Supporting Information

Phosphinines *versus* Mesoionic Carbenes: A Comparison of Structurally Related Ligands in Au(I)-Catalysis

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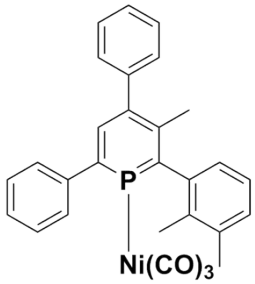
Synthesis of [(*rac*-2)Ni(CO)$_3$]



Caution: [Ni(CO)$_4$] is highly toxic and potentially carcinogenic. It can be absorbed through the skin or inhaled due to its high volatility. Vapors of [Ni(CO)$_4$] can autoignite. All manipulations must be done with extreme care in a well-ventilated fumehood.

Under vacuum 0.6 mL of THF were condensed in a Young NMR tube containing *rac*-**2** (6 mg, 0.0164 mmol). Afterwards, roughly 2 equivalents of [Ni(CO)$_4$] were condensed in the same tube using a condensation line. The tube was slowly heated up to room temperature and the reaction progress was monitored by $^{31}P\{^{1}H\}$ NMR, degassing the tube until full conversion. The volatiles were removed *in vacuo*, yielding the product quantitatively. IR spectra were measured in DCM.

IR (DCM): 2077 (m), 2007.5 (bs) cm^{-1}.

NMR spectroscopy

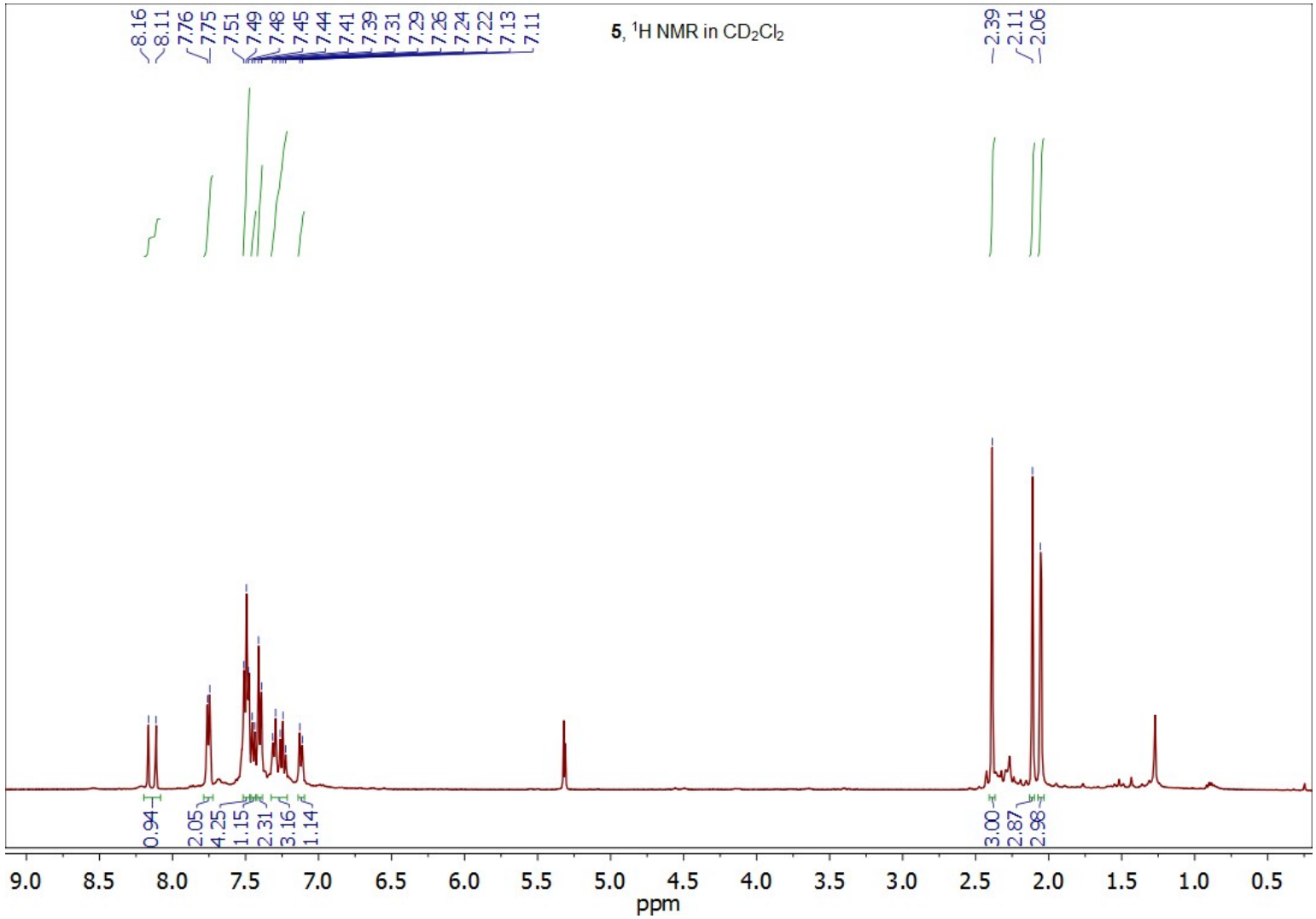


Figure S1: ^{1}H NMR spectra of Complex **5** in CD_2Cl_2

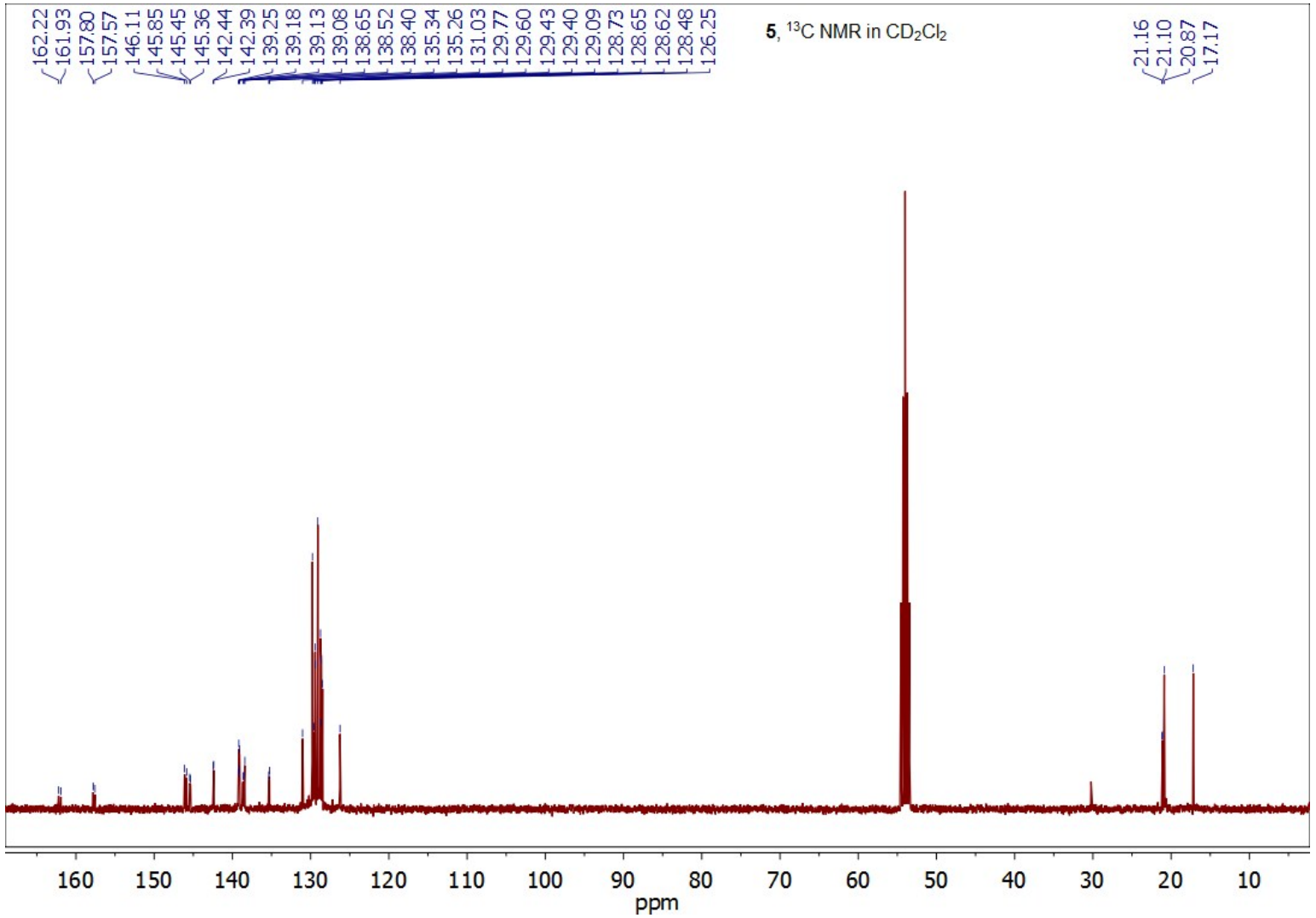


Figure S2: $^{13}C\{^{1}H\}$ NMR spectra of Complex **5** in CD_2Cl_2

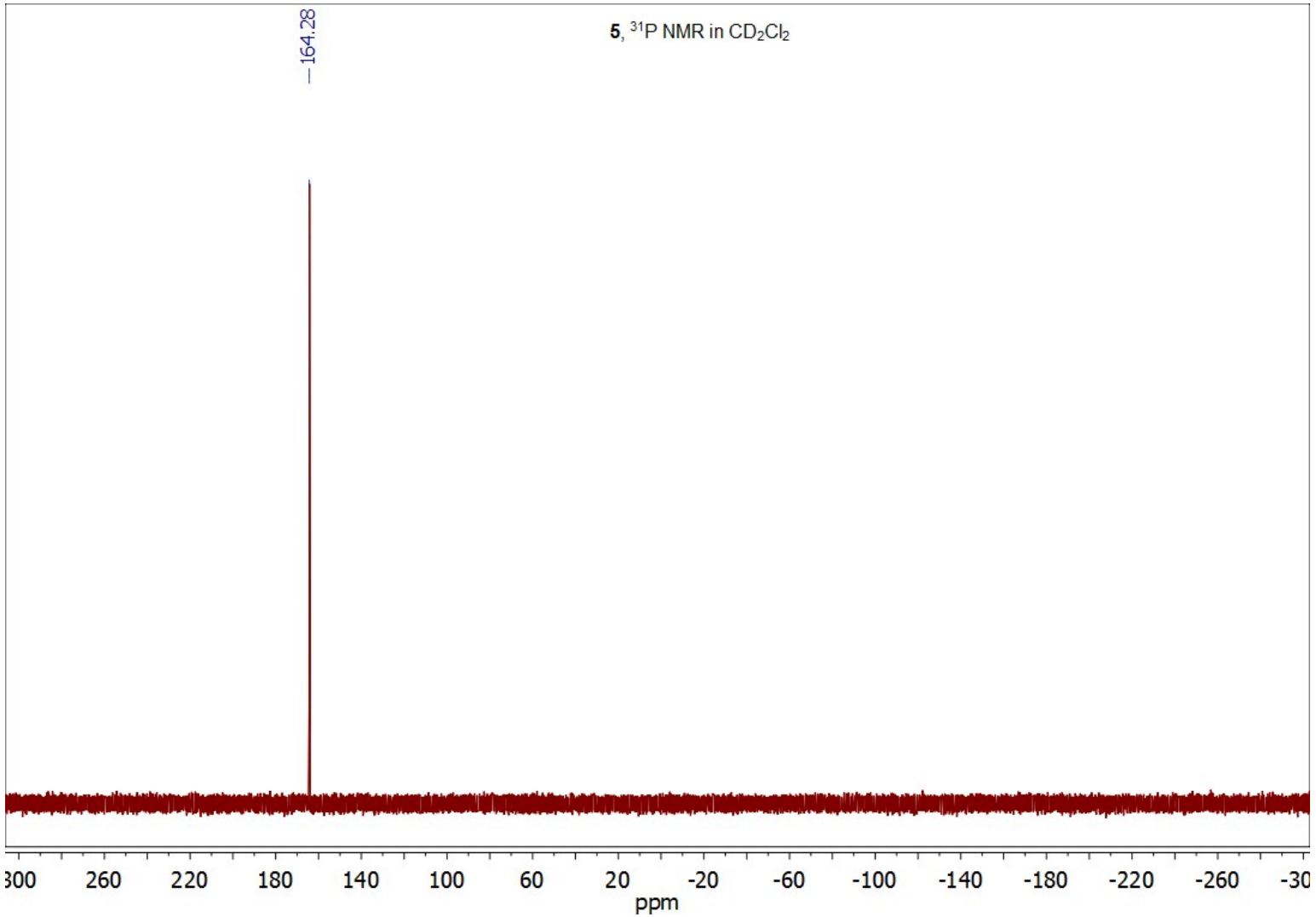


Figure S3: $^{31}P\{^{1}H\}$ NMR spectra of Complex **5** in CD_2Cl_2

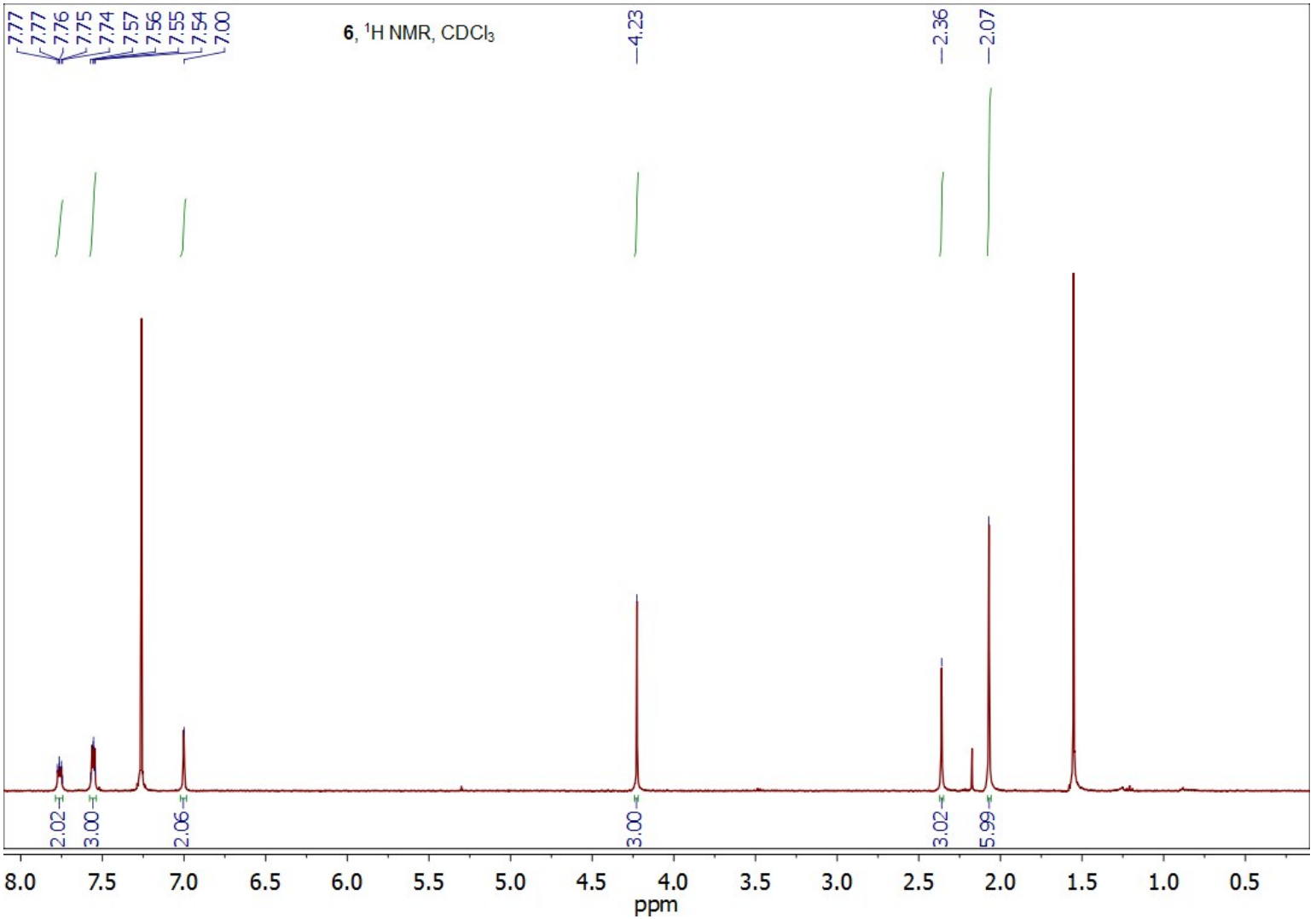


Figure S4: ^{1}H NMR spectra of Complex **6** in $CDCl_3$

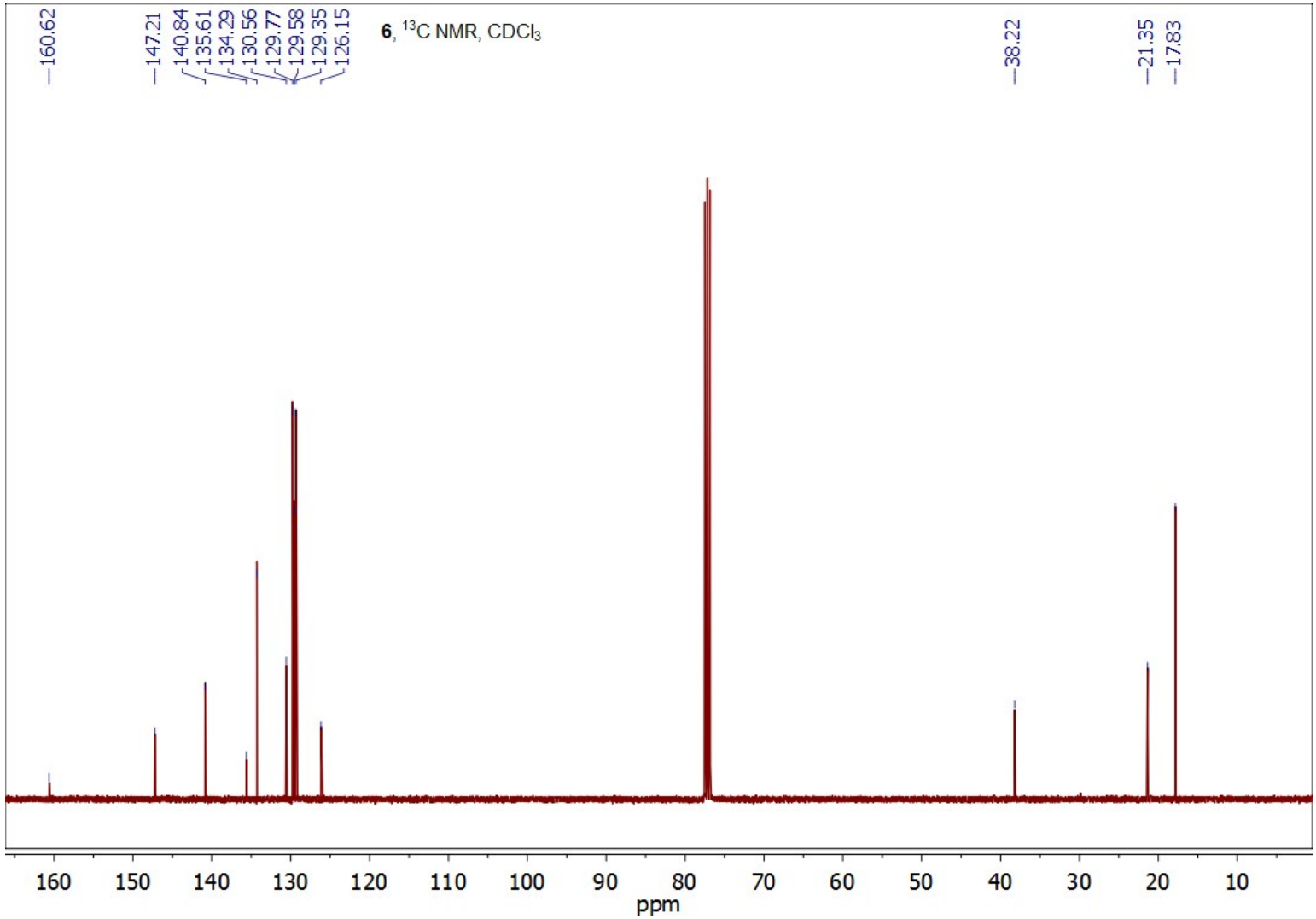


Figure S5: $^{13}C\{^{1}H\}$ NMR spectra of Complex **6** in $CDCl_3$

X-ray Data

Table S1: Parameters for the Data Collection[a] and Structure Refinement for Complex **6**[1]

	6
Chemical formular	$C_{18}H_{19}AuClN_3$
M_r	509,78
Crystal system, space group	monoclinic, $P2_1/c$
Temperature (K)	140(2)
a, b, c (Å)	20.988(5), 6.425(5),13.166(5)
α, β, γ (°)	90, 100.804(5), 90
V (Å^3)	1743.9(16)
Z	4
Density (g/cm^3)	1.942
F000	976
Radiation type	Mo $K\alpha$
μ (mm^{-1})	8.591
Crystal size (mm)	0.48 x 0.36 x 0.34
meas. refl.	11174
indep. ref.	3985
obsvd. [I > 2σ(I)] refl.	2647
R_{int}	0.0621
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0370, 0.1095, 0.0836
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.687, –1.405
CCDC	1015504

[a] Collected on a Bruker Smart AXS duo using Mo $K\alpha$ radiation (λ = 0.71069 Å) at 140(2) K.

Table S2: Selected measured bond length in Å of complexes **6**

	6
C1 - C2	1.394(11)
C1 - N3	1.384(10)
C2 - N1	1.360(10)
N1 - N2	1.316(9)
N2 - N3	1.342(8)
C2 - C5	1.478(11)
N3 - C20	1.439(10)
N1 - C50	1.462(10)
Au1 - C1	1.973(1)
Au1 - Cl1	2.281(2)

Table S3: Selected measured bond angles in ° of complex **6**

	6
C1 - C2 - N1	107.1(7)
C2 - C1 - N3	102.0(7)
C1 - N3 - N2	114.5(7)
C2 - N1 - N2	113.2(6)
N1 - N2 - N3	103.2(6)
C1 - Au1 - Cl1	176.7(2)

Table S4: Selected bond angles[b] in ° of complex **6**

	6
Trz - Ar(over C2)	51.7(2)
Trz - Ar(over N3)	86.5(2)

[b]Measured with the program Diamond 3.1

Calculation of the buried volume

The buried volume $\%V_{bur}$ was calculated according to literature.[2] The recommended parameters have been used: 3.50 Å was selected as the value for the sphere radius, both 2.00 and 2.28 Å were considered as distances for the metal–ligand bond, hydrogen atoms were omitted, mesh spacing was set to 0.10 and scaled Bondi radii were used.

The data was obtained starting from the crystal structures of the gold complexes **4**[3], ***rac*-5** and **6**.

Ligand	**1**	***rac*-2**	**mesoionic carbene**
$\%V_{bur}$ at 2.00 Å	33.1	33.8	31.8
$\%V_{bur}$ at 2.28 Å	29.2	29.7	27.8

Literature

1 a) G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution and Refinement, University of Göttingen: Göttingen, Germany, 1997; b) SAINT+, Data Integration Engine, Version 8.27b©, Bruker AXS Inc., Madison, Wisconsin, USA, 1997–2012; c) G. M. Sheldrick, *Acta Cryst.* 2008, **64**, 112; d) Bruker, APEX2, Bruker AXS Inc., Madison, Wisconsin, USA, 2012; e) G. M. Sheldrick, SHELXL Version 2014/7, Program for Chrystal Structure Solution and Refinement, University of Göttingen: Göttingen, Germany, 2014; f) G.

M. Sheldrick, *Acta Cryst.* 2015, **71**, 3; g) G. M. Sheldrick, SADABS. Program for Empirical Absorption Correction. University of Gottingen: Göttingen Germany, SADABS Ver. 2008/1.

2 a) H. Clavier, S. P. Nolan, *Chem. Commun.* 2010, **46**, 841. b) A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* 2009, 1759. c) https://www.molnac.unisa.it/OMtools/sambvca2.0/index.html

3 J. Stott, C. Bruhn, U. Siemeling, *Z. Naturforsch.* 2013, **68b**, 853.