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Supporting Information

Metal-Catalyzed Reactivity Reversal in the Sulfonylation Reaction of α-Allenols: Controlled Synthesis of 4-(Arylsulfonyl)-2,5-Dihydrofurans

Fernando Herrera, Pablo Esteban, Amparo Luna,* and Pedro Almendros*

Supporting Information for the Paper

Metal-Catalyzed Reactivity Reversal in the Sulfonylation Reaction of α-Allenols: Controlled Synthesis of 4-(Arylsulfonyl)-2,5-dihydrofurans

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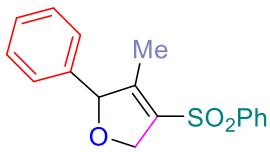
1. General Methods: ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AMX-500, or Bruker Avance-DPX 300. NMR spectra were recorded in $CDCl_3$ or CD_3CN solution, except otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), $CDCl_3$ (^{1}H, 7.27 ppm; ^{13}C, 76.9 ppm) and CD_3CN (^{1}H, 1.94 ppm; ^{13}C, 118.3 ppm). Low- and high-resolution mass spectra were taken on an AGILENT 6520 Accurate Mass QTOF LC/MS spectrometer using the electronic impact (EI) or electrospray modes (ES) unless otherwise stated. IR spectra were recorded on a Bruker Tensor 27

spectrometer. All commercially available compounds were used without further purification.

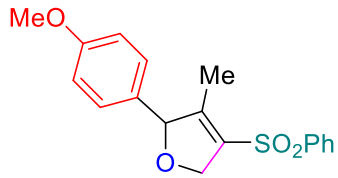
2. General procedure for the preparation of compounds 3a-o and 4a-b

$Cu(OAc)_2$ (10 mol %), sodium salt **2** (2.0 mmol) and $AgNO_3$ (2.0 mmol) were added to a solution of allene **1** (1.0 mmol) in acetonitrile (10 mL). The reaction mixture was stirred at 100 °C in a sealed tube until the starting material disappeared as indicated by TLC. The reaction mixture was cooled to room temperature, was diluted with ethyl acetate (3×5 mL), and the ethyl acetate layer was separated from the aqueous layer. The organic extract was washed with brine, dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. Chromatography of the residue using hexanes/ethyl acetate mixtures gave analytically pure compounds. Spectroscopic and analytical data for pure forms of compounds **3** and **4** follow.



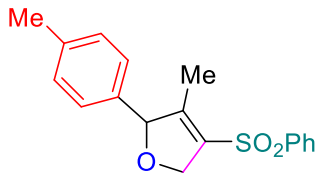
3a

Sulfone-3a. From 53 mg (0.33 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, gave compound **3a** (67 mg, 68%) as a yellow oil; ^{1}H NMR (500 MHz, CD_3CN, 25 ^{o}C) δ 7.94 (m, 2H), 7.75 (m, 1H), 7.66 (m, 2H), 7.36 (m, 3H), 7.19 (m, 2H), 5.65 (t, *J* = 4.7 Hz, 1H), 4.95 (ddq, *J* = 11.4, 5.6, 1.9 Hz, 1H), 4.81 (ddq, *J* = 11.8, 4.1, 2.1 Hz, 1H), 1.85 (m, 3H); ^{13}C NMR (125 MHz, CD_3CN, 25 ^{o}C) δ 152.3, 141.9, 140.6, 135.1 (2C), 133.0, 130.8 (2C), 129.8 (2C), 128.1 (2C), 128.0 (2C), 93.7, 75.6, 11.7; IR ($CHCl_3$, cm^{-1}): ν 1300, 1005. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{17}O_3S$ 301.08929; Found 301.08885.



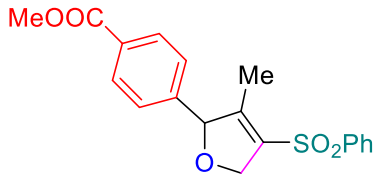
3b

Sulfone-3b. From 34.8 mg (0.18 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3b** (37 mg, 62%) as a yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ 7.95 (m, 2H), 7.69 (m, 1H), 7.61 (m, 2H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.57 (t, *J* = 4.5 Hz, 1H), 4.97 (m, 1H), 4.82 (ddq, *J* = 9.6, 3.9, 2.1 Hz, 1H), 3.81 (s, 3H), 1.94 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$, 25 ^{o}C) δ 160.1, 150.9, 140.8, 133.8, 132.0, 130.9, 129.5 (2C), 128.5 (2C), 127.2 (2C), 114.2 (2C), 92.8, 74.6, 55.3, 11.4; IR ($CHCl_3$, cm^{-1}): ν 1324, 995. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}O_4S$ 331.09986; Found 331.10036.



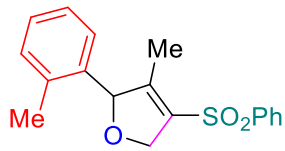
3c

Sulfone-3c. From 48 mg (0.28 mmol) of the corresponding α -allenic alcohol, and after chromatography of the residue using hexanes/ diethyl ether (7:3) as eluent, gave compound **3c** (52 mg, 59%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ 7.95 (m, 2H), 7.69 (m, 1H), 7.61 (m, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 5.58 (t, *J* = 4.4 Hz, 1H), 4.99 (ddq, *J* = 11.3, 5.6, 2.0 Hz, 1H), 4.84 (ddq, *J* = 11.6, 4.1, 2.1 Hz, 1H), 2.35 (s, 3H), 1.94 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ 150.9, 140.8, 138.8, 135.8, 133.8, 132.0, 129.5 (2C), 129.5 (2C), 127.2 (2C), 127.0 (2C), 93.0, 74.8, 21.2, 11.4; IR ($CHCl_3$, cm^{-1}): ν 1318, 996. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}O_3S$ 315.10494; Found 315.10413.



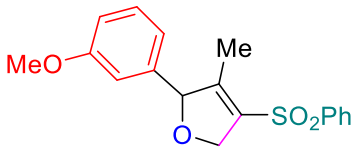
3d

Sulfone-3d. From 51 mg (0.23 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3d** (51.5 mg, 63%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.94 (m, 2H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.61 (m, 2H), 7.27 (m, 2H), 5.66 (t, *J* = 4.5 Hz, 1H), 5.03 (m, 1H), 4.89 (m, 1H), 3.93 (s, 3H), 1.94 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 166.6, 149.9, 143.7, 140.6, 134.0, 132.6, 130.7, 130.1 (2C), 129.5 (2C), 127.2 (2C), 126.9 (2C), 92.5, 75.2, 52.2, 11.3; IR ($CHCl_3$, cm^{-1}): ν 1315, 1008. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{18}NaO_5S$ 381.07672; Found 381.07508.



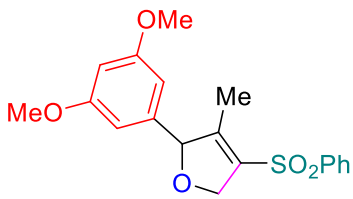
3e

Sulfone-3e. From 64.6 mg (0.37 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3e** (76 mg, 66%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 7.87 (m, 2H), 7.60 (m, 1H), 7.52 (m, 2H), 7.09 (m, 3H), 6.94 (m, 1H), 5.83 (t, *J* = 4.5 Hz, 1H), 4.82 (m, 2H), 2.18 (s, 3H), 1.87 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 150.8, 140.7, 136.4, 136.2, 133.8, 132.3, 131.1, 129.5 (2C), 128.8, 128.0, 127.2 (2C), 126.5, 90.5, 74.5, 18.9, 11.4; IR ($CHCl_3$, cm^{-1}): ν 1310, 998. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}O_3S$ 315.10494; Found 315.10476.



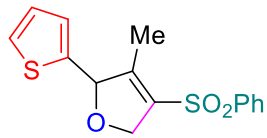
3f

Sulfone-3f. From 189 mg (0.99 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using toluene as eluent, gave compound **3f** (206 mg, 63%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 7.95 (m, 2H), 7.68 (m, 1H), 7.60 (m, 2H), 7.27 (m, 1H), 6.87 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 6.76 (m, 1H), 6.69 (m, 1H), 5.58 (t, *J* = 4.3 Hz, 1H), 5.0 (ddq, *J* = 11.4, 5.7, 1.9 Hz, 1H), 4.86 (ddq, *J* = 11.6, 4.1, 2.1 Hz, 1H), 3.77 (s, 3H), 1.96 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 160.0, 150.7, 140.8, 140.3, 133.8, 132.1, 129.9, 129.5 (2C), 127.2 (2C), 119.3, 114.4, 112.5, 93.0, 74.9, 55.2, 11.4; IR ($CHCl_3$, cm^{-1}): ν 1306, 996. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{19}O_4S$ 331.09986; Found 331.10083.



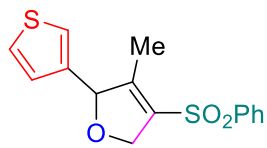
3g

Sulfone-3g. From 91.6 mg (0.42 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (13:1) as eluent, gave compound **3g** (104 mg, 69%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 7.94 (m, 2H), 7.72–7.57 (m, 3H), 6.42 (t, *J* = 2.3 Hz, 1H), 6.30 (d, *J* = 2.2 Hz, 2H), 5.53 (t, *J* = 4.3 Hz, 1H), 4.99 (m, 1H), 4.86 (ddq, *J* = 9.7, 3.8, 2.0 Hz, 1H), 3.75 (s, 6H), 1.97 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 161.1 (2C), 150.7, 141.1, 140.8, 133.8, 132.1, 129.5 (2C), 127.2 (2C), 104.9 (2C), 100.6, 93.1, 75.0, 55.3 (2C), 11.4; IR ($CHCl_3$, cm^{-1}): ν 1318, 997. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{21}O_5S$ 361.11042; Found 361.11141.



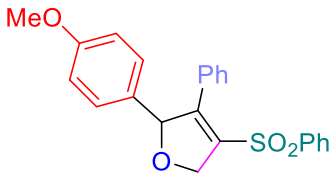
3h

Sulfone-3h. From 80 mg (0.48 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (14:1) as eluent, gave compound **3h** (98 mg, 68%) as a pale brown oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 7.95 (m, 2H), 7.69 (m, 1H), 7.61 (m, 2H), 7.32 (m, 1H), 6.99 (m, 2H), 5.91 (t, J = 4.3 Hz, 1H), 4.91 (ddq, J = 11.2, 5.7, 1.9 Hz, 1H), 4.82 (ddq, J = 11.8, 4.1, 2.0 Hz, 1H), 2.03 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 149.7, 142.2, 140.6, 133.9, 132.5, 129.5 (2C), 127.2 (2C), 126.9, 126.8, 126.3, 88.1, 74.1, 11.3; IR ($CHCl_3$, cm^{-1}): ν 1305, 1030. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{14}NaO_3S_2$ 329.02766; Found 329.02719.



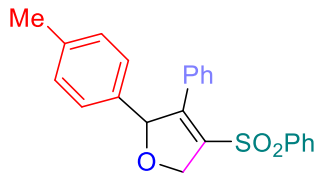
3i

Sulfone-3i. From 138 mg (0.80 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3i** (150 mg, 61%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 7.95 (m, 2H), 7.69 (m, 1H), 7.61 (m, 2H), 7.32 (dd, J = 5.0, 2.9 Hz, 1H), 7.22 (m, 1H), 6.87 (dd, J = 5.0, 1.3 Hz, 0H), 5.73 (t, J = 4.3 Hz, 1H), 4.94 (ddq, J = 11.3, 5.7, 1.9 Hz, 1H), 4.81 (m, 1H), 2.00 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 150.2, 140.7, 139.8, 133.8, 132.2, 129.5 (2C), 127.2 (2C), 127.1, 125.5, 123.7, 88.4, 74.3, 11.3; IR ($CHCl_3$, cm^{-1}): ν 1311, 998. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{14}NaO_3S_2$ 329.02766; Found 329.02807.



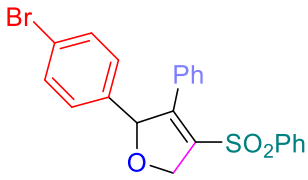
3j

Sulfone-3j. From 44 mg (0.17 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/diethyl ether (7:3) as eluent, gave compound **3j** (47 mg, 71%) as a brown oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 7.63 (m, 2H), 7.56 (m, 1H), 7.42 (m, 2H), 7.21 (m, 3H), 7.04 (d, *J* = 8.7 Hz, 2H), 6.93 (m, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 5.94 (dd, *J* = 6.0, 3.7 Hz, 1H), 5.31 (dd, *J* = 12.6, 6.0 Hz, 1H), 5.12 (dd, *J* = 12.6, 3.7 Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 159.9, 151.4, 140.3, 135.3, 133.6 (2C), 130.6, 129.0, 128.9 (2C), 128.5 (4C), 127.9 (2C), 127.6 (2C), 114.0 (2C), 93.1, 75.6, 55.2; IR ($CHCl_3$, cm^{-1}): ν 1306, 998. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{20}NaO_4S$ 415.09745; Found 415.09904.



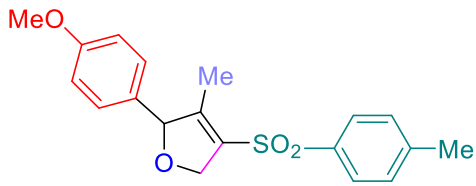
3k

Sulfone-3k. From 78 mg (0.33 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3k** (62 mg, 50%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 7.63 (m, 2H), 7.56 (m, 1H), 7.41 (m, 2H), 7.22 (m, 3H), 7.07–6.92 (m, 6H), 5.95 (dd, *J* = 6.0, 3.7 Hz, 1H), 5.33 (dd, *J* = 12.6, 6.0 Hz, 1H), 5.14 (dd, *J* = 12.6, 3.7 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 151.4, 140.3, 138.5, 135.5, 135.3, 133.6, 130.0, 129.3 (2C), 129.0, 128.9 (2C), 128.5 (2C), 127.9 (2C), 127.6 (2C), 127.0 (2C), 93.4, 75.8, 21.2; IR ($CHCl_3$, cm^{-1}): ν 1307, 1018. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{21}O_3S$ 377.12059; Found 377.12068.



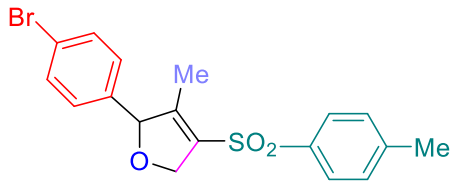
3l

Sulfone-3l. From 113 mg (0.37 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3l** (111 mg, 68%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 7.61 (m, 2H), 7.55 (m, 1H), 7.47–7.34 (m, 4H), 7.32–7.18 (m, 3H), 6.97 (d, J = 8.3 Hz, 2H), 6.92 (m, 2H), 5.95 (dd, J = 6.1, 3.9 Hz, 1H), 5.34 (dd, J = 12.7, 6.1 Hz, 1H), 5.15 (dd, J = 12.7, 3.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 150.7, 140.1, 137.6, 135.8, 133.7, 131.7 (2C), 129.6, 129.2, 129.0 (2C), 128.6 (2C), 128.4 (2C), 128.0 (2C), 127.6 (2C), 122.7, 92.8, 76.1; IR ($CHCl_3$, cm^{-1}): ν 1308, 998. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}BrO_3S$ 441.01545; Found 441.01574.



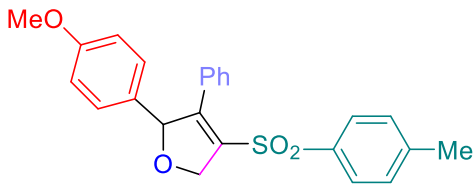
3m

Sulfone-3m. From 63 mg (0.33 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3m** (67 mg, 59%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 7.82 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 5.55 (t, J = 4.4 Hz, 1H), 4.96 (m, 1H), 4.80 (ddq, J = 11.6, 4.1, 2.0 Hz, 1H), 3.81 (s, 3H), 2.48 (s, 3H), 1.92 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 160.1, 150.2, 144.9, 137.9, 132.3, 130.9, 130.1 (2C), 128.5 (2C), 127.3 (2C), 114.2 (2C), 92.7, 74.6, 55.3, 21.7, 11.4; IR ($CHCl_3$, cm^{-1}): ν 1312, 996. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}NaO_4S$ 367.09745; Found 367.09654.



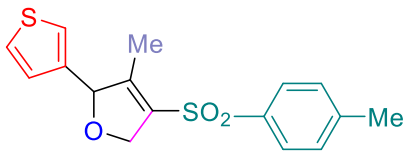
3n

Sulfone-3n. From 105 mg (0.44 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3n** (102 mg, 59%) as a pale green oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 5.55 (t, *J* = 4.4 Hz, 1H), 4.98 (ddq, *J* = 11.5, 5.7, 1.9 Hz, 1H), 4.84 (ddq, *J* = 9.6, 3.9, 2.1 Hz, 1H), 2.48 (s, 3H), 1.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 149.3, 145.0, 138.0, 137.7, 132.9, 132.0 (2C), 130.1 (2C), 128.7 (2C), 127.3 (2C), 122.9, 92.4, 75.0, 21.7, 11.2.; IR ($CHCl_3$, cm^{-1}): ν 1308, 998. HRMS (ESI-TOF) m/z: [*M* + NH_4]$^+$ Calcd for $C_{18}H_{21}BrNO_3S$ 410.04200; Found 410.03970.



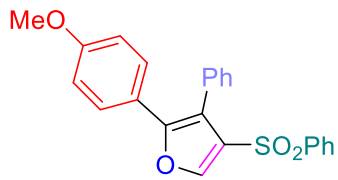
3o

Sulfone-3o. From 74 mg (0.29 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3o** (76 mg, 65%) as a brown oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.27–7.15 (m, 5H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.95 (m, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 5.93 (dd, *J* = 5.9, 3.7 Hz, 1H), 5.29 (dd, *J* = 12.6, 6.0 Hz, 1H), 5.10 (dd, *J* = 12.6, 3.7 Hz, 1H), 3.76 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 159.8, 150.8, 144.7, 135.5, 130.7, 130.4, 130.1, 129.6 (2C), 128.9, 128.5(2C), 128.4 (2C), 127.8 (2C), 127.6 (2C), 113.9 (2C), 93.1, 75.6, 55.2, 21.6; IR ($CHCl_3$, cm^{-1}): ν 1310, 996. HRMS (ESI-TOF) m/z: [*M* + H]$^+$ Calcd for $C_{24}H_{23}O_4S$ 407.13116; Found 407.13201.



3p

Sulfone-3p. From 65 mg (0.40 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **3p** (95 mg, 74%) as a yellow oil; ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.39 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.32 (dd, *J* = 2.8, 1.0 Hz, 1H), 6.86 (dd, *J* = 5.0, 1.2 Hz, 1H), 5.76 (t, *J* = 4.3 Hz, 1H), 4.87 (ddq, *J* = 11.4, 5.6, 1.9 Hz, 1H), 4.74 (ddq, *J* = 11.7, 4.1, 2.0 Hz, 1H), 2.46 (s, 3H), 1.88 (m, 3H); ^{13}C NMR (125 MHz, CD_3CN, 25 ºC) δ 151.3, 146.4, 141.6, 139.0, 133.3, 131.3 (2C), 128.2, 128.1 (2C), 126.8, 124.9, 89.1, 75.0, 21.7, 11.6; IR ($CHCl_3$, cm^{-1}): ν 1306, 997. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{17}NaO_3S_2$ 321.06191; Found 321.06201.

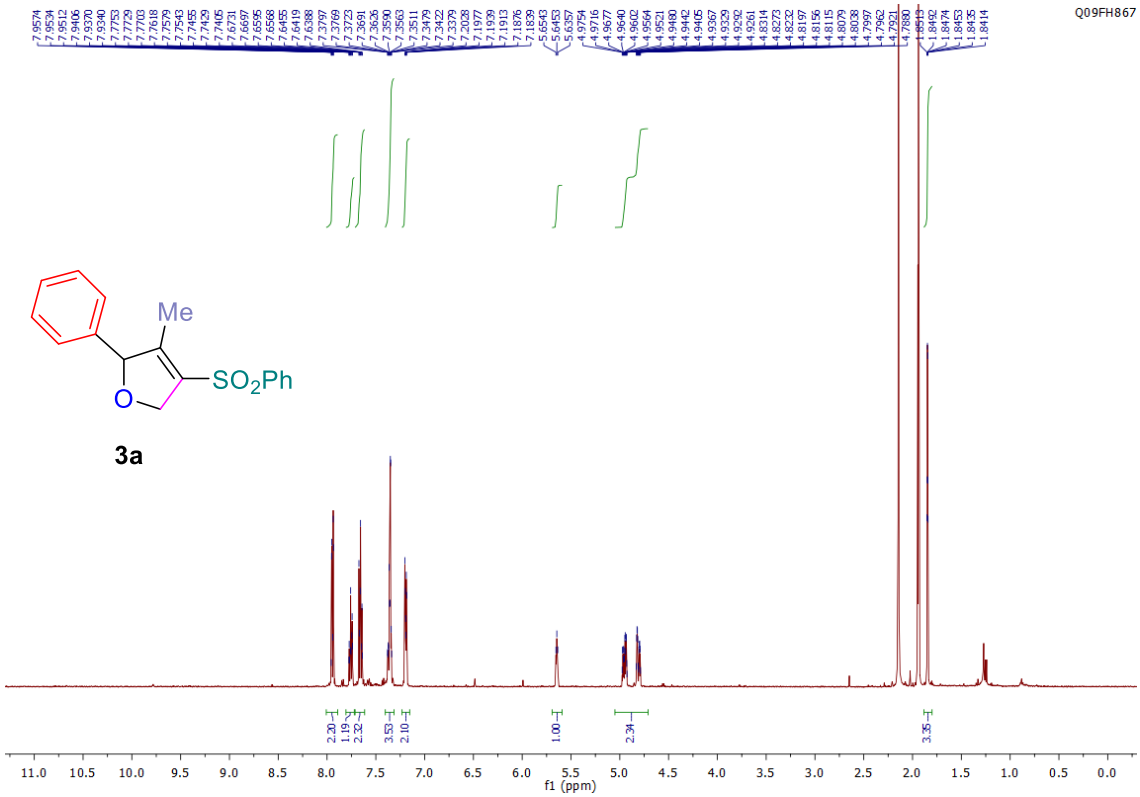


4a

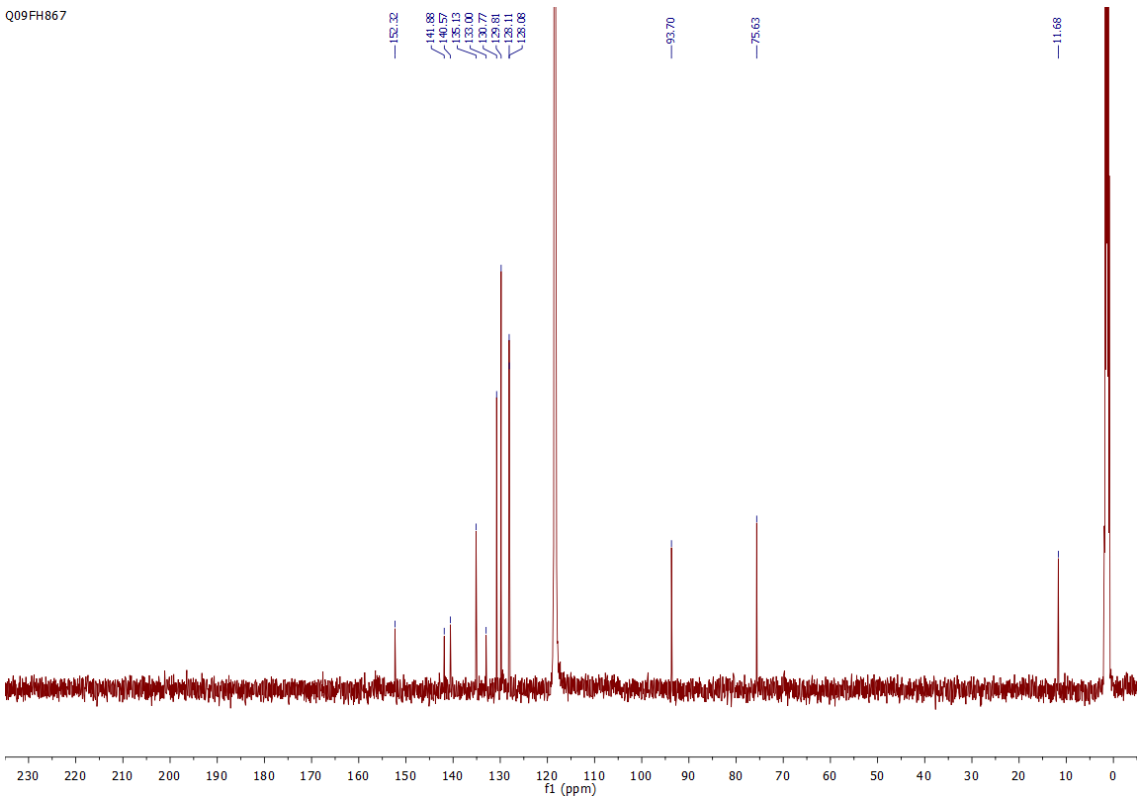
Sulfone-4a. From 47 mg (0.18 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **4a** (42 mg, 60%) as a yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 8.19 (s, 1H), 7.49–7.25 (m, 8H), 7.23 (d, *J* = 9.1 Hz, 2H), 7.10 (m, 2H), 6.74 (d, *J* = 9.1 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 ºC) δ 159.6, 152.0, 144.9, 140.7, 133.0, 130.8 (2C), 130.0, 128.6 (2C), 128.5 (2C), 128.2 (2C), 127.8 (2C), 127.3 (2C), 122.0, 117.6, 113.9 (2C), 55.2; IR ($CHCl_3$, cm^{-1}): ν 1324, 992. HRMS (ESI-TOF) m/z: [*M* + Ha]$^+$ Calcd for $C_{23}H_{19}O_4S$ 391.09986; Found 391.10038.

3. NMR Spectra

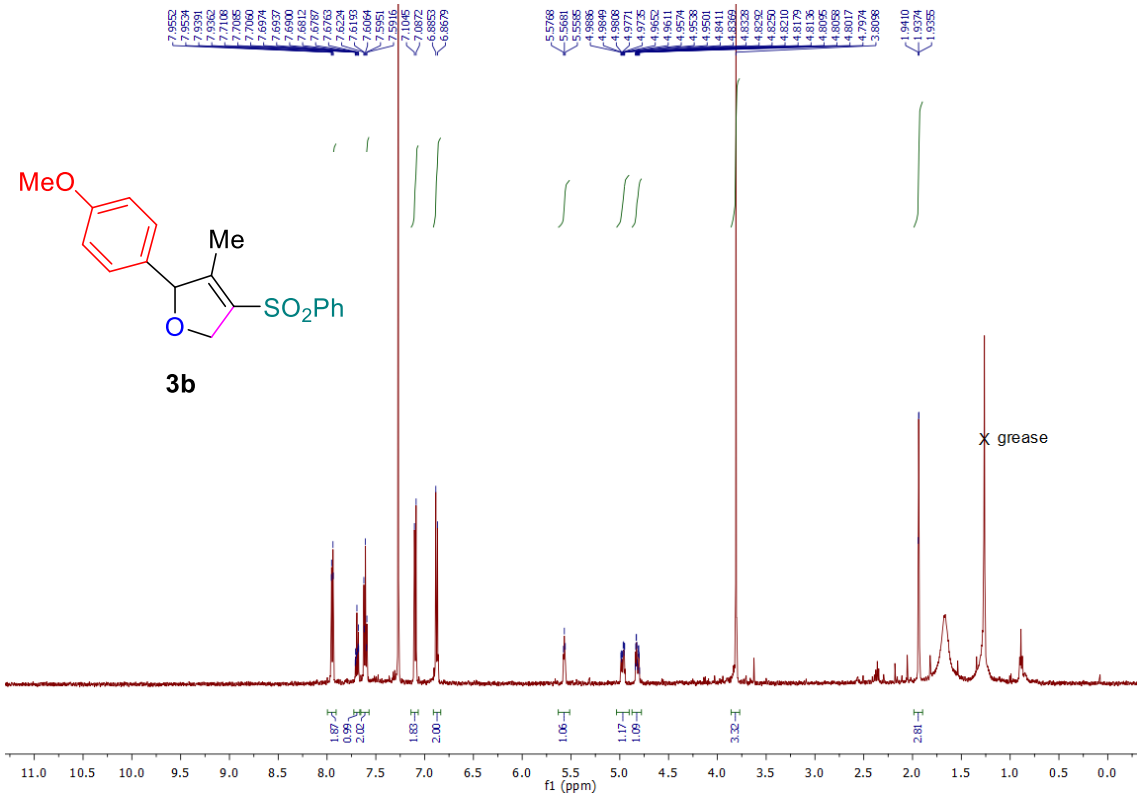
^{1}H NMR spectrum of **3a** in CD_3CN at 500 MHz



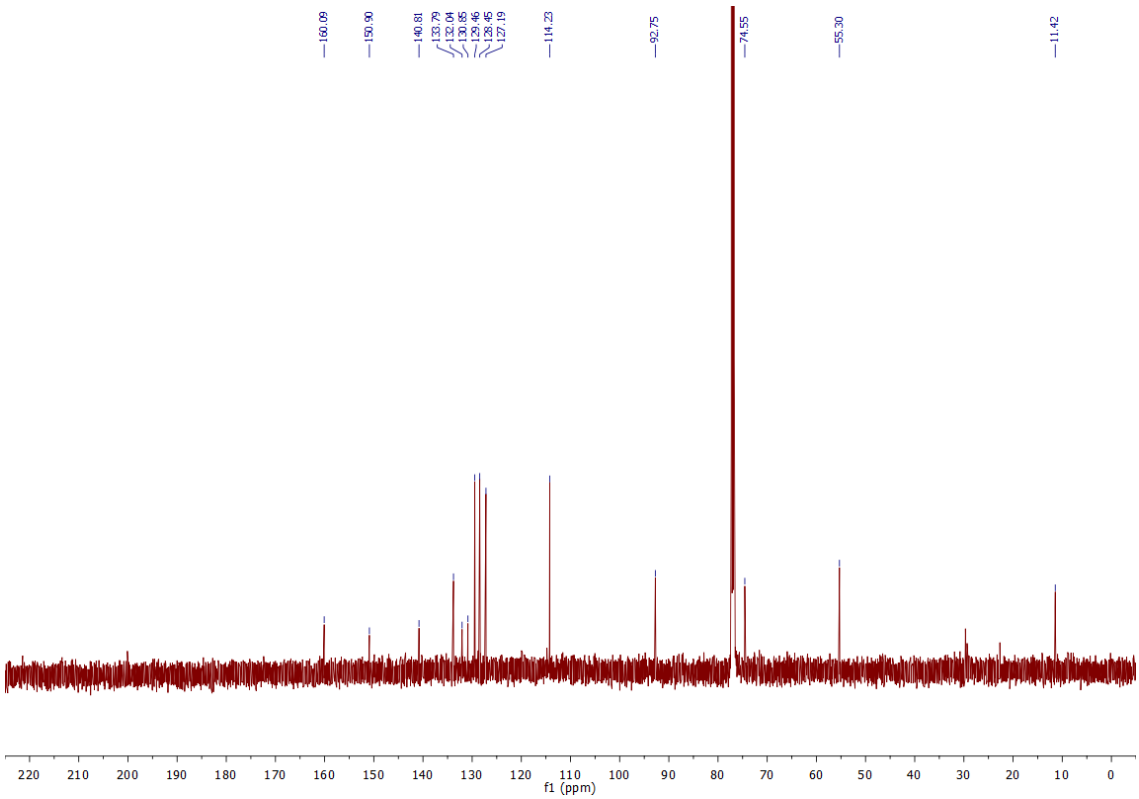
^{13}C NMR spectrum of **3a** in CD_3CN at 125 MHz



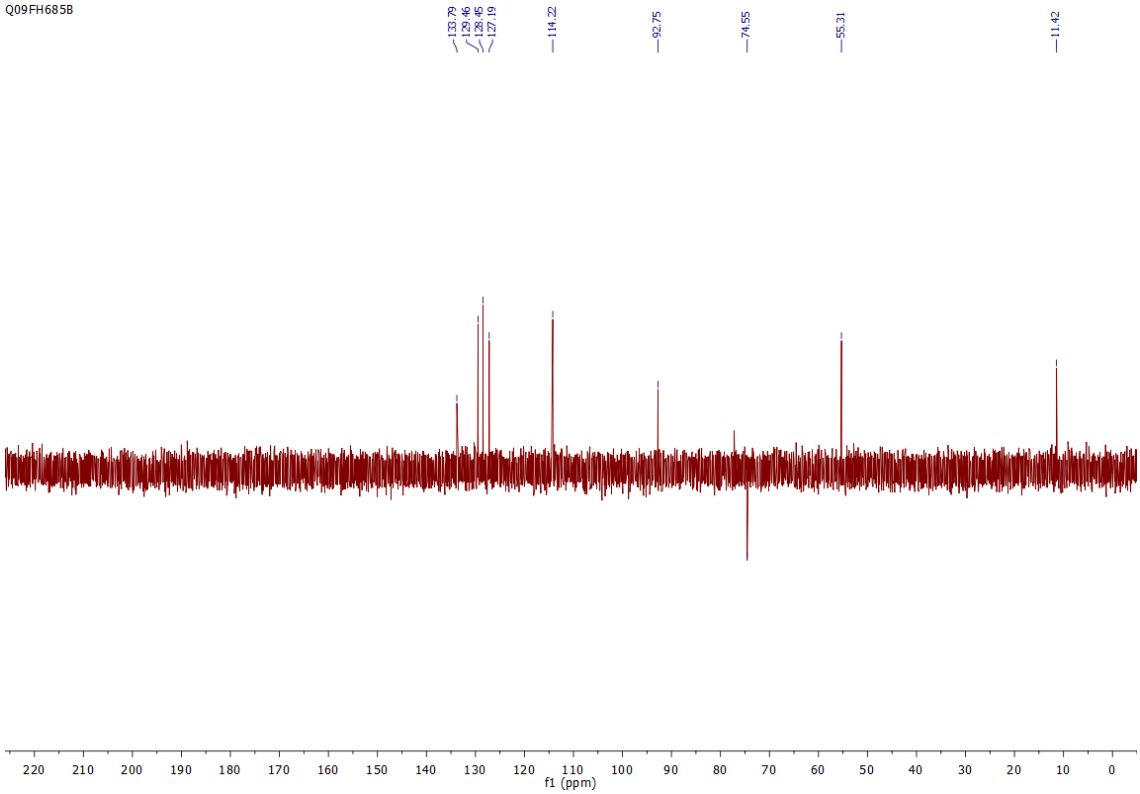
^{1}H NMR spectrum of **3b** in $CDCl_3$ at 500 MHz



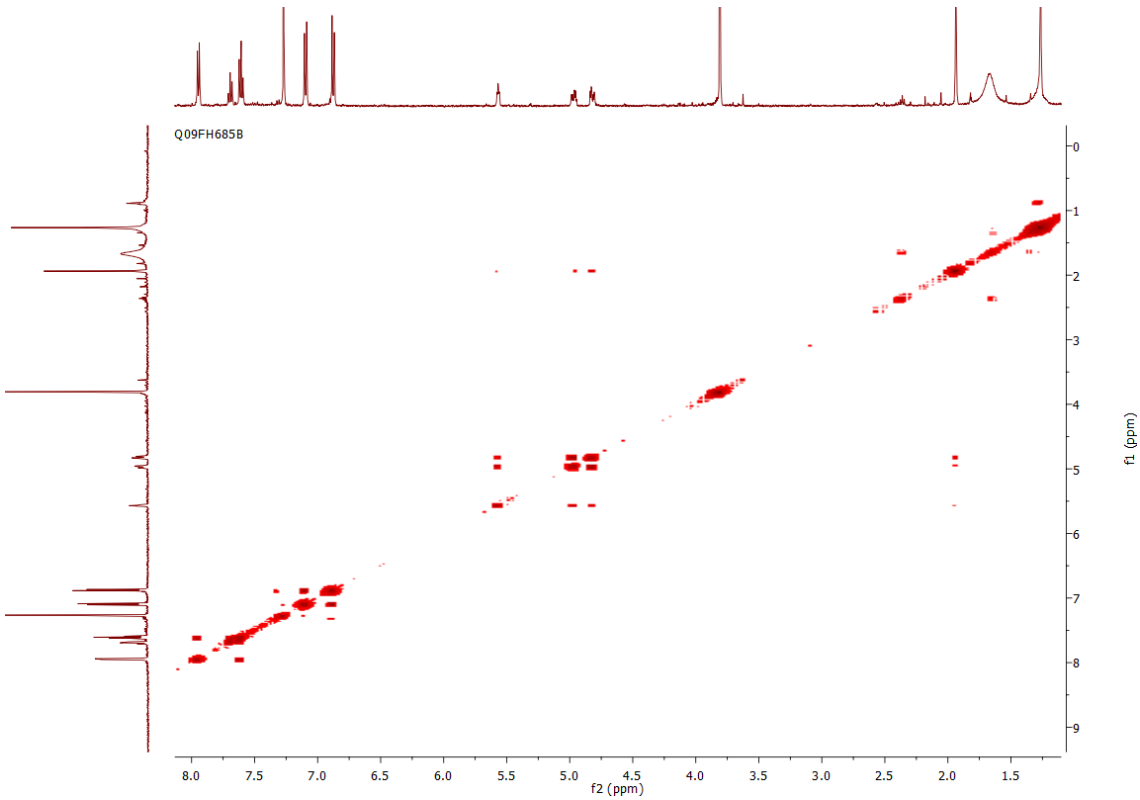
^{13}C NMR spectrum of **3b** in $CDCl_3$ at 125 MHz



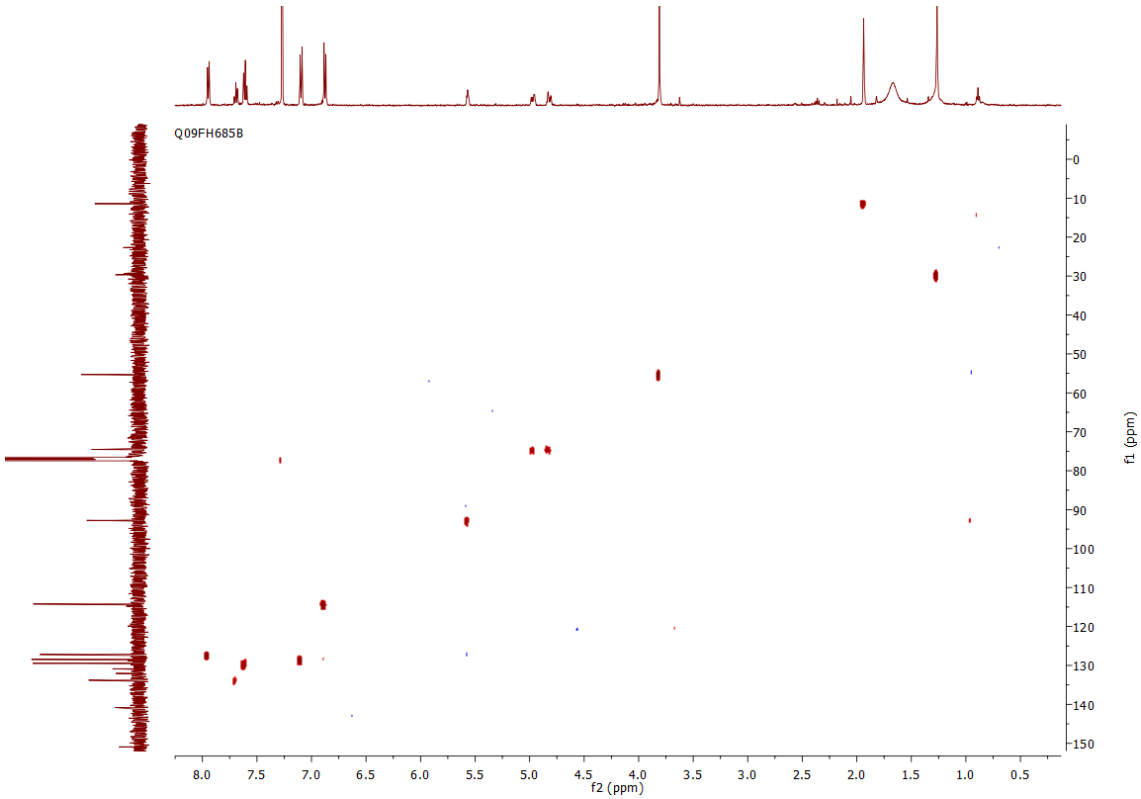
DEPT NMR spectrum of **3b** in $CDCl_3$ at 75 MHz



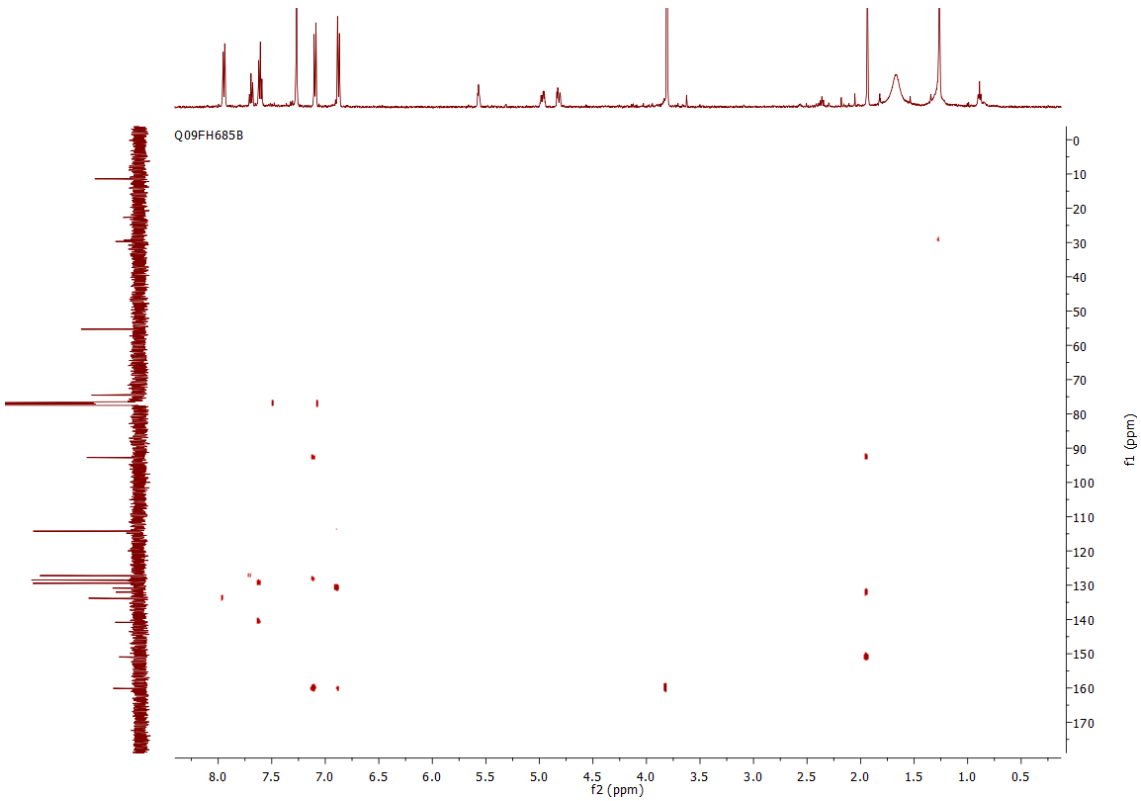
Two-dimensional COSY NMR spectrum ^{1}H-^{1}H of **3b** in $CDCl_3$ at 300 MHz



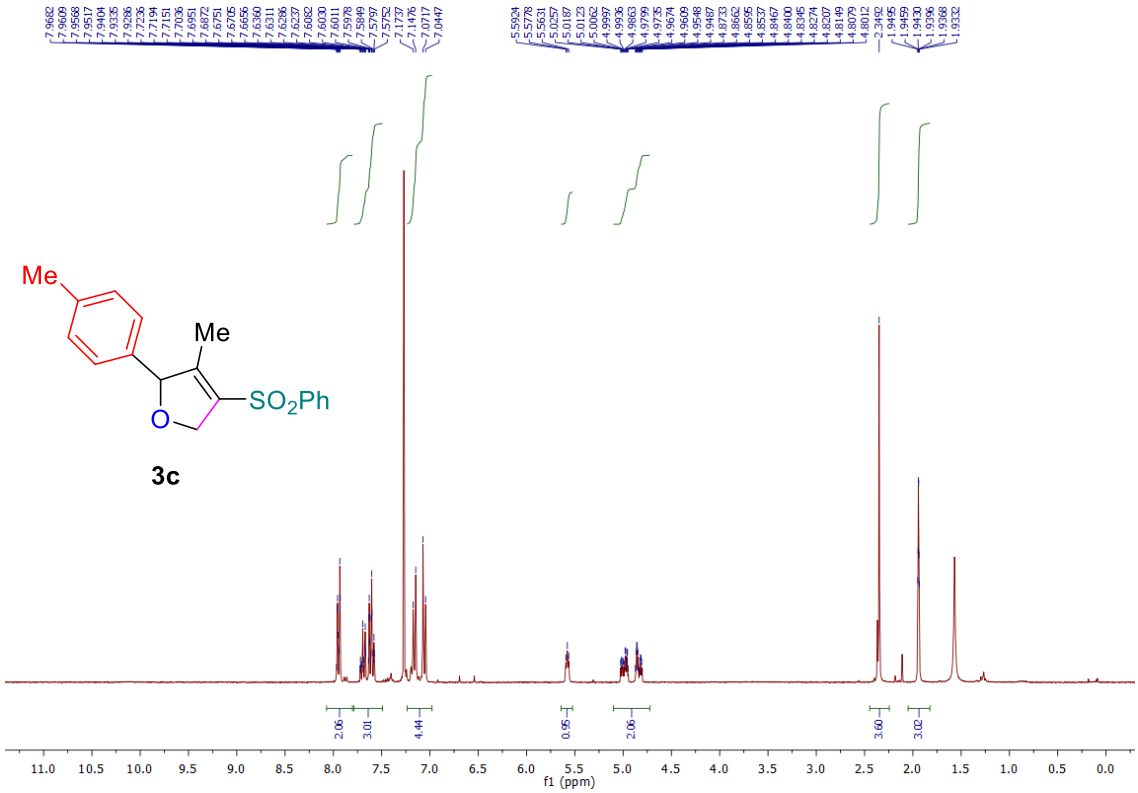
Two-dimensional HMQC NMR spectrum ^{1}H-^{13}C of **3b** in $CDCl_3$



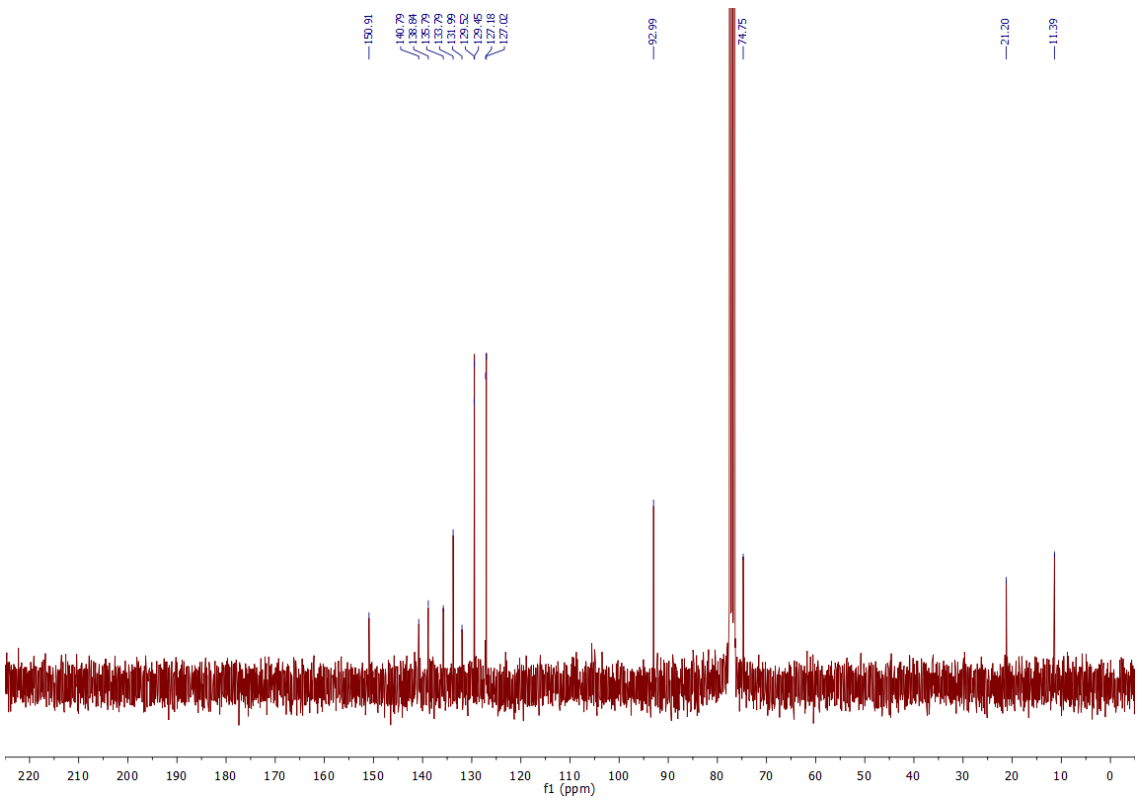
Two-dimensional HMBC NMR spectrum ^{1}H-^{13}C of **3b** in $CDCl_3$



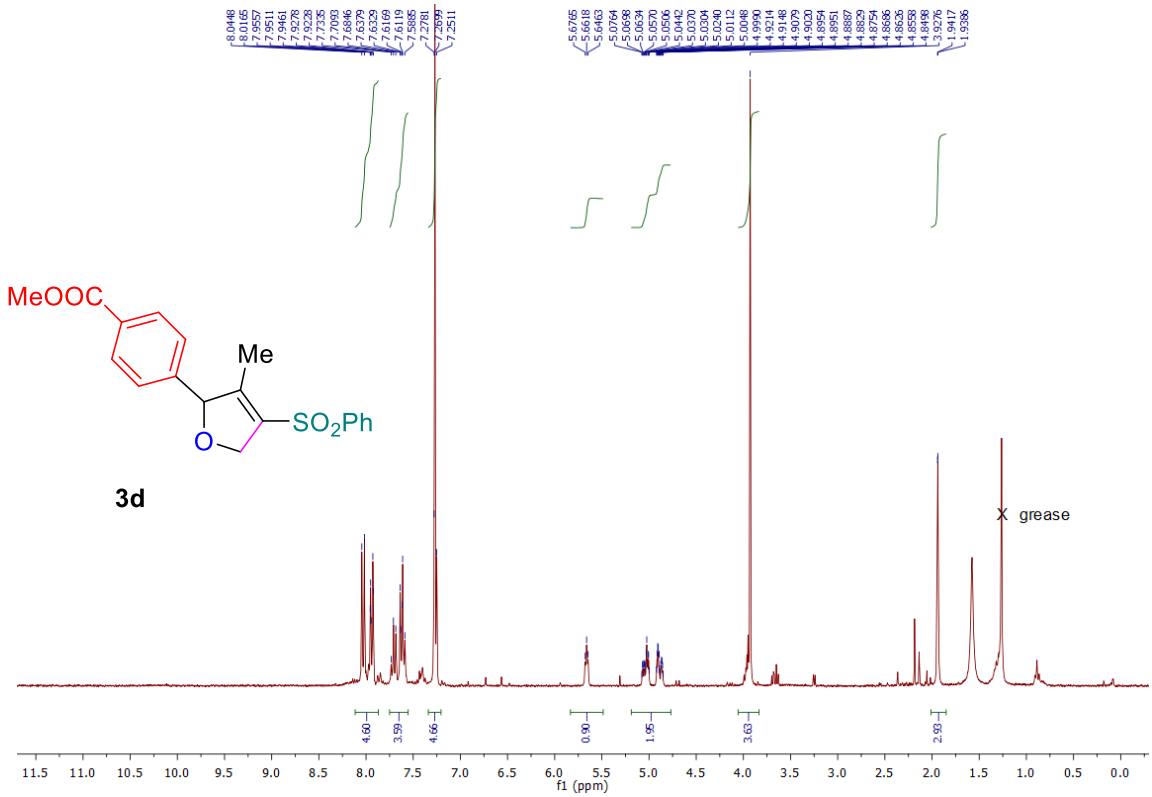
^{1}H NMR spectrum of **3c** in $CDCl_3$ at 300 MHz



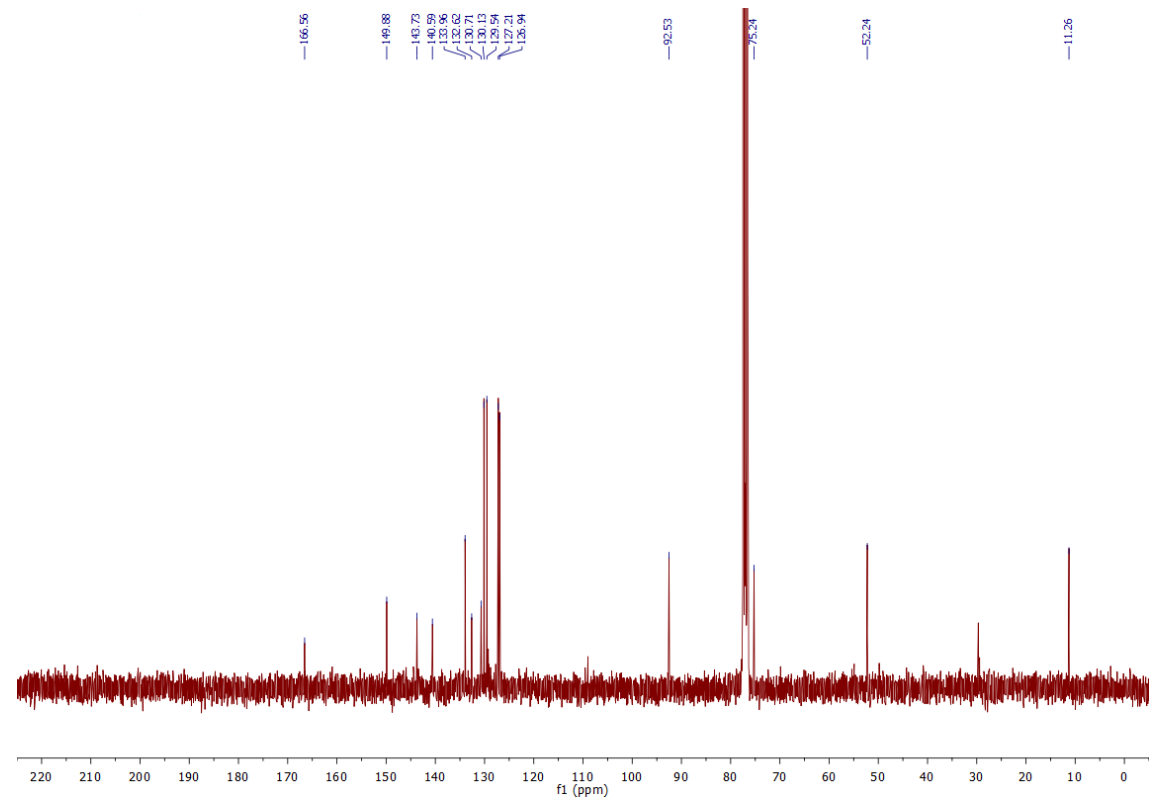
^{13}C NMR spectrum of **3c** in $CDCl_3$ at 75 MHz



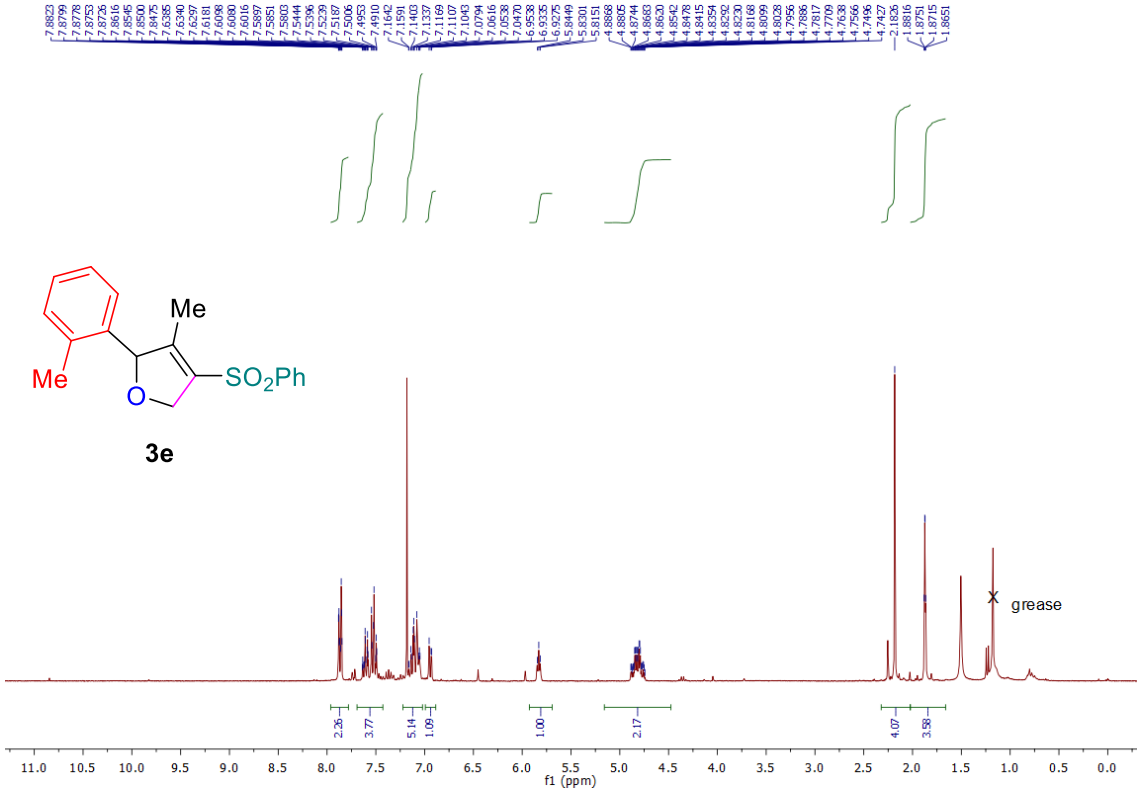
^{1}H NMR spectrum of **3d** in $CDCl_3$ at 300 MHz



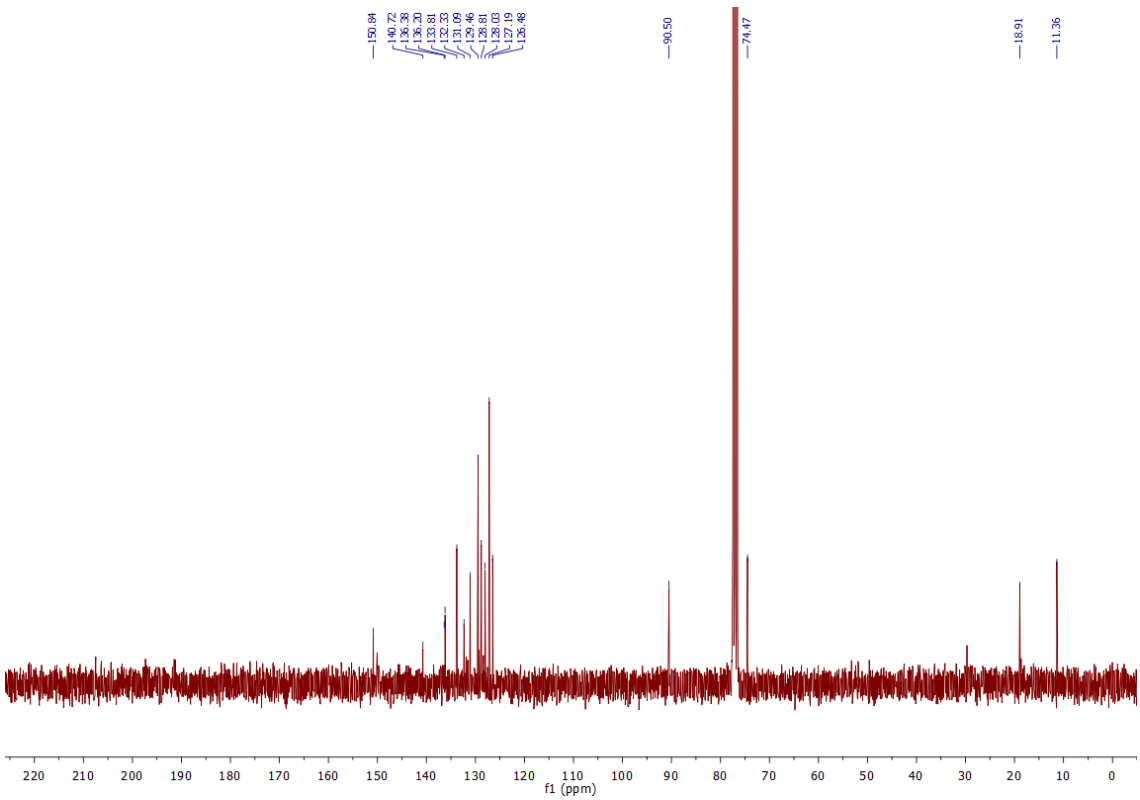
^{13}C NMR spectrum of 3**d** in $CDCl_3$ at 75 MHz



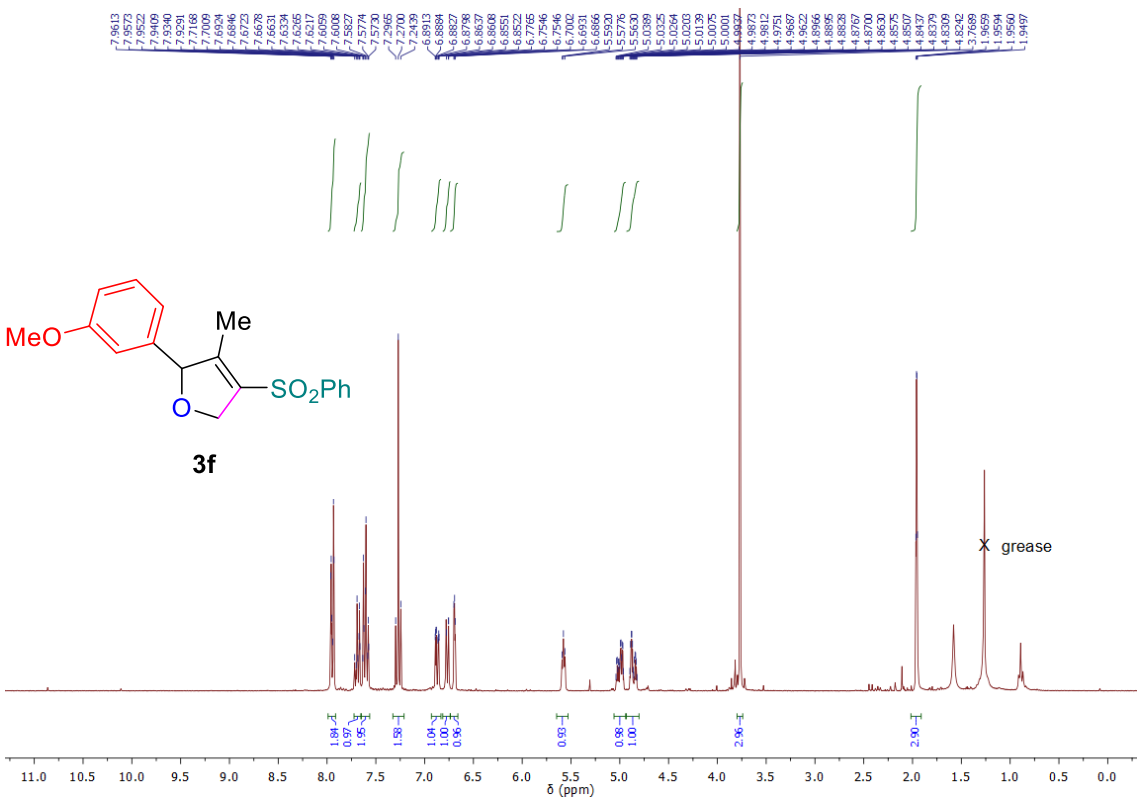
^{1}H NMR spectrum of **3e** in $CDCl_3$ at 300 MHz



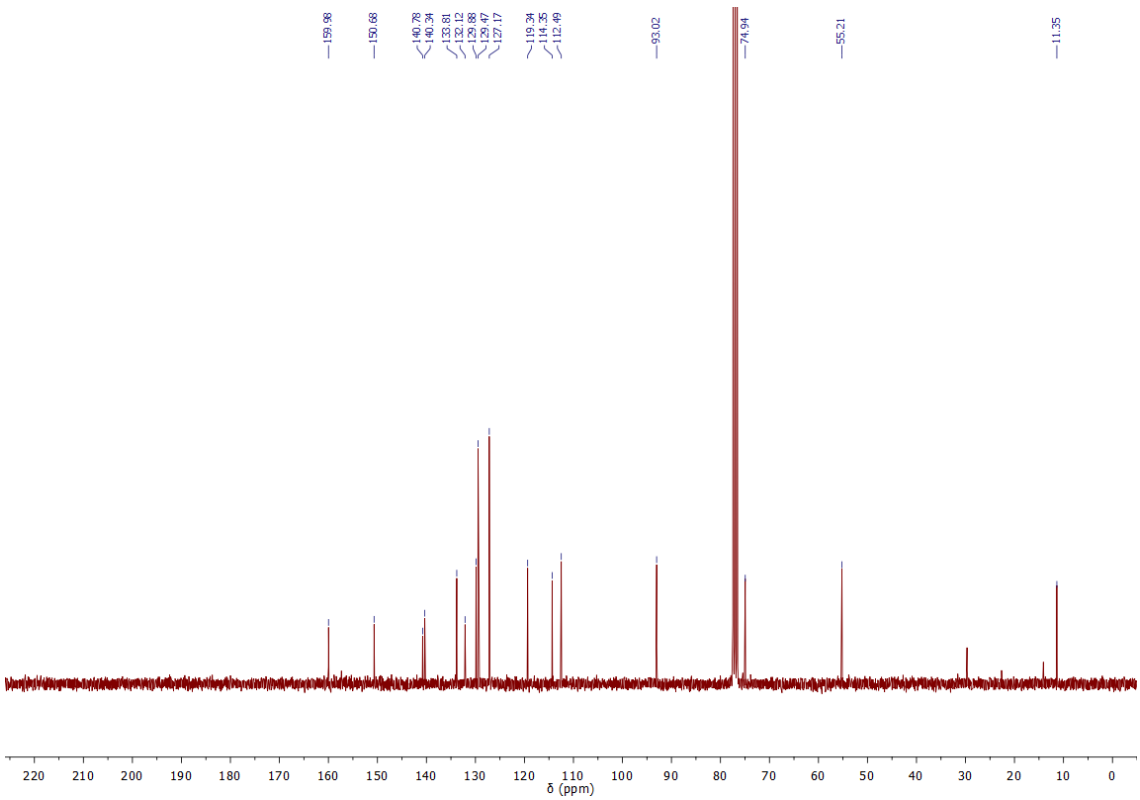
^{13}C NMR spectrum of 3**e** in $CDCl_3$ at 75 MHz



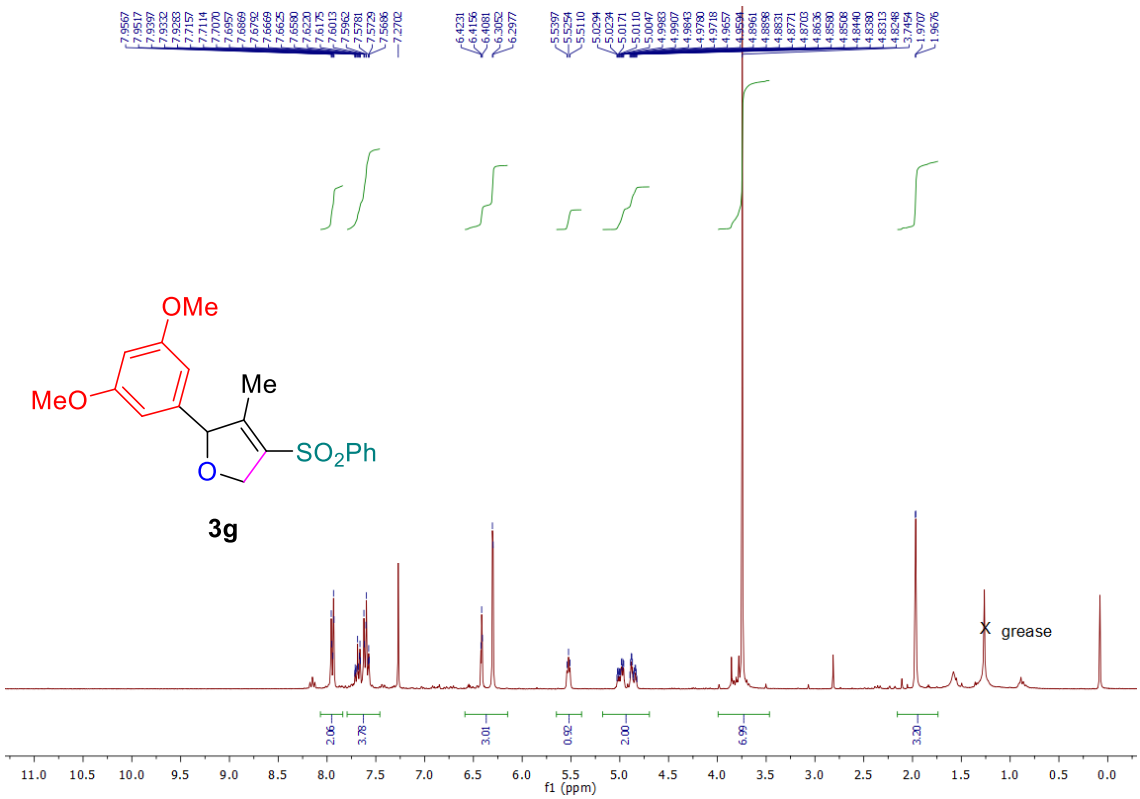
^{1}H NMR spectrum of **3f** in $CDCl_3$ at 300 MHz



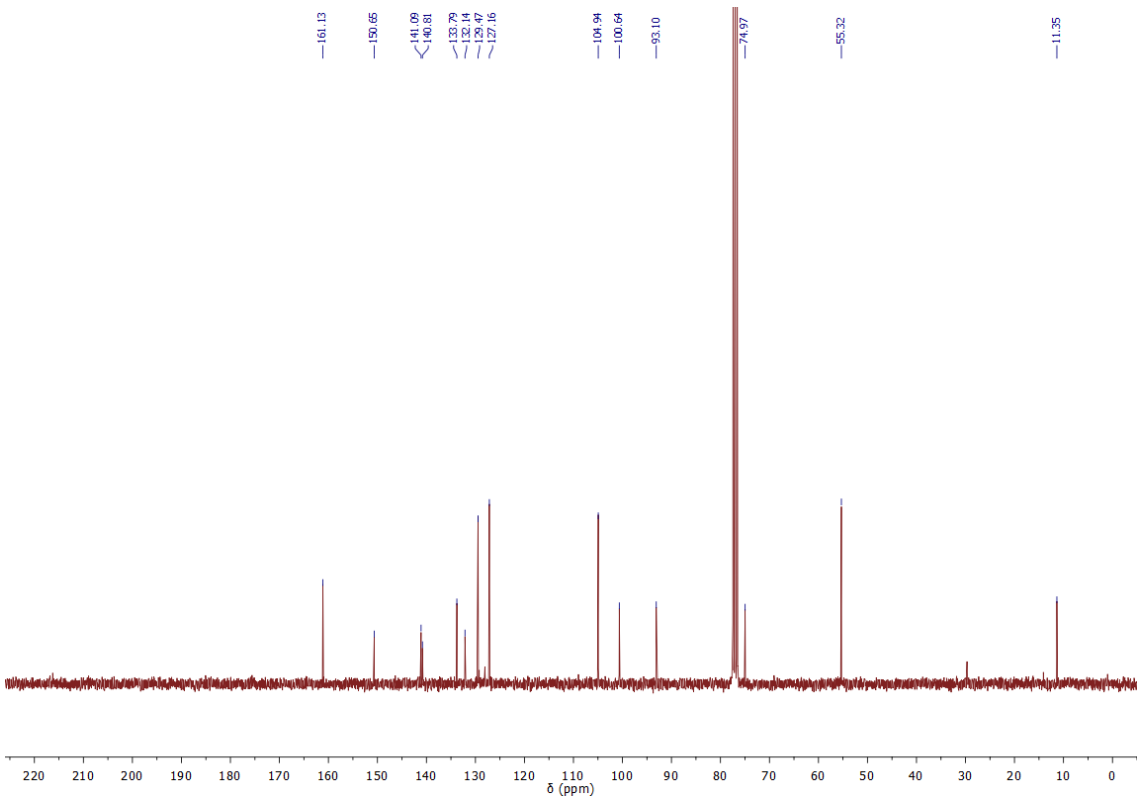
^{13}C NMR spectrum of 3**f** in $CDCl_3$ at 75 MHz



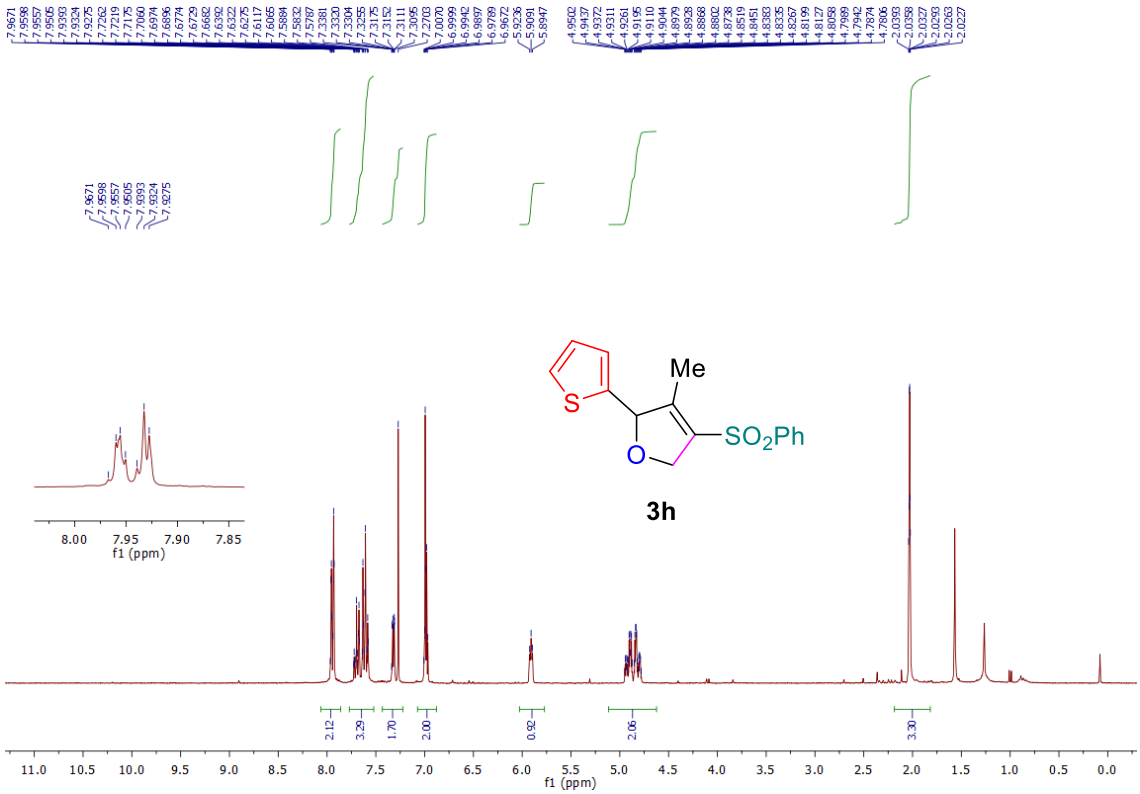
^{1}H NMR spectrum of **3g** in $CDCl_3$ at 300 MHz



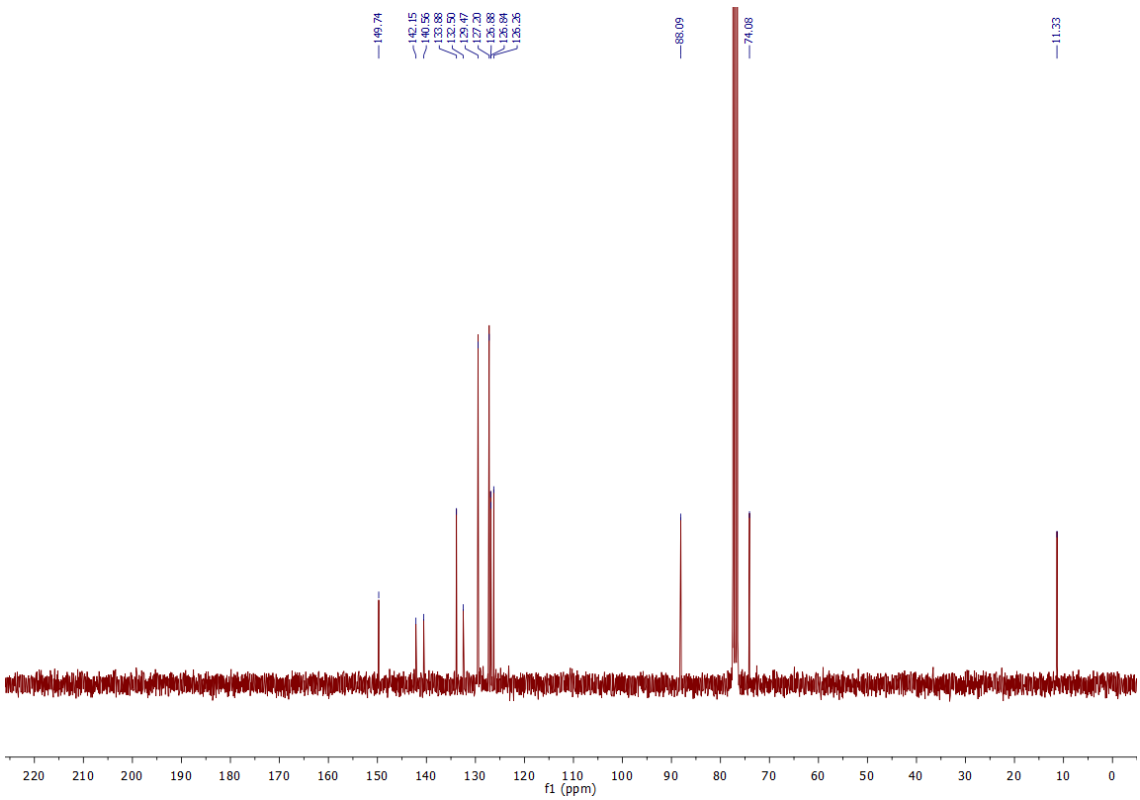
^{13}C NMR spectrum of 3**g** in $CDCl_3$ at 75 MHz



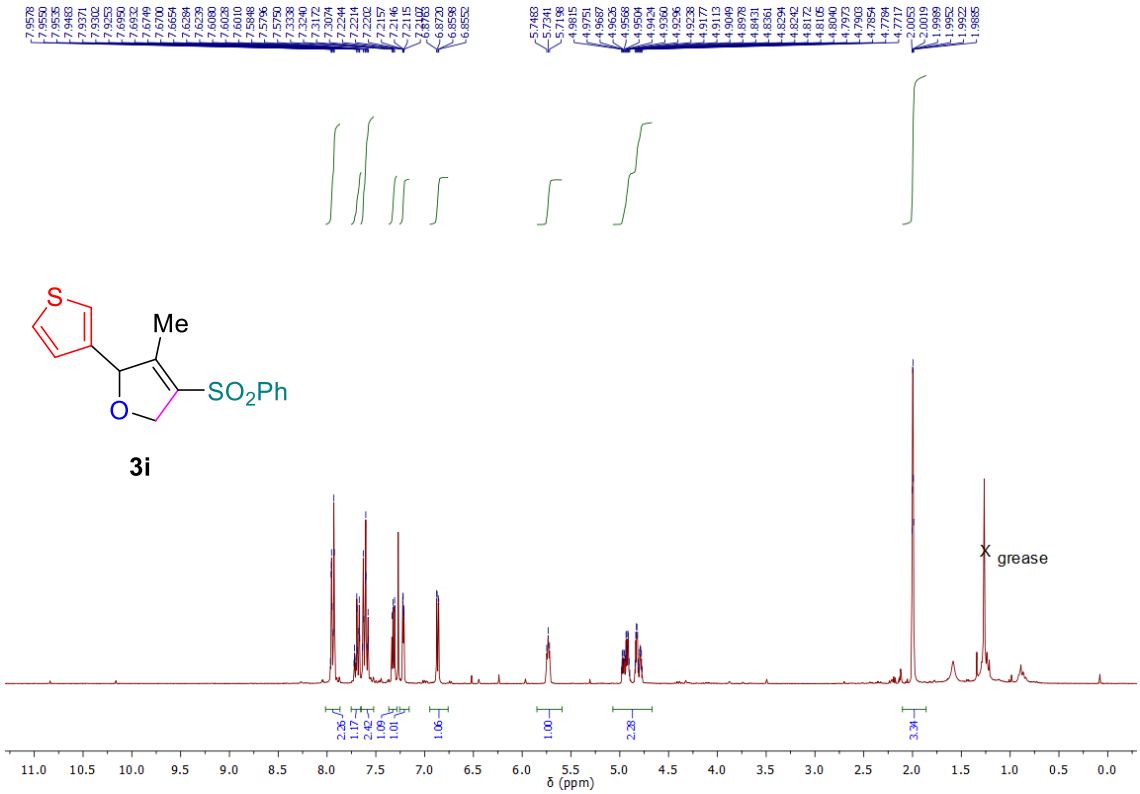
^{1}H NMR spectrum of **3h** in $CDCl_3$ at 300 MHz



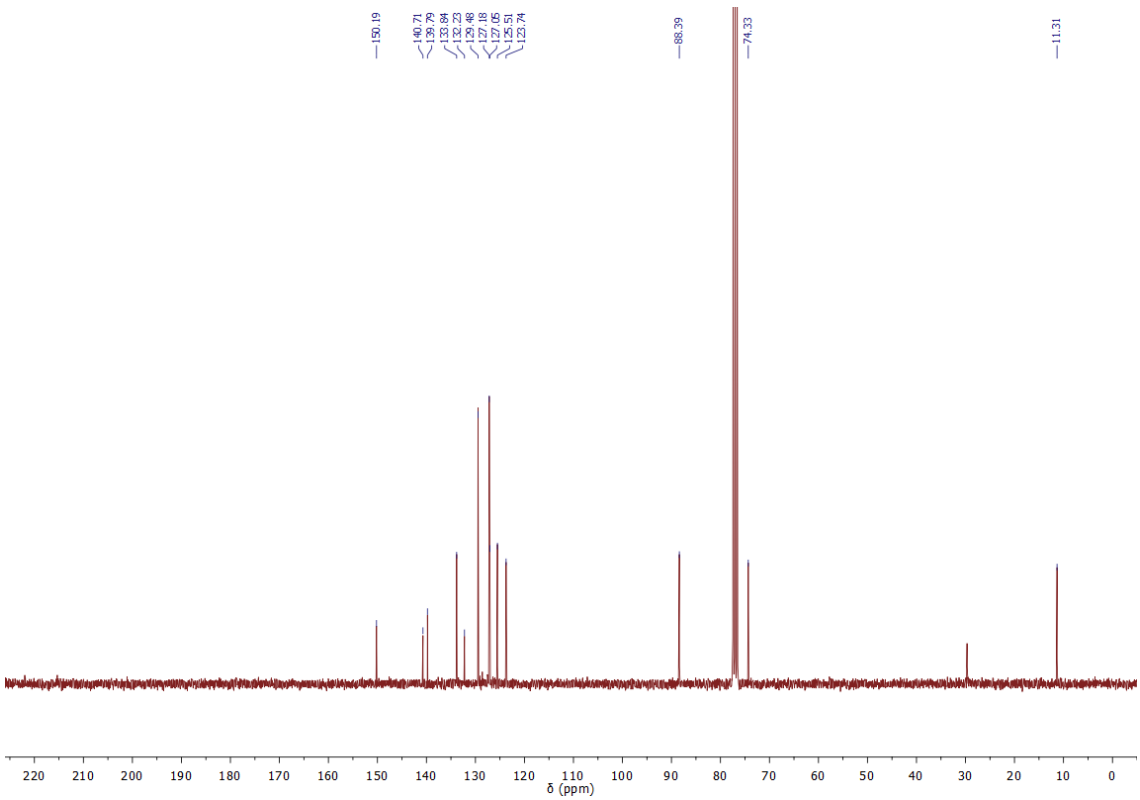
^{13}C NMR spectrum of 3**h** in $CDCl_3$ at 75 MHz



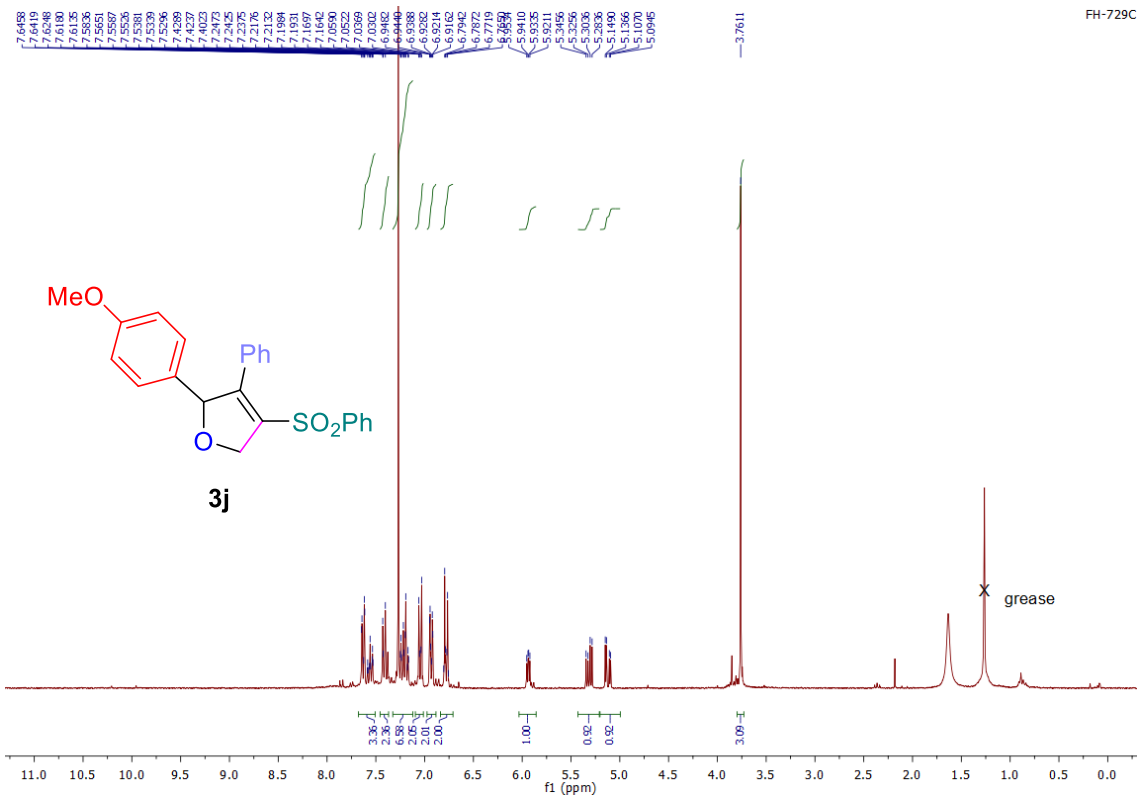
^{1}H NMR spectrum of **3i** in $CDCl_3$ at 300 MHz



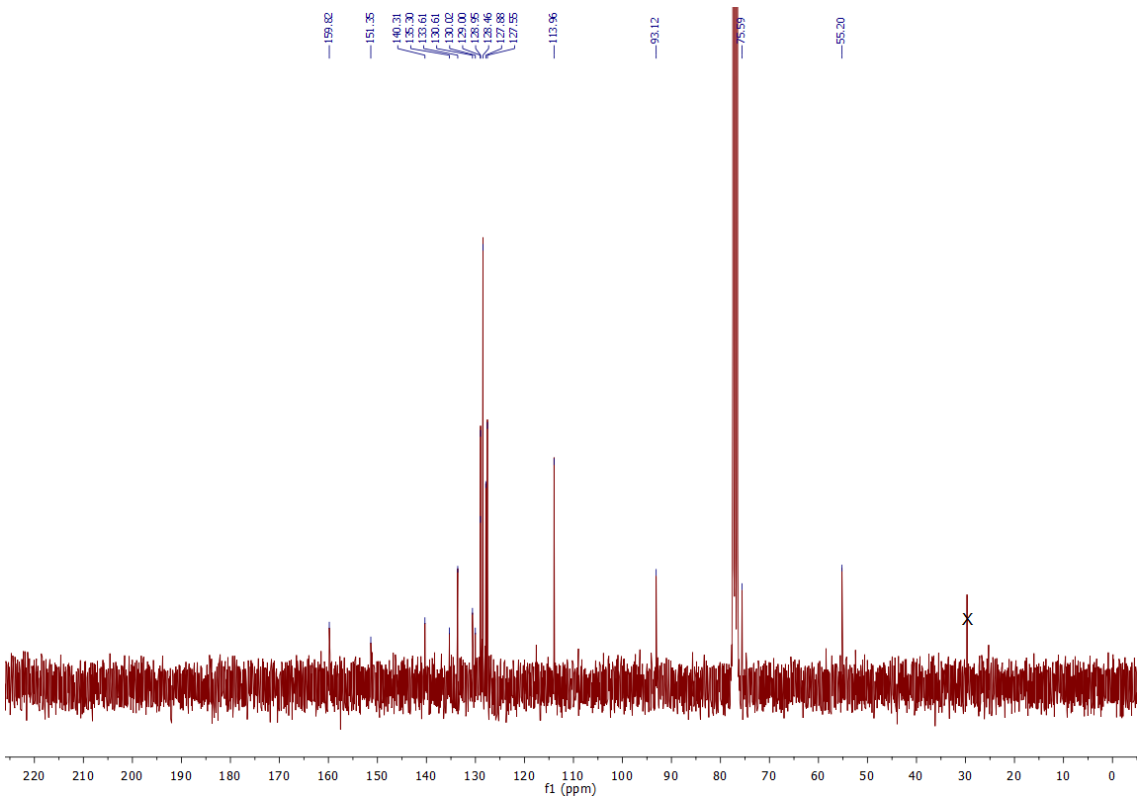
^{13}C NMR spectrum of 3**i** in $CDCl_3$ at 75 MHz



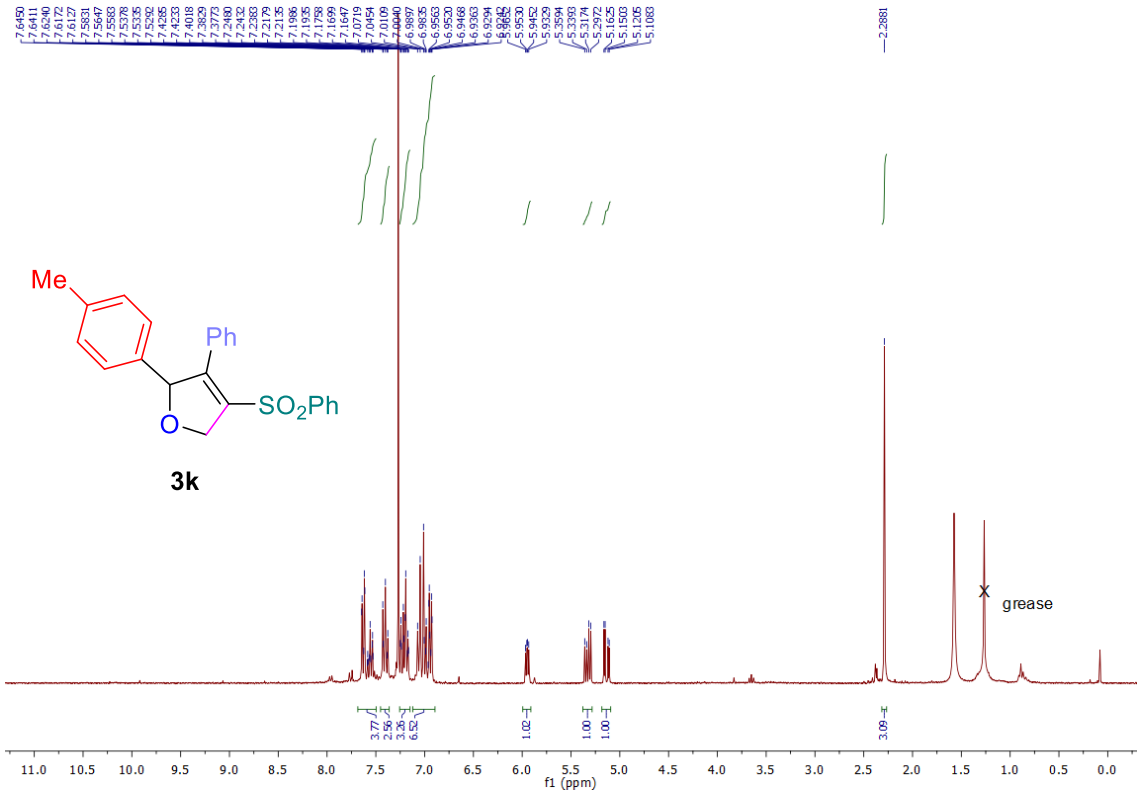
^{1}H NMR spectrum of **3j** in $CDCl_3$ at 300 MHz



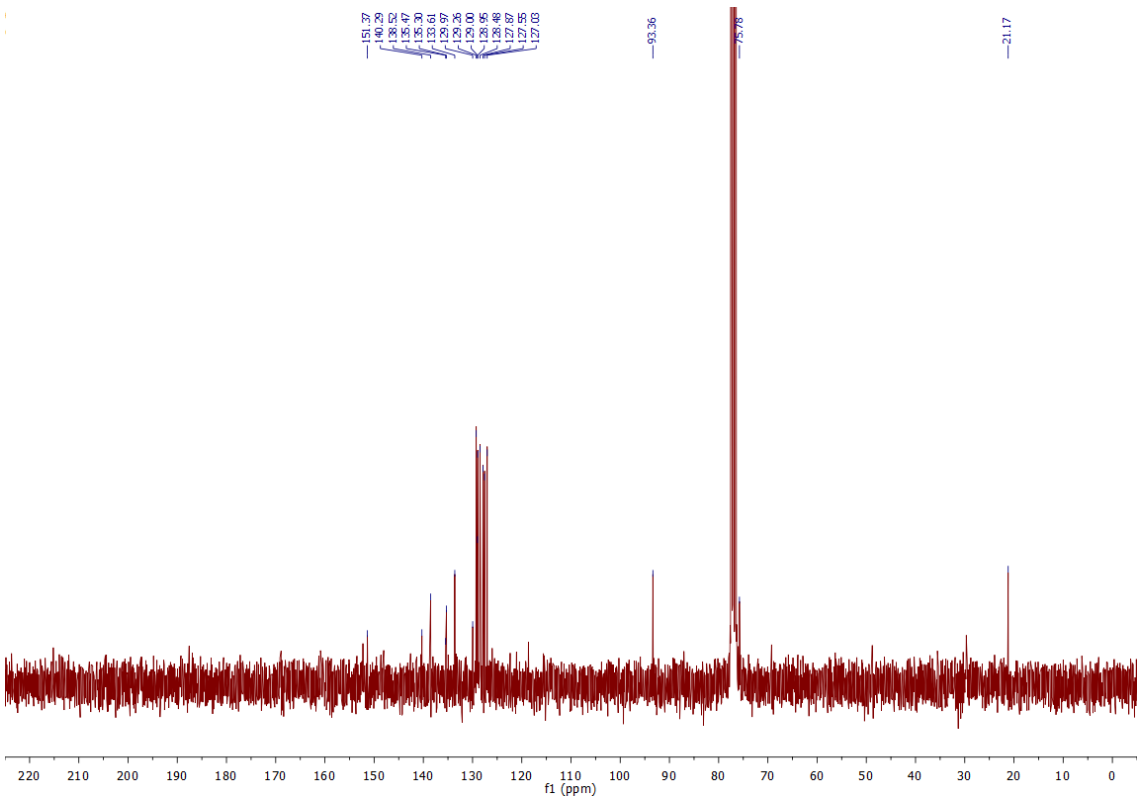
^{13}C NMR spectrum of 3**j** in $CDCl_3$ at 75 MHz



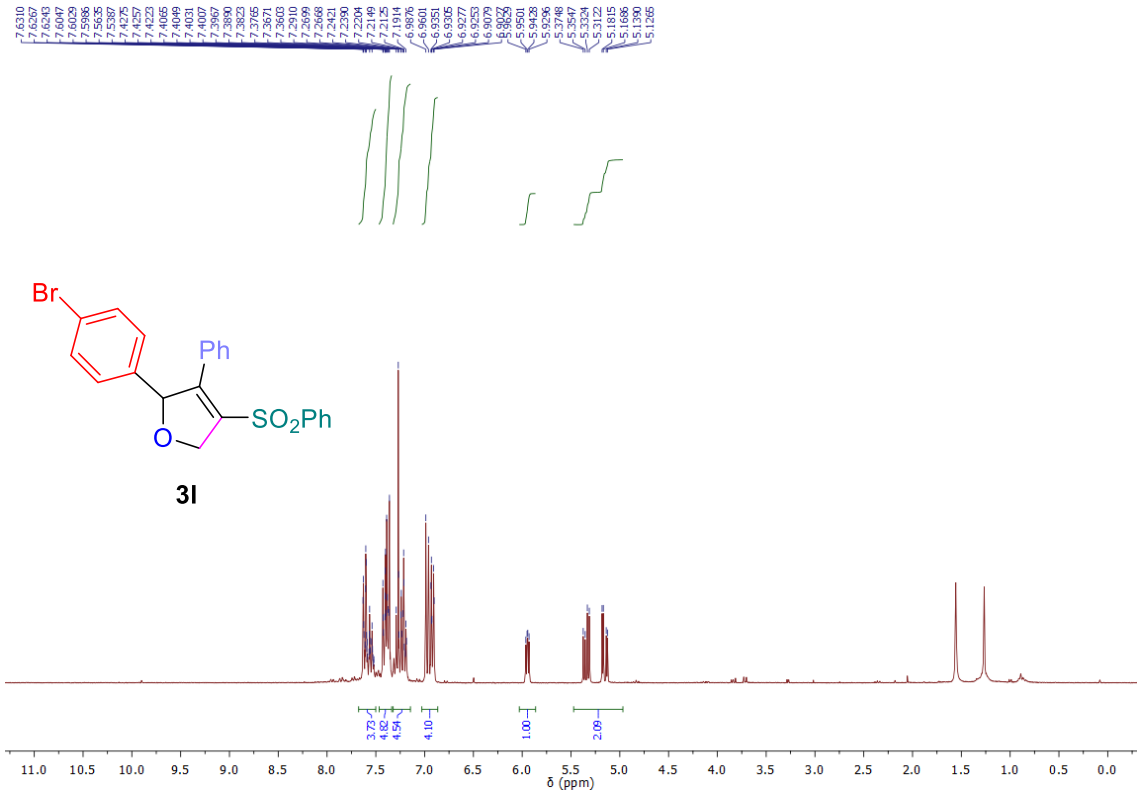
^{1}H NMR spectrum of **3k** in $CDCl_3$ at 300 MHz



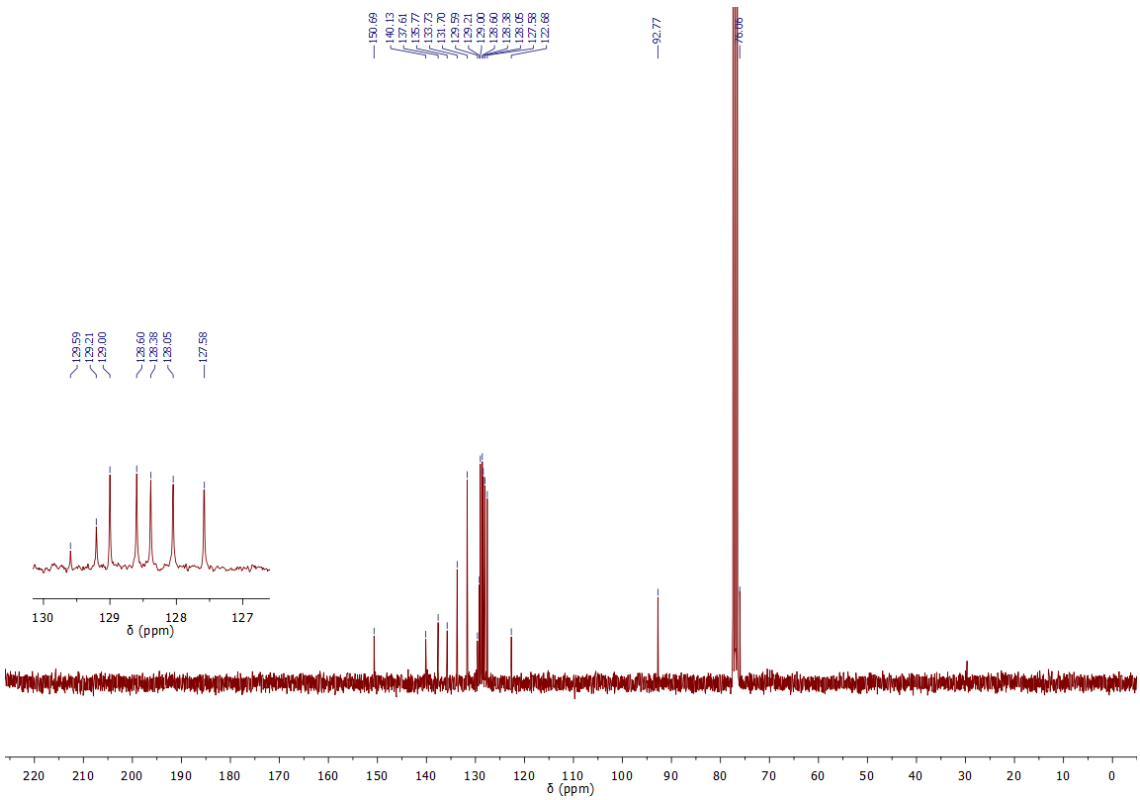
^{13}C NMR spectrum of 3**k** in $CDCl_3$ at 75 MHz



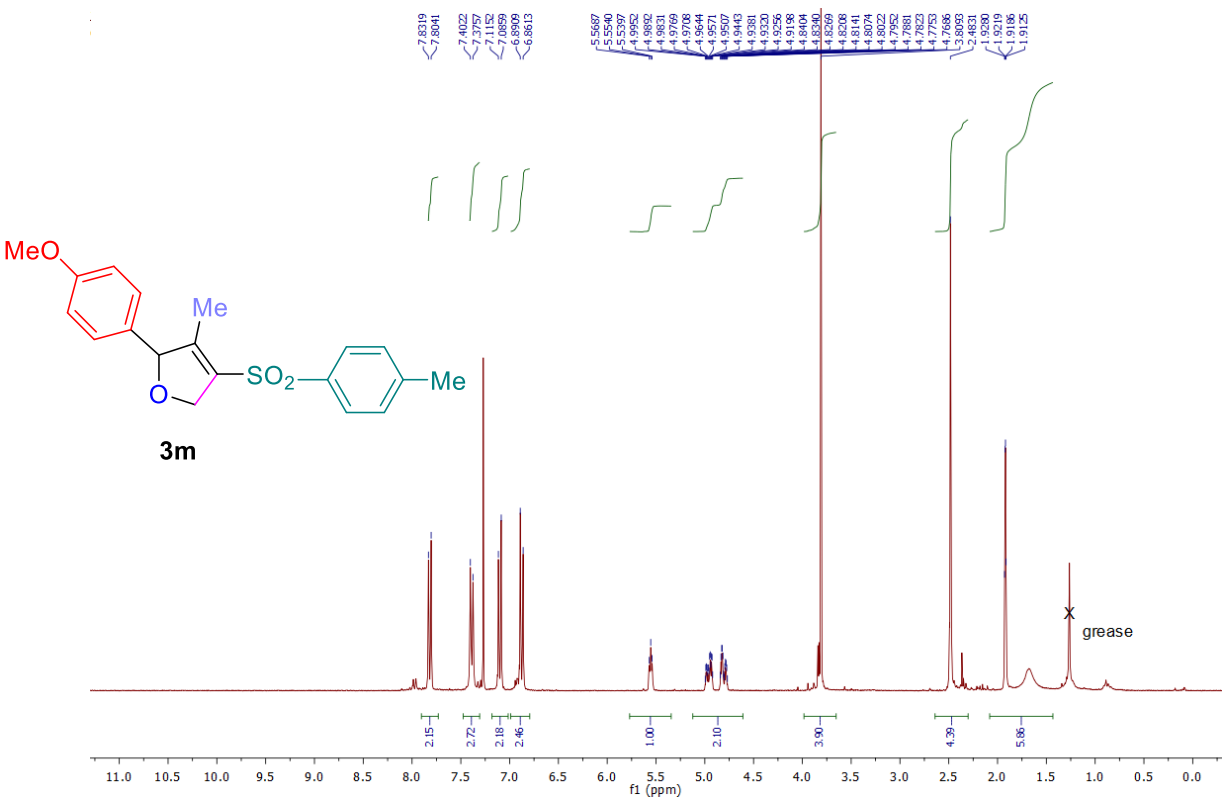
^{1}H NMR spectrum of **3l** in $CDCl_3$ at 300 MHz



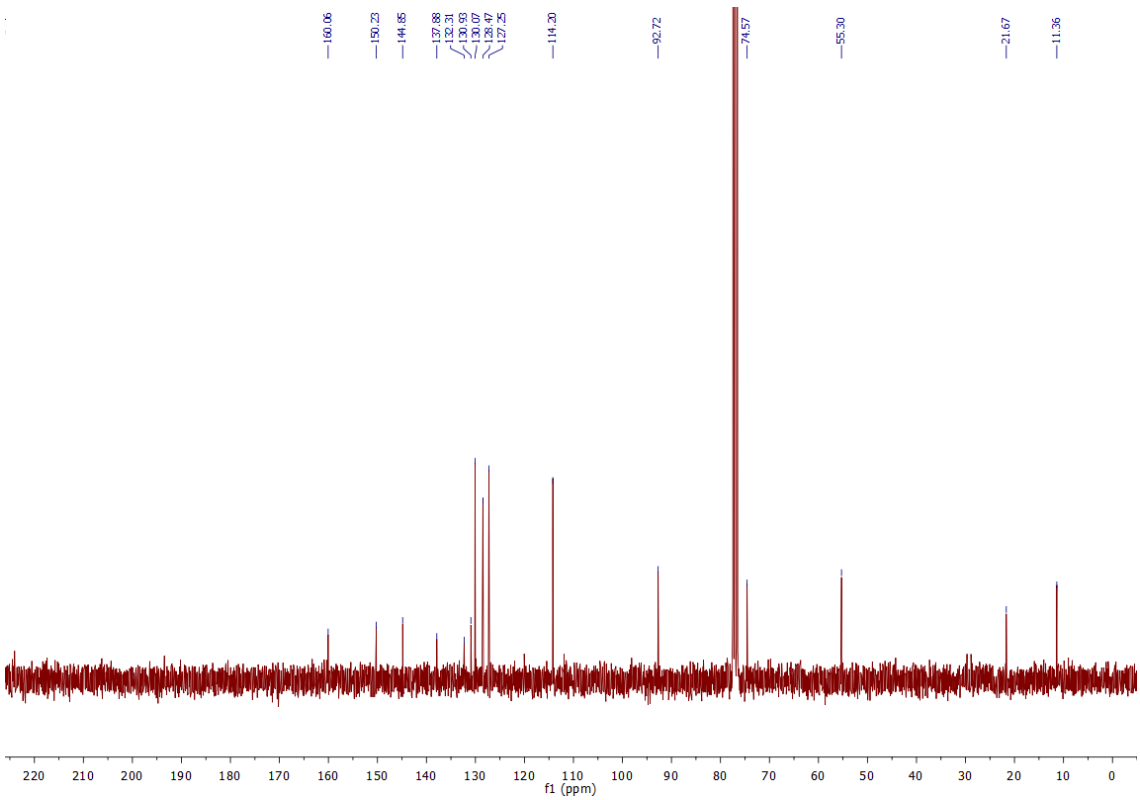
^{13}C NMR spectrum of **3l** in $CDCl_3$ at 75 MHz



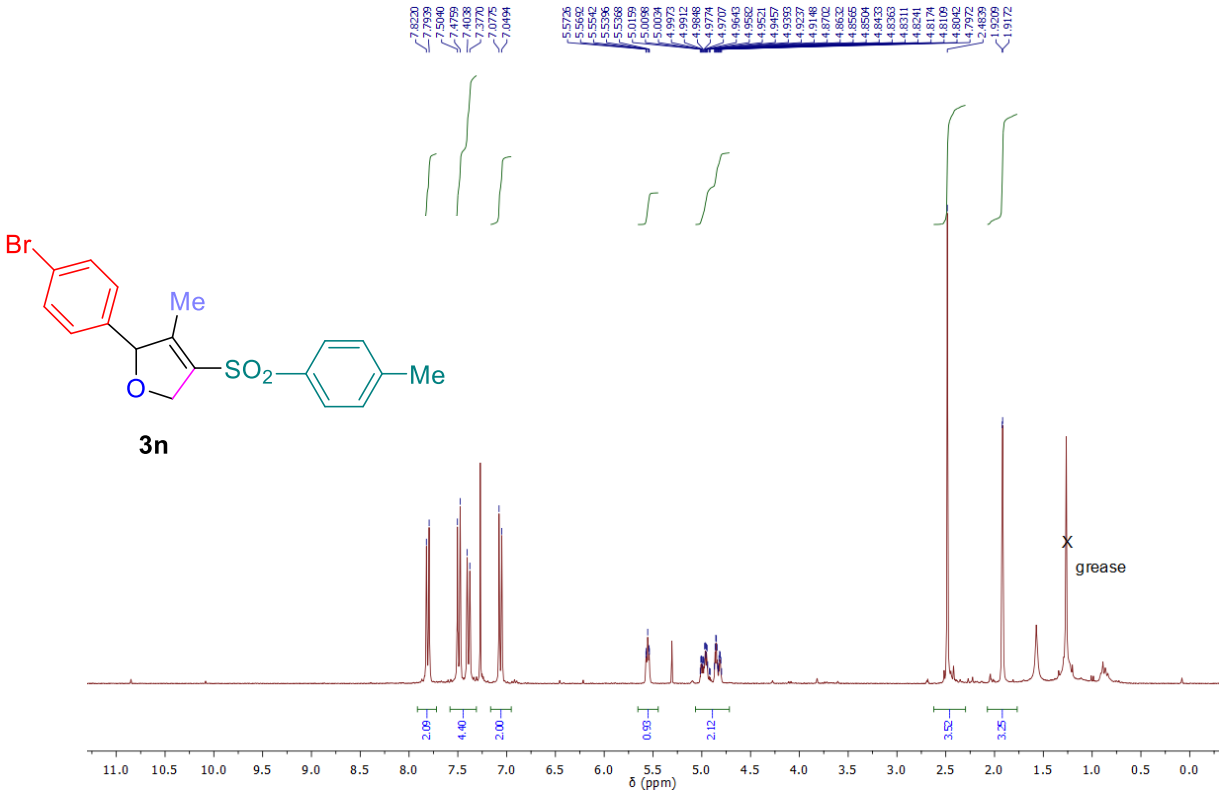
^{1}H NMR spectrum of **3m** in $CDCl_3$ at 300 MHz



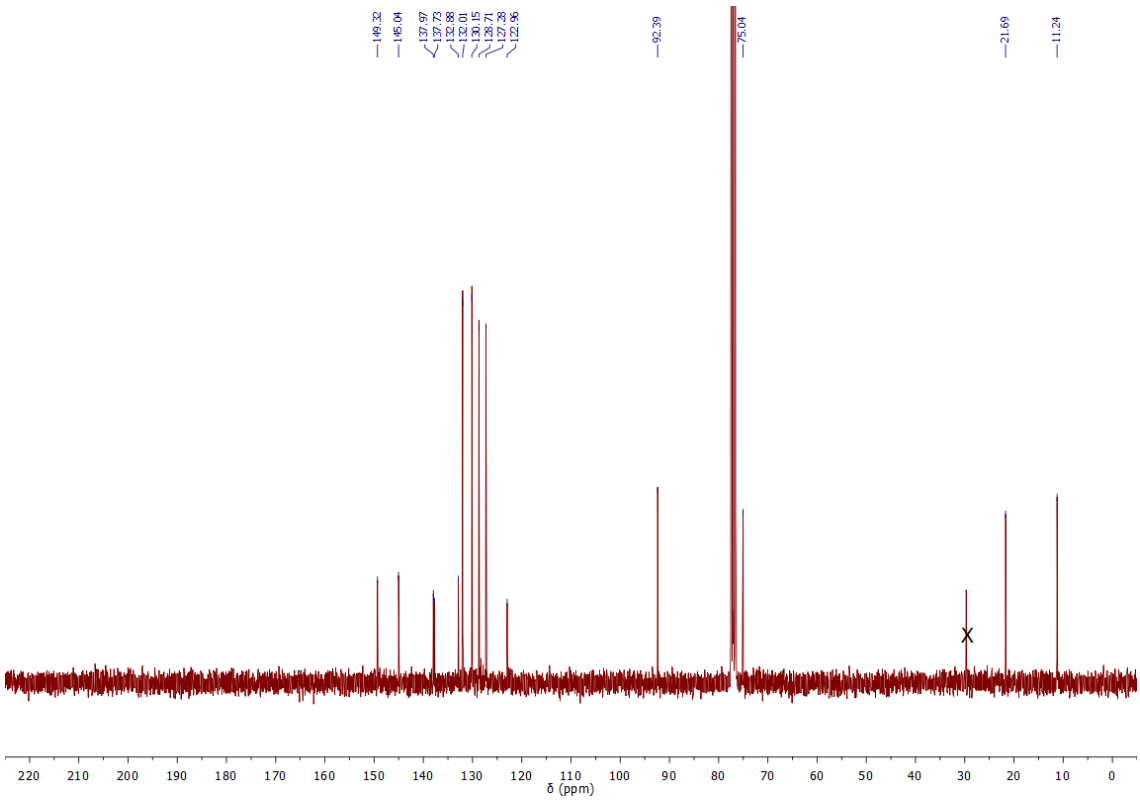
^{13}C NMR spectrum of **3m** in $CDCl_3$ at 75 MHz



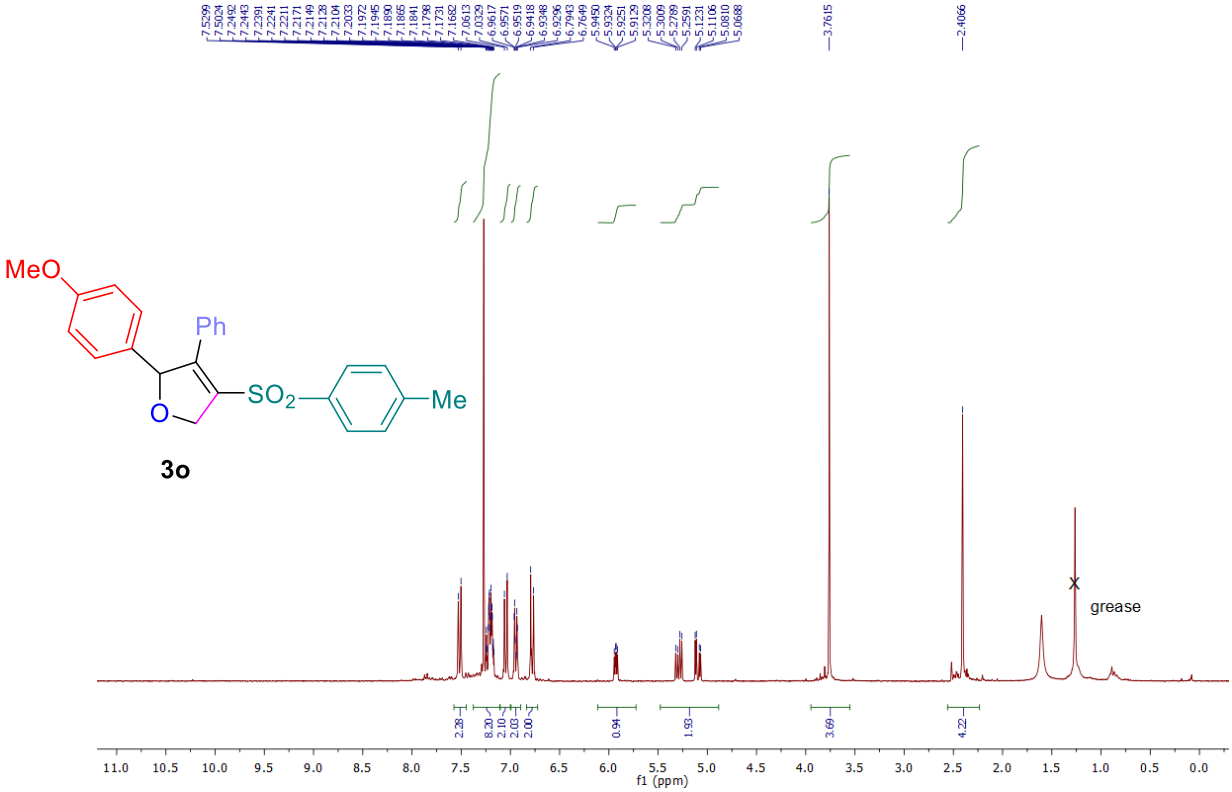
^{1}H NMR spectrum of **3n** in $CDCl_3$ at 300 MHz



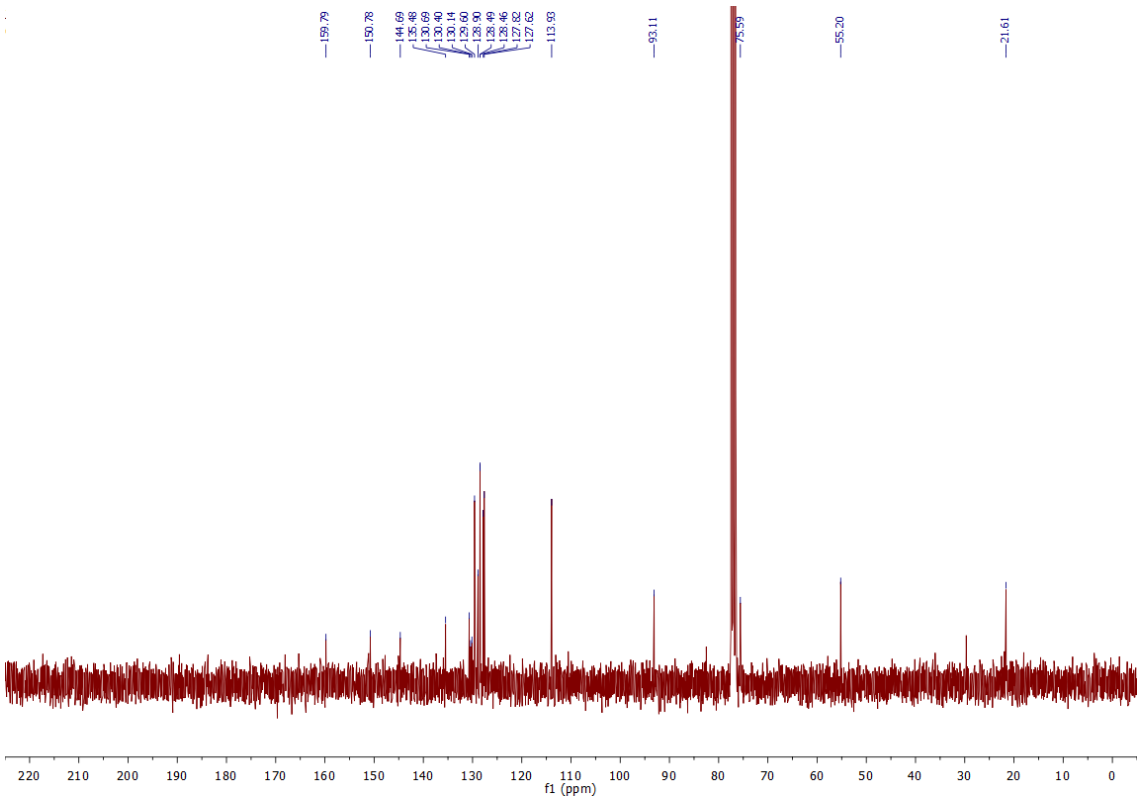
^{13}C NMR spectrum of **3n** in $CDCl_3$ at 75 MHz



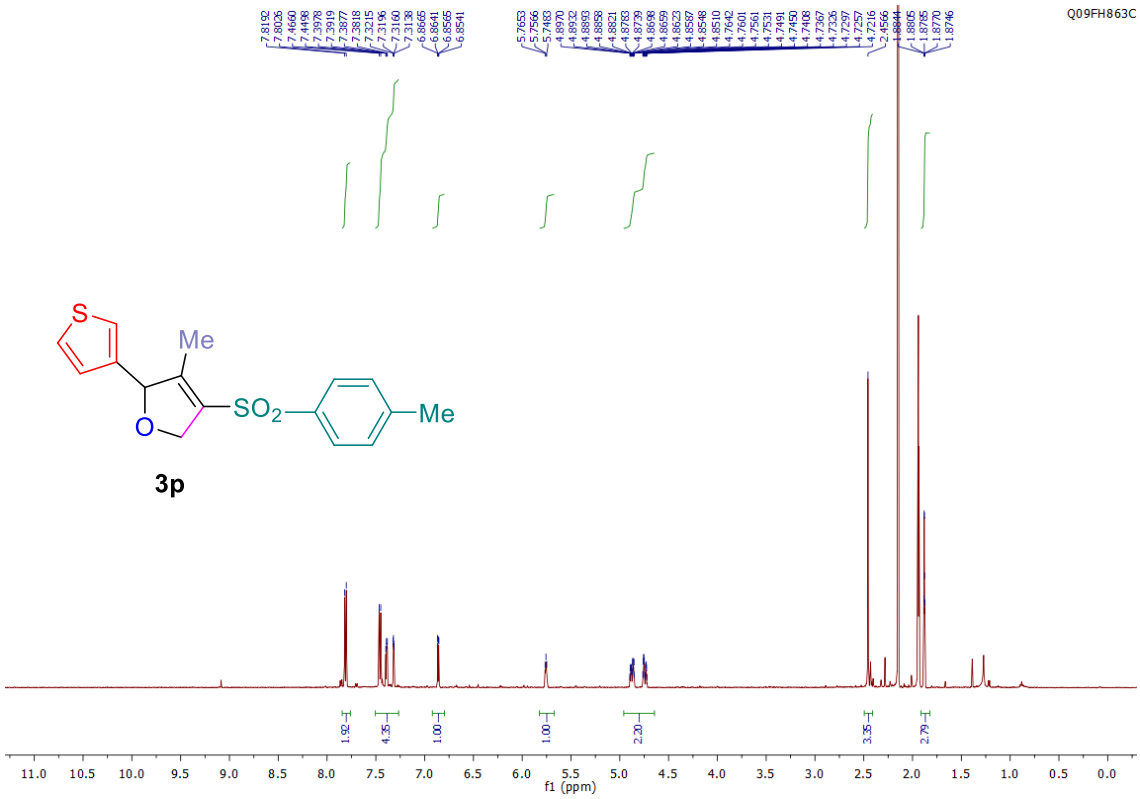
^{1}H NMR spectrum of **3o** in $CDCl_3$ at 300 MHz



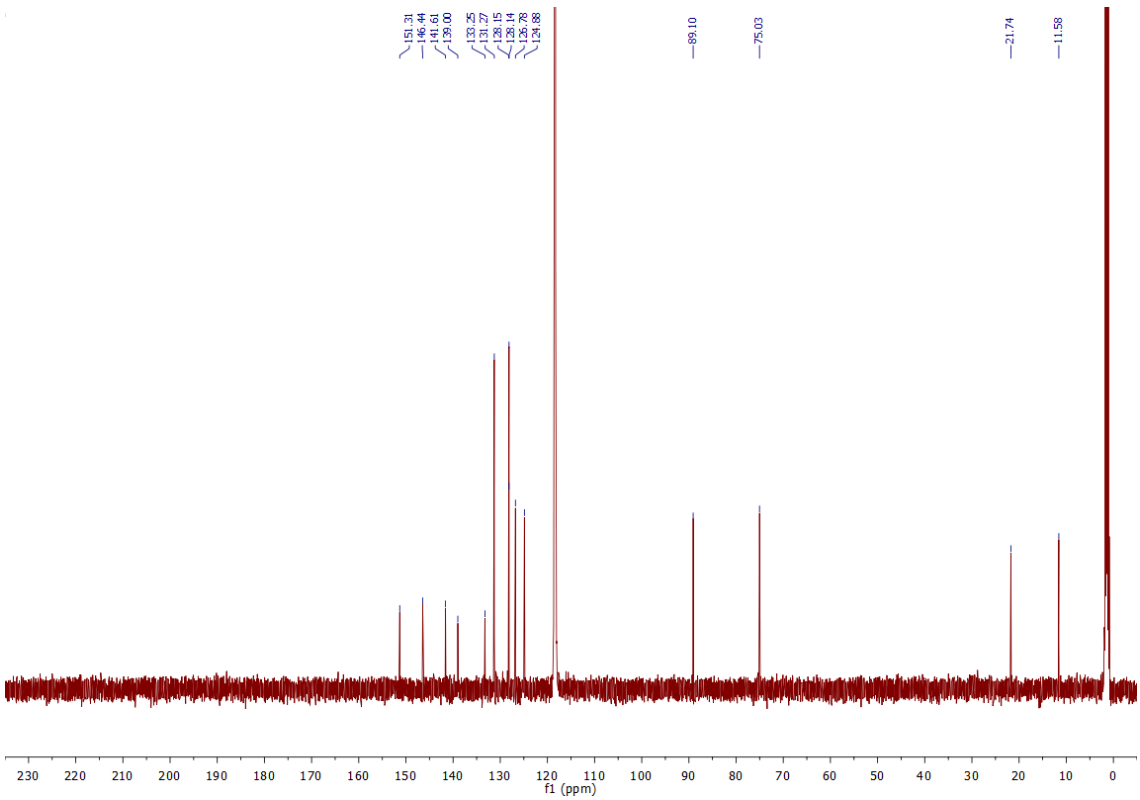
^{13}C NMR spectrum of **3o** in $CDCl_3$ at 75 MHz



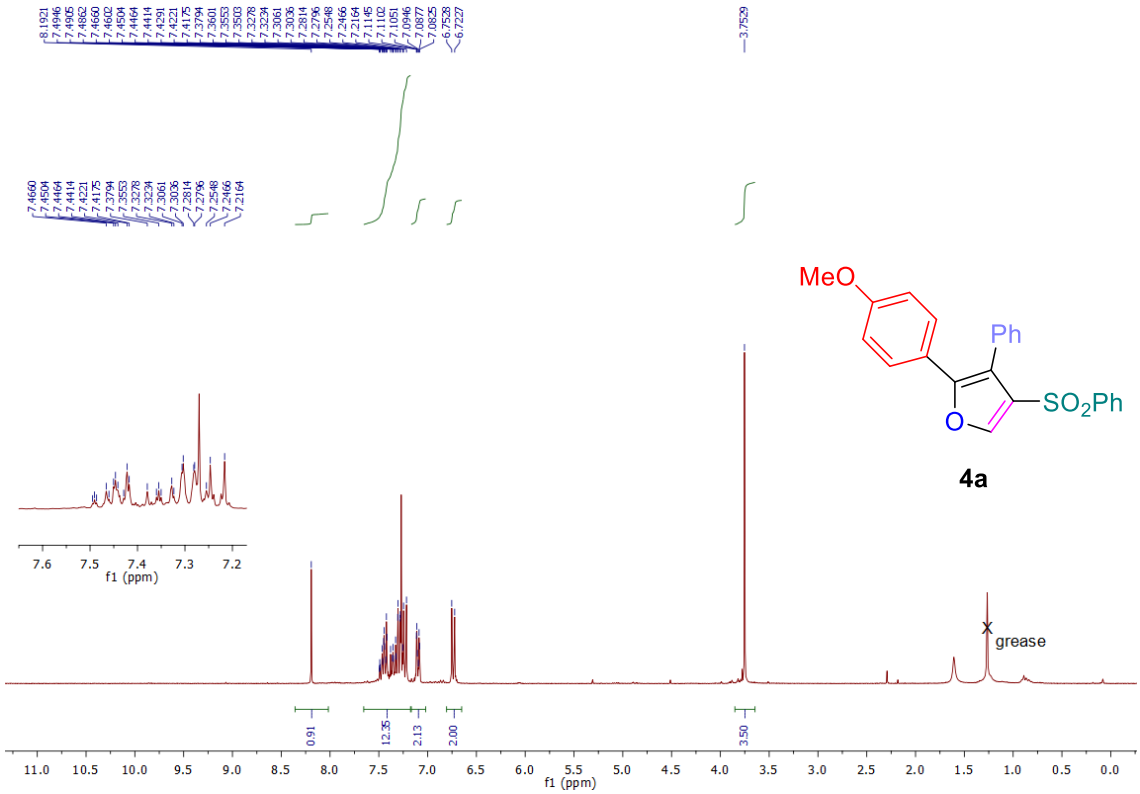
^{1}H NMR spectrum of **3p** in CD_3CN at 500 MHz



^{13}C NMR spectrum of **3p** in $CDCl_3$ at 125 MHz



^{1}H NMR spectrum of **4a** in $CDCl_3$ at 300 MHz



^{13}C NMR spectrum of **4a** in $CDCl_3$ at 75 MHz