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Supporting information

A new method for detecting intramolecular H-bonds of aromatic amides based on de-shielding effect of carbonyl on β-protons

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1. General information

All reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), and column chromatography purifications were carried out using silica gel. *N*-Phenylbenzamide (**PhB**) was bought from Anhui Senrise Technology Co., Ltd. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on the Bruker AVANCEⅢ 500. To avoid the effect of molecular aggregation on chemical shifts, the concentration of most solution was equal to 1.0 mmol/L. The compounds were dried in vacuum at 50°C for 12 hours. The deuterated solvents for ^{1}H NMR experiments were dried with 4Å molecular sieves in advance, and the preparation of solutions of amide compounds was carefully operated in an anhydrous glove box. Chemical shifts for protons are referenced to solvent residual peak in the NMR solvent ($CDCl_3$ = δ 7.26 ppm, DMSO-d_6 = 2.50 ppm, CD_3NO_2 = 4.33 ppm and CD_3CN = 1.94 ppm for ^{1}H NMR spectra), and the signals of tetramethylsilane (TMS) in chloroform, acetonitrile and DMSO locate between –0.01 and +0.01 ppm in the stack plots of ^{1}H NMR spectra (Figures S19 – S36). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. When the NMR spectra were recorded, the temperature of sample was set to 298 K. After a sample was loaded, its temperature was continuously measured and controlled by the NMR spectrometer. The measurement temperature is calibrated every two weeks by using an internal standard method with the standard sample of 80% ethylene glycol in DMSO-d_6 for 290 K~430 K.

2. Synthetic and characterization data

2-Methoxy-*N*-propylbenzamide (1a)

2-Methoxybenzoic acid (2.0 g, 13.1 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid

chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (2.5 mL, 30.2 mmol) and triethylamine (2 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.35 g (91%) of colorless oil. ^{1}H NMR (500 MHz, Chloroform-d) δ: 8.24 (dd, J = 7.8, 1.8 Hz, 1H, Ar H), 7.89 (s, 1H, CONH), 7.53–7.41 (m, 1H, Ar H), 7.11 (t, J = 7.6 Hz, 1H, Ar H), 7.00 (d, J = 8.3 Hz, 1H, Ar H), 3.99 (s, 3H, OCH_3), 3.53–3.38 (m, 2H, CH_2), 1.68 (p, J = 7.3 Hz, 2H, CH_2), 1.02 (t, J = 7.5 Hz, 3H, CH_3).

N^1,N^3-Dipropyl-4-methoxy-1,3-benzenedicarboxamide (1b)

A mixture of 4-Methoxy-1,3-benzenedicarboxylic acid dimethyl ester (2.0 g, 8.9 mmol) and potassium hydroxide (1.0 g, 17.9 mmol) was dissolved in MeOH (50 mL) and water (10 mL). The mixture was refluxed for 12 hours. Water (100 mL) was added to cause precipitation while acidifying with HCl. After removing part of the solvent, the solid was collected, washed with water, to give the desired acid, 4-Methoxy-1,2-benzenedicarboxylic acid, 1.5 g (88%) of white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 12.89 (s, 2H, COOH), 8.20 (d, *J* = 2.8 Hz, 1H, Ar H), 8.05 (d, *J* = 8.3 Hz, 1H, Ar H), 7.22 (d, *J* = 8.8 Hz, 1H, Ar H), 3.89 (s, 3H, OCH_3).

4-Methoxy-1,2-benzenedicarboxylic acid (1.5 g, 7.65 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (1.5 mL, 18.4 mmol) and triethylamine (3 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.0 g (90%) of white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 8.47 (d, *J* = 2.5 Hz, 1H, Ar H), 8.11 (dd, *J* = 8.7, 2.4 Hz, 1H, Ar H), 7.85 (s, 1H, CONH), 7.06 (d,

J = 8.7 Hz, 1H, Ar H), 6.33 (s, 1H, CONH), 4.02 (s, 3H, OCH_3), 3.43 (dtd, *J* = 17.4, 7.2, 5.6 Hz, 4H, CH_2), 1.64 (dh, *J* = 9.6, 7.3 Hz, 4H, CH_2), 0.99 (dt, *J* = 11.2, 7.4 Hz, 6H, CH_3).

N^1,N^3-Dipropyl-2-methoxy-1,3-benzenedicarboxamide (1c)

A suspension of 2-Methoxy-1,3-dimethylbenzene (5.0 g, 36.7 mmol), potassium permanganate (29.0 g, 183.5 mmol), and potassium hydroxide (6.2 g, 0.11 mol) in water (250 mL) was stirred at 80°C for 3 h and then cooled to room temperature. The solid was filtered off, and the filtrate was acidified with concentrated hydrochloric acid to pH= 7. The resulting precipitate was filtered, washed with water, and dried in vacuum. Recrystallization from ethanol gave 5.0 g (70%) of white solid, 2-Methoxy-1,3-benzenedicarboxylic acid. ^{1}H NMR (500 MHz, DMSO-d_6) δ: 13.10 (s, 2H, COOH), 7.81 (d, *J* = 7.6 Hz, 2H, Ar H), 7.26 (t, *J* = 7.7 Hz, 1H, Ar H), 3.81 (s, 3H, OCH_3).

2-Methoxy-1,3-benzenedicarboxylic acid (2.0 g, 10.2 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (2 mL, 24.5 mmol) and triethylamine (3 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.6 g (88%) of white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 8.07 (dd, *J* = 7.7, 2.3 Hz, 2H, Ar H), 7.41–7.27 (m, 3H, Ar H, CONH), 3.86 (s, 3H,OCH_3), 3.51–3.40 (m, 4H, CH_2), 1.66 (h, *J* = 7.3 Hz, 4H, CH_2), 1.01 (t, *J* = 7.4 Hz, 6H, CH_3).

4-Methoxy-*N*-propylbenzamide (1d)

4-Methoxybenzoic acid (2.0 g, 13.1 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride

was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (2.5 mL, 30.2 mmol) and triethylamine (2 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.45 g (95%) of white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 7.73 (d, *J* = 8.7 Hz, 2H, Ar H), 6.92 (d, *J* = 8.7 Hz, 2H, Ar H), 6.02 (s, 1H, CONH), 3.85 (s, 3H, OCH_3), 3.41 (q, *J* = 6.7 Hz, 2H, CH_2), 1.64 (dt, *J* = 14.7, 7.4 Hz, 2H, CH_2), 0.99 (t, *J* = 7.4 Hz, 3H, CH_3).

N^1,N^3-Dipropyl-5-methoxy-1,3-benzenedicarboxamide (1e)

5-Methoxy-1,3-benzenedicarboxylic acid (2.0 g, 10.2 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (2 mL, 24.5 mmol) and triethylamine (3 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.7 g (92%) of white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 7.68 (t, *J* = 1.5 Hz, 1H, Ar H), 7.42 (d, *J* = 1.5 Hz, 2H, Ar H), 6.34 (t, *J* = 5.9 Hz, 2H, CONH), 3.86 (s, 3H, OCH_3), 3.44–3.37 (m, 4H, CH_2), 1.63 (q, *J* = 7.3 Hz, 4H, CH_2), 0.98 (t, *J* = 7.4 Hz, 6H, CH_3).

2-Methoxy-*N*-(2-methoxyphenyl)benzamide (1f)

2-Methoxybenzoic acid (1.5 g, 9.87 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride was distilled off and residue was dried under vacuum to give yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of

o-anisidine (1.336 g, 10.85 mmol) and triethylamine (3 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.05 g (82%) of white solid. ^{1}H NMR (500 MHz, Chloroform-d) δ: 10.59 (s, 1H, NH), 8.65 (dd, J = 7.9, 1.6 Hz, 1H, Ar-H), 8.31 (dd, J = 7.8, 1.7 Hz, 1H, Ar-H), 7.56 – 7.43 (m, 1H, Ar-H), 7.13 (t, J = 7.6 Hz, 1H, Ar-H), 7.08 – 6.98 (m, 3H, Ar-H), 6.95 – 6.87 (m, 1H, Ar-H), 4.07 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3).

_N_-Propyl-2-pyridinecarboxamide (2a)

2-Pyridinecarboxylic acid (1.0 g, 8.13 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (0.8 mL, 30.2 mmol) and triethylamine (1 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 1.3 g (90%) of yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 8.55 (d, *J* = 4.8 Hz, 1H, Ar H), 8.22 (d, *J* = 7.8 Hz, 1H, Ar H), 8.10 (s, 1H, CONH), 7.86 (td, *J* = 7.7, 1.7 Hz, 1H, Ar H), 7.43 (ddd, *J* = 7.6, 4.8, 1.3 Hz, 1H, Ar H), 3.45 (q, *J* = 6.8 Hz, 2H, CH_2), 1.67 (h, *J* = 7.4 Hz, 2H, CH_2), 1.00 (t, *J* = 7.4 Hz, 3H, CH_3).

_N_-Propyl-4-pyrimidinecarboxamide (2b)

4-Pyrimidinecarboxylic acid (1.5 g, 12.1 mmol) was suspended in dry dichloromethane (15 mL) with oxalyl chloride (5 mL) and stirred for 8 hours at room temperature. Excess of oxalyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (1.2 mL, 14.52 mmol) and triethylamine (2 mL). The resulting mixture was stirred overnight at

room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 1.7 g (80%) of yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 9.24 (s, 1H), 8.97 (t, *J* = 4.7 Hz, 1H), 8.13 (t, *J* = 4.5 Hz, 1H), 8.02 (s, 1H), 3.46 (q, *J* = 6.2, 5.5 Hz, 2H), 1.74 – 1.62 (m, 2H), 1.01 (td, *J* = 7.6, 3.5 Hz, 3H).

N^4,N^6-Dipropyl-4,6-pyrimidinedicarboxamide (2c)

4,6-Pyrimidinedicarboxylic acid (2.0 g, 11.9 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (2.4 mL, 28.6 mmol) and triethylamine (3 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.8 g (93%) of colorless oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 9.20 (s, 1H, Ar H), 8.87 (s, 1H, Ar H), 7.96 (s, 2H, CONH), 3.46 (q, *J* = 6.7 Hz, 4H, CH_2), 1.72–1.62 (m, 4H, CH_2), 1.00 (t, *J* = 7.3 Hz, 6H, CH_3).

***N*-Propyl-4-pyridinecarboxamide (2d)**

4-Pyridylcarboxylic acid (2.0 g, 16.3 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (1.6 mL, 19.5 mmol) and triethylamine (2 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.5 g (88%) of orange solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 8.72 (d, *J* = 6.1 Hz, 2H, Ar

H), 7.63 (d, *J* = 6.1 Hz, 2H, Ar H), 6.46 (s, 1H, CONH), 3.47–3.38 (m, 2H, CH_2), 1.65 (h, *J* = 7.4 Hz, 2H, CH_2), 0.98 (t, *J* = 7.4 Hz, 3H, CH_3).

_N_-(pyridin-2-yl)-2-pyridinecarboxamide (2e)

2-Pyridinecarboxylic acid (1.5 g, 12.2 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride was distilled off and residue was dried under vacuum to give yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of 2-aminopyridine (1.26 g, 13.4 mmol) and triethylamine (1 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with water, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 1.92 (79%) of white solid. ^{1}H NMR (500 MHz, Chloroform-d) δ: 10.55 (s, 1H, NH), 8.64 (d, J = 4.6 Hz, 1H, Ar-H), 8.43 (d, J = 8.3 Hz, 1H, Ar-H), 8.37 (d, J = 4.8 Hz, 1H, Ar-H), 8.30 (d, J = 8.5 Hz, 1H, Ar-H), 7.91 (td, J = 7.7, 1.5 Hz, 1H, Ar-H), 7.81 – 7.72 (m, 1H, Ar-H), 7.54 – 7.45 (m, 1H, Ar-H), 7.12 – 7.04 (m, 1H, Ar-H).

2-Fluoro-*N*-propyl-benzamide (3a)

2-Fluorobenzoic acid (2.0 g, 14.3 mmol) was suspended in dry dichloromethane (15 mL) with oxalyl chloride (5 mL) and stirred for 8 hours at room temperature. Excess of oxalyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (1.4 mL, 17.2 mmol) and triethylamine (2 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.4 g (86%) of yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 8.10 (td, *J* = 7.9, 1.9 Hz, 1H, Ar H), 7.50–7.42 (m, 1H, Ar H), 7.26 (td, *J* = 7.6, 1.2 Hz, 1H, Ar H), 7.11 (ddd, *J* = 12.2, 8.3, 1.1 Hz, 1H, Ar H), 6.74 (s, 1H, CONH), 3.45 (tdd, *J* =

7.2, 5.6, 1.5 Hz, 2H, CH_2), 1.65 (q, *J* = 7.3 Hz, 2H, CH_2), 0.99 (t, *J* = 7.4 Hz, 3H, CH_3).

2-Fluoro-*N*-propyl-3-pyridinecarboxamide (3b)

2-Fluoro-3-pyridinecarboxylic acid (2.0 g, 14.2 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (1.4 mL, 17.0 mmol) and triethylamine (2 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.5 g (91%) of yellow oil. ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 8.59 (ddd, *J* = 9.8, 7.5, 2.1 Hz, 1H, Ar H), 8.32 (dt, *J* = 4.7, 1.7 Hz, 1H, Ar H), 7.36 (ddd, *J* = 7.4, 4.8, 2.4 Hz, 1H, Ar H), 6.85 (s, 1H, CONH), 3.46 (tdd, *J* = 7.2, 5.7, 1.4 Hz, 2H, CH_2), 1.67 (q, *J* = 7.3 Hz, 2H, CH_2), 1.00 (t, *J* = 7.4 Hz, 3H, CH_3).

4-Fluoro-*N*-propyl-benzamide (3c)

4-Fluorobenzoic acid (2.0 g, 14.3 mmol) was suspended in dry dichloromethane (15 mL) with oxalyl chloride (5 mL) and stirred for 8 hours at room temperature. Excess of oxalyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (1.4 mL, 17.2 mmol) and triethylamine (2 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.6 g (95%) of white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ: 7.77 (dd, *J* = 8.5, 5.4 Hz, 2H, Ar H), 7.10 (t, *J* = 8.4 Hz, 2H, Ar H), 6.09 (s, 1H, CONH), 3.41 (q, *J* = 6.7 Hz, 2H, CH_2), 1.64 (q, *J* = 7.3 Hz, 2H, CH_2), 0.99 (t, *J* = 7.4 Hz, 3H, CH_3).

2-Fluoro-*N*-(2-fluorophenyl)benzamide (3d)

2-Fluorobenzoic acid (1.5 g, 10.71 mmol) was suspended in dry dichloromethane (15 mL) with oxalyl chloride (5 mL) and stirred for 8 hours at room temperature. Excess of oxalyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of 2-Fluoroaniline (1.12 mL, 11.78 mmol) and triethylamine (2 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.35 (94%) of white solid. ^{1}H NMR (500 MHz, Chloroform-d) δ: 8.79 (d, J = 14.0 Hz, 1H, NH), 8.51 (t, J = 8.0 Hz, 1H, Ar-H), 8.19 (t, J = 7.7 Hz, 1H, Ar-H), 7.55 (q, J = 6.7, 6.3 Hz, 1H, Ar-H), 7.33 (t, J = 7.6 Hz, 1H, Ar-H), 7.24 – 7.07 (m, 4H, Ar-H).

2-Fluoro-*N*-(4-methyl-2-fluorophenyl)benzamide (3e)

2-Fluorobenzoic acid (1.5 g, 10.71 mmol) was suspended in dry dichloromethane (15 mL) with oxalyl chloride (5 mL) and stirred for 8 hours at room temperature. Excess of oxalyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of 2-Fluoro-4-methylaniline (1.36 mL, 11.78 mmol) and triethylamine (2 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.4 g (91%) of white solid. ^{1}H NMR (500 MHz, Chloroform-d) δ: 8.70 (d, J = 15.3 Hz, 1H, NH), 8.33 (t, J = 8.2 Hz, 1H, Ar-H), 8.18 (t, J = 7.9 Hz, 1H, Ar-H), 7.53 (q, J = 7.1 Hz, 1H, Ar-H), 7.32 (t, J = 7.6 Hz, 1H, Ar-H), 7.19 (dd, J = 12.2, 8.3 Hz, 1H, Ar-H), 7.02 – 6.92 (m, 2H, Ar-H), 2.34 (s, 3H, OCH_3).

***N*-Propylbenzamide (PB)**

Benzenecarboxylic acid (2.0 g, 16.4 mmol) was suspended in thionyl chloride (15 mL) with 3 drops of DMF and refluxed for 8 hours. Excess of thionyl chloride was distilled off and residue was dried under vacuum to give a yellow oil. Acid chloride was dissolved in dry dichloromethane (20 mL) followed by addition of *N*-propylamine (1.6 mL, 19.7 mmol) and triethylamine (2 mL). The resulting mixture was stirred overnight at room temperature. After that, the reaction mixture was washed with 1 mol/L HCl solution, saturated $NaHCO_3$ solution, and organic layer was dried over $MgSO_4$. Evaporation of solvent gave 2.8 g (96%) of white solid. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.2 Hz, 2H, Ar H), 7.49 (t, *J* = 7.4 Hz, 1H, Ar H), 7.42 (t, *J* = 7.6 Hz, 2H, Ar H), 6.19 (s, 1H, CONH), 3.42 (q, *J* = 6.7 Hz, 2H, CH_2), 1.64 (h, *J* = 7.4 Hz, 2H, CH_2), 0.99 (t, *J* = 7.4 Hz, 3H, CH_3).

3. ^{1}H NMR spectra of compounds in $CDCl_3$

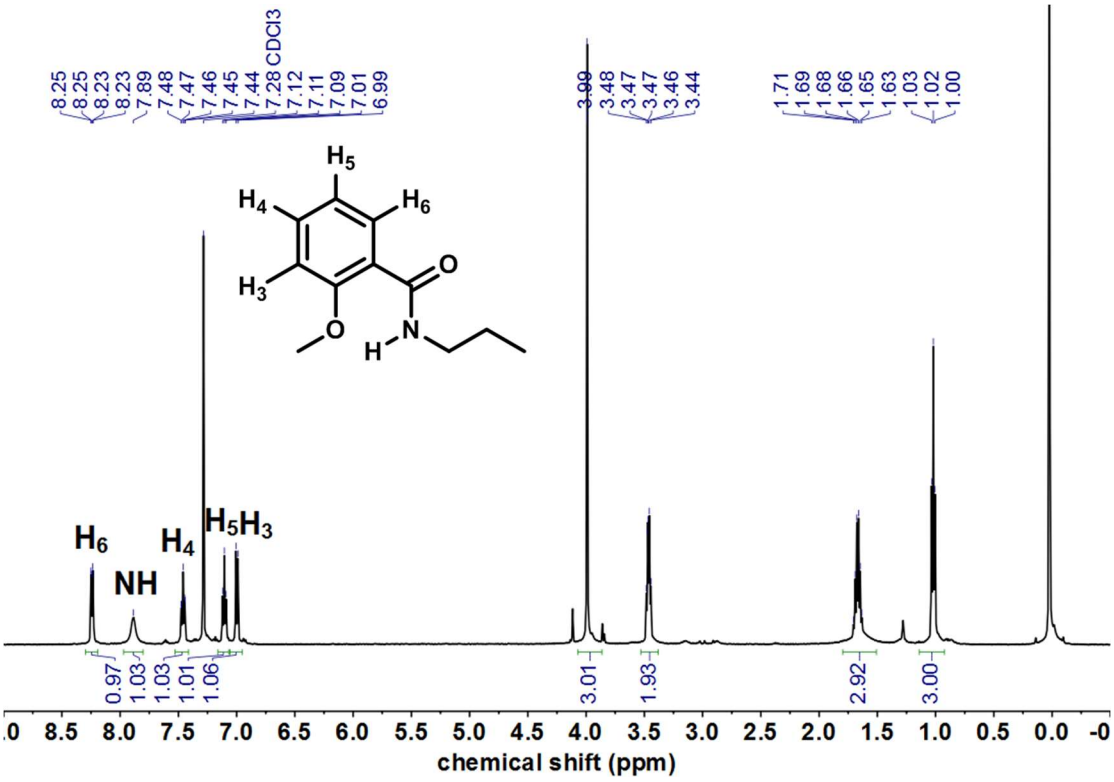

Figure S1. ^{1}H NMR (500 MHz, 298 K) spectrum of **1a** in $CDCl_3$.

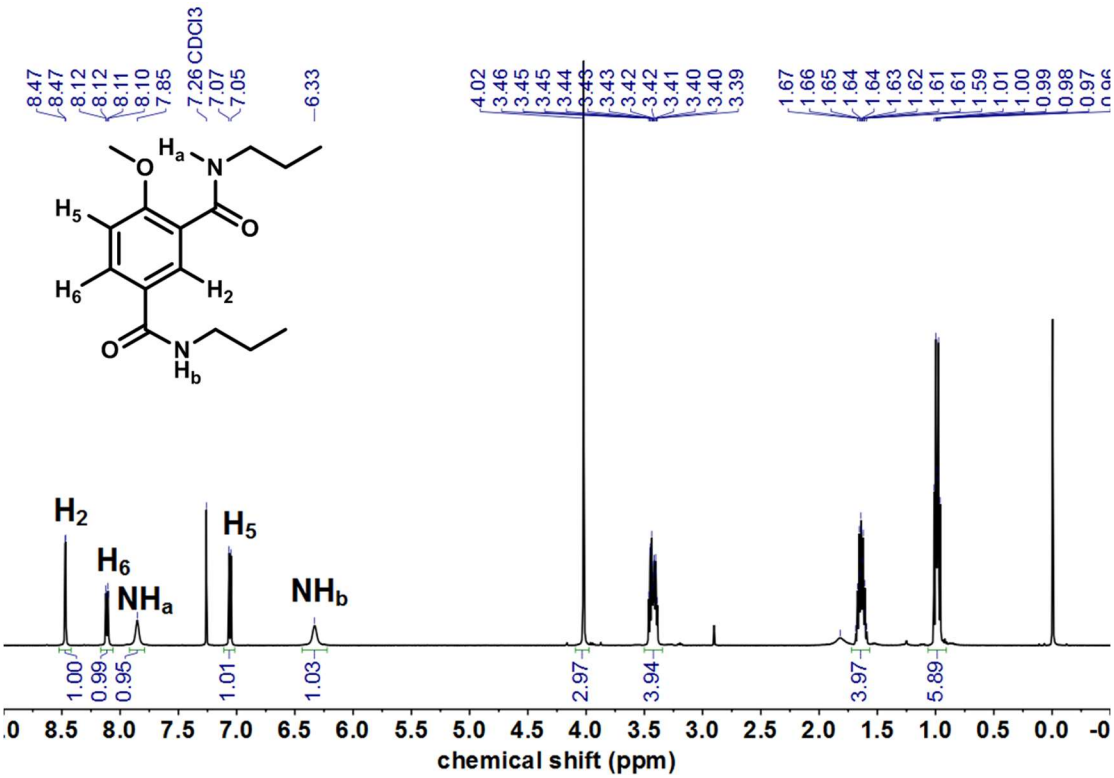

Figure S2. ^{1}H NMR (500 MHz, 298 K) spectrum of **1b** in $CDCl_3$.

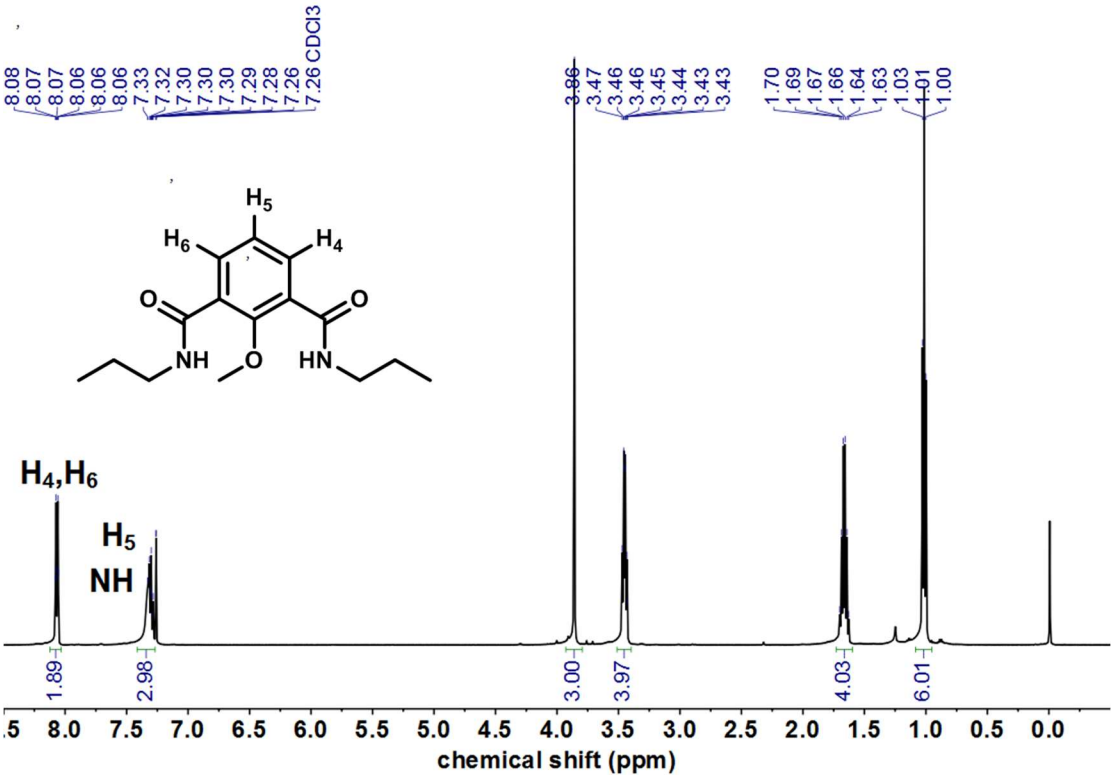

Figure S3. ^{1}H NMR (500 MHz, 298 K) spectrum of **1c** in $CDCl_3$.

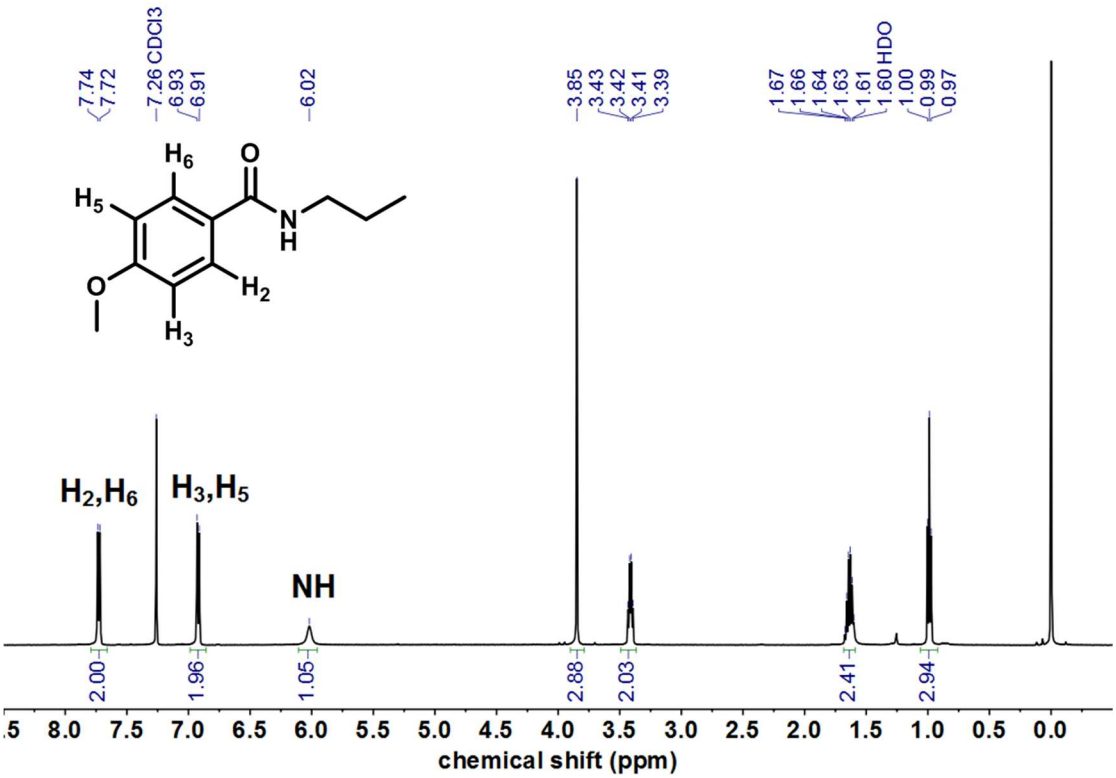

Figure S4. ^{1}H NMR (500 MHz, 298 K) spectrum of **1d** in $CDCl_3$.

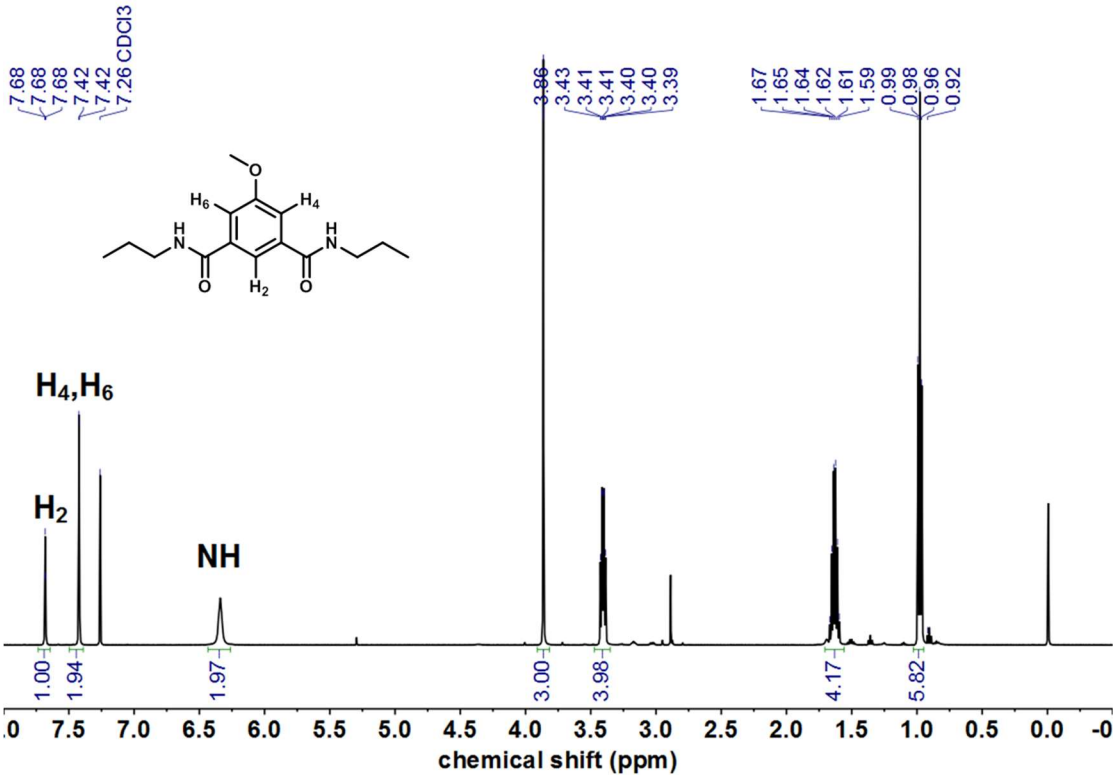

Figure S5. ^{1}H NMR (500 MHz, 298 K) spectrum of **1e** in $CDCl_3$.

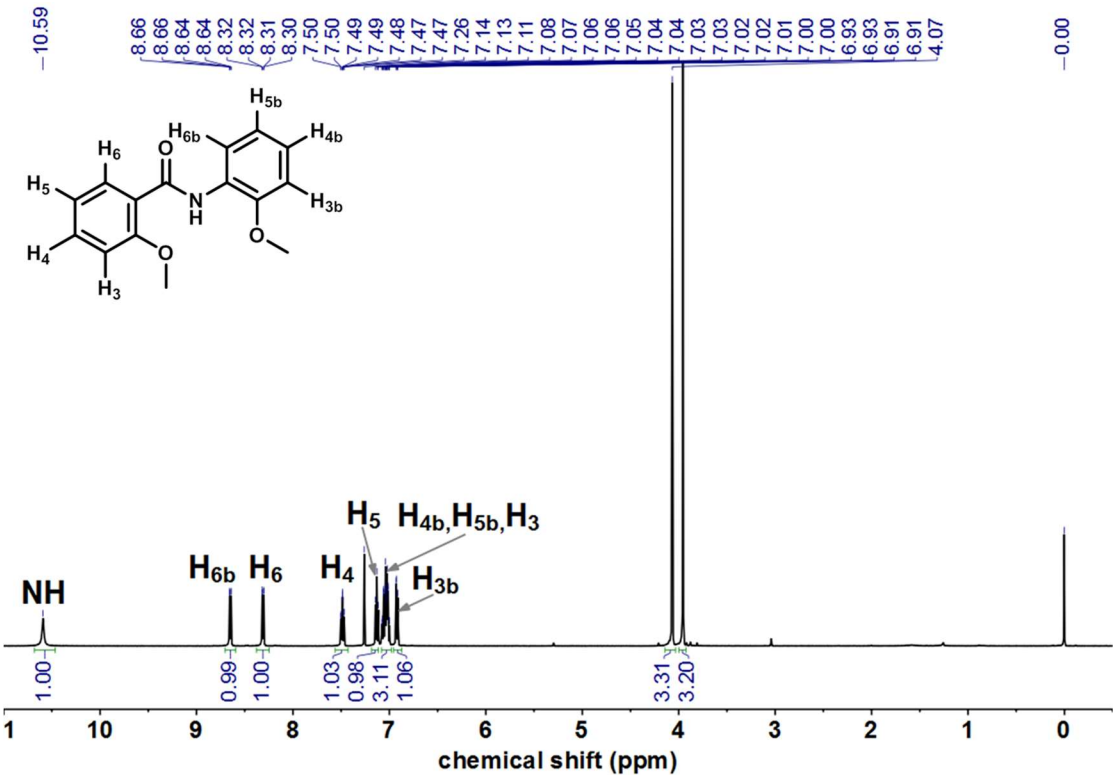

Figure S6. ^{1}H NMR (500 MHz, 298 K) spectrum of **1f** in $CDCl_3$.

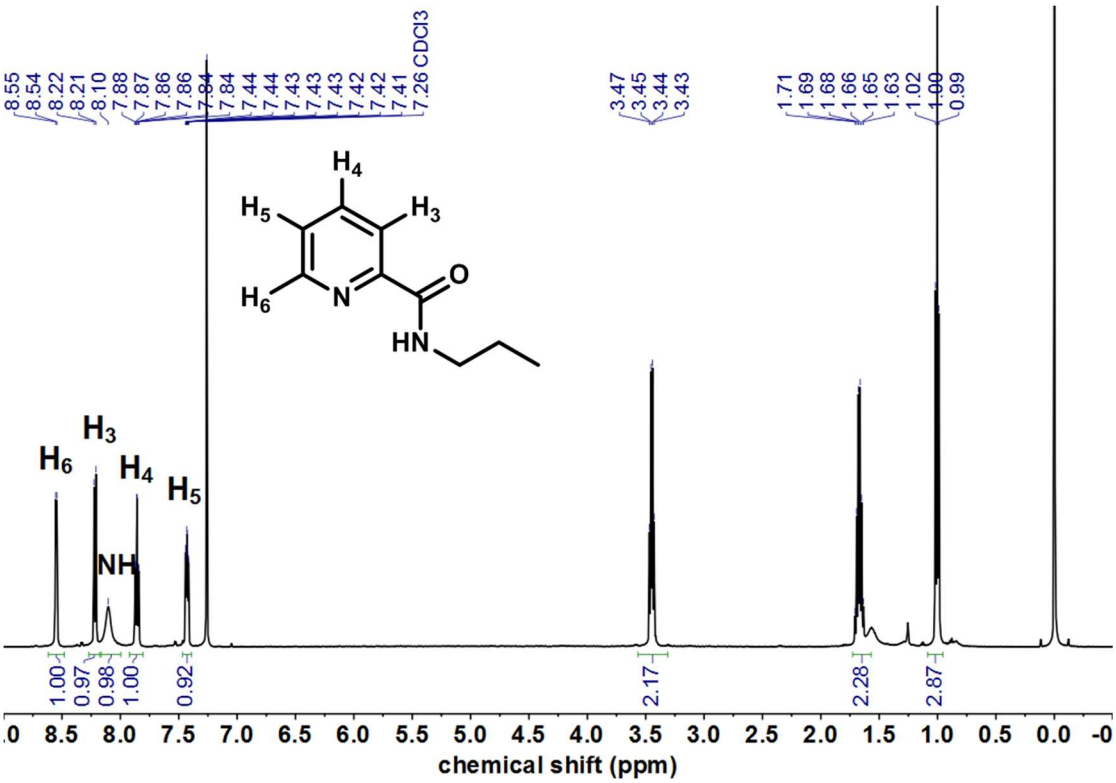

Figure S7. ^{1}H NMR (500 MHz, 298 K) spectrum of **2a** in $CDCl_3$.

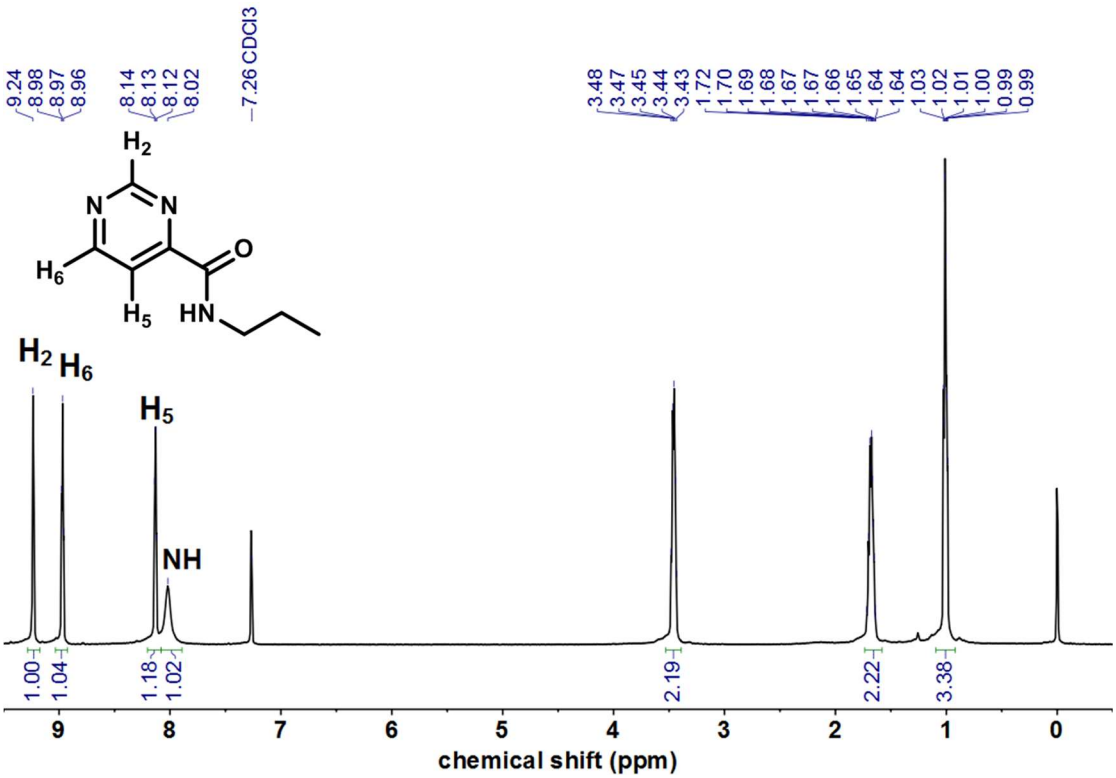

Figure S8. ^{1}H NMR (500 MHz, 298 K) spectrum of **2b** in $CDCl_3$.

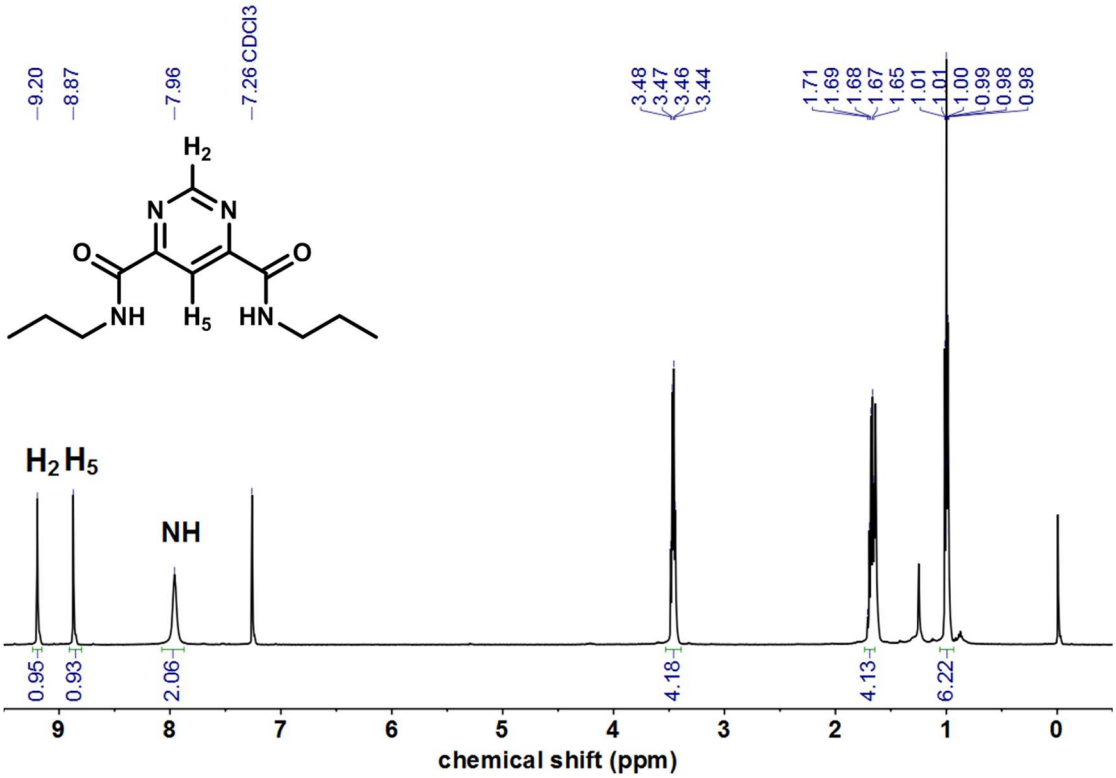

Figure S9. ^{1}H NMR (500 MHz, 298 K) spectrum of **2c** in $CDCl_3$.

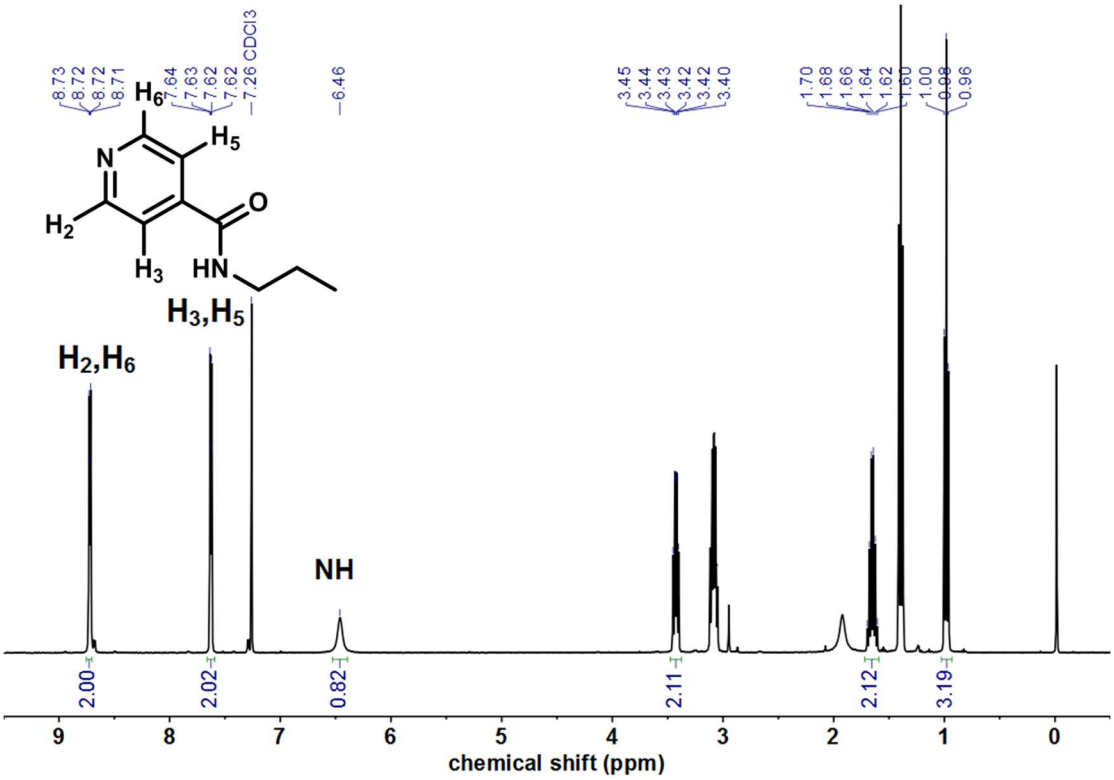

Figure S10. ^{1}H NMR (500 MHz, 298 K) spectrum of **2d** in $CDCl_3$.

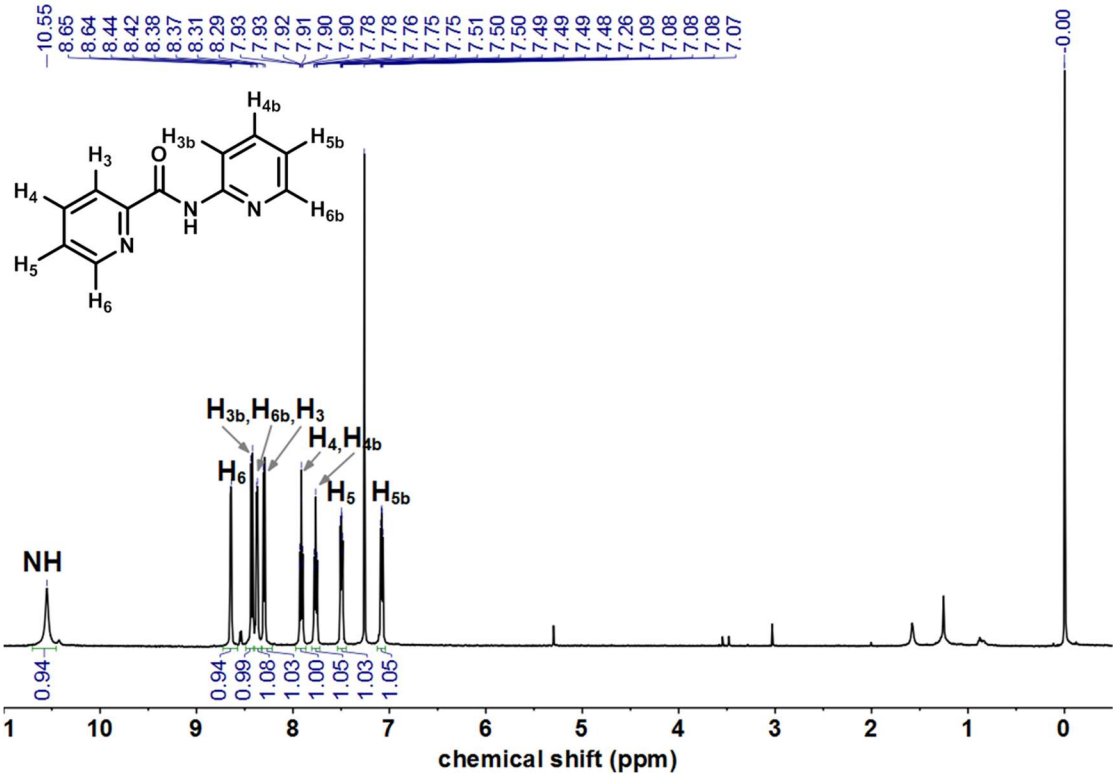

Figure S11. ^{1}H NMR (500 MHz, 298 K) spectrum of **2e** in $CDCl_3$.

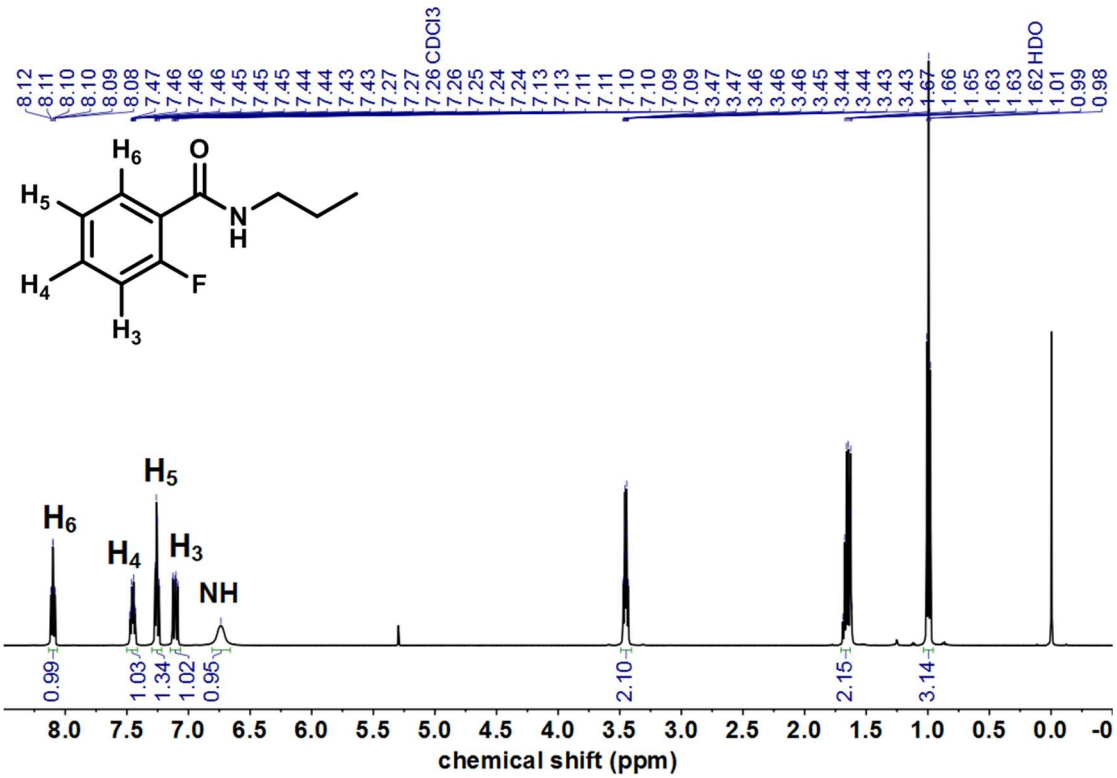

Figure S12. ^{1}H NMR (500 MHz, 298 K) spectrum of **3a** in $CDCl_3$.

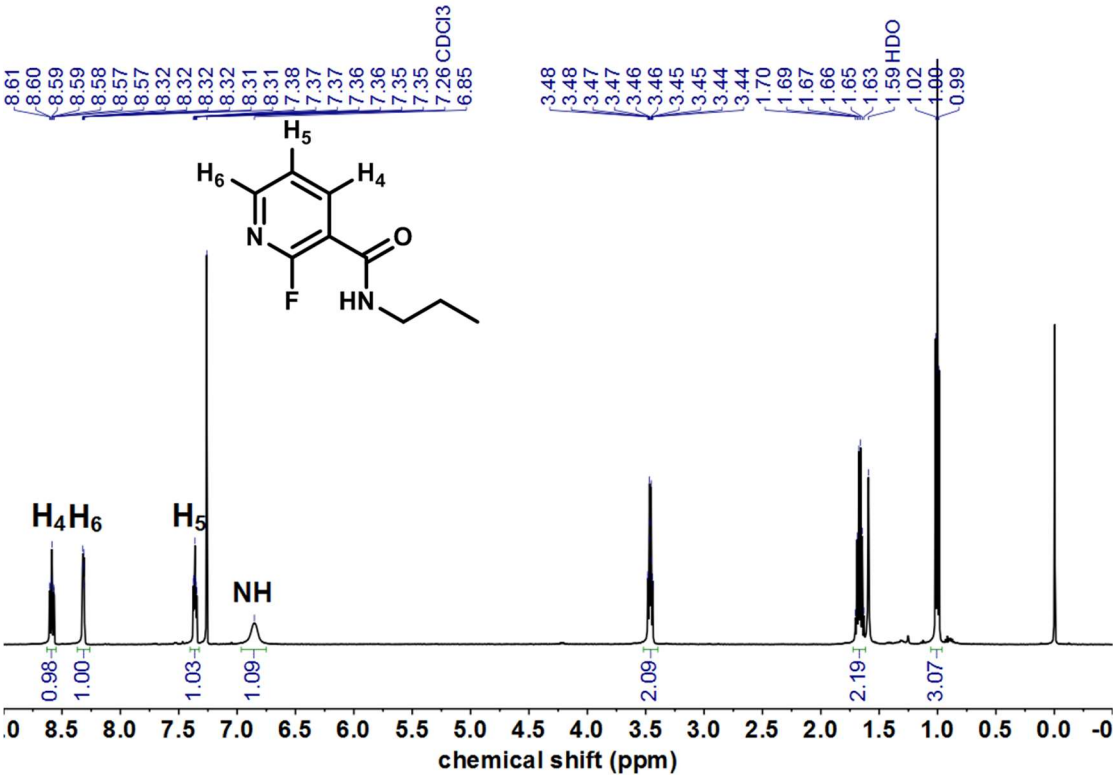

Figure S13. ^{1}H NMR (500 MHz, 298 K) spectrum of **3b** in $CDCl_3$.

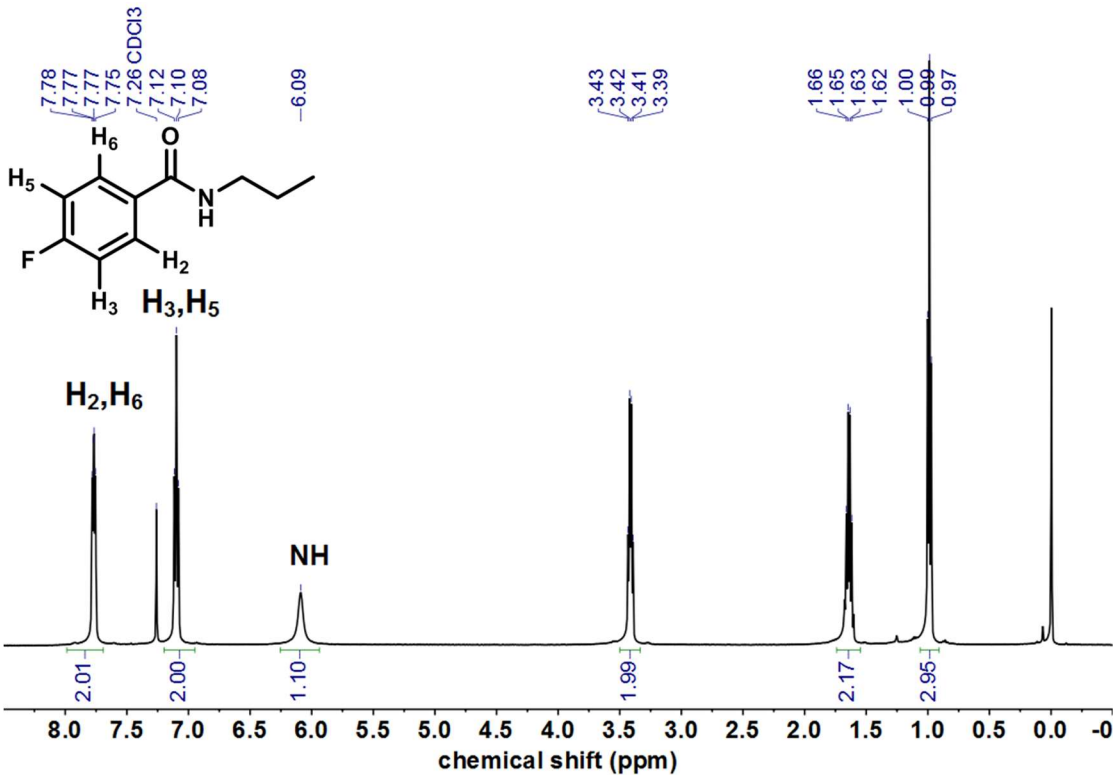

Figure S14. ^{1}H NMR (500 MHz, 298 K) spectrum of **3c** in $CDCl_3$.

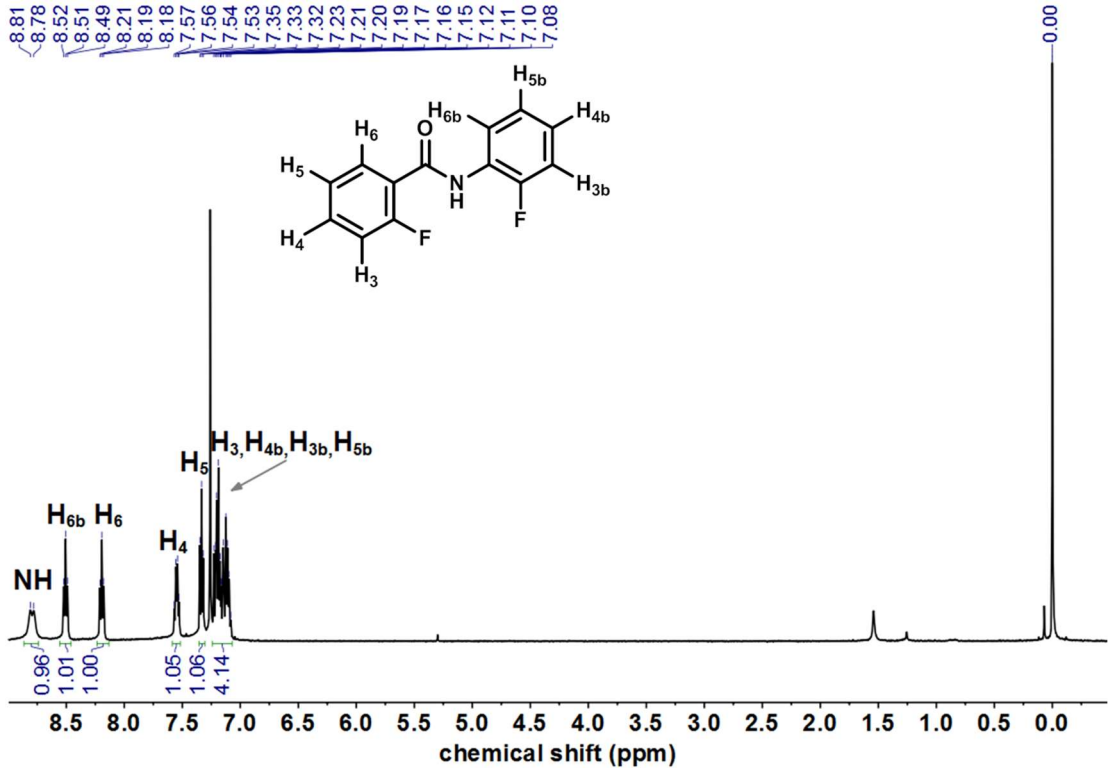

Figure S15. ^{1}H NMR (500 MHz, 298 K) spectrum of **3d** in $CDCl_3$.

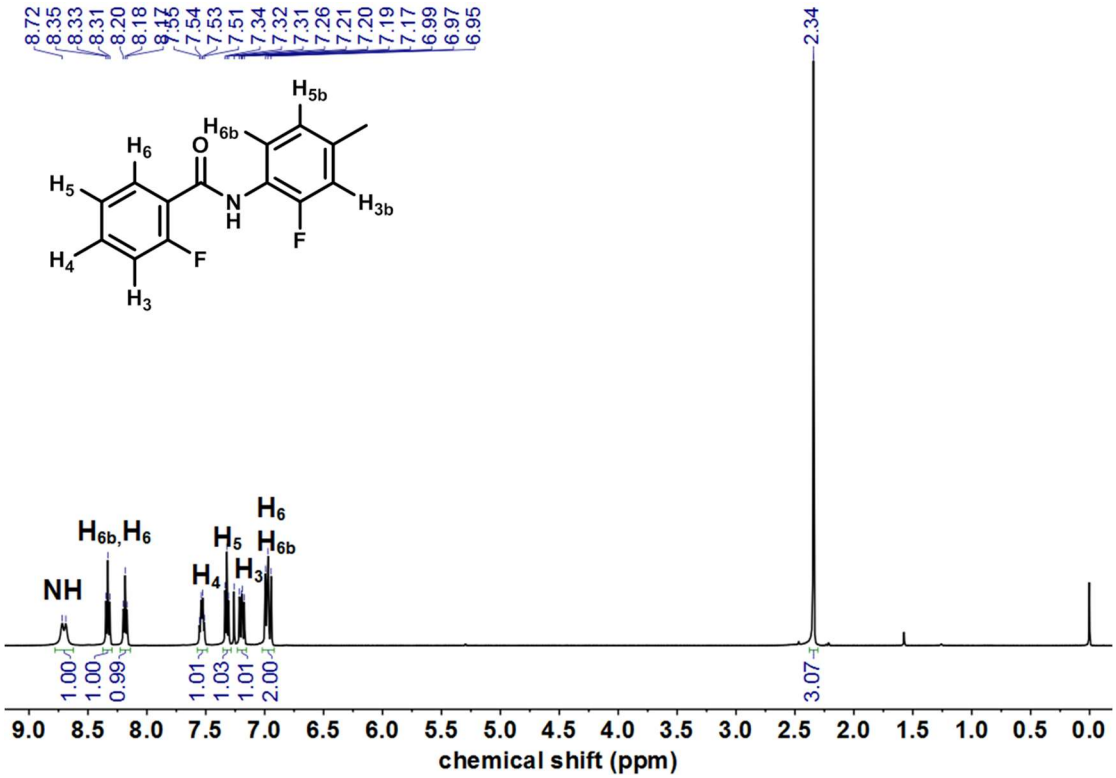

Figure S16. ^{1}H NMR (500 MHz, 298 K) spectrum of **3e** in $CDCl_3$.

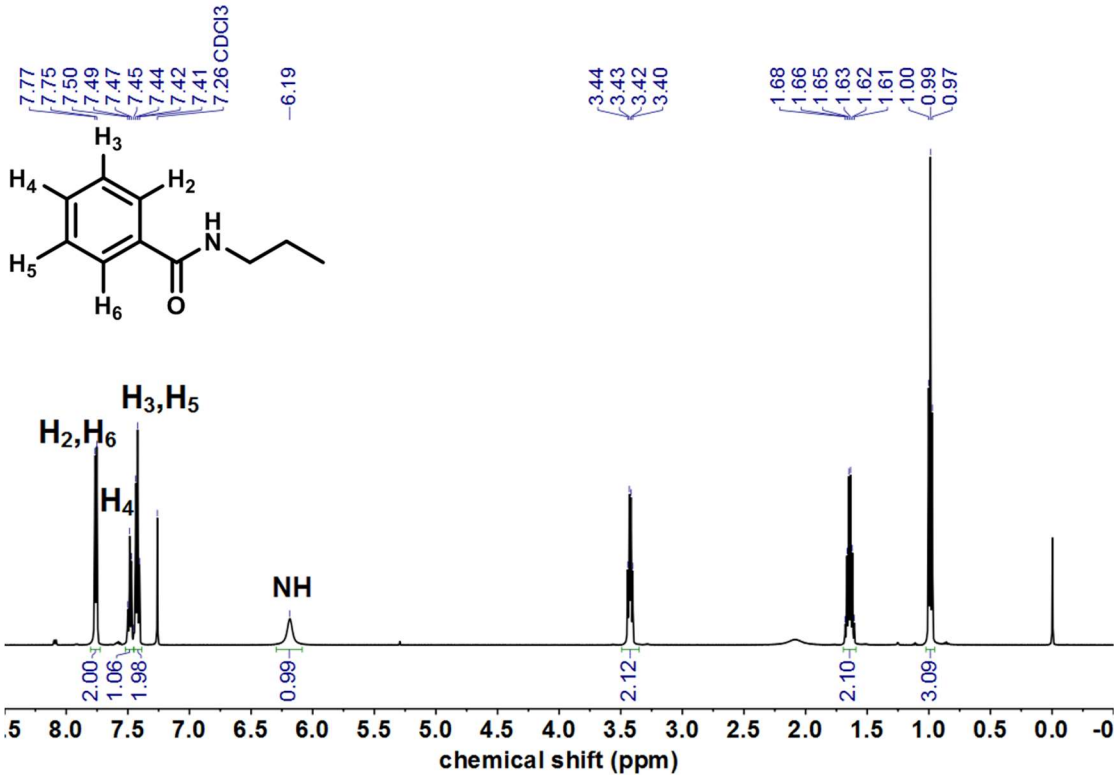

Figure S17. ^{1}H NMR (500 MHz, 298 K) spectrum of **PB** in $CDCl_3$.

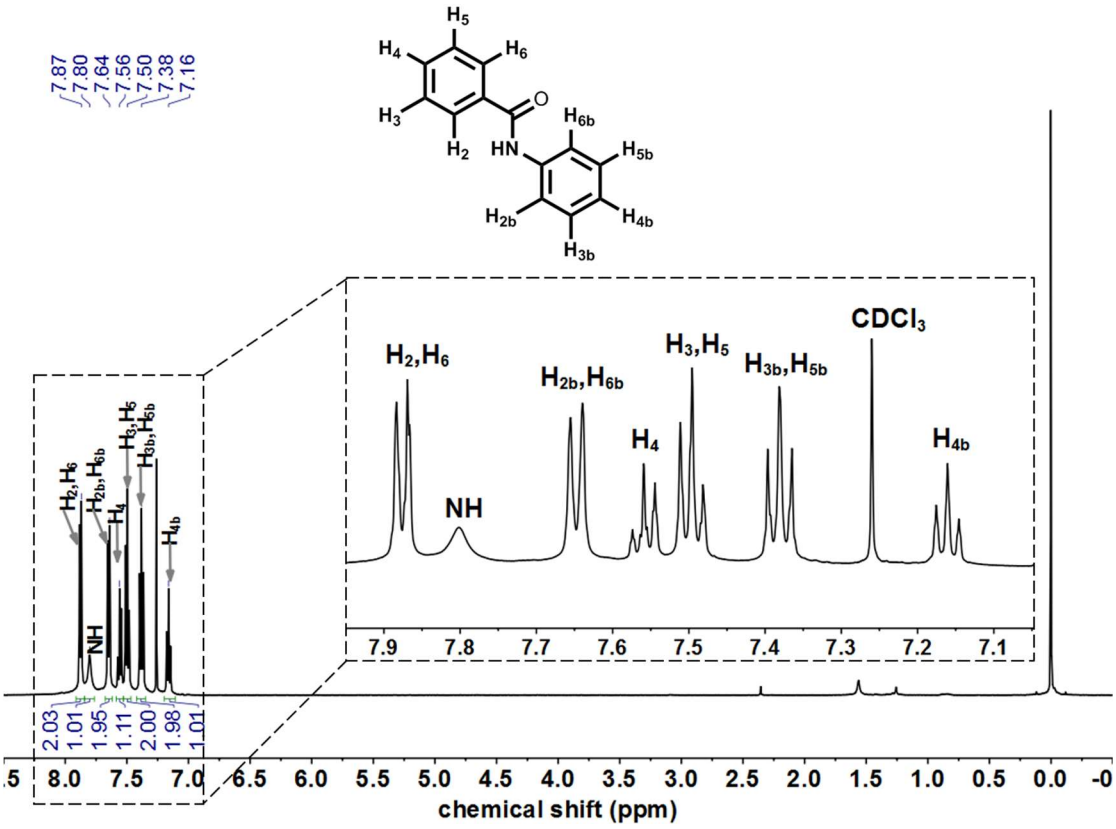

Figure S18. ^{1}H NMR (500 MHz, 298 K) spectrum of **PhB** in $CDCl_3$.

4. Stack plots of partial ^{1}H NMR spectra of compounds

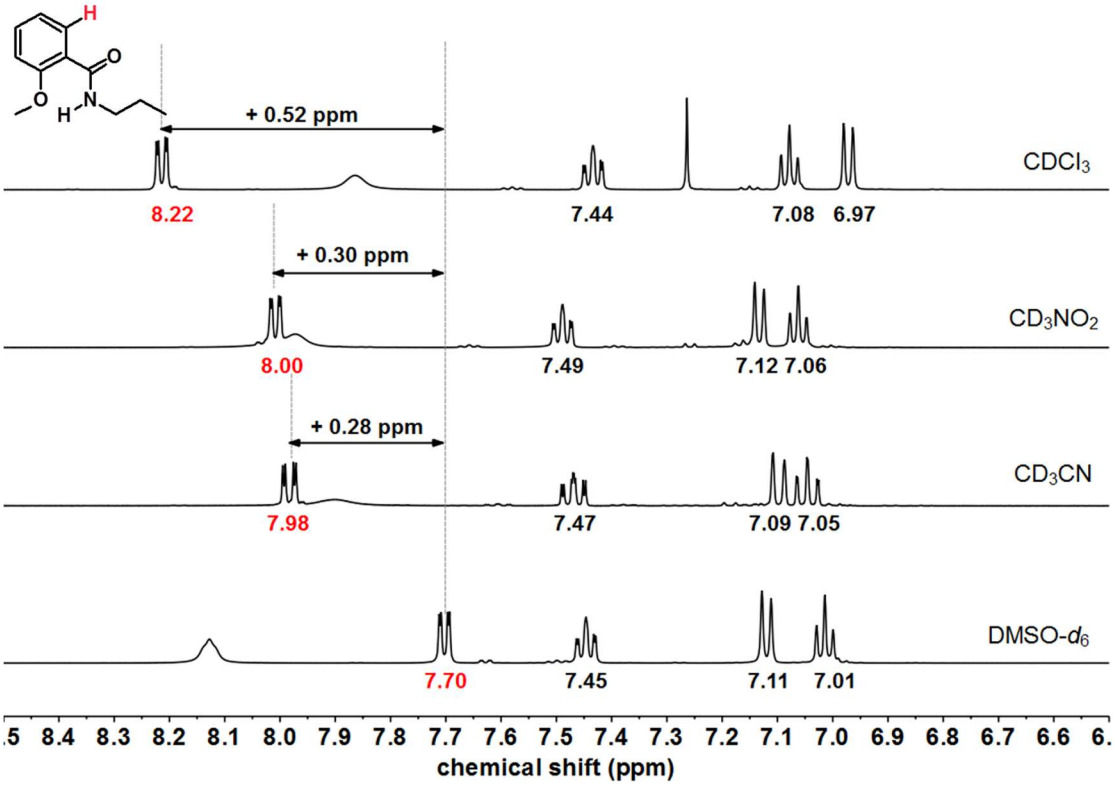

Figure S19. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **1a**.

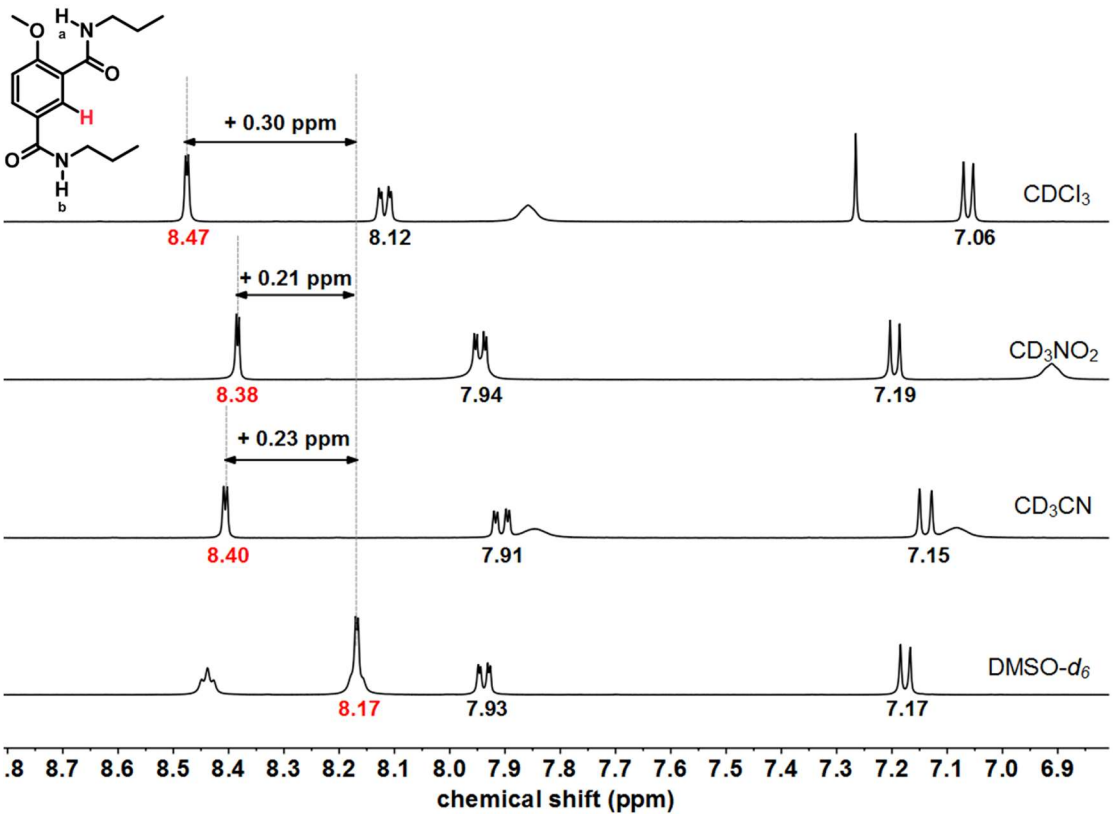

Figure S20. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **1b** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

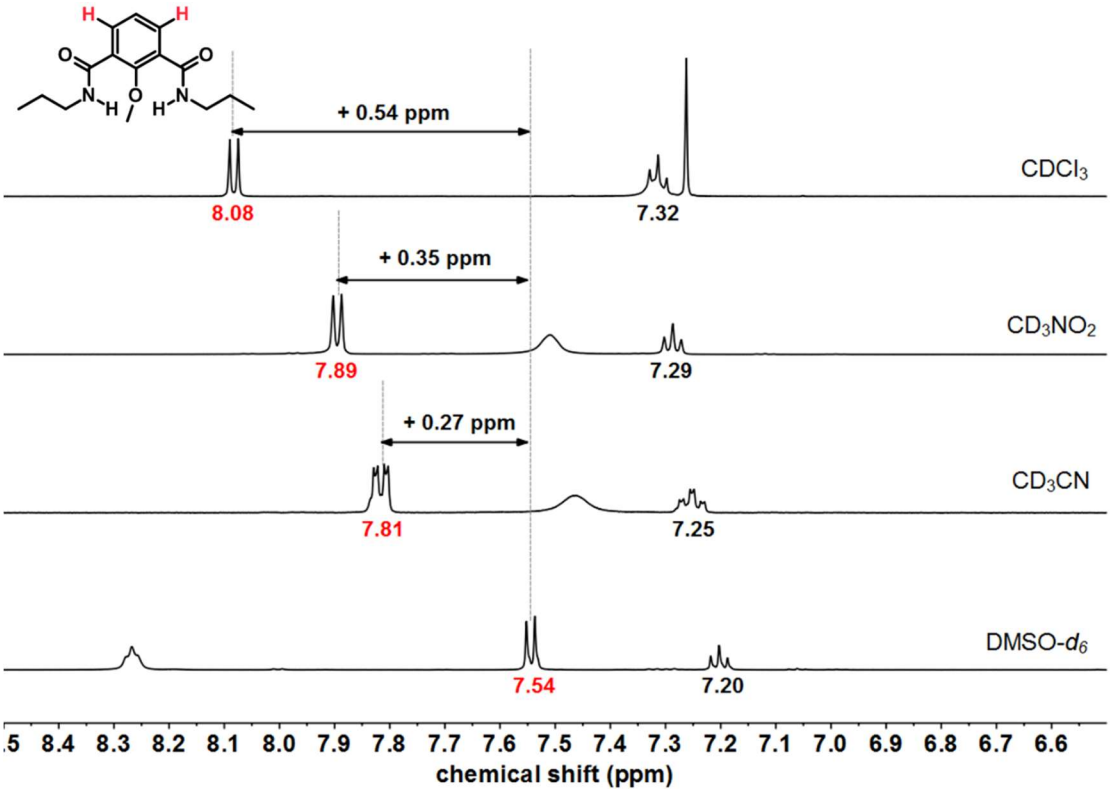

Figure S21. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **1c** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

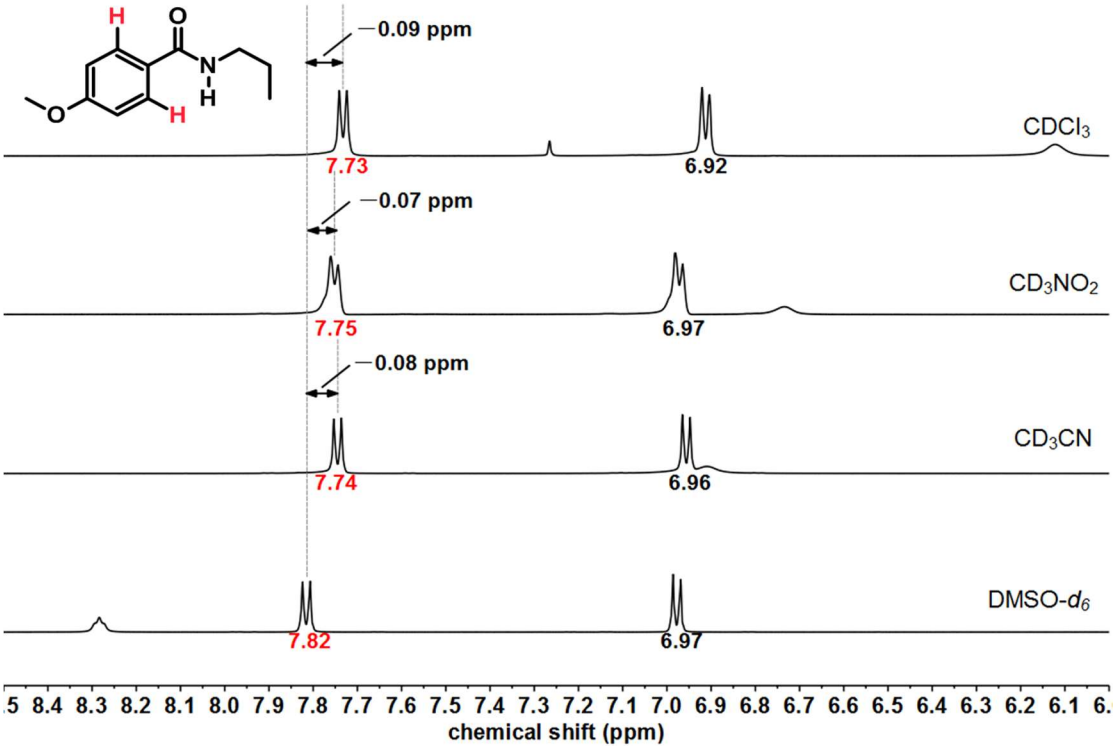

Figure S22. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **1d** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

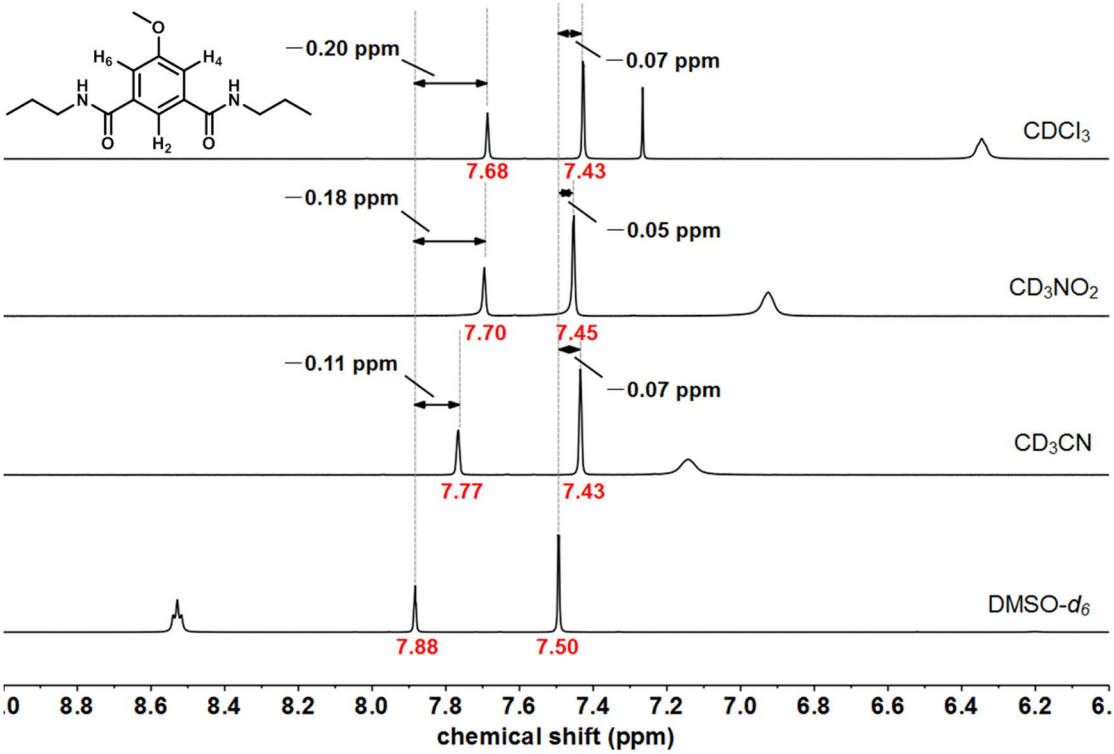

Figure S23. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **1e** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

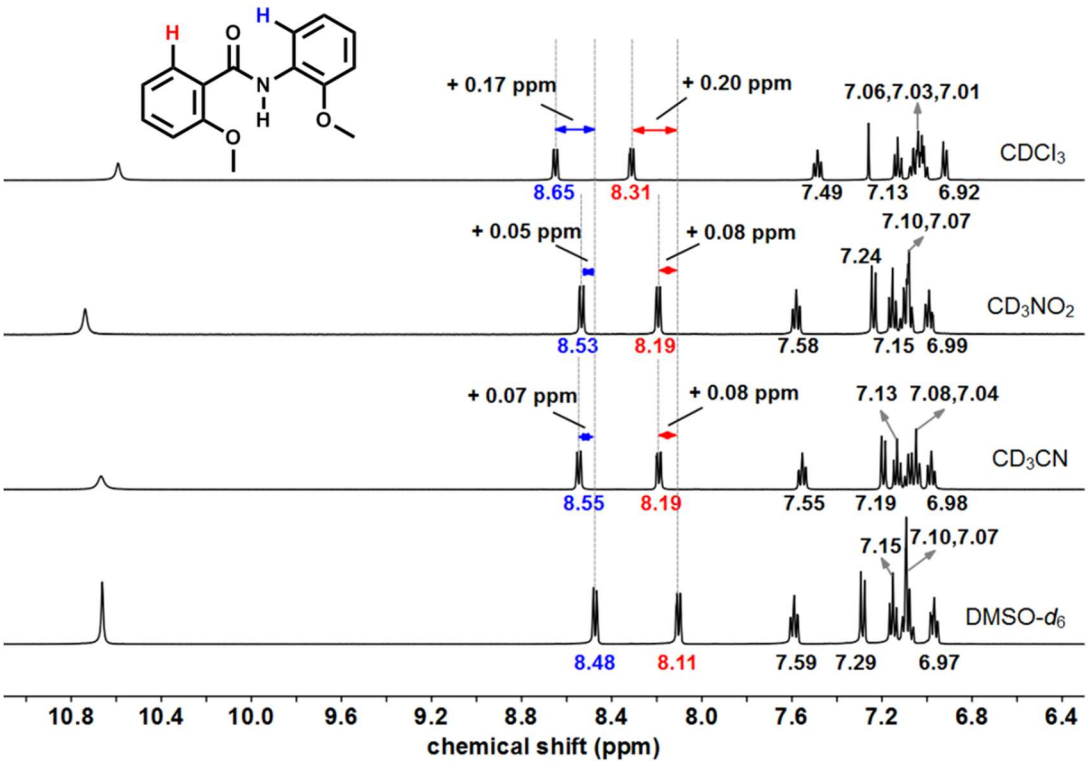

Figure S24. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **1f** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

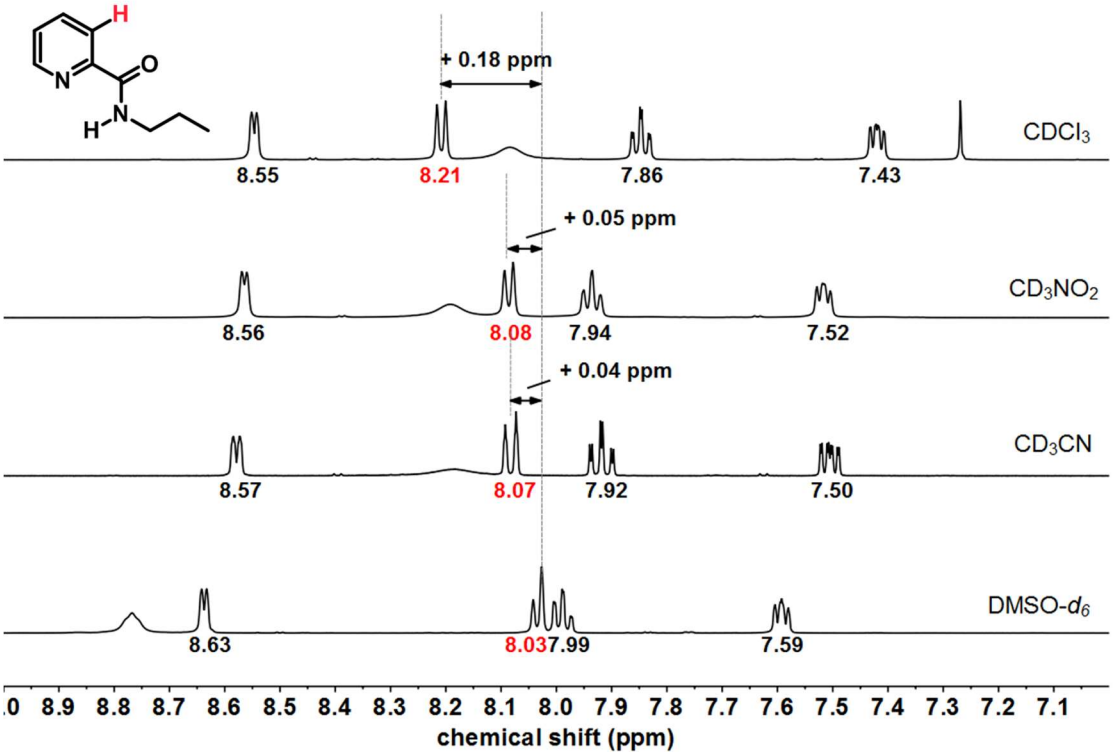

Figure S25. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **2a** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

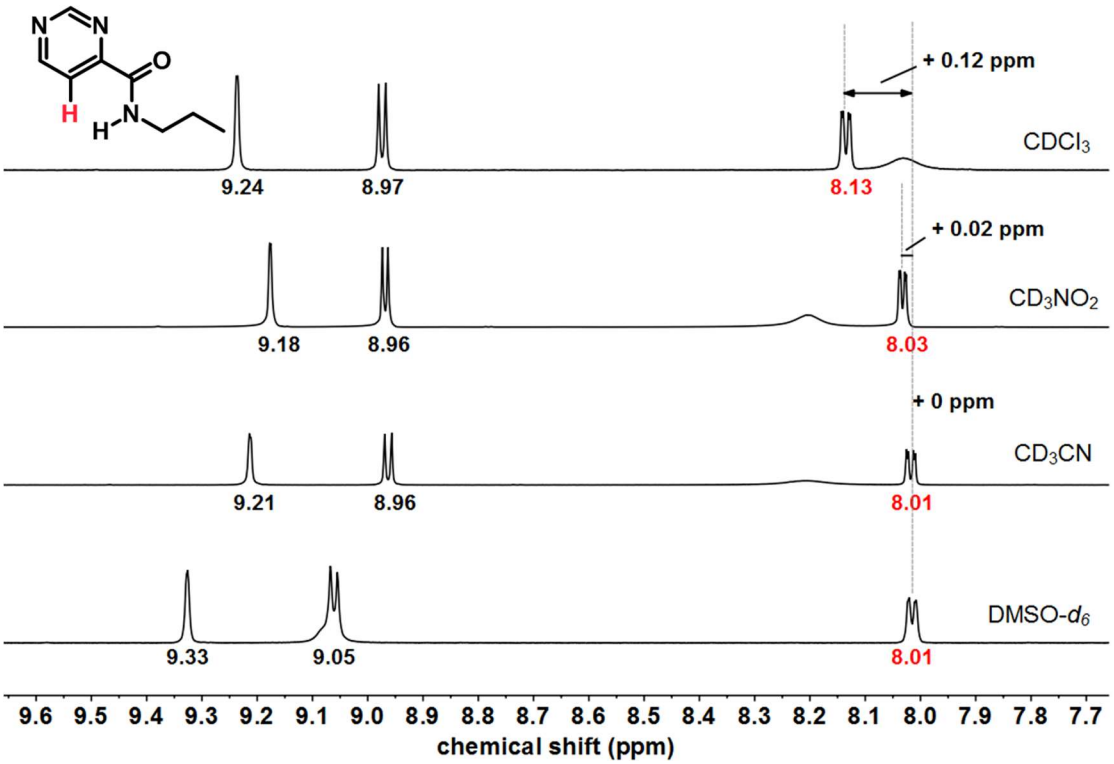

Figure S26. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **2b** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

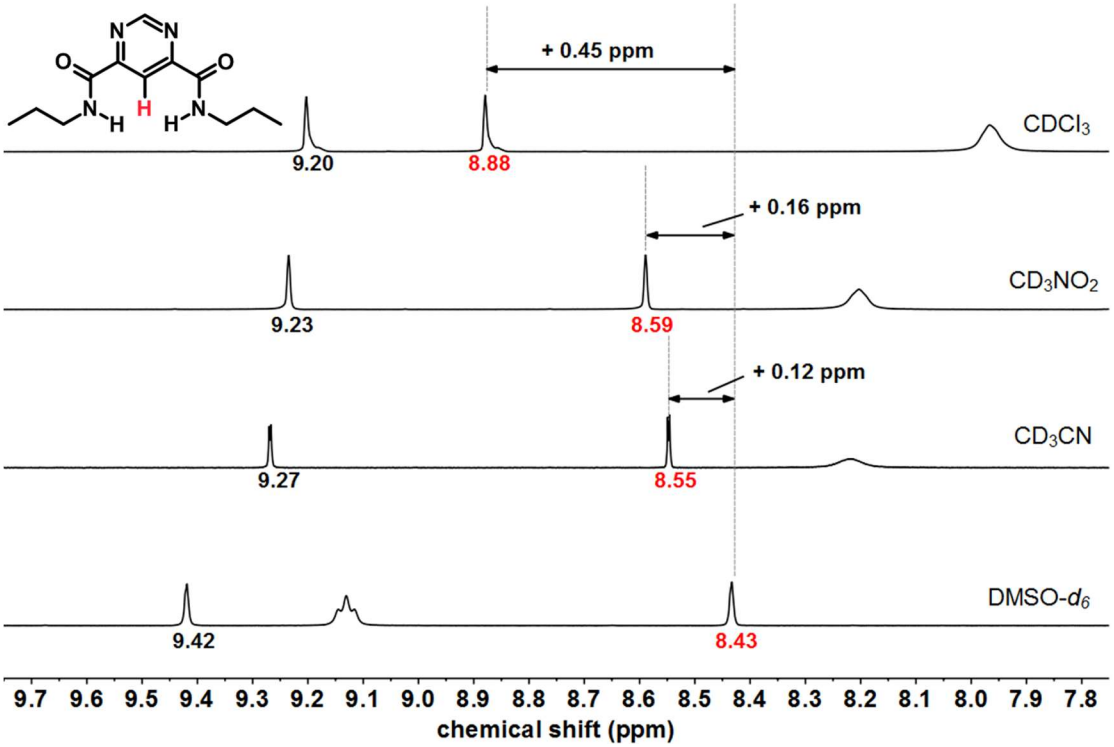

Figure S27. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **2c** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

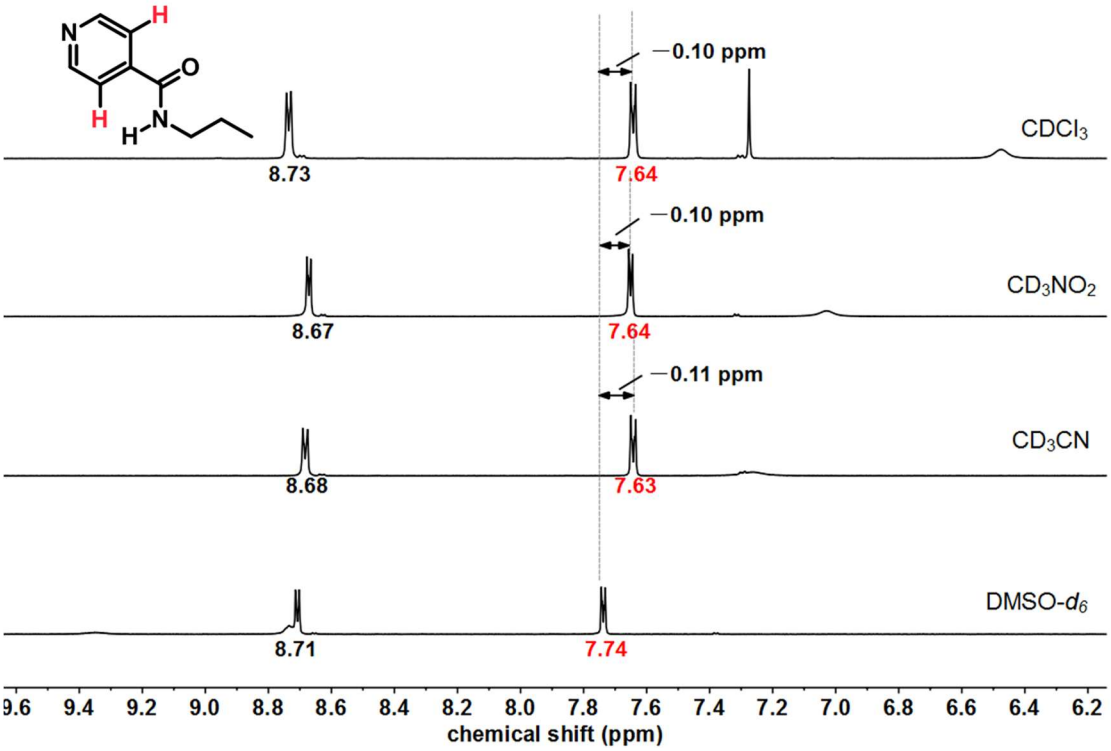

Figure S28. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **2d** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

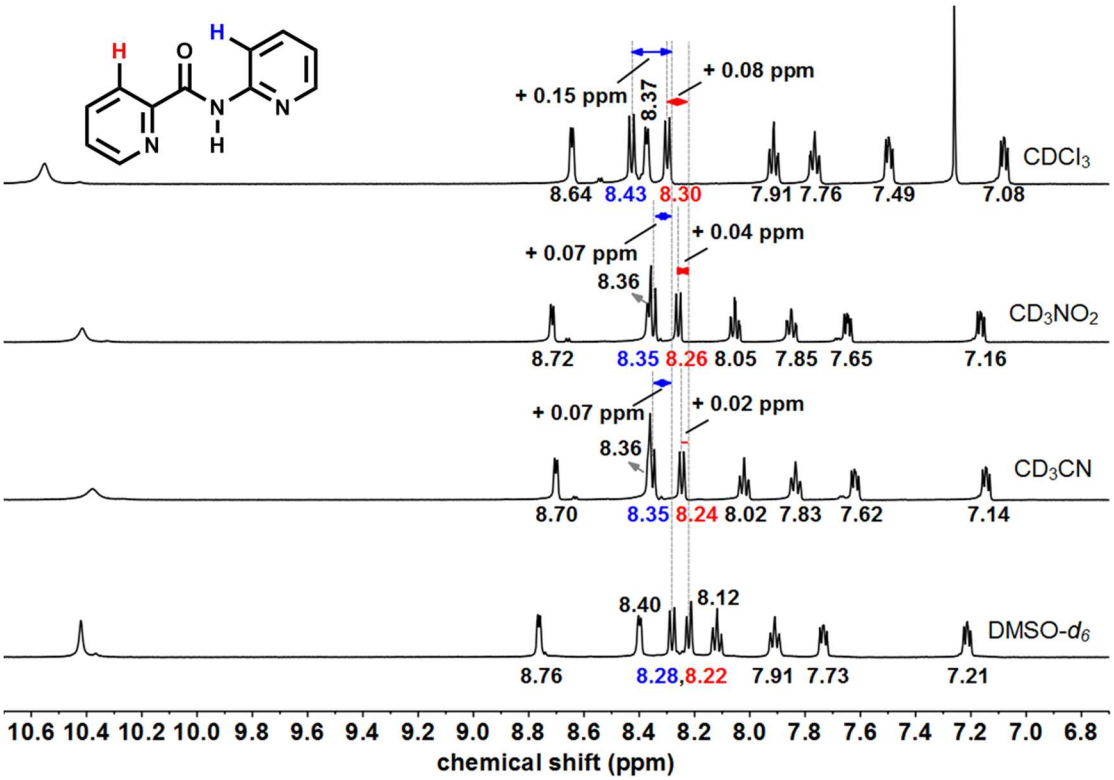

Figure S29. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **2e** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

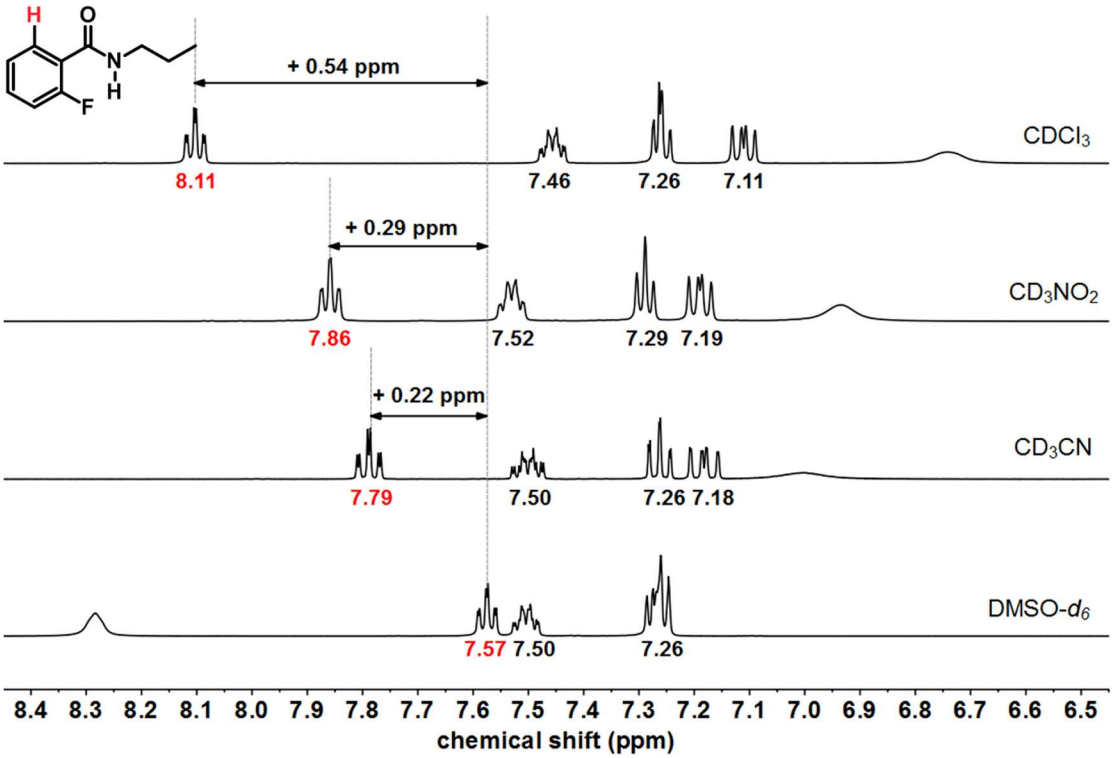

Figure S30. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **3a** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

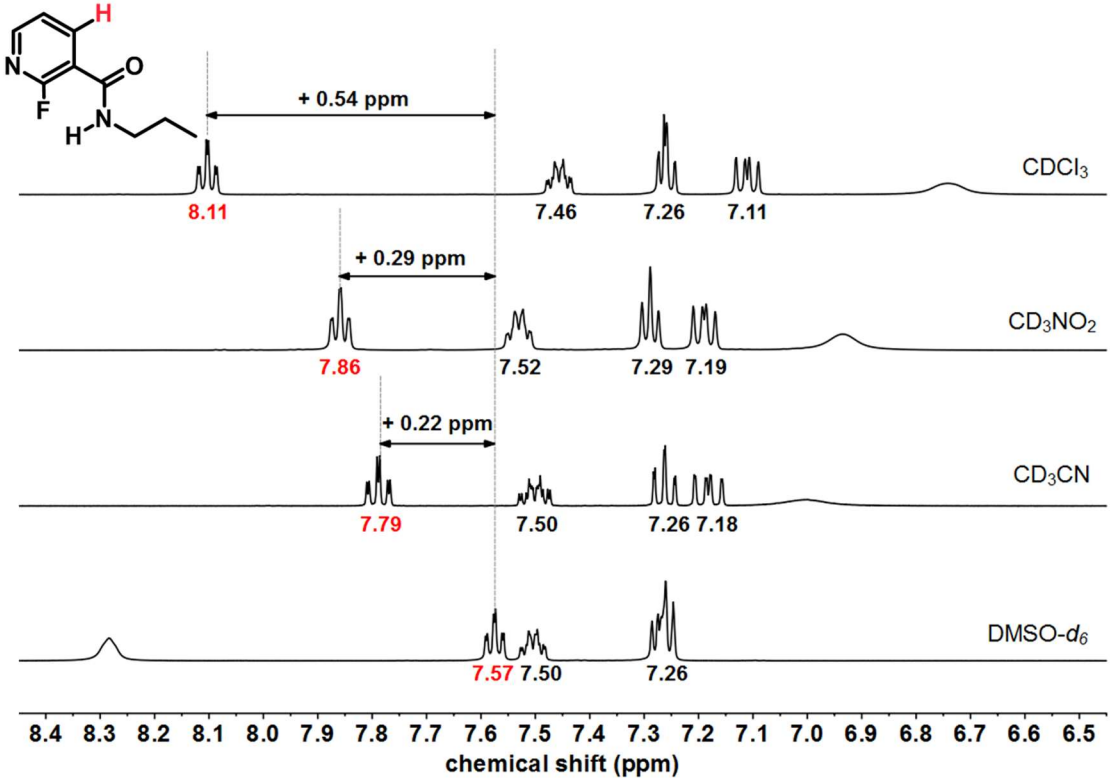

Figure S31. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **3b** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

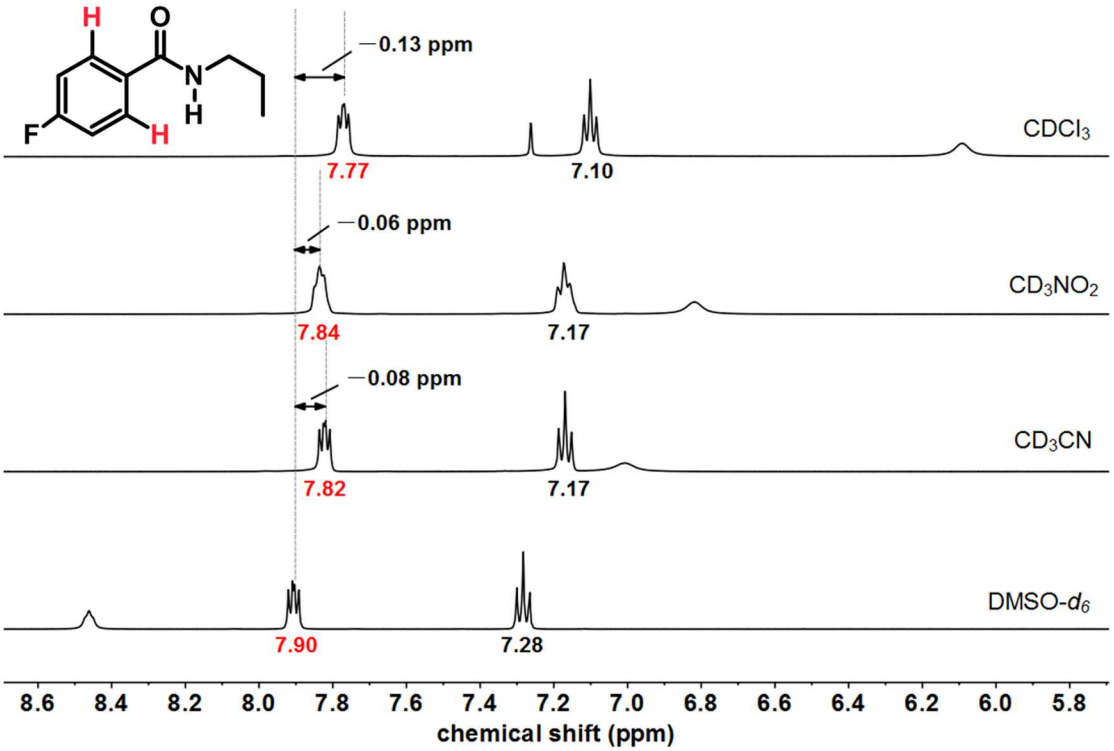

Figure S32. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **3c** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

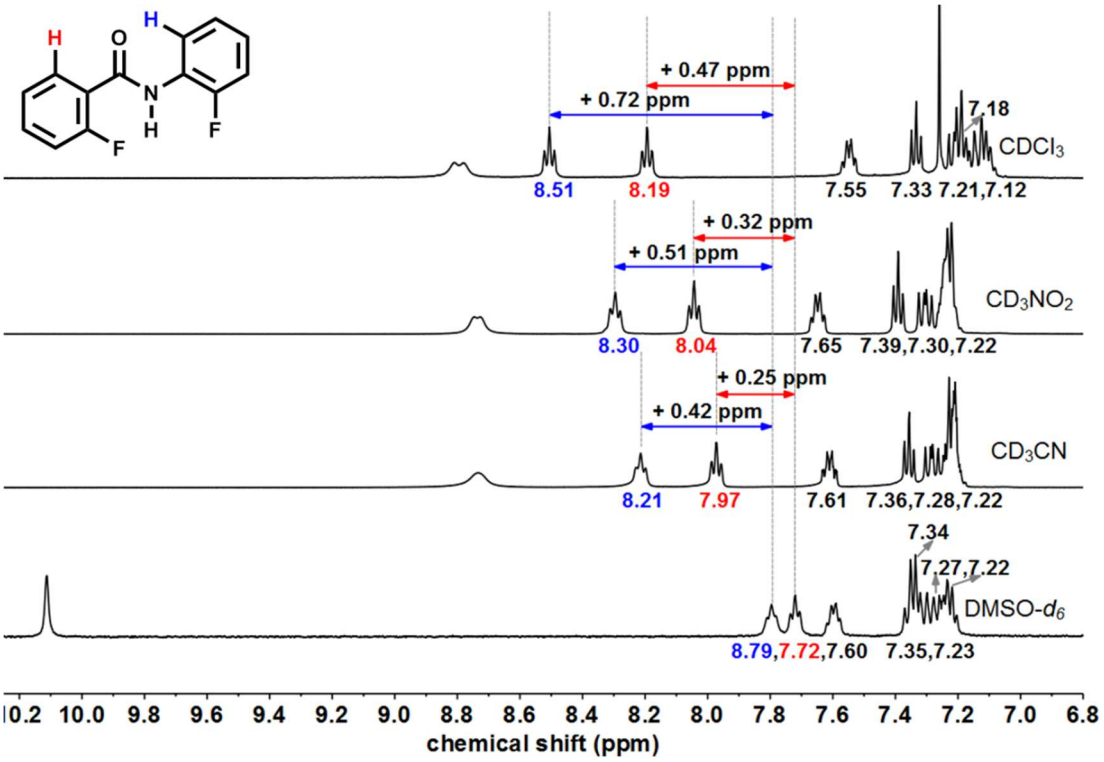

Figure S33. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **3d** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

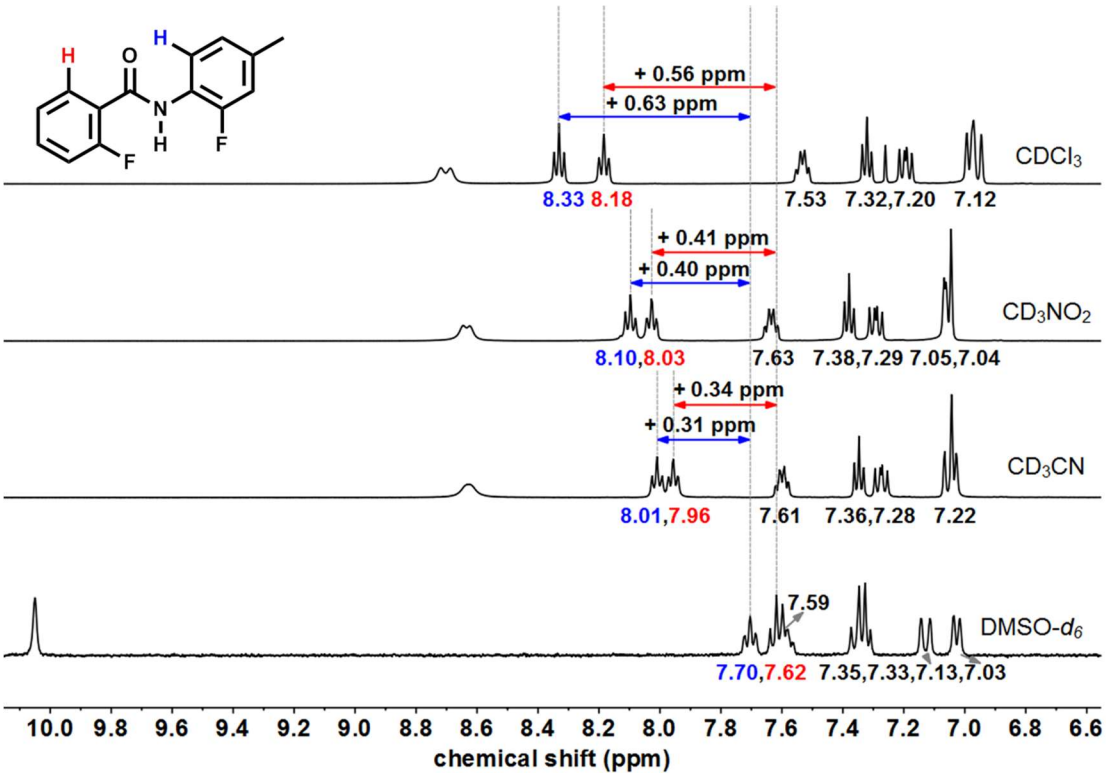

Figure S34. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **3e** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

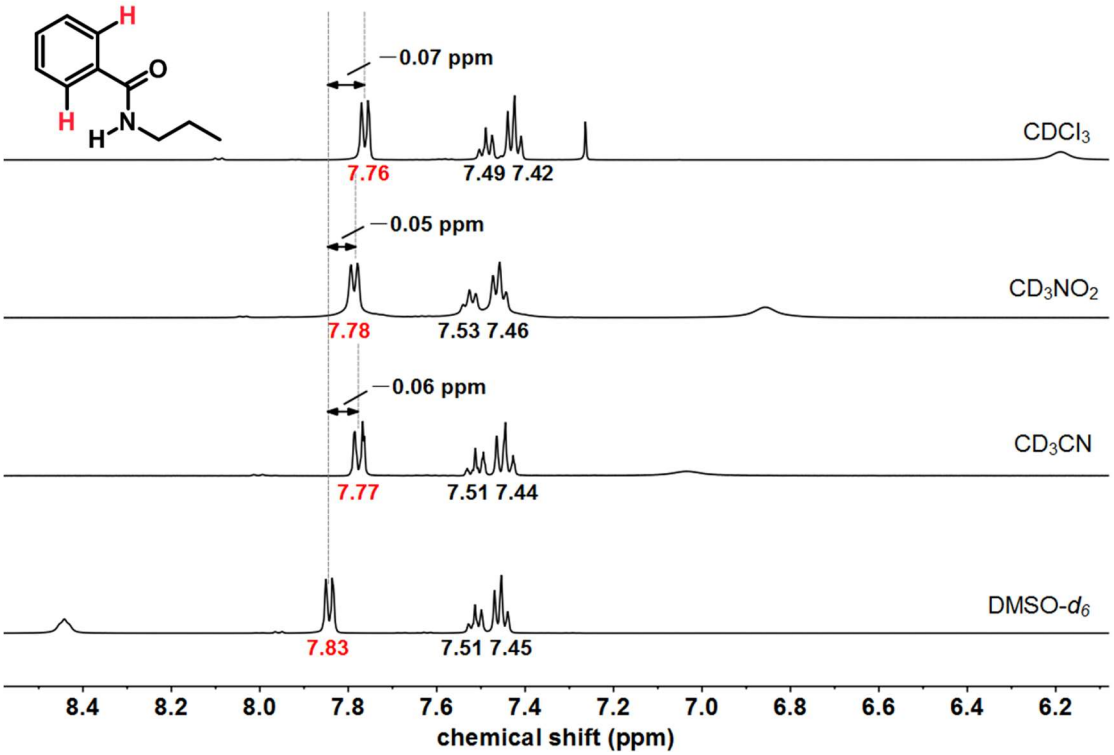

Figure S35. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **PB** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

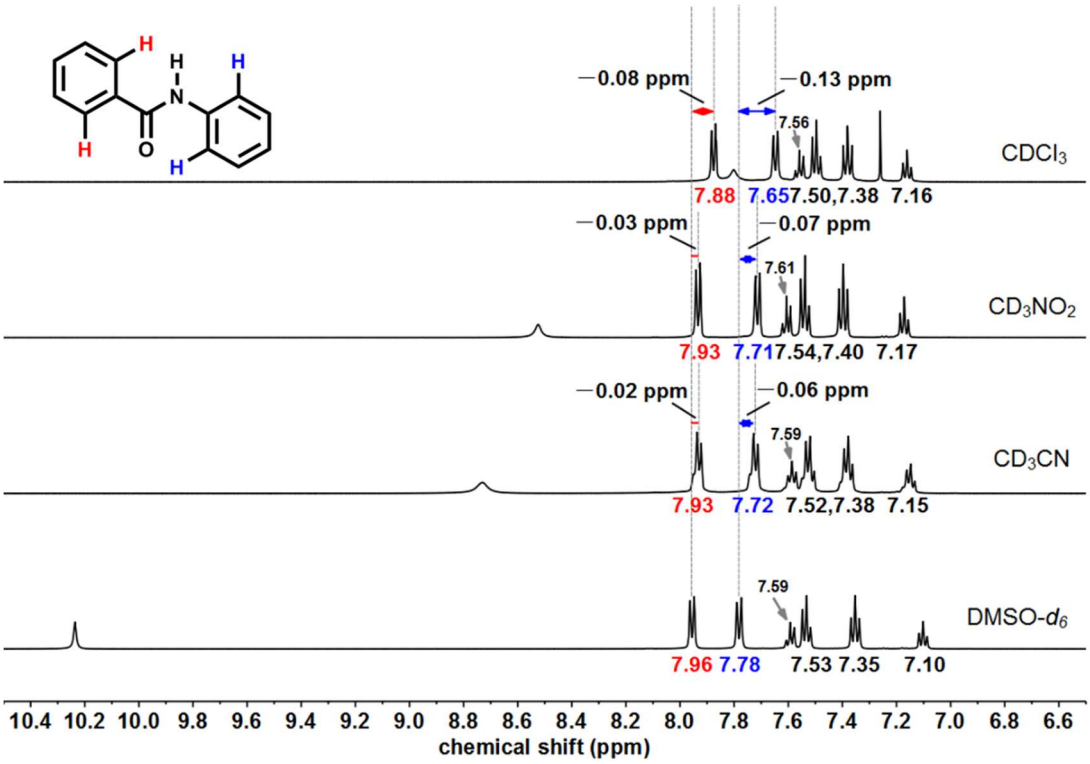

Figure S36. Stack plots of partial ^{1}H NMR (500 MHz, 298 K) spectra of **PhB** in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6.

5. Table S1. Chemical shifts of nonβH of compounds

Table S1. Chemical shifts of nonβH of *N*-alkyl aromatic amides in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6 and their solvent-related changes.

nonβH	δ($CDCl_3$)	δ(CD_3NO_2)	δ(CD_3CN)	δ(DMSO)	Δ($\delta_{nonβH}$)-1[a]	Δ($\delta_{nonβH}$)-2	Δ($\delta_{nonβH}$)-3
H3 of 1a	6.97	7.12	7.09	7.11	−0.14	0.01	−0.02
H4 of 1a	7.44	7.49	7.47	7.45	−0.01	0.04	0.02
H5 of 1a	7.08	7.06	7.05	7.01	0.07	0.05	0.04
H5 of 1b	7.06	7.19	7.15	7.17	−0.11	0.02	−0.02
H5 of 1c	7.32	7.29	7.25	7.20	0.12	0.09	0.05
H3,H5 of 1d	6.92	6.97	6.96	6.97	−0.05	0.00	−0.01
H4 of 2a	7.86	7.94	7.92	7.99	−0.13	−0.05	−0.07
H5 of 2a	7.43	7.52	7.50	7.59	−0.16	−0.07	−0.09
H6 of 2a	8.55	8.56	8.57	8.63	−0.08	−0.07	−0.06
H2 of 2b	9.24	9.18	9.21	9.33	−0.09	−0.15	−0.12
H6 of 2b	8.97	8.96	8.96	9.05	−0.08	−0.09	−0.09
H2 of 2c	9.20	9.23	9.27	9.42	−0.22	−0.19	−0.15
H2,H6 of 2d	8.73	8.67	8.68	8.71	0.02	−0.04	−0.03
H3 of 3a	7.11	7.19	7.18	7.26	−0.15	−0.07	−0.08
H4 of 3a	7.46	7.52	7.50	7.50	−0.04	0.02	0.00
H5 of 3a	7.26	7.29	7.26	7.26	0.00	0.03	0.00
H5 of 3b	7.36	7.42	7.38	7.45	−0.09	−0.03	−0.07
H6 of 3b	8.32	8.29	8.28	8.33	−0.01	−0.04	−0.05
H3,H5 of 3c	7.10	7.17	7.17	7.28	−0.18	−0.11	−0.11
H3,H5 of PB	7.42	7.46	7.44	7.45	−0.03	0.01	−0.01
H4 of PB	7.49	7.53	7.51	7.51	−0.02	0.02	0.00

[a] $\Delta(\delta_{nonβH})\text{-}1 = \delta_{nonβH}(CDCl_3) - \delta_{nonβH}(DMSO)$, $\Delta(\delta_{nonβH})\text{-}2 = \delta_{nonβH}(CD_3NO_2) - \delta_{nonβH}(DMSO)$, $\Delta(\delta_{nonβH})\text{-}3 = \delta_{nonβH}(CD_3CN) - \delta_{nonβH}(DMSO)$.

Table S2. Chemical shifts of aromatic protons except βH and γH of *N*-aryl aromatic amides (**1f**, **2e**, **3d**, **3e** and **PhB**) in $CDCl_3$, CD_3NO_2, CD_3CN and DMSO-d_6 and their solvent-related changes.

	δ($CDCl_3$)	δ(CD_3NO_2)	δ(CD_3CN)	δ(DMSO)	Δ(δ)-1[a]	Δ(δ)-2	Δ(δ)-3
H3 of 1f	7.03	7.24	7.19	7.29	−0.26	−0.05	−0.10
H4 of 1f	7.49	7.58	7.55	7.59	−0.10	−0.01	−0.04
H5 of 1f	7.13	7.15	7.13	7.15	−0.02	0.00	−0.02
H3b of 1f	6.92	7.07	7.04	7.07	−0.15	0.00	−0.03
H4b of 1f	7.06	7.10	7.08	7.10	−0.04	0.00	−0.02
H5b of 1f	7.01	6.99	6.98	6.97	0.04	0.02	0.01
H4 of 2e	7.91	8.05	8.02	8.12	−0.21	−0.07	−0.10
H5 of 2e	7.49	7.65	7.62	7.73	−0.24	−0.08	−0.11
H6 of 2e	8.64	8.72	8.70	8.76	−0.12	−0.04	−0.06
H4b of 2e	7.76	7.85	7.83	7.91	−0.15	−0.06	−0.08
H5b of 2e	7.08	7.16	7.14	7.21	−0.13	−0.05	−0.07
H6b of 2e	8.37	8.36	8.36	8.40	−0.03	−0.04	−0.04
H3 of 3d	7.21	7.30	7.28	7.34	−0.13	−0.04	−0.06
H4 of 3d	7.55	7.65	7.61	7.60	−0.05	0.05	0.01
H5 of 3d	7.33	7.39	7.36	7.35	−0.02	0.04	0.01
H3b of 3d	7.12	7.22	7.22	7.23	−0.11	−0.01	−0.01
H4b of 3d	7.18	7.30	7.28	7.27	−0.09	0.03	0.01
H5b of 3d	7.12	7.22	7.22	7.22	−0.10	0.00	0.00
H3 of 3e	7.20	7.29	7.27	7.33	−0.13	−0.04	−0.06
H4 of 3e	7.53	7.63	7.60	7.59	−0.06	0.04	0.01
H5 of 3e	7.32	7.38	7.35	7.35	−0.03	0.03	0.00
H3b of 3e	6.97	7.04	7.04	7.13	−0.16	−0.09	−0.09
H5b of 3e	6.97	7.05	7.05	7.03	−0.06	0.02	0.02
H4 of PhB	7.56	7.61	7.59	7.59	−0.03	0.02	0.00
H4b of PhB	7.16	7.17	7.15	7.10	0.06	0.07	0.05
H3,H5 of PhB	7.50	7.54	7.52	7.53	−0.03	0.01	−0.01
H3b,H5b of PhB	7.38	7.4	7.38	7.35	0.03	0.05	0.03

[a] Δ(δ)-1 = δ($CDCl_3$) − δ(DMSO), Δ(δ)-2 = δ(CD_3NO_2) − δ(DMSO), Δ(δ)-3 = δ(CD_3CN) − δ(DMSO).