

Heterogeneous Fe-N-C Cocatalyst for Hydroquinone Oxidation Enables Aerobic Oxidation of Primary Alcohols to Aldehydes

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Table of Contents

1. General Considerations	S2
2. Ir-catalyzed benzyl alcohol oxidation with catalytic BQ and homogeneous electron transfer mediator	S2
3. Source, synthesis and characterization of Fe-N-C catalysts	S4
3a. ICP-OES Analysis of Fe Content.....	S4
3b. X-Ray Photoelectron Spectroscopy (XPS)	S4
3c. ⁵⁷ Fe Mössbauer Spectroscopy	S7
4. General Method for Aerobic Hydroquinone (HQ) Oxidation	S8
5. General Method for Alcohol Oxidation with Stoichiometric Quinone Derivatives	S12
6. General Method for Aerobic Benzyl Alcohol Oxidation with Catalytic BQ.....	S13
7. General Method for Aerobic Alcohol Oxidation with Catalytic HQ.....	S19
8. Compound Characterization	S20
9. References.....	S23
10. NMR Spectra.....	S25

1. General Considerations

Commercially available organic compounds and solvents were purchased from Sigma Aldrich or Thermo Scientific and used as received unless otherwise noted. Co(salen) hydrate, Co(salophen) hydrate, and iron(II) phthalocyanine (Fe(Pc)) were purchased from Sigma Aldrich. Platinum and palladium on carbon (5 wt %) were sourced from Johnson-Matthey and Sigma Aldrich, respectively. Reaction vials were placed in a 19-well aluminum block that was raised from the surface of the stir plate by 0.5 inches to prevent reaction heating via conduction of heat generated by the stirring motor. Chromatography was performed using an automated Biotage Isolera® with reusable 25 g Biotage® Silicycle cartridges or standard silica cartridges. NMR spectra (^1H and ^{13}C) were obtained with a Bruker Avance III 500 MHz spectrometer with reference to residual solvent peaks: CDCl_3 peaks at 7.26 ppm (^1H) and 77.16 ppm (^{13}C). Multiplicities are described using the following abbreviations: s = singlet, bs = broad singlet, d = doublet, dd = doublet of doublet, dt = doublet of triplet, t = triplet, m = multiplet. High-resolution mass spectra were obtained using a Thermo Q Exactive™ Plus via ASAP-MS in the mass spectrometry facility at the University of Wisconsin-Madison. Samples were submitted to the facility and facility staff ran the samples. *Note* – caution should be used when conducting reactions in organic solvents using oxygen gas. Efforts should be made to stay below the limiting oxygen concentration (LOC) of the solvent and/or reagents used in the reaction.^[1]

The complex $[\text{Ir}(\text{trop}_2\text{DAD})\text{OTf}]$ (**Ir-2**) was synthesized following the known literature procedure.^[2] Characterization data for the catalyst is as follows:

^1H NMR (500 MHz, CD_2Cl_2) δ 9.37 (s, 2H), 7.61 (dd, $J = 7.0, 2.0$ Hz, 4H), 7.48 (dd, $J = 7.0, 1.9$ Hz, 4H), 7.39 (pd, $J = 7.4, 1.7$ Hz, 8H), 6.42 (s, 2H), 5.70 (s, 4H).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.1, 139.4, 133.5, 130.5, 130.5, 129.2, 128.7, 75.8, 74.5.

^{19}F NMR (377 MHz, CDCl_3) δ -76.95.

UV-vis in THF, λ (nm): 413.9, 340.1 279.1.

HRMS (ESI) exact mass calculated for $[\text{M-OTf}]^+$, $[\text{IrC}_{32}\text{H}_{26}\text{N}_2]^+$: 629.1569, found m/z 629.1696.

2. Ir-catalyzed benzyl alcohol oxidation with catalytic BQ and homogeneous electron transfer mediator

Each reaction vial (8 mL, 2 drams) was charged with benzyl alcohol (5 mmol, 520 μL), BQ (10 mol %, 0.5 mmol, 54 mg), 0.05 mol % $[\text{Ir}(\text{trop}_2\text{DAD})\text{OTf}]$, **Ir-2** (0.0025 mmol, 1.75 mg) as an alcohol oxidation catalyst, a homogeneous HQ oxidation catalyst (0.1 mol %), 0.1 mol % NaO^tBu (0.56 mg, 2.5 μL from 2 M NaO^tBu solution), and 1,3,5-trimethoxybenzene (28 mg, 0.166 mmol) as an internal standard in 1.5 mL THF. The reaction solution was charged with 1 atm O_2 (a slow sparge of O_2 bubbles, originating from an O_2 tank) and stirred at 1000 rpm. Reaction aliquots (20 μL) were taken out every 30 min or 1 hour using a pipette and diluted with 0.5 mL of CDCl_3 . The reaction aliquot was then filtered through a 13 mm syringe filter with a 0.2 μm PTFE membrane (VWR) and analyzed by ^1H NMR spectroscopy.

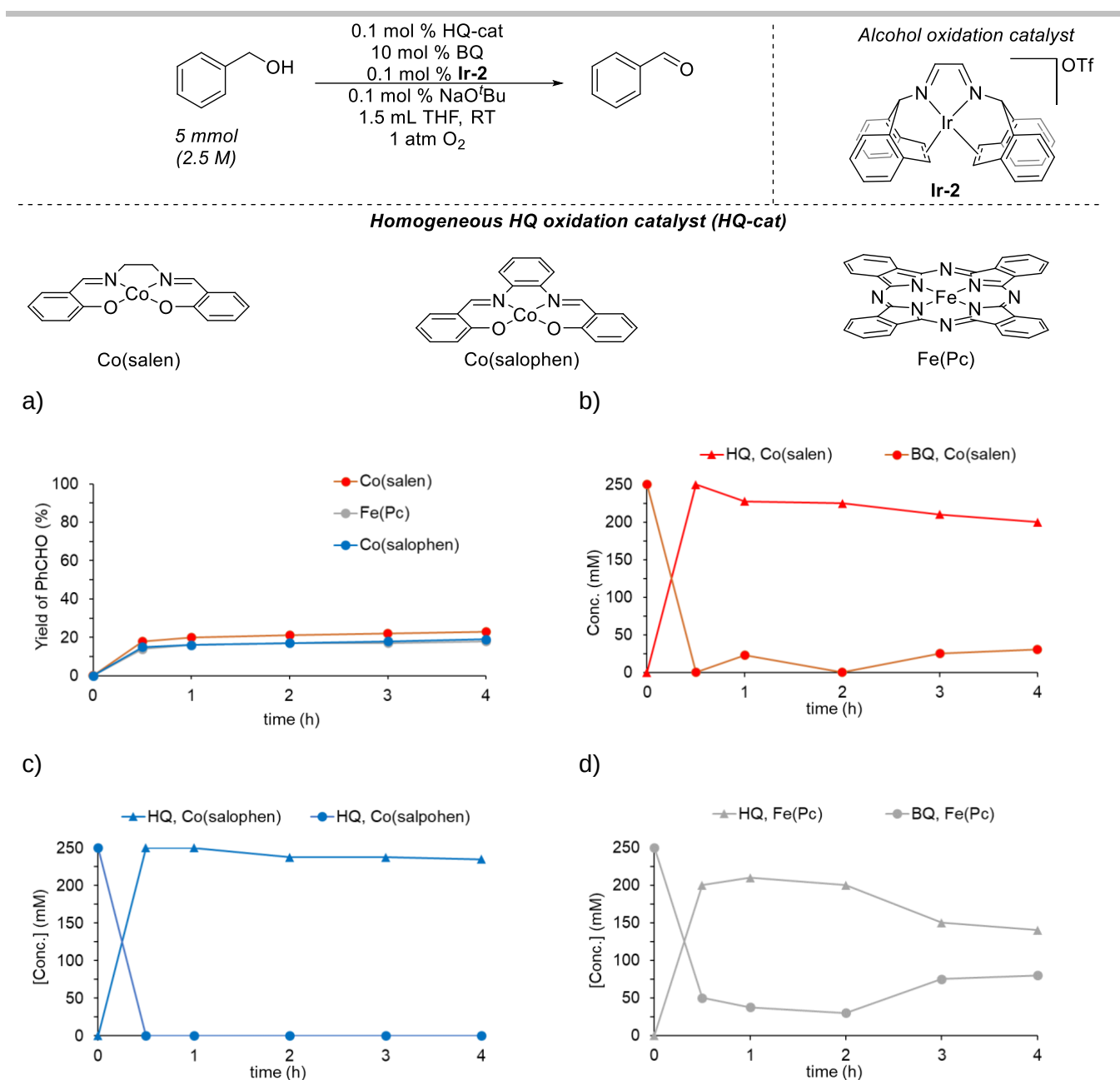


Figure S1. Aerobic oxidation of benzyl alcohol with catalytic BQ. a) Time course for aerobic benzyl alcohol oxidation in the presence of 0.1 mol % homogeneous HQ oxidation catalyst, 0.1 mol % Ir-2, and 10 mol % BQ in THF. HQ and BQ speciation during the reactions run with b) Co(salen); c) Co(salophen) and d) Fe(Pc).

The homogeneous catalysts Co(salen), Co(salophen), and Fe(Pc) were not able to regenerate BQ efficiently during the reaction to maintain catalytic activity (after 30 min, almost all of the quinone is present as HQ (triangle data points), which cannot assist with catalytic turnover).

3. Source, synthesis and characterization of Fe-N-C catalysts

A commercially available Fe-N-C catalyst was sourced from Pajarito Powder^[3] (product number PMF-011904) and abbreviated as “PAJ-Fe-N-C” in this report. Several other previously reported Fe-N-C materials including Fe-Phen-C,^[4,5] Fe-Pc-C,^[6] and Fe-PANI-C^[7] which were synthesized according to the literature procedures (Phen = 1,10-phenanthroline, Pc = phthalocyanine; PANI = polyaniline). The ICP-OES, XPS and Mössbauer data of these materials have been provided below.

3a. ICP-OES Analysis of Fe Content

The Fe content in each of the catalysts was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

PAJ-Fe-N-C^[8]: 0.55 wt% Fe

Fe-Phen-C^[9]: 0.6 wt% Fe

Fe-Pc-C^[9]: 0.63 wt%

Fe-PANI-C^[8]: 1.2 wt% Fe

3b. X-Ray Photoelectron Spectroscopy (XPS)

Spectra were collected using a Thermo Scientific K-alpha XPS equipped with a monochromatic Al K α X-ray source and spot size of 400 μ m. The powder samples were pressed onto the sample holder and mounted on a sample stage placed in the analysis chamber. The X-ray gun was operated at 15 kV and 20 mA. All spectra are referenced to the low binding energy carbon peak set at 284.8 eV. Elemental scan was done for N 1s from 392 to 410 eV with step size of 0.1 eV and pass energy of 50 eV. Elemental scan was done for Fe 2p from 700 eV to 740 eV with a step size of 0.1 eV and pass energy of 50 eV. CasaXPS software was used to perform the least-squares curve-fitting procedure using a mixture of Gaussian (70%) and Lorentzian (30%) functions, and a Shirley background. XPS data for Fe-PANI-C were reported previously.^[10]

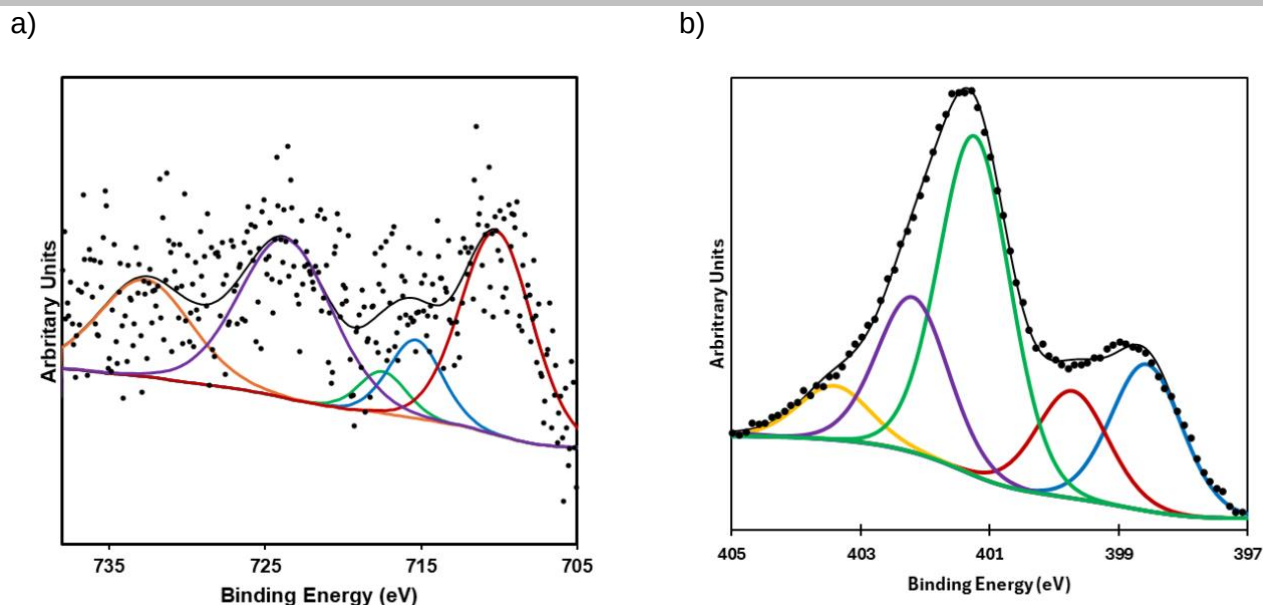


Figure S2. XPS data for PAJ-Fe-N-C. (a) Fitted Fe2p spectrum and (b) N1s spectrum. The Fe2p spectrum was fit using a peak for Fe2p_{1/2} (purple), Fe2p_{3/2} (red), multiplets (blue and orange), and a satellite (green). The N1s spectrum was fit using a peak for pyridinic (blue), FeN_x (red), pyrrolic (green), quaternary (purple), graphitic (yellow), and various peaks for NO_x species (gray).

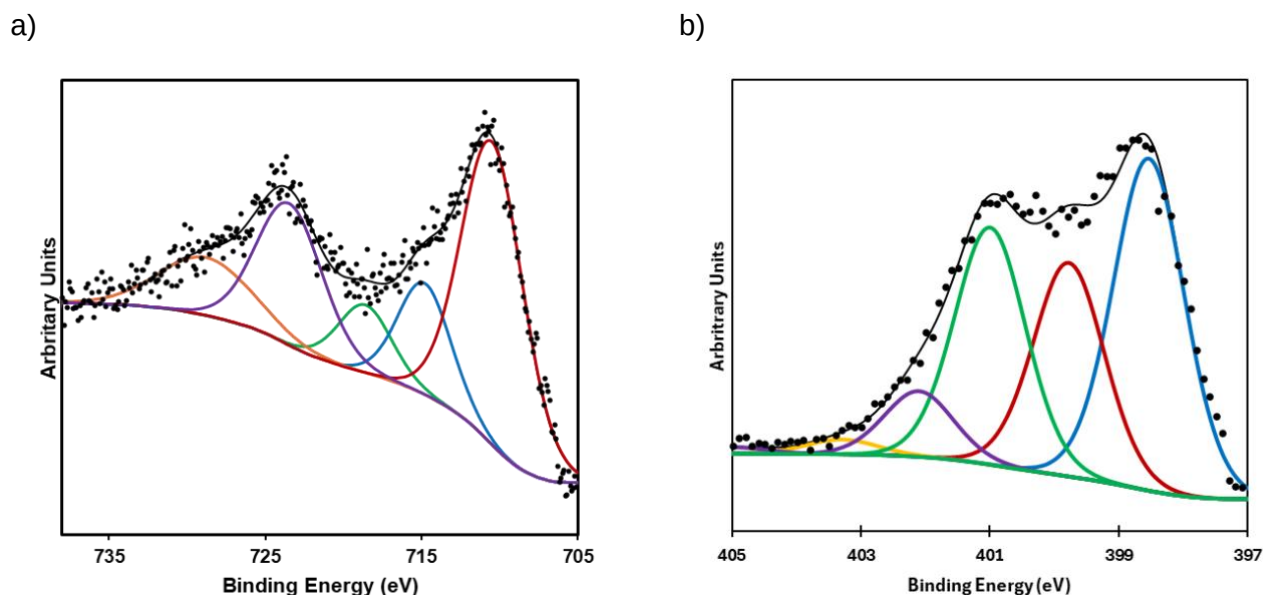


Figure S3. XPS data for Fe-Phen-C. (a) Fitted Fe2p spectrum and (b) N1s spectrum. The Fe2p spectrum was fit using a peak for Fe2p_{1/2} (purple), Fe2p_{3/2} (red), multiplets (blue and orange), and a satellite (green). The N1s spectrum was fit using a peak for pyridinic (blue), FeN_x (red), pyrrolic (green), quaternary (purple), graphitic (yellow), and various peaks for NO_x species (gray).

a) b)

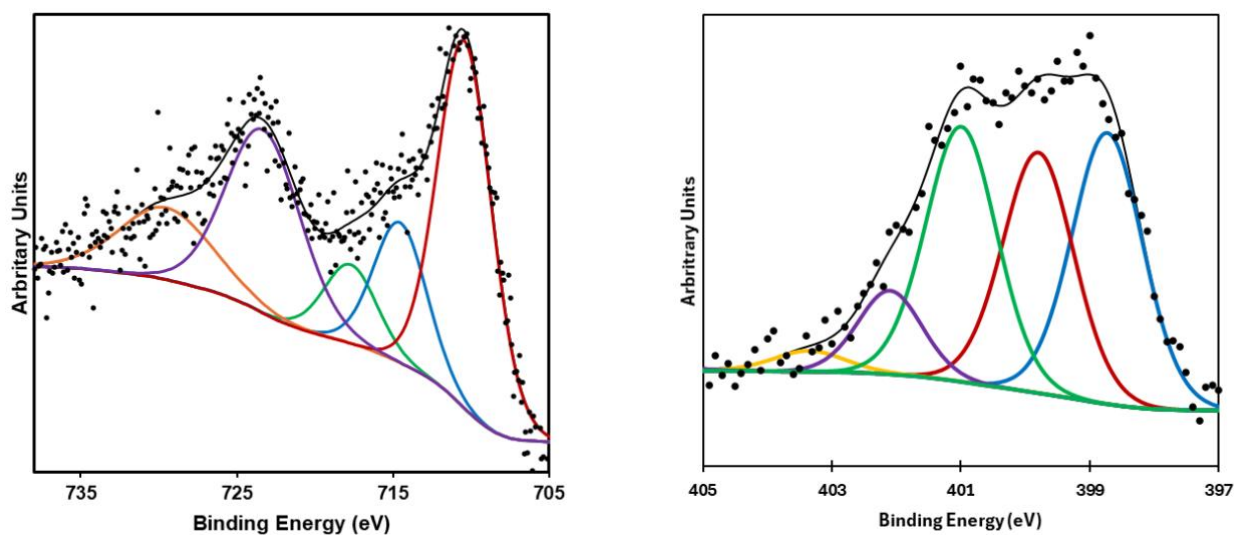


Figure S4. XPS data for Fe-Pc-C. (a) Fitted Fe2p spectrum and (b) N1s spectrum. The Fe2p spectrum was fit using a peak for Fe2p_{1/2} (purple), Fe2p_{3/2} (red), multiplets (blue and orange), and a satellite (green). The N1s spectrum was fit using a peak for pyridinic (blue), FeN_x (red), pyrrolic (green), quaternary (purple), graphitic (yellow), and various peaks for NO_x species (gray).

3c. ^{57}Fe Mössbauer Spectroscopy

^{57}Fe Mössbauer spectra were collected on a 1024 channel See Co model W304 resonant gamma ray spectrometer using ^{57}Co on Rh foil as a gamma-ray source. Isomer shifts were referenced to α -Fe foil at room temperature. Fe-N-C samples were loaded into the sample chamber and spectra were collected under vacuum with a source velocity range of $\pm 10 \text{ mm s}^{-1}$. Fe-N-C samples were cooled to 4.2 K using a Janis model SHI-850 cryostat controlled by a Lakeshore model 336 temperature controller. Peak identities are defined as follows (using notation introduced in ref. [11]): **D1**: $\text{Fe}^{\text{III}}\text{N}_x$, **D3**: $\text{FeCl}_2 \cdot \text{H}_2\text{O}$, **S1**: FeO_x , **S2**: α -Fe, **S3**: Fe_xC_y . Peak fit initial guesses and identities follow the protocols previously published.^[8] ^{57}Fe Mössbauer spectra for PAJ-Fe-N-C and Fe-PANI-C were reported previously.^[8]

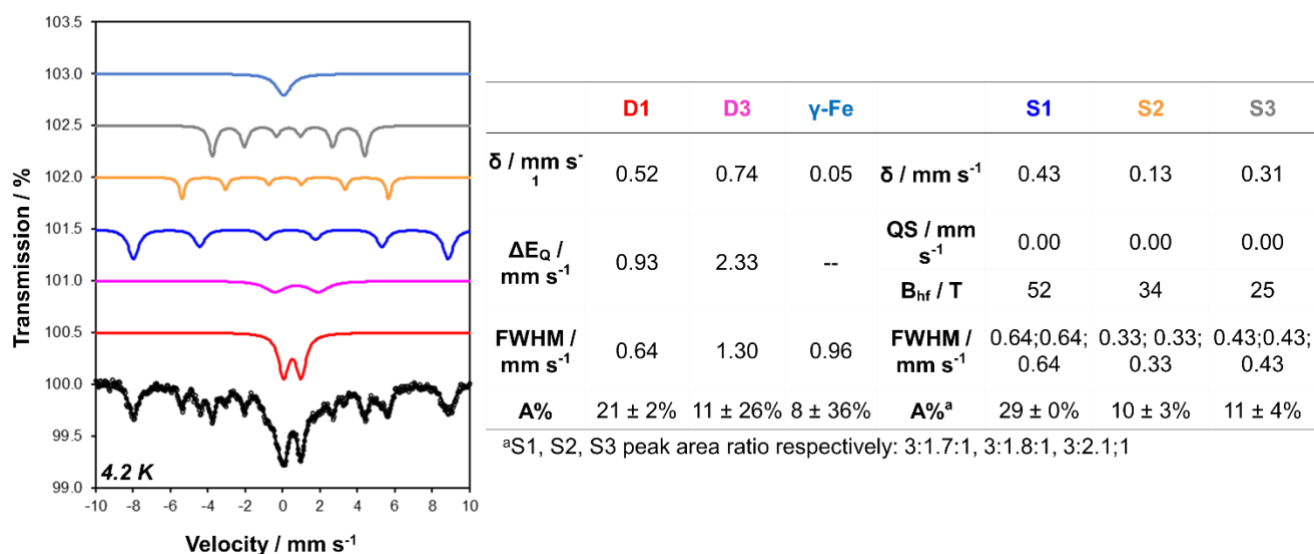


Figure S5. ^{57}Fe Mössbauer spectrum (4.2 K) and fitting parameters of Fe-Phen-C.

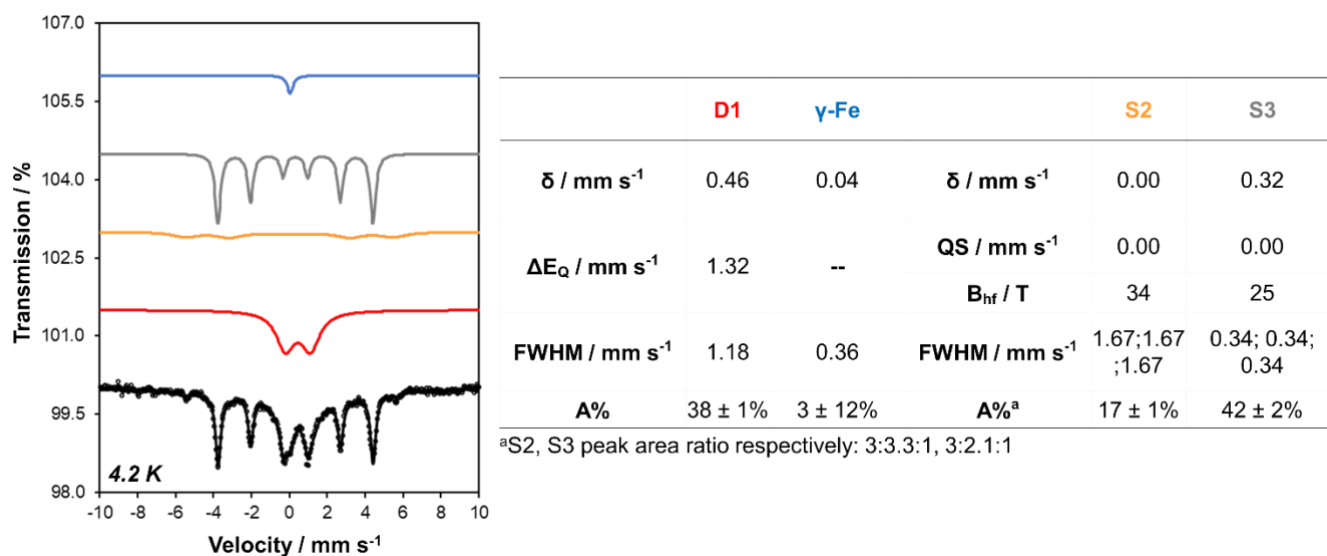


Figure S6. ^{57}Fe Mössbauer spectrum (4.2 K) and fitting parameters of Fe-Pc-C.

4. General Method for Aerobic Hydroquinone (HQ) Oxidation

Each reaction vial (8 mL, 2 drams) was charged with hydroquinone (HQ, 0.5 mmol, 55 mg), 2 mL THF (250 mM), catalyst (homogeneous or heterogeneous, various metal loadings), base additive (0 or 1 mol %), and 1,3,5-trimethoxybenzene (0.166 mmol, 28 mg, 0.33 equiv with respect to HQ) as an internal standard. The reaction solution was then charged with 1 atm O₂ (a slow sparge of O₂ bubbles, originating from an O₂ tank) and stirred at 1000 rpm. Reaction aliquots (20 µL) were taken out every 20 min using a pipette and diluted with 0.5 mL of CDCl₃. Each diluted aliquot was then filtered through a 13 mm syringe filter with a 0.2 µm PTFE membrane (VWR) and analyzed by ¹H NMR spectroscopy.

Catalysts and loadings (based on metal content mol %) used:

1 mol % Co(salen) = 1.72 mg

1 mol % Co(salophen) = 1.96 mg

1 mol % Fe(Pc) = 2.84 mg

1 mol % PAJ-Fe-NC (0.55 wt % Fe in PAJ-Fe-N-C) = 51 mg

0.3 mol % PAJ-Fe-N-C = 15 mg

0.1 mol % PAJ-Fe-N-C = 5 mg

0.3 mol % Fe-Phen-C (0.6 wt % Fe in Fe-Phen-C) = 14 mg

0.3 mol % Fe-Pc-C (0.63 wt % Fe in Fe-Pc-C) = 13.3 mg

0.3 mol % Fe-PANI-C (1.2 wt % Fe in Fe-Pc-C) = 7 mg

1 mol % Pt/C = 20 mg (5 wt % Pt in Pt/C)

1 mol % Pd/C = 11 mg (5 wt % Pd in Pd/C).

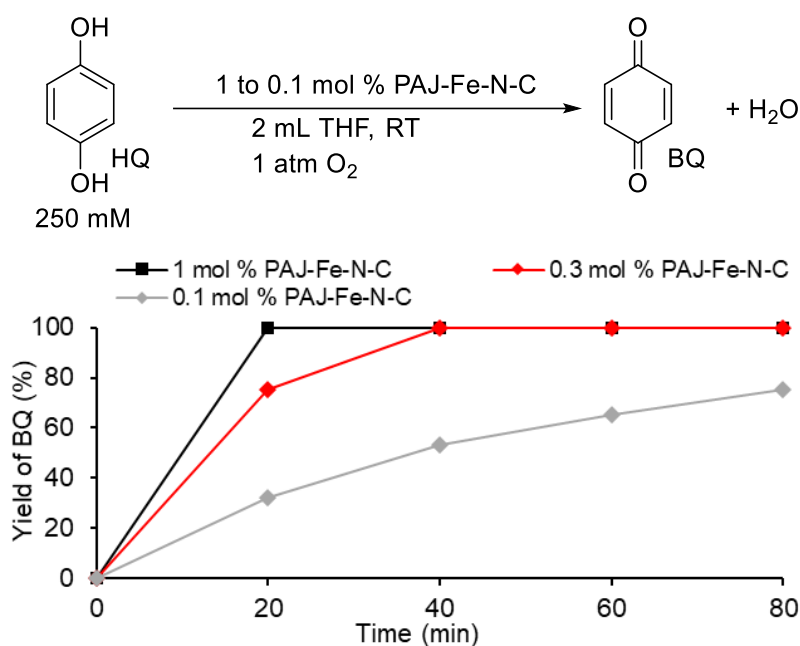


Figure S7. Variation of PAJ-Fe-N-C loading on aerobic oxidation of hydroquinone, HQ (250 mM) to benzoquinone, BQ in 2 mL THF under 1 atm O₂.

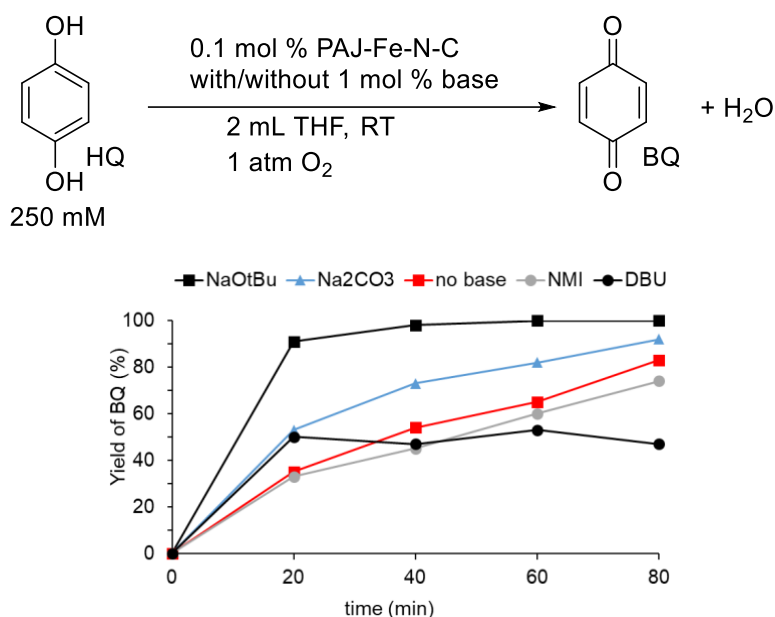
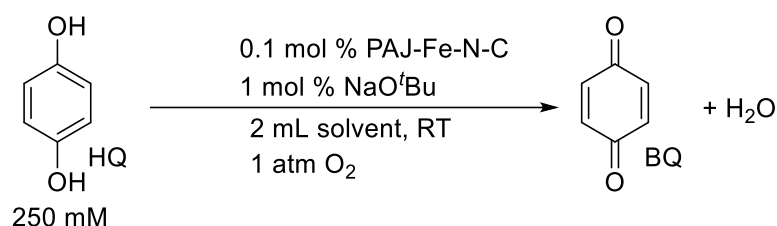


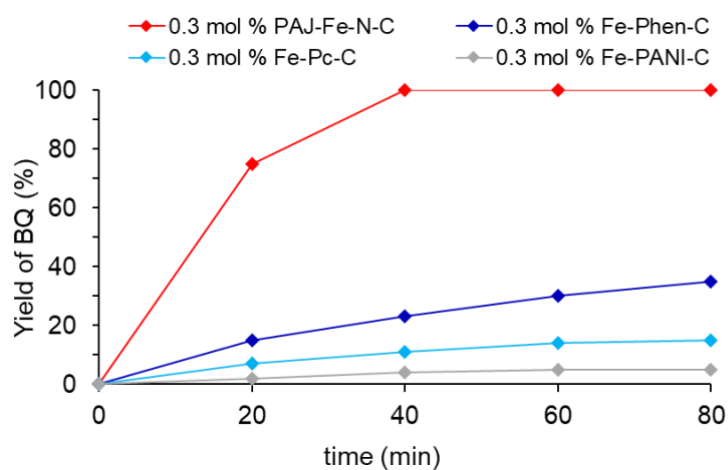
Figure S8. Effect of bases on aerobic oxidation of hydroquinone, HQ (250 mM) to benzoquinone, BQ in 2 mL THF under 1 atm O₂ in presence of 0.1 mol % PAJ-Fe-N-C.

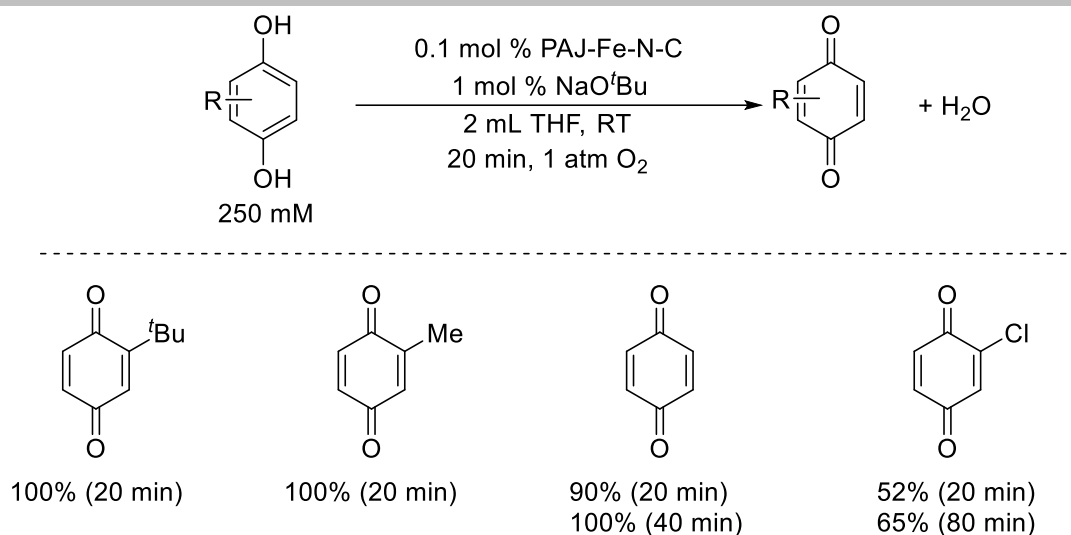
HQ oxidation is facilitated by the addition of inorganic bases; however, BQ decomposes in the presence of organic bases such as NMI (N-methyl Imidazole) or DBU (1,8-Diazabicyclo [5.4.0] undec-7-ene).

Table S1. Aerobic hydroquinone oxidation in various solvents.

Entry	Solvent	Conv. HQ (%)	Yield of BQ (%)
1	MeOH	65	0
2	MeCN	85	85
3	DCM	100	100
4	H ₂ O	83	34
5	THF	100	100
6	Me-THF	83	83
7	EtOAc	100	100
8	Acetone	90	95
9	THF/PhCH ₂ OH	100	100
10	THF/Octanol	100	100

Reaction conditions: Following the above general procedure with 0.1 mol % PAJ-Fe-N-C (5.1 mg) and 1 mol % NaO^tBu (0.48 mg, 2.5 μ L from 2 M NaO^tBu in THF), varying solvent.

**Figure S9.** Various Fe-N-C catalysts for aerobic oxidation of hydroquinone HQ (250 mM) to benzoquinone, BQ in 2 mL THF under 1 atm O₂.



Figures S10. Yields of substituted BQ at 0.1 mol % PAJ-Fe-N-C loading. Reactions were run following the above general procedure using 0.5 mmol of a substituted HQ and 1 mol % NaO^tBu (0.48 mg, 2.5 μ L from 2 M NaO^tBu in THF).

Electron-rich hydroquinones are easy to oxidize, whereas electron-deficient hydroquinones such as 2-chlorohydroquinone are difficult to oxidize and did not achieve full conversion within 80 min.

5. General Method for Alcohol Oxidation with Stoichiometric Quinone Derivatives

Each reaction vial (8 mL, 2 drams) was charged with benzyl alcohol (5 mmol, 520 μ L), 1.2 equiv of a quinone derivative (6 mmol), 0.05 mol % [Ir(trop₂DAD)]OTf (**Ir-2**, 0.1 μ mol, 1.75 mg) as a catalyst, 0.1 mol % NaO^tBu (0.48 mg, 2.5 μ L from 2 M NaO^tBu solution) as a base, and 1,3,5-trimethoxybenzene (28 mg, 0.166 mmol) as an internal standard in 1.5 mL THF. The reaction was carried out at room temperature for 20 min. Reaction aliquots (20 μ L) were diluted with 0.5 mL CDCl₃ and analyzed by ¹H NMR spectroscopy.

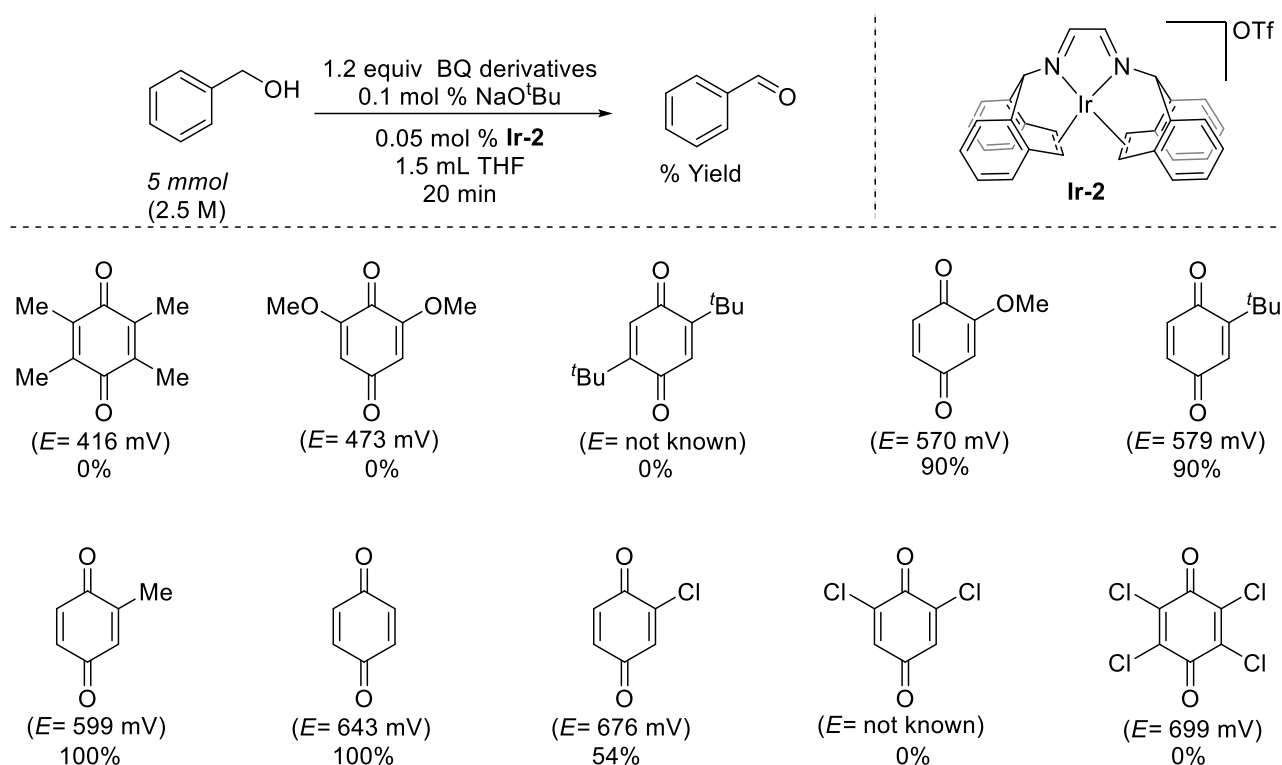


Figure S11. Yields of benzaldehyde for **Ir-2** catalyzed benzyl alcohol oxidation using stoichiometric quinone derivatives as the oxidant.

Quinones with redox potentials ($2 e^-/2 H^+$) ranging from approximately 570 mV to 676 mV, when substituted with either weak electron-donating or weak electron-withdrawing groups, lead to good product yield. Among these, unsubstituted benzoquinone (BQ), with a redox potential of 643 mV, is the most reactive and optimal for this reaction. In contrast, quinones that are either highly electron-rich or highly electron-deficient show no reactivity. This poor performance could be rationalized by steric factors, as these quinones are also more substituted, in addition to electronic effects (e.g., low potential quinones may be insufficiently oxidizing to support regeneration of the Ir catalyst). A similar reactivity trend was observed in a Pd-catalyzed allylic acetoxylation reaction.^[12]

6. General Method for Aerobic Benzyl Alcohol Oxidation with Catalytic BQ

Each reaction vial (8 mL, 2 drams) was charged with benzyl alcohol (5 mmol, 520 μ L), BQ (10 mol %, 0.5 mmol, 54 mg), 0.05 mol % **Ir-2** (0.0025 mmol, 1.75 mg) as an alcohol oxidation catalyst, a homogeneous or heterogeneous HQ oxidation catalyst (0.1 mol %), 0.1 mol % NaO^tBu (0.56 mg, 2.5 μ L from 2 M NaO^tBu solution), and 1,3,5-trimethoxybenzene (28 mg, 0.166 mmol) as an internal standard in 1.5 mL THF. The reaction solution was charged with 1 atm O₂ (a slow sparge of O₂ bubbles, originating from an O₂ tank) and stirred at 1000 rpm. Reaction aliquots (20 μ L) were taken out every 1 hour using a pipette and diluted with 0.5 mL of CDCl₃. The reaction aliquot was then filtered through a 13 mm syringe filter with a 0.2 μ m PTFE membrane (VWR) and analyzed by ¹H NMR spectroscopy.

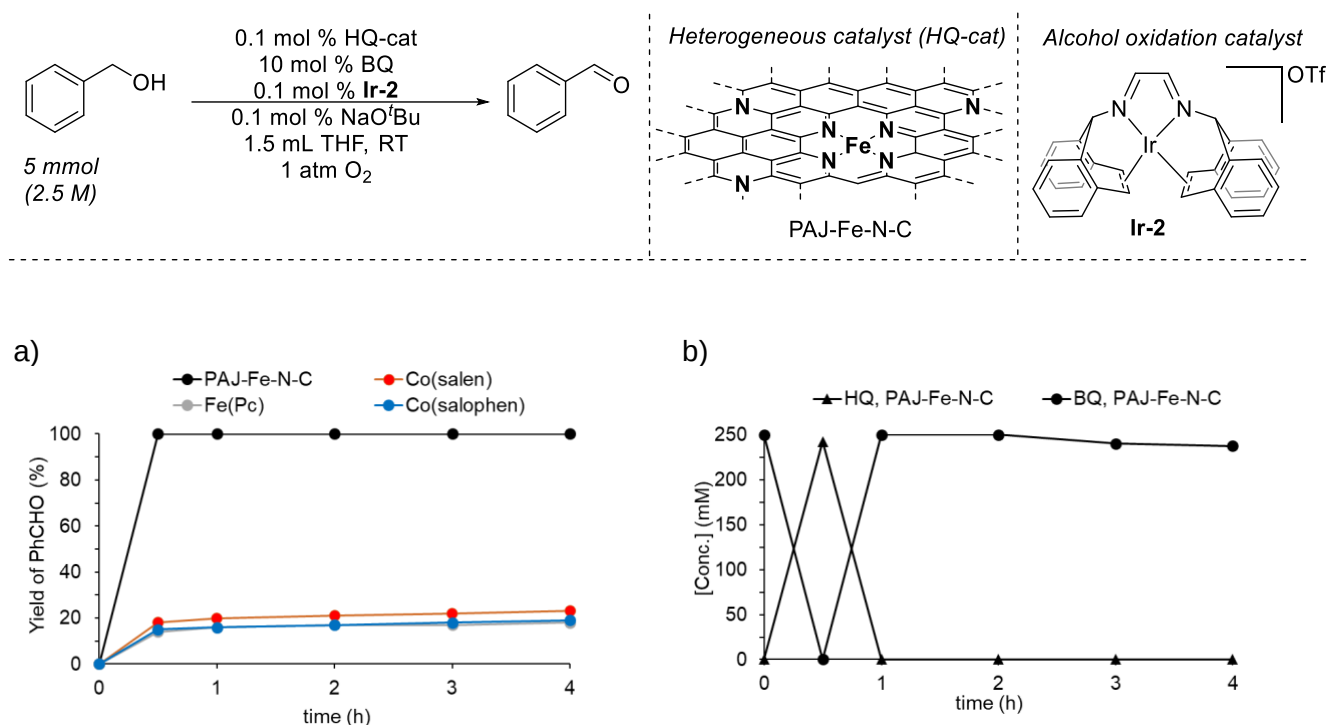


Figure S12. Aerobic oxidation of benzyl alcohol with catalytic BQ. a) Time course for aerobic benzyl alcohol oxidation in the presence of 0.1 mol % homogeneous or heterogeneous HQ oxidation catalyst, 0.1 mol % **Ir-2**, and 10 mol % BQ in THF. b) HQ and BQ speciation during the reactions with PAJ-Fe-N-C.

Use of the PAJ-Fe-N-C cocatalyst supports full conversion of benzyl alcohol to benzaldehyde within 30 min, shows exclusive formation of BQ after 1 h (no benzyl alcohol left) supporting the ability of PAJ-Fe-N-C to efficiently reoxidize HQ to BQ.

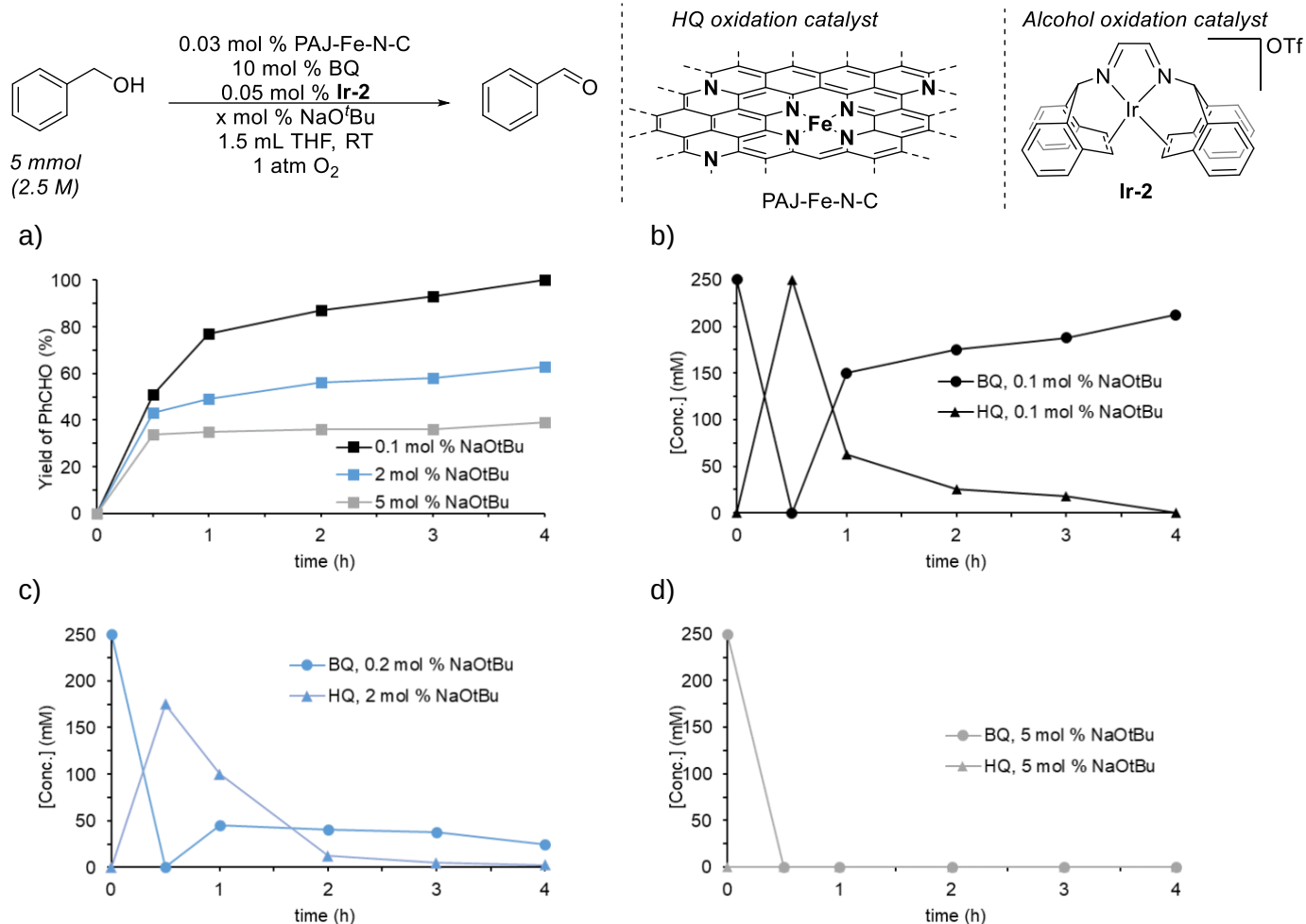


Figure S13. Aerobic benzyl alcohol oxidation with 10 mol % BQ and varied NaO^tBu loading. a) Time courses for reactions with varying NaO^tBu loading. b) HQ and BQ speciation throughout the reaction with 0.1 mol % NaO^tBu. c) HQ and BQ speciation throughout the reaction with 2 mol % NaO^tBu. d) HQ and BQ speciation throughout the reaction with 5 mol % NaO^tBu.

A higher loading of NaO^tBu results in quinone decomposition over time and therefore limits the reactivity for aldehyde formation.

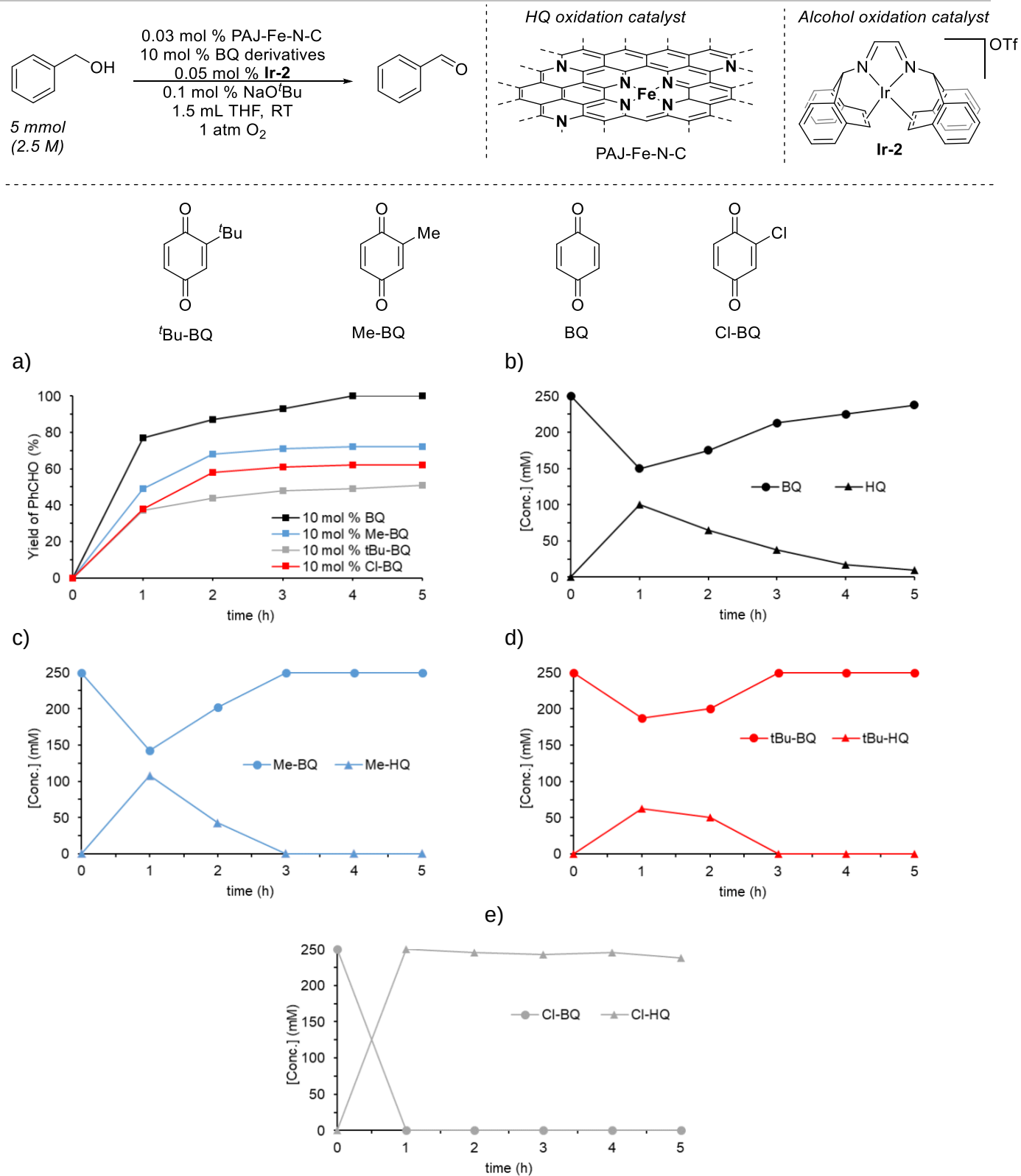


Figure S14. Aerobic benzyl alcohol oxidation with 10 mol % benzoquinone derivatives. a) Time course of the reactions. Hydroquinone/benzoquinone speciation throughout their reactions: b) HQ/BQ; c) Me-HQ/Me-BQ; d) ^tBu-HQ/^tBu-BQ and e) Cl-HQ/Cl-BQ speciation.

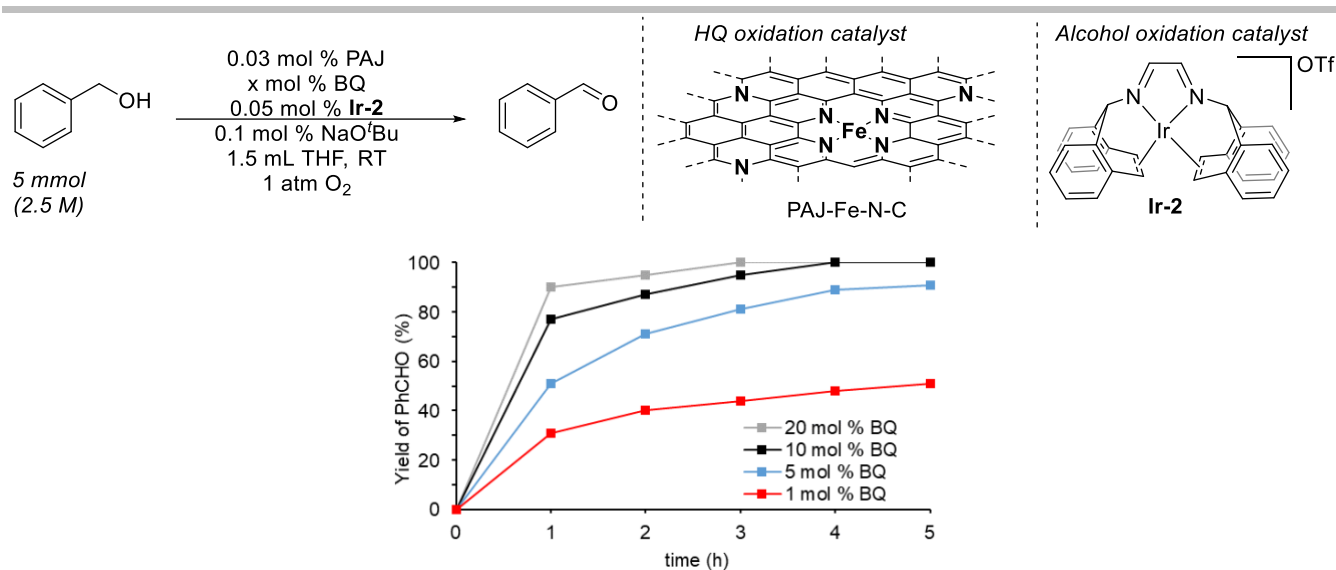
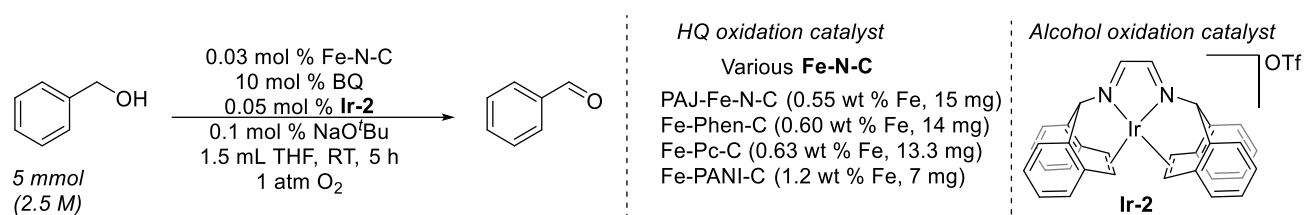


Figure S15. Time courses for aerobic benzyl alcohol oxidation with various loadings of BQ.

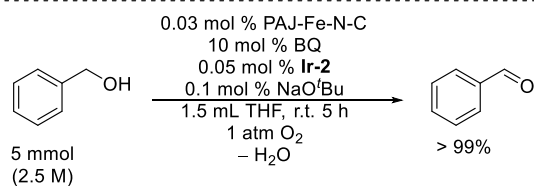
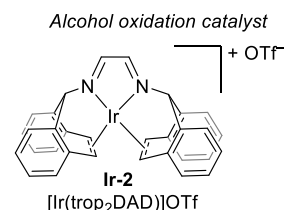
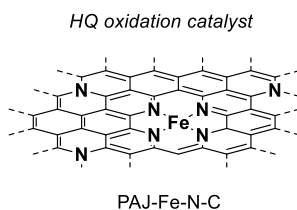
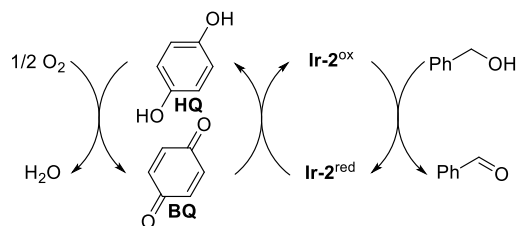
Table S2. Aerobic benzyl alcohol oxidation with various Fe-N-C catalysts reported in the literature.



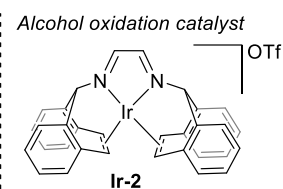
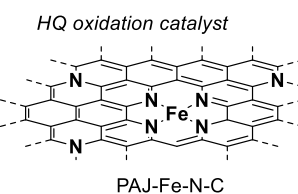
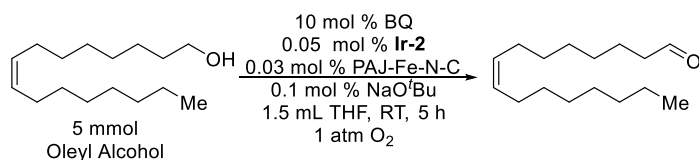
Entry	Fe-N-C	Conv. (%)	Yield of PhCHO (%)
1	PAJ-Fe-N-C (0.55 wt % Fe) ^[8]	100	>99
2	Fe-Phen-C (0.60 wt % Fe) ^[9]	66	66
3	Fe-Pc-C (0.63 wt % Fe) ^[9]	35	35
4	Fe-PANI-C (1.2 wt % Fe) ^[8]	11	11

Table S3. Control experiments.

Control experiment for aerobic oxidation of benzyl alcohol to benzaldehyde



Entry	Deviation from standard conditions	Yield of PhCHO (%)
1	none	99
2	No PAJ Fe-N-C	10
3	No BQ	0
4	No Ir-2	0
5	Under N ₂	10

Table S4. Reaction optimization for oleyl alcohol (seed oil)

Entry	BQ (mol %)	Ir-2 (mol %)	PAJ-Fe-N-C (mol %)	Conv. (%)	Yield (%)
1	10	0.05	0.03	30	29
2	10	0.05	0.1	65	61
3	10	0.1	0.1	82	79
4	20	0.1	0.1	100	>99

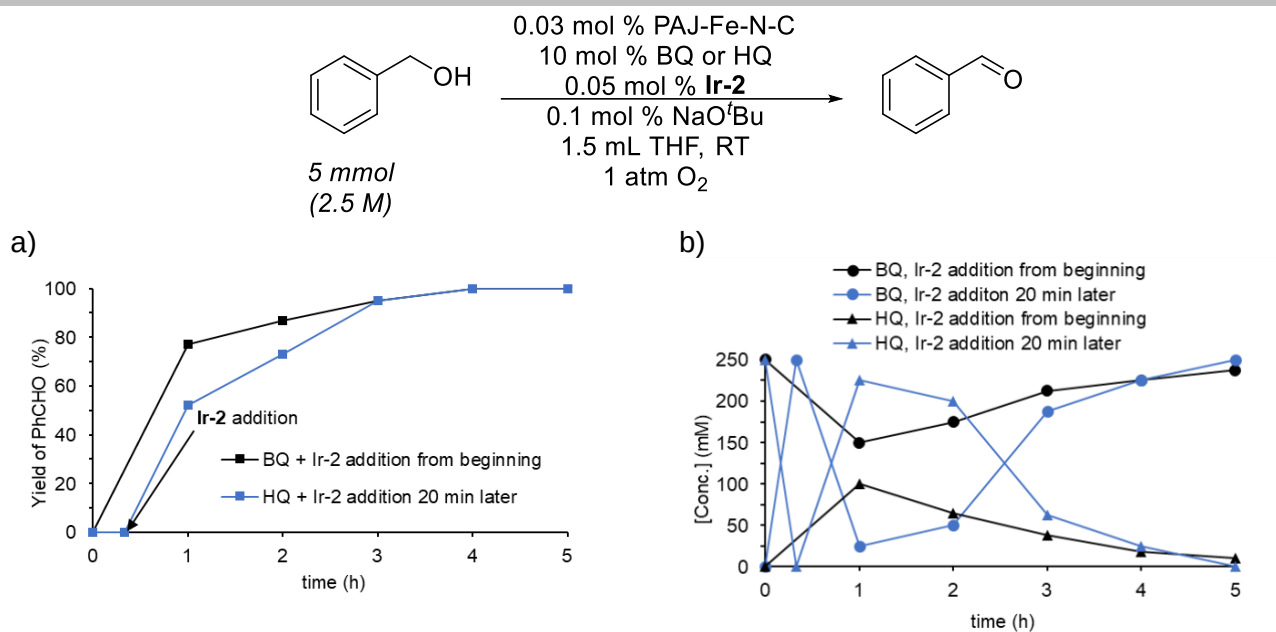


Figure S16. Comparison of aerobic benzyl alcohol oxidation using catalytic BQ and catalytic HQ. a) Time courses of the reaction starting with BQ and the reaction starting with HQ (the **Ir-2** is added 20 min later when all HQ was oxidized to BQ). b) HQ and BQ speciation throughout the reactions in (a).

7. General Method for Aerobic Alcohol Oxidation with Catalytic HQ.

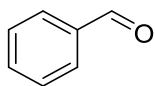
Method A for benzylic alcohols

Each reaction vial (8 mL, 2 drams) was charged with 5 mmol alcohol, 10 mol % HQ (0.5 mmol, 55 mg), 0.03 mol % PAJ-Fe-N-C (based on metal content loading, 15 mg), and 0.1 mol % NaO^tBu (0.48 mg, 2.5 μ L from 2 M NaO^tBu solution) in 1.5 mL. The reaction solution was charged with 1 atm O₂ (a slow sparge of O₂ bubbles, originating from an O₂ tank) and stirred at 1000 rpm for 10 min. Then, 0.05 mol % **Ir-2** (0.0025 mmol, 1.75 mg) was added to the reaction mixture and the reaction was carried out for 5 h. The reaction mixture was diluted with 5 mL THF and filtered through a 47 mm syringe filter with a 0.2 μ m PTFE membrane (VWR). The filtrate was concentrated to ~2 mL and purified via column chromatography.

Method B for Aliphatic alcohols

Each reaction vial (8 mL, 2 drams) was charged with 5 mmol alcohol, 10 mol % HQ (0.5 mmol, 55 mg), 0.03 mol % PAJ-Fe-N-C (based on metal content loading, 15 mg), and 0.1 mol % NaO^tBu (0.48 mg, 2.5 μ L from 2 M NaO^tBu solution) in 1.5 mL THF. The reaction solution was charged with 1 atm O₂ (a slow sparge of O₂ bubbles, originating from an O₂ tank) and stirred at 1000 rpm for 10 min. Then, 0.1 mol % **Ir-2** (0.005 mmol, 3.5 mg) was added to the reaction mixture and the reaction was carried out for 5 h. The reaction mixture was diluted with 5 mL THF and filtered with 47 mm syringe filter with 0.2 μ m PTFE membrane (VWR). The filtrate was concentrated to ~2 mL and purified via column chromatography.

8. Compound Characterization



2a

Benzaldehyde, **2a**

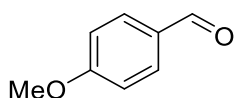
Prepared via Method A, from benzyl alcohol, **1a** (540.7 mg, 522 μ L, 5 mmol). The crude residue was purified by column chromatography on silica gel with an eluent gradient from 100 % pentane to 20 % ethyl acetate in pentane to afford **2a** (yield: 503.5 mg, 4.75 mmol, 96 % yield) as a colorless liquid.

Characterization data matches with the literature values.^[13]

^1H NMR (500 MHz, CDCl_3) δ 10.02 (s, 1H), 7.88 (dd, J = 8.2, 1.5 Hz, 2H), 7.70 – 7.58 (m, 1H), 7.52 (dd, J = 8.3, 7.0 Hz, 2H).

^{13}C NMR (126 MHz, CDCl_3) δ 192.5, 136.5, 134.6, 129.8, 129.1.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ ($\text{C}_7\text{H}_7\text{O}$) Calcd: 107.0491; Found: 107.0495.



2b

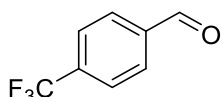
4-Methoxybenzaldehyde, **2b**

Prepared via Method A, from 4-methoxy benzyl alcohol, **1b** (690.8 mg, 622 μ L, 5 mmol). The crude residue was purified by column chromatography on silica gel with an eluent gradient from 100 % pentane to 15 % ethyl acetate in pentane to afford **2b** (yield: 632 mg, 4.65 mmol, 93 % yield) as a light brown liquid. Characterization data matches with the literature values.^[13]

^1H NMR (500 MHz, CDCl_3) δ 9.89 (s, 1H), 7.84 (d, J = 8.7 Hz, 2H), 7.00 (d, J = 8.7 Hz, 2H), 3.89 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 190.9, 164.8, 132.1, 130.1, 114.5, 55.7.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ ($\text{C}_8\text{H}_9\text{O}_2$) Calcd: 137.0597; Found: 137.0597.



2c

4-(Trifluoromethyl)benzaldehyde, **2c**

Prepared Method A, from (4-(trifluoromethyl)phenyl)methanol, **1c** (880 mg, 684.3 μ L, 5 mmol). The crude residue was purified by column chromatography on silica gel with an eluent gradient from 100 % pentane to 15 % ethyl acetate in pentane to afford **2c** (yield: 835 mg, 4.8 mmol, 96 % yield) as a white solid.

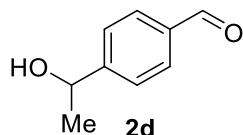
Characterization data matches with the literature values.^[14]

^1H NMR (500 MHz, CDCl_3) δ 10.09 (s, 1H), 8.00 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 8.0 Hz, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 191.2, 138.8 (d, *J* = 1.3 Hz), 135.8 (q, *J* = 32.7 Hz), 130.0, 126.3 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 272.9 Hz).

¹⁹F NMR (377 MHz, CDCl₃) δ -63.3.

HRMS (ESI) *m/z*: [M+H]⁺ (C₈H₆F₃O) Calcd: 175.0365; Found: 175.0365.



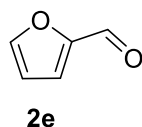
4-(1-Hydroxyethyl)benzaldehyde, **2d**

Prepared via Method A, from 1-(4-(hydroxymethyl)phenyl)ethan-1-ol, **1d** (671 mg, 5 mmol). The crude residue was purified by column chromatography on silica gel with an eluent gradient from 100 % pentane to 15 % ethyl acetate in pentane to afford **2d** (yield: 668 mg, 4.45 mmol, 89 % yield) as a colorless liquid. Characterization data matches with the literature values.^[15]

¹H NMR (500 MHz, CDCl₃) δ 9.97 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 4.97 (q, *J* = 6.5 Hz, 1H), 2.24 (s, 1H), 1.50 (d, *J* = 6.5 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 192.1, 152.8, 135.7, 130.2, 126.0, 70.0, 25.5.

HRMS (ESI) *m/z*: [M+H]⁺ (C₉H₁₁O₂) Calcd: 151.0754; Found: 151.0753.



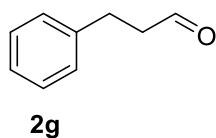
Furan-2-carbaldehyde, **2e**

Prepared via Method A, from furan-2-ylmethanol, **1e** (545 mg, 495 μL, 5 mmol). The crude residue was purified by column chromatography on silica gel with an eluent gradient from 100 % pentane to 15 % ethyl acetate in pentane to afford **2e** (yield: 432 mg, 4.5 mmol, 90 % yield) as a light brown liquid. Characterization data matches with the literature values.^[15]

¹H NMR (500 MHz, CDCl₃) δ 9.64 (s, 1H), 8.05 – 7.52 (m, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 6.58 (dd, *J* = 3.6, 1.7 Hz, 1H).

¹³C NMR (126 MHz, CDCl₃) δ 178.0, 153.0, 148.2, 121.1, 112.7.

HRMS (ESI) *m/z*: [M+H]⁺ (C₅H₅O₂) Calcd: 97.0284; Found: 97.0288.



3-Phenylpropanal, **2g**

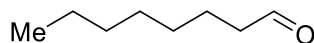
Prepared via Method A, from 3-phenylpropan-1-ol, **1g** (680 mg, 680 μL, 5 mmol). The crude residue was purified by column chromatography on silica gel with an eluent gradient from 100 % pentane to 15 %

ethyl acetate in pentane to afford **2g** (yield: 640 mg, 4.7 mmol, 94 % yield) as a colorless liquid. Characterization data matches with the literature values.^[15]

¹H NMR (500 MHz, CDCl₃) δ 9.83 (t, *J* = 1.8 Hz, 1H), 7.30 (dd, *J* = 8.2, 6.8 Hz, 3H), 7.21 (ddd, *J* = 8.2, 7.0, 1.7 Hz, 5H), 2.97 (t, *J* = 7.6 Hz, 3H), 2.79 (td, *J* = 7.6, 1.4 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 201.7, 140.5, 128.8, 128.4, 126.5, 45.4, 28.3.

HRMS (ESI) *m/z*: [M+H]⁺ (C₉H₁₁O) Calcd: 133.0648; Found: 133.0647.



2h

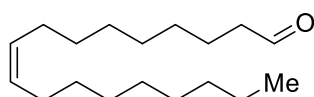
Octanal, **2h**

Prepared via Method B, from octan-1-ol, **1h** (651 mg, 784 μL, 5 mmol). The crude residue was purified by column chromatography on silica gel with an eluent gradient from 100 % pentane to 15 % ethyl acetate in pentane to afford **2h** (yield: 590 mg, 4.6 mmol, 92 % yield) as a colorless liquid. Characterization data matches with the literature values.^[16]

¹H NMR (500 MHz, CDCl₃) δ 9.76 (t, *J* = 1.9 Hz, 1H), 2.41 (td, *J* = 7.4, 1.9 Hz, 2H), 1.62 (td, *J* = 9.1, 8.2, 6.2 Hz, 2H), 1.38 – 1.19 (m, 8H), 0.97 – 0.81 (m, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 203.1, 44.1, 31.8, 29.3, 29.2, 22.7, 22.2, 14.2.

HRMS (ESI) *m/z*: [M+H]⁺ (C₈H₁₇O) Calcd: 129.1274; Found: 129.1275.



2i

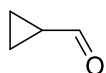
Olealdehyde, **2i**

Prepared via Method B, from (Z)-octadec-9-en-1-ol (Oleyl alcohol), **1i** (1342 mg, 1580 μL, 5 mmol). The crude residue was purified by column chromatography on silica gel with an eluent gradient from 100 % pentane to 15 % ethyl acetate in pentane to afford **2i** (yield: 1212 mg, 4.55 mmol, 91 % yield) as a colorless liquid. Characterization data matches with the literature values.^[17]

¹H NMR (500 MHz, CDCl₃) δ 9.71 (t, *J* = 1.9 Hz, 1H), 5.41 – 5.21 (m, 2H), 2.36 (td, *J* = 7.3, 1.9 Hz, 2H), 2.02 – 1.87 (m, 4H), 1.58 (p, *J* = 7.3, 6.5 Hz, 2H), 1.37 – 1.12 (m, 20H), 0.84 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 202.5, 130.0, 129.7, 43.9, 32.0, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 29.2, 29.1, 27.3, 27.2, 22.7, 22.1, 14.1.

HRMS (ESI) *m/z*: [M+H]⁺ (C₁₈H₃₅O) Calcd: 267.2682; Found: 267.2680.



2j

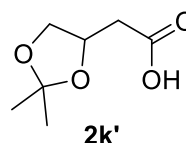
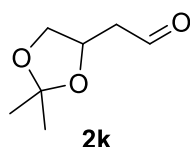
Cyclopropanecarbaldehyde, **2j**

Prepared via Method B, from cyclopropylmethanol, **1j** (360 mg, 405 μ L, 5 mmol). The crude residue was purified by column chromatography on silica gel with an eluent gradient from 100 % pentane to 15 % ethyl acetate in pentane to afford **2j** (yield: 143.2 mg, 2.04 mmol, 41 % yield) as a colorless liquid. The isolated yield is lower than the crude NMR yield due to evaporation of the product while removing solvent with the rotavap. Characterization data matches with the literature values.^[18]

^1H NMR (500 MHz, CDCl_3) δ 8.91 (d, J = 5.9 Hz, 1H), 2.24 – 1.47 (m, 1H), 1.07 (m, 4H).

^{13}C NMR (126 MHz, CDCl_3) δ 201.7, 22.8, 7.5.

HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ ($\text{C}_4\text{H}_7\text{O}$) Calcd: 71.0491; Found: 71.0499.



2-(2,2-dimethyl-1,3-dioxolan-4-yl)acetaldehyde, **2k**; 2-(2,2-dimethyl-1,3-dioxolan-4-yl)acetic acid, **2k'**

Prepared via Method B, from 2-(2,2-dimethyl-1,3-dioxolan-4-yl)ethan-1-ol, **1k** (731 mg, 709 μ L, 5 mmol). The crude residue was purified by column chromatography on silica gel with an eluent gradient from 100 % pentane to 20 % ethyl acetate in pentane to afford **2k** (yield: 432 mg, 3 mmol, 60 % yield) as a colorless liquid from the first eluted fraction. Increasing to 30 % ethyl acetate in pentane eluted another product, the overoxidized carboxylic acid **2k'** (yield: 228 mg, 1.425 mmol, 28 % yield) as a colorless oily liquid. Characterization data matches with the literature values.^[15]

2k

^1H NMR (500 MHz, CDCl_3) δ 9.70 (t, J = 1.6 Hz, 1H), 4.43 (p, J = 6.3 Hz, 1H), 4.08 (dd, J = 8.4, 6.1 Hz, 1H), 3.49 (dd, J = 8.3, 6.7 Hz, 1H), 2.73 (ddd, J = 17.2, 6.6, 1.9 Hz, 1H), 2.55 (ddd, J = 17.1, 6.0, 1.4 Hz, 1H), 1.31 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 199.9, 109.1, 70.6, 69.0, 47.6, 26.7, 25.4.

HRMS (ESI) m/z : $[(\text{M}-\text{H}_2\text{O})+\text{H}]^+$ ($\text{C}_7\text{H}_{11}\text{O}_2$) Calcd: 127.0754; Found: 127.0755.

2k'

^1H NMR (500 MHz, CDCl_3) ^1H NMR (500 MHz, CDCl_3) δ 10.92 (bs, 1H), 4.45 (p, J = 6.4 Hz, 1H), 4.14 (dd, J = 8.4, 6.0 Hz, 1H), 3.64 (dd, J = 8.4, 6.3 Hz, 1H), 2.71 (dd, J = 16.2, 6.6 Hz, 1H), 2.54 (dd, J = 16.2, 6.8 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H).

^{13}C NMR (126 MHz, CDCl_3) δ 176.3, 109.6, 71.9, 69.1, 38.9, 26.9, 25.5.

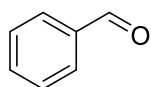
HRMS (ESI) m/z : $[(\text{M}-\text{H})^-]$ ($\text{C}_7\text{H}_{11}\text{O}_4$) Calcd: 159.0663; Found: 159.0653.

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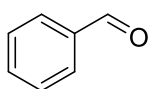
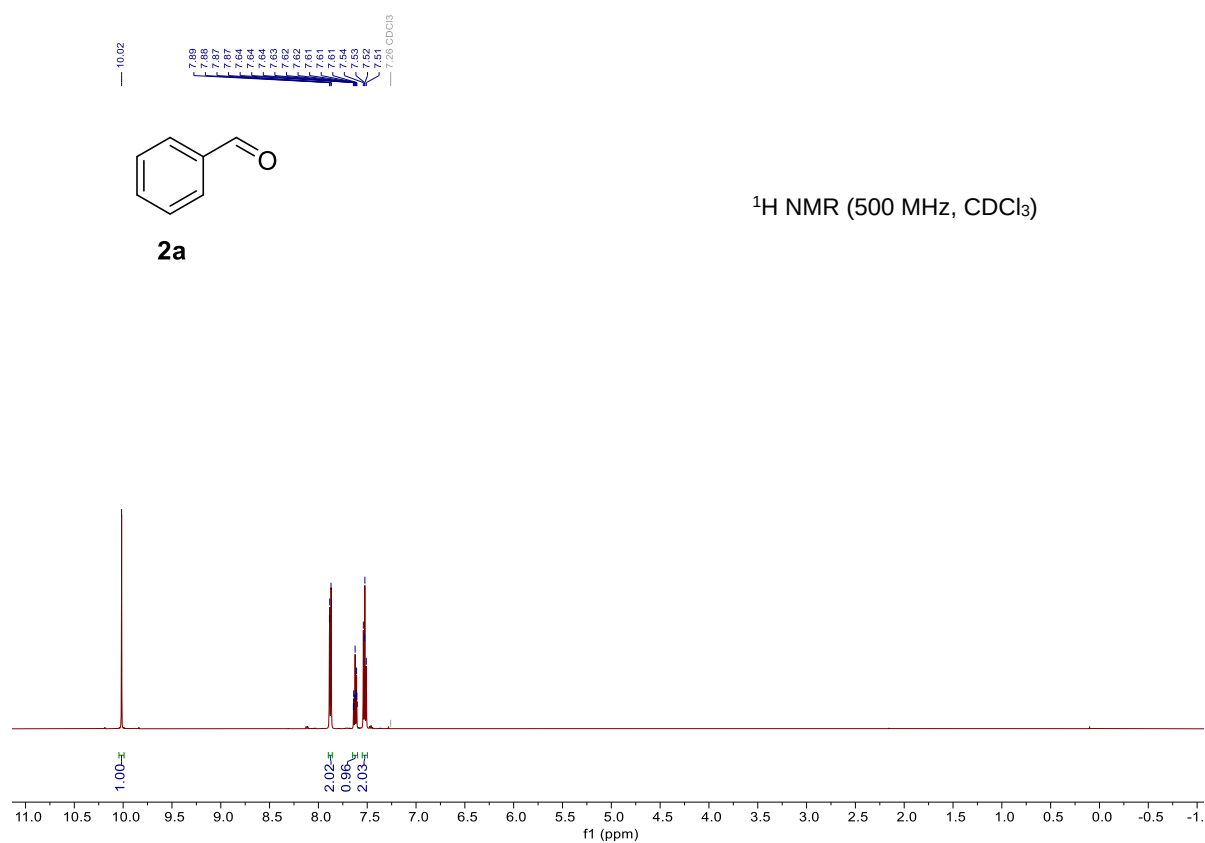
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10. NMR Spectra



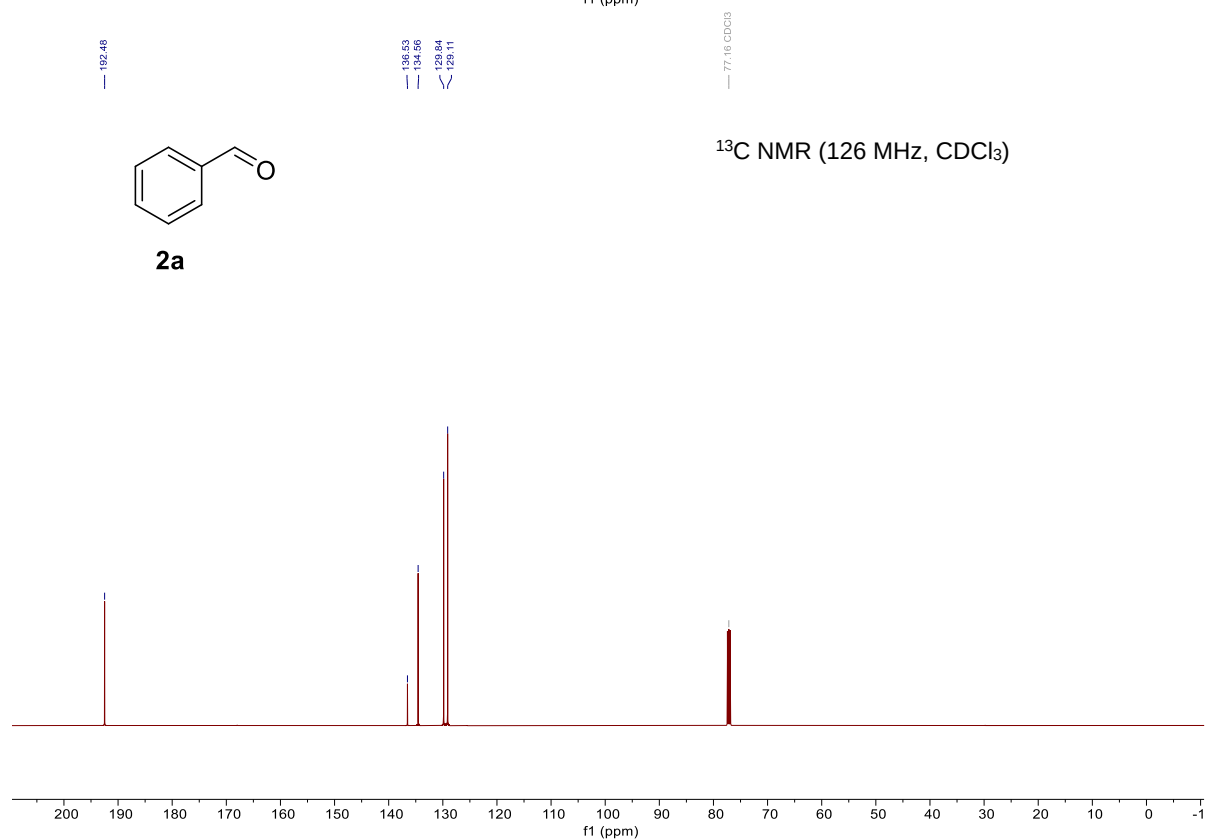
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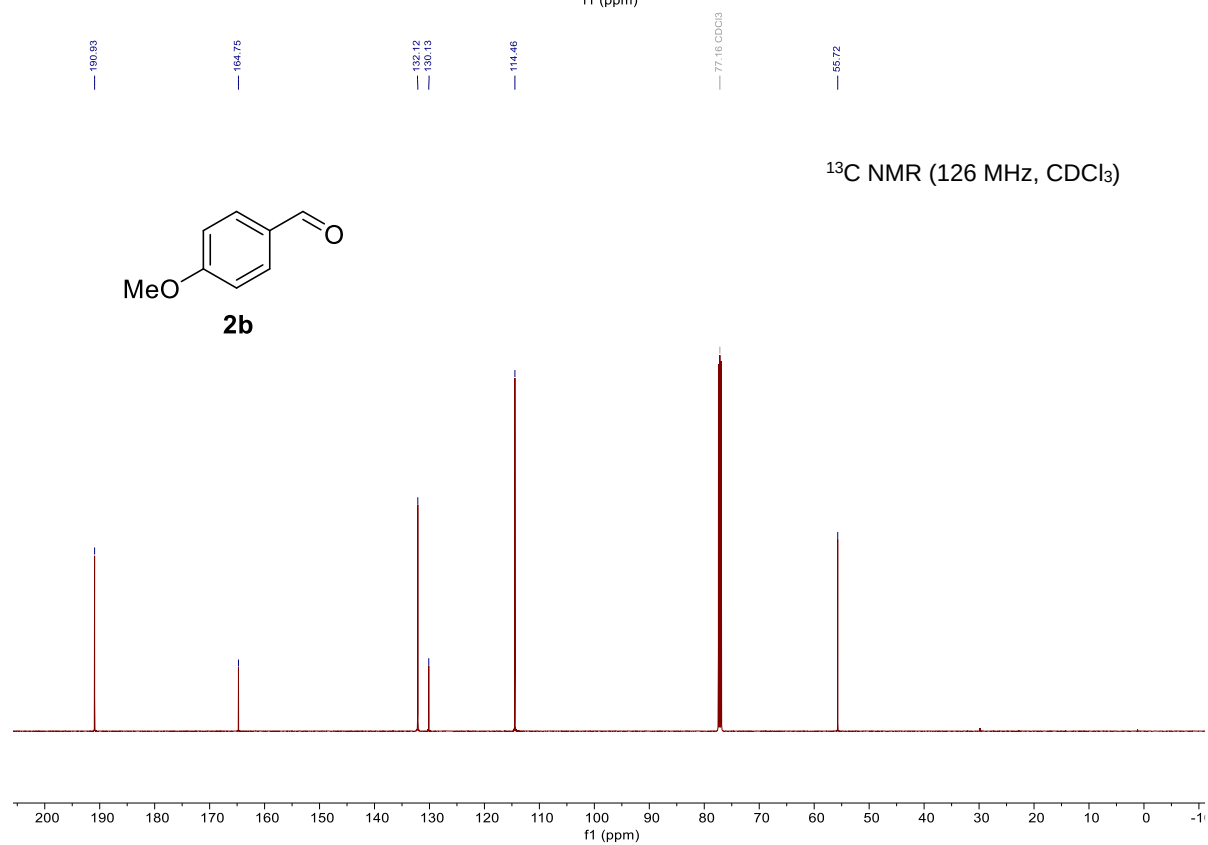
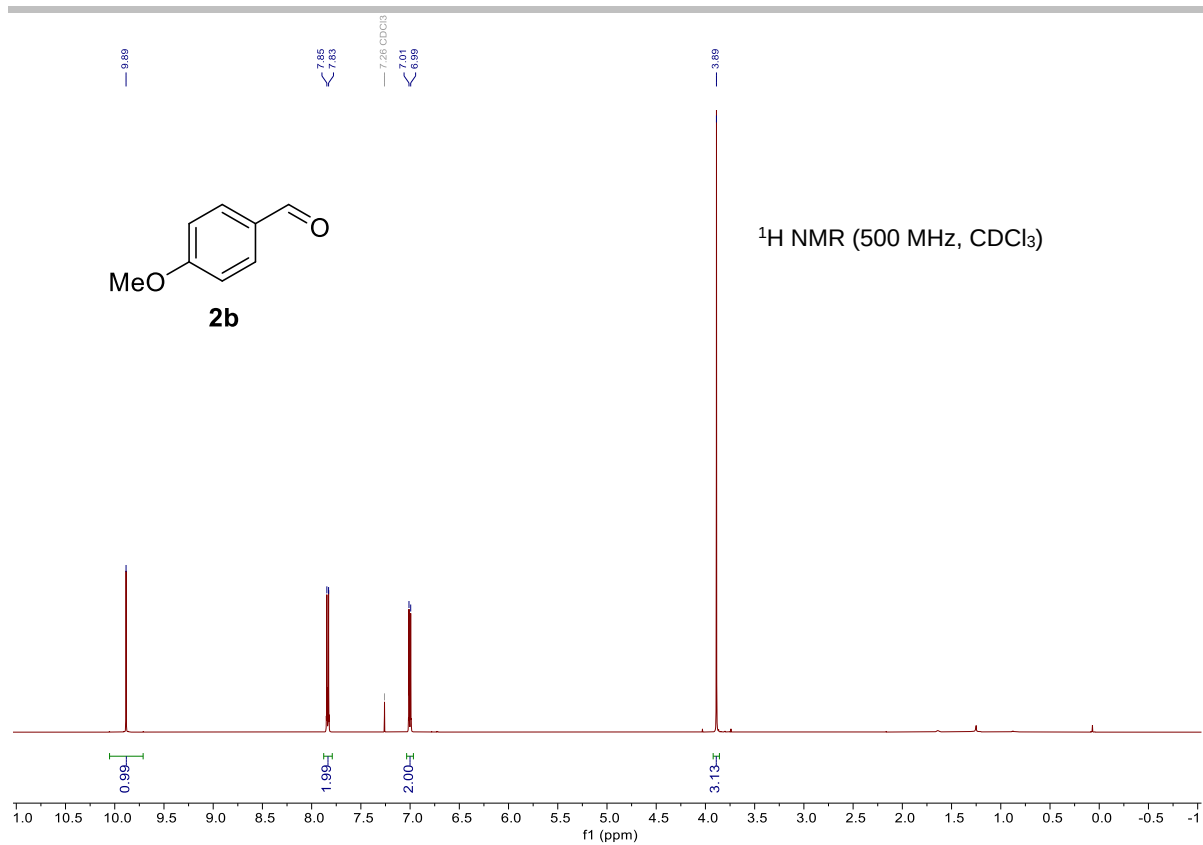
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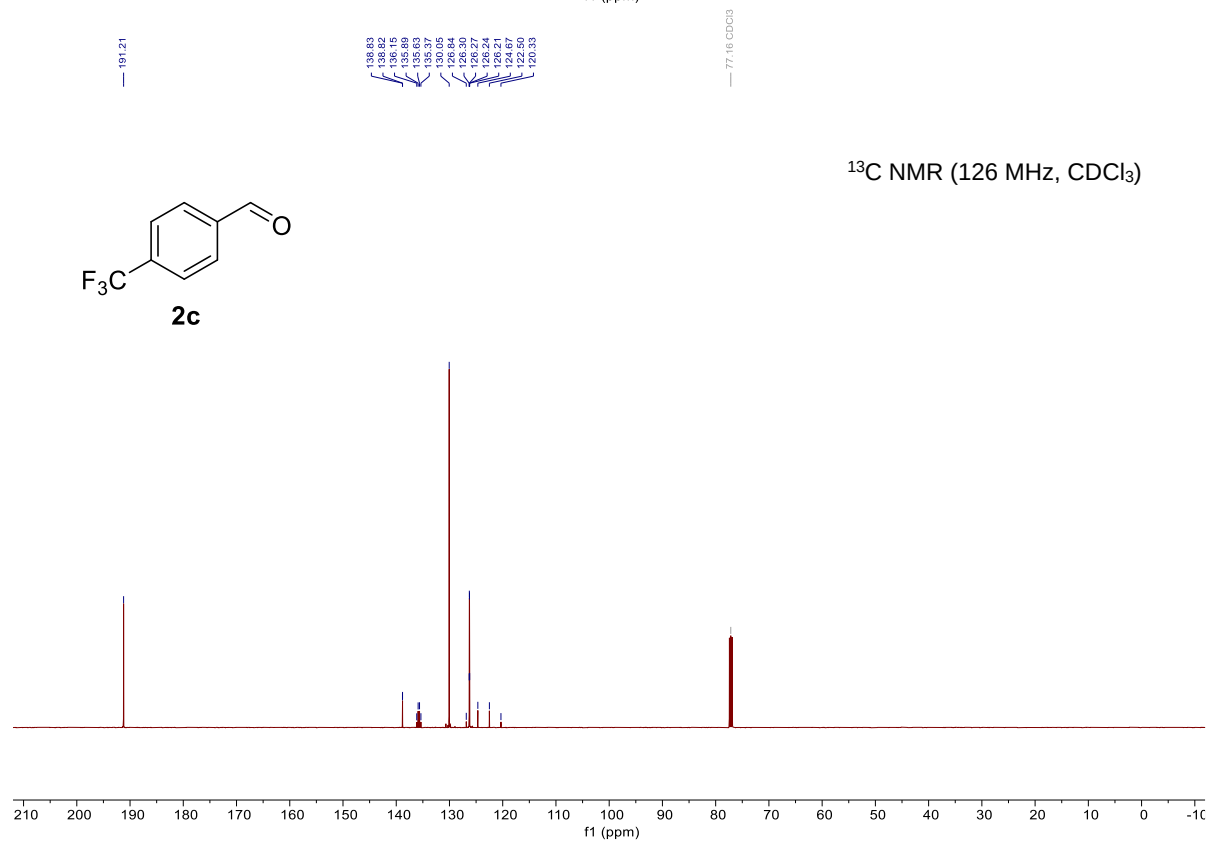
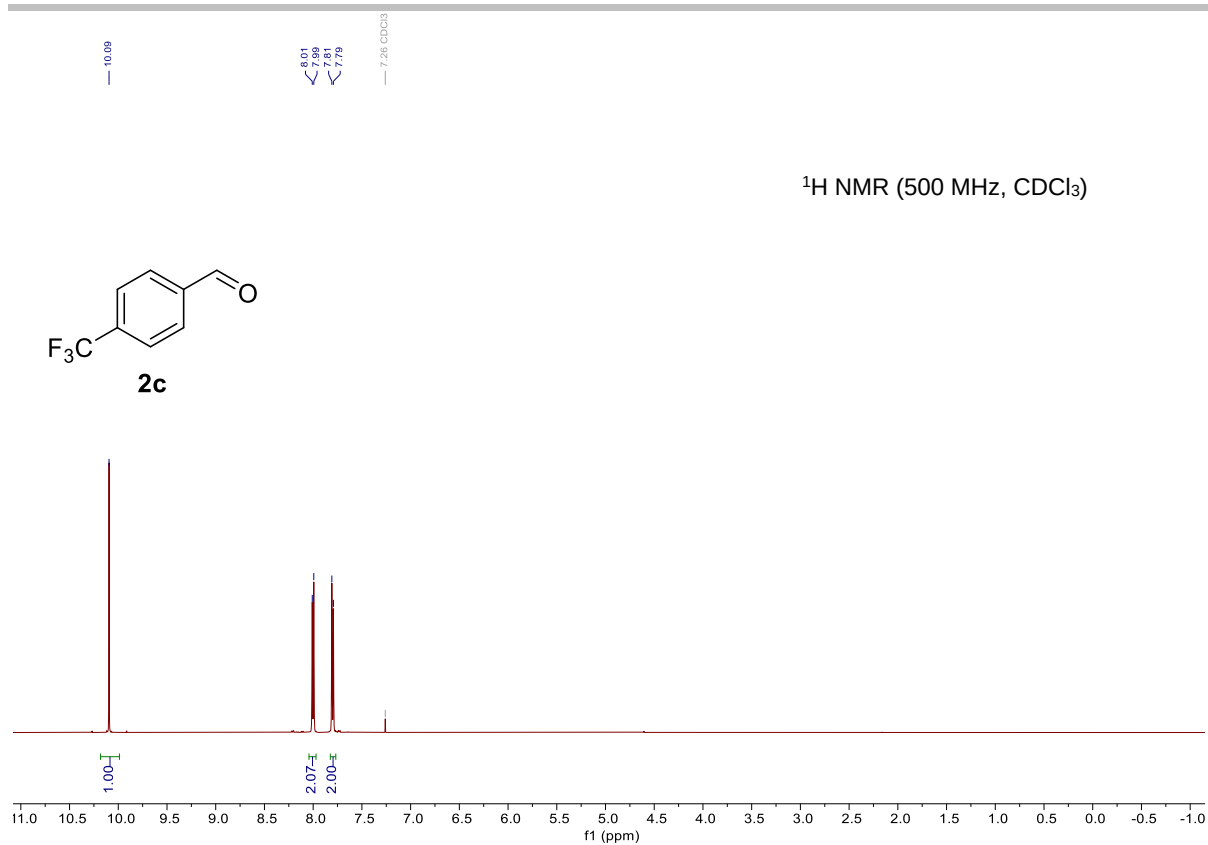


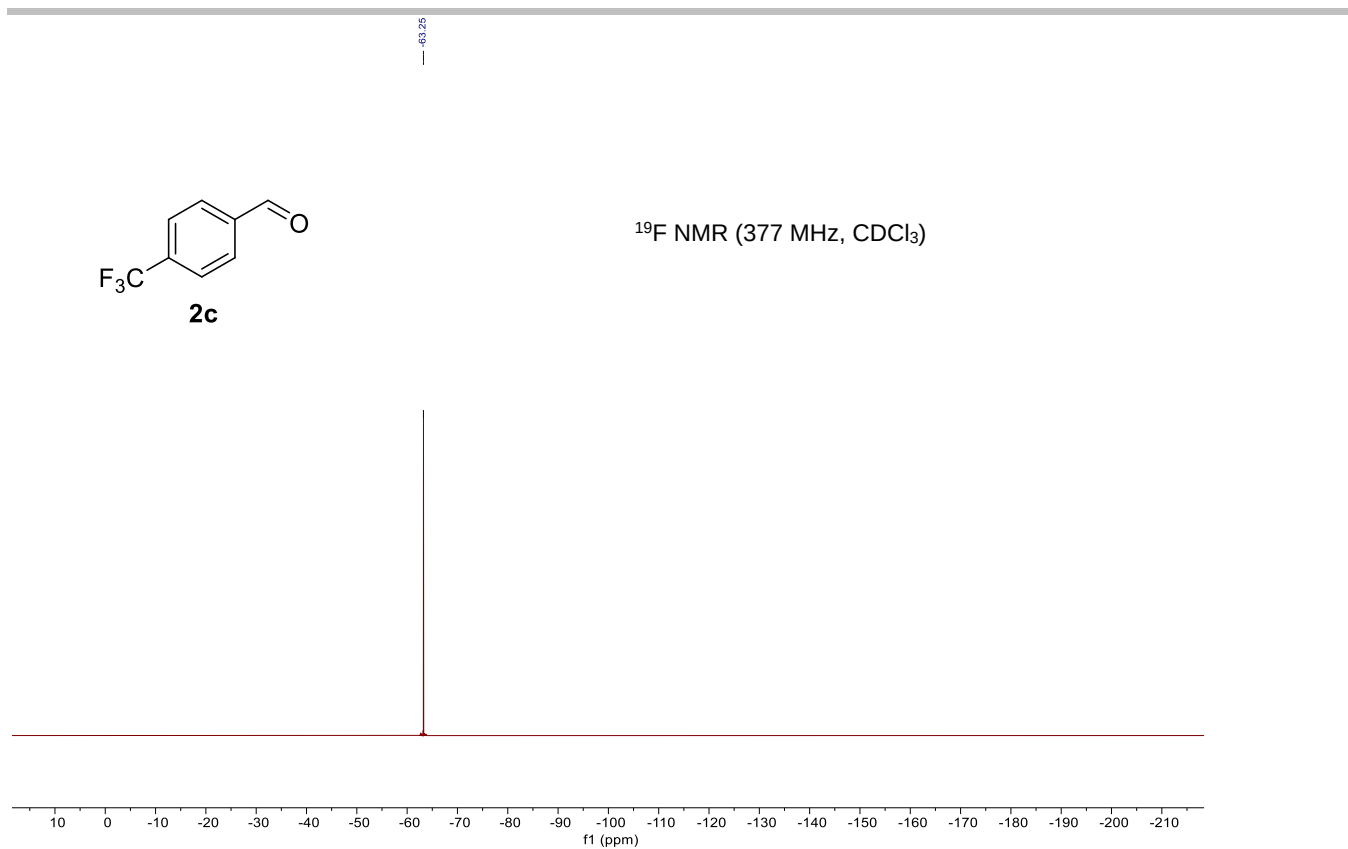
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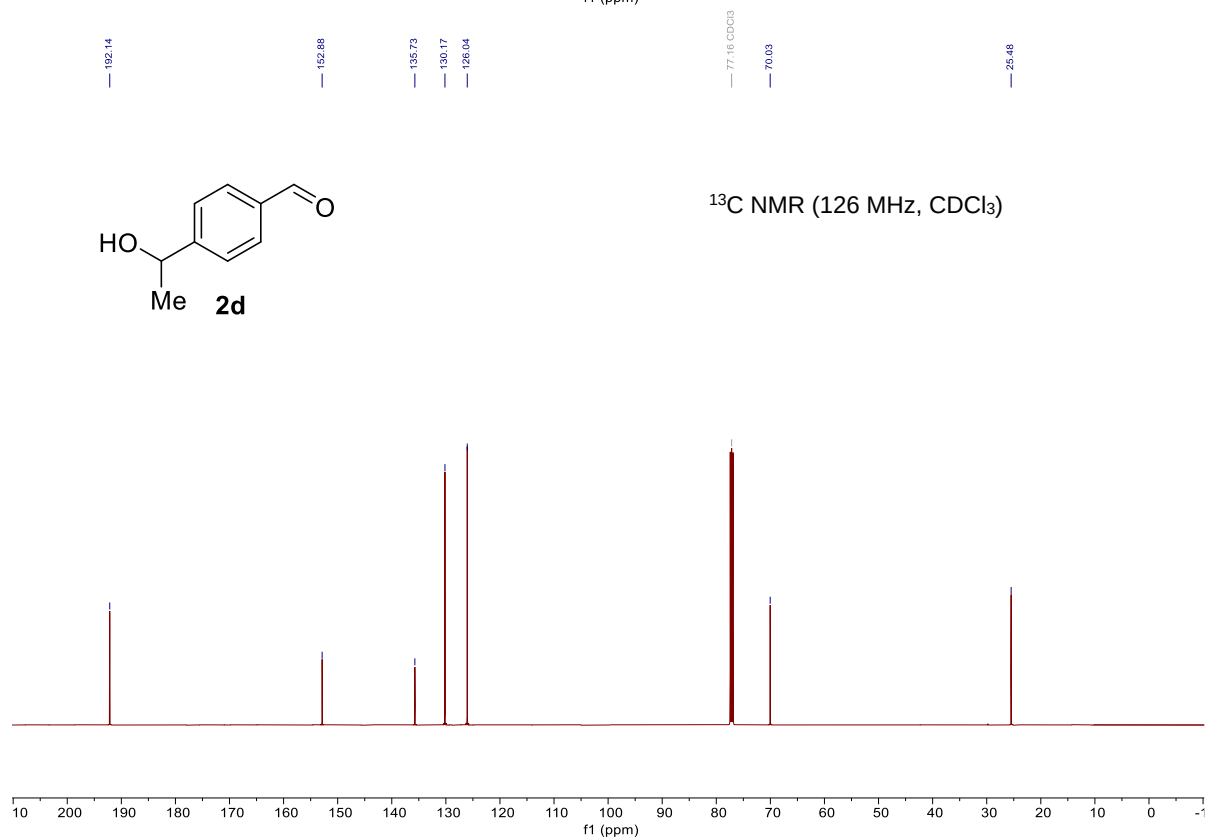
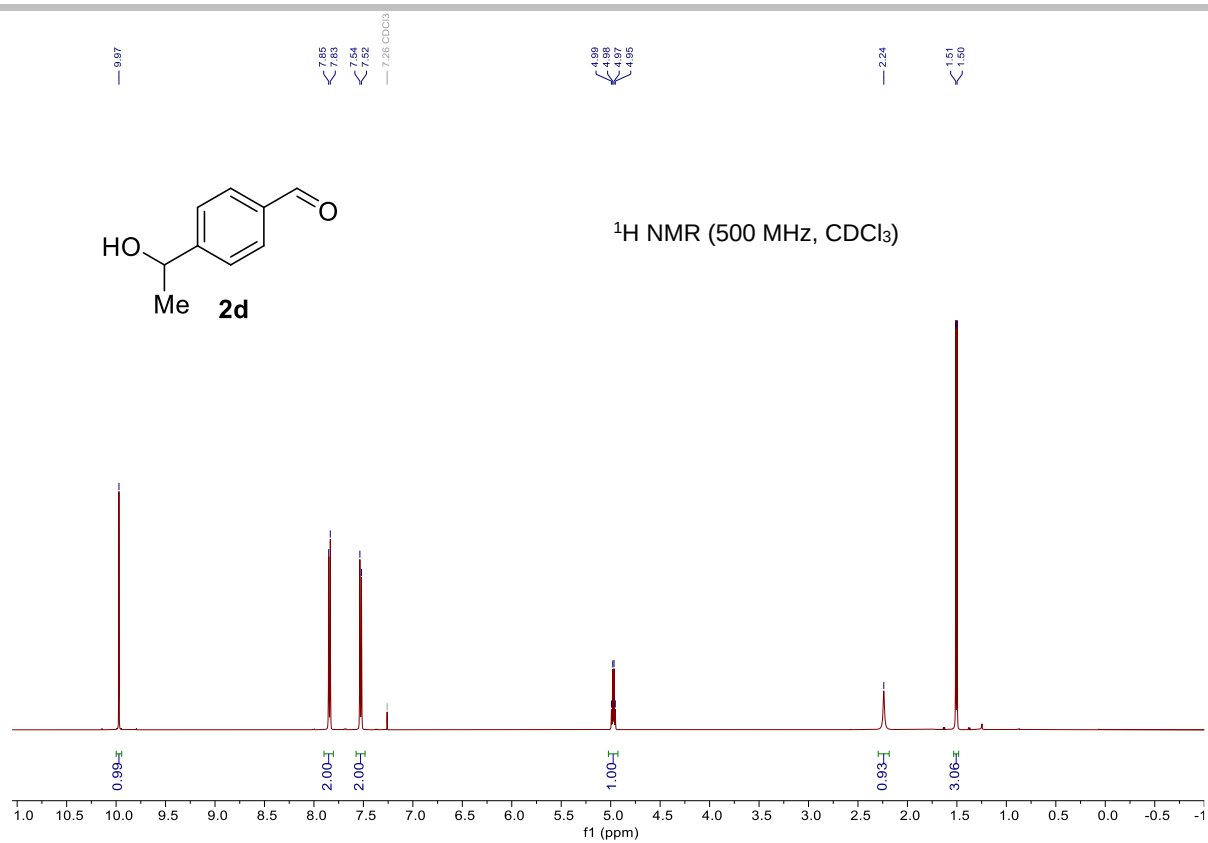
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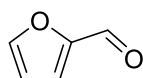






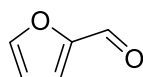
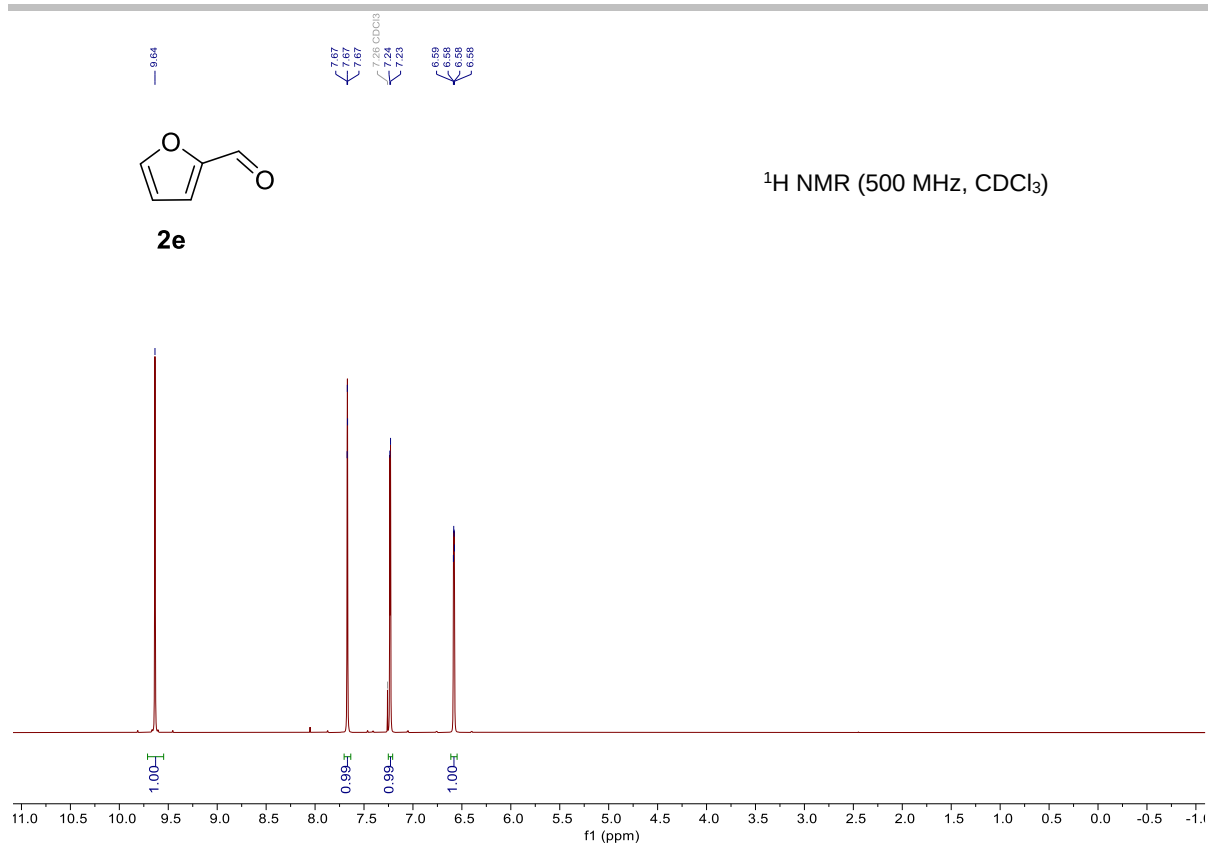






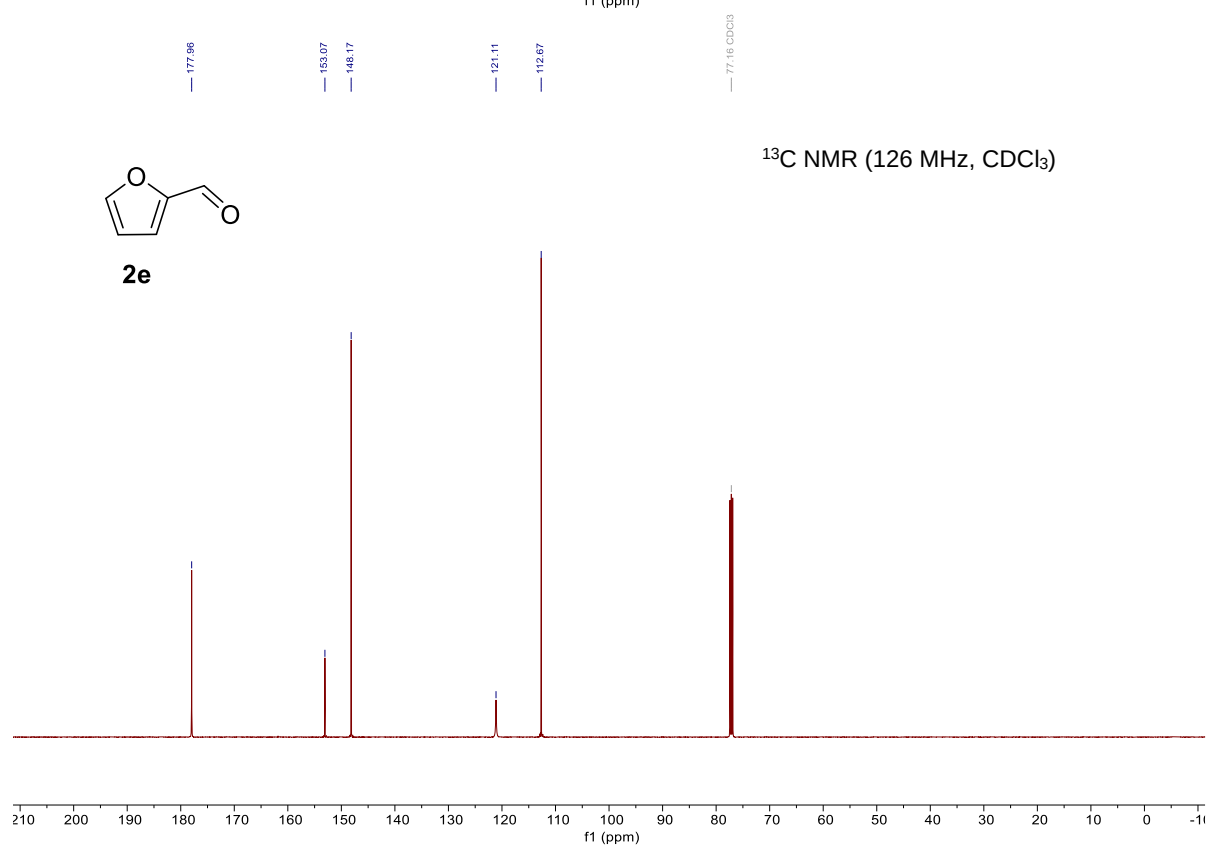
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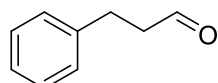
¹H NMR (500 MHz, CDCl₃)



2e

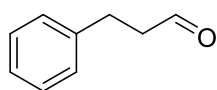
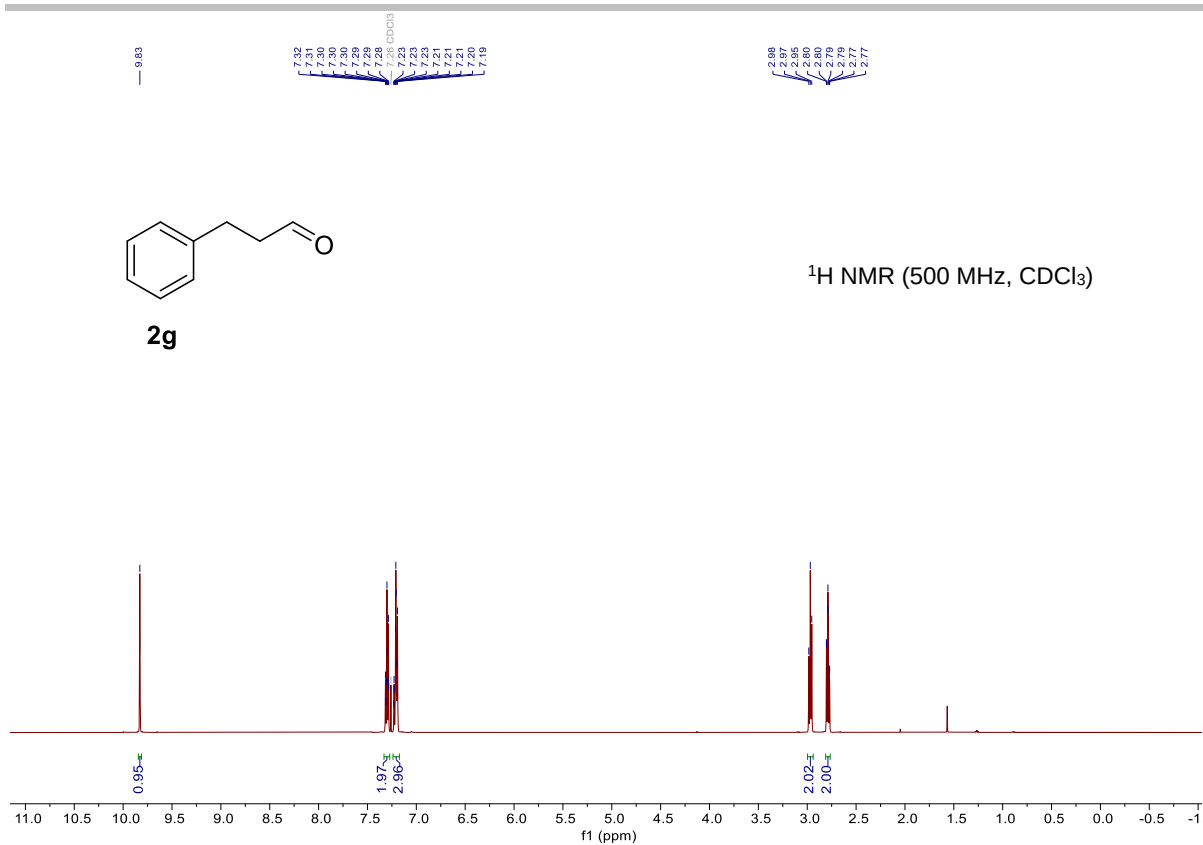
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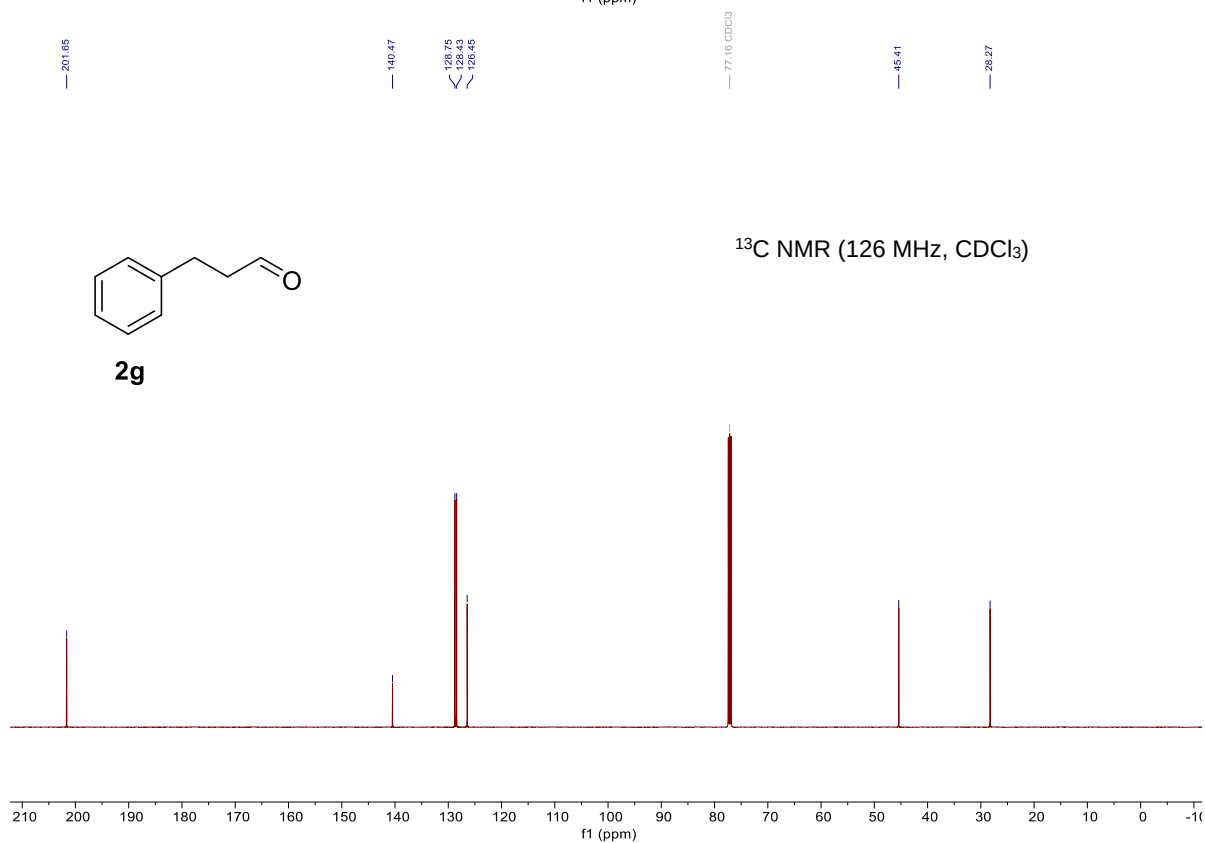
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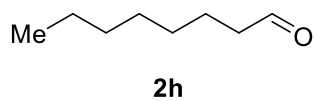
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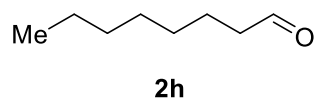
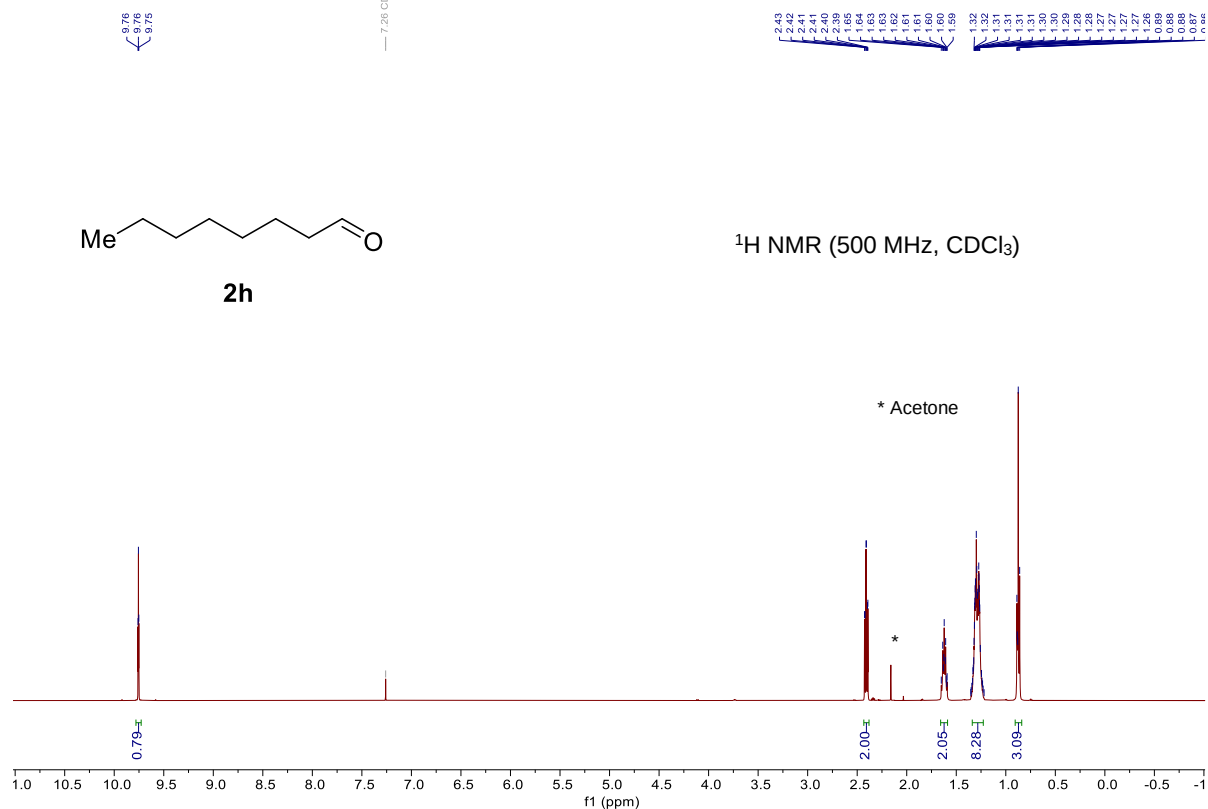
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¹³C NMR (126 MHz, CDCl₃)

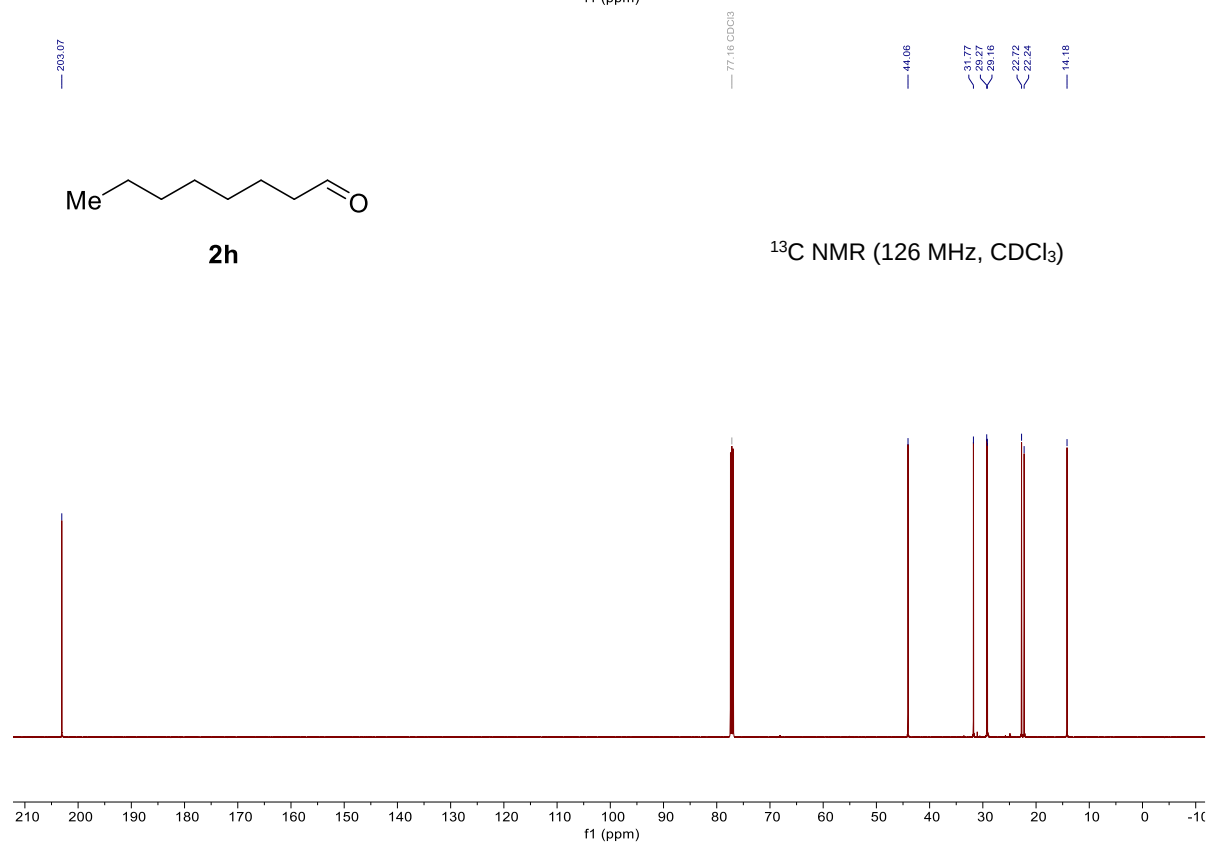


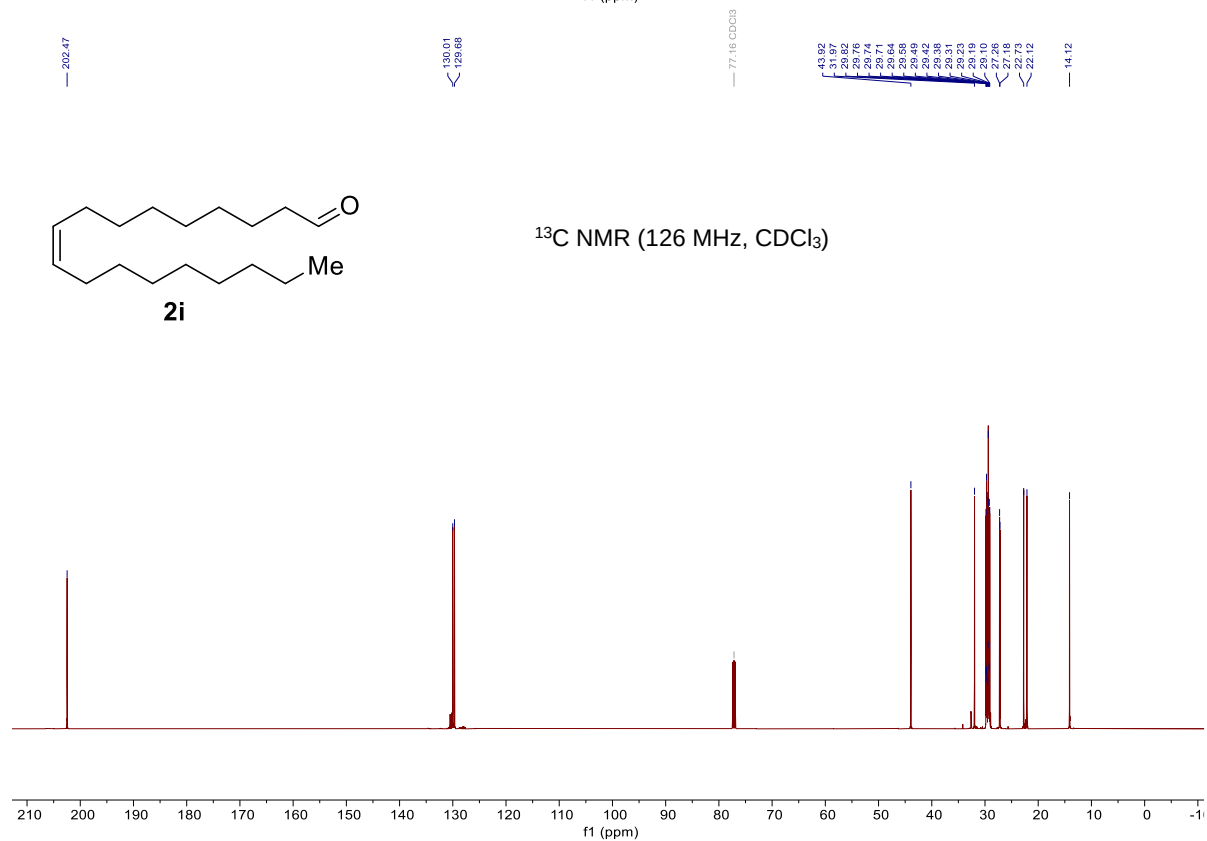
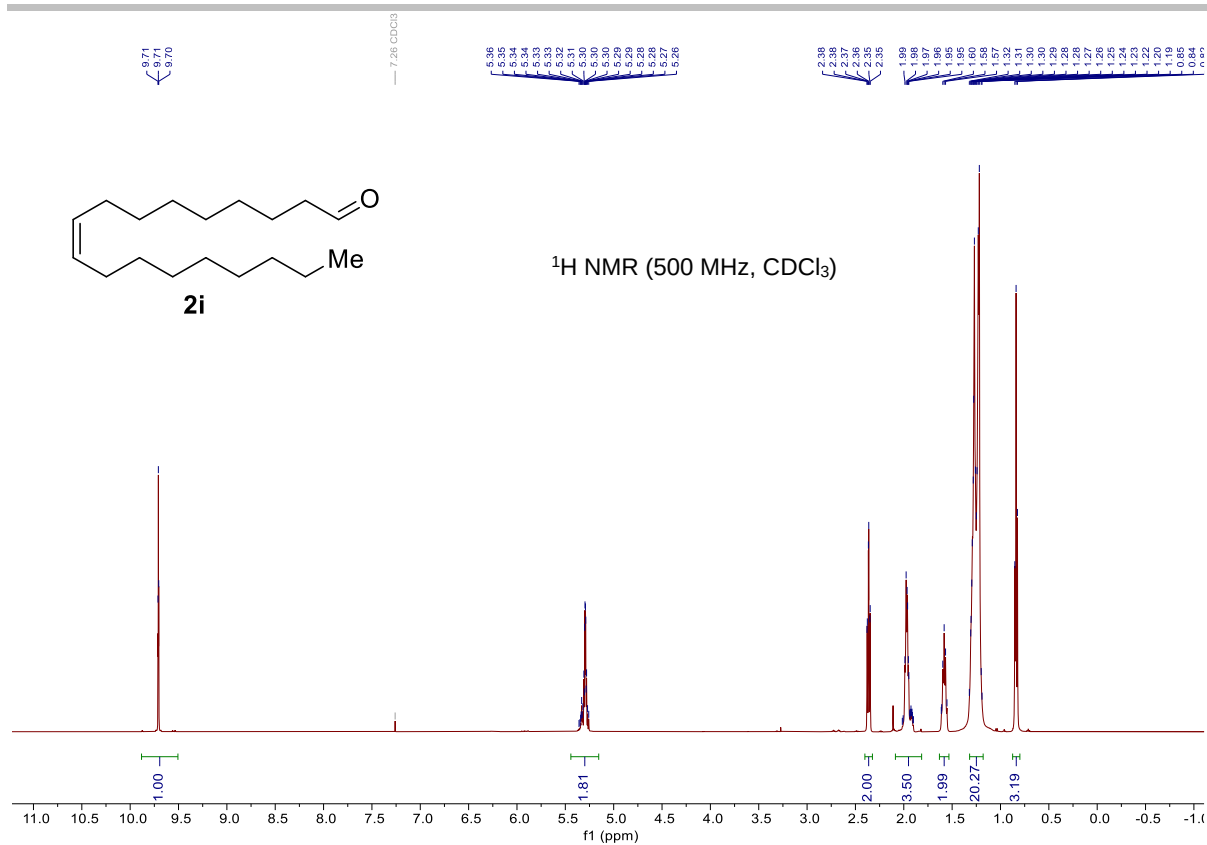


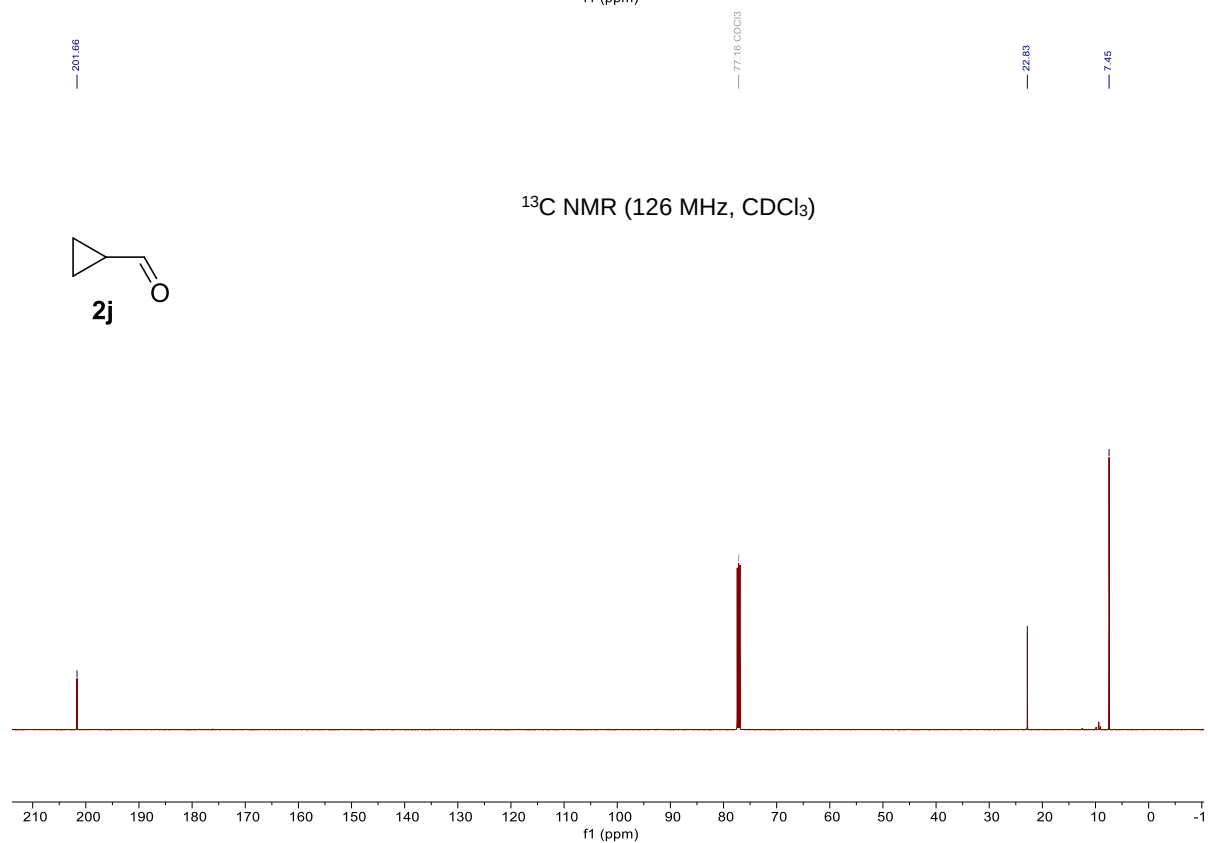
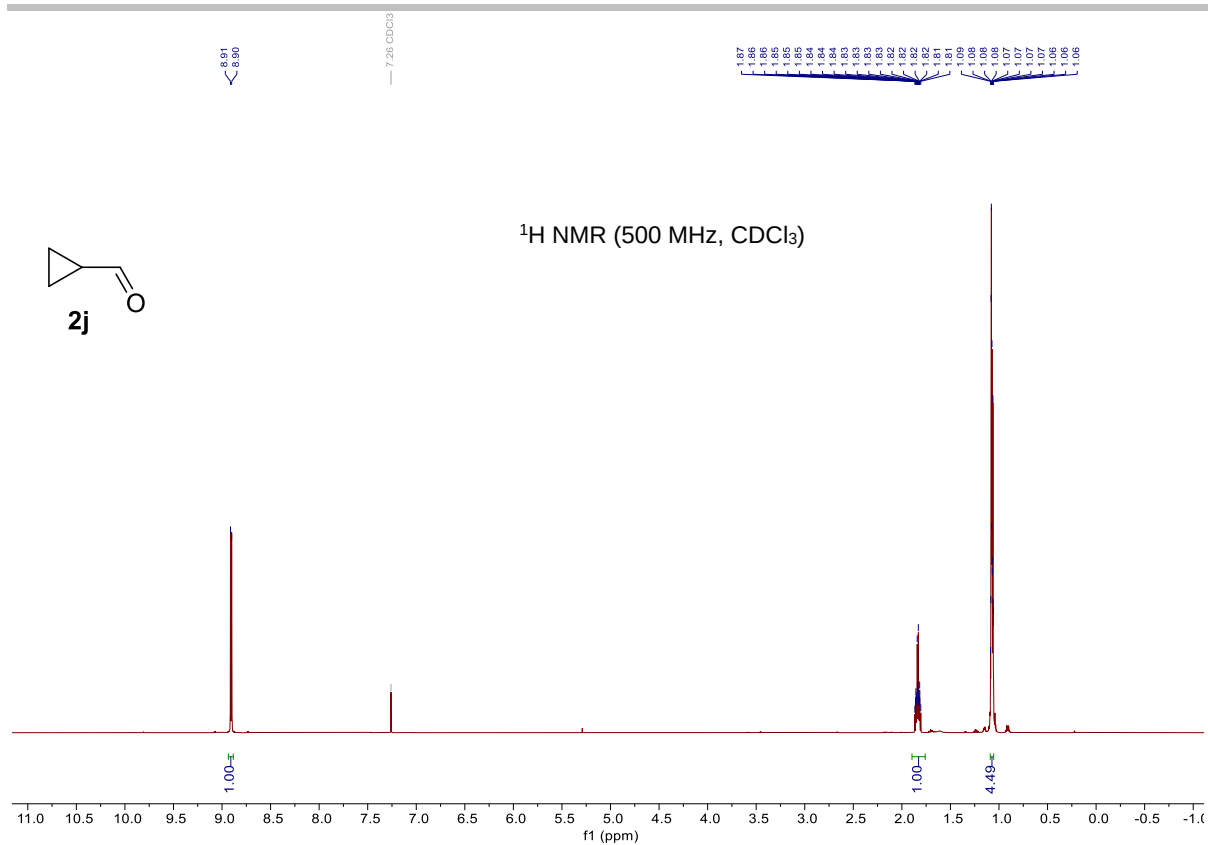
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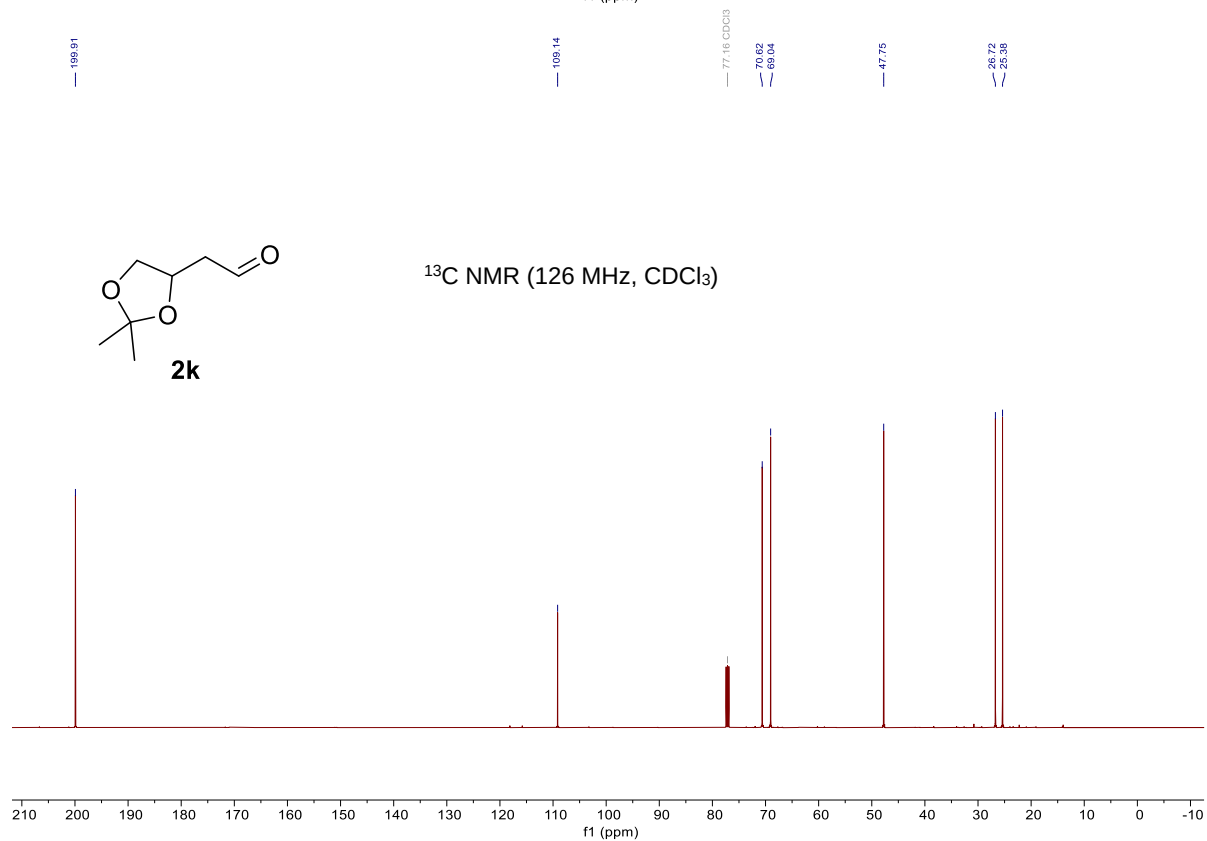
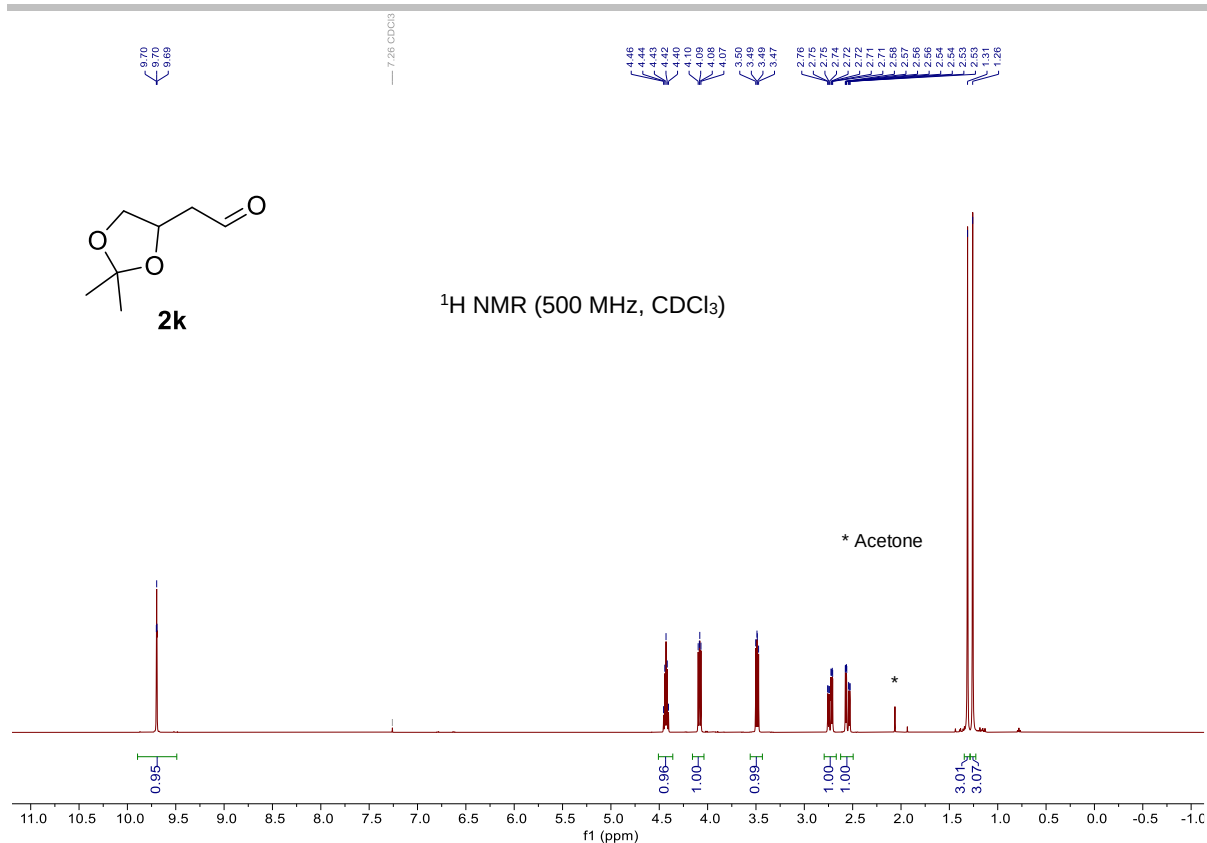


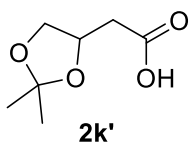
¹³C NMR (126 MHz, CDCl₃)



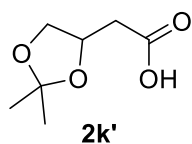
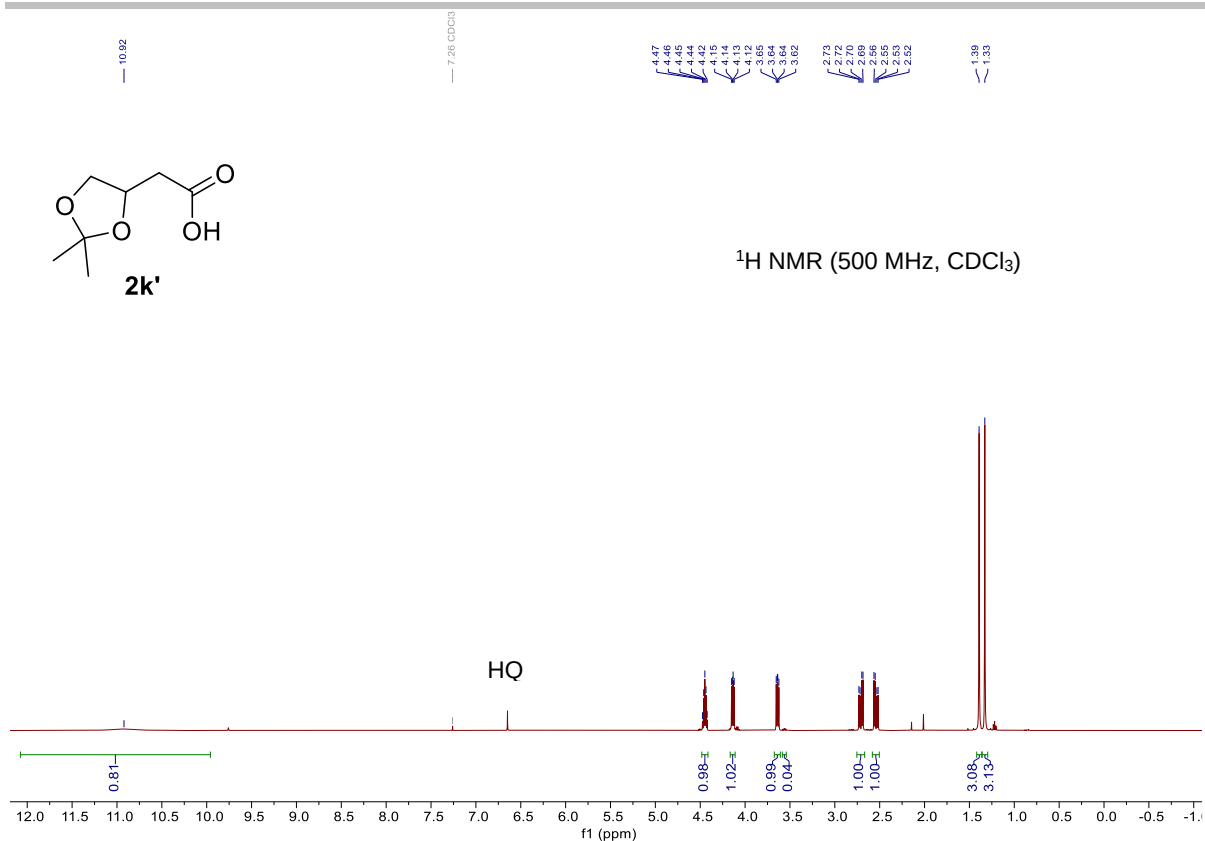








¹H NMR (500 MHz, CDCl₃)



¹³C NMR (126 MHz, CDCl₃)

