Supporting Information

Chemical Communications

A white light emitting reconfigurable pyrazoline-naphthalimide logic gate with magnesium, sodium and proton inputs

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Table of Contents

Chemicals

Acenaphthene (99%, BDH), acetylchloride (98%, Sigma-Aldrich), benzo-15-crown-5 ether (98%, TCI), benzaldehyde (99%, Sigma-Aldrich), hexamethylenetetramine (99%, Sigma-Aldrich), 4-hydrazinobenzoic acid (97%, Sigma-Aldrich), trifluoroacetic acid (99%, Sigma-Aldrich), tetramethylammonium hydroxide (2.5 M, Sigma-Aldrich), anhydrous aluminium chloride (98.5%, Acros Organics) were used as received. Aniline (Hopkins and Williams) was distilled prior to use. The solvents were HPLC grade. Rhodamine B (Sigma-Aldrich) was used as supplied. Sodium perchlorate and magnesium perchlorate (BDH) salts were dried and stored in a desiccator.

Column chromatography was performed using sand (50-70 mesh), high purity grade silica gel (pore size 60 Å, 70-230 mesh, 63-200 μm) or aluminium oxide (pore size 60 Å, 50-200 μm). Thin-layer chromatography (TLC) was performed using silica gel on aluminium foils (pore size 60 Å) or aluminium oxide neutral (pore size 60 Å) from Sigma-Aldrich. NMR spectra were recorded in deuterated chloroform (99.8% atom D, 0.05% (v/v) TMS, Sigma-Aldrich) or (99.6 atom% stabilized with silver chip, TCI). FTIR spectra were measured with potassium bromide (99%, Fischer) dried in an oven at 200 ^{o}C and compressed with a handheld press into discs. Vanillin and caffeine analytical standards (Sigma-Aldrich) were used as melting point standards.

Instrumentation

Synthetic reactions were carried out in round-bottom flasks fitted with a reflux condenser on IKA C-MAG HP 7 hot plates equipped with a ETS-D5 temperature probe. A Stuart RE300D8 rotatory evaporator and water bath set was used for solvent removal under vacuum. Nuclear magnetic resonance (NMR) spectra were measured on a Bruker Avance III HD NMR spectrometer equipped with an Ascend 500 MHz superconducting magnet operating at 500.13 MHz and 125.76 MHz for ^{1}H and ^{13}C respectively. Chemical shifts were calibrated versus TMS at 0.00 ppm or versus the solvent peak ($CHCl_3$) at 7.26 ppm and ($CDCl_3$) at 77.00 ppm for ^{1}H and ^{13}C, respectively. Data were acquired using a 5 mm PABBO probe and analysed using the software TopSpin version 3.2. Infra-red spectra were measured using a Shimadzu IR-Affinity1 spectrophotometer calibrated against a polystyrene film standard at 1602 cm^{-1}. Spectra were interpreted using SpectraGraph V1.2. High resolution mass spectrometry were measured by Medac Ltd. using a Waters LC premier instrument. Melting points were measured on a Stuart SMP11 melting point apparatus and are corrected. Naked eye emission was observed using a dual-wavelength UVGL-58 handheld lamp (254 nm and 365 nm).

Ultraviolet-visible absorbance and steady-state emission spectra were recorded on JASCO V-650 and Jasco FP-8300 spectrophotometers connected to a desktop computer at room temperature. Solutions were contained within 3.0 mL Suprasil quartz cuvettes (QS-101-10-40) with a 1.0 cm path length. For the fluorescence experiments, dilute solutions with an optical density (OD) below 0.10 were used at the excitation wavelengths of 472 nm and 470 nm to avoid reabsorption effects. Excitation and emission slit widths were set at 2.5 nm. Rhodamine B was used as the fluorescence quantum yields standard (Φ_F = 0.53 in MeOH).[S1]

The fluorescence quantum yields were determined using the following equation

$$\Phi_F = \Phi_{ref} x \frac{I_F}{I_{ref}} x \frac{A_{ref}}{A} x \frac{n^2}{n_{ref}^2}$$

where Φ_F is the relative fluorescence quantum yield of the sample, Φ_{ref} is the fluorescence quantum yield of the reference standard, I_F is the emission area of the sample, I_{ref} is the emission area of the reference standard, A_{ref} is the absorbance of the reference standard, A is the absorbance of the sample, n is the solvent refractive index of the sample, and n_{ref} is the solvent refractive index of the reference standard.

pH titrations in acetonitrile were performed using standard solutions of 1 M, 0.1 M, 0.01 M and 0.001 M of methanesulfonic acid (MSA) and tetramethylammonium hydroxide (TMAH). The pH titrations were carried out by adding an aliquot of TMAH and then titrating with MSA solutions. Aliquots were added using Gibson micropipettes. After each aliquot, a sample from the solution was transferred into a quartz cuvette, the absorbance and emission spectra were measured, and the sample within the cuvette returned to the original solution. Metal ion titrations for compound **2** were carried out using a similar procedure with known equivalents of $NaClO_4$ or $Mg(ClO_4)_2$. *Caution*: *perchlorate salts present a potential explosion hazard and should be handled with care.*

Synthesis and Characterisation

The synthetic strategy for compounds **1** and **2**, shown in Scheme S1, was adapted from references S2 and S3.

1-(1,2-Dihydroacenaphthylen-5-yl)ethanone (**4**)

In a two-necked 250 mL round-bottom flask, acenaphthene (22 g, 0.15 mol) was dissolved in 100 mL of dry dichloromethane. Anhydrous aluminium chloride (25 g, 0.19 mol) and acetylchloride (13 mL, 0.19 mol) were stirred in a 100 mL round-bottom flask for 1 hour in 50 mL of sieve-dried dichloromethane and over an ice bath at 5 °C added to the acenaphthene solution and stirred for 24 hours. The reaction mixture was poured over 50 mL of conc. HCl and 250 g of ice, extracted with CH_2Cl_2 (3×50 mL), washed with 50 mL of 10% sodium carbonate and saturated NaCl solutions, and dried over magnesium sulfate. The solution was removed by rotary evaporator to dryness to yield a brown solid, which was purified by silica gel chromatography with hexane and gradually increasing to 5% ethyl acetate. The off-white solid was recrystallised from petroleum ether in 60% yield (18.5 g).[S2] m.p. 62.2-62.8 ^{o}C; ^{1}H NMR ($CDCl_3$, ppm): δ_H 2.72 (3H, s), 3.39-3.45 (4H, m), 7.30 (1H, d, J = 7.3 Hz), 7.37 (1H, d, J = 6.9 Hz), 7.60 (1H, dd, J = 8.6, 6.9 Hz), 8.07 (1H, d, J = 7.3 Hz), 8.72 (1H, dd, J = 8.6, 0.5 Hz); ^{13}C NMR ($CDCl_3$, ppm): δ_C 28.92 (CH_3), 30.33 (CH_2), 30.47 (CH_2), 118.04 (CH), 120.35 (CH), 122.54 (CH), 129.26 (C), 130.17 (C), 130.43 (CH), 132.82 (CH), 139.74 (C), 146.07 (C), 153.17 (C), 200.23 (C=O); ^{13}C NMR ($CDCl_3$, ppm): δ_C (^{13}C DEPT) = 28.92 (↑), 30.33 (↓), 30.47 (↓), 118.04 (↑), 120.35 (↑), 122.54 (↑), 129.26 (-), 130.17 (-), 130.43 (↑), 132.82 (↑), 139.74 (-), 146.07 (-), 153.17 (-), 200.23 (-); IR (KBr/cm^{-1}): 3040 (=C-H), 2946 (C-H), 2922 (C-H), 1661 (C=O), 1598 (C=C), 1499 (C=C), 1269 (C-O), 1232 (C-O), 841 (Ar-H), 776 (Ar-H).

6-Acetylbenzo[de]isochromene-1,3-dione (**5**)

In a two-necked flask 250 mL round-bottom flask, 150 mL of glacial acetic acid, **4** (9.0 g, 50 mmol) and sodium dichromate dihydrate (50 g, 0.17 mol) were added and the reaction refluxed for 24 hours. The mixture was poured over 200 g of ice while stirring with a magnetic stir bar and filtered under gravity to yield a green precipitate, which was washed with boiling 10% NaOH for 1 hour. After cooling, the solution was acidified to pH 3 with conc. sulfuric acid resulting in a precipitate, which was recrystallised from 95% ethanol to give dark yellow needles in 48% yield (5.7 g).[S2] m.p. 186.1-187.0 ^{o}C; ^{1}H NMR ($CDCl_3$, ppm): δ_H 2.83 (3H, s), 7.92 (1H, dd, J = 8.5 Hz, 7.3 Hz), 8.17 (1H, d, J = 7.6 Hz), 8.69 (2H, m), 9.05 (1H, dd, J = 8.7 Hz, 0.8 Hz); ^{13}C NMR ($CDCl_3$, ppm): δ_C 30.12 (CH_3), 118.85 (C), 121.64 (C), 128.13 (CH), 128.71 (C), 129.18 (CH), 130.82 (C), 132.15 (CH), 133.80 (CH), 134.15 (CH), 141.47 (C), 159.80 (C=O), 160.14 (C=O), 200.45 (C=O); ^{13}C NMR ($CDCl_3$, ppm): δ_C (^{13}C DEPT) = 30.12

(↑), 118.88 (-), 121.64 (-), 128.13 (↑), 128.71 (-), 129.18 (↑), 130.82 (-), 132.15 (↑), 133.80 (↑), 134.15 (↑), 141.47 (-), 159.80 (-), 160.14 (-), 200.45 (-); IR (KBr/cm^{-1}): 3102 (=C-H), 3097 (=C-H), 3046 (=C-H), 1783 (C=O), 1738 (C=O), 1679 (C=O), 1593 (C=C), 1512 (C=C), 1132 (C-O), 1030 (C-O), 863 (Ar-H), 784 (Ar-H).

6-Acetyl-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**6**)

In a 50 mL round-bottom flask, 6-acetylbenzo[de]isochromene-1,3-dione **5** (500 mg, 2.1 mmol) and aniline (0.38 mL, 4.2 mmol) were added to 15 mL of glacial acetic acid and refluxed for 24 hours. Upon cooling 20 mL of 10% HCl was added. The flask was placed in a fridge for 1 hour and the resulting suspension vacuum filtered. The precipitate was washed with cold distilled water (2×10 mL), 10 mL of ethanol and 5 mL of diethyl ether and dried under vacuum to give a light beige powder in 82% yield (538 mg).[1] m.p. 210.0-211.0 ^{o}C; ^{1}H NMR ($CDCl_3$, ppm): δ_H 2.83 (3H, s), 7.32 (2H, m), 7.49 (1H, m), 7.56 (2H, m), 7.89 (1H, dd, J = 8.6 Hz, 7.4 Hz), 8.16 (1H, d, J = 7.6 Hz), 8.69 (2H, m), 9.01 (1H, dd, J = 8.7 Hz, 0.8 Hz); ^{13}C NMR ($CDCl_3$, ppm): δ_C 30.13 (CH_3), 122.82 (C), 125.64 (C), 128.01 (CH), 128.53 (CH), 128.72 (CH), 128.92 (CH), 129.13 (C),129.54 (CH), 130.33 (CH), 131.92 (CH), 132.85 (CH), 135.04 (C), 140.51 (C), 163.63 (C=O),164.01 (C=O), 200.92 (C=O); ^{13}C NMR ($CDCl_3$/MeOD, ppm): δ_C (^{13}C DEPT) = 30.21 (↑), 123.54 (-), 126.23 (-), 129.04 (↑), 129.23 (↑), 129.35 (↑), 129.42 (-), 129.54 (↑), 129.97 (-), 130.01 (↑), 131.12 (↑), 132.52 (↑), 133.73 (↑), 136.04 (-), 141.75 (-), 164.73 (-), 165.35 (-), 202.59 (-); IR (KBr/cm^{-1}): 3058 (=C-H), 3042 (=C-H), 1715, (C=O), 1663 (C=O), 1558 (C=C), 1490 (C=C), 1430 (C-N), 1243 (C-O), 1139 (C-O), 896 (Ar-H), 786 (Ar-H).

6-Cinnamoyl-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**7**)

4-Acetyl-*N*-phenyl-1,8-naphthalimide (158 mg, 0.501 mmol), benzaldehyde (1.5 eqv., 80 mg, 0.75 mmol) and 1 mL of triethylamine were added to 10 mL of anhydrous ethanol in a 50 mL round-bottom flask. To the flask was added 2 g of 3Å molecular sieves. The reaction mixture was purged with nitrogen and refluxed whilst monitoring via TLC for reaction completion. The mixture was filtered, and the sieves washed with dichloromethane, and the solution evaporated under vacuum. The crude residue was used directly for the preparation of **1**.

6-(3-(2,3,5,6,8,9,11,12-Octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecin-15-yl)-acryl oyl)-2-phenyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (**8**)

4-Acetyl-*N*-phenyl-1,8-naphthalimide (158 mg, 0.501 mmol) and 4-formylbenzo-15-crown-5 (223 mg, 0752 mmol) were reflux for 72 hours and afforded a brown oil (405 mg). The crude product was used directly for the preparation of **2**.

4-Formylbenzo-15-crown-5 ether was synthesised from benzo-15-crown-5 ether (750 mg, 2.8 mmol), hexamethylenetetramine (800 mg, 5.6 mmol) and trifluoroacetic acid (5 mL) at 90 ^{o}C for 24 hours and recrystallised from petroleum ether to give 273 mg of an off-white powder in 33% yield.[S4]

Ethyl4-(3-(1,3-dioxo-2-phenyl-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)-5-phenyl-4,5-dihydro-1H-pyrazol-1-yl)benzoate (**1**)

A crude mixture of compound **7** (145 mg, ca. 0.25 mmol) and 4-hydrazinobenzoic acid (150 mg, 1.0 mmol) were dissolved in 10 mL of ethanol, 10 mL of acetonitrile and 0.5 mL of 37% HCl under an inert atmosphere of argon. On completion after 48 hours, confirmed by TLC, the solution was removed by rotary evaporator under vacuum. The residue was extracted with dichloromethane (2×20 mL) and washed with 10% HCl and 10% NaOH. The solvent was removed under vacuum and the crude product purified via column chromatography on silica using 2% ethyl acetate in hexane to give a bright orange powder in 20% yield (40 mg). m.p. > 300 ^{o}C; ^{1}H NMR ($CDCl_3$, ppm): δ_H 1.39 (3H, t, J = 7.1 Hz), 3.52 (1H, dd, J = 16.9 Hz, 6.1 Hz), 4.22 (1H, dd, J = 16.9 Hz, 12.5 Hz), 4.35 (2H, q, J = 6.5 Hz), 5.55 (1H, dd, J = 12.5 Hz, 6.1 Hz), 7.19 (2H, d, J = 8.8 Hz), 7.37 (7H, m), 7.52 (1H, d, J = 7.3 Hz), 7.58 (2H, d, J = 7.8 Hz), 7.71 (1H, d, J = 7.8 Hz), 7.98 (2H, d, J = 8.8 Hz) , 8.02 (1H, dd, J = 8.6 Hz, 7.5 Hz), 8.62 (1H, d, J = 7.8 Hz), 8.78 (1H, d, J = 7.2 Hz), 10.02 (1H, d, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$, ppm): δ_C 14.70 (CH_3), 45.50 (CH_2), 60.40 (CH_2), 63.20 (CH), 113.08 (CH), 121.91 (C), 122.64 (C), 123.01 (C), 125.63 (CH), 126.89 (CH), 128.16 (CH), 128.28 (CH), 128.61 (CH), 128.79 (CH), 129.07 (C), 129.41 (CH), 129.49 (C), 129.55 (CH), 130.90 (CH), 131.19 (CH), 131.78 (CH), 134.48 (CH), 134.77 (C), 135.33 (C), 140.85 (C), 146.59 (C), 147.45 (C), 163.91 (C=O), 164.38 (C=O), 166.52 (C=O); ^{13}C NMR ($CDCl_3$, ppm): δ_C (^{13}C DEPT) = 14.70 (↑), 45.50 (↓), 60.40 (↓), 63.20 (↑), 113.08 (↑), 121.91 (-), 122.64 (-), 123.01 (-), 125.63 (↑), 126.89 (↑), 128.16 (↑), 128.28 (↑), 128.61 (↑), 128.79 (↑), 129.07 (-), 129.41 (↑), 129.49 (-), 129.55 (↑), 130.90 (↑), 131.19 (↑), 131.78 (↑), 134.48 (↑), 134.77 (-), 135.33 (-), 140.85 (-), 146.59 (-), 147.45(-), 163.91 (-), 164.38 (-), 166.52 (-); IR (KBr/cm^{-1}): 3068 (=C-H), 2982 (C-H), 1708 (C=O), 1669

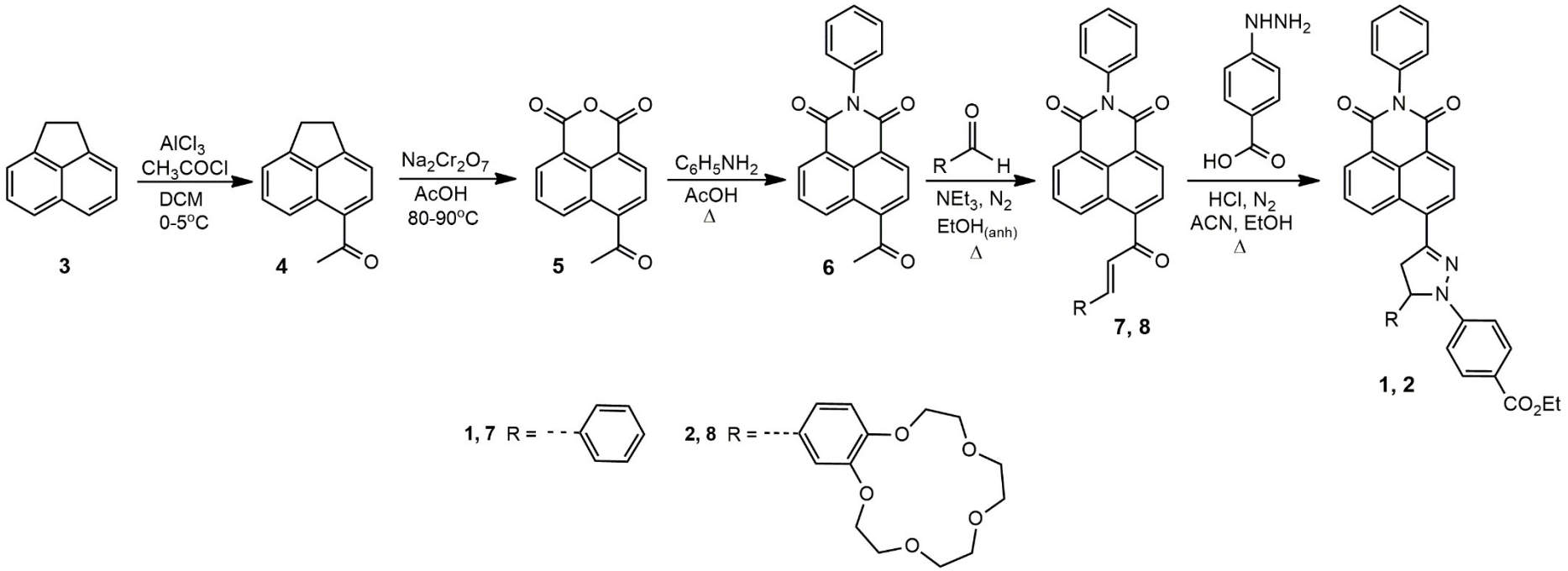
(C=O), 1654 (C=O), 1605 (C=C), 1507 (C=C), 1274 (C-O), 1103 (C-O), 1022 (C-O), 846 (Ar-H), 782 (Ar-H), 768 (Ar-H); HRMS ESI $[M+H]^+$ ($C_{36}H_{28}N_3O_4$): 566.2081 (calc. mass: 566.2080).

Ethyl-4-(3-(1,3-dioxo-2-phenyl-2,3-dihydro-1H-benzo[de]isoquinolin-6-yl)-5-(2,3,5,6,8,9,11,12-octahydrobenzo[b][1,4,7,10,13]pentaoxacyclopentadecin-15-yl)-4,5-dihydro-1H-pyrazol-1-yl)benzoate (**2**)

A crude mixture of compound **8** (320 mg, 0.53 mmol) and 4-hydrazinobenzoic acid (300 mg, 2.0 mmol) were reacted for 72 hours. The crude residue was purified by column chromatography on neutral alumina using 1% methanol in CH_2Cl_2 to give an orange powder in 10% yield (38 mg). m.p. > 300 ^oC; ^1H NMR ($CDCl_3$, ppm): δ_H 1.37 (3H, t, J = 7.0 Hz), 3.54 (1H, dd, J = 16.9 Hz, 6.0 Hz), 3.73 (8H, m), 3.93 (4H, m), 4.10 (1H, m), 4.17 (4H, m), 4.34 (2H, d, J = 8.9 Hz), 5.42 (1H, dd, J = 12.5 Hz, 6.0 Hz), 6.82 (1H, d, J = 2.4 Hz), 6.88 (1H, dd, J = 8.3 Hz, 2.4 Hz), 7.06 (1H, d, J = 8.3 Hz), 7.19 (2H, d, J = 8.9 Hz), 7.32 (2H, d, J = 6.8 Hz), 7.50 (1H, m), 7.55 (2H, m), 7.70 (1H, d, J = 7.7 Hz), 7.90 (2H, d, J = 8.9 Hz), 8.05 (1H, dd, J = 8.6 Hz, 7.4 Hz), 8.62 (1H, d, J = 7.7 Hz), 8.78 (1H, d, J = 7.4 Hz), 10.1 (1H, d, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$, ppm): δ_C 14.65 (CH_3), 45.52 (CH_2), 60.50 (CH_2), 63.80 (CH), 69.18 (CH_2), 69.23 (CH_2), 69.54 (CH_2), 69.61 (CH_2), 70.61 (CH_2), 70.69 (CH_2), 71.25 (CH_2), 71.34 (CH_2), 113.08 (CH), 115.07 (CH), 115.14 (CH), 119.15 (CH), 121.89 (C), 122.62 (C), 123.11 (C), 125.67 (CH), 126.91 (CH), 128.26 (CH), 128.64 (CH), 128.79 (CH), 129.04 (C), 129.48 (CH), 129.54 (C), 130.91 (CH), 131.78 (CH), 134.58 (CH), 134.73 (C), 140.87 (C), 146.39 (C), 147.48 (C), 149.38 (C), 149.74 (C), 163.93 (C=O), 164.42 (C=O), 166.49 (C=O); ^{13}C NMR ($CDCl_3$, ppm): δ_C (^{13}C DEPT) = 14.65 (↑), 45.52 (↓), 60.50 (↓), 63.80 (↑), 69.18 (↓), 69.23 (↓), 69.54 (↓), 69.61 (↓), 70.61 (↓), 70.69 (↓), 71.25 (↓), 71.34 (↓), 113.08 (↑), 115.07 (↑), 115.14 (↑), 119.15 (↑), 121.89 (-), 122.62 (-), 123.11 (-), 125.67 (↑), 126.91 (↑), 128.26 (↑), 128.64 (↑), 128.79 (↑), 129.04 (-), 129.48 (↑), 129.54 (-), 130.91 (↑), 131.78 (↑), 134.58 (↑), 134.73 (-), 140.87 (-), 146.39 (-), 147.48 (-), 149.38 (-), 149.74 (-), 163.93 (-), 164.42 (-), 166.49 (-); IR (KBr) $\tilde{\nu}$ cm^{-1}: 3014 (=C-H), 2921 (C-H), 2853 (-OCH_2-), 1709 (C=O), 1667 (C=O), 1590, (C=C), 1514 (C=C), 1268 (C-O), 1241 (C-O), 1134 (C-O), 923 (Ar-H), 840 (Ar-H), 754 (Ar-H); ESI $[M+Na]^+$ ($C_{44}H_{41}N_3O_9Na$): 778.2737 (calc. mass: 778.2741).

Table S1. Truth table for a three-input two-output double INH logic gate array. The labels A-F correspond to the vials in Fig. 3.

Vial	$Input_1$ (H^+)	$Input_2$ (Na^+)	$Input_3$ (Mg^{2+})	$Output_1$ (Orange)	$Output_2$ (White)
A	0	0	0	0	0
B	0	1	0	1	0
C	0	0	1	0	1
D	1	0	0	0	0
E	1	1	0	0	0
F	1	0	1	0	0



Scheme S1 The synthesis of 3-pyrazolinylnaphthalimide compounds **1** and **2**.

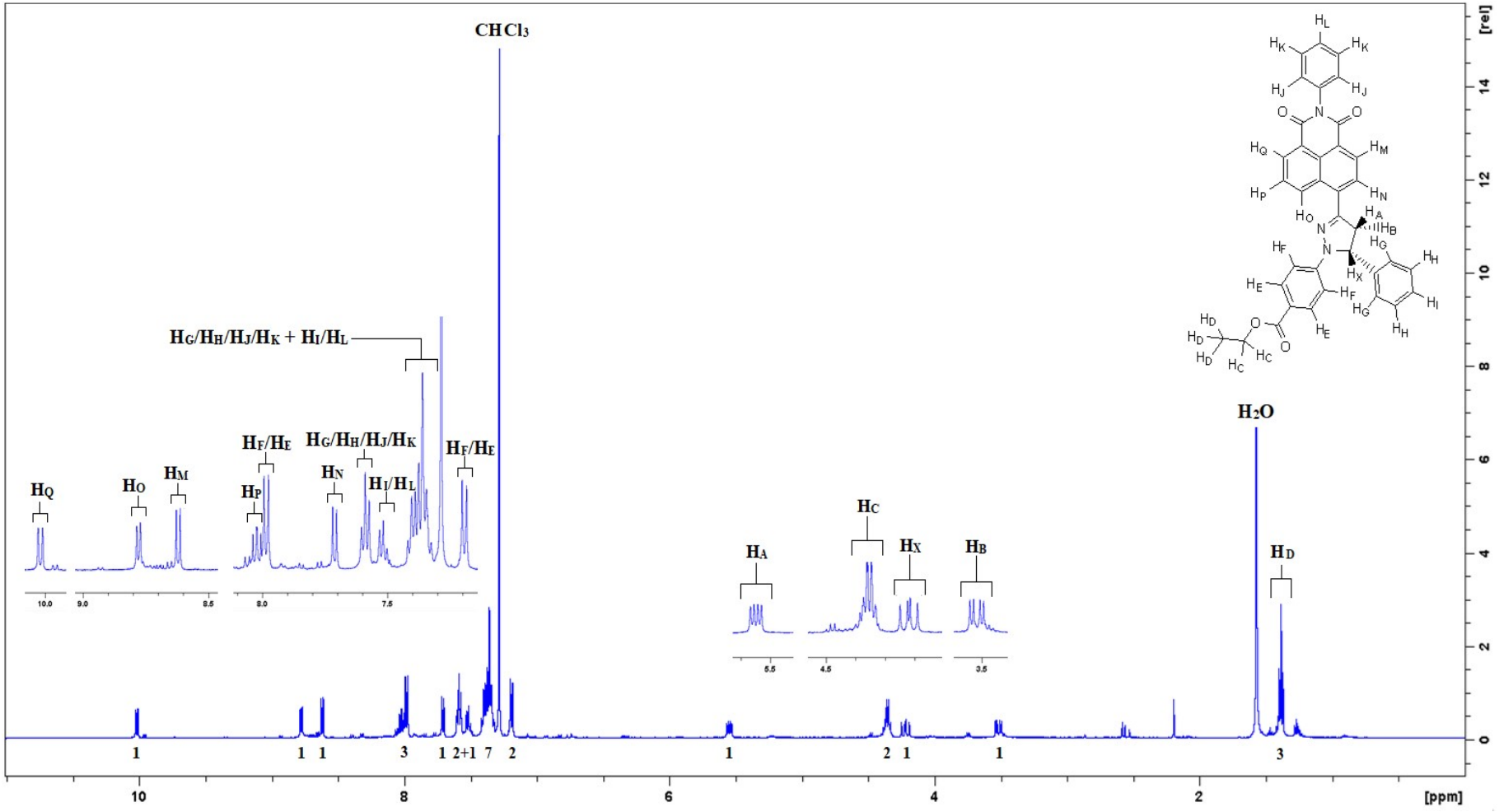


Fig. S1 The ^{1}H NMR spectrum of **1** in $CDCl_3$.

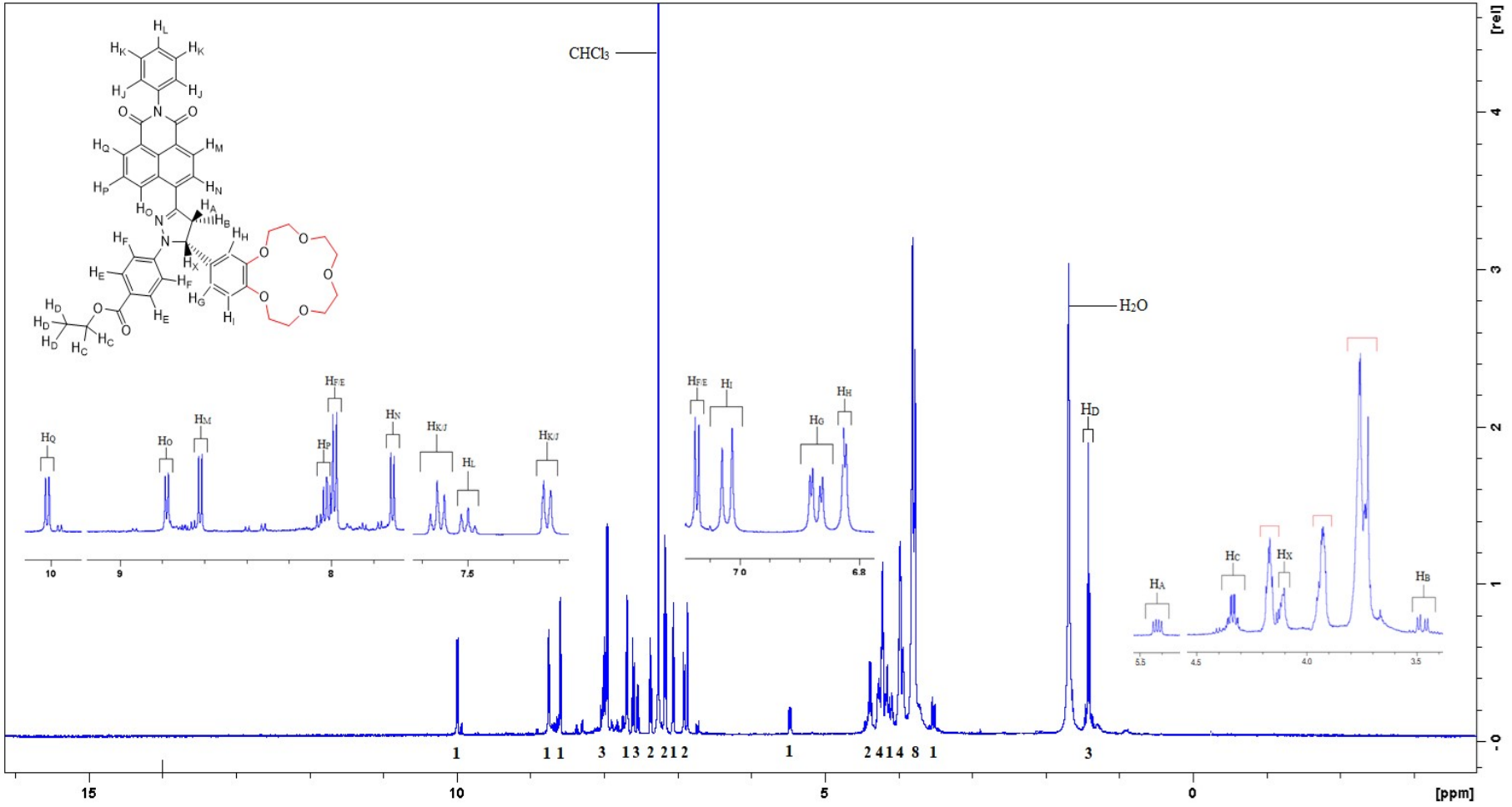


Fig. S2 The ^{1}H NMR spectrum of **2** in $CDCl_3$.

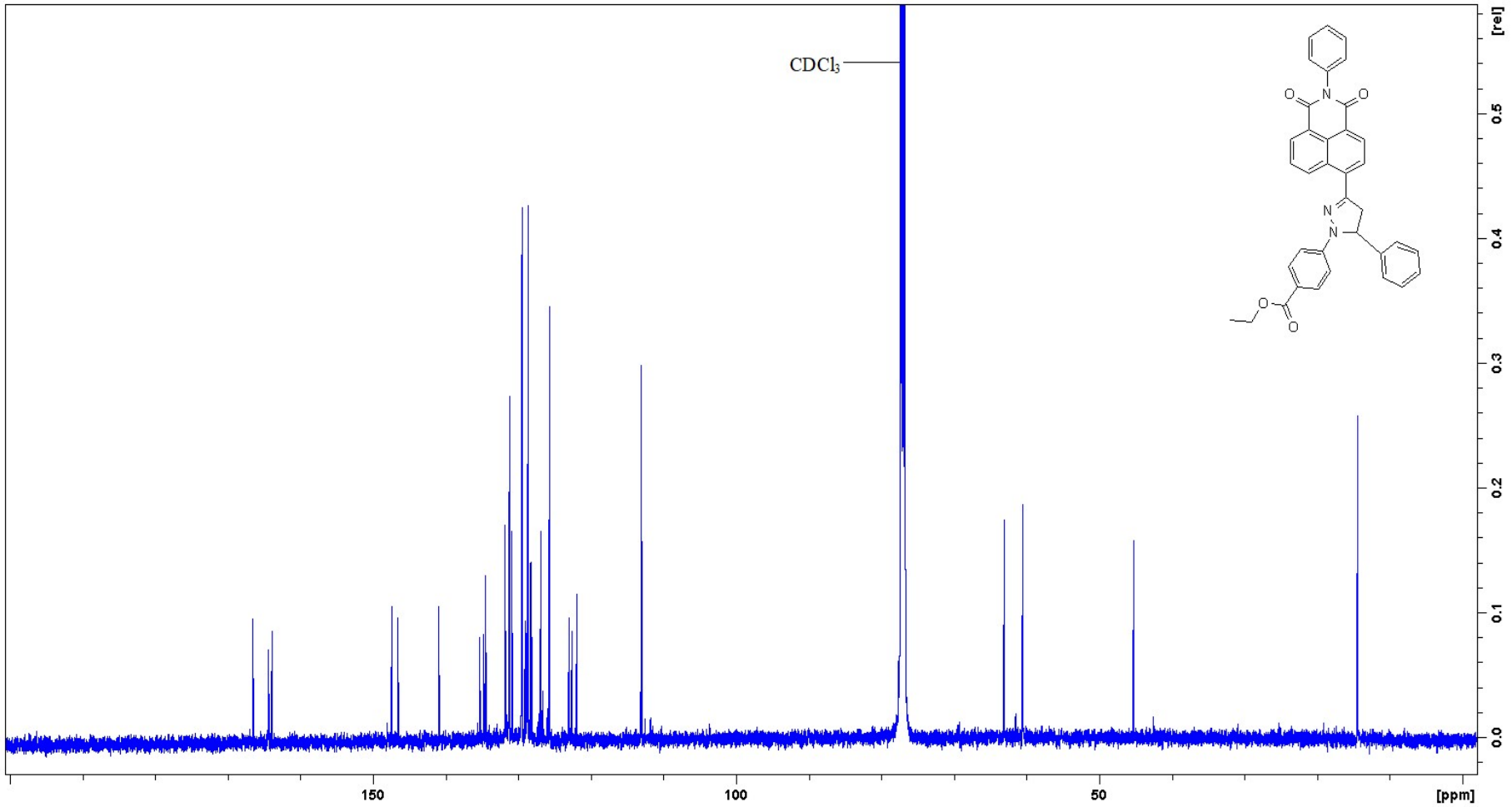


Fig. S3 The ^{13}C NMR spectrum of **1** in $CDCl_3$.

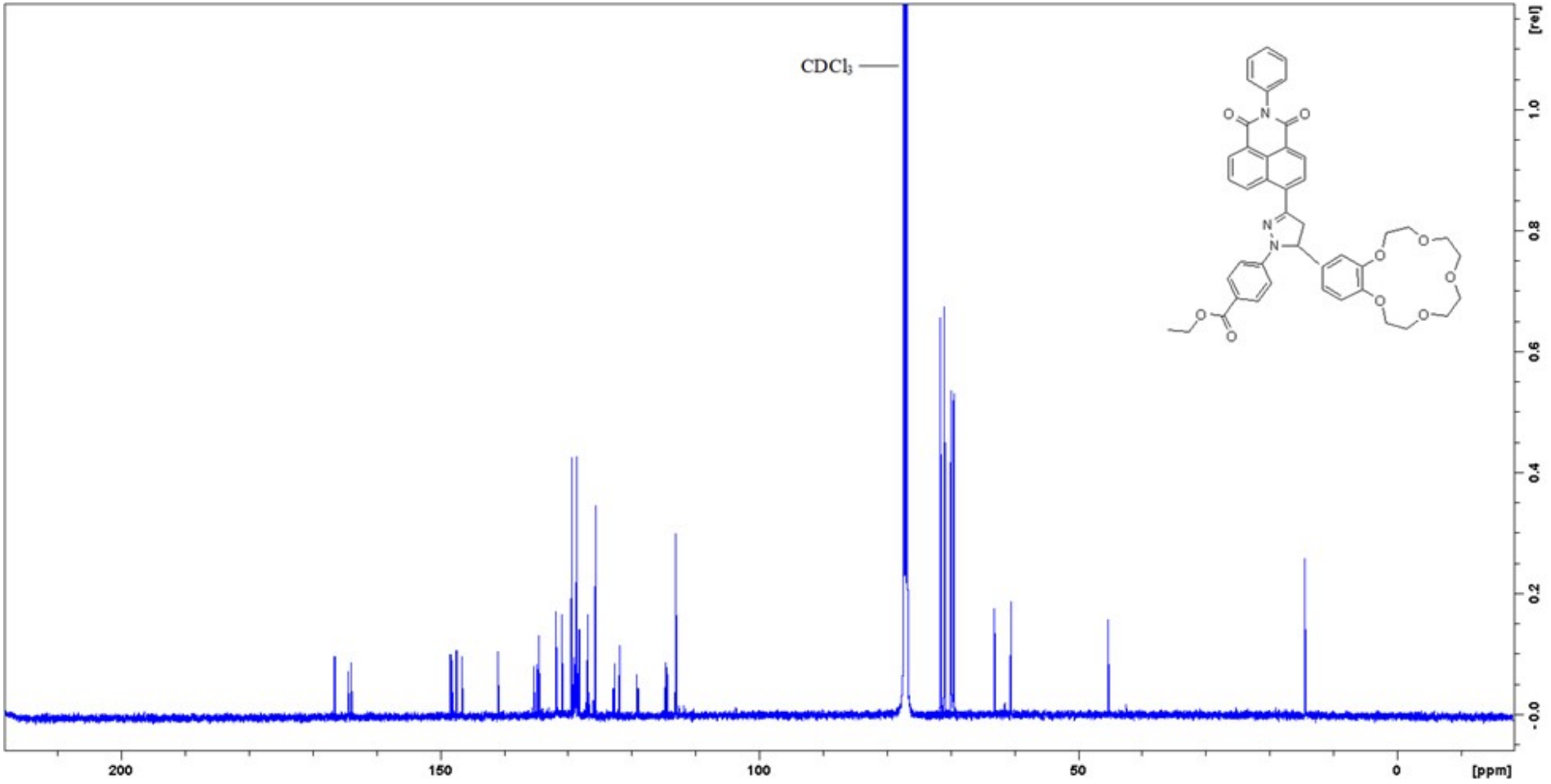


Fig. S4 The ^{13}C NMR spectrum of **2** in $CDCl_3$.

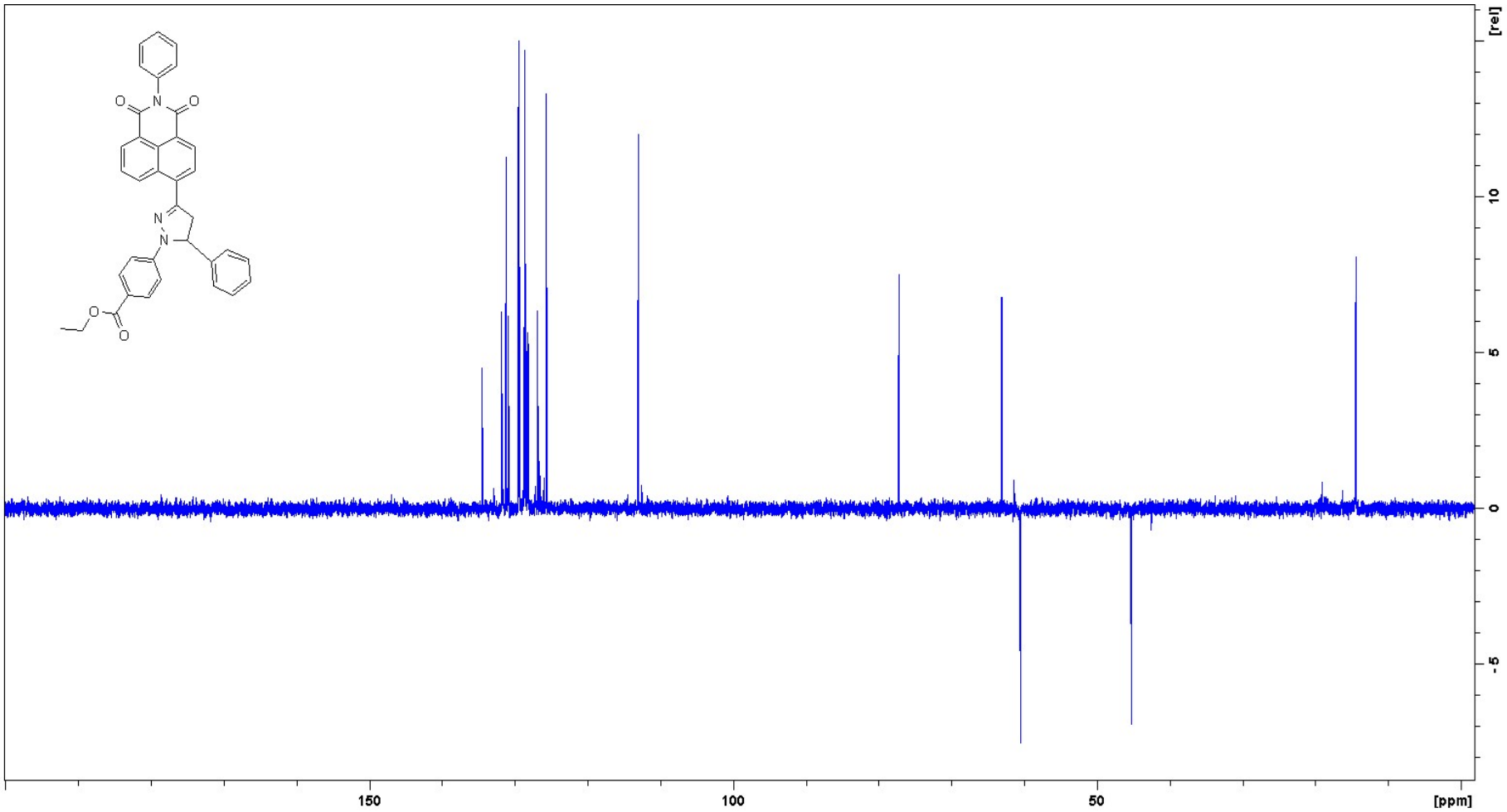


Fig. S5 The ^{13}C DEPT(135) NMR spectrum of **1** in $CDCl_3$.

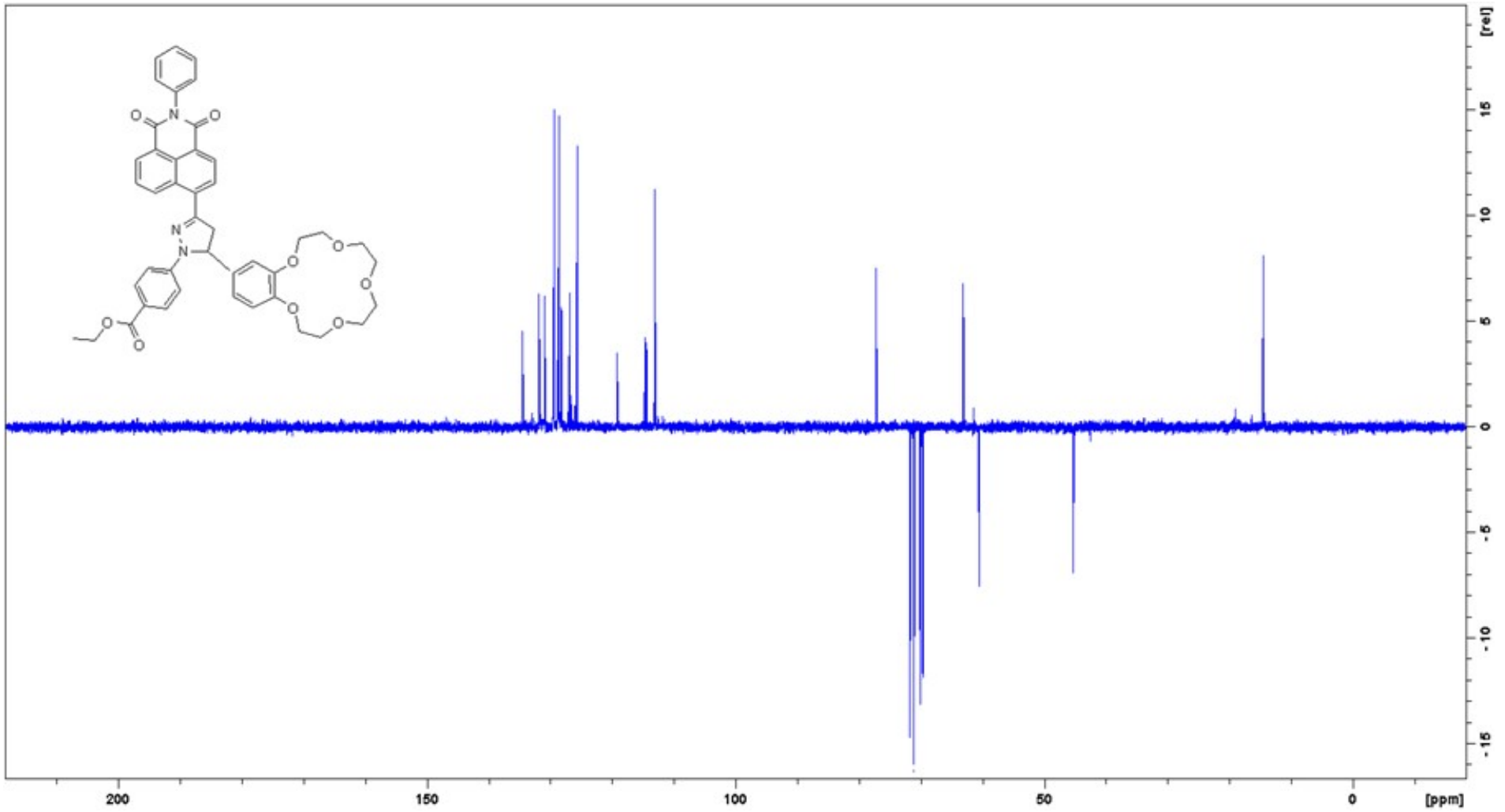


Fig. S6 The ^{13}C DEPT(135) NMR spectrum of **2** in $CDCl_3$.

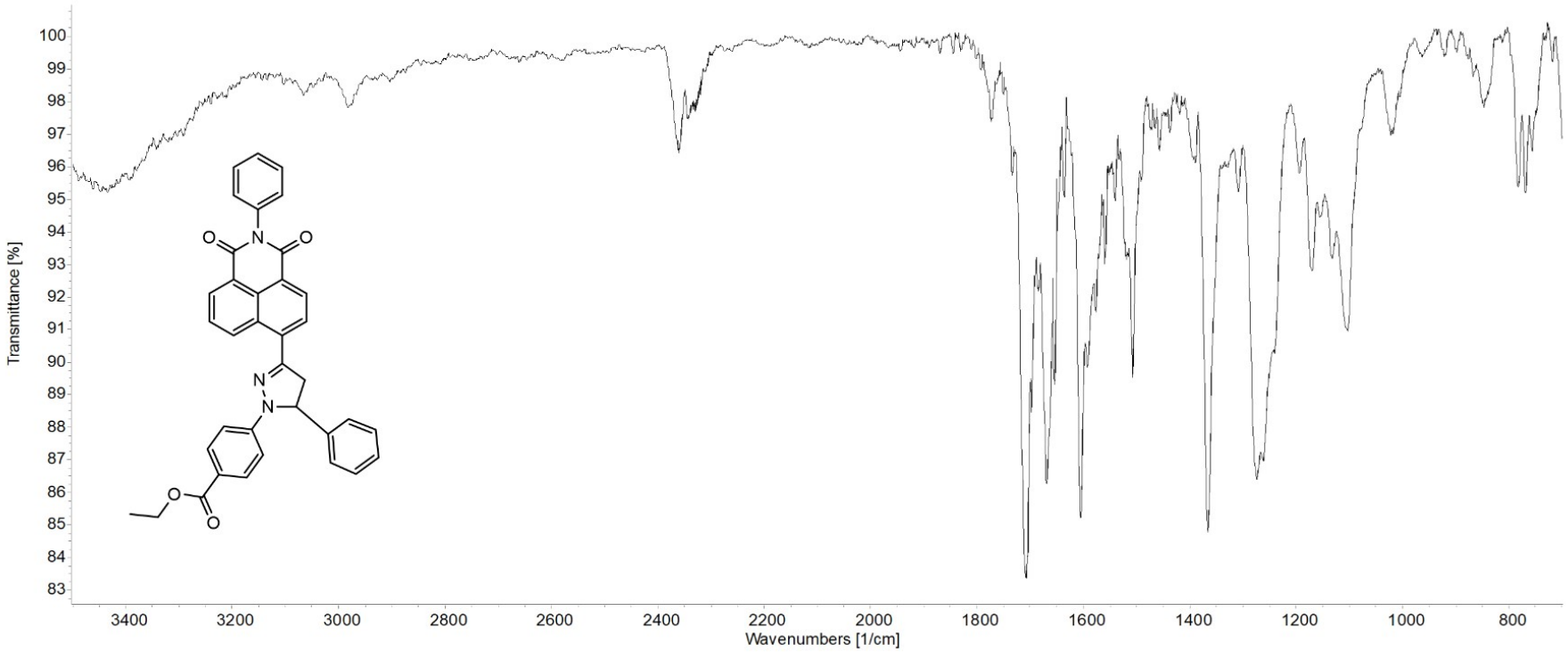


Fig. S7 The IR spectrum of **1** as a KBr disc.

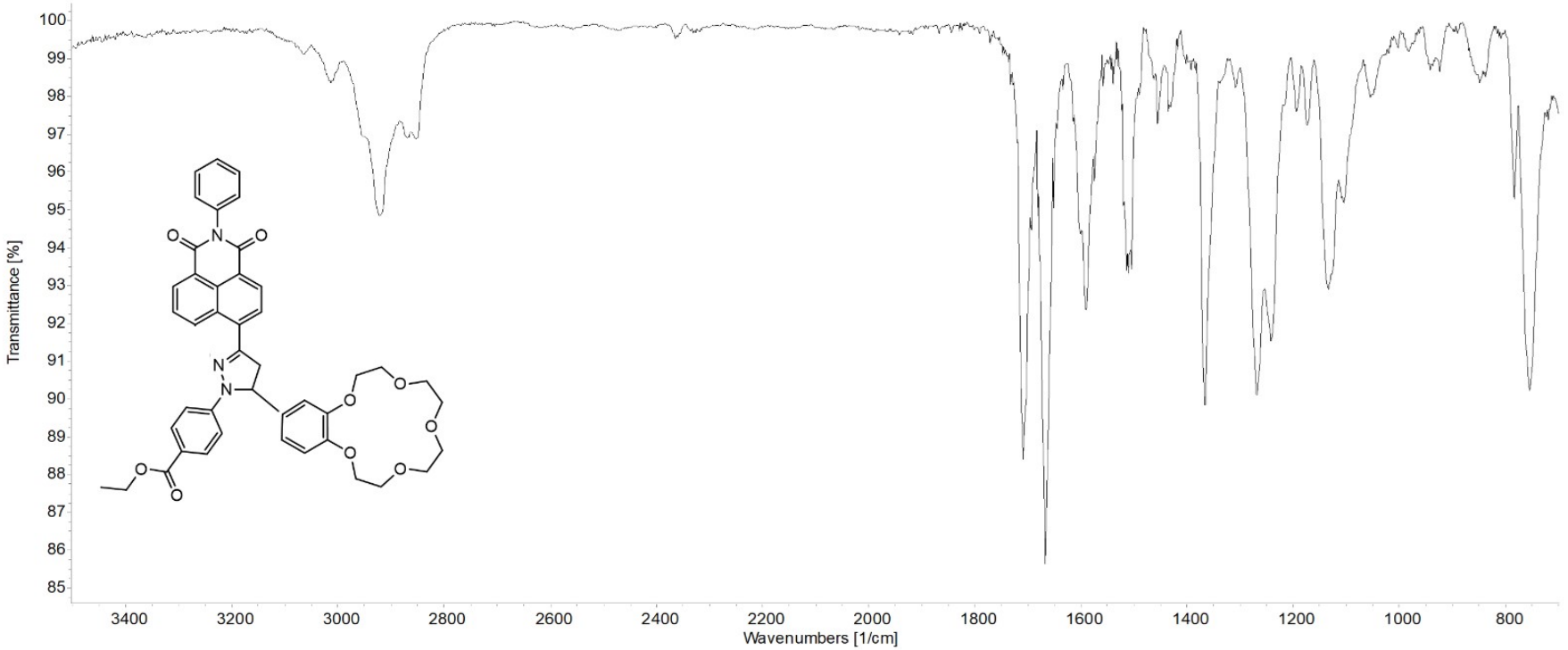


Fig. S8 The IR spectrum of **2** as a KBr disc.

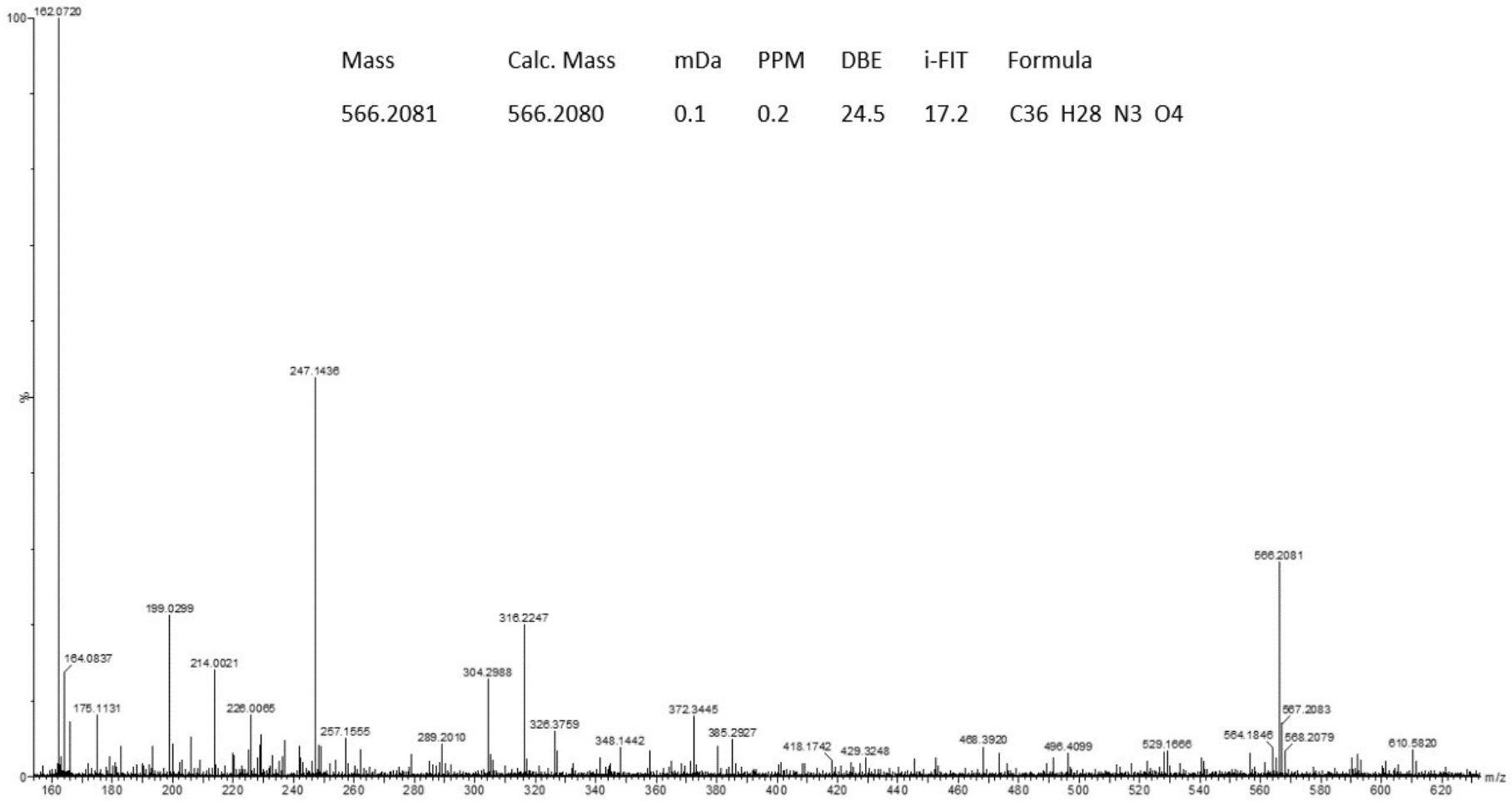


Fig. S9 The mass spectrum and HRMS data of **1**.

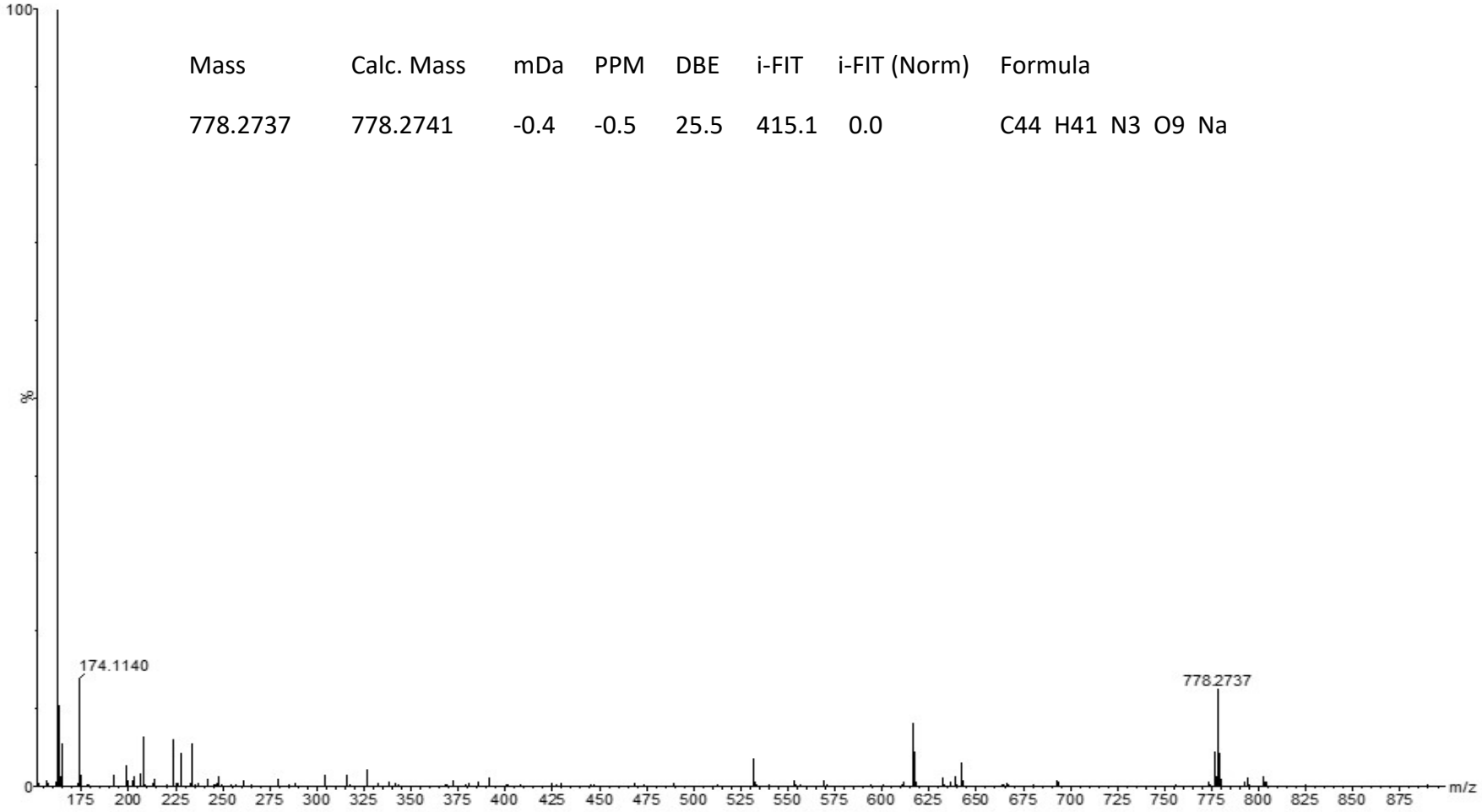


Fig. S10 The mass spectrum and HRMS data of **2**.

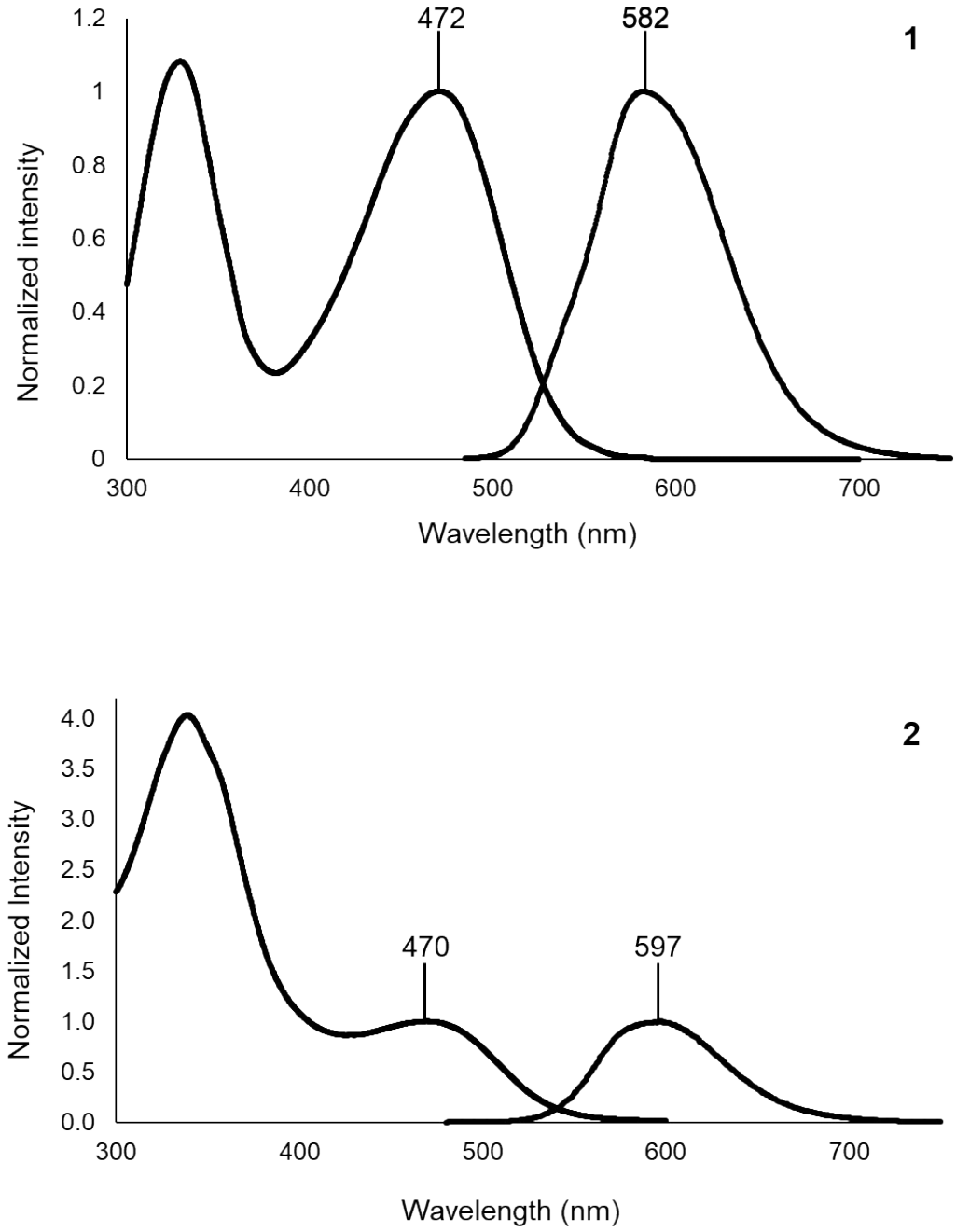


Fig. S11 Normalised absorption spectra (left) and emission spectra (λ_{ex} = 472 nm, 470 nm) (right) for **1** and **2** in acetonitrile.

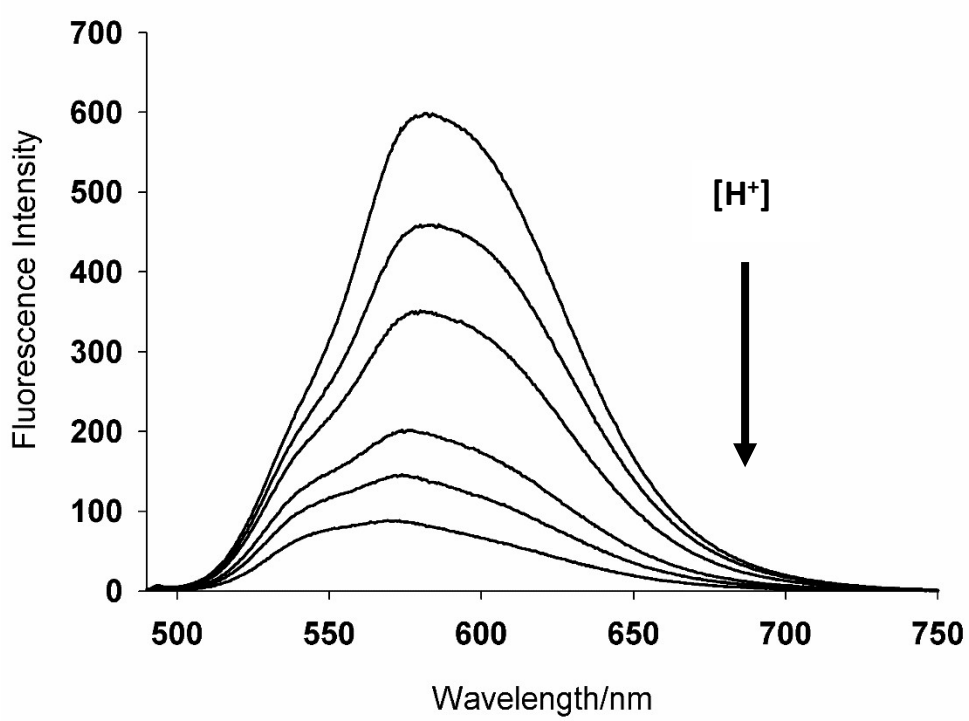


Fig. S12 Fluorescence emission spectra of 3 μM **1** in acetonitrile (λ_{ex} = 470 nm) as a function of acid $p\beta_{H^+} = -\log [H^+]$ in order of increasing concentration and decreasing intensity: 4.79, 3.18, 1.93, 0.96, 0.52 and 0.24.

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