Decarbonylation of Phenylacetic Acids by High Valent Transition Metal Halides

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Supporting Information

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Spectroscopic data of carboxylic acids.

A)CPh_3CO_2H. IR (solid state): ν/cm^{-1} = 3056w, 2789w, 2611w, 1693vs (C=O), 1597w, 1488m, 1445m, 1405w, 1282m-sh, 1258m, 1190w-m, 1084w, 1035w, 1002w, 943w-br, 906w, 759m, 733s, 697vs, 667m-s. ^{1}H NMR (dmso-d_6): δ/ppm = 7.28, 7.15 (m, 15 H, Ph); 3.5 (br, 1 H, OH). $^{13}C\{^1H\}$ NMR (dmso-d_6): δ/ppm = 174.8 (C=O); 143.7 (*ipso*-Ph), 130.4, 128.1, 127.1 (Ph); 67.4 (*C*Ph_3).

B) $CMe(Ph)_2CO_2H$. IR (solid state): ν/cm^{-1} = 3088w, 3063w, 3024w, 3003w, 2985w, 2945w, 2825w, 1697s (C=O), 1598w, 1581w, 1494m, 1462w-m, 1445m, 1409w-m, 1379w, 1293m, 1275m-s, 1213w-m, 1200w-m, 1125w-m, 1070w-m-sh, 1052w, 1030w-m, 937m-br, 922m, 882w, 838w, 773w, 757m-s, 734m-s, 697vs, 657m-s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.36-7.25 (10 H, Ph); 1.95 (s, 3 H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 180.9 (OCO); 144.4 (*ipso*-Ph); 128.7, 128.6, 127.6 (Ph); 56.9 (*C*Ph_2); 27.2 (Me).

C) $CMe_2(Ph)CO_2H$. IR (solid state): ν/cm^{-1} = 2974w, 2115w, 1694vs (C=O), 1497w, 1471w, 1446w, 1438w, 1404w, 1365w, 1293m, 1176w, 1160w-m, 1102w, 1078w, 1030w, 1013w, 938m, 840w, 776w, 756w, 731m, 697s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ/ppm = 7.43 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, *ortho* H); 7.37 (t, $^3J_{HH}$ = 7.6 Hz, 2 H, *meta* H); 7.29 (d, $^3J_{HH}$ = 7.2 Hz, 1 H, *para* H); 1.63 (s, 3H).; 1.63 (s, 6 H, Me). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 182.9 (C=O); 143.8 (*ipso*-Ph); 128.5, 127.0, 125.8 (Ph); 46.3 (*C*Me_2); 26.2 (Me).

D) $CPh_2(CH_2CH_2Br)CO_2H$. IR (solid state): ν/cm^{-1} = 3058w, 2983w, 2932w, 2815w, 2684w, 2639w, 2516w, 1958w, 1900w, 1815w, 1771w, 1702vs, 1599w-m, 1494m-s, 1440m-sh, 1402m, 1335w, 1306w-m, 1270s, 1229w, 1209w, 1178w, 1162w, 1147w-m, 1088w, 1066w, 1034w, 1015w-m, 915m-br, 841w, 785w-m, 756s, 740m, 726m-s, 687vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ/ppm = 10.58 (br, 1 H, OH); 7.40-7.31 (m, 10 H, Ph); 3.15-3.11 (m, 2 H, $BrCH_2$); 3.01-2.97 (m, 2 H, CH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ/ppm = 179.9 (C=O); 141.0 (*ipso*-Ph); 128.7, 128.4, 127.6 (Ph); 60.6 (*C*Ph_2); 41.6 (CH_2); 28.8 ($BrCH_2$).

E) $CHPh_2CO_2H$. IR (solid state): ν/cm^{-1} = 3025w, 2903w, 2703w, 2604w, 1956w, 1699s (C=O), 1600w-m, 1581w, 1497m, 1449m-sh, 1410m, 1314m-sh, 1282w, 1222s, 1183w-br, 1080w, 1033w-

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

F) MeC≡CCO$_2$H. IR (solid state): ν/cm^{-1} = 2801w, 2624m, 2479w-m, 2321w, 2246vs (C≡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}. ^{1}H NMR ($CDCl_3$): δ/ppm = 11.33 (s, 1H, OH); 2.01 (s, 3 H, Me). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ/ppm = 158.6 (C=O); 88.8(CO–*C*≡C); 71.9(C≡*C*–Me); 3.8 (Me).

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

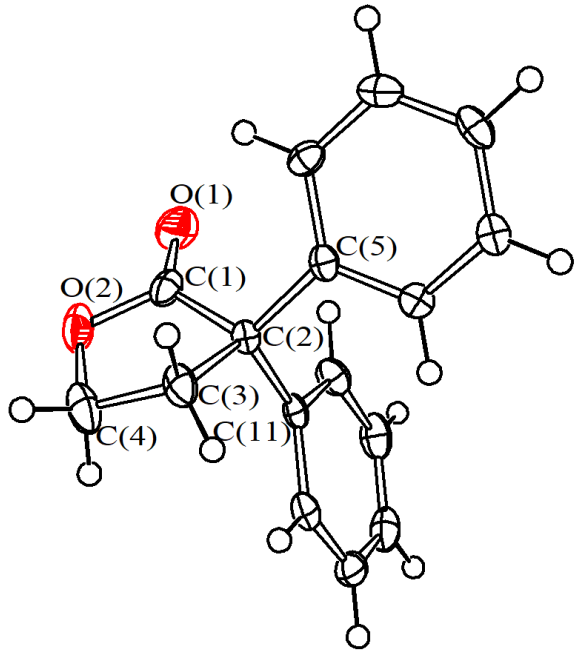

Table S1. Selected bond lengths (Å) and angles (deg) for **6**.

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)=CHCO$_2$H, **8**. Displacement ellipsoids are at the 50% probability level.

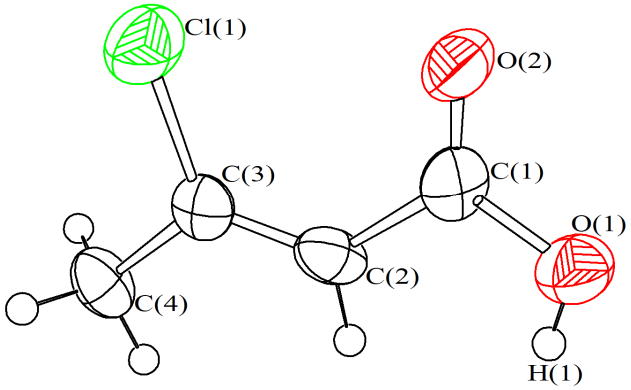

Table S2. Selected bond lengths (Å) and angles (deg) for MeC(Cl)=CHCO$_2$H, **8**.

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)=CHCO$_2$H, **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 $CPh_2(CH_2CH_2Br)CO_2H$ (**A1**). Displacement ellipsoids are at the 50% probability level.

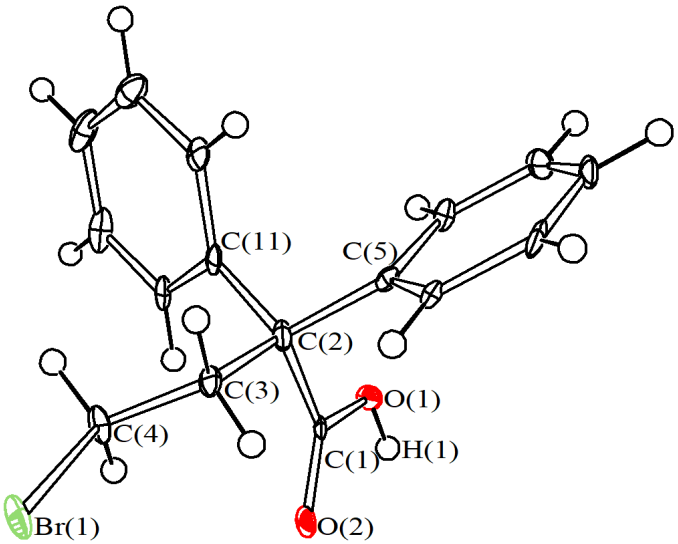

Table S4. Selected bond lengths (Å) and angles (deg) for $CPh_2(CH_2CH_2Br)CO_2H$, **A1**.

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 $CPh_2(CH_2CH_2Br)CO_2H$, **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 $CPh_2(CH_2CH_3)CO_2H$, **A2**. Displacement ellipsoids are at the 50% probability level.

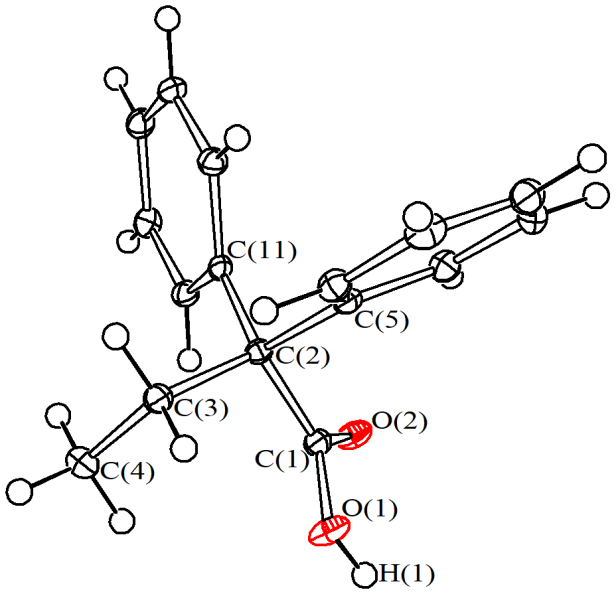

Table S6. Selected bond lengths (Å) and angles (deg) for $CPh_2(CH_2CH_3)CO_2H$, **A2**.

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 $CPh_2(CH_2CH_3)CO_2H$, **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. ^{1}H NMR spectrum (401 MHz, CD_2Cl_2) of $[CPh_3][MoOCl_4]$, **1**.

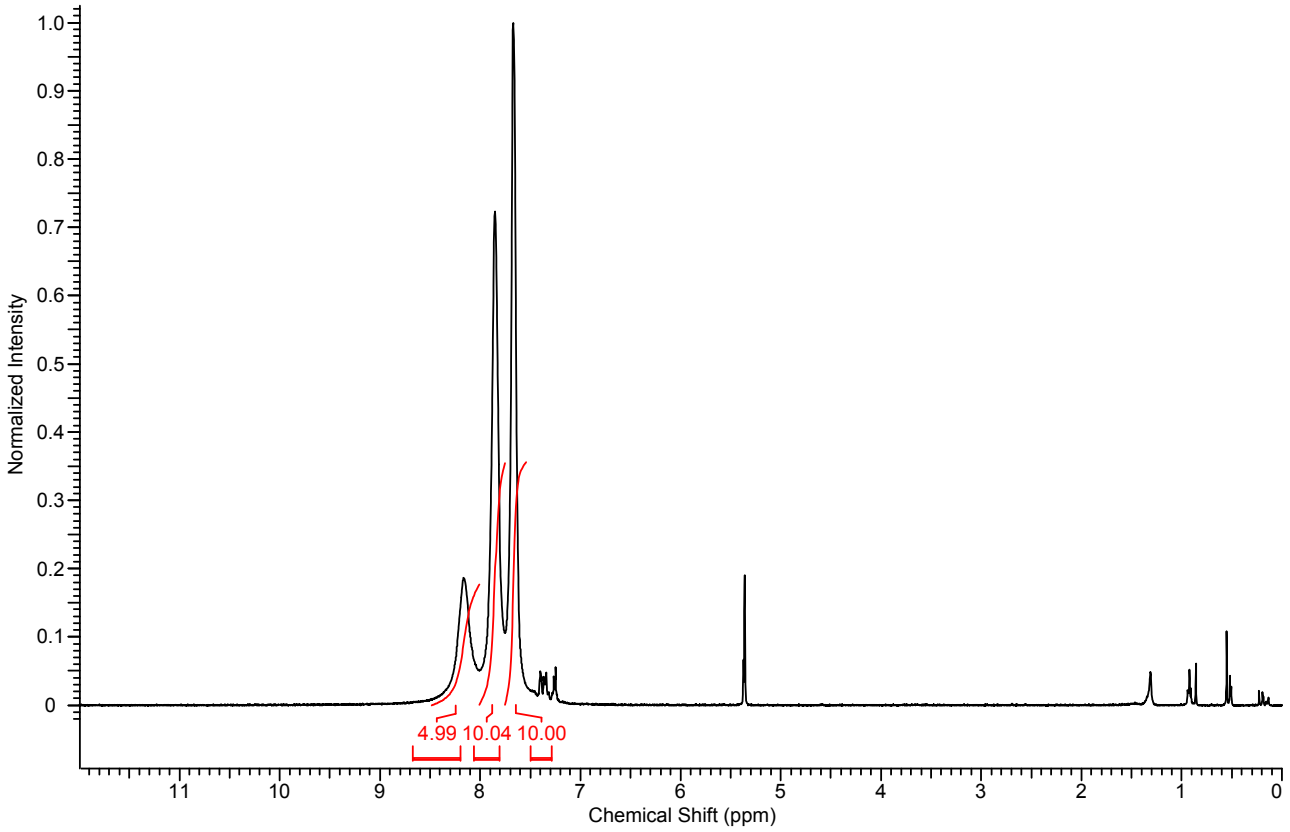

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of $[CPh_3][MoOCl_4]$, **1**.

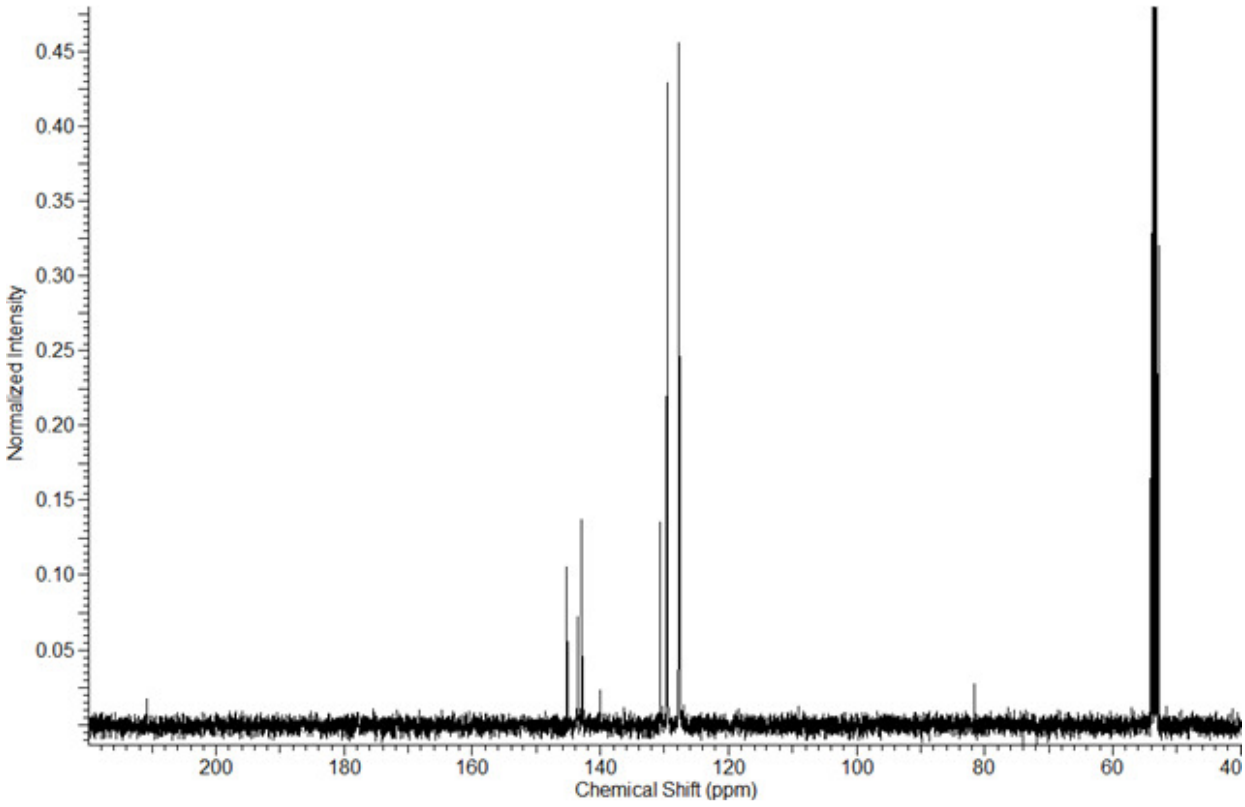

Figure S19. ^{19}F NMR spectrum (CD_3CN) of $[CPh_3][NbF_6]$, **2**.

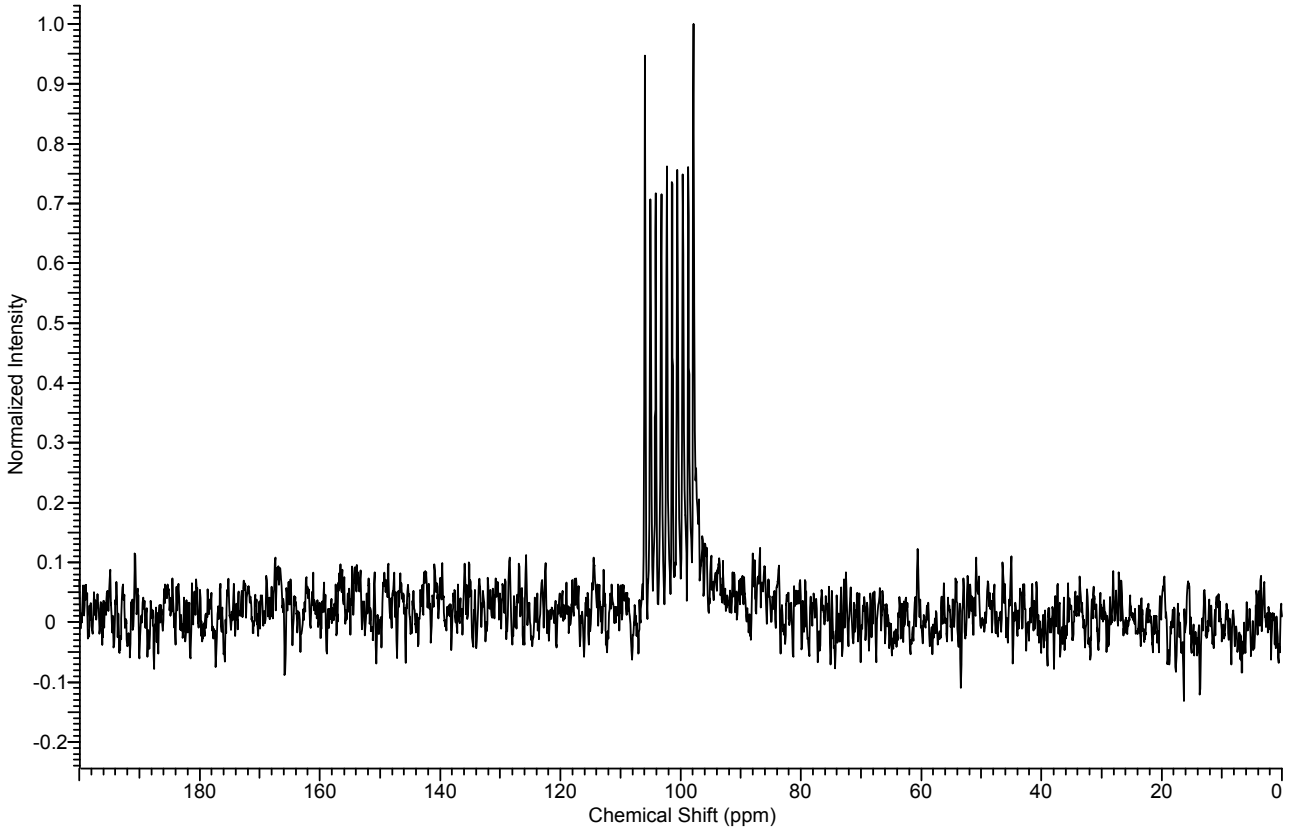

Figure S20. ^{93}Nb NMR spectrum (CD_3CN) of $[CPh_3][NbF_6]$, **2**.

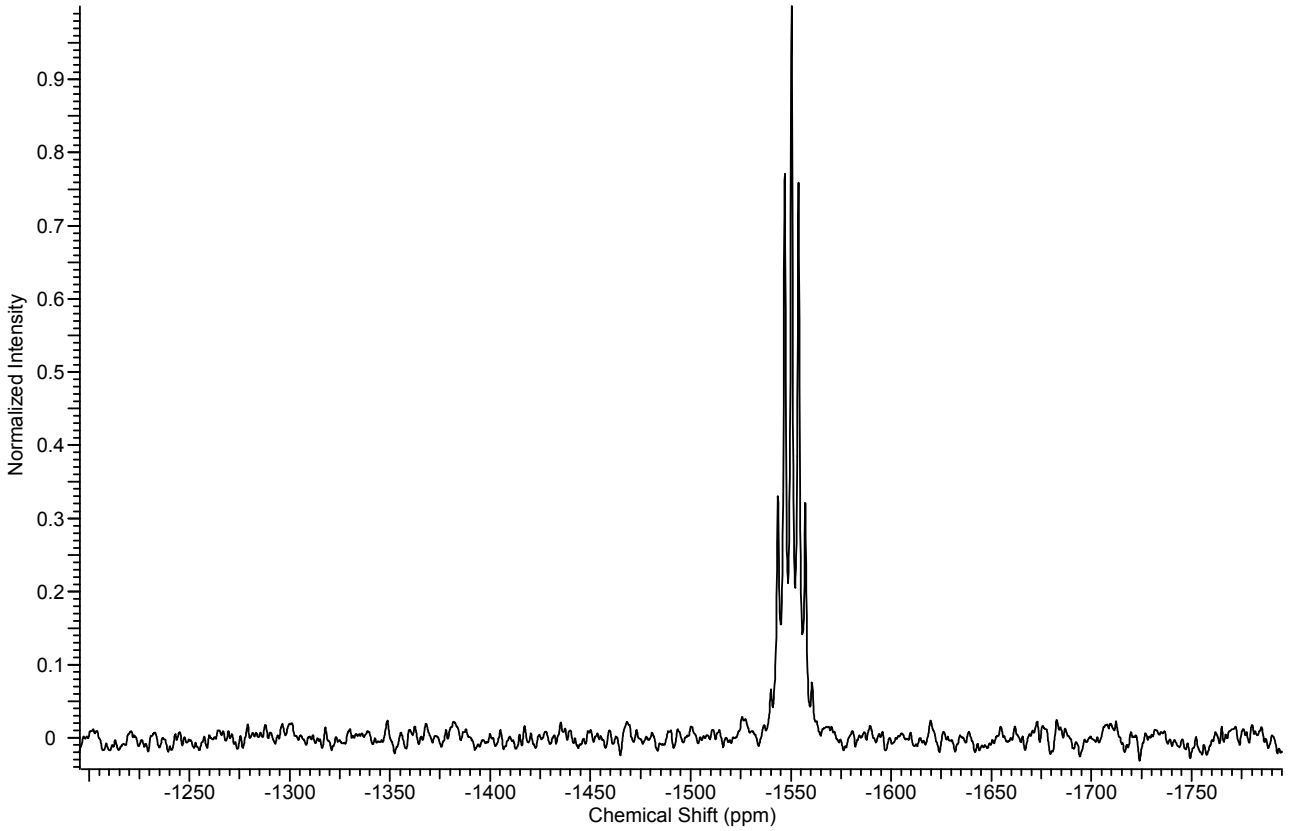

Figure S21. ^{1}H NMR spectrum (401 MHz, CD_2Cl_2) of $[CPh_3][NbCl_6]$, **3**.

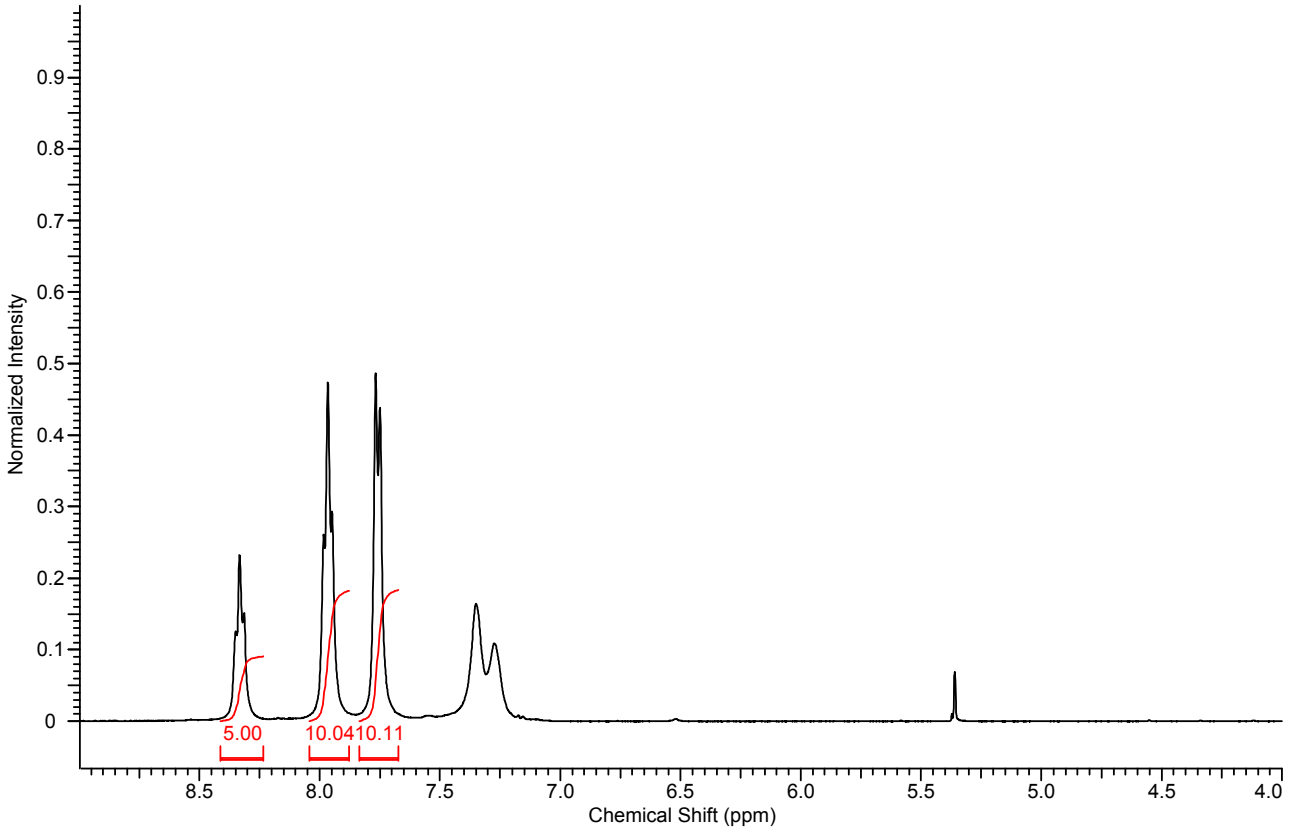

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of $[CPh_3][NbCl_6]$, **3**.

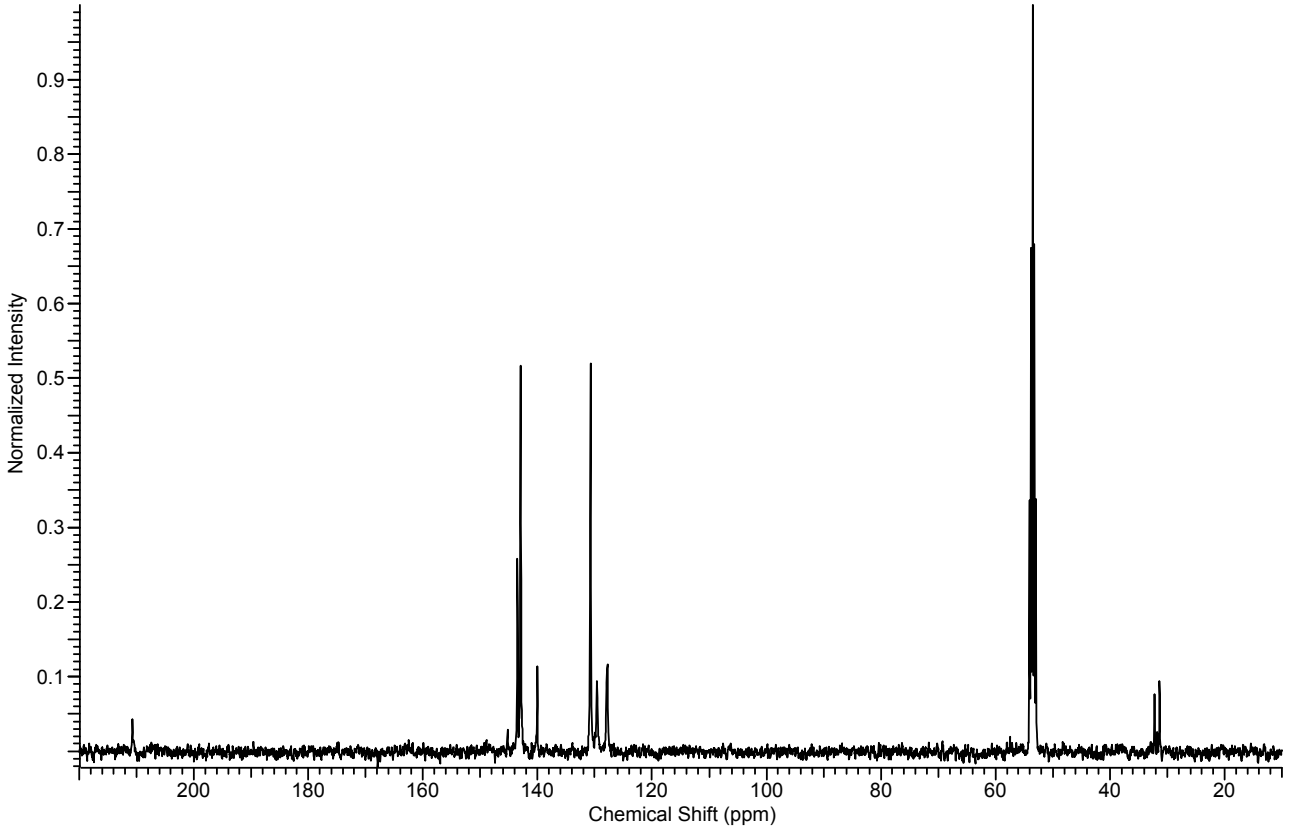

Figure S23. ^{1}H NMR spectrum (401 MHz, CD_2Cl_2) of **5a**.

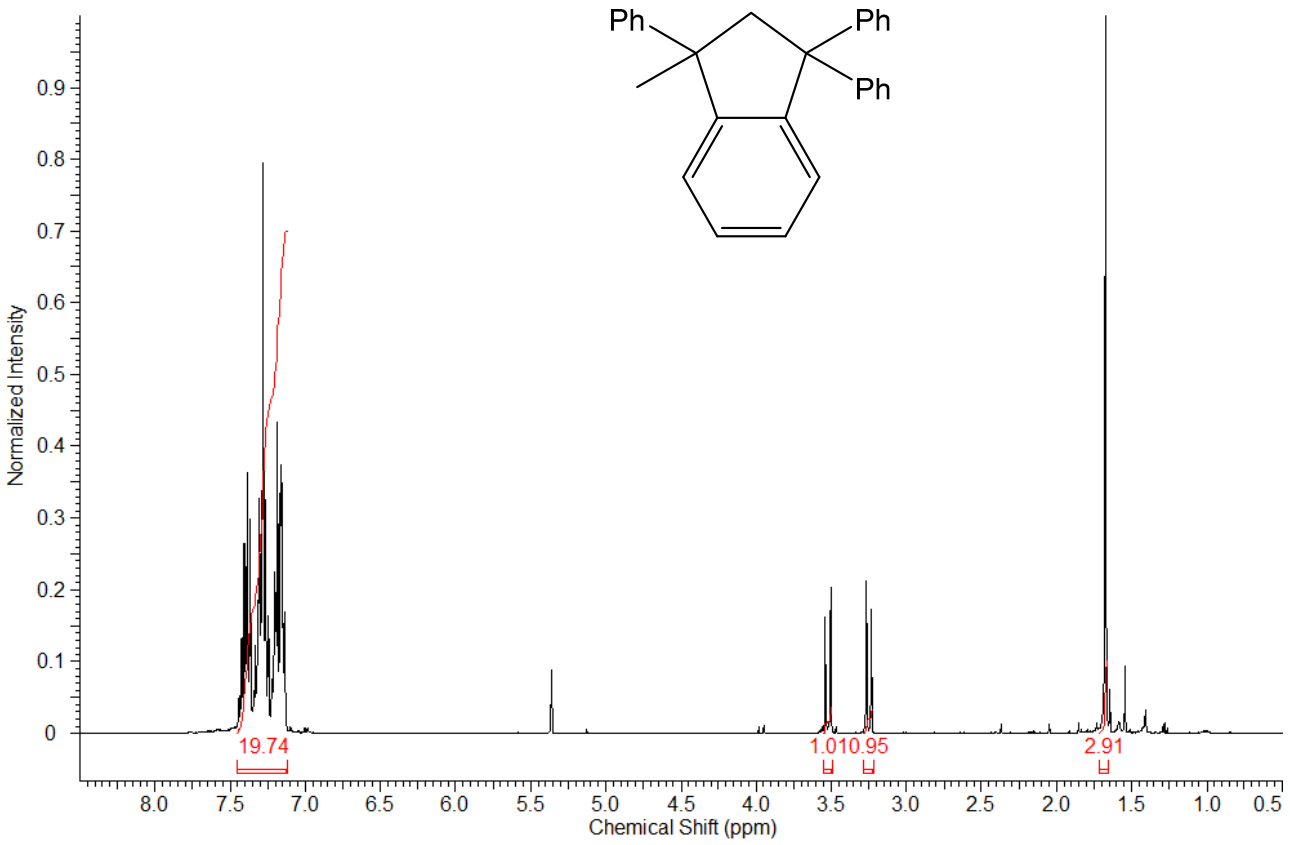

Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **5a**.

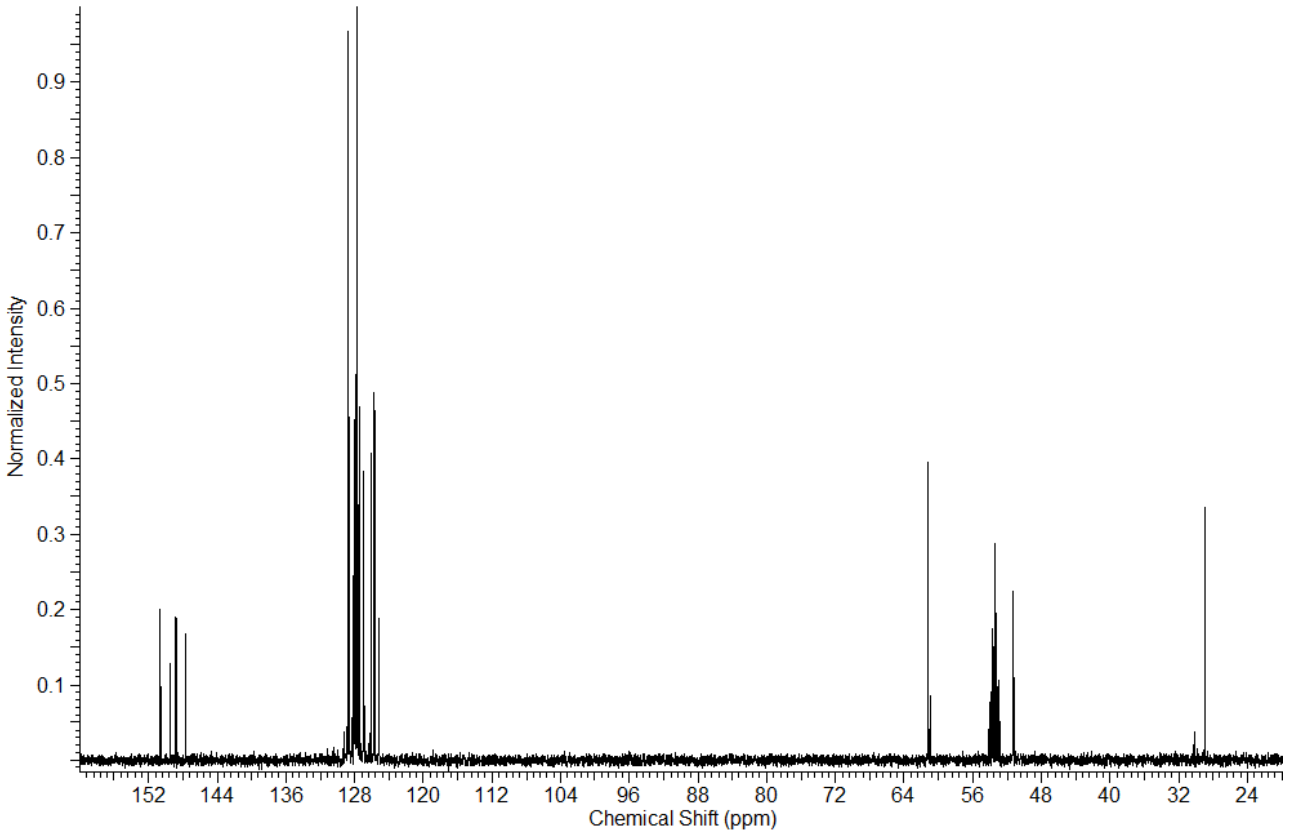

Figure S25. ^{1}H NMR spectrum (401 MHz, CD_2Cl_2) of **5b**.

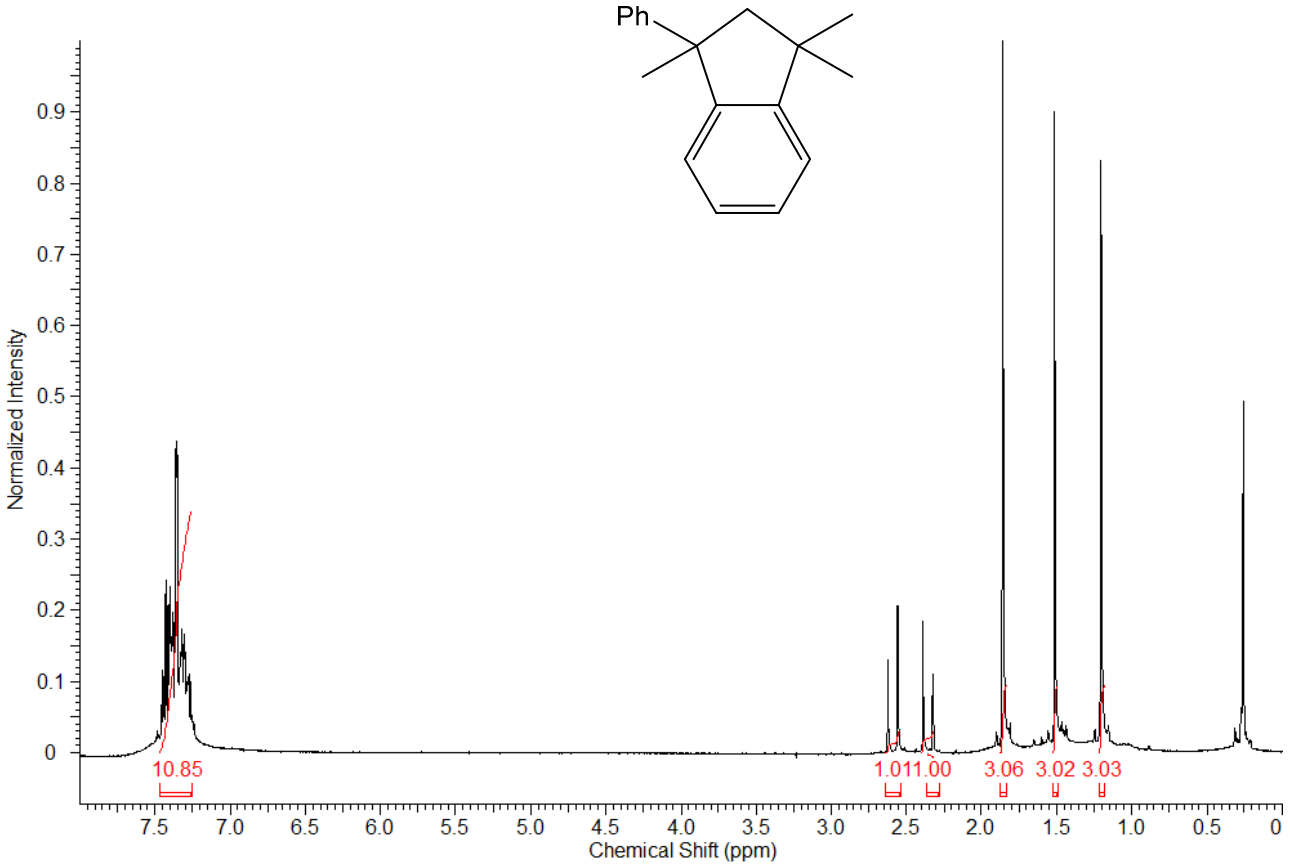

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of **5b**.

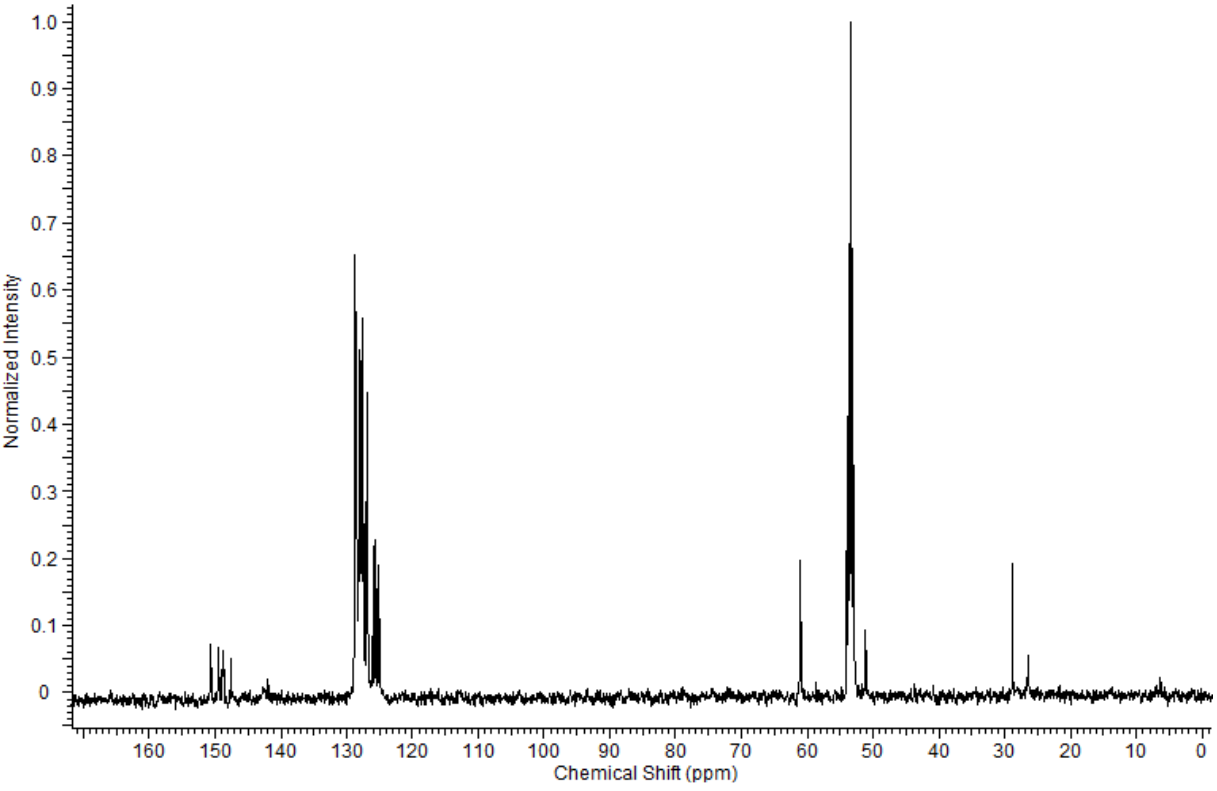

Figure S27. ^{1}H NMR spectrum (401 MHz, CD_2Cl_2) of $NbCl_4(O_2CCHPh_2)$, **6**.

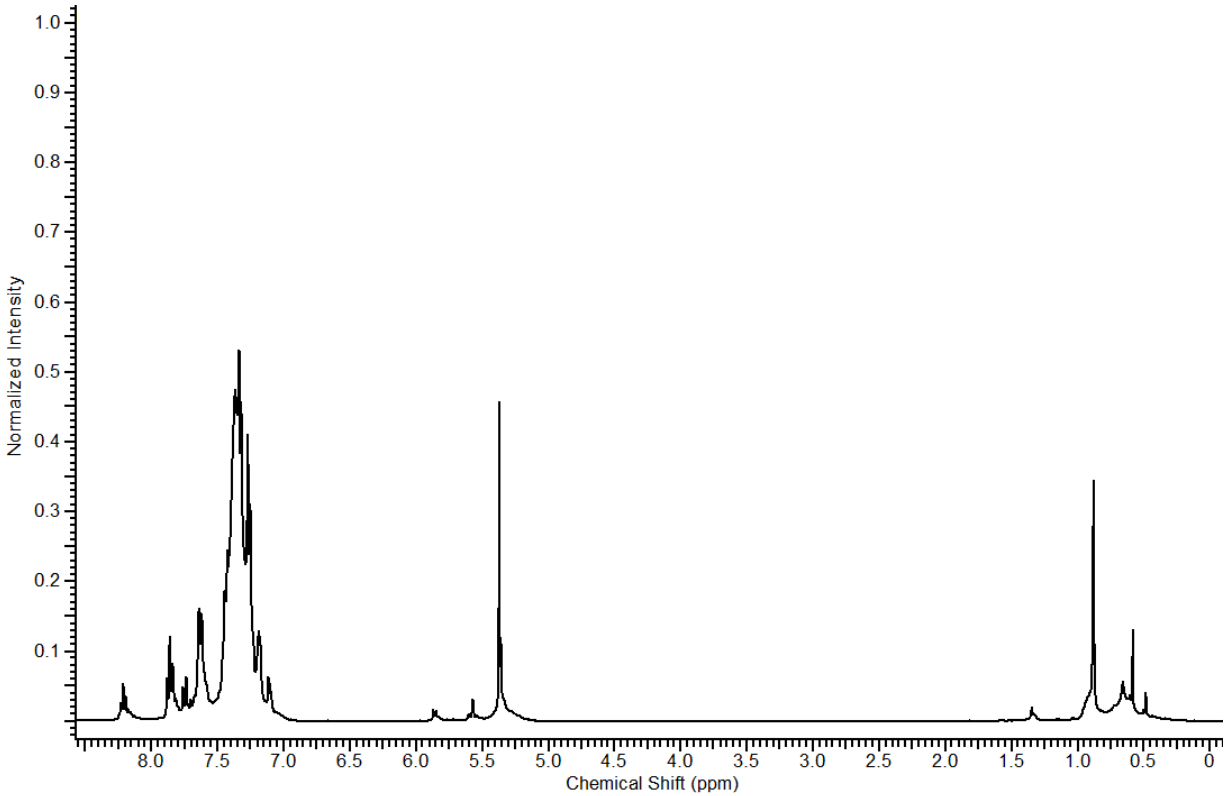

Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, CD_2Cl_2) of $NbCl_4(O_2CCHPh_2)$, **6**.

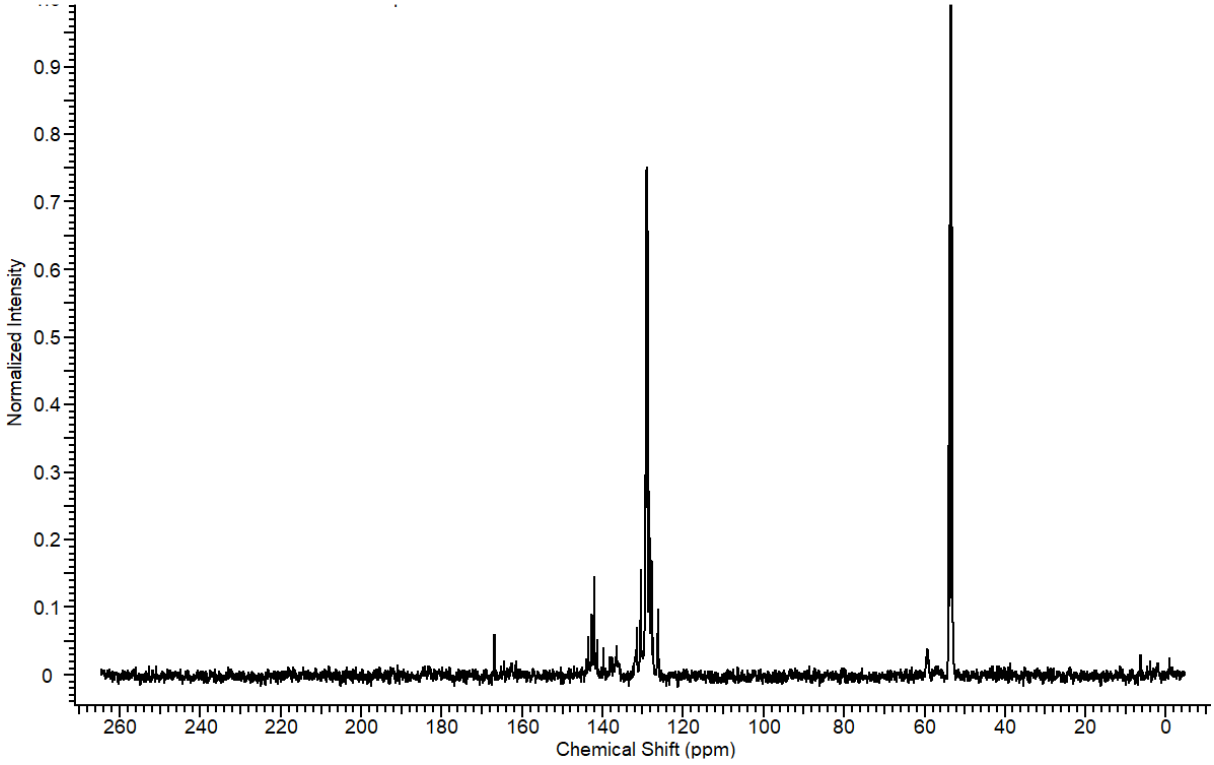

Figure S29. ^{1}H NMR spectrum (401 MHz, $CDCl_3$) of 3,3-diphenyldihydrofuran-2(3H)-one, **7**.

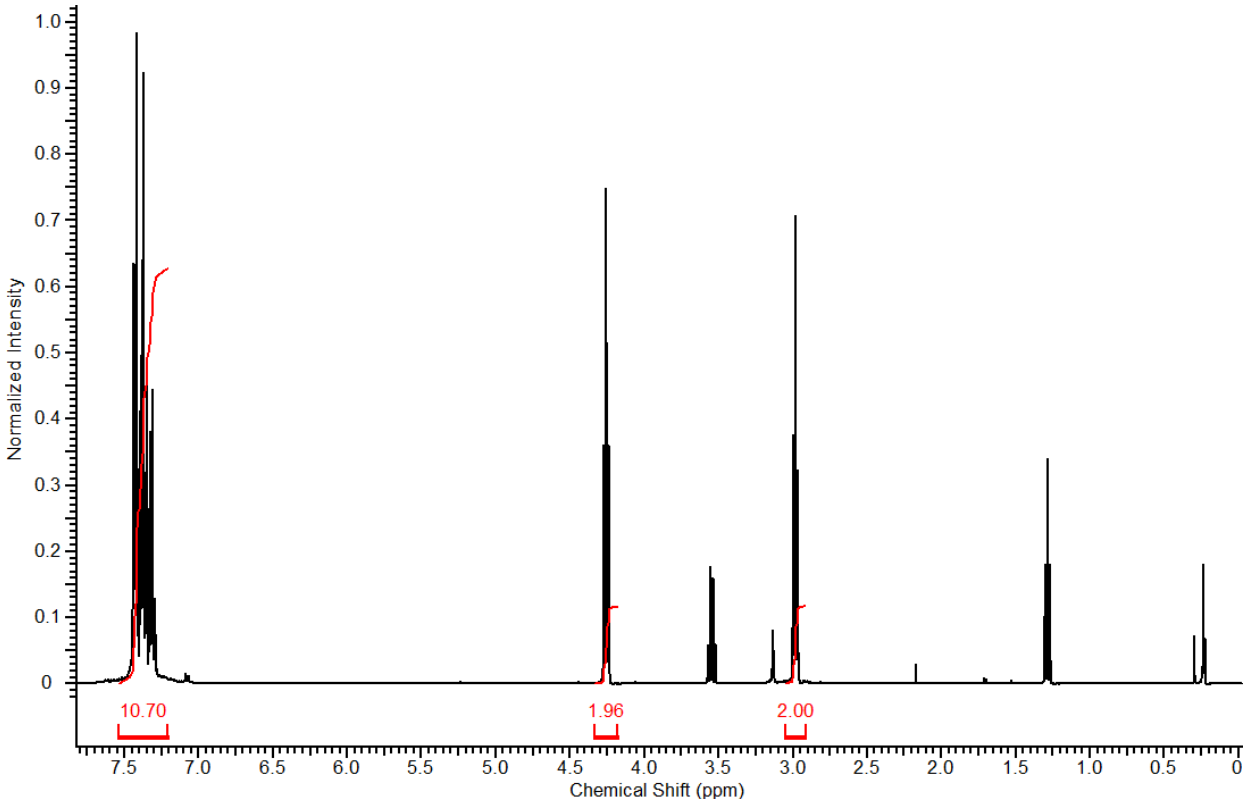

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of 3,3-diphenyldihydrofuran-2(3H)-one, **7**.

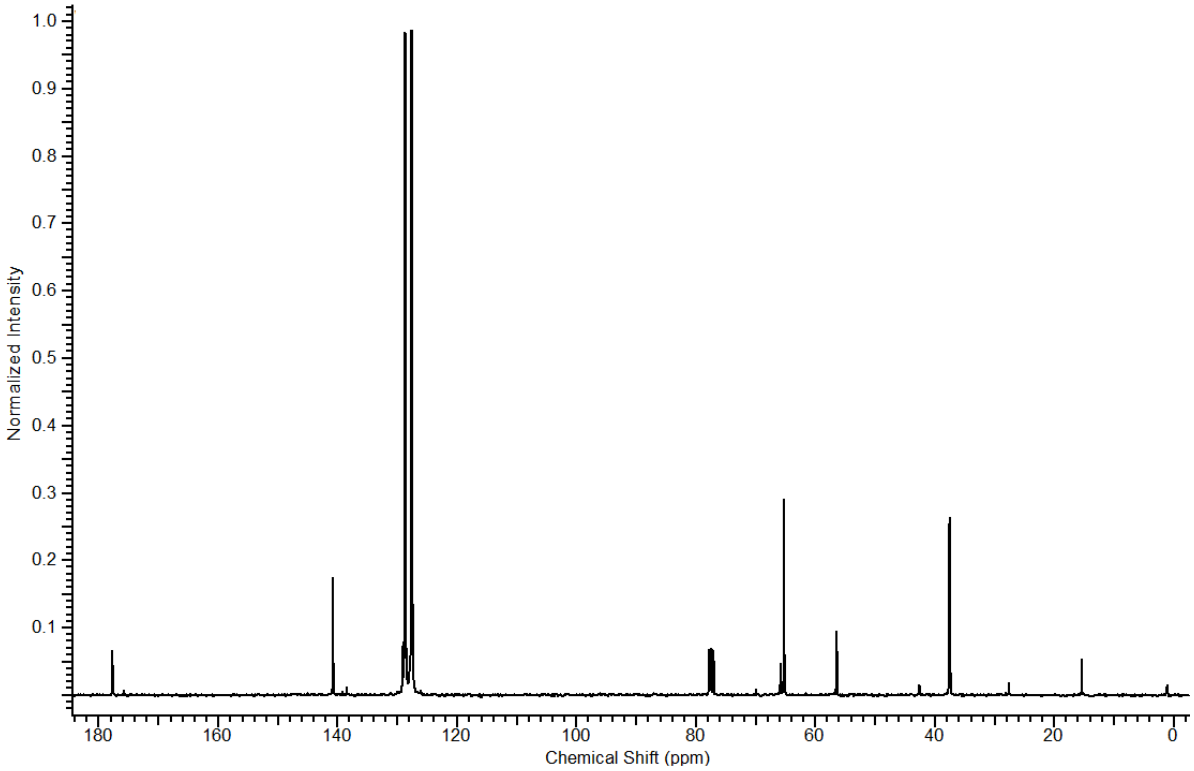

Figure S31. ^{1}H NMR spectrum (401 MHz, $CDCl_3$) of MeC(Cl)=CHCOOH, **8**.

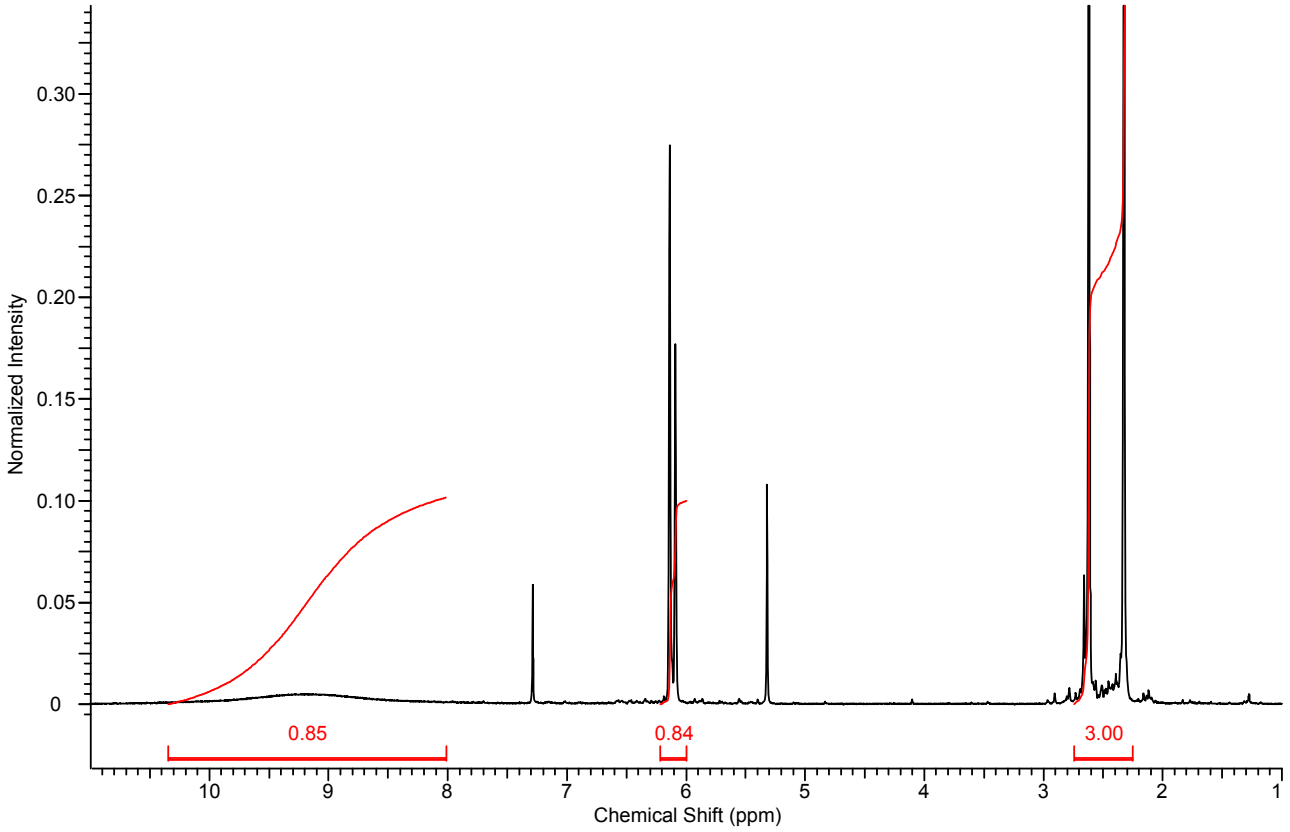

Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of MeC(Cl)=CHCOOH, **8**.

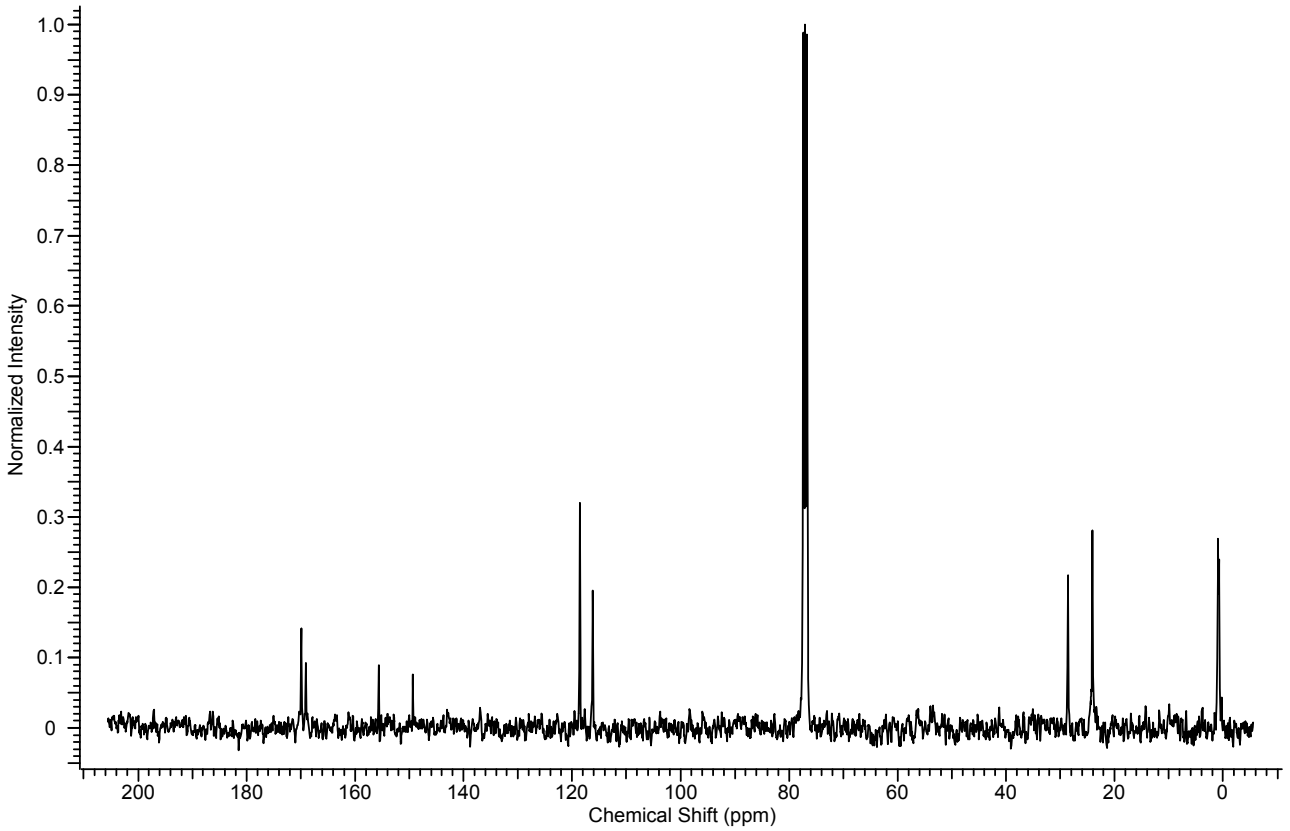

Figure S33. IR (ATR) spectrum of $[CPh_3][MoOCl_4]$, **1**.

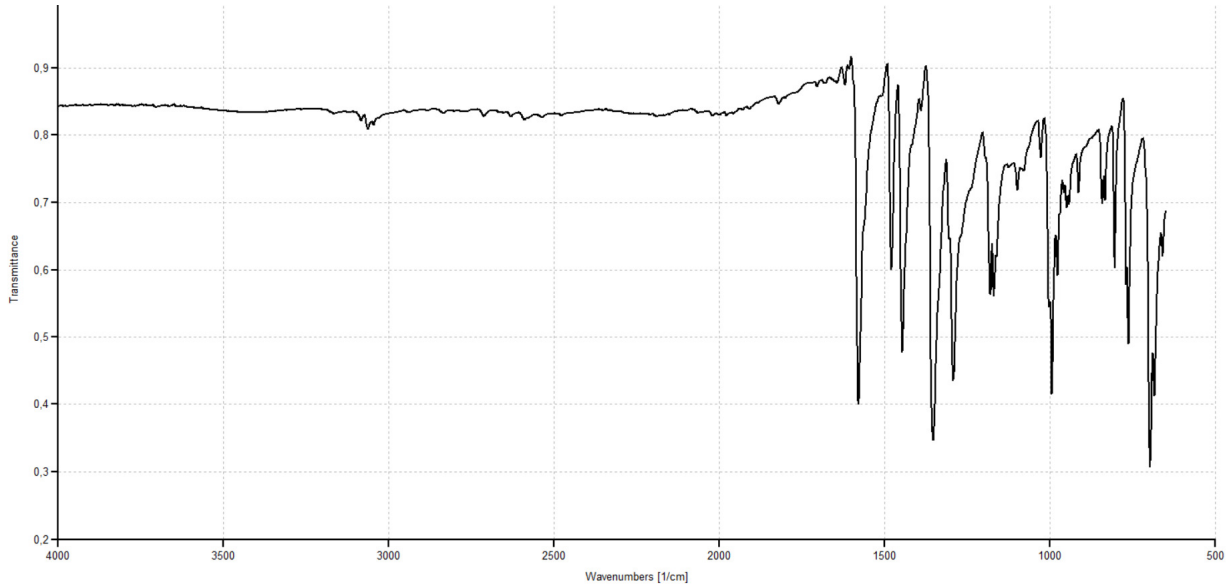

Figure S34. IR (ATR) spectrum of $[CPh_3][NbF_6]$, **2**.

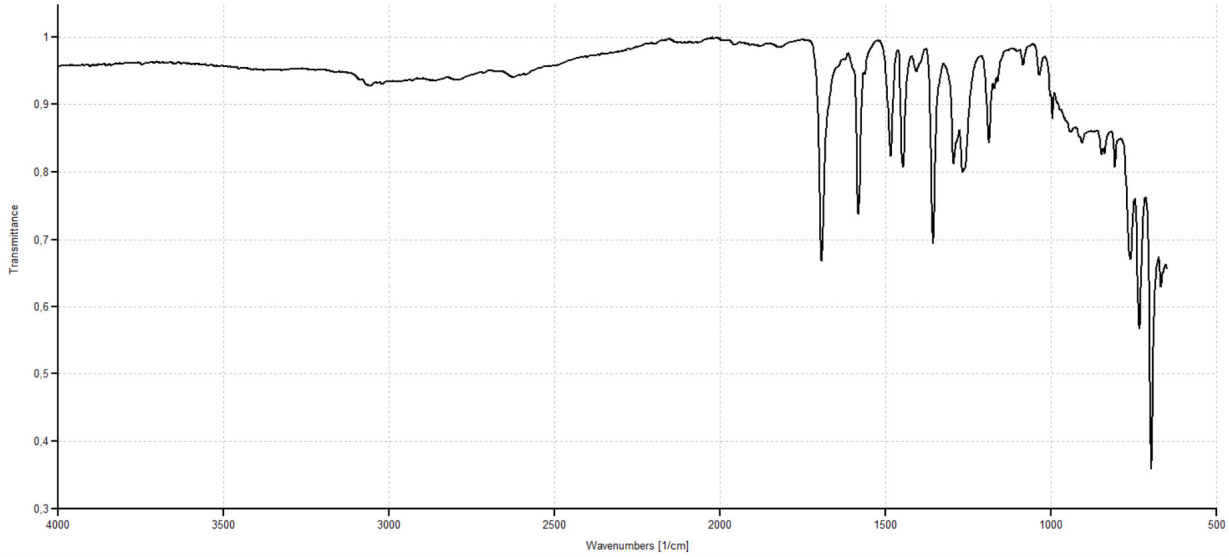

Figure S35. IR (ATR) spectrum of $[CPh_3][NbCl_6]$, **3**.

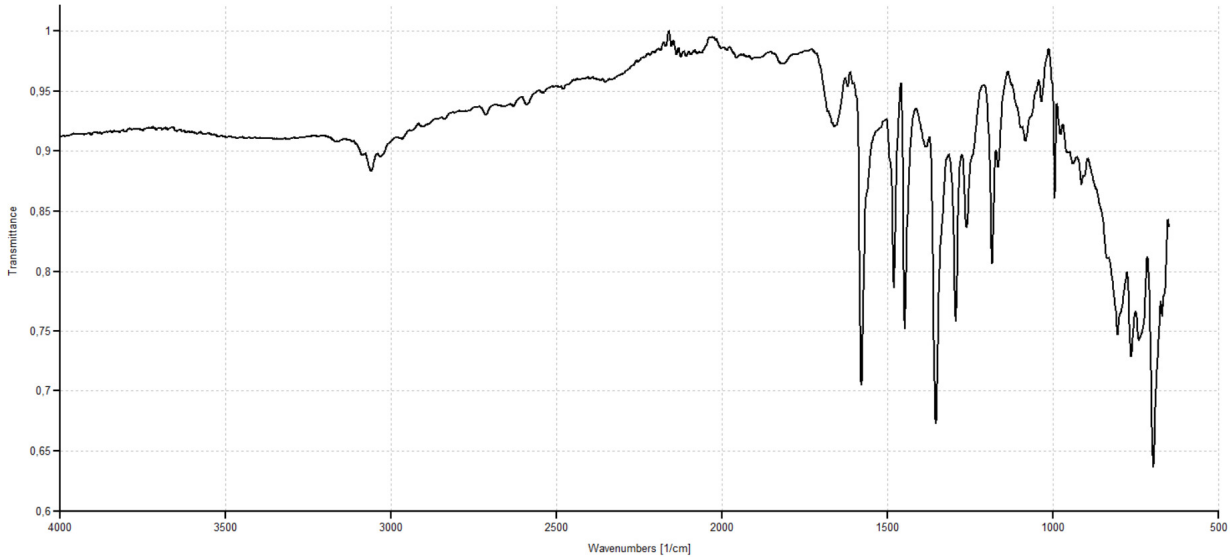

Figure S36. IR (ATR) spectrum of $[CPh_3][Ti_2Cl_8(\mu\text{-}\kappa^2\text{-}O_2CCPh_3)]$, **4**.

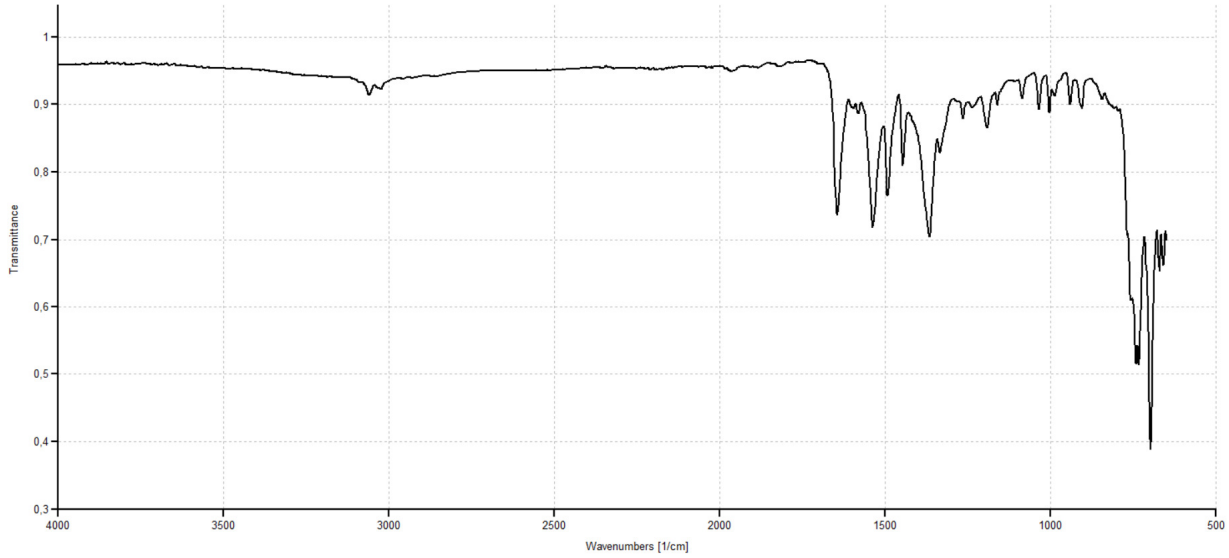

Figure S37. IR (ATR) spectrum of $NbCl_4(O_2CCHPh_2)$, **6**.

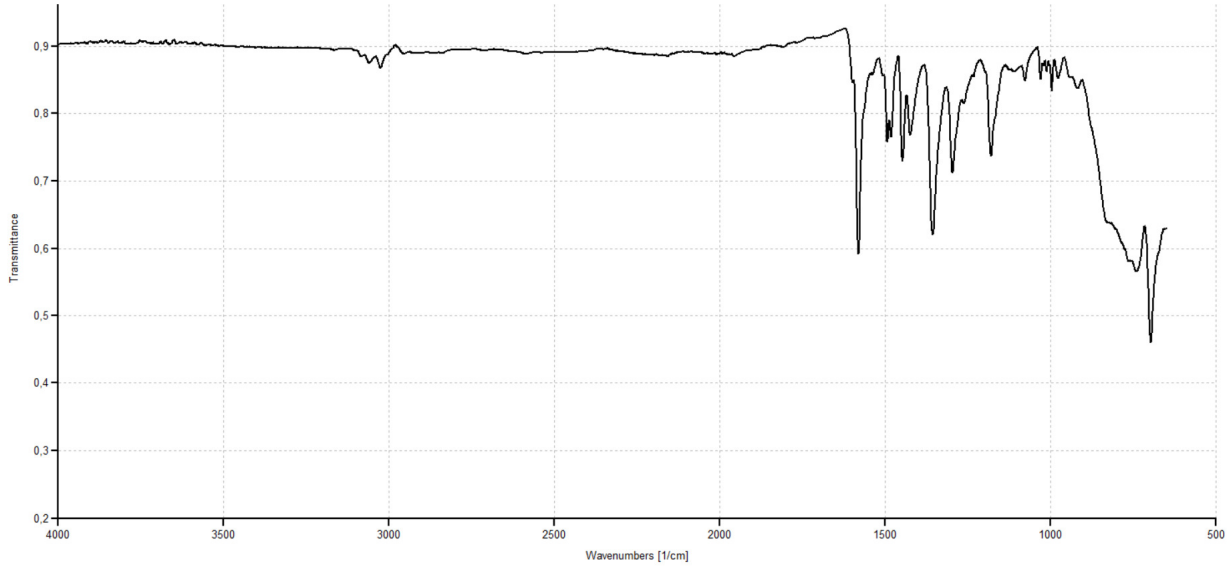

Figure S38. IR (ATR) spectrum of 3,3-diphenyldihydrofuran-2(3H)-one, **7**.

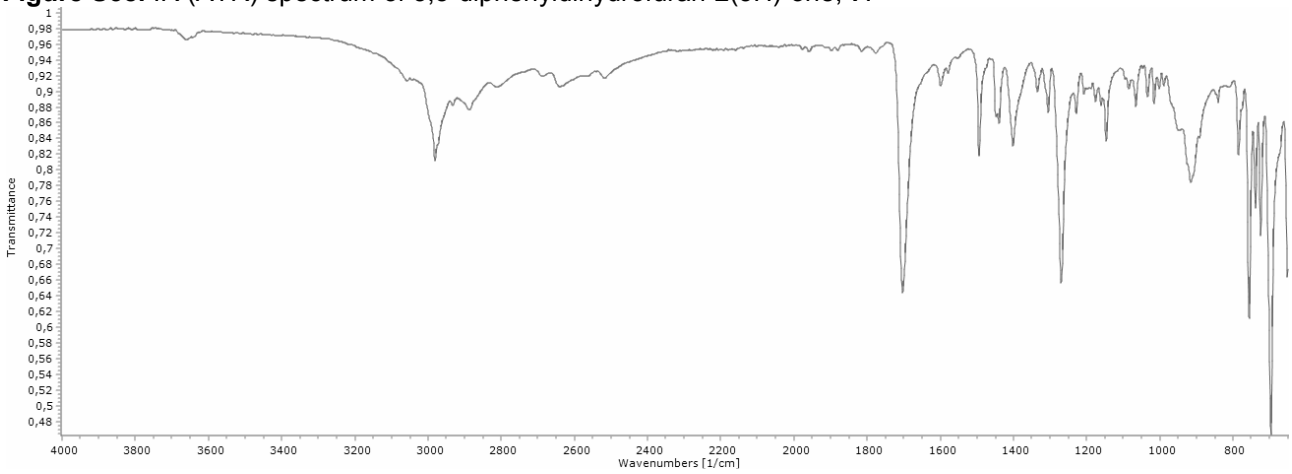

Figure S39. IR (ATR) spectrum of MeC(Cl)=CHCOOH, **8**.