

Supplementary Materials: Cathodic Aromatic C,C Cross-Coupling Reaction via Single Electron Transfer Pathway

1. Linear Sweep Voltammograms for Reduction of Arylhalides and Arenes.

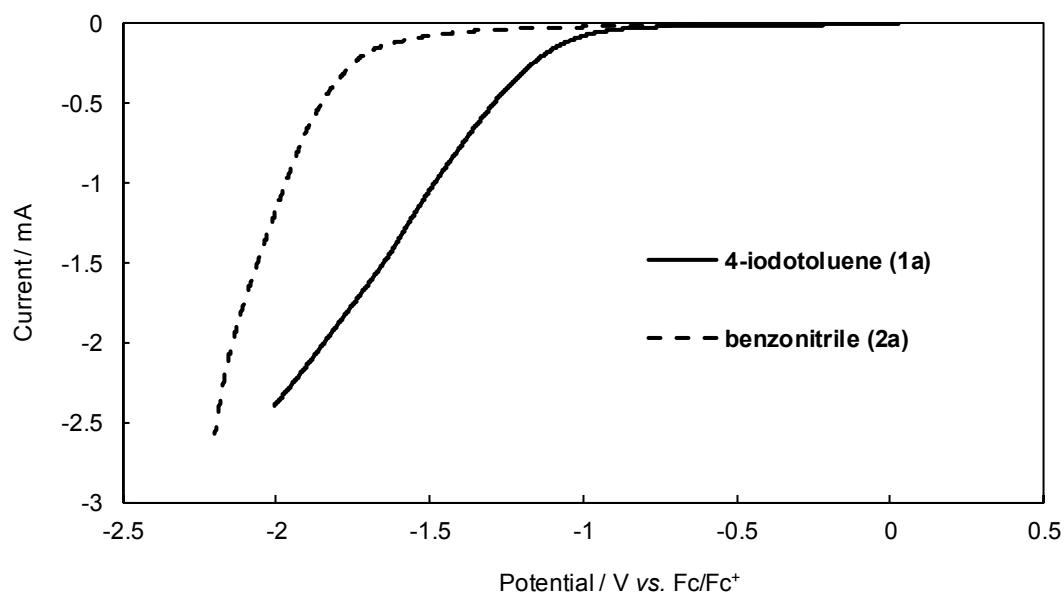


Figure S1. Linear sweep voltammograms of benzonitrile and 4-iodotoluene in DMF (10 mL) at 25°C at the scan rate 0.1 V s⁻¹ on Pt electrode.

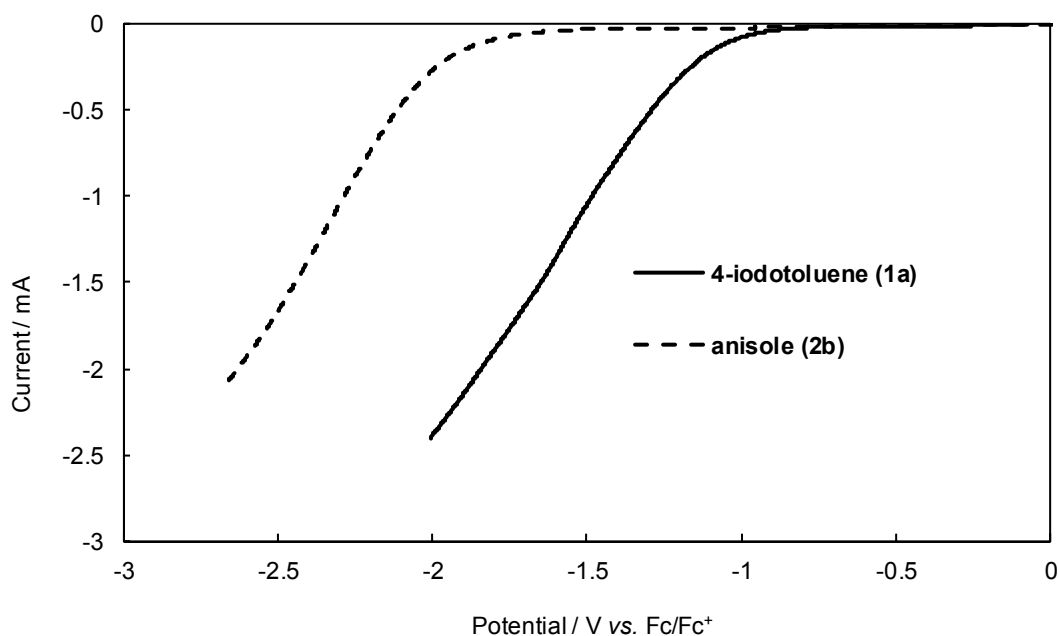


Figure S2. Linear sweep voltammograms of anisole and 4-iodotoluene in DMF (10 mL) at 25°C at the scan rate 0.1 V s⁻¹ on Pt working electrode.

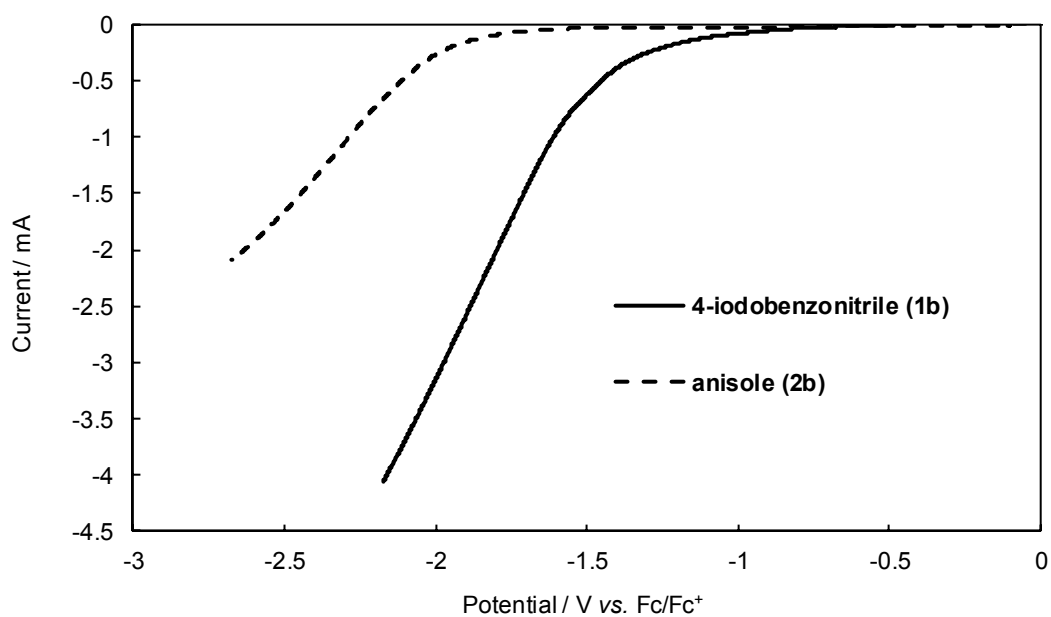


Figure S3. Linear sweep voltammograms of anisole and 4-iodobenzonitrile in DMF (10 mL) at 25°C at the scan rate 0.1 V s⁻¹ on Pt working electrode.

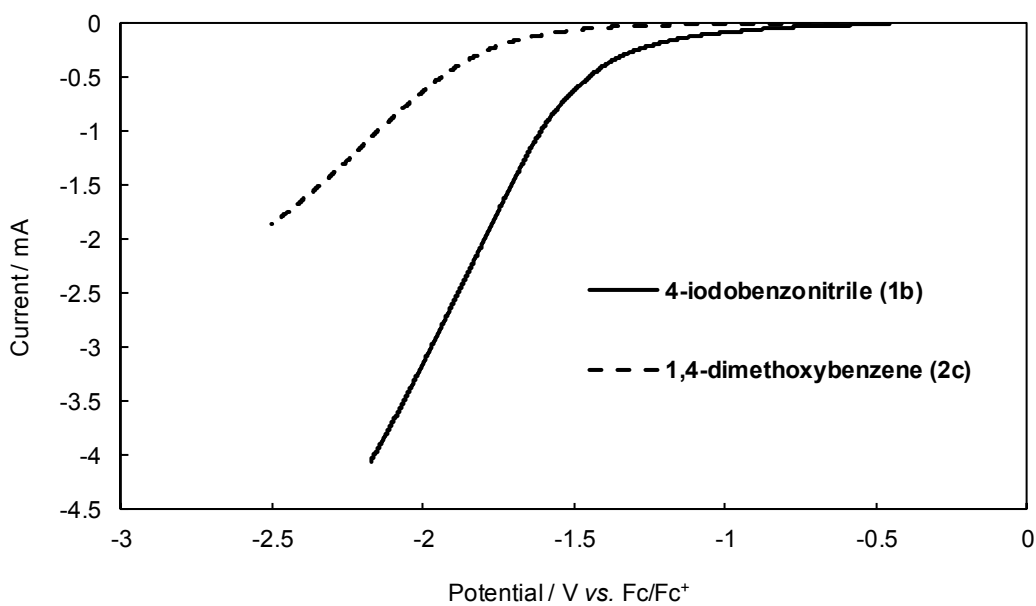


Figure S4. Linear sweep voltammograms of 1,4-dimethoxybenzene and 4-iodobenzonitrile in DMF (10 mL) at 25°C at the scan rate 0.1 V s⁻¹ on Pt working electrode.

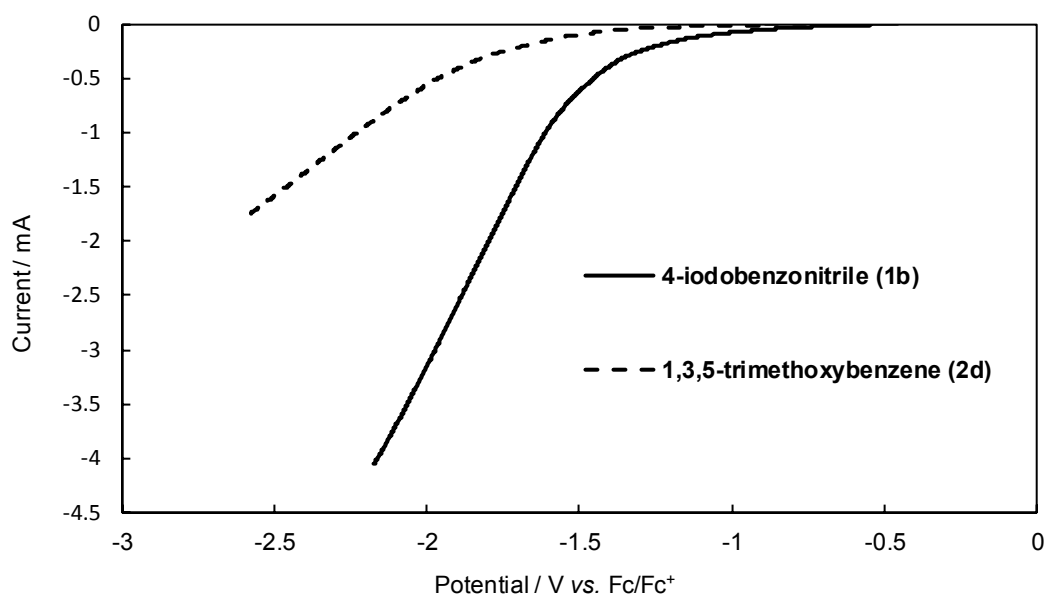


Figure S5. Linear sweep voltammograms of 1,3,5-trimethoxybenzene and 4-iodobenzonitrile in DMF (10 mL) at 25°C at the scan rate 0.1 V s⁻¹ on Pt working electrode.

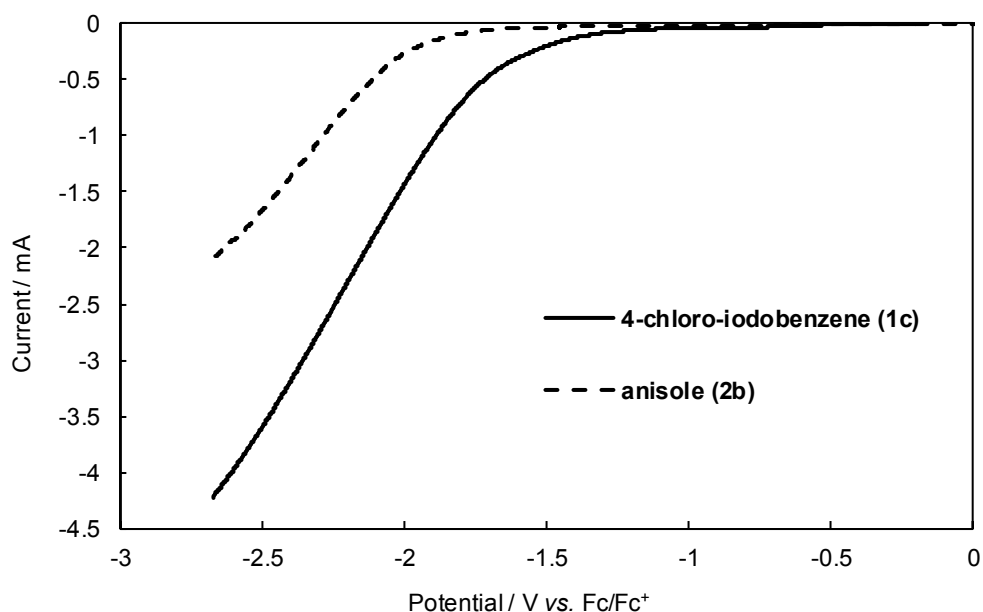


Figure S6. Linear sweep voltammograms of anisole and 4-chloro-iodobenzene in DMF (10 mL) at 25°C at the scan rate 0.1 V s⁻¹ on Pt working electrode.

2. Determination of ¹H NMR Yields of 3b, 3c, 3d, and 3e

After the electrolysis, crude products were subjected to short silica gel column chromatography (solvent: chloroform) in order to remove supporting electrolytes. Then, the formation of cross coupling products were confirmed by capillary GC-MS analysis. The base peaks of **3b**, **3c**, **3d**, **3e**, and **3f** were observed at 198.05, 209.05, 239.05, 269.10, and 218.90, respectively. Nitromethane (0.75 μL, 0.014 mmol) as an internal standard was added to 0.2 mL of evaporated residues. The NMR yields of **3b**, **3c**, **3d**, and **3e** were determined by following equation (3).

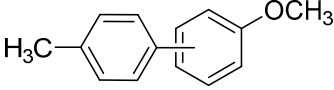
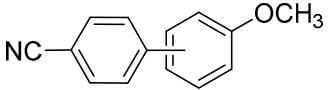
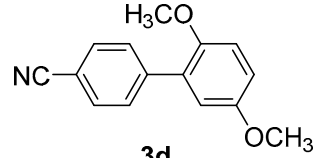
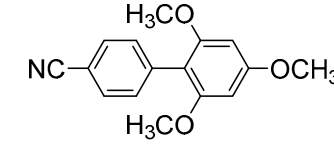
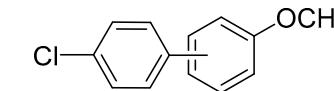
$$I_1 / N_1 = I_2 / N_2 \quad \text{---(1)}$$

$$N_2 / 0.2 = N_3 / V \quad \text{---(2)}$$

$$\text{Yield (\%)} = N_3 / N_{\text{arylhalide}} \cdot 100\% \quad \text{---(3)}$$

where I_1 and I_2 are NMR integral values of nitromethane and product peaks, respectively; N_1 , N_2 , and N_3 are mole quantities of nitromethane in NMR sample, product in 0.2 mL of evaporated residue, and product in total evaporated residue, respectively; V are volume of total evaporation residue. Details are shown in Table S1.

Table S1. Detail values for ^1H NMR yields determination

| Cross-coupling product | I_1 | I_2 | V / mL | Yield (%) |
|--|-------|--------------------------------|-----------------|---------------------------------|
|  3b | 10 | o : m : p = 4,26 : 0 : 5.87 | 6.0 | 47 (o : m : p = 42 : 0 : 58) |
|  3c | 10 | o : m : p = 0 : 0 : 13.36 | 5.0 | 52 (o : m : p = 0 : 0 : 100) |
|  3d | 10 | 8.94 | 6.0 | 42 |
|  3e | 10 | 6.82 | 4.0 | 11 |
|  3f | 10 | o : m : p = 0 : 2.54 : 7.99 | 6.0 | 49 (o : m : p = 0 : 24 : 76) |

3. Schematic illustration of H-type divided cell.

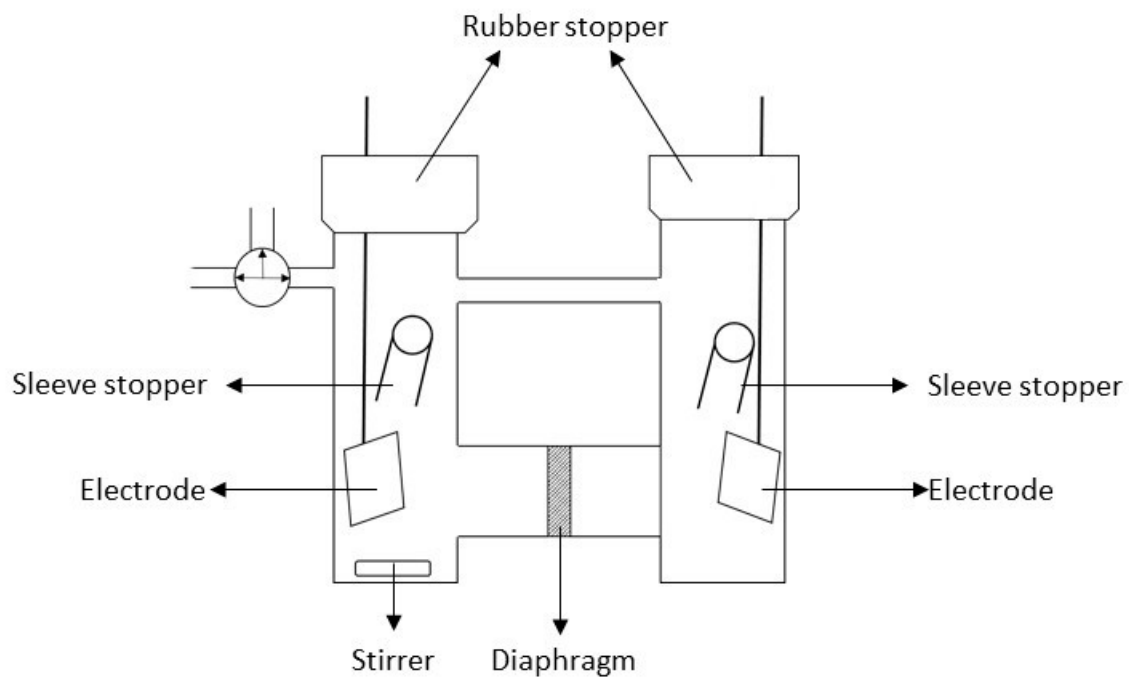
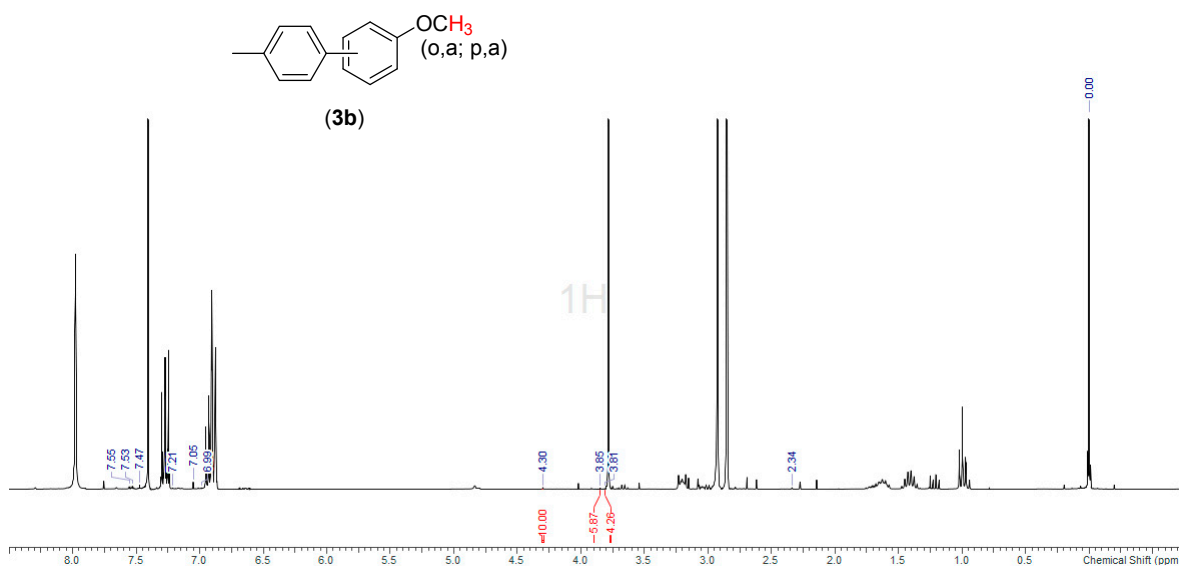


Figure S7. Schematic illustration of H-type divided cell.

4. ^1H NMR Spectra

The yields of **3b**, **3c**, **3d**, **3e**, and **3f** were calculated by ^1H NMR measurements of these reaction mixtures with nitromethane (at 4.30 ppm) as an internal standard. Characteristic peaks of purpose products were determined by referring to the previous synthetic reports [1-8].



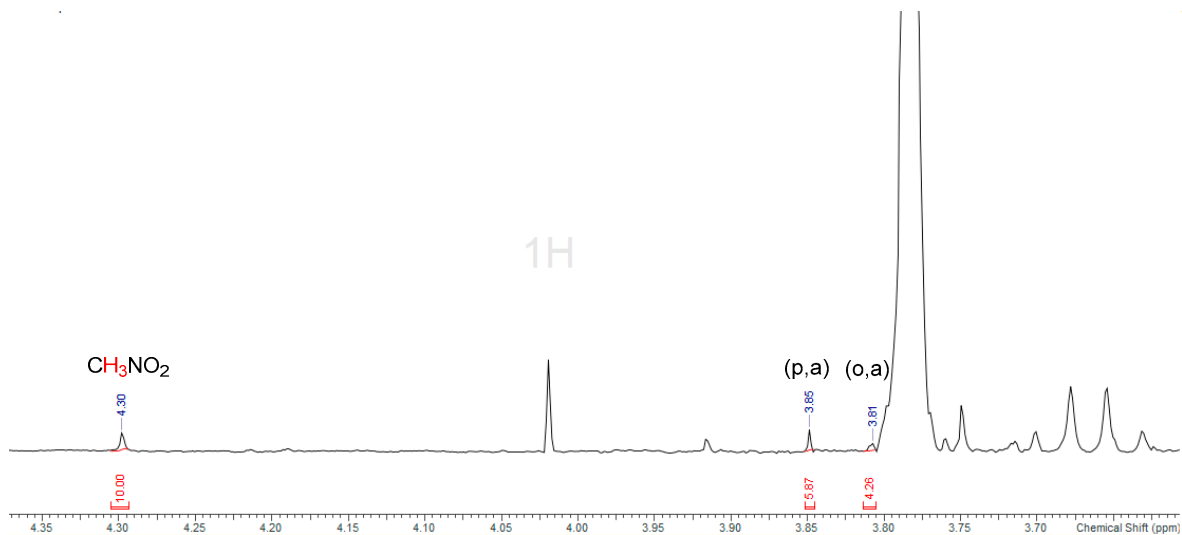


Figure S8. ^1H NMR spectrum of reaction mixture of Entry 2 in Table 3 (synthesis of **3b**).

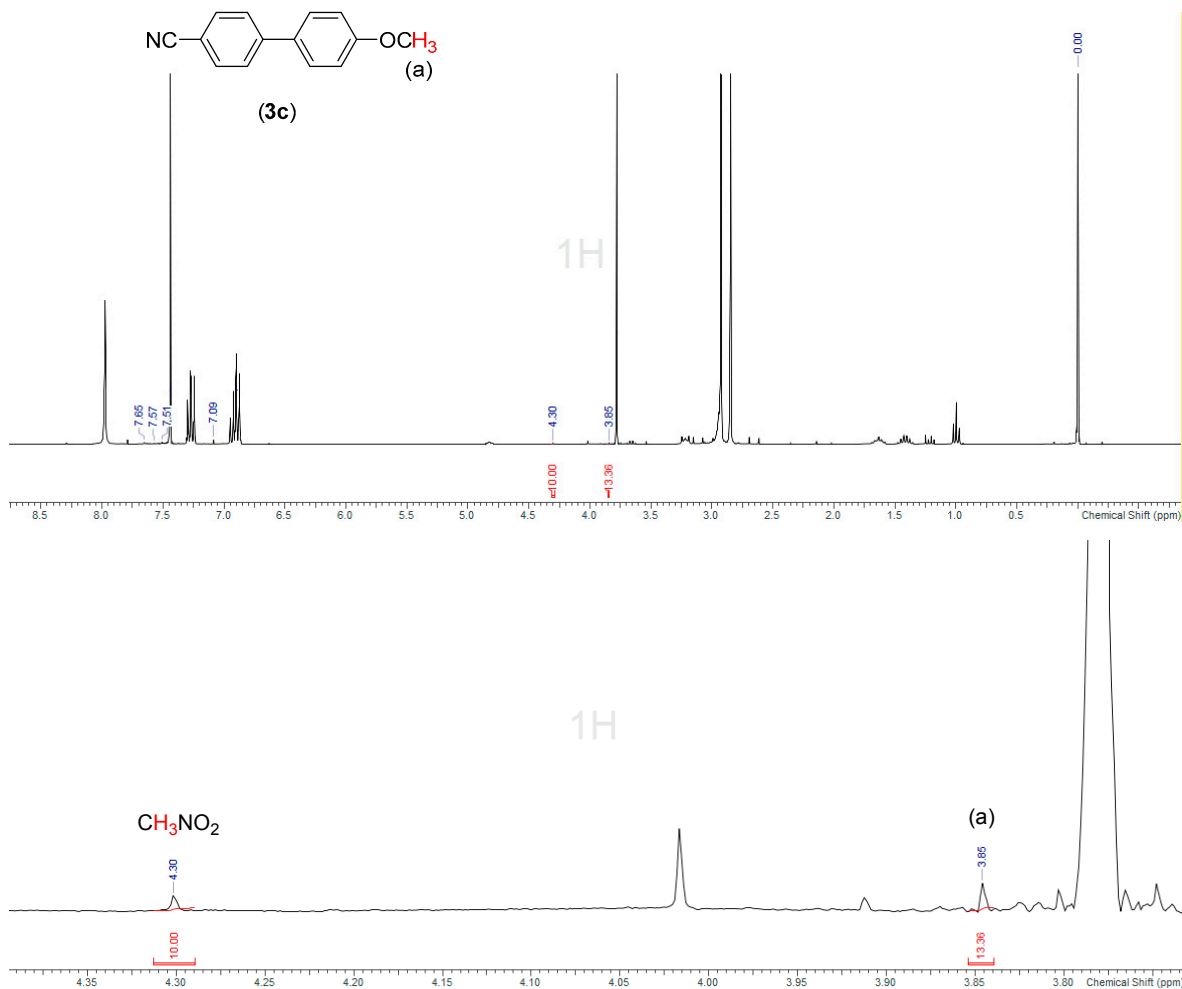


Figure S9. ^1H NMR spectrum of reaction mixture of Entry 3 in Table 3 (synthesis of **3c**).

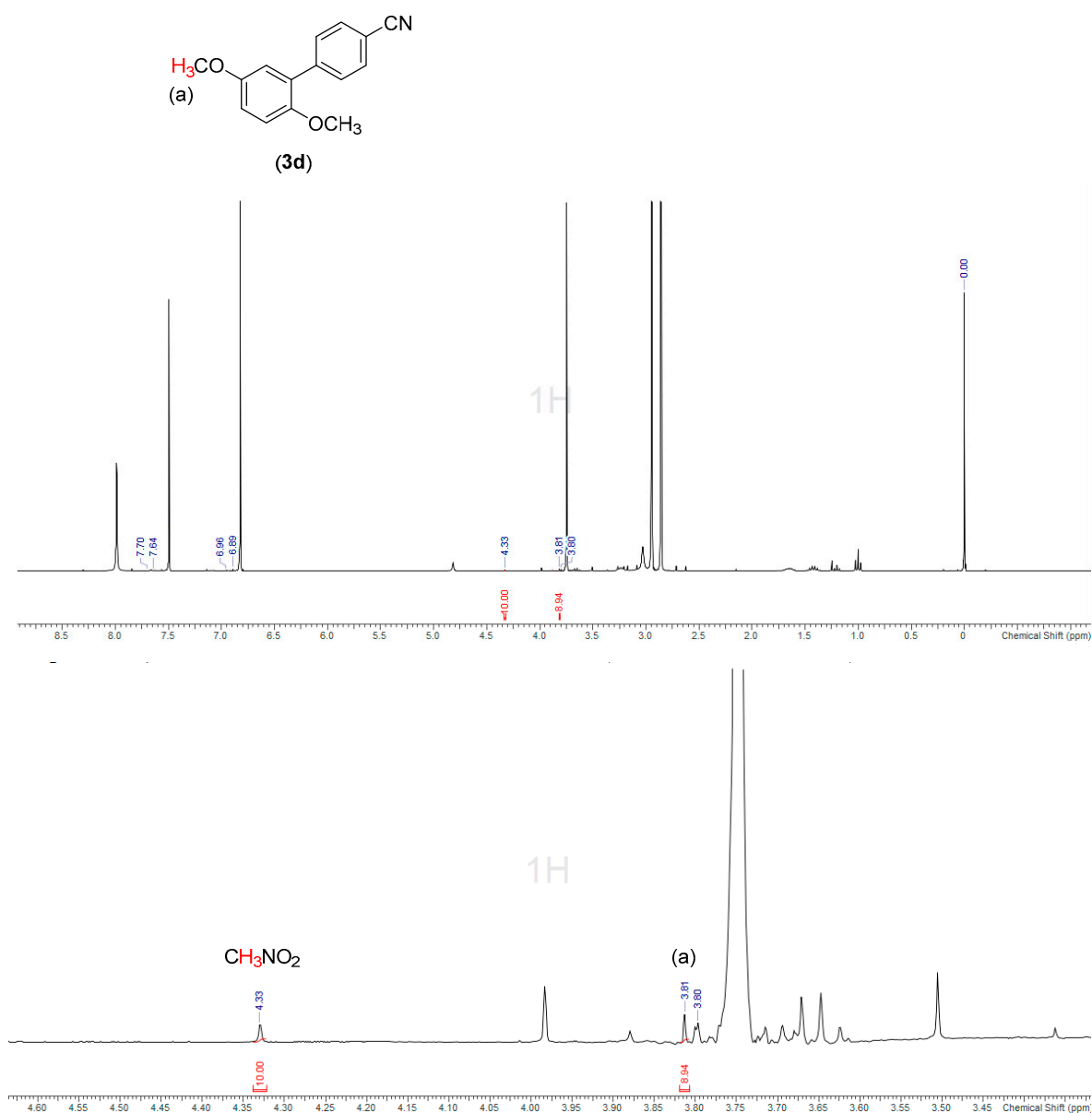


Figure S10. ^1H NMR spectrum of reaction mixture of Entry 4 in Table 3 (synthesis of **3d**).

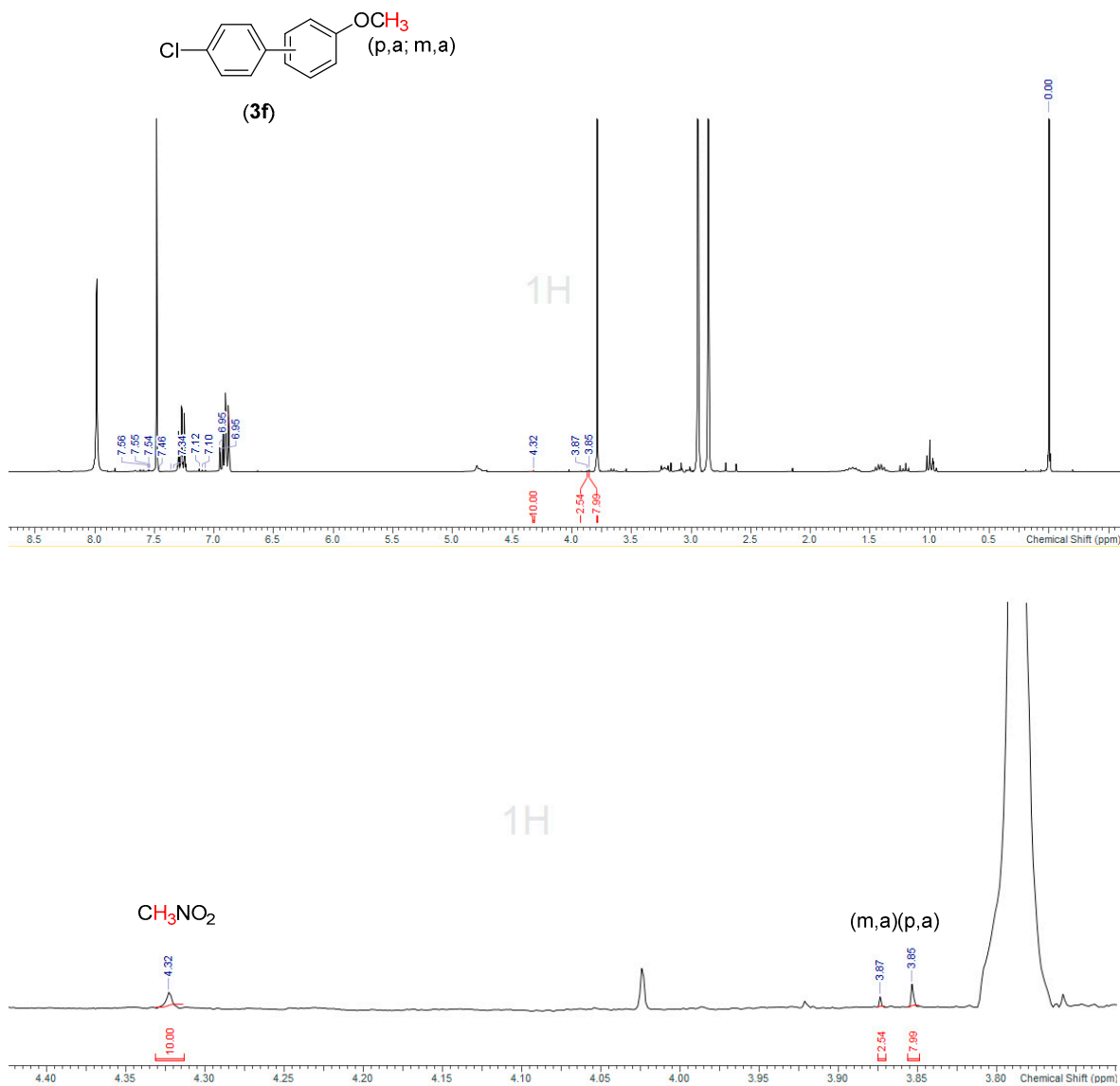


Figure S12. ^1H NMR spectrum of reaction mixture of Entry 6 in Table 3 (synthesis of **3f**).

References

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