

Supplementary Information

Understanding the Effect of Specific Adsorption on Vibrational Stark Effect of Adsorbates on Electrode Surface via Surface Enhanced Spectroscopies

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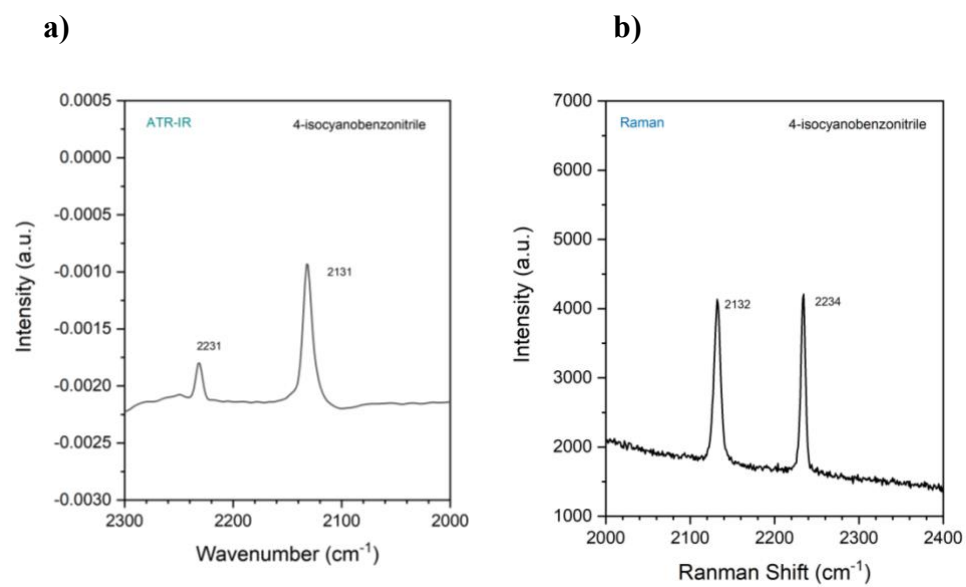


Fig. S1 IR and Raman spectra of bulk 4-isocyanobenzonitrile.

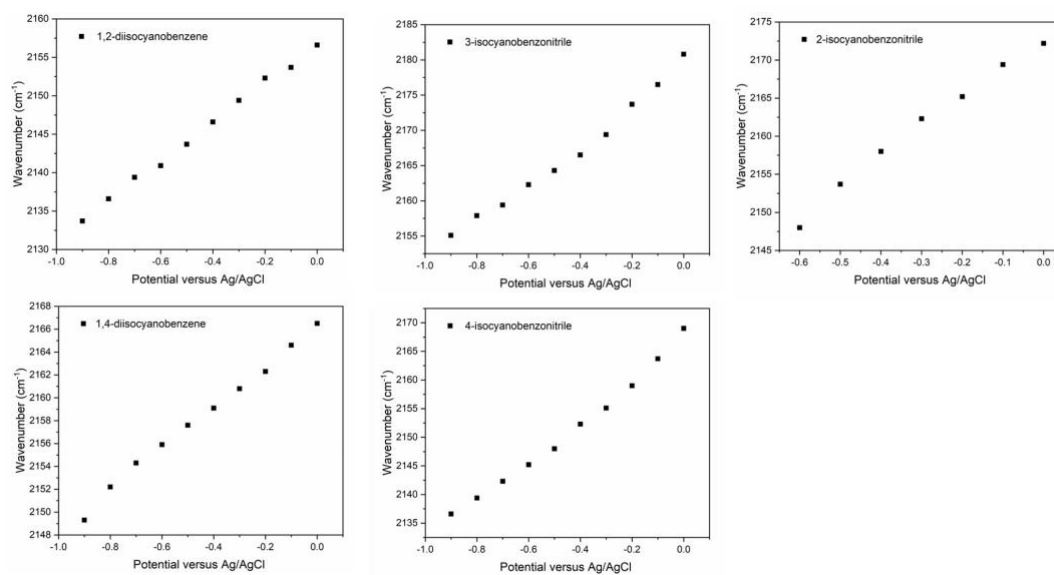


Fig. S2 Potential-dependent wavenumbers of molecules adsorbed on an Au electrode in 0.1 M NaClO₄.

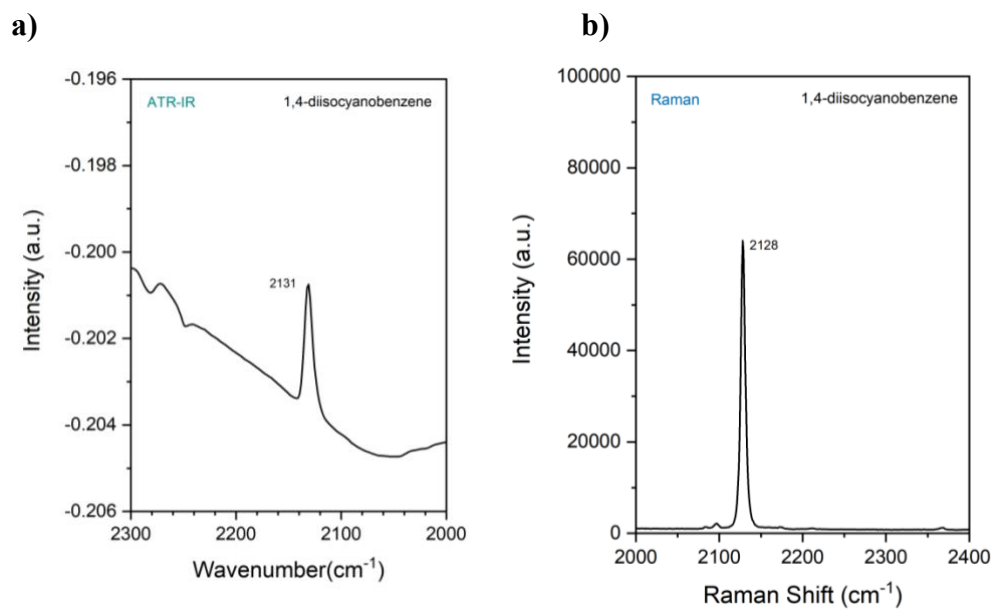


Fig. S3 IR and Raman spectra of bulk 1,4-diisocyanobenzene.

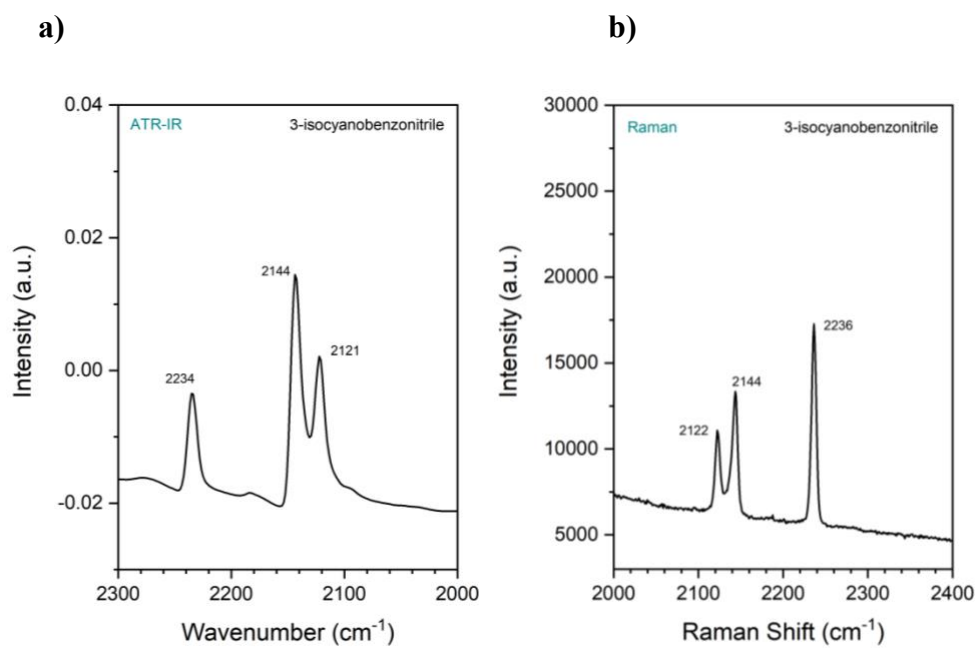


Fig. S4 IR and Raman spectra of bulk 3-isocyanobenzonitrile.

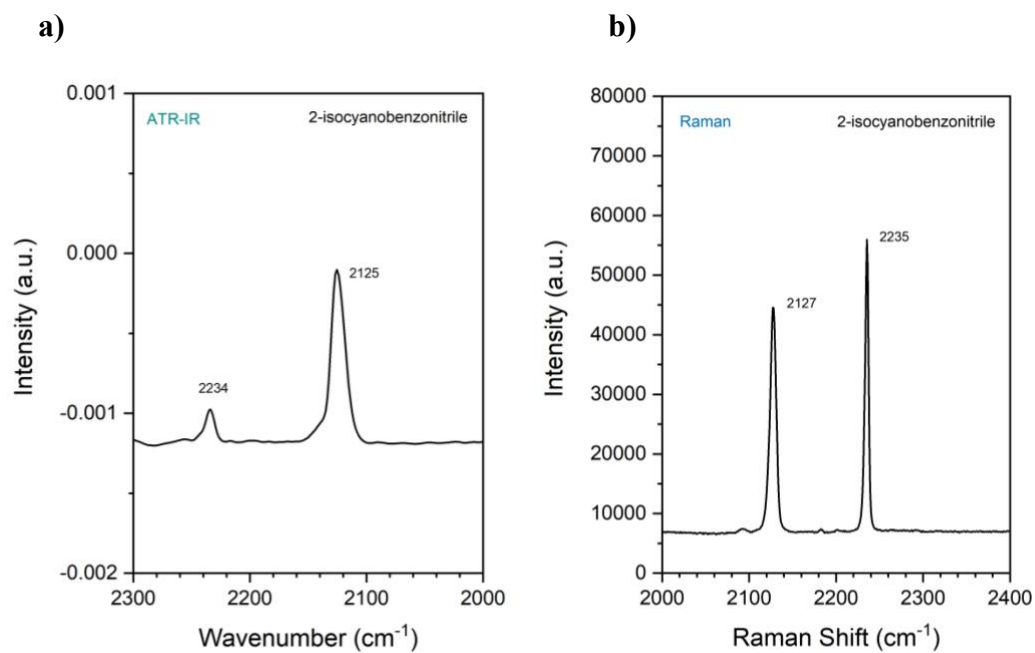


Fig. S5 IR and Raman spectra of bulk 2-isocyanobenzonitrile.

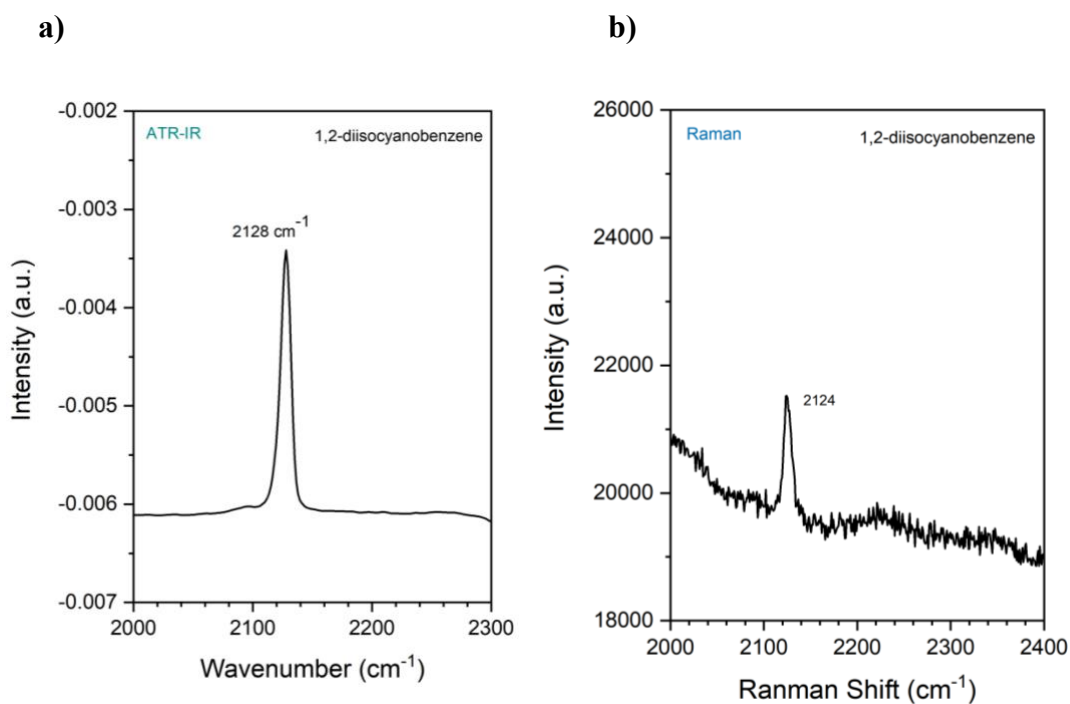


Fig. S6 IR and Raman spectra of bulk 1,2-diisocyanobenzene.

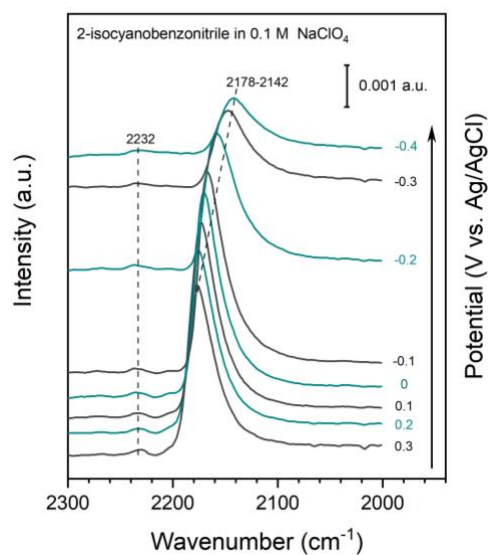


Fig. S7 Potential-dependent ATR-SEIRA spectra of 2-isocyanobenzonitrile adsorbed on Au film electrode in 0.1 M NaClO₄.

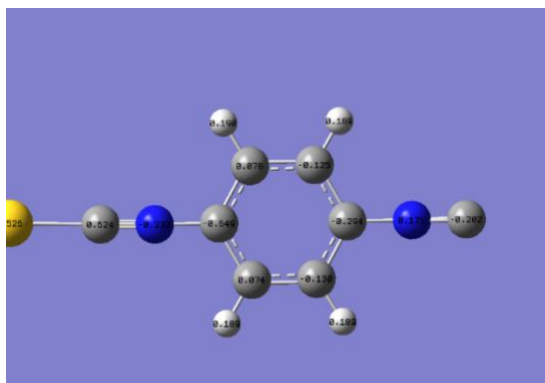
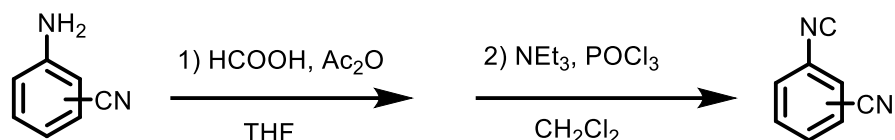
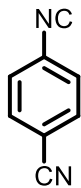


Fig. S8 DFT-calculated Mulliken charge of adsorbed 1,4-diisocyanobenzene on Au.

General Synthesis Procedure for isocyanobenzonitrile



First, an acetic anhydride (1.2 mL) and formic acid (0.6 mL) mixture was heated to 55 °C for 2 h to yield acetic formic anhydride. Aminobenzonitrile (5 mmol) and THF (15 mL) were added to an oven-dried flask, and then cooled to 0 °C. The obtained acetic formic anhydride was dropped slowly to the solution at 0 °C, and then the mixture was warmed to room temperature and stirred for 2 h. Then, the reaction solution was quenched by a Na₂CO₃ solution and extracted with ethyl acetate (EA) three times. The combined organic layer was dried over Na₂SO₄ salt powder and evaporated under vacuum to yield formamide. NEt₃ (5 mL, 30 mmol) and the obtained formamide were added to an oven-dried flask with 20 mL of CH₂Cl₂ under the Ar atmosphere and cooled to 0 °C. POCl₃ (0.6 mL, 6 mmol) was added dropwise and the reaction solution was stirred for 2 h at 0 °C. Then, the mixture was quenched by a Na₂CO₃ solution and stirred for 20 min. The mixture was extracted with CH₂Cl₂ three times, dried over Na₂SO₄ salt powder and evaporated under vacuum to obtain the crude product. The crude product was purified by column chromatography on silica gel to yield the desired isocyanobenzonitrile used in spectroscopic experiments.



^1H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, $J = 8.3$ Hz, 2H), 7.50 (d, $J = 8.3$ Hz, 2H).

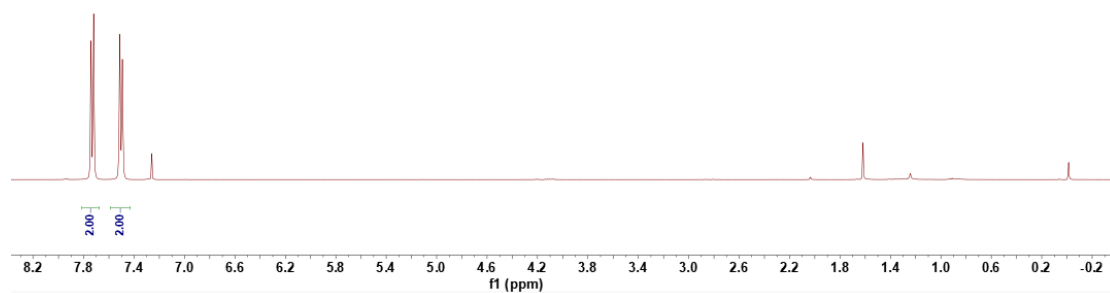
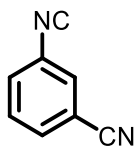


Fig. S8 ^1H -NMR spectrum of 4-isocyanobenzonitrile.



^1H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.55 (m, 4H).

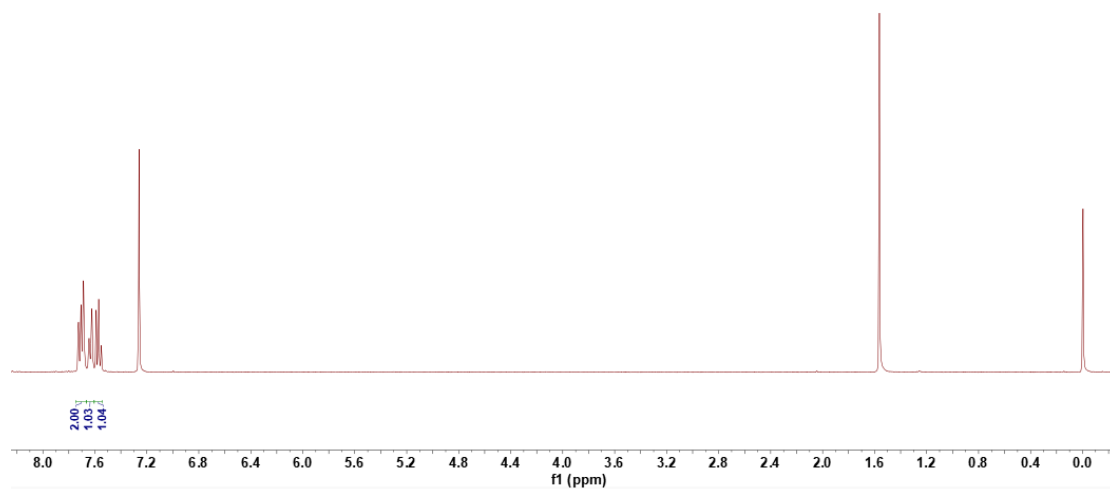
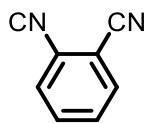


Fig. S9 ^1H -NMR spectrum of 3-isocyanobenzonitrile.



^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.68 (m, 2H), 7.58 – 7.54 (m, 2H).

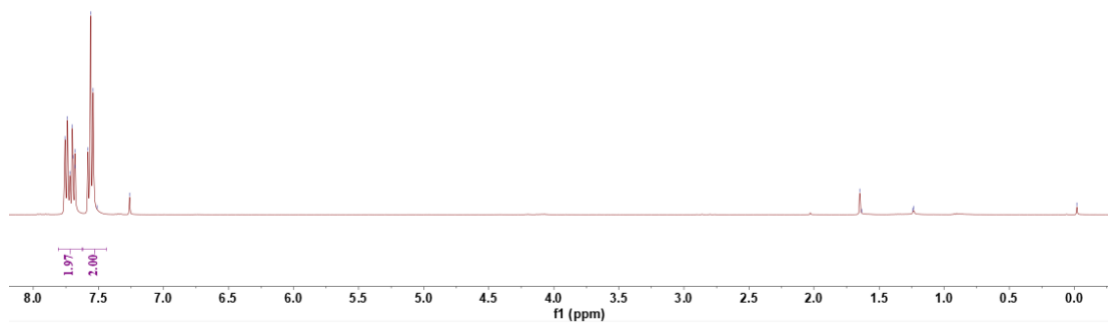
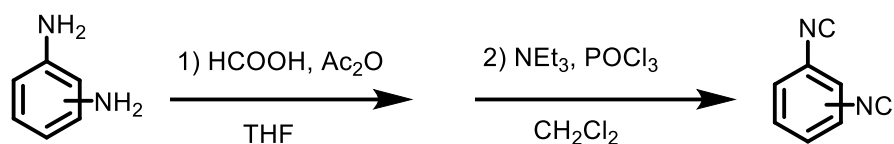
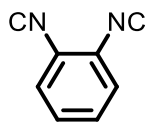


Fig. S10 ^1H -NMR spectrum of 2-isocyanobenzonitrile.

General Procedure for preparation of diisocyanobenzene



A mixture of formic acid (1.5 mL) and acetic anhydride (3.2 mL) was heated to 55 °C for 2 h and then cooled to 0 °C. A solution of diaminobenzene (6 mmol) in THF (10 mL) was added dropwise to the above solution at 0 °C, and then the mixture was warmed to room temperature and stirred for 2 h. Then, the reaction solution was quenched by a Na_2CO_3 solution and extracted with EA three times. The combined organic layer was dried over Na_2SO_4 salt powder and evaporated under vacuum to give formamide. To an oven-dried flask CH_2Cl_2 (25 mL), NEt_3 (72 mmol) and the obtained formamide were added under the Ar atmosphere and cooled to 0 °C. POCl_3 (14.4 mmol) was added dropwise, and the reaction solution was stirred for 2 h at 0 °C. Then, the mixture was quenched by a Na_2CO_3 solution and stirred for 20 min. The mixture was extracted with CH_2Cl_2 three times, dried over Na_2SO_4 salt powder and evaporated under vacuum to afford crude product. The crude product was purified by column chromatography on silica gel to afford the desired diisocyanobenzene used in spectroscopic experiments.



^1H NMR (400 MHz, Chloroform-*d*) δ 7.53-7.43 (m, 4H)

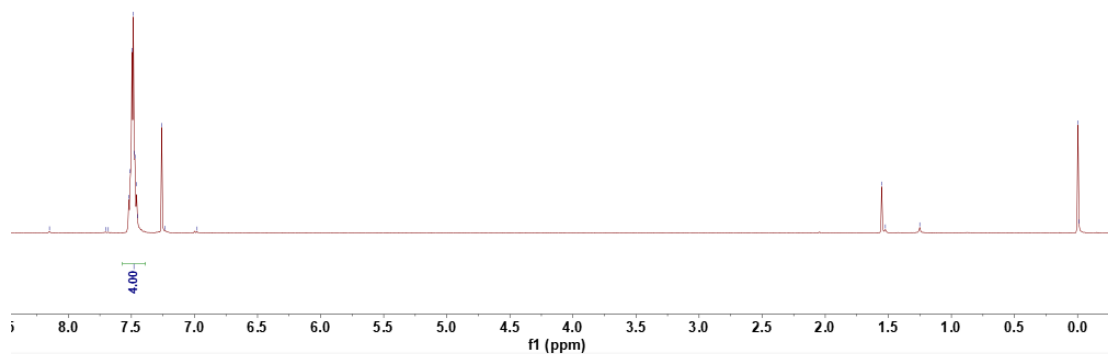
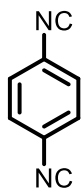


Fig. S11 ^1H -NMR spectrum of 1,2-dicyanobenzene



^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 (s, 4H).

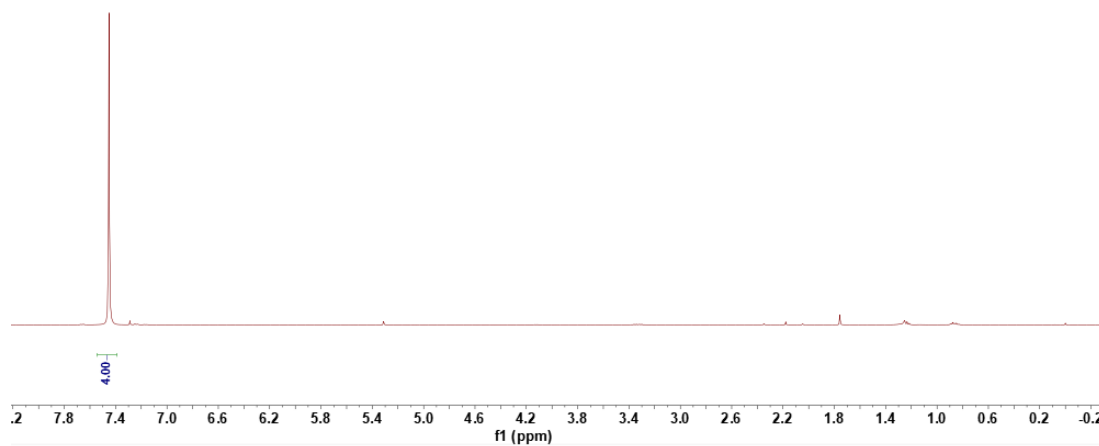


Fig. S12 ^1H -NMR spectrum of 1,4-dicyanobenzene