Supplementary Information

A Mild Synthetic Route to Diaryl α-Nitroso Pyrroles

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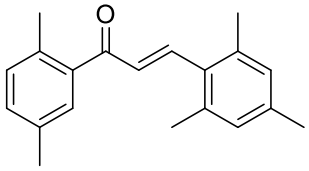
Experimental Procedures

All NMR spectra were recorded using a 500 MHz spectrometer unless otherwise noted. ^{1}H chemical shifts are reported in ppm relative to tetramethylsilane using the residual solvent signal as an internal standard. Coupling constants are given in the units of Hz. ^{13}C NMR spectra were recorded using the proton decoupled UDEFT pulse sequence, and chemical shifts are reported in ppm using the residual solvent signal as an internal standard. ^{19}F NMR spectra were recorded using a proton decoupled pulse and chemical shifts are reported in ppm. All chemicals and solvents were purchased and used as received unless otherwise indicated. Note that for best results the $NOBF_4$ must be of high quality and stored in a freezer under N_2. Thin-layer chromatography was performed on commercially prepared silica plates and column chromatography was performed using 320-400 mesh silica. Solutions of air and moisture-sensitive compounds were introduced via syringe under inert conditions, unless otherwise noted. Mass spectra were obtained using TOF and LCQ Duo ion trap instruments operating in ESI+/- or APCI-mode, as indicated.

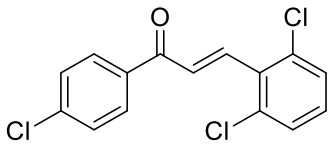
Chalcones

Chalcones **1a**,[1] **1b**,[2] **1d**,[3] **1g**,[4] **1h**,[5] **1i**,[6] **1j**,[7] **1k**,[7] **1m**,[1] **1n**,[1] **1o**,[8] **1p**,[9] and **1q**,[1] were synthesised according to literature procedures.

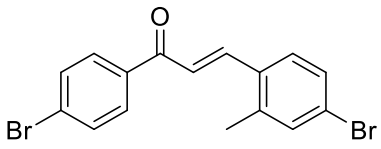
General Procedure 1 (GP1) for the synthesis of Chalcones, 1a-q Modifying a reported procedure,[1] potassium hydroxide (58.3 mmol, 2.5 eq.) was added to a stirring solution of a benzaldehyde (23.3 mmol, 1 eq.) and acetophenone (23.3 mmol, 1 eq.) in methanol (20 mL). The reaction mixture was stirred at room temperature for 1 h. The resulting precipitate was isolated via filtration, washed with methanol and cold pentane, and then dried under vacuum to afford the desired chalcone.



(E)-1-(2,5-Dimethylphenyl)-3-(2,4,6-trimethylphenyl)-2-propen-1-one (1c) The title compound was synthesised from 2,4,6-trimethylbenzaldehyde and 2,5-dimethylacetophenone according to GP1 and was isolated as a yellow solid (5.1 g, 78%).^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.62 (d, *J* = 16.4 Hz, 1H), 7.28 (s, 1H), 7.11-7.19 (m, 2H), 6.90 (s, 2H), 6.73 (d, *J* = 16.4 Hz, 1H), 2.41 (s, 3H), 2.33 (s, 3H), 2.32 (s, 6H), 2.27 (s, 3H). $^{13}C\{^{1}H\}$ NMR (125 Hz, $CDCl_3$) δ: 196.9, 144.6, 139.1, 138.8, 137.1, 135.1, 133.9, 131.9, 131.3, 129.4, 128.8, 21.3, 21.2, 21.0, 19.9, two signals missing. HRMS-ESI (*m/z*): $[M + Na]^+$ calc'd for $C_{20}H_{22}NaO$ 301.1563, found 301.1559.



(E)-1-(4-Chlorophenyl)-3-(2,6-dichlorophenyl)-2-propen-1-one (1e) The title compound was synthesised from 2,6-dichlorobenzaldehyde and 4-chloroacetophenone, according to GP1, and was isolated as a yellow solid (4.79 g, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: = 7.96 (d, *J* = 8.6 Hz, 2H), 7.85 (d, *J* = 16.0 Hz, 1H), 7.62 (d, *J* = 16.0 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 8.1 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (125 Hz, $CDCl_3$) δ: 189.1, 139.7, 138.4, 136.1, 135.3, 132.5, 130.2, 130.0, 130.1, 129.1, 129.0. HRMS-ESI$^+$ (m/z): $[M + Na]^+$ calc'd for $C_{15}H_9Cl_3NaO$ 332.9617, found 332.9611.

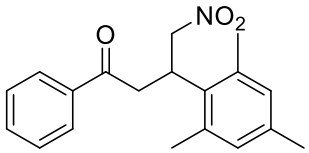


(E)-1-(4-Bromo-, 2 methylphenyl)-3-(2,4,6-trimethylphenyl)-2-propen-1-one (1f) According to a modified version of GP1, the title compound was synthesised from 4-bromo-2-methylbenzaldehyde (5.02 mmol) and 4'-bromoacetophenone (5.02 mmol) and was isolated as a yellow solid (1.71 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 15.6 Hz, 1H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.35-7.43 (m, 3H), 2.45 (s, 3H). $^{13}C\{^{1}H\}$ NMR (125 Hz, $CDCl_3$) δ: 189.1, 141.8, 140.5, 136.9, 134.0, 132.8, 132.1, 130.2, 129.7, 128.2, 127.9, 124.8, 122.9, 19.8. HRMS-ESI$^+$ (*m/z*): $[M + Na]^+$ calc'd for $C_{16}H_{12}Br_2NaO$ 400.9147, found 400.9150.

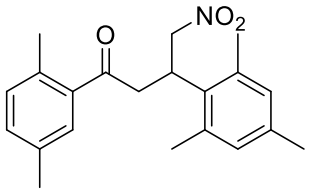
4-Nitrobutan-1-ones

4-Nitrobutan-1-ones **2a**,[1] **2d**,[10] **2h**,[11] **2i**,[10] **2m**,[1] **2n**,[1] **2o**,[12] **2p**,[13] and **2q**[1] were synthesised according to literature procedures.

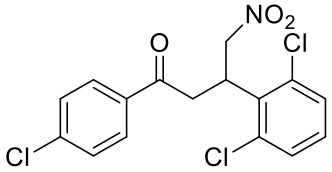
General procedure 2 (GP2) for the synthesis of nitrobutan-1-ones (2a-q) Modifying a reported procedure,[1] a solution of 1,3-diarylpropenone **1a-p** (6 mmol, 1 eq.) in ethanol (20 mL) was added 1,8-diazabicyclo(5.4.0)undec-7-ene (30 mmol, 5 eq.) and nitromethane (30 mmol, 5 eq.). The mixture was then heated at 65 ℃ for 1 h before being allowed to cool to room temperature. The solution was acidified to pH 2 with 1 M hydrochloric acid, and then extracted with CH_2Cl_2 (2x100 mL). The aqueous layer was back-extracted with a further portion of CH_2Cl_2 (100 mL), and the combined organic fractions were washed with water (100 mL) and brine (100 mL), then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and the resulting oil purified by column chromatography on silica (5→100% ethyl acetate in hexanes) to provide the desired product.



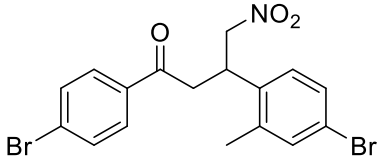
4-Nitro-1-phenyl-3-(2,4,6-trimethylphenyl)butan-1-one (2b) The title compound was synthesised from **1b**,[2] according to GP2, and was isolated as an orange oil (1.37 g, 74%). NMR data was in accordance with literature.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.92-7.98 (m, 2H), 7.55-7.60 (m, 1H), 7.43-7.49 (m, 2H), 6.86 (m, 2H), 4.84-4.99 (m, 2H), 4.72-4.81 (dd, *J* = 12.0 Hz, 8.1 Hz, 1H), 3.46-3.62 (m, 2H), 2.47 (s, 6H), 2.26 (s, 3H).



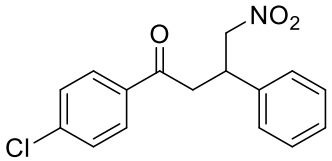
1-(2,5-Dimethylphenyl)-4-nitro-3-(2,4,6-trimethylphenyl)butan-1-one (2c) The title compound was synthesised from **1c**, according to GP2, and was isolated as a white crystalline solid (1.28 g, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (s, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H) 6.78-6.85 (m, 2H), 4.82-4.89 (m, 1H), 4.74-4.82 (m, 1H), 4.67-4.74 (m, 1H), 3.34-3.48 (m, 2H), 2.41 (s, 3H), 2.33 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H), 2.23 (s, 3H). ^{13}C{^{1}H} NMR (125 Hz, $CDCl_3$) δ: 201.4, 137.8, 137.3, 137.2, 135.9, 135.4, 135.4, 132.5, 132.4, 132.1, 131.4, 130.0, 128.9, 78.3, 43.5, 34.6, 21.7, 21.2, 21.0, 20.8, 20.5. HRMS-ESI$^+$ (*m/z*): [M + Na]$^+$ calc'd for $C_{21}H_{25}NNaO_3$: 362.1724; found 362.1727.



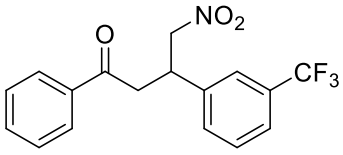
3-(2,6-Dichlorophenyl)-4-nitro-1-(4-chlorophenyl)-butan-1-one (2e) The title compound was synthesised from **1e**, according to GP2, and was isolated as a yellow solid (1.51 g, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.85-7.95 (m, 2H), 7.41-7.50 (m, 2H), 7.35-7.41 (m, 1H), 7.27-7.33 (m, 1H), 7.14 (t, *J* = 7.9 Hz, 1H), 5.25-5.35 (m, 1H), 4.94-5.08 (m, 2H), 3.68 (d, *J* = 6.8 Hz, 2H). ^{13}C{^{1}H} NMR (125 Hz, $CDCl_3$) δ: 195.5, 140.3, 137.2, 134.5, 134.4, 130.2, 129.6, 129.4, 129.2, 76.4, 39.1, 35.5. HRMS-ESI$^+$ (*m/z*): [M + Na]$^+$ $C_{16}H_{12}Cl_3NNaO_3$: 393.9772; found 393.9775.



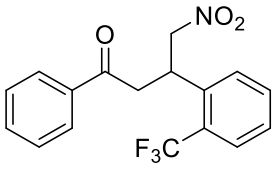
3-(2-Methyl-4-bromophenyl)-4-nitro-1-(4-bromophenyl)-butan-1-one (2f) The title compound was synthesised from **1f**, according to GP2, and the crude product was isolated as a yellow oil (1.69 g, 64%) that was used in the following step without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.34-37 (m, 1H), 7.28-7.32 (m, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 4.71-4.77 (m, 1H), 4.58-4.64 (m, 1H), 4.45 (q, *J* = 7.2 Hz, 1H), 3.31-3.46 (m, 2H), 2.46 (s, 3H). ^{13}C{^{1}H} NMR (125 Hz, $CDCl_3$) δ: 195.7, 139.1, 136.4, 135.0, 134.2, 132.3, 129.8, 129.6, 129.1, 127.1, 121.5, 78.9, 41.4, 34.1, 19.6. HRMS-ESI$^-$ (*m/z*): [M - H]$^-$ calc'd for $C_{17}H_{14}Br_2NO_3$: 437.9346; found 437.9333.



1-(4-Chloro-phenyl)-4-nitro-3-phenyl-butan-1-one (2g) The title compound was synthesised from **1g**,[4] according to GP2, and was used in the subsequent step without further purification.



4-Nitro-1-phenyl-3-[3-(trifluoromethyl)phenyl]-1-butan-1-one (2j) The title compound was synthesised from **1j**,[7] according to GP2, and was used in the subsequent step without further purification.



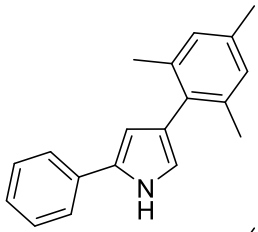
4-Nitro-1-phenyl-3-[2-(trifluoromethyl)phenyl]-1-butan-1-one (2k) The title compound was synthesised from **1k**,[7] according to GP2, and was used in the subsequent step without further purification.

Pyrroles

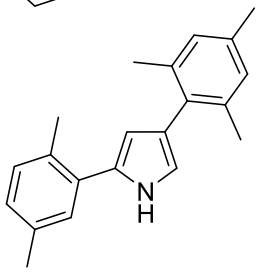
Pyrrole **3a** was synthesised with slight modifications to literature procedure.[1]

General procedure 3 (GP3) for the synthesis of 2,4-diaryl-1*H*-pyrroles (3a-g, 3i-j, 3m-n, 3p-q) Modifying a reported procedure,[1] a solution of potassium hydroxide (40 mmol, 5 eq.) in methanol (124 mL) was added the 4-nitrobutan-1-one **2a-q** (8 mmol, 1 eq.) and the mixture was stirred for 1 h at room temperature. The mixture was then added dropwise to a solution of concentrated sulfuric acid (12 mL) in methanol (20 mL) at 0 °C. The solution was allowed to warm to room temperature and then stirred for a further 1 h. Water (100 mL) and ice (100 mL) were added, and the mixture was neutralised with aqueous 4 M sodium hydroxide and then extracted with CH_2Cl_2 (2 x 250 mL). The combined organics were washed with water (100 mL) and brine (50 mL), then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* to provide a crude oil, which was carried into the next stage without further purification. To the intermediate compound was added acetic acid (27 mL) and ammonium acetate (40 mmol, 5 eq.), and the resulting mixture was heated at 100 °C for 1 h. The reaction mixture was allowed to cool to room temperature, and ice (100 mL) was then added. The mixture was carefully neutralised with 4 M aq. sodium hydroxide to result in the generation of a precipitate which was isolated by filtration. The crude product was further purified by the dissolution of the solid in a small amount of CH_2Cl_2, followed by the addition of pentane and isolation of the resulting precipitate via filtration.

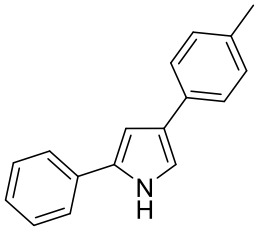
General procedure 4 (GP4) for the synthesis of 2,4-diaryl-1*H*-pyrroles, (3h, 3k, 3l, 3o) Modifying a reported procedure,[14] a mixture of the 4-nitrobutan-1-one (2 mmol, 1 eq.), sulfur (6 mmol, 3 eq.), and ammonium acetate (12 mmol, 6 eq.) were combined in morpholine (2.5 mL), and the resulting mixture was heated at 80 °C for 30 min. The reaction mixture was then cooled to ambient temperature and diluted with ethyl acetate (50 mL). The solid was removed by filtration. The organic layer was washed with water (50 mL) and brine (50 mL), dried over anhydrous Na_2SO_4, and then concentrated *in vacuo*. The resulting material was purified by column chromatography on silica to provide the desired product.



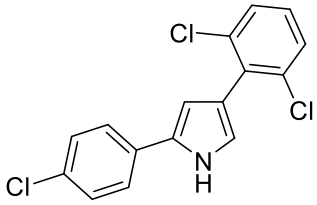
2-Phenyl-4-(2,4,6-trimethylphenyl)-1*H*-pyrrole (3b) The title compound was synthesised from **2b**, according to GP3, and was isolated as a purple solid (920 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.42 (br s, 1H), 7.50-7.54 (m, 2H), 7.37-7.44 (m, 2H), 7.21-7.26 (m, 1H), 6.98 (s, 2H), 6.66-6.70 (s, 1H), 6.43-6.46 (m, 1H), 2.36 (s, 3H), 2.23 (s, 6H). ^{13}C{^{1}H} NMR (125 Hz, $CDCl_3$) δ: 137.7, 136.2, 133.3, 132.9, 131.8, 129.0, 128.1, 126.2, 124.1, 123.6, 117.6, 107.8, 21.3, 21.1. HRMS-ESI$^+$ (*m/z*): $[M + H]^+$ calc'd for $C_{19}H_{20}N$: 262.1590; found 262.1591.



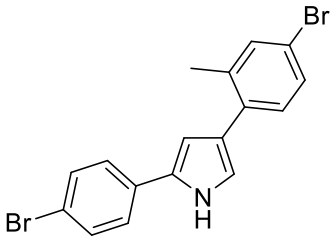
2-(2,5-Dimethylphenyl)-4-(2,4,6-trimethylphenyl)-1*H*-pyrrole (3c) The title compound was synthesised from **2c**, according to GP3 and was isolated as a purple solid (1.13 g, 49%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.52 (br s, 1H), 7.52-7.55(m, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.25 (s, 2H), 6.94-96 (m, 1H), 6.51-6.54 (m, 1H), 2.74 (s, 3H), 2.67 (s, 3H), 2.63 (s, 3H), 2.52 (s, 6H). ^{13}C{^{1}H} NMR (125 Hz, $CDCl_3$) δ: 137.8, 136.1, 135.6, 133.6, 132.8, 132.0, 131.2, 131.0, 128.2, 128.1, 127.5, 123.1, 116.5, 110.8, 21.3, 21.1, 21.0, 1 signal missing. HRMS-ESI$^+$ (*m/z*): $[M + H]^+$ calc'd for $C_{21}H_{24}N$: 290.1903, found 290.1903.



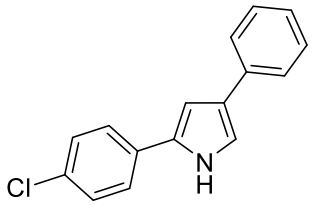
4-(4-Methylphenyl)-2-phenyl-1*H*-pyrrole (3d) According to an amended version of GP3, the requisite 4-nitrobutan-1-one, **2d**,[10] (6.98 mmol, 1 eq.) was reacted with potassium hydroxide (34.9 mmol, 5 eq.) in methanol (63 mL). After 1 hour, the mixture was added dropwise to a solution of concentrated sulfuric acid (9.2 mL) in methanol (50 mL) stirring at 0 °C. After the mixture was neutralised with 4 M aq. potassium hydroxide, the intermediate product was isolated by filtration and dried overnight in a vacuum desiccator. To the intermediate compound was added acetic acid (26 mL) and ammonium acetate (17.5 mmol, 2.5 eq.), and the resulting mixture heated at 100 °C for 1 h. After the mixture was neutralised with aqueous 4 M potassium hydroxide the crude material was extracted with CH_2Cl_2 (50 mL) and the organic later washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and the resulting material was purified by dissolution in a small amount of ethyl acetate, followed by the addition of hexanes and isolation of the precipitate *via* filtration to obtain the desired compound as a crystalline silver solid (0.15 g, 9%). NMR data were found to be in accordance with literature.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (br s, 1H), 7.52 (d, *J* = 6.9 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.39 (t, *J* = 6.9 Hz, 2H), 7.24 (t, *J* = 6.9 Hz, 1H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.12 (br s, 1H), 6.80 (br s, 1H), 2.36 (s, 3H).



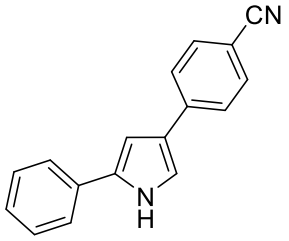
4-(2,6-Dichloro-phenyl)-2-(4-chloro-phenyl)-1*H*-pyrrole (3e) The title compound was synthesised from **2e**, according to GP3, and was isolated as a purple solid (1.31 g, 51%). ^{1}H NMR (500 MHz, CD_3NO_2) δ: 8.22 (br s, 1H), 7.95 (d, *J* = 7.1 Hz, 2H), 7.44 (m, 1H), 7.32 (d, *J* = 7.1 Hz, 2H), 7.16 (m, 1H), 7.06 (m, 1H), 6.94 (m, 1H), 6.69 (m, 1H). ^{13}C{^{1}H} NMR (125 Hz, $CDCl_3$) δ: 137.6, 136.0, 135.4, 133.4, 132.7, 131.8, 131.1, 130.9, 128.0, 127.9, 127.3, 123.0. HRMS-ESI$^+$ (*m/z*): [M - H]$^-$ calc'd for $C_{16}H_9Cl_3N$: 319.9806; found 319.9806.



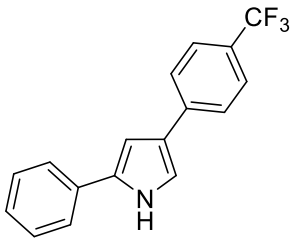
4-(4-Bromo-2-methylphenyl)-2-(4-bromophenyl)-1*H*-pyrrole (3f) The title compound was synthesised from **2f**, according to GP3, and was isolated as a purple solid (657 mg, 21%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.44 (br s, 1H), 7.48-7.53 (m, 2H), 7.41-7.30 (m, 4H), 7.24 (overlapping with solvent, 1H), 6.91-6.96 (m, 1H), 6.59-6.66 (m, 1H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (125 Hz, $CDCl_3$) δ: 137.6, 134.4, 133.4, 132.2, 131.4, 131.2, 130.8, 129.0, 125.5, 125.4, 120.2, 119.9, 118.3, 107.4, 21.3. HRMS-ESI$^+$ (*m/z*): [M + H]$^+$ calc'd $C_{17}H_{14}Br_2N$ for 389.9488, found 389.9499



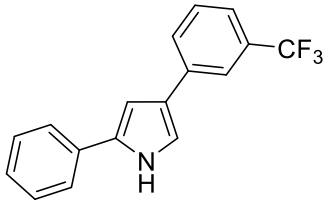
4-Phenyl- 2-(4-chloro-phenyl)-1*H*-pyrrole (3g) The title compound was synthesised from **2g**, according to a modified version of GP3 yielding 52 mg (15%). NMR data was found to be in accordance with literature.[15] ^{1}H NMR (400 MHz; $CDCl_3$) δ: 8.40 (bs, 1H), 7.56 (d, *J* = 7.2 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 8.4 Hz, 4H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.12-7.17 (m, 1H), 6.78-6.83 (m, 1H).



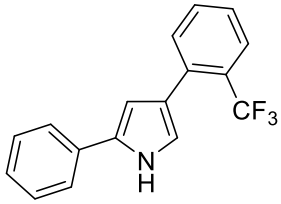
4-(4-Cyanophenyl)-2-phenyl-1*H*-pyrrole (3h) According to GP4, the title compound was synthesised from **2h**[11] and was isolated as a yellow solid after purification by column chromatography on silica (5→20% ethyl acetate in hexanes) (190 mg, 39%). NMR data were found to be in accordance with literature.[16] ^{1}H NMR (400 MHz; DMSO-d_6) δ: 11.69 (s, 1H), 7.81 (d, *J* = 8.5 Hz 2H), 7.75 (d, *J* = 8.5 Hz 2H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.58 (m, 1H), 7.39 (t, *J* = 7.8 Hz 2H), 7.20 (t, *J* = 7.4 Hz 1H), 7.09(m, 1H).



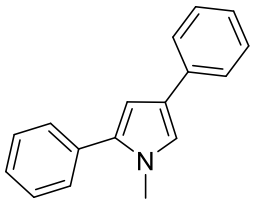
2-Phenyl-4-[4-(trifluoromethyl)phenyl]-1*H*-pyrrole (3i) According to an amended version of GP3, the requisite nitrobutan-1-one, **2i**,[10] (3.97 mmol, 1 eq.) was reacted with potassium hydroxide (19.9 mmol, 5 eq.) in methanol (35 mL). After 1 hour, the mixture was added dropwise to a solution of concentrated sulfuric acid (5.2 mL) in methanol (28 mL) at 0 °C. After the mixture was neutralised with aqueous 4 M potassium hydroxide, the intermediate product was isolated by filtration and dried overnight in a vacuum desiccator. To the intermediate compound was added acetic acid (15 mL) and ammonium acetate (9.88 mmol, 2.5 eq.), and the resulting mixture heated at 100 °C for 1 h. After the mixture was neutralised with aqueous 4 M potassium hydroxide the crude material was extracted with CH_2Cl_2 (30 mL) and the organic later washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and the resulting material was purified by dissolution in a small amount of ethyl acetate, followed by the addition of pentane and isolation of the precipitate *via* filtration to obtain the desired compound as a crystalline silver solid (0.54 g, 48%). NMR data were found to be in accordance with literature.[17] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (bs, 1H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.53 (dd, *J* = 7.7, 1.3 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.27 (tt, *J* = 7.7, 1.3 Hz, 1H), 7.20-7.23 (m, 1H), 6.82-6.85 (m, 1H).



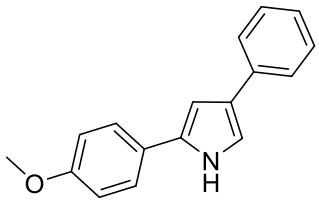
2-Phenyl-4-[3-(trifluoromethyl)phenyl]-1*H*-pyrrole (3j) According to an amended version of GP3, the requisite nitrobutan-1-one, **2j**, (7.09 mmol, 1 eq.) was reacted with potassium hydroxide (35.6 mmol, 5 eq.) in methanol (60 mL). After 1 hour, the mixture was then added dropwise to a solution of concentrated sulfuric acid (9.3 mL) in methanol (50 mL) at 0 °C. After the mixture was neutralised with aqueous 4 M potassium hydroxide the intermediate product was isolated by filtration and dried overnight in a vacuum desiccator. To the intermediate compound was added acetic acid (27 mL) and ammonium acetate (17.7 mmol, 2.5 eq.), and the resulting mixture heated at 100 °C for 1 h. After the mixture was neutralised with aqueous 4 M potassium hydroxide the crude material was extracted with CH_2Cl_2 (50 mL) and the organic later washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and the resulting material was purified by dissolution in a small amount of CH_2Cl_2, followed by the addition of hexanes and isolation of the precipitate *via* filtration to obtain the desired compound as a crystalline silver solid (0.27 g, 13%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (bs, 1H), 7.80 (s, 1H), 7.73 (d, *J* = 6.9 Hz, 1H), 7.53 (d, *J* = 6.9 Hz, 2H), 7.37-7.50 (m, 4H), 7.27 (t, *J* = 6.9 Hz, $CDCl_3$ shoulder), 7.16-7.22 (m, 1H), 6.81-6.87 (m, 1H). ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) *δ*: -62.7 (s). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 136.5, 133.7, 132.3, 131.3, 131.0, 129.2, 128.4, 126.9, 125.5, 124.1, 123.2, 122.4, 121.9, 116.1, 104.0. HRMS-ESI$^-$ *m/z* [M - H]$^-$ calc'd for $C_{17}H_{11}F_3N$: 286.0849; found 286.0845.



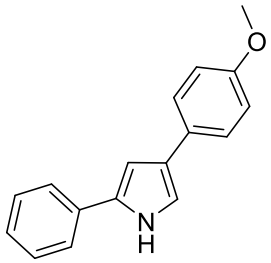
2-Phenyl-4-(2-(trifluoromethyl) phenyl)-1*H*-pyrrole (3k) According to GP4, the title compound was synthesised from **2k** and was isolated as a white solid after purification by column chromatography on silica (5→20% ethyl acetate/hexanes) and then recrystallisation in a mixture of dichloromethane/hexanes (184 mg, 32%). ^{1}H NMR (400 MHz; $CDCl_3$) δ: 8.50 (s, 1H), 7.77 (d, *J* = 7.7 Hz 1H), 7.53-7.50 (m, 4H), 7.41-7.35 (m, 3H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.99 (m, 1H), 6.68 (m, 1H). ^{19}F{1H} NMR (377 MHz; $CDCl_3$) δ: -57.8 (s). ^{13}C{^{1}H} NMR (101 MHz; $CDCl_3$) δ: 135.8, 132.5, 132.3, 132.1, 131.6, 129.1, 127.9 (q, *J* = 130 Hz), 126.6, 126.4, 126.0, 124.0, 123.3, 118.3 (q, *J* = 3.0 Hz), 107.6, one carbon signal missing. HRMS-ESI$^-$ *m/z* [M - H]$^-$ calc'd for $C_{17}H_{11}F_3N$: 286.0849; found 286.0848.



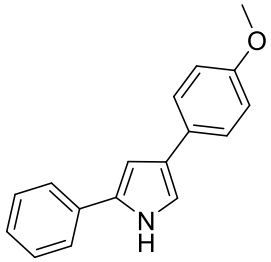
1-Methyl-2,4-diphenyl-1*H*-pyrrole (3l) The title compound was synthesised from **3l** according to a modified literature procedure.[18] In a thick-walled glass pressure flask, **3l** (140 mg, 0.64 mmol, 1 eq.), was dissolved in a suspension of potassium carbonate (277 mg, 38 mmol, 60 eq.) in acetonitrile (65 mL). Iodomethane (1.2 mL, 19 mmol, 30 eq.), was added and the vessel was sealed and heated to 85 °C overnight. Once cooled to room temperature, the mixture was quenched with 4 M aq. potassium hydroxide (20 mL). The organic layer was extracted with CH_2Cl_2 (150 mL), washed with brine, dried over sodium sulfate, and concentrated *in vacuo*. The product was purified from unreacted starting material by column chromatography (0→50% ethyl acetate in hexanes) to yield a pale pink solid (46 mg, 32%). NMR data was found to be in accordance with literature.[19] ^{1}H NMR (400 MHz; $CDCl_3$) δ: 7.54 (d, *J* = 7.2 Hz, 2H), 7.40-7.47 (m, 4H), 7.30-7.37 (m, 3H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.00-7.04 (m, 1H), 6.51-6.56 (m, 1H), 3.70 (s, 3H).



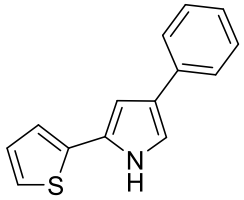
2-(4-Methoxyphenyl)-4-phenyl-1*H*-pyrrole (3m) According to an amended version of GP3, the requisite 4-nitrobutan-1-one, **2m**,[1] (8.18 mmol, 1 eq.) was reacted with potassium hydroxide (40.9 mmol, 5 eq.) in methanol (70 mL). After 1 hour, the mixture was then added dropwise to a solution of concentrated sulfuric acid (11 mL) in methanol (59 mL) at 0 °C. After the mixture was neutralised with aqueous 4 M potassium hydroxide the intermediate product was isolated by filtration and dried overnight in a vacuum desiccator. To the intermediate compound was added acetic acid (30 mL) and ammonium acetate (20.4 mmol, 2.5 eq.), and the resulting mixture heated at 100 °C for 1 h. After the mixture was neutralised with 4 M aq. potassium hydroxide the crude material was extracted with CH_2Cl_2 (60 mL) and the organic later washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and the resulting material was purified by dissolution in a small amount of ethyl acetate, followed by the addition of hexanes and isolation of the precipitate *via* filtration to obtain the desired compound as a crystalline silver solid (0.37 g, 18%). NMR data were found to be in accordance with literature.[14] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.28 (bs, 1H), 7.56-7.64 (m, 4H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.25-7.28 (m, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 8.9 Hz, 2H), 6.78-6.82 (m, 1H), 3.77 (s, 3H).



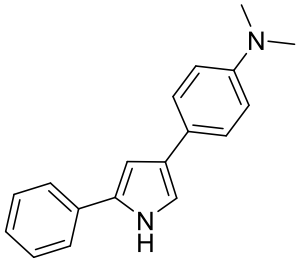
4-(4-Methoxyphenyl)-2-phenyl-1*H*-pyrrole (3n) According to an amended version of GP3, the requisite 4-nitrobutan-1-one, **2n**,[1] (6.98 mmol, 1 eq.) was reacted with potassium hydroxide (34.9 mmol, 5 eq.) in methanol (63 mL). After 1 hour, the mixture was added dropwise to a solution of concentrated sulfuric acid (9.2 mL) in methanol (50 mL) at 0 °C. After the mixture was neutralised with aqueous 4 M aq. potassium hydroxide the intermediate product was isolated by filtration and dried overnight in a vacuum desiccator. To the intermediate compound was added acetic acid (26 mL) and ammonium acetate (17.5 mmol, 2.5 eq.), and the resulting mixture heated at 100 °C for 1 h. After the mixture was neutralised with aqueous 4 M potassium hydroxide the crude material was extracted with CH_2Cl_2 (50 mL) and the organic later washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and the resulting material was purified by dissolution in a small amount of ethyl acetate, followed by the addition of hexanes and isolation of the precipitate *via* filtration to obtain the desired compound as a crystalline silver solid (0.15 g, 9%). NMR data were found to be in accordance with literature.[14] ^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.33 (bs, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 9.1 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.20-7.23 (m, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J* = 9.1 Hz, 2H), 6.85-6.88 (m, 1H), 3.75 (s, 3H).



4-(4-Hydroxyphenyl)-2-phenyl-1*H*-pyrrole (3o) According to GP4, the title compound was synthesised from 4-nitrobutan-1-one **2o**[12] and was isolated as a light yellow solid after purification by column chromatography on silica (5→30% ethyl acetate in hexanes) (24 mg, 5%). ^{1}H NMR (400 MHz; DMSO-d_6) δ: 11.27 (s, 1H), 9.17 (s, 1H), 7.66 (d, *J* = 7.1 Hz 2H), 7.40 (d, *J* = 8.5 Hz 2H), 7.26 (t, *J* = 7.8 Hz 2H), 7.19-7.12 (m, 2H), 6.82 (m, 1H), 6.73 (d, *J* = 8.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz; DMSO-d_6) δ: 155.6, 133.3, 132.3, 129.1, 127.3, 126.1, 126.0, 125.5, 123.8, 115.8, 115.7, 103.4. HRMS-ESI$^-$ *m/z* [M - H]$^-$ calc'd for $C_{16}H_{12}NO$: 234.0924; found 234.0918.

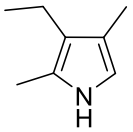


4-Phenyl-2-(2-thienyl)-1*H*-pyrrole (3p) The title compound was synthesised from 4-nitrobutan-1-one **2p**[13] according to a slight modification of GP3. The crude product was purified by column chromatography (0→60% CH_2Cl_2 in hexanes), followed by precipitation in CH_2Cl_2 and pentane to yield the off-white solid product (0.148 g, 17%). NMR data was found to be in accordance with literature.[20] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.30 (bs, 1H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.14-7.23 (m, 2H), 7.01-7.11 (m, 3H), 6.71 (bs, 1H).



N,N-Dimethyl-4-(5-phenyl-1*H*-pyrrol-3-yl)benzenamine (3q) According to an amended version of GP3, the requisite 4-nitrobutan-1-one, **2q**,[1] (1.67 mmol, 1 eq.) was reacted with potassium hydroxide (8.35 mmol, 5 eq.) in methanol (15 mL). After 1 hour, the mixture was added dropwise to a solution of concentrated sulfuric acid (2.2 mL) in methanol (12 mL) at 0 °C. After the mixture was neutralised with aqueous 4 M potassium hydroxide the intermediate product was isolated by filtration and dried overnight in a vacuum desiccator. To the intermediate compound was added acetic acid (6.2 mL) and ammonium acetate (4.18 mmol, 2.5 eq.), and the resulting mixture heated at 100 °C for 1 h. After the mixture was neutralised with aqueous 4 M potassium hydroxide the crude material was extracted with CH_2Cl_2 (15 mL) and the organic later washed with water and brine, and then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*, and the resulting material was purified by dissolution in a small amount of ethyl acetate, followed by the addition of hexanes and isolation of the precipitate *via* filtration to obtain the desired compound as a crystalline silver solid (80 mg, 18%). NMR data were found to be in accordance with literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.39 (bs, 1H), 7.51 (d, *J* = 7.9 Hz, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.9 Hz, 1H), 7.03-7.07 (m, 1H), 6.84 (bs, 2H), 6.75-6.78 (m, 1H), 2.98 (s, 6H).

Phenylmethyl 2,4-dimethyl-1H-pyrrole-3-carboxylate (7a) The title compound was synthesised following literature procedures.[21]



3-Ethyl-2,4-dimethyl-1*H*-pyrrole (7b) The title compound was synthesised in a three-step procedure from ethyl acetoacetate, following modifications of reported procedures, as follows.[22,23]

Step 1 Preparation of 2,4-dimethyl-3-acetyl-5-carbethyoxypyrrole: ethyl acetoacetate (104 g, 0.80 mol, 1.1 eq.) and glacial acetic acid (310 mL, 4.92 mol, 6.6 eq.) was stirred at 0 ℃ using an overhead stirrer. A solution of sodium nitrite (63.7 g, 0.75 mol, 1 eq.) in de-ionised water (105 mL) was added, with the rate of addition sufficiently slow to maintain the temperature of the reaction mixture below 12 °C. The mixture was stirred in the ice bath for 3 h, then allowed to stand at room temperature, without stirring, for an additional 16 h. The stirring was resumed and acetylacetone (90.2 g, 0.9 mol, 1.2 eq.) was added followed by portion-wise addition of solid zinc powder (117 g, 1.78 mol, 2.4 eq.) while maintaining the temperature of the reaction mixture below 60 °C. The mixture was heated at reflux temperature for 2 h, then decanted directly into ice water (4 L). The resulting solid precipitate was isolated via filtration, and dissolved in a minimum amount of hot 95% ethanol. The residual zinc solid was removed by filtration. The product crystallised from the ethanolic mixture overnight. Two crops of crystallisations yielded the product as a white solid (94 g, 0.45 mol, 56%).

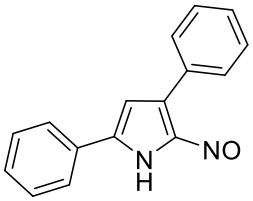
Step 2 Preparation of 2,4-dimethyl-3-ethyl-5-carbethoxypyrrole: 2,4-dimethyl-3-acetyl-5-carbethoxypyrrole (63.0 g, 0.301 mol, 1 eq.) was dissolved in dry THF (2 L) under nitrogen, and the solution was cooled in an ice bath. A 1 M solution of BH_3•THF (600 mL, 0.601 mol, 2 eq.) was added dropwise over 30 min. The mixture was allowed to warm to room temperature and stirred for 16 h. Methanol was slowly added to quench the unreacted BH_3•THF. The solvent was removed *in vacuo* and the resulting solid was crystalised from hexanes to yield the desired product as of an off-white solid (41.5 g, 0.213 mol, 71%). Additional product was isolated from the crystallisation filtrate using column chromatography, eluting with 5% ethyl acetate in hexanes (12.3 g, 0.063 mol, 21%). Thus the total yield was 53.8 g (0.276 mol, 92%).

Step 3 Preparation of 3-ethyl-2,4-dimethylpyrrole (cryptopyrrole, **7b**): ethyl 4-ethyl-3,5-dimethylpyrrole-2-carboxylate (6.67 g, 34 mmol, 1 eq.) and sodium hydroxide (13.40 g, 335 mmol, 9.9 eq.) were suspended in ethylene glycol (135 mL). The mixture was degassed with nitrogen and the slurry heated to 198 °C for 1 h using an aluminium block. After cooling to 170 °C and transferring to a separatory funnel, cold degassed brine:water (50:50) solution (500 mL) was added. The aqueous layer was extracted with degassed hexane (2 x 350 mL). The organic layers were dried over Na_2SO_4, then concentrated *in vacuo*. The crude dark orange oil and was purified by vacuum distillation using a Kugelrohr short path distillation apparatus (bp. 150 ℃ under reduced pressure) to provide the title compound as a colourless oil (3.39 g, 28 mmol, 80%). NMR data is in accordance with literature.[23] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (bs, 1H), 6.41 (bs, 1H), 2.44 (q, *J* = 7.6 Hz, 2H), 2.21 (s, 3H), 2.8 (s, 3H), 1.12 (t, *J* = 7.6 Hz, 3H).

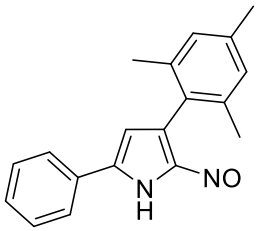
Nitroso pyrroles

General procedure 5 (GP5) for the synthesis of nitroso pyrroles (4a-l): Pyrrole **3a-l** (50 mg, 1 eq.) was dissolved in anhydrous acetonitrile (5 mL) under a nitrogen atmosphere and the solution cooled to -5 °C using an ice/acetone bath. $NOBF_4$ (0.9 eq), was weighed in a nitrogen-filled glovebox, and separated into three portions. The three portions of $NOBF_4$ were added to the stirring solution of pyrrole about 15 seconds apart with a flow of nitrogen maintained during the additions. The resulting solution was stirred for 5-10 minutes, in the cold bath, at which point all pyrrole starting material was consumed according to analysis by TLC. The reaction mixture was added to water (20 mL) and extracted into CH_2Cl_2 (2 x 20 mL). The combined organics were dried over anhydrous Na_2SO_4, then concentrated *in vacuo*. The resulting solid was purified by column chromatography on silica using a gradient of ethyl acetate/hexanes to provide the desired 2-nitroso pyrrole as a green solid that stained orange on silica TLC plates when visualised with vanillin stain and heat.

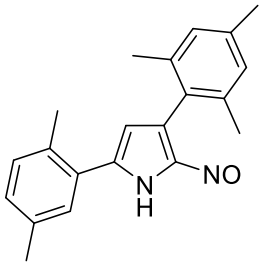
General procedure 6 (GP6) for the synthesis of nitroso pyrroles with electron donating character (4m-q) Pyrrole **3m-q** (0.23 mmol, 1 eq.) was dissolved in anhydrous 1,2-dimethoxyethane (5 mL) alongside (suspended) anhydrous potassium carbonate (65 mg, 0.47 mmol, 2 eq.) under a nitrogen atmosphere, and the mixture cooled to -5 to -10 °C (achieved using an ice/acetone bath). A solution of $NOBF_4$ (30 mg, 0.26 mmol, 1.1 eq.) in 1,2-dimethoxyethane (4.5 mL) was added dropwise at a rate of 1 mL/min using a syringe pump. The resulting solution was stirred for one additional minute, in the cold bath, at which point all pyrrole starting material was consumed according to analysis by TLC. The reaction mixture was added to water (20 mL) at room temperature and extracted into CH_2Cl_2 (2 x 20 mL). The combined organics were washed with a saturated aqueous solution of sodium bicarbonate, dried over anhydrous Na_2SO_4, then concentrated *in vacuo*. The resulting solid was wet-loaded onto a silica chromatography column using CH_2Cl_2, and purified using a gradient of ethyl acetate/dichloromethane as eluent to afford the desired 2-nitroso pyrrole as a green solid.



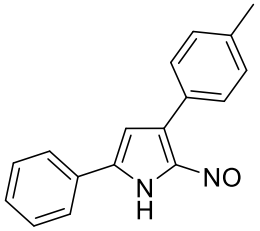
2-Nitroso-3,5-diphenyl-1*H*-pyrrole (4a) The title compound was synthesised from **3a** according to GP5 and was isolated as a green solid (37 mg, 60%). NMR data were found to be in accordance with literature.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.16-8.21 (m, 2H), 7.79-7.83 (m, 2H), 7.45-7.55 (m, 6H), 7.15 (s, 1H).



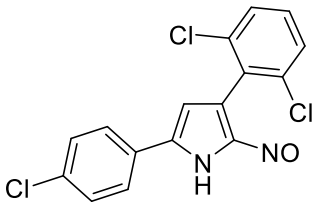
2-Nitroso-5-phenyl-3-(2,4,6-trimethylphenyl)-1*H*-pyrrole (4b) The title compound was synthesised from **3b** according to GP5 and was isolated as a green solid (41 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.84-7.88 (m, 2H), 7.44-7.52 (m, 3H), 7.01 (s, 2H), 6.84 (s, 1H), 2.35 (s, 3H), 2.23 (s, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 163.1, 143.9, 138.1, 137.2, 131.2, 129.4, 128.9, 128.3, 127.0, 116.5, 21.1, 21.0, 2 signals missing. HRMS-ESI$^+$ (*m/z*): $[M + Na]^+$ calc'd for $C_{19}H_{18}N_2NaO$: 313.1309; found 313.1311.



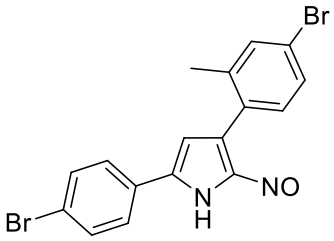
5-(2,5-Dimethylphenyl)-2-nitroso-3-(2,4,6-trimethylphenyl)-1*H*-pyrrole (4c) The title compound was synthesised from **3c** according to GP5 and was isolated as a green solid (43 mg, 59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35 (s, 1H), 7.18-7.22 (m, 2H), 7.02 (s, 2H), 6.63 (s, 1H), 2.48 (s, 3H), 2.37 (s, 3H), 2.35 (s, 3H), 2.25 (s, 6H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 137.6, 136.0, 135.4, 133.4, 132.7, 131.8, 131.1, 130.9, 128.0, 127.9, 127.3, 123.0, 23.7, 21.2, 21.1, 20.9 HRMS-ESI$^+$ (*m/z*): $[M + Na]^+$ calc'd for $C_{21}H_{22}N_2NaO$: 341.1621; found 341.1624.



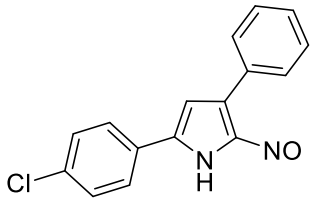
3-(4-Methylphenyl)-2-nitroso-5-phenyl-1*H*-pyrrole (4d) The title compound was synthesised from **3d** according to GP5 and was isolated as a green solid (38 mg, 59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.09 (d, *J* = 8.5 Hz, 2H), 7.78-7.80 (m, 2H), 7.50-7.52 (m, 3H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.12 (s, 1H), 2.43 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 135.5, 133.1, 132.8, 132.7, 129.5, 129.1, 126.8, 126.6, 125.3, 124.0, 115.4, 21.3. HRMS-ESI$^+$ (*m/z*): $[M + H]^+$ calc'd for $C_{17}H_{15}N_2O$ 263.1179, found, 263.1187.



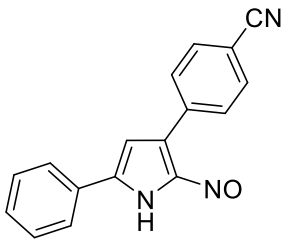
3-(2,6-Diclorophenyl)-5-(4-chlorophenyl)-2-nitroso-1*H*-pyrrole (4e) The title compound was synthesised from **3e** according to GP5 and was isolated as a green solid (35 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.16-8.19 (m, 2H), 7.80-7.83 (m, 2H), 7.47-7.51 (m, 2H), 7.14 (s, 1H), 6.77-6.78 (m, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 147.6, 145.0, 139.4, 137.4, 136.7, 134.8, 133.4, 132.7, 131.1, 130.9, 128.0, 127.9. HRMS-ESI$^+$ (*m/z*): $[M + H]^+$ calc'd for $C_{16}H_{10}Cl_3N_2O$: 352.6110 found 352.6113.



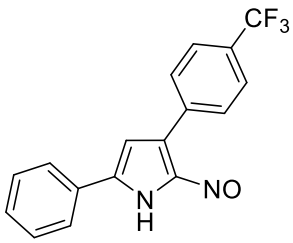
3-(4-Bromo-2-methylphenyl)-5-(4-bromophenyl)-2-nitroso-1*H*-pyrrole (4f) The title compound was synthesised from **3f** according to GP5 and was isolated as a green solid (37 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.49- 7.54 (m, 2H), 7.42-7.47 (m, 1H), 6.94 (s, 1H), 2.45 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 163.2, 139.2, 133.7, 133.4, 132.9, 130.6, 129.1, 128.6, 128.4, 126.3, 123.5, 116.7 21.1, 2 signals missing. HRMS-ESI$^+$ (*m/z*): $[M + H]^+$ calc'd for $C_{17}H_{13}Br_2N_2O$: 418.9390; found 418.9389.



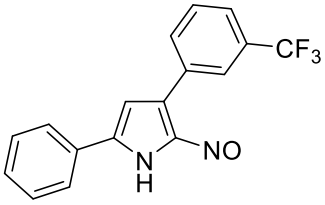
5-(4-Chlorophenyl)-2-nitroso-3-phenyl-1*H*-pyrrole (4g) The title compound was synthesised from **3g** (48 mg, 0.19 mmol) according to a slight modification of GP5. An additional portion of $NOBF_4$ (5 mg, 0.04 mmol) was added after 5 min. to force the reaction to completion. Purification yielded a bright green solid (22 mg, 45%).^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.12-8.17 (m, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.46-7.53 (m, 5H), 7.14, (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 163.3, 142.3, 137.8, 131.8, 129.9, 129.9, 129.7, 129.0, 128.3, 114.0, 2 signals missing. HRMS-ESI (*m/z*): $[M+H]^+$ calc'd for $C_{16}H_{12}ClN_2O$: 283.0633; found 283.0635.



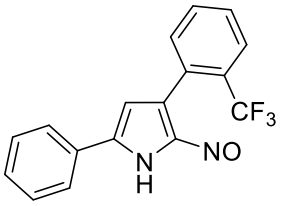
3-(4-Cyanophenyl)-2-nitroso-5-phenyl-1*H*-pyrrole (4h) The title compound was synthesised from **3h** according to GP5 and was isolated as a green solid (38 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.30 (d, *J* = 8.3 Hz 2H), 7.73-7.83 (m, 4H), 7.48-7.56 (m, 3H), 7.18 (s, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 162.24, 136.4, 132.6, 131.7, 130.2, 129.7, 126.9, 118.8, 113.0 3 signals missing. HRMS-ESI$^+$ (*m/z*): $[M + H]^+$ calc'd for $C_{17}H_{12}N_3O$ 274.0975, found 274.0984.



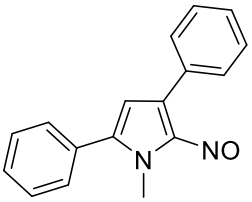
3-[4-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4i) The title compound was synthesised according to an amended version of GP5, from **3i** (80 mg) and was isolated as a green solid (41 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.30 (d, *J* = 8.1 Hz, 2H), 7.78-7.85 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.49-7.55 (m, 3H), 7.19 (s, 1H). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$) δ: -62.77 (s). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 162.5, 135.3, 131.5, 131.4, 129.8, 129.6, 128.9, 126.8, 125.7 (q, *J* = 3.6), 113.0, 2 signals missing. HRMS-ESI$^-$ (m/z): $[M - H]^-$ calc'd for $C_{17}H_{10}F_3N_2O$: 315.0751; found 315.0740.



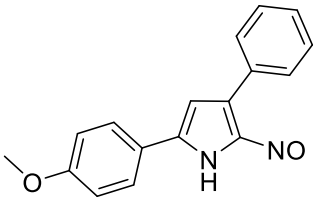
3-[3-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4j) The title compound was synthesised from **3j** according to GP5 and was isolated as a green solid, (39 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.44 (d, *J* = 8.0 Hz, 1H), 8.37 (s, 1H), 7.78-7.84 (m, 2H), 7.72 (d, *J* = 7.6 1H), 7.63 (t, *J* = 8.0, 1H), 7.49-7.57 (m, 3H), 7.20 (s, 1H). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$) *δ*: -62.67 (s). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) *δ*: 162.4, 133.0, 132.6, 131.6, 131.4 (q, 32.6 Hz), 129.6, 129.4, 128.9, 126.8, 126.0, 4 signals missing. HRMS-ESI$^-$ (m/z): [M - H]$^-$ calc'd for $C_{17}H_{10}F_3N_2O$ 315.0751, found 315.0741.



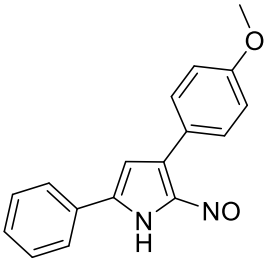
3-[2-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4k) The title compound was synthesised from **3k** (54 mg mg, 0.19 mmol) according to a slight modification of GP5. An additional portion of $NOBF_4$ (3 mg, 0.03 mmol) was added at the 5-minute mark to force the reaction to completion. Purification yielded a green solid (39 mg, 66%).^{1}H NMR (400 MHz, $CDCl_3$) δ:7.77-7.88 (m, 4H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.58 (t, *J* = 7.8, 1H), 7.45-7.54 (m, 3H), 7.08 (s, 1H). ^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$) δ: -57.36 (s). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 163.5, 147.2, 140.3, 134.3, 131.5, 131.4, 130.7, 129.5, 129.3, 129.2, 128.9, 127.1, 126.5 (q, *J* = 5.2 Hz), 124.2 (q, *J* = 275 Hz), 116.9. HRMS-ESI$^+$ (*m/z*): [M + Na]$^+$ calc'd for $C_{17}H_{11}F_3N_2NaO$: 339.0716; found 339.0712.



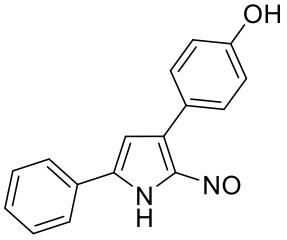
1-Methyl-2-nitroso 3,5-diphenyl-1*H*-pyrrole (4l) The title compound was synthesised from **3l** (62 mg, 0.27 mmol) according to a slight modification of GP5. An additional 2 mg of $NOBF_4$ was added at the 5-minute mark to force the reaction to completion. Purification yielded a crystalline green solid (45 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 7.2 Hz, 2H), 7.41-7.53 (m, 8H), 6.70 (s, 1H), 3.62 (s, 3H) ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 160.4, 145.1, 142.6, 133.1, 130.4, 130.2, 129.4, 129.2, 129.0, 128.7, 112.4, 36.1, 1 signal missing. HRMS-ESI (*m/z*): [M+Na]$^+$ calc'd for $C_{17}H_{14}N_2NaO$ 285.0998, found 285.1002.



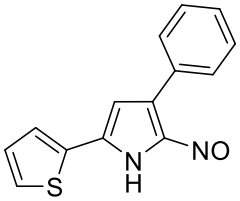
5-(4-Methoxyphenyl)-2-nitroso-3-phenyl-1*H*-pyrrole (4m) The title compound was synthesised from pyrrole **3m** according to GP6, yielding a green solid (10 mg, 16%), whose NMR data is in accordance with literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.08-8.15 (m, 2H), 7.85, (d, *J* = 8.8 Hz, 2H), 7.42-7.51 (m, 3H), 7.15 (s, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H).



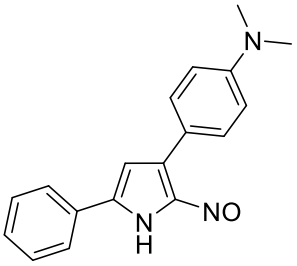
3-(4-Methoxyphenyl)-2-nitroso-5-phenyl-1*H*-pyrrole (4n) The title compound was synthesised from pyrrole **3m** according to GP6. After the initial column the product was cleaned up through successive precipitations with CH_2Cl_2 and pentane yielding a yellow brown solid (1 mg, 6%), that stains purple on TLC when heated with vanillin. The NMR data is in accordance with literature.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.17 (d, *J* = 8.8 Hz, 2H), 7.76-7.81 (m, 2H), 7.47-7.53 (m, 3H), 7.07 (s, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H).



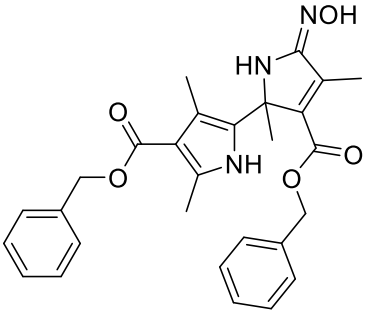
3-(4-Hydroxyphenyl)-2-nitroso-5-phenyl-1*H*-pyrrole (4o) The title compound was synthesised from pyrrole **3o** according to GP6. After the initial column, the product was further purified by washing with CH_2Cl_2 to yield a dark green solid (5 mg, 12%). ^{1}H NMR (500 MHz, THF-d_6) δ: 8.14 (d, *J* = 8.6 Hz, 2H), 7.94 (d, *J* = 6.8 Hz, 2H), 7.40-7.47 (m, 3H), 7.18 (s, 1H), 6.82-6.86 (m, 2H). ^{13}C{^{1}H} NMR (125 MHz, THF-d_6) *δ*: 163.3, 159.0, 130.8, 130.5, 129.8, 128.7, 126.8, 126.3, 124.2, 115.4, 2 signals missing. HRMS-ESI$^+$ (*m/z*): [M + H]$^+$ calc'd for $C_{16}H_{13}N_2O_2$: 265.0972; found 265.0976.



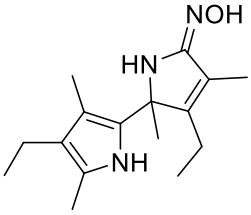
2-Nitroso-5-phenyl-3-(2-thienyl)-1*H*-pyrrole (4p) The title compound was synthesised from pyrrole **3p** according to GP6. The crude product showed a distinctive yellow spot by TLC. The initial column could not fully purify this compound. Precipitation from CH_2Cl_2 and pentane yielded milligram quantities of a green solid that could not be further purified. HRMS-ESI$^+$ (*m/z*): $[M + H]^+$ calc'd for $C_{14}H_{11}N_2OS$: 255.0587; found 255.0594.



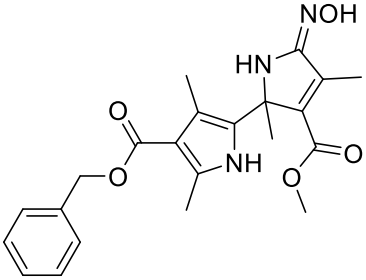
3-(4,4-Dimehtylaminophenyl)-phenyl-2-nitroso-1H-pyrrole (4q) The title compound was synthesised from pyrrole 3q according to GP6. The crude product showed a distinctive yellow spot by TLC. The initial column yielded milligram quantities of a grey/green solid that could not be further purified. HRMS-ESI$^+$ (*m/z*): $[M + H]^+$ calc'd for $C_{18}H_{18}N_3O$: 292.1444; found 292.1446



3,4'-Bis(benzylester)-2,3',4,5'-Butamethyl-[2,2'-bi-1*H*-pyrrol]-5(2H)-one oxime (8a) The title compound was synthesised from pyrrole **7a** according to GP6. **8a**stained mauve with vanillin and heat by TLC and was isolated by column chromatography (0→30% ethyl acetate in hexanes) to provide the title product as a white solid (3 mg, 5%) along with a close traveling byproduct**.** ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.12 (br s, 1H), 7.31-7.42 (m, 2H), 7.29-7.37 (m, 6H), 7.18-7.20 (m, 2H), 5.61 (br s, 1H), 5.26 (s, 2H), 5.20 (d, *J* = 11.3 Hz, 1H), 5.08 (d, *J* = 11.3 Hz, 1H), 2.35 (s, 3H), 2.19 (s, 3H), 2.13 (s, 3H), 1.86 (s, 3H).. ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 165.9, 163.3, 157.1, 141.7, 139.2, 137.1, 135.3, 134.6, 128.8, 128.5, 128.3, 128.2, 127.9, 124.3, 118.7, 111.8, 66.9, 65.4, 65.2, 26.6, 14.2, 11.0, 10.9, 1 signal missing. HRMS-ESI$^+$ (m/z): $[M + H]^+$ calc'd for $C_{28}H_{30}N_3O_5$ 488.2180, found 488.2179.



2,3',4,5'-Butamethyl-3,4'-diethyl-[2,2'-bi-1*H*-pyrrol]-5(2H)-one oxime (8b) The title compound was synthesised from **7b** according to GP6, and required a second chromatographic purification step (0→100% ethyl acetate in CH_2Cl_2) to provide the title product as a red-brown solid (7 mg, 5%) along with a close traveling impurity. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (br s, 1H), 5.42 (br s, 1H), 2.33 (q, *J* = 7.5 Hz, 2H), 2.04-2.18 (m, 5H), 2.00 (s, 3H), 1.78 (s, 3H), 1.71 (s, 3H), 1.01 (t, *J* = 7.5 Hz, 3H), 0.80 (t, *J* = 7.6 Hz, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 159.6, 155.5, 123.8, 122.4, 122.3, 121.3, 114.4, 67.2, 25.3, 18.8, 17.6, 16.0, 13.0, 11.1, 10.2, 8.5. HRMS-ESI$^+$ (*m/z*): $[M + H]^+$ calc'd for $C_{16}H_{26}N_3O$ 276.2070, found 276.2075.

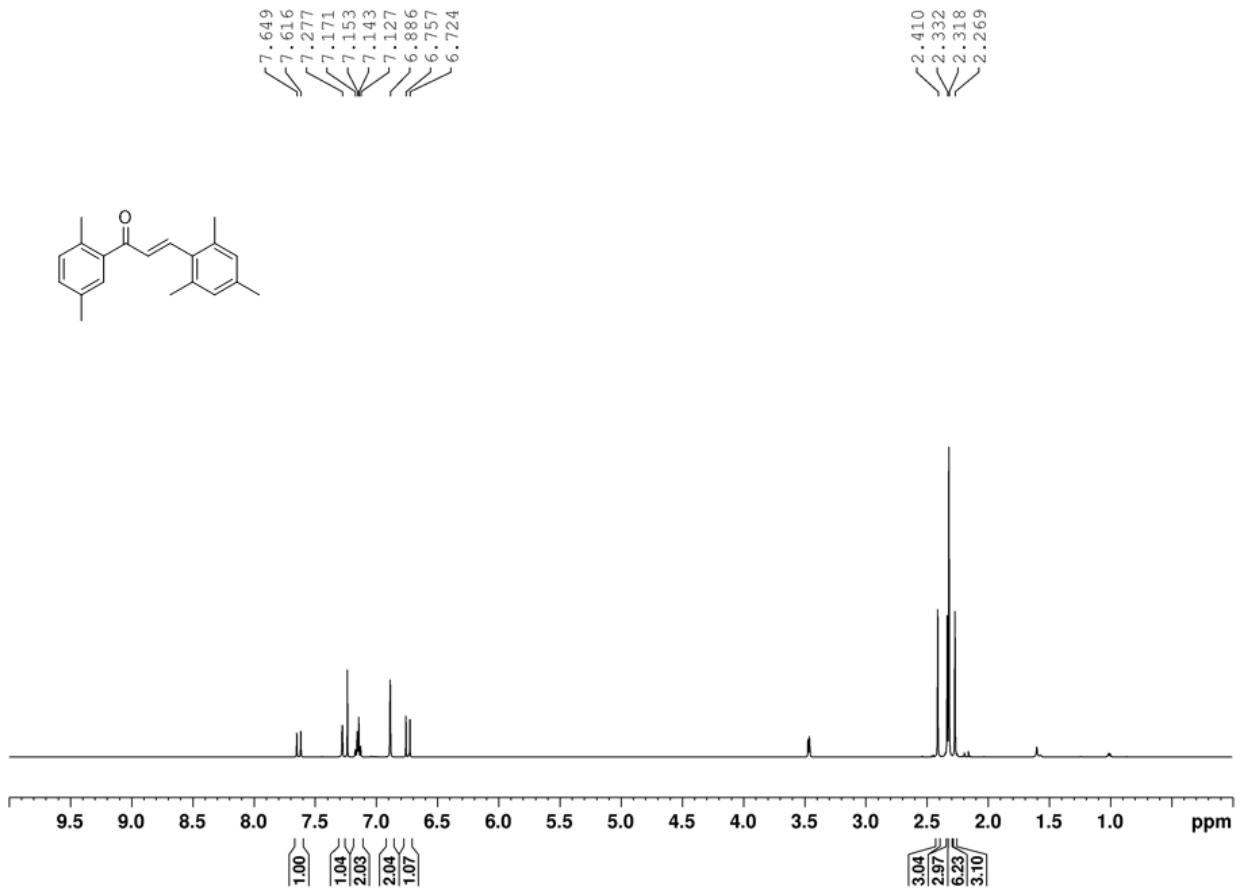


4'-Benzylester-2,3',4,5'-Butamethyl-3-methylester-[2,2'-bi-1*H*-pyrrol]-5(2H)-one oxime (8c) The title compound was synthesised from 8a (14 mg, 0.029 mmol) and potassium hydroxide (16 mg, 0.29 mmol), dissolved in methanol (1 mL). The mixture was heated at 65 ºC for 1h. Upon completion of the reaction the mixture was diluted with water and extracted with CH_2Cl_2. The organic layers were washed with brine, dried over sodium sulfate then concentrated *in vacuo*. The product was slowly crystalised from pentane diffusing into chloroform to provide the title compound as a crystalline white solid (7 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (br s, 1H), 7.27-7.43 (m 5H), 6.71 (br, 1H), 5.52 (s, 1H), 5.24 (s, 2H), 3.74 (s, 3H), 2.44 (s, 3H), 2.19 (s, 3 H), 2.18 (s, 3H), 1.89 (s, 3H).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 166.0, 164.2, 157.3, 141.0, 139.1, 137.1, 134.6, 128.6, 128.2, 128.0, 124.6, 118.5, 111.8, 65.6, 65.3, 51.9, 26.7, 14.6, 11.1, 11.0. HRMS-ESI$^+$ (*m/z*): $[M + H]^+$ calc'd for $C_{22}H_{26}N_3O_5$ 412.1867, found 412.1875.

Nuclear Magnetic Resonance Data

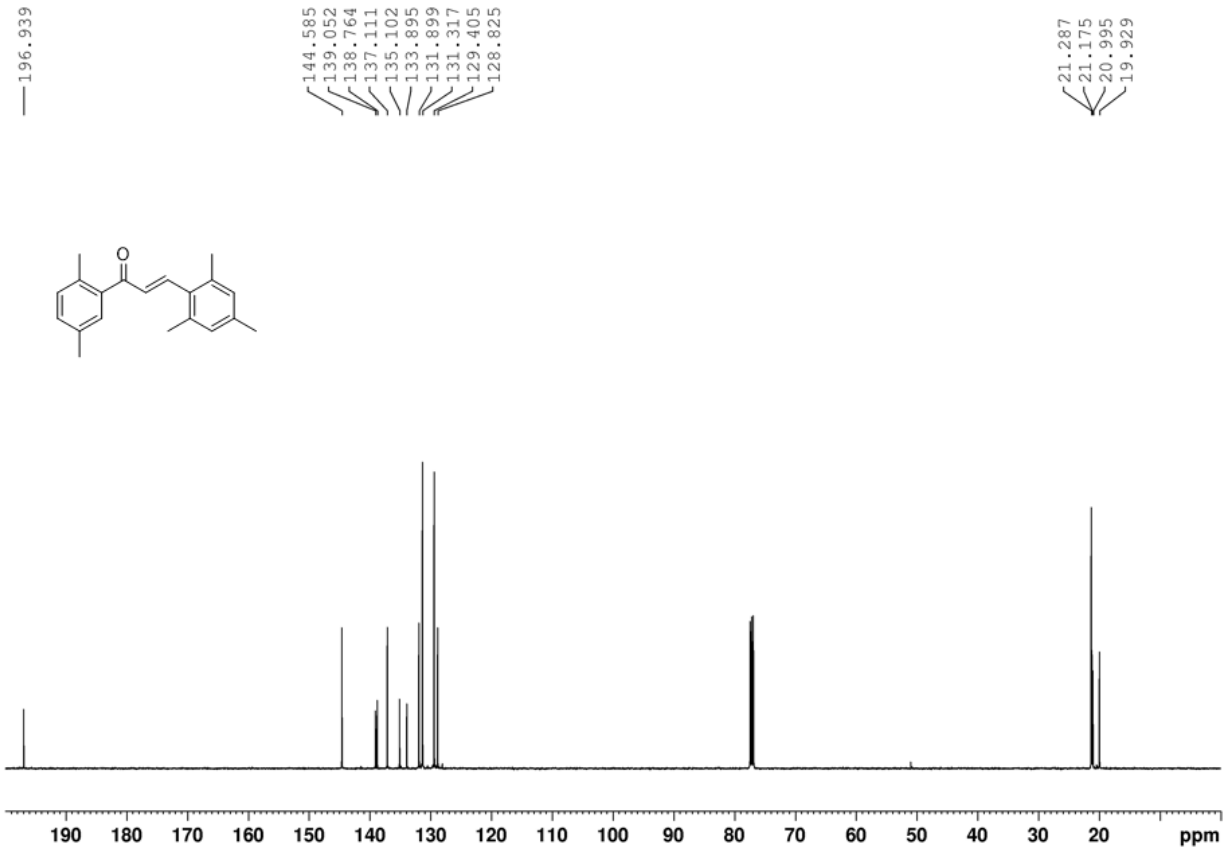
(2E)-1-(2,5-Dimethylphenyl)-3-(2,4,6-trimethylphenyl)-2-propen-1-one (1c)

^{1}H NMR (500 MHz) spectrum of compound **1c** in $CDCl_3$



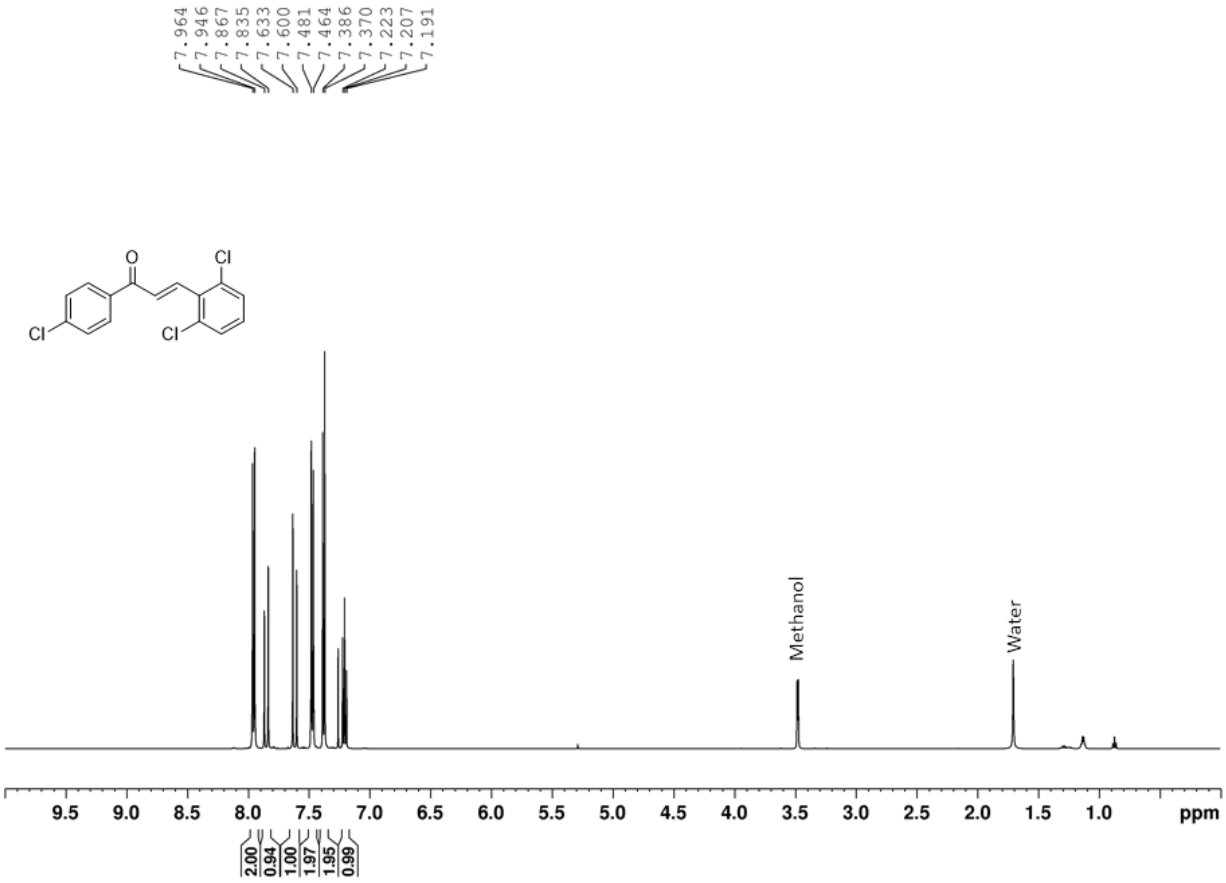
(2E)-1-(2,5-Dimethylphenyl)-3-(2,4,6-trimethylphenyl)-2-propen-1-one (1c)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **1c** in $CDCl_3$



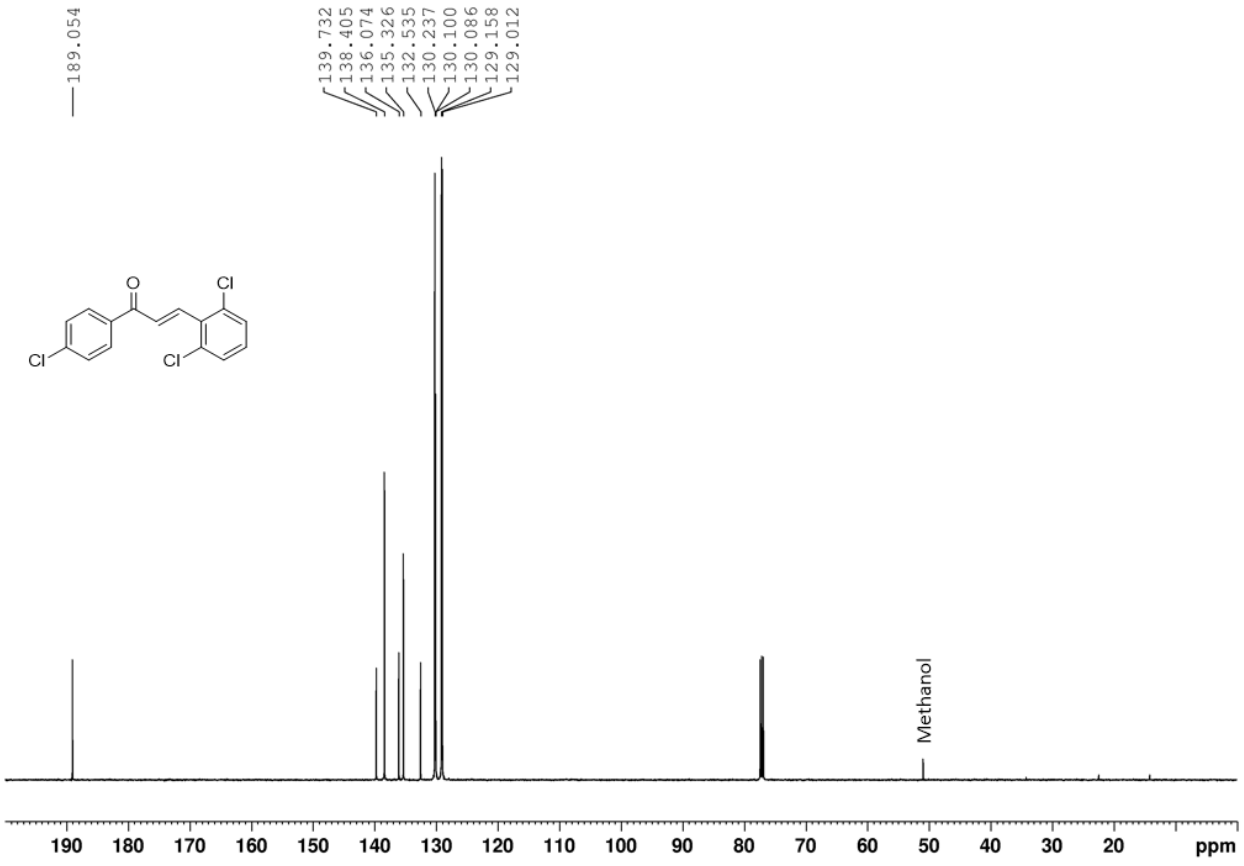
(2E)-1-(4-Chlorophenyl)-3-(2,6-dichlorophenyl)-2-propen-1-one (1e)

^{1}H NMR (500 MHz) spectrum of compound **1e** in $CDCl_3$



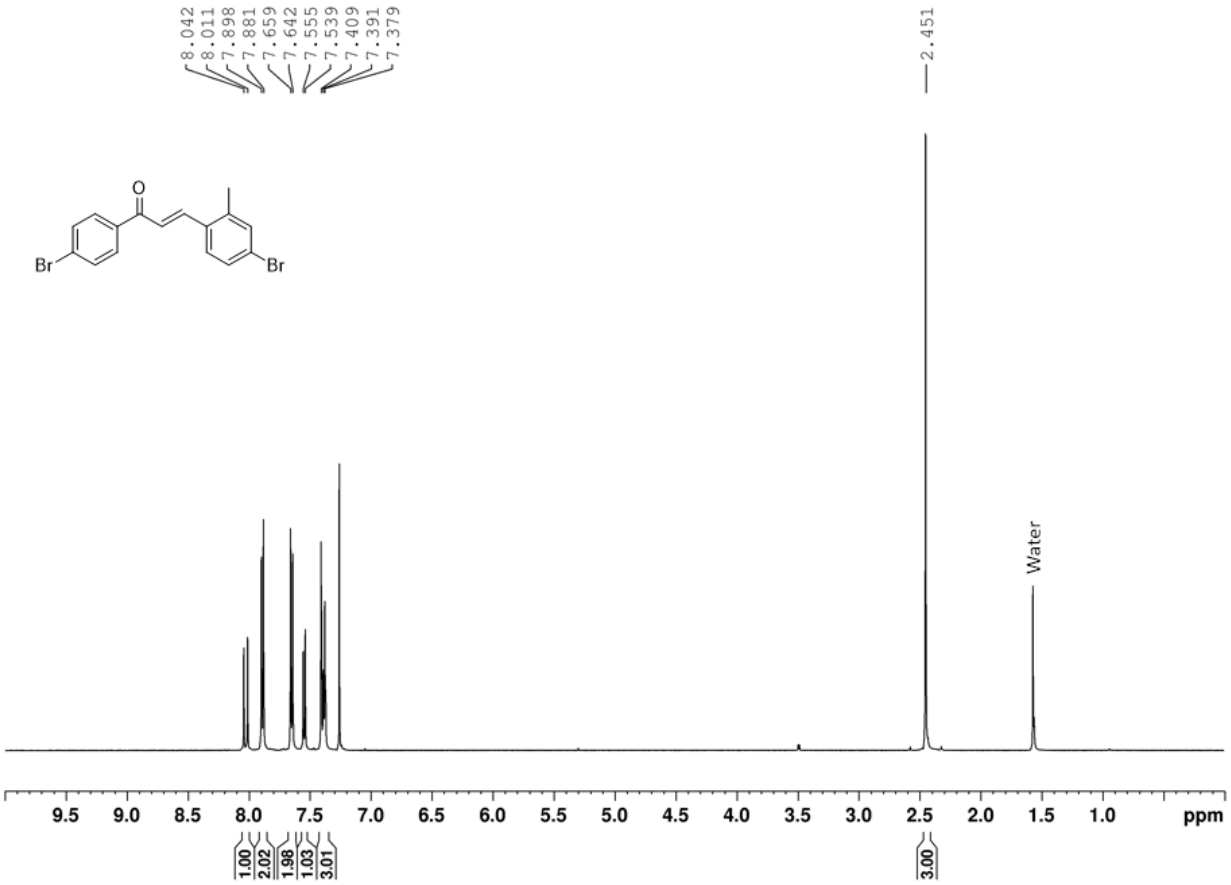
(2E)-1-(4-Chlorophenyl)-3-(2,6-dichlorophenyl)-2-propen-1-one (1e)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **1e** in $CDCl_3$



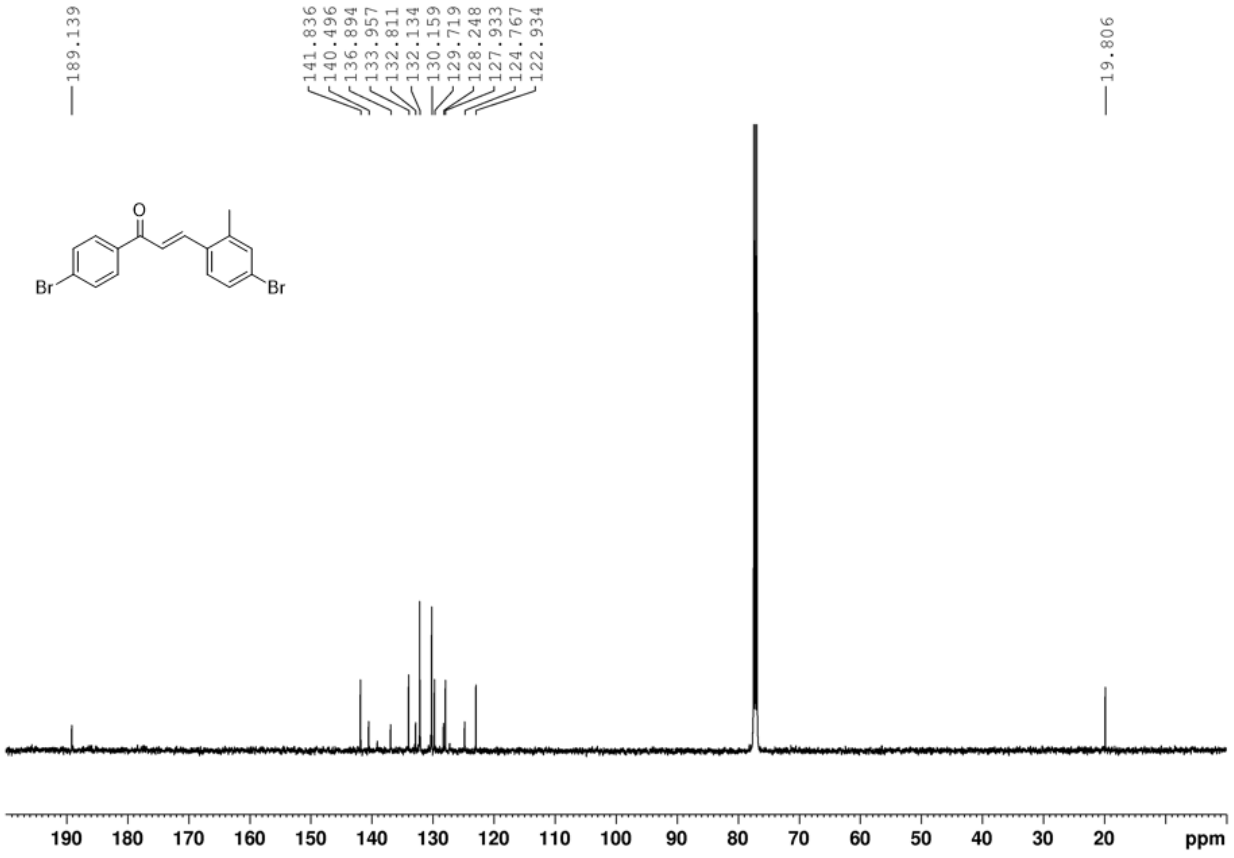
(2E)-1-(4-Bromo-, 2 methylphenyl)-3-(2,4,6-trimethylphenyl)-2-propen-1-one (1f)

^{1}H NMR (500 MHz) spectrum of compound **1f** in $CDCl_3$



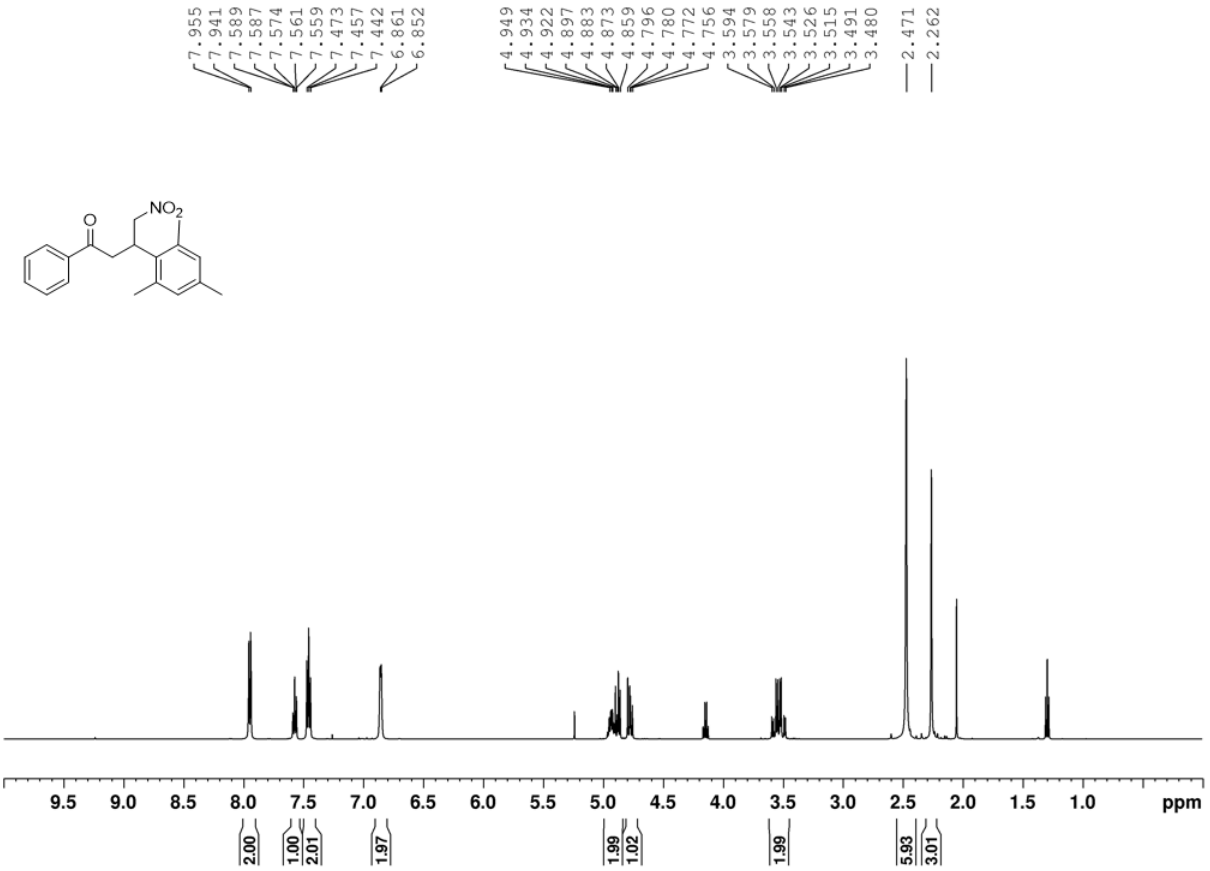
(2E)-1-(4-Bromo-, 2 methylphenyl)-3-(2,4,6-trimethylphenyl)-2-propen-1-one (1f)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **1f** in $CDCl_3$



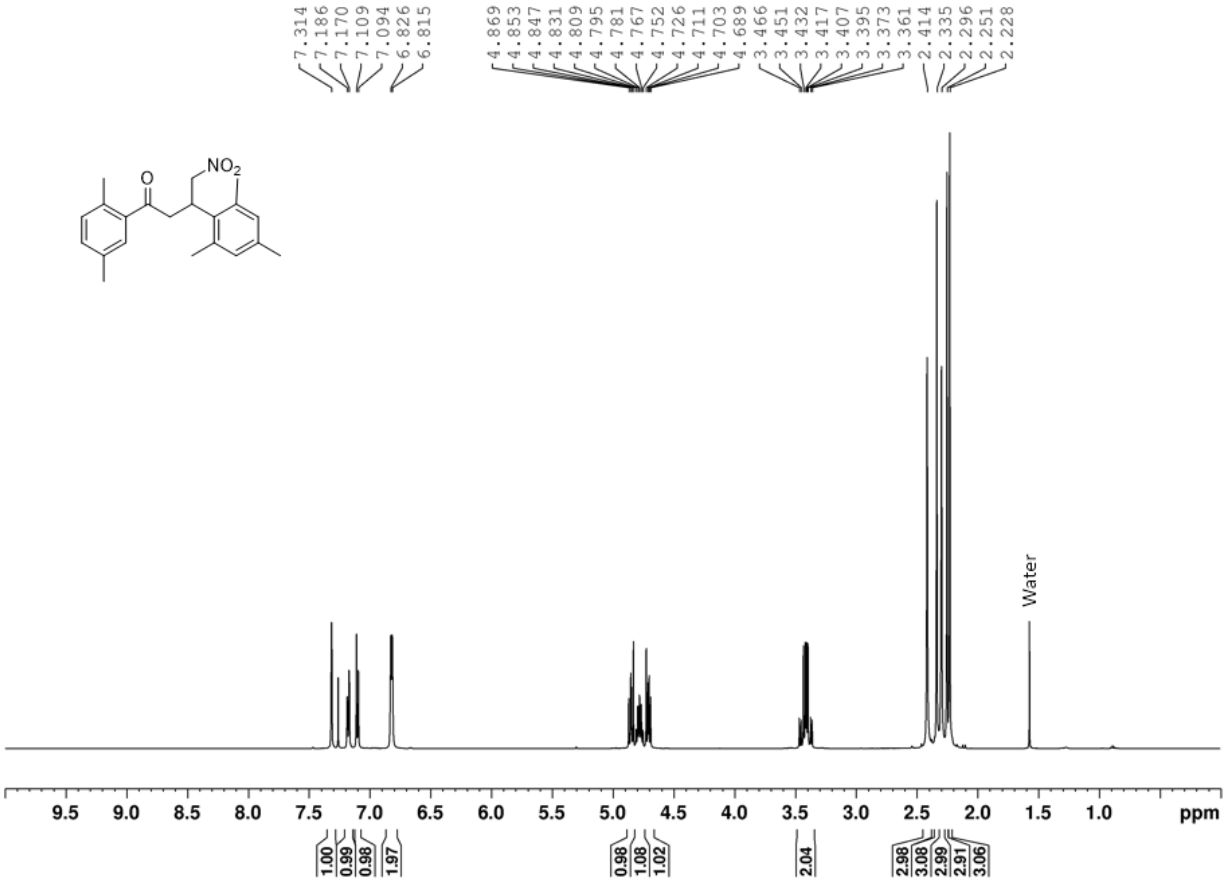
4-Nitro-1-phenyl-3-(2,4,6-trimethylphenyl)butan-1-one (2b)

^{1}H NMR (500 MHz) spectrum of compound **2b** in $CDCl_3$



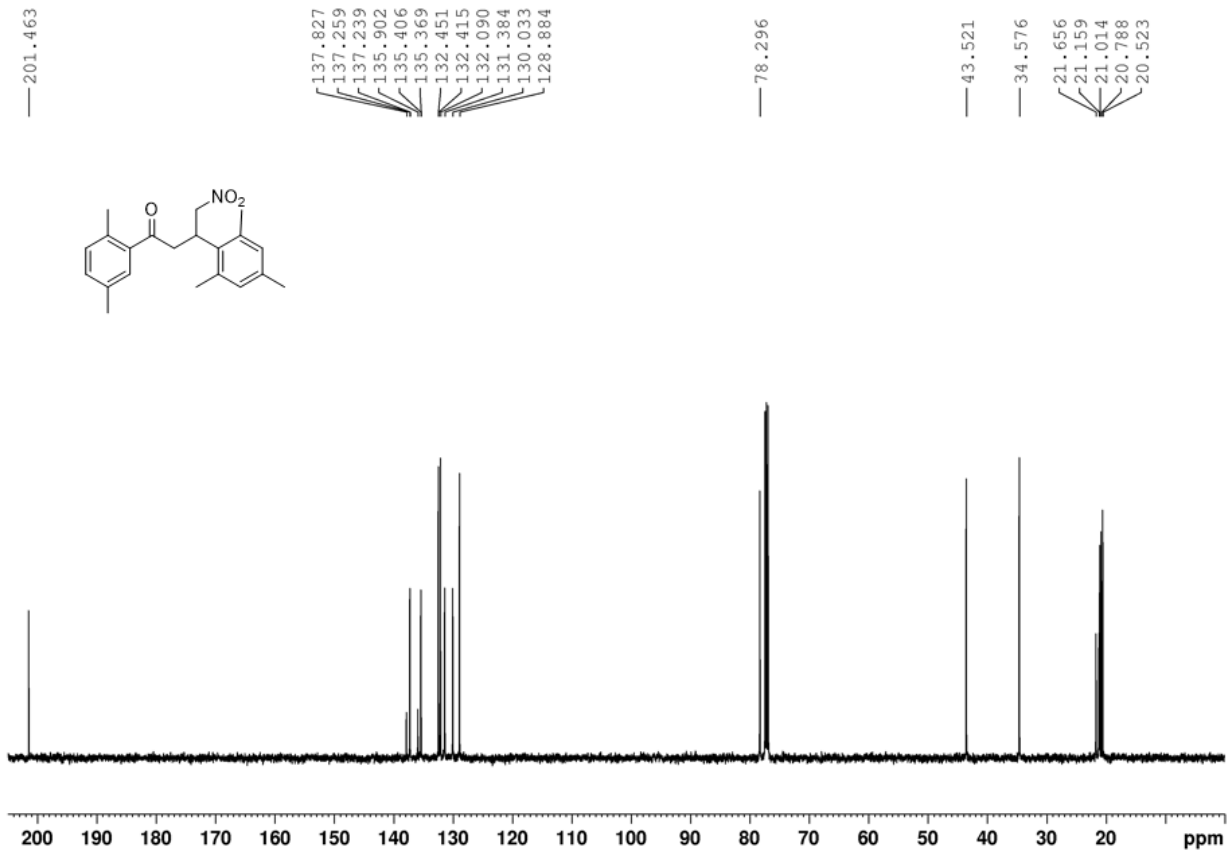
1-(2,5-Dimethylphenyl)-4-nitro-3-(2,4,6-trimethylphenyl)butan-1-one (2c)

^{1}H NMR (500 MHz) spectrum of compound **2c** in $CDCl_3$



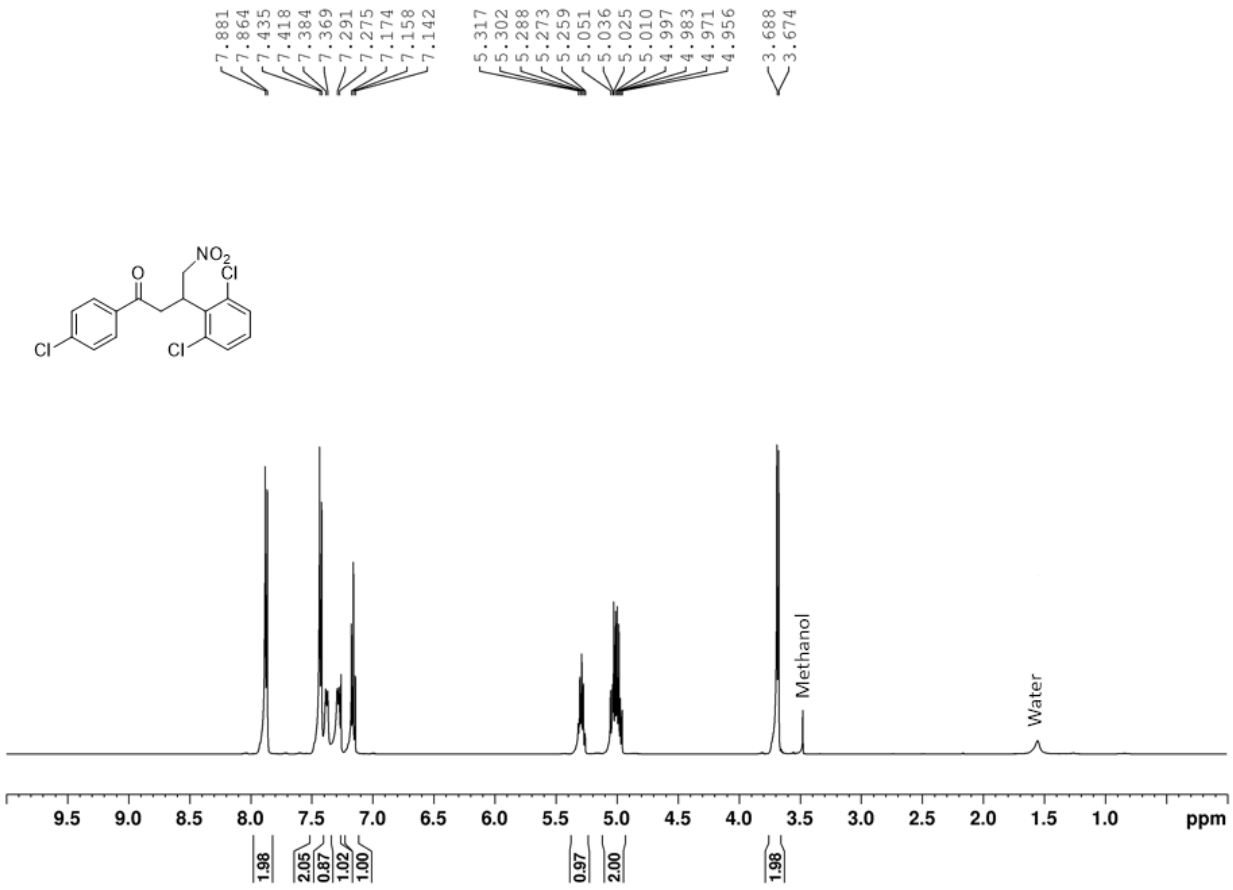
1-(2,5-Dimethylphenyl)-4-nitro-3-(2,4,6-trimethylphenyl)butan-1-one (2c)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **2c** in $CDCl_3$



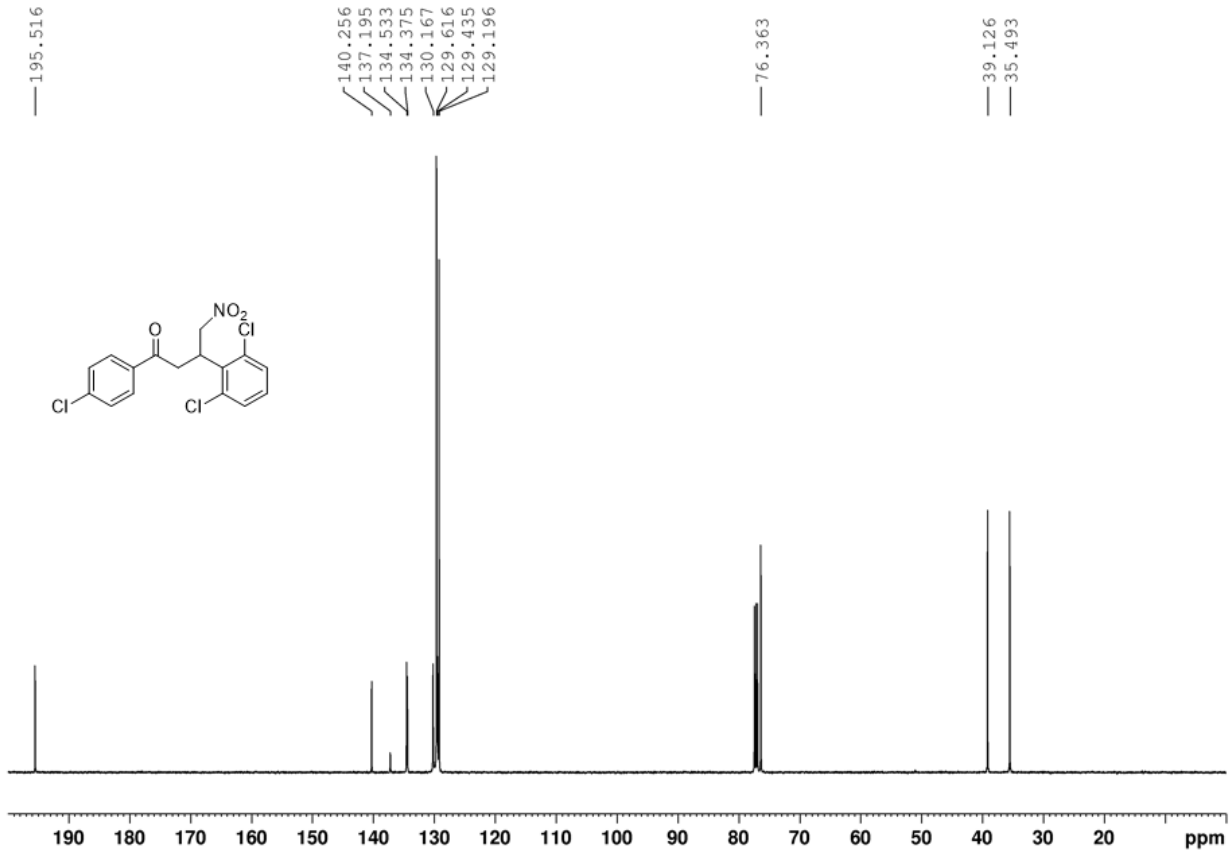
3-(2,6-Dichloro-phenyl)-4-nitro-1-(4-chloro-phenyl)-butan-1-one (2e)

^{1}H NMR (500 MHz) spectrum of compound **2e** in $CDCl_3$



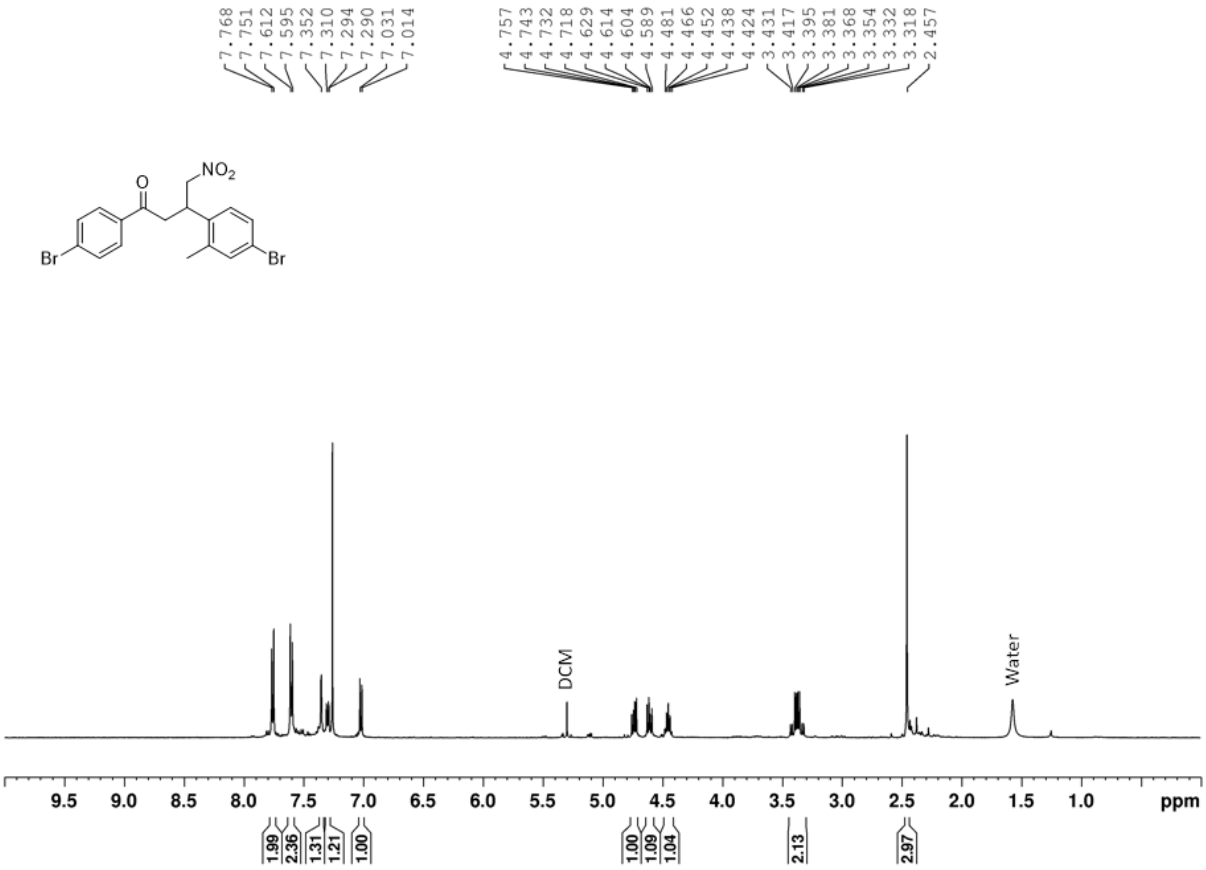
3-(2,6-Dichloro-phenyl)-4-nitro-1-(4-chloro-phenyl)-butan-1-one (2e)

^{1}H NMR (126 MHz) spectrum of compound **2e** in $CDCl_3$



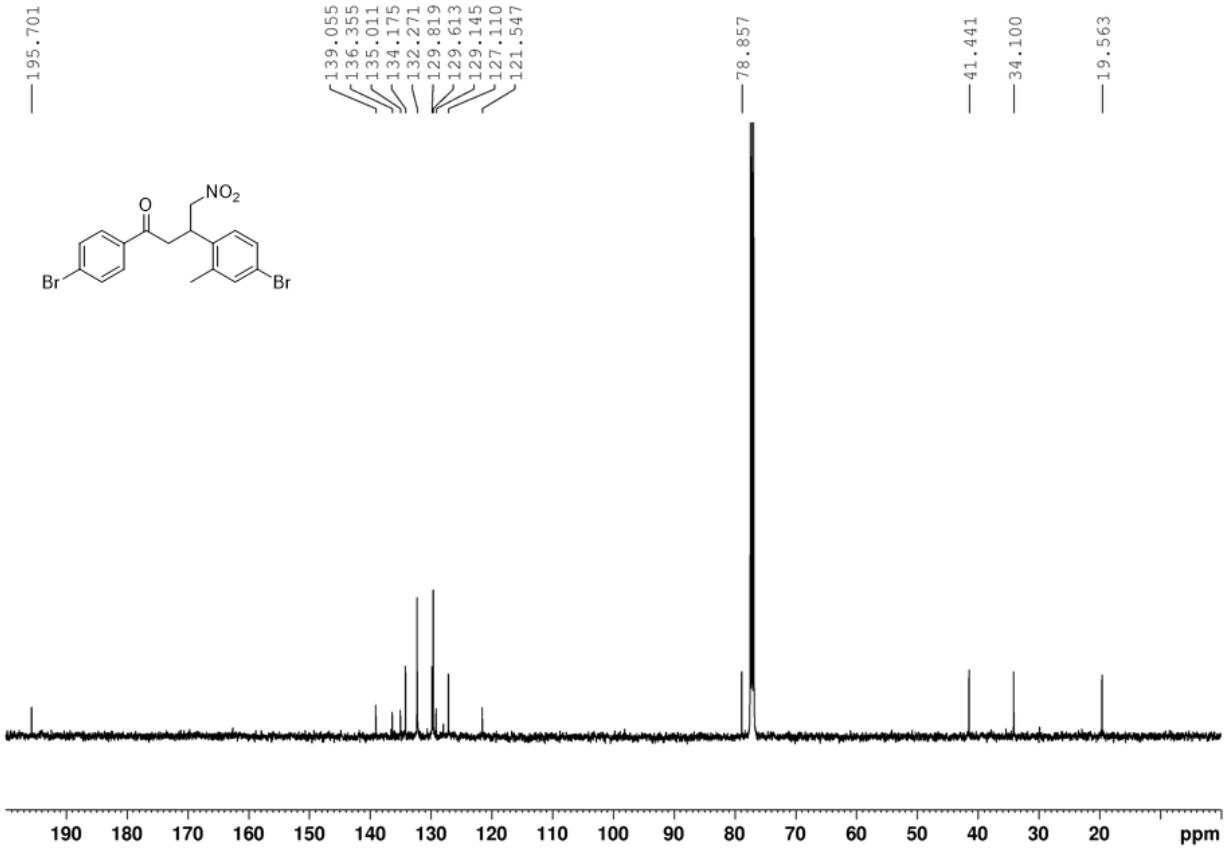
3-(2-Methyl-4-bromo-phenyl)-4-nitro-1-(4-bromo-phenyl)-butan-1-one (2f)

^{1}H NMR (500 MHz) spectrum of compound **2f** in $CDCl_3$



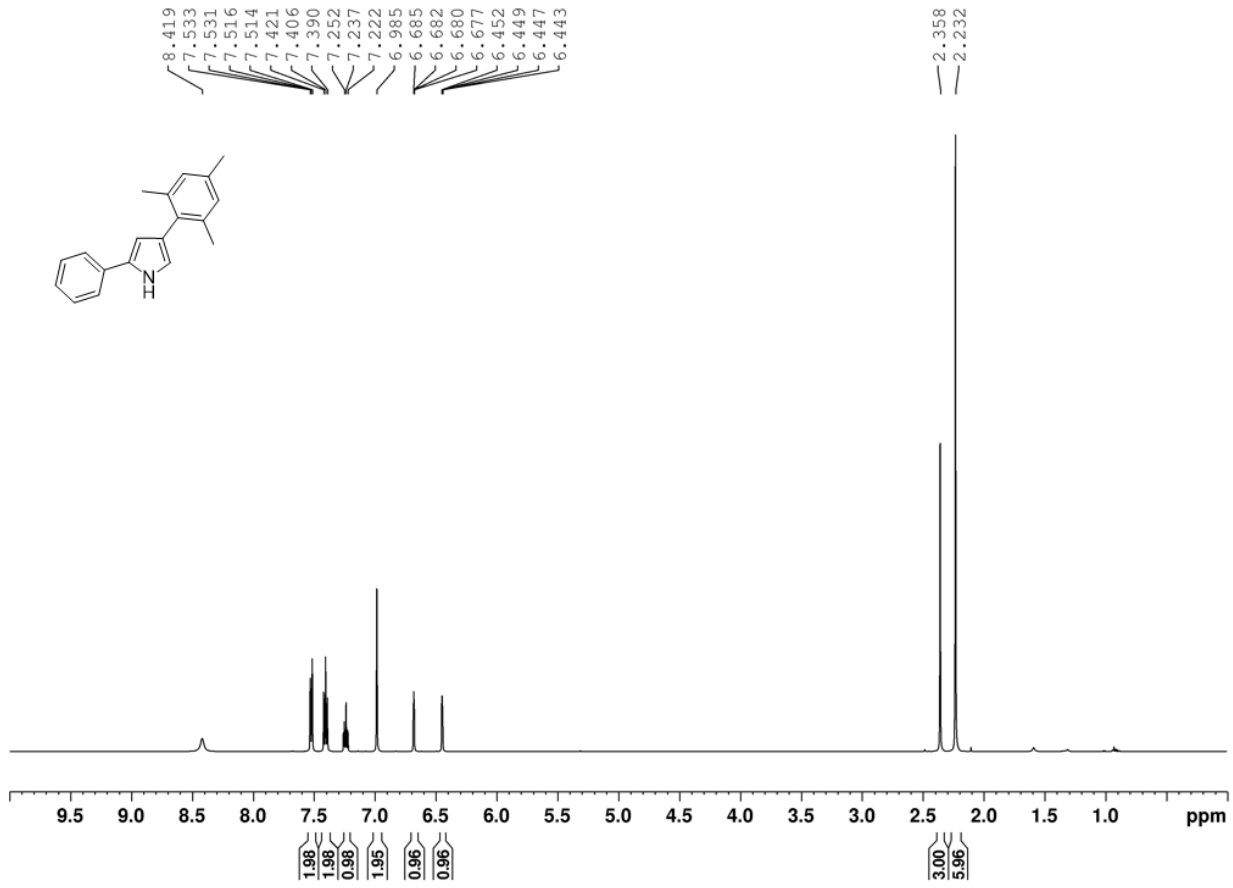
3-(2-Methyl-4-bromo-phenyl)-4-nitro-1-(4-bromo-phenyl)-butan-1-one (2f)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **2f** in $CDCl_3$



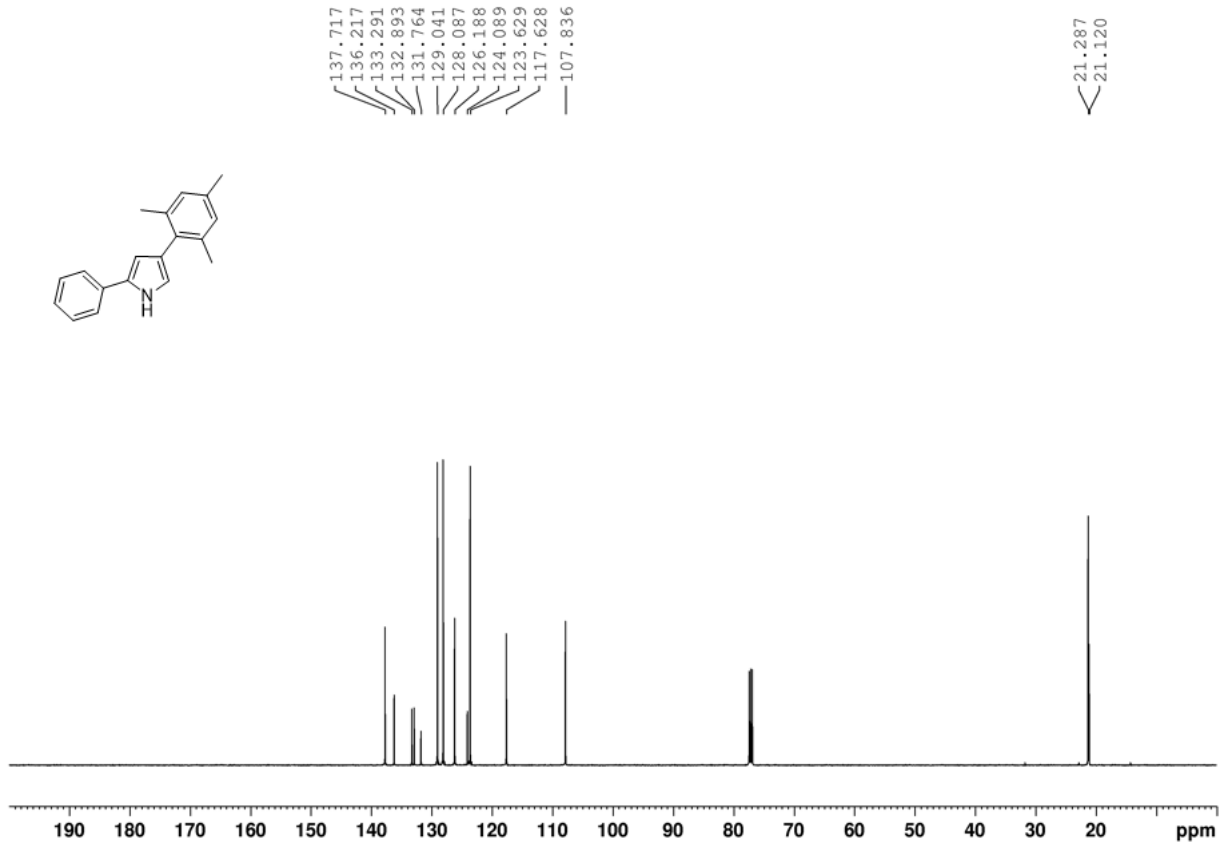
2-Phenyl-4-(2,4,6-trimethylphenyl)-1*H*-pyrrole (3b)

^{1}H NMR (500 MHz) spectrum of compound **3b** in $CDCl_3$



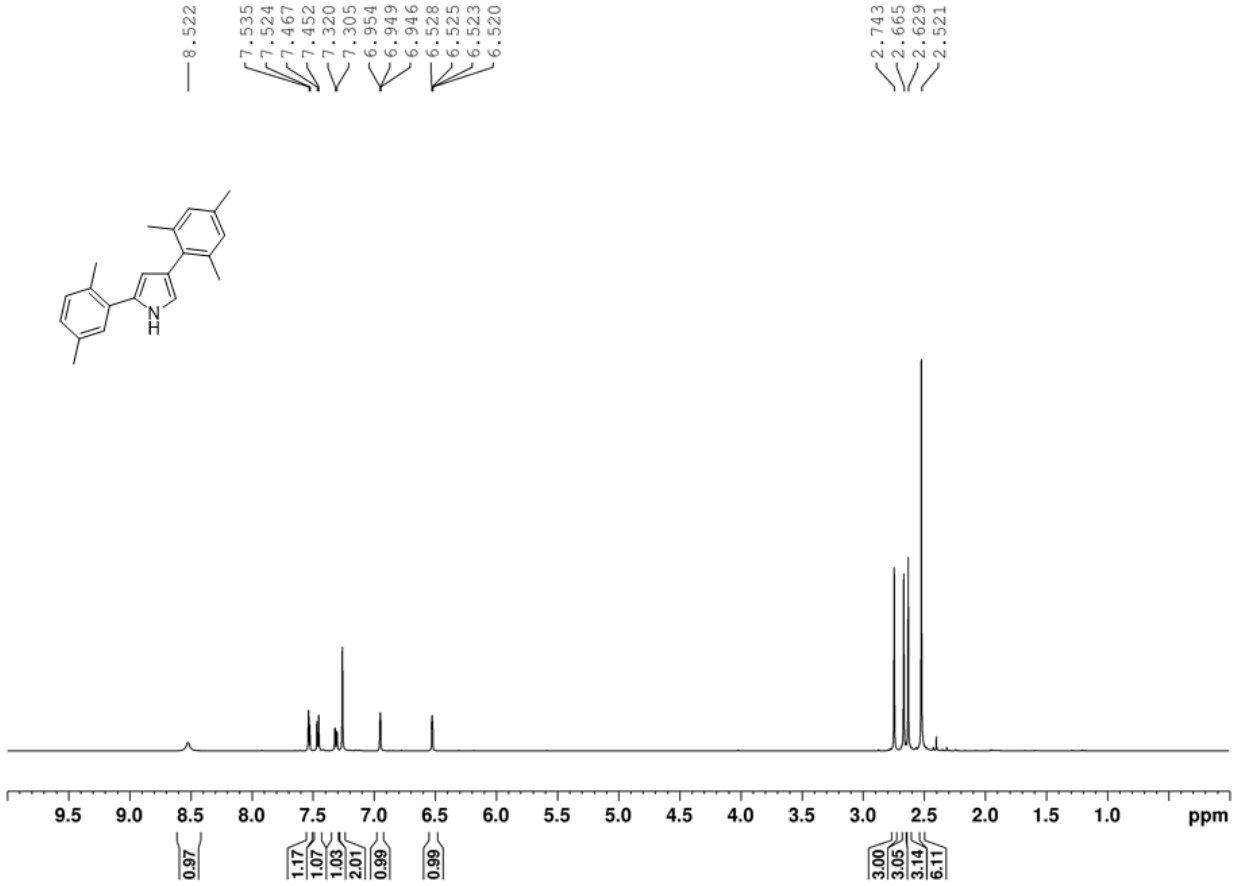
2-Phenyl-4-(2,4,6-trimethylphenyl)-1*H*-pyrrole (3b)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **3b** in $CDCl_3$



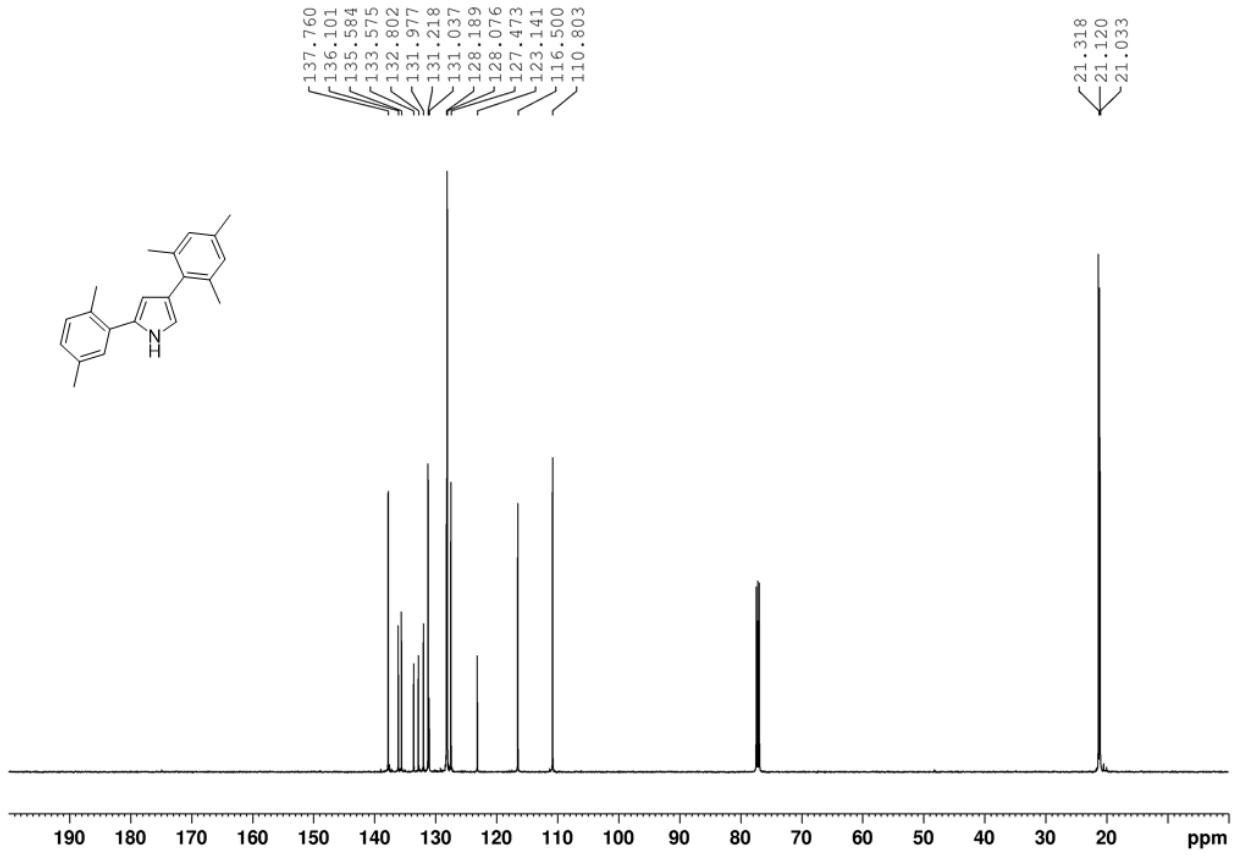
2-(2,5-Dimethylphenyl)-4-(2,4,6-trimethylphenyl)-1*H*-pyrrole (3c)

^{1}H NMR (500 MHz) spectrum of compound **3c** in $CDCl_3$



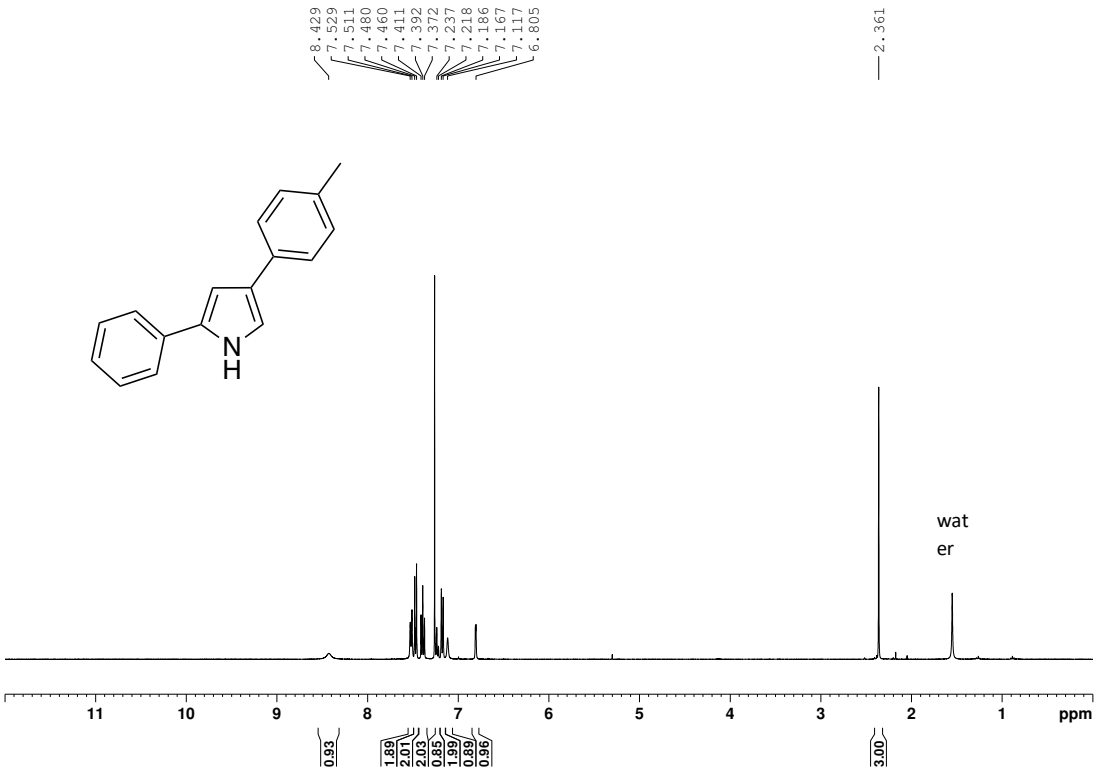
2-(2,5-Dimethylphenyl)-4-(2,4,6-trimethylphenyl)-1*H*-pyrrole (3c)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **3c** in $CDCl_3$



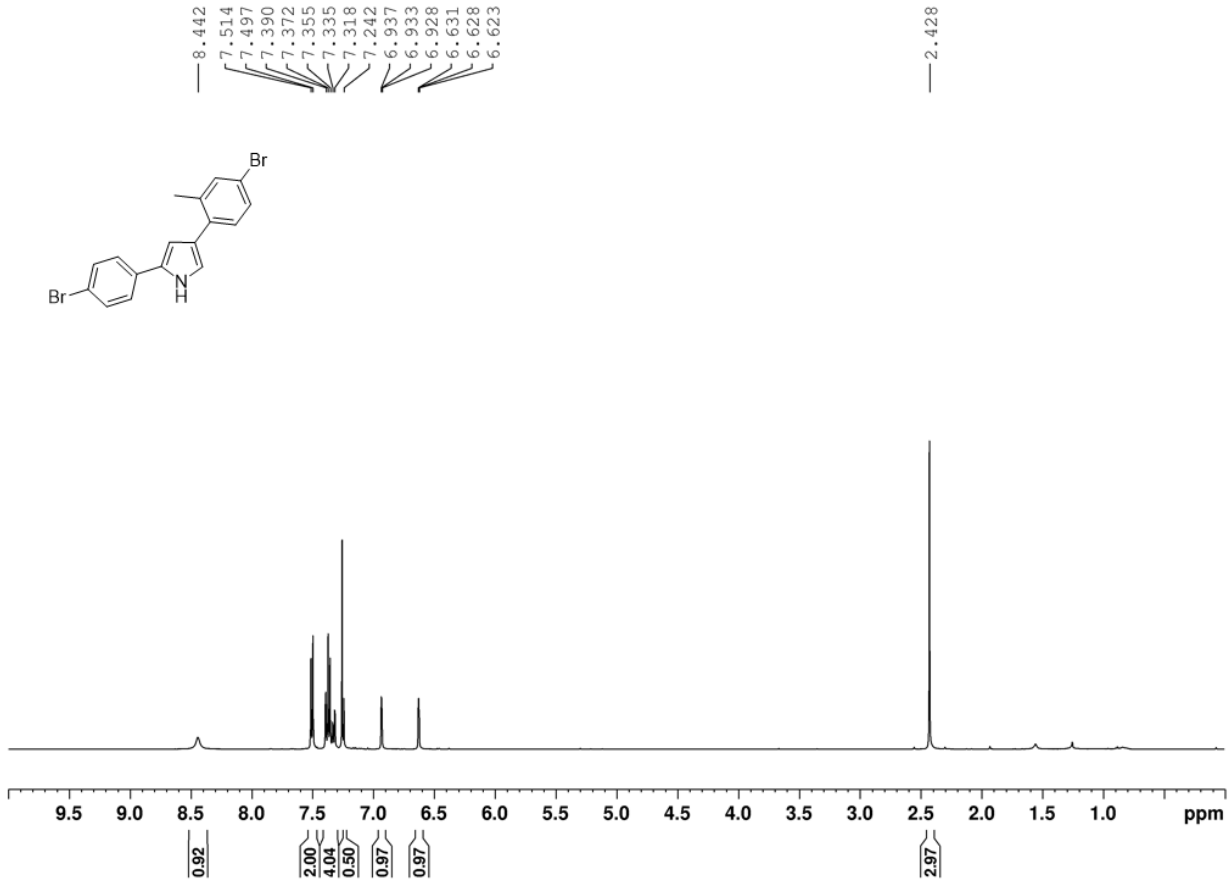
4-(4-Methylphenyl)-2-phenyl-1*H*-pyrrole (3d)

^{1}H NMR (400 MHz) spectrum of compound **3d** in $CDCl_3$



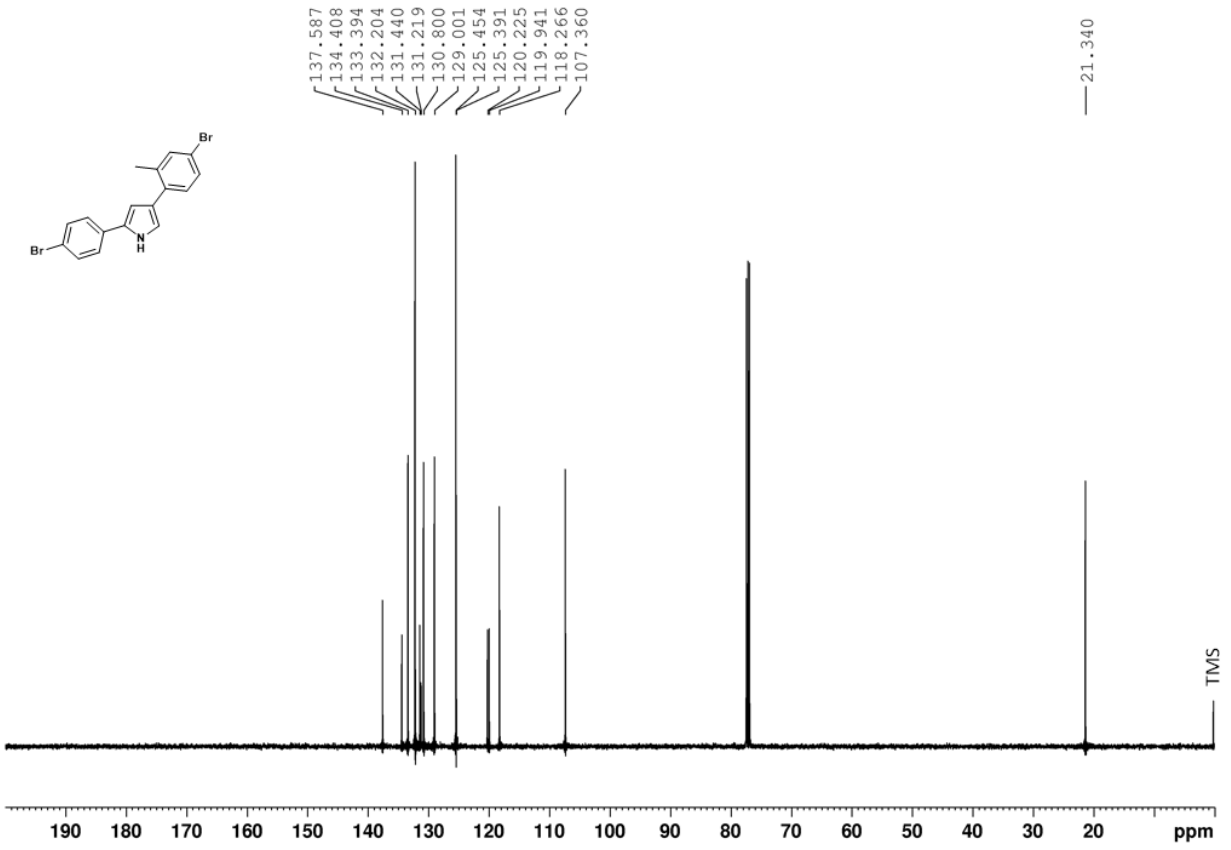
4-(4-Bromo-2-methylphenyl)-2-(4-bromophenyl)-1*H*-pyrrole (3f)

^{1}H NMR (500 MHz) spectrum of compound **3f** in $CDCl_3$



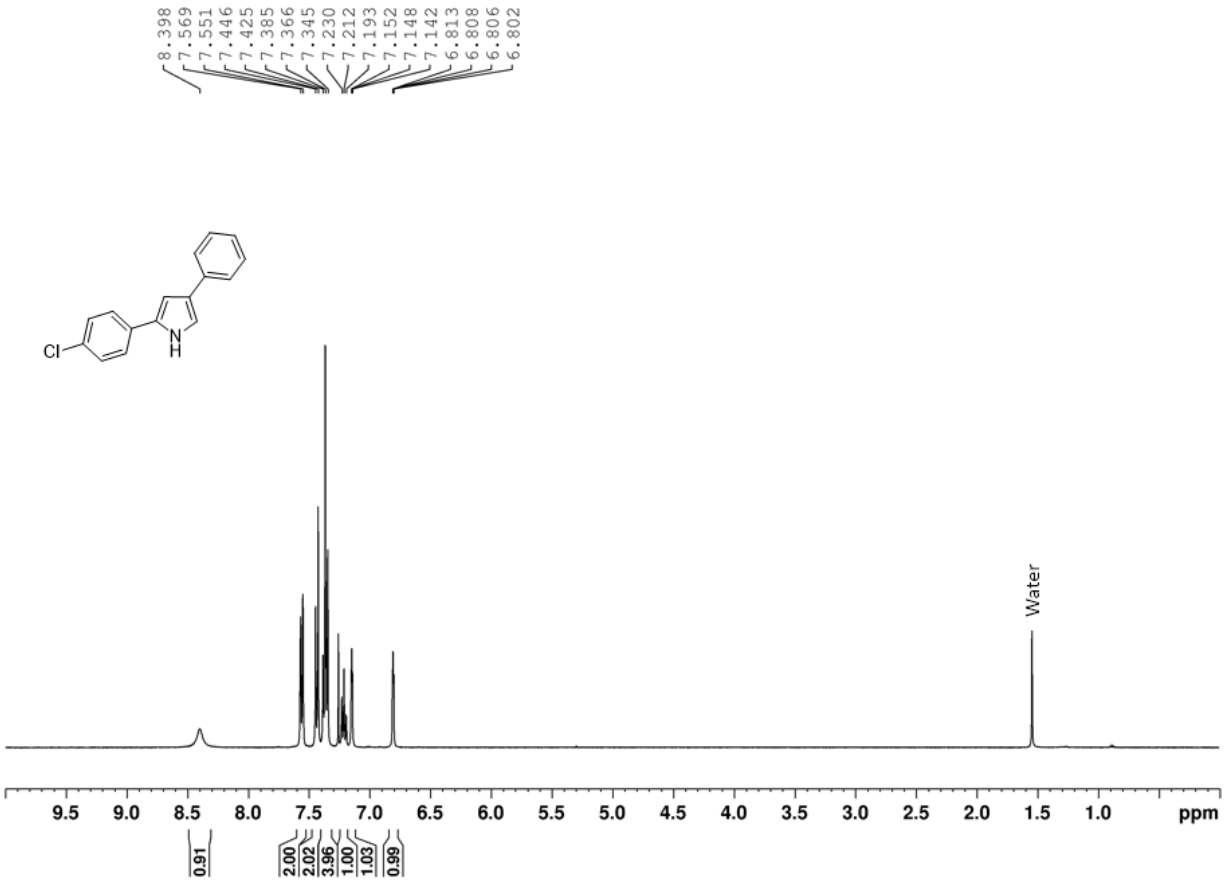
4-(4-Bromo-2-methylphenyl)-2-(4-bromophenyl)-1*H*-pyrrole (3f)

$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of compound **3f** in $CDCl_3$



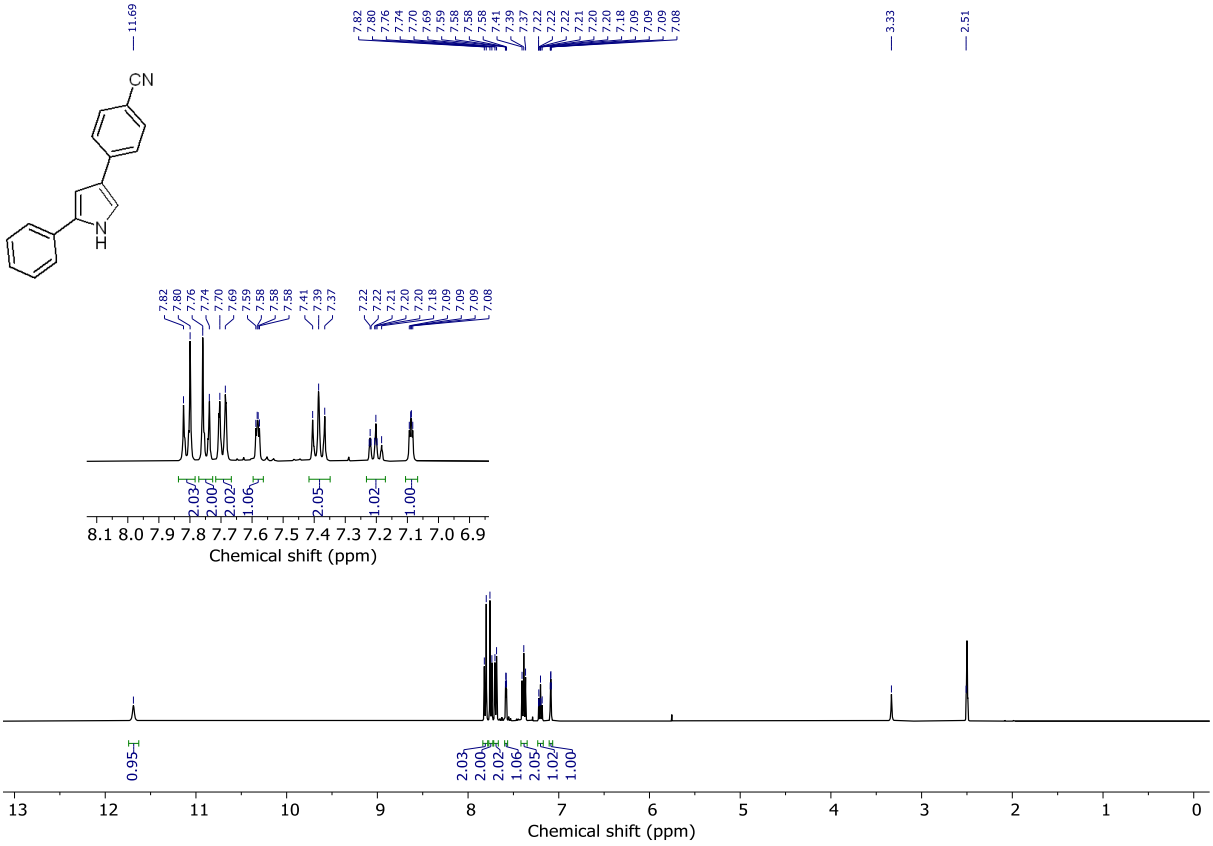
4-Phenyl- 2-(4-chloro-phenyl)-1*H*-pyrrole (3g)

^{1}H NMR (400 MHz) spectrum of compound **3g** in $CDCl_3$



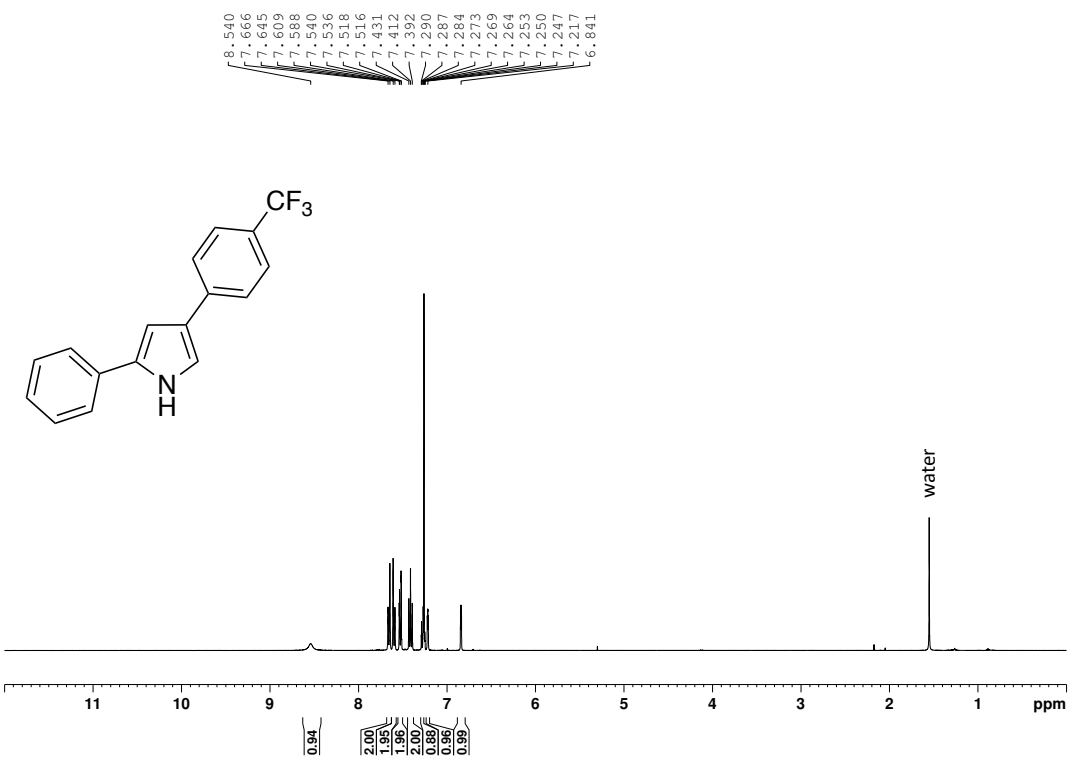
4-(4-Cyanophenyl)-2-phenyl-1*H*-pyrrole (3h)

^{1}H NMR (400 MHz) spectrum of compound **3h** in DMSO-d_6



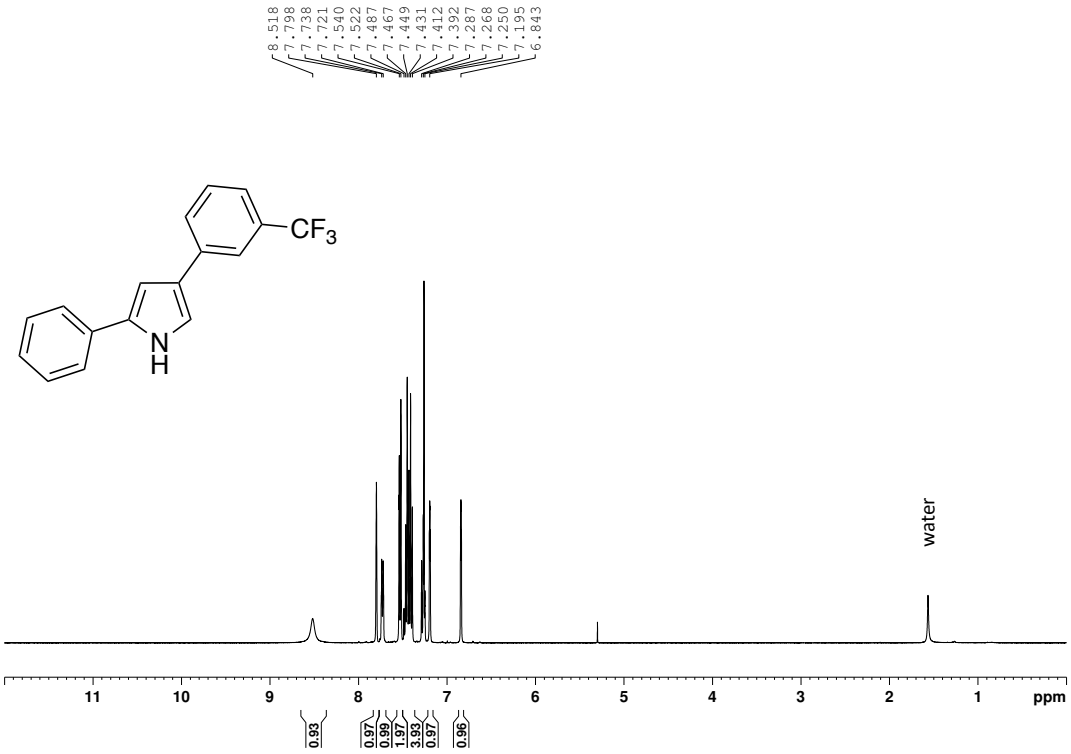
2-Phenyl-4-[4-(trifluoromethyl)phenyl]-1*H*-pyrrole (3i)

^{1}H NMR (400 MHz) spectrum of compound **3i** in $CDCl_3$



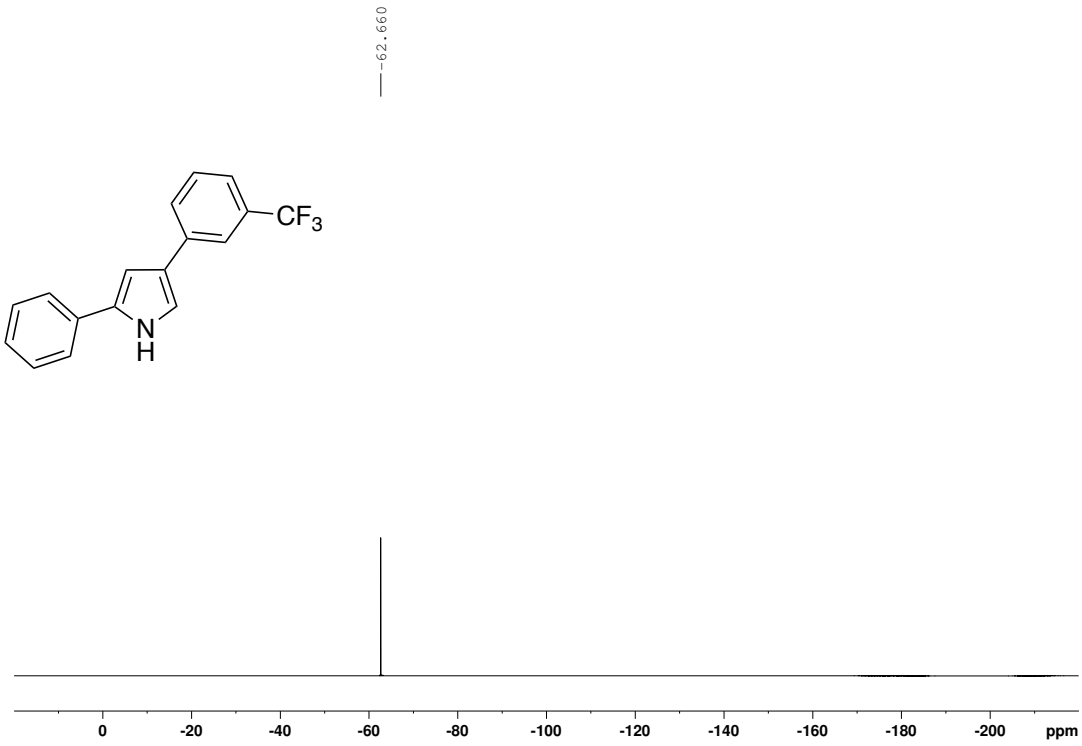
2-Phenyl-4-[3-(trifluoromethyl)phenyl]-1*H*-pyrrole (3j)

^{1}H NMR (400 MHz) spectrum of compound **3j** in $CDCl_3$



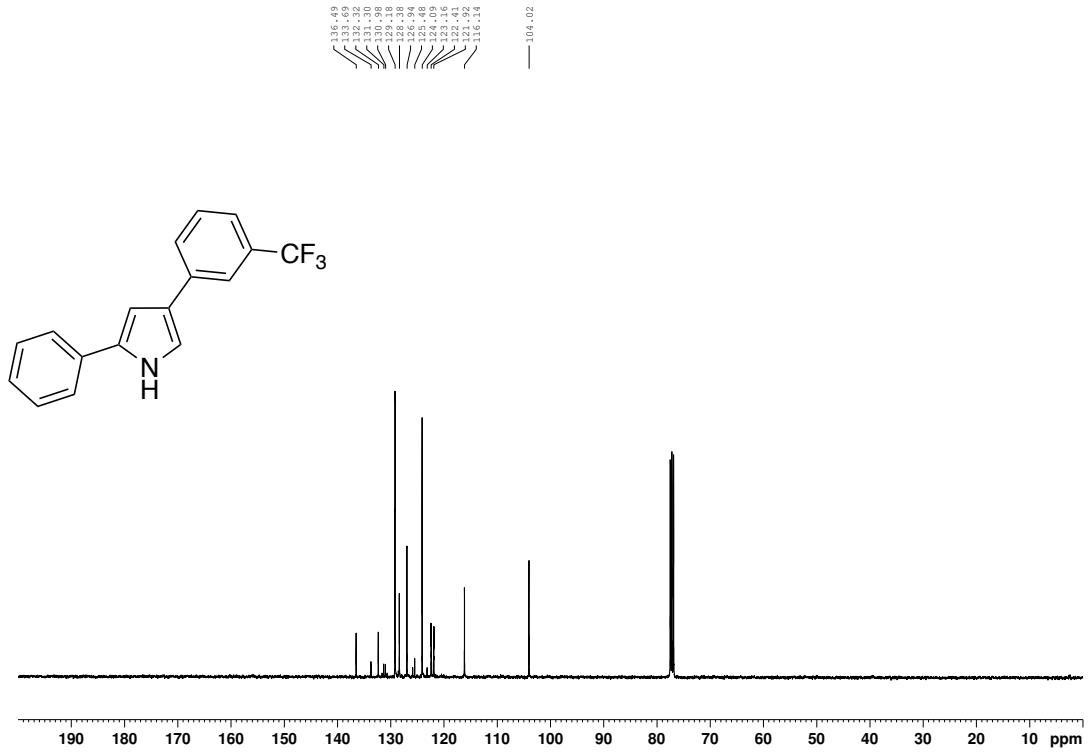
2-Phenyl-4-[3-(trifluoromethyl)phenyl]-1*H*-pyrrole (3j)

$^{19}F\{^{1}H\}$ NMR (377 MHz) spectrum of compound **3j** in $CDCl_3$



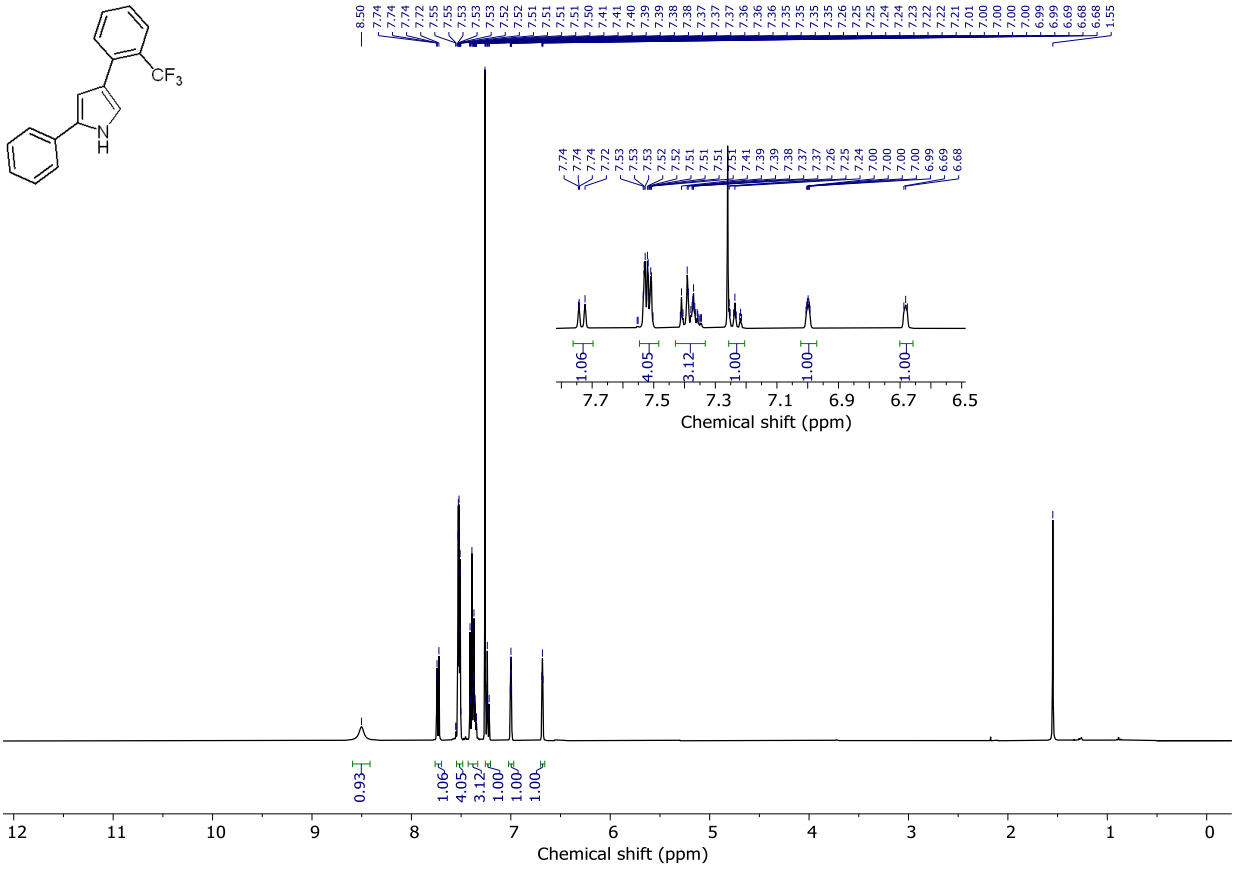
2-Phenyl-4-[3-(trifluoromethyl)phenyl]-1*H*-pyrrole (3j)

$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of compound **3j** in $CDCl_3$



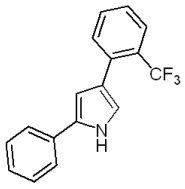
2-Phenyl-4-(2-(trifluoromethyl) phenyl)-1*H*-pyrrole (3k)

^{1}H NMR (400 MHz) spectrum of compound **3k** in $CDCl_3$



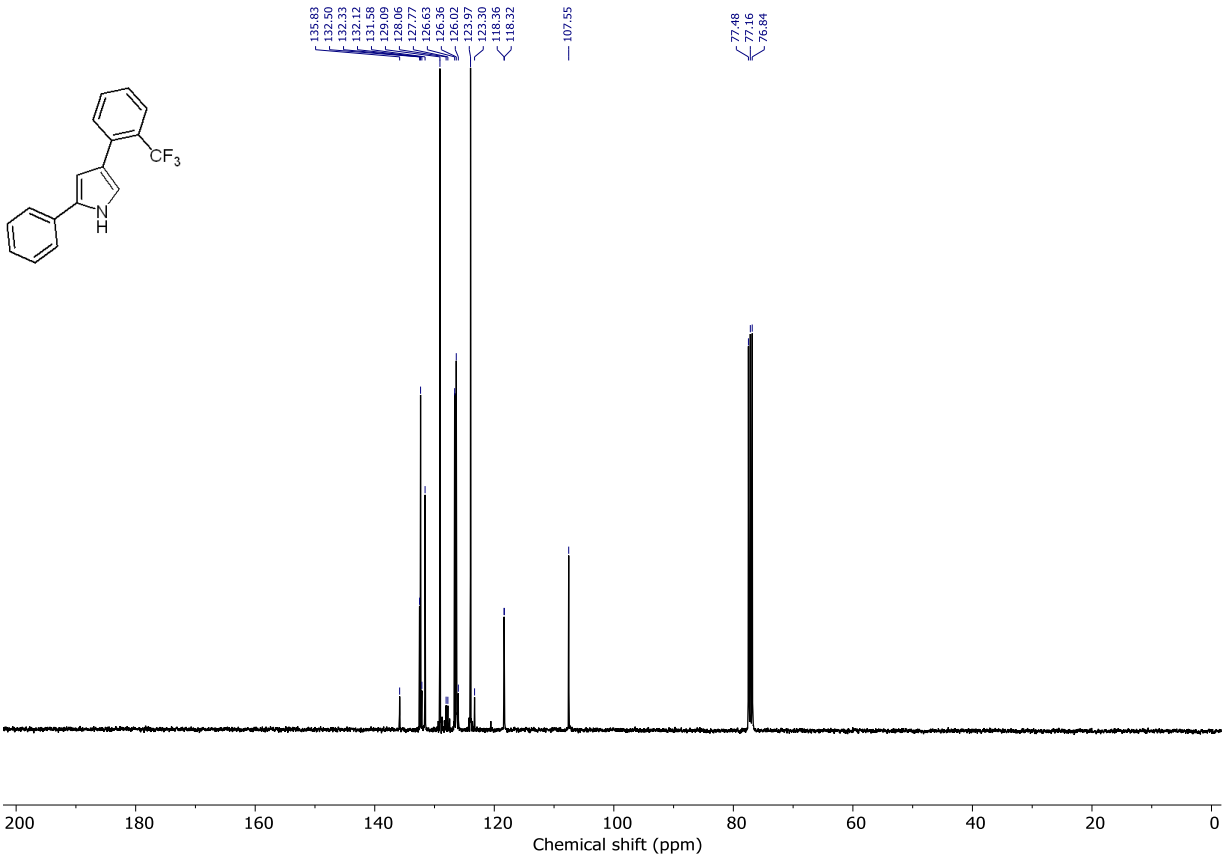
2-Phenyl-4-(2-(trifluoromethyl) phenyl)-1*H*-pyrrole (3k)

$^{19}F\{^{1}H\}$ NMR (377 MHz) spectrum of compound **3k** in $CDCl_3$



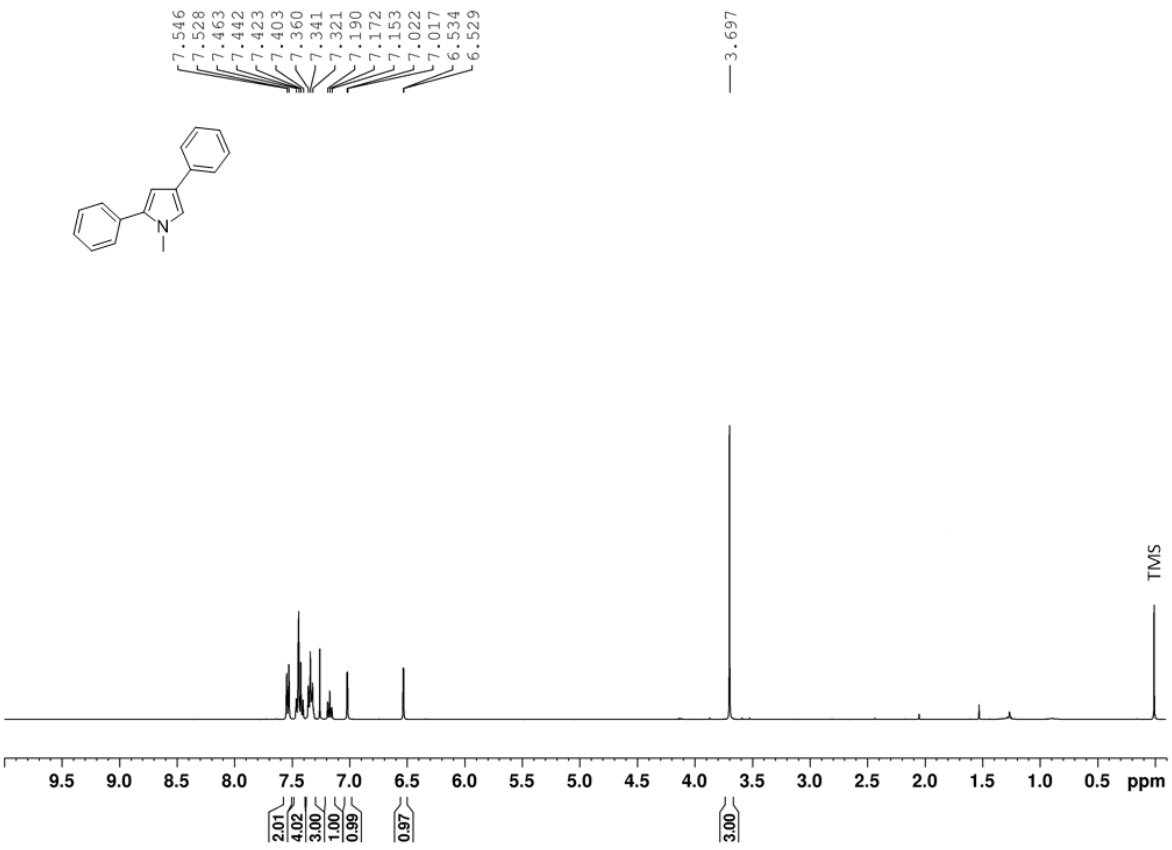
2-Phenyl-4-(2-(trifluoromethyl) phenyl)-1*H*-pyrrole (3k)

$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of compound **3k** in $CDCl_3$



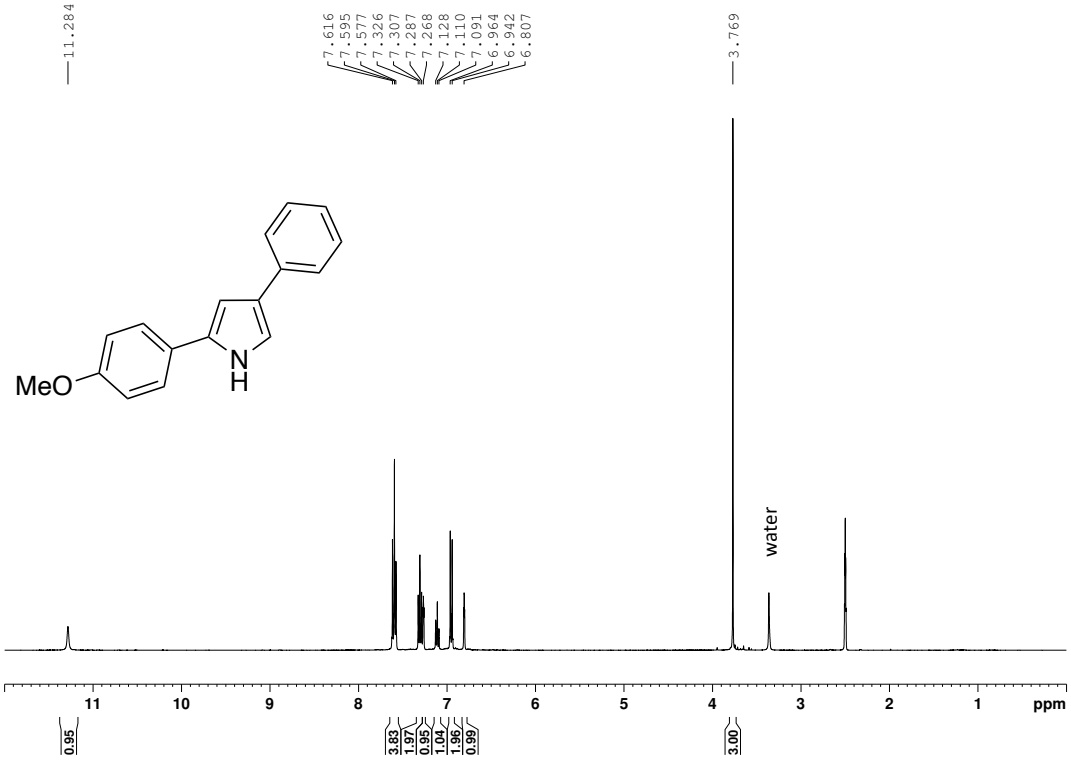
1-Methyl-2,4-diphenyl-1*H*-pyrrole (3l)

^{1}H NMR (400 MHz) spectrum of compound **3l** in $CDCl_3$



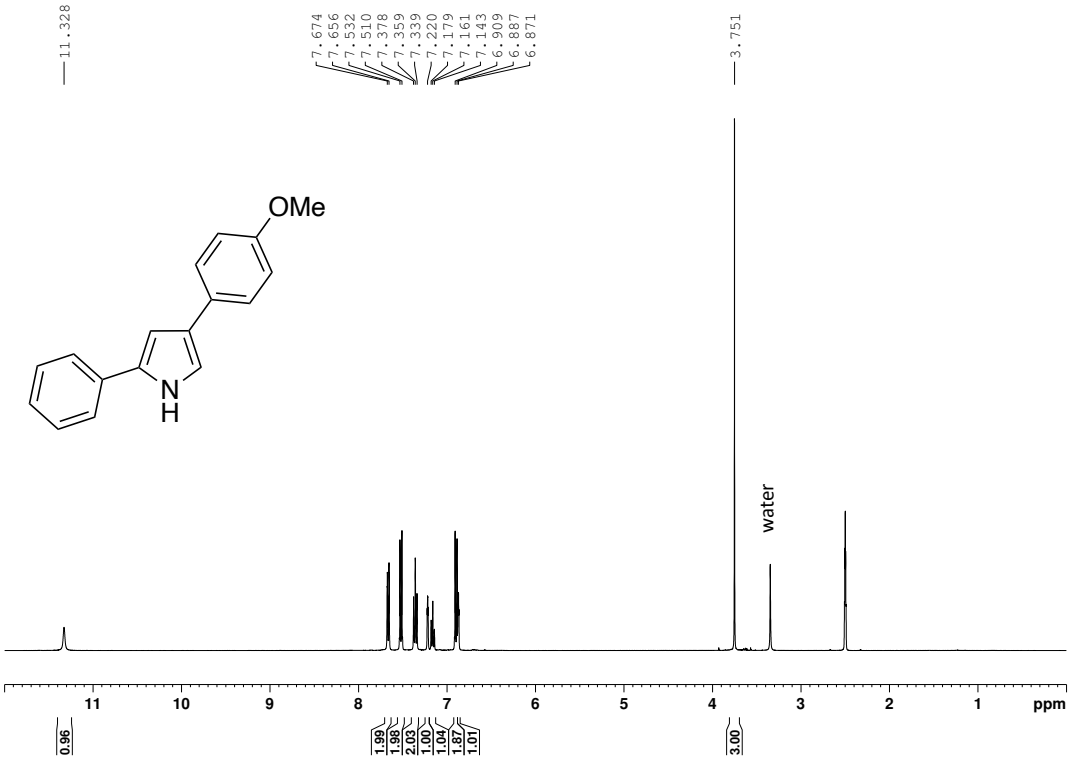
2-(4-Methoxyphenyl)-4-phenyl-1*H*-pyrrole (3m)

^{1}H NMR (400 MHz) spectrum of compound **3m** in DMSO-d_6



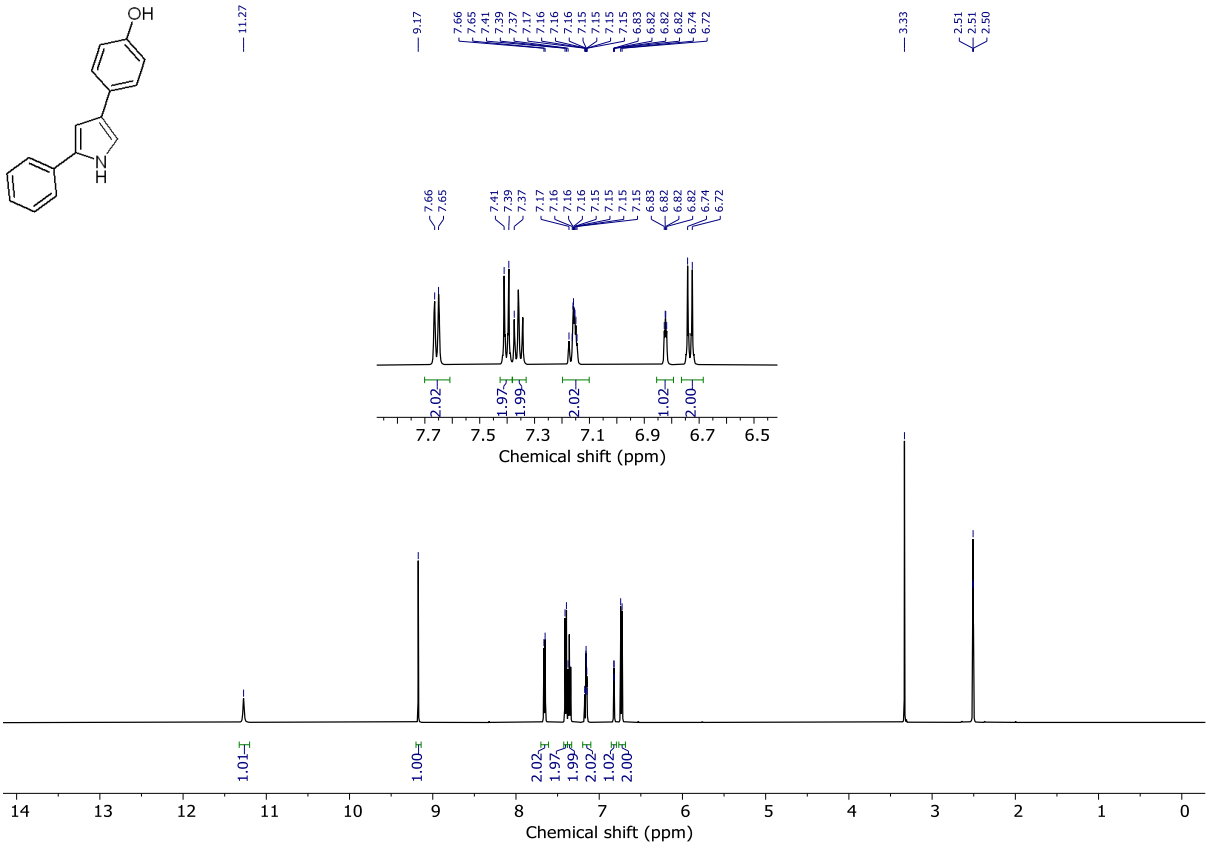
4-(4-Methoxyphenyl)-2-phenyl-1*H*-pyrrole (3n)

^{1}H NMR (400 MHz) spectrum of compound **3n** in DMSO-d_6



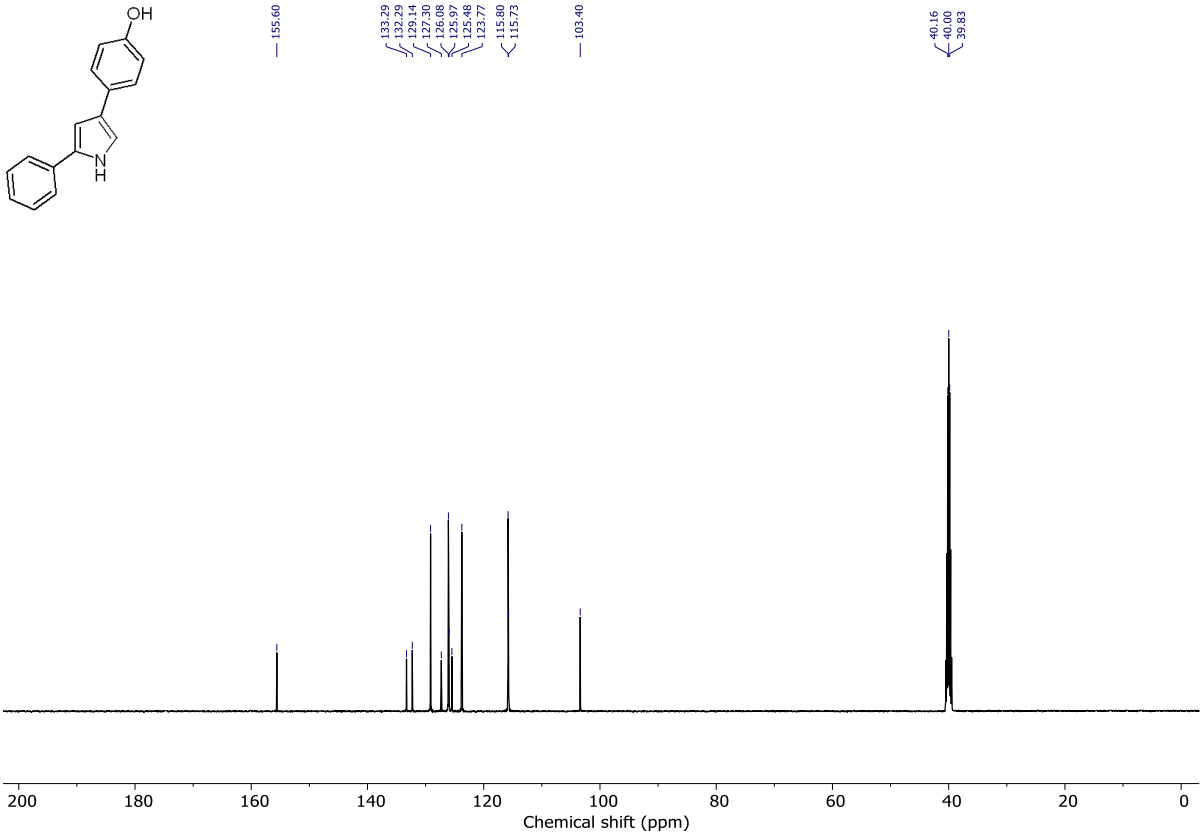
4-(4-Hydroxyphenyl)-2-phenyl-1*H*-pyrrole (3o)

^{1}H NMR (500 MHz) spectrum of compound **3o** in DMSO-d_6



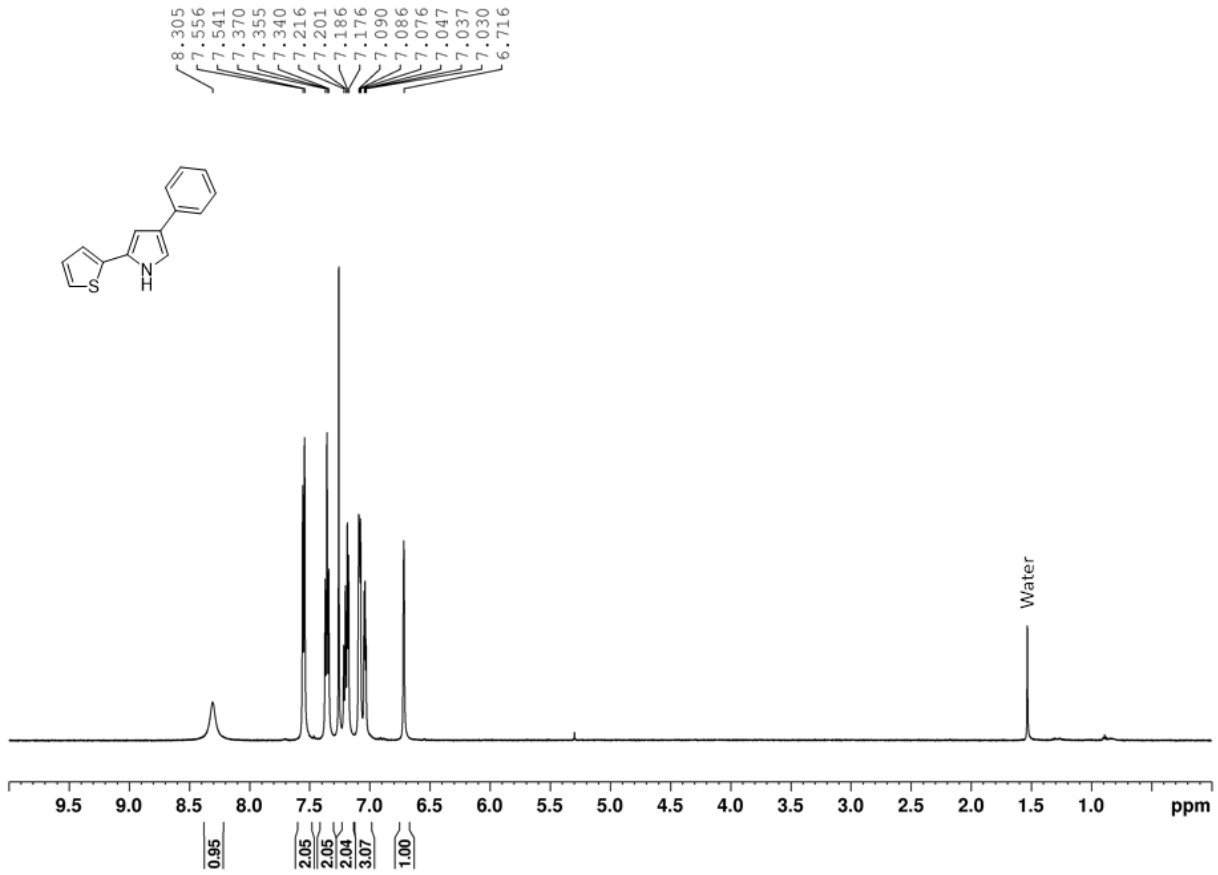
4-(4-Hydroxyphenyl)-2-phenyl-1*H*-pyrrole (3o)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **3o** in $CDCl_3$



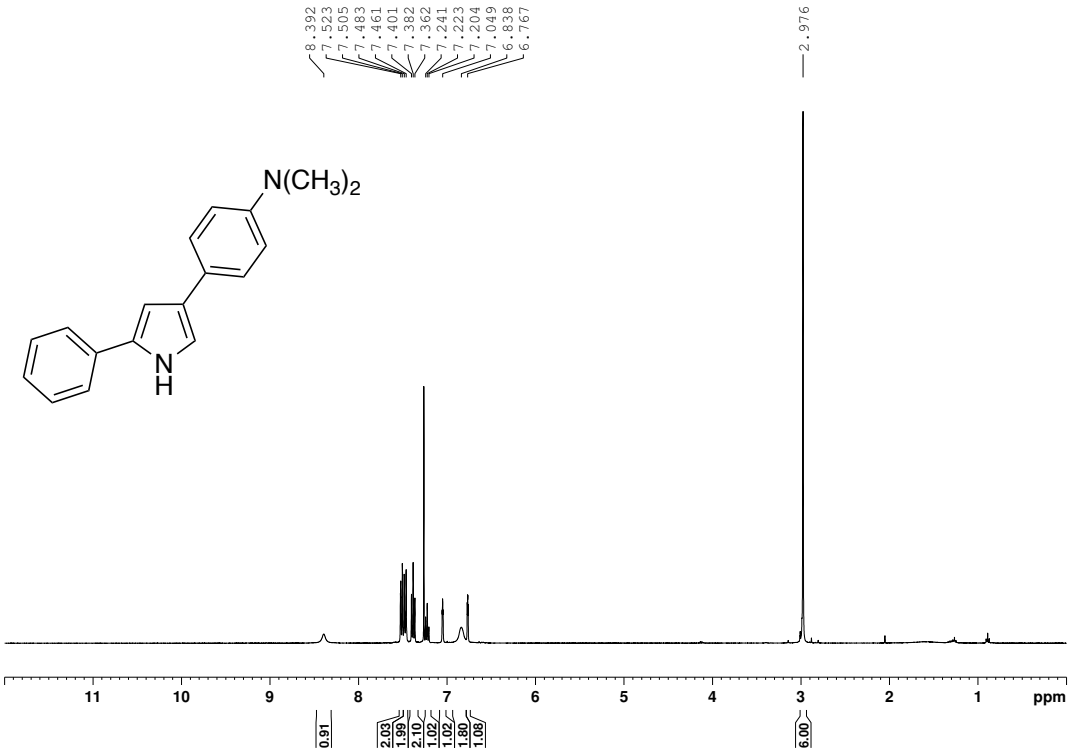
4-Phenyl-2-(2-thienyl)-1*H*-pyrrole (3p)

^{1}H NMR (500 MHz) spectrum of compound **3p** in $CDCl_3$



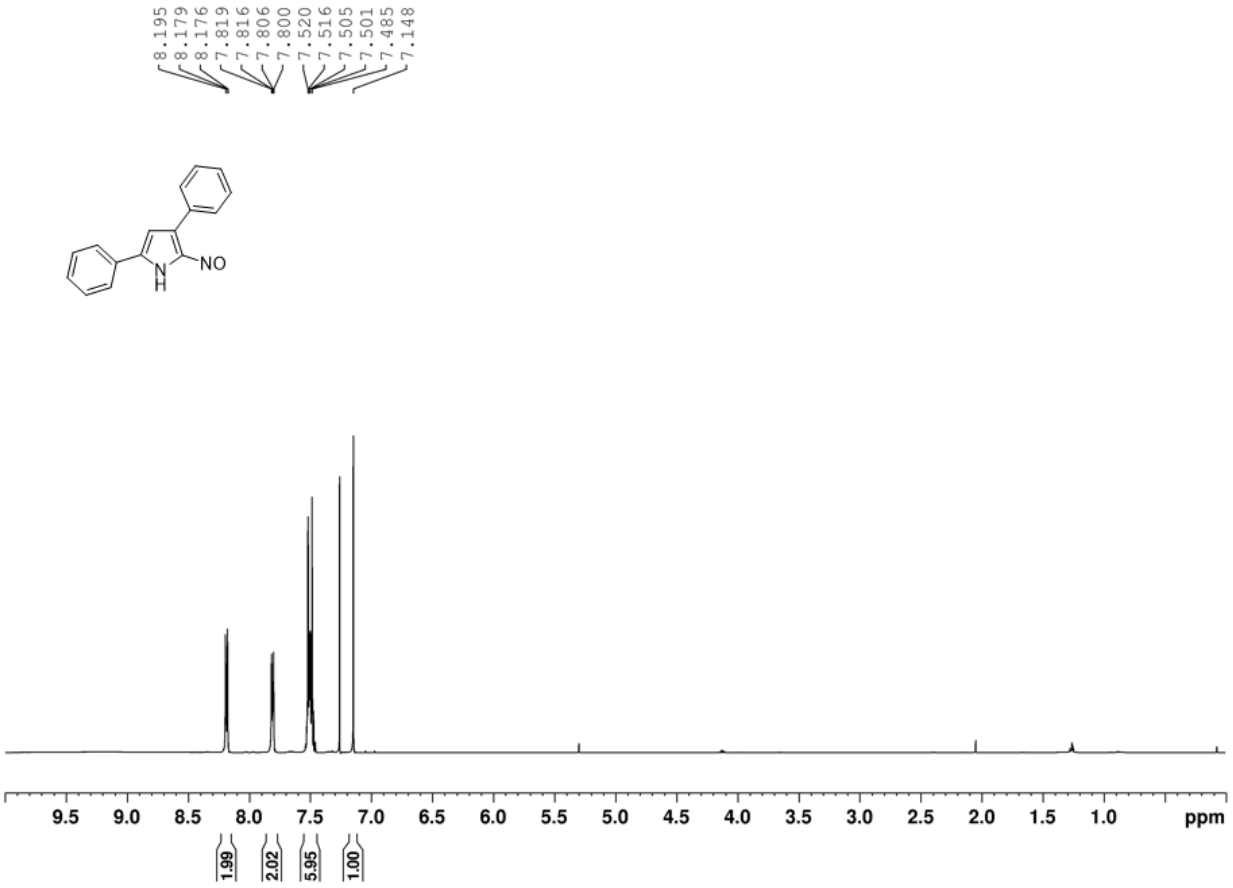
N,N-Dimethyl-4-(5-phenyl-1*H*-pyrrol-3-yl)benzenamine (3q)

^{1}H NMR (400 MHz) spectrum of compound **3q** in $CDCl_3$



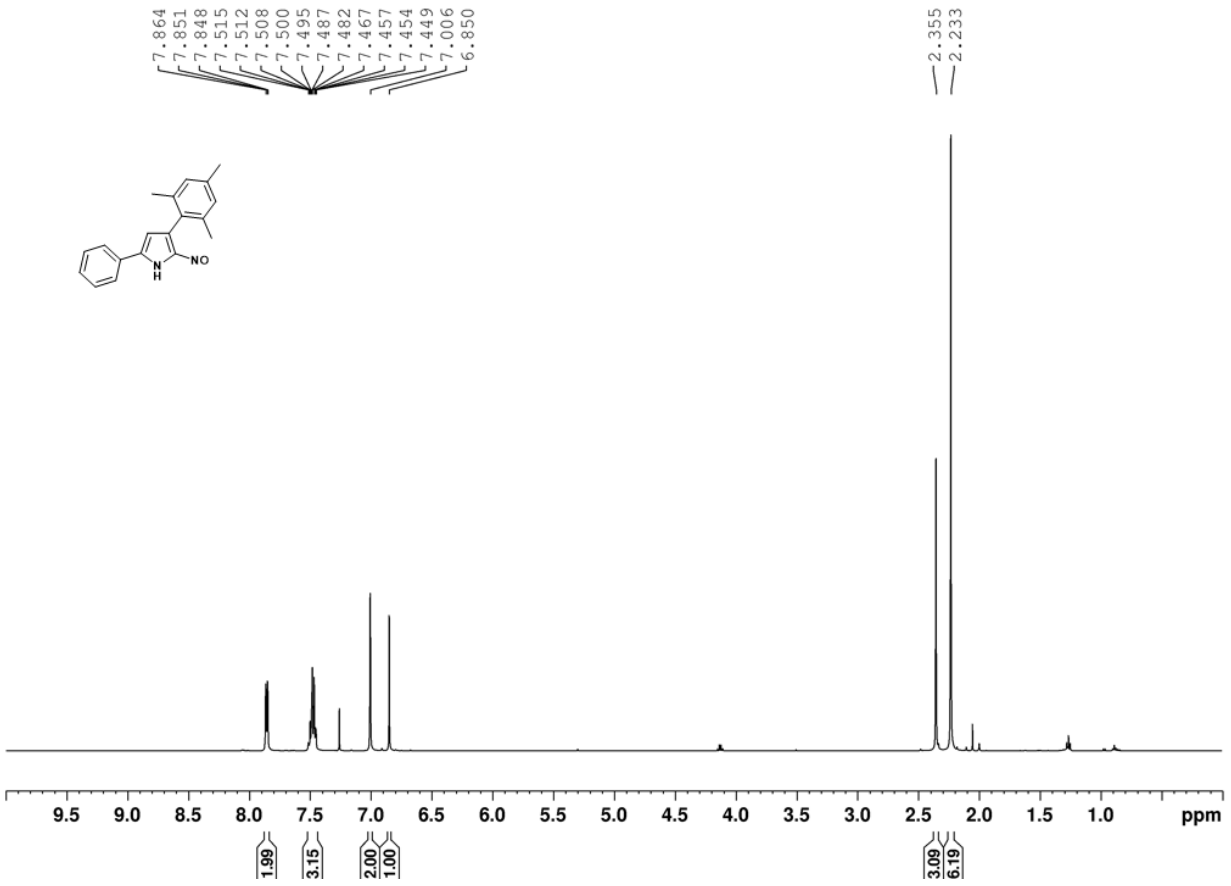
2-Nitroso-3,5-diphenyl-1*H*-pyrrole (4a)

^{1}H NMR (500 MHz) spectrum of compound **4a** in $CDCl_3$



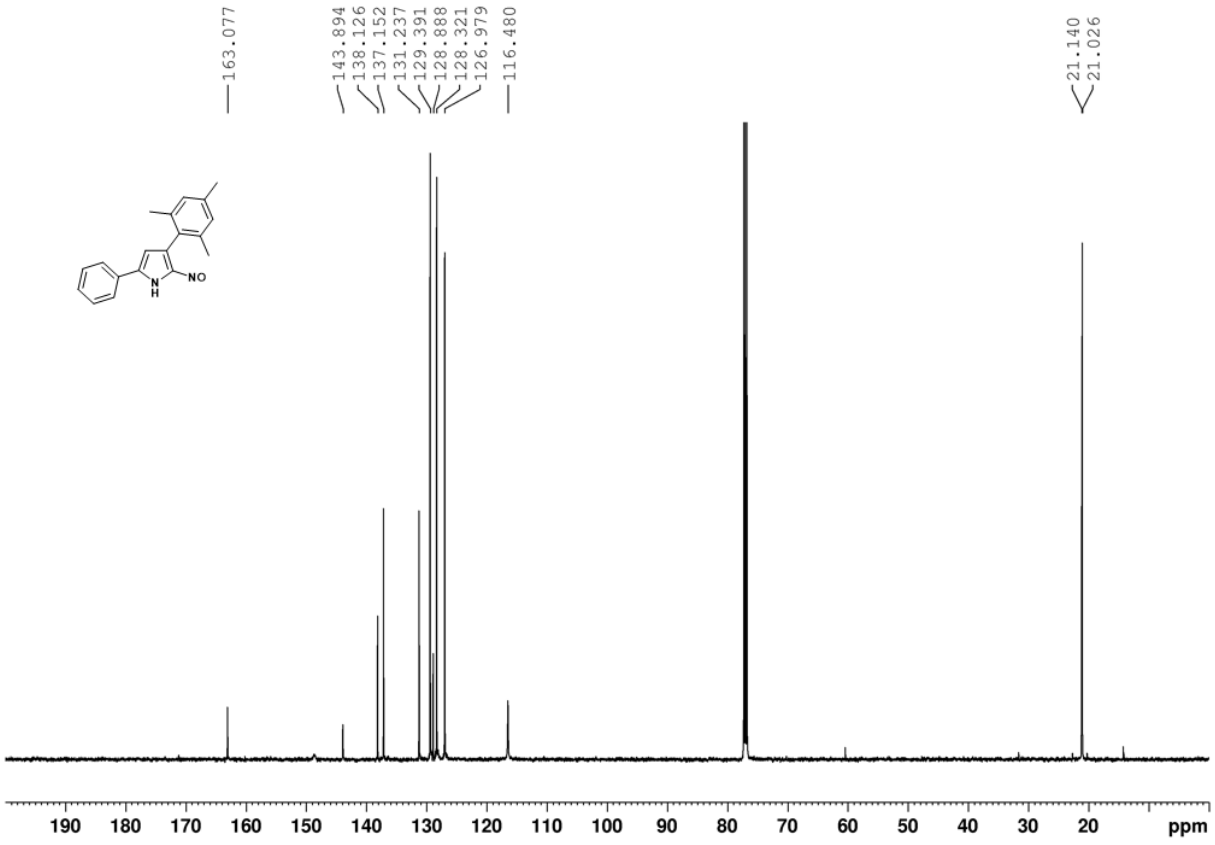
2-Nitroso-5-phenyl-3-(2,4,6-trimethylphenyl)-1*H*-pyrrole (4b)

^{1}H NMR (500 MHz) spectrum of compound **4b** in $CDCl_3$



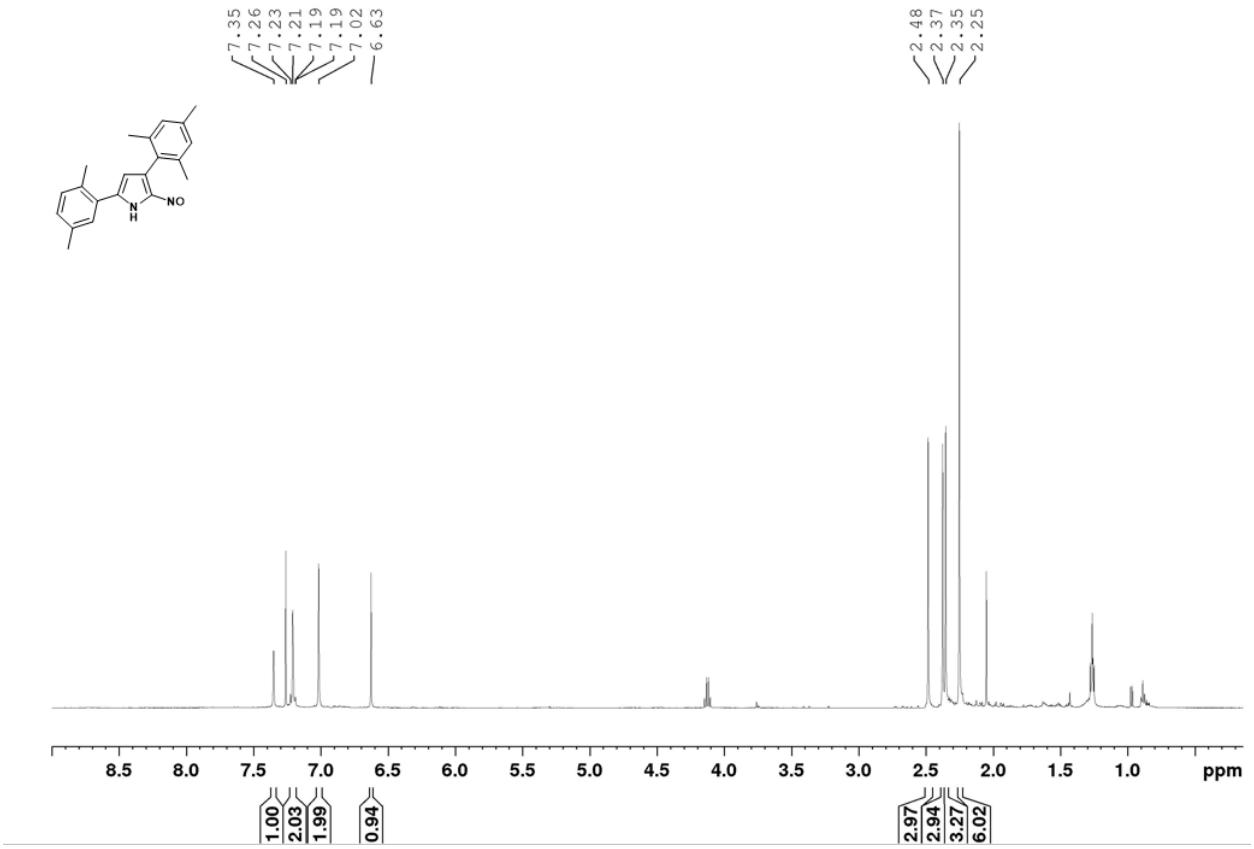
2-Nitroso-5-phenyl-3-(2,4,6-trimethylphenyl)-1*H*-pyrrole (4b)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4b** in $CDCl_3$



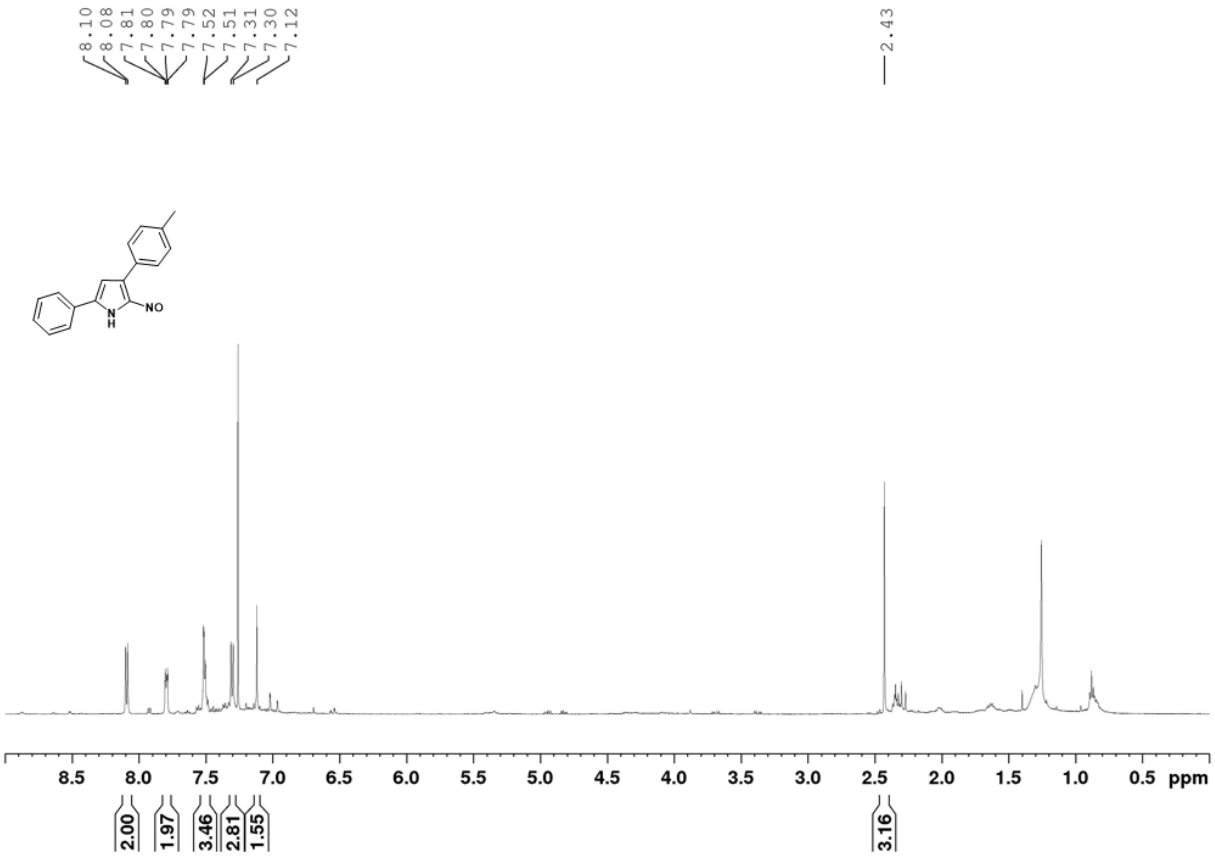
5-(2,5-Dimethylphenyl)-2-nitroso-3-(2,4,6-trimethylphenyl)-1*H*-pyrrole (4c)

^{1}H NMR (500 MHz) spectrum of compound **4c** in $CDCl_3$



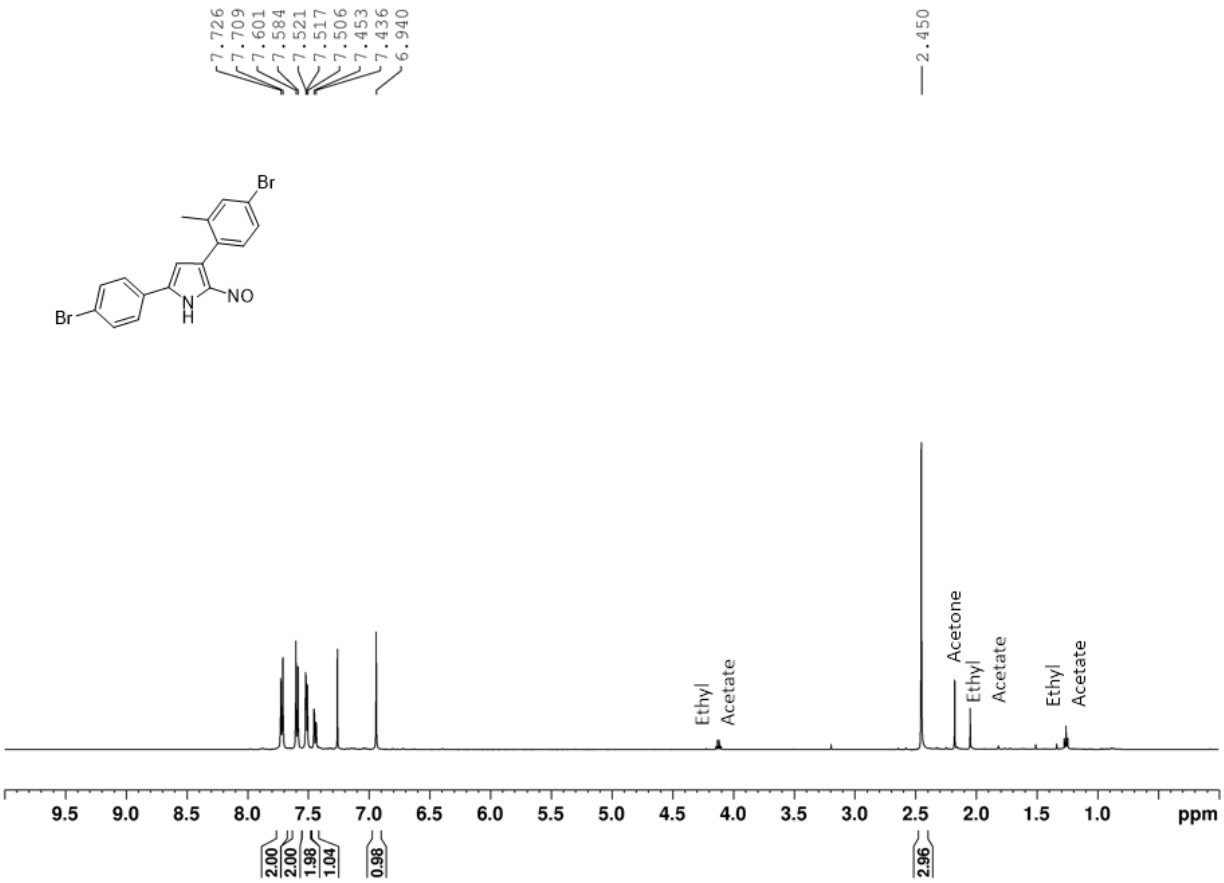
3-(4-Methylphenyl)-2-nitroso-5-phenyl-1*H*-pyrrole (4d)

^{1}H NMR (400 MHz) spectrum of compound **4d** in $CDCl_3$



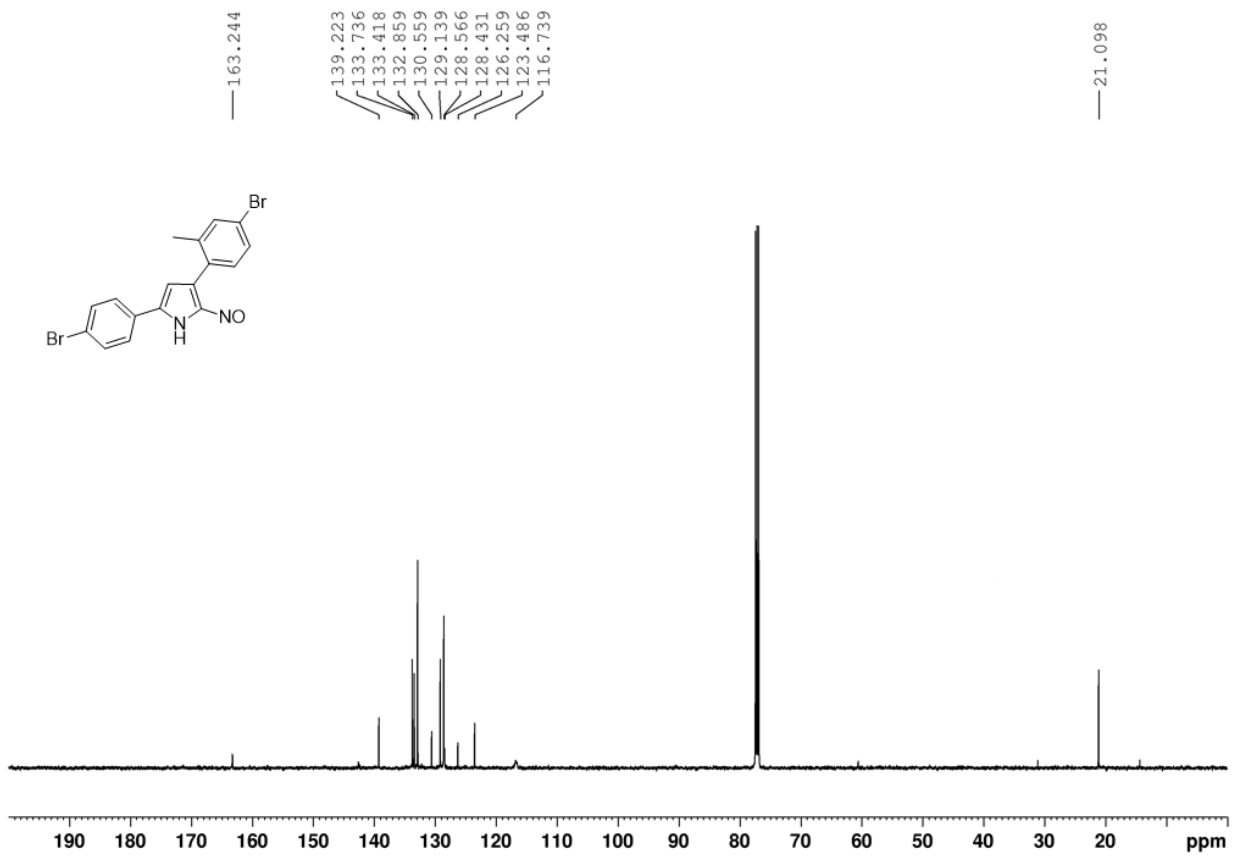
3-(4-Bromo-2-methylphenyl)-5-(4-bromophenyl)-2-nitroso-1*H*-pyrrole (4f)

^{1}H NMR (500 MHz) spectrum of compound **4f** in $CDCl_3$



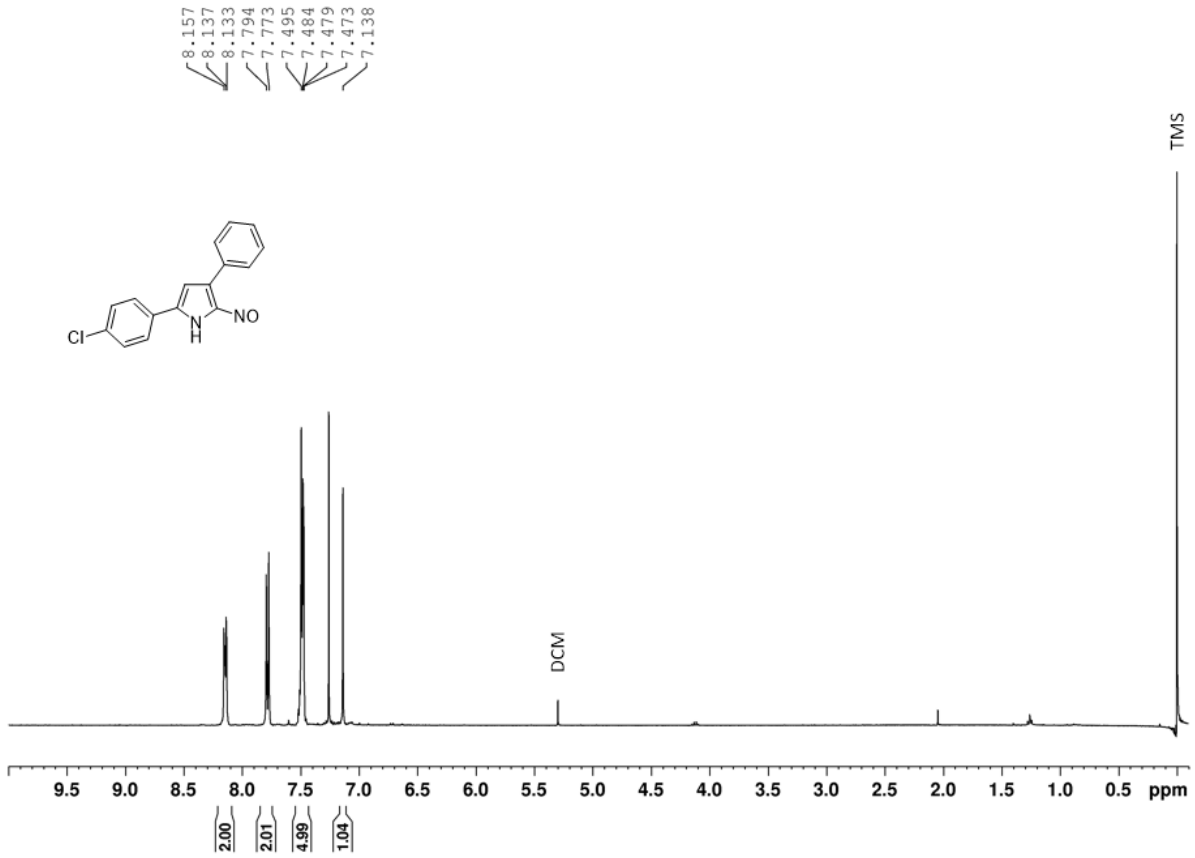
3-(4-Bromo-2-methylphenyl)-5-(4-bromophenyl)-2-nitroso-1*H*-pyrrole (4f)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4f** in $CDCl_3$



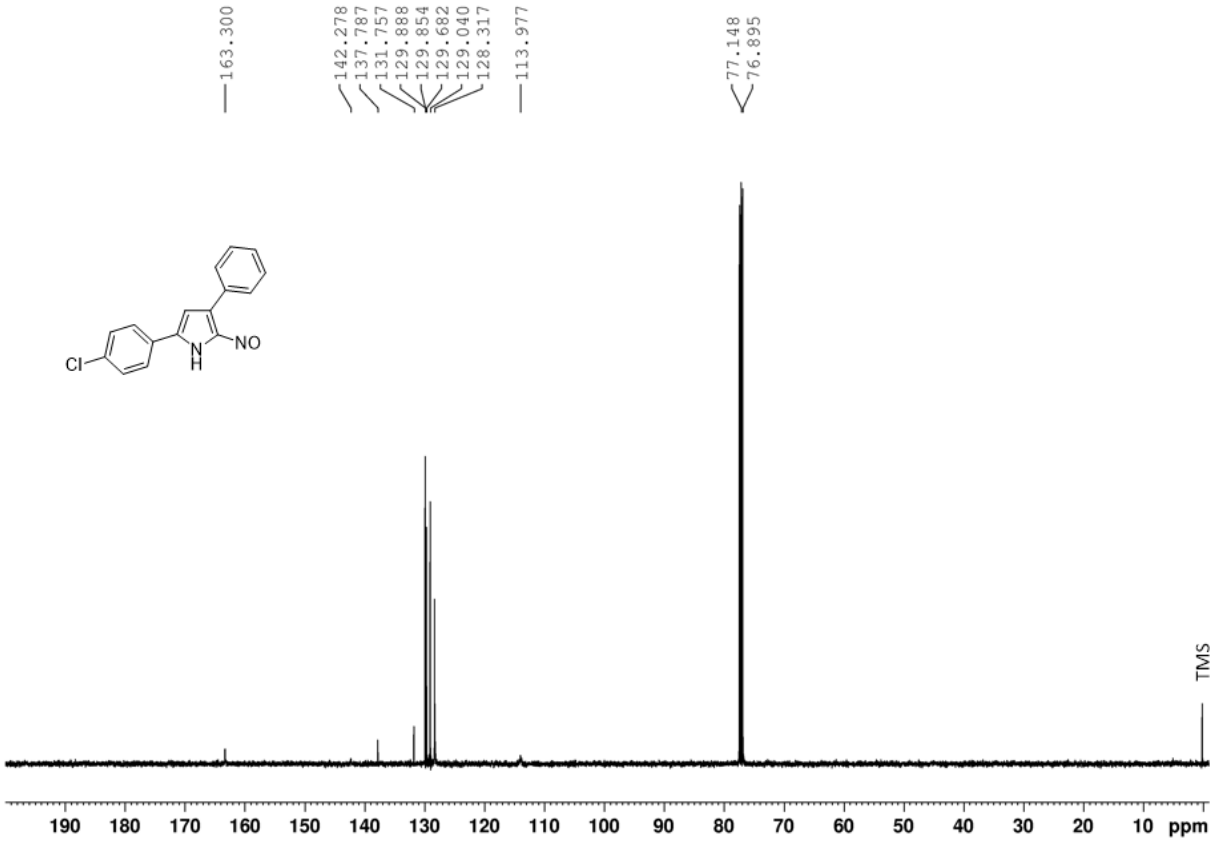
5-(4-Chlorobenzene)-2-nitroso-3-phenyl-1H-pyrrole (4g)

^{1}H NMR (400 MHz) spectrum of compound **4g** in $CDCl_3$



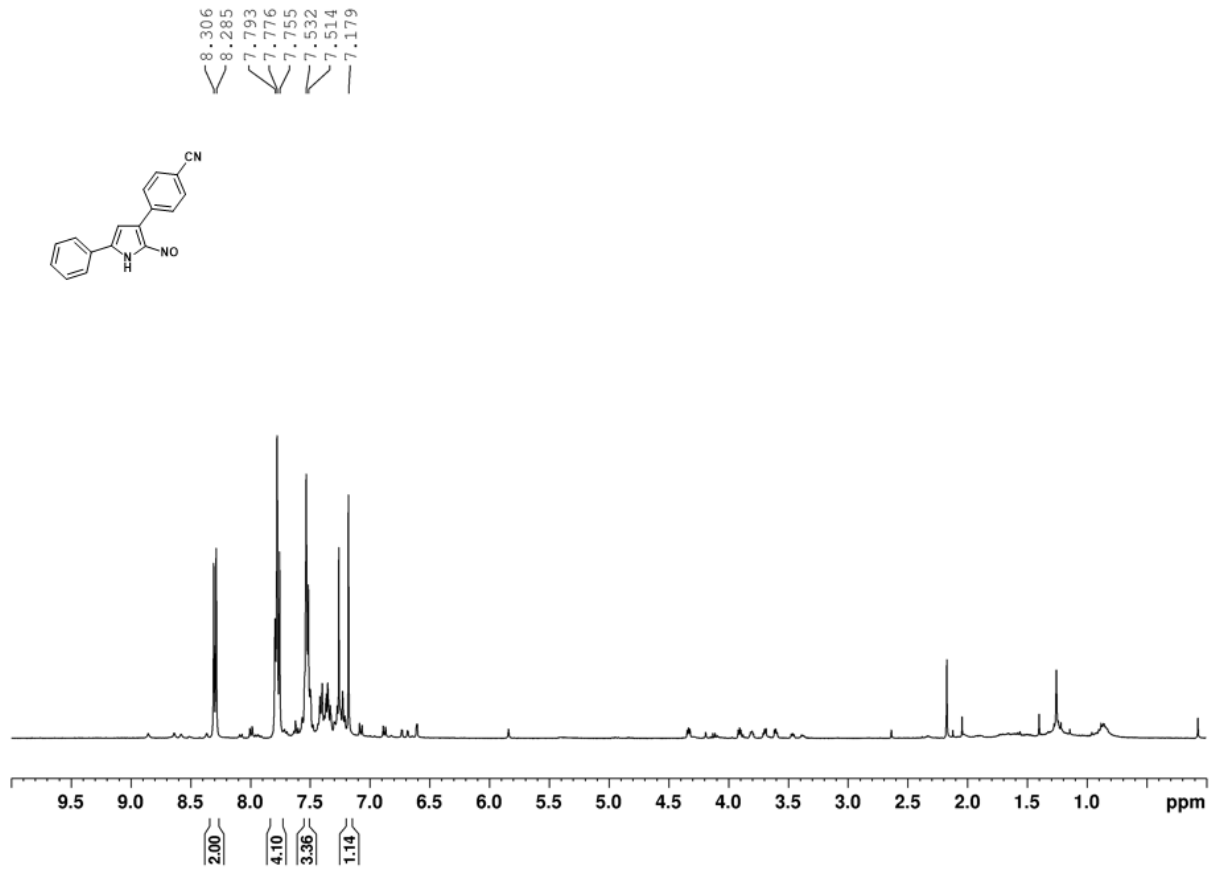
3-(4-Bromo-2-methylphenyl)-5-(4-bromophenyl)-2-nitroso-1*H*-pyrrole (4f)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4g** in $CDCl_3$



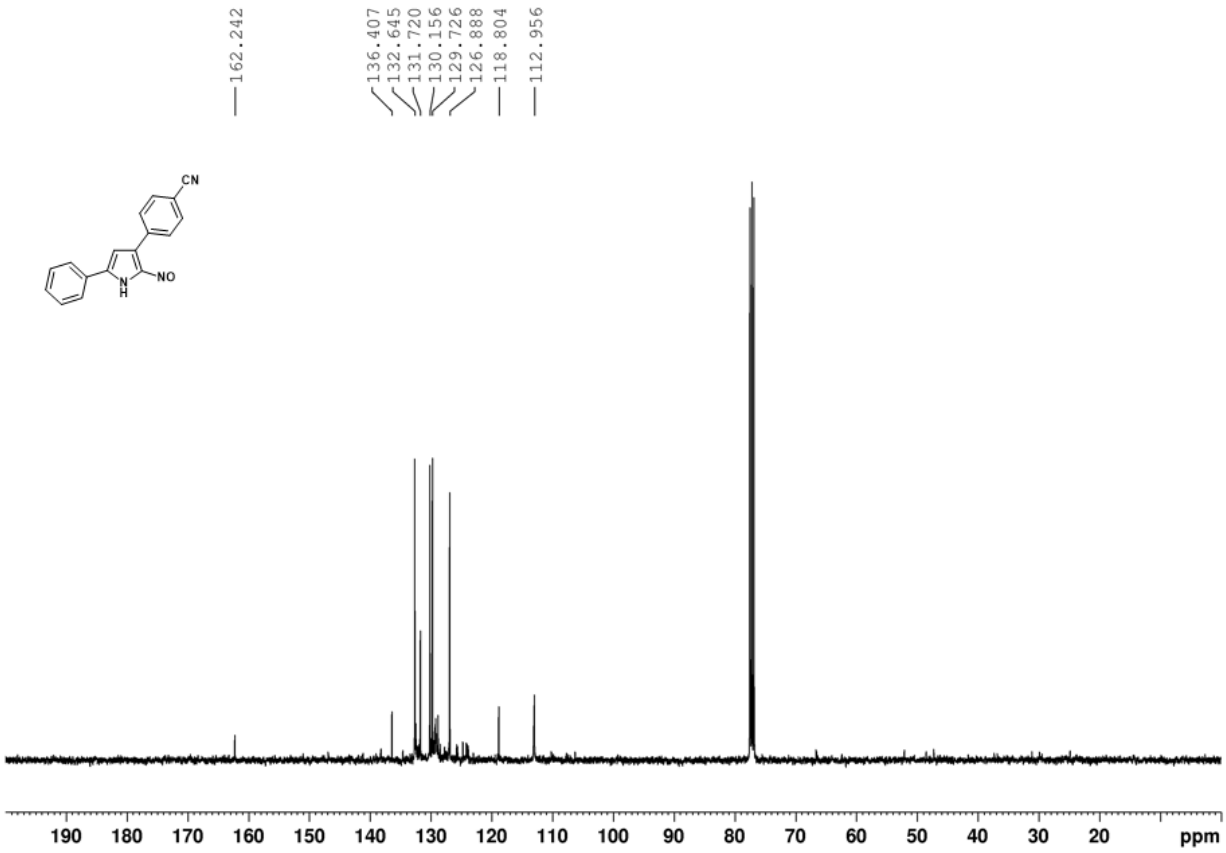
3-(4-Cyanophenyl)-2-nitroso-5-phenyl-1*H*-pyrrole (4h)

^{1}H NMR (400 MHz) spectrum of compound **4h** in $CDCl_3$



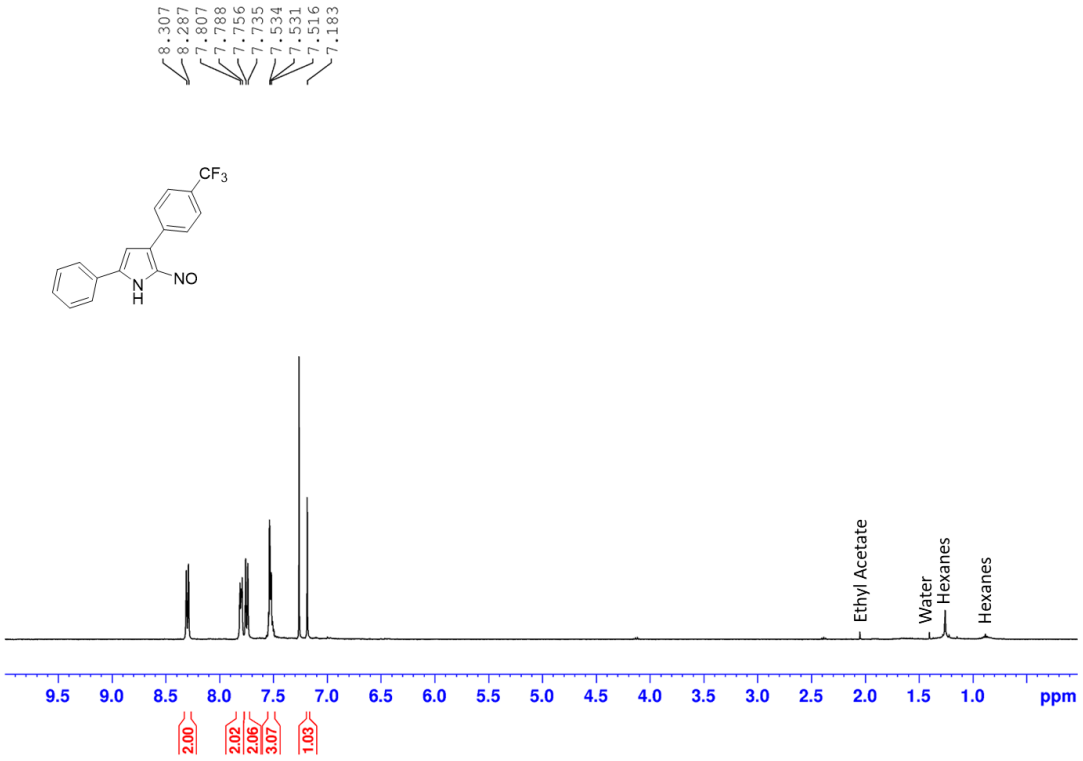
3-(4-Cyanophenyl)-2-nitroso-5-phenyl-1*H*-pyrrole (4h)

$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of compound **4h** in $CDCl_3$



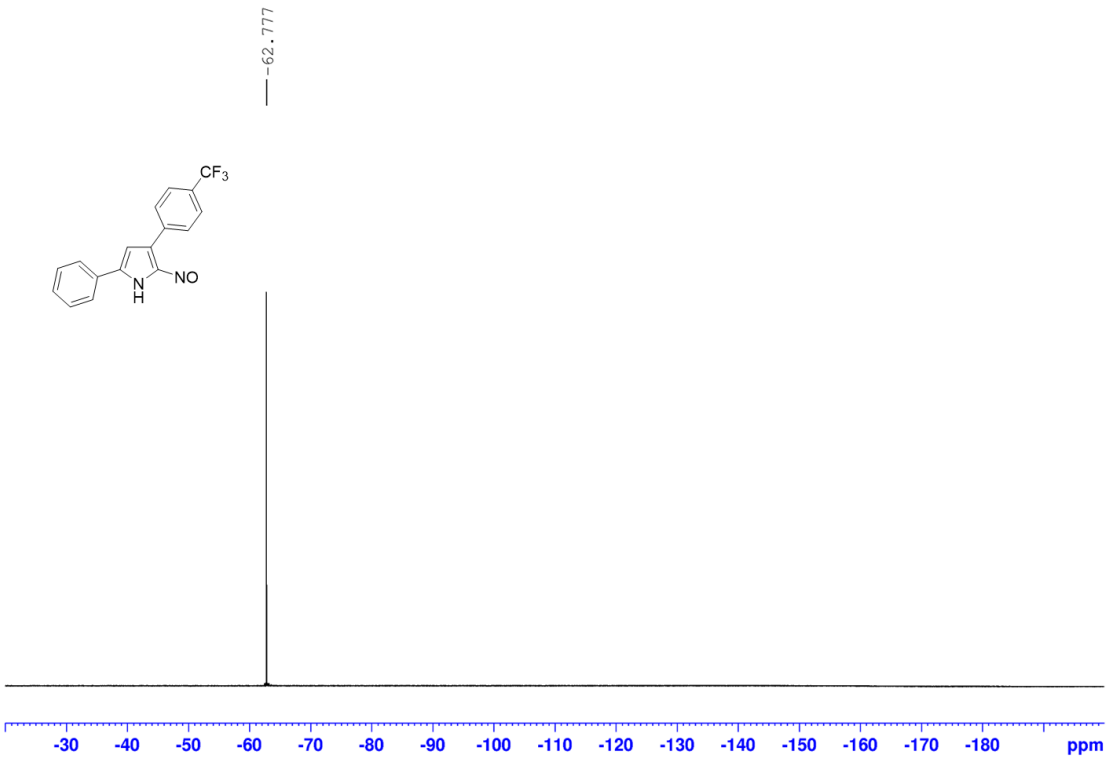
3-[4-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4i)

^{1}H NMR (400 MHz) spectrum of compound **4i** in $CDCl_3$



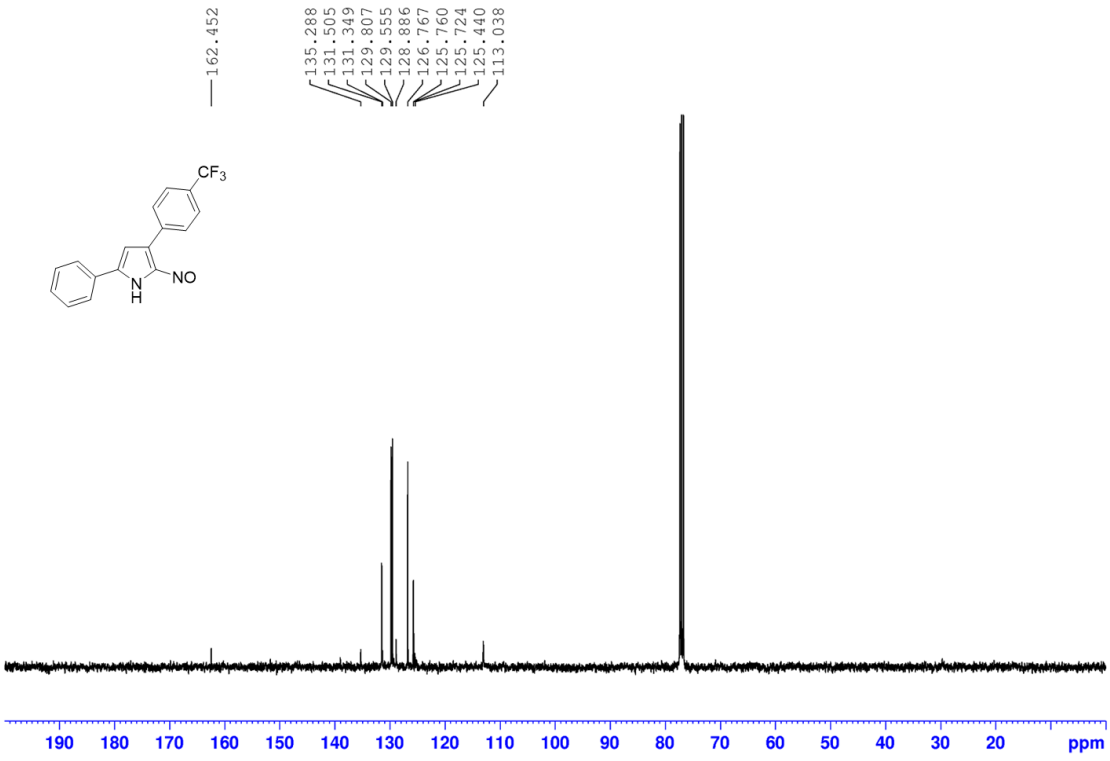
3-[4-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4i)

$^{19}F\{^{1}H\}$ NMR (377 MHz) spectrum of compound **4i** in $CDCl_3$



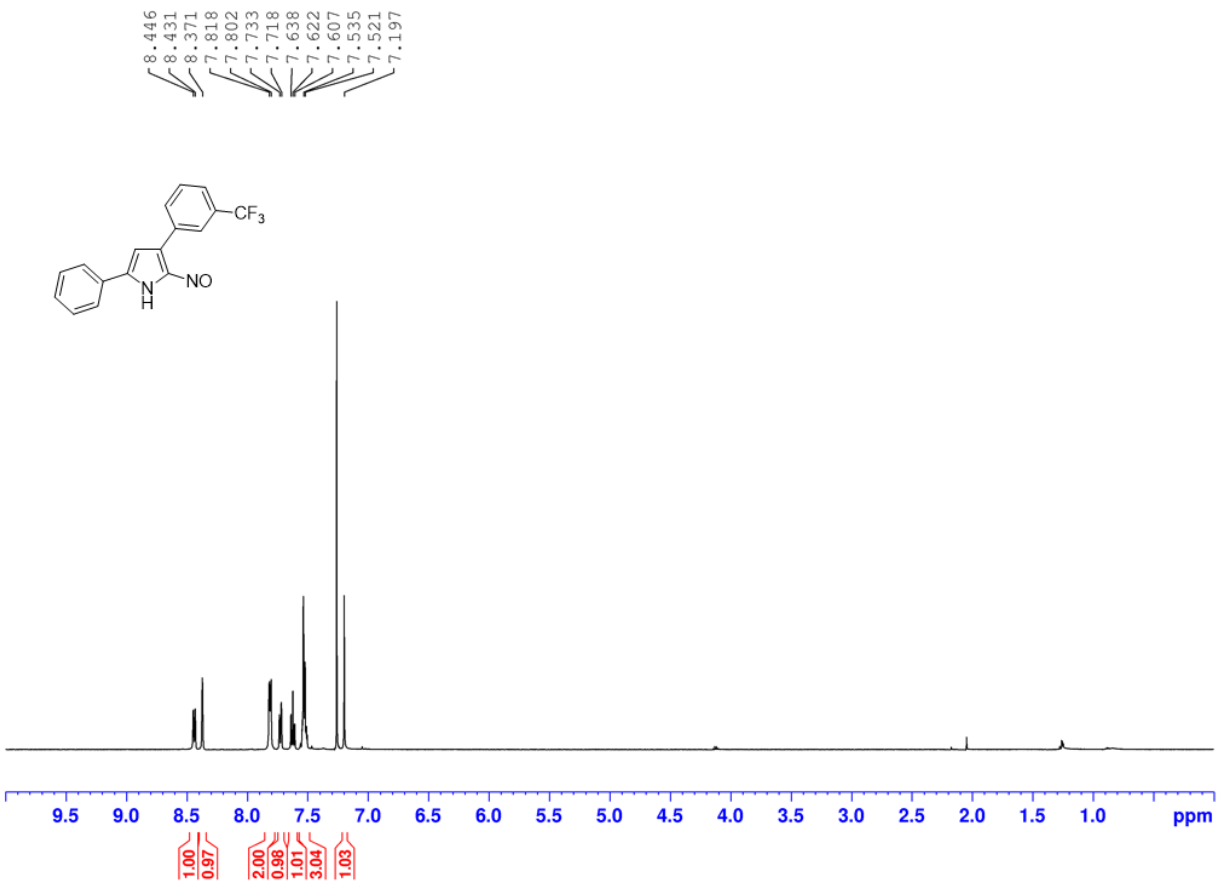
3-[4-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4i)

$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of compound **4i** in $CDCl_3$



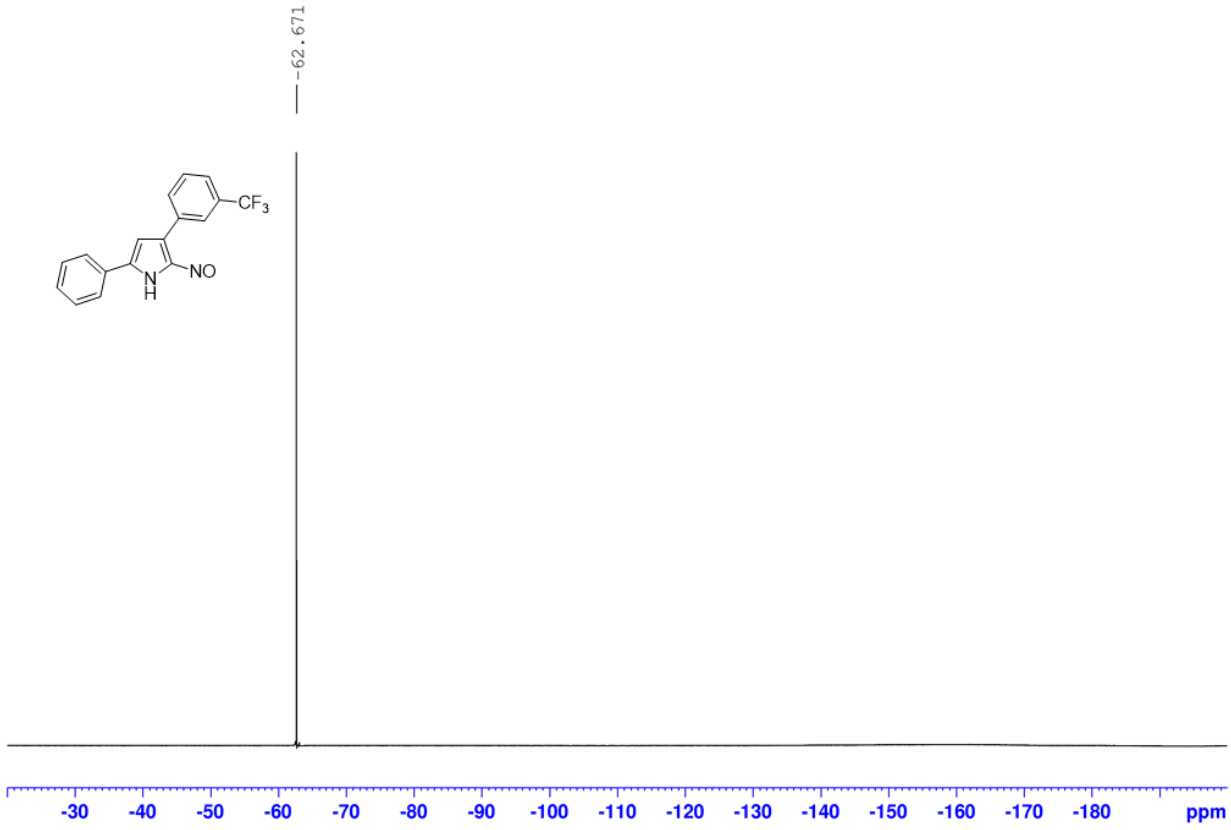
3-[3-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4j)

^{1}H NMR (400 MHz) spectrum of compound **4j** in $CDCl_3$



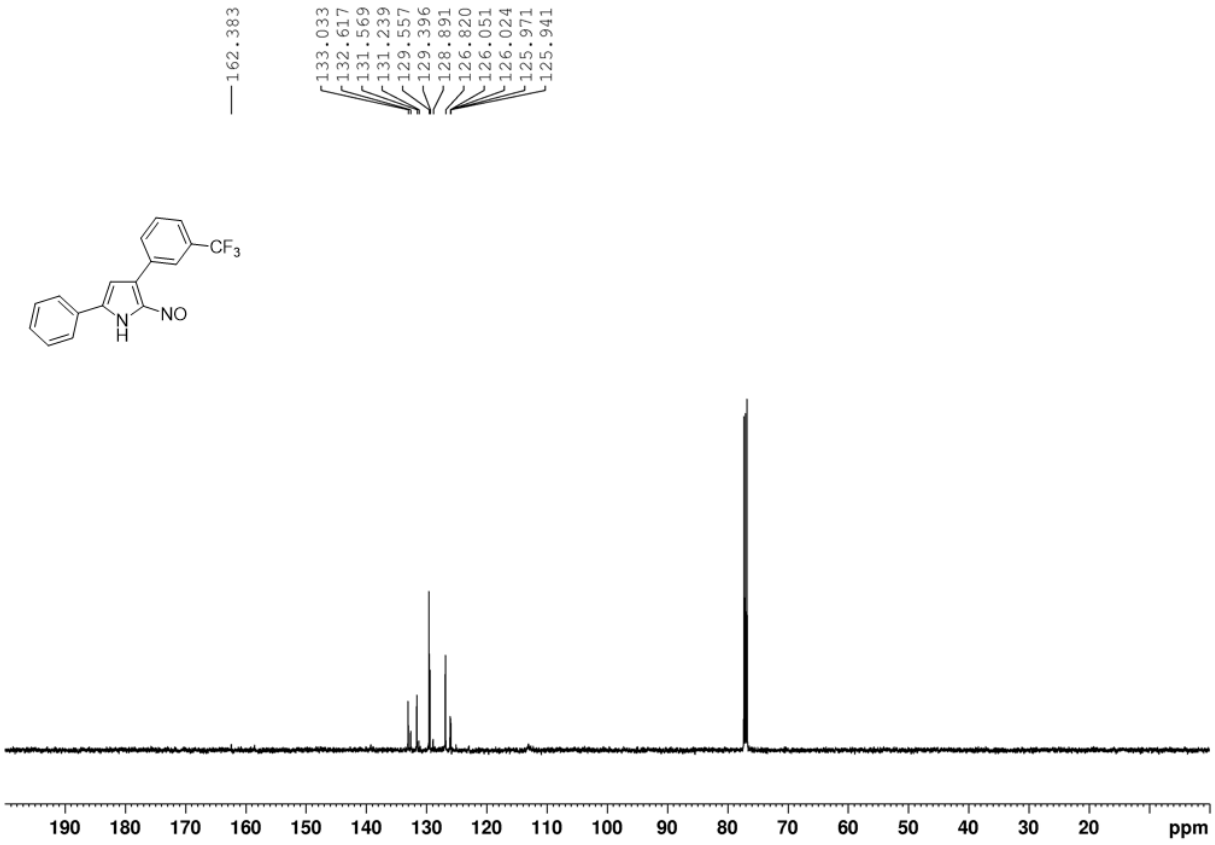
3-[3-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4j)

$^{19}F\{^{1}H\}$ NMR (377 MHz) spectrum of compound **4j** in $CDCl_3$



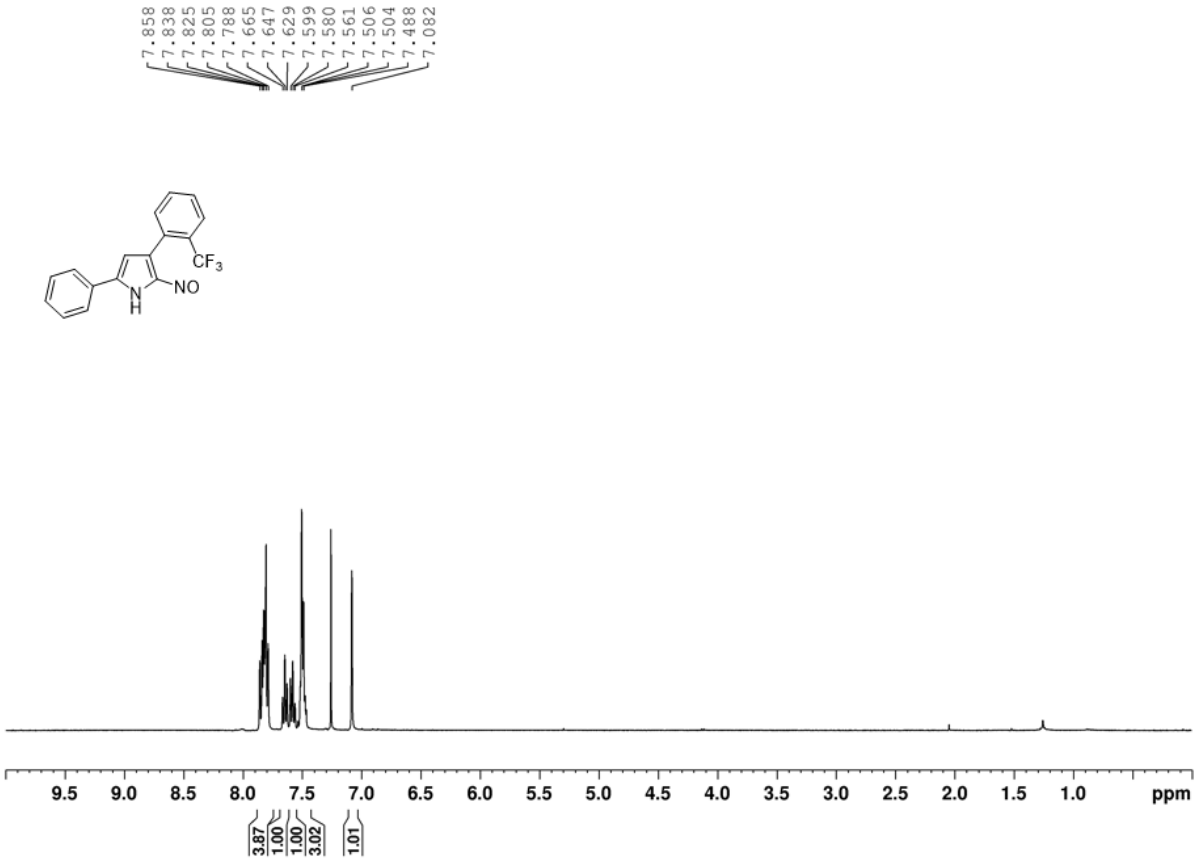
3-[3-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4j)

$^{13}C\{^{1}H\}$ NMR (101 MHz) spectrum of compound **4j** in $CDCl_3$



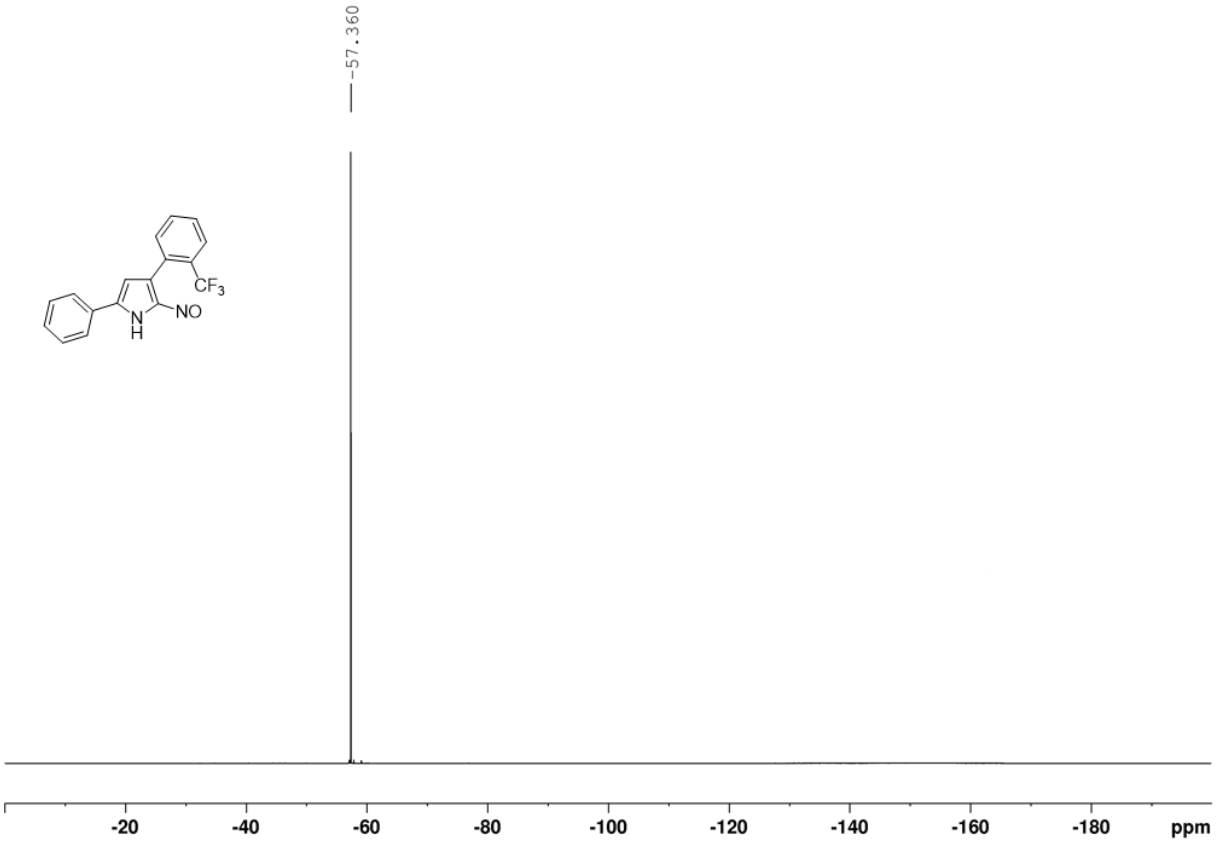
3-[2-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4k)

^{1}H NMR (400 MHz) spectrum of compound **4k** in $CDCl_3$



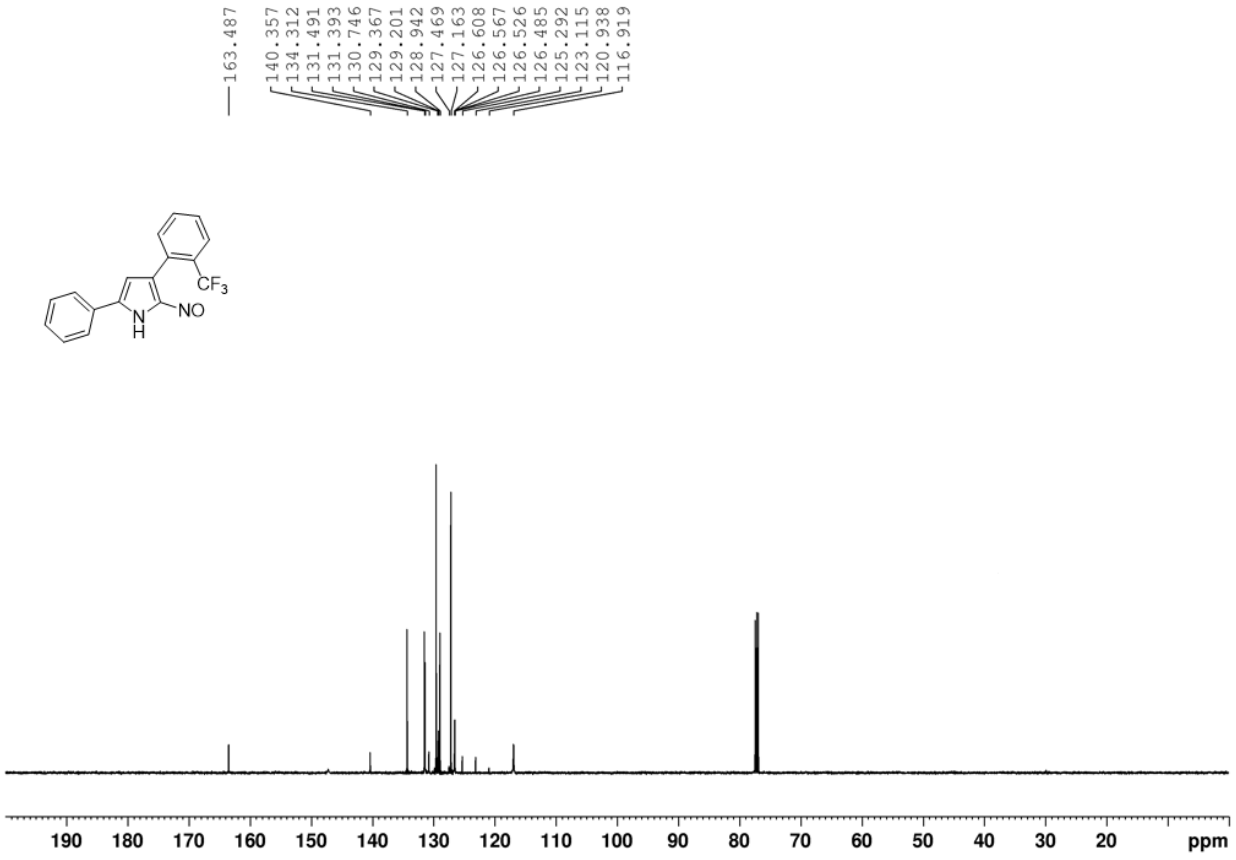
3-[2-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4k)

$^{19}F\{^{1}H\}$ NMR (377 MHz) spectrum of compound **4k** in $CDCl_3$



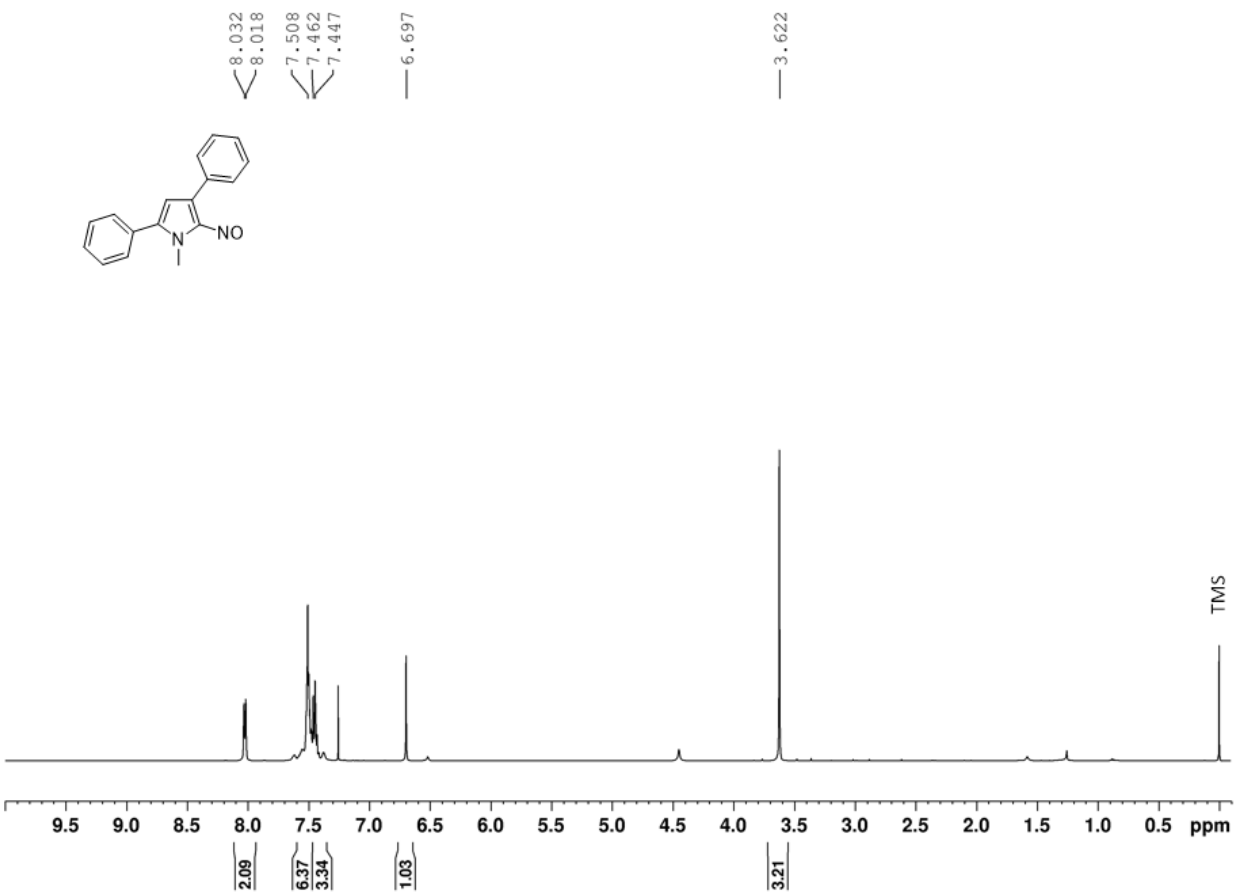
3-[2-(Trifluoromethyl)phenyl]-2-nitroso-5-phenyl-1*H*-pyrrole (4k)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4k** in $CDCl_3$



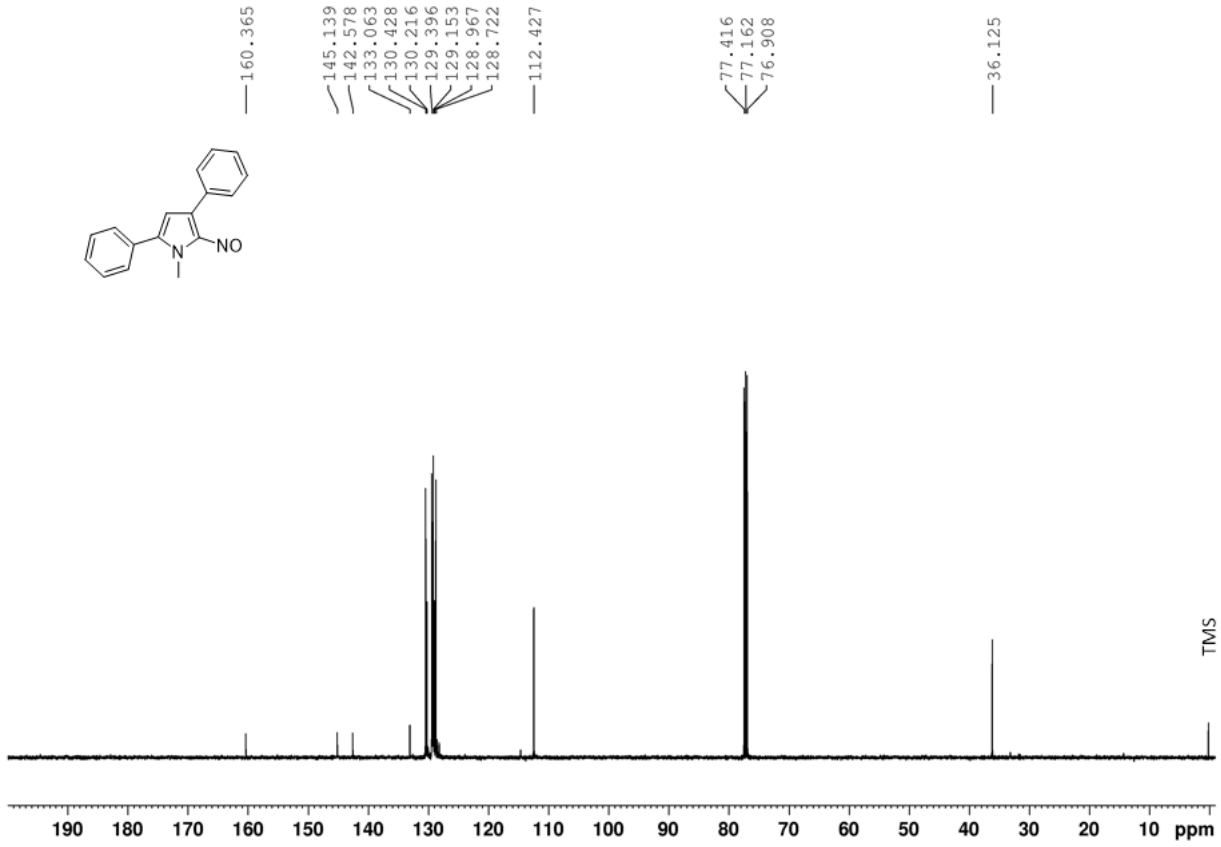
1-Methyl-2-nitroso 3,5-diphenyl-1*H*-pyrrole (4l)

^{1}H NMR (500 MHz) spectrum of compound **4l** in $CDCl_3$



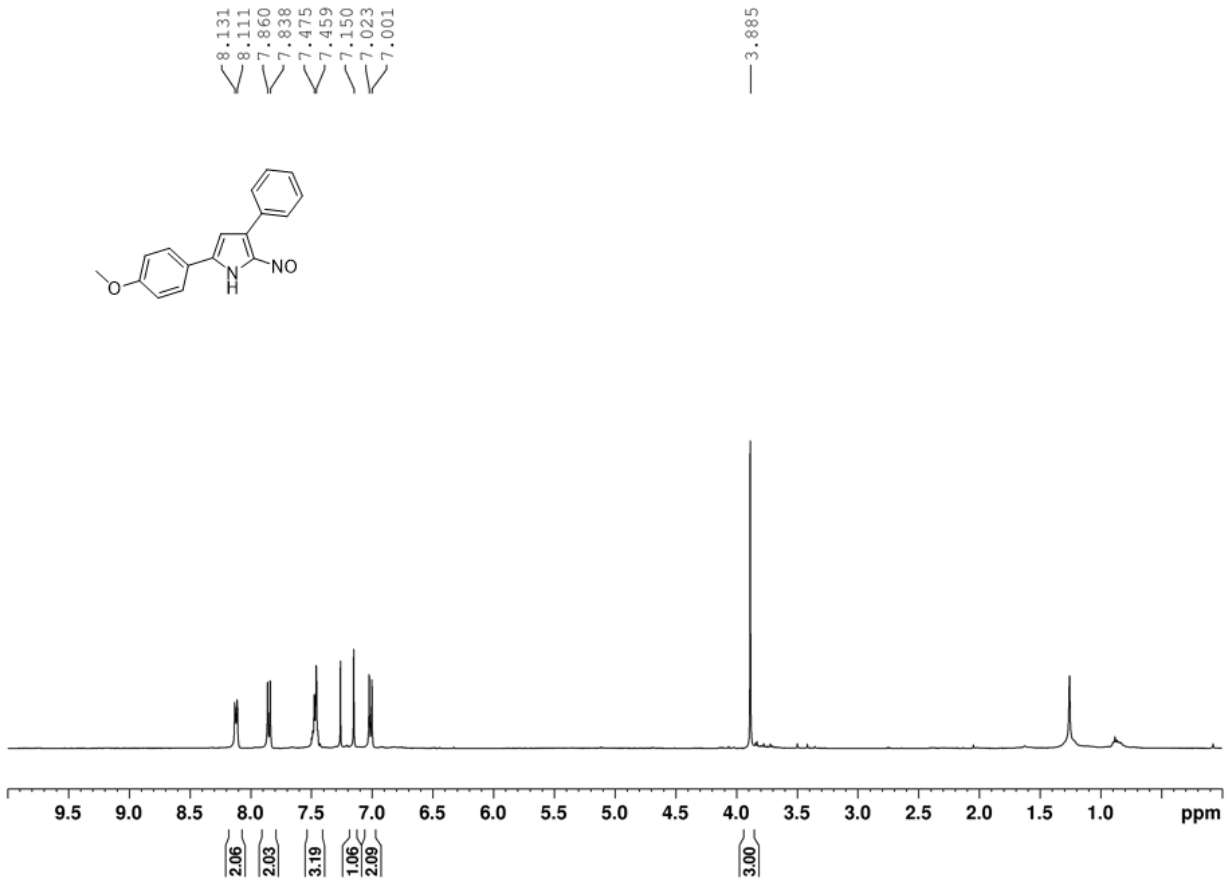
1-Methyl-2-nitroso 3,5-diphenyl-1*H*-pyrrole (4l)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4j** in $CDCl_3$



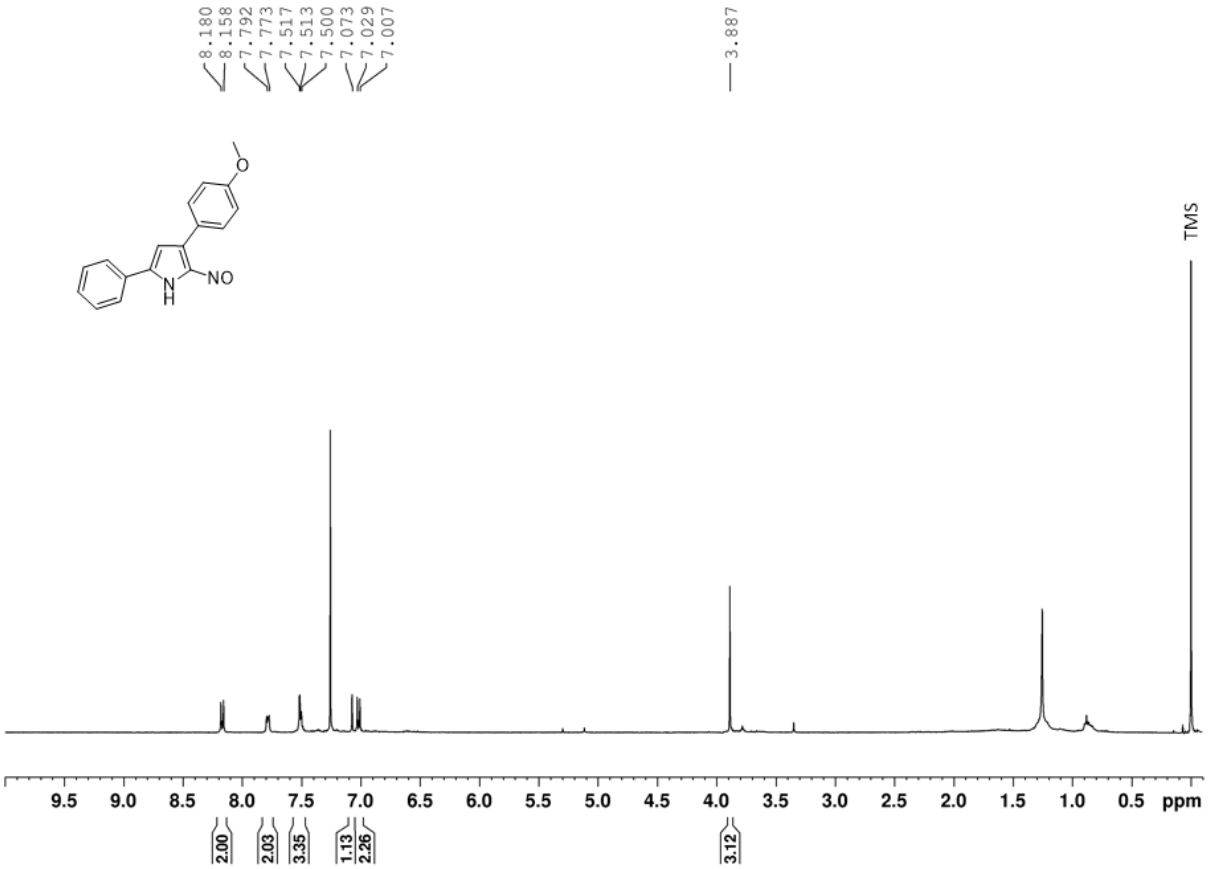
5-(4-Methoxyphenyl)-2-nitroso-3-phenyl-1*H*-pyrrole (4m)

^{1}H NMR (400 MHz) spectrum of compound **4m** in $CDCl_3$



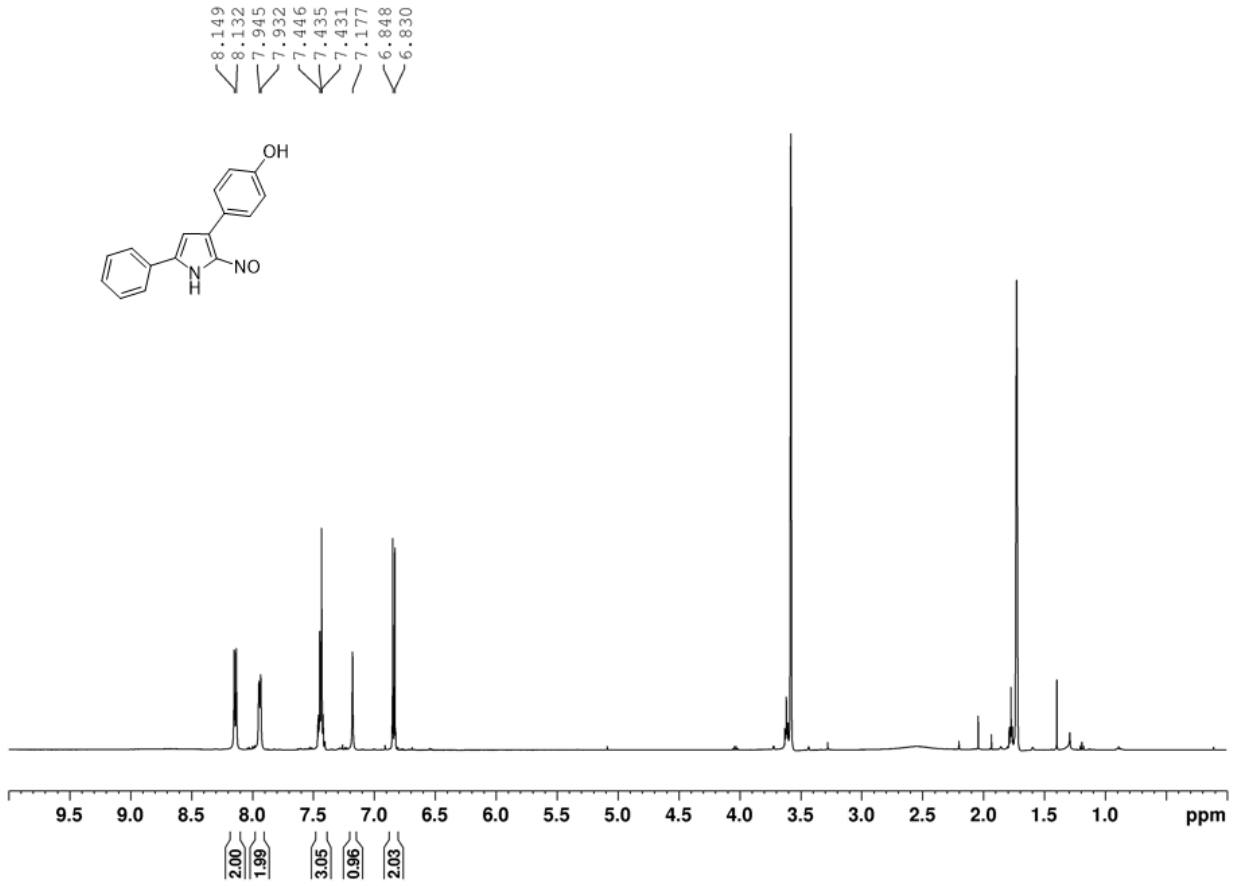
3-(4-Methoxyphenyl)-2-nitroso-5-phenyl-1*H*-pyrrole (4n)

^{1}H NMR (400 MHz) spectrum of compound **4n** in $CDCl_3$



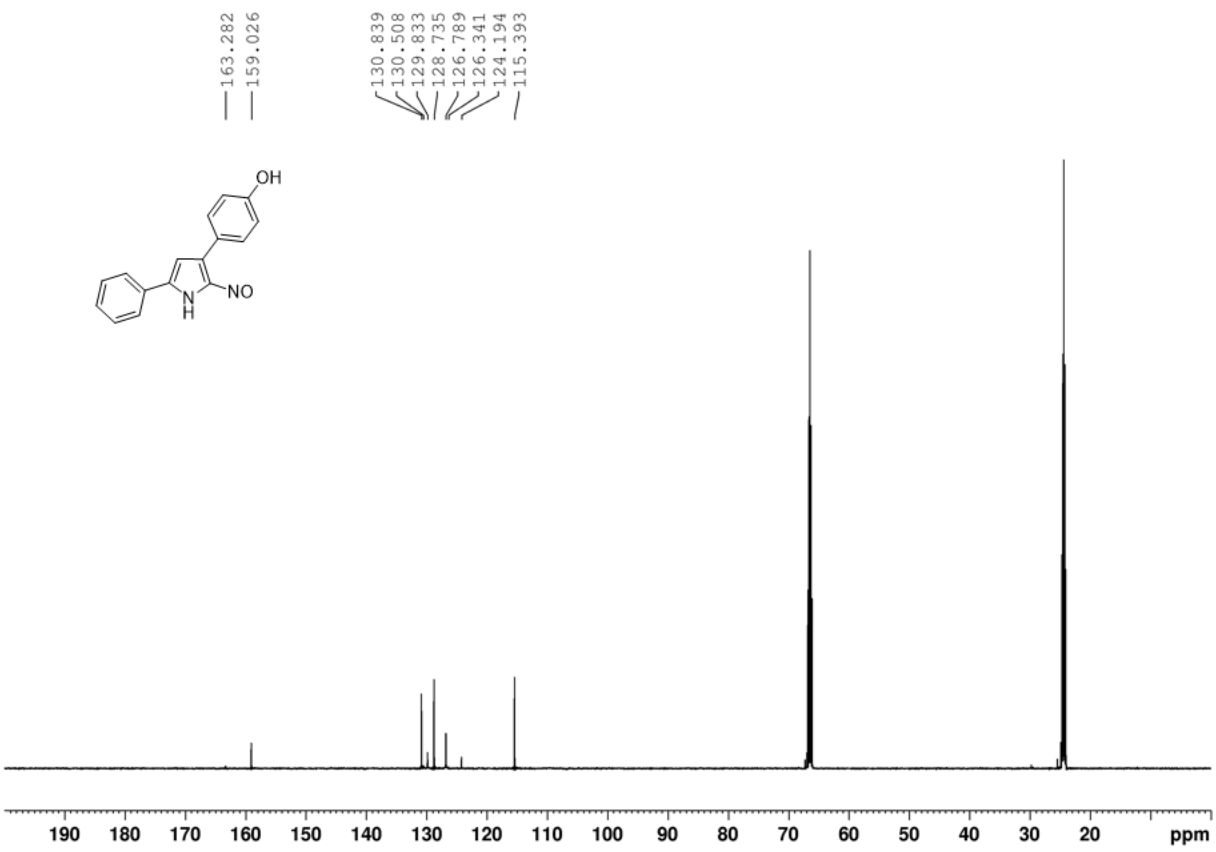
3-(4-Hydroxyphenyl)-2-nitroso-5-phenyl-1*H*-pyrrole (4o)

^{1}H NMR (500 MHz) spectrum of compound **4o** in THF-d_8



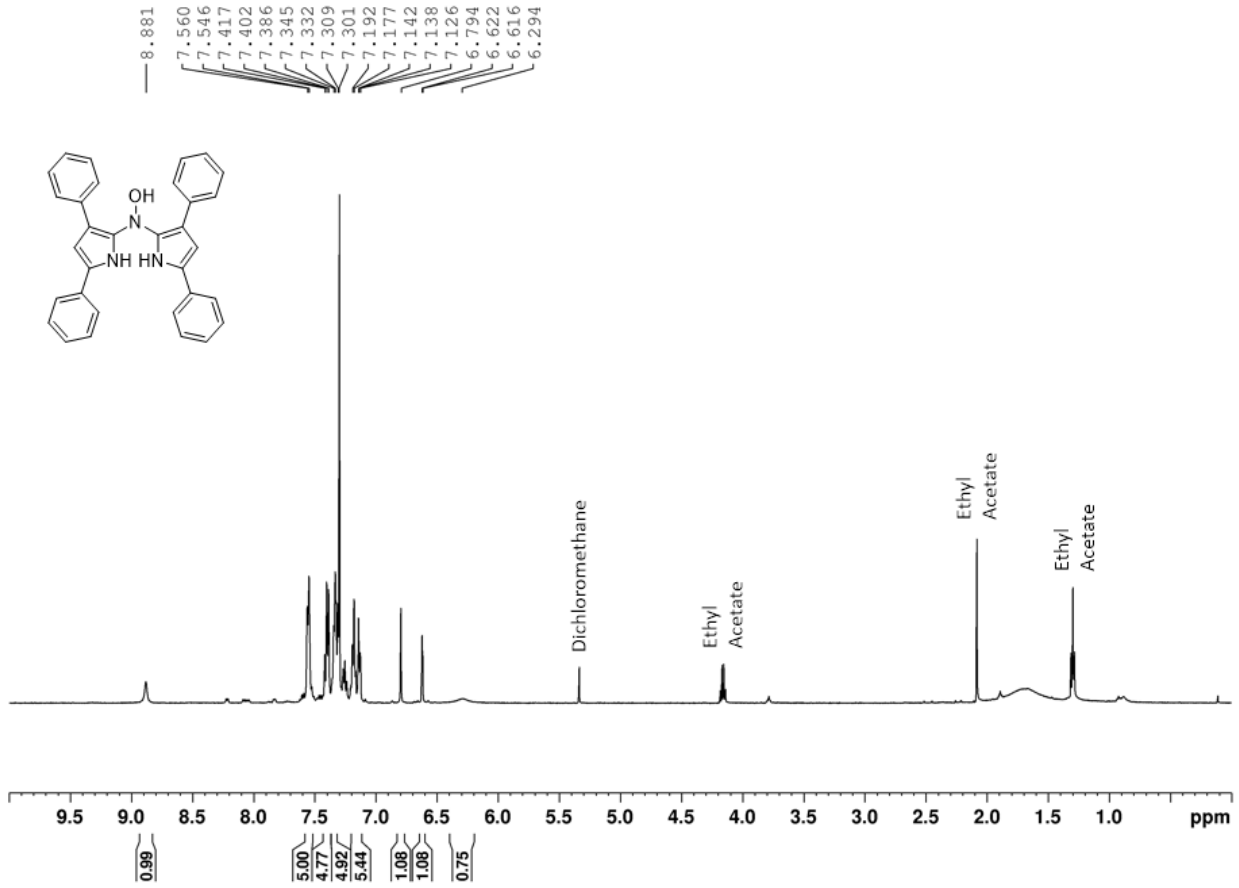
3-(4-Hydroxyphenyl)-2-nitroso-5-phenyl-1*H*-pyrrole (4o)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **4o** in THF-d_6



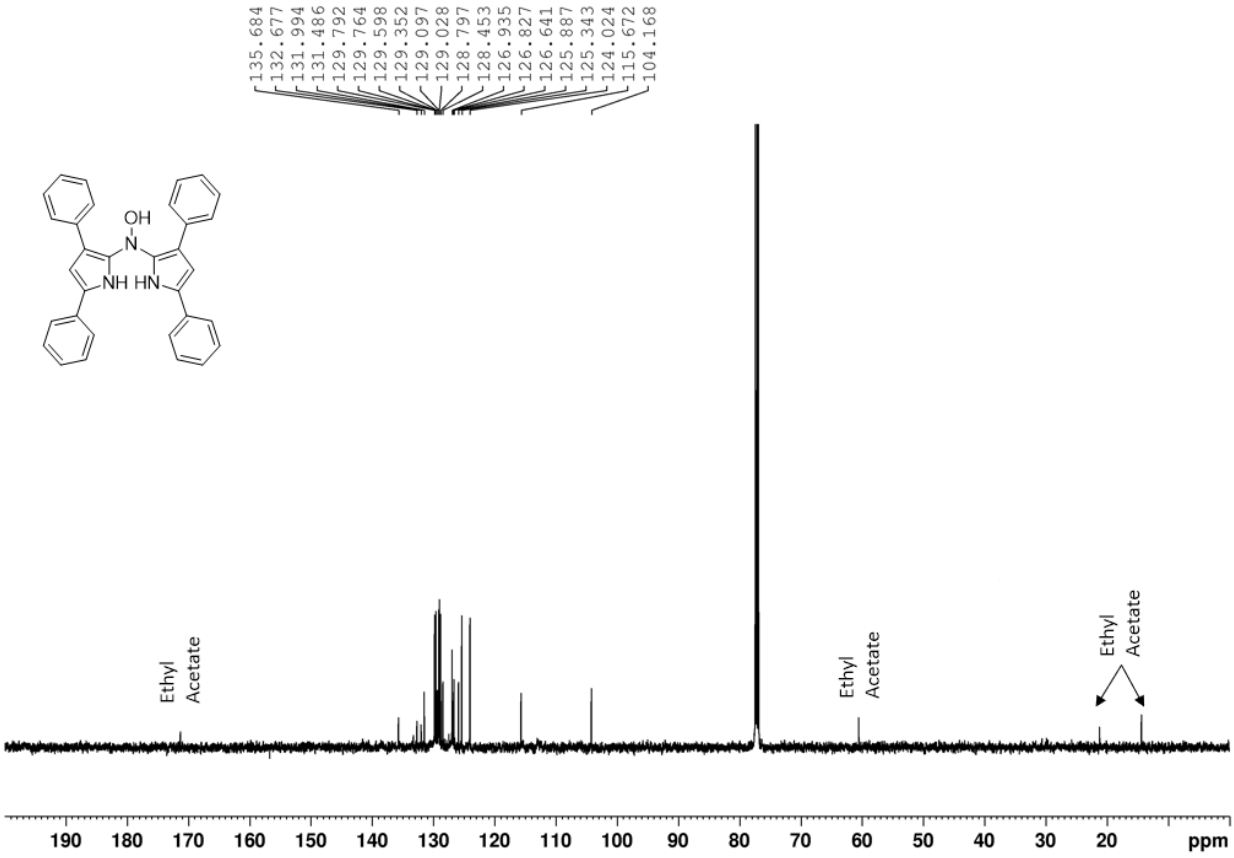
***N*-(3,5-diphenyl-1*H*-pyrrol-2-yl)-*N*-hydroxy-3,5-diphenyl-1*H*-pyrrol-2-amine (6)**

^{1}H NMR (500 MHz) spectrum of compound **6** in $CDCl_3$



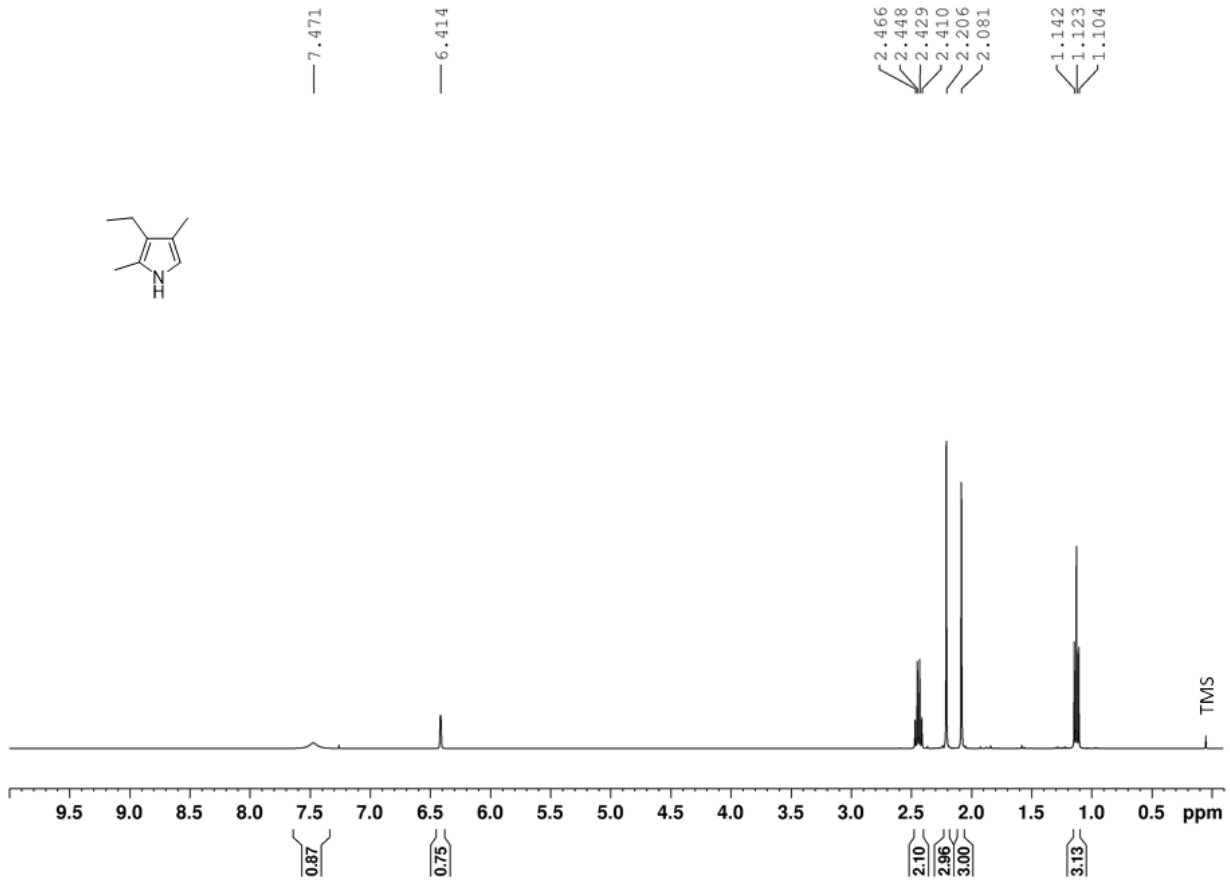
***N*-(3,5-diphenyl-1*H*-pyrrol-2-yl)-*N*-hydroxy-3,5-diphenyl-1*H*-pyrrol-2-amine (6)**

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **6** in $CDCl_3$



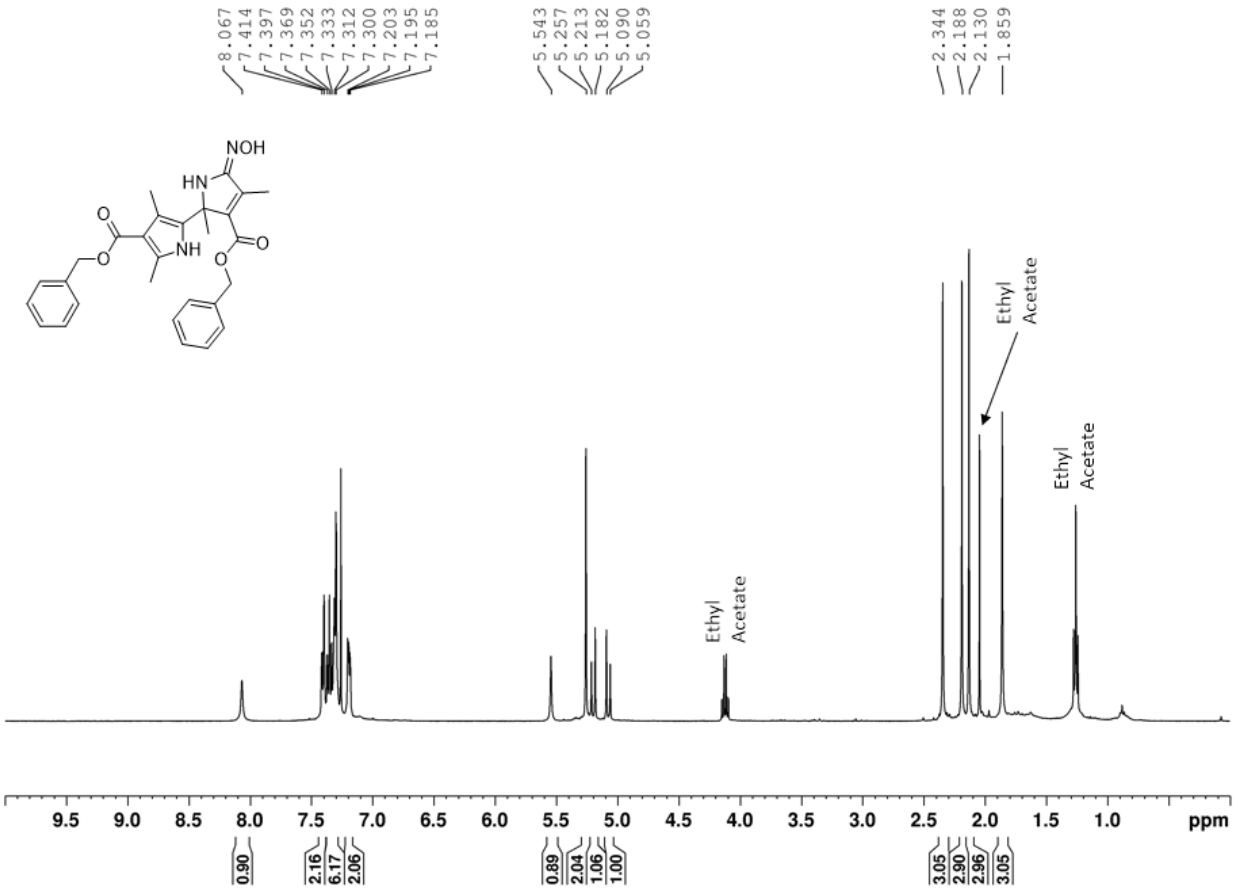
3-Ethyl-2,4-dimethyl-1*H*-pyrrole (7b)

^{1}H NMR (400 MHz) spectrum of compound **7b** in $CDCl_3$



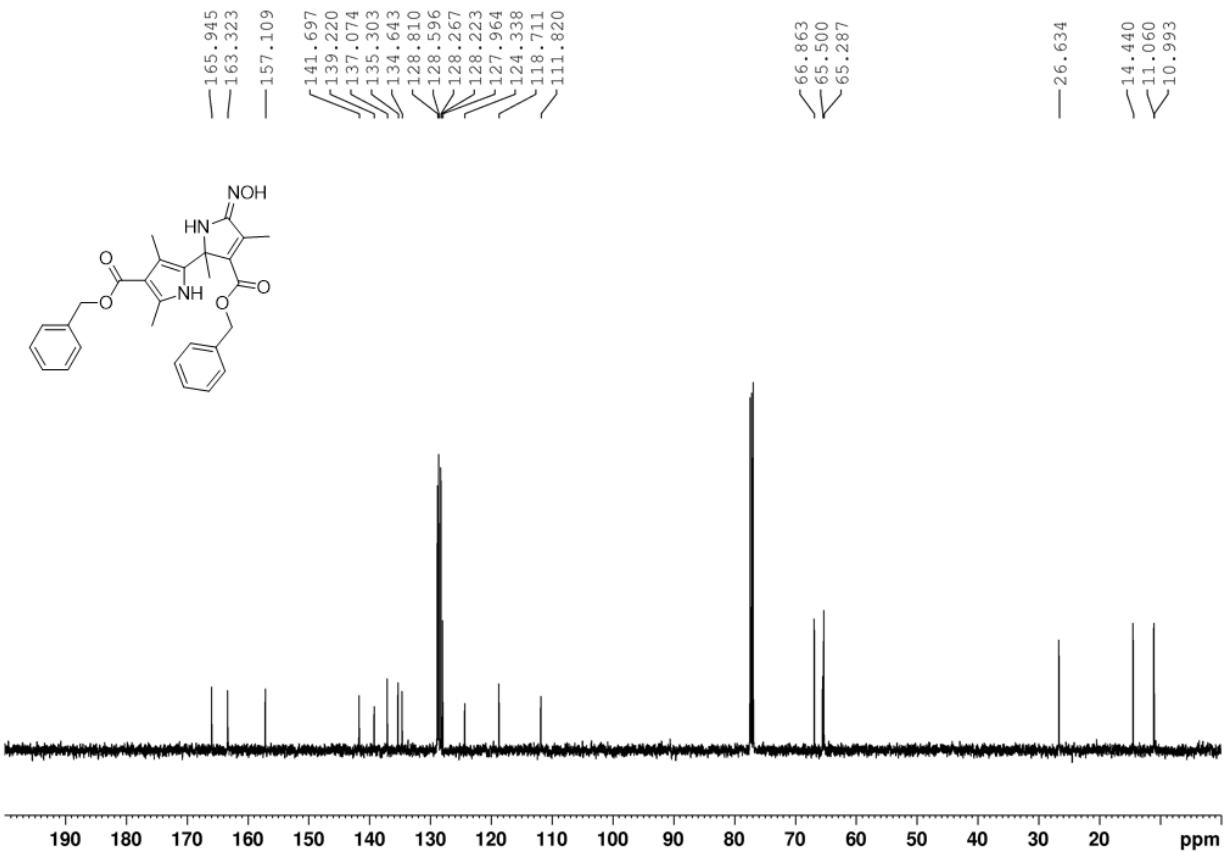
3,4′-Bis(benzylester)-2,3′,4,5′-Butamethyl-[2,2′-bi-1*H*-pyrrol]-5(2H)-one oxime (8a)

^{1}H NMR (400 MHz) spectrum of compound **8a** in $CDCl_3$



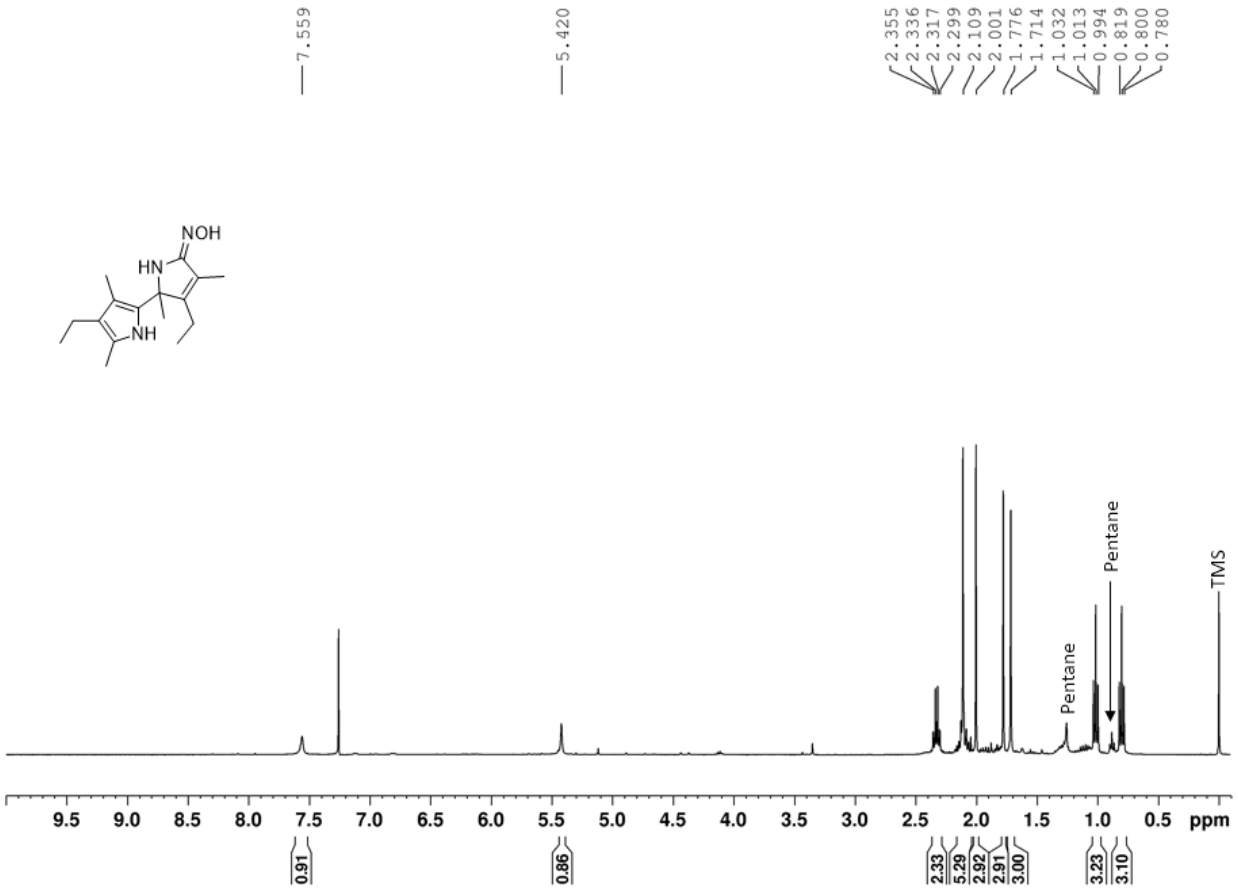
3,4′-Bis(benzylester)-2,3′,4,5′-Butamethyl-[2,2′-bi-1*H*-pyrrol]-5(2H)-one oxime (8a)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **8a** in $CDCl_3$



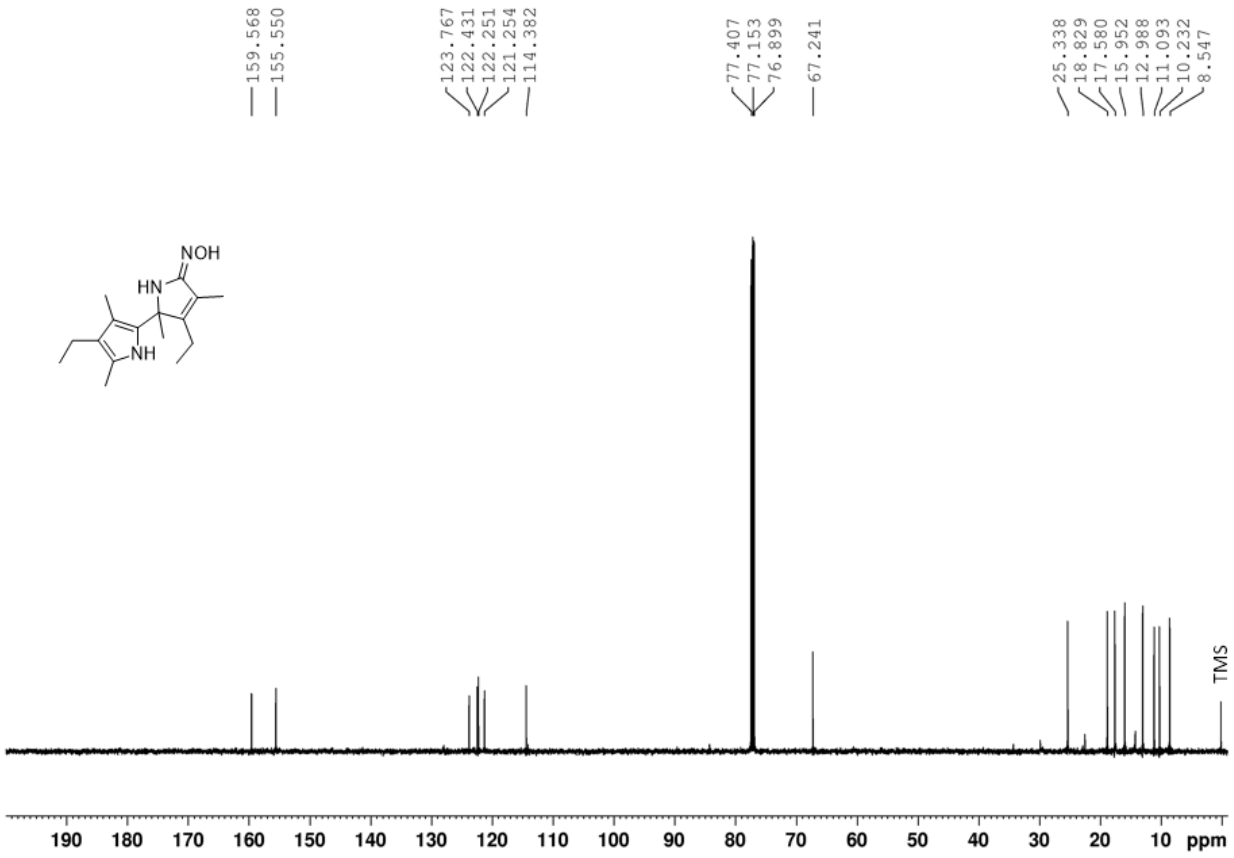
2,3′,4,5′-Butamethyl-3,4'-diethyl-[2,2′-bi-1*H*-pyrrol]-5(2H)-one oxime (8b)

^{1}H NMR (400 MHz) spectrum of compound **8b** in $CDCl_3$



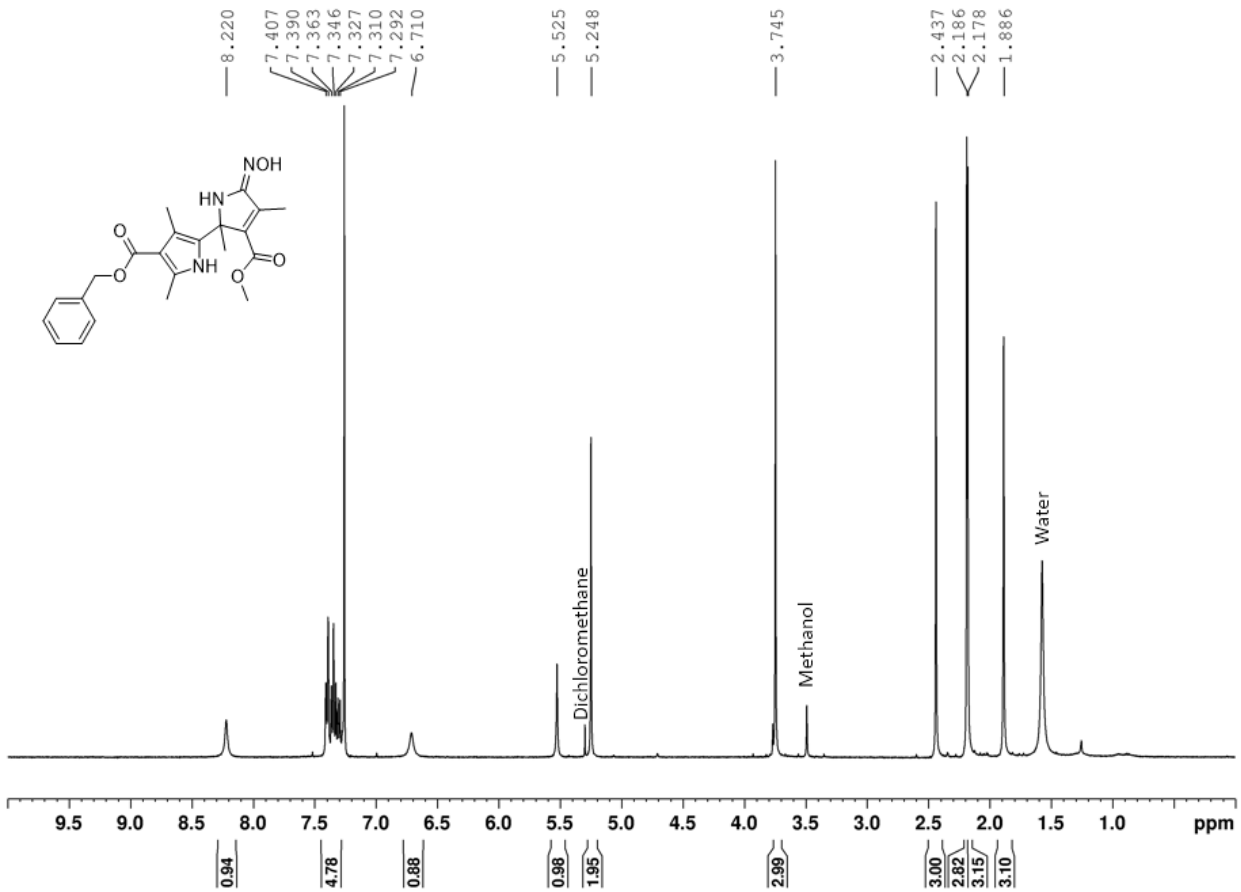
2,3′,4,5′-Butamethyl-3,4'-diethyl-[2,2′-bi-1*H*-pyrrol]-5(2H)-one oxime (8b)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **8b** in $CDCl_3$



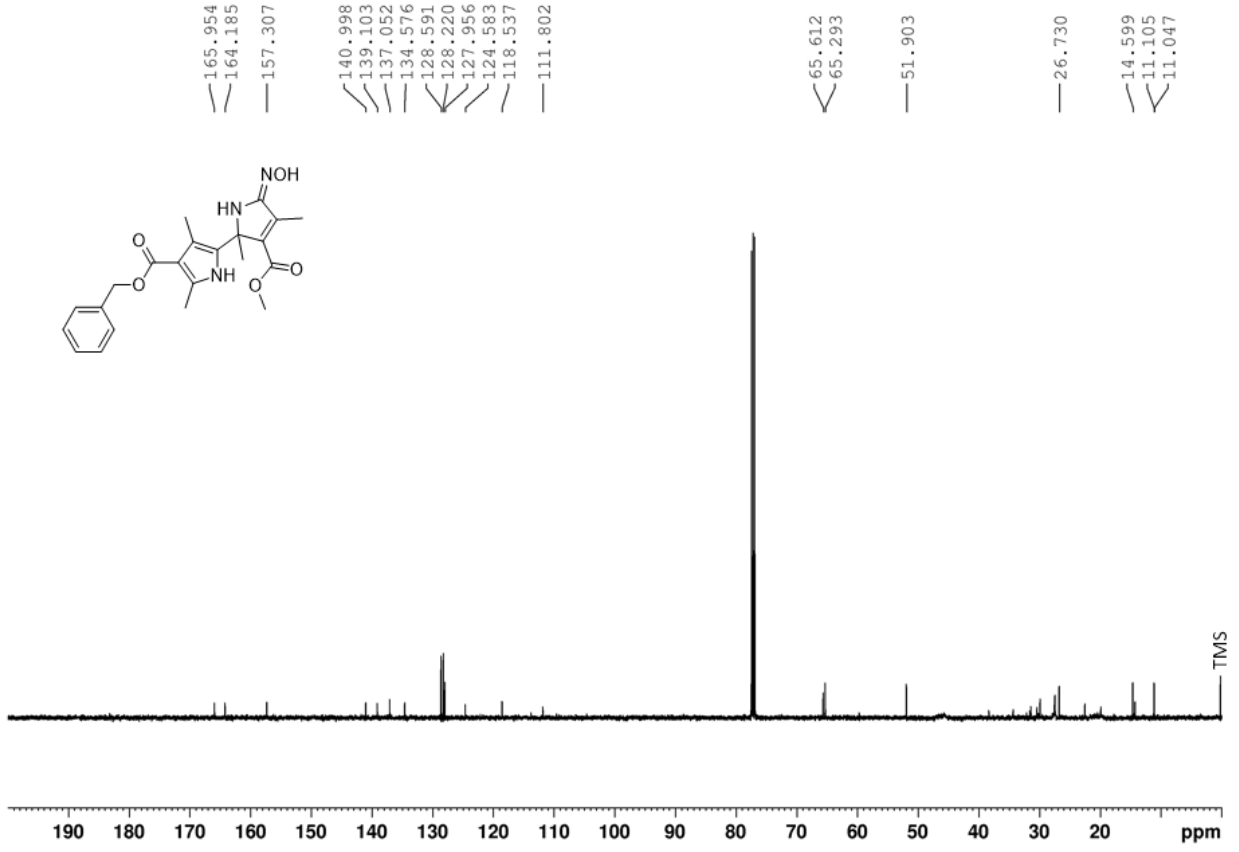
4'-Benzylester-2,3',4,5'-Butamethyl-3-methylester-[2,2'-bi-1*H*-pyrrol]-5(2H)-one oxime (8c)

^{1}H NMR (400 MHz) spectrum of compound **8c** in $CDCl_3$



4'-Benzylester-2,3',4,5'-Butamethyl-3-methylester-[2,2'-bi-1*H*-pyrrol]-5(2H)-one oxime (8c)

$^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound **8c** in $CDCl_3$



Crystallographic Data

The crystal chosen was attached to the tip of a MicroLoop with Paratone-N oil. Measurements were made on a Bruker D8 VENTURE diffractometer equipped with a PHOTON III CMOS detector using monochromated Cu Kα radiation (λ = 1.54178 Å) from an Incoatec micro-focus sealed tube for compound **4a** and monochromated Mo Kα radiation (λ = 0.71073 Å) from an Incoatec microfocus sealed tube for compound **8c**, both at 150 K.[24] The initial orientation and unit cell were indexed using a least-squares analysis of the reflections collected from a 180° phi-scan, 1° per frame, and 5 seconds per frame for **4a** and 10 seconds for **8c**. For data collection, a strategy was calculated to maximize data completeness and multiplicity, in a reasonable amount of time, and then implemented using the Bruker Apex 4 software suite.[24] The crystal to detector distance was set to 4.0 cm and 15 second frames were collected for **4a** (1.0° per frame) and **8c** (0.5° per frame). In each case, cell refinement and data reduction were performed with the Bruker SAINT[25] software, which corrects for beam inhomogeneity, possible crystal decay, and Lorentz and polarisation effects. A multi-scan absorption correction was applied (SADABS).[26] The structures were solved using SHELXT-2014[27] and were refined using a full-matrix least-squares method on F^2 with SHELXL-2019[27]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon were included at geometrically idealized positions and allowed to ride on the atom to which they were bonded. The isotropic thermal parameters of the hydrogen atoms were fixed at $1.2U_{eq}$ of the parent carbon atom or $1.5U_{eq}$ for methyl hydrogens. The positions of the hydrogen atoms bonded to nitrogen and oxygen were located in near final Fourier difference maps. They were refined isotropically, with U_{iso}H set equal to $1.5U_{eq}$N in compound **4a**, and with the N-H and O-H bond lengths restrained to reasonable values.

2-Nitroso-3,5-diphenyl-1*H*-pyrrole (4a)

Data was collected and integrated to try and reach a maximum resolution of 0.80 Å. However, the maximum resolution obtained was only 0.81 Å (θ_{max} = 72.37°). This must have occurred for geometric reasons, as the ratio of I/σ(I) was still large at 0.81 Å. All of this data was used in the refinement.

The molecule crystallized in the centrosymmetric Triclinic space group *P*-1, with two molecules of the compound in the asymmetric unit. Pairs of these two molecules are held together in the lattice as a hydrogen bonded dimer.

4'-benzylester-2,3',4,5'-Butamethyl-3-methylester-[2,2'-bi-1*H*-pyrrol]-5(2H)-one oxime (8c)

Data was collected to try and reach a maximum resolution of 0.60 Å but the final data set was integrated only to a resolution of 0.70 Å (θ_{max} = 30.52°). During data processing, a second small twin component was detected in the crystal. The data was treated and the structure was refined using both the twinned and untwinned data sets. The statistical results were best when the twin component was not included. In the twin refinements, the second component refined to a contribution of less than 0.5 %. Proper integration of such a small second component was likely why the results using the twin data sets were not as good. At the end of the regular data processing, the second component of the twin could no longer be detected. However, its presence can still be observed in a comparison of the major differences in the F_{obs}^2 and F_{calc}^2 values for the strong reflections. Four reflections, which were at least partially obscured by the beam stop, were removed from the final refinement because of poor agreement between F_{obs}^2 and F_{calc}^2. An extinction parameter was refined.

The compound crystallized in the centrosymmetric Triclinic space group *P*-1 with two unique molecules in the asymmetric unit. There was no solvent found in the lattice. The structure was found to be disordered. In each molecule, disorder of the -$CH_2(C_6H_5)$ group was modelled using two parts which were restrained to have similar geometries. The length of the bonds from the disordered to the ordered part of the molecules were restrained to be similar in both molecules. The anisotropic displacement parameters of the disordered carbon atoms in each ring were also restrained to be similar. Finally, a rigid bond restraint was placed over all of the atoms in the molecule. The occupancies of the two parts of the disordered group were refined to total one using a different free variable for each molecule. The final occupancies obtained were 61.6(10) % and 38.4 % for parts 1 and 2 of molecule 1, respectively. For molecule two, the corresponding values refined to 68.8(18) % and 31.2 %.

Data for compounds 4a and 8c

Table S1. NH and OH hydrogen bonds in the compounds studied [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Compound **4a**				
N(1)-H(1N)...O(2)	0.906(17)	2.088(18)	2.994(3)	177(3)
N(3)-H(3N)...O(1)	0.886(17)	2.025(18)	2.899(3)	168(3)
Compound **8c**				
O(5)-H(5O)...O(5)#1	0.863(17)	2.54(2)	3.151(2)	128(2)
O(5)-H(5O)...N(3)#1	0.863(17)	1.896(18)	2.7296(17)	162(3)
O(10)-H(10O)...O(10)#2	0.862(16)	2.59(2)	3.178(2)	127(2)
O(10)-H(10O)...N(6)#2	0.862(16)	1.912(18)	2.7366(16)	160(3)
N(1)-H(1N)...O(10)#3	0.884(15)	2.112(16)	2.9826(19)	168(2)
N(2)-H(2N)...O(8)	0.871(16)	2.17(2)	2.8930(17)	141(2)
N(4)-H(4N)...O(5)	0.889(15)	2.090(16)	2.966(2)	168(2)
N(5)-H(5N)...O(3)#4	0.872(15)	2.169(18)	2.9099(17)	142.5(19)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y,-z+1 #2 -x+2,-y+1,-z #3 x-1,y,z #4 x+1,y,z

Table S2: Crystal data and structure refinement details.

Identification code	**4a**	**8c**
CCDC deposit number	2324181	2324182
Empirical formula	$C_{32}H_{24}N_4O_2$	$C_{44}H_{50}N_6O_{10}$
Formula weight	496.55	822.90
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
Unit cell dimensions (Å and º)	*a* = 9.4686(3)	*a* = 10.8638(5)
	b = 9.5459(4)	*b* = 12.1680(6)
	c = 14.1712(5)	*c* = 16.7951(8)
	α = 90.7407(19)	*α* = 73.7257(17)
	β = 94.8288(17)	*β* = 84.4334(17)
	γ = 107.1627(16)	*γ* = 82.2936(17)
Volume (Å^3)	1218.54(8)	2107.82(18)
Z	2	2
Density (calculated, Mg/m^3)	1.353	1.297
Absorption coefficient (mm^{-1})	0.688	0.093
F(000)	520	872
Crystal size (mm^3)	0.106x0.075x0.020	0.150x0.090x0.057
Theta range of data (º)	3.132 to 72.374	1.895 to 30.521
Index ranges (*h*, *k*, *l*)	-10/11, -11/11, -17/17	-15/15, -17/17, -23/23
Reflections collected	48742	154108
Independent reflections	4807	12867
R(int)	0.0438	0.0464
Completeness (%) to angle (°)	100.0 (67.679)	99.9 (25.242)
Max. and min. transmission	0.7536 and 0.6456	0.7453 and 0.6418
Data / restrains / parameters	4807 / 2 / 350	12867 / 1078 / 722
Goodness-of-fit on F^2	1.206	1.122
Final R indices [I>2sigma(I)]	R1 = 0.0681	R1 = 0.0644
	wR2 = 0.1250	wR2 = 0.1613
R indices (all data)	R1 = 0.0937	R1 = 0.0931
	wR2 = 0.1460	wR2 = 0.2034
Extinction coefficient	0.0027(4)	0.081(4)
Largest diff. peak and hole (e.Å^{-3})	0.291 and -0.319	0.447 and -0.494

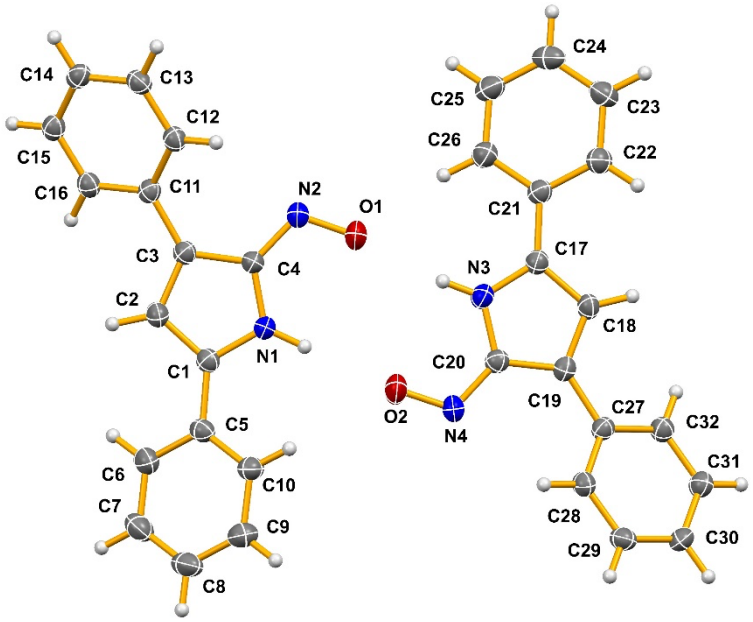


Figure S1. Structure of Compound **4a** with full labelling. Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms are included but have not been labelled.

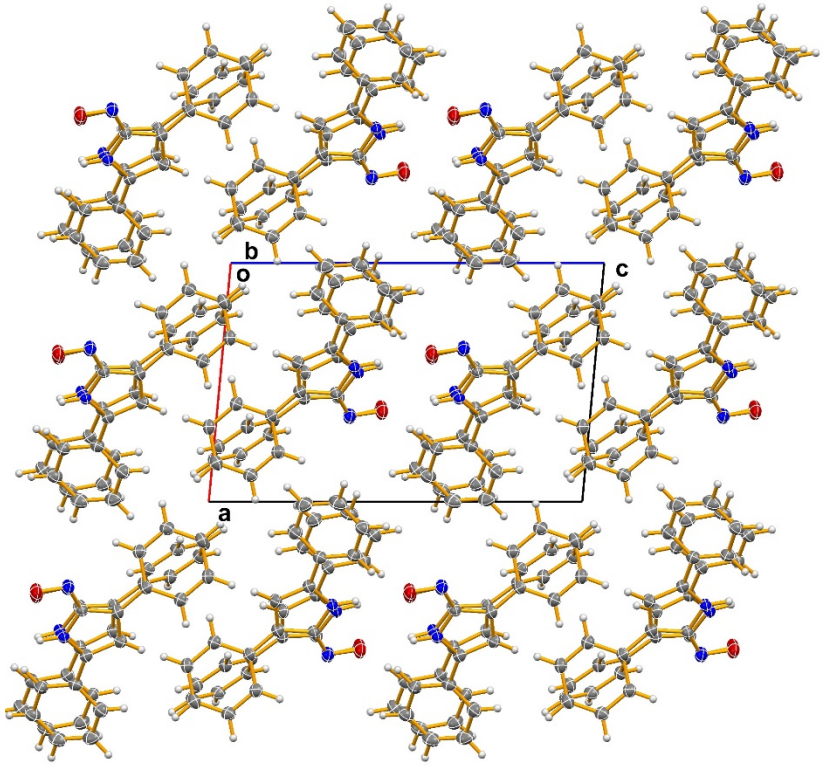


Figure S2. Packing diagram of Compound **4a** viewed down the *B*-axis.

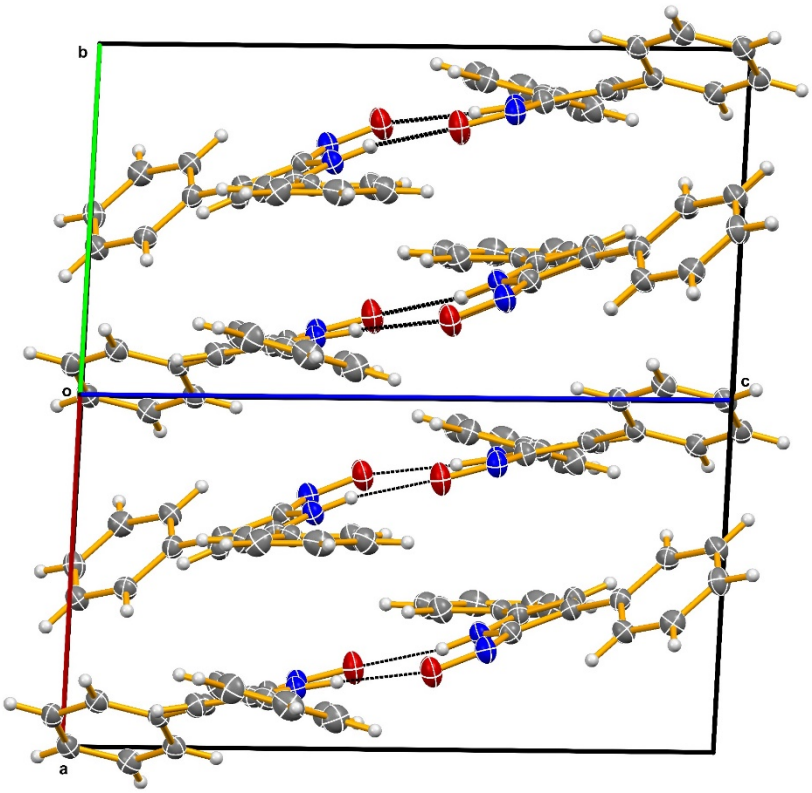


Figure S3. Packing of Compound **4a** drawn to show the layering of the hydrogen bonded dimers (dashed lines) and the alternating orientations of the pendant phenyl rings.

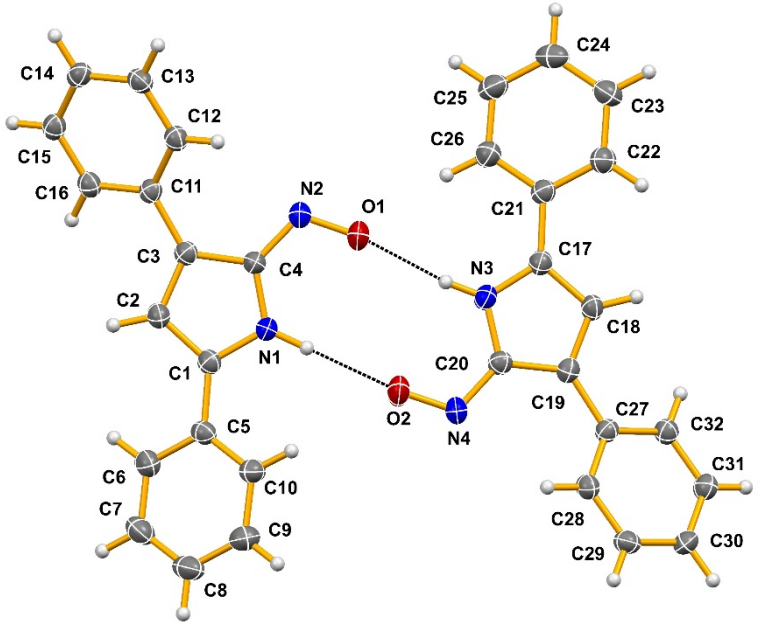
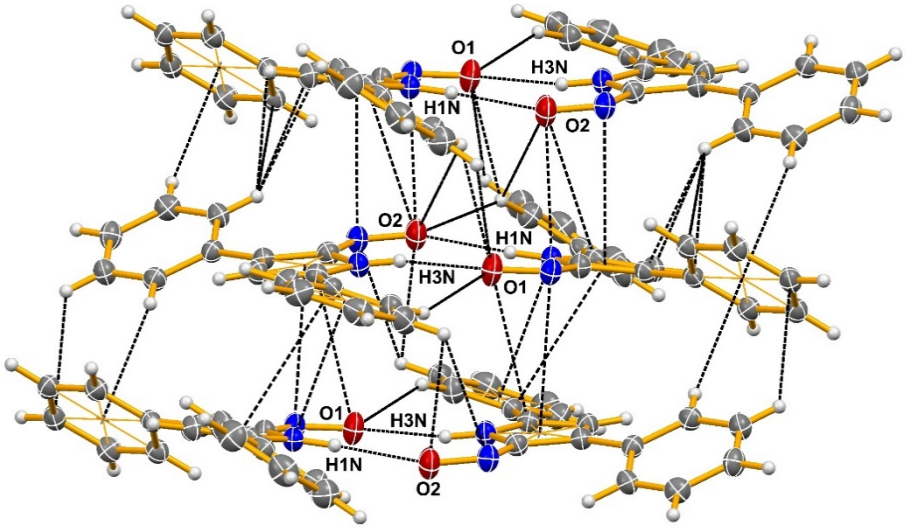


Figure S4. Structure of Compound **4a** showing the N-H…O hydrogen bonds (dashed lines, Table S1) that join the two independent molecules into a dimer in the solid state. Only selected atoms have been labelled.



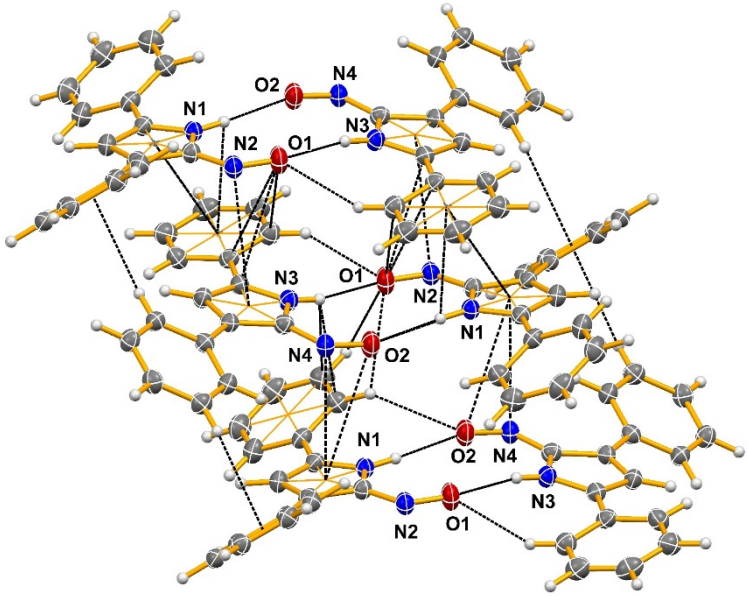


Figure S5. Two different views of the intermolecular interactions (to the sum of the van der Waals radii plus 0.2 Å; dashed lines) found in Compound **4a**. In addition to the N-H…O hydrogen bonds that join the two independent molecules into a dimer, there are a number of perpendicular interactions between the planes, including stacking contacts between rings (minimum 3.777(2) Å between the 5-membered ring (N1, C1-C4) and the 6-membered ring (C21-C26; symmetry 1-*x*, -*y*, -*z*); C-H…O, C-H…N and C-H…ring hydrogen bonds; and O and N contacts to ring electron density in the planes both above and below the central plane. Interactions involving electron density in a ring as the acceptor may be directed toward the ring centroid or may involve specific bonds or atoms. Only the non-carbon atoms have been labelled for clarity.

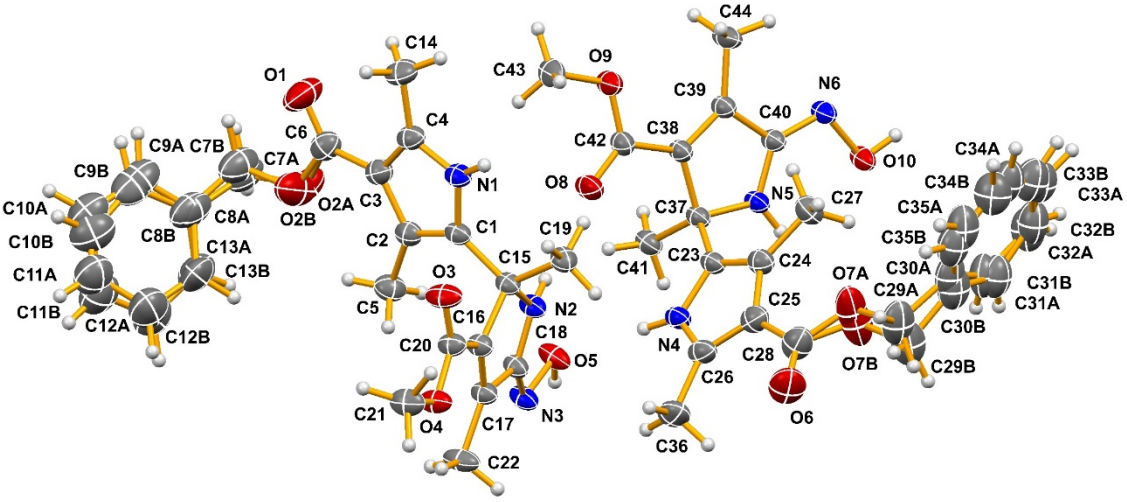
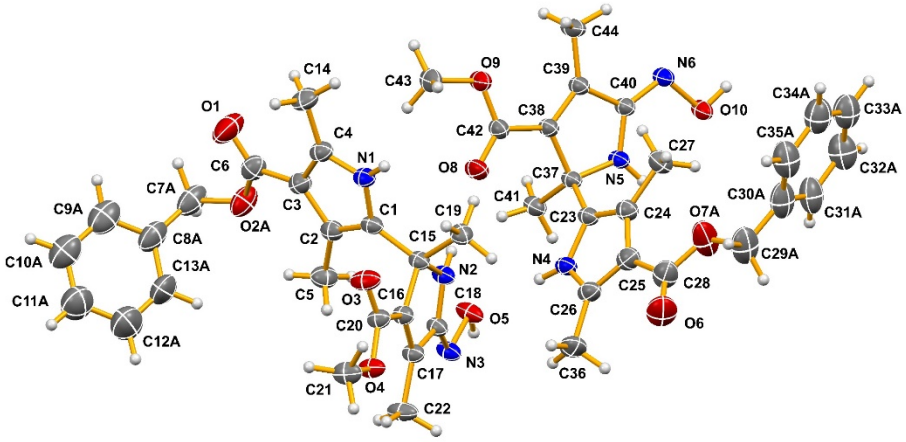


Figure S6. Structure of Compound **8c** with full labelling. Disorder has not been removed. Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms are included but have not been labelled.



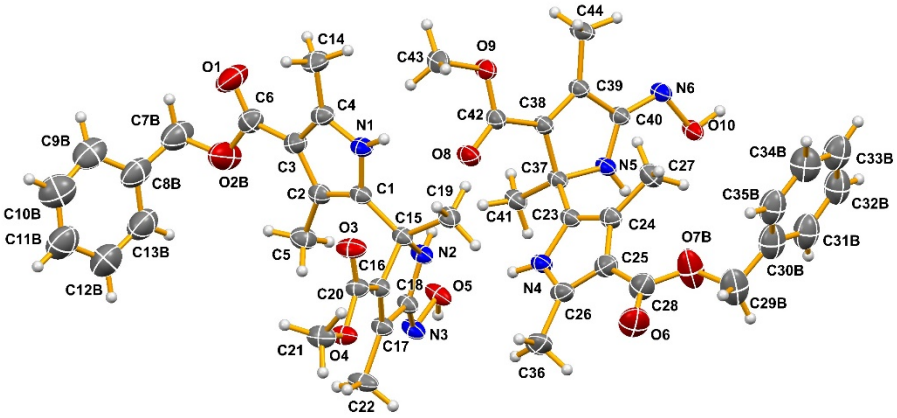


Figure S7. The two components of the disordered model used to refine the structure of Compound **8c** shown with full labelling. Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms are included but have not been labelled.

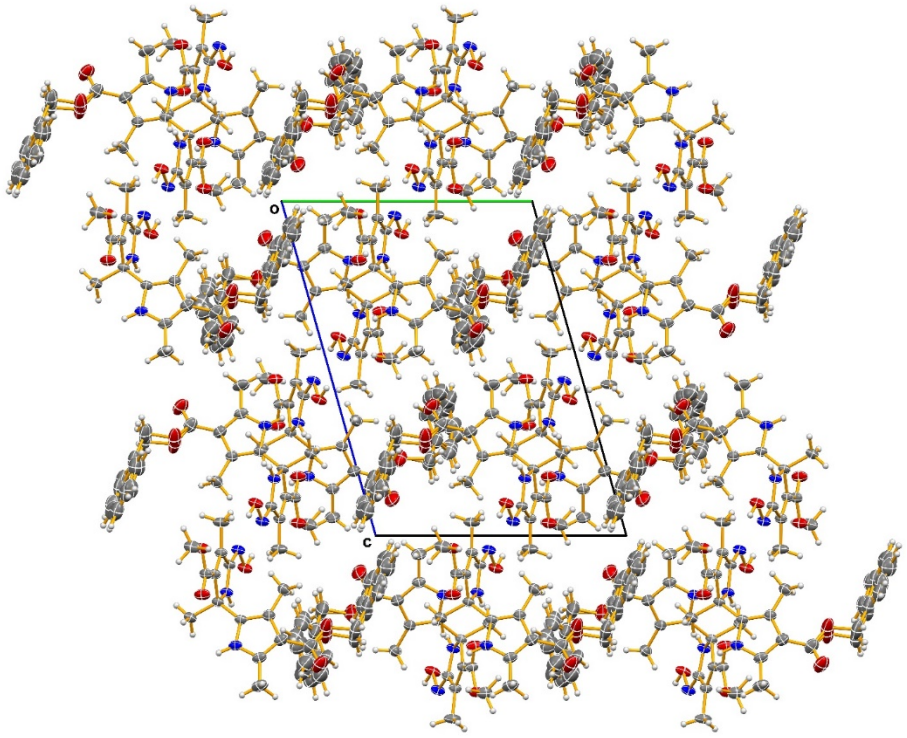


Figure S8. Packing diagram of Compound **8c** viewed down the *A*-axis.

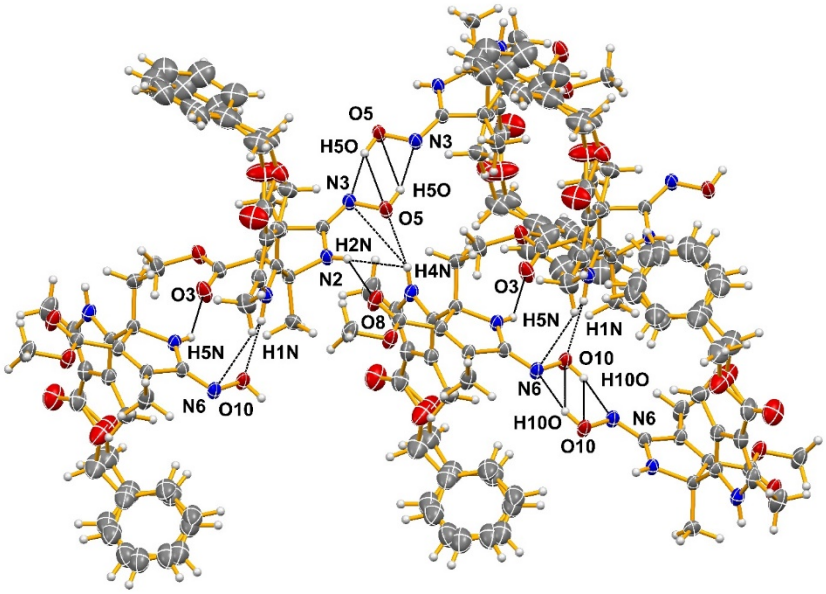
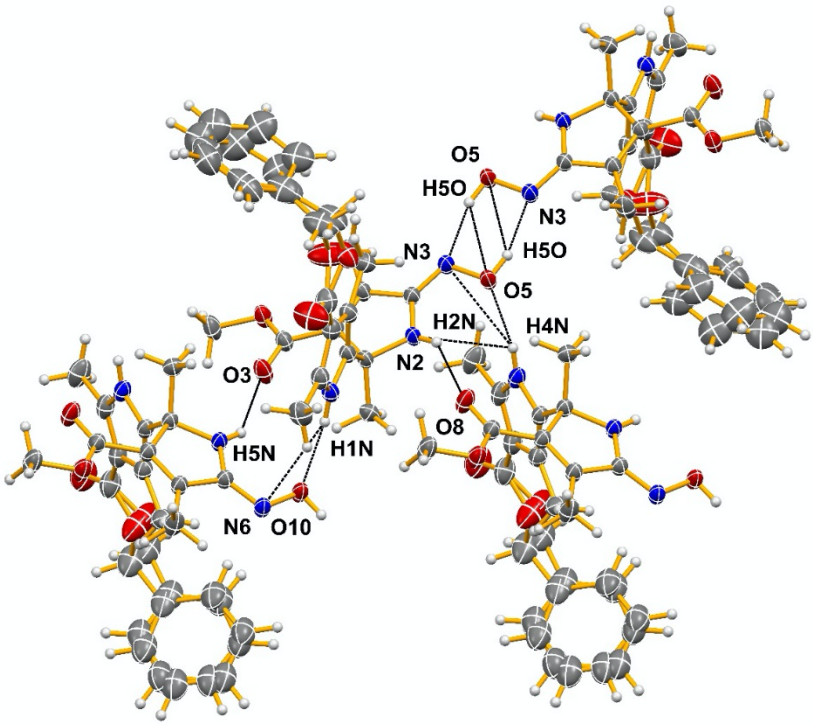


Figure S9. Structure of Compound **8c** showing the N-H..N and N-H…O hydrogen bonds (dashed lines, Table S1). Disorder has not been removed. Only selected atoms have been labelled.



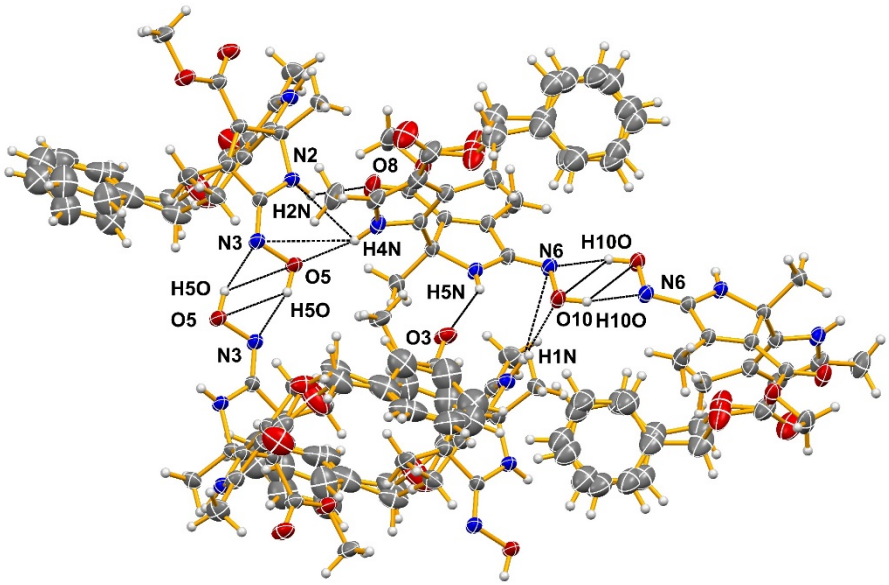


Figure S10. Structures of the two independent molecules in Compound **8c** showing their individual N-H..N and N-H…O hydrogen bonds (dashed lines, centered on molecule 1 top and molecule 2 bottom, Table S1). Disorder has not been removed. Only selected atoms have been labelled.

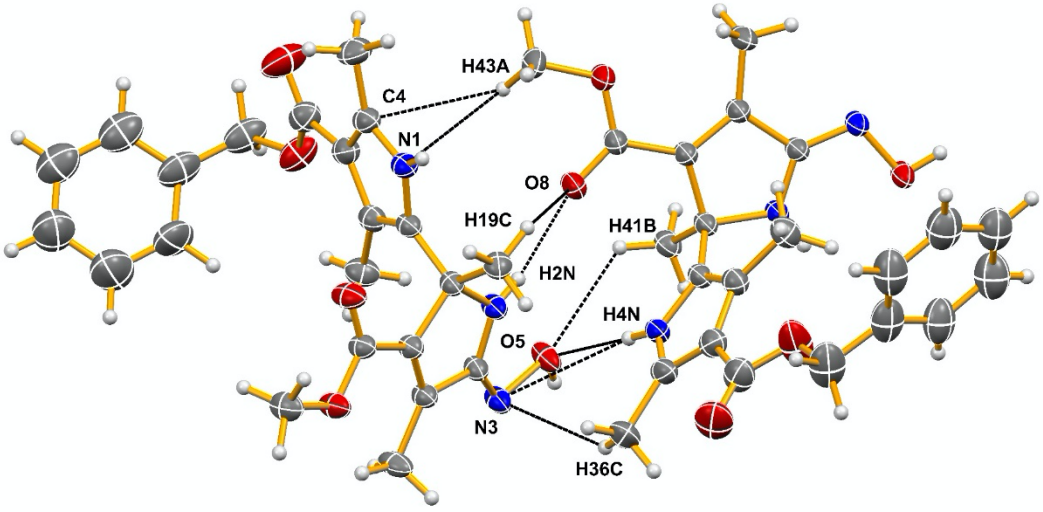


Figure S11. Contacts between the two independent molecules in the structure of compound **8c**. C/N-H..N and C/N-H…O hydrogen bonds (to the sum of the van der Waals radii plus 0.2 Å) are shown with dashed lines. Disorder has been removed. Only selected atoms have been labelled.

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