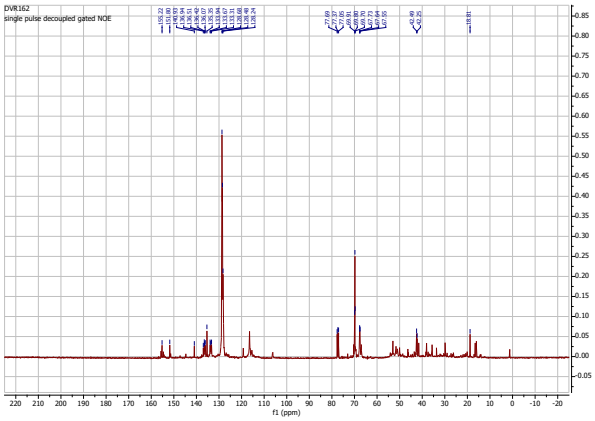
^{1}H-NMR spectrum of benzyl allyl(3-methyl-1-vinylcyclopent-2-en-1-yl)carbamate



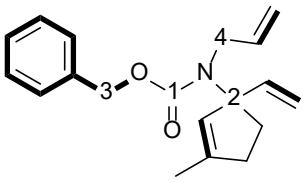


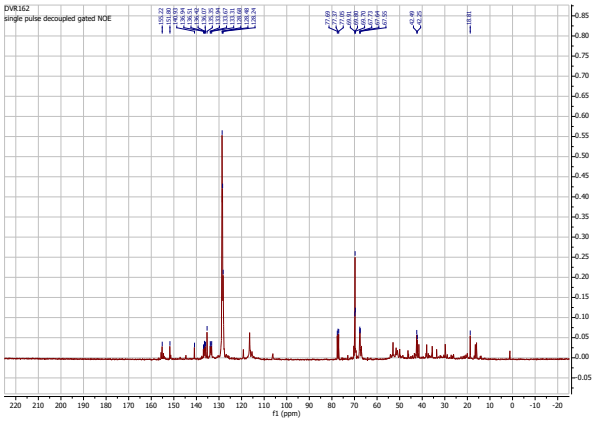
^{1}H-NMR spectrum of the signals of phenyl ring as well as protons due to the allylic and homoallylic part with CH_2 protons directly attached to the oxygen atom δ_H 7.40 (dd, *J* =1.6 and 8.0 Hz, 1H), 7.39 (d, *J* =1.6 Hz, 1H), 7.37 (dd *J* = 0.8 and 2.6 Hz, 1H), 7.35 (dd, *J* = 2.0 and 5.2 Hz, 1H), 7.34 (d, *J* =4.0 Hz, 1H), 5.82-5.95 (m, 2H), 5.89 (d, *J* =4.2 Hz, 1H), 5.11 (dd, *J* = 4.4 and 9.8 Hz, 1H), 5.01 (dd, *J* =8.0 and 21.4 Hz, 1H), 5.19 (s, 2H), 5.22 (dd, *J* =2.0 and 7.2 Hz, 1H) 5.18 (dd, *J* =2 and 7.2 Hz, 1H).



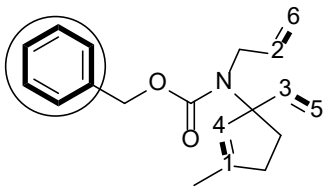


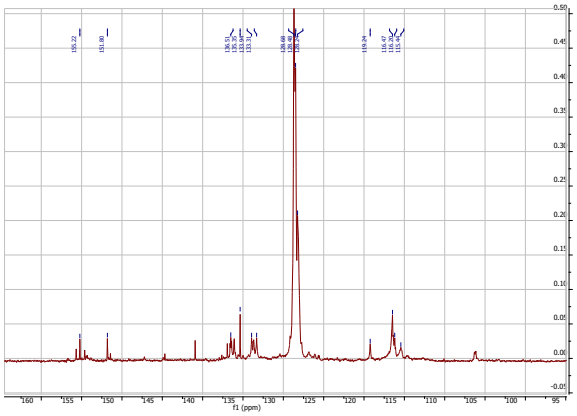
^{13}C-NMR spectrum of benzyl allyl(3-methyl-1-vinylcyclopent-2-en-1-yl)carbamate





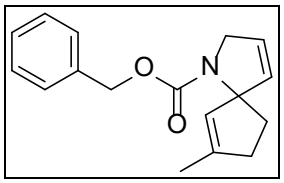
δ_C 155.2 ppm (1) (due to the ester carbonyl carbon atom), as well as 69.8 ppm (2) for the quaternary carbon with methylene carbon atoms at 67.7 (3), 53.0 (4) ppm respectively.



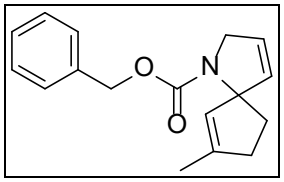


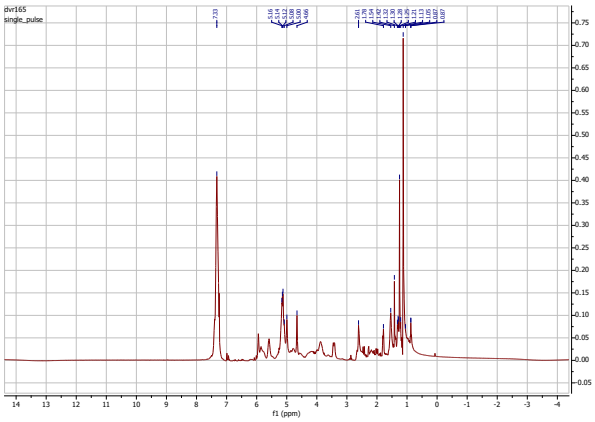
^{13}C-NMR spectrum of the signals of the carbon atoms due to the phenyl ring carbon atoms as well as homoallylic and allylic carbon atoms with the quaternary and methine carbon atoms of the cyclopentene ring δ_C 140.9(1), 136.9 (2), 136.5, 136.1(3), 135.4(4), 133.9(5), 133.7, 133.3, 128.7, 128.5, 128.2, 116.5(6) (others are due to the aromatic carbon atoms).

Benzyl 7-methyl-1-azaspiro[4.4]nona-3,6-diene-1-carboxylate (6a) (new compound)

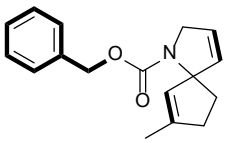


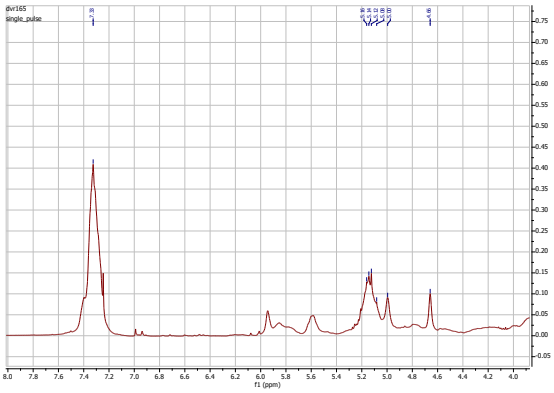
Color: Thick Dark Brown oil; Yield: 412 mg, 65 % chemical yield. FT-IR (KBr, ν, cm^{-1}) : 3010, 2962, 1719, 1225. Purified by Flash Column Chromatography, (1:5:1 % Et_3N, EtOAc, Hexane). ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 7.37 (d, J =18.8 Hz, 1H), 7.35 (d, J =8.0 Hz, 1H), 7.33 (d, J = 4.8 Hz, 1H), 7.29 (d, J = 10 Hz, 1H) 7.31 (d, J = 10 Hz, 1H), 5.94 (s, 1H), 5.59 (d, J = 5.6 Hz,1H), 5.00 (s, 1H), 5.17 (d, J = 6.8 Hz, 1H), 5.15 (d, J = 6.8 Hz, 1H), 3.87 (dd, J =6.8 and 14.4 Hz, 1H), 3.43 (dd, J =2.8 and 14.0 Hz, 1H), 2.63 (dd, J = 4.0 and 21.8 Hz, 1H), 1.79 (d, J =10.2 Hz, 1H), 1.54 (broad singlet, 1H), 1.31 (dd, J =4.4 and 15.6 Hz, 1H), 1.25 (s, 3H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 154.4, (for carbonyl carbon of ester part) 149.0, 136.6, 136.0, 135.1, 128.5 (high intensity for 2 carbon atoms), 128.0, 126.6, 126.0, 125.6, 67.7, 67.4, 53.6, 42.8, 37.3, 29.8. $C_{17}H_{20}NO_2$, HRMS-ESI, $[M+H]^+$ Calculated mass; 270.1494, Found mass; 270.1493.



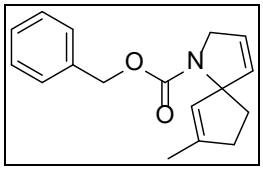


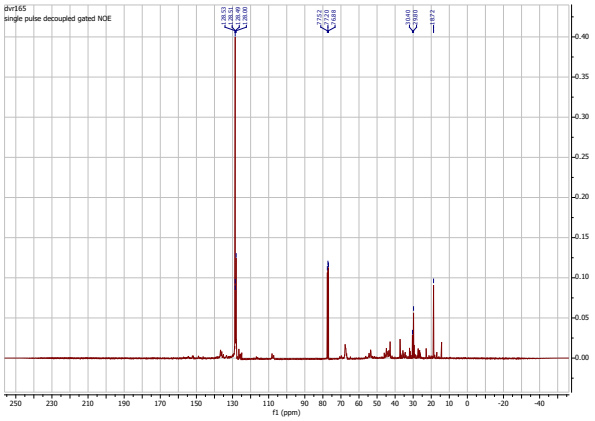
^{1}H-NMR spectrum of Benzyl 7-methyl-1-azaspiro[4.4]nona-3,6-diene-1-carboxylate



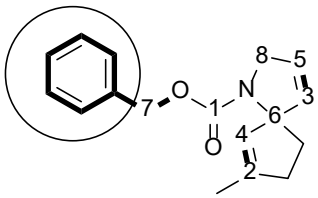


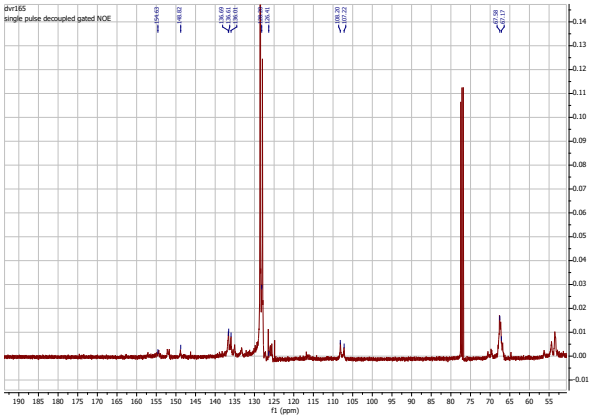
^{1}H-NMR spectrum of the signals due to the phenyl ring as well as methine protons of the dihydropyrrole and cyclopentene ring δ_H 7.37 (d, J =18.8 Hz, 1H), 7.35 (d, J =8.0 Hz, 1H), 7.33 (d, J = 4.8 Hz, 1H), 7.29 (d, J = 10 Hz, 1H) 7.31 (d, J = 10 Hz, 1H), 5.94 (s, 1H), 5.59 (d, J = 5.6 Hz,1H), 5.00 (s, 1H), 5.17 (d, J = 6.8 Hz, 1H), 5.15 (d, J = 6.8 Hz, 1H).





^{13}C-NMR spectrum of the Benzyl 7-methyl-1-azaspiro[4.4]nona-3,6-diene-1-carboxylate

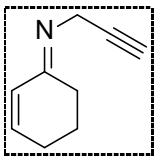




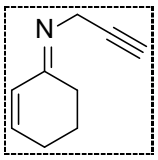
^{13}C-NMR spectrum at δ_C 154.4 ppm (1) (for the carbonyl carbon of ester part) as well as carbon atoms of the aromatic ring with methine carbon atoms of the dihydropyrrole ring and methine carbon of the cyclopentene ring with quaternary carbon directly attached to the methyl group; 149.0 (2), 136.6 (3), 136.0 (4), 135.1, 128.5 (high intensity for 2 carbon atoms), 128.0, 126.6, 126.0 125.6 (5) furthermore signals at 67.7 (6) ppm for the quaternary carbon atom and 67.4 ppm (7) and 53.6 ppm (8) for the carbon atoms directly attached to oxgen and nitrogen atoms respectively.

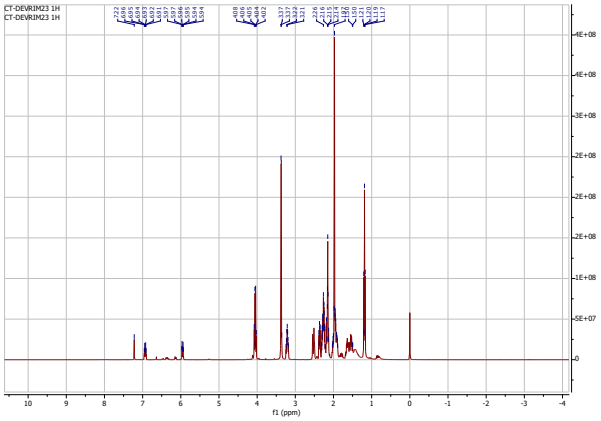
(IMINE COMPOUNDS CAN NOT BE PRUFIED THEY ARE EASILY DECOMPOSED ON SILICA GEL SO ^{1}H AND ^{13}C-NMR SPECTRA ARE TAKEN IMMIDIATELY SUBJECTED TO FURTHER REACTION)

(E)-N-(cyclohex-2-en-1-ylidene)prop-2-yn-1-amine 3c (Crude NMR)

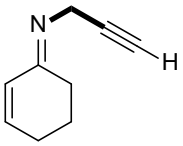


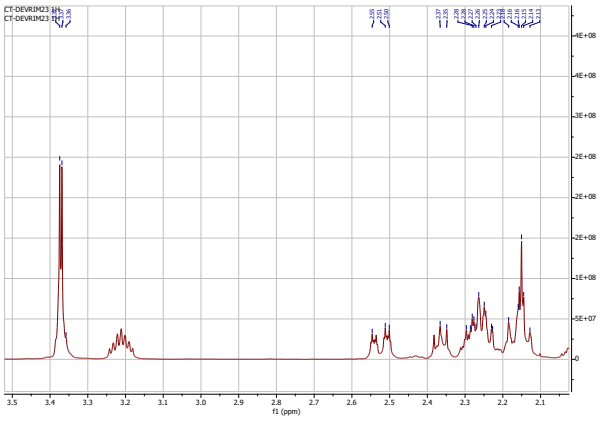
Color: Dark Brown oil FT-IR (KBr, *ν*, cm^{-1}): 3315, 2267 cm^{-1}. ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 6.94 (td, *J* = 4.2 and 5.0 Hz, 1H), 5.95 (td, *J* = 2.0 and 10.1 Hz, 1H), 3.37 (d, *J*= 2.4 Hz, 2H), 3.18-3.24 (m, 1H), 2.52 (dd, *J* = 4.0 and 13.8 Hz, 1H), 2.37 (t, *J* = 6.4 Hz, 1H), 2.29 (td, 2.0 and 6.2 Hz, 1H), 2.24 (dd, *J* =1.6 and 7.4 Hz, 1H), 2.15 (t, *J*= 2.0 Hz, 1H, (-C≡C-*H))*, 2.13-2.19 (m, 1H), 1.96 (dd, *J* = 3.5 and 4.4 Hz, 1H), 1.91 (dd, *J* = 4.0 and 5.4 Hz, 1H), 1.94-2.04 (m, 1H), 1.60-1.68 (m, 1H), 1.50-1.59 (m, 1H). ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 182.9, 170.1, 129.6, 81.9, 71.6, 47.9, 41.0, 38.1, 35.0, 30.4, 25.7, 22.7, 21.8.



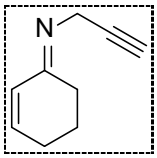


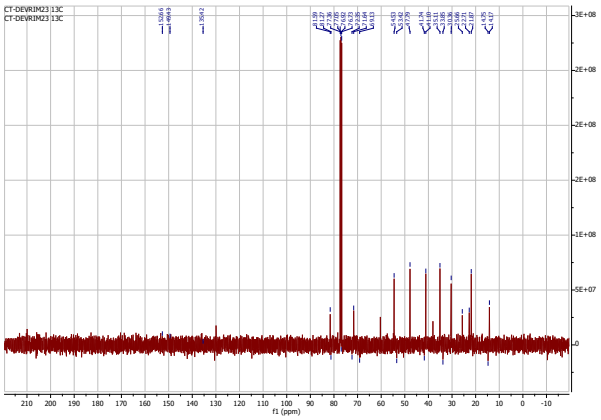
^{1}H-NMR spectrum of (E)-N-(cyclohex-2-en-1-ylidene)prop-2-yn-1-amine (Crude NMR)



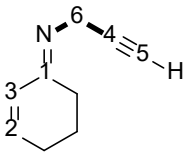


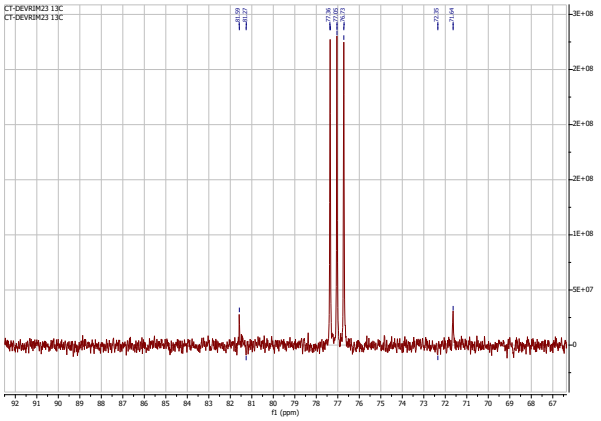
^{1}H-NMR spectrum of the signals due to the acetylenic proton as well as methylene protons directly attached to the nitrogen atom δ_h 3.37 (d, *J*= 2.4 Hz, 2H), 3.18-3.24 (m, 1H), 2.52 (dd, *J* = 4.0 and 13.8 Hz, 1H), 2.37 (t, *J* = 6.4 Hz, 1H) , 2.29 (td, 2.0 and 6.2 Hz, 1H), 2.24 (dd, *J* =1.6 and 7.4 Hz, 1H), 2.15 (t, *J* = 2.0 Hz, 1H, (-C≡C-*H))*





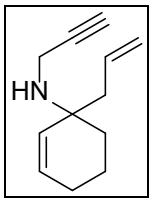
^{13}C-NMR spectrum of (E)-N-(cyclohex-2-en-1-ylidene)prop-2-yn-1-amine (Crude NMR)



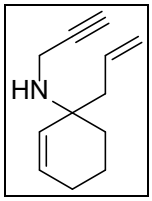


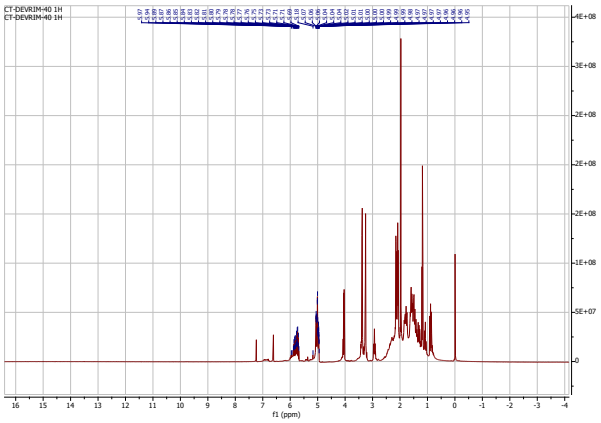
^{13}C-NMR spectrum of the signals due to the triple bond carbon atoms, δ_C 81.9 (4), 71.6 (5) ppm, (-C≡C-). Furthermore the ^{13}C-NMR signals at 182.9 (2), 170.1(1), 129.6 (3) ppm for the olefinic carbon atoms as well as imine carbon atom respectively finally methylene carbon at 47.9 ppm (6).

1-allyl-N-(prop-2-yn-1-yl)cyclohex-2-enamine (12b) (new compound)

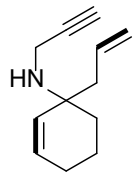


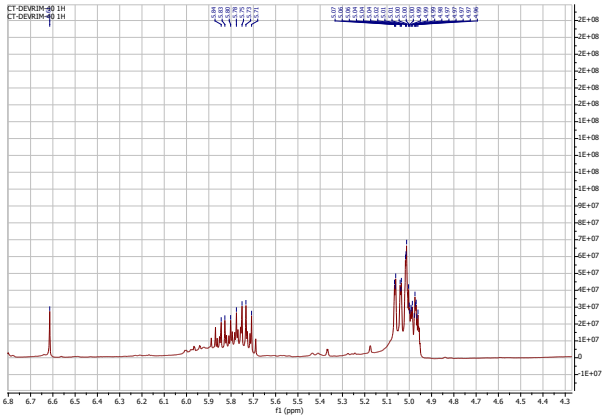
Color: Dark Brown oil Yield:1.10 g, 72 % chemical yield, FT-IR (KBr, *ν*, cm^{-1}): 3317, 3092, 2130,1650 cm^{-1}. Purified by Flash Column Chromatography, (1:1:1% Et_3N, EtOAc, Hexane) ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 5.69-5.90 (m, 1H), 5.05 (dd, *J* = 2.0 and 10.0 Hz, 1H), 5.01 (t, *J* = 1.0 Hz, 1H), 5.00 (ddd, *J* = 1.2, 3.2 and 4.0 Hz, 1H), 4.97 (pd, *J* = 1.2 and 5.6 Hz, 1H), 3.39 (dd, *J* = 2.4 and 5.0 Hz, 1H), 3.38 (dd, *J* = 2.4 and 5.4 Hz, 1H), 3.26 (t, N-*H*, *J* = 2.8 Hz, 1H), 2.15 (dd, *J* = 2.4 and 4.4 Hz, 1H), 2.13 (t, *J* = 2.6 Hz, 1H), 2.10 (dd, *J* = 0.4 and 6.0 Hz, 1H), 2.08 (d, *J* = 7 Hz, 1H), 1.83 (dd, *J* = 4.0 and 10.6 Hz, 1H), 1.77 (dd, *J* = 3.6 and 12.2 Hz, 1H), 1.62 (dd, 1H, *J* = 1.2 and 2.8 Hz), 1.56 (dd, *J* = 3.6 and 10.6 Hz,1H), 1.50 (dd, *J* = 3.2 and 6.2 Hz, 1H) ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 134.4, 133.3, 118.0, 117.0, 83.5, 82.0, 71.2, 70.2, 54.8, 43.6, 41.2, 35.3, 32.4, 19.5. $C_{12}H_{18}N$, HRMS-ESI, $[M+H]^+$ Calculated mass; 176.1439, Found mass; 176.1423.



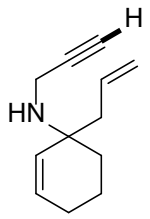


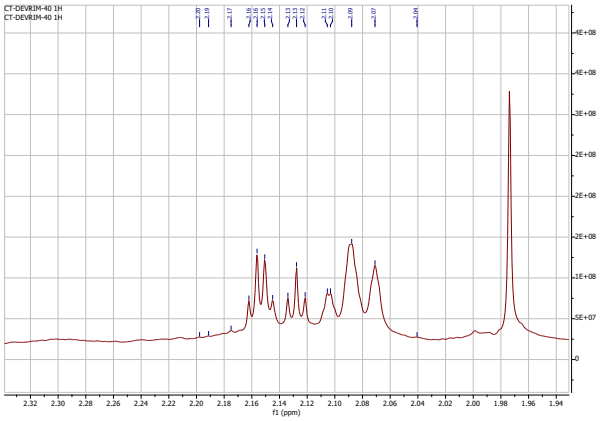
^{1}H-NMR spectrum of 1-allyl-N-(prop-2-yn-1-yl)cyclohex-2-enamine



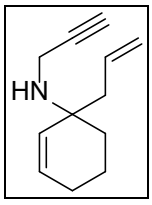


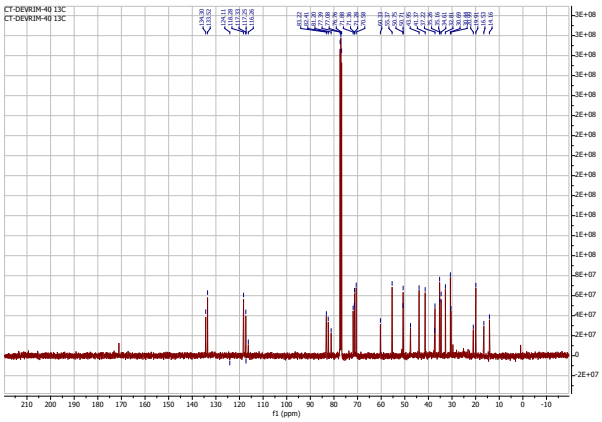
^{1}H-NMR spectrum of the signals of allylic protons as well as olefinic protons of the cyclohexene ring δ_H 5.69-5.90 (m, 1H), 5.05 (dd, J = 2.0 and 10.0 Hz, 1H), 5.01 (t, J = 1.0 Hz, 1H), 5.00 (ddd, J = 1.2, 3.2 and 4.0 Hz, 1H), 4.97 (pd, J = 1.2 and 5.6 Hz, 1H).



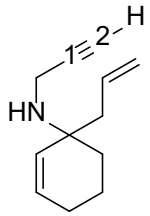


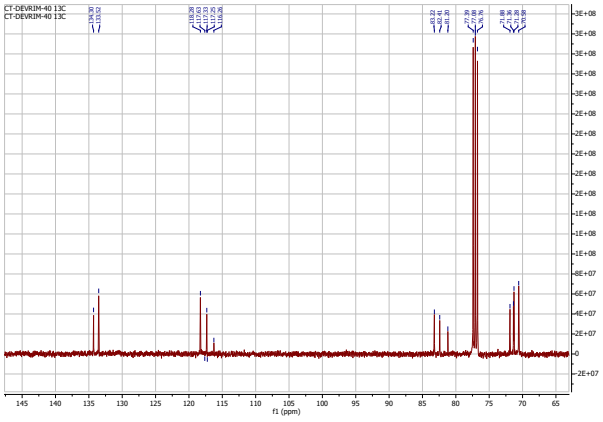
^{1}H-NMR spectrum of the signals of the acetylenic proton δ_H 2.13 (t, J = 2.6 Hz, 1H).



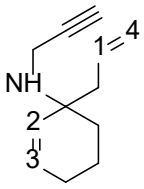


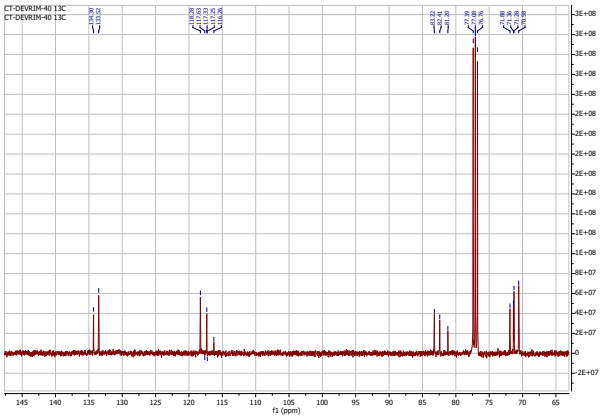
^{13}C-NMR spectrum of 1-allyl-N-(prop-2-yn-1-yl)cyclohex-2-enamine



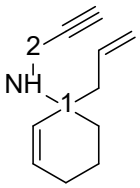


^{13}C-NMR spectrum of the signals at δ_C 82.0 (1), 71.2 (2) ppm for the acetylenic carbon atoms.



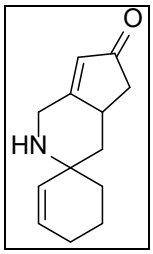


^{13}C-NMR spectrum of the signals at δ_C 134.4 (1), 133.3 (2), 118.0 (3), 117.0 ppm (4) for the homoallylic carbon atoms and olefinic carbons of the cyclohexene ring.

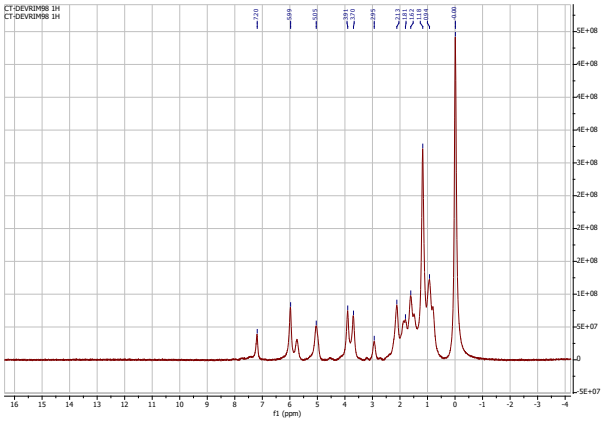


^{13}C-NMR spectrum of the signals at 54.8 (1), 43.6 (2), for the quaternary carbon and methylene carbon atoms directly attached to the nitrogen atom.

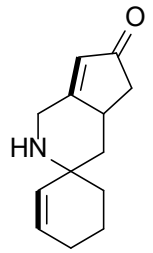
1',2',4a',5'-tetrahydrospiro[cyclohex[2]ene-1,3'-cyclopenta[c]pyridin]-6'(4'H)-one (13b) (new compound)

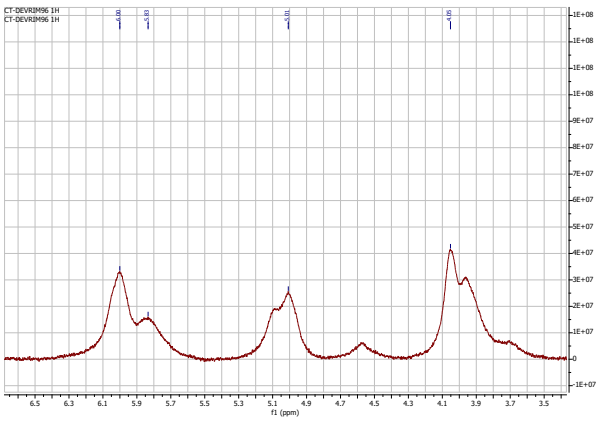


Color: Dark yellow oil. FT-IR (KBr, ν, cm^{-1}) : 2929, 2915, 1677 (C=O) ,^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): δ_H 5.99 (s, 1H), 5.65-5.85 (m, 1H), 5.05 (d, *J* = 6.4 Hz, 1H), 3.91 (d, *J*= 2.8 Hz, 1H), 3.70 (d, *J* = 2.4 Hz, 1H), 2.86-3.05 (m, 1H), 2.03-2.30 (m, 2H), 1.88 (dd, *J* = 3.2 anfd 5.6 Hz, 1H), 1.80 (dd, *J* = 6.8 and 15.6 Hz, 1H), 1.61(dd, *J* = 5.2 and 9.4 Hz, 1H), 1.50 (dd, *J* = 2.4 and 5.6 Hz, 1H), 1.07-1.31 (m, 3H), 0.94 (dd, *J* = 2.8 and 6.8 Hz, 1H), 0.82 (dd, *J* = 2.0 and 6.2 Hz, 1H) ^{13}C-NMR (100 MHz, $CDCl_3$, δ, ppm): δ_C 200.2, according to the carbonyl group, 171.7, 136.8, 133.2, 118.0, 60.9, 55.1, 51.3, 49.4, 44.4, 42.8, 31.8, 27.3.

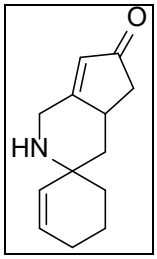


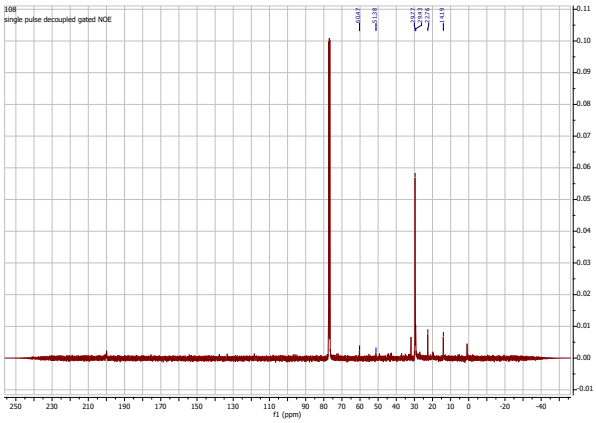
^{1}H-NMR spectrum of 1',2',4a',5'-tetrahydrospiro[cyclohex[2]ene-1,3'-cyclopenta[c]pyridin]-6'(4'H)-one



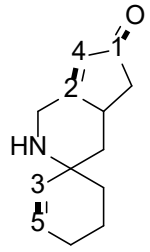


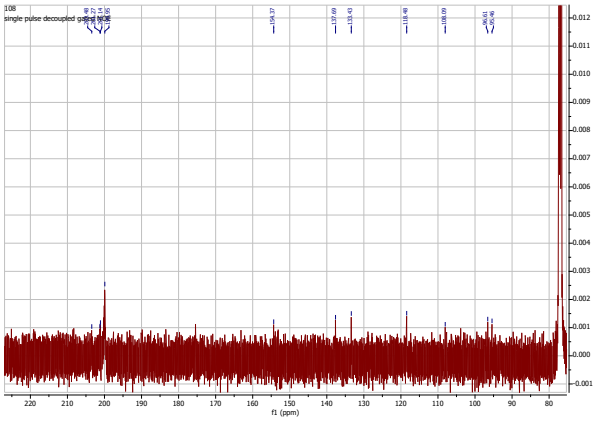
^{1}H-NMR spectrum of the signals due to the olefinic protons δ_H 5.99 (s, 1H), 5.65-5.85 (m, 1H), 5.05 (d, J = 6.4 Hz, 1H).



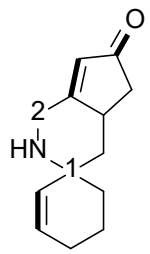


^{13}C-NMR spectrum of 1',2',4a',5'-tetrahydrospiro[cyclohex[2]ene-1,3'-cyclopenta[c]pyridin]-6'(4'H)-one

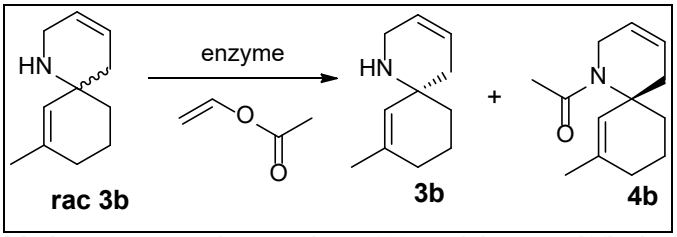




^{13}C-NMR spectrum of the signals δ_C 200.2 (1) due to the carbonyl carbon atom, at 171.7 (2), 136.8 (3) ppm for the quaternary carbon and methine carbon of cyclopentenone ring, as well as methine carbon atoms of the cyclohexene ring at 133.2 (4), 118.0 (5) ppm.



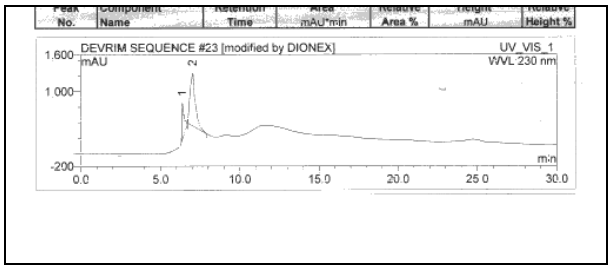
^{13}C-NMR spectrum of the signals at δ_C 60.9 (1), 55.1 (2) ppm for the quaternary carbon atom and methylene carbon directly attached to nitrogen atom respectively.



[7] Scheme S2. Enzymatic kinetic resolution of (±)-8-methyl-1-azaspiro[5,5]undeca-3,7-diene *rac* 3b

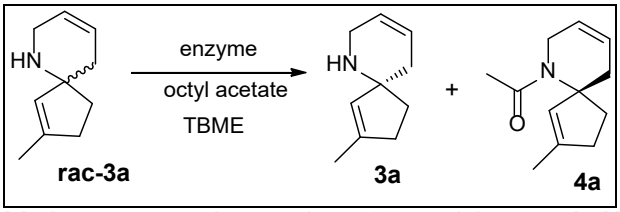
[8] Table S2. Enzymatic kinetic resolution of (±)-8-methyl-1-azaspiro[5,5]undeca-3,7-diene *rac* 3b

Product	**Enzyme**	**Temperature (^{0}C)**	**Time(hr)**	**ee (%)**	**$[\alpha]_D^{18}$ (c, solvent)**
(-)-8-methyl-1-azaspiro[5,5]undeca-3,7-diene **3b**	CAL-A-CLEA	40	85	2	- 1.82 (c=0.25, **$CHCl_3$**)
(+)-1-(8-methyl-1-azaspiro[5,5]undeca-3,7-dien-1-il)ethan-1-one **4b**	CAL-A-CLEA	40	85	30	+8.21 (c=0.25, **$CHCl_3$**)
(-)-8-methyl-1-azaspiro[5,5]undeca-3,7-diene **3b**	CAL-B-recombinant from Aspergillus oryzae	40	85	20	+8.88 (c=0.25, **$CHCl_3$**)
(+)-1-(8-methyll-1-azaspiro[5,5]undeca-3,7-dien-1-il)ethan-1-one **4b**	CAL-B-recombinant from Aspergillus oryzae	40	85	55	-15.37 (c=0.25, **$CHCl_3$**)



HPLC Chromatogram of (-)-1-(8-methyl-1-azaspiro[5,5]undeca-3,7-dien-1-il)ethan-1-one **3b**

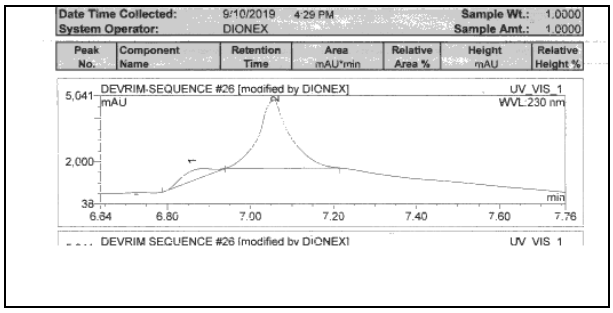
HPLC conditıons: CHIRALPAK OD-H, flow rate = 0.5 ml/min t_{r1} = 6.38 min, t_{r2} = 7.03 minwavelength: 230 nm. ENZYME**:** CAL-B-recombinant from Aspergillus oryzae.



[9] Scheme S3 Enzymatic kinetic resolution of (±)-2-methyl-6-azaspiro[4,5]deca-1,8-diene *rac* 3a

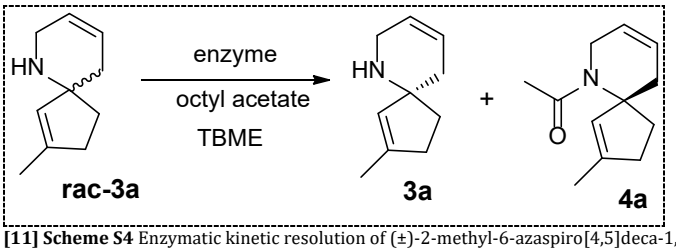
[10] Table S3. Enzymatic kinetic resolution of (±)-2-methyl-6-azaspiro[4,5]deca-1,8-diene ***rac* 3a**

Product	**Enzyme**	**Temperature (°C)**	**Time (hr)**	**ee (%)**	**$[\alpha]_D^{19}$ (c, solvent)**
(+)-2-methyl-6-azaspiro[4,5]deca-1,8-diene **(3a)**	*CAL-B-recombinant from Aspergillus oryzae*	40	78	77	+17.84 (c=0.25, **$CHCl_3$**)
(-)-1-(2-methyl-6-azaspiro[4,5]deca-1,8-dien-6-il)ethanone **(4a)**	*CAL-B-recombinant from Aspergillus oryzae*	40	78	52	-18.50 (c=0.25, **$CHCl_3$**)



HPLC Chromatogram of (+)-2-methyl-6-azaspiro[4,5]deca-1,8-diene **3a**

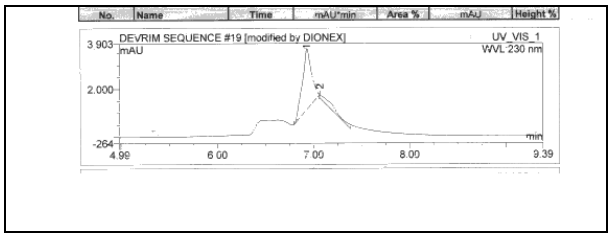
HPLC conditions: CHIRALPAK OD-H, flow rate = 0.5 ml/min t_{r1} = 6.86 min t_{r2} = 7.06 minwavelength: 230 nm. ENZYME: CAL-B-recombinant from Aspergillus oryzae, Acyl donor: octyl acetate.



[11] Scheme S4 Enzymatic kinetic resolution of (±)-2-methyl-6-azaspiro[4,5]deca-1,8-diene *rac-3a*

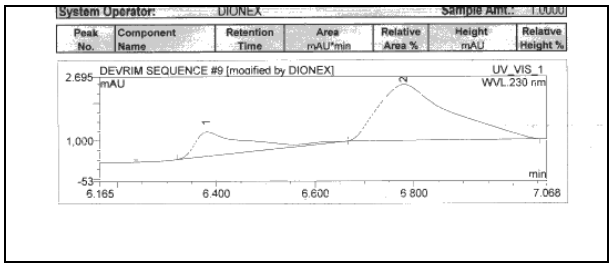
[12] Table S4. Enzymatic kinetic resolution of (±)-2-methyl-6-azaspiro[4,5]deca-1,8-diene rac-3a

Product	**Enzyme**	**Temperature (⁰C)**	**Time (hr)**	**ee (%)**	**$[\alpha]_D^{18}$ (c, solvent)**
(-)-2-methyl-6-azaspiro[4,5]deca-1,8-diene **(3a)**	CAL-A-CLEA	40	78	25	- 6.94 (c=0.25, $CHCl_3$)
(+)-1-(2-metil-6-azaspiro[4,5]deca-1,8-diene-6-il)ethanone **(4a)**	CAL-A-CLEA	40	78	55	+22.56 (c=0.25, $CHCl_3$)
(+)-2-methyl-6-azaspiro[4,5]deca-1,8-diene **(3a)**	CAL-B-recombinant from Aspergillus oryzae	40	85	60	+15.55 (c=0.25, $CHCl_3$)
(-)-1-(2-methyl-6-azaspiro[4,5]deca-1,8-dien-6-il)ethanone (**4a**)	CAL-B-recombinant from Aspergillus oryzae	40	85	75	-33.54 (c=0.25, $CHCl_3$)



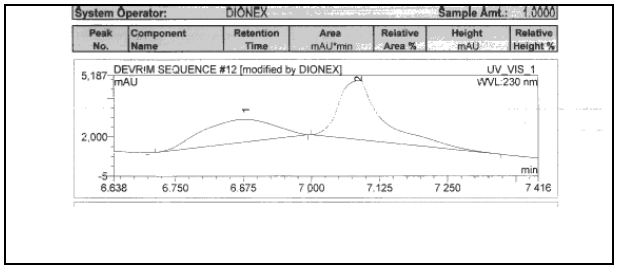
HPLC Chromatogram of (-)-1-(2-methyl-6-azaspiro[4,5]deca-1,8-diene-6-il)ethanone **4a**

HPLC conditıons: CHIRALPAK OD-H, flow rate = 0.5 ml/min t_{r1} = 6.93 min, t_{r2} = 7.06 min Wavelength: 230 nm. ENZYME: CAL-B-recombinant from Aspergillus oryzae



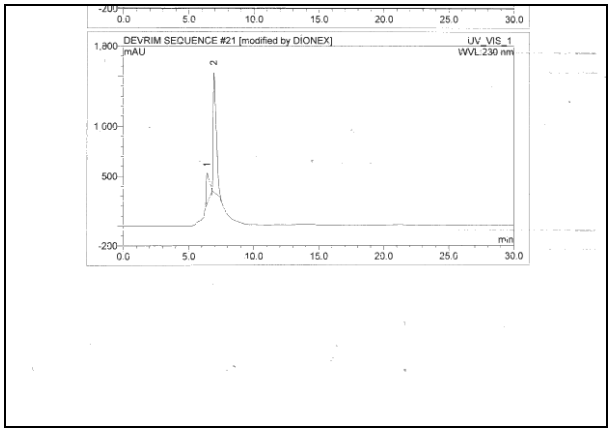
HPLC Chromatogram of (+)-1-(2-methyl-6-azaspiro[4,5]deca-1,8-diene-6-il)ethanone **4a**

HPLC conditions: CHIRALPAK OD-H, flow rate = 0.5 ml/min t_{r1} = 6.38 min, t_{r2} = 6.78 min. Wavelength: 230 nm. ENZYME: CAL-A-CLEA.



HPLC Chromatogram of (-)-2-methyl-6-azaspiro[4,5]deca-1,8-diene **3a**

HPLC conditions: CHIRALPAK OD-H, flow rate = 0.5 ml/min t_{r1} = 6.88 min, t_{r2} = 7.08 min. Wavelength: 230 nm. ENZYME: CAL-A-CLEA.



HPLC Chromatogram of (+)-2-methyl-6-azaspiro[4,5]deca-1,8-diene **3a**

HPLC conditions: CHIRALPAK OD-H, flow rate = 0.5 ml/min t_{r1} = 6.41 min, t_{r2} = 6.91 min. Wavelength: 230 nm. ENZYME: CAL-B-recombinant from Aspergillus oryzae.

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†ENZYMATIC KINETIC RESOLUTION REACTIONS ARE STUDIED IN MICROSCALE SUCH AS WITH (100 mg-200 mg substrates) SO THE HPLC CHROMATOGRAMS ARE TAKEN ONLY FOR CHIRAL ALCOHOLS 3a-3b and CHIRAL ACETATES 4a-4b

ABSOLUTE CONFIGURATION OF CHIRAL ALCOHOLS 3a-3b AND CORRESPONDING ACETATES 4a-4b ARE NOT KNOWN; THE CONFIGURATION SHOWN ONLY TO INDICATE THE CHIRALITY OF THEM.