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Confluence of Disparate Carbido Chemistries: $[WRuAu_2(\mu\text{-}C)_2Cl_2(CO)_2(PCy_3)_2(Tp^*)]$

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Materials and methods

The complex $[RuAu(\mu\text{-}^{13}C)Cl_3(PCy_3)_2]$ (**3**) was prepared according to the published procedure,[1] while $[W(\equiv CSn^nBu_3)(CO)_2(Tp^*)]$ (**2b**) was prepared via the modification described below of published procedures for $[W(\equiv CSnMe_3)(CO)_2(Tp^*)]$ (**2a**) and $[Mo(\equiv CSnPh_3)(CO)_2(Tp^*)]$.[2] All other reagents were purchased from commercial suppliers and used as received. Solvents were dried by distillation under nitrogen from either CaH_2 (CH_2Cl_2) or sodium/benzophenone (ethers, parafins). Elemental analyses were carried out by the microanalytical services of the Department of Chemistry, University of Copenhagen using a FlashEA 1112 instrument.

NMR spectra were recorded using an 800 or 500 MHz Bruker instrument with a cryoprobe (^1H and $^{13}C\{^1H\}$ NMR) or a 400 Mhz Bruker instrument with broadband probe (^1H and $^{31}P\{^1H\}$ NMR). Residual solvent signals were used for calibration (CD_2Cl2 or $CDCl_3$). IR spectra were recorded using Agilent Technologies Cary 630 FTIR or Perkin Elmar Spectrum One FTIR instruments.

X-ray crystallographic studies were carried out on an Agilent Xcalibur CCD instrument, and structures were solved in Olex2 using the olex2.solve[3] program (Charge Flipping) and refined using SHELXL.[4] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters (U_{iso} = 1.2 U_{eq} of the parent atom for BH, CH and CH_2 groups, and U_{iso} = 1.5 U_{eq} of the parent atom for CH_3 groups). Disorder was treated by applying the ISOR command with appropriate parameters.

Synthesis of $[W(\equiv CSn^nBu_3)(CO)_2(Tp^*)]$ (2b)

Tri-*n*-butylchlorostannane, $^nBu_3SnCl$, was purged with dry nitrogen gas for 30 minutes. In a Schlenk flask, the complex $[W(\equiv CBr)(CO)_2(Tp^*)]$ (0.21 g, 0.33 mmol) was dissolved in degassed THF (20 mL) and the solution was cooled in a dry ice/acetone bath for 15 minutes before an *n*-hexane solution of ^{n}BuLi (2.5 M, 0.18 mL, 0.45 mmol) was syringed slowly into the solution. The yellow solution was stirred for a further 15 minutes before Sn^nBu_3Cl (0.12 mL, 0.44 mmol) was added. The reaction mixture was stirred at this temperature for 90 minutes and then allowed to slowly warm to room temperature (ν_{CO} = 1974, 1884 cm^{-1}). The bright yellow solution was freed of volatiles under reduced pressure before being extracted with cold *n*-hexane (2 x 30 mL). The extracts were cannula-filtered to a pre-dried Schlenk flask and then concentrated under reduced pressure to provide yellow starbursts. Crystals suitable for diffractometry were obtained by vapour diffusion between DCM and *n*-hexane (1:2, – 18 ˚C). Yield: 0.26 g (91%). IR (CH_2Cl_2, cm^{-1}): 1975, 1881 (ν_{CO}). NMR ($CDCl_3$, 25 °C) ^1H NMR (400 MHz, $CDCl_3$) 5.91 (s, 2 H, pzH), 5.72 (s, 1 H, pzH), 2.63 (s, 6 H, $pzCH_3$), 2.40 (s, 3 H, $pzCH_3$), 2.35 (s, 6 H, $pzCH_3$), 2.29 (s, 3 H, $pzCH_3$), 1.57, 1.33 (m x 2, 6 H x 2, $SnCH_2CH_2CH_2$), 0.99 (t, 6 H, $SnCH_2$, $^3J_{HH}$ = 8 Hz), 0.89 (t, 9 H, CH_2CH_3). $^{13}C\{^1H\}$ (201 MHz): δ_H = 346.8 (W≡C, $^1J_{WC}$ = 165), 226.5 (CO, $^1J_{WC}$ = 177 Hz), 152.2, 151.1, 144.9, 144.4 [1:2:1:2C, $C^{3,5}$(pz)], 106.5, 106.4 [C^4(pz)], 29.32 ($SnCH_2CH_2$), 27.49 (CH_2CH_3), 13.8, 13.7, 13.6, 12.7 (2:2:1:1C, $pzCH_3$), 12.11 ($SnCH_2$, $^1J_{SnC}$ = 320, 336), 8.79 ($SnCH_2CH_2$, $^1J_{SnC}$ = 299, 312 Hz). ESI-MS (+, MeCN): *m/z* = 841.3 $[MH]^+$. *Crystal data for* **2b**: $C_{30}H_{49}BN_6O_2SnW$, M_r = 839.11, T = 150(2) K, orthorhombic, space group *Pnma*, a = 15.1363(2) Å, b = 15.7836(2) Å, c = 14.4560(2) Å, V = 3453.62(8) Å^3, Z = 4, D_{calc} = 1.614 Mgm^{-3}, μ(Mo Kα) = 12.08 mm^{-1}, yellow block, 0.09 x 0.06 x 0.04 mm, 53,910 measured reflections with θ_{max} = 72.5 ˚, 3,545 independent reflections, 3,545 absorption-corrected data used in F^2 refinement, 228 parameters, 58 restraints, R_1 = 0.067, wR_2 = 0.152 for 3,245 reflections with $I > 2\sigma(I)$. CCDC 1847568.

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CCDC 1847568 - 1847569 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

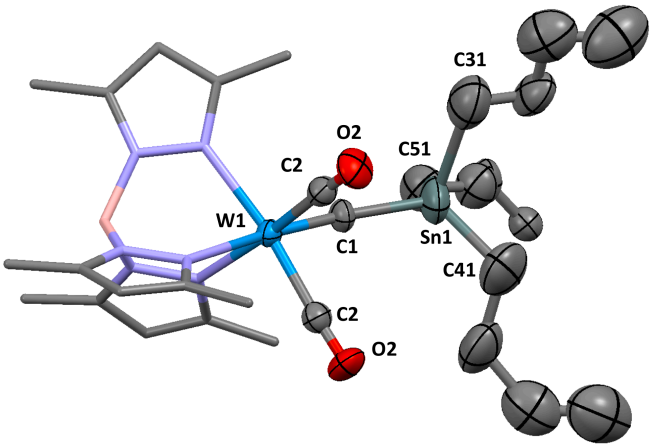

Figure S1. Molecular structure of **2b** in a crystal (50% displacement ellipsoids, hydrogen atom omitted and pyrazolyl groups simplified). Selected bond lengths (Å) and angles (°): W1–C2 1.999(8), W1–C1 1.822(10), W1–C2 1.999(8), Sn1–C1 2.127(10), Sn1–C1–W1 172.3(7).

Synthesis of [WRuAu$_2$(μ-C)$_2$Cl$_3$(CO)$_2$(PCy$_3$)$_2$(Tp*)] (5)

A mixture of [RuAu(μ-^{13}C)Cl$_3$(PCy$_3$)$_2$] (**3**: 45.7 mg, 46.7 μmol; 100% ^{13}C enriched at the carbido) and [W(≡CSn^{n}Bu$_3$)(CO)$_2$(Tp*)] (39.2 mg, 46.7 μmol) were dissolved in chloroform (0.4 mL) and heated until all solids had dissolved. The dark orange reaction mixture was left standing for one day and then subjected to diethyl ether vapor diffusion over three days. Orange crystals of **5** were separated from the mother liquor by decanting, washed with diethyl ether (3 x 2 ml), and air-dried. Yield: 16.8 mg, 9.74 μmol, 41.7% based on the Au content of ^{13}C-**3**. Elemental analysis, calculated for $C_{55}H_{88}Au_2BCl_3N_6O_2P_2RuW$: C: 38.33%, H: 5.15%, N: 4.88%; found: 38.88%, H: 5.60%, N: 5.24%. NMR (CD_2Cl_2, 25°C), ^{1}H (500 MHz): δ_H = 1.31 – 1.19 (m, 18H, Cy), 1.66 – 1.55 (m, 12H, Cy), 1.77 – 1.70 (m, 6H, Cy), 1.90 – 1.79 (m, 12H, Cy), 2.16 – 2.04 (m, 12H, Cy), 2.31 (s, 3 H, pzCH$_3$), 2.36 (s, 6 H, pzCH$_3$), 2.49 (s, 3 H, pzCH$_3$), 2.56 (s, 6 H, pzCH$_3$), 2.70 – 2.61 (m, 6 H, Cy), 5.88 (s, 1 H, pzH), 5.98 (s, 2 H, pzH). ^{13}C{^{1}H} (126 MHz): δ_C = 420.11 (br., Ru≡CAu), 395.83 (t, $^3J_{PC}$ = 6.2 Hz due to reformed **3**), 220.55 (CO), 153.65, 152.39, 146.36, 146.24 [1:2:1:2C, C^{3,5}(pz)], 108.16, 107.54 [1:2C, C^4(pz)], 32.68 (t, *J* = 9.9 Hz, Cy), 30.67 (Cy), 28.45 (t, *J* = 5.7 Hz, Cy), 27.01 (Cy), 18.18, 15.81, 13.12, 13.08 (2:1:1:2C, pzCH$_3$). ^{31}P{^{1}H} (202 MHz) δ_P = 43.57. IR (solid ATR, cm^{-1}): 1994, 1913 (ν_{CO}, See also Table S1). *Crystal data for* **5**: $C_{55}H_{88}Au_2BCl_3N_6O_2P_2RuW$, M_r = 839.11, *T* = 150(2) K, triclinic, space group *P*-1 (No. 2), *a* = 13.8516(3) Å, *b* = 14.6061(3) Å, *c* = 17.1538(4) Å, α = 73.1381(17)°, β = 81.6834(17)°, γ = 65.5781(18)° *V* = 3022.91(11) Å^3, *Z* = 2, D_{calc} = 1.893 Mgm^{-3}, μ(Mo Kα) = 7.210 mm^{-1}, yellow-orange prism, 0.33 x 0.12 x 0.06 mm, 61,102 measured reflections with θ_{max} = 52.0°, 12,338 independent absorption-corrected data used in F^2 refinement, 704 parameters, 6 restraints, R_1 = 0.032, wR_2 = 0.07 for 10,824 reflections with $I > 2\sigma(I)$. CCDC 1847569.

Note: the formation of WRuAu$_2$ proceeds *via* an equilibrium. When single crystals of WRuAu$_2$ are dissolved for NMR analysis, the appearance of new resonances is evident within the course of minutes (e.g. a ^{1}H resonance from (Cy$_3$P)$_2$Cl$_2$Ru≡^{13}C–AuCl at 2.2 ppm). Consequently, NMR characterization must be carried out immediately after dissolution.

Table S1. Representative IR data for (OC)$_2$(Tp*)W≡C–[M] complexes

[M]	Medium	ν_{CO}/cm^{-1}	
RuAu$_2$Cl$_3$(PCy$_3$)$_2$ (**5**)	Solid ATR	1994,	1913
SnMe$_3$ (**2a**)	Nujol[6]	1971,	1877
Sn^{n}Bu$_3$ (**2b**)	CH_2Cl_2	1975,	1881
Au (**7**)	CH_2Cl_2[6]	1979,	1900
AuPEt$_3$	KBr[6]	1944,	1851
AuAsPh$_3$	CH_2Cl_2[6]	1998,	1915
NiCl(PEt$_3$)$_2$	CH_2Cl_2[5]	1936,	1843

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Table S2. Cartesian Coordinates (Å) for $WAu(\mu\text{-}CH)Cl(CO)_2(\eta\text{-}C_5H_5)$ (B3LYP-LANL2DZ)

Atom	*x*	*y*	*z*
W1	-0.0493014	-0.4933060	0.4422646
H1	2.2694038	1.4047092	-0.7806006
C1	1.2017677	1.4181776	-0.6168394
C5	0.5392110	1.8862814	0.5583671
H5	0.4002895	0.5287944	-2.5097746
H7	1.0120402	2.3368120	1.4181694
C4	-0.8859238	1.7293906	0.3595593
H8	-1.6589533	2.0638935	1.0342222
C3	-1.0842082	1.1417755	-0.9321488
H9	-2.0323562	0.9363238	-1.4045740
C2	0.2142640	0.9397193	-1.5287113
C6	-0.2244351	-0.4590422	2.4222890
O1	-0.3731239	-0.4268718	3.5872807
C7	1.7099532	-1.4174754	0.6629008
O2	2.7668003	-1.9135576	0.7772780
Au1	-0.5397150	-2.6041333	-1.3591629
C8	-1.1332314	-2.0263966	0.5831611
H6	-1.8094825	-2.7228470	1.0734730
Cl1	-0.2944207	-3.5770907	-3.5401160

Figure S1. Optimised Geometry (B3LYP-LANL2DZ) for $WAu(\mu\text{-}CH)Cl(CO)_2(\eta\text{-}C_5H_5)$

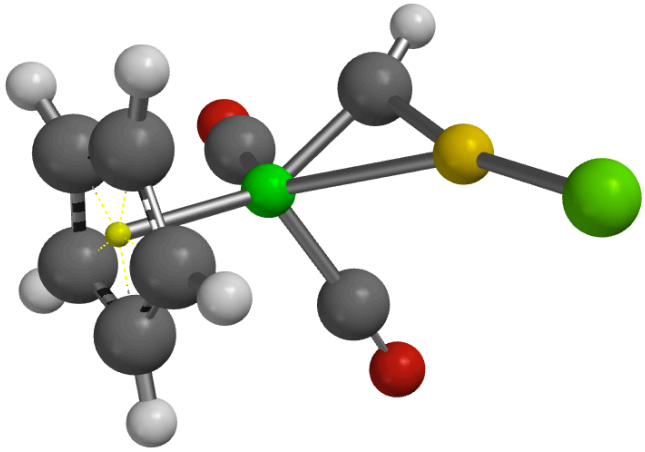

Figure S2. Calculated IR Spectrum for $WAu(\mu\text{-}CH)Cl(CO)_2(\eta\text{-}C_5H_5)$

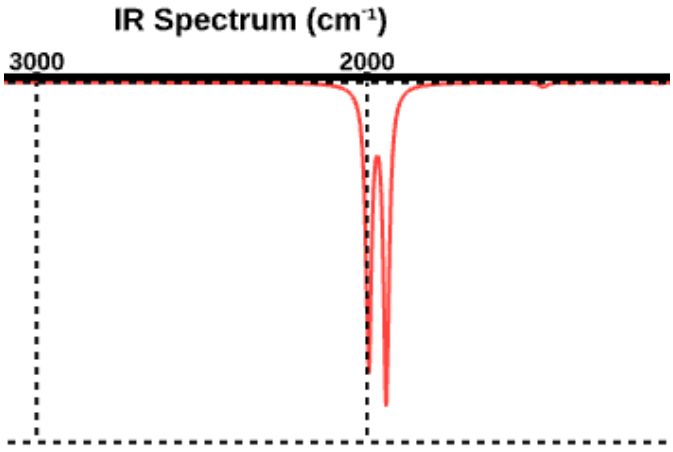

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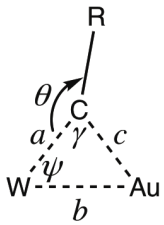
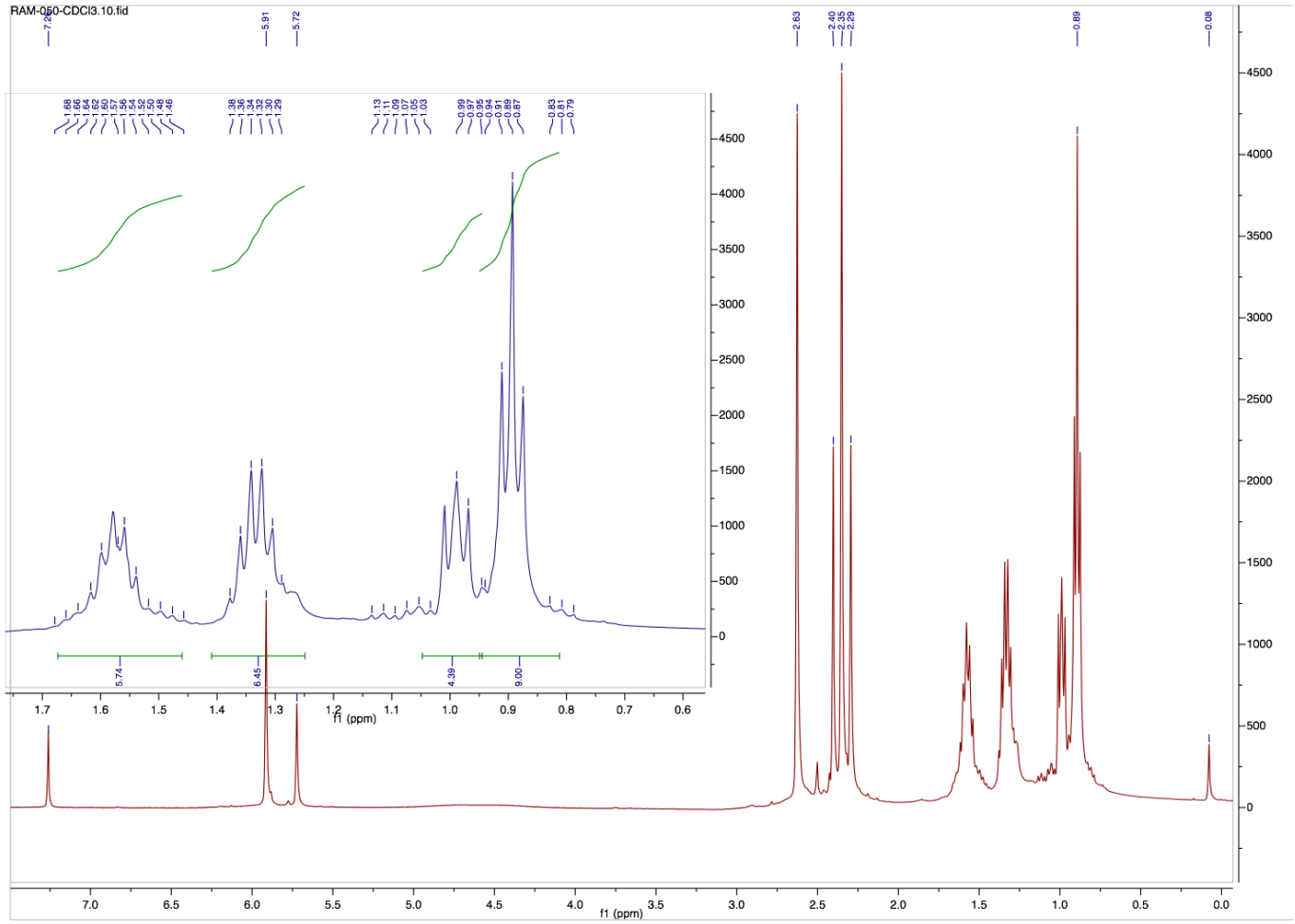
Table S3. Selected Geometric Features for WC^3Au Connectivities from the CCDC.[1]

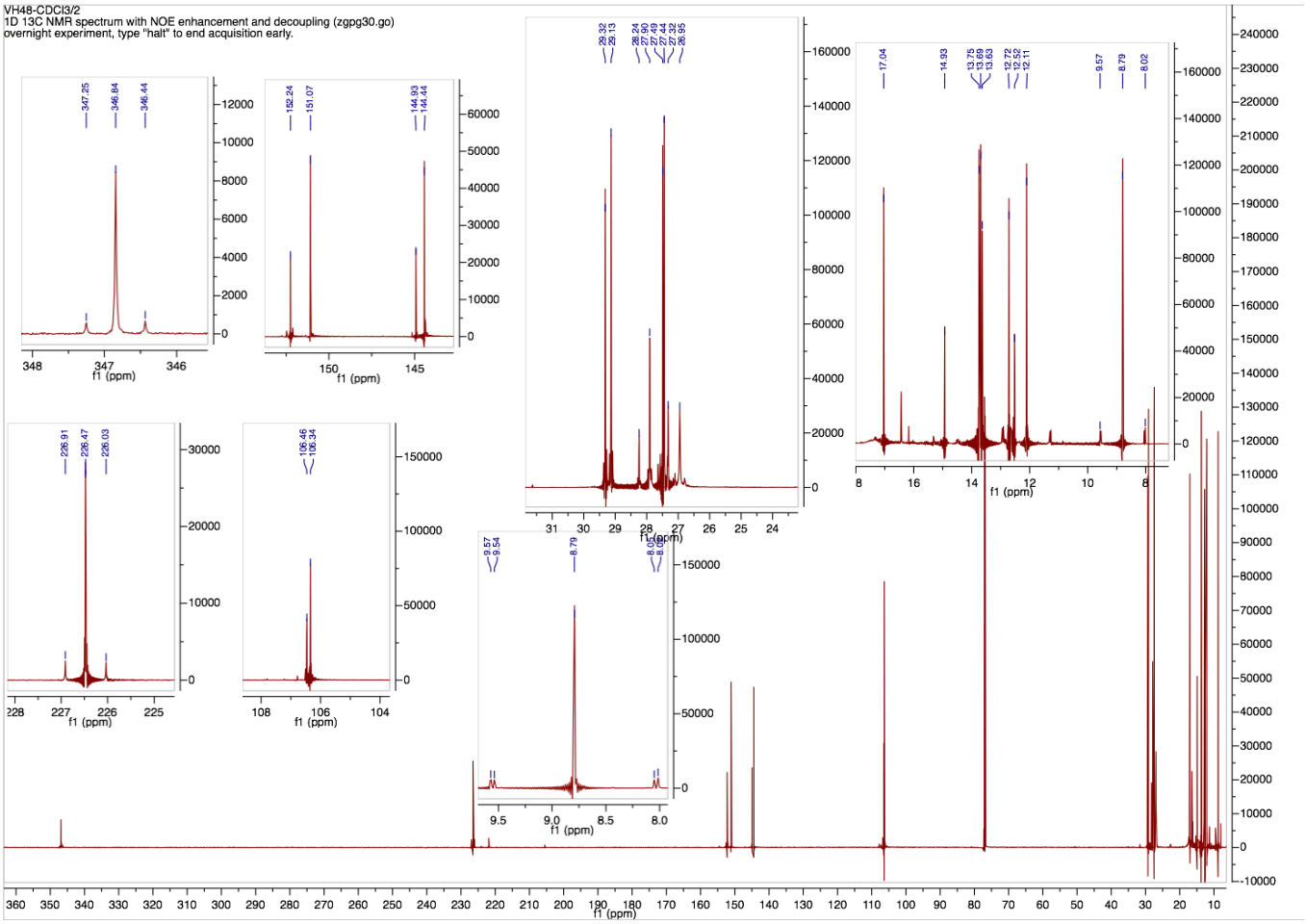


Complex	Ref	*a*	*b*	*c*	*θ*	*ψ*	*γ*
$[W_2Au(\mu\text{-}CC_6H_4Me\text{-}4)_2(CO)_4(\eta\text{-}C_5H_5)]^+$	7	1.832	2.752	2.119	50.31	87.99	160.86
$[WAu(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_2(PPh_3)(C_2B_9H_9Me_2)]$	8	1.88	2.781	2.194	51.88	85.74	162.77
$[WAu(\mu\text{-}CS)(CO)_2(PPh_3)\{HB(pz)_3\}]$	9	1.911	2.825	2.161	49.83	87.64	165.78
$[WAu(\mu\text{-}CS)(CO)_2(PPh_3)\{HB(pz)_3\}]$	9	1.904	2.823	2.151	49.6	88.01	167.34
$[WAu(\mu\text{-}CPPh_2AuCl)(CO)_2(Tp^*)]$	10	1.898	2.801	2.031	46.47	90.89	145.13
$[WAu(\mu\text{-}CPPh_2AuCl)(CO)_2(Tp^*)]$	10	1.907	2.794	2.043	46.98	89.99	146.63
$[W_2Au_2(\mu\text{-}C_2PPhAuCl)(CO)_4(Tp^*)_2]$	10	1.872	2.827	2.038	46.06	92.52	148.60
	10	1.882	2.769	2.020	46.85	90.32	148.80
$[WAu(\mu\text{-}CC_6H_4Me\text{-}4)Br(C_6F_5)(CO)_2(bipy)]$	11	1.89	2.783	2.080	48.36	88.88	151.28
$[WAuRh(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_3(PPh_3)(\eta\text{-}C_5H_5)(C_2B_9H_{11})]$	12	1.904	2.731	2.180	50.99	85.03	156.05
$[WAu(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_2(\eta\text{-}C_5H_5)(C_2B_9H_9Me_2)]^-$	13	1.906	2.697	2.105	50.95	84.34	158.23
$[WAu(\mu\text{-}CC^tBu)(NO)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$	14	2.119	2.803	2.262	52.51	79.48	172.63
$[WAu(\mu\text{-}CC_3H_2NS\text{-}NC_5H_{10}\text{-}3)BrCl(CO)_2(py)_2$	15	1.889	2.738	2.028	46.79	90.44	152.38
$[W_2Au(\mu\text{-}CC_6H_4Me\text{-}4)_2Cl_2(bipy)_2(CO)_4]$	16	1.875	2.789	2.154	44.23	93.32	147.28
	16	1.945	2.773	1.937	50.38	85.55	156.66
$[W_2Au_2(\mu\text{-}CC_6H_4Me\text{-}4)_2(\mu\text{-}dppb)(CO)_4(C_2B_9H_9Me_2)_2]$	17	1.871	2.799	2.195	51.51	86.61	161.76
$[W_4Au_4(\mu\text{-}C)_4(CO)_8(Tp^*)_4]$ (**7**)	6	1.846	2.846	2.032	45.38	94.33	160.30
	6	1.867	2.822	2.143	49.40	89.18	167.64
	6	1.897	2.841	2.090	47.36	90.74	163.50
	6	1.871	2.825	2.102	48.08	90.44	165.10
"$WAu(\mu\text{-}CH)Cl(CO)_2(\eta\text{-}C_5H_5)$" (B3LYP-LANL2DZ)	*a*	*1.883*	*2.818*	*2.112*	*48.53*	*89.55*	*155.94*

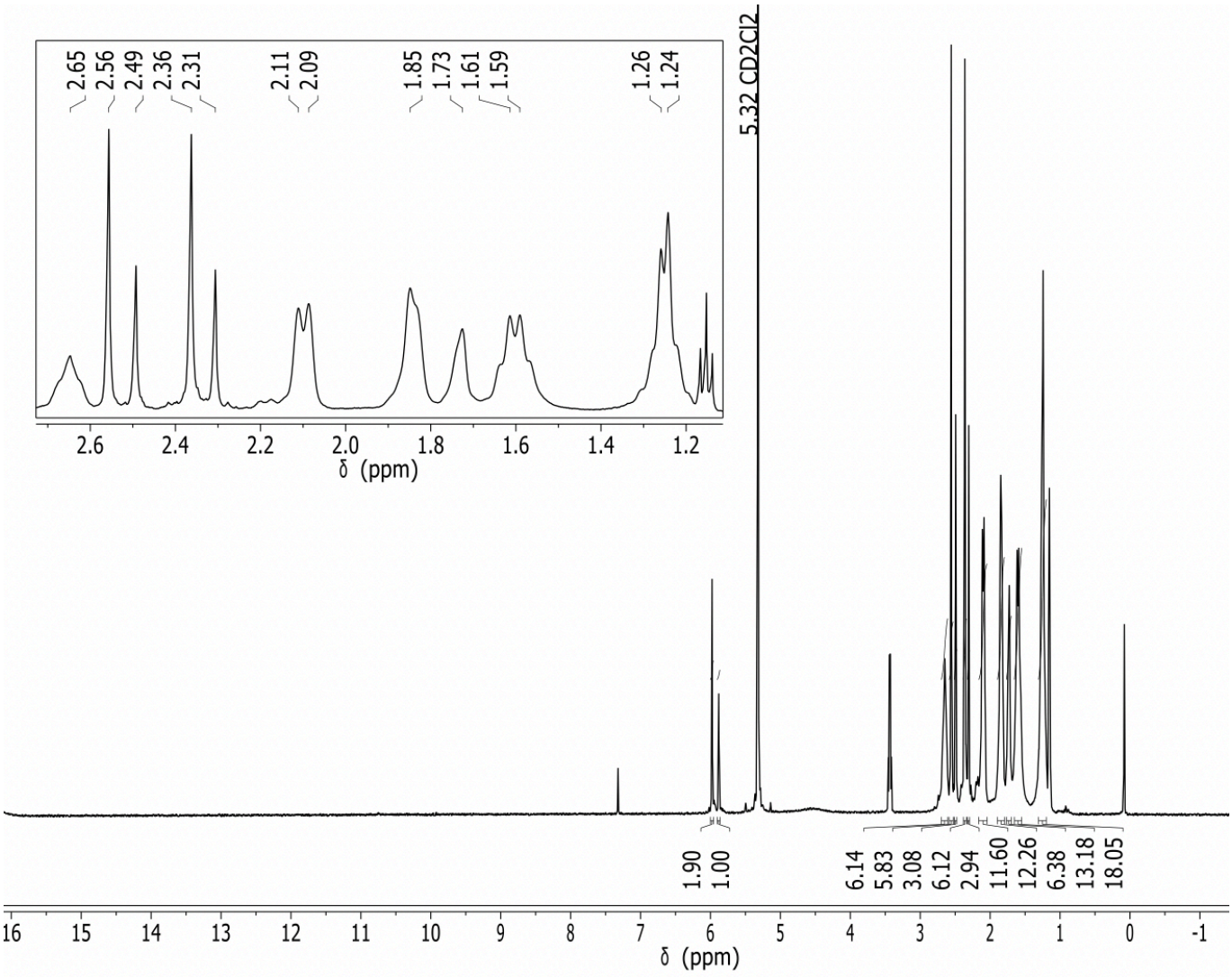
[a] This work.



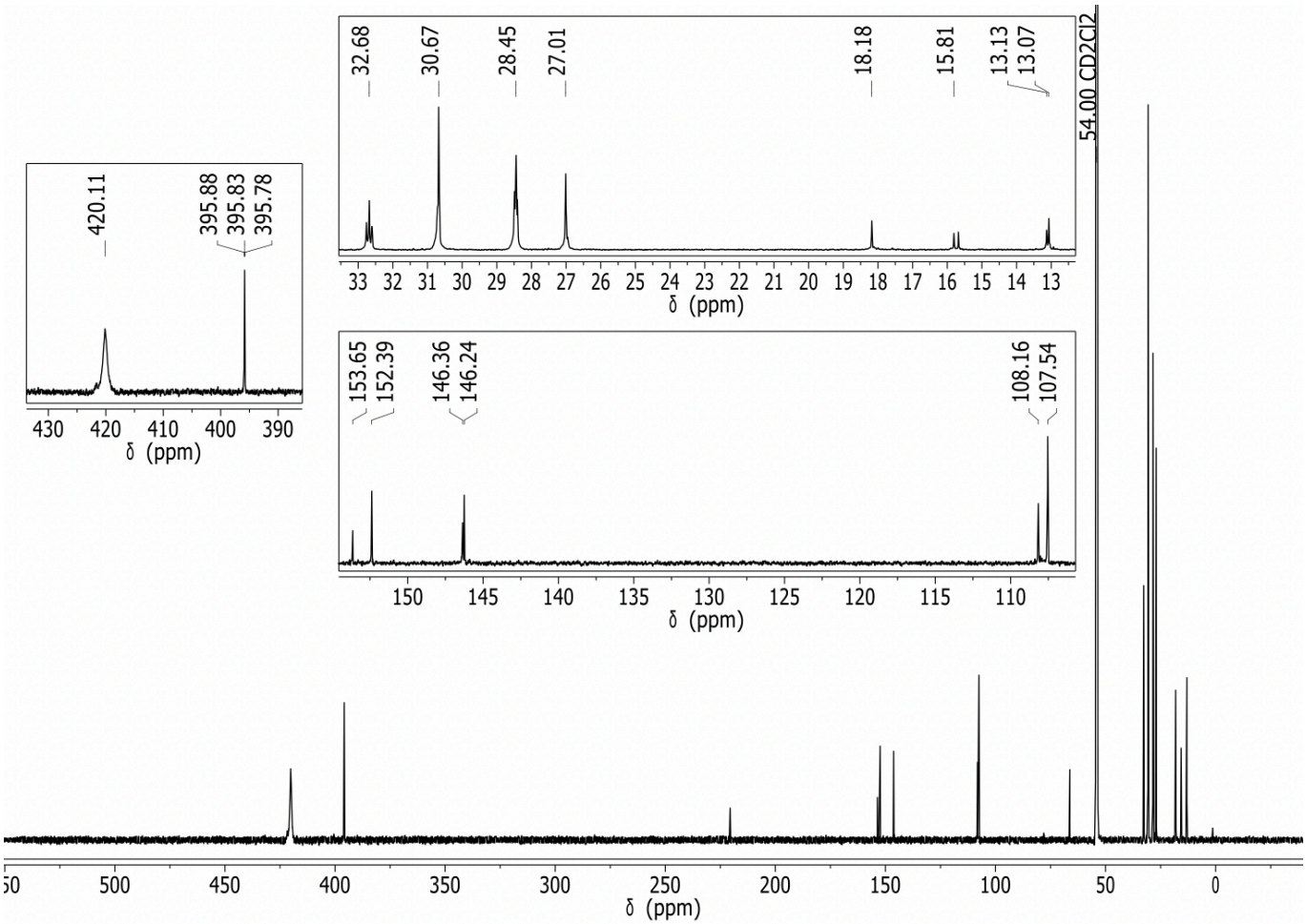
^{1}H NMR Spectrum of [W(CS^{n}Bu$_3$)(CO)$_2$(Tp*)] (**2b**)



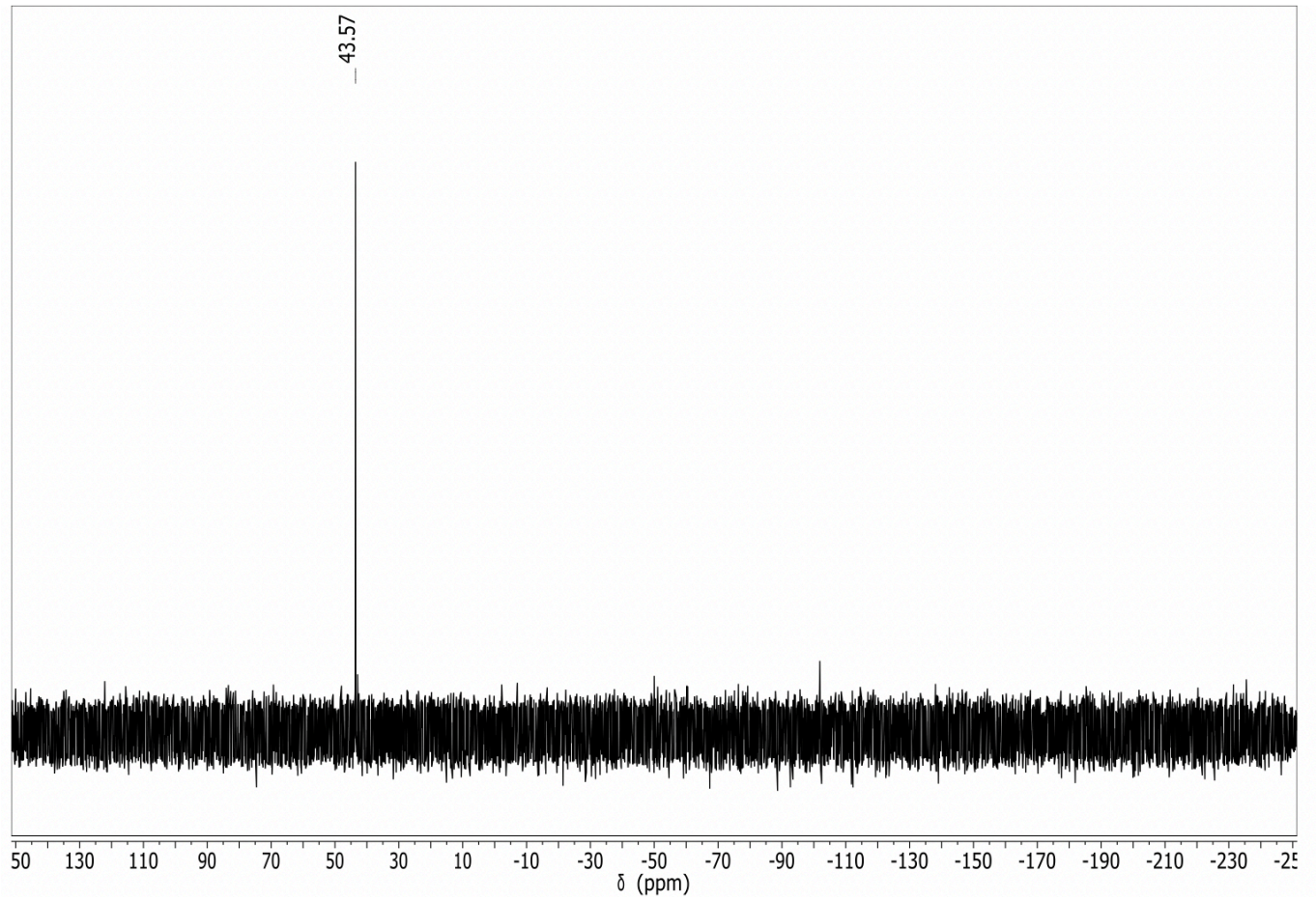
$^{13}C\{^{1}H\}$ NMR Spectrum of [W(CSn^{n}Bu$_3$)(CO)$_2$(Tp*)] (**2b**)



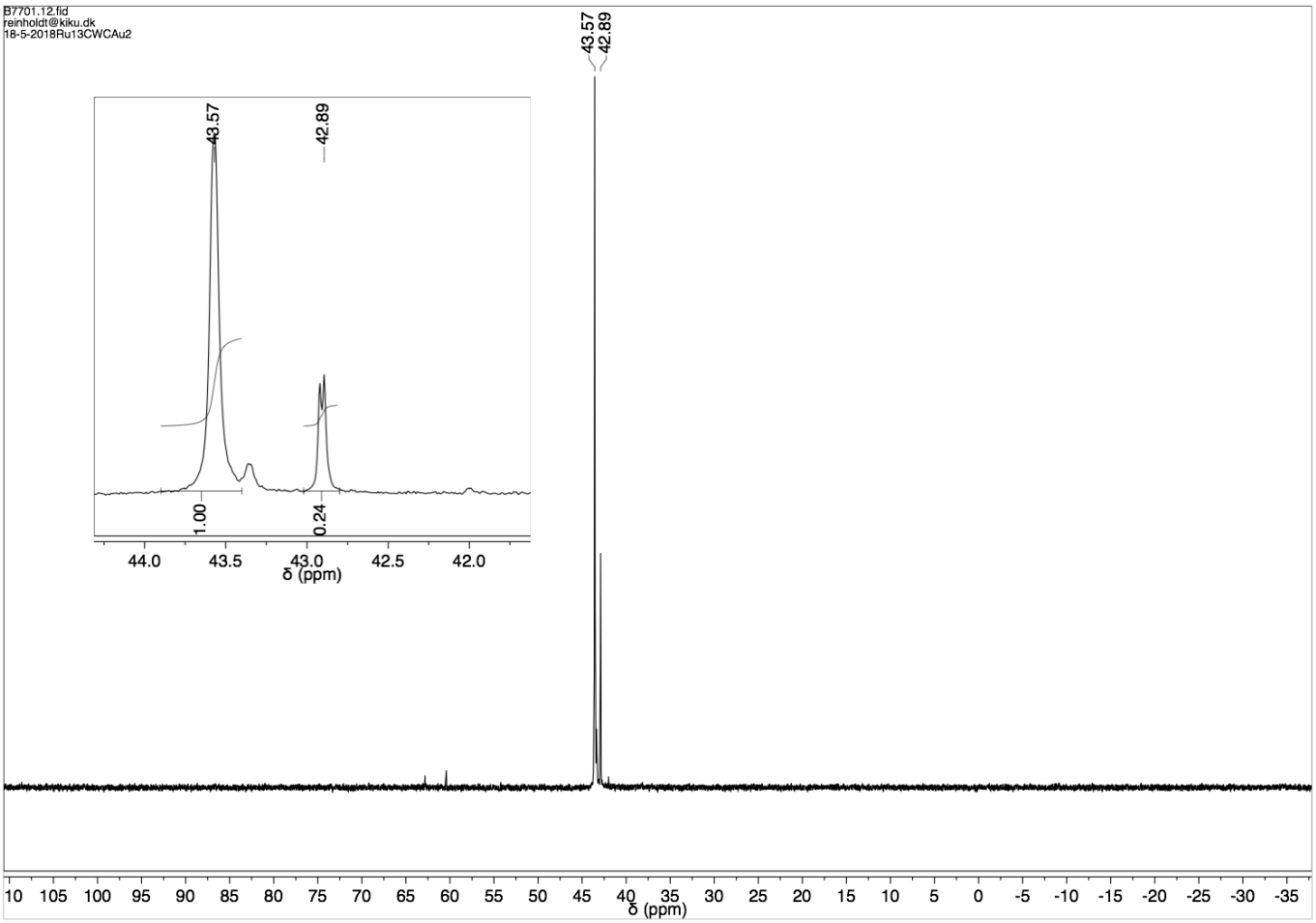
^{1}H NMR spectrum of **5**. Chloroform residue: 7.32 ppm, diethyl ether residue 1.15 and 3.43 ppm



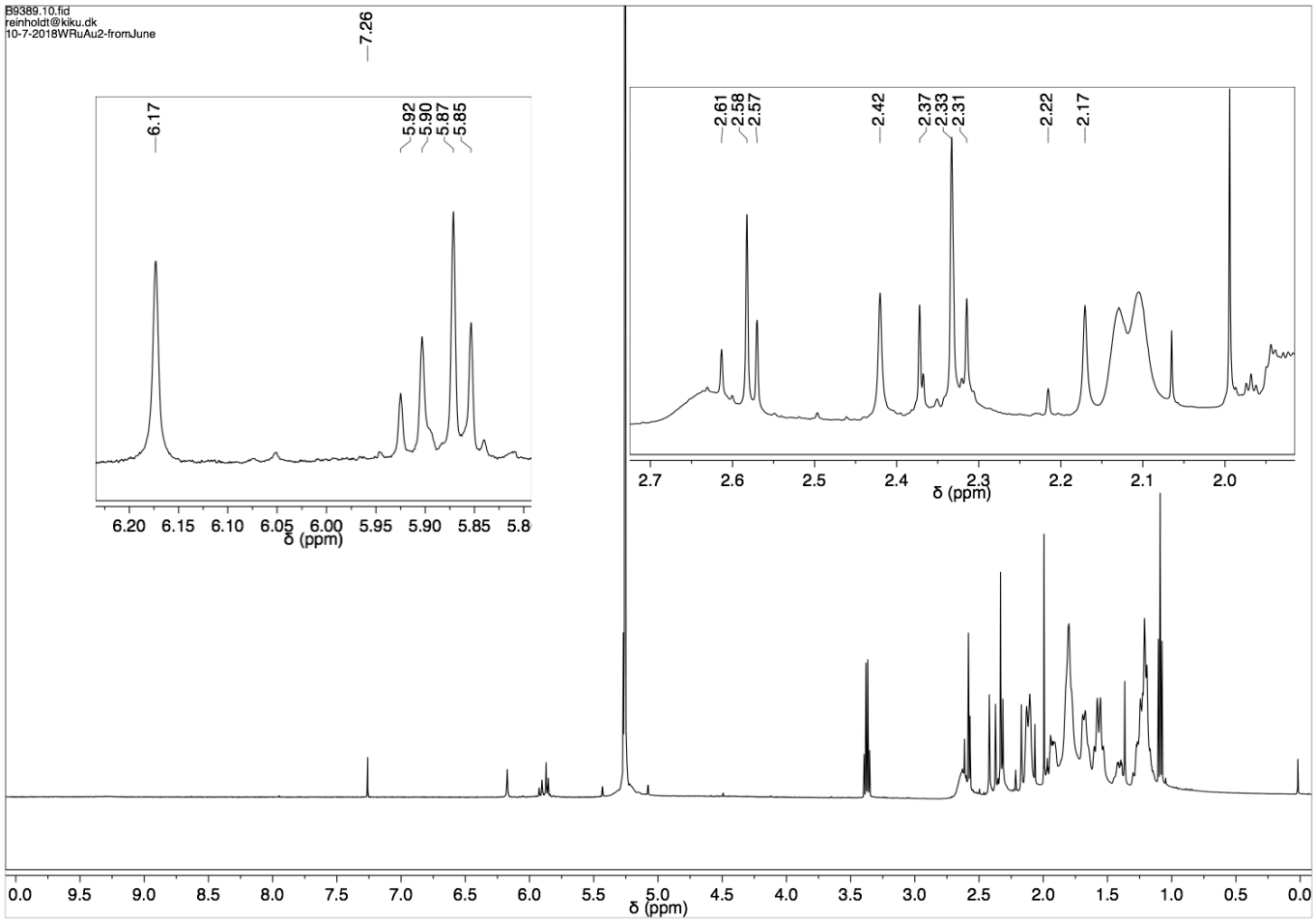
$^{13}C\{^{1}H\}$ NMR spectrum ^{13}C-**5**. Diethyl ether residue: 15.68 and 66.23 ppm. NB: The spectrum was measured for a sample of **5** prepared from **3** that was 100% ^{13}C-enriched at the carbido carbon in combination with **2b** prepared from natural abundance $W(CO)_6$. The absence of any ^{13}C enrichment in the tungsten bound carbide resonance provides evidence that the two carbidos retain their individual identities throughout. Within the acquisition period (during which decomposition to **3** and **7** was clearly proceeding) insufficient signal/noise was achieved to unambiguously locate the second carbido resonance for **5** or for the resulting carbido resonance for **7** (δ_C = 361.7, $^{1}J_{WC}$ = 75.5 Hz, see reference 6)



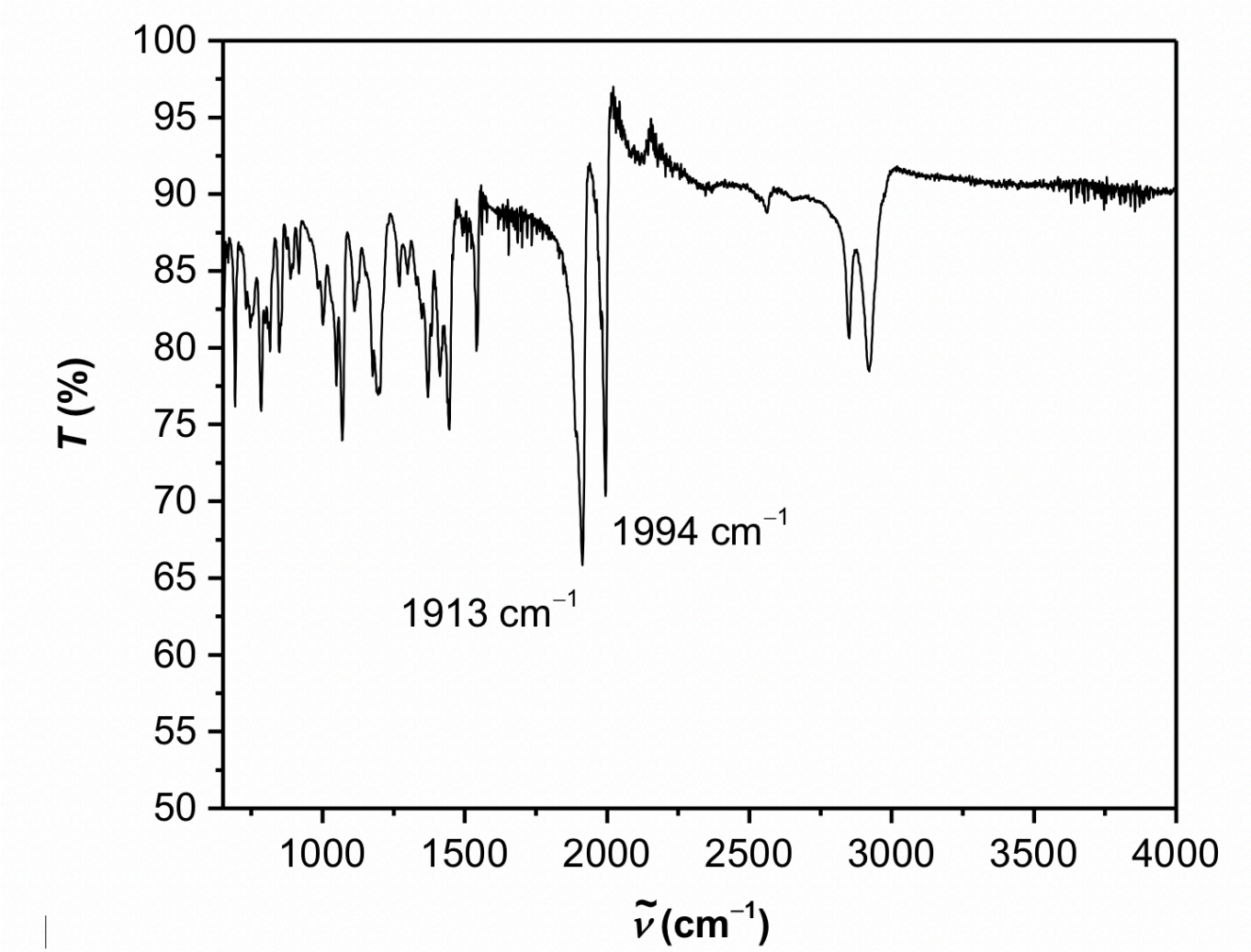
$^{31}P\{^{1}H\}$ NMR spectrum of freshly prepared **5**



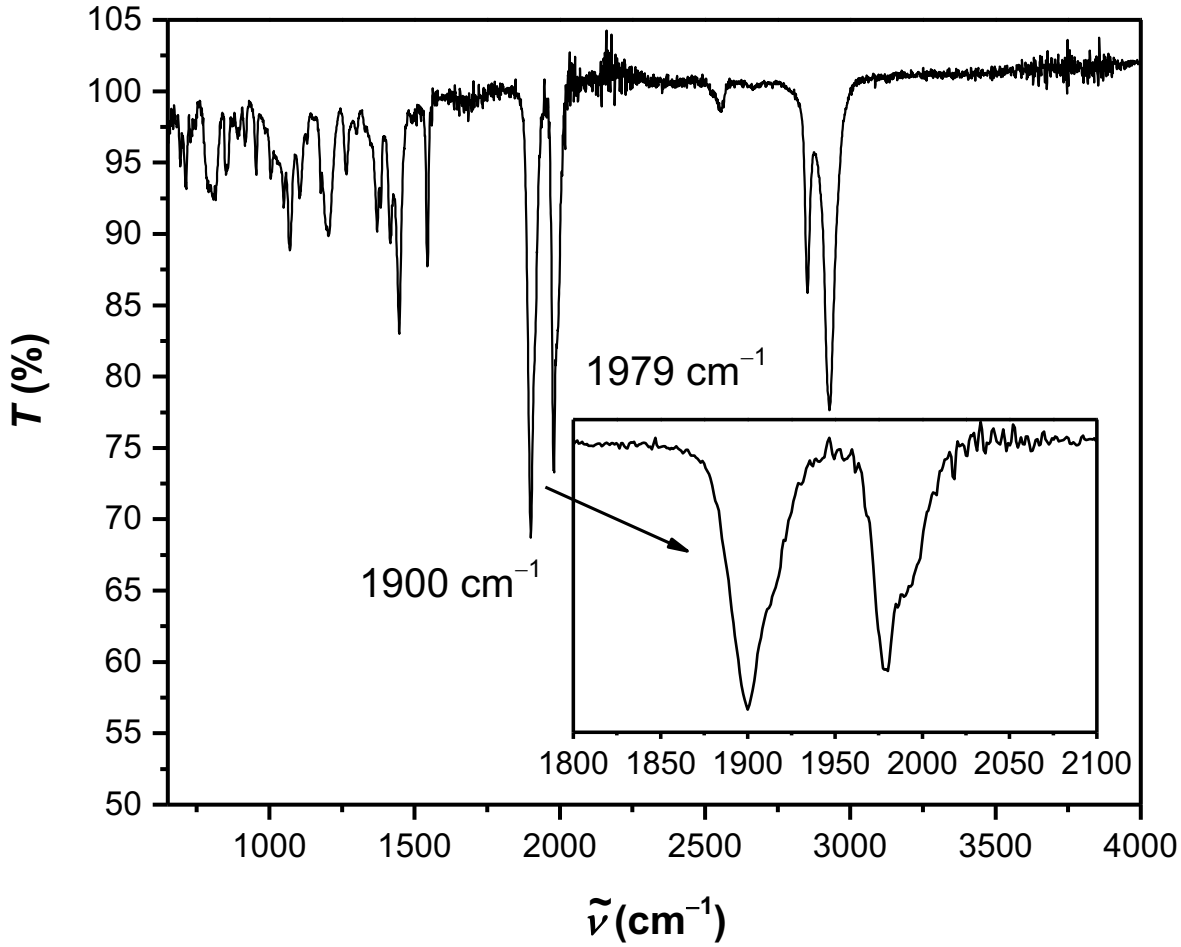
$^{31}P\{^{1}H\}$ NMR spectrum of **5** (δ_P = 43.57) after ^{13}C NMR acquisition showing ca 20% conversion to **3** (δ_P = 42.89)



^{1}H NMR of aged sample of **5** showing complete conversion to **7** and **3**.



IR spectrum of **5**



IR spectrum of **5** after standing in CD_2Cl_2 solution for 4 hours showing conversion to **7** (From ref. 6: IR (ν_{CO}, cm^{-1}) CH_2Cl_2: 1979, 1900; Nujol: 1974, 1900).