Supporting Information

for

Synthesis and Properties of BF_2-3,3'-Dimethyldiarylazadipyrromethene Near Infrared Fluorophores

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Experimental

General Methods. All reactions involving air-sensitive reagents were performed under nitrogen in oven-dried glassware using syringe-septum cap technique. All solvents were purified and degassed before use. Chromatographic separation was carried out under pressure on Merck silica gel 60 using flash-column techniques. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm silica gel coated aluminum plates (60 Merck F_{254}) using UV light (254 nm) as visualizing agent. Unless it is specified, all reagents were used as received without further purifications. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature at 300 MHz or 400 MHz and 75 MHz or 100 MHz respectively, and calibrated using residual non-deuterated solvent as an internal reference.

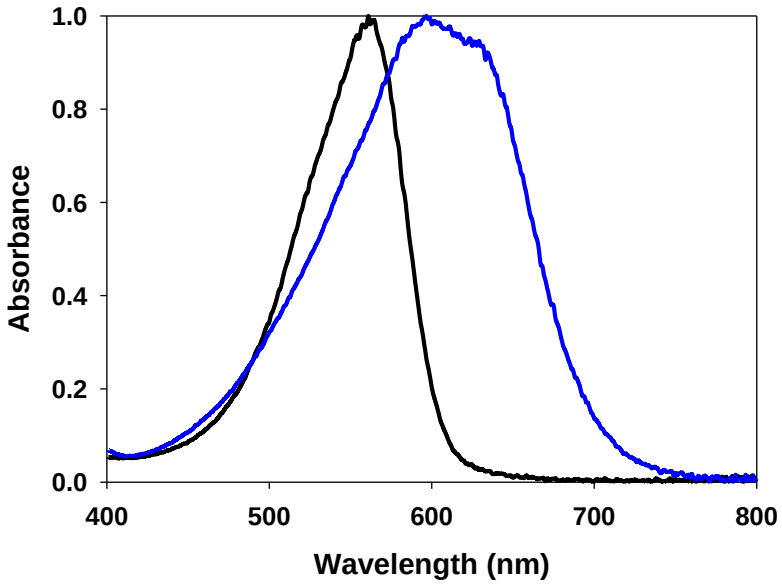
Repeat of Procedure for the Claimed Synthesis of 4.[1]

A mixture of 4-oxo-4-phenylbutanenitrile (200 mg, 1.26 mmol) and hydroxylamine hydrochloride (344 mg, 5.04 mmol) in EtOH (2 mL) was heated under reflux for 2 h during which time the reaction solution becomes blue. The mixture was cooled, and dark blue precipitate was collected (168 mg, 0.54 mmol, 85%), washed with HPLC-grade acetone, de-ionized water and dried under vacuum to give the product as a dark blue solid (93 mg, 0.30 mmol, 47%), mp 276-277 °C. The solid decomposed as a solution in THF, acetone, MeOH and CH_3CN but was sufficiently stable in DMSO to obtain analytical data. ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.78 (br, 2H), 7.97-7.91 (m, 4H), 7.60-7.57 (m, 6H), 7.35 (d, J = 1.6 Hz, 1H), 7.33 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 170.70, 158.80, 152.00, 148.41, 137.00, 132.60, 131.72, 130.86, 129.85, 129.83, 128.50, 128.47, 127.25, 126.77, 103.91, 103.23. IR (KBr disc): 3428, 3118, 1669, 892 cm^{-1}. λ_{max} abs ($CHCl_3$): 596 nm, (ε = 17,000 L mol^{-1}cm^{-1}). ES-HRMS $[M+H]^+$: 314.1304, $C_{20}H_{16}N_3O$ requires 314.1293.

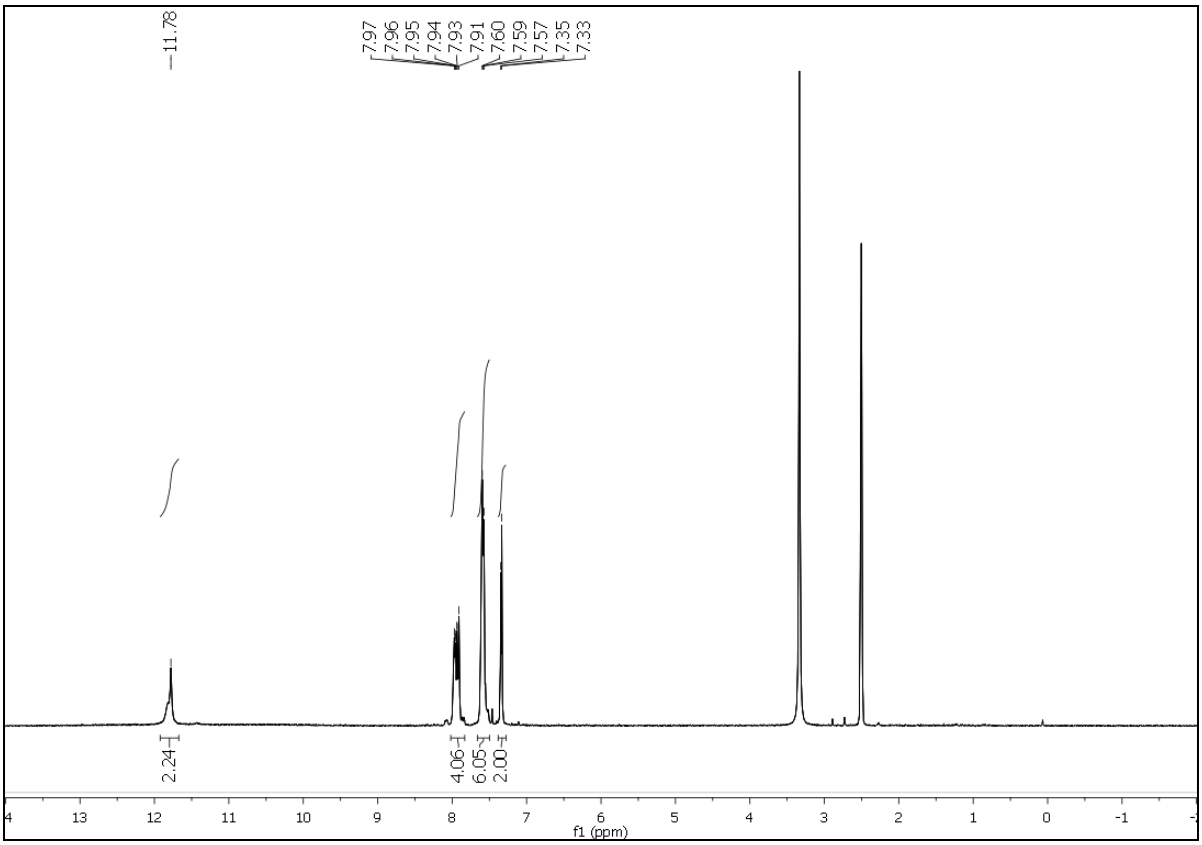
Analytical data is not consistent with the structure assigned as compound **4** in the literature.[1-3]

1. Knott, E.B. *J. Chem. Soc.* **1947**, 1196.
2. Sathyamoorthi, G.; Soong, M.-L.; Ross, T.W.; Boyer, J.H. *Heteroatom Chem*. **1993**, *4*, 603.
3. Bird, C.W. and Jiang, L. *Tetrahedron Lett.* **1992**, *33*, 7253.

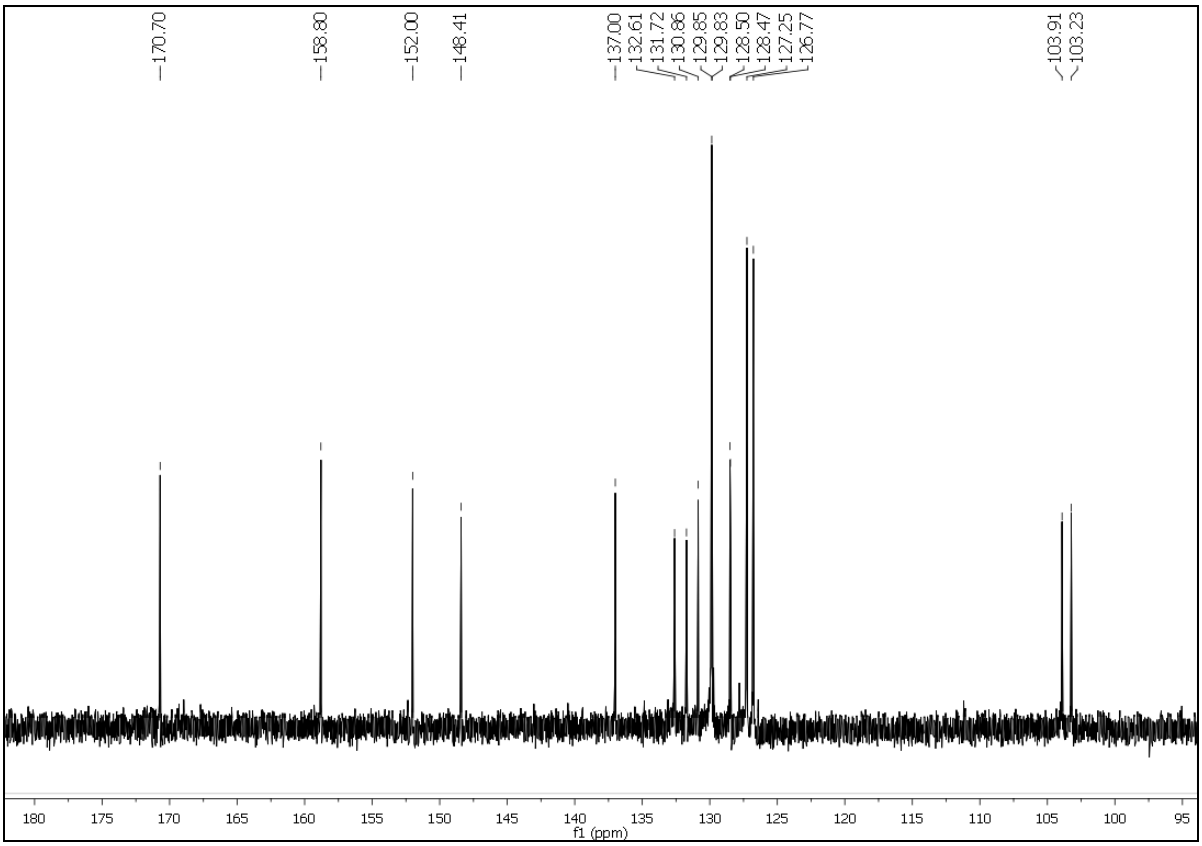
Figure S1. Normalized UV-visible absorption spectra of incorrectly assigned structure **4** (blue) and **9a** (black) in $CHCl_3$.



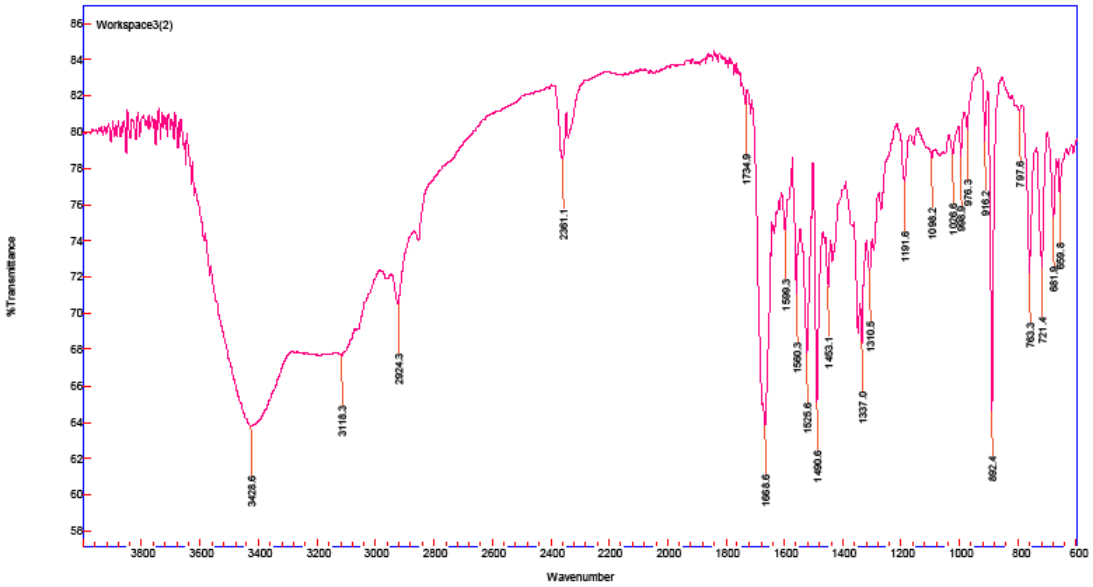
^{1}H NMR (400 MHz, DMSO-d_6) of Dark Blue Precipitate



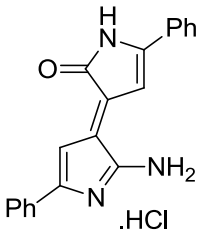
^{13}C NMR (100M Hz, DMSO-d_6) of Dark Blue Precipitate



IR Spectrum of Dark Blue Precipitate



A plausible structure which is consistent with the analytical data is shown below (though other closely related structures could also be envisaged).



Synthesis of (*E*)-1-phenylbut-2-en-1-ol 10a.[4] A solution of crotoaldehyde (1 g, 14.26 mmol) in THF (5 mL) at 0 °C was treated dropwise with phenyllithium (1.8 M in Bu_2O, 9.51 mL, 17.12 mmol) and stirred for 15 min. The reaction mixture was stirred for an additional 1 h at rt and the reaction quenched with saturated ammonium chloride solution (15 mL). Following extraction with diethyl ether (3 x 30 mL), the combined organic layers were washed with brine (30 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 4:1 cyclohexane:ethyl acetate gave the product **10a** as a colorless oil (1.35 g, 64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.29 (m, 5H), 5.78-5.66 (m, 2H), 5.12 (d, *J*=3.8 Hz, 1H), 3.06 (s, 1H), 1.75 (d, *J* = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.57, 133.81, 128.41, 127.38, 127.10, 126.26, 75.01, 17.75. ES-HRMS $[M+Na]^+$: 171.0792, $C_{10}H_{12}ONa$ requires 171.0786.

4. Procedure adapted from R. Shintani, K. Takatsu, T. Hayashi, *Org, Lett*. **2008**, *10*, 1191.

Synthesis of (*E*)-1-(4-methoxyphenyl)but-2-en-1-ol 10b. A solution of crotoaldehyde (1.5 g, 21.39 mmol) in THF (10 mL) at 0 °C was treated dropwise with 4-methoxyphenylmagnesium bromide (0.5 M in THF, 51.36 mL, 25.68 mmol) and stirred for 15 min. The reaction mixture was stirred for an additional 1 h at rt and quenched with saturated ammonium chloride solution (40 mL). Following extraction with ethyl acetate (3 x 30 mL), the combined organic layers were washed with brine (30 mL), dried over sodium sulfate and concentrated to dryness. Purification by silica gel chromatography eluting with 4:1 cyclohexane:ethyl acetate gave the product **10b** as a colorless oil (3.24 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J*=8.8 Hz, 2H), 6.85 (d, *J*=8.8 Hz, 2H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.12 (dd, *J* = 15.9, 6.6 Hz, 1H), 4.49-4.44 (m, 1H), 3.80 (s, 3H), 1.59 (br, 1H), 1.36 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.22, 131.37, 129.39, 128.98, 127.59, 113.97, 69.09, 55.26, 23.44. ES-HRMS $[M-OH]^+$: 161.0960, $C_{11}H_{13}O$ requires 161.0966.

Synthesis of (*E*)-1-phenylbut-2-en-1-one 11a. *trans*-1-Phenylbut-2-en-1-ol **10a** (1.20 g, 8.10 mmol) and MnO_2 (3.40 g, 40.5 mmol) were stirred for 12 h at room temperature in dry diethyl ether (25 mL). The black slurry was filtered through celite, and the celite washed with diethyl ether (4x30 mL) and the combined phases of diethyl ether were evaporated under reduced pressure. Purification by silica gel chromatography eluting with 5:1 cyclohexane:ethyl acetate which gave the product **11a** as an orange oil (971 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.89 (m, 2H), 7.65-7.41 (m, 3H), 7.11-6.99 (m, 1H), 6.93 (d, *J* = 15.3, 1H), 2.02 (dd, *J* = 6.7, 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.74, 145.00, 137.89, 132.53, 128.46, 128.45, 127.51, 18.57. EI-HRMS $[M]^+$: 146.0735, $C_{10}H_{10}O$ requires 146.0732.

Synthesis of (*E*)-1-(4-methoxyphenyl)but-2-en-1-one 11b. (*E*)-1-(4-methoxyphenyl)but-2-en-1-ol **10b** (3.2 g, 17.96 mmol) and MnO_2 (15.61 g, 179.6 mmol) were stirred for 20 h at room temperature in dry diethyl ether (40 mL). The black slurry was filtered through celite and the celite washed with diethyl ether (4x30 mL) and the combined phases of diethyl ether were evaporated under reduced pressure. Purification by silica gel chromatography eluting with 4:1 cyclohexane:ethyl acetate which gave the product **11b** as an orange oil (2.30 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.9 Hz, 2H), 7.00-6.91 (m, 1H), 6.84-6.80 (m, 3H), 3.74 (s, 3H), 1.87 (dd, *J* = 6.7, 1.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.66, 163.19, 143.70, 130.65, 130.60, 127.01, 113.63, 55.29, 18.39. ES-HRMS $[M+H]^+$: 177.0923, $C_{11}H_{13}O_2$ requires 177.0923.

Synthesis of 3-methyl-4-nitro-1-phenylbutan-1-one 12a. (*E*)-1-Phenylbut-2-en-1-one **11a** (900 mg, 6.16 mmol) in EtOH (15 mL) was treated with nitromethane (1.65 mL, 30.8 mmol) and diethylamine (DEA) (3.18 mL, 30.8 mmol) and the mixture heated under reflux for 4 h. The solution was cooled, treated with aqueous HCl (5 M, 60 mL) and extracted with CH_2Cl_2 (3x40 mL). The combined organic layers were washed with brine, dried over sodium sulfate and the solvent removed under reduced pressure. Purification by silica gel chromatography eluting with 5:1 cyclohexane:ethyl acetate gave the product **12a** as a yellow oil (1.04 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99-7.88 (m, 2H), 7.60-7.52 (m, 1H), 7.49-7.41 (m, 2H), 4.51 (dd, *J* = 12.0, 5.9 Hz, 1H), 4.40 (dd, *J* = 12.0, 6.3 Hz, 1H), 3.13 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.98 (dd, *J* = 18.8, 6.3 Hz, 1H), 2.97-2.92 (m, 1H), 1.13 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.72, 136.57, 133.45, 128.70, 127.96, 80.48, 41.71, 28.59, 17.55. ES-HRMS $[M+Na]^+$: 230.0787, $C_{11}H_{13}NO_3Na$ requires 230.0793.

Synthesis of 1-(4-methoxyphenyl)-3-methyl-4-nitrobutan-1-one 12b. (*E*)-1-(4-methoxyphenyl)but-2-en-1-one **11b** (2 g, 11.35 mmol) in EtOH (30 mL) was treated with nitromethane (3.05 mL, 56.75 mmol) and diethylamine (5.86 mL, 56.75 mmol) and the mixture was heated under reflux for 5 h. The solution was cooled, treated with aqueous HCl (5 M, 60 mL) and extracted with CH_2Cl_2 (3x50 mL). The combined organic layers were washed with brine, dried over sodium sulfate and the solvent removed under reduced pressure. Purification by silica gel chromatography eluting with 4:1 cyclohexane:ethyl acetate gave the product **12b** as a light yellow oil (2.10 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.9 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.53 (dd, *J* = 11.9, 5.9 Hz, 1H), 4.42 (dd, *J* = 11.9, 6.5 Hz, 1H), 3.88 (s, 3H), 3.09 (dd, *J* = 16.3, 6.0 Hz, 1H), 3.03-2.92 (m, 2H), 1.14 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.16, 163.74, 130.28, 129.69, 113.83, 80.59, 55.48, 41.34, 28.76, 17.58. ES-HRMS $[M+Na]^+$: 260.0905, $C_{12}H_{15}NO_4Na$ requires 260.0899.

Synthesis of (*Z*)-3-methyl-*N*-(3-methyl-5-phenyl-2*H*-pyrrol-2-ylidene)-5-phenyl-1*H*-pyrrol-2-amine 8a. A mixture of 3-methyl-4-nitro-1-phenylbutan-1-one **12a** (600 mg, 2.89 mmol) and NH_4OAc (7.81 g, 101.34 mmol) in EtOH (20 mL) was heated under reflux for 6 h. The solvent was reduced under vacuum to half of the volume and the mixture cooled with a NaCl/ice bath. The precipitate was filtered and the residue washed with cold EtOH, saturated $NaHCO_3$, deionized H_2O and was dried under vacuum to give **8a** as a dark blue solid (89 mg, 0.27 mmol, 19%), mp 122-123 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.9 Hz, 4H), 7.57-7.39 (m, 6H), 6.75 (s, 2H), 2.38 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.90, 150.22, 141.39, 132.48, 129.58, 128.99, 126.34, 116.75, 11.37. λ_{max} abs ($CHCl_3$): 561 nm. ES-HRMS $[M+H]^+$: 326.1648, $C_{22}H_{20}N_3$ requires 326.1657.

Synthesis of (*Z*)-5-(4-methoxyphenyl)-*N*-(5-(4-methoxyphenyl)-3-methyl-2*H*-pyrrol-2-ylidene)-3-methyl-1*H*-pyrrol-2-amine 8b. Method A: A mixture of 1-(4-methoxyphenyl)-3-methyl-4-nitrobutan-1-one **12b** (300 mg, 1.26 mmol) and NH_4OAc (3.49 g, 44 mmol) in MeOH (8 mL) was heated under reflux for 10 h. The solution was cooled, treated with saturated $NaHCO_3$ (20 mL) and extracted with ethyl acetate (3x30 mL). The combined organic layers were washed with water, brine, dried over sodium sulfate and the solvent removed under reduced pressure. Purification by silica gel chromatography eluting with 5:1 cyclohexane:ethyl acetate which gave the product **8b** as a dark blue solid (68 mg, 0.18 mmol, 28%).

Method B: A mixture of 1-(4-methoxyphenyl)-3-methyl-4-nitrobutan-1-one **12b** (2.00 g, 8.43 mmol) and NH_4OAc (22.74 g, 295 mmol) in EtOH (55 mL) was heated under reflux for 6 h. The solvent was reduced under vacuum to half of the volume and the mixture cooled with a NaCl/ice bath. The precipitate was filtered and the residue washed with cold EtOH, saturated $NaHCO_3$, deionized H_2O and was dried under vacuum to give **8b** as a dark blue solid (422 mg, 1.09 mmol, 26%), mp 207-208 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.8 Hz, 4H), 6.98 (d, *J* = 8.8 Hz, 4H), 6.63 (s, 2H), 3.87 (s, 6H), 2.32 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.84, 154.04, 149.87, 140.82, 127.82, 125.37, 116.06, 114.46, 55.41, 11.31. λ_{max} abs ($CHCl_3$): 579 nm. ES-HRMS $[M+H]^+$: 386.1862, $C_{24}H_{24}N_3O_2$ requires 386.1869.

Synthesis of (*Z*)-4-(5-(5-(4-methoxyphenyl)-3-methyl-2*H*-pyrrol-2-ylideneamino)-4-methyl-1*H*-pyrrol-2-yl)phenol 8c. A solution of **8b** (300 mg, 0.78 mmol) in dry CH_2Cl_2 (10 mL) at -78 °C was treated dropwise with BBr_3 (1 M in CH_2Cl_2, 2.34 mL, 2.34 mmol) and stirred for 3 h. The reaction mixture was warmed to room temperature for further 30 min. After cooling to 0 °C, the reaction was slowly quenched with saturated sodium bicarbonate (20 mL), the organic layer separated and the aqueous layer extracted with CH_2Cl_2 (2x40 mL). The combined organic layers

were washed with saturated sodium bicarbonate, deionized H_2O and brine, and dried (Na_2SO_4), filtered and concentrated under reduced pressure. Purification by silica gel chromatography eluting with 5:1 cyclohexane:ethyl acetate gave **8c** as dark blue solid (57 mg, 20%), mp 110-111 °C. ^{1}H NMR (400 MHz, CD_3OD): δ 7.77 (dd, *J* = 8.7, 6.1 Hz, 4H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.76 (s, 1H), 6.70 (s, 1H), 3.86 (s, 3H), 2.28 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, CD_3OD): δ 161.02, 156.69, 155.35, 151.91, 150.72, 148.16, 141.42, 139.10, 127.96, 127.18, 124.83, 123.78, 116.71, 115.69, 114.90, 114.25, 54.50, 9.96, 9.89. λ_{max} abs ($CHCl_3$): 580 nm. ES-HRMS $[M+H]^+$: 372.1722, $C_{23}H_{21}N_3O_2$ requires 372.1712.

Synthesis of BF_2 chelated (Z)-3-methyl-*N*-(3-methyl-5-phenyl-2*H*-pyrrol-2-ylidene)-5-phenyl-1*H*-pyrrol-2-amine 13a. A solution of **8a** (70 mg, 0.21 mmol) in dry CH_2Cl_2 (10 mL) was treated with diisopropylethylamine (DIPEA) (0.36 mL, 2.10 mmol), $BF_3.OC_4H_{10}$ (0.37 mL, 2.94 mmol) and stirred at rt under N_2 for 6 h. The reaction mixture was washed with deionized H_2O (3x20 mL), brine, dried over Na_2SO_4, filtered and concentrated to dryness under reduced pressure. Purification by silica gel chromatography eluting with 9:1 cyclohexane:ethyl acetate gave **13a** as a red metallic solid (69 mg, 90%), mp 139-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 6.7, 3.0 Hz, 4H), 7.50-7.36 (m, 6H), 6.59 (s, 2H), 2.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.41, 146.53, 144.22, 131.63, 130.55, 129.45 (t, *J* = 4.4 Hz), 128.45, 121.80, 11.29. ^{19}F NMR (375 MHz, $CDCl_3$): δ -132.70. λ_{max} abs ($CHCl_3$): 618 nm. HRMS $[M+Na]^+$: 396.1476, $C_{22}H_{18}BF_2N_3Na$ requires 396.1460.

Synthesis of BF_2 chelated (Z)-5-(4-methoxyphenyl)-*N*-(5-(4-methoxyphenyl)-3-methyl-2*H*-pyrrol-2-ylidene)-3-methyl-1*H*-pyrrol-2-amine 13b. A solution of **8b** (100 mg, 0.26 mmol) in dry CH_2Cl_2 (15 mL) was treated with diisopropylethylamine (DIPEA) (0.45 mL, 2.60 mmol) and $BF_3.OC_4H_{10}$ (0.46 mL, 3.64 mmol), and stirred at rt under N_2 for 6 h. The reaction mixture was washed with H_2O (3x20 mL), brine, dried over Na_2SO_4, filtered and concentrated to dryness under reduced pressure. Purification by silica gel chromatography eluting with 5:1 cyclohexane:ethyl acetate gave **13b** as red metallic solid (93 mg, 83%), mp 212-213 °C . ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, *J* = 9.1 Hz, 4H), 6.95 (d, *J* = 9.1 Hz, 4H), 6.59 (s, 2H), 3.85 (s, 3H), 2.38 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.59, 157.98, 146.24, 143.03, 131.41 (t, *J* = 5.0 Hz), 124.21, 121.19, 114.09, 55.34, 11.20. ^{19}F NMR (375 MHz, $CDCl_3$): δ -133.28. λ_{max} abs ($CHCl_3$): 648 nm. ES-HRMS $[M+H]^+$: 434.1864, $C_{24}H_{23}BF_2N_3O_2$ requires 434.1851.

Synthesis of BF_2 chelated (*Z*)-4-(5-(5-(4-methoxyphenyl)-3-methyl-2*H*-pyrrol-2-ylideneamino)-4-methyl-1*H*-pyrrol-2-yl)phenol 13c. A solution of **8c** (50 mg, 0.13 mmol) in dry CH_2Cl_2 (10 mL) was treated with diisopropylethylamine (DIPEA) (0.23 mL, 1.34 mmol) and

$BF_3O.C_4H_{10}$ (0.24 mL, 1.88 mmol), and stirred at rt under N_2 for 6 h. The reaction mixture was washed with H_2O (3x20 mL), brine, dried over Na_2SO_4, filtered and concentrated to dryness under reduced pressure. Purification by silica gel chromatography eluting with 4:1 cyclohexane:ethyl acetate gave **13c** as red metallic solid (43 mg, 78%), mp 158-159 °C. ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 10.42 (br, 1H), 8.03-7.98 (m, 4H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.02 (s, 1H), 6.93 (s, 1H), 6.89 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.31 (s, 6H). ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 161.82, 161.34, 158.86, 156.45, 146.20, 145.38, 143.27, 141.93, 132.44, 131.67, 123.91, 122.60, 121.88, 121.83, 116.29, 114.76, 55.92, 11.48, 11.43. ^{19}F NMR (375 MHz, DMSO-d$_6$) δ -131.6. λ_{max} abs ($CHCl_3$): 651 nm. ES-HRMS [M-H]$^-$: 418.1544, $C_{23}H_{19}BF_2N_3O_2$ requires 418.1538.

Synthesis of BF_2 chelate of (Z)-3-(4-(5-(5-(4-methoxyphenyl)-3-methyl-2H-pyrrol-2-ylideneamino)-4-methyl-1*H*-pyrrol-2-yl)phenoxy)propane-1-sulfonate cesium salt 13d. A solution of **13c** (30 mg, 0.07 mmol) and Cs_2CO_3 (35 mg, 0.11 mmol) in dry THF (8 mL) was treated with propane-1,3-sultone (26 mg, 0.21 mmol) and heated reflux for 1 h under a N_2 atmosphere. The reaction mixture was cooled to rt, the solvent was removed under reduced pressure. Acetone (5 mL) was added and sonicated for 10 min, the solid was filtered, washed fully with acetone, dried under vacuum gave the product **13d** as a dark blue solid (29 mg, 62%), mp 257-258°C. For NMR analysis the compound was transformed into tetrabutylammonium salt by extraction of aqueous solution of **13d** with $CHCl_3$ in presence of tetrabutylammonium chloride. The organic phase was washed with water three times, dried and evaporated. ^{1}H NMR of **13d** ($^+NBu_4$) (400 MHz, $CDCl_3$): δ 8.02-7.95 (m, 4H), 7.00-6.91 (m, 4H), 6.62 (s, 1H), 6.59 (s, 1H), 4.21 (t, *J* = 6.6 Hz, 2H) 3.87 (s, 3H), 3.33-3.22 (m, 8H), 3.01-2.98 (m, 2H), 2.36 (s, 6H), 2.34-2.30 (m, 2H), 1.72-1.54 (m, 8H), 1.47-1.38 (m, 8H), 0.99 (t, *J* = 7.3 Hz, 12H). ^{19}F NMR (375 MHz, $CDCl_3$): δ -133.26. λ_{max} abs (PBS): 664 nm, λ_{max} em (PBS): 695 nm. ES-HRMS [M-Cs]$^-$: 540.1580, $C_{26}H_{25}BF_2N_3O_5S$ requires 540.1582.

Table S1

Effects of the Solvent Polarity on the Absorption Spectra of 13a-c

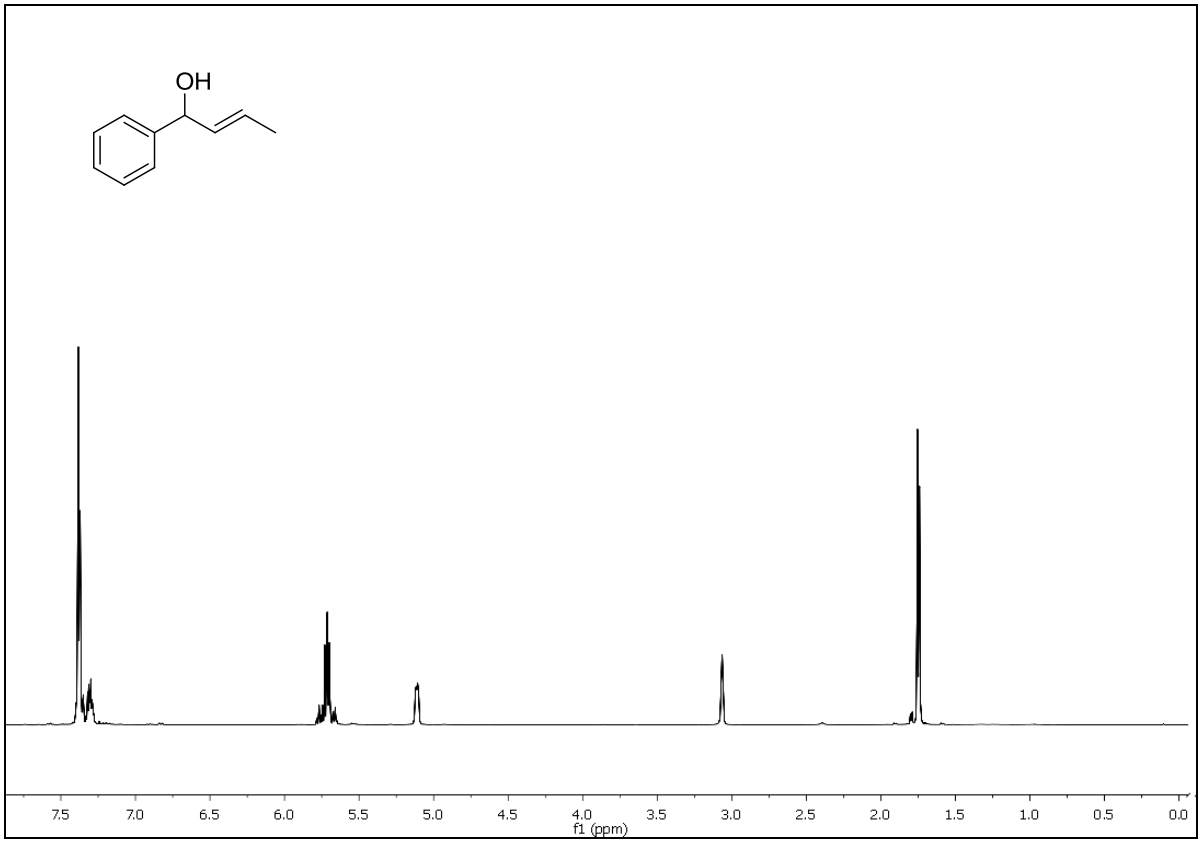
	$\lambda_{max\ abs}$ (fwhm)/nm				
	Cyclohexane	Toluene	THF	CH_3CN	MeOH
13a	613(46)	623(47)	618(51)	613(54)	612(49)
13b	647(52)	654(52)	656(54)	642(61)	647(55)
13c	642(50)	653(50)	655(57)	646(65)	652(57)

Effects of the Solvent Polarity on the Fluorescence Spectra of 13a-c

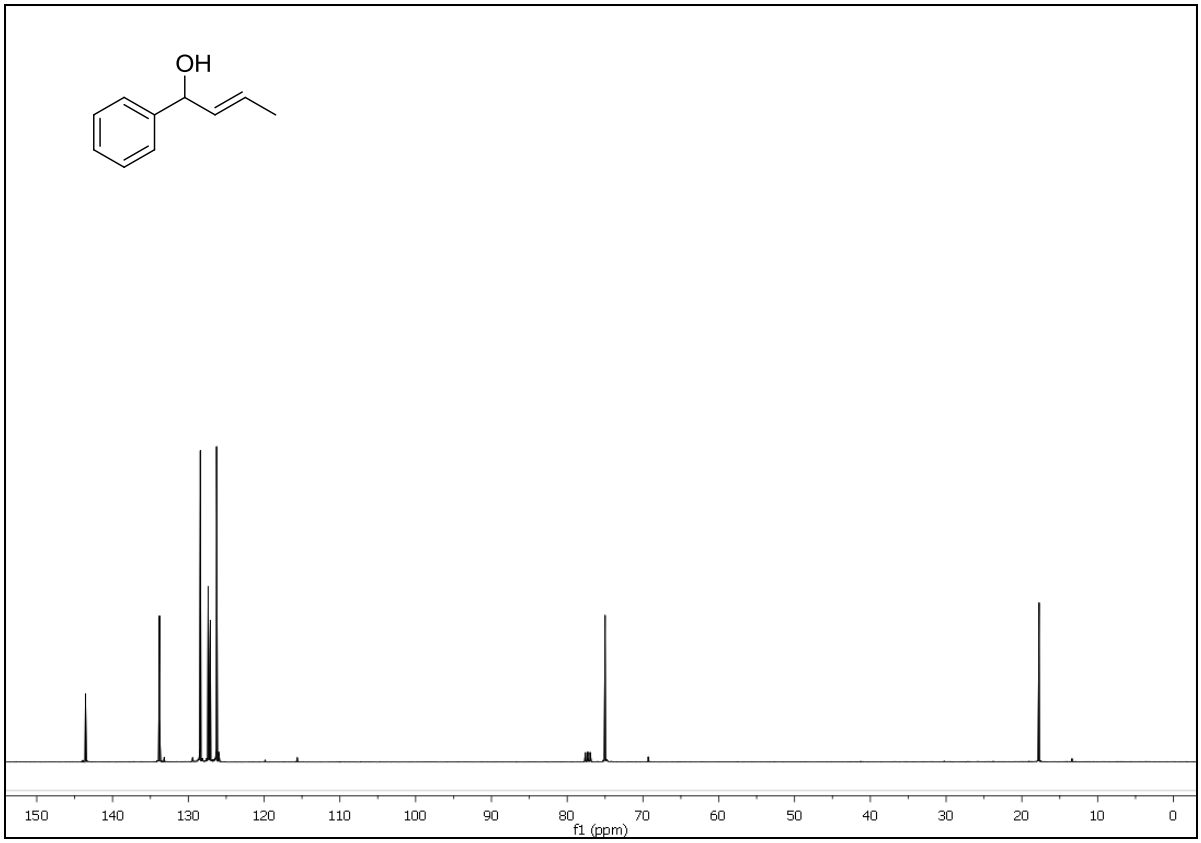
	$\lambda_{max\ abs}$ (Stoke shift)/nm				
	Cyclohexane	Toluene	THF	CH_3CN	MeOH
13a	634(21)	644(21)	640(22)	635(22)	634(22)
13b	667(20)	679(25)	676(20)	675(33)	673(26)
13c	662(20)	674(21)	678(23)	674(28)	678(26)

(*E*)-1-Phenylbut-2-en-1-ol 10a.

^{1}H NMR (400 MHz, $CDCl_3$)

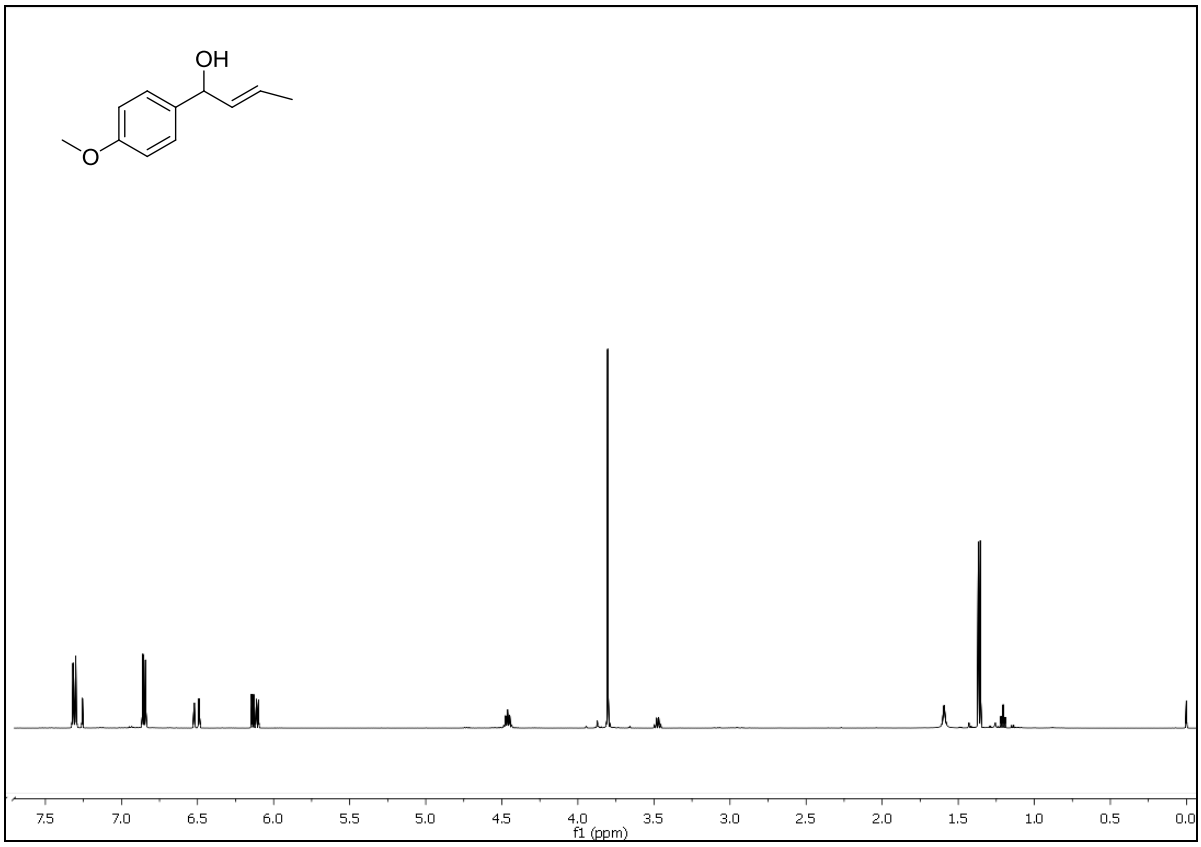


^{13}C NMR (100 MHz, $CDCl_3$)

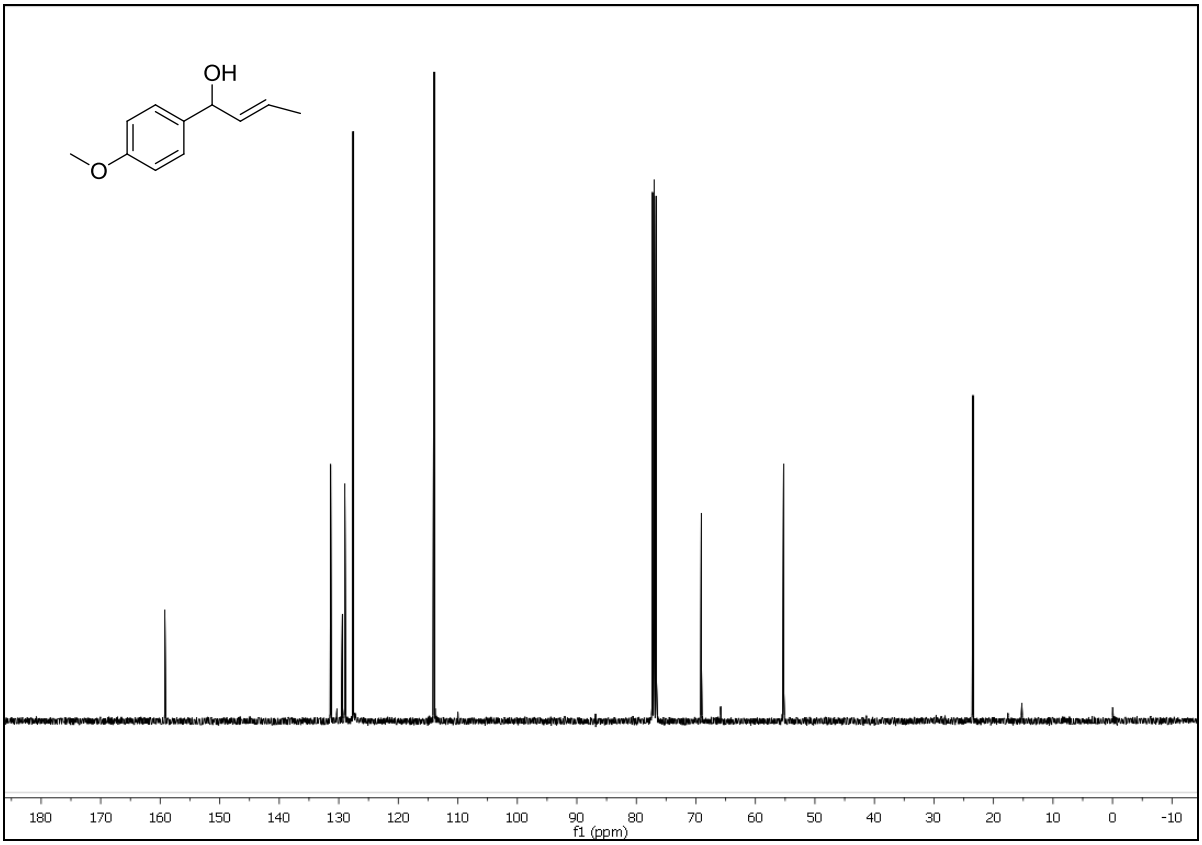


(*E*)-1-(4-Methoxyphenyl)but-2-en-1-one 10b.

^{1}H NMR (400 MHz, $CDCl_3$)

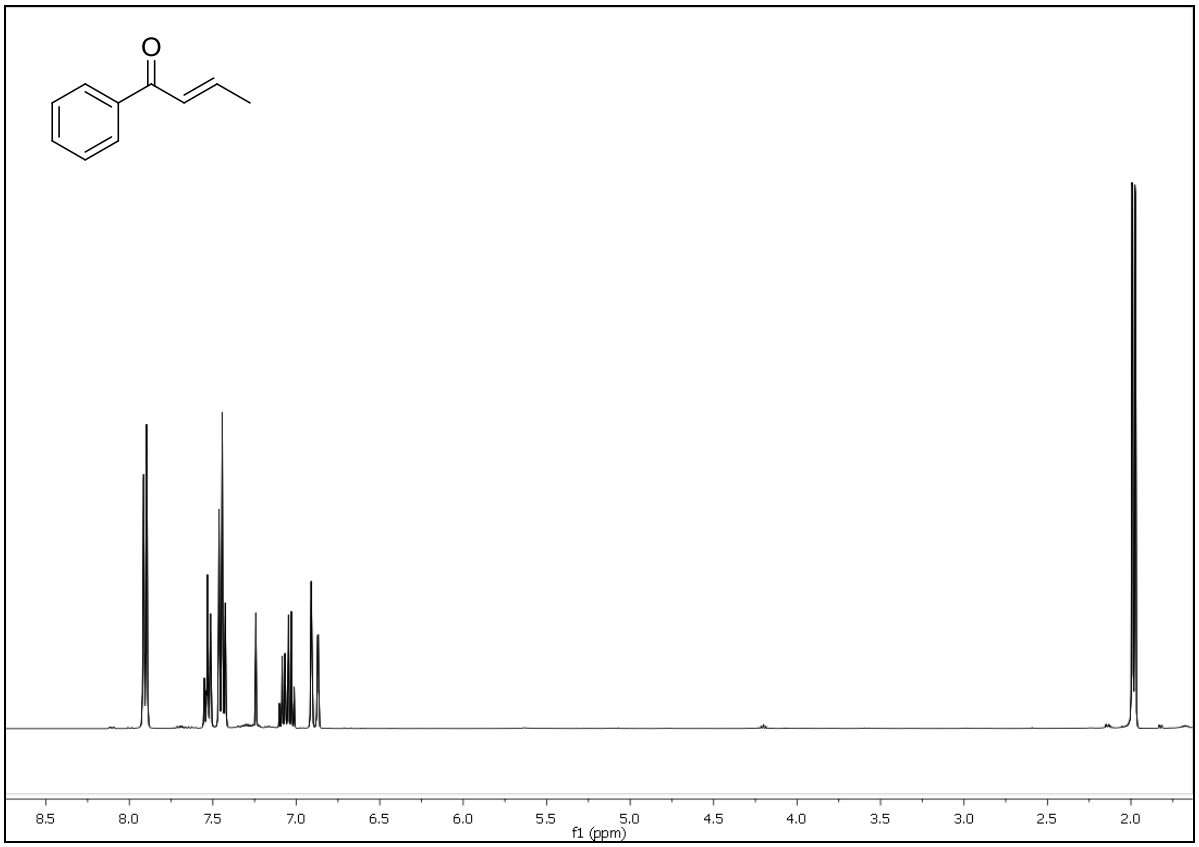


^{13}C NMR (100 MHz, $CDCl_3$)

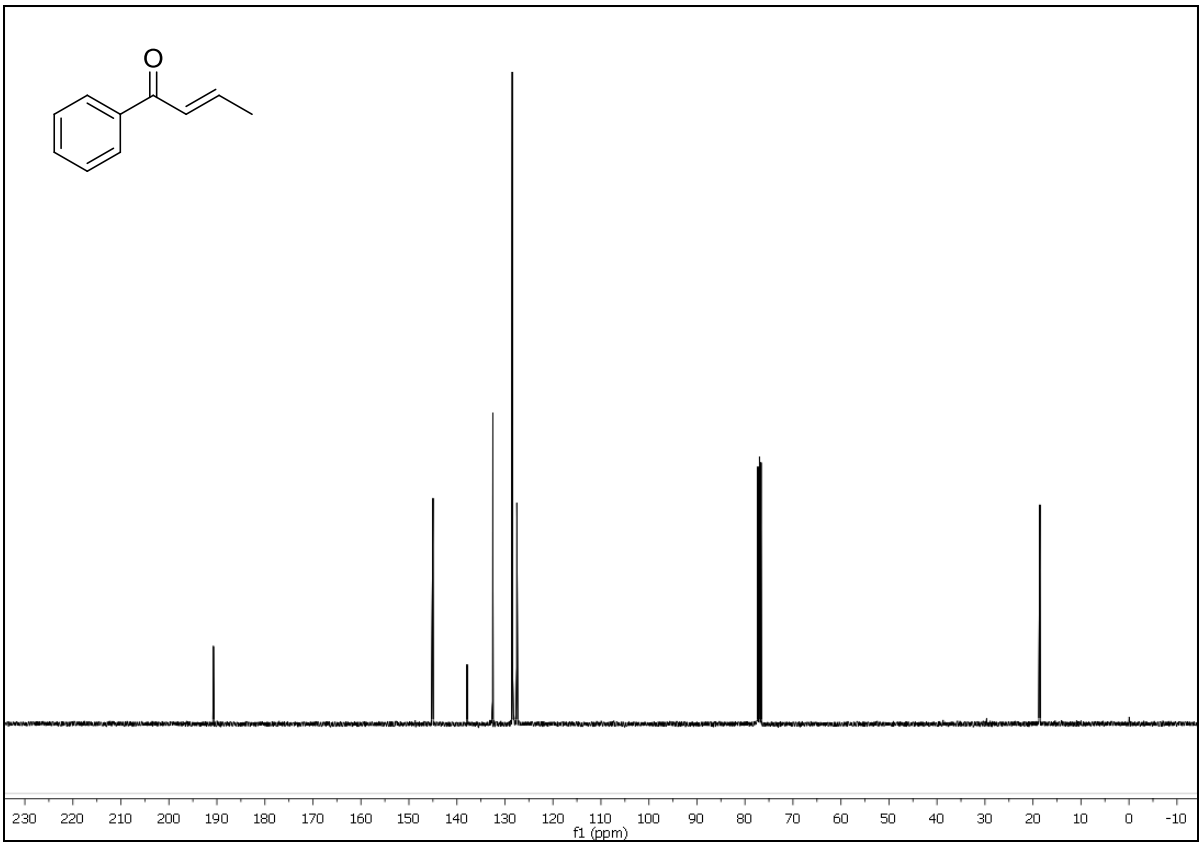


(*E*)-1-Phenylbut-2-en-1-one 11a.

^{1}H NMR (400 MHz, $CDCl_3$)

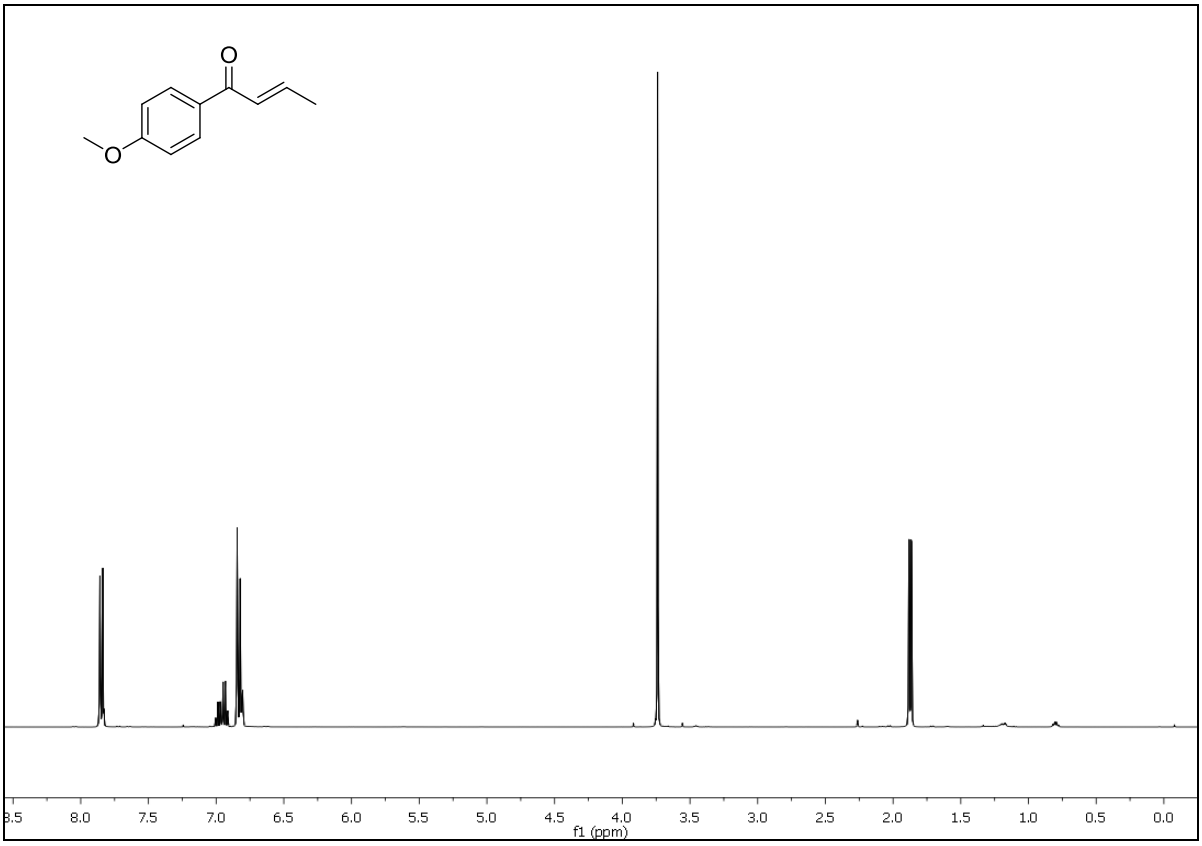


^{13}C NMR (100 MHz, $CDCl_3$)

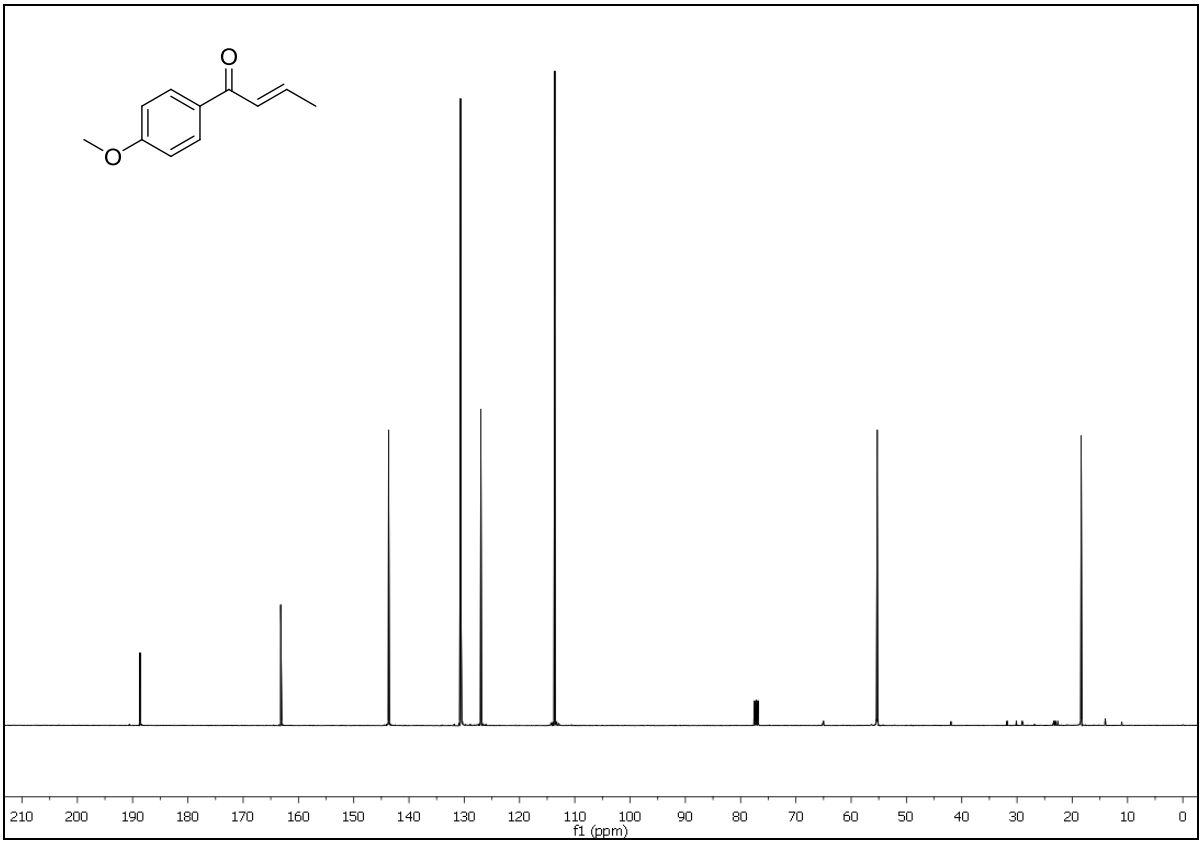


(*E*)-1-(4-Methoxyphenyl)but-2-en-1-one 11b.

^{1}H NMR (400 MHz, $CDCl_3$)

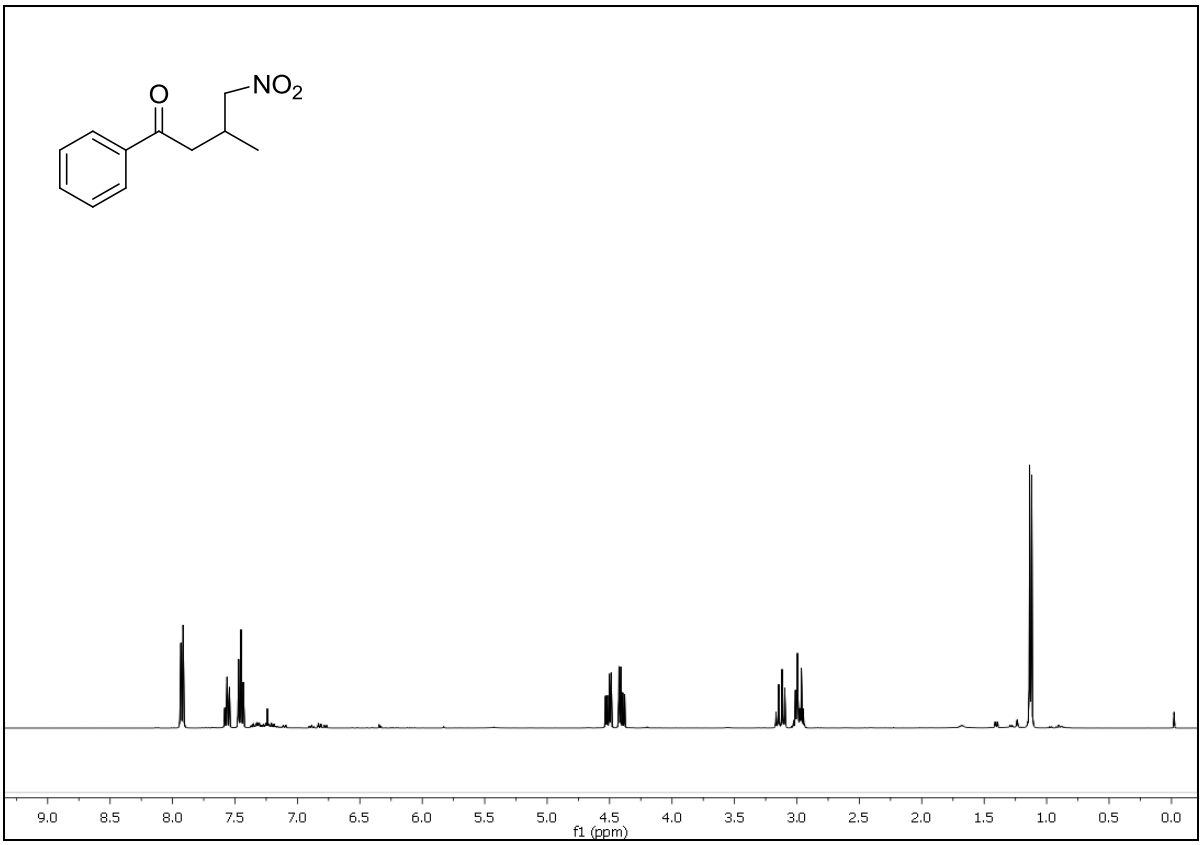


^{13}C NMR (100 MHz, $CDCl_3$)

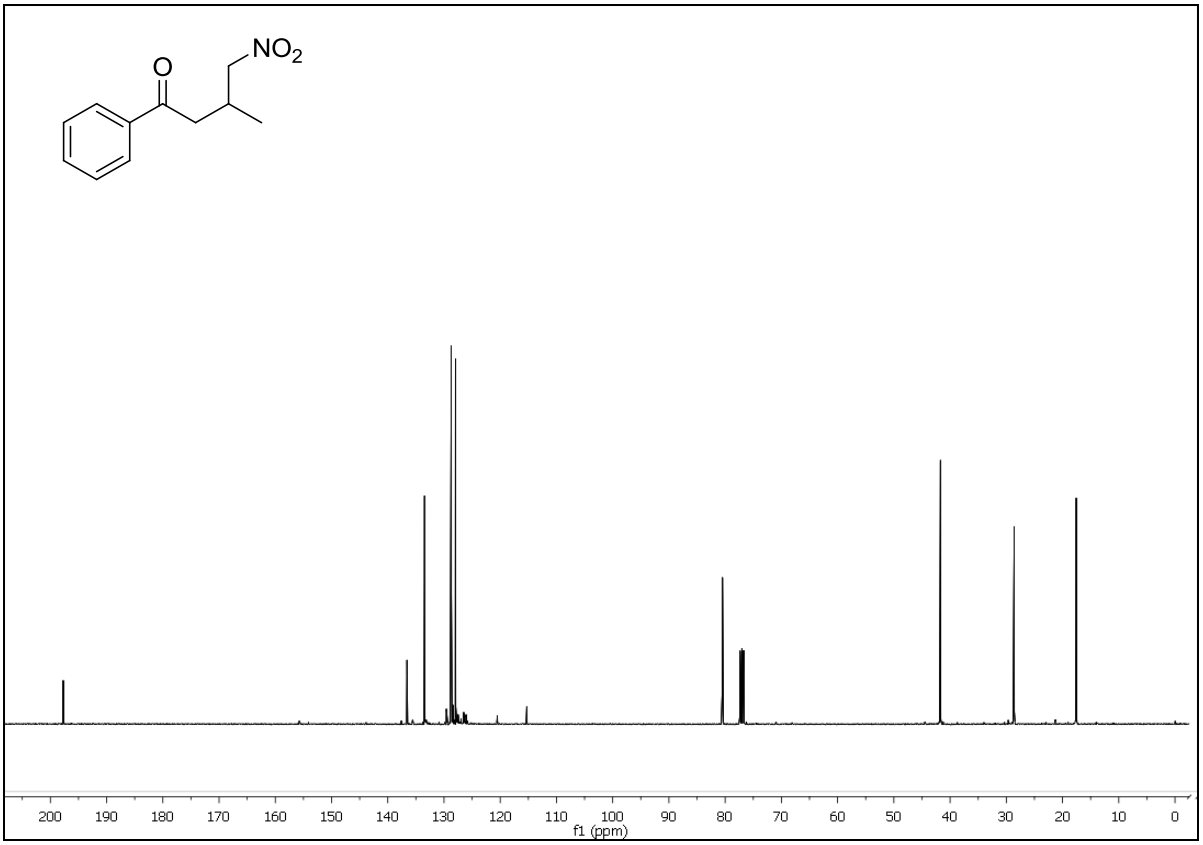


3-Methyl-4-nitro-1-phenylbutan-1-one 12a.

^{1}H NMR (400 MHz, $CDCl_3$)

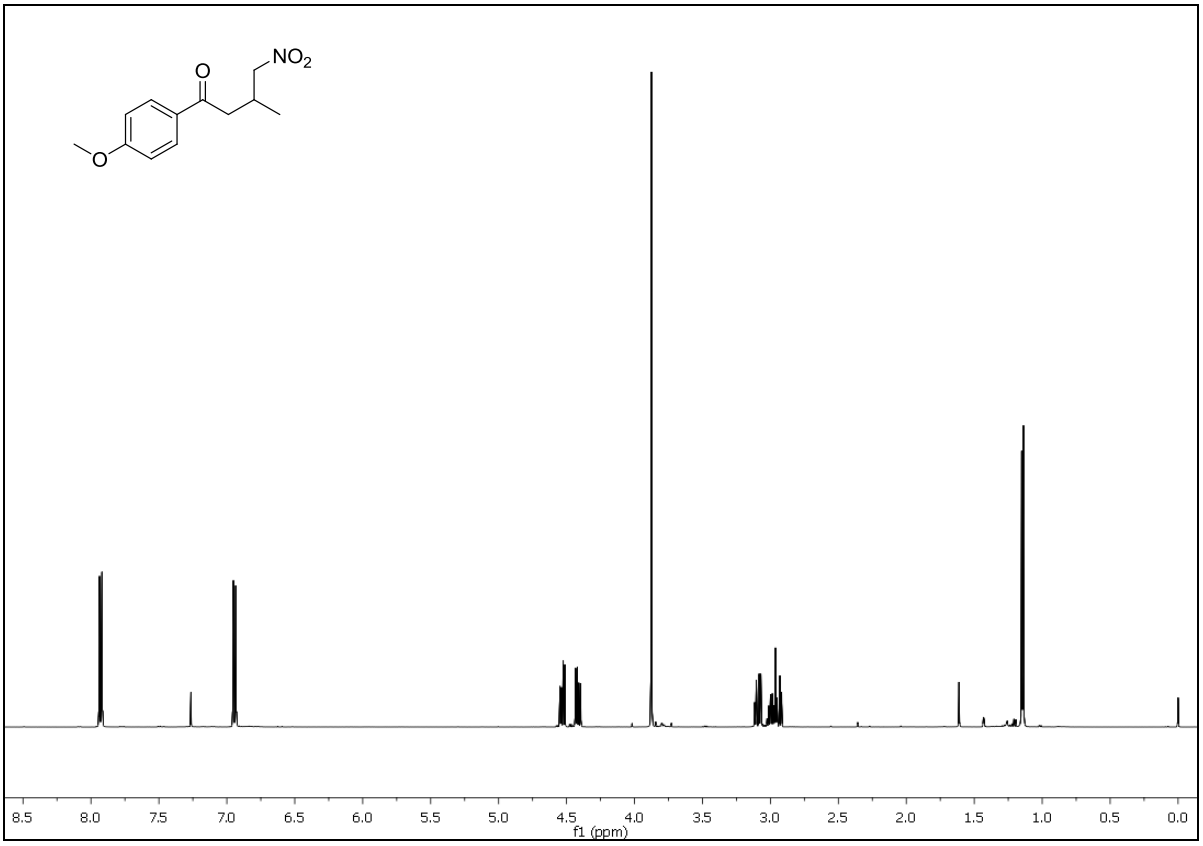


^{13}C NMR (100 MHz, $CDCl_3$)

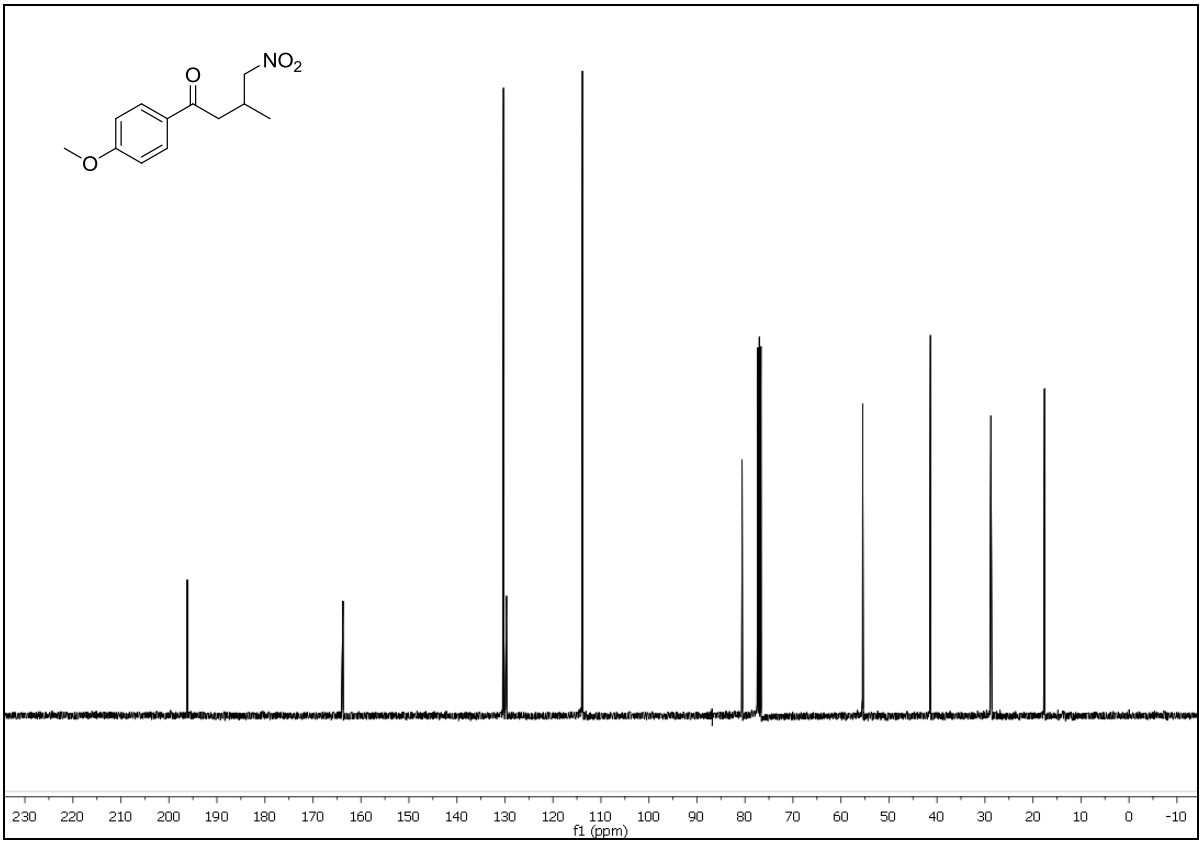


1-(4-Methoxyphenyl)-3-methyl-4-nitrobutan-1-one 12b.

^{1}H NMR (400 MHz, $CDCl_3$)

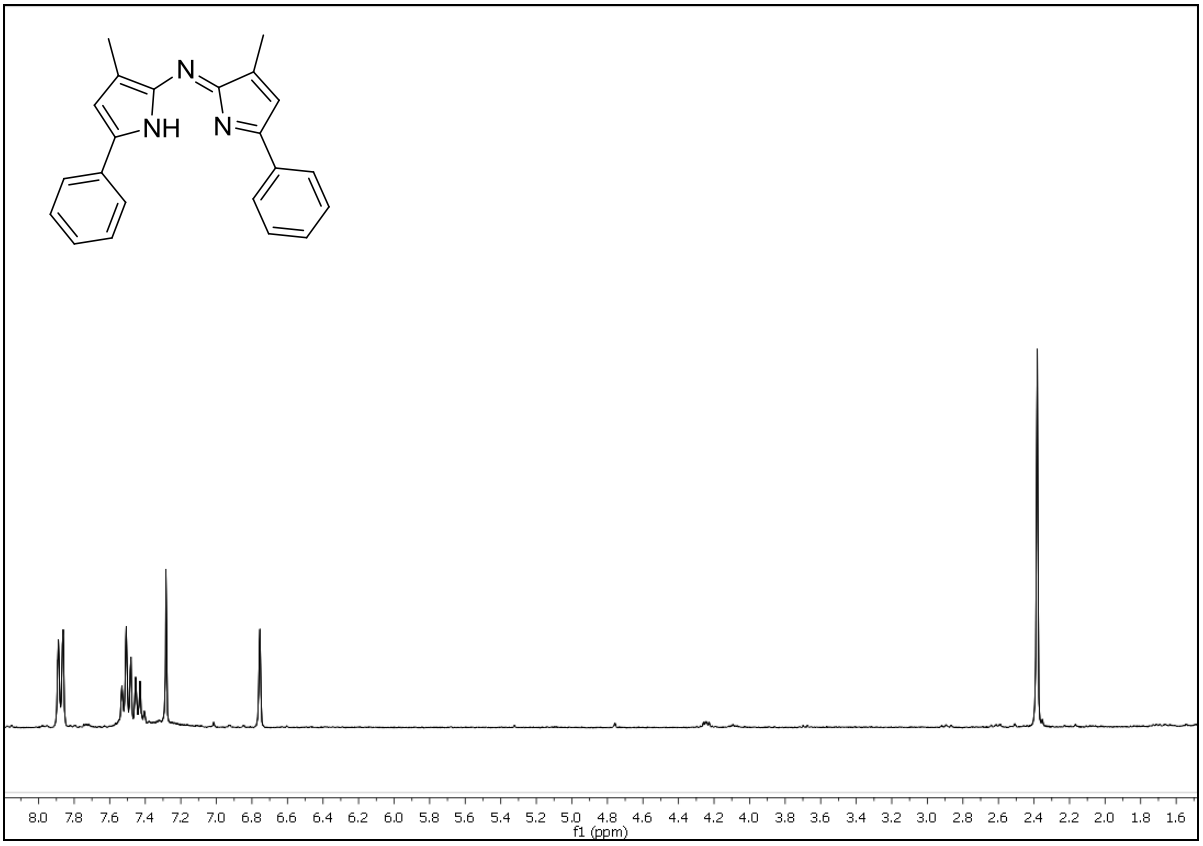


^{13}C NMR (100 MHz, $CDCl_3$)

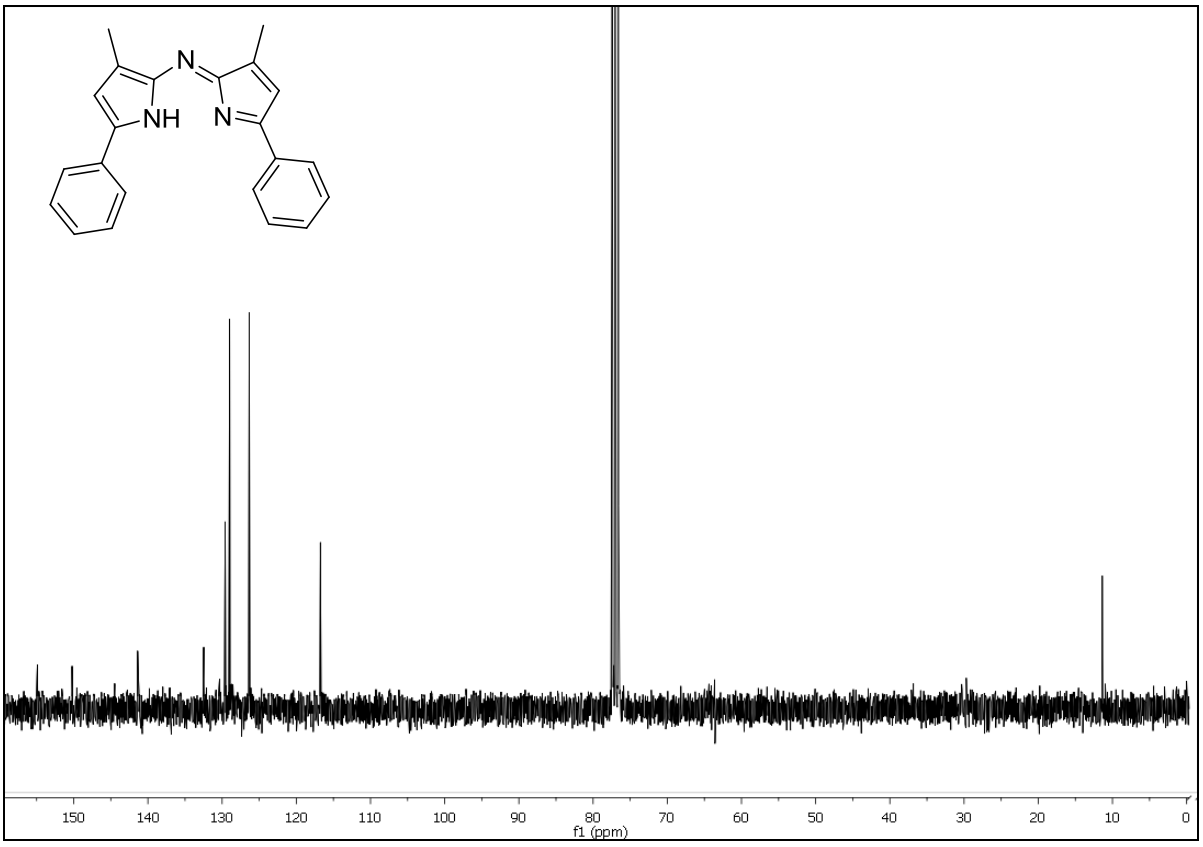


(*Z*)-3-Methyl-*N*-(3-methyl-5-phenyl-2*H*-pyrrol-2-ylidene)-5-phenyl-1*H*-pyrrol-2-amine 8a.

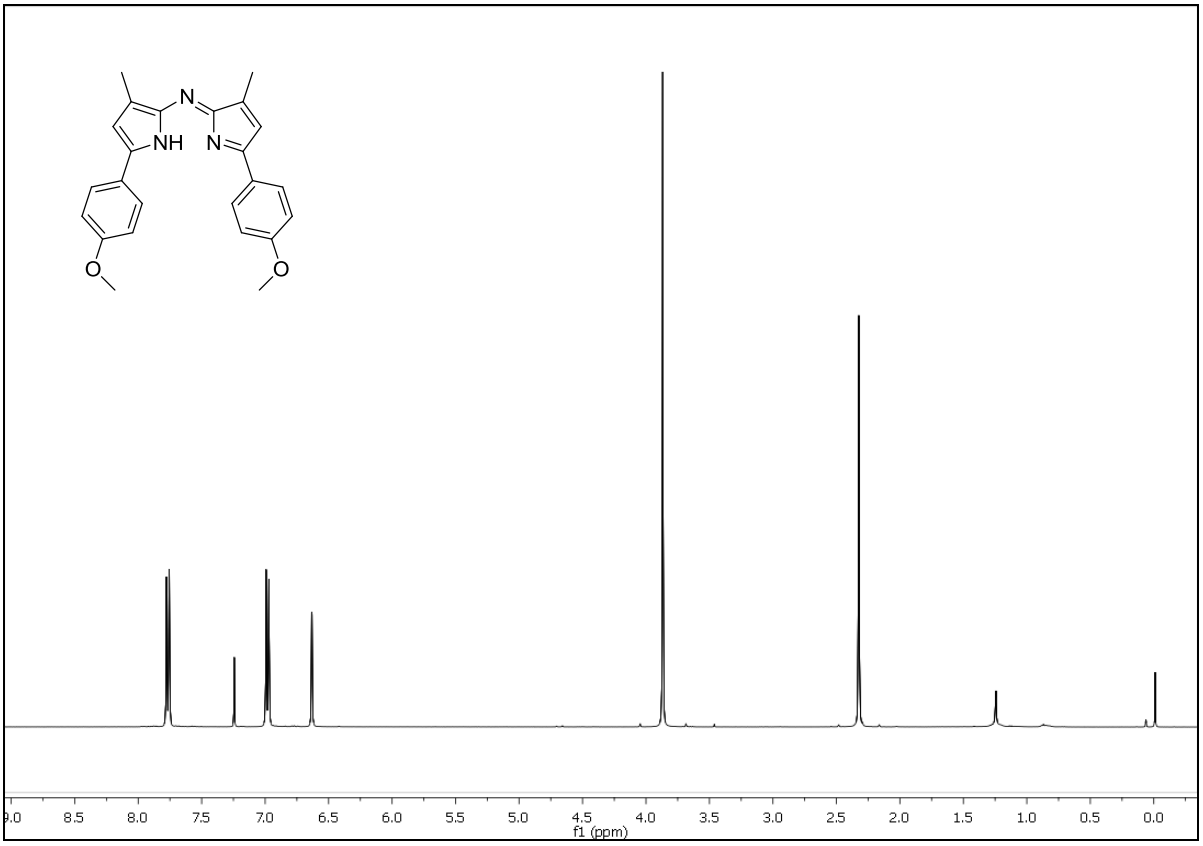
^{1}H NMR (300 MHz, $CDCl_3$)



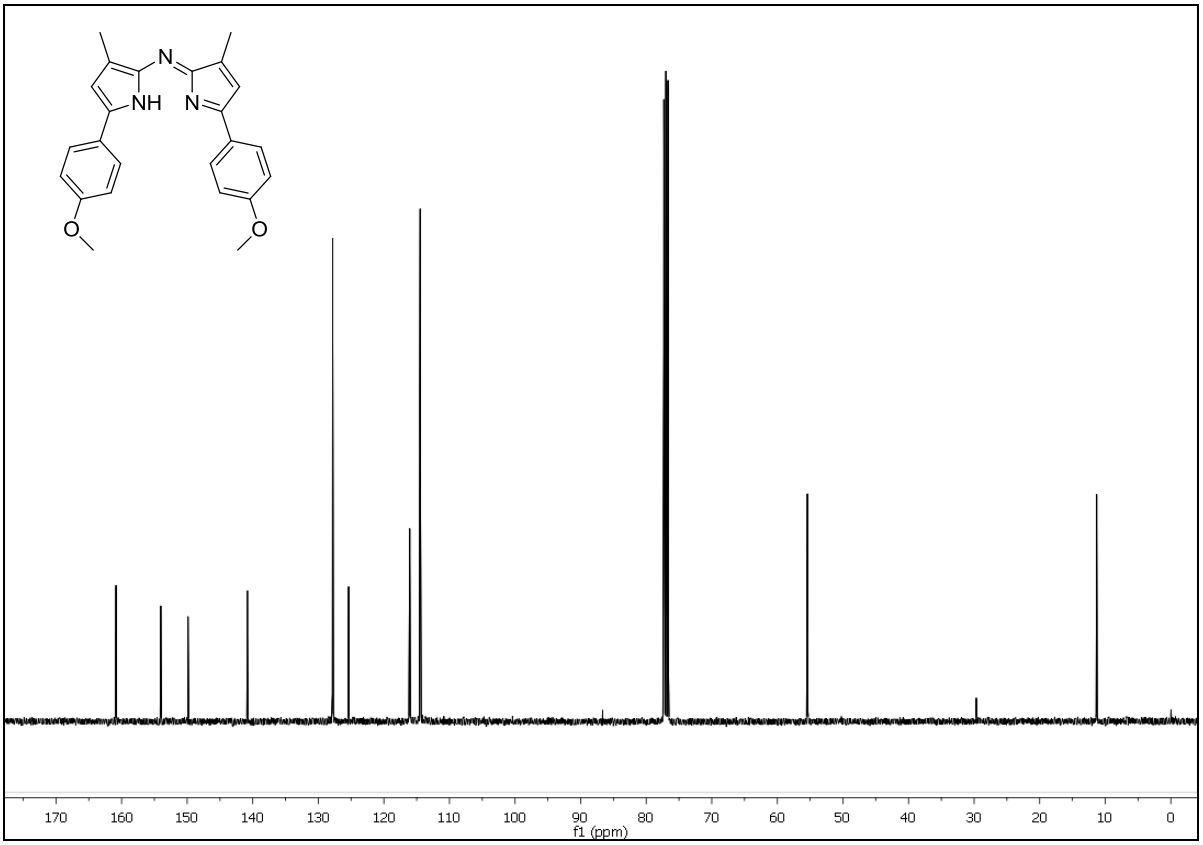
^{13}C NMR (75 MHz, $CDCl_3$)



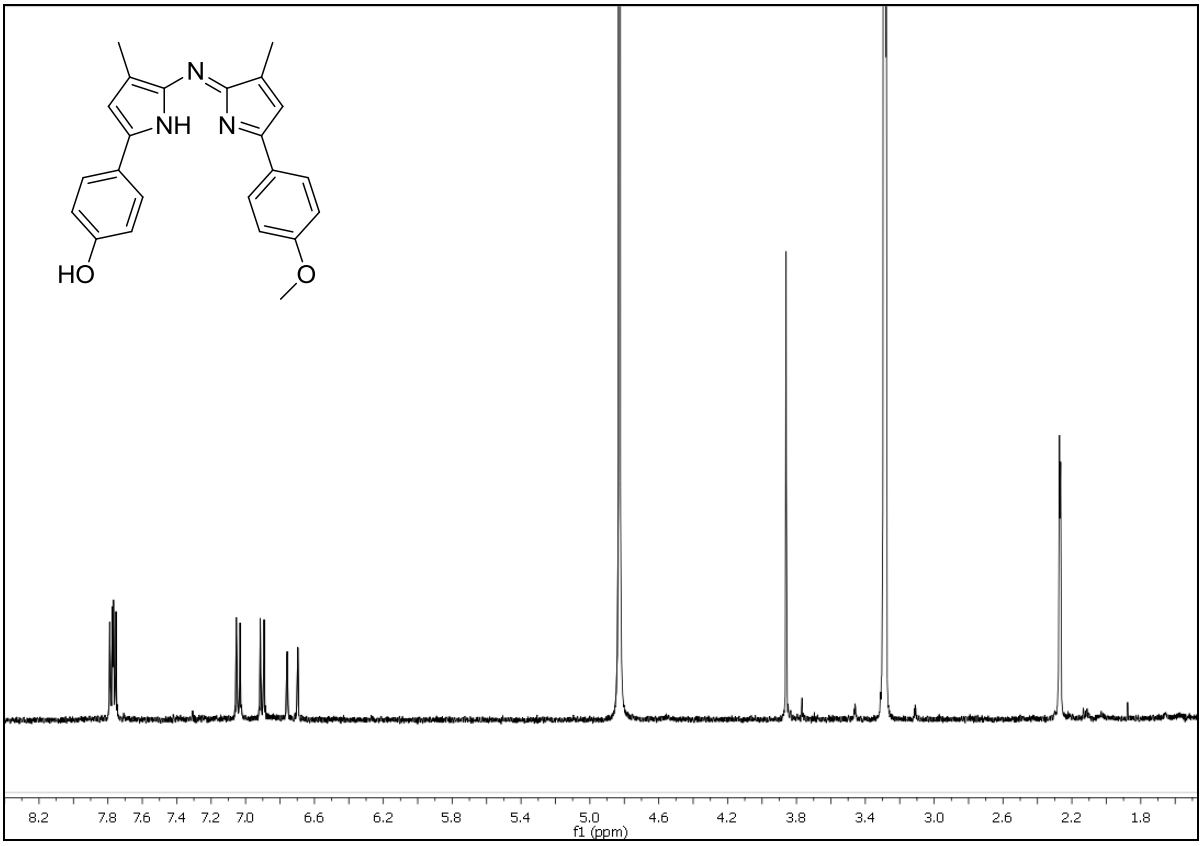
(*Z*)-5-(4-Methoxyphenyl)-*N*-(5-(4-methoxyphenyl)-3-methyl-2*H*-pyrrol-2-ylidene)-3-methyl-1*H*-pyrrol-2-amine 8b. ^{1}H NMR (400 MHz, $CDCl_3$)



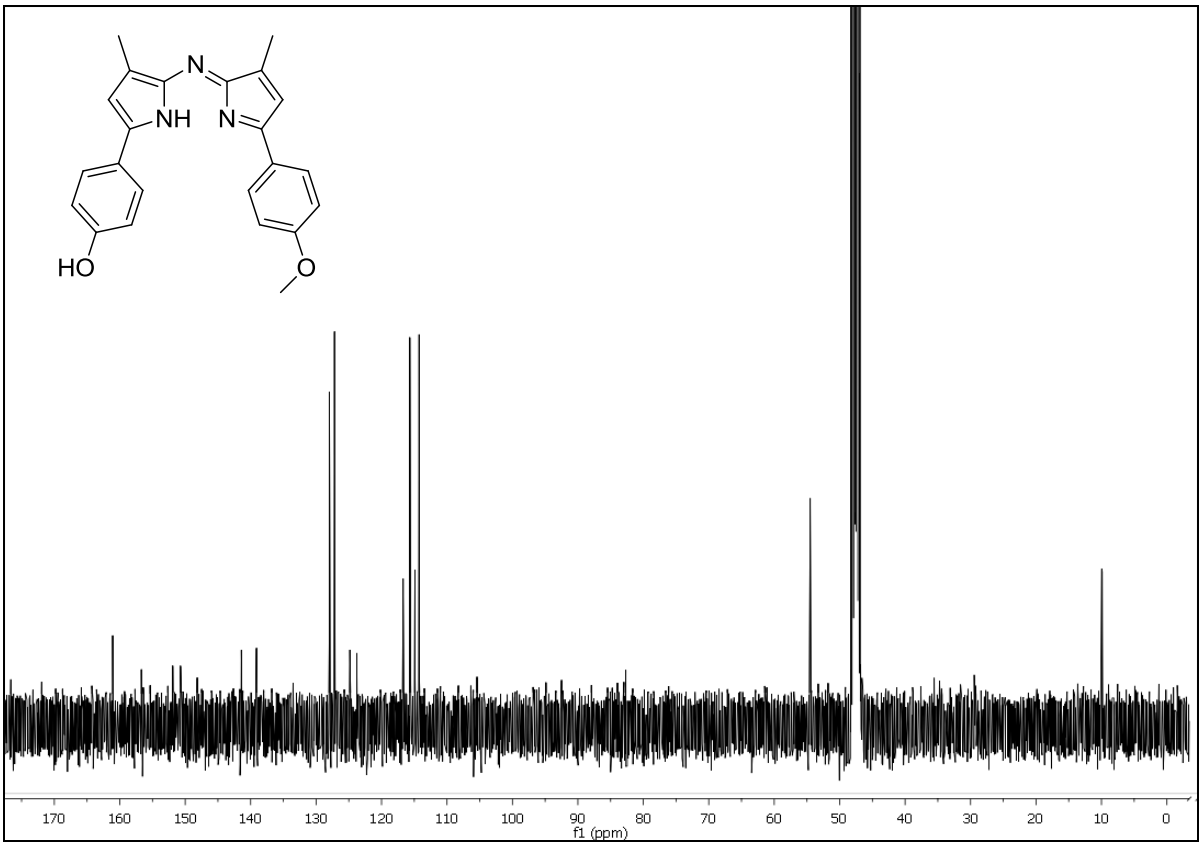
^{13}C NMR (100 MHz, $CDCl_3$)



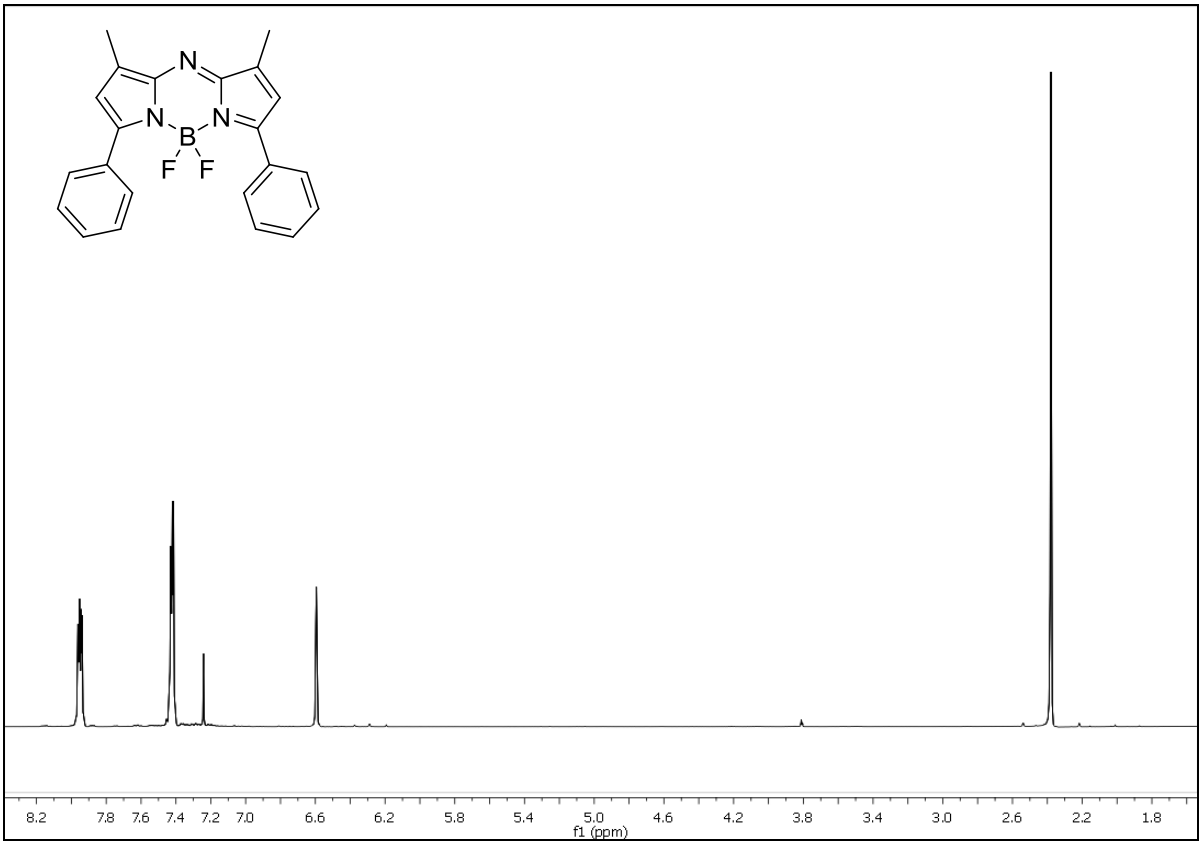
(*Z*)-4-(5-(5-(4-Methoxyphenyl)-3-methyl-2*H*-pyrrol-2-ylideneamino)-4-methyl-1*H*-pyrrol-2-yl)phenol 8c. ^{1}H NMR (400 MHz, CD_3OD)



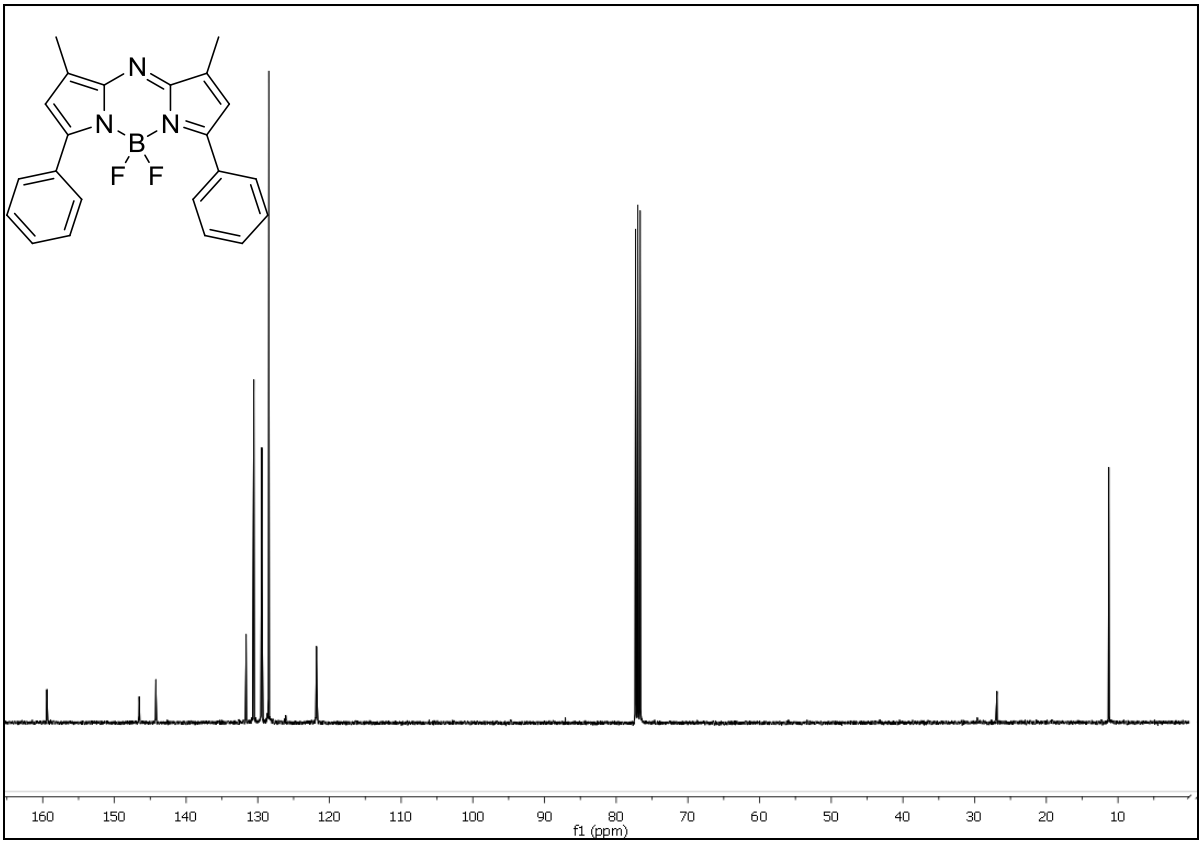
^{13}C NMR (100 MHz, CD_3OD)



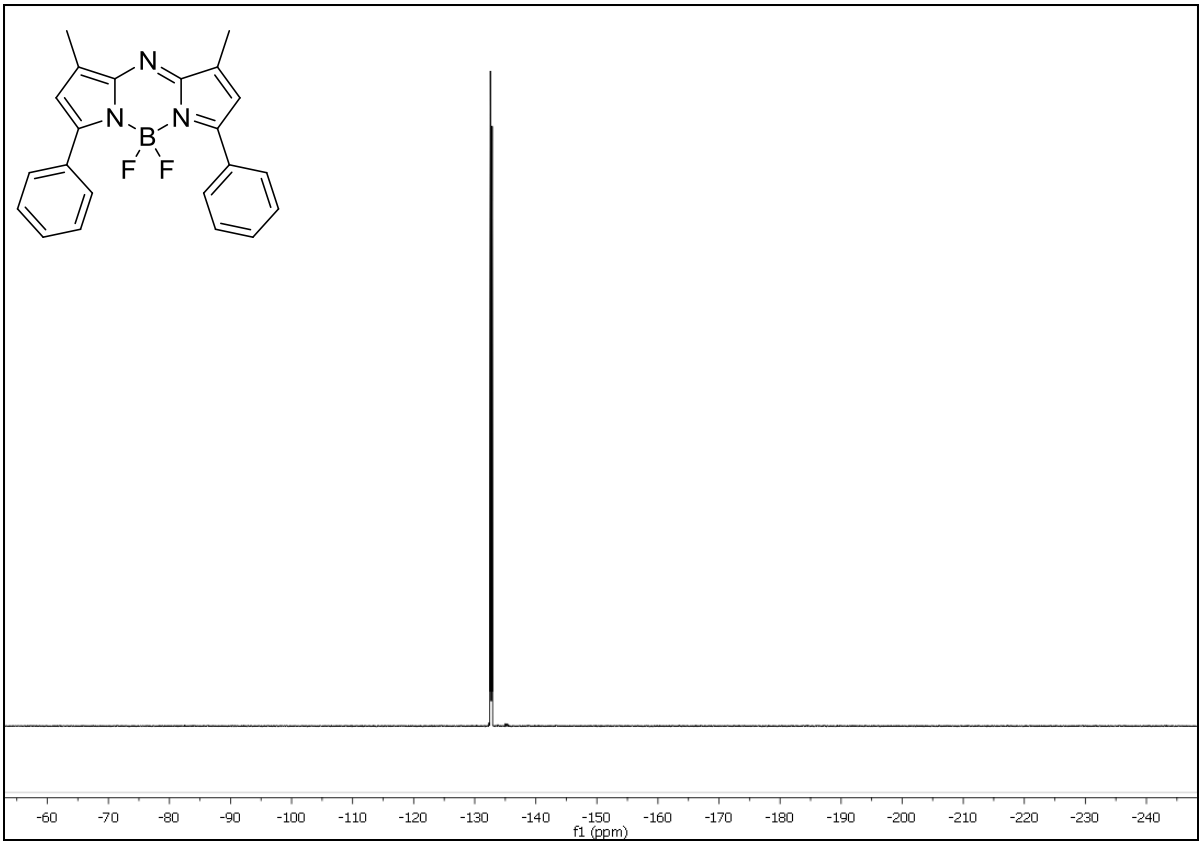
BF_2 chelate of (*Z*)-3-methyl-*N*-(3-methyl-5-phenyl-2*H*-pyrrol-2-ylidene)-5-phenyl-1*H*-pyrrol-2-amine 13a. ^{1}H NMR (400 MHz, $CDCl_3$)



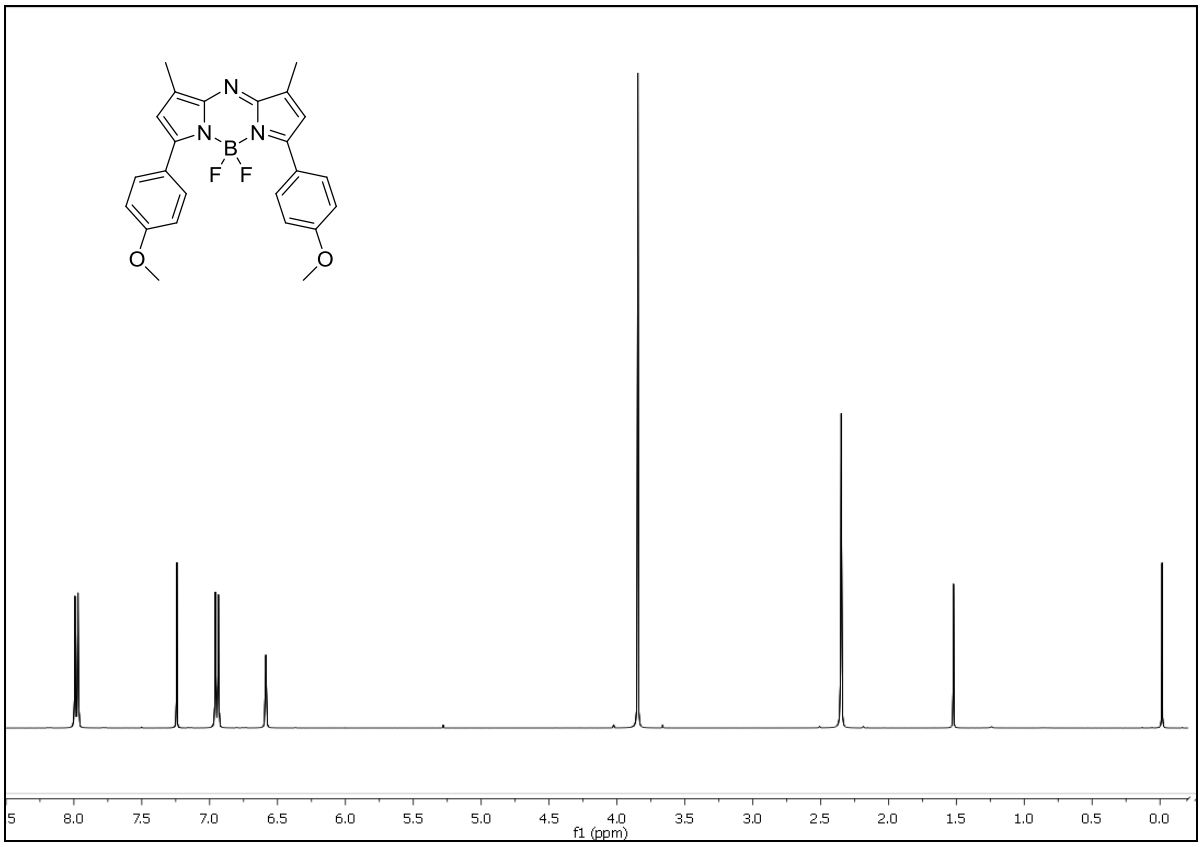
^{13}C NMR (100 MHz, $CDCl_3$)



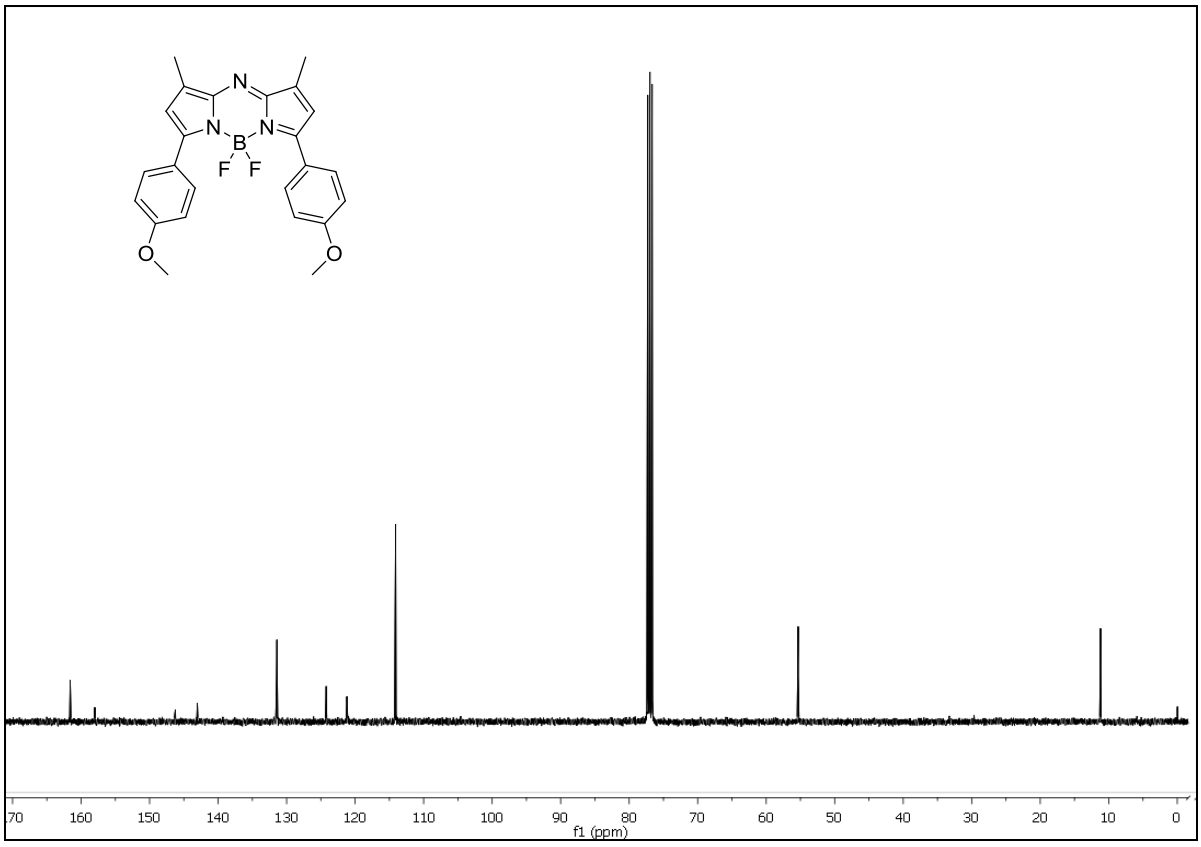
^{19}F NMR (375 MHz, $CDCl_3$)



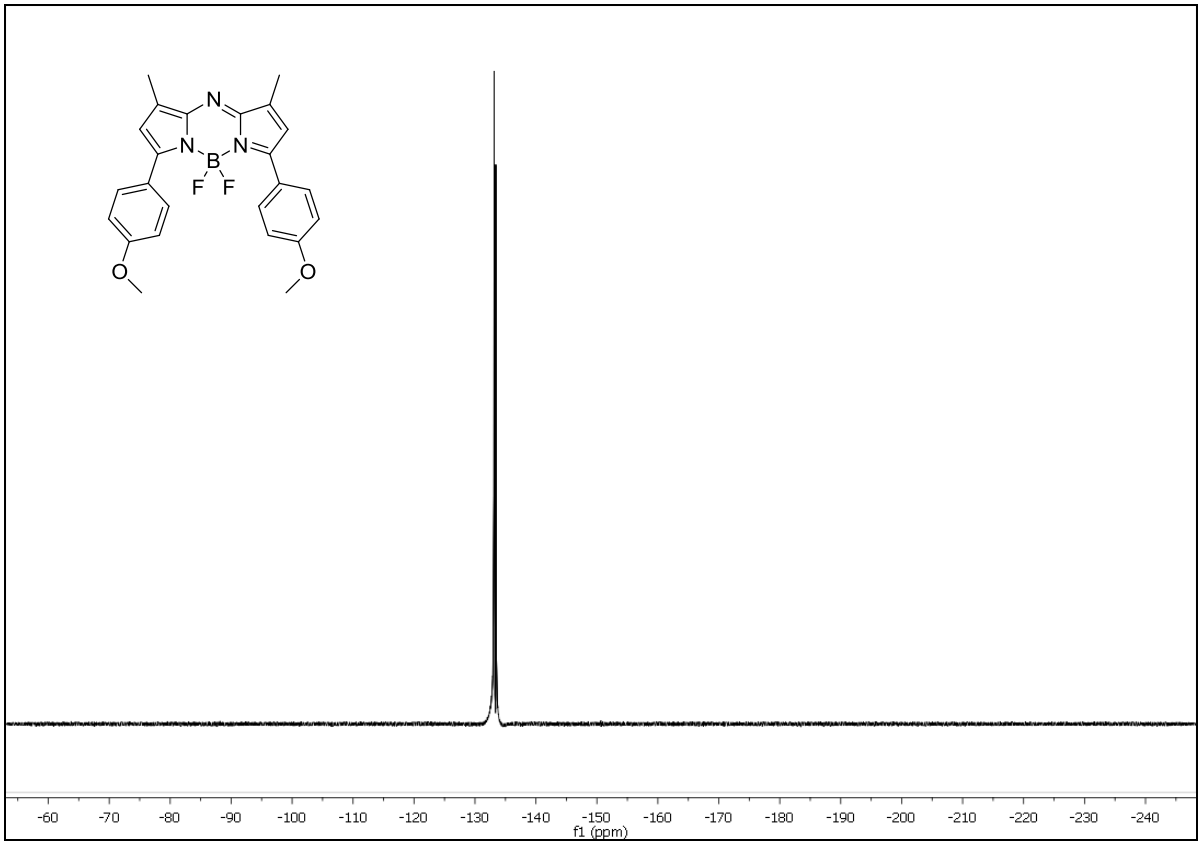
BF_2 chelate of (*Z*)-5-(4-methoxyphenyl)-*N*-(5-(4-methoxyphenyl)-3-methyl-2*H*-pyrrol-2-ylidene)-3-methyl-1*H*-pyrrol-2-amine 13b. ^{1}H NMR (400 MHz, $CDCl_3$)



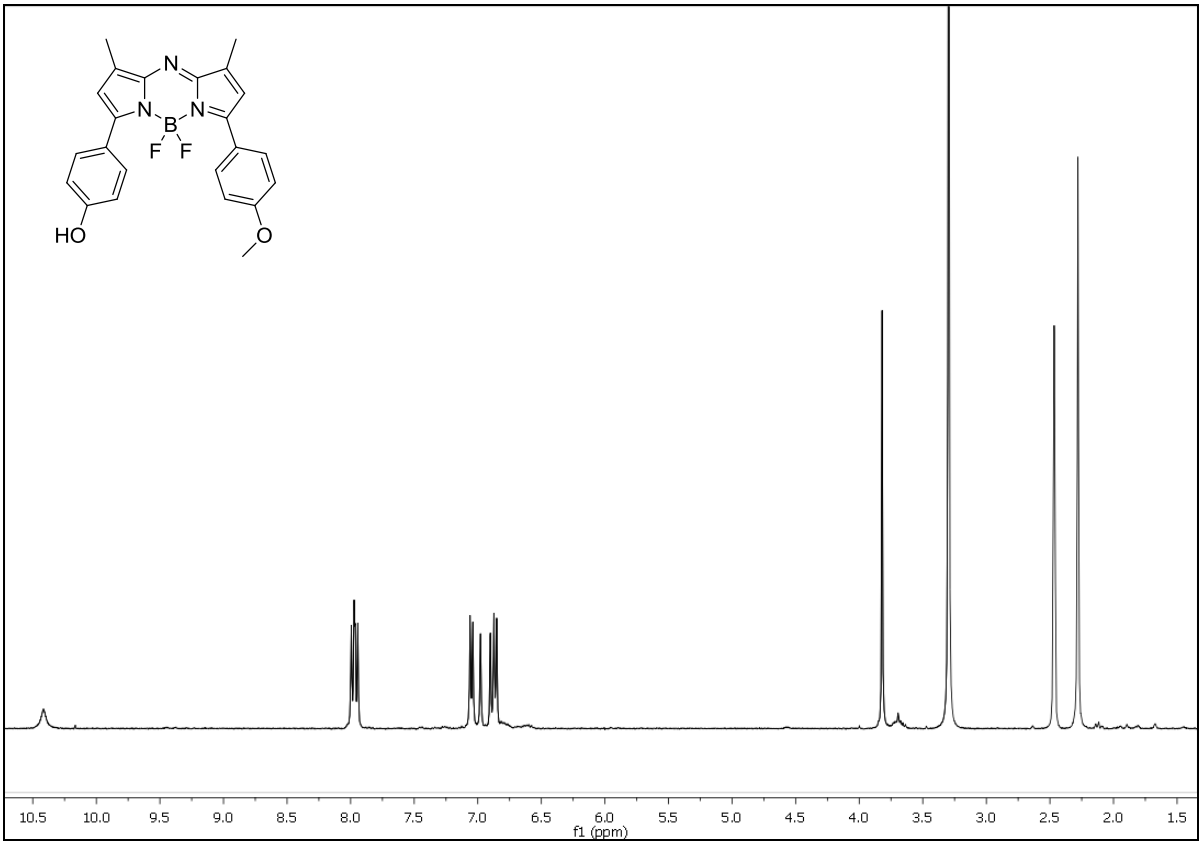
^{13}C NMR (100 MHz, $CDCl_3$)



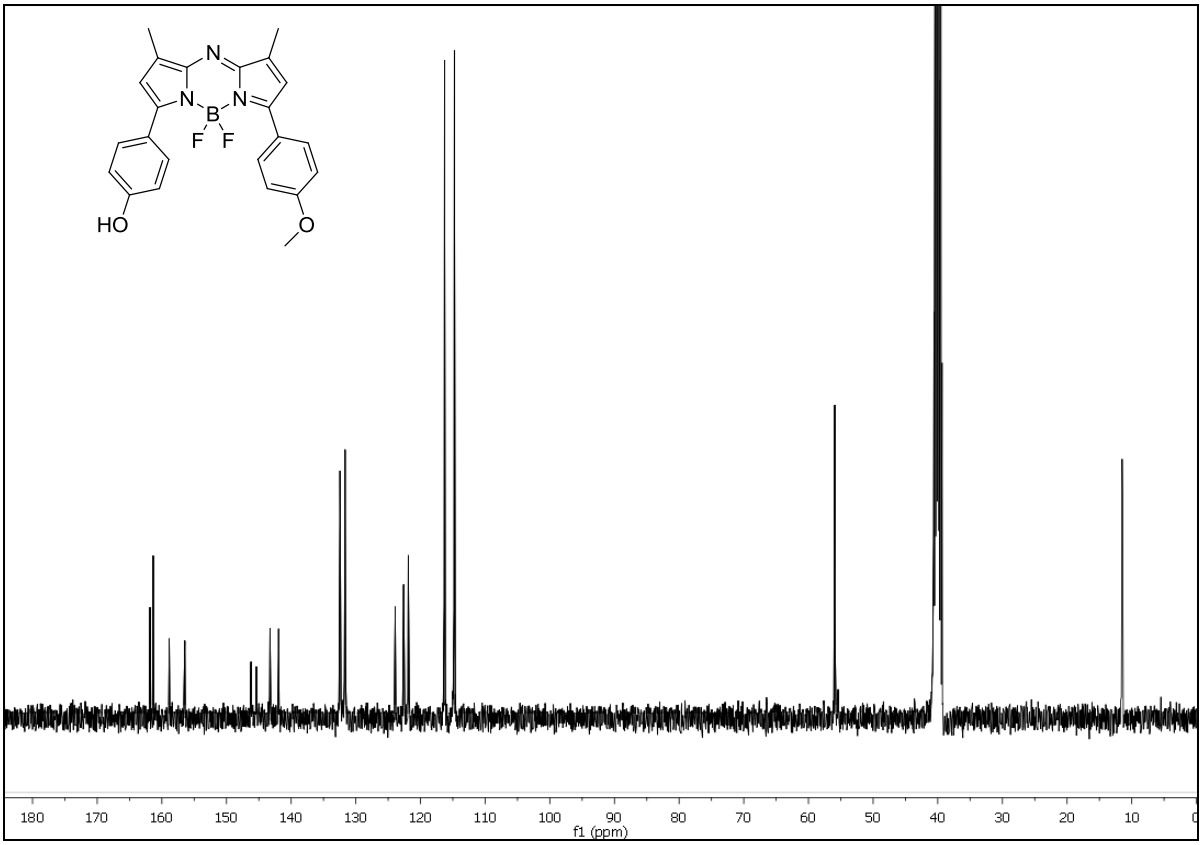
^{19}F NMR (375 MHz, $CDCl_3$)



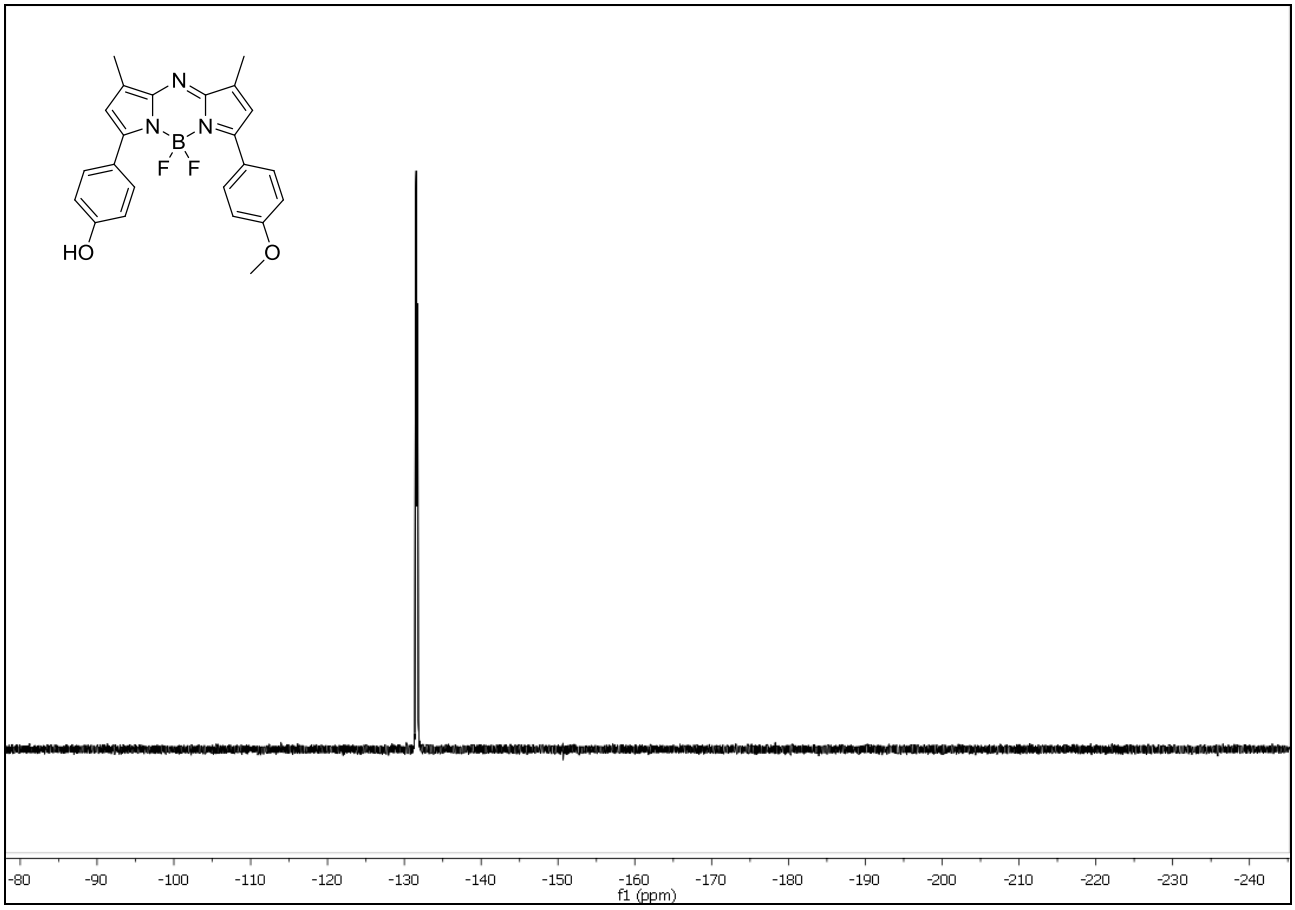
BF_2 chelate of (*Z*)-4-(5-(5-(4-methoxyphenyl)-3-methyl-2*H*-pyrrol-2-ylideneamino)-4-methyl-1*H*-pyrrol-2-yl)phenol 13c. ^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)

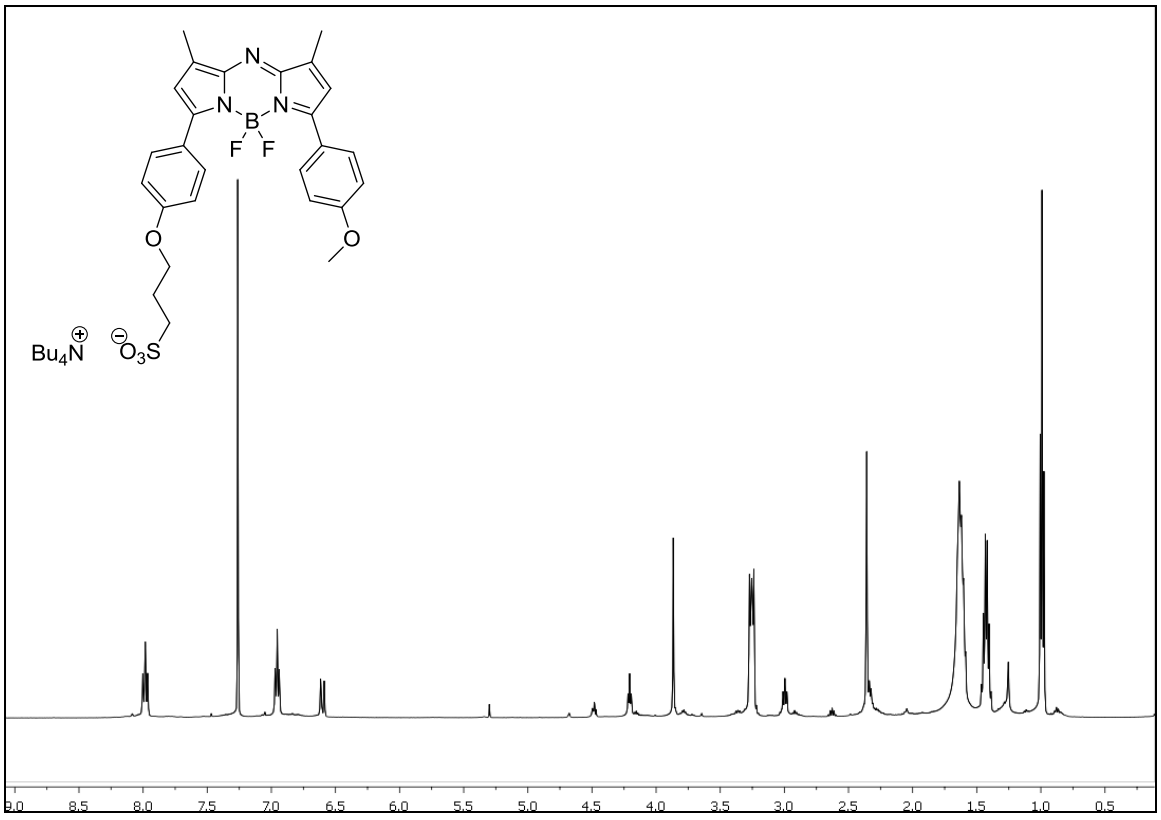


^{19}F NMR (375 MHz, DMSO-d_6)

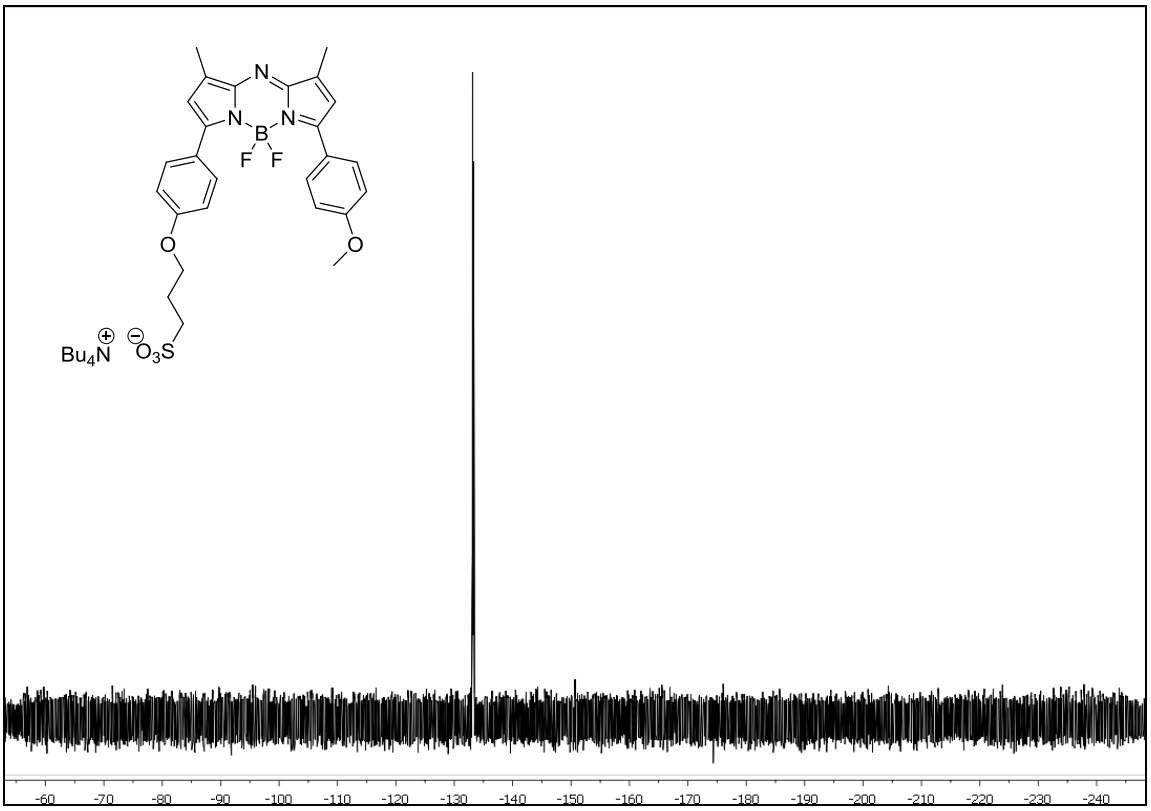


BF_2 chelate of (Z)-3-(4-(5-(5-(4-methoxyphenyl)-3-methyl-2H-pyrrol-2-ylideneamino)-4-methyl-1*H*-pyrrol-2-yl)phenoxy)propane-1-sulfonate 13d.

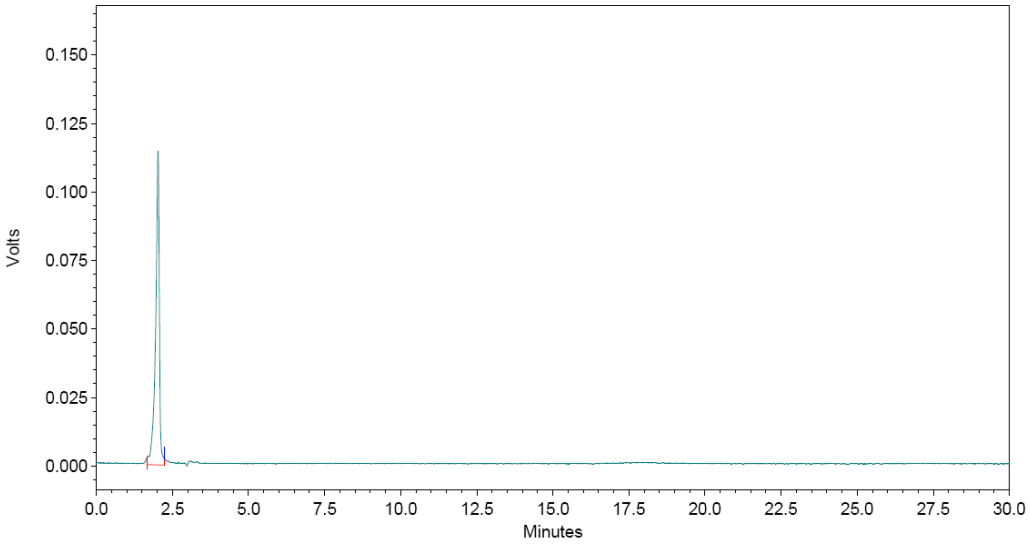
^{1}H NMR (400 MHz, $CDCl_3$)



^{19}F NMR (375 MHz, $CDCl_3$)



HPLC analyses of **13d**



Eluent: 20% H_2O in acetonitrile, flow rate: 0.8ml/min.

Retention times: 2.1 min. Wavelength at 600 (nm).

X-Ray Structural Data for **13b**

Table 1. Crystal data and structure refinement for **13b**.

Identification code	**13b**	
Empirical formula	$C_{24}\,H_{22}\,B\,N_3\,O_2\,F_2$	
Formula weight	433.26	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$ (#14)	
Unit cell dimensions	a = 14.0790(5) Å	α= 90°.
	b = 14.3782(4) Å	β= 91.267(3)°.
	c = 10.0650(3) Å	γ = 90°.
Volume	2036.97(11) $Å^3$	
Z	4	
Density (calculated)	1.413 Mg/m^3	
Absorption coefficient	0.852 mm^{-1}	
F(000)	904	
Crystal size	0.2985 x 0.0571 x 0.0154 mm^3	
Theta range for data collection	3.14 to 66.96°.	
Index ranges	–16<=h<=14, –17<=k<=16, –11<=l<=11	
Reflections collected	14145	
Independent reflections	3561 [R(int) = 0.0429]	
Completeness to theta = 66.96°	98.5 %	
Absorption correction	Analytical	
Max. and min. transmission	0.986 and 0.883	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	3561 / 0 / 293	
Goodness–of–fit on F^2	1.028	
Final R indices [I>2sigma(I)]	R1 = 0.0399, wR2 = 0.0995	
R indices (all data)	R1 = 0.0542, wR2 = 0.1096	
Largest diff. peak and hole	0.222 and –0.207 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **13b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
B	7092(2)	5027(1)	1250(2)	23(1)
F(1)	8032(1)	5310(1)	1409(1)	28(1)
F(2)	6895(1)	4302(1)	2115(1)	29(1)
N(1)	6877(1)	4697(1)	–205(1)	22(1)
C(1)	6195(1)	5135(1)	–1011(2)	22(1)
C(2)	6134(1)	4684(1)	–2266(2)	24(1)
C(5)	5503(1)	4991(1)	–3386(2)	29(1)
C(3)	6764(1)	3955(1)	–2190(2)	25(1)
C(4)	7219(1)	3958(1)	–915(2)	23(1)
C(6)	7900(1)	3257(1)	–457(2)	23(1)
C(7)	8566(1)	3382(1)	579(2)	28(1)
C(8)	9176(1)	2677(1)	988(2)	28(1)
C(9)	9139(1)	1818(1)	360(2)	26(1)
O(1)	9689(1)	1077(1)	705(1)	32(1)

C(12)	10335(1)	1189(1)	1813(2)	32(1)
C(10)	8496(1)	1682(1)	–695(2)	28(1)
C(11)	7892(1)	2384(1)	–1092(2)	26(1)
N(2)	5666(1)	5854(1)	–656(1)	23(1)
C(13)	5795(1)	6218(1)	539(2)	22(1)
C(14)	5376(1)	7060(1)	1000(2)	24(1)
C(17)	4639(1)	7606(1)	254(2)	28(1)
C(15)	5820(1)	7253(1)	2191(2)	25(1)
C(16)	6473(1)	6532(1)	2495(2)	23(1)
N(3)	6448(1)	5891(1)	1493(1)	22(1)
C(18)	7070(1)	6497(1)	3701(2)	23(1)
C(19)	7392(1)	7340(1)	4253(2)	25(1)
C(20)	7952(1)	7357(1)	5399(2)	27(1)
C(21)	8191(1)	6525(1)	6037(2)	25(1)
O(2)	8739(1)	6608(1)	7168(1)	30(1)
C(24)	8887(2)	5785(1)	7942(2)	37(1)
C(22)	7872(1)	5682(1)	5516(2)	26(1)
C(23)	7322(1)	5674(1)	4354(2)	26(1)

Table 3. Bond lengths [Å] and angles [°] for **13b**.

B–F(1)	1.390(2)
B–F(2)	1.391(2)
B–N(3)	1.560(2)
B–N(1)	1.562(2)
N(1)–C(4)	1.374(2)
N(1)–C(1)	1.393(2)
C(1)–N(2)	1.328(2)
C(1)–C(2)	1.420(2)
C(2)–C(3)	1.373(3)
C(2)–C(5)	1.487(3)
C(5)–H(5A)	0.9800
C(5)–H(5B)	0.9800
C(5)–H(5C)	0.9800
C(3)–C(4)	1.422(2)
C(3)–H(3)	0.9500
C(4)–C(6)	1.459(3)
C(6)–C(7)	1.399(3)
C(6)–C(11)	1.409(2)
C(7)–C(8)	1.385(3)
C(7)–H(7)	0.9500
C(8)–C(9)	1.387(3)
C(8)–H(8)	0.9500
C(9)–O(1)	1.358(2)
C(9)–C(10)	1.394(3)
O(1)–C(12)	1.433(2)
C(12)–H(12A)	0.9800
C(12)–H(12B)	0.9800
C(12)–H(12C)	0.9800
C(10)–C(11)	1.374(3)
C(10)–H(10)	0.9500
C(11)–H(11)	0.9500
N(2)–C(13)	1.320(2)
C(13)–N(3)	1.397(2)
C(13)–C(14)	1.428(2)

C(14)–C(15)	1.368(3)
C(14)–C(17)	1.491(3)
C(17)–H(17A)	0.9800
C(17)–H(17B)	0.9800
C(17)–H(17C)	0.9800
C(15)–C(16)	1.415(3)
C(15)–H(15)	0.9500
C(16)–N(3)	1.367(2)
C(16)–C(18)	1.462(3)
C(18)–C(23)	1.396(2)
C(18)–C(19)	1.404(2)
C(19)–C(20)	1.383(3)
C(19)–H(19)	0.9500
C(20)–C(21)	1.395(3)
C(20)–H(20)	0.9500
C(21)–O(2)	1.367(2)
C(21)–C(22)	1.390(3)
O(2)–C(24)	1.429(2)
C(24)–H(24A)	0.9800
C(24)–H(24B)	0.9800
C(24)–H(24C)	0.9800
C(22)–C(23)	1.388(3)
C(22)–H(22)	0.9500
C(23)–H(23)	0.9500

F(1)–B–F(2)	110.51(15)
F(1)–B–N(3)	107.73(14)
F(2)–B–N(3)	111.97(15)
F(1)–B–N(1)	111.19(15)
F(2)–B–N(1)	108.72(14)
N(3)–B–N(1)	106.67(14)
C(4)–N(1)–C(1)	106.90(14)
C(4)–N(1)–B	131.24(15)
C(1)–N(1)–B	121.75(14)
N(2)–C(1)–N(1)	125.29(15)
N(2)–C(1)–C(2)	124.83(16)
N(1)–C(1)–C(2)	109.87(15)
C(3)–C(2)–C(1)	105.79(16)
C(3)–C(2)–C(5)	129.98(16)
C(1)–C(2)–C(5)	124.23(16)
C(2)–C(5)–H(5A)	109.5
C(2)–C(5)–H(5B)	109.5
H(5A)–C(5)–H(5B)	109.5
C(2)–C(5)–H(5C)	109.5
H(5A)–C(5)–H(5C)	109.5
H(5B)–C(5)–H(5C)	109.5
C(2)–C(3)–C(4)	109.02(15)
C(2)–C(3)–H(3)	125.5
C(4)–C(3)–H(3)	125.5
N(1)–C(4)–C(3)	108.38(15)
N(1)–C(4)–C(6)	127.28(16)
C(3)–C(4)–C(6)	124.29(15)
C(7)–C(6)–C(11)	116.85(16)
C(7)–C(6)–C(4)	124.89(15)
C(11)–C(6)–C(4)	118.26(16)
C(8)–C(7)–C(6)	121.88(16)

C(8)–C(7)–H(7)	119.1
C(6)–C(7)–H(7)	119.1
C(7)–C(8)–C(9)	120.00(17)
C(7)–C(8)–H(8)	120.0
C(9)–C(8)–H(8)	120.0
O(1)–C(9)–C(8)	124.54(17)
O(1)–C(9)–C(10)	116.20(15)
C(8)–C(9)–C(10)	119.26(16)
C(9)–O(1)–C(12)	117.33(14)
O(1)–C(12)–H(12A)	109.5
O(1)–C(12)–H(12B)	109.5
H(12A)–C(12)–H(12B)	109.5
O(1)–C(12)–H(12C)	109.5
H(12A)–C(12)–H(12C)	109.5
H(12B)–C(12)–H(12C)	109.5
C(11)–C(10)–C(9)	120.41(16)
C(11)–C(10)–H(10)	119.8
C(9)–C(10)–H(10)	119.8
C(10)–C(11)–C(6)	121.58(18)
C(10)–C(11)–H(11)	119.2
C(6)–C(11)–H(11)	119.2
C(13)–N(2)–C(1)	119.18(15)
N(2)–C(13)–N(3)	124.59(15)
N(2)–C(13)–C(14)	125.65(16)
N(3)–C(13)–C(14)	109.40(15)
C(15)–C(14)–C(13)	105.84(15)
C(15)–C(14)–C(17)	129.30(16)
C(13)–C(14)–C(17)	124.80(16)
C(14)–C(17)–H(17A)	109.5
C(14)–C(17)–H(17B)	109.5
H(17A)–C(17)–H(17B)	109.5
C(14)–C(17)–H(17C)	109.5
H(17A)–C(17)–H(17C)	109.5
H(17B)–C(17)–H(17C)	109.5
C(14)–C(15)–C(16)	108.86(15)
C(14)–C(15)–H(15)	125.6
C(16)–C(15)–H(15)	125.6
N(3)–C(16)–C(15)	109.16(15)
N(3)–C(16)–C(18)	126.49(15)
C(15)–C(16)–C(18)	124.35(15)
C(16)–N(3)–C(13)	106.65(14)
C(16)–N(3)–B	130.31(15)
C(13)–N(3)–B	122.45(14)
C(23)–C(18)–C(19)	118.00(16)
C(23)–C(18)–C(16)	123.75(15)
C(19)–C(18)–C(16)	118.24(15)
C(20)–C(19)–C(18)	121.17(16)
C(20)–C(19)–H(19)	119.4
C(18)–C(19)–H(19)	119.4
C(19)–C(20)–C(21)	119.74(16)

C(19)–C(20)–H(20)	120.1
C(21)–C(20)–H(20)	120.1
O(2)–C(21)–C(22)	124.16(16)
O(2)–C(21)–C(20)	115.72(15)
C(22)–C(21)–C(20)	120.11(17)
C(21)–O(2)–C(24)	117.04(14)
O(2)–C(24)–H(24A)	109.5
O(2)–C(24)–H(24B)	109.5
H(24A)–C(24)–H(24B)	109.5
O(2)–C(24)–H(24C)	109.5
H(24A)–C(24)–H(24C)	109.5
H(24B)–C(24)–H(24C)	109.5
C(23)–C(22)–C(21)	119.61(16)
C(23)–C(22)–H(22)	120.2
C(21)–C(22)–H(22)	120.2
C(22)–C(23)–C(18)	121.36(16)
C(22)–C(23)–H(23)	119.3
C(18)–C(23)–H(23)	119.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **13b**. The anisotropic displacement factor exponent takes the form: $–2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B	30(1)	17(1)	23(1)	–1(1)	–3(1)	1(1)
F(1)	31(1)	22(1)	31(1)	–7(1)	–6(1)	2(1)
F(2)	45(1)	17(1)	23(1)	2(1)	–4(1)	2(1)
N(1)	28(1)	15(1)	23(1)	1(1)	–2(1)	0(1)
C(1)	27(1)	15(1)	24(1)	4(1)	–3(1)	–3(1)
C(2)	32(1)	16(1)	25(1)	3(1)	–4(1)	–5(1)
C(5)	40(1)	22(1)	25(1)	1(1)	–8(1)	–1(1)
C(3)	33(1)	18(1)	23(1)	–1(1)	–3(1)	–3(1)
C(4)	30(1)	17(1)	22(1)	0(1)	0(1)	–3(1)
C(6)	29(1)	18(1)	23(1)	0(1)	0(1)	–1(1)
C(7)	35(1)	20(1)	27(1)	–4(1)	–4(1)	3(1)
C(8)	32(1)	25(1)	26(1)	–2(1)	–5(1)	1(1)
C(9)	28(1)	20(1)	30(1)	3(1)	1(1)	2(1)
O(1)	36(1)	20(1)	39(1)	0(1)	–8(1)	6(1)
C(12)	31(1)	29(1)	35(1)	6(1)	–6(1)	2(1)
C(10)	35(1)	18(1)	31(1)	–5(1)	–2(1)	1(1)
C(11)	31(1)	22(1)	26(1)	–2(1)	–1(1)	–1(1)
N(2)	29(1)	14(1)	26(1)	3(1)	–2(1)	–3(1)
C(13)	26(1)	17(1)	24(1)	3(1)	–2(1)	–3(1)
C(14)	27(1)	18(1)	27(1)	3(1)	3(1)	–2(1)
C(17)	34(1)	20(1)	30(1)	3(1)	0(1)	4(1)
C(15)	33(1)	17(1)	25(1)	–1(1)	2(1)	0(1)
C(16)	28(1)	17(1)	24(1)	1(1)	3(1)	–2(1)
N(3)	28(1)	16(1)	22(1)	2(1)	–2(1)	–1(1)
C(18)	28(1)	21(1)	21(1)	0(1)	1(1)	2(1)
C(19)	30(1)	19(1)	27(1)	–1(1)	3(1)	2(1)

C(20)	33(1)	19(1)	28(1)	–5(1)	3(1)	0(1)
C(21)	29(1)	25(1)	22(1)	–4(1)	1(1)	0(1)
O(2)	40(1)	24(1)	25(1)	–3(1)	–6(1)	–1(1)
C(24)	52(1)	29(1)	31(1)	1(1)	–13(1)	–2(1)
C(22)	36(1)	19(1)	24(1)	1(1)	0(1)	0(1)
C(23)	34(1)	20(1)	24(1)	–2(1)	0(1)	–1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **13b**.

Atom	x	y	z	U(eq)
H(5A)	5759	5559	–3777	44
H(5B)	4865	5113	–3056	44
H(5C)	5469	4501	–4062	44
H(3)	6877	3520	–2878	30
H(7)	8602	3967	1016	33
H(8)	9619	2781	1697	34
H(12A)	10773	1702	1635	48
H(12B)	10697	614	1950	48
H(12C)	9977	1329	2613	48
H(10)	8476	1100	–1142	34
H(11)	7458	2278	–1813	31
H(17A)	4243	7941	883	42
H(17B)	4241	7184	–282	42
H(17C)	4949	8053	–330	42
H(15)	5709	7785	2725	30
H(19)	7221	7909	3832	30
H(20)	8173	7932	5751	32
H(24A)	8271	5517	8169	56
H(24B)	9243	5942	8759	56
H(24C)	9248	5333	7428	56
H(22)	8030	5115	5953	32
H(23)	7113	5096	3996	31

Table 6. Torsion angles [°] for **13b**.

F(1)–B–N(1)–C(4)	65.0(2)
F(2)–B–N(1)–C(4)	–56.8(2)
N(3)–B–N(1)–C(4)	–177.77(16)
F(1)–B–N(1)–C(1)	–119.13(16)
F(2)–B–N(1)–C(1)	118.98(16)
N(3)–B–N(1)–C(1)	–1.9(2)
C(4)–N(1)–C(1)–N(2)	176.50(16)
B–N(1)–C(1)–N(2)	–0.2(2)
C(4)–N(1)–C(1)–C(2)	–2.19(18)
B–N(1)–C(1)–C(2)	–178.91(14)
N(2)–C(1)–C(2)–C(3)	–176.93(16)
N(1)–C(1)–C(2)–C(3)	1.77(19)
N(2)–C(1)–C(2)–C(5)	3.6(3)
N(1)–C(1)–C(2)–C(5)	–177.71(16)
C(1)–C(2)–C(3)–C(4)	–0.67(19)
C(5)–C(2)–C(3)–C(4)	178.77(18)
C(1)–N(1)–C(4)–C(3)	1.73(18)

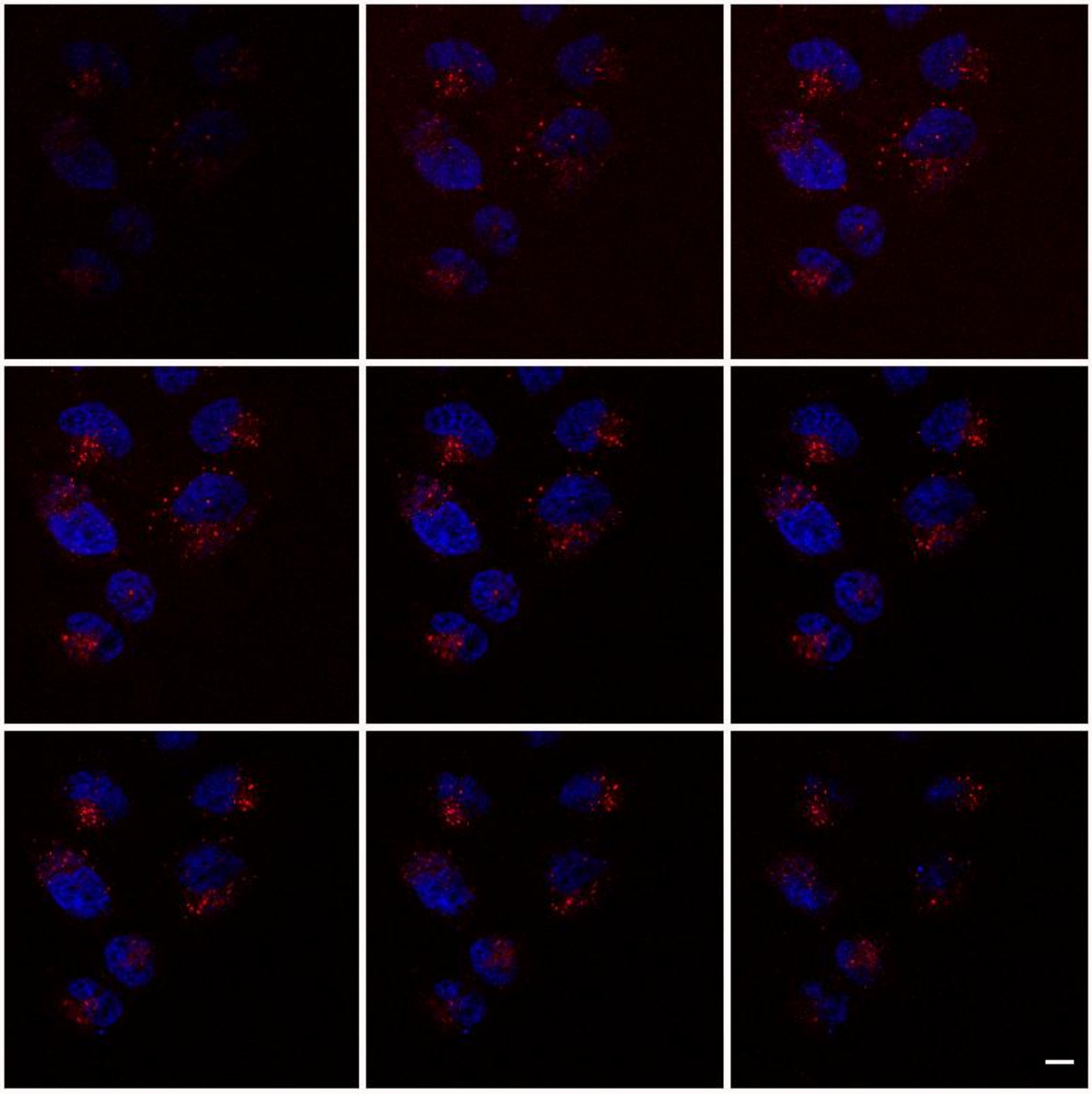
B–N(1)–C(4)–C(3)	178.03(16)
C(1)–N(1)–C(4)–C(6)	–175.81(16)
B–N(1)–C(4)–C(6)	0.5(3)
C(2)–C(3)–C(4)–N(1)	–0.66(19)
C(2)–C(3)–C(4)–C(6)	176.97(16)
N(1)–C(4)–C(6)–C(7)	–23.9(3)
C(3)–C(4)–C(6)–C(7)	158.97(18)
N(1)–C(4)–C(6)–C(11)	155.80(17)
C(3)–C(4)–C(6)–C(11)	–21.4(3)
C(11)–C(6)–C(7)–C(8)	–1.5(3)
C(4)–C(6)–C(7)–C(8)	178.19(17)
C(6)–C(7)–C(8)–C(9)	0.3(3)
C(7)–C(8)–C(9)–O(1)	–178.38(17)
C(7)–C(8)–C(9)–C(10)	1.1(3)
C(8)–C(9)–O(1)–C(12)	1.4(3)
C(10)–C(9)–O(1)–C(12)	–178.08(16)
O(1)–C(9)–C(10)–C(11)	178.24(16)
C(8)–C(9)–C(10)–C(11)	–1.3(3)
C(9)–C(10)–C(11)–C(6)	0.1(3)
C(7)–C(6)–C(11)–C(10)	1.3(3)
C(4)–C(6)–C(11)–C(10)	–178.39(17)
N(1)–C(1)–N(2)–C(13)	2.0(2)
C(2)–C(1)–N(2)–C(13)	–179.52(16)
C(1)–N(2)–C(13)–N(3)	–1.1(2)
C(1)–N(2)–C(13)–C(14)	171.20(16)
N(2)–C(13)–C(14)–C(15)	–170.12(17)
N(3)–C(13)–C(14)–C(15)	3.20(19)
N(2)–C(13)–C(14)–C(17)	7.3(3)
N(3)–C(13)–C(14)–C(17)	–179.38(15)
C(13)–C(14)–C(15)–C(16)	–2.30(19)
C(17)–C(14)–C(15)–C(16)	–179.56(17)
C(14)–C(15)–C(16)–N(3)	0.6(2)
C(14)–C(15)–C(16)–C(18)	–179.30(16)
C(15)–C(16)–N(3)–C(13)	1.37(18)
C(18)–C(16)–N(3)–C(13)	–178.70(16)
C(15)–C(16)–N(3)–B	172.51(16)
C(18)–C(16)–N(3)–B	–7.6(3)
N(2)–C(13)–N(3)–C(16)	170.58(16)
C(14)–C(13)–N(3)–C(16)	–2.83(18)
N(2)–C(13)–N(3)–B	–1.4(2)
C(14)–C(13)–N(3)–B	–174.82(15)
F(1)–B–N(3)–C(16)	–47.8(2)
F(2)–B–N(3)–C(16)	73.9(2)
N(1)–B–N(3)–C(16)	–167.23(15)
F(1)–B–N(3)–C(13)	122.15(16)
F(2)–B–N(3)–C(13)	–116.13(17)
N(1)–B–N(3)–C(13)	2.7(2)
N(3)–C(16)–C(18)–C(23)	–34.2(3)
C(15)–C(16)–C(18)–C(23)	145.70(18)
N(3)–C(16)–C(18)–C(19)	147.31(17)
C(15)–C(16)–C(18)–C(19)	–32.8(3)
C(23)–C(18)–C(19)–C(20)	0.9(3)
C(16)–C(18)–C(19)–C(20)	179.43(16)
C(18)–C(19)–C(20)–C(21)	–1.2(3)
C(19)–C(20)–C(21)–O(2)	–179.44(16)
C(19)–C(20)–C(21)–C(22)	0.5(3)

C(22)–C(21)–O(2)–C(24)	–8.3(3)
C(20)–C(21)–O(2)–C(24)	171.64(17)
O(2)–C(21)–C(22)–C(23)	–179.62(16)
C(20)–C(21)–C(22)–C(23)	0.5(3)
C(21)–C(22)–C(23)–C(18)	–0.8(3)
C(19)–C(18)–C(23)–C(22)	0.1(3)
C(16)–C(18)–C(23)–C(22)	–178.37(17)

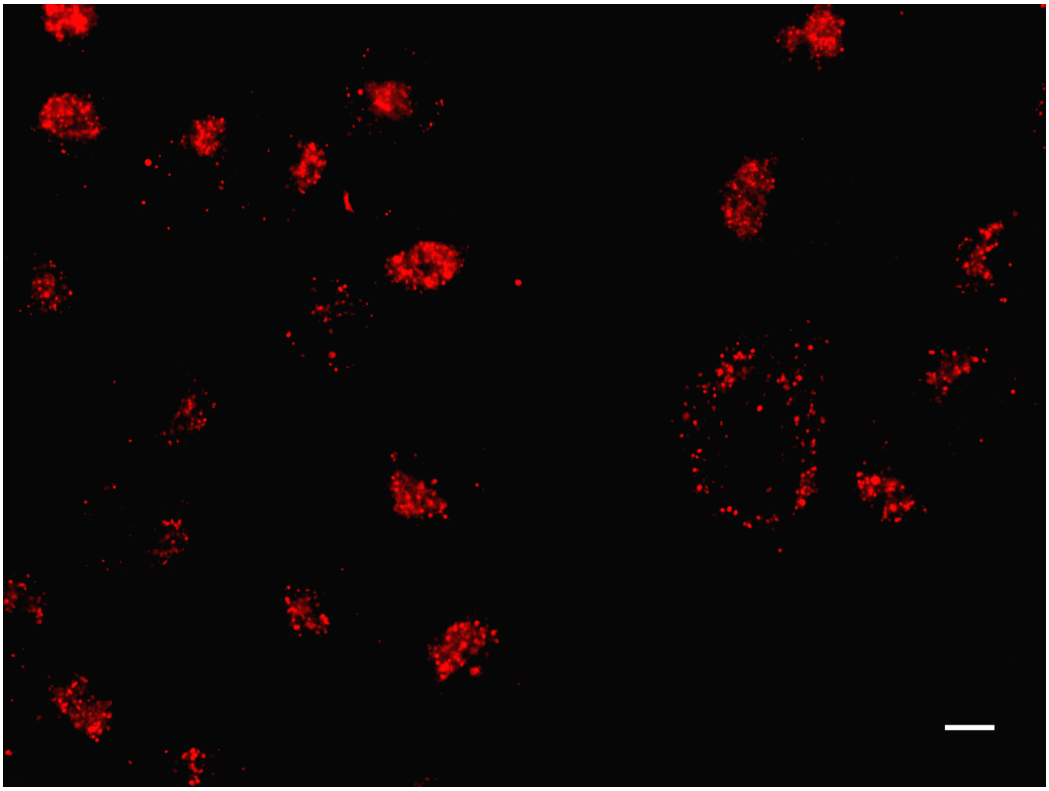
Symmetry transformations used to generate equivalent atoms:

Figure S2: Confocal Z-Stack Imaging of 13d in HeLa cells

Individual cellular focal plane sections showing localization of 13d (red color) and nuclei (blue color) with DAPI.



Confocal Imaging of 13d (red color) in HeLa cells



Confocal Imaging of 13d in HeLa cells
Localization of 13d (red color) and nuclei (blue color) with DAPI.