Supporting Information

Highly Photostable Near-Infrared Fluorescent pH Indicators and Sensors based on BF_2-Chelated Tetraarylazadipyrromethene Dyes

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EXPERIMENTAL

Measurements of pH gradients in the gastric cavity of a symbiont bearing coral (Goniopora sp.)

The coral was sampled from the reef flat off Heron Island, Great Barrier Reef, Australia. After sampling, the coral was kept at Heron Island Research Station in an outdoor aquarium continuously flushed with aerated seawater from the reef flat. Prior to pH measurements, coral specimen was transferred to a flow chamber with aerated seawater (pH ~8.1) at 26 °C and at a flow rate of approximately 3 cm s^{-1}. The coral was illuminated with an incident irradiance of ~150 µmol·photons $m^{-2}\cdot s^{-1}$ from a fiber-optic halogen lamp Schott kl2500 LCD (www.schott.com). The pH optode was mounted in a manual micromanipulator MM33 (Märtzhäuser, www.marzhauser.com) that was attached to a heavy stand. The optode tip was carefully positioned towards and into the mouth opening of a single coral polyp; this was done by observation under a dissection microscope SM-6TZ-54S, Amscope (www.amscope.com) equipped with a CCD camera.

Solution preparation for titration curves

Indicators **1** - **8** were dissolved in THF (10 ml). For absorption measurements 200 µl (90 µl for fluorescence measurements) of this solution was diluted with 25 ml of ethanol. Prior to absorption (fluorescence) measurements ethanolic solution was diluted with aqueous buffer 1:1. Final concentration of solutions were for absorption measurements **1** – 3.19×10^{-6} M, **2** – 3.10×10^{-6} M, **3** – 3.37×10^{-6} M, **4** – 3.27×10^{-6} M, **5** – 3.32×10^{-6} M, **6** – 3.01×10^{-6} M, **7**- 2.55×10^{-6} M, **8** – 3.23×10^{-6} M, and fluorescence measurements **1** – 1.45×10^{-6} M, **2** – 1.41×10^{-6} M, **3** – 1.53×10^{-6} M, **4** – 1.49×10^{-6} M, **5** – 1.51×10^{-6} M, **6** – 1.37×10^{-6} M, **7**- 1.16×10^{-6} M, **8** – 1.47×10^{-6} M.

Synthesis

1-(3-chloro-4-hydroxyphenyl)-3-phenylpropenone (2a): 3'-chloro-4'-hydroxyacetophenone (1 eq, 2 g, 11.7 mmol) and benzaldehyde (1 eq, 1.24 g, 11.7 mmol) were dissolved in absolute ethanol (10 ml). 10 ml of aqueous potassium hydroxide solution (3 eq, 1.96 g, 35.1 mmol) was added dropwise. Resulting solution was stirred for 8-12 hours, during which the product precipitated as the potassium salt. The solution/suspension was poured into 1 M HCl (10 ml), and further concentrated HCl was added until the solution was acidic. Obtained yellow solid was washed with water and used in further synthesis without purification. (2.7 g, 77%)

1-(3-chloro-4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (2b): A solution of 1-(3-chloro-4-hydroxyphenyl)-3-phenylpropenone (2a) (1eq, 2 g, 7.7 mmol), nitromethane (20 eq, 8,35 ml, 154.7 mmol) and KOH (1.2 eq, 0.52 g, 9.28 mmol) in EtOH (10 ml) was heated at 60 ºC under reflux for 12 h. After cooling to room temperature, the solvent was removed in vacuo and oily residue obtained was acidified with 4 M HCl and partitioned between EtOAc (50 ml) and H_2O (50 ml). The organic layer was separated, dried over sodium sulfate and evaporated under reduced pressure. The obtained product was used for further synthesis without purification. (2.4 g, 73%)

[5-(3-chloro-4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (2c): 1-(3-chloro-4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (2b) (1 eq, 1 g, 3.7 mmol), 1,3-diphenyl-4-nitro-butan-1-on (1b) (1 eq, 0.99 g, 3.7 mmol) and ammonium acetate (35 eq, 8.03 g, 129 mmol) in butanol (50 ml) were heated under reflux for 24 h. The reaction was cooled to room temperature, the crude product was purified by column chromatography on silica with dichloromethane (after eluting symmetric byproduct with hexane/dichloromethane 3:1 v/v) to yield to product 2c as a blue-black solid. Product was recrystallized from hexane/tetrahydrofuran mixture as green metallic crystals (0.26 g, 17%). ^{1}H NMR (300 MHz, DMSO-d6) δ 8.26-8.27 (d, J = 2 Hz, 1H), 8.06-8.13 (t, J = 6.5 Hz, 4H), 7.99-8.02 (dd, J = 8.7 Hz, 2.1 Hz, 1H), 7.92-7.95 (d, J = 7.4 Hz, 2H), 7.83 (s, 1H), 7.32-7.61 (t, J = 7.5 Hz, 10H), 7.04-7.06 (d, J = 8.6 Hz, 1H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH^+] found 499.1473, calculated 499.1451.

BF_2 chelate of [5-(3-chloro-4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (2): Compound 2c (0.24 g, 0.48 mmol) was dissolved in dry CH_2Cl_2 (50 ml), treated with diisopropylethylamine (10 eq, 0.79 ml, 4.8 mmol) and BF_3 diethyletherate (15 eq, 0.92 ml, 7.2 mmol) and stirred under argon for 24 h. Purification by column chromatography on silica eluting with CH_2Cl_2 and recrystallization from hexane/tetrahydrofurane gave the product 2 as a red metallic solid (0.20 g, 43 %). ^{1}H NMR (300 MHz, DMSO-d6) δ 8.30-8.29 (d, J = 2.1 Hz, 1 H), 8.21 – 8.07 (m, 7 H), 7.76 (s, 1 H), 7.58 – 7.45 (m, 10 H), 7.13- 7.16 (d, J = 8.7 Hz, 1 H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH^+] found 546.1490, calculated 546.1470.

1-(3-methyl-4-hydroxyphenyl)-3-phenylpropenone (3a): 3'-methyl-4'-hydroxyacetophenone (1 eq, 2 g, 14.7 mmol) and benzaldehyde (1 eq, 1.55 g, 11.8 mmol) were dissolved in absolute ethanol (10 ml). 10 ml of aqueous potassium hydroxide solution (3 eq, 1.98 g, 35.4 mmol) was added dropwise. Resulting solution was stirred for 8-12 hours, during which the product precipitated as the potassium salt. The solution/suspension was poured into 1 M HCl (10 ml), and further concentrated HCl was added until the solution was acidic. Obtained yellow solid was washed with water and used in further synthesis without purification. (3.5 g, 93%)

1-(3-methyl-4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (3b): A solution of 1-(3-methyl-4-hydroxyphenyl)-3-phenylpropenone (3) (1eq, 2 g, 12.05 mmol), nitromethane (20 eq, 16.6 ml, 240.96 mmol) and KOH (1.2 eq, 0.81 g, 14.46 mmol) in EtOH (10 ml) was heated at 60 ºC under reflux for 12 h. After cooling to room temperature, the solvent was removed in vacuo and oily residue obtained was acidified with 4 M HCl and partitioned between EtOAc (50 ml) and H_2O (50 ml). The organic layer was separated, dried over sodium sulfate and evaporated under reduced pressure. The obtained product was used for further synthesis without purification. (1.33 g, 53%)

[5-(3-methyl-4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (3c): 1-(3-methyl-4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (3a) (1 eq, 1 g, 3.7 mmol), 1,3-diphenyl-4-nitro-butan-1-on (1b) (1 eq, 0.99 g, 3.7 mmol) and ammonium acetate (35 eq, 8.03 g, 129 mmol) in butanol (50 ml) were heated under reflux for 24 h. The reaction was cooled to room temperature, the crude product was purified by column chromatography on silica with dichloromethane (after eluting symmetric byproduct with hexane/dichloromethane 3:1 v/v) to yield to product 3c as a blue-black solid. Product was recrystalized from hexane/tetrahydrofuran mixture as green metallic crystals (0.26 g, 10%). ^{1}H NMR (300 MHz, DMSO-d6) δ 8.05 – 8.13 (m, 5 H), 7.93-7.95 (d, *J* = 7.6 Hz, 3 H), 7.80 (s, 1 H), 7.56-7.61 (m, 2 H), 7.32 – 7.51 (m, 8 H), 7.00-7.03 (d, *J* = 8.4 Hz, 1 H), 2.29 (s, 3 H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH^+] found 479.1998, calculated 479.1998.

BF_2 chelate of [5-(3-methyl-4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (3): Compound 3c (0.19 g, 0.39 mmol) was dissolved in dry CH_2Cl_2 (50 ml), treated with diisopropylethylamine (10 eq, 0.65 ml, 3.9 mmol) and BF_3 diethyletherate (15 eq, 0.75 ml, 5.85 mmol) and stirred under argon for 24 h. Purification by column chromatography on silica eluting with CH_2Cl_2 gave the product 3 as a red metallic solid (0.22 g, 66 %). ^{1}H NMR (300 MHz, DMSO-d6) δ 10.74 (s, 1 H), 8.04 – 8.22(m, 8 H), 7.82 (s, 1 H), 7.39 – 7.59 (m, 10 H), 6.97 (m, 1 H), 2.21 (s, 3H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH$^+$] found 526.2020, calculated 526.2017.

1-(3,5-dimethyl-4-hydroxyphenyl)-3-phenylpropenone (4a): 3’,5’-dimethyl-4’-hydroxyacetophenone (1 eq, 2 g, 12.1 mmol) and benzaldehyde (1 eq, 1.29 g, 12.1 mmol) were dissolved in absolute ethanol (10 ml). 10 ml of aqueous potassium hydroxide solution (3 eq, 2.04 g, 36.3 mmol) was added dropwise. Resulting solution was stirred for 8-12 hours, during which the product precipitated as the potassium salt. The solution/suspension was poured into 1 M HCl (10 ml), and further concentrated HCl was added until the solution was acidic. Obtained yellow solid was washed with water and used in further synthesis without purification. (3.3 g, 95%)

1-(3,5-dimethyl-4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (4b): A solution of 1-(3,5-dimethyl-4-hydroxyphenyl)-3-phenylpropenone (4a) (1eq, 2 g, 7.93 mmol), nitromethane (20 eq, 16.6 ml, 240.96 mmol) and KOH (1.2 eq, 0.81 g, 14.46 mmol) in EtOH (10 ml) was heated at 60 ºC under reflux for 12 h. After cooling to room temperature, the solvent was removed in vacuo and oily residue obtained was acidified with 4 M HCl and partitioned between EtOAc (50 ml) and H_2O (50 ml). The organic layer was separated, dried over sodium sulfate and evaporated under reduced pressure. The obtained product was used for further synthesis without purification. (1.6 g, 65%)

[5-(3,5-dimethyl-4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (4c): 1-(3,5-dimethyl-4-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (4b) (1 eq, 1 g, 3.2 mmol), 1,3-diphenyl-4-nitro-butan-1-on (1b) (1 eq, 1 g, 3.2 mmol) and ammonium acetate (35 eq, 8.03 g, 112 mmol) in butanol (50 ml) were heated under reflux for 24 h. The reaction was cooled to room temperature, the crude product was purified by column chromatography on silica with dichloromethane (after eluting symmetric byproduct with hexane/dichloromethane 3:1 v/v) to yield to product 5 as a blue-black solid. Product was recrystallized from hexane/tetrahydrofuran mixture as green metallic crystals (0.43 g, 20%). ^{1}H NMR (300 MHz, DMSO-d6) δ 8.09-8.15 (m, 4H), 7.93-7.96 (m, 2H), 7.89 (s, 2H), 7.81 (s, 1H), 7.31-7.60 (m, 10H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH$^+$] found 493.2198, calculated 493.2154.

BF_2 chelate of [5-(3,5-dimethyl-4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (4): Compound 4c (0.19 g, 0.39 mmol) was dissolved in dry CH_2Cl_2 (50 ml), treated with diisopropylethylamine (10 eq, 0.65 ml, 3.9 mmol) and BF_3 diethyletherate (15 eq, 0.75 ml, 5.85 mmol) and stirred under argon for 24 h. Purification by column chromatography on silica eluting with CH_2Cl_2 gave the product 4 as a red metallic solid (0.28 g, 62 %). ^{1}H NMR (300 MHz, DMSO-d6) δ 9.66 (s, 1H), 8.06 – 8.22 (m, 6H), 8.01 (s, 2H), 7.82 (s, 1H), 7.42 – 7.58 (m, 9 H), 7.40 (s, 1H), 2.26 (s, 6 H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH$^+$] found 540.2192, calculated 540.2173.

1-phenyl-4-nitro-3-(4-hydroxyphenyl)-butan-1-one (5a): A solution of 1-phenyl-3-(4-hydroxyphenyl)-propenone (1eq, 2 g, 8.9 mmol), nitromethane (20 eq, 10.8 ml, 178.3 mmol) and KOH (1.2 eq, 0.59 g, 10.68 mmol) in EtOH (10 ml) was heated at 60 ºC under reflux for 12 h. After cooling to room temperature, the solvent was removed in vacuo and oily residue obtained was acidified with 4 M HCl and partitioned between EtOAc (50 ml) and H_2O (50 ml). The organic layer was separated, dried over sodium sulfate and evaporated under reduced pressure. The obtained product was used for further synthesis without purification. (1.5 g, 60%)

[5-phenyl-3-(4-hydroxyphenyl)-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (5b): 1-phenyl-4-nitro-3-(4-hydroxyphenyl)-butan-1-one (5a) (1 eq, 1 g, 3.5 mmol), 1,3-diphenyl-4-nitro-butan-1-on (1b) (1 eq, 1 g, 3.5 mmol) and ammonium acetate (35 eq, 7.6 g, 122 mmol) in butanol (50 ml) were heated under reflux for 24 h. The reaction was cooled to room temperature, the crude product was purified by column chromatography on silica with dichloromethane (after eluting symmetric byproduct with hexane/dichloromethane 3:1 v/v) to yield to product 6b as a blue-black solid. Product was recrystallized from hexane/tetrahydrofuran mixture as green metallic crystals (0.32 g, 20%). ^{1}H NMR (300 MHz, DMSO-d6) δ 8.14 – 7.99 (m, 8 H), 7.66 – 7.38 (m, 11 H), 6.88- 6.85 (d, J = 8.7 Hz, 2 H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH$^+$] found 465.1876, calculated 465.1841.

BF_2 chelate of [5-phenyl-3-(4-hydroxyphenyl)-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (5): Compound 5b (0.22 g, 0.47 mmol) was dissolved in dry CH_2Cl_2 (50 ml), treated with diisopropylethylamine (10 eq, 0.61 ml, 4.7 mmol) and BF_3 diethyletherate (15 eq, 0.9 ml, 7.05 mmol) and stirred under argon for 24 h. Purification by column chromatography on silica eluting with CH_2Cl_2 and recrystallization from hexane/tetrahydrofurane gave the product 5 as a red metallic solid (

0.17 g, 36 %). ^{1}H NMR (300 MHz, DMSO-d6) δ 10.22 (s, 1H), 8.08- 8.13 (d, *J* = 13 Hz, 8 H), 7.45-7.56 (m, 11 H), 6.92-6.95 (d, *J* = 8.5 Hz, 2 H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH$^+$] found 512.1888, calculated 512.186.

1-(3-hydroxyphenyl)-3-phenylpropenone (6a): 3'-hydroxyacetophenone (1 eq, 2 g, 14.7 mmol) and benzaldehyde (1 eq, 1.56 g, 14.7 mmol) were dissolved in absolute tetrahydrofurane (10 ml). Sodium hydride (3 eq, 1.06 g, 44.1 mmol) was added dropwise. Resulting solution was stirred for 8-12 hours, during which the product precipitated as the potassium salt. The solution/suspension was poured into 1 M HCl (10 ml), and further concentrated HCl was added until the solution was acidic. Obtained yellow solid was washed with water and used in further synthesis without purification. (2.98 g, 91%)

1-(3-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (6b): A solution of 1-(3-hydroxyphenyl)-3-phenylpropenone (3) (1eq, 2 g, 7 mmol), nitromethane (20 eq, 7.57 ml, 140.2 mmol) and KOH (1.2 eq, 0.47 g, 8.4 mmol) in EtOH (10 ml) was heated at 60 ºC under reflux for 12 h. After cooling to room temperature, the solvent was removed in vacuo and oily residue obtained was acidified with 4 M HCl and partitioned between EtOAc (50 ml) and H_2O (50 ml). The organic layer was separated, dried over sodium sulfate and evaporated under reduced pressure. The obtained product was used for further synthesis without purification. (0.99 g, 60%)

[5-(3-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (6c): 1-(3-hydroxyphenyl)-4-nitro-3-phenylbutan-1-one (6b) (1 eq, 1 g, 3.5 mmol), 1,3-diphenyl-4-nitro-butan-1-on (1b) (1 eq, 0.94 g, 3.5 mmol) and ammonium acetate (35 eq, 7.6 g, 122.5 mmol) in butanol (50 ml) were heated under reflux for 24 h. The reaction was cooled to room temperature, the crude product was purified by column chromatography on silica with dichloromethane (after eluting symmetric byproduct with hexane/dichloromethane 3:1 v/v) to yield to product 6c as a blue-black solid. Product was recrystalized from hexane/tetrahydrofuran mixture as green metallic crystals (0.20 g, 17%). ^{1}H NMR (300 MHz, Chloroform-d) δ 6.97-7.00 (dd, *J* = 9.7 Hz, 1H), 7.39-7.66 (m, 13H), 7.71 (m, 1H), 8.10-8.12 (d, *J* = 7.3 Hz, 6H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH$^+$] found 465.1853, calculated 465.1841.

BF_2 chelate of [5-(3-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (6): Compound 6c (0.19 g, 0.4 mmol) was dissolved in dry CH_2Cl_2 (50 ml), treated with diisopropylethylamine (10 eq, 0.7 ml, 4 mmol) and BF_3 diethyletherate (15 eq, 0.81 ml, 6 mmol) and stirred under argon for 24 h. Purification by column chromatography on silica eluting with CH_2Cl_2 and recrystallization from hexane/tetrahydrofurane gave the product 6 as a red metallic solid (0.08 g, 36 %). ^{1}H NMR (300 MHz, Chloroform-d) δ 8.02-8.09 (m, 6H), 7.59-7.61 (t, *J* = 2.3 Hz, 1H), 7.44-7.56 (m, 10H), 7.34-7.39 (t, *J* = 8 Hz, 1H), 6.97-7.01 (m, 3H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH$^+$] found 512.193, calculated 512.186.

1-phenyl-4-nitro-3-(4-methoxyphenyl)-butan-1-one (7a): A solution of 1-phenyl-3-(4-methoxyphenyl)-propenone (1 eq, 2 g, 8.4 mmol), nitromethane (20 eq, 10.25 ml, 168 mmol) and KOH (0.2 eq, 0.09 g, 1.7 mmol) in EtOH (10 ml) was heated at 60 ºC under reflux for 12 h. After cooling to room temperature, the solvent was removed in vacuo and oily residue obtained was partitioned between EtOAc (50 ml) and H_2O (50 ml). The organic layer was separated, dried over sodium sulfate and evaporated under reduced pressure. The obtained product was used for further synthesis without purification. (2.5 g, 82%)

[5-(4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-(4-methoxyphenyl)-3-phenylpyrrol-2-ylidene]amine (7b): Compound 7a (1eq, 1.0 g, 4.4 mmol), compound 1b (1eq, 0.93 g, 4.4 mmol) and ammonium acetate (35 eq, 9.55 g, 154 mmol) in butanol (50 ml) were heated under reflux for 24 h. The reaction was cooled to room temperature, the crude product was purified by column chromatography on silica with dichloromethane (after eluting symmetric byproduct with toluene/dichloromethane 3:1 v/v) to yield to product 7b as a blue-black solid. Product was recrystallized from hexane/tetrahydrofuran mixture as green metallic crystals (0.13 g, 8%). ^{1}H NMR (300 MHz, DMSO-d6) δ 8.08-8.10 (d, *J* = 7.3 Hz, 4 H), 7.97-8.01 (dd, *J* = 8.7, 3.3 Hz, 4 H), 7.60 (s, 1 H), 7.53 (s, 1 H), 7.34 – 7.49 (m, 2H), 7.18-7.21 (d, *J* = 8.8 Hz, 2 H), 7.01-7.04 (d, *J* = 8.7 Hz, 2 H), 3.89 (s, 3 H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH$^+$] found 495.1984, calculated 495.1947.

BF_2 chelate of [5-(4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-(4-methoxyphenyl)-3-phenylpyrrol-2-ylidene]amine (7): Compound 7b (0.1 g, 0.20 mmol) was dissolved in dry CH_2Cl_2 (50 ml), treated with diisopropylethylamine (10 eq, 0.39 ml, 2 mmol) and BF_3 diethyletherate (15 eq, 0.38 ml, 3 mmol) and stirred under argon for 24 h. Purification by column chromatography on silica eluting with CH_2Cl_2 and recrystallization from hexane/tetrahydrofurane gave the product 7 as a red metallic solid (0.079 g, 53 %). ^{1}H NMR (300 MHz, DMSO-d) δ 8.11-8.19 (m, 8 H), 7.68 (s, 1 H), 7.42-7.57

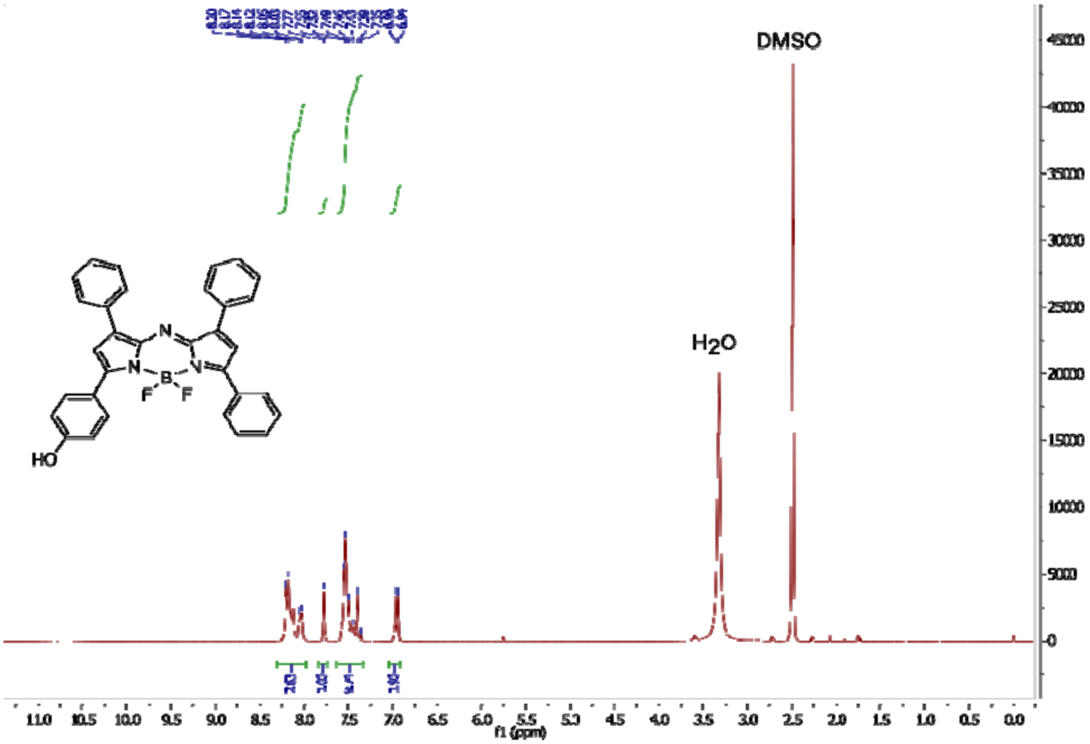
(m, 7 H), 7.12-7.15 (d, *J* = 9.0 Hz, 2 H), 6.87-6.90 (d, *J* = 8.9 Hz, 2 H), 3.88 (s, 3 H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH^+] found 542.203, calculated 542.196.

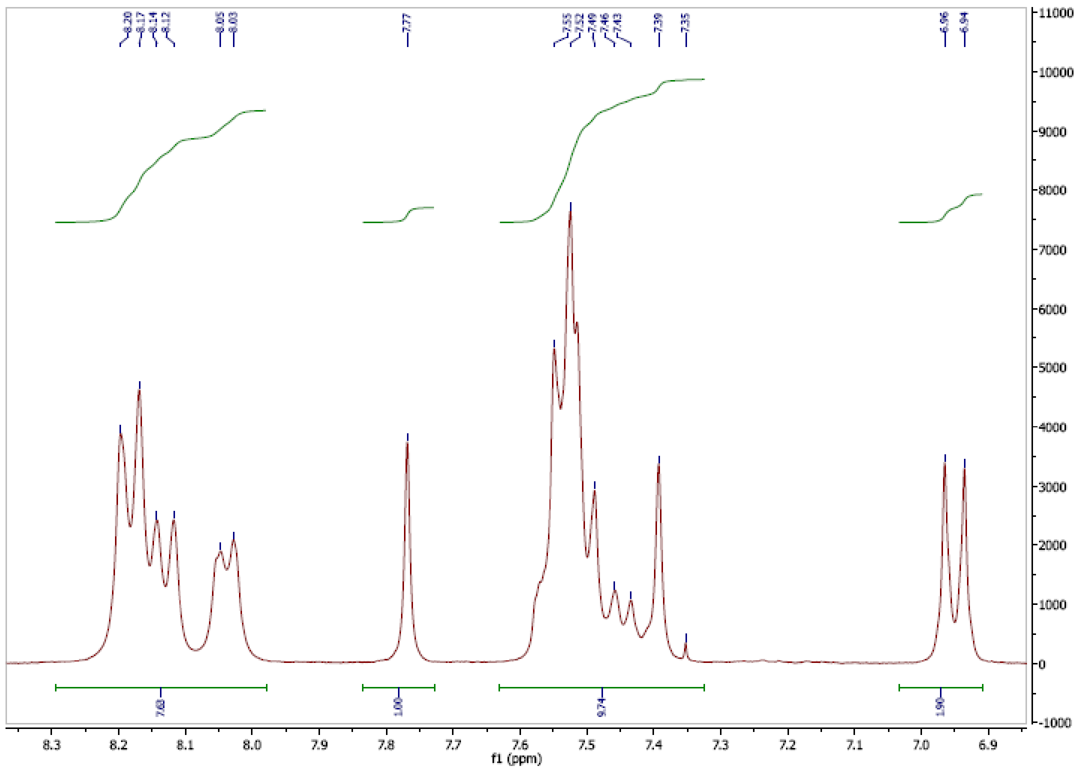
1-(4-methoxyphenyl)-4-nitro-3-(4-methoxyphenyl)-butan-1-one (8a). A solution of 1-(4-methoxyphenyl)-3-(4-methoxyphenyl)-propenone (1 eq, 2 g, 8.4 mmol), nitromethane (20 eq, 10.25 ml, 168 mmol) and KOH (0.2 eq, 0.09 g, 1.68 mmol) in EtOH (10 ml) was heated at 60 ºC under reflux for 12 h. After cooling to room temperature, the solvent was removed in vacuo and oily residue obtained was partitioned between EtOAc (50 ml) and H_2O (50 ml). The organic layer was separated, dried over sodium sulfate and evaporated under reduced pressure. The obtained product was used for further synthesis without purification. (2.2 g, 92%)

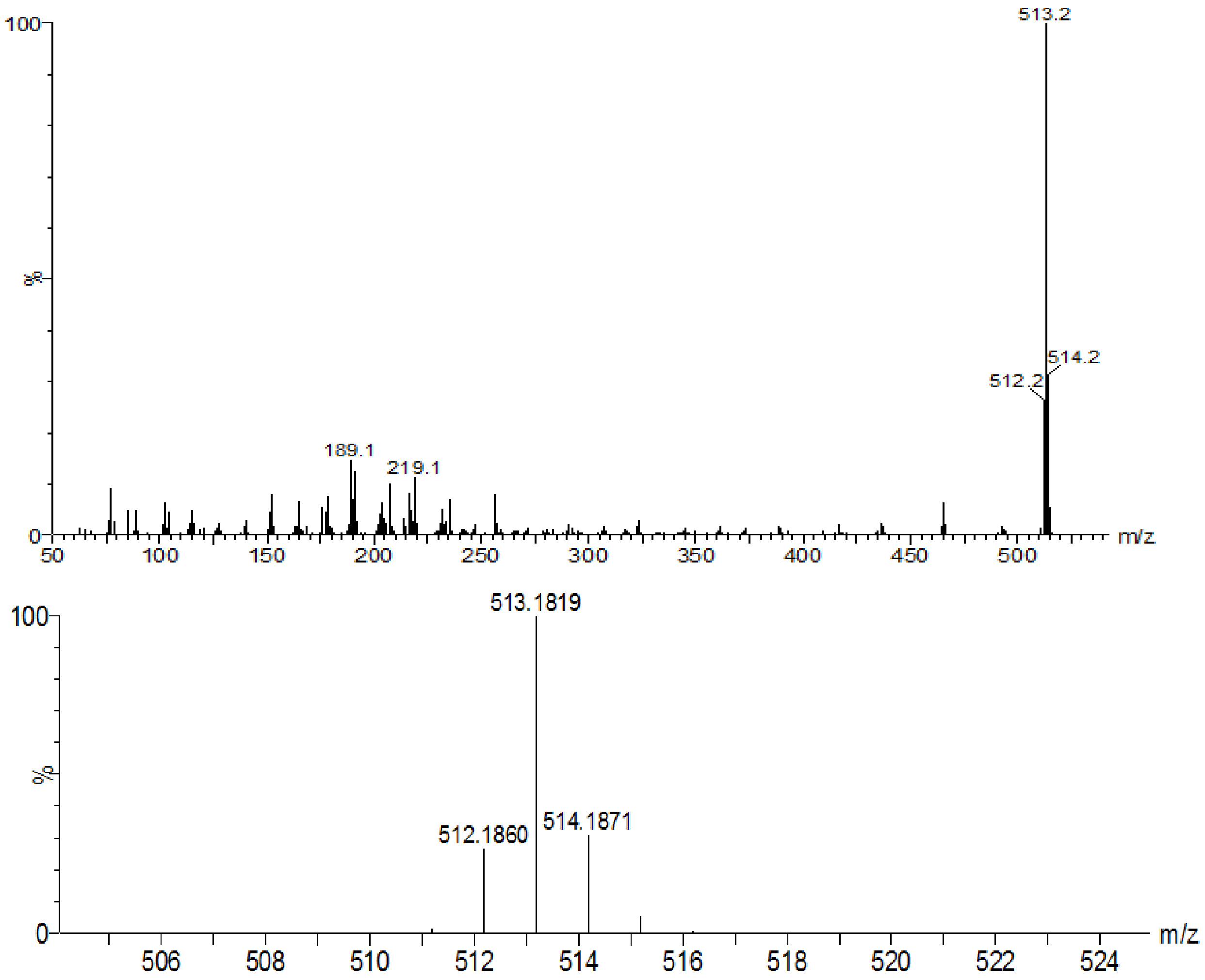
[5-(4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-(4-methoxyphenyl)-3-(4-methoxy phenyl)-pyrrol-2-ylidene]amine (8b): Compound 8a (1eq, 1.0 g, 4.4 mmol), compound 1b (1eq, 0.93 g, 4.4 mmol) and ammonium acetate (35 eq, 9.55 g, 154 mmol) in butanol (50 ml) were heated under reflux for 24 h. The reaction was cooled to room temperature, the crude product was purified by column chromatography on silica eluting with dichloromethane (after eluting symmetric byproduct with toluene/dichloromethane 3:1 v/v) to yield to product 8b as a blue-black solid. Product was recrystallized from hexane/tetrahydrofuran mixture as green metallic crystals (0.39 g, 20%). ^{1}H NMR (300 MHz, DMSO-d6) δ 8.08-8.13 (m, 4H), 7.92 – 7.95 (m, 2 H), 7.87 (s, 2 H), 7.78 (s, 1 H), 7.54-7.59 (t, 2 H), 7.32-7.50 (m, 8 H), 2.31 (s, 2 H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH^+] found 525.2096, calculated 525.2053.

BF_2 chelate of [5-(4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-(4-methoxyphenyl)-3-(4-methoxy phenyl)-pyrrol-2-ylidene]amine (8): Compound 8b (0.22 g, 0.42 mmol) was dissolved in dry CH_2Cl_2 (50 ml), treated with diisopropylethylamine (10 eq, 0.71 ml, 4.2 mmol) and BF_3 diethyletherate (15 eq, 0.8 ml, 6.3 mmol) and stirred under argon for 24 h. Purification by column chromatography on silica eluting with CH_2Cl_2 and recrystallization from hexane/tetrahydrofurane gave the product 8 as a red metallic solid (0.19 g, 78 %). ^{1}H NMR (300 MHz, DMSO-d6) δ 10.46 (s, 1 H), 8.08 - 8.20 (m, 8 H), 7.46-7.59 (m, 5 H), 7.08-7.11 (dd, *J* = 12.9, 9.0 Hz, 4 H), 6.92-6.95 (d, *J* = 8.9 Hz, 2 H), 3.89 (s, 3 H), 3.87 (s, 3 H). Electron impact-direct insertion-time of flight (EI-DI-TOF) m/z [MH^+] found 572.2072, calculated 572.2129.

BF$_2$ chelate of [5-(4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (1).

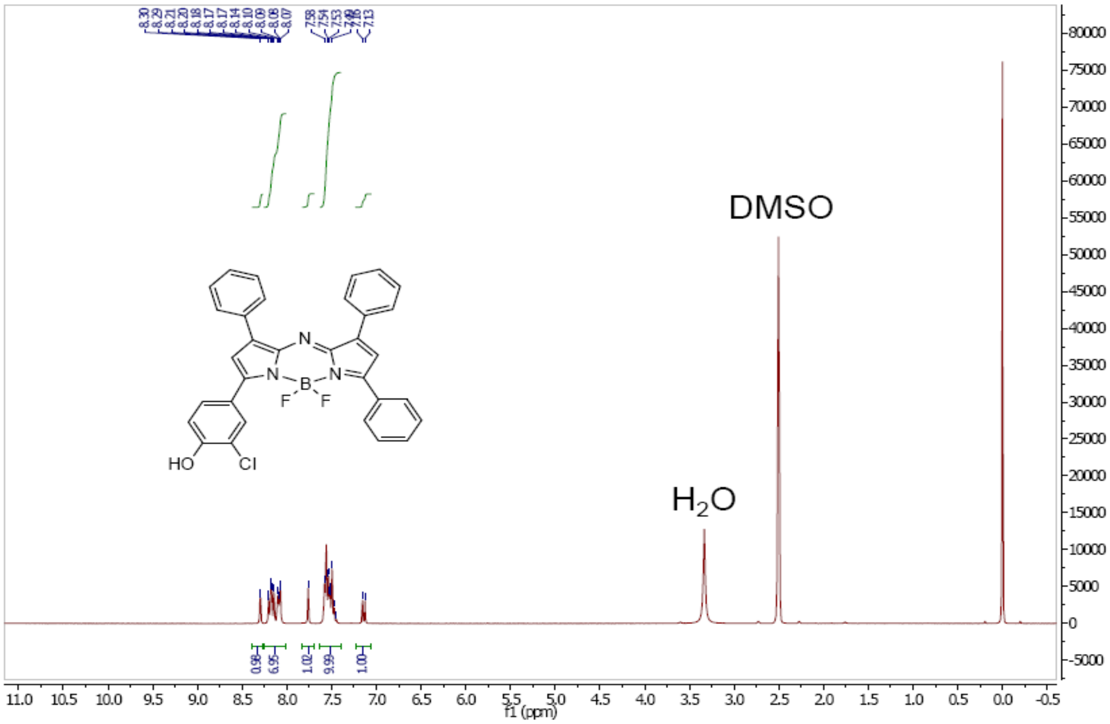


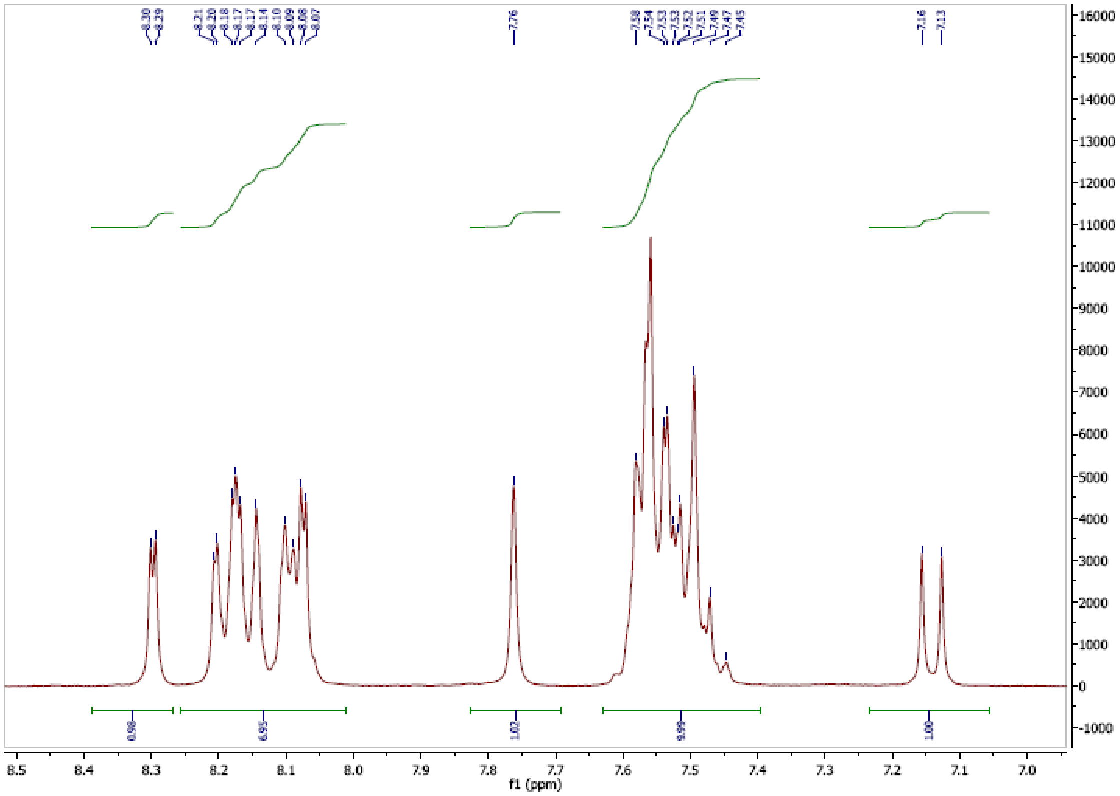


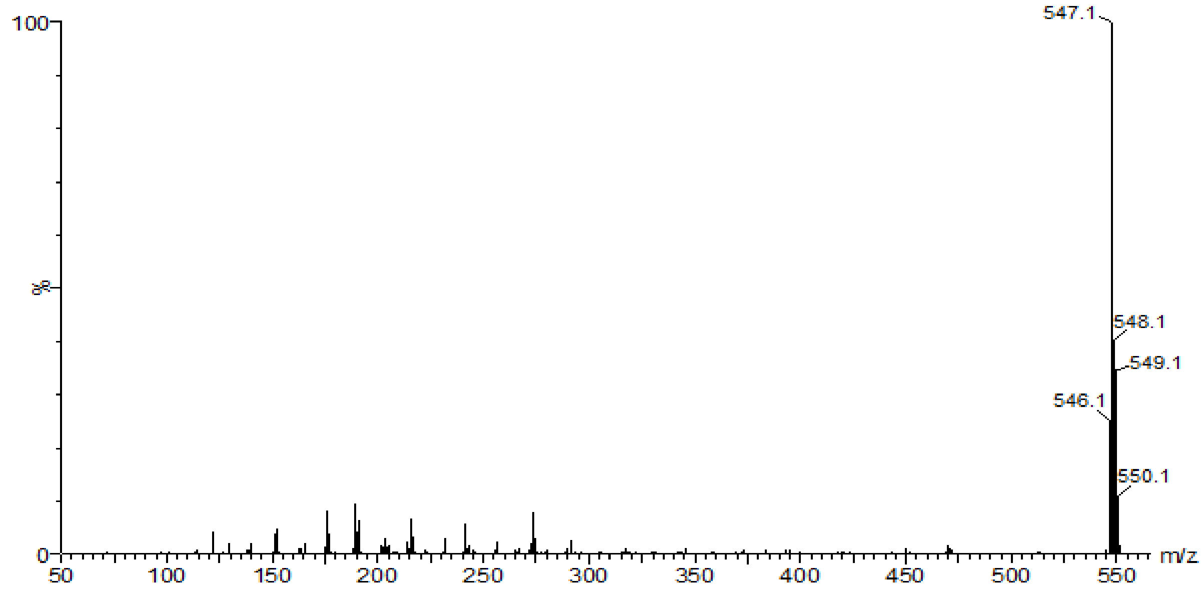


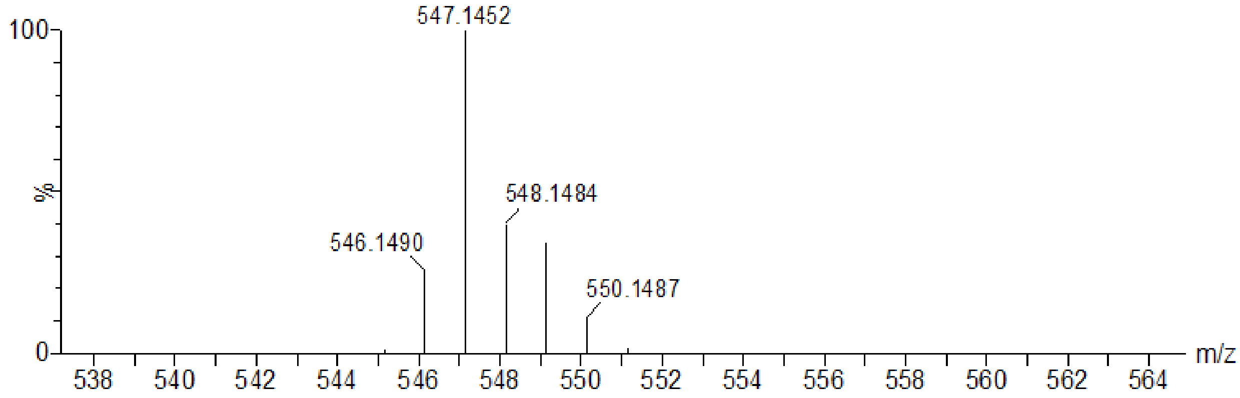
^{1}H NMR and mass spectra of **1** in DMSO.

BF_2 chelate of [5-(3-chloro-4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (2)



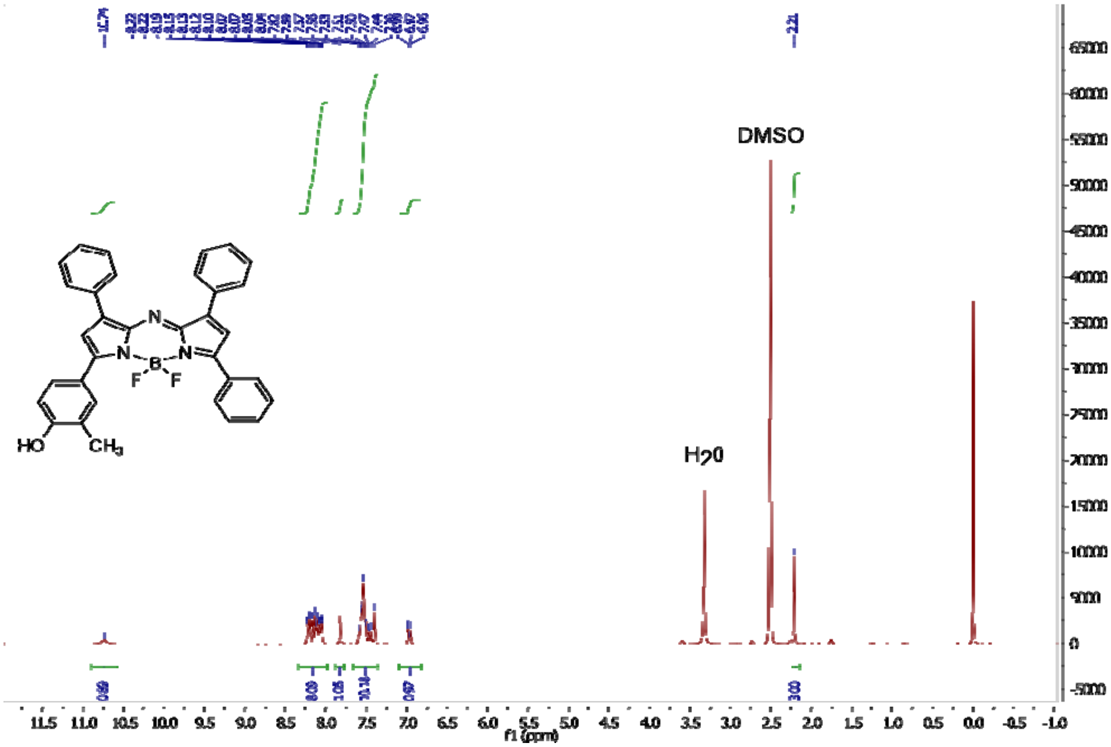


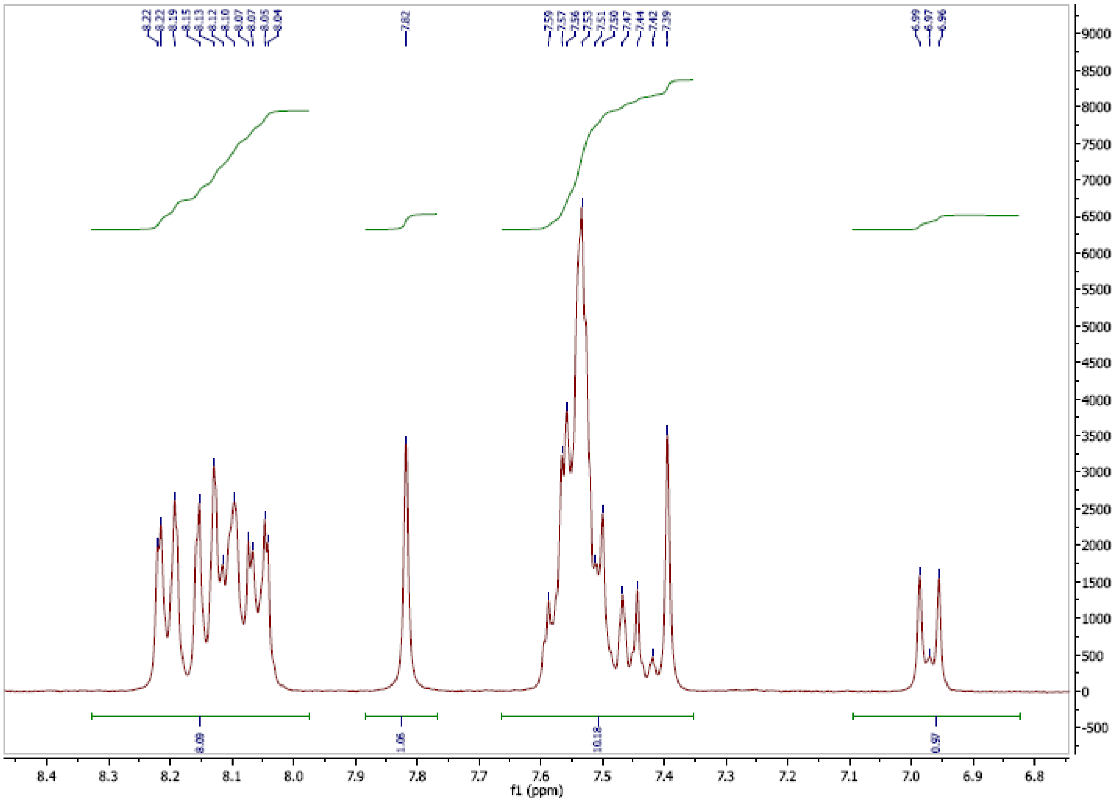


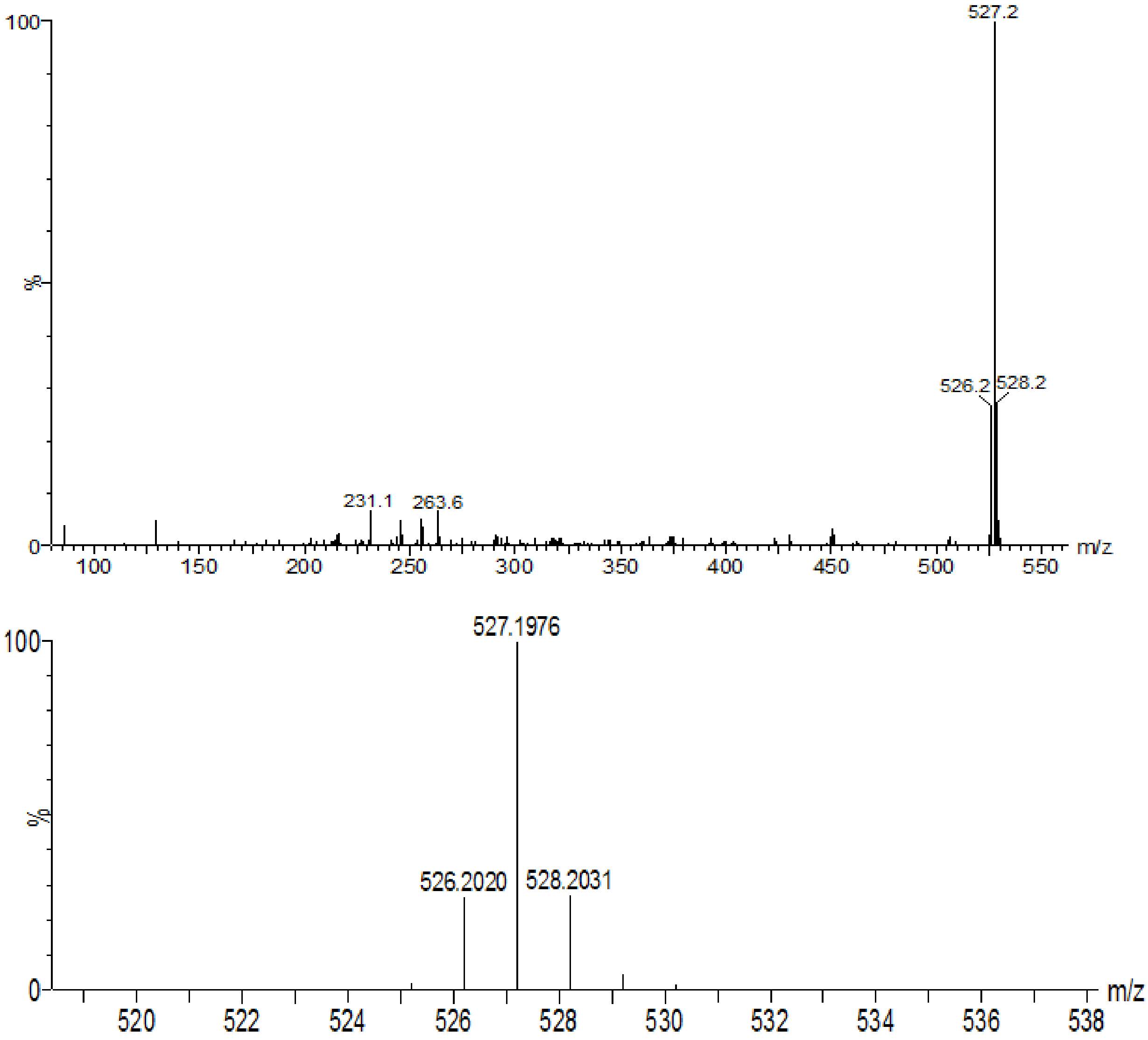


^{1}H NMR and mass spectra of **2** in DMSO.

BF_2 chelate of [5-(3-methyl-4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (3)

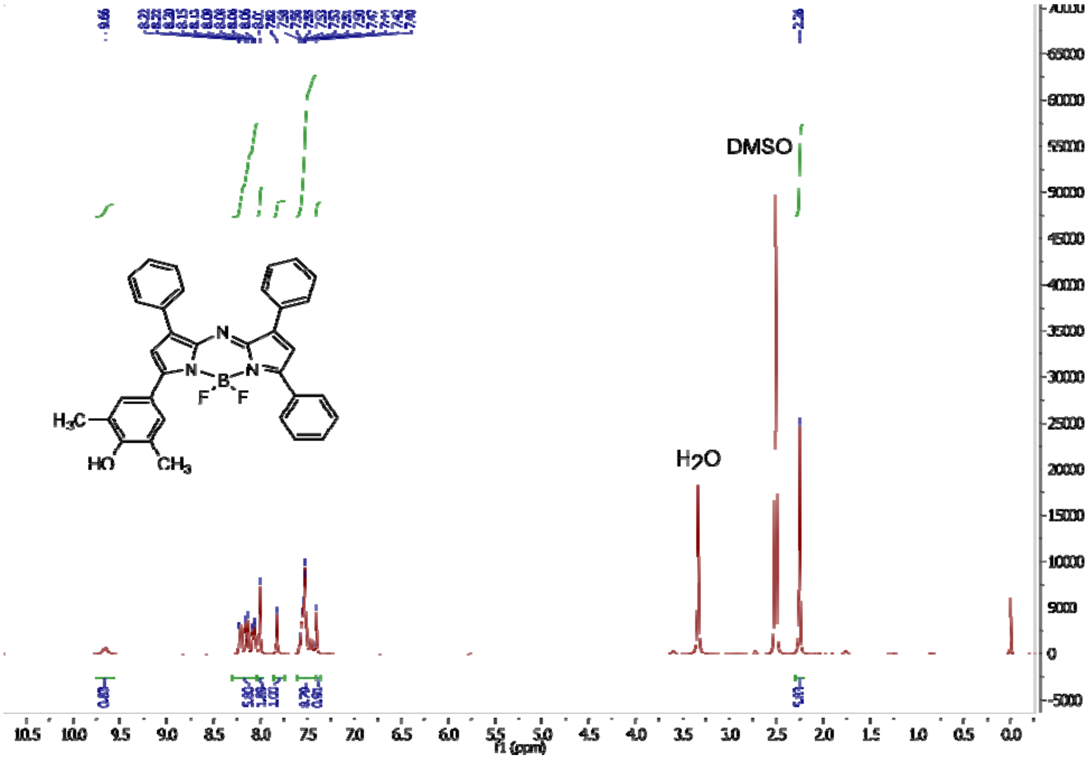


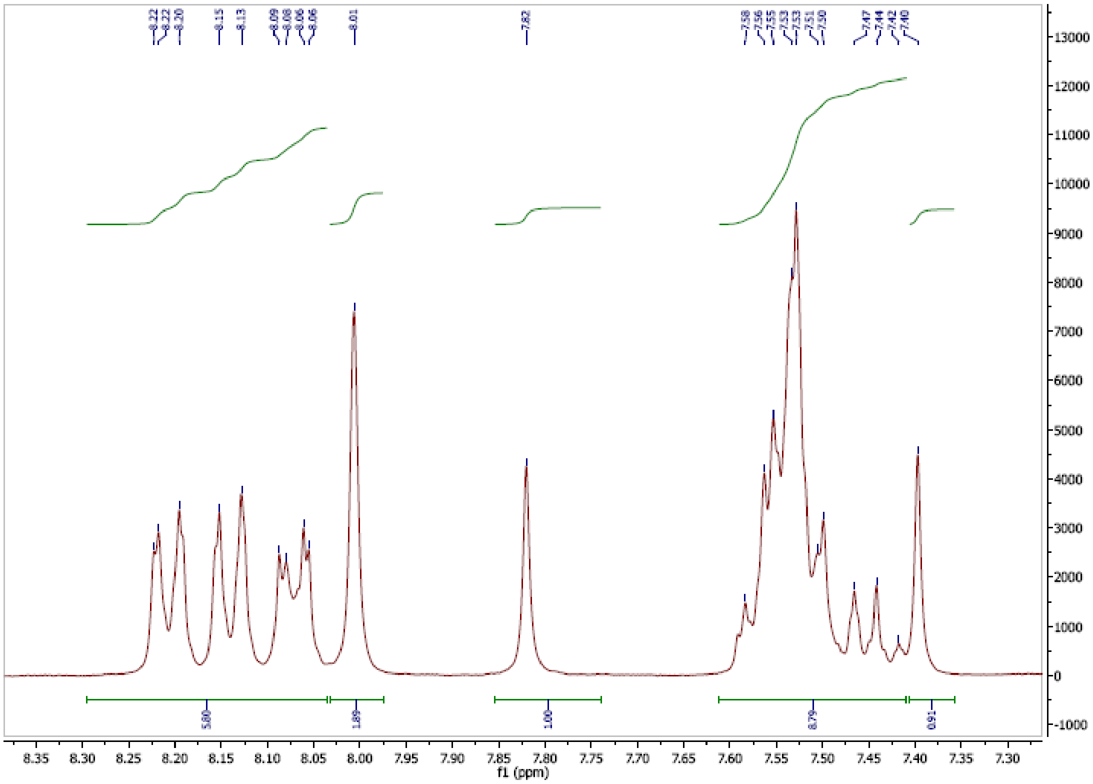


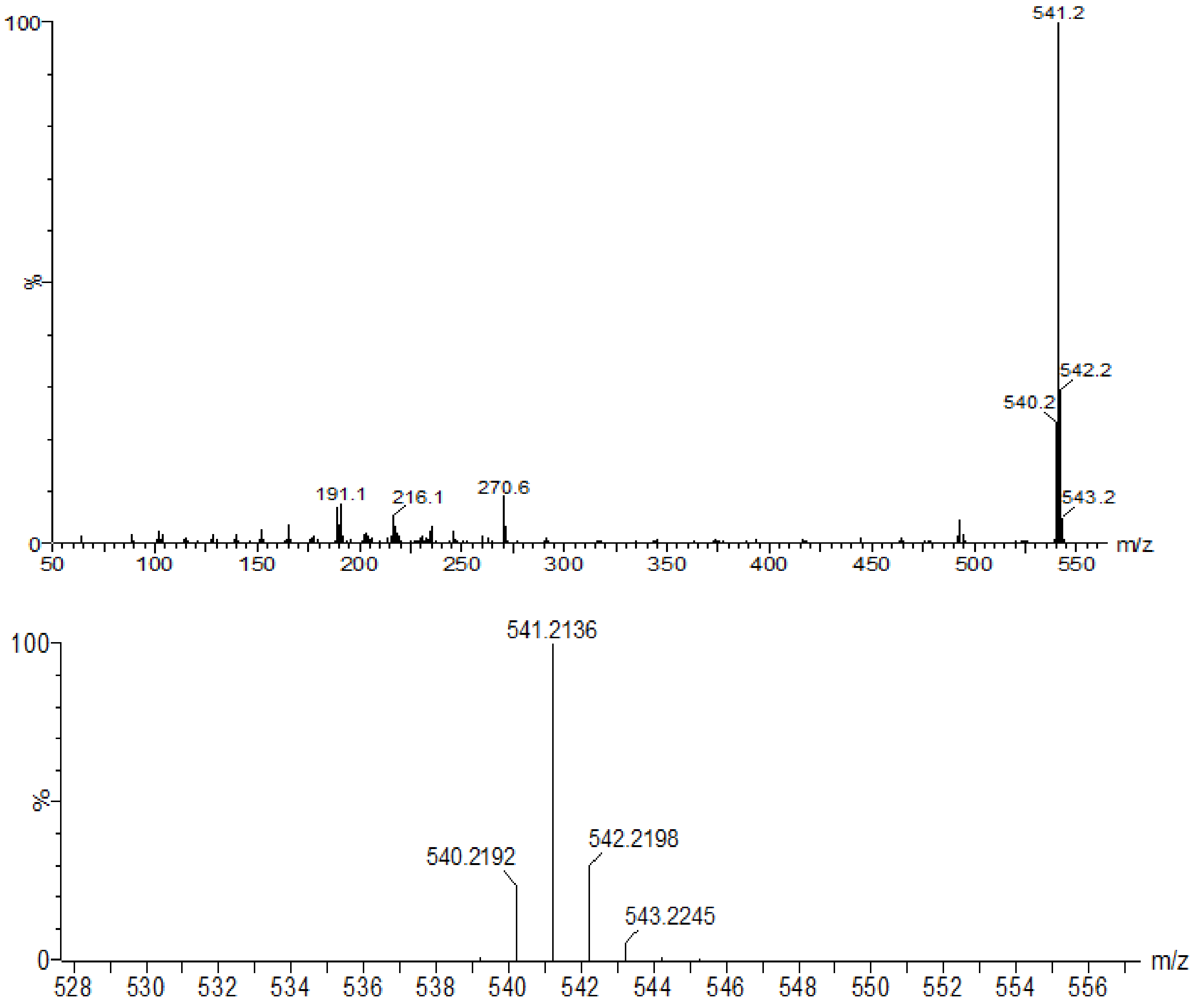


^{1}H NMR and mass spectra of **3** in DMSO.

BF_2 chelate of [5-(3,5-dimethyl-4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (4)

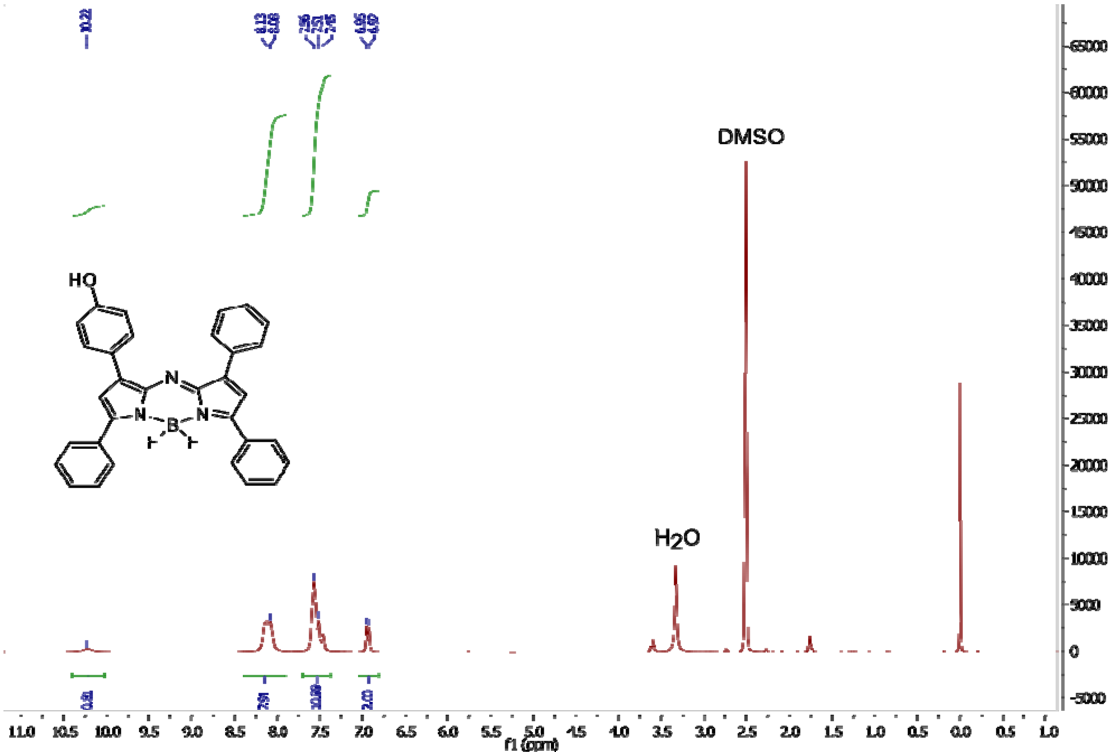


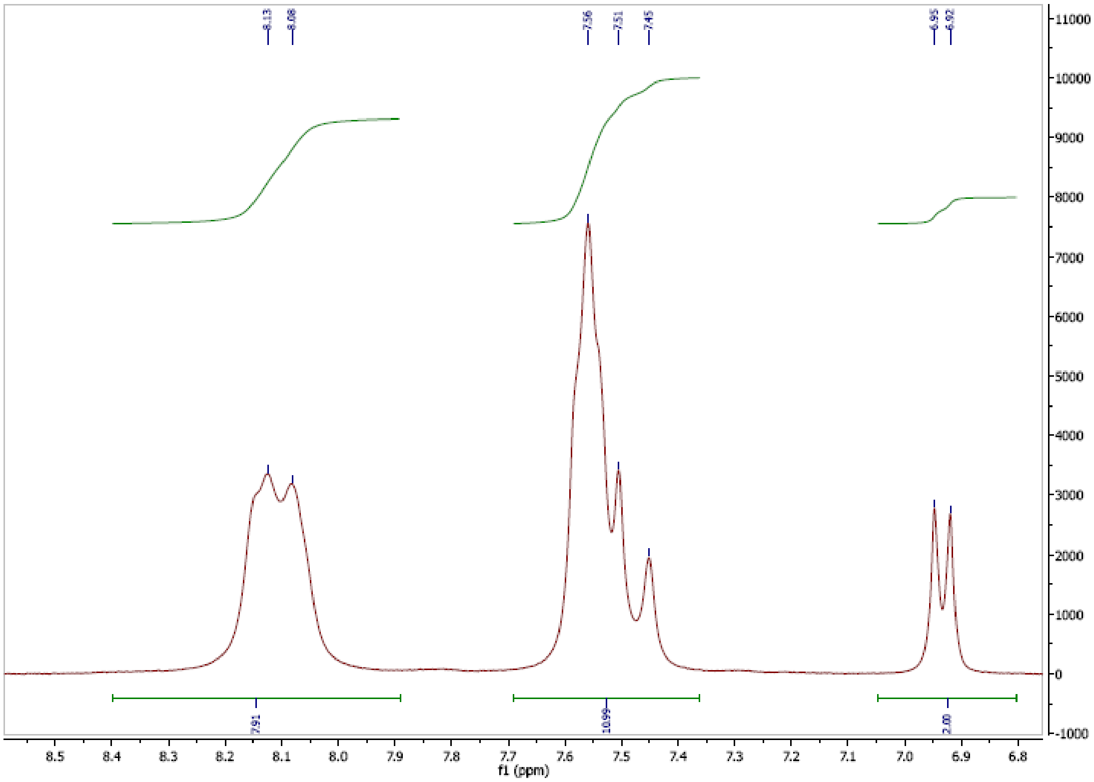


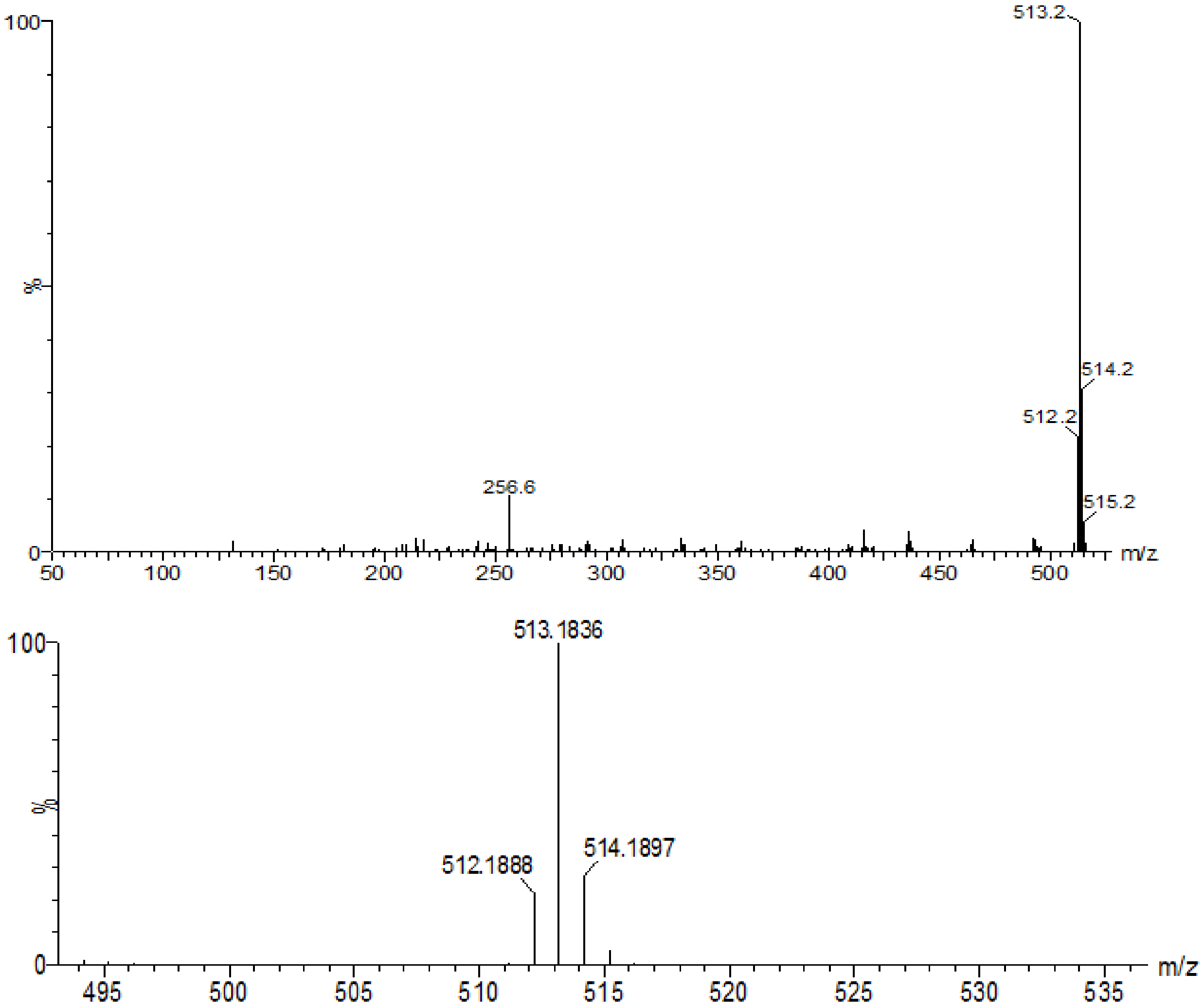


^{1}H NMR and mass spectra of **4** in DMSO.

BF_2 chelate of [5-phenyl-3-(4-hydroxyphenyl)-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (5)

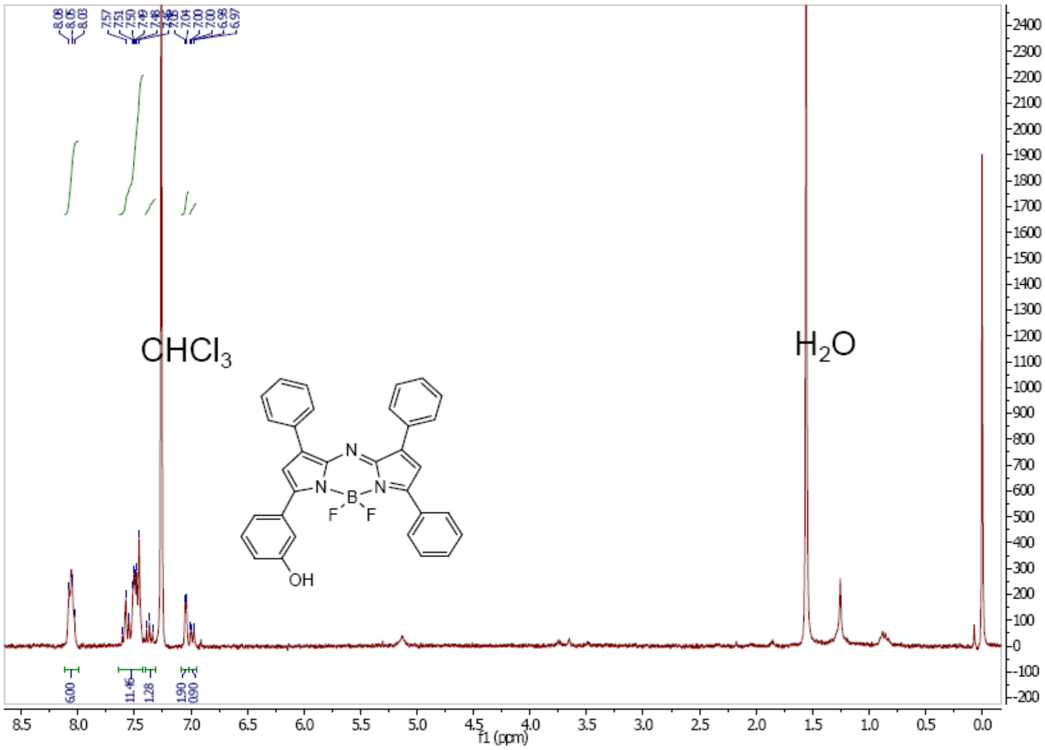


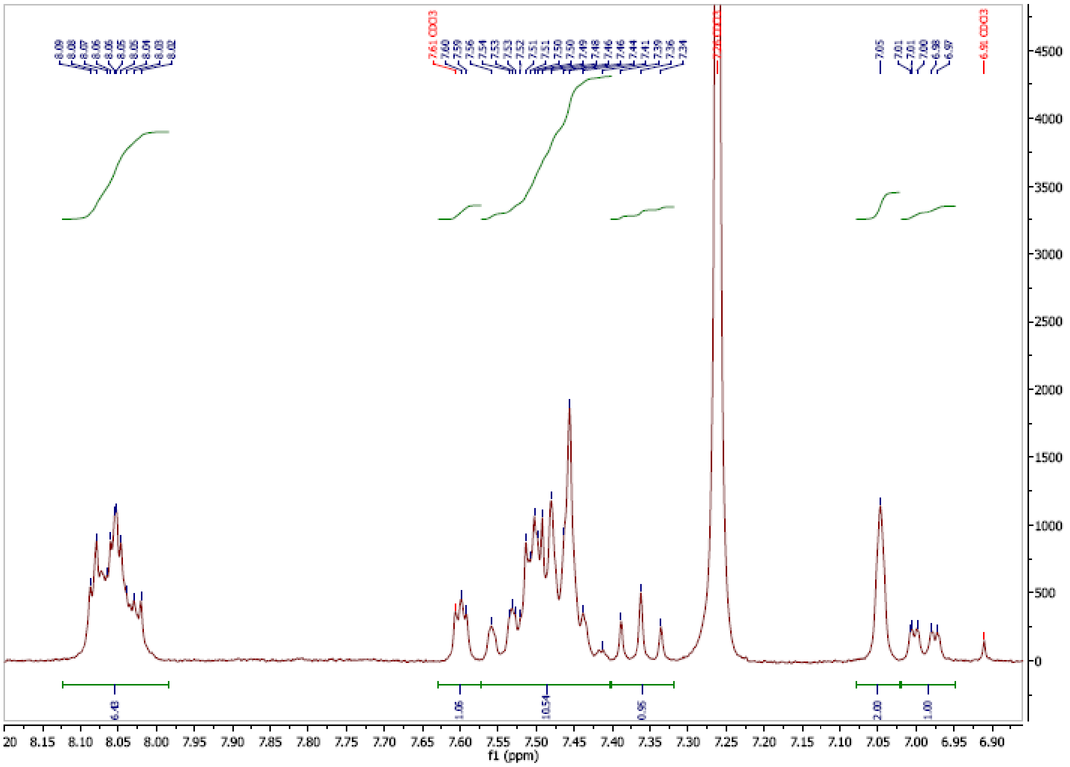


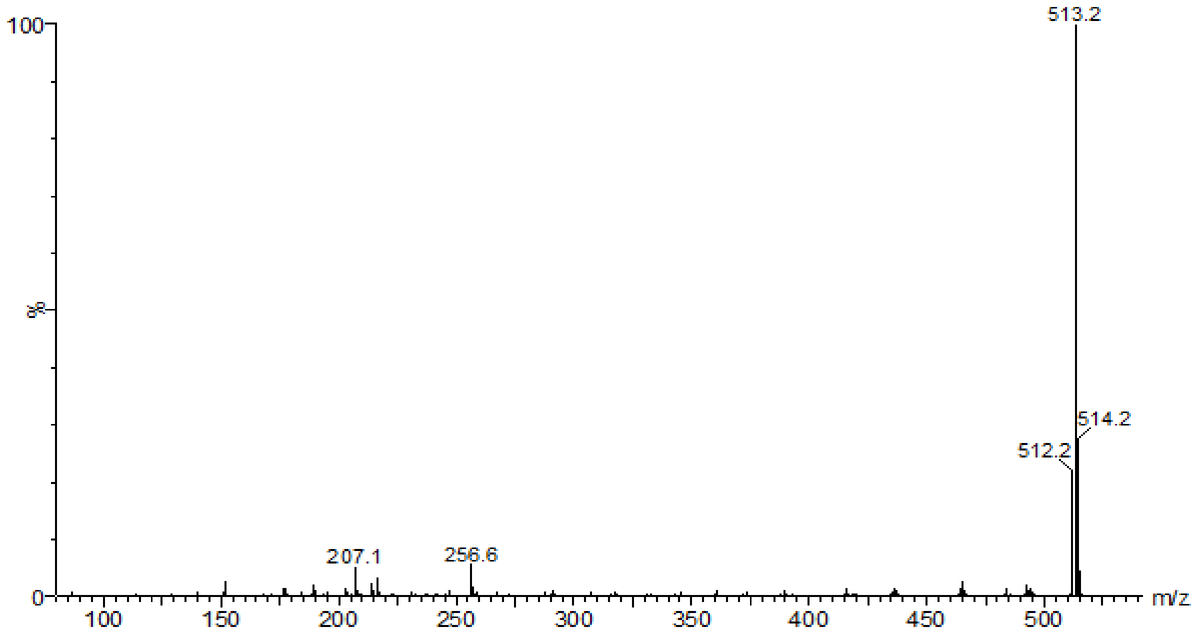


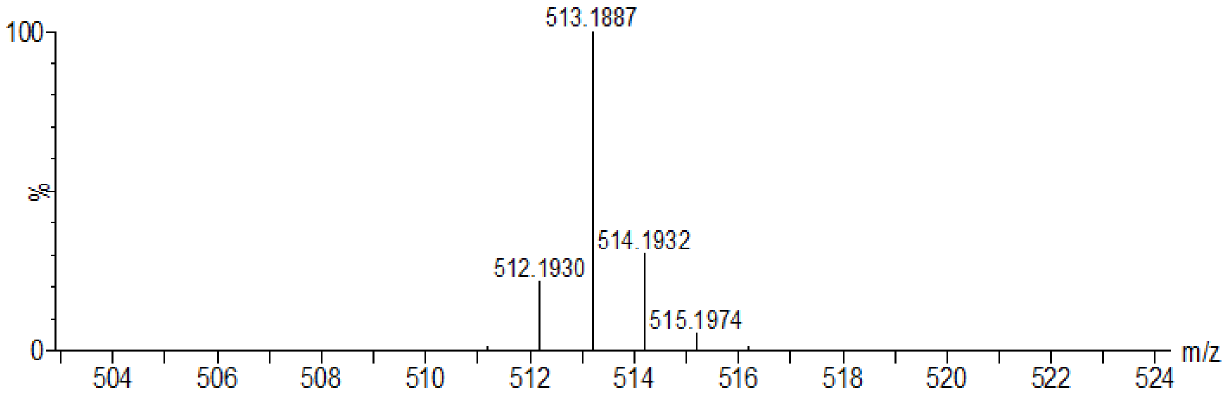
^{1}H NMR and mass spectra of **5** in DMSO.

BF_2 chelate of [5-(3-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-phenyl-3-phenylpyrrol-2-ylidene]amine (6)



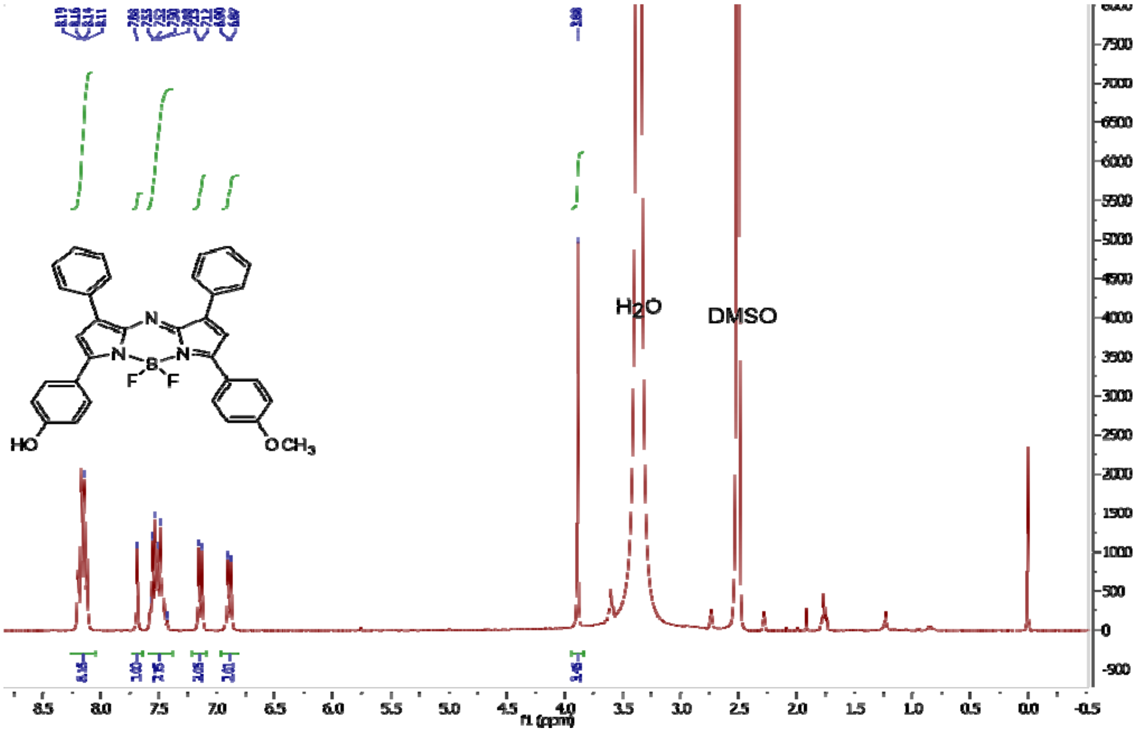


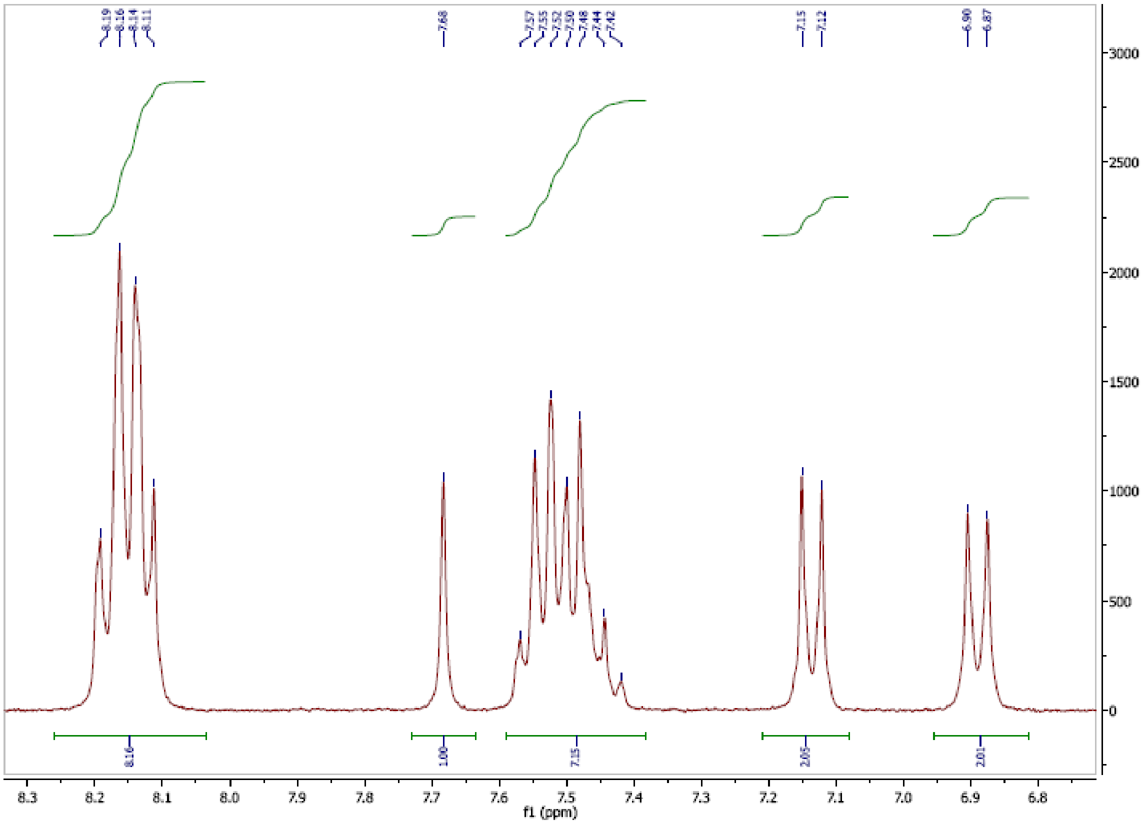


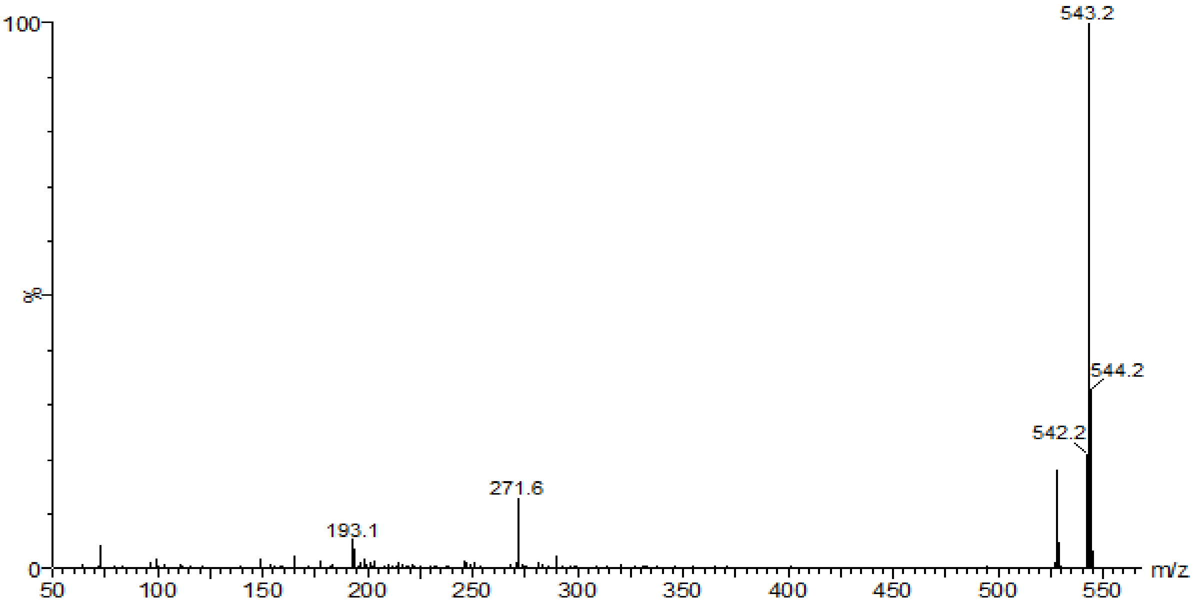


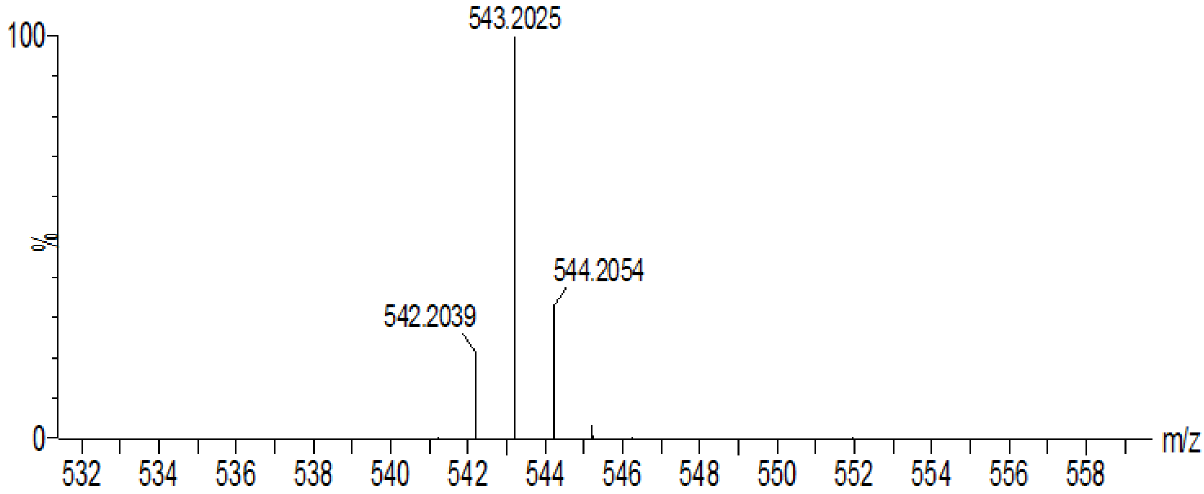
^{1}H NMR and mass spectra of **6** in $CDCl_3$.

BF_2 chelate of [5-(4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-(4-methoxyphenyl)-3-phenylpyrrol-2-ylidene]amine (7)



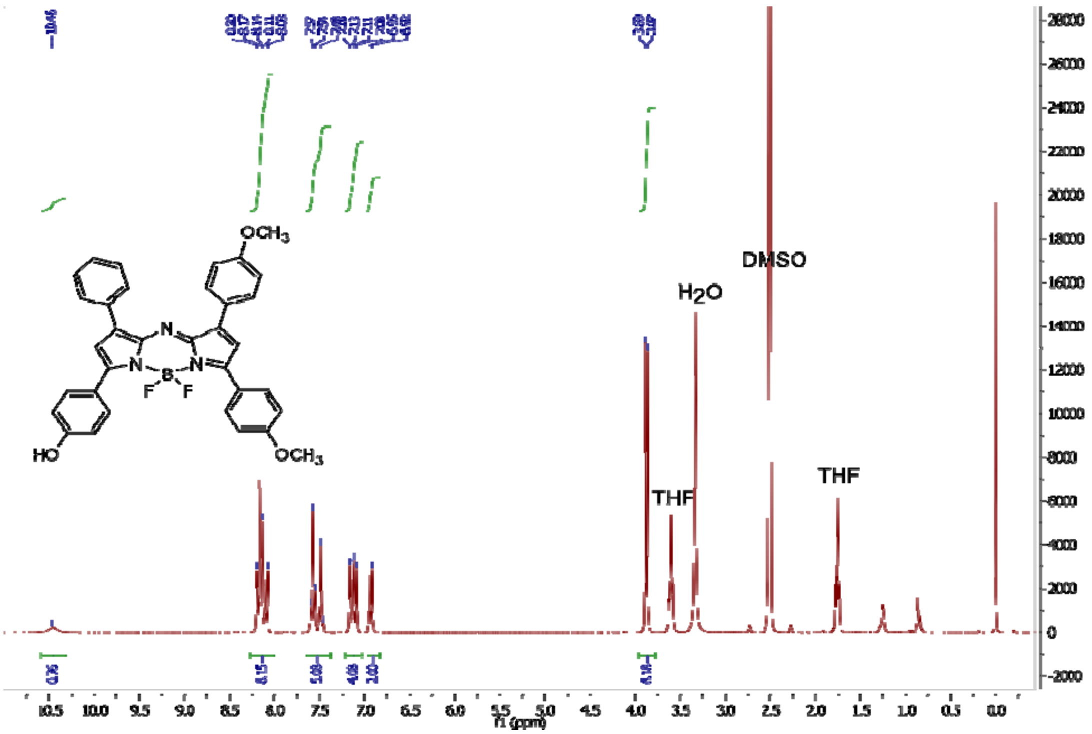


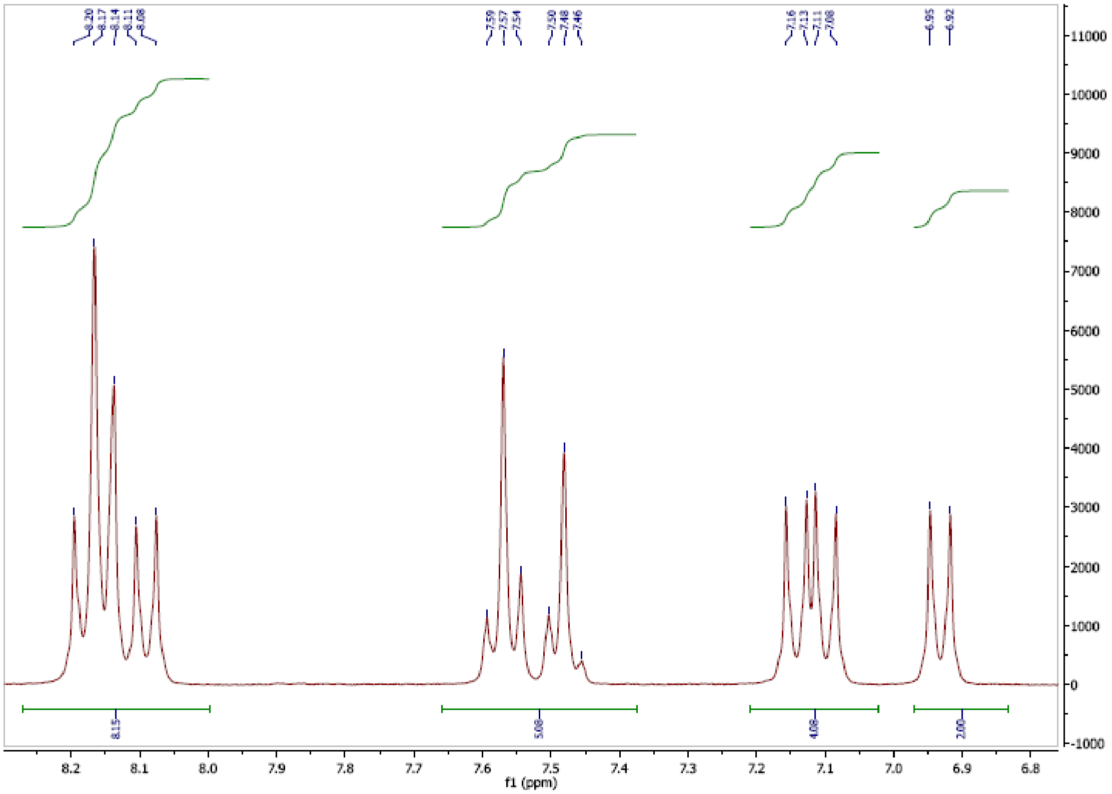


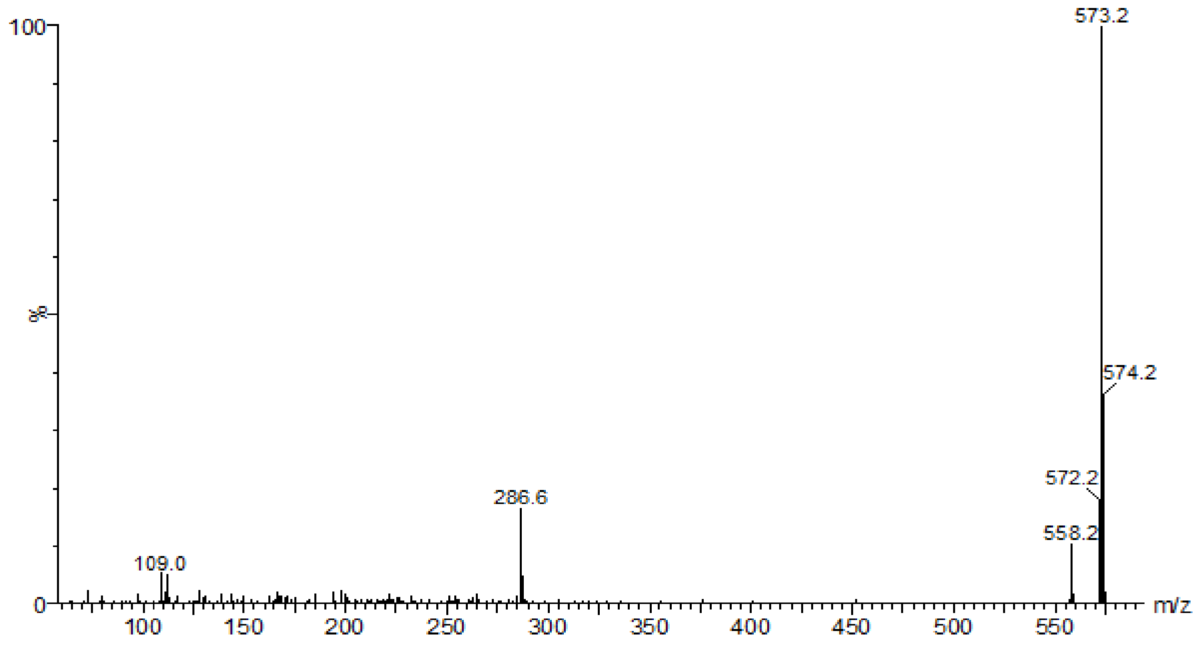


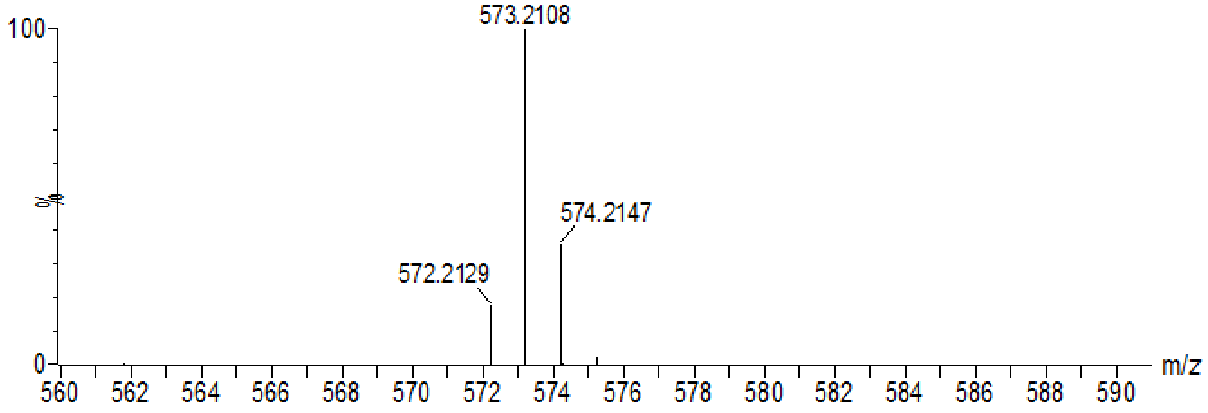
^{1}H NMR and mass spectra of **7** in DMSO.

BF$_2$ chelate of [5-(4-hydroxyphenyl)-3-phenyl-1H-pyrrol-2-yl]-[5-(4-methoxyphenyl)-3-phenylpyrrol-2-ylidene]amine (8)









^{1}H NMR and mass spectra of **8** in DMSO.

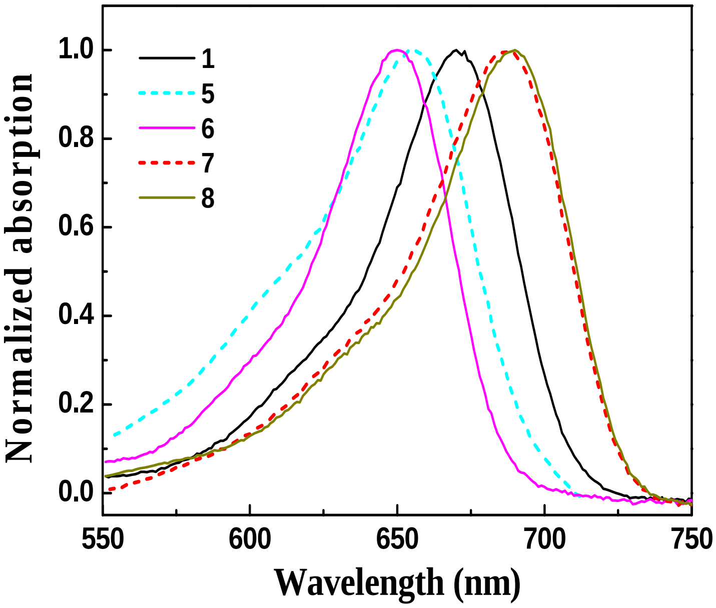


Figure S1. Normalized absorption spectra of pH sensor dye no. **1**, **5**, **6**, **7** and **8** in EtOH/H_2O, IS=0.02 M.

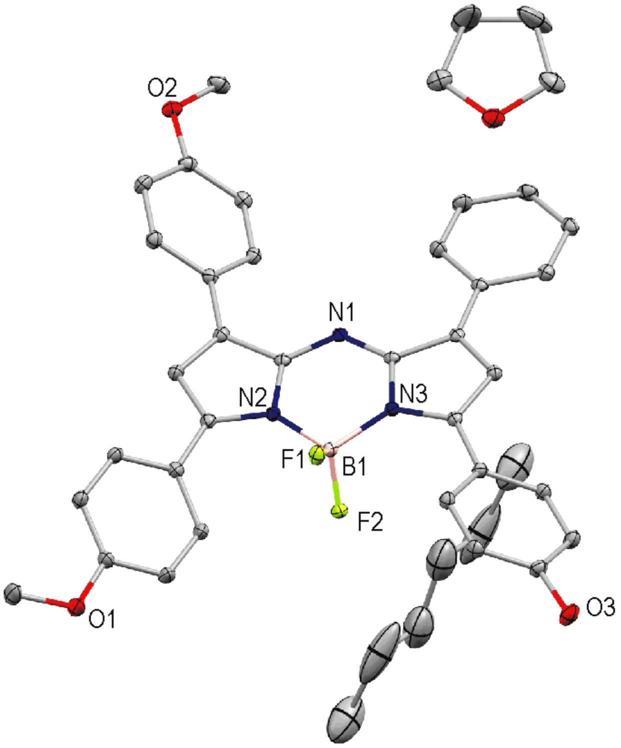


Figure S2. Crystal structure of **8.**

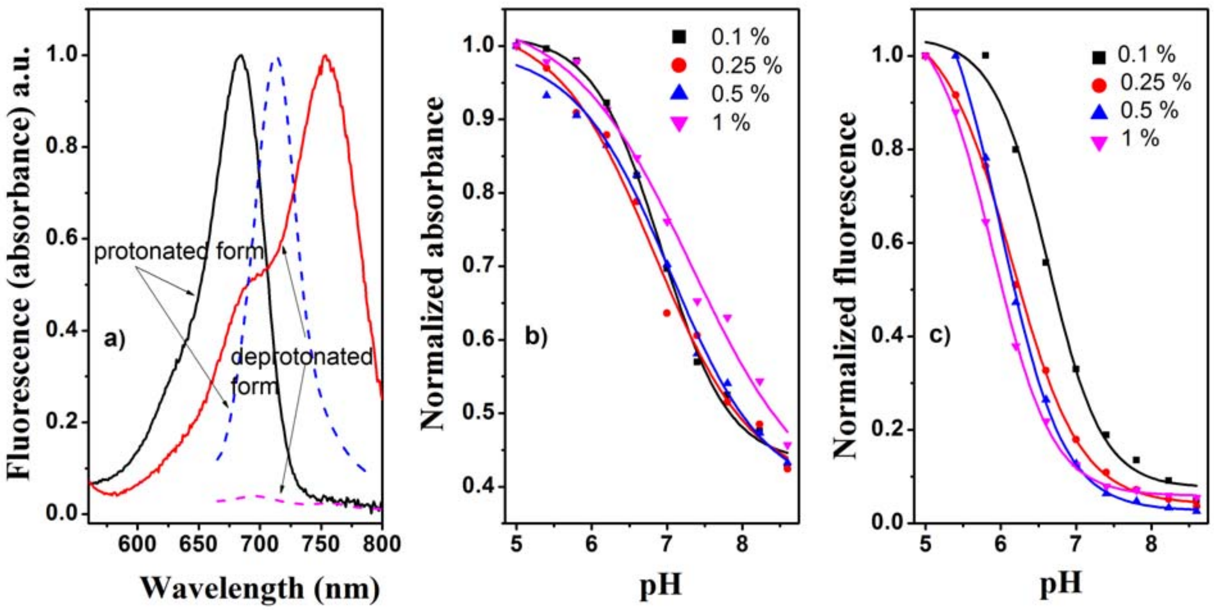


Figure S3. a) Absorbance (solid lines) and fluorescence spectra (dashed lines) of **2** in hydrogel D4 (excited at 650 nm), absorption (b) and fluorescence (c) calibration plots for different concentrations of indicator **2** in hydrogel D4.

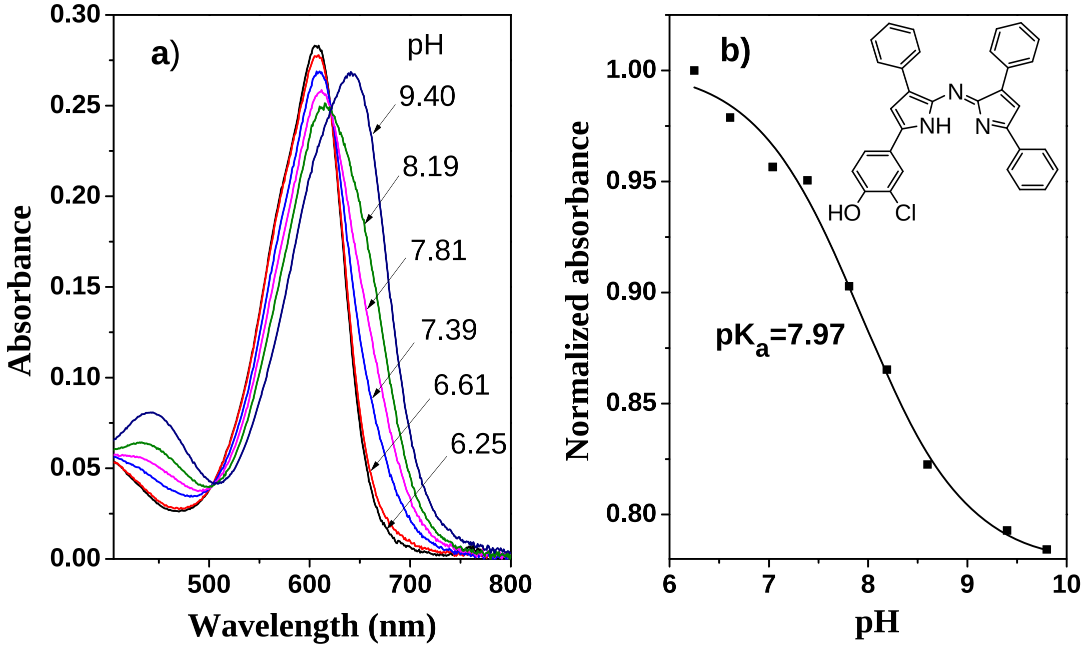


Figure S4. a) pH dependence of absorbance (left) and calibration curve (right) for azadipyrromethene corresponding to the pH indicator **2** in ethanol/aqueous buffer solution.

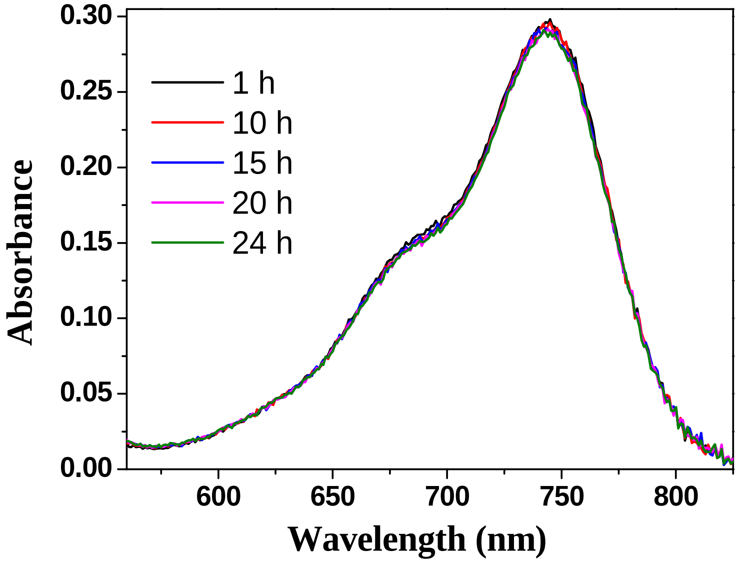


Figure S5. Leaching of aza-BODIPY pH probe **1** determined from the absorption measurements (pH 10, IS=0.02 M).

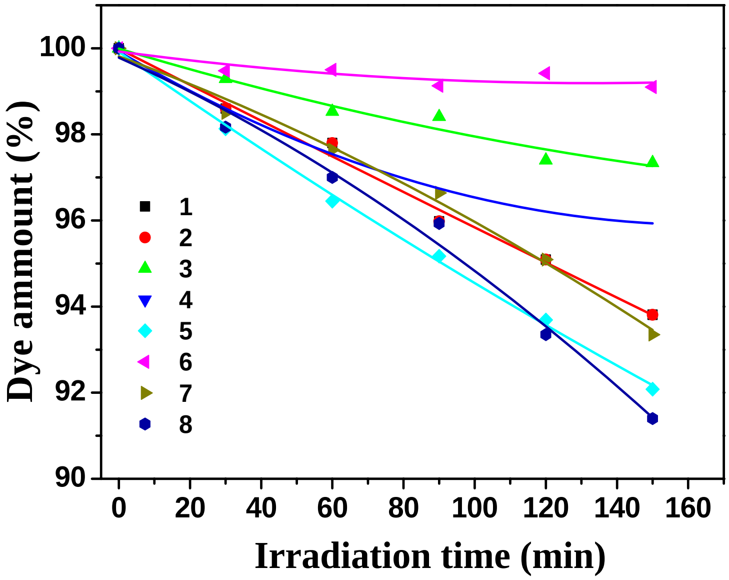


Figure S6. Photobleaching profiles for aza-BODIPY fluorescent pH probes in dimethylformamide determined from the absorption measurements.

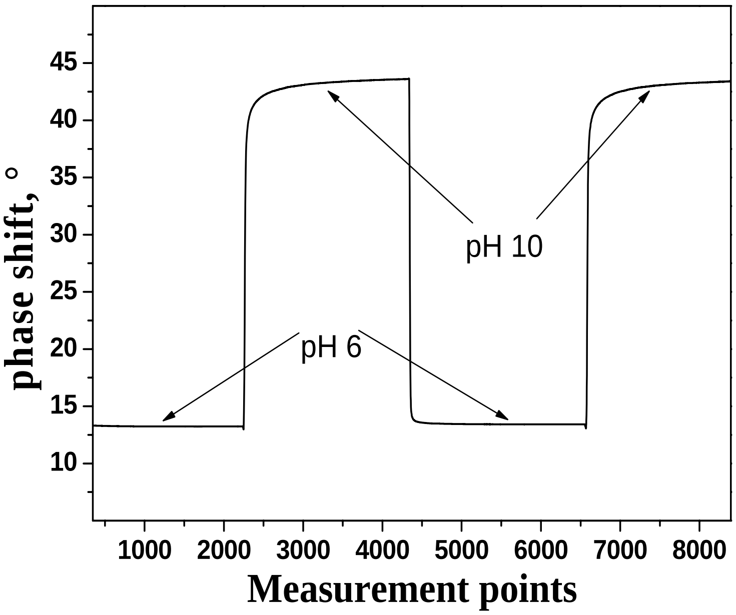


Figure S7. Photobleaching of DLR referenced fiber-optic sensor based on **1** (100% light intensity, 200 ms integration time, IS=0.02 M). Each measurement point in the experiment corresponds to the light doses accumulated in 50 measurement points at standard settings.

Table 1. Crystal data and structure refinement for rf354_fin.

Identification code	rf354_fin	
Empirical formula	C41 H41 B F2 N3 O4	
Formula weight	688.58	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.9037(19) Å	α= 90°.
	b = 14.469(2) Å	β= 99.652(4)°.
	c = 17.351(3) Å	γ = 90°.
Volume	3441.3(8) Å^3	
Z	4	
Density (calculated)	1.329 Mg/m^3	
Absorption coefficient	0.092 mm^{-1}	
F(000)	1452	
Crystal size	0.34 x 0.31 x 0.29 mm^3	
Theta range for data collection	1.74 to 26.00°.	
Index ranges	-17<=h<=17, -17<=k<=17, -21<=l<=21	
Reflections collected	151076	
Independent reflections	6772 [R(int) = 0.0368]	
Completeness to theta = 26.00°	100.0 %	
Absorption correction	None	

Max. and min. transmission	0.9739 and 0.9688
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6772 / 0 / 464
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0661, wR2 = 0.1717
R indices (all data)	R1 = 0.0726, wR2 = 0.1823
Largest diff. peak and hole	1.322 and -1.168 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for rf354_fin. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	3905(1)	5729(1)	2123(1)	24(1)
F(2)	2937(1)	6865(1)	2483(1)	26(1)
B(1)	3468(2)	6066(2)	2726(1)	18(1)
N(2)	2797(1)	5300(1)	2977(1)	17(1)
N(3)	4224(1)	6315(1)	3469(1)	17(1)
N(1)	3468(1)	5374(1)	4346(1)	16(1)
O(2)	1750(1)	2151(1)	6440(1)	29(1)
O(1)	1045(2)	4683(1)	-742(1)	34(1)
O(3)	6322(2)	9366(1)	1449(1)	33(1)
C(3)	2208(2)	4258(2)	3790(1)	19(1)
C(7)	5368(2)	6995(2)	4373(1)	19(1)
C(2)	1797(2)	4073(2)	3027(1)	20(1)
C(6)	4840(2)	6426(2)	4791(1)	17(1)
C(5)	4123(2)	5993(2)	4212(1)	16(1)
C(1)	2161(2)	4714(2)	2533(1)	19(1)
C(8)	4973(2)	6941(2)	3570(1)	18(1)
C(4)	2852(2)	5024(2)	3755(1)	17(1)
C(21)	2221(2)	4142(2)	5236(1)	20(1)

C(20)	2122(2)	3638(2)	5900(1)	21(1)
C(11)	1609(2)	5480(2)	417(2)	30(1)
C(9)	1893(2)	4728(2)	1680(1)	20(1)
C(16)	2084(2)	3740(2)	4496(1)	19(1)
C(12)	1315(2)	4646(2)	51(1)	24(1)
C(17)	1834(2)	2799(2)	4435(1)	23(1)
C(13)	1313(2)	3851(2)	495(1)	23(1)
C(19)	1880(2)	2708(2)	5829(1)	23(1)
C(14)	1596(2)	3899(2)	1300(1)	22(1)
C(10)	1890(2)	5523(2)	1215(1)	26(1)
C(18)	1734(2)	2290(2)	5092(1)	25(1)
C(22)	1965(2)	2533(2)	7209(1)	32(1)
C(15)	694(2)	3854(2)	-1132(2)	36(1)
C(23)	4967(2)	6335(2)	5648(1)	18(1)
C(29)	5298(2)	7526(2)	2972(1)	18(1)
C(27)	5801(2)	6819(2)	6929(1)	24(1)
C(33)	5580(2)	7902(2)	1662(1)	22(1)
C(24)	4395(2)	5742(2)	6021(1)	25(1)
C(28)	5676(2)	6867(2)	6117(1)	21(1)
C(34)	5251(2)	7296(2)	2181(1)	21(1)
C(32)	5974(2)	8754(2)	1922(1)	23(1)
C(30)	5690(2)	8394(2)	3216(1)	22(1)
C(26)	5221(2)	6236(2)	7288(1)	27(1)

C(31)	6022(2)	8994(2)	2704(1)	25(1)
C(25)	4527(2)	5696(2)	6831(2)	30(1)
C(38)	1831(2)	7085(2)	4819(2)	36(1)
C(35)	1403(6)	7335(3)	4014(2)	112(3)
C(41)	466(5)	9720(5)	5217(4)	108(2)
C(40)	634(7)	10000(5)	5936(5)	156(4)
O(4)	1316(2)	6284(1)	5014(1)	35(1)
C(37)	557(2)	6046(2)	4378(2)	42(1)
C(36)	646(3)	6700(4)	3727(2)	81(2)
C(39)	1709(5)	9535(4)	6384(5)	118(3)

Table 3. Bond lengths [Å] and angles [°] for rf354_fin.

F(1)-B(1)	1.384(3)
F(2)-B(1)	1.397(3)
B(1)-N(2)	1.557(3)
B(1)-N(3)	1.562(3)
N(2)-C(1)	1.366(3)
N(2)-C(4)	1.398(3)
N(3)-C(8)	1.369(3)
N(3)-C(5)	1.400(3)
N(1)-C(4)	1.322(3)
N(1)-C(5)	1.325(3)
O(2)-C(19)	1.368(3)
O(2)-C(22)	1.429(3)
O(1)-C(12)	1.364(3)
O(1)-C(15)	1.424(3)
O(3)-C(32)	1.352(3)
C(3)-C(2)	1.377(3)
C(3)-C(4)	1.433(3)
C(3)-C(16)	1.470(3)
C(7)-C(6)	1.387(3)
C(7)-C(8)	1.411(3)
C(2)-C(1)	1.414(3)

C(6)-C(5)	1.435(3)
C(6)-C(23)	1.474(3)
C(1)-C(9)	1.464(3)
C(8)-C(29)	1.469(3)
C(21)-C(20)	1.389(3)
C(21)-C(16)	1.394(3)
C(20)-C(19)	1.387(3)
C(11)-C(10)	1.376(3)
C(11)-C(12)	1.392(3)
C(9)-C(14)	1.397(3)
C(9)-C(10)	1.405(3)
C(16)-C(17)	1.405(3)
C(12)-C(13)	1.384(3)
C(17)-C(18)	1.384(3)
C(13)-C(14)	1.388(3)
C(19)-C(18)	1.398(3)
C(23)-C(28)	1.400(3)
C(23)-C(24)	1.400(3)
C(29)-C(34)	1.403(3)
C(29)-C(30)	1.406(3)
C(27)-C(26)	1.385(4)
C(27)-C(28)	1.392(3)
C(33)-C(34)	1.388(3)

C(33)-C(32)	1.392(3)
C(24)-C(25)	1.388(3)
C(32)-C(31)	1.392(3)
C(30)-C(31)	1.377(3)
C(26)-C(25)	1.383(4)
C(38)-O(4)	1.432(3)
C(38)-C(35)	1.468(5)
C(35)-C(36)	1.423(7)
C(41)-C(40)	1.295(10)
C(41)-C(41)#1	1.604(14)
C(40)-C(39)	1.703(12)
O(4)-C(37)	1.435(4)
C(37)-C(36)	1.495(5)

F(1)-B(1)-F(2)	109.86(18)
F(1)-B(1)-N(2)	108.66(18)
F(2)-B(1)-N(2)	111.19(19)
F(1)-B(1)-N(3)	112.69(19)
F(2)-B(1)-N(3)	107.89(18)
N(2)-B(1)-N(3)	106.54(17)
C(1)-N(2)-C(4)	107.02(18)
C(1)-N(2)-B(1)	130.24(18)
C(4)-N(2)-B(1)	122.34(18)

C(8)-N(3)-C(5)	107.06(18)
C(8)-N(3)-B(1)	130.53(18)
C(5)-N(3)-B(1)	121.75(18)
C(4)-N(1)-C(5)	119.80(19)
C(19)-O(2)-C(22)	117.5(2)
C(12)-O(1)-C(15)	117.45(19)
C(2)-C(3)-C(4)	105.73(19)
C(2)-C(3)-C(16)	127.8(2)
C(4)-C(3)-C(16)	126.3(2)
C(6)-C(7)-C(8)	109.30(19)
C(3)-C(2)-C(1)	108.8(2)
C(7)-C(6)-C(5)	105.06(19)
C(7)-C(6)-C(23)	126.6(2)
C(5)-C(6)-C(23)	128.2(2)
N(1)-C(5)-N(3)	124.36(19)
N(1)-C(5)-C(6)	126.1(2)
N(3)-C(5)-C(6)	109.53(18)
N(2)-C(1)-C(2)	109.21(19)
N(2)-C(1)-C(9)	126.3(2)
C(2)-C(1)-C(9)	124.4(2)
N(3)-C(8)-C(7)	108.99(19)
N(3)-C(8)-C(29)	127.44(19)
C(7)-C(8)-C(29)	123.4(2)

N(1)-C(4)-N(2)	124.3(2)
N(1)-C(4)-C(3)	126.2(2)
N(2)-C(4)-C(3)	109.21(18)
C(20)-C(21)-C(16)	121.8(2)
C(19)-C(20)-C(21)	119.4(2)
C(10)-C(11)-C(12)	120.7(2)
C(14)-C(9)-C(10)	117.3(2)
C(14)-C(9)-C(1)	118.1(2)
C(10)-C(9)-C(1)	124.6(2)
C(21)-C(16)-C(17)	117.9(2)
C(21)-C(16)-C(3)	122.5(2)
C(17)-C(16)-C(3)	119.6(2)
O(1)-C(12)-C(13)	124.6(2)
O(1)-C(12)-C(11)	115.8(2)
C(13)-C(12)-C(11)	119.6(2)
C(18)-C(17)-C(16)	120.8(2)
C(12)-C(13)-C(14)	119.4(2)
O(2)-C(19)-C(20)	124.3(2)
O(2)-C(19)-C(18)	115.8(2)
C(20)-C(19)-C(18)	119.8(2)
C(13)-C(14)-C(9)	122.0(2)
C(11)-C(10)-C(9)	120.9(2)
C(17)-C(18)-C(19)	120.2(2)

C(28)-C(23)-C(24)	117.9(2)
C(28)-C(23)-C(6)	119.4(2)
C(24)-C(23)-C(6)	122.7(2)
C(34)-C(29)-C(30)	117.3(2)
C(34)-C(29)-C(8)	125.9(2)
C(30)-C(29)-C(8)	116.81(19)
C(26)-C(27)-C(28)	120.1(2)
C(34)-C(33)-C(32)	120.3(2)
C(25)-C(24)-C(23)	120.6(2)
C(27)-C(28)-C(23)	121.1(2)
C(33)-C(34)-C(29)	121.2(2)
O(3)-C(32)-C(33)	123.1(2)
O(3)-C(32)-C(31)	117.6(2)
C(33)-C(32)-C(31)	119.3(2)
C(31)-C(30)-C(29)	121.6(2)
C(25)-C(26)-C(27)	119.3(2)
C(30)-C(31)-C(32)	120.3(2)
C(26)-C(25)-C(24)	120.9(2)
O(4)-C(38)-C(35)	106.6(3)
C(36)-C(35)-C(38)	109.3(3)
C(40)-C(41)-C(41)#1	107.2(9)
C(41)-C(40)-C(39)	108.6(6)
C(38)-O(4)-C(37)	110.2(2)

O(4)-C(37)-C(36)	106.6(3)
C(35)-C(36)-C(37)	107.1(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+1

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for rf354_fin. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	30(1)	24(1)	17(1)	-4(1)	6(1)	-7(1)
F(2)	30(1)	16(1)	27(1)	3(1)	-7(1)	0(1)
B(1)	22(1)	15(1)	16(1)	1(1)	0(1)	-2(1)
N(2)	18(1)	16(1)	16(1)	0(1)	2(1)	1(1)
N(3)	18(1)	15(1)	16(1)	0(1)	3(1)	0(1)
N(1)	17(1)	14(1)	19(1)	0(1)	3(1)	3(1)
O(2)	35(1)	30(1)	23(1)	8(1)	6(1)	-4(1)
O(1)	51(1)	29(1)	18(1)	2(1)	-3(1)	-13(1)
O(3)	54(1)	25(1)	22(1)	0(1)	13(1)	-12(1)
C(3)	18(1)	17(1)	21(1)	0(1)	5(1)	1(1)
C(7)	18(1)	19(1)	19(1)	-2(1)	2(1)	-1(1)
C(2)	20(1)	19(1)	21(1)	0(1)	3(1)	-3(1)
C(6)	17(1)	14(1)	19(1)	-1(1)	3(1)	4(1)
C(5)	18(1)	15(1)	16(1)	1(1)	4(1)	3(1)
C(1)	19(1)	16(1)	21(1)	0(1)	3(1)	1(1)
C(8)	18(1)	16(1)	19(1)	-2(1)	3(1)	2(1)
C(4)	17(1)	16(1)	17(1)	1(1)	4(1)	4(1)
C(21)	17(1)	18(1)	24(1)	-1(1)	5(1)	0(1)

C(20)	19(1)	25(1)	19(1)	-2(1)	5(1)	1(1)
C(11)	40(1)	22(1)	25(1)	7(1)	-5(1)	-8(1)
C(9)	18(1)	20(1)	20(1)	1(1)	1(1)	-1(1)
C(16)	16(1)	21(1)	20(1)	2(1)	4(1)	0(1)
C(12)	27(1)	25(1)	19(1)	1(1)	0(1)	-5(1)
C(17)	25(1)	22(1)	22(1)	-2(1)	4(1)	-3(1)
C(13)	30(1)	19(1)	21(1)	-2(1)	4(1)	-7(1)
C(19)	20(1)	26(1)	22(1)	6(1)	5(1)	1(1)
C(14)	28(1)	18(1)	22(1)	3(1)	5(1)	-4(1)
C(10)	32(1)	17(1)	26(1)	2(1)	-5(1)	-4(1)
C(18)	28(1)	20(1)	28(1)	2(1)	8(1)	-3(1)
C(22)	31(1)	44(2)	21(1)	8(1)	5(1)	0(1)
C(15)	53(2)	32(1)	21(1)	-3(1)	0(1)	-13(1)
C(23)	19(1)	16(1)	18(1)	0(1)	3(1)	5(1)
C(29)	19(1)	19(1)	18(1)	1(1)	3(1)	0(1)
C(27)	28(1)	24(1)	20(1)	-4(1)	0(1)	2(1)
C(33)	26(1)	26(1)	16(1)	-2(1)	5(1)	-2(1)
C(24)	29(1)	25(1)	21(1)	0(1)	2(1)	-4(1)
C(28)	22(1)	21(1)	20(1)	-2(1)	4(1)	2(1)
C(34)	22(1)	20(1)	20(1)	-2(1)	3(1)	-2(1)
C(32)	28(1)	21(1)	21(1)	3(1)	7(1)	-2(1)
C(30)	27(1)	22(1)	16(1)	-1(1)	4(1)	-2(1)
C(26)	38(1)	27(1)	15(1)	0(1)	4(1)	3(1)

C(31)	34(1)	18(1)	23(1)	-3(1)	6(1)	-6(1)
C(25)	38(1)	29(1)	22(1)	5(1)	6(1)	-6(1)
C(38)	40(2)	33(1)	36(2)	3(1)	15(1)	6(1)
C(35)	214(7)	67(3)	39(2)	24(2)	-27(3)	-61(4)
C(41)	125(5)	94(4)	109(5)	-11(4)	34(4)	-44(4)
C(40)	221(9)	79(4)	216(9)	-53(5)	174(8)	-68(5)
O(4)	46(1)	36(1)	24(1)	4(1)	6(1)	-3(1)
C(37)	28(1)	59(2)	37(2)	5(1)	2(1)	5(1)
C(36)	45(2)	146(5)	46(2)	48(3)	-8(2)	-14(2)
C(39)	86(4)	88(4)	197(8)	-11(4)	74(5)	-9(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3})

for rf354_fin.

	x	y	z	U(eq)
H(3)	6274	9143	997	49
H(7)	5911	7363	4593	22
H(2)	1344	3593	2861	24
H(21)	2386	4778	5288	24
H(20)	2220	3927	6398	25
H(11)	1615	6024	112	36
H(17)	1732	2509	3937	27
H(13)	1120	3278	250	28
H(14)	1588	3352	1602	27
H(10)	2084	6099	1455	32
H(18)	1566	1653	5042	30
H(22A)	2640	2756	7307	48
H(22B)	1881	2057	7593	48
H(22C)	1521	3049	7254	48
H(15A)	1223	3399	-1085	54
H(15B)	460	3986	-1686	54
H(15C)	156	3606	-895	54

H(27)	6284	7188	7238	29
H(33)	5536	7735	1128	27
H(24)	3913	5367	5717	30
H(28)	6080	7268	5877	25
H(34)	4989	6715	1997	25
H(30)	5727	8570	3748	26
H(26)	5299	6206	7842	32
H(31)	6286	9576	2885	30
H(25)	4134	5288	7075	36
H(38A)	2534	6946	4855	43
H(38B)	1756	7599	5180	43
H(35A)	1136	7970	4003	134
H(35B)	1913	7319	3678	134
H(41A)	333	9048	5195	130
H(41B)	1039	9843	4961	130
H(40A)	98	9802	6208	188
H(40B)	673	10683	5953	188
H(37A)	-91	6108	4538	50
H(37B)	636	5400	4211	50
H(36A)	809	6359	3271	97
H(36B)	23	7033	3562	97
H(39A)	1686	8862	6325	177
H(39B)	1816	9695	6940	177

H(39C)	2245	9782	6143	177

Table 6. Torsion angles [°] for rf354_fin.

F(1)-B(1)-N(2)-C(1)	-43.2(3)
F(2)-B(1)-N(2)-C(1)	77.8(3)
N(3)-B(1)-N(2)-C(1)	-164.8(2)
F(1)-B(1)-N(2)-C(4)	128.6(2)
F(2)-B(1)-N(2)-C(4)	-110.4(2)
N(3)-B(1)-N(2)-C(4)	6.9(3)
F(1)-B(1)-N(3)-C(8)	60.9(3)
F(2)-B(1)-N(3)-C(8)	-60.5(3)
N(2)-B(1)-N(3)-C(8)	180.0(2)
F(1)-B(1)-N(3)-C(5)	-129.7(2)
F(2)-B(1)-N(3)-C(5)	108.8(2)
N(2)-B(1)-N(3)-C(5)	-10.6(3)
C(4)-C(3)-C(2)-C(1)	-1.0(2)
C(16)-C(3)-C(2)-C(1)	-176.4(2)
C(8)-C(7)-C(6)-C(5)	1.9(2)
C(8)-C(7)-C(6)-C(23)	-175.2(2)
C(4)-N(1)-C(5)-N(3)	-0.4(3)
C(4)-N(1)-C(5)-C(6)	-179.5(2)
C(8)-N(3)-C(5)-N(1)	-179.9(2)
B(1)-N(3)-C(5)-N(1)	8.5(3)
C(8)-N(3)-C(5)-C(6)	-0.7(2)

B(1)-N(3)-C(5)-C(6)	-172.27(18)
C(7)-C(6)-C(5)-N(1)	178.4(2)
C(23)-C(6)-C(5)-N(1)	-4.5(4)
C(7)-C(6)-C(5)-N(3)	-0.8(2)
C(23)-C(6)-C(5)-N(3)	176.28(19)
C(4)-N(2)-C(1)-C(2)	0.9(2)
B(1)-N(2)-C(1)-C(2)	173.6(2)
C(4)-N(2)-C(1)-C(9)	-178.5(2)
B(1)-N(2)-C(1)-C(9)	-5.8(4)
C(3)-C(2)-C(1)-N(2)	0.1(3)
C(3)-C(2)-C(1)-C(9)	179.6(2)
C(5)-N(3)-C(8)-C(7)	1.9(2)
B(1)-N(3)-C(8)-C(7)	172.5(2)
C(5)-N(3)-C(8)-C(29)	-174.1(2)
B(1)-N(3)-C(8)-C(29)	-3.5(4)
C(6)-C(7)-C(8)-N(3)	-2.5(2)
C(6)-C(7)-C(8)-C(29)	173.7(2)
C(5)-N(1)-C(4)-N(2)	-3.9(3)
C(5)-N(1)-C(4)-C(3)	170.0(2)
C(1)-N(2)-C(4)-N(1)	173.2(2)
B(1)-N(2)-C(4)-N(1)	-0.2(3)
C(1)-N(2)-C(4)-C(3)	-1.6(2)
B(1)-N(2)-C(4)-C(3)	-174.98(19)

C(2)-C(3)-C(4)-N(1)	-173.0(2)
C(16)-C(3)-C(4)-N(1)	2.5(4)
C(2)-C(3)-C(4)-N(2)	1.6(2)
C(16)-C(3)-C(4)-N(2)	177.1(2)
C(16)-C(21)-C(20)-C(19)	-0.1(3)
N(2)-C(1)-C(9)-C(14)	152.8(2)
C(2)-C(1)-C(9)-C(14)	-26.6(3)
N(2)-C(1)-C(9)-C(10)	-28.9(4)
C(2)-C(1)-C(9)-C(10)	151.7(2)
C(20)-C(21)-C(16)-C(17)	0.4(3)
C(20)-C(21)-C(16)-C(3)	-178.5(2)
C(2)-C(3)-C(16)-C(21)	-155.9(2)
C(4)-C(3)-C(16)-C(21)	29.6(3)
C(2)-C(3)-C(16)-C(17)	25.2(3)
C(4)-C(3)-C(16)-C(17)	-149.3(2)
C(15)-O(1)-C(12)-C(13)	3.1(4)
C(15)-O(1)-C(12)-C(11)	-176.9(3)
C(10)-C(11)-C(12)-O(1)	179.5(2)
C(10)-C(11)-C(12)-C(13)	-0.5(4)
C(21)-C(16)-C(17)-C(18)	-0.4(3)
C(3)-C(16)-C(17)-C(18)	178.5(2)
O(1)-C(12)-C(13)-C(14)	-179.5(2)
C(11)-C(12)-C(13)-C(14)	0.6(4)

C(22)-O(2)-C(19)-C(20)	-5.9(3)
C(22)-O(2)-C(19)-C(18)	175.3(2)
C(21)-C(20)-C(19)-O(2)	-179.0(2)
C(21)-C(20)-C(19)-C(18)	-0.3(3)
C(12)-C(13)-C(14)-C(9)	-0.6(4)
C(10)-C(9)-C(14)-C(13)	0.4(4)
C(1)-C(9)-C(14)-C(13)	178.9(2)
C(12)-C(11)-C(10)-C(9)	0.4(4)
C(14)-C(9)-C(10)-C(11)	-0.4(4)
C(1)-C(9)-C(10)-C(11)	-178.7(2)
C(16)-C(17)-C(18)-C(19)	0.1(4)
O(2)-C(19)-C(18)-C(17)	179.0(2)
C(20)-C(19)-C(18)-C(17)	0.2(4)
C(7)-C(6)-C(23)-C(28)	0.7(3)
C(5)-C(6)-C(23)-C(28)	-175.8(2)
C(7)-C(6)-C(23)-C(24)	179.8(2)
C(5)-C(6)-C(23)-C(24)	3.3(4)
N(3)-C(8)-C(29)-C(34)	-31.6(4)
C(7)-C(8)-C(29)-C(34)	152.9(2)
N(3)-C(8)-C(29)-C(30)	148.5(2)
C(7)-C(8)-C(29)-C(30)	-27.0(3)
C(28)-C(23)-C(24)-C(25)	0.7(3)
C(6)-C(23)-C(24)-C(25)	-178.4(2)

C(26)-C(27)-C(28)-C(23)	0.2(4)
C(24)-C(23)-C(28)-C(27)	-0.9(3)
C(6)-C(23)-C(28)-C(27)	178.2(2)
C(32)-C(33)-C(34)-C(29)	0.6(4)
C(30)-C(29)-C(34)-C(33)	0.0(3)
C(8)-C(29)-C(34)-C(33)	-179.9(2)
C(34)-C(33)-C(32)-O(3)	178.8(2)
C(34)-C(33)-C(32)-C(31)	-0.8(4)
C(34)-C(29)-C(30)-C(31)	-0.4(3)
C(8)-C(29)-C(30)-C(31)	179.6(2)
C(28)-C(27)-C(26)-C(25)	0.7(4)
C(29)-C(30)-C(31)-C(32)	0.2(4)
O(3)-C(32)-C(31)-C(30)	-179.2(2)
C(33)-C(32)-C(31)-C(30)	0.4(4)
C(27)-C(26)-C(25)-C(24)	-0.9(4)
C(23)-C(24)-C(25)-C(26)	0.2(4)
O(4)-C(38)-C(35)-C(36)	-0.1(6)
C(41)#1-C(41)-C(40)-C(39)	-172.2(5)
C(35)-C(38)-O(4)-C(37)	-2.4(4)
C(38)-O(4)-C(37)-C(36)	3.9(4)
C(38)-C(35)-C(36)-C(37)	2.4(7)
O(4)-C(37)-C(36)-C(35)	-3.8(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+2,-z+1