

# Straightforward Formation of Carbocations from Tertiary Carboxylic Acids via CO Release at Room Temperature

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**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.  $\text{WCl}_6$  (99.9%) and  $\text{PCl}_5$  (98%) were purchased from Strem and stored in sealed tubes under argon atmosphere.  $\text{WOCl}_4$  <sup>1</sup> was prepared according to the literature. Organic reactants were purchased from Sigma-Aldrich or TCI Europe, were of the highest purity available and stored under nitrogen atmosphere as received. 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  $^1\text{H}$  and  $^{13}\text{C}$  were referenced to the non-deuterated aliquot of the solvent.  $^1\text{H}$  and  $^{13}\text{C}$  Spectra were assigned with the assistance of  $^1\text{H}$ - $^{13}\text{C}$  (*gs*-HSQC and *gs*-HMBC) correlation experiments.<sup>2</sup> 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 <sup>3</sup> on solutions prepared by dissolution of the solids in aqueous KOH at boiling temperature, followed by cooling down to room temperature and addition of  $\text{HNO}_3$  up to neutralization.

### Spectroscopic data of carboxylic acids.

**A) Ph<sub>3</sub>CCO<sub>2</sub>H.** IR (solid state):  $\nu/\text{cm}^{-1}$  = 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. <sup>1</sup>H NMR (dmsO-d<sub>6</sub>):  $\delta/\text{ppm}$  = 7.28, 7.15 (m, 15 H, Ph); 3.5 (br, 1 H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (dmsO-d<sub>6</sub>):  $\delta/\text{ppm}$  = 174.8 (C=O); 143.7 (*ipso*-Ph), 130.4, 128.1, 127.1 (Ph); 67.4 (CPh<sub>3</sub>).

**B) CEt(Ph)<sub>2</sub>CO<sub>2</sub>H.** IR (solid state):  $\nu/\text{cm}^{-1}$  = 3060w, 2987w, 2967w, 2941w, 2883w, 1695s (C=O), 1597w, 1492m, 1459w, 1444m, 1402w, 1376w, 1316m, 1281w, 1255s, 1196m, 1159w, 1126w, 1093w, 1032w, 1002vw, 917m, 898w-sh, 802m, 760s, 729s, 700vs. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta/\text{ppm}$  = 7.36-7.27 (m, 10 H, Ph); 2.45 (q, <sup>3</sup>J<sub>HH</sub> = 7.34 Hz, 2 H, CH<sub>2</sub>); 0.79 (t, <sup>3</sup>J<sub>HH</sub> = 7.34 Hz, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta/\text{ppm}$  = 179.8 (C=O); 142.3 (*ipso*-Ph); 129.1, 127.9, 126.9 (Ph); 60.7 (CPh<sub>2</sub>); 30.8 (CH<sub>2</sub>); 9.8 (Me).

**C) CMe(Ph)<sub>2</sub>CO<sub>2</sub>H.** IR (solid state):  $\nu/\text{cm}^{-1}$  = 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  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta/\text{ppm}$  = 7.36-7.25 (10 H, Ph); 1.95 (s, 3 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta/\text{ppm}$  = 180.9 (OCO); 144.4 (*ipso*-Ph); 128.7, 128.6, 127.6 (Ph); 56.9 (CPh<sub>2</sub>); 27.2 (Me).

**D) CMe<sub>2</sub>(Ph)CO<sub>2</sub>H.** IR (solid state):  $\nu/\text{cm}^{-1}$  = 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  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta/\text{ppm}$  = 7.43 (d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 H, *ortho* H); 7.37 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 H, *meta* H); 7.29 (d, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 1 H, *para* H); 1.63 (s, 3H); 1.63 (s, 6 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta/\text{ppm}$  = 182.9 (C=O); 143.8 (*ipso*-Ph); 128.5, 127.0, 125.8 (Ph); 46.3 (CMe<sub>2</sub>); 26.2 (Me).

## Synthesis and characterization of carboxylic acid chlorides.

*General procedure.* In a Schlenk tube, a solution of the carboxylic acid reactant (ca. 0.50 mmol) in  $\text{CDCl}_3$  (ca. 4 mL) was treated with  $\text{PCl}_5$  (1.0 eq.). The mixture was stirred at room temperature for 2 h. An aliquot (0.5 mL) of the resulting solution was analyzed by NMR spectroscopy. The  $^{31}\text{P}$  spectrum clearly showed the presence of  $\text{POCl}_3$  ( $\delta$  = ca. 4 ppm) as unique phosphorus species.<sup>4</sup> The solution resulted unchanged after stirring 24-48 hours at room temperature. The solution was dried under vacuum, and the colourless residue characterized by IR spectroscopy.

**A)  $\text{Ph}_3\text{CC(O)Cl}$ .** IR (solid state):  $\nu/\text{cm}^{-1}$  = 3059w, 3034w, 1804m, 1790m-s, 1770s (C=O), 1594w, 1494s, 1443s, 1322w, 1186w, 1157w, 1087m, 1034m, 1009m-s, 994m-s, 941w, 917w, 901w, 790s, 753s, 729vs, 697vs, 666vs.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.43-7.31 (Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 175.6 (C=O), 141.0 (*ipso*-Ph), 130.4, 128.3, 127.6 (Ph), 76.3 ( $\text{CPh}_3$ ).

**B)  $\text{CEt(Ph)}_2\text{C(O)Cl}$ .** IR (solid state):  $\nu/\text{cm}^{-1}$  = 3061vw, 2981w, 2940vw, 2882vw, 1796s, 1770s-sh (C=O), 1495m, 1445m, 1383w, 1297vs, 1094w, 1033w, 1014w, 967m, 912w, 807s, 756w, 731vs, 699vs.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.40-7.33 (10 H, Ph); 2.57 (q,  $^3J_{\text{HH}}$  = 7.34 Hz, 2 H,  $\text{CH}_2$ ); 0.86 (t,  $^3J_{\text{HH}}$  = 7.34 Hz, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 176.3 (C=O); 139.9 (*ipso*-Ph); 129.4, 128.3, 127.7 (Ph); 70.3 ( $\text{CPh}_2$ ); 32.0 ( $\text{CH}_2$ ); 9.6 ( $\text{CH}_3$ ).

**C)  $\text{CMe(Ph)}_2\text{C(O)Cl}$ .** IR (solid state):  $\nu/\text{cm}^{-1}$  = 3061w, 3027w, 2999w, 1775vs (C=O), 1599w, 1495m, 1460w-m, 1444m, 1377m, 1336w, 1297w, 1223w, 1189w, 1159w, 1127w, 1082w, 1027w-m, 929s, 903s, 779m-s, 759m, 746m, 729vs, 695vs, 654vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.39, 7.29 (m, 10 H, Ph), 2.13 (s, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 177.6 (CO), 141.5 (*ipso*-Ph), 128.5, 128.3, 127.8 (Ph), 66.0 ( $\text{CPh}_3$ ), 27.9 (Me).

**D)  $\text{CMe}_2(\text{Ph})\text{C(O)Cl}$ .** IR (solid state):  $\nu/\text{cm}^{-1}$  = 3062w, 2982w, 2939vw, 1820w-sh, 1780s (C=O), 1753w-sh, 1601w, 1584w, 1496m, 1461w, 1448m, 1388w, 1368w, 1238w, 1191w, 1157w, 1105w, 1077w, 1031w, 1015w, 944s, 909w, 874vs, 755s, 696vs  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.44-7.33 (5 H, Ph); 1.73 (s, 6 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 178.9 (C=O); 141.5 (*ipso*-Ph); 128.9, 127.8, 126.1 (Ph); 56.8 ( $\text{CMe}_2$ ); 26.5 (Me).

### Reaction of $\text{WCl}_6$ with triphenylacetic acid.

**A) NMR study: detection of  $\text{Ph}_3\text{CCl}$ , **2**, and  $[\text{CPh}_3]^+$ .** A suspension of  $\text{WCl}_6$  (108 mg, 0.272 mmol) in  $\text{CD}_2\text{Cl}_2$  (5 mL) was treated with  $\text{Ph}_3\text{CCO}_2\text{H}$  (81 mg, 0.281 mmol), and the mixture was stirred at room temperature for 72 hours. During this period of time, the system was purged with nitrogen in order to dynamically remove the released gas. Aliquots of the reaction solution were analyzed by NMR spectroscopy at different times. The  $^1\text{H}$  spectrum after ca. 20 minutes evidenced the prevalent presence of  $\text{Ph}_3\text{CC}(\text{O})\text{Cl}$ .  $^1\text{H}$  and  $^{13}\text{C}$  spectra at the end were as follows. The  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta/\text{ppm}$  = 8.31 (d,  $^3J_{\text{HH}}$  = 6.8 Hz, 1 H, *para* H); 7.96 (t,  $^3J_{\text{HH}}$  = 6.8 Hz, 2 H, *meta* H); 7.75 (d,  $^3J_{\text{HH}}$  = 7.0 Hz, 2 H, *ortho* H).  $2/[\text{CPh}_3]^+$  ratio = 2.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 210.0 (br,  $\text{CPh}_3$ ), 143.5, 142.9, 140.0, 130.7 (Ph).

**B) Isolation of  $[\text{CPh}_3][\text{WOCl}_5]$ , **1**.** A suspension of  $\text{Ph}_3\text{CCO}_2\text{H}$  (367 mg, 1.262 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was treated with  $\text{WCl}_6$  (505 mg, 1.273 mmol), and the mixture was stirred at room temperature for 18 hours. During this period of time, the system was purged with nitrogen in order to dynamically remove the released gas: a silver chloride precipitation test evidenced the formation of  $\text{HCl}$ , while GC analysis (*vide infra*) allowed to detect carbon monoxide. Removal of the volatiles gave a red-orange solid residue, which was washed with hexane (50 mL) and dried under vacuum. Thus **1** was isolated as an orange solid. Yield 252 mg, 32%. Anal. Calcd for  $\text{C}_{19}\text{H}_{15}\text{Cl}_5\text{OW}$ : C, 36.78; H, 2.44; Cl, 28.57. Found: C, 36.49; H, 2.48; Cl, 28.38. IR (solid state):  $\nu/\text{cm}^{-1}$  = 3060w, 1577vs, 1558w-m, 1480m, 1447s, 1352vs, 1292vs, 1183m-s, 1163w-m, 1125w, 1110w, 1085w, 993m-s ( $\nu_{\text{W=O}}$ ), 977m, 965m-s, 914w-m, 841m, 807w-m, 767m-s, 740w-m, 696vs.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta/\text{ppm}$  = 8.16, 7.85, 7.67 ppm (m, 5 H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 210.0 (br,  $\text{CPh}_3$ ), 143.4, 143.0, 140.4, 131.1 (Ph).

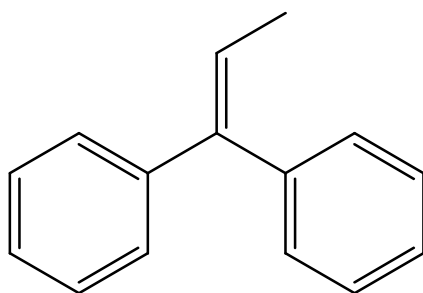
Crystals of **1** suitable for X-ray analysis were collected from a dichloromethane reaction solution layered with hexane and stored at  $-30^\circ\text{C}$  for one week.

**C) Reaction of  $\text{Ph}_3\text{CC}(\text{O})\text{Cl}$  with  $\text{WOCl}_4$ .** A solution of  $\text{CPh}_3\text{C}(\text{O})\text{Cl}$  (obtained from  $\text{CPh}_3\text{CO}_2\text{H}$ , 153 mg, 0.531 mmol, and  $\text{PCl}_5$ , 119 mg, 0.571 mmol, *vide supra*) in  $\text{CD}_2\text{Cl}_2$  (5 mL) was treated

with  $\text{WOCl}_4$  (182 mg, 0.533 mmol). The resulting orange-brown mixture was allowed to stir at room temperature for 5 days. NMR analysis on the final orange-red solution allowed for the identification of **1** and **2**. **1/2** ratio = 1:1.

**D) Reaction of  $\text{Ph}_3\text{CCO}_2\text{H}$  with  $\text{WOCl}_4$ .** The reaction of  $\text{WOCl}_4$  (302 mg, 0.884 mmol) with  $\text{Ph}_3\text{CCO}_2\text{H}$  (255 mg, 0.884mmol) was carried out with a procedure analogous to that described for  $\text{WCl}_6/\text{Ph}_3\text{CCO}_2\text{H}$ . Evolution of CO was detected by GC (*vide infra*).

**Reaction of  $\text{WCl}_6$  with  $\text{Ph}_2(\text{Et})\text{CCO}_2\text{H}$ : formation of prop-1-ene-1,1-diylidibenzene, **3** (Chart 1).**



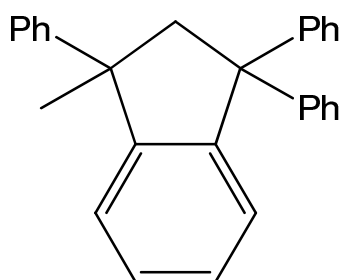
**Chart 1.** Structure of **3**.

A solution of  $\text{Ph}_2(\text{Et})\text{CCO}_2\text{H}$  (295 mg, 1.23 mmol) in dichloromethane (15 mL) was treated with  $\text{WCl}_6$  (162 mg, 0.409 mmol), and the mixture was allowed to stir at room temperature for 22 hours. The resulting dark-red solution was added of  $\text{H}_2\text{O}$  (ca. 3 mL). A yellow solid (**3**) was obtained after filtration through alumina column, using dichloromethane as eluent. Yield 148 mg, 62%. Anal. Calcd for  $\text{C}_{15}\text{H}_{14}$ : C, 92.74; H, 7.26. Found: C, 90.13; H, 7.48. IR (solid state):  $\nu/\text{cm}^{-1}$  = 3080vw, 3056w, 3025w, 2911w, 1598w, 1494m, 1441m, 1355w, 1073w, 1031w, 964w, 914w, 891w, 840w, 756s, 695vs.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.51-7.31 (10H, Ph); 6.31 (q,  $^3J_{\text{HH}}$  = 6.85 Hz, 1 H, CH); 1.89 (d,  $^3J_{\text{HH}}$  = 6.85 Hz, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 143.1, 142.6, 140.1 (arom C +  $\text{CPh}_2$ ); 130.2, 128.5, 128.2, 127.3, 127.0, 126.9 (Ph); 124.2 (CH); 15.8 (Me). When the same reaction was repeated in  $\text{CD}_2\text{Cl}_2$ , NMR analysis of an aliquot of the reaction mixture after ca. 20 minutes evidenced the prevalent presence of  $\text{CPh}_2(\text{Et})\text{C}(=\text{O})\text{Cl}$ .

## Synthesis of indenenes.

*General procedure.* In a Schlenk tube,  $\text{WCl}_6$  was added to a solution of the carboxylic acid in  $\text{CH}_2\text{Cl}_2$  (ca. 20 mL). The obtained mixture was stirred at room temperature for the appropriate time, which was determined by monitoring the reaction evolution by NMR. Formation of  $\text{HCl}$  was observed by means of silver chloride precipitation test. At the end, the mixture was treated with  $\text{H}_2\text{O}$  (ca. 2 mL), and the resulting mixture was allowed to stir at room temperature for 24 hours. The solution was separated from the precipitate by filtration. The precipitate was then dissolved in a saturated  $\text{NaHCO}_3$  solution, and, after liquid\liquid extraction with diethyl ether, the organic phase was added to the filtrated solution. After drying under vacuum, the residue was dissolved in diethyl ether and filtrated on an alumina column using diethyl ether/ $\text{CH}_2\text{Cl}_2$  mixture (ca. 1:1) as eluent. The eluted solution was dried under vacuum thus affording a colourless residue.

### A) Synthesis of 1-methyl-1,3,3-triphenyl-2,3-dihydro-1H-indene, **4a** (Chart 2), and detection of $[\text{CPh}_2(\text{Me})]^+$ .<sup>5</sup>



**Chart 2.** Structure of **4a**.

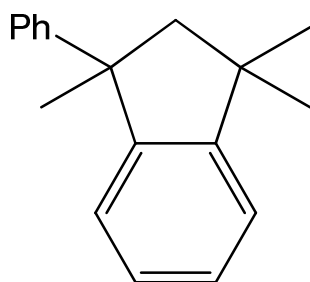
From  $\text{WCl}_6$  (190 mg, 0.479 mmol) and 2,2-diphenylpropionic acid (210 mg, 0.928 mmol), reaction time = 7 days. Colourless solid, yield 106 mg (63%). Anal. Calcd for  $\text{C}_{28}\text{H}_{24}$ : C, 93.29; H, 6.71. Found: C, 91.16; H, 6.84. IR (solid state):  $\nu/\text{cm}^{-1}$  = 3057w, 3028w, 2970w, 2868w, 1594m, 1488m, 1475w-sh, 1444m, 1373w, 1306w, 1250w, 1223w, 1154w, 1119w, 1071w, 1054w, 1028m, 945w, 910w, 765w, 749s, 698vs.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 7.49-7.14 (19 H, arom CH); 3.60, 3.28 (d, 2 H,  $^2J_{\text{HH}} = 13.52$  Hz,  $\text{CH}_2$ ); 1.71 (s, 3 H, Me).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta/\text{ppm}$  = 150.6, 149.4, 148.9, 148.6, 147.5 (arom +  $\text{CPh}_2$ ); 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 (CH<sub>2</sub>); 51.2 (CMePh); 28.9 (Me). Crystals suitable for X-ray analysis were obtained from a concentrated diethyl ether solution, at -30 °C.

When the same reaction was repeated in CD<sub>2</sub>Cl<sub>2</sub>, NMR analysis of an aliquot of the reaction mixture after ca. 20 minutes pointed out the prevalent presence of CPh<sub>2</sub>(Me)C(O)Cl. The <sup>1</sup>H NMR spectrum after 2 h displayed minor signals at ca. 7.8 (Ph) and 3.9 ppm (Me), attributed to [CPh<sub>2</sub>(Me)]<sup>+</sup>.<sup>6</sup> These signals completely disappeared after 24 h.

### B) Synthesis of 1,1,3-trimethyl-3-phenyl-2,3-dihydro-1H-indene, 4b (Chart 3).<sup>7</sup>



**Chart 3.** Structure of **4b**.

From WCl<sub>6</sub> (133 mg, 0.335 mmol) and 2-methyl-2-phenylpropanoic acid (110 mg, 0.670 mmol), reaction time = 7 days. Light yellow solid, yield 70 mg (88%). Anal. Calcd for C<sub>18</sub>H<sub>20</sub>: C, 91.47; H, 8.53. Found: C, 90.12; H, 8.79. IR (solid state):  $\nu/\text{cm}^{-1}$  = 3029w, 3025w, 2929w, 1598w-m, 1493s, 1441s, 1378w, 1354w, 1181w, 1107w, 1073w, 1031w, 964w, 9113w, 891w, 840w, 769s, 755vs, 694vs. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta/\text{ppm}$  = 7.38-7.19 (9 H, arom CH); 2.50, 2.27 (d, <sup>2</sup>J<sub>HH</sub> = 13.20 Hz, 2 H, CH<sub>2</sub>); 1.77, 1.42, 1.11 (s, 9 H, Me). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta/\text{ppm}$  = 152.3, 151.1, 148.9 (arom C); 128.0, 127.3, 126.7, 125.5, 125.1, 122.6 (arom CH); 59.3 (CH<sub>2</sub>); 50.9, 42.9 (CMe); 31.0, 30.7, 30.4 (Me).

When the same reaction was repeated in CD<sub>2</sub>Cl<sub>2</sub>, NMR analysis of an aliquot of the reaction mixture after ca. 20 minutes pointed out the prevalent presence of CPh(Me)<sub>2</sub>C(O)Cl.

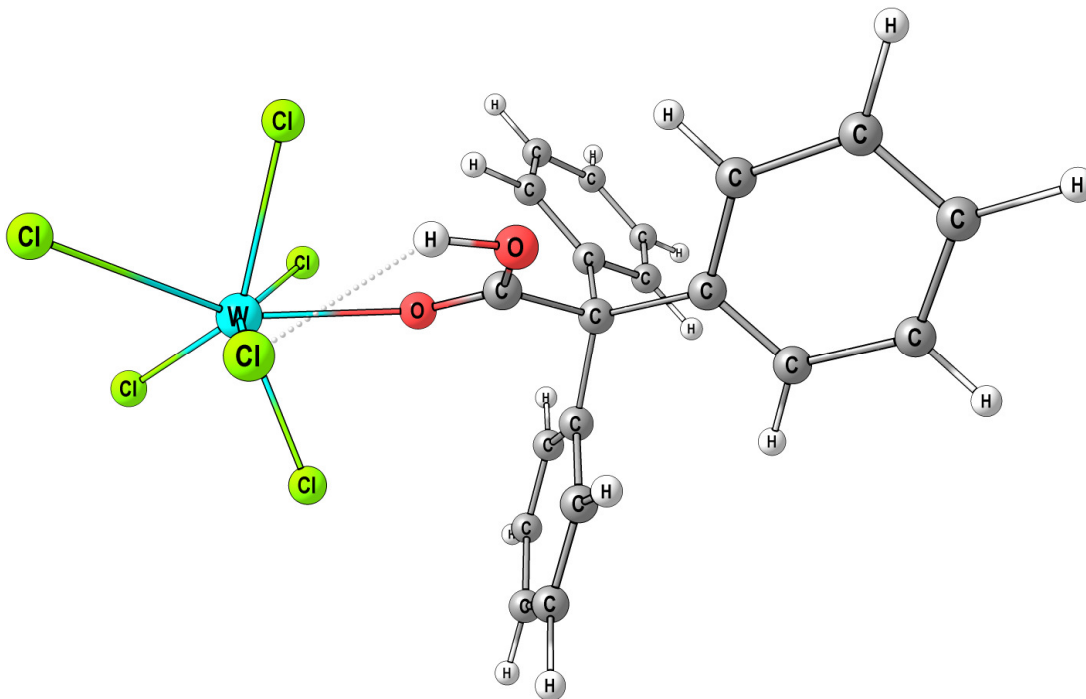
### C) Isolation and characterization of WO<sub>2</sub>Cl<sub>2</sub>.

The reaction of WCl<sub>6</sub> (283 mg, 0.714 mmol) with 2-methyl-2-phenylpropanoic acid (243 mg, 1.48 mmol) was carried out in CH<sub>2</sub>Cl<sub>2</sub> (15 mL), and the mixture was stirred at room temperature for 6

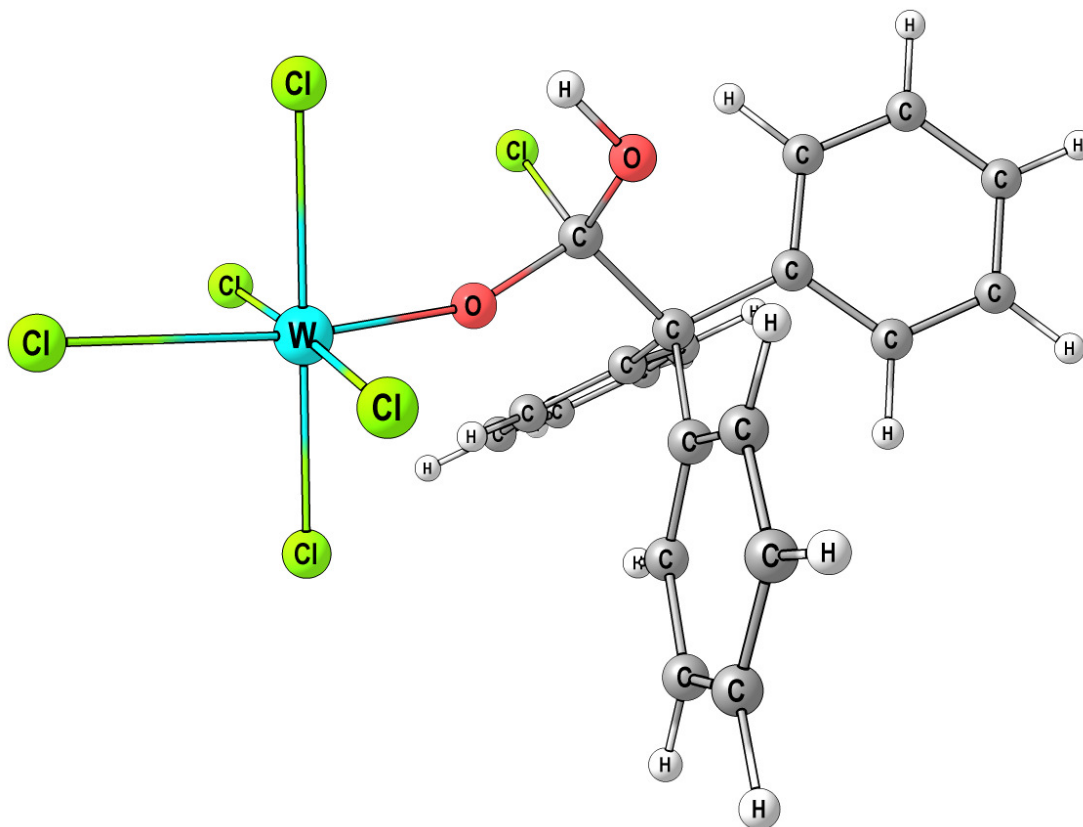
hours. A dark red solution over a dark precipitate was obtained. The precipitate,  $\text{WO}_2\text{Cl}_2$ , was separated from the solution and washed with  $\text{CHCl}_3$  (ca. 30 mL), thus affording a microcrystalline gray-green solid. Yield 152 mg, 74%. IR: 797vs, 699m  $\text{cm}^{-1}$ . [Errore. Il segnalibro non è definito.] Anal. Calcd for  $\text{Cl}_2\text{O}_2\text{W}$ : Cl, 24.73. Found: Cl, 24.39. A similar outcome was achieved starting from  $\text{WCl}_6$  (ca. 0.70 mmol) and 2,2-diphenylpropionic acid (2 eq.).

**Gas-chromatographic analyses.** A mixture of metal compound (ca. 1 mmol) and the appropriate carboxylic acid (1 eq.) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was stirred at room temperature for 72 hours in a Schlenk tube tapped with a silicon stopper. Then 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  $\text{WCl}_6/\text{Ph}_3\text{CCO}_2\text{H}$ : 57%;  $\text{WOCl}_4/\text{Ph}_3\text{CCO}_2\text{H}$ : 52%;  $\text{WCl}_6/\text{Ph}_2(\text{Me})\text{CCO}_2\text{H}$ : 52%;  $\text{WCl}_6/\text{Ph}(\text{Me})_2\text{CCO}_2\text{H}$ : 54%;  $\text{WCl}_6/\text{CPh}_2(\text{Et})\text{CO}_2\text{H}$ : 48%;  $\text{WCl}_6/\text{CPh}_2(\text{Pr})\text{CO}_2\text{H}$ : 21%;  $\text{WCl}_6/\text{CPh}_2(\text{CH}_2\text{CH}_2\text{Br})\text{CO}_2\text{H}$ : 6%;  $\text{WCl}_6/\text{CPh}(\text{C}_5\text{H}_{10})\text{CO}_2\text{H}$  (1-phenyl-1-cyclohexanecarboxylic acid): 35%.

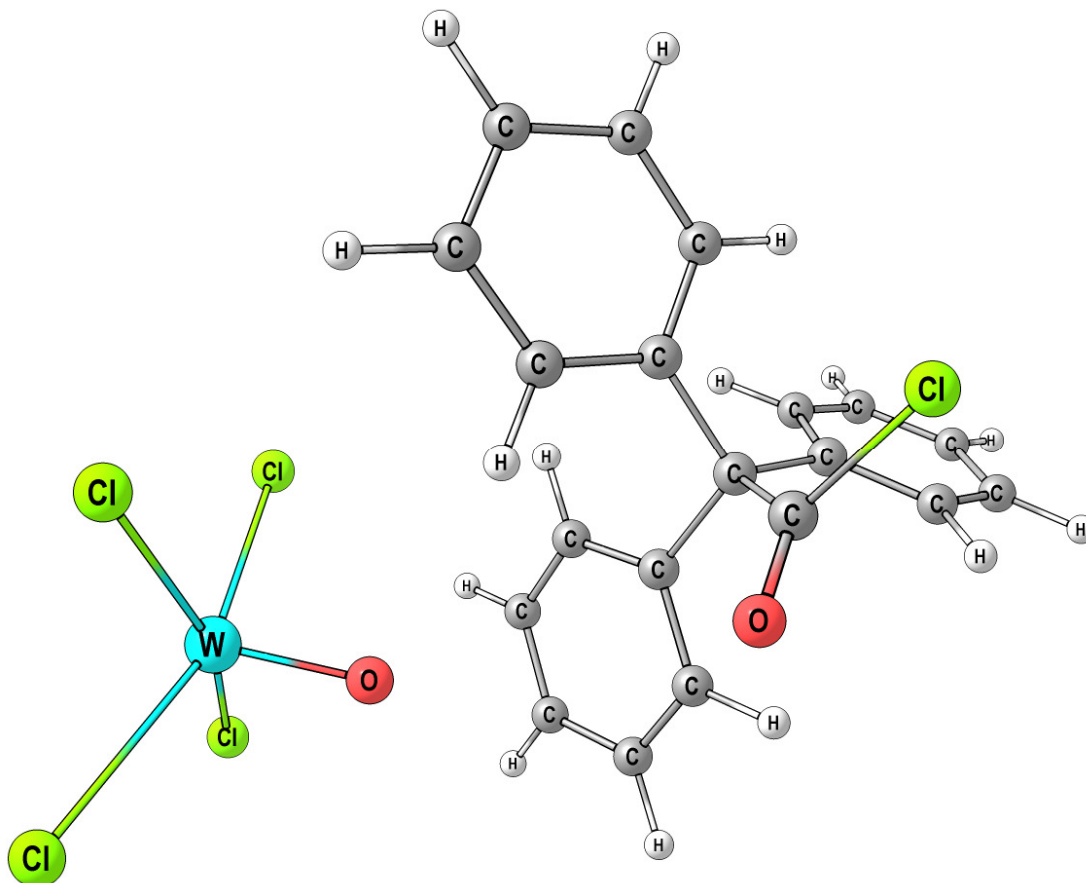
**Figure S1.** DFT-optimized geometry of  $[\text{WCl}_6\{\text{OC}(\text{OH})\text{CPh}_3\}]$  **(a)** (C-PCM- $\omega$ B97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å): W-Cl 2.302, 2.324, 2.331, 2.354, 2.418, 2.432; W-O 2.208; C=O 1.240; C-O(H) 1.289; C-CPh<sub>3</sub> 1.531; O-H 0.983; H---Cl 2.112. Selected computed angles (°): O-W-Cl 72.6, 72.8, 74.7, 78.9, 137.0, 144.6; W-O-C 144.3; O-C-O 124.5; C-O-H 110.8; O-H-Cl 141.5.



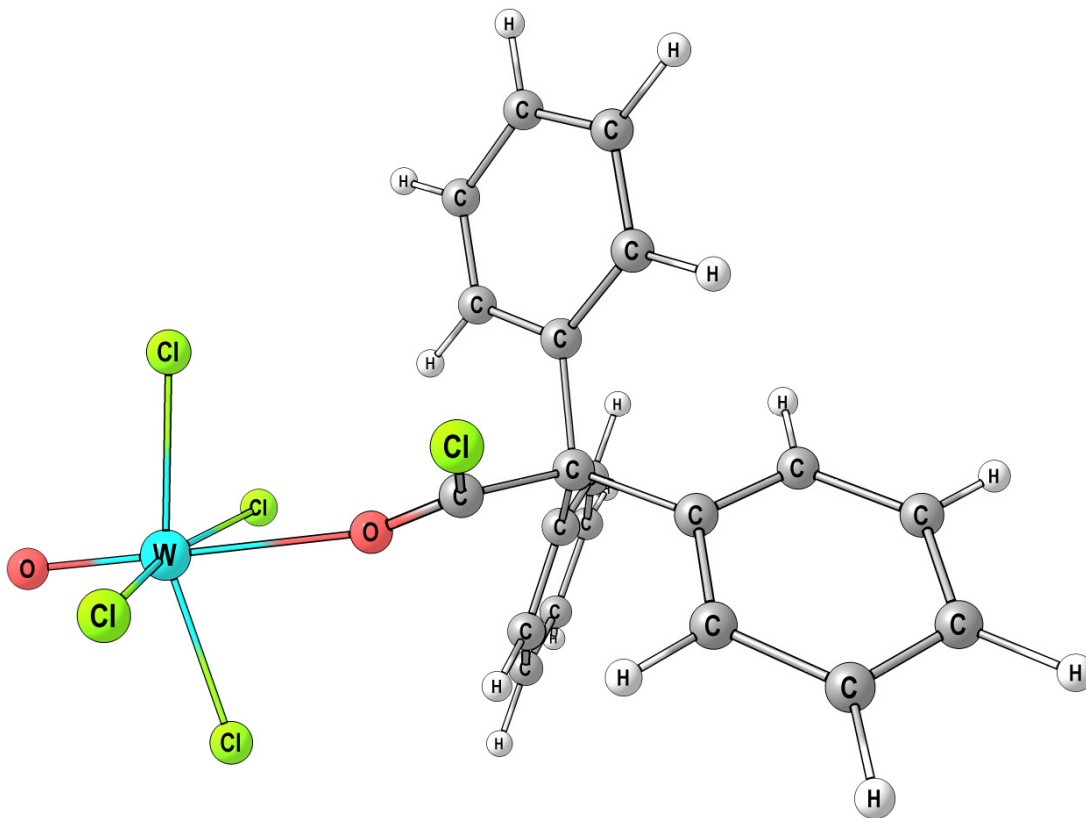
**Figure S2.** DFT-optimized geometry of  $[\text{WCl}_5\{\text{OCCl}(\text{OH})\text{CPh}_3\}]$  **(b)** (C-PCM- $\omega$ B97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å): W-Cl 2.293, 2.302, 2.309, 2.312, 2.364; W-O 1.821; C-O 1.433; C-O(H) 1.344; C-CPh<sub>3</sub> 1.581; C-Cl 1.810; O-H 0.972. Selected computed angles (°): O-W-Cl 85.7, 94.6, 90.5, 92.8, 172.0; W-O-C 157.0; O-C-O 108.8; O-C-Cl 103.5, 110.5.



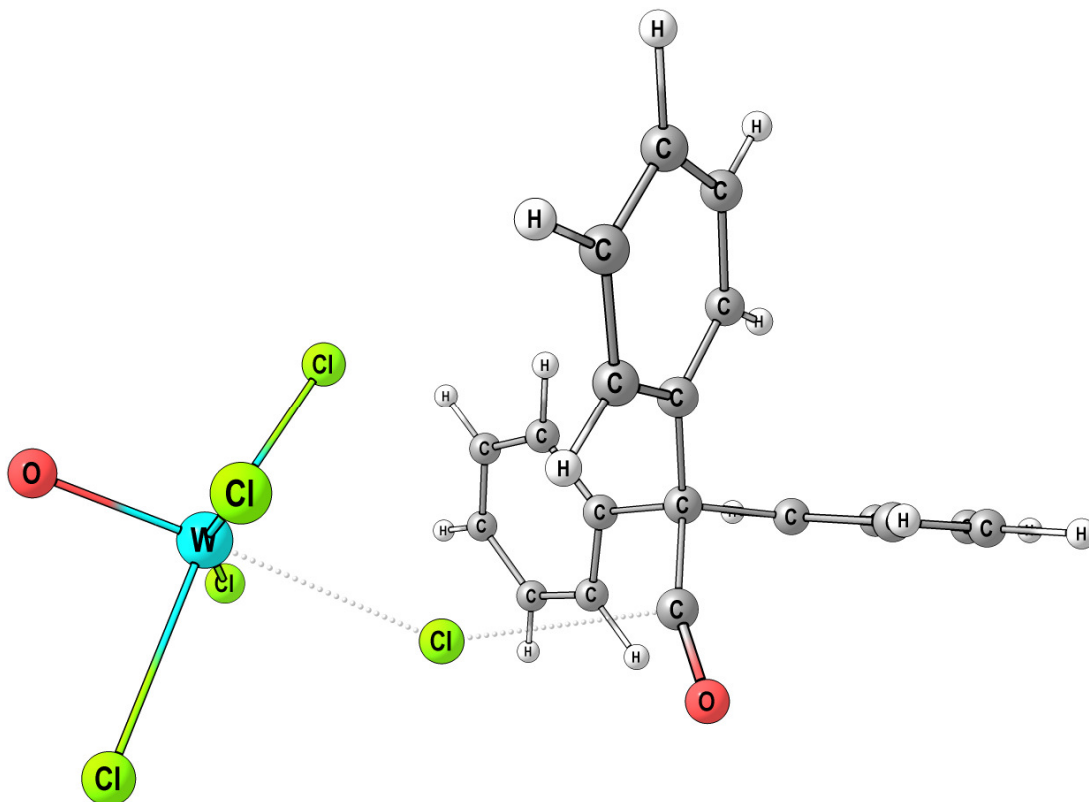
**Figure S3.** DFT-optimized geometry of  $[\text{WOCl}_4] + \text{OCClCPh}_3$  (**c**) (C-PCM- $\omega$ B97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å): W-Cl 2.315, 2.316, 2.320, 2.327; W=O 1.654; C=O 1.184; C-CPh<sub>3</sub> 1.544; C-Cl 1.787. Selected computed angles (°): O=W-Cl 99.5, 99.9, 100.7, 100.7; O-C-Cl 118.8.



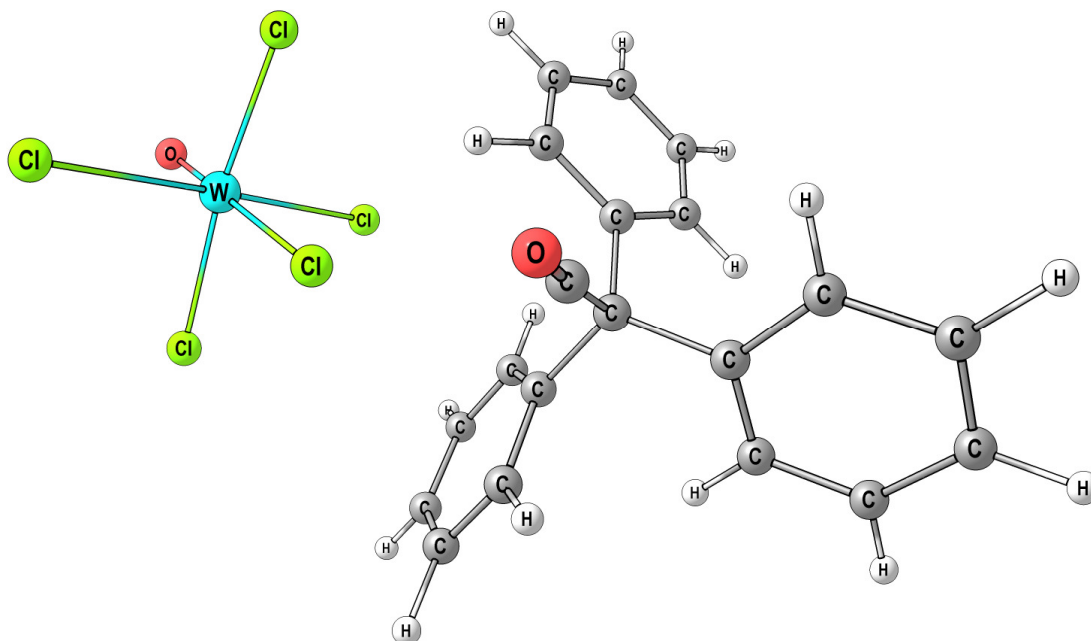
**Figure S4.** DFT-optimized geometry of  $[\text{WOCl}_4(\text{OCClCPh}_3)]$  (**d**) (C-PCM- $\omega$ B97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å): W-Cl 2.316, 2.318, 2.321, 2.328; W=O 1.660; W-O 2.389; C=O 1.203; C-CPh<sub>3</sub> 1.534; C-Cl 1.737. Selected computed angles (°): O=W-Cl 98.7, 98.8, 100.1, 100.3; O=W-O 178.8; O-C-Cl 119.2.



**Figure S5.** DFT-optimized geometry of  $[\text{WOCl}_4\cdots\text{Cl}\cdots\text{C}(\text{O})\text{CPh}_3]$  (**ts1**) (C-PCM- $\omega$ B97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å): W-Cl 2.328, 2.330, 2.332, 2.344; W=O 1.668; W $\cdots$ Cl 2.660; C=O 1.123; C-CPh<sub>3</sub> 1.488; C $\cdots$ Cl 2.670. Selected computed angles (°): O=W-Cl 95.5, 96.1, 96.3, 96.7; O=W $\cdots$ Cl 177.9; O-C $\cdots$ Cl 94.6. Imaginary frequency  $i76.2\text{ cm}^{-1}$ .

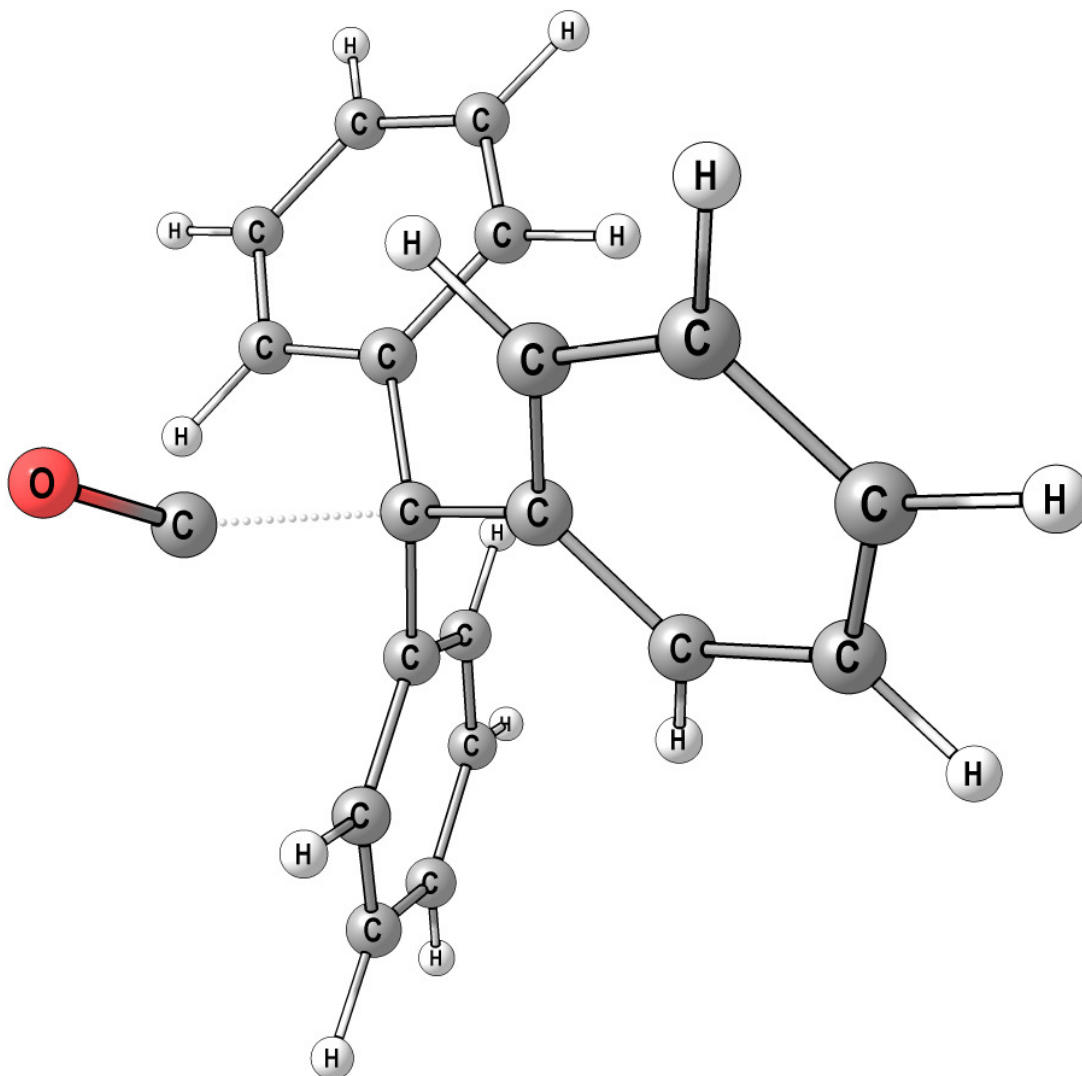


**Figure S6.** DFT-optimized geometry of  $[\text{OCCPh}_3][\text{WOCl}_5]$  (**e**) (C-PCM- $\omega$ B97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å): W-Cl 2.333, 2.335, 2.341, 2.353, 2.583; W=O 1.673; C=O 1.118; C- $\text{CPh}_3$  1.469. Selected computed angles ( $^\circ$ ): O=W-Cl 94.3, 95.0, 95.3, 95.8, 178.4; O-C-C 172.2.

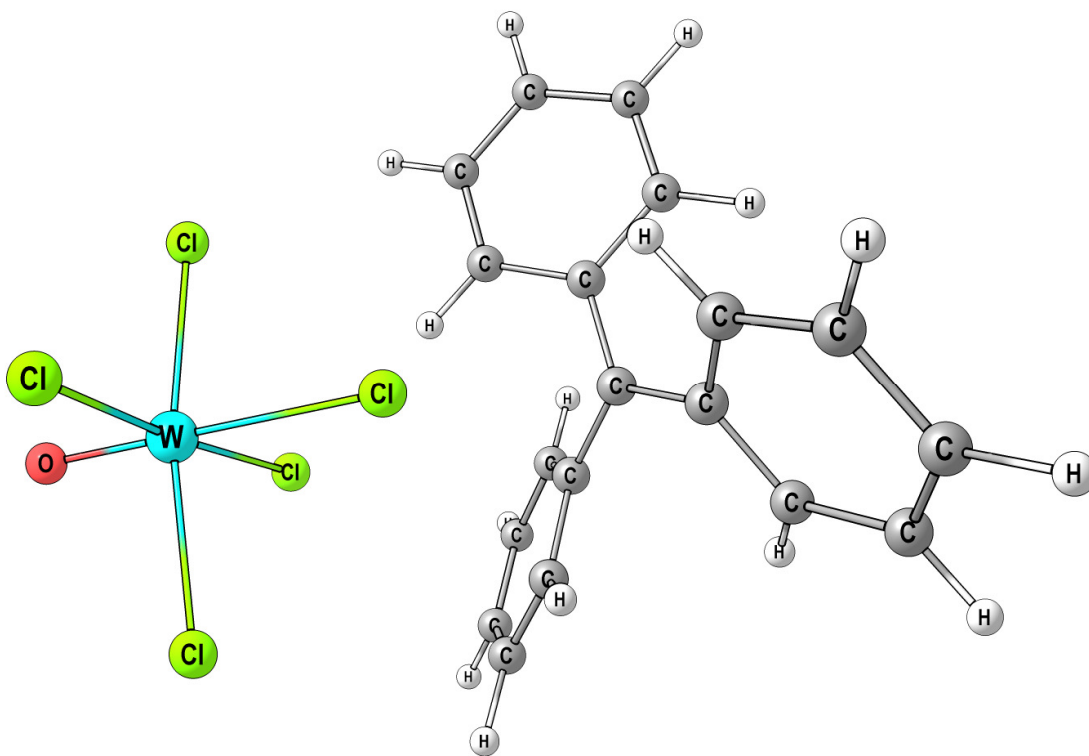




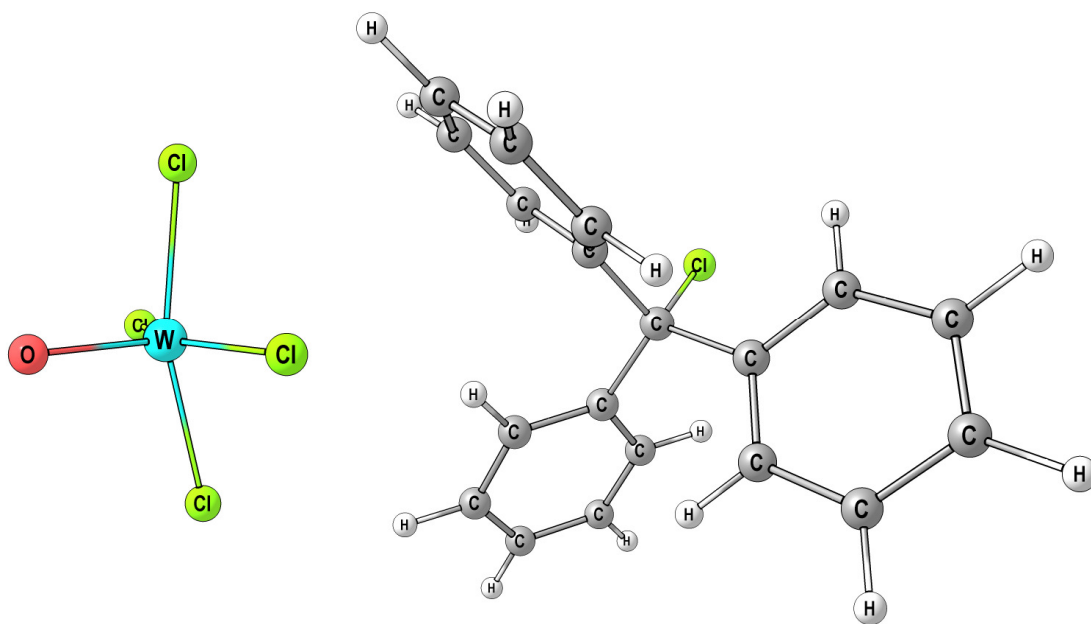
**Figure S7.** DFT-optimized geometry of  $[\text{CPh}_3\cdots\text{CO}]^+$  (**ts2**) (C-PCM- $\omega$ B97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å): C $\cdots$ C(CO) 1.867; C=O 1.132; C-C(Ph) 1.503, 1.504, 1.506. Selected computed angles ( $^\circ$ ): C(CO)-C-C(Ph) 99.3, 99.5, 103.5. Imaginary frequency  $i424.4\text{ cm}^{-1}$ .



**Figure S8.** DFT-optimized geometry of  $[\text{CPh}_3][\text{WOCl}_5]$  (**f**) (C-PCM- $\omega$ B97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å): W-Cl 2.335, 2.341, 2.345, 2.359, 2.545; W=O 1.676; C-C(Ph) 1.446, 1.448, 1.451. Selected computed angles (°): O=W-Cl 94.2, 94.3, 94.7, 95.0, 179.2; C(Ph)-C-C(Ph) 119.8, 119.8, 120.4.



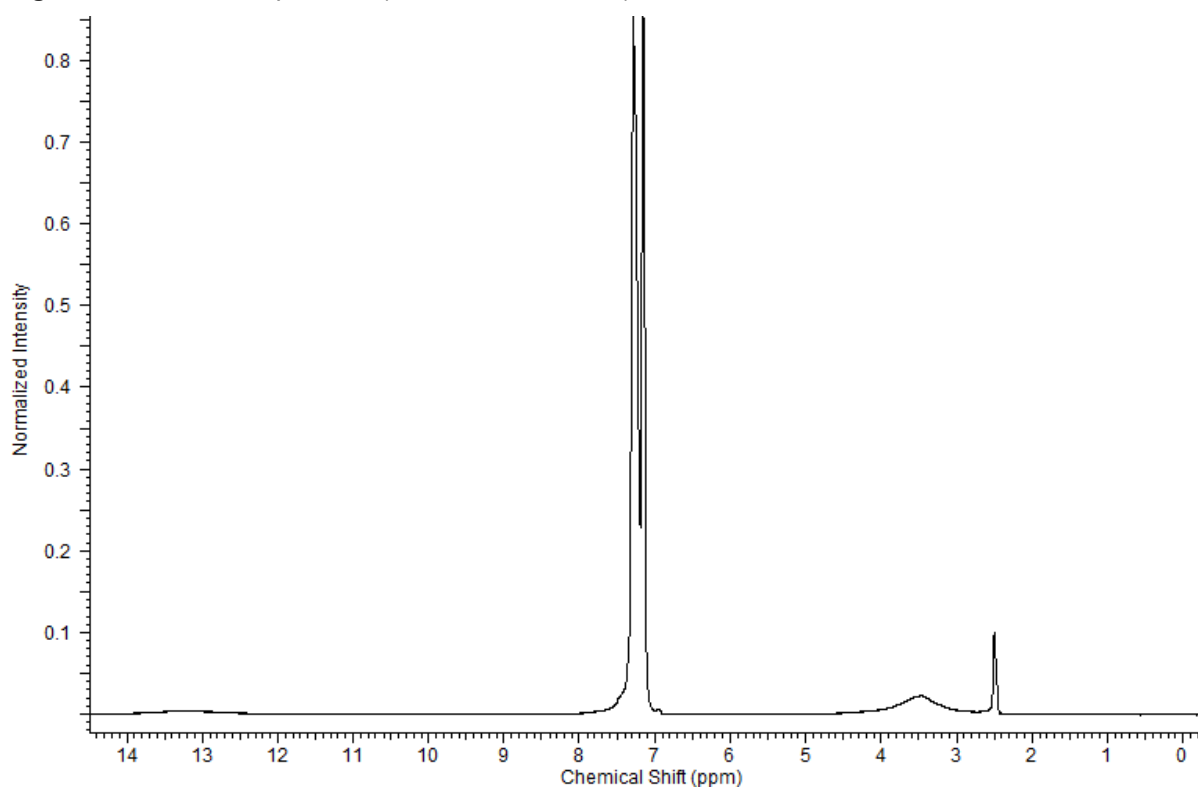
**Figure S9.** DFT-optimized geometry of  $[\text{WOCl}_4] + \text{Ph}_3\text{CCl}$  (**g**) (C-PCM- $\omega$ B97X calculations, dichloromethane as continuous medium). Selected computed bond lengths (Å): W-Cl 2.310, 2.311, 2.315, 2.335; W=O 1.655; C-Cl 1.839. Selected computed angles (°): O=W-Cl 98.5, 98.6, 103.1, 103.2.



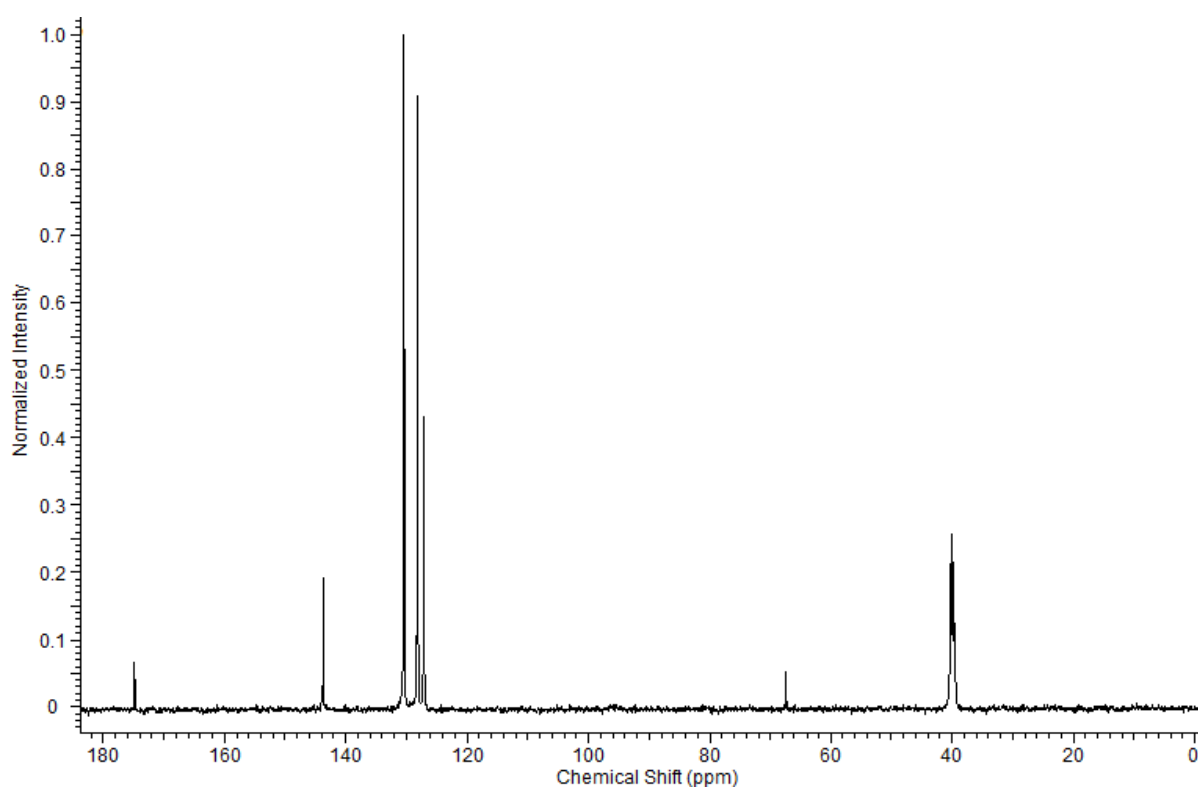
**Computational details.**

The electronic structures of the compounds were optimized using the range-separated  $\omega$ B97X DFT functional<sup>8</sup> in combination with Ahlrichs' split-valence polarized basis set, with ECP on the W centre.<sup>9</sup> The "restricted" formalism was always applied. The C-PCM implicit solvation model ( $\epsilon = 9.08$ ) was added to  $\omega$ B97X calculations.<sup>10</sup> The stationary points were characterized by IR simulations (harmonic approximation), from which zero-point vibrational energies and thermal corrections ( $T = 298.15\text{K}$ ) were obtained.<sup>11</sup> The software used was Gaussian 09.<sup>12</sup>

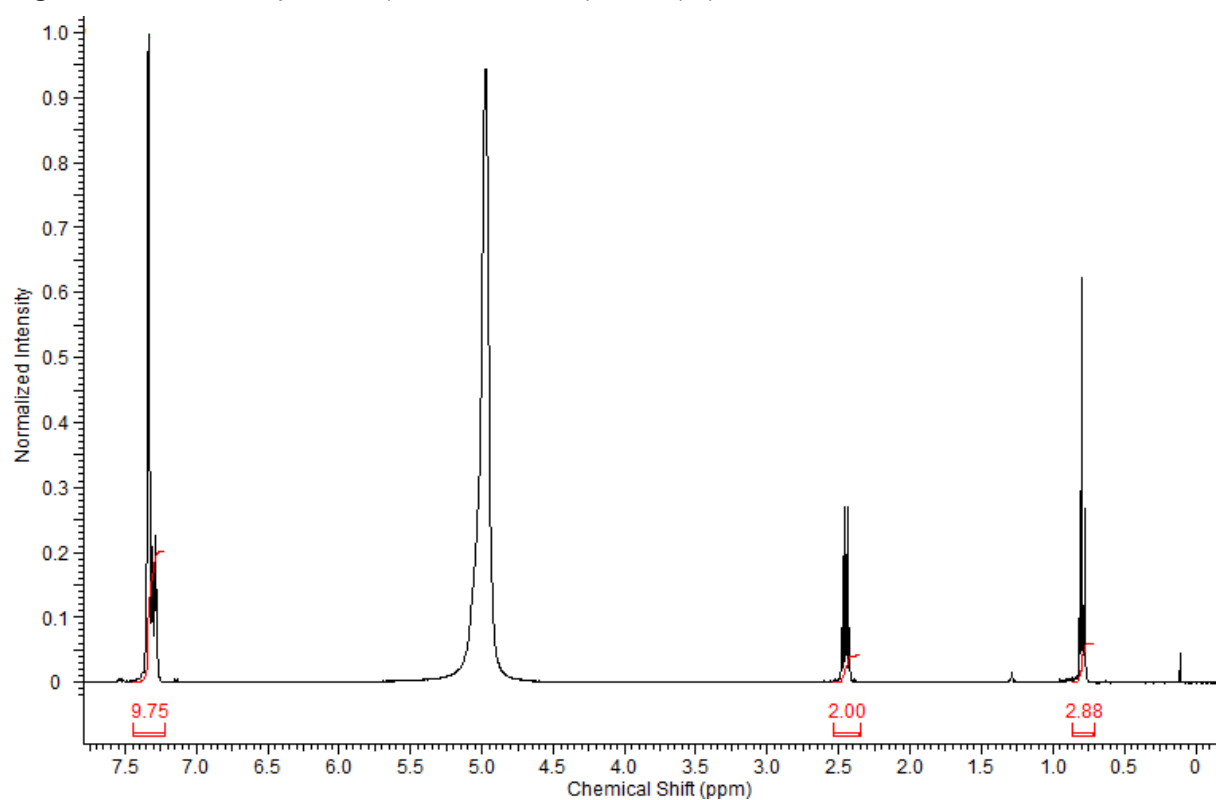
**Figure S10.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{DMSO-d}_6$ ) of  $\text{Ph}_3\text{CCO}_2\text{H}$ .



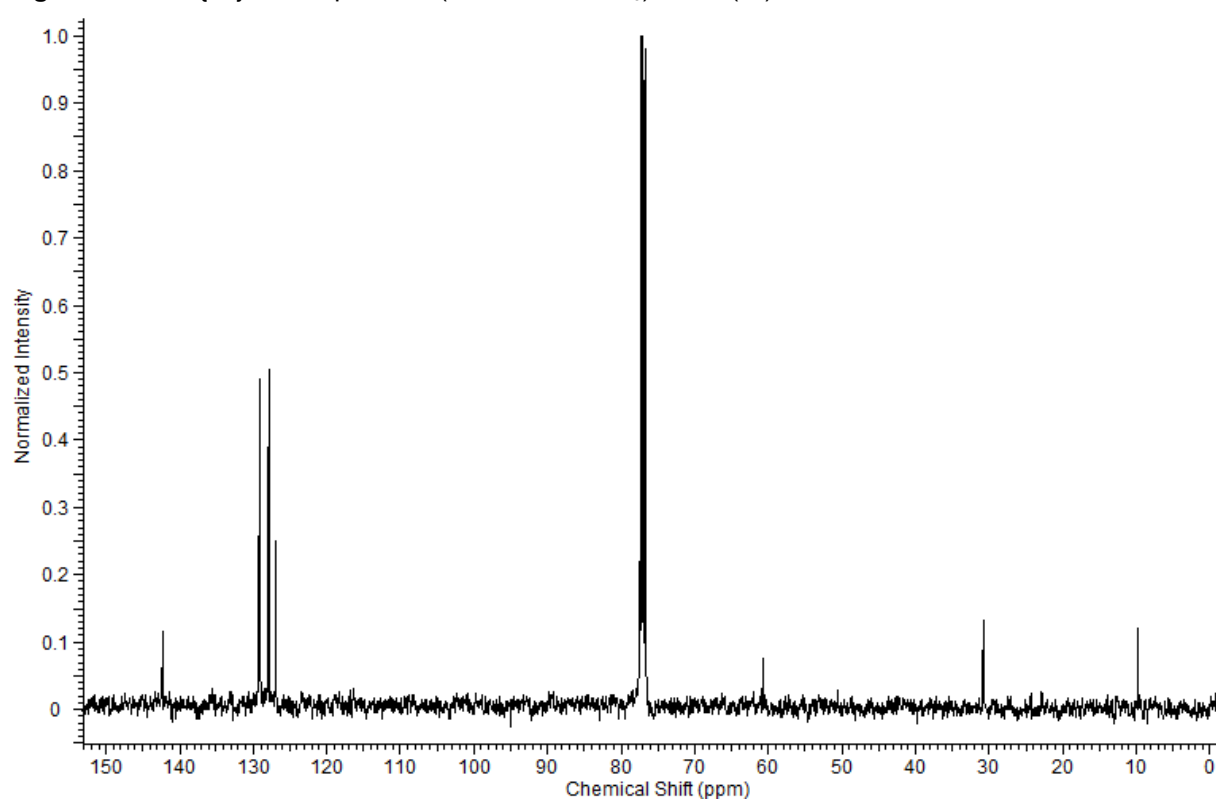
**Figure S11.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{DMSO-d}_6$ ) of  $\text{Ph}_3\text{CCO}_2\text{H}$ .



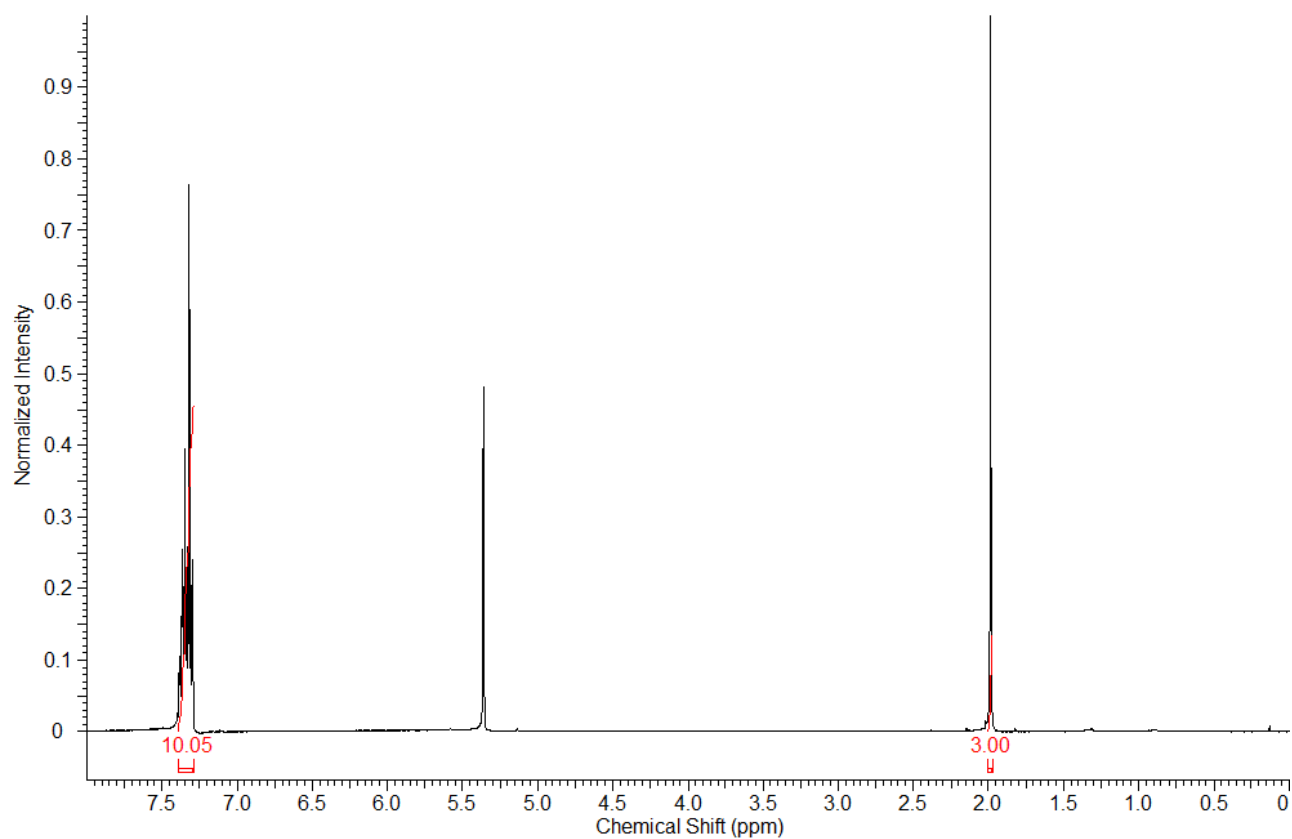
**Figure S12.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{CDCl}_3$ ) of  $\text{Ph}_2(\text{Et})\text{CCO}_2\text{H}$ .



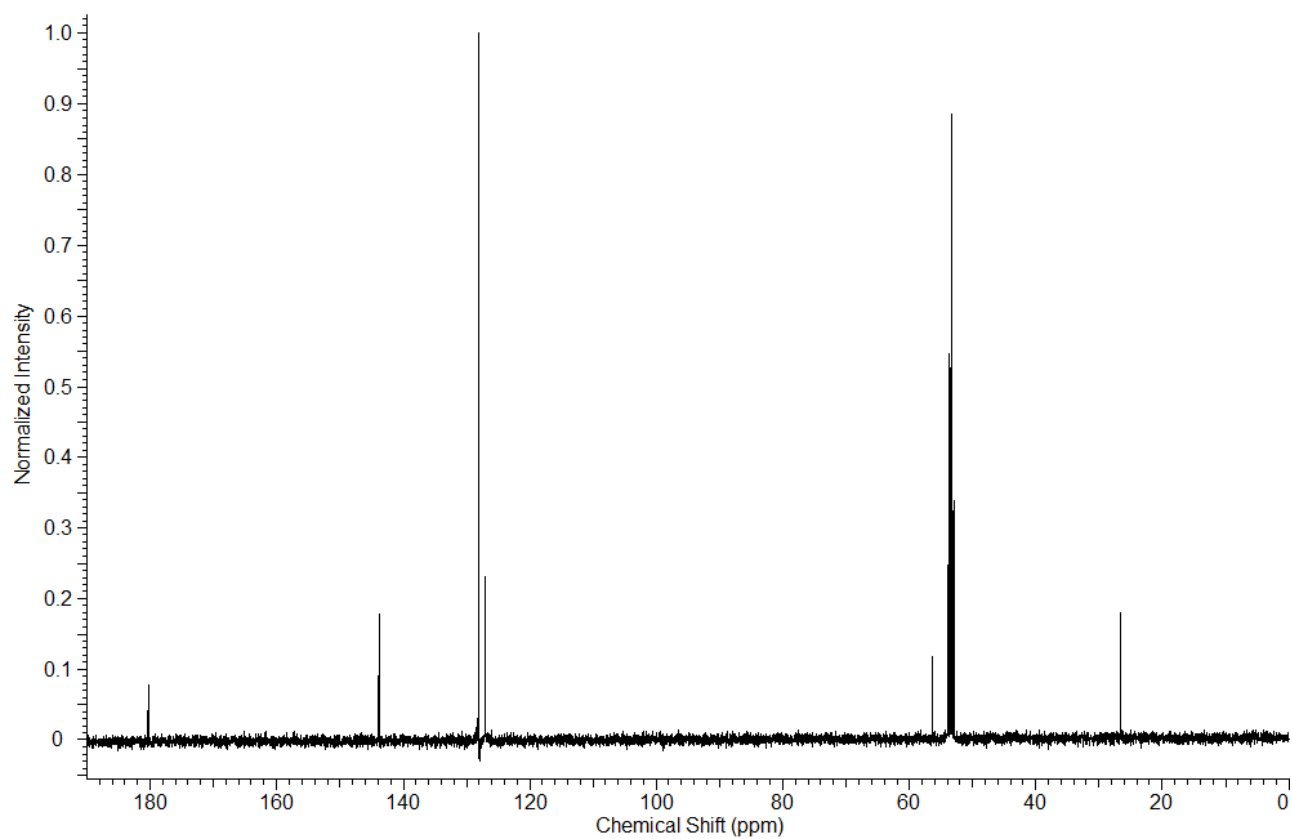
**Figure S13.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of  $\text{Ph}_2(\text{Et})\text{CCO}_2\text{H}$ .



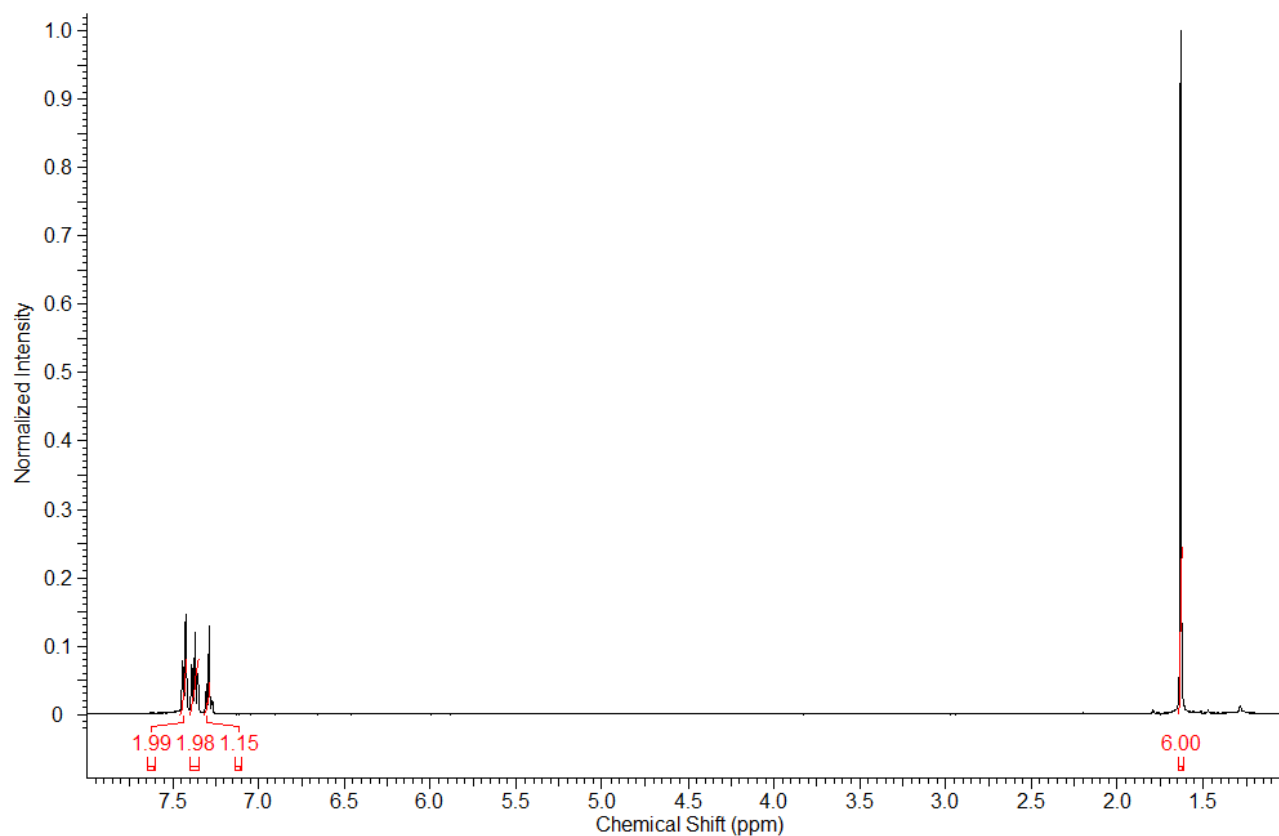
**Figure S14.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{CD}_2\text{Cl}_2$ ) of  $\text{Ph}_2(\text{Me})\text{CCO}_2\text{H}$ .



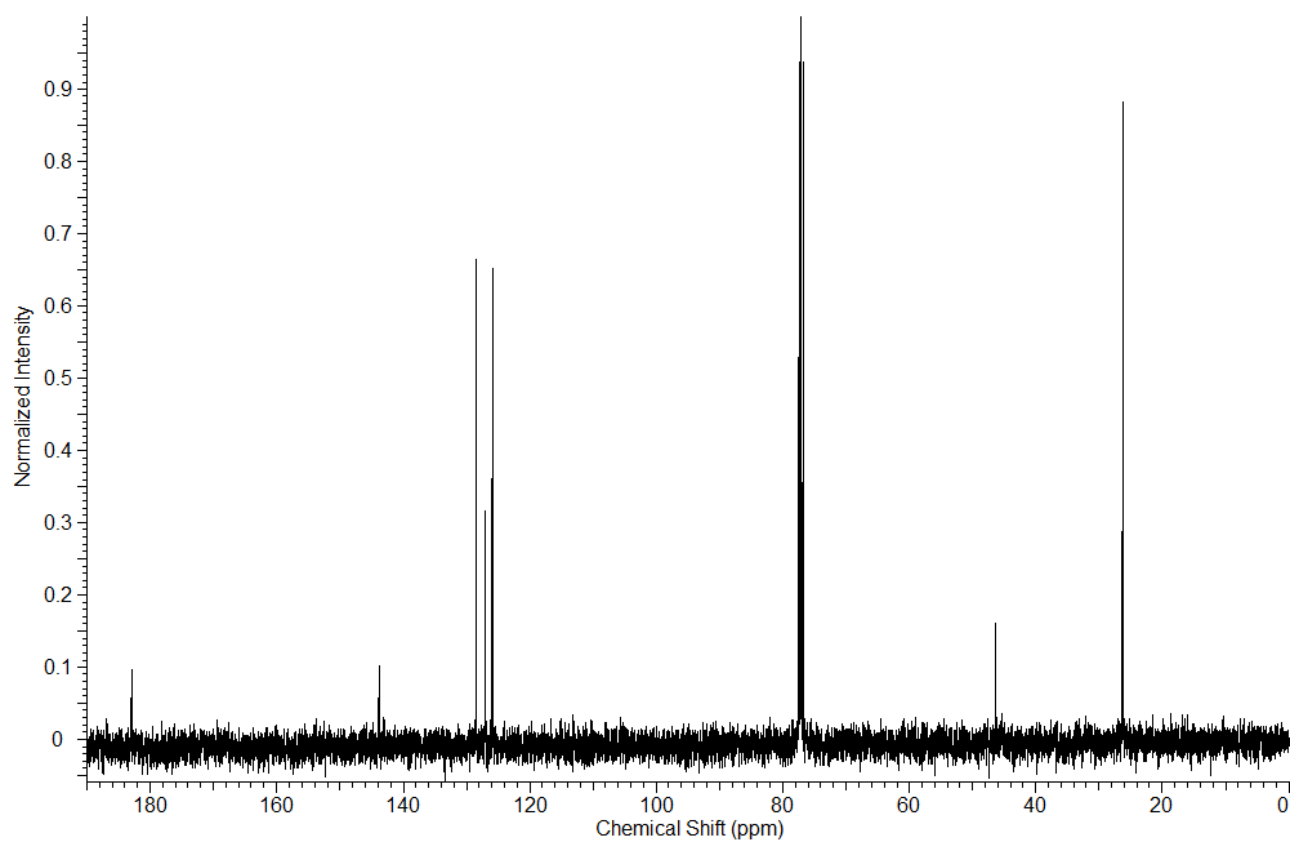
**Figure S15.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CD}_2\text{Cl}_2$ ) of  $\text{Ph}_2(\text{Me})\text{CCO}_2\text{H}$ .



**Figure S16.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{CDCl}_3$ ) of  $\text{Ph}_2(\text{Me})\text{CCO}_2\text{H}$ .

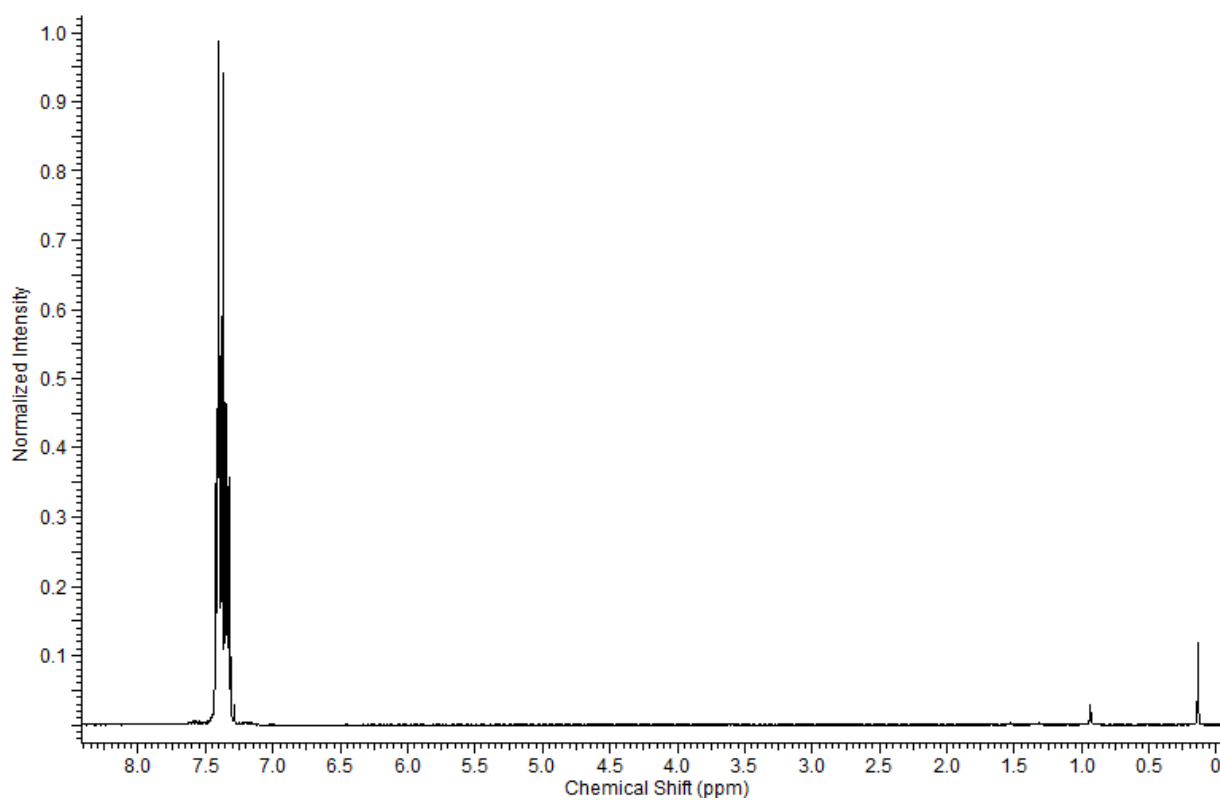


**Figure S17.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of  $\text{Ph}_2(\text{Me})\text{CCO}_2\text{H}$ .

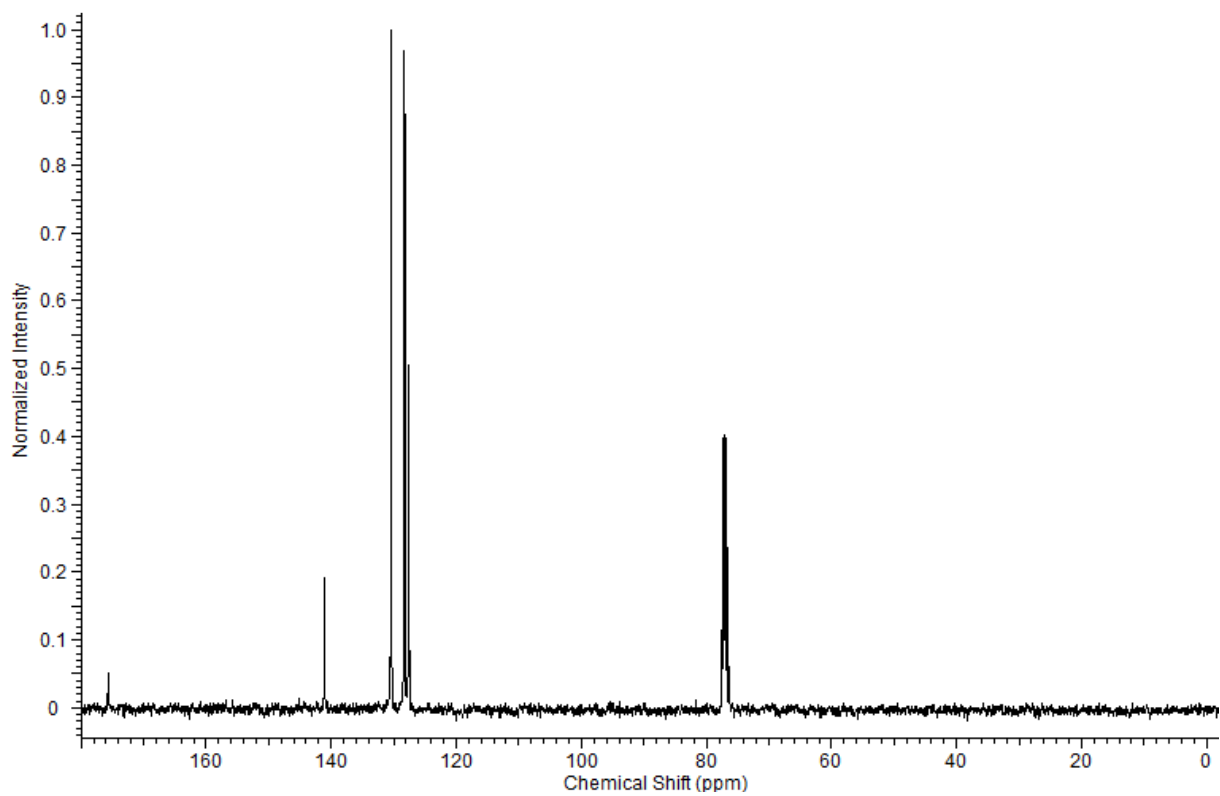




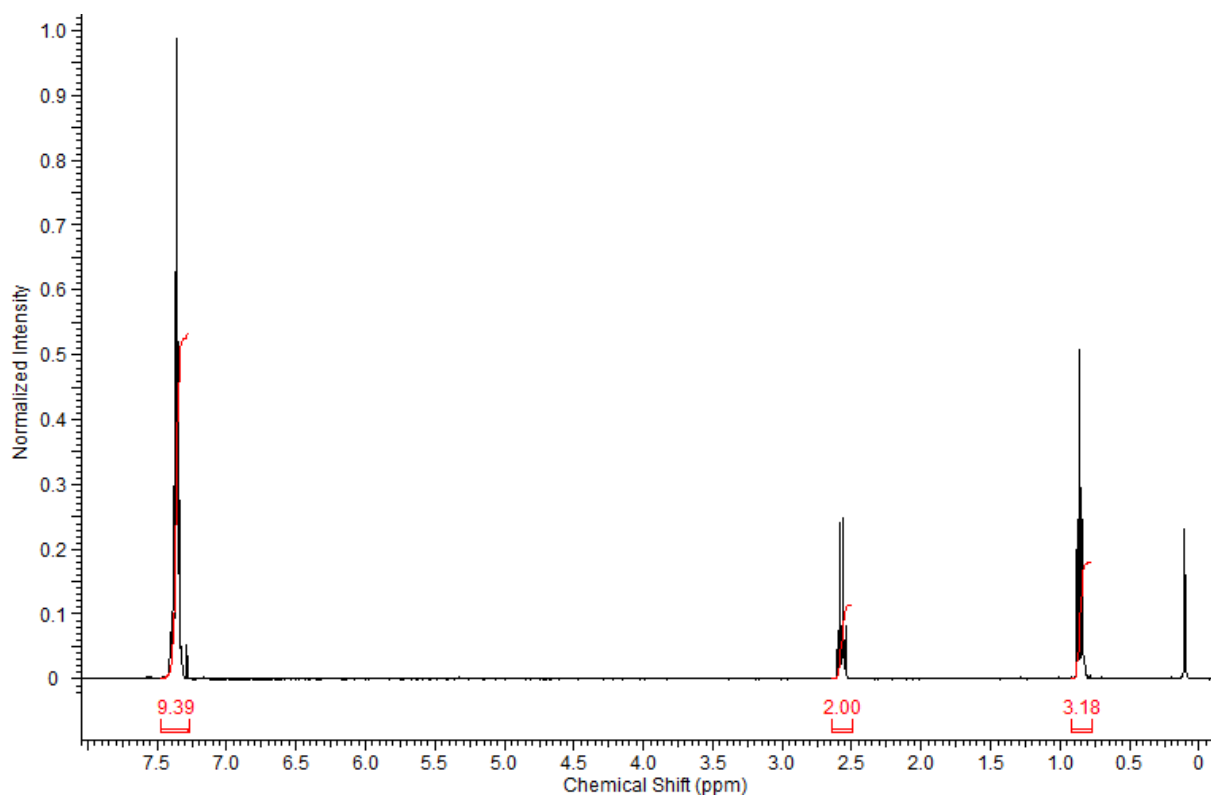
**Figure S18.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{CDCl}_3$ ) of  $\text{Ph}_3\text{CC}(\text{O})\text{Cl}$ .



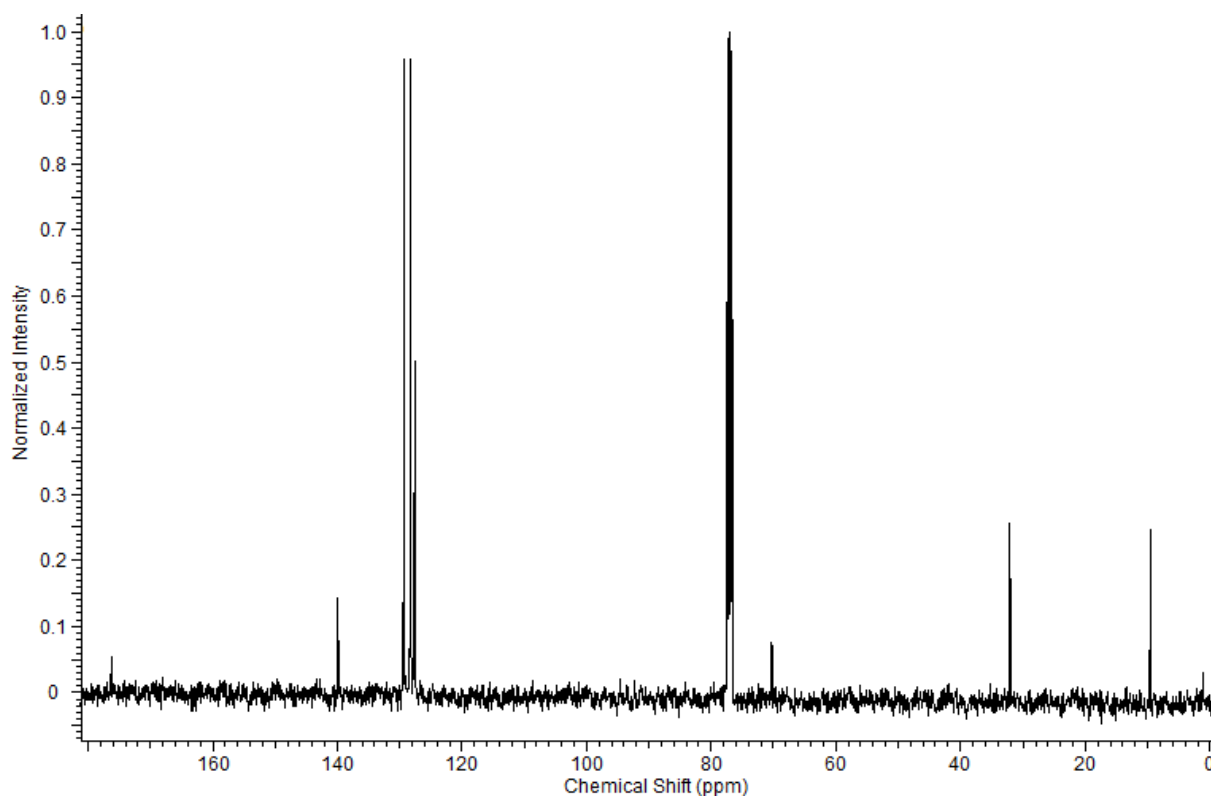
**Figure S19.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of  $\text{Ph}_3\text{CC}(\text{O})\text{Cl}$ .



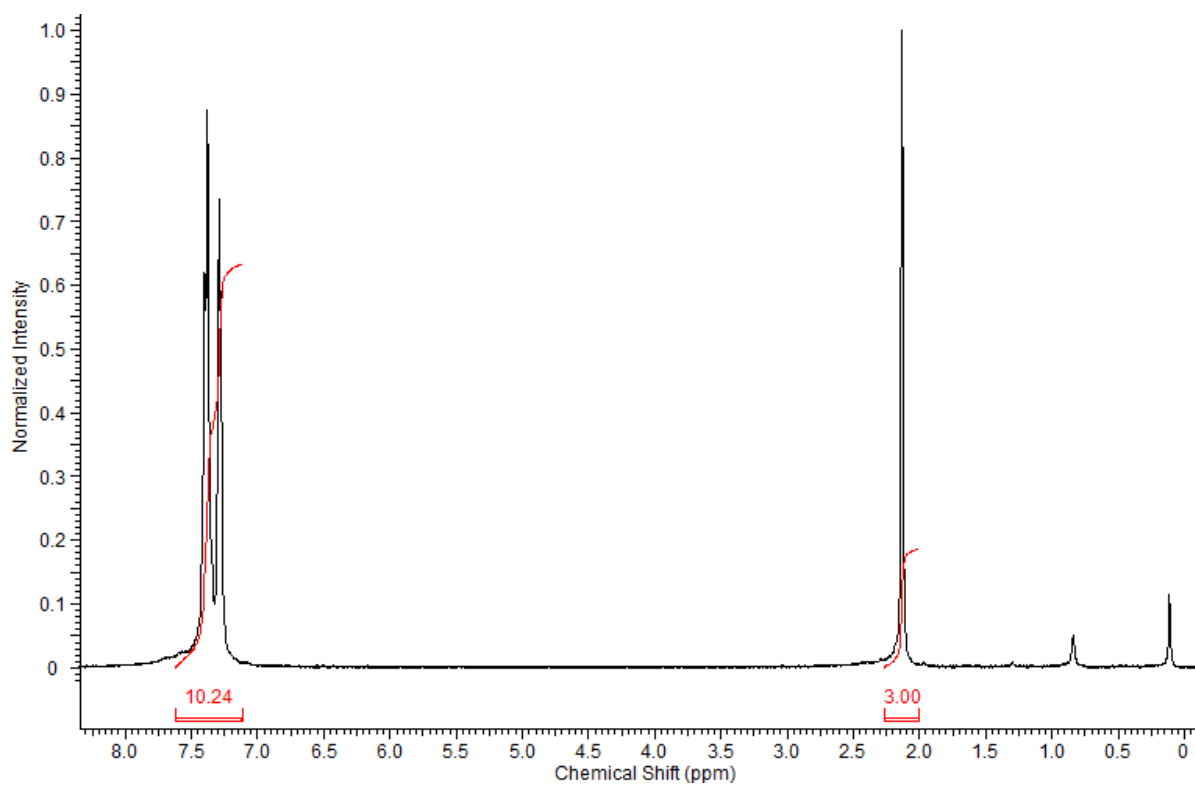
**Figure S20.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{CDCl}_3$ ) of  $\text{Ph}_2(\text{Et})\text{CC}(\text{O})\text{Cl}$ .



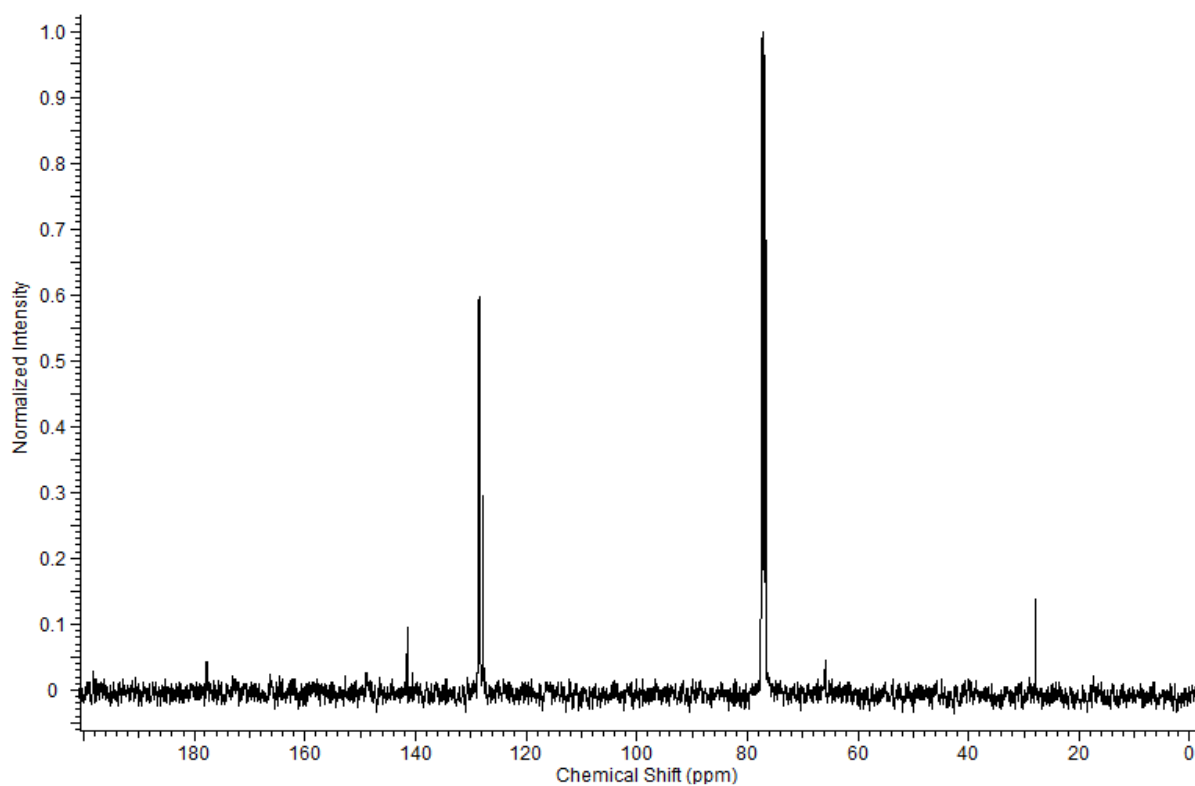
**Figure S21.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of  $\text{Ph}_2(\text{Et})\text{CC}(\text{O})\text{Cl}$ .



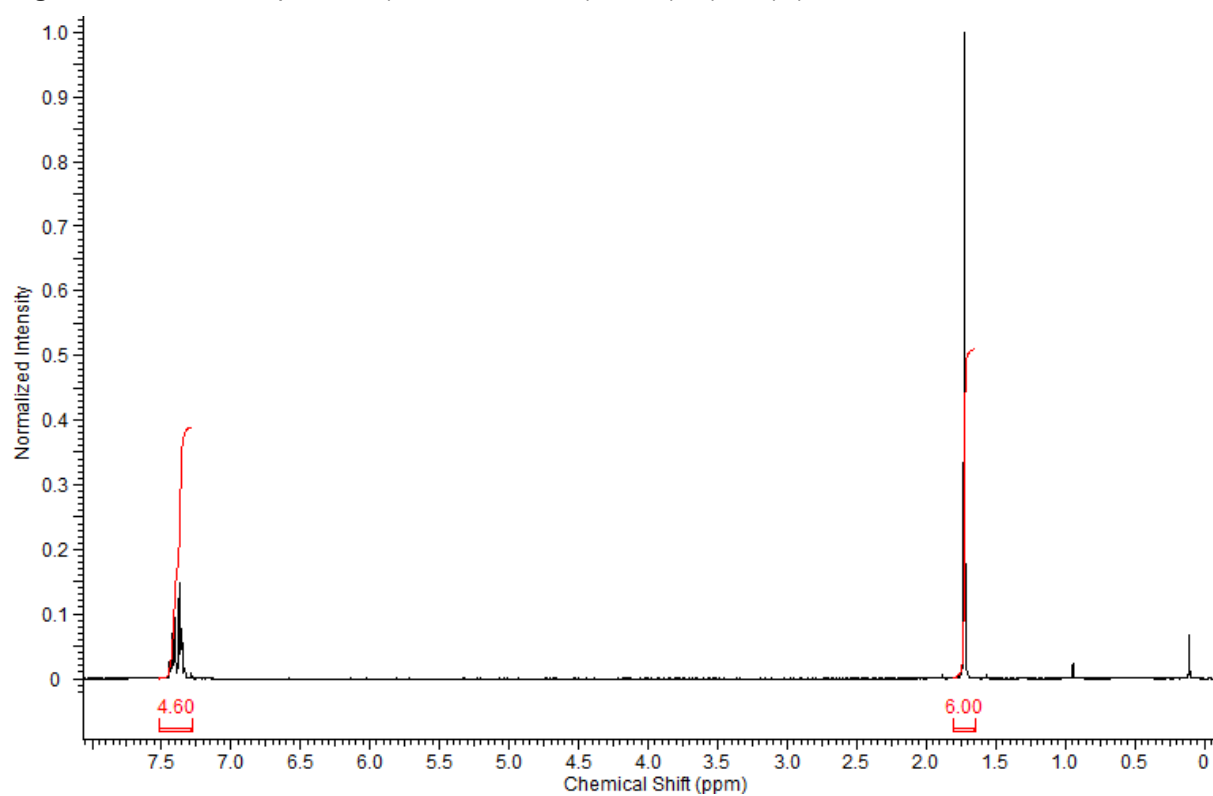
**Figure S22.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{CDCl}_3$ ) of  $\text{Ph}_2(\text{Me})\text{CC}(\text{O})\text{Cl}$ .



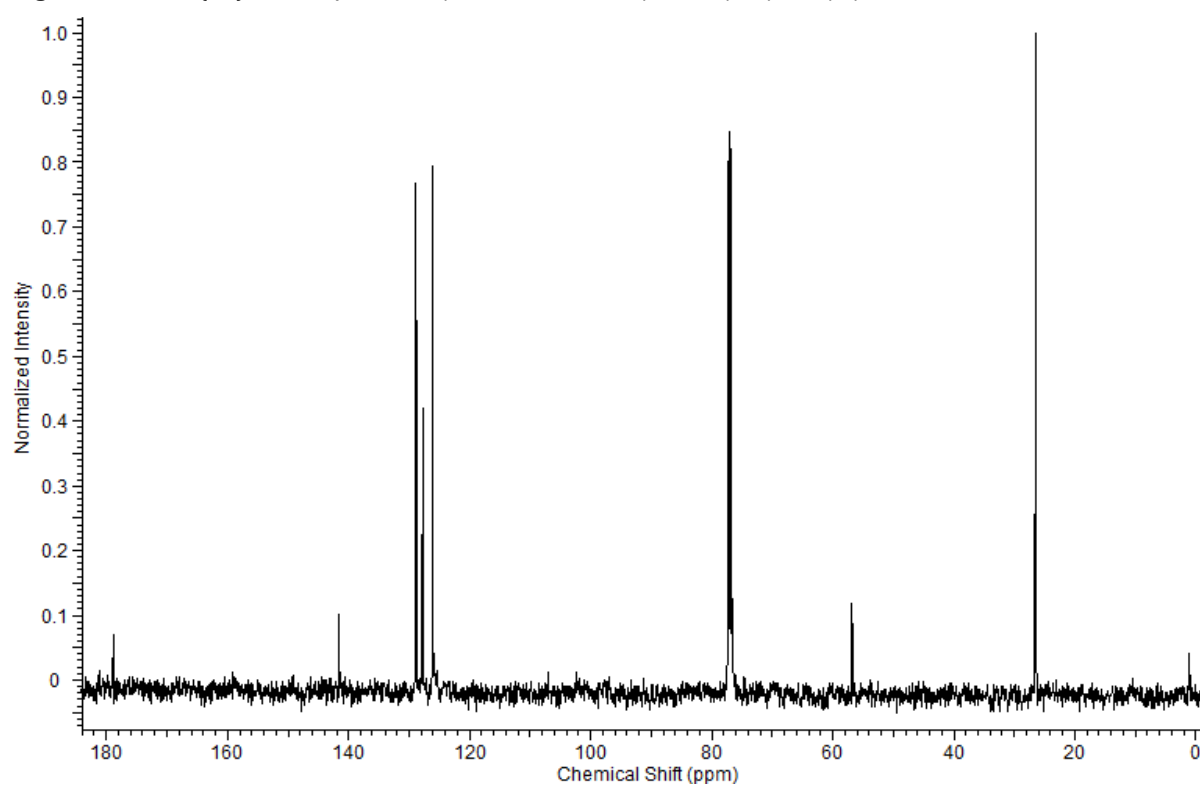
**Figure S23.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of  $\text{CMe}(\text{Ph})_2\text{C}(\text{O})\text{Cl}$ .



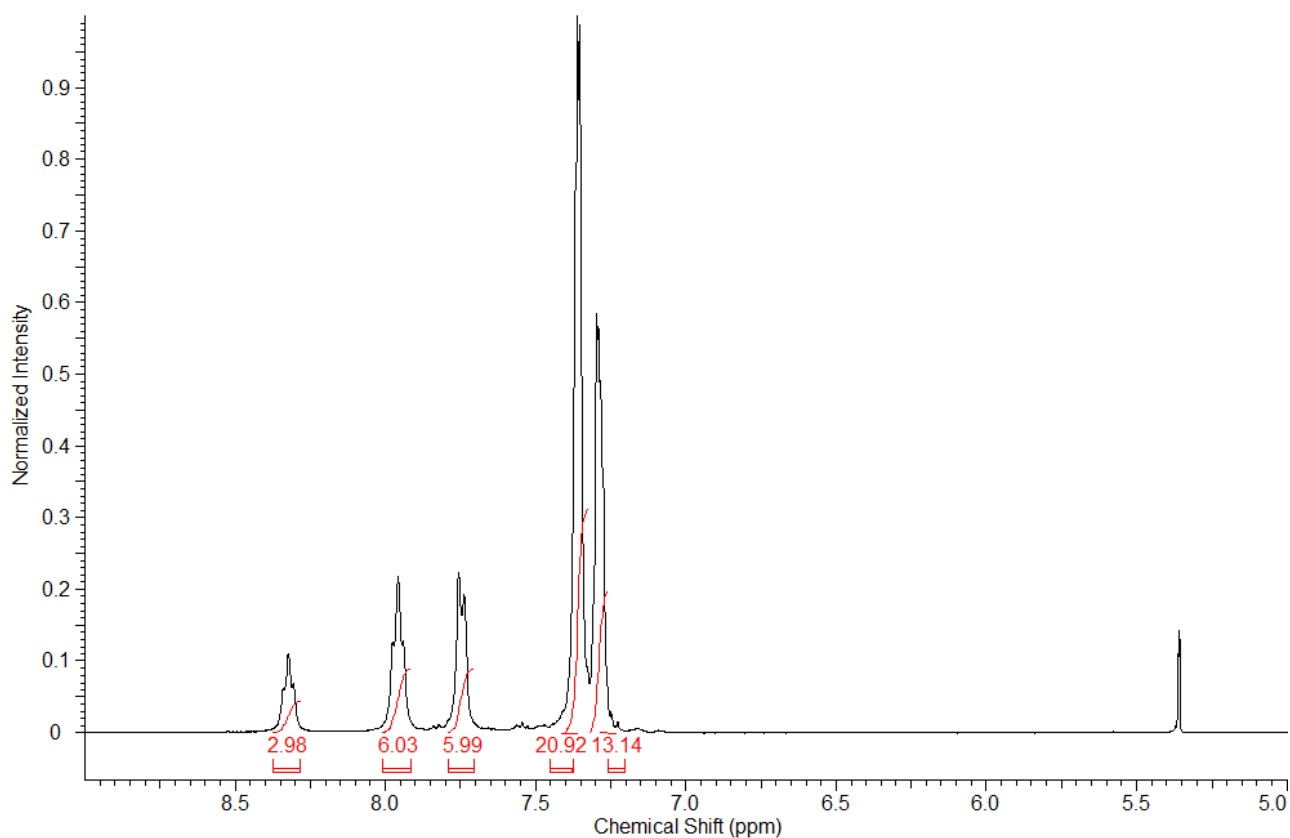
**Figure S24.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{CDCl}_3$ ) of  $\text{Ph}(\text{Me})_2\text{CC}(\text{O})\text{Cl}$ .



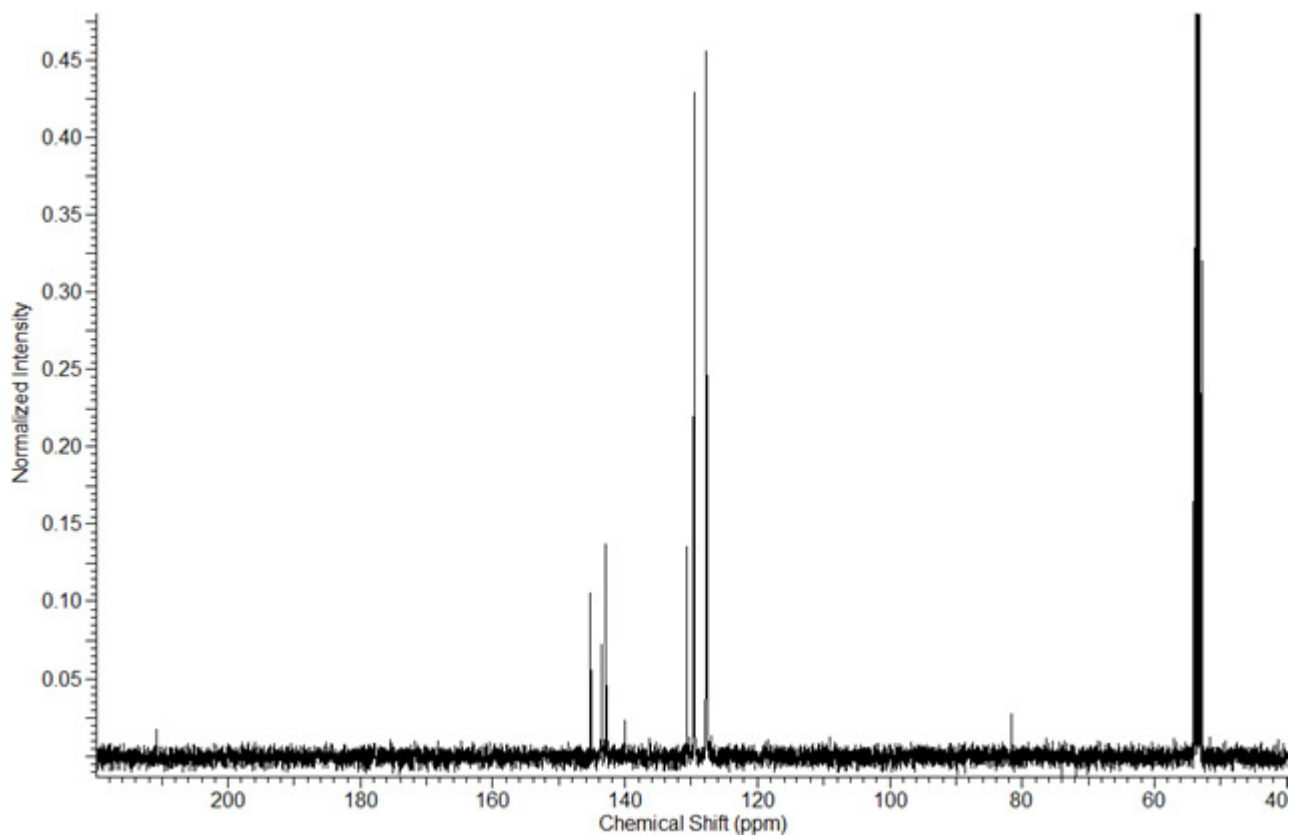
**Figure S25.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of  $\text{Ph}(\text{Me})_2\text{CC}(\text{O})\text{Cl}$ .



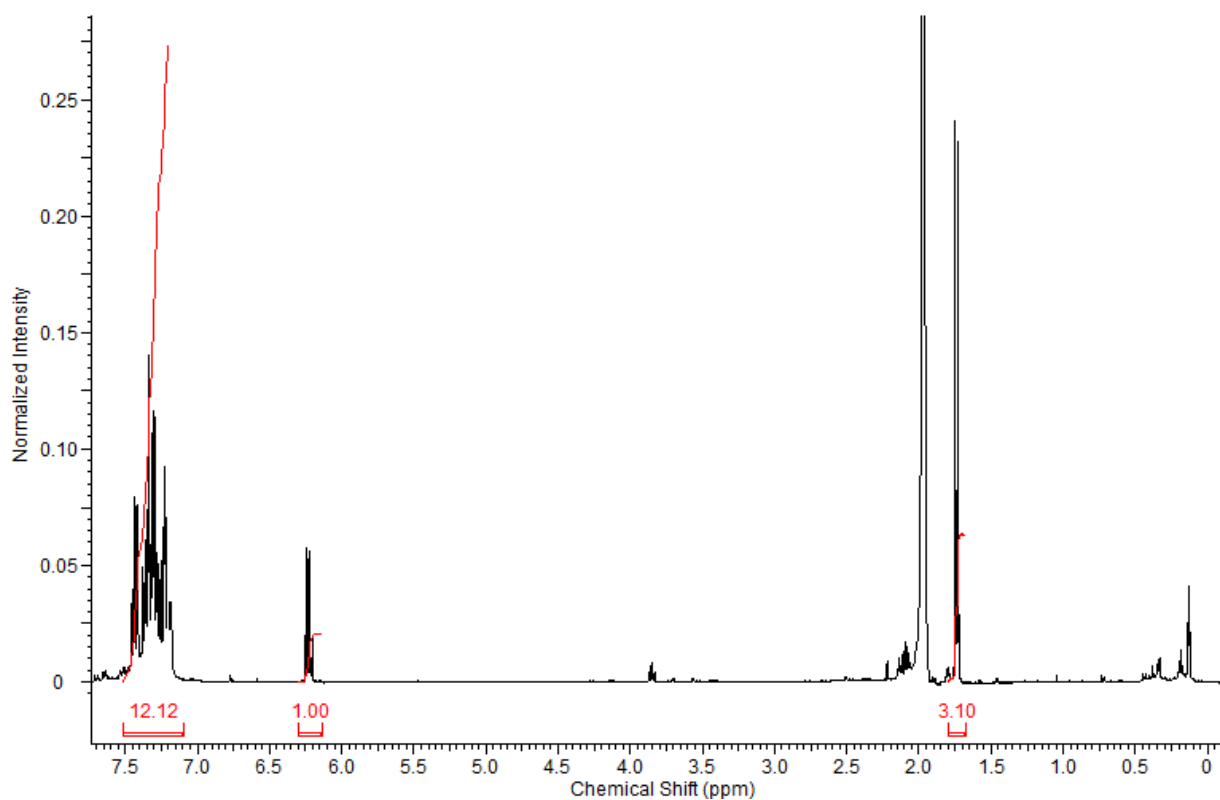
**Figure S26.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{CDCl}_3$ ) of the mixture obtained from  $\text{WCl}_6/\text{Ph}_3\text{CCO}_2\text{H}$  (**1** + **2**).



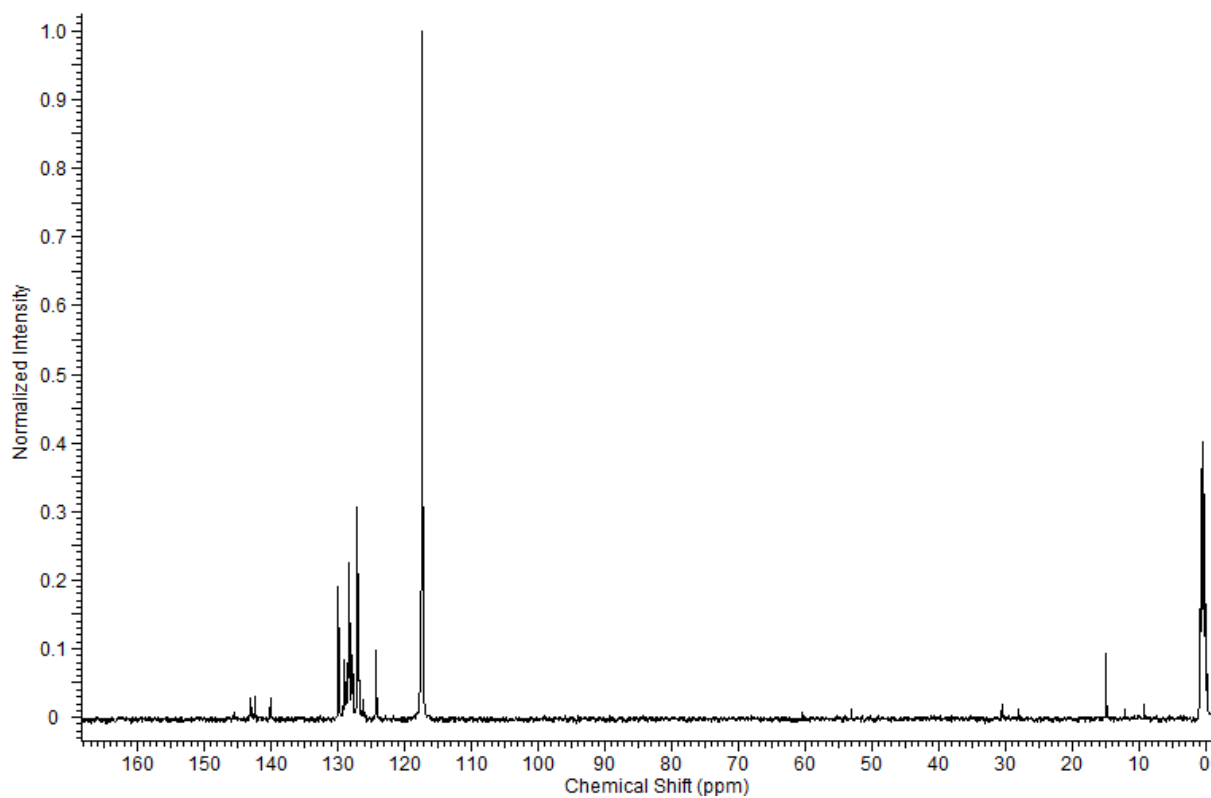
**Figure S27.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of the mixture obtained from  $\text{WCl}_6/\text{Ph}_3\text{CCO}_2\text{H}$  (**1** + **2**).



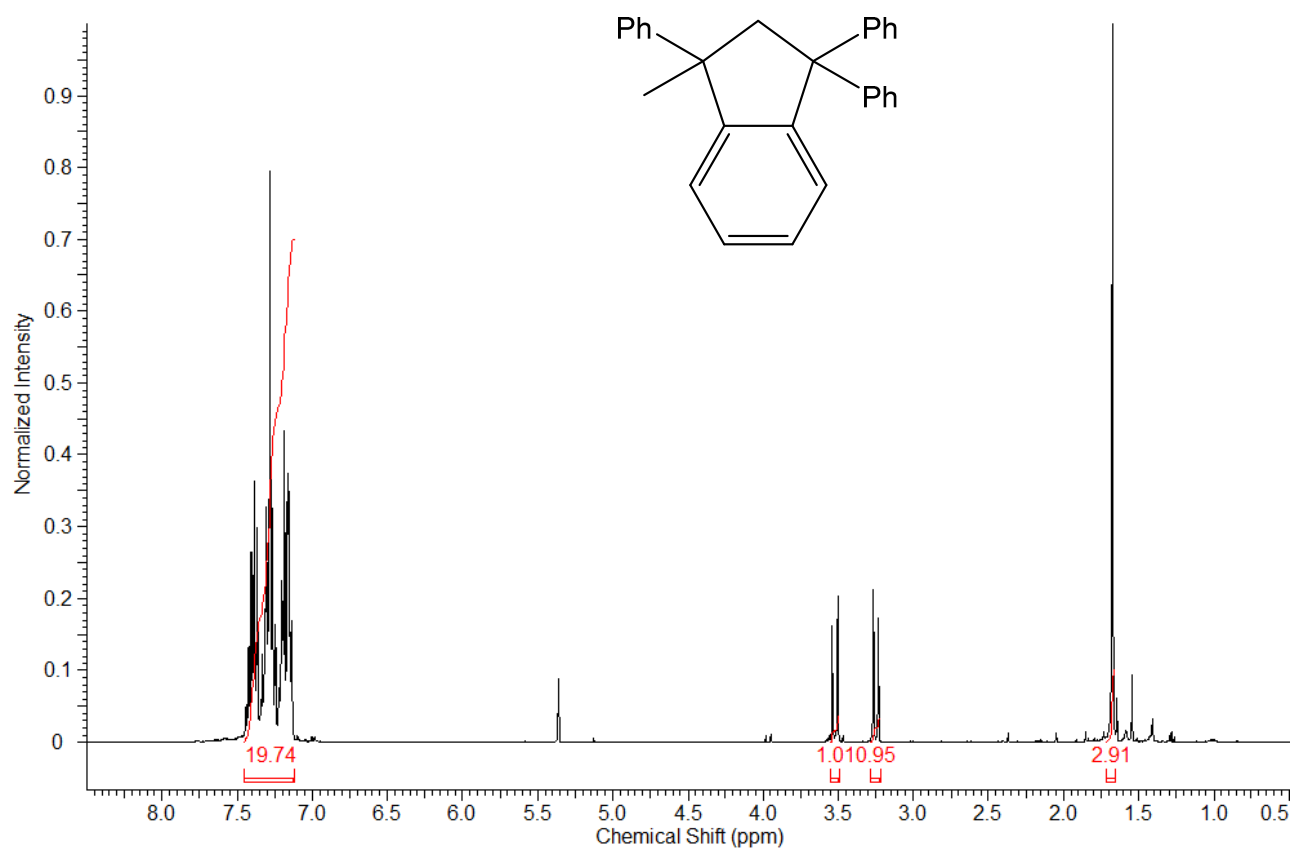
**Figure S28.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{CD}_3\text{CN}$ ) of  $\text{Ph}_2\text{C}=\text{CH}(\text{Me})$ , **3**.



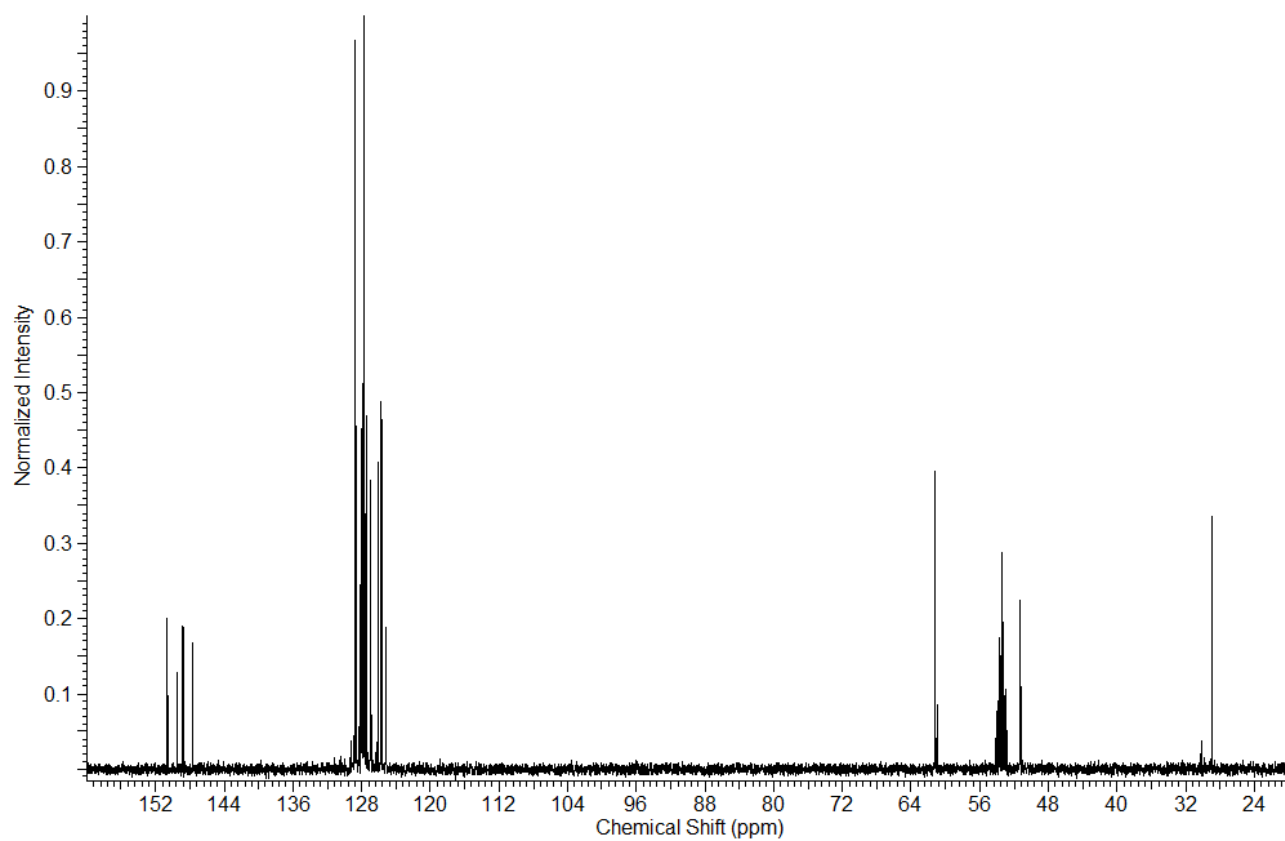
**Figure S29.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CD}_3\text{CN}$ ) of  $\text{Ph}_2\text{C}=\text{CH}(\text{Me})$ , **3**.



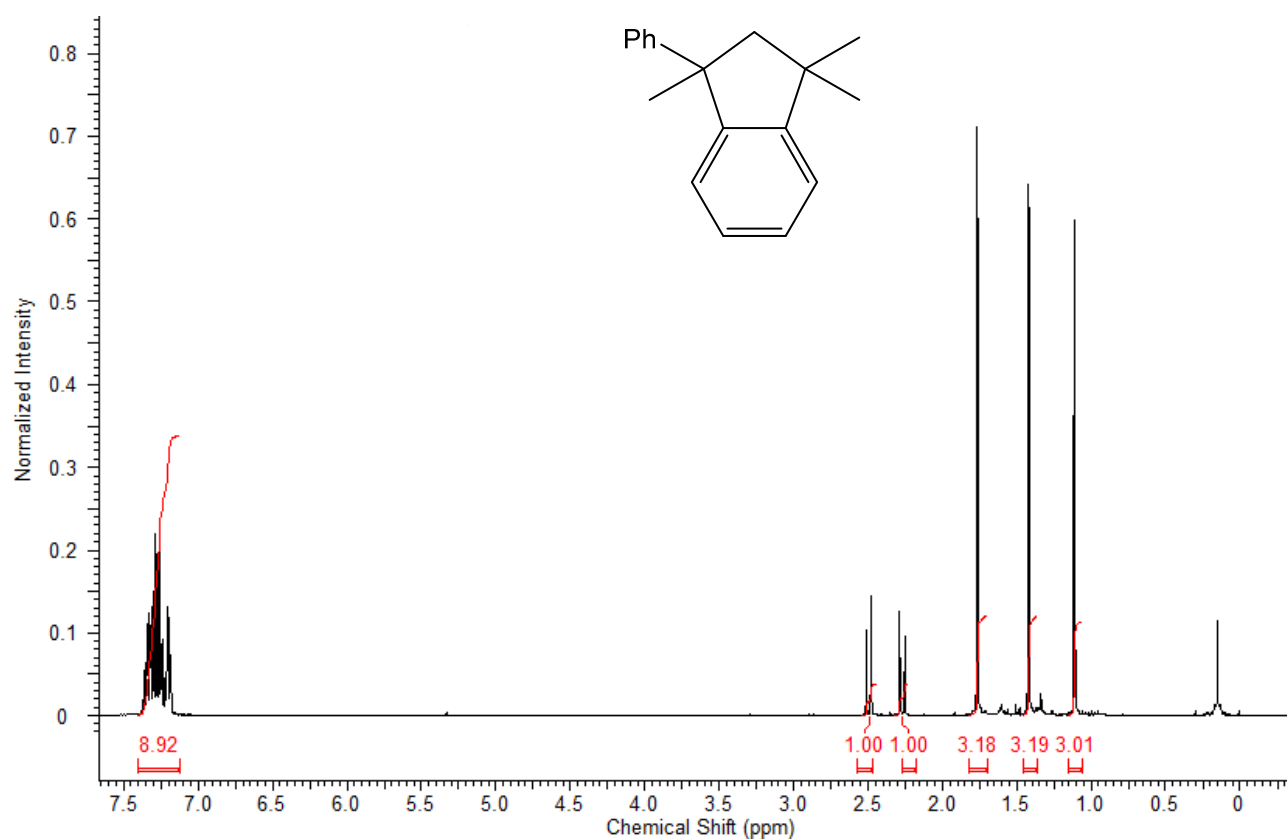
**Figure S30.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **4a**.



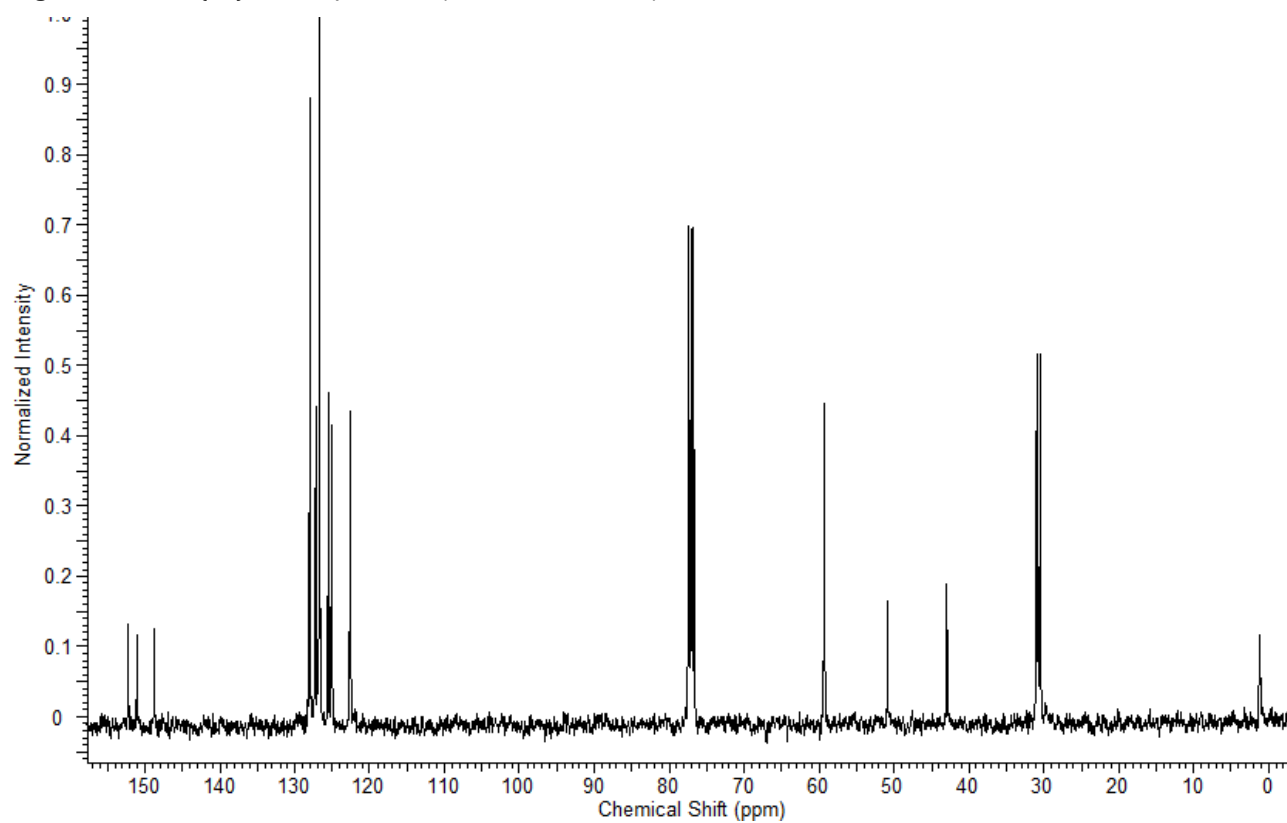
**Figure S31.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **4a**.



**Figure S32.**  $^1\text{H}$  NMR spectrum (401 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **4b**.



**Figure S33.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum (101 MHz,  $\text{CD}_2\text{Cl}_2$ ) of **4b**.



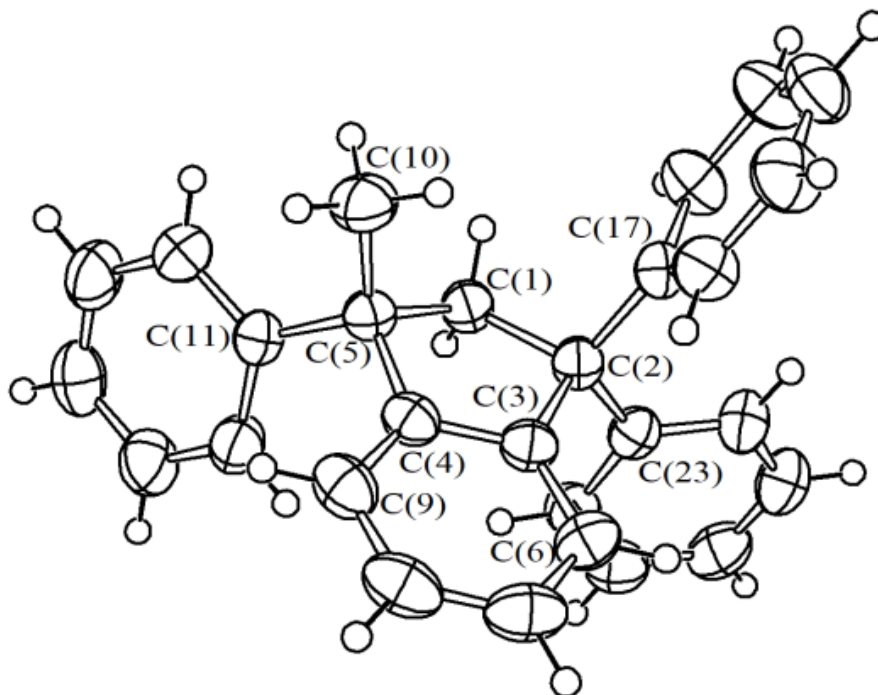


**X-ray Crystallographic Studies.** Crystal data and collection details for **1** and **4a** are reported in Table S1. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using *Mo-K $\alpha$*  radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).<sup>13</sup> Structures were solved by direct methods and refined by full-matrix least-squares based on all data using *F<sup>2</sup>*.<sup>14</sup> Hydrogen atoms were fixed at calculated positions and refined by a riding model. The molecular structure of **4a** contains a chiral carbon atom and, since it crystallizes in the centrosymmetric space group *P2<sub>1</sub>/n*, both the enantiomers are present within the unit cell in a 1:1 ratio.

**Table S1.** Crystal data and experimental details for [CPh<sub>3</sub>][WOCl<sub>5</sub>], **1**, and (C<sub>6</sub>H<sub>4</sub>)C(Ph)<sub>2</sub>CH<sub>2</sub>C(Me)(Ph), **4a**.

	<b>1</b>	<b>4a</b>
Formula	C <sub>19</sub> H <sub>15</sub> Cl <sub>5</sub> OW	C <sub>28</sub> H <sub>24</sub>
<i>F</i> <sub>w</sub>	620.41	360.47
$\lambda$ , Å	0.71073	0.71073
Temperature, K	100(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
<i>a</i> , Å	14.275(2)	11.0309(3)
<i>b</i> , Å	7.9205(11)	17.4337(5)
<i>c</i> , Å	18.698(3)	11.3811(3)
$\beta$ , °	103.080(2)	111.847(2)
Cell volume, Å <sup>3</sup>	2059.2(5)	2031.50(10)
<i>Z</i>	4	4
<i>D</i> <sub>c</sub> , g cm <sup>-3</sup>	2.001	1.179
$\mu$ , mm <sup>-1</sup>	6.265	0.066
<i>F</i> (000)	1184	768
$\theta$ limits, °	1.465 - 25.049	2.195 - 26.999
Reflections collected	16758	34185
Independent reflections	3654 [R <sub>int</sub> = 0.0568]	4436 [R <sub>int</sub> = 0.0409]
Data / restraints / parameters	3654 / 1 / 235	4436 / 0 / 254
Goodness on fit on <i>F</i> <sup>2</sup>	1.076	1.024
<i>R</i> 1 (> 2 $\sigma$ ( <i>I</i> ))	0.0374	0.0406
<i>wR</i> 2 (all data)	0.0875	0.1099
Largest diff. peak and hole, e.Å <sup>-3</sup>	2.845 / -1.399	0.185 / -0.146

**Figure S34.** Molecular structure of **4a** with key atoms labelled. Thermal ellipsoids are at the 50% probability level. Selected bond distances (Å) and angles (°): C(1)–C(2) 1.5662(17), C(2)–C(3) 1.5270(17), C(3)–C(4) 1.3868(18), C(4)–C(5) 1.5191(18), C(1)–C(5) 1.5599(17), C(5)–C(1)–C(2) 107.99(10), C(1)–C(2)–C(3) 101.16(10), C(2)–C(3)–C(4) 111.91(11), C(3)–C(4)–C(5) 112.14(11), C(4)–C(5)–C(1) 113.65(10).



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