# Supplementary Material (ESI) for Chemical Communications


# Chemical Communications

# Electronic Supporting Information

# Impact of a Conformationally Restricted Receptor on the $BF_2$ Chelated Azadiyrromethene Fluorosensing Platform

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**General Experimental**

THF was distilled under $N_2$ over sodium wire and benzophenone. Cyclohexane, 1,4-dioxane and chloroform were distilled over $K_2CO_3$. DMF was distilled under reduced pressure over $K_2CO_3$.

Solutions for the solvent studies were prepared from a stock solution of **1** (0.005 mmol in 10 mL THF). 1 mL was diluted into 25 mL of either cyclohexane, DMF, 1,4-dioxane or THF to provide a second stock solution from which further dilutions were made to give the desired concentration.

Fluorescence measurements were recorded with the following setting; both slit widths 5 nm, excitation wavelength 630 nm.

Cremophor EL formulation procedure.

**1a** or **1b** (1 mg) was dissolved in THF (0.5 mL) to which Cremophor EL (0.2 mL) was added and the mixture was sonicated for 30 minutes. The THF was removed under reduced pressure and the resulting blue oil was made up to 25 mL with saline solution to give a stock solution. Further dilutions were made as required to give the necessary concentration.

**4-(4-Dimethylamino-2,6-dimethyl-phenyl)-2-phenyl-1*H*-pyrrole**.

3-(4-Dimethylamino-2,6-dimethyl-phenyl)-5-phenyl-1*H*-pyrrole-2-carboxylic acid ethyl ester[1] (1.0 g, 2.76 mmol) was dissolved in ethanol (20 mL), 10% NaOH solution (10 mL) was added and the solution was heated under reflux for 1 hour. The reaction was allowed to cool to room temperature, concentrated to half the original volume, neutralized with 1M HCl and the resulting precipitate was isolated by filtration. The precipitate was air-dried. This crude material was dissolved in ethanolamine (3 mL) and the solution was heated under reflux for 1 hour. The reaction was allowed to cool, poured into cold water (50 mL) and the resulting precipitate was isolated by filtration (0.74 g, 92%), m.p. 109-111 ºC. $^{1}$H NMR (300 MHz, DMSO-$d_6$) δ: 11.25 (bs, 1H), 7.67 (d, $J$ = 7.3 Hz, 2H), 7.35-7.40 (m, 2H), 7.17 (t, $J$ = 7.3 Hz, 1H), 6.68 (m, 1H), 6.50 (s, 2H), 6.42 (d, $J$ = 1.7 Hz, 1H), 2.90 (s, 6H), 2.14 (s, 6H). $^{13}$C NMR (75 MHz, DMSO-$d_6$) δ: 149.3, 137.3, 133.4, 131.0, 129.0, 125.6, 125.2, 123.5, 123.0, 118.7, 112.2, 107.8, 40.8, 22.1. IR (KBr disc) cm$^{-1}$: 3432. ES-MS: *m/z* $[M + H]^+$ 291.1. HRMS Calcd for $C_{20}H_{23}N_2$ $[M + H]^+$: 291.1861, found 291.1873.

1. J. Killoran, J.F. Gallagher, P.V. Murphy, D.F. O'Shea, *New J. Chem*. 2005, **29**, 1258.

**2-Nitroso-3-(4-dimethylamino-2,6-dimethyl-phenyl)-5-phenyl-1*H*-pyrrole (3b).**

[3,5-Dimethyl-4-(5-phenyl-1*H*-pyrrol-3-yl)-phenyl]-dimethyl-amine (0.21 g, 0.7 mmol) was dissolved in acetic acid (5 mL) and the solution was cooled on an ice bath. Concentrated HCl (0.1 mL) was added and the reaction mixture was cooled on an ice bath. A solution of sodium nitrite (0.06 g, 0.79 mmol) in water (5 mL) was added drop-wise over 10 minutes to give a brown orange solution that was left to stir for 20 minutes. The solution was poured over a saturated sodium acetate solution (30 mL) and the resulting brown precipitate was isolated by filtration. Recrystallization from ether/cyclohexane gave **3b** as a dark brown solid (0.12 g, 52%), m.p. 189-191 ºC. $^{1}$H NMR (300 MHz, $CDCl_3$) δ: 7.82-7.85 (m, 2H), 7.46-7.49 (m, 3H), 6.82 (s, 1H), 6.55 (s, 2H), 2.98 (s, 6H), 2.25 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 163.6, 150.6, 144.6, 138.1, 131.2, 129.6, 129.5, 129.4, 127.0, 119.9, 117.1, 111.8, 40.5, 21.8. IR (KBr disc) cm$^{-1}$: 3281, 1500. ES-MS: *m/z* $[M + H]^+$ 320.2. HRMS Calcd for $C_{20}H_{22}N_3O$ $[M + H]^+$: 320.1763, found 320.1770.

**(3,5-Diphenyl-1*H*-pyrrol-2-yl)-[3-(4-dimethylamino-2,6-dimethyl-phenyl)-5-phenyl-pyrrol-2-ylidene]-amine (4b).** [3,5-Dimethyl-4-(2-nitroso-5-phenyl-1*H*-pyrrol-3-yl)-phenyl]-dimethyl-amine **3b** (0.09 g, 0.28 mmol) and 2,4-diphenyl-1*H*-pyrrole **2b** (0.075 g, 0. 34mmol) were dissolved in acetic acid (5 mL) and acetic anhydride (1 mL) and heated at 100 ºC for 1 hours. During the course of the reaction an intense blue color formed. The reaction mixture was allowed to cool to room temperature, washed with a saturated sodium bicarbonate solution (100 mL) and water (50 mL) and the resulting precipitate was isolated by filtration, leaving a colorless filtrate. Purification by silica gel column chromatography eluting with $CH_2Cl_2$/hexane (1:1) gave **4b** as a dark colored solid (0 016g, 11%), m.p. 209-211ºC. $^1$H NMR (300 MHz, $CDCl_3$) δ: 7.96-8.01 (m, 4H), 7.88 (d, *J* = 7.32 Hz, 2H), 7.40-7.56 (m, 6H), 7.19-7.23 (m, 3H), 7.13 (s, 1H), 6.95 (s, 1H), 6.56 (s, 2H), 3.00 (s, 6H), 2.25 (s, 6H), (NH not observed). $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 159.9, 153.2, 150.4, 150.1, 147.0, 146.0, 139.0, 137.7, 133.6, 132.7, 131.9, 130.3, 129.4, 129.1, 129.0, 128.2, 128.1, 127.4, 126.9, 125.9, 122.6, 120.2, 112.3, 111.8, 40.8, 21.8. IR (KBr disc) cm$^{-1}$: 1604, 1542. $\lambda_{max}$ ($CHCl_3$) nm: 587. HRMS Calcd for $C_{36}H_{33}N_4$ $[M + H]^+$: 521.2705, found 521.2690.

**$BF_2$ Chelated-(3,5-Diphenyl-1*H*-pyrrol-2-yl)-[3-(4-dimethylamino-phenyl)-5-phenyl-pyrrol-2-ylidene]-amine (1a).** (3,5-Diphenyl-1*H*-pyrrol-2-yl)-[3-(4-dimethylamino-phenyl)-5-phenyl-pyrrol-2-ylidene]-amine[2] **4a** (0.076 g, 0.15 mmol) was dissolved in dry $CH_2Cl_2$ (25 mL), treated with diisopropylethylamine (0.27 mL, 1.54 mmol) and boron trifluoride diethyletherate (0.27 mL, 2.16 mmol), and stirred at room temperature under nitrogen for 6 hours. The mixture was diluted with $CH_2Cl_2$ (30 mL), washed with water (2 x 50 mL), and organic layer was dried over sodium sulfate and evaporated to dryness. Purification by column chromatography on silica eluting with $CH_2Cl_2$/hexane (3:1) gave **1a** as a metallic brown solid (0.067 g, 93%), m.p. 244-245 ˚C. $^1$H NMR (300 MHz, $CDCl_3$) δ: 8.12 (d, *J* = 8.9 Hz, 2H), 7.99-8.07 (m, 6H), 7.38-7.49 (m, 9H), 6.96 (s, 1H), 6.84 (s, 1H), 6.74 (d, *J* = 8.9 Hz, 2H), 3.09 (s, 6H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ: 155.6, 151.5, 146.2, 144.2, 141.4, 133.1, 132.3, 131.9, 131.2, 130.7, 129.9, 129.5, 129.3, 128.7, 128.5, 128.4, 128.4, 120.5,

117.8, 115.5, 111.9, 40.1. IR (KBr disc) $cm^{-1}$: 1600, 1488. $\lambda_{max}$ ($CHCl_3$) nm: 610, 726. HRMS Calcd for $C_{34}H_{28}N_4BF_2$ $[M + H]^+$: 541.2375, found 541.2380.

2. Hall, M.J.; McDonnell, S.O.; Killoran, J.; O'Shea, D.F. *J. Org. Chem*. **2005**, *70*, 5571.

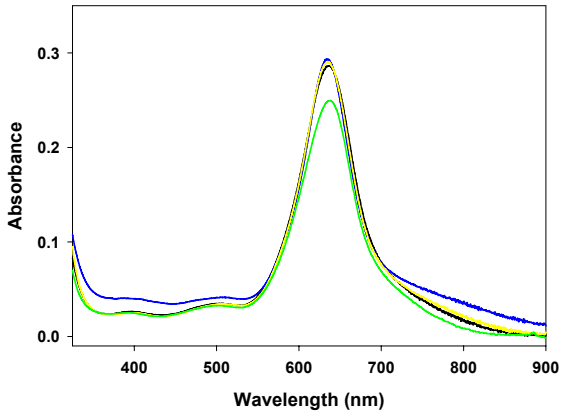
**$BF_2$ Chelated-(3,5-diphenyl-1*H*-pyrrol-2-yl)-[3-(4-dimethylamino-2,6-dimethyl-phenyl)-5-phenyl-pyrrol-2-ylidene]-amine (1b).** (3,5-Diphenyl-1*H*-pyrrol-2-yl)-[3-(4-dimethylamino-2,6-dimethyl-phenyl)-5-phenyl-pyrrol-2-ylidene]-amine **4b** (0.016 g, 0.03 mmol) was dissolved in dry $CH_2Cl_2$ (5 mL), treated with diisopropylamine (0.05 mL, 0.3 mmol) and boron trifluoride diethyletherate (0.05 mL, 0.43 mmol), and stirred at room temperature under nitrogen for 6 hours. The mixture was diluted with $CH_2Cl_2$ (20 mL), washed with water (2 x 25 mL), and organic layer was dried over sodium sulfate and evaporated to dryness. Purification by column chromatography on silica eluting with $CH_2Cl_2$/hexane (3:1) gave **1b** as a metallic brown solid (0.011 g, 63%), m.p. 231-232 ˚C. $^1$H NMR ($CDCl_3$) δ: 8.04-8.08 (m, 2H), 7.95-8.02 (m, 4H), 7.46-7.50 (m, 6H), 7.29-7.31 (m, 3H), 6.96 (s, 1H), 6.75 (s, 1H), 6.54 (s, 2H), 3.01 (s, 6H), 2.30 (s, 6H). $^{13}$C NMR ($CDCl_3$) δ: 160.0, 158.6, 150.5, 147.5, 144.9, 142.8, 138.1, 132.3, 131.9, 131.5, 130.9, 130.5, 129.7, 129.4, 129.1, 128.8, 128.6, 128.5, 123.6, 118.4, 111.8, 40.5, 22.1. IR (KBr disc) $cm^{-1}$: 1600, 1513. $\lambda_{max}$ ($CHCl_3$) nm: 637. HRMS Calcd for $C_{36}H_{32}BF_2N_4$ $[M + H]^+$: 569.2688, found 569.2715.

**Table 1**. Absorbance Spectral Characteristics of **1b** in nm.

| entry | **1b** | DMF | THF | 1,4-dioxane | cyclohexane |
|---|---|---|---|---|---|
| 1 | abs.[a] | 635 | 635 | 635 | 636 |
| 2 | abs./$H^{+}$ [b] | 649 | 645 | 645 | 643 |

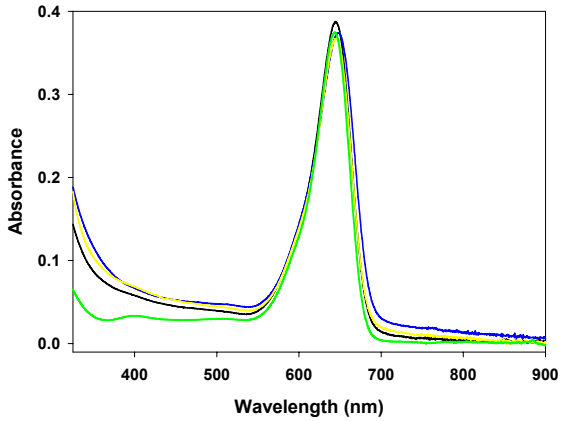
[a] Concentration of 5 x $10^{-6}$ M. [b] Trifluoroacetic acid added until maximum peak intensity was reached.

**Figure 1.** Absorbance spectra; organic solvent study of **1b**




Absorbance Spectra of **1b** at 5 x $10^{-6}$ M in DMF (blue), THF (yellow), 1,4-dioxane (black), cyclohexane (green).

**Figure 2.** Absorbance spectra; organic solvent study of **1b**



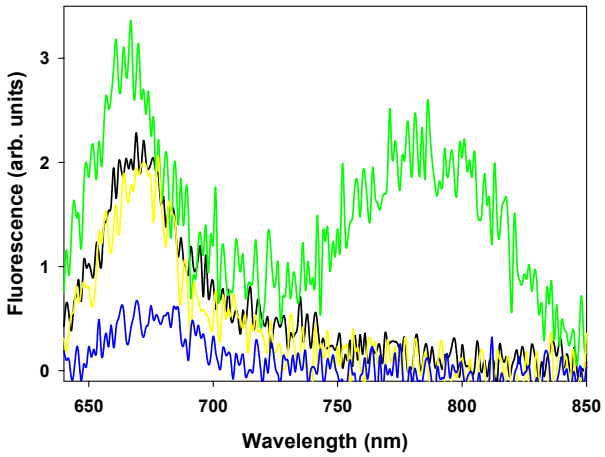

Absorbance Spectra of **1b** at 5 x $10^{-6}$ M in DMF + trifluoroacetic acid (blue), THF + trifluoroacetic acid (yellow), 1,4-dioxane + trifluoroacetic acid (black), cyclohexane + trifluoroacetic acid (green).

**Table 2**. Fluorescence Spectral Characteristics of **1b** in nm.

| entry | **1b** | DMF | THF | 1,4-dioxane | cyclohexane |
|---|---|---|---|---|---|
| 1 | flu.[a] | 669 | 672 | 672 | 667, 786 |
| 2 | flu./$H^+$ [b] | 673 | 669 | 670 | 665 |

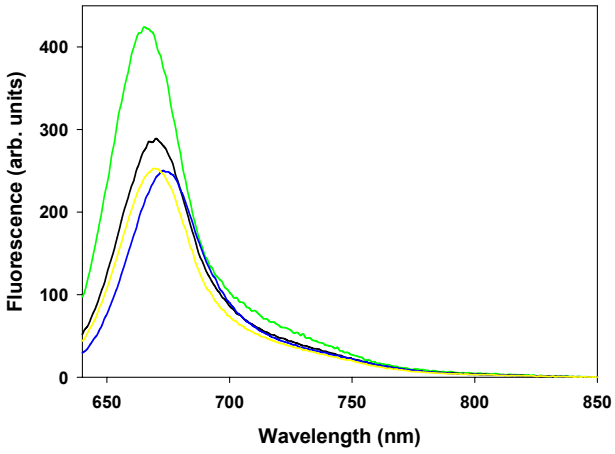
[a] concentration of 5 x $10^{-7}$ M.
[b] Trifluoroacetic acid added until maximum peak intensity was reached.

**Figure 3.** Fluorescence Organic solvent study of **1b**



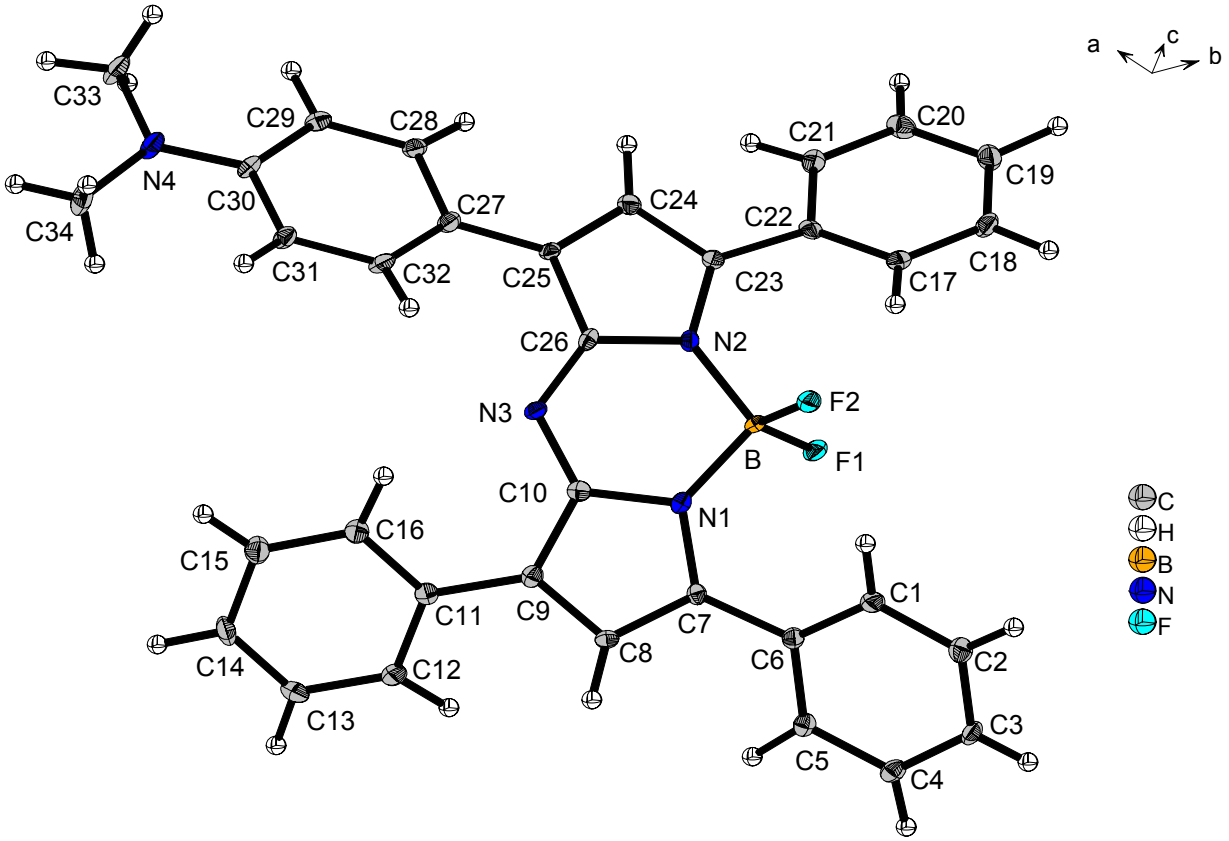

Fluorescence Spectra of **1b** at 5 x $10^{-7}$ M in DMF (blue), THF (yellow), 1,4-dioxane (black), cyclohexane (green).

**Figure 4.** Fluorescence Organic Solvent Study of **1b**.




Fluorescence Spectra of **1b** at 5 x $10^{-7}$ M in DMF + trifluoroacetic acid (blue), THF + trifluoroacetic acid (yellow), 1,4-dioxane + trifluoroacetic acid (black), cyclohexane + trifluoroacetic acid (green).

ORTEP Diagram of **1a**

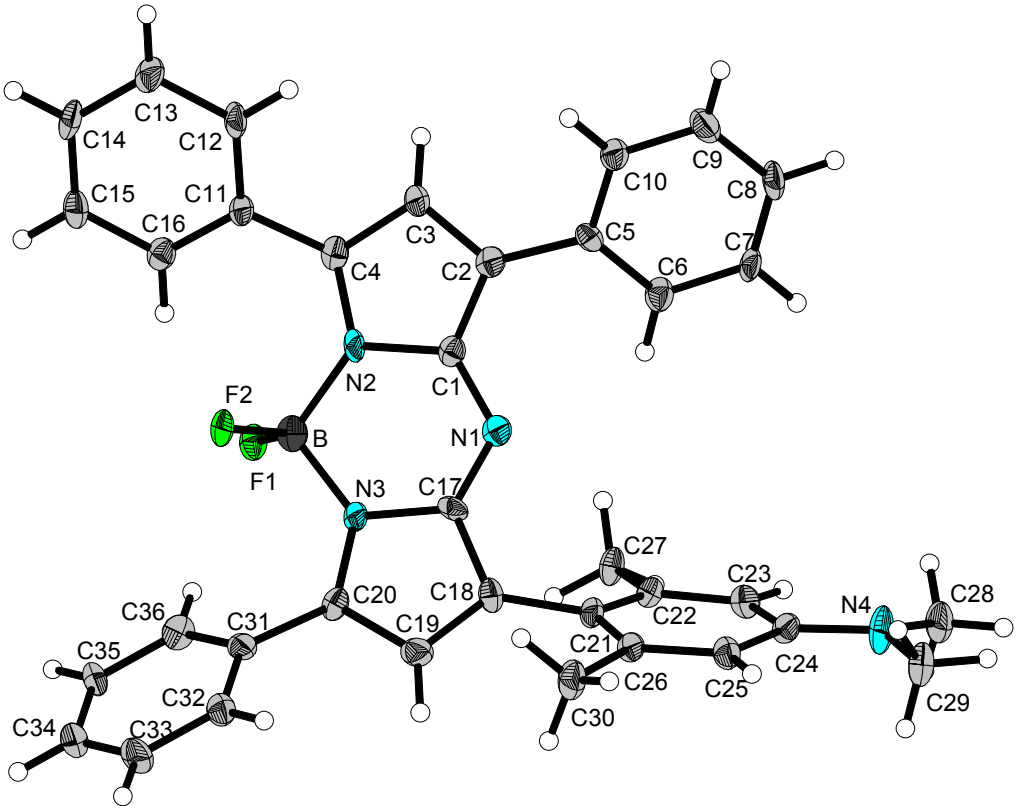



**1a;** Thermal ellipsoids are drawn on the 50% probability level.

**Table 1**. Crystal data and structure refinement for **1a**.

| | | |
|---|---|---|
| Identification code | **1a** | |
| Empirical formula | $C_{34}\ H_{27}\ B\ N_4\ F_2$ | |
| Formula weight | 540.41 | |
| Temperature | 113(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Triclinic | |
| Space group | P–1 (#2) | |
| Unit cell dimensions | a = 10.755(3) Å | α= 91.726(6)°. |
| | b = 10.824(3) Å | β= 113.148(5)°. |
| | c = 12.163(4) Å | γ = 96.565(6)°. |
| Volume | 1288.9(7) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.392 $Mg/m^3$ | |
| Absorption coefficient | 0.092 $mm^{-1}$ | |
| F(000) | 564 | |
| Crystal size | 0.50 x 0.30 x 0.04 $mm^3$ | |
| Theta range for data collection | 1.83 to 26.00°. | |
| Index ranges | –13<=h<=13, –13<=k<=13, –14<=l<=14 | |
| Reflections collected | 9788 | |
| Independent reflections | 4977 [R(int) = 0.0530] | |
| Completeness to theta = 26.00° | 97.9 % | |
| Absorption correction | Semi–empirical from equivalents | |
| Max. and min. transmission | 0.9963 and 0.6896 | |
| Refinement method | Full–matrix least–squares on $F^2$ | |
| Data / restraints / parameters | 4977 / 0 / 456 | |
| Goodness–of–fit on $F^2$ | 1.189 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0944, wR2 = 0.2168 | |
| R indices (all data) | R1 = 0.1443, wR2 = 0.2358 | |
| Largest diff. peak and hole | 0.380 and –0.367 $e.Å^{-3}$ | |

ORTEP Diagram of **1b**




**1b;** Thermal ellipsoids are drawn on the 50% probability level.

**Table 1**. Crystal data and structure refinement for **1b**.

| | | |
|---|---|---|
| Identification code | **1b** | |
| Empirical formula | C36 H31 B N4 F2 | |
| Formula weight | 568.46 | |
| Temperature | 293(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | C2 | |
| Unit cell dimensions | a = 42.555(7) Å | α= 90°. |
| | b = 5.3195(9) Å | β= 103.405(4)°. |
| | c = 12.781(2) Å | γ = 90°. |
| Volume | 2814.3(8) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.342 $Mg/m^3$ | |
| Absorption coefficient | 0.088 $mm^{-1}$ | |
| F(000) | 1192 | |
| Crystal size | 0.60 x 0.10 x 0.01 $mm^3$ | |
| Theta range for data collection | 1.64 to 23.98°. | |
| Index ranges | -48<=h<=48, -5<=k<=5, -14<=l<=14 | |
| Reflections collected | 8078 | |
| Independent reflections | 3777 [R(int) = 0.0602] | |
| Completeness to theta = 23.98° | 89.7 % | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 0.9991 and 0.5272 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3777 / 1 / 392 | |
| Goodness-of-fit on $F^2$ | 1.014 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0509, wR2 = 0.0981 | |
| R indices (all data) | R1 = 0.0854, wR2 = 0.1109 | |
| Absolute structure parameter | 1.8(13) | |
| Largest diff. peak and hole | 0.258 and -0.253 $e.Å^{-3}$ | |