Supporting Information for:

Solvents and their hydrogen bonding properties as general considerations in carbon dioxide reduction by molecular catalysts

*Xiaohan Li and Jeffrey J. Warren**

Department of Chemistry
Simon Fraser University,
8888 University Drive, Burnaby BC V5A 1S6, Canada
*jjwarren@sfu.ca

Contents

Instrumentation

^{1}H NMR spectra were collected on a Bruker Avance III 400 MHz spectrometer. ^{1}H DOSY data were collected on Avance II 600 MHz spectrometer equipped with a 5 mm Bruker QNP cryoprobe. ^{19}F DOSY data were collected on Avance II 600 MHz spectrometer (^{19}F frequency = 564.97 MHz) equipped with a 5 mm Bruker QCI cryoprobe. Diffusion coefficients were obtained using MesterNova's built-in Bayesian DOSY transform algorithm following the user manual. Infrared spectra were collected on a Perkin Elmer Spectrum 2 FT-IR equipped with an attenuated total reflectance (ATR) accessory (germanium crystal: 4000-700 cm^{-1}).IR samples were recorded using pure solid samples. UV-vis spectra were collected using a Cary 100Bio spectrometer.

Characterization of complexes

BrRe(CO_3)(2,2´-bipyridine).[1] ^{1}H NMR (400 MHz, CD_3CN): δ = 7.63 (ddd, 2H); 8.19 (td, 2H); 8.43 (dt, 2H); 9.04 (d, 2H). ATR-FTIR (cm^{-1}): 2009, 1871. UV-vis: 370 nm (MLCT)

BrRe(CO_3)(4,4´-dimethoxy-2,2´-bipyridine).[2] ^{1}H NMR (400 MHz, CD_3CN): δ = 4.04 (s, 6H), 7.13 (dd, 2H); 7.89 (d, 2H); 8.78 (d, 2H). ATR-FTIR (cm^{-1}): 2020, 1877. UV-vis: 356 nm (MLCT)

BrRe(CO_3)(4,4´-di-*tert*-butyl-2,2´-bipyridine).[3] ^{1}H NMR (400 MHz, CD_3CN): δ = 1.45 (s, 18H), 7.64 (dd, 2H); 8.41 (d, 2H); 8.90 (d, 2H). ATR-FTIR (cm^{-1}): 2019, 1886, 1876. UV-vis: 365 nm (MLCT)

BrRe(CO_3)(2-(2´-quinolyl)benzimidazole).[4] ^{1}H NMR (400 MHz, 80% CD_3CN + 20% DMSO-d_6): δ = 7.57 (m, 2H); 7.81 (m, 1H); 7.86 (m, 1H); 8.03 (m, 1H); 8.10 (ddd 1H); 8.18 (dd,1H); 8.60 (d, 1H); 8.84 (dd, 2H). ATR-FTIR (cm^{-1}): 2017, 1901. UV-vis: 353 (shoulder) and 365 nm (MLCT)

Determination of k_{obs}

$$\frac{i_{cat}}{i_p} = \frac{1}{0.446}\sqrt{\frac{n'RT}{nF\nu}k_{obs}} \quad (1)$$

The ratio of the catalytic peak current densities (i_{cat}, i_p) is obtained from the cyclic voltammograms. Then k_{obs}, the intrinsic catalytic rate constant, can be solved by using equation 1, where R is the universal gas constant (R=8.3144598 J mol^{-1} K^{-1}), T is the temperature in kelvin (K) , F is the Faraday constant (F=96485.3321 s A mol^{-1}), υ is scan rate (all CVs collected in this paper were collected at υ=0.1 V), n is the number of electrons transferred from the electrode per catalyst (n = 2), n′ is the catalyst required for complete turnover (n′ = 1).

Potential correction to H_2

$$Correction = E - E(Fc) + E(H_2) + 0.591(pK_a) \quad (2)$$

E in this equation represents the original potential values obtained from the CV measurements. The first correction component is the ferrocene standard versus silver (E(Fc)), this number varies depending on the solvent and time of CV collection. The following is the correction of H^+/H_2 versus ferrocene ($E(H_2)$), in DMF is –0.662 V and in acetonitrile is –0.028 V. The last correction for phenol involves the pK_a of the solvent (pK_a(DMF)=18.9, pK_a(MeCN)=29), this component is excluded for CVs obtained under argon.

Cyclic voltammograms under argon

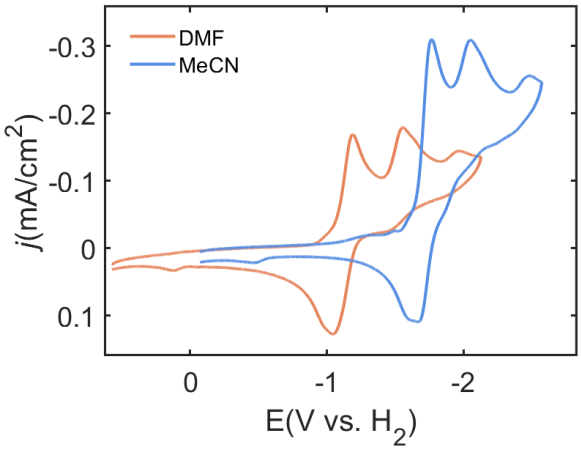

Figure S1. Cyclic voltammograms for $BrRe(CO)_3bpy$ (1 mM) in DMF and acetonitrile under argon. Scan rate was 100 mV s^{-1} and the supporting electrolyte was 100 mM $^nBu_4NPF_6$.

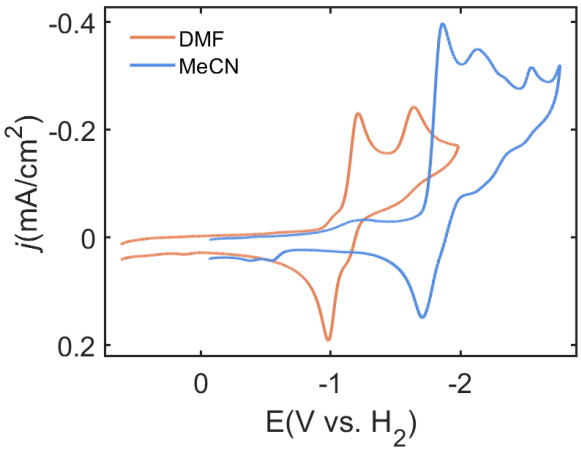

Figure S2. Cyclic voltammograms for $BrRe(CO)_3{}^tBubpy$ (1 mM) in DMF and acetonitrile under argon. Scan rate was 100 mV s^{-1} and the supporting electrolyte was 100 mM $^nBu_4NPF_6$.

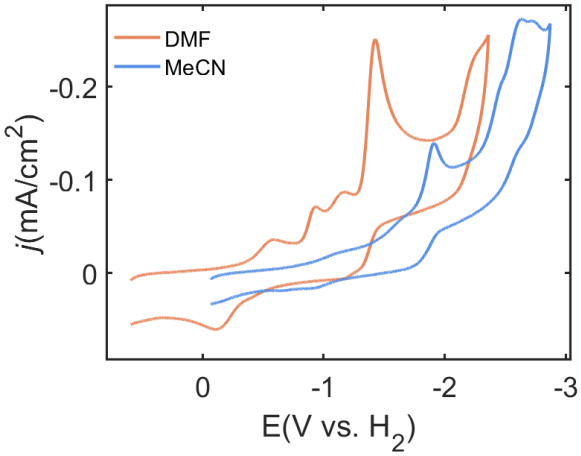

Figure S3. Cyclic voltammograms for $BrRe(CO)_3QuBIm$ (1 mM) in DMF and acetonitrile under argon. Scan rate was 100 mV s^{-1} and the supporting electrolyte was 100 mM $^nBu_4NPF_6$.

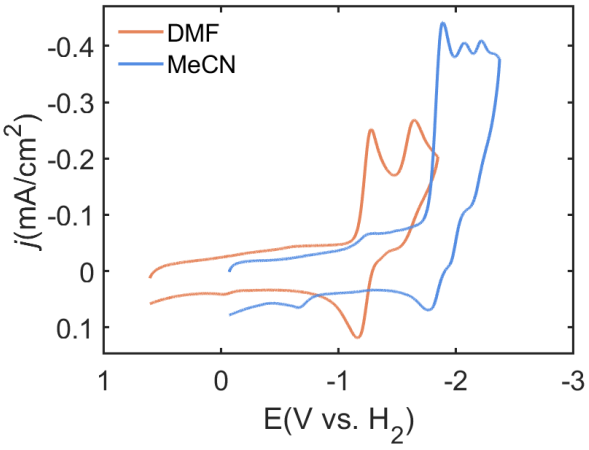

Figure S4. Cyclic voltammograms for $BrRe(CO)_3OMe_2bpy$ (1 mM) in DMF and acetonitrile under argon. Scan rate was 100 mV s^{-1} and the supporting electrolyte was 100 mM $^nBu_4NPF_6$.

Cyclic voltammograms versus ferrocenium/ferrocene (Fc^{+0}) reference

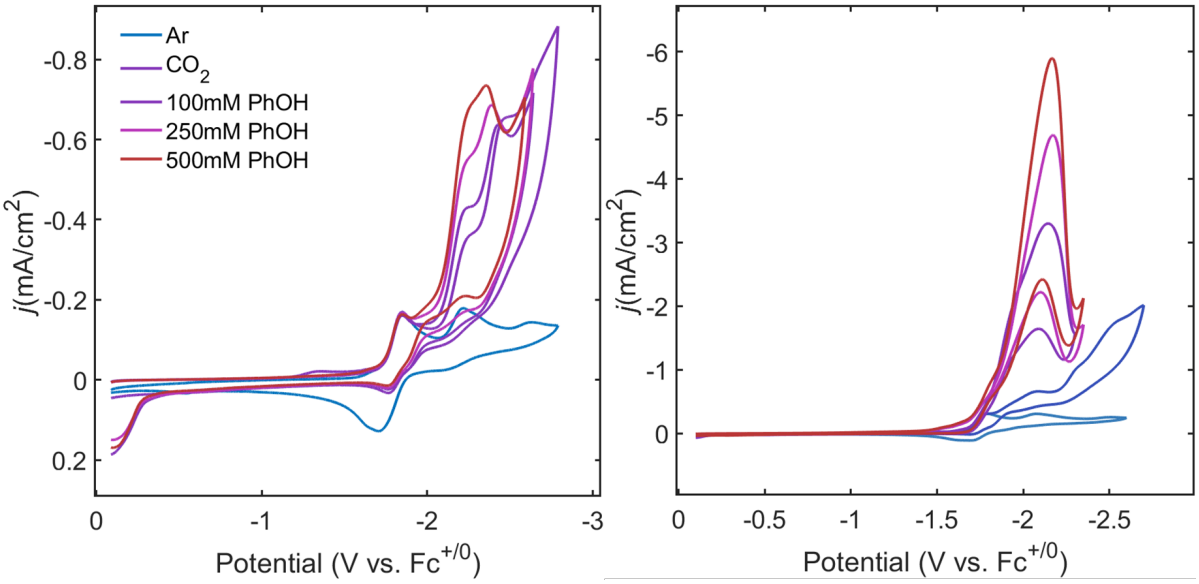

Figure S5. CV data $BrRe(CO)_3$bpy in DMF (left) and acetonitrile (right) with respect to the ferrocenium/ferrocene ($Fc^{+/0}$) couple.

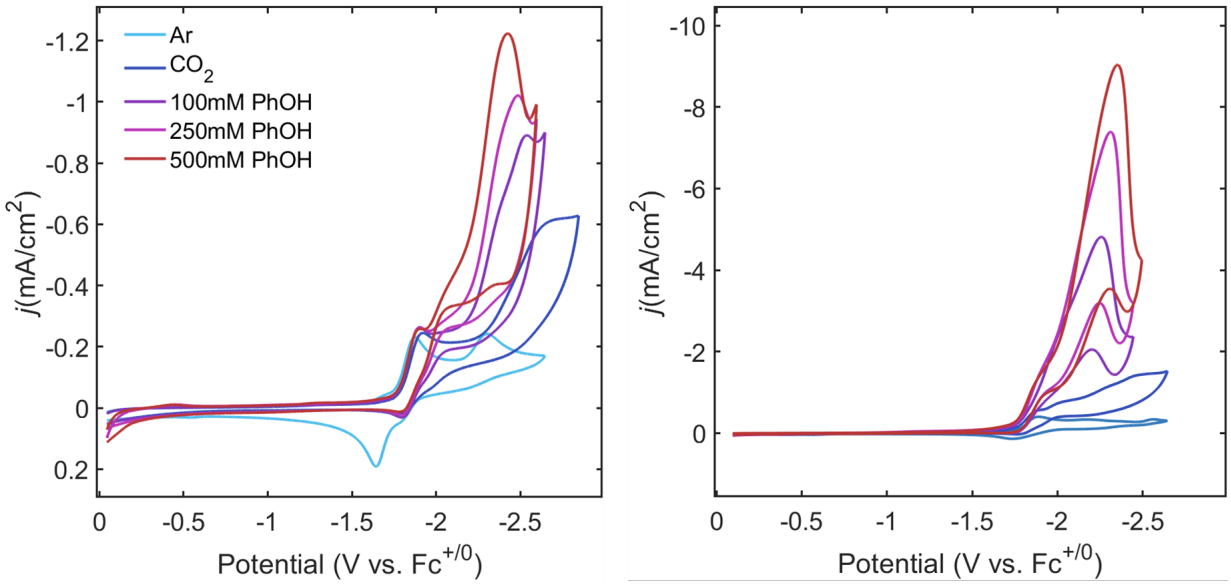

Figure S6. $BrRe(CO)_3{}^t$Bubpy in DMF (left) and acetonitrile (right) with respect to the ferrocenium/ferrocene ($Fc^{+/0}$) couple.

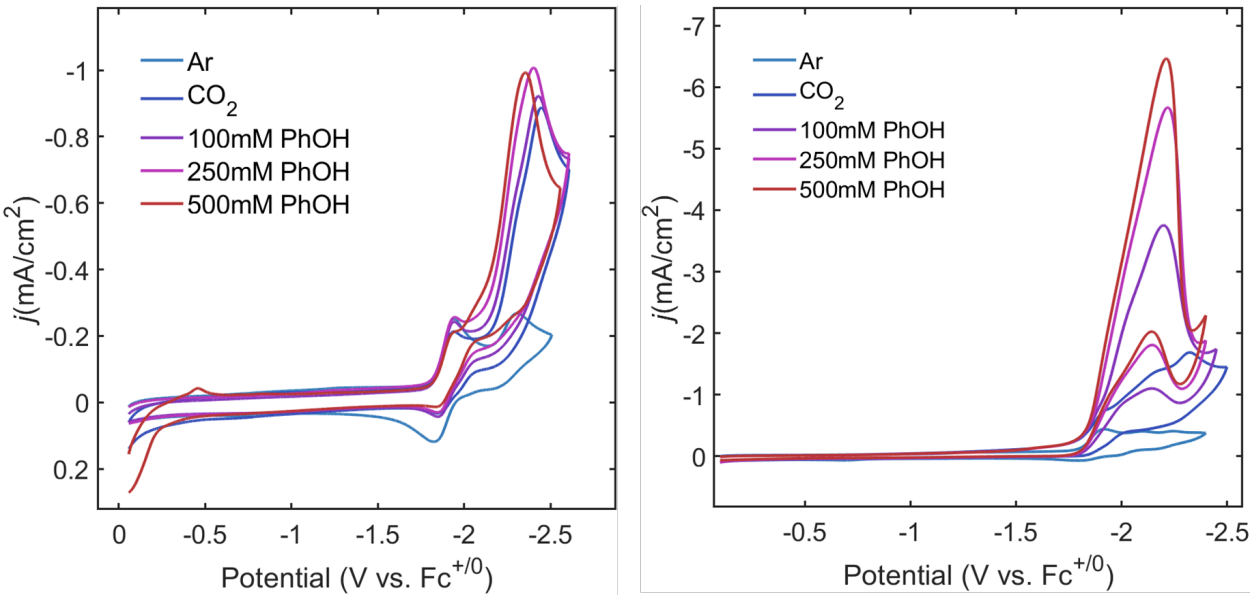

Figure S7. $BrRe(CO)_3OMebpy$ in DMF (left) and acetonitrile (right) with respect to the ferrocenium/ferrocene ($Fc^{+/0}$) couple.

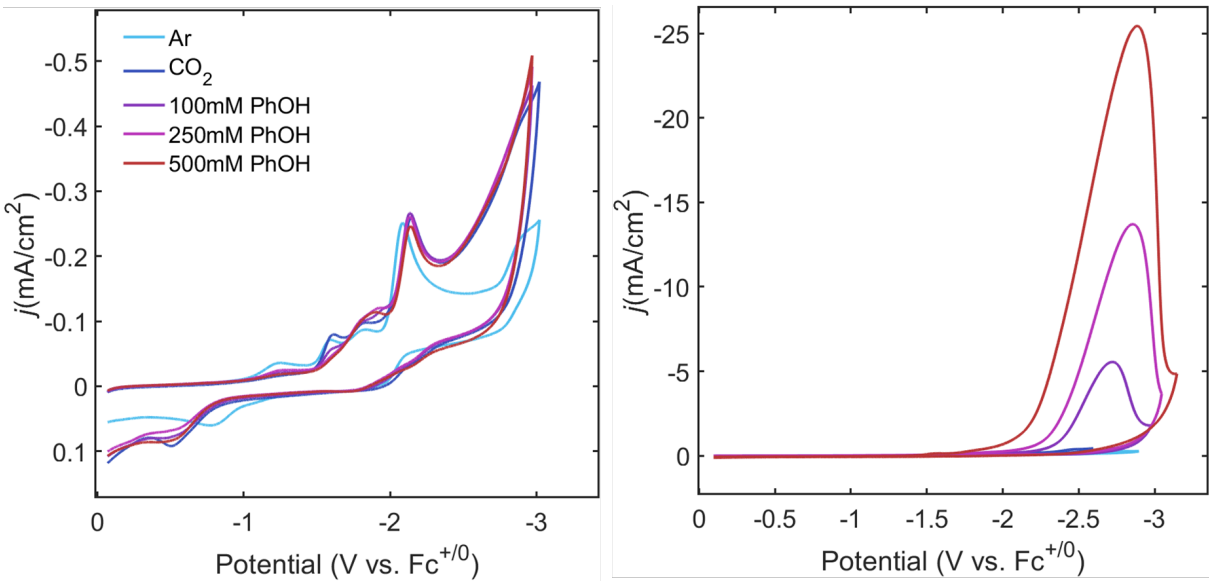

Figure S8. $BrRe(CO)_3QuBIm$ in DMF (left) and acetonitrile (right) with respect to the ferrocenium/ferrocene ($Fc^{+/0}$) couple.

DOSY NMR spectra

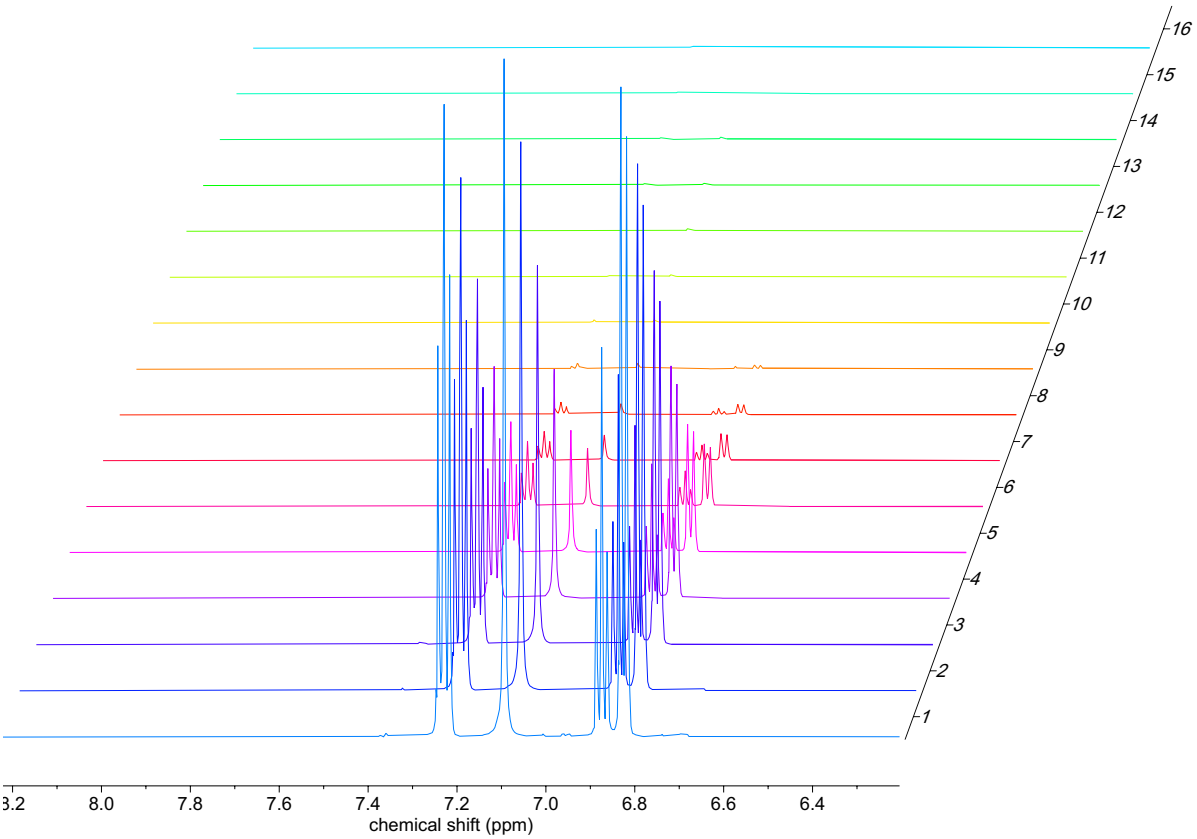

Figure S9. ^{1}H DOSY spectra of phenol in CD_3CN.

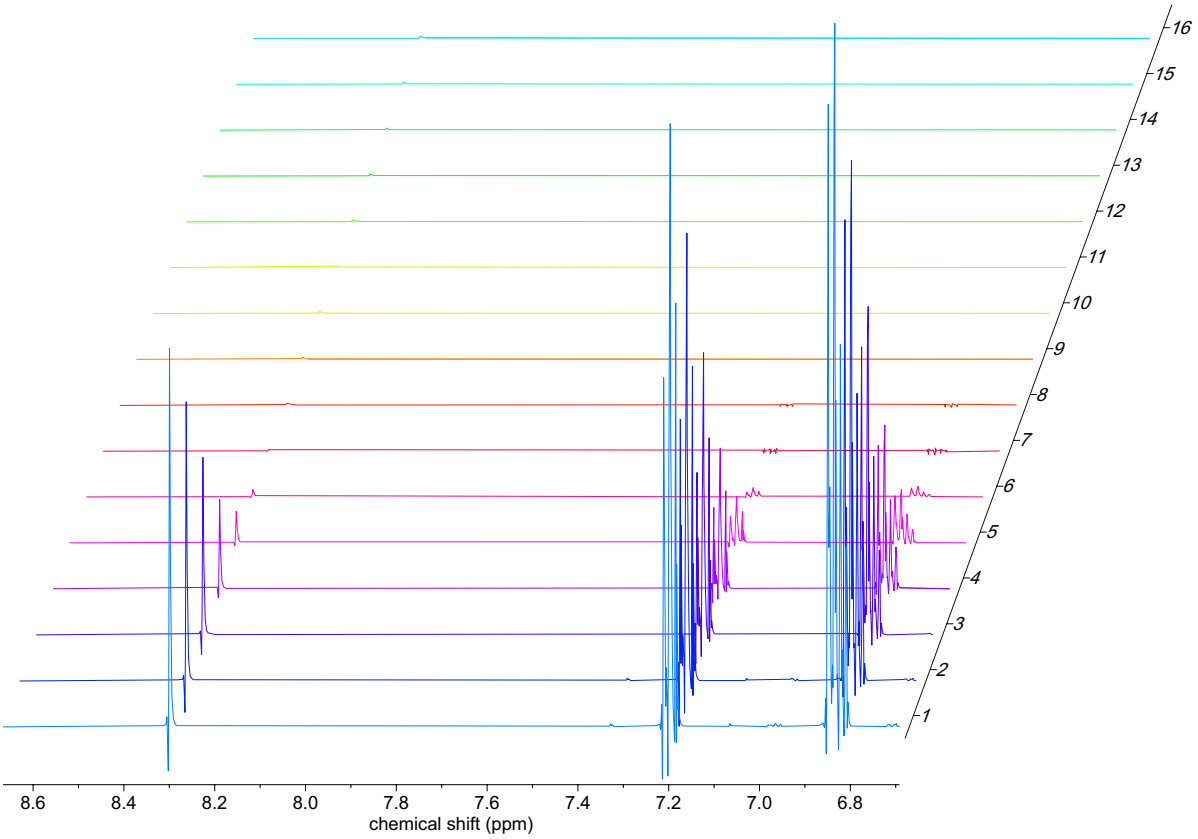

Figure S10. ^{1}H DOSY spectra of phenol in $(CD_3)_2CO$.

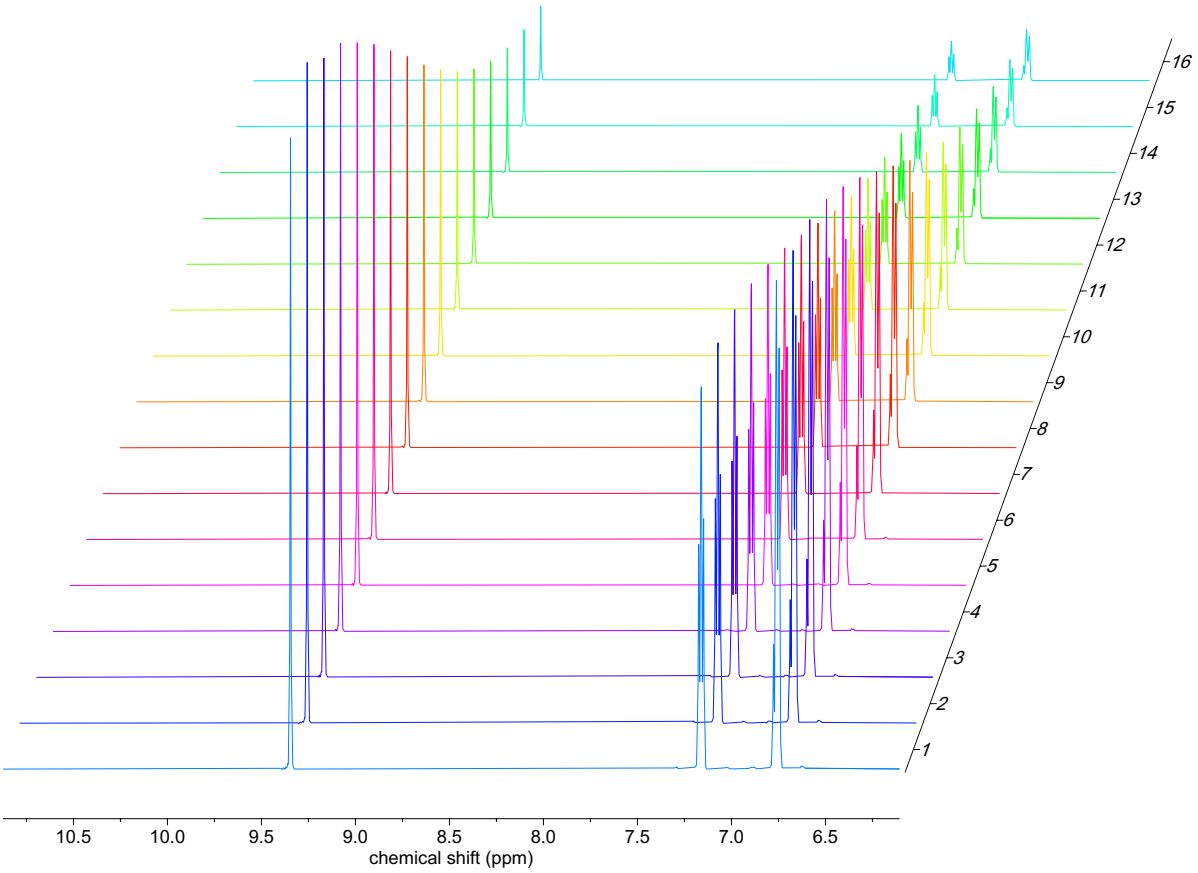

Figure S11. ^{1}H DOSY spectra of phenol in $(CD_3)_2SO$.

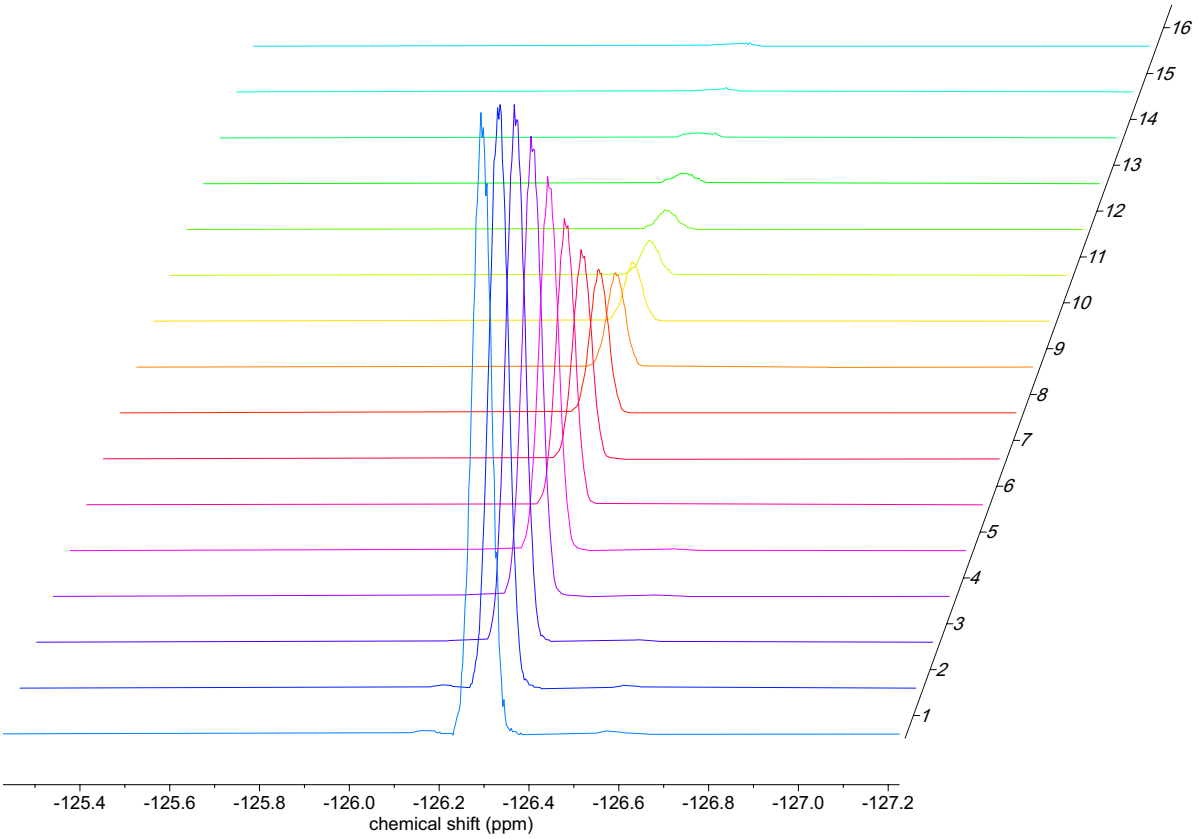

Figure S12. ^{19}F DOSY spectra of 4-fluorophenol in CH_3CN.

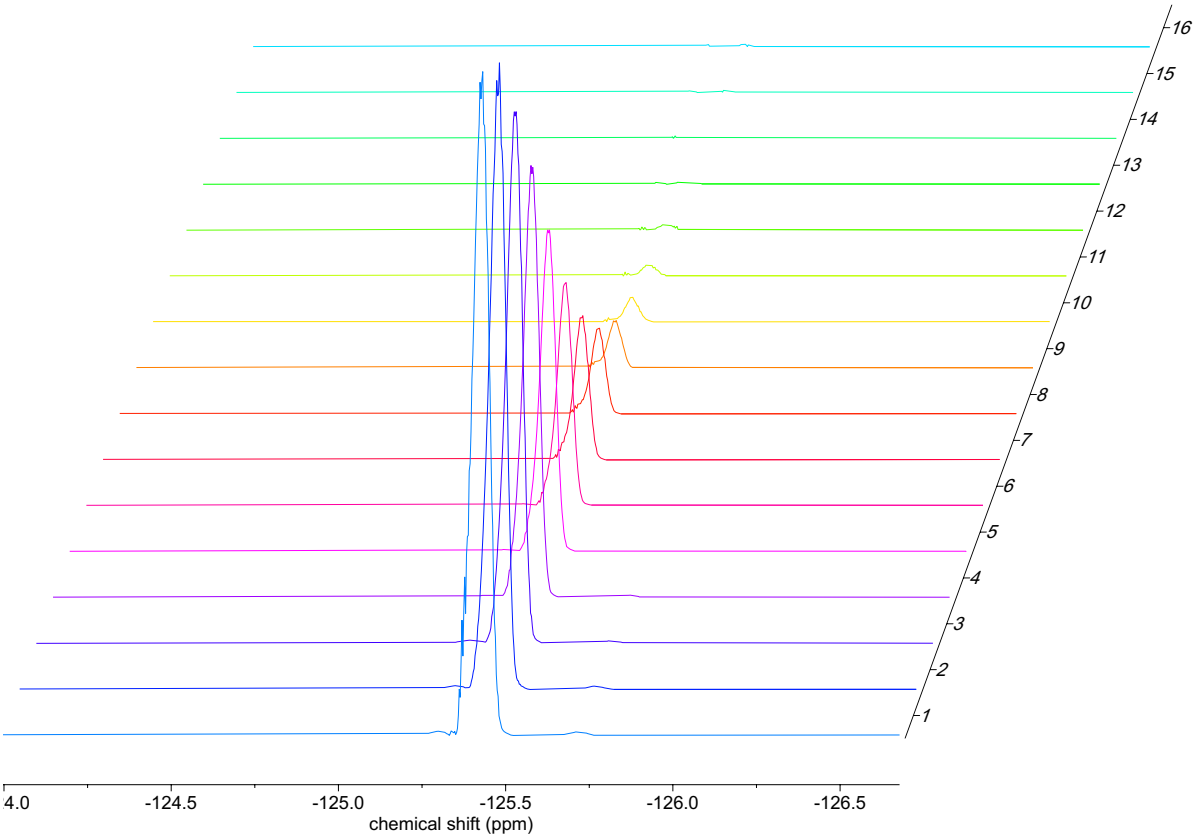

Figure S13. ^{19}F DOSY spectra of 4-fluorophenol in CH_3CN.