SUPPORTING INFORMATION

Hydride, Hydrogen Atom, Proton and Electron Transfer Driving Forces of Various Five-membered Heterocyclic Organic Hydrides and Their Reaction Intermediates in Acetonitrile

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CONTENTS

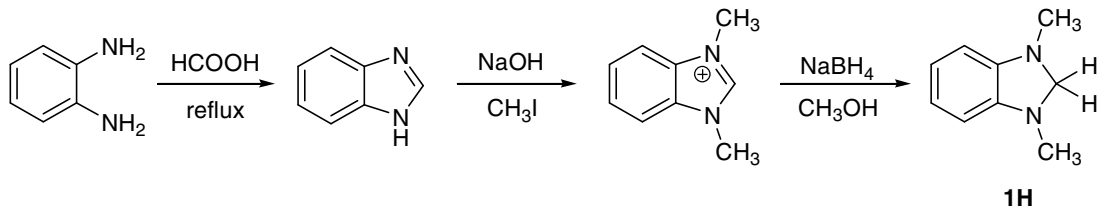
SI–1. General Methods

Solvents and reagents were obtained from commercial sources and used as received. ^{1}H NMR spectra were recorded in $CDCl_3$ and d_6-DMSO on 400 MHz or 300MHz NMR spectrometer. The chemical shifts (δ) were described in parts per million (ppm) downfield from tetramethylsilane (TMS, 0.00 ppm) as an internal standard.

All reagents of commercial quality were from freshly opened containers or were purified according to the standard methods before use. Reagent grade acetonitrile was refluxed over $KMnO_4$ and K_2CO_3 for several hours and was distilled over P_2O_5 under argon twice before use. The commercial tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, Aldrich) was recrystallized from CH_2Cl_2/Et_2O and dried in vacuo at 110 ^oC overnight before preparation of a supporting electrolyte solution.

Acetonitrile containing 0.1 M tetra-n-butylammonium hexafluorophosphate ($TBAPF_6$) was used as solvent in electrochemical measurements. Ferrocene/ferrocenium redox couple (Fc/Fc^+) was used as an internal reference for all measurements. All electrochemical measurements were performed under dry nitrogen atmosphere using 0.1 V/s scan rate, unless otherwise specified, the concentration of samples was 10^{-3} M.

SI-2. Synthetic Route of 1H [S1]

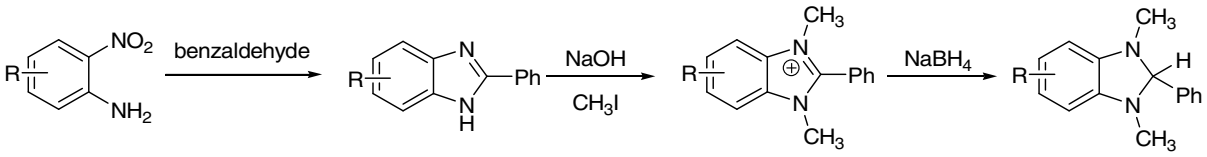


1H

2.7 g (0.025 mol) of *p*-phenylenediamine was placed in a 50 mL round bottomed flask and 90% of formic acid (1.6 mL, 0.034 mol) was added. The mixture was heated at 100oC in oil

bath for 2 h. After cooled to room temperature, 10% sodium hydroxide aqueous solution was slowly added till the mixture can make litmus appear just alkaline. The crude benzimidazole was filtrated and washed with ice-cold water, drained well and washed again with 10 mL cold water. Dissolved the crude product in 50mL boiling water, 0.2 g active carbon was added and boiled for 15 min. The mixture was filtered rapidly through a preheated buchner funnel and flask. After the filtration was cooled to about 10°C, the benzimidazole was separated and washed with 10 mL cooled water. The obtained white solid was dried at 100 °C and then treated with methyl iodide in 10 mL methanol containing 0.1 g NaOH. The mixture was refluxed for 10 h, and then the solvent was removed under reduced pressure. The crude product was recrystallized with absolute ethanol to give pure product $\mathbf{1^+I^-}$. To the solution of $\mathbf{1^+I^-}$ in 10mL methanol was slowly added appropriate amount of $NaBH_4$. The mixture was stirred for 30 min under N_2 atmosphere then compound **1H** was obtained by silica-gel chromatography (yield, 65%). ^{1}H NMR ($CDCl_3$, 400 M): δ6.69 (dd, 2H), 6.43 (dd, 2H), 4.33 (s, 2H), 2.74 (s, 6H); ESI-MS/M^+ = 148.16; Anal. Calcd for $C_9H_{12}N_2$ (148.2): C, 72.94; H, 8.16; N, 18.9. Found: C, 72.99; H, 8.14; N, 18.85.

SI-3. Synthetic Route of 2H [S2]



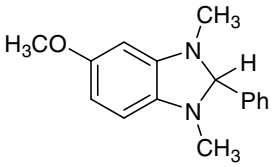
M **2⁺** **2H**

Preparation of 7 or 8 substituted-2-phenyl benzoimdazole (M). A solution of substituted o-nitroaniline (2.0 mmol) and benzaldehyde (2.0 mmol) in ethanol (10 mL) was treated with 1M $Na_2S_2O_4$ (3.0 mmol, 6mL). The reaction mixture was heated for 5-7 h, cooled to room temperature and then treated dropwise with 5N aq NH_4OH (4 mL), and precipitation was immediately formed which was then filtered, washed with water and dried under reduced pressure to afford the desired product in satisfactory purity.

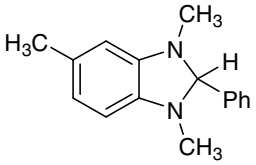
Preparation of N, N'-dimethyl-7 or 8 substituted-2-phenyl benzo[d]imidazolium iodide

(2^+I^-). To the methanol solution of substituted-2-phenyl-benzoimdazole (**M**), methyl iodide and appropriate amount of NaOH in 10 mL methanol was added, the mixture was heated at 120 ^oC for 12 h in a sealed tube to give a faint yellow solid. The crude product was washed with a small amount of acetone and recrystallized from absolute ethanol to give yellow crystalline solid. The yield is over 80%.

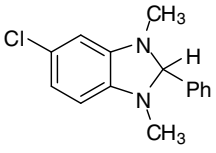
Preparation of 2H. A solution (20 mL) of compound **3** (1eq.) in methanol (25 mL) was reduced by $NaBH_4$ (1.5eq.) to give a white solid. The white solid was recrystallized from ethanol-H_2O (2:1, v/v) to give a colorless crystalline product. The yield is over 65%.



^1H NMR ($CDCl_3$, 400 M): δ7.56 (d, 2H), 7.41 (m, 3H), 6.33 (d, 1H), 6.21 (d, 1H), 6.12 (s, 1H), 4.77 (s, 1H), 3.76(s, 3H), 2.53 (s, 6H); ESI-MS/M^+ = 254.15; Anal. Calcd for $C_{16}H_{18}N_2O$ (254.3): C, 75.56; H, 7.13; N, 11.01; Found: C, 75.52; H, 7.14; N, 11.05.

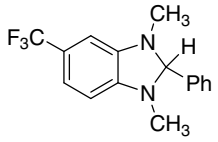


^1H NMR ($CDCl_3$, 400 M): δ 7.56 (d, 2H), 7.41 (m, 3H), 6.33 (d, 1H), 6.21 (d, 1H), 6.12 (s, 1H), 4.77 (s, 1H), 3.76(s, 3H), 2.53 (s, 6H); ESI-MS/M^+ = 238.15; Anal. Calcd for $C_{16}H_{18}N_2$ (238.3): C, 80.63; H, 7.61; N, 11.75. Found: C, 80.62; H, 7.59; N, 11.73.

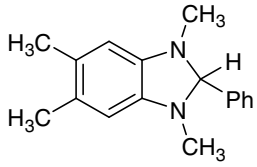


^1H NMR ($CDCl_3$, 400 M): δ 7.58 (m, 2H), 7.41 (m, 3H), 6.72 (dd, 2H), 6.43 (dd, 2H), 4.87 (s,

1H), 2.56 (s, 6H); ESI-MS/M^+ = 258.07; Anal. Calcd for $C_{15}H_{15}N_2Cl$ (258.8): C, 69.63; H, 5.84; N, 10.83. Found: C, 69.59; H, 5.86; N, 10.80.

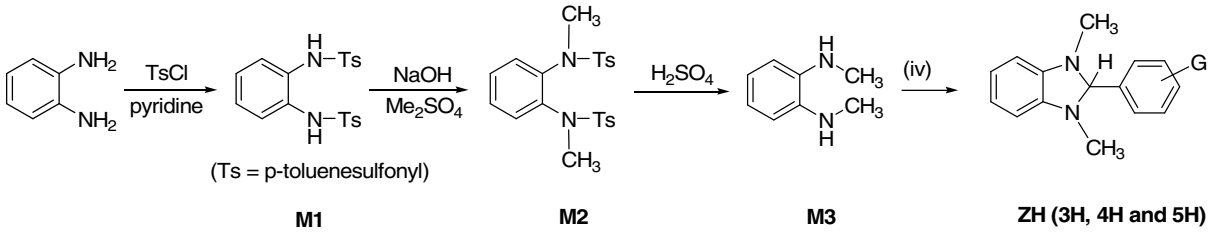


^{1}H NMR ($CDCl_3$, 400 M): δ 7.53 (m, 2H), 7.42 (m, 3H), 6.97 (d, 1H), 6.50 (s, 1H), 6.33 (d, 1H), 5.17 (s, 1H), 2.59 (s, 6H); ESI-MS/M^+ = 292.13; Anal. Calcd for $C_{16}H_{15}N_2F_3$ (292.3): C, 65.74; H, 5.17; N, 9.58; F, 19.50. Found: C, 65.76; H, 5.19; N, 9.54; F, 19.58.



^{1}H NMR ($CDCl_3$, 400 M): δ 7.56 (d, 2H), 7.40 (d, 2H), 6.29 (s, 2H), 4.66 (s, 1H), 2.52 (s, 6H), 2.18 (s, 6H); ESI-MS/M^+ = 252.16; Anal. Calcd for $C_{17}H_{20}N_2$ (252.4): C, 80.91; H, 7.99; N, 11.10. Found: C, 80.89; H, 7.97; N, 11.13.

SI-4. Synthetic Route of ZH (3H, 4H and 5H) [S3]



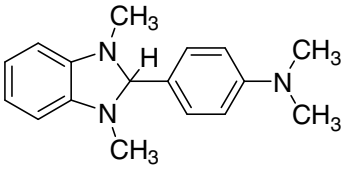
Preparation of *N, N'*-di (*p*-toluenesulufonyl)-*o*-phenylenediamine (M1). A solution of *o*-phenylenediamine (50 mmol) in dry pyridine (50 mL) was added to a solution of *p*-toluenesulfonyl chloride (100 mmol) in dry pyridine (40 mL). The resulted mixture was stirred at room temperature for 18 h. By slow addition of 15% aqueous HCl, a precipitate was

formed. The solid were dissolved in EtOH (140 mL) and refluxed for 4 h, and then stored in a refrigerator for crystallization. After filtration, *N,N'*-di(*p*-toluenesulufonyl)-*o*-phenylene-diamine (**M1**) was obtained as faint solid (36 mmol, 70%), mp. 201.5~203.0 ^{o}C.

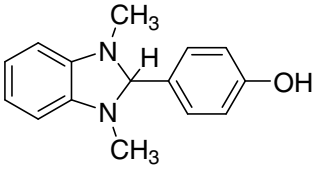
Preparation of *N,N'*-dimethyl-*N,N'*-di(*p*-toluenesulufonyl)-*o*-phenylenediamine (M2). *N,N'*-di(*p*-toluenesulufonyl)-*o*-phenylenediamine (20 g) was boiled in aqueous solution of sodium hydroxide (4N, 25 mL). Dimethyl sulfate (10mL) was added to the cooled suspension and the mixture was gently boiled for 5 min. After cooled to room temperature, the suspension was stirred well and 4N NaOH (25 mL) and dimethyl sulfate (10mL) were added again, and then the mixture was boiled for 5min. After two treatments, the educt was filtered from the hot mixture and boiled with 0.75N NaOH (400 mL), the insoluble part was crystallized from ethanol to give colorless crystals in good yields. Mp. 180.0~185.0 ^{o}C.

Preparation of *N,N'*-dimethyl-*o*-phenylenediamine (M3). *N,N'*-dimethyl-*N,N'*-di(*p*-toluenesulufonyl)-*o*-phenylenediamine (**M2**) (22g) was heated in conc. sulfuric acid (20mL) on a stream bath for 4 h, the mixture was poured into the crushed ice (200 g) and neutralized with 4N NaOH aqueous solution. The residue was extracted with ether. The ether layer was washed with water and brine, respectively, and dried over Na_2SO_4, concentrated then dried to give crude product **M3.** This crude product was used for the following reactions without further purification.

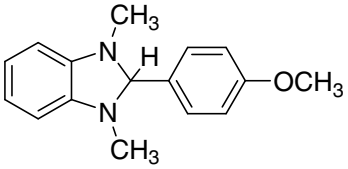
General procedure for preparation of 3H, 4H and 5H. To the solution of substituted *N, N'*-dimethyl-*o*-phenylenediamine (**M3**) (0.01mol) in minimum quantity of methanol was added appropriate amount of aromatic aldehyde (0.01mol) with vigorously shaking at room temperature, and then a drop of glacial acetic acid was added. After 15-45 min, the crude product was separated from the reaction mixture by filtration, and then washed with cold methanol and recrystallized from petroleum ether to give the corresponding pure 1,3-dimethyl-2-arylbenzimidazoles **3H, 4H** and **5H**.



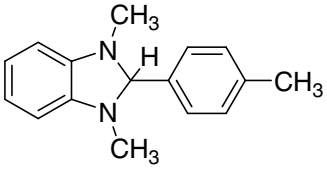
^{1}H NMR ($CDCl_3$, 400 M): δ 7.42 (d, 2H), 6.74 (d, 2H), 6.69 (dd, 2H), 6.42 (dd, 2H), 4.78 (s, 1H), 2.99 (s, 6H), 2.55 (s, 6H); ESI-MS/M^+ = 267.16; Anal. Calcd for $C_{17}H_{21}N_3$ (267.4): C, 76.37; H, 7.92; N, 15.92. Found: C, 76.4; H, 7.93; N, 15.89.



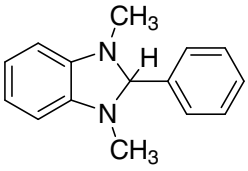
^{1}H NMR ($CDCl_3$, 400 M): δ 7.43 (d, 2H), 6.85 (d, 2H), 6.72 (dd, 2H), 6.43 (dd, 2H), 4.78 (s, 1H), 2.54 (s, 6H); ESI-MS/(M-1) = 239.13; Anal. Calcd for $C_{15}H_{16}N_2O$ (240.3): C, 74.97; H, 6.71; N, 11.66. Found: C, 75.0; H, 6.69; N, 11.68.



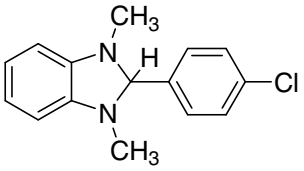
^{1}H NMR ($CDCl_3$, 400 M): δ 7.48 (d, 2H), 6.93 (d, 2H), 6.71 (dd, 2H), 6.42 (2H), 4.82 (s, 1H), 3.83 (s, 3H), 2.54 (s, 6H); ESI-MS/M^+ = 254.14; Anal. Calcd for $C_{16}H_{18}N_2O$ (254.4): C, 75.56; H, 7.13; N, 11.01. Found: C, 75.51; H, 7.15; N, 11.06.



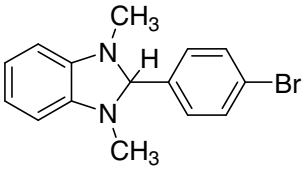
^{1}H NMR ($CDCl_3$, 400 M): δ 7.46 (d, 2H), 7.22 (d, 2H), 6.70 (dd, 2H), 6.42 (2H), 4.84 (s, 1H), 2.55 (s, 6H), 2.39 (s, 3H); ESI-MS/M^+ = 238.16; Anal. Calcd for $C_{16}H_{18}N_2O$ (238.3): C, 80.63; H, 7.61; N, 11.75. Found: C, 80.65; H, 7.63; N, 11.72.



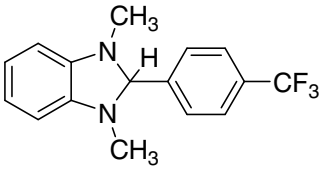
^{1}H NMR ($CDCl_3$, 400 M): δ 7.58 (m, 2H), 7.41 (m, 3H), 6.72 (dd, 2H), 6.43 (dd, 2H), 4.87 (s, 1H), 2.56 (s, 6H); ESI-MS/M^+ = 223.65; Anal. Calcd for $C_{15}H_{16}N_2$ (224.3): C, 80.32; H, 7.19; N, 12.49. Found: C, 80.28; H, 7.21; N, 12.53.



^{1}H NMR ($CDCl_3$, 400 M): δ 7.53 (d, 2H), 7.39 (d, 2H), 6.73 (dd, 2H), 6.44 (2H), 4.85 (s, 1H), 2.55 (s, 6H); ESI-MS/M^+ = 258.59; Anal. Calcd for $C_{15}H_{15}N_2Cl$ (258.8): C, 69.63; H, 5.84; N, 10.83. Found: C, 69.6; H, 5.86; N, 10.85.

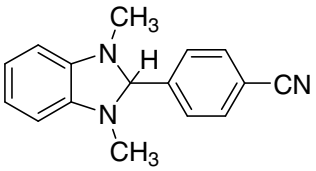


^{1}H NMR ($CDCl_3$, 400 M): δ 7.53 (d, 2H), 7.39 (d, 2H), 6.73 (dd, 2H), 6.44 (2H), 4.85 (s, 1H), 2.55 (s, 6H); ESI-MS/M^+ = 302.05; Anal. Calcd for $C_{15}H_{15}N_2Br$ (303.2): C, 59.43; H, 4.99; N, 9.24. Found: C, 59.4; H, 5.04; N, 9.21.

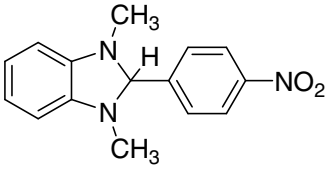


^{1}H NMR ($CDCl_3$, 400 M): δ 7.69 (m, 4H), 6.75 (dd, 2H), 6.46 (dd, 2H), 4.94 (s, 1H), 2.57 (s, 6H); ESI-MS/M^+ = 292.13; Anal. Calcd for $C_{16}H_{15}N_2F_3$ (292.3): C, 65.74; H, 5.17; N, 9.58.

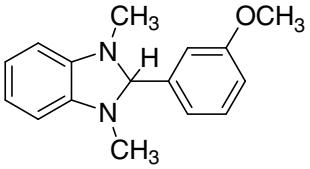
Found: C, 65.78; H, 5.16; N, 9.53.



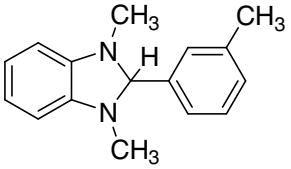
^{1}H NMR ($CDCl_3$, 400 M): δ 7.72 (m, 4H), 6.75 (dd, 2H), 6.46 (2H), 4.94 (s, 1H), 2.57 (s, 6H); ESI-MS/M^+ = 249.15; Anal. Calcd for $C_{16}H_{15}N_3$ (249.3): C, 77.08; H, 6.06; N, 16.85. Found: C, 77.13; H, 6.04; N, 16.81.



^{1}H NMR ($CDCl_3$, 400 M): δ 8.27 (d, 2H), 7.79 (d, 2H), 6.76 (dd, 2H), 6.47 (dd, 2H), 5.00 (s, 1H), 2.548 (s, 6H); ESI-MS/M^+ = 269.13; Anal. Calcd for $C_{15}H_{15}N_3O_2$ (269.3): C, 66.9; H, 5.61; N, 15.6. Found: C, 66.94; H, 5.63; N, 15.51.

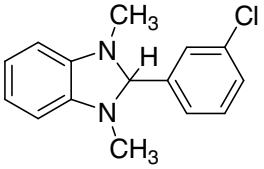


^{1}H NMR ($CDCl_3$, 400 M): δ 7.59 (s, 1H), 7.20 (m, 3H), 6.71 (dd, 2H), 6.42 (m, 2H), 4.86 (s, 1H), 3.84 (s, 3H), 2.55 (s, 6H); ESI-MS/M^+ = 254.13; Anal. Calcd for $C_{16}H_{18}N_2O$ (254.4): C, 75.56; H, 7.13; N, 11.01. Found: C, 75.52; H, 7.12; N, 11.08.

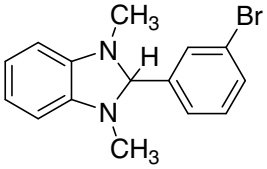


^{1}H NMR ($CDCl_3$, 400 M): δ 7.56 (s, 1H), 7.40 (m, 3H), 6.71 (dd, 2H), 6.43 (m, 2H), 4.86 (s,

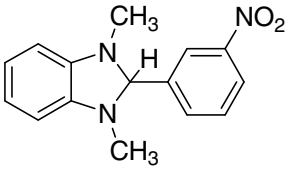
1H), 2.55 (s, 6H), 2.38 (s, 3H); ESI-MS/M^+ = 238.15; Anal. Calcd for $C_{16}H_{18}N_2O$ (238.3): C, 80.63; H, 7.61; N, 11.75. Found: C, 80.62; H, 7.61; N, 11.78.



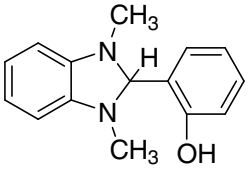
^{1}H NMR ($CDCl_3$, 400 M): δ 7.60 (s, 1H), 7.51 (m, 3 H), 6.64 (dd, 2H), 6.47 (dd, 2H), 4.91 (s, 1H), 2.55 (s, 6 H); ESI-MS/M^+ = 258.35; Anal. Calcd for $C_{15}H_{15}N_2Cl$ (258.8): C, 69.63; H, 5.84; N, 10.83. Found: C, 69.61; H, 5.85; N, 10.87.



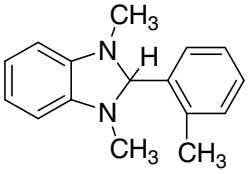
^{1}H NMR ($CDCl_3$, 400 M): δ 7.61 (s, 1H), 7.50 (m, 3H), 6.64 (dd, 2 H), 6.47 (dd, 2H), 4.91 (s, 1H), 2.55 (s, 6 H); ESI-MS/M^+ = 302.43; Anal. Calcd for $C_{15}H_{15}N_2Br$ (303.2): C, 59.43; H, 4.99; N, 9.24. Found: C, 59.45; H, 5.01; N, 9.25.



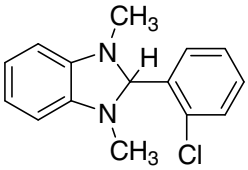
^{1}H NMR ($CDCl_3$, 400 M): δ 8.23 (s, 1H), 7.75 (m, 3H), 6.74 (dd, 2H), 6.44 (dd, 2H), 4.98 (s, 1H), 2.55 (s, 6H); ESI-MS/M^+ = 269.15; Anal. Calcd for $C_{15}H_{15}N_3O_2$ (269.3): C, 66.9; H, 5.61; N, 15.6. Found: C, 66.92; H, 5.65; N, 15.54.



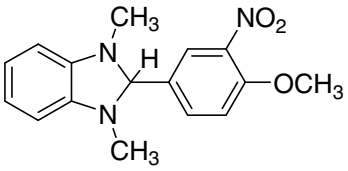
^{1}H NMR ($CDCl_3$, 400 M): δ 9.138 (s, ~1H), 7.32 (t, 1H), 7.07 (d, 1H), 6.95-6.81 (m, 4H), 6.60 (dd, 2H), 4.69 (s, 1H), 2.64 (s, 6H); ESI-MS/ (M-1) = 239.15; Anal. Calcd for $C_{15}H_{16}N_2O$ (240.3): C, 74.97; H, 6.71; N, 11.66. Found: C, 75.01; H, 6.68; N, 11.65.



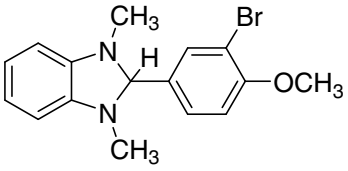
^{1}H NMR ($CDCl_3$, 400 M): δ 7.55 (d, 1H), 7.28-7.17 (m, 2H), 6.70 (dd, 2H), 6.421 (2H), 5.12 (s, 1H), 2.55 (s, 6H), 2.44 (s, 3H); ESI-MS/M^+ = 238.16; Anal. Calcd for $C_{16}H_{18}N_2O$ (238.3): C, 80.63; H, 7.61; N, 11.75. Found: C, 80.61; H, 7.64; N, 11.75.



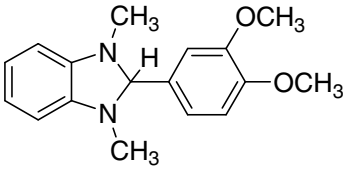
^{1}H NMR ($CDCl_3$, 400 M): δ 7.91 (d, 1H), 7.40-7.30 (d, 2H), 6.72 (dd, 2H), 6.43 (2H), 5.70 (s, 1H), 2.60 (s, 6H); ESI-MS/M^+ = 258.59; Anal. Calcd for $C_{15}H_{15}N_2Cl$ (258.8): C, 69.63; H, 5.84; N, 10.83. Found: C, 69.65; H, 5.87; N, 10.79.



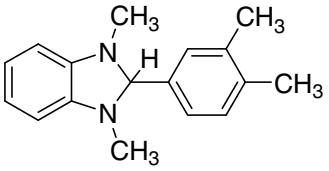
^{1}H NMR ($CDCl_3$, 400 M): δ 8.06 (s, 1H), 7.82 (dd, 1H), 7.15 (d, 1H), 6.73 (dd, 2H), 6.46 (dd, 2H), 4.89 (s, 1H), 4.01 (s, 3H), 2.57 (s, 6H); ESI-MS/M^+ = 299.15; Anal. Calcd for $C_{16}H_{17}N_3O_3$ (299.3): C, 64.2; H, 5.72; N, 14.04. Found: C, 64.26; H, 5.69; N, 14.08.



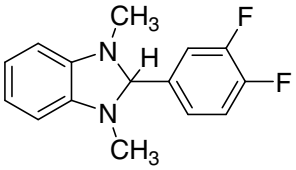
^{1}H NMR ($CDCl_3$, 400 M): δ 7.80 (s, 1H), 7.46 (d, 1H), 6.92 (d, 1H), 6.73 (dd, 2H), 6.34 (dd, 2H), 4.80 (1H), 3.93 (s, 3H), 2.55 (s, 6H); ESI-MS/M^+ =332.15; Anal. Calcd for $C_{16}H_{17}N_2BrO$ (333.2): C, 56.67; H, 5.14; N, 8.41. Found: C, 56.61; H, 5.18; N, 8.42.



^{1}H NMR ($CDCl_3$, 400 M): δ 7.23 (s, 1H), 7.01 (d, 1H), 6.99 (d, 1H), 6.73 (dd, 2H), 6.45 (dd, 2H), 4.84 (s, 1H), 3.90 (s, 6H), 2.56 (s, 6H); ESI-MS/M^+ =284.25; Anal. Calcd for $C_{17}H_{20}N_2O_2$ (284.4): C, 71.81; H, 7.09; N, 9.85. Found: C, 71.79; H, 7.11; N, 9.86.

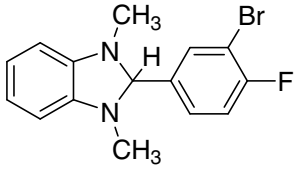


^{1}H NMR ($CDCl_3$, 400 M): δ 7.37 (s, 1H), 7.261 (d, 1H), 7.18 (d, 1H), 6.72 (dd, 2H), 6.43 (dd, 2H), 4.80 (s, 1H), 2.56 (s, 6H), 2.30 (s, 6H); ESI-MS/M^+ =252.26; Anal. Calcd for $C_{17}H_{20}N_2$ (252.4): C, 80.91; H, 7.99; N, 11.1. Found: C, 80.94; H, 7.94; N, 11.12.

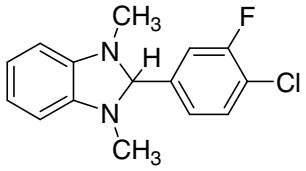


^{1}H NMR ($CDCl_3$, 400 M): δ 7.50-7.20 (m, 3H), 6.74 (m, 2H), 6.45 (m, 2H), 4.84 (s, 1H), 2.56 (s, 6H); ESI-MS/M^+ =260.15; Anal. Calcd for $C_{15}H_{14}N_2F_2$ (260.3): C, 69.22; H, 5.42; N, 10.76.

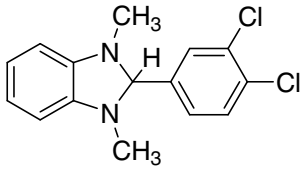
Found: C, 69.2; H, 5.45; N, 10.8.



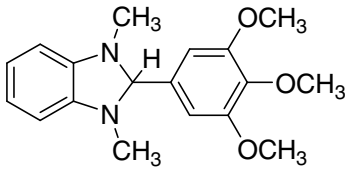
^{1}H NMR ($CDCl_3$, 400 M): δ 7.82 (d, 1H), 7.50 (m, 1H), 7.17 (t, 1H), 6.74 (dd, 2H), 6.45 (dd, 2H), 4.85 (s, 1H), 2.56 (s, 6H); ESI-MS/M^+ =321.04; Anal. Calcd for $C_{15}H_{14}N_2BrF$ (321.2): C, 56.09; H, 4.39; N, 8.72. Found: C, 56.11; H, 4.41; N, 8.69.



^{1}H NMR ($CDCl_3$, 400 M): δ 7.46-7.42 (m, 2H), 7.29 (d, 1H), 6.74 (dd, 2H), 6.45 (dd, 2H), 4.86 (s, 1H), 2.57 (s, 6H); ESI-MS/M^+ = 276.15; Anal. Calcd for $C_{15}H_{14}N_2ClF$ (276.7): C, 65.1; H, 5.1; N, 10.12. Found: C, 65.13; H, 4.96; N, 10.15.

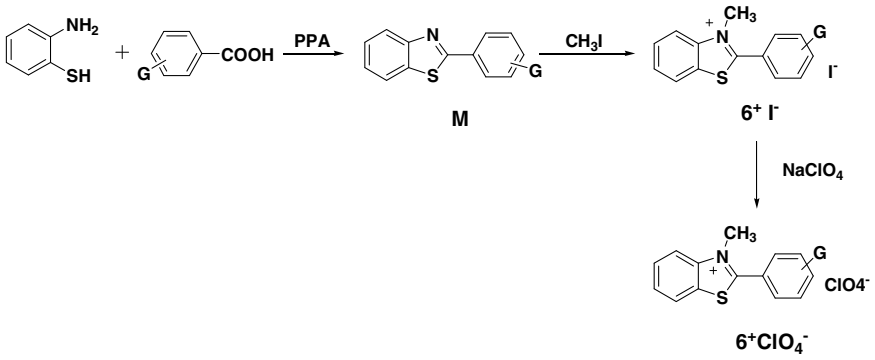


^{1}H NMR ($CDCl_3$, 400 M): δ 7.82 (s, 1H), 7.47 (d, 1H), 6.96 (d, 1H), 6.73 (dd, 2H), 6.35 (dd, 2H), 4.86 (s, 1H), 2.55 (s, 6H); ESI-MS/M^+ = 293.13; Anal. Calcd for $C_{15}H_{14}N_2Cl_2$ (293.2): C, 61.45; H, 4.81; N, 9.55. Found: C, 61.42; H, 4.82; N, 9.53.



^{1}H NMR ($CDCl_3$, 400 M): δ 6.80 (s, 2H), 6.74 (m, 2H), 6.45 (m, 2H), 4.79(s, 1H), 3.89 (s, 9H), 2.59 (s, 6H); ESI-MS/M^+ =314.25; Anal. Calcd for $C_{18}H_{22}N_2O_2$ (314.4): C, 68.77; H, 7.05; N, 8.91. Found: C, 68.75; H, 7.08; N, 8.93.

SI-5. Synthetic Route of $6^+ClO_4^-$ [S4]

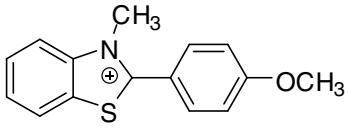


Preparation of 2-p-substituentphenyl-benzothiazole(M). A mixture of 1.3 equiv of benzoic acid (3.00 g) , 1 equiv of 2-aminothiophenol (2.38 g) and polyphosphoric acid (6.39 g) was heated with stirring at 150 ^{o}C for 2 h. After cooled to about 50 ^{o}C, a brown solid was separated. 50mL 7 % NH_4OH was added to neutralize the excess acid, and then stirred for 2 h. The yellow solid was filtered, thoroughly rinsed with the NH_4OH solution (50 mL), and dried and then purified by silica-gel chromatography to give pure 2-phenylbenzothiazole (3.99g), mp. 112.5 ^{o}C. The yield was generally over 85%. The product was identified by ^{1}H NMR.

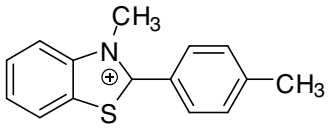
Preparation of N-methyl-2-p-substituentphenyl-benzothiazolium iodide (6^+I^-). Methyl iodide (12.6 g) was added to a solution of 2-phenylbenzothiazole (3.98 g) in 15 mL methanol. The mixture was heated at 120 ^{o}C for 12 h in a sealed tube to give dark brown solids. The crude product was washed with a small amount of acetone and recrystallized from absolute ethanol to give yellow crystalline solids. The yield was over 75%.

Preparation of N-methyl-2-p-substituentphenyl-benzothiazolium perchlorate (6^+ClO4^-).

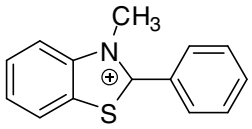
The iodide was exchanged by perchlorate ion as follows: compound **5** (3.00 g) was dissolved in 100 mL hot water and then 30 mL hot aqueous solution containing an excess of $NaClO_4$ (10.0 g) was added. The exchange reaction took place instantaneously and the perchlorate salt precipitated. The pale yellow solid of N-methyl-2-p-substituentphenyl-benzothiazolium percholorate was recrystallized from absolute ethanol.



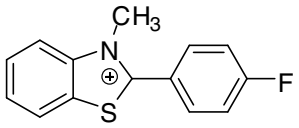
^{1}H NMR (d_6-DMSO, 400 M): δ 8.46 (d, 1H), 8.35 (d, 1H), 7.96 (dd, 1H), 7.91 (d, 2H), 7.85 (dd, 1H), 7.32 (d, 2H), 4.26 (s, 3H), 3.94 (s, 3H); ESI-MS/M^+ = 256.08.



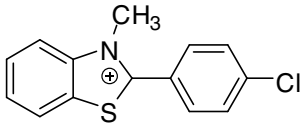
^{1}H NMR (d_6-DMSO, 400 M): δ 8.53 (d, 1H), 8.42 (d, 1H), 7.98(dd, 1H), 7.91 (d, 2H), 7.85 (dd, 1H), 7.62 (d, 2H), 4.25 (s, 3H), 3.32 (s, 3H); ESI-MS/M^+ = 240.15.



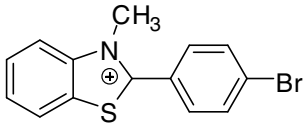
^{1}H NMR (d_6-DMSO, 400 M): δ 8.56 (d, 1H), 8.42 (d, 1H), 7.99 (dd, 1H), 7.98 (d, 2H), 7.92 (dd, 2H), 7.88 (m, 1H), 7.80 (d, 2H), 4.26 (s, 3H); ESI-MS/M^+ = 226.09.



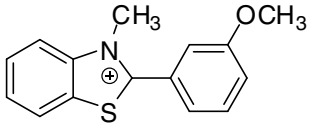
^{1}H NMR (d_6-DMSO, 400 M): δ 8.55 (d, 1H), 8.44 (d, 1H), 8.06(dd, 1H), 8.02 (dd, 1H), 7.93 (dd, 1H), 7.66 (d, 2H), 4.23 (s, 3H); ESI-MS/M^+ = 244.06.



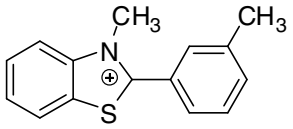
^{1}H NMR (d_6-DMSO, 400 M): δ 8.56 (d, 1H), 8.45 (d, 1H), 8.07 (dd, 2H), 8.04 (dd, 1H), 7.96 (d, 2H), 7.92 (dd, 1H), 4.23 (s, 3H); ESI-MS/M^+ = 260.25.



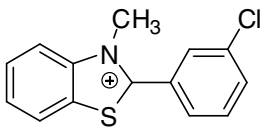
^{1}H NMR (d_6-DMSO, 400 M): δ 8.56 (d, 1H), 8.44 (d, 1H), 8.07 (dd, 2H), 8.03 (dd, 1H), 7.96 (d, 2H), 7.93 (dd, 1H), 4.23 (s, 3 H); ESI-MS/M^+ = 305.13.



^{1}H NMR (d_6-DMSO, 400 M): δ 8.53 (d, 1 H), 8.41 (d, 1 H), 7.99 (dd, 1H), 7.91 (d, 1H), 7.89 (t, 1H), 7.87 (d, 1H), 7.79 (d, 1H), 4.22 (s, 3H), 3.93 (s, 3H); ESI-MS/M^+ = 256.08.



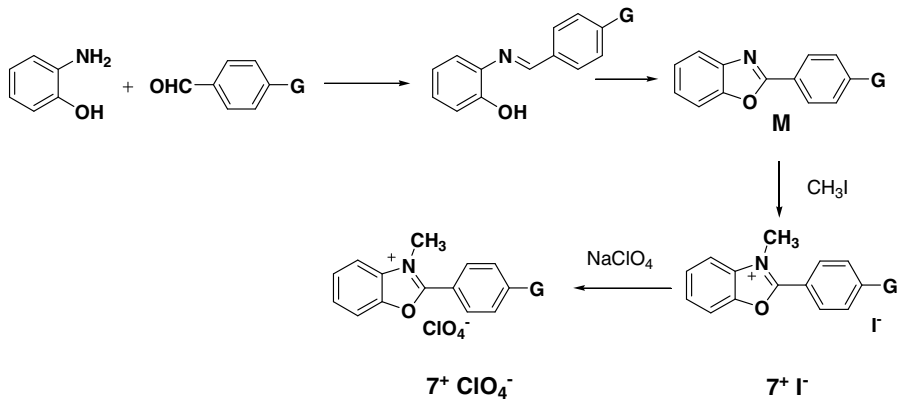
^{1}H NMR (d_6-DMSO, 400M): δ 8.55 (d, 1H), 8.43 (d, 1H), 7.98 (dd, 1H), 7.92 (d, 1H), 7.90 (t,1H), 7.86 (d, 1H), 7.78 (d, 1H), 4.23 (s, 3H), 3.31 (s, 3H), 3.31 (s, 3H); ESI-MS/M^+ = 240.15.



^{1}H NMR (d_6-DMSO, 400 M): δ 8.57 (d, 1H), 8.46 (d, 1H), 8.03 (dd, 1H), 7.94 (d, 1H), 7.93 (t,

1H), 7.91 (d, 1H), 7.81 (d, 1H), 4.23 (s, 3H); ESI-MS/M^+ = 260.23.

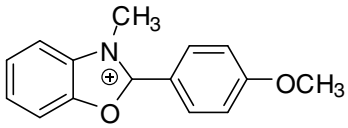
SI-6. Synthetic Route of $7^+ClO_4^-$



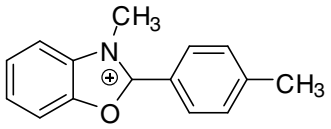
Preparation of 2-p-substituentphenyl-benzooxazone (M).[S5] The corresponding aromatic aldehyde (1.0 mmol) was added to a solution of 2-aminophenol (0.109 g, 1.0 mmol) in MeOH (5 mL). The resulted mixture was heated at 45 ^oC for 12 h. After concentration under reduced pressure, the residue was dissolved in CH_2Cl_2 (10 mL) and then DDQ (0.250 g, 1.1 mmol) was added. After stirred at room temperature for 30 min, the resulted mixture was diluted with additional CH_2Cl_2 (10 mL), then washed sequentially with saturated Na_2CO_3 (10mL×2) and brine (10 mL), respectively. The organic layer was dried over anhydrous Na_2SO_4. After evaporation, the crude product was purified by flash column chromatography (10% EtOAc in hexane) to afford the desired product (0.187 g, 83%).

Preparation of N-methyl-2-p-substituentphenyl-benzooxazonium iodide (7^+I^-).[S6] Methyl iodide (0.015mol) was added into a solution of 2-phenylbenzooxazone (0.01mol) in methanol, and the mixture was heated at 150 ^oC for 18 h in a sealed tube to give dark brown solids. The crude product was rinsed with a small amount of acetone to remove unreacted reactants and recrystallized from absolute ethanol to give yellow crystalline solids. The yield was over 85%.

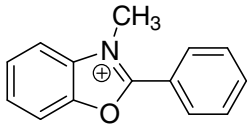
Preparation of N-methyl-2-p-substituentphenyl-benzooxazonium perchlorate ($7^+ClO_4^-$). The iodide was exchanged by perchlorate ion as follows: compound **5** was dissolved in 100 mL of hot water and treated with 30 mL of hot aqueous solution containing an excess of $NaClO_4$. The exchange reaction took place instantaneously and a precipitate was formed. The faint yellow solid of N-methyl-2-*p*-substituentphenyl-benzooxazonium perchlorate was recrystallized from absolute ethanol. The yield was over 50%.



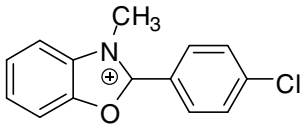
^{1}H NMR (d_6-DMSO, 400 M): δ 8.03 (s, 2H), 7.76 (s, 2H), 7.60 (s, 2H), 7.14 (s, 2H), 4.12 (s, 3H), 3.80 (s, 3H); ESI-MS/M^+ = 240.10.



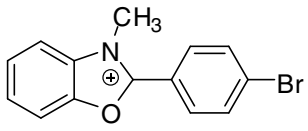
^{1}H NMR (d_6-DMSO, 400 M): δ 8.26-8.12 (m, 4H), 7.82 (d, 2H), 7.62 (d, 2H), 4.26 (s, 3H), 2.94 (s, 3H); ESI-MS/M^+ = 224.13.



^{1}H NMR (d_6-DMSO, 400 M): δ 8.27-8.18 (m, 3H), 8.14-8.12 (d, 2H), 7.83 (dd, 2H), 7.62 (d, 2H), 4.27 (s, 3H); ESI-MS/M^+ = 210.10.

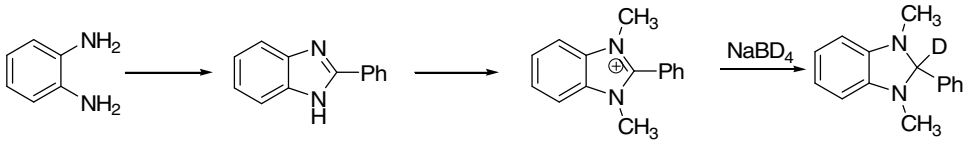


^{1}H NMR (d_6-DMSO, 400 M): δ 8.52-8.26 (m, 4H), 7.80 (d, 2H), 7.69 (d, 2H), 4.28 (s, 3H); ESI-MS/M^+ =244.13;



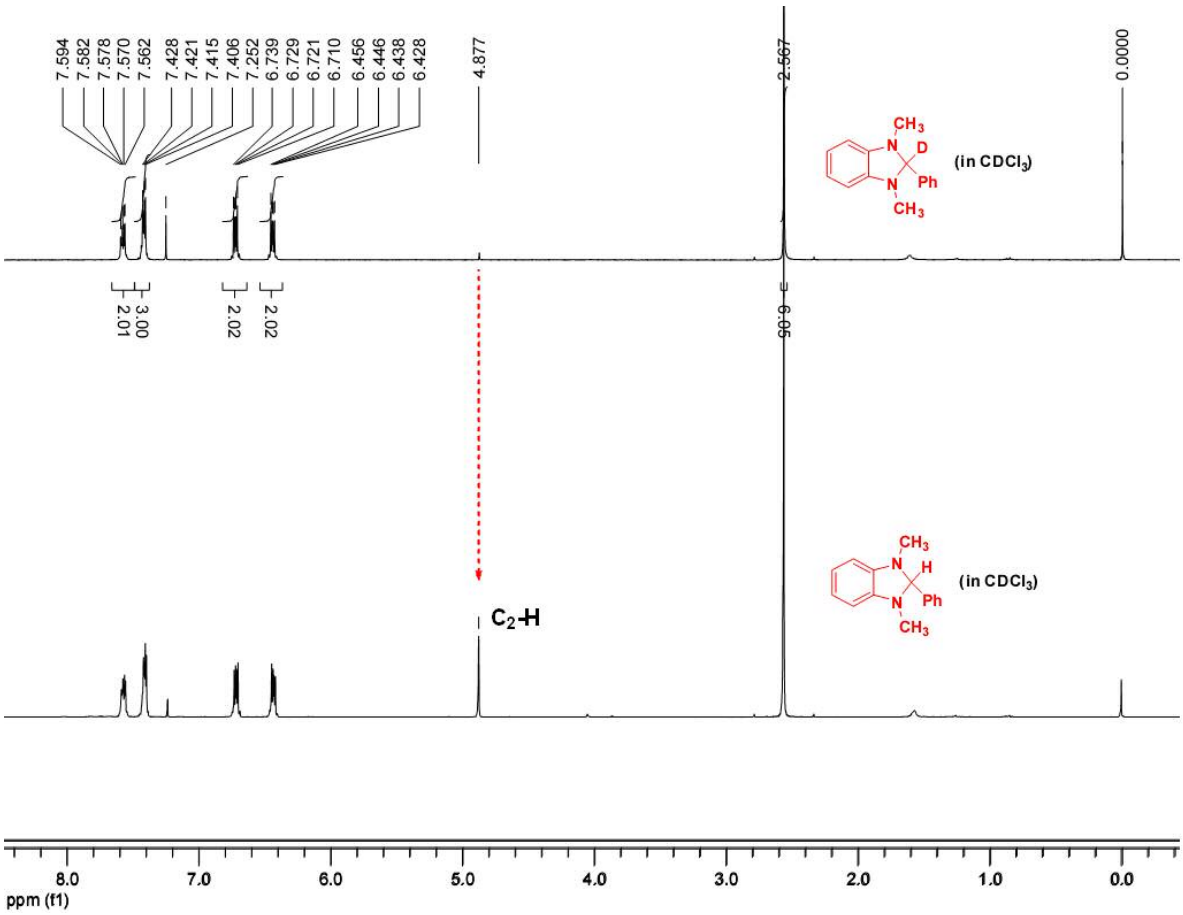
^{1}H NMR (d_6-DMSO, 400 M): δ 8.51-8.27 (m, 4H), 7.81 (d, 2H), 7.68 (d, 2H), 4.28 (s, 3H); ESI-MS/M^+ = 288.75.

SI-7. Synthesis Route of 2-deuterated 3H (G = H) (3D) and its ^{1}H NMR Paragraph [S7]

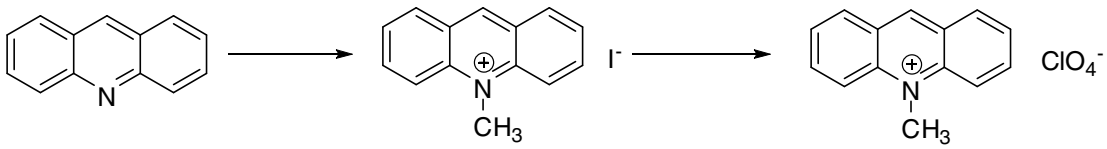


2-deuterated **3H** (**3D**)

A mixture of 0.03 mol of o-phenylenediamine dichloride, 20mL of water and 0.09 mol of benzoic acid was heated under reflux for 5 h. After cooled to room temperature, the mixture was adjusted to distinctly basic by addition of concentrated ammonia aqueous solution dropwise and a precipitate was formed. It was recrystallized from 10 percent aqueous ethanol. The obtained 2-phenylbenzimidazole was treated with methyl iodide in 10 mL methanol containing 0.02mol NaOH at 110 ^{o}C in sealed tube. The mixture was refluxed for 10 h then the solvent was removed under reduced pressure. The crude product was recrystallized from absolute ethanol. An appropriate amount of $NaBD_4$ was slowly added intro a solution of this crude product in 10mL methanol. The mixture was stirred for 30 min under N_2 atmosphere then compound **3D** was obtained by silica-gel chromatography (yield = 65%). ^{1}H NMR ($CDCl_3$, 400M): δ 7.58 (m, 2H), 7.41 (m, 3H), 6.72 (dd, 2H), 6.43 (dd, 2H), 2.56 (s, 6H); ESI-MS/M^+ = 224.58. The ^{1}H NMR spectrum of **3H** and **3D** were given below.



SI-8. Synthetic Route of $AcrH^+ClO_4^-$ [S8]



0.03mol methyl iodide was added to a solution of 0.01mol acridine in 50mL methanol. The mixture was stirred for 5 days at room temperature. The red precipitate was filtrated and recrystallized from water/ethanol. The iodide was exchanged by perchlorate ion as follows: Acridium iodide was dissolved in 100 mL hot water and treated by 30 mL hot aqueous solution containing an excess amount of $NaClO_4$. The exchange reaction took place instantaneously and then the perchlorate salt was precipitated. The yellow solid of N-methylacridium perchlorate was recrystallized from aqueous ethanol for three times. The yield was over 50%.

SI-9. Analysis of Products

N-methyl acridinium ion ($AcrH^+ClO_4^-$) (0.5mmol) was added into a solution of 1,3-dimethyl-2,3-dihydro-2-phenylbenzo[d]imidiazole **1H** (0.5mmol) in 10mL deaerated acetonitrile under argon atmosphere. After stirred at room temperature for ten minutes, the reaction mixture was isolated by preparative thin-layer chromatography to give 9,10-dihydroacridine ($AcrH_2$) and the salt of **1H** ($\mathbf{1}^+ClO_4^-$) as the final products.

$\mathbf{6}^+ClO_4^-$ or $\mathbf{7}^+ClO_4^-$ (0.5mmol) was added into a solution of 1,3-dimethyl-2,3-dihydro-2-phenylbenzo[d]imidiazole [**3H** (G = H)] (0.5mmol) in 10 mL deaerated acetonitrile under argon atmosphere. Ten minutes later, the reaction mixture was extracted with CH_2Cl_2 and isolated by preparative TLC to give **6H** or **7H**. ^{1}H NMR ($CDCl_3$, 400M): **6H** (G = H): δ 7.56 (d, 2 H), 7.38 (m, 3H), 7.02 (dd, 1H), 6.99 (d, 1H) , 6.72 (m, 2H), 6.42 (d, 1H), 5.98 (s, 1H), 2.63 (s, 3H); **7H** (G = H): δ 7.39-7.25 (m, 7H), 6.68-6.48 (m, 2H), 6.282 (s, 1H), 2.869 (s, 3H).

SI-10. References

(S1) Furniss, B. S., Hannnaford, A. J.; Smith, P. W.; Tatchell, A. R. *Vogel's textbook of Pratical Organic Chemistry*, 5th ed, 1989, Lasercomp Times New Roman.

(S2) Lee, I. H.; Jeoung, E. H.; Kreevoy, M. M. ***J.*** *Am. Chem. Soc.* **1997,** *119*, 2722.

(S3) (a) Lau, K. S. Y.; Basiulis, D. I. *Tetrahedron Lett.* **1981**, *22*, 1175. (b) Reddy, A.; Pandu, R.; Veeranagaiah, V.; Ratnam, C. V., *Indian J. Chem., Section B,* **1985**, *2*4, 367.

(S4) Lee, I.-S. H.; Ji, Y. R.; Jeoung, E. H. *J. Phys. Chem. A.* **2006,** *110*, 3875.

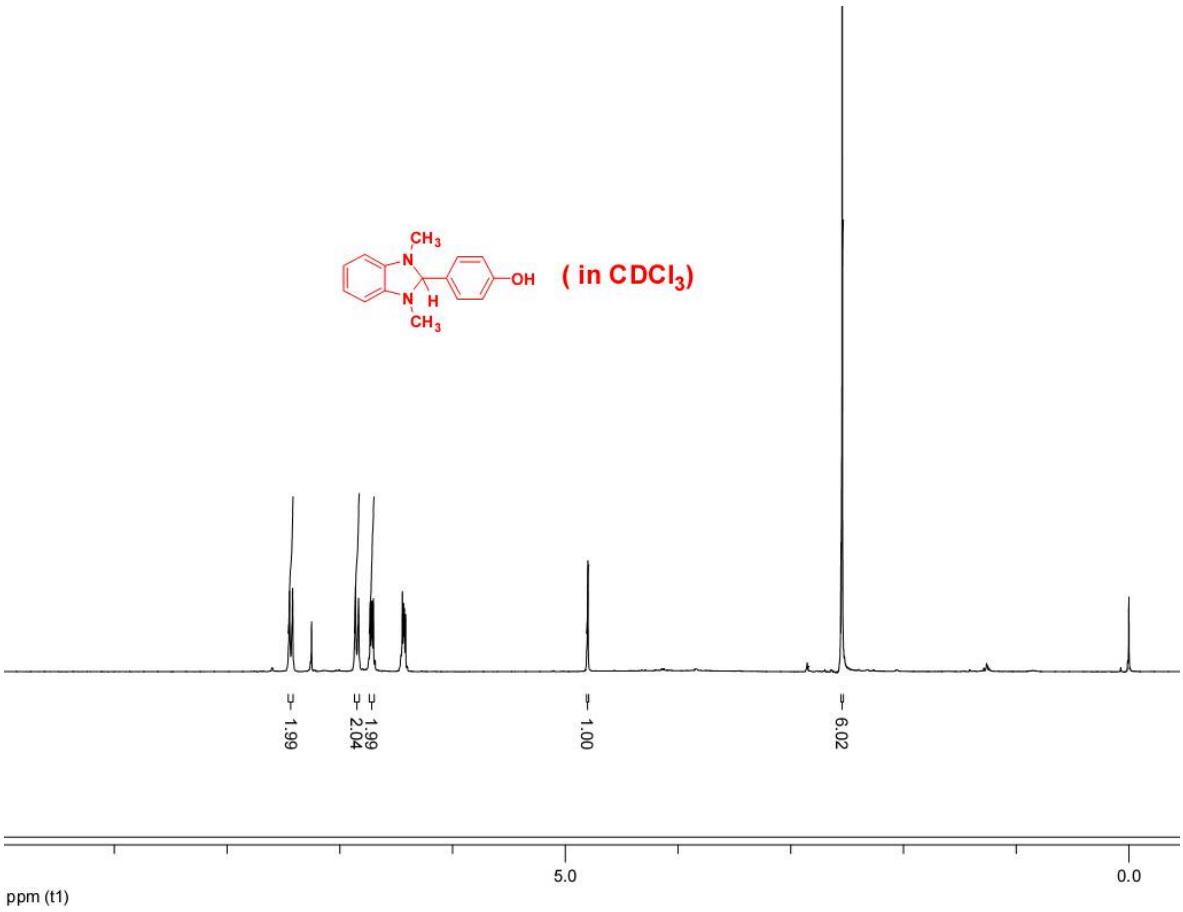
(S5) Chang, J.-B.; Zhao, K.; Pan, S.-F. *Tetrahedron Lett.* **2002**, *43*, 951-954.

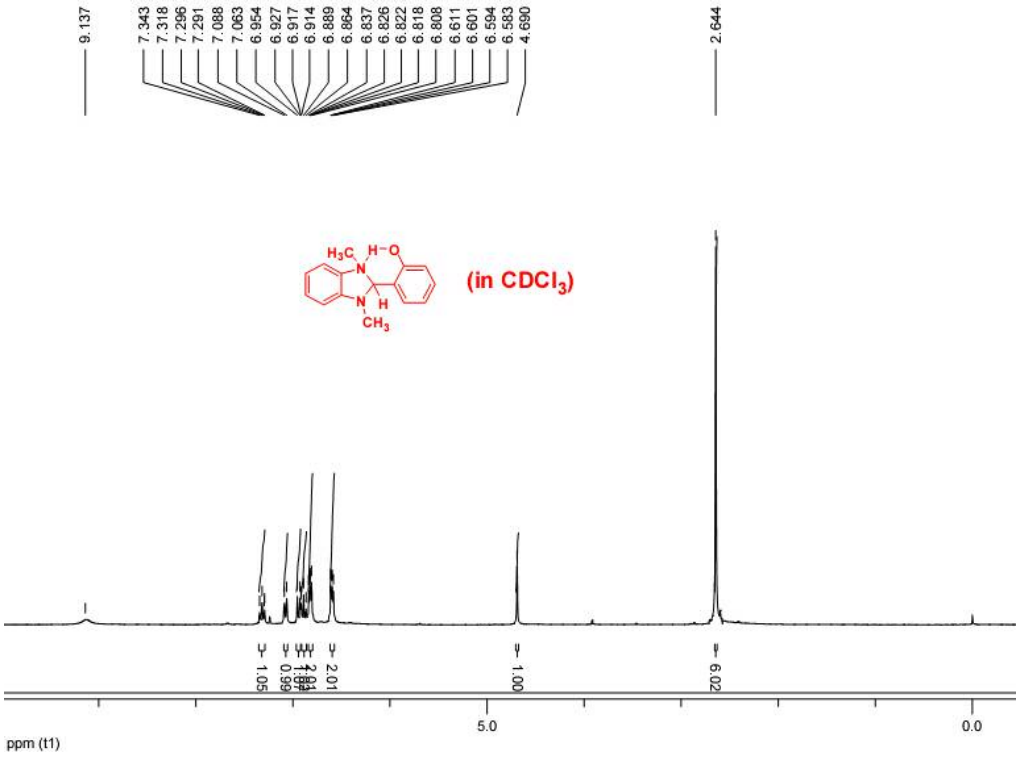
(S6) Cook, M. J.; Katritzky, A. R.; Page, A. D.; Tack, R. D.; Witek, H. *Tetrahedron* **1976**, *32*, 1773.

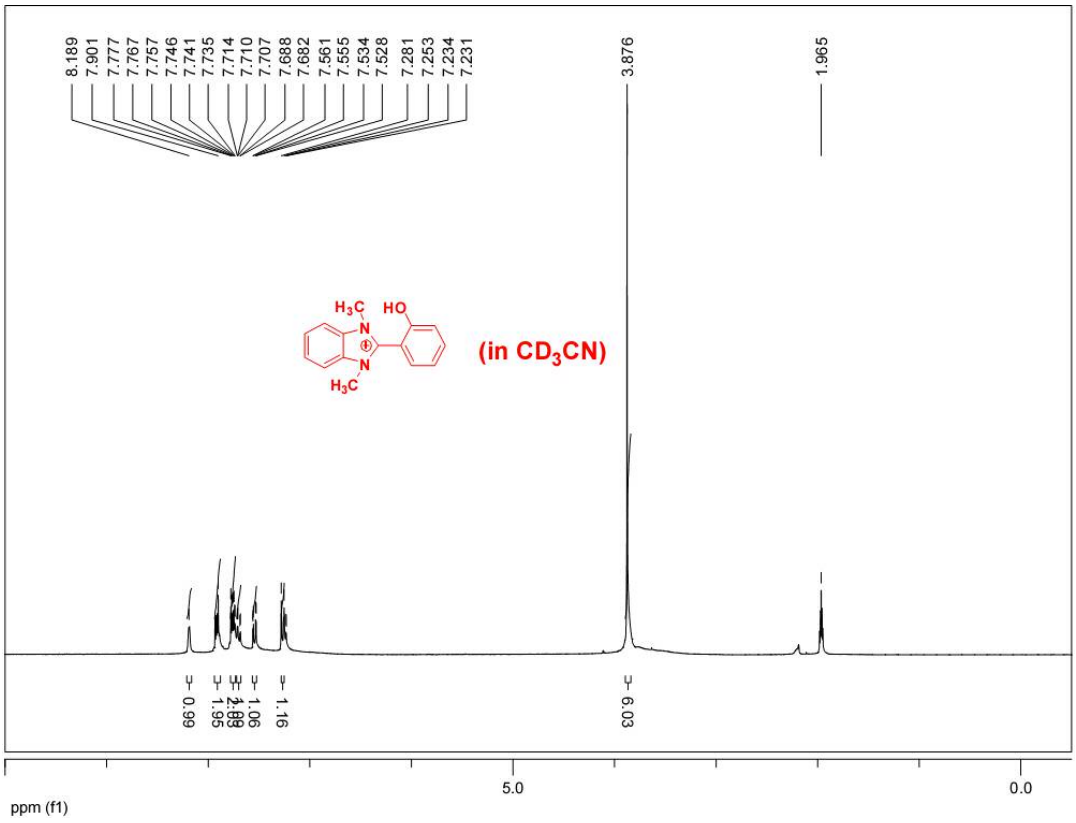
(S7) Lee, I. H.; Jeoung, E. H.; Kreevoy, M. M. *J. Am. Chem. Soc.* **1997,** *123*, 7492.

(S8) Fujita, M.; Fukuzumi, S. *J. Chem. Soc., Perkin Trans. 2.* **1993**, 1915.

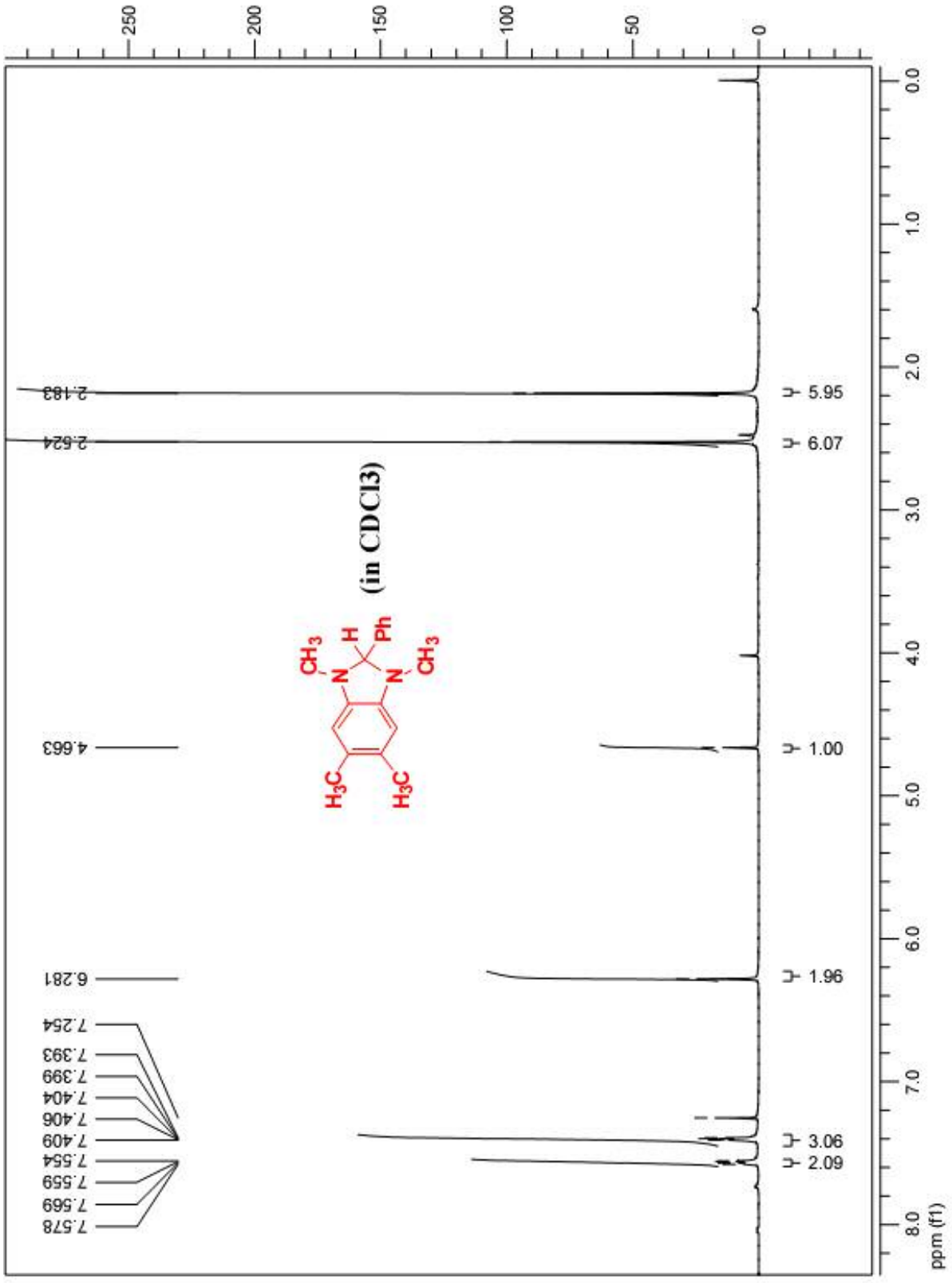
SI-11. ^{1}HNMR Spectra of *p*-OH-3H, *o*-OH-3H and *o*-OH-3^{+}

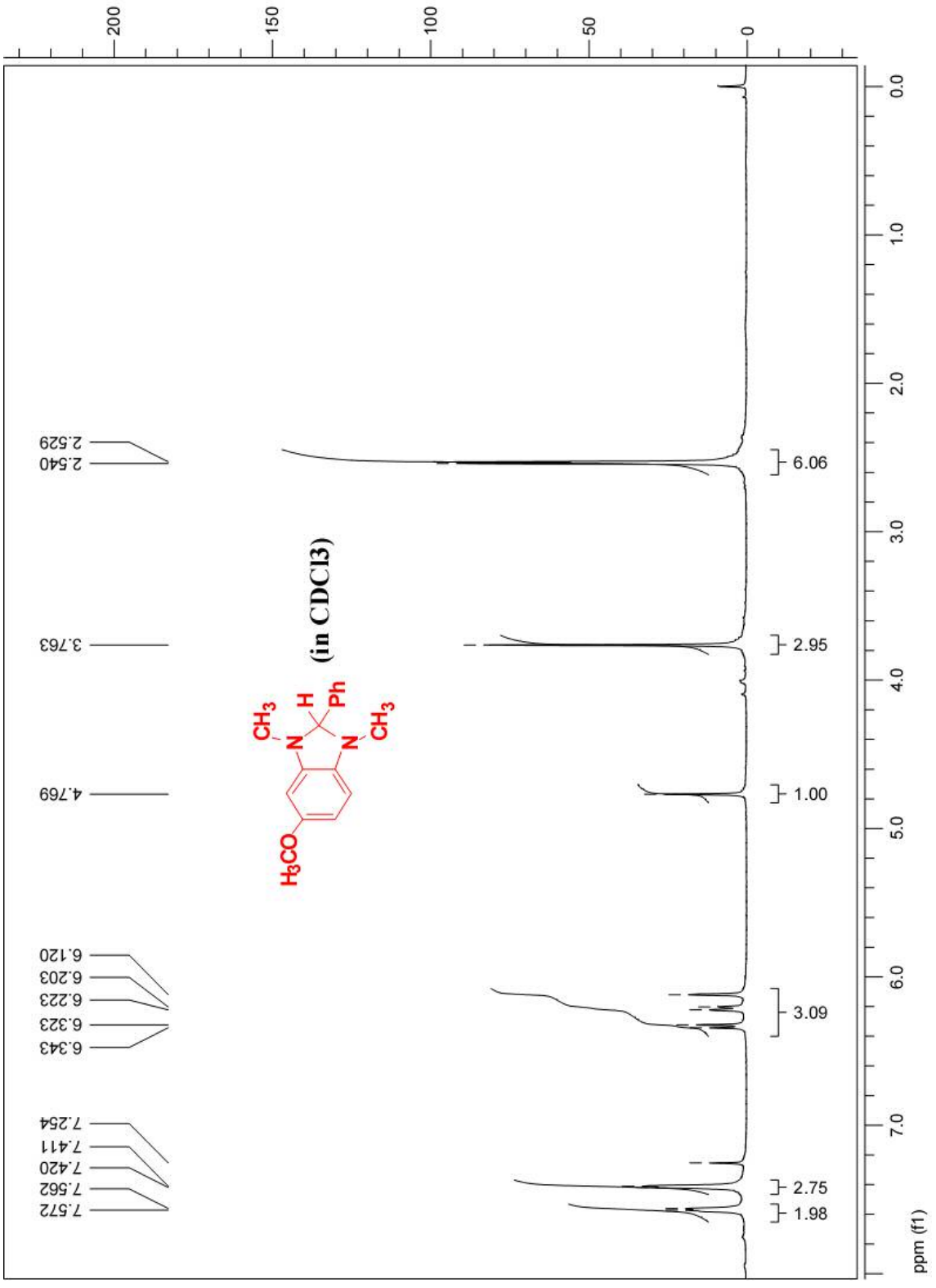


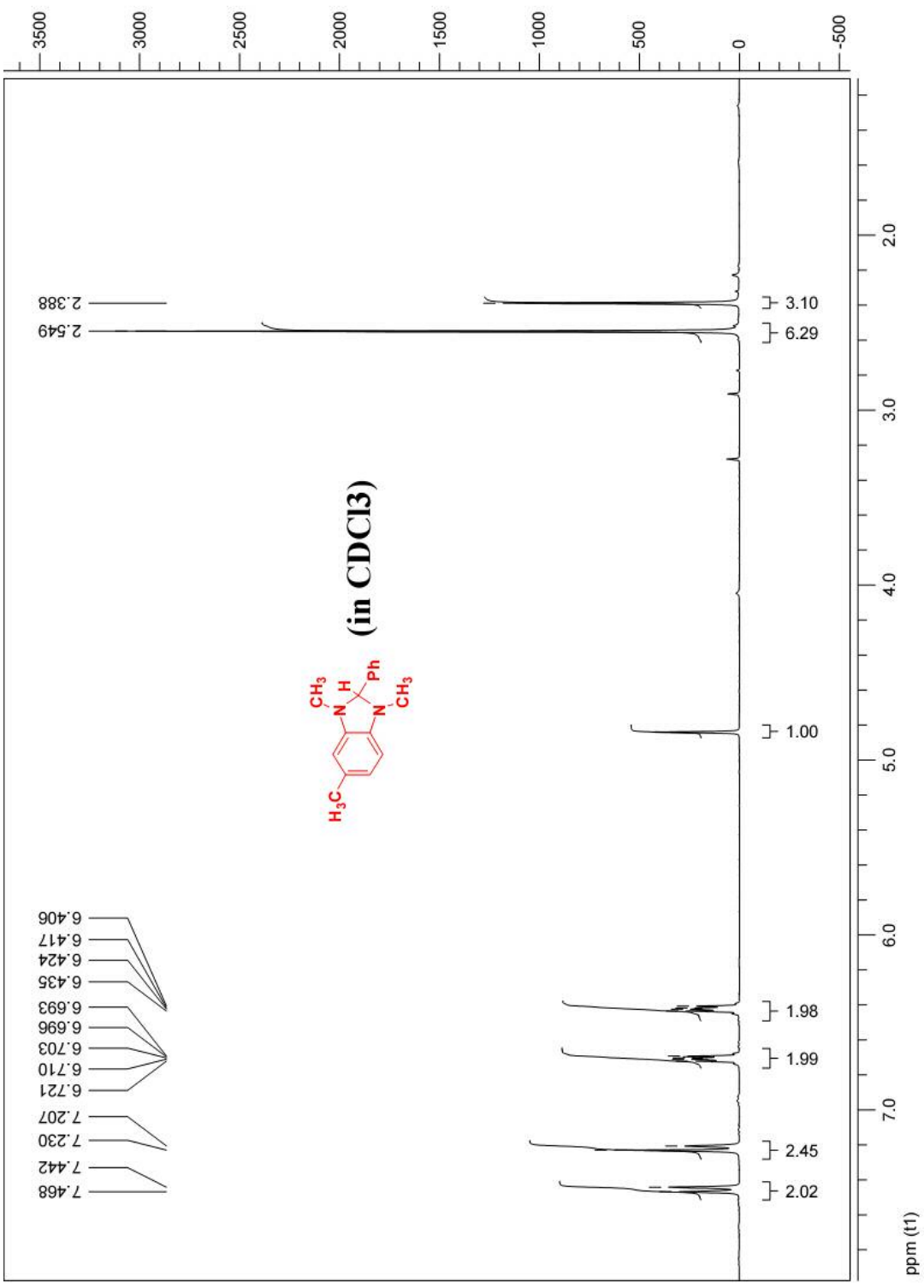

9.137
7.343
7.318
7.296
7.291
7.088
7.063
6.954
6.927
6.917
6.914
6.889
6.864
6.837
6.826
6.822
6.818
6.808
6.611
6.601
6.594
6.583
4.690
2.644
(in CDCl3)
1.05
0.99
2.01
1.00
6.02
5.0
0.0
ppm (t1)

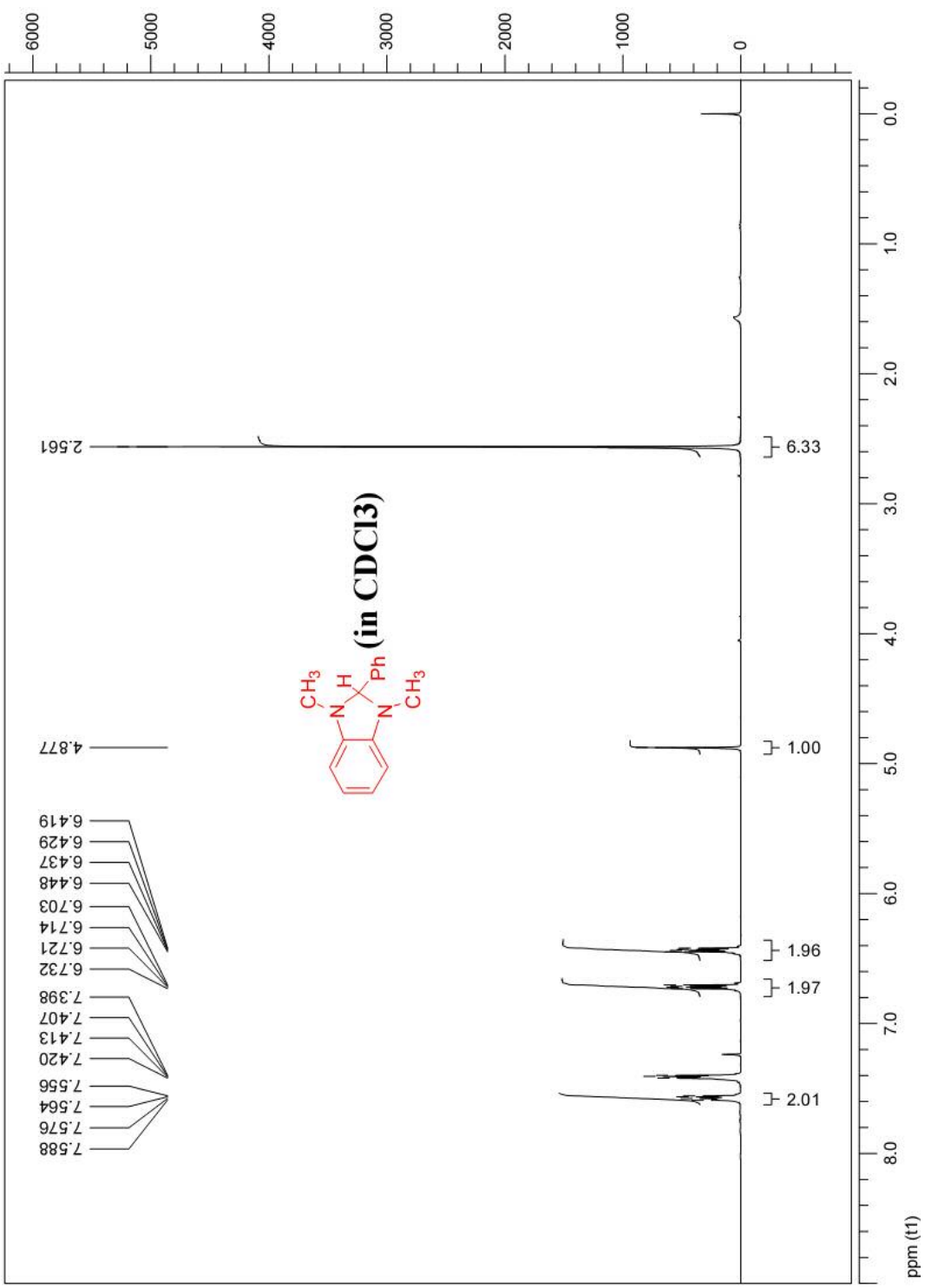

8.189
7.901
7.777
7.767
7.757
7.746
7.741
7.735
7.714
7.710
7.707
7.688
7.682
7.561
7.555
7.534
7.528
7.281
7.253
7.234
7.231
3.876
1.965
(in CD3CN)
0.99
1.96
1.90
1.16
6.03
5.0
0.0
ppm (f1)

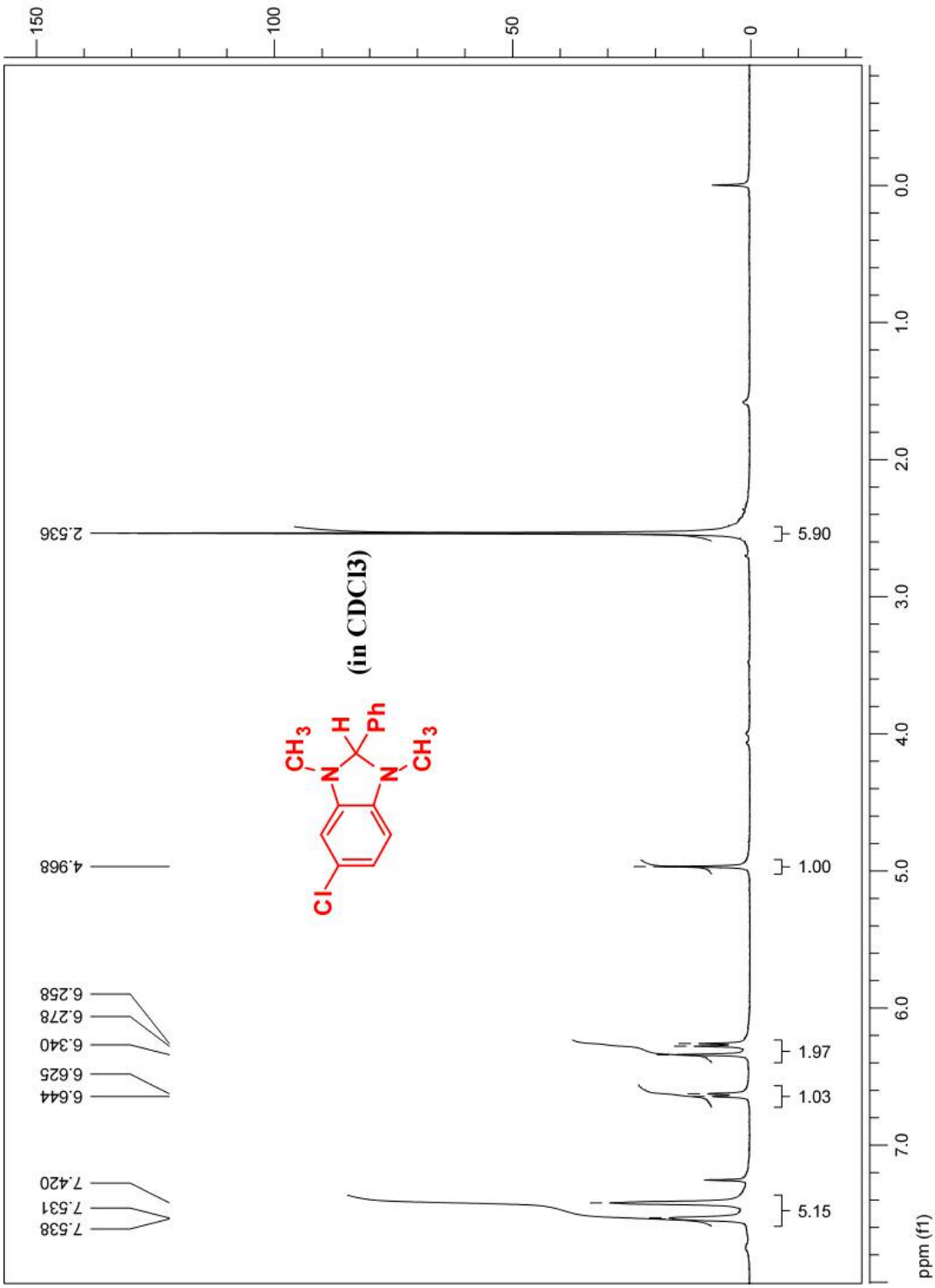
SI-12. Representative ^{1}H NMR Graphs of ZH and Z^{+}

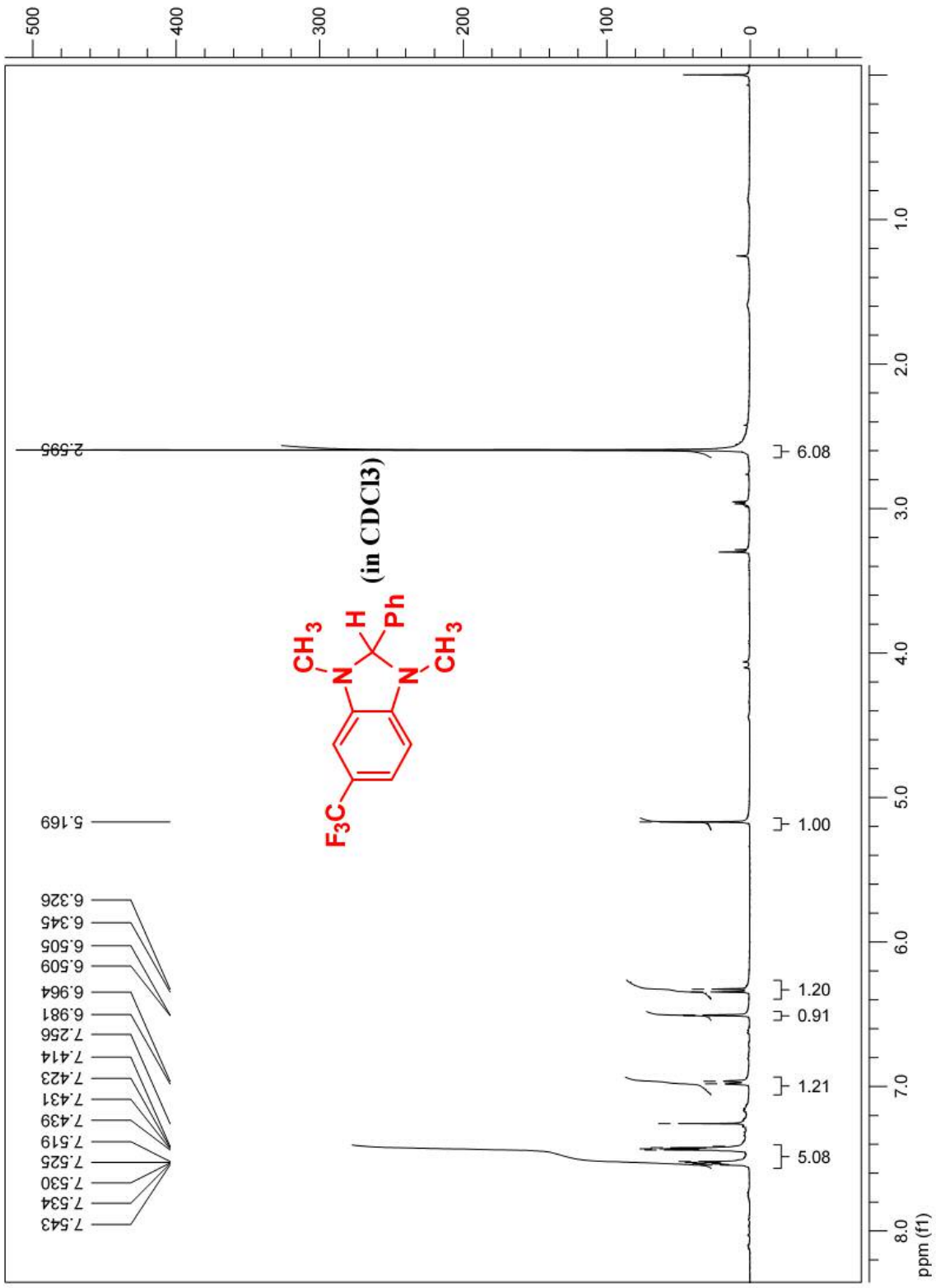



(in CDCl3)
2.529
2.540
3.763
4.769
6.120
6.203
6.223
6.323
6.343
7.254
7.411
7.420
7.562
7.572
6.06
2.95
1.00
3.09
2.75
1.98
ppm (f1)


(in CDCl3)
2.388
2.549
6.406
6.417
6.424
6.435
6.693
6.696
6.703
6.710
6.721
7.207
7.230
7.442
7.468
3.10
6.29
1.00
1.98
1.99
2.45
2.02
ppm (t1)


(in CDCl3)
2.561
4.877
6.419
6.429
6.437
6.448
6.703
6.714
6.721
6.732
7.398
7.407
7.413
7.420
7.556
7.564
7.576
7.588
6.33
1.00
1.96
1.97
2.01
ppm (t1)


150
100
50
0
2.536
4.968
6.258
6.278
6.340
6.625
6.644
7.420
7.531
7.538
5.90
1.00
1.97
1.03
5.15
(in CDCl3)
CH3
H
Ph
N
N
CH3
Cl
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
ppm (f1)


(in CDCl3)
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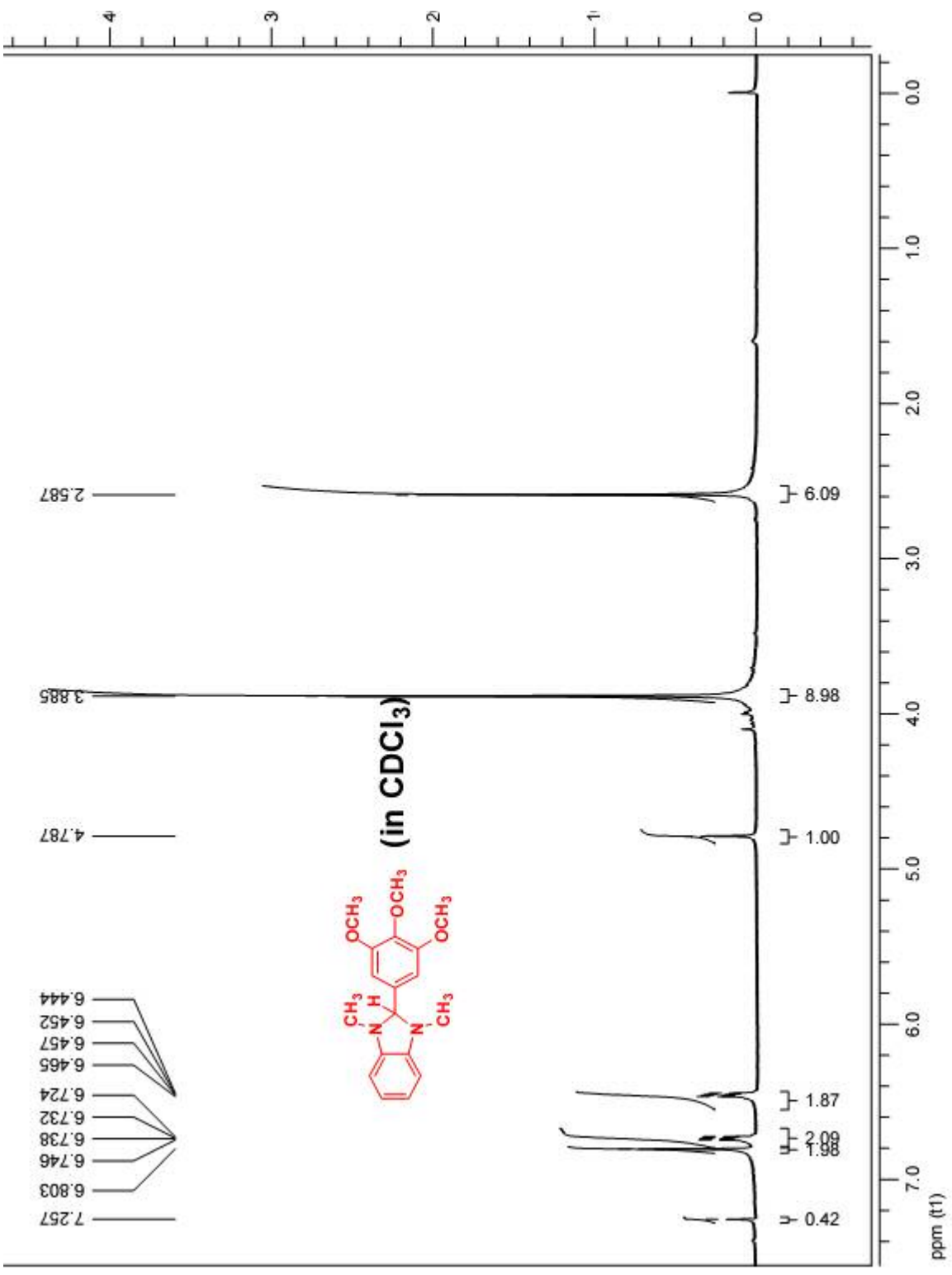
5.169
6.326
6.345
6.505
6.509
6.964
6.981
7.256
7.414
7.423
7.431
7.439
7.519
7.525
7.530
7.534
7.543
6.08
1.00
1.20
0.91
1.21
5.08
ppm (f1)


(in CDCl3)
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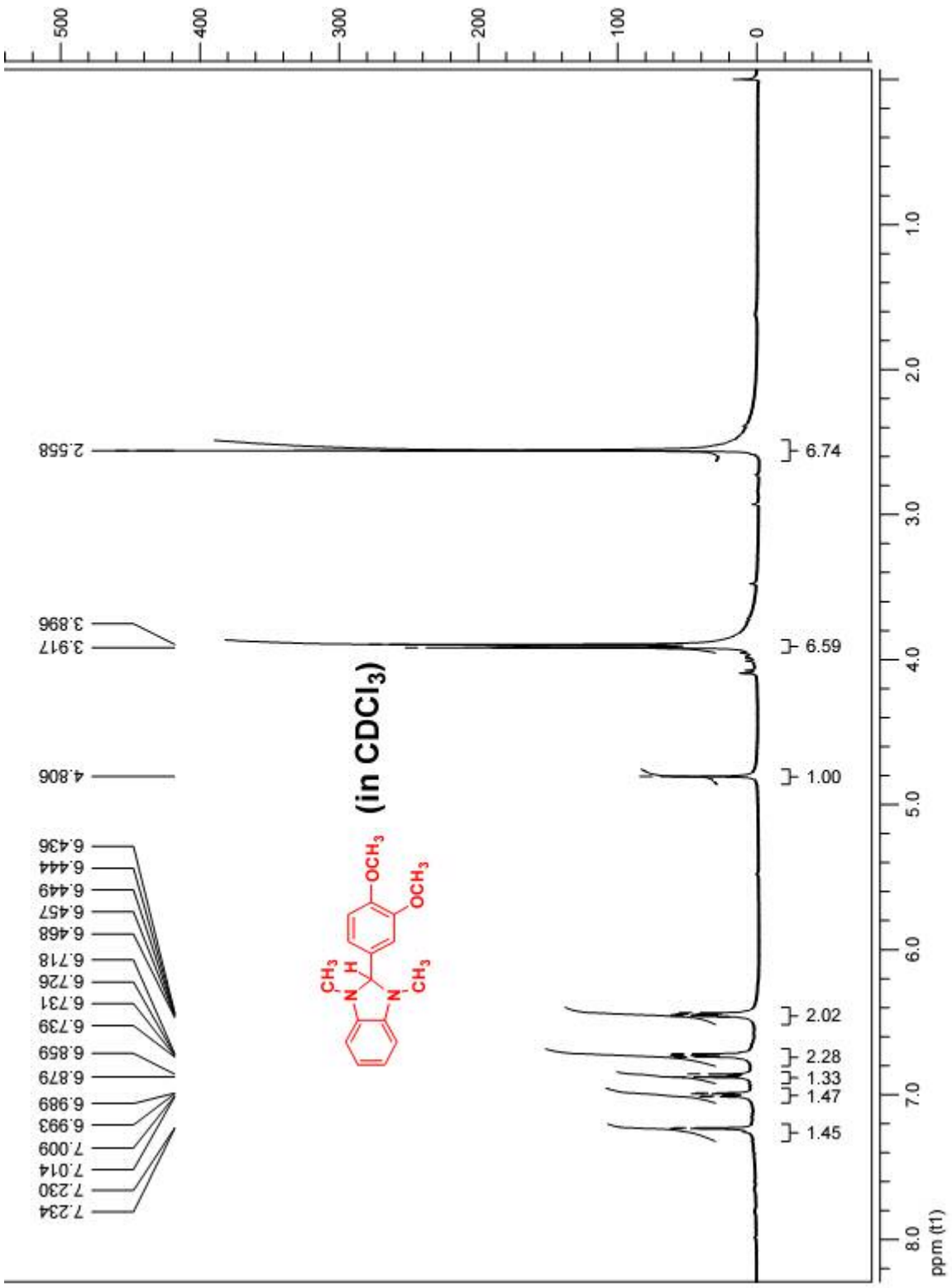
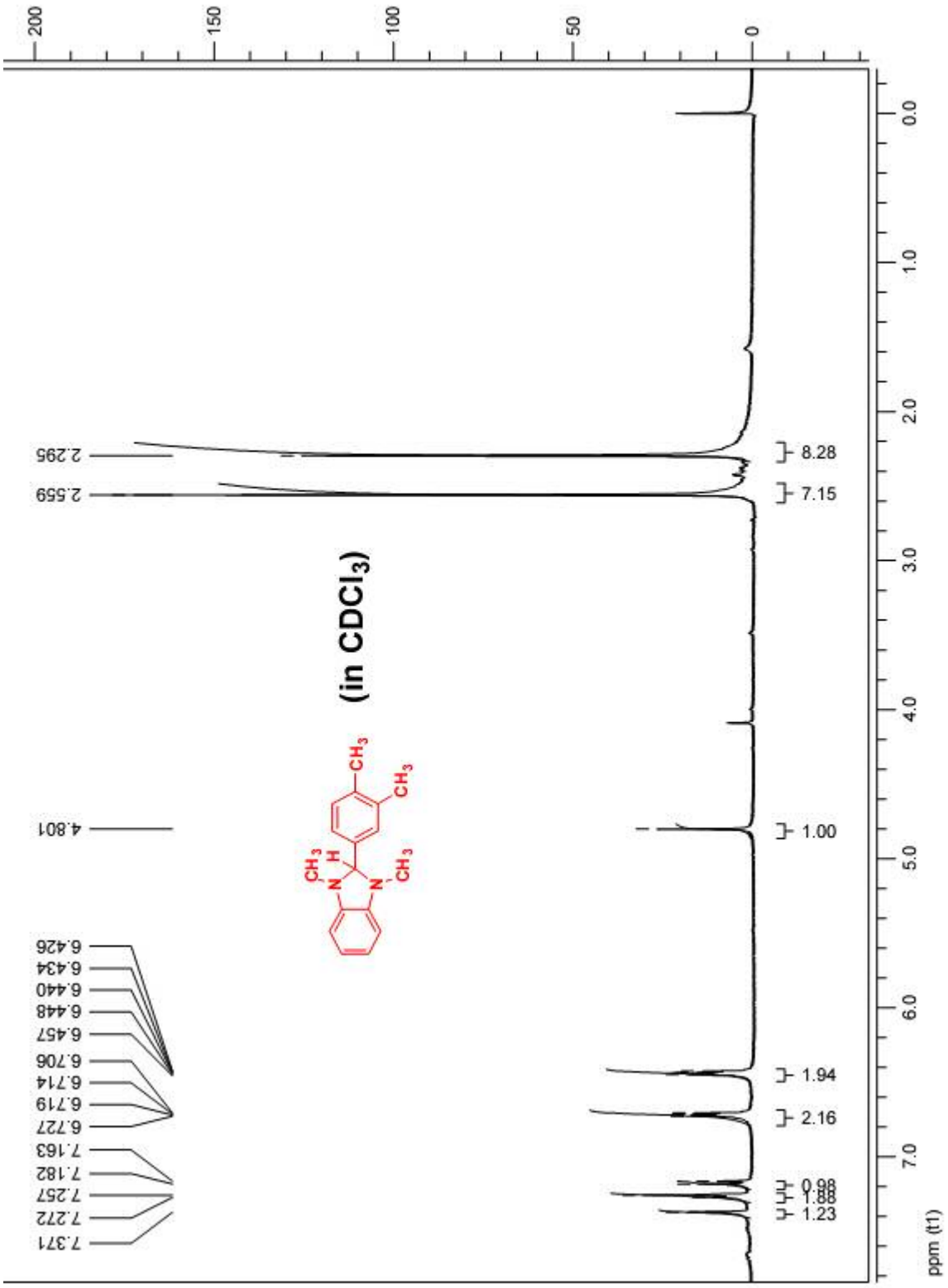
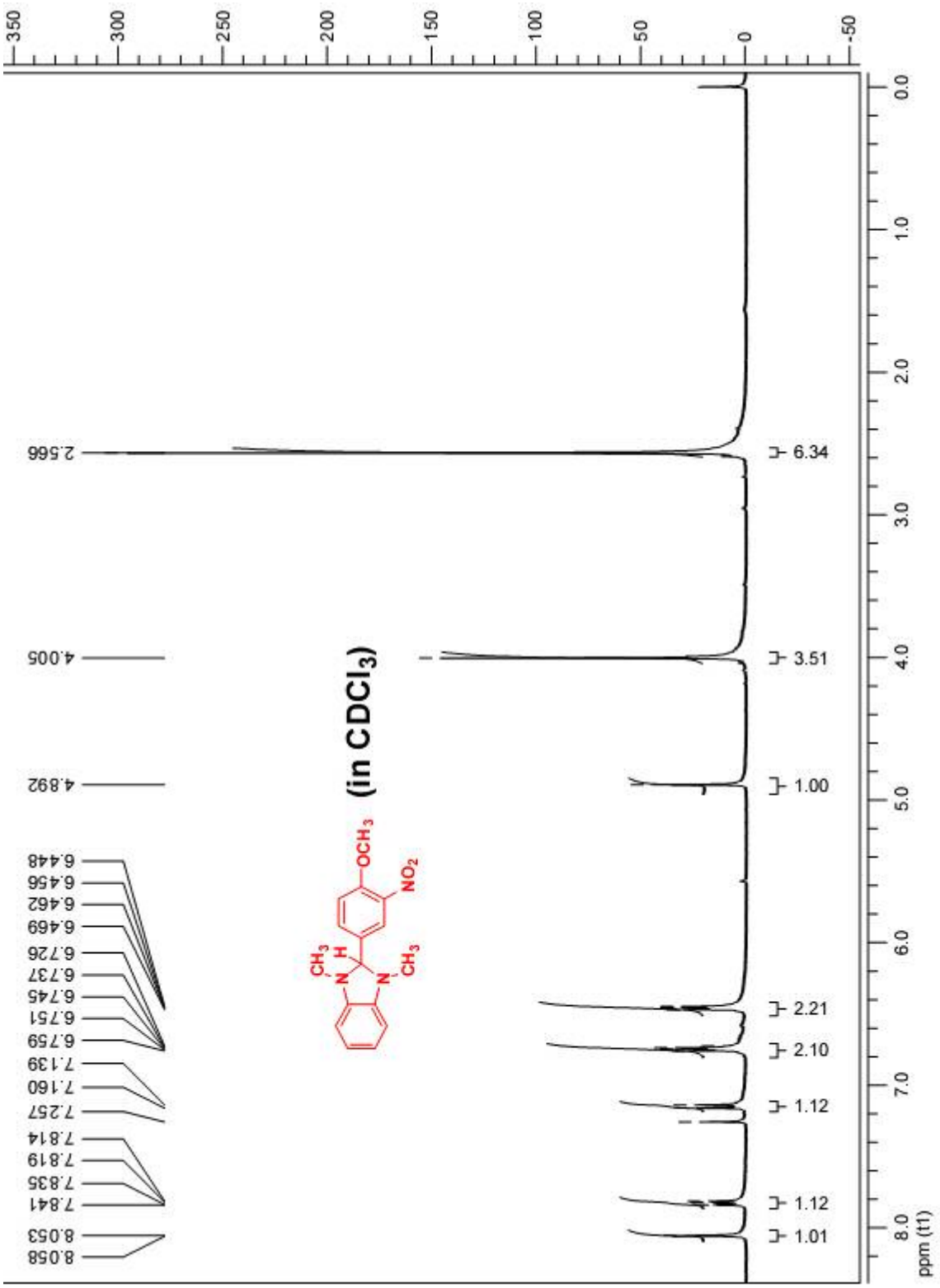
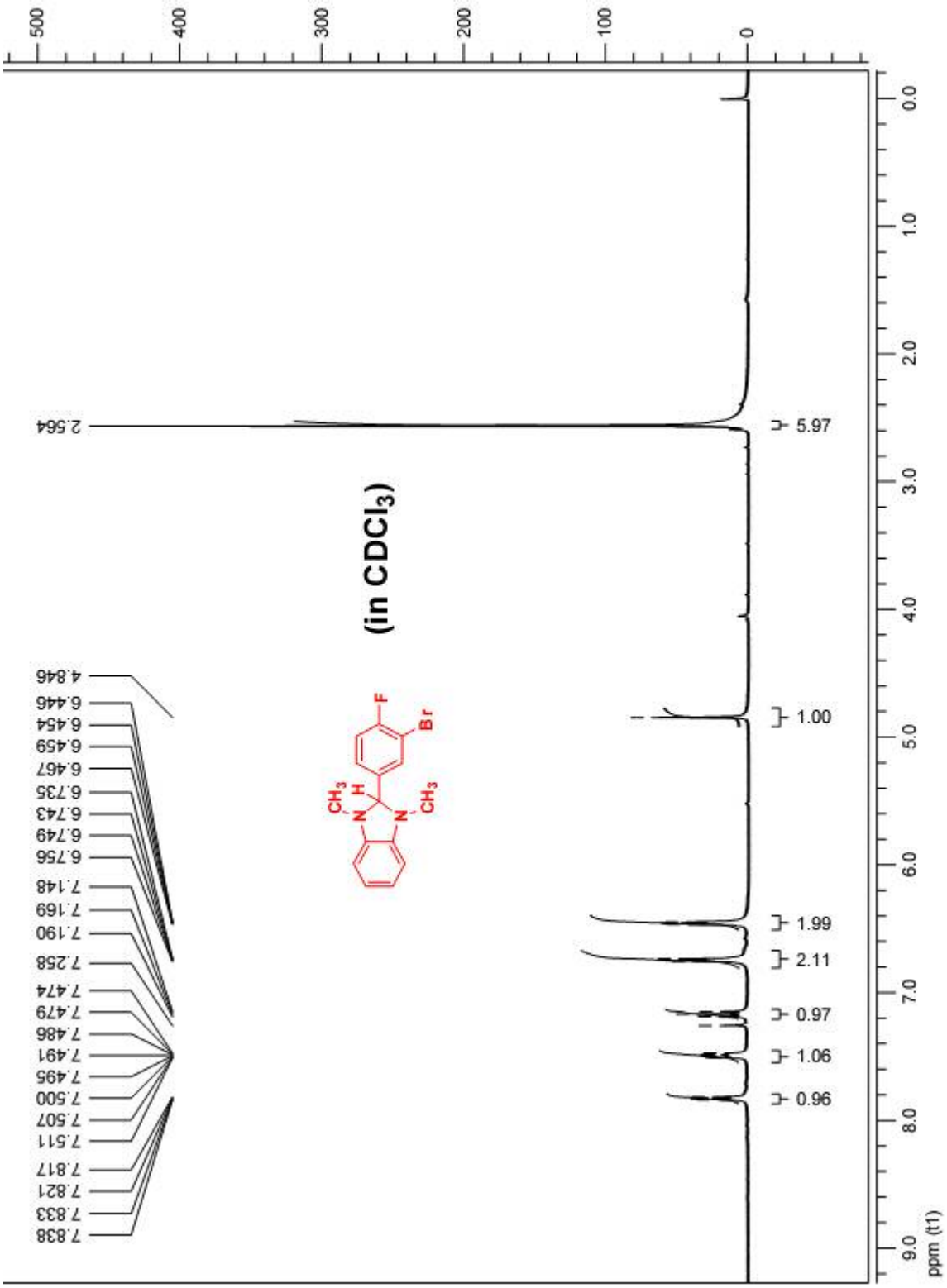
3.885
4.787
6.444
6.452
6.457
6.465
6.724
6.732
6.738
6.746
6.803
7.257
6.09
8.98
1.00
1.87
2.09
1.98
0.42
ppm (t1)


500
400
300
200
100
0
2.558
3.896
3.917
4.806
6.436
6.444
6.449
6.457
6.468
6.718
6.726
6.731
6.739
6.859
6.879
6.989
6.993
7.009
7.014
7.230
7.234
(in CDCl3)
OCH3
OCH3
CH3
H
N
N
CH3
6.74
6.59
1.00
2.02
2.28
1.33
1.47
1.45
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (t1)


(in CDCl3)
2.295
2.559
4.801
6.426
6.434
6.440
6.448
6.457
6.706
6.714
6.719
6.727
7.163
7.182
7.257
7.272
7.371
8.28
7.15
1.00
1.94
2.16
0.98
1.88
1.23
ppm (t1)


(in CDCl3)
OCH3
NO2
CH3
H
N
N
CH3
2.566
4.005
4.892
6.448
6.456
6.462
6.469
6.726
6.737
6.745
6.751
6.759
7.139
7.160
7.257
7.814
7.819
7.835
7.841
8.053
8.058
6.34
3.51
1.00
2.21
2.10
1.12
1.12
1.01
ppm (t1)


(in $CDCl_3$)
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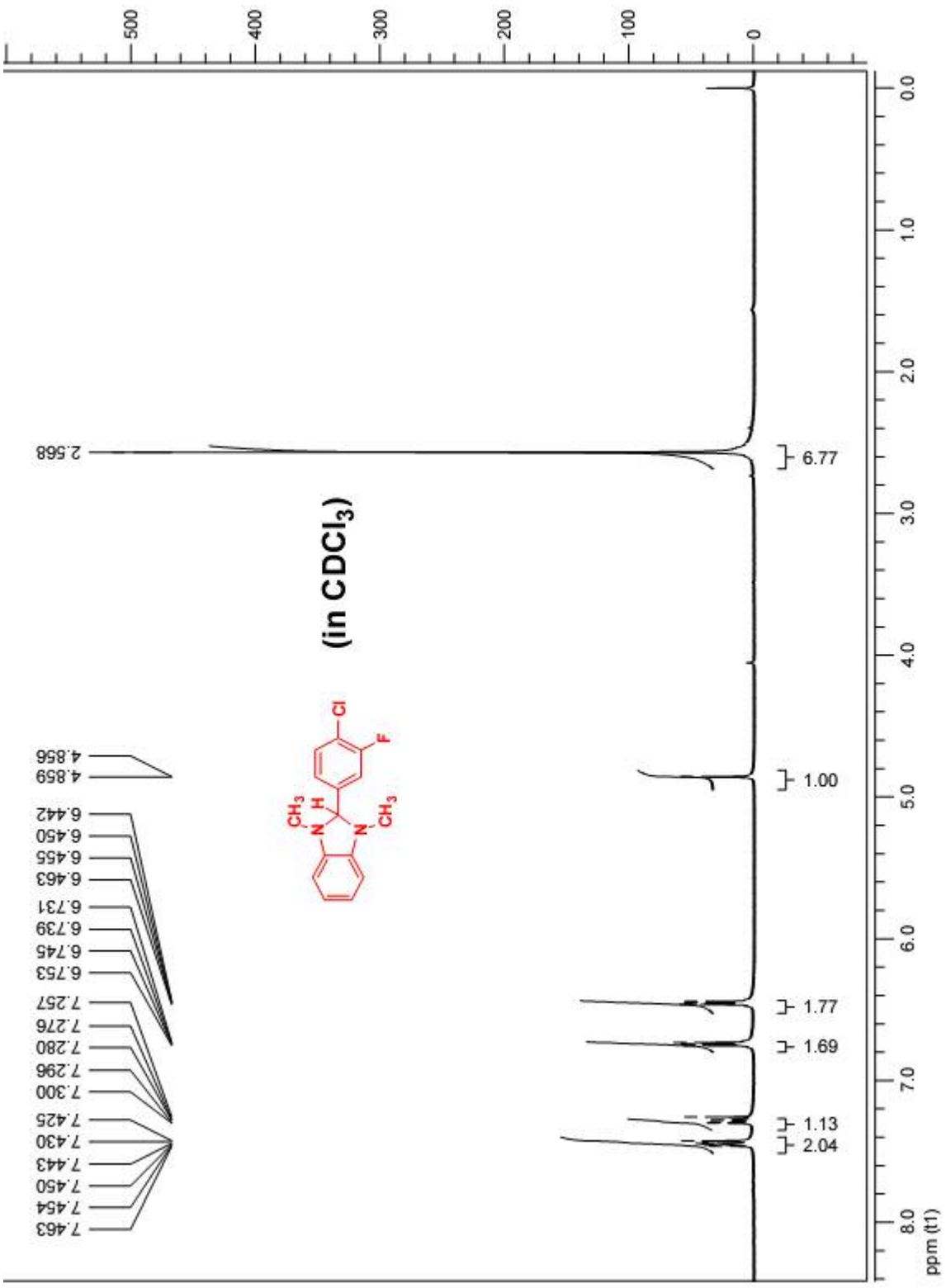
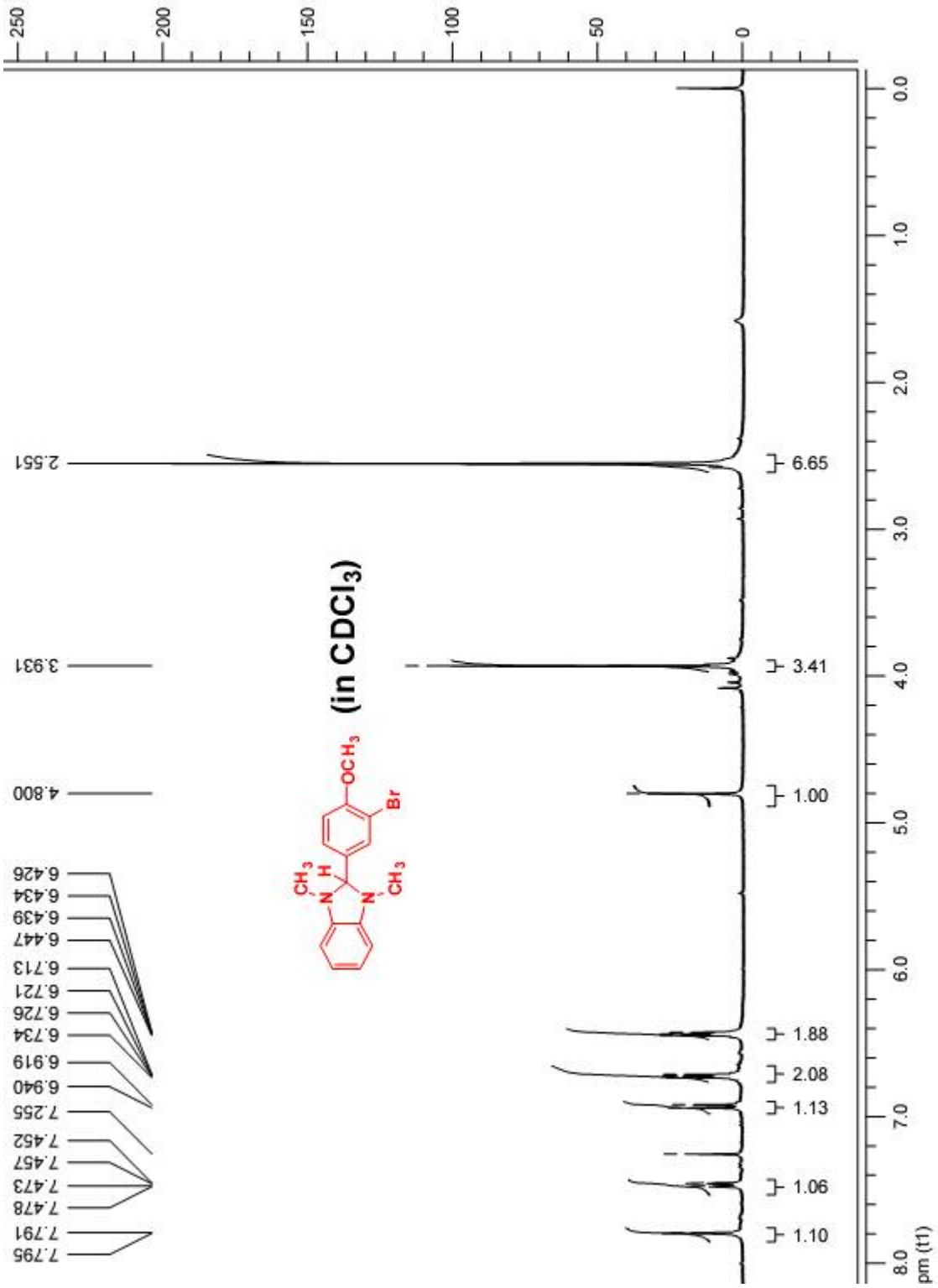
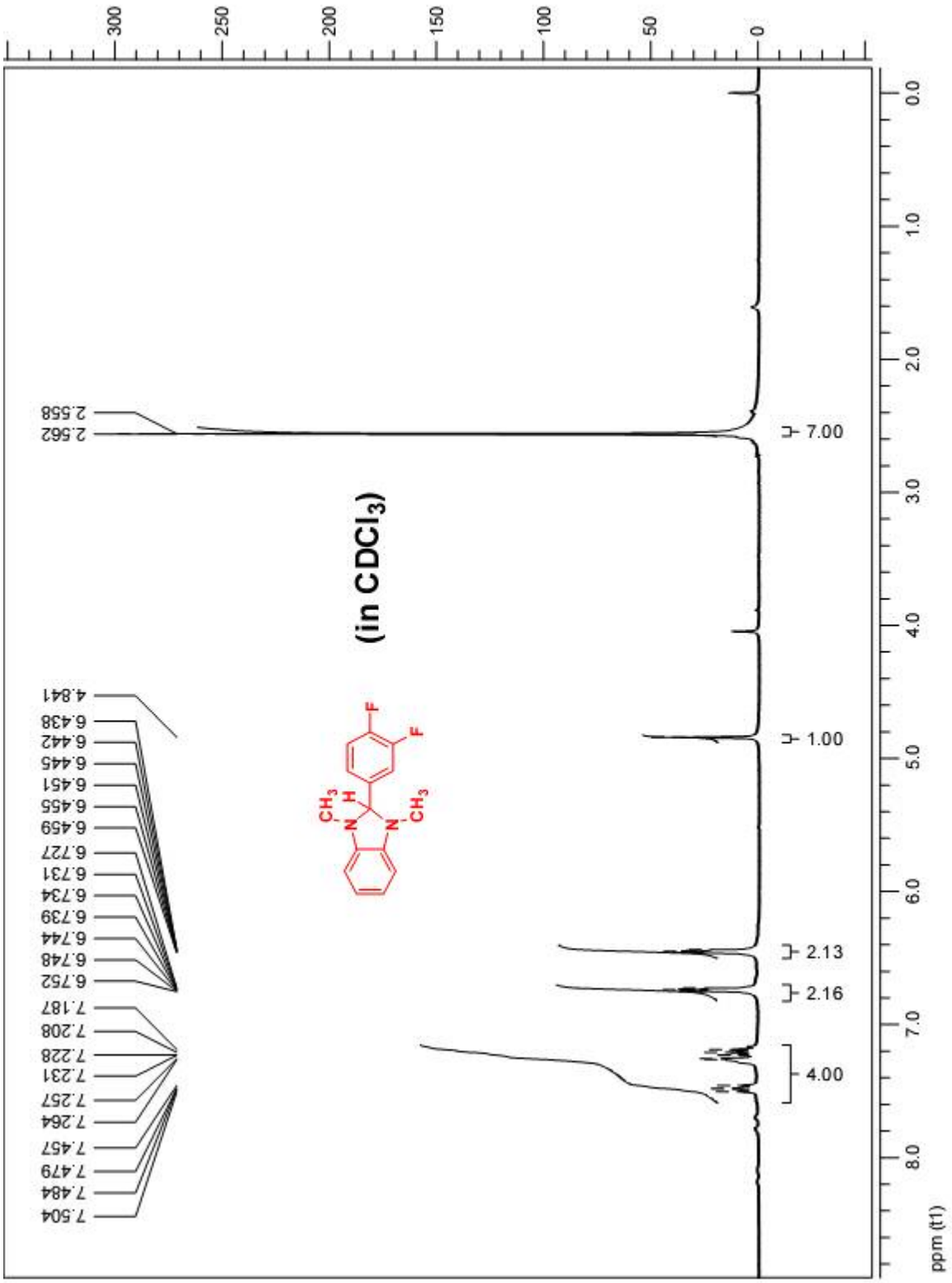
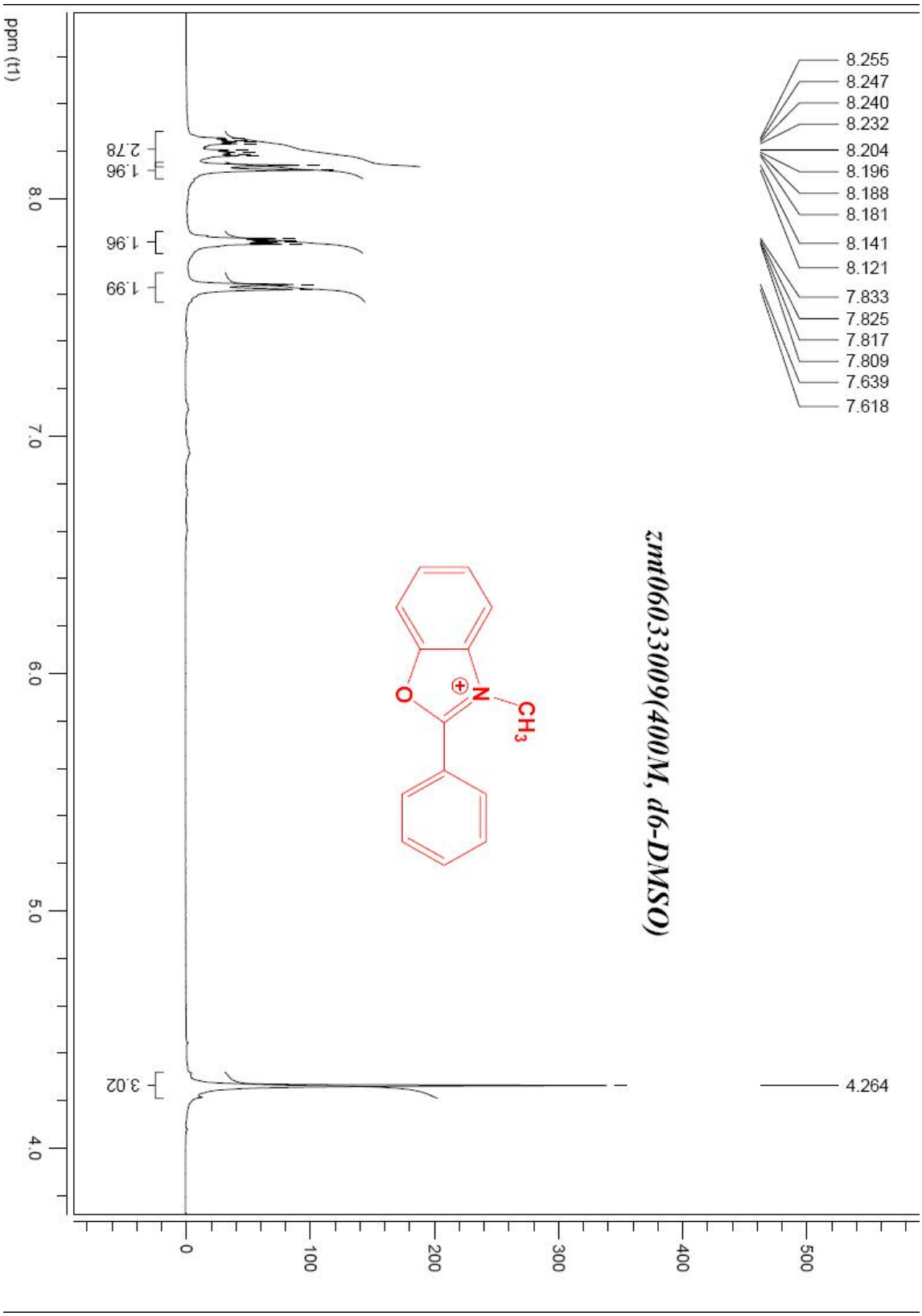
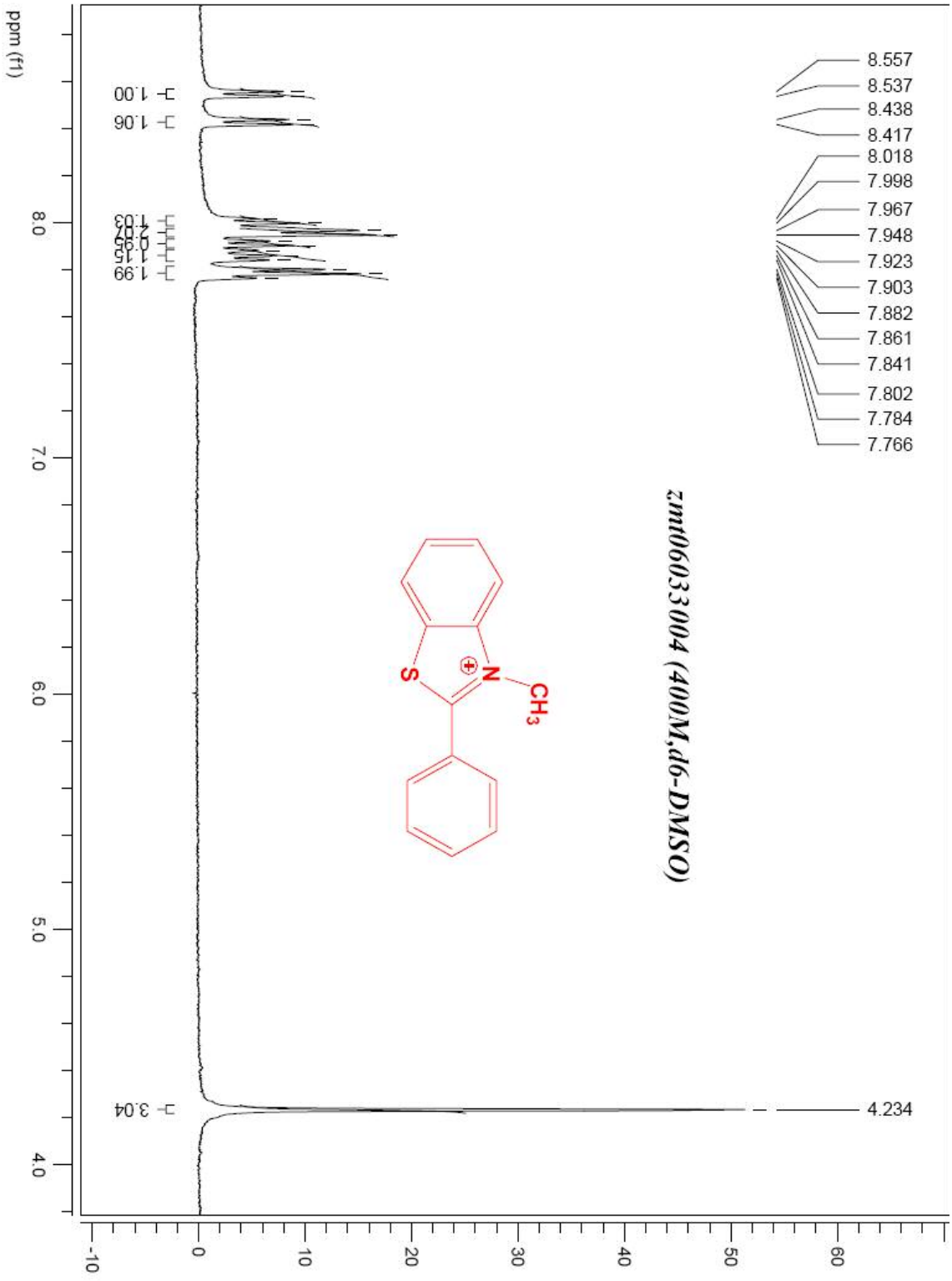
6.454
6.459
6.467
6.735
6.743
6.749
6.756
7.148
7.169
7.190
7.258
7.474
7.479
7.486
7.491
7.495
7.500
7.507
7.511
7.817
7.821
7.833
7.838
5.97
1.00
1.99
2.11
0.97
1.06
0.96
ppm (t1)


(in CDCl3)
2.568
4.856
4.859
6.442
6.450
6.455
6.463
6.731
6.739
6.745
6.753
7.257
7.276
7.280
7.296
7.300
7.425
7.430
7.443
7.450
7.454
7.463
6.77
1.00
1.77
1.69
1.13
2.04
ppm (t1)


(in CDCl3)
2.551
3.931
4.800
6.426
6.434
6.439
6.447
6.713
6.721
6.726
6.734
6.919
6.940
7.255
7.452
7.457
7.473
7.478
7.791
7.795
6.65
3.41
1.00
1.88
2.08
1.13
1.06
1.10
pm (t1)


(in CDCl3)
2.562
2.558
4.841
6.438
6.442
6.445
6.451
6.455
6.459
6.727
6.731
6.734
6.739
6.744
6.748
6.752
7.187
7.208
7.228
7.231
7.257
7.264
7.457
7.479
7.484
7.504
7.00
1.00
2.13
2.16
4.00
ppm (t1)

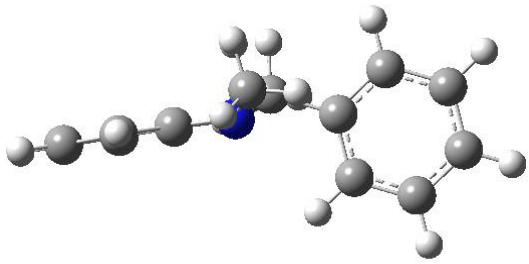

ppm (t1)
8.0
7.0
6.0
5.0
4.0
0
100
200
300
400
500
2.78
1.96
1.96
1.99
3.02
8.255
8.247
8.240
8.232
8.204
8.196
8.188
8.181
8.141
8.121
7.833
7.825
7.817
7.809
7.639
7.618
4.264
O
N
CH3
zmt060330009(400M, d6-DMSO)


8.557
8.537
8.438
8.417
8.018
7.998
7.967
7.948
7.923
7.903
7.882
7.861
7.841
7.802
7.784
7.766
4.234
3.04
1.00
1.06
1.03
2.05
0.99
1.15
1.99
zmt060330004 (400M,d6-DMSO)
S
N
CH3
ppm (f1)

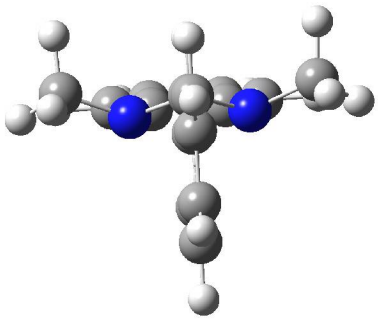
SI-13. Conformations of 3H (G = H) and Its Radical Cation $3H^{+\bullet}$ (G = H)

The geometries of the molecules were optimized at B3LYP/6-31+G* method, and each optimized structure was checked by the frequency calculation at the same level of the optimizations to be a real minimum without any imaginary frequency.

Scheme SI-1. The Conformation of **3H** (G = H)

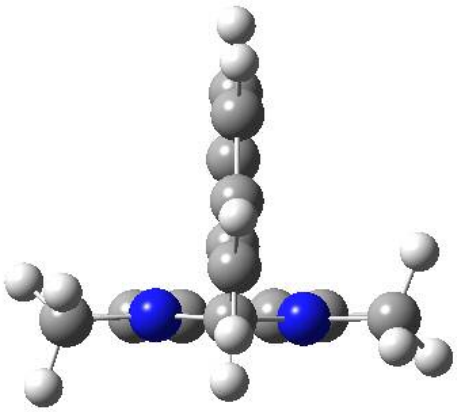


side-view

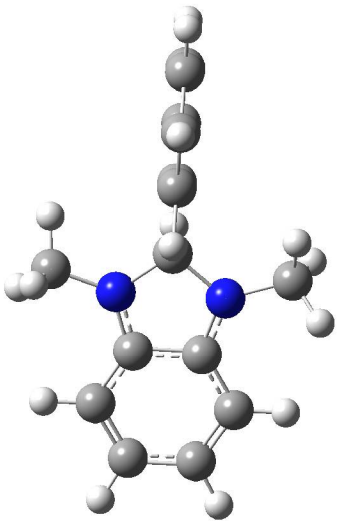


side-view

Scheme SI-2. The Conformation of the Radical Cation $\mathbf{3H^{+\bullet}}$ (G = H)



side-view



face-view

The absolute energies (in Hartrees) and optimized geometries of 3H and its radical cation, together with a reference to the program we used to carry out the calculations:

3H (G = H):

Energy HF = -690.7499388

Optimized structures:

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.962740	1.419448	0.207598
2	6	0	-4.159803	0.696949	0.384410
3	6	0	-1.783452	0.705439	0.041295
4	1	0	-2.971502	2.505569	0.198269
5	6	0	-4.159938	-0.696696	0.383806
6	6	0	-1.783595	-0.705313	0.040696
7	7	0	-0.457409	1.145400	-0.100138
8	1	0	-5.092938	1.239309	0.511111
9	6	0	-2.963004	-1.419258	0.206364
10	7	0	-0.457630	-1.145432	-0.101074
11	6	0	0.313352	0.000099	-0.610707
12	6	0	-0.170822	2.444036	-0.677942
13	1	0	-5.093175	-1.238988	0.510035
14	6	0	1.764614	-0.000160	-0.164660
15	6	0	-0.171371	-2.443636	-0.680061
16	1	0	-2.971944	-2.505369	0.196104
17	1	0	0.290535	0.000573	-1.729178
18	1	0	-0.700045	3.219808	-0.117544
19	1	0	0.901308	2.646328	-0.601057
20	1	0	-0.470898	2.508983	-1.739620
21	6	0	2.795598	0.001547	-1.109531
22	6	0	2.087476	-0.001954	1.199993
23	1	0	-0.700207	-3.219858	-0.119914
24	1	0	-0.472102	-2.507783	-1.741599
25	1	0	0.900814	-2.645928	-0.603985
26	6	0	4.135218	0.001534	-0.703899
27	6	0	3.421299	-0.001999	1.607815
28	1	0	2.550579	0.002870	-2.170181
29	1	0	1.284685	-0.003315	1.931810
30	6	0	4.449205	-0.000234	0.656237
31	1	0	4.927154	0.002879	-1.448663
32	1	0	3.662593	-0.003405	2.667951
33	1	0	5.488182	-0.000261	0.976455

Radical Cation $3H^{+\bullet}$ (G = H):
Energy HF = -690.5243447
Optimized structure

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.827833	-1.464505	0.261688
2	6	0	3.940827	-0.756140	0.685776
3	6	0	1.709971	-0.719557	-0.155771
4	1	0	2.819661	-2.548931	0.253170
5	6	0	3.961857	0.667228	0.703405
6	6	0	1.724978	0.718683	-0.121615
7	7	0	0.507593	-1.117669	-0.629171
8	1	0	4.823196	-1.297455	1.012555
9	6	0	2.867942	1.418894	0.304245
10	7	0	0.516761	1.164039	-0.537092
11	6	0	-0.348116	0.040674	-0.930086
12	6	0	0.052624	-2.490674	-0.805616
13	1	0	4.861509	1.173971	1.038406
14	6	0	-1.698764	0.018784	-0.233987
15	6	0	0.126333	2.552113	-0.741761
16	1	0	2.894919	2.502943	0.317365
17	1	0	-0.511263	0.080375	-2.020479
18	1	0	-0.344099	-2.895530	0.132209
19	1	0	-0.736764	-2.512929	-1.559446
20	1	0	0.885236	-3.109340	-1.149343
21	6	0	-2.869221	0.033125	-1.001011
22	6	0	-1.780071	-0.018391	1.166288
23	1	0	0.558831	3.173900	0.045501
24	1	0	0.466580	2.914873	-1.719562
25	1	0	-0.961345	2.626311	-0.684915
26	6	0	-4.118793	0.008977	-0.373225
27	6	0	-3.027102	-0.042276	1.789503
28	1	0	-2.811167	0.063799	-2.087309
29	1	0	-0.874619	-0.025257	1.769200
30	6	0	-4.197164	-0.029268	1.019957
31	1	0	-5.024336	0.020553	-0.972700
32	1	0	-3.088687	-0.069943	2.873588
33	1	0	-5.166922	-0.047948	1.508859

Reference:

Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.01; Gaussian, Inc.: Wallingford, CT, 2004.

Acknowledgment. We are also grateful to the computational support of Nankai University ISC, and the technical support of the Center for Theoretical and Computational Chemistry, College of Chemistry of Nankai University.

SI-14. Plots of ΔH_H^-(ZH), ΔH_H(ZH), ΔH_P($ZH^{+\bullet}$) and ΔH_H($ZH^{+\bullet}$) as well as E_{ox}(ZH) and E_{red}(Z^+) against the Sum of Hammett Substituent Parameters σ_p and σ_m

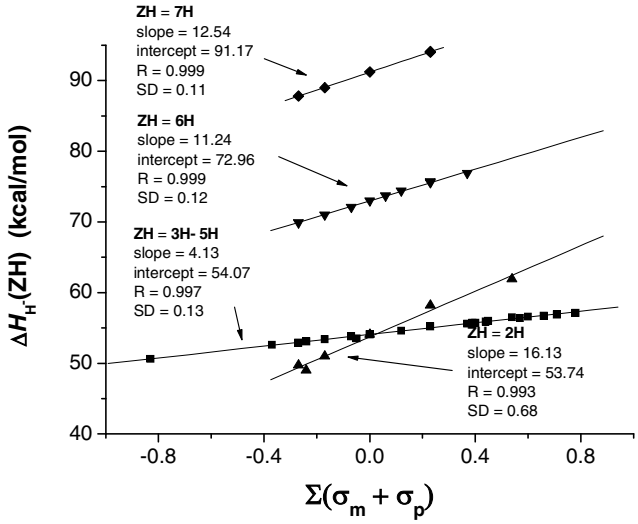


Figure S1. Plot of ΔH_H^-(**ZH**) against the sum of Hammett substituent parameters σ_p and σ_m.

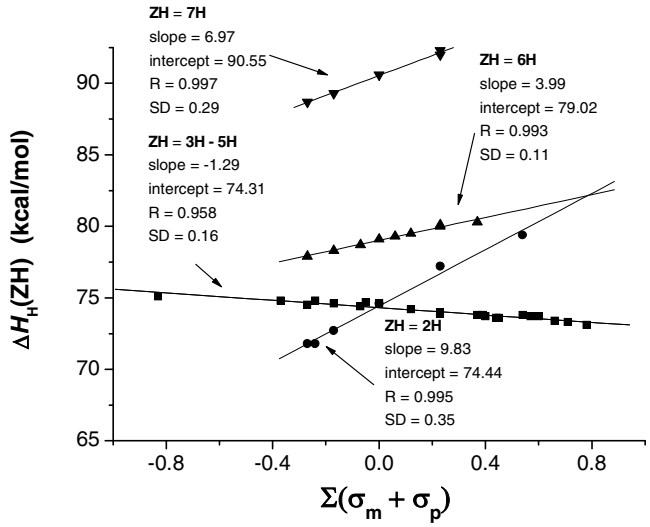


Figure S2. Plot of ΔH_H(**ZH**) against the sum of Hammett substituent parameters σ_p and σ_m.

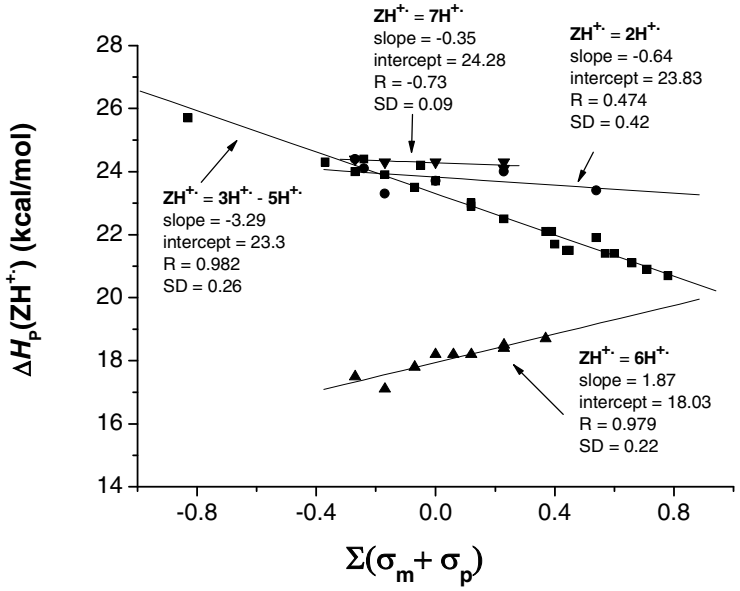


Figure S3. Plot of $\Delta H_P(\mathbf{ZH})^{+\bullet}$ against the sum of Hammett substituent parameters σ_p and σ_m.

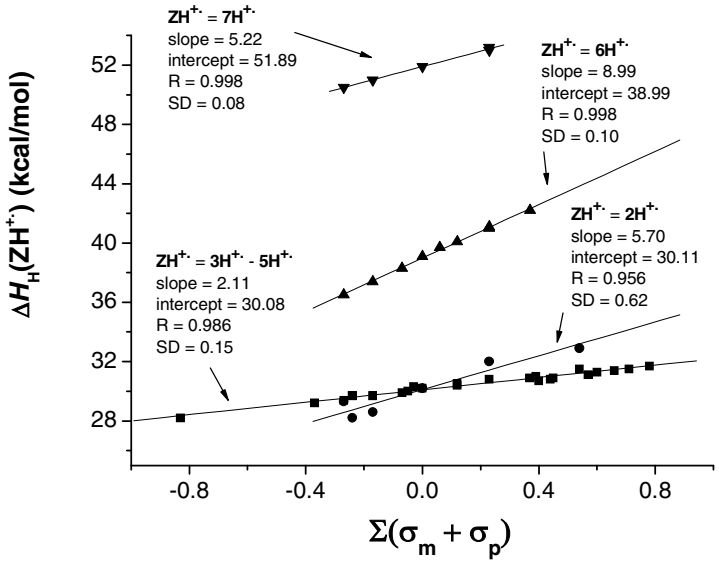


Figure S4. Plot of $\Delta H_H(\mathbf{ZH}^{+\bullet})$ against the sum of Hammett substituent parameters σ_p and σ_m.

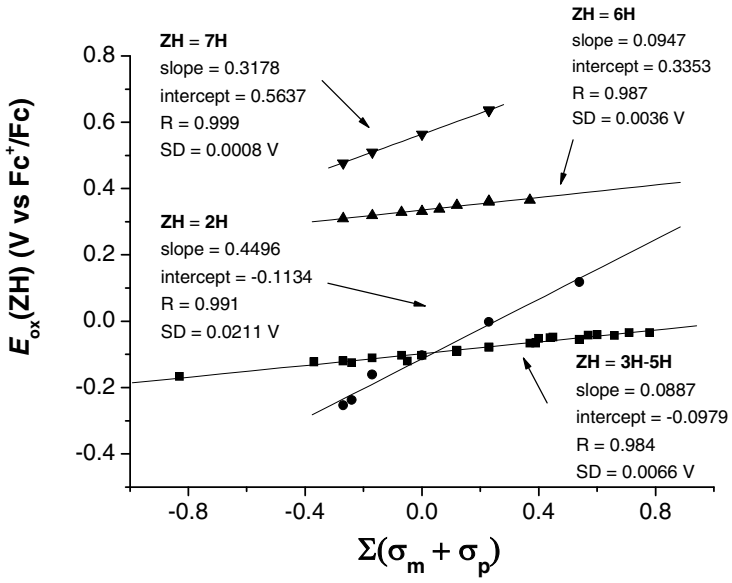


Figure S5. Plot of E_{ox}(**ZH**) against the sum of Hammett substituent parameters σ_p and σ_m.

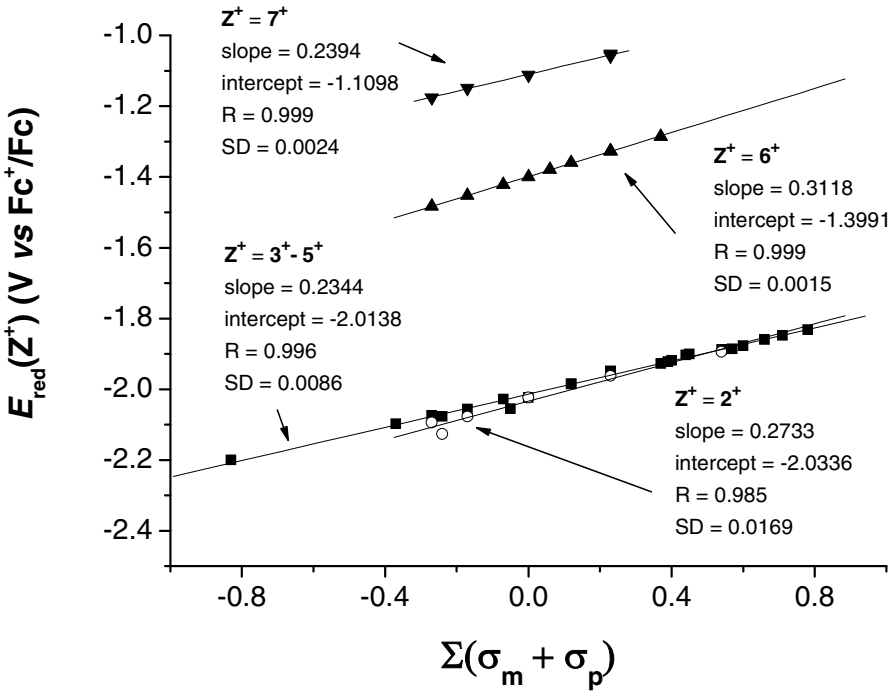


Figure S6. Plot of E_{red}($\mathbf{Z}^+$) against the sum of Hammett substituent parameters σ_p and σ_m.

SI-15. Dual-correlations of the effective charge on the C(2) in $ZH^{+\bullet}$, $Z^{\bullet}$, and Z^{+} with F and R of the groups: $N(Me)C_6H_5$, SC_6H_5 and OC_6H_5

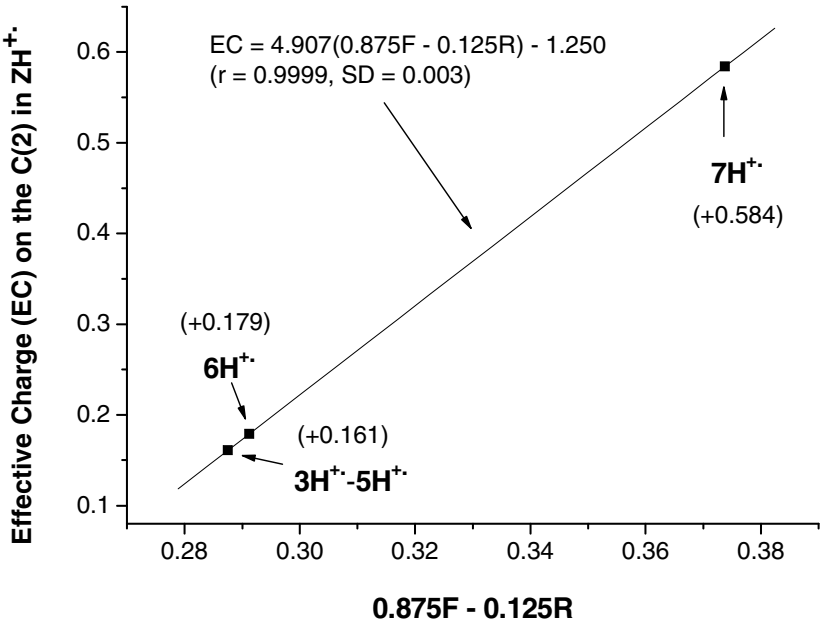


Figure S7. Dual-correlation of the effective charge on the C(2) in $\mathbf{3H^{+\bullet}}$-$\mathbf{5H^{+\bullet}}$, $\mathbf{6H^{+\bullet}}$and $\mathbf{7H^{+\bullet}}$ with the inductive and resonance parameters (F and R) of the groups: $N(Me)C_6H_5$, SC_6H_5 and OC_6H_5.

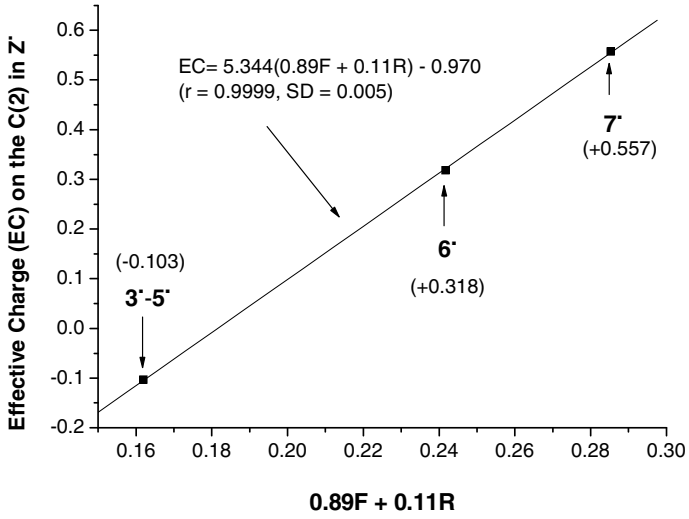


Figure S8. Dual-parameter correlation of the effective charge on the C(2) in **3**$^{\bullet}$-**5**$^{\bullet}$, **6**$^{\bullet}$ and **7**$^{\bullet}$ with the inductive and resonance parameters (F and R) of the groups: $N(Me)C_6H_5$, SC_6H_5 and OC_6H_5.

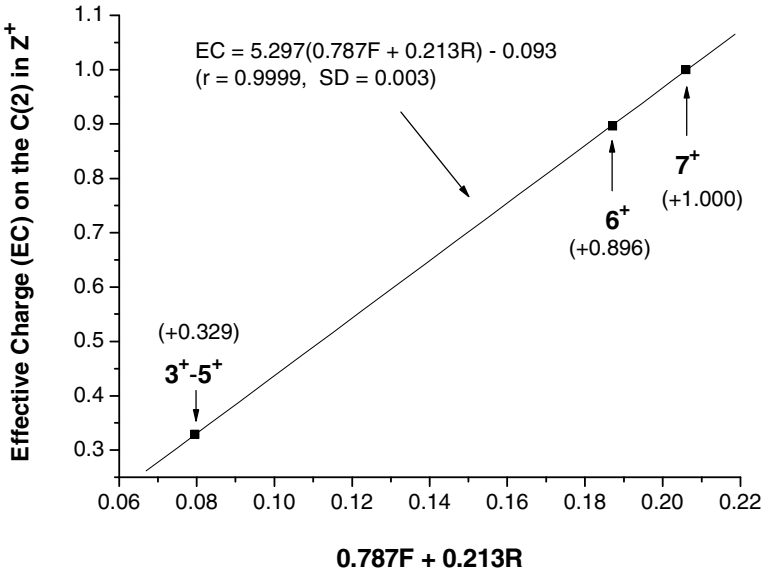
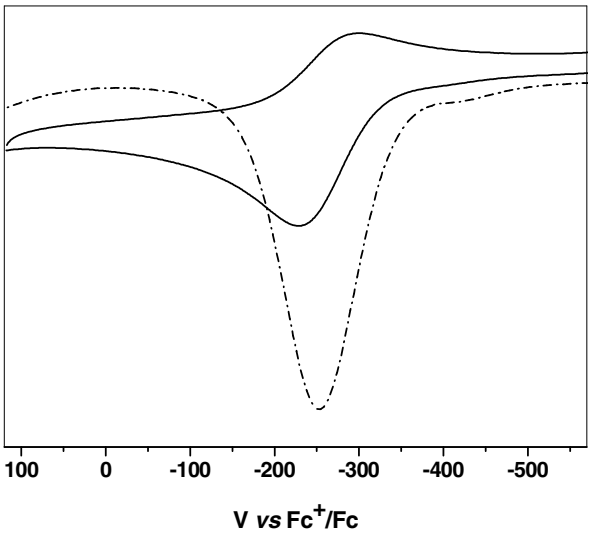


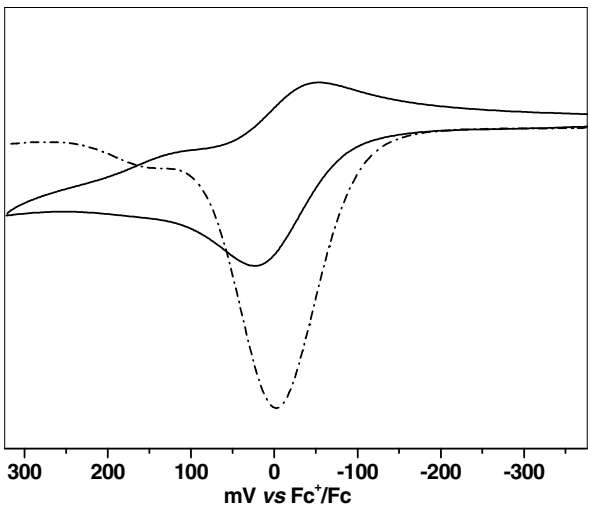
Figure S9. Dual-correlation of the effective charge on the C(2) in **3**$^{+}$-**5**$^{+}$, **6**$^{+}$ and **7**$^{+}$ with the inductive and resonance parameters (F and R) of the groups: $N(Me)C_6H_5$, SC_6H_5 and OC_6H_5.

SI-16. CV and OSWV Graphs of Some Representative ZH and Z^+

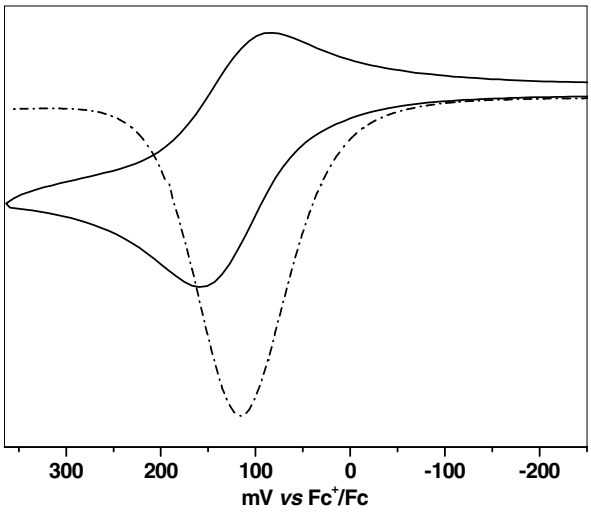
(1) 2H (G-CH_3O, m-H):



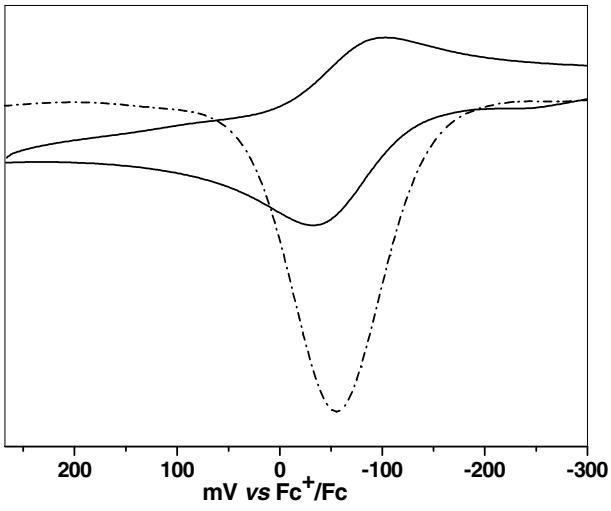
(2) 2H (p-Cl, m-H):



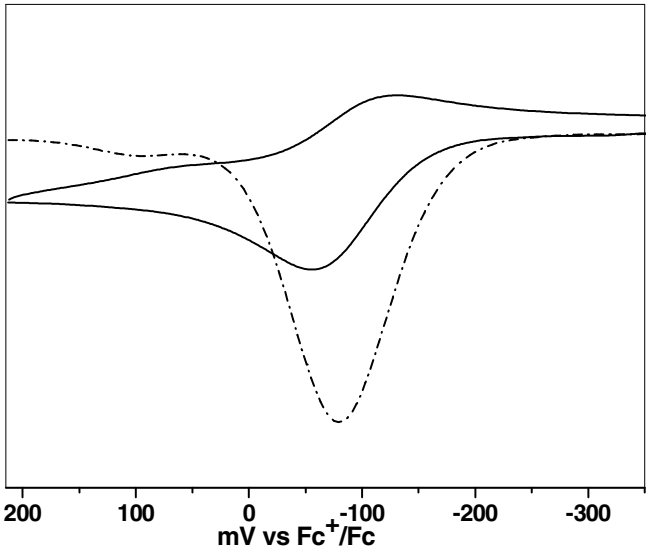
(3) 2H (p-CF3, m-H):



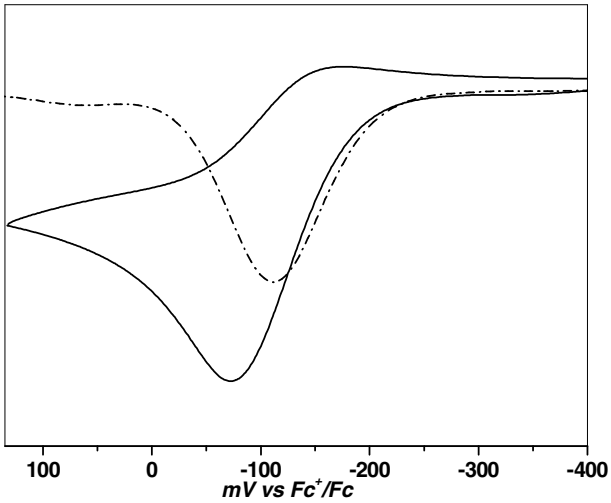
(4) 3H (p-CF_3):



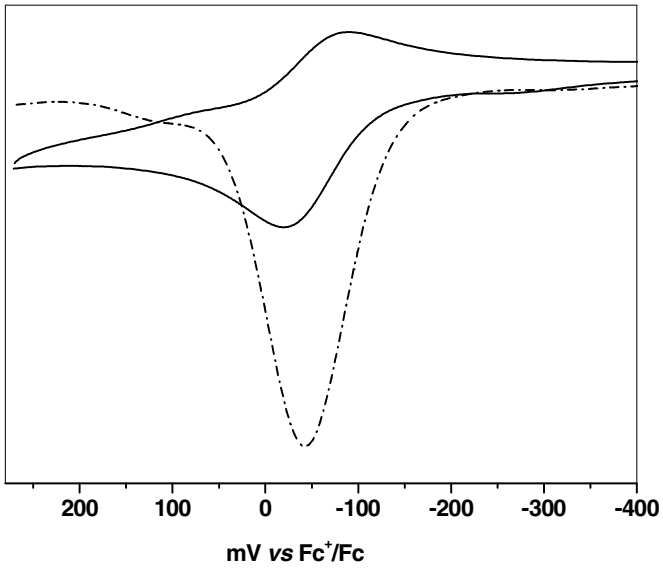
(5) 3H (p-Cl):



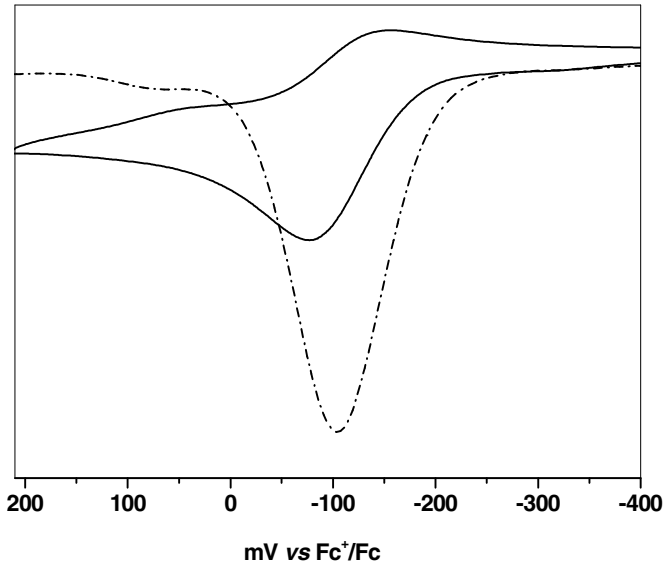
(6) 3H (p-CH_3):



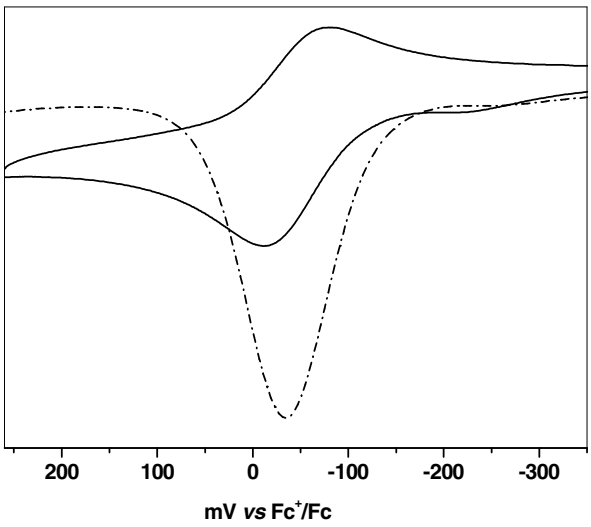
(7) 3H (p-CN):



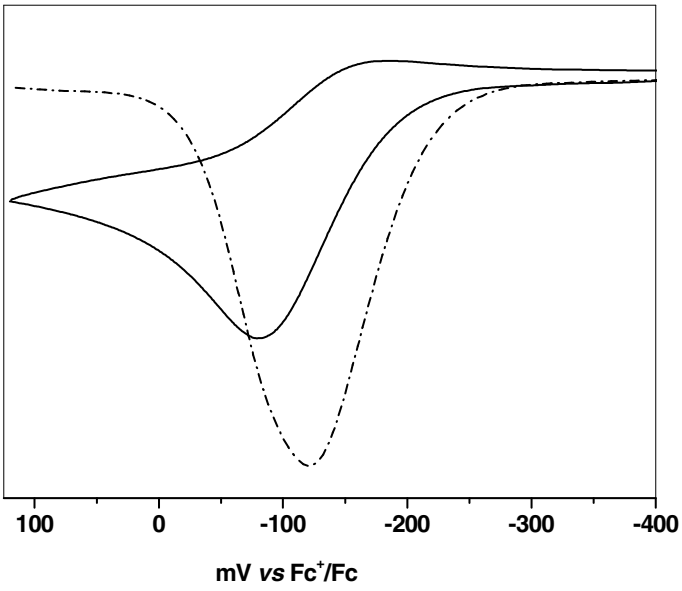
(8) 3H (p-H):



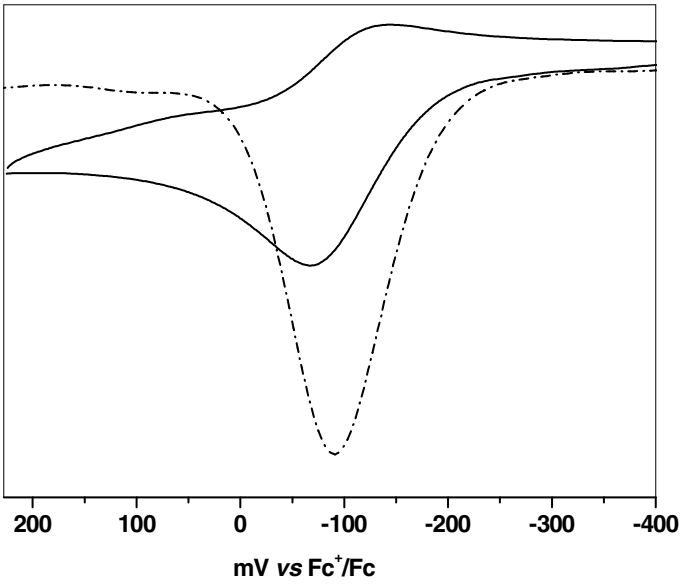
(9) 3H (G = NO_2):



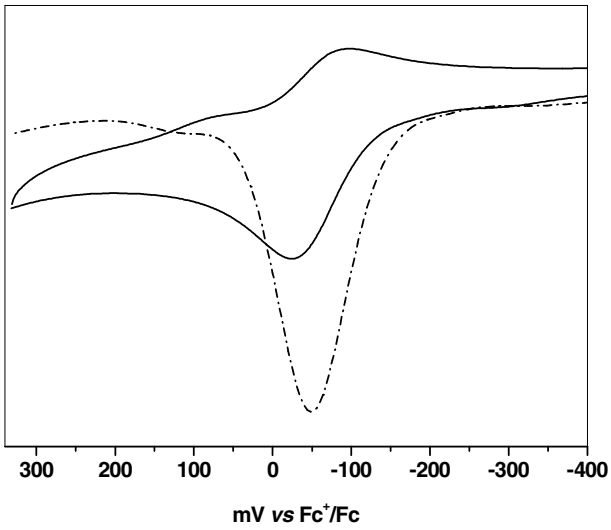
(10) 3H (G = CH_3O):



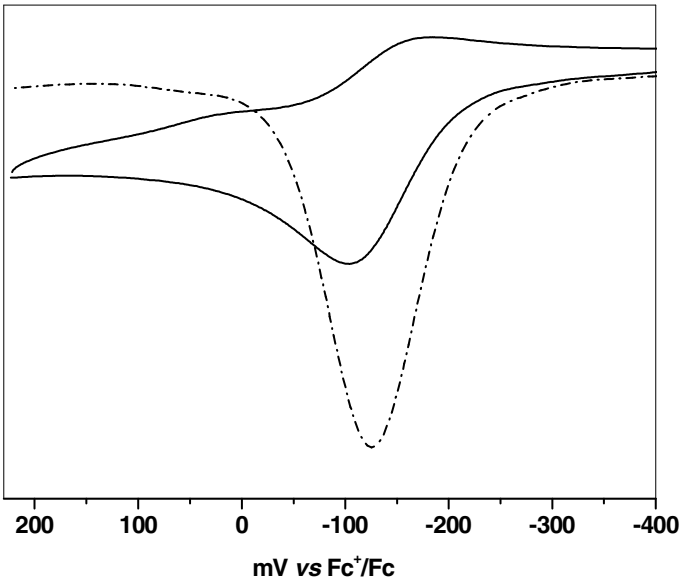
(11) 4H (*m*-Br, *p*-CH_3O):



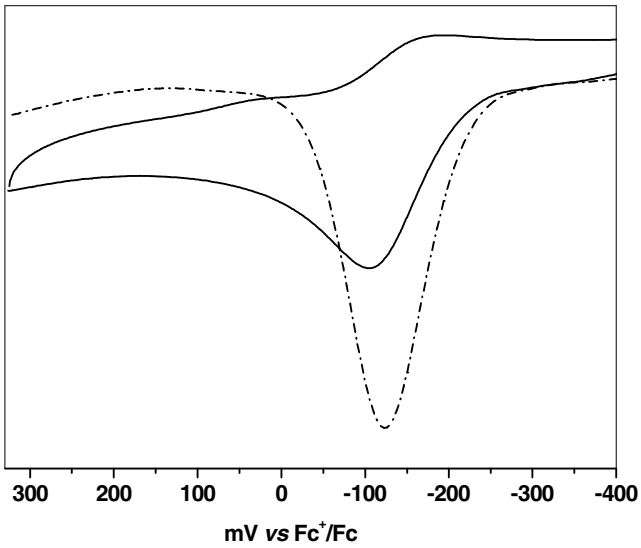
(12) 4H (*m*-Br, *p*-F):



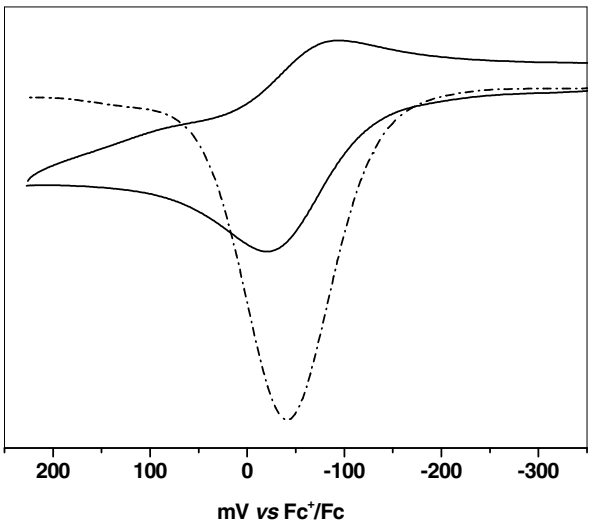
(13) 4H (*m*-CH_3, *p*-CH_3):



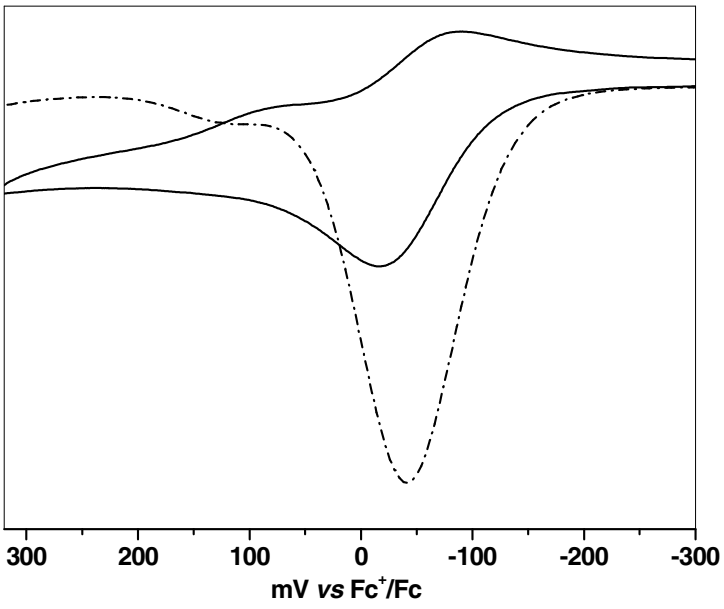
(14) 4H (*m*-CH_3O, *p*-CH_3O):



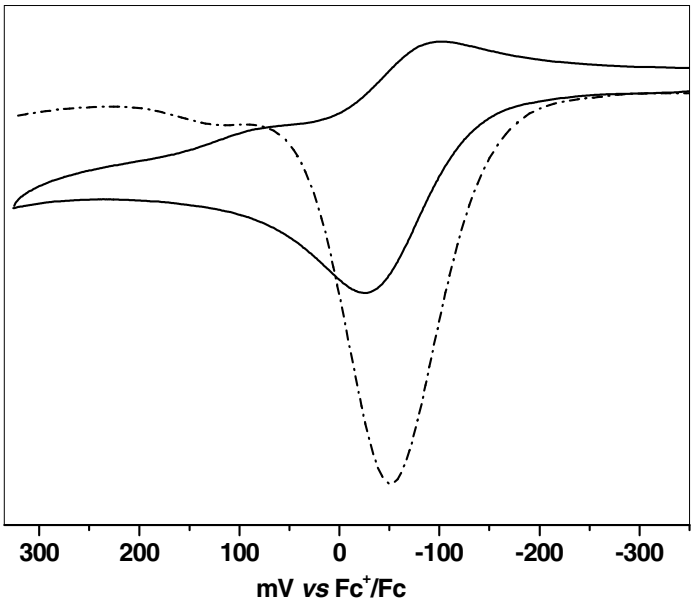
(15) 4H (*m*-Cl, *p*-Cl):



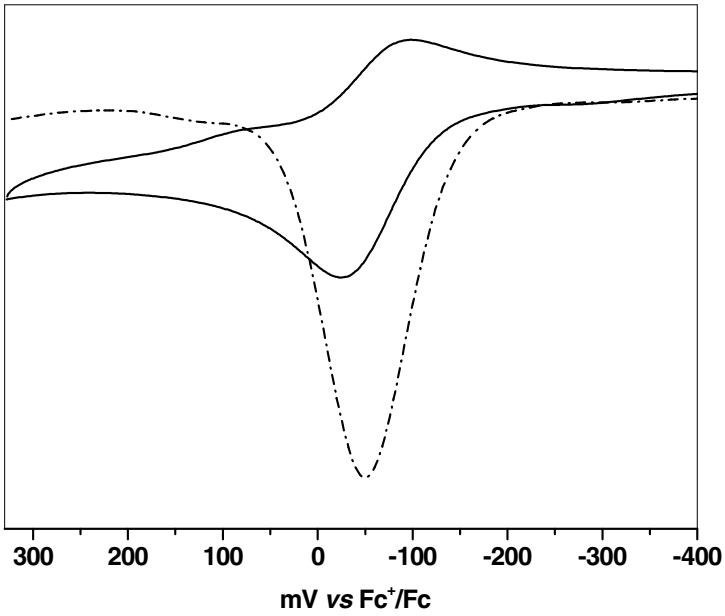
(16) 4H (*m*-F, *p*-Cl):



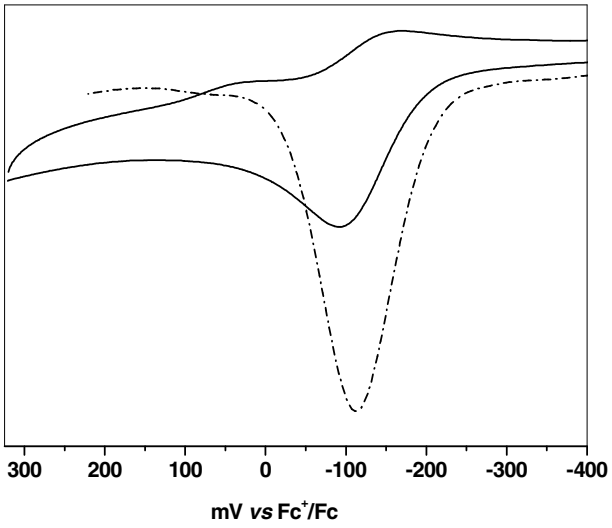
(17) 4H (*m*-NO_2, *p*-CH_3O):



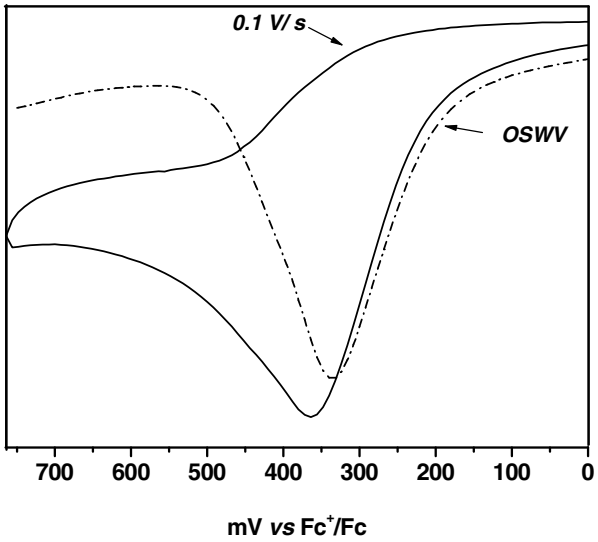
(18) 4H (*m*-F, *p*-F):



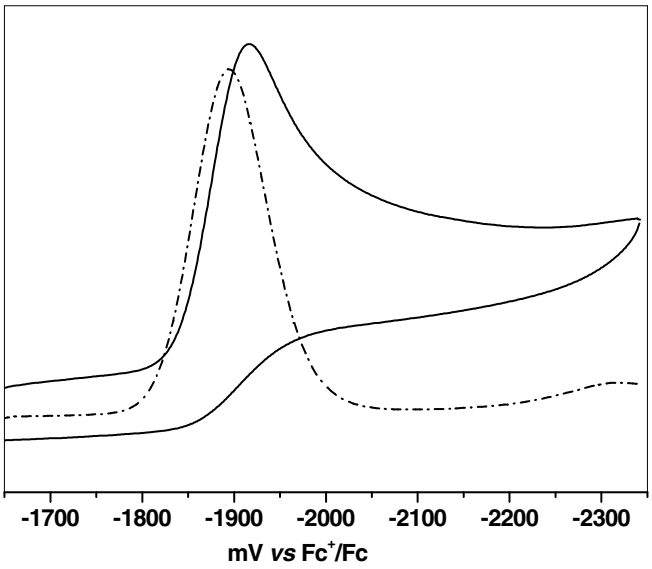
(19) 5H:


300
200
100
0
-100
-200
-300
-400
mV vs Fc+/Fc

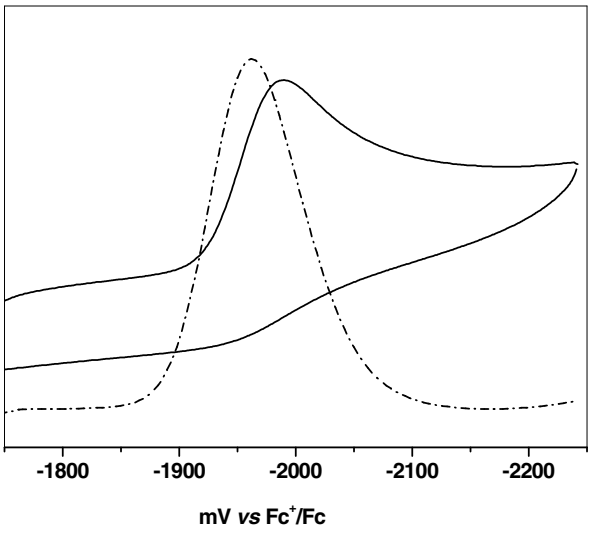
(20) 6H (p-H):


0.1 V/ s
OSWV
700
600
500
400
300
200
100
0
mV vs Fc+/Fc

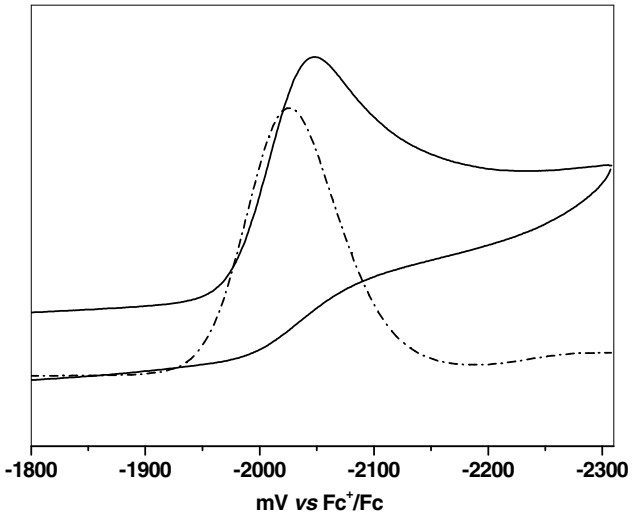
(21) 2^+ (p-CF_3, m-H):



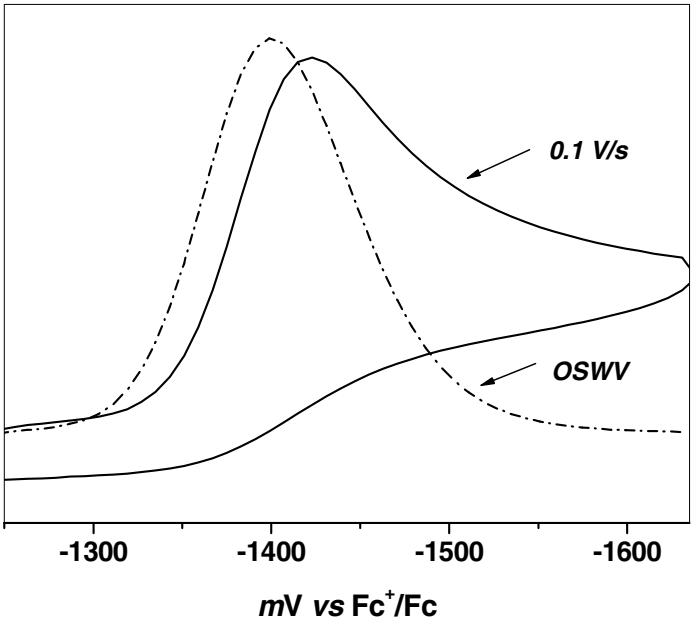
(22) 2^+ (p-Cl, m-H):



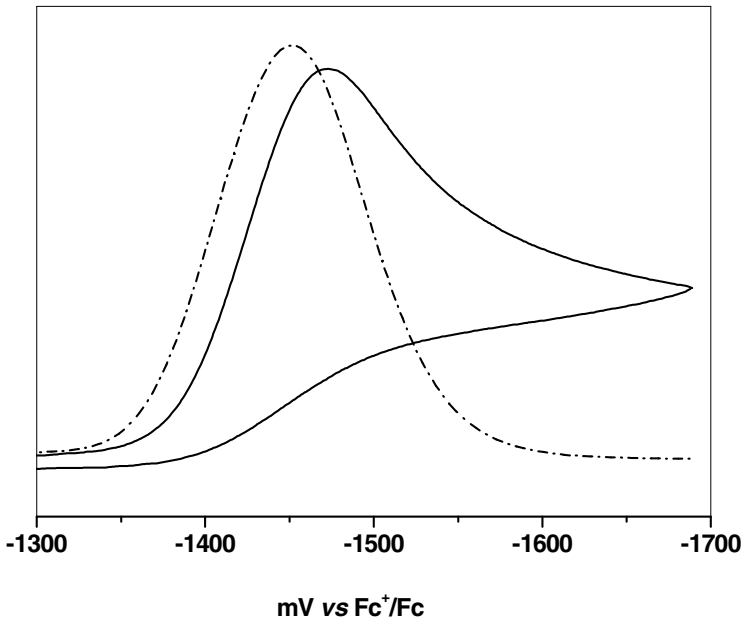
(23) 3^+ (p-H):


-1800
-1900
-2000
-2100
-2200
-2300
mV vs Fc+/Fc

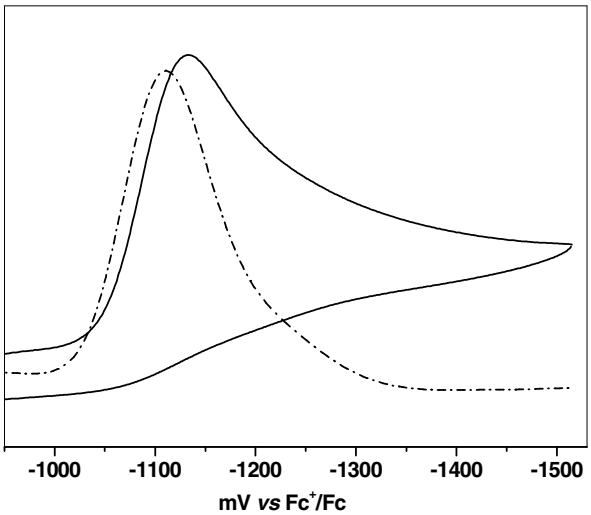
(24) 6^+ (p-H):


0.1 V/s
OSWV
-1300
-1400
-1500
-1600
mV vs Fc+/Fc

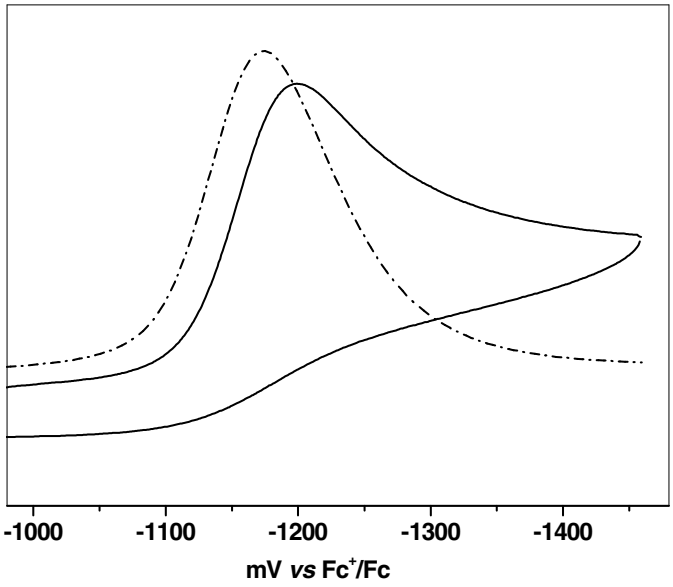
(25) 6^+ (p-CH_3):



(26) 7^+ (p-H):

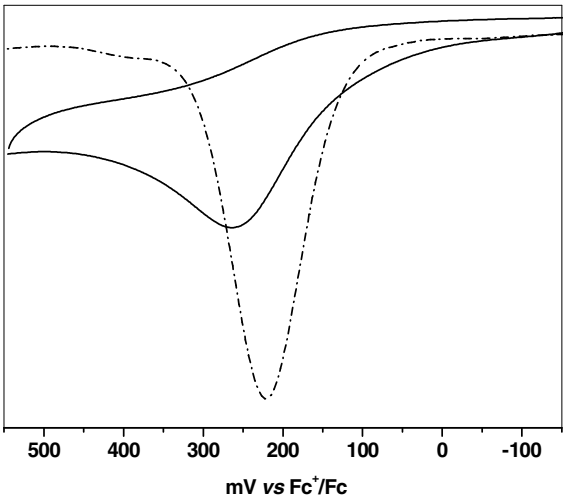


(27) 7^+ (p-CH_3O):

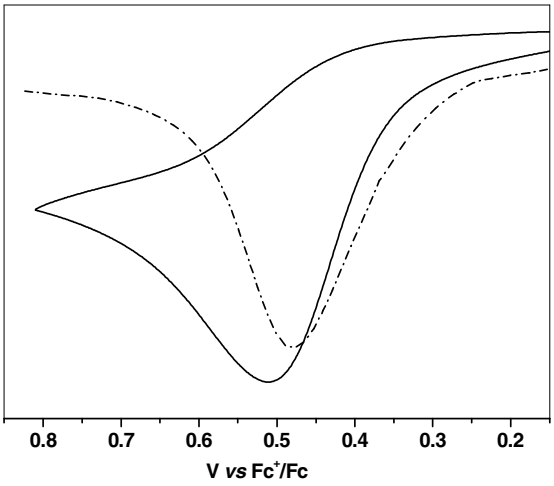


SI-17. CV and OSWV Graphs of BNAH, HEH and $AcrH_2$ as well as BNA^+, HE^+ and $AcrH^+$

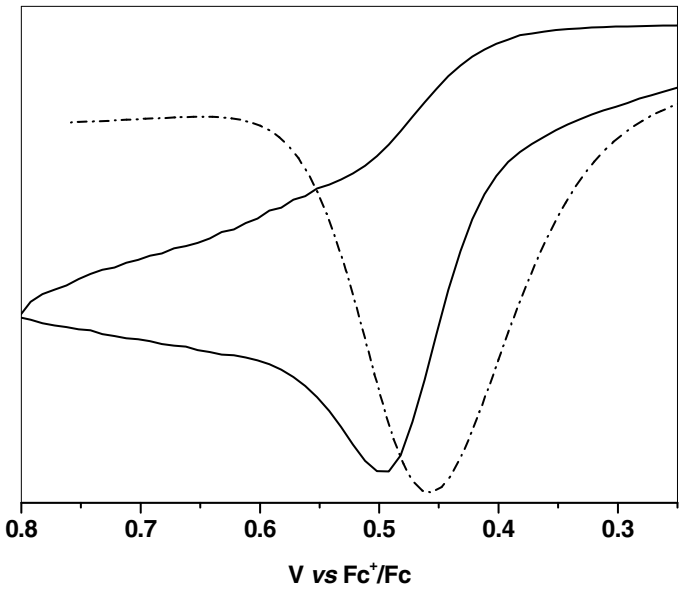
(1) BNAH:



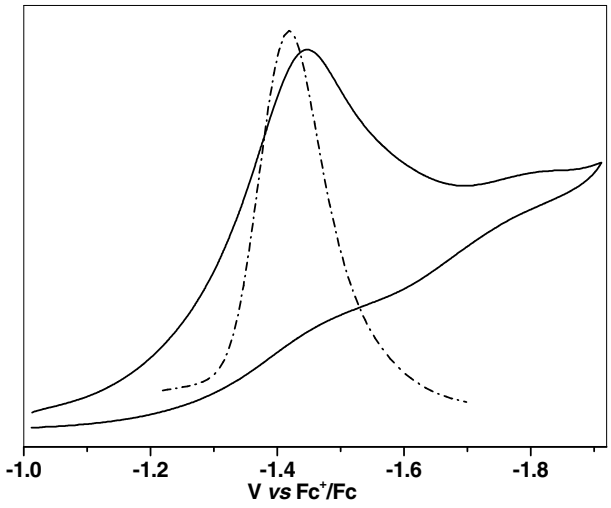
(2) HEH:



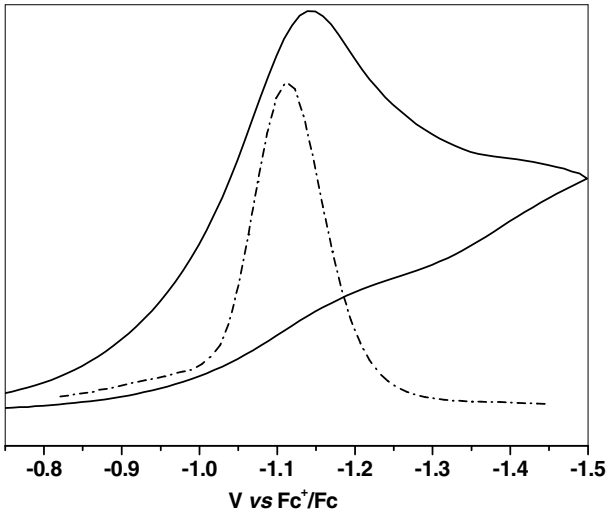
(3) $AcrH_2$:



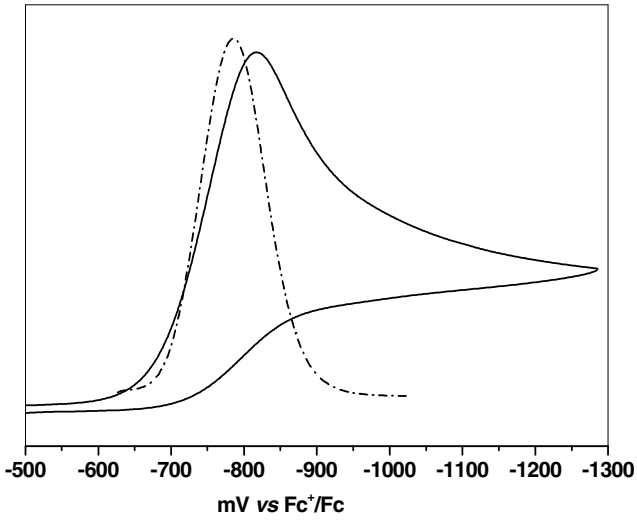
(4) BNA^+:



(5) HE^+:


-0.8
-0.9
-1.0
-1.1
-1.2
-1.3
-1.4
-1.5
V vs Fc+/Fc

(6) $AcrH^+$:


-500
-600
-700
-800
-900
-1000
-1100
-1200
-1300
mV vs Fc+/Fc

SI-18. Derivation of Eqs (4) and (6):

Derivation of Eq (4) in the Text:

$$\mathbf{ZH} \xrightarrow{(1)} \mathbf{Z}^{\oplus} + H^{\ominus} \qquad \Delta H(1) = \Delta H_H\text{-}(\mathbf{ZH})$$

$$AcrH_2 \xrightarrow{(2)} AcrH^{\oplus} + H^{\ominus} \qquad \Delta H(2) = \Delta H_H\text{-}(AcrH_2)$$

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(1) - (2):

$$\mathbf{ZH} - AcrH_2 \xrightarrow{(3)} \mathbf{Z}^{\oplus} + H^{\ominus} - AcrH^{\oplus} - H^{\ominus}$$

$$\Delta H(3) = \Delta H(1) - \Delta H(2) = \Delta H_H\text{-}(\mathbf{ZH}) - \Delta H_H\text{-}(AcrH_2)$$

$$\mathbf{ZH} + AcrH \xrightarrow{(3)} \mathbf{Z} + AcrH_2$$

$$\Delta H_r = \Delta H(3) = \Delta H_H\text{-}(\mathbf{ZH}) - \Delta H_H\text{-}(AcrH_2)$$

$$\boxed{\Delta H_H\text{-}(\mathbf{ZH}) = \Delta H_H\text{-}(AcrH_2) + \Delta H_r}$$

Derivation of Eq (6) in the Text:

$$\mathbf{3H} \xrightarrow{(1)} \mathbf{3}^{\oplus} + \mathbf{H}^{\ominus} \qquad \Delta H(1) = \Delta H_{\mathrm{H}}\text{-}(\mathbf{3H})$$

$$\mathbf{ZH} \xrightarrow{(2)} \mathbf{Z}^{\oplus} + \mathbf{H}^{\ominus} \qquad \Delta H(2) = \Delta H_{\mathrm{H}}\text{-}(\mathbf{ZH})$$

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(1) + (2):

$$\mathbf{3H - ZH} \xrightarrow{(3)} \mathbf{3}^{\oplus} + \mathbf{H}^{\ominus} - \mathbf{Z}^{\oplus} - \mathbf{H}^{\ominus}$$

$$\Delta H(3) = \Delta H(1) - \Delta H(2) = \Delta H_{\mathrm{H}}\text{-}(\mathbf{3H}) - \Delta H_{\mathrm{H}}\text{-}(\mathbf{ZH})$$

$$\mathbf{3H} + \mathbf{Z}^{\oplus} \xrightarrow{(3)} \mathbf{3}^{\oplus} + \mathbf{ZH}$$

$$\Delta H_{\mathrm{r}} = \Delta H(3) = \Delta H_{\mathrm{H}}\text{-}(3\mathrm{H}) - \Delta H_{\mathrm{H}}\text{-}(\mathrm{ZH})$$

$$\boxed{\Delta H_{\mathrm{H}}\text{-}(\mathbf{ZH}) = \Delta H_{\mathrm{H}}\text{-}(\mathbf{3H}) - \Delta H_{\mathrm{r}}}$$