

Supporting information

Wacker-type oxidation of styrenes with Markovnikov selectivity using copper as a site-selective sequential photooxidant-photoreductant

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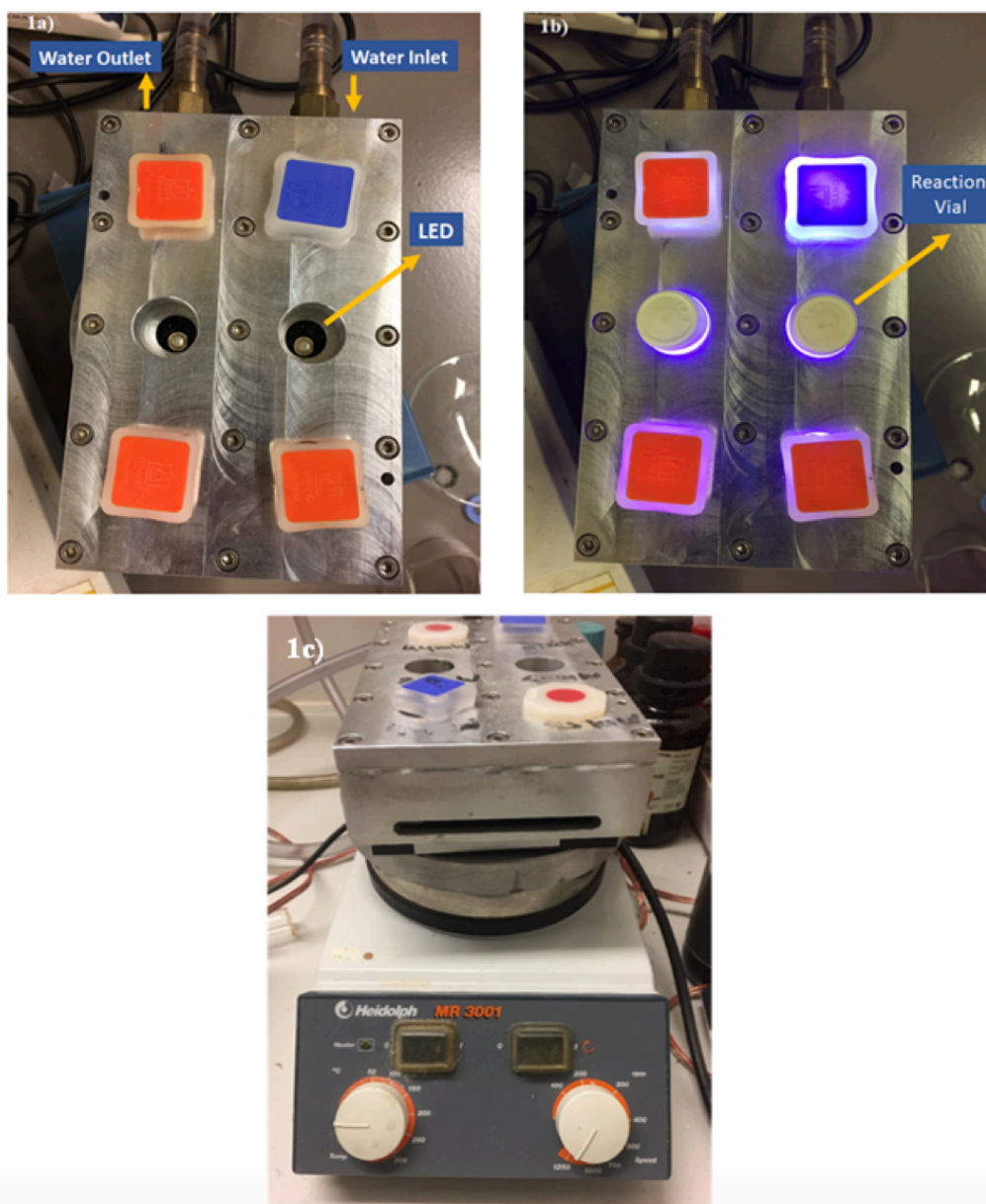
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1. General information

We employed commercially available chemicals without further purification. The synthesized compounds underwent purification following standard procedures. All photochemical reactions took place in oven-dried glassware under atmospheric conditions unless otherwise specified. Reaction mixtures underwent degassing through three freeze-pump-thaw cycles. Prior to use, petroleum ether (hexanes) and ethyl acetate (EtOAc) were distilled. Yields reported refer to isolated compounds, unless specified otherwise. For thin-layer chromatography (TLC), we utilized precoated aluminum sheets (Merck silica gel 60 F254). Visualization was achieved using UV light ($\lambda = 254$ nm). Staining was performed with vanillin (6.0 g vanillin, 100.0 mL ethanol (95%), and 1.0 mL conc. sulfuric acid), potassium permanganate (1.0 g KMnO_4 , 2.0 g Na_2CO_3 , and 100.0 mL distilled water), or Seebach's stain (0.5 g cer. ammonium molybdate, 12.0 g ammonium molybdate, 15.0 mL conc. sulfuric acid, and 235 mL water) followed by heating. Column chromatography involved silica gel (Merck, Geduran 80, 0.063 – 0.200 mm particle size) and flash silica gel (Merck, 0.040 – 0.200 mm particle size). $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra¹ were recorded on Avance III Systems from Bruker, Rheinstetten: (i) Bruker Avance 300 FT-NMR (for 300 MHz $^1\text{H-NMR}$ and 75 MHz $^{13}\text{C-NMR}$) (ii) Bruker Avance 400 FT-NMR (for 400 MHz $^1\text{H-NMR}$ and 101 MHz $^{13}\text{C-NMR}$ and 377 MHz $^{19}\text{F-NMR}$). Field strengths are expressed in MHz, and chemical shifts are reported relative to the solvent residual peak of commercially available NMR solvents CDCl_3 : δ ppm = 7.26; D_2O : δ ppm = 4.79, and DMSO-d_6 : δ ppm = 2.5. Peak multiplicities are designated as follows: s–singlet, d–doublet, dd–doublet of doublet, ddd–doublet of doublet of doublet, dt–doublet of triplet, dtd–doublet of triplet of doublet, t–triplet, td–triplet of doublet, q–quartet, p–pentet, m–multiplet. FTIR spectroscopy was performed on a Cary 630 FTIR spectrometer. Solid and liquid compounds were measured neatly, and the wave numbers are reported as cm^{-1} . Mass spectra were recorded by the Central Analytical Laboratory at the Department of Chemistry of the University of Regensburg on a Varian MAT311A, Finnigan MAT 95, Thermoquest Finnigan TSQ 7000, or Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS. High-resolution mass spectra were performed using electrospray ionization (ESI) or electron ionization (EI) with a quadrupole time-of-flight (Q-TOF) detector." The irradiation was done using Inolux IN-C68QABTMU2 – UV LED (3.08 W electric power @700mA, $\lambda = 365$ nm).

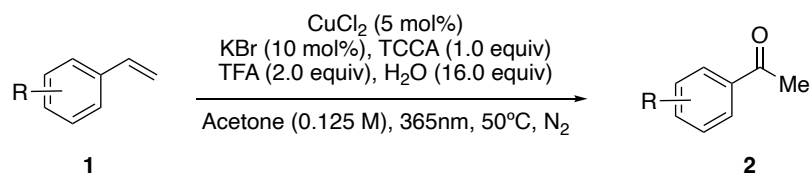
Photochemical setup:



Safety Statement:

Ultra-violet LEDs is harmful for skin and eyes. Caution must be taken during the handling of the LEDs and safety equipment should be worn before switching the LEDs on.

2. Experimental procedures:



General procedure 1 (G.P.1)

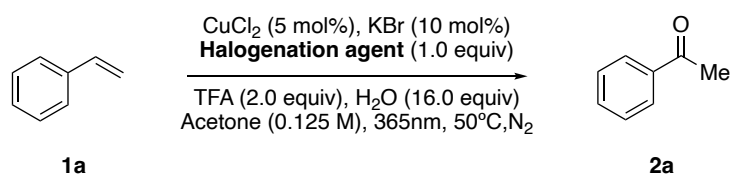
A glass vial was loaded with trichloroisocyanuric acid (TCCA) (0.5 mmol, 1.0 equiv), copper (II) chloride (0.025 mmol, 5 mol%) and potassium bromide (0.05 mmol, 10 mol%) in 4 mL of acetone. A stirring bar was added and the vial was capped with a rubber septum. The reaction mixture was then degassed by nitrogen. Afterwards, water (8.0 mmol, 16.0 equiv), trifluoroacetic acid (1.0 mmol, 2.0 equiv) and the olefin (0.5 mmol, 1.0 equiv) were consecutively injected into the mixture. The vial was then placed in a cooling block and irradiated from the bottom side by a 365 nm LED (3W electrical power) for 16 hours at 50°C. After completion, the solvent was removed in *vacuo*. The crude mixture was then dissolved in 2 mL of dichloromethane and 2 mL of H₂O and transferred into a separatory funnel. The aqueous layer was extracted two times with 4 mL of DCM. The combined organic layers were dried over MgSO₄, filtered and evaporated under reduced pressure. Purification by flash column chromatography furnished the desired products.

General procedure 2 (G.P.2)

G.P.2 is identical to G.P.1 except tribromoisocyanuric acid (TBCA) (0.5 mmol, 1.0 equiv) was used instead of TCCA and the reaction was conducted at room temperature instead of 50°C.

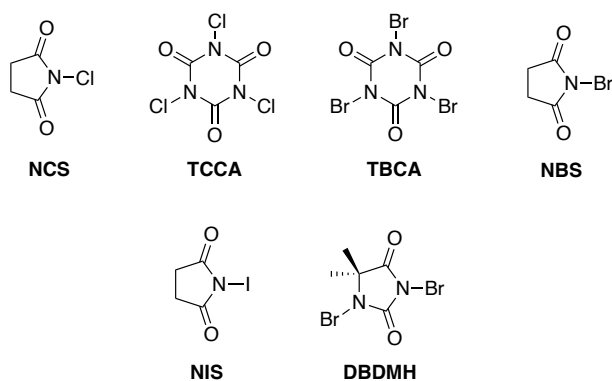
3. Reaction optimization:

Halogenation agent screening:

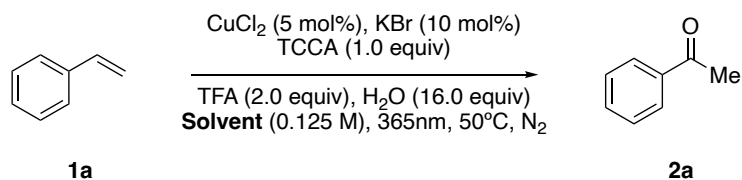


Entry	Halogenation agent	Yield ^a (%)
1	NCS	5%
2	NBS	24%
3	NIS	16%
4	TCCA	89% (34%) ^b
5	TBCA	75% (56%) ^c
6	DBDMH	37%

^a ¹H-NMR yield using tetrachloroethane as internal standard, ^b reaction at room temperature, ^c reaction under 400 nm



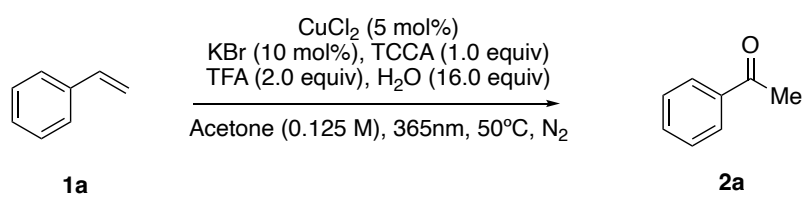
Solvent screening:



Entry	Solvent	Yield ^a (%)
1	Acetone	89%
2	MeCN	60%
3	DCM	c.r.m.
4	CHCl ₃	c.r.m.
5	MeOH	c.r.m.
6	Benzene	c.r.m.

^a ¹H-NMR yield using tetrachloroethane as internal standard

Control experiments:



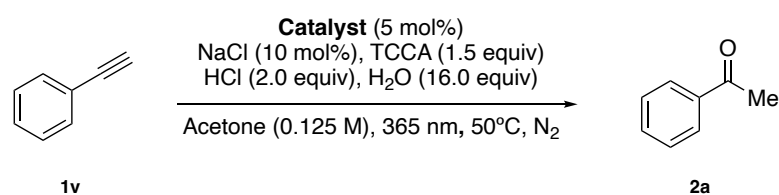
Entry	Conditions	Yield ^a (%)
1	-	89%
2	No light	-
3	No CuCl ₂	25 %

^a ¹H-NMR-yield using tetrachloroethane as internal standard

4. Optimization using phenylacetylene:

A glass vial was loaded with trichloroisocyanuric acid (TCCA) (174.3 mg, 0.75 mmol, 1.5 equiv), copper (II) acetate (4.54 mg, 0.025 mmol, 5 mol%) and sodium chloride (2.9 mg, 0.05 mmol, 10 mol%) in 4 mL of acetone. A stirring bar was added and the vial was capped with a rubber septum. The reaction mixture was then degassed by nitrogen. Afterwards, water (144 mg, 8.0 mmol, 16.0 equiv), hydrochloric acid (1.0 mmol, 2.0 equiv) and phenylacetylene **1v** (51.1 mg, 0.5 mmol, 1.0 equiv) were consecutively injected into the mixture. The vial was then placed in a cooling block and irradiated from the bottom side by a 365 nm LED (3W electrical power) for 16 hours at 50°C. After completion, the solvent was removed in *vacuo*. The crude mixture was then dissolved in 2 mL of dichloromethane and 2 mL of H₂O and transferred into a separatory funnel. The aqueous layer was extracted two times with 4 mL of DCM. The combined organic layers were dried over MgSO₄, filtered and evaporated under reduced pressure. The crude mixture was analyzed via ¹H-NMR using tetrachloroethane as an internal standard.

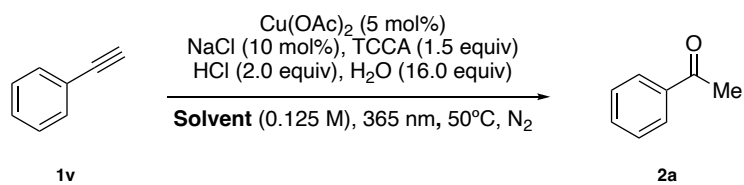
Catalyst screening:



Entry	Catalyst	Yield ^a (%)
1	FeCl ₃	49 %
2	CeCl ₃	24 %
3	Fe(acac) ₃	48 %
4	Cu(acac) ₂	49 %
5	CuCl ₂	42 %
6	Cu(OAc) ₂	45% (45%) ^b

^a ¹H-NMR-yield using tetrachloroethane as internal standard, ^b 10 mol% of Cu(OAc)₂

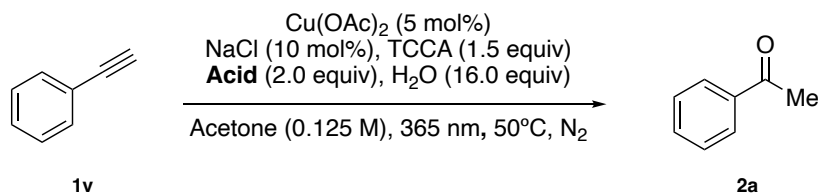
Solvent screening:



Entry	Solvent	Yield ^a (%)
1	Acetone	49%
2	MeCN	44 %
3	EtOAc	35 %
4	DCE	c.r.m.
5	MeOH	c.r.m.
6	DMF	c.r.m.

^a ¹H-NMR-yield using tetrachloroethane as internal standard

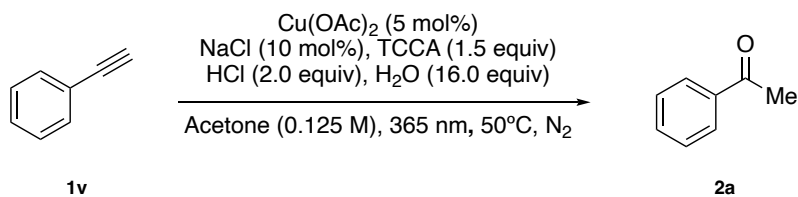
Acid screening:



Entry	Acid	Yield ^a (%)
1	TFA	45%
2	TFAA	16%
3	H ₂ SO ₄	36%
4	PTSA	n.r.
5	MeCO ₂ H	26%

^a ¹H-NMR-yield using tetrachloroethane as internal standard

Control experiments:



Entry	Conditions	Yield ^a (%)
1	No Cu(OAc) ₂	14 %
2	No TCCA	n.r.
3	No HCl	18 %
4	No NaCl	48 %
5	400 nm irradiation	31 %
6	No Light	0 %

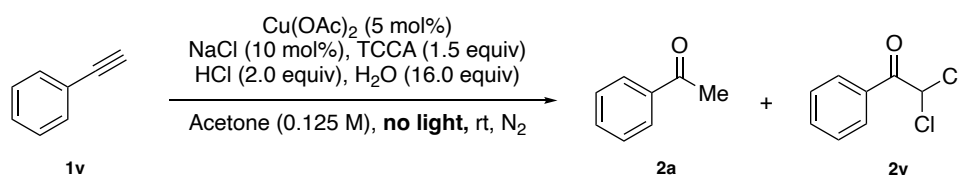
^a ¹H-NMR-yield using tetrachloroethane as internal standard

Phenylacetylene: Dark experiments

A glass vial was loaded with trichloroisocyanuric acid (TCCA) (174.3 mg, 0.75 mmol, 1.5 equiv), copper (II) acetate (4.54 mg, 0.025 mmol, 5 mol%) and sodium chloride (2.9 mg, 0.05 mmol, 10 mol%) in 4 mL of acetone. A stirring bar was added and the vial was capped with a rubber septum. The reaction mixture was then degassed by nitrogen. Afterwards, water (144 mg, 8.0 mmol, 16.0 equiv), hydrochloric acid (1.0 mmol, 2.0 equiv) and phenylacetylene **1v** (51.1 mg, 0.5 mmol, 1.0 equiv) were consecutively injected into the mixture. The vial was then covered with an aluminum foil and stirred for 24h. After completion, the solvent was removed in *vacuo*. The crude mixture was then dissolved in 2 mL of dichloromethane and 2 mL of H₂O and transferred into a separatory funnel. The aqueous layer was extracted two times with 4 mL of DCM. The combined organic layers were dried over MgSO₄, filtered and evaporated under reduced pressure. The crude mixture was analyzed via ¹H-NMR using tetrachloroethane as an internal standard.

2,2-dichloro-1-phenylethan-1-one (2v)

¹H-NMR (300 MHz, CDCl₃): 8.08 (d, 2H), 7.65 (t, 2H), 7.51 (t, 2H), 6.70 (s, 1H). ¹³C-NMR (75 MHz, CDCl₃): 185.94, 134.62, 131.35, 129.77, 128.97, 67.82. HRMS (EI) m/z calculated for C₈H₆Cl₂O (M⁺) 187.9797 found 187.9799. IR (neat, cm⁻¹): 1704, 1595, 1450, 1278, 1220, 812, 776, 687, 654.

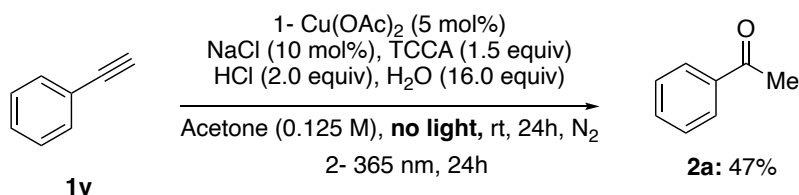


Entry	Conditions	2a ^a (%)	2v ^a (%)
1	-	-	79%
2	Under air	-	86 %
3	No NaCl	-	86 %
4	1.0 equiv of TCCA	-	79 %
5	No $\text{Cu}(\text{OAc})_2$	-	88 %

^a ¹H-NMR-yield using tetrachloroethane as internal standard

Dark-light experiment:

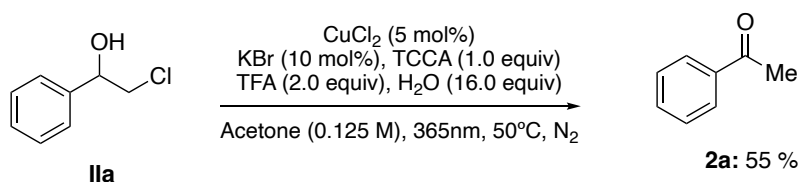
A glass vial was loaded with trichloroisocyanuric acid (TCCA) (174.3 mg, 0.75 mmol, 1.5 equiv), copper (II) acetate (4.54 mg, 0.025 mmol, 5 mol%) and sodium chloride (2.9 mg, 0.05 mmol, 10 mol%) in 4 mL of acetone. A stirring bar was added and the vial was capped with a rubber septum. The reaction mixture was then degassed by nitrogen. Afterwards, water (144 g, 8.0 mmol, 16.0 equiv), hydrochloric acid (1.0 mmol, 2.0 equiv) and phenylacetylene **1v** (51.1 mg, 0.5 mmol, 1.0 equiv) were consecutively injected into the mixture. The vial was then covered with an aluminum foil and stirred for 24h. After completion, the vial was placed in a cooling block and irradiated from the bottom side by a 365 nm LED (3W electrical power) for 24 hours at 50°C. The solvent was then removed in *vacuo*. The crude mixture was then dissolved in 2 mL of dichloromethane and 2 mL of H_2O and transferred into a separatory funnel. The aqueous layer was extracted two times with 4 mL of DCM. The combined organic layers were dried over MgSO_4 , filtered and evaporated under reduced pressure. The crude mixture was analyzed via ¹H-NMR using tetrachloroethane as an internal standard.



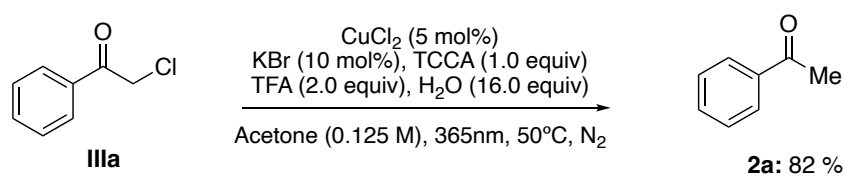
5. Testing intermediates:

In order to prove the validity of our proposed reaction pathway, we have subjected both conceptualized intermediates **IIa** and **IIIa** to our standard conditions following GP1.

Starting from chlorohydrin:



Starting from 2-Chloroacetophenon:

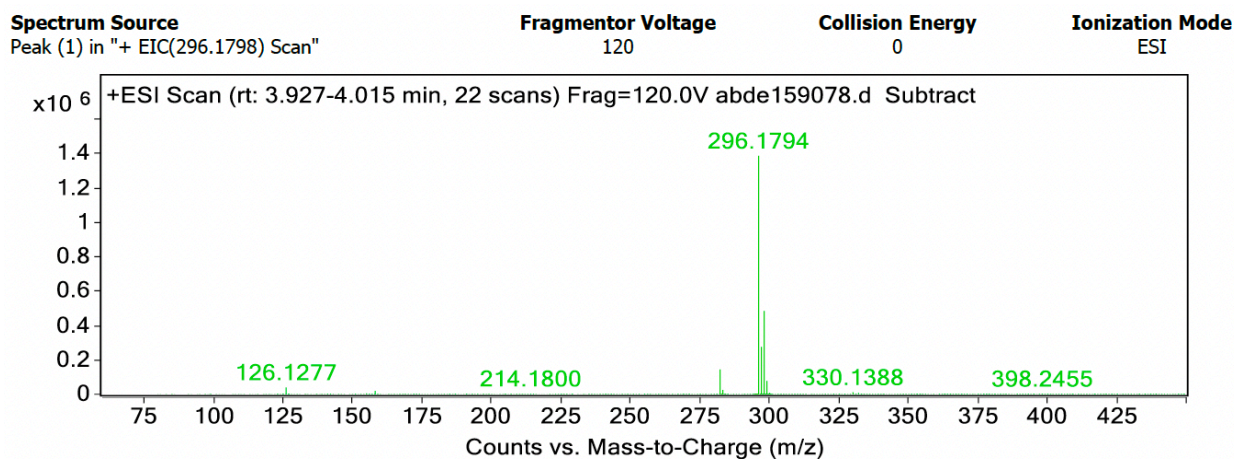
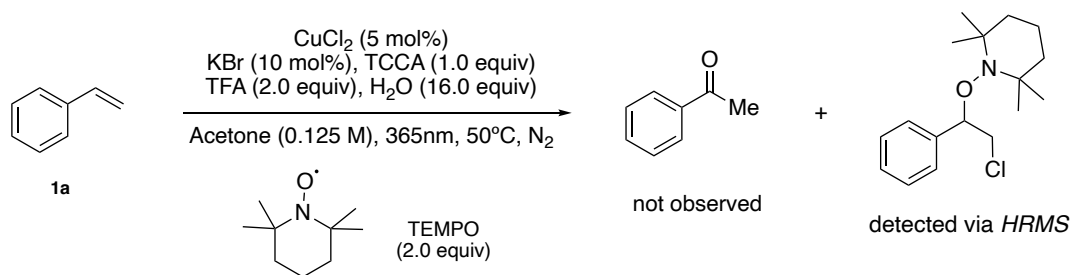


6. Radical trapping experiments:

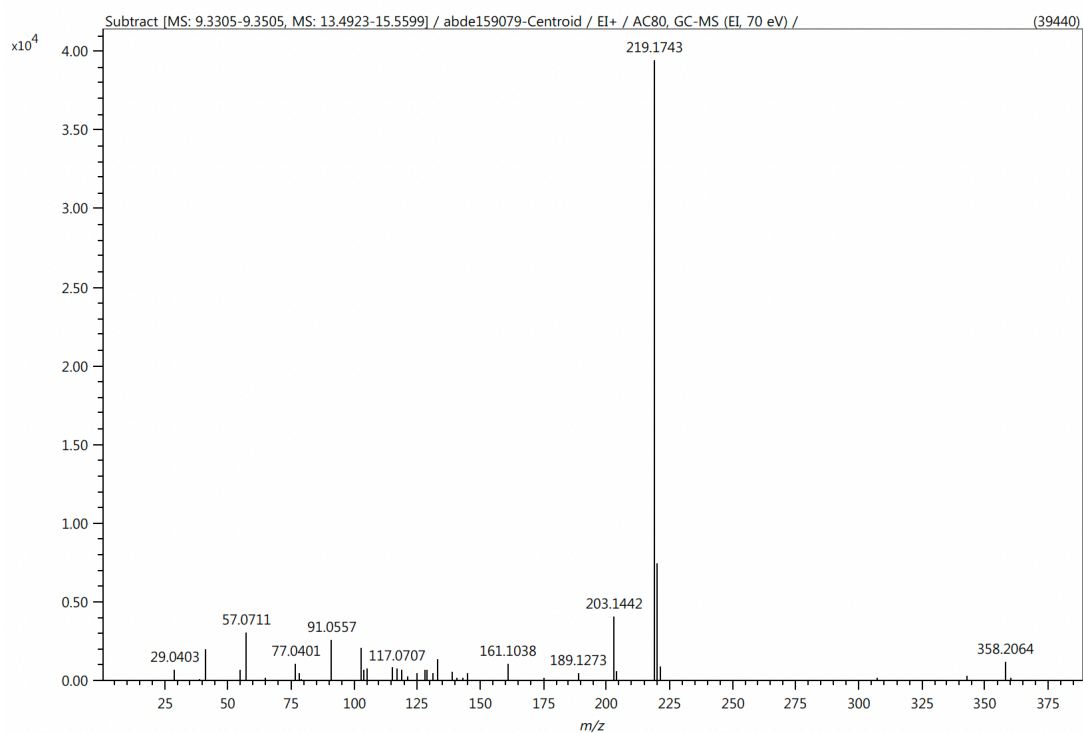
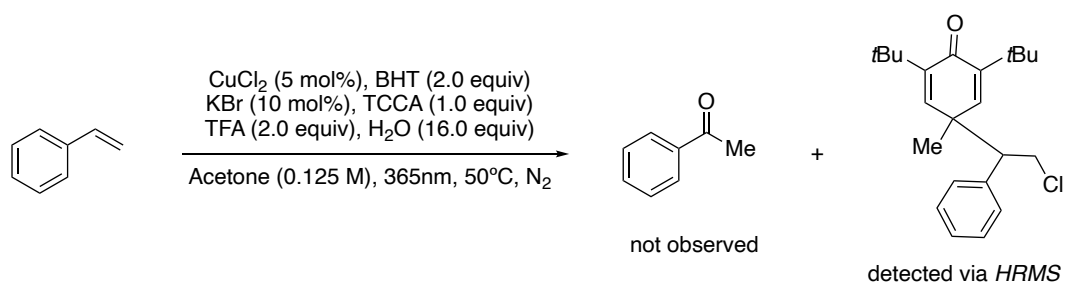
Experimental procedure:

A glass vial was loaded with trichloroisocyanuric acid (58.0 mg, 0.25 mmol, 1.0 equiv), copper (II) chloride (1.68 mg, 0.0125 mmol, 5 mol%), potassium bromide (2.98 mg, 0.025 mmol, 10 mol%) and the radical trapping reagent (0.5 mmol, 2 equiv) in 2 mL of acetone. A stirring bar was added and the vial was capped with a rubber septum. The reaction mixture was then degassed using nitrogen. Afterwards, water (72.0 mg, 4.0 mmol, 16.0 equiv), trifluoroacetic acid (57 mg, 0.5 mmol, 2.0 equiv) and styrene (26.1 mg, 0.25 mmol, 1.0 equiv) were consecutively injected into the reaction mixture. The vial was then irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C. After completion, an aliquot (100 μ L) was taken, diluted with DCM (500 μ L), dried over MgSO₄ and filtered. The remaining solution was passed through a syringe filter for further GC-MS analysis.

TEMPO trapping:



BHT trapping:



7. ¹⁸O-labelling experiment:

An oven dried vial was equipped with trichloroisocyanuric acid (58.0 mg, 0.25 mmol, 1.0 equiv), copper (II) chloride (1.68 mg, 0.0125 mmol, 5 mol%) and potassium bromide (2.98 mg, 0.025 mmol, 10 mol%) in 2 mL of solvent. A stirring bar was added and the vial was capped with a rubber septum. The reaction mixture was then degassed by nitrogen. Afterwards, H₂¹⁸O (80.1 mg, 4.0 mmol, 16.0 equiv), trifluoroacetic acid (57.0 mg, 0.5 mmol, 2.0 equiv) and styrene (26.1 mg, 0.25 mmol, 1.0 equiv) were consecutively injected into the mixture. The reaction was irradiated for 16h at 50°C. After completion, the reaction mixture was allowed to cool down to room temperature and charged with trimethoxybenzene as ¹H NMR internal standard. An aliquot (100 μL) was taken, diluted with DCM (500 μL), dried over MgSO₄ and filtered. The remaining solution was passed through a syringe filter for further GC-MS analysis. The ¹⁸O enrichment percentage was determined according to literature² using the following formula.

¹⁸O enrichment equation:

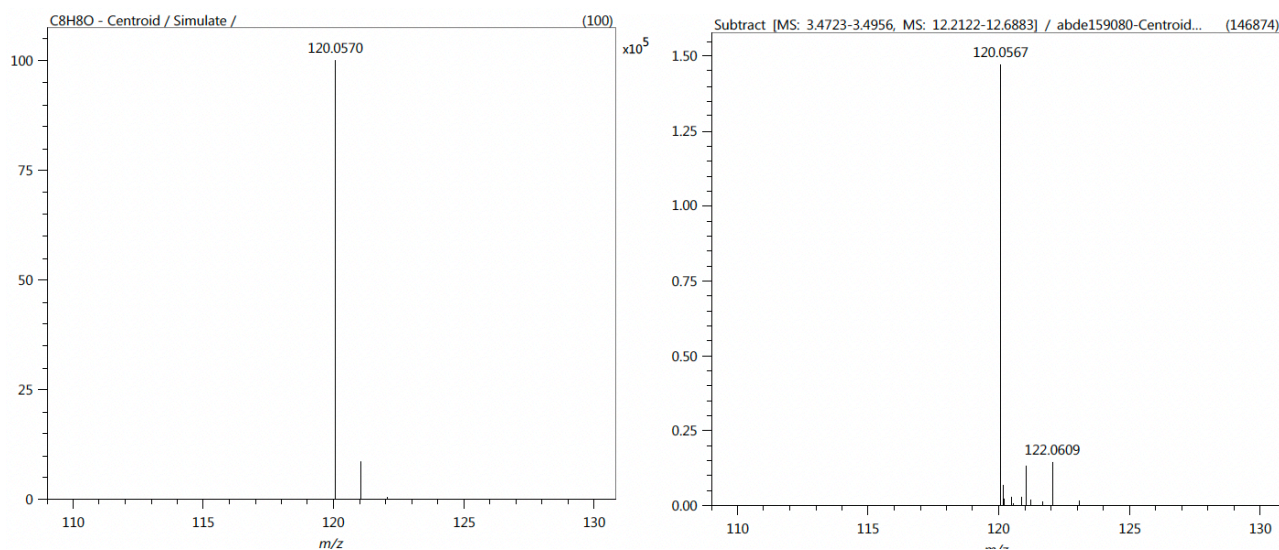
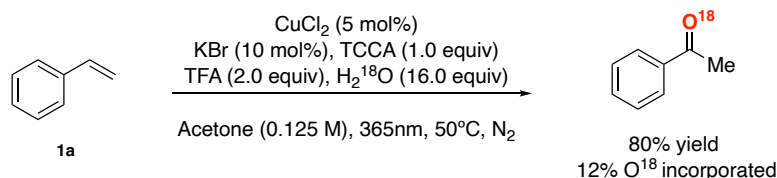
$$100 \cdot \frac{Rx - Ro}{1 + (Rx - Ro)} ; \quad R = \frac{m/z + 2}{m/z + 0}$$

Rx = experimental

Ro = formula isotopic distribution

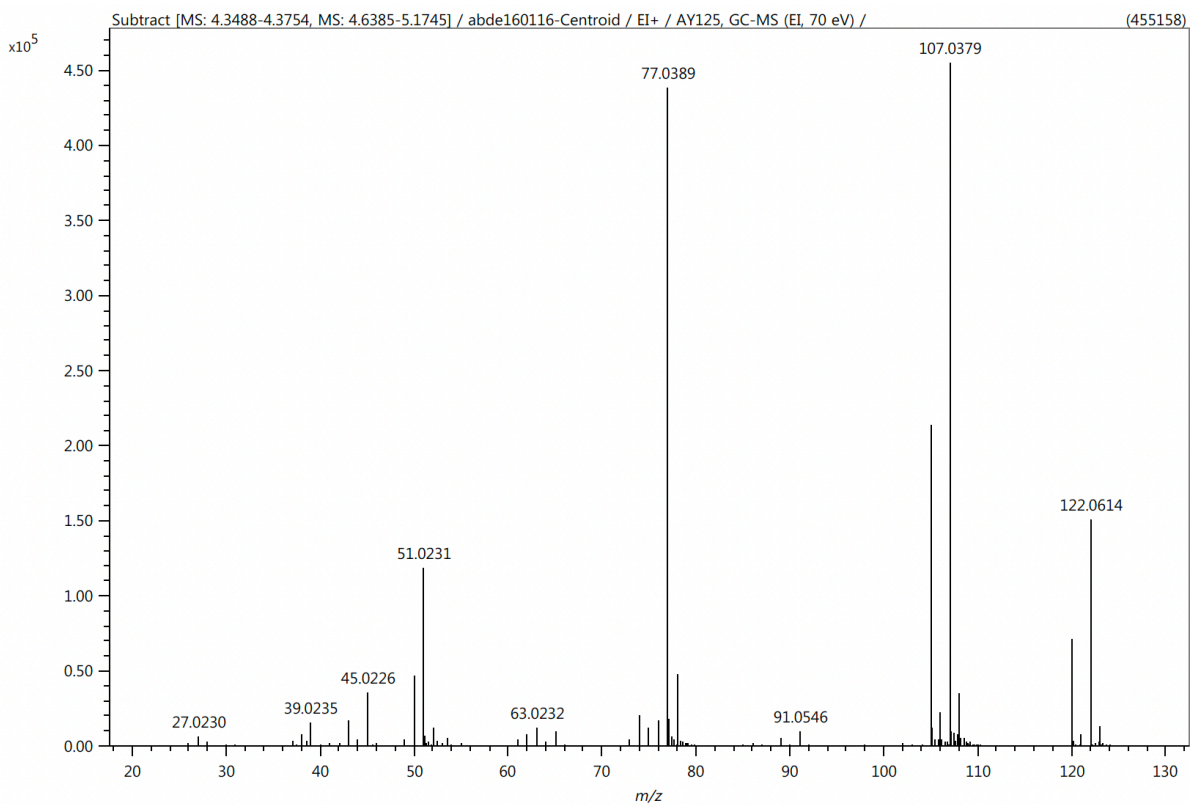
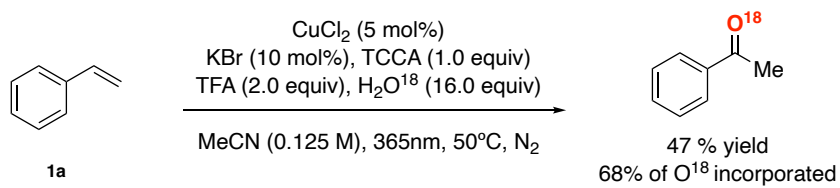
The ¹⁸O labelling was conducted in acetone and in MeCN as solvents. This was due to the low enrichment we obtained in acetone caused by self-condensation (catalyzed by TFA) present which released an extra amount of H₂¹⁶O and perturbed the experiment. However, in MeCN, 68% incorporation was observed.

In acetone:

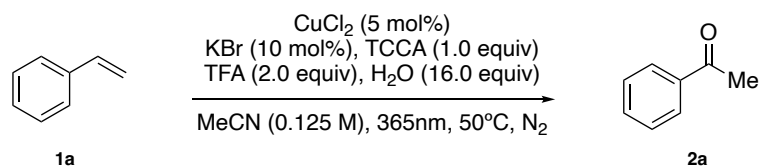


Acetophenone: Simulated spectra (left) vs measured spectra (right)

In MeCN:



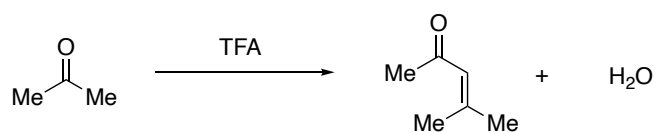
Formation of water through acetone:



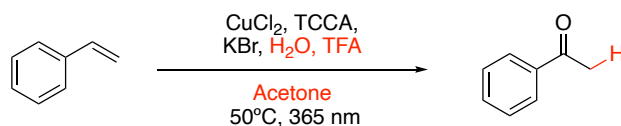
Entry	Conditions	Yield ^a (%)
1	-	60 %
2	No H_2O , 16 equiv of acetone	50 %
3	No H_2O , no acetone	0 %

^a $^1\text{H-NMR}$ -yield using tetrachloroethane as internal standard

Formation of water (side-reaction)



8. D-labelling experiments



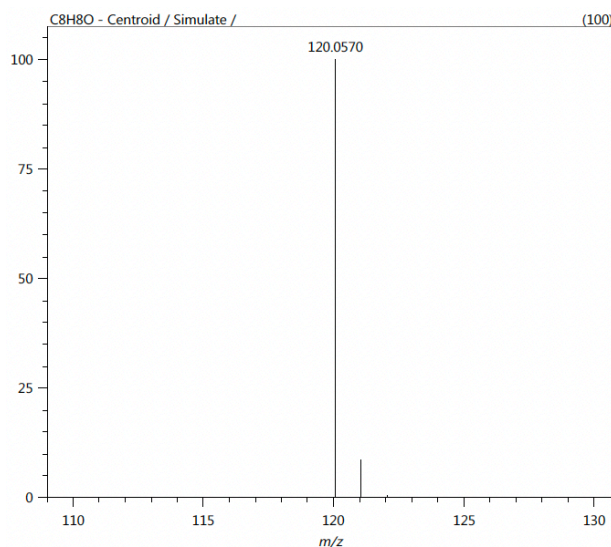
From a general point of view, the reaction consists of the addition of a hydrogen and oxygen atoms over an unsaturated olefin. Looking at the standard conditions, the source of the hydrogen atom can whether be H_2O , TFA or acetone. We have decided to perform deuteration labelling experiments to determine the nature of the H-donor for our system.

Procedure:

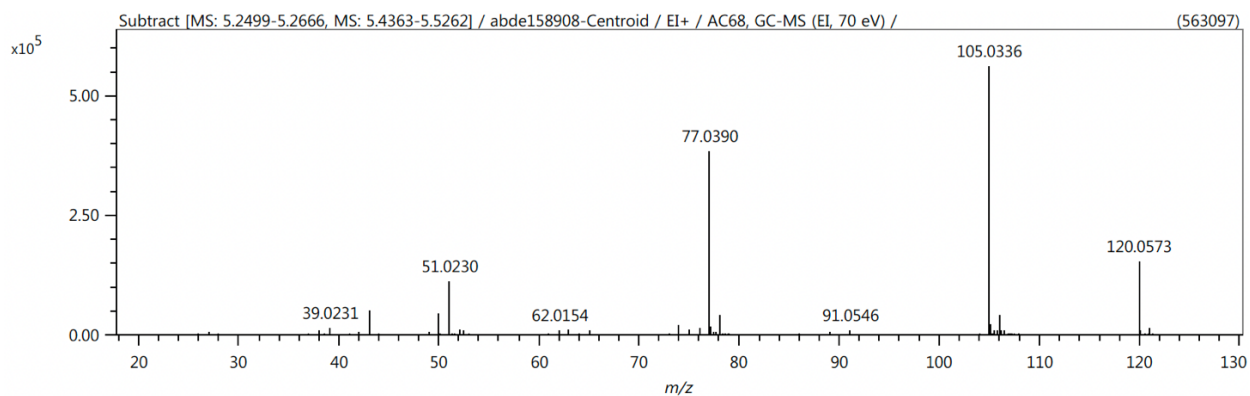
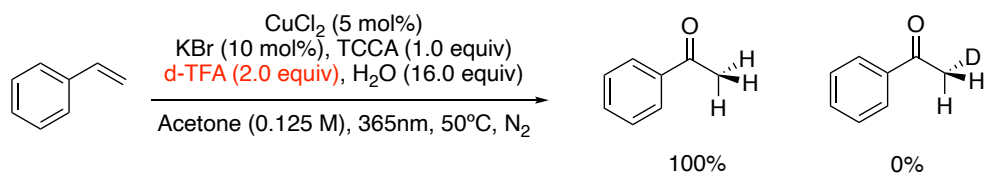
The reaction was set-up using the general procedure (G.P.1) while using the correspondent deuterated reagent. After completion, the reaction was allowed to cool to room temperature. An aliquot (100 μL) was taken, diluted with DCM (500 μL), dried over MgSO_4 and filtered. The remaining solution was passed through a syringe filter for further GC-MS analysis. The Deuterium incorporation was calculated using the formula:

$$R = 100 \cdot \frac{m/z + x}{\sum m/z + x}$$

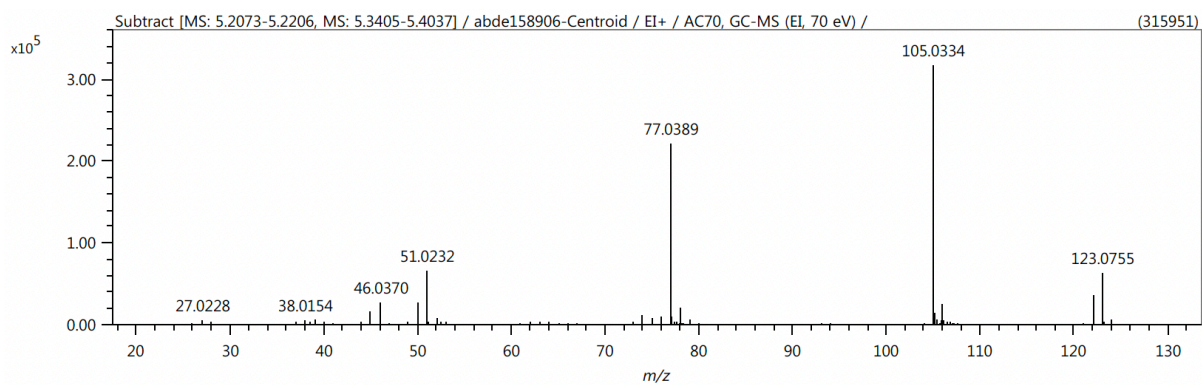
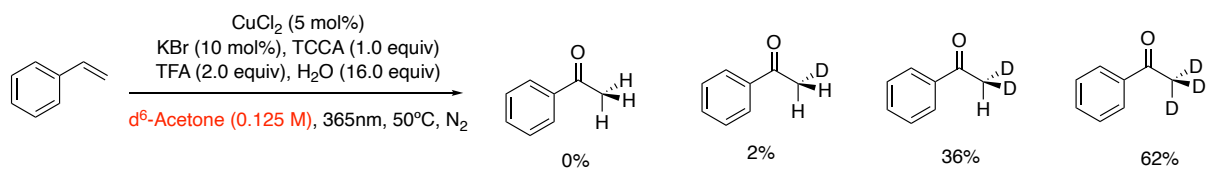
Simulated Mass spectra of acetophenone:



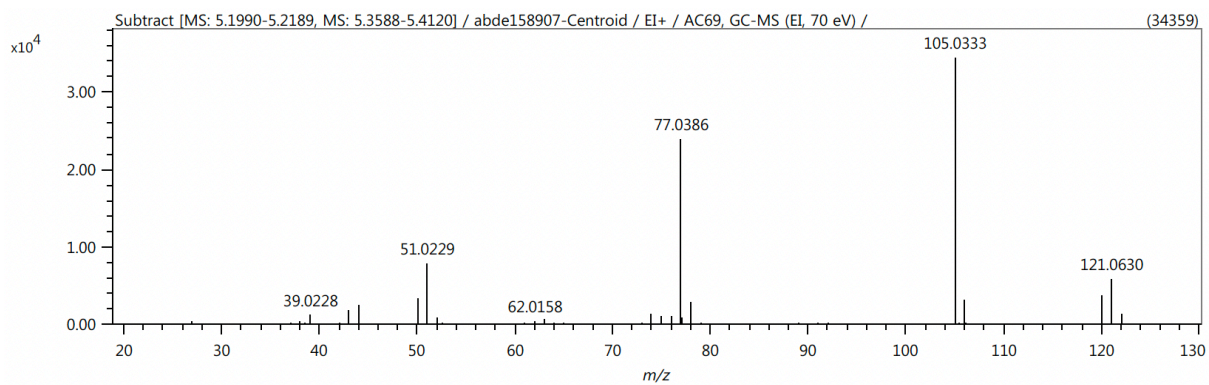
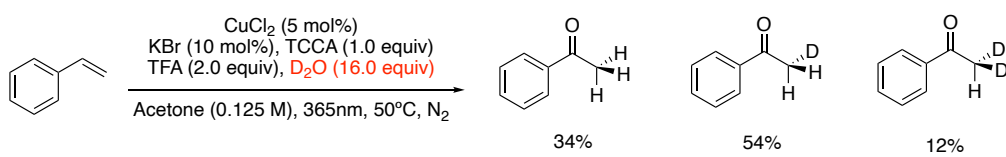
Using *d*-TFA:



Using *d*⁶-acetone:



Using D₂O:



9. UV-vis measurements:

UV-vis measurements were recorded using a SPECTRORECORD 200 PLUS spectrophotometer by analytikjena, while employing a Macro cell type 110-QS quartz cuvette with a PTFE stopper (Hellma Analytics quartz cuvette, 10×10 mm, 3.5 mL). The measurements were recorded using acetone as a solvent.

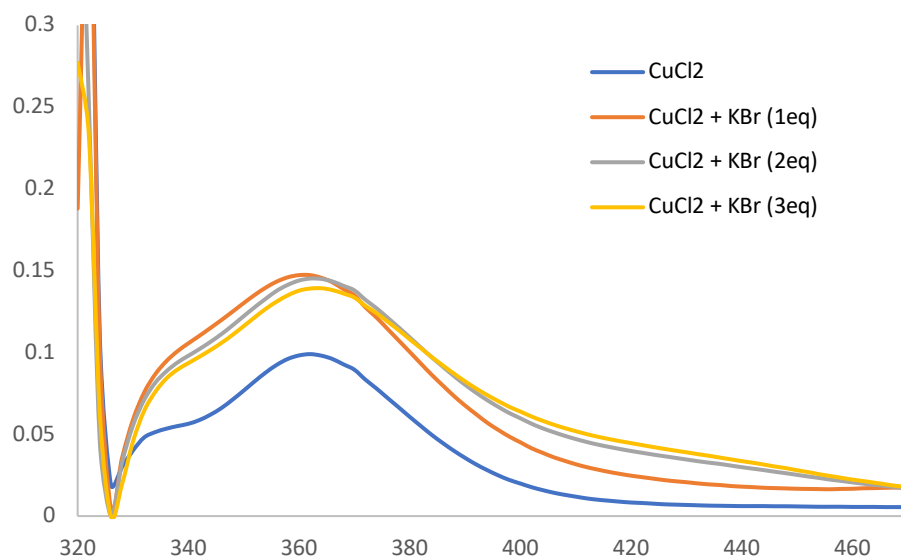


Figure 1: Absorption profile of CuCl₂ and KBr mixtures

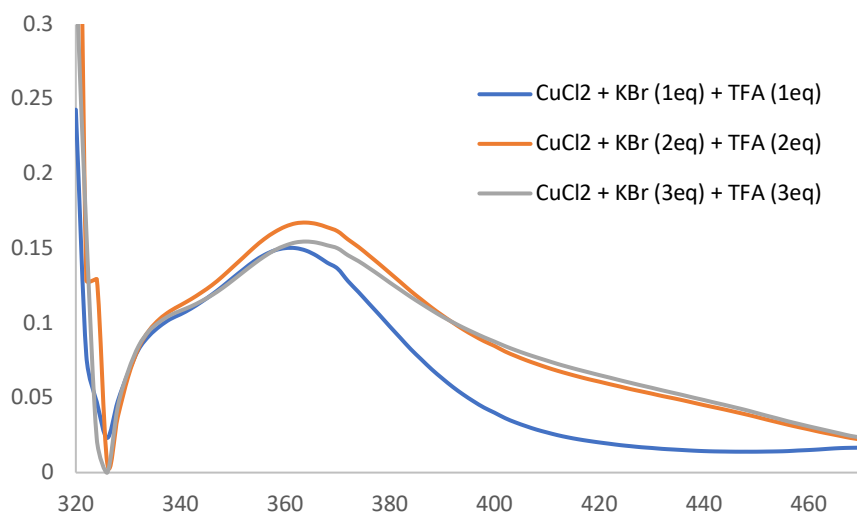


Figure 2: Absorption profile of CuCl₂, KBr and TFA mixtures

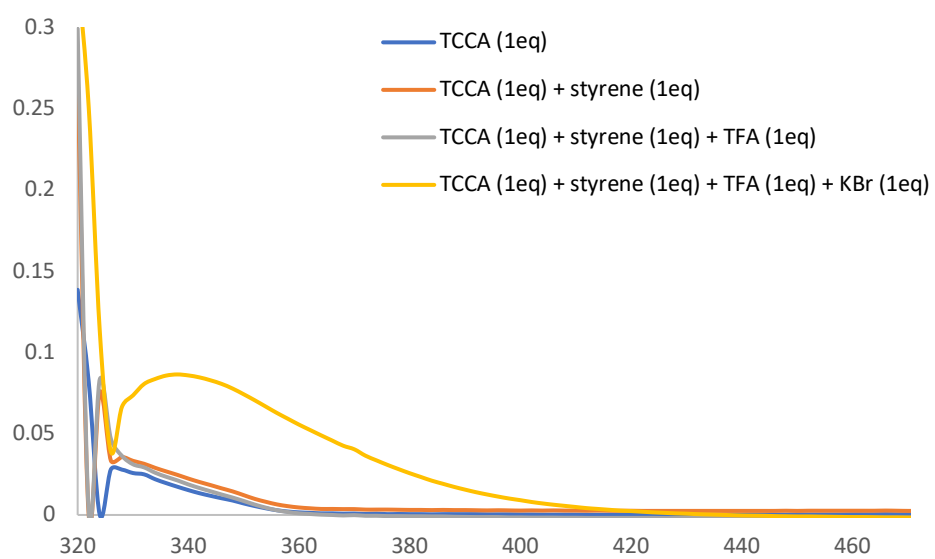


Figure 3: Absorption profile of other reaction components

10. Role of Copper:

Copper-TCCA fluorescence quenching:

The interaction between the catalyst CuCl_2 and TCCA was assessed by recording fluorescence emission spectra through irradiation at 365 nm. These measurements were conducted using a HORIBA Fluoromax-4 from Horiba Scientific, employing a High Precision Cell 117100F-10-40 quartz cuvette with a screw cap (Hellma Analytics quartz cuvette, dimensions: 10×10 mm, capacity: 3.5 mL)

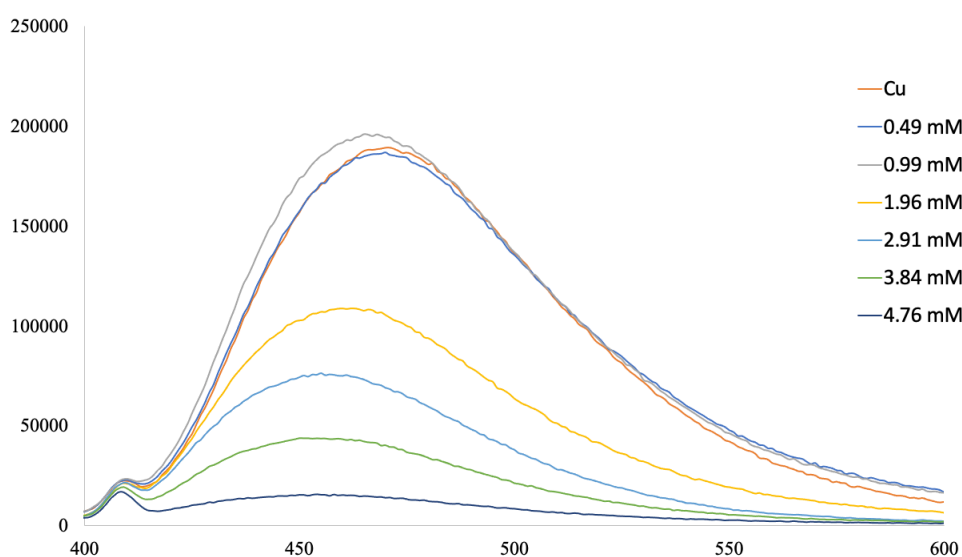


Figure 4: CuCl_2 emission quenching using TCCA as quencher

TCCA was proven to quench the photocatalyst. The Stern-Volmer plot and quenching constants were calculated. solutions under nitrogen atmosphere were freshly prepared prior to the measurements. The mixtures were irradiated at 365nm and the data for the plot was collected from the maximum emission wavelength (466 nm).

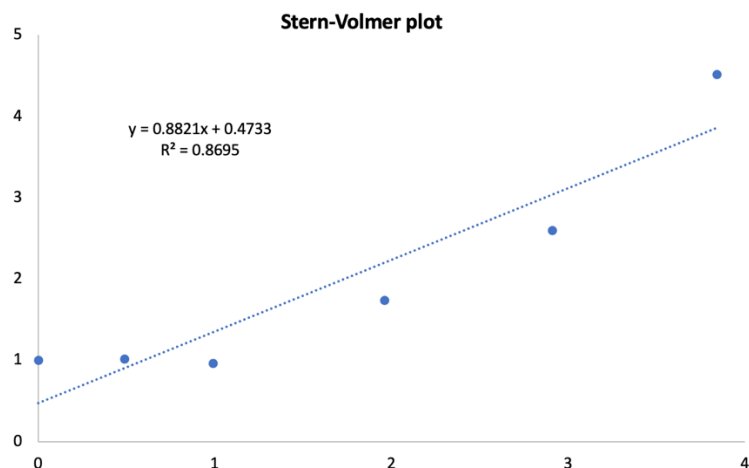


Figure 5: Stern-Volmer quenching plot of CuCl_2 using TCCA as quencher

Copper interaction with intermediates:

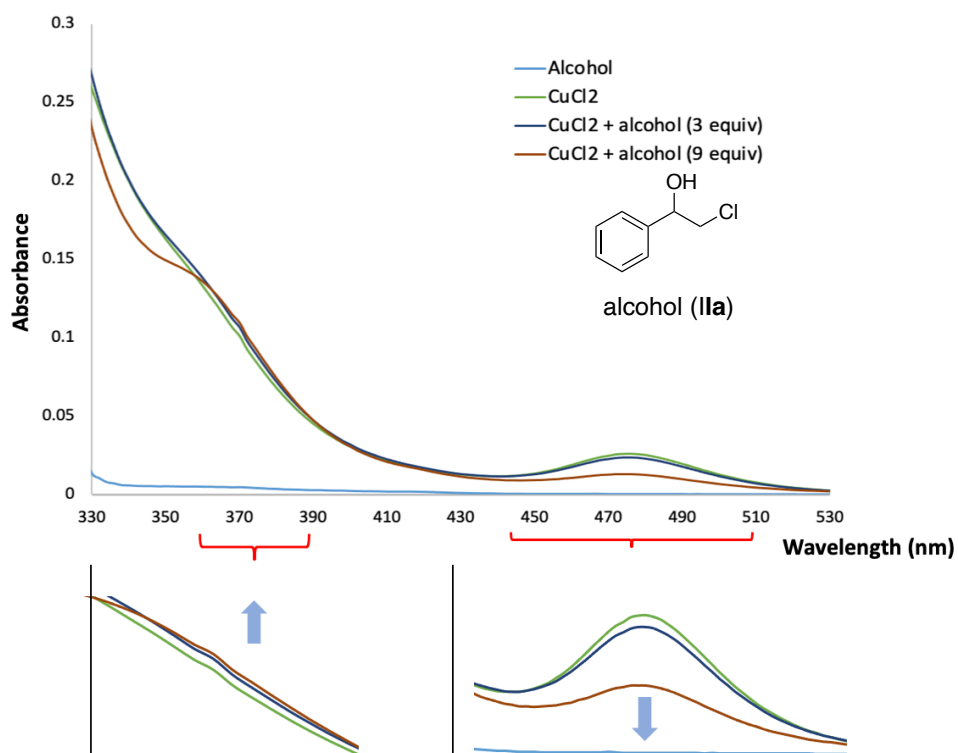


Figure 6: Absorbance variation of copper-alcohol complex

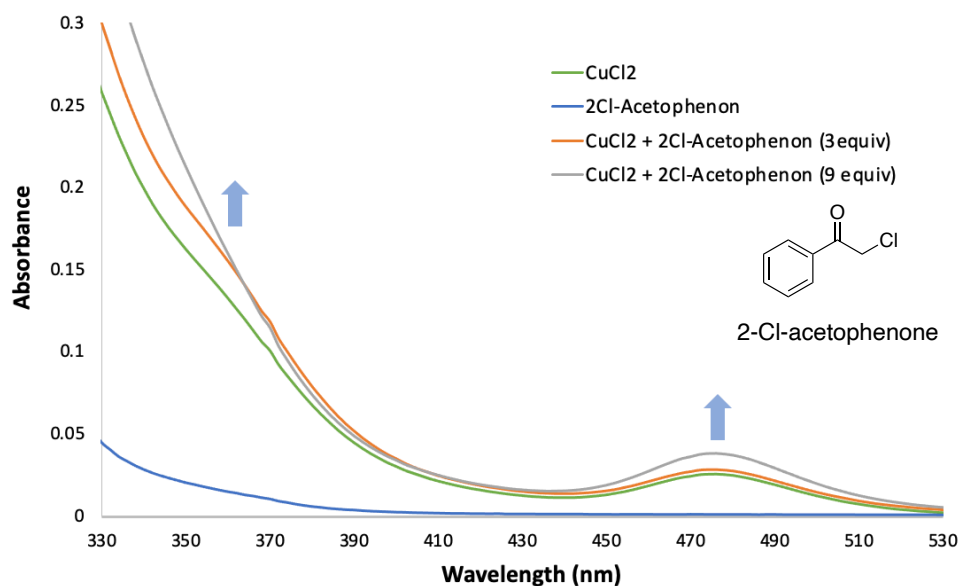
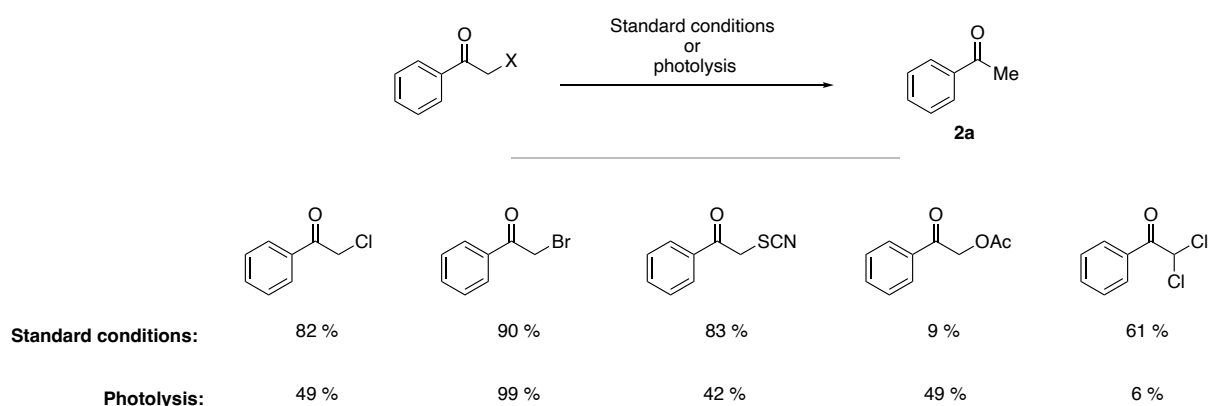


Figure 7: Absorbance variation of copper-2-chloroacetophenone complex

11. Reductive dehalogenation:

Procedure under standard conditions: The reaction was performed following G.P.1 using α -substituted acetophenone instead of styrene.

Procedure of the photolysis reactions: In an oven dried vial, 2-chloroacetophenone (0.25 mmol) was diluted in acetone (2 mL). The vial was charged with a stirring bar, capped with a rubber septum and bubbled with nitrogen. The reaction was then irradiated at 365 nm for 16 hours at 50°C. Afterwards, the reaction was concentrated in *vacuo*, charged with tetrachloroethane ($^1\text{H-NMR}$ internal standard), dissolved in CDCl_3 and added directly to an NMR tube for quantitative analysis.

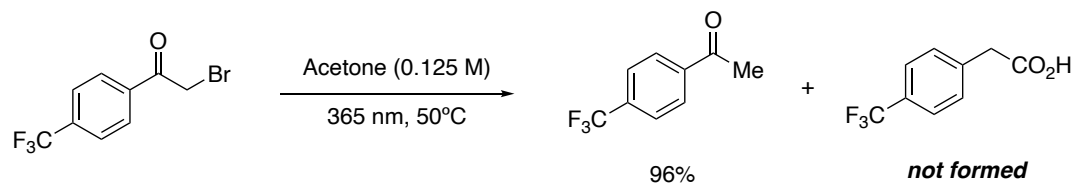
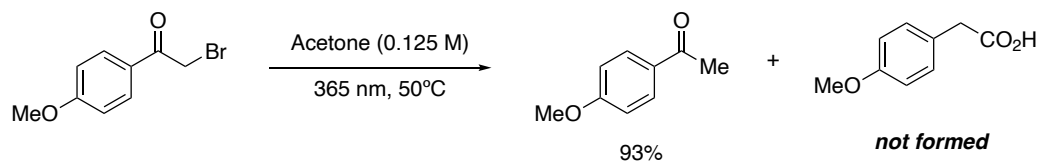


Reductive dehalogenation: case of substituted styrenes

We were interested to evaluate the substituents effects on the homolysis of 2-haloacetophenone derivatives to understand why certain electron rich styrenes do not afford the desired acetophenone when TCCA was used.

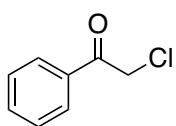


In the case of 2-bromoacetophenones, the outcome is independent of the electronics involved in the phenyl ring and let to the corresponding acetophenones selectively.



12. Cyclic voltammetry analysis:

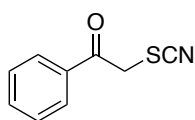
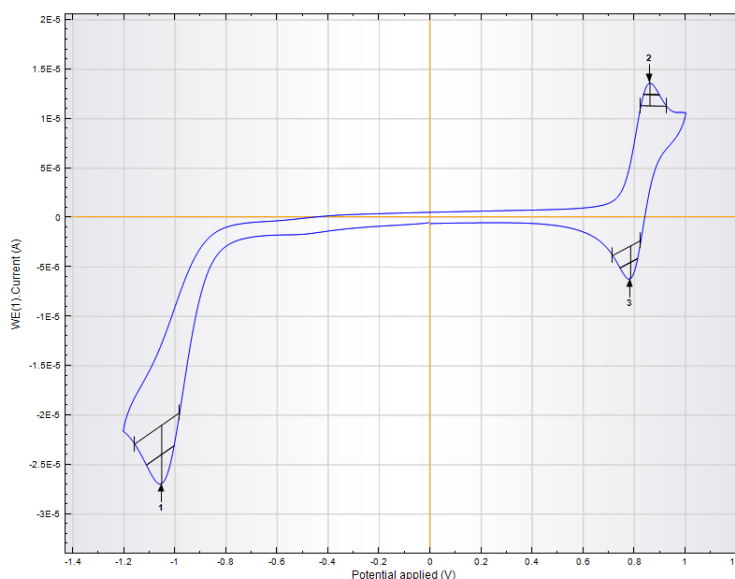
Cyclic voltammetry was measured on a three-electrode potentiostat galvanostat PGSTAT302N from Metrohm Autolab using a glassy carbon working electrode (3mm in diameter), a platinum wire as counter electrode and a silver wire as a reference electrode. The cyclic voltammograms were recorded in acetone with NBu_4BF_4 as electrolyte using ferrocene (Fc/Fc^+) as an internal standard. Measurements were carried out at room temperature with a scan rate of 50 mV/s. Potentials vs SCE were calculated using the formula: $E_{\text{SCE}} = E_{\text{Fc}/\text{Fc}^+} + 0.38 \text{ V}$.



2-chloro-1-phenylethan-1-one

$E_{\text{red}} = -1.50 \text{ V vs SCE}$

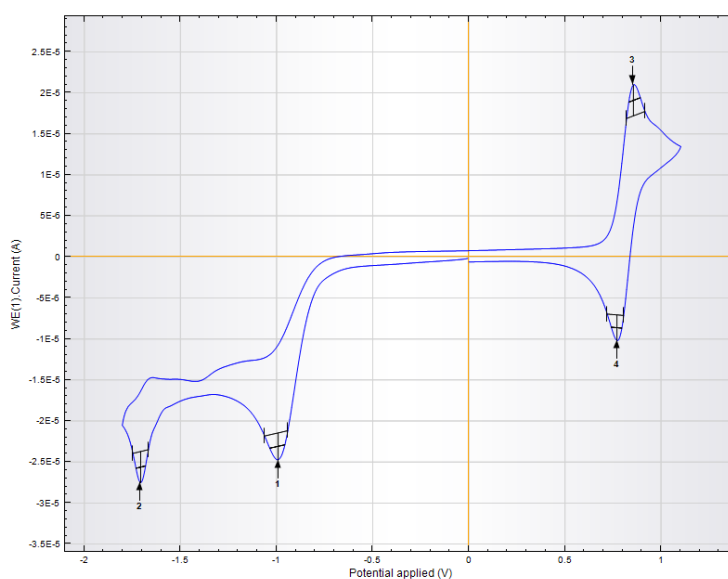
Index	Peak position vs Ferrocene
1	-1.0524
2	0.86105
3	0.78552

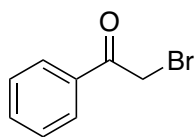


1-phenyl-2-thiocyanatoethan-1-one

$E_{\text{red}} = -1.43 \text{ V vs SCE}$

Index	Peak position vs Ferrocene
1	-0.99197
2	-1.707
3	0.85602
4	0.77042

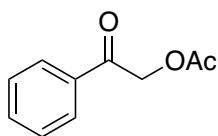
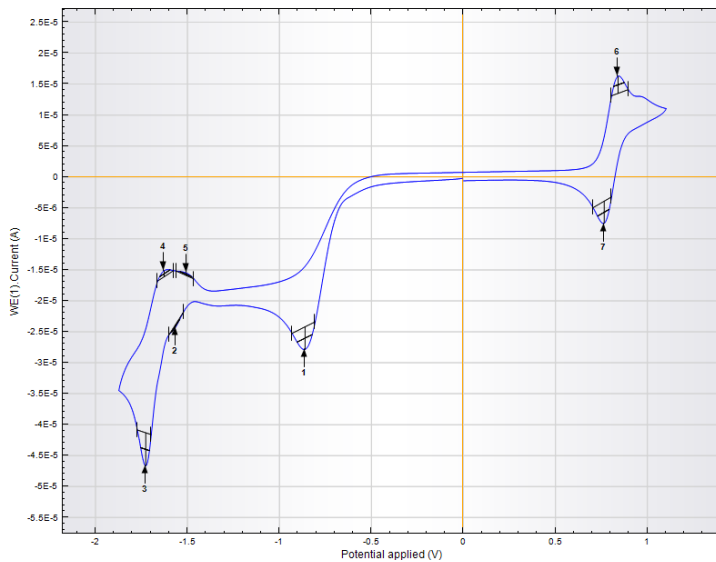




2-bromo-1-phenylethan-1-one

$E_{red} = -1.28$ V vs SCE

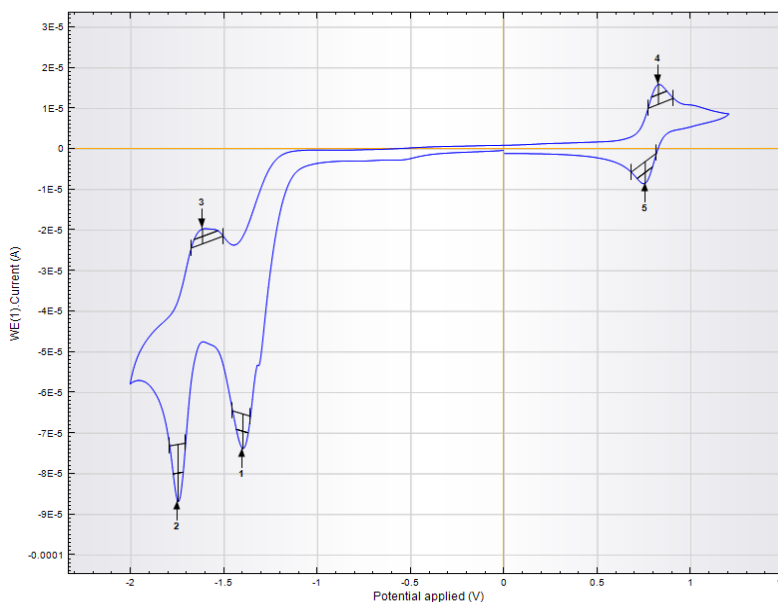
Index	Peak position vs Ferrocene
1	-0.86105
2	-1.566
3	-1.7271
4	-1.6264
5	-1.5056
6	0.84091
7	0.76538

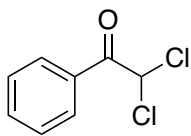


2-oxo-2-phenylethyl acetate

$E_{red} = -1.81$ V vs SCE

Index	Peak position vs Ferrocene
1	-1.3998
2	-1.7473
3	-1.6164
4	0.82581
5	0.75531



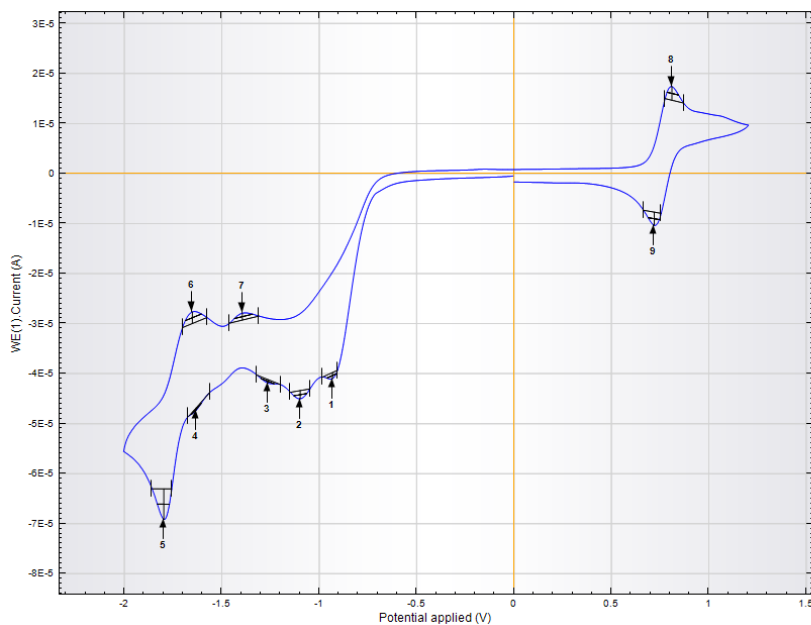


2,2-dichloro-1-phenylethan-1-one

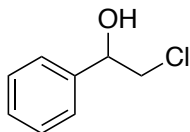
$E_{red} = -1.32 \text{ V vs SCE}$

Index **Peak position vs Ferrocene**

1	-0.93155
2	-1.0977
3	-1.2639
4	-1.6315
5	-1.7976
6	-1.6516
7	-1.3948
8	0.8107
9	0.72006



13. Spectral data:

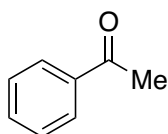


2-chloro-1-phenylethan-1-ol (**IIa**)

Following G.P.1 using styrene (**1a**) (52.1 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone in dark for 16 hours at room temperature yielded 75% of 2-chloro-1-phenylethan-1-ol (**IIa**) (58.5 mg, 0.375 mmol) after flash chromatography on silica (hexanes : EtOAc).

¹H-NMR (300 MHz, CDCl₃): 7.41-7.29 (m, 5H), 4.88 (dd, *J*=8.61 Hz, 1H), 3.76-3.60 (m, 2H), 2.80 (s, 1H). ¹³C-NMR (75 MHz, CDCl₃): 140.03, 128.71, 128.50, 126.13, 74.10, 50.85.

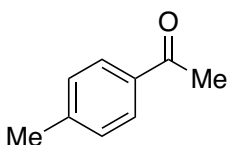
HRMS (EI) *m/z* calculated for C₈H₉ClONa (M⁺) 179.0239 found 179.0241. IR (neat, cm⁻¹): 3367, 2005, 2989, 1275, 1260, 767



Acetophenone (**2a**)

Following G.P.1 using styrene (**1a**) (52.1 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom using a 365 nm LED for 16 hours at 50°C yielded 85% of acetophenone (**2a**) (51.1 mg, 0.425 mmol) after flash chromatography on silica (hexanes : EtOAc).

¹H-NMR (300 MHz, CDCl₃): 7.90 (d, 2H), 7.50 (t, 1H), 7.39 (t, 2H), 2.53 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): 197.97, 137.08, 133.06, 128.54, 128.26, 26.51. HRMS (EI) *m/z* calculated for C₈H₈O (M⁺) 120.0569 found 120.0572. IR (neat, cm⁻¹): 1681, 1599, 1449, 1356, 1263, 1177, 1077, 1025, 954, 760, 689.

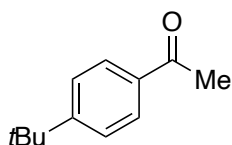


1-(*p*-tolyl)ethan-1-one (**2b**)

Following G.P.2 using 4-methylstyrene (**1b**) (59.1 mg, 0.5 mmol, 1 equiv), tribromoisocyanuric acid (TBCA) (183mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of

acetone irradiated from the bottom side by a 365 nm LED for 16 hours at room temperature yielded 44% of 1-(*p*-tolyl)ethan-1-one (**2b**) (29.5 mg, 0.22 mmol) after flash chromatography on silica (hexanes : EtOAc).

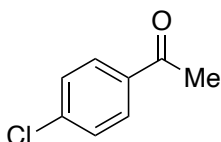
¹H-NMR (300 MHz, CDCl₃): 7.82 (d, 2H), 7.21 (d, 2H), 2.53 (s, 3H), 2.37 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): 197.79, 143.86, 134.70, 129.24, 128.44, 26.51, 21.62. HRMS (EI) m/z calculated for C₉H₁₀O (M⁺) 134.0726 found 134.0729. IR (neat, cm⁻¹): 1677, 1606, 1405, 1356, 1267, 1181, 1017, 954, 812, 711, 670.



1-(4-(*tert*-butyl)phenyl)ethan-1-one (**2c**)

Following G.P.2 using 4-*tert*-butylstyrene (**1c**) (80.13 mg, 0.5 mmol, 1 equiv), tribromoisocyanuric acid (TBICA) (183mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at room temperature yielded 58% of 1-(4-(*tert*-butyl)phenyl)ethan-1-one (**2c**) (51.1 mg, 0.29 mmol) after flash chromatography on silica (hexanes : EtOAc).

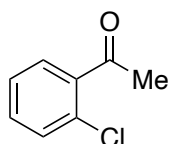
¹H-NMR (300 MHz, CDCl₃): 7.89 (d, 2H), 7.46 (d, 2H), 2.56 (s, 3H), 1.32 (s, 9H). ¹³C-NMR (75 MHz, CDCl₃): 197.81, 156.81, 134.63, 128.32, 125.52, 35.11, 31.11, 26.56. HRMS (EI) m/z calculated for C₁₂H₁₆O (M⁺) 176.1201 found 176.1195. IR (neat, cm⁻¹): 2963, 2870, 1681, 1606, 1405, 1356, 1267, 1192, 1110, 1013, 957, 834



1-(4-chlorophenyl)ethan-1-one (**2d**)

Following G.P.1 using 4-chlorostyrene (**1d**) (69.3 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 60% of 1-(4-chlorophenyl)ethan-1-one (**2d**) (46.4 mg, 0.3 mmol) after flash chromatography on silica (hexanes : EtOAc).

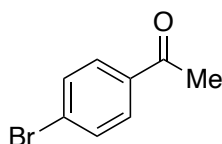
¹H-NMR (300 MHz, CDCl₃): 7.86 (d, 2H), 7.39 (d, 2H), 2.55 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): 196.79, 139.54, 135.45, 129.73, 128.88, 26.55. HRMS (EI) m/z calculated for C₈H₇OCl (M⁺) 154.0179 found 154.0176. IR (neat, cm⁻¹): 1684, 1587, 1394, 1356, 1256, 1092, 1013, 954, 820, 760.



1-(2-chlorophenyl)ethan-1-one (2e)

Following G.P.1 using 2-chlorostyrene (**1e**) (69.3 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 42% of 1-(2-chlorophenyl)ethan-1-one (**2e**) (32.5 mg, 0.21 mmol) after flash chromatography on silica (hexanes : EtOAc).

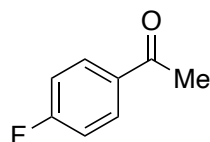
¹H-NMR (300 MHz, CDCl₃): 7.52 (d, 1H), 7.41-7.33 (m, 2H), 7.32-7.27 (m, 1H), 2.62 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): 139.16, 132.01, 131.31, 130.66, 129.41, 126.96, 30.72. HRMS (EI) m/z calculated for C₈H₇OCl (M⁺) 154.0179 found 154.0184. IR (neat, cm⁻¹): 1692, 1591, 1468, 1431, 1356, 1274, 1237, 1095, 1043, 961, 752, 670.



1-(4-bromophenyl)ethan-1-one (2f)

Following G.P.2 using 4-bromostyrene (**1f**) (91.6 mg, 0.5 mmol, 1 equiv), tribromoisocyanuric acid (TBCA) (183mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at room temperature yielded 67% of 1-(4-bromophenyl)ethan-1-one (**2f**) (66.7 mg, 0.335 mmol) after flash chromatography on silica (hexanes : EtOAc).

¹H-NMR (300 MHz, CDCl₃): 7.81 (d, 2H), 7.60 (d, 2H), 2.58 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): 197.03, 135.86, 131.92, 129.87, 128.33, 26.56. HRMS (EI) m/z calculated for C₈H₇OBr (M⁺) 197.9674 found 197.9678. IR (neat, cm⁻¹): 1677, 1584, 1479, 1423, 1394, 1356, 1263, 1078, 1006, 957, 820, 745

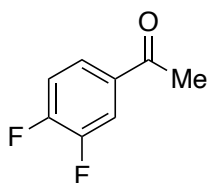


1-(4-fluorophenyl)ethan-1-one (2g)

Following G.P.1 using 4-fluorostyrene (**1g**) (61.1 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 70% of 1-(4-

fluorophenyl)ethan-1-one (**2g**) (48.35 mg, 0.35 mmol) after flash chromatography on silica (hexanes : EtOAc).

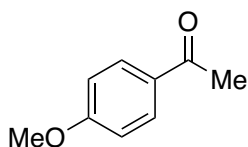
¹H-NMR (400 MHz, CDCl₃): 7.91 (q, 2H), 7.05 (t, 2H), 2.52 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃): 196.38, 166.98, 164.45, 133.59 (d, *J*¹ = 3Hz), 130.91 (d, *J*¹ = 9Hz), 115.58 (d, *J*¹ = 22Hz), 26.43. ¹⁹F (282 MHz, CDCl₃): -105.94 (s, 1F). HRMS (EI) *m/z* calculated for C₈H₇OF (M⁺) 138.0475 found 138.0477. IR (neat, cm⁻¹): 1681, 1595, 1505, 1408, 1356, 1263, 1226, 1155, 1103, 957, 834.



1-(3,4-difluorophenyl)ethan-1-one (**2h**)

Following G.P.1 using 3,4-difluorostyrene (**1h**) (70.1 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 71% of 1-(3,4-difluorophenyl)ethan-1-one (**2h**) (55.4 mg, 0.355 mmol) after flash chromatography on silica (hexanes : EtOAc).

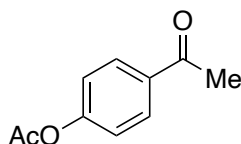
¹H-NMR (400 MHz, CDCl₃): 7.81-7.70 (m, 2H), 7.30-7.20 (m, 1H), 2.58 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃): 195.35, 153.22 (dd, *J*¹ = 14Hz, *J*³ = 329Hz), 150.69 (dd, *J*¹ = 14 Hz, *J*³ = 330Hz), 134.22 (t, *J*¹ = 4Hz), 125.36 (q, *J*¹ = 4Hz, *J*³ = 8Hz), 117.42 (d, *J*¹ = 18Hz), 26.35. ¹⁹F (282 MHz, CDCl₃): -130.54 (s, 1F), -136.79 (s, 1F). HRMS (EI) *m/z* calculated for C₈H₆OF₂ (M⁺) 156.0381 found 156.0377. IR (neat, cm⁻¹): 1688, 1610, 1513, 1423, 1360, 1282, 1185, 1114, 898, 820, 775.



1-(4-methoxyphenyl)ethan-1-one (**2i**)

Following G.P.2 using 4-methoxystyrene (**1i**) (67.1 mg, 0.5 mmol, 1 equiv), tribromoisocyanuric acid (TBCA) (183mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at room temperature yielded 36% of 1-(4-methoxyphenyl)ethan-1-one (**2i**) (27.0 mg, 0.18 mmol) after flash chromatography on silica (hexanes : EtOAc).

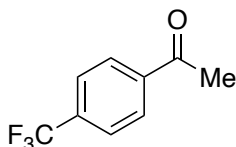
¹H-NMR (300 MHz, CDCl₃): 7.93 (d, 2H), 6.93 (d, 2H), 3.87 (s, 3H), 2.56 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): 196.80, 163.51, 130.62, 130.39, 113.71, 55.49, 26.37. HRMS (EI) *m/z* calculated for C₉H₁₀O₂ (M⁺) 150.0675 found 150.0676. IR (neat, cm⁻¹): 1666, 1595, 1505, 1416, 1356, 1244, 1174, 1110, 1021, 954, 831.



4-acetylphenyl acetate (**2j**)

Following G.P.1 using 4-acetoxystyrene (**1j**) (81.1 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 62% of 4-acetylphenyl acetate (**2j**) (55.2 mg, 0.31 mmol) after flash chromatography on silica (hexanes : EtOAc).

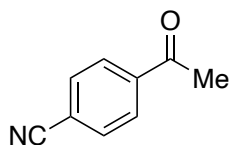
¹H-NMR (300 MHz, CDCl₃): 7.99 (d, 2H), 7.19 (d, 2H), 2.59 (s, 3H), 2.32 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): 196.84, 168.86, 154.36, 134.75, 129.95, 121.78, 26.60, 21.15. HRMS (EI) m/z calculated for C₁₀H₁₀O₃ (M⁺) 178.0624 found 178.0622. IR (neat, cm⁻¹): 1759, 1681, 1599, 1505, 1412, 1360, 1263, 1185, 1013, 849.



1-(4-(trifluoromethyl)phenyl)ethan-1-one (**2k**)

Following G.P.1 using 4-trifluoromethylstyrene (**1k**) (86.1 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 88% of 1-(4-(trifluoromethyl)phenyl)ethan-1-one (**2k**) (82.8 mg, 0.44 mmol) after flash chromatography on silica (hexanes : EtOAc).

¹H-NMR (400 MHz, CDCl₃): 8.05 (d, 2H), 7.73 (d, 2H), 2.64 (s, 3H). ¹³C-NMR (101 MHz, CDCl₃): 196.98, 139.71, 134.44 (q, *J*¹ = 33Hz, *J*³ = 68Hz), 128.64, 127.70 (q, *J*¹ = 4Hz, *J*³ = 7Hz), 124.97, 122.26, 26.79. ¹⁹F (282 MHz, CDCl₃): -63.63 (s, 3F). HRMS (EI) m/z calculated for C₉H₇OF₃ (M⁺) 188.0443 found 188.0447. IR (neat, cm⁻¹): 1692, 1513, 1408, 1323, 1263, 1166, 1125, 1058, 1013, 961, 834, 719.

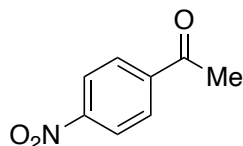


4-acetylbenzotrile (**2l**)

Following G.P.1 using 4-cyanostyrene (**1l**) (64.6 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 45% of 4-

acetylbenzointrile (**2l**) (32.7 mg, 0.225 mmol) after flash chromatography on silica (hexanes : EtOAc).

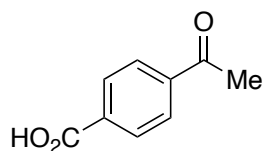
$^1\text{H-NMR}$ (300 MHz, CDCl_3): 8.04 (d, 2H), 7.77 (d, 2H), 2.64 (s, 3H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 196.54, 139.96, 132.55, 128.73, 117.95, 116.46, 26.79. HRMS (EI) m/z calculated for $\text{C}_9\text{H}_7\text{NO}$ (M^+) 145.0522 found 145.0520. IR (neat, cm^{-1}): 2228, 1684, 1602, 1561, 1401, 1353, 1259, 954, 827.



1-(4-nitrophenyl)ethan-1-one (**2m**)

Following G.P.2 using 4-nitrostyrene (**1m**) (74.6 mg, 0.5 mmol, 1 equiv), tribromoisocyanuric acid (TBICA) (183mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at room temperature yielded 26% of 1-(4-nitrophenyl)ethan-1-one (**2m**) (21.5 mg, 0.13 mmol) after flash chromatography on silica (hexanes : EtOAc).

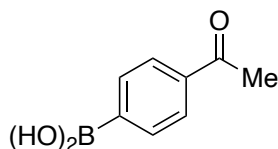
$^1\text{H-NMR}$ (300 MHz, CDCl_3): 8.30 (d, 2H), 8.10 (d, 2H), 2.67 (s, 3H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 196.35, 150.38, 141.40, 129.34, 123.89, 27.03. HRMS (EI) m/z calculated for $\text{C}_8\text{H}_7\text{NO}_3$ (M^+) 165.0420 found 165.0424. IR (neat, cm^{-1}): 3362, 3108, 1692, 1606, 1520, 1431, 1341, 1319, 1244, 1103, 1006, 961, 857, 745, 693.



4-acetylbenzoic acid (**2n**)

Following G.P.1 using 4-vinylbenzoic acid (**1n**) (74.1 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TBICA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 55% of 4-acetylbenzoic acid (**2n**) (45.1 mg, 0.275 mmol) after flash chromatography on silica (hexanes : EtOAc).

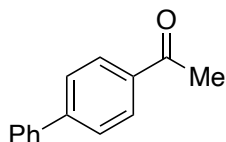
$^1\text{H-NMR}$ (300 MHz, DMSO-d_6): 13.31 (s, 1H), 8.04 (s, 4H), 2.61 (s, 3H). $^{13}\text{C-NMR}$ (75 MHz, DMSO-d_6): 198.16, 167.11, 140.27, 134.96, 130.00, 128.77, 27.45. HRMS (EI) m/z calculated for $\text{C}_9\text{H}_8\text{O}_3$ (M^+) 164.0468 found 164.0463. IR (neat, cm^{-1}): 2810, 2661, 2542, 1669, 1569, 1423, 1364, 1289, 1248, 1118, 931, 868, 771, 730, 693.



(4-acetylphenyl)boronic acid (**2o**)

Following G.P.1 using 4-vinylphenylboronic acid (**1o**) (74 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 59% of (4-acetylphenyl)boronic acid (**2o**) (48.4 mg, 0.295 mmol) after flash chromatography on silica (hexanes : EtOAc).

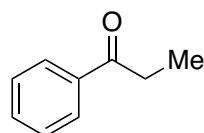
¹H-NMR (300 MHz, DMSO-d⁶): 8.28 (s, 2H), 7.90 (s, 4H), 2.58 (s, 3H). ¹³C-NMR (75 MHz, DMSO-d⁶): 198.72, 138.30, 134.70, 127.42, 27.28. HRMS (ESI) m/z calculated for C₈H₉BO₃ (M+H⁺) 165.0722 found 165.0722. IR (neat, cm⁻¹): 3425, 3198, 1662, 1505, 1401, 1334, 1271, 1170, 1170, 1103, 1006, 834, 745, 700.



1-([1,1'-biphenyl]-4-yl)ethan-1-one (**2p**)

Following G.P.1 using 4-vinyl biphenyl (**1p**) (90.13 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 60% of 1-([1,1'-biphenyl]-4-yl)ethan-1-one (**2p**) (58.9 mg, 0.3 mmol) after flash chromatography on silica (hexanes : EtOAc).

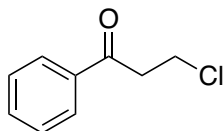
¹H-NMR (300 MHz, CDCl₃): 8.03 (d, 2H), 7.69 (d, 2H), 7.63 (d, 2H), 7.51-7.36 (m, 3H), 2.64 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): 197.81, 145.82, 139.90, 135.87, 128.97 (d, *J*¹ = 3Hz), 128.27, 127.28 (d, *J*¹ = 3Hz), 26.72. HRMS (EI) m/z calculated for C₁₄H₁₂O (M⁺) 196.0882 found 196.0881. IR (neat, cm⁻¹): 1677, 1599, 1356, 1259, 957, 834, 764, 719, 689.



Propiophenone (**2q**)

Following G.P.1 using trans-β-methylstyrene (**1q**) (59.1 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 75% of propiophenone (**2q**) (50.31 mg, 0.375 mmol) after flash chromatography on silica (hexanes : EtOAc).

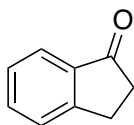
$^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.92 (d, 2H), 7.50 (t, 1H), 7.40 (t, 1H), 2.94 (q, 2H), 1.18 (t, 3H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 200.77, 136.89, 132.88, 128.55, 127.96, 31.75, 8.22. HRMS (EI) m/z calculated for $\text{C}_9\text{H}_{10}\text{O}$ (M^+) 134.0726 found 134.0729. IR (neat, cm^{-1}): 1684, 1595, 1449, 1349, 1218, 1077, 1013, 950, 745, 689.



3-chloro-1-phenylpropan-1-one (2r)

Following G.P.1 using cinnamyl chloride (**1r**) (76.3 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 40% of 3-chloro-1-phenylpropan-1-one (**2r**) (33.7 mg, 0.2 mmol) after flash chromatography on silica (hexanes : EtOAc).

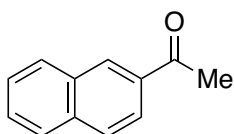
$^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.96 (d, 2H), 7.59 (t, 1H), 7.48 (t, 2H), 3.93 (t, 2H), 3.46 (t, 2H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 196.75, 136.38, 133.60, 128.79, 128.09, 41.31, 38.72. HRMS (EI) m/z calculated for $\text{C}_9\text{H}_9\text{OCl}$ (M^+) 168.0336 found 168.0335. IR (neat, cm^{-1}): 1677, 1595, 1446, 1353, 1267, 1200, 1066, 976, 741, 715.



2,3-dihydro-1H-inden-1-one (2s)

Following G.P.1 using indene (**1s**) (58.1 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 26% of 2,3-dihydro-1H-inden-1-one (**2s**) (17.2 mg, 0.13 mmol) after flash chromatography on silica (hexanes : EtOAc).

$^1\text{H-NMR}$ (300 MHz, CDCl_3): 7.75 (d, 1H), 7.58 (t, 1H), 7.47 (d, 1H), 7.36 (t, 1H), 3.14 (t, 2H), 2.71-2.64 (m, 2H). $^{13}\text{C-NMR}$ (75 MHz, CDCl_3): 207.13, 155.20, 137.11, 134.63, 127.31, 126.73, 123.74, 36.25, 25.83. HRMS (EI) m/z calculated for $\text{C}_9\text{H}_8\text{O}$ (M^+) 132.0569 found 132.0572. IR (neat, cm^{-1}): 1699, 1584, 1394, 1326, 1274, 1241, 1148, 1032, 823, 767.

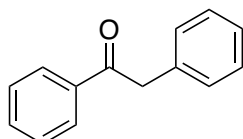


1-(naphthalen-2-yl)ethan-1-one (2t)

Following G.P.2 using 2-vinylnaphthalene (**1t**) (77.1 mg, 0.5 mmol, 1 equiv), tribromoisocyanuric acid (TBICA) (183mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144

mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at room temperature yielded 27% of 1-(naphthalen-2-yl)ethan-1-one (**2t**) (23.0 mg, 0.135 mmol) after flash chromatography on silica (hexanes : EtOAc).

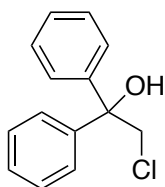
¹H-NMR (300 MHz, CDCl₃): 8.46 (s, 1H), 8.05-8.01 (m, 1H), 7.96 (d, 1H), 7.91-7.85 (m, 2H), 7.63-7.51 (m, 2H), 2.72 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): 198.16, 135.62, 134.51, 132.54, 130.24, 129.59, 128.51, 128.46, 127.82, 126.82, 123.93, 26.74. HRMS (EI) m/z calculated for C₁₂H₁₀O (M⁺H⁺) 171.0809 found 171.0804. IR (neat, cm⁻¹): 1669, 1364, 1267, 1222, 1189, 868, 834, 752



1,2-diphenylethan-1-one (**2u**)

Following G.P.1 using trans-stilbene (**1u**) (90.12 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 30% of 1,2-diphenylethan-1-one (**2u**) (29.4 mg, 0.15 mmol) after flash chromatography on silica (hexanes : EtOAc).

¹H-NMR (300 MHz, CDCl₃): 8.02 (d, 2H), 7.56 (t, 1H), 7.46 (t, 2H), 7.37-7.22 (m, 5H), 4.29 (s, 2H). ¹³C-NMR (75 MHz, CDCl₃): 197.66, 136.63, 134.58, 133.21, 129.51, 128.69 (t, *J*¹ = 4Hz), 126.94, 45.54. HRMS m/z calculated for C₁₄H₁₂O (M⁺) 198.0882 found 196.0882. IR (neat, cm⁻¹): 1740, 1681, 1580, 1446, 1334, 1215, 1073, 987, 752, 685.



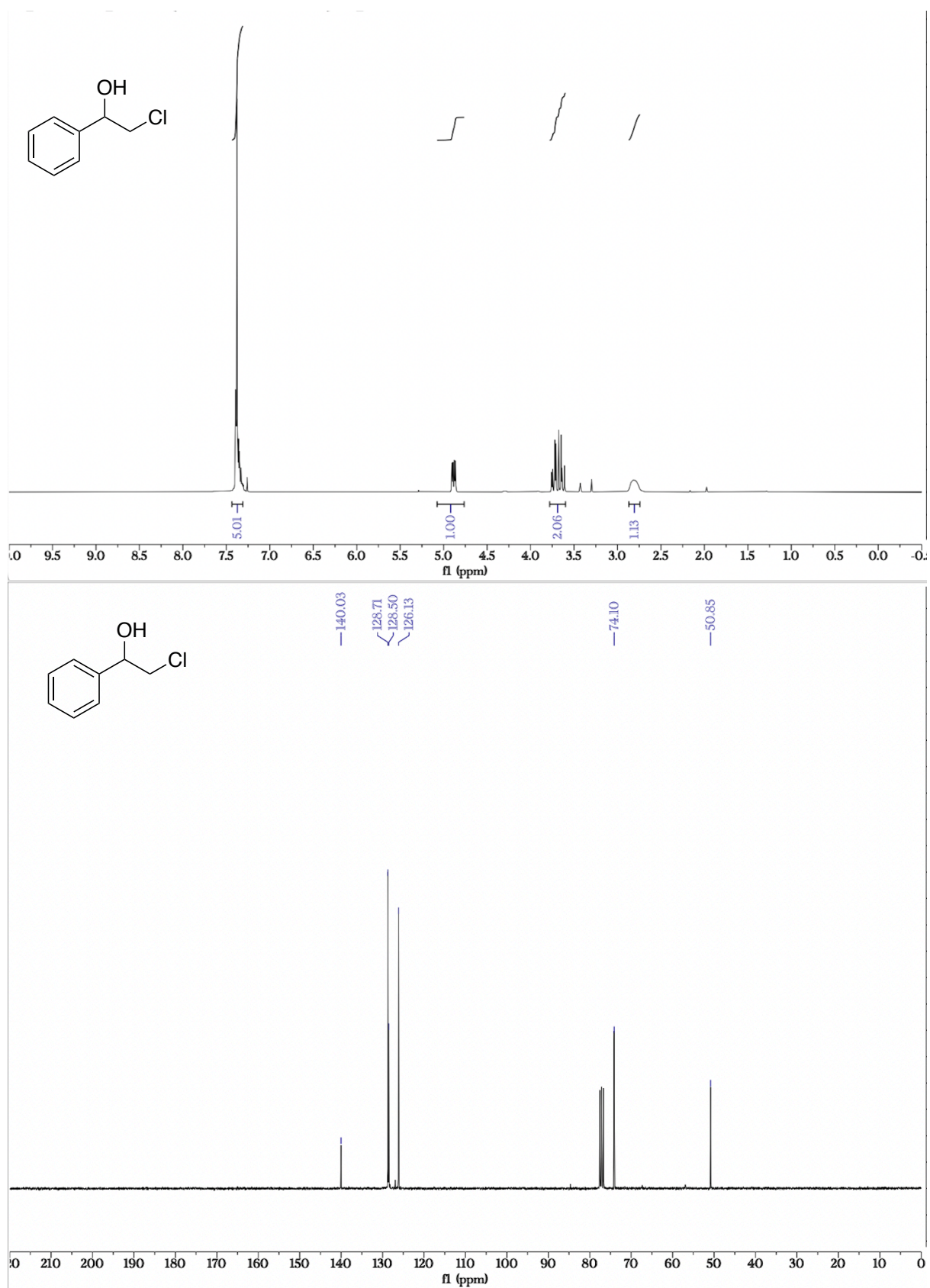
2-chloro-1,1-diphenylethan-1-ol (**2w**):

Following G.P.1 using 1,1-diphenylethylene (**1w**) (90.12 mg, 0.5 mmol, 1 equiv), trichloroisocyanuric acid (TCCA) (116.2 mg, 0.5 mmol, 1.0 equiv), copper (II) chloride (3.36 mg, 0.025 mmol, 5 mol%) and potassium bromide (5.95 mg, 0.05 mmol, 10 mol%), water (144 mg, 8.0 mmol, 16.0 equiv) and trifluoroacetic acid (114 mg, 1.0 mmol, 2.0 equiv) in 4 mL of acetone irradiated from the bottom side by a 365 nm LED for 16 hours at 50°C yielded 53% of 2-chloro-1,1-diphenylethan-1-ol (**2w**) (61.67 mg, 0.265 mmol) after flash chromatography on silica (hexanes : EtOAc).

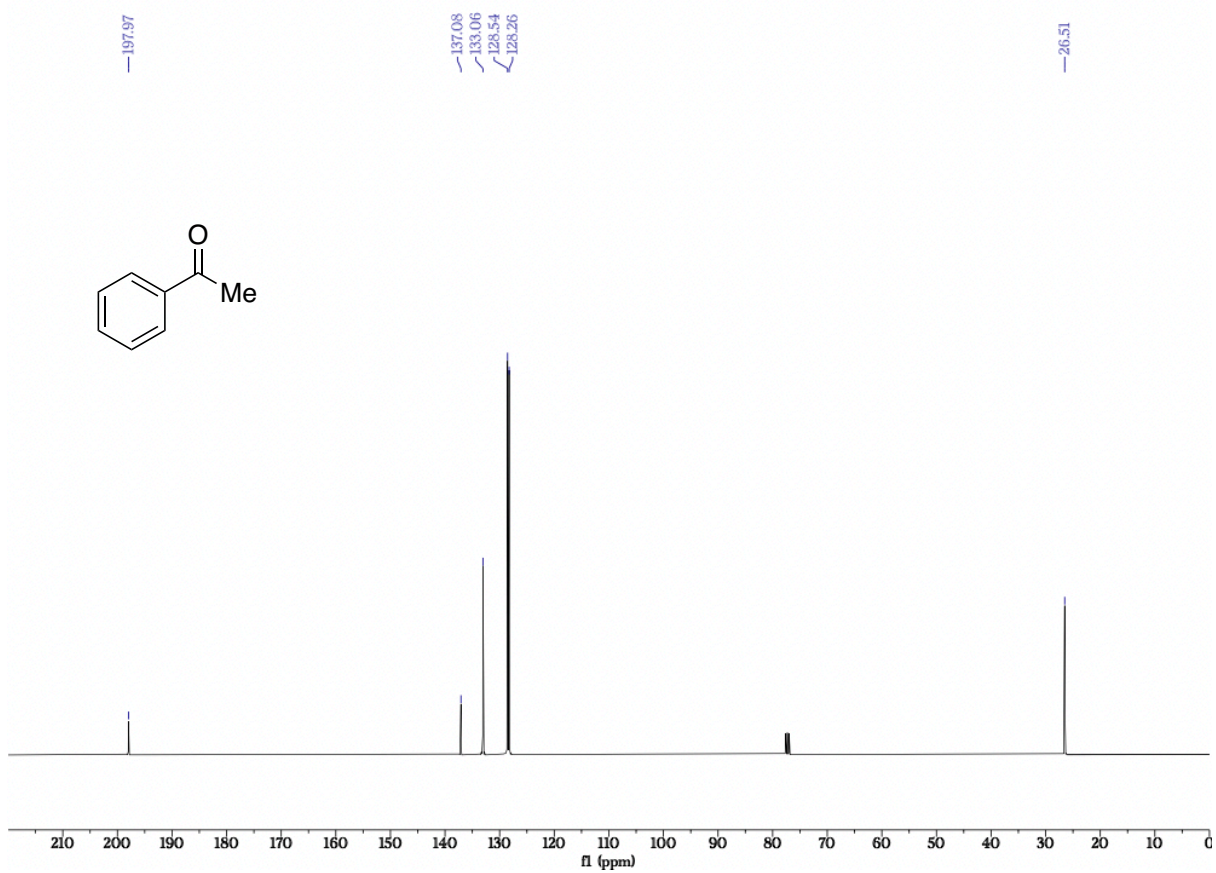
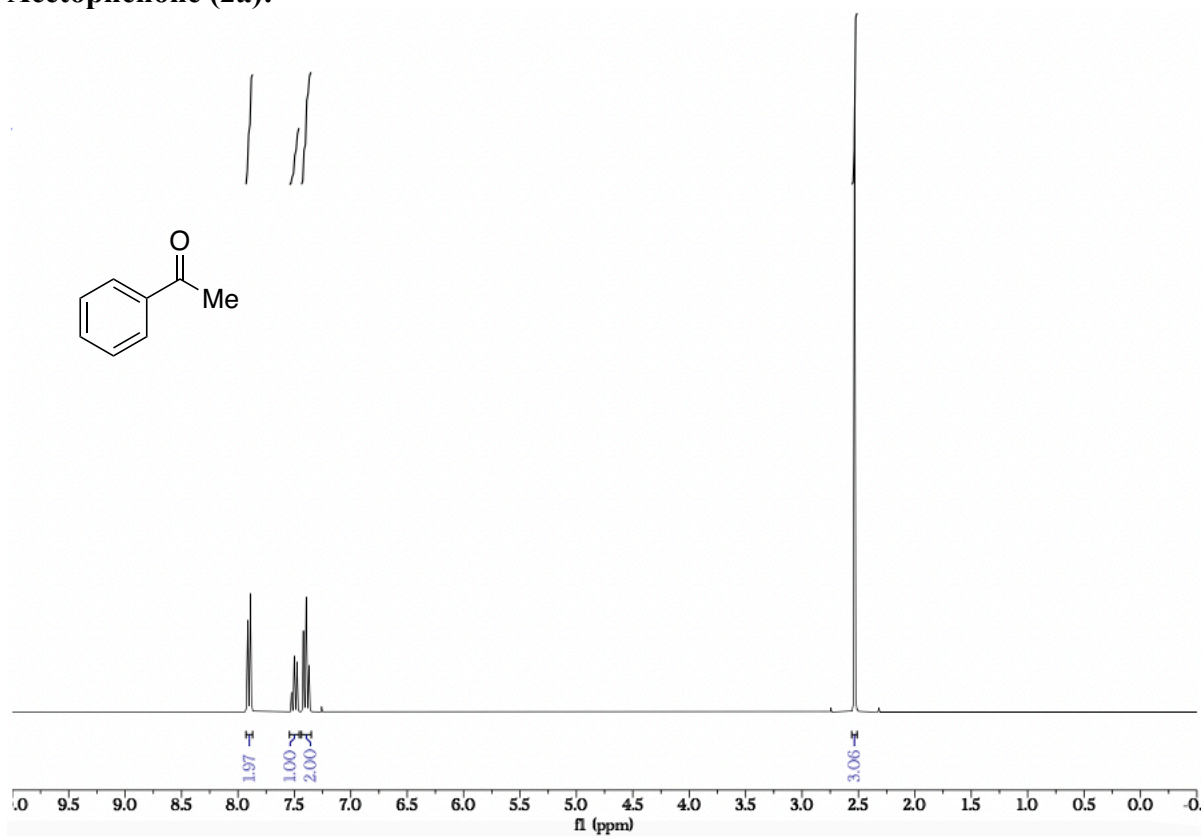
¹H-NMR (300 MHz, CDCl₃): 7.46 (d, 4H), 7.40-7.27 (m, 6H), 4.21 (s, 2H), 3.18 (s, 1H). ¹³C-NMR (75 MHz, CDCl₃): 143.28, 128.43, 127.77, 126.43, 126.11, 77.90, 53.26. HRMS (ESI) m/z calculated for C₁₄H₁₃ClO (M⁺) 232.0654 found 232.0660. IR (neat, cm⁻¹): 3548, 3060, 3026, 2963, 1599, 1490, 1446, 1334, 1267, 1166, 1062, 1010, 752, 723, 693.

14. Copies of NMR spectra:

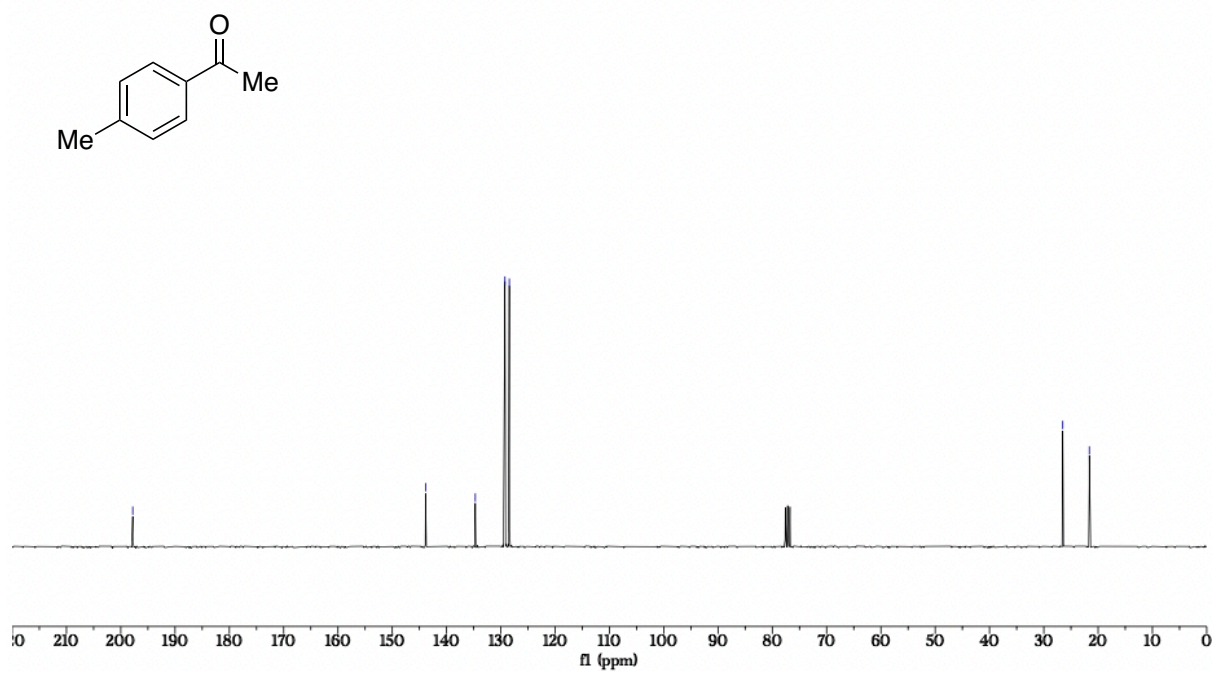
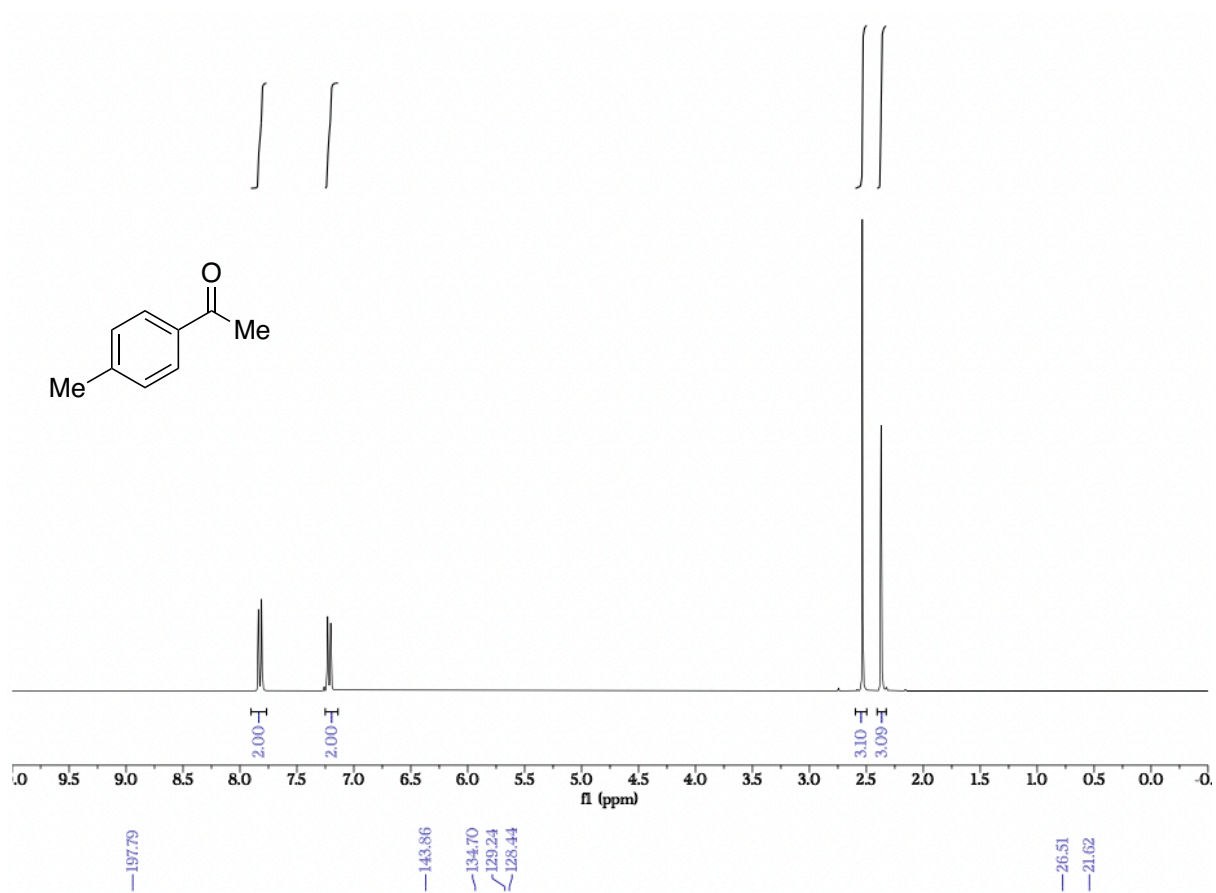
2-chloro-1-phenylethan-1-ol (IIa)



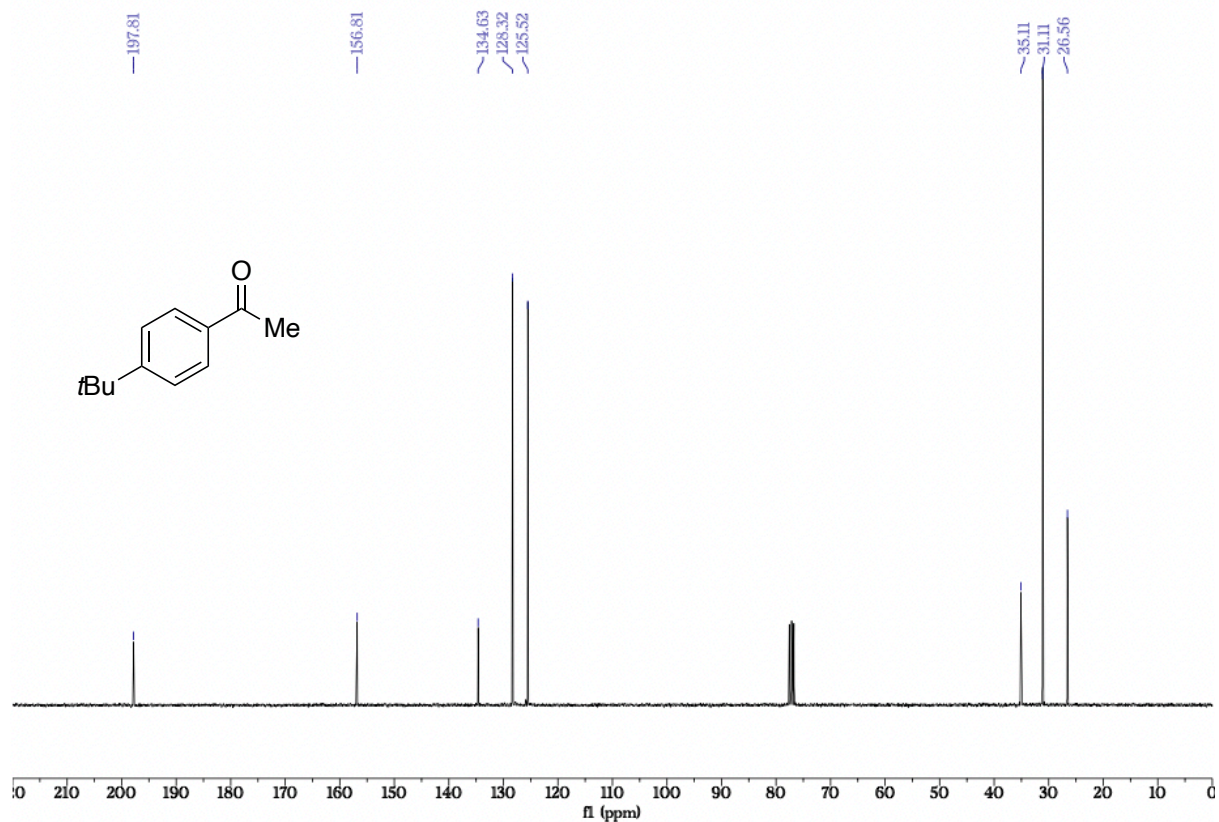
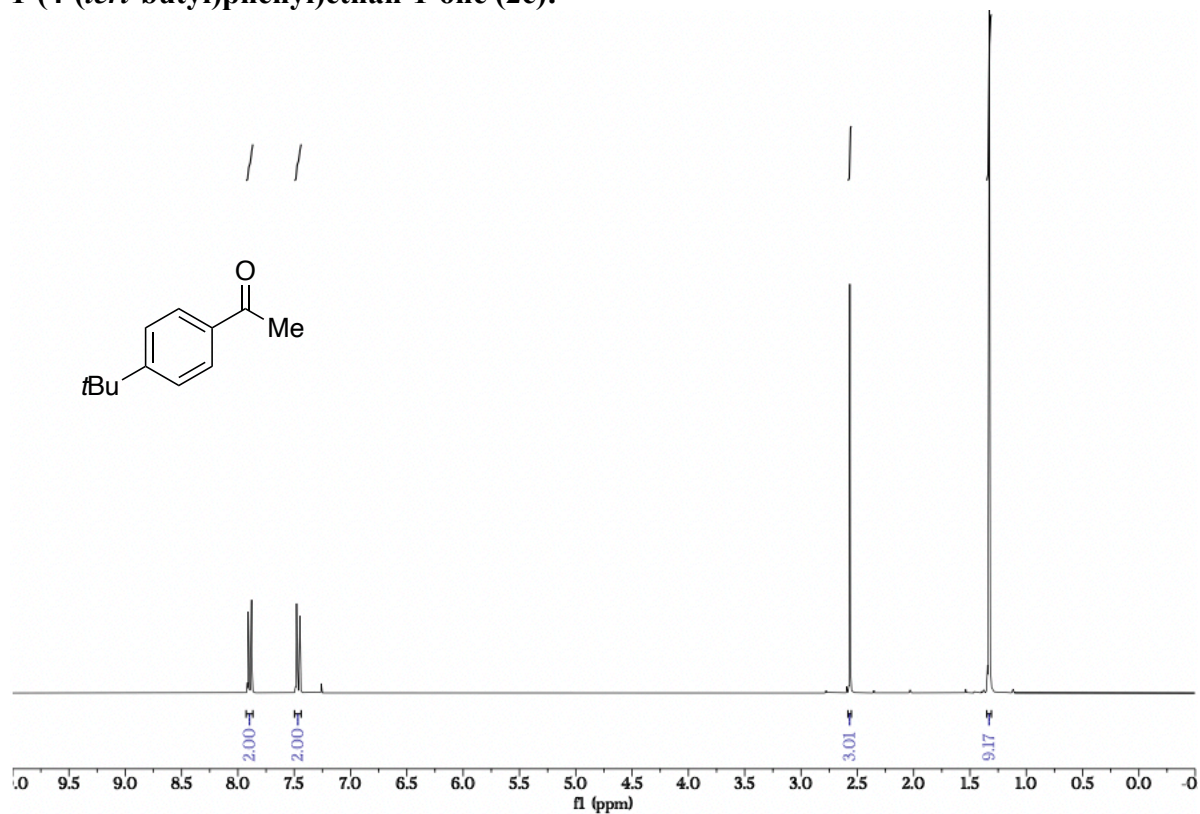
Acetophenone (2a):



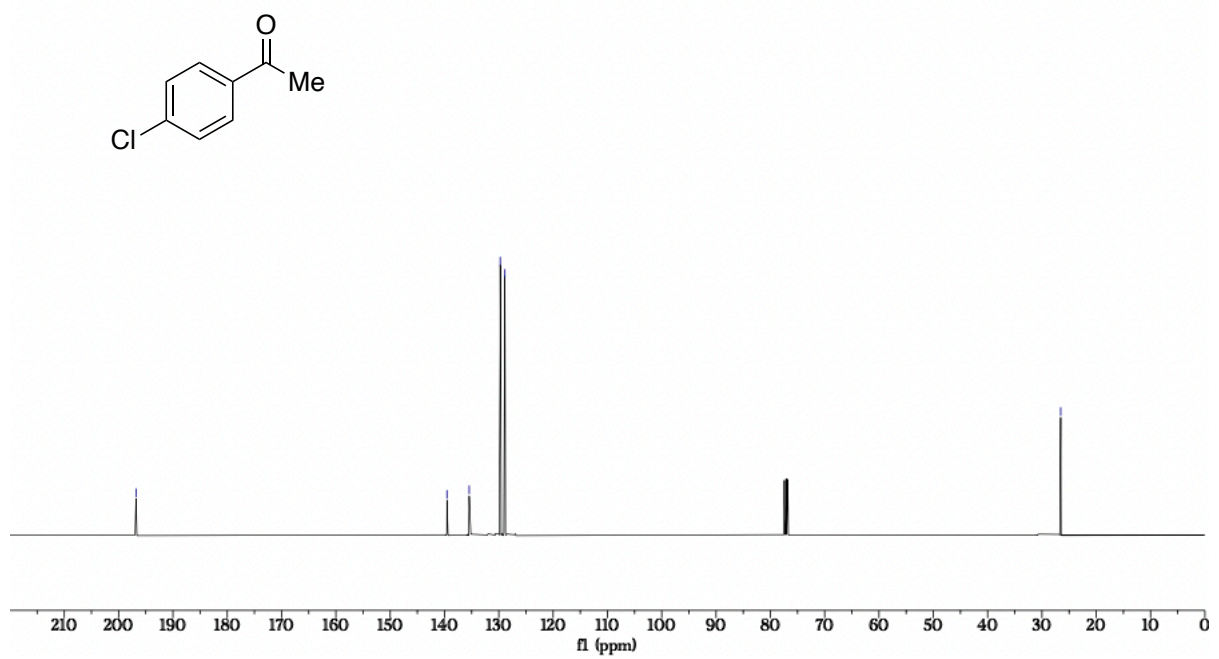
1-(*p*-tolyl)ethan-1-one (2b):



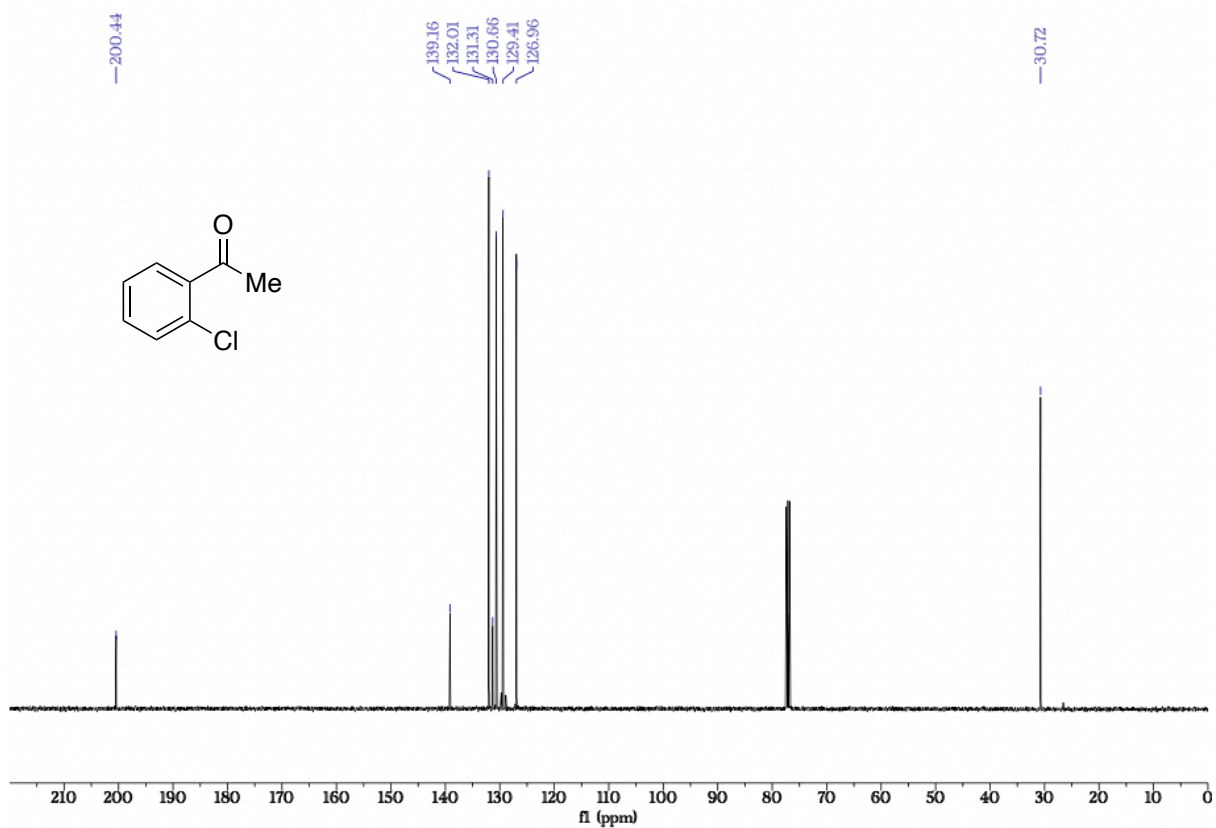
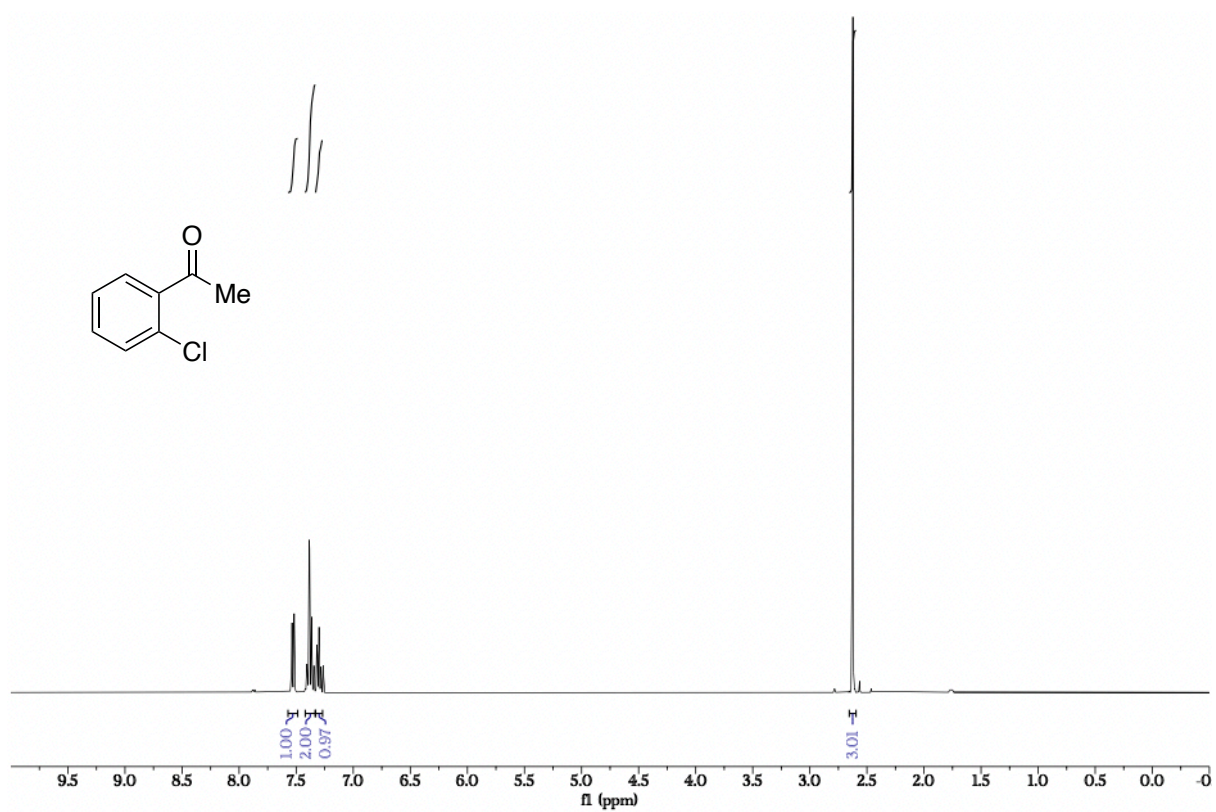
1-(4-(*tert*-butyl)phenyl)ethan-1-one (2c):



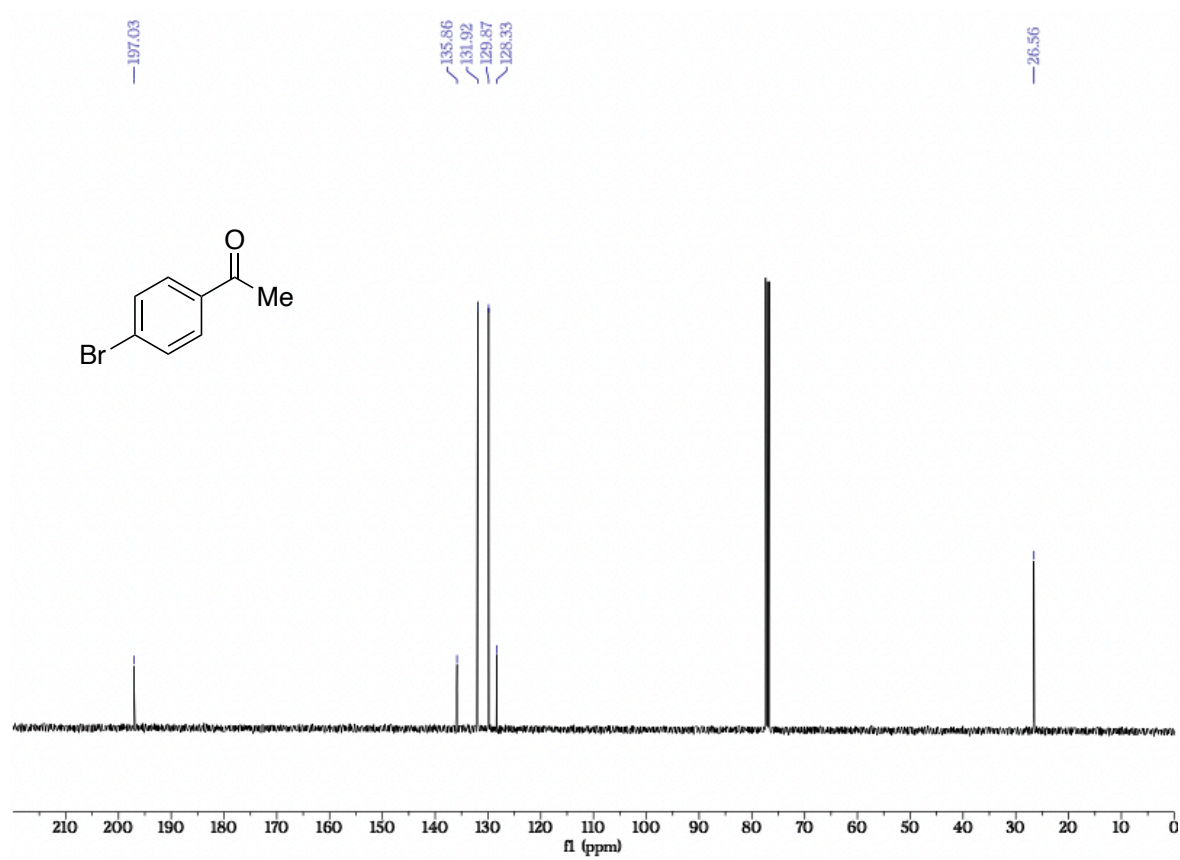
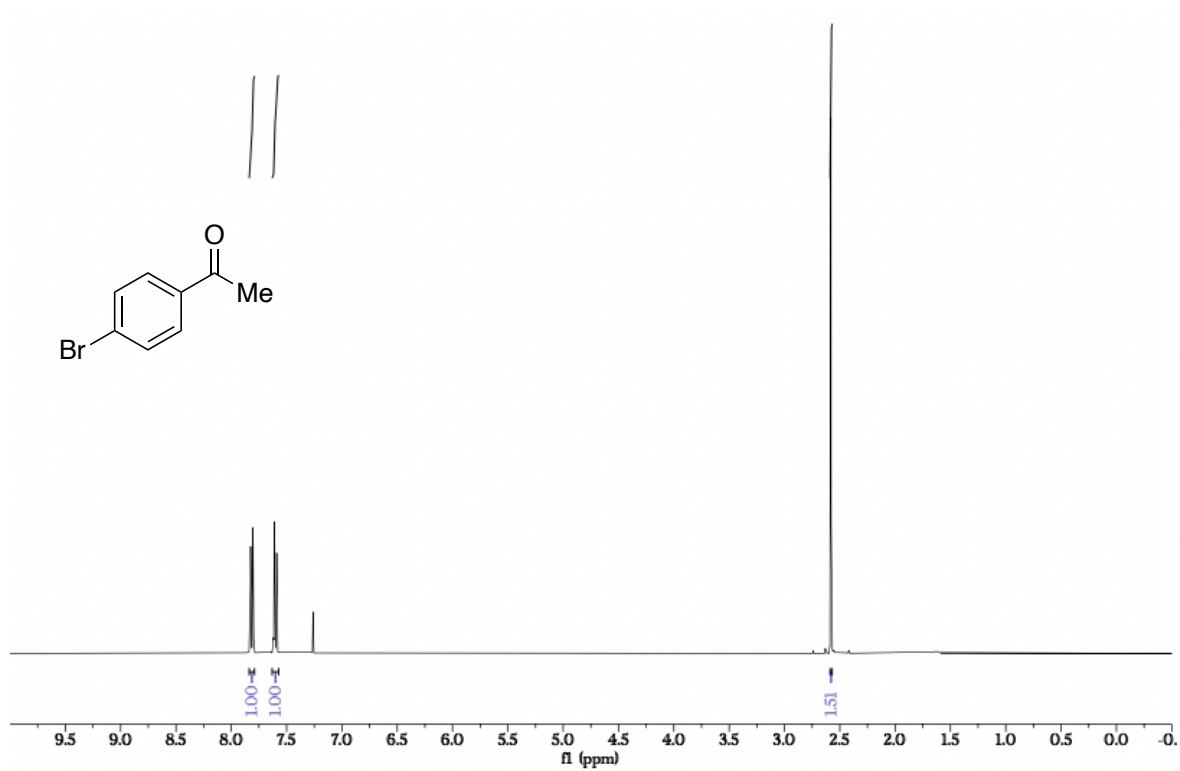
1-(4-chlorophenyl)ethan-1-one (2d):



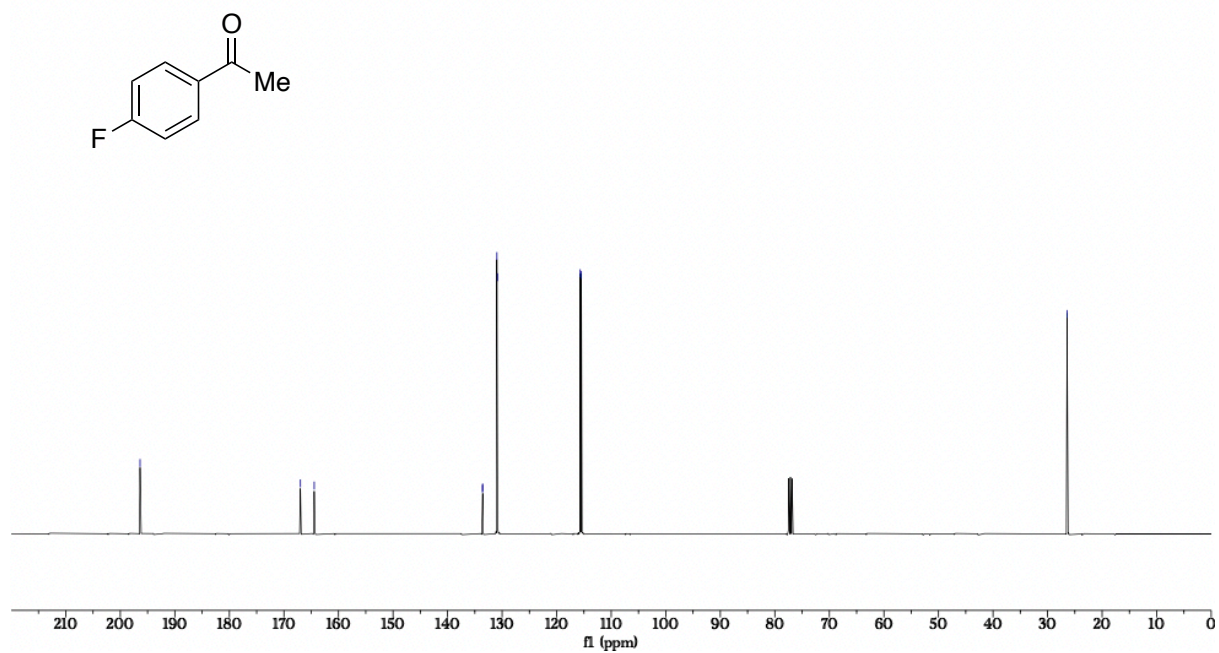
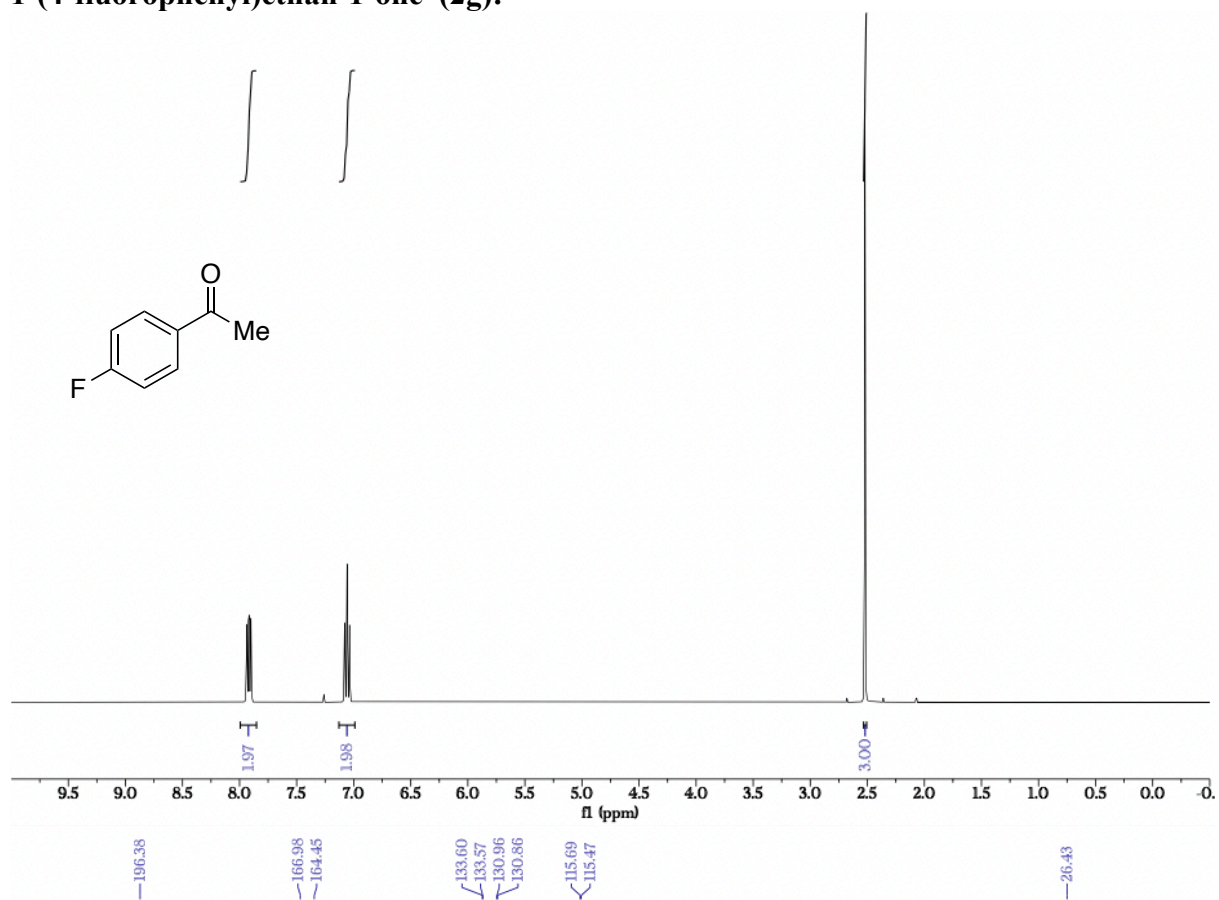
1-(2-chlorophenyl)ethan-1-one (2e):

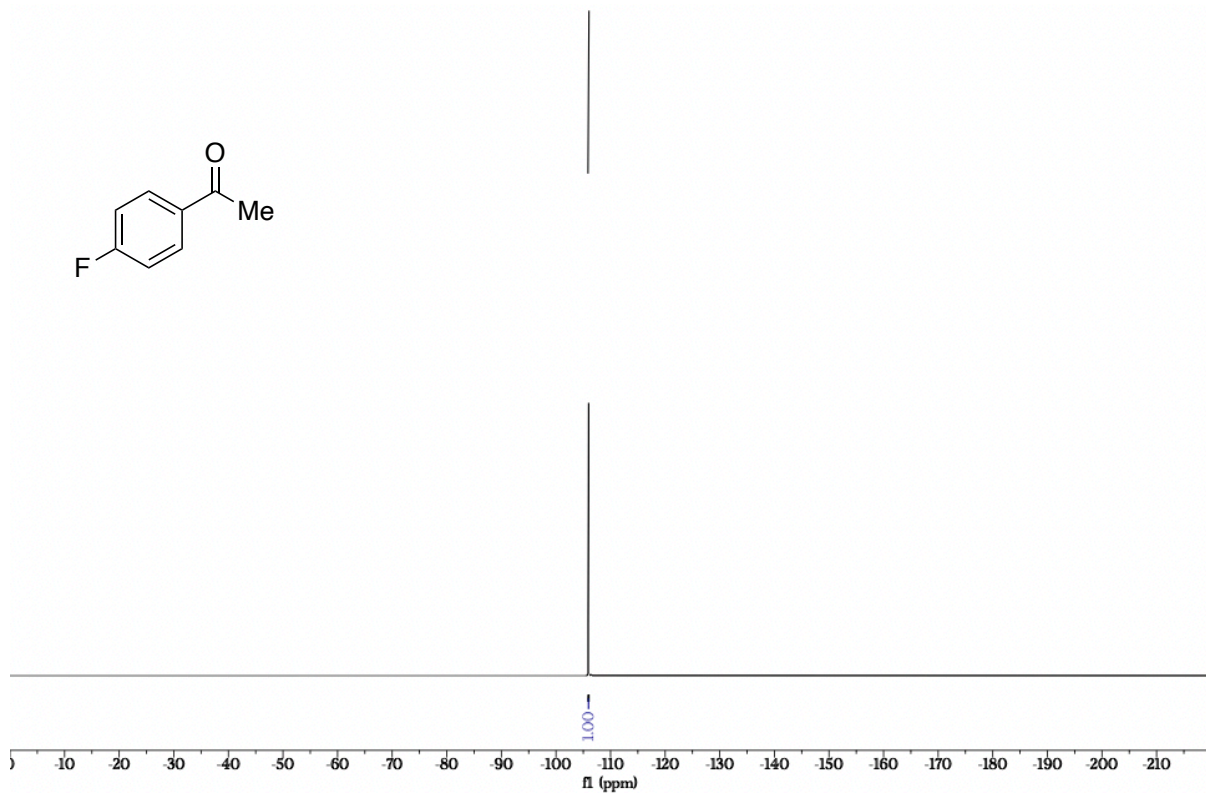
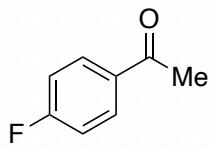


1-(4-bromophenyl)ethan-1-one (2f):

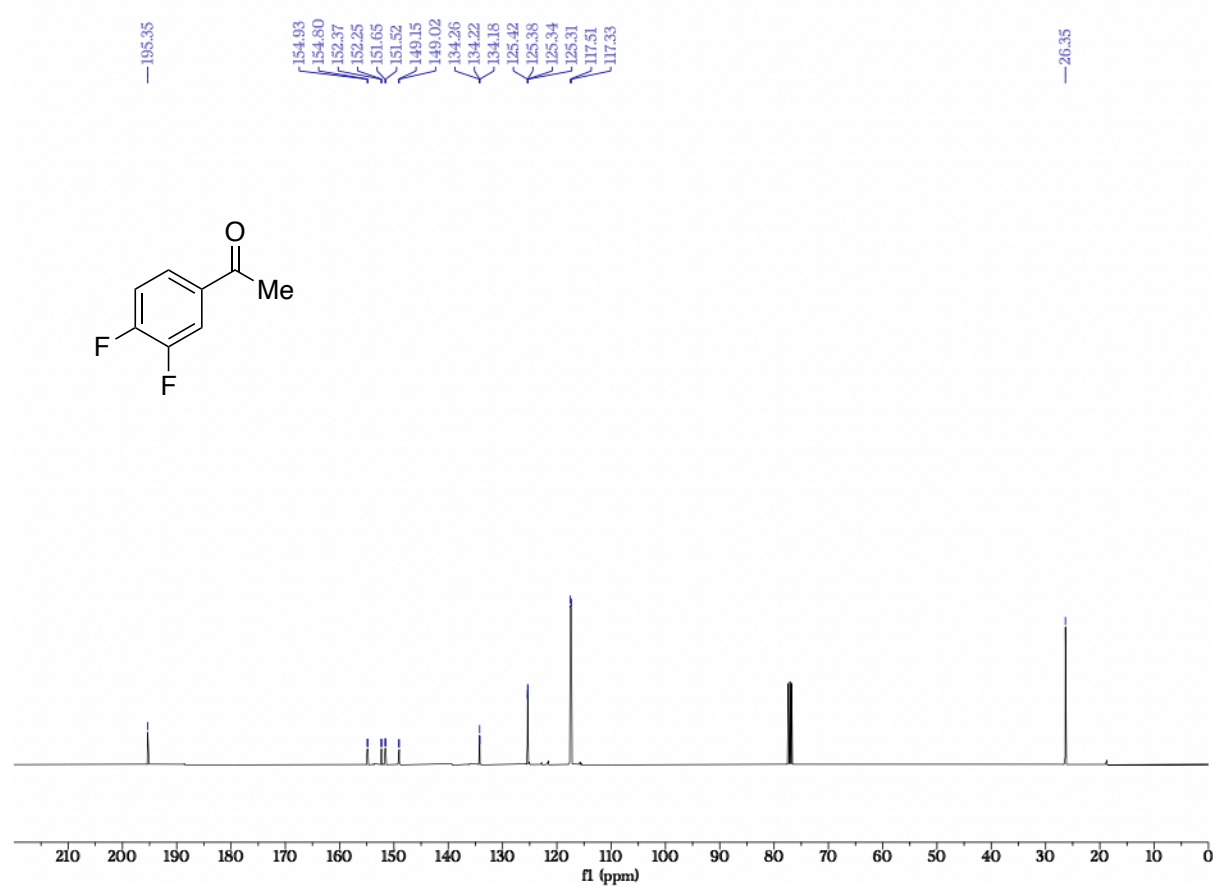
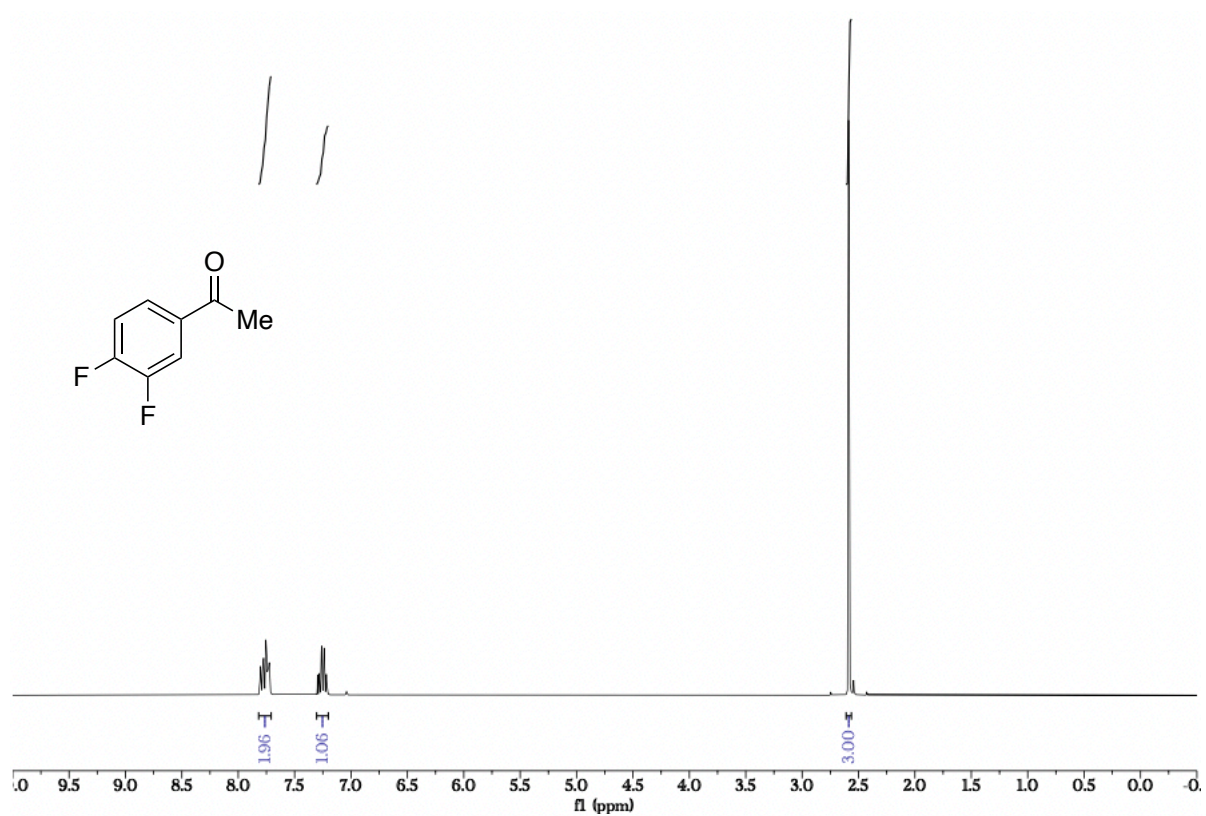


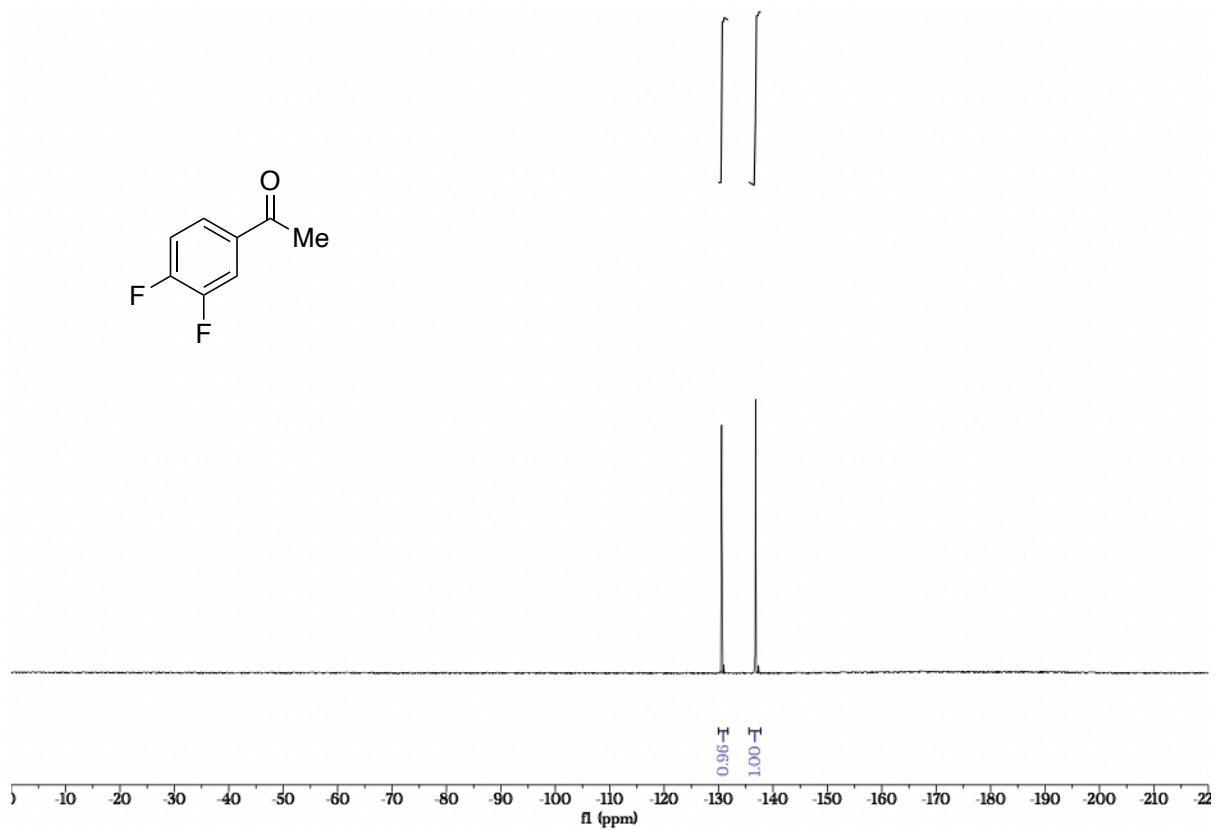
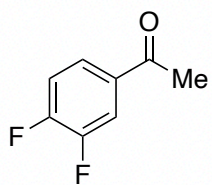
1-(4-fluorophenyl)ethan-1-one (2g):



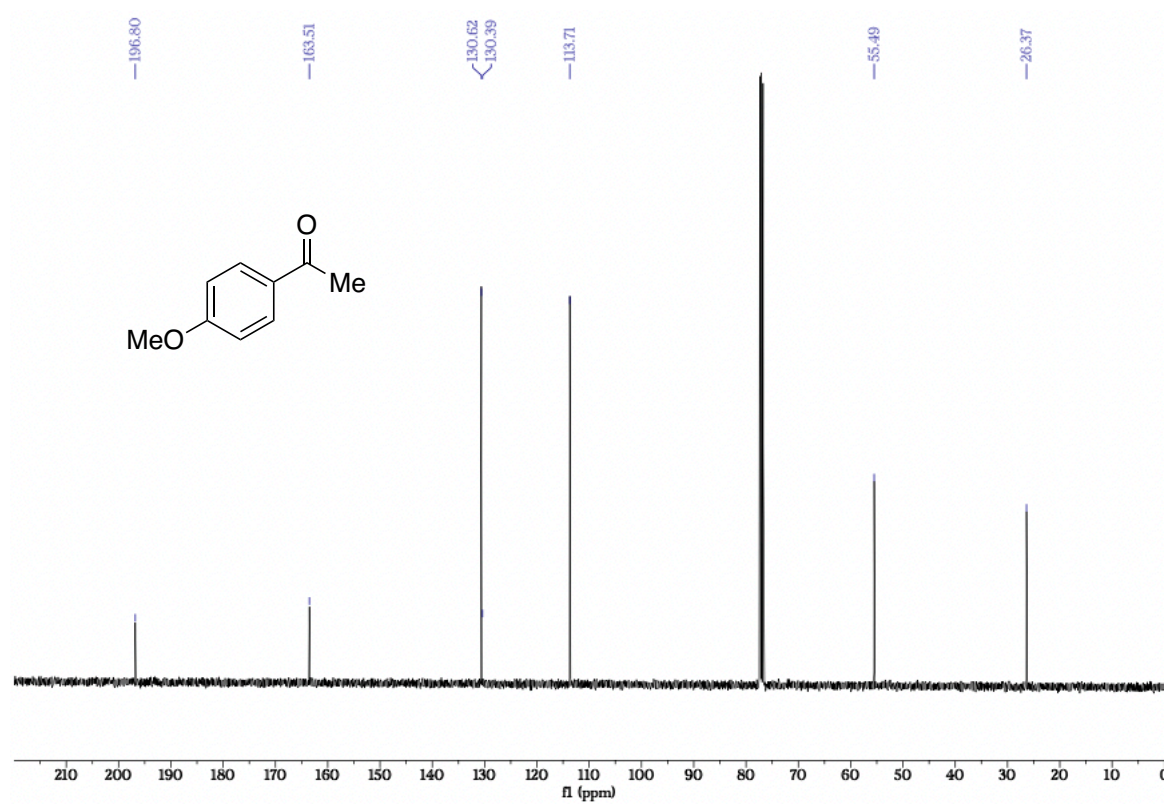
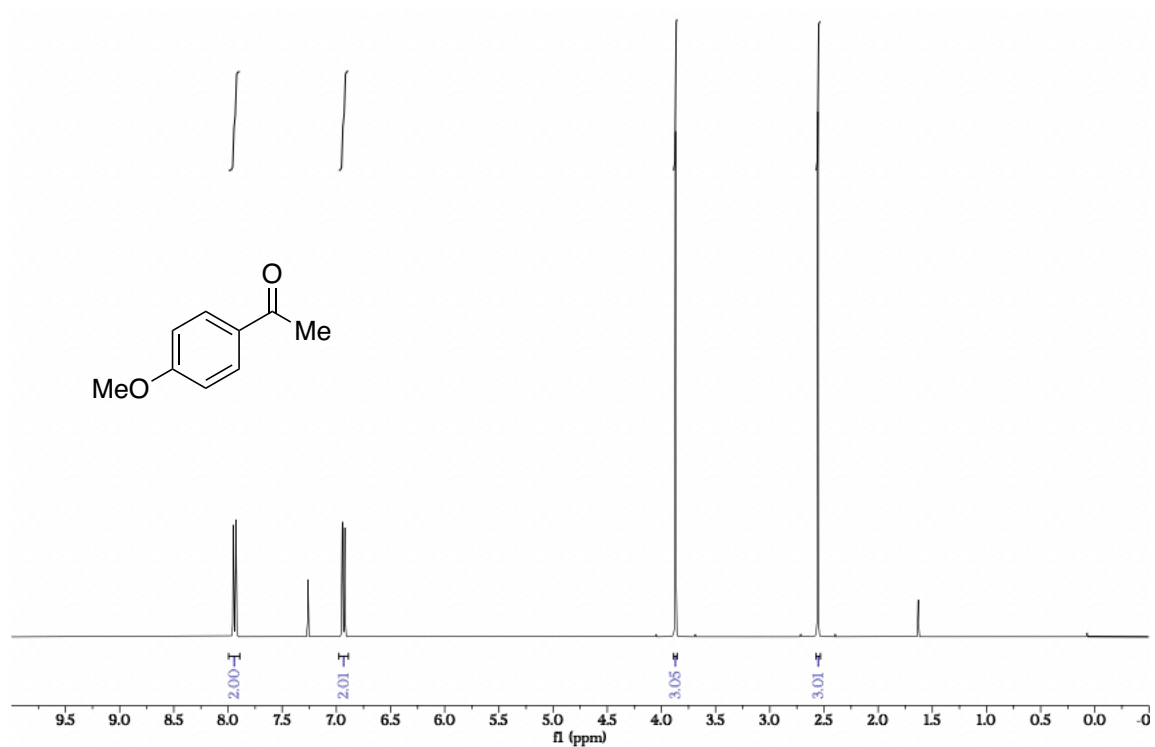


1-(3,4-difluorophenyl)ethan-1-one (2h):

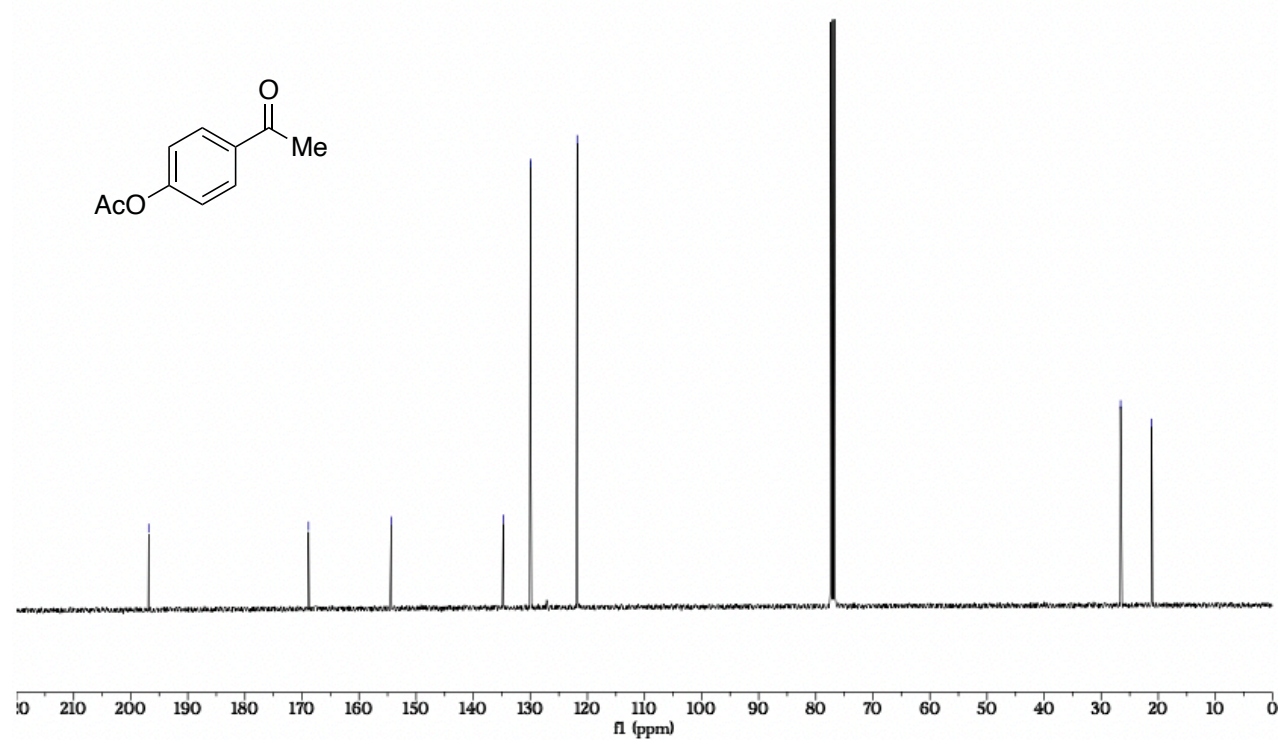
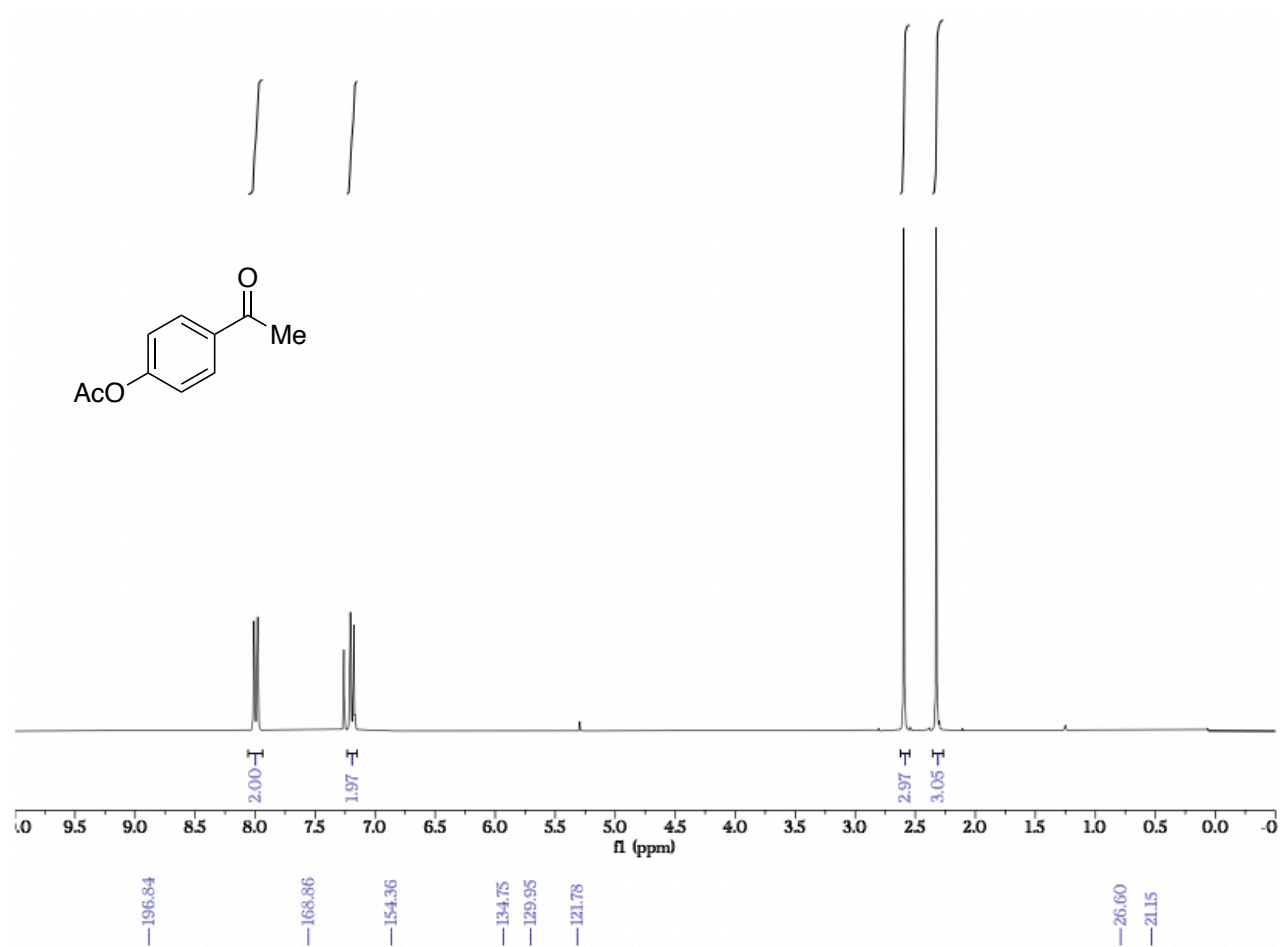




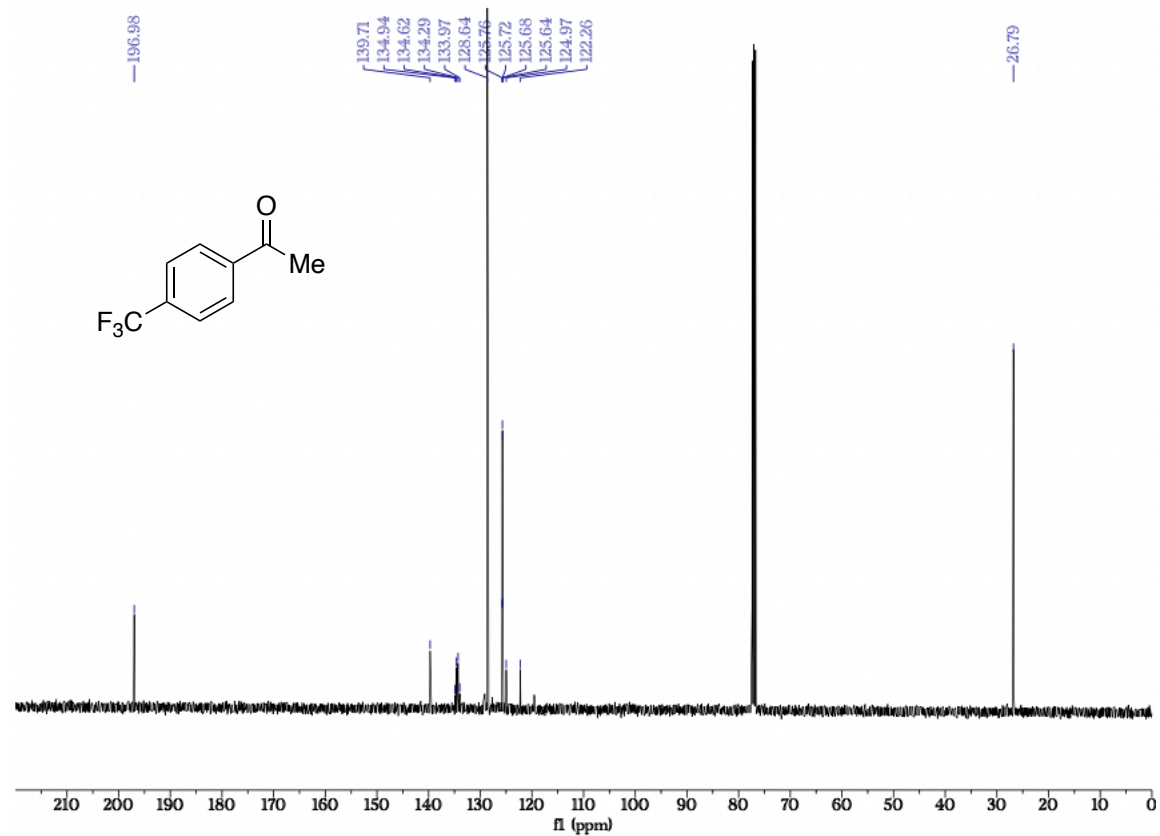
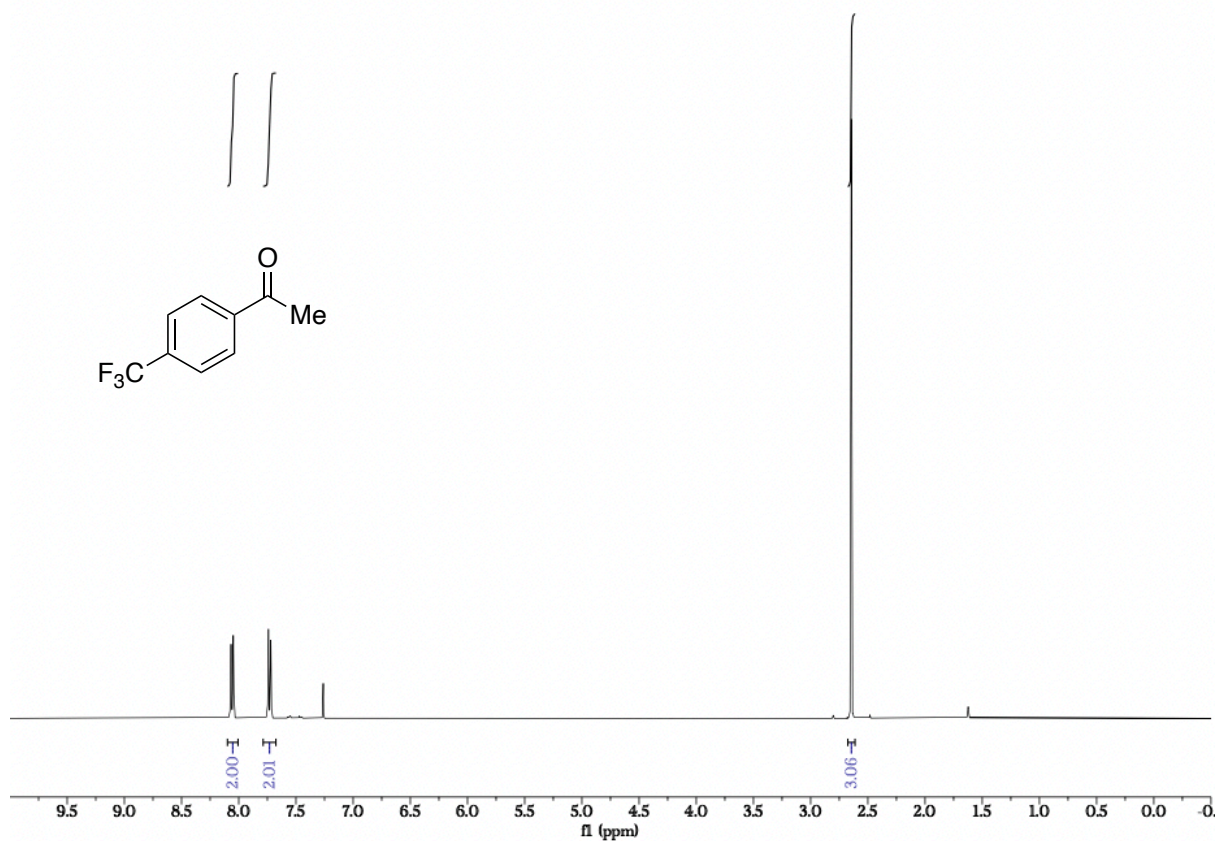
1-(4-methoxyphenyl)ethan-1-one (2i):

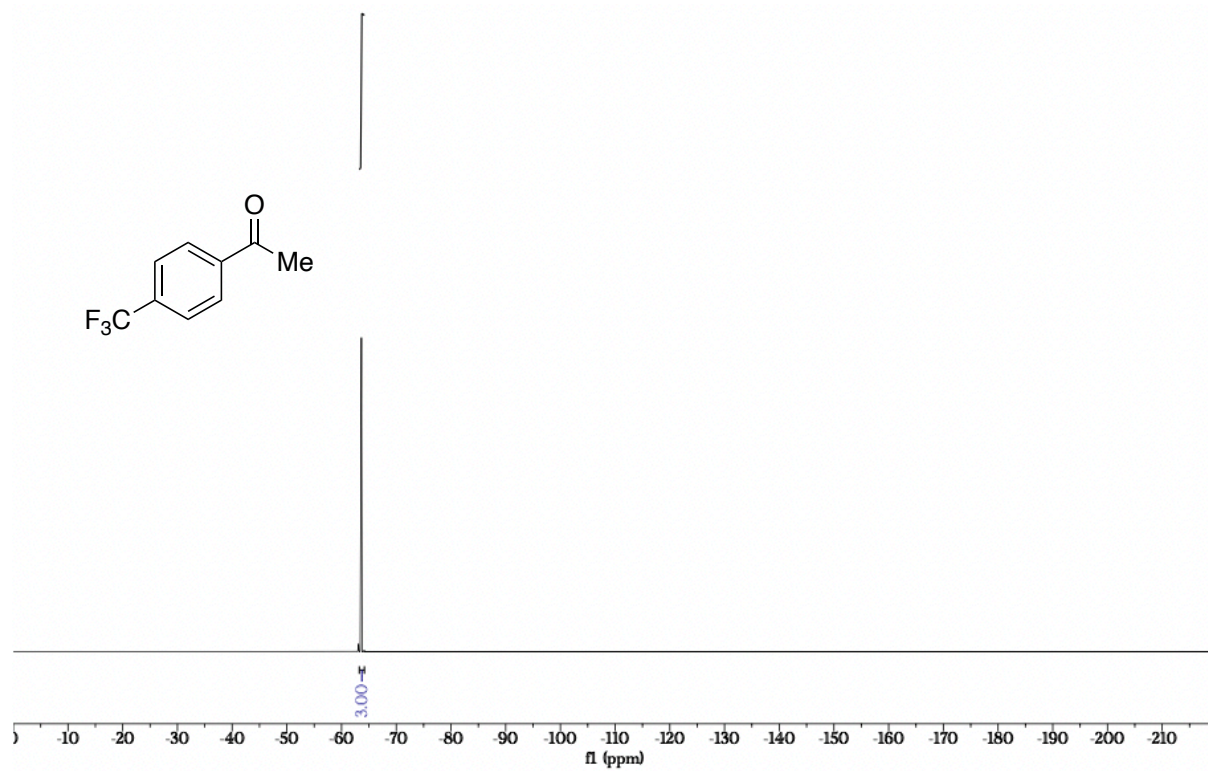


4-acetylphenyl acetate (2j):

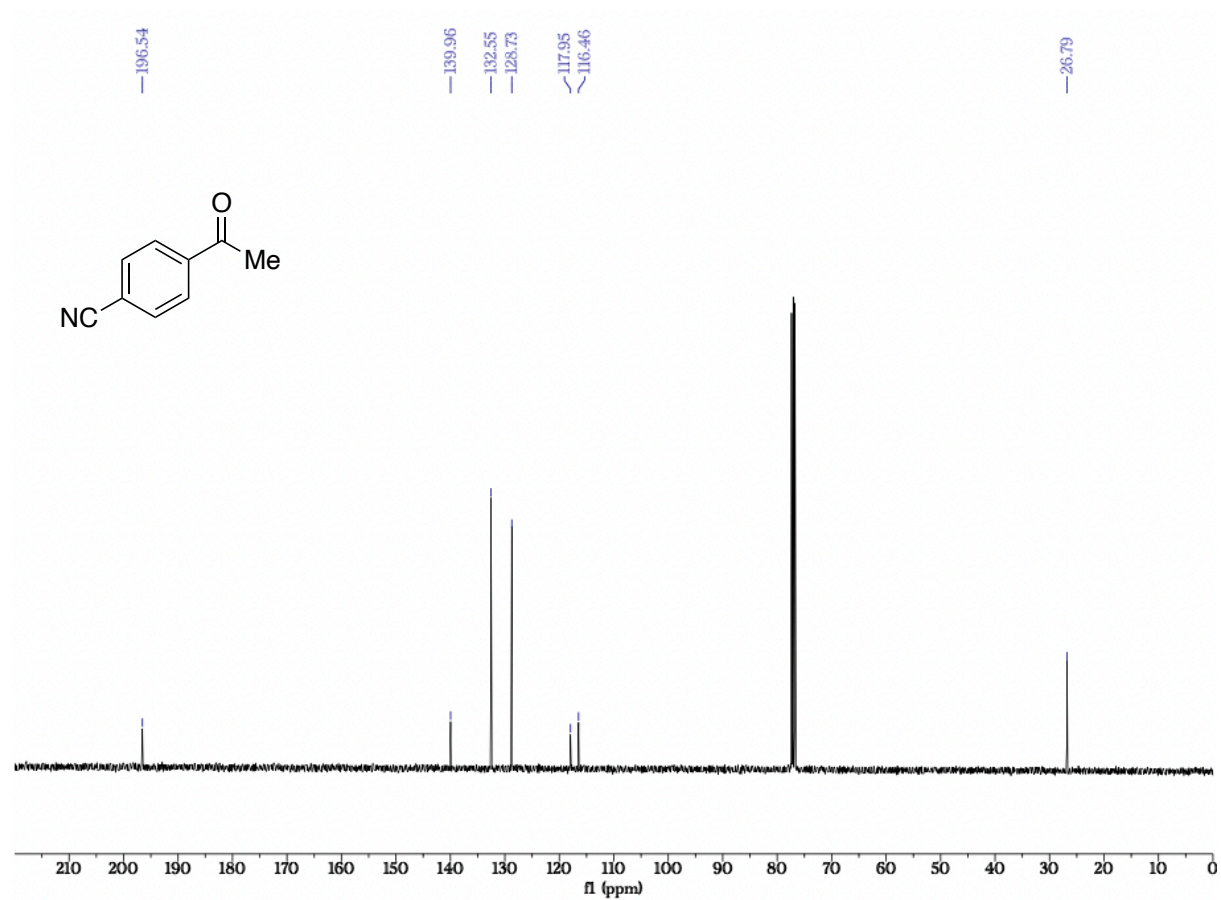
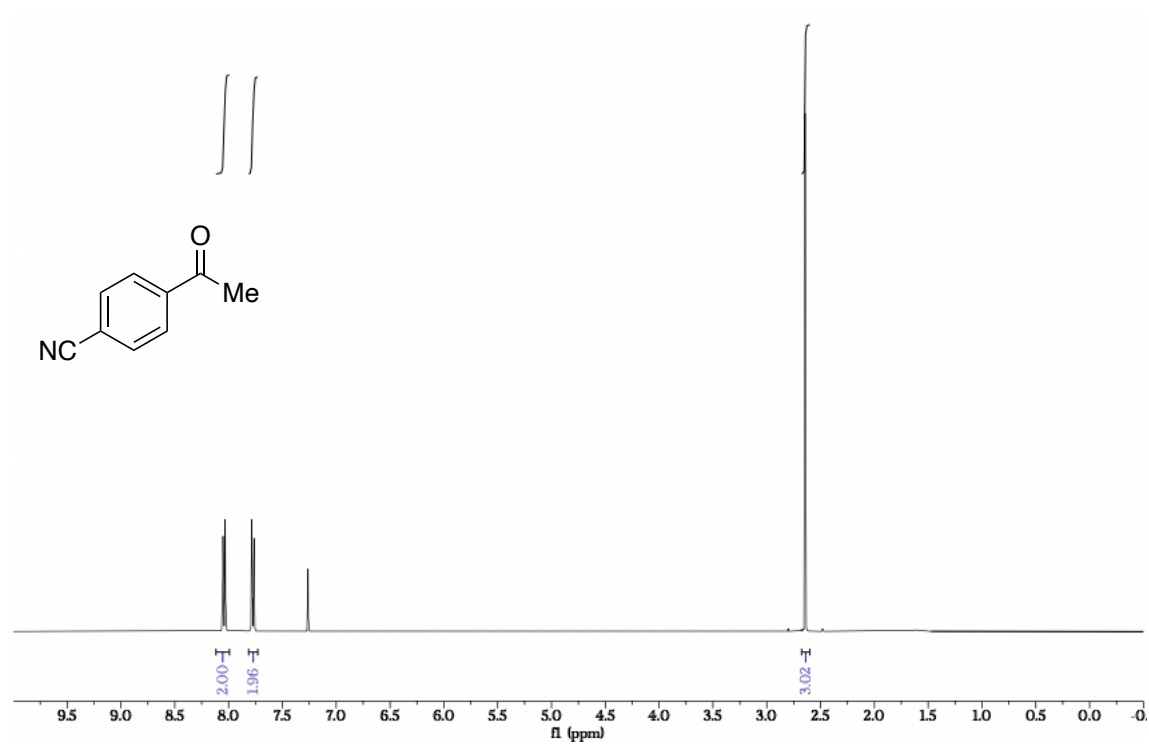


1-(4-(trifluoromethyl)phenyl)ethan-1-one (2k):

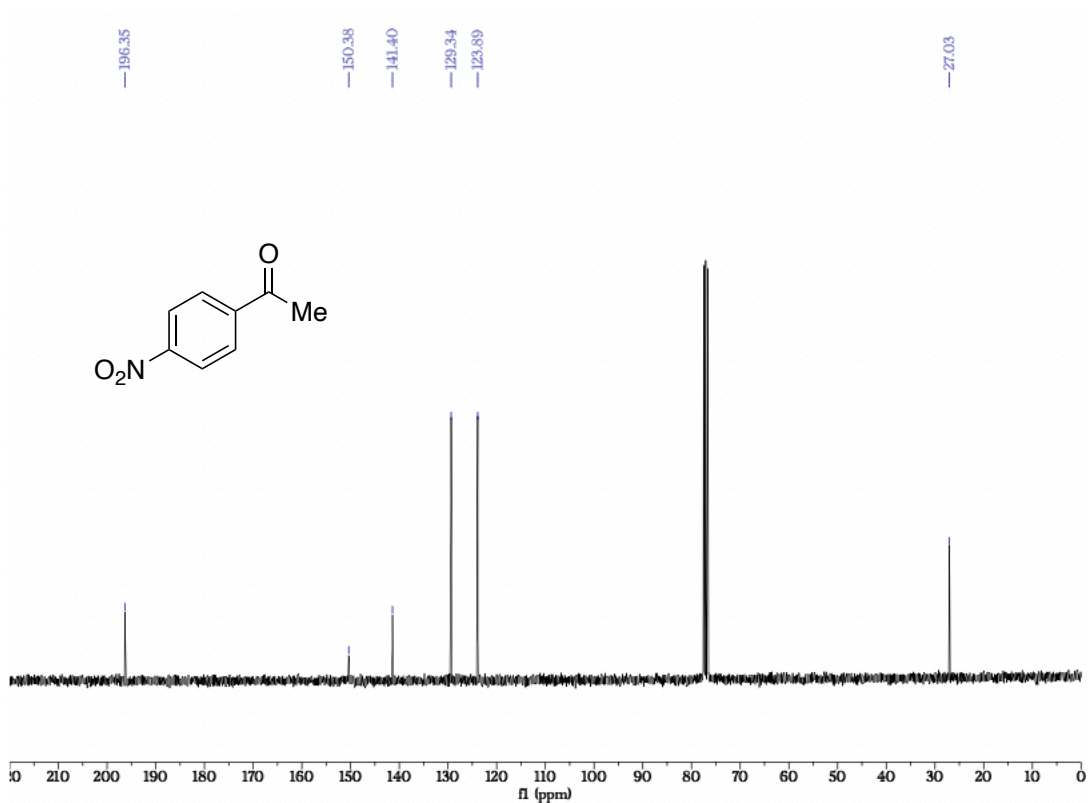
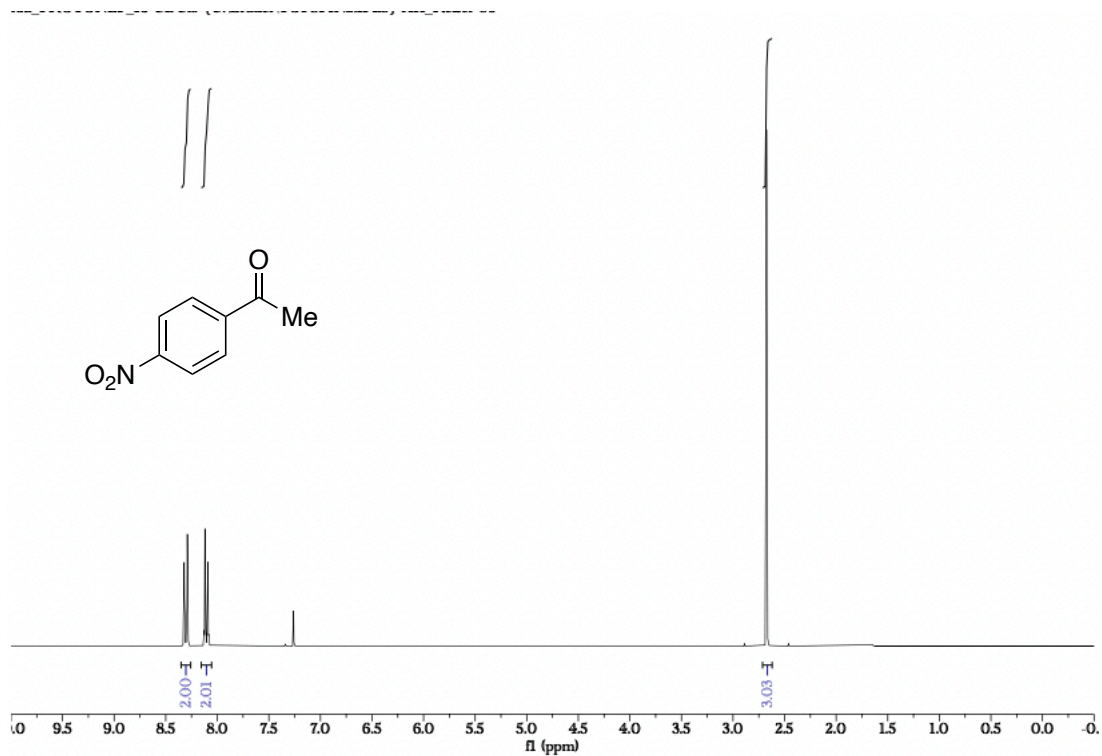




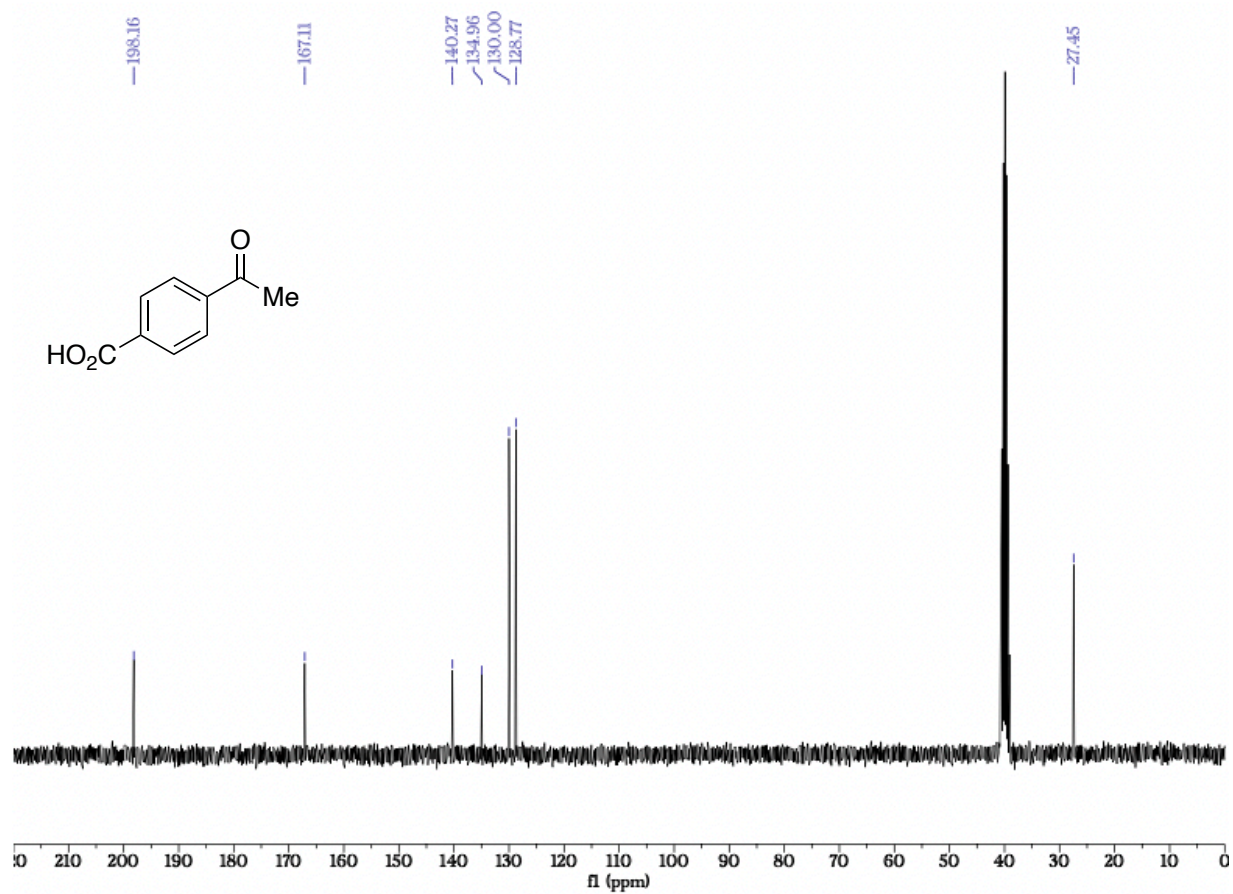
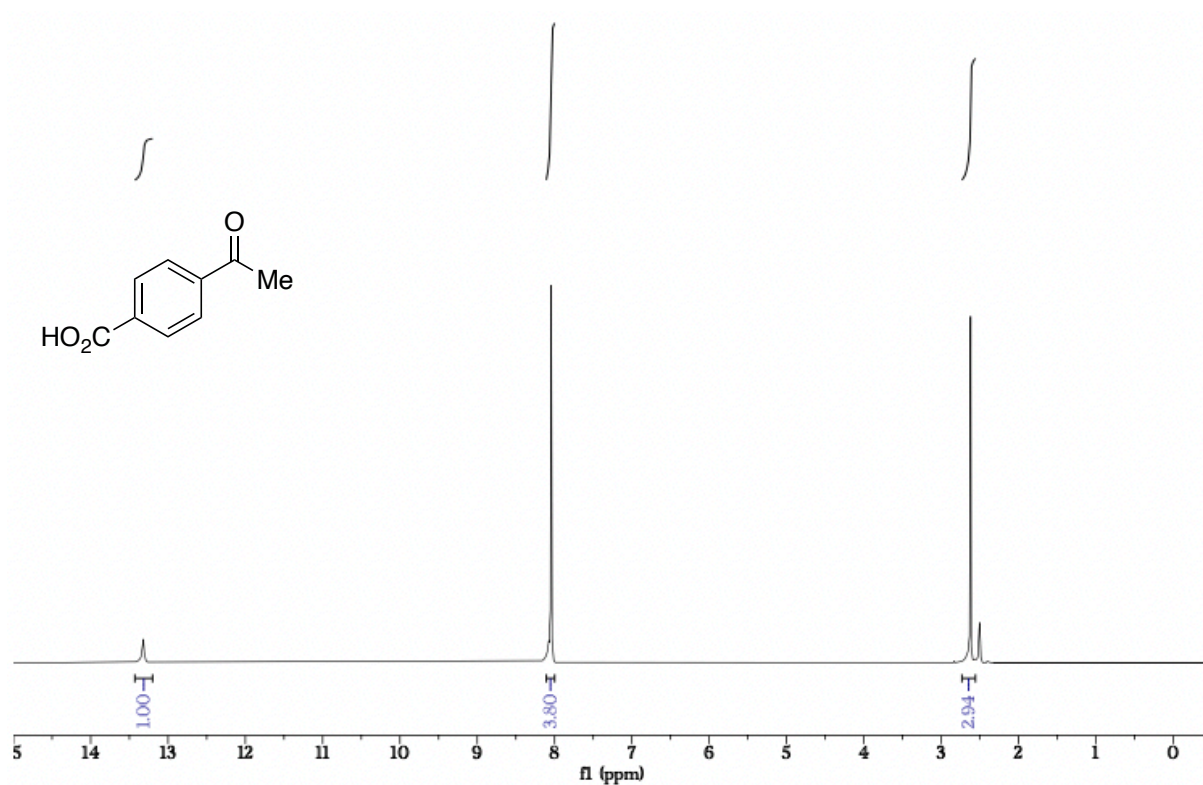
4-acetylbenzotrile (2l):



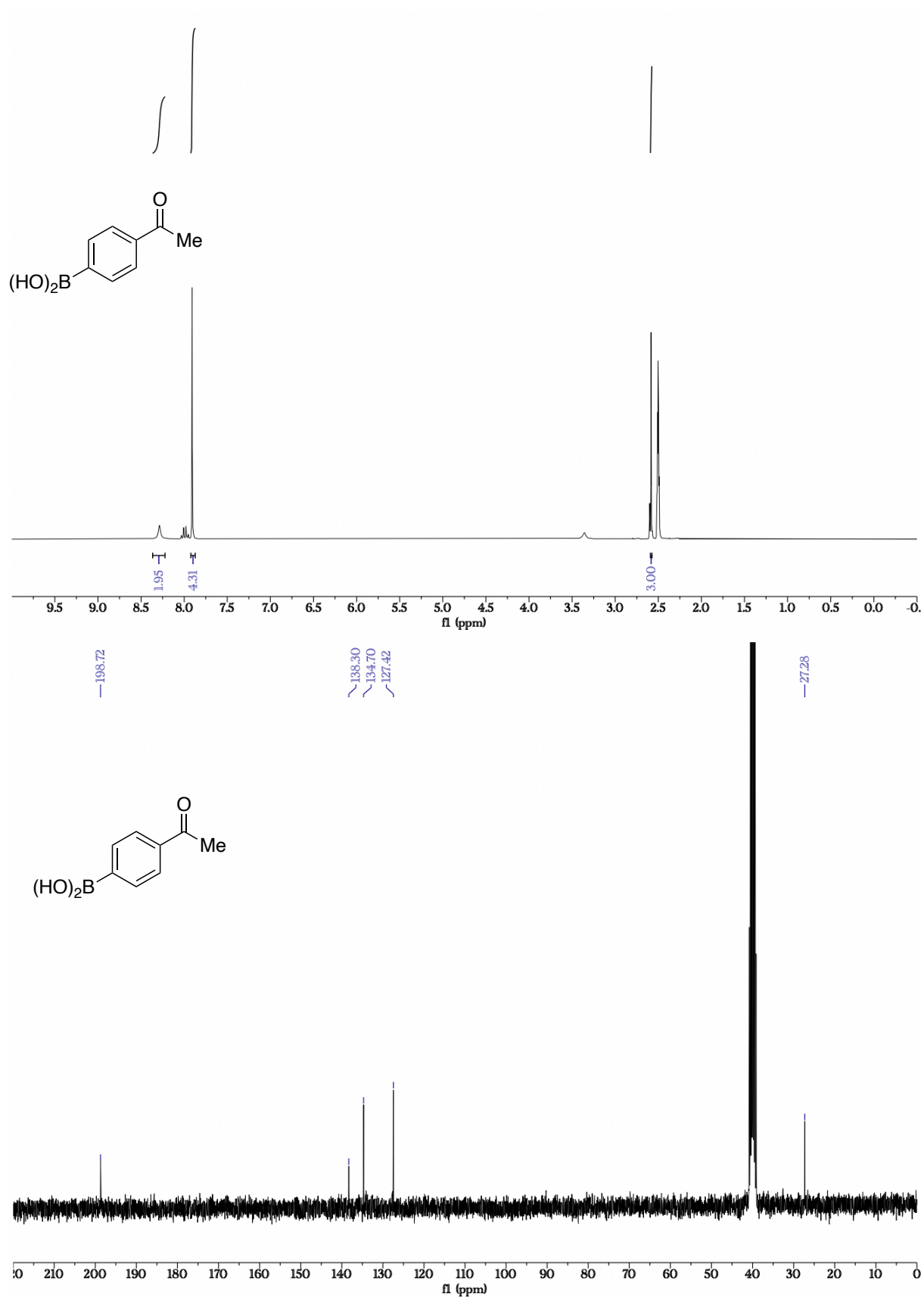
1-(4-nitrophenyl)ethan-1-one (2m):



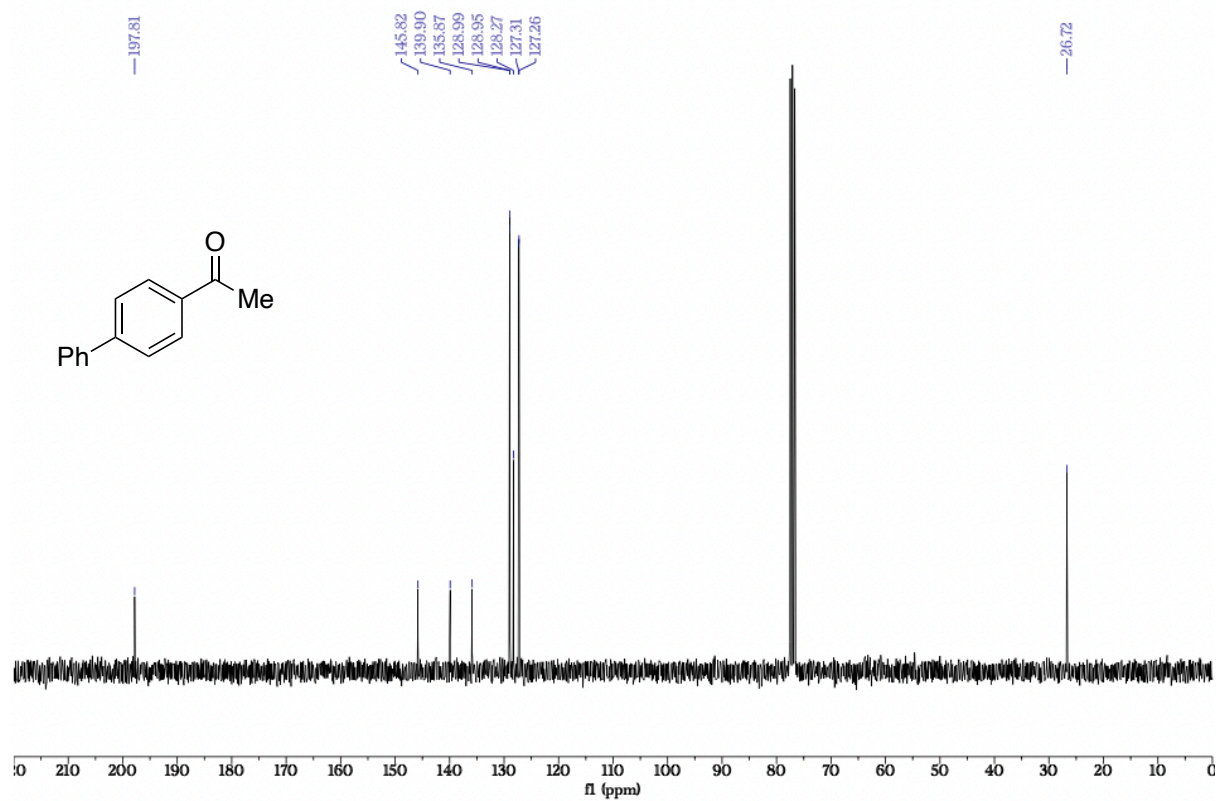
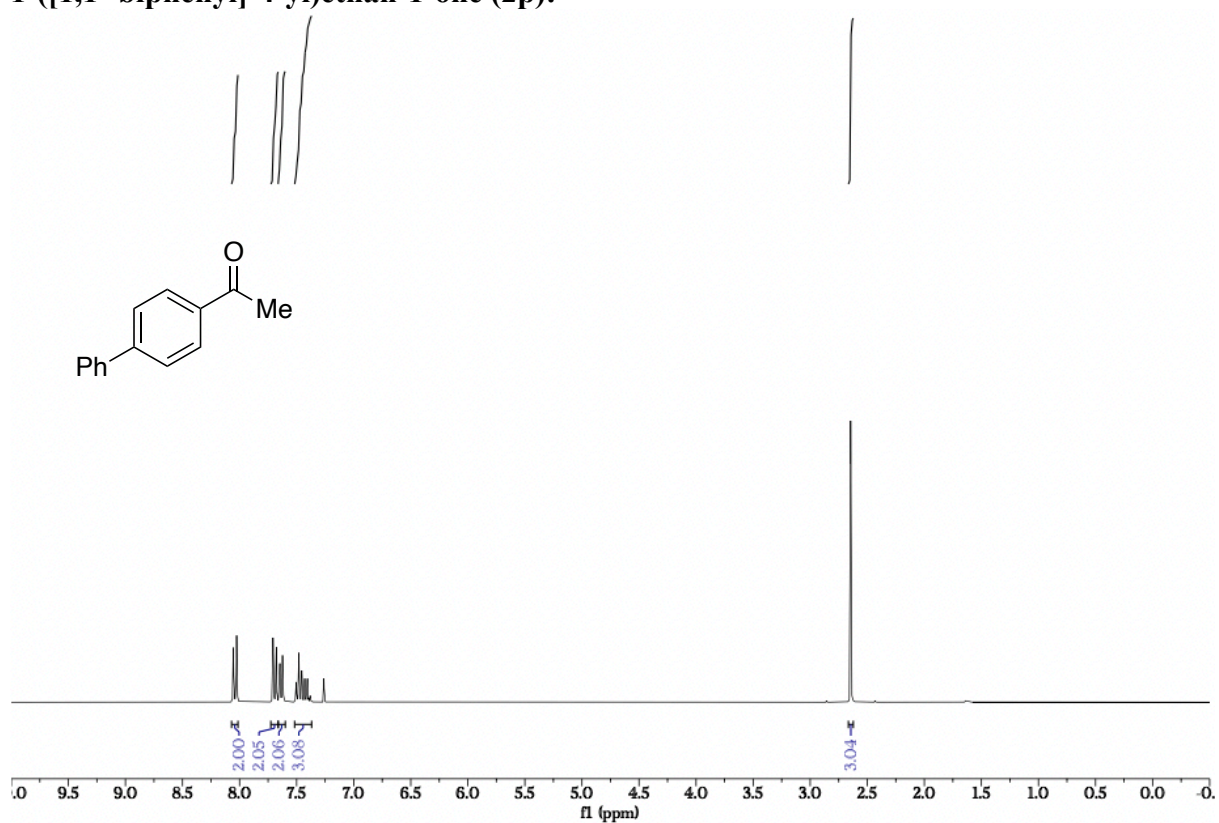
4-acetylbenzoic acid (2n):



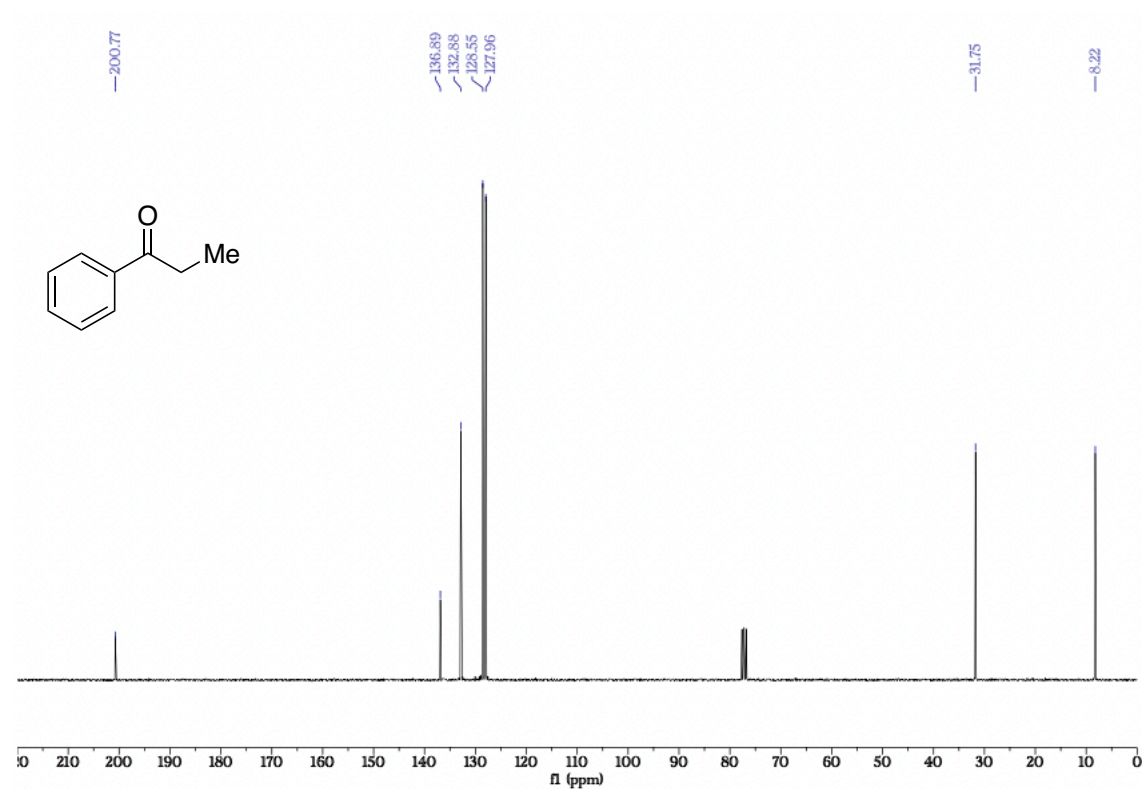
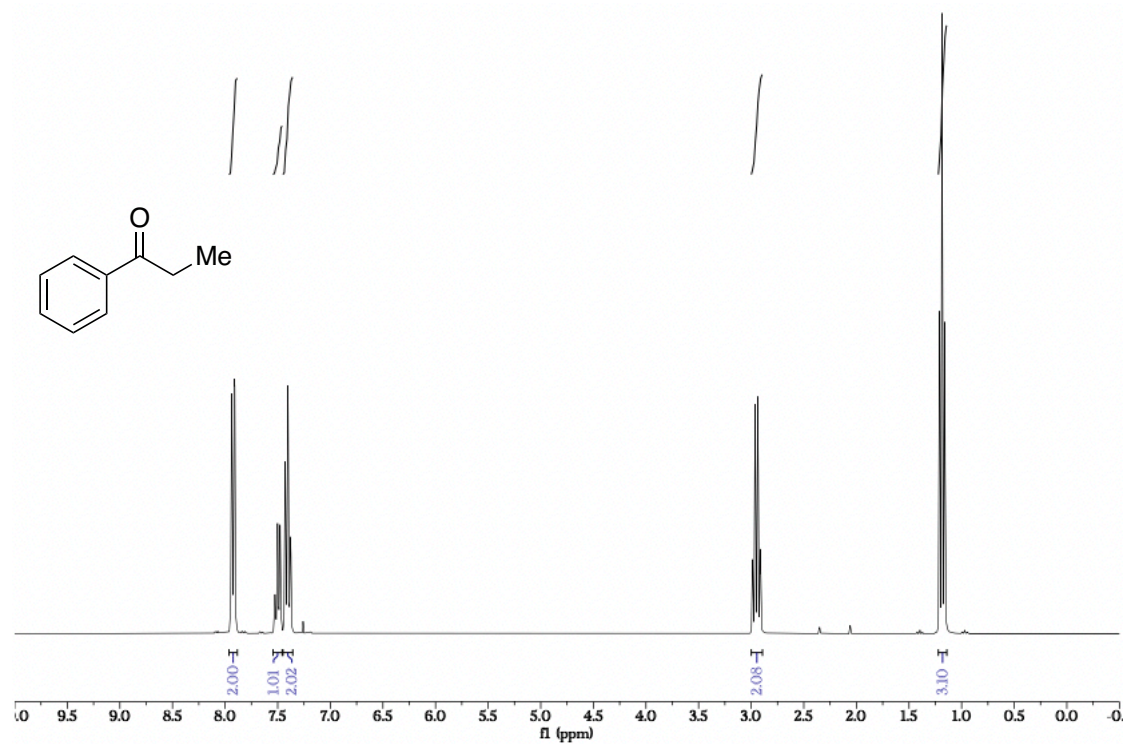
(4-acetylphenyl)boronic acid (2o):



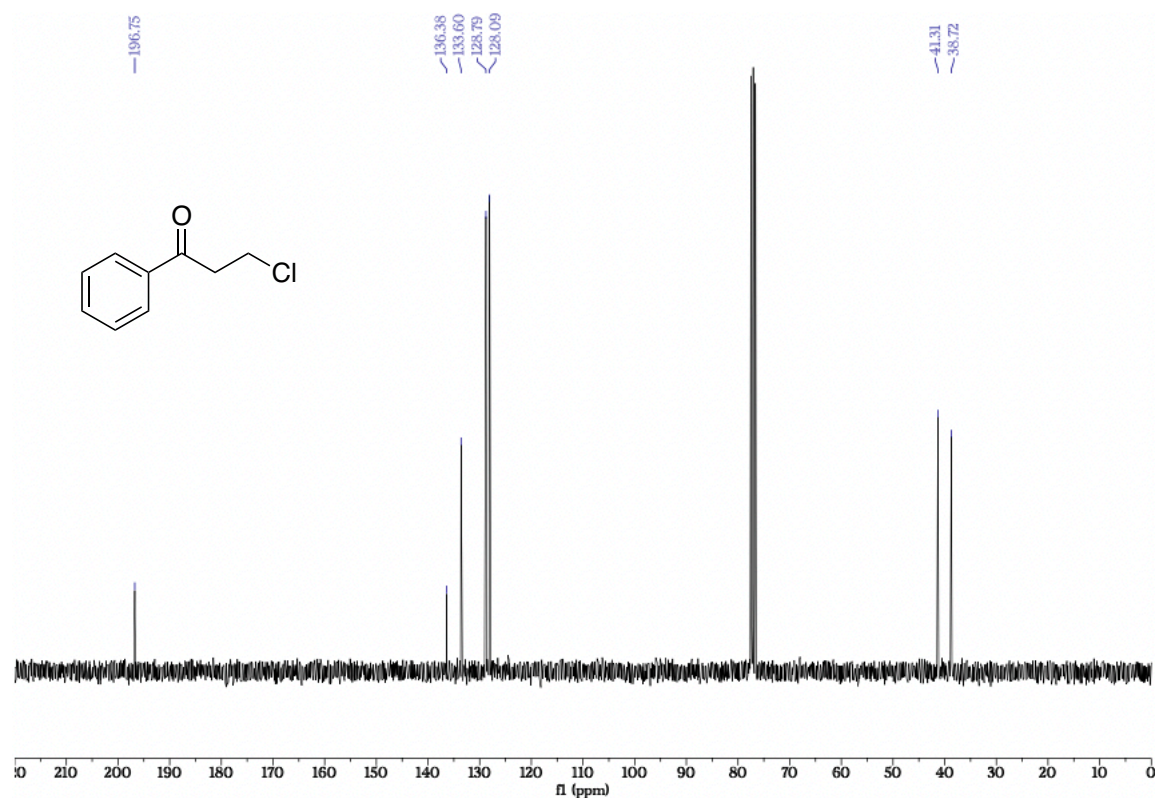
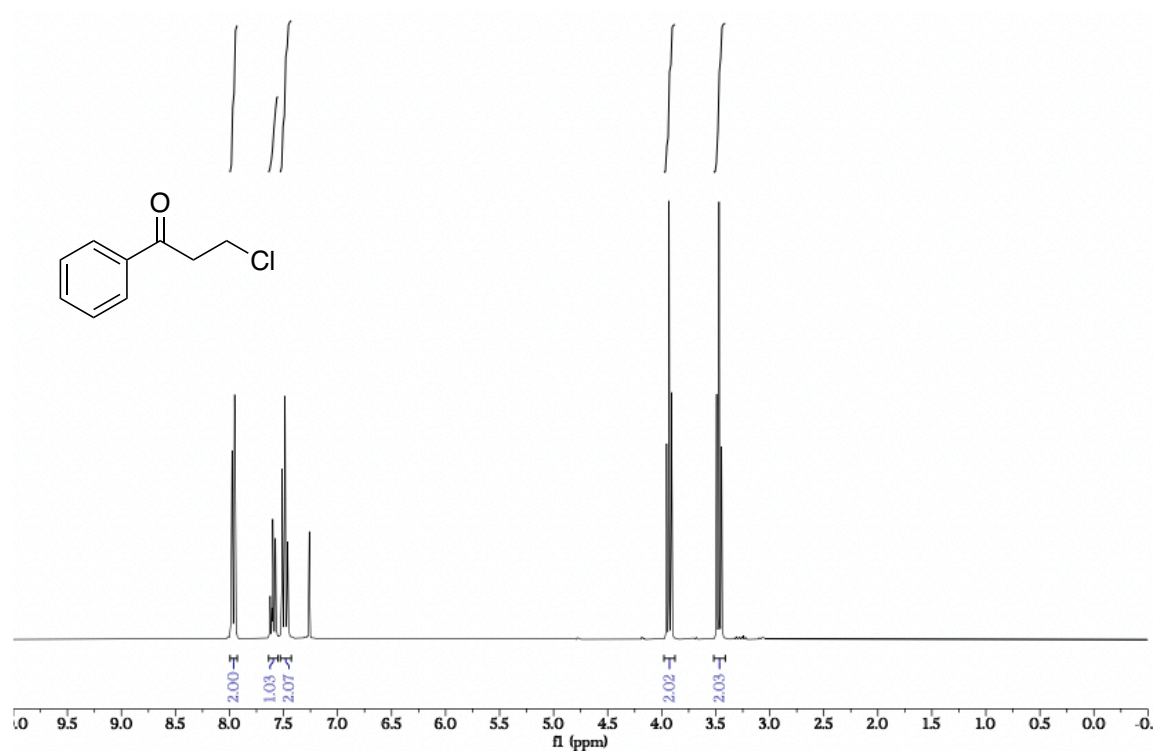
1-([1,1'-biphenyl]-4-yl)ethan-1-one (2p):



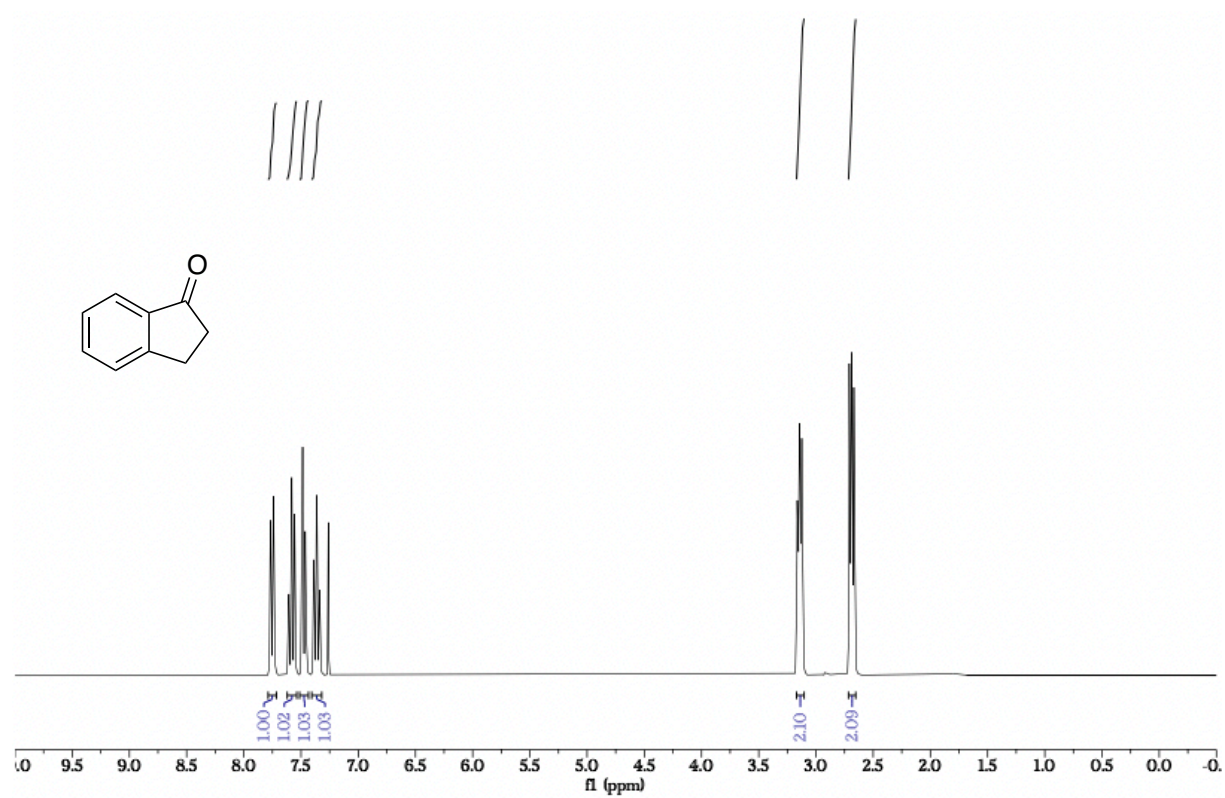
Propiophenone (2q):



3-chloro-1-phenylpropan-1-one (2r):



2,3-dihydro-1H-inden-1-one (2s):



207.13

155.20

137.11

134.63

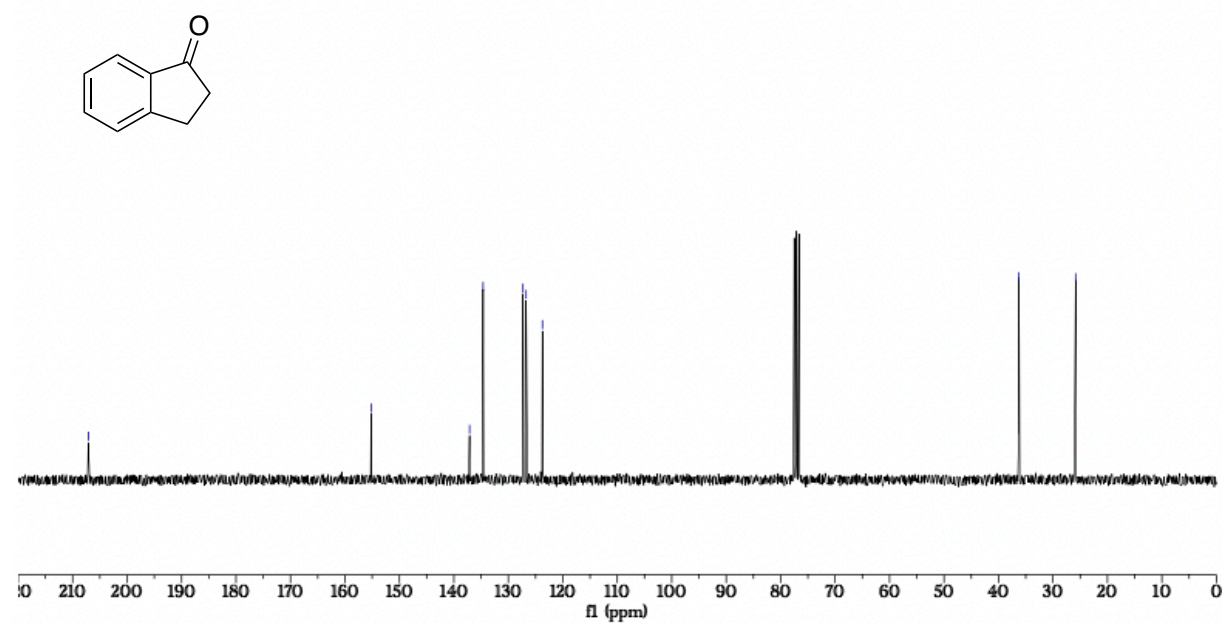
127.31

126.73

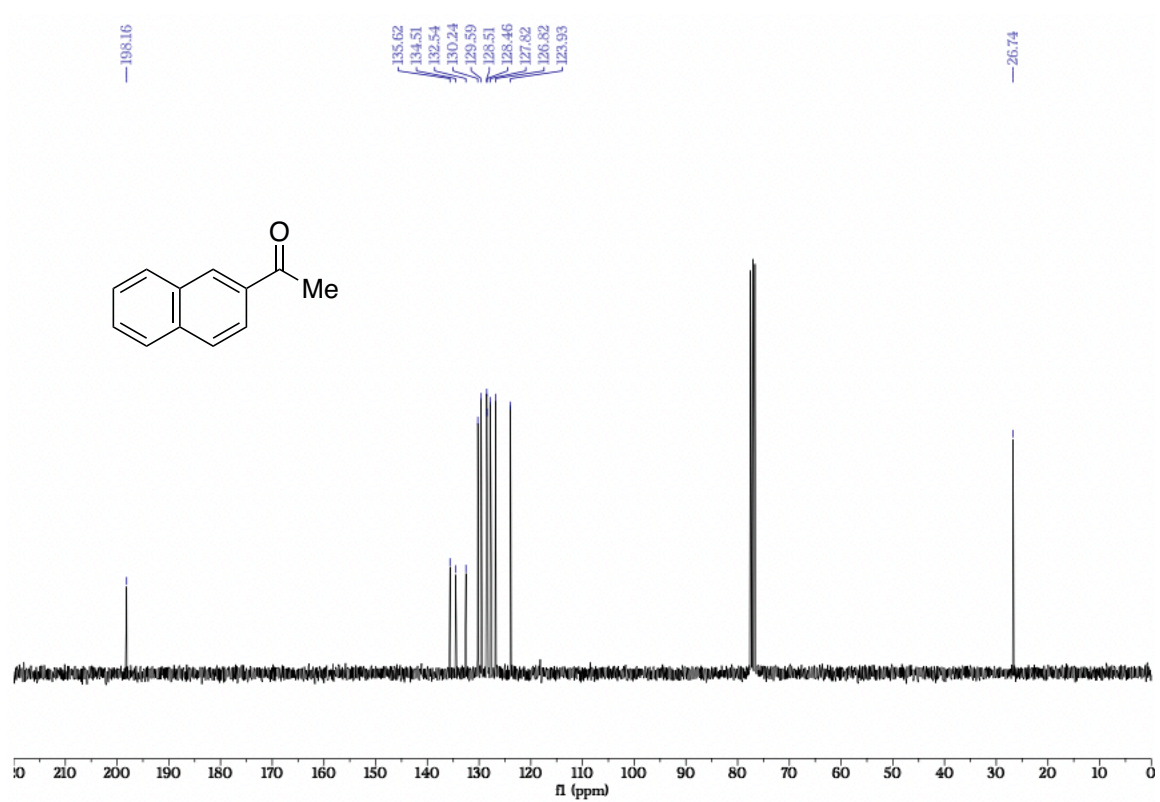
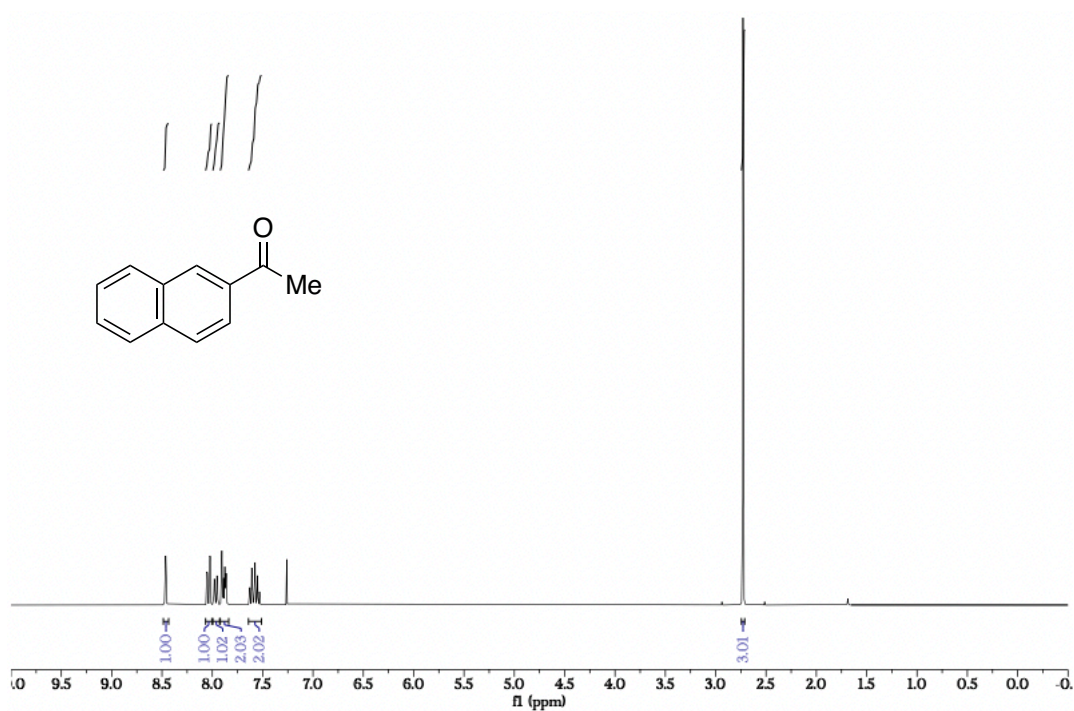
123.74

36.25

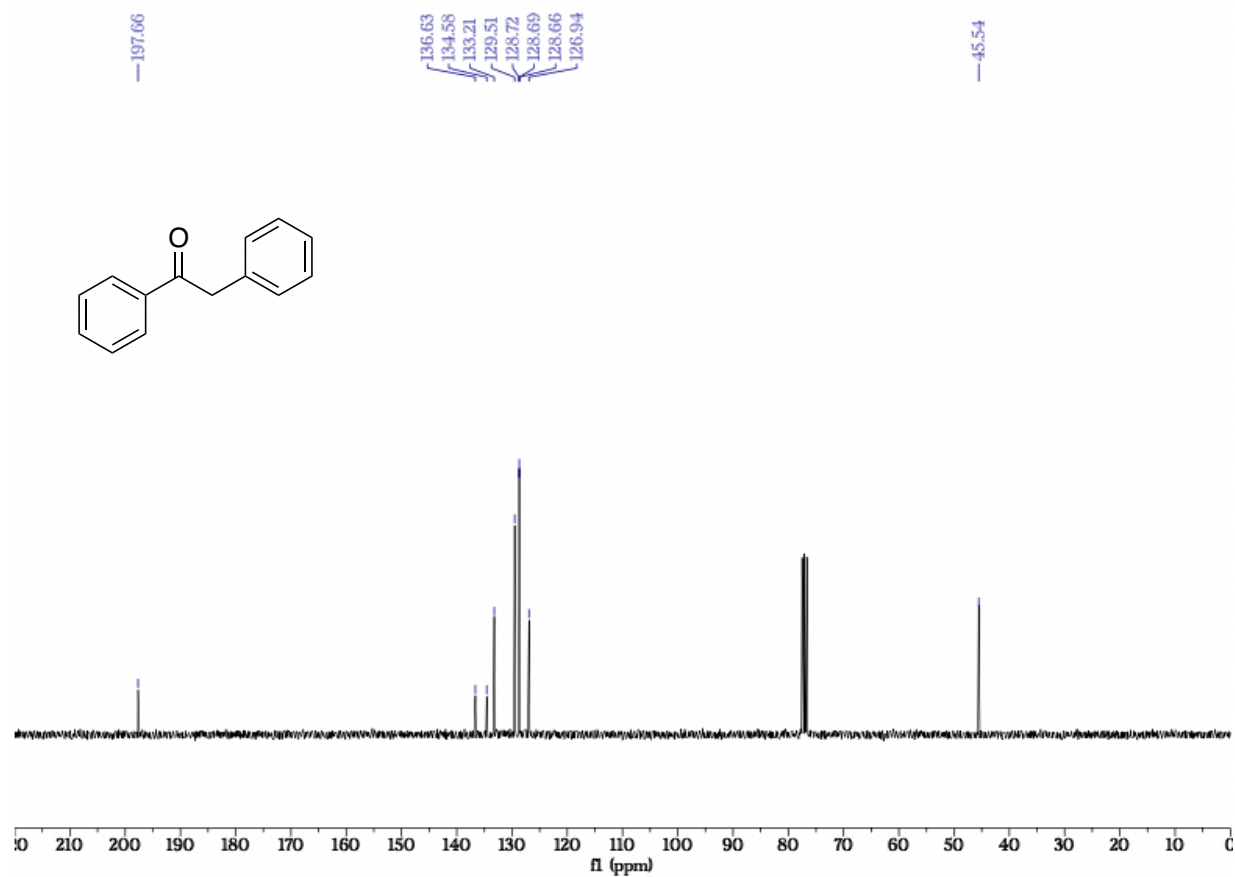
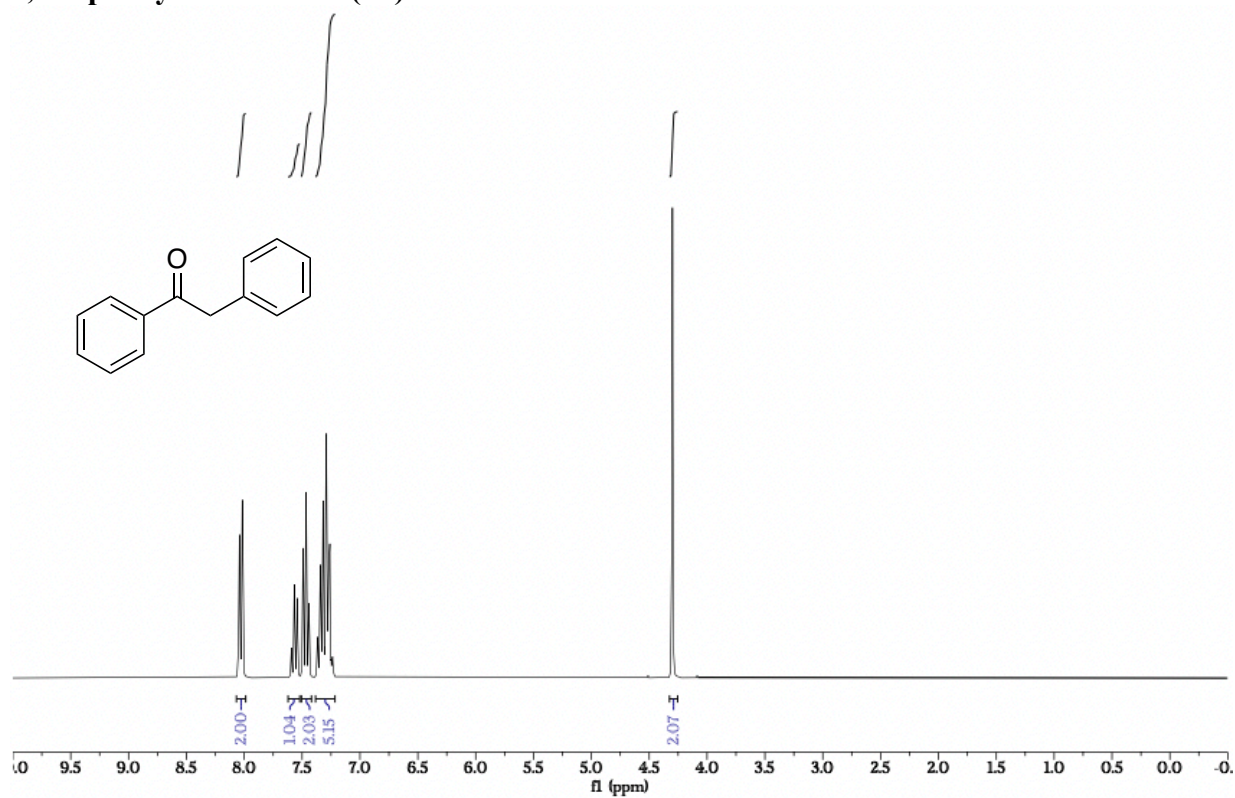
25.83



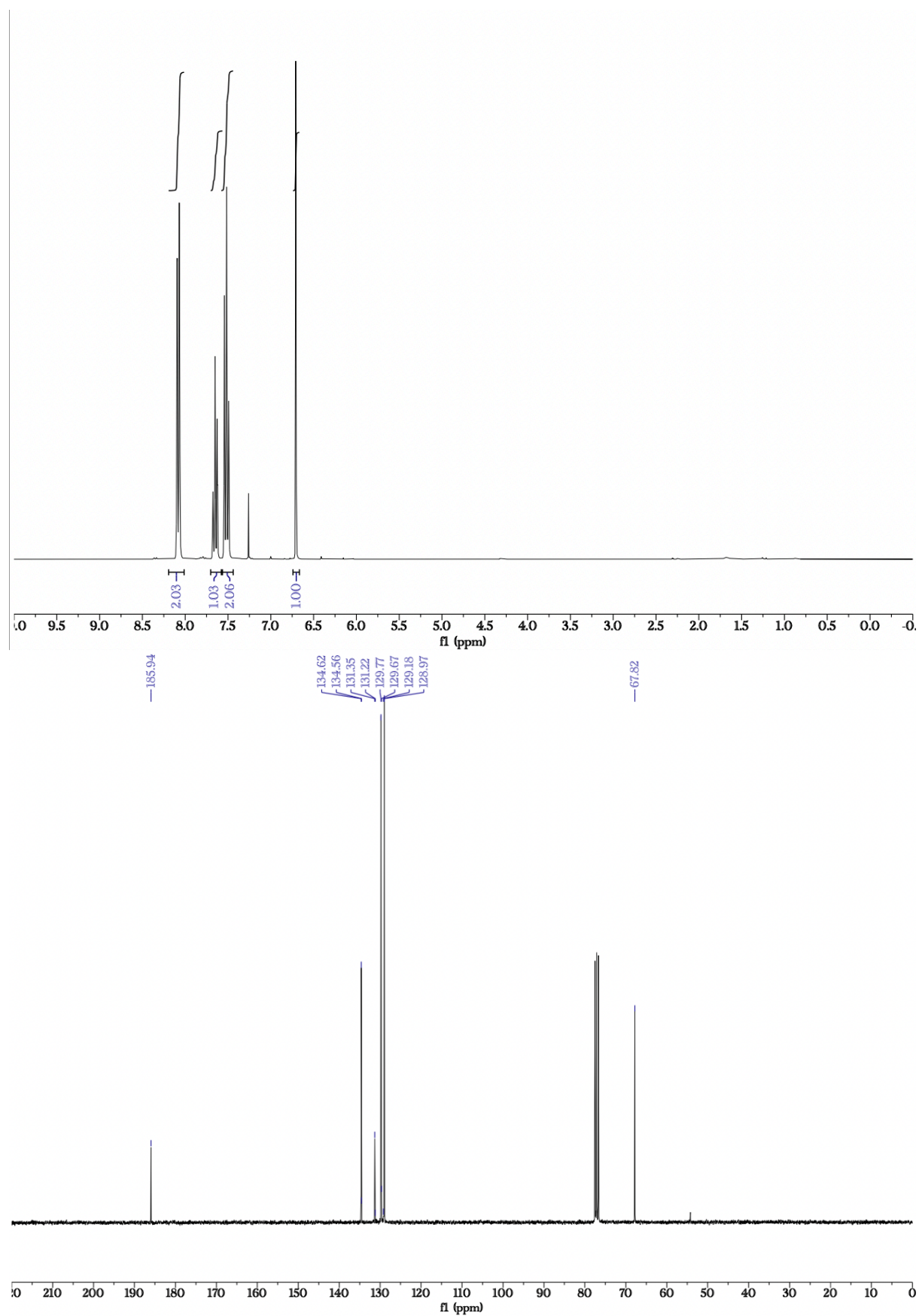
1-(naphthalen-2-yl)ethan-1-one (2t):



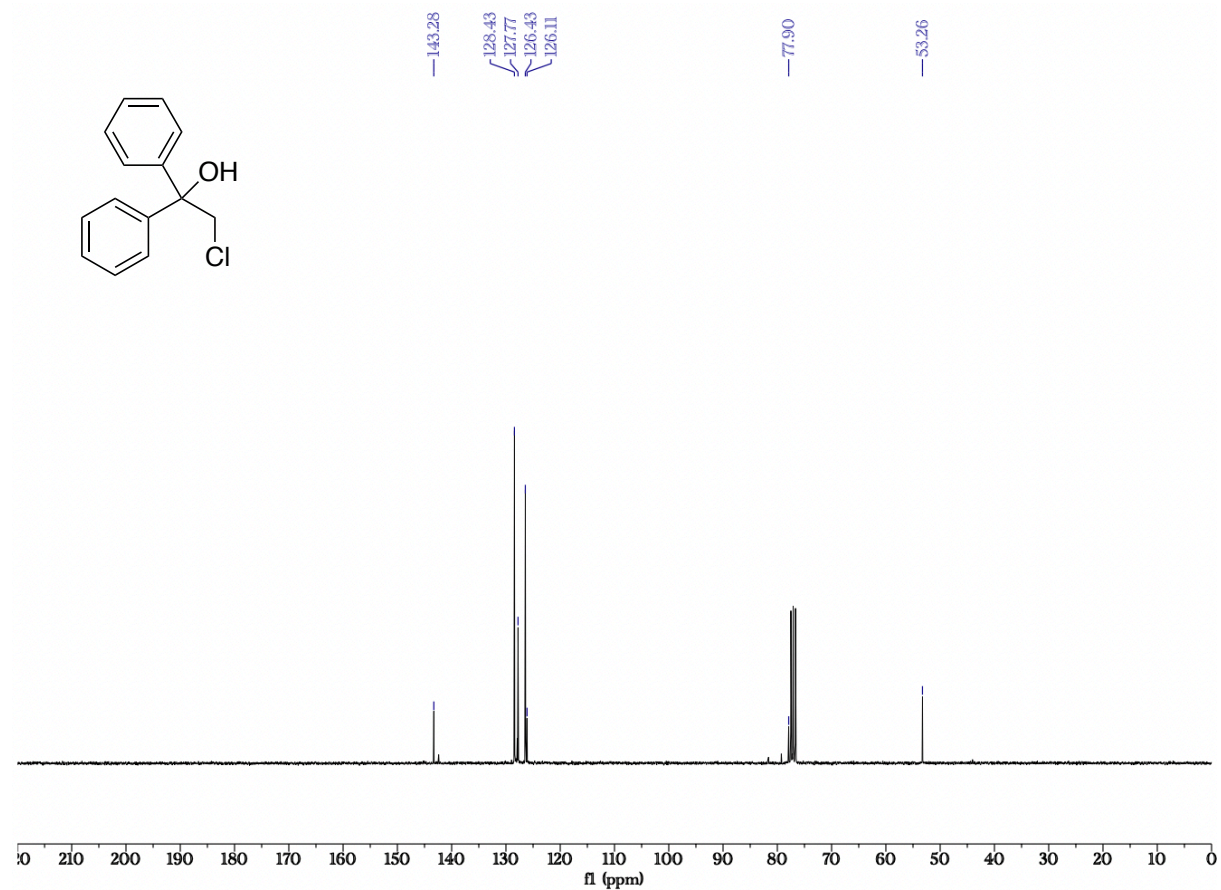
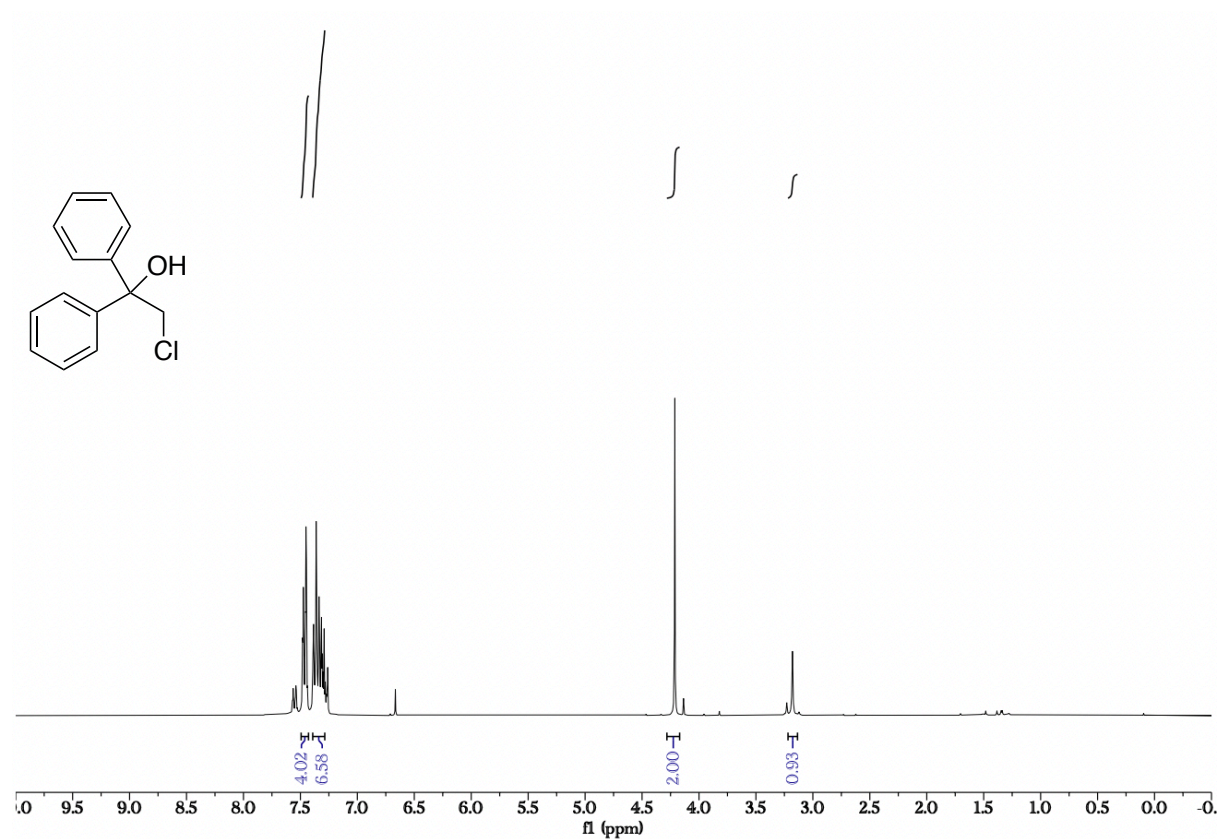
1,2-diphenylethan-1-one (2u):



2,2-dichloro-1-phenylethan-1-one (2v)



2-chloro-1,1-diphenylethan-1-ol (2w):



15. References:

- 1 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.
- 2 E. E. Tredget, N. Forsyth, A. Uji-Friedland, M. Chambers, A. Ghahary, P. G. Scott, A. M. Hogg and J. F. Burke, *J. Chromatogr. B Biomed. Sci. Appl.*, 1993, **612**, 7–19.