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Title:	Synthesis and durability of benzophenone derivatives as carriers in nonaqueous redox flow batteries
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Synthesis and durability of benzophenone derivatives as carriers in nonaqueous redox flow batteries

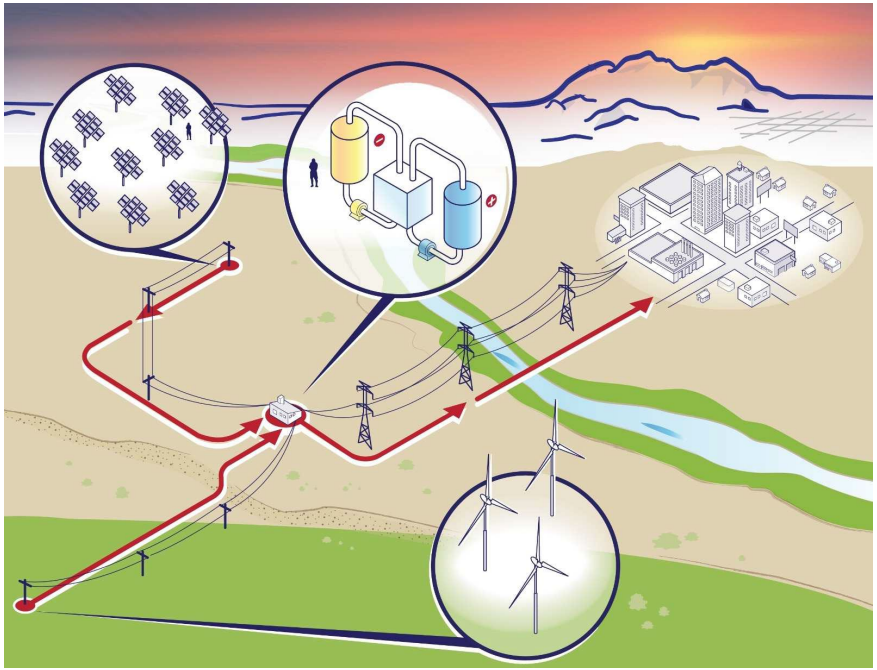
Kate Jesse, Benjamin Davis, Sandipkumar Mauya, and Rangachary Mukundan

MPA-11: Materials, Synthesis, and Integrated Devices

03/20/2022

LA-UR-22-22511

Long duration energy storage systems



US Department of Energy Goal: reduce the cost of grid-scale energy storage by 90% for systems that store energy for 10+ hours by 2035

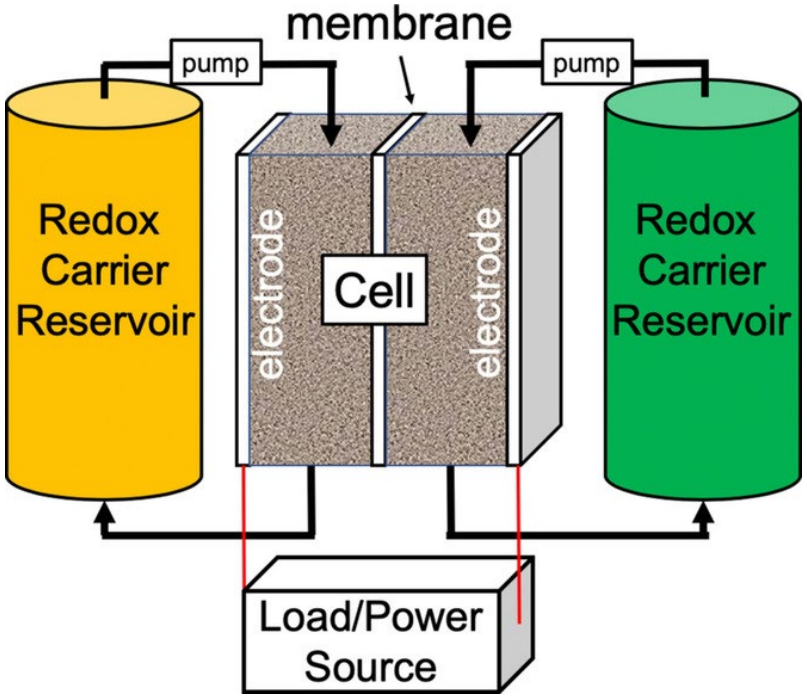
Essential for the development of a low cost, reliable electric grid

Cheaper, more efficient energy storage will make it easier to capture and store energy from renewable sources

The Biden-Harris Administration has a goal of net-zero carbon emissions by 2050

[1] U.S. Department of Energy. *Long Duration Storage Shot : An Introduction*; 2021.
[2]The Climate Group. How California is Driving the Energy storage Market Through State Legislation; 2017.

Redox flow batteries for energy storage



Redox flow batteries (RFB's) could be used to store energy from intermittent energy generation sources such as, wind and solar energy

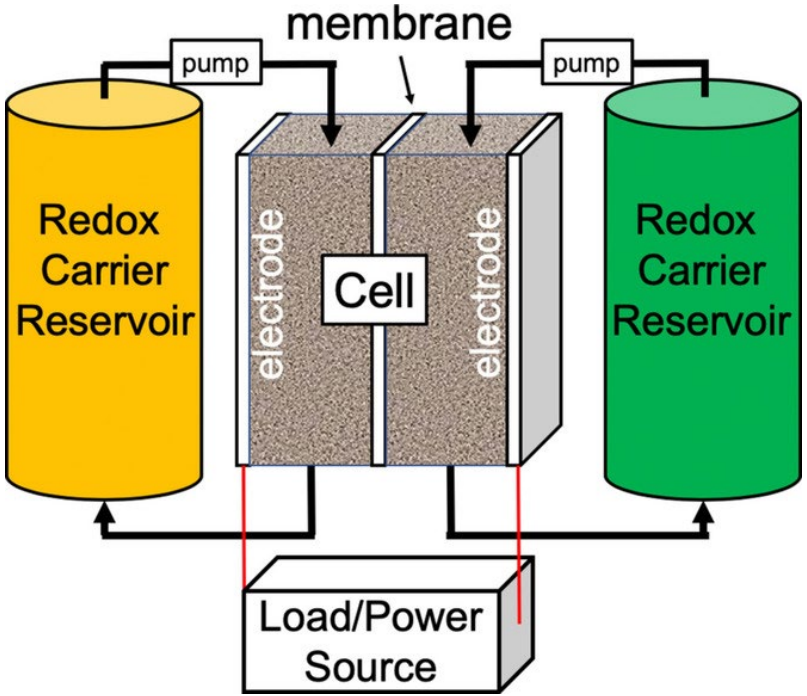
RFB's allow for long term energy storage in various redox states of a molecule

RFB's store power and energy separately, allowing power and energy to be scaled individually as needed for a given application

Carrier material can be easily replaced at the end of its lifetime

[1] Palmer, T. C. *ChemSusChem* **2021**, *14* (5), 1214–1228.
[2] Cao, J. et. al.. *Energy and Fuels* **2020**, *34* (11), 13384–13411.
[3] Darling, R. M. et. al. *Energy Environ. Sci.* **2014**, *7* (11), 3459–3477.
[4] Chu, T., et. al., *ChemSusChem* **2019**, *12*, 1304–1309.

Features of the ideal RFB



The ideal RFB will be low in cost and high volumetric energy density

$$E_{vol} = nV_{cell}FC_{active}$$

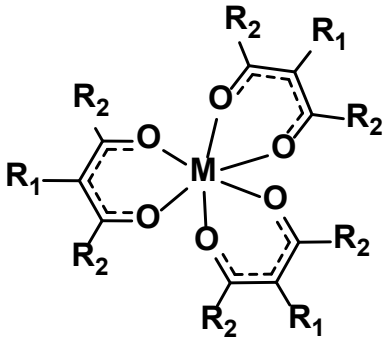
n = numbers of electrons transferred
V_{cell} = cell voltage
F = faraday's constant
C_{active} = concentration of active species

Non-aqueous redox flow batteries can take advantage of a larger solvent window (~5.5 V for MeCN) relative to water (~1.8 V)

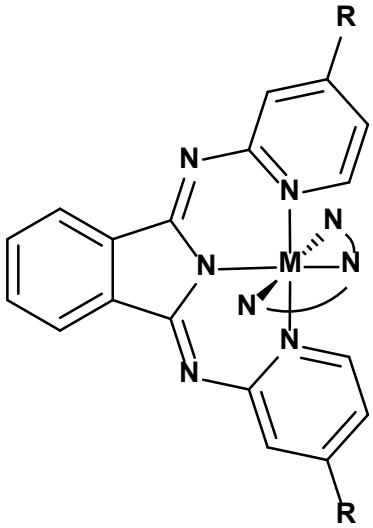
Water-in salt window is closer to 3.2 V, but this is still lower than non-aqueous solvents

[1] Palmer, T. C. *ChemSusChem* **2021**, *14* (5), 1214–1228.
[2] Cao, J. et. al.. *Energy and Fuels* **2020**, *34* (11), 13384–13411.
[3] Darling, R. M. et. al. *Energy Environ. Sci.* **2014**, *7* (11), 3459–3477.
[4] Leonard, D. P., et. al., *ACS Energy Lett.* **2018**, *3*, 373–374.
[5] Chu, T., et. al., *ChemSusChem* **2019**, *12*, 1304–1309.

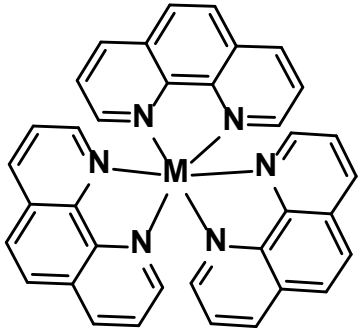
Inorganic carriers in RFB's



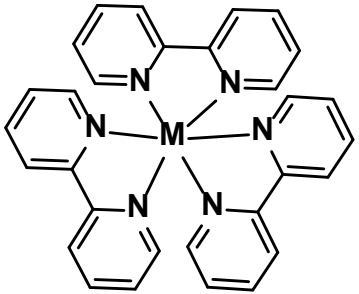
M = V, Cr, Mn, U, Ru



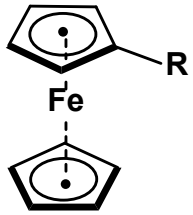
M = Mg, Mn, Fe, Co, Ni, Zn

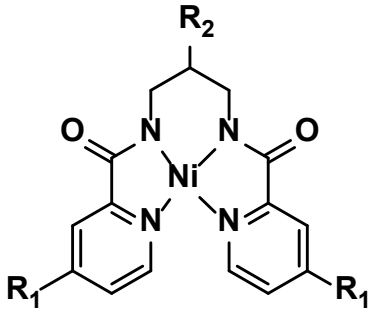


M = Fe, Ru, Ni, Co



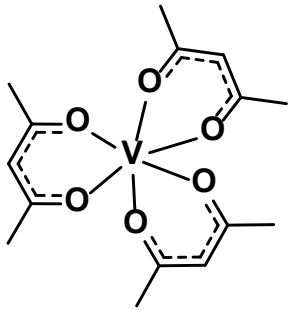
M = Fe, Ru, Ni, Co



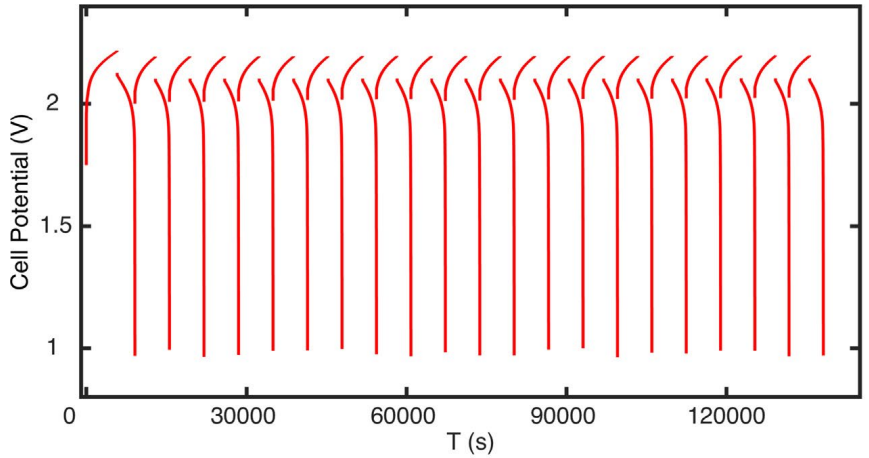


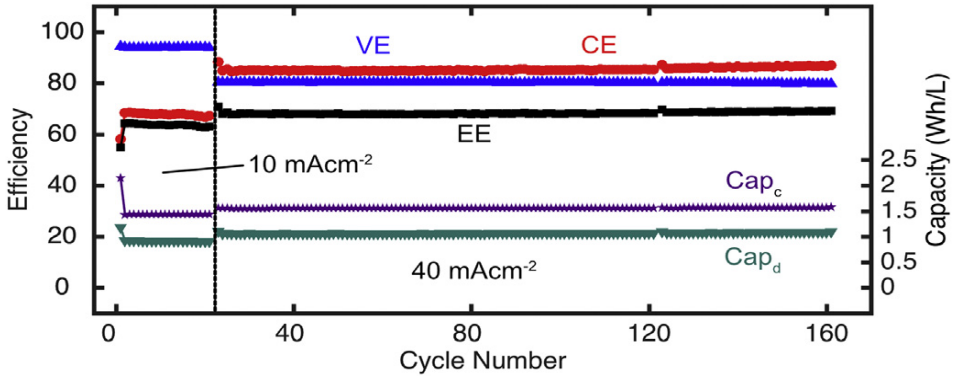
[1] Palmer, T. C., et. al., *ChemSusChem* **2021**, *14* (5), 1214–1228.
(2) Cabrera, P. J. et. al., *Inorg. Chem.* **2015**, *54*, 10214–10223.
[3] Sevov, C. S., et. al., *J. Am. Chem. Soc.* **2016**, *138*, 15378–15384.
[4] Saraidaridis, J. D.; Monroe, C. W. *J. Power Souces* **2019**, *412*, 384–390.
[5] Chu, T., et. al., *ChemSusChem* **2019**, *12*, 1304–1309.
[6] Zhen, Y., et. al., *J. Power Souces* **2020**, *445*, 1–8.
[7] Suttil, J. A., et. al., *J. Mater. Chem. A* **2015**, *3*, 7929–7938.

$V(acac)_3$ as an inorganic carrier in RFB's

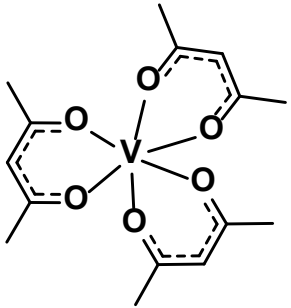


Saraidaridis, J. D.; Monroe, C. W. *J. Power Souces* **2019**, *412*, 384–390.

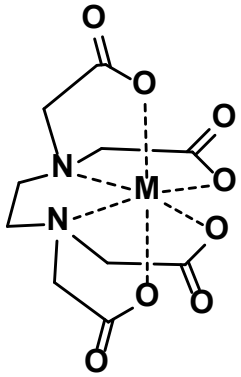




Commercialization of RFB's with inorganic carriers



UniEnergy Technologies



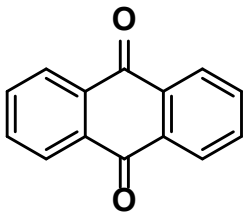
Sun Catalytix / Lockheed Martin

It takes many years to commercialize this technology after the initial discovery

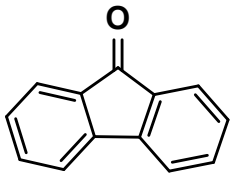
Vanadium is too high in cost for commercialization on the scale needed to meet national and state-wide energy storage goals

Organic carriers in RFB's

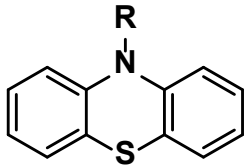
Negolytes



[1]Wu, M., et. al., *J. Mater. Chem. A* **2021**, *47*.
[2] Lantz, A. W., et. al., P. G. *Appl. Energy Mater.* **2019**, *2*, 7893–7902.
[3] Wu, M., et. al.,. *Batter. Supercaps* **2022**, 1–7.

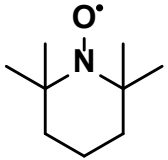


Feng, Ruozhu, et. al., *Science*. **2021**. *372,* 836-840.

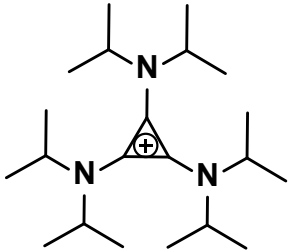


Attanayake, N. H., et. al., *Chem. Mater.* **2019**, *31* (12), 4353–4363.

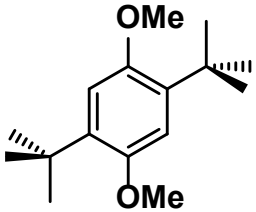
Posolytes



Xing, X.; Huo, Y.; Wang, X.; Zhao, Y. *Int. J. Hydrogen Energy* **2017**, *42*, 17488–17494.

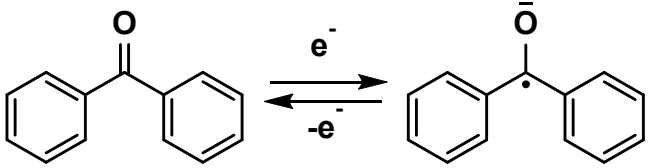


[1] Yan, Y.; Vaid T.P.; Sanford, M.S. *J. Am. Chem. Soc.* **2020**, *10*, 17564–17571.
[2] Yan, Y., et. al., *J. Am. Chem. Soc.* **2019**, *141*, 15301-15306.
[3] Yan, Y., et. al., *J. Am. Chem. Soc.* **2021**



Wang, X., et. al., *Int. J. Electrochem. Sci.* **2018**, *13* (7), 6676–6683.

Benzophenone derivative are promising candidates for negolytes in an RFB



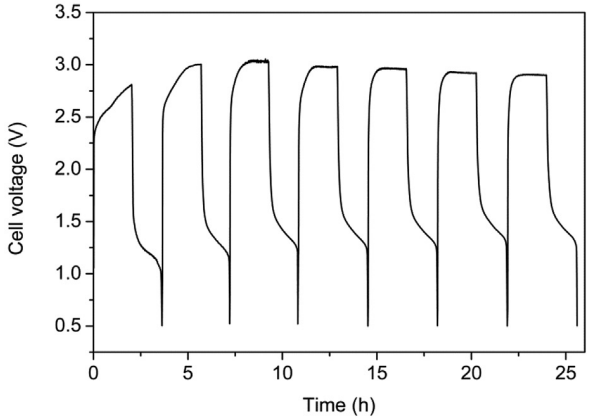
Highly soluble in MeCN → 3.7(1) M

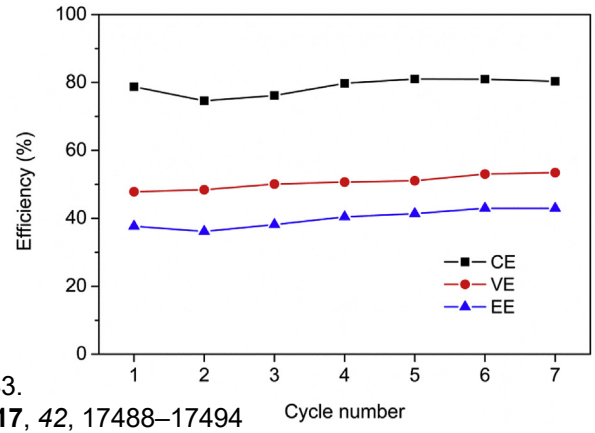
Reversible redox couple at -2.16 V vs. Ag/Ag^+ in MeCN

Conjugated pi system allows for delocalization of spin and charge density in the radical anion

Highly modifiable on the aromatic rings

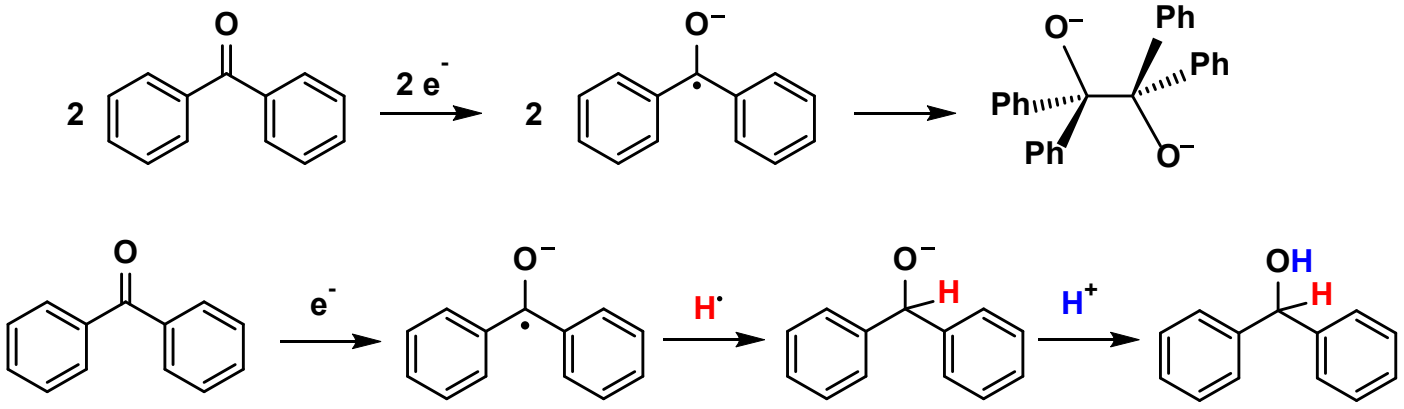
Downside: Not stable to extensive cycling





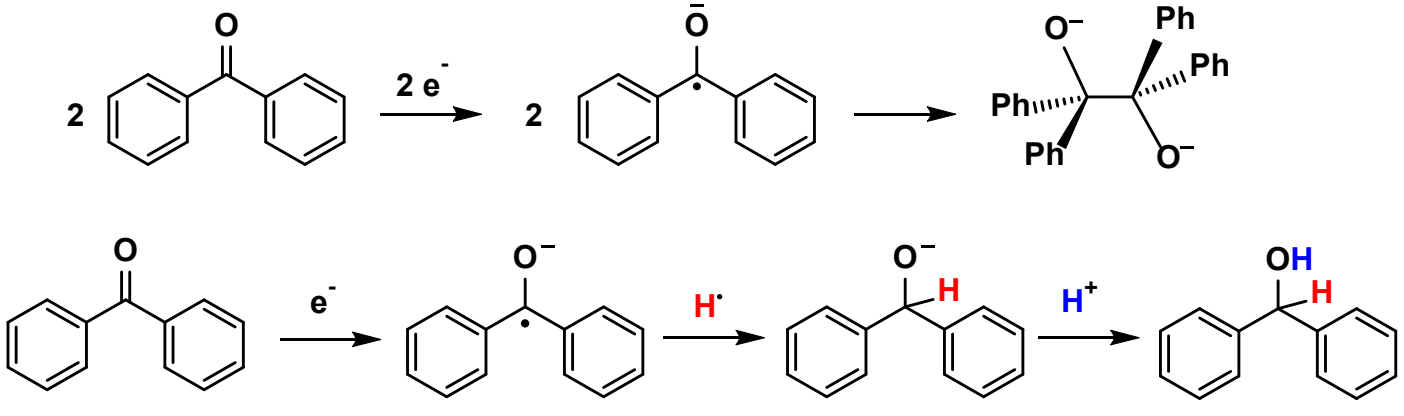
[1] Wang, X., et. al., *Int. J. Electrochem. Sci.* **2018**, *13* (7), 6676–6683.
[2] Xing, X.; Huo, Y.; Wang, X.; Zhao, Y. *Int. J. Hydrogen Energy* **2017**, *42*, 17488–17494

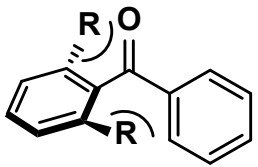
Possible degradation pathways of benzophenone radical anions



In all cases the major decomposition product determined by GCMS is diphenylmethanol

Sterically bulky benzophenones should block these degradation pathways



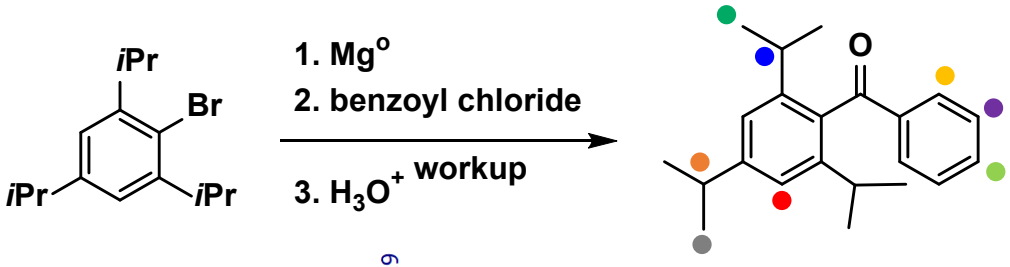


R = ^{i}Pr, ^{t}Bu

Benefits of asymmetry

- Increased solubility
- Delocalization of charge and spin density onto phenyl ring
- Straightforward synthetic route

Synthesis of 2,4,6-Triisopropylbenzophenone



IR, C=O stretch: 1662 cm^{-1}

Solubility in MeCN: 350(3) mM

^{1}H NMR: CD_3CN

Fleukke, K. H.; Van der Stelt, C.; Nauta, W. T. *Recueil* **1962**, *81*, 93–101.

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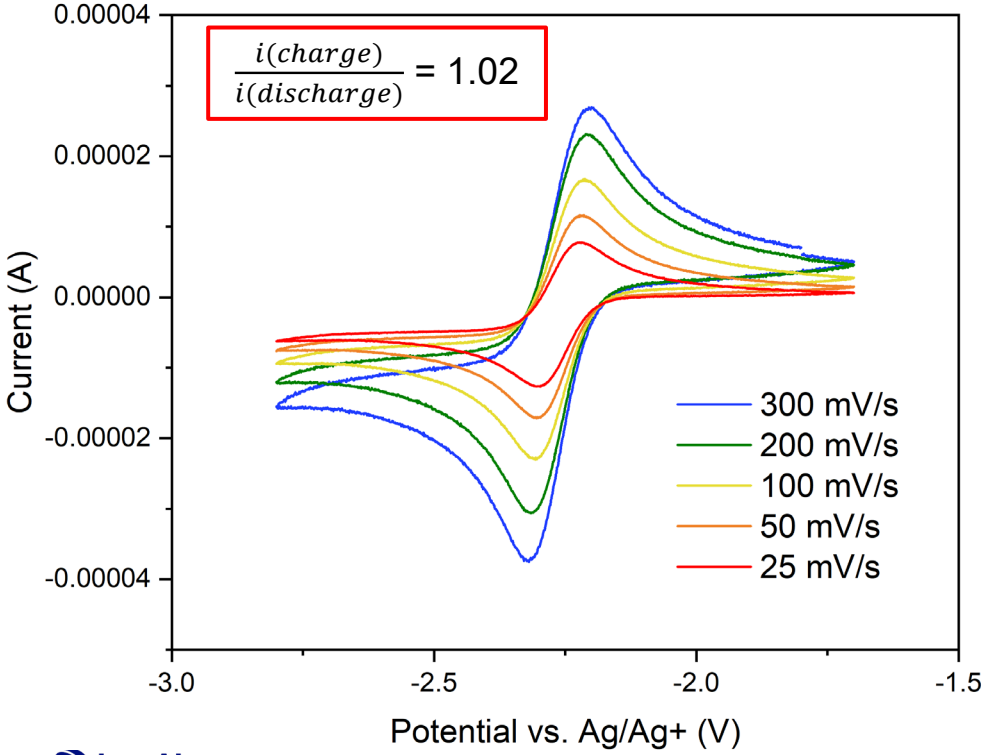
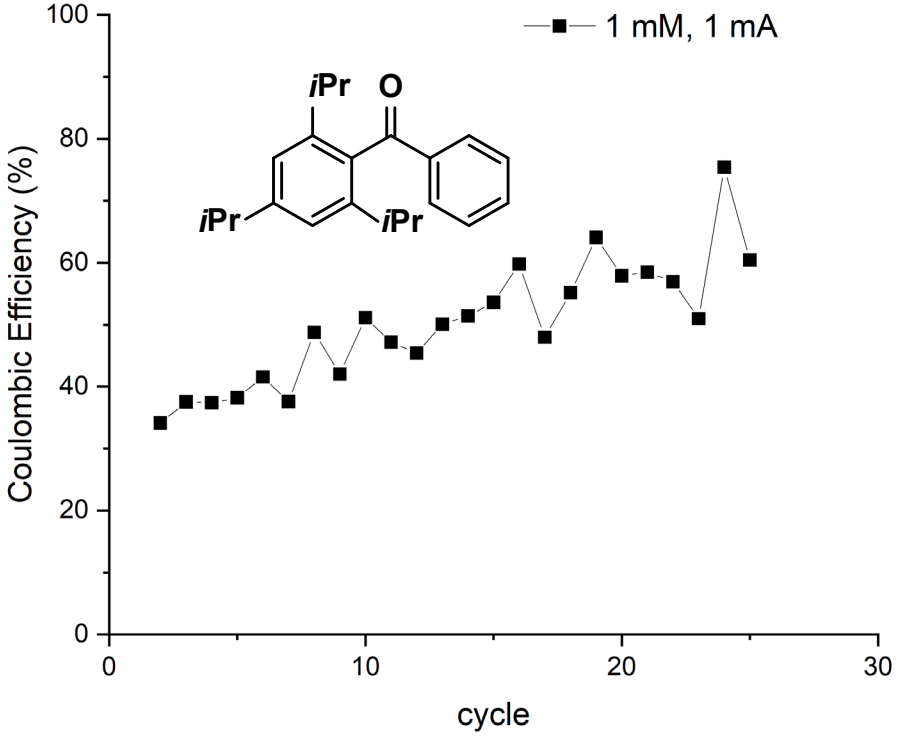
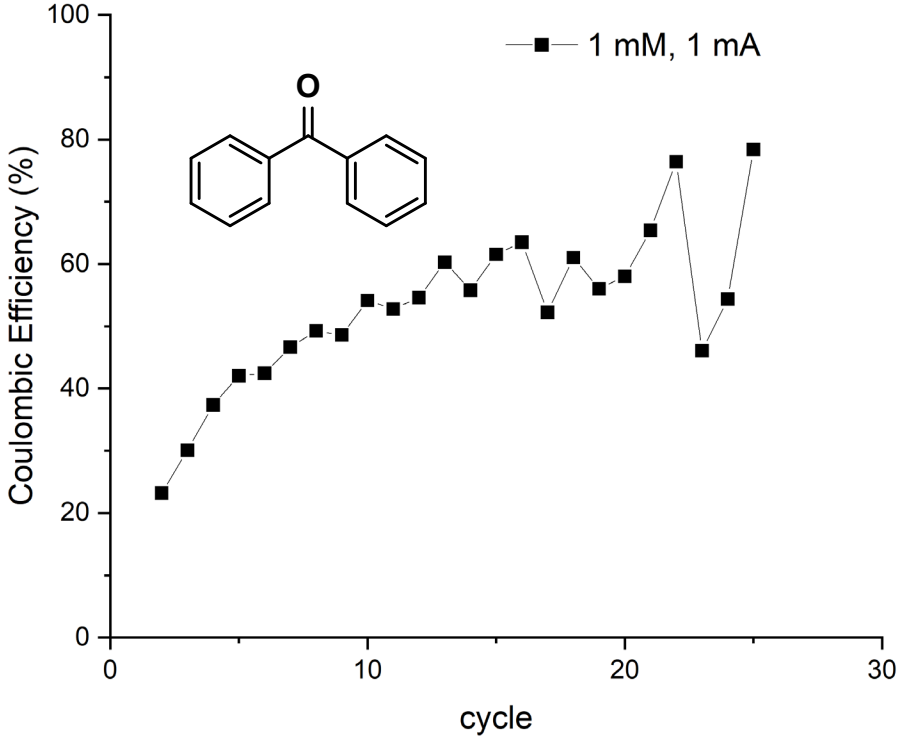
Electrochemical characterization of the reversibility of 2,4,6-Triisopropylbenzophenone



Scan rate (mV/s)	E_a (V)	E_c (V)	ΔE (mV)
300	-2.319	-2.2047	114.3
200	-2.3116	-2.2112	100.4
100	-2.3041	-2.2122	91.9
50	-2.3051	-2.2218	83.3
25	-2.2977	-2.2272	70.5

Bulk electrolysis of 2,4,6-Triisopropylbenzophenone, 100% SOC





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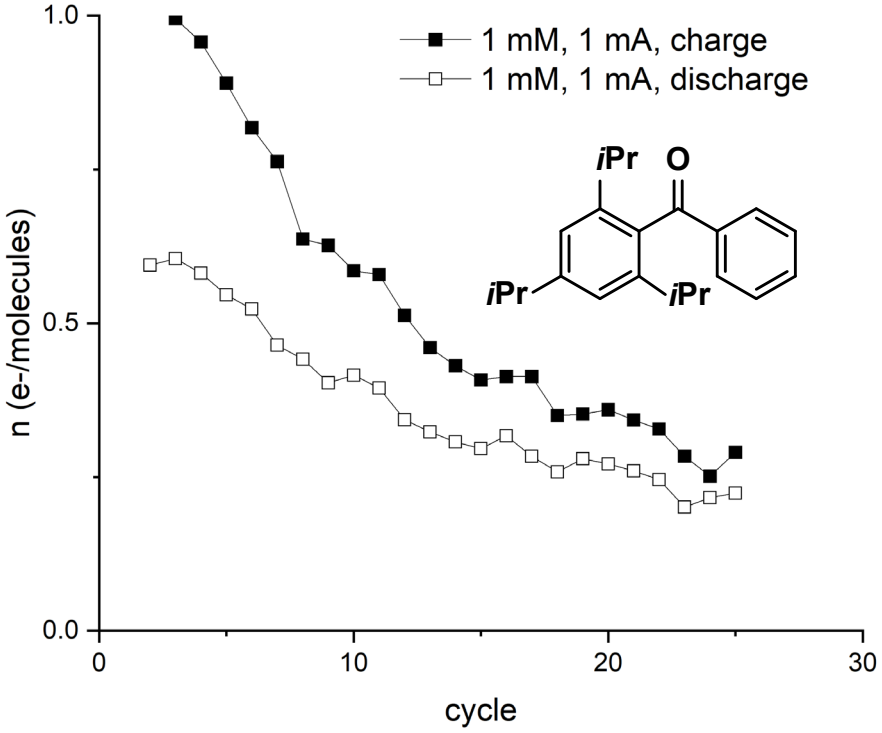
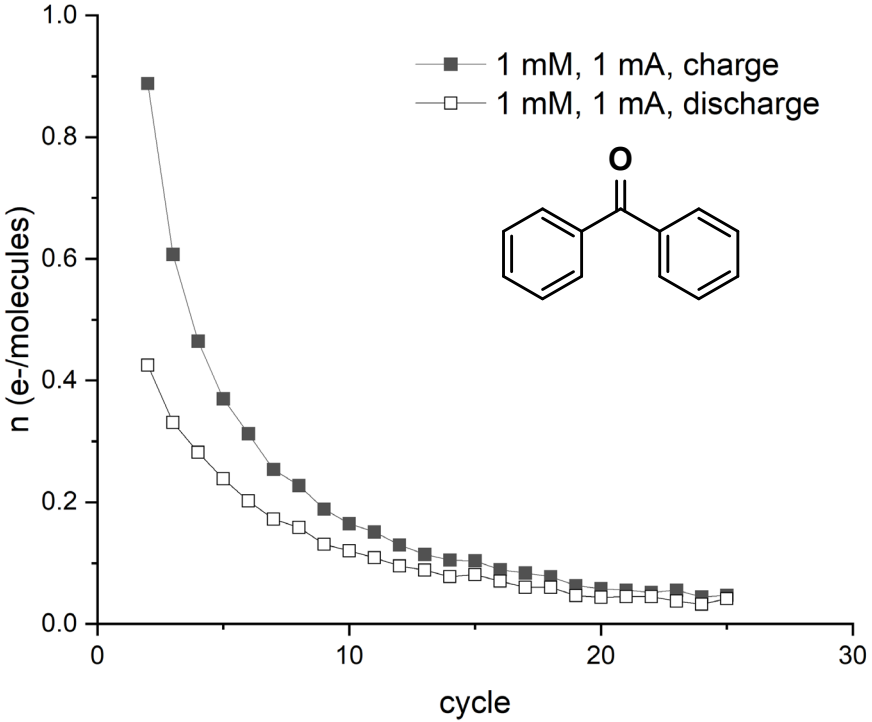
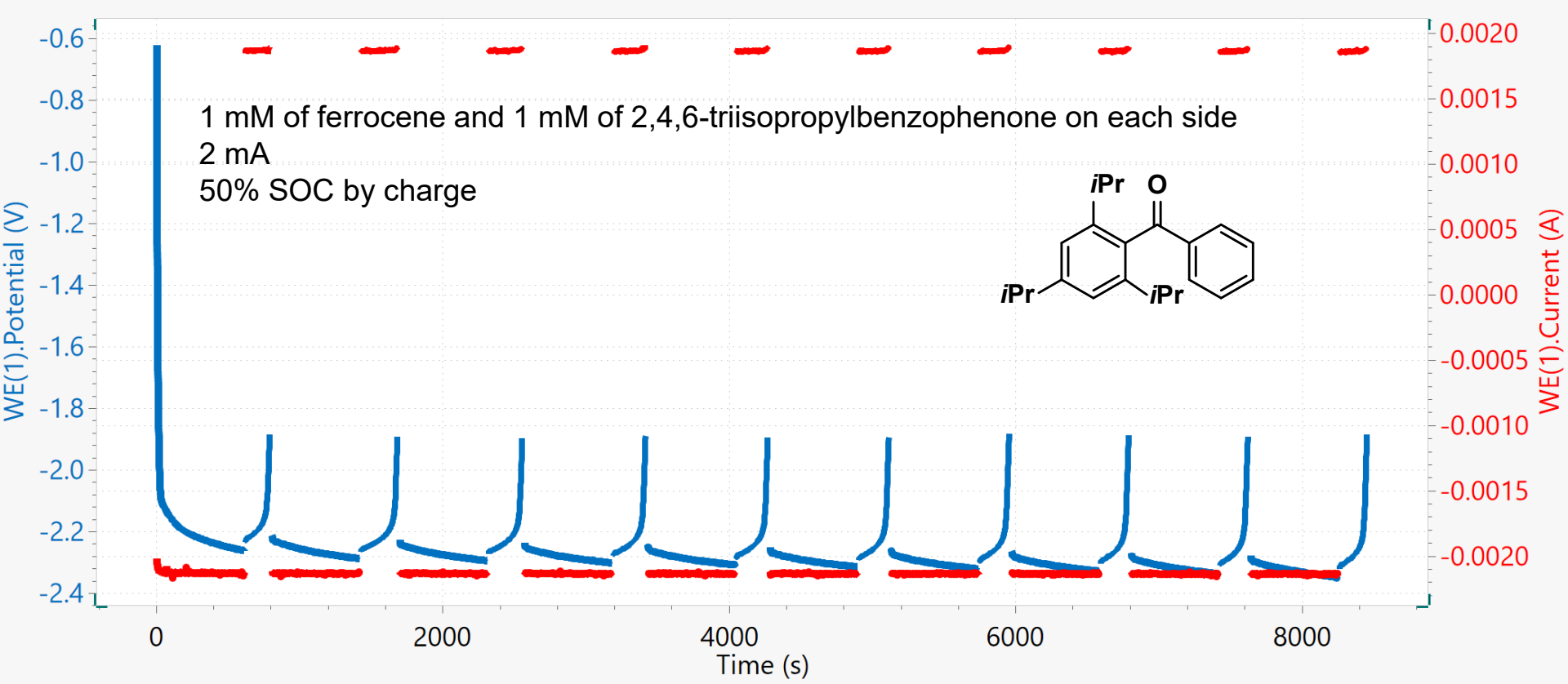


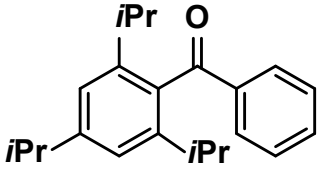


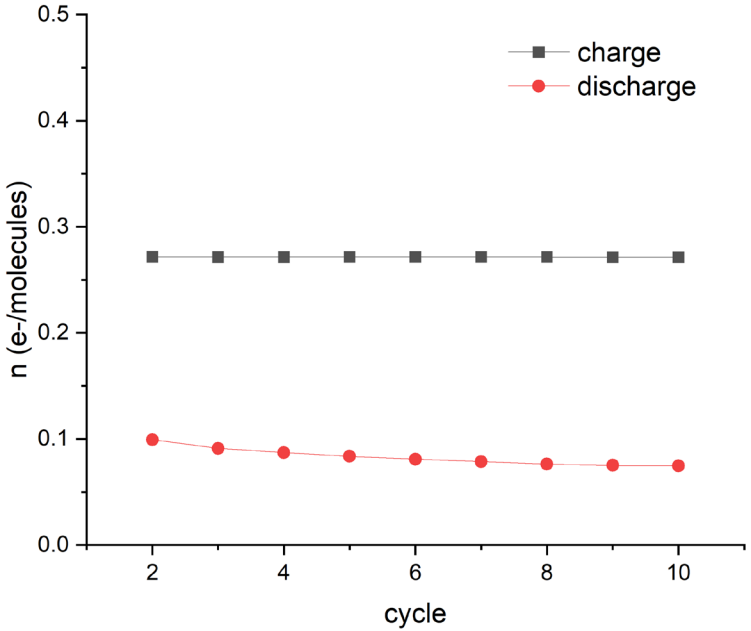
Reversibility in MeCN with 100 mM $TBAPF_6$

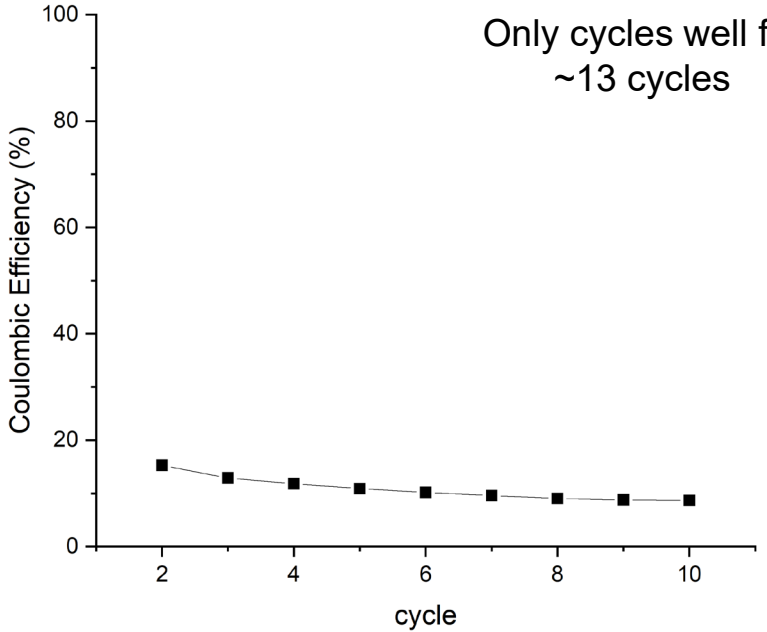


Reversibility in MeCN with 100 mM $TBAPF_6$

1 mM of ferrocene and 1 mM of 2,4,6-triisopropylbenzophenone on each side
2 mA
50% SOC by charge

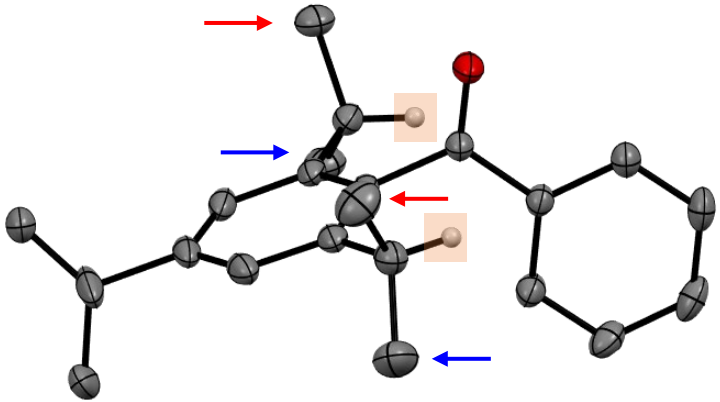






Only cycles well for ~13 cycles

Solid and solution state conformation of 2,4,6-Triisopropylbenzophenone



Equivalent isopropyl protons
Inequivalent isopropyl -CH_3 groups

^{1}H NMR: CD_3CN

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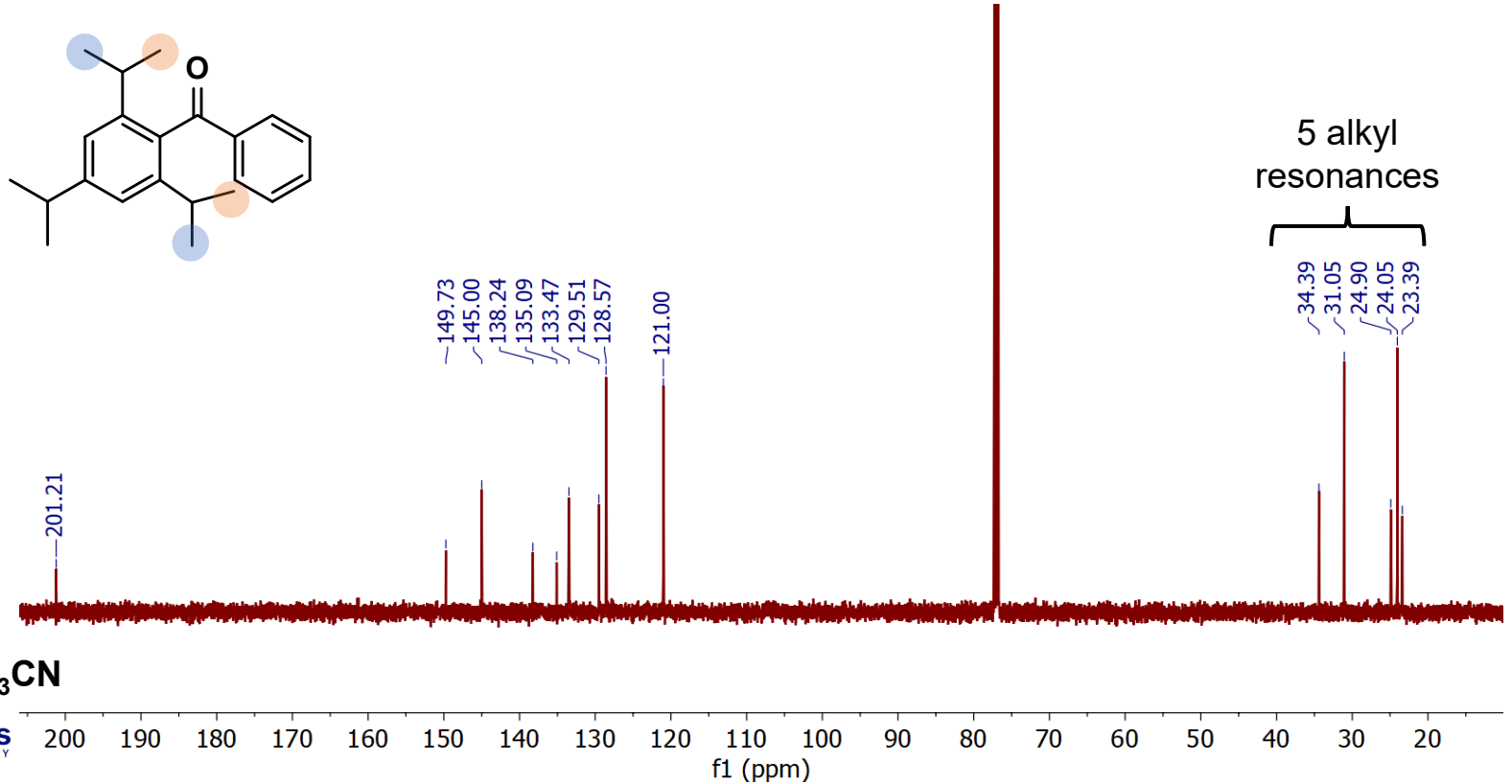
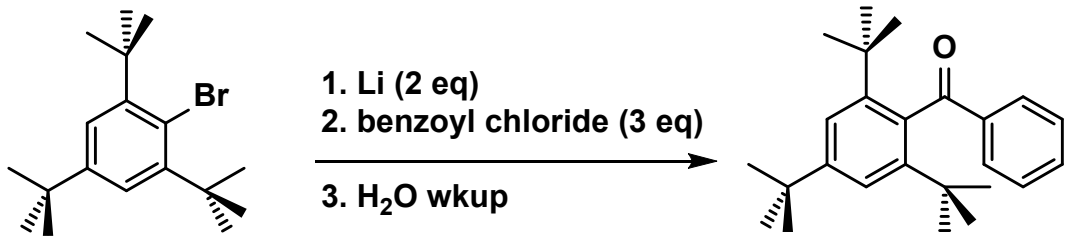
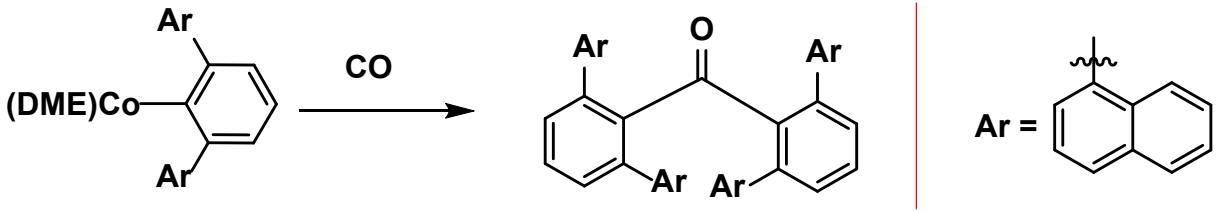
Solid and solution state conformation of 2,4,6-Triisopropylbenzophenone



^{1}H NMR: CD_3CN

Future directions





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Emily Thompson