Pyrrolesulfonium salts: Stable, accessible and versatile pseudohalides for Stille couplings.

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ELECTRONIC SUPPORTING INFORMATION

General Experimental Details, Synthetic chemistry and compound characterisation.

Reagents

Reagents were purchased from Fluorochem, Merck and Tokyo Chemical Industries. Trifluoromethanesulfonic anhydride was purchased from Merck only and used within 30 days of opening.

Solvents

Reactions were carried out under an atmosphere of nitrogen, by purging the vessel with a flow of nitrogen. Dichloromethane, toluene and methanol were dried and degassed by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system. DMF and *t*-butanol were commercial anhydrous grade, over 4Å molecular sieves. Pet Ether refers to petroleum ether, bp 40-60 °C. Solvents were removed using Büchi rotary evaporators and with high vacuum on a Schlenk line.

Melting Points

Capillary melting points were recorded on a Büchi 535 melting point apparatus and are uncorrected.

NMR Spectroscopy

^{1}H, ^{13}C and ^{19}F NMR spectra were obtained using a 500 MHz Agilent ProPulse 500 or a 400 MHz Bruker Avance NEO NMR spectrometer, for which proton decoupling was active for ^{13}C NMR. Spectra were acquired at 298 K and were referenced to residual solvent peaks. Chemical shifts are reported in parts per million (ppm) relative to residual chloroform (δ = 7.26 ppm, ^{1}H; 77.16 ppm, ^{13}C) or DMSO (δ = 2.50 ppm, ^{1}H; 39.52 ppm, ^{13}C)**.** Coupling constants, *J*, reported in Hz, were calculated using MestreNova x64 to the nearest 0.1 Hz. ^{1}H and ^{13}C{^{1}H} assignments for novel compounds are corroborated though 2D NMR experiments (COSY, NOESY, HSQC, HMBC).

Infrared Spectroscopy

Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum 100 ATR-FTIR spectrometer with only selected absorbances quoted as ν in cm^{-1} .

Mass Spectrometry

For mass spectrometry a microTOF electrospray time-of-flight (ESITOF) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) was used. Data are reported in the form of *m/z*. The observed mass and isotope pattern matched the corresponding theoretical values as calculated from the expected molecular formula.

Chromatography

Analytical thin-layer chromatography was performed on Merck silica gel 60 F254 aluminium-backed plates. Visualisation was accomplished with UV light (254 nm), and vanillin stain. Automated flash column chromatography (normal phase) was performed using a Teledyne ISCO CombiFlash NextGen 300+ system equipped with UV and ELSD detectors, using 4 - 40g silica columns. RediSep® Bronze columns (40 - 60 µm particle size) were used for the purification of all compounds, except *N*-trisyl protected Stille coupling products **5a**-**5j**, for which RediSep® Gold columns (20 - 40 µm particle size) were required to achieve the stated isolated yields.

X-ray Crystallography

Intensity data for **2•PF$_6$** were collected at 150(2) K on a Rigaku Xcalibur, EosS2 single crystal diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) and for **5f** on a Rigaku SuperNova Dual EosS2 single crystal diffractometer using monochromated Cu-Kα radiation (λ = 1.54184 Å). Unit cell determination, data collection data reduction and absorption correction were performed using the CrysAlisPro software[1]. The structures were solved with SHELXT[2] and refined by a full-matrix least-squares procedure based on F^2 (SHELXL-2018-19/3)[2]. All non-hydrogen atoms were refined anisotropically. Additional programmes used for analysing data and their graphical manipulation included SHELXle[3], ORTEP3 for windows[4] and Mercury.[5]

Preparation of pyrrolylsulfonium salts 2•OTf, 4•OTf and 10•OTf-13•OTf

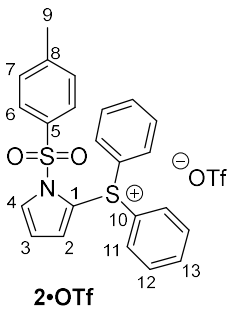
General Procedure A for the Synthesis of Pyrrolyl Sulfonium salts

The pyrrole (1.0 equiv) was added to a stirred solution of sulfoxide (1.0 equiv) in dry CH_2Cl_2 (c = 0.32 M) in a round bottom flask under a nitrogen atmosphere. Trifluoromethanesulfonic anhydride (2.0 equiv) was added dropwise at stated temperature, and then stirred until consumption of pyrrole via TLC. The reaction was diluted with CH_2Cl_2, and washed with 1 M Na_2CO_3 (aq), and then with brine. The aqueous phases were combined and extracted with CH_2Cl_2 (x 3). The organic phases were then combined. (An additional wash with KPF_6 (aq) may also be performed to effect anion exchange at this point if required). The combined organic phase was then dried over $MgSO_4$ and filtered, then the filtrate was concentrated in *vacuo.* Purification was performed by dissolution of the crude material in MeCN, which was then extracted with 3 portions of an equal volume of hexane. The MeCN layer was then concentrated to dryness and the material was triturated with hexane before drying under high vacuum.

General Procedure B for the Synthesis/isomerisation of Pyrrolyl Sulfonium salts with added Brønsted acid.

The pyrrole (1.0 equiv) was added to a stirred solution of sulfoxide (1.0 equiv) in dry CH_2Cl_2 (c = 0.32 M) in a round bottom flask under a nitrogen atmosphere, followed by trifluoromethanesulfonic acid(3.0 equiv). Trifluoromethanesulfonic anhydride (2.0 equiv) was added dropwise at stated temperature, and then stirred until until full isomerisation observed via ^{1}H-NMR spectroscopy of reaction aliquots. The reaction was diluted with CH_2Cl_2, and washed with 1 M Na_2CO_3 (aq), and then with brine. The aqueous phases were combined and extracted with CH_2Cl_2 (x 3). The organic phases were then combined. (An additional wash with KPF_6 (aq) may also be performed to effect anion exchange at this point if required). The combined organic phase was then dried over $MgSO_4$ and filtered, then the filtrate was concentrated in *vacuo.* Purification was performed by dissolution of the crude material in MeCN, which was then extracted with 3 portions of an equal volume of hexane. The MeCN layer was then concentrated to dryness and the material was triturated with hexane before drying under high vacuum.

Diphenyl(1-(*p*-toluenesulfonyl)-1*H*-pyrrol-2-yl)sulfonium trifluoromethanesulfonate (2•OTf)

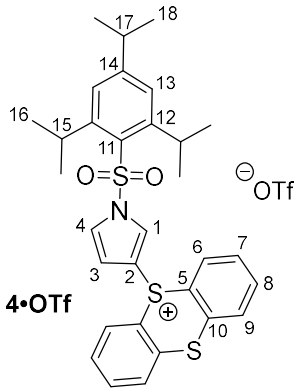


2•OTf

The starting material (*N*-tosylpyrrole) was prepared as reported previously.[6] **2•OTf** was prepared using *General Procedure A* (reaction time: 5 h), followed by recrystallisation from MeOH. Black crystals, 85%, m.p. 97-98 °C.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 (dd, *J* = 3.3, 1.7 Hz, 1H, H^4), 7.91–7.85 (m, 2H, H^{13}), 7.81–7.74 (m, 8H, $H1^{11,12}$), 7.71 (d, *J* = 8.4 Hz, 2H, H^6), 7.41 (d, *J* = 8.4 Hz, 2H, H^7), 6.81–6.71 (m, 1H, H^3), 6.67 (dd, *J* = 4.0, 1.7 Hz, 1H, H^2), 2.08 (s, 3H, H^9) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 147.4 (C^8), 134.7 (C^{13}), 133.0 (C^5), 131.8 (C^4), 131.5 (C^{11}/C^{12}), 130.8 (C^{11}/C^{12}), 130.7 (C^7), 127.8 (C^2), 127.5 (C^6), 125.2 (C^{10}), 115.4 (C^3), 111.0 (C^1), 21.2 (C^9) ppm. HRMS (ESI+): calc. for $C_{23}H_{20}NO_2S_2$ $[M]^+$ 406.0930, found 406.0928. IR (neat) 3056.2, 1476.2, 1593.9, 1192.0, 1379.3, 815.6 cm^{-1}

5-(1-((2,4,6-Triisopropylphenyl)sulfonyl)-1*H*-pyrrol-3-yl)-5*H*-thianthren-5-ium trifluoromethane sulfonate (4•OTf)

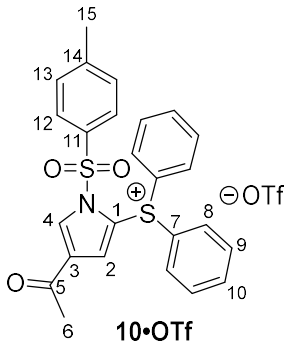


4•OTf

The starting material (*N*-trisylpyrrole) was prepared as reported previously.[7] **4•OTf** was prepared using *General Procedure B* (reaction time: 3 h), followed by purification by column chromatography (SiO_2, CH_2Cl_2–MeOH). Grey powder, 84%, m.p. 80-85°C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 7.5 Hz, 2H, H^6), 7.83 – 7.74 (m, 3H, H^1), 7.72 (dd, *J* = 7.9, 1.2 Hz, 2H), 7.64 (dd, *J* = 7.5, 1.3 Hz, 2H), 7.19 (s, 2H, H^{13}), 7.03 (dd, *J* = 3.4, 2.2 Hz, 1H, H^4), 6.57 (dd, *J* = 3.1, 1.2 Hz, 1H, H^3), 3.88 (hept, *J* = 6.8 Hz, 2H, H^{15}), 2.90 (h, *J* = 7.1 Hz, 1H, H^{17}), 1.25 (d, *J* = 6.9 Hz, 6H, H^{18}), 1.09 (d, *J* = 6.6 Hz, 12H, H^{16}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5, 152.4, 135.5, 134.44, 134.41, 130.4, 129.8, 128.5, 125.8, 125.0, 123.0, 120.5, 112.0, 107.5, 34.5, 30.0, 24.6, 23.5 ppm. HRMS (ESI+) m/z calcd. for ($C_{31}H_{34}NO_2S_3$) $[M]^+$ 548.1746, found 548.1479. IR (neat) 2960.8, 1598.0, 1254.4, 884.2 cm^{-1}

(4-Acetyl-1-(*p*-toluenesulfonyl)-1*H*-pyrrol-2-yl)diphenylsulfonium trifluoromethanesulfonate (10•OTf)

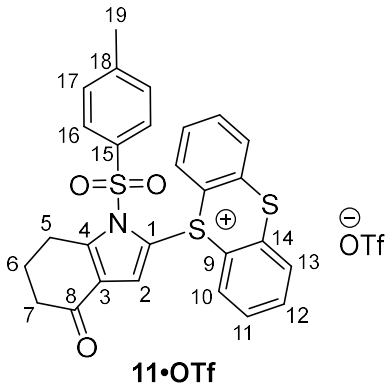


10•OTf

The starting material (3-acetyl-*N*-tosylpyrrole) was prepared as reported previously.[6] **10•OTf** was prepared using *General Procedure A*, followed by purification by column chromatography (SiO_2, CH_2Cl_2–MeOH). Brown gum, 23%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 1.9 Hz, 1H, H^4), 8.13–8.07 (m, 2H, H^{12}), 7.80–7.64 (m, 10H, H^{8-10}), 7.56–7.52 (m, 2H, H^{13}), 6.86 (d, *J* = 1.9 Hz, 1H, H^2), 2.47 (s, 3H, H^{15}), 2.46 (s, 3H, H^6) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9 (C^5), 148.7, 134.9, 133.0, 132.1 (C^4), 131.9, 131.72, 131.65, 131.3, 130.9, 128.6 (C^{12}), 124.5 (C^2), 112.8, 27.4 (C^6), 21.6 (C^{15}) ppm. HRMS (ESI^+): calc. $C_{25}H_{22}NO_3S_2^+$ $[M]^+$ 448.1036, found 448.1039. IR (neat) 1681.7, 1260.7, 1146.3, 752.0 cm^{-1}

5-(4-Oxo-1-(*p*-toluenesulfonyl)-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (11•OTf)

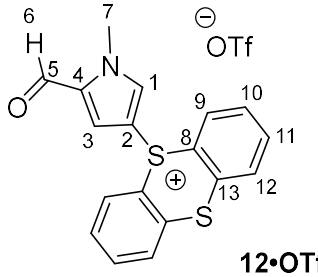


11•OTf

The starting material (1-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-4*H*-indol-4-one) was prepared as reported previously.[8] **11•OTf** was prepared using *General Procedure A*, followed by purification by column chromatography (SiO_2, CH_2Cl_2–MeOH). Beige powder, 60%

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 7.4, 2.0 Hz, 2H, H^{10}), 7.88 (dd, *J* = 7.5, 1.5 Hz, 2H, H^{13}), 7.79–7.70 (m, 6H, $H^{11,12,16}$), 7.42 (d, *J* = 8.0 Hz, 2H, H^{17}), 6.96 (s, 1H, H^2), 2.76 (t, *J* = 6.1 Hz, 2H, H^5), 2.50–2.42 (m, 2H, H^7), 2.44 (3H, s, H^{19}), 2.06 (app quint, *J* = 6.2 Hz, 2H, H^6) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.0 (C^8), 147.9, 146.6, 142.2, 137.0, 135.7 (C^{10}), 134.6, 132.5, 131.1 (C^{17}), 130.4 (C^{13}), 130.1, 128.3, 127.3 (C^2), 121.5, 118.4, 36.5 (C^7), 22.8 (C^6), 22.5 (C^5), 22.0 (C^{19}) ppm. HRMS (ESI$^+$): calc. $C_{27}H_{22}NO_3S_3^+$ $[M]^+$ 504.0756, found 504.0749. IR (neat) 1673.1, 1430.6, 1387.4, 1028.7, 911.0 cm^{-1}

5-(5-Formyl-1-methyl-1*H*-pyrrol-3-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (12•OTf)

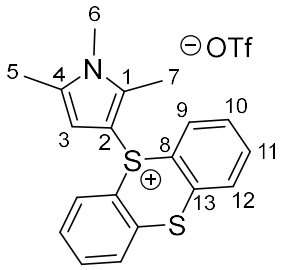


12•OTf

The starting material (1-methyl-2-pyrrolecarboxaldehyde) was purchased from Fluorochem. **12•OTf** was prepared using *General Procedure A*; product precipitated from the CH_2Cl_2 reaction solvent upon standing. White powder, 47%, m.p. 108-111 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.51 (s, 1H, H^6), 8.43 (dd, *J* = 7.8, 1.4 Hz, 2H, H^9), 8.26 (d, *J* = 1.9 Hz, 1H, H^1), 7.82 (dd, *J* = 7.8, 1.3 Hz, 2H, H, H^{12}), 7.73 (app td, *J* = 7.8, 1.6 Hz, 2H, H^{11}), 7.67 (app td, *J* = 7.8, 1.4 Hz, 2H, H^{10}), 7.12 (d, *J* = 1.9 Hz, 1H, H^3), 3.96 (s, 3H, H^7) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 179.5 (C^5), 137.4 (C^1), 135.5 (C^8), 134.4 (C^{11}), 134.1 (C^4), 133.9 (C^9), 130.5 (C^{10}), 130.1 (C^{12}), 122.7 (C^3), 121.5 (C^{13}), 103.3 (C^2), 37.9 (C^7) ppm. HRMS (ESI$^+$): calc. $C_{18}H_{15}NOS_2^+$ $[M]^+$ 324.0511, found 342.0827. IR (neat) 1660.3, 1443.4, 1003.1, 701.9 cm^{-1}.

5-(1,2,5-Trimethyl-1*H*-pyrrol-3-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate (13•OTf)



13•OTf

The starting material (1-methyl-2-pyrrolecarboxaldehyde) was purchased from Tokyo Chemical Industries. **13•OTf** was prepared using *General Procedure A*. Brown amorphous solid, 75%

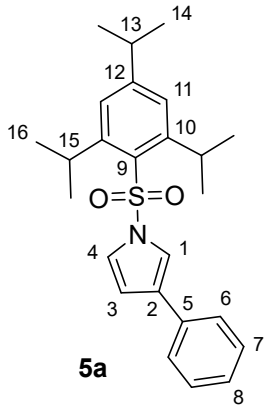
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.76 (m, 2H, H^9), 7.67–7.56 (m, 6H, $H^{10\text{-}12}$), 5.97 (s, 1H, H^3), 3.62 (s, 3H, H^6), 2.55 (s, 3H, H^7), 2.30 (s, 3H, H^5) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 136.3, 132.8, 132.7, 130.33, 130.25, 128.8, 127.4, 105.7, 86.9, 32.0, 12.9, 11.5 ppm. HRMS (ESI+) m/z calcd. for ($C_{19}H_{18}NS_2$) $[M]^+$ 324.0875, found 324.0870. IR (neat) 3107.0, 1444.0, 812.2, 706.0 cm^{-1}.

General method for Optimised Stille Cross-Couplings:

$Pd_2(dba)_3$ (2 mol%), $AsPh_3$ (16 mol%), pyrrolyl sulfonium salt (1.0 equiv) and tributylorganostannane (2.2 equiv) were added to a round bottom flask and 3 evacuation/N_2 fill cycles were performed. DMF (dry, c = 0.12 M) was added, and the reaction was stirred at 50 ^oC for 16-20 hours. The reaction was then concentrated under vacuum and filtered through a plug of celite with CH_2Cl_2. The filtrate was concentrated under vacuum, and the crude mixture purified via column chromatography (SiO_2, EtOAc–Pet Ether).

NOTE: See the section on chromatography in the "General Experimental Details" for details of the stationary phases used for chromatographic purification of the coupling products.

3-Phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (5a)

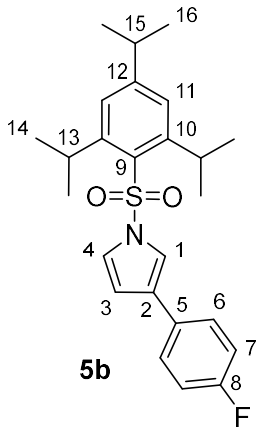


5a

White powder, 76%, m.p. 108-111 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.8 Hz, 2H, H^{6}), 7.38–7.32 (m, 3H, $H^{4,7}$), 7.23 (t, *J* = 7.2 Hz, 1H, H^{8}), 7.21 (s, 2H, H^{11}), 7.13 (dd, *J* = 2.8, 2.8 Hz, 1H, H^{1}), 6.58 (dd, *J* = 3.4, 1.7 Hz, 1H, H^{3}), 4.21 (hept, *J* = 6.7 Hz, 2H, H^{15}), 2.92 (hept, *J* = 6.8 Hz, 1H, H^{13}), 1.26 (d, *J* = 6.9 Hz, 6H, H^{14}), 1.21 (d, *J* = 6.8 Hz, 12H, H^{16}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8 (C^{12}), 151.7 (C^{10}), 134.0 (C^{5}), 131.0 (C^{9}), 128.9 (C^{7}), 128.4 (C^{2}), 127.0 (C^{8}), 125.8 (C^{6}), 124.5 (C^{11}), 120.9 (C^{1}), 115.7 (C^{4}), 110.8 (C^{3}), 34.4 (C^{13}), 29.8 (C^{15}), 24.8 (C^{16}), 23.6 (C^{14}) ppm. HRMS (ESI+) m/z calcd. for ($C_{25}H_{31}NO_2S$) $[M+H]^+$ 410.2154, found 410.2153. IR (neat) 3137.7, 1447.2, 1263.4, 768.0 cm^{-1}

3-(4-Fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (5b)

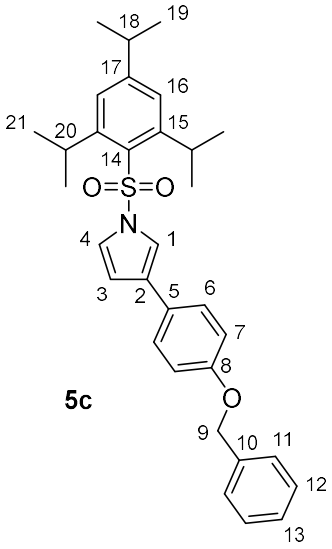


5b

White powder, 58%, m.p. 105-110 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.39 (m, 2H, H^{6}), 7.29 (app t, *J* = 2.0 Hz, 1H, H^{1}), 7.21 (s, 2H, H^{11}), 7.12 (dd, *J* = 3.3, 2.3 Hz, 1H, H^{4}), 7.03 (app t, *J* = 8.7 Hz, 2H, H^{7}), 6.52 (dd, *J* = 3.3, 1.7 Hz, 1H, H^{3}), 4.20 (hept, *J* = 6.8 Hz, 2H, H^{13}), 2.92 (hept, *J* = 6.9 Hz, 1H, H^{15}), 1.26 (d, *J* = 6.9 Hz, 6H, H^{16}), 1.20 (d, *J* = 6.8 Hz, 12H, H^{14}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0 ($^{1}J_{CF}$ = 245.7 Hz, C^{8}), 154.9 (C^{12}), 151.7 (C^{10}), 130.9 (C^{9}), 130.2 ($^{4}J_{CF}$ = 3.3 Hz, C^{5}), 127.5 (C^{2}), 127.3 ($^{3}J_{CF}$ = 7.9 Hz, C^{6}), 124.5 (C^{11}), 121.0 (C^{4}), 115.8 ($^{2}J_{CF}$ = 21.6 Hz, C^{7}), 115.4 (C^{1}), 110.7 (C^{3}), 34.4 (C^{15}), 29.8 (C^{13}), 24.8 (C^{14}), 23.6 (C^{16}) ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.7 (tt, *J* = 9.1, 4.6 Hz). HRMS (ESI+) m/z calcd. for ($C_{25}H_{31}FNO_2S$) $[M+Na]^+$ 450.1873; found 450.1885. IR (neat) 2964.0, 1344.9, 1060.8, 778.0 cm^{-1}.

3-(4-(Benzyloxy)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (5c)

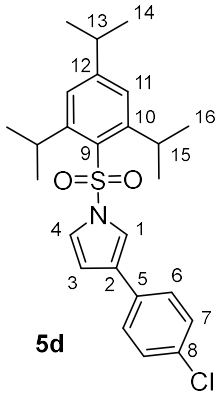


5c

White powder, 75%, m.p. 140-142 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.35 (m, 6H, $H^{6,11,12}$), 7.34-7.30 (m, 1H, H^{13}), 7.24 (app t, *J* = 2.0 Hz, 1H, H^{1}), 7.20 (s, 2H, H^{16}), 7.10 (dd, *J* = 3.2, 2.2 Hz, 1H, H^{4}), 6.96 (d, *J* = 8.8 Hz, 2H, H^{7}), 6.51 (dd, *J* = 3.3, 1.7 Hz, 1H, H^{3}), 5.07 (s, 2H, H^{9}), 4.20 (hept, *J* = 6.7 Hz, 2H, H^{20}), 2.91 (hept, *J* = 6.9 Hz, 1H, H^{18}), 1.26 (d, *J* = 6.9 Hz, 6H, H^{19}), 1.20 (d, *J* = 6.7 Hz, 12H, H^{21}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.0 (C^{8}), 154.7 (C^{17}), 151.7 (C^{15}), 137.1 (C^{10}), 131.1 (C^{14}), 128.8 (C^{12}), 128.12 (C^{13}), 128.09 (C^{2}), 127.6 (C^{11}), 127.0 (C^{5}) 126.9 (C^{6}), 124.5 (C^{16}), 120.8 (C^{4}), 115.3 (C^{7}), 114.9 (C^{1}), 110.7 (C^{3}), 70.2 (C^{9}), 34.4 (C^{18}), 29.7 (C^{20}), 24.8 (C^{21}), 23.6 (C^{19}) ppm. HRMS (ESI+) m/z calcd. for ($C_{32}H_{37}NO_3S$) $[M+H]^+$ 516.2567, found 516.2565. IR (neat) 2693.3, 1363.6, 1052.2, 795.0 cm^{-1}.

3-(4-Chlorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (5d)

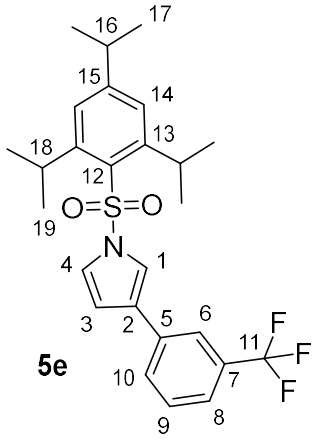


5d

White powder, 54%, m.p. 85-89 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.6 Hz, 2H, H^{6}), 7.34–7.28 (m, 3H, $H^{4or1,7}$), 7.21 (s, 2H), 7.11 (dd, *J* = 3.3, 2.3 Hz, 1H, H^{1or4}), 6.53 (dd, *J* = 3.3, 1.7 Hz, 1H, H^{3}), 4.19 (hept, *J* = 6.8 Hz, 2H, H^{15}), 2.92 (hept, *J* = 6.9 Hz, 1H, H^{13}), 1.26 (d, *J* = 6.9 Hz, 6H, H^{14}), 1.20 (d, *J* = 6.8 Hz, 12H, H^{16}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (C^{12}), 151.8 (C^{10}), 132.6 (C^{5}/C^{8}), 132.5 (C^{5}/C^{8}), 130.8 (C^{9}), 129.0 (C^{7}), 127.2 (C^{2}), 127.0 (C^{6}), 124.6 (C^{11}), 121.1 (C^{1}), 115.8 (C^{4}), 110.6 (C^{3}), 34.4 (C^{13}), 29.8 (C^{15}), 24.8 (C^{16}), 23.6 (C^{14}) ppm. HRMS (ESI+) m/z calcd. for ($C_{25}H_{30}ClNO_2S$) $[M+Na]^+$ 466.1583, found 466.1590. IR (neat) 1585.0, 1042.1, 839.2 cm^{-1}

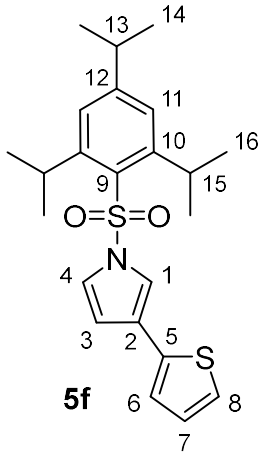
3-(3-(Trifluoromethyl)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (5e)



White crystals, 72%, m.p. 60-63 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70–7.68 (m, 1H, H^6), 7.64 (dd, *J* = 7.2, 1.8 Hz, 1H, H^{10}), 7.50–7.43 (m, 2H, $H^{8,9}$), 7.41 (dd, *J* = 2.0, 2.0 Hz, 1H, H^1), 7.22 (s, 2H, H^{14}), 7.13 (dd, *J* = 3.3, 2.3 Hz, 1H, H^4), 6.59 (dd, *J* = 3.3, 1.7 Hz, 1H, H^3), 4.19 (hept, *J* = 6.8 Hz, 2H, H^{18}), 2.92 (hept, *J* = 6.9 Hz, 1H, H^{16}), 1.26 (d, *J* = 6.9 Hz, 6H, H^{17}), 1.21 (d, *J* = 6.8 Hz, 12zH, H^{19}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1 (C^{15}), 151.8 (C^{13}), 134.9 (C^5), 131.3 (q, $^{2}J_{CF}$ = 32 Hz, C^7), 130.7 (C^{12}), 129.4 (C^9), 128.9 (C^{10}), 127.0 (C^2), 126.7 (q, $^{1}J_{CF}$ = 240.4 Hz, C^{11}), 124.6 (C^{14}), 123.5 (q, $^{3}J_{CF}$ = 3.9 Hz, C^8), 122.4 (q, $^{3}J_{CF}$ = 3.7 Hz, C^6), 121.3 (C^4), 116.2 (C^1), 110.5 (C^3), 34.4 (C^{16}), 29.8 (C^{18}), 24.8 (C^{19}), 23.6 (C^{17}) ppm. HRMS (ESI+) m/z calcd. for ($C_{26}H_{30}F_3NO_2S$) $[M+H]^+$ 478.2028, found 478.2029. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.76 ppm. IR (neat) 2959.4, 1598.1, 1124.5, 790.9 cm^{-1}.

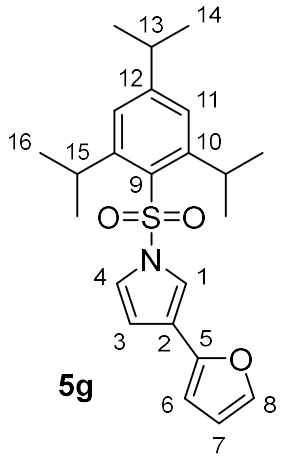
3-(Thiophen-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (5f)



Colourless crystals, 80%, m.p. 113-118 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (app t, *J* = 2.0 Hz, 1H, H^4), 7.20 (s, 2H, H^{11}), 7.15 (dd, *J* = 5.1, 1.2 Hz, 1H, H^8), 7.08 (dd, *J* = 3.3, 2.3 Hz, H^1), 7.07 (dd, J = 3.6, 1.2 Hz, H^6), 6.99 (dd, *J* = 5.1, 3.6 Hz, 1H, H^7), 6.47 (dd, *J* = 3.3, 1.7 Hz, 1H, H^3), 4.19 (hept, *J* = 6.8 Hz, 2H, H^{15}), 2.91 (hept, *J* = 6.8 Hz, 1H, H^{13}), 1.26 (d, *J* = 6.9 Hz, 6H, H^{14}), 1.20 (d, *J* = 6.7 Hz, 12H, H^{16}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (C^{12}), 151.8 (C^{10}), 137.1 (C^5), 130.9 (C^9), 127.7 (C^7), 124.6 (C^{11}), 123.5 (C^8), 123.0 (C^6), 122.4 (C^2), 120.9 (C^1), 115.5 (C^4), 111.2 (C^3), 34.4 (C^{13}), 29.8 (C^{15}), 24.8 (C^{16}), 23.6 (C^{14}) ppm. HRMS (ESI+) m/z calcd. for ($C_{23}H_{29}NO_2S_3$) $[M+H]^+$ 416.1713, found 416.1714. IR (neat) 2954.2, 2925.8, 1593.7, 1260.2, 1029.5, 750.0 cm^{-1}.

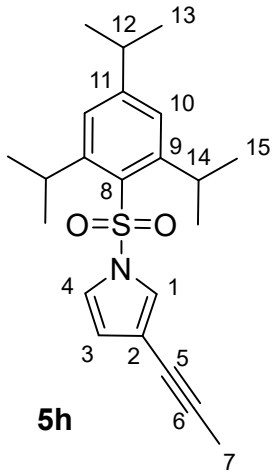
3-(Furan-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (5g)



White powder, 77%, m.p. 122-125 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 1.8, 0.8 Hz, 1H, H^{8}), 7.31 (dd, *J* = 2.3, 1.6 Hz, 1H, H^{1or4}), 7.22 (s, 2H, H^{11}), 7.12 (dd, *J* = 3.3, 2.3 Hz, 1H, H^{1or4}), 6.49 (dd, *J* = 3.3, 1.6 Hz, 1H, H^{3}), 6.39 (dd, *J* = 3.3, 1.8 Hz, 1H, H^{7}), 6.36 (dd, *J* = 3.4, 0.8 Hz, 1H, H^{6},), 4.20 (hept, *J* = 6.8 Hz, 2H, H^{15}), 2.92 (hept, *J* = 6.9 Hz, 1H, H^{13}), 1.27 (d, *J* = 7.0 Hz, 6H, C^{14}), 1.21 (d, *J* = 6.8 Hz, 12H, C^{16}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (C^{12}), 151.8 (C^{10}), 149.4 (C^{5}), 141.1 (C^{8}), 130.8 (C^{9}), 124.5 (C^{11}), 120.8 (C^{1or4}), 119.5 (C^{2}), 115.0 (C^{1or4}), 111.3 (C^{7}), 109.6 (C^{3}), 104.6 (C^{6}), 34.4 (C^{15}), 29.7 (C^{15}), 24.8 (C^{16}), 23.6 (C^{14}) ppm. HRMS (ESI+) m/z calcd. for ($C_{23}H_{29}NO_3S$) $[M+H]^+$ 400.1941, found 400.1942. IR (neat) 1593.4, 1475.4, 1222.0, 815.7, 745.9 cm^{-1}.

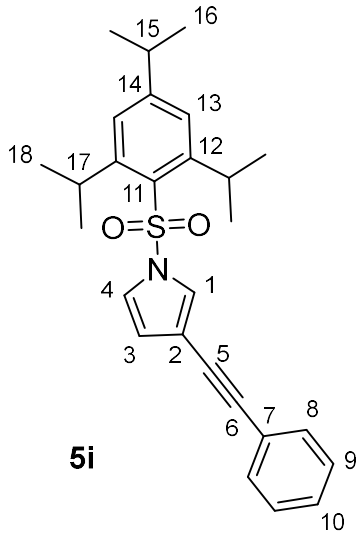
3-(Prop-1-yn-1-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (5h)



White powder, 71%, m.p. 130-133 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 2H, H^{10}), 7.09 (dd, *J* = 2.0, 2.0 Hz, 1H, H^{4}), 7.01 (dd, *J* = 3.2, 2.3 Hz, 1H, H^{1}), 6.26 (dd, *J* = 3.2, 1.6 Hz, 1H, H^{3}), 4.10 (hept, *J* = 6.7 Hz, 2H, H^{14}), 2.90 (hept, *J* = 7.0 Hz, 1H, H^{12}), 1.98 (s, 3H, H^{7}), 1.25 (d, *J* = 6.9 Hz, 6H, H^{13}), 1.17 (d, *J* = 6.8 Hz, 12H, H^{15}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0 (C^{11}), 151.8 (C^{9}), 130.6 (C^{8}), 124.5 (C^{10}), 122.4 (C^{4}), 119.8 (C^{1}), 114.8 (C^{3}), 109.4 (C^{2}), 86.1 (C^{5or6}), 72.9 (C^{5or6}), 34.4 (C^{12}), 29.7 (C^{14}), 24.8 (C^{15}), 23.6 (C^{13}), 4.4 (C^{7}) ppm. HRMS (ESI+) m/z calcd. for ($C_{22}H_{29}NO_2S$) $[M+H]^+$ 372.1997, found 372.1995. IR (neat) 2960.1, 1459.1, 950.7, 589.9 cm^{-1}.

3-(Phenylethynyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole (5i)

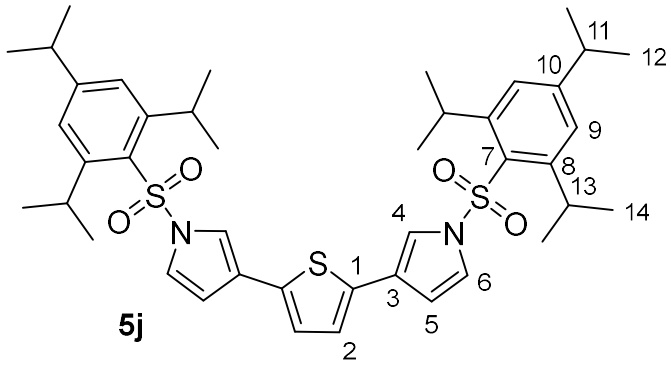


5i

Beige solid, 71%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2H, H^8), 7.35-7.29 (m, 3H, H^9, H^{10}), 7.27-7.25 (m, 1H, H^4) 7.21 (s, 2H, H^{13}), 7.06 (app t, *J* = 2.7 Hz, 1H, H^1), 6.40 (dd, *J* = 3.2, 1.6 Hz, 1H, H^3), 4.14 (hept, *J* = 6.7 Hz, 2H, H^{17}), 2.92 (hept, *J* = 7.0 Hz, 1H, H^{15}), 1.26 (d, *J* = 7.0 Hz, 6H, H^{16}), 1.20 (d, *J* = 6.7 Hz, 12H, H^{18}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2 (C^{14}), 151.9 (C^{12}), 131.5 (C^8), 130.4 (C^{11}), 128.4 (C^9), 128.2 (C^{10}), 124.6 (C^{13}), 123.4 (C^7), 122.9 (C^4), 120.1 (C^1), 114.8 (C^3), 108.8 (C^2), 89.7 (C^6), 82.9 (C^5), 34.4 (C^{15}), 29.8 (C^{17}), 24.8 (C^{18}), 23.6 (C^{16}) ppm. HRMS (ESI+) m/z calcd. for ($C_{27}H_{31}NO_2S$) $[M+H]^+$ 434.2154; found 434.2149. IR (neat) 3145.7, 2850.4, 2237.0, 1292.0, 702.0 cm^{-1}.

2,5-Bis(1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrol-3-yl)thiophene (5j)

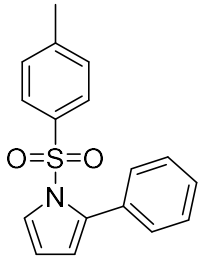


5j

Yellow powder, 63% m.p. 180-185 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 2.3, 1.7 Hz, 2H, H^4), 7.20 (s, 4H, H^9), 7.07 (dd, *J* = 3.3, 2.3 Hz, 2H, H^6), 6.94 (s, 2H, H^2), 6.45 (dd, *J* = 3.3, 1.7 Hz, 2H, H^5), 4.17 (hept, *J* = 6.7 Hz, 4H, H^{13}), 2.91 (hept, *J* = 6.9 Hz, 2H, H^{11}), 1.26 (d, *J* = 6.9 Hz, 12H, H^{12}), 1.20 (d, *J* = 6.8 Hz, 24H, H^{14}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.9 (C^{10}), 151.8 (C^8), 135.0 (C^1), 130.8 (C^7), 124.6 (C^9), 123.5 (C^2), 122.3 (C^3), 120.9 (C^6), 115.3 (C^4), 110.9 (C^5), 34.4 (C^{11}), 29.8 (C^{13}), 24.8 (C^{14}), 23.6 (C^{12}) ppm. HRMS (ESI+) m/z calcd. for ($C_{42}H_{54}N_2O_4S_3$) $[M+H]^+$ 747.3319, found 747.3326. IR (neat) 2954.2, 2925.8, 1551.1, 1171.3, 837.0 cm^{-1}.

2-Phenyl-1-(*p*-toluenesulfonyl)-1*H*-pyrrole (7a)

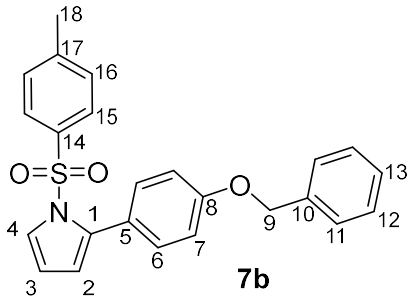


7a

White powder, 71%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 3.5, 1.7 Hz, 1H), 7.39 – 7.20 (m, 8H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.31 (app t, *J* = 3.3 Hz, 1H), 6.16 (dd, *J* = 3.4, 1.8 Hz, 1H), 2.36 (s, 3H) ppm. Data in agreement with those previously reported.[9]

2-(4-(Benzyloxy)phenyl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole (7b)

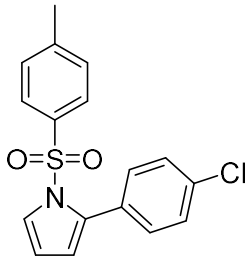


7b

White powder, 54%, m.p. 110-113 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.0 Hz, 2H, H^{11}), 7.45–7.40 (m, 3H, $H^{4,12}$), 7.36 (t, *J* = 7.2 Hz, 1H, H^{13}), 7.22 (d, *J* = 8.3 Hz, 2H, H^{15}), 7.14 (d, *J* = 8.1 Hz, 2H, H^6), 7.07 (d, *J* = 8.1 Hz, 2H, H^{16}), 6.91 (d, *J* = 8.1 Hz, 1H, H^7), 6.29 (dd, *J* = 3.3, 0.9 Hz, 1H, H^3), 6.10 (dd, *J* = 3.3, 1.6 Hz, 1H, H^2), 5.12 (s, 2H, H^9), 2.34 (s, 3H, H^{18}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8 (C^8), 144.6 (C^{17}), 136.9 (C^{14}), 135.71 (C^1/C^{10}), 135.69 (C^1/C^{10}), 132.3 (C^6), 129.3 (C^{16}), 128.7 (C^{12}), 128.1 (C^{13}), 127.6 (C^{11}), 127.2 (C^{15}), 124.0 (C^5), 123.7 (C^4), 115.3 (C^2), 113.8 (C^7), 111.9 (C^3), 70.0 (C^9), 21.6 (C^{18}) ppm. HRMS (ESI+) m/z calcd. for ($C_{24}H_{21}NO_3S$) $[M+H]^+$ 404.1318, found 404.1316. IR (neat) 1507.8, 1131.0, 1064.3, 748.8, 670.1 cm^{-1}

2-(4-Chlorophenyl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole (7c)

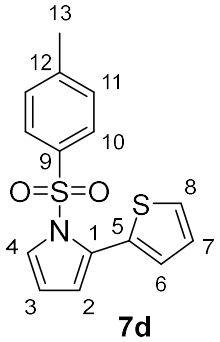


7c

Pale yellow solid, 51%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 3.4, 1.7 Hz, 1H), 7.32–7.22 (m, 4H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.30 (app t, *J* = 3.3 Hz, 1H), 6.15 (dd, *J* = 3.3, 1.8 Hz, 1H), 2.36 (s, 3H) ppm. Data in agreement with those previously reported.[10]

2-(Thiophen-2-yl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole (7d)

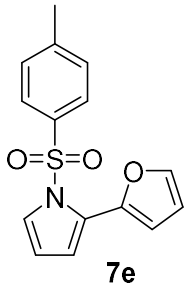


7d

White powder, 70%, m.p. 61-64 °C

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 3.3, 1.9 Hz, 1H, H^4), 7.31 (d, *J* = 8.4 Hz, 2H, H^{10}), 7.28 (dd, *J* = 5.2, 1.2 Hz, 1H, H^8), 7.14 (dd, *J* = 3.6, 1.2 Hz, 1H, H^6), 7.12 (d, *J* = 7.9 Hz, 2H, H^{11}), 7.03 (dd, *J* = 5.2, 3.6 Hz, 1H, H^7), 6.33–6.25 (m, 2H, $H^{2,3}$), 2.36 (s, 3H, H^{13}) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9 (C^{12}), 135.5 (C^9), 131.3 (C^5), 130.5 (C^6), 129.6 (C^{11}), 127.4 (C^{10}), 127.0 (C^7/C^8), 126.9 (C^7/C^8), 124.7 (C^4), 117.6 (C^2/C^3), 113.6 (C^1), 111.6 (C^2/C^3), 21.8 (C^{13}) ppm. HRMS (ESI+) m/z calcd. for ($C_{15}H_{13}NO_2S_2$) $[M+H]^+$ 304.0461, found 304.0463. IR (neat) 2920.3, 2853.6, 1440.3, 998.0 cm^{-1}

2-(Furan-2-yl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole (7e)

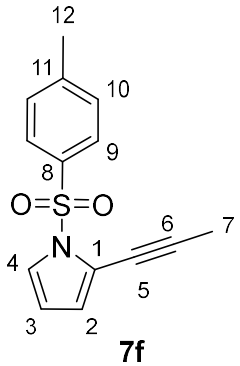


7e

Pale yellow solid, 58%

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.46–7.44 (m, 1H), 7.40–7.39 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.59 (d, *J* = 3.6 Hz, 1H), 6.45–6.42 (m, 2H), 6.32–6.30 (m, 1H), 2.38 (s, 3H) ppm. Data in agreement with those previously reported.[11]

2-(Prop-1-yn-1-yl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole (7f)

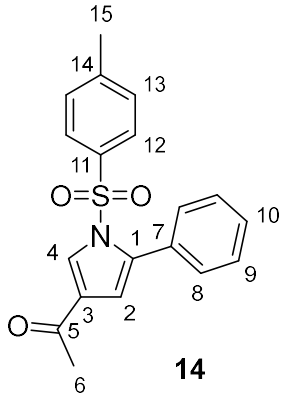


7f

White powder, 65%, m.p. 100-105 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H, H^{9}), 7.34–7.28 (m, 3H, $H^{4,10}$), 6.38 (dd, *J* = 3.6, 1.7 Hz, 1H, H^{2}), 6.17 (app t, *J* = 3.4 Hz, 1H, H^{3}), 2.42 (s, 3H, H^{12}), 2.07 (s, 3H, H^{7}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3 (C^{8}), 135.7 (C^{11}), 129.8 (C^{10}), 127.9 (C^{9}), 122.7 (C^{4}), 120.1 (C^{2}), 116.2 (C^{1}), 111.4 (C^{3}), 91.9 (C^{6}), 70.2 (C^{5}), 21.9 (C^{12}), 4.9 (C^{7}) ppm. HRMS (ESI+) m/z calcd. for ($C_{14}H_{13}NO_2S$) $[M+Na]^+$ 282.0565, found 282.0560. IR (neat) 1292.4, 1177.6, 1053.1, 702.3 cm^{-1}

1-(5-Phenyl-1-(*p*-toluenesulfonyl)-1*H*-pyrrol-3-yl)ethan-1-one (14)

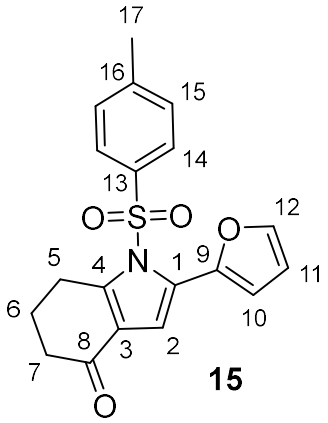


14

White powder, 65%, m.p. 108-111 ºC

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 1.9 Hz, 1H, H^4), 7.42–7.34 (m, 1H, H^{10}), 7.31-7.26 (m, 2H, H^9), 7.20 (d, *J* = 8.5 Hz, 2H, H^{12}), 7.18–7.14 (m, 2H, H^8), 7.10 (d, *J* = 8.2 Hz, 2H, H^{13}), 6.53 (d, *J* = 2.0 Hz, 1H, H^2), 2.47 (s, 3H, H^6), 2.37 (s, 3H, H^{15}) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.2 (C^5), 145.7 (C^{14}), 136.8 (C^1), 134.8 (C^{11}), 131.3 (C^8), 130.4 (C^7), 129.8 (C^{13}), 129.0 (C^{10}), 127.8 (C^9/C^{12}), 127.7 (C^9/C^{12}), 127.6 (C^4), 127.1 (C^3), 113.7 (C^2), 27.3 (C^6), 21.8 (C^{15}) ppm. HRMS (ESI+) m/z calcd. for ($C_{19}H_{17}NO_3S$) $[M+H]^+$ 340.1002, found 340.1000. IR (neat) 2925.3, 1704.5, 1449.4, 1326.6, 1011.5, 837.8 cm^{-1}.

2-(Furan-2-yl)-1-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-4H-indol-4-one (15)

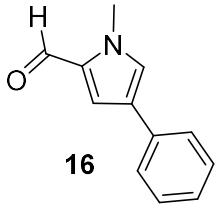


15

Beige powder, 66%, m.p. 177-180 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H, H^{14}), 7.63 (s, 1H, H^2), 7.40 (dd, *J* = 3.4, 0.8 Hz, 1H, H^{10}), 7.38-7.33 (m, 3H, $H^{15,12}$), 6.43 (dd, *J* = 3.4, 1.8 Hz, 1H, H^{11}), 3.01 (t, *J* = 6.2 Hz, 2H, H^5), 2.50-2.45 (m, 2H, H^7), 2.44 (s, 3H, H^{17}), 2.09 (tt, *J* = 7.8, 6.4 Hz, 2H, H^6) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0 (C^8), 147.6 (C^9), 146.2 (C^{16}), 144.7 (C^4), 141.4 (C^{12}), 135.2 (C^{13}), 130.6 (C^{15}), 127.4 (C^{14}), 120.6 (C^3), 118.6 (C^2), 116.8 (C^1), 111.7 (C^{11}), 110.8 (C^{10}), 38.7 (C^7), 23.4 (C^5), 23.0 (C^6), 21.9 (C^{17}) ppm. HRMS (ESI+) m/z calcd. for ($C_{19}H_{17}NO_4S$) $[M+H]^+$ 356.0951; found 356.0958. IR (neat) 2922.9, 1671.4, 14336, 1258.8, 821.1 cm^{-1}.

1-Methyl-4-phenyl-1*H*-pyrrole-2-carbaldehyde (16)

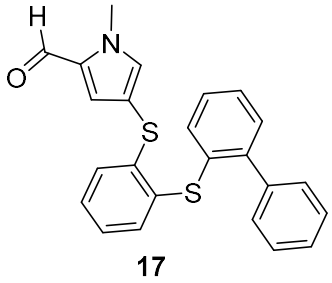


16

White powder, 30% conv.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 7.51–7.47 (m, 2H), 7.47 (dd, *J* = 7.7, 7.7 Hz, 2H), 7.34–7.29 (m, 1H), 7.27–7.25 (m, 2H), 4.08 (s, 3H) ppm. **16** clearly identifiable in crude ^{1}H-NMR spectrum, but only trace amounts of pure product isolated from column (most **16** co-eluted with **17**). Data in agreement with those previously reported.[12]

4-((2-([1,1'-Biphenyl]-2-ylthio)phenyl)thio)-1-methyl-1*H*-pyrrole-2-carbaldehyde (17)

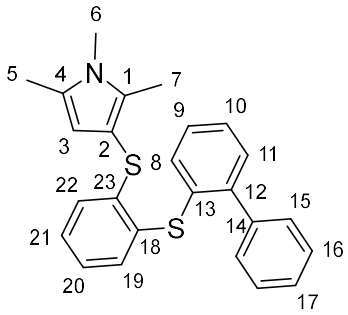


17

White powder, 30% conv, m.p. 97-101 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.55 (s, 1H), 7.53–7.46 (m, 2H), 7.45–7.34 (m, 3H), 7.33–7.27 (m, 2H), 7.25–7.20 (m, 2H), 7.19–7.10 (m, 1H), 7.08–7.00 (m, 2H), 6.97 (s, 2H), 6.92 (dd, *J* = 8.0, 1.4 Hz, 1H), 3.96 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 179.7, 143.5, 142.5, 140.6, 137.1, 134.7, 134.6, 133.2, 131.7, 130.7, 129.8, 129.5, 129.4, 128.7, 128.20, 128.17, 127.7, 127.1, 126.5, 126.0, 110.9, 37.0 ppm. HRMS (ESI$^+$): calc. $C_{24}H_{19}NOS_2^+$ $[M+Na]^+$ 424.0806, found 424.0819. IR (neat) 2961.3, 1666.4, 1289.5, 705.7 cm^{-1}. Only trace amounts of pure product isolated from column (most **17** co-eluted with **16**).

3-((2-([1,1'-Biphenyl]-2-ylthio)phenyl)thio)-1,2,5-trimethyl-1*H*-pyrrole (18)

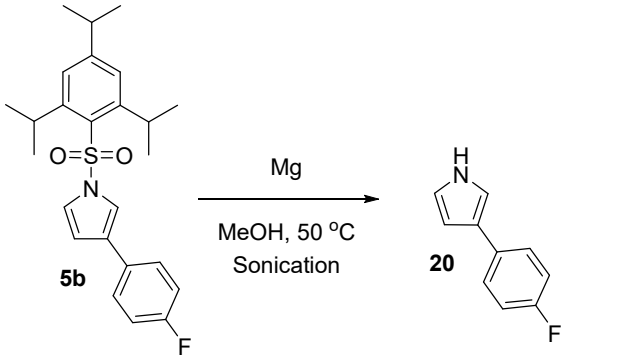


18

White powder, 78% NMR conv

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 6.9 Hz, 2H, H^{15}), 7.43 (app t, *J* = 7.5 Hz, 2H, H^{16}), 7.37 (t, *J* = 7.3 Hz, 1H, H^{17}), 7.29–7.16 (m, 4H, $H^{8\text{-}11}$), 7.10 (app td, *J* = 7.6, 1.4 Hz, 1H, H^{21}), 7.00 (dd, *J* = 7.5, 1.6 Hz, 1H, H^{19}), 6.96 (ddd, *J* = 7.5, 7.5, 1.4 Hz, 1H, H^{20}), 6.77 (dd, *J* = 8.0, 1.4 Hz, 1H, H^{22}), 5.88 (s, 1H, H^{3}), 3.44 (s, 3H, H^{6}), 2.22 (s, 3H, H^{5}), 2.12 (s, 3H, H^{7}) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6 (C^{18}), 141.6 (C^{13}), 140.8 (C^{14}), 135.5 (C^{12}), 135.2 (C^{8} or C^{11}), 134.0 (C^{1}), 130.5 (C^{8} or C^{11}), 129.6 (C^{15}), 129.4 (C^{23}), 128.74 (C^{21}), 128.70 (C^{4}), 128.6 (C^{19}), 128.2 (C^{16}), 128.0 (C^{9} or C^{10}), 127.6 (C^{17}), 125.9 (C^{9} or C^{10}), 125.7 (C^{22}), 124.7 (C^{20}), 111.5 (C^{3}), 102.9 (C^{2}), 31.2 (C^{6}), 12.6 (C^{5}), 10.6 (C^{7}) ppm. HRMS (ESI+) m/z calcd. for ($C_{25}H_{23}NS_2$) $[M+Na]^+$ 424.1170, found 424.1164. Only trace amounts of pure product isolated from column, melting point and IR data not obtained.

Deprotection of 3-(4-Fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole

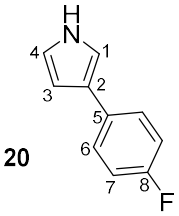


73% NMR conversion
unstable to purification

Procedure:

3-(4-Fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5b** (0.176 mmol, 75 mg) was added to magnesium metal (3.52 mmol, 61 mg) in dry methanol (2.2 ml). The flask was then sonicated for 5 hours at 50 °C. The reaction mixture was poured onto 1M HCl (aq) then neutralised with 1M $NaHCO_3$ (aq) and extracted with CH_2Cl_2 (x3). The mixture was then dried over $MgSO_4$ and filtered, then the filtrate was concentrated *in vacuo*. Trimethoxybenzene internal standard (0.059 mmol) was added, from a stock solution to the crude mixture. A conversion of 73% to desired product was determined by integration of the ^{1}H-NMR spectrum. Attempted further purification by chromatography on silica led to decomposition of the product.

3-(4-Fluorophenyl)-1*H*-pyrrole 20



20

Crude brown solid, 73% NMR conv

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (br s, 1H, N-H), 7.48 (dd, *J* = 8.5, 5.5 Hz, 2H, H^6), 7.06-6.98 (m, 3H, H^1, H^7), 6.84-6.81 (m, 1H, H^4), 6.52-6.46 (m, 1H, H^3) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4 (d, $^1J_{CF}$ = 243.4 Hz, C^8), 132.1 (C^5), 126.8 (d, $^3J_{CF}$ = 7.8 Hz, C^6), 124.3 (C^2), 119.1 (C^4), 115.5 (d, $^2J_{CF}$ = 21.3 Hz, C^7), 114.4 (C^1), 106.7 (C^3) ppm. HRMS (ESI+) m/z calcd. for ($C_{10}H_7FN$) $[M-H]^-$ 160.0568; found 160.0563.

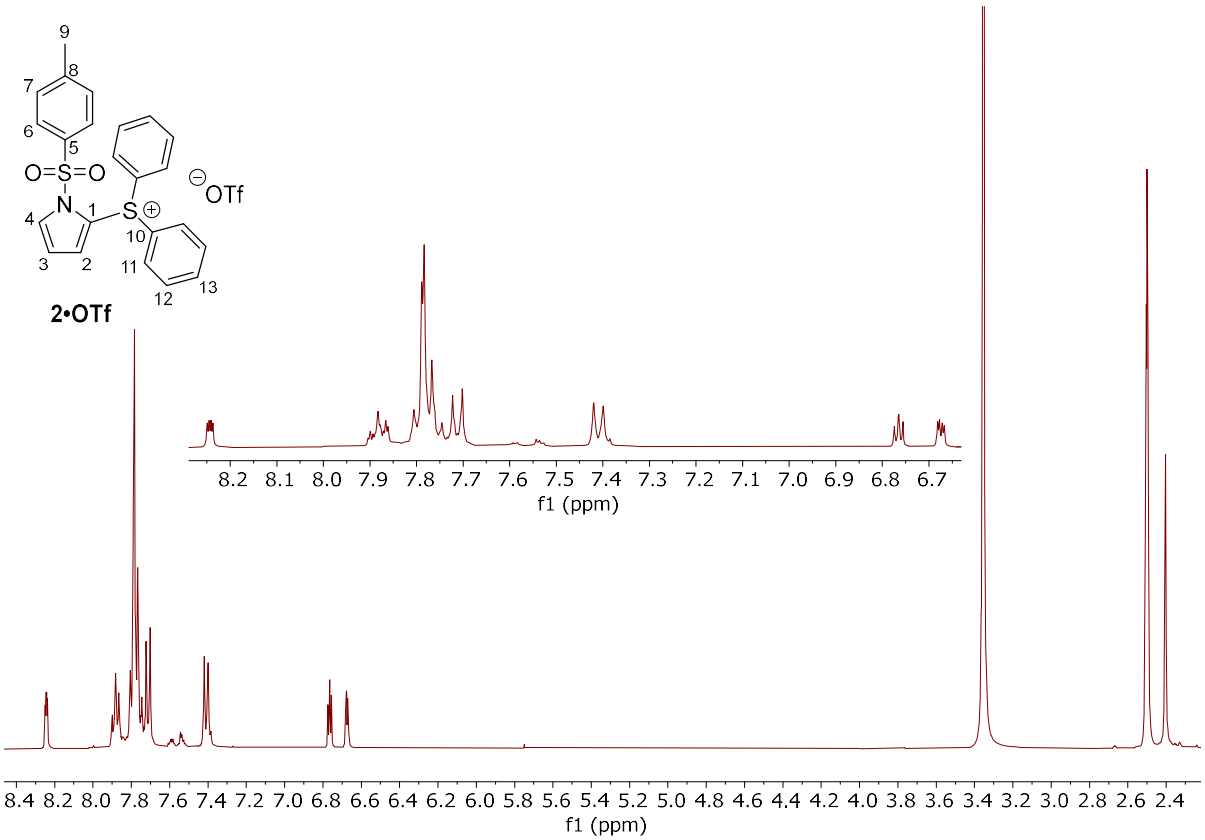


*Figure S1: [1]H-NMR spectrum of Diphenyl(1-(p-toluenesulfonyl)-1H-pyrrol-2-yl)sulfonium trifluoromethanesulfonate **2•OTf** in DMSO-d_6*

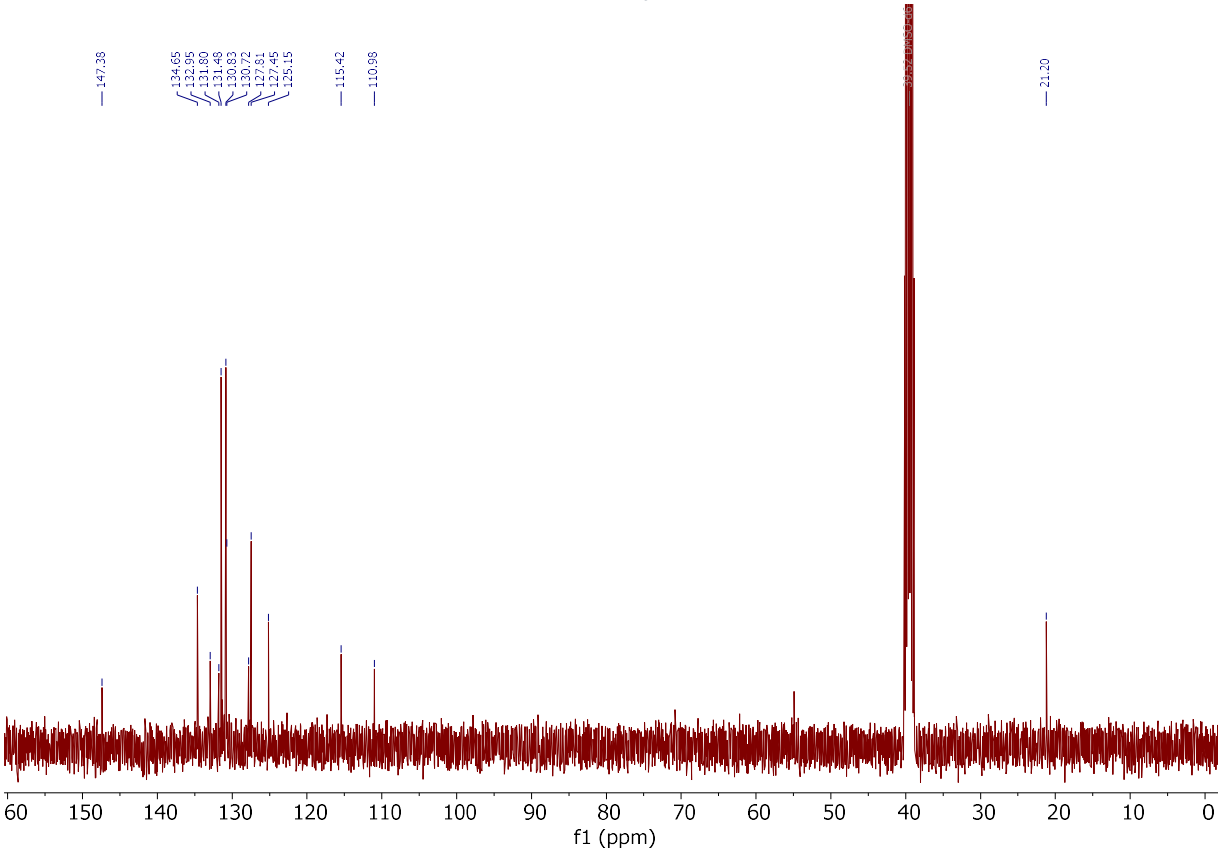


*Figure S2: [13]C NMR spectrum of Diphenyl(1-(p-toluenesulfonyl)-1H-pyrrol-2-yl)sulfonium trifluoromethanesulfonate **2•OTf** in DMSO-d_6*

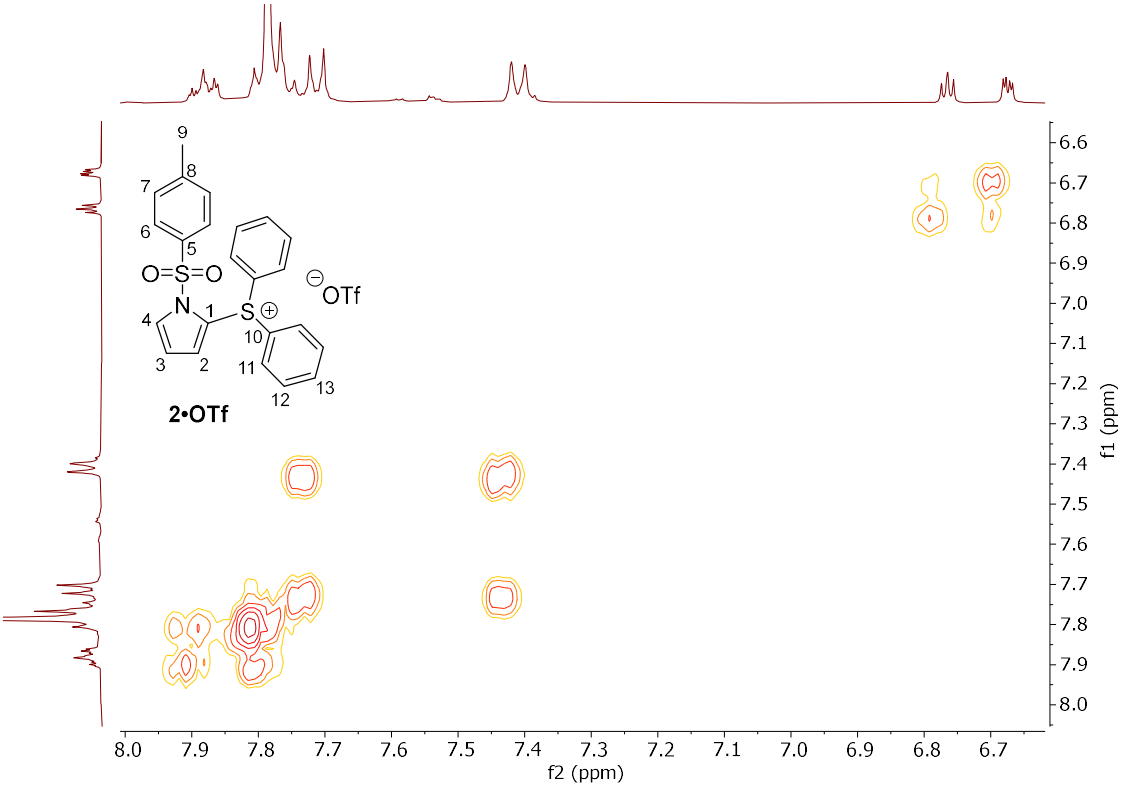


Figure S3: COSY NMR spectrum of Diphenyl(1-(p-toluenesulfonyl)-1H-pyrrol-2-yl)sulfonium trifluoromethanesulfonate ***2•OTf*** *in DMSO-d_6*

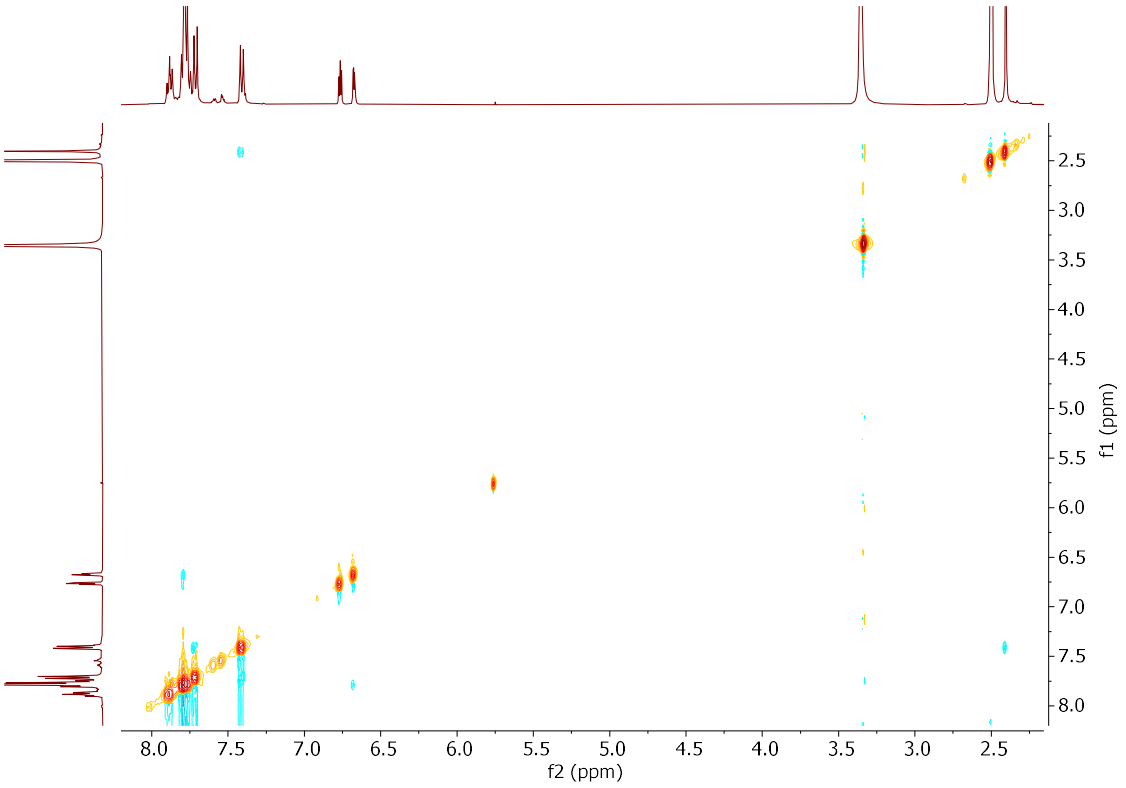


Figure S4: NOESY NMR spectrum of Diphenyl(1-(p-toluenesulfonyl)-1H-pyrrol-2-yl)sulfonium trifluoromethanesulfonate ***2•OTf*** *in DMSO-d_6*

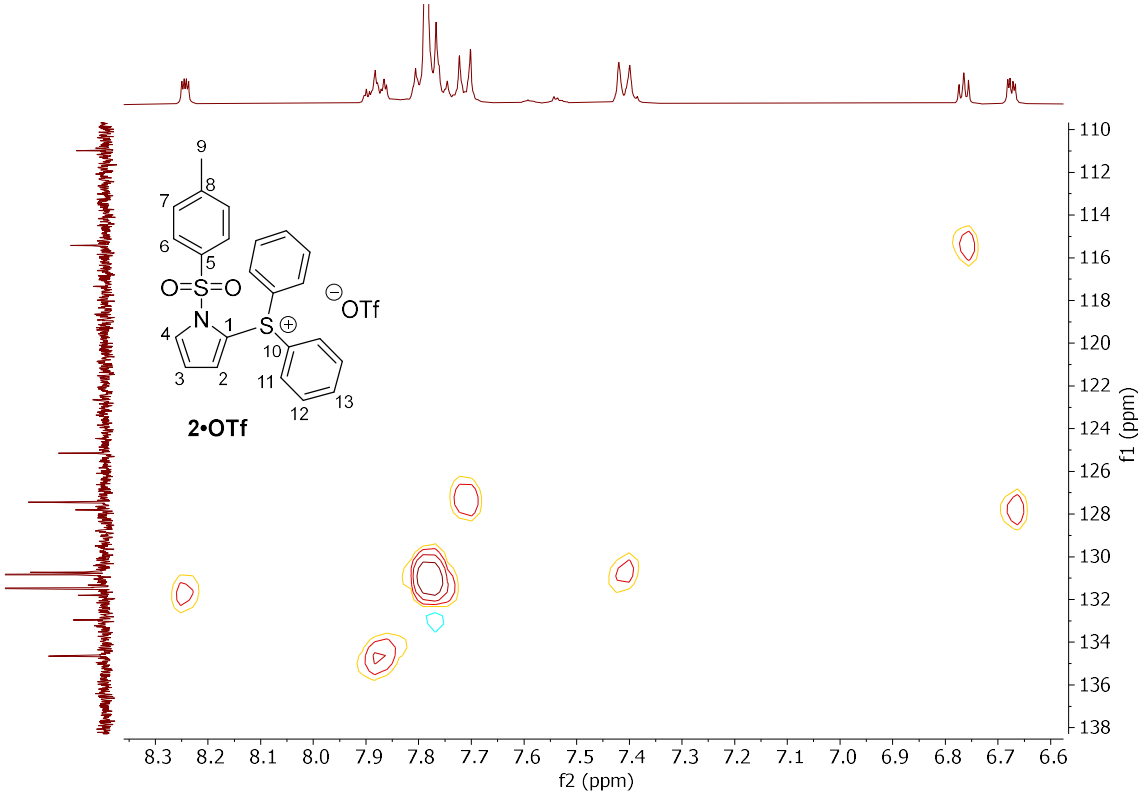


Figure S5: HSQC NMR spectrum of Diphenyl(1-(p-toluenesulfonyl)-1H-pyrrol-2-yl)sulfonium trifluoromethanesulfonate ***2•OTf*** *in DMSO-d_6*

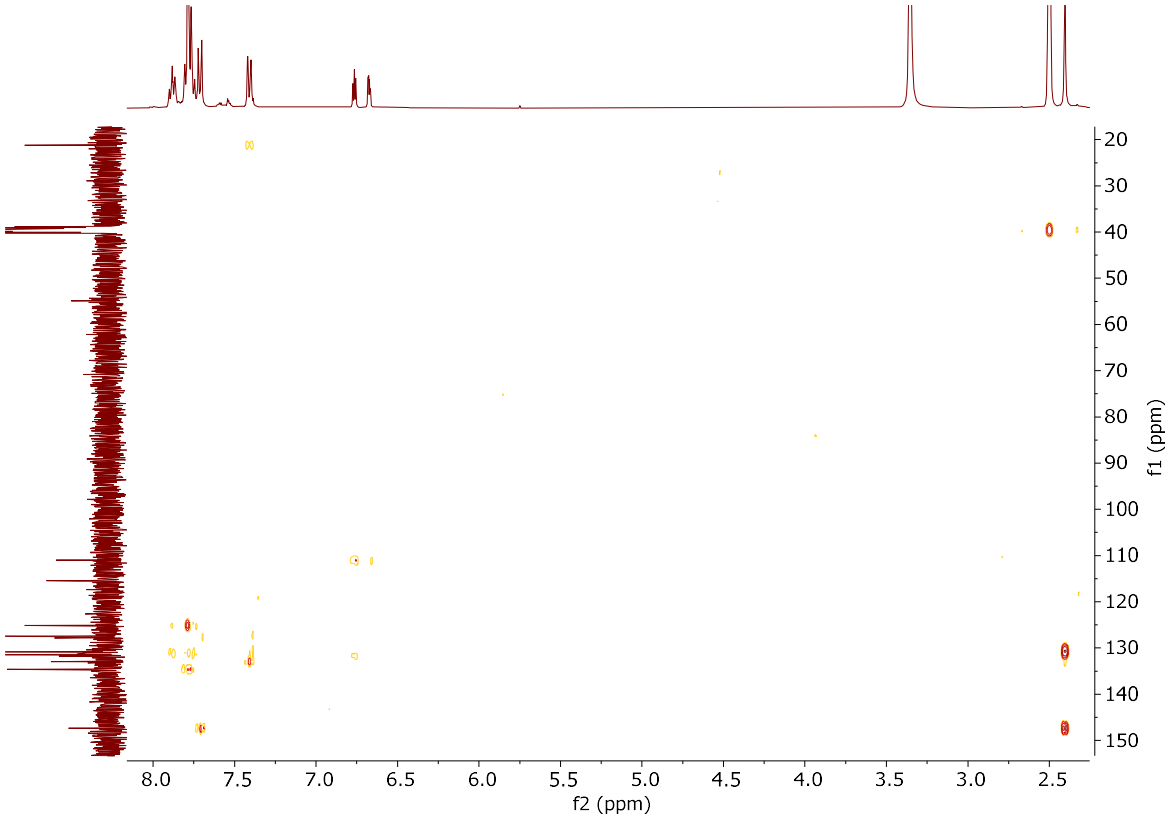


Figure S6: HMBC NMR spectrum of Diphenyl(1-(p-toluenesulfonyl)-1H-pyrrol-2-yl)sulfonium trifluoromethanesulfonate ***2•OTf*** *in DMSO-d_6*

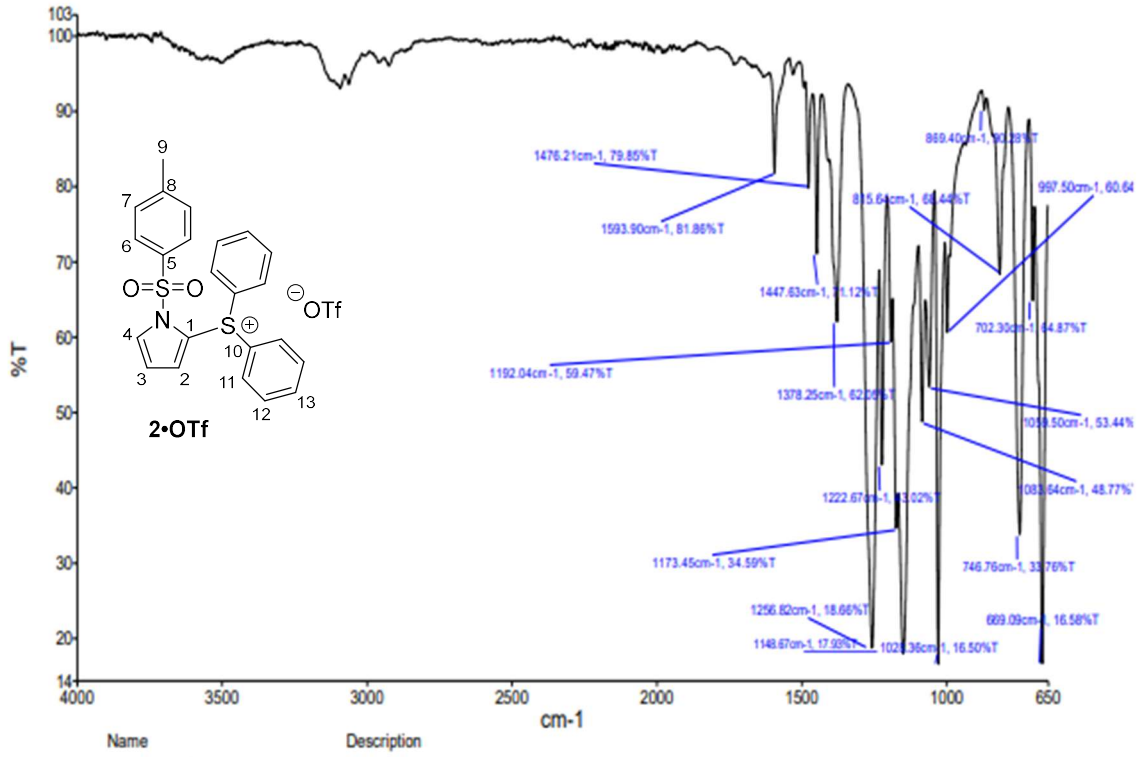


*Figure S7: IR spectrum of Diphenyl(1-(*p*-toluenesulfonyl)-1*H*-pyrrol-2-yl)sulfonium trifluoromethanesulfonate* ***2•OTf***

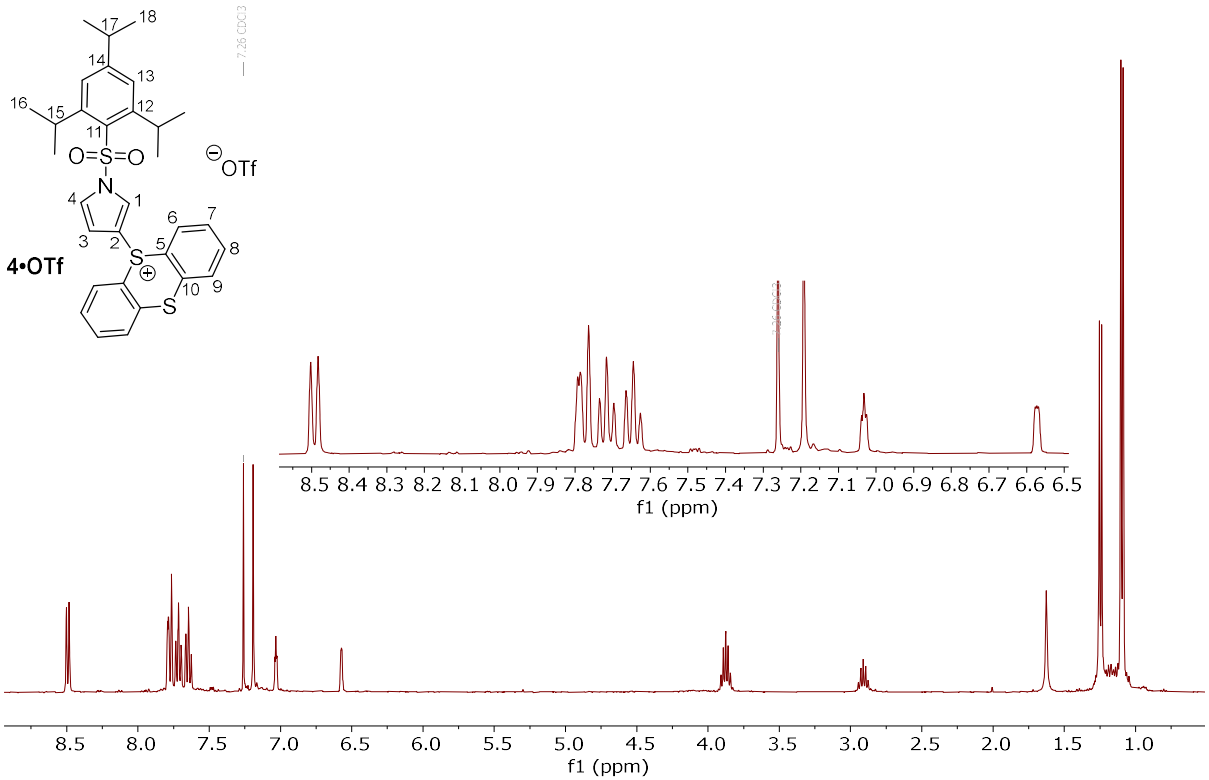


*Fig S8: ^{1}H NMR spectrum of 5-(1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrol-3-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate **4•OTf** in $CDCl_3$*

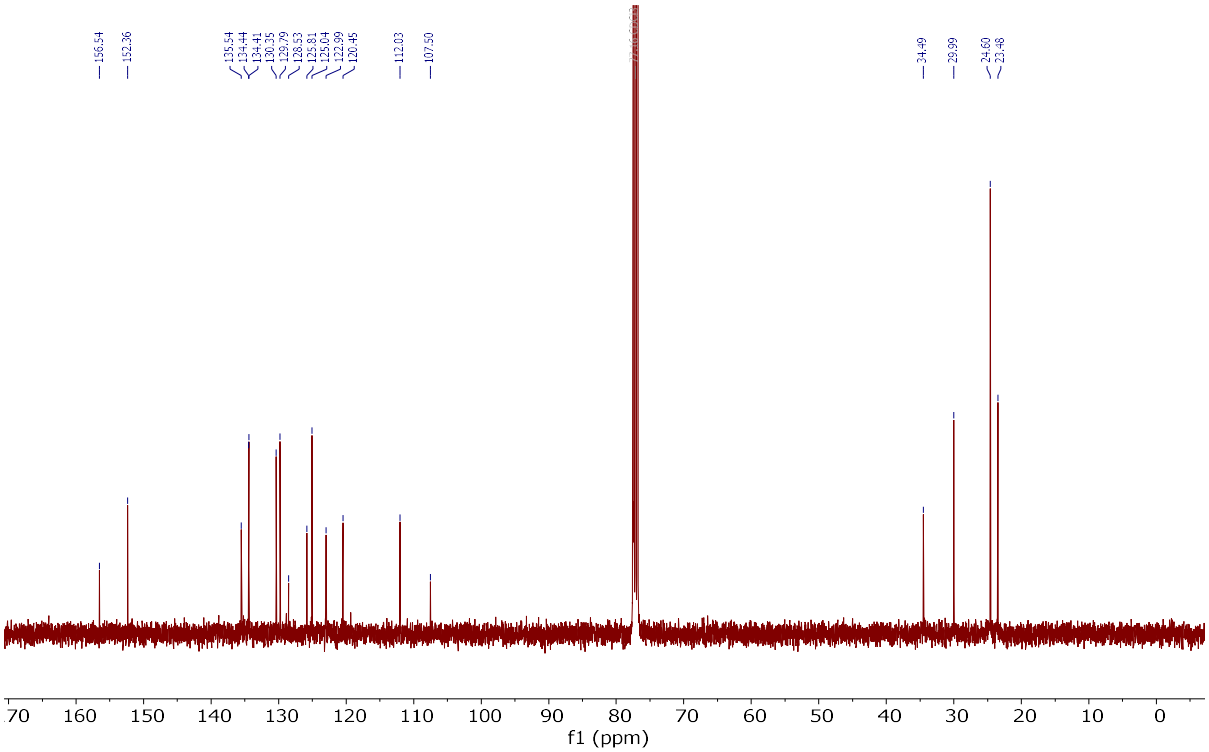


*Fig S9: ^{13}C NMR spectrum of 5-(1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrol-3-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate **4•OTf** in $CDCl_3$*

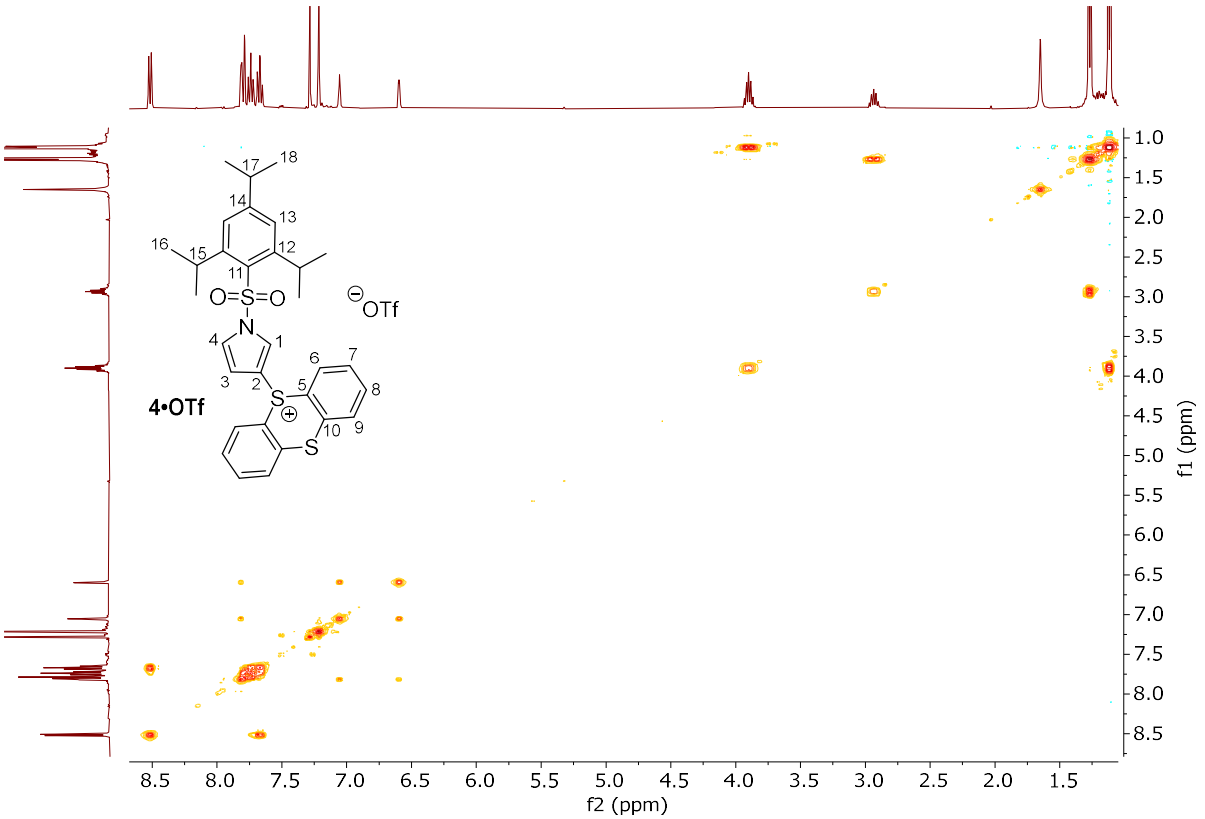


*Fig S10: COSY NMR spectrum of 5-(1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrol-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate **4•OTf** in $CDCl_3$*

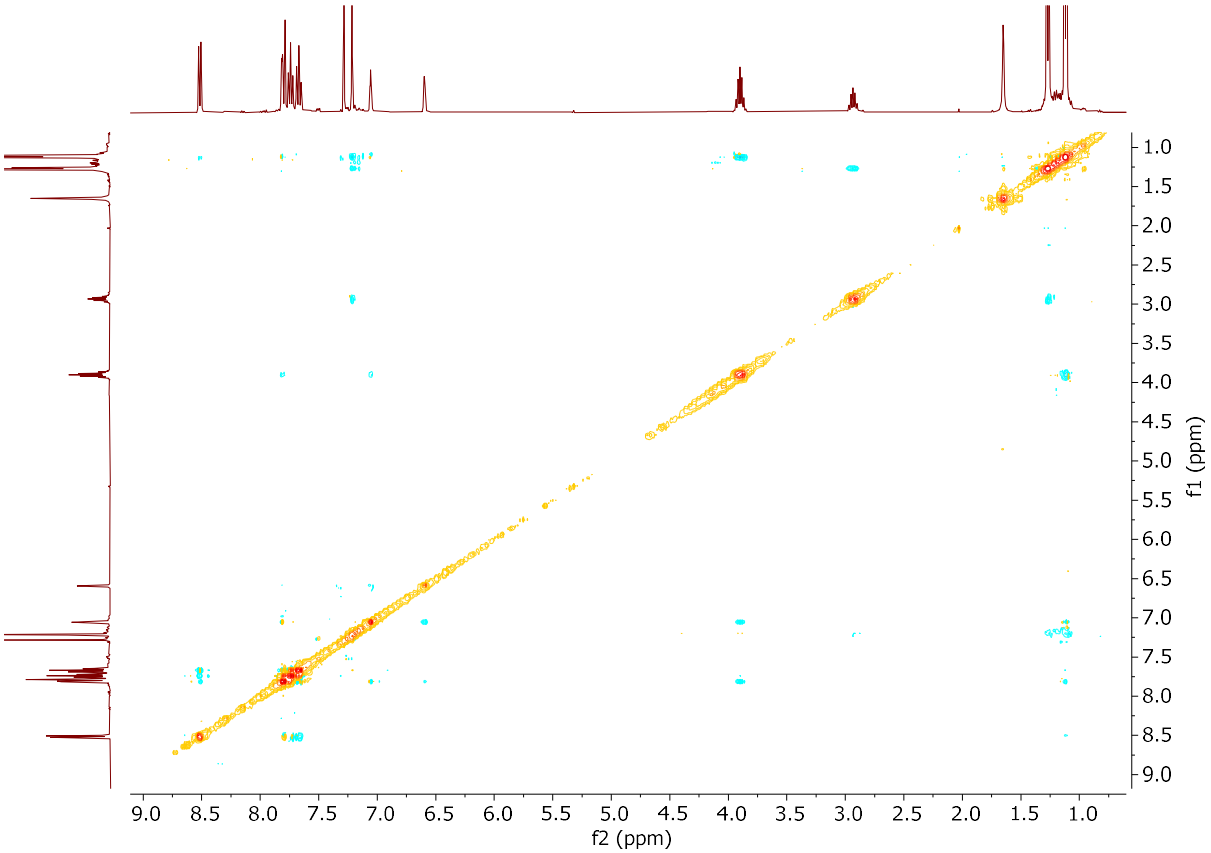


*Fig S11: NOESY NMR spectrum of 5-(1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrol-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate **4•OTf** in $CDCl_3$*

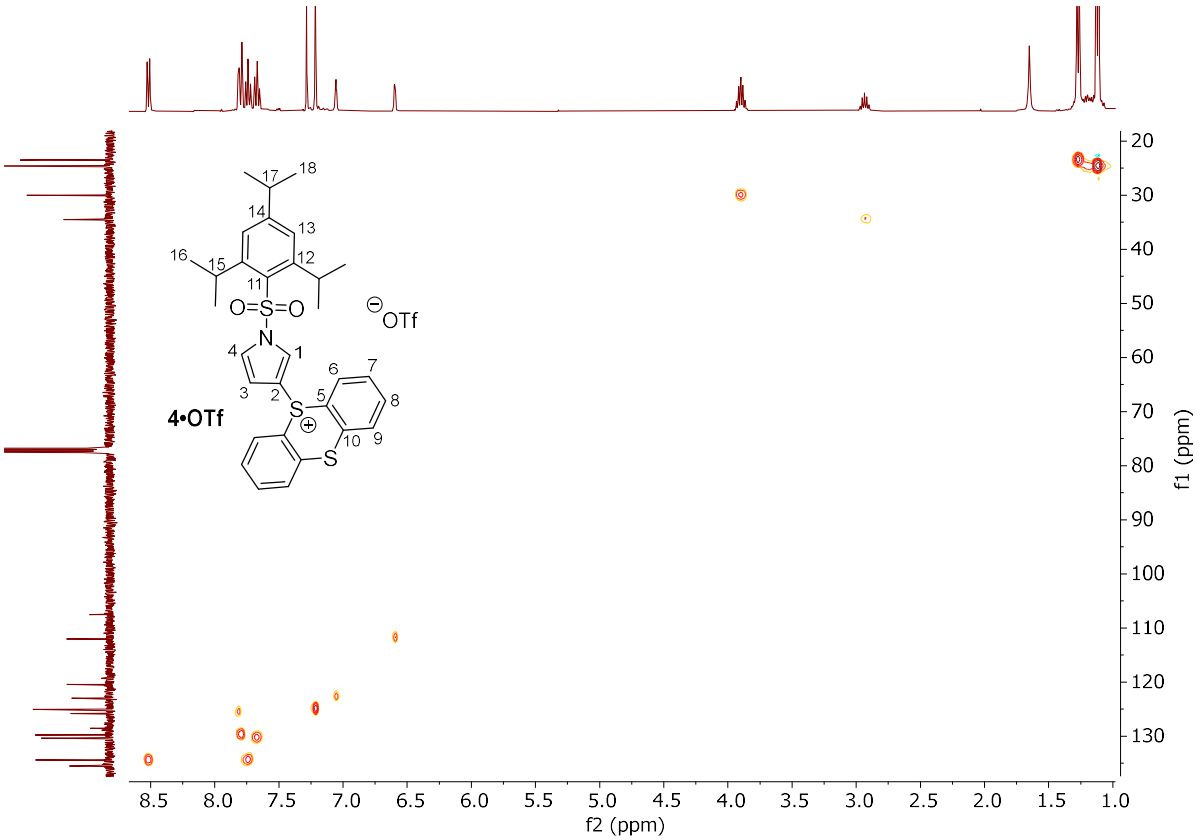


*Fig S12: HSQC NMR spectrum of 5-(1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrol-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate **4•OTf** in $CDCl_3$*

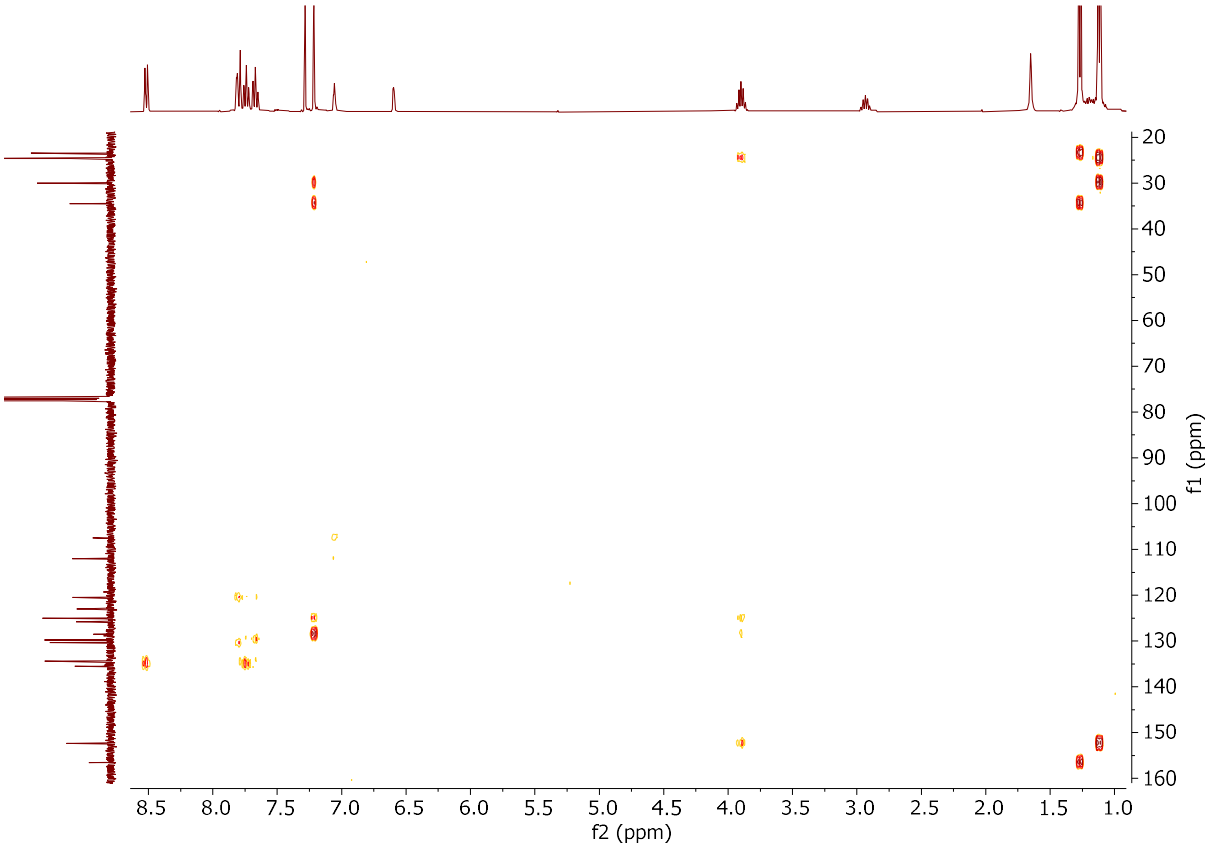


*Fig S13: HMBC NMR spectrum of 5-(1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrol-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate **4•OTf** in $CDCl_3$*

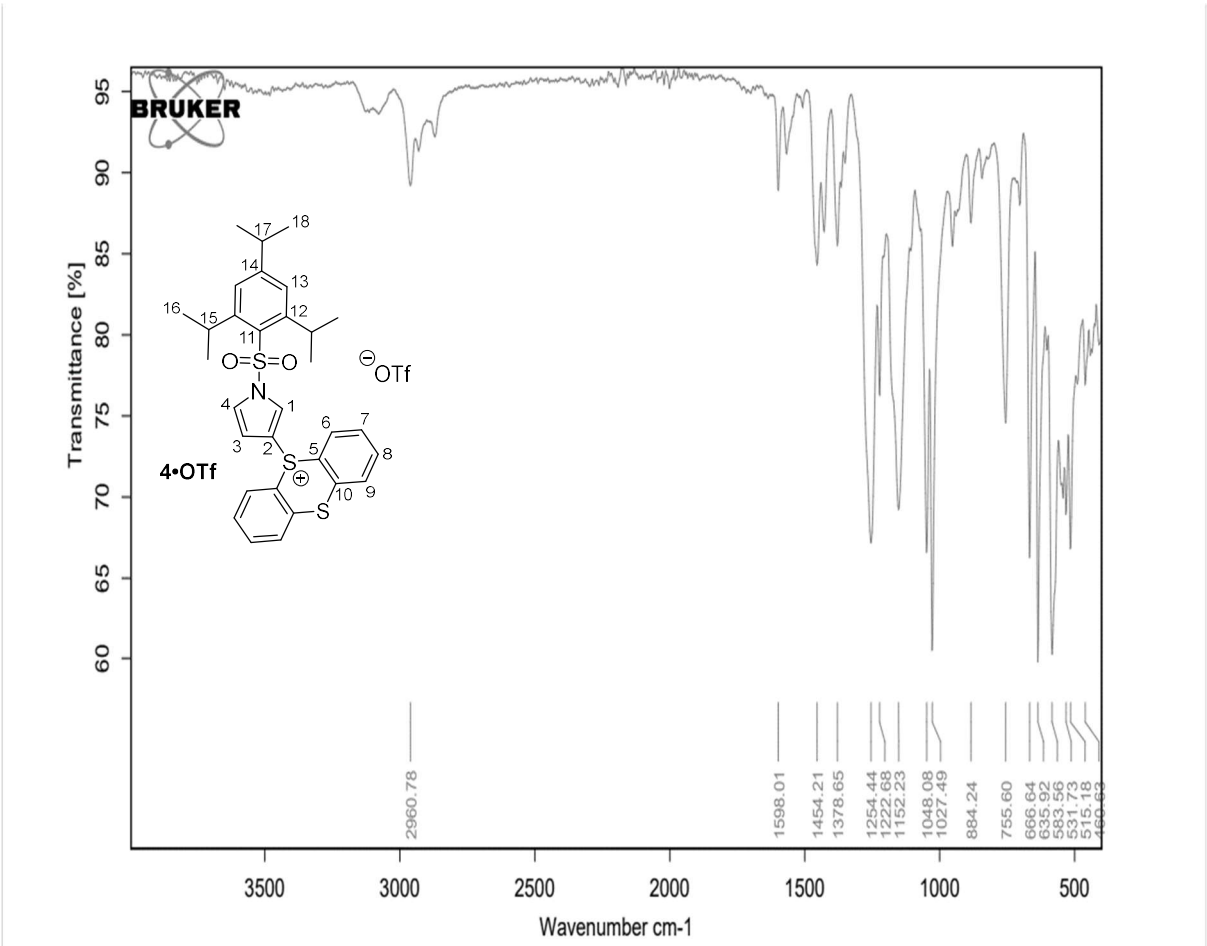


*Fig S14: IR spectrum of 5-(1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrol-3-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate* ***4•OTf****.*

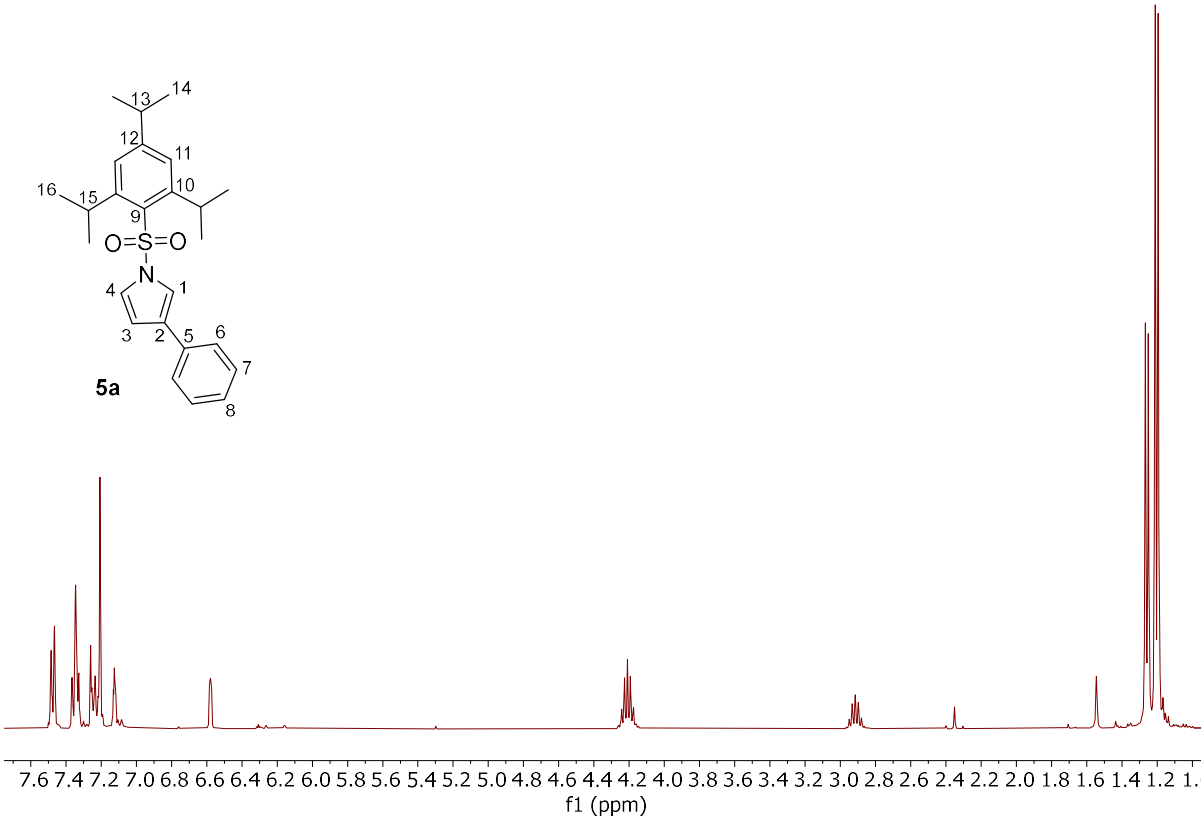


*Figure S15: [1]H NMR spectrum of 3-phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5a** in $CDCl_3$*

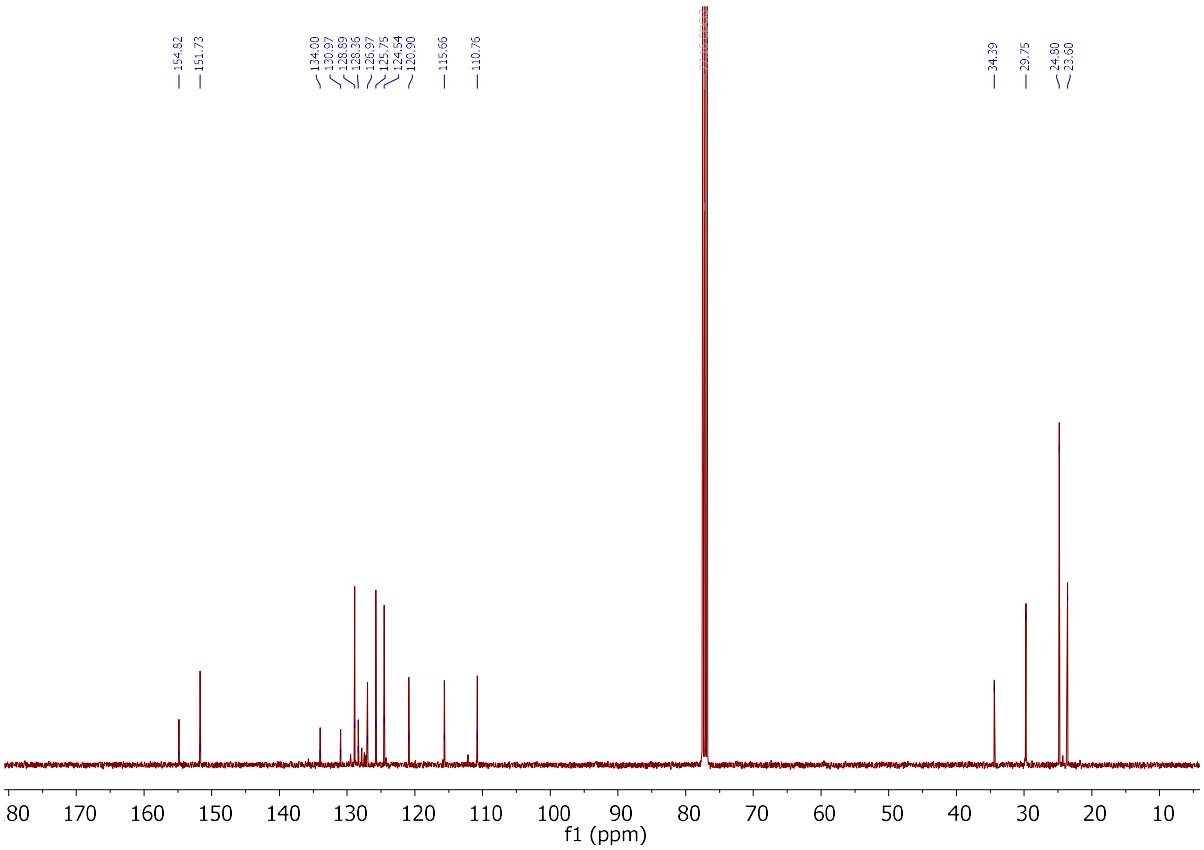


*Figure S16: [13]C NMR spectrum of 3-phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5a** in $CDCl_3$*

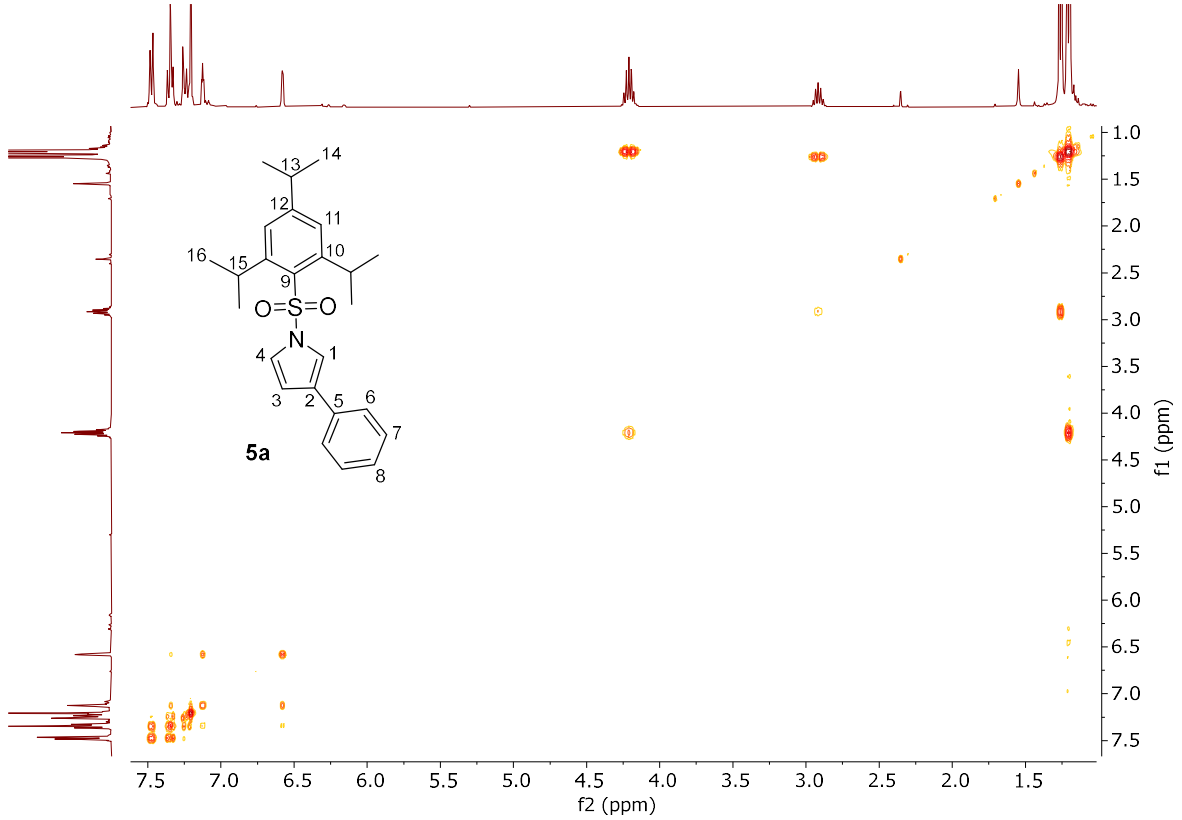


*Figure S17: COSY NMR spectrum of 3-phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5a** in $CDCl_3$*

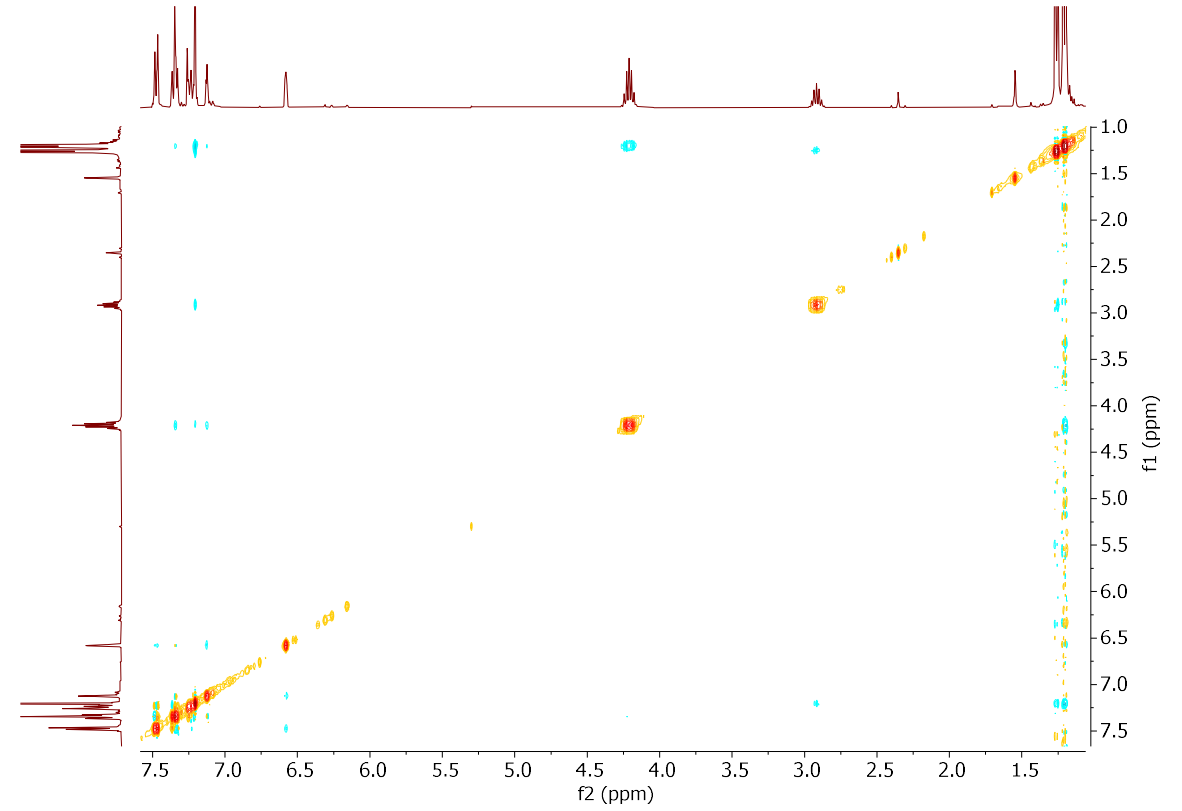


*Figure S18: NOESY NMR spectrum of 3-phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5a** in $CDCl_3$*

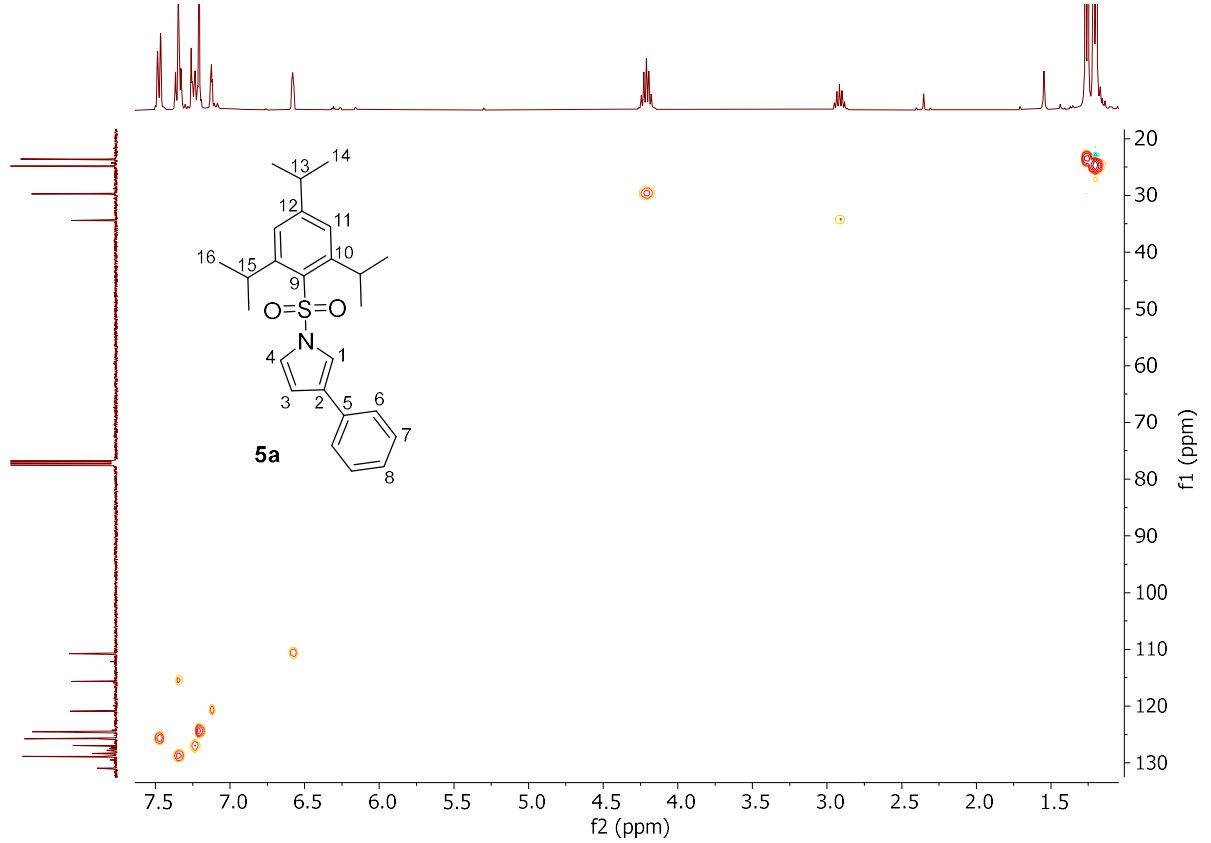


*Figure S19: HSQC NMR spectrum of 3-phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5a** in $CDCl_3$*

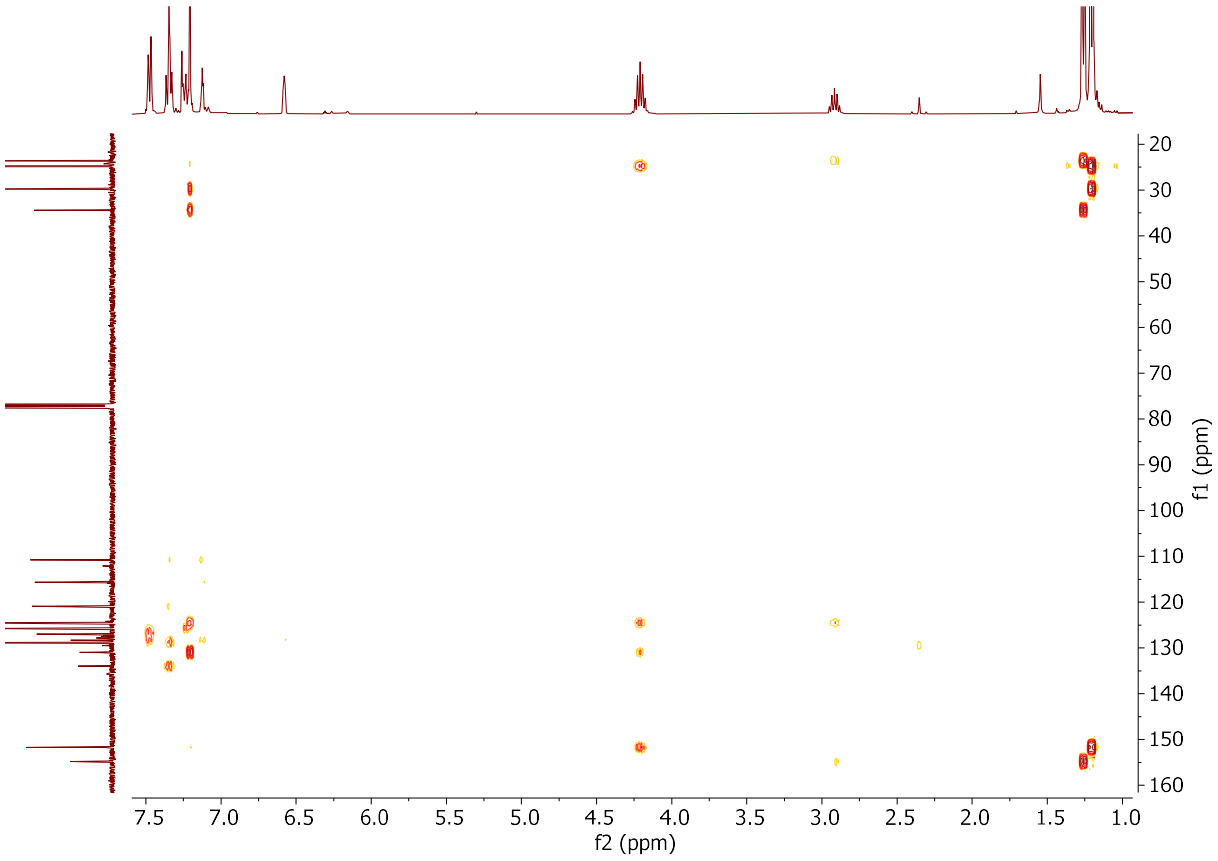


*Figure S20: HMBC NMR NMR spectrum of 3-phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5a** in $CDCl_3$.*

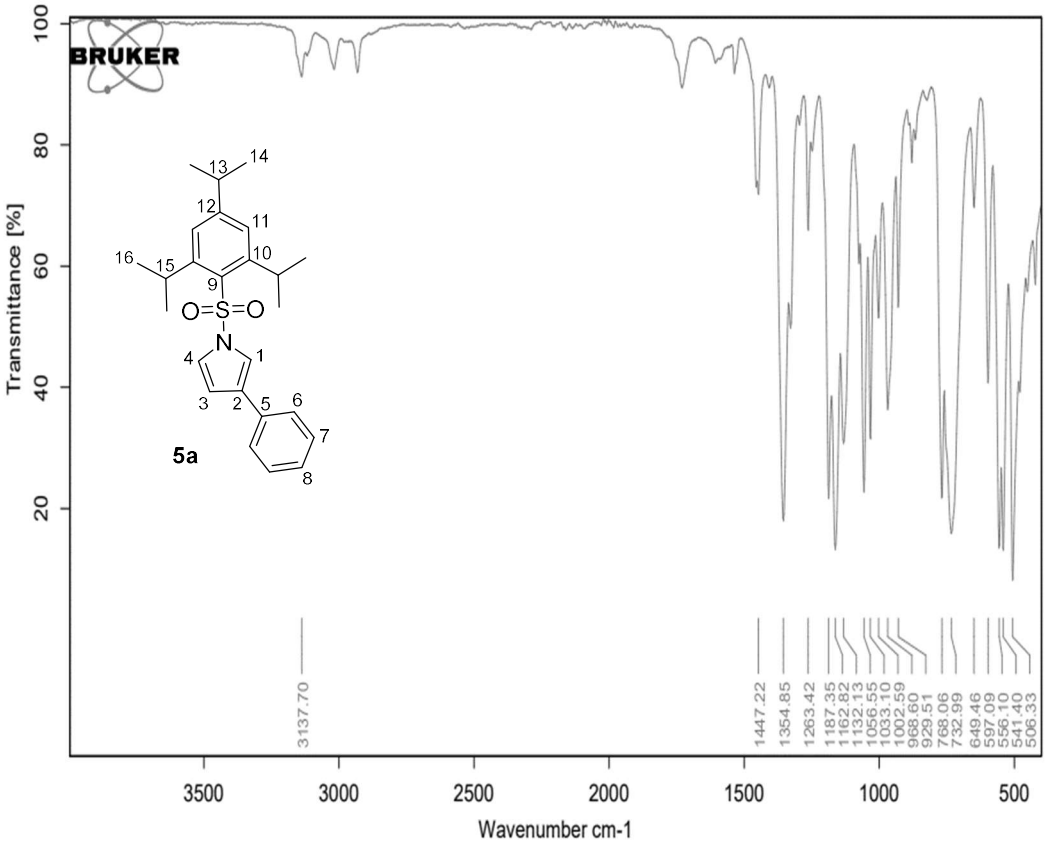


*Figure S21: IR spectrum of 3-phenyl-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5a***

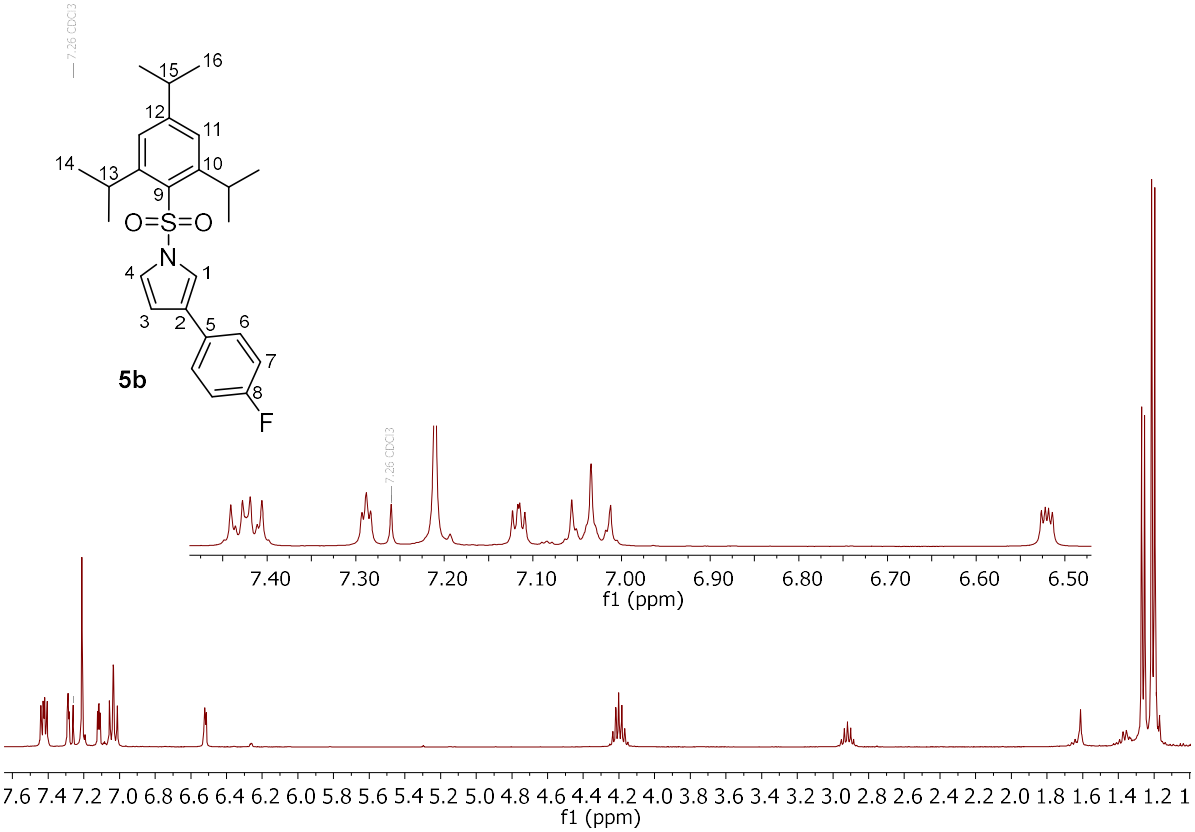


*Figure S22: [1]H NMR spectrum of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5b** in $CDCl_3$*

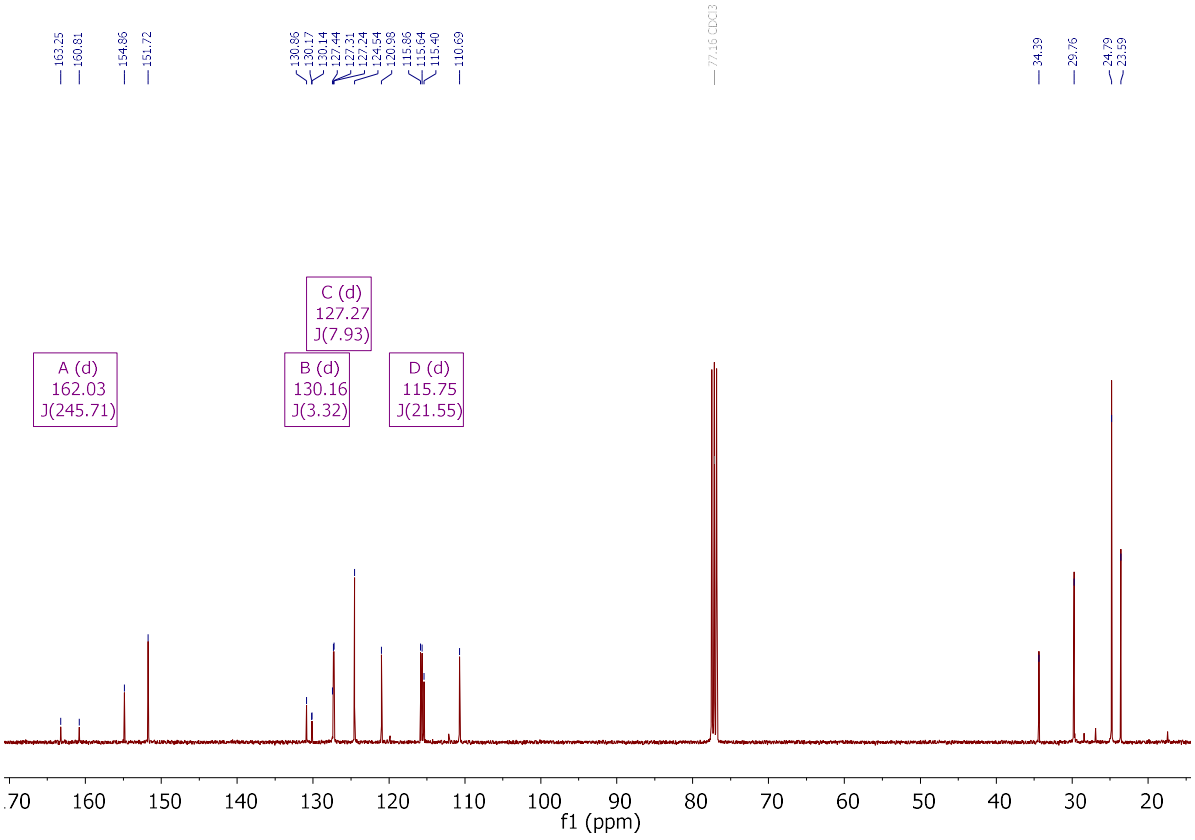


*Figure S23: [13]C NMR spectrum of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5b** in $CDCl_3$*

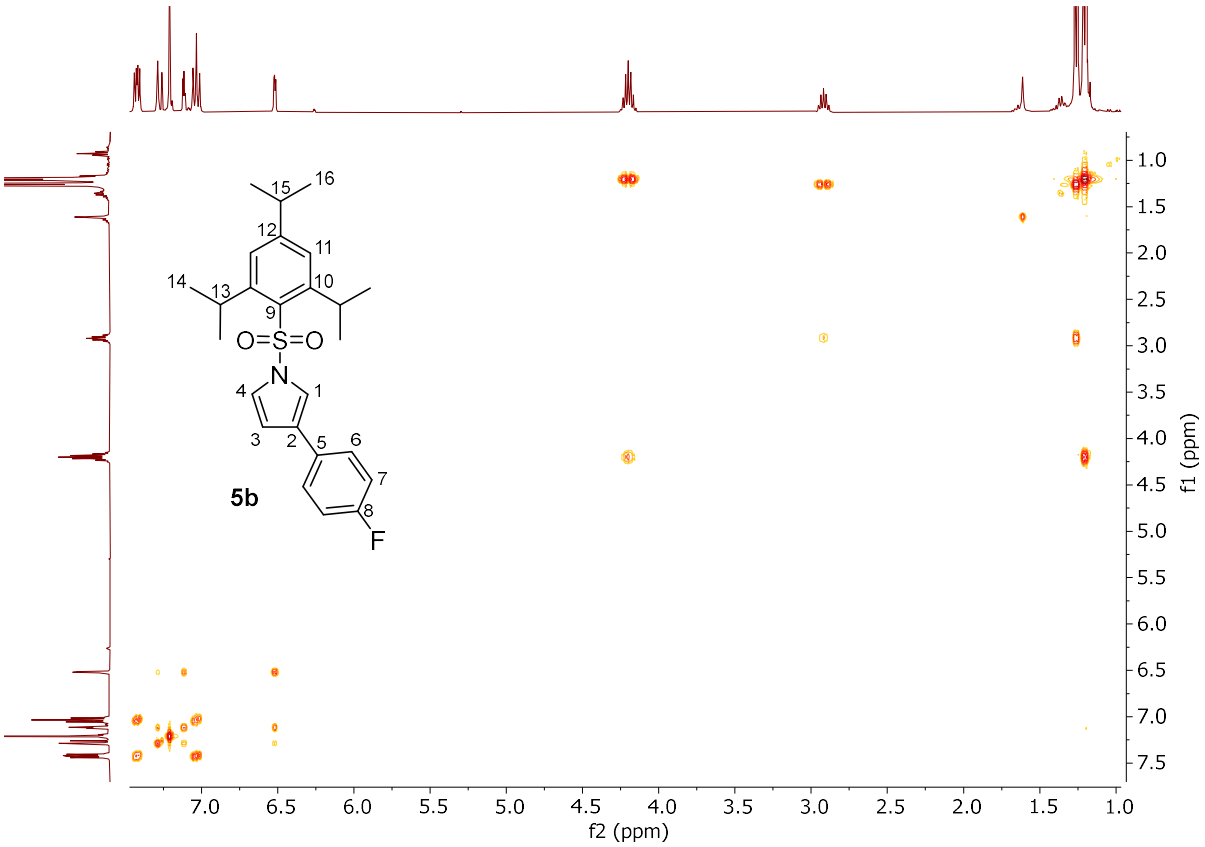


*Figure S24: COSY NMR spectrum of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5b** in $CDCl_3$*

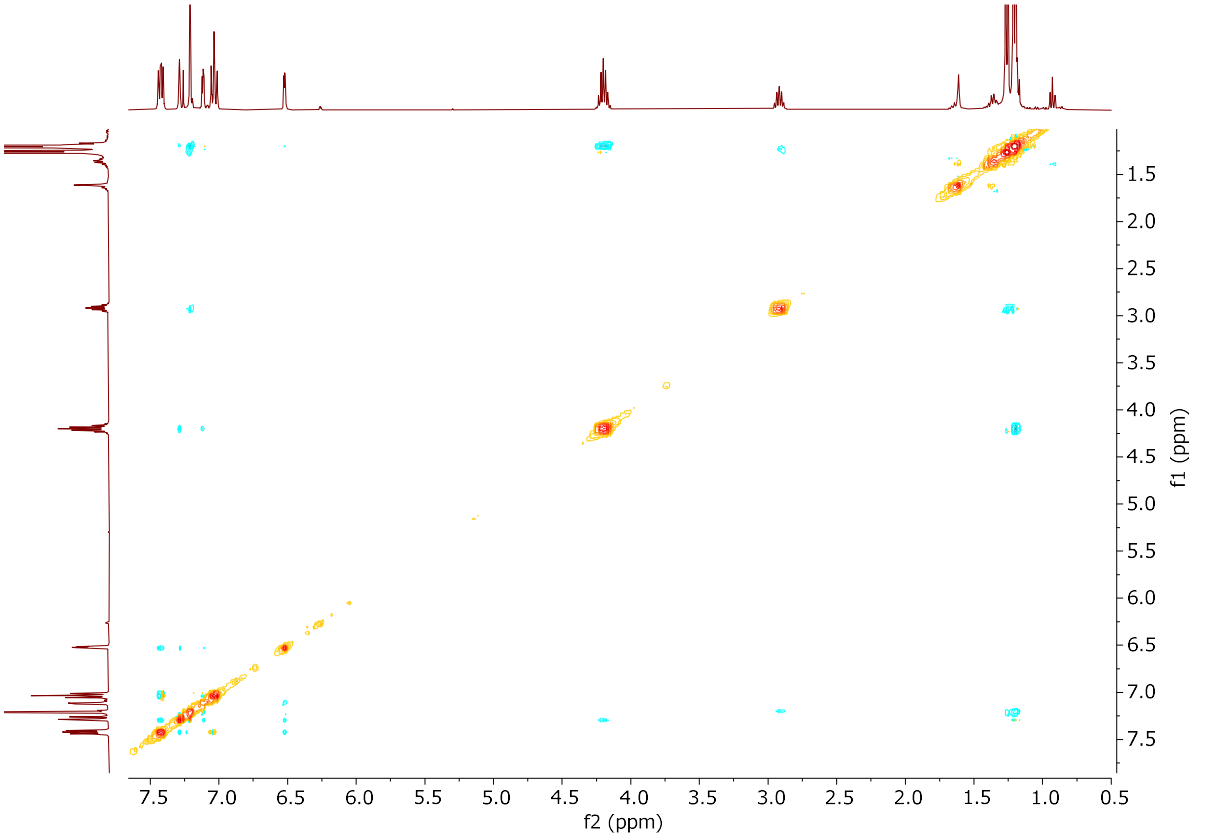


*Figure S25: NOESY NMR spectrum of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5b** in $CDCl_3$*

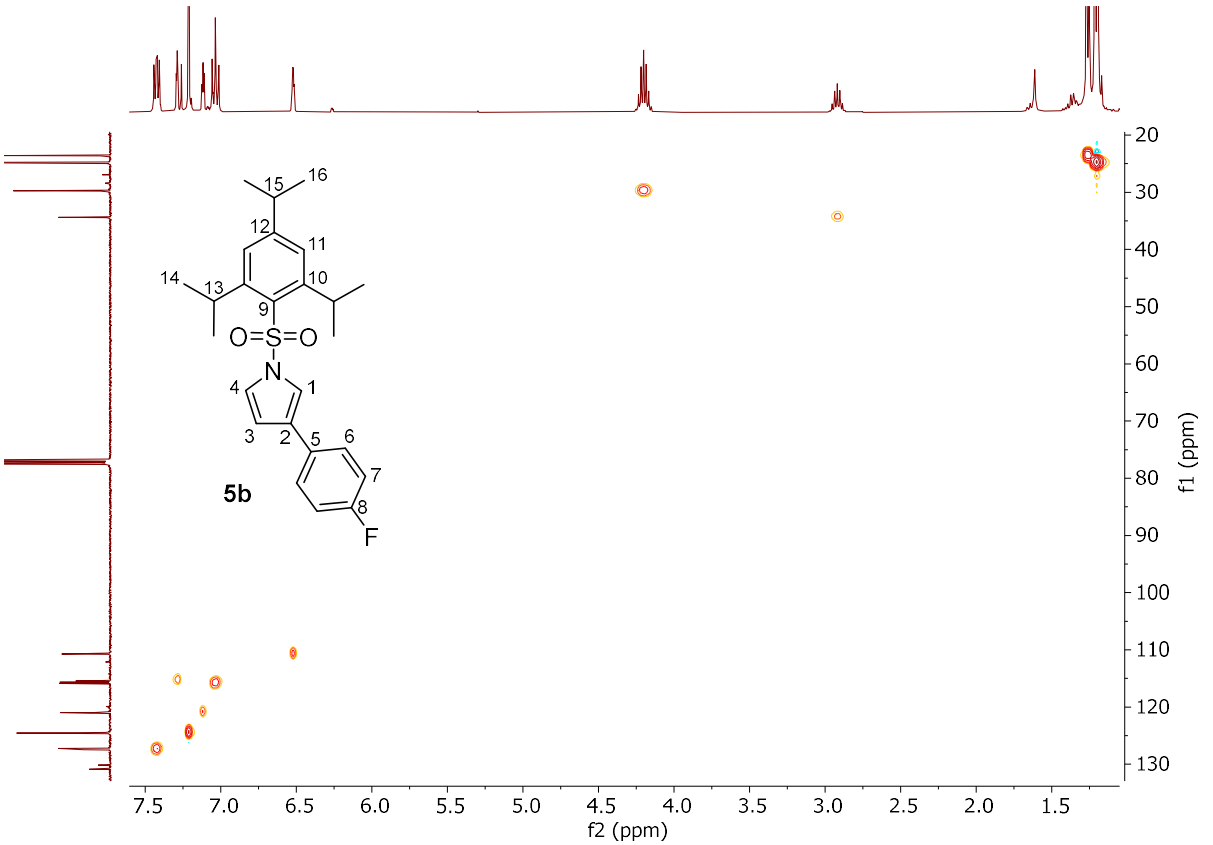


*Figure S26: HSQC NMR spectrum of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5b** in $CDCl_3$*

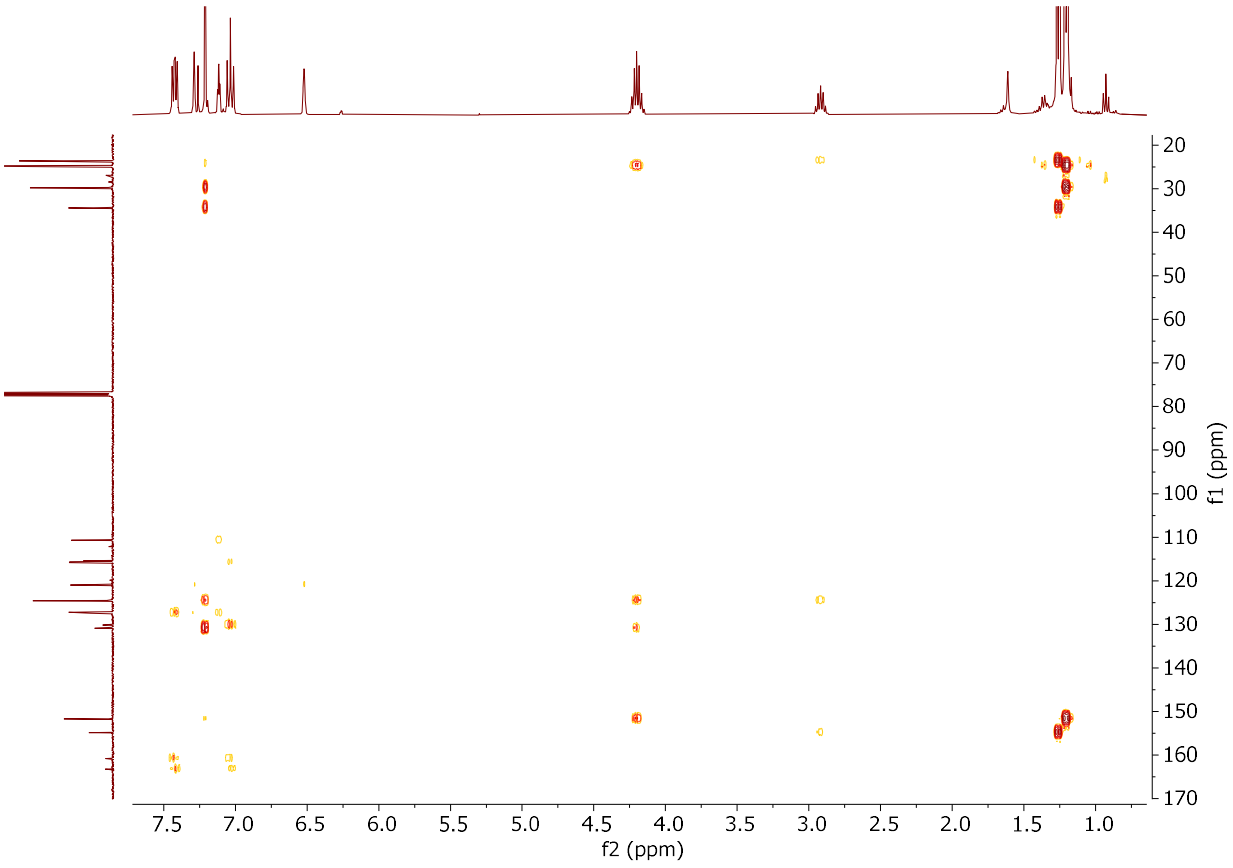


*Figure S27: HMBC NMR spectrum of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5b** in $CDCl_3$*

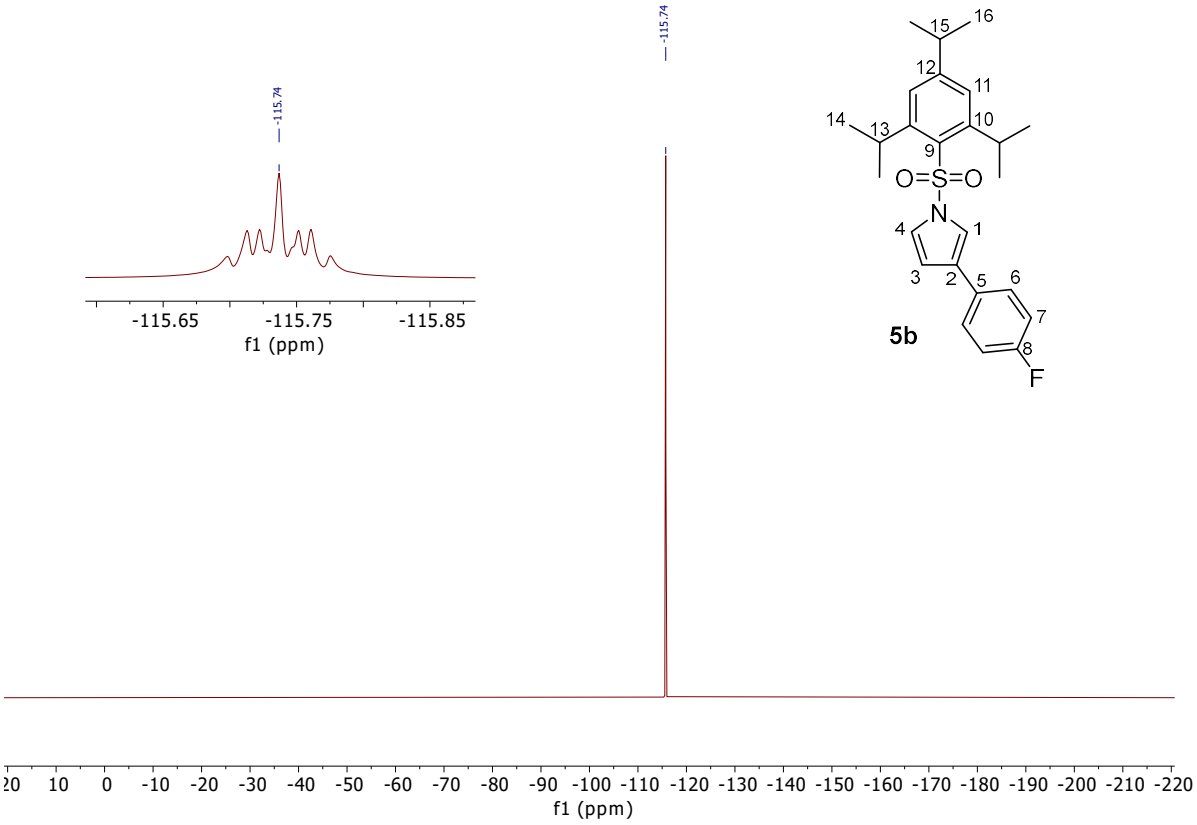


*Figure S28: ^{19}F NMR spectrum of NMR spectrum of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5b** in $CDCl_3$*

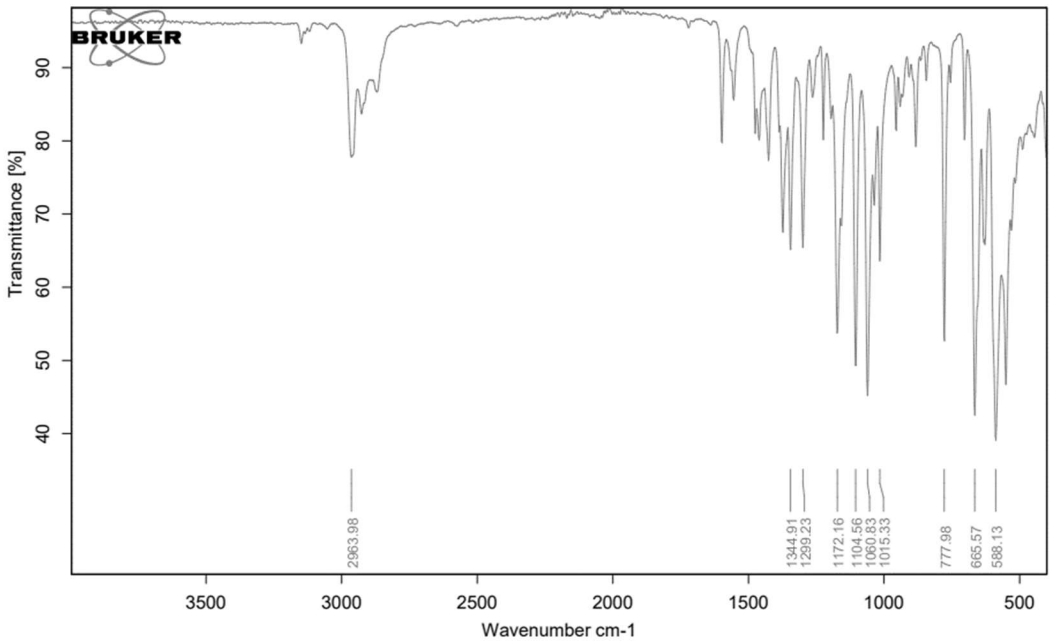


*Figure S29: IR spectrum of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5b**.*

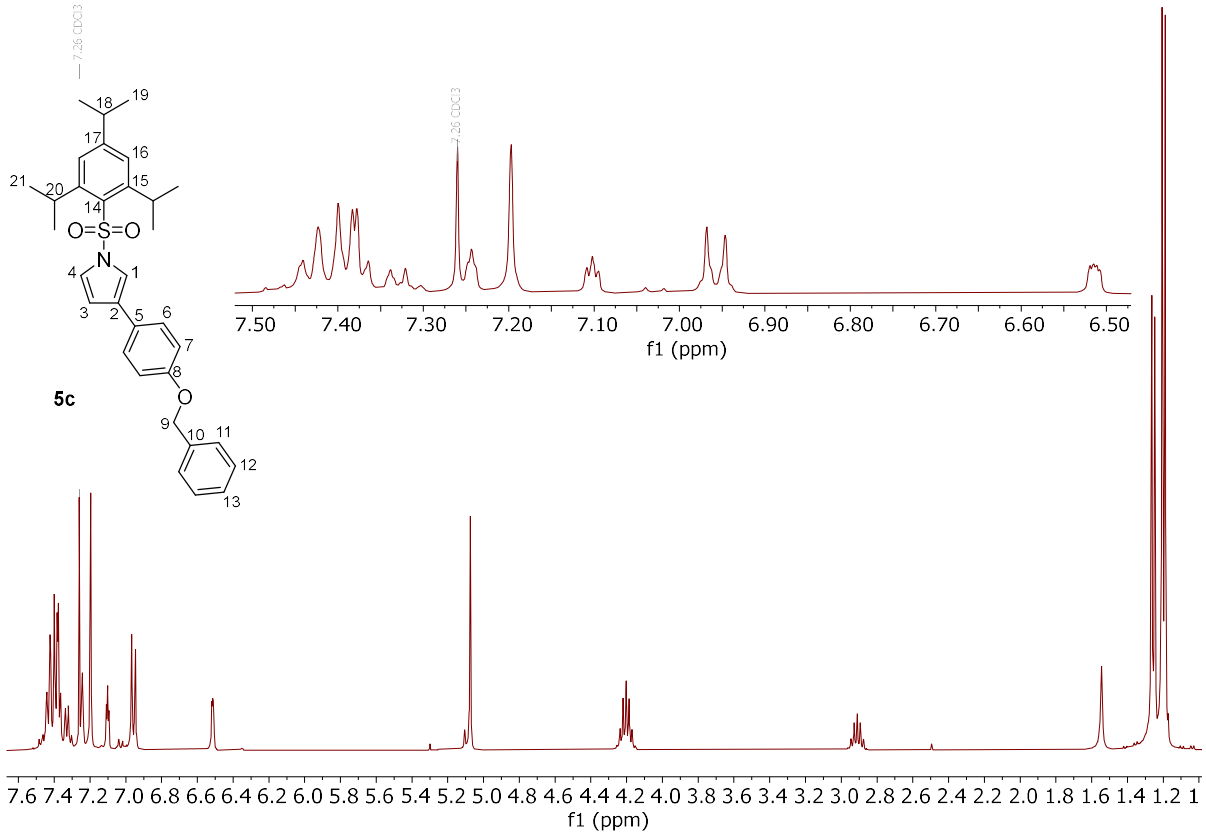


*Figure S30: ^{1}H NMR spectrum of 3-(4-(benzyloxy)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5c** in $CDCl_3$*

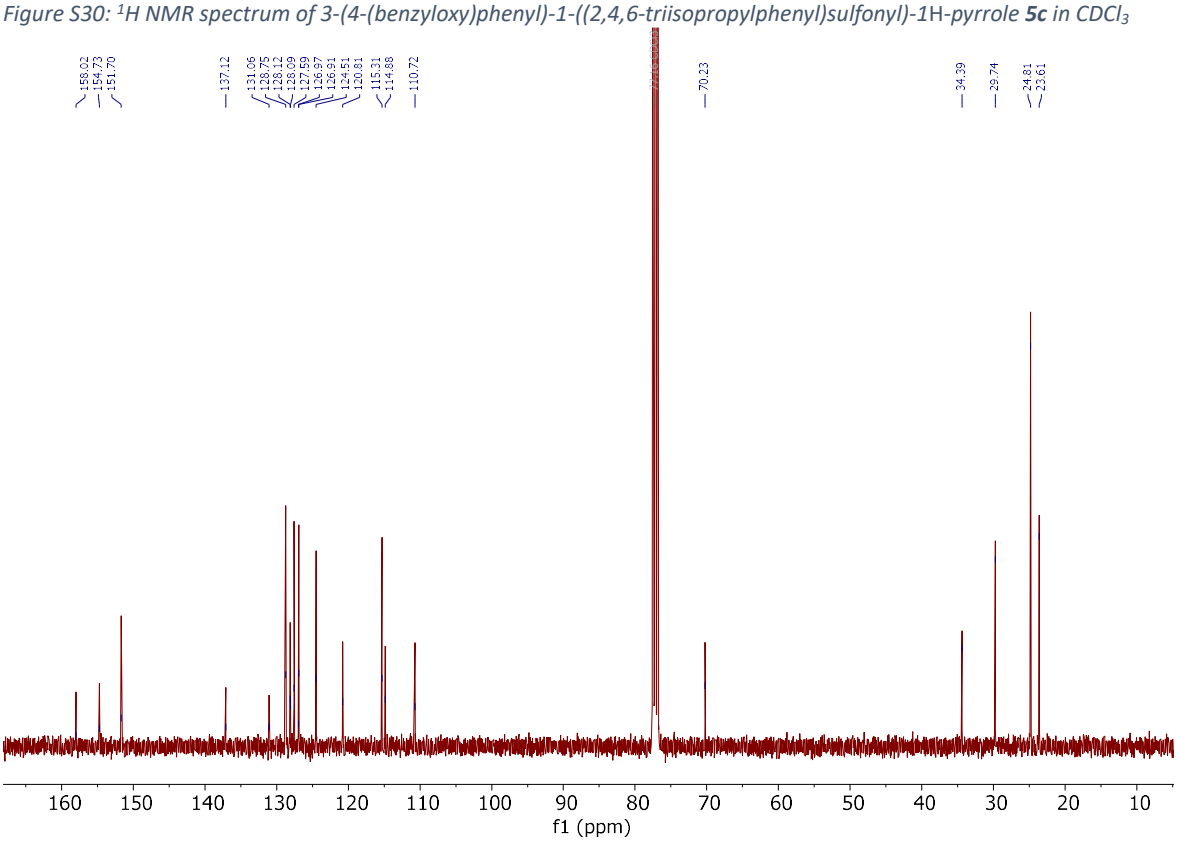


*Figure S31: ^{13}C NMR spectrum of 3-(4-(benzyloxy)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5c** in $CDCl_3$*

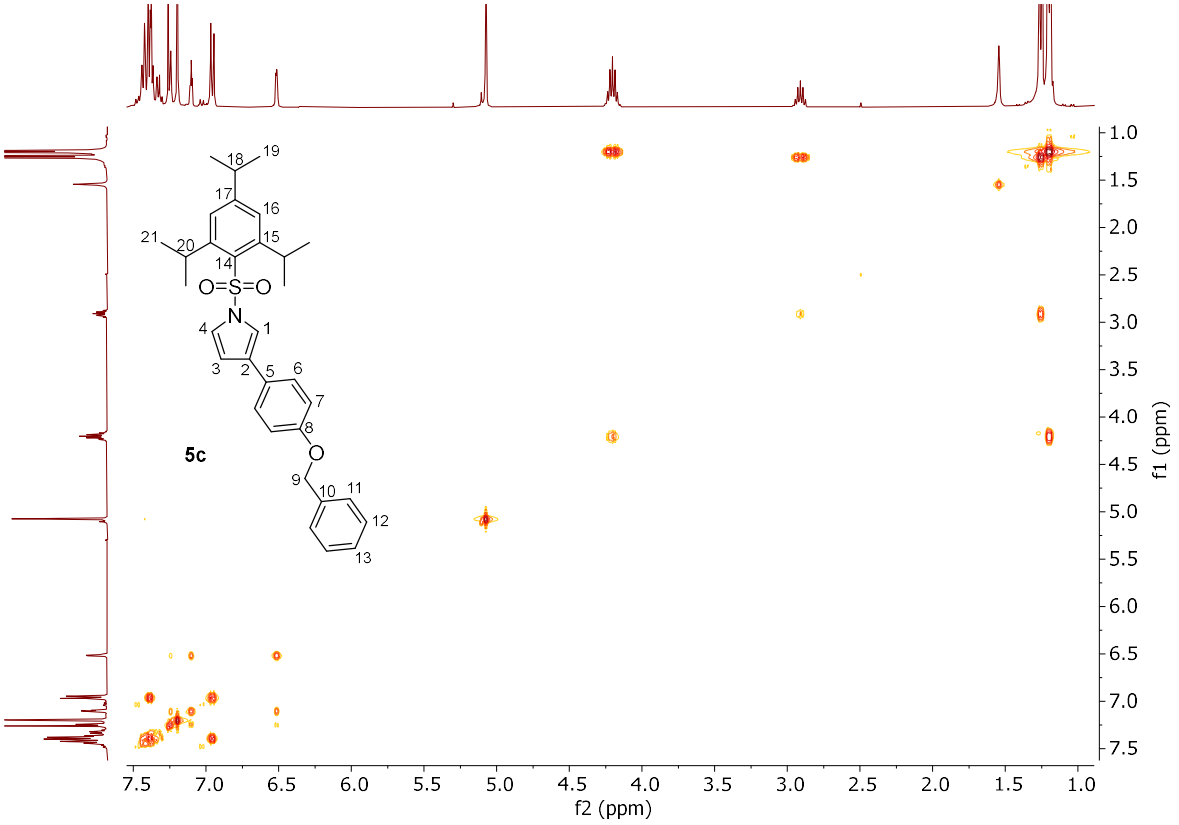


*Figure S32: COSY NMR spectrum of 3-(4-(benzyloxy)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5c** in $CDCl_3$*

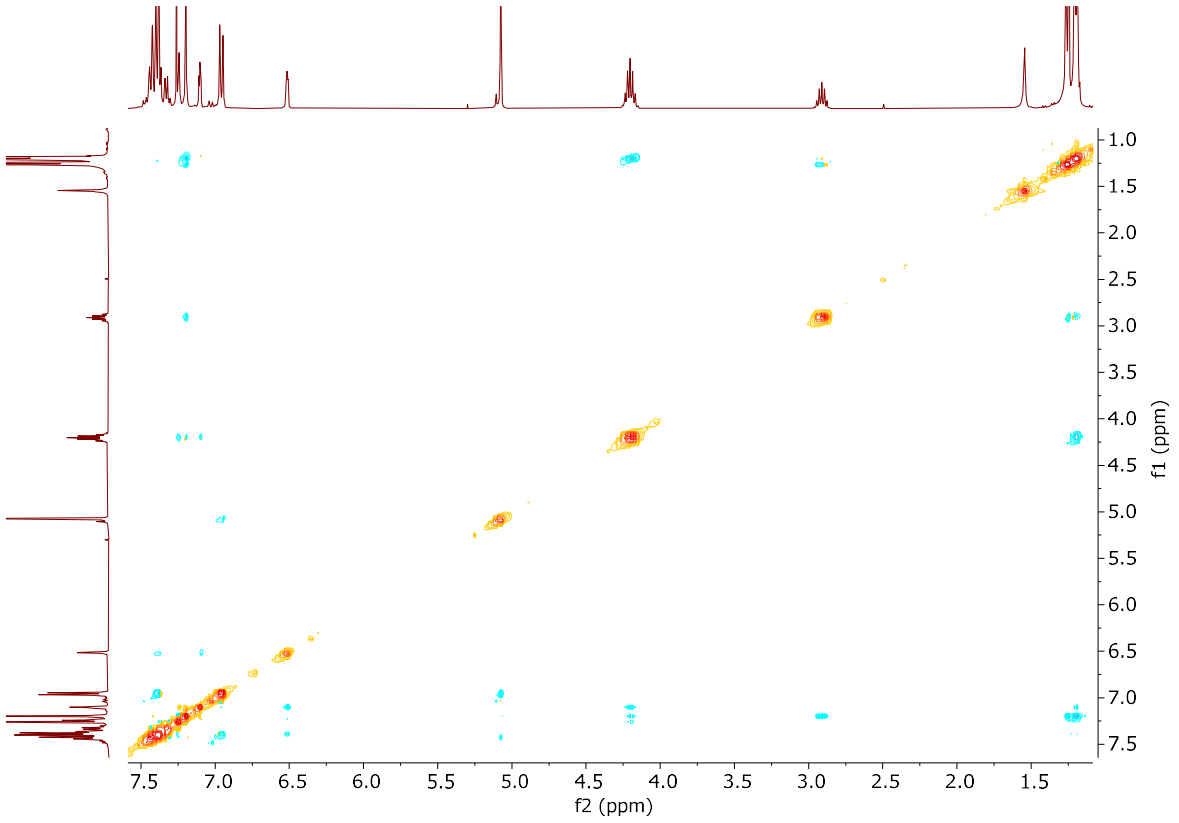


*Figure S33: NOESY NMR spectrum of 3-(4-(benzyloxy)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5c** in $CDCl_3$*

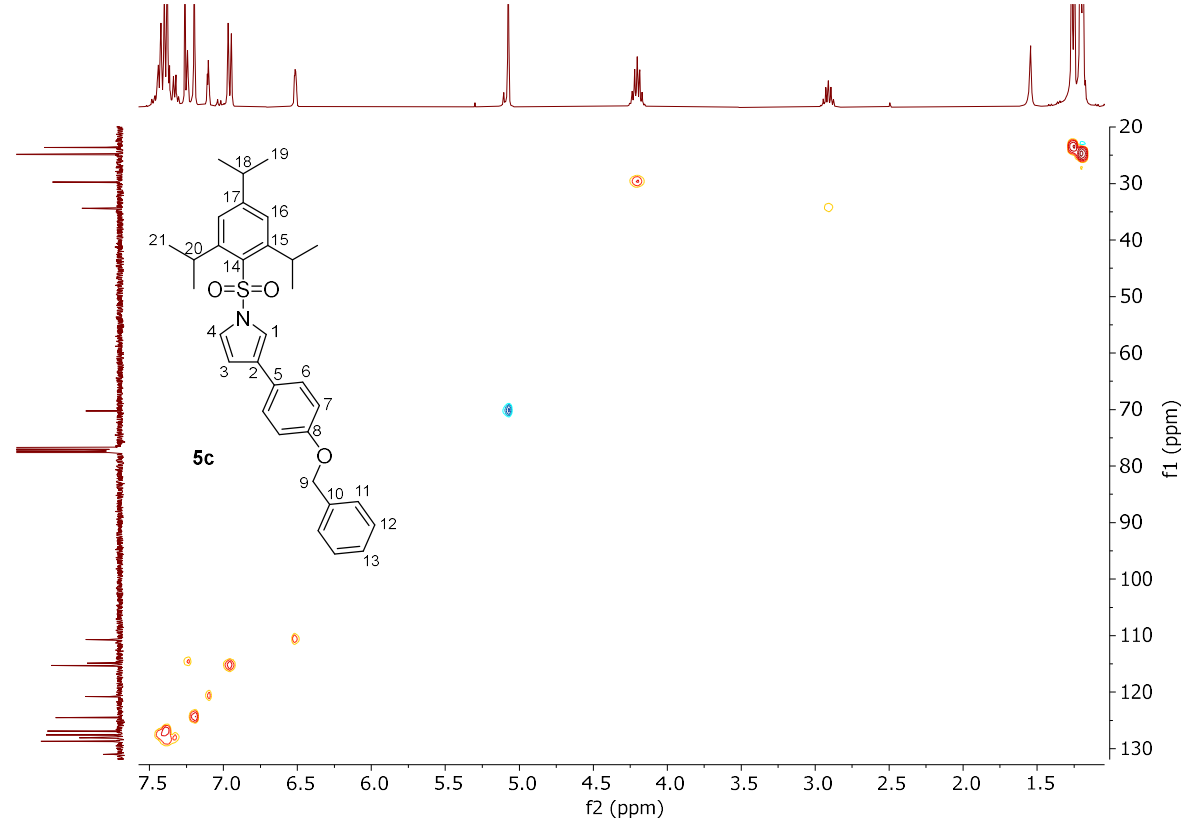


*Figure S34: HSQC NMR spectrum of 3-(4-(benzyloxy)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5c** in $CDCl_3$*

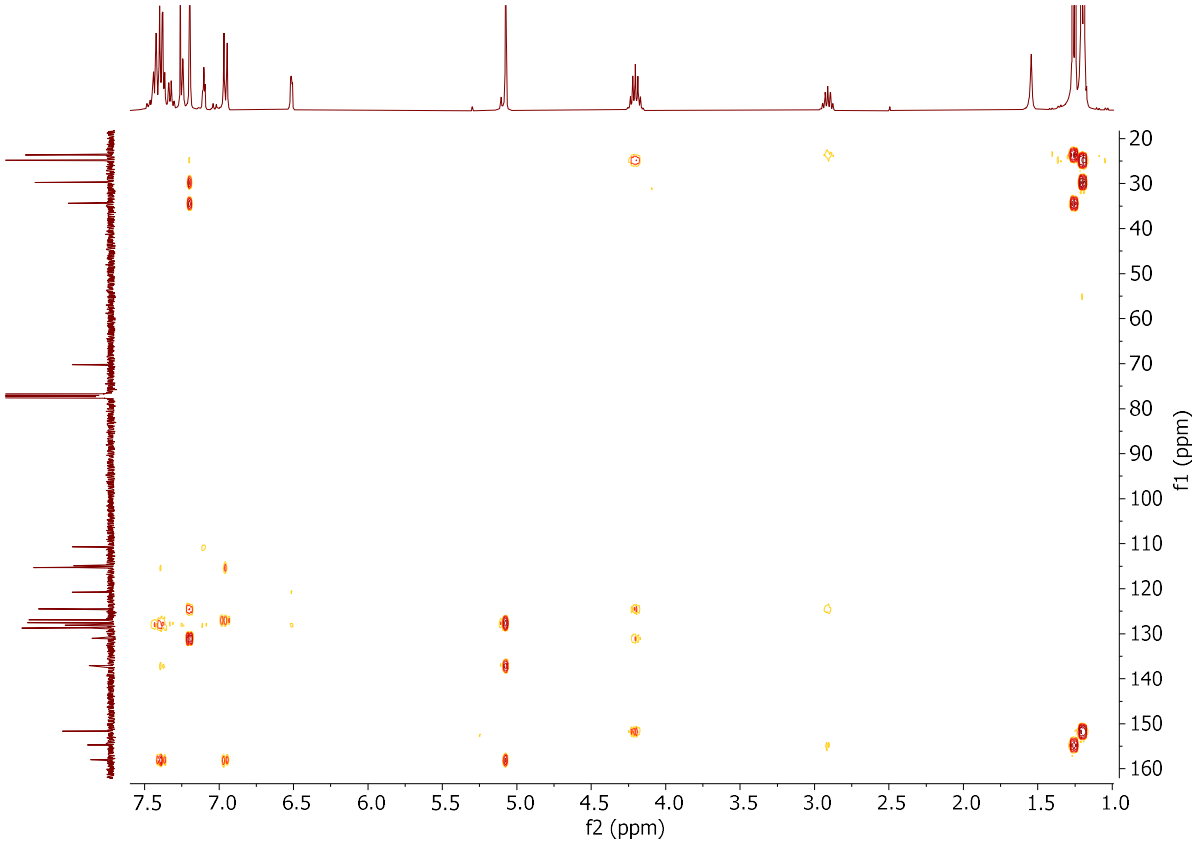


*Figure S35: HMBC NMR spectrum of 3-(4-(benzyloxy)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5c** in $CDCl_3$*

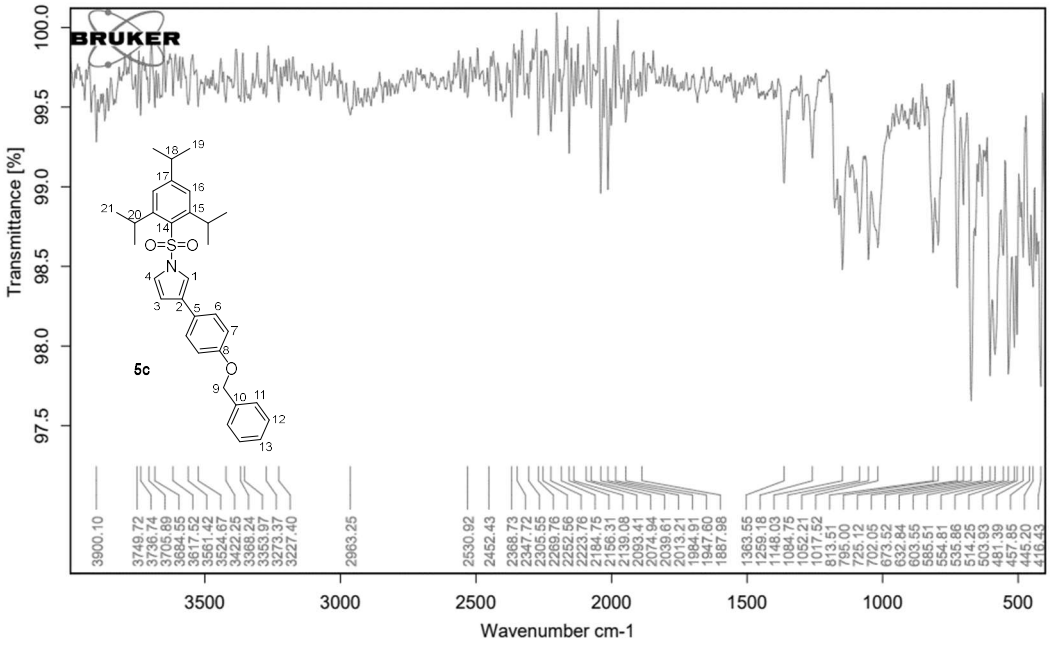


*Figure S36: IR spectrum of 3-(4-(benzyloxy)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5c***

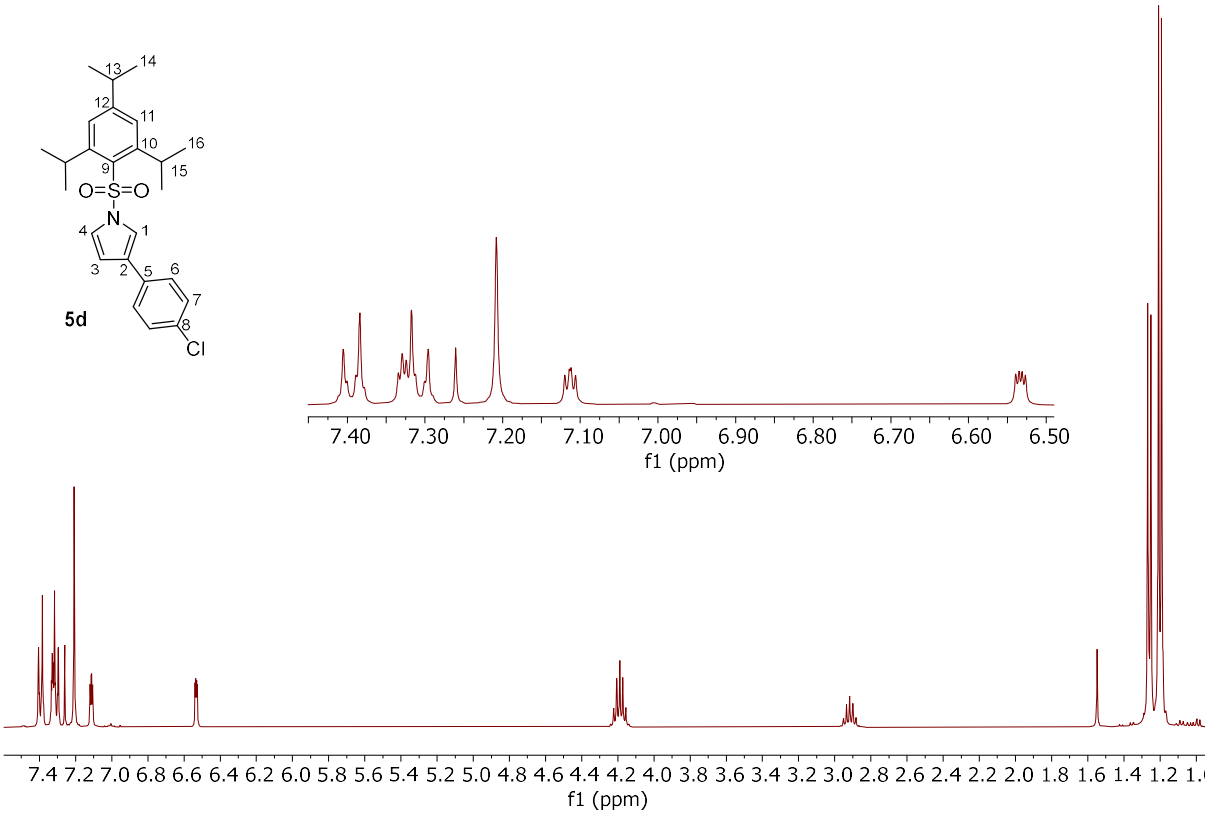


*Figure S37: ^{1}H NMR spectrum of 3-(4-chlorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5d** in $CDCl_3$*

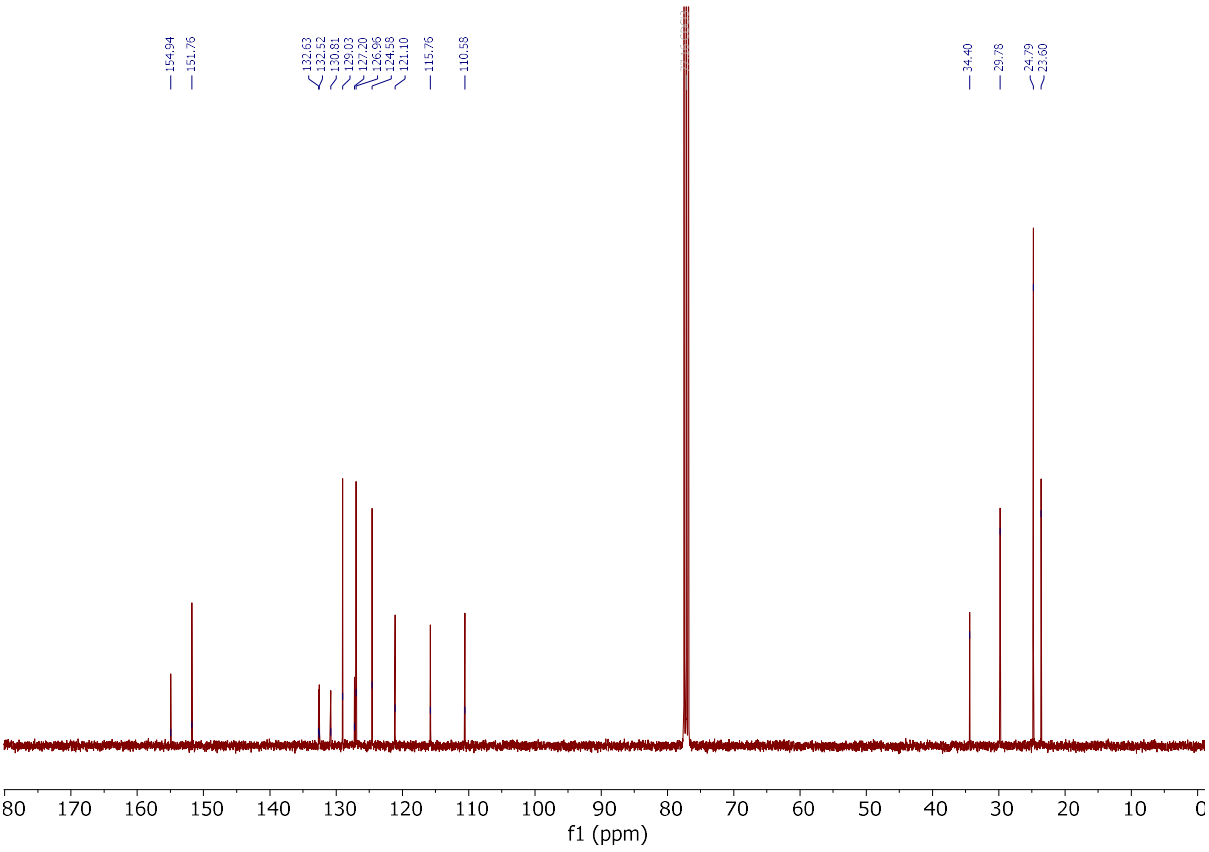


*Figure S38: ^{13}C NMR spectrum of 3-(4-chlorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5d** in $CDCl_3$.*

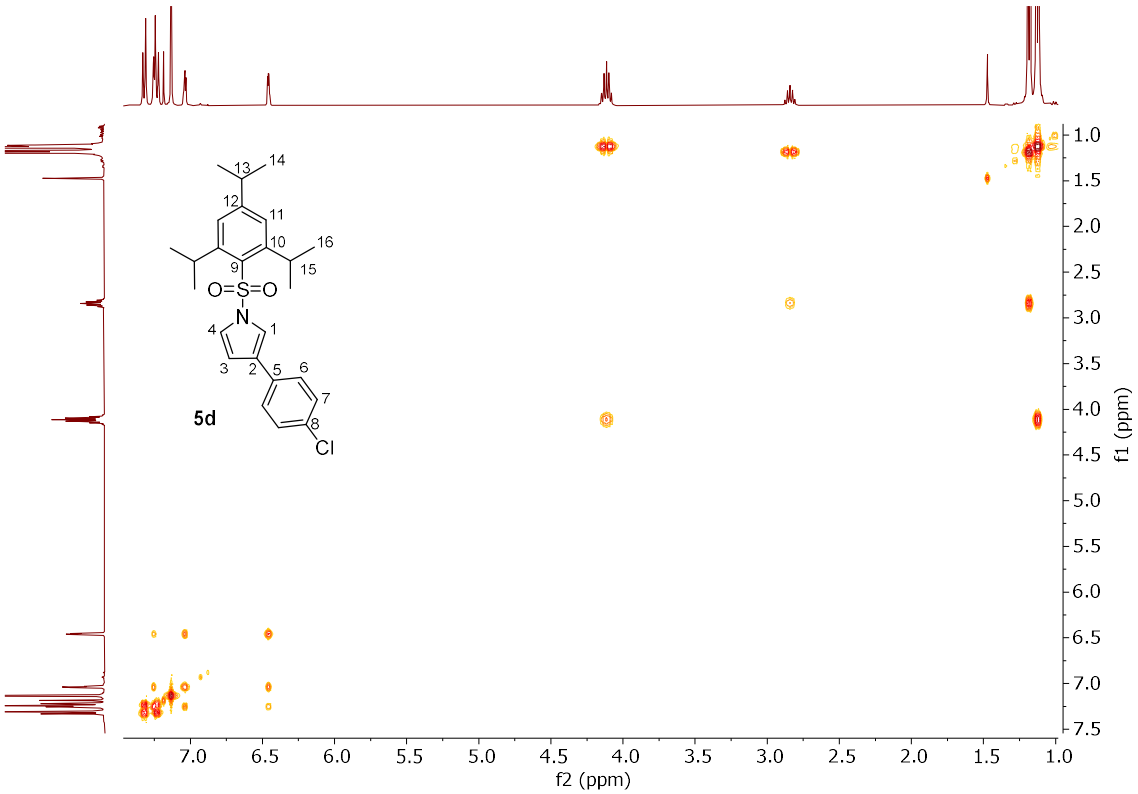


*Figure S39: COSY NMR spectrum of 3-(4-chlorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5d** in $CDCl_3$.*

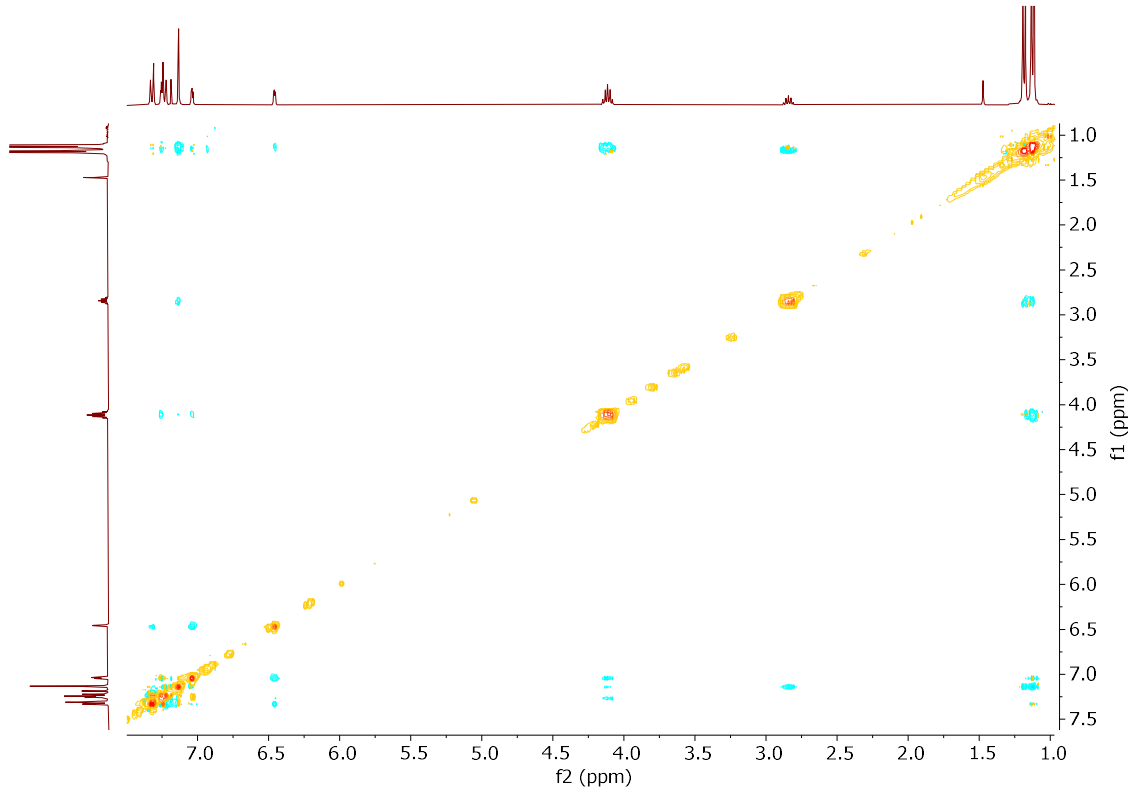


*Figure S40: NOESY NMR spectrum of 3-(4-chlorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5d** in $CDCl_3$.*

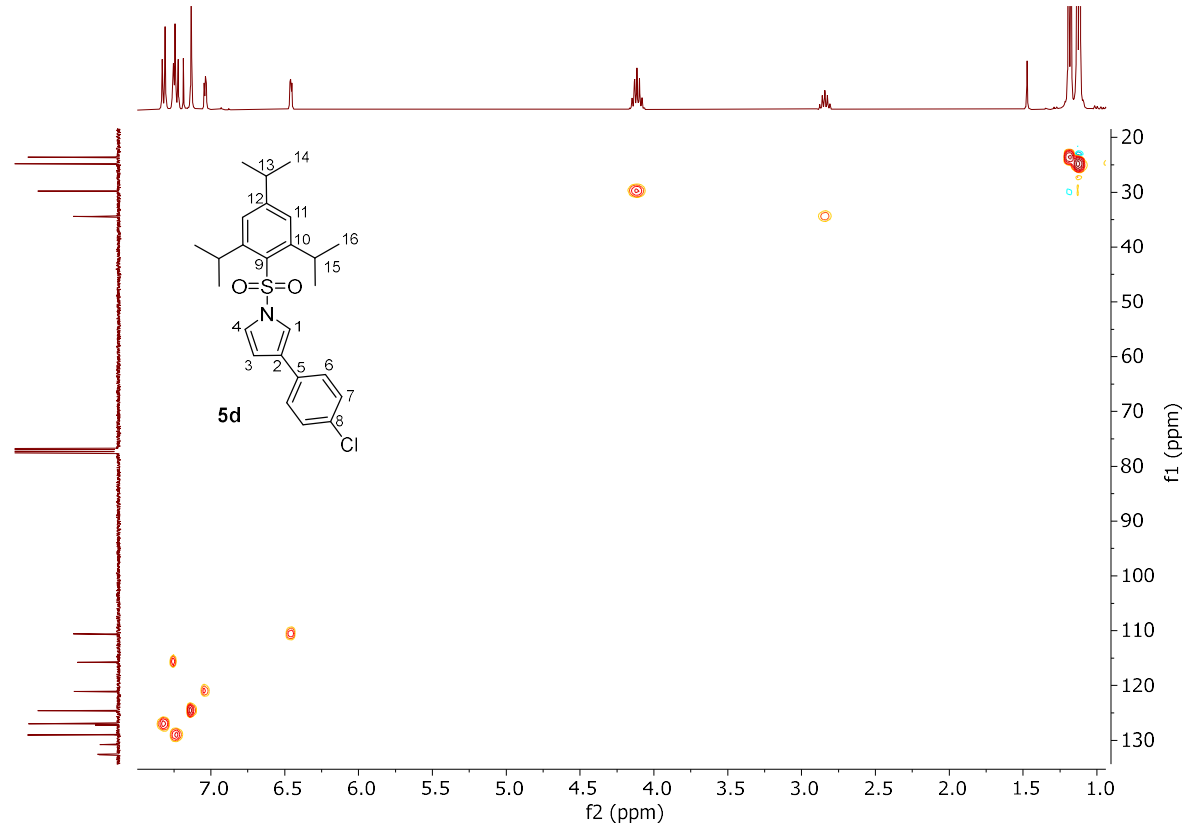


*Figure S41: HSQC NMR spectrum of 3-(4-chlorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5d** in $CDCl_3$.*

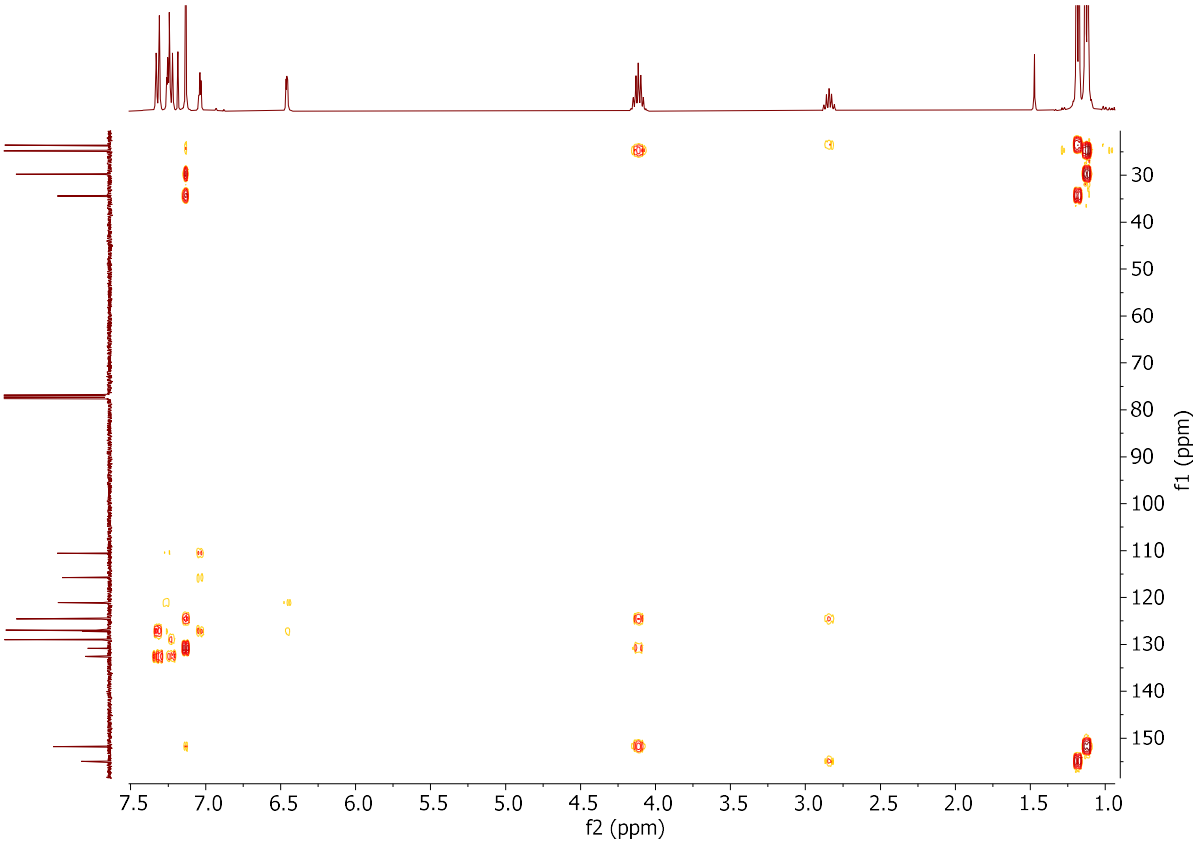


*Figure S42: HMBC NMR spectrum of 3-(4-chlorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5d** in $CDCl_3$.*

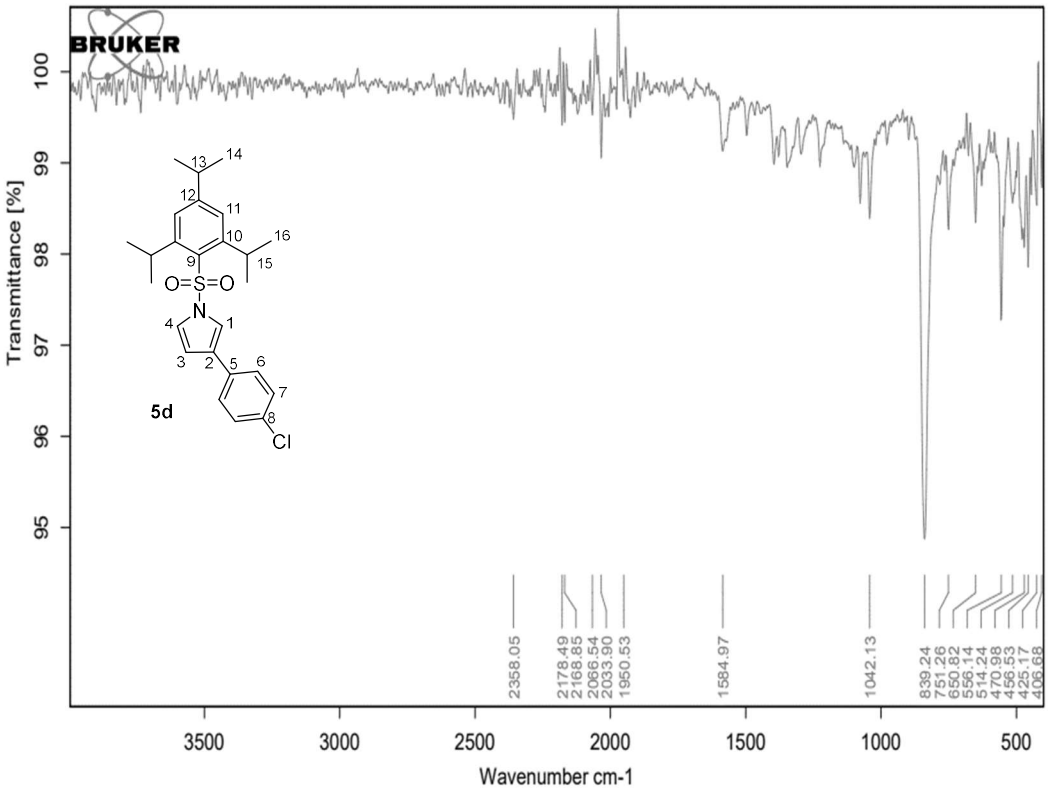


*Figure S43: 1IR spectrum of 3-(4-chlorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5d***

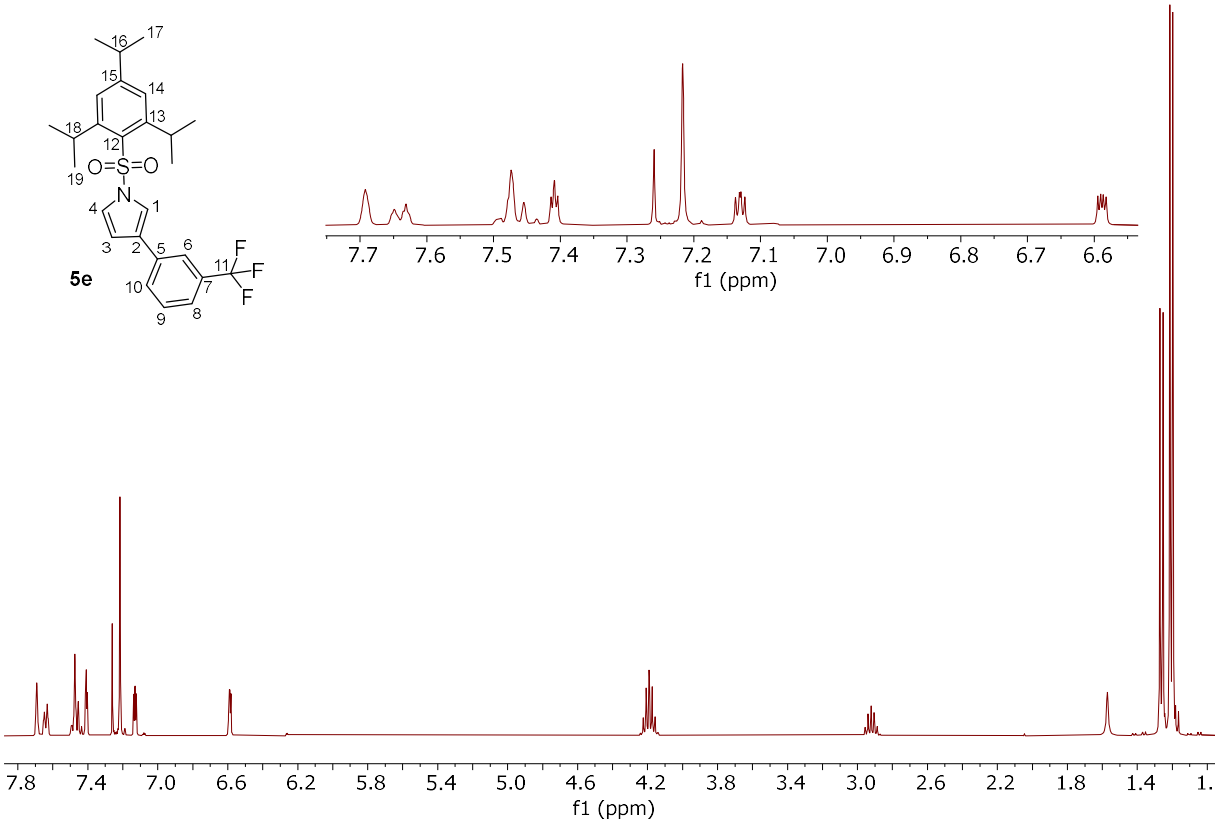


*Figure S44: ^{1}H NMR spectrum of 3-(3-(trifluoromethyl)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5e** in $CDCl_3$*

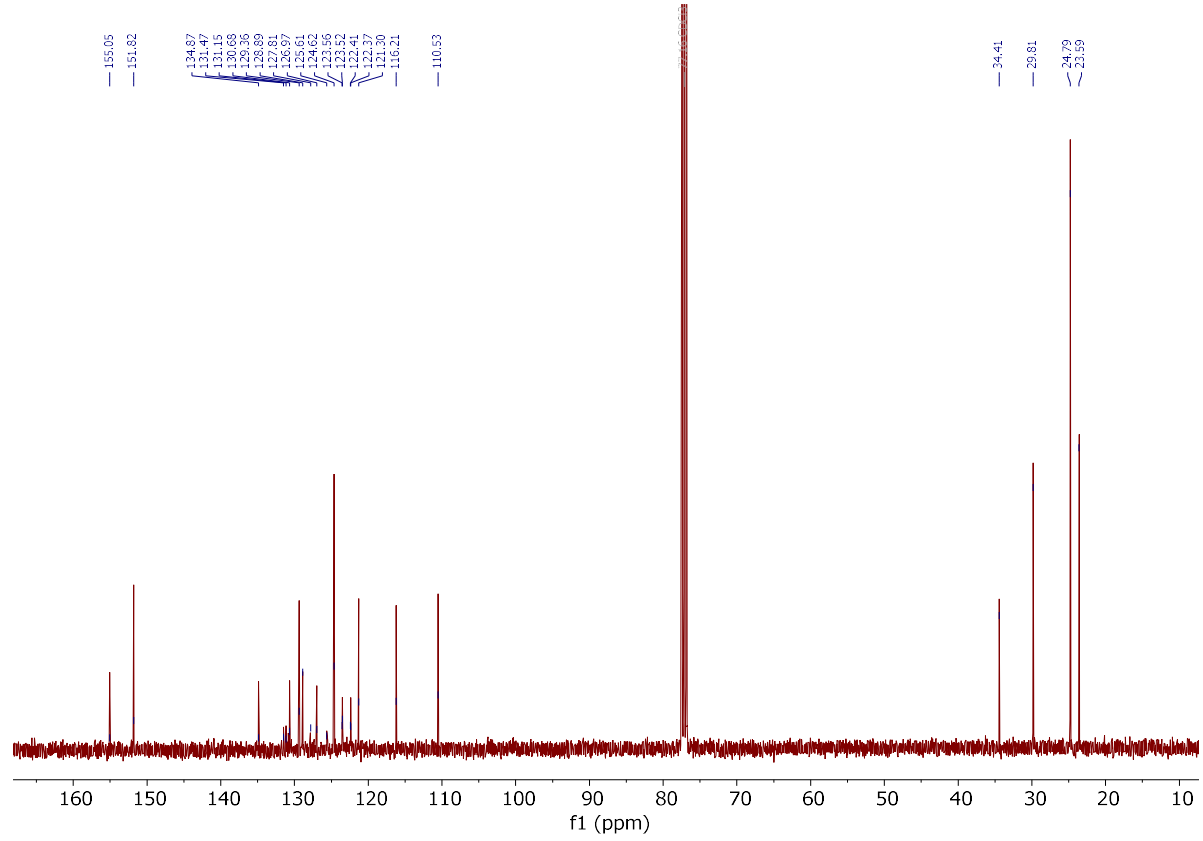


*Figure S45: ^{13}C NMR spectrum of 3-(3-(trifluoromethyl)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5e** in $CDCl_3$*

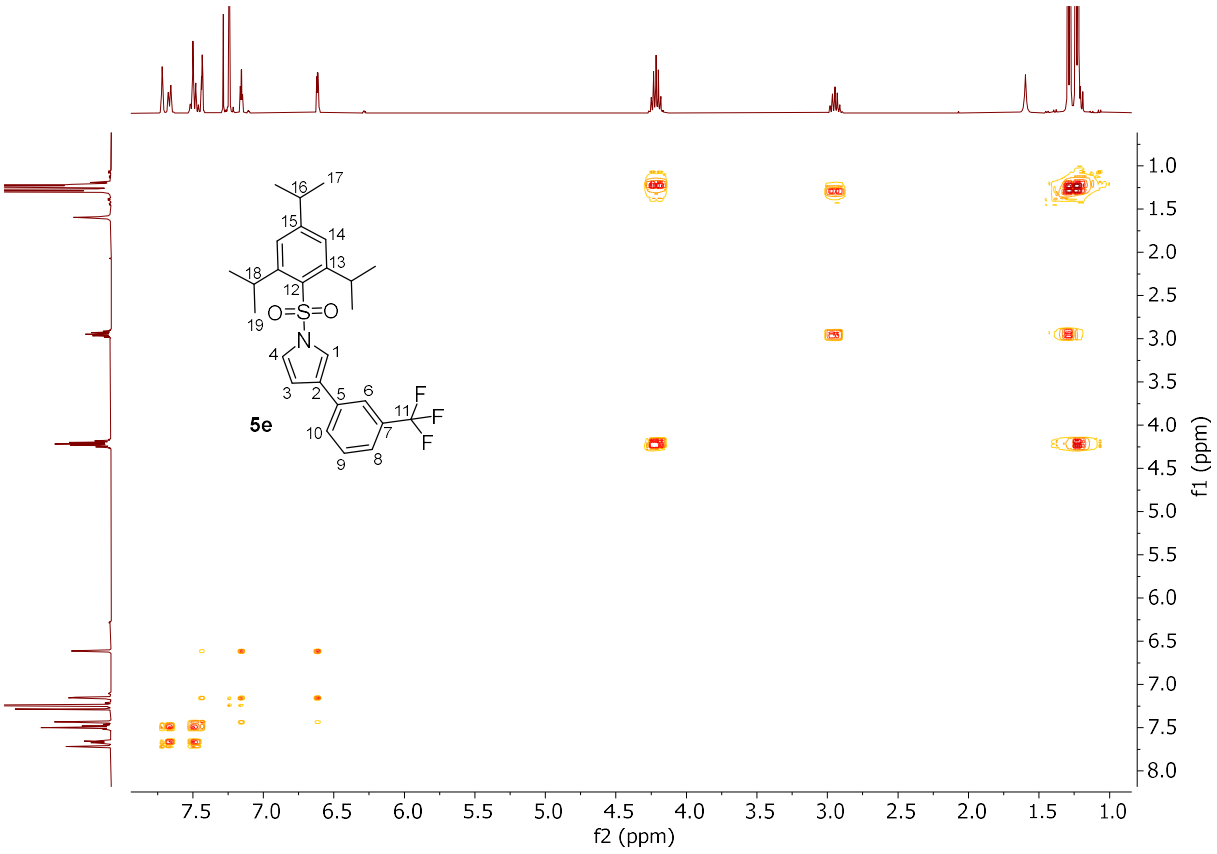


*Figure S46: COSY spectrum of 3-(3-(trifluoromethyl)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5e** in $CDCl_3$*

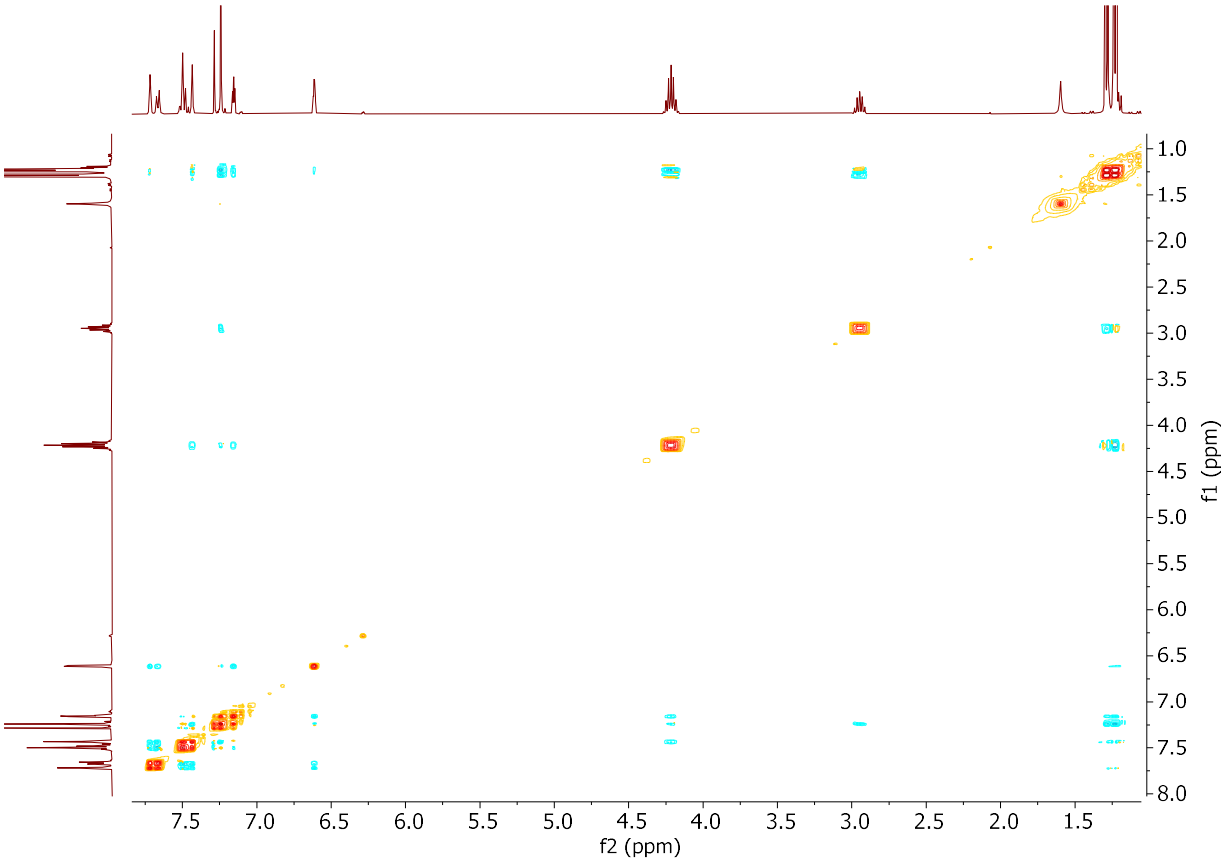


*Figure S47: NOESY spectrum of 3-(3-(trifluoromethyl)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5e** in $CDCl_3$*

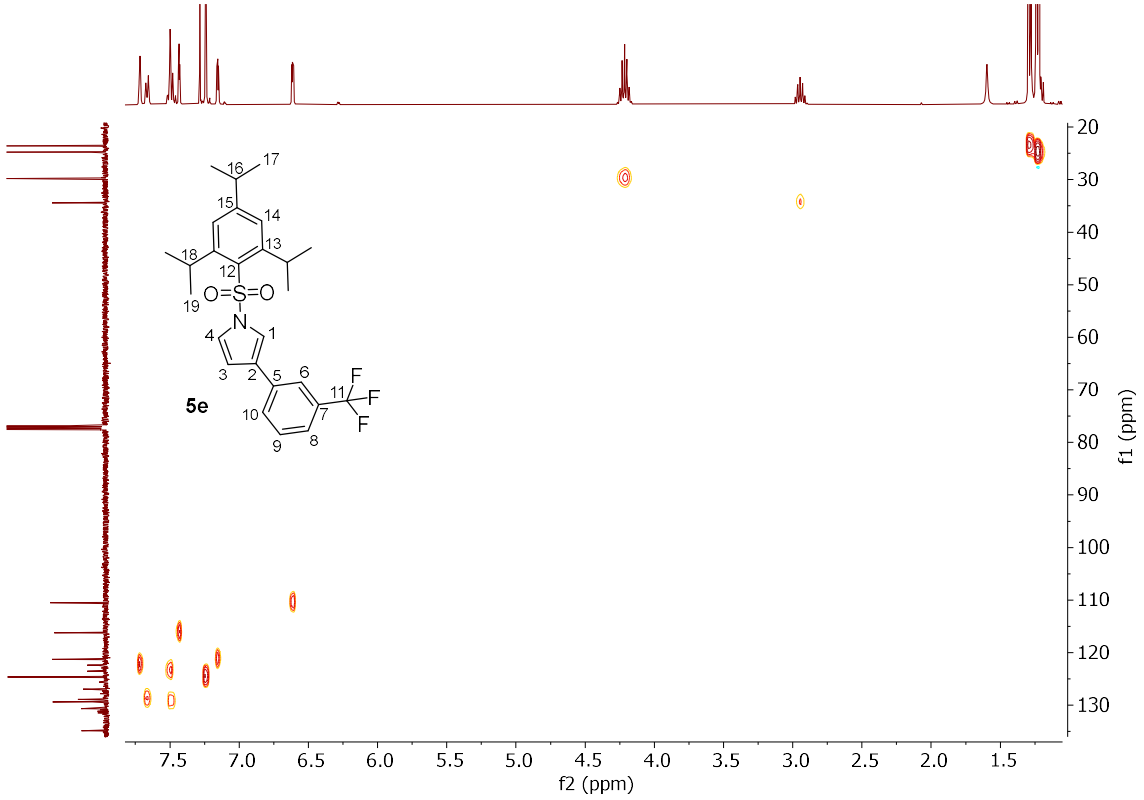


*Figure S48: HSQC spectrum of 3-(3-(trifluoromethyl)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5e** in $CDCl_3$*

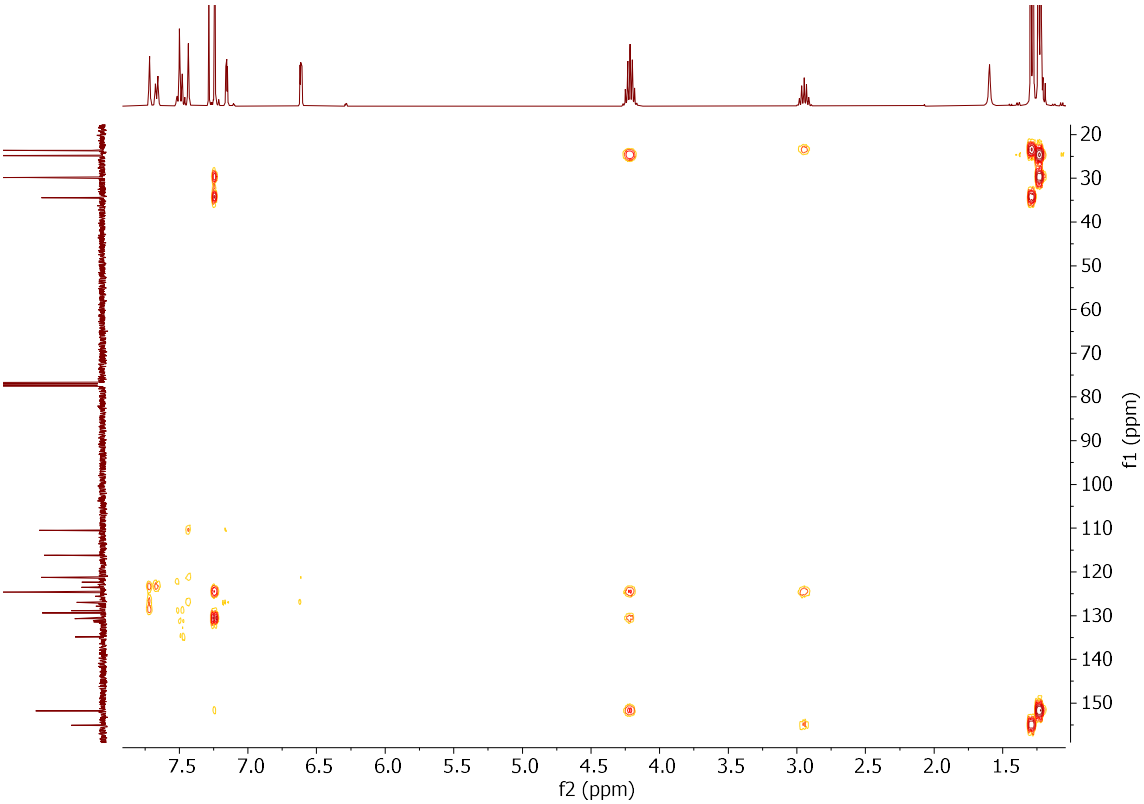


*Figure S49: HMBC spectrum of 3-(3-(trifluoromethyl)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5e** in $CDCl_3$*

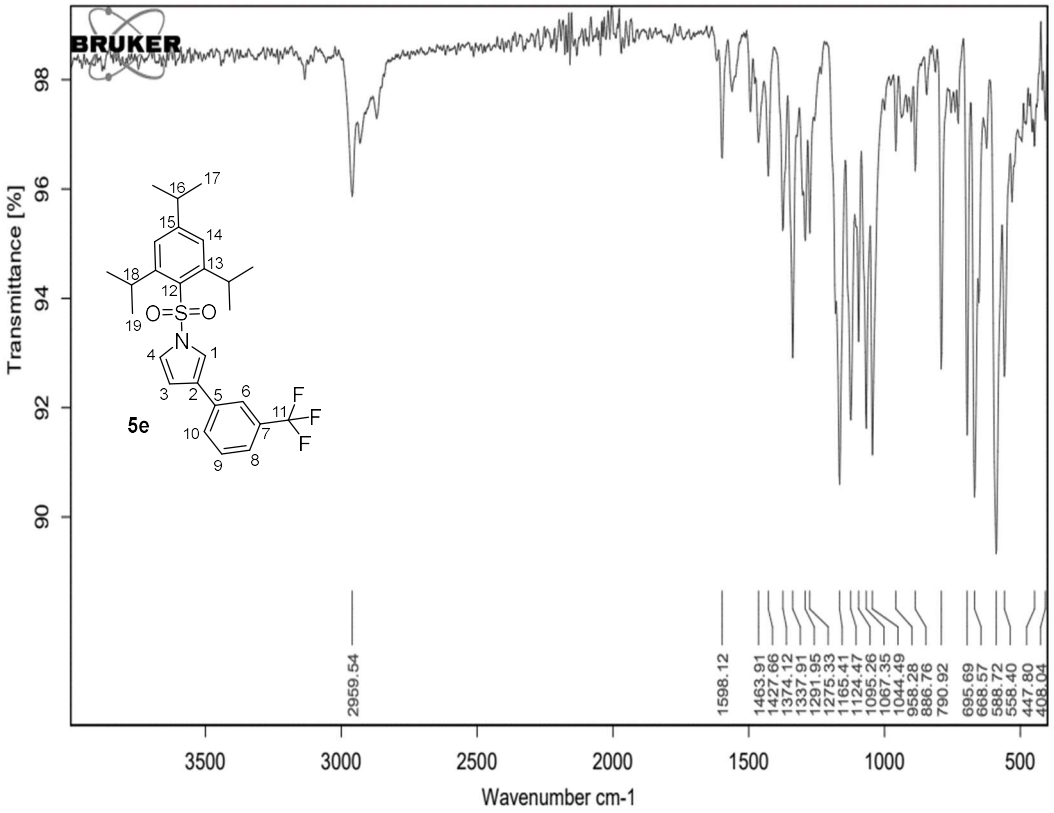


*Figure S50: IR spectrum of 3-(3-(trifluoromethyl)phenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5e***

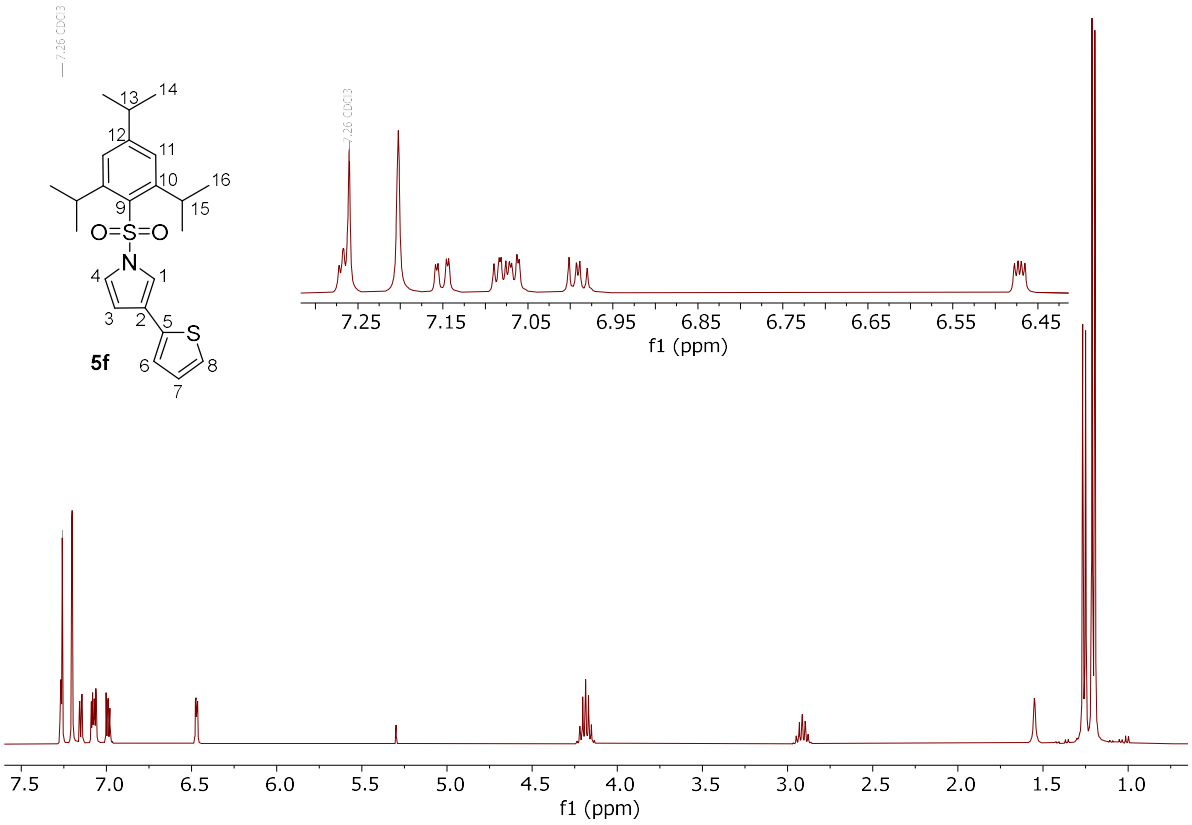


*Figure S51: ^{1}H NMR of 3-(thiophen-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5f** in $CDCl_3$*

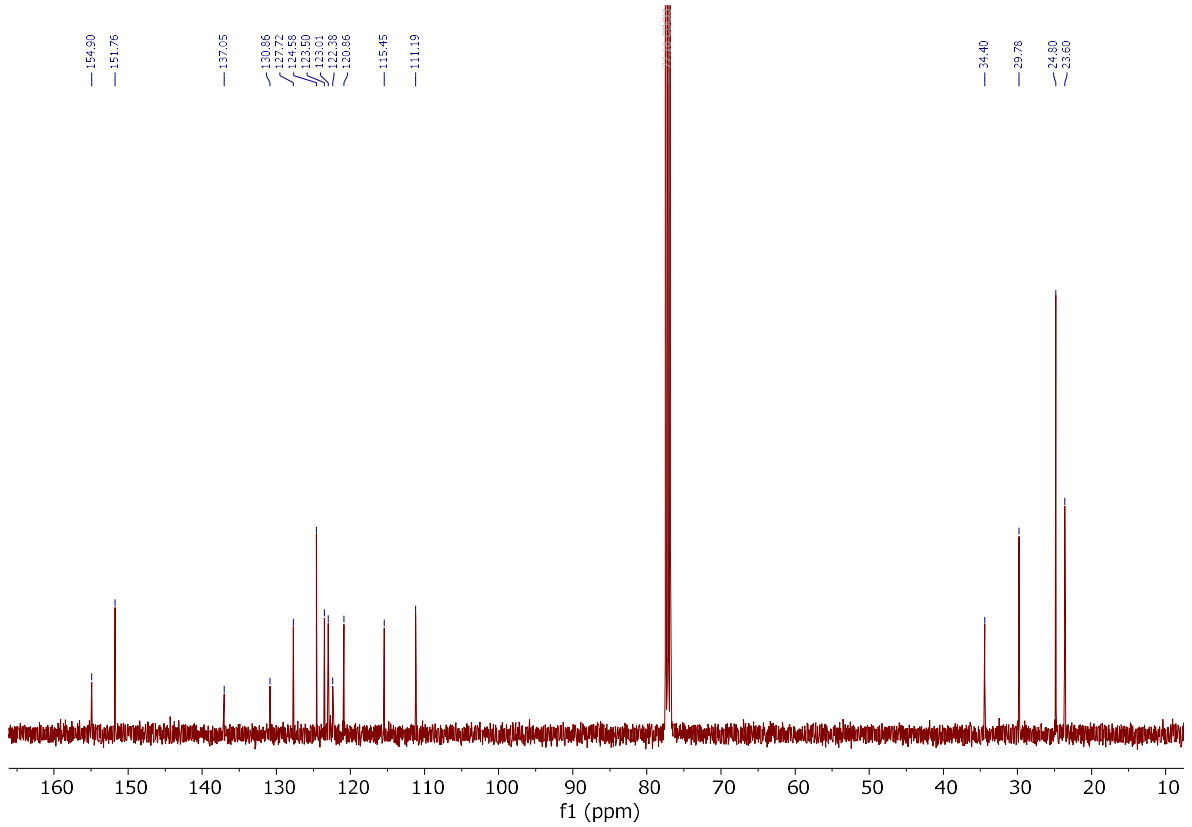


*Figure S52: ^{13}C NMR of 3-(thiophen-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5f** in $CDCl_3$*

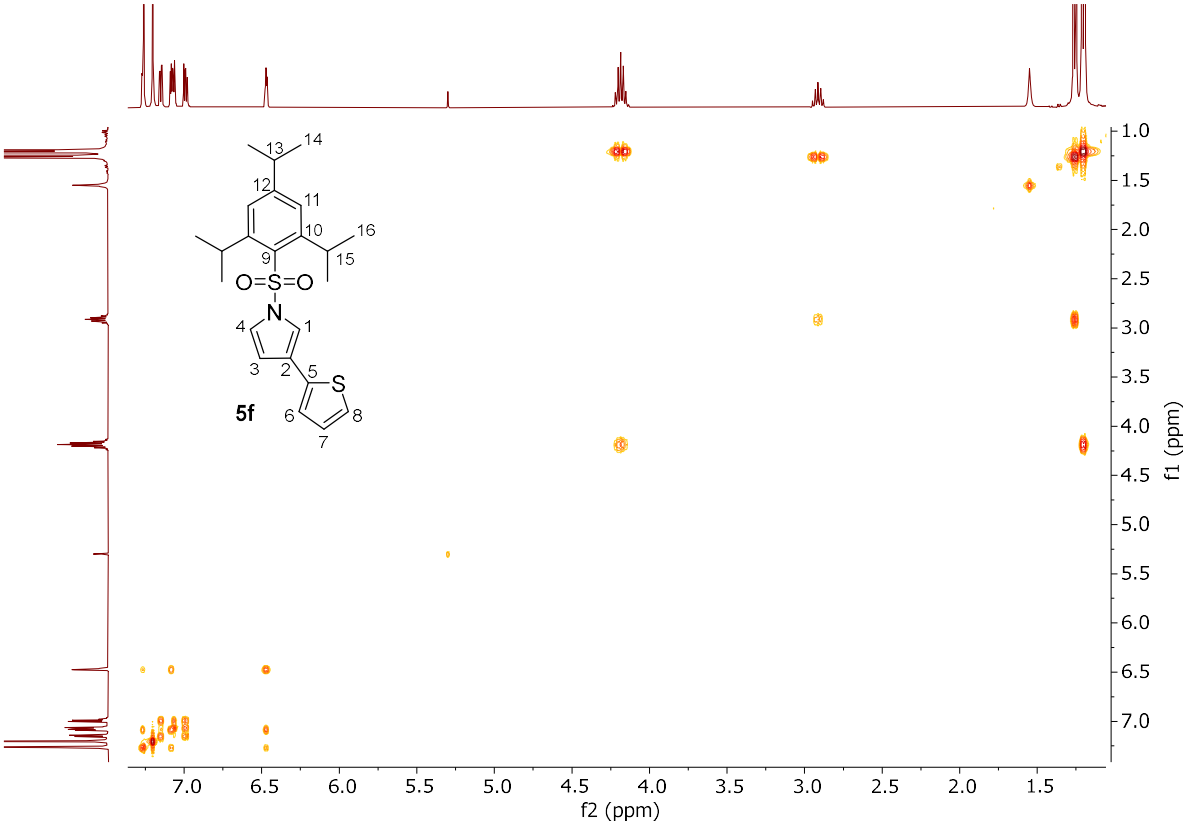


*Figure S53: COSY NMR of 3-(thiophen-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5f** in $CDCl_3$*

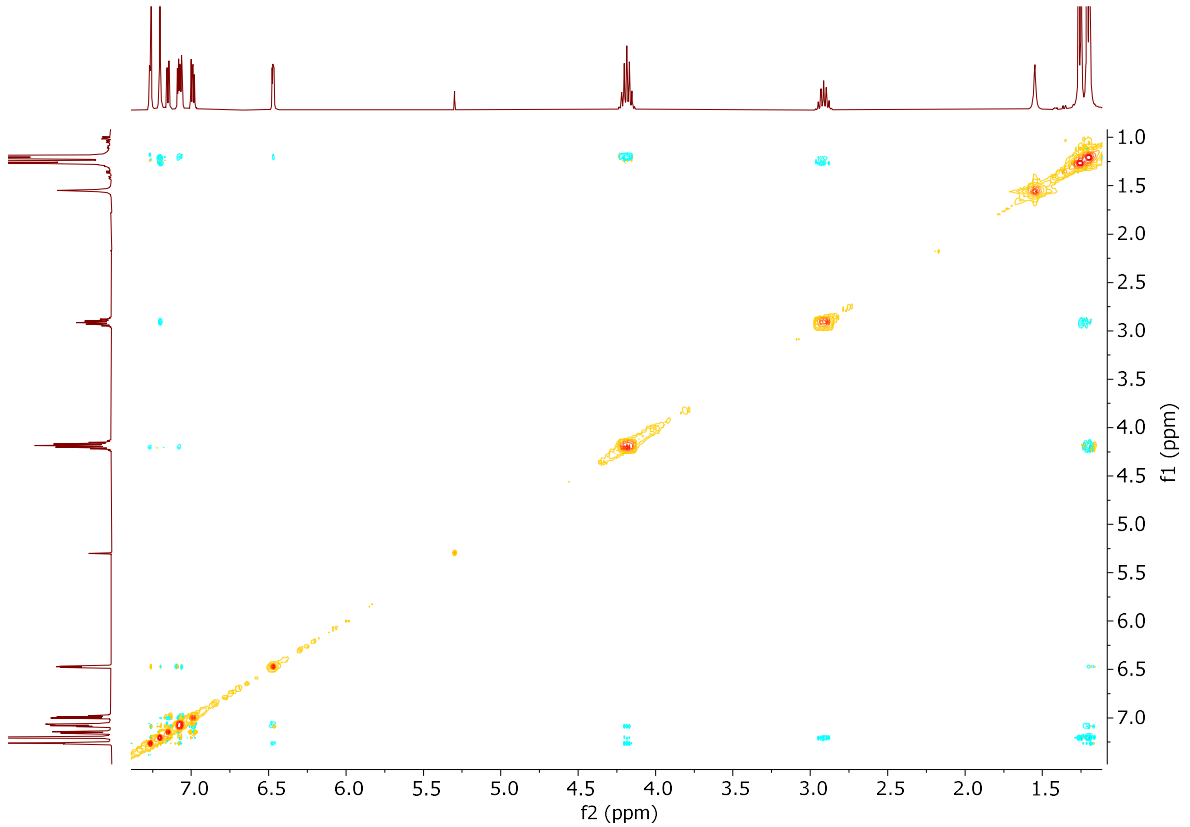


*Figure S54: NOESY NMR of 3-(thiophen-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5f** in $CDCl_3$*

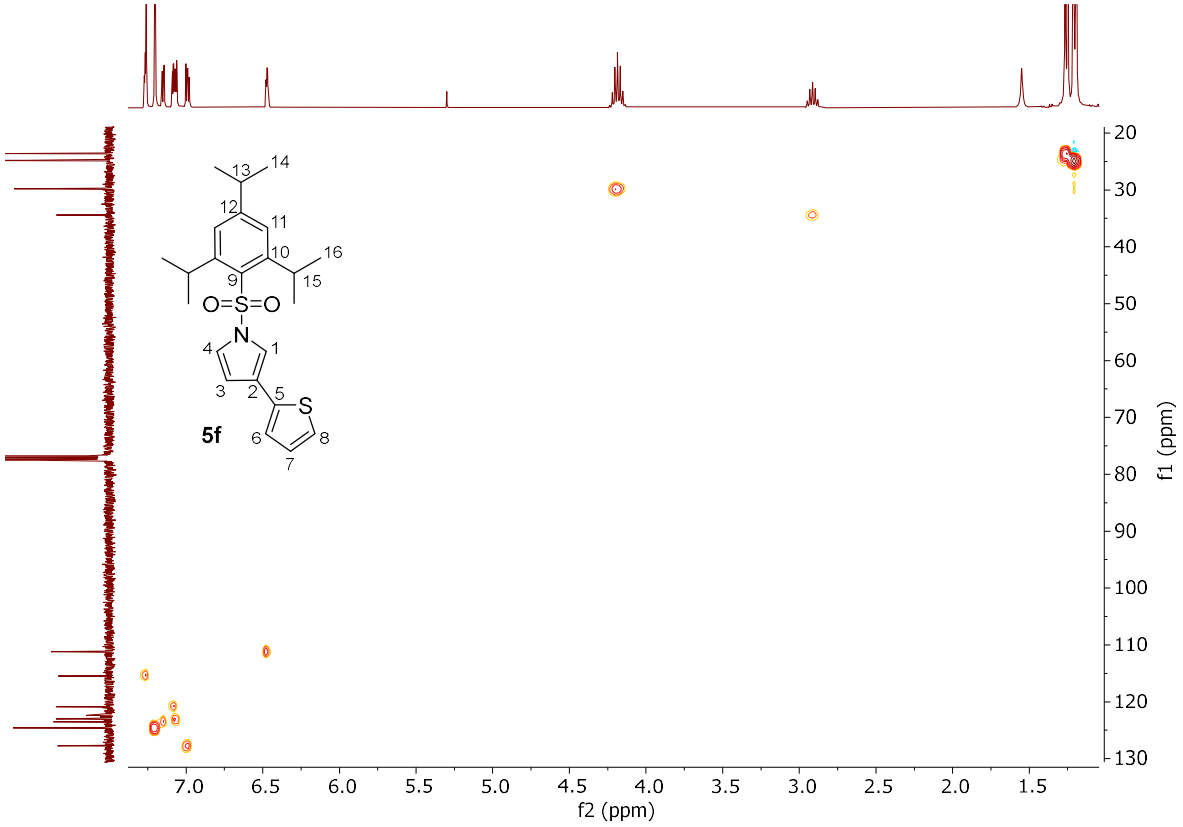


*Figure S55: HSQC NMR of 3-(thiophen-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5f** in $CDCl_3$*

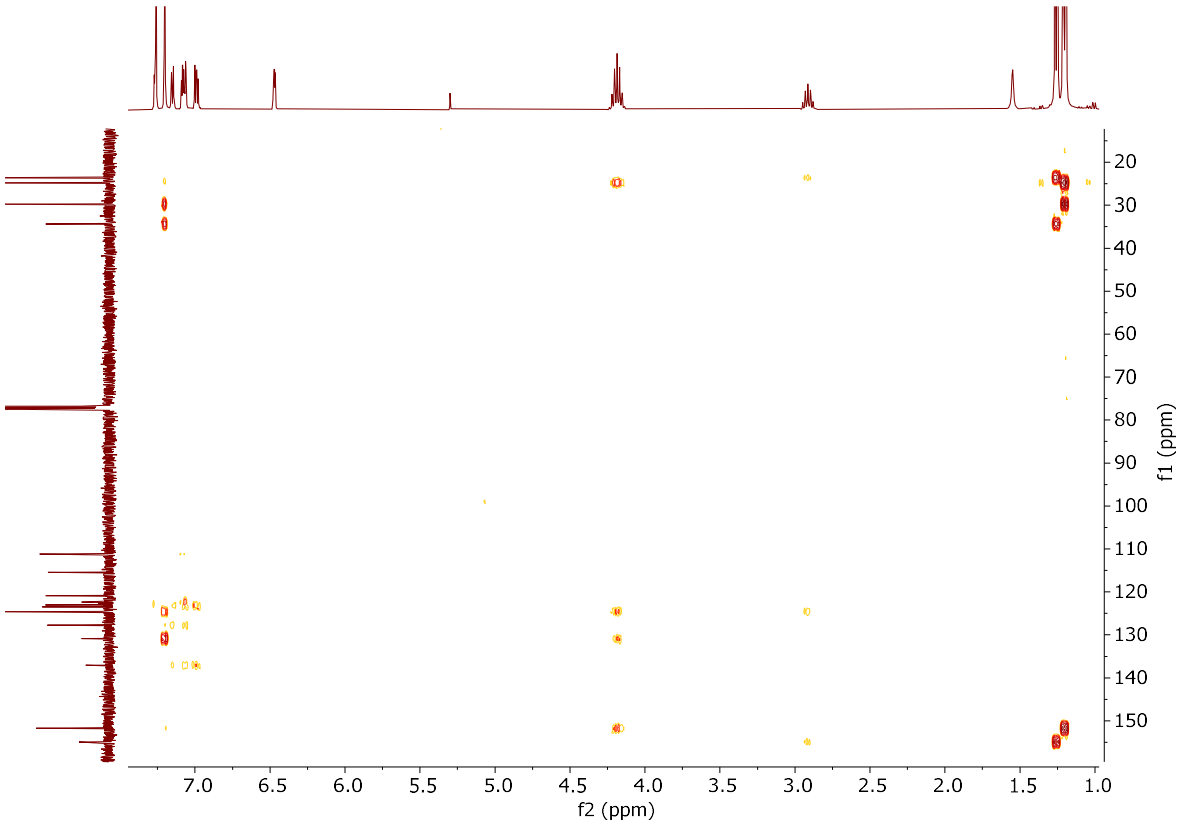


*Figure S56: HMBC NMR of 3-(thiophen-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5f** in $CDCl_3$*

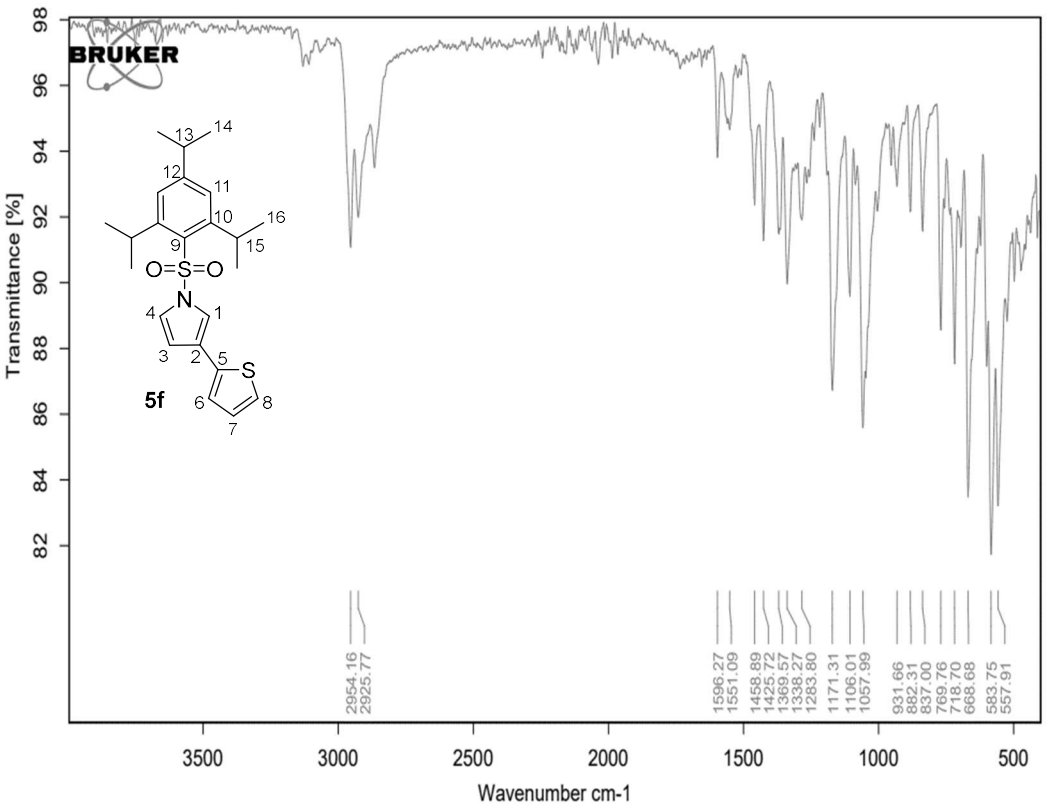


*Figure S57: IR spectrum of 3-(thiophen-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5f***

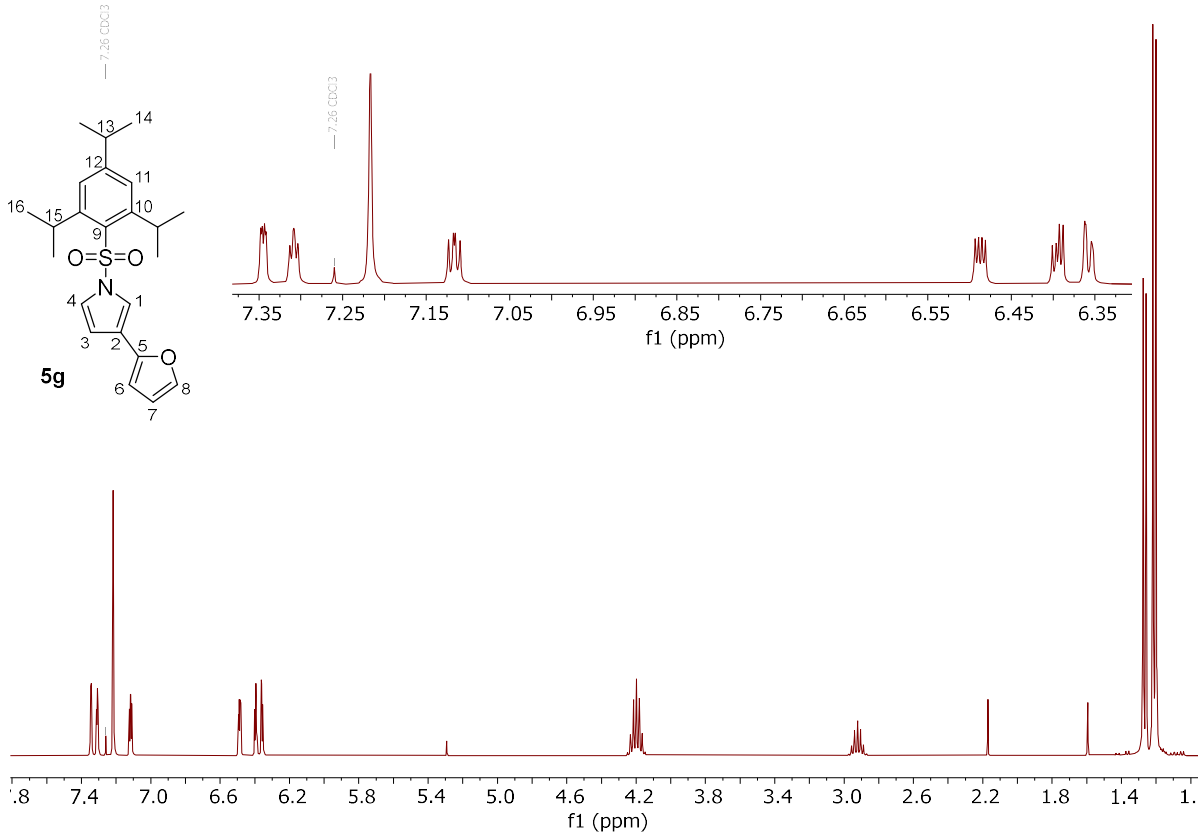


*Figure S58: [1]H NMR spectrum of 3-(furan-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5g** in $CDCl_3$*

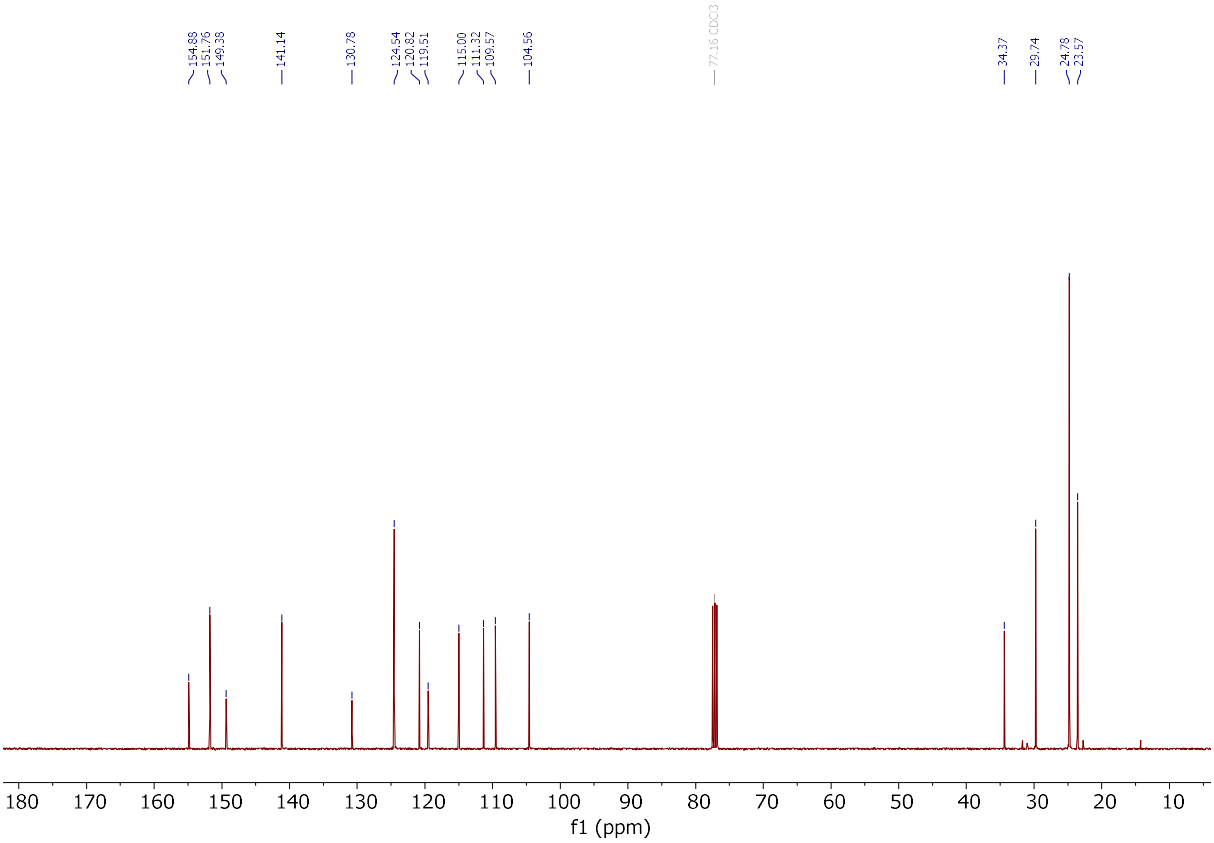


*Figure S59: [13]C NMR spectrum of 3-(furan-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5g** in $CDCl_3$*

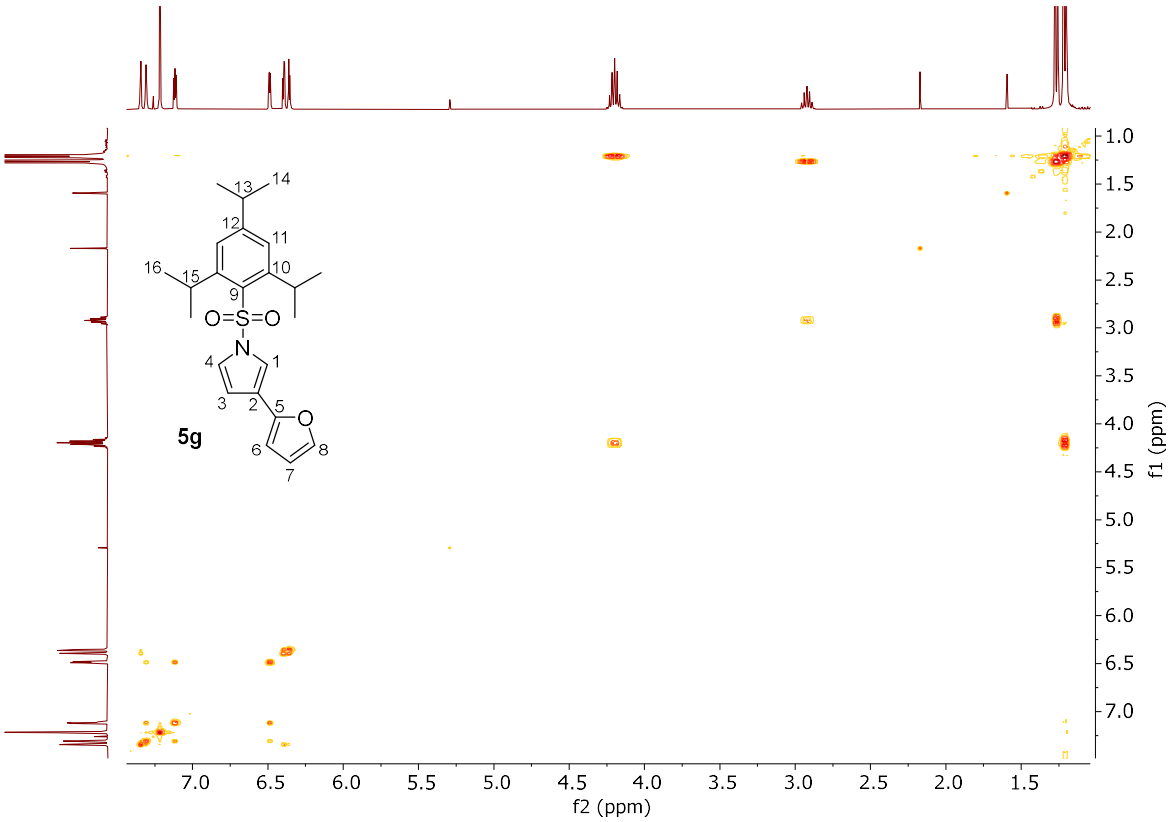


*Figure S60: COSY NMR spectrum of 3-(furan-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5g** in $CDCl_3$*

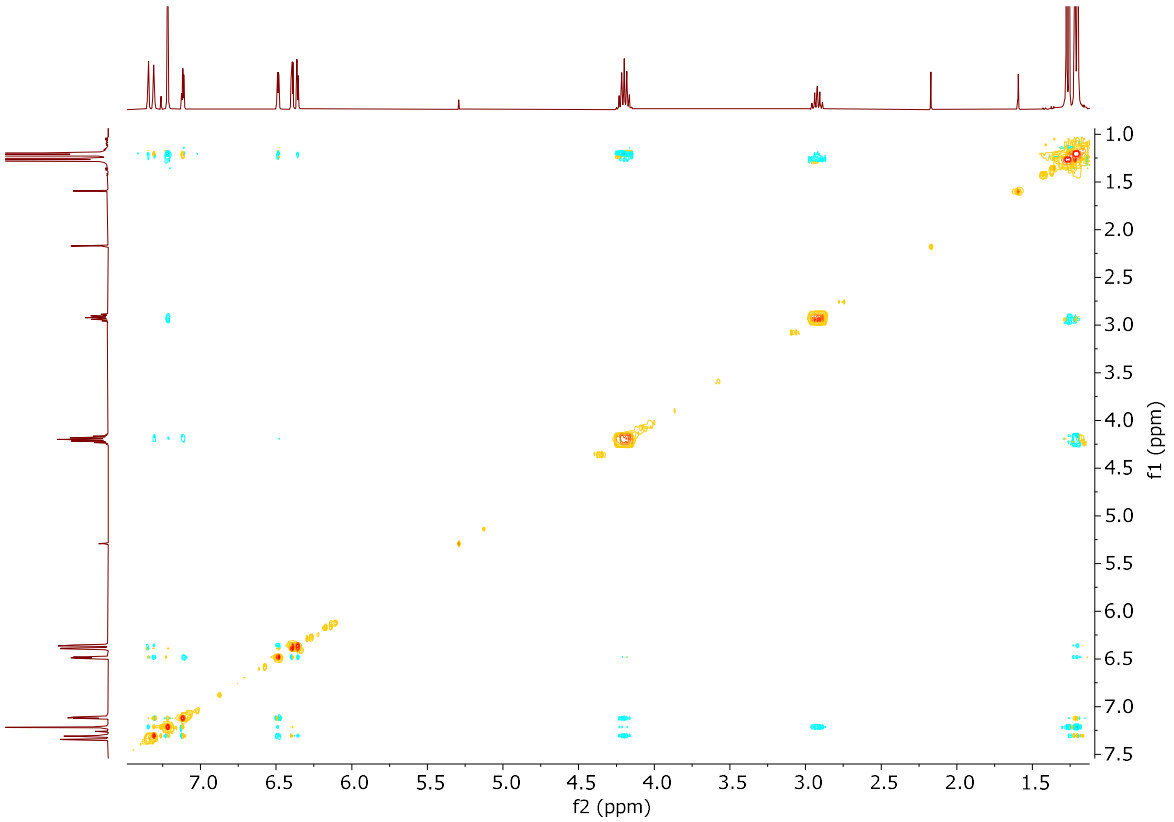


*Figure S61: NOESY NMR spectrum of 3-(furan-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5g** in $CDCl_3$*

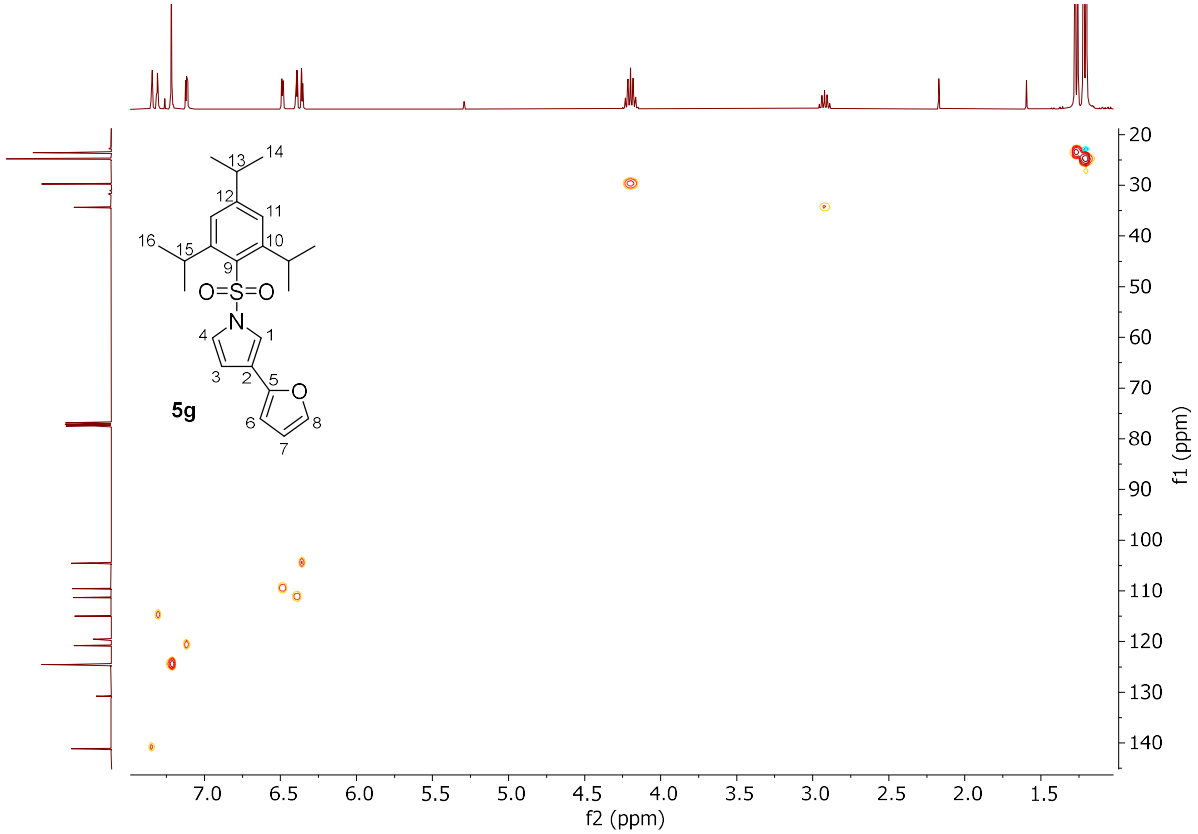


*Figure S62: HSQC NMR spectrum of 3-(furan-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5g** in $CDCl_3$*

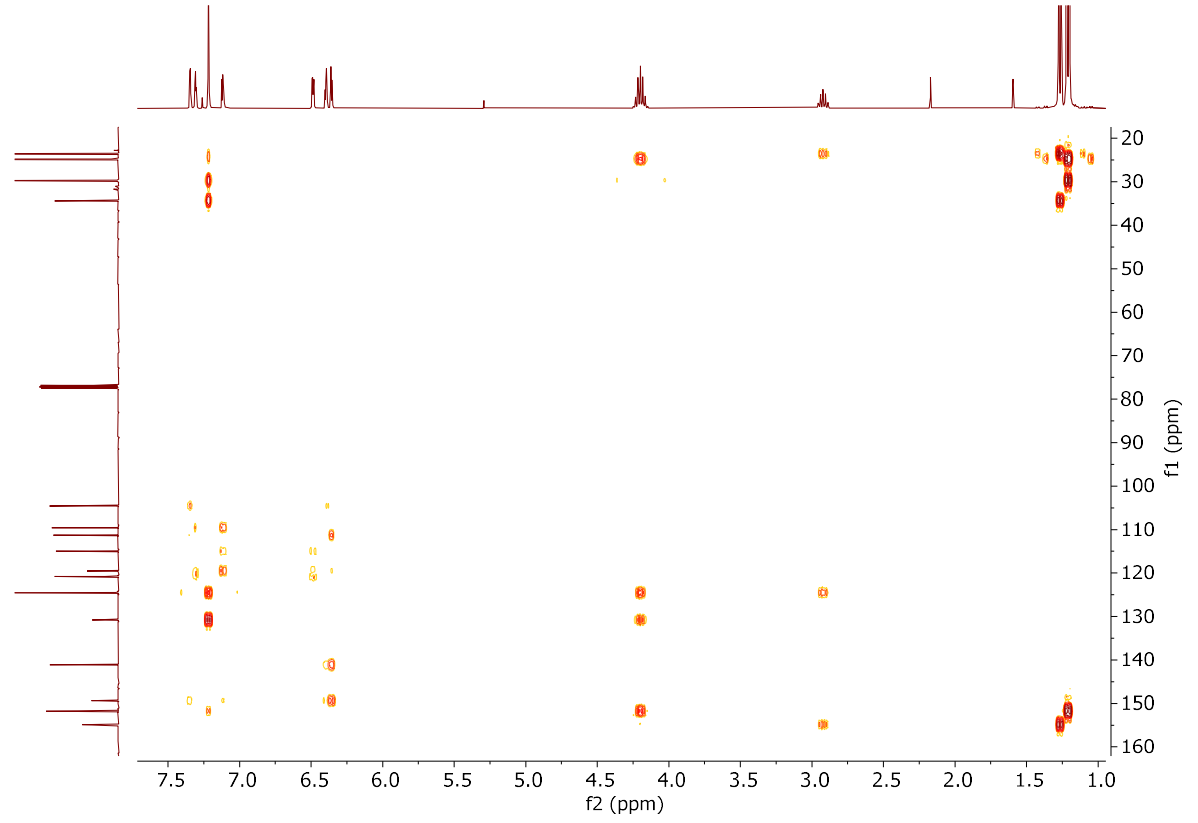


*Figure S63: HMBC NMR spectrum of 3-(furan-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5g** in $CDCl_3$*

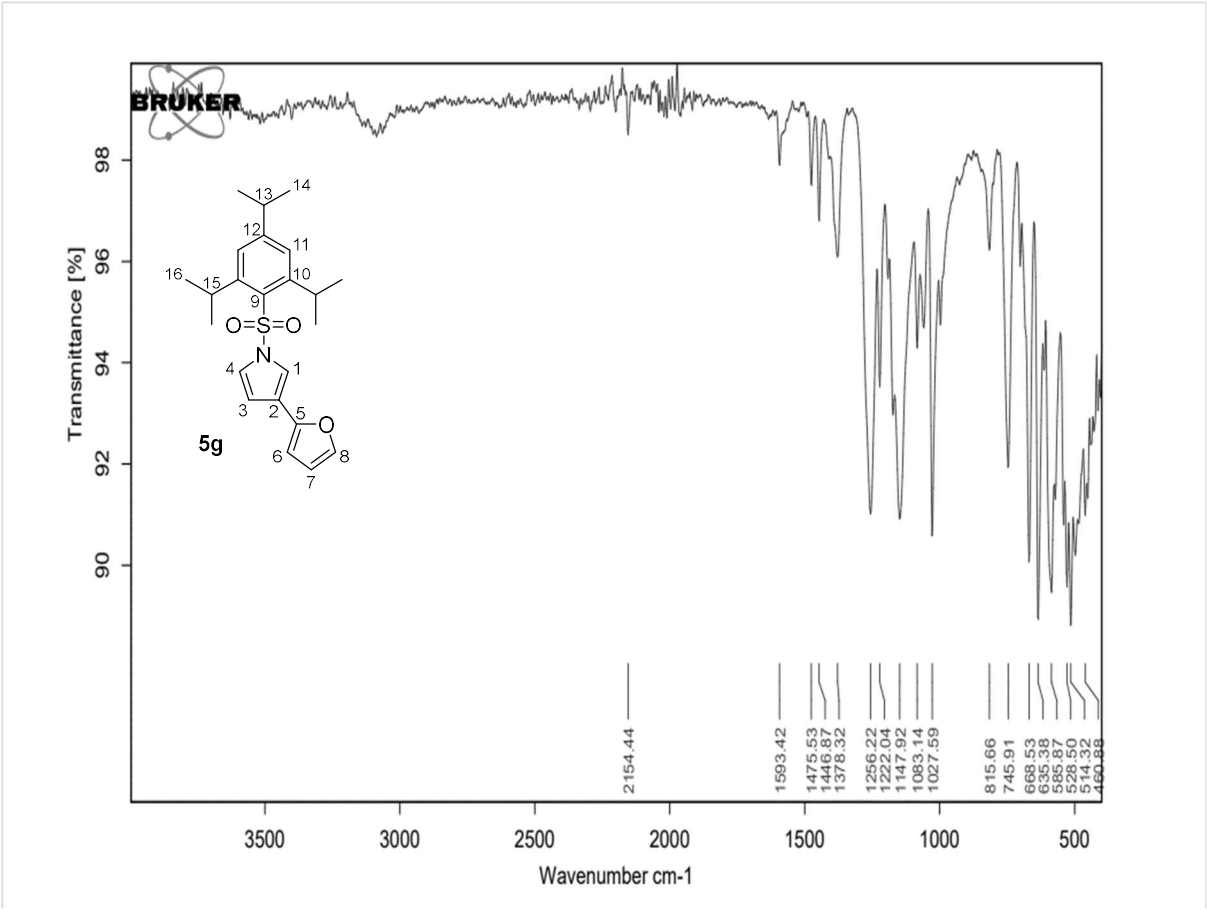


*Figure S64: IR spectrum of 3-(furan-2-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5g***

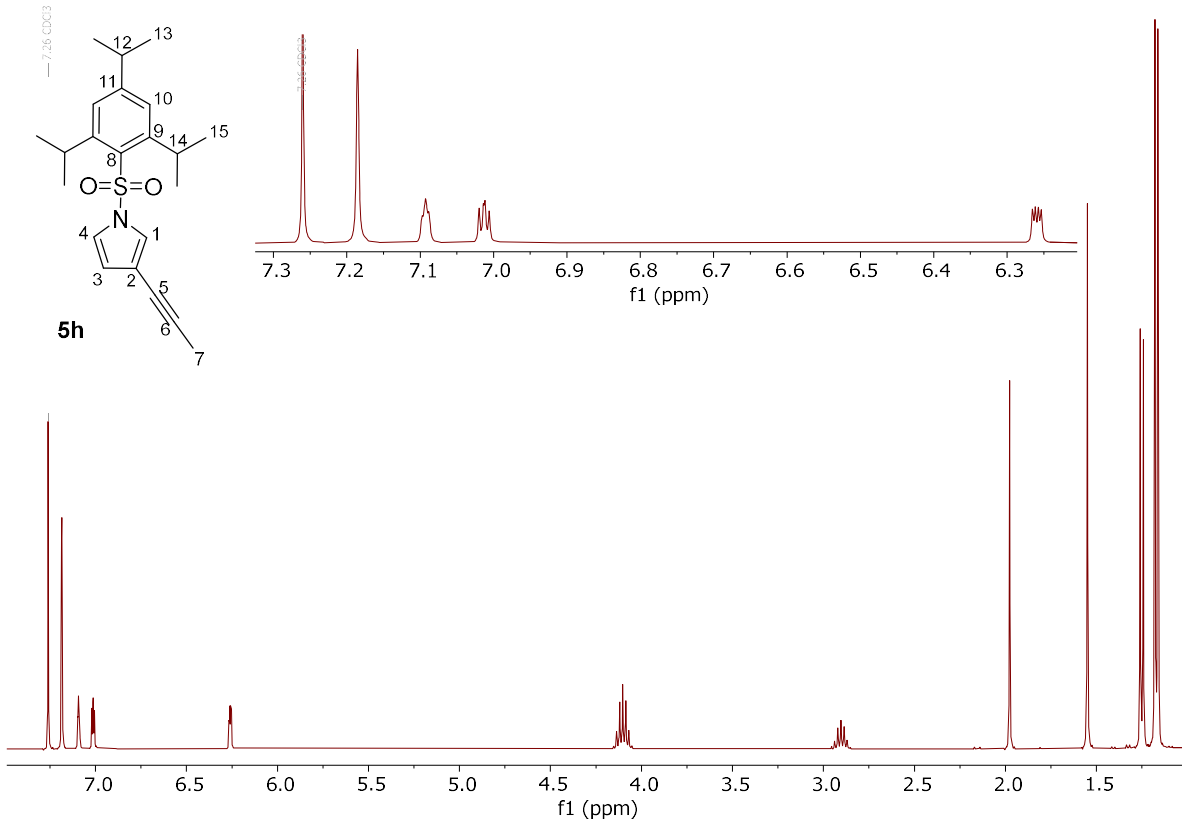


*Figure S65: [1]H NMR spectrum of 3-(prop-1-yn-1-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5h** in $CDCl_3$*

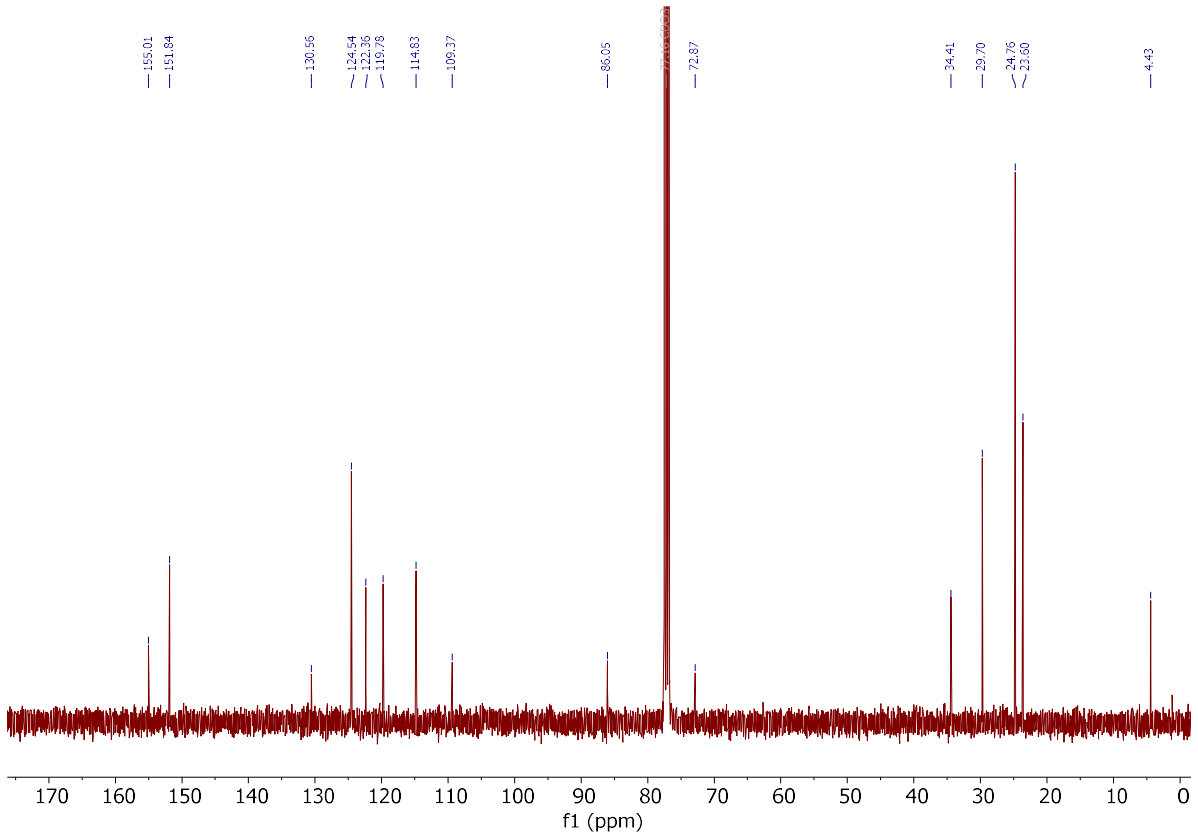


*Figure S66: [13]C NMR spectrum of 3-(prop-1-yn-1-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5h** in $CDCl_3$*

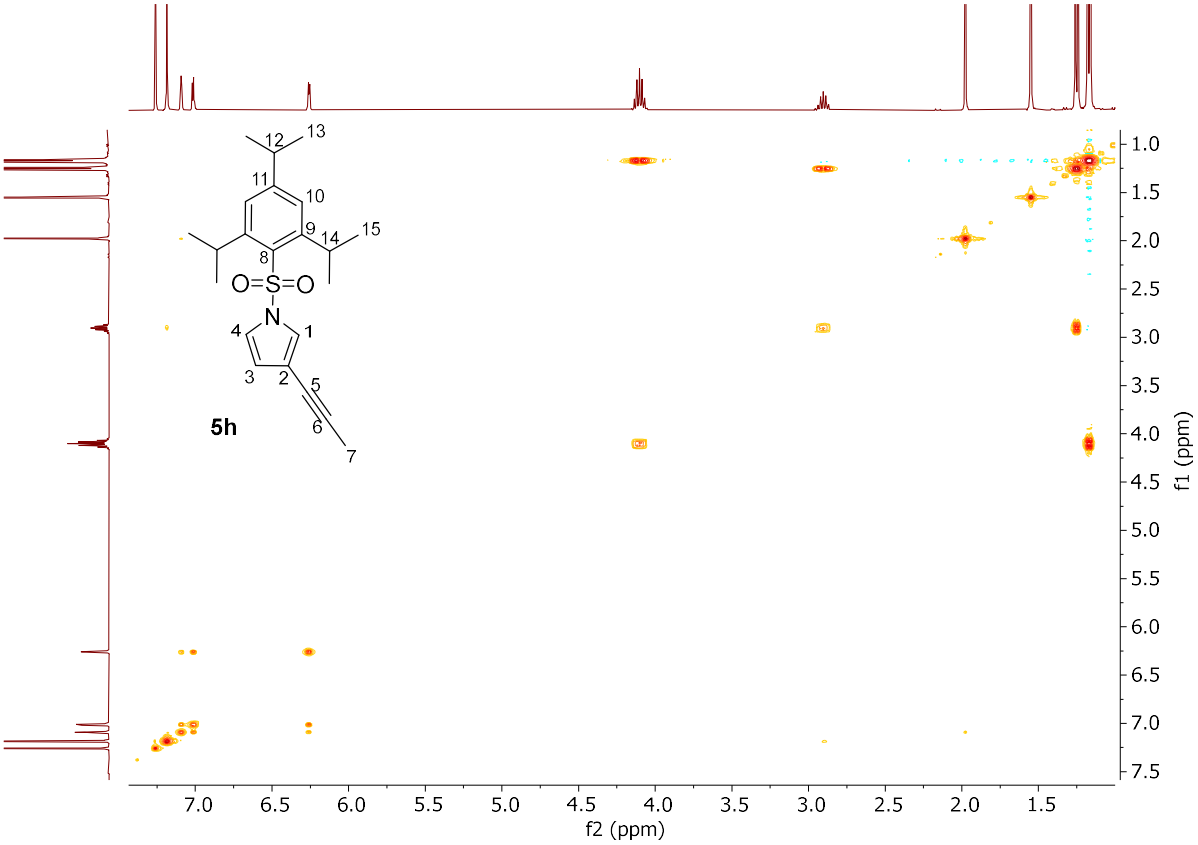


*Figure S67: COSY NMR spectrum of 3-(prop-1-yn-1-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5h** in $CDCl_3$*

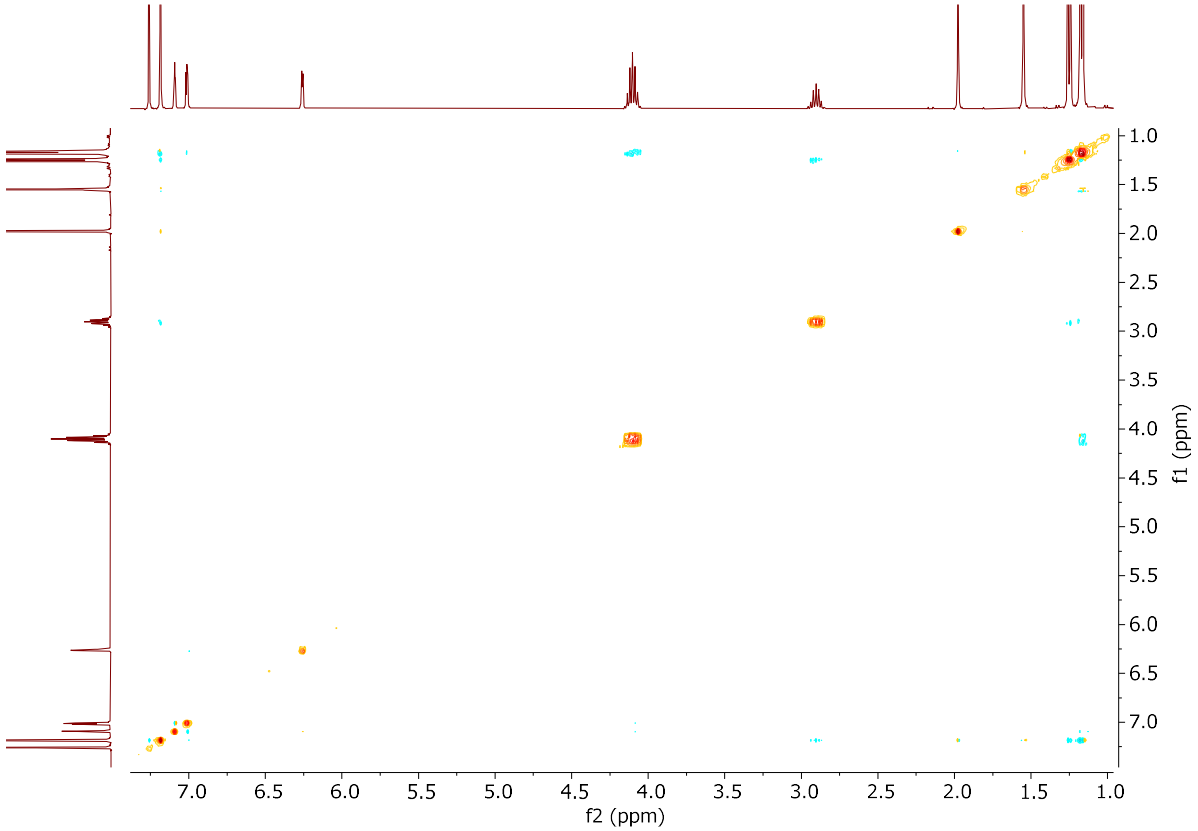


*Figure S68: NOESY NMR spectrum of 3-(prop-1-yn-1-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5h** in $CDCl_3$*

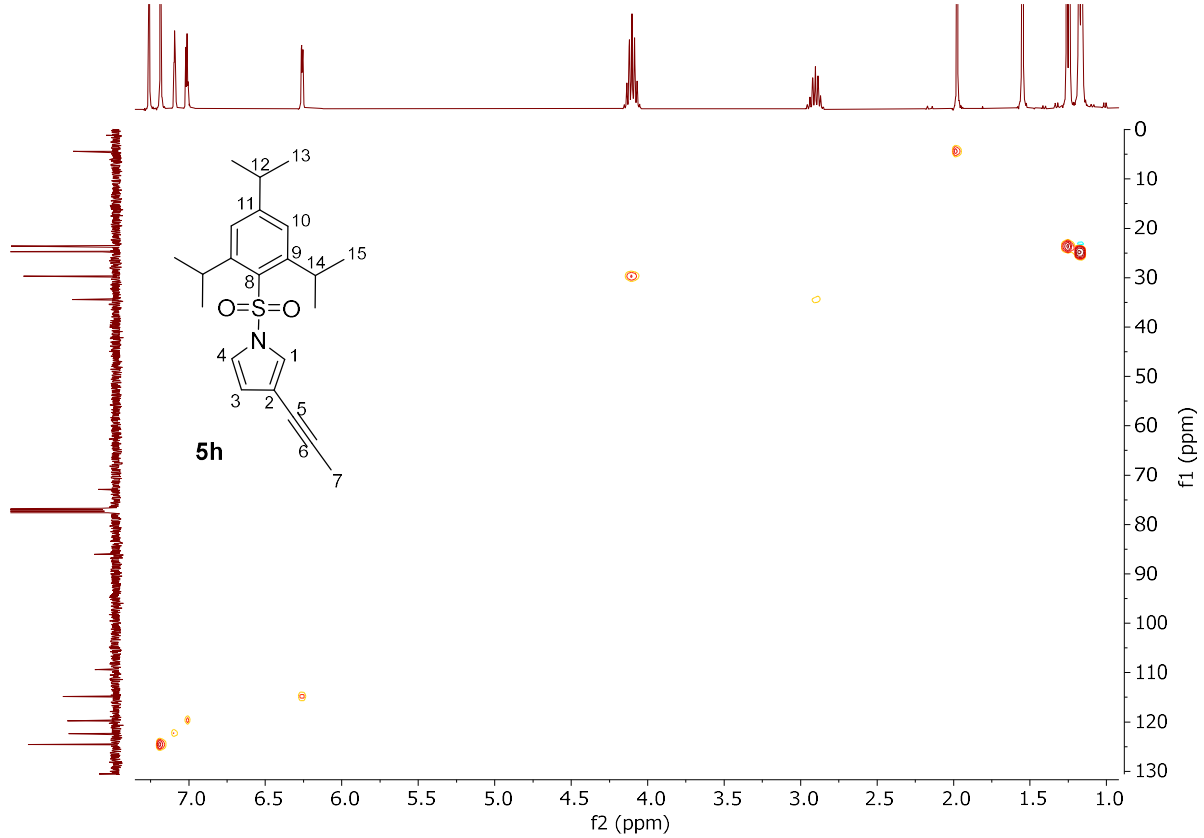


*Figure S69: HSQC NMR spectrum of 3-(prop-1-yn-1-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5h** in $CDCl_3$*

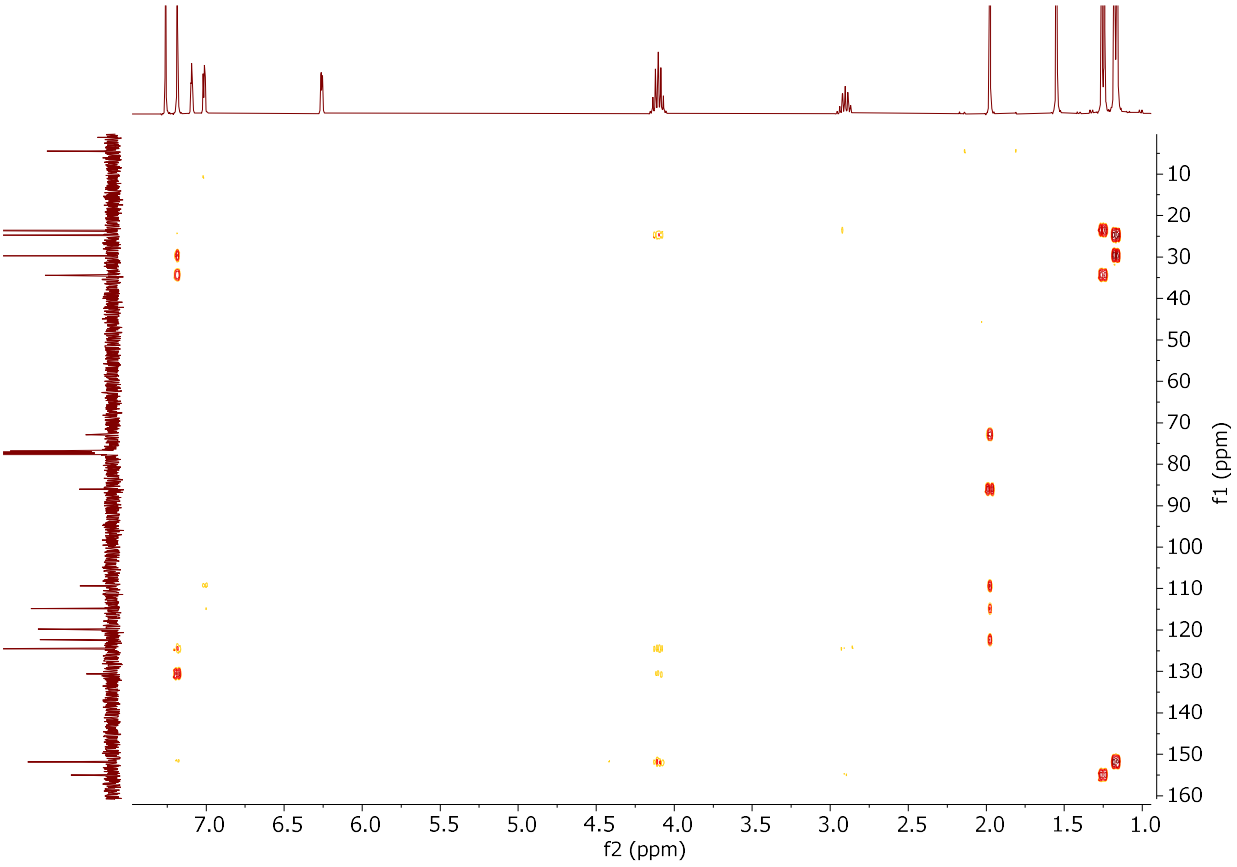


*Figure S70: HMBC NMR spectrum of 3-(prop-1-yn-1-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5h** in $CDCl_3$*

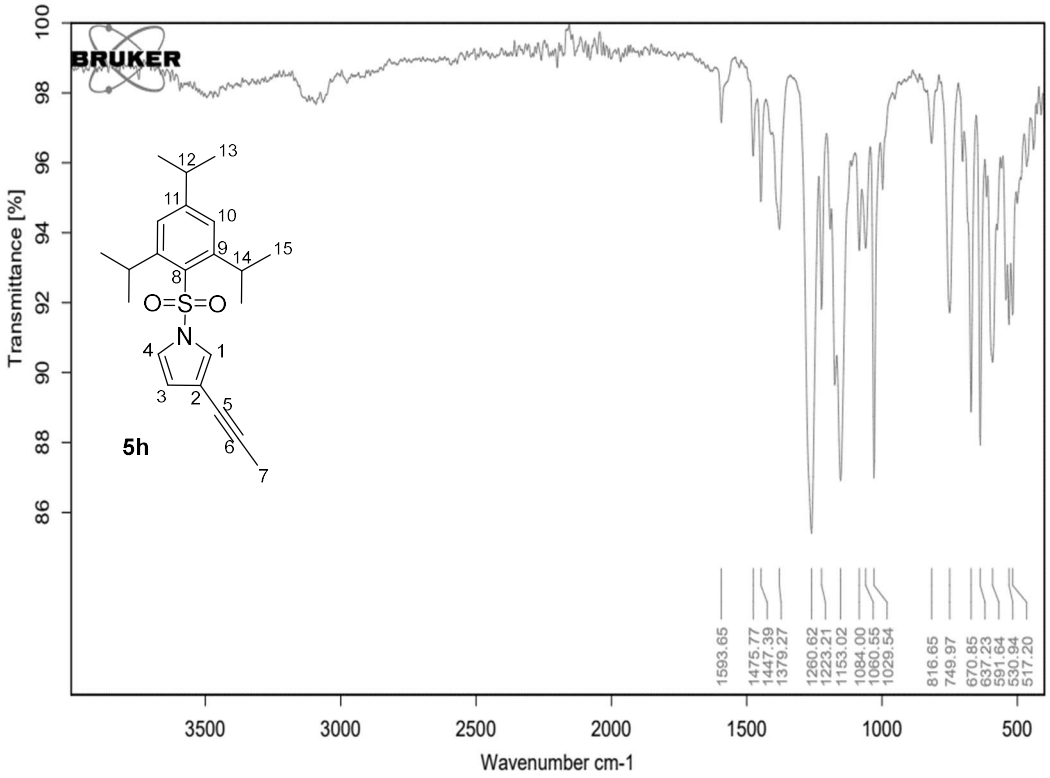


*Figure S71: IR spectrum of 3-(prop-1-yn-1-yl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5h***

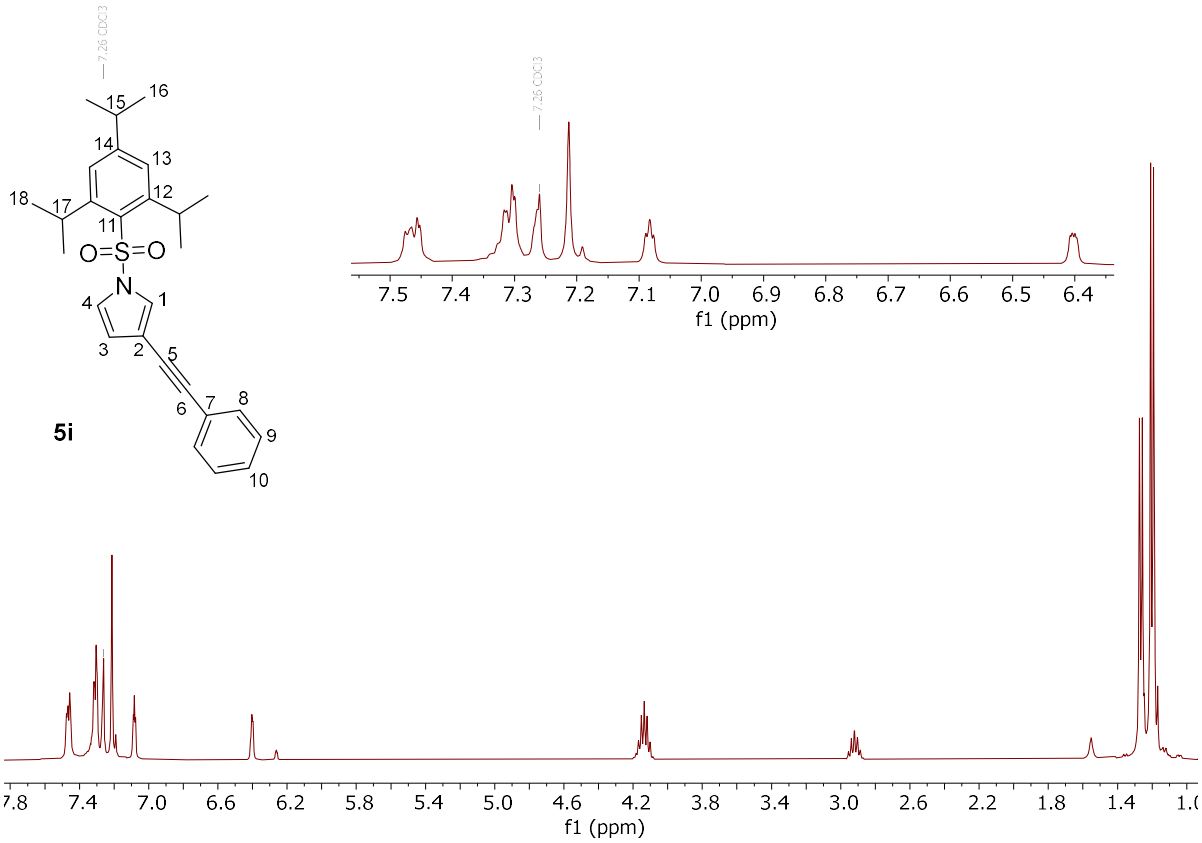


*Figure S72: ^{1}H NMR spectrum of 3-(phenylethynyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5i** in $CDCl_3$*

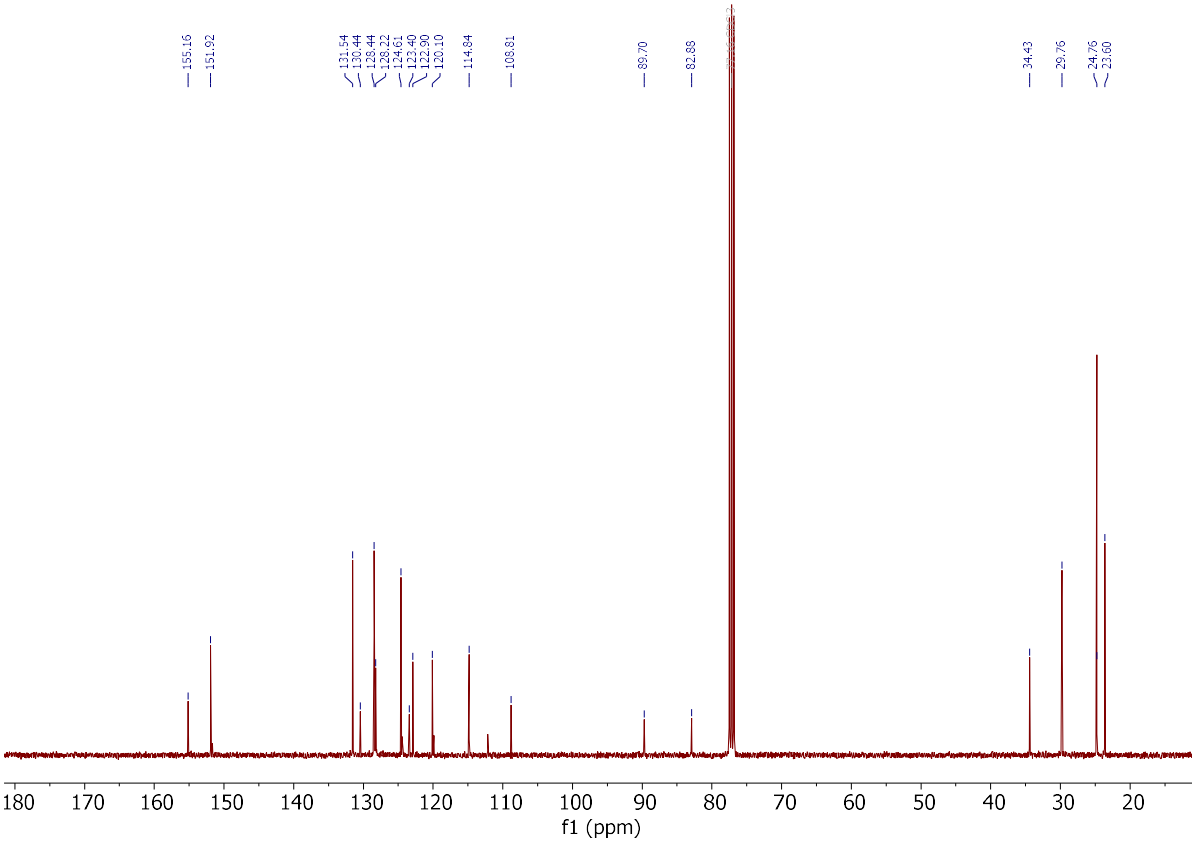


*Figure S73: ^{13}C NMR spectrum of 3-(phenylethynyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5i** in $CDCl_3$*

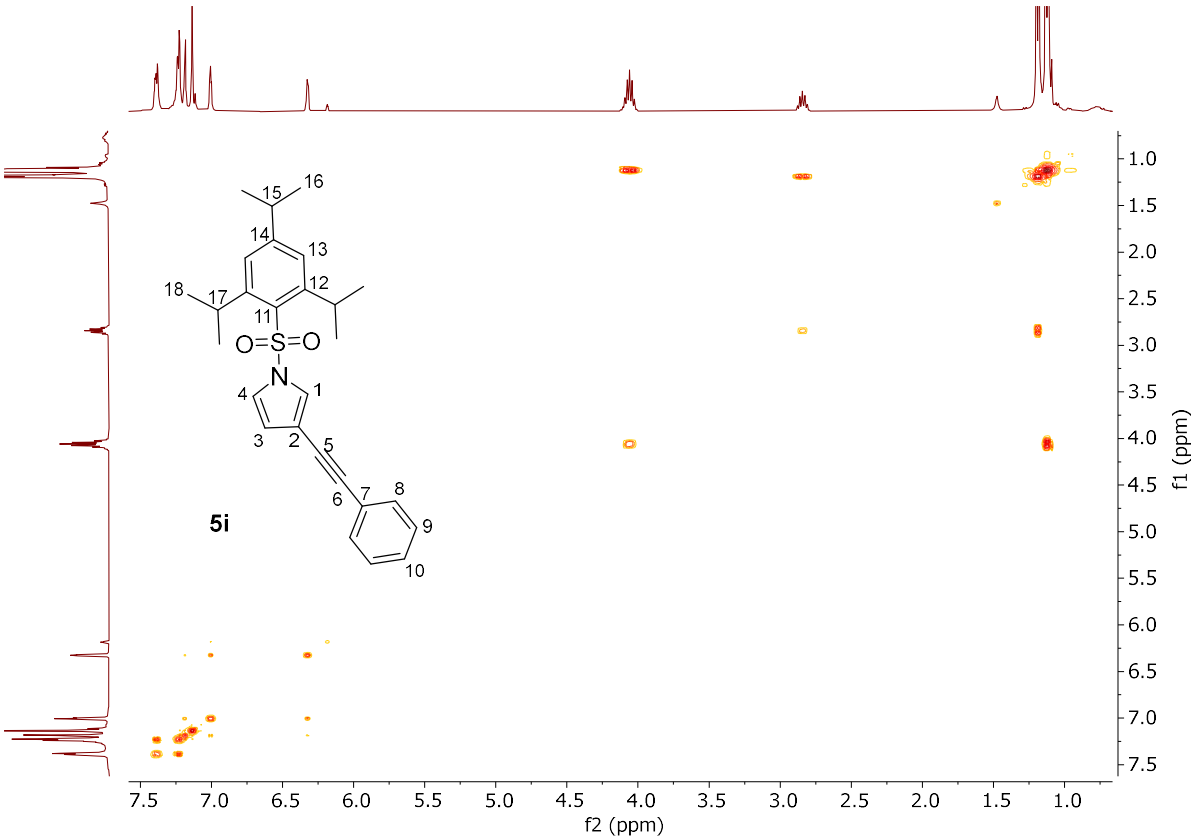


*Figure S74: COSY NMR spectrum of 3-(phenylethynyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5i** in $CDCl_3$*

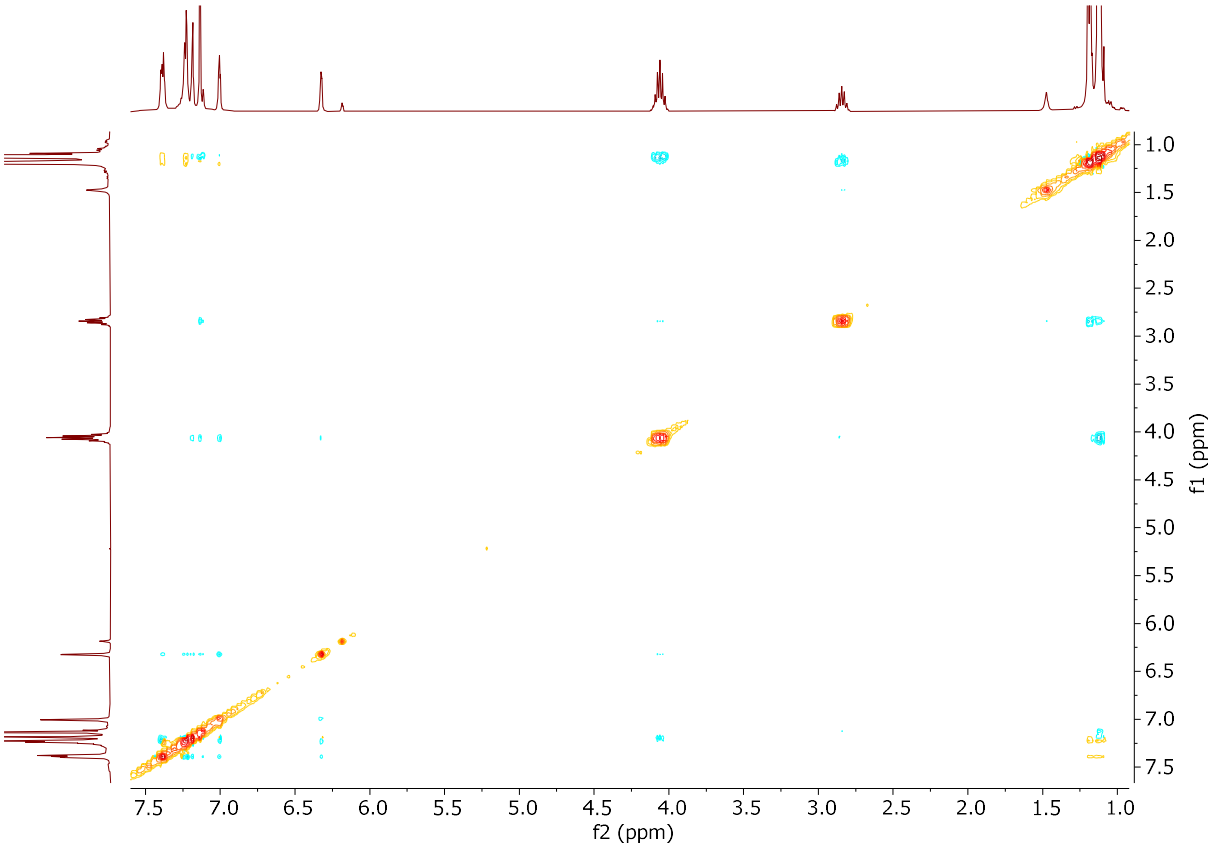


*Figure S75: NOESY NMR spectrum of 3-(phenylethynyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5i** in $CDCl_3$*

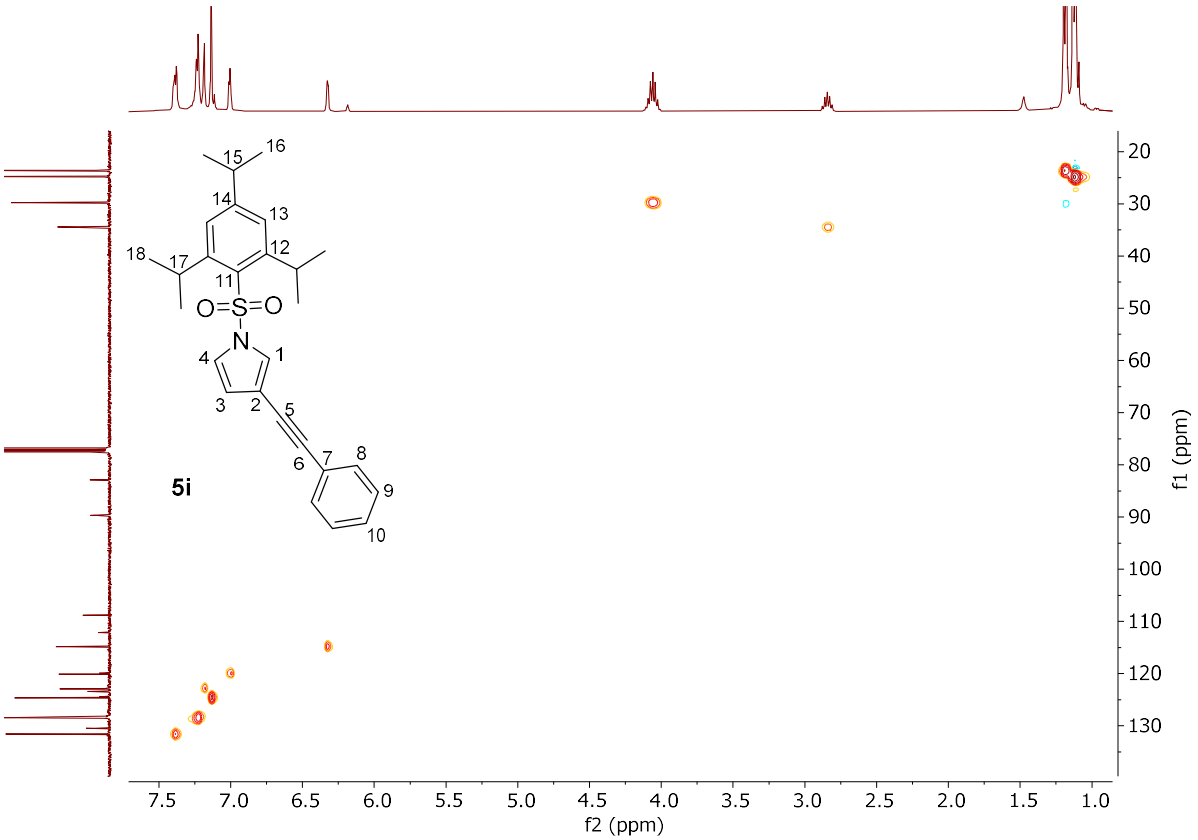


*Figure S76: HSQC NMR NMR spectrum of 3-(phenylethynyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5i** in $CDCl_3$*

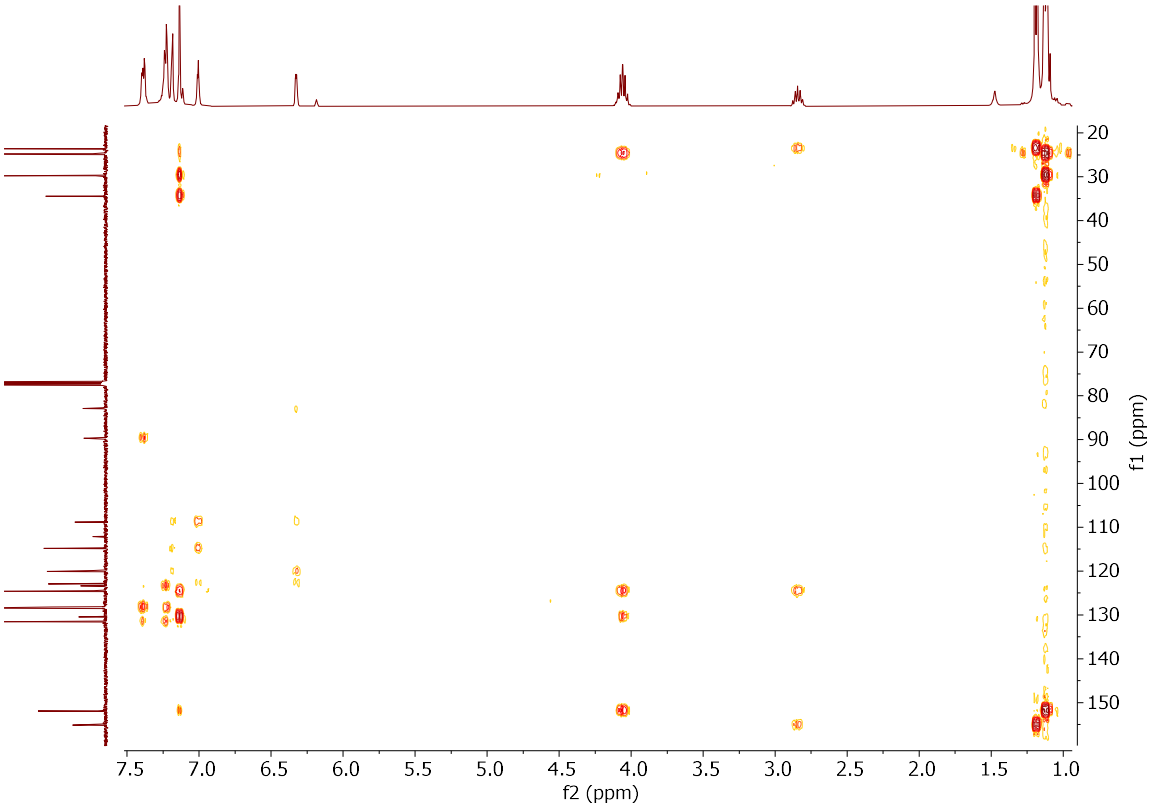


*Figure S77: HMBC NMR spectrum of 3-(phenylethynyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **5i** in $CDCl_3$*

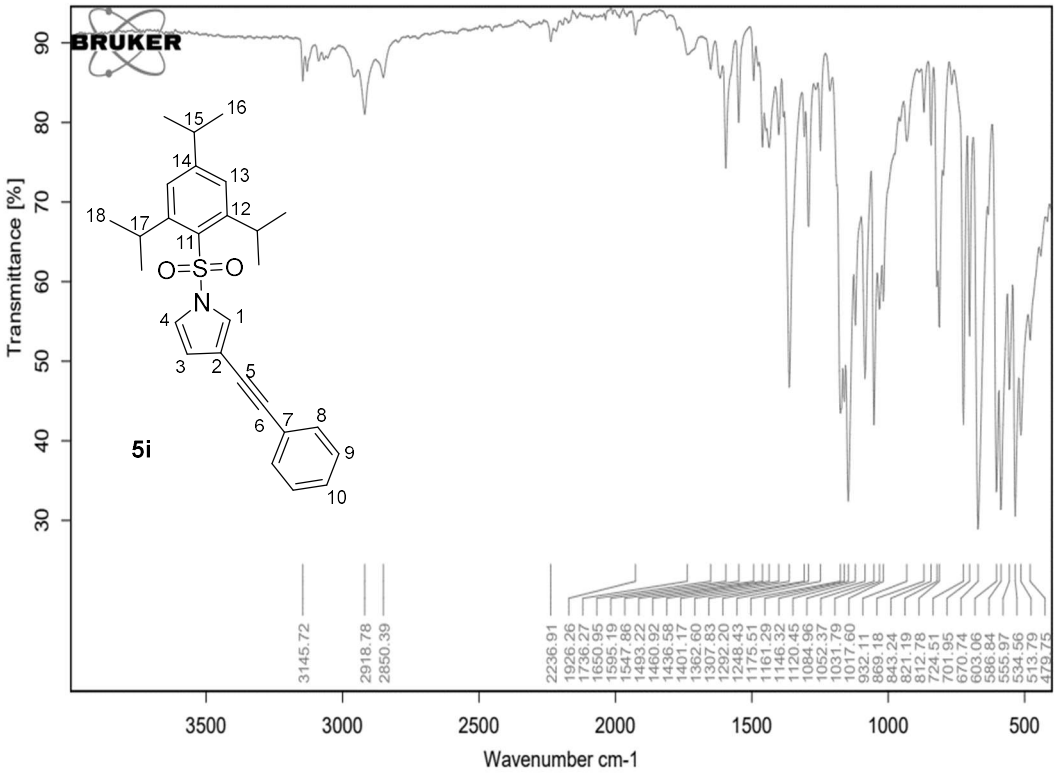


*Figure S78: IR spectrum of 3-(phenylethynyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **5i***

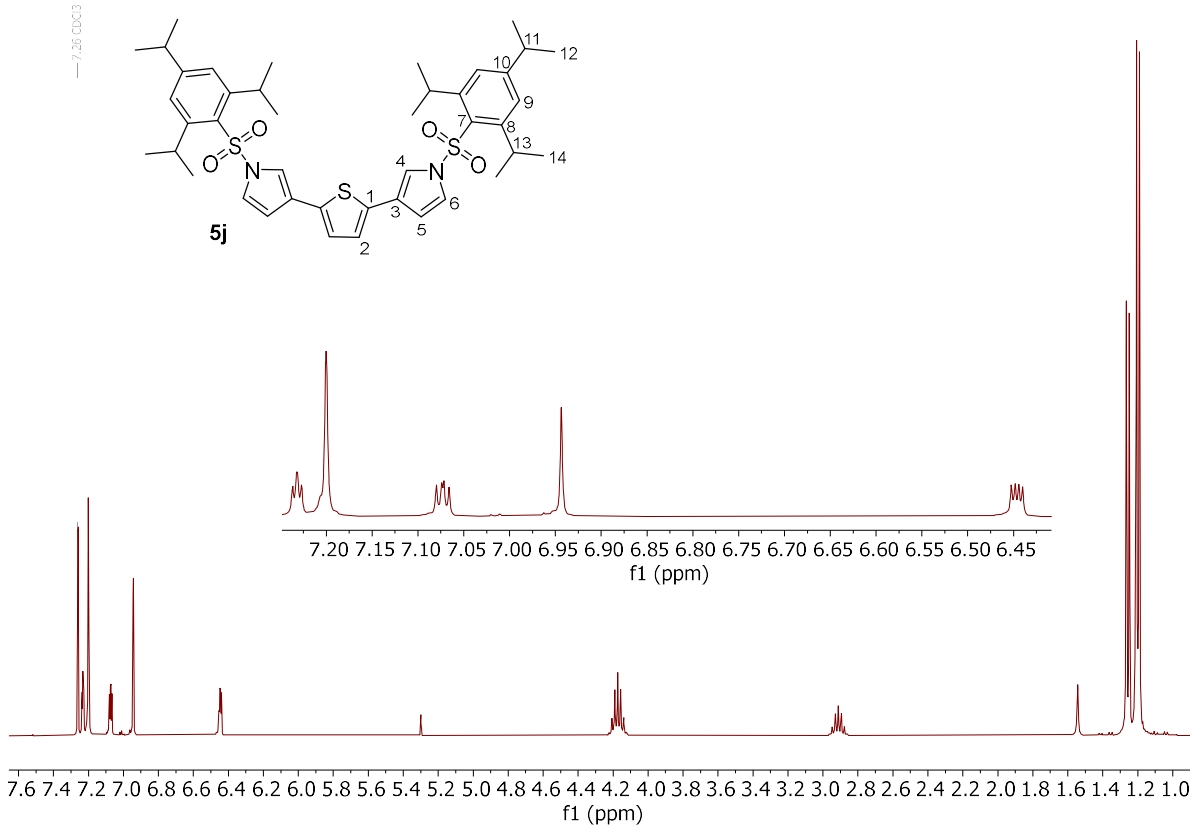


*Figure S79: ^{1}H NMR spectrum of 2,5-bis(1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrol-3-yl)thiophene **5j** in $CDCl_3$*

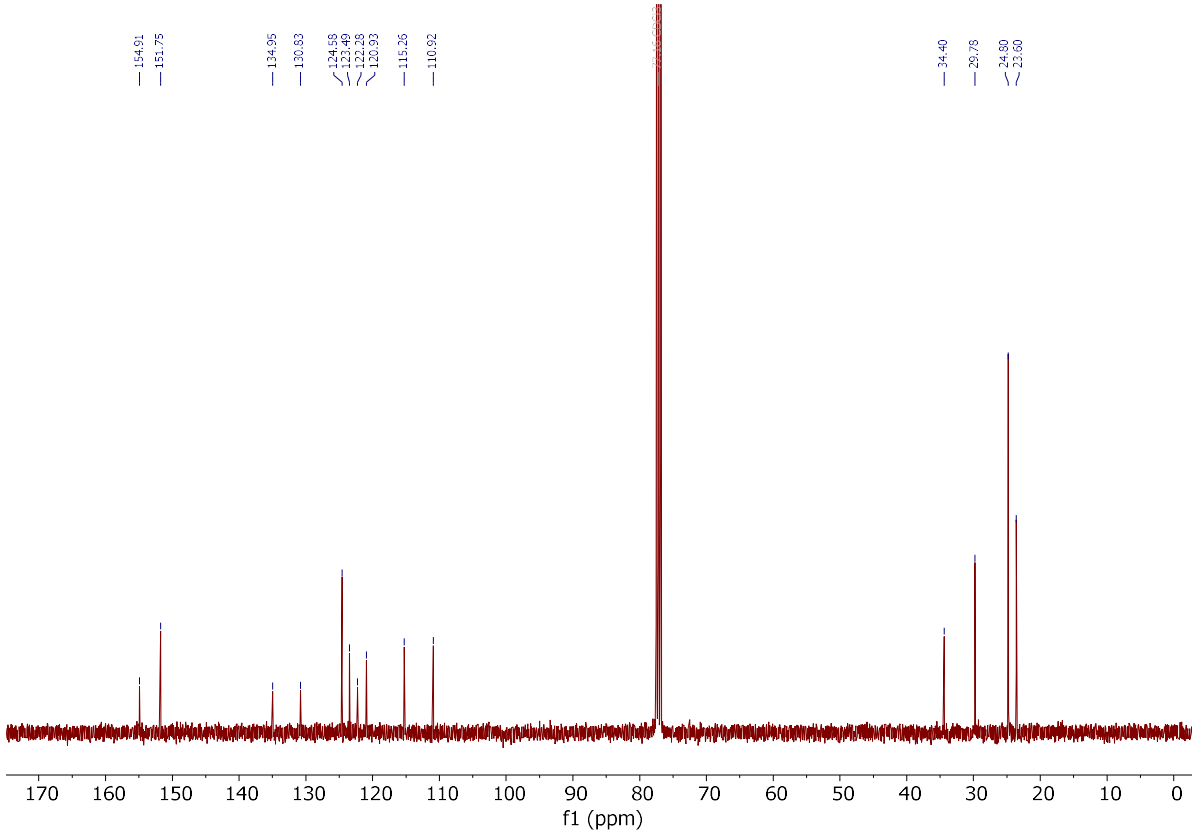


*Figure S80: ^{13}C NMR spectrum of 2,5-bis(1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrol-3-yl)thiophene **5j** in $CDCl_3$*

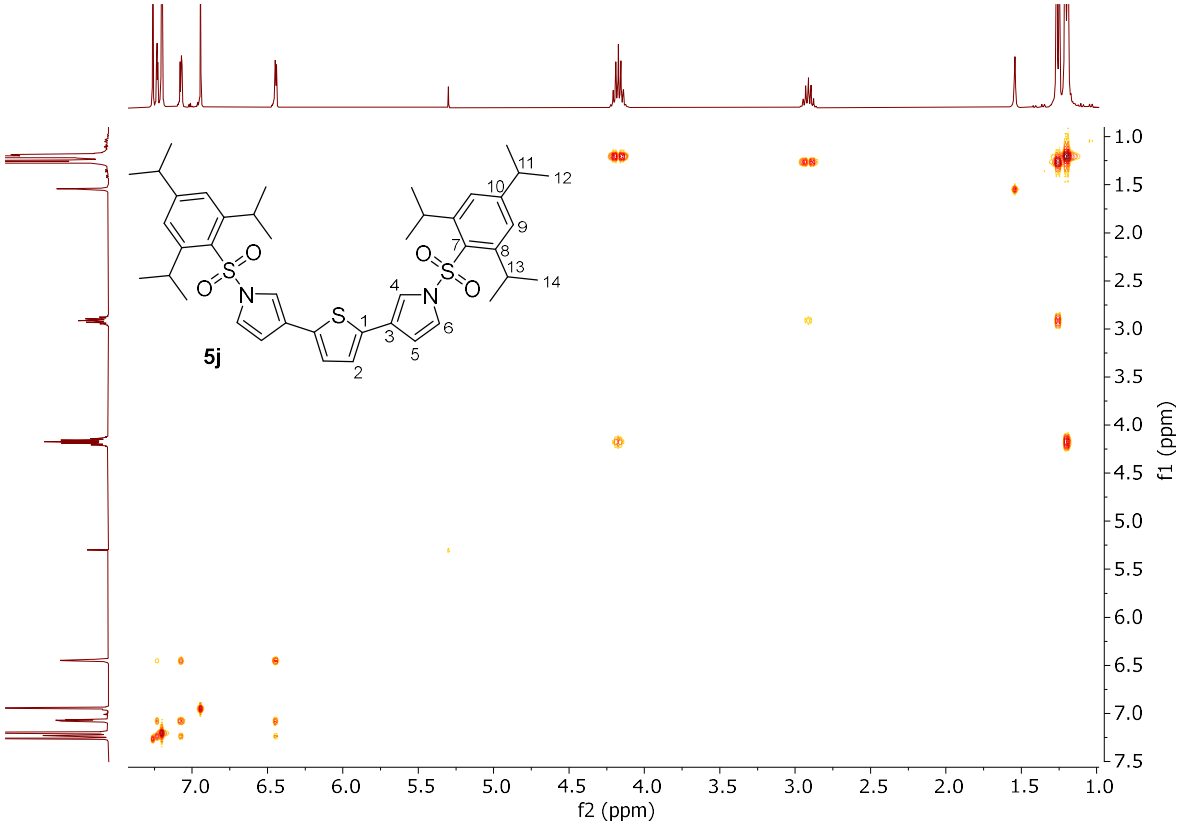


*Figure S81: COSY NMR spectrum of 2,5-bis(1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrol-3-yl)thiophene **5j** in $CDCl_3$*

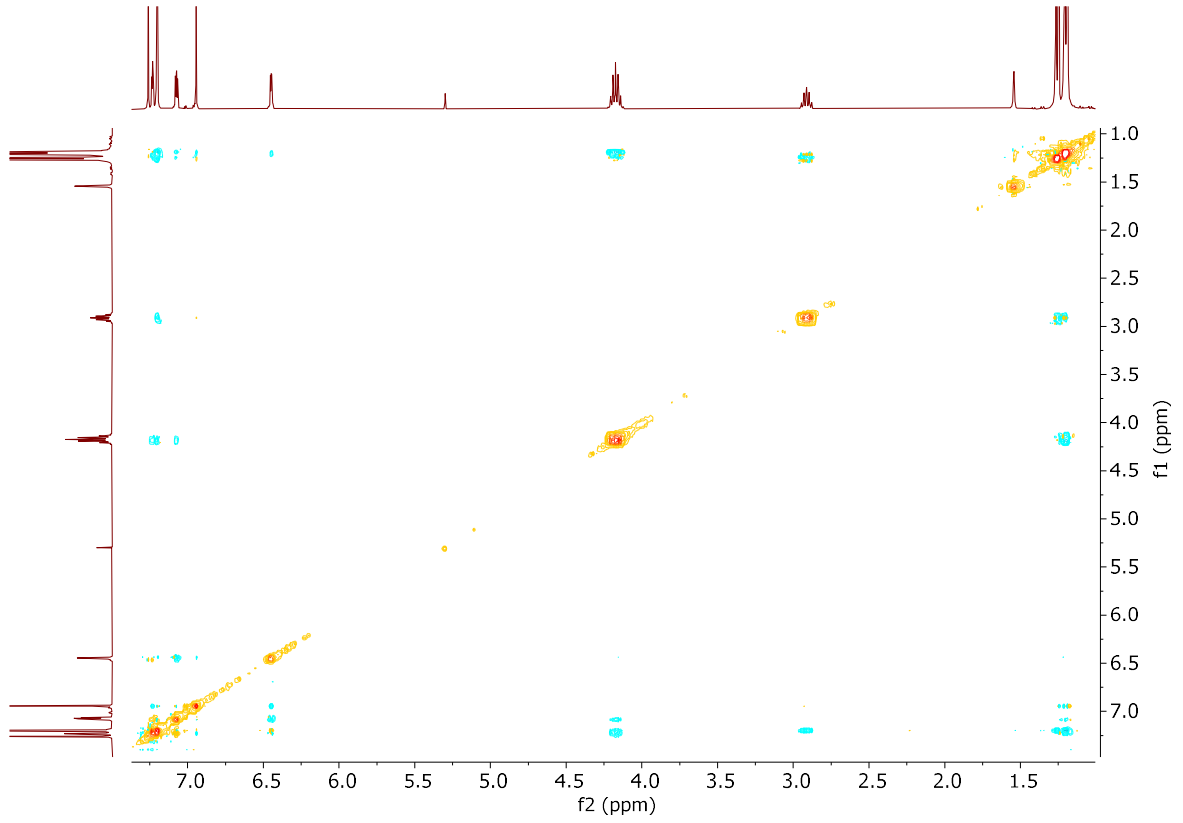


*Figure S82: NOESY NMR spectrum of 2,5-bis(1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrol-3-yl)thiophene **5j** in $CDCl_3$*

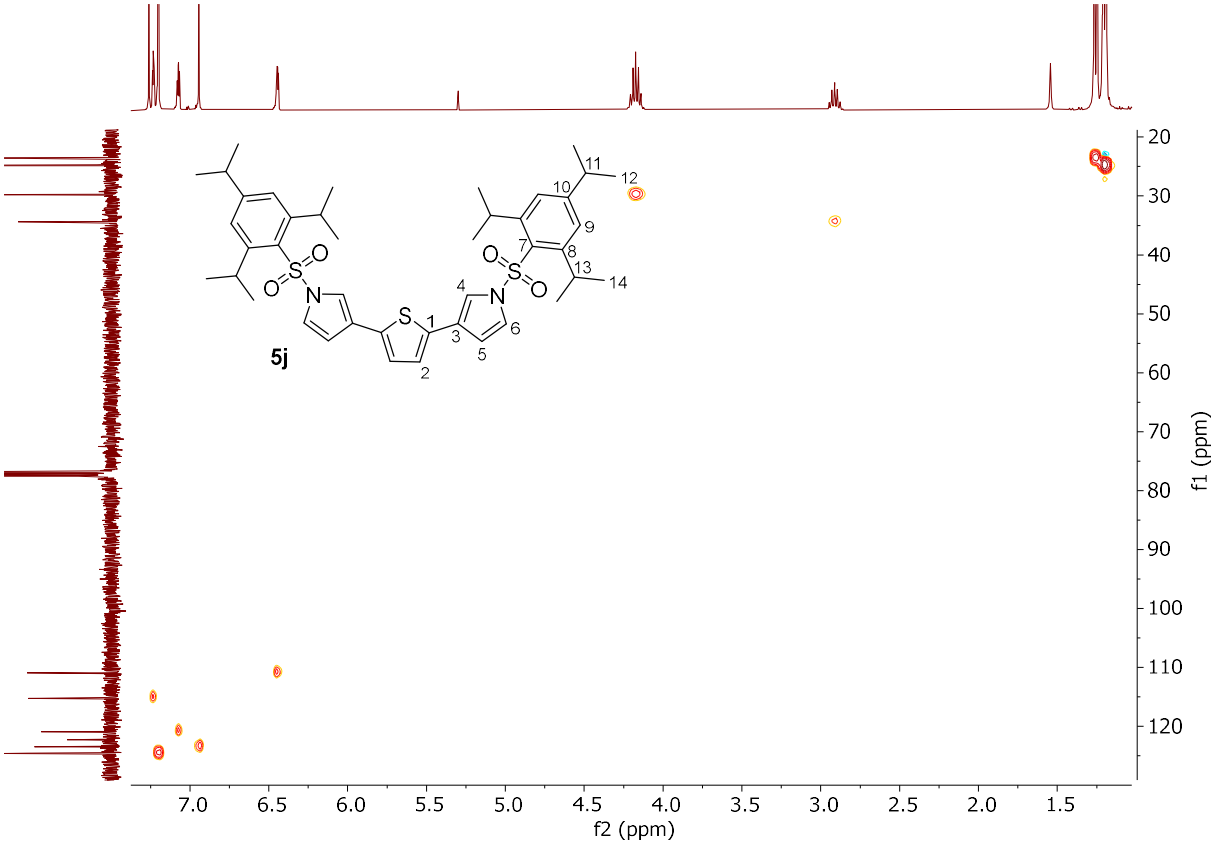


*Figure S83: HSQC NMR spectrum of 2,5-bis(1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrol-3-yl)thiophene **5j** in $CDCl_3$*

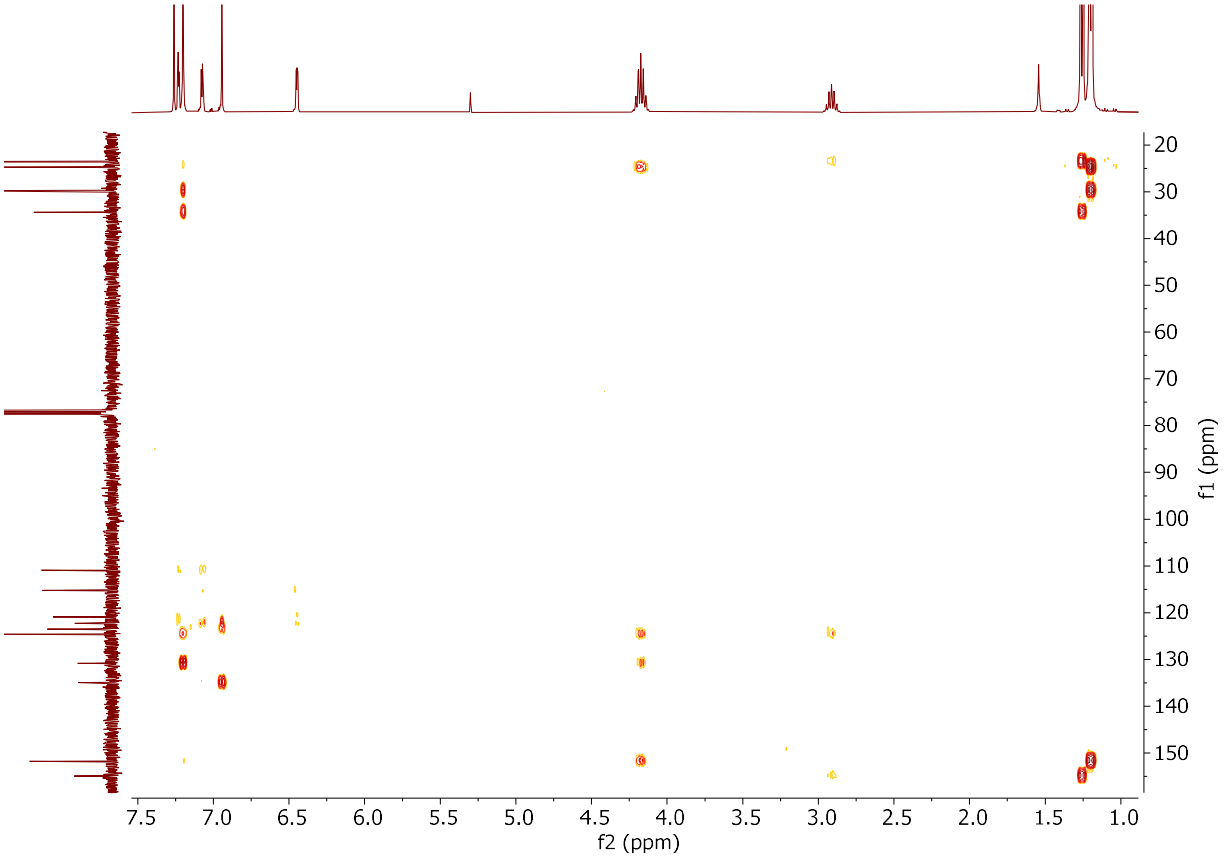


*Figure S84: HMBC NMR spectrum of 2,5-bis(1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrol-3-yl)thiophene **5j** in $CDCl_3$*

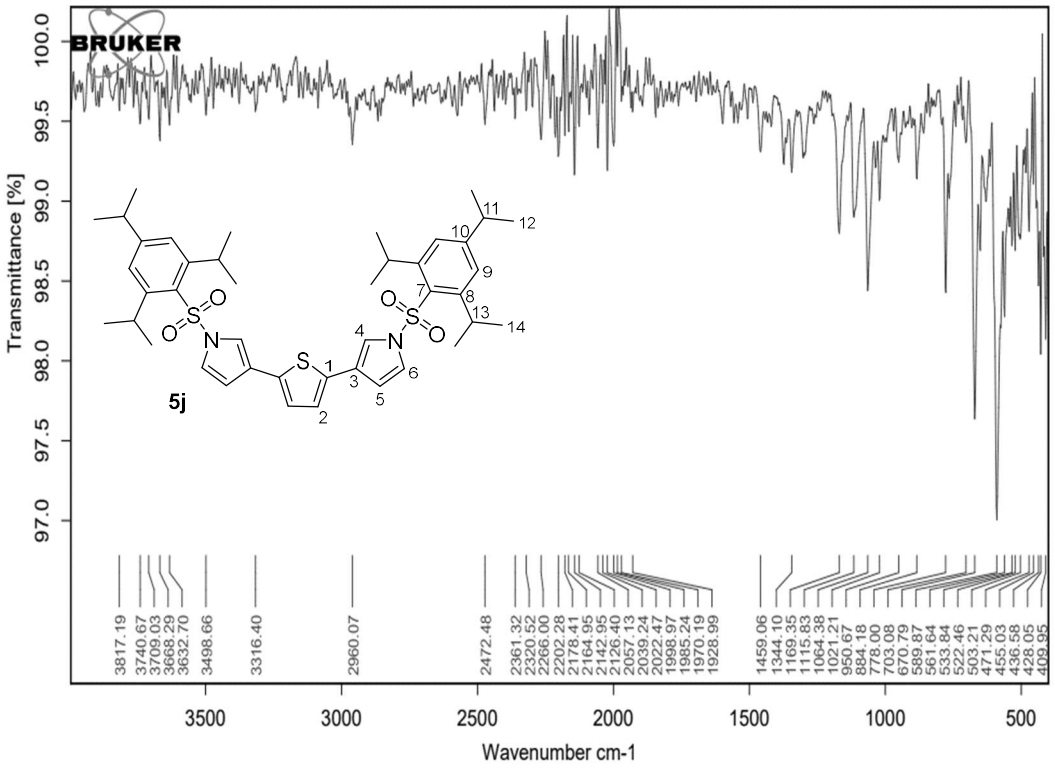


*Figure S85: IR spectrum of spectrum of 2,5-bis(1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrol-3-yl)thiophene **5j***

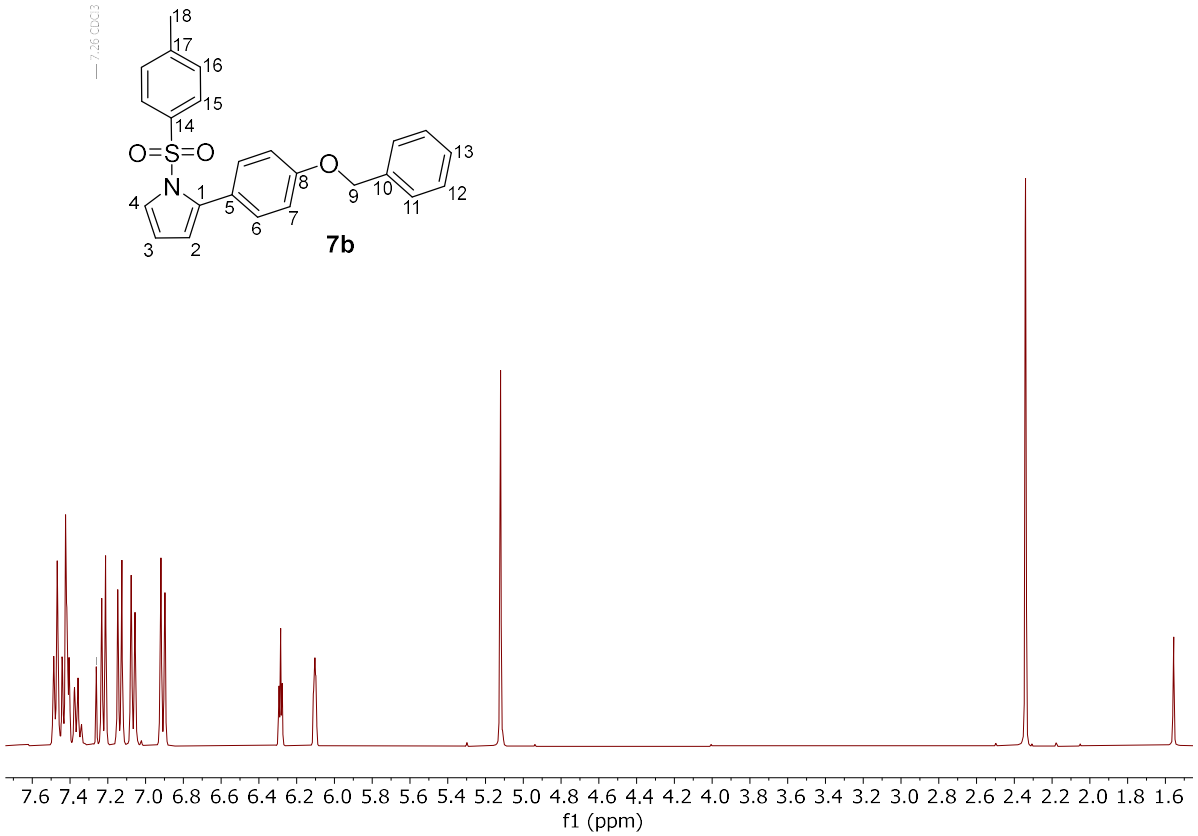


*Figure S86: ^{1}H NMR spectrum of 2-(4-(benzyloxy)phenyl)-1-(p-toluenesulfonyl)-1H-pyrrole **7b** in $CDCl_3$.*

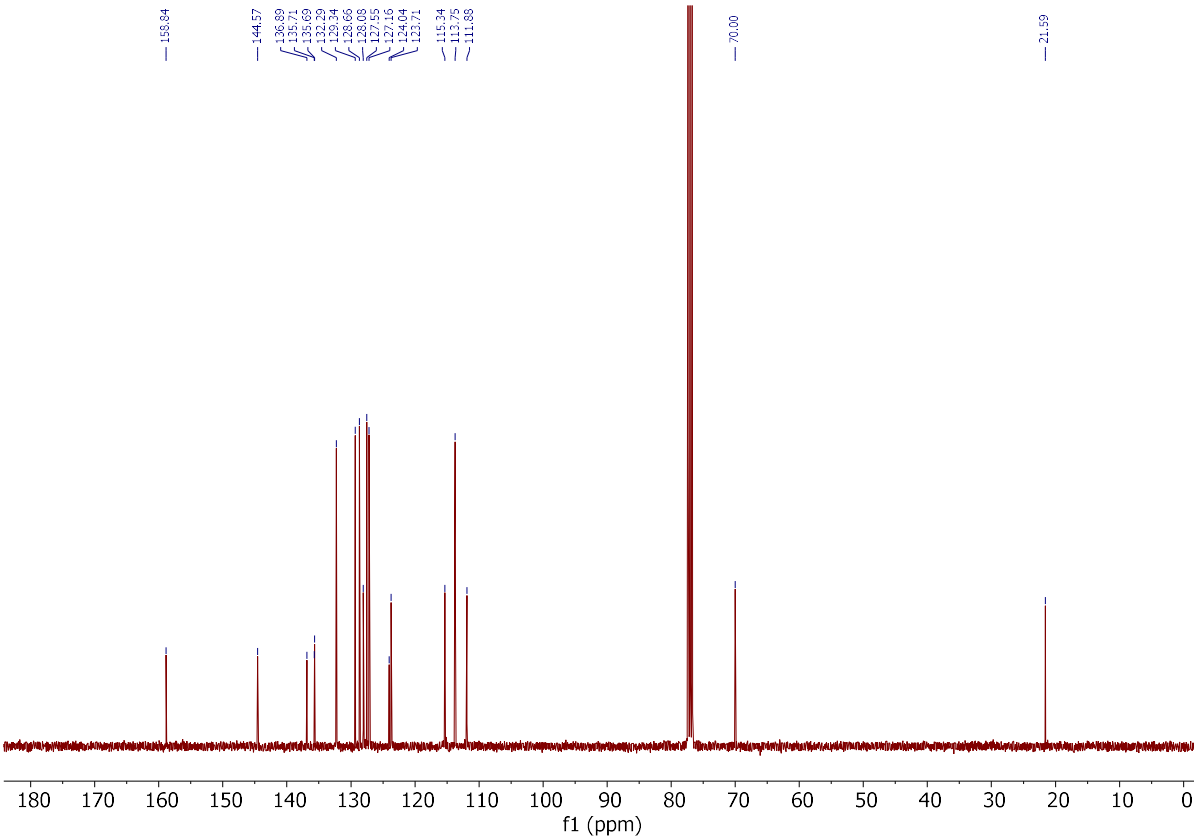


*Figure S87: ^{13}C NMR spectrum of 2-(4-(benzyloxy)phenyl)-1-(p-toluenesulfonyl)-1H-pyrrole **7b** in $CDCl_3$.*

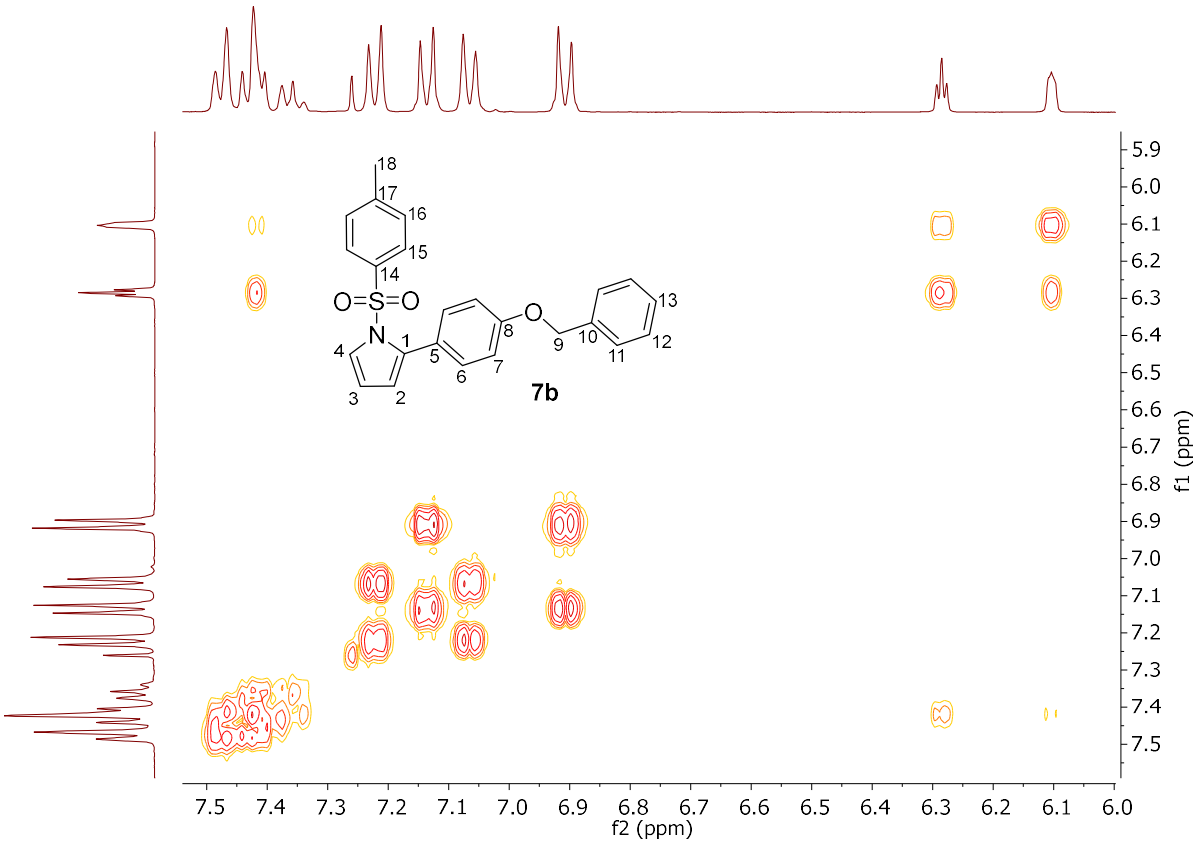


*Figure S88: COSY NMR spectrum of 2-(4-(benzyloxy)phenyl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole **7b** in $CDCl_3$.*

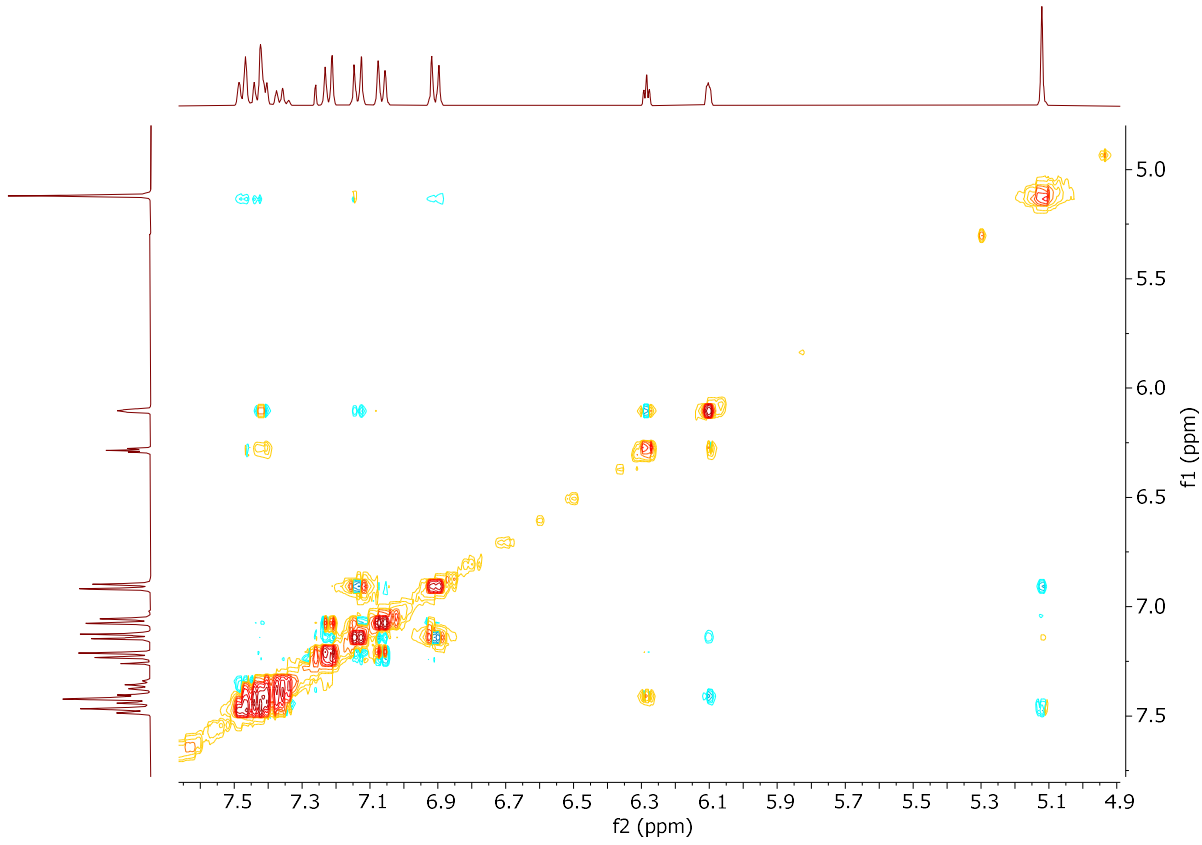


*Figure S89: NOESY NMR spectrum of 2-(4-(benzyloxy)phenyl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole **7b** in $CDCl_3$.*

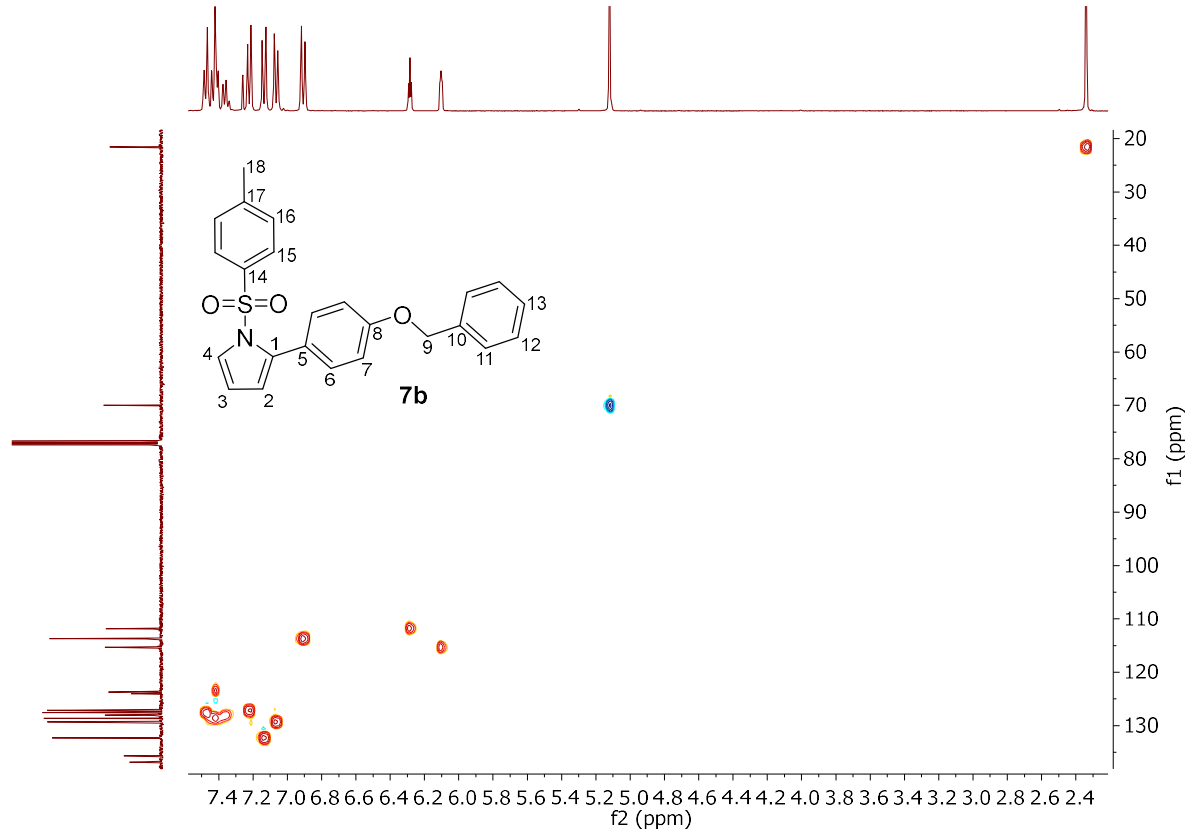


*Figure S90: HSQC NMR spectrum of 2-(4-(benzyloxy)phenyl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole **7b** in $CDCl_3$.*

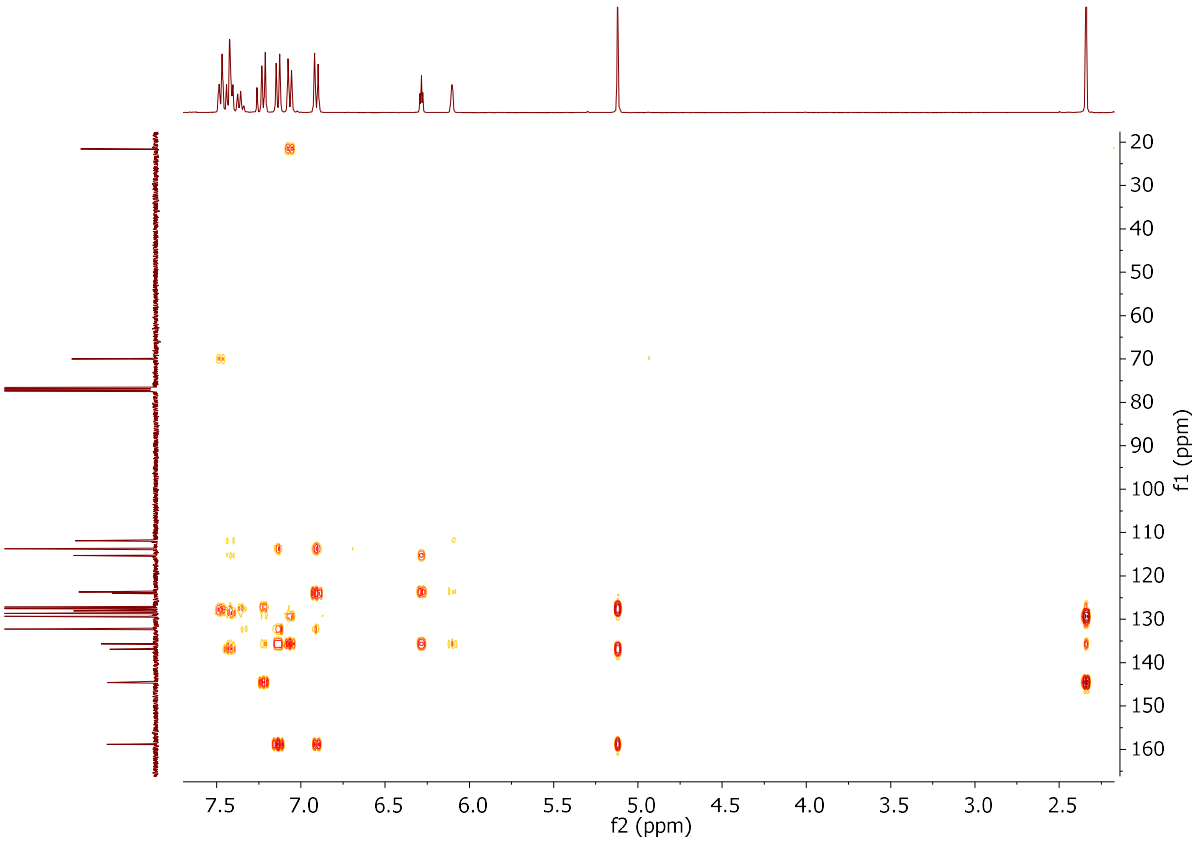


*Figure S91: HMBC NMR spectrum of 2-(4-(benzyloxy)phenyl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole **7b** in $CDCl_3$.*

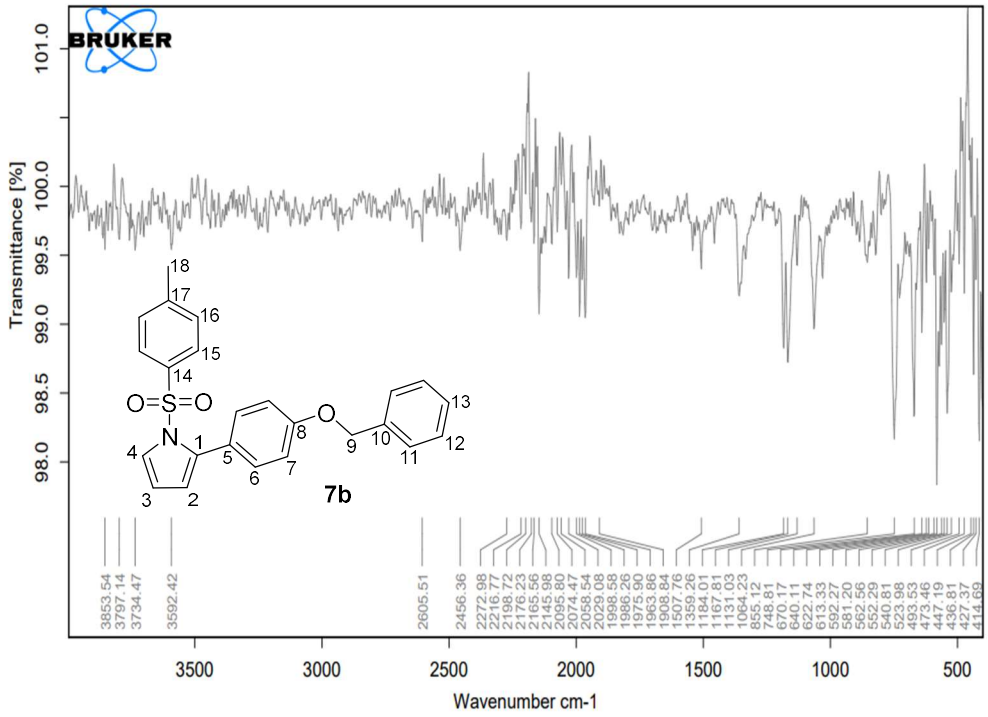


*Figure S92: IR spectrum of 2-(4-(benzyloxy)phenyl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole **7b**.*

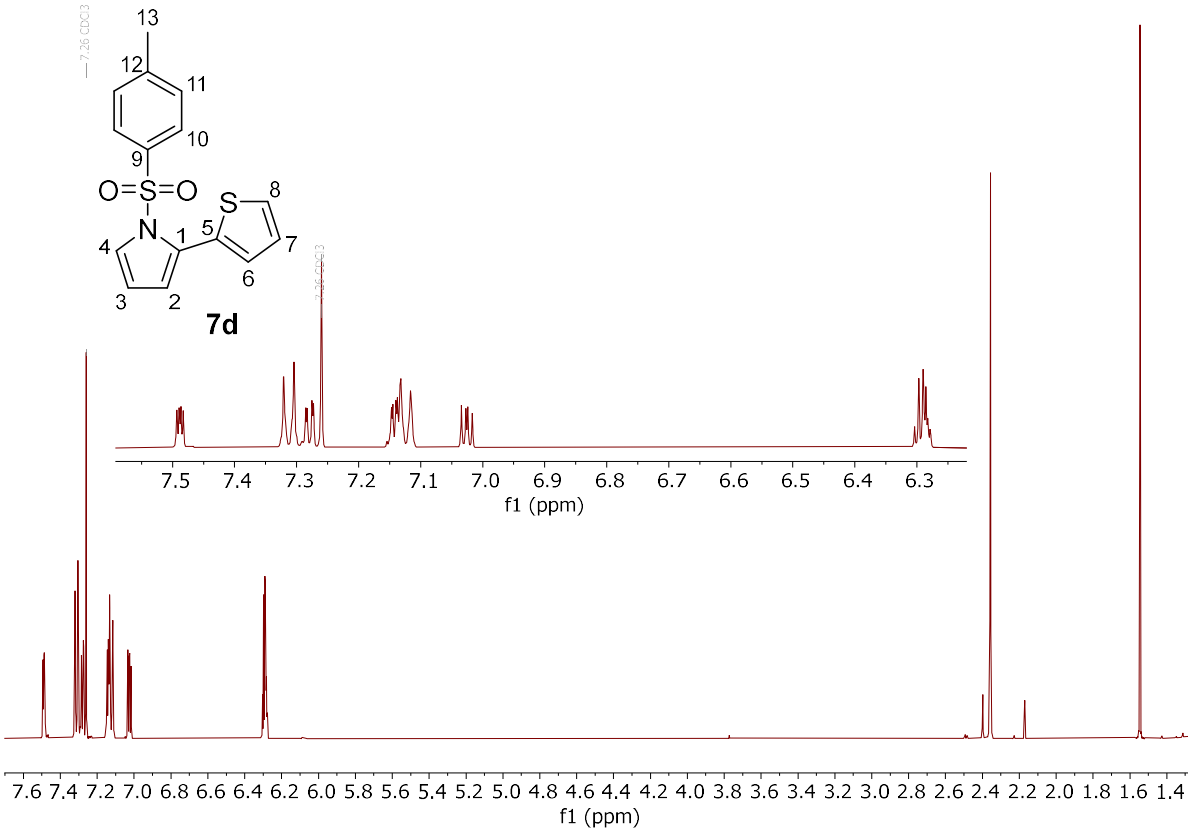


*Figure S93: [1]H NMR spectrum of 2-(thiophen-2-yl)-1-(p-toluenesulfonyl)-1H-pyrrole **7d** in $CDCl_3$*

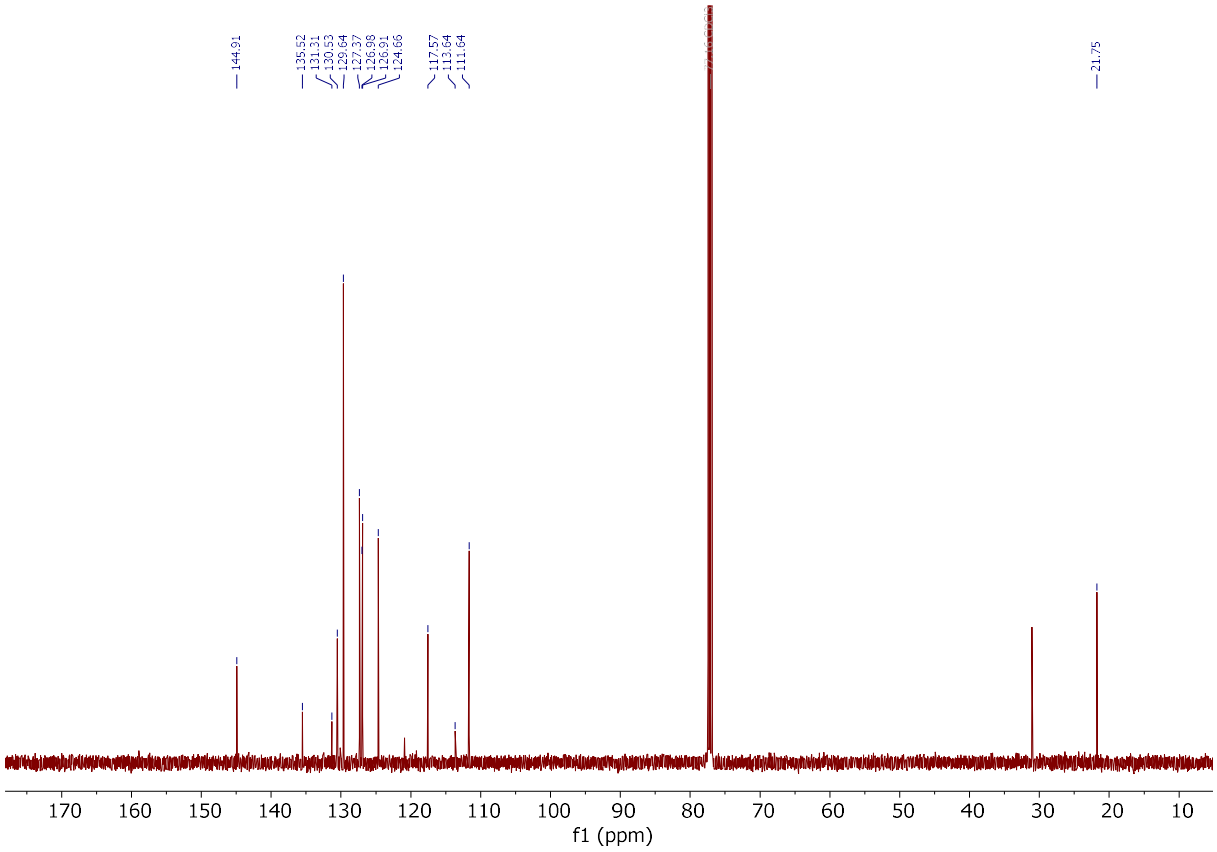


*Figure S94: [13]C NMR spectrum of NMR spectrum of 2-(thiophen-2-yl)-1-(p-toluenesulfonyl)-1H-pyrrole **7d** in $CDCl_3$*

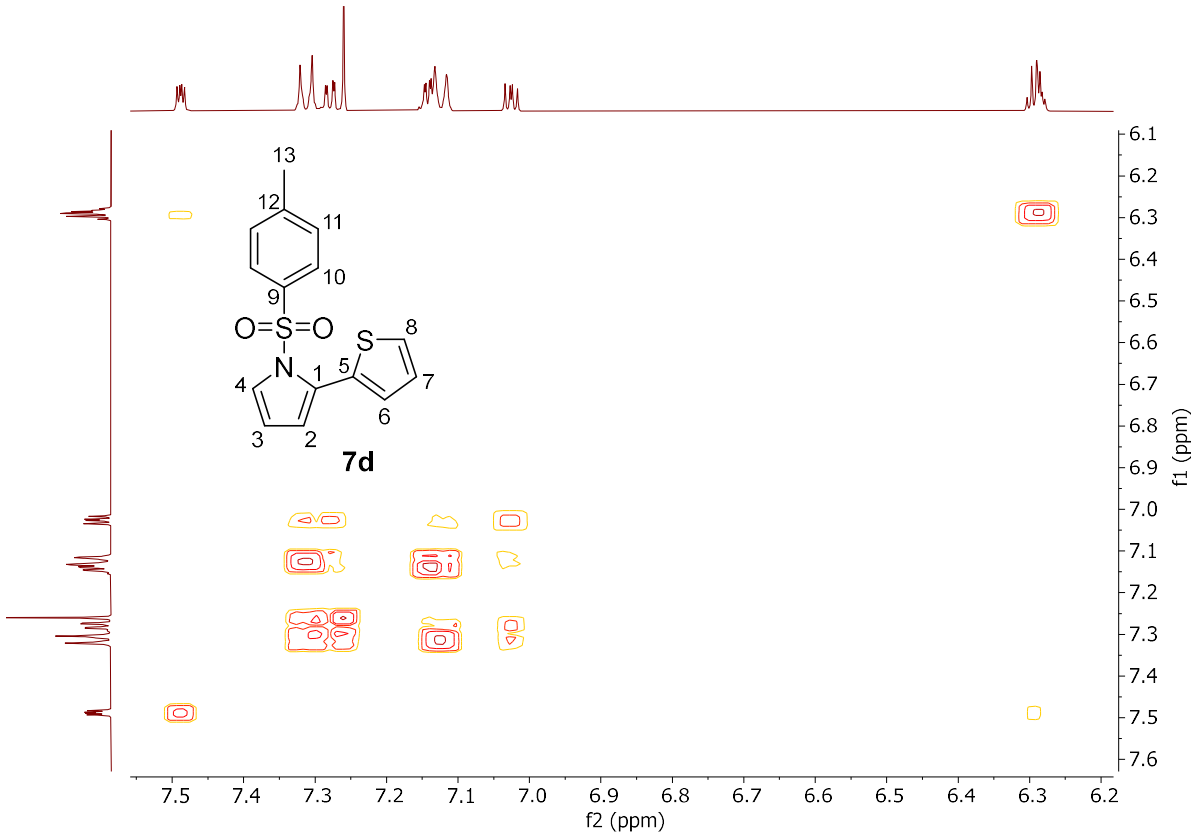


*Figure S95: COSY NMR spectrum of 2-(thiophen-2-yl)-1-(p-toluenesulfonyl)-1H-pyrrole **7d** in $CDCl_3$*

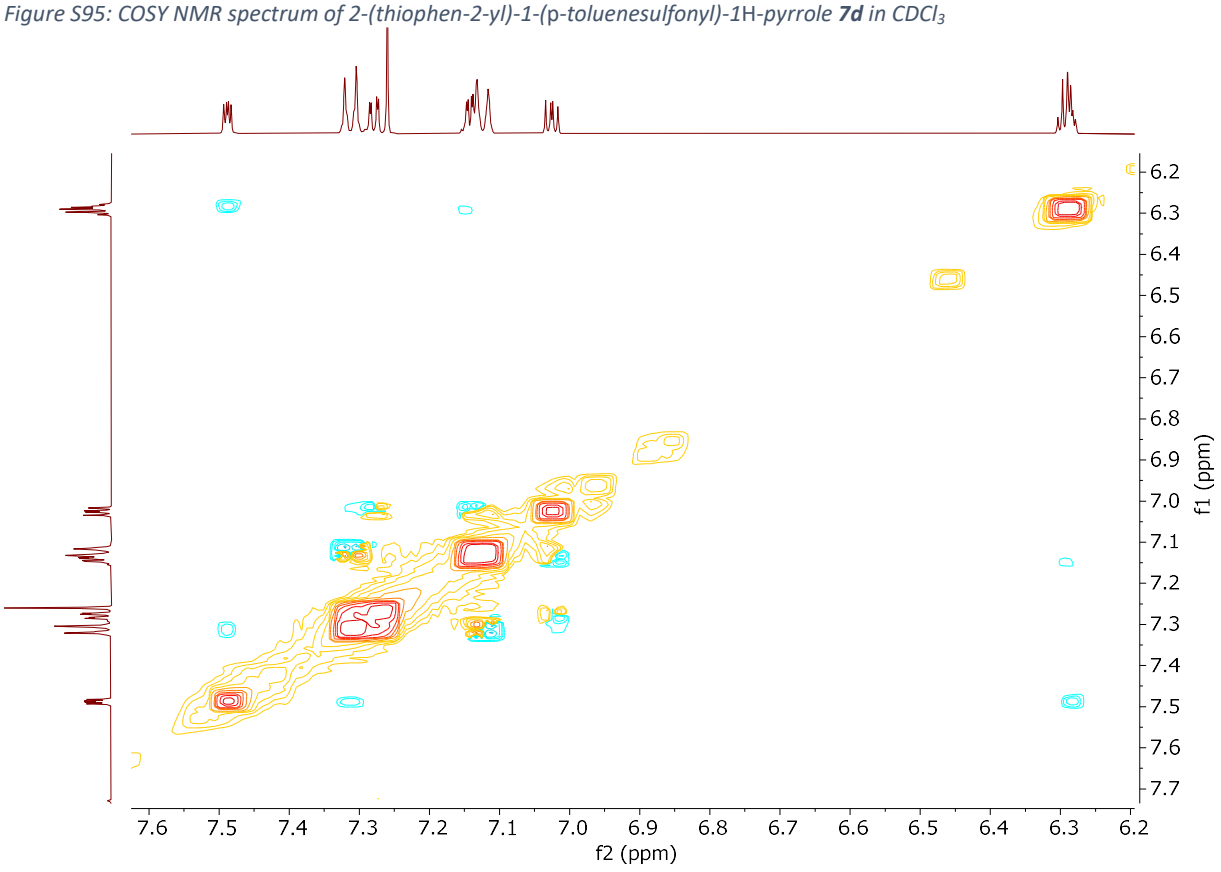


*Figure S96: NOESY NMR spectrum of 2-(thiophen-2-yl)-1-(p-toluenesulfonyl)-1H-pyrrole **7d** in $CDCl_3$*

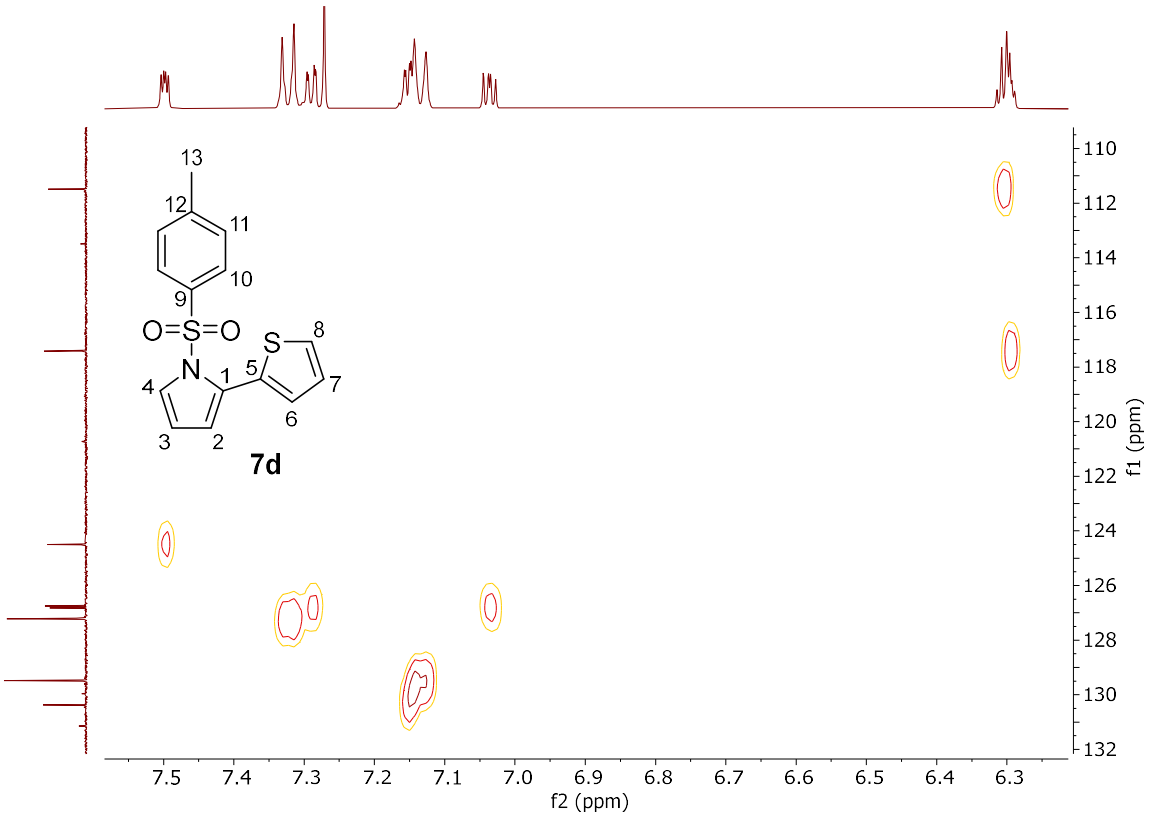


*Figure S97: HSQC NMR spectrum of 2-(thiophen-2-yl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole **7d** in $CDCl_3$*

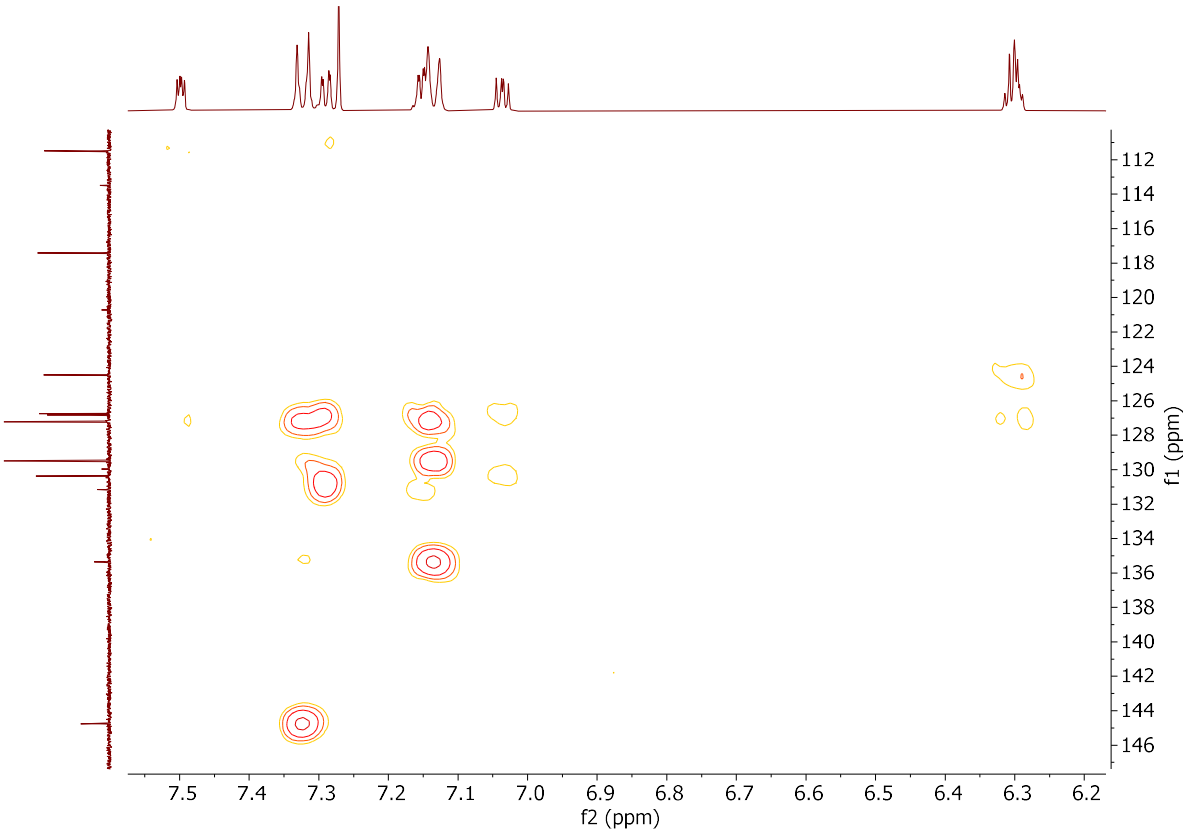


*Figure S98: HMBC NMR spectrum of 2-(thiophen-2-yl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole **7d** in $CDCl_3$*

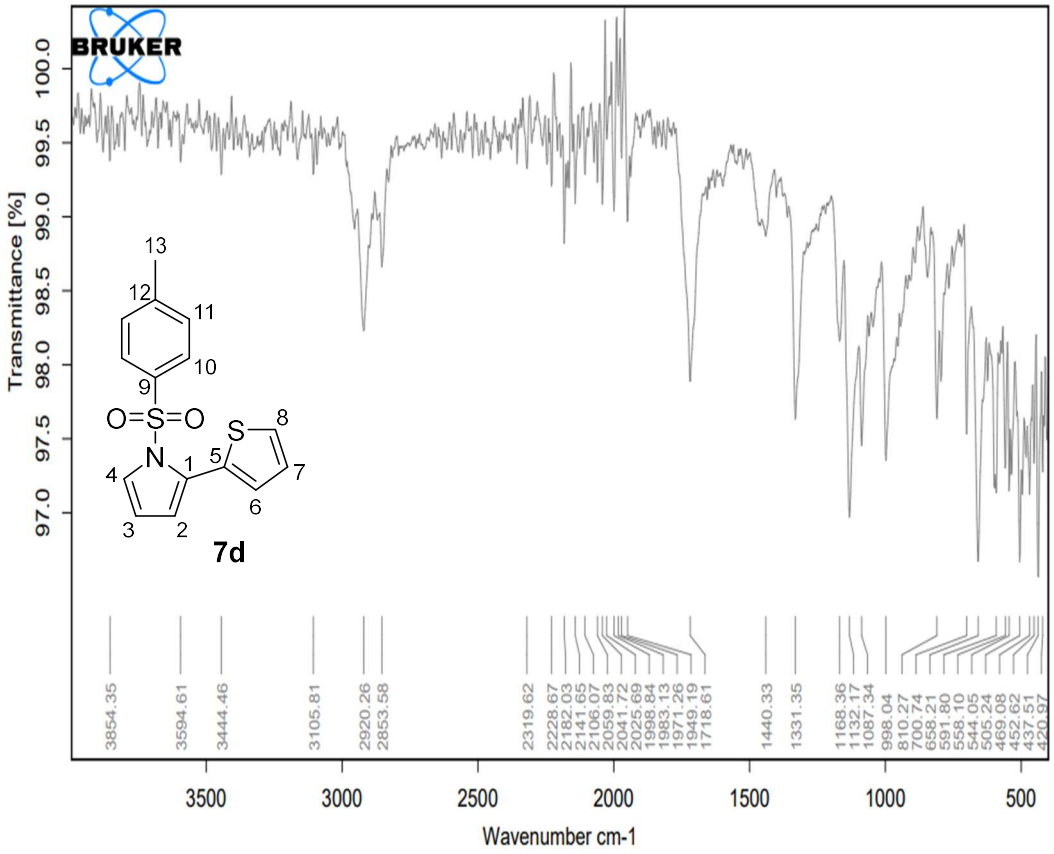


*Figure S99: IR NMR spectrum of 2-(thiophen-2-yl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole* ***7d***

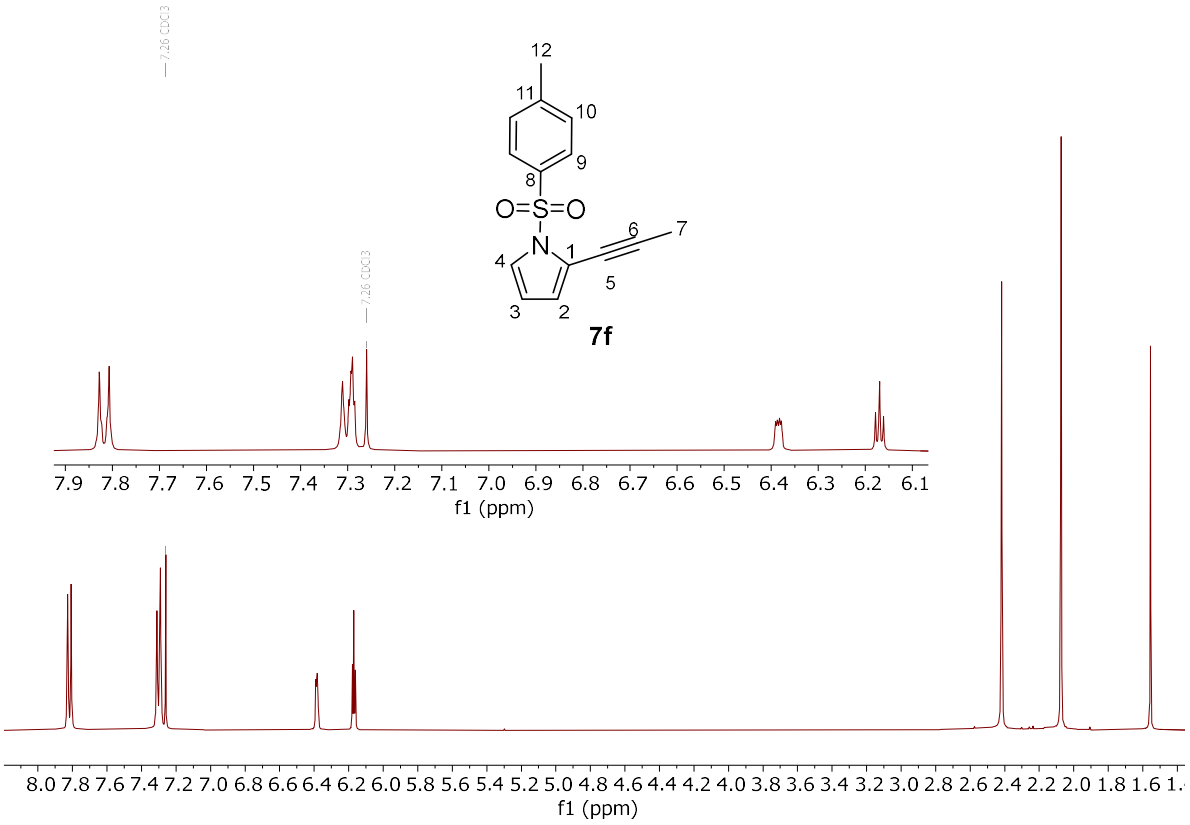


*Figure S100: ^{1}H NMR spectrum of 2-(prop-1-yn-1-yl)-1-(p-toluenesulfonyl)-1H-pyrrole **7f** in $CDCl_3$*

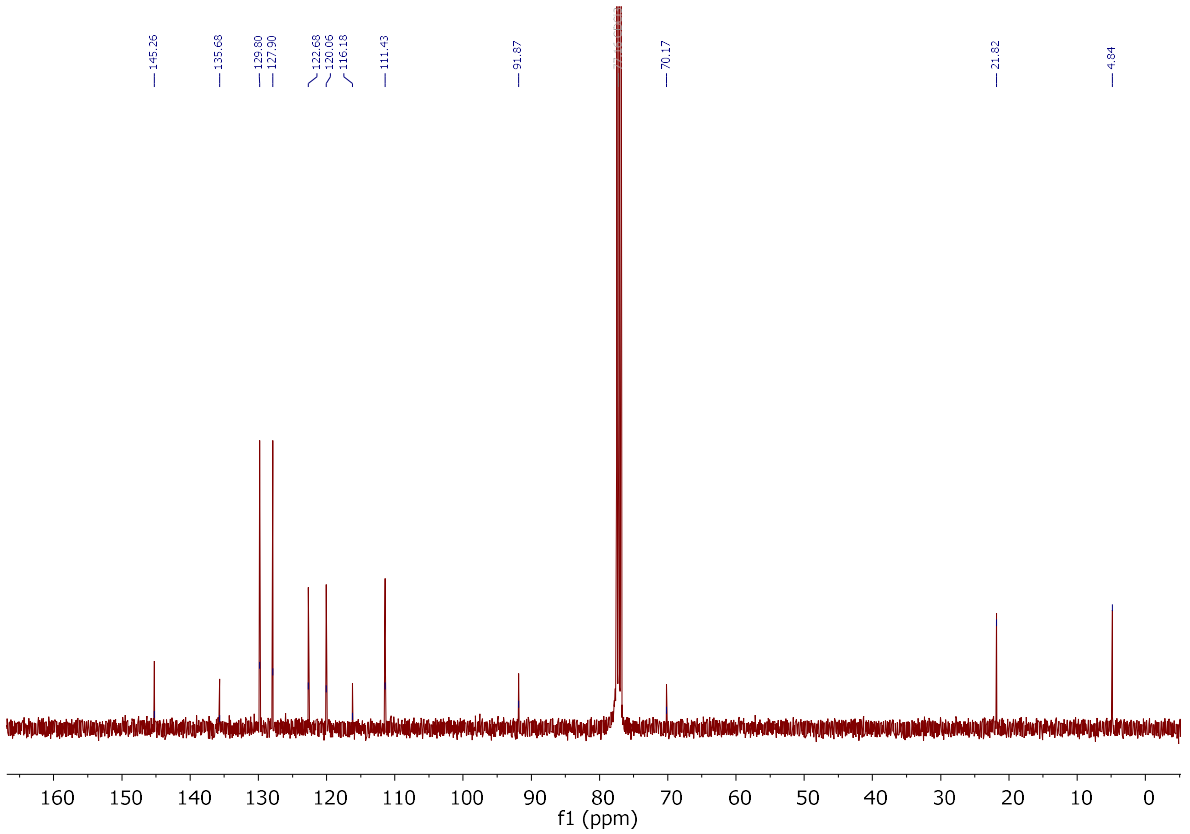


*Figure S101: ^{13}C NMR spectrum of 2-(prop-1-yn-1-yl)-1-(p-toluenesulfonyl)-1H-pyrrole **7f** in $CDCl_3$*

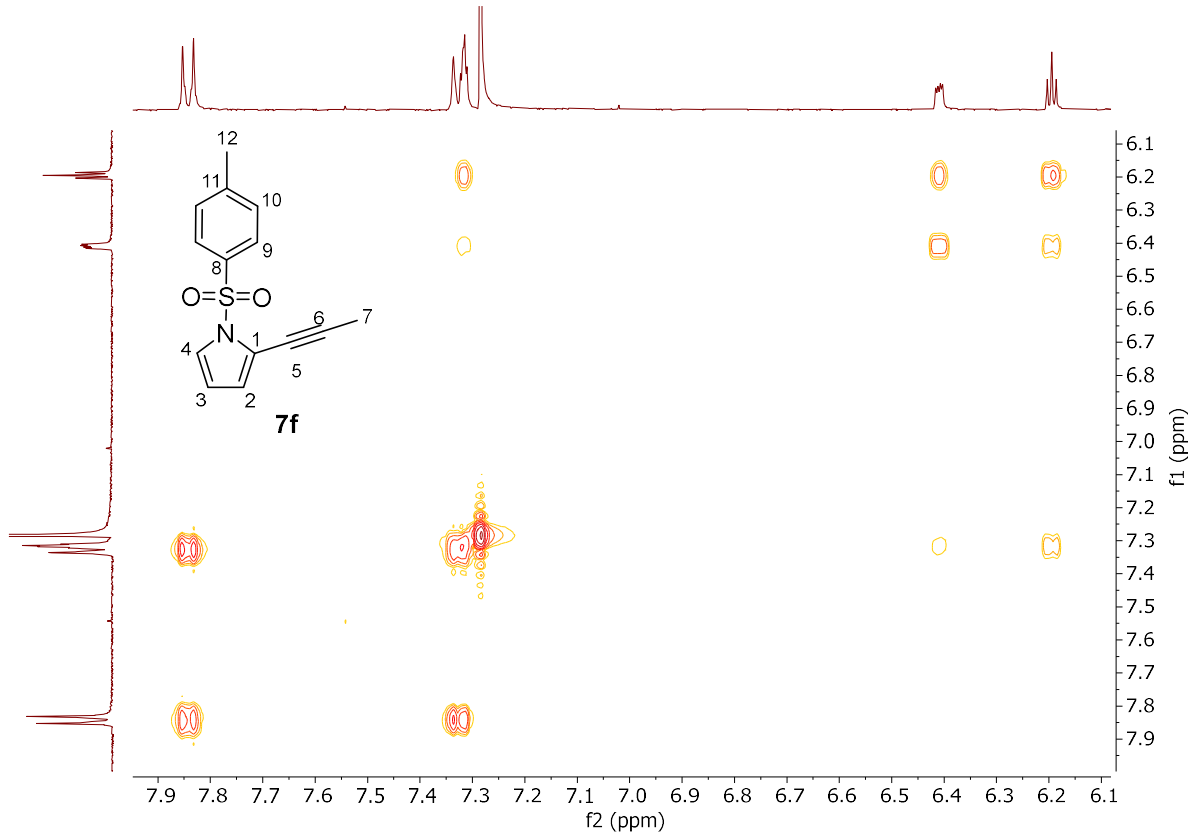


*Figure S102: COSY NMR spectrum of 2-(prop-1-yn-1-yl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole **7f** in $CDCl_3$*

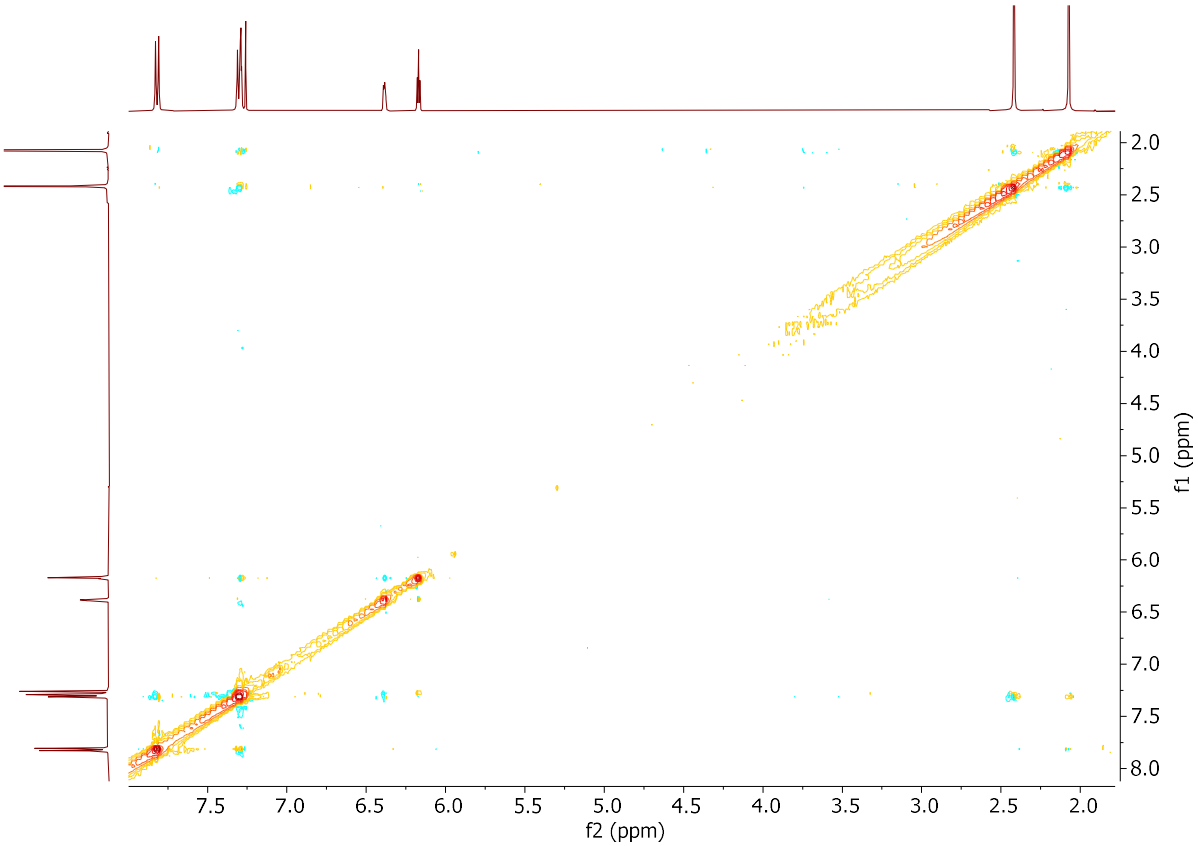


*Figure S103: NOESY NMR spectrum of 2-(prop-1-yn-1-yl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole **7f** in $CDCl_3$*

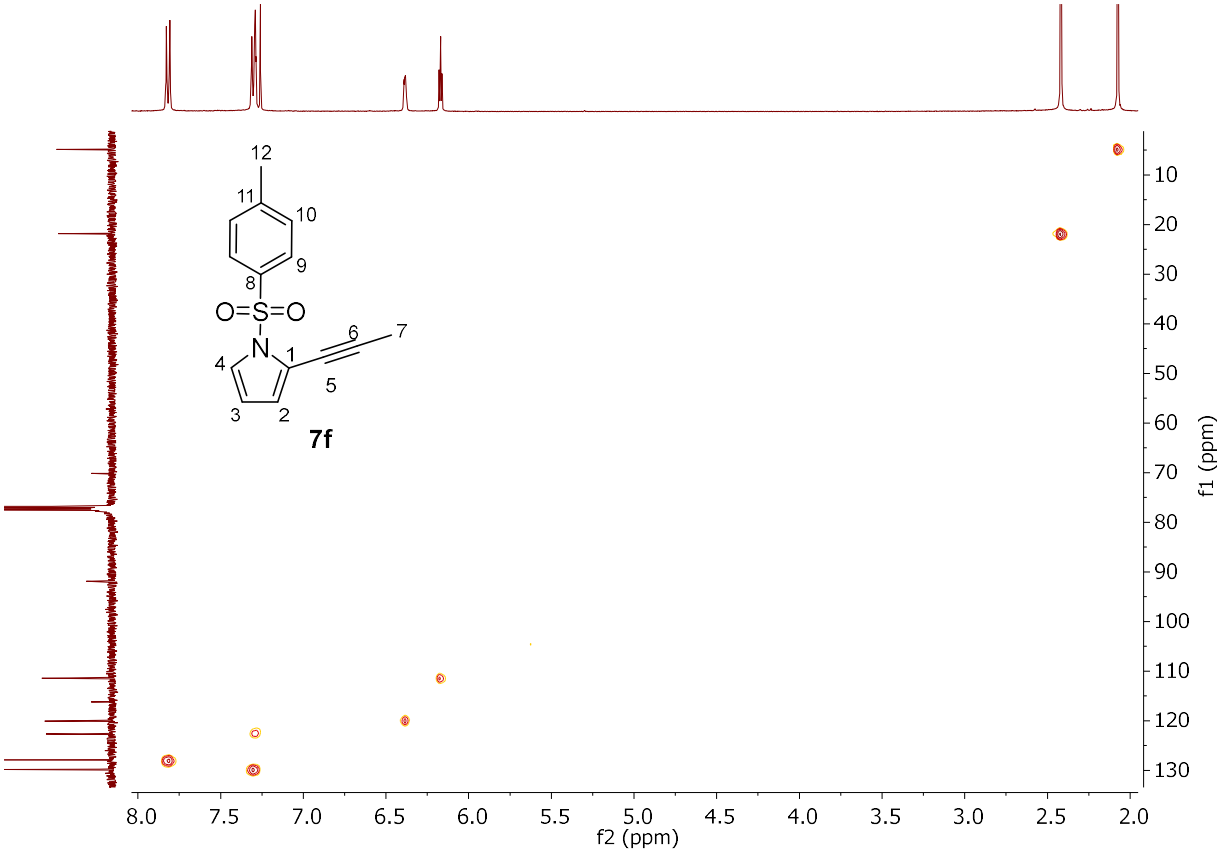


*Figure S104: HSQC NMR spectrum of 2-(prop-1-yn-1-yl)-1-(p-toluenesulfonyl)-1H-pyrrole **7f** in $CDCl_3$*

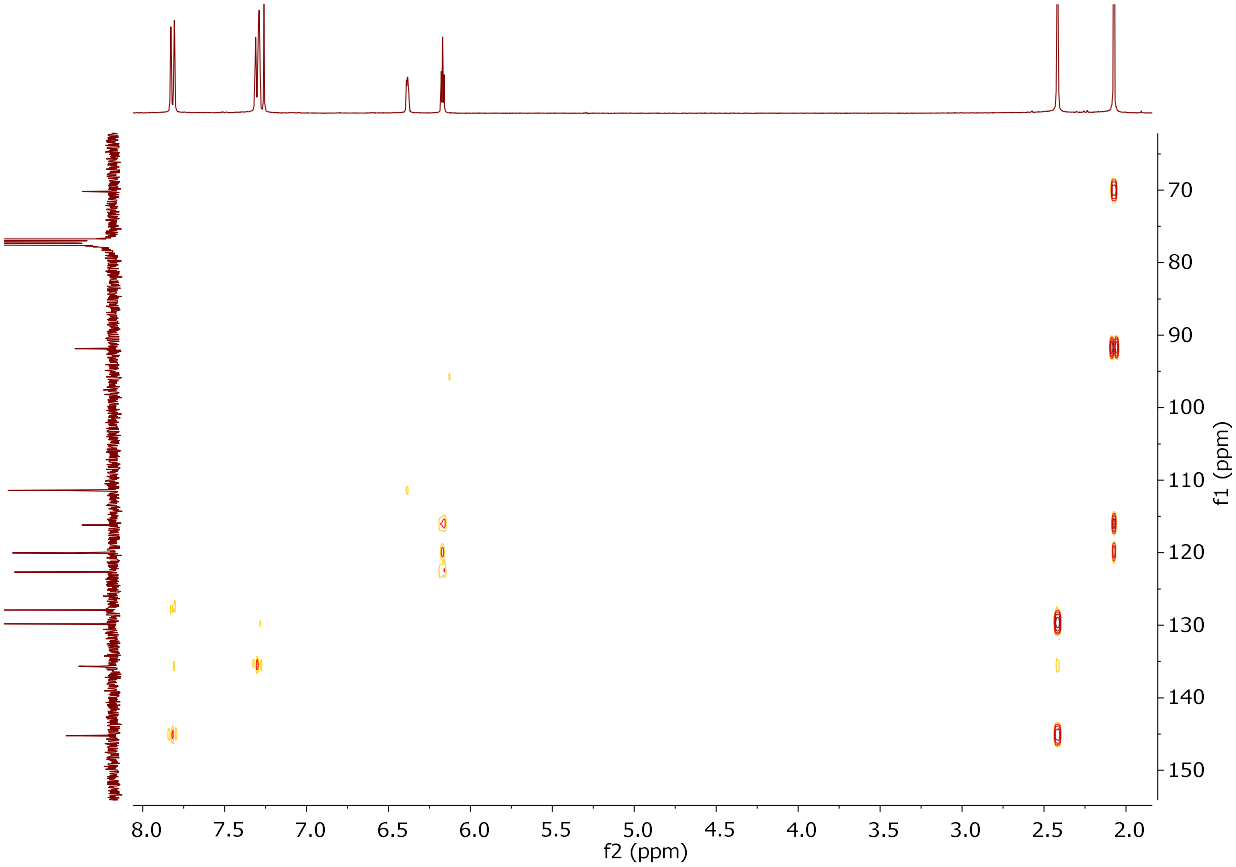


*Figure S105: HMBC NMR spectrum of 2-(prop-1-yn-1-yl)-1-(p-toluenesulfonyl)-1H-pyrrole **7f** in $CDCl_3$*

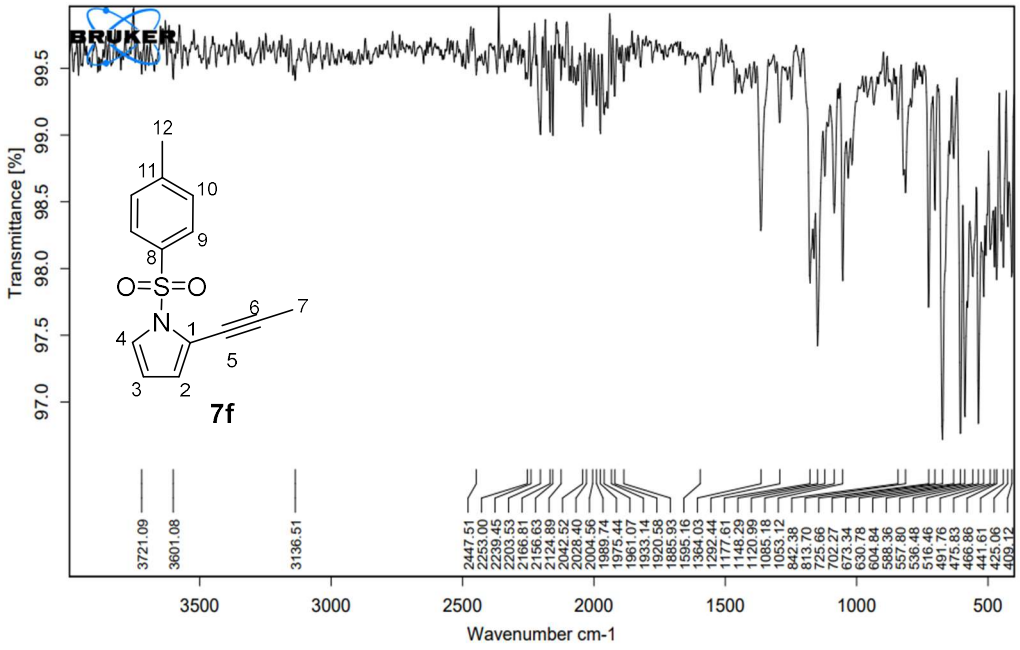


*Figure S106: IR spectrum of 2-(prop-1-yn-1-yl)-1-(*p*-toluenesulfonyl)-1*H*-pyrrole **7f***

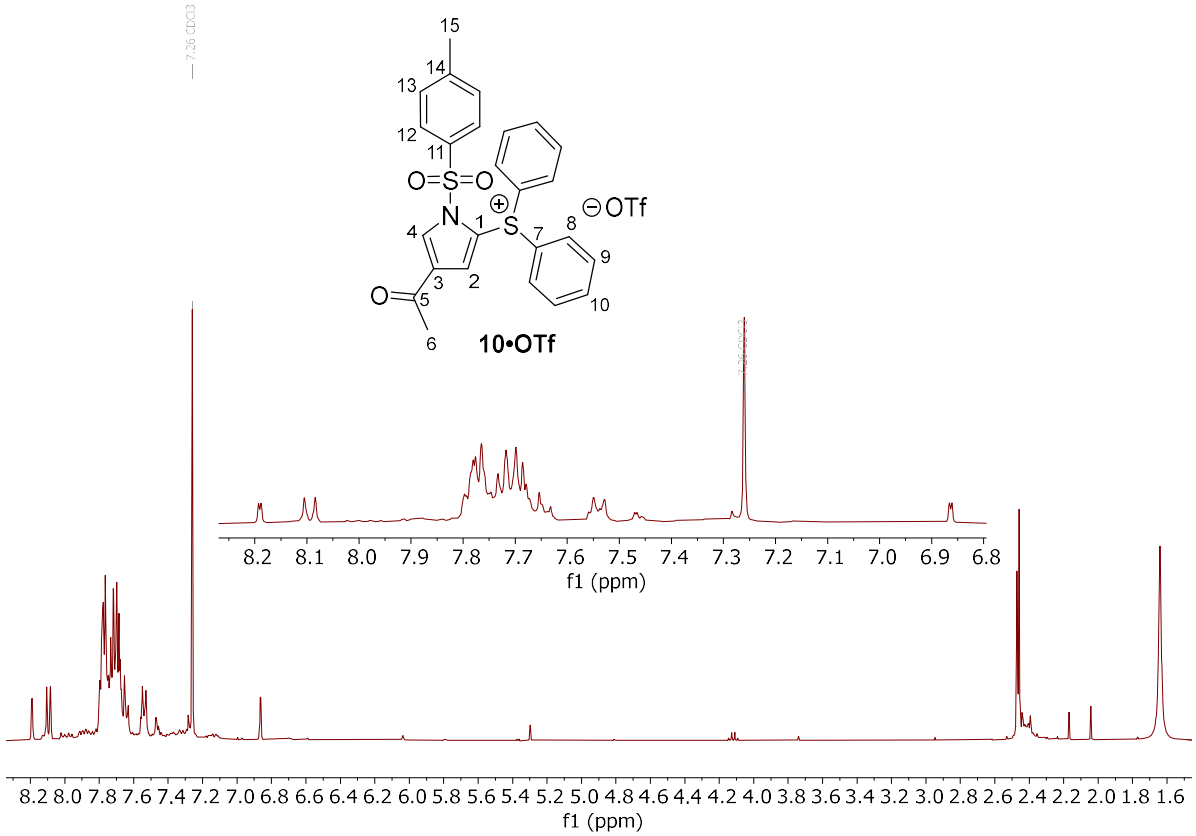


*Figure S107: ^{1}H NMR spectrum of (4-acetyl-1-(p-toluenesulfonyl)-1H-pyrrol-2-yl)diphenylsulfonium trifluromethanesulfonate **10•OTf** in $CDCl_3$*

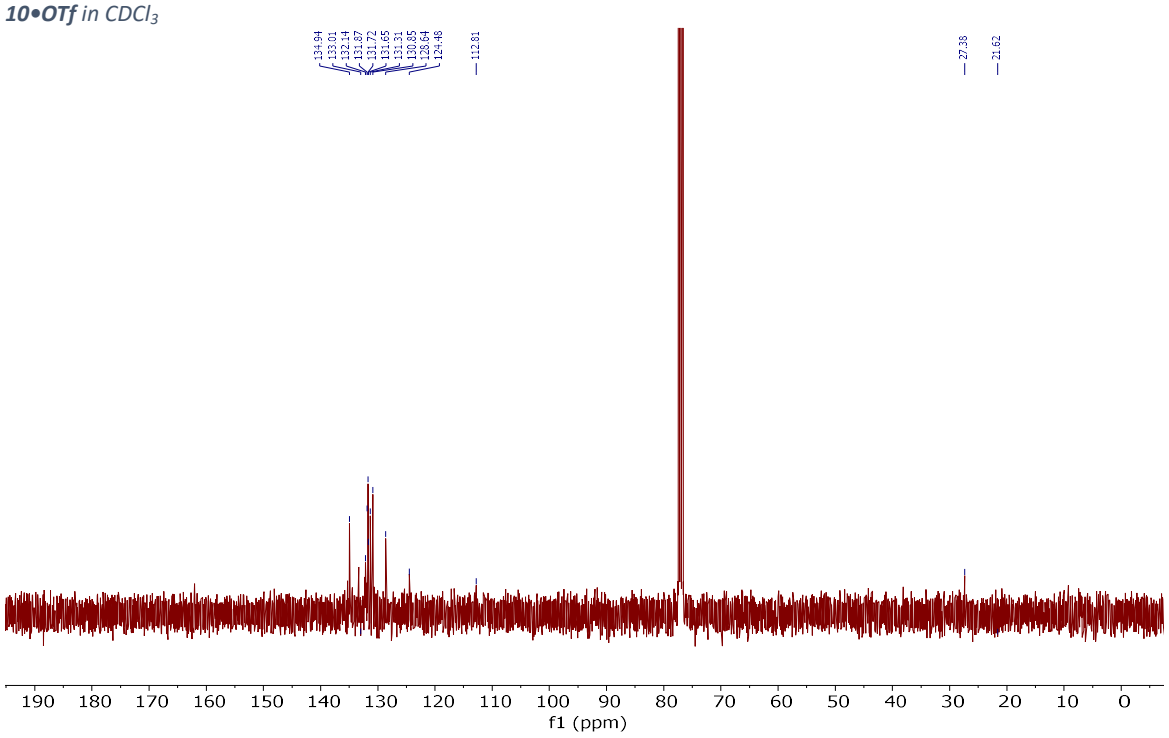


*Figure S108: ^{13}C NMR spectrum of (4-acetyl-1-(p-toluenesulfonyl)-1H-pyrrol-2-yl)diphenylsulfonium trifluromethanesulfonate **10•OTf** in $CDCl_3$*

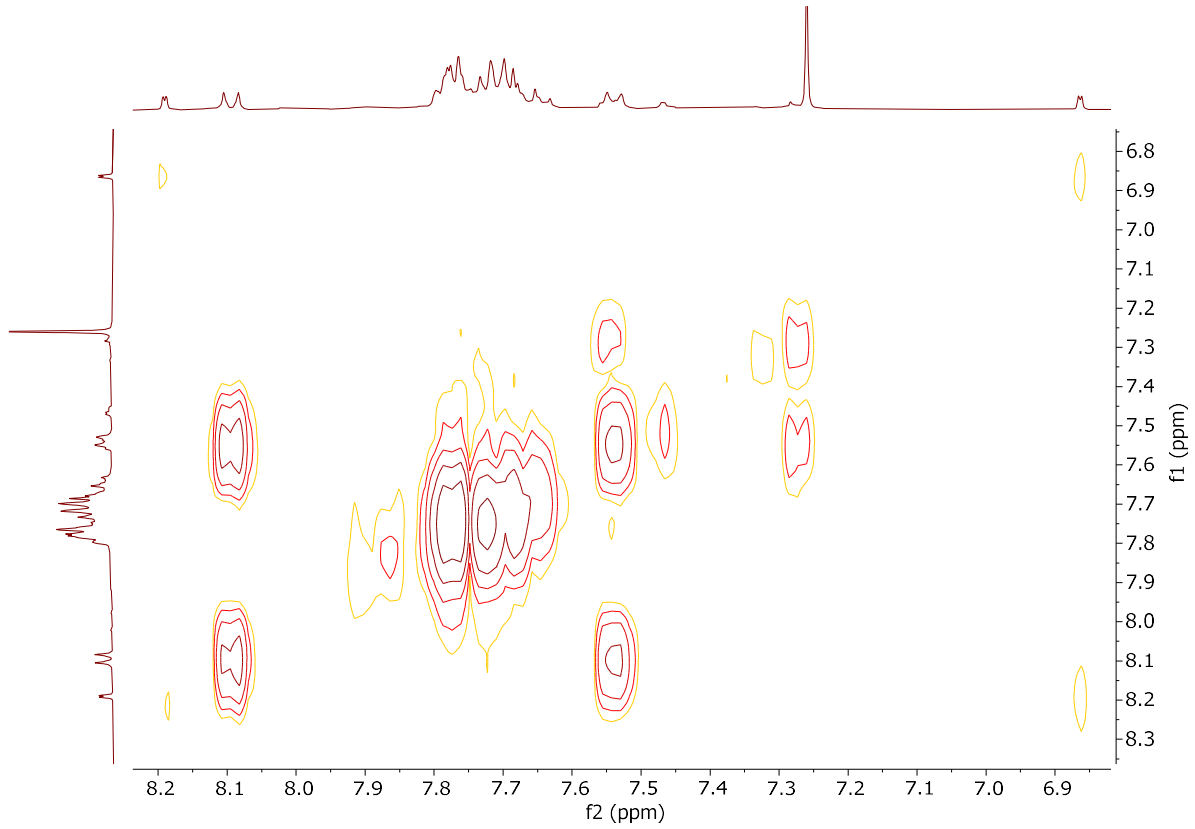


*Figure S109: COSY NMR spectrum of (4-acetyl-1-(p-toluenesulfonyl)-1H-pyrrol-2-yl)diphenylsulfonium trifluromethanesulfonate **10•OTf** in $CDCl_3$*

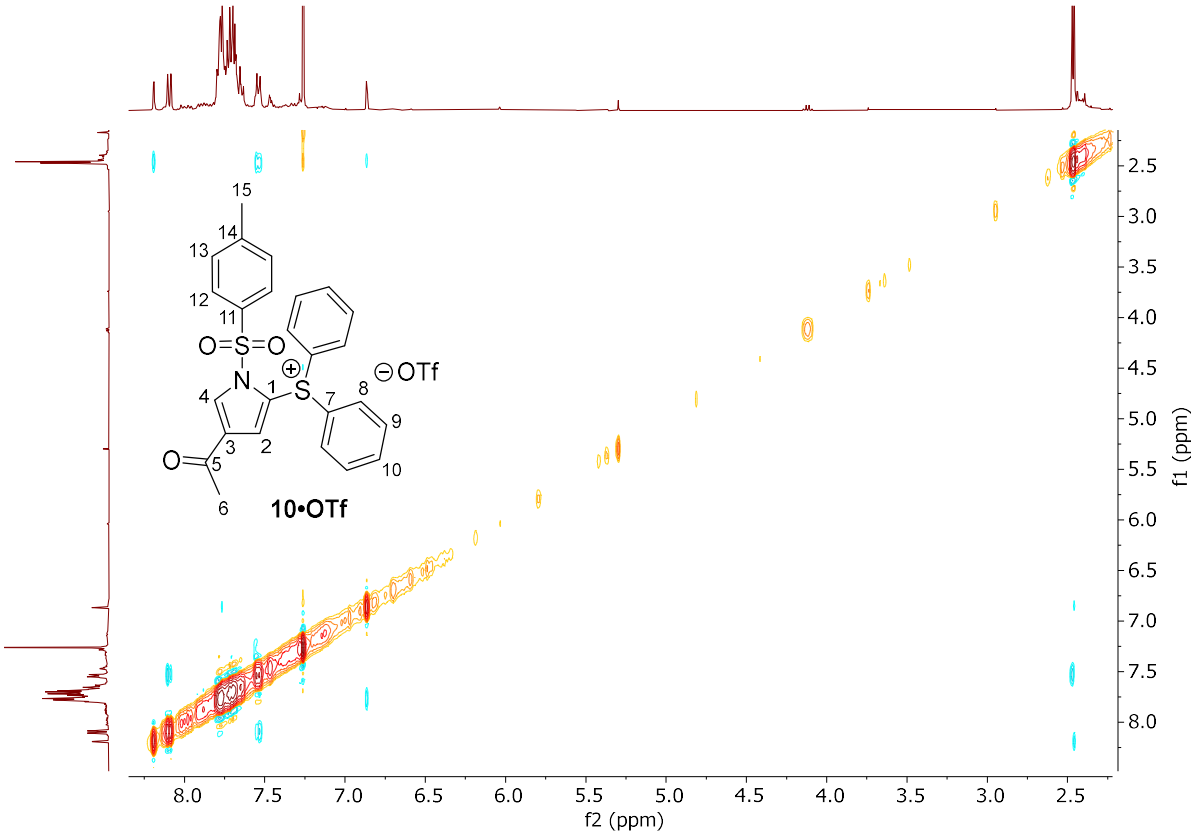


*Figure S110: NOESY NMR spectrum of (4-acetyl-1-(p-toluenesulfonyl)-1H-pyrrol-2-yl)diphenylsulfonium trifluromethanesulfonate **10•OTf** in $CDCl_3$*

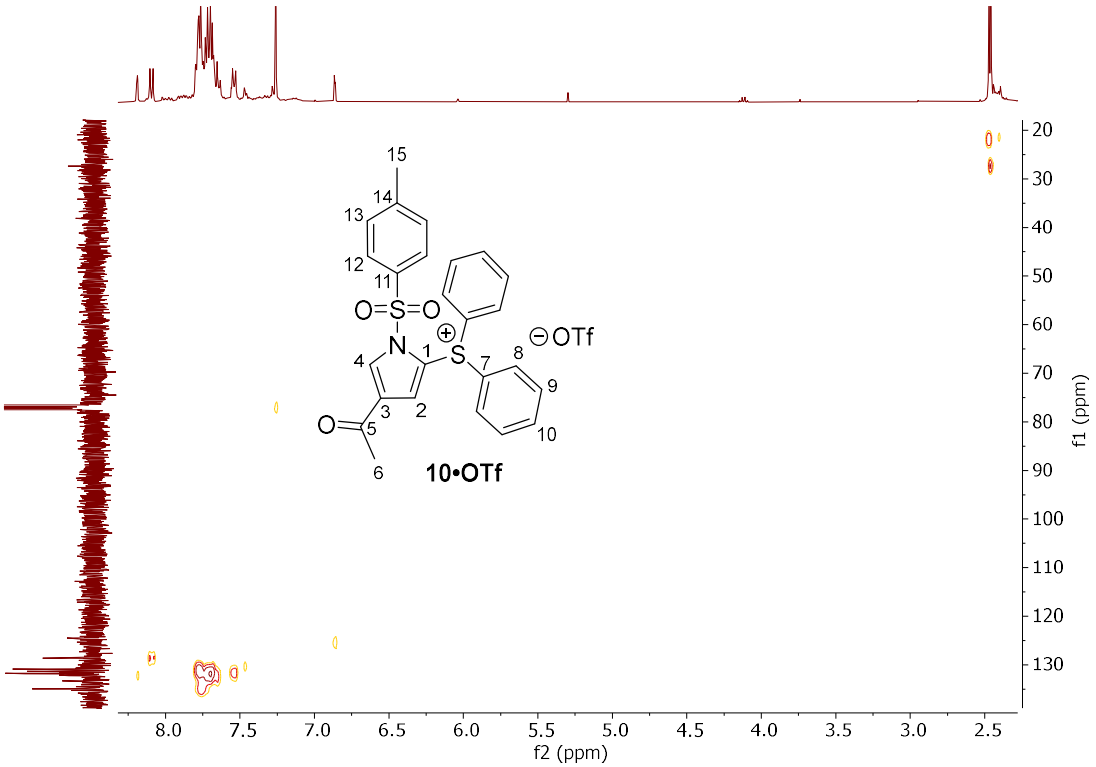


*Figure S111: HSQC NMR spectrum of (4-acetyl-1-(*p*-toluenesulfonyl)-1*H*-pyrrol-2-yl)diphenylsulfonium trifluromethanesulfonate **10•OTf** in $CDCl_3$*

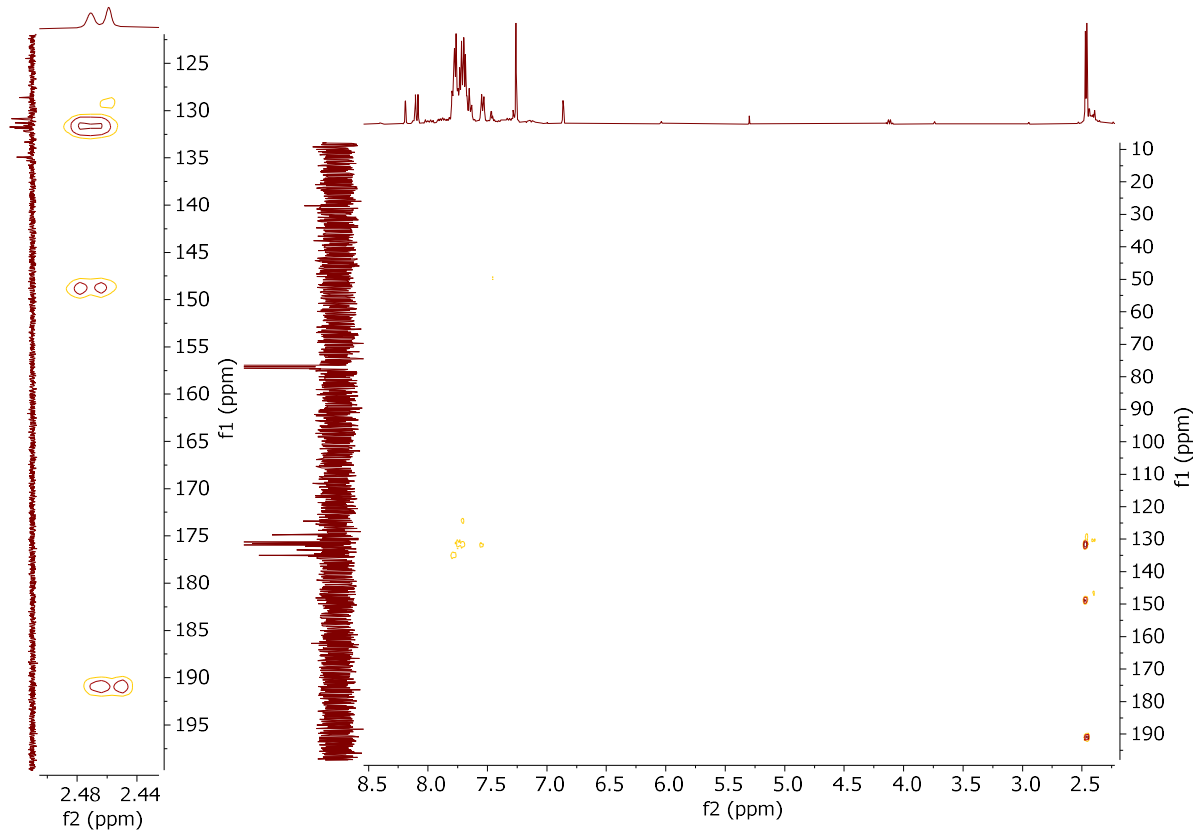


*Figure S112: HMBC NMR spectrum of (4-acetyl-1-(*p*-toluenesulfonyl)-1*H*-pyrrol-2-yl)diphenylsulfonium trifluromethanesulfonate **10•OTf** in $CDCl_3$*

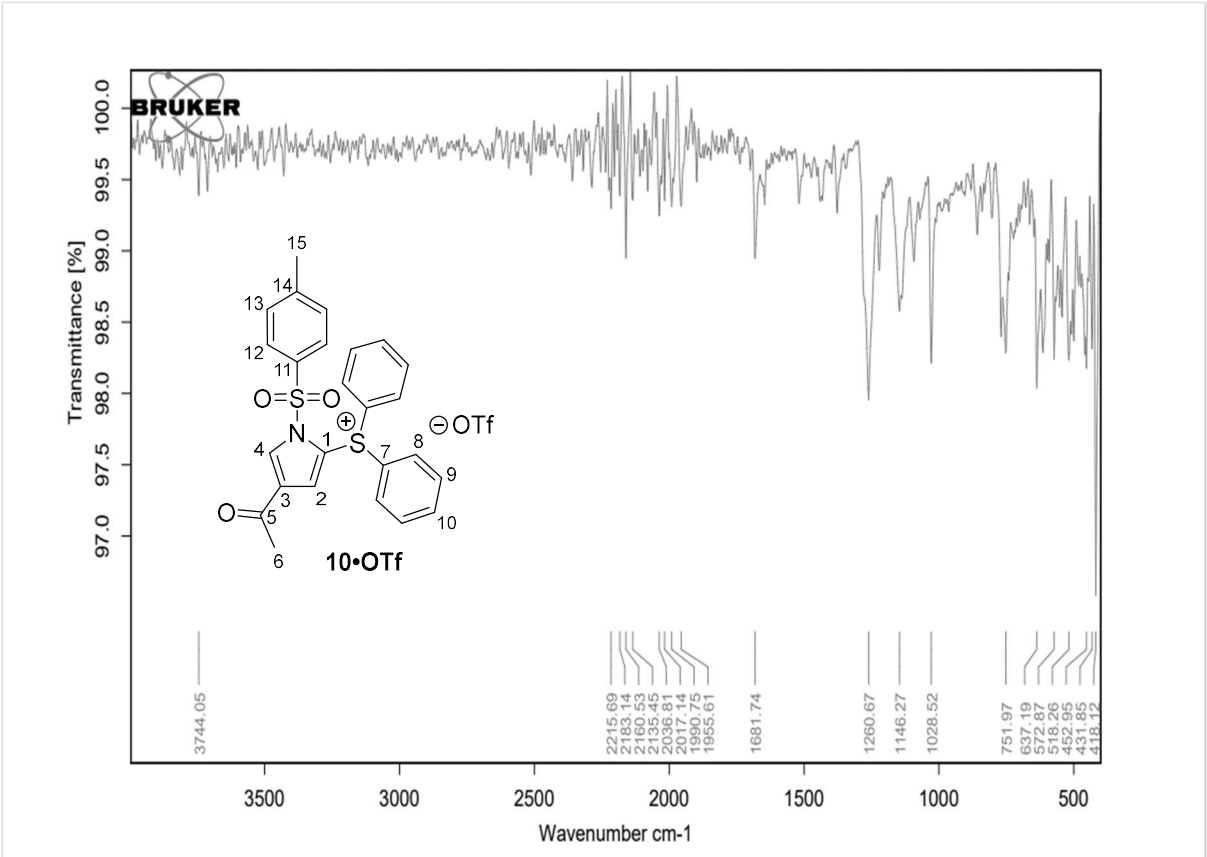


*Figure S113: IR spectrum of (4-acetyl-1-(*p*-toluenesulfonyl)-1*H*-pyrrol-2-yl)diphenylsulfonium trifluoromethanesulfonate* ***10•OTf***

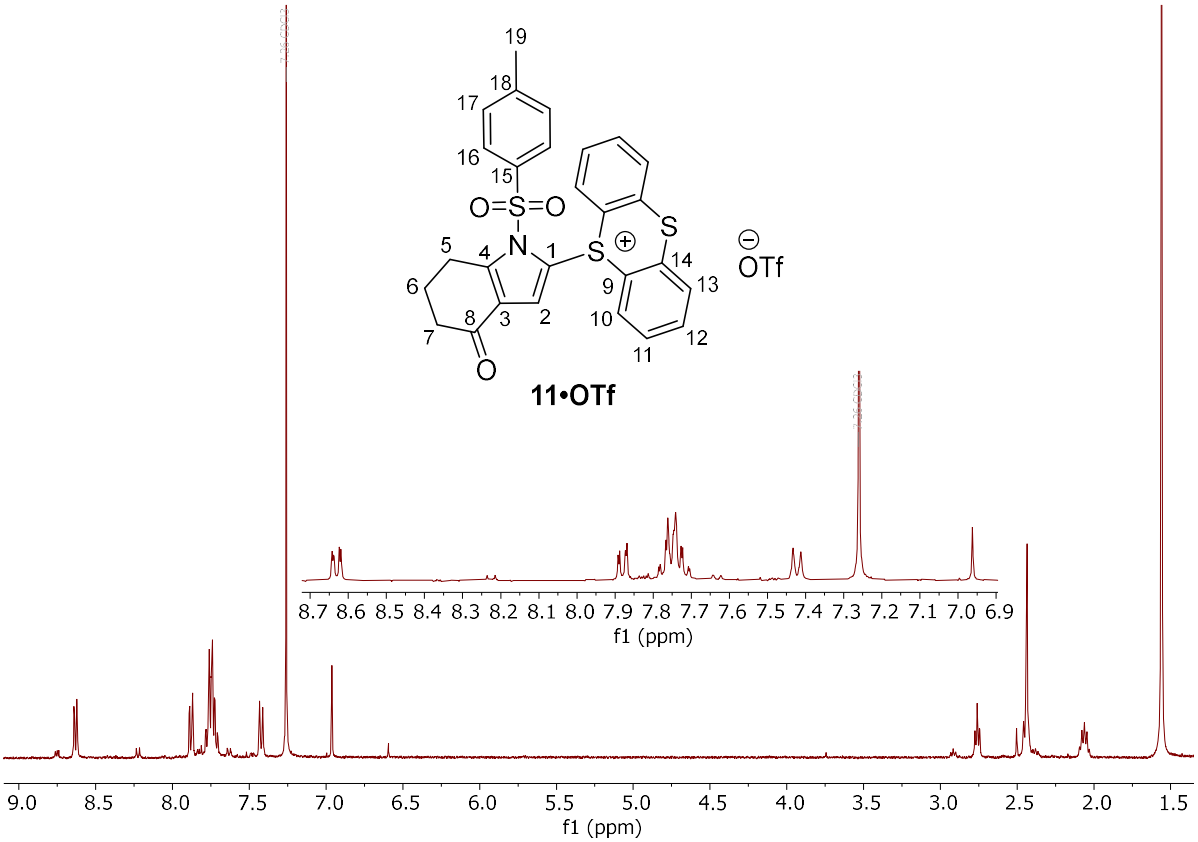


*Figure S114: [1]H NMR spectrum of 5-(4-oxo-1-(p-toluenesulfonyl)-4,5,6,7-tetrahydro-1H-indol-2-yl)-5H-thianthren-5-ium trifluoromethanesulfonate **11•OTf** in $CDCl_3$*

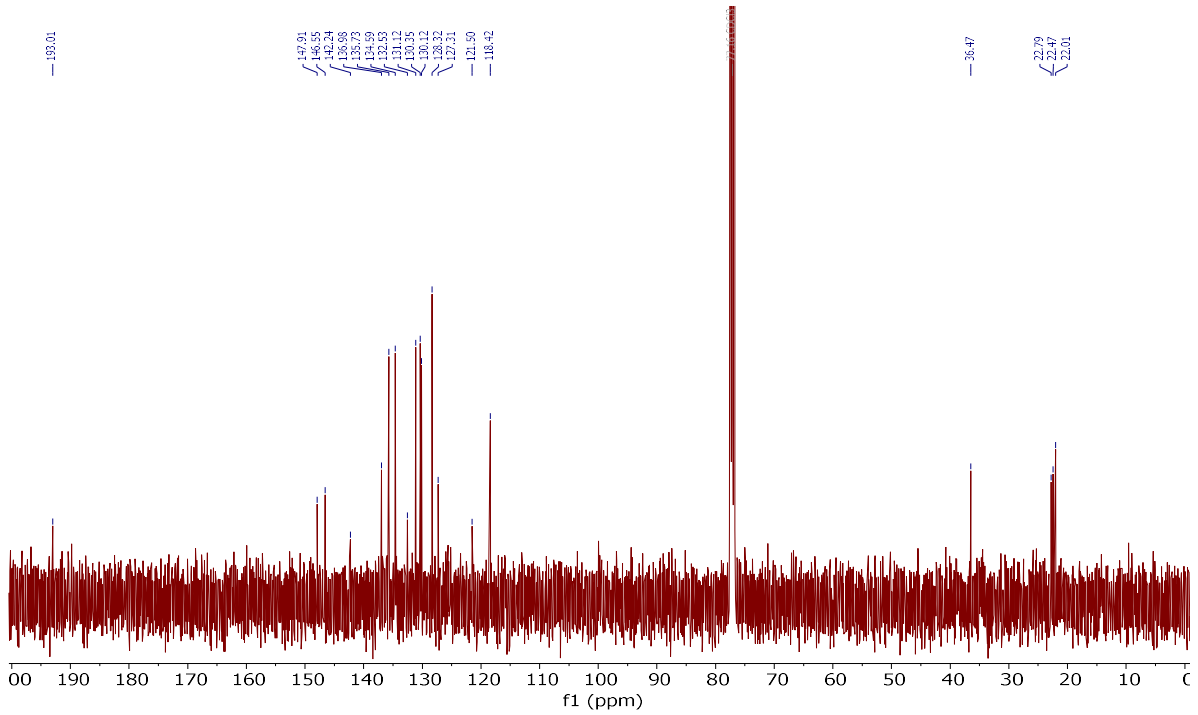


*Figure S115: [13]C NMR spectrum of 5-(4-oxo-1-(p-toluenesulfonyl)-4,5,6,7-tetrahydro-1H-indol-2-yl)-5H-thianthren-5-ium trifluoromethanesulfonate **11•OTf** in $CDCl_3$*

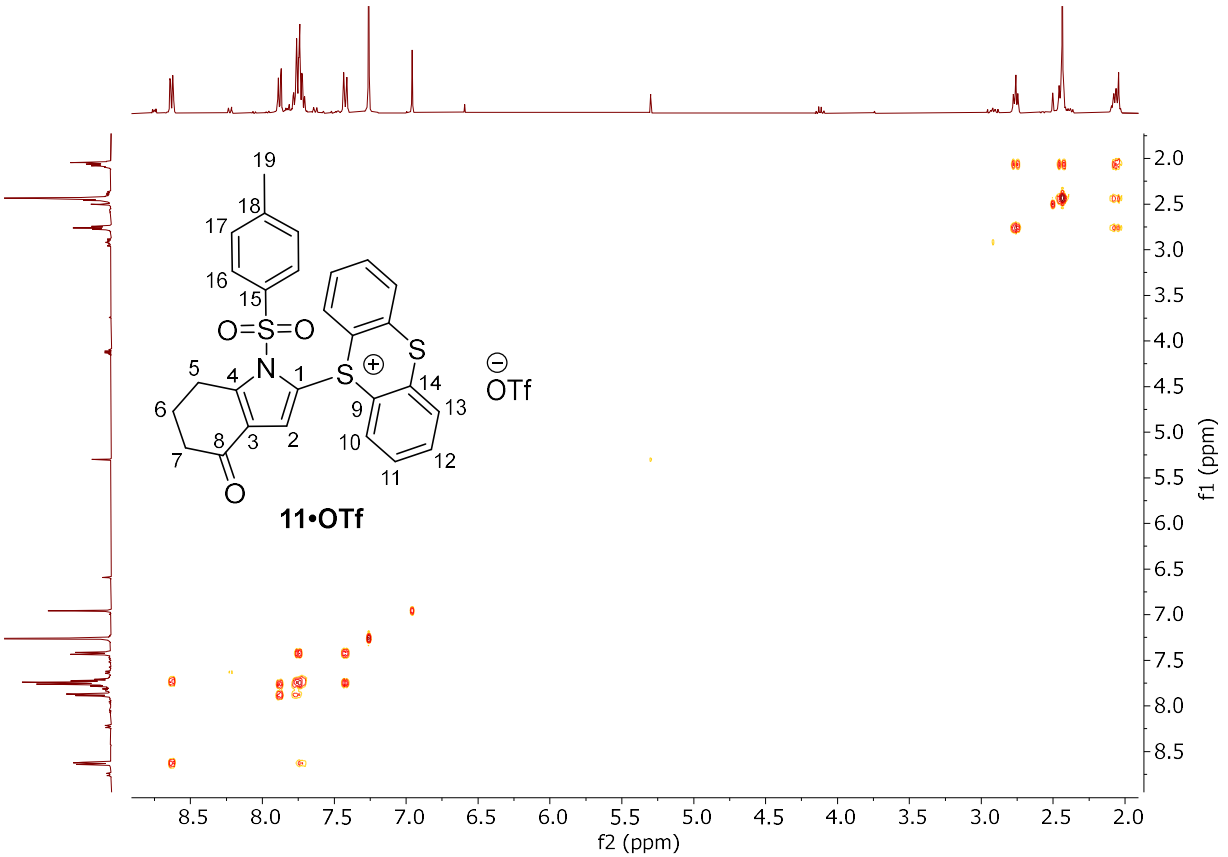


*Figure S116: COSY NMR spectrum of 5-(4-oxo-1-(p-toluenesulfonyl)-4,5,6,7-tetrahydro-1H-indol-2-yl)-5H-thianthren-5-ium trifluoromethanesulfonate **11•OTf** in $CDCl_3$*

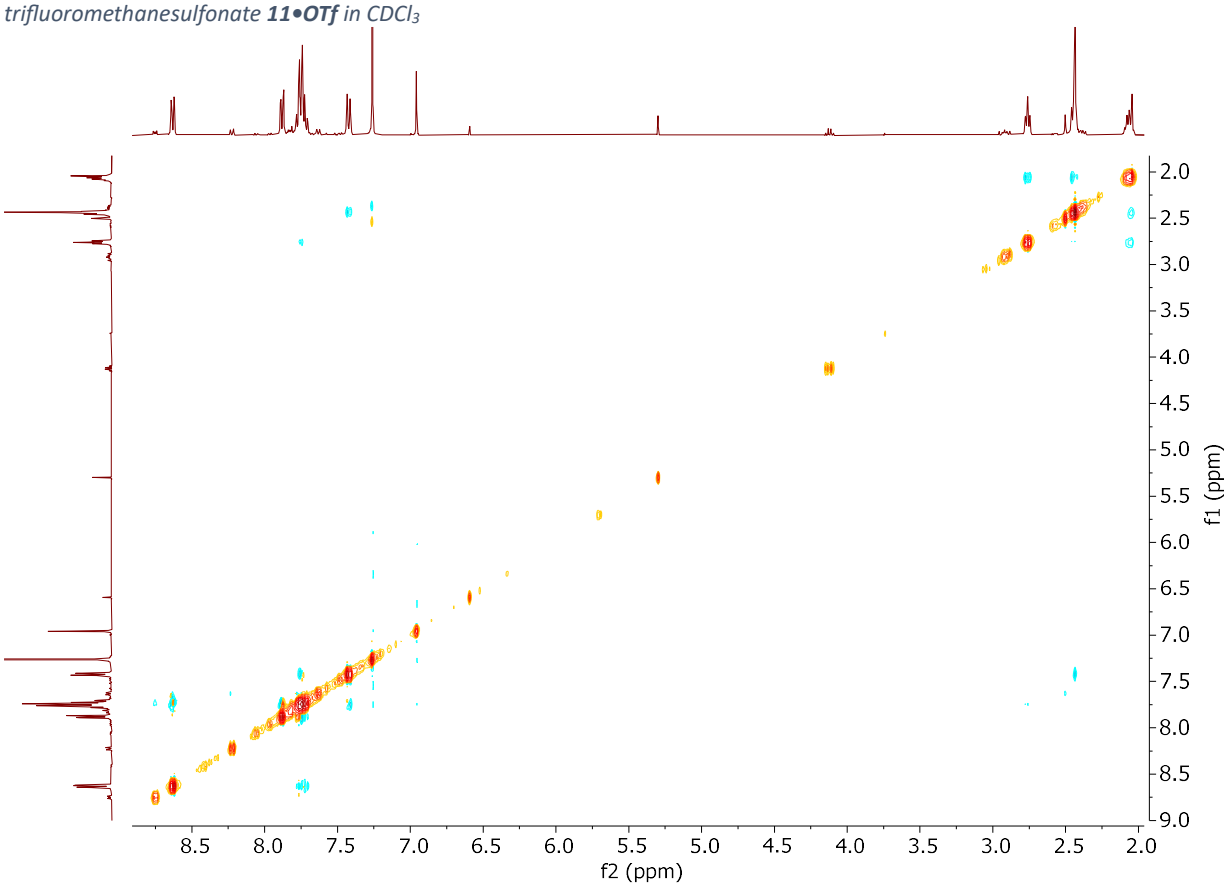


*Figure S117: NOESY NMR spectrum of 5-(4-oxo-1-(p-toluenesulfonyl)-4,5,6,7-tetrahydro-1H-indol-2-yl)-5H-thianthren-5-ium trifluoromethanesulfonate **11•OTf** in $CDCl_3$*

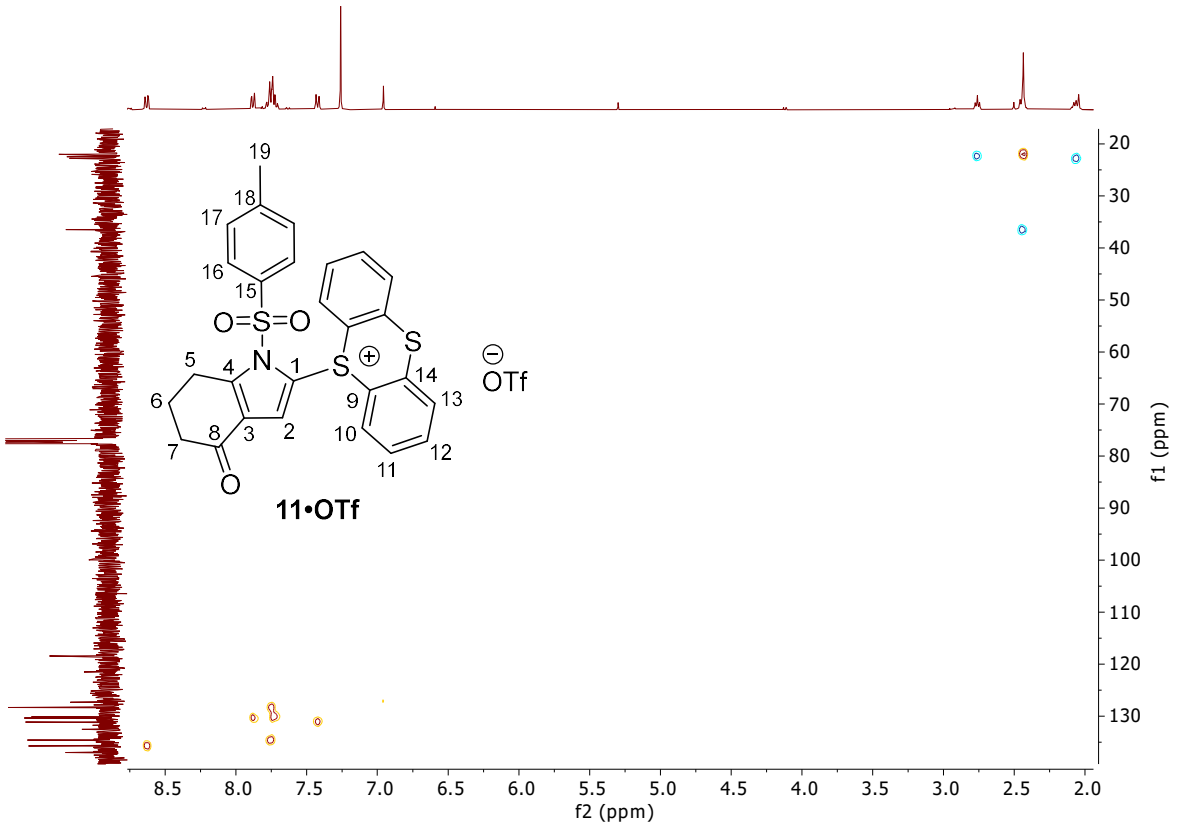


*Figure S118: HSQC NMR spectrum of 5-(4-oxo-1-(*p*-toluenesulfonyl)-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate **11•OTf** in $CDCl_3$*

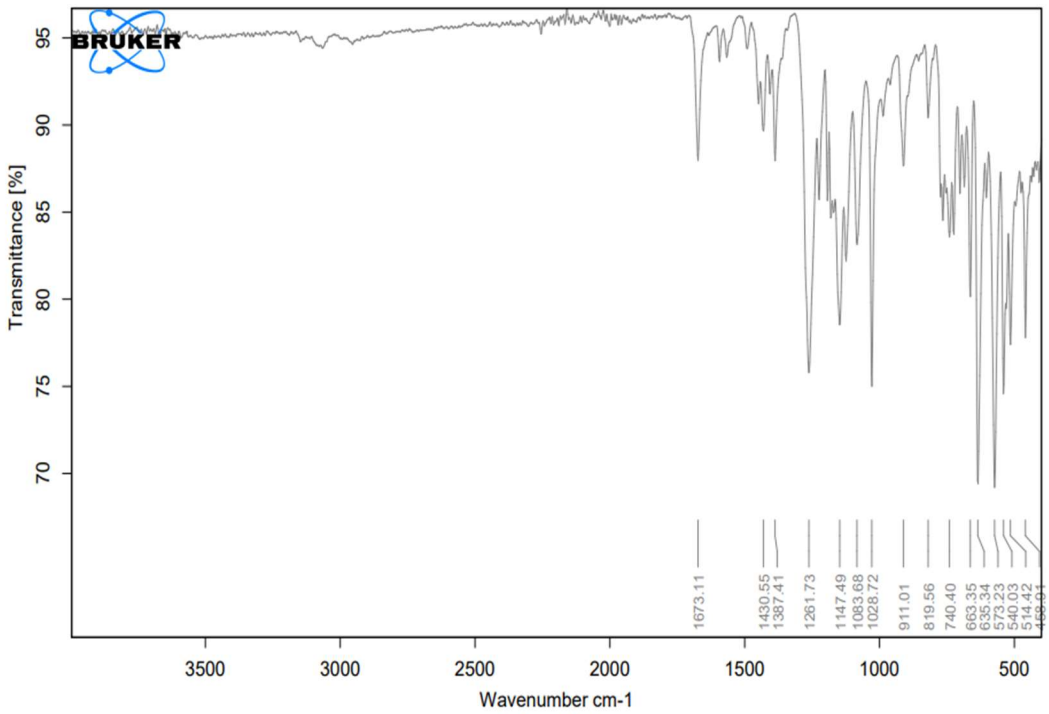


*Figure S119: IR spectrum of 5-(4-oxo-1-(*p*-toluenesulfonyl)-4,5,6,7-tetrahydro-1*H*-indol-2-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate **11•OTf***

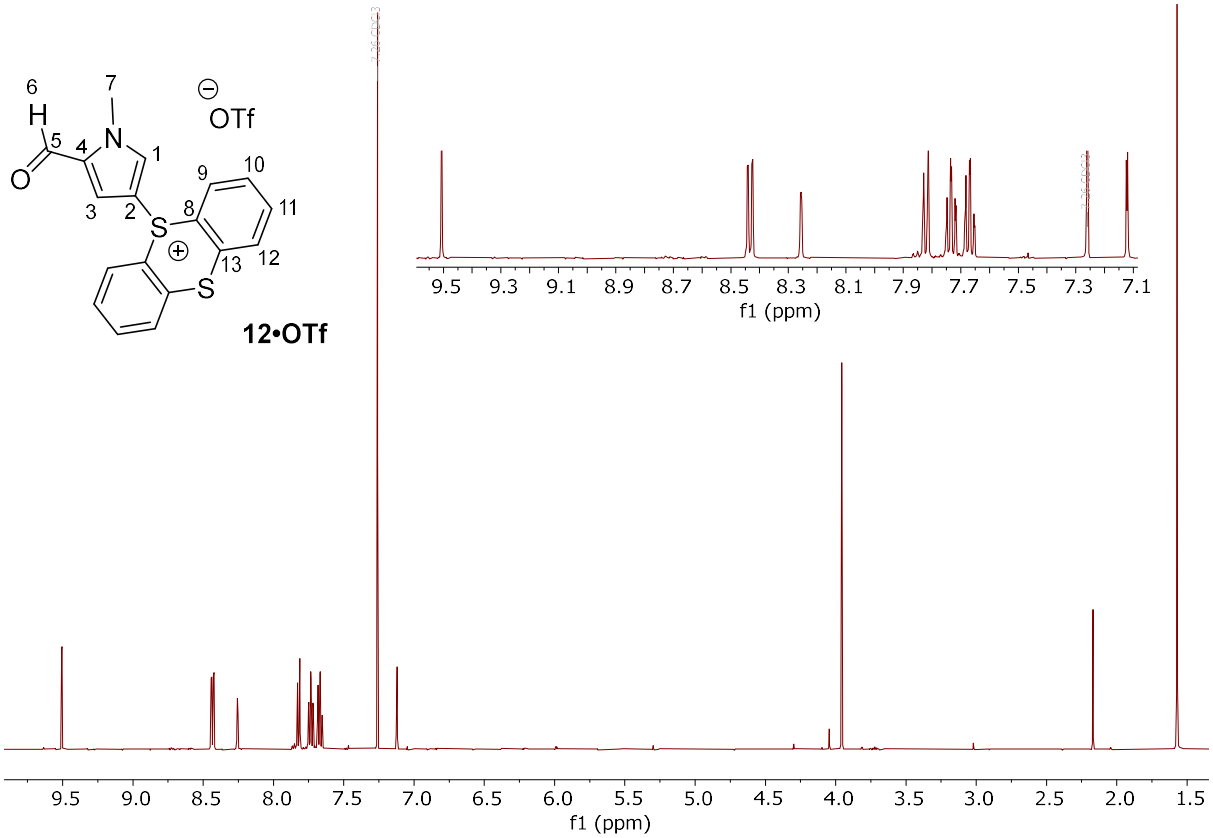


Figure S120: ^{1}H NMR spectrum of 5-(5-formyl-1-methyl-1H-pyrrol-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate ***12•OTf*** *in $CDCl_3$*

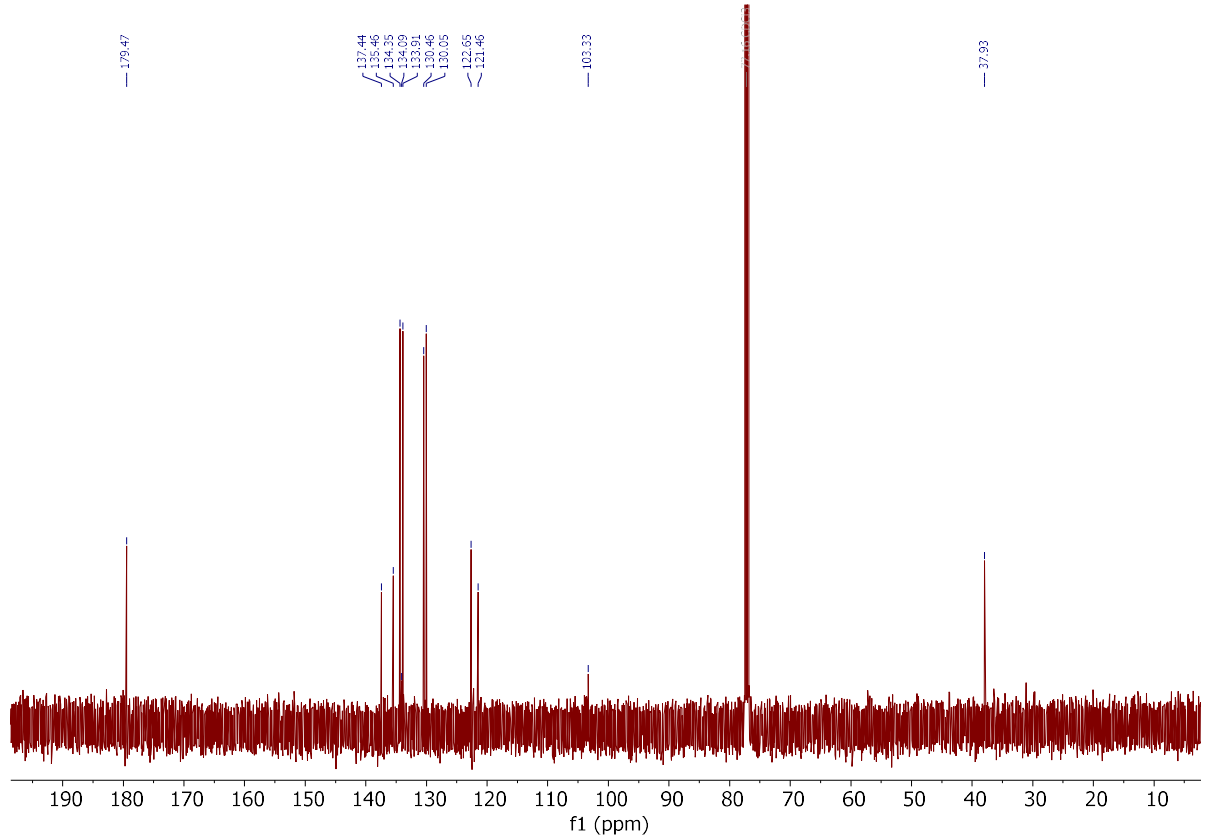


Figure S121: ^{13}C NMR spectrum of 5-(5-formyl-1-methyl-1H-pyrrol-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate ***12•OTf*** *in $CDCl_3$*

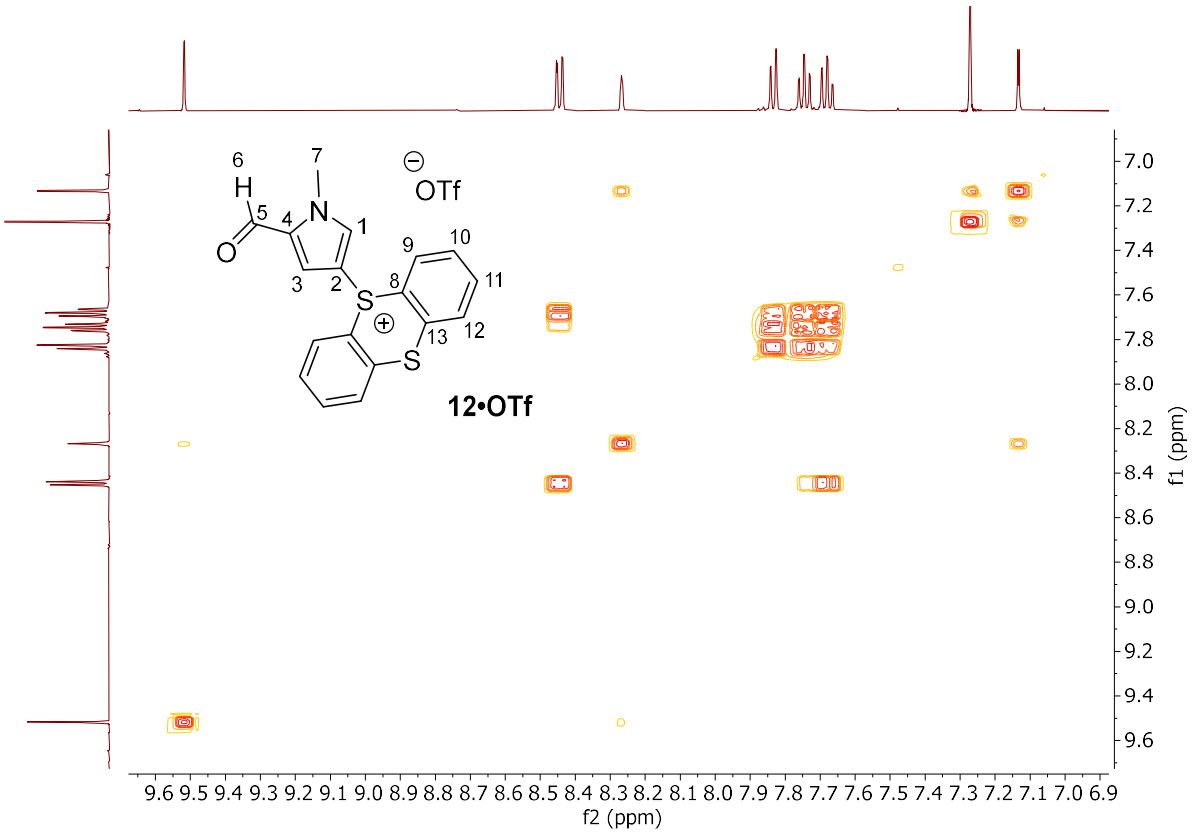


*Figure S122: COSY NMR spectrum of 5-(5-formyl-1-methyl-1*H*-pyrrol-3-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate* ***12•OTf*** *in $CDCl_3$*

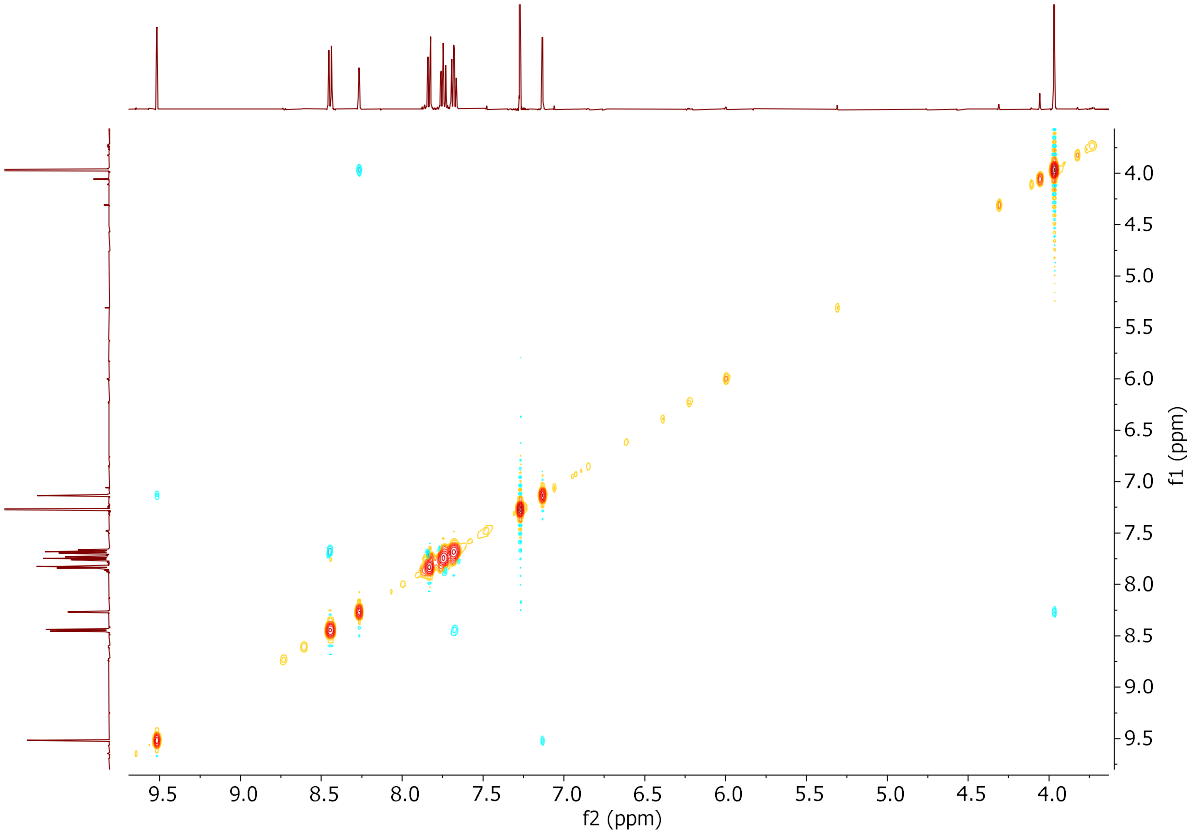


*Figure S123: NOESY NMR spectrum of 5-(5-formyl-1-methyl-1*H*-pyrrol-3-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate* ***12•OTf*** *in $CDCl_3$*

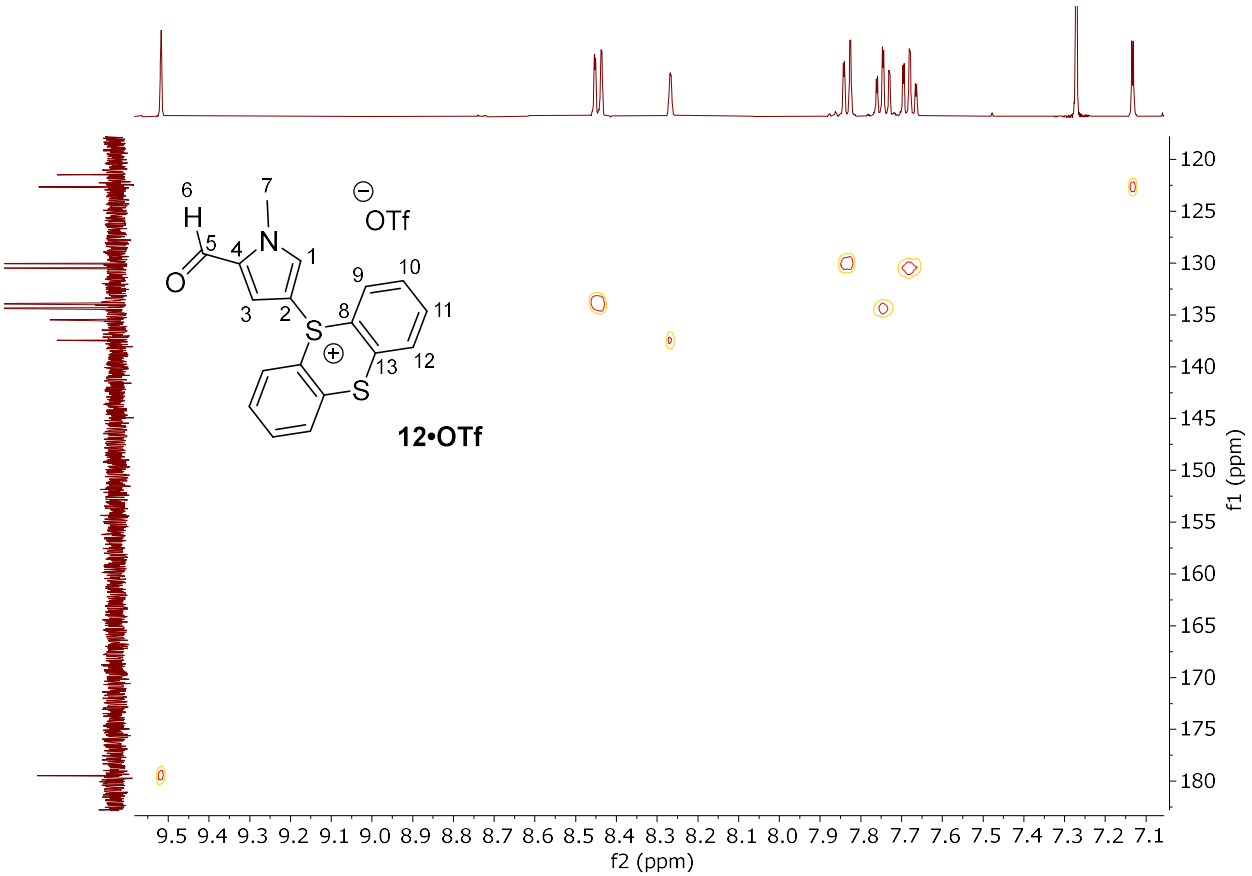


Figure S124: HSQC NMR spectrum of 5-(5-formyl-1-methyl-1H-pyrrol-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate ***12•OTf*** *in $CDCl_3$*

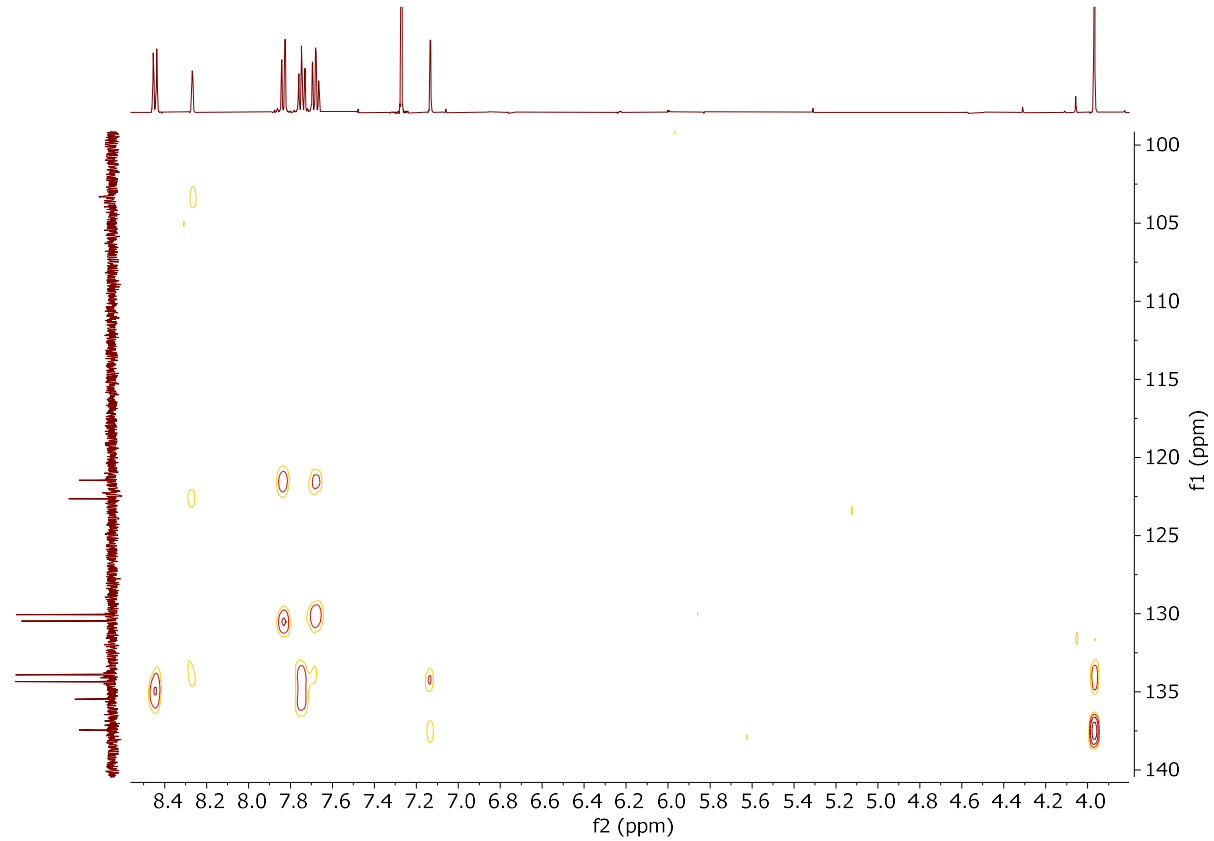


Figure S125: HMBC NMR spectrum of 5-(5-formyl-1-methyl-1H-pyrrol-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate ***12•OTf*** *in $CDCl_3$*

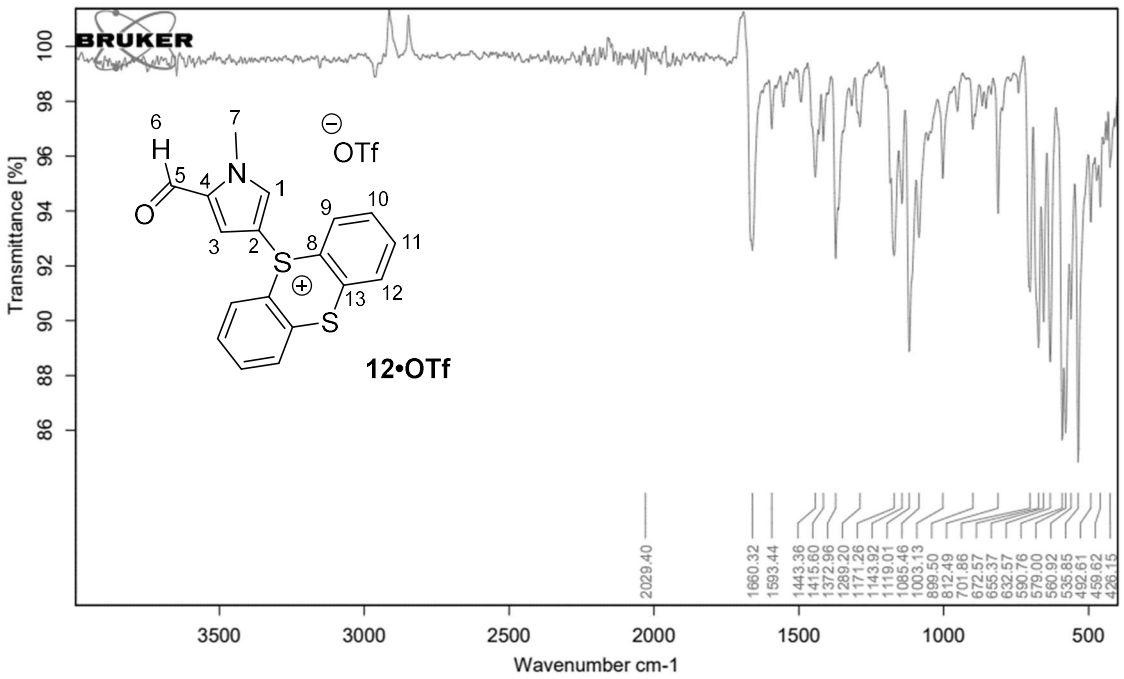


*Figure S126: IR spectrum of 5-(5-formyl-1-methyl-1*H*-pyrrol-3-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate* ***12•OTf***

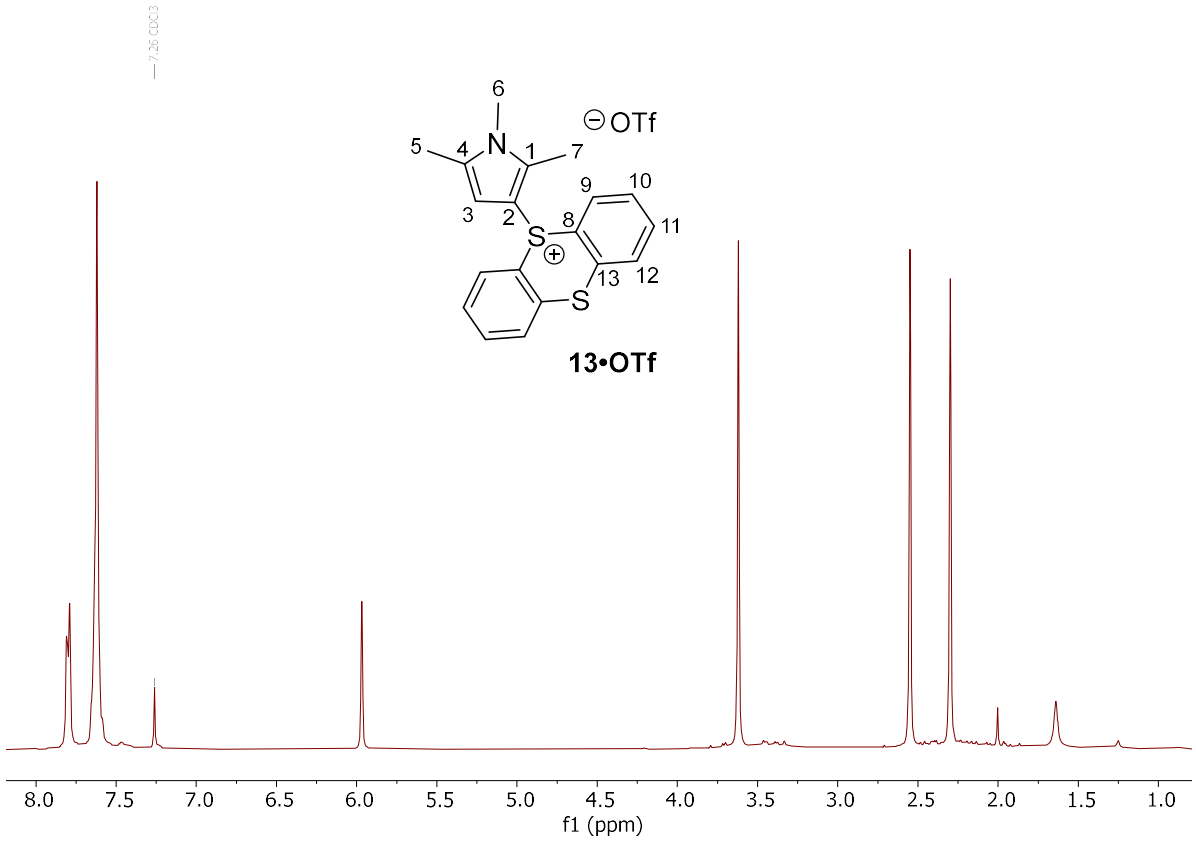


*Figure S127: ^{1}H NMR spectrum of 5-(1,2,5-trimethyl-1*H*-pyrrol-3-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate **13•OTf** in $CDCl_3$*

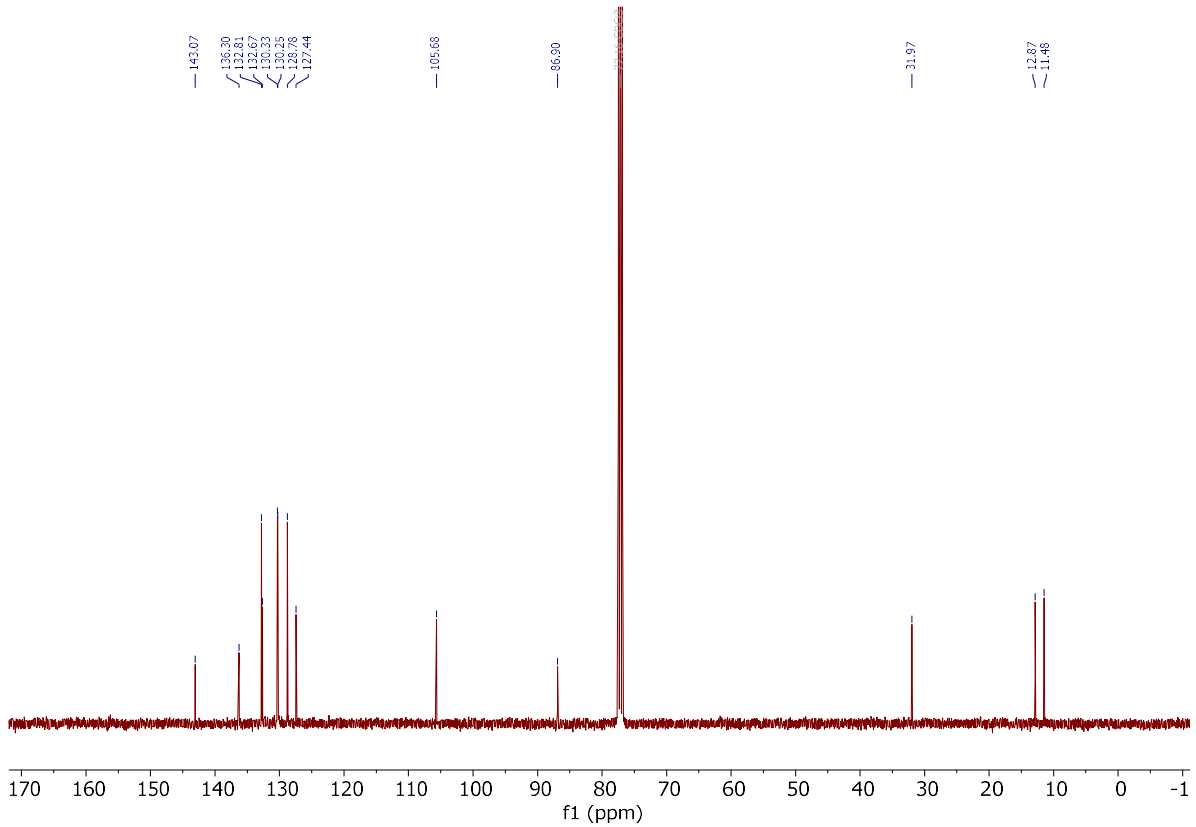


*Figure S128: ^{13}C NMR spectrum of 5-(1,2,5-trimethyl-1*H*-pyrrol-3-yl)-5*H*-thianthren-5-ium trifluoromethanesulfonate **13•OTf** in $CDCl_3$*

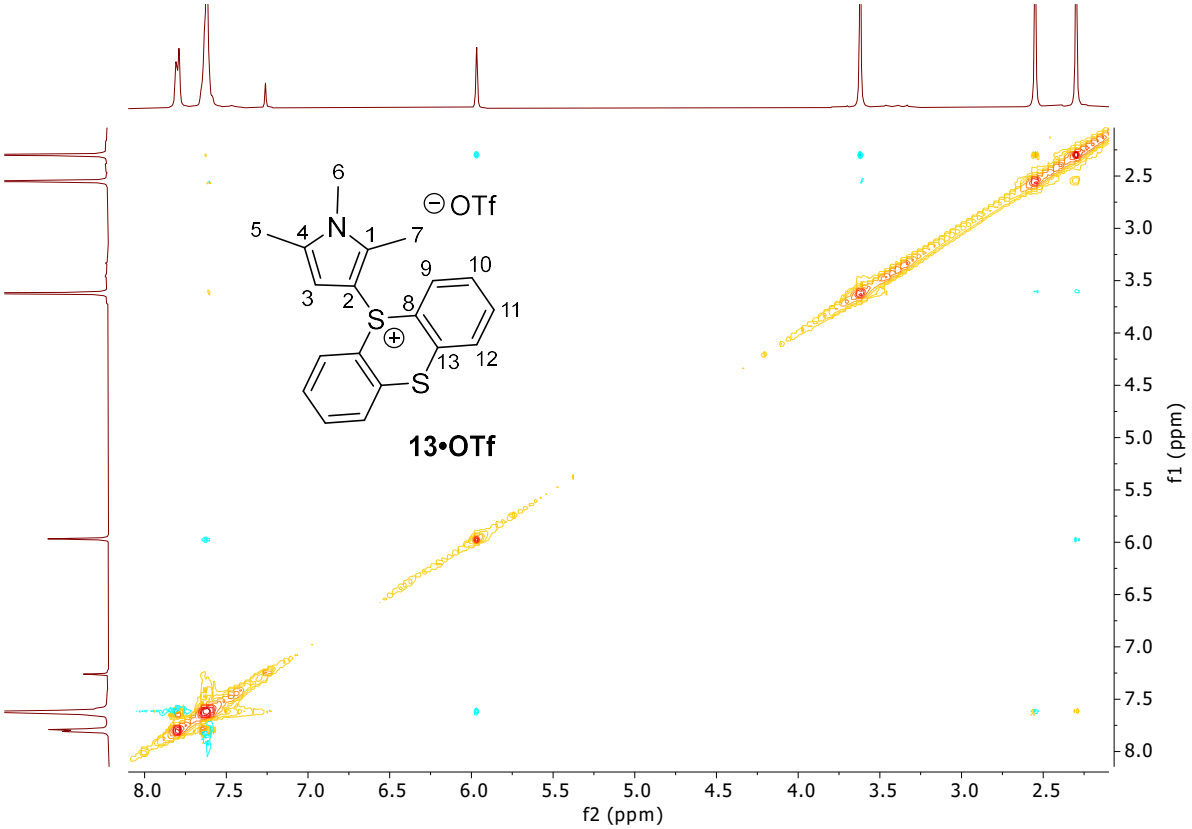


Figure S129: NOESY NMR spectrum of 5-(1,2,5-trimethyl-1H-pyrrol-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate ***13•OTf*** *in* $CDCl_3$

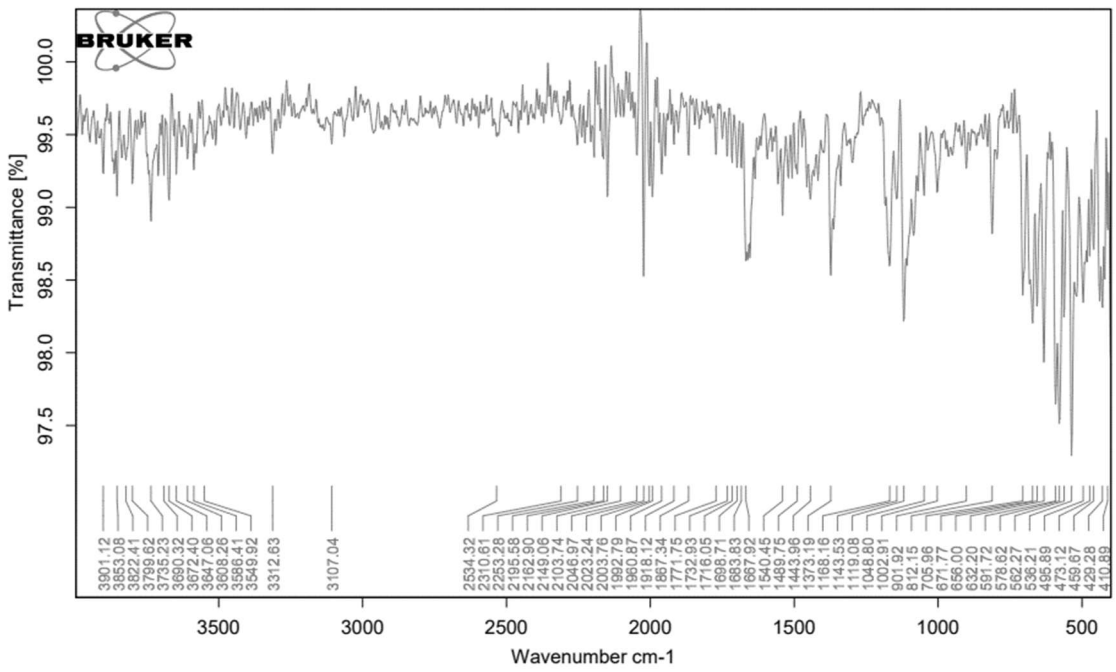


Figure S130: IR spectrum of 5-(1,2,5-trimethyl-1H-pyrrol-3-yl)-5H-thianthren-5-ium trifluoromethanesulfonate ***13•OTf***

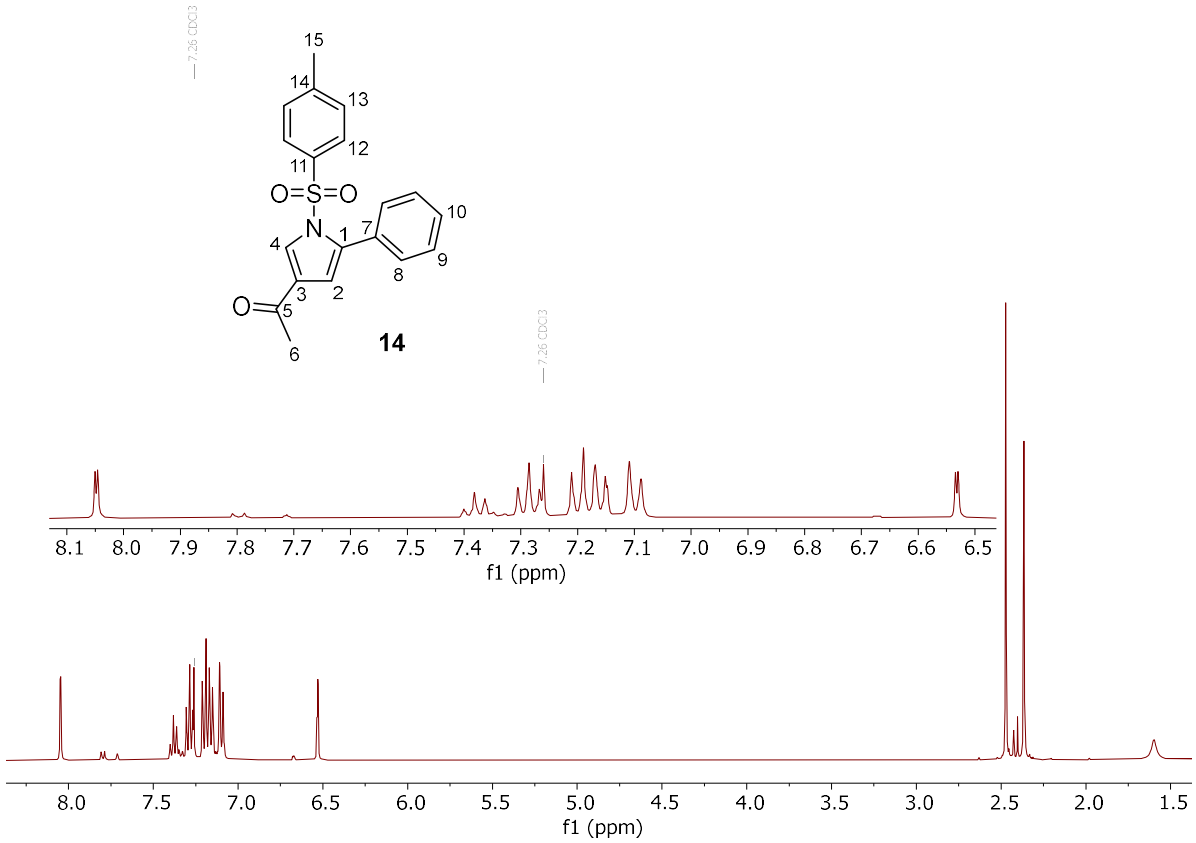


*Figure S131: ^{1}H NMR spectrum of 1-(5-phenyl-1-(p-toluenesulfonyl)-1H-pyrrol-3-yl)ethan-1-one **14** in $CDCl_3$*

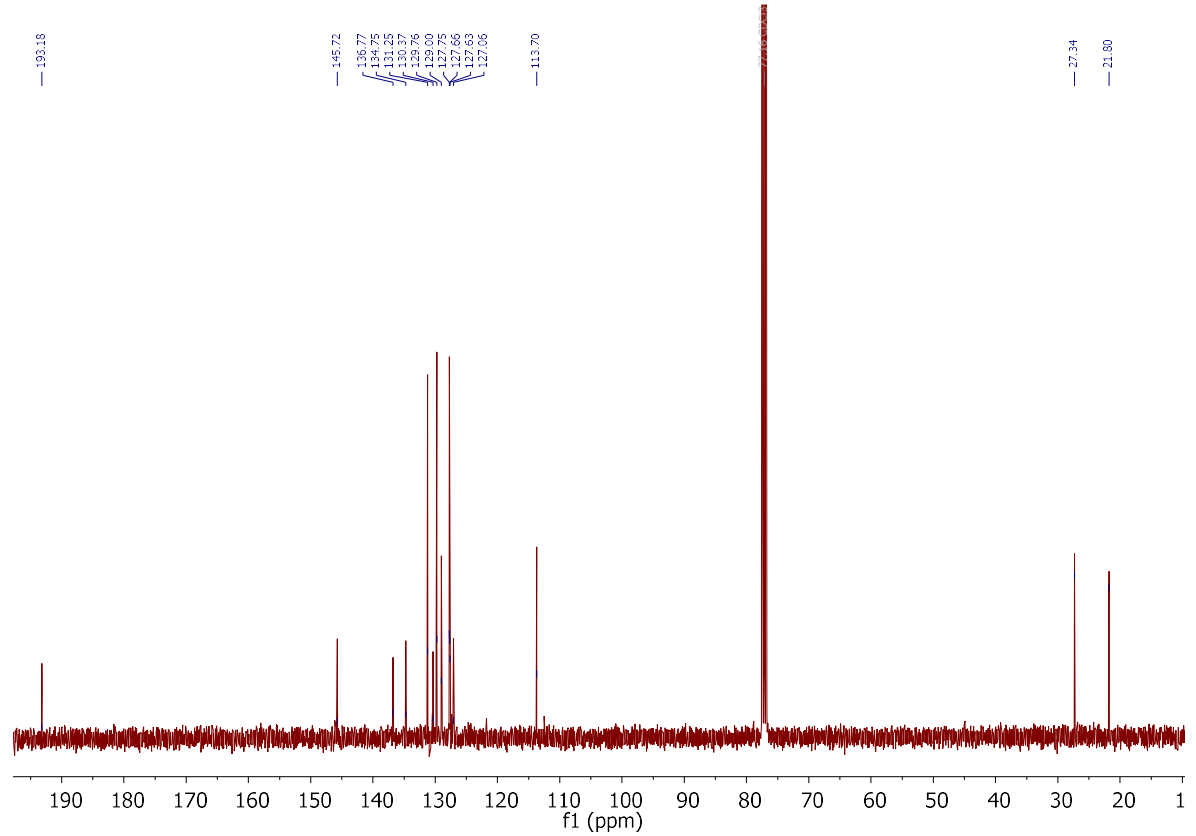


*Figure S132: ^{13}C NMR spectrum of 1-(5-phenyl-1-(p-toluenesulfonyl)-1H-pyrrol-3-yl)ethan-1-one **14** in $CDCl_3$*

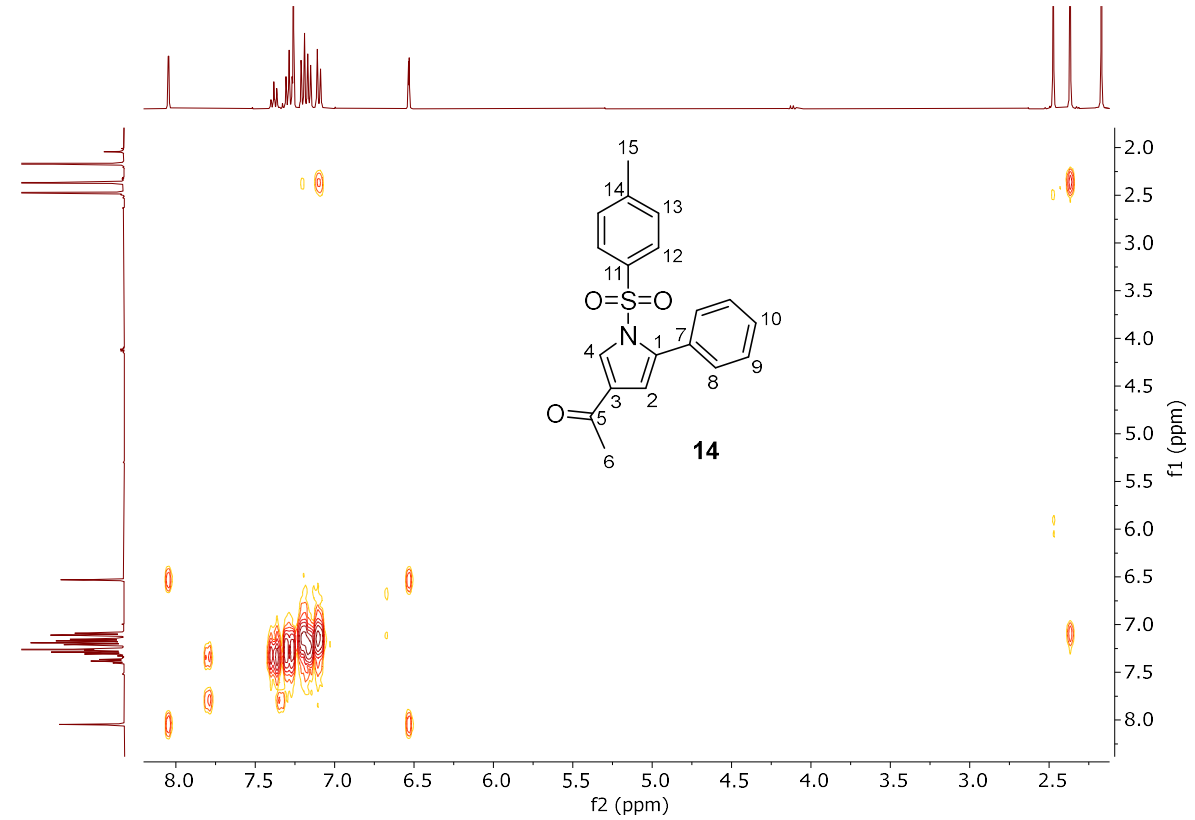


*Figure S133: COSY NMR spectrum of 1-(5-phenyl-1-(p-toluenesulfonyl)-1H-pyrrol-3-yl)ethan-1-one **14** in $CDCl_3$*

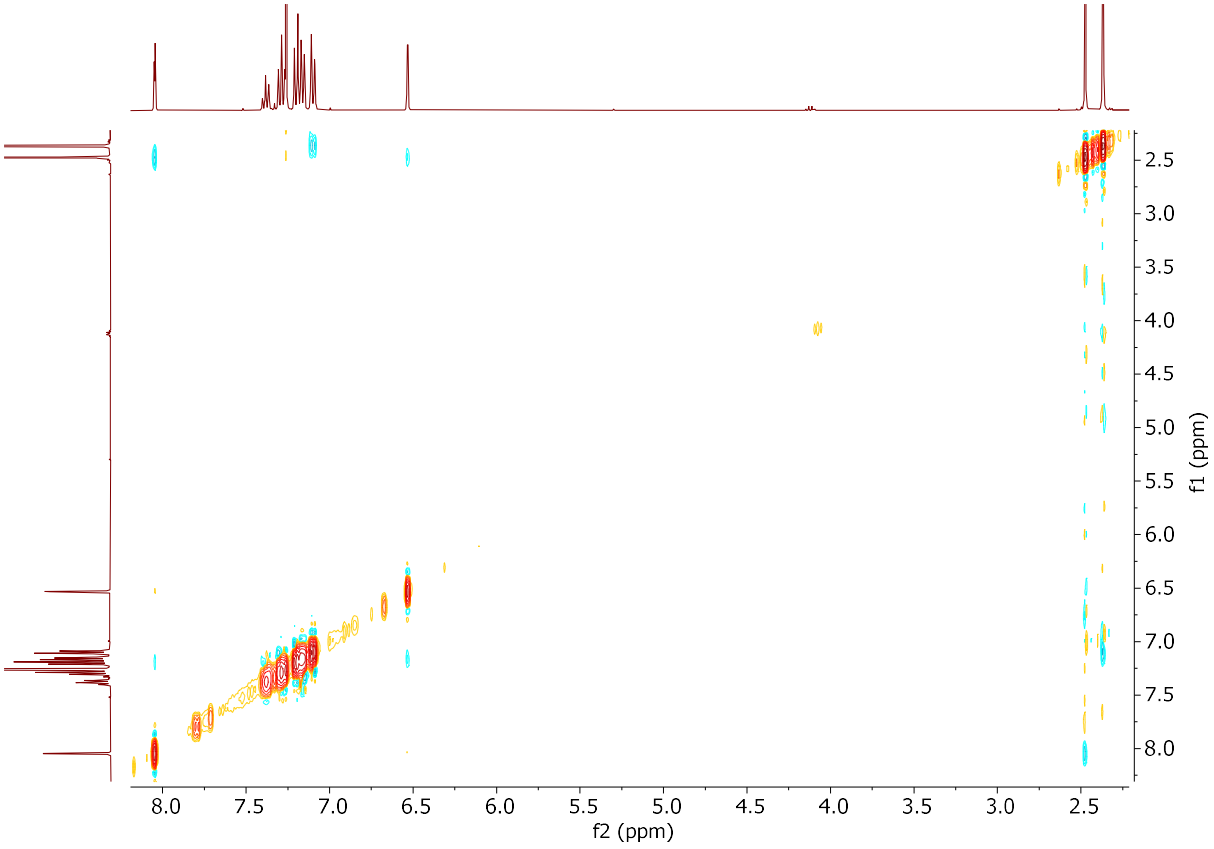


*Figure S134: NOESY NMR spectrum of 1-(5-phenyl-1-(p-toluenesulfonyl)-1H-pyrrol-3-yl)ethan-1-one **14** in $CDCl_3$*

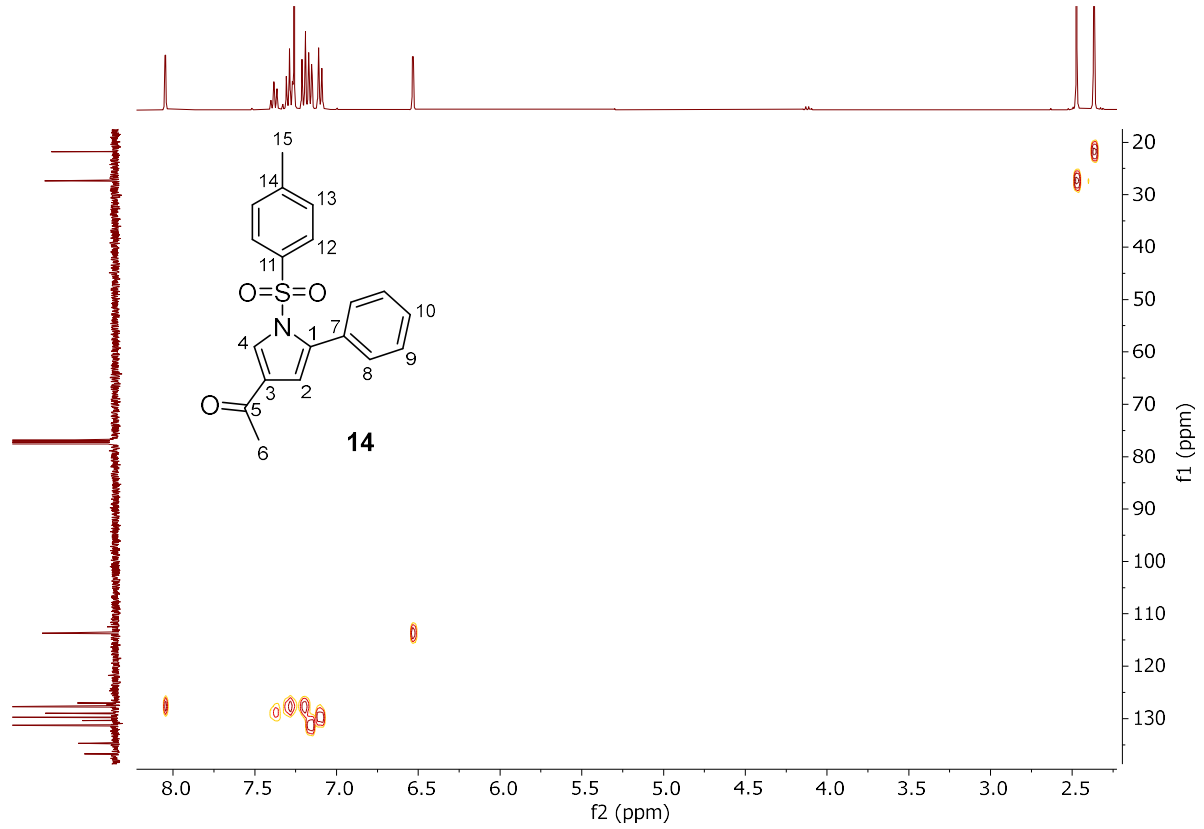


*Figure S135: HSQC NMR spectrum of 1-(5-phenyl-1-(*p*-toluenesulfonyl)-1*H*-pyrrol-3-yl)ethan-1-one **14** in $CDCl_3$*

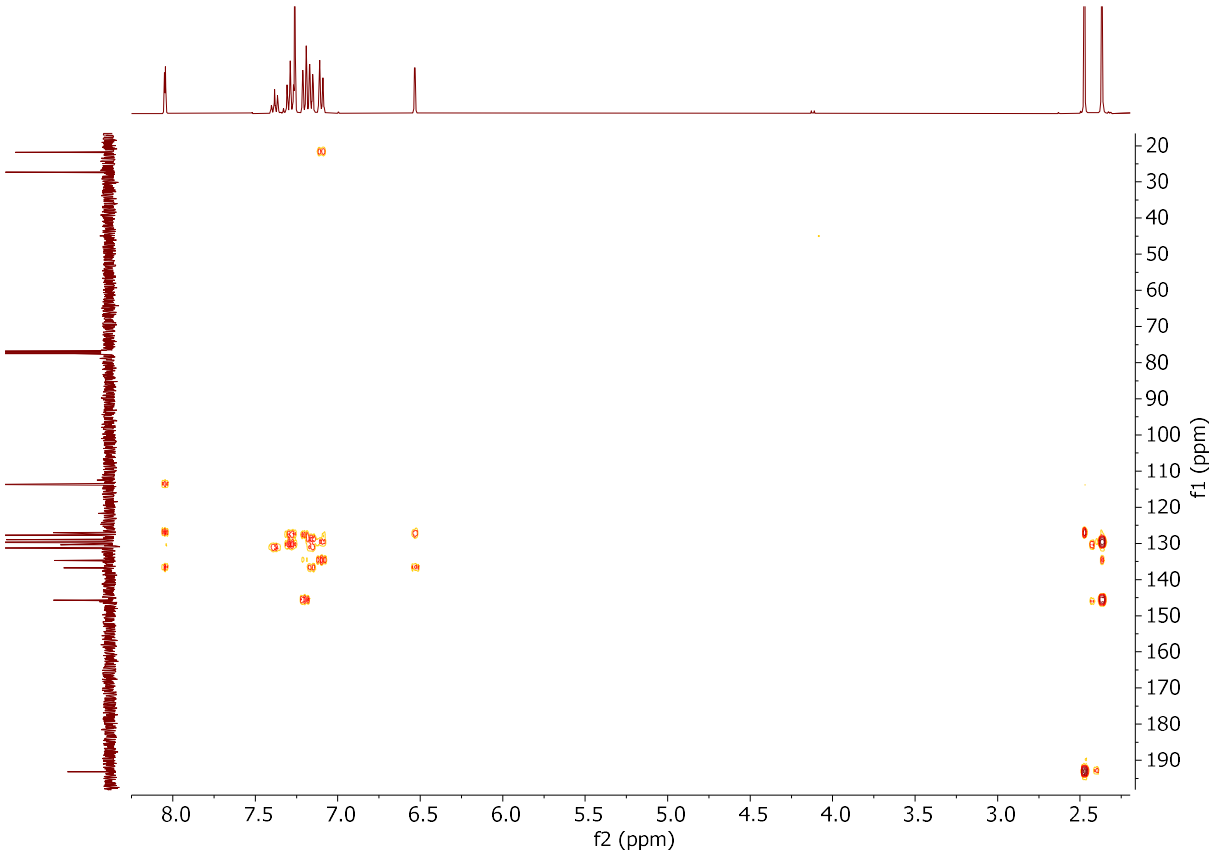


*Figure S136: HMBC NMR spectrum of 1-(5-phenyl-1-(*p*-toluenesulfonyl)-1*H*-pyrrol-3-yl)ethan-1-one **14** in $CDCl_3$*

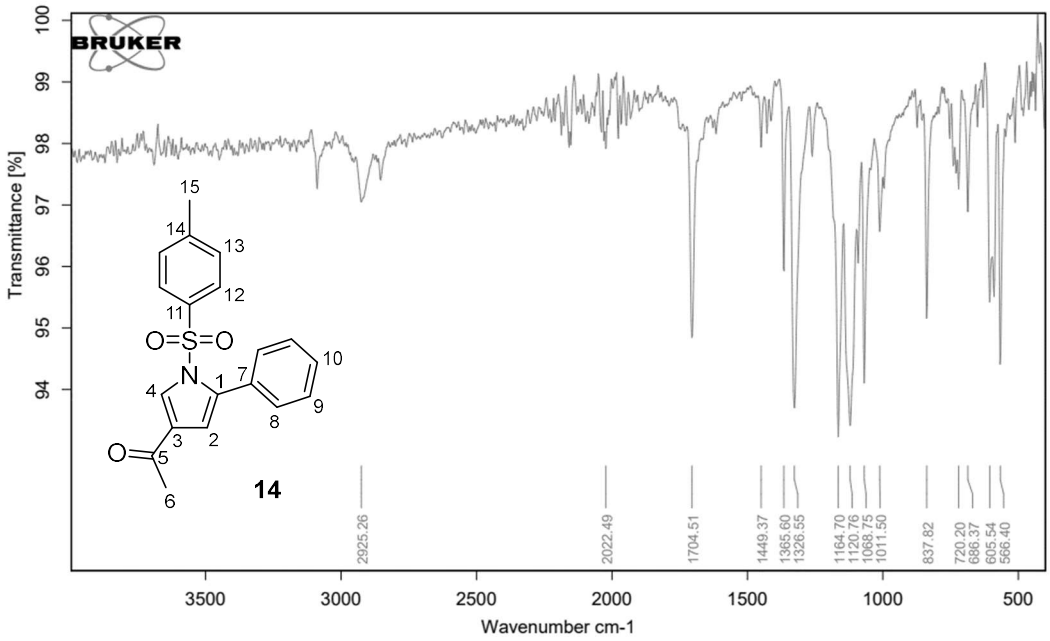


*Figure S137: IR spectrum of 1-(5-phenyl-1-(*p*-toluenesulfonyl)-1*H*-pyrrol-3-yl)ethan-1-one* ***14***

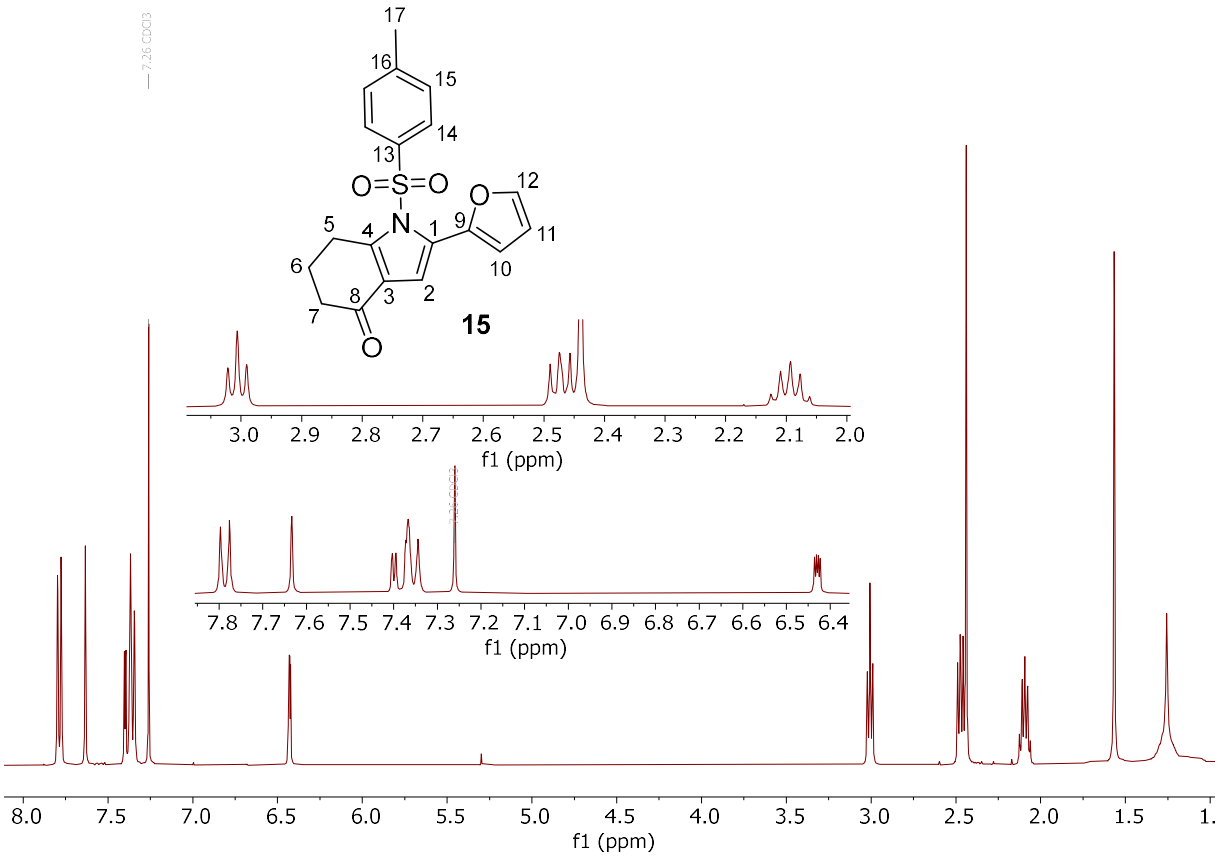


*Figure S138: ^{1}H NMR spectrum of 2-(furan-2-yl)-1-(p-toluenesulfonyl)-1,5,6,7-tetrahydro-4H-indol-4-one **15** in $CDCl_3$.*

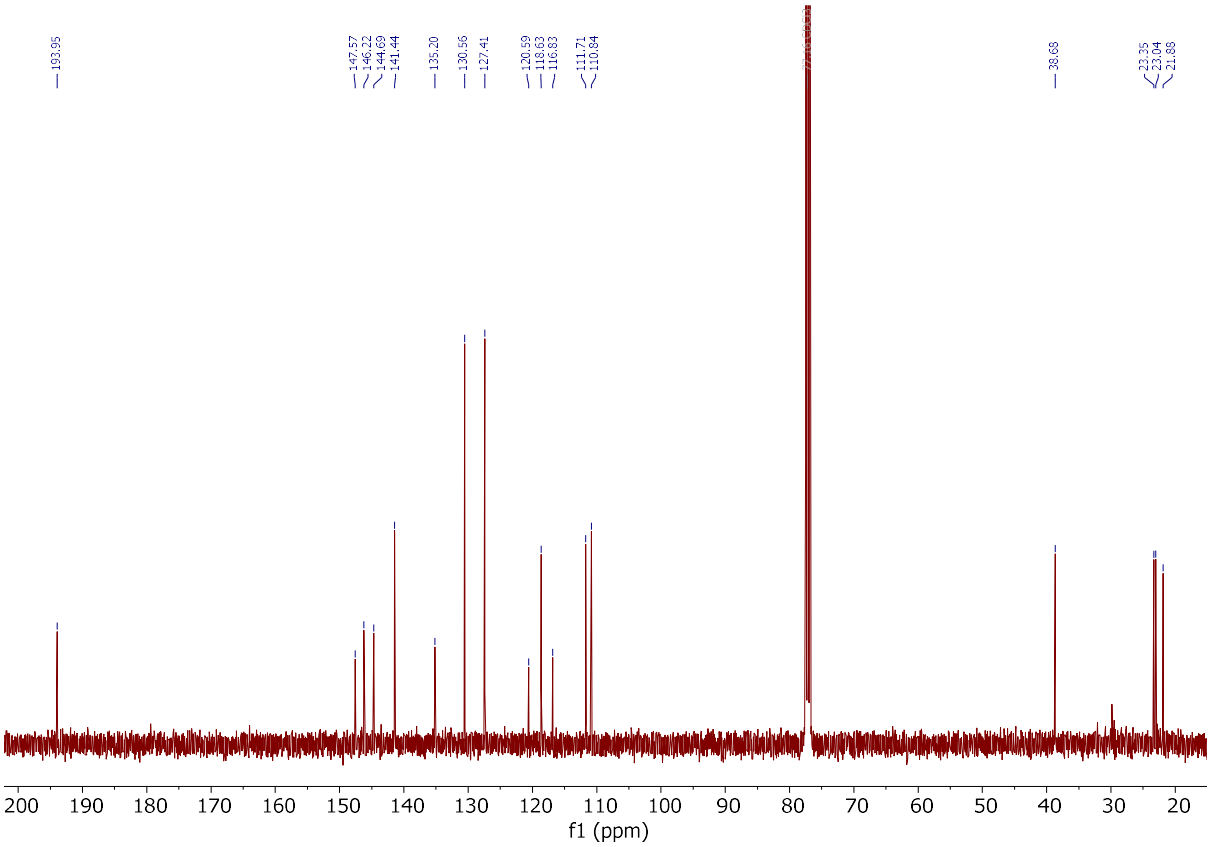


*Figure S139: ^{13}C NMR spectrum of 2-(furan-2-yl)-1-(p-toluenesulfonyl)-1,5,6,7-tetrahydro-4H-indol-4-one **15** in $CDCl_3$.*

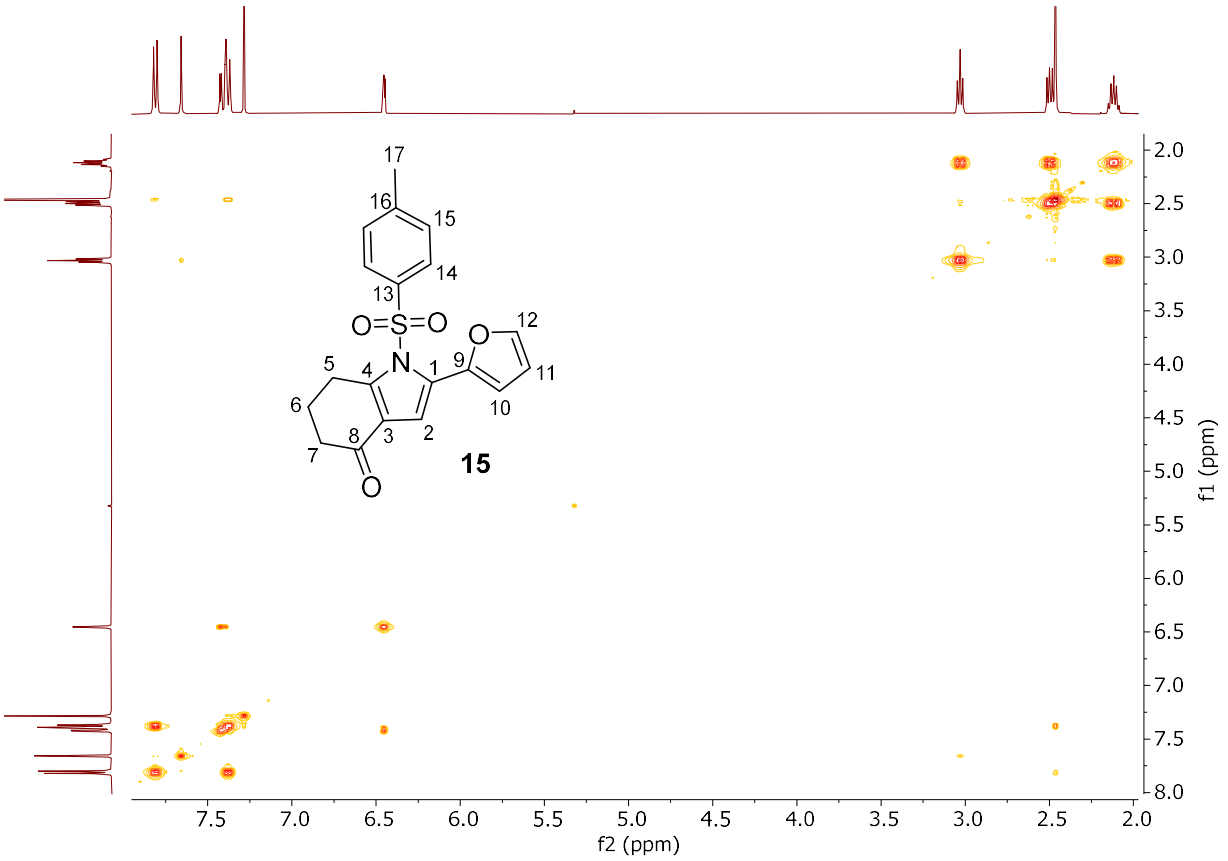


*Figure S140: COSY NMR spectrum of 2-(furan-2-yl)-1-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-4*H*-indol-4-one **15** in $CDCl_3$.*

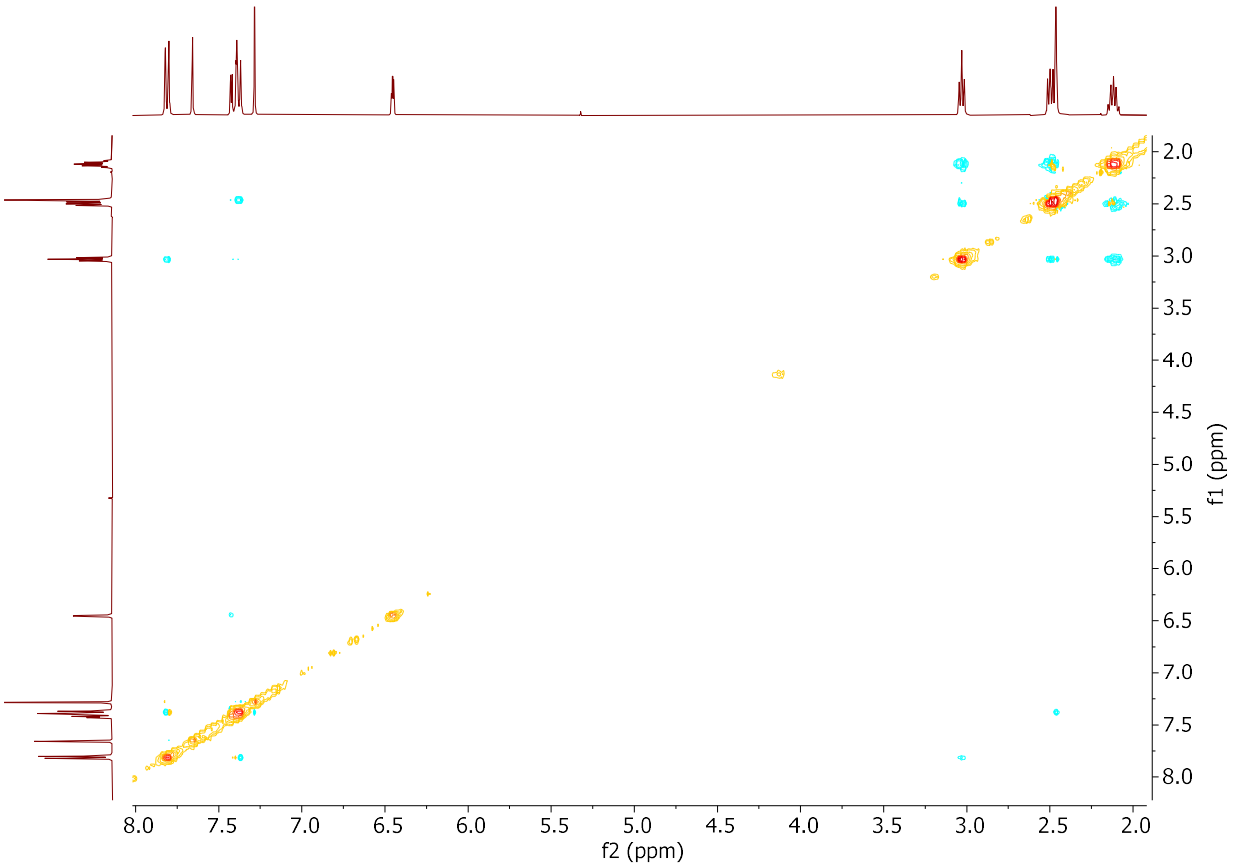


*Figure S141: NOESY NMR spectrum of 2-(furan-2-yl)-1-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-4*H*-indol-4-one **15** in $CDCl_3$.*

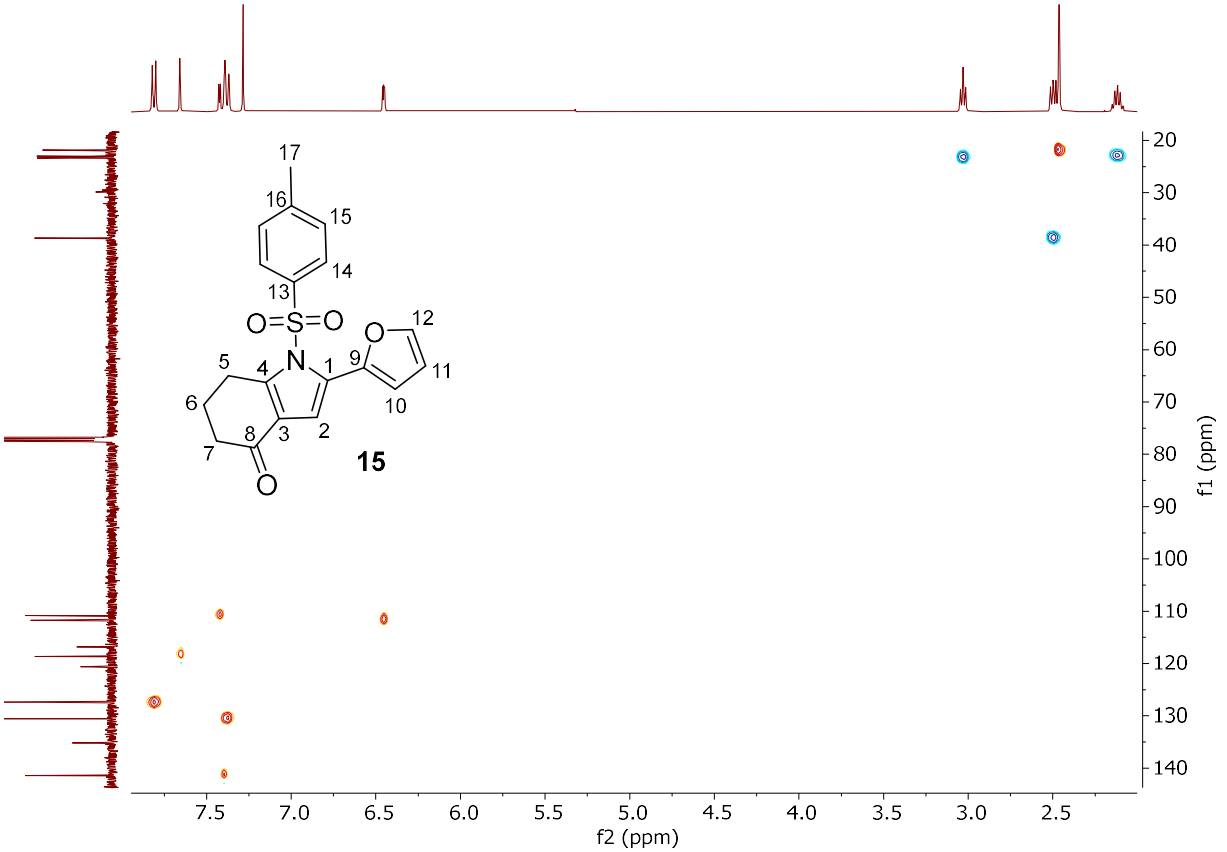


*Figure S142: HSQC NMR spectrum of 2-(furan-2-yl)-1-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-4*H*-indol-4-one **15** in $CDCl_3$.*

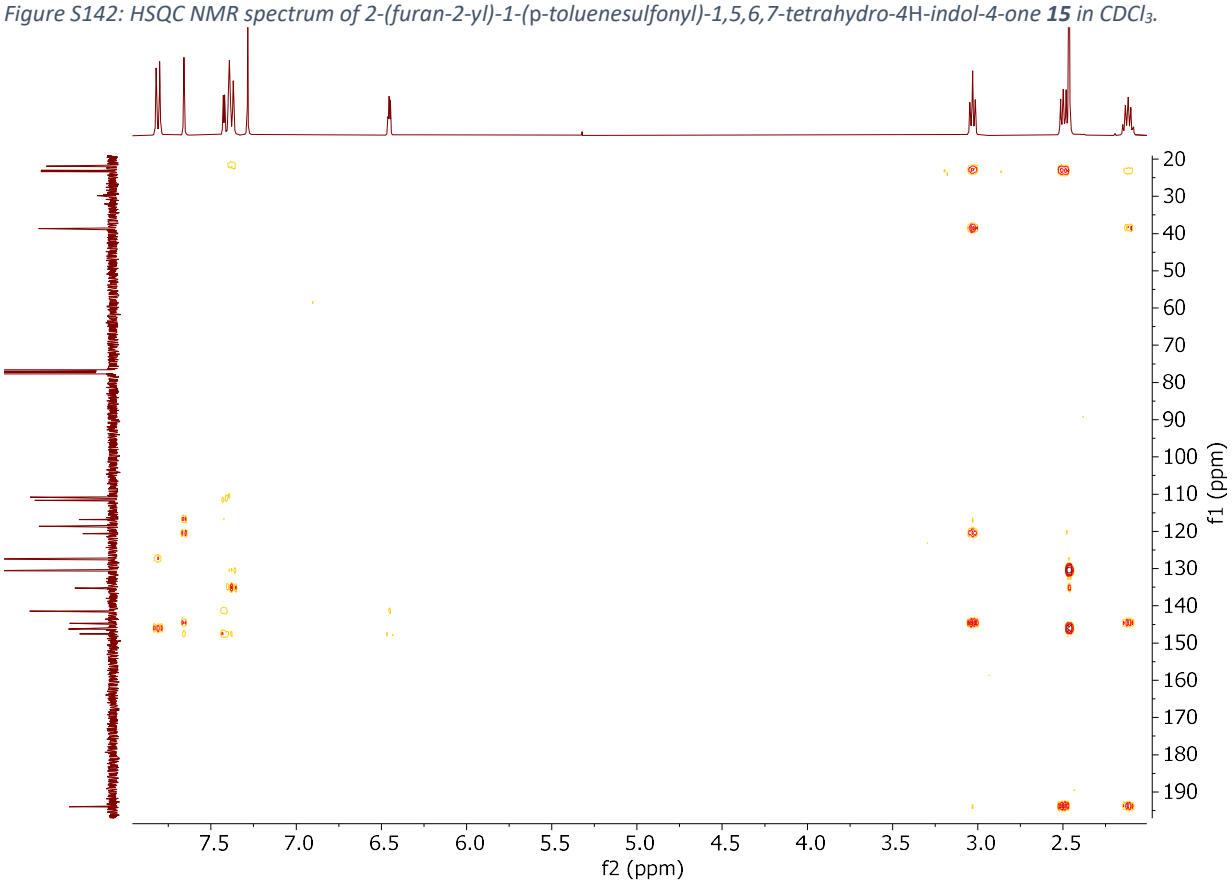


*Figure S143: HMBC NMR spectrum of 2-(furan-2-yl)-1-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-4*H*-indol-4-one **15** in $CDCl_3$.*

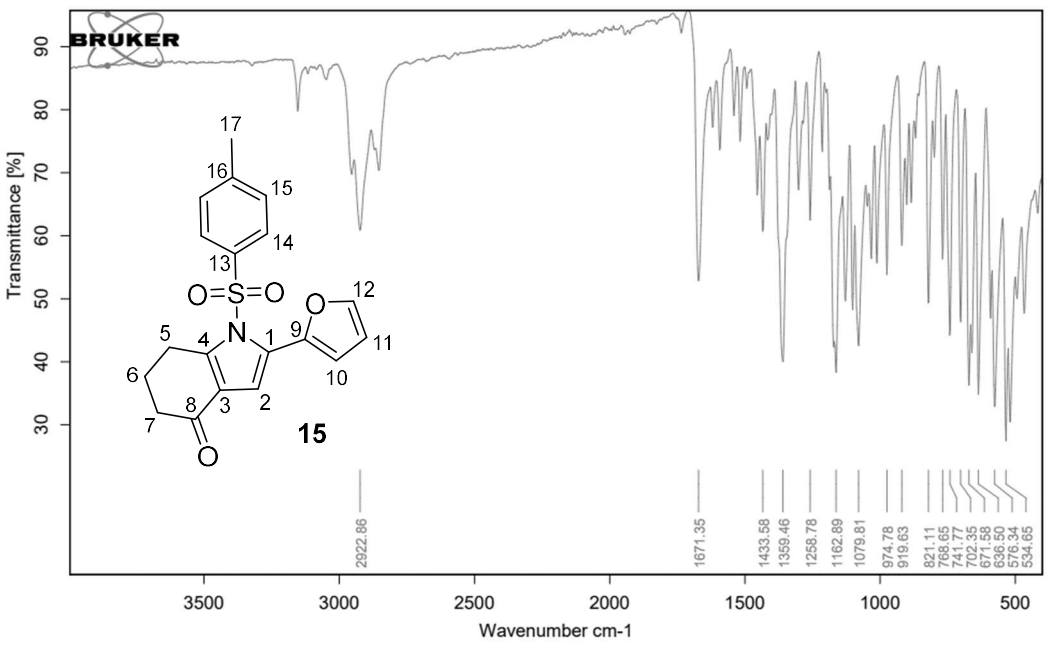


*Figure S144: IR Spectrum of spectrum of 2-(furan-2-yl)-1-(*p*-toluenesulfonyl)-1,5,6,7-tetrahydro-4*H*-indol-4-one* ***15***

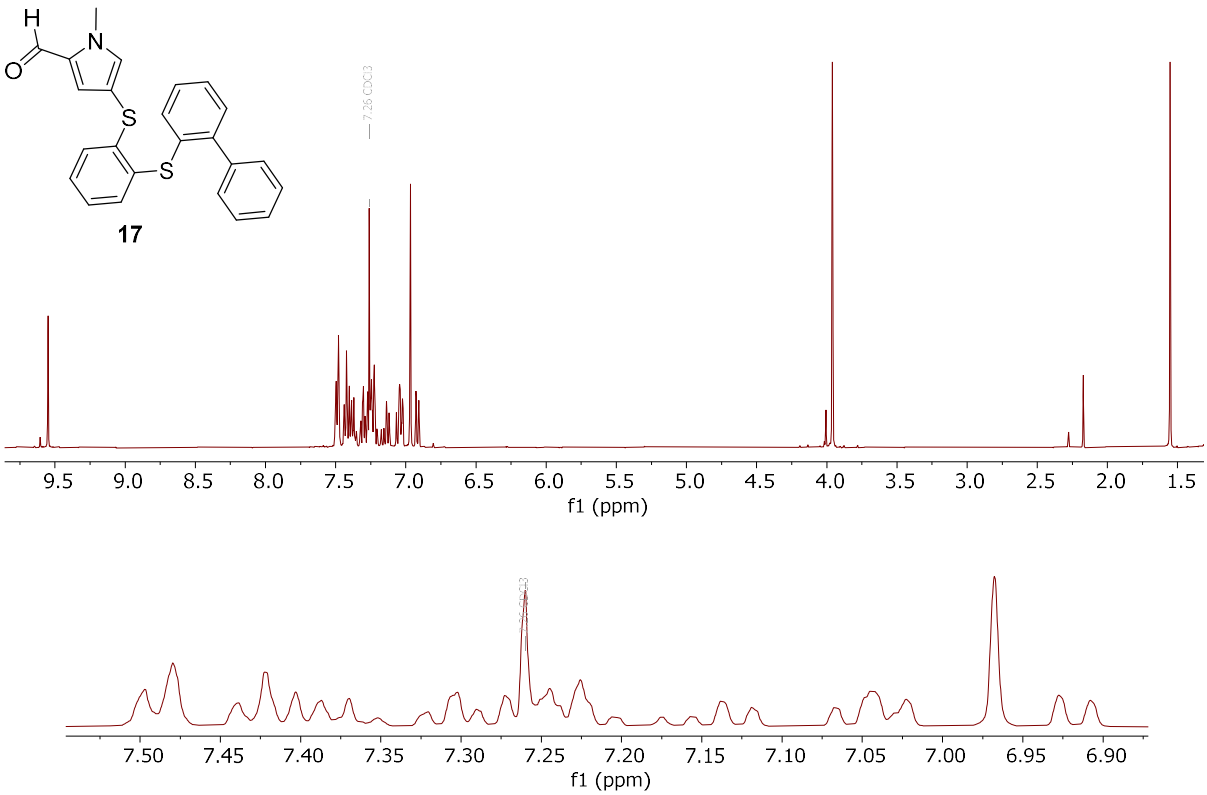


*Figure S145: [1]H NMR spectrum of 4-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1-methyl-1*H*-pyrrole-2-carbaldehyde **17** in $CDCl_3$*

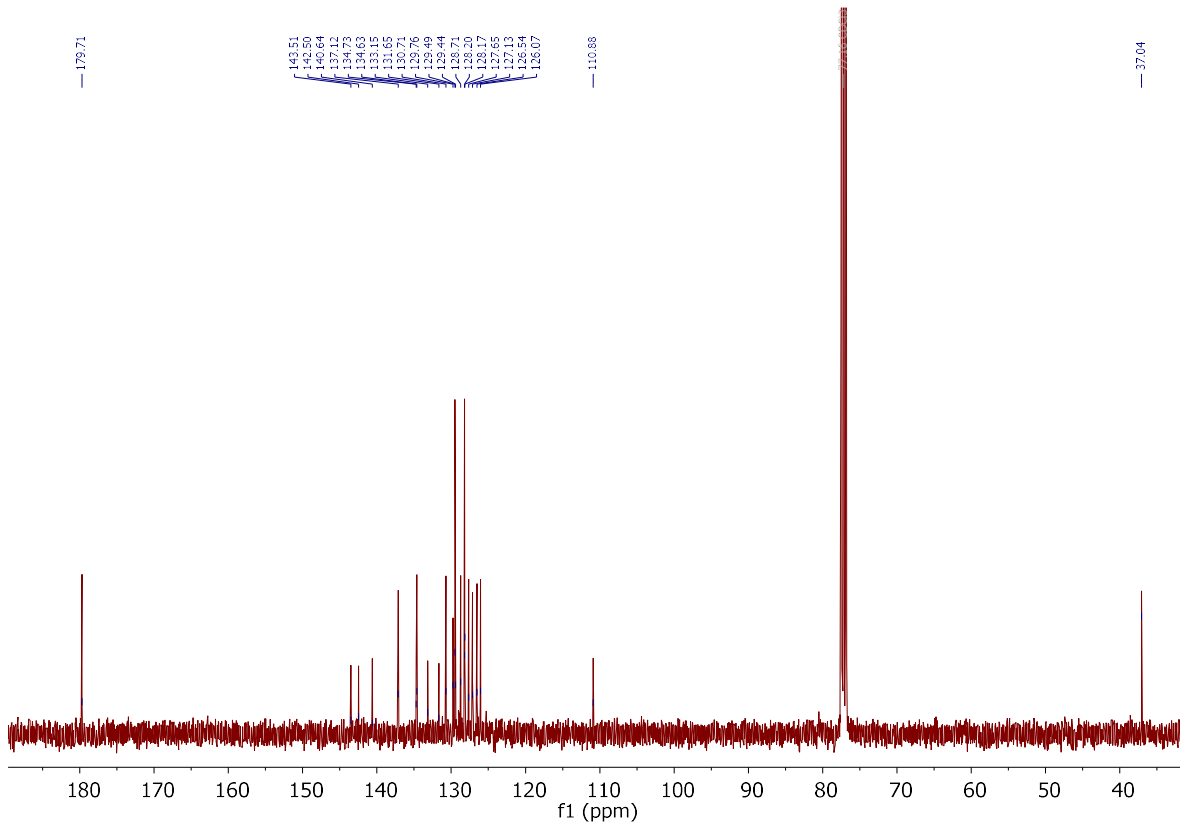


*Figure S146: [13]C NMR spectrum of 4-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1-methyl-1*H*-pyrrole-2-carbaldehyde **17** in $CDCl_3$*

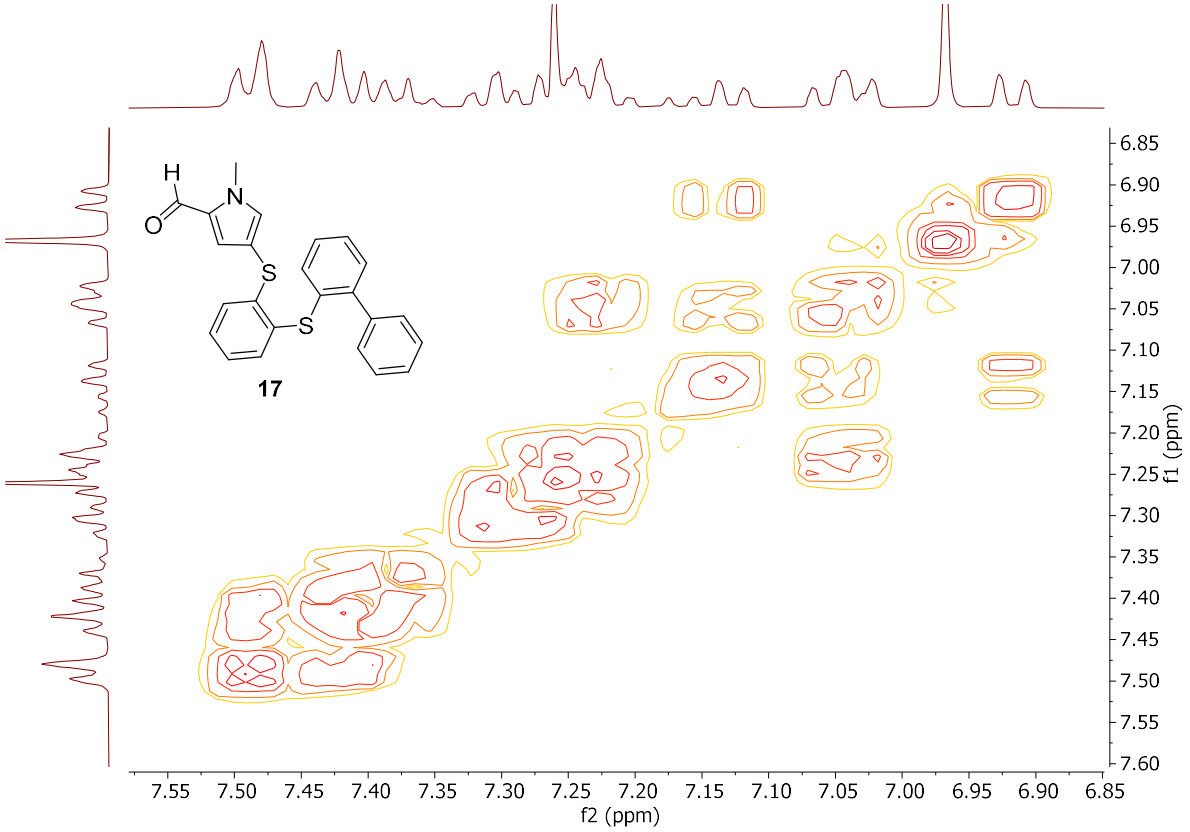


*Figure S147: COSY spectrum of 4-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1-methyl-1H-pyrrole-2-carbaldehyde **17** in $CDCl_3$*

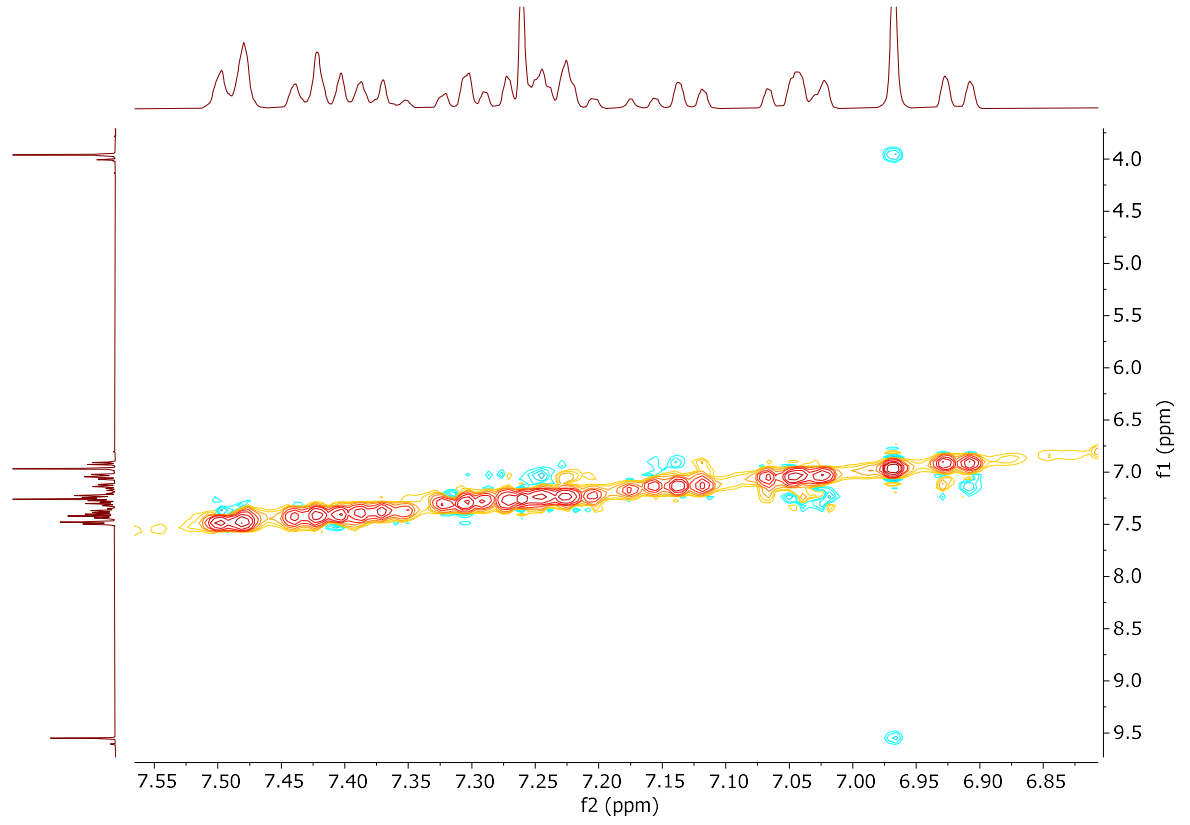


*Figure S148: NOESY spectrum of 4-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1-methyl-1H-pyrrole-2-carbaldehyde **17** in $CDCl_3$*

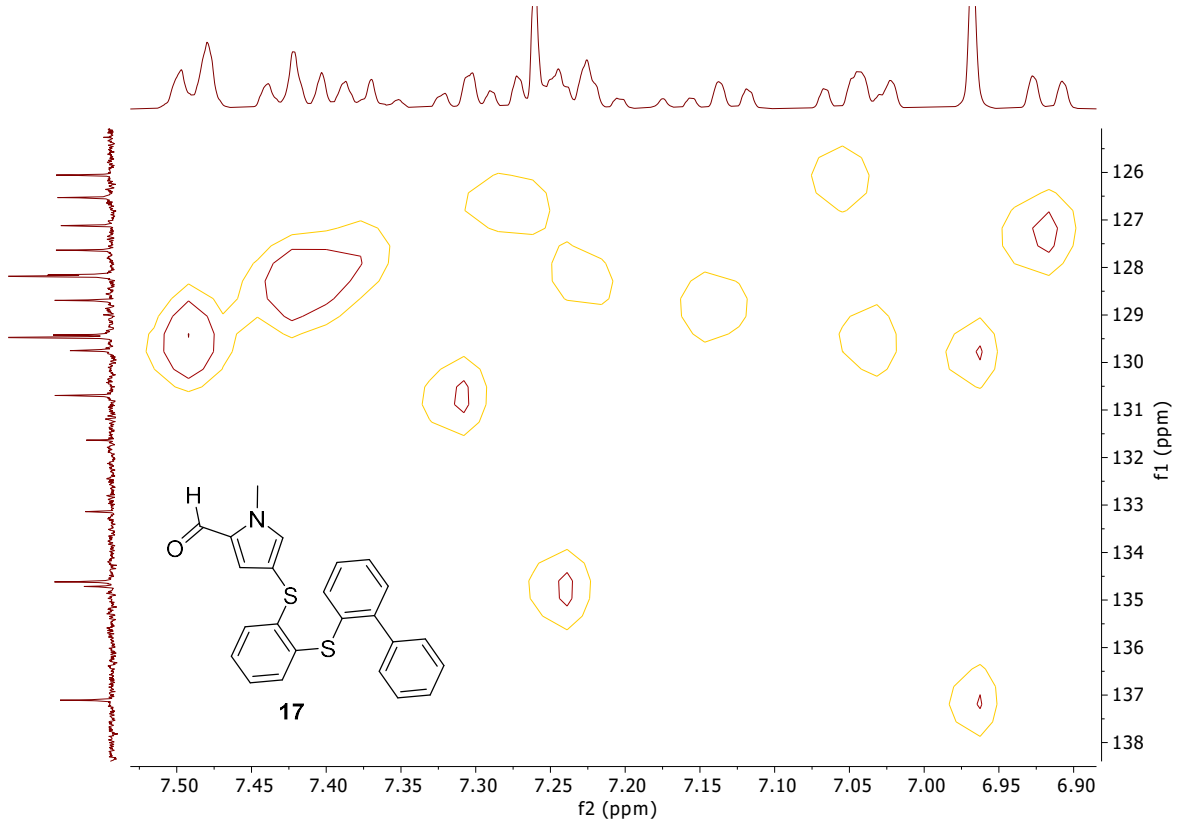


*Figure S149: HSQC spectrum of 4-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1-methyl-1*H*-pyrrole-2-carbaldehyde **17** in $CDCl_3$*

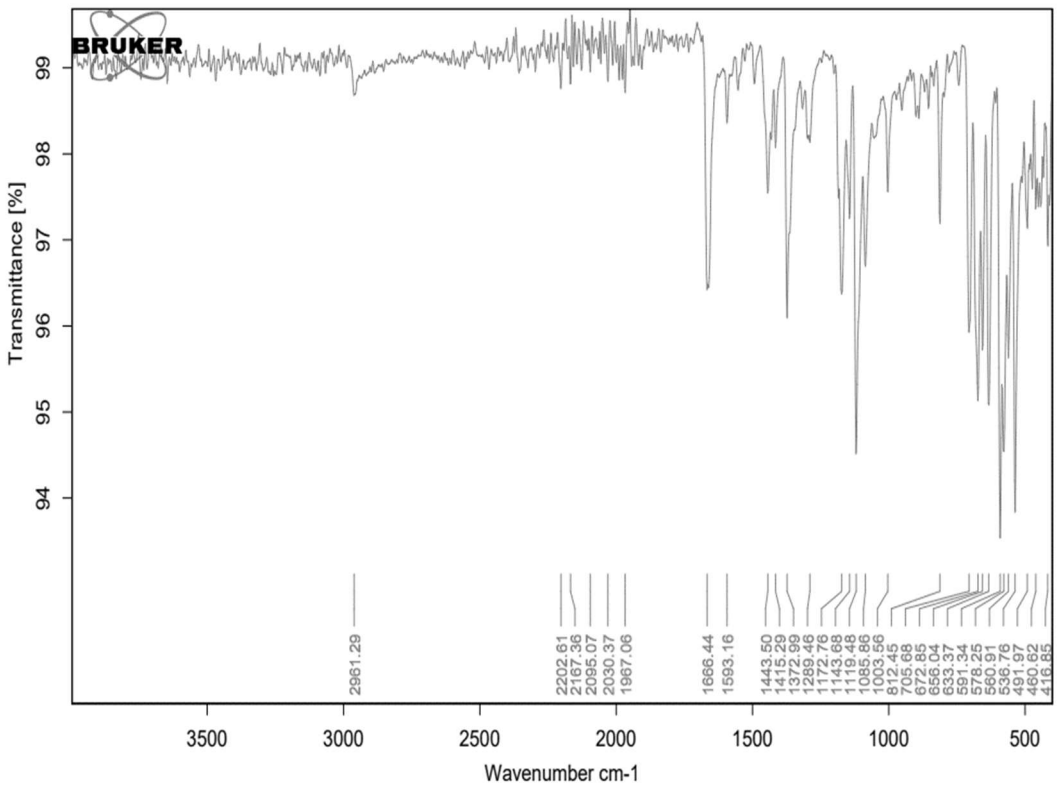


*Figure S150: IR spectrum of spectrum of 4-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1-methyl-1*H*-pyrrole-2-carbaldehyde **17***

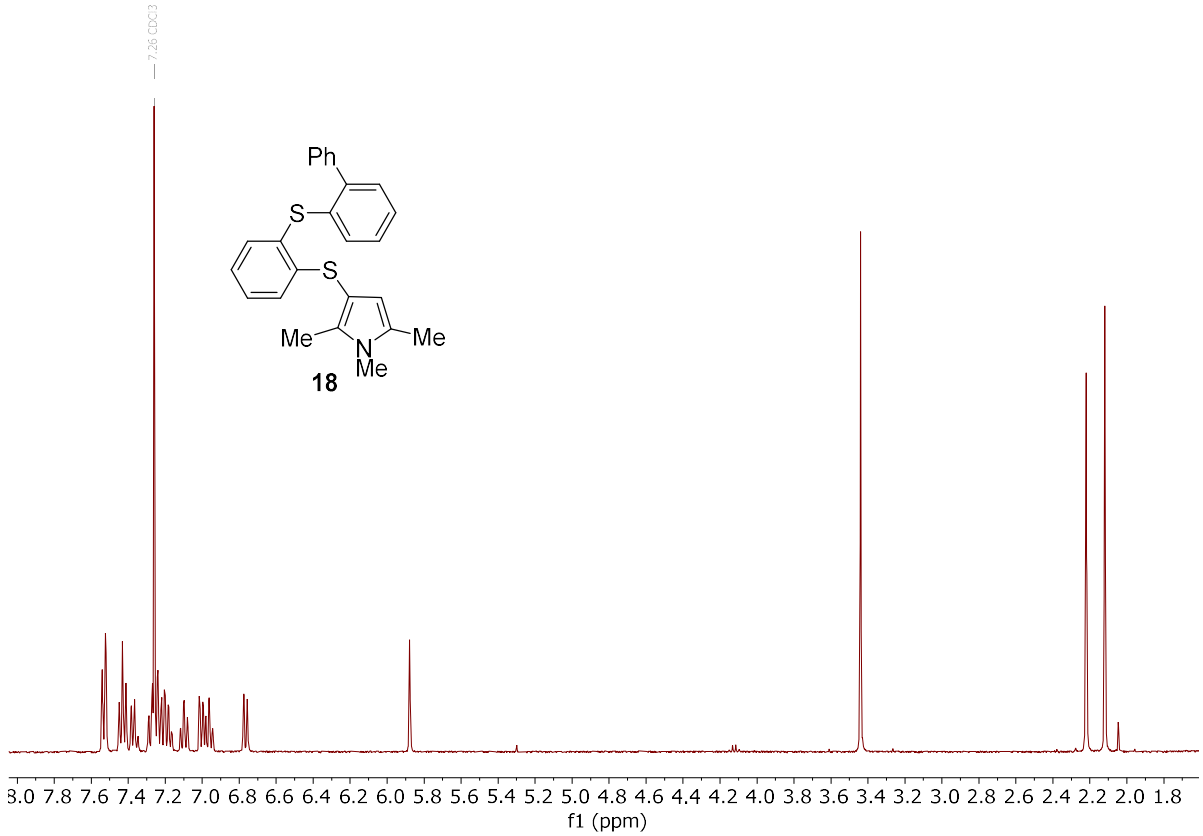


*Figure S151: ^{1}H NMR spectrum of 3-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1,2,5-trimethyl-1*H*-pyrrole **18** in $CDCl_3$*

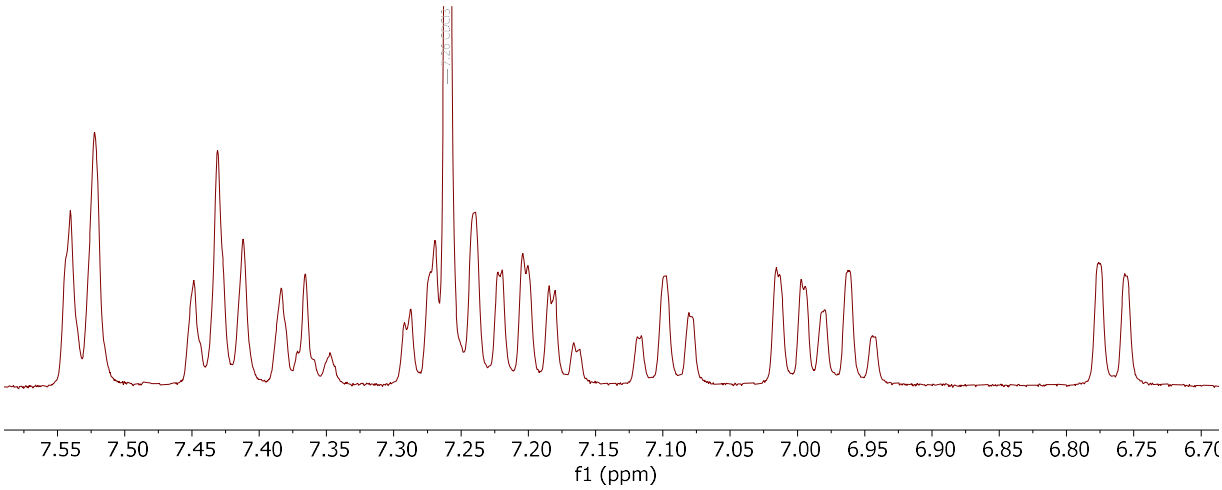


*Figure S152: Zoomed region of ^{1}H NMR spectrum of 3-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1,2,5-trimethyl-1*H*-pyrrole **18** in $CDCl_3$*

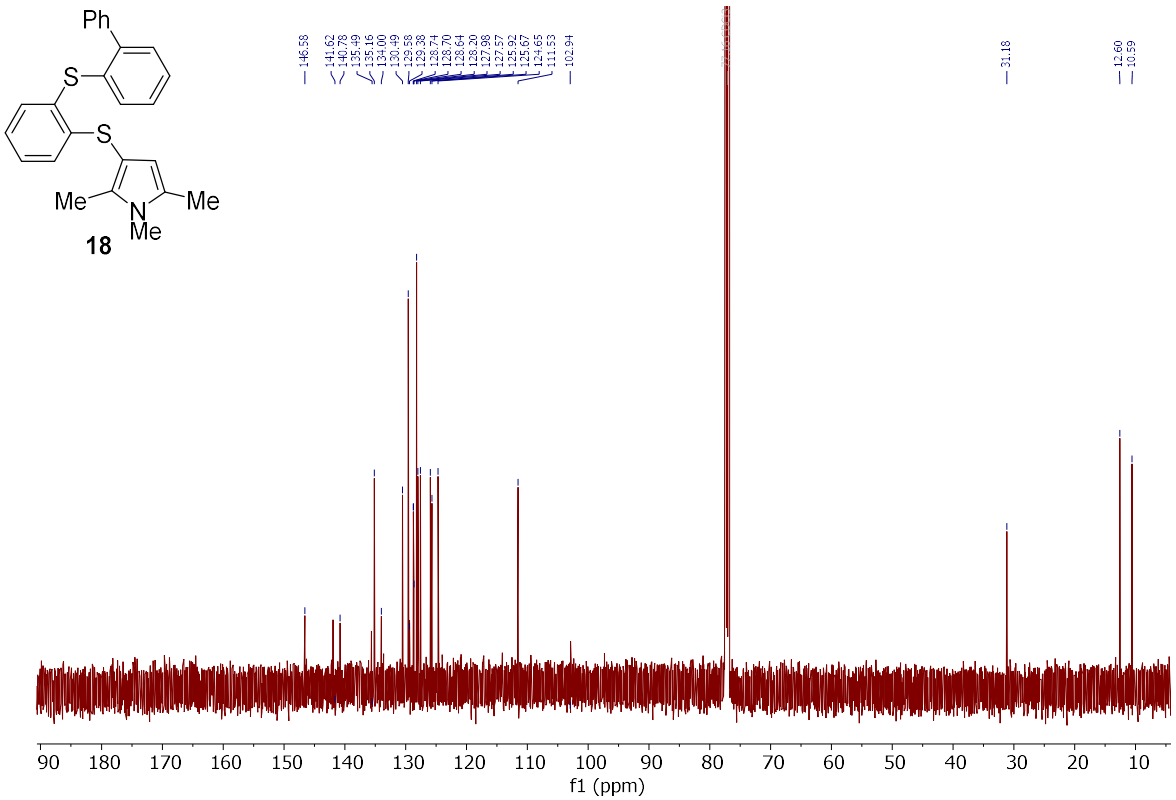


*Figure S153: ^{13}C NMR spectrum of 3-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1,2,5-trimethyl-1H-pyrrole **18** in $CDCl_3$*

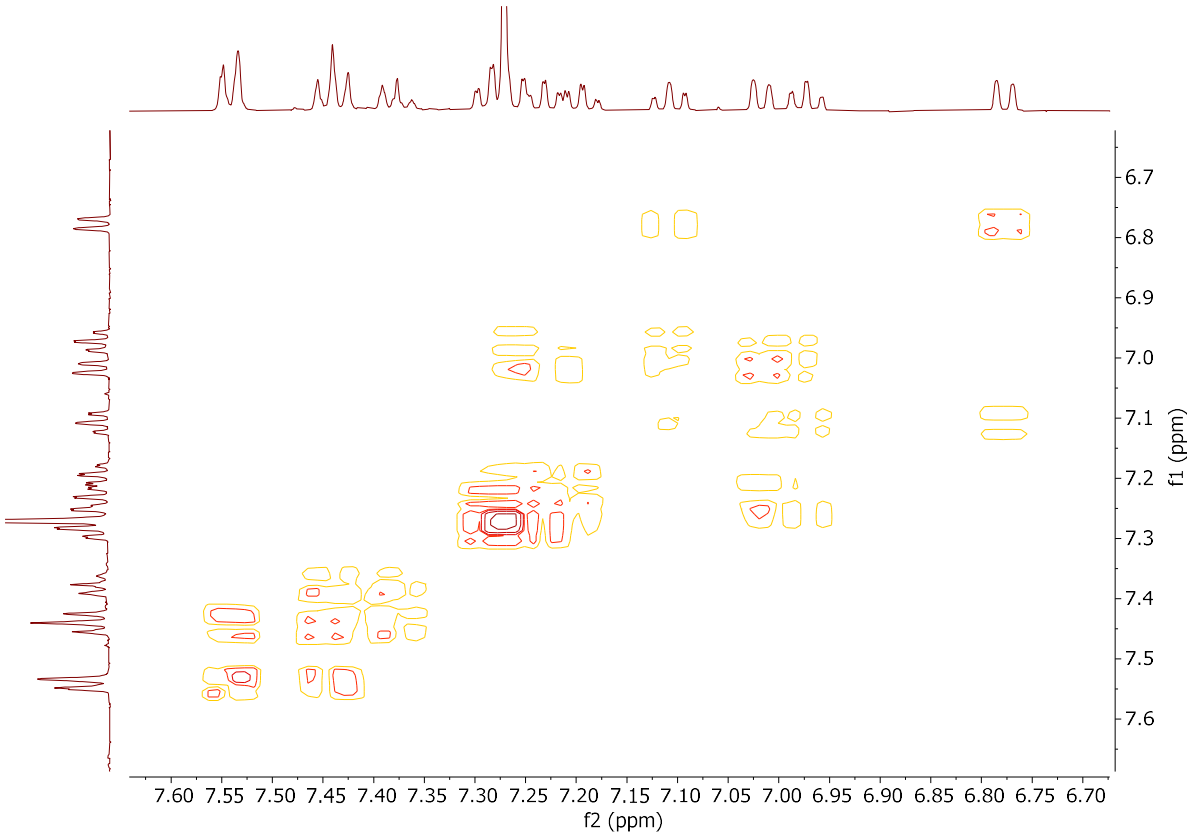


*Figure S154: COSY spectrum of 3-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1,2,5-trimethyl-1H-pyrrole **18** in $CDCl_3$*

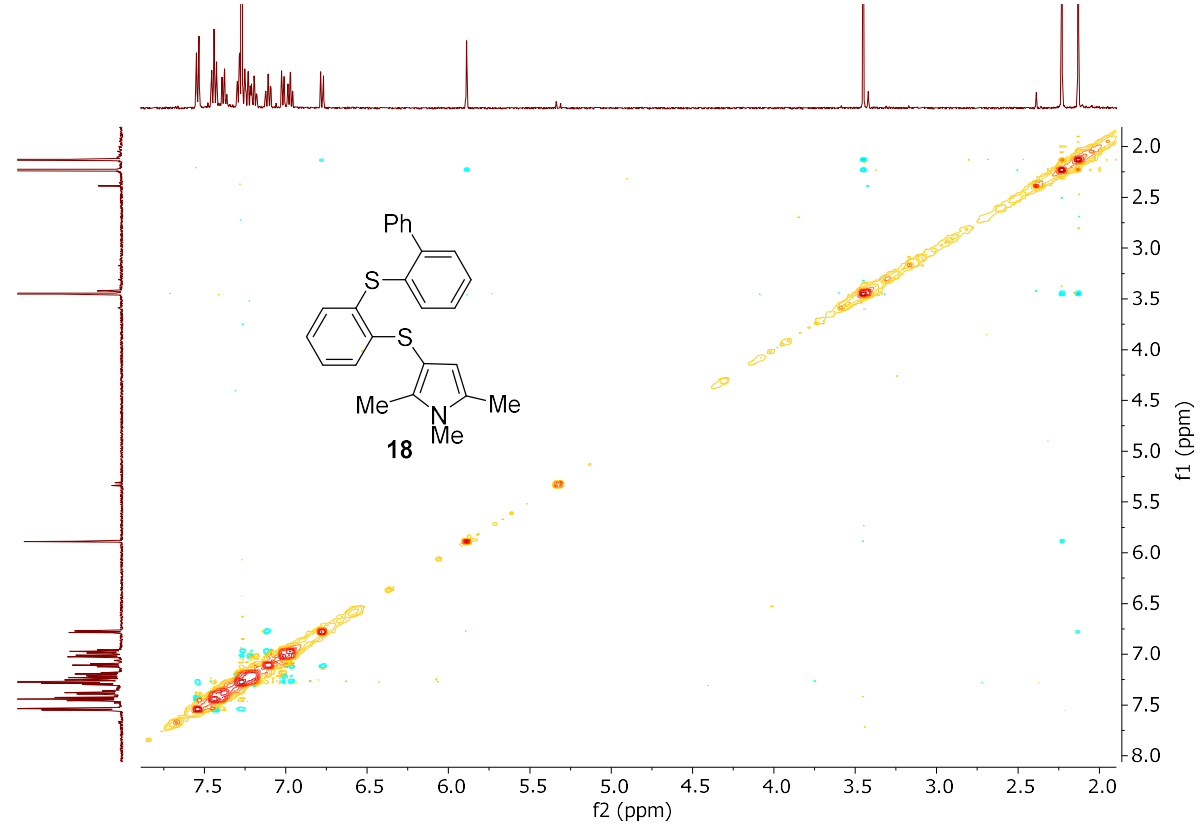


*Figure S155: NOESY spectrum of 3-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1,2,5-trimethyl-1H-pyrrole **18** in $CDCl_3$*

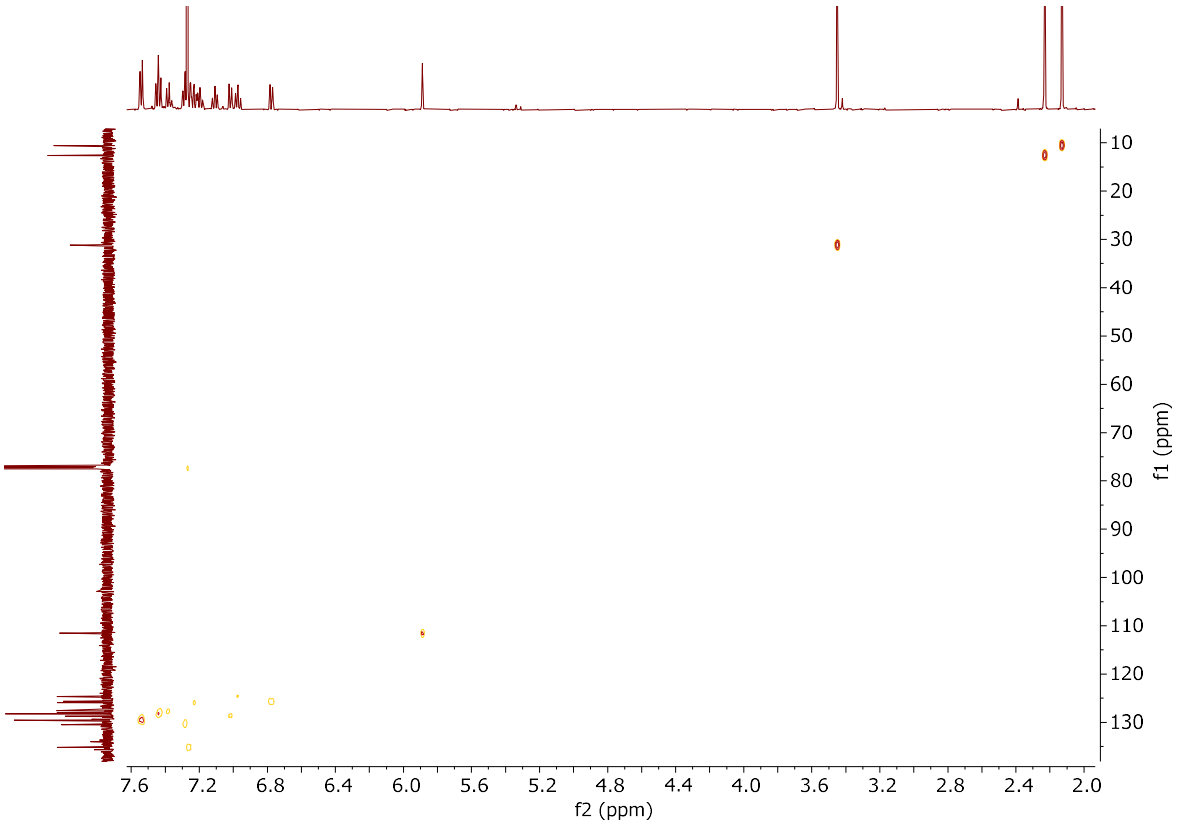


*Figure S156: HSQC spectrum of 3-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1,2,5-trimethyl-1H-pyrrole **18** in $CDCl_3$*

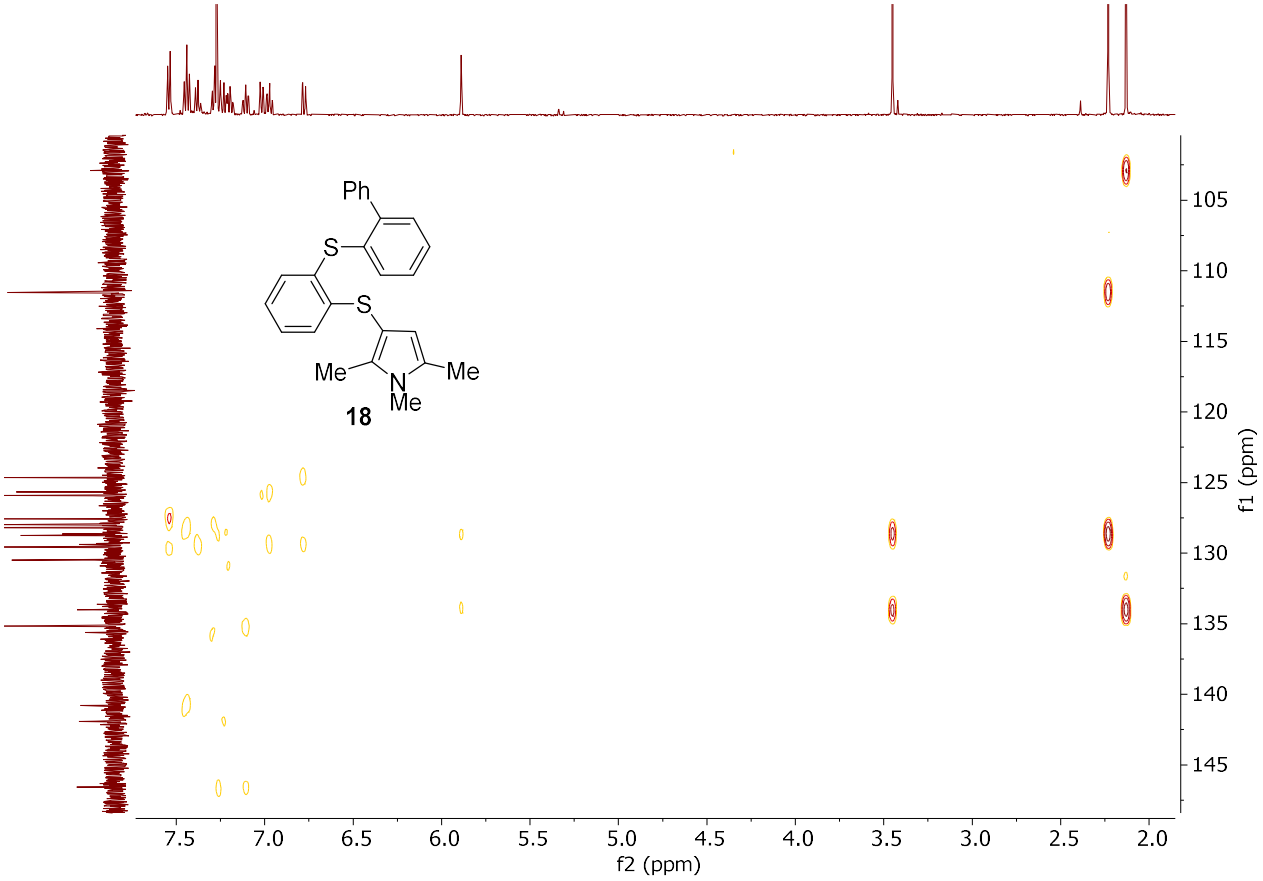


*Figure S157: HMBC spectrum of 3-((2-([1,1'-biphenyl]-2-ylthio)phenyl)thio)-1,2,5-trimethyl-1*H*-pyrrole **18** in $CDCl_3$*

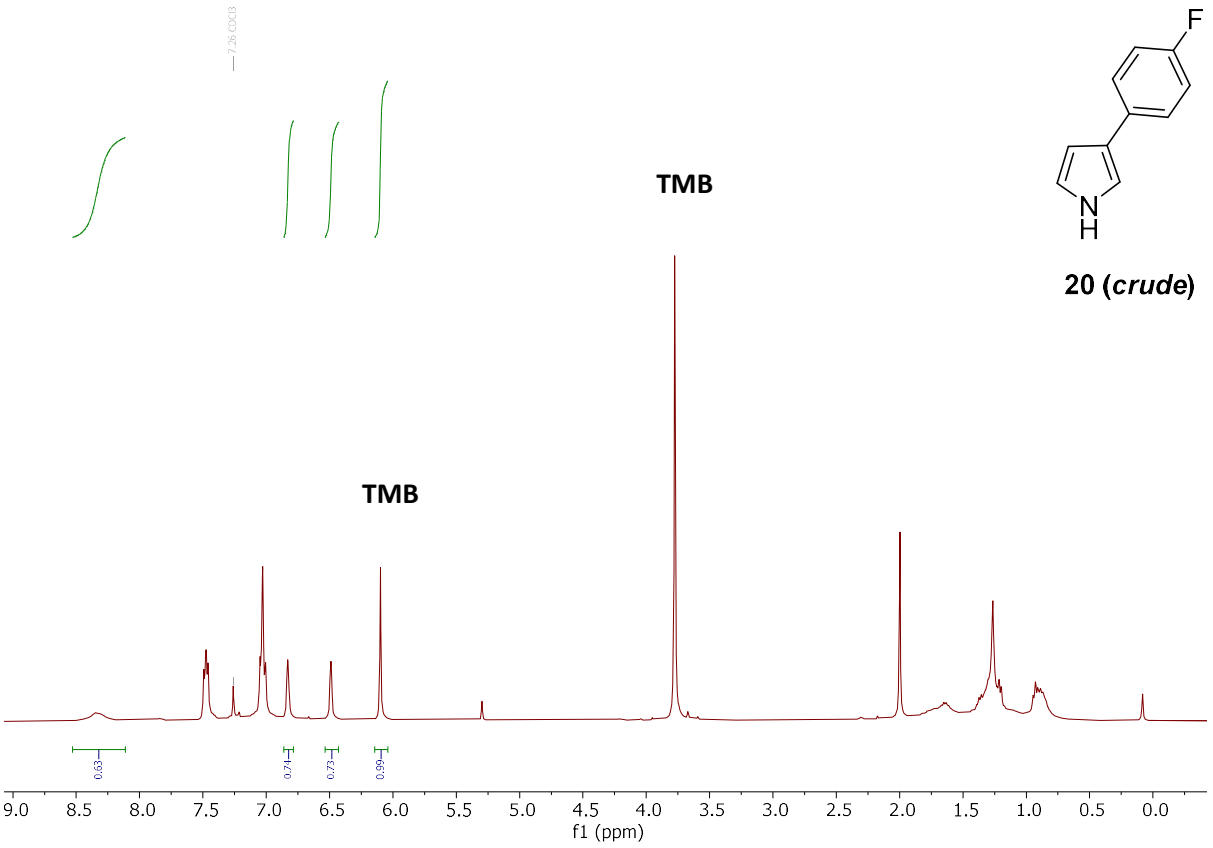


*Figure S158: ^{1}H Crude NMR of deprotection of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **20** in $CDCl_3$ with trimethoxy benzene (**TMB**) internal standard.*

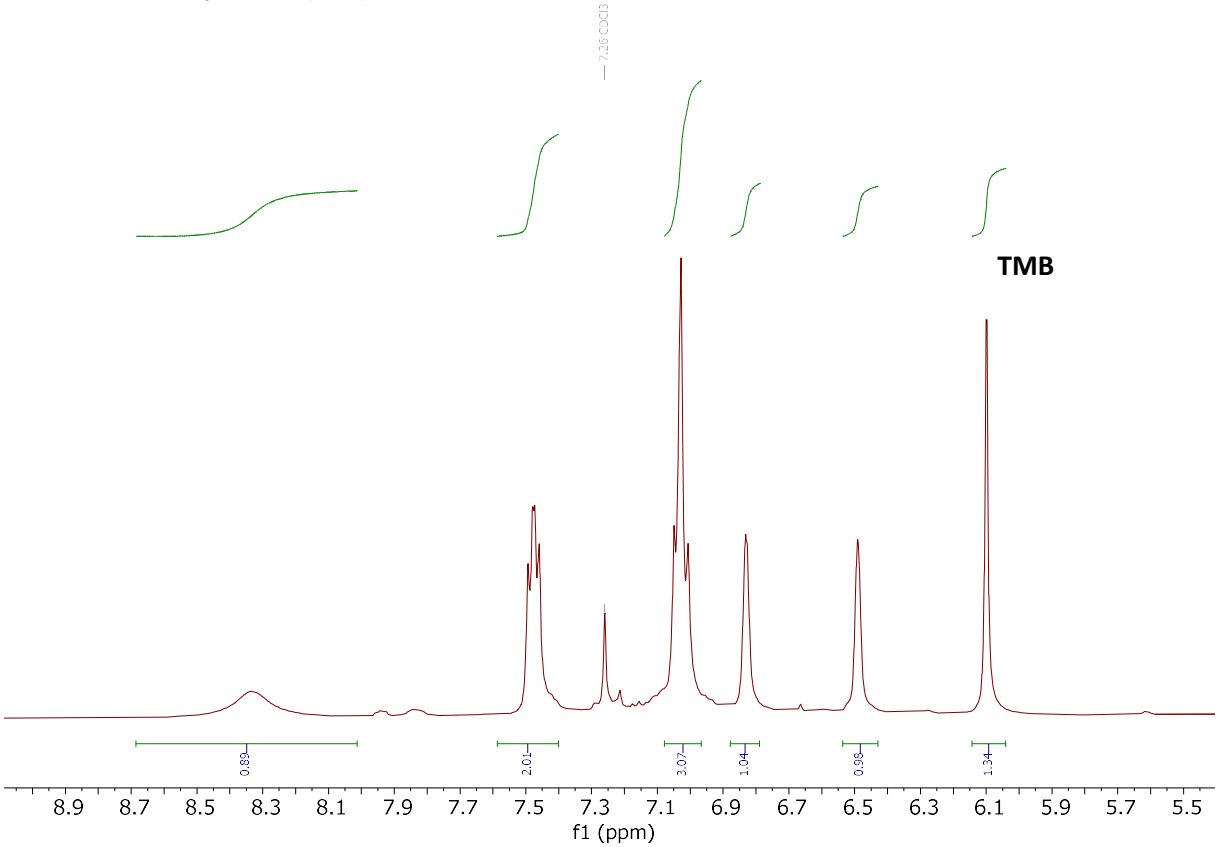


*Figure S159: Zoomed region of ^{1}H Crude NMR of deprotection of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **20** in $CDCl_3$ with trimethoxy benzene (**TMB**) internal standard*

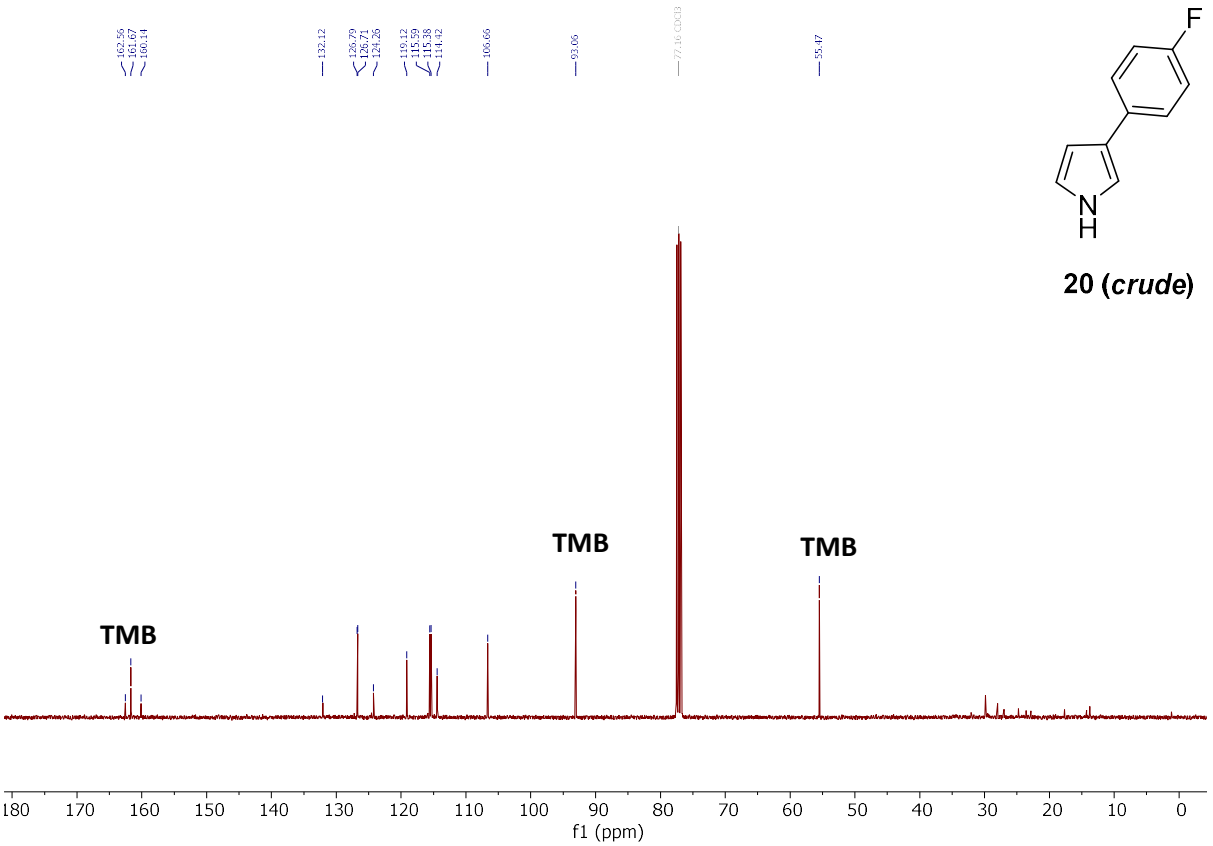


Figure S160: ^{13}C Crude NMR of deprotection of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole in $CDCl_3$ with trimethoxy benzene (TMB) internal standard

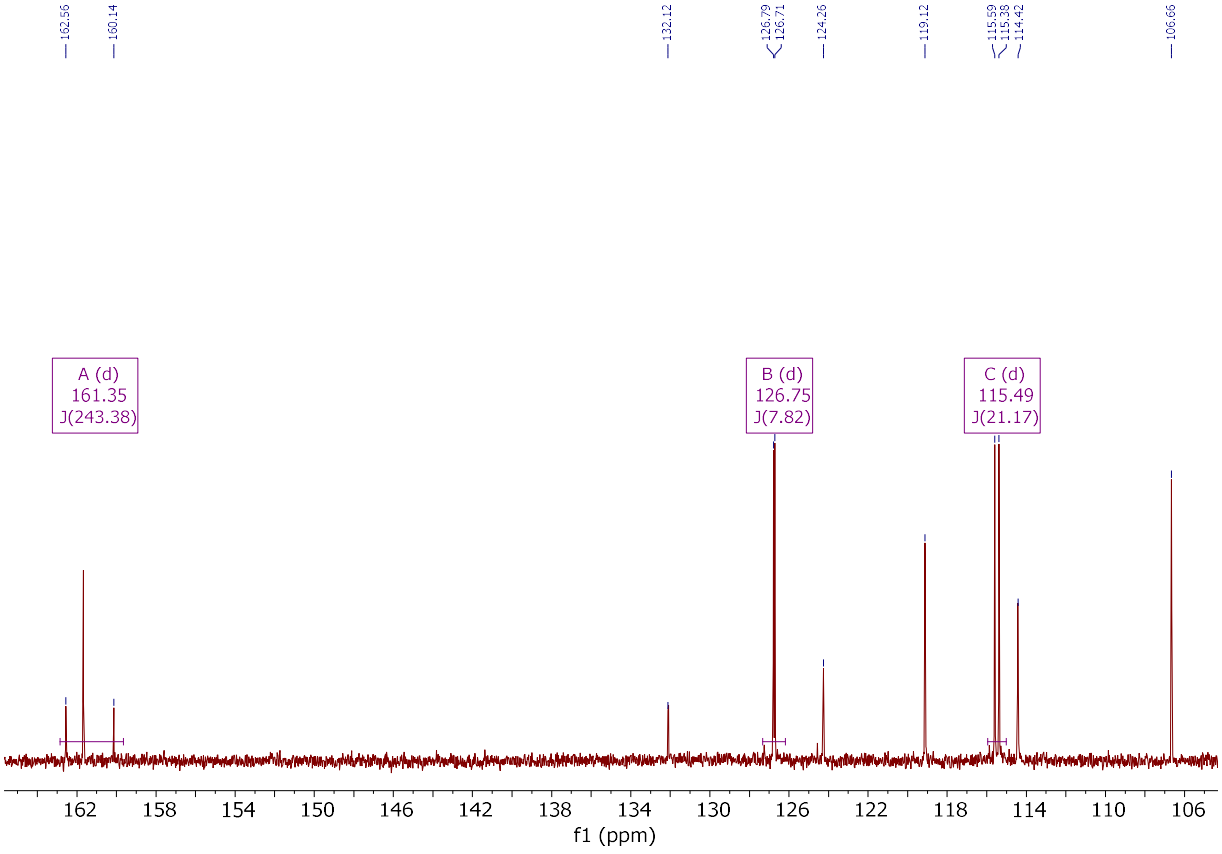


Figure S161: Zoomed region of ^{13}C Crude NMR of deprotection of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole in $CDCl_3$ with trimethoxy benzene (TMB) internal standard

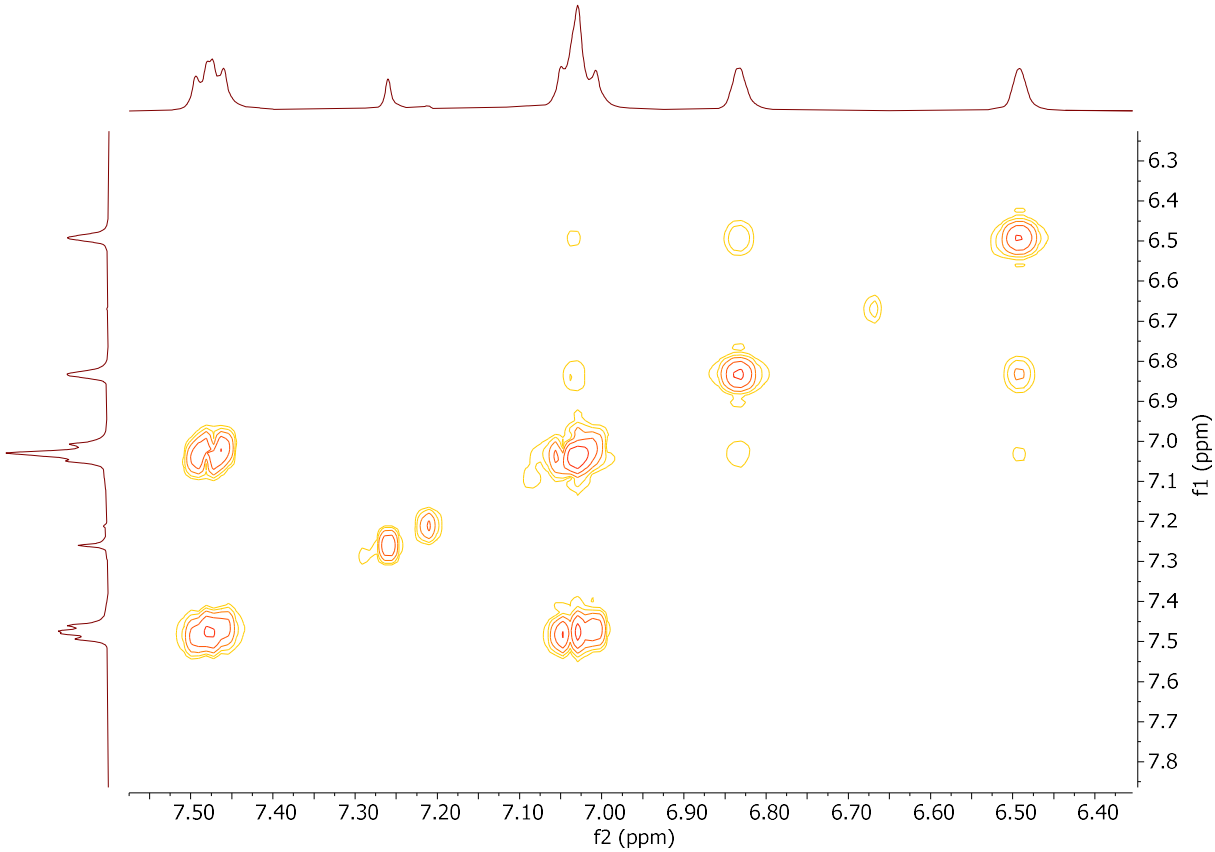


*Figure S162: Crude COSY NMR of deprotection of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **20** in $CDCl_3$ with trimethoxy benzene (TMB) internal standard*

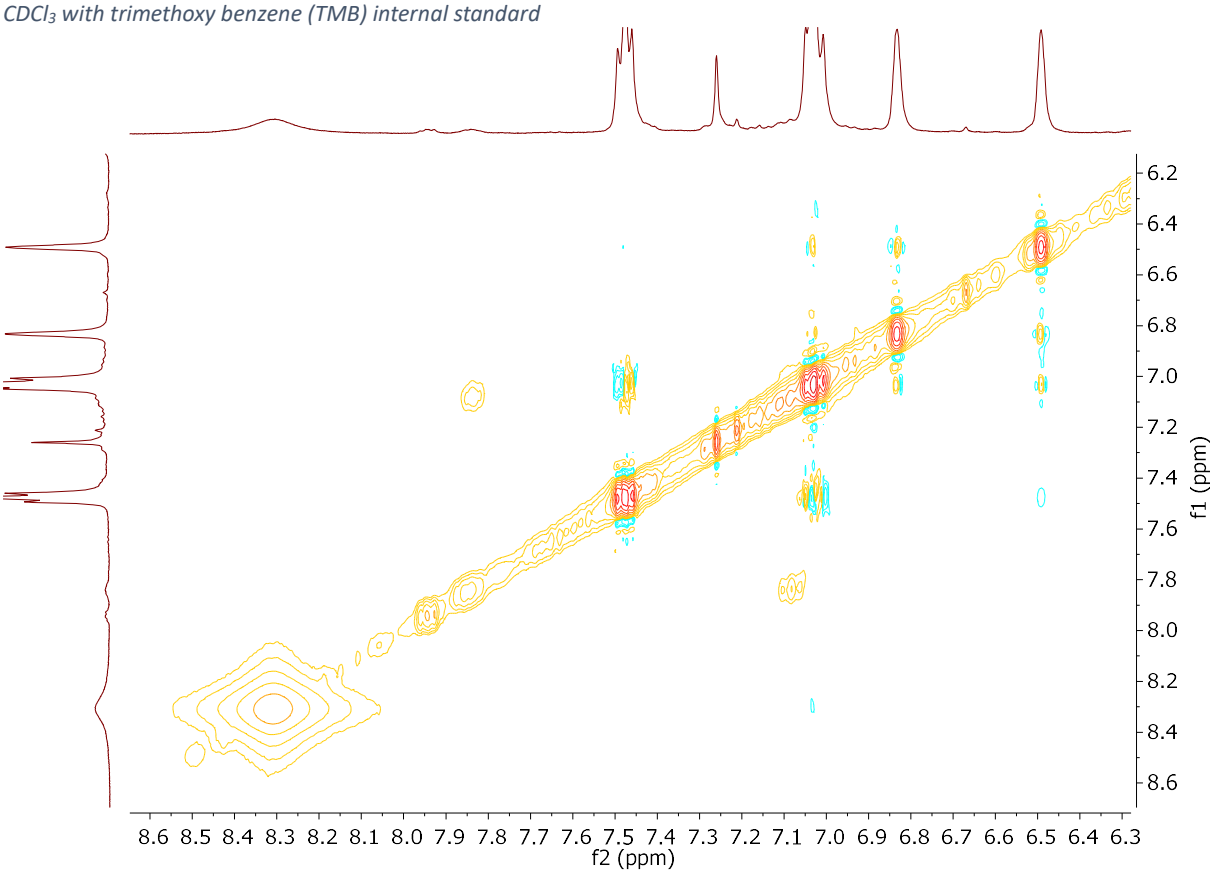


*Figure S163: Crude NOESY NMR of deprotection of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1H-pyrrole **20** with trimethoxy benzene (TMB) internal standard*

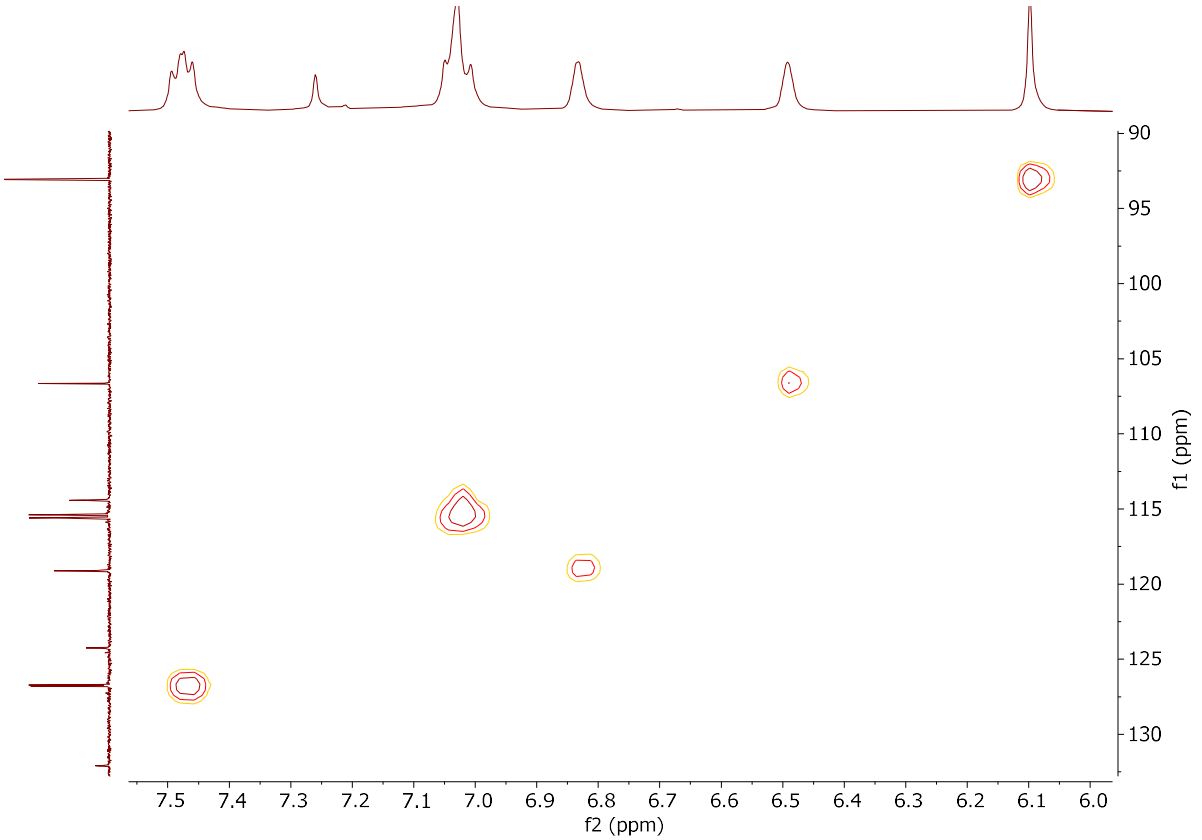


*Figure S164: Crude HSQC NMR of deprotection of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **20** with trimethoxy benzene (TMB) internal standard*

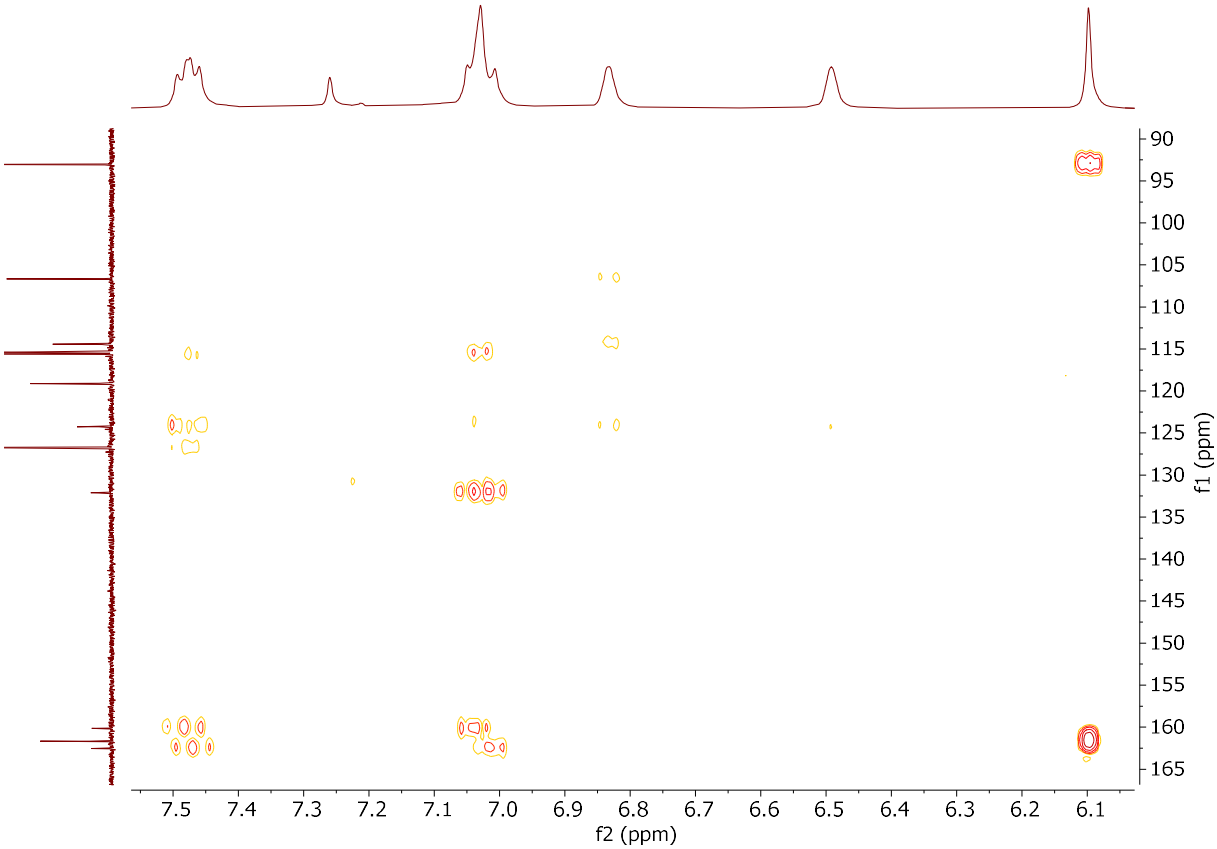


*Figure S165: Crude HMBC NMR of deprotection of 3-(4-fluorophenyl)-1-((2,4,6-triisopropylphenyl)sulfonyl)-1*H*-pyrrole **20** with trimethoxy benzene (TMB) internal standard.*

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