Supporting Information

Reactions of dinuclear Ni_2 complexes $[Ni(RN_{Py}S_4)]_2$ ($RN_{Py}S_4$ = 2,6-bis(2-mercaptophenylthiomethyl-4-R-pyridine) with $Fe(CO)_3$(BDA) (BDA = benzylidene acetone) leading to heterodinuclear NiFe and mononuclear Fe complexes related to the active sites of [NiFe]- and [Fe]-hydrogenases

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Contents:

I. Preparation of new starting material 2,6-bis[(tosyloxy)methyl]-4-methylthiopyridine and its precursor 2,6-bis(hydroxymethyl)-4-methylthiopyridine

(1) Preparation of 2,6-bis(hydroxymethyl)-4-methylthiopyridine

This new precursor was prepared from the previously reported compound 2,6-bis(hydroxymethyl)-4-bromopyridine (J. Kupai, P. Huszthy, K. Székely, T. Tóth and L. Párkányi, *ARKIVOC*, 2011 (ix), 77-93). A mixture consisting of 2,6-bis(hydroxymethyl)-4-bromopyridine (2.18 g, 10 mmol), 15% aqueous solution of sodium thiomethoxide (7 mL, 15 mmol) and 50 mL of ethanol was stirred at reflux for 12 h. After cooling to room temperature, the volatiles were removed at reduced pressure to leave a viscous yellow residue. To this residue were added ethyl acetate (20 mL) and water (20 mL), and then the aqueous phase was separated from organic phase. After the aqueous phase was extracted with ethyl acetate (20 mL×5), the extracts were combined with the above separated organic phase, dried over anhydrous $MgSO_4$, filtered, and evaporated to give 2,6-bis(hydroxymethyl)-4-methylthiopyridine (1.60 g, 86%) as a light-yellow solid, mp 94–96 °C. Anal. Calcd for $C_8H_{11}NO_2S$: C, 51.87; H, 5.99; N, 7.56. Found: C, 51.74; H, 5.71; N, 7.33. IR (KBr disk): 3360 (vs), 2956 (vs), 1633 (s), 1553 (s), 1057 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.50 (s, 3H, CH_3), 2.89 (br.s, 2H, 2OH), 4.71 (s, 4H, $2CH_2$), 7.00 (s, 2H, C_5H_2N), ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 14.0 (CH_3), 64.5 (CH_2), 115.5, 152.8, 158.3 (C_5H_2N) ppm. MS (ESI, CH_2Cl_2): m/z 186.1 [M^+].

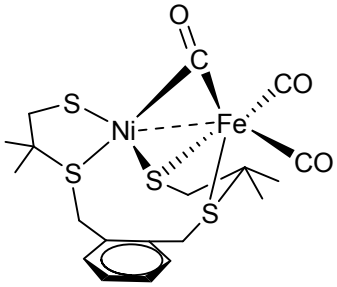
(2) Preparation of 2,6-bis[(tosyloxy)methyl]-4-methythiopyridine

This new starting material was prepared from the above-prepared precursor by using a reported procedure with some modifications (J. Kupai, P. Huszthy, K. Székely, T. Tóth and L. Párkányi, *ARKIVOC*, 2011 (ix), 77-93). To a stirred mixture consisting of 2,6-bis(hydroxymethyl)-4-methylthiopyridine (1.85 g, 10 mmol), CH_2Cl_2 (60 mL), and 40 % aqueous KOH solution (60 mL) was added tosyl chloride (3.81 g, 20 mmol). The mixture was stirred at 0 °C for 1 h and at room temperature for about 4 h until the fluorescence TLC analysis showed that the starting material 2,6-bis(hydroxymethyl)-4-methylthiopyridine was completely consumed. After water (60 mL) was added, the resulting mixture was extracted with CH_2Cl_2 (60 mL×3) and then the combined organic phase was dried over anhydrous $MgSO_4$. After removal of the drying agent and volatiles, the residue was recrystallyzed from CH_2Cl_2/hexane to give 2,6-bis[(tosyloxy)methyl]-4-methylthiopyridine (4.11 g, 83%) as a white solid, mp 96–98°C. Anal. Calcd for $C_{22}H_{23}NO_6S_3$： C, 53.53; H, 4.70; N, 2.84. Found: C, 53.35; H, 4.75; N, 2.70. IR (KBr disk): 2869 (w), 1588 (s), 1364 (s), 1176 (vs), 814 (s), 667 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): 2.43 (s, 9H, SCH_3, $2C_6H_4CH_3$), 4.98 (s, 4H, $2CH_2$), 7.03 (s, 2H, C_5H_2N), 7.31 (d, J = 7.6 Hz, 4H of $2C_6H_4$), 7.77 (d, J = 7.6 Hz, 4H of $2C_6H_4$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): 13.9 (CH_3), 21.8 ($C_6H_4CH_3$), 71.4 (CH_2), 117.2, 128.2, 130.1, 132.8, 145.4, 153.1, 153.4 (C_6H_4, C_5H_2N) ppm. MS (ESI, CH_2Cl_2): m/z 494.1 [M^+].

II. The expected effective magnetic moment for 1a, 1e, 1f, and 1g.

Since **1a, 1e, 1f,** and **1g** are octahedral Ni(II) complexes, their expected μ_{eff} value can be calculated as 2.83 μ_B according to the formula $\mu_{eff} = \sqrt{n(n+2)}\,\mu_B$, where n = 2 (namely two unpaired electrons). [J. C. Bailar, H. J. Emelèus, S. R. Nyholm and A. F. Trotman-Dickenson, *Comprehensive Inorganic Chemistry,* Pergamon: Oxford, U.K., Vol. 3, 1973]

III. Molecular structure of Lubitz compound



IV. Molecular structure of 3g

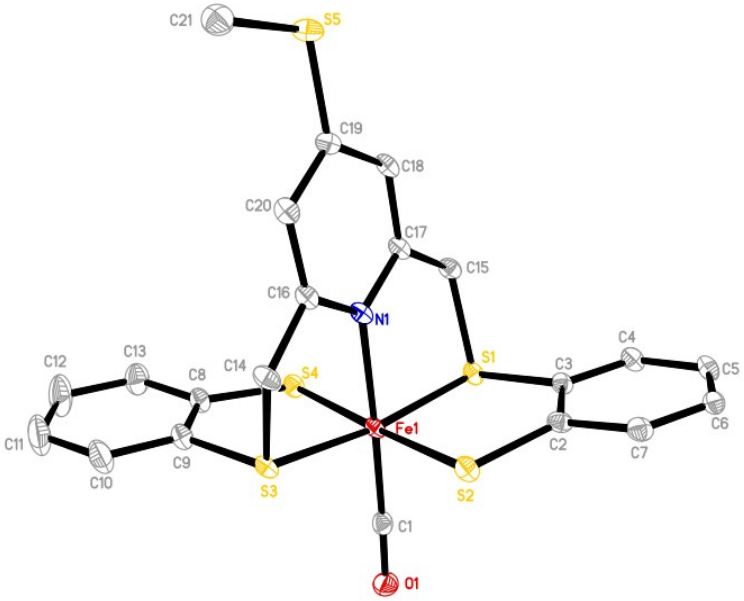


Fig. S1 Molecular structure of **3g** with 30% probability level ellipsoids.

V. *In situ* IR spectra for conversion of the isolated 2e into 3e and *in situ* IR spectra of the isolated 3e

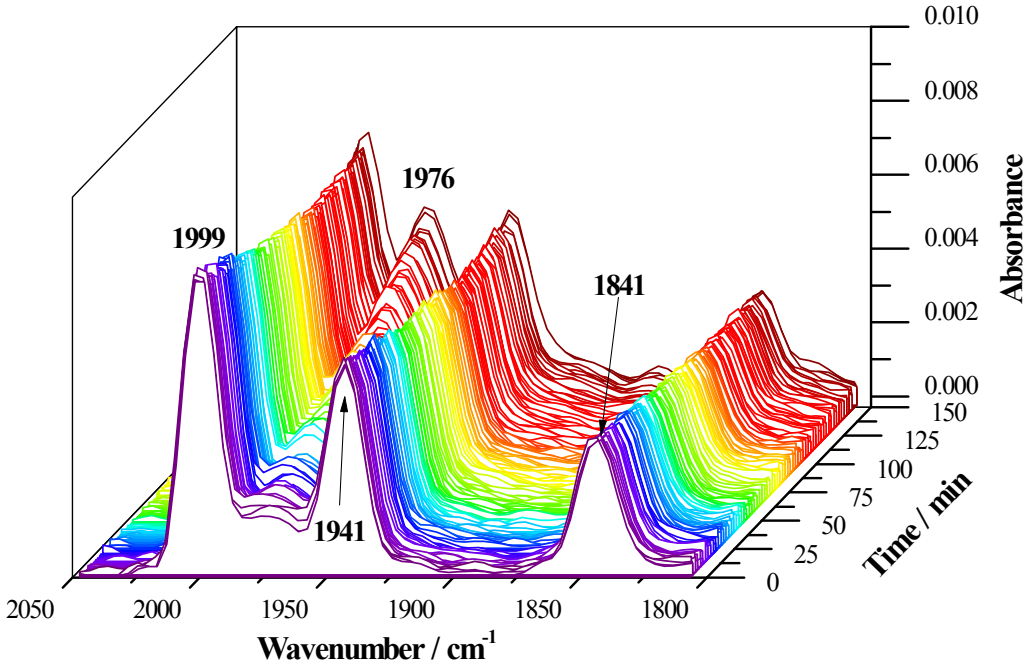


Fig. S2 *In situ* IR spectra for conversion of the isolated **2e** into **3e** in THF at room temperature.

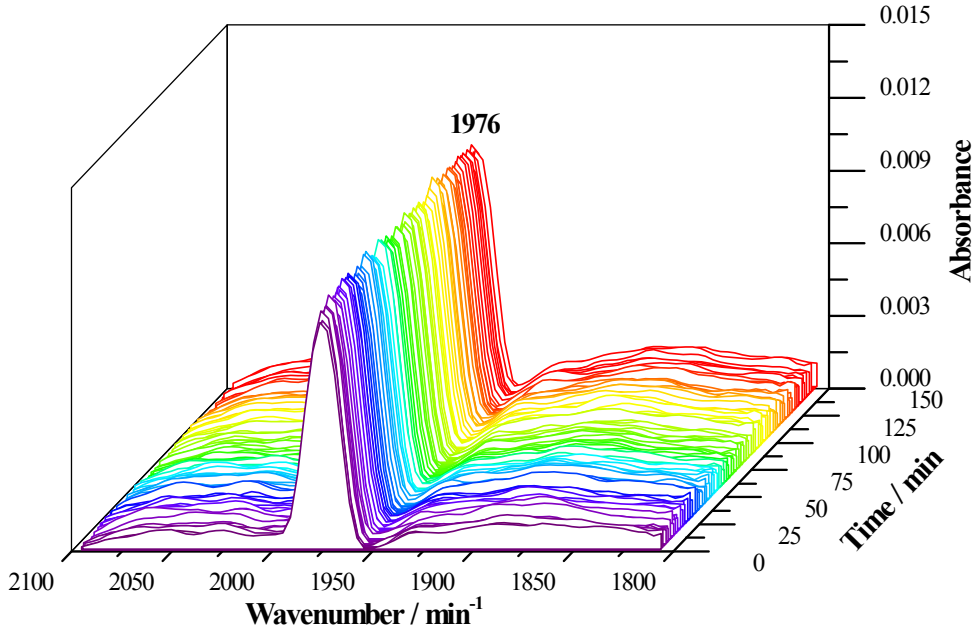


Fig. S3 *In situ* IR spectra of the isolated **3e** in THF at room temperature.

VI. Thermal decomposition experiment of 2e to give 3e

A 50 mL three-necked flask equipped with a magnetic stir-bar, two serum caps, and a N_2 inlet tube was charged with **2e** (0.100 g, 0.16 mmol) and THF (10 mL). The brown red solution was stirred at 25^{o}C for 6 h to give a red solution. After solvent was removed at reduced pressure, the residue was subjected to flash column chromatography. Elution with CH_2Cl_2/acetone (v/v = 40:1) developed a red band, from which **3e** (0.067 g, 81%) was obtained as a red solid.

VII. ^{1}H NMR and IR spectra of 2b-2g

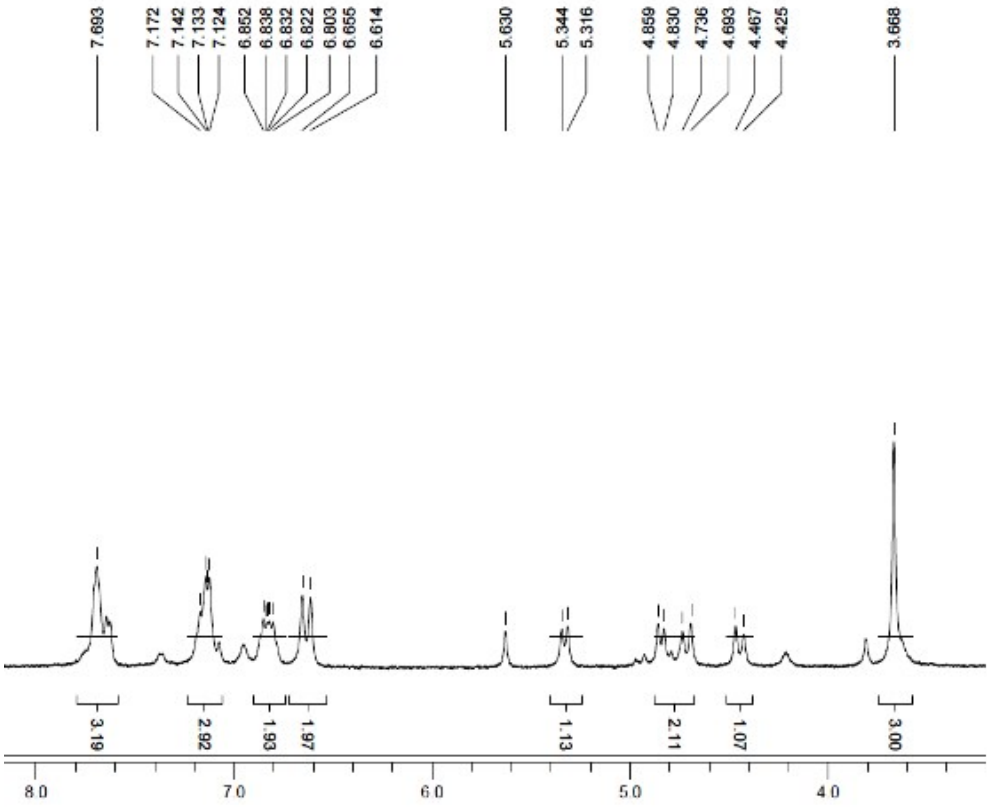


Fig. S4. ^{1}H NMR spectrum of **2b**

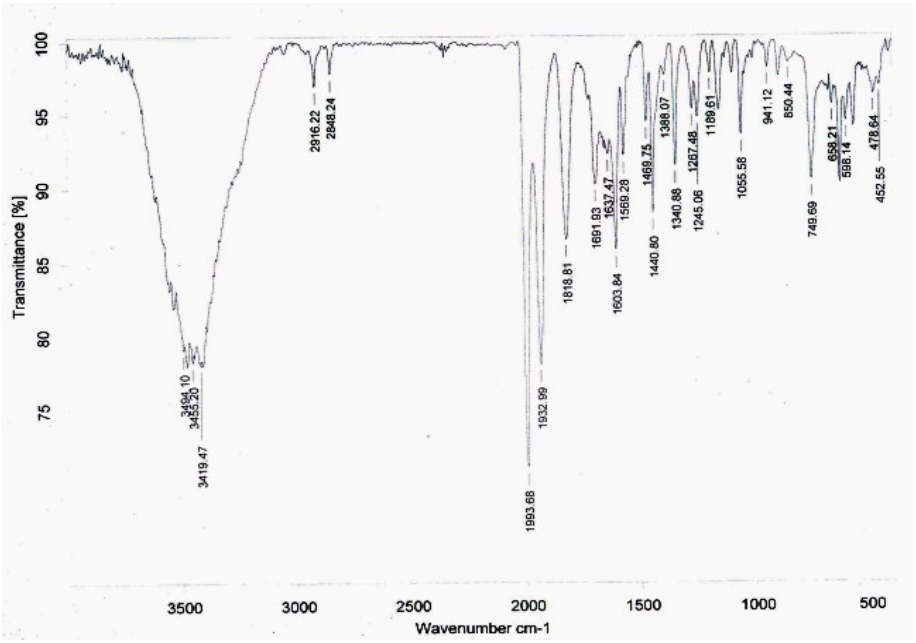


Fig. S5. IR spectrum of **2b**

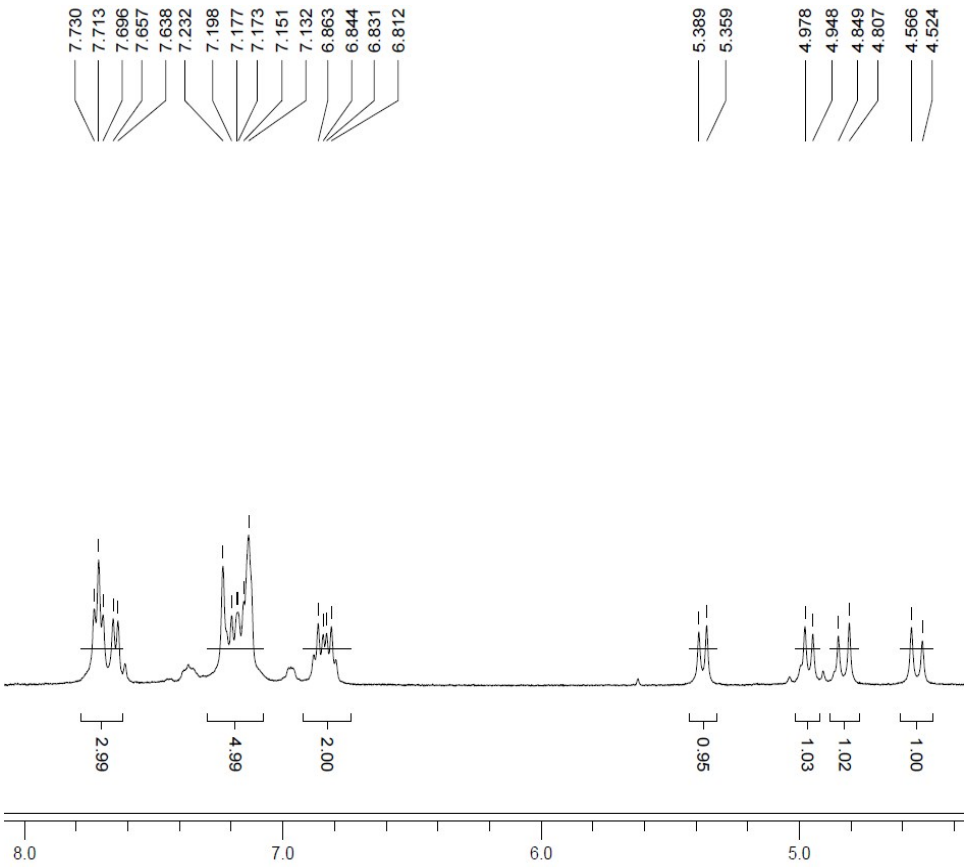


Fig. S6 ^{1}H NMR spectrum of **2c**

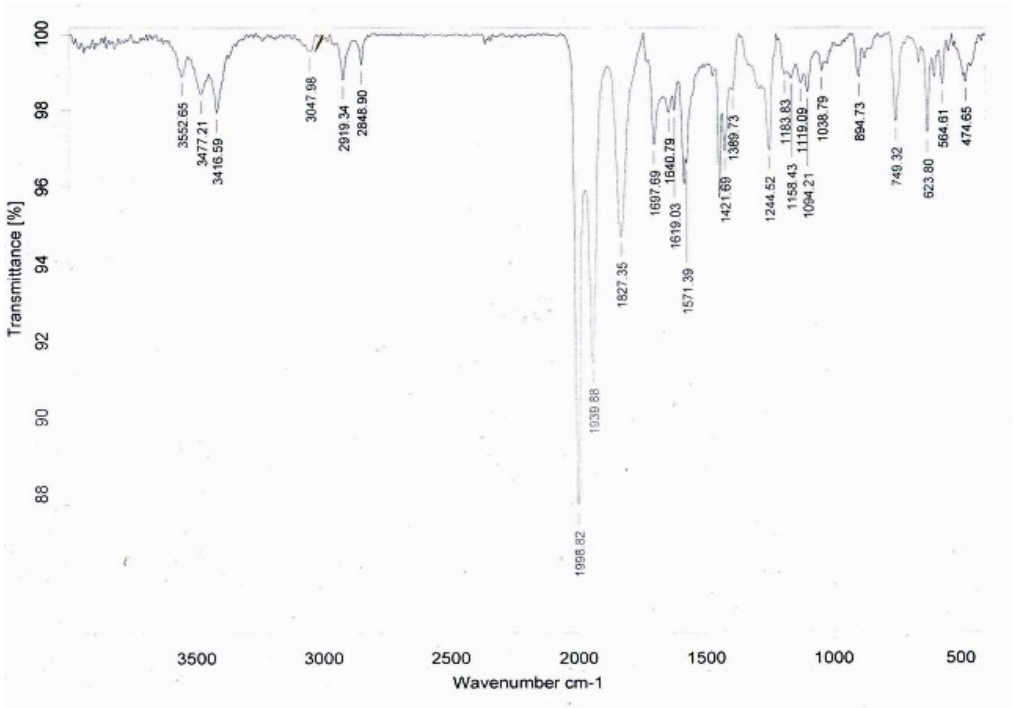


Fig. S7 IR spectrum of **2c**

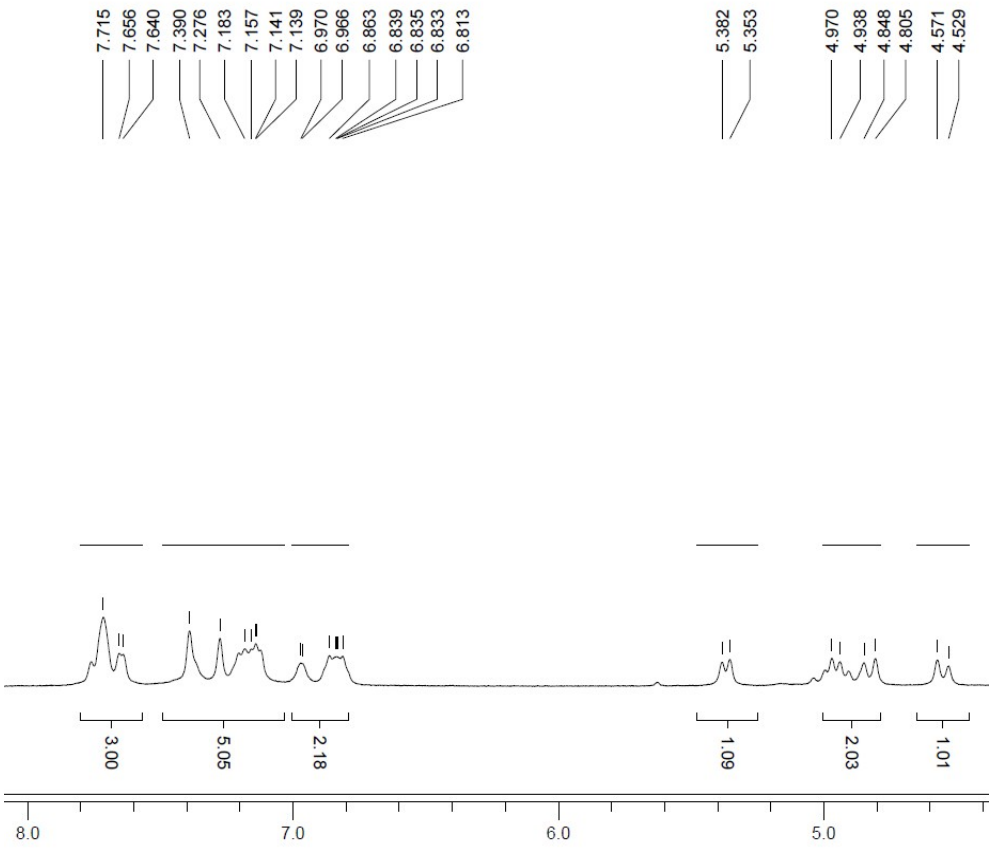


Fig. S8 ^{1}H NMR spectrum of **2d**

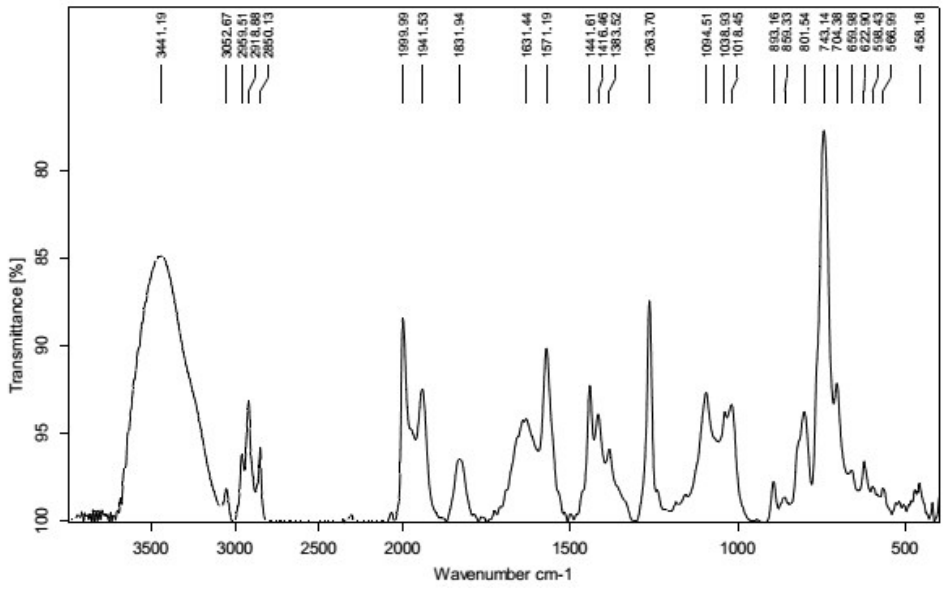


Fig. S9 IR spectrum of **2d**

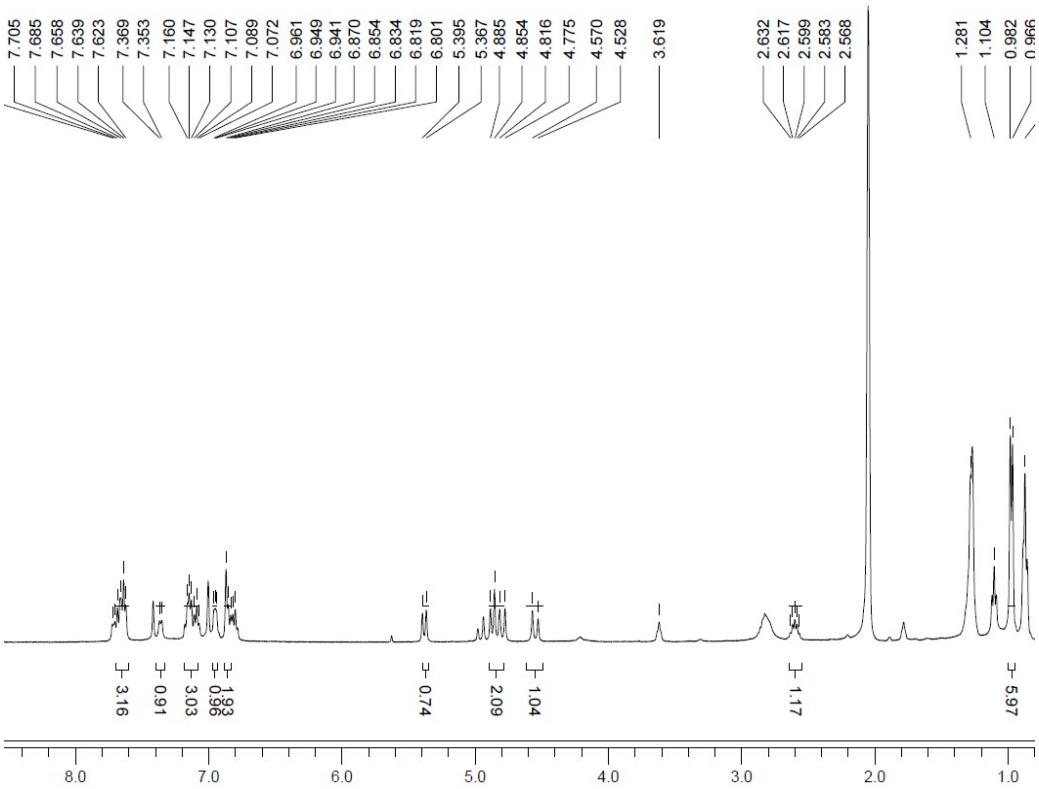


Fig. S10 ^{1}H NMR spectrum of **2e**

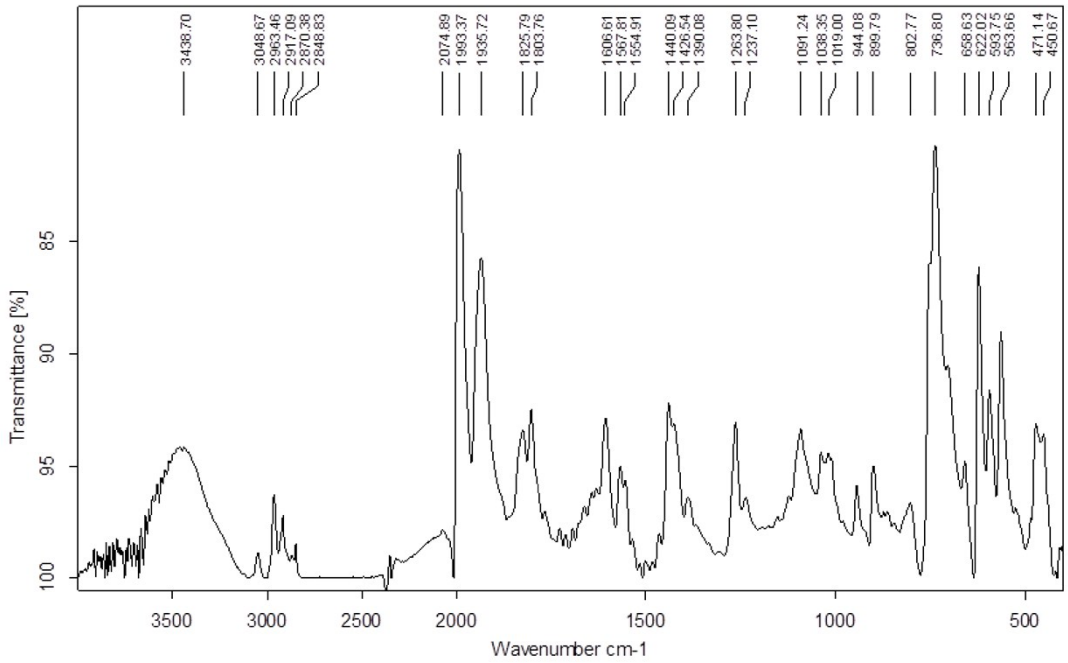


Fig. S11 IR spectrum of **2e**

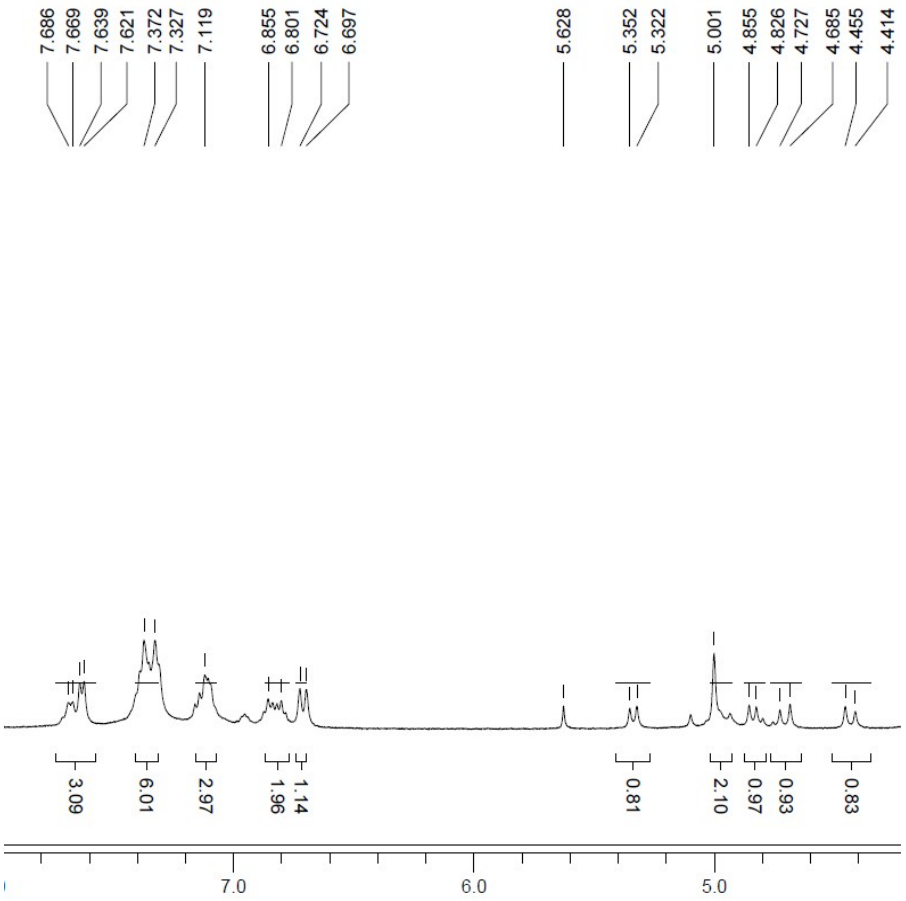


Fig. S12 ^{1}H NMR spectrum of **2f**

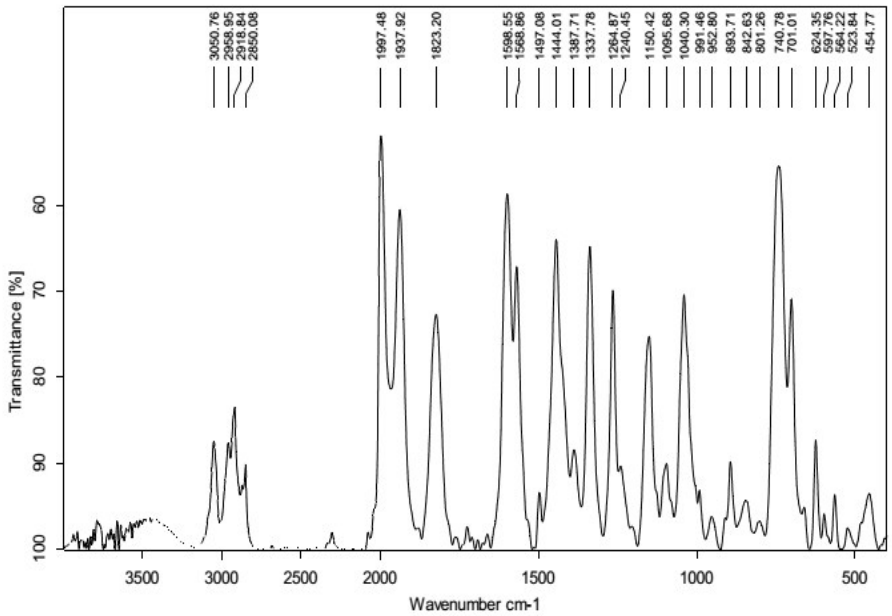


Fig. S13 IR spectrum of **2f**

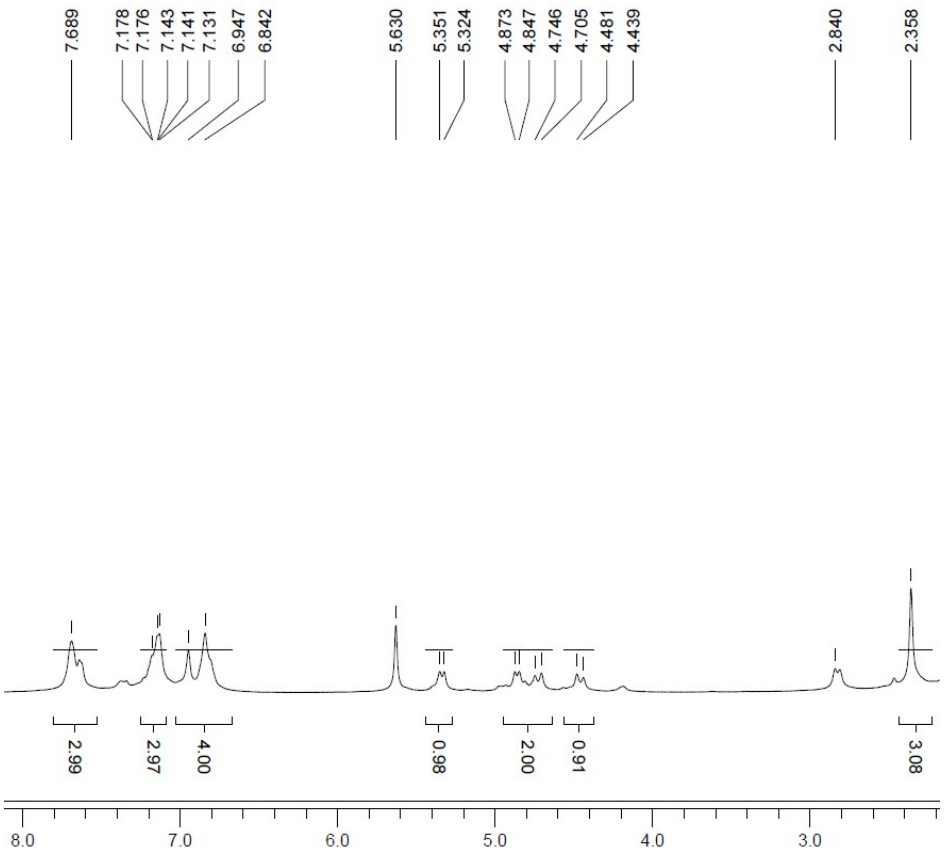


Fig. S14 ^{1}H NMR spectrum of **2g**

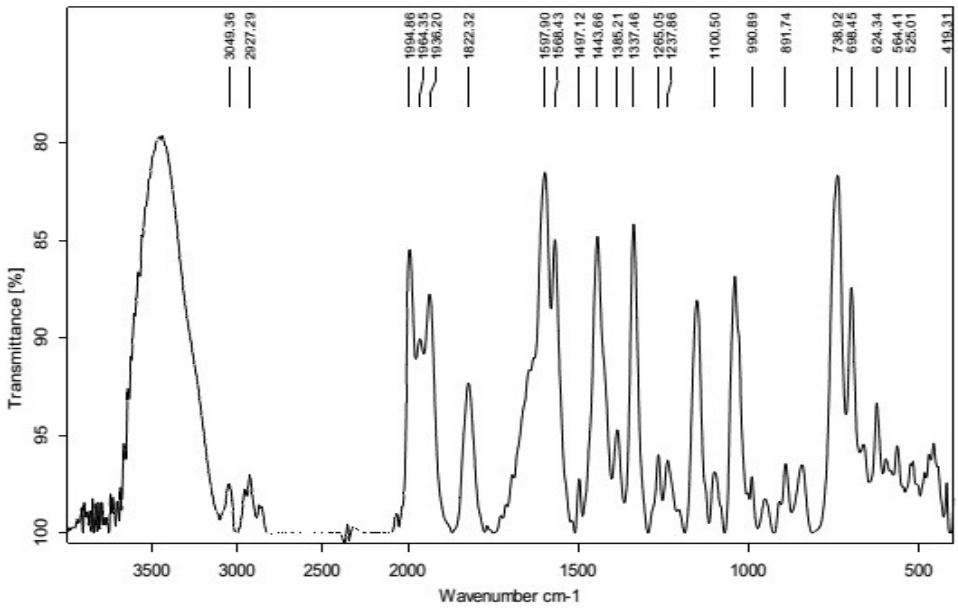


Fig. S15 IR spectrum of **2g**