Supporting Information

Highly Photostable Near-Infrared Fluorescent pH Indicators and Sensors based on BF$_2$-Chelated Tetraarylazadipyromethene Dyes

Tijana Jokic,$^a$ Sergey M. Borisov,$^{a,*}$ Robert Saf,$^b$ Daniel A. Nielsen,$^c$ Michael Kühl,$^{c,d,e}$ and Ingo Klimant$^a$

$^a$Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Stremayrgasse 9, 8010, Graz, Austria
$^b$Institute of Chemistry and Technology of Materials, Graz University of Technology, Stremayrgasse 9, 8010, Graz, Austria
$^c$ Plant Functional Biology and Climate Change Cluster, Department of Environmental Science, University of Technology, Sydney, PO Box 123, Broadway NSW, Australia
$^d$ Singapore Centre on Environmental Life Sciences Engineering, School of Biological Sciences, Nanyang Technological University, Singapore
$^e$ Marine Biology Section, Department of Biology, University of Copenhagen, Strandpromenaden 5, DK-3000 Helsingør, Denmark.

* Corresponding author. E-mail: sergey.borisov@tugraz.at
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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 \(~150 \mu\text{mol}\cdot\text{photons m}^{-2}\cdot\text{s}^{-1}\) from a fiber-optic halogen lamp Schott kl2500 LCD (www.schott.com). The pH optode was mounted in a manual micromanipulator MM33 (Märthhäuser, www.marthhauser.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 \times 10^{-6} M, 2 – 3.10 \times 10^{-6} M, 3 – 3.37 \times 10^{-6} M, 4 – 3.27 \times 10^{-6} M, 5 – 3.32 \times 10^{-6} M, 6 – 3.01 \times 10^{-6} M, 7 - 2.55 \times 10^{-6} M, 8 – 3.23 \times 10^{-6} M, and fluorescence measurements 1 – 1.45 \times 10^{-6} M, 2 – 1.41 \times 10^{-6} M, 3 – 1.53 \times 10^{-6} M, 4 – 1.49 \times 10^{-6} M, 5 – 1.51 \times 10^{-6} M, 6 – 1.37 \times 10^{-6} M, 7 - 1.16 \times 10^{-6} M, 8 – 1.47 \times 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) (1 eq, 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 °C 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 H₂O (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%). ¹H 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. 

BF₂ 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 CH₂Cl₂ (50 ml), treated with diisopropylethylamine (10 eq, 0.79 ml, 4.8 mmol) and BF₃ diethyletherate (15 eq, 0.92 ml, 7.2 mmol) and stirred under argon for 24 h. Purification by column chromatography on silica eluting with CH₂Cl₂ and recrystallization from hexane/tetrahydrofuran gave the product 2 as a red metallic solid (0.20 g, 43 %). ¹H NMR (300 MHz, DMSO-d6) δ 8.30-8.29 (d, J = 2 Hz, 1H), 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) (1 eq, 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 °C 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 H₂O (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 recrystallized from hexane/tetrahydrofuran mixture as green metallic crystals (0.26 g, 10%). ¹H 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.

BF₂ 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 CH₂Cl₂ (50 ml), treated with diisopropylethylamine (10 eq, 0.65 ml, 3.9 mmol) and BF₃ diethyletherate (15 eq, 0.75 ml, 5.85 mmol) and stirred under argon for 24 h. Purification by column chromatography on silica eluting with CH₂Cl₂ gave the product 3 as a red metallic solid (0.22 g, 66 %). ¹H 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) (1 eq, 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 H₂O (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%). ¹H 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$_2$Cl$_2$ (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$_2$Cl$_2$ 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$_2$O (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-nitrobutan-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$_2$Cl$_2$ (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$_2$Cl$_2$ 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 tetrahydrofuran (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) (1 eq, 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$_2$O (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-nitrobutan-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 recrystallized 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$_2$Cl$_2$ (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 CH₂Cl₂ and recrystallization from hexane/tetrahydrofuran gave the product 6 as a red metallic solid (0.08 g, 36%). ¹H 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 H₂O (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 (1 eq, 1.0 g, 4.4 mmol), compound 1b (1 eq, 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%). ¹H 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.

BF₂ 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 CH₂Cl₂ (50 ml), treated with diisopropylethylamine (10 eq, 0.39 ml, 2 mmol) and BF₃ diethyletherate (15 eq, 0.38 ml, 3 mmol) and stirred under argon for 24 h. Purification by column chromatography on silica eluting with CH₂Cl₂ and recrystallization from hexane/tetrahydrofuran gave the product 7 as a red metallic solid (0.079 g, 53 %). ¹H 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 H₂O (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-methoxyphenyl)-pyrrol-2-ylidene]amine (8b): Compound 8a (1 eq, 1.0 g, 4.4 mmol), compound 1b (1 eq, 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%). ¹H 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.

BF₂ 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 CH₂Cl₂ (50 ml), treated with diisopropylethylamine (10 eq, 0.71 ml, 4.2 mmol) and BF₃ diethyletherate (15 eq, 0.8 ml, 6.3 mmol) and stirred under argon for 24 h. Purification by column chromatography on silica eluting with CH₂Cl₂ and recrystallization from hexane/tetrahydrofurane gave the product 8 as a red metallic solid ( 0.19 g, 78 %). ¹H 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 $\mathbf{1}$ 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.
BF₂ 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-yldene]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/H₂O, 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 azadipyromethene 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.

| Property                        | Value                                      |
|---------------------------------|--------------------------------------------|
| 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) Å³                               |
| Z                               | 4                                          |
| Density (calculated)            | 1.329 Mg/m³                                |
| Absorption coefficient          | 0.092 mm⁻¹                                 |
| F(000)                          | 1452                                       |
| Crystal size                    | 0.34 x 0.31 x 0.29 mm³                     |
| 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 F² |
| **Data / restraints / parameters** | 6772 / 0 / 464 |
| **Goodness-of-fit on F²**     | 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 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)|
| \( C(n) \) | 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) |
| Atom | C(31)  | C(25)  | C(38)  | C(35)  | C(41)  | C(40)  | O(4)   | C(37)  | C(36)  | C(39)  |
|------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
|      | 6022(2)| 8994(2)| 2704(1)| 25(1)  | 4527(2)| 5696(2)| 6831(2)| 30(1)  | 1831(2)| 7085(2)| 4819(2)| 36(1)  |
|      | 1303(6)| 7335(3)| 4014(2)| 112(3) | 1403(6)| 7335(3)| 4014(2)| 112(3) | 1831(2)| 7085(2)| 4819(2)| 36(1)  |
|      | 466(5) | 9720(5)| 5217(4)| 108(2) | 634(7) | 10000(5)| 5936(5)| 156(4) | 1316(2)| 6284(1)| 5014(1)| 35(1)  |
|      | 557(2) | 6046(2)| 4378(2)| 42(1)  | 646(3) | 6700(4)| 3727(2)| 81(2)  | 557(2) | 6046(2)| 4378(2)| 42(1)  |
|      | 1709(5)| 9535(4)| 6384(5)| 118(3) |        |        |        |        |        |        |        |        |
Table 3. Bond lengths [Å] and angles [°] for rf354_fin.

| Bond                  | Length [Å] |
|-----------------------|------------|
| 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)   |
| Bond          | Distance (Å) |
|--------------|--------------|
| 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)
| Bond                  | Angle (°)       |
|----------------------|-----------------|
| 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)        |
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 (Å² x 10³) for rf354_fin. The anisotropic displacement factor exponent takes the form: \(-2\pi^2 [ h^2 U_{11} + ... + 2 h k a^* b^* U_{12} ]\)

|     | 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 |
| H(33) | 5536 | 7735 | 1128 |
| H(24) | 3913 | 5367 | 5717 |
| H(28) | 6080 | 7268 | 5877 |
| H(34) | 4989 | 6715 | 1997 |
| H(30) | 5727 | 8570 | 3748 |
| H(26) | 5299 | 6206 | 7842 |
| H(31) | 6286 | 9576 | 2885 |
| H(25) | 4134 | 5288 | 7075 |
| H(38A) | 2534 | 6946 | 4855 |
| H(38B) | 1756 | 7599 | 5180 |
| H(35A) | 1136 | 7970 | 4003 |
| H(35B) | 1913 | 7319 | 3678 |
| H(41A) | 333 | 9048 | 5195 |
| H(41B) | 1039 | 9843 | 4961 |
| H(40A) | 98 | 9802 | 6208 |
| H(40B) | 673 | 10683 | 5953 |
| H(37A) | -91 | 6108 | 4538 |
| H(37B) | 636 | 5400 | 4211 |
| H(36A) | 809 | 6359 | 3271 |
| H(36B) | 23 | 7033 | 3562 |
| H(39A) | 1686 | 8862 | 6325 |
| H(39B) | 1816 | 9695 | 6940 |
| H(39C) |    2245 |    9782 |    6143 |    177 |
Table 6. Torsion angles [°] for rf354_fin.

| Bond Sequence                  | Torsion Angle [°] |
|--------------------------------|-------------------|
| 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)           |
| Bond/Rotation | Angle (deg) |
|---------------|-------------|
| 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(10)-C(11)-C(12)-C(13)  -176.9(3)
C(15)-O(1)-C(12)-C(13)  3.1(4)
C(15)-O(1)-C(12)-C(11)  179.5(2)
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)
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