

**Decarbonylation of Phenylacetic Acids by High Valent
Transition Metal Halides**

Journal:	<i>Dalton Transactions</i>
Manuscript ID	DT-ART-02-2019-000551.R1
Article Type:	Paper
Date Submitted by the Author:	n/a
Complete List of Authors:	Pampaloni, Guido; Universita di Pisa, Dipartimento di Chimica e Chimica Industriale Bartalucci, Niccolò; Universita degli Studi di Pisa, Dipartimento di Chimica e Chimica Industriale Marchetti, Fabio; Universita' di Pisa, Chimica e Chimica Industriale Zacchini, Stefano; Universita di Bologna, Dipartimento di Chimica Industriale "Toso Montanari"

Dalton Transactions

Guidelines to Referees

Communications & Papers

The international journal for high quality, original research in inorganic and organometallic chemistry

<http://www.rsc.org/dalton>



Dalton Transactions wishes to encourage high quality articles reporting exciting new developments in inorganic chemistry.

For an article to be accepted, it must report new, high-quality research and make a significant contribution to the field.

Manuscripts that describe purely physical, crystallographic or computational studies must include the clear relevance of the work to the broad inorganic chemistry readership of *Dalton Transactions*.

Communications must report chemistry of sufficient importance and impact to justify preliminary publication. **Papers** should report more complete studies.

Dalton Transactions' Impact Factor is 4.099 (2017 Journal Citation Reports®)

Routine or unnecessarily fragmented work, however competently researched and reported, should not be recommended for publication.

Thank you very much for your assistance in evaluating this manuscript

Dr Andrew Shore (dalton@rsc.org)
Royal Society of Chemistry
Editor, *Dalton Transactions*

Professor John Arnold
University of California, Berkeley
Chair, *Dalton Transactions* Editorial Board

General Guidance (for further details, see the RSC [Refereeing Procedure and Policy](#))

When preparing your report, please:

- Comment on the **originality**, **importance**, **impact** and **scientific reliability** of the work
- State clearly whether you would like to see the paper accepted or rejected and give detailed comments (with references, as appropriate) that will help both the Editor to make a decision on the paper and the authors to improve it

Please inform the Editor if:

- There is a conflict of interest
- There is a significant part of the work which you are not able to referee with confidence
- If the work, or a significant part of the work, has previously been published, including online publication (e.g. on a preprint server/open access server)
- You believe the work, or a significant part of the work, is currently submitted elsewhere
- The work represents part of an unduly fragmented investigation

Decarbonylation of Phenylacetic Acids by High Valent Transition Metal

Halides

Niccolò Bartalucci,^a Fabio Marchetti,^a Stefano Zacchini,^{b,*} Guido Pampaloni^{a,*}

^a*Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Via G. Moruzzi 13, I-56124 Pisa, Italy.*

^b*Dipartimento di Chimica Industriale “Toso Montanari”, Università di Bologna, Viale Risorgimento 4, I-40136 Bologna, Italy.*

Abstract

Triphenylacetic acid underwent unusual decarbonylation when allowed to react with a series of halides of groups 4-6 metals in their highest oxidation state, in dichloromethane at ambient temperature. Thus, the reaction of CPh_3COOH with MoCl_5 , in 1:1 molar ratio, afforded the trityl salt $[\text{CPh}_3][\text{MoOCl}_4]$, **1**, in 79% yield, while the 1:2 reaction of CPh_3COOH with NbF_5 afforded $[\text{CPh}_3][\text{NbF}_6]$, **2**, in 70% yield NbOF_3 being the metal co-product. CPh_3COOH reacted with NbCl_5 , TiF_4 and WOCl_4 to give mixtures of compounds, however the cation $[\text{CPh}_3]^+$ was NMR identified in each case. $[\text{CPh}_3][\text{NbCl}_6]$, **3**, was isolated from NbCl_5 and CPh_3COCl , prior generated from CPh_3COOH and PCl_5 . The reaction of CPh_3COOH with TiCl_4 was non-selective, and the salt $[\text{CPh}_3][\text{Ti}_2\text{Cl}_8(\mu-\kappa^2\text{-O}_2\text{CCPh}_3)]$, **4**, was obtained in 18% yield. The decarbonylation reactions of $\text{CMe}(\text{Ph})_2\text{COCl}$ and $\text{CMe}_2(\text{Ph})\text{COCl}$ by means of NbCl_5 led to the indanes **5a-b**, which were isolated in 79-97% yields after hydrolysis of the mixtures and subsequent alumina filtration of the organic phases. The reactions of $\text{CH}(\text{Ph})_2\text{COOH}$ with NbCl_5 and WCl_6 afforded $\text{NbCl}_4(\text{OOCCHPh}_2)$, **6**, and CHPh_2COCl , respectively, as the prevalent species. $\text{CPh}_2(\text{CH}_2\text{CH}_2\text{Br})\text{COOH}$ did not undergo CO release when allowed to interact with WCl_6 , instead selective intramolecular condensation to $\overline{\text{C}(\text{Ph})_2\text{C}(=\text{O})\text{OCH}_2\text{CH}_2}$, **7**, occurred. $\text{MeC}\equiv\text{CCOOH}$ underwent hydrochlorination by WCl_6 to give $\text{MeC}(\text{Cl})=\text{CHCOOH}$, **8**, in 72% yield. All the products were fully characterized by elemental analysis, IR and multinuclear NMR spectroscopy. In addition, the solid state structures of **1**, **2**, **4**, **7**, **8** were elucidated by X-ray diffraction.

Introduction

Early transition metal halides, containing the metal in an oxidation state higher than +4, are featured by a strong Lewis acidic character^[1] and a quite positive oxidation potential.^[2] These peculiar characteristics give rise to several transformations on organic substrates, such as the formation of C-C

bonds,^[3] the dehydrogenative coupling of arenes,^[4] the functionalization of alkenes,^[5] the polymerization of alkynes^[6] and several cycloaddition reactions.^[7]

In the recent years, we have studied the reactivity of high valent groups 4, 5 and 6 metal halides with Lewis bases pointing out a marked difference of reactivity when moving from group 4 to group 6 elements.

For example, TiCl_4 generally reacts with oxygen donors affording hexacoordinate complexes, and activation of the ligands is observed at high temperature only.^[8] On the other hand, in view of the lower M-Cl bond energy^[9] and the higher oxidation state, MoCl_5 and WCl_6 make possible stoichiometric modifications of simple molecules through unconventional pathways even at room temperature or below. In particular, tungsten hexachloride shows examples which include the conversion of imines into aza-2-allenium and nitrilium cations,^[10] the former being generated via unusual N_2 elimination, and of α -diimines into quinoxalium salts.^[11]

Unique reactivity patterns have been observed with niobium and tantalum pentahalides^[1c,7,12] and, considering also the relative cheapness and the substantial non-toxicity of the related metal elements,^[13] a significant advance in the use of these systems as promoters for organic transformations has been experienced in the last years.^[7,14] When compared to the heavier halides of Group 6, NbX_5 ($\text{X} = \text{F}, \text{Cl}$) are more inert towards reduction processes, and are characterized by relatively strong niobium-halide bonds,^[9] thus disfavoring halide/oxygen exchange reactions.^[15] As a matter of fact, NbF_5 forms adducts when allowed to react with alcohols and carboxylic acids,^[16] while NbCl_5 in the same conditions affords metal alcoholates/carboxylates through HCl release.^[14e, 17] The formation of metal carboxylates is also the typical reactivity displayed by low- or medium valent transition metal chlorides with carboxylic acids,^[18] including CPh_3COOH .^[19] On the other hand, the reactivity of simple carboxylic acids (RCOOH) with MoCl_5 and WCl_6 shows similitudes with the behaviour of PCl_5 ,^[20] thus Cl/O exchange takes place with formation of the corresponding acyl chlorides RC(O)Cl . This outcome, however, is

often accompanied by side reactions,^[21] possibly giving an explanation why the interaction of Group 6 high valent metal halides with carboxylic acids (and their acyl chloride counterparts), especially the ones bearing an additional functional group, has been sparingly explored heretofore.

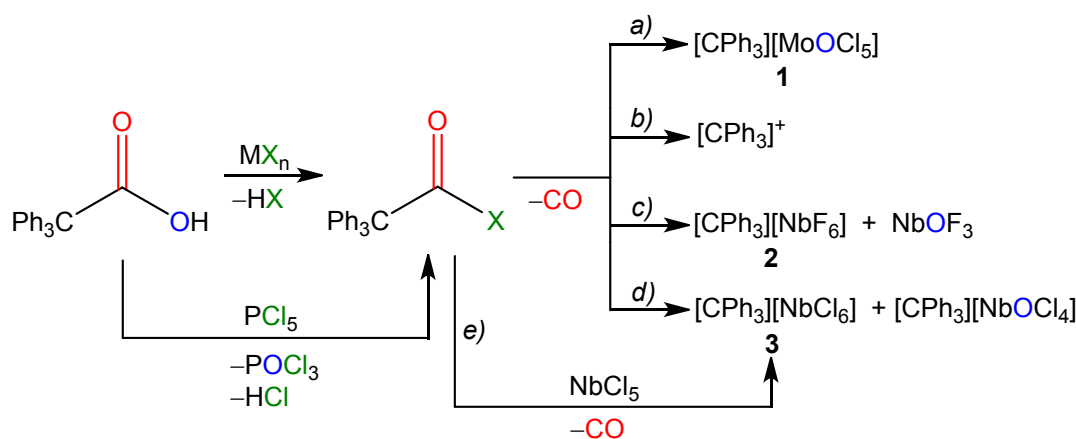
In the framework of our project, aimed to develop the chemistry of homoleptic halides of early transition metals, and following our recent communication on the unusual reactivity exhibited by WCl_6 with CPh_3COOH and related carboxylic acids,^[22] herein we report an extension of this study to other halides of high valent groups 4-6 metals.

Results and discussion

1. Decarbonylation reactions of triphenylacetic acid.

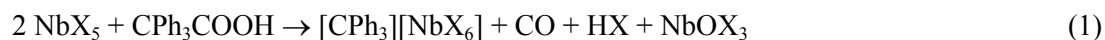
The 1:1 molar reactions of triphenylacetic acid with a series of high valent metal chlorides/fluorides, i.e. MoCl_5 , WOCl_4 , NbCl_5 , NbF_5 or TiF_4 , were carried out in dichloromethane at ambient temperature and cleanly proceeded with CO extrusion (detected by gas-chromatography), to give the trityl cation associated to various counteranions (Scheme 1). Similarly to what found for the $\text{CPh}_3\text{COOH}/\text{WCl}_6$ reaction system,^[22] the preliminary formation of CPh_3COX ($\text{X} = \text{Cl}$ or F), resulting from halide/oxygen exchange between the organic substrate and the metal halide, is likely to precede the CO release step. Indeed, CPh_3COCl was NMR detected along the pathways to **1** and **3**. Olah observed a very unstable coordination complex between CPh_3COF and SbF_5 , decarbonylating to $[\text{CPh}_3]^+$.^[23]

The reaction involving MoCl_5 straightforwardly afforded **1**, isolated in 78% yield, wherein the anion is the Cl/O exchange metal product (Scheme 1a). On the other hand, the cation $[\text{CPh}_3]^+$ was clearly recognized by ^{13}C NMR in the reaction mixtures obtained from $\text{CPh}_3\text{COOH}/\text{WOCl}_4$ and $\text{CPh}_3\text{COOH}/\text{TiF}_4$ (diagnostic resonance at ca. 210 ppm), but the clean isolation of products failed (Scheme 1b). The ^{19}F NMR spectrum of $\text{CPh}_3\text{COOH}/\text{TiF}_4$ displayed a complicated set of signals.



Scheme 1. Decarbonylation of triphenylacetic acid and triphenylacetic acid chloride by reactions with high valent halides. MX_n = MoCl₅ (a); WOCl₄ or TiF₄ (b); NbF₅ (c); NbCl₅ (d).

The combination of CPh₃COOH with niobium pentahalides yielded **2-3** in admixture with niobium oxo-halide co-products (Scheme 1c-d), and the optimal stoichiometry for these reactions resulted to be Nb/acid 2:1 (Eqn. 1). In other terms, it appears that half of the metal reactant serves the halide/O exchange, whereas the remaining aliquot is employed to form the anion within **2-3**. NbOF₃ was easily separated by precipitation and characterized by IR spectroscopy (typical band at 995 cm⁻¹),^[24] thus allowing the isolation of **2**.



X = F, Cl

Both anions [NbCl₆]⁻ (δ = 8.8 ppm)^[25] and [NbOCl₄]⁻ (δ = -343 ppm)^[26] were identified by ⁹³Nb NMR in the reaction system CPh₃COOH/NbCl₅, but the isolation of a well-defined product was not possible in this case. The IR spectrum of the solid residue suggested the presence of NbOCl₃ (broad absorption at 780 cm⁻¹).^[27]

In order to cleanly generate **3**, CPh₃COCl was prior generated from CPh₃COOH and PCl₅, and then allowed to react with NbCl₅ (Scheme 1e).

Compounds **1-3** were characterized by elemental analysis, IR and multinuclear NMR spectroscopy. Salient data are represented by IR band due to the Mo=O moiety in **1** ($\nu = 993 \text{ cm}^{-1}$)^[28] and ^{19}F NMR resonance related to the $[\text{NbF}_6]^-$ anion in **2** (decet centred at 102 ppm).^[29] Furthermore, the solid state structures of **1** and **2** were elucidated by single crystal X-ray diffraction studies. Views of these structures are shown in Figures 1 and 2, while relevant bonding parameters are reported in Tables 1-2.

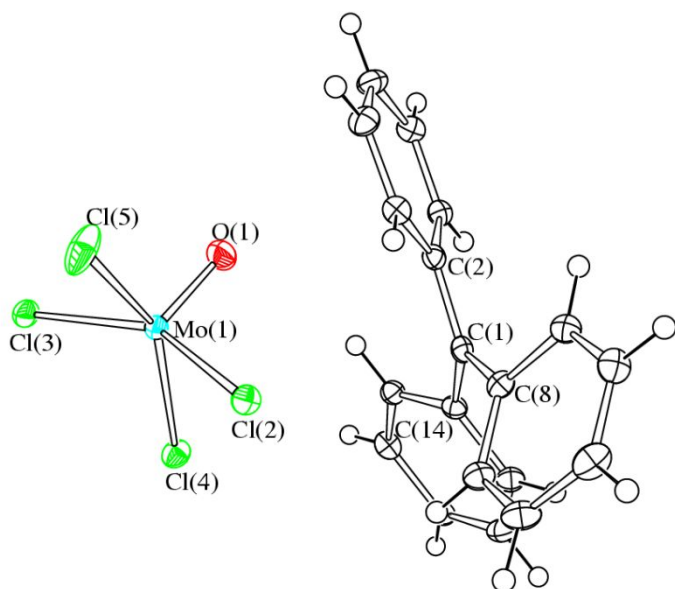


Figure 1. Molecular structure of $[\text{CPh}_3][\text{MoOCl}_4]$, **1**, with key atoms labelled. Thermal ellipsoids are at the 50% probability level.

Table 1. Selected bond distances (\AA) and angles ($^\circ$) for **1**.

Mo(1)–O(1)	1.6549(14)	Mo(1)–Cl(2)	2.3527(5)
Mo(1)–Cl(3)	2.3484(5)	Mo(1)–Cl(4)	2.3427(5)
Mo(1)–Cl(5)	2.3320(6)	C(1)–C(2)	1.444(2)
C(1)–C(8)	1.455(2)	C(1)–C(14)	1.442(2)
O(1)–Mo(1)–Cl(2)	105.27(5)	O(1)–Mo(1)–Cl(3)	104.49(5)
O(1)–Mo(1)–Cl(4)	105.66(5)	O(1)–Mo(1)–Cl(5)	105.51(6)
Cl(2)–Mo(1)–Cl(3)	150.226(17)	Cl(4)–Mo(1)–Cl(5)	148.82(2)
C(2)–C(1)–C(8)	119.34(15)	C(2)–C(1)–C(14)	121.35(15)
C(8)–C(1)–C(14)	119.31(15)		

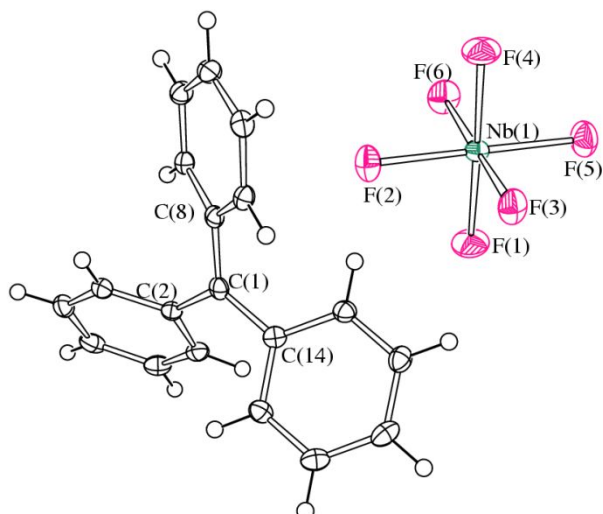


Figure 2. Molecular structure of $[\text{CPh}_3][\text{NbF}_6]$, **2**, with key atoms labelled. Thermal ellipsoids are at the 50% probability level.

Table 2. Selected bond distances (Å) and angles (°) for **2**.

Nb(1)–F(1)	1.8698(13)	Nb(1)–F(2)	1.8963(13)
Nb(1)–F(3)	1.8885(13)	Nb(1)–F(4)	1.8774(13)
Nb(1)–F(5)	1.8919(14)	Nb(1)–F(6)	1.8892(13)
C(1)–C(2)	1.447(3)	C(1)–C(8)	1.440(3)
C(1)–C(14)	1.452(3)		
F(1)–Nb(1)–F(4)	178.25(6)	F(2)–Nb(1)–F(5)	179.20(5)
F(3)–Nb(1)–F(6)	178.39(6)	C(2)–C(1)–C(8)	120.79(18)
C(2)–C(1)–C(14)	118.87(18)	C(8)–C(1)–C(14)	120.29(18)

The solid state structure of **1** is an ionic packing of $[\text{CPh}_3]^+$ cations and $[\text{MoOCl}_4]^-$ anions. The former cation has been previously characterized with miscellaneous anions showing very similar bonding parameters.^[30] The $[\text{MoOCl}_4]^-$ anion displays a distorted square-pyramidal structure as previously found in other $[\text{MoOCl}_4]^-$ salts.^[17^a, 28^f, 31] The Mo(1)–O(1) bond [1.6549(14) Å] reveals a strong π -character, as expected for a Mo(V)=O unit.^[32] The $[\text{MoOCl}_4]^-$ anions may be found in the solid state in different forms: (A) isolated anions; (B) weak intermolecular adducts with a donor atom of the cation or the co-crystallized solvent molecule; (C) dimeric $\{[\text{MoOCl}_4]^- \}_2$ units; (D) infinite $\{[\text{MoOCl}_4]^- \}_\infty$ chains.^[31] In the case of **1**, the $[\text{MoOCl}_4]^-$ anions are isolated (A). The solid state structure of **2** consists of an ionic packing of $[\text{CPh}_3]^+$ cations and $[\text{NbF}_6]^-$ anions,^[15^b, 25^c, 33] which have been previously described in the literature.

The study of the reactivity of triphenylacetic acid with metal halides was extended to titanium tetrachloride. The 1:1 molar reaction afforded a complicated mixture of products. Fractional crystallization of the raw material afforded a 18% yield of the crystalline salt $[\text{CPh}_3][\text{Ti}_2\text{Cl}_8(\text{O}_2\text{CCPh}_3)]$, **4**. This outcome indicates that TiCl_4 exhibits a hybrid behaviour towards triphenylacetic acid, the latter being partially converted into carboxylate and partially decarbonylated, thus determining the non-selectivity of the reaction. The scarcely soluble compound **4** was characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction. The solid state structure of **4** consists of an ionic packing of $[\text{CPh}_3]^+$ cations and $[\text{Ti}_2\text{Cl}_8(\text{O}_2\text{CCPh}_3)]^-$ anions. The latter anion is unprecedented and closely related to the previously reported neutral species $\text{Ti}_2\text{Cl}_7(\text{O}_2\text{CR})(\text{RCOOH})$ ($\text{R} = p\text{-C}_6\text{H}_4\text{Cl}$, $\text{CH}=\text{CHMe}$),^[34] wherein a terminal chloride ligand has been replaced by a O-bonded CPh_3COO fragment. Thus, $[\text{Ti}_2\text{Cl}_8(\text{O}_2\text{CCPh}_3)]^-$ is a dimeric anion, composed by two distorted octahedral $\text{Ti}(\text{IV})$ centres, each bonded to three terminal and two μ -bridging chlorides as well as the O-atom of a bridging $[\text{Ph}_3\text{CCOO}]^-$ carboxylate ligand. All bonding parameters closely resemble those reported in the case of $\text{Ti}_2\text{Cl}_7(\text{O}_2\text{CR})(\text{RCOOH})$.^[34] The carboxylate ligand gives rise to a strong IR absorption at 1644 cm^{-1} , to be compared with the value 1693 cm^{-1} , characteristic of CPh_3COOH .

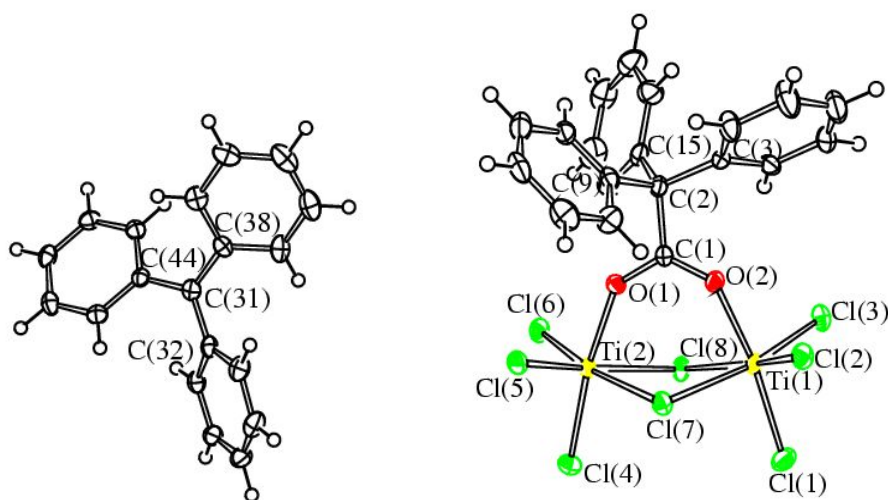


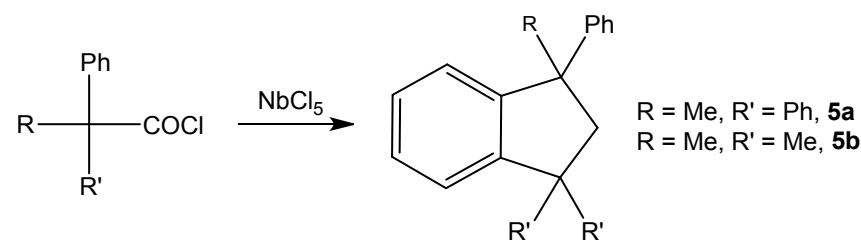
Figure 3. Molecular structure of $[\text{CPh}_3][\text{Ti}_2\text{Cl}_8(\text{OCCPh}_3)]$, **4**, with key atoms labelled. Thermal ellipsoids are at the 50% probability level.

Table 3. Selected bond distances (Å) and angles (°) for **4**.

Ti(1)–O(2)	2.008(4)	Ti(2)–O(1)	2.000(3)
Ti(1)–Cl(1)	2.2406(16)	Ti(2)–Cl(4)	2.2402(16)
Ti(1)–Cl(2)	2.2165(16)	Ti(2)–Cl(5)	2.2205(16)
Ti(1)–Cl(3)	2.2368(16)	Ti(2)–Cl(6)	2.2272(16)
Ti(1)–Cl(7)	2.4790(15)	Ti(2)–Cl(7)	2.4835(15)
Ti(1)–Cl(8)	2.5054(15)	Ti(2)–Cl(8)	2.5051(15)
C(1)–O(1)	1.262(6)	C(1)–O(2)	1.249(6)
C(1)–C(2)	1.534(7)	C(2)–C(3)	1.550(7)
C(2)–C(9)	1.536(7)	C(2)–C(15)	1.560(7)
C(31)–C(32)	1.447(7)	C(31)–C(38)	1.433(7)
C(31)–C(44)	1.454(7)		
O(2)–Ti(1)–Cl(1)	170.42(11)	O(1)–Ti(2)–Cl(4)	171.96(11)
Cl(2)–Ti(1)–Cl(8)	166.45(6)	Cl(5)–Ti(2)–Cl(8)	165.76(6)
Cl(3)–Ti(1)–Cl(7)	168.12(6)	Cl(6)–Ti(2)–Cl(7)	168.41(6)
Cl(2)–Ti(1)–Cl(3)	99.84(6)	Cl(5)–Ti(2)–Cl(6)	101.52(6)
Cl(7)–Ti(1)–Cl(8)	79.15(5)	Cl(7)–Ti(2)–Cl(8)	79.07(5)
Ti(1)–Cl(7)–Ti(2)	97.73(5)	Ti(1)–Cl(8)–Ti(2)	96.48(5)
Ti(1)–O(2)–C(1)	141.4(3)	Ti(2)–O(1)–C(1)	140.1(3)
O(1)–C(1)–O(2)	123.2(5)	O(1)–C(1)–C(2)	116.7(4)
O(2)–C(1)–C(2)	120.1(4)	C(1)–C(2)–C(3)	109.8(4)
C(1)–C(2)–C(9)	105.4(4)	C(1)–C(2)–C(15)	110.3(4)
C(32)–C(31)–C(38)	119.8(5)	C(32)–C(31)–C(44)	118.7(5)
C(38)–C(31)–C(44)	119.8(5)		

2. Decarbonylation reactions and activation reactions of mono- and diphenylacetic acids.

The reactions of $\text{CMePh}_2\text{COCl}$ and $\text{CMe}_2\text{PhCOCl}$ with NbCl_5 proceed as reported in Scheme 2 affording the indanes **5a-b**, which were isolated in good yields (after hydrolysis of the mixtures and subsequent alumina filtration of the organic phases) and characterized analytically and spectroscopically. Compound **5b** was also obtained, although in a lower yield, by using NbOCl_3 in the place of NbCl_5 .



Scheme 2. Synthesis of indanes by reaction of phenylacetic acids with NbCl_5 .

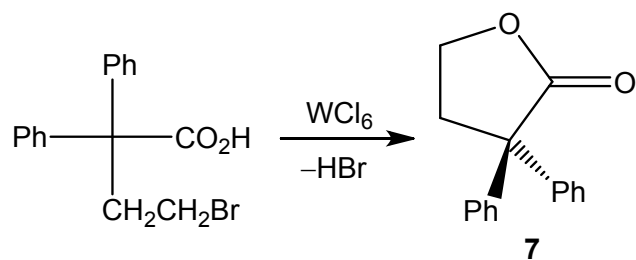
Indanes were previously obtained by elaborated protocols consisting in dimerization of cyclobutenes constructed by coupling of C_2 blocks.^[35]

The reactivity of diphenylacetic acid was investigated towards NbCl_5 and WCl_6 . Both reactions failed to produce decarbonylation products, and instead evidenced the typical reactivity of the two chlorides towards carboxylic acids.^[17^b, c, 21^a, 36] Thus, $\text{NbCl}_4(\text{O}_2\text{CCHPh}_2)$, **6**, was isolated in good yield and fully characterized (Eqn. 2), while CHPh_2COCl was the only species NMR detected in the WCl_6/acid reaction solution (Eqn. 3).



It is presumable that the relative instability of the carbocation $[\text{CHPh}_2]^+$ ^[37] is responsible for not observing decarbonylation from diphenylacetic acid.^[22]

The interaction of 4-bromo-2,2-diphenylbutyric acid with WCl_6 led to cyclization of the organic substrate via HBr release, affording **7** in high yield. In this case, the presence of bromine as a β -substituent is the key for inhibiting the decarbonylation pathway.



The product **7** was purified by alumina chromatography and characterized by analytical and spectroscopic techniques, and its identity confirmed by X-ray diffraction (Figure S1 and Table S1). The ester group manifests itself with a strong IR absorption at 1762 cm^{-1} and a ^{13}C NMR resonance at 177.8 ppm .

Finally, the reaction of WCl_6 with an alkynyl carboxylic acid, i.e. $\text{MeC}\equiv\text{CCOOH}$, was investigated in dichloromethane. This reaction resulted in the prevalent hydrochlorination of the triple carbon-carbon

bond, affording $\text{MeC}(\text{Cl})=\text{CHCOOH}$, **8**, which was identified by IR and NMR spectroscopy and X-ray diffraction (Figure S2 and Table S2).

Conclusions

The carboxylic acid function, in organic chemistry, can act as a leaving one, with elimination of either carbon dioxide or, less frequently, carbon monoxide. The decarbonylation reactions, leading to alkenes or C–C coupling products, are usually promoted by low valent transition metal compounds and take place under harsh conditions (typically, temperatures above 150 °C).^[22]

We have previously found that the decarbonylation pathway is straightforward for α -phenylacetic acids at room temperature in the presence of WCl_6 , through the preliminary formation of the related carboxylic acid chlorides. Herein, we have demonstrated that this non-conventional mode of reactivity has some general character, thus working with a series of homoleptic halides of high valent transition metals belonging to groups 4-6. However, a minimum oxidation state of +5 for the metal centre seems necessary to make the reaction selective. It should be remarked that triphenylacetic acid typically reacts with low- or medium valent transition metal chlorides affording metal triphenyl-acetates via HCl elimination.^[19] Our results indicate that the α -carbon in the carboxylic acid must be fully substituted in order to permit the CO release and the relative stabilization of the descending radical cation, and that the substitution at the β -carbon may also play an important role. The radical cations may then be converted *in situ* into indanes depending on the specific stability/chemistry of the former.

This paper confirms the potential of high valent transition metal halides as promoters of valuable organic transformations, in view of their possible dual role as halogenating agents and oxidants.

Experimental Section.

Methods and materials. *Warning:* all the metal products reported in this paper are highly moisture-sensitive, thus rigorously anhydrous conditions were required for the reaction and crystallization procedures. The reaction vessels were oven dried at 140 °C prior to use, evacuated (10^{-2} mmHg) and then filled with argon. MoCl_5 (99.6% purity), NbCl_5 (99+%), NbF_5 (99.5%) and TiF_4 (98%) were purchased from Strem and stored in sealed tubes under argon atmosphere. TiCl_4 (99.0+%) and carboxylic acids (>97%) were purchased from Sigma-Aldrich or TCI Europe and stored under argon atmosphere as received. WOCl_4 ^[38] and NbOCl_3 ^[27] were prepared according to the literature. Once isolated, the metal products were conserved in sealed glass tubes under nitrogen. Solvents (Sigma-Aldrich) were distilled before use from appropriate drying agents. Infrared spectra were recorded at 298 K on a FT IR-Perkin Elmer Spectrometer, equipped with a UATR sampling accessory. NMR spectra were recorded at 293 K on a Bruker Avance II DRX400 instrument equipped with a BBFO broadband probe. The chemical shifts for ^1H and ^{13}C were referenced to the non-deuterated aliquot of the solvent; the chemical shifts for ^{19}F and ^{93}Nb were referenced, respectively, to CFCl_3 and $[\text{NEt}_4][\text{NbCl}_6]$ as external references. Gas-chromatographic analyses were carried out on a Dani 3200 instrument, equipped with capillary column with molecular sieves (2m; 0.25in ID), using Ar at $p = 1.5$ atm as a gas carrier, at 50 °C. Carbon and hydrogen analyses were performed on a Vario MICRO cube instrument (Elementar). The chloride content was determined by the Mohr method^[39] on solutions prepared by dissolution of the solids in aqueous KOH at boiling temperature, followed by cooling down to ambient temperature and addition of HNO_3 up to neutralization. Titanium content was determined spectrophotometrically by measuring the 410 nm absorbance of an aqueous solution after treatment with few drops of 30% aqueous H_2O_2 (UV-VIS spectrum was recorded with Perkin-Elmer Lambda EZ201 spectrophotometer at 293 K).

Reaction of MoCl₅ with triphenylacetic acid: synthesis of [CPh₃][MoOCl₄], 1. A suspension of MoCl₅ (0.250 g, 0.915 mmol) in CH₂Cl₂ (15 mL) was treated with CPh₃COOH (0.270 g, 0.936 mmol). The mixture was stirred at ambient temperature for 18 hours, then the final brown solution was concentrated to *ca.* 3 mL and added of hexane (30 mL). The resulting precipitate was washed with pentane (20 mL) and dried under vacuum: compound **1** was isolated as a dark-red powder. Yield 0.359 g, 79%. Anal. Calcd for C₁₉H₁₅Cl₄MoO: C, 45.91; H, 3.04; Cl, 28.53. Found: C, 46.06; H, 3.02; Cl, 28.31. IR (solid state): ν/cm^{-1} = 3062vw, 1579vs, 1479m, 1446s, 1385w, 1352vs, 1292s, 1180m, 1169m, 1098w, 1029w, 993vs (Mo=O), 976w, 949w, 913w, 841w-m, 803m, 768m-sh, 762m, 697vs, 684s. ¹H NMR (CD₂Cl₂): δ/ppm = 8.5, 8.1 (br, Ph). ¹³C{¹H} NMR (CD₂Cl₂): δ/ppm = 211.6 (CPh₃), 148.3, 147.5, 141.3, 135.1 (Ph). Crystals of **1** suitable for X-ray analysis were collected from a dichloromethane reaction solution layered with hexane and settled aside at -30°C for one week.

Reaction of NbF₅ with triphenylacetic acid: synthesis of [CPh₃][NbF₆], 2, and NbOF₃. The reaction of NbF₅ (0.200 g, 1.06 mmol) with CPh₃COOH (0.154 g, 0.534 mmol) was carried out with a procedure analogous to that described for MoCl₅/CPh₃COOH. The final yellow solution was separated from a pale-yellow precipitate by filtration. IR analysis on the precipitate clearly evidenced the presence of a strong band at 995 cm⁻¹ ($\nu_{\text{Nb=O}}$, NbOF₃). Compound **2** was recovered from the solution as a yellow solid after work-up. Yield 0.167 g, 70%. Crystals of **2** suitable for X-ray analysis were collected from a dichloromethane reaction solution layered with hexane and stored at -30°C for one week. Anal. Calcd for C₁₉H₁₅F₆Nb: C, 50.69; H, 3.36; Nb, 20.64. Found: C, 50.64; H, 3.41; Nb, 20.43. IR (solid state): ν/cm^{-1} = 2958w, 2925w, 1581vs, 1483m, 1449s, 1355vs, 1294s, 1186m, 1169w-m, 1030w, 995w-m, 982w-br, 914w, 846m, 837m, 806m, 765m, 733w, 699vs. ¹H NMR (CD₃CN): δ/ppm = 8.30, 7.88, 7.76 (m, CPh₃). ¹³C{¹H} NMR (CD₃CN): δ/ppm = 212.0 (CPh₃), 143.1, 140.2, 130.1 (Ph). ¹⁹F NMR

(CD₃CN): $\delta/\text{ppm} = 102$ (decet, $^1J_{\text{NbF}} = 3.4 \cdot 10^2$ Hz, NbF₆⁻). ⁹³Nb NMR (CD₃CN): $\delta/\text{ppm} = -1556$ (hept, $^1J_{\text{NbF}} = 3.4 \cdot 10^2$ Hz, NbF₆⁻).

Reaction of NbCl₅ with triphenylacetic acid: identification of [CPh₃]⁺, [NbCl₆]⁻, [NbOCl₄]⁻ and

NbOCl₃. The reaction of NbCl₅ (0.110 g, 0.407 mmol) with CPh₃COOH (0.125 g, 0.433 mmol) was carried out with in CD₂Cl₂ (5 mL). The reaction solution was analyzed by NMR spectroscopy after 72 hours. ¹H NMR (CD₂Cl₂): $\delta/\text{ppm} = 8.31$ (t, $^3J_{\text{HH}} = 7.4$ Hz, 3 H, [CPh₃]⁺_{para}); 7.94 (t, $^3J_{\text{HH}} = 7.6$ Hz, 6 H, [CPh₃]⁺_{meta}); 7.73 (d, J = 7.5 Hz, 6 H, [CPh₃]⁺_{ortho}); 7.32-7.27 (m, CPh₃Cl). ¹³C{¹H} NMR (CD₂Cl₂): $\delta/\text{ppm} = 210.7$ (CPh₃), 143.5, 142.8, 140.0, 130.7 (Ph). ⁹³Nb NMR (CD₂Cl₂): $\delta/\text{ppm} = 6.6$ ($\Delta\nu^{1/2} = 138$ Hz, NbCl₆⁻); -107.2 ($\Delta\nu^{1/2} = 142$ Hz, minor); -358 ($\Delta\nu^{1/2} = 2 \cdot 10^3$ Hz, NbOCl₄⁻); -588 ($\Delta\nu^{1/2} = 6 \cdot 10^4$ Hz, minor). Ratio NbCl₆⁻/NbOCl₄⁻ $\cong 2 : 5$. The IR spectrum of the solid residue obtained by elimination of volatile materials appeared as follows. IR (solid state): $\nu/\text{cm}^{-1} = 3059\text{vw}$, 1579vs, 1481s, 1447m-s, 1353vs, 1293s, 1183m, 1165w, 1083w, 994m, 835m-sh, 804m, 780br ($\nu_{\text{Nb=O}}$, NbOCl₃), 763s, 696vs.

Reaction of NbCl₅ with triphenylacetic acid chloride: synthesis of [CPh₃][NbCl₆], 3. A solution of CPh₃COOH (172 mg, 0.60 mmol) in CD₂Cl₂ (5 mL) was treated with PCl₅ (123 mg, 0.59 mmol). The mixture was left stirred at ambient temperature for 3 hours. Then NbCl₅ (155 mg, 0.57 mmol) was added, and the resulting mixture was stirred at ambient temperature for 48 hours. The volatiles were removed under vacuum, the residue was repeatedly washed with hexane (3 x 20 mL) and then dried under vacuum. Anal. Calcd for C₁₉H₁₅Cl₆Nb: C, 41.57; H, 2.75; Cl, 38.75. Found: C, 41.03; H, 2.88; Cl, 38.66. ¹H NMR (CD₂Cl₂): $\delta/\text{ppm} = 8.27$, 7.90, 7.71 (m, 15 H, Ph). ¹³C{¹H} NMR (CD₂Cl₂): $\delta/\text{ppm} = 211.5$ (CPh₃), 143.6, 140.8, 131.4, 128.5 (Ph). ⁹³Nb NMR (CD₂Cl₂): $\delta/\text{ppm} = 7.0$ (NbCl₆⁻).

Reactions of $\text{WOCl}_4/\text{TiF}_4$ with triphenylacetic acid: identification of $[\text{CPh}_3]^+$. The reactions of TiF_4 or WOCl_4 (ca. 1 mmol) with 0.5 eq. of CPh_3COOH was carried out with a procedure analogous to that described for $\text{MoCl}_5/\text{CPh}_3\text{COOH}$. The final mixture was eliminated of the volatile materials, then the resulting residue was dried under vacuum.

From TiF_4 . IR (yellow solid): $\nu/\text{cm}^{-1} = 3061\text{vw}, 1581\text{s}, 1485\text{m}, 1446\text{m}, 1357\text{s}, 1295\text{w}, 1187\text{w}, 866\text{m}, 796\text{vs}, 758\text{s}, 731\text{s}, 694\text{vs}$. $^1\text{H NMR}$ (CD_3CN): $\delta/\text{ppm} = 8.30, 7.89, 7.72$ (m, CPh_3).

From WOCl_4 . IR (orange solid): $\nu/\text{cm}^{-1} = 3060\text{vw}, 1579\text{vs}, 1481\text{s}, 1447\text{m-s}, 1353\text{vs}, 1293\text{s}, 1183\text{m}, 1165\text{w-m}, 1083\text{w}, 974\text{m}, 832\text{m}, 804\text{m}, 760\text{s}, 696\text{vs}$. $^1\text{H NMR}$ (CD_2Cl_2): $\delta/\text{ppm} = 8.20, 7.89, 7.67$ ppm (m, CPh_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta/\text{ppm} = 210.2$ (CPh_3), 143.4, 142.9, 140.1, 130.9 (Ph).

Reaction of TiCl_4 with triphenylacetic acid: isolation of $[\text{CPh}_3][\text{Ti}_2\text{Cl}_8(\mu-\kappa^2\text{-O}_2\text{CCPh}_3)]$, **4.** The reaction of CPh_3COOH (0.280 g, 0.971 mmol) with TiCl_4 (1.0 M solution in heptane, 0.97 mL) was carried out with a procedure analogous to that described for $\text{MoCl}_5/\text{CPh}_3\text{COOH}$. IR and NMR analyses on the obtained orange solid residue suggested the formation of a complicated mixture of products. Yellow crystals of **3** suitable for X-ray analysis were isolated from a CH_2Cl_2 reaction mixture layered with hexane and settled aside at $-30\text{ }^\circ\text{C}$ for 72 h. Yield 0.080 g, 18%. Anal. Calcd for $\text{C}_{39}\text{H}_{30}\text{Cl}_8\text{O}_2\text{Ti}_2$: C, 51.47; H, 3.32; Cl, 31.17; Ti, 10.52. Found: C, 51.35; H, 3.28; Cl, 31.05; Ti, 10.64. IR (solid state): $\nu/\text{cm}^{-1} = 3059\text{w}, 3023\text{w}, 1644\text{s}(\nu_{\text{COO}}), 1580\text{w}, 1537\text{s}, 1493\text{s}, 1446\text{m}, 1365\text{s}, 1334\text{m}, 1264\text{w}, 1191\text{w}, 1160\text{w}, 1085\text{w}, 1034\text{w}, 1002\text{w}, 986\text{w}, 940\text{w}, 904\text{w}, 753\text{s-sh}, 740\text{vs}, 697\text{vs}, 669\text{s}, 658$.

Reaction of NbCl_5 with 2,2-diphenylpropionic acid chloride: synthesis of 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene, **5a, (Chart 1).**^[22,40]

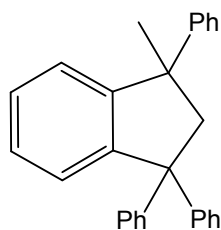


Chart 1. Structure of **5a**.

A solution of CMePh₂COOH (229 mg, 1.01 mmol) in dichloromethane (10 mL) was treated with PCl₅ (209 mg, 1.00 mmol), and the resulting mixture was left stirring at ambient temperature for 2 hours. Then NbCl₅ (91 mg, 0.34 mmol) was added, and the mixture was stirred for additional 48 hours. An excess of H₂O (ca. 5 mmol) was added to the final solution, and the so obtained mixture was stirred for 12 hours. Afterwards the organic phase was separated and filtered through an alumina column using diethyl ether as eluent. The product was isolated as a colourless solid upon removal of the volatiles under vacuum. Yield 176 mg, 97%. ¹H NMR (CD₂Cl₂): δ/ppm = 7.49-7.14 (19 H, arom CH); 3.60, 3.28 (d, ²J_{HH} = 13.52 Hz, 2 H, CH₂); 1.71 (s, 3 H, Me). ¹³C {¹H} NMR (CD₂Cl₂): δ/ppm = 150.6, 149.4, 148.9, 148.6, 147.5 (arom + CPh₂); 128.8, 128.7, 128.0, 127.9, 127.6, 127.4, 126.9, 126.0, 125.7, 125.6, 125.1 (arom); 61.4 (CH₂); 51.2 (Me).

Reaction of niobium chlorides with 2-methyl-2-phenylpropanoic acid chloride: synthesis of 1,1,3-trimethyl-3-phenyl-2,3-dihydro-1H-indene, 5b, (Chart 2).^[22,41]

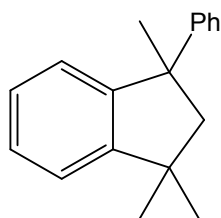


Chart 2. Structure of **5b**.

A solution of $\text{CMe}_2\text{PhCOOH}$ (154 mg, 0.94 mmol) in dichloromethane (10 mL) was treated with PCl_5 (200 mg, 0.96 mmol). The resulting solution was left stirring at ambient temperature for ca. 2 hours. Then NbCl_5 (85 mg, 0.31 mmol) was added, and the mixture was stirred for additional 48 hours. An excess of H_2O (ca. 5 mmol) was added to the final solution, and the so obtained mixture was stirred for 12 hours. Afterwards the organic phase was separated and filtered through an alumina column using diethyl ether as eluent. The product was isolated as a colourless solid upon removal of the volatiles under vacuum and characterized by elemental analysis and ^1H NMR. Yield 88 mg, 79%.

In a different experiment, a dichloromethane solution of freshly prepared 2-methyl-2-phenylpropanoyl chloride was added of 1 eq. of NbOCl_3 , and the mixture was left stirring at ambient temperature for 5 days. Treatment with water and successive work-up were performed as described above. In this case. the title product was isolated in 70% yield.

Reactions of CHPh_2COOH with metal chlorides.

A) Synthesis of $\text{NbCl}_4(\text{O}_2\text{CCHPh}_2)$, **6.** A solution of $\text{CH}(\text{Ph})_2\text{COOH}$ (230 mg, 1.08 mmol) in CH_2Cl_2 (10 mL) was added of NbCl_5 (292 mg, 1.08 mmol). The mixture was stirred at room temperature for 18 hours. The resulting red solution was eliminated of the volatiles, then the residue was washed with hexane (2 x 10 mL) and dried under vacuum. A red solid was obtained. Yield 338 mg, 70%. Anal. Calcd for $\text{C}_{14}\text{H}_{11}\text{Cl}_4\text{NbO}_2$: C, 37.71; H, 2.49; Cl, 31.80. Found: C, 37.25; H, 2.50; Cl, 31.70. IR (solid state): $\nu/\text{cm}^{-1} = 3060\text{w}, 3027\text{w}, 1579\text{s}, 1481\text{m}, 1447\text{m}, 1416\text{m}, 1354\text{s}, 1295\text{m}, 1261\text{w-m}, 1180\text{m}, 1079\text{w}, 1000\text{w}, 995\text{w}, 978\text{w}, 920\text{w}, 800\text{vs-br}, 733\text{vs}, 694\text{vs}$. ^1H NMR (CD_2Cl_2): $\delta/\text{ppm} = 7.44\text{-}7.12$ (10 H, Ph); 5.37 (s, 1 H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta/\text{ppm} = 167.2$ (OCO); 143.5-126.1 (Ph); 59.1 (CH). ^{93}Nb NMR (CDCl_3): $\delta/\text{ppm} = -234$ ($\Delta\nu^{1/2} = 2.7 \cdot 10^3$ Hz).

B) Formation of CHPh_2COCl . A solution of $\text{CH}(\text{Ph})_2\text{COOH}$ (269 mg, 1.27 mmol) in CD_2Cl_2 (2 mL) was added of WCl_6 (251 mg, 0.633 mmol). A light red solution formed after 18 hours, which was

analyzed by NMR spectroscopy. The analysis clearly evidenced the formation of $\text{CH}(\text{Ph})_2\text{C}(\text{O})\text{Cl}$,^[42] in admixture with a secondary, non-identified species [^1H : $\delta/\text{ppm} = 7.50\text{-}7.38$ (Ph), 5.40 (CH); $^{13}\text{C}\{^1\text{H}\}$: $\delta/\text{ppm} = 182.3$ (C=O), 136.4 (*ipso*-Ph), 129.1, 128.8, 128.2 (Ph), 57.2 (CH)]. The solution was dried under vacuum, then the residue was characterized by IR spectroscopy. IR (solid state): $\nu/\text{cm}^{-1} = 1702\text{s}, 1659\text{s}, 1599\text{s}, 1581\text{s}$.

Reactions of WCl_6 with 4-bromo-2,2-diphenylbutyric acid: synthesis of 3,3-diphenyldihydrofuran-2(3H)-one, 7, (Chart 3).^[43]

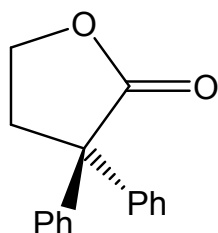


Chart 3. Structure of 7.

The title compound was obtained by a procedure similar to that described for **5a**, from WCl_6 (188 mg, 0.474 mmol) and $\text{CPh}_2(\text{CH}_2\text{CH}_2\text{Br})\text{COOH}$ (303 mg, 0.949 mmol), reaction time: 26 h. The product was isolated as colourless crystals upon crystallization from a diethyl ether/pentane mixture, at $-30\text{ }^\circ\text{C}$. Yield 197 mg, 72%. Anal. Calcd for $\text{C}_{16}\text{H}_{14}\text{O}_2$: C, 80.65; H, 5.92. Found: C, 79.75; H, 5.80. IR (solid state): $\nu/\text{cm}^{-1} = 3056\text{w}, 2988\text{w}, 2912\text{w}, 1762\text{vs}$ (C=O), 1596w, 1493m, 1446m, 1369m, 1340w, 1322w, 1226w, 1207w, 1160s, 1090w-m, 1021s, 1000w-m, 954m, 916w, 897w, 834w, 772m, 753s, 725w, 698vs, 675m. ^1H NMR (CDCl_3): $\delta/\text{ppm} = 7.44\text{-}7.29$ (10 H, Ph); 4.25 (t, 2 H, $J = 6.36$ Hz, Ph_2CCH_2); 2.98 (t, 2 H, $J = 6.36, 6.85$ Hz, CH_2Br). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): $\delta/\text{ppm} = 177.8$ (C=O); 140.8 (*ipso*-Ph); 128.8, 127.7, 127.6 (Ph); 65.3 (Ph_2CCH_2); 56.5 (CPh_2); 37.5 (CH_2Br).

Reaction of MeC≡CCOOH with WCl₆: synthesis of MeC(Cl)=CHCOOH, **8.** MeC≡CCOOH (85 mg, 1.01 mmol) and WCl₆ (415 mg, 1.05 mmol) were allowed to react in dichloromethane (30 mL) at room temperature for 7 days. During this period, the progress of the reaction was evaluated by NMR analysis performed on aliquots of the reaction mixture. The final dark red/brown solution was treated with water. The organic phase was then recovered by filtration, and after removal of the volatiles, **8** was recovered as a dark brown solid. Yield 88 mg, 72%. Anal. Calcd. for C₄H₅ClO₂: C, 39.86; H, 4.18; Cl, 29.41; O, 26.55. Found: C, 39.71; H, 4.23; Cl, 29.11; O, 26.38. ¹H NMR (CDCl₃): δ/ppm = 9.2 (br); 6.14, 6.09 (s, 1H, CH *cis* + *trans*); 2.62, 2.33 (s, 3 H, Me *cis* + *trans*). ¹³C{¹H} NMR (CDCl₃): δ/ppm = 170.0, 169.2 (C=O *cis* + *trans*); 155.79, 149.50 (=CCl *cis* + *trans*); 118.74, 116.35 (=CH *cis* + *trans*); 28.73, 24.17 (Me *cis* + *trans*).

X-ray quality crystals of **8** were collected from a concentrated solution of the crude product in hexane, stored at -30°C.

Gas chromatographic analyses.

A mixture of metal compound (ca. 1 mmol) and the appropriate carboxylic acid (1 eq.) in CH₂Cl₂ (10 mL) was stirred at ambient temperature for 72 hours in a Schlenk tube tapped with a silicon stopper. An aliquot of the reaction atmosphere was withdrawn by a 1 mL syringe through the stopper and injected into the GC instrument. The yields of CO formation were estimated based on analyses of gaseous standard mixtures containing known amounts of CO. From MoCl₅/CPh₃COOH: 45%; from NbF₅/CPh₃COOH: 38%; from NbCl₅/CPh₃COOH: 39%; from TiF₄/CPh₃COOH: 9.4%; WCl₆/CPh₂(CH₂CH₂Br)COOH: 3.1%; from WCl₆/CHPh₂COOH: 0%.

X-ray Crystallographic studies. Crystal data and collection details for **1**, **2**, **4**·2CH₂Cl₂, **6**, **8**, **A1** and **A2** are reported in Table 4. The diffraction experiments were carried out on a Bruker APEX II

diffractometer equipped with a CCD detector (**1**, **2**, **4**·2CH₂Cl₂) or a PHOTON100 detector (**6**, **8**, **A1**, **A2**) using *Mo-K α* radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).^[44] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2 .^[45] Hydrogen atoms were fixed at calculated positions and refined by a riding model. One CH₂Cl₂ molecule of **4**·2CH₂Cl₂ is disordered and, thus, it has been split into two positions and refined isotropically using one occupancy factor per disordered group. The CH₂Cl₂ molecules of **4**·2CH₂Cl₂ have been restrained to have similar geometries (SAME line in SHELXL; s.u. 0.02) and their C–Cl distances have been restrained to 1.75 Å (s.u. 0.02).

Table 4. Crystal data and experimental details for [CPh₃][MoOCl₄], **1**, [CPh₃][NbF₆], **2**, [CPh₃][Ti₂Cl₈(μ - κ^2 -O₂CCPh₃)], **4**·2CH₂Cl₂, $\overline{\text{C}}(\text{Ph})_2\text{C}(\text{=O})\text{OCH}_2\text{CH}_2$, **6**, MeC(Cl)=CHCOOH, **8**, CPh₂(CH₂CH₂Br)COOH, **A1** and CPh₂(CH₂CH₃)COOH, **A2**.

	1	2	4 ·2CH ₂ Cl ₂	6	A1	A2	8
Formula	C ₁₉ H ₁₅ Cl ₄ MoO	C ₁₉ H ₁₅ F ₆ Nb	C ₄₁ H ₃₄ Cl ₁₂ O ₂ Ti ₂	C ₁₆ H ₁₄ O ₂	C ₁₆ H ₁₅ BrO ₂	C ₁₆ H ₁₆ O ₂	C ₄ H ₅ ClO ₂
F_w	497.05	450.22	1079.88	238.27	319.19	240.29	120.53
λ , Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature, K	100(2)	100(2)	100(2)	100(2)	100(2)	100(2)	292(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	P2 ₁ /n	P2 ₁ /c	P2 ₁ /n	Pc	Pccn	P2 ₁ /n	P2 ₁ /n
a , Å	8.9934(15)	8.5095(15)	17.897(3)	7.3476(6)	14.500(3)	9.062(9)	5.387(15)
b , Å	19.335(3)	12.681(2)	10.5524(18)	15.2022(11)	26.776(6)	14.647(14)	9.02(3)
c , Å	11.3379(19)	16.036(3)	25.825(5)	10.9707(9)	7.1309(15)	9.918(10)	11.16(3)
β , °	98.547(2)	94.183(2)	106.889(2)	91.960(3)	90	96.13(2)	101.87(5)
Cell volume, Å ³	1949.6(6)	1725.9(5)	4666.8(14)	1224.71(17)	2768.6(10)	1309(2)	531(3)
Z	4	4	4	4	8	4	4
D_c , g cm ⁻³	1.693	1.733	1.537	1.292	1.532	1.219	1.509
μ , mm ⁻¹	1.225	0.757	1.064	0.084	2.964	0.079	0.597
$F(000)$	988	896	2176	504	1296	512	248
θ limits, °	2.100 - 26.996	2.050 - 27.000	1.234 - 25.026	1.339 - 25.998	1.597 - 24.997	2.490 - 27.990	2.929 - 24.999
Reflections collected	21352	18372	43028	14249	17881	14653	3721
Independent reflections	4254 [$R_{\text{int}} = 0.0254$]	3763 [$R_{\text{int}} = 0.0335$]	8248 [$R_{\text{int}} = 0.0717$]	4780 [$R_{\text{int}} = 0.0446$]	2442 [$R_{\text{int}} = 0.0841$]	3146 [$R_{\text{int}} = 0.0291$]	925 [$R_{\text{int}} = 0.2230$]
Data / restraints / parameters	4254 / 0 / 226	3763 / 0 / 235	8248 / 27 / 512	4780 / 2 / 325	2442 / 24 / 173	3146 / 0 / 165	925 / 0 / 66
Goodness on fit on F^2	1.104	1.044	1.045	1.070	1.247	1.081	1.081
$R1$ ($I > 2\sigma(I)$)	0.0227	0.0266	0.0617	0.0489	0.0590	0.0458	0.1338
$wR2$ (all data)	0.0560	0.0647	0.1896	0.0995	0.1285	0.1114	0.3275
Largest diff. peak and hole, e.Å ⁻³	0.528 / -0.587	0.365 / -0.458	2.805 / -1.361	0.192 / -0.272	0.867 / -0.805	0.382 / -0.233	0.550 / -0.511

Acknowledgement

We thank the University of Pisa (Fondi di Ateneo) for funding. We are grateful to Mr. Francesco del Cima and Dr. Debora Preti for the execution of GC analyses.

Supporting Information. Spectroscopic data of carboxylic acids, **figures of the IR and NMR spectra of products**. X-ray structures of **6**, **8**, **A1** and **A2**. CCDC reference numbers 1891866 (**1**), 1891867 (**2**), 1891868 (**4**·2CH₂Cl₂), 1891869 (**6**), 1891870 (**8**), 189186671 (**A1**) and 1891872 (**A2**) contain the supplementary crystallographic data for the X-ray studies reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; e-mail: deposit@ccdc.cam.ac.uk).

References and Notes

- [1] Selected references: (a) S. M. Coman, M. Verziu, A. Tirsoaga, B. Jurca, C. Teodorescu, V. Kuncser, V. I. Parvulescu, G. Scholz and E. Kemnitz, *ACS Catal.*, 2015, **5**, 3013-3026. (b) S. Afewerki and A. Còrdova, *Chem. Rev.*, 2016, **116**, 13512-13570. (c) M. M. Rahman, M. D. Smith, J. A. Amaya, T. M. Makris and D. V. Peryshkov, *Inorg. Chem.*, 2017, **56**, 11798-11803. (d) M. Bortoluzzi, E. Ferretti, M. Hayatifar, F. Marchetti, G. Pampaloni and S. Zacchini, *Eur. J. Inorg. Chem.*, 2016, 3838-3845. (e) H. Tsurugi, H. Tanahashi, H. Nishiyama, W. Fegler, T. Saito, A. Sauer, J. Okuda and K. Mashima, *J. Am. Chem. Soc.*, 2013, **135**, 5986-5989.
- [2] (a) N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877-910. (b) F. Marchetti, G. Pampaloni and C. Pinzino, *Chem. Eur. J.*, 2013, **19**, 13962-13969. (c) O. B. Babushkina and S. Ekres, *Electrochim. Acta*, 2010, **56**, 867-877.

-
- [3] (a) K. Hackeloer, G. Schnakenburg and S. R. Waldvogel, *Org. Lett.*, 2011, **13**, 916-919. (b) K. Wehming, M. Schubert, G. Schnakenburg and S. R. Waldvogel, *Chem. Eur. J.*, 2014, **20**, 12463-12469. (c) M. Schubert, S. Trosien, L. Schulz, C. Brandscheid, D. Schollmeyer and S. R. Waldvogel, *Eur. J. Org. Chem.*, 2014, 7091-7094. (d) M. A. Zolfigol, A. R. Moosavi-Zare, P. Arghavani-Hadi, A. Zare, V. Khakyzadeh and G. Darvishi, *RSC Adv.*, 2012, **2**, 3618-3620.
- [4] S. R. Waldvogel and S. Trosien, *Chem. Commun.*, 2012, **48**, 9109-9119.
- [5] L. Ferrand, Y. Tang, C. Aubert, L. Fensterbank, V. Mouriès-Mansuy, M. Petit and M. Amatore, *Org. Lett.*, 2017, **19**, 2062-2065.
- [6] (a) A. Kanazawa, S. Kanaoka and S. Aoshima, *Macromolecules*, 2009, **42**, 3965-3972. (b) I. V. Tatarinova, O. A. Tarasova, M. V. Markova, L. V. Morozova, A. I. Mikhaleva and B. A. Trofimov, *J. Organomet. Chem.*, 2012, **706-707**, 124-127.
- [7] Y. Satoh and Y. Obora, *Eur. J. Org. Chem.*, 2015, 5041-5054, and references therein.
- [8] F. Marchetti, G. Pampaloni and L. Biancalana, *Inorg. Chim. Acta*, 2012, **385**, 135-139.
- [9] D. V. Drobot and E. A. Pisarev, *Russ. J. Coord. Chem.*, 1981, **26**, 1-8.
- [10] M. Bortoluzzi, T. Funaioli, F. Marchetti, G. Pampaloni, C. Pinzino and S. Zacchini, *Chem. Commun.*, 2017, **53**, 364-367.
- [11] N. Bartalucci, M. Bortoluzzi, T. Funaioli, F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2017, **46**, 12780-12784.
- [12] a) E. Solari, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Chem. Commun.*, 1991, 841-843. (b) M. Aresta, A. Dibenedetto, P. Stufano, B. M. Aresta, S. Maggi, I. Pápai, T. A. Rokob and B. Gabriele, *Dalton Trans.*, 2010, **39**, 6985-6992. (c) F. Marchetti, C. Pinzino, S. Zacchini and G. Pampaloni, *Angew. Chem. Int. Ed.*, 2010, **49**, 5268-5272.

-
- [13] See for instance: (a) D. Zhao, K. Chang, T. Ebel, M. Qian, R. Willumeit, M. Yan and F. Pyczak, *J. Mech. Behav. Biomed. Mater.*, 2013, **28**, 171-182. (b) I. Jirka, M. Vandrovcova, O. Frank, Z. Tolde, J. Plsek, T. Luxbacher, L. Bacakova and V. Stary, *Mat. Sci. Eng. C: Mater. Biol. Appl.*, 2013, **33**, 1636-1645.
- [14] (a) L. Ferrand, Y. Tang, C. Aubert, L. Fensterbank, V. Mouriès-Mansuy, M. Petit and M. Amatore, *Org. Lett.*, 2017, **219**, 2062-2065. (b) M. E. Wilhelm, M. H. Antofer, R. M. Reich, V. D'Elia, J.-M. Basset, W. A. Herrmann, M. Cokoja and F. E. Kuhn, *Catal. Sci. Tech.*, 2014, **4**, 1638-1643. (c) F. C. Redshaw, M. Walton, L. Clowes, D. L. Hughes, A.-M. Fuller, Y. Chao, A. Walton, V. Sumerin, P. Elo, I. Soshnikov, W. Zhao and W.-H. Sun, *Chem. Eur. J.*, 2013, **19**, 8884-8899. (d) S. L. Benjamin, W. Levason and G. Reid, *Chem. Soc. Rev.*, 2013, **42**, 1460-1499. (e) F. Marchetti and G. Pampaloni, *Chem. Commun.*, 2012, **48**, 635-653, and references therein. (f) A. M. Raspolli Galletti and G. Pampaloni, *Coord. Chem. Rev.*, 2010, **254**, 525-536, and references therein.
- [15] (a) F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2007, 4343-4351. (b) R. Bini, C. Chiappe, F. Marchetti, G. Pampaloni and S. Zacchini, *Inorg. Chem.*, 2010, **49**, 339-351.
- [16] F. Marchetti, G. Pampaloni and S. Zacchini, *J. Fluorine Chem.*, 2010, **131**, 21-28.
- [17] (a) F. Marchetti, G. Pampaloni and S. Zacchini, *Polyhedron*, 2015, **85**, 369-375. (b) F. Marchetti, G. Pampaloni and S. Zacchini, *Polyhedron*, 2008, **27**, 1969-1976, and references therein. (c) D. A. Brown, W. Errington and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.* **1993**, 1163-1164.
- [18] (a) C. Oldham, *Carboxylates, Squarates and Related Species in Comprehensive Coordination Chemistry*, G. Wilkinson, R. D. Gillard and J. A. McCleverty, Eds., Pergamon Press, Oxford, 1987. (b) R. C. Merhotra and R. Bohra, *Metal Carboxylates*, Academic Press, London, 1983. (c) U. Casellato, P. Vigato and M. Vidali, *Coord. Chem. Rev.*, 1978, **26**, 85-159.

-
- [19] (a) D. M. Roitershtein, A. A. Vinogradov, A. A. Vinogradov, K. A. Lyssenko, Y. V. Nelyubina, I. V. Ananov, I. E. Nifantev, V. A. Yakovlev and N. N. Kostitsyna, *Organometallics*, 2013, **32**, 1272-1286. (b) M. Czakler and U. Schubert, *Inorg. Chim. Acta*, 2018, **471**, 567–569. (c) L. H. Do, S. J. Lippard, *J. Am. Chem. Soc.*, 2011, **133**, 10568-10581. (d) A. Grala, M. Wolska-Pietkiewicz, A. Wojewódzka, M. Dabergut, I. Justyniak and J. Lewiński, *Organometallics*, 2015, **34**, 4959–4964.
- [20] (a) M. Bortoluzzi, F. Marchetti, M. G. Murralli and G. Pampaloni, *Inorg. Chim. Acta*, 2015, **427**, 150-154. (b) A. L. Fuentes de Arriba, L. Simón, C. Raposo, V. Alcázar and J. R. Morán, *Tetrahedron*, 2009, **65**, 4841-4845. (c) K. Griesbaum, A. R. Bandyopadhyay and M. Meister, *Can. J. Chem.*, 1986, **64**, 1553-1559.
- [21] (a) M. Bortoluzzi, F. Guarra, F. Marchetti, G. Pampaloni and S. Zacchini, *Polyhedron*, 2015, **99**, 141–146. (b) N. Bartalucci, L. Biancalana, M. Bortoluzzi, G. Pampaloni, L. Giordano, S. Zacchini and F. Marchetti, *ChemistrySelect*, 2018, **3**, 8844-8848.
- [22] N. Bartalucci, M. Bortoluzzi, S. Zacchini, G. Pampaloni and F. Marchetti, *Dalton Trans.*, 2019, **48**, 1574-1577.
- [23] G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Bastien and E. B. Baker, *J. Am. Chem. Soc.*, 1963, **85**, 1328-1334.
- [24] (a) J. Köhler, A. Simon, L. van Wüllen, S. Cordier, T. Roisnel, M. Poulain and M. Somer, *Z. Anorg. Allg. Chem.*, 2002, **628**, 2683-2690. (b) W. Levason, G. Reid, J. Trayer and W. Zhang, *Dalton Trans.*, 2014, **43**, 3649-3659. (c) M. Bortoluzzi, E. Ferretti, F. Marchetti, G. Pampaloni and S. Zacchini, *J. Coord. Chem.*, 2016, **69**, 2766–2774.
- [25] (a) M. Bortoluzzi, M. Hayatifar, F. Marchetti, G. Pampaloni and S. Zacchini, *Inorg. Chem.*, 2015, **54**, 4047-4055. (b) S. L. Benjamin, Y.-P. Chang, C. Gurnani, A. L. Hector, M. Huggon, W. Levason and G. Reid, *Dalton Trans.*, 2014, **43**, 16640-16648. (c) W. Levason, M. E. Light, G.

- Reid and W. Zhang, *Dalton Trans.*, 2014, **43**, 9557-9566. (d) F. Marchetti and G. Pampaloni, *Inorg. Chim. Acta*, 2011, **376**, 123–128. (e) F. Marchetti, G. Pampaloni and S. Zacchini, *RSC Adv.*, 2014, **4**, 60878-60882.
- [26] The solid obtained by reacting NbOCl₃ (0.130 g, 0.604 mmol) with [NBu₄]Cl (0.167 g, 0.601 mmol) for 18 h in CH₂Cl₂ (10 mL), after solvent elimination, was analyzed by ⁹³Nb NMR in CD₂Cl₂. The spectrum consisted of a resonance at $\delta = -350$ ppm ($\Delta\nu^{1/2} = 10^3$ Hz, NbOCl₄⁻).
- [27] V. C. Gibson, T. P. Kee and A. Shaw, *Polyhedron*, 1988, **7**, 2217-2219
- [28] (a) L. Favero, F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2014, **43**, 495-504. (b) B. Modéc, M. Šala and R. Clérac, *Eur. J. Inorg. Chem.*, 2010, 542-553. (c) R. Aguado, J. Escribano, M. R. Pedrosa, A. De Cian, R. Sanz and F. J. Arnàiz, *Polyhedron*, 2007, **26**, 3842-3848. (d) F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2013, **42**, 15226-15234. (e) F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2013, **42**, 2477-2487. (f) M. Bortoluzzi, G. Bresciani, F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2015, **44**, 10030-10037.
- [29] (a) W. Levason, G. Reid and W. Zhang, *J. Fluorine Chem.*, 2015, **172**, 62-67. (b) M. Bortoluzzi, F. Marchetti, G. Pampaloni, M. Pucino and S. Zacchini, *Dalton Trans.*, 2013, **42**, 13054-13064. (c) M. Jura, W. Levason, R. Ratnani, G. Reid and M. Webster, *Dalton Trans.*, 2010, **39**, 883-891. (d) M. Bortoluzzi, E. Ferretti, F. Marchetti, G. Pampaloni and S. Zacchini, *Dalton Trans.*, 2016, **45**, 6939-6948.
- [30] (a) S. Garratt, A. Guerrero, D. L. Hughes and M. Bochmann, *Angew. Chem. Int. Ed.*, 2014, **43**, 2166-2169. (b) U. P. Preiss, G. Steinfeld, H. Scherer, A. M. T. Erle, B. Benkmil, A. Kraft and I. Krossing, *Z. Anorg. Allg. Chem.*, 2013, **639**, 714-721. (c) A. Kraft, N. Trapp, D. Himmel, H. Bohrer, P. Schluter, H. Scherer and I. Krossing, *Chem. Eur. J.*, 2012, **18**, 9371-9380. (d) M. A.

- Avelar, F. S. Tham and C. A. Reed, *Angew. Chem. Int. Ed.*, 2009, **48**, 3491-3493. (e) A. Lehmann, A. Schulz and A. Villinger, *Angew. Chem. Int. Ed.*, 2009, **48**, 7444-7447. (f) M.-C. Chen, J. A. S. Roberts, A. M. Seyam, L. Li, C. Zuccaccia, N. G. Stahl and T. J. Marks, *Organometallics*, 2006, **25**, 2833-2850. (g) S. P. Lewis, N. J. Taylor, W. E. Piers and S. Collins, *J. Am. Chem. Soc.*, 2003, **125**, 14686-14687. (h) J. Zhou, S. J. Lancaster, D. A. Walker, S. Beck, M. Thorton-Pett and M. Bochmann, *J. Am. Chem. Soc.*, 2001, **123**, 223-237. (i) F. Calderazzo, P. Pallavicini, G. Pampaloni and P. F. Zanazzi, *J. Chem. Soc., Dalton Trans.*, 1990, 2743-2746.
- [31] (a) P. Klinzing, A. El-Kholi, U. Müller, K. Dehnicke and K. Findeisen, *Z. Anorg. Allg. Chem.*, 1989, **569**, 83-90. (b) C. D. Garner, L. H. Hill, F. E. Mabbs, D. L. McFadden and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 1977, 853-858.
- [32] (a) C. Limberg, R. Boese and B. Schiemenz, *J. Chem. Soc., Dalton Trans.*, 1997, 1633-1638. (b) D.L. Kepert and R. Mandyczewsky, *J. Chem. Soc. A*, 1968, 530-533.
- [33] (a) R. Haiges, P. Deokar and K. Christe, *Z. Anorg. Allg. Chem.*, 2014, **640**, 1568-1575.
- [34] N. W. Alcock, D. A. Brown, T. F. Illson, S. M. Roe and M. G. H. Wallbridge, *J. Chem. Soc., Dalton Trans.*, 1991, 873-881.
- [35] V. López-Carrillo and A. M. Echavarren, *J. Am. Chem. Soc.*, 2010, **132**, 9292-9294.
- [36] D. A. Brown, M. G. H. Wallbridge, W.-S. Li and M. McPartlin, *Polyhedron*, 1994, **13**, 2265-2270.
- [37] (a) S.Radharishnan, J. Mieres-Perez, M. S. Gudipati and W. Sander, *J. Phys. Chem. A*, 2017, **121**, 6405-6412. (b) P. Costa, M. Fernandez-Oliva, E. Sanchez-Garcia and W. Sander, *J. Am. Chem. Soc.*, 2014, **136**, 15625-15630. (c) T. A. Nigst, J. Ammer and H. Mayr, *J. Phys. Chem. A*, 2012, **116**, 8494-8499. (d) T. Bally, S. Matzinger, L. Truttman, M. S. Platz, A. Admasu, F. Gerson, A. Arnold and R. Schmidlin, *J. Am. Chem. Soc.*, 1993, **115**, 7007-8.
- [38] V. C. Gibson, T. P. Kee and A. Shaw, *Polyhedron*, 1990, **9**, 2293-2298.

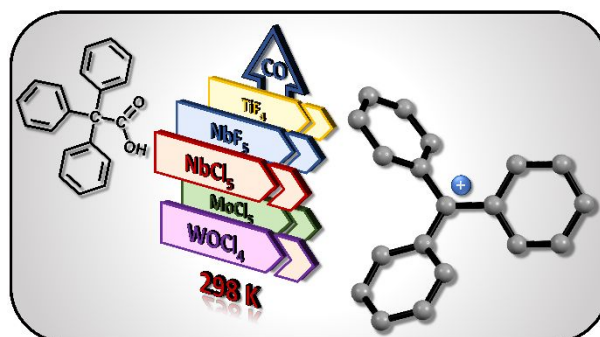
-
- [39] D. A. Skoog, D. M. West, F. J. Holler and S. R. Crouch, *Fundamentals of Analytical Chemistry*, 8th Edition, Thomson Learning Inc, Belmont, CA, 2004.
- [40] D. Basavaiah and K. R. Reddy, *Org. Lett.*, 2007, **9**, 57-60.
- [41] V. López-Carrillo and A. M. Echavarren, *J. Am. Chem. Soc.*, 2010, **132**, 9292-9294.
- [42] P. V. Fish, A. D. Brown, E. Evrard and L. R. Roberts, *Bioorg. Med. Chem.*, 2008, **7**, 1871-1876.
- [43] a) M. M. Kayser, *Can. J. Chem.*, 1983, **61**, 439-441. (b) A. Haahr, *Tetrahedron Lett.*, 2011, **52**, 3020-3022.
- [44] G. M. Sheldrick, *SADABS-2008/1 - Bruker AXS Area Detector Scaling and Absorption Correction*, Bruker AXS: Madison, Wisconsin, USA, 2008.
- [45] G.M. Shekdrick, Crystal structure refinement with SHELXL *Acta Cryst. C*, 2015, **71**, 3-8.

Decarbonylation of Triphenylacetic Acid by High Valent Transition Metal Halides, and Effect of the Replacement of Phenyl Groups

Niccolò Bartalucci, Fabio Marchetti, Stefano Zacchini, Guido Pampaloni

Table of Contents Synopsis

The unusual decarbonylation of α -phenyl carboxylic acids with suitable substituents is a general reaction promoted at room temperature by homoleptic halides of high valent transition metals.



Decarbonylation of Phenylacetic Acids by High Valent Transition Metal Halides

Niccolò Bartalucci, Fabio Marchetti, Stefano Zacchini, Guido Pampaloni

Supporting Information

<u>Table of contents</u>	<i>Pages</i>
Spectroscopic data of carboxylic acids	S2
Figure S1, Table S1: ORTEP drawing of 6 , and selected bonding parameters	S4
Figure S2, Tables S2-S3: ORTEP drawing of 8 , and selected bonding parameters	S5
Figure S3, Tables S4-S5: ORTEP drawing of $\text{CPh}_2(\text{CH}_2\text{CH}_2\text{Br})\text{CO}_2\text{H}$ (A1), and selected bonding parameters	S6
Figure S4, Tables S6-S7: ORTEP drawing of $\text{CPh}_2(\text{CH}_2\text{CH}_3)\text{CO}_2\text{H}$ (A2), and selected bonding parameters	S7
Figures S5-S32: NMR spectra of products	S8-S15
Figures S33-S39: IR spectra of products	S16-S18

Spectroscopic data of carboxylic acids.

A) CPh₃CO₂H. IR (solid state): $\nu/\text{cm}^{-1} = 3056\text{w}, 2789\text{w}, 2611\text{w}, 1693\text{vs} (\text{C}=\text{O}), 1597\text{w}, 1488\text{m}, 1445\text{m}, 1405\text{w}, 1282\text{m-sh}, 1258\text{m}, 1190\text{w-m}, 1084\text{w}, 1035\text{w}, 1002\text{w}, 943\text{w-br}, 906\text{w}, 759\text{m}, 733\text{s}, 697\text{vs}, 667\text{m-s}$. ¹H NMR (dms_o-d₆): $\delta/\text{ppm} = 7.28, 7.15 (\text{m}, 15 \text{ H}, \text{Ph}); 3.5 (\text{br}, 1 \text{ H}, \text{OH})$. ¹³C{¹H} NMR (dms_o-d₆): $\delta/\text{ppm} = 174.8 (\text{C}=\text{O}); 143.7 (\text{ipso-Ph}), 130.4, 128.1, 127.1 (\text{Ph}); 67.4 (\text{CPh}_3)$.

B) CMe(Ph)₂CO₂H. IR (solid state): $\nu/\text{cm}^{-1} = 3088\text{w}, 3063\text{w}, 3024\text{w}, 3003\text{w}, 2985\text{w}, 2945\text{w}, 2825\text{w}, 1697\text{s} (\text{C}=\text{O}), 1598\text{w}, 1581\text{w}, 1494\text{m}, 1462\text{w-m}, 1445\text{m}, 1409\text{w-m}, 1379\text{w}, 1293\text{m}, 1275\text{m-s}, 1213\text{w-m}, 1200\text{w-m}, 1125\text{w-m}, 1070\text{w-m-sh}, 1052\text{w}, 1030\text{w-m}, 937\text{m-br}, 922\text{m}, 882\text{w}, 838\text{w}, 773\text{w}, 757\text{m-s}, 734\text{m-s}, 697\text{vs}, 657\text{m-s}$ cm^{-1} . ¹H NMR (CDCl₃): $\delta/\text{ppm} = 7.36\text{-}7.25 (10 \text{ H}, \text{Ph}); 1.95 (\text{s}, 3 \text{ H}, \text{Me})$. ¹³C{¹H} NMR (CDCl₃): $\delta/\text{ppm} = 180.9 (\text{OCO}); 144.4 (\text{ipso-Ph}); 128.7, 128.6, 127.6 (\text{Ph}); 56.9 (\text{CPh}_2); 27.2 (\text{Me})$.

C) CMe₂(Ph)CO₂H. IR (solid state): $\nu/\text{cm}^{-1} = 2974\text{w}, 2115\text{w}, 1694\text{vs} (\text{C}=\text{O}), 1497\text{w}, 1471\text{w}, 1446\text{w}, 1438\text{w}, 1404\text{w}, 1365\text{w}, 1293\text{m}, 1176\text{w}, 1160\text{w-m}, 1102\text{w}, 1078\text{w}, 1030\text{w}, 1013\text{w}, 938\text{m}, 840\text{w}, 776\text{w}, 756\text{w}, 731\text{m}, 697\text{s}$ cm^{-1} . ¹H NMR (CDCl₃): $\delta/\text{ppm} = 7.43 (\text{d}, {}^3J_{\text{HH}} = 7.6 \text{ Hz}, 2 \text{ H}, \text{ortho H}); 7.37 (\text{t}, {}^3J_{\text{HH}} = 7.6 \text{ Hz}, 2 \text{ H}, \text{meta H}); 7.29 (\text{d}, {}^3J_{\text{HH}} = 7.2 \text{ Hz}, 1 \text{ H}, \text{para H}); 1.63 (\text{s}, 3\text{H}); 1.63 (\text{s}, 6 \text{ H}, \text{Me})$. ¹³C{¹H} NMR (CDCl₃): $\delta/\text{ppm} = 182.9 (\text{C}=\text{O}); 143.8 (\text{ipso-Ph}); 128.5, 127.0, 125.8 (\text{Ph}); 46.3 (\text{CMe}_2); 26.2 (\text{Me})$.

D) CPh₂(CH₂CH₂Br)CO₂H. IR (solid state): $\nu/\text{cm}^{-1} = 3058\text{w}, 2983\text{w}, 2932\text{w}, 2815\text{w}, 2684\text{w}, 2639\text{w}, 2516\text{w}, 1958\text{w}, 1900\text{w}, 1815\text{w}, 1771\text{w}, 1702\text{vs}, 1599\text{w-m}, 1494\text{m-s}, 1440\text{m-sh}, 1402\text{m}, 1335\text{w}, 1306\text{w-m}, 1270\text{s}, 1229\text{w}, 1209\text{w}, 1178\text{w}, 1162\text{w}, 1147\text{w-m}, 1088\text{w}, 1066\text{w}, 1034\text{w}, 1015\text{w-m}, 915\text{m-br}, 841\text{w}, 785\text{w-m}, 756\text{s}, 740\text{m}, 726\text{m-s}, 687\text{vs}$ cm^{-1} . ¹H NMR (CDCl₃): $\delta/\text{ppm} = 10.58 (\text{br}, 1 \text{ H}, \text{OH}); 7.40\text{-}7.31 (\text{m}, 10 \text{ H}, \text{Ph}); 3.15\text{-}3.11 (\text{m}, 2 \text{ H}, \text{BrCH}_2); 3.01\text{-}2.97 (\text{m}, 2 \text{ H}, \text{CH}_2)$. ¹³C{¹H} NMR (CDCl₃): $\delta/\text{ppm} = 179.9 (\text{C}=\text{O}); 141.0 (\text{ipso-Ph}); 128.7, 128.4, 127.6 (\text{Ph}); 60.6 (\text{CPh}_2); 41.6 (\text{CH}_2); 28.8 (\text{BrCH}_2)$.

E) CHPh₂CO₂H. IR (solid state): $\nu/\text{cm}^{-1} = 3025\text{w}, 2903\text{w}, 2703\text{w}, 2604\text{w}, 1956\text{w}, 1699\text{s} (\text{C}=\text{O}), 1600\text{w-m}, 1581\text{w}, 1497\text{m}, 1449\text{m-sh}, 1410\text{m}, 1314\text{m-sh}, 1282\text{w}, 1222\text{s}, 1183\text{w-br}, 1080\text{w}, 1033\text{w-}$

m, 1003w, 933m-s-br, 886w, 768w, 749m-s, 731s, 695vs, 666m-s cm^{-1} . ^1H NMR (CDCl_3): δ/ppm = 11.2 (s, br, 1 H, OH); 7.74 – 6.98 (m, 10 H, Ph); 5.11 (s, 1 H, CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ/ppm = 179.0 (C=O); 137.9, 128.7, 127.6 (Ph); 57.1 (CH).

F) MeC \equiv CCO $_2$ H. IR (solid state): ν/cm^{-1} = 2801w, 2624m, 2479w-m, 2321w, 2246vs (C \equiv C), 2138w-m, 2041w, 1997w, 1699s (C=O), 1661s, 1635s, 1567m-s, 1506w, 1439w-m, 1399s, 1368m, 1242vs-br, 1074m-s, 1025w-m, 854m-s-br, 778s, 751vs, 731s cm^{-1} . ^1H NMR (CDCl_3): δ/ppm = 11.33 (s, 1H, OH); 2.01 (s, 3 H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ/ppm = 158.6 (C=O); 88.8(CO–C \equiv C); 71.9(C \equiv C–Me); 3.8 (Me).

Figure S1. ORTEP drawing of the structure of **6**. Displacement ellipsoids are at the 50% probability level.

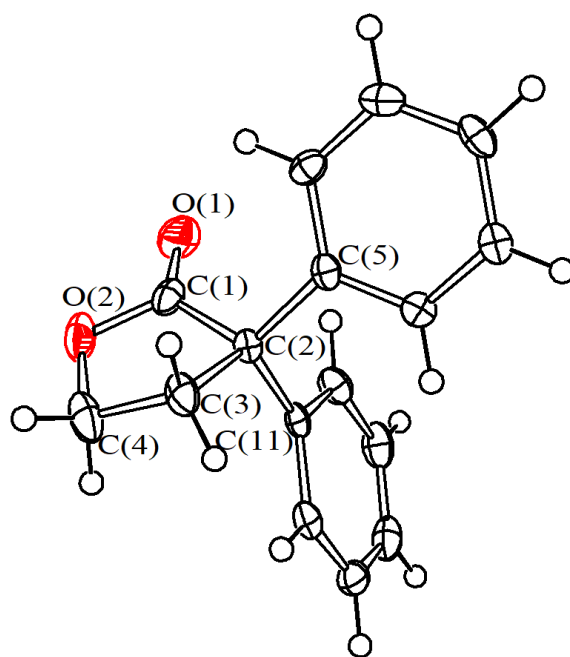


Table S1. Selected bond lengths (Å) and angles (deg) for **6**.

C(1)-O(1)	1.187(4)	C(1)-O(2)	1.341(4)
C(1)-C(2)	1.538(5)	C(2)-C(3)	1.541(4)
C(3)-C(4)	1.510(5)	C(4)-O(2)	1.454(5)
C(2)-C(5)	1.532(4)	C(2)-C(11)	1.540(5)
O(2)-C(1)-C(2)	128.5(3)	O(2)-C(1)-O(1)	121.9(3)
O(1)-C(1)-C(2)	109.6(3)	C(1)-C(2)-C(3)	100.9(3)
C(2)-C(3)-C(4)	102.3(3)	C(3)-C(4)-O(2)	104.3(3)
C(4)-O(2)-C(1)	110.9(3)	C(5)-C(2)-C(11)	110.5(3)

Figure S2. ORTEP drawing of the structure of MeC(Cl)=CHCO₂H, **8**. Displacement ellipsoids are at the 50% probability level.

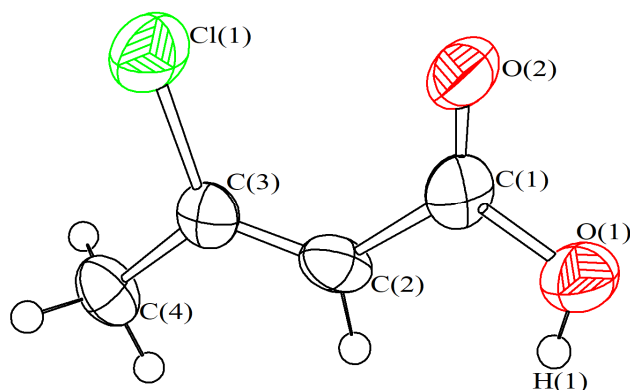


Table S2. Selected bond lengths (Å) and angles (deg) for MeC(Cl)=CHCO₂H, **8**.

C(1)-O(1)	1.351(13)	C(1)-O(2)	1.179(13)
C(1)-C(2)	1.507(15)	C(2)-C(3)	1.331(14)
C(3)-C(4)	1.496(14)	C(3)-Cl(1)	1.709(12)
O(1)-C(1)-O(2)	122.5(10)	O(1)-C(1)-C(2)	109.2(11)
O(2)-C(1)-C(2)	128.3(10)	C(1)-C(2)-C(3)	126.8(11)
C(2)-C(3)-C(4)	122.9(11)	C(2)-C(3)-Cl(1)	122.6(9)
C(4)-C(3)-Cl(1)	114.5(8)		

Table S3. Hydrogen bonds for MeC(Cl)=CHCO₂H, **8** [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)···Cl(1)#1	0.82	2.62	3.370(12)	153.5

Symmetry transformations used to generate equivalent atoms: #1 $x-1/2, -y+1/2, z+1/2$.

Figure S3. ORTEP drawing of the structure of $\text{CPh}_2(\text{CH}_2\text{CH}_2\text{Br})\text{CO}_2\text{H}$ (**A1**). Displacement ellipsoids are at the 50% probability level.

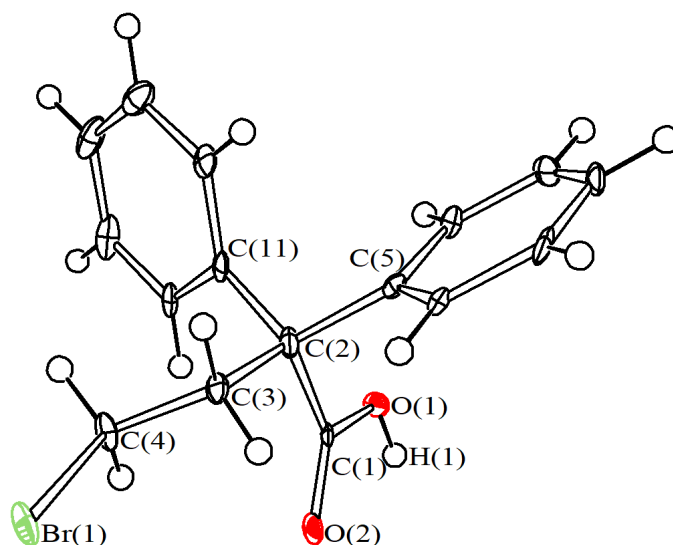


Table S4. Selected bond lengths (Å) and angles (deg) for $\text{CPh}_2(\text{CH}_2\text{CH}_2\text{Br})\text{CO}_2\text{H}$, **A1**.

C(1)-O(1)	1.307(6)	C(1)-O(2)	1.222(6)
C(1)-C(2)	1.539(6)	C(2)-C(3)	1.548(7)
C(3)-C(4)	1.520(7)	C(4)-Br(1)	1.965(5)
C(2)-C(5)	1.541(7)	C(2)-C(11)	1.544(7)
O(1)-C(1)-O(2)	123.9(4)	O(1)-C(1)-C(2)	114.0(4)
O(2)-C(1)-C(2)	122.1(4)	C(1)-C(2)-C(3)	109.1(4)
C(2)-C(3)-C(4)	112.8(4)	C(3)-C(4)-Br(1)	108.6(3)
C(5)-C(2)-C(11)	111.6(4)		

Table S5. Hydrogen bonds for $\text{CPh}_2(\text{CH}_2\text{CH}_2\text{Br})\text{CO}_2\text{H}$, **A1** [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)#1	0.84	1.80	2.637(5)	170.8

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z.

Figure S4. ORTEP drawing of the structure of $\text{CPh}_2(\text{CH}_2\text{CH}_3)\text{CO}_2\text{H}$, **A2**. Displacement ellipsoids are at the 50% probability level.

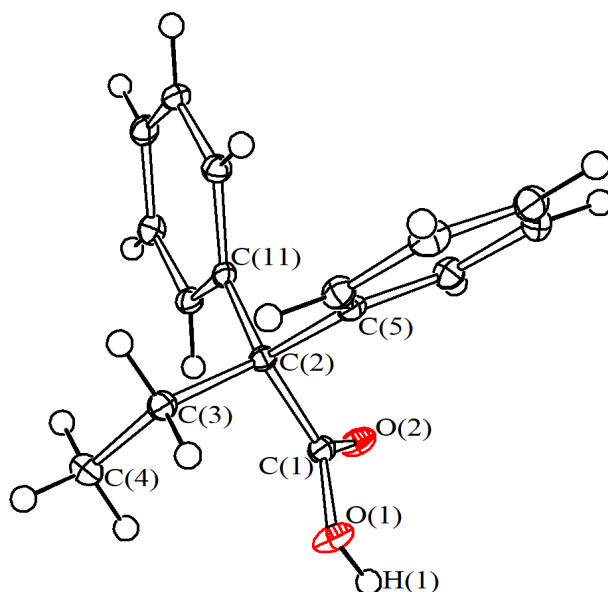


Table S6. Selected bond lengths (Å) and angles (deg) for $\text{CPh}_2(\text{CH}_2\text{CH}_3)\text{CO}_2\text{H}$, **A2**.

C(1)-O(1)	1.3300(18)	C(1)-O(2)	1.2330(18)
C(1)-C(2)	1.5436(18)	C(2)-C(3)	1.563(2)
C(3)-C(4)	1.536(2)		
C(2)-C(5)	1.557(2)	C(2)-C(11)	1.547(2)
O(1)-C(1)-O(2)	122.48(11)	O(1)-C(1)-C(2)	113.02(11)
O(2)-C(1)-C(2)	124.40(12)	C(1)-C(2)-C(3)	109.13(11)
C(2)-C(3)-C(4)	114.38(10)	C(5)-C(2)-C(11)	109.70(10)

Table S7. Hydrogen bonds for $\text{CPh}_2(\text{CH}_2\text{CH}_3)\text{CO}_2\text{H}$, **A2** [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(2)#1	0.84	1.85	2.681(2)	173.3

Symmetry transformations used to generate equivalent atoms: #1 -x+2, -y+1, -z+1.

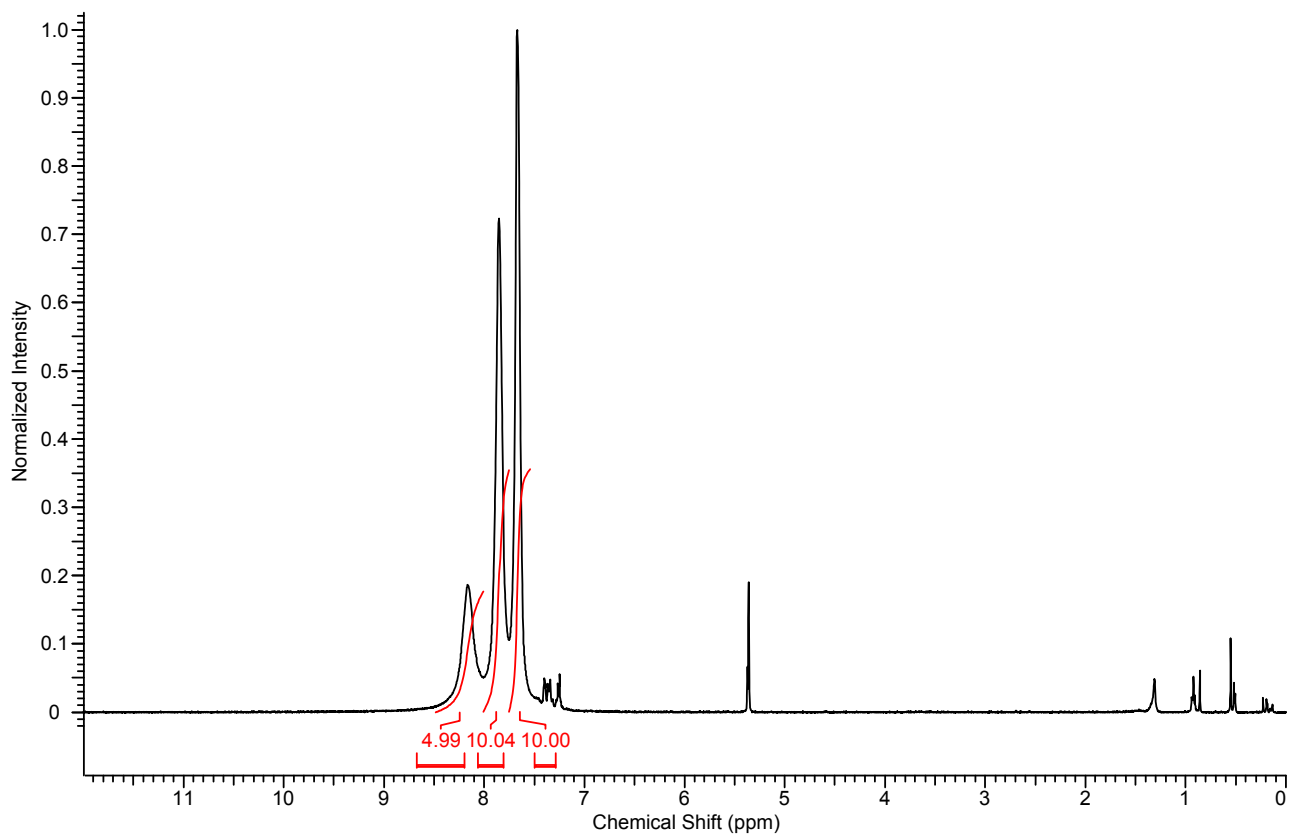
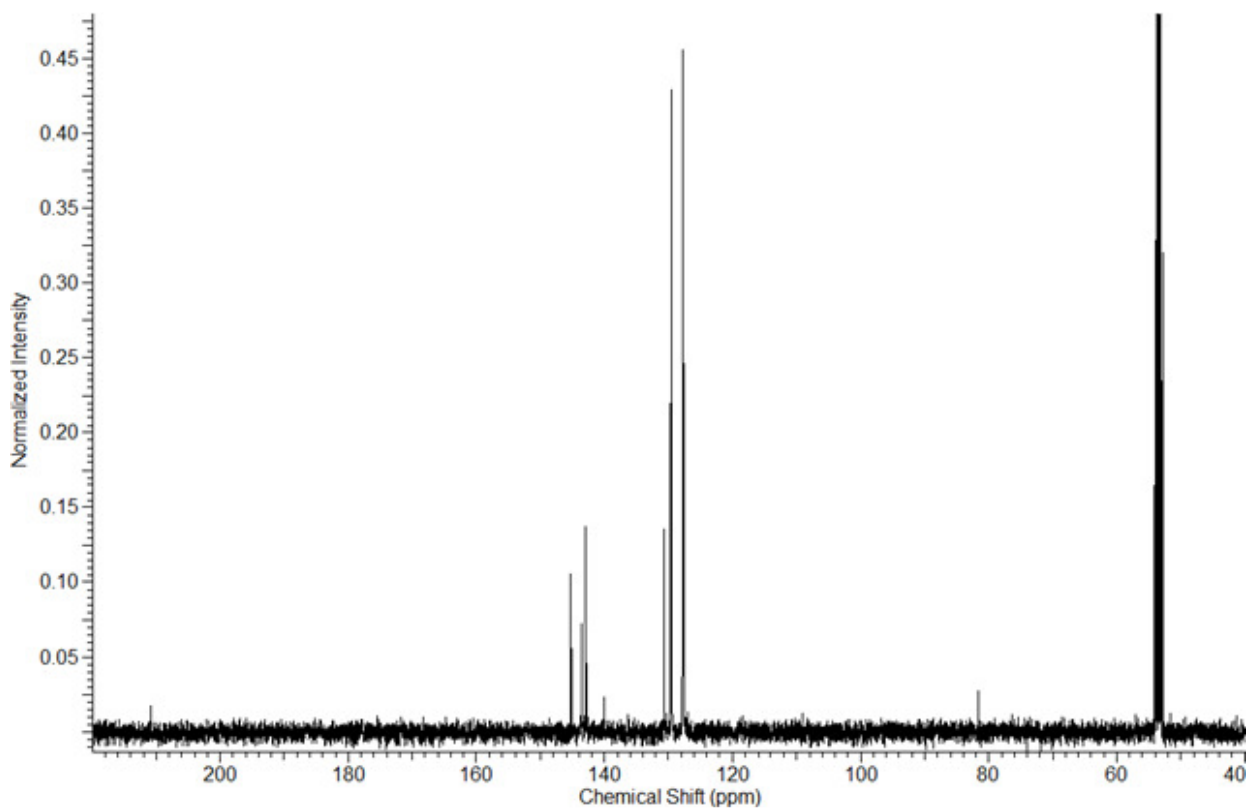
Figure S17. ^1H NMR spectrum (401 MHz, CD_2Cl_2) of $[\text{CPh}_3][\text{MoOCl}_4]$, **1**.**Figure S18.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2) of $[\text{CPh}_3][\text{MoOCl}_4]$, **1**.

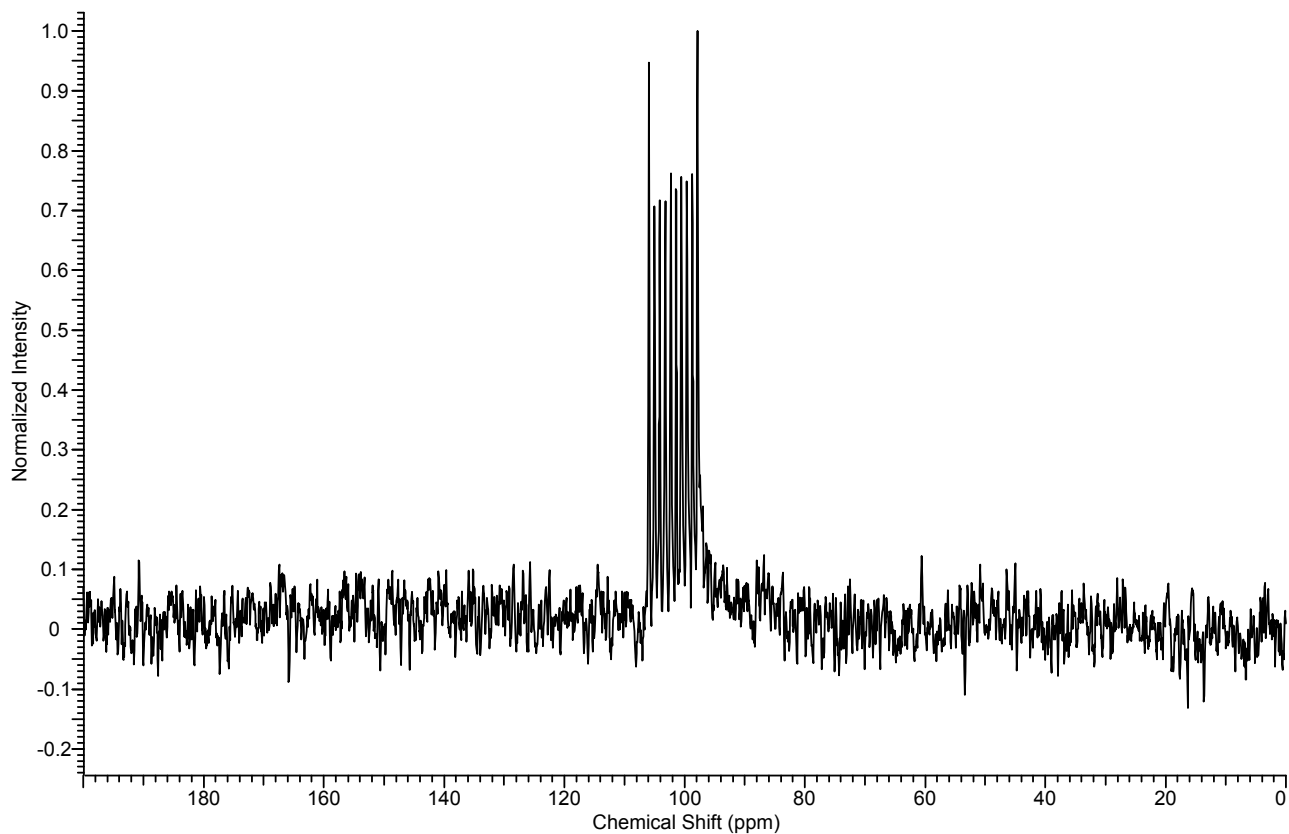
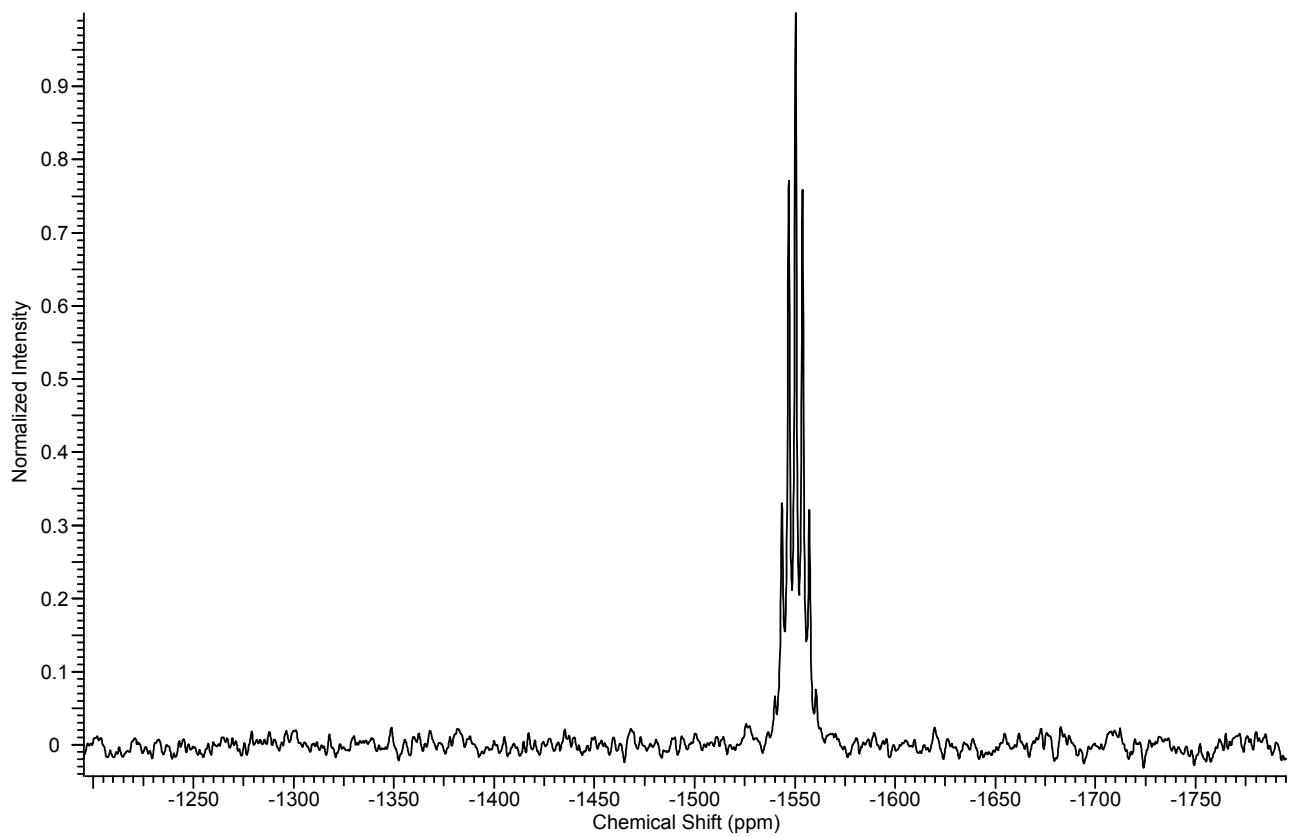
Figure S19. ^{19}F NMR spectrum (CD_3CN) of $[\text{CPh}_3][\text{NbF}_6]$, **2**.**Figure S20.** ^{93}Nb NMR spectrum (CD_3CN) of $[\text{CPh}_3][\text{NbF}_6]$, **2**.

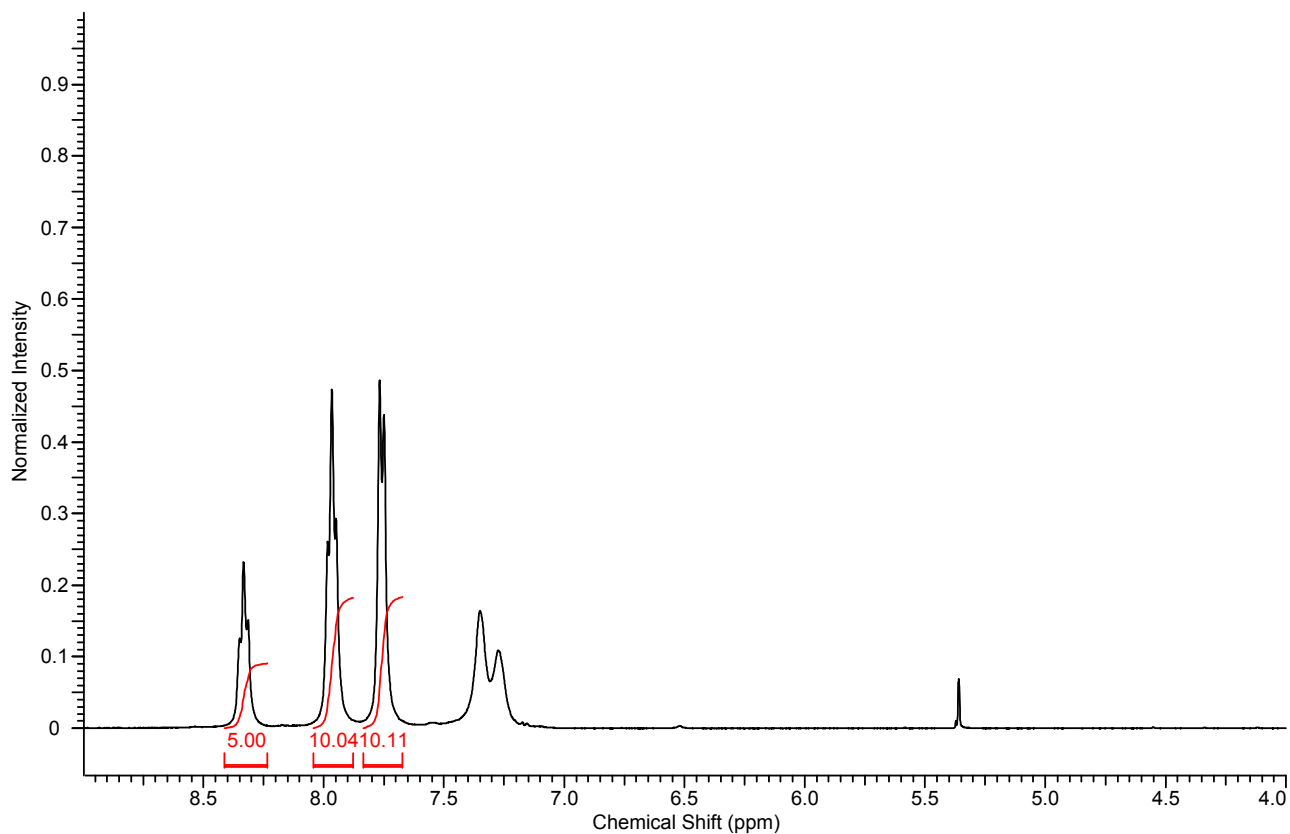
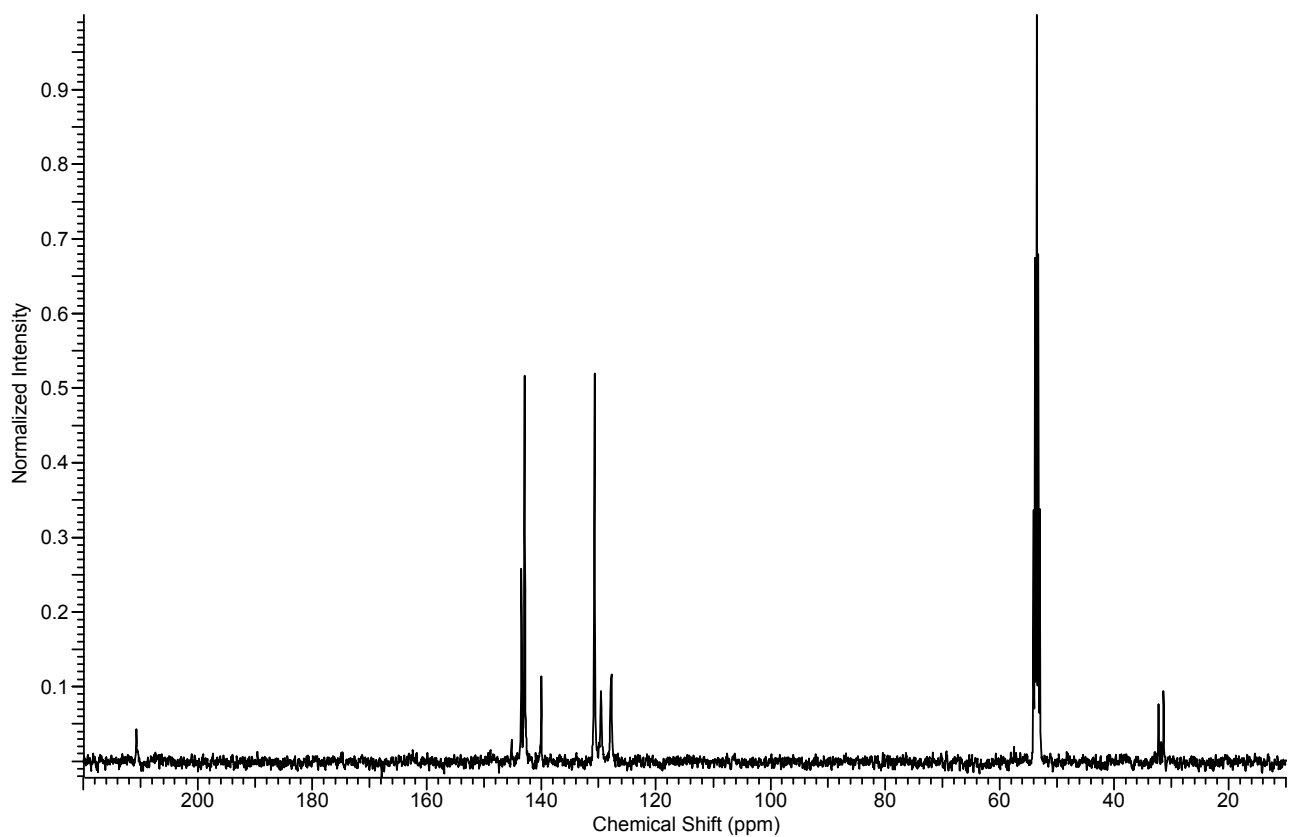
Figure S21. ^1H NMR spectrum (401 MHz, CD_2Cl_2) of $[\text{CPh}_3][\text{NbCl}_6]$, **3**.**Figure S22.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2) of $[\text{CPh}_3][\text{NbCl}_6]$, **3**.

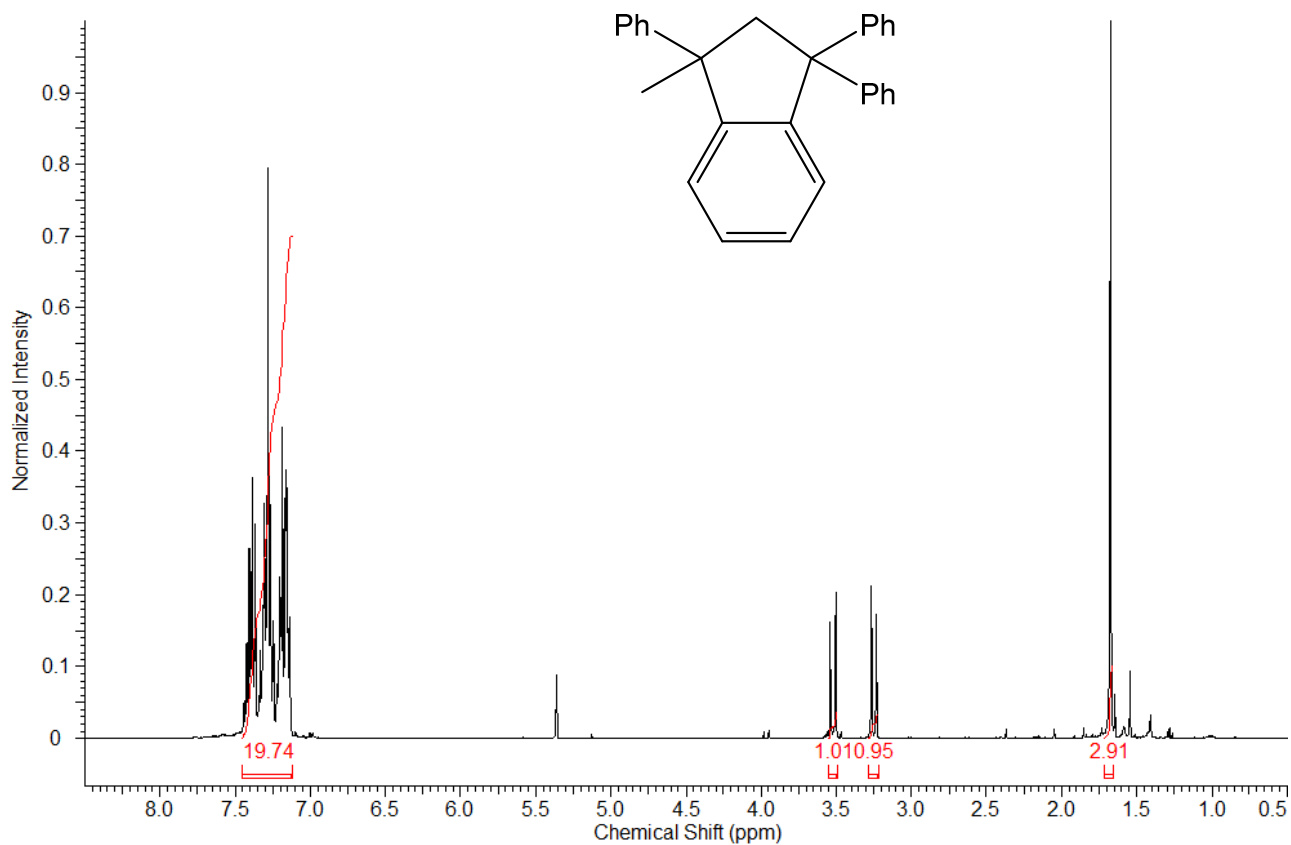
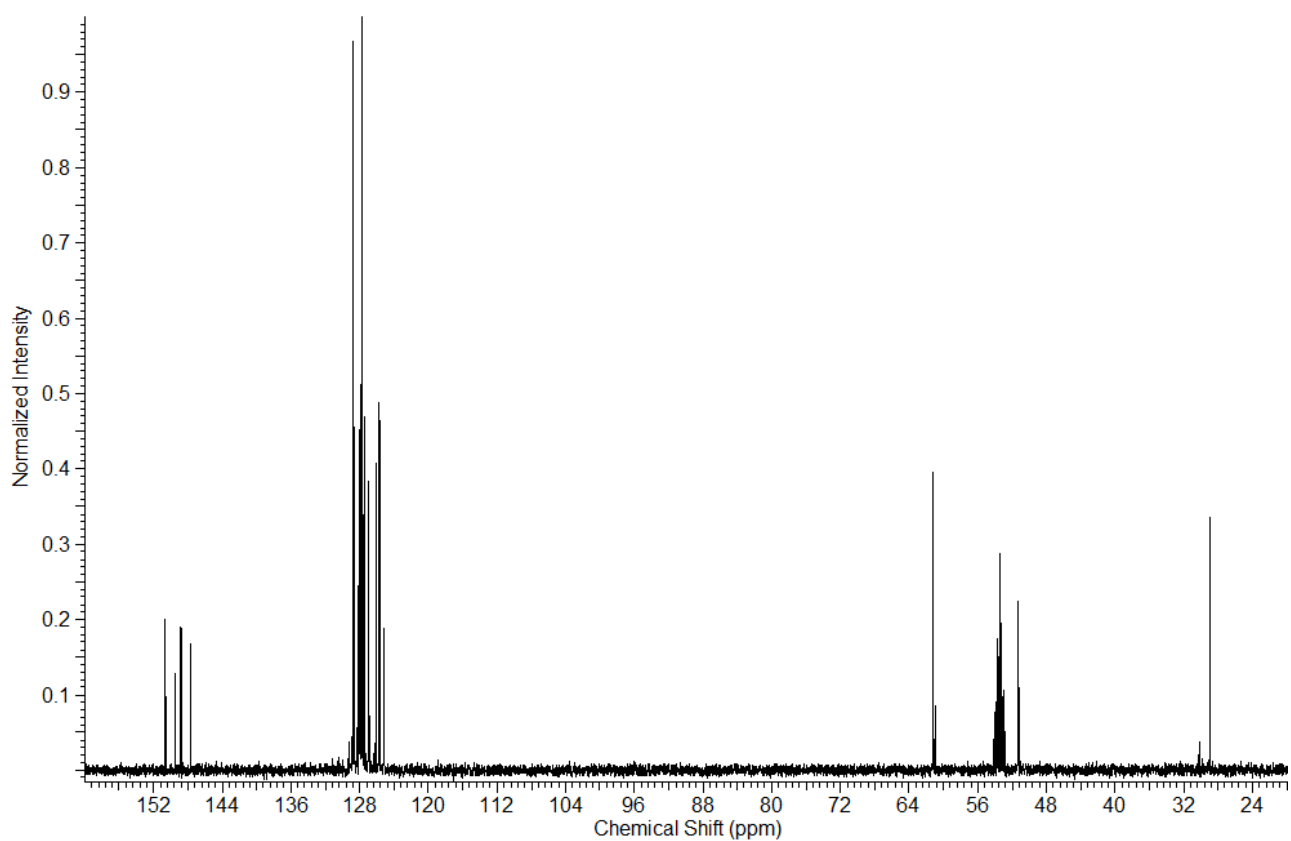
Figure S23. ^1H NMR spectrum (401 MHz, CD_2Cl_2) of **5a**.**Figure S24.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **5a**.

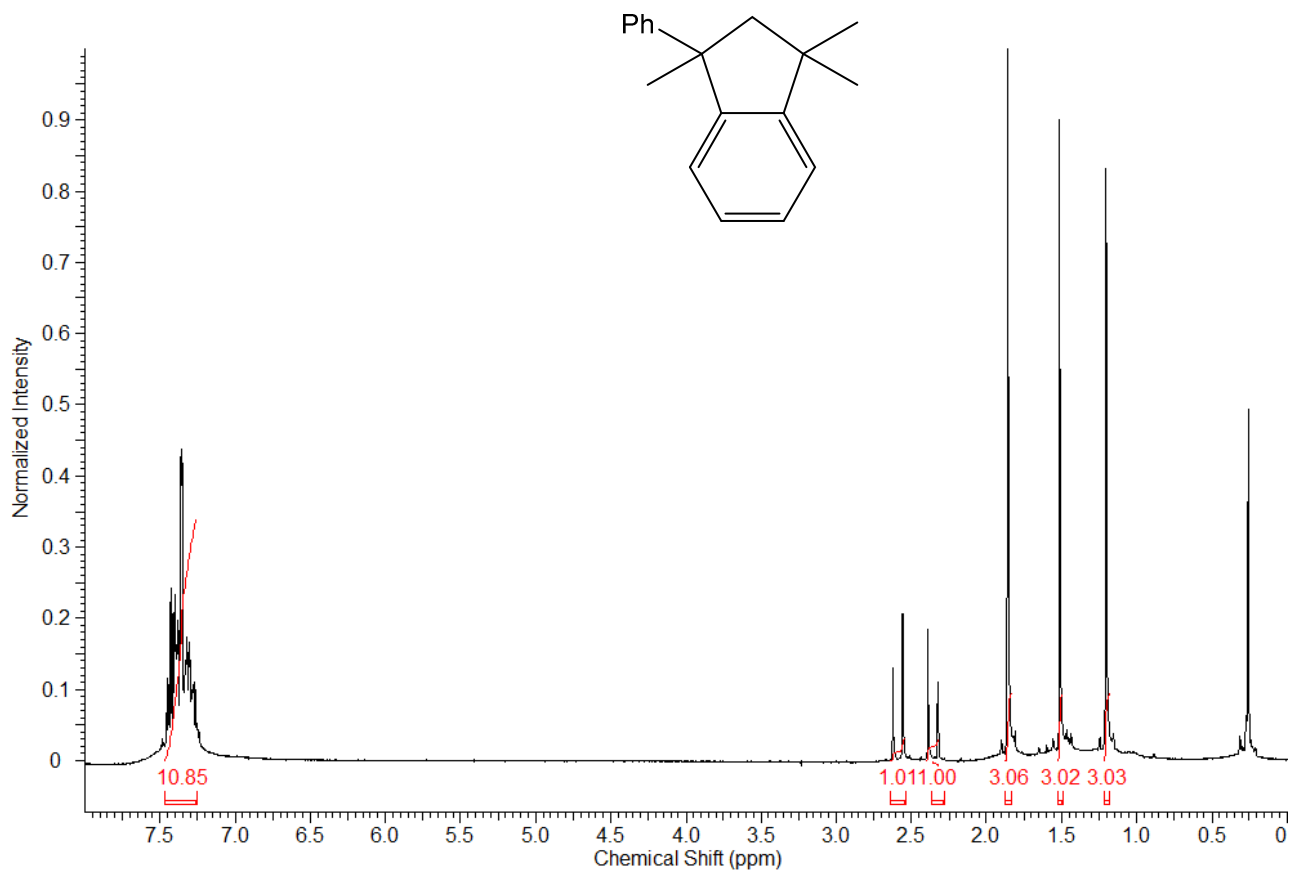
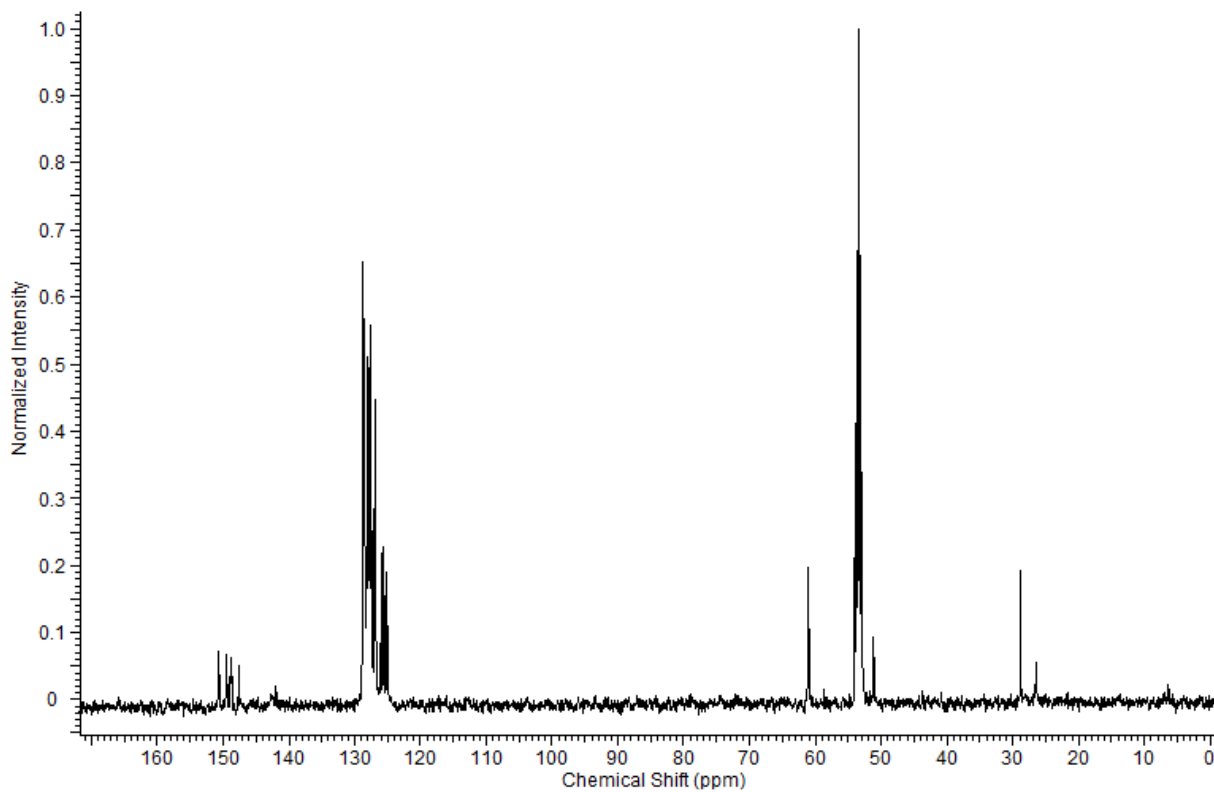
Figure S25. ^1H NMR spectrum (401 MHz, CD_2Cl_2) of **5b**.**Figure S26.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **5b**.

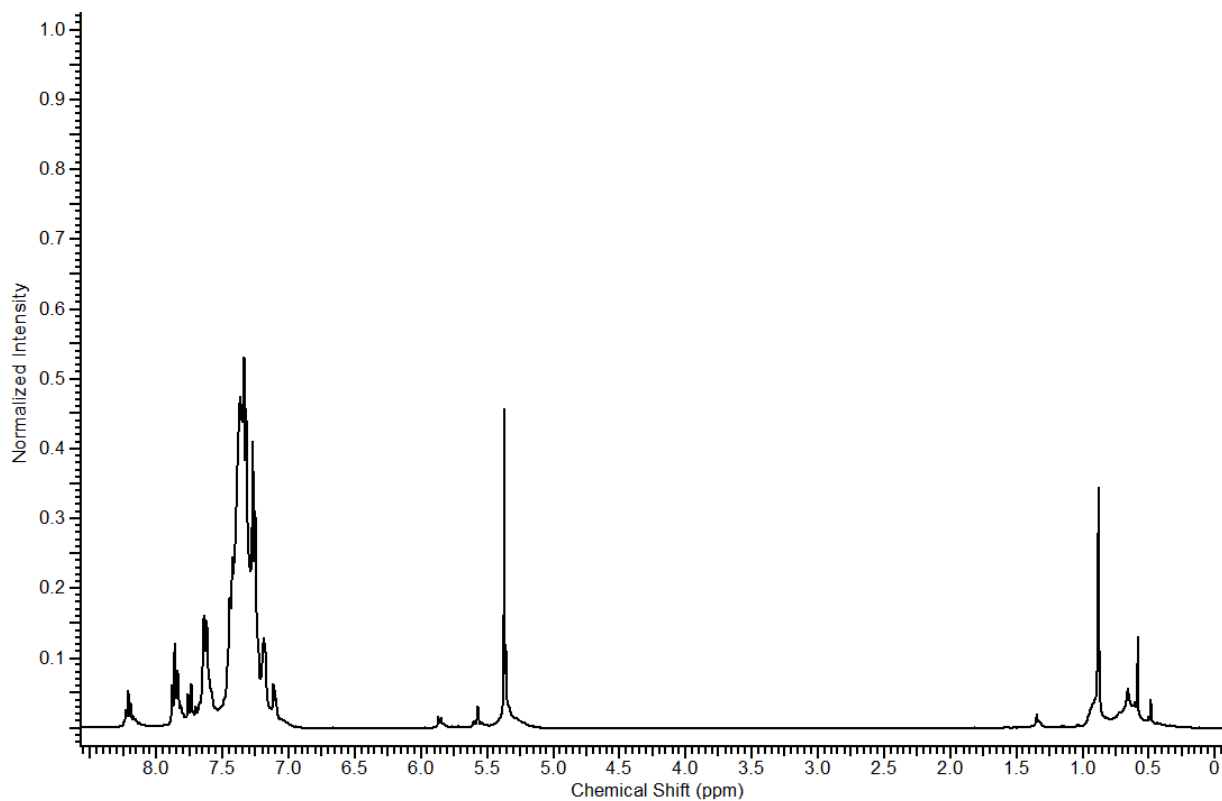
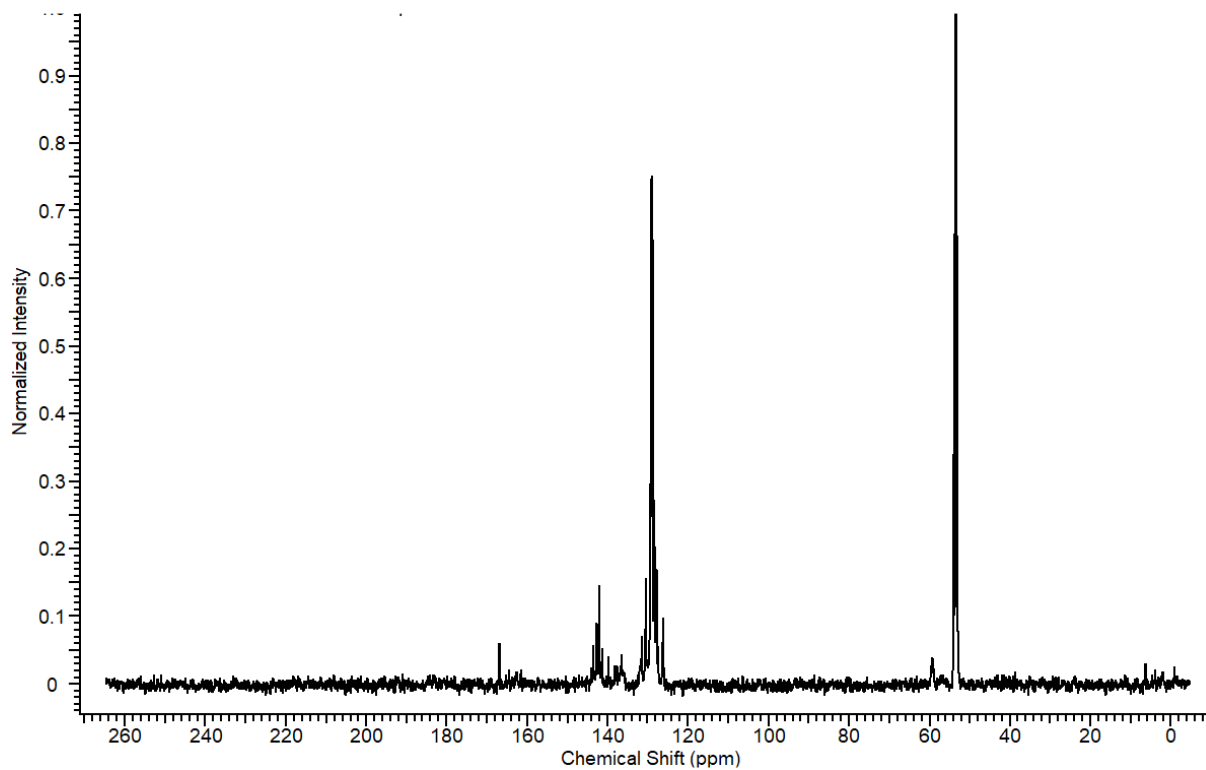
Figure S27. ^1H NMR spectrum (401 MHz, CD_2Cl_2) of $\text{NbCl}_4(\text{O}_2\text{CCHPh}_2)$, **6**.**Figure S28.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CD_2Cl_2) of $\text{NbCl}_4(\text{O}_2\text{CCHPh}_2)$, **6**.

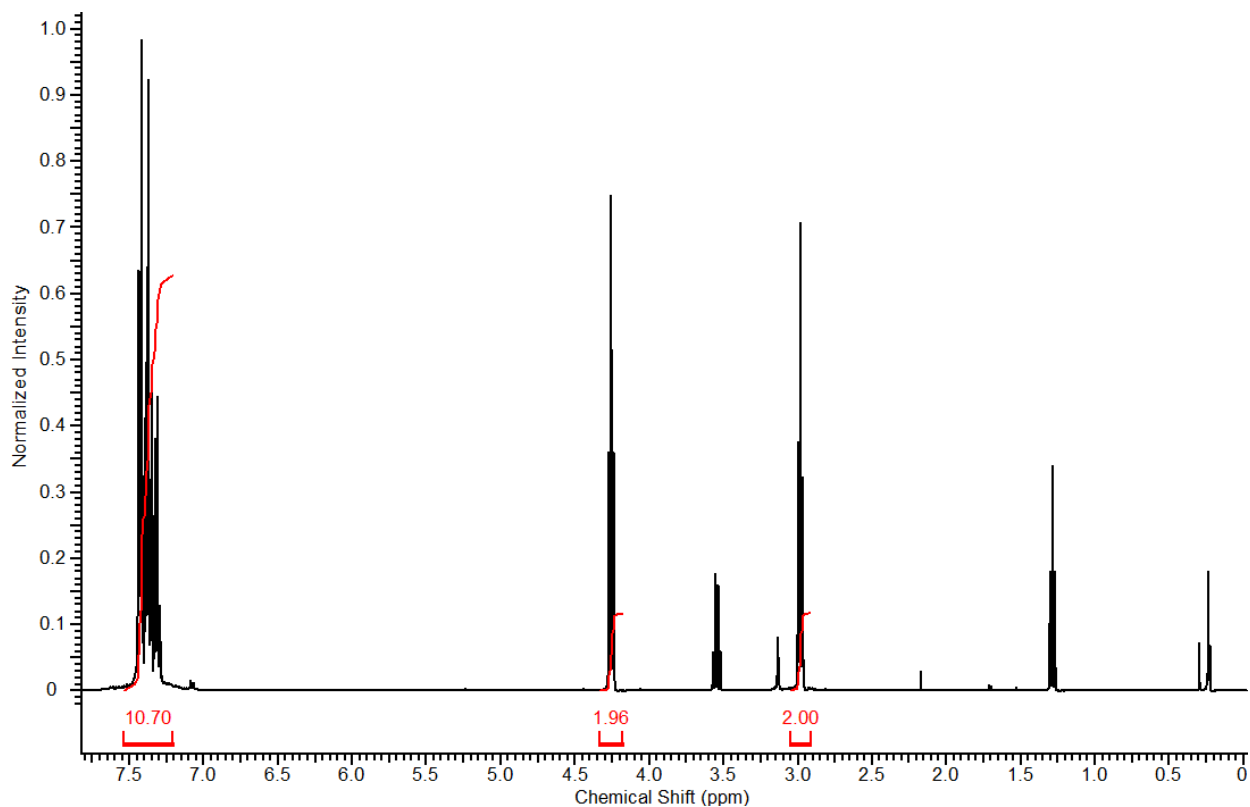
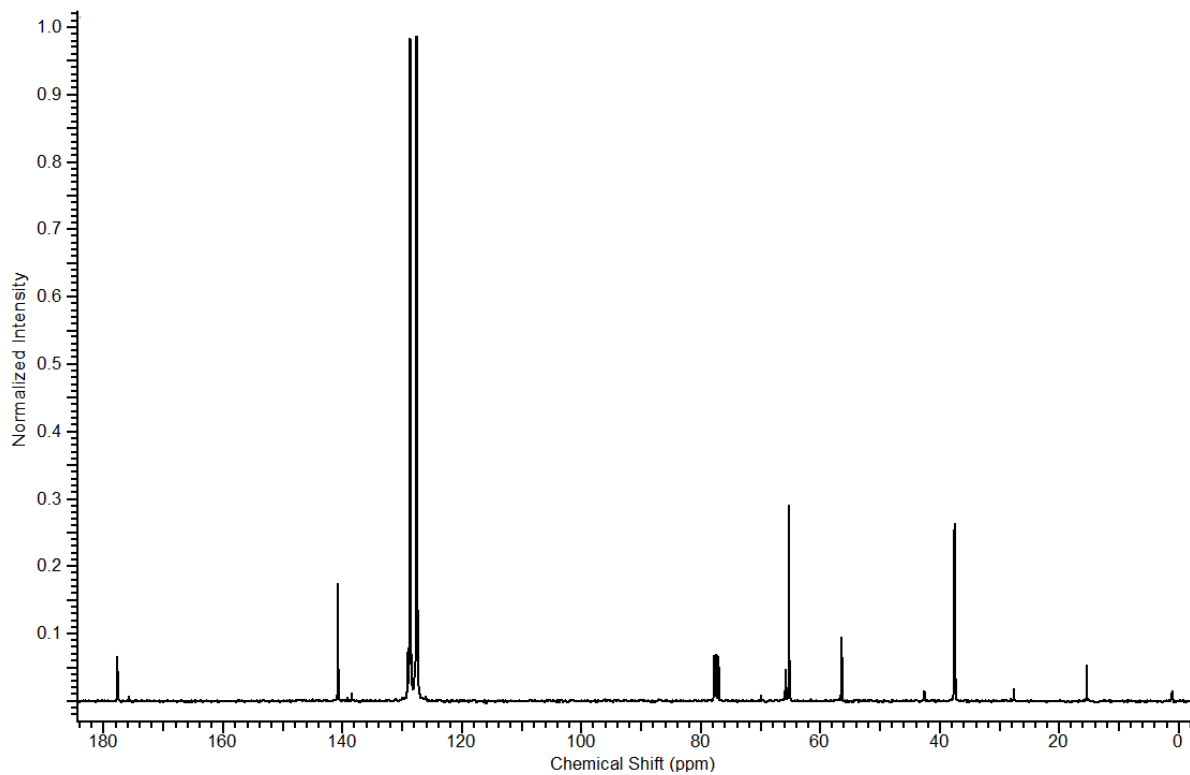
Figure S29. ^1H NMR spectrum (401 MHz, CDCl_3) of 3,3-diphenyldihydrofuran-2(3H)-one, **7**.**Figure S30.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of 3,3-diphenyldihydrofuran-2(3H)-one, **7**.

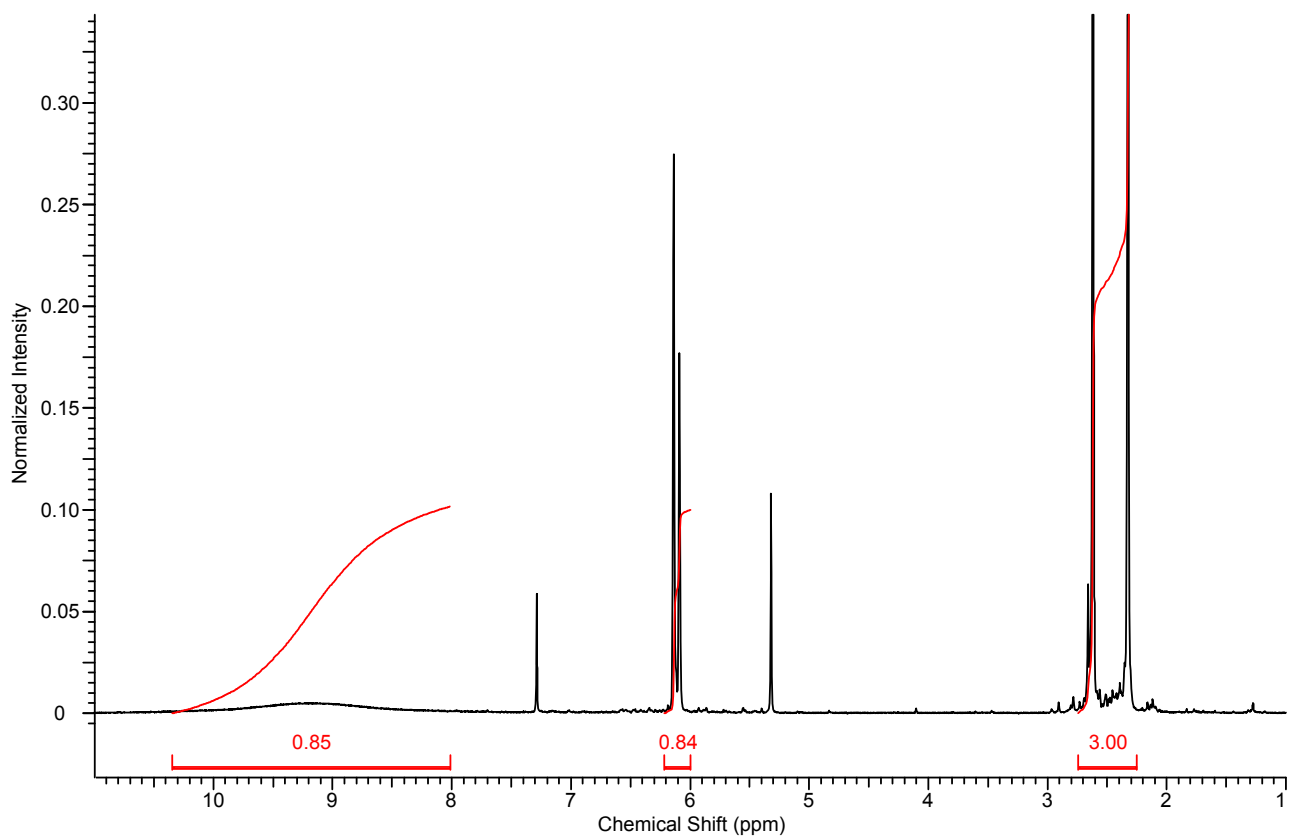
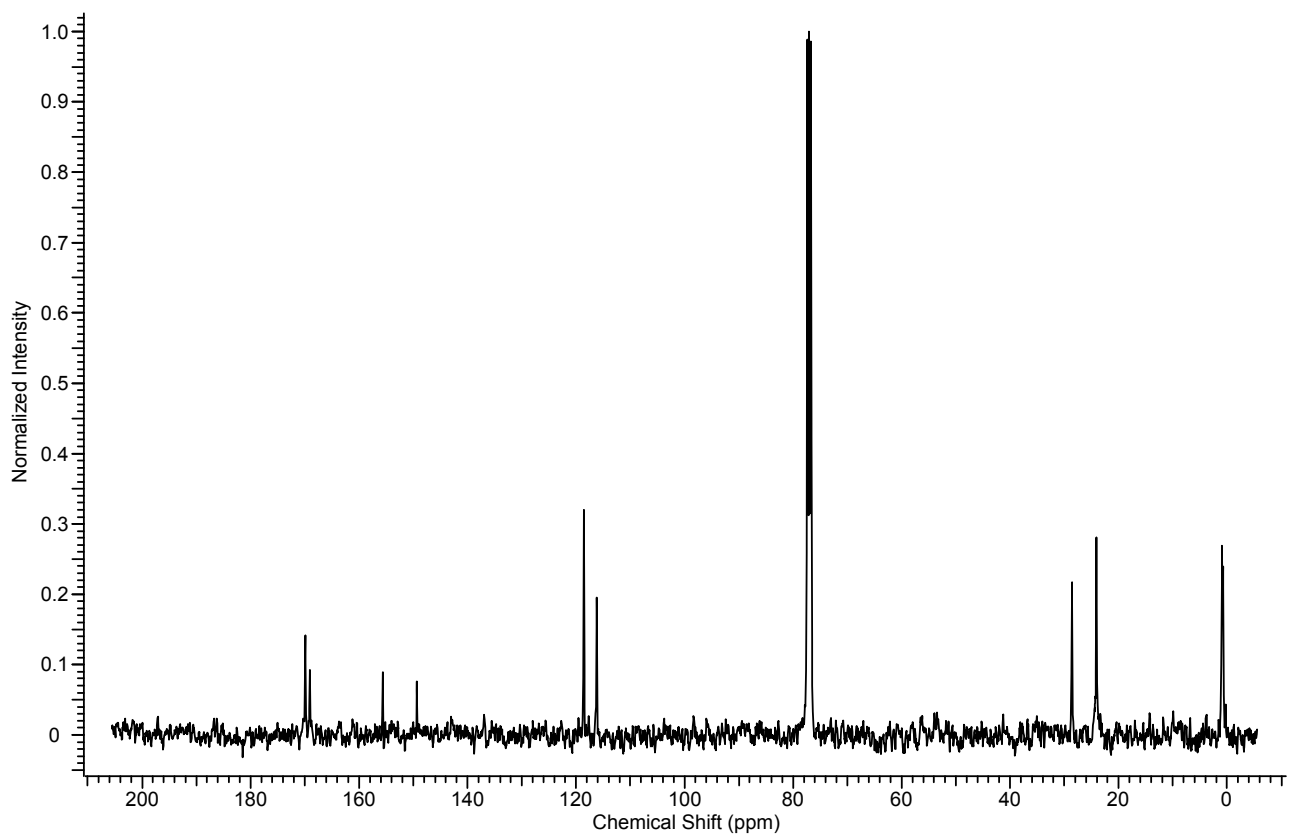
Figure S31. ^1H NMR spectrum (401 MHz, CDCl_3) of $\text{MeC}(\text{Cl})=\text{CHCOOH}$, **8**.**Figure S32.** $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (101 MHz, CDCl_3) of $\text{MeC}(\text{Cl})=\text{CHCOOH}$, **8**.

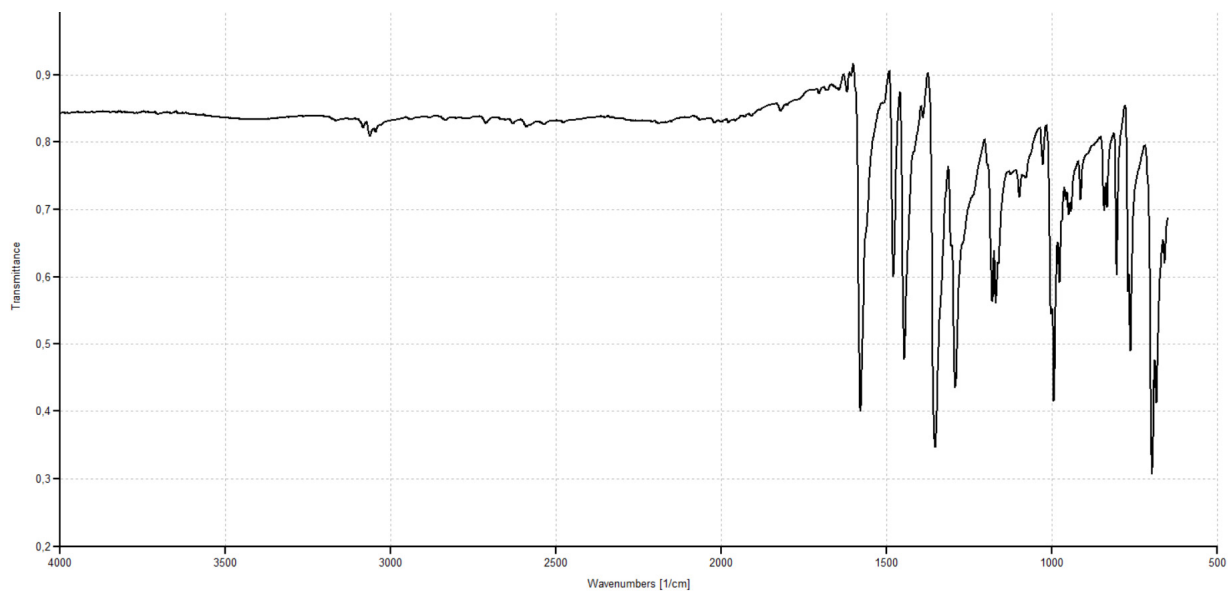
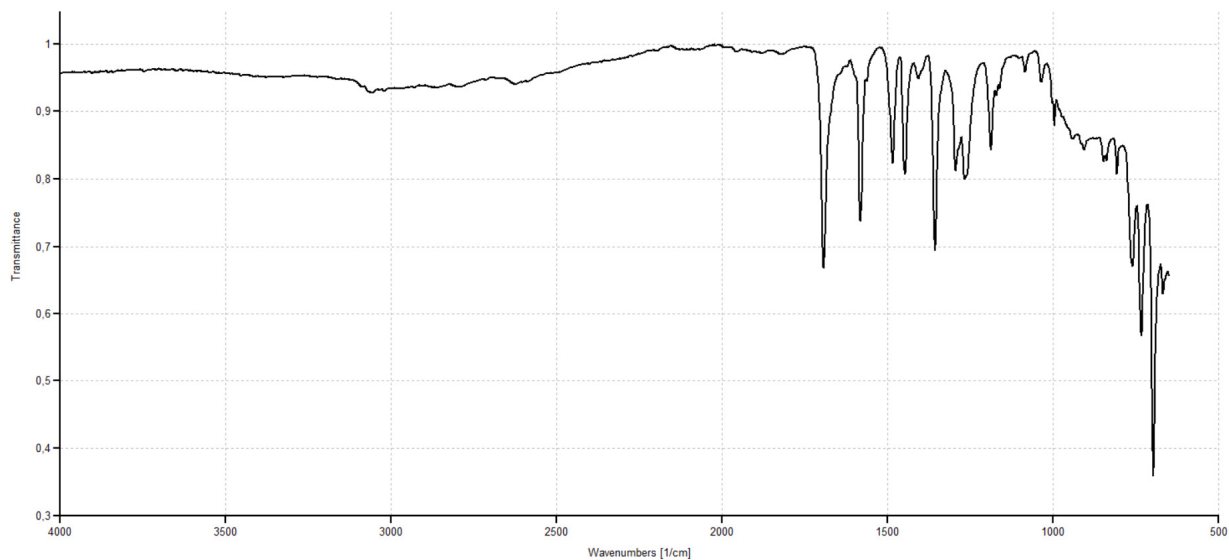
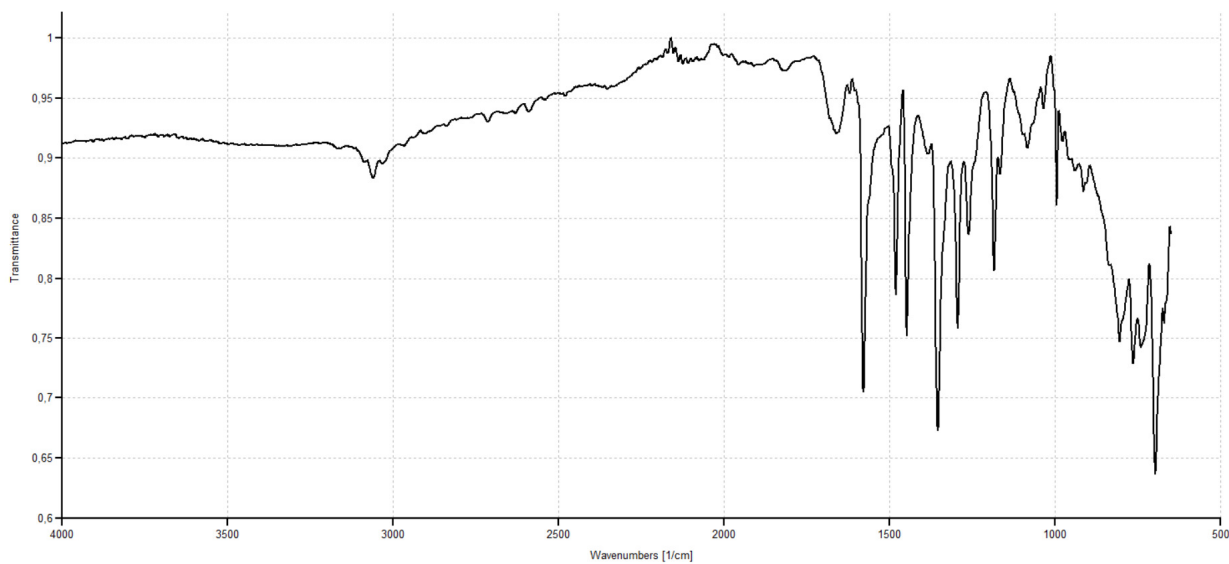
Figure S33. IR (ATR) spectrum of $[\text{CPh}_3][\text{MoOCl}_4]$, **1**.**Figure S34.** IR (ATR) spectrum of $[\text{CPh}_3][\text{NbF}_6]$, **2**.**Figure S35.** IR (ATR) spectrum of $[\text{CPh}_3][\text{NbCl}_6]$, **3**.

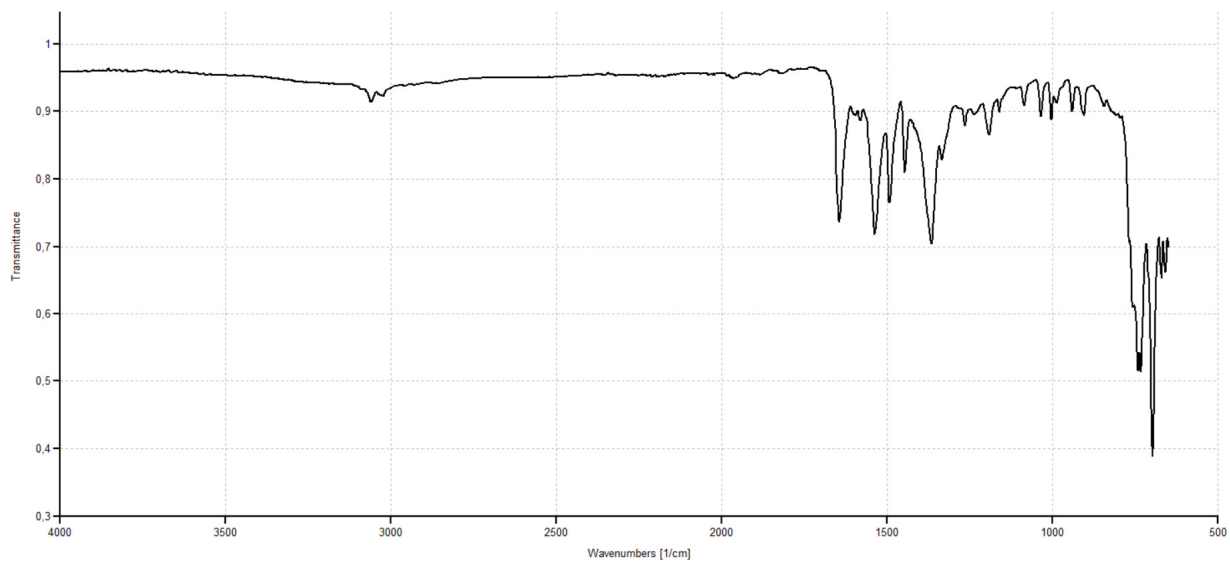
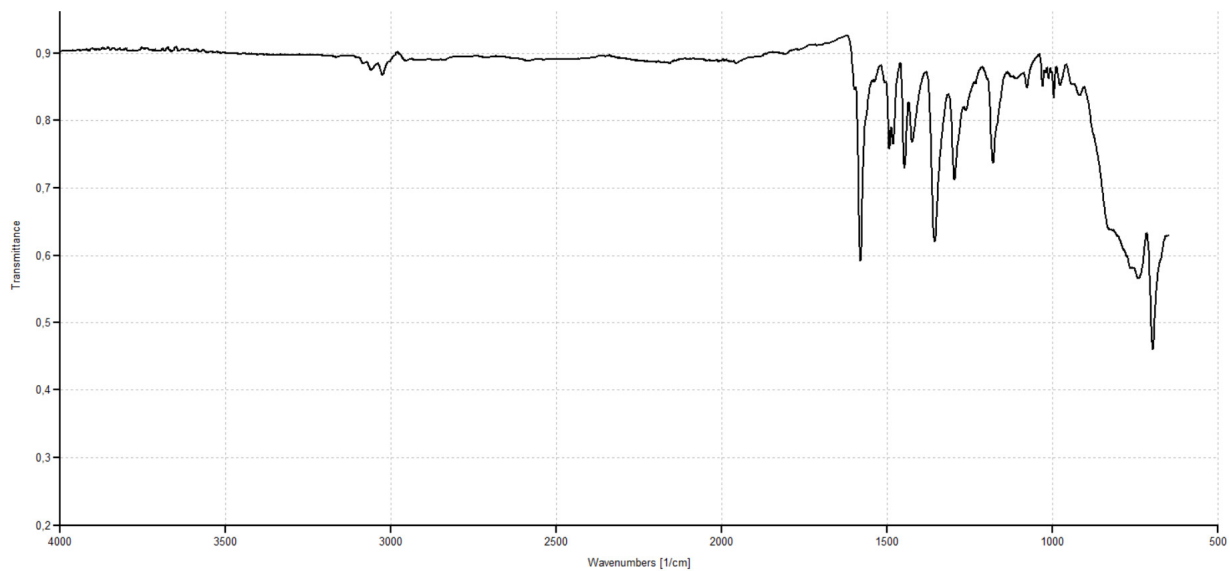
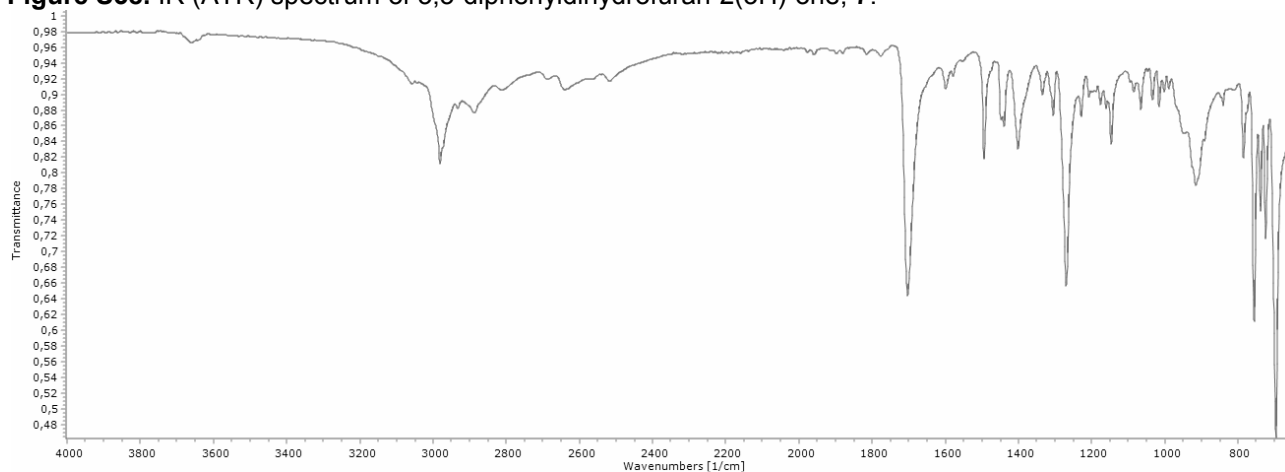
Figure S36. IR (ATR) spectrum of $[\text{CPh}_3][\text{Ti}_2\text{Cl}_8(\mu-\kappa^2\text{-O}_2\text{CCPh}_3)]$, **4**.**Figure S37.** IR (ATR) spectrum of $\text{NbCl}_4(\text{O}_2\text{CCHPh}_2)$, **6**.

Figure S38. IR (ATR) spectrum of 3,3-diphenyldihydrofuran-2(3H)-one, **7**.**Figure S39.** IR (ATR) spectrum of $\text{MeC}(\text{Cl})=\text{CHCOOH}$, **8**.