

Electronic Supporting information

Gold-Allenylidenes – An Experimental and Theoretical Study**

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1. General Methods

Chemicals were purchased from commercial suppliers and used as delivered. Dry solvents were dispensed from solvent purification system MB SPS-800. Oxygen-free, anhydrous reactions were carried out under an atmosphere of nitrogen. Reaction steps involving the synthesis of phosphorous ligands were carried out using dry and degassed solvents. To degas the solvents, nitrogen was bubbled through them for at least 1 hour. NMR spectra were, if not mentioned otherwise, recorded at room temperature on the following spectrometers: Bruker ARX-250, Bruker Avance DRX-300 or Bruker Avance 500, Bruker Avance 600. Chemical shifts are given in ppm and coupling constants in Hz. ^1H and ^{13}C spectra are calibrated in relation to deuterated solvents (CDCl_3 : 7.26 / 77.16 ppm; CD_2Cl_2 : 5.32 / 53.80 ppm; C_6D_6 : 7.15 / 128.06 ppm; d_6 -DMSO: 2.50 / 39.52 ppm; d_6 -acetone: 2.05 / 29.84). ^{31}P spectra were calibrated in relation to the reference measurement of phosphoric acid (0.00 ppm). ^{19}F spectra were calibrated in relation to the reference measurement of 1,2-difluorobenzene (-139 ppm). The following abbreviations were used for ^1H NMR to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), pent (pentet), sext (sextet), sept (septet), decet (decet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet), td (triplet of doublet), qd (quartet of doublet), tt (triplet of triplet), ddd (doublet of doublet of doublet), ddt (doublet of doublet of triplet), bs (broad singlet). All ^{13}C NMR spectra were measured with ^1H decoupling. The multiplicities mentioned in this spectra [s (singlet, quaternary carbon), d (doublet, CH-group), t (triplet, CH_2 -group), q (quartet, CH_3 group)] were determined by DEPT135 and HSQC spectra. In addition, for new compounds HMBC and H,H-COSY spectra were taken. For phosphorous and fluorine containing compounds, the second multiplicity refers to the ^{31}P - or ^{19}F -coupling. All ^{13}C spectra of phosphorous containing compounds were also measured with ^{31}P -decoupling. Mass spectra (MS and HRMS) were determined in the chemistry department of the University Heidelberg under the direction of Dr. J. Gross. FAB + spectra were obtained using a JEOL JMS-700 spectrometer. For the FAB-matrix, 3-nitrobenzyl alcohol (NBA) or *o*-nitrophenyl octyl ether (NPOE) was used. For ESI+ spectra, a Bruker ApexQe FT-ICR-MS spectrometer was used. Infrared Spectroscopy (IR) was processed on an FT-IR BRUKER (IF528), IR PERKIN ELMER (283) or FT-IR Bruker Vektor 22. The solvent or matrix is denoted in brackets. For the most significant bands, the wave number (cm^{-1}) is given. X-ray crystal structure analyses were measured on Bruker Smart CCD or Bruker Smart APEX instrument using Mo-K α radiation. Diffraction intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS based on the Laue symmetry of reciprocal space. Heavy atom diffractions were solved by direct methods and refined against F2 with the full matrix least square algorithm. Hydrogen atoms were either isotropically refined or calculated. The structures were solved and refined using the SHELXTL software package. GasChromatography / Mass

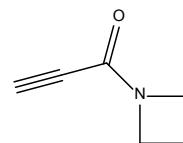
Spectrometry (GC MS) were carried out on two different systems: 1. HP 5972 Mass Selective Detector, coupled with a HP 5890 SERIES II plus Gas Chromatograph. 2. Agilent 5975C Mass Selective Detector, coupled with an Agilent 7890A Gas Chromatograph. In both cases, as a capillary column, an OPTIMA 5 cross-linked Methyl Silicone column (30 m x, 0.32 mm, 0.25 µm) was employed, and helium was used as the carrier gas. Gas Chromatography (GC) was carried out on a HP 5890 SERIES II plus Gas Chromatograph. As a capillary column, an OPTIMA 5 cross-linked Methyl Silicone column (30 m x, 0.32 mm, 0.25 µm) was employed, and nitrogen was used as the carrier gas. Melting points were measured in open glass capillaries in a Büchi melting point apparatus (according to Dr. Tottoli) and were not corrected. Flash column chromatography was accomplished using Silica gel 60 (0.04 - 0.063 mm /230 - 400 mesh ASTM purchased from Macherey-Nagel) or Aluminium oxide (neutral) (purchased from Macherey-Nagel). Analytical Thin Layer Chromatography (TLC) was carried out on precoated plastic sheets (Macherey- Nagel POLYGRAM® SIL G/UV₂₅₄ or POLYGRAM® ALOX N/UV₂₅₄). Detection was accomplished using UV-light (254 nm), KMnO₄ (in 1.5M Na₂CO₃ (aq.)), molybdatophosphoric acid (5 % in ethanol), or vanillin/H₂SO₄ (in ethanol).

2. Synthesis of starting materials

General Procedure A: In situ-alkylation

To a solution of gold-acetylide or propiolamide (1 eq) in CD₂Cl₂ (0.6 mmol) was added methyl triflate (1.2 eq), stirred for some minutes (10-60 min), transferred into an NMR tube and the NMR measured at room temperature.

1-(azetidin-1-yl)prop-2-yn-1-one (9)

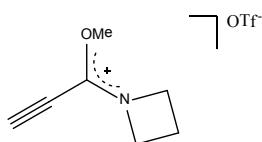


Azetidin (590 µL, 8.76 mmol) was dissolved in MeOH/H₂O (10 mL/10 mL), cooled to -50 °C and methyl propiolate (779 µL, 8.76 mmol) slowly added at this temperature. The solution was stirred at -50°C for 4 h and then 1M HCl solution (5 mL) added. The solution was stirred for 12 h and then the aqueous solution extracted with CH₂Cl₂ (50 mL). The organic phase was washed with sat. NaHCO₃ (50 mL) followed by brine (50 mL), dried over Na₂SO₄ and the solvent evaporated. The solid was purified by recrystallization from hot hexanes/ethyl acetate to afford colourless needles (838 mg, 88%).

IR (KBr) ν_{max} = 3201 cm⁻¹, 3048, 3019, 2973, 2954, 2884, 2102, 1902, 1623, 1455, 1432, 1295, 1267, 1245, 1186, 1168, 1129, 1038, 920, 862, 772, 736, 724, 665; ¹H NMR (500 MHz, CD₂Cl₂) δ = 2.29 (tt, J

= 7.7 Hz, 7.7 Hz, 2H), 3.03 (s, 1H), 3.99 (t, J = 7.8 Hz, 2H), 4.19 (t, J = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 16.0 (t), 48.7 (t), 50.9 (t), 75.2 (s), 77.5 (d), 153.0 (s); MS-EI + (m/z): 109.1 [M] $^+$ (65), 101 (8), 80 (12), 54 (11), 53 (100), 42 (51); HRMS-EI + (m/z): calcd for $\text{C}_6\text{H}_7\text{NO}$, 109.0528; found, 109.0530.

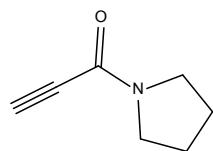
Methylated Compound 9



For preparation see General Procedure A; *in situ* characterisation:

^1H NMR (500 MHz, CD_2Cl_2) δ = 2.61 (tt, J = 8.0 Hz, 2H), 4.32 (s, 3H), 4.55 (t, J = 8.1 Hz, 2H), 4.69 (t, J = 8.0 Hz, 2H), 4.93 (s, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 16.6 (t), 54.8 (t), 55.9 (t), 63.5 (q), 65.5 (s), 101.7 (d), 121.2 (qs, $J(^{13}\text{C}-^{19}\text{F})$ = 320 Hz), 154.9 (s).

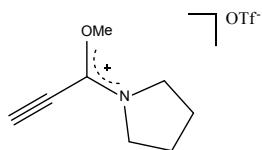
1-(pyrrolidin-1-yl)prop-2-yn-1-one (2)



A slightly modified procedure from Ref.^[1] was followed for the synthesis of compound **2**. Pyrrolidine (1.23 mL, 15.0 mmol) was dissolved in MeOH/H₂O (50 mL/50 mL), cooled to -50 °C and methyl propiolate (1.30 mL, 15.0 mmol) slowly added at this temperature. The solution was stirred at -50°C for 4 h and then 1M HCl solution (100 mL) added. The solution was stirred for 12 h and then the aqueous solution extracted with CH₂Cl₂ (150 mL). The organic phase was washed with sat. NaHCO₃ (50 mL) followed by brine (50 mL), dried over Na₂SO₄ and the solvent evaporated. The solid was purified by recrystallization from hot hexanes/ethyl acetate to afford colorless needles (1.34 g, 72 %). The compound is literature known.^[1]

^1H NMR (500 MHz, CD_2Cl_2) δ = 1.86-1.95 (m, 4H), 3.07 (s, 1H), 3.40 (t, J = 6.3 Hz, 2H), 3.62 (t, J = 6.3 Hz, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 25.1 (t), 25.9 (t), 45.7 (t), 48.6 (t), 76.9 (d), 77.5 (s), 151.6 (s).

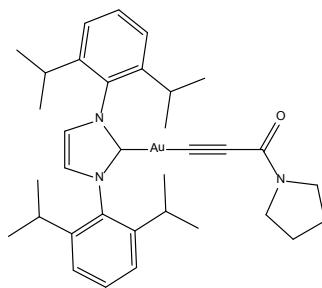
Methylated compound 8



For preparation see General Procedure A; *in situ* characterisation:

^1H NMR (500 MHz, CD_2Cl_2) δ = 2.11-2.16 (m, 4H), 3.83 (t, J = 5.8 Hz, 2H), 4.03 (t, J = 5.8 Hz, 2H), 4.38 (s, 3H), 4.99 (s, 1H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 25.0 (t, 2C), 51.4 (t), 54.1 (t), 63.7 (q), 67.6 (s), 101.6 (d), 119.8 (qs, $J(^{13}\text{C}-^{19}\text{F})$ = 320 Hz), 154.2 (s).

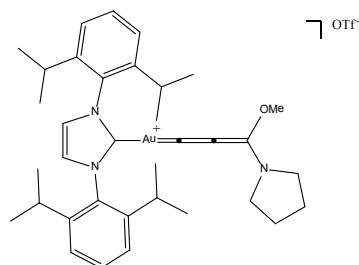
Compound 4



To a solution of IPrAuCl (100 mg, 0.161 mmol) in $\text{CH}_2\text{Cl}_2/\text{NEt}_3$ (1 mL/0.5 mL) was added 1-(pyrrolidin-1-yl)prop-2-yn-1-one (21.9 mg, 0.178, 1.1 eq.) and stirred in the dark at room temperature for 24h. After evaporation of the solvent the crude material was purified by flash column chromatography (neutral alox; EtOAc:PE = 1:1 to 2:1) to afford compound 4 as a white solid (92 mg, 81%).

R_f = 0.12 (alex; EtOAc:PE = 1:1); IR (thin film) ν_{max} = 2963 cm^{-1} , 2869, 2117, 1598, 1470, 1413, 1364, 1330, 1256, 1218, 1194, 1117, 1060, 947, 804, 759, 740; ^1H NMR (600 MHz, CD_2Cl_2) δ = 1.23 (d, J = 6.9 Hz, 12H), 1.34 (d, J = 6.9 Hz, 12H), 1.74-1.78 (m, 4H), 3.24 (t, J = 6.4 Hz, 2H), 3.46 (d, J = 6.2 Hz, 2H), 7.22 (s, 2H), 7.36 (d, J = 7.8 Hz, 4H), 7.57 (t, J = 8.0 Hz, 2H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ = 24.3 (q, 4C), 24.8 (q, 4C), 25.4 (t), 25.9 (t), 29.4 (d, 4C), 45.2 (t), 48.5 (t), 97.3 (s), 124.1 (d, 2C), 124.8 (d, 4C), 131.2 (d, 2C), 132.4 (s), 134.6 (s, 2C), 146.4 (s, 4C), 153.8 (s), 190.4 (s); HRMS-ESI + (m/z): calcd for $\text{C}_{34}\text{H}_{45}\text{AuN}_3\text{O}$, 708.3228.

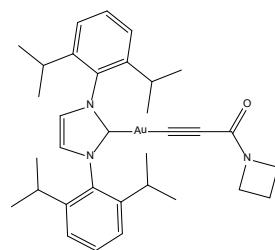
Compound 5



In a Schlenk flask under N₂ atmosphere Au-acetylide **4** (30mg, 42.3 μmol) was dissolved in CH₂Cl₂ (1 mL) and at room temperature methyl triflate (5.3 μL, 46.6 μL, 1.1 eq.) added. The solution was stirred at room temperature for 1 h and then stored at -30°C. Slow diffusion of pentane into this solution at -30°C afforded colourless crystals of compound **5** (26.2 mg, 72%).

IR (KBr) ν_{max} = 2964 cm⁻¹, 2871, 2115, 1627, 1554, 1468, 1417, 1366, 1326, 1273, 1223, 1154, 1061, 1032, 914, 808, 760, 705, 638, 572; ¹H NMR (600 MHz, CD₂Cl₂) δ = 1.25 (d, *J* = 6.9 Hz, 12H), 1.31 (d, *J* = 6.9 Hz, 12H), 1.96-2.05 (m, 4H), 2.54 (sept., *J* = 6.9 Hz, 4H), 3.58 (t, *J* = 6.7 Hz, 2H), 3.72 (t, *J* = 6.9 Hz, 2H), 4.10 (s, 3H), 7.30 (s, 2H), 7.36 (d, *J* = 7.6 Hz, 4H), 7.57 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (125 MHz, CD₂Cl₂) δ = 24.3 (q, 4C), 24.9 (q, 4C), 25.0 (t), 25.3 (t), 49.8 (t), 53.2 (t), 87.5 (s), 124.8 (d, 2C), 124.9 (d, 4C), 131.4 (d, 2C), 134.2 (s, 2C), 146.4 (s, 4C), 153.3 (s), 169.5 (s), 187.1 (s); HRMS-ESI + (m/z): calcd for C₃₅H₄₇AuN₃O, 722.3379 [M-NTf₂]⁺; found, 722.3373.

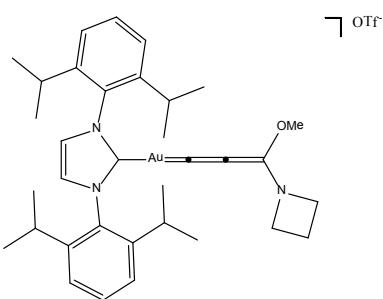
Compound **10**



To a solution of IPrAuCl (100 mg, 0.161 mmol) in CH₂Cl₂/NEt₃ (1 mL/0.5 mL) was added 1-(azetidin-1-yl)prop-2-yn-1-one (19.3 mg, 0.177 mmol, 1.1 eq.) and stirred for 20h at room temperature. The solvent was evaporated and the solid purified by column chromatography (neutral Alox; PE : EtOAc = 1:2) to afford compound **10** as white solid (89 mg, 0.128 mmol, 80%).

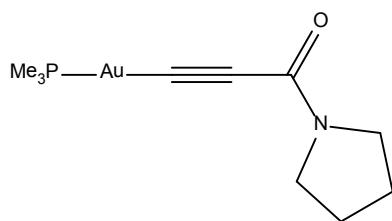
R_f = 0.33 (silica gel, PE:EA = 1:2); IR (KBr) 3108 cm⁻¹, 3073, 2961, 2869, 2121, 1606, 1554, 1471, 1414, 1364, 1352, 1329, 1293, 1257, 1215, 1181, 1157, 1120, 1059, 947, 804, 759; ¹H NMR (300 MHz, CD₂Cl₂) δ = 1.22 (d, *J* = 6.9 Hz, 12H), 1.33 (d, *J* = 6.9 Hz, 12H), 2.10 (tt, *J* = 7.7 Hz, 7.9 Hz, 2H), 2.55 (sept., *J* = 7.0 Hz, 4H), 3.81 (t, *J* = 7.8 Hz, 2H), 4.00 (t, *J* = 7.5 Hz, 2H), 7.21 (s, 2H), 7.35 (d, *J* = 7.9 Hz, 4H), 7.57 (t, *J* = 7.9 Hz, 2H); ¹³C NMR (125 MHz, CD₂Cl₂) δ = 15.7 (t), 24.3 (q, 4C), 24.8 (q, 4C), 29.4 (d, 4C), 48.2 (t), 50.6 (t), 94.6 (s), 124.1 (d, 2C), 124.8 (d, 4C), 131.2 (d, 2C), 133.8 (s), 134.6 (s, 2C), 146.4 (s, 4C), 155.8 (s), 190.2 (s); HRMS-ESI + (m/z): calcd for C₃₃H₄₃AuN₃O [M+H]⁺, 694.3072; found, 694.3076 [M+H]⁺.

Alkylated Compound of **10**



^1H NMR (500 MHz, CD_2Cl_2) δ = 1.24 (d, J = 6.9 Hz, 12H), 1.30 (d, J = 6.9 Hz, 12H), 2.42-2.49 (m, 2H), 2.53 (sept., J = 6.8 Hz, 4H), 4.04 (s, 3H), 4.29 (t, J = 7.4 Hz, 2H), 4.33 (t, J = 7.4 Hz, 2H), 7.30 (s, 2H), 7.36 (d, J = 7.8 Hz, 4H), 7.57 (t, J = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 16.4 (t), 24.2 (q, 4C), 24.9 (q, 4C), 29.3 (d, 4C), 53.3 (t), 54.3 (t), 61.9 (q), 84.9 (s), 124.8 (d, 2C), 124.8 (d, 4C), 131.3 (d, 2C), 134.2 (s, 2C), 146.3 (s, 4C), 154.1 (s), 169.8 (s), 186.9 (s).

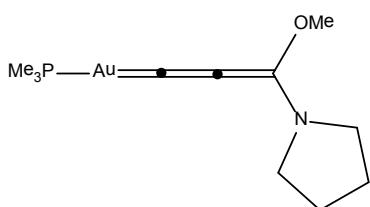
Compound 7



To a solution of trimethylphosphine gold(I) chloride (100 mg, 0.324 mmol) in $\text{CH}_2\text{Cl}_2/\text{NEt}_3$ (4 mL/1mL) was added 1-(pyrrolidin-1-yl)prop-2-yn-1-one (44.3 mg, 0.360 mmol, 1.1 eq.) and the solution stirred for 12 h in the dark at room temperature. After evaporation of the solvent the crude material was purified by column chromatography (neutral alox; CH_2Cl_2 :acetone: 20:1) to afford compound 6 as white solid (99.8 mg, 0.252 mmol, 70 %).

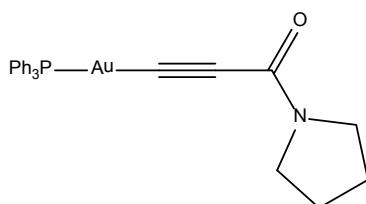
R_f = 0.24 (neutral alox; CH_2Cl_2 :acetone = 10:1); IR (KBr) ν_{\max} = 2971 cm^{-1} , 2872, 2113, 1597, 1405, 1337, 1292, 1222, 1193, 1116, 1046, 1005, 958, 866, 739, 683, 661, 567; ^1H NMR (500 MHz, CD_2Cl_2) δ = 1.52 (d, $J(\text{P}^{31}-\text{H})$ = 10.3 Hz, 9H), 1.82-1.89 (m, 4H), 3.35 (t, J = 6.9 Hz, 2H), 3.62 (t, J = 6.9 Hz, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ = 15.9 (dq, $J(\text{P}^{31}-\text{C}^{13})$ = 36.7 Hz, 25.4 (t), 26.0 (t), 45.4 (t), 48.8 (t), 97.1 (ds, $J(\text{P}^{31}-\text{C}^{13})$ = 27.4 Hz), 136.5 (ds, $J(\text{P}^{31}-\text{C}^{13})$ = 146.6), 153.5 (s); ^{31}P NMR (120 MHz, CD_2Cl_2) δ = 0.7; HRMS-ESI + (m/z): calcd for $\text{C}_{10}\text{H}_{18}\text{AuNOP} [\text{M}+\text{H}]^+$, 396.0792 $[\text{M}+\text{H}]^+$.

Alkylated compound of 7



¹H NMR (500 MHz, CD₂Cl₂) δ = 1.53 (d, *J*(³¹P-¹H) = 10.3 Hz), 1.98-2.04 (m, 4H), 3.58-3.65 (m, 2H), 3.83-3.89 (m, 2H), 4.21 (s, 3H); ¹³C NMR (125 MHz, CD₂Cl₂) δ = 15.4 (qd, *J*(³¹P-¹³C) = 38.6 Hz), 25.0 (t), 25.3 (t), 50.0 (t), 54.0 (t), 62.5 (q), 87.1 (s), 121.6 (sq, *J*(¹⁹F-¹³C) = 320 Hz, OTf), 153.4 (s), 170.3 (s); ³¹P NMR (120 MHz, CD₂Cl₂) δ = 0.7.

Compound 6

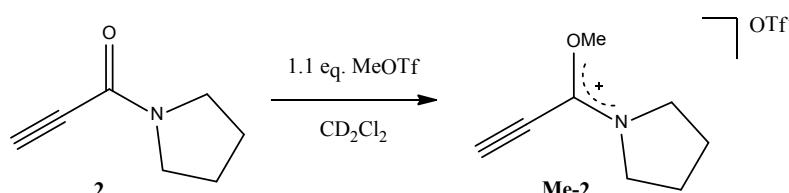


To a solution of IPrAuCl (150 mg, 0.303 mmol) in CH₂Cl₂/NEt₃ (2 mL/1 mL) was added at room temperature 1-(pyrrolidin-1-yl)prop-2-yn-1-one (37.3 mg, 0.303 mmol, 1.0 eq.) and the solution stirred in the dark for 15 h. After evaporation of the solvent the crude material was purified by flash column chromatography (neutral alox; PE : EtOAc = 1:2) to afford compound 6 as colourless solid (120 mg, 69%).

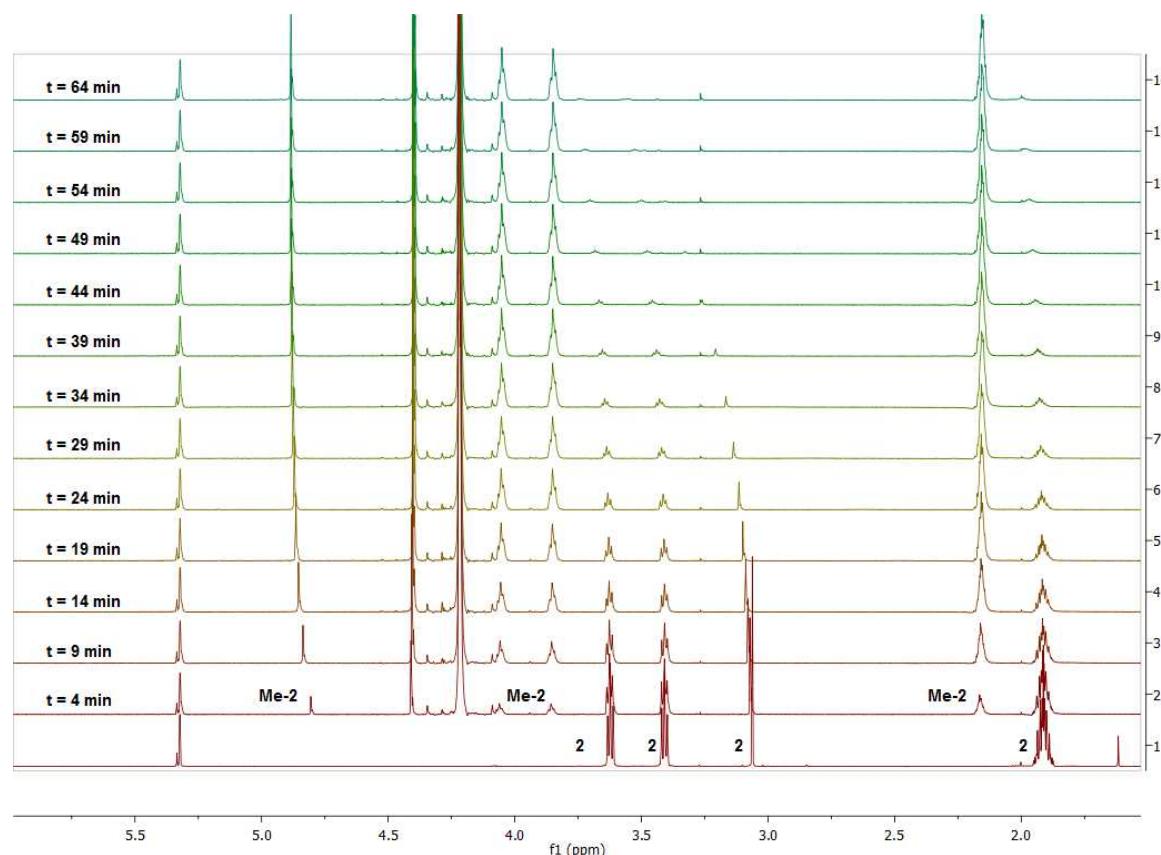
R_f = 0.29 (neutral alox; PE:EA = 1:2); IR (KBr) ν_{max} = 3050 cm⁻¹, 2967, 2869, 2117, 1605, 1480, 1435, 1408, 1336, 1311, 1222, 1192, 1100, 1044, 1027, 998, 911, 853, 746, 710, 694, 618, 567; ¹H NMR (400 MHz, CD₂Cl₂) δ = 1.84-1.91 (m, 4H), 3.38 (t, *J* = 6.9 Hz, 2H), 3.68 (t, *J* = 6.9 Hz, 2H), 7.44-7.55 (m, 15H); ¹³C NMR (100 MHz, CD₂Cl₂) δ = 25.4 (t), 26.0 (t), 45.4 (t), 48.8 (t), 96.6 (s), 129.7 (dd, *J*(³¹P-¹³C) = 11 Hz), 130.8 (dq, *J*(³¹P-¹³C) = 50.0 Hz), 132.0 (dd, *J*(³¹P-¹³C) = 2.0 Hz), 134.7 (d, *J*(³¹P-¹³C) = 14.9 Hz), 135.6 (s), 153.5 (s); ³¹P NMR (162 MHz, CD₂Cl₂) δ = 36.0; HRMS-ESI + (m/z): calcd for C₂₅H₂₄AuNOP [M+H]⁺, 582.1261; found, 582.1278 [M+H]⁺.

3. Methylation kinetic

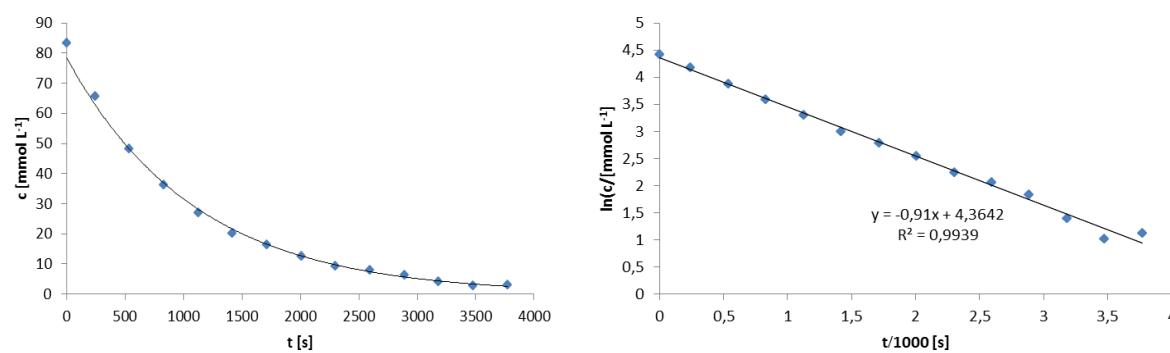
Methylation kinetic of compound 2



From a standard solution of 1-(pyrrolidin-1-yl)prop-2-yn-1-one (**2**) (12.3 mg, 100 µmol in 1.2 mL CD₂Cl₂) 0.6 mL (50 µmol) was transferred into a NMR-tube. A proton NMR was measured, excess MeOTf (34.0 µL, 300 µmol, 6 eq.) was added and the kinetics followed by ¹H NMR (600 MHz) at T = 298K.



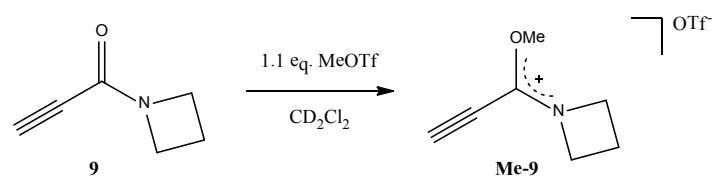
Plot-concentration of **2** vs. time and determination of pseudo-first order rate constant



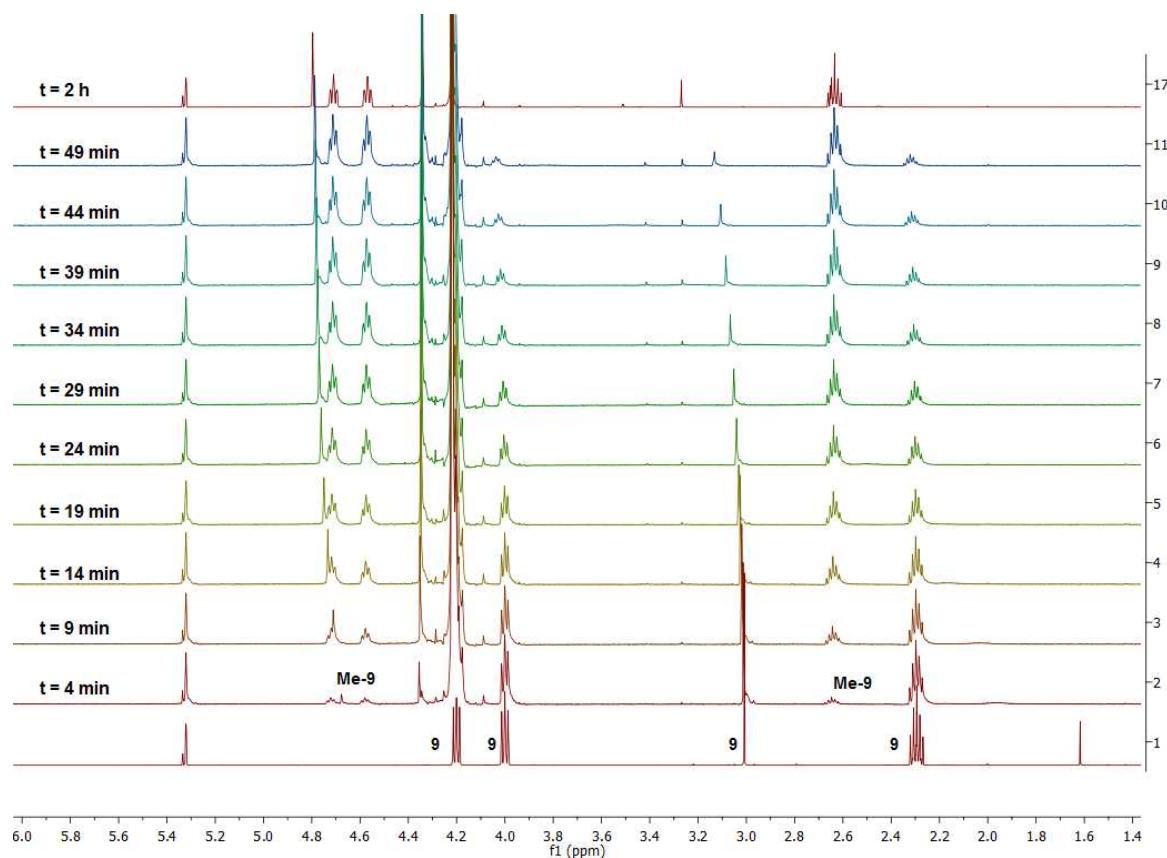
In case of excess MeOTf → pseudo-first order

$$r = -\frac{d[2]}{dt} = k_{p1,0}^{298K} \cdot [2] \rightarrow k = 0.910 \cdot 10^{-3} \text{ s}^{-1}$$

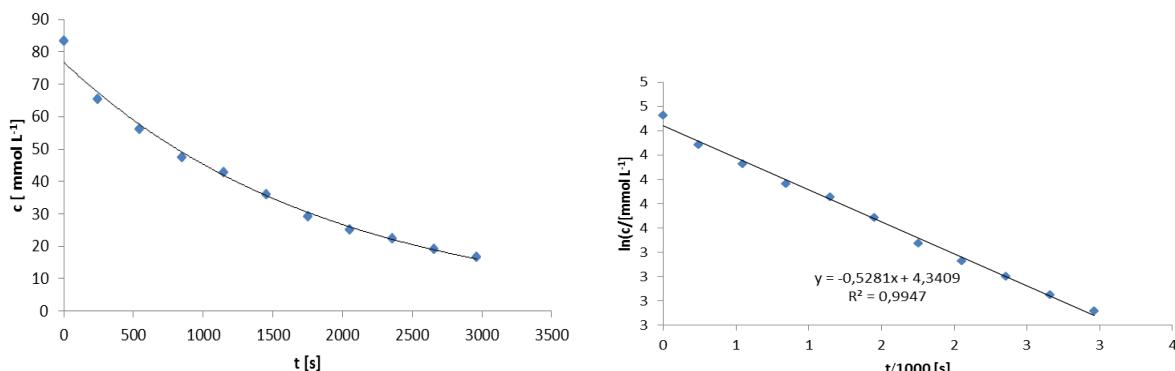
Methylation kinetic of compound 9



From a standard solution of 1-(azetidin-1-yl)prop-2-yn-1-one (**9**) (10.9 mg, 100 µmol in 1.2 mL CD₂Cl₂) 0.6 mL (50 µmol) was transferred into a NMR-tube. A proton NMR was measured, excess MeOTf (34.0 µL, 300 µmol, 6 eq.) was added and the kinetics followed by ¹H NMR (600 MHz) at T = 298K.



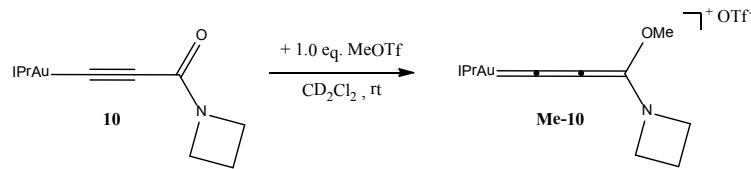
Plot-concentration of **9 vs. time and determination of pseudo-first order rate constant**



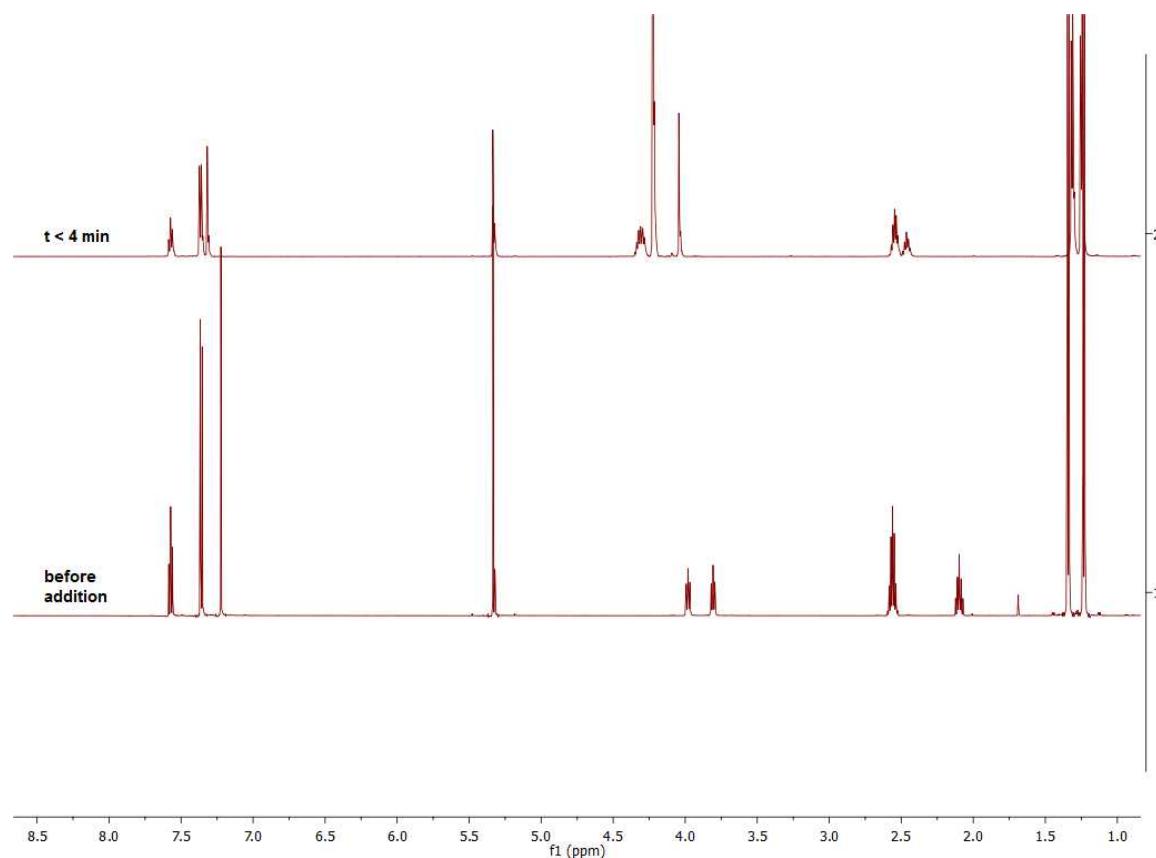
In case of excess MeOTf -> pseudo-first order

$$r = -d[9]/dt = k_{p1.0}^{298K} \cdot [9] \rightarrow k = 0.528 \cdot 10^{-3} \text{ s}^{-1}$$

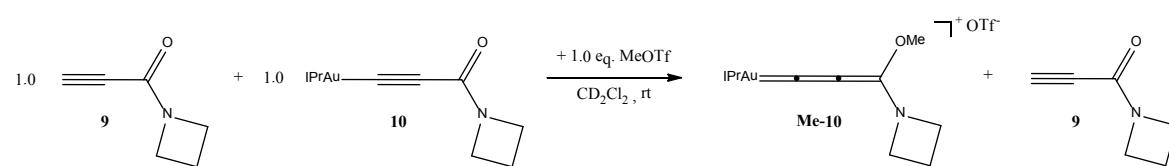
Methylation kinetic of compound **10**



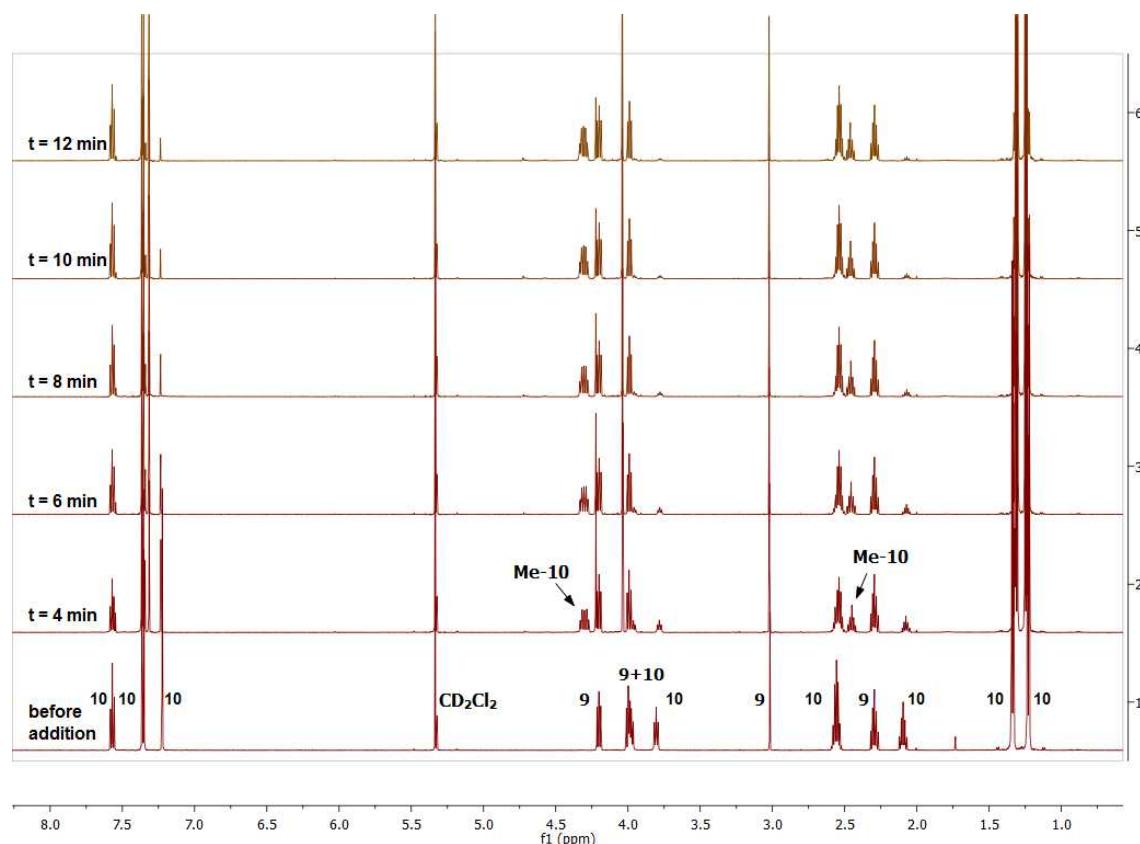
Identical conditions: To a solution of gold-complex **10** (34.7 mg, 50 µmol) in 0.6 mL CD_2Cl_2 was added excess MeOTf (34.0 µL, 300 µmol, 6 eq.) and the kinetics followed by ^1H NMR (600 MHz) at $T = 298\text{K}$. Compared to the kinetics with the free amides the reaction, under identical conditions (pseudo-first order conditions) full conversion was observed in less than 4 min (corresponds to mixing time and sample insertion)! To gain further inside a competition experiment was performed (see below) confirming this rate acceleration effect.



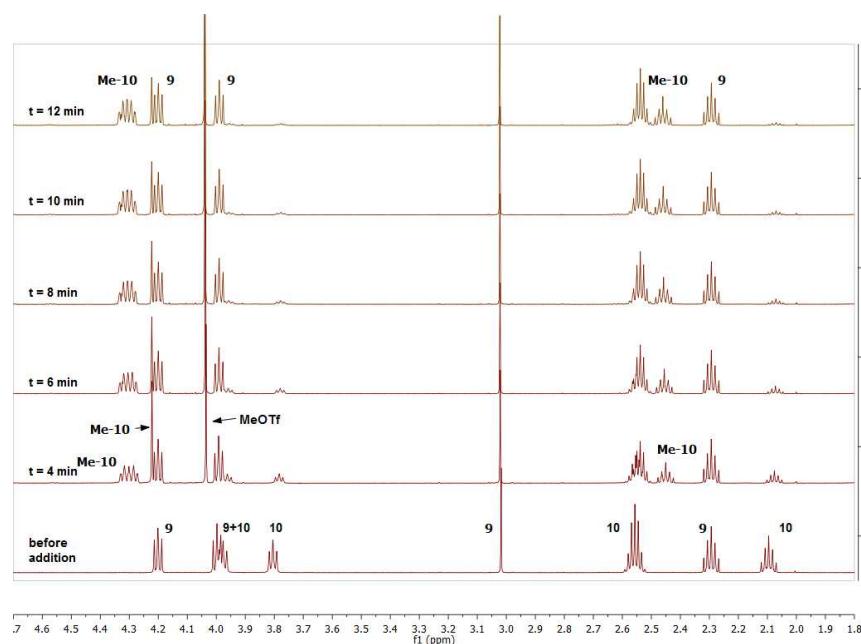
Methylation competition experiment:



To a 1:1 solution of 1-(azetidin-1-yl)prop-2-yn-1-one (**9**) (5.5 mg, 50.0 μ mol) and gold-complex **10** (34.7 mg, 50 μ mol) in CD_2Cl_2 (0.6 mL) in a NMR-tube was added 1.0 equivalent of MeOTf (5.7 μ L, 50.0 μ mol) and the NMR-spectrum directly measured as function of time (see below).

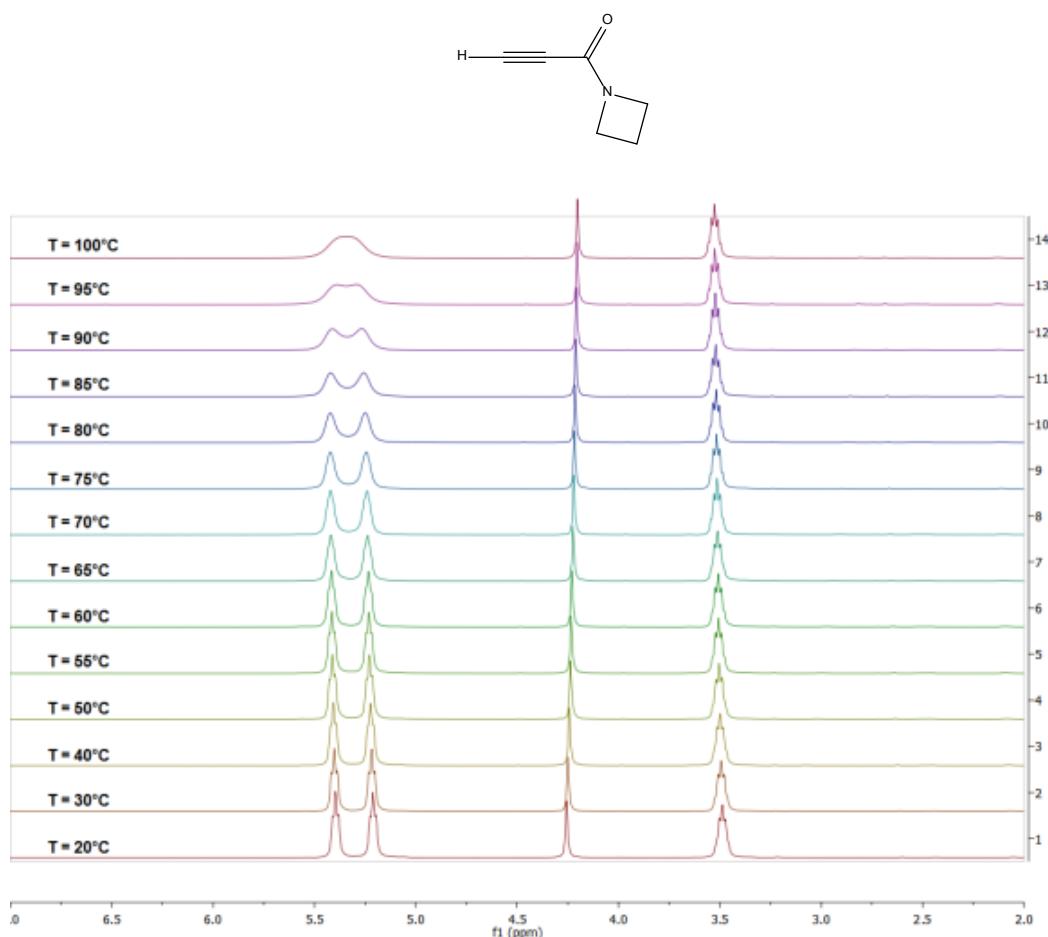


Enlargement of the ¹H-NMR region at 4.7 ppm – 1.8 ppm

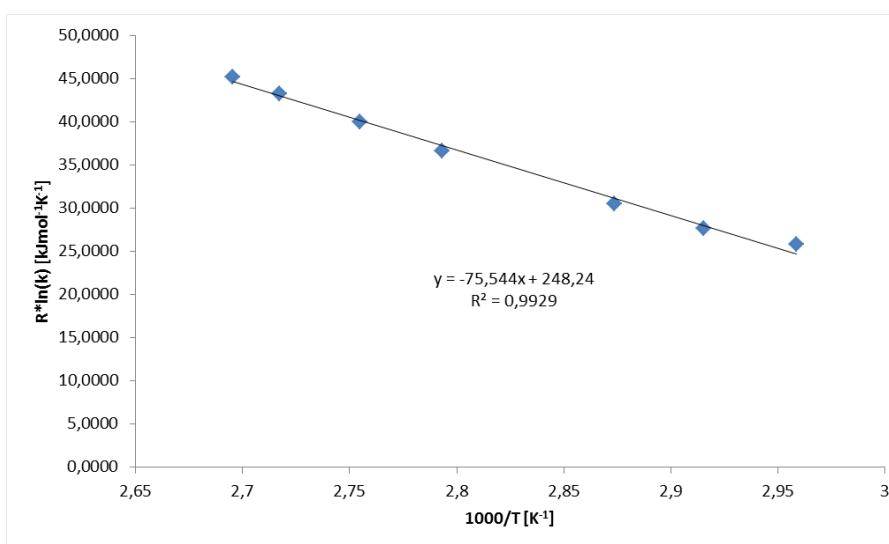


4. Temperature-dependent NMR-rotation barriers

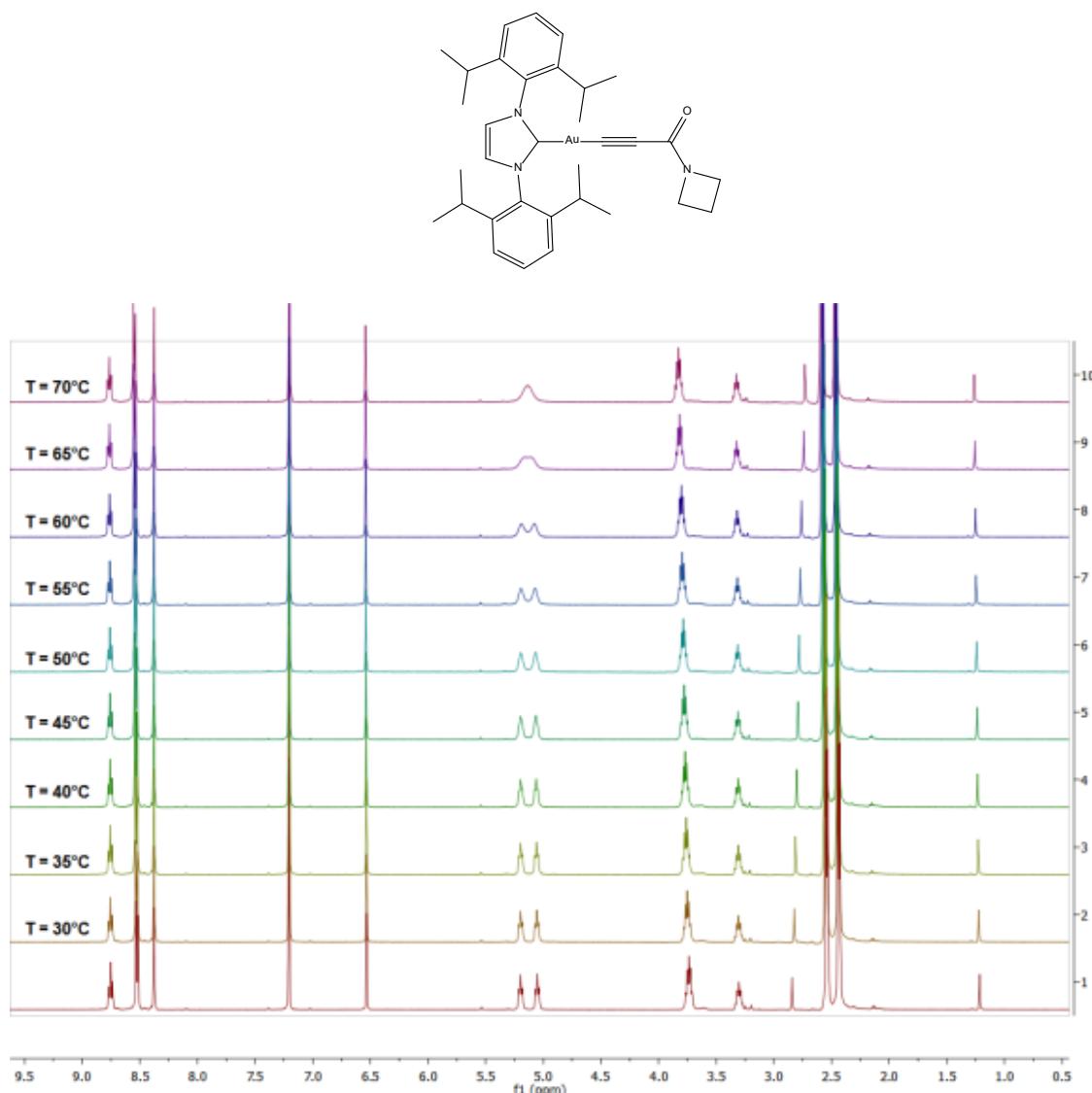
- Rotation barrier of 1-(azetidin-1-yl)prop-2-yn-1-one (**9**)



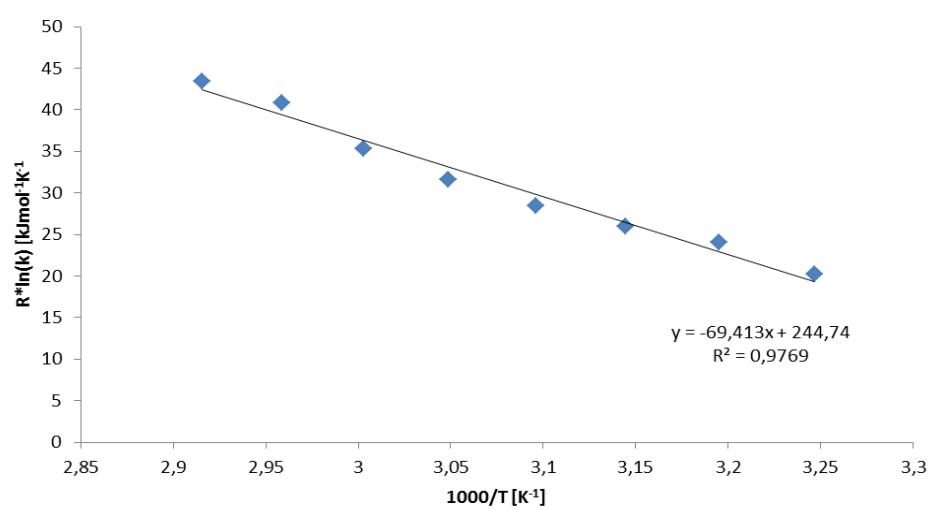
Lineshape fitting was performed with TOPSPIN DNMR module;^[2] Arrhenius-Plot:



- Rotation barrier of Au-acetylide (10)

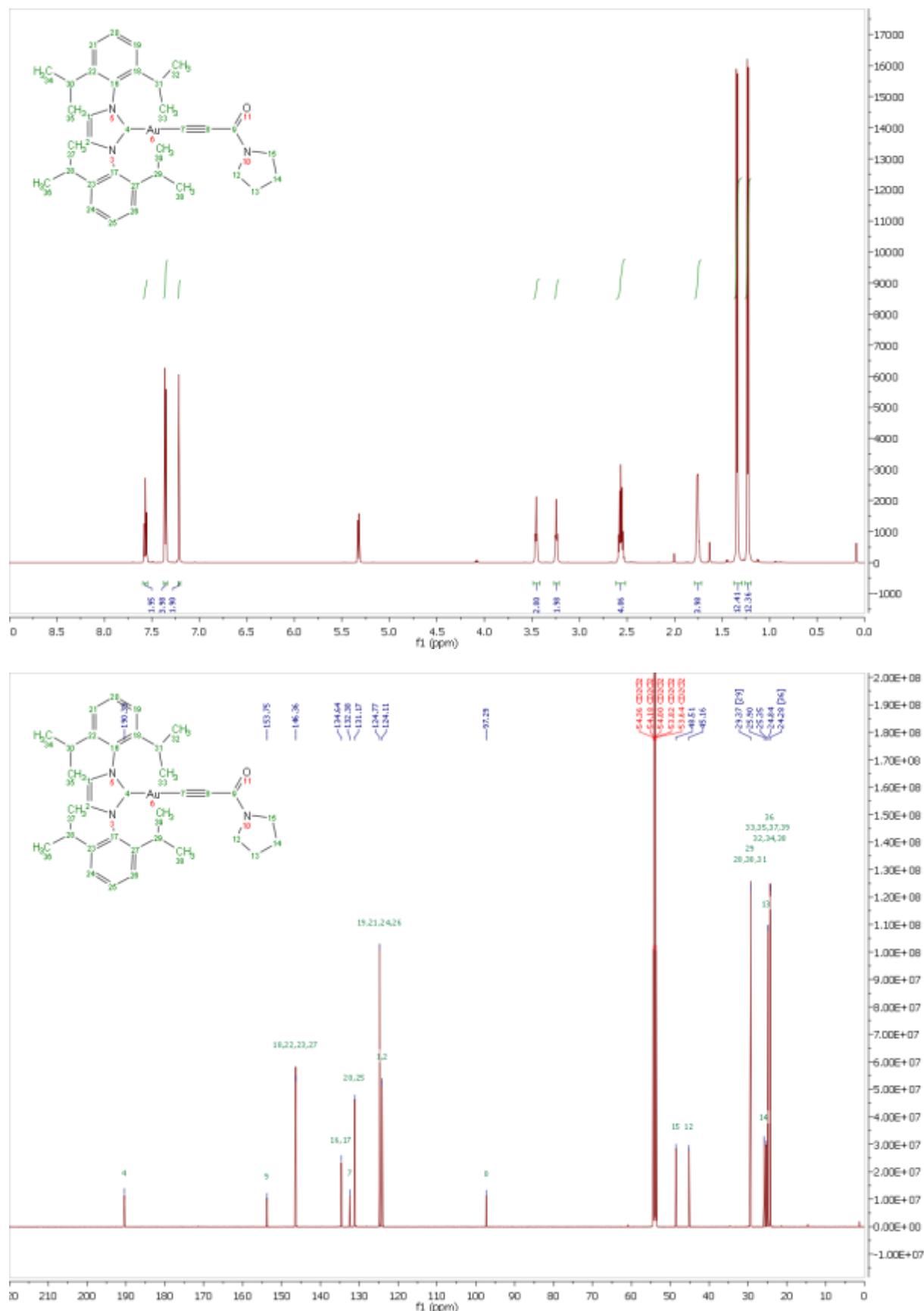


Lineshape fitting was performed with TOPSPIN DNMR module; Arrhenius-Plot:

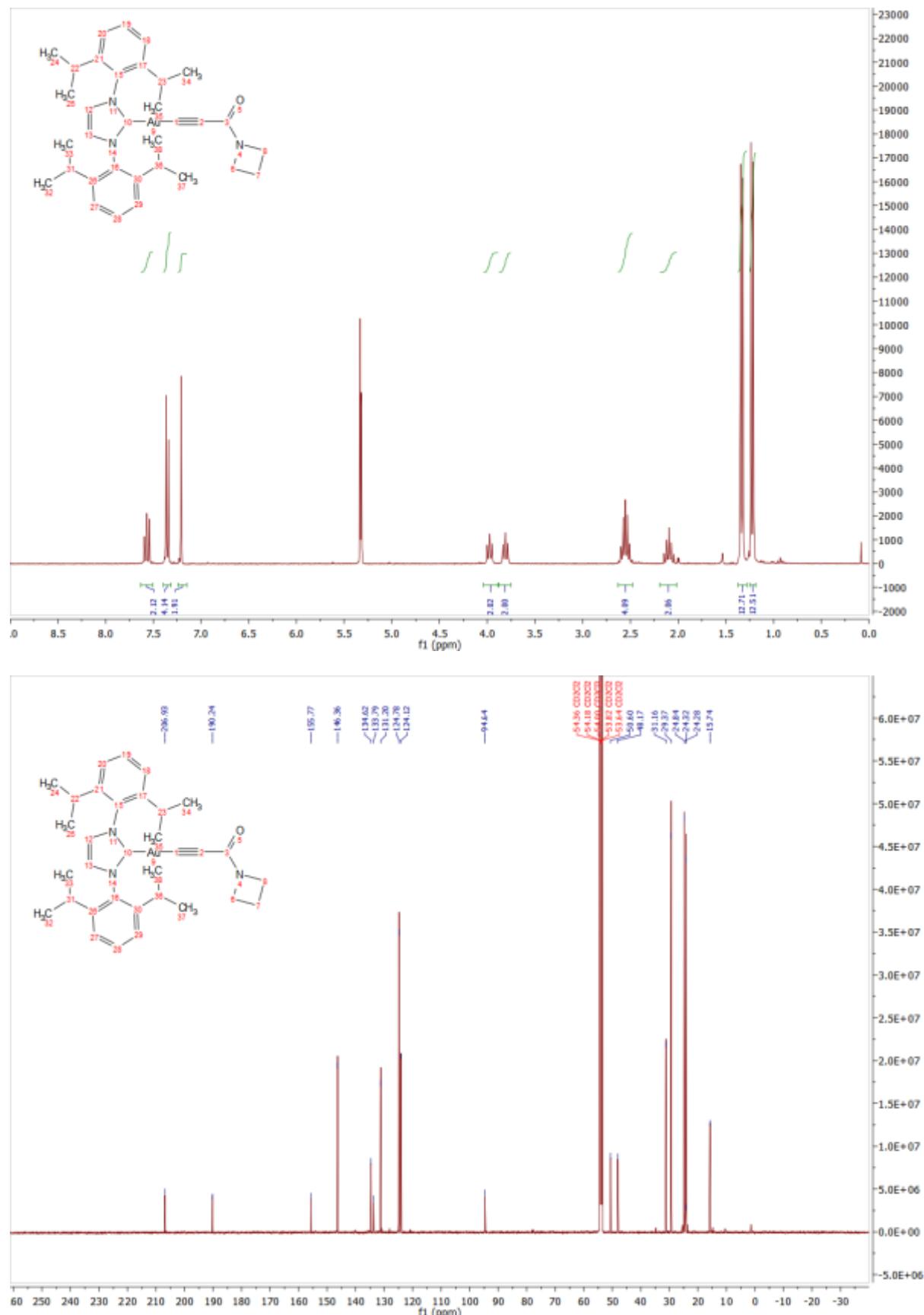


5. NMR Spectra

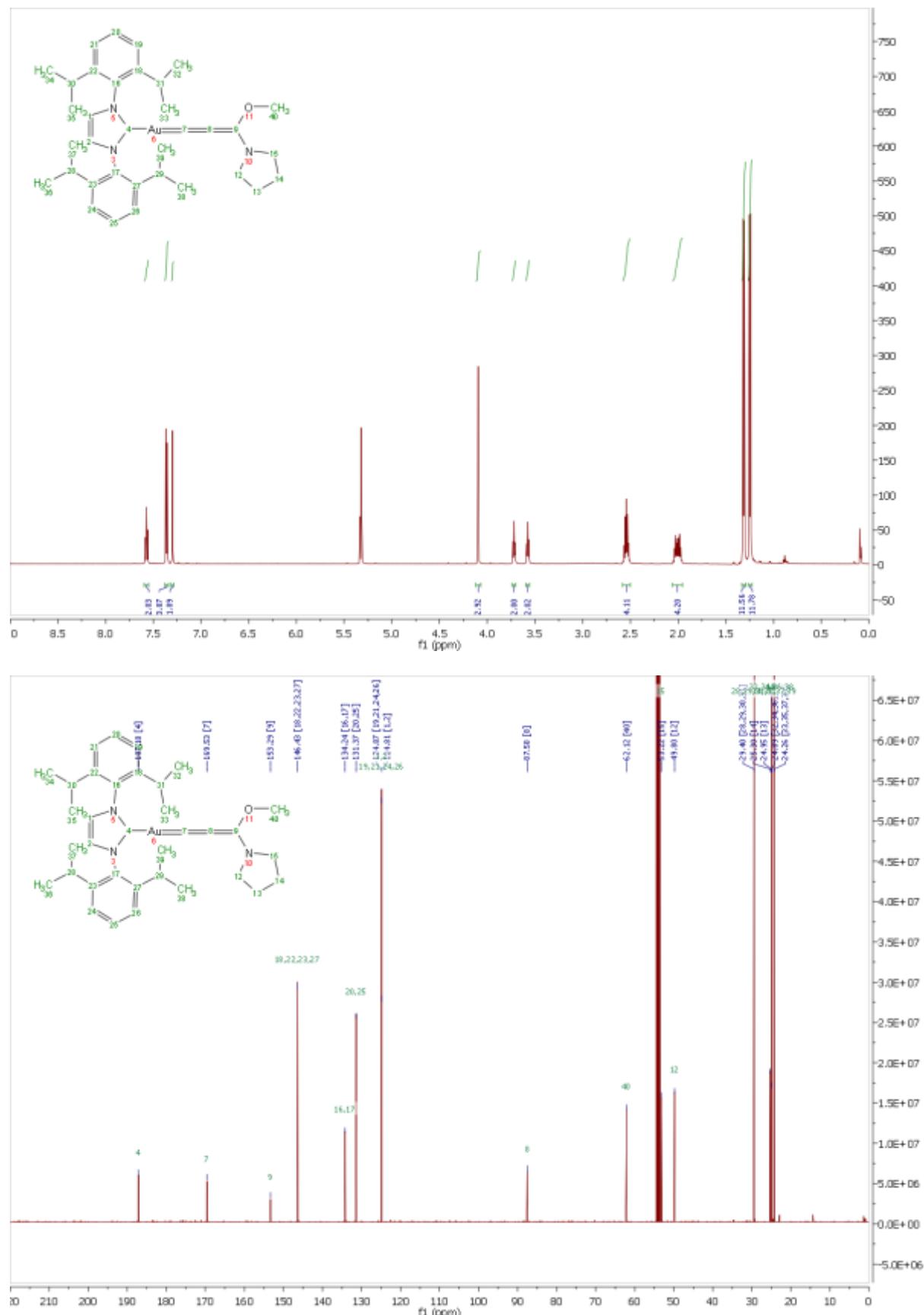
^1H NMR and ^{13}C NMR of compound 4



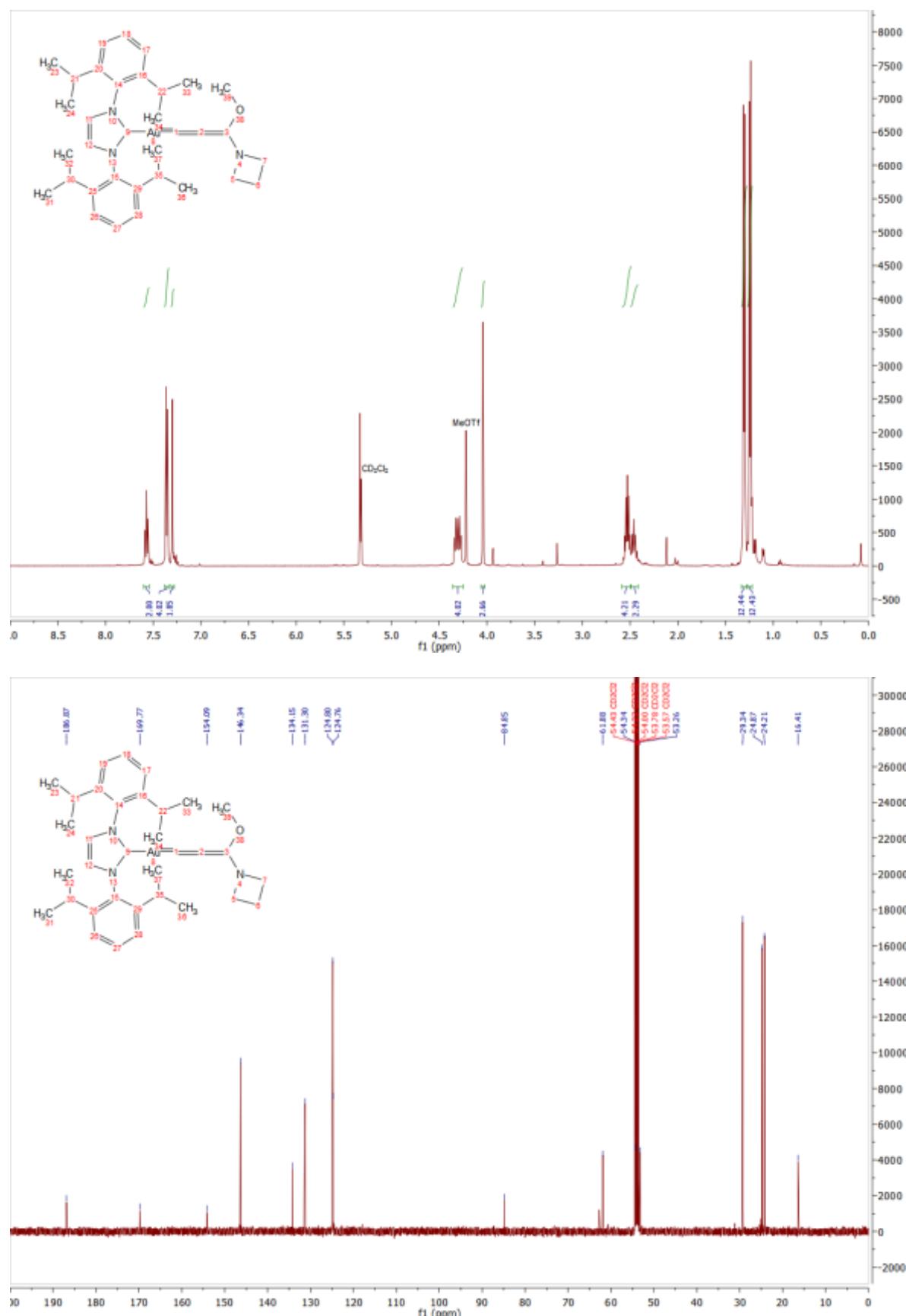
¹H NMR and ¹³C NMR of compound **10**



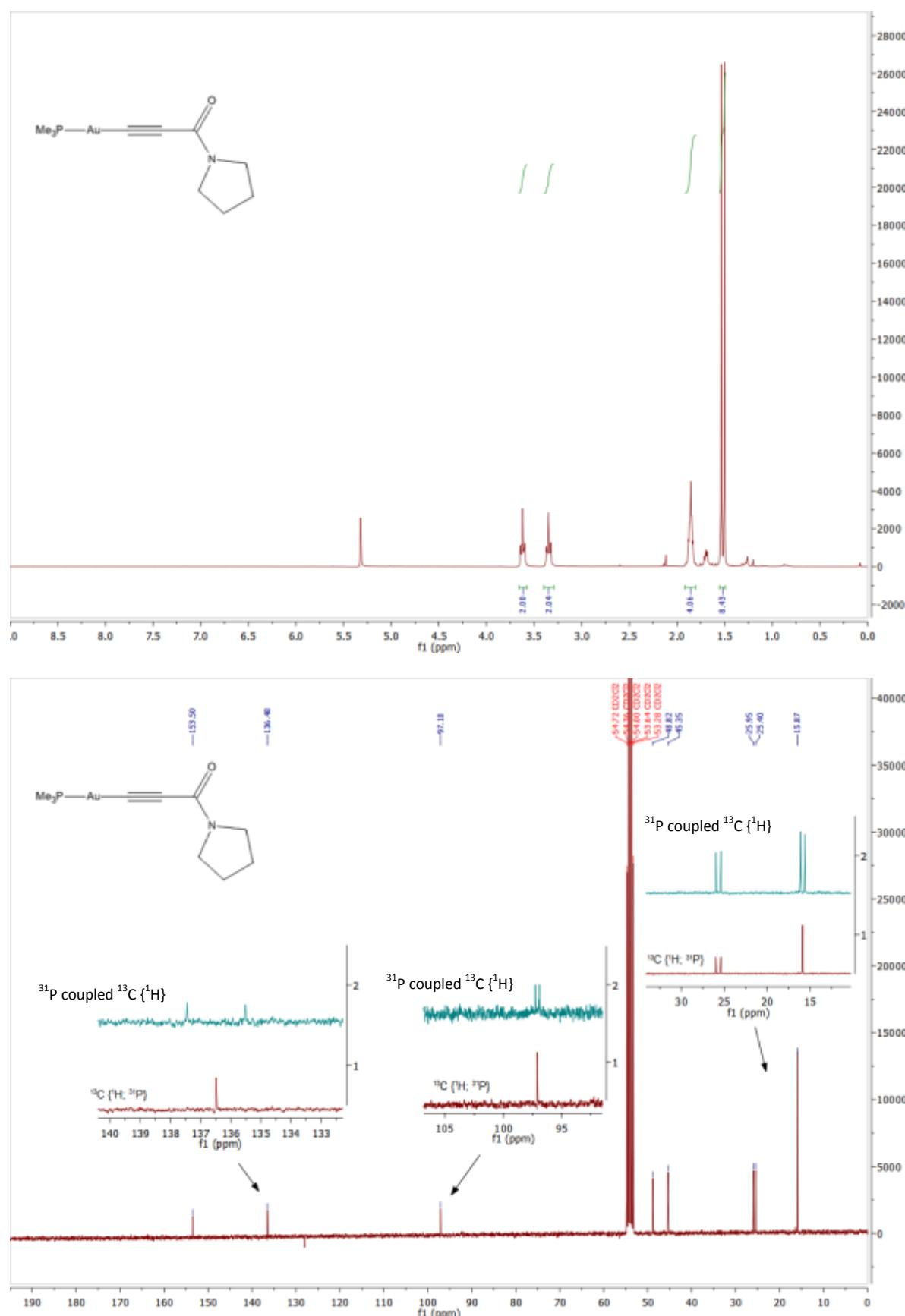
¹H NMR and ¹³C NMR of compound 5



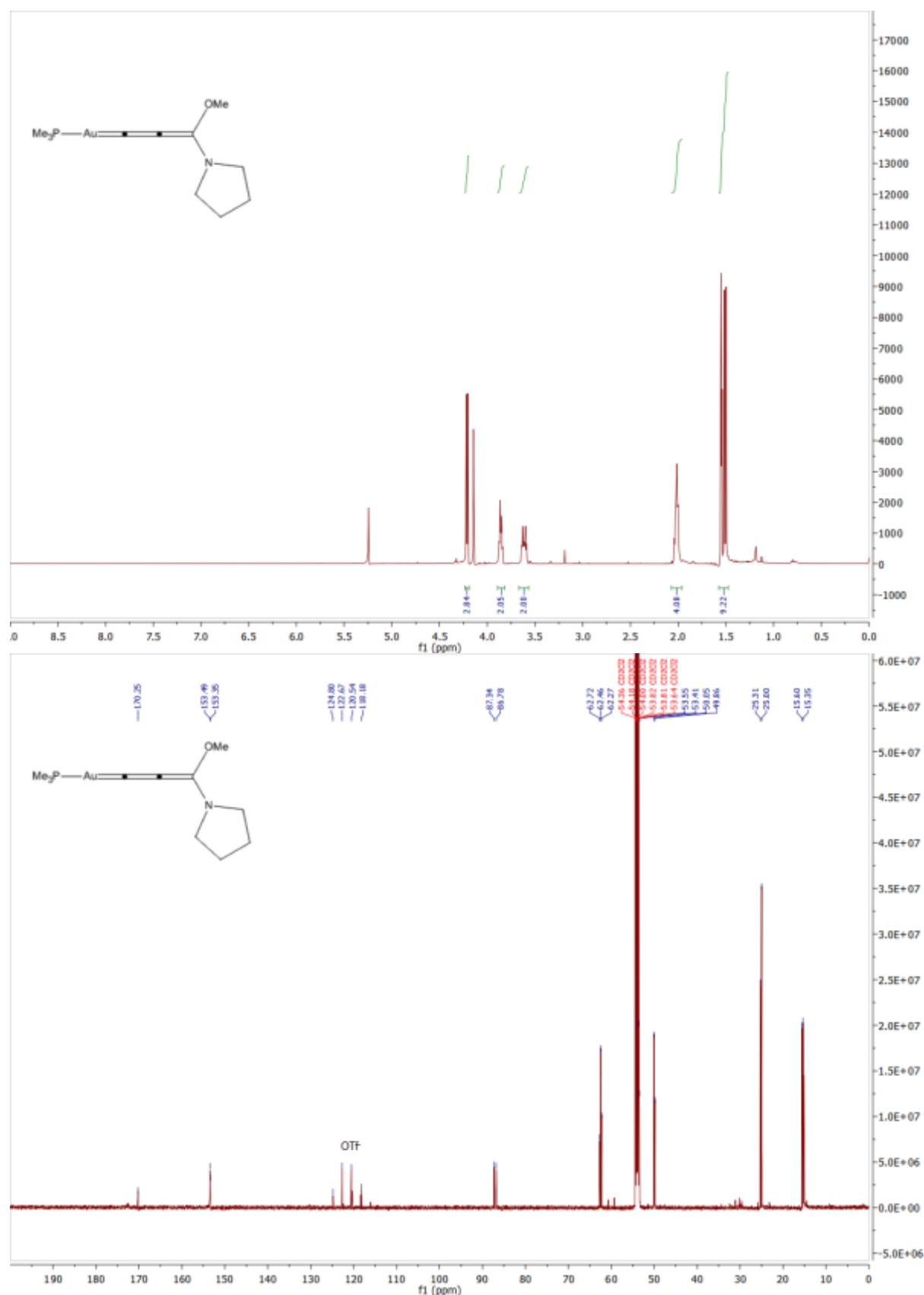
¹H NMR and ¹³C NMR of methylated compound **10**



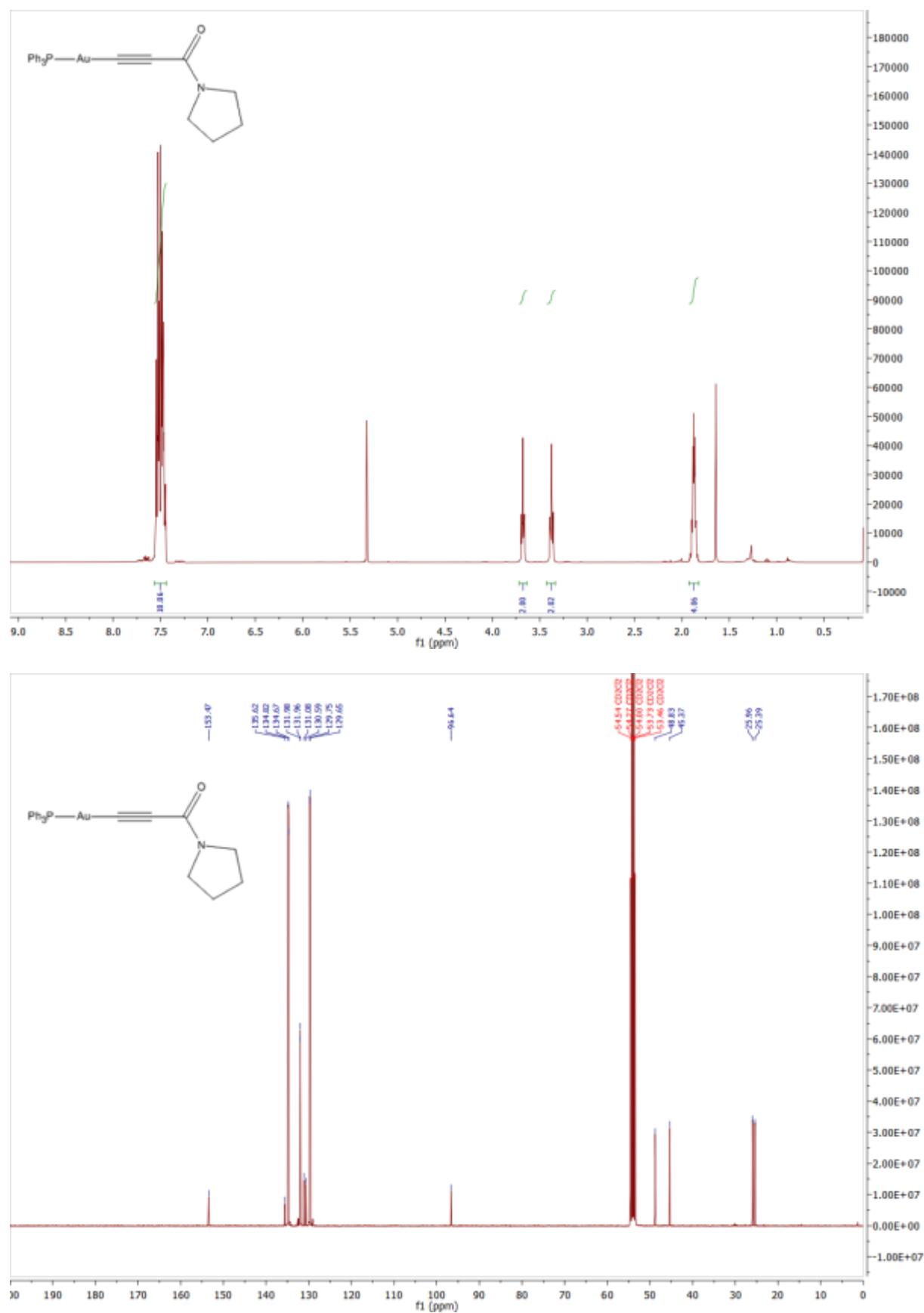
^1H NMR and ^{13}C NMR of compound 6



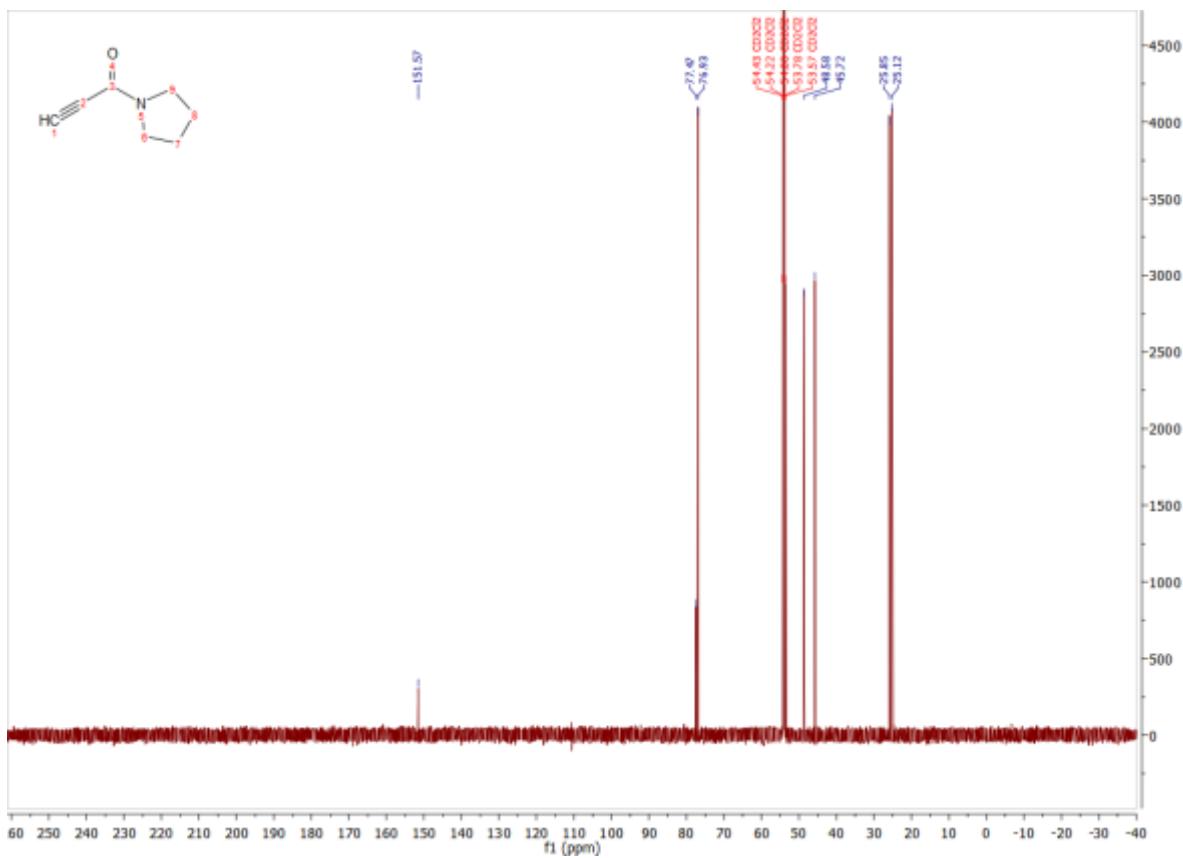
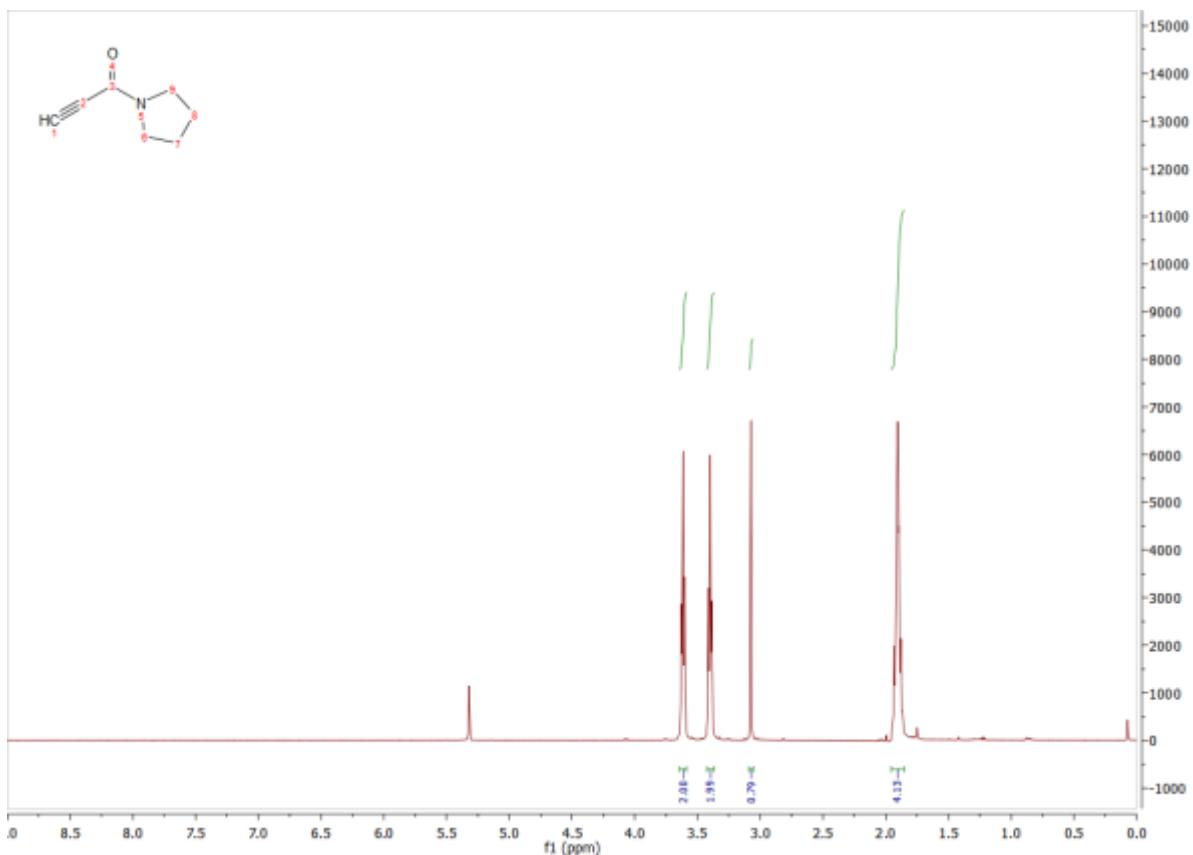
¹H NMR and ¹³C NMR of methylated compound 5



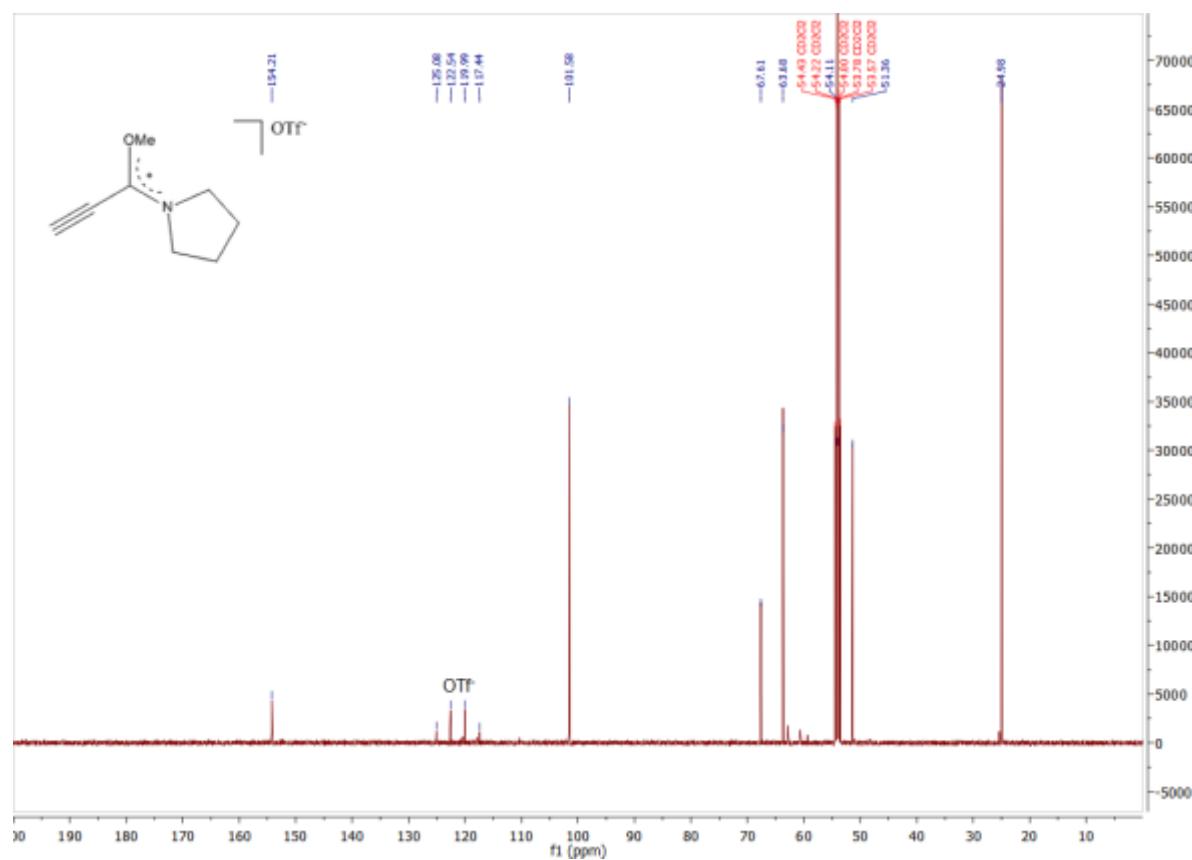
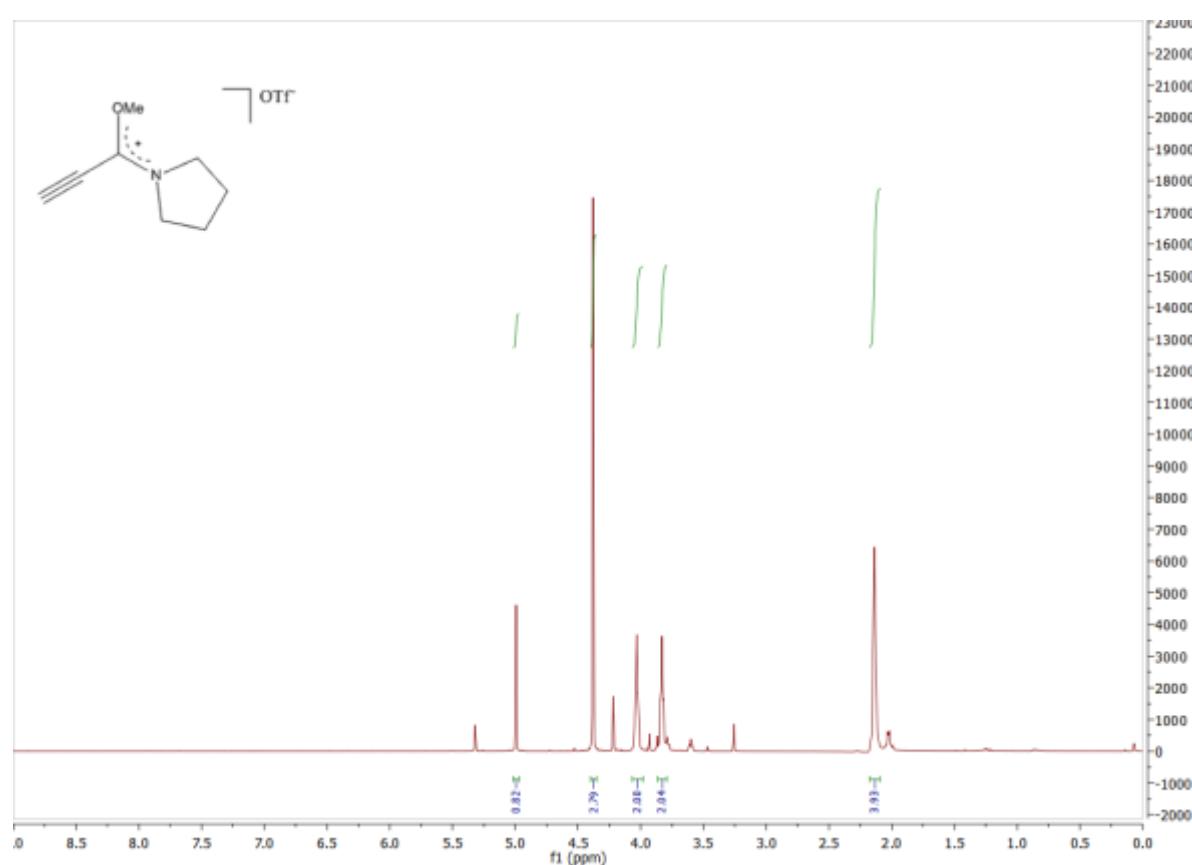
¹H NMR and ¹³C NMR of compound 6



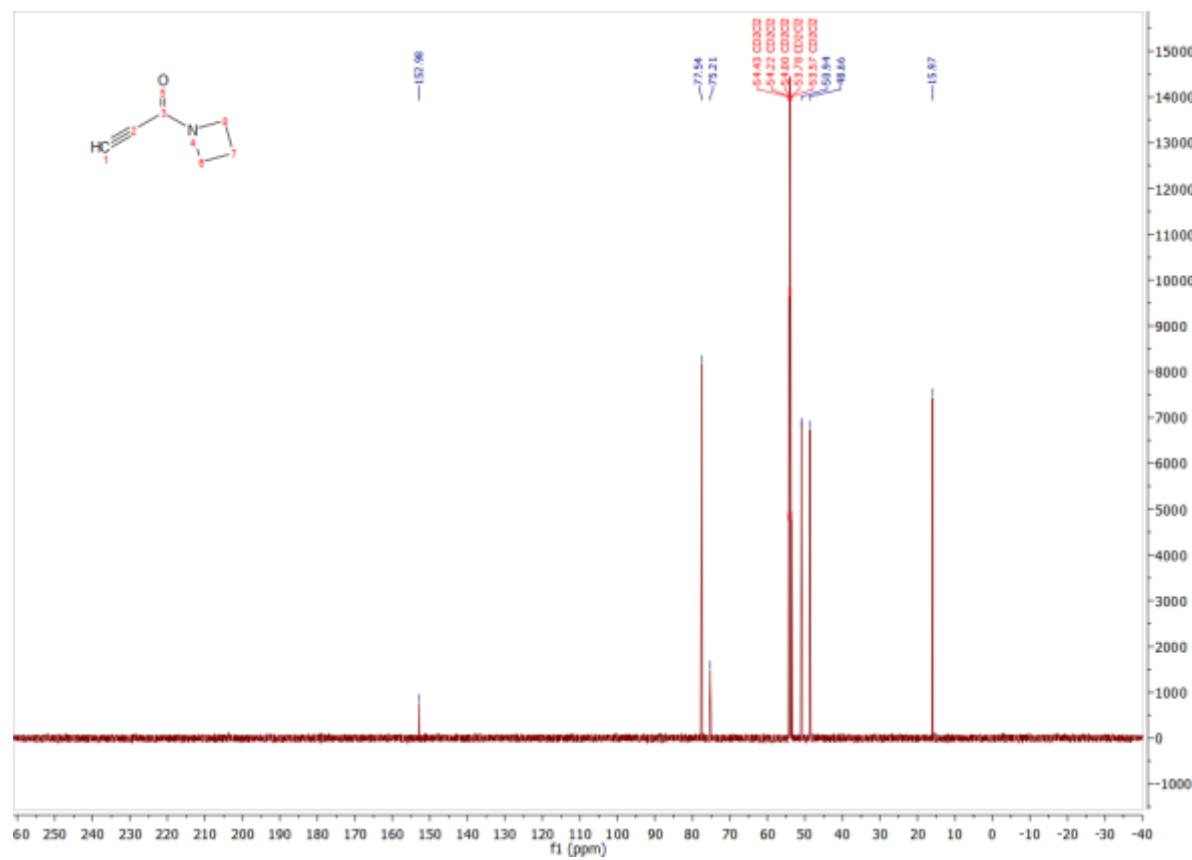
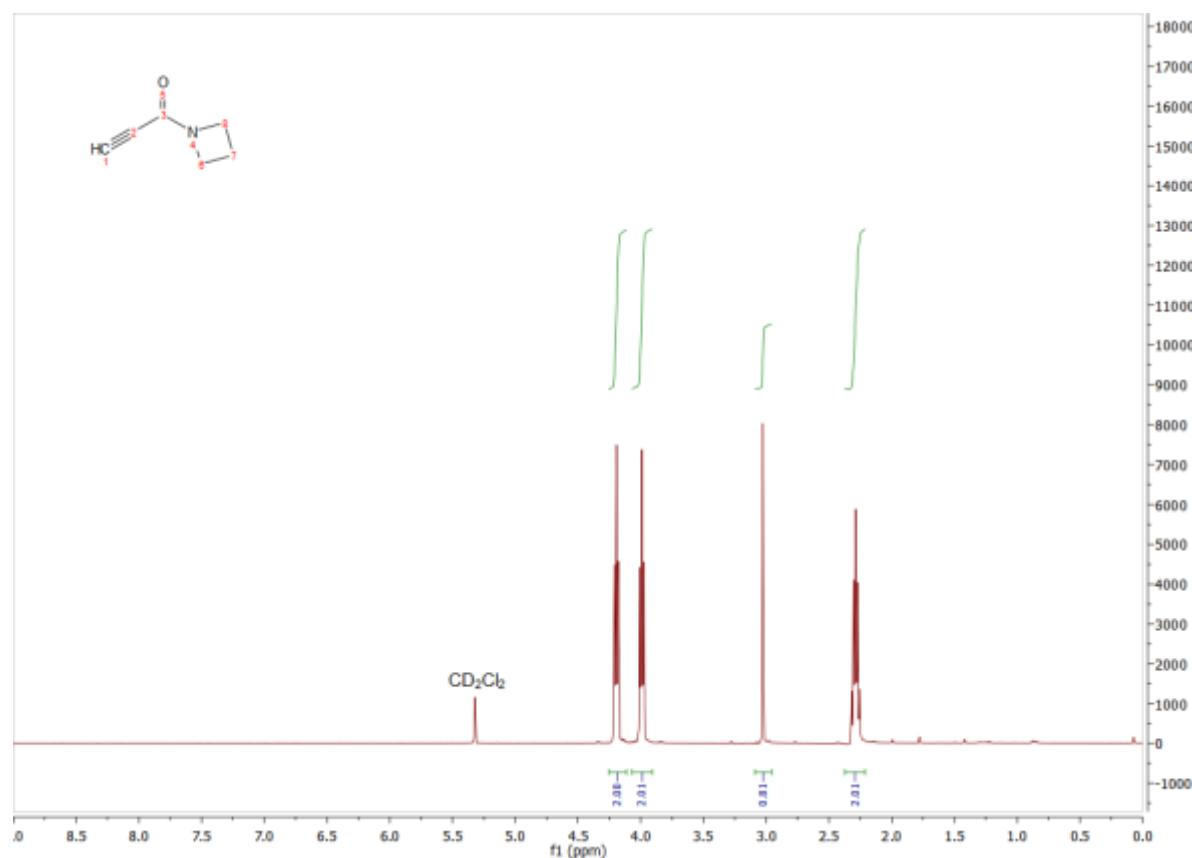
¹H NMR and ¹³C NMR of compound 2



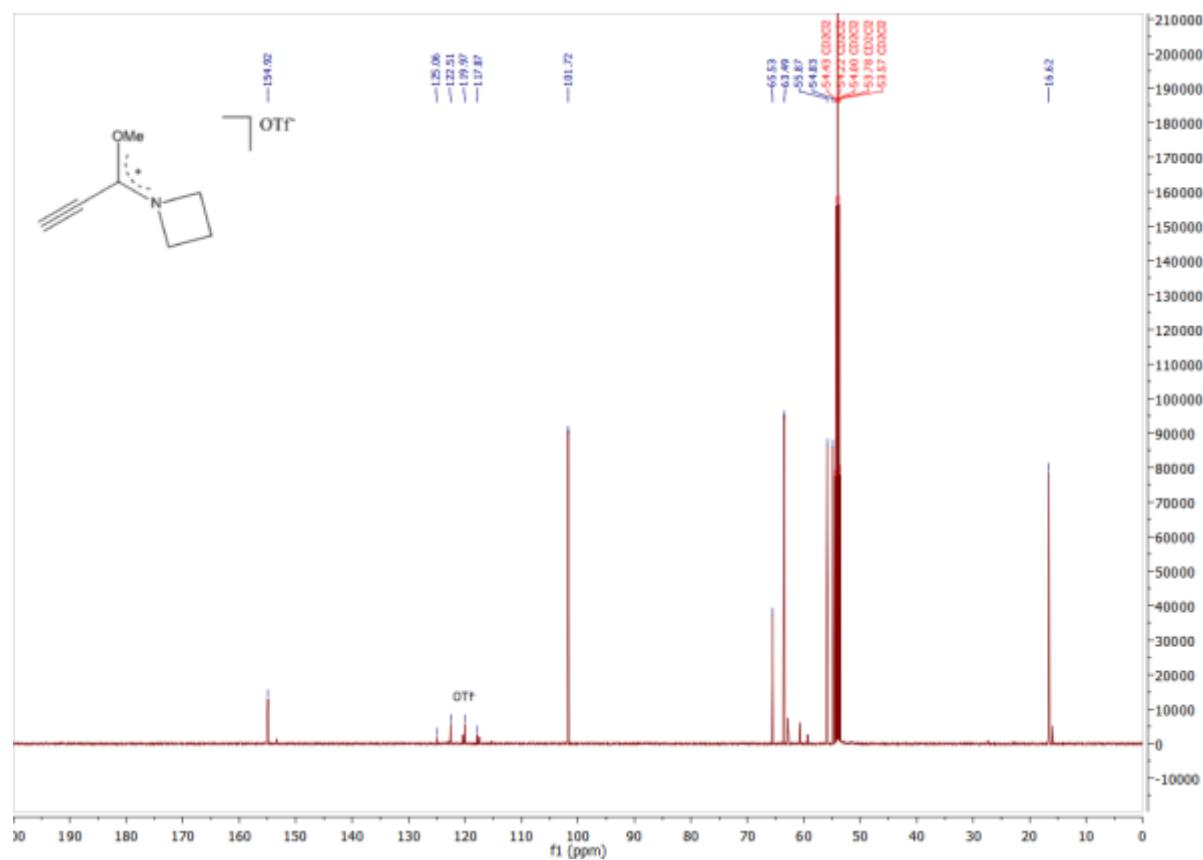
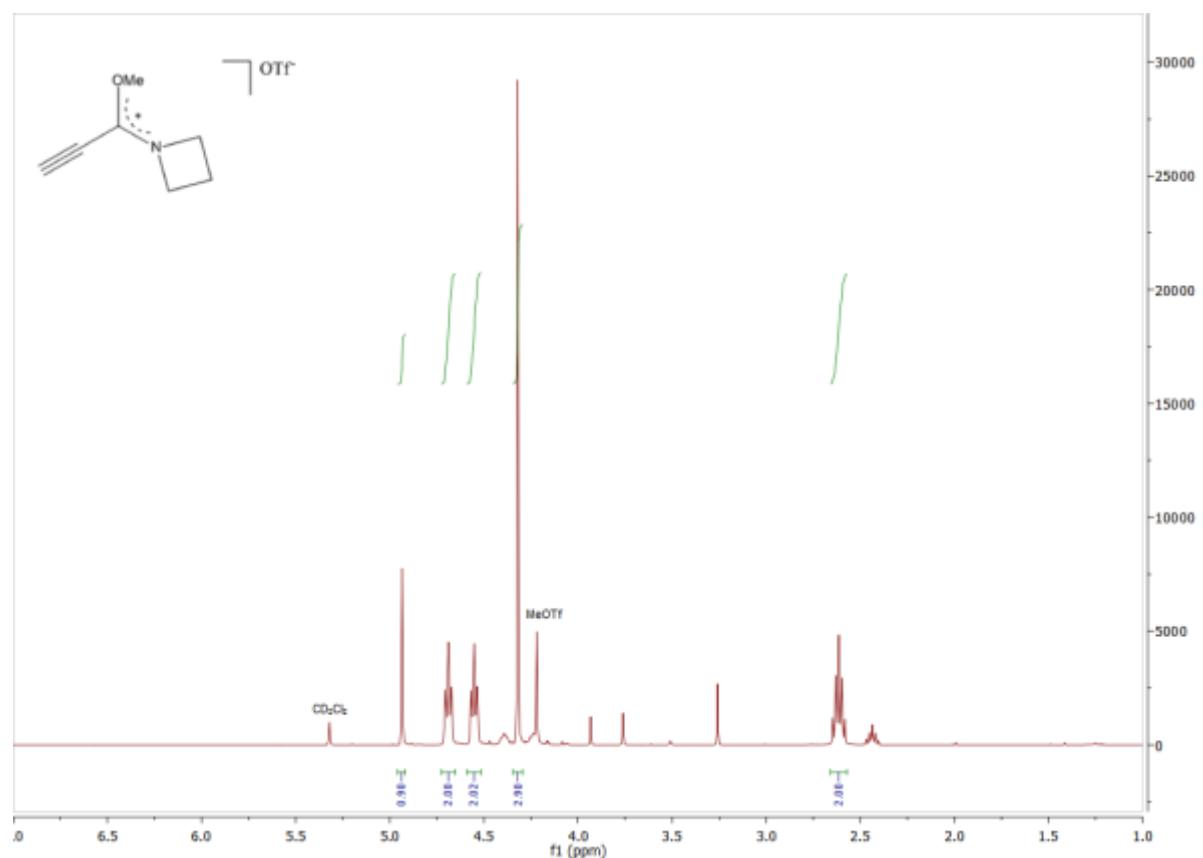
¹H NMR and ¹³C NMR of methylated compound **8**



^1H NMR and ^{13}C NMR of compound 9

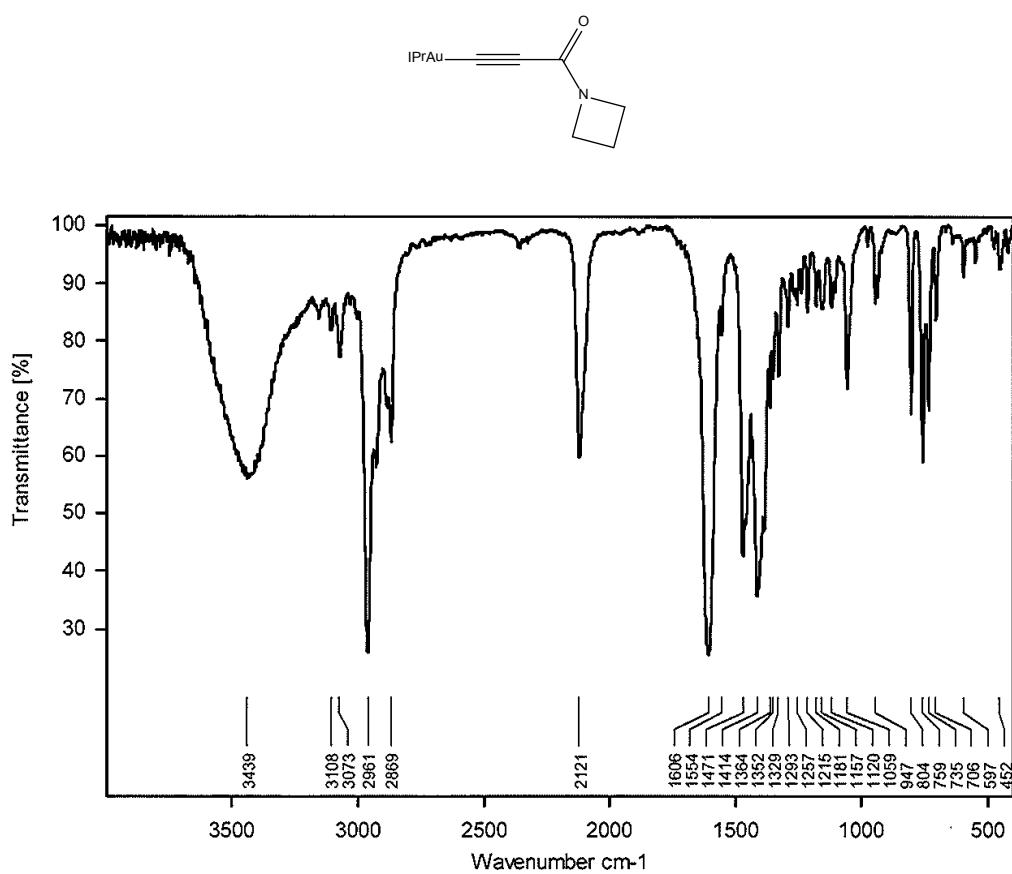


¹H NMR and ¹³C NMR of methylated compound 9

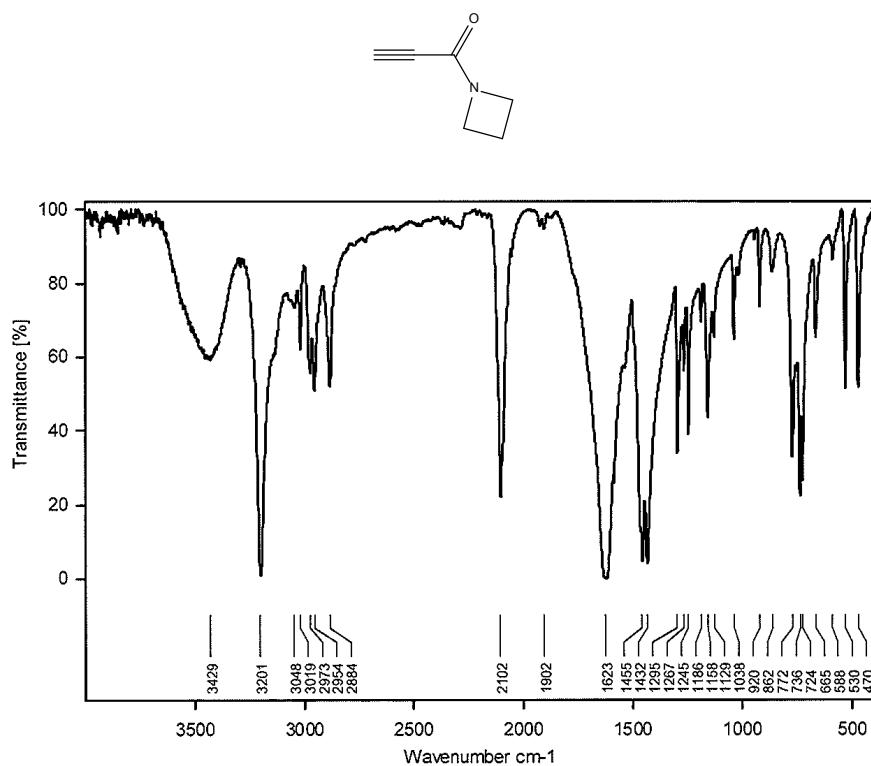


6. IR spectra

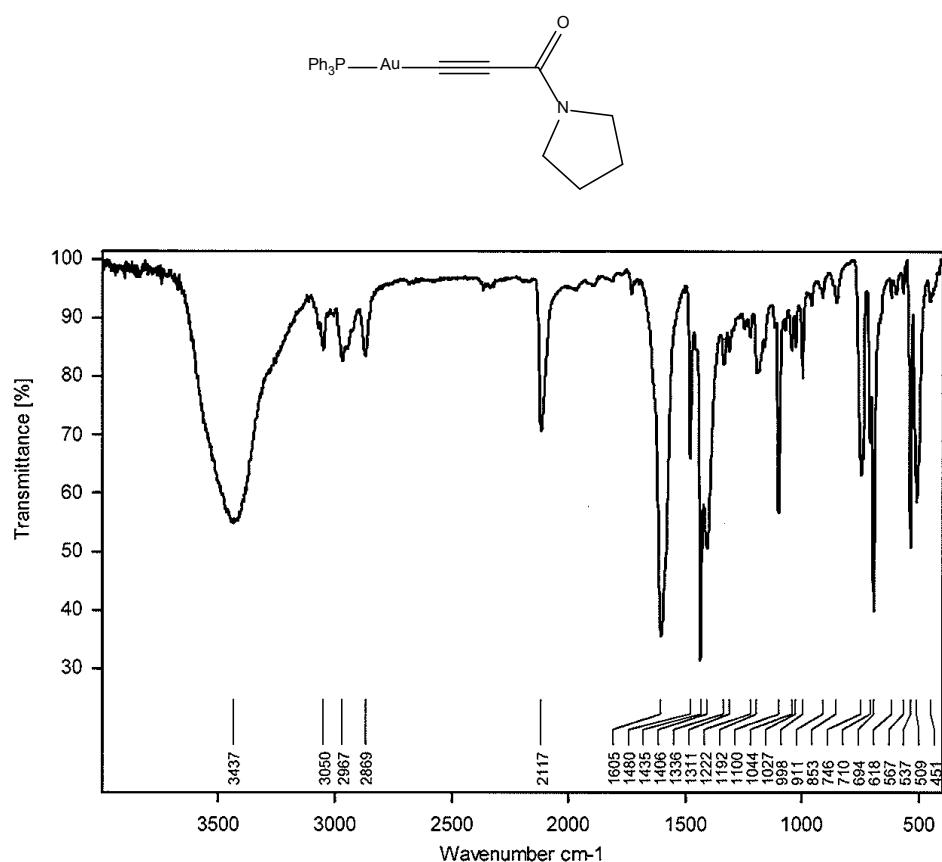
Compound 10



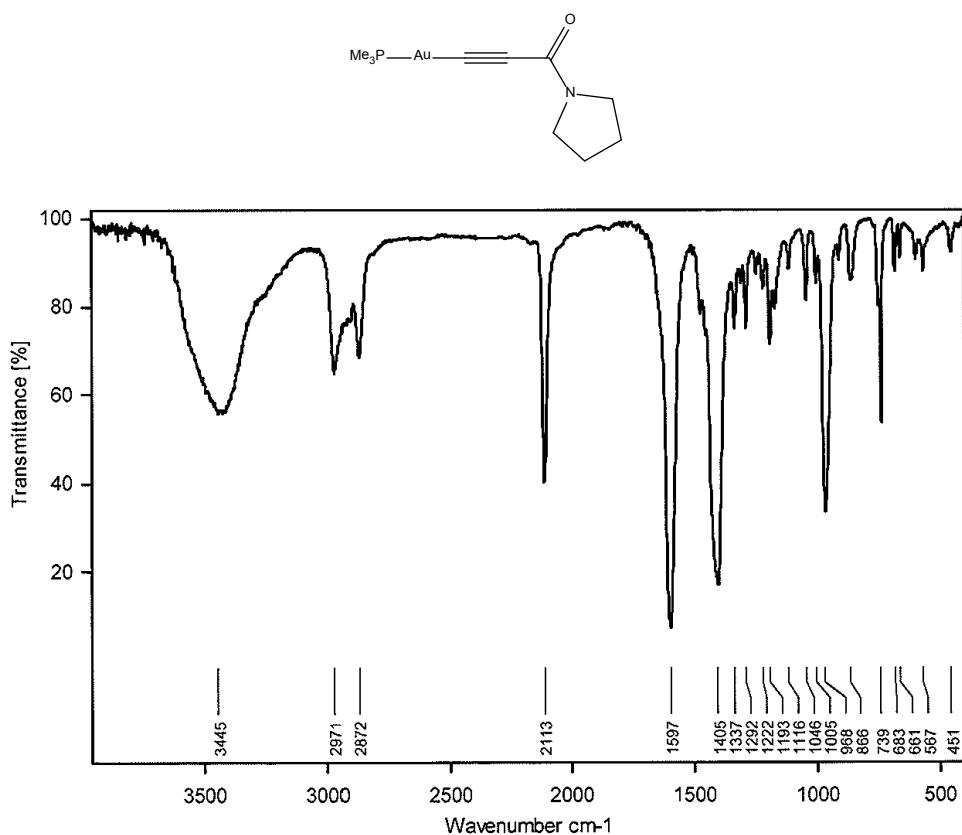
Compound 9



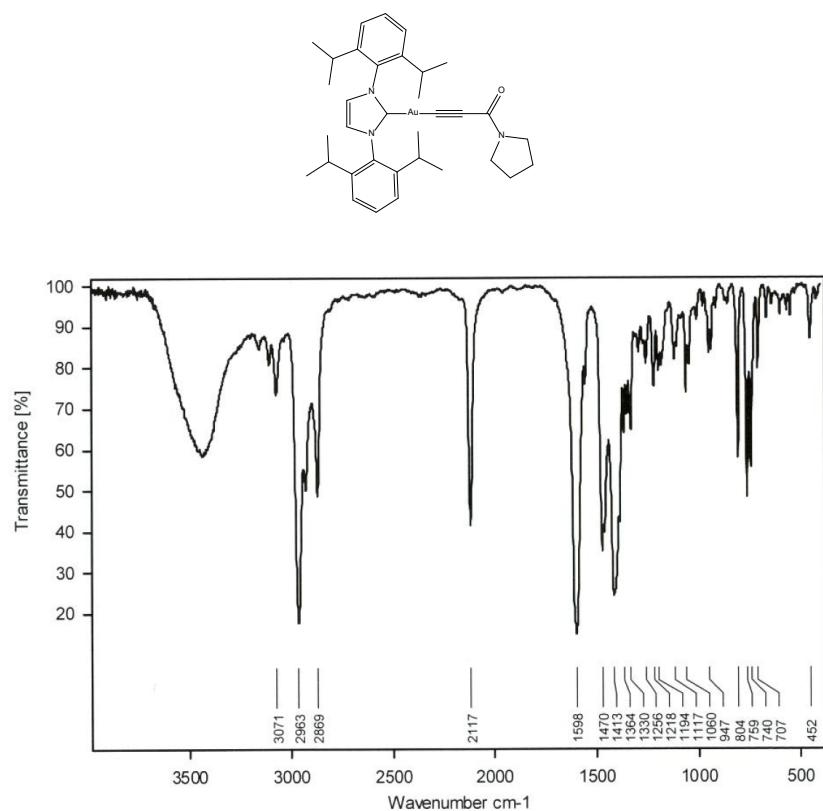
Compound 6



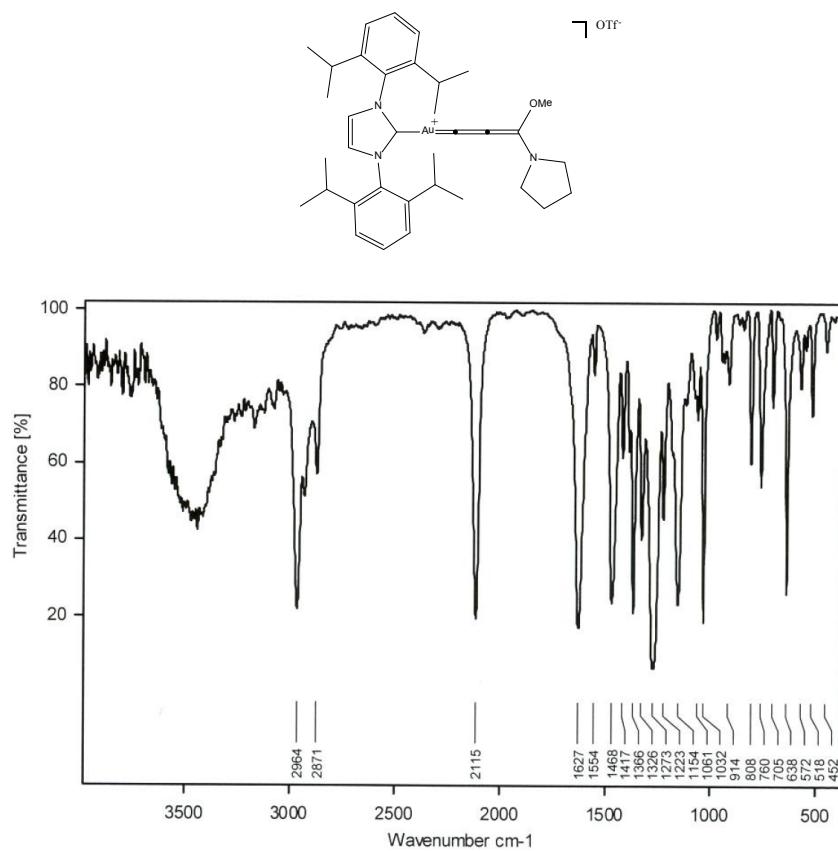
Compound 7



Compound 4

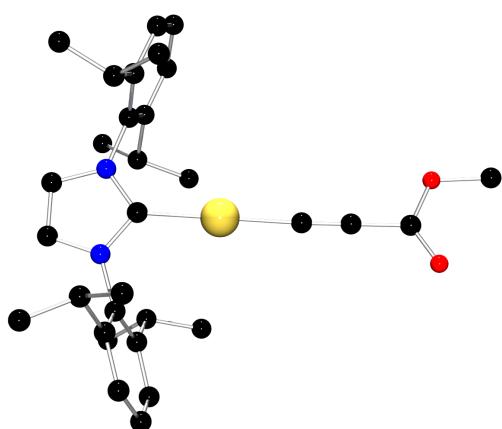


Compound 5

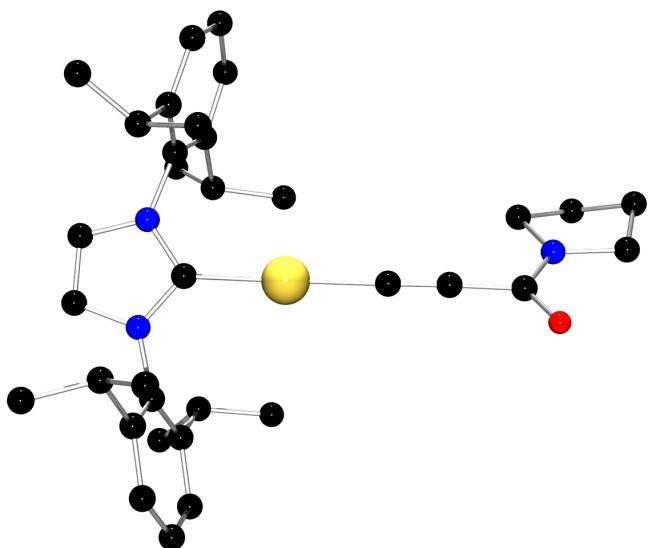


7. X-ray data

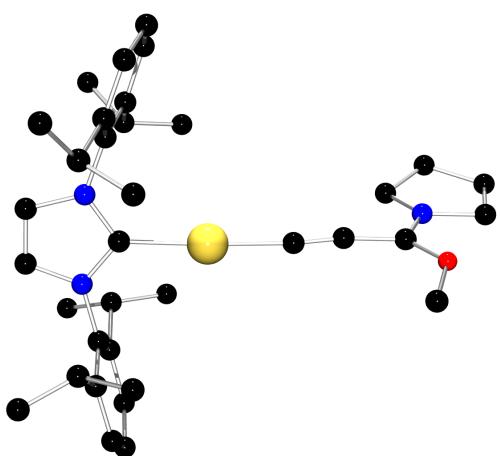
The crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.



Compound **3**; colourless crystal (polyhedron), dimensions $0.16 \times 0.14 \times 0.10 \text{ mm}^3$, crystal system monoclinic, space group $P2_1/n$, $Z=4$, $a=12.2769(4) \text{ \AA}$, $b=12.2829(5) \text{ \AA}$, $c=22.2697(8) \text{ \AA}$, $\alpha=90 \text{ deg}$, $\beta=91.868(2) \text{ deg}$, $\gamma=90 \text{ deg}$, $V=3356.4(2) \text{ \AA}^3$, $\rho=1.491 \text{ g/cm}^3$, $T=200(2) \text{ K}$, $\Theta_{\max}=30.69 \text{ deg}$, radiation Mo Kalpha, $\lambda=0.71073 \text{ \AA}$, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 7.12 and a completeness of 99.7% to a resolution of 0.70 \AA , 75424 reflections measured, 10380 unique ($R(\text{int})=0.0453$), 7907 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS¹ based on the Laue symmetry of the reciprocal space, $\mu=4.57 \text{ mm}^{-1}$, $T_{\min}=0.53$, $T_{\max}=0.66$, structure solved by direct methods and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package⁴, 352 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.01 for observed reflections, final residual values $R1(F)=0.028$, $wR(F^2)=0.063$ for observed reflections, residual electron density -1.04 to 1.08 $e\text{\AA}^{-3}$.



Compound **4**; colourless crystal (plate), dimensions $0.52 \times 0.48 \times 0.06$ mm 3 , crystal system monoclinic, space group P2₁/n, Z=4, $a=10.2357(3)$ Å, $b=12.3159(3)$ Å, $c=28.5345(7)$ Å, alpha=90 deg, beta=96.224(2) deg, gamma=90 deg, $V=3575.91(16)$ Å 3 , rho=1.472 g/cm 3 , T=203(2) K, Theta_{max}=27.56 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 4.90 and a completeness of 99.5% to a resolution of 0.77Å, 41179 reflections measured, 8216 unique ($R(\text{int})=0.0631$), 6846 observed ($I > 2\sigma$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS¹ based on the Laue symmetry of the reciprocal space, mu=4.29mm $^{-1}$, $T_{\min}=0.21$, $T_{\max}=0.78$, structure solved by direct methods and refined against F 2 with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package², 379 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.03 for observed reflections, final residual values R1(F)=0.034, wR(F 2)=0.075 for observed reflections, residual electron density -1.56 to 1.10 eÅ $^{-3}$.

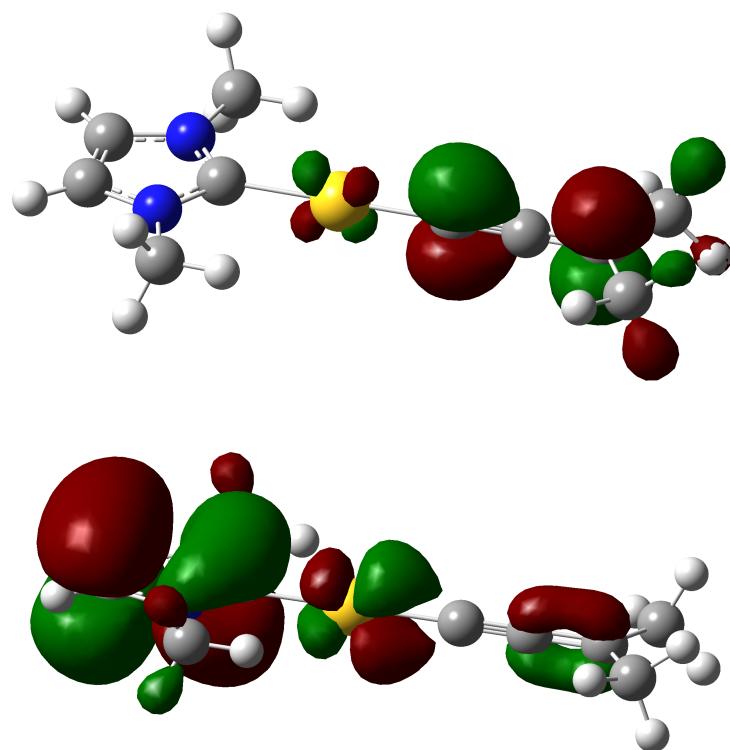


Compound **5**; colourless crystal (needle), dimensions $0.71 \times 0.05 \times 0.05$ mm³, crystal system tetragonal, space group P4₁, Z=16, a=27.6000(18) Å, b=27.6000(18) Å, c=21.2131(13) Å, alpha=90 deg, beta=90 deg, gamma=90 deg, V=16159.3(18) Å³, rho=1.497 g/cm³, T=200(2) K, Theta_{max}= 25.37 deg, radiation Mo Kalpha, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 7.47 and a completeness of 99.9% to a resolution of 0.83Å, 175832 reflections measured, 29623 unique ($R(int)=0.0586$), 21579 observed ($I > 2s(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS³ based on the Laue symmetry of the reciprocal space, mu=3.81mm⁻¹, T_{min}=0.17, T_{max}=0.84, structure solved by direct methods and refined against F² with a Full-matrix least-squares algorithm using the SHELXTL (Version 2008/4) software package⁴, 1775 parameters refined, hydrogen atoms were treated using appropriate riding models, Flack absolute structure parameter 0.098(8), goodness of fit 1.02 for observed reflections, final residual values R1(F)=0.056, wR(F²)=0.131 for observed reflections, residual electron density -0.60 to 1.62 eÅ⁻³.

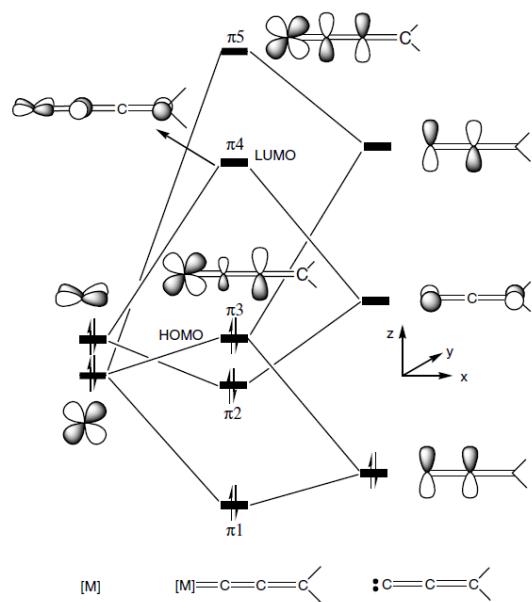
8. Computational methods

All geometry optimisations were performed by employing the Gaussian09 program package.^[5] The theoretical approach is based on density functional theory (DFT),^[6,7] in combination with the hybrid B3LYP functional,^[8] the M06 functional^[9] and the TPSS functional^[10] together with a relativistic pseudopotential for Au.^[11] The pseudopotential basis set and the all-electron basis sets for the other light elements (H, C, S, P) were of cc-pVTZ quality. Geometries were fully optimized without symmetry restrictions and minima on the energy surface uniquely characterized by occurrence of none imaginary frequency. Gibbs free energies are calculated for standard temperature and pressure (298.15 K, 1 atm) and are corrected in respect to zero point energies which are calculated based on gas phase frequency calculations. Natural charges were calculated utilising the NBO5 program.^[12]

9. HOMO and LUMO visualisation



Calculated LUMO (top) and HOMO (down) of $\text{Au}^{\text{NHC/II}}$ (isocontour value of 0.05 for LUMO 0.02 for HOMO)



Orbital diagram for allenylidene-complexes from Ref.¹³

10. References

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- [3] Program SADABS 2008/1 for absorption correction; G. M. Sheldrick, Bruker Analytical X-ray Division, Madison, Wisconsin 2008.
- [4] Software package SHELXTL 2008/4 for structure solution and refinement; Sheldrick, G.M. (2008). *Acta Cryst. A*64, 112-122.
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