Electronic Supplementary Material (ESI) for ChemComm.

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1. General information

NMR Spectroscopy. ^{1}H NMR spectra were recorded on high-field spectrometers (^{1}H 600.15 MHz and 500 MHz, 13C 150 MHz), equipped with a broadband inverse gradient probehead. Spectra were referenced to the residual solvent signal (chloroform-*d*, 7.24 ppm). Two dimensional NMR spectra were recorded with 2048 data points in the t_2 domain and up to 1024 points in the t_1 domain, with a 1s recovery delay.

Mass Spectrometry. High resolution and accurate mass spectra were recorded on a Shimadzu qTOF LCMS-9030 spectrometer using the electrospray technique.

GC-MS/FID. GC-FID: The Agilent 8890 gas chromatograph equipped with an FID detector was used for the analysis. The samples were loaded onto an Agilent 19091S-433UI column measuring 30 m x 250 µm x 0.25 µm with an HP-5ms Ultra Intert phase using an Agilent 7693A autosampler. The sample was flowing at 1 mL/min at 12.052 psi, while the Post Run was 2 mL/min. Initially, the oven temperature of 50°C was maintained for 1 minute, then increased by 30°C/min until it reached 250°C and was maintained for 3 minutes. Post Run was performed at 300°C for 2 minutes. The results were recorded thanks to the FID detector.

GC-MS: The Agilent 8890 gas chromatograph coupled with an Agilent 5977B mass spectrometer was used for the analysis. Samples were applied to an Agilent 122-5532 column measuring 30 m x 250 µm x 0.25 µm with a DB-5 m phase using the autosampler. Sample flowed with 1 mL/min movement at 12.052 psi, while Post Run Level flow was 2 mL/min. The oven parameters were the same as for the GC-FID measurement. The results were recorded using electron ionization (EI) mass spectroscopy in the scope of the scanning obligation in the range from 30.00 to 350.00. The airfoil clearance in 2.6 min was used, step 0.1 m/z with frequency 4.4 scans/sec and cycle time 117.45 ms.

Theoretical calculations. Geometry optimizations were carried out with the Gaussian 16 software package.[1] Becke's three-parameter exchange functionals with the gradient corrected correlation formula of Lee, Yang, and Parr (DFT-B3LYP)[2,3] were used with the 6-31G(d,p) basis set (PCM=Water). The structures were found to have converged to a minimum on the potential energy. Proton and carbon chemical shifts were calculated using the GIAO method and referenced to the absolute shielding of tetramethylsilane calculated at the same level of theory.

Flash chromatography. Flash Teledyne ISCO CombiFlash Rf integrated with ELS and UV-Vis light scattering detector was used. The test mixture with celite was placed in a RediSep® Rf precolumn and connected to the Flash liquid chromatography. A Teledyne Silica RediSep® Rf HP Gold 80 g column was used, and ethyl acetate and petroleum ether were used as eluents with a gradient change for separating the compounds contained in the oil over some time.

2. Experimental

Solvents and reagents: All solvents (Ethyl Acetate, Chloroform, Petroleum Ether (40-60), *n*-hexane), if not indicated differently, were used without purification. Dichloromethane was distilled over CaH_2. Acetonitrile was dried by passing through a silica column with the MBraun drying system. Chloroform-*d* was prepared directly before use by passing through a basic alumina column.

2.1. Synthesis of porphyrins and catalysts

Synthesis of H_2TPP (ligand for cat. 1, and cat. 4)

Ligand H_2TPP was synthesized using a procedure by Das et. al.[4]

Synthesis of *meta*-benziporphrin (ligand for cat. 2)

Ligand (TPBP)H was synthesized using a procedure by Stępień et. al.[5]

Synthesis of meso-tetrakis(2-methylphenyl)porphyrin (ligand for cat. 5)

meso-Tetrakis(2-methylphenyl)porphyrin was synthesized using a procedure by Lindsey et. al.[6]

Synthesis of meso-tetrakis(2-nitrophenyl)porphyrin (ligand for cat. 6)

meso-Tetrakis(2-nitrophenyl)porphyrin was synthesized using a procedure by Sharghi et. al. [7]

Synthesis of H_2TPFPP (ligand for cat. 3, cat. 7, and cat. 8)

To a 1 L round-bottom flask containing a stir bar were added CH_2Cl_2 (0.5 L), pyrrole (0.694 mL, 10.0 mmol), and pentafluorobenzaldehyde (1.23 mL, 10.0 mmol). After stirring briefly, the reaction was initiated by adding $BF_3{\cdot}OEt_2$ (1.23 mL, 10.0 mmol). The flask was tightly capped, and the reaction mixture was stirred at room temperature overnight. At a reaction time of 19 h, the reaction mixture was oxidized by adding DDQ (2.50 g, 11.0 mmol) at room temperature. After ~1 min, triethylamine (5.58 mL, 40.0 mmol, 4.00 equiv. relative to the acid) was added, and the mixture was stirred at room temperature. After 1 h, the reaction mixture was filtered through a pad of silica gel and eluted with CH_2Cl_2. The first fraction was concentrated into a dark, purple film. The analytical data match those of the reported molecule.[8]

Synthesis of catalyst 1

Catalyst 1 was synthesized using a procedure by Eder et al.[9]

Synthesis of catalyst 2

meta-Benziporphyrin (20 mg, 0.032 mmol, 1 equiv.) and $[Ru_3(CO)_{12}]$ (61 mg, 0.096 mmol, 3 equiv.) were refluxed in *o*-dichlorobenzene (under nitrogen) for four hours. The mixture was then chromatographed (silica gel, dichloromethane). The third dark green fraction is **cat. 2**. Yield - 61%.

^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ = 7.54–7.61 (m, 6,11,16,21-*o*-Ph), 7.54 (d, ^3J = 7.8 Hz, 2,4-H), 7.39–7.49 (m, 6,11,16,21-*m,p*-Ph), 7.07 (s, 13,14-H), 7.00 (t, ^3J = 7.6 Hz, 3-H), 6.86 (d, ^3J = 5.1 Hz, 8,19-H), 6.84 (d, ^3J = 5.2 Hz, 9,18-H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ = 191.0, 158.3, 154.9, 147.2, 144.2, 143.3, 143.0, 141.6, 137.2, 136.7, 136.4, 135.2, 134.2(2x), 132.5, 131.1(2x), 128.4, 128.1(2x), 127.5, 126.4(2x), 125.8, 117.9.

HRMS (ESI+) *m/z* $[M]^+$ 753.1354 calcd. $C_{47}H_{29}N_3ORu^+$ 753.1356

IR: ν_{CO} = 1939 cm^{-1}

Synthesis of catalyst 3

Catalyst 3 was synthesized using a procedure by Chen et al.[10]

Synthesis of catalysts 4-6

To a 50 mL round-bottom flask equipped with a stirring bar were added proper ligand (1 mmol) and $MnCl_2 \cdot 4H_2O$ (990 mg, 5 mmol). After dimethylformamide (50 mL) was placed in the flask, the reaction mixture was stirred and heated at 153 °C under air until UV-vis showed no free ligand left (2–4 hrs). The mixture was cooled to room temperature. After that, 10 mL conc. HCl (36%) to the mixture was added and stirred for about 15 minutes. The formed precipitate was filtered under reduced pressure. The sediment was washed with deionized water until the filtrate was almost colorless. The product was left overnight to dry under reduced pressure. The analytical data match those of the reported molecule.[11-13]

Synthesis of catalyst 7

Catalyst 7 was synthesized using a procedure by Castro et al.[14]

Synthesis of catalyst 8

To a 50 mL round-bottom flask equipped with a stirring bar were added H_2TPFPP (973 mg, 1 mmol) and $MnCl_2 \cdot 4H_2O$ (990 mg, 5 mmol). After dimethylformamide (50 mL) was placed in the flask, the reaction mixture was stirred and heated at 153 °C under air overnight until UV-vis showed no free H_2TPFPP left. The mixture was cooled to room temperature. After 10 mL conc. HCl (36%) to the mixture was added and stirred for about 15 minutes. The formed precipitate was filtered under reduced pressure. The sediment was washed with deionized water until the filtrate was almost colorless. The product was left overnight to dry under reduced pressure. The final product looked like a brownish powder. The analytical data match those of the reported molecule.[15]

Synthesis of 1B

1B was synthesized using an analogous procedure by Li et al.[16] To a 100 mL flask charged with a solution of 4-pentylphenol (5 mmol, 1 equiv.) in MeCN (10 mL) was added KOH (15 mmol, 3 equiv.). The reaction mixture was stirred at room temperature for 5 minutes, and iodomethane (7.5 mmol, 1.5 equiv.) was added. After stirring at 80 °C for 2 hours, the reaction mixture was quenched with saturated NH_4Cl, washed with water, dried over Na_2SO_4. Then product was isolated by flash chromatography using hexane and ethyl acetate (8:1) as the eluent on silical gel to afford substrate **1B** in 82% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.07 (d, ^3J = 8.5 Hz, 2H), 6.81 (d, ^3J = 8.6 Hz, 2H), 2.59 – 2.36 (m, 2H), 1.66 – 1.44 (m, 2H), 1.38 – 1.15 (m, 4H), 0.87 (t, ^3J = 7.0 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 157.6, 135.1, 129.2(2x), 113.7(2x), 55.3, 35.0, 31.5, 22.6, 14.3.

Oxidation of arylalkane to 1,4-diketone – a general method

In a 4 mL vial, the right amounts of proper catalyst (1,1%mol) and acetonitrile (27,5 μl) were placed (25 μl of solvent to 1%mol of catalyst). Then it was equipped with a stir bar and mixed for about 10 minutes. To an another 4 mL vial Oxone® (9 mg, 0.029 mmol, 0.29 equiv.), and (diacetoxyiodo)benzene (428 mg, 1.328 mmol, 13 equiv.) were added. After that, a stirring bar and catalyst were added (1,1 mg in 27.5 μl MeCN). Then a right substrate (0.1 mmol, 1 equiv.) and 1 mL

of deionized water were placed in a vial and closed by the cap. The reaction mixture was stirred for 24 h at 25 °C.

Extraction of 1,4-diketone

After 24 h the reaction mixture was placed in a separating funnel, and isolated 1,4-diketone was extracted from a water phase using ethyl acetate. After, it was measured using NMR and GC-MS. Finally, the pure product was isolated with flash chromatography.

Oxidation of arylalkane to 1,4-diketone – more details

Some of the substrates used in the experiments in the presence of oxygen are decomposed. Therefore, the appropriate amount of substrates were taken out of the glove box before the experiment.

The experiment was started by weighing the appropriate amount of the catalyst on an analytical balance and dissolving it in the proper amount of solvent, using a Hamilton microlitre syringe to ensure greater accuracy. Then, the correct amounts of oxidant were weighed into each of the 4 mL vials in which the reactions were carried out, the proper amount of additives was added, and the magnetic stirring bar was placed. The appropriate amount of catalyst, substrate, and water, the main reaction medium, were added sequentially. The vials were then placed in a metal heat plate and agitated for an appropriate time. The desired product was then extracted from the aqueous phase. A separating funnel was used for this, and the extractant was ethyl acetate. The water layer was checked for the presence of 1,4-diketone, albeit negative. The extractant was evaporated on an evaporator under reduced pressure of 230 hPa at a temperature of 50 °C, which positively resulted in the use of 4-pentylbromobenzene to obtain an oily, light yellowish liquid.

2.2 Optimization of Reaction Conditions

Figure S1.

Two methods were used to determine the efficiency of 1,4-diketone formation. The first one used was the NMR spectroscopy and 1,3,5-trimethoxybenzene (TMB) as the internal standard. TMB was chosen due to the lack of interference of the signal from the aryl ring protons (marked **a**) with the signals belonging to the protons **2b** marked in the spectrum (Figure S1) as **b** and **c**. To calculate the efficiency, the peak belonging to the standard substance was integrated as one and a half because this signal corresponds to three protons, while the signals belonging to **2b** correspond to two

protons. The integration of peaks **b** or **c** multiplied by 100 determines the percentage yield. For example, in the shown spectrum (Figure S1), the 1,4-diketone formation efficiency is 28%.

Another method of checking efficiency was based on using gas chromatography with an FID detector. The calibration curve had to be prepared for the correct reaction efficiency reading. Ten solutions with known concentrations of TMB and **2b** were made, and their signals were recorded on the chromatograph. The left peak shown in Figure S2 corresponds to the standard, while the right one to **2b**. Below the chromatogram there are shown the obtained signals' retention times, surface areas, and heights.

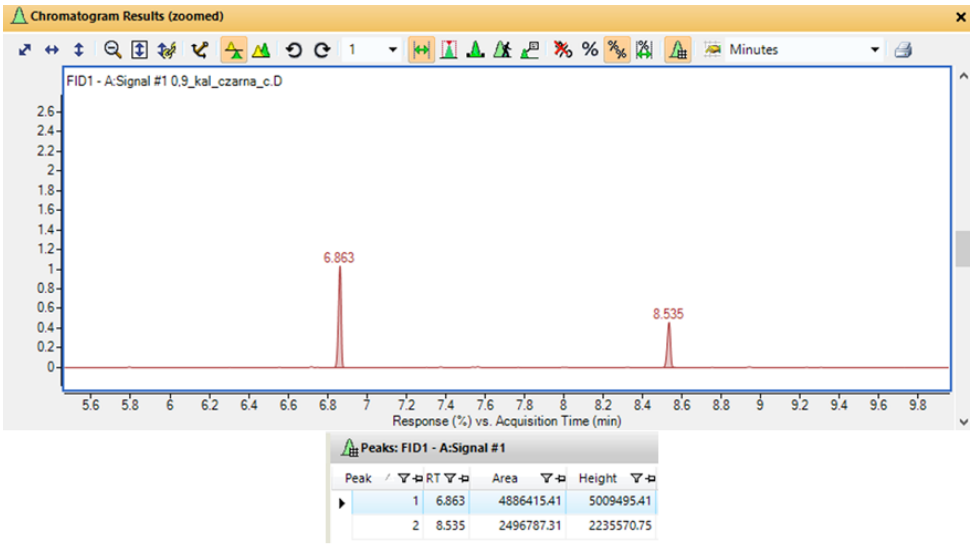


Figure S2.

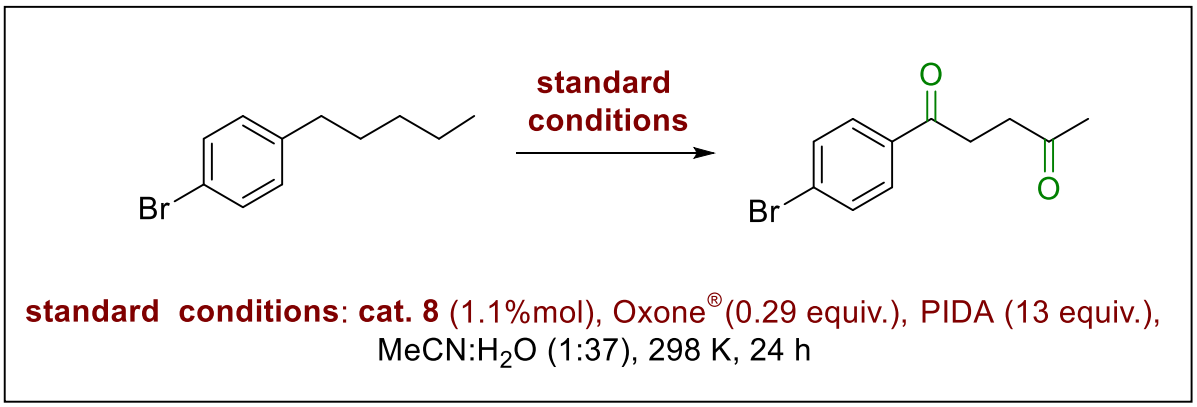
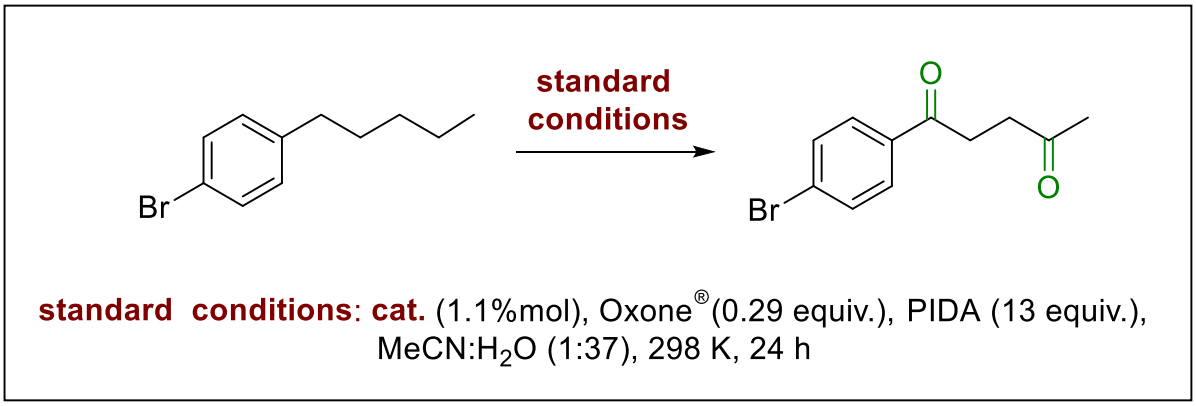
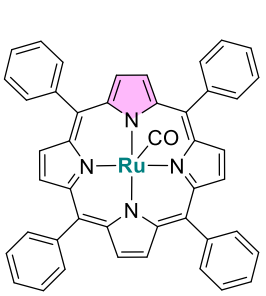


Table 1. Optimization of oxidation of arylalkanes to 1,4-diketones.

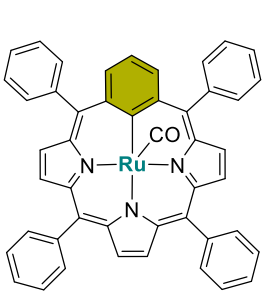
Lp.	***Conditions***	***α-Monoketone***	***1,4-Diketone***
1.	*Standard*	*26%*	***54%***
2.	*w/o catalyst 8*	*traces*	***Traces***
3.	*w/o oxidant 1 (PIDA)*	*-*	***-***
4.	*w/o oxidant 2 (Oxone)*	*53%*	***42%***
5.	*with 100 µl of 0.1 M HCl*	*64%*	***29%***

6.	*with 100 µl of 0.1 M Cs_2CO_3*	*61%*	***36%***

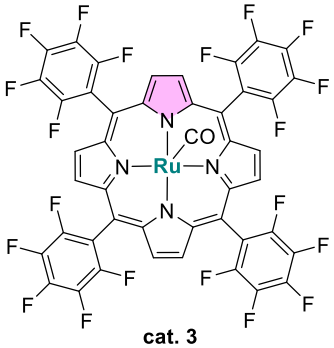




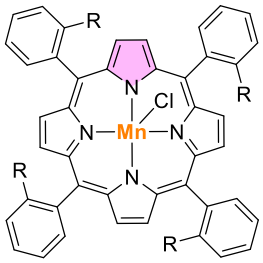
cat. 1



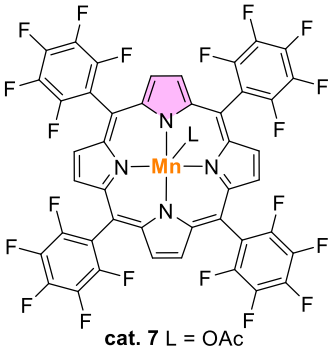
cat. 2



cat. 3



cat. 4 R = H
cat. 5 R = CH_3
cat. 6 R = NO_2



cat. 7 L = OAc
cat. 8 L = Cl

Table 2. Optimization of oxidation of arylalkanes to 1,4-diketones.

Lp.	***Catalyst***	***1,4-Diketone***
1.	*cat. 8*	***54%***
2.	*cat. 1/2/4/ 5/6*	***n.d.***
3.	*cat. 3*	***traces***
4.	*cat. 7*	***54%***
5.	*w/o catalyst*	***n.d.***

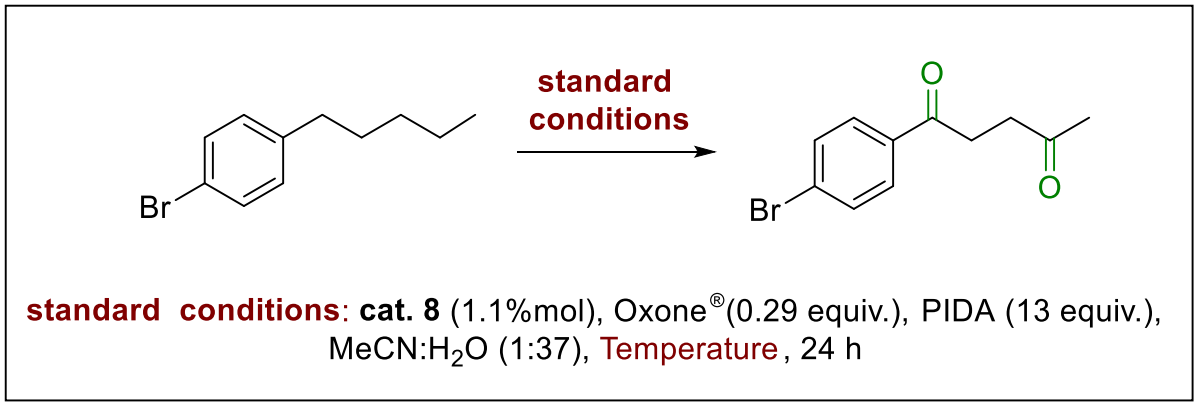


Table 3. Optimization of oxidation of arylalkanes to 1,4-diketones.

Lp.	*Temperature*	*α-Monoketone*	*1,4-Diketone*
1.	*25 °C*	*34%*	***54%***
2.	*40 °C*	*21%*	***30%***
3.	*60 °C*	*20%*	***11%***
4.	*80 °C*	*24%*	***3%***

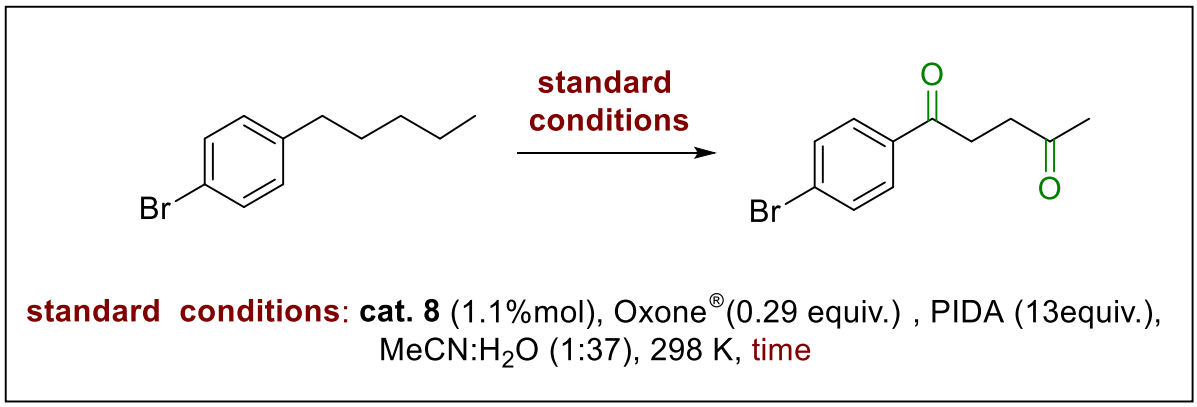


Table 4. Optimization of oxidation of arylalkanes to 1,4-diketones.

Lp.	*Time*	*Conversion*	*α-Monoketone*	*1,4-Diketone*
1.	*1 h*	*78%*	*30%*	***13%***
2.	*5 h*	*98%*	*34%*	***49%***
3.	*24 h*	*100%*	*10%*	***54%***
4.	*48 h*	*100%*	*4%*	***32%***
5.	*72 h*	*100%*	*3%*	***34%***

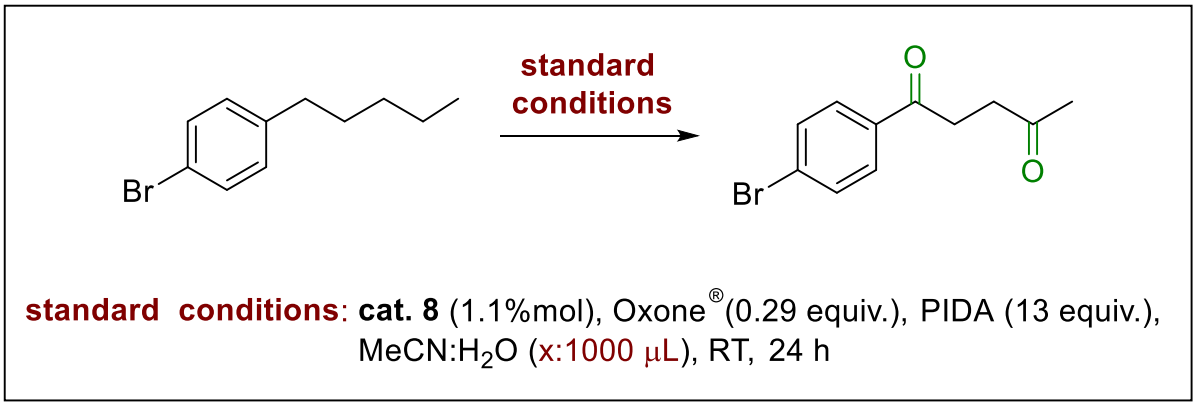
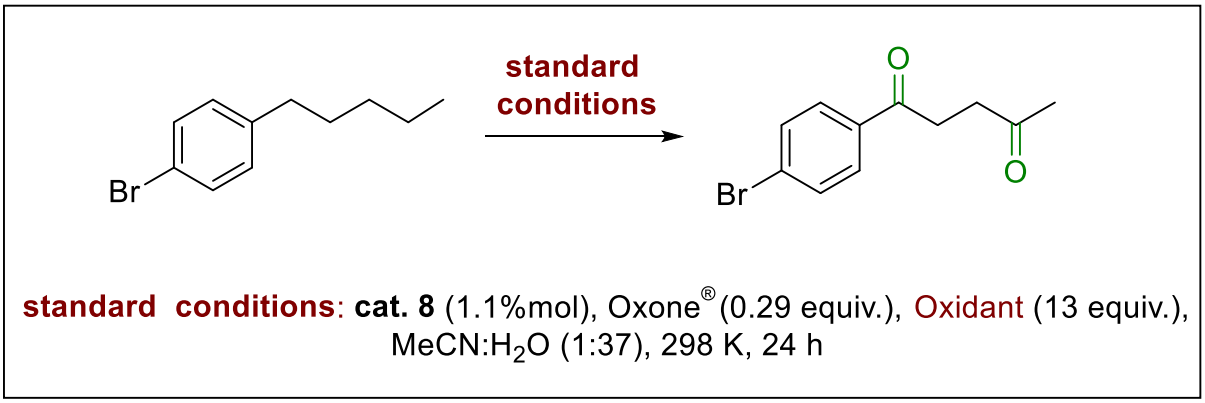
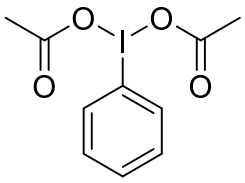


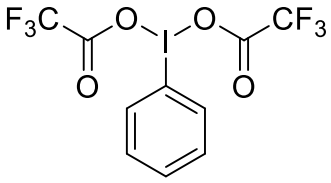
Table 5. Optimization of oxidation of arylalkanes to 1,4-diketones.

Lp.	*MeCN*	*1,4-Diketone*
1.	*27.5 μl*	***57%***
2.	*250 μl*	***17%***
3.	*500 μl*	***11%***
4.	*750 μl*	***5%***
5.	*1000 μl*	***<1%***

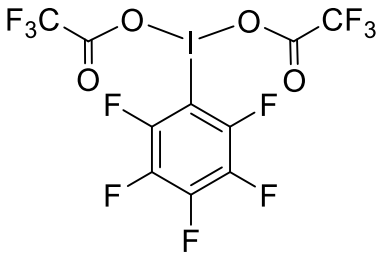




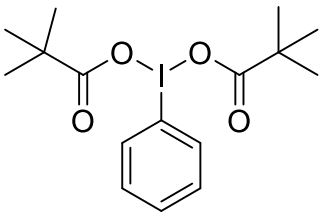
PIDA 5A



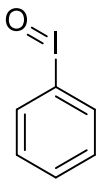
PIFA 5B



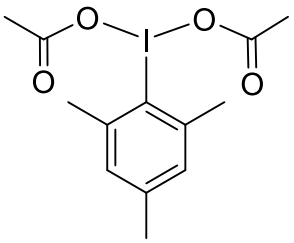
5C



5D



5E



5F

Table 6. Optimization of oxidation of arylalkanes to 1,4-diketones.

Lp.	*Oxidant*	*1,4-Diketone*	*Substrate: Monoketone*
1.	*5A*	***54%***	-
2.	*5B*	-	*5:1*
3.	*5C*	-	*42:1*
4.	*5D*	***17%***	*1:2.6*
5.	*5E*	-	*30:1*
6.	*5F*	-	*11:1*

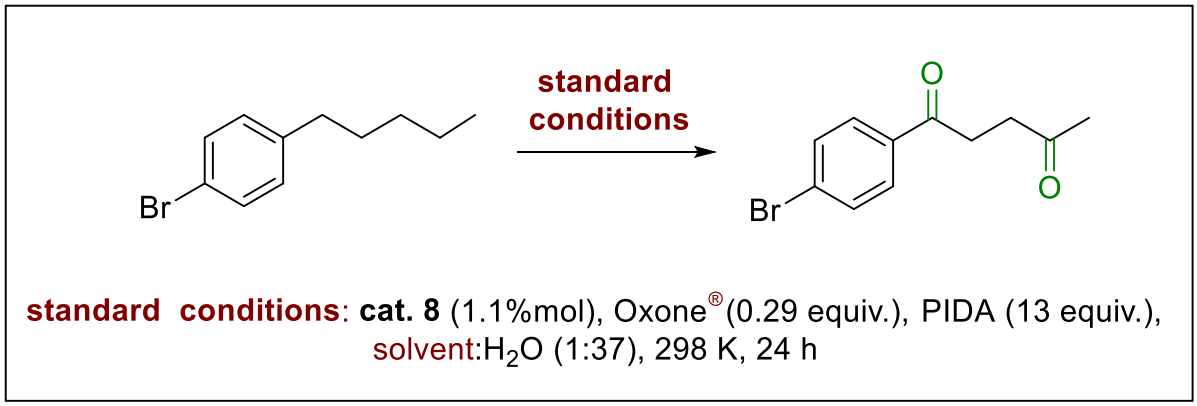
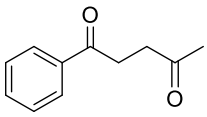


Table 7. Optimization of oxidation of arylalkanes to 1,4-diketones.

Lp.	*Solvent*	*α-Monoketone*	*1,4-Diketone*
1.	*Acetonitrile*	*26%*	***54%***
2.	*Propionitrile*	*3%*	***50%***
3.	*Dichloromethane*	*10%*	***41%***
4.	*DMF*	*28%*	***5%***
5.	-	*61%*	***20%***

3. Oxidation of arylalkanes to 1,4-diketones

1-phenylpentane-1,4-dione (2a)



The compound **2a** was prepared according to the general procedure by reaction of *n*-amylbenzene (17.3 µL, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 85:15) to give yellowish oil. Yield: 45% (isolated: 32%, 5.6 mg).

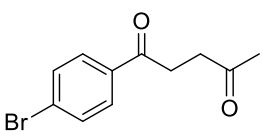
^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.96 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.62 –7.49 (m, 1H), 7.44 (dd, *J* = 10.7, 4.8 Hz, 2H), 3.26 (dd, *J* = 6.9, 6.3 Hz, 2H), 2.87 (dd, *J* = 6.9, 6.3 Hz, 2H), 2.24 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 207.3, 198.5, 136.7, 133.2, 128.6(2x), 128.1(2x), 37.1, 32.4, 30.1.

HRMS (ESI+) *m/z* $[M+H]^+$ 177.093 calcd. $C_{11}H_{13}O_2^+$ 177.092

The analytical data match those of the reported molecule.[17]

1-(4-bromophenyl)pentane-1,4-dione (2b)



The compound **2b** was prepared according to the general procedure by reaction of 1-bromo-4-pentylbenzene (18.7 µL, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 80:20) to give yellowish oil. Yield: 54% (isolated: 43%, 10.9 mg).

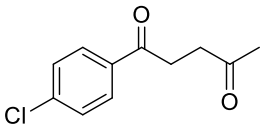
1g-scale: In a 10 mL vial, the catalyst **8** (1,1%mol) and acetonitrile (1210 μl) were placed. Then it was equipped with a stir bar and mixed for about 10 minutes. Next, to a 100 mL flask Oxone® (396 mg, 1.28 mmol, 0.29 equiv.) and (diacetoxyiodo)benzene (18.83 g, 58.43 mmol, 13 equiv.) were added. After that, a huge stirring bar and catalyst were added (48,4 mg in 1210 μl MeCN). Then a 1-bromo-4-pentylbenzene (827.8 μl, 4.4 mmol, 1 equiv.) and 44 mL of deionized water were placed in a flask and closed by the cap. Finally, the reaction mixture was stirred for 24 h at 25 °C. Isolated yield = 48% (539 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.82 (d, ^3J = 8.7 Hz, 2H), 7.59 (d, ^3J = 8.7 Hz, 2H), 3.21 (t, *J* = 6.8, 6.2 Hz, 2H), 2.87(t, *J* = 6.8, 6.2 Hz, 2H), 2.23 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 207.1, 135.4, 131.9(2x), 129.6(2x), 128.4, 37.0, 32.3, 30.1.

HRMS (ESI+) *m/z* $[M+Na]^+$ 276.986 calcd. $C_{11}H_{11}BrNaO_2^+$ 276.984

1-(4-chlorophenyl)pentane-1,4-dione (2c)



The compound **2c** was prepared according to the general procedure by reaction of 1-chloro-4-pentylbenzene (18.4 μL, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 80:20) to give whitish solid. Yield: 47% (isolated: 35%, 7.4 mg).

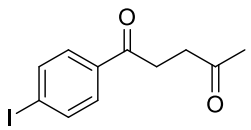
1 mmol-scale: In a 4 mL vial, the catalyst 8 (1,1%mol) and acetonitrile (275 μl) were placed. Then it was equipped with a stir bar and mixed for about 10 minutes. To a 50 mL flask Oxone® (90 mg, 0.29 mmol, 0.29 equiv.), and (diacetoxyiodo)benzene (4280 mg, 13.28 mmol, 13 equiv.) were added. After that, a big stirring bar and catalyst were added. Then a 1-chloro-4-pentylbenzene (184 μL, 1.0 mmol) and 10 mL of deionized water were placed in a flask and closed by the cap. The reaction mixture was stirred for 24 h at 25 °C. Isolated yield: 45% (94.5 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.90 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 3.1 (dd *J* = 7.1, 6.2 Hz, 2H), 2.89 (dd, *J* = 7.1, 6.2 Hz, 2H), 2.23 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 207.1, 197.3, 139.6, 135.0, 129.5(2x), 128.9(2x), 37.0, 32.4, 30.1.

HRMS (ESI+) *m/z* $[M+Na]^+$ 233.035 calcd. $C_{11}H_{121}ClNaO_2^+$ 233.037

1-(4-iodophenyl)pentane-1,4-dione (2d)



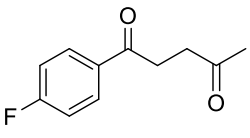
The compound **2d** was prepared according to the general procedure by reaction of 1-iodo-4-pentylbenzene (19.9 μL, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 80:20) to give yellowish solid. Yield: 63% (isolated: 52%, 15.9 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.5 Hz, 2H), 7.67 (d, *J* = 8.5 Hz, 2H), 3.20 (dd, *J* = 7.0, 6.2 Hz, 2H), 2.86 (dd, *J* = 7.0, 6.2 Hz, 2H), 2.23 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 207.1, 197.8, 137.9(2x), 129.5(2x), 101.1, 37.0, 32.3, 30.1.

HRMS (ESI+) *m/z* $[M+H]^+$ 302.986 calcd. $C_{11}H_{12}IO_2^+$ 302.988

1-(4-fluorophenyl)pentane-1,4-dione (2e)



The compound **2e** was prepared according to the general procedure by reaction of 1-fluoro-4-pentylbenzene (17.7 µL, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 85:15) to give yellowish oil. Yield: 56% (isolated: 32%, 11,3 mg).

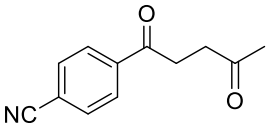
1g-scale: In a 10 mL vial, the catalyst **8** (1,1%mol) and acetonitrile (1650 µl) were placed. Then it was equipped with a stir bar and mixed for about 10 minutes. Next, to a 250 mL flask Oxone® (541 mg, 1.75 mmol, 0.29 equiv.) and (diacetoxyiodo)benzene (25.77 g, 79.94 mmol, 13 equiv.) were added. After that, a huge stirring bar and catalyst were added (66,2 mg in 1650 µl MeCN). Then a 1-fluoro-4-pentylbenzene (1063.8 µl, 6.0 mmol, 1 equiv.) and 60 mL of deionized water were placed in a flask and closed by the cap. Finally, the reaction mixture was stirred for 24 h at 25 °C. Isolated yield = 49% (573 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.99 (d, J = 8.6, 2H), 7.11 (d, J = 8.6 Hz, 2H), 3.22 (dd, J = 7.1, 6.4 Hz, 2H), 2.87 (dd, J = 7.1, 6.4 Hz, 2H), 2.24 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 207.3, 196.9, 166.6, 164.9, 133.2, 130.7, 115.8, 115.6, 37.0, 32.3, 30.1.

HRMS (ESI+) *m/z* $[M+H]^+$ 198.082 calcd. $C_{11}H_{12}FO_2^+$ 198.081

4-(4-oxopentanoyl)benzonitrile (2f)



The compound **2f** was prepared according to the general procedure by reaction of 4-pentylbenzonitrile (18.2 µL, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 75:25) to give yellowish solid. Yield: 50% yield (isolated: 38%, 7.7 mg).

1 mmol-scale: In a 4 mL vial, the catalyst 8 (1,1%mol) and acetonitrile (275 µl) were placed. Then it was equipped with a stir bar and mixed for about 10 minutes. To a 50 mL flask Oxone® (90 mg, 0.29 mmol, 0.29 equiv.) and (diacetoxyiodo)benzene (4280 mg, 13.28 mmol, 13 equiv.) were added. After that, a big stirring bar and catalyst were added. Then 4-pentylbenzonitrile (182 µL, 1.0 mmol) and 10 mL of deionized water were placed in a flask and closed by the cap. The reaction mixture was stirred for 24 h at 25 °C. Isolated yield: 48% (96.4 mg).

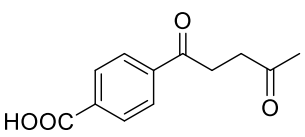
^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 3.23 (dd, *J* = 6.9, 6.3 Hz, 2H), 2.90 (dd, *J* = 6.9, 6.3 Hz, 2H), 2.24 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 206.8, 197.3, 139.7, 132.5(2x), 128.5(2x), 117.9, 116.5, 37.0, 32.6, 30.00

HRMS (ESI+) *m/z* $[M+Na]^+$ 224.070 calcd. $C_{12}H_{11}NNaO_2^+$ 224.069

The analytical data match those of the reported molecule.[18]

4-(4-oxopentanoyl)benzoic acid (2g)



The compound **2g** was prepared according to the general procedure by reaction of 4-pentylbenzaldehyde (18.4 µL, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 70:30) to give whitish solid. Yield: 31% yield (isolated: 19%, 4.2 mg).

1 mmol-scale: In a 4 mL vial, the catalyst 8 (1,1%mol) and acetonitrile (275 µl) were placed. Then it was equipped with a stir bar and mixed for about 10 minutes. To a 50 mL flask Oxone® (90 mg, 0.29 mmol, 0.29 equiv.) and (diacetoxyiodo)benzene (4280 mg, 13.28 mmol, 13 equiv.) were added. After that, a big stirring bar and catalyst were added. Then 4-pentylbenzaldehyde (184 µL, 1.0

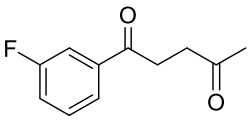
mmol) and 10 mL of deionized water were placed in a flask and closed by the cap. The reaction mixture was stirred for 24 h at 25 °C. Isolated yield: 30% (66.0 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.17 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 3.28 (dd, *J* = 7.0, 6.2 Hz, 2H), 2.91 (dd, *J* = 7.0, 6.2 Hz, 2H), 2.25 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ: 207.0, 198.0, 169.4, 140.5, 132.8, 130.5(2x), 128.1(2x), 37.1, 32.8, 30.0.

HRMS (ESI+) *m/z* $[M+Na]^+$ 243.065 calcd. $C_{12}H_{12}NaO_4^+$ 243.063

1-(3-fluorophenyl)pentane-1,4-dione (2h)



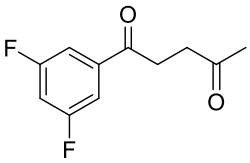
The compound **2h** was prepared according to the general procedure by reaction of 1-fluoro-3-pentylbenzene (17.7 µL, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 80:20) to give colorless oil. Yield: 39% (isolated: 32%, 6.1 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.70 (dt, J = 7.7, 1.3 Hz, 1H), 7.59 (ddd, J = 9.5, 2.6, 1.5 Hz, 1H), 7.38 (td, J = 8.0, 5.5 Hz, 1H), 7.30 – 7.10 (m, 1H), 3.18 (dd, J = 6.9, 5.6 Hz, 2H), 2.83 (dd, J = 6.9, 5.6 Hz, 2H), 2.19 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ: 207.0, 197.3, 162.8, 138.8, 130.3, 123.8, 120.2, 114.9, 37.0, 32.5, 30.1.

HRMS (ESI+) *m/z* $[M+Na]^+$ 217.067 calcd. $C_{11}H_{11}FNaO_2^+$ 217.064

1-(3,5-difluorophenyl)pentane-1,4-dione (2i)



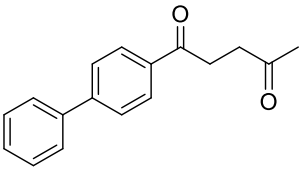
The compound **2i** was prepared according to the general procedure by reaction of 1,3-difluoro-5-pentylbenzene (18.0 µL, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 80:20) to give whitish solid. Yield: 45% (isolated: 41%, 9.5 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.46 (dd, J = 7.8, 2.1 Hz, 2H), 7.05-6.90 (m, 1H), 3.18 (dd, J = 6.9, 5.4 Hz, 2H), 2.88 (dd, J = 7.0, 5.6 Hz, 2H), 2.23 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ: 206.6, 196.2, 164.2, 162.3, 139.6, 111.2, 111.00, 108.43, 36.9, 32.5, 30.0.

HRMS (ESI+) *m/z* $[M+Na]^+$ 235.054 calcd. $C_{11}H_{10}F_2NaO_2^+$ 235.055

1-([1,1'-biphenyl]-4-yl)pentane-1,4-dione (2j)



The compound **2j** was prepared according to the general procedure by reaction of 4-pentyl-1,1'-biphenyl (23.1 µL, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 85:15) to give white solid. Yield: 26% (isolated: 21%, 5.3mg).

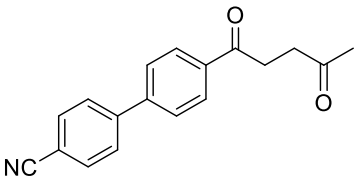
1 mmol-scale: In a 4 mL vial, the catalyst 8 (1,1%mol) and acetonitrile (275 µl) were placed. Then it was equipped with a stir bar and mixed for about 10 minutes. To a 50 mL flask Oxone® (90 mg, 0.29 mmol, 0.29 equiv.) and (diacetoxyiodo)benzene (4280 mg, 13.28 mmol, 13 equiv.) were added. After that, a big stirring bar and catalyst were added. Then 4-pentyl-1,1'-biphenyl (231 µL, 1.0 mmol) and 10 mL of deionized water were placed in a flask and closed by the cap. The reaction mixture was stirred for 24 h at 25 °C. Isolated yield: 28% (70.6 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.46-7.44 (m, 2H), 7.39-7.37 (m, 1H), 3.29 (dd, *J* = 7.0, 6.3 Hz, 2H), 2.90 (dd, *J* = 7.0, 6.3 Hz, 2H), 2.25 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 207.3, 198.1, 145.9, 139.9, 135.4, 128.9(2x), 128.7(2x), 128.2, 127.3(2x), 127.2(2x), 37.1, 32.5, 30.1.

HRMS (ESI+) *m/z* $[M+H]^+$ 253.123 calcd. $C_{17}H_{17}O_2^+$ 253.123

4'-(4-oxopentanoyl)-[1,1'-biphenyl]-4-carbonitrile (2k)



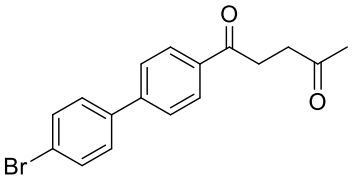
The compound **2k** was prepared according to the general procedure by reaction of 4-cyano-4'-pentyl-1,1'-biphenyl (24.7 µL, 0.1 mmol). It was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 80:20) to give yellowish solid. Yield: 34% (isolated: 30%, 8.3 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.70 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 3.28 (dd, *J* = 6.9, 6.2 Hz, 2H), 2.90 (dd, *J* = 6.9, 6.2 Hz, 2H), 2.25 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 207.2, 197.9, 144.3, 143.6, 136.5, 132.7(2x), 128.9(2x), 127.9(2x), 127.5(2x), 118.6, 111.9, 37.1, 32.5, 30.1.

HRMS (ESI+) *m/z* $[M+H]^+$ 278.118 calcd. $C_{18}H_{16}NO_2^+$ 278.116

1-(4'-bromo-[1,1'-biphenyl]-4-yl)pentane-1,4-dione (2l)



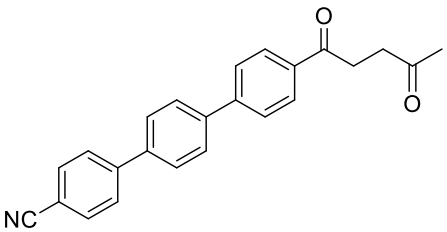
The compound **2l** was prepared according to the general procedure by reaction of 4-bromo-4'-pentyl-1,1'-biphenyl (30.3 mg, 0.1 mmol). It was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 75:25) to give yellowish solid. Yield: 30% (isolated: 23%, 7.6 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 3.28 (dd, *J* = 6.9, 6.3 Hz, 2H), 2.90 (dd, *J* = 6.9, 6.3 Hz, 2H), 2.25 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 207.3, 198.0, 144.6, 138.8, 135.7, 132.1(2x), 128.8(2x), 128.8(2x), 127.1(2x), 122.7, 37.1, 32.5, 30.1.

HRMS (ESI+) *m/z* $[M+Na]^+$ 353.018 calcd. $C_{17}H_{15}BrNaO_2^+$ 353.015

4''-(4-oxopentanoyl)-[1,1':4',1''-terphenyl]-4-carbonitrile (2m)



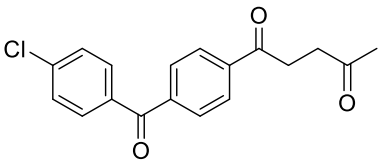
The compound **2m** was prepared according to the general procedure by reaction of 4-cyano-4''-pentyl-*p*-terphenyl (32.5 mg, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 65:35) to give white solid. Yield: 21% (isolated: 16%, 5.6 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.07 (d, *J* = 8.4 Hz, 2H), 7.76 – 7.64 (m, 6H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 3.30 (dd, *J* =6.9, 6.0 Hz, 2H), 2.91 (dd, *J* = 6.9, 6.0 Hz, 2H), 2.26 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 207.4, 198.1, 144.8, 140.3, 139.0, 135.8, 132.8(2x), 128.9(3x), 128.1(3x), 127.9(2x), 127.7(2x) 127.3(2x), 127.2, 37.2, 32.6, 29.8.

HRMS (ESI+) *m/z* $[M+Na]^+$ 376.135 calcd. $C_{24}H_{19}NNaO_2^+$ 376.131

1-(4-(4-chlorobenzoyl)phenyl)pentane-1,4-dione (2n)



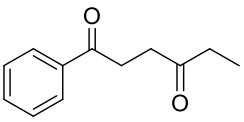
The compound **2n** was prepared according to the general procedure by reaction of 4-Chloro-4'-*n*-pentylbenzophenone (28.7 mg, 0.1 mmol). It was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 60:40) to give a pinkish solid. Yield: 45% (Isolated: 41%, 12.8 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.06 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.6 Hz, 2H), 3.29 (dd, *J* = 6.8, 5.5 Hz, 2H), 2.92 (dd, *J* = 6.8, 5.5 Hz, 2H), 2.25 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 207.0, 198.0, 194.7, 141.0, 139.4, 135.2, 131.5, 129.9, 128.9, 128.0, 37.0, 32.7, 30.0.

HRMS (ESI+) *m/z* $[M+H]^+$ 315.079 calcd. $C_{18}H_{16}ClO_3^+$ 315.077

1-phenylhexane-1,4-dione (2o)



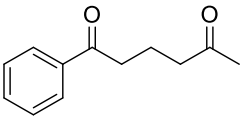
The compound **2o** was prepared according to the general procedure by reaction of *n*-hexylbenzene (18.9 µL, 0.1 mmol). It was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 85:15) to give a pinkish solid. Yield: 16% (isolated: 12%, 2.3 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.01 – 7.89 (m, 2H), 7.57 – 7.53 (m, 1H), 7.46 – 7.43 (m, 2H), 3.27 (dd, *J* = 6.9, 6.1 Hz, 2H), 2.84 (dd, *J* = 6.9, 6.1 Hz, 2H), 2.55 (q, *J* = 7.4 Hz, 2H), 1.08 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 210.1, 198.7, 136.8, 133.1, 128.6(2x), 128.1(2x), 36.1, 35.8, 32.4, 7.9.

HRMS (ESI+) *m/z* $[M+H]^+$ 191.107 calcd. $C_{12}H_{15}O_2^+$ 191.105

1-phenylhexane-1,5-dione (2p)



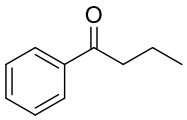
The compound **2p** was prepared according to the general procedure by reaction of *n*-hexylbenzene (18.9 µL, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 80:20) to give white solid. Yield: 32% (isolated: 24%, 4.6 mg).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.95 – 7.93 (m, 2H), 7.55 – 7.53 (m, 1H), 7.46 – 7.43 (m, 2H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.55 (t, *J* = 7.0 Hz, 2H), 2.13 (s, 3H), 2.00 (k, *J* = 7.0 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ: 208.5, 199.9, 136.9, 133.1, 128.6(2x), 128.1(2x), 42.6, 37.4, 29.9, 18.2.

HRMS (ESI+) *m/z* $[M+H]^+$ 191.107 calcd. $C_{12}H_{15}O_2^+$ 191.106

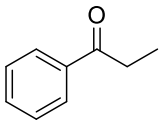
1-phenylbutan-1-one (2r)



The compound **2r** was prepared according to the general procedure by reaction of *n*-butylbenzene (15.6 µL, 0.1 mmol). Yield: 51%.

The analytical data match those of the reported molecule.[19]

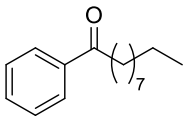
1-phenylpropan-1-one (2s)



The compound **2s** was prepared according to the general procedure by reaction of *n*-propylbenzene (14 µL, 0.1 mmol). Yield: 58%.

The analytical data match those of the reported molecule.[20]

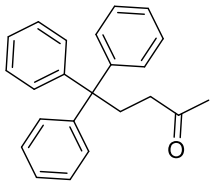
1-phenyldecan-1-one (2t)



The compound **2t** was prepared according to the general procedure by reaction of 1-decylbenzene (18.7 µL, 0.1 mmol). Yield: 37%.

The analytical data match those of the reported molecule. [21]

5,5,5-triphenylpentan-2-one (2u)



The compound **2u** was prepared according to the general procedure by reaction of 1,1,1-triphenylpentane (28.7 mg, 0.1 mmol) and was isolated by column chromatography (silica gel, hexane to hexane/ethyl acetate 80:20) to give white solid. Yield: 58% (Isolated: 50%, 15.7 mg).

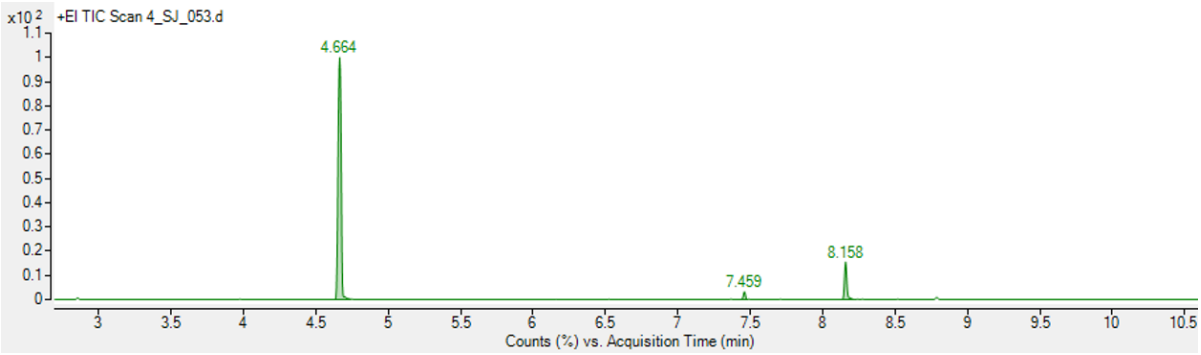
^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.31 – 7.16 (m, 12H), 7.11 (m, 3H), 2.94 – 2.75 (m, 2H), 2.29 – 2.10 (m, 2H), 1.92 (s, 3H).

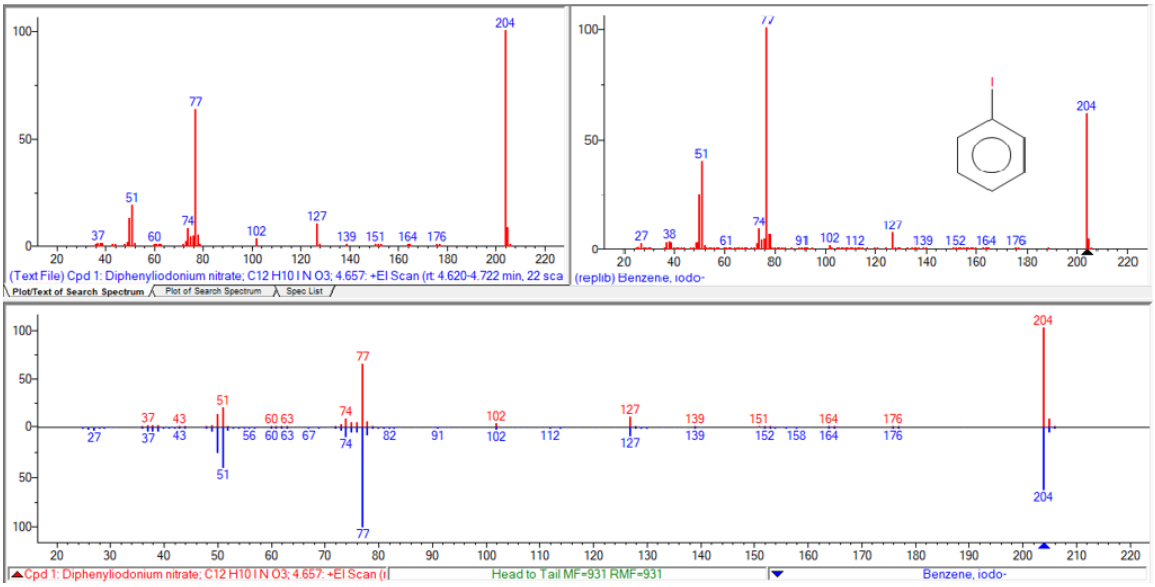
^{13}C NMR (150 MHz, $CDCl_3$) δ: 208.4, 146.8(3x), 129.1(6x), 128.0(6x), 126.0(3x), 55.9, 40.4, 33.4, 30.2.

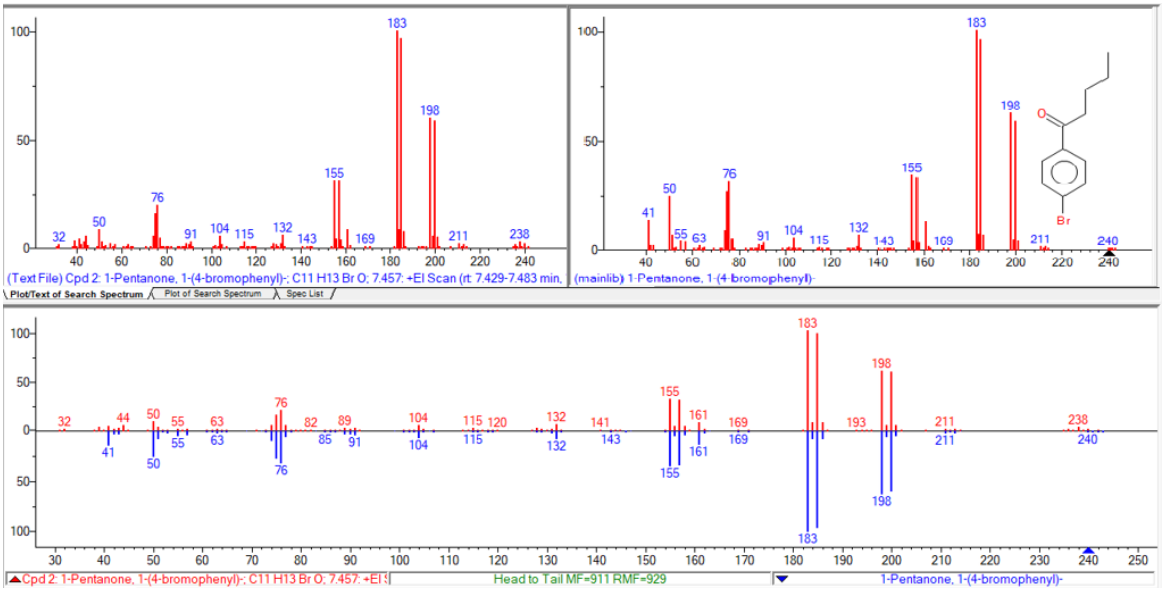
HRMS (ESI+) *m/z* $[M+Na]^+$ 337.159 calcd. $C_{23}H_{22}NaO^+$ 337.157

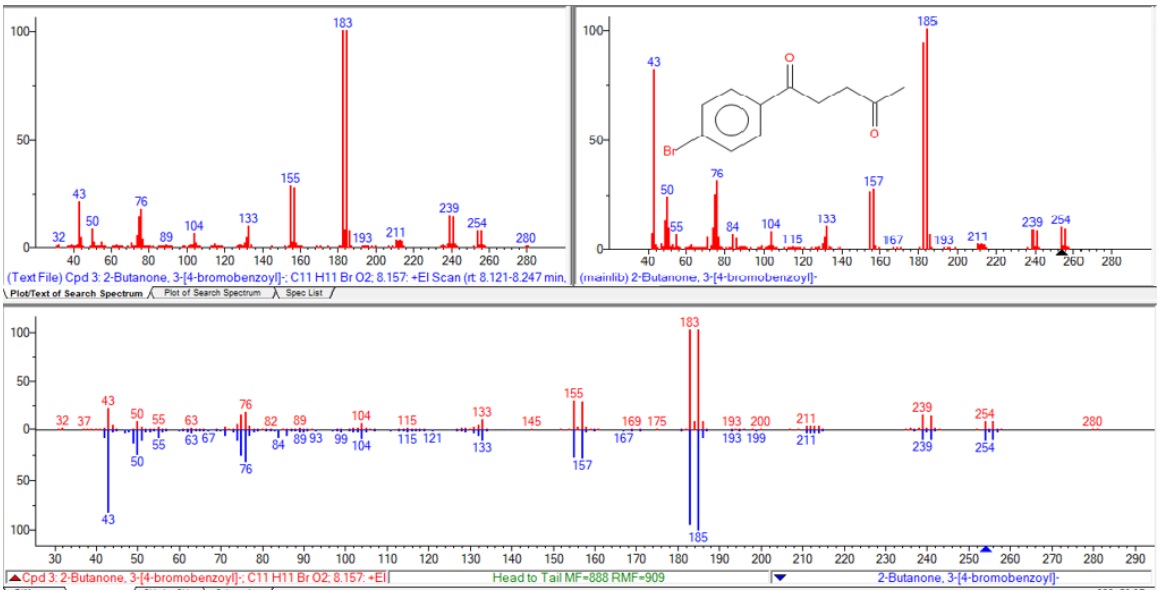
4. GC-MS analyses

4.1. Analyses of the reaction mixture

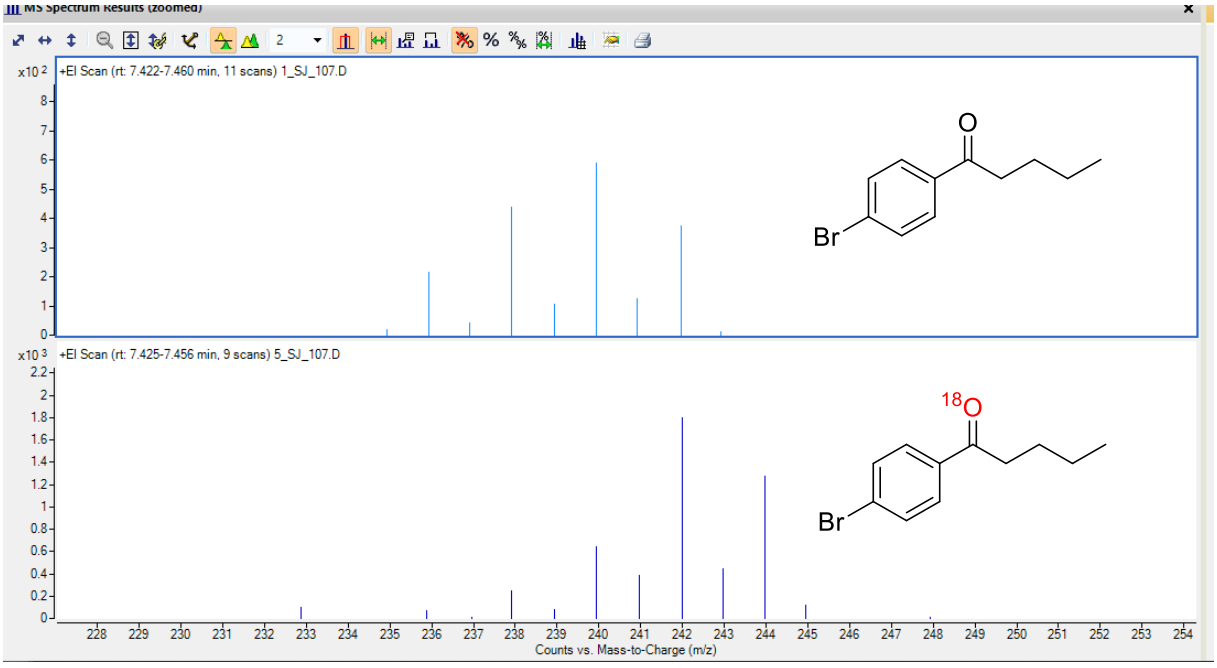








4.2. Analyses of reaction with $H_2{}^{18}O$



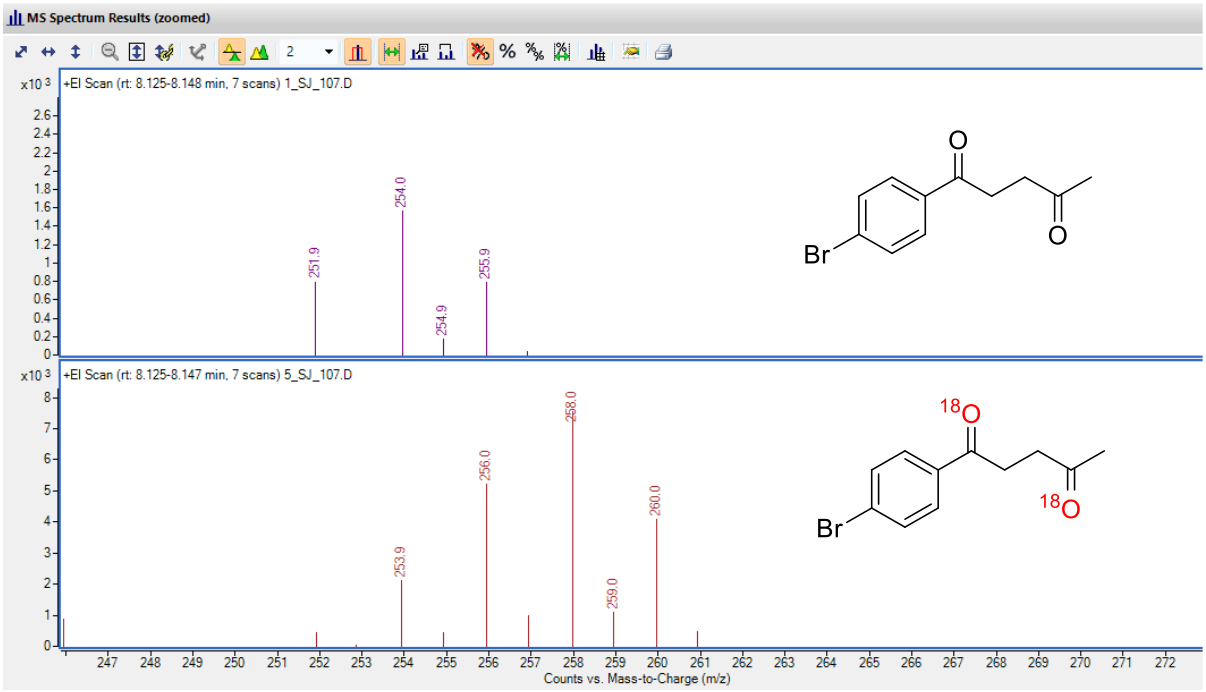
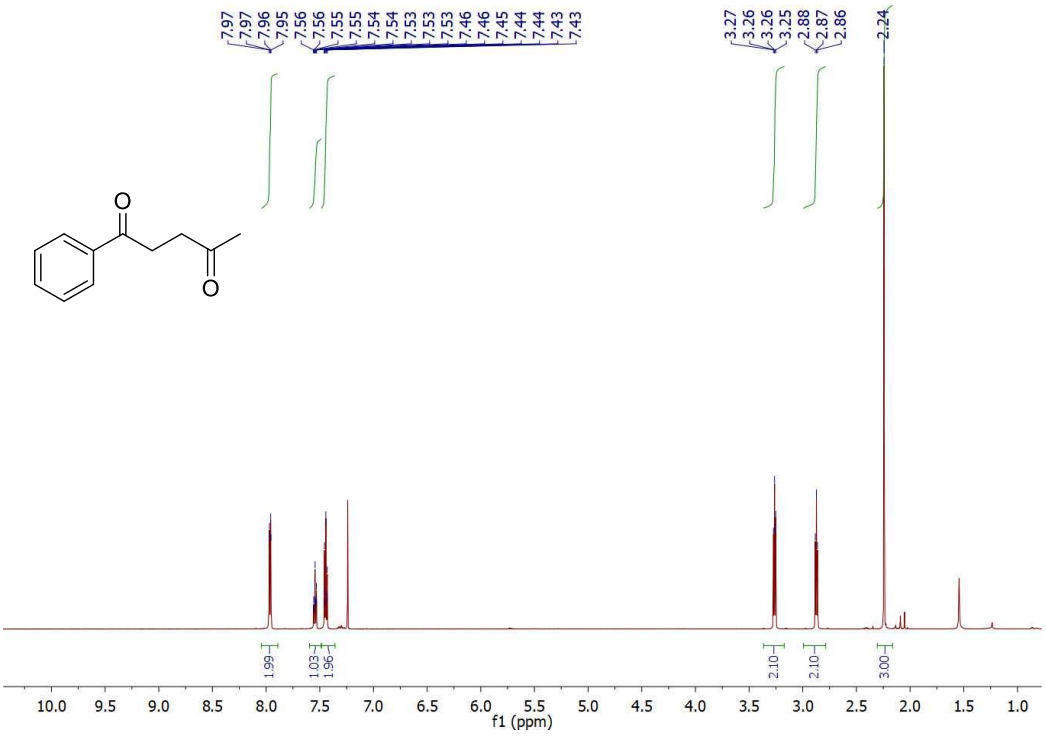
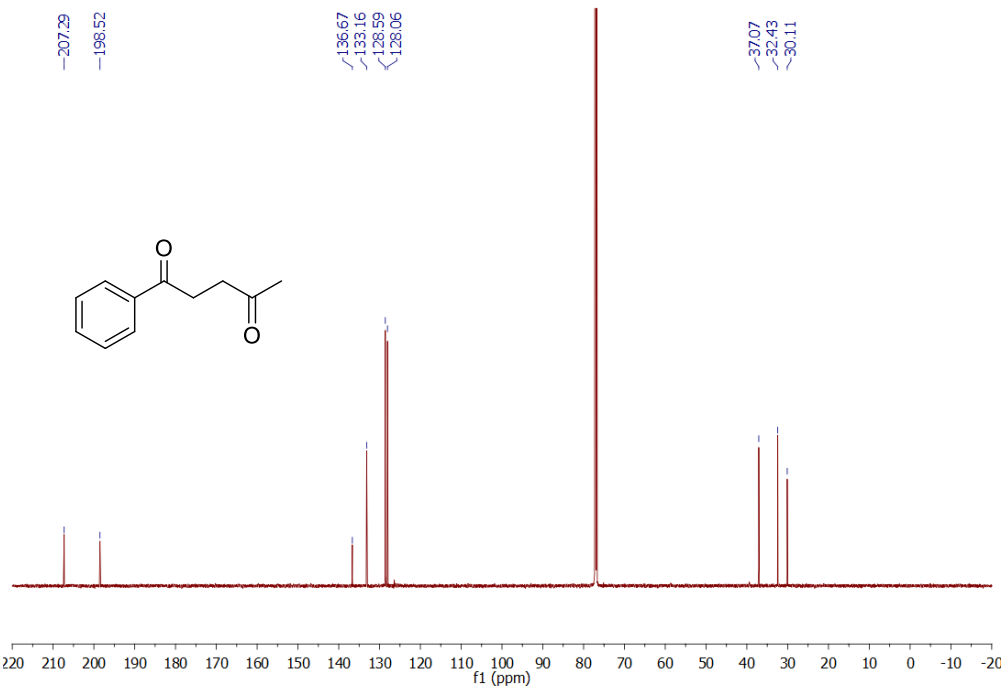
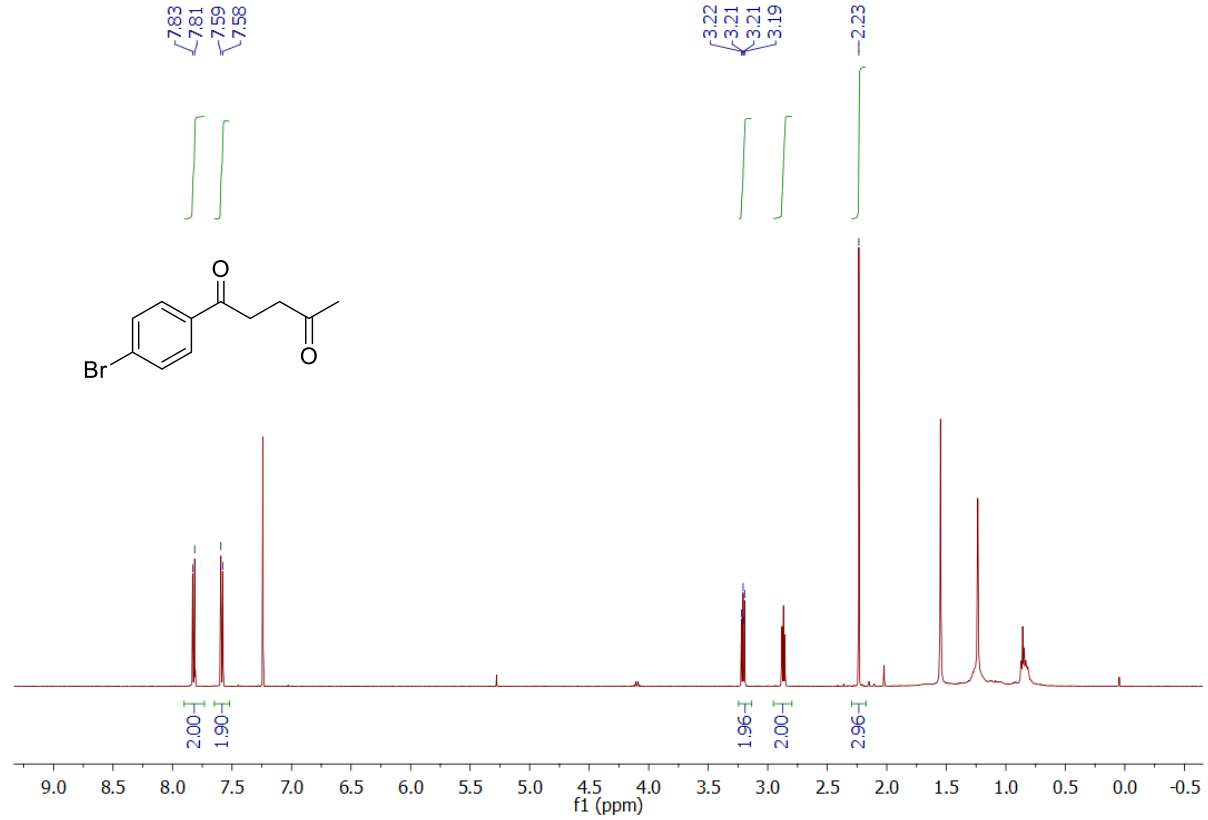


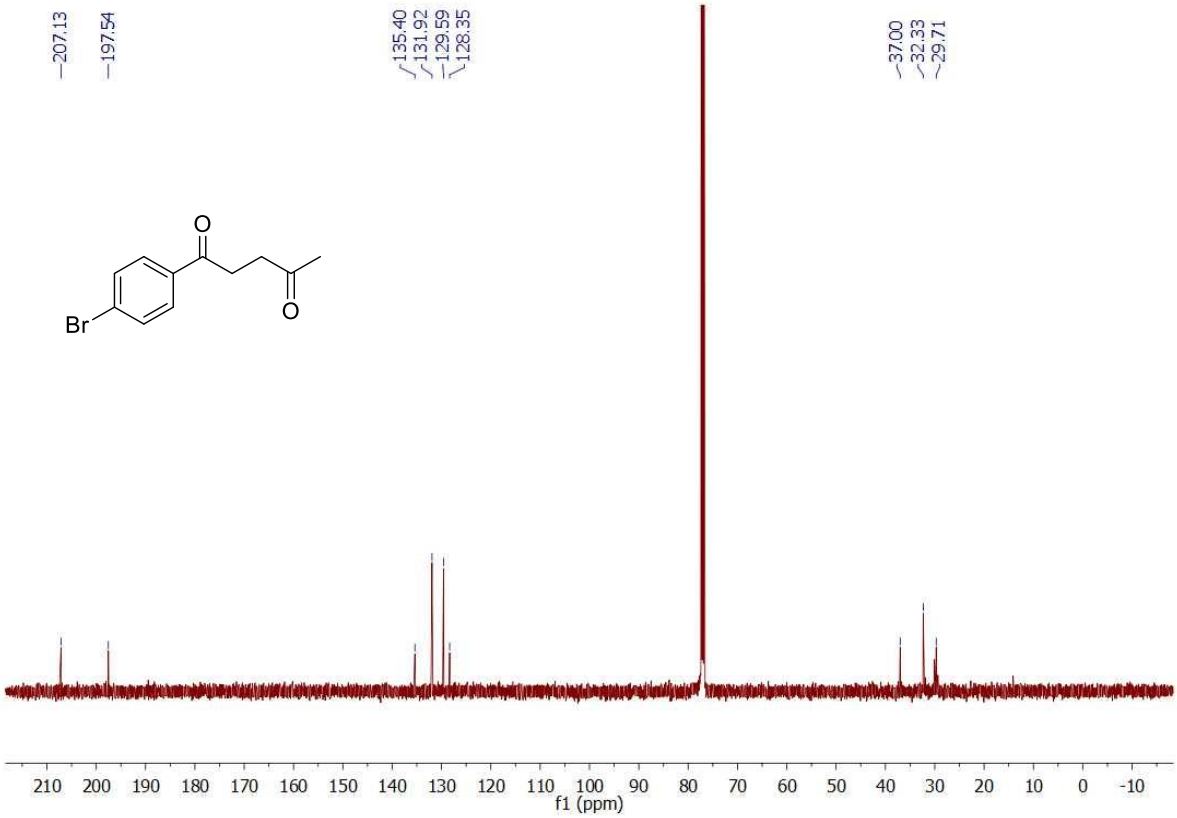
Figure S3. GC-MS after reaction with $H_2{}^{18}O$.

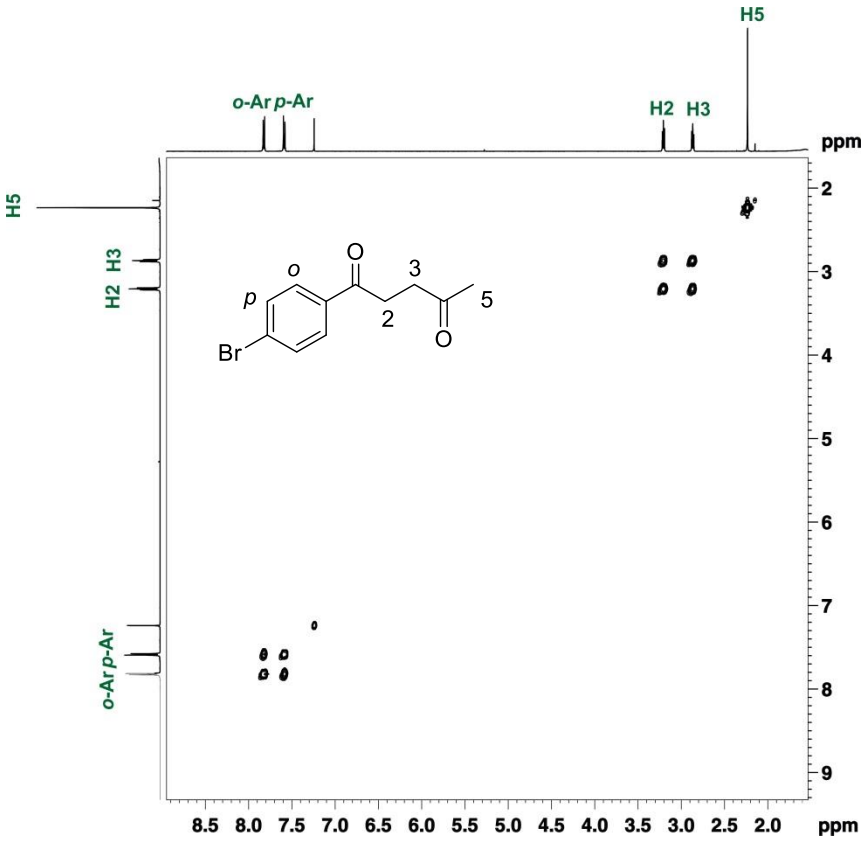
5. **NMR spectra**



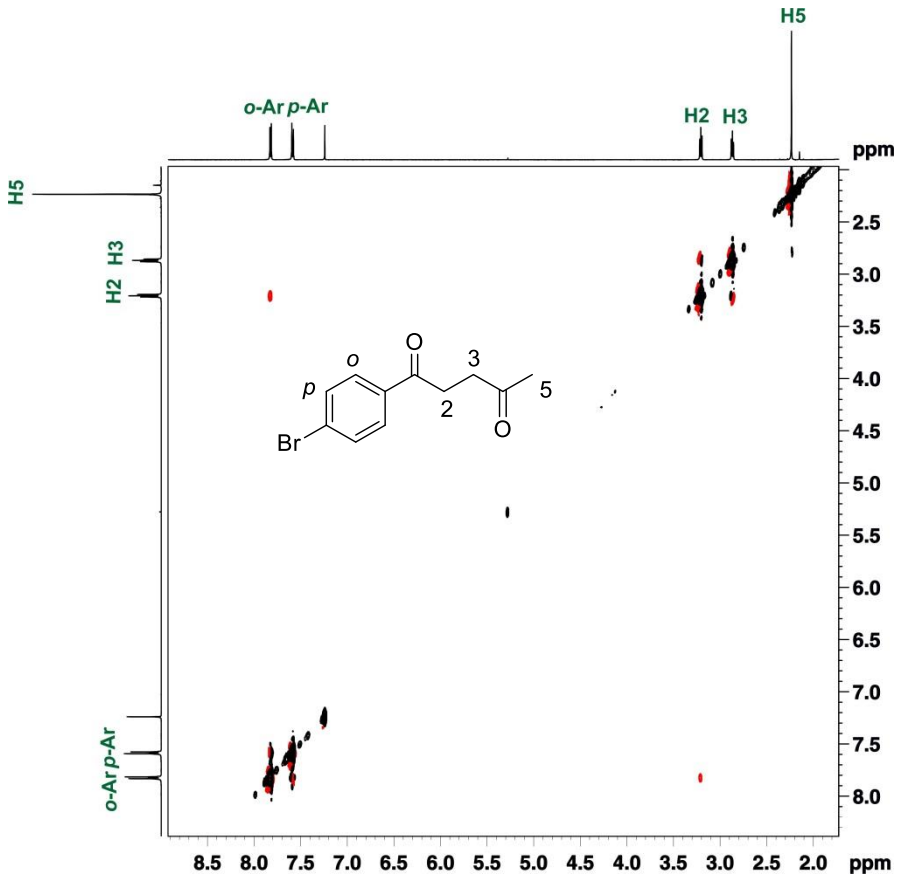

207.29
198.52
136.67
133.16
128.59
128.06
37.07
32.43
30.11
O
O
f1 (ppm)


7.83
7.81
7.59
7.58
3.22
3.21
3.21
3.19
2.23
O
O
Br
2.00
1.90
1.96
2.00
2.96
f1 (ppm)

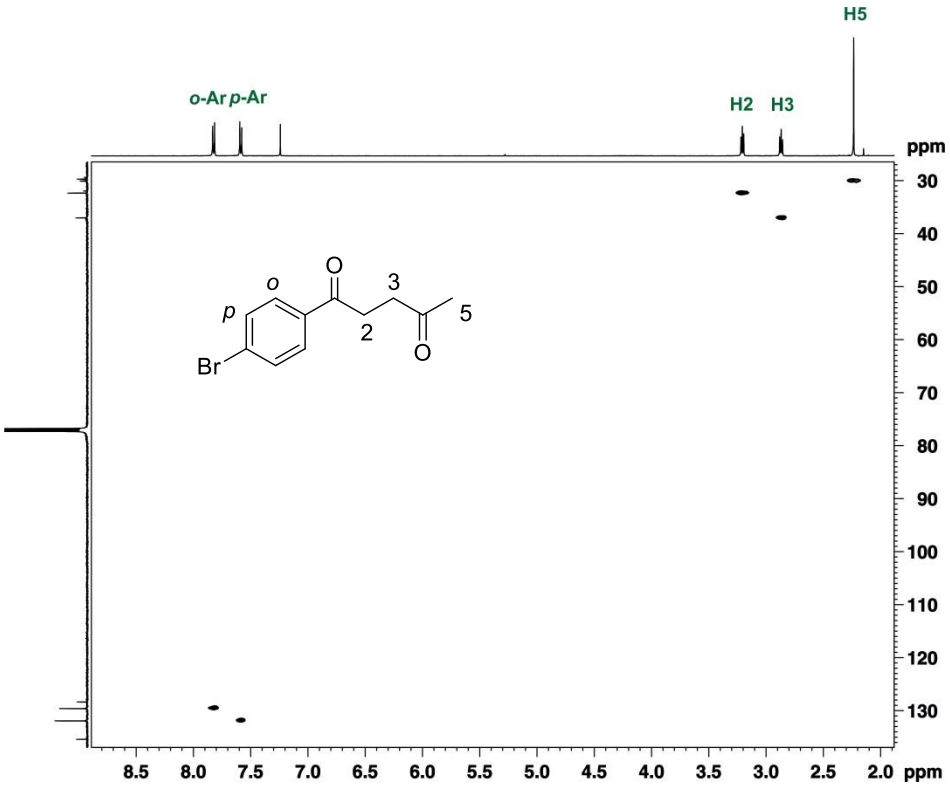




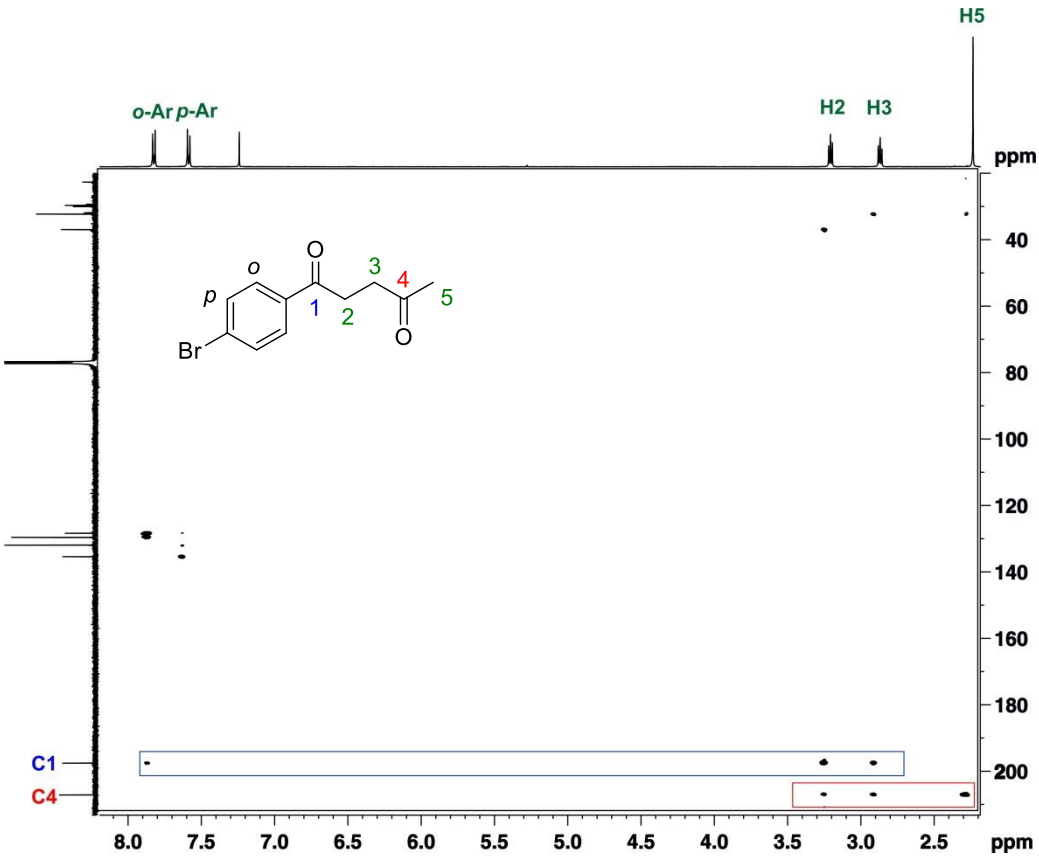
Part of COSY spectrum of 2b.



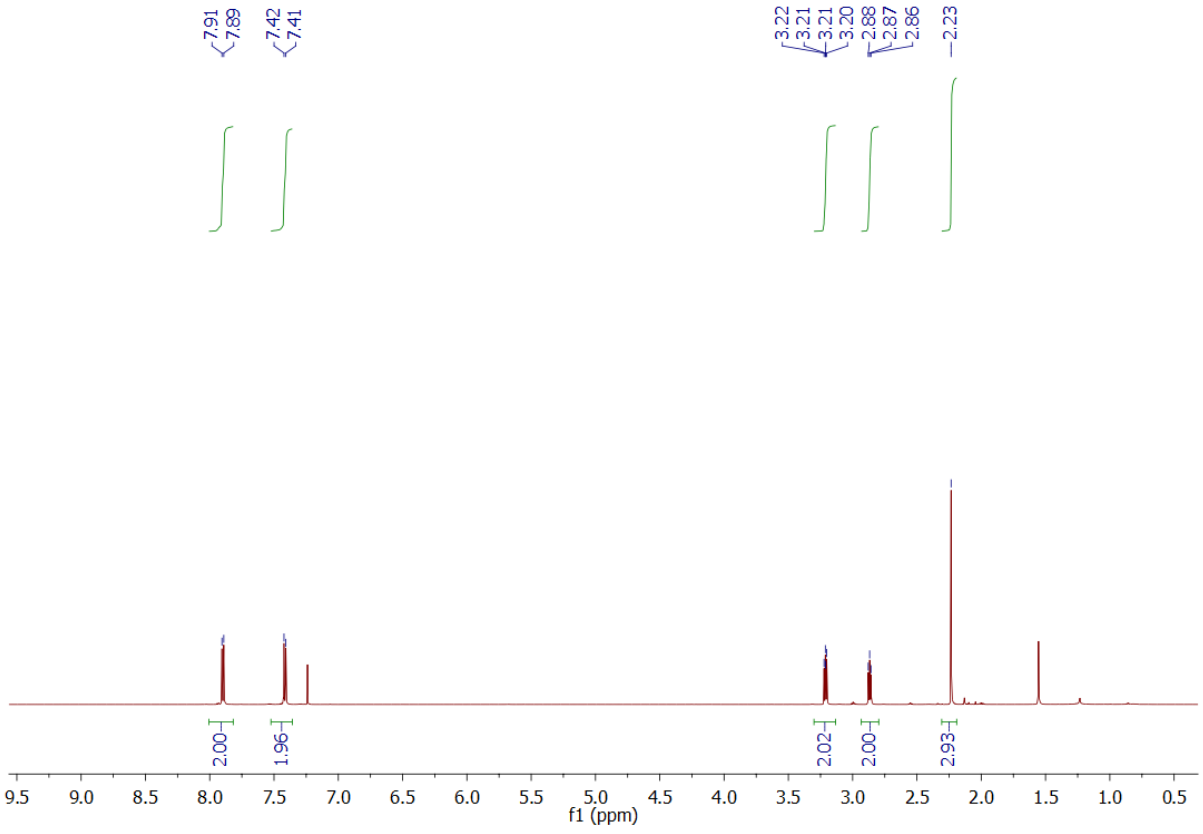
Part of NOESY spectrum of 2b.

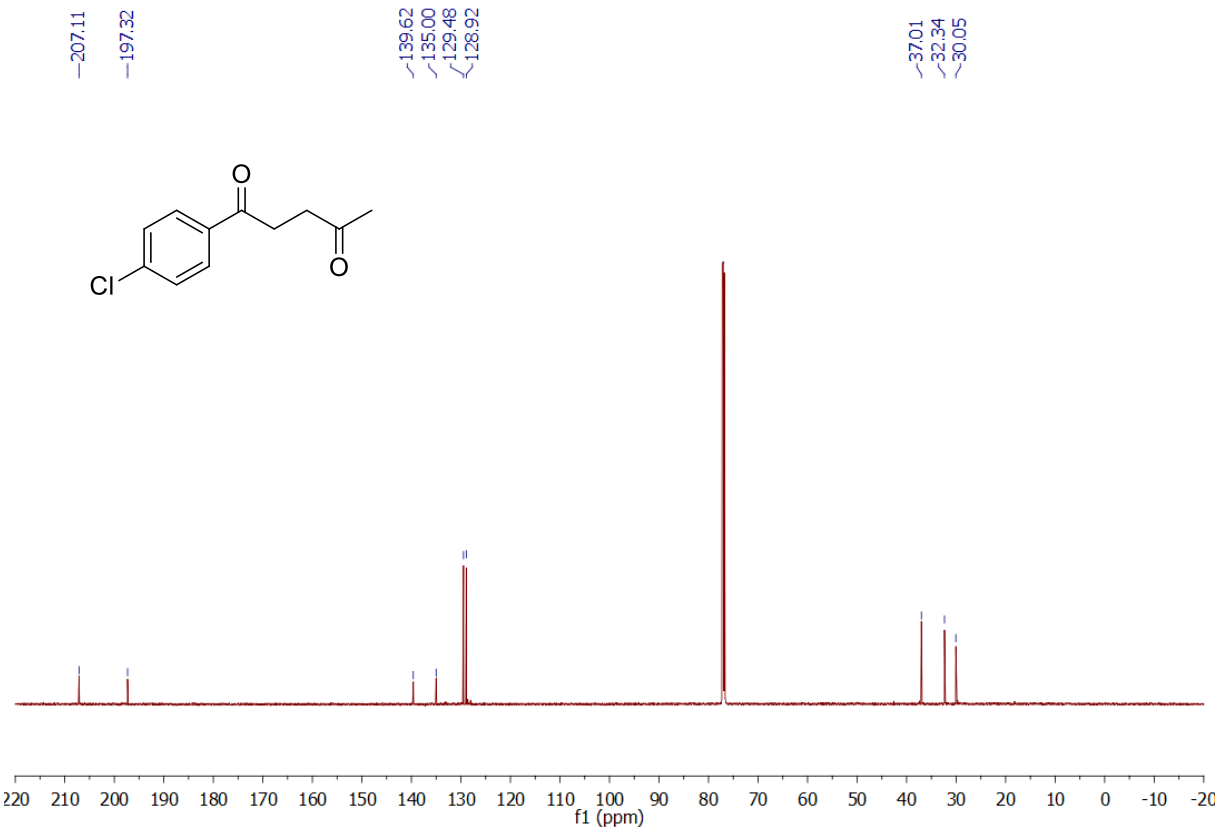


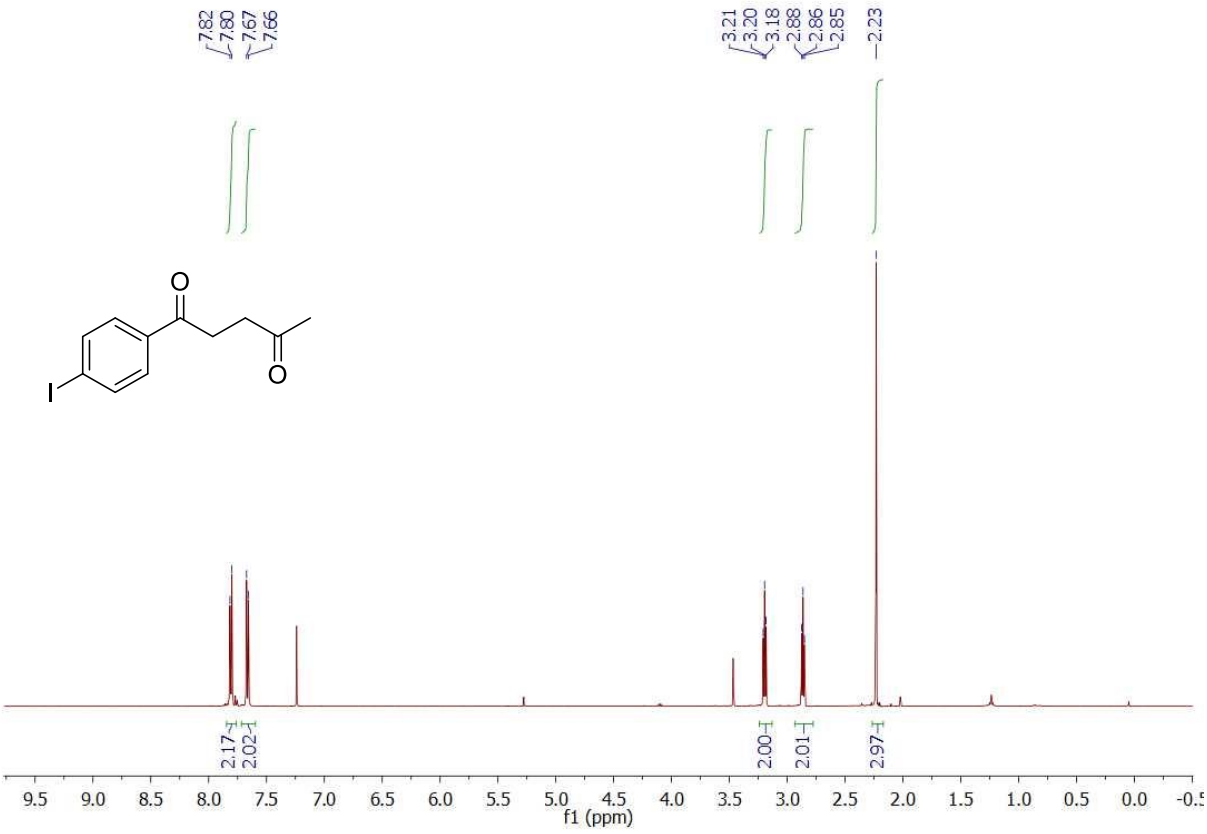
Part of HSQC spectrum of 2b.

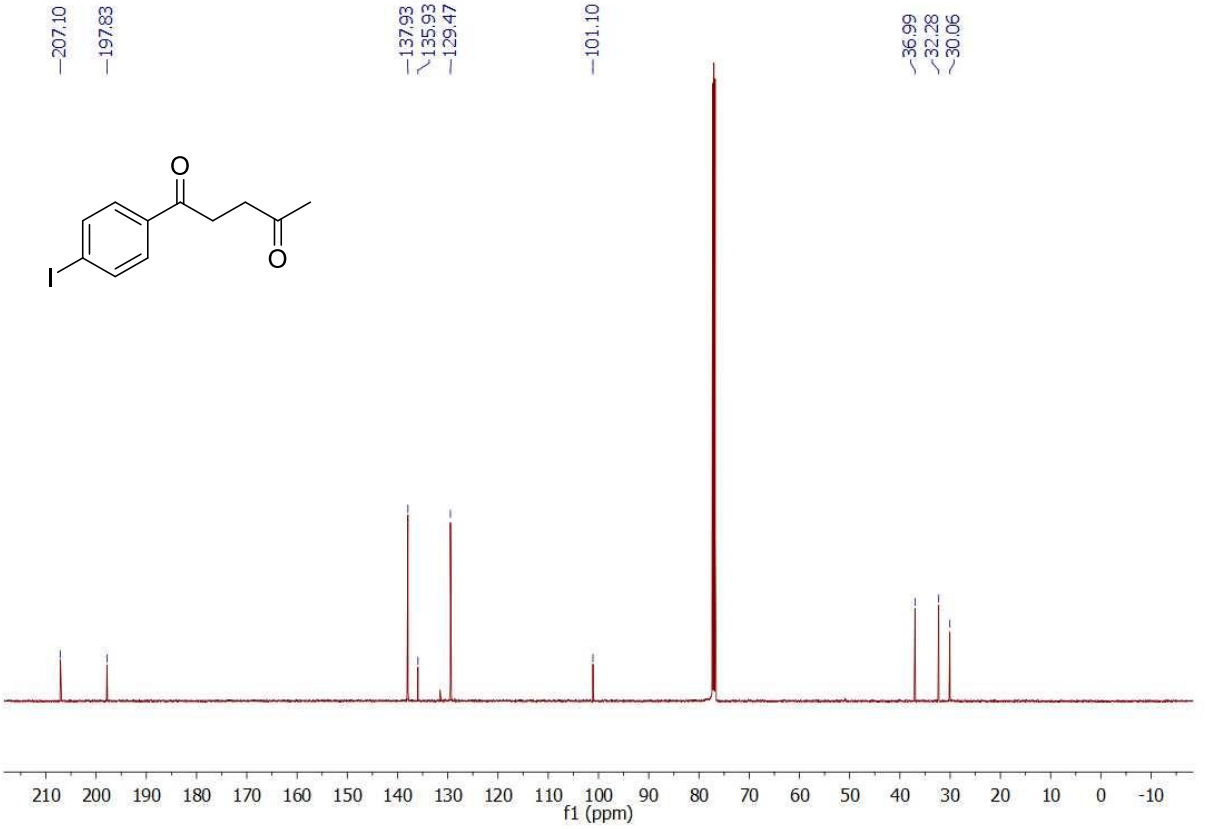


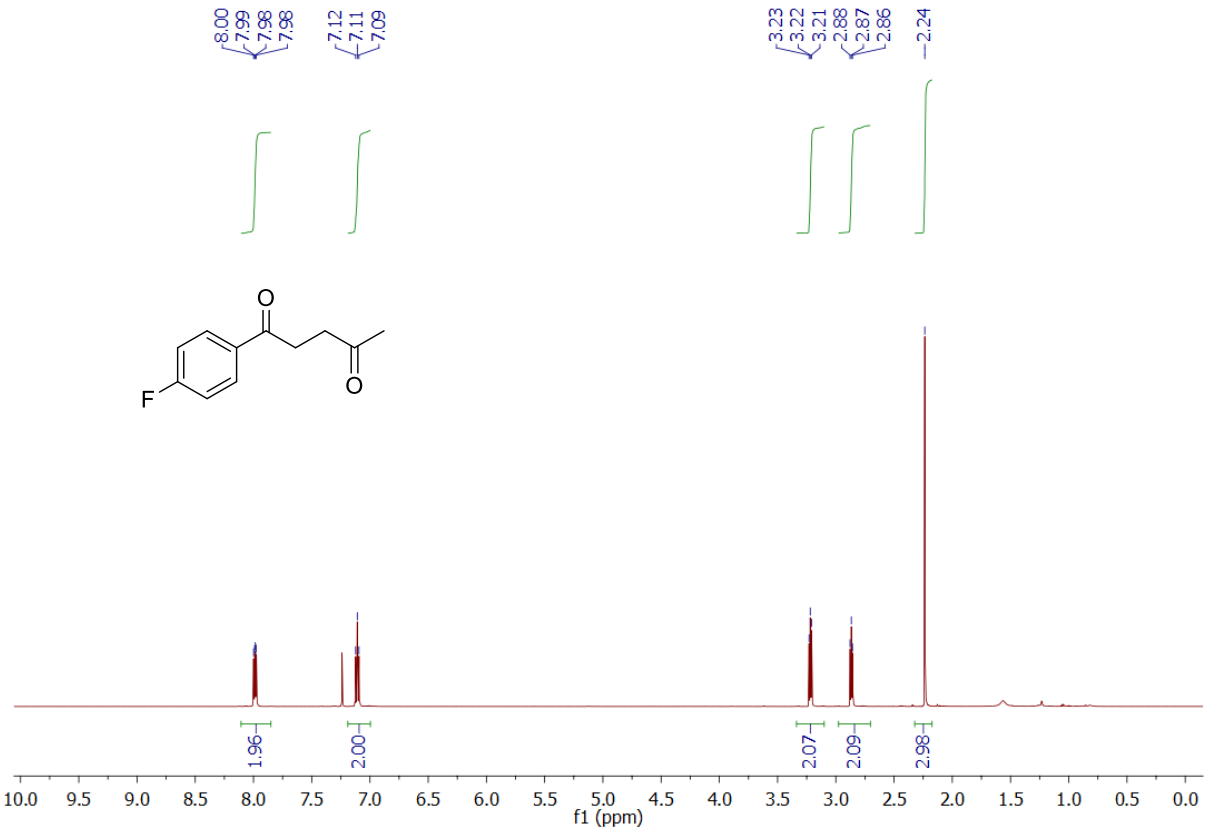
Part of HMBC spectrum of 2b.

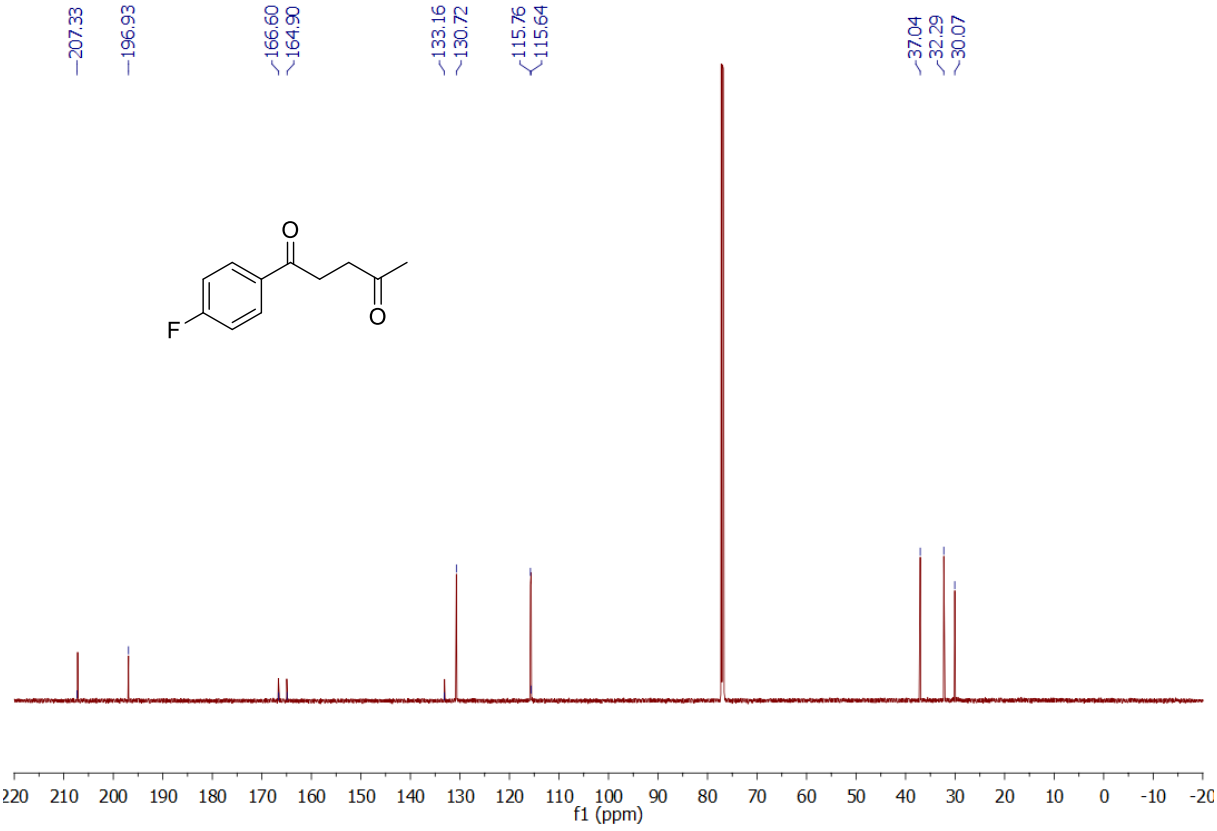


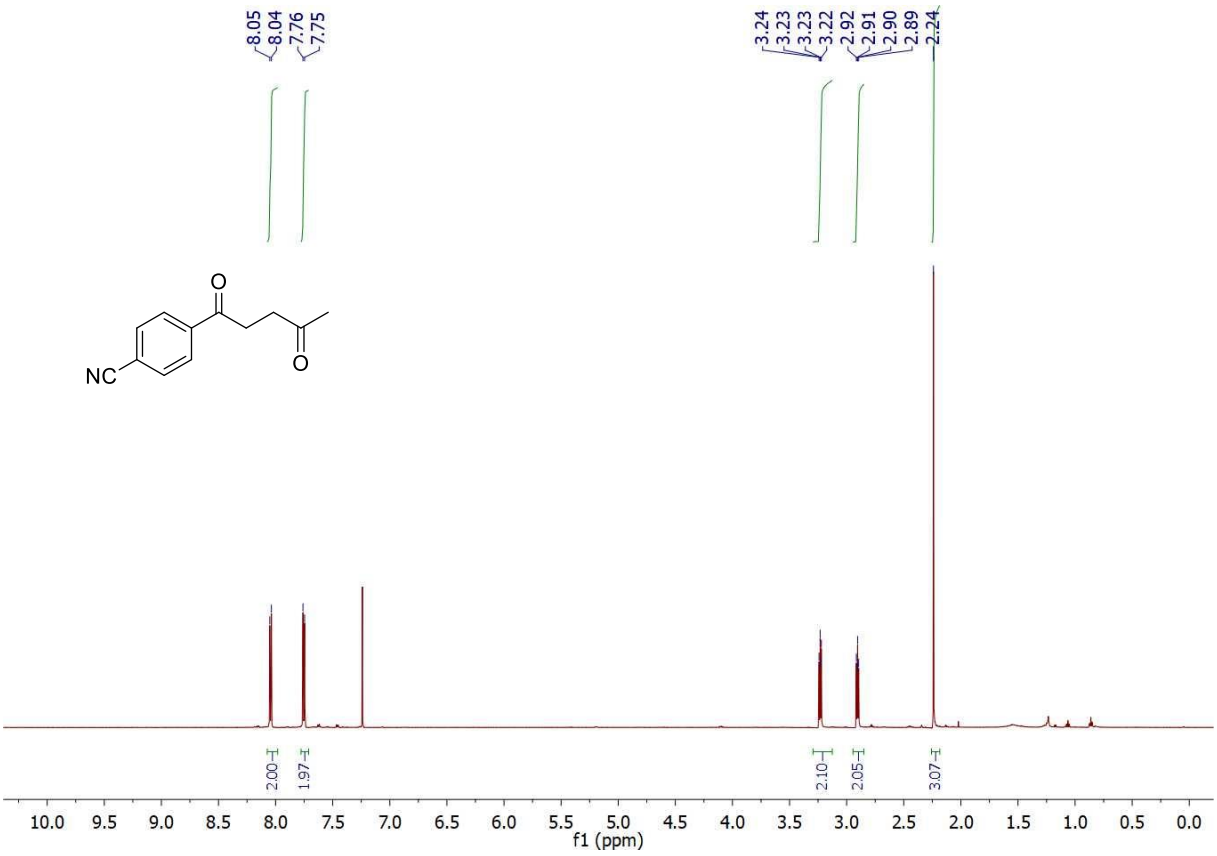

207.11
197.32
139.62
135.00
129.48
128.92
37.01
32.34
30.05
O
O
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

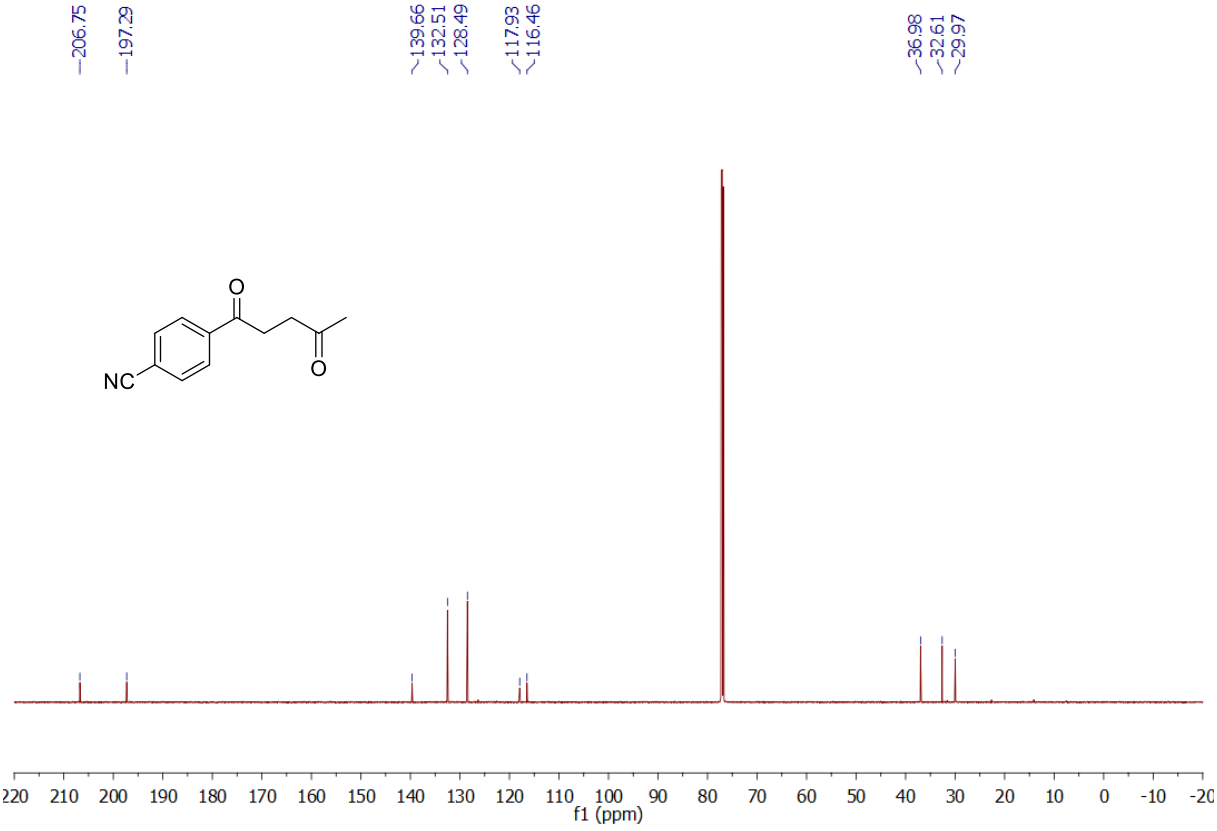

7.82
7.80
7.67
7.66
3.21
3.20
3.18
2.88
2.86
2.85
2.23
O
O
I
2.17
2.02
2.00
2.01
2.97
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

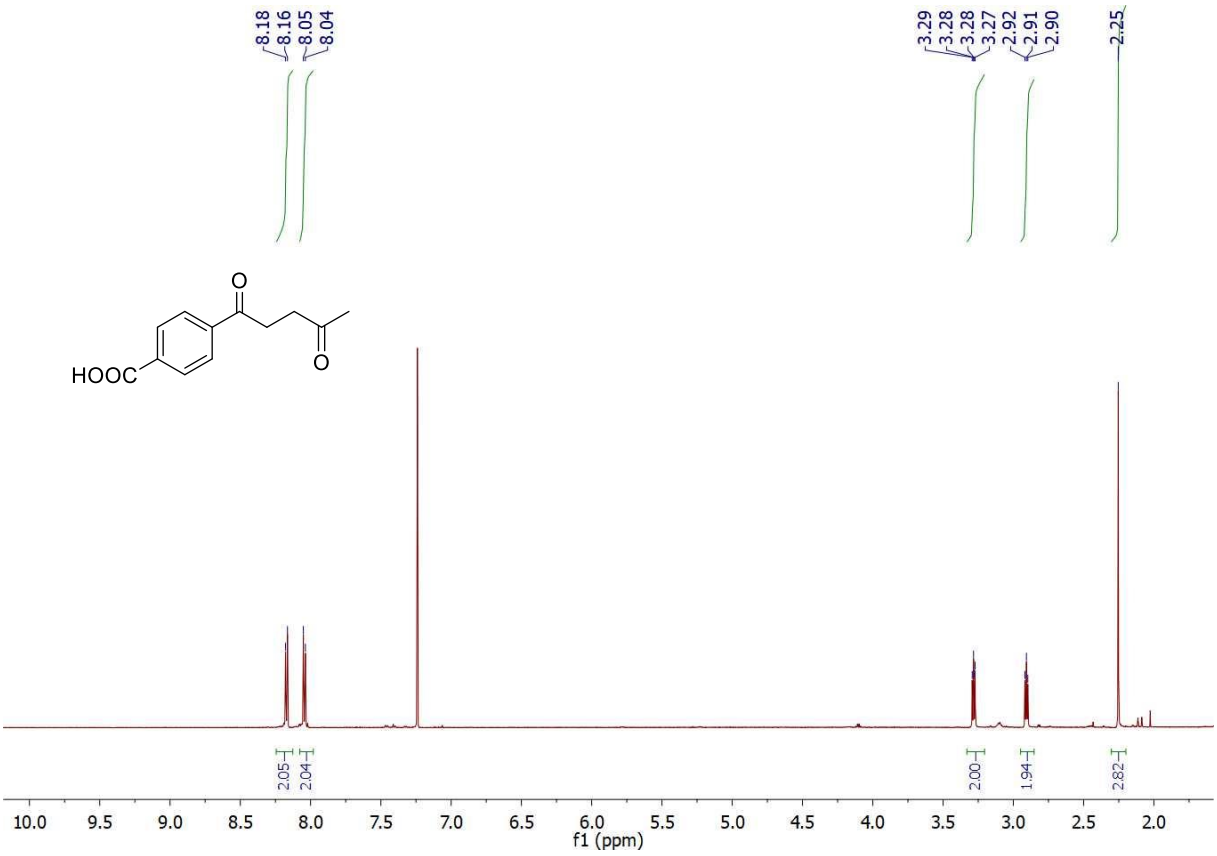

207.10
197.83
137.93
135.93
129.47
101.10
36.99
32.28
30.06
O
O
I
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

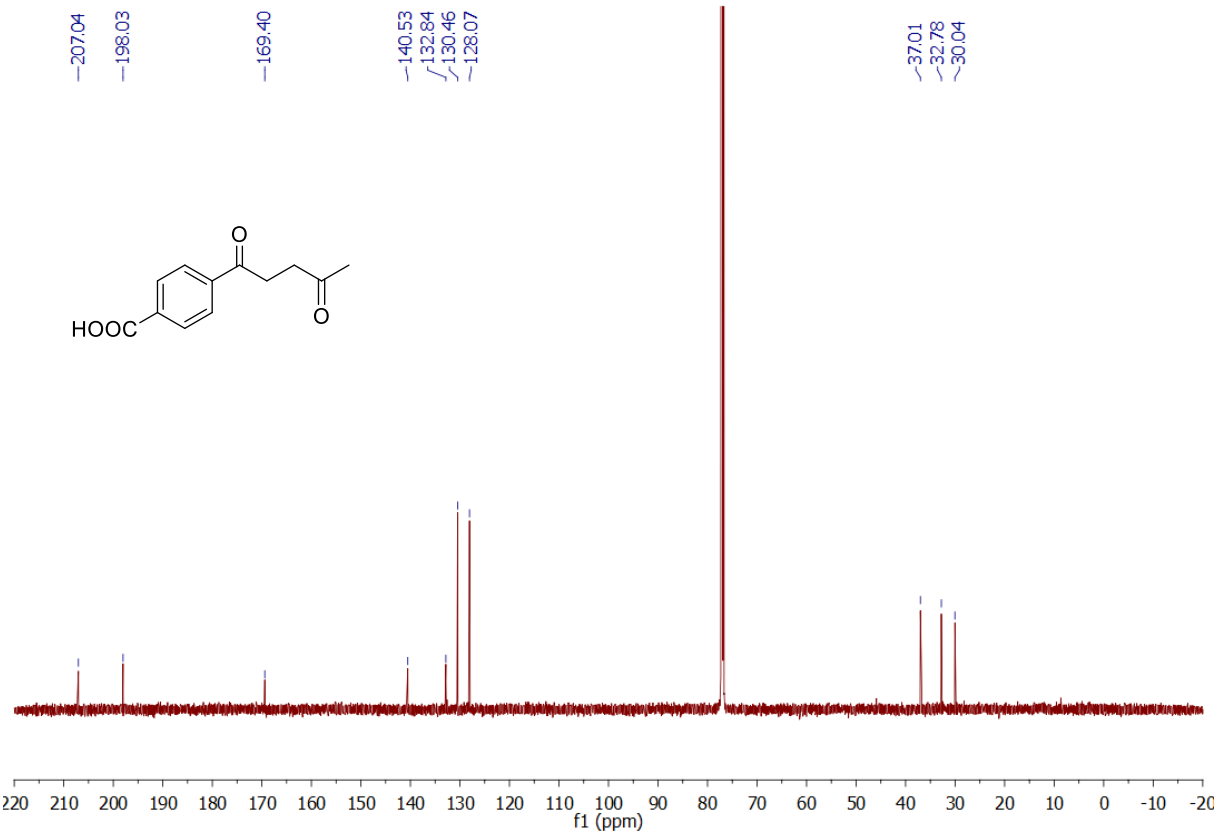

8.00
7.99
7.98
7.98
7.12
7.11
7.09
3.23
3.22
3.21
2.88
2.87
2.86
2.24
O
O
F
1.96
2.00
2.07
2.09
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

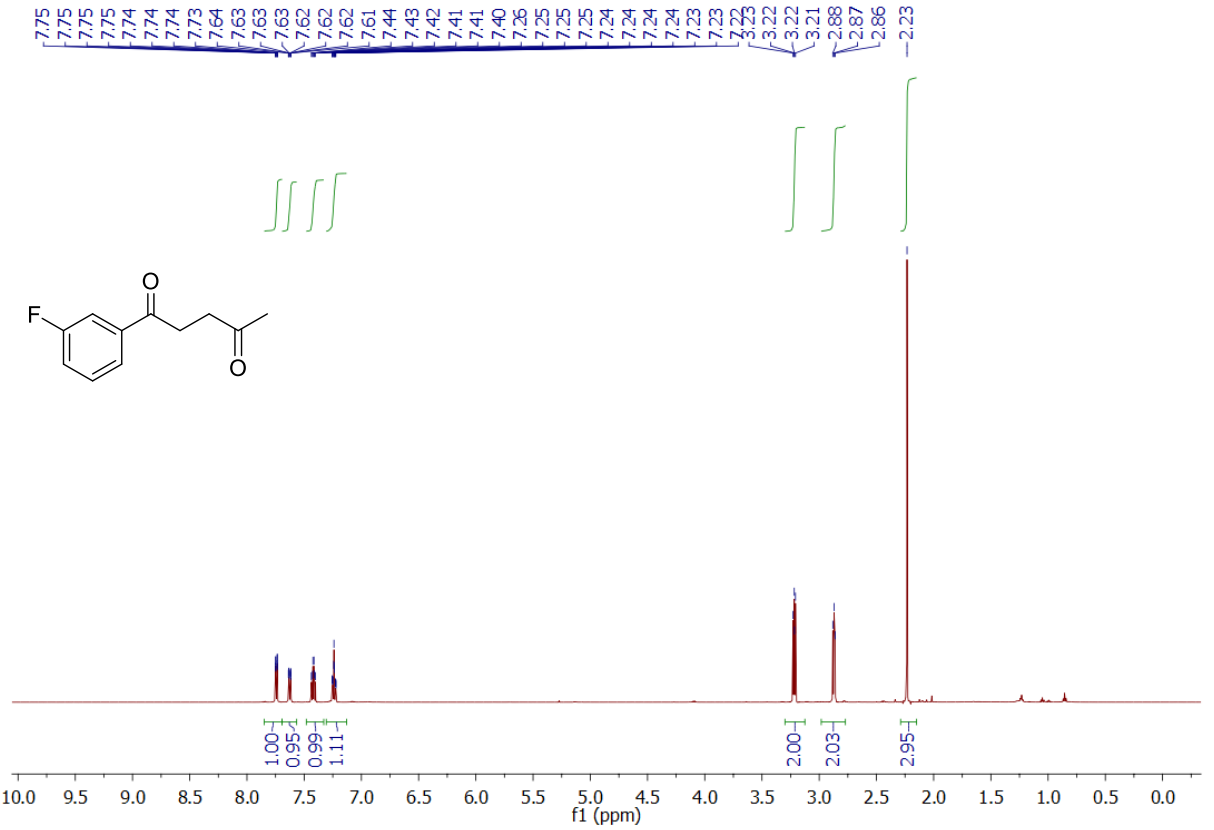

207.33
196.93
166.60
164.90
133.16
130.72
115.76
115.64
37.04
32.29
30.07
O
O
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

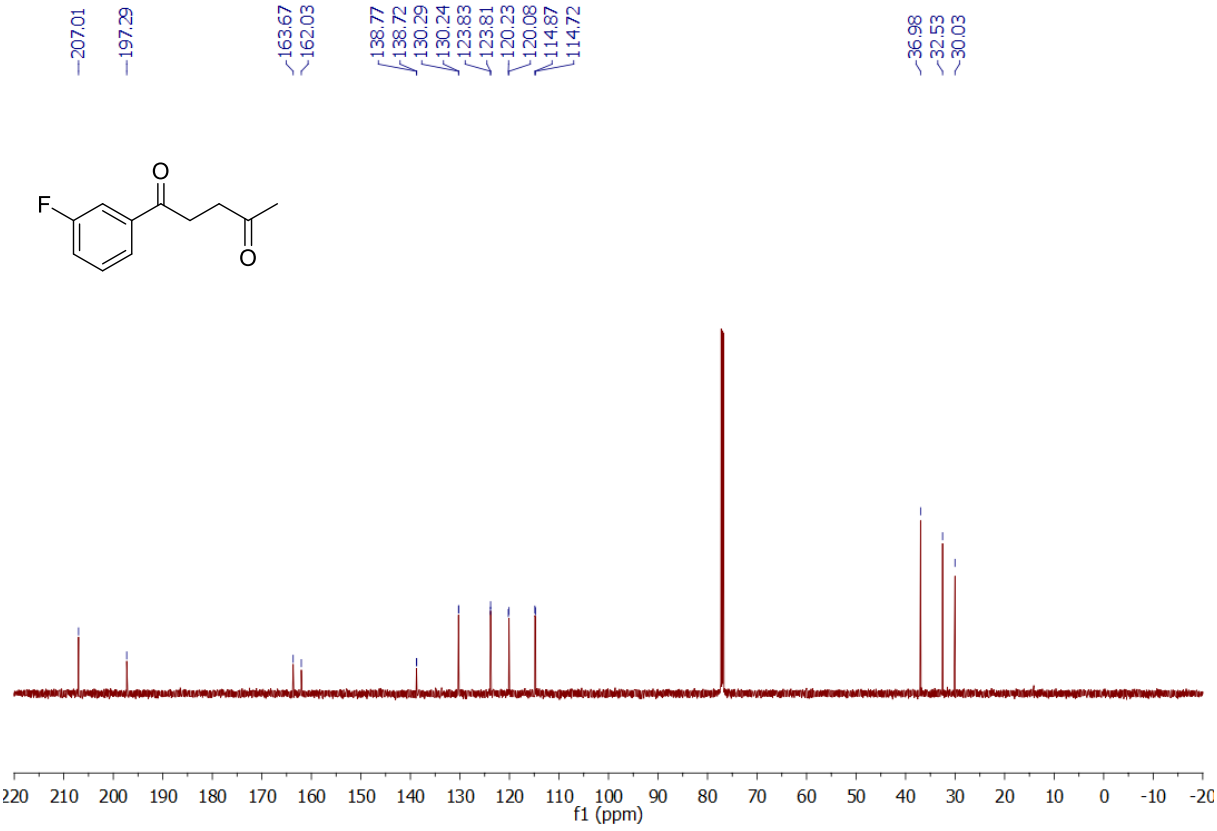

8.05
8.04
7.76
7.75
3.24
3.23
3.23
3.22
2.92
2.91
2.90
2.89
2.24
O
O
NC
2.00
1.97
2.10
2.05
3.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

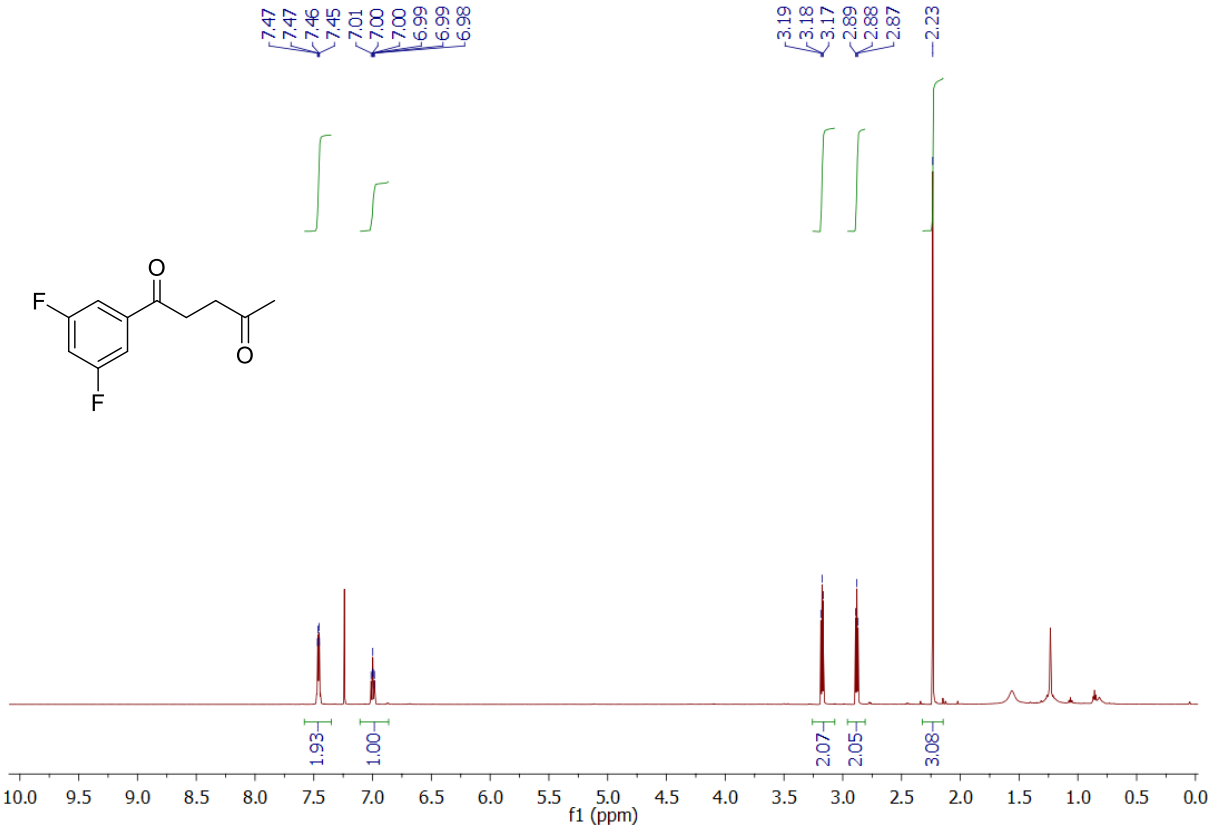

206.75
197.29
139.66
132.51
128.49
117.93
116.46
36.98
32.61
29.97
O
O
NC
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


8.18
8.16
8.05
8.04
3.29
3.28
3.28
3.27
2.92
2.91
2.90
2.25
HOOC
O
O
2.05
2.04
2.00
1.94
2.82
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


207.04
198.03
169.40
140.53
132.84
130.46
128.07
37.01
32.78
30.04
HOOC
O
O
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


7.75 7.75 7.75 7.75 7.74 7.74 7.73 7.64 7.63 7.63 7.63 7.62 7.62 7.62 7.61 7.44 7.43 7.42 7.41 7.41 7.40 7.26 7.25 7.25 7.25 7.24 7.24 7.24 7.24 7.23 7.23 7.22 3.23 3.22 3.22 3.21 2.88 2.87 2.86 2.23
F
O
O
1.00 0.95 0.99 1.11 2.00 2.03 2.95
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


207.01 197.29 163.67 162.03 138.77 138.72 130.29 130.24 123.83 123.81 120.23 120.08 114.87 114.72 36.98 32.53 30.03
F
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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7.47
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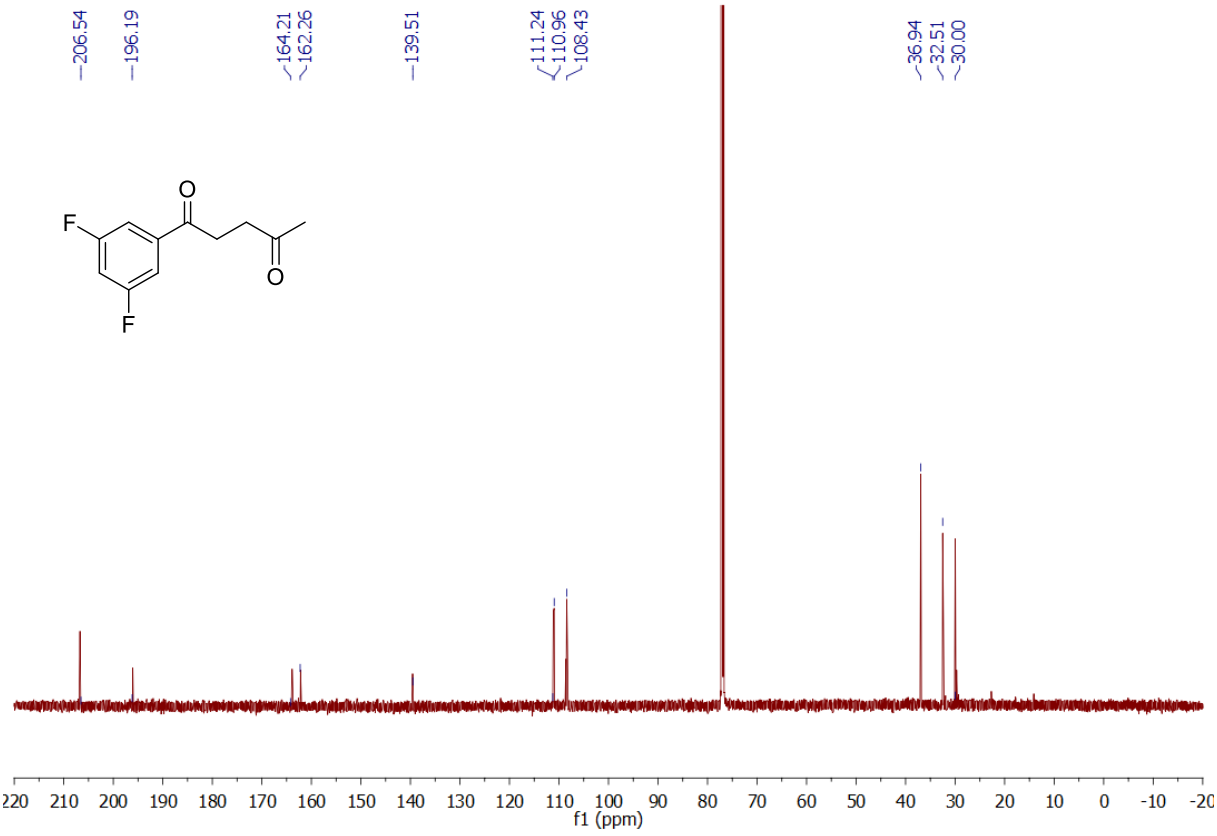
7.45
7.01
7.00
7.00
6.99
6.99
6.98
3.19
3.18
3.17
2.89
2.88
2.87
2.23
F
O
O
F
1.93
1.00
2.07
2.05
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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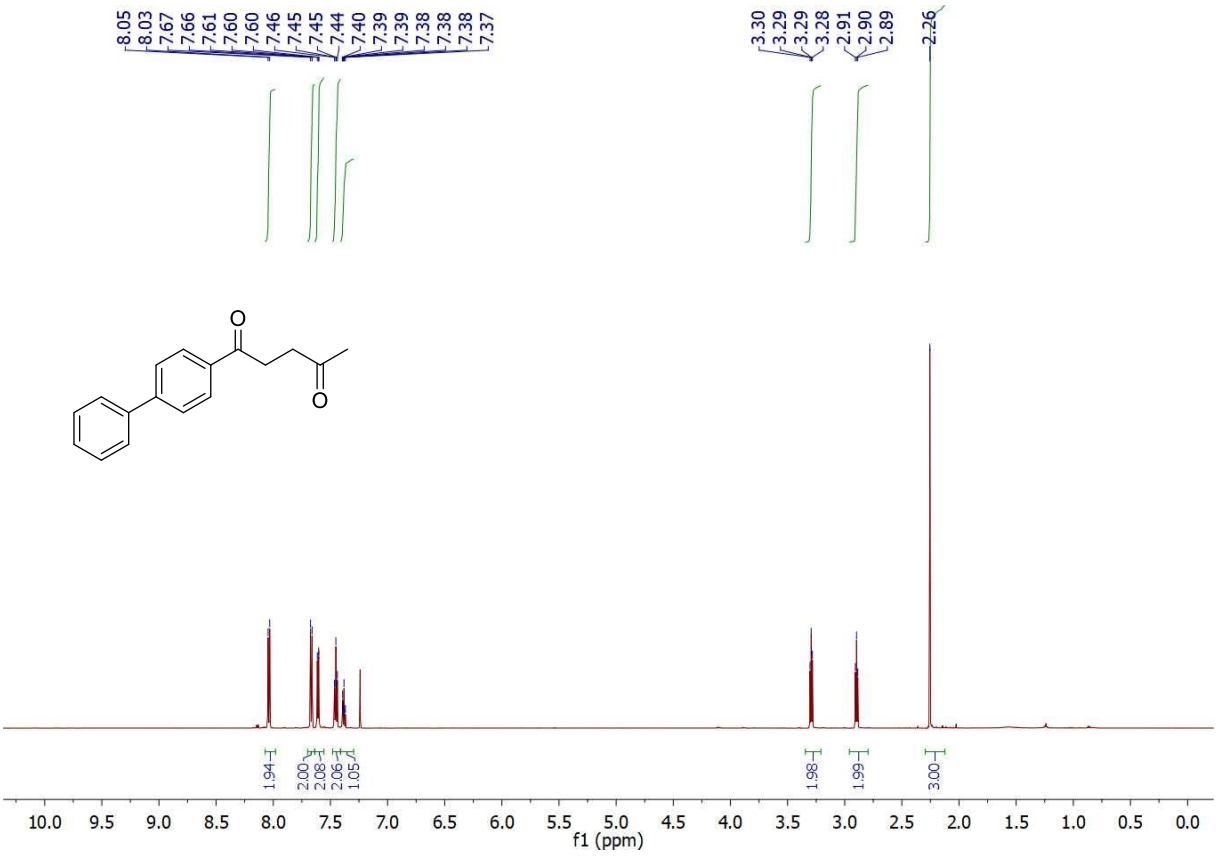
162.26
139.51
111.24
110.96
108.43
36.94
32.51
30.00
F
O
O
F
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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8.03
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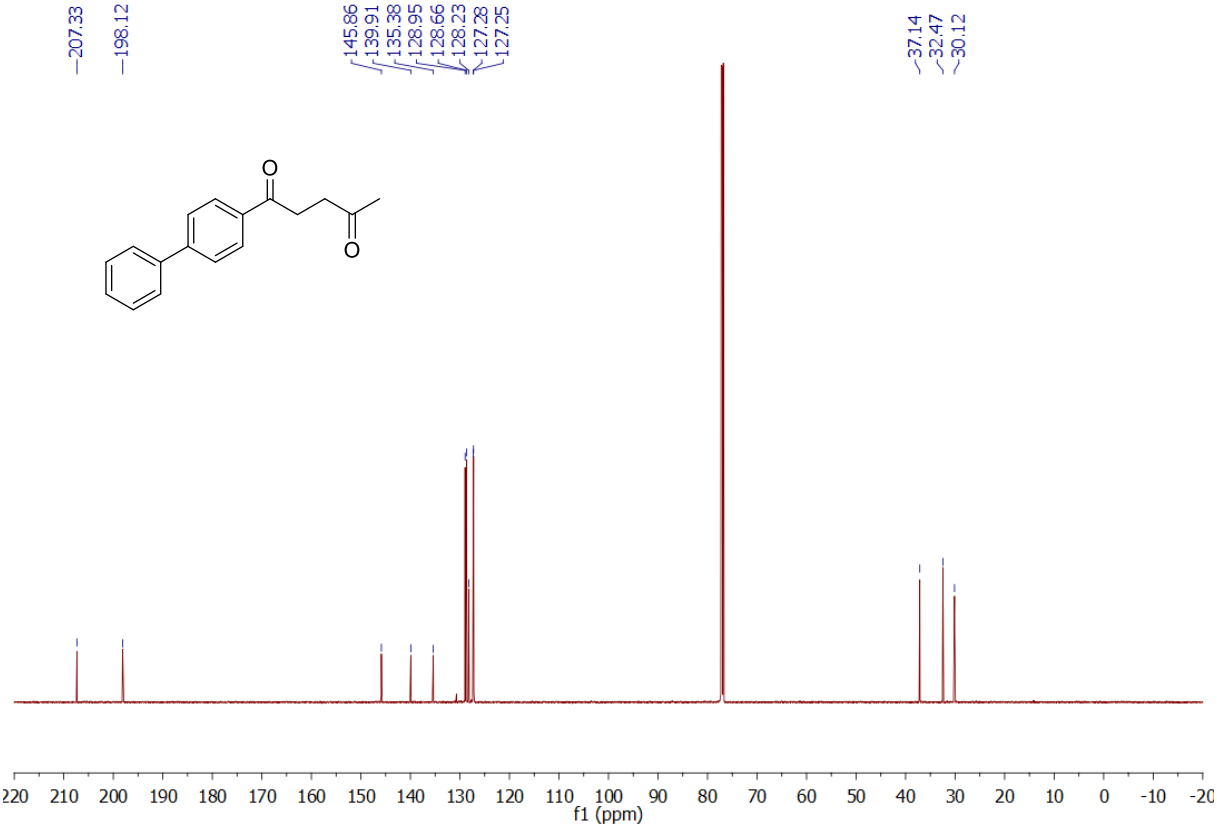
7.66
7.61
7.60
7.60
7.46
7.45
7.45
7.44
7.40
7.39
7.39
7.38
7.38
7.38
7.37
3.30
3.29
3.29
3.28
2.91
2.90
2.89
2.26
O
O
1.94
2.00
2.08
2.06
1.05
1.98
1.99
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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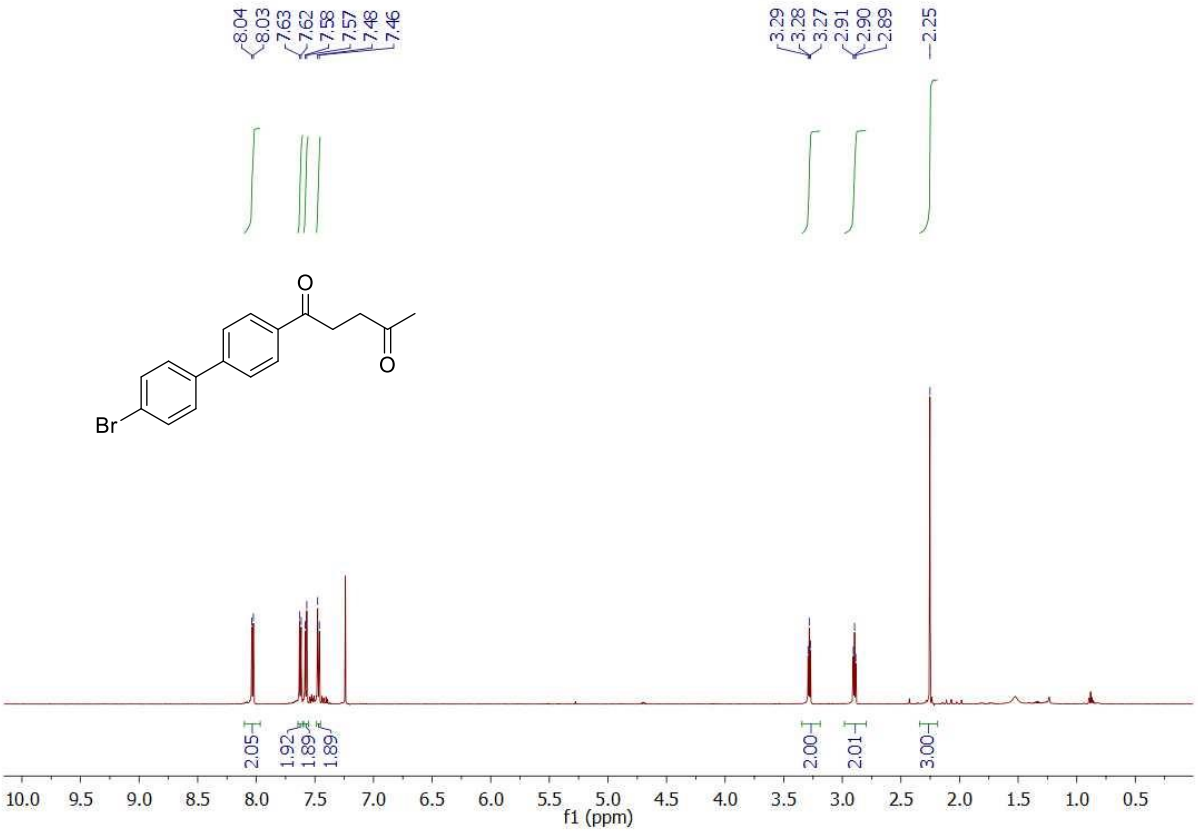
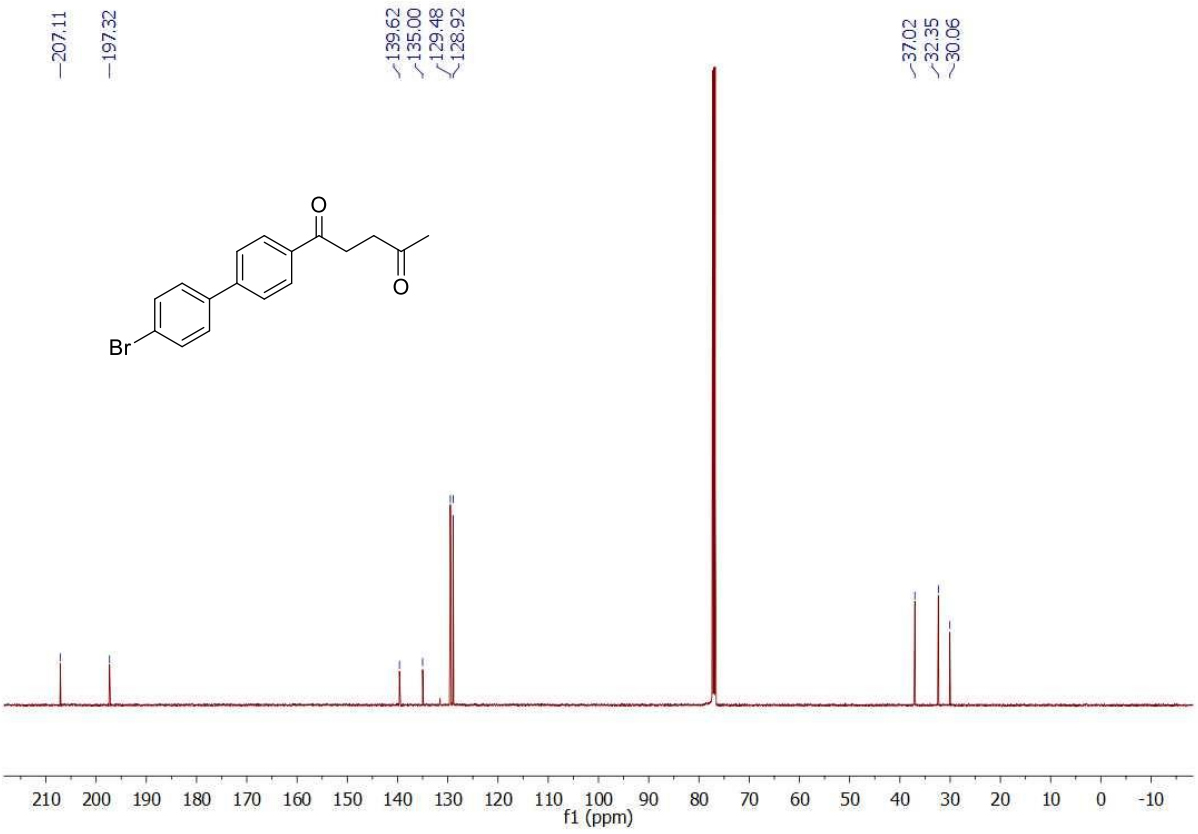
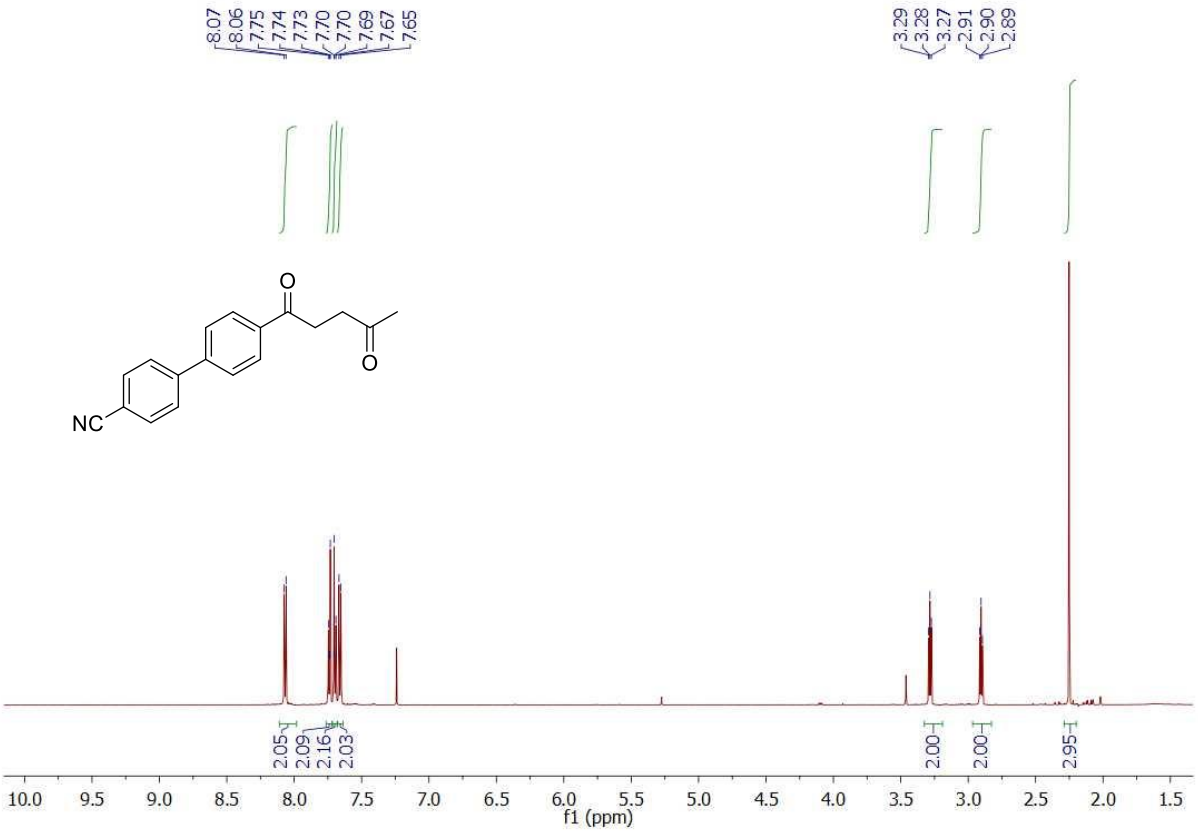
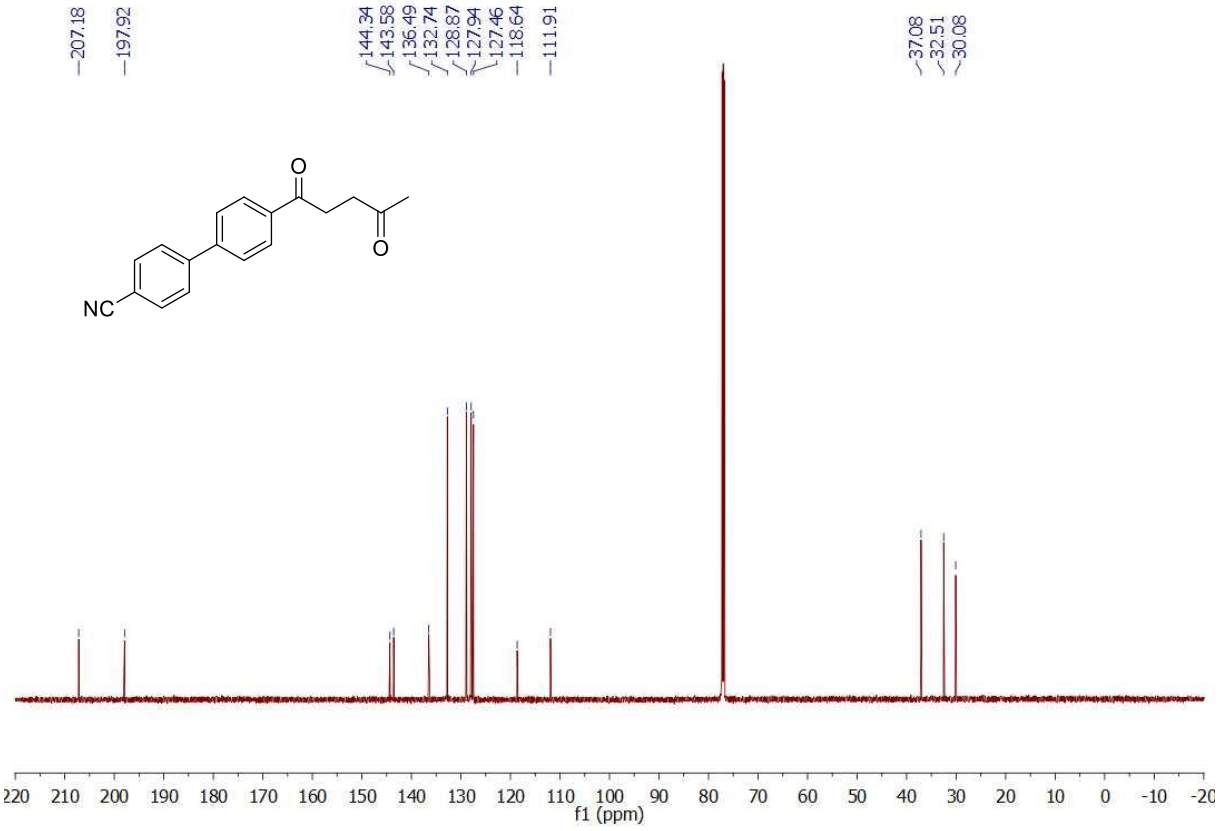
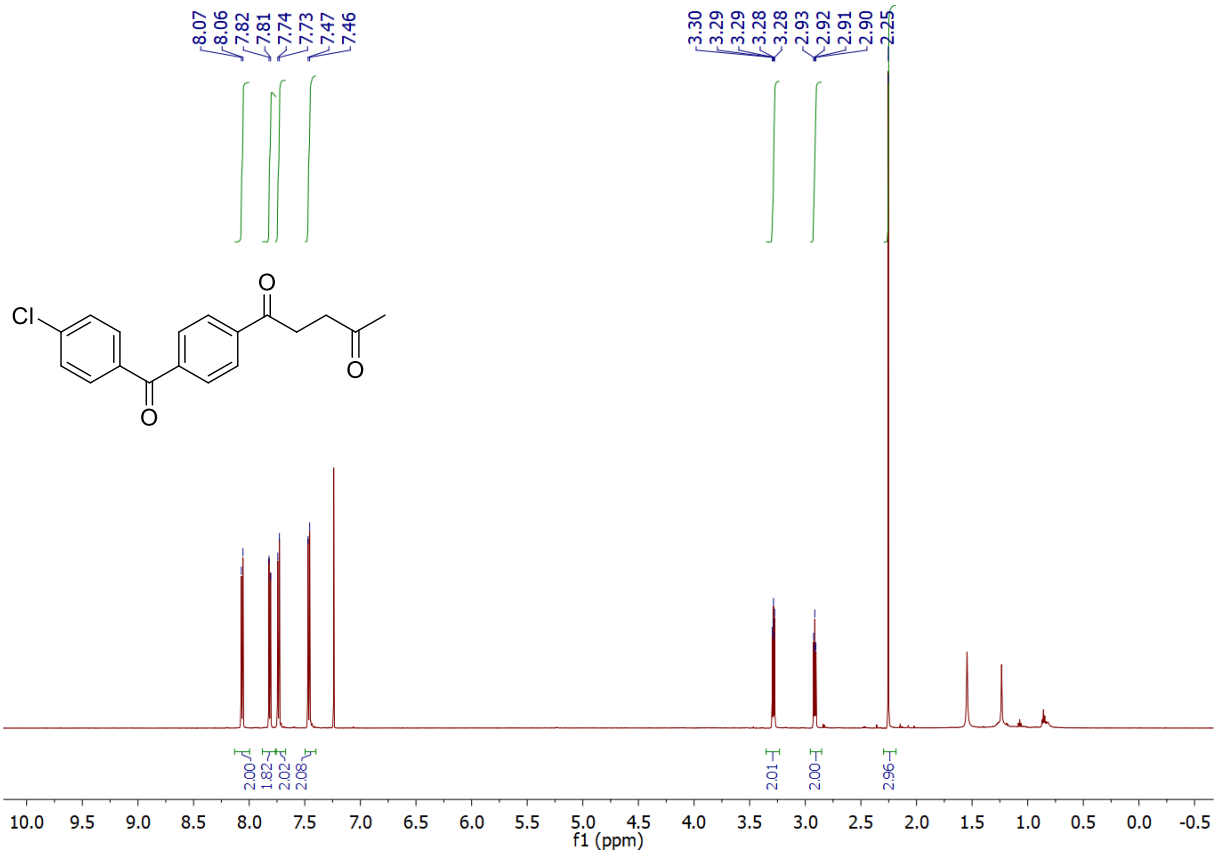
135.38
128.95
128.66
128.23
127.28
127.25
37.14
32.47
30.12
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

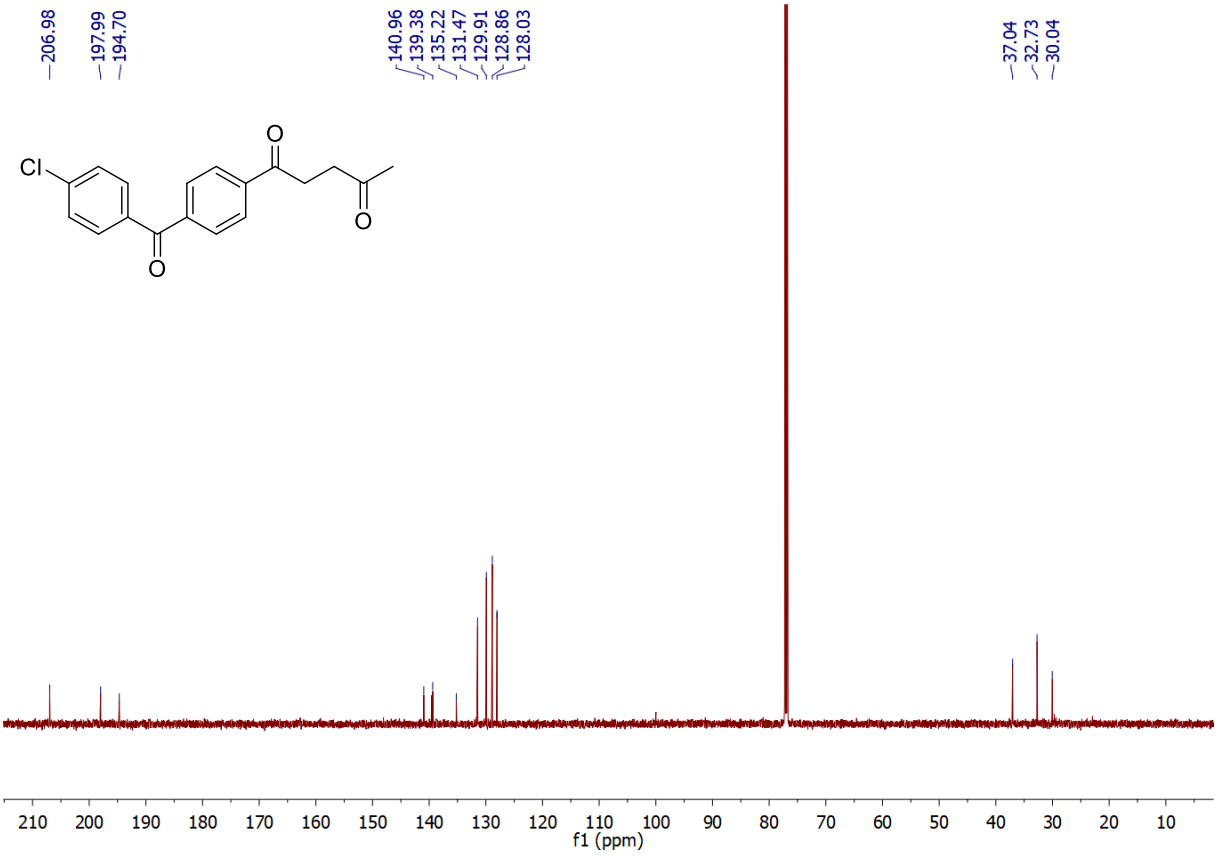

8.04
8.03
7.63
7.62
7.58
7.57
7.48
7.46
3.29
3.28
3.27
2.91
2.90
2.89
2.25
O
O
Br
2.05
1.92
1.89
1.89
2.00
2.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

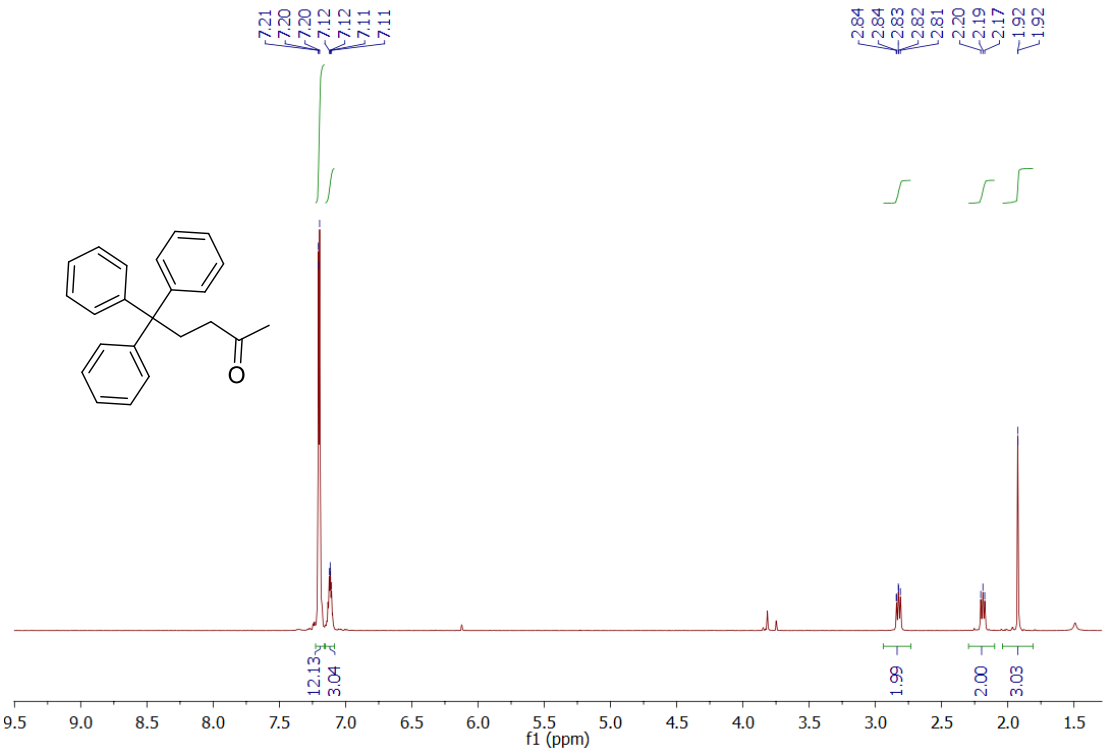

207.11
197.32
139.62
135.00
129.48
128.92
37.02
32.35
30.06
O
O
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

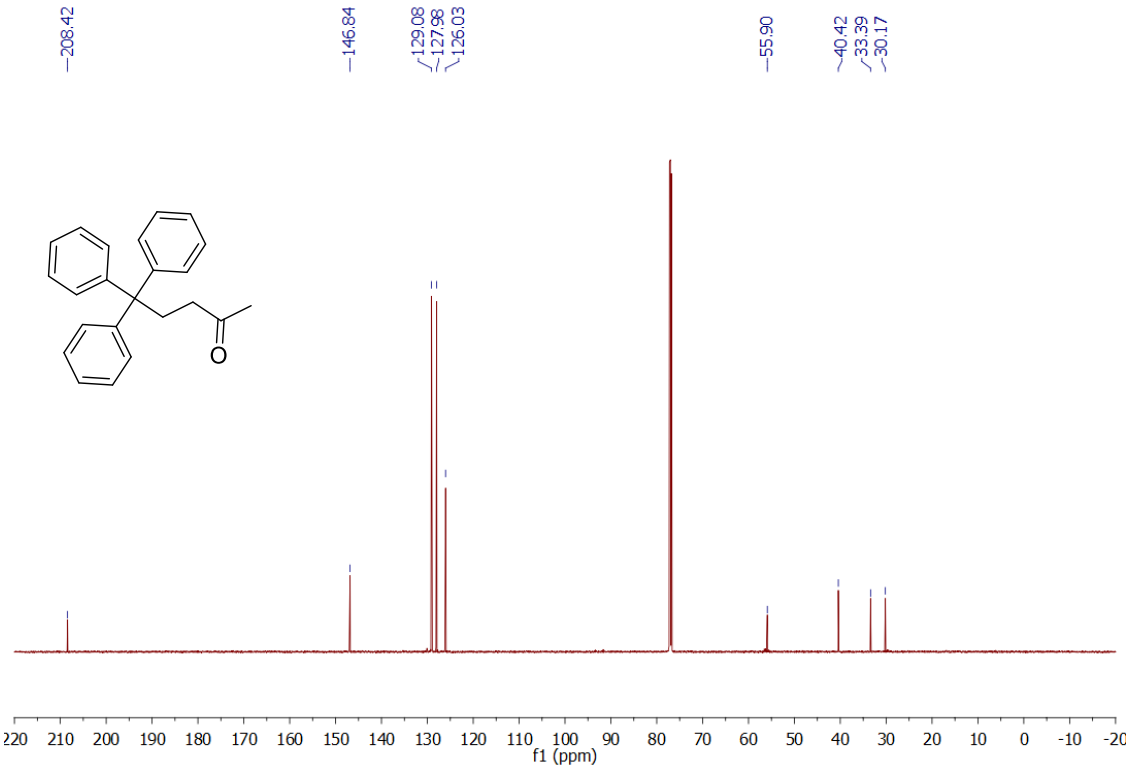

8.07
8.06
7.75
7.74
7.73
7.70
7.70
7.69
7.67
7.65
3.29
3.28
3.27
2.91
2.90
2.89
O
O
NC
2.05
2.09
2.16
2.03
2.00
2.00
2.95
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

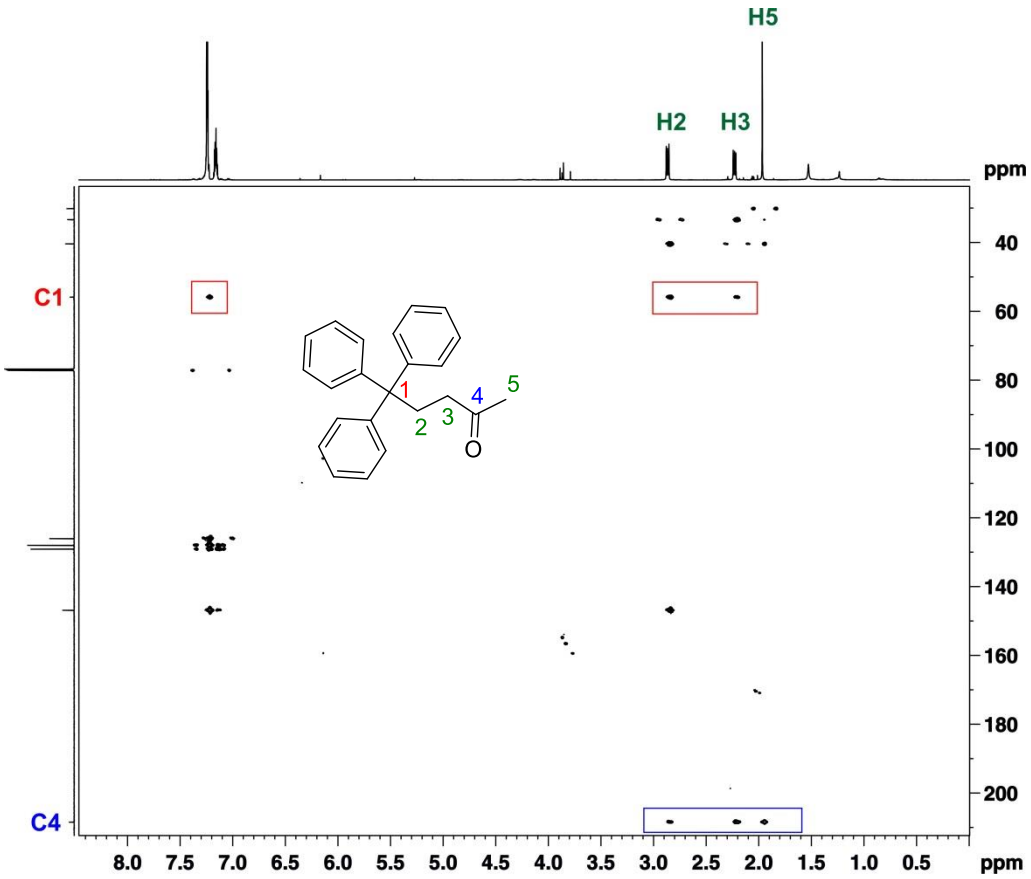

207.18
197.92
144.34
143.58
136.49
132.74
128.87
127.94
127.46
118.64
111.91
37.08
32.51
30.08
O
O
NC
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


8.07
8.06
7.82
7.81
7.74
7.73
7.47
7.46
3.30
3.29
3.29
3.28
3.28
2.93
2.92
2.91
2.90
2.25
Cl
O
O
O
2.00
1.82
2.02
2.08
2.01
2.00
2.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

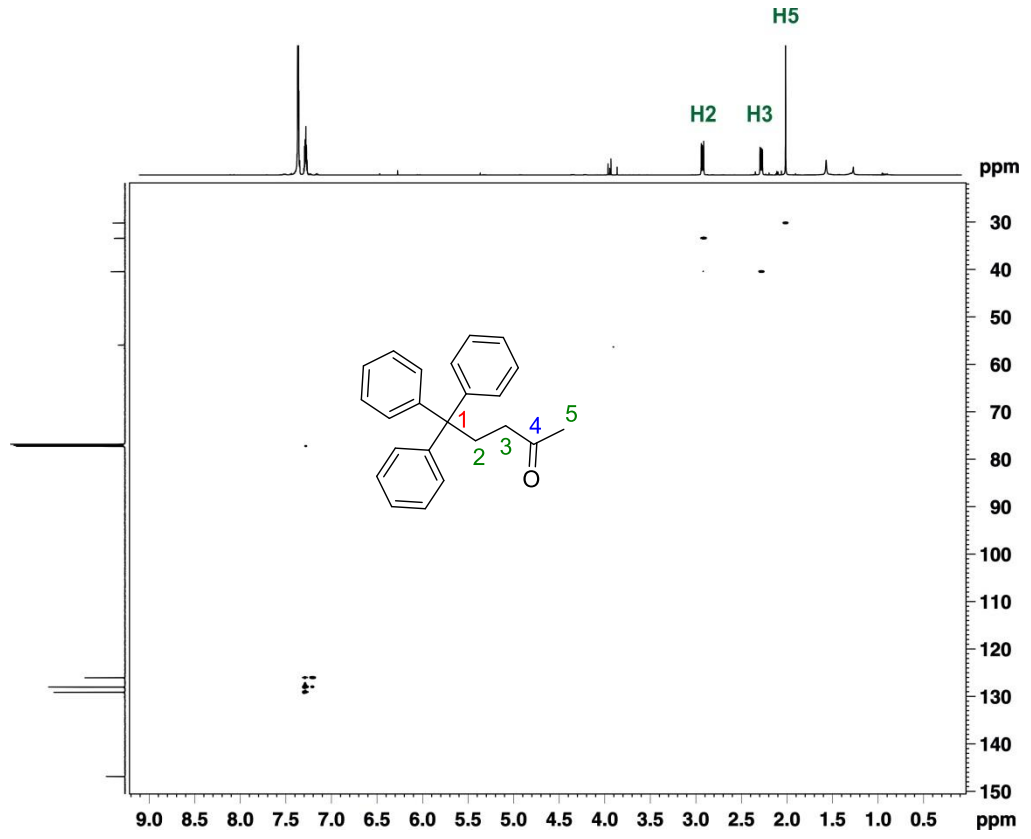

206.98
197.99
194.70
140.96
139.38
135.22
131.47
129.91
128.86
128.03
37.04
32.73
30.04
Cl
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.21
7.20
7.20
7.12
7.12
7.11
7.11
2.84
2.84
2.83
2.82
2.81
2.20
2.19
2.17
1.92
1.92
O
12.13
3.04
1.99
2.00
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

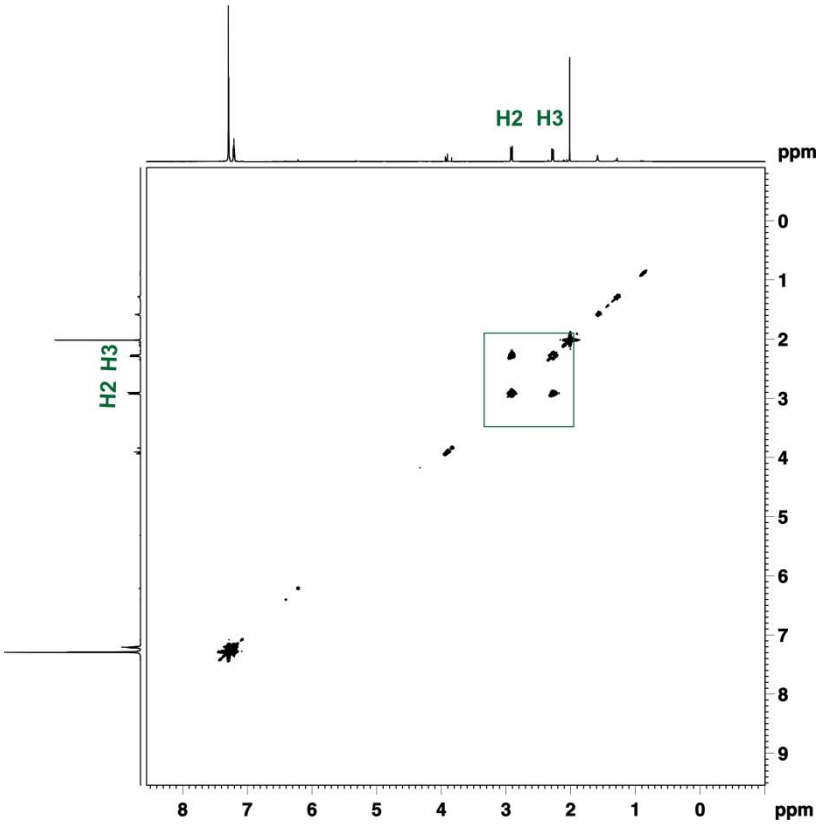

208.42
146.84
129.08
127.98
126.03
55.90
40.42
33.39
30.17
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



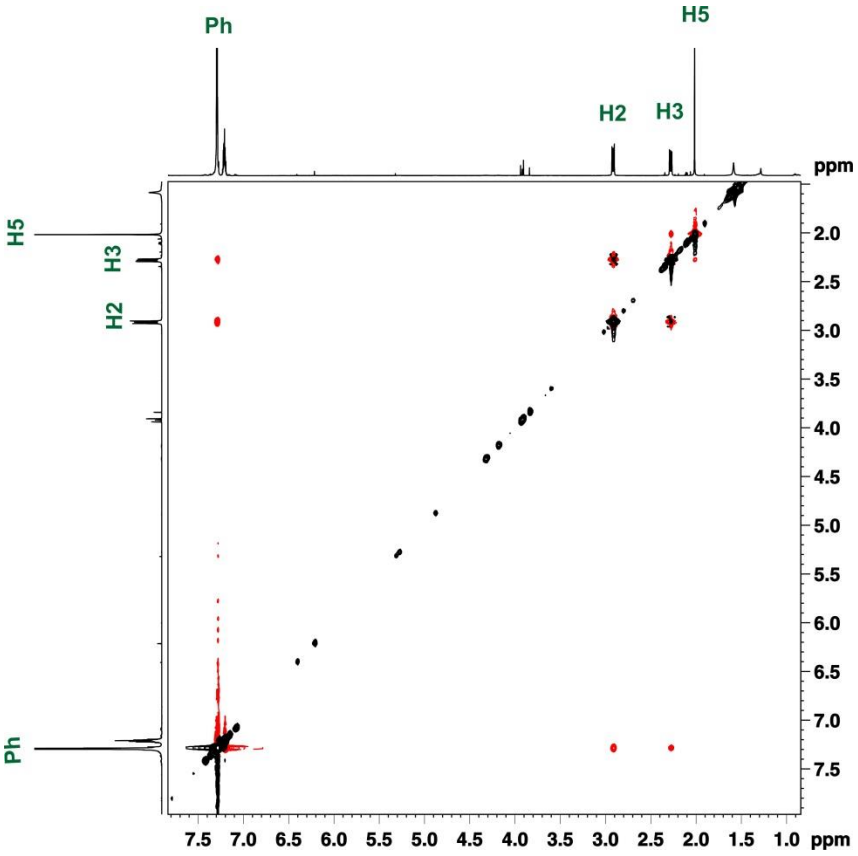
Part of HMBC spectrum of 2u.



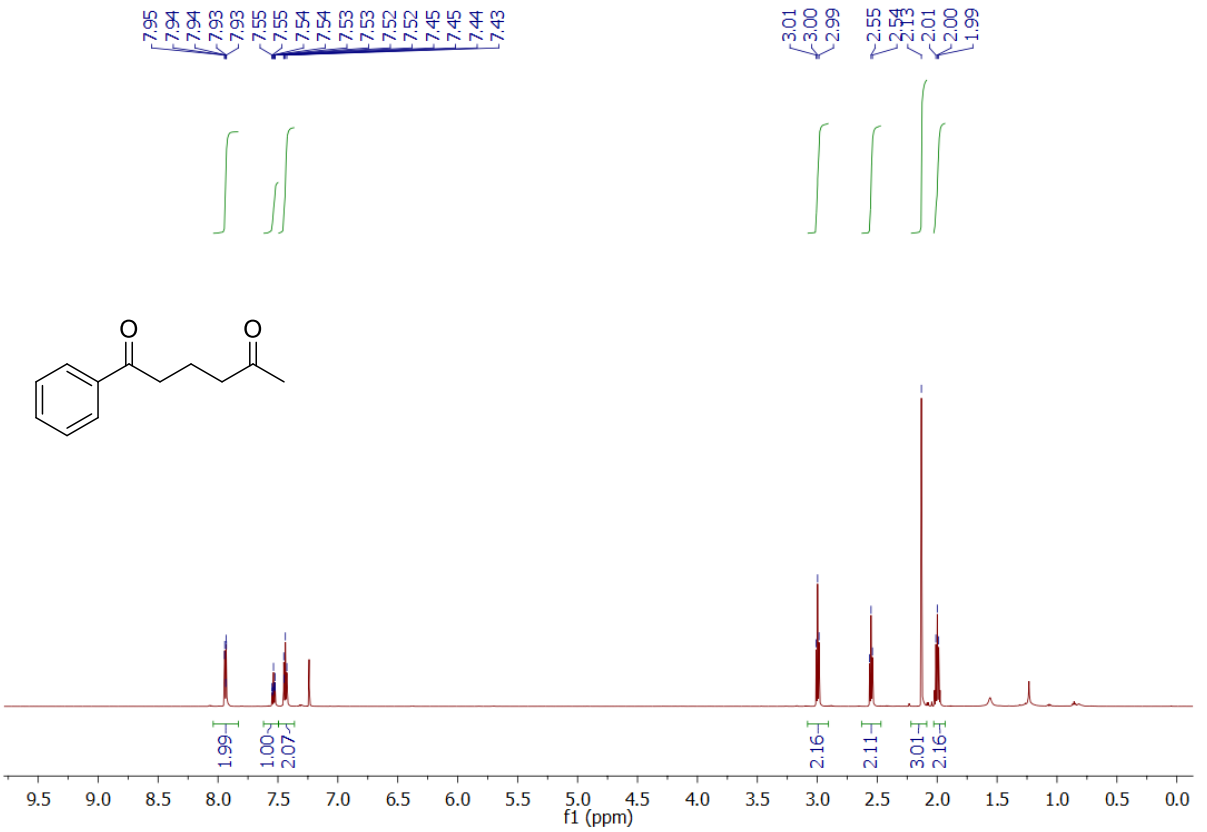
Part of HSQC spectrum of 2u.

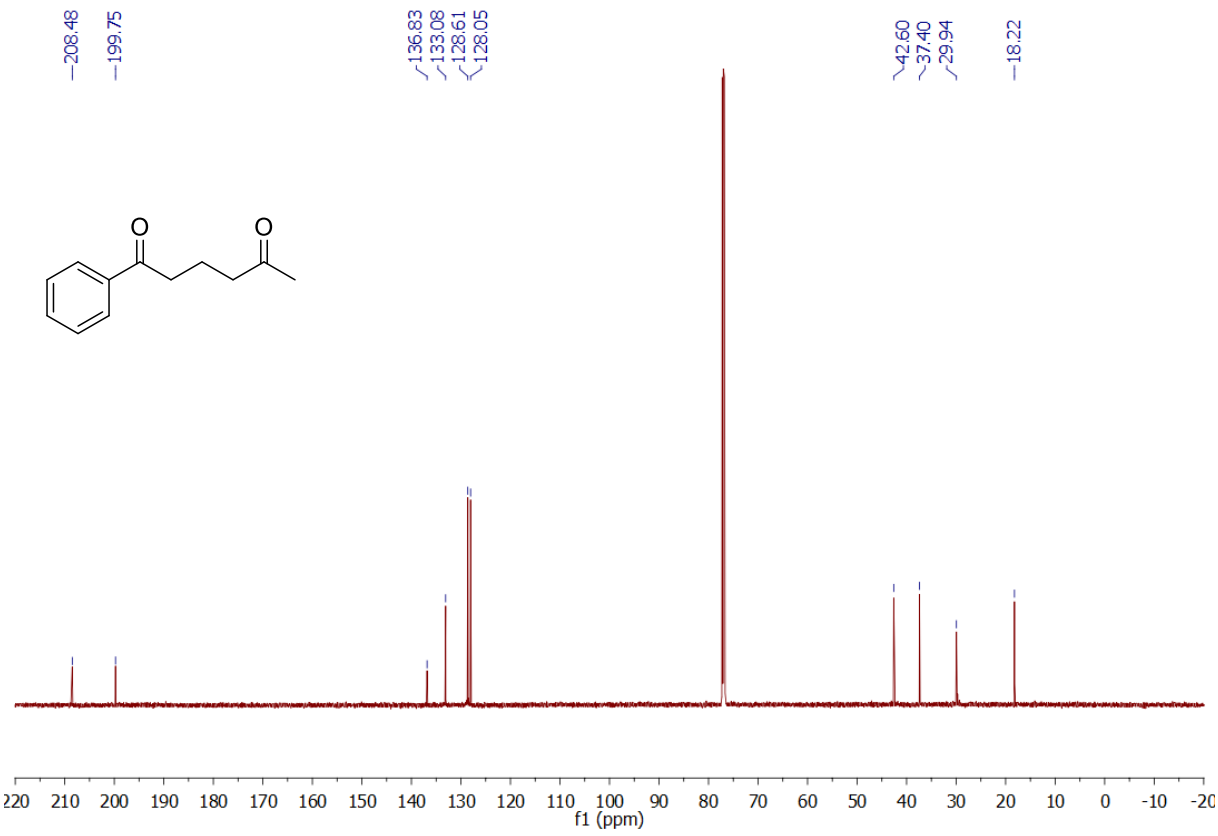


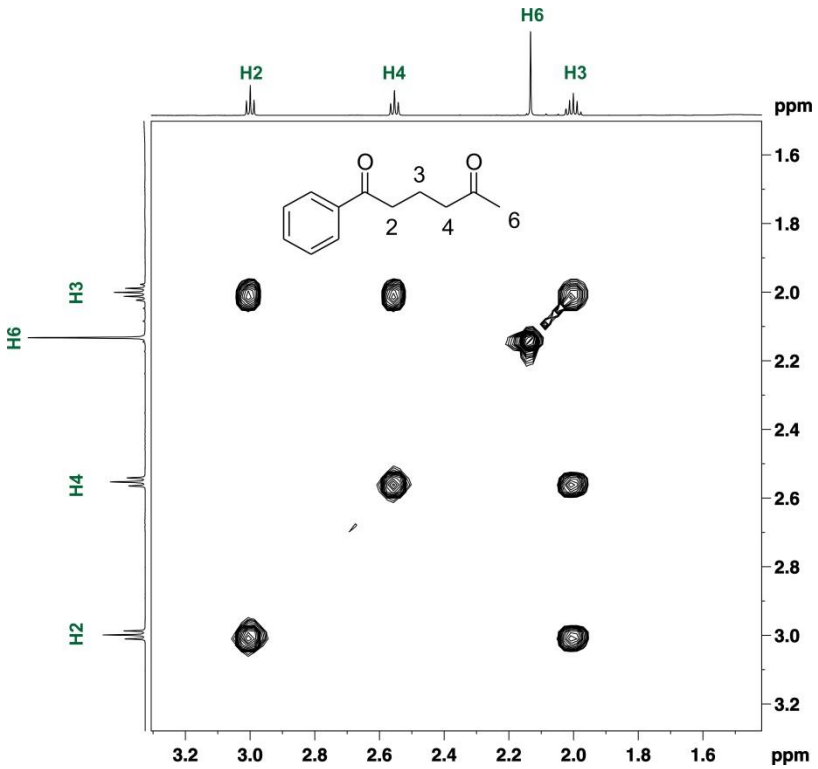
Part of COSY spectrum of 2u.



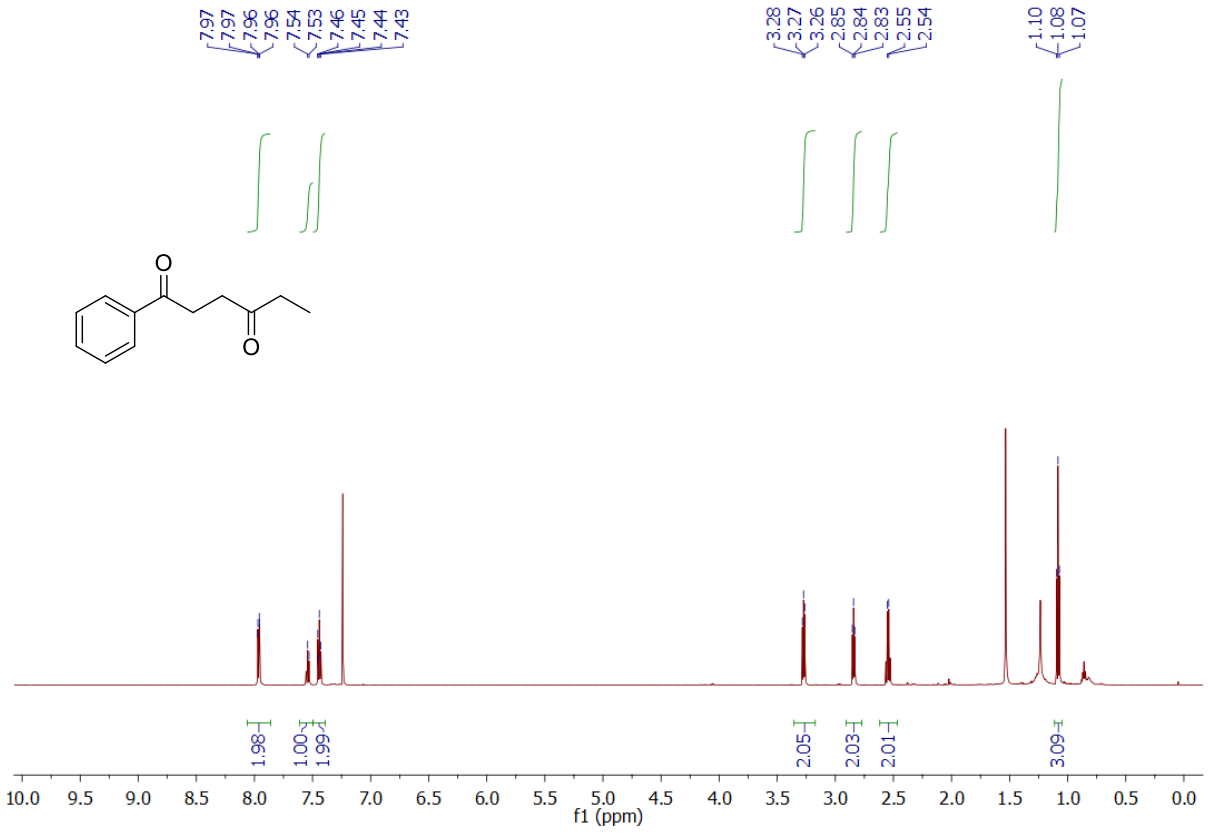
Part of NOESY spectrum of 2u.

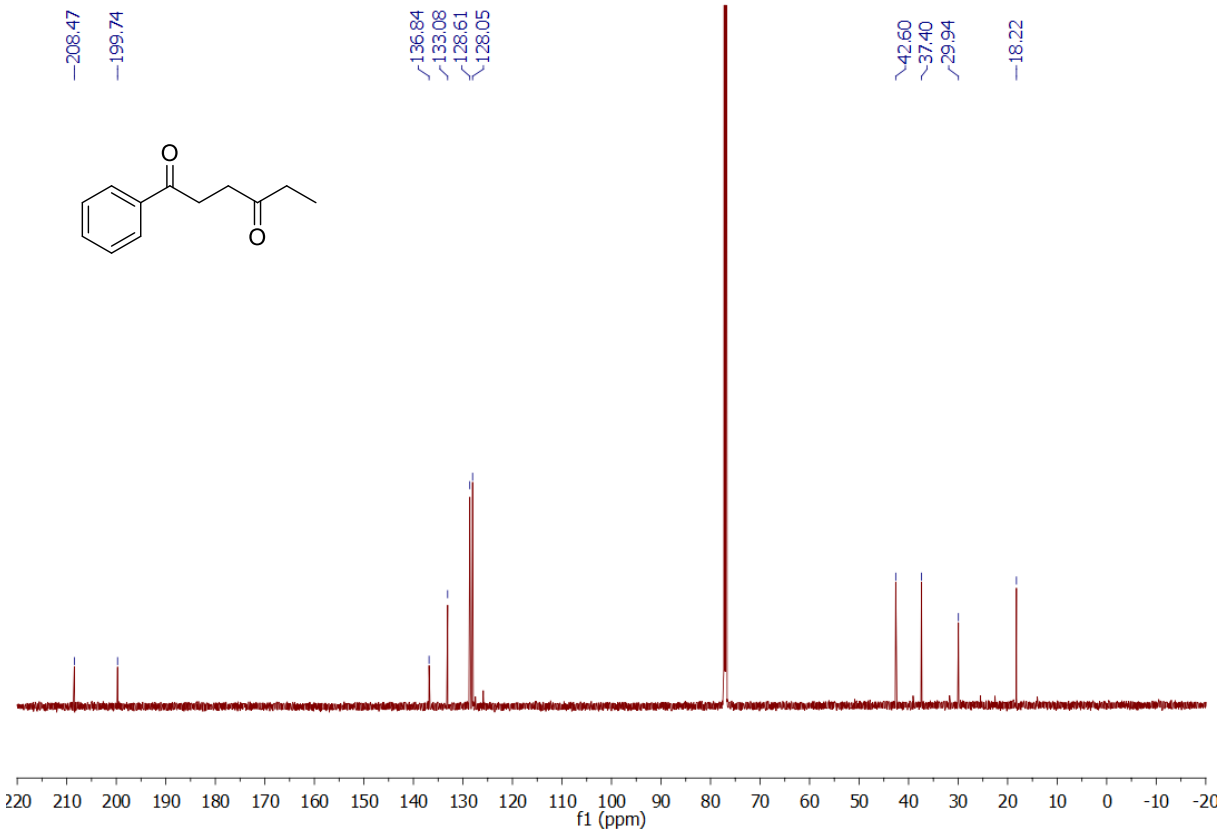

7.95
7.94
7.94
7.93
7.93
7.55
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.45
7.44
7.43
3.01
3.00
2.99
2.55
2.54
2.13
2.01
2.00
1.99
O
O
1.99
1.00
2.07
2.16
2.11
3.01
2.16
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

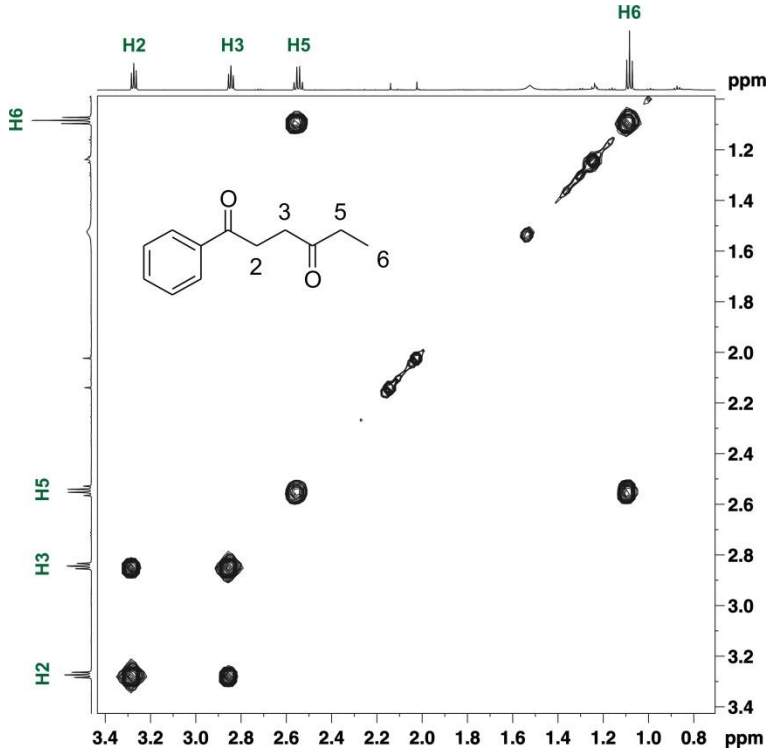

208.48
199.75
136.83
133.08
128.61
128.05
42.60
37.40
29.94
18.22
O
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)



Part of COSY spectrum of 2p.







Part of COSY spectrum of 2o.

6. DFT calculations

6.1. Optimized geometry

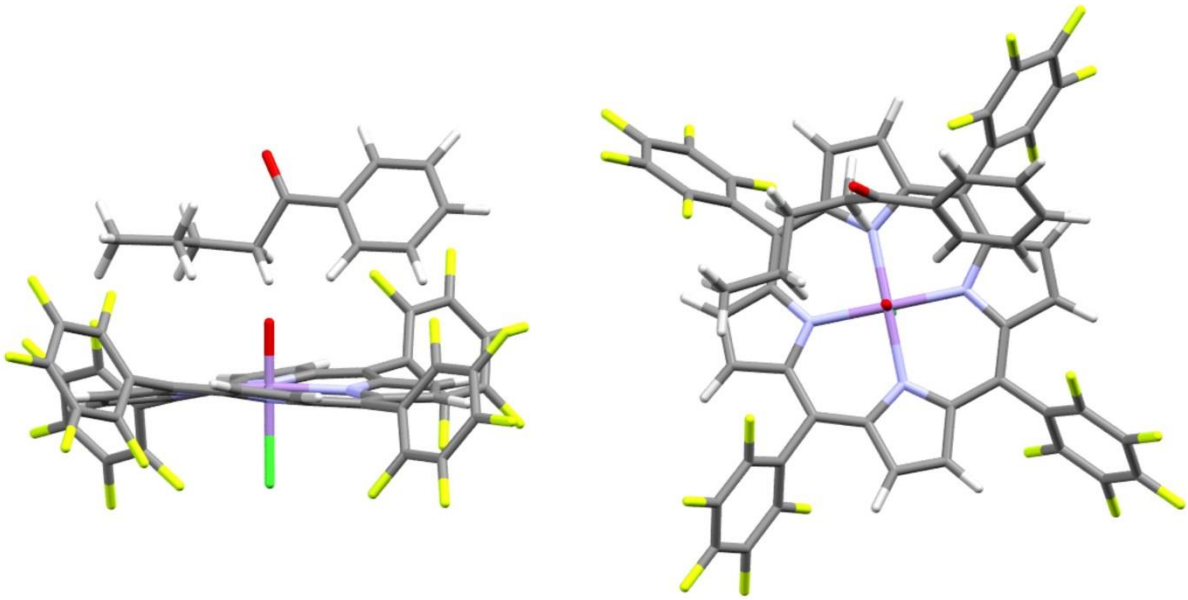


Figure S4. DFT-optimized molecular structure of **Mn^{V}-oxo-S**.

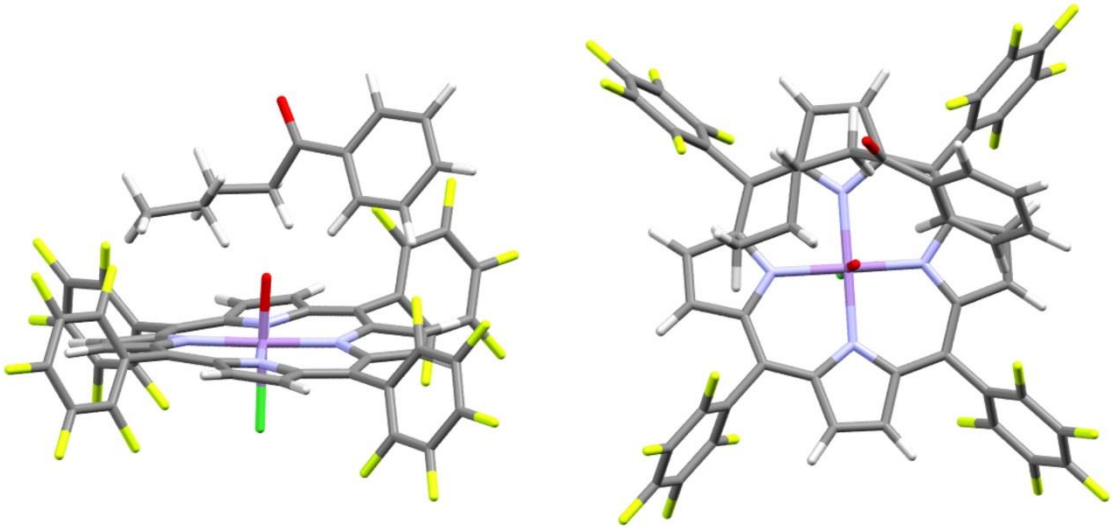


Figure S5. DFT-optimized molecular structure of **Mn-TS-S4**. Activation in position 4.

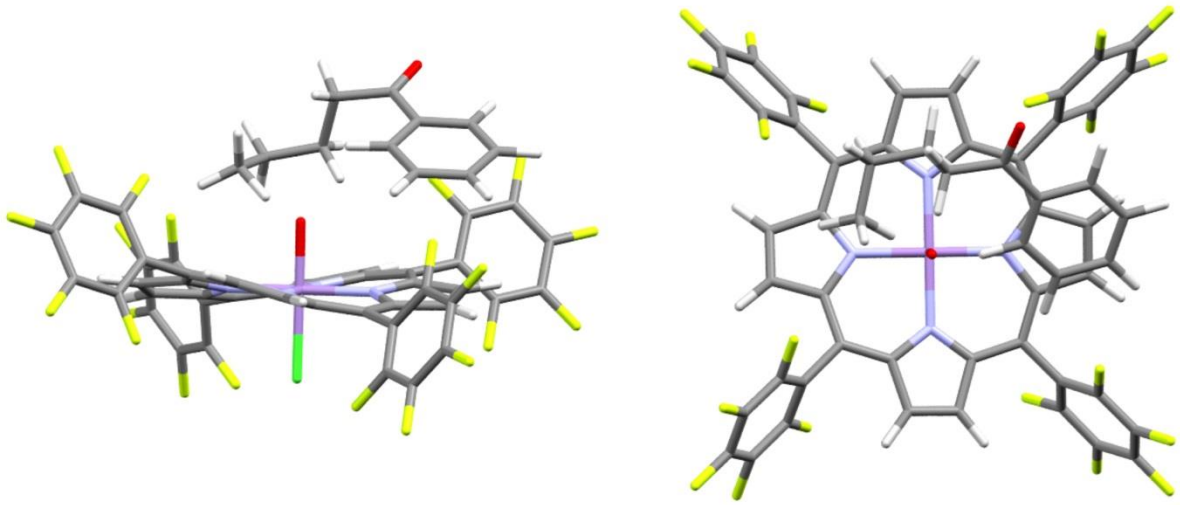


Figure S6. DFT-optimized molecular structure of **Mn-TS-S5**. Activation in position 5.

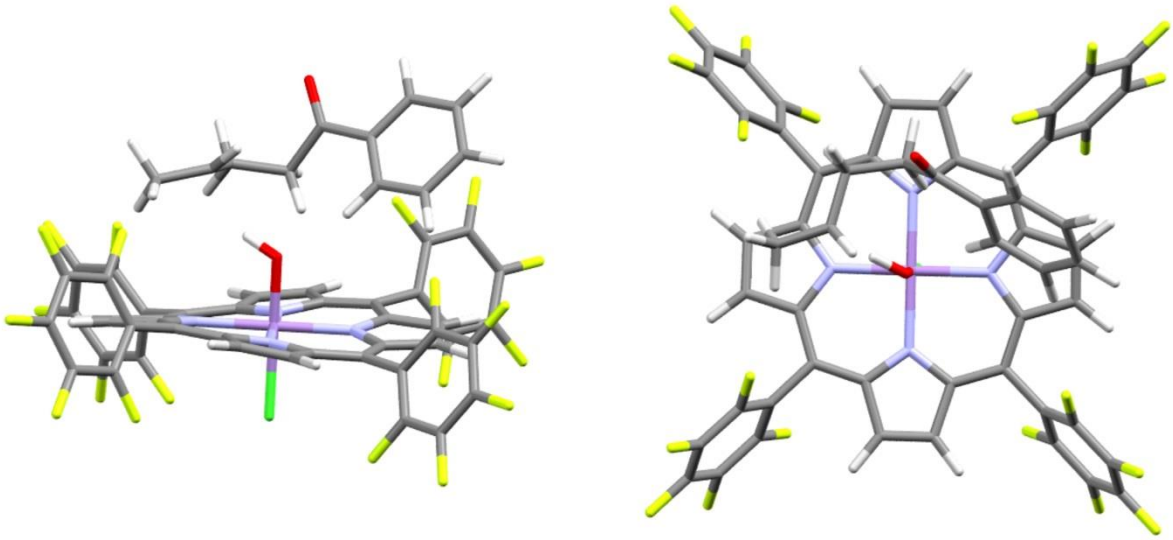


Figure S7. DFT-optimized molecular structure of **Mn^{IV}-OH-S4**.

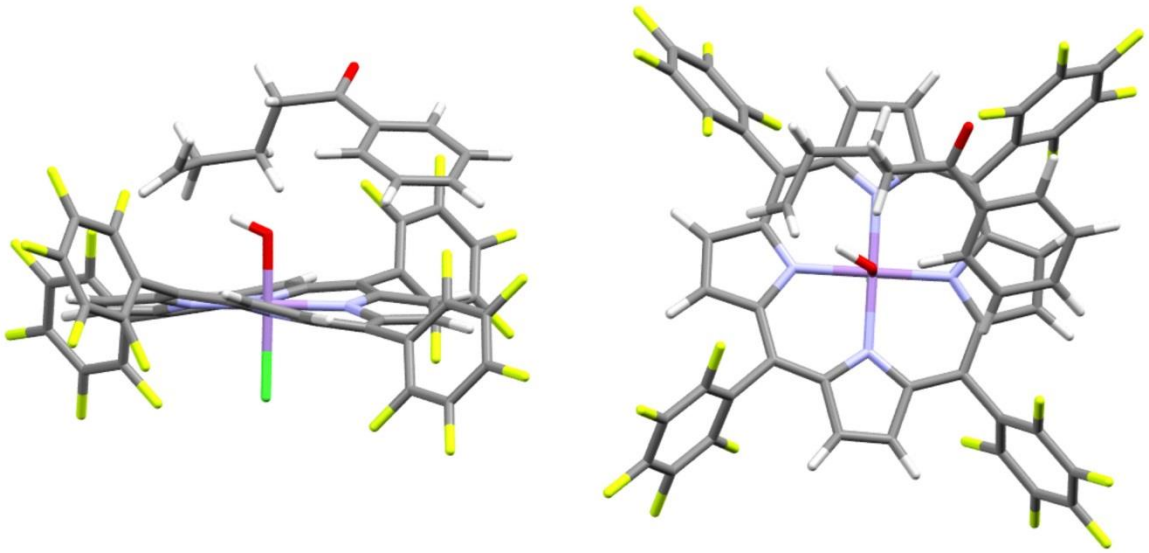


Figure S8. DFT-optimized molecular structure of **Mn^{IV}-OH-S5**.

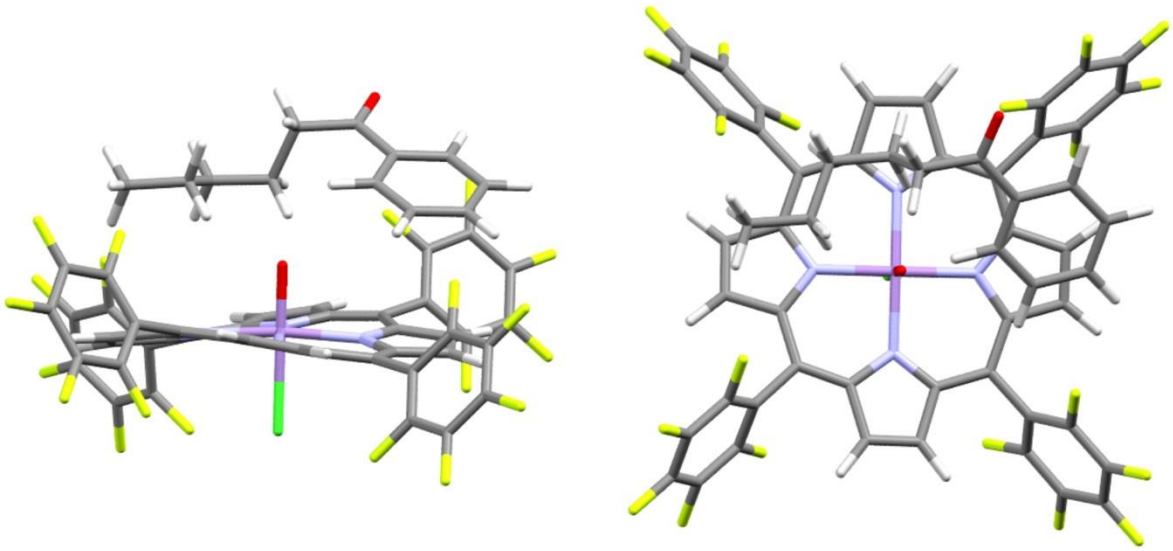


Figure S9. DFT-optimized molecular structure of **Mn^{V}-oxo-Hex**.

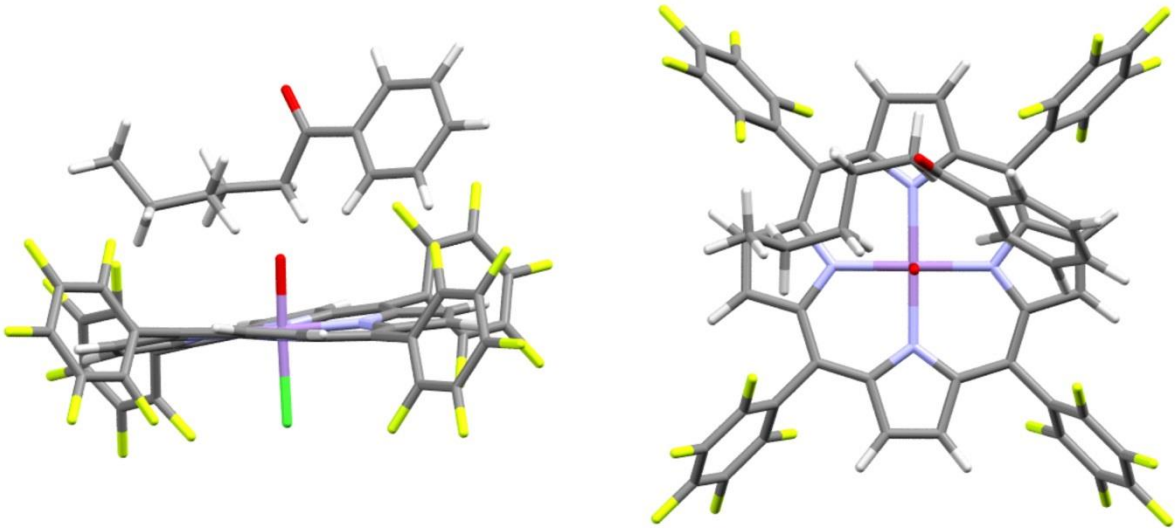


Figure S10. DFT-optimized molecular structure of **Mn-TS-Hex4**. Activation in position 4.

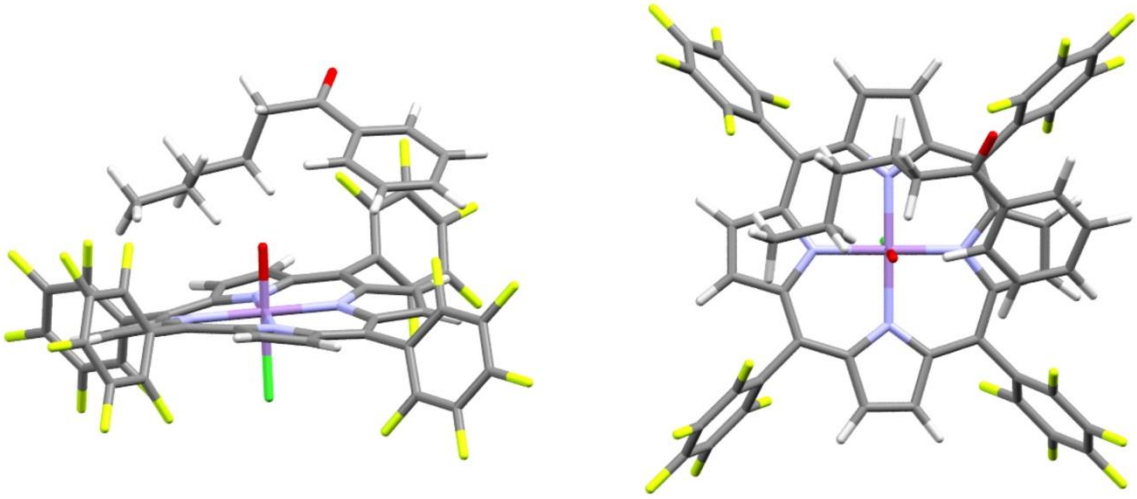


Figure S11. DFT-optimized molecular structure of **Mn-TS-Hex5**. Activation in position 5.

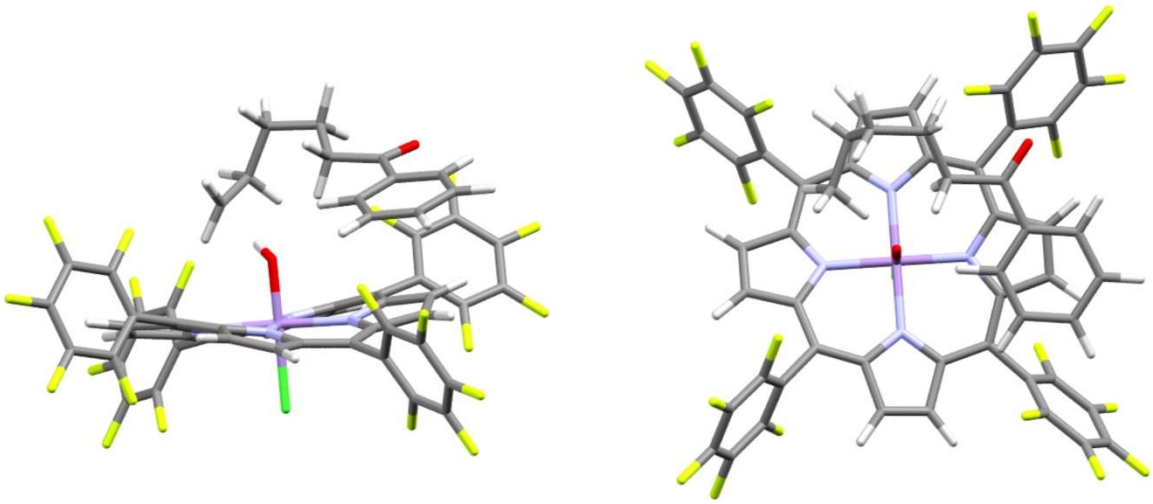


Figure S12. DFT-optimized molecular structure of **Mn-TS-Hex6**. Activation in position 6.

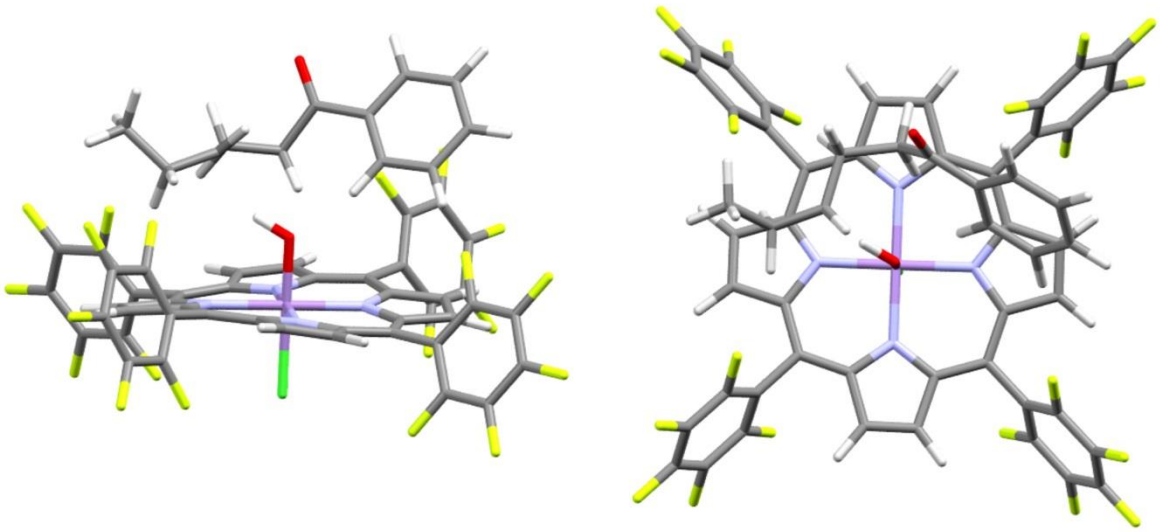


Figure S13. DFT-optimized molecular structure of **Mn^{IV}-OH-Hex4**.

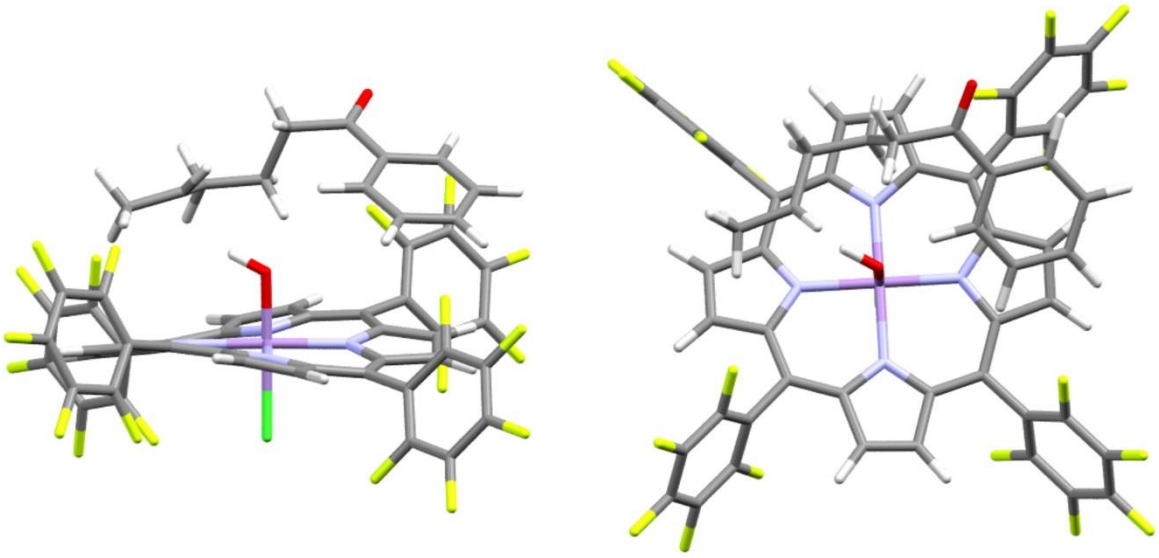


Figure S14. DFT-optimized molecular structure of **Mn^{IV}-OH-Hex5**.

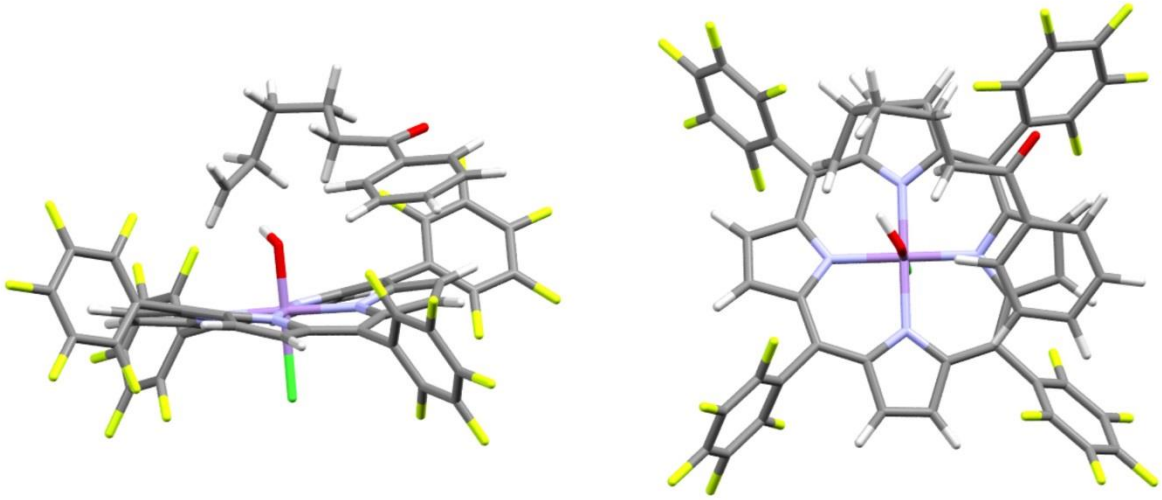


Figure S15. DFT-optimized molecular structure of **Mn^{IV}-OH-Hex6**.

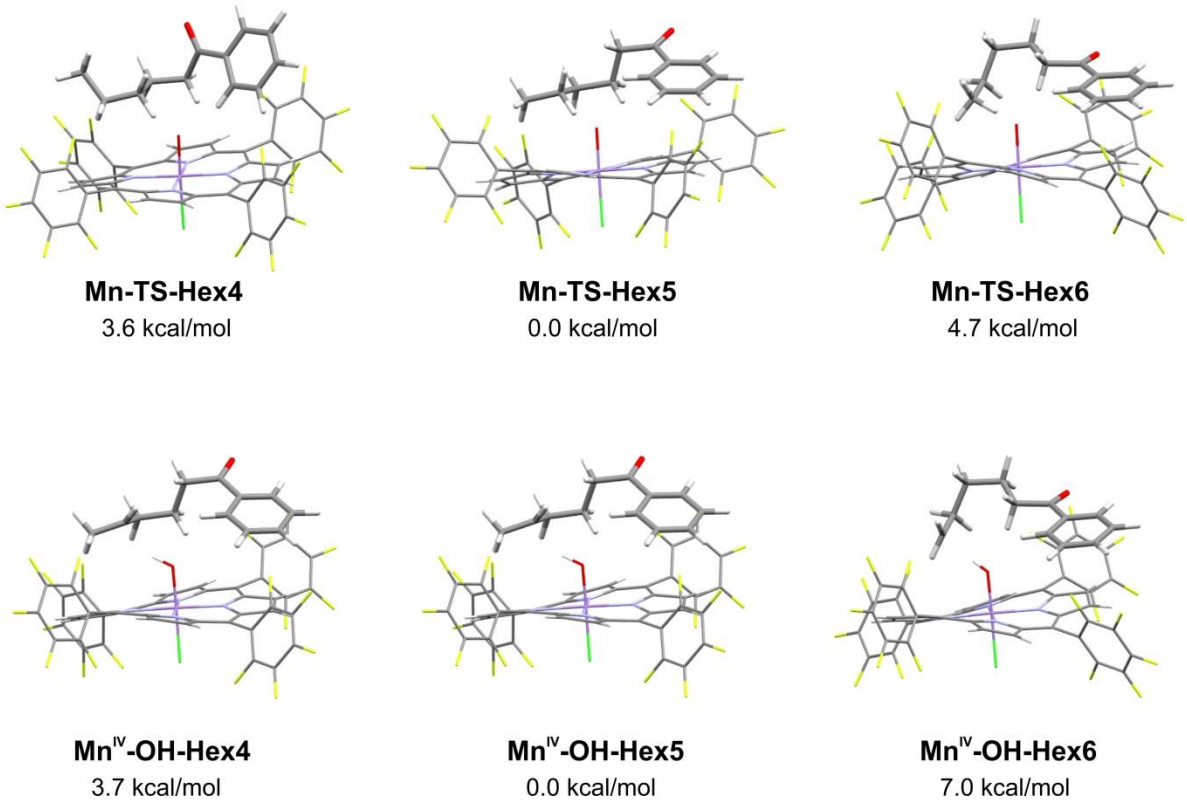


Figure S16. DFT-optimized molecular structure - energy differences between **Mn-TS-Hex4**, **Mn-TS-Hex5**, **Mn-TS-Hex6**.

6.2. Cartesian coordinates

C	-0.04150500	-3.99903700	-0.83806300
C	-1.36614200	-3.72081500	-0.71606700
C	-1.48691600	-2.28264300	-0.64662000
C	-2.69047700	-1.59226100	-0.63740300
C	-2.80822100	-0.18423000	-0.73698700
C	-4.06250900	0.52614900	-0.86457100
C	-3.75937100	1.84461200	-0.97217500
C	-2.32238800	1.95570100	-0.85723800
C	-1.62641700	3.15198700	-0.77119300
C	-0.23132100	3.26866500	-0.55317600
C	0.43584200	4.51422600	-0.23780500
C	1.73262700	4.20949200	0.02397000
C	1.87371800	2.78250200	-0.16108400
C	-3.94309400	-2.38778300	-0.54920300
C	-4.24734100	-3.13527800	0.59268400
C	-4.85778100	-2.42882100	-1.60555700
C	-5.42524900	-3.86633400	0.69572000
F	-3.39557500	-3.16634800	1.62482100
C	-6.03934200	-3.15542500	-1.52506800
F	-4.60175800	-1.75394200	-2.73498800
C	-6.32345000	-3.87540900	-0.36739600
F	-5.69448800	-4.56192600	1.80430300
F	-6.89446800	-3.17637200	-2.55143700
F	-7.45341300	-4.57706200	-0.27988400
C	-2.40712700	4.41562000	-0.82002800
C	-2.24008600	5.32280300	-1.86886800

C	3.05549500	2.07129000	-0.03160000
C	2.06075200	-2.60475600	-0.91425500
C	0.65317900	-2.73228000	-0.82735100
N	-0.22908500	-1.70671300	-0.70340100
N	-1.76836700	0.69018300	-0.74274300
N	0.64866400	2.23802100	-0.51729400
N	2.17172600	-0.18592200	-0.48707700
C	2.75358500	-1.41995800	-0.73058200
C	4.19274100	-1.29223600	-0.69463900
C	3.19117400	0.67951500	-0.26920300
C	4.46437000	0.00227500	-0.38430700
Mn	0.19950800	0.26596900	-0.52333900
H	5.43058200	0.46990300	-0.27649700
H	4.89494000	-2.08962200	-0.88075300
H	0.42856500	-4.96679900	-0.91795100
H	-2.19066800	-4.41634000	-0.71103900
H	-5.04153000	0.07533600	-0.86791000
H	-4.44113300	2.66975500	-1.10443600
H	-0.03918500	5.48152400	-0.18999900
H	2.52237900	4.88189000	0.31999700
C	2.82941000	-3.84106900	-1.22059600
C	2.71217900	-4.43935100	-2.47867500
C	3.67118900	-4.45626100	-0.29274700
C	3.40696600	-5.59698200	-2.80727000
F	1.91201300	-3.88938100	-3.40169800
C	4.37475900	-5.61594700	-0.59815100
F	3.80645500	-3.94123400	0.93834100
C	4.24250200	-6.18545100	-1.86134600
F	3.28243100	-6.14297900	-4.02021300
F	5.16808200	-6.18664600	0.31279200
F	4.91401300	-7.29631200	-2.16483700
C	1.24690900	-2.73523300	2.94979800
H	1.36531700	-3.42804300	3.79096400
H	1.67744300	-3.22765600	2.07153700
C	2.01418000	-1.43530800	3.22368000
H	1.60608300	-0.96536900	4.12854600
H	1.81776700	-0.73784900	2.40210200
C	-3.31281900	4.75176200	0.18990900
C	-2.95144400	6.51535700	-1.92344800
F	-1.37543400	5.04502100	-2.85361900
C	-4.03387700	5.93965900	0.15564300
F	-3.49657800	3.92527700	1.22943200
C	-3.85139600	6.82217400	-0.90589200
F	-2.78087100	7.36274300	-2.94220200
F	-4.89119700	6.24183300	1.13493200
F	-4.53878200	7.96364000	-0.94763000
C	4.28548800	2.80193700	0.36648100
C	4.87174700	3.77263200	-0.44911500
C	4.91150800	2.51418300	1.58292200
C	6.03129100	4.43928700	-0.06913900
F	4.32166800	4.07462500	-1.63234200
C	6.07007200	3.16823700	1.98230100
F	4.38195200	1.59083900	2.39827900
C	6.63039100	4.13450400	1.15007900
F	6.57640600	5.36070400	-0.86863300
F	6.64342500	2.88227700	3.15460900
F	7.74179400	4.76937500	1.52254300
C	-3.35611000	-1.63901800	4.70379700
C	-4.56734300	-0.96212200	4.59493100
C	-4.74143000	-0.00111200	3.59402200
C	-3.70210900	0.27450800	2.70384800
C	-2.49857900	-0.42649600	2.78905700
C	-2.31760100	-1.38950600	3.79380100
H	-3.20015100	-2.37860700	5.48184500
H	-5.37398000	-1.17727900	5.28886200
H	-5.68267200	0.53416700	3.51353200
H	-3.82691100	1.03955500	1.94440100
H	-1.69270900	-0.19562200	2.09926900
C	-1.04629100	-2.16774600	3.94119900
O	-0.71499700	-2.59924400	5.04257000
C	-0.24126100	-2.48583200	2.69486600
H	-0.35754000	-1.69535500	1.95283700
H	-0.72218400	-3.37873700	2.26921000
H	3.95522000	-2.06937000	2.47649900

C	3.52155200	-1.63921900	3.38420400
O	0.08451400	0.28096000	1.12938000
Cl	0.37334300	0.31783000	-2.98703600
H	4.03205900	-0.69038500	3.57582700
H	3.74818900	-2.31833000	4.21452500

Figure S17. Cartesian coordinates for **Mn^{V}-oxo-S**.

C	-0.16083500	-4.04744100	-0.87940300
C	-1.47467100	-3.70005600	-0.80546200
C	-1.52596100	-2.26359200	-0.71226600
C	-2.70444200	-1.51704000	-0.68632800
C	-2.74471000	-0.12740700	-0.71555200
C	-3.95110800	0.64437000	-0.83803500
C	-3.58674400	1.95142700	-0.94273600
C	-2.15316700	2.00521000	-0.83438500
C	-1.41300400	3.18237400	-0.77589600
C	-0.03821600	3.22386300	-0.54801500
C	0.70311800	4.43100800	-0.27226200
C	1.97534800	4.05833900	0.02601600
C	2.03504600	2.62251400	-0.09155200
C	3.19005100	1.86779800	0.07599600
C	1.99535600	-2.77044700	-0.80660300
C	0.60328600	-2.82693000	-0.81671100
N	-0.24944700	-1.75090800	-0.71606900
N	-1.64986700	0.72351500	-0.71032800
N	0.79321300	2.13507000	-0.45064200
N	2.19324500	-0.35210000	-0.35790500
C	2.72463900	-1.60366600	-0.58583300
C	4.15943800	-1.54425200	-0.49014300
C	3.25751000	0.48497300	-0.11147100
C	4.48678300	-0.25992500	-0.17503700
Mn	0.26644500	0.19603100	-0.56425700
H	5.47100900	0.15747300	-0.02800200
H	4.82502800	-2.37969300	-0.64374100
H	0.26133500	-5.03794800	-0.95244700
H	-2.33581900	-4.34986400	-0.82753200
H	-4.94888100	0.23458600	-0.85052400
C	-2.14350300	4.47575600	-0.86068500
C	-1.99346900	5.32023800	-1.96179300
C	-2.99081400	4.90006600	0.16521700
C	-2.66035800	6.53754800	-2.04747600
F	-1.18573100	4.96221600	-2.96980300
C	-3.67306800	6.10942000	0.09915500
F	-3.16335800	4.13144100	1.25246400
C	-3.50368900	6.93072900	-1.01223900
F	-2.50089200	7.32693800	-3.11513800
F	-4.47891400	6.49172400	1.09558900
F	-4.15063500	8.09587500	-1.08483200
C	4.45558800	2.58528600	0.39506900
C	5.11366100	3.35067100	-0.56978300
C	5.03508400	2.51143600	1.66218000
C	6.30058100	4.01878100	-0.29066600
F	4.59816800	3.45318300	-1.80280100
C	6.22326900	3.16788100	1.96440000
F	4.44078000	1.79939300	2.63193800
C	6.85646200	3.92384800	0.98216200
F	6.91165100	4.74370800	-1.23379900
F	6.75472500	3.08307700	3.18860900
F	7.99594000	4.56018800	1.26127900
C	-3.70962800	-1.05586900	4.84271900
C	-4.70659700	-0.08688200	4.79847100
C	-4.70388900	0.87071600	3.77866700
C	-3.70553200	0.85046700	2.80341000
C	-2.72205600	-0.13842300	2.82893000
C	-2.71509400	-1.09881500	3.85230600
H	-3.68825800	-1.79818100	5.63306400
H	-5.48258200	-0.07100800	5.55733600

H	-4.23038200	2.80737500	-1.07306700
H	0.28594600	5.42621600	-0.27468900
H	2.80369700	4.69018000	0.30734100
C	2.74110000	-4.04376000	-1.00421100
C	2.79849700	-4.64884800	-2.26114800
C	3.39452200	-4.68639000	0.04798000
C	3.48040500	-5.84271900	-2.46934400
F	2.18211500	-4.07550800	-3.30397600
C	4.08589300	-5.87856600	-0.13534200
F	3.35692600	-4.15895400	1.28281700
C	4.12763100	-6.45693500	-1.40091900
F	3.52208100	-6.39933700	-3.68448000
F	4.70065500	-6.47350700	0.89227600
F	4.78652800	-7.60205500	-1.58920800
C	-3.99788000	-2.25638400	-0.70017300
C	-4.46422800	-2.93624200	0.42594100
C	-4.78912100	-2.30323600	-1.85002400
C	-5.66945300	-3.62995200	0.41783900
F	-3.74357200	-2.93741400	1.55685800
C	-6.00011500	-2.98554100	-1.88111100
F	-4.38629200	-1.67066000	-2.96139700
C	-6.43950800	-3.65261400	-0.74108500
F	-6.09139300	-4.26991300	1.51371800
F	-6.73813800	-3.01086000	-2.99612800
F	-7.59911500	-4.31311900	-0.75952000
H	-5.47647700	1.63300200	3.74899900
H	-3.68865800	1.60711300	2.02629800
H	-1.93728000	-0.12857400	2.08208200
C	-1.66399000	-2.15565800	3.95000300
O	-1.42738600	-2.69812900	5.02652700
C	-0.91961900	-2.60352400	2.70029600
H	-1.16276300	-1.98008900	1.84475600
H	-1.30199200	-3.60635700	2.47639600
C	0.60044200	-2.65860300	2.89030200
H	0.82583100	-3.21469800	3.81051600
H	1.05193100	-3.21722900	2.06526200
C	1.23377000	-1.27833900	2.98016700
H	0.80743500	-0.69772400	3.80780700
H	0.85429200	-0.67397600	2.05255700
C	2.74969200	-1.25124600	3.00019900
H	3.16910900	-1.84173400	2.18352900
H	3.13851800	-0.23344800	2.92609100
H	3.11796100	-1.68094800	3.94149000
O	0.00217000	0.20084500	1.21005100
Cl	0.55597700	0.24845600	-2.88280800

Figure S18. Cartesian coordinates for **Mn-TS-S4**.

C	0.69359900	-3.97355300	-0.97183800
C	-0.64509200	-3.90086800	-0.73336300
C	-0.97748200	-2.50446800	-0.60965300
C	-2.27751700	-2.00667500	-0.48791000
C	-2.59610400	-0.65260700	-0.56927900
C	-3.93061700	-0.13399300	-0.71607200
C	-3.82288100	1.20117800	-0.95288700
C	-2.42617500	1.53708600	-0.87216000
C	-1.92451100	2.83706100	-0.86892800
C	-0.59334000	3.14895700	-0.58619000
C	-0.11951100	4.46708300	-0.23900600
F	-6.56580700	-5.63144500	0.05675100
C	-2.87031100	3.96753600	-1.07314400
C	-2.79771800	4.75293400	-2.22588400
C	-3.84165900	4.30628900	-0.12891300
C	-3.65875100	5.82346200	-2.44100300
F	-1.87814800	4.47747500	-3.16130100
C	-4.71753600	5.36811500	-0.32349300
F	-3.95031700	3.60086200	1.00971800
C	-4.62272600	6.12966100	-1.48486700
F	-3.56928200	6.55466700	-3.55705900
F	-5.63815300	5.66787100	0.59891100

C	1.17560900	4.33481300	0.15632500
C	1.52784700	2.94547100	-0.00132600
C	2.80400000	2.41724600	0.17048600
C	2.54933500	-2.28418100	-1.05900900
C	1.19942200	-2.62343100	-0.96609400
N	0.16125100	-1.74597900	-0.74861200
N	-1.68903500	0.38878800	-0.65713700
N	0.42784200	2.24277600	-0.45294700
N	2.28301500	0.10025500	-0.50553800
C	3.04578000	-1.00277200	-0.81793700
C	4.44101200	-0.66536300	-0.70366900
C	3.15398800	1.10251400	-0.15492600
C	4.50704400	0.62316100	-0.26353300
Mn	0.29078100	0.25016600	-0.58282300
H	5.39005000	1.21182800	-0.06698000
H	5.26127900	-1.33117900	-0.92363500
H	1.29420100	-4.85882600	-1.11430400
H	-1.35254800	-4.71349100	-0.67312500
H	-4.83478200	-0.71743400	-0.65221000
H	-4.62089700	1.90446200	-1.13266600
H	-0.72035200	5.36358200	-0.25410800
H	1.83862400	5.10702400	0.51446300
C	3.52200400	-3.38180600	-1.31069200
C	3.60942500	-3.99335300	-2.56238900
C	4.36548400	-3.85511200	-0.30355100
C	4.50174700	-5.03092700	-2.81011300
F	2.81605300	-3.58167600	-3.56119100
C	5.26886400	-4.88756500	-0.52814300
F	4.31050500	-3.31435200	0.92443400
C	5.33522400	-5.47619800	-1.78810600
F	4.56724300	-5.59749500	-4.01977400
F	6.06383900	-5.32256300	0.45538200
F	6.19708800	-6.46973800	-2.01513600
C	-3.39316400	-2.98582400	-0.36126500
C	-3.56540100	-3.74173900	0.79977500
C	-4.31397800	-3.18911300	-1.39230100
C	-4.62848800	-4.62312800	0.95710800
F	-5.45608800	7.15348700	-1.68085200
C	3.88224200	3.29666200	0.69441300
C	4.39651000	4.36927100	-0.03590900
C	4.43665800	3.05010300	1.95312900
C	5.41076100	5.17729700	0.46655200
F	3.91203000	4.64137600	-1.25615400
C	5.45417800	3.84111700	2.47377800
F	3.98307100	2.02621100	2.69194200
C	5.94080700	4.90952000	1.72544200
F	5.88571600	6.19908500	-0.25413700
F	5.96336700	3.58658700	3.68408700
F	6.91661600	5.67724600	2.21537500
C	-4.16572400	-1.48068500	3.50977600
C	-4.98859100	-0.53793100	2.90410200
C	-4.44533200	0.66232100	2.43277600
C	-3.07735500	0.90385600	2.55510900
C	-2.25017500	-0.04592300	3.15136400
C	-2.78785200	-1.24315000	3.64497400
H	-4.56482000	-2.41963800	3.87692400
H	-6.05070000	-0.73388300	2.79547000
H	-5.08087200	1.40194700	1.95815900
H	-2.65401300	1.82550600	2.17333800
H	-1.18798500	0.14995200	3.20386200
C	-1.95061200	-2.28897400	4.30823600
O	-2.47690000	-3.23956600	4.87974600
C	1.55967200	-2.49099200	2.61455400
H	2.12011500	-2.99061000	3.42020500
H	1.84277300	-2.99724500	1.68860900
C	1.99778600	-1.04265700	2.55048400
H	1.89795900	-0.48948700	3.48768100
H	1.22556600	-0.45976800	1.82419800
O	0.18965700	0.18184500	1.21360000
Cl	0.43371900	0.38832700	-2.92066900
H	2.98404200	-0.88521200	2.11050600
C	0.05297400	-2.67409500	2.83630800
H	-0.47654400	-2.12676200	2.05365800
H	-0.20888800	-3.73010900	2.71930300

F	-2.68683400	-3.63522500	1.80617600
C	-5.38302800	-4.06874500	-1.26180200
F	-4.18696200	-2.51636500	-2.54569900
C	-5.54181800	-4.78627600	-0.07964700
F	-4.77401500	-5.31031500	2.09540200
F	-6.25185100	-4.23460500	-2.26514800
C	-0.43869500	-2.19312500	4.21654700
H	-0.11041000	-1.16604100	4.39751400
H	-0.01971800	-2.82411500	5.00499000

Figure S19. Cartesian coordinates for **Mn-TS-S5**.

C	-0.15836700	-4.02192200	-0.90255300
C	-1.47143400	-3.67787100	-0.80922400
C	-1.52739100	-2.24190700	-0.70601500
C	-2.70759500	-1.50150900	-0.67233700
C	-2.75354900	-0.10898200	-0.70764800
C	-3.96538700	0.66121300	-0.82181200
C	-3.60239700	1.96734200	-0.92956800
C	-2.16554800	2.01837500	-0.83093700
C	-1.42321700	3.19634000	-0.76943500
C	-0.04724700	3.24149600	-0.54908000
C	0.69176100	4.44898700	-0.27217700
C	1.96723400	4.07892500	0.01971800
C	2.03104500	2.64394000	-0.10409700
C	3.19004100	1.88835500	0.05785200
C	1.99751300	-2.74522500	-0.84868600
C	0.60525000	-2.80163000	-0.83921500
N	-0.24854000	-1.72732800	-0.71852600
N	-1.66639600	0.73945800	-0.71120000
N	0.79274700	2.15674300	-0.46039700
N	2.19807900	-0.32749400	-0.40528700
C	2.72930200	-1.58078600	-0.62781500
C	4.16281200	-1.52295600	-0.51235900
C	3.26055500	0.50966500	-0.13972300
C	4.48814500	-0.24106200	-0.18824300
Mn	0.26896200	0.21625600	-0.55827500
H	5.47150900	0.17276300	-0.02586200
H	4.82862600	-2.35998600	-0.65627600
F	-6.79724900	-2.95835700	-2.90914500
F	-7.59627300	-4.31173100	-0.67969100
C	-2.15515200	4.48981900	-0.84716700
C	-2.01808100	5.33314100	-1.95078900
C	-2.99109000	4.91499100	0.18750500
C	-2.68648600	6.55007700	-2.03044300
F	-1.22192600	4.97441100	-2.96780700
C	-3.67458100	6.12402900	0.12786500
F	-3.15080100	4.14823400	1.27812200
C	-3.51823600	6.94414600	-0.98627100
F	-2.53943500	7.33835500	-3.10085100
F	-4.46928900	6.50720900	1.13302600
F	-4.16655200	8.10903500	-1.05290500
C	4.45060700	2.60060700	0.40485400
C	5.11467200	3.39943900	-0.52789700
C	5.02177000	2.48306900	1.67278000
C	6.29864000	4.05890300	-0.21687100
F	4.60850400	3.54440600	-1.76066700
C	6.20747100	3.12853500	2.00606500
F	4.42151800	1.73544500	2.61206100
C	6.84640500	3.91925300	1.05529100
F	6.91548400	4.81696700	-1.12987400
F	6.73129900	3.00038000	3.22989600
F	7.98367600	4.54600500	1.36418200
C	-3.76252900	-1.18093300	4.71592800
C	-4.76431200	-0.21855400	4.64666300
C	-4.69952200	0.78707000	3.67623900

H	0.26447900	-5.01093600	-0.99060100
H	-2.33064700	-4.33026900	-0.82861100
H	-4.96287000	0.25071000	-0.82291400
H	-4.24626300	2.82441000	-1.05146900
H	0.27219900	5.44321900	-0.26923600
H	2.79439700	4.71297000	0.29964600
C	2.73980100	-4.01745000	-1.06851600
C	2.79955600	-4.59471400	-2.33842300
C	3.38610000	-4.68702400	-0.02932600
C	3.47650900	-5.78697200	-2.57094000
F	2.18927300	-3.99563800	-3.37032700
C	4.07315200	-5.87787300	-0.23644300
F	3.34740500	-4.18786300	1.21775600
C	4.11708900	-6.42802200	-1.51436600
F	3.51981100	-6.31659900	-3.79808700
F	4.68168000	-6.49798400	0.77999000
F	4.77163900	-7.57167600	-1.72593200
C	-3.99758800	-2.24652200	-0.67100500
C	-4.43206100	-2.95523800	0.45044700
C	-4.81938300	-2.27196700	-1.80025500
C	-5.63568800	-3.65151400	0.45951500
F	-3.67956900	-2.98556300	1.56023400
C	-6.02990100	-2.95573200	-1.81368300
F	-4.44782500	-1.61706100	-2.90980600
C	-6.43761200	-3.64914600	-0.67770700
F	-6.02545200	-4.31829600	1.55142000
C	-3.63402500	0.82111400	2.77540500
C	-2.64358500	-0.16027900	2.82354600
C	-2.69978800	-1.16882900	3.79802500
H	-3.78965000	-1.96066200	5.46921500
H	-5.59253800	-0.24532000	5.34782200
H	-5.47667700	1.54370200	3.62709000
H	-3.57120300	1.61363000	2.03739800
H	-1.81157700	-0.10859300	2.13110300
C	-1.65254100	-2.22712600	3.91837900
O	-1.48434900	-2.81668000	4.98281600
C	-0.83518400	-2.62450500	2.69759800
H	-0.97856400	-1.92929400	1.87555300
H	-1.25319800	-3.58333700	2.36891100
C	0.66214300	-2.79742200	2.99923000
H	0.75462900	-3.45011100	3.88398500
H	1.14505500	-3.33285900	2.17554800
C	1.37521500	-1.50772700	3.25300200
H	0.87292000	-0.77803200	3.88823000
H	0.74575900	-0.43346200	1.67033400
C	2.85590500	-1.39666300	3.11221900
H	3.22512200	-1.98358500	2.26746500
H	3.18144200	-0.36027100	2.98701100
H	3.36650000	-1.78143200	4.01207200
O	0.11435800	0.17923500	1.23295100
Cl	0.48686200	0.29932500	-2.88674800

Figure S20. Cartesian coordinates for **Mn^{IV}-OH-S4.**

C	0.54408000	-3.98029400	-0.96270600
C	-0.79355800	-3.85953700	-0.74030500
C	-1.07823100	-2.45259300	-0.61508900
C	-2.36086100	-1.91113300	-0.51104500
C	-2.63295400	-0.54506700	-0.59536300
C	-3.94985400	0.02137300	-0.74746700
C	-3.79252800	1.35336900	-0.96928000
C	-2.38306000	1.63559800	-0.87612200
C	-1.83335500	2.91678200	-0.84900600
F	-4.95098400	-5.15953100	2.04681100
F	-6.41070300	-3.99511200	-2.29702800
F	-6.76034600	-5.40359900	0.01277000
C	-2.73916900	4.08244400	-1.03725400
C	-2.63888100	4.88355100	-2.17682000
C	-3.69980200	4.43778000	-0.08812900
C	-3.46301900	5.98599100	-2.37466600
F	-1.72779500	4.59298200	-3.11602700
C	-4.53944100	5.53136800	-0.26587400

C	-0.49319200	3.17986100	-0.55943600
C	0.02632800	4.48073600	-0.21450600
C	1.31891600	4.30548000	0.17319200
C	1.62219200	2.90427000	0.01846000
C	2.88191200	2.33296400	0.19062800
C	2.46200700	-2.36160500	-1.02808900
C	1.09974200	-2.65052900	-0.94392200
N	0.09167000	-1.73586600	-0.73488600
N	-1.69310700	0.46048100	-0.67040200
N	0.49948200	2.24049400	-0.42746900
N	2.27753600	0.02874800	-0.46500200
C	3.00299300	-1.10119700	-0.77598900
C	4.40809500	-0.81272600	-0.65524100
C	3.18397300	1.00404600	-0.11676300
C	4.51837300	0.47305500	-0.21736000
Mn	0.29220700	0.25176300	-0.55293600
H	5.42166900	1.02884900	-0.01751900
H	5.20513300	-1.50827300	-0.86822400
H	1.11351400	-4.88622300	-1.10322100
H	-1.53048400	-4.64637400	-0.69369600
H	-4.87451300	-0.53010500	-0.69467800
H	-4.56266100	2.08810000	-1.14495700
H	-0.54371400	5.39714500	-0.22773000
H	2.00988600	5.05523300	0.52622500
C	3.39193600	-3.49021600	-1.30398600
C	3.44300700	-4.08137700	-2.56794800
C	4.22896800	-4.01412800	-0.31706800
C	4.29195300	-5.14725800	-2.84552500
F	2.65531500	-3.62135900	-3.55000100
C	5.08961200	-5.07591700	-0.57113300
F	4.21025000	-3.49652700	0.92244300
C	5.11944200	-5.64311400	-1.84210300
F	4.32215400	-5.69273100	-4.06618000
F	5.87817500	-5.55865200	0.39502100
F	5.93990600	-6.66435000	-2.09750800
C	-3.50827200	-2.85339200	-0.39216200
C	-3.69945800	-3.61624300	0.76159900
F	-3.83311800	3.71742700	1.03848900
C	-4.41740200	6.30855100	-1.41432700
F	-3.34749700	6.73228800	-3.47834300
F	-5.45100100	5.84655700	0.66047400
F	-5.21562800	7.36300200	-1.59399900
C	3.99404300	3.18612300	0.68737300
C	4.53462100	4.22452900	-0.07308400
C	4.55590100	2.94963400	1.94451800
C	5.58219000	5.00844500	0.39806700
F	4.04370100	4.48576100	-1.29314300
C	5.60701900	3.71644100	2.43406600
F	4.07863500	1.95820300	2.71167100
C	6.11986000	4.75052900	1.65580000
F	6.08164300	5.99738800	-0.35142800
F	6.12336300	3.47124100	3.64334400
F	7.12758700	5.49516200	2.11600700
C	-4.18932500	-1.38979300	3.49764700
C	-4.97987400	-0.41664800	2.89780000
C	-4.39635000	0.76725900	2.43236300
C	-3.02134300	0.96202900	2.55611900
C	-2.22650200	-0.01823000	3.14761200
C	-2.80356400	-1.19985300	3.63281300
H	-4.61951400	-2.31738500	3.85839000
H	-6.04798400	-0.57616000	2.78828900
H	-5.00656600	1.53010400	1.96134100
H	-2.56741400	1.87090900	2.17867600
H	-1.15828700	0.14048000	3.19851800
C	-2.00229200	-2.28016100	4.28300800
O	-2.56116100	-3.22134600	4.83944600
C	1.53376100	-2.81710800	2.70322500
H	1.92479800	-3.46058500	3.51272700
H	1.79217100	-3.32914800	1.77230700
C	2.23044600	-1.49953000	2.75505200
H	2.01693700	-0.79290100	3.55248200
H	0.98171000	-0.36218300	1.58488100
O	0.22116200	0.15126500	1.23778400
Cl	0.43739900	0.40670900	-2.88694100

C	-4.43845100	-3.01850600	-1.42165000
C	-4.78887300	-4.46537600	0.91497200
F	-2.81225400	-3.54961900	1.76394200
C	-5.53398200	-3.86560800	-1.29515000
F	-4.29399300	-2.34131200	-2.57044600
C	-5.71101100	-4.58938100	-0.11944500
H	3.15644500	-1.35452400	2.20815700
C	0.00023900	-2.75968200	2.83316600
H	-0.40656200	-2.12804000	2.04088800
H	-0.40142800	-3.76530200	2.67608700
C	-0.48583800	-2.24214900	4.20154400
H	-0.11294200	-1.22963800	4.37872400
H	-0.10389900	-2.88657500	4.99830400

Figure S21. Cartesian coordinates for **Mn^{IV}-OH-S5.**

C	-0.10907800	-4.01235900	-0.94130800
C	-1.41688200	-3.67804200	-0.76509700
C	-1.47366000	-2.24479900	-0.62047500
C	-2.65446900	-1.50157100	-0.56926200
C	-2.69601600	-0.10791900	-0.63266600
C	-3.89751300	0.66725200	-0.81690100
C	-3.51983100	1.96084100	-0.99352000
C	-2.08789500	2.00859000	-0.84575200
C	-1.33941400	3.18321400	-0.78522300
C	0.02150800	3.22314200	-0.47905500
C	0.75071000	4.42442100	-0.15283100
C	2.00425300	4.04390900	0.21506100
C	2.06917700	2.60986900	0.07789100
C	3.22400000	1.84770000	0.24037100
C	2.04335100	-2.72386000	-0.93968300
C	0.65312900	-2.79126600	-0.87444200
N	-0.19870100	-1.72755800	-0.67546800
N	-1.60413700	0.73351500	-0.64664700
N	0.84657100	2.13383200	-0.34301700
N	2.24564000	-0.33989500	-0.35542400
C	2.77871700	-1.57117500	-0.67124500
C	4.21314000	-1.51336200	-0.56822500
C	3.30407700	0.48211700	-0.03821200
C	4.53501700	-0.25679000	-0.15008200
Mn	0.31914600	0.20291500	-0.47655500
H	5.51734100	0.14888700	0.03809300
H	4.88067200	-2.33640000	-0.77368900
H	0.31223300	-4.99519900	-1.08882200
C	-2.94597600	4.98192800	-0.04048900
C	-2.43475400	6.47980600	-2.31526100
F	-0.93372200	4.83026600	-3.04176200
C	-3.59848300	6.19576600	-0.22306500
F	-3.20849000	4.28745200	1.07969500
C	-3.33849900	6.94735000	-1.36552800
F	-2.18721200	7.20174000	-3.41349800
F	-4.46133900	6.64858100	0.69286400
F	-3.95625300	8.11601500	-1.55006900
C	4.47647600	2.54167400	0.64828700
C	5.17434500	3.36633400	-0.23588800
C	5.00769300	2.37630900	1.92790900
C	6.35393800	4.00360000	0.13303400
F	4.70720100	3.55778100	-1.47764000
C	6.18819700	2.99843500	2.31887200
F	4.37042200	1.60484200	2.82299000
C	6.86202100	3.81514700	1.41533200
F	7.00425300	4.78697700	-0.73430600
F	6.67335100	2.82398200	3.55291900
F	7.99489500	4.41996500	1.77939500
C	-4.68628300	-0.70298700	3.28231500
C	-5.22677000	0.43064800	2.68623000
C	-4.39095500	1.49010000	2.31691500
C	-3.01560000	1.40008300	2.52916400
C	-2.47212800	0.26052500	3.11883000
C	-3.30397000	-0.79752900	3.51303500
H	-5.31454800	-1.53737500	3.57356200
H	-6.29546000	0.49275700	2.50643100

H	-2.27329800	-4.33439400	-0.76505700
H	-4.89994700	0.27125600	-0.81007600
H	-4.15406300	2.81467600	-1.17410200
H	0.33772900	5.42145200	-0.17076200
H	2.81819000	4.67137900	0.54478300
C	2.78390900	-3.97401600	-1.27044700
C	2.90972800	-4.39024700	-2.59672600
C	3.36471200	-4.77506300	-0.28795400
C	3.59093900	-5.55371300	-2.93803100
F	2.36484900	-3.65770100	-3.57772200
C	4.05196800	-5.94211000	-0.60305800
F	3.26306200	-4.42947500	1.00633400
C	4.16391100	-6.33047300	-1.93508900
F	3.69971600	-5.92867000	-4.21716900
F	4.59790500	-6.69191100	0.36034200
F	4.82039200	-7.44903700	-2.25049100
C	-3.94644000	-2.24228300	-0.53923700
C	-4.32375800	-2.99416700	0.57487700
C	-4.83630500	-2.21842300	-1.61660600
C	-5.54775700	-3.64817500	0.64749300
F	-3.48971000	-3.11049000	1.61737600
C	-6.06481200	-2.86843400	-1.57132200
F	-4.52063400	-1.54466800	-2.73267900
C	-6.42299300	-3.58348400	-0.43201800
F	-5.88316000	-4.33556600	1.74481200
F	-6.89767900	-2.81825600	-2.61684000
H	-4.80499800	2.37718600	1.85054100
H	-2.36661500	2.21193300	2.22211000
H	-1.39927500	0.20131500	3.24266400
C	-2.78013500	-2.03187700	4.17305700
O	-3.55184100	-2.87249500	4.62586400
C	0.82461500	-2.91390900	2.93572200
H	1.06091600	-3.65227400	3.72526600
H	1.15245000	-3.38578900	2.00170800
C	1.62903300	-1.67537700	3.17224000
H	1.22320700	-0.92380200	3.84788900
H	0.82137200	-0.51866700	1.70128800
O	0.18097200	0.11614400	1.31124500
Cl	0.54099000	0.33416400	-2.81273200
C	3.10660500	-1.67112100	2.96966700
C	-0.69622200	-2.70334700	2.89430800
H	-0.93668300	-1.96597400	2.12537700
H	-1.17979000	-3.63845500	2.59704500
C	-1.28059200	-2.25308800	4.24889100
H	-0.78656100	-1.33784900	4.58842400
H	-1.10510900	-3.02572600	5.00245600
H	3.62089000	-2.11226500	3.84118700
H	3.39772100	-2.26551700	2.10074600
H	3.50161300	-0.65887600	2.85162800
F	-7.60074500	-4.20920600	-0.37816000
C	-2.04123800	4.48132600	-0.97856200
C	-1.79941800	5.25954700	-2.11272100

Figure S22. Cartesian coordinates for **Mn^{V}-oxo-Hex**.

C	0.25994200	-4.01082200	-0.95739800
C	-1.08472000	-3.82434200	-0.85820800
C	-1.30678500	-2.40466000	-0.75948200
C	-2.56586600	-1.80528700	-0.71091400
C	-2.77325200	-0.43065900	-0.72832800
C	-4.06522700	0.19140800	-0.82888600
C	-3.86196500	1.53387000	-0.92172400
C	-2.44395600	1.75847400	-0.82836100
C	-1.85031800	3.01534400	-0.75964000
F	-7.08205000	-5.17908800	-0.73351500
C	-2.73237100	4.21200800	-0.81626800
C	-2.69816800	5.08407400	-1.90569600
C	-3.61329500	4.51588200	0.22388900
C	-3.50898900	6.21228700	-1.96649900
F	-1.86435100	4.84110700	-2.92663200
C	-4.43790000	5.63424000	0.18286900
F	-3.67869600	3.71744300	1.30135800
C	-4.38213000	6.48550300	-0.91744000

C	-0.48738600	3.21916800	-0.54896800
C	0.10582800	4.50177400	-0.25650800
C	1.41993600	4.28192100	0.00990900
C	1.65356200	2.86759700	-0.14495700
C	2.89697700	2.25800600	-0.02457600
C	2.24700000	-2.48315300	-0.93001000
C	0.87220400	-2.70729300	-0.90565400
N	-0.10150700	-1.74182700	-0.78450100
N	-1.78867300	0.54569400	-0.72592500
N	0.47255300	2.23860000	-0.49123200
N	2.16388300	-0.06057100	-0.46904000
C	2.83550700	-1.23693300	-0.72631500
C	4.25484300	-1.00448900	-0.67520400
C	3.12623900	0.89670900	-0.24299200
C	4.43406700	0.30776900	-0.35581700
Mn	0.18015900	0.25223500	-0.62223200
H	5.36480800	0.84053500	-0.23593500
H	5.01093500	-1.75236300	-0.85880700
H	0.79756400	-4.94276800	-1.04177000
H	-1.86171000	-4.57310300	-0.86601600
H	-5.00650900	-0.33544400	-0.83572500
H	-4.60491900	2.30800400	-1.03425200
H	-0.43027100	5.43784800	-0.22592700
H	2.16935700	5.00485000	0.29278200
C	3.13560500	-3.65788200	-1.14791100
C	3.24459100	-4.24369300	-2.41048700
C	3.87576400	-4.22586300	-0.11020400
C	4.05903300	-5.34746300	-2.63851400
F	2.54918000	-3.73979500	-3.43932100
C	4.69906300	-5.32763900	-0.31340800
F	3.79561300	-3.71500900	1.12963100
C	4.78919100	-5.88880800	-1.58422300
F	4.14755200	-5.88722700	-3.85870800
F	5.39460400	-5.85330200	0.70040200
F	5.57457900	-6.94770400	-1.79116100
C	-3.76119700	-2.69500300	-0.71125500
C	-4.13322800	-3.41941800	0.42192500
F	-3.45877100	7.02995000	-3.02353200
F	-5.27261800	5.90184000	1.19281900
F	-5.16688300	7.56396900	-0.96621200
C	4.07442200	3.11819100	0.27725500
C	4.58241600	4.00705400	-0.67286400
C	4.72113700	3.06107200	1.51271800
C	5.68600100	4.81055600	-0.40933900
F	4.00061600	4.09878400	-1.87693900
C	5.82921300	3.85137900	1.79810100
F	4.27333800	2.23252000	2.46826600
C	6.31129700	4.72936000	0.83174000
F	6.15291100	5.65128500	-1.33863200
F	6.42683800	3.77820000	2.99217500
F	7.37283400	5.49405900	1.09521200
C	-3.48653100	-1.47217000	4.86403800
C	-4.58597100	-0.62012700	4.85367800
C	-4.72356200	0.32880500	3.83500400
C	-3.76185500	0.41698600	2.82721500
C	-2.67372500	-0.45580500	2.81983200
C	-2.52610800	-1.40657100	3.84163300
H	-3.35654700	-2.20531700	5.65255600
H	-5.33341900	-0.68847100	5.63784500
H	-5.57683100	1.00019500	3.83149300
H	-3.85527700	1.16826700	2.05037900
H	-1.91946200	-0.35985400	2.04832000
C	-1.36113200	-2.33936100	3.90473800
O	-1.03490400	-2.85306300	4.97194900
C	-0.60722600	-2.70006100	2.63284100
H	-0.93454800	-2.09856500	1.78995100
H	-0.89065800	-3.73521100	2.40856900
C	0.91469700	-2.59943900	2.78678600
H	1.21218300	-3.14065300	3.69407600
H	1.40199200	-3.09913500	1.94457100
C	1.39744700	-1.15896400	2.87775200
H	0.94920500	-0.64699600	3.73983600
H	0.92008000	-0.58841900	1.97990500
C	2.90176100	-0.94253600	2.82983200

C	-4.54906200	-2.84393700	-1.85465500
C	-5.24400500	-4.25613000	0.42654800
F	-3.40997800	-3.32474300	1.54714500
C	-5.66673900	-3.67078500	-1.87332800
F	-4.23498900	-2.17185600	-2.97136700
C	-6.01295700	-4.38012500	-0.72665900
F	-5.57671300	-4.93637600	1.52880900
F	-6.40383900	-3.79338700	-2.98250000
H	3.31217400	-1.42867000	1.94156400
H	3.11106600	0.12658200	2.73139300
O	-0.04317900	0.21027000	1.15665500
Cl	0.40638800	0.36312100	-2.94672800
C	3.61848200	-1.48619300	4.07585500
H	3.50798700	-2.57182700	4.15559800
H	4.68841200	-1.26009800	4.03038800
H	3.21649200	-1.03825500	4.99093900

Figure S23. Cartesian coordinates for **Mn-TS-Hex4**.

C	-0.36434000	-4.01476400	-0.89912500
C	-1.64973900	-3.59060400	-0.75469800
C	-1.60906100	-2.15663900	-0.61745600
C	-2.73717200	-1.33356200	-0.57374900
C	-2.68147100	0.05767800	-0.61152900
C	-3.82423700	0.91248700	-0.79302200
C	-3.36144500	2.18184500	-0.94778900
C	-1.93285100	2.13649000	-0.79107800
C	-1.11187700	3.25934600	-0.72730000
C	0.24926700	3.20596300	-0.42707500
C	1.06003400	4.35523200	-0.10416300
C	2.28972500	3.89085800	0.24414800
C	2.25757900	2.45637300	0.09995800
C	3.36196500	1.62321500	0.23936100
C	1.86883100	-2.87256300	-0.88140700
C	0.47668600	-2.84629200	-0.82962600
N	-0.30354100	-1.72596800	-0.65448300
N	-1.52982600	0.82789400	-0.60332400
N	0.99699200	2.06180000	-0.30460800
N	2.23014400	-0.50175900	-0.31386700
C	2.67816100	-1.76543000	-0.63241100
C	4.11582700	-1.79701300	-0.56997400
C	3.34605900	0.25247600	-0.03413800
C	4.52648200	-0.55881300	-0.17493500
Mn	0.34156600	0.17010900	-0.45790400
H	5.53677000	-0.21240900	-0.01961500
H	4.72604200	-2.65943400	-0.79107400
F	-6.99427200	-2.33296000	-2.76137600
F	-7.86011100	-3.69827100	-0.56422400
C	-1.72578200	4.60109800	-0.92064700
C	-1.42972300	5.36040400	-2.05498000
C	-2.59706400	5.16220900	0.01474500
C	-1.98013500	6.62082500	-2.25958700
F	-0.59322600	4.87260200	-2.98180500
C	-3.16532200	6.41743200	-0.17004300
F	-2.90978400	4.48770800	1.13420200
C	-2.85236900	7.14904200	-1.31216000
F	-1.68152600	7.32351300	-3.35747100
F	-3.99759100	6.92805800	0.74364400
F	-3.38859200	8.35689900	-1.49851600
C	4.66950000	2.24273100	0.59381100
C	5.38974700	2.99129600	-0.33929100
C	5.22912400	2.08750200	1.86222500
C	6.61840000	3.56339500	-0.02895100
F	4.89551100	3.17079000	-1.57223900
C	6.45832200	2.64621400	2.19537900
F	4.57459700	1.39123000	2.80468300
C	7.15370800	3.38659200	1.24393200
F	7.28875400	4.27379400	-0.94255300
F	6.96984000	2.48319700	3.42027500
F	8.33328100	3.92947600	1.55285500
C	-4.79972400	-0.39072200	3.23996000
C	-5.24848100	0.78999100	2.65866700
C	-4.33355900	1.79325000	2.32229300

H	-0.00863200	-5.02577300	-1.02646500
H	-2.54881600	-4.18695600	-0.76620700
H	-4.85064400	0.58362000	-0.80043900
H	-3.93781300	3.07668300	-1.12337200
H	0.71345700	5.37736600	-0.11249200
H	3.14792500	4.46086700	0.56568900
C	2.52491900	-4.17765700	-1.17159000
C	2.53952600	-4.69443300	-2.46822900
C	3.13047400	-4.93713300	-0.17016800
C	3.13667000	-5.91517600	-2.76361500
F	1.96504500	-4.00661100	-3.46468300
C	3.73618400	-6.15916400	-0.44044400
F	3.12859000	-4.49693000	1.09870300
C	3.73838500	-6.64739900	-1.74410000
F	3.14008200	-6.38593200	-4.01536100
F	4.30675700	-6.86770600	0.53973600
F	4.31576600	-7.81963300	-2.01597000
C	-4.07858500	-1.98199000	-0.58557700
C	-4.54245000	-2.71480900	0.50809300
C	-4.93018000	-1.88549300	-1.68958000
C	-5.80912900	-3.28623900	0.53314100
F	-3.75416600	-2.89491700	1.57663500
C	-6.20054200	-2.45097800	-1.69128000
F	-4.53412000	-1.22103000	-2.78528600
C	-6.64222600	-3.15237900	-0.57299000
F	-6.22558000	-3.96040600	1.61056500
C	-2.97132000	1.60065100	2.55176000
C	-2.52013900	0.41388900	3.12533100
C	-3.43183200	-0.58839900	3.48808200
H	-5.49067900	-1.18246200	3.50749000
H	-6.30712200	0.93235200	2.46555600
H	-4.67590300	2.71654400	1.86805200
H	-2.26096700	2.36930100	2.27075100
H	-1.45654200	0.27612900	3.26621800
C	-3.00655300	-1.86623300	4.13726800
O	-3.84170200	-2.65035100	4.57833300
C	0.55852600	-2.81306200	2.85407600
H	0.85958100	-3.46023500	3.69271100
H	0.86914700	-3.33647600	1.94387100
C	1.32342300	-1.50248600	2.95816300
H	1.01516600	-0.91521700	3.83090500
H	0.93596500	-0.82226300	2.07818700
O	0.12148800	0.13646200	1.32393900
Cl	0.60726400	0.26786500	-2.78948600
C	2.83303600	-1.61738700	2.88723400
C	-0.96400100	-2.63891500	2.84876300
H	-1.22654400	-1.90411100	2.08460600
H	-1.44455900	-3.57872700	2.56138200
C	-1.52776400	-2.19383100	4.21471700
H	-0.97761800	-1.32259200	4.58277800
H	-1.40833400	-2.99648600	4.94719800
H	3.20681100	-2.11035600	3.79502100
H	3.15085000	-2.21867200	2.03459300
H	3.31292100	-0.63914800	2.82262200

Figure S24. Cartesian coordinates for **Mn-TS-Hex5**.

C	1.76674300	-3.69425800	-1.14731000
C	0.46614100	-3.98193000	-0.85855400
C	-0.18922100	-2.73370600	-0.56144000
C	-1.56620600	-2.59019600	-0.33381200
C	-2.22667600	-1.36370400	-0.34383000
C	-3.65745000	-1.18618500	-0.32053600
C	-3.90702100	0.11410500	-0.62937000
C	-4.24312700	2.68550500	-2.59503300
C	-4.30555400	3.87901700	-0.53640800
C	-5.38517000	3.34674100	-3.03076800
F	-3.68608900	1.78507900	-3.41757000
C	-5.44882900	4.55411200	-0.94996900
F	-3.83117200	4.16966400	0.68749000
C	-5.99100100	4.28671000	-2.20254400

C	-2.63159400	0.77436100	-0.76247100
C	-2.46968100	2.15336600	-0.92938900
C	-1.26596200	2.80951700	-0.66752900
C	-1.10392200	4.23427000	-0.51459900
C	0.14916900	4.44691700	-0.02621300
C	0.80541500	3.16533400	0.03803300
C	2.16107100	2.97718400	0.29640700
C	3.14762800	-1.59102900	-1.05347300
C	1.93155500	-2.27210300	-0.99182400
N	0.72067300	-1.70956800	-0.64914500
N	-1.62354800	-0.13790500	-0.57288900
N	-0.08230200	2.18059700	-0.34828500
N	2.27387300	0.62348800	-0.42111800
C	3.29935800	-0.24294600	-0.71983900
C	4.56040500	0.40871200	-0.47438500
C	2.84773500	1.78878400	0.02541900
C	4.28151200	1.65164700	0.01329600
Mn	0.31974100	0.23882000	-0.48068200
H	4.98032800	2.41977600	0.30778100
H	5.52966600	-0.04225800	-0.62393900
H	2.54700000	-4.38163000	-1.43632700
H	-0.01737900	-4.94638900	-0.87997300
H	-4.37684100	-1.95777100	-0.09832500
H	-4.86512500	0.60479600	-0.69425200
H	-1.86190000	4.97333200	-0.72009100
H	0.60181200	5.39040700	0.23702200
C	4.37910300	-2.36737200	-1.35785000
C	5.07596500	-2.17446500	-2.55156400
C	4.89791800	-3.29418700	-0.45150400
C	6.23906600	-2.87947000	-2.84212700
F	4.62430400	-1.28878400	-3.45042800
C	6.05600800	-4.01409200	-0.72142200
F	4.27615200	-3.50368200	0.72000400
C	6.72764900	-3.80329300	-1.92270400
F	6.88582400	-2.67932600	-3.99551200
F	6.53237400	-4.89539100	0.16457600
F	7.84212900	-4.48674200	-2.19184600
F	-5.90024500	3.08906800	-4.23753700
F	-6.03242400	5.44832700	-0.14497500
F	-7.08803000	4.92869300	-2.60834900
C	2.95901700	4.12845500	0.80126900
C	3.32975400	5.19299700	-0.02066000
C	3.38852200	4.15833700	2.12902700
C	4.08797200	6.25650000	0.45714100
F	2.94866100	5.20710400	-1.30623700
C	4.15193600	5.20787000	2.62822200
F	3.06453200	3.15310000	2.95543300
C	4.50131200	6.26003900	1.78637700
F	4.42881600	7.26661800	-0.35082100
F	4.54910300	5.21408700	3.90552700
F	5.23239700	7.27421700	2.25468600
C	-4.72268500	-0.78773500	2.96392800
C	-5.48821600	0.31928100	2.61097900
C	-4.86191000	1.53273200	2.30947000
C	-3.47010100	1.62863800	2.35640900
C	-2.70252400	0.52162200	2.70583300
C	-3.32347800	-0.69630500	3.02044800
H	-5.18832400	-1.73722900	3.20403100
H	-6.57008300	0.24076700	2.57083600
H	-5.45355600	2.40036300	2.03483000
H	-2.98125400	2.56196400	2.10921500
H	-1.62300700	0.60369600	2.69596600
C	-2.53503800	-1.89970800	3.43110300
O	-3.08871300	-2.98085600	3.61209300
C	1.19963900	-2.72852300	4.28235100
H	1.48579800	-1.85449500	4.88230700
H	1.62561100	-3.59771200	4.79643500
C	2.16796300	-1.20619300	2.40991100
H	1.21703500	-0.65150800	1.89188200
O	0.24937000	0.11674900	1.31793800
Cl	0.40530300	0.40378600	-2.82564600
C	-0.32694500	-2.88366400	4.28839200
H	-0.60392300	-3.82533600	3.81293400
H	-0.67652700	-2.95011700	5.32574700

C	-2.37134700	-3.83058900	-0.17713500
C	-2.14567600	-4.69316800	0.89768100
C	-3.36336900	-4.20252300	-1.08945700
C	-2.89630700	-5.84471800	1.09618700
F	-1.16263400	-4.42147000	1.76706900
C	-4.12920000	-5.34985300	-0.91356800
F	-3.59909200	-3.45038200	-2.17426500
C	-3.89635100	-6.17179800	0.18535100
F	-2.65931700	-6.63792900	2.14624900
F	-5.07536500	-5.67558400	-1.80126300
F	-4.62485500	-7.27627900	0.35970600
C	-3.67056200	2.92964800	-1.34067300
C	-1.03935900	-1.73210100	3.59084500
H	-0.64778600	-1.57583500	2.57840600
H	-0.83627800	-0.79176200	4.11471500
C	1.85145000	-2.61240000	2.88722300
H	1.25493400	-3.14705800	2.13642400
H	2.81533800	-3.14184300	2.90450000
H	2.44424700	-0.51482900	3.21111900
H	2.91167700	-1.18622000	1.61411600

Figure S25. Cartesian coordinates for **Mn-TS-Hex6**.

C	0.37723300	-3.97404500	-0.97422000
C	-0.97157800	-3.82958000	-0.87002800
C	-1.24040200	-2.41770000	-0.77017600
C	-2.51747700	-1.86260100	-0.71990500
C	-2.77236700	-0.49273000	-0.73602800
C	-4.08764600	0.08775000	-0.82501500
C	-3.92678900	1.43588500	-0.90283400
C	-2.51305600	1.70067300	-0.81368700
C	-1.95654700	2.97553000	-0.72781200
C	-0.59895800	3.22315600	-0.53043400
C	-0.04582400	4.52144400	-0.23220300
C	1.28011100	4.34462800	0.01106100
C	1.55979400	2.94102800	-0.16347300
C	2.82664400	2.36990600	-0.06421000
C	2.31751000	-2.38843700	-0.96799300
C	0.95013000	-2.65294100	-0.92614500
N	-0.05306300	-1.71740600	-0.79892000
N	-1.82544600	0.50963800	-0.72914700
N	0.39953700	2.27826600	-0.49935300
N	2.16401200	0.03400300	-0.52834500
C	2.87031000	-1.12409800	-0.77978200
C	4.28196800	-0.84867600	-0.72413900
F	-6.34987000	-3.92200000	-2.93906300
F	-6.92788700	-5.37531200	-0.70455300
C	-2.87770200	4.14393100	-0.75982300
C	-2.88881200	5.02641200	-1.84128500
C	-3.75426900	4.40809600	0.29462900
C	-3.73904200	6.12625900	-1.88076500
F	-2.06171200	4.82154200	-2.87605100
C	-4.61765000	5.49738800	0.27524000
F	-3.77726300	3.59917500	1.36614100
C	-4.60703400	6.35944300	-0.81792600
F	-3.73177700	6.95450400	-2.93085700
F	-5.44722500	5.72688500	1.29885800
F	-5.42950900	7.41031700	-0.84623800
C	3.97629100	3.25947700	0.25640000
C	4.45026800	4.19634000	-0.66427700
C	4.63142700	3.18037800	1.48656200
C	5.52756800	5.02695700	-0.37660700
F	3.86015700	4.31042600	-1.86253100
C	5.71388500	3.99674200	1.79540000
F	4.21792300	2.30105000	2.41210400
C	6.16154900	4.92349400	0.85835100
F	5.96164600	5.91491700	-1.27768600

C	3.09732800	1.02160000	-0.29647100
C	4.42164800	0.46749800	-0.40463900
Mn	0.17063900	0.28128000	-0.62205900
H	5.33659700	1.02610200	-0.28083300
H	5.06037900	-1.57473400	-0.90174800
H	0.94276900	-4.88889700	-1.06253600
H	-1.72385600	-4.60304900	-0.87785100
H	-5.01178900	-0.46857900	-0.82944800
H	-4.69314200	2.18915200	-0.99895300
H	-0.61291800	5.43828900	-0.18323500
H	2.00812000	5.09068400	0.28992400
C	3.23961700	-3.53839500	-1.18079100
C	3.36029600	-4.13225600	-2.43855300
C	4.00264900	-4.07481400	-0.14277000
C	4.20677200	-5.21290900	-2.66123800
F	2.64413200	-3.65982800	-3.46812700
C	4.85843500	-5.15246100	-0.34030900
F	3.91535700	-3.55444700	1.09328800
C	4.95921500	-5.72198900	-1.60657600
F	4.30508000	-5.76085400	-3.87708700
F	5.57570600	-5.64654900	0.67428100
F	5.77609400	-6.75782600	-1.80863100
C	-3.68150900	-2.79244100	-0.71294200
C	-4.00085800	-3.55484100	0.41174800
C	-4.49456900	-2.94203100	-1.83867600
C	-5.08581300	-4.42447600	0.42672800
F	-3.24830200	-3.46763200	1.51845400
C	-5.58776100	-3.80117200	-1.84660100
F	-4.23045200	-2.23901900	-2.94947500
C	-5.88268600	-4.54517900	-0.70768900
F	-5.36743700	-5.13944400	1.52134700
F	6.32061700	3.90130600	2.98344900
F	7.19839300	5.71386600	1.14432900
C	-3.49634700	-1.71132200	4.73252200
C	-4.62184000	-0.89483800	4.69924200
C	-4.72860500	0.10654100	3.72813100
C	-3.70923600	0.28284800	2.79121700
C	-2.59241900	-0.55308800	2.80466400
C	-2.47684500	-1.55682300	3.77901700
H	-3.39087200	-2.48516200	5.48499100
H	-5.41403600	-1.03209100	5.42853200
H	-5.60320500	0.74956900	3.70653300
H	-3.78080000	1.07371400	2.05247900
H	-1.79868000	-0.38860300	2.08567200
C	-1.29135100	-2.46145400	3.86244900
O	-1.01488700	-3.02815700	4.91670700
C	-0.45814300	-2.73437400	2.61860000
H	-0.71909800	-2.06353900	1.80546100
H	-0.74195200	-3.74229200	2.29352600
C	1.05638400	-2.69124600	2.88394600
H	1.26126100	-3.33984800	3.75157200
H	1.59092100	-3.13322500	2.03736000
C	1.57565300	-1.31439300	3.15112000
H	1.02403900	-0.70787800	3.86971900
H	0.77567000	-0.32784600	1.59329200
C	2.99972100	-0.94989000	2.87853900
H	3.28109100	-1.28240500	1.87472200
H	3.12405300	0.13682500	2.90526400
O	0.06072000	0.19687300	1.17124300
Cl	0.31467400	0.42776900	-2.95401300
C	3.98357400	-1.59751200	3.88045200
H	3.93490300	-2.68865600	3.82074400
H	5.00983600	-1.29022800	3.65560400
H	3.75324100	-1.30046900	4.90810500

Figure S26. Cartesian coordinates for **Mn^{IV}-OH-Hex4**.

C	0.04567500	-4.01042800	-0.90861500
C	-1.27963800	-3.74420500	-0.77234000
C	-2.76428400	6.44244200	-2.14446600
F	-1.15563300	4.91069800	-2.90218400

C	-1.40937600	-2.30840800	-0.65867300
C	-2.61691300	-1.62398300	-0.63887400
C	-2.73907300	-0.21279500	-0.73302000
C	-3.98915800	0.49784900	-0.91143000
C	-3.68151200	1.81180600	-1.04192500
C	-2.25018100	1.92577900	-0.87398500
C	-1.55910200	3.12142500	-0.76847800
C	-0.17716800	3.23775100	-0.47167800
C	0.47479900	4.48286600	-0.12260300
C	1.76077500	4.17804900	0.18971900
C	1.91172500	2.75223400	-0.00099100
C	3.09494900	2.04578400	0.13079400
C	2.14003700	-2.59931700	-0.93761000
C	0.73309300	-2.73976600	-0.85676700
N	-0.15512800	-1.72541600	-0.70076100
N	-1.70131100	0.66098900	-0.71741600
N	0.69923200	2.20828600	-0.40045200
N	2.23311300	-0.20138800	-0.40569500
C	2.82524600	-1.41979500	-0.69959600
C	4.26339900	-1.28296700	-0.64962600
C	3.24411200	0.66213000	-0.14686000
C	4.52336300	-0.00102900	-0.28073200
Mn	0.25935400	0.23722300	-0.45458300
H	5.48513200	0.46807000	-0.14286100
H	4.97207000	-2.06808500	-0.86225000
H	0.52202900	-4.97159300	-1.02429000
H	-2.10007100	-4.44446300	-0.78795300
H	-4.96983600	0.05327600	-0.92865000
H	-4.35891200	2.63467200	-1.20680900
H	-0.00357700	5.44950000	-0.09243200
H	2.53899700	4.84952800	0.51729800
C	2.91483500	-3.81523200	-1.30638800
C	2.81429600	-4.33350800	-2.60076600
C	3.74394200	-4.48778900	-0.40784900
C	3.51610100	-5.46677800	-2.99328300
F	2.02433800	-3.72742900	-3.49725600
C	4.45473400	-5.62446100	-0.77740700
C	-3.98302200	5.98077400	-0.11411200
F	-3.54610300	4.01864800	1.08971400
C	-3.72199500	6.80900800	-1.20233400
F	-2.51671900	7.23747800	-3.18922200
F	-4.89497000	6.33882200	0.79431300
F	-4.38873700	7.95497400	-1.34180400
C	4.31761600	2.78017900	0.54709100
C	4.91481100	3.74568700	-0.26646600
C	4.92547100	2.50178100	1.77390400
C	6.06914500	4.41490000	0.12502300
F	4.38046400	4.03998600	-1.45886700
C	6.07885200	3.15800000	2.18521700
F	4.38132200	1.58756400	2.59003500
C	6.65131400	4.11808900	1.35433700
F	6.62523600	5.33142700	-0.67278500
F	6.63478000	2.88053100	3.36809000
F	7.75771400	4.75549700	1.73806500
C	-4.42930200	-1.14102600	3.31624600
C	-5.12012000	-0.08536700	2.73306600
C	-4.42636900	1.05753200	2.31852300
C	-3.04219800	1.12538900	2.47106900
C	-2.34665100	0.06188800	3.04421000
C	-3.03565400	-1.07622800	3.48456700
H	-4.94488100	-2.03934600	3.63744100
H	-6.19550700	-0.14771400	2.59881000
H	-4.95898700	1.88598300	1.86427900
H	-2.50156400	2.00060100	2.13114400
H	-1.26863700	0.11983800	3.10727100
C	-2.34276800	-2.23748900	4.12173400
O	-2.99370300	-3.17663000	4.57345000
C	1.32529800	-2.83156600	2.90340200
H	1.57573700	-3.57659000	3.67268400
H	1.67742700	-3.25019000	1.95321600
C	2.08644400	-1.52876600	3.17823600
H	1.77235200	-1.11494600	4.14541500
H	1.79474400	-0.79402000	2.42006500
O	0.11730700	0.19923200	1.19294100

F	3.86106000	-4.05316000	0.85540700
C	4.34061900	-6.11279500	-2.07570600
F	3.40819800	-5.93524400	-4.23998300
F	5.23730700	-6.25082100	0.10620800
F	5.01898800	-7.20115500	-2.44037600
C	-3.86432400	-2.42238200	-0.52124000
C	-4.10531900	-3.19696500	0.61830700
C	-4.85146700	-2.42571000	-1.51163400
C	-5.30326300	-3.87332700	0.80921600
F	-3.17062300	-3.30034900	1.57008900
C	-6.04988800	-3.11084400	-1.35136600
F	-4.65734700	-1.75007600	-2.65307900
C	-6.28014700	-3.82994500	-0.18099600
F	-5.51592700	-4.56207300	1.93468400
F	-6.97579800	-3.09004200	-2.31447000
Cl	0.47877900	0.35707800	-2.92728800
C	3.60610800	-1.70904400	3.18340900
C	-0.19880700	-2.66463500	2.82516600
H	-0.43343300	-1.90447000	2.07499900
H	-0.65389300	-3.60474600	2.49350700
C	-0.82756100	-2.26529100	4.17848400
H	-0.44288400	-1.29144900	4.49467900
H	-0.55296000	-2.99889600	4.94239700
H	3.91960500	-2.42578800	3.95187400
H	3.96033000	-2.08325100	2.21936500
H	4.11769700	-0.76191100	3.37730600
F	-7.43000600	-4.48297400	-0.01517400
C	-2.32160900	4.39006900	-0.91084900
C	-2.07597500	5.24540400	-1.98806300
C	-3.28260700	4.78773900	0.02141800

Figure S27. Cartesian coordinates for **Mn^{IV}-OH-Hex5**.

C	1.75632700	-3.63302000	-1.26926100
C	0.44401100	-3.91844400	-1.04068600
C	-0.21039400	-2.68000600	-0.70748700
C	-1.58815100	-2.54063300	-0.50202500
C	-2.24363900	-1.30941600	-0.47646800
C	-3.67442700	-1.12736200	-0.43300400
C	-3.91924100	0.18609100	-0.68054700
C	-2.64007600	0.84278400	-0.80069800
C	-2.47341900	2.22545800	-0.90809300
C	-1.26240200	2.87152300	-0.65478700
C	-1.09711300	4.29438000	-0.49194100
C	0.16653700	4.50163100	-0.02924100
C	0.81737800	3.21654000	0.02197100
C	2.17093600	3.02091700	0.29310800
C	3.15770000	-1.56028400	-1.01932200
C	1.93116000	-2.22353400	-1.03919800
N	0.71332700	-1.66041700	-0.71327200
N	-1.63631800	-0.08488300	-0.66810500
N	-0.07600600	2.23883700	-0.35859000
N	2.28006700	0.65945400	-0.40585400
F	-4.67599500	-7.21566100	0.13242900
C	-3.68218400	3.03078500	-1.23010000
C	-4.29058900	2.89600600	-2.48251900
C	-4.28712800	3.90607800	-0.32562300
C	-5.44265200	3.59499000	-2.82371700
F	-3.76100700	2.06778000	-3.39397900
C	-5.43994200	4.61576000	-0.64268600
F	-3.77187600	4.07952900	0.90389900
C	-6.01903000	4.45979800	-1.89804900
F	-5.99583700	3.44491400	-4.03191200
F	-5.99724500	5.43611500	0.25444700
F	-7.12543400	5.13616700	-2.21289600
C	2.96994500	4.17646000	0.78774200
C	3.35652300	5.22101100	-0.05249000
C	3.38008400	4.23525200	2.12043400
C	4.11331400	6.29155900	0.41151100
F	2.99124600	5.20878900	-1.34265700
C	4.14210800	5.29216500	2.60625000
F	3.04007100	3.25081900	2.96507900
C	4.50840400	6.32332300	1.74590900

C	3.30761600	-0.22280600	-0.64629400
C	4.56409400	0.41191300	-0.33953200
C	2.84977200	1.82364200	0.05668100
C	4.28055100	1.66422300	0.11676200
Mn	0.31917700	0.28886300	-0.51187500
H	4.97500700	2.42524900	0.43864000
H	5.53217100	-0.05604800	-0.43445400
H	2.53909300	-4.31492500	-1.56381900
H	-0.04820400	-4.87498100	-1.12546700
H	-4.39536500	-1.90401000	-0.23517400
H	-4.87465200	0.68541800	-0.71266900
H	-1.85891100	5.03469500	-0.67993700
H	0.62771100	5.44169000	0.23141900
C	4.39094600	-2.34115600	-1.30397700
C	5.15249300	-2.08610800	-2.44631900
C	4.84626000	-3.33863000	-0.43874800
C	6.31592100	-2.79478500	-2.72542700
F	4.76385400	-1.13483800	-3.30689200
C	6.00383000	-4.06317600	-0.69847100
F	4.16213900	-3.61744700	0.68261900
C	6.74048300	-3.78769100	-1.84721100
F	7.02360200	-2.53290200	-3.82962700
F	6.41722600	-5.01172900	0.14883400
F	7.85487700	-4.47525900	-2.10552200
C	-2.39458300	-3.78257000	-0.37396700
C	-2.15350700	-4.67622900	0.67235100
C	-3.40934100	-4.12342200	-1.27350500
C	-2.91423200	-5.82176400	0.86329600
F	-1.14932300	-4.43689500	1.52783900
C	-4.18386800	-5.26640200	-1.10723900
F	-3.66084400	-3.34380500	-2.33517200
C	-3.93755900	-6.11632800	-0.03259900
F	-2.66392400	-6.63929600	1.89121100
F	-5.15186500	-5.56169100	-1.98203900
F	4.46953000	7.28197600	-0.41411100
F	4.52153800	5.32538600	3.88859000
F	5.23816500	7.34441200	2.20124700
C	-4.65817000	-0.98203500	2.93368700
C	-5.38320300	0.16825100	2.63997000
C	-4.71293600	1.36822200	2.38239900
C	-3.31809600	1.40732300	2.41240400
C	-2.59020500	0.25821800	2.71018100
C	-3.25536900	-0.94658000	2.98030500
H	-5.15862500	-1.92200500	3.13820100
H	-6.46774500	0.13385600	2.61125700
H	-5.27326600	2.26910300	2.15382200
H	-2.79674100	2.33082000	2.19275200
H	-1.50887500	0.29880900	2.68409200
C	-2.51726500	-2.19688500	3.33751700
O	-3.11551200	-3.26401800	3.44554400
C	1.10572500	-3.30238400	4.37608300
H	1.41545200	-2.47982100	5.03406900
H	1.41596600	-4.22472800	4.87941500
C	2.21888000	-1.79346300	2.62797800
H	0.87718500	-0.56987100	1.58995900
O	0.25656700	0.12152900	1.27908200
Cl	0.43664600	0.51295500	-2.84254800
C	-0.42431200	-3.32969400	4.25841300
H	-0.73491300	-4.23139100	3.72809800
H	-0.85591900	-3.40409400	5.26379100
C	-1.01641300	-2.10997500	3.55710100
H	-0.56741400	-1.96678200	2.56633300
H	-0.78317700	-1.19588400	4.11321900
C	1.86724300	-3.18301500	3.03908600
H	1.31424200	-3.68980300	2.23388500
H	2.81065000	-3.75156200	3.11267900
H	2.24717600	-0.99892300	3.36927700
H	2.79797100	-1.64394900	1.72263200

Figure S28. Cartesian coordinates for **Mn^{IV}-OH-Hex6**.

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