Supporting Information for the Paper

Visible-Light-Mediated Ru-Catalyzed Synthesis of 3-(Arylsulfonyl)but-3-enals via Coupling of α-Allenols with Diazonium Salts and Sulfur Dioxide

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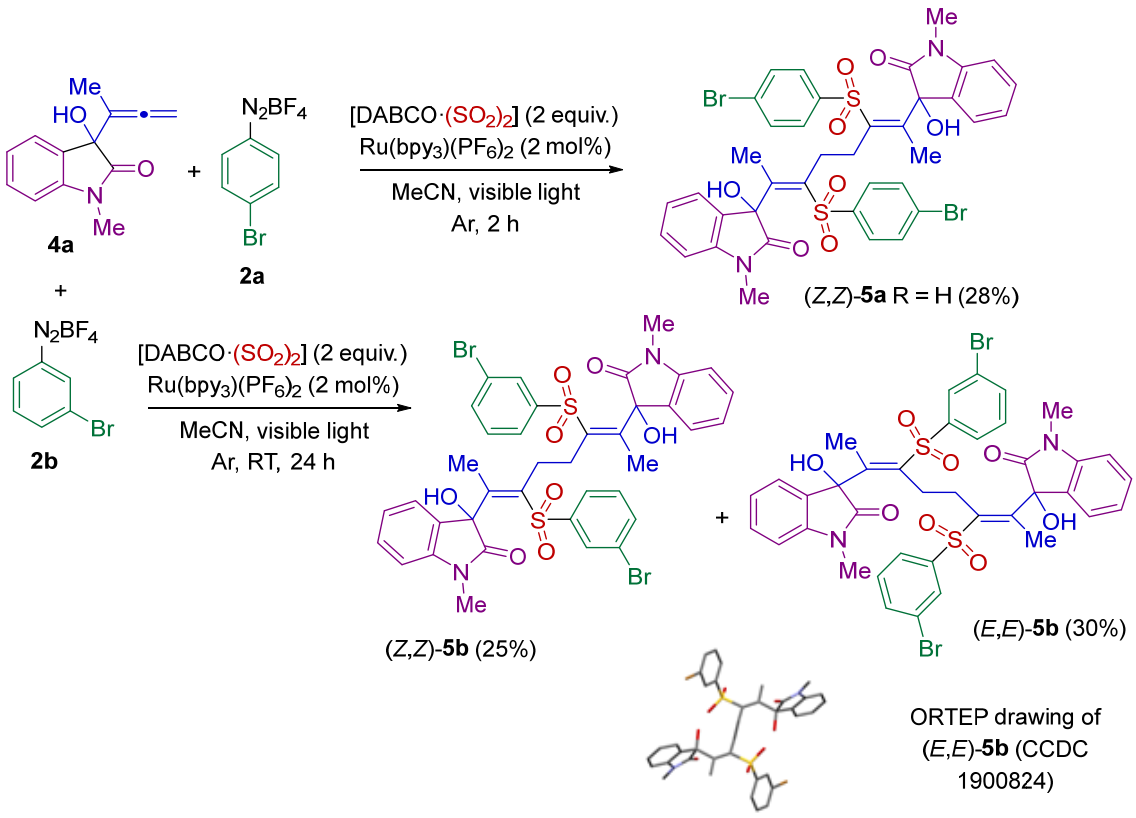
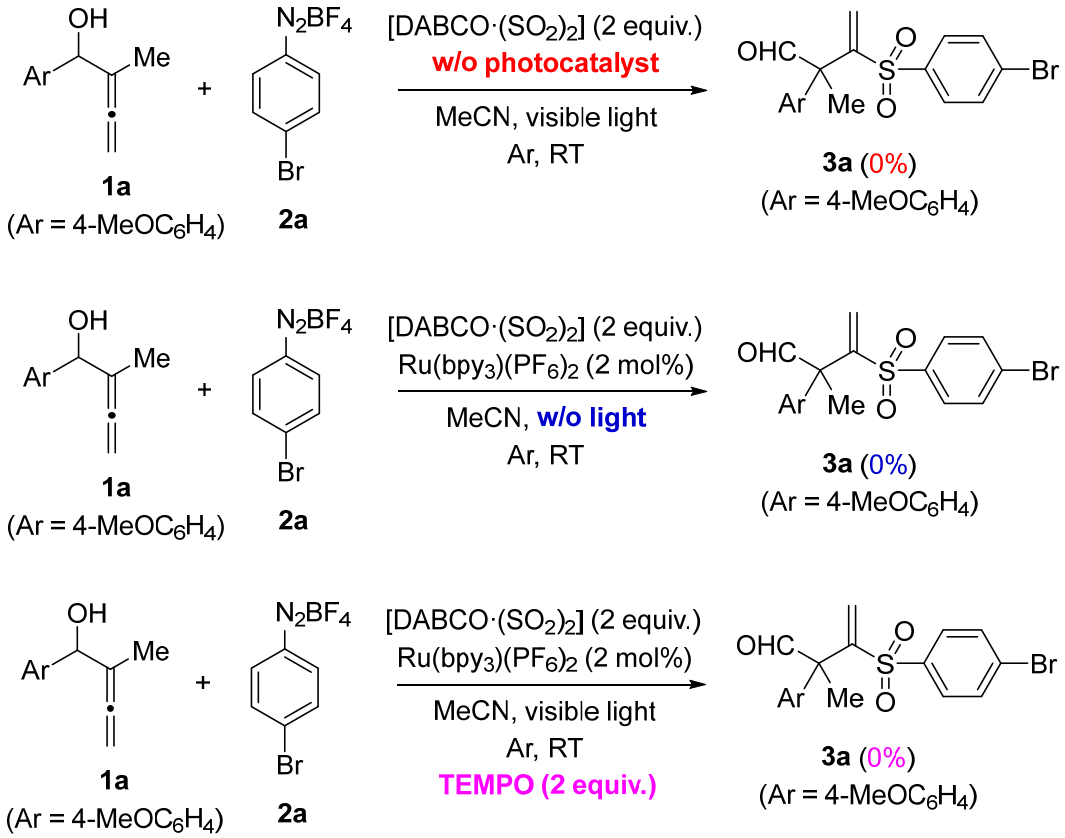
1. General Methods: ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Bruker Avance AMX-700, Bruker AMX-500, or Bruker Avance-DPX 300. NMR spectra were recorded in $CDCl_3$ or CD_3CN, solutions, except otherwise stated. Chemical shifts are given in ppm relative to TMS (^{1}H, 0.0 ppm), $CDCl_3$ (^{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. White LED (10 W, 175-250V, ROBLAN Led lamps) was used for light irradiation.

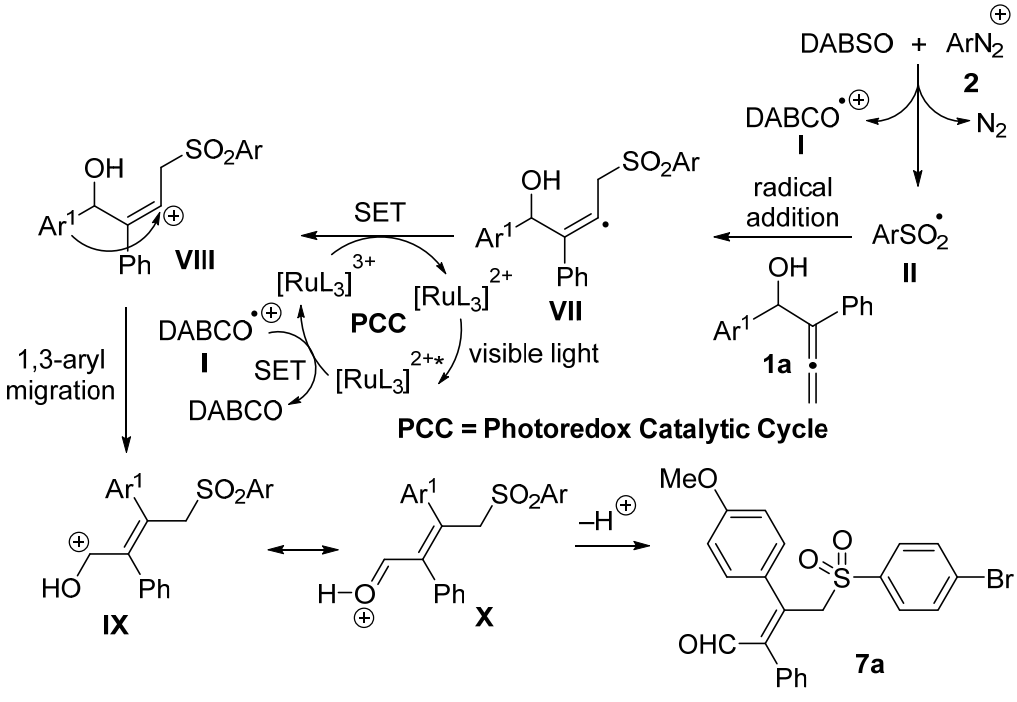
2. Scheme S1. Sulfonylation-Rearrangement Cascade of Allenols 4a,b under Photocatalysis. Preparation of 3,6-Bis[(aryl)sulfonyl-octa-2,6-dienyl]bis(indolin-2-ones) 5a,b



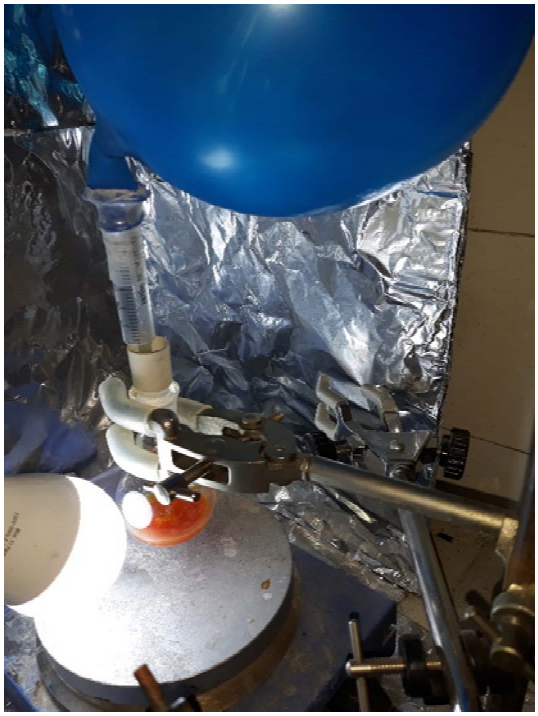
3. Scheme S2. Control and Radical Inhibition Experiments



4. Scheme S3. Rationalization for the formation of side product 7a



5. Figure S1. Photographic depiction of the reaction setup



6. Experimental Procedures. Synthesis and Characterization

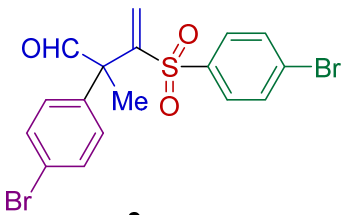
Allenols 1 and 4 were prepared as reported in previous works (Alcaide, B.; Almendros, P.; Martínez del Campo, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 4501; Alcaide, B.; Almendros, P.; Martínez del Campo, T.; Carrascosa, R. *Chem. Asian J.* **2008**, *3*, 1140; Alcaide, B.; Almendros, P.; Fernández, I.; Martínez del Campo, T.; Naranjo, T. *Adv. Synth. Catal.* **2013**, *355*, 2681; Alcaide, B.; Almendros, P.; Luna, A.; Soriano, E. *J. Org. Chem.* **2015**, *80*, 7050; Alcaide, B.; Almendros, P.; González, A. M.; Luna, A.; Martínez-Ramírez, S. *Adv. Synth. Catal.* **2016**, *358*, 2000; Li, W.; Lin, Z.; Chen, L.; Tian, X.; Wang, Y.; Huang, S. H.; Hong, R. *Tetrahedron Lett.* **2016**, *57*, 603; Alcaide, B.; Almendros, P.; Cembellín, S.; Martínez del Campo, T. *Adv. Synth. Catal.* **2015**, *357*, 1070; Alcaide, B.; Almendros, P.; Cembellín, S.; Martínez del Campo, T.; Palop, G. *Chem. Eur. J.* **2017**, *23*, 13754; Zaky, M.; Li, Z.; Morgan, T. D. R.; Lefort, F. M.; Boyd, R. J.; Burnell, D. J. *J. Org. Chem.* **2019**, *84*, 13665); **using the following procedure: Indium-promoted reaction between 3-substituted prop-2-ynyl bromides and aldehydes. General procedure for the synthesis of α-allenols 1 and 4.** 1-Bromo-2-butyne or 1-bromo-3-phenyl-2-propyne (3.0 mmol) was added to a well stirred suspension of the corresponding aldehyde (1.0 mmol) and indium powder (6.0 mmol) in THF/NH_4Cl (aq. sat.)

(1:5, 5 mL) at 0 ºC. After disappearance of the starting material (TLC) the mixture was extracted with ethyl acetate (3 x 5 mL). The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes or dichloromethane/ethyl acetate mixtures gave analytically pure compounds **1** and **4**.

Aryldiazonium salts 2 were prepared according to the method of Bunnett (Broxton, T. J.; Bunnett, J. F.; Paik, C. H. *J. Org. Chem.* **1977**, *42*, 643; Hanson, P.; Jones, J. R.; Taylor, A. B.; Walton, P. H.; Timms, A. W. *J. Chem. Soc., Perkin Trans. 2,* **2002**, 1135; Kumar, P.; Shu, X.-Z.; Zhang, M.; He, Y.; Frei, H.; Toste, F. D. *J. Am. Chem. Soc.* **2014**, *136*, 5844; Srivastava, A.; Sah, C.; Devi, S.; Venkataramani, S. *Chem. Eur. J.* **2019**, *25*, 11924); **using the following procedure:** To a stirred solution of the appropriate aniline (10 mmol) in a mixture of 50% fluoroboric acid (3 ml) and distilled water (3 ml), was added a solution of sodium nitrite (690 mg) in water (3 ml) at 0 ºC. The mixture was stirred for 30 minutes and the thick precipitate was collected and re-dissolved in acetone. The diazonium tetrafluoroborate was precipitated by the addition of diethyl ether, collected and dry under air.

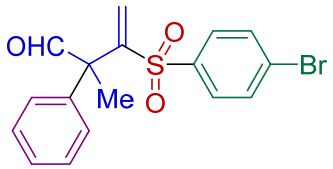
General procedure for the preparation of compounds 3a-r, 5a-b and 6a-e

General method for light-induced transformation of α-allenic alcohols **1**: To a solution of diazonium salts **2** (0.75 mmol), [DABCO·$(SO_2)_2$] (1.0 mmol) in acetonitrile (3.5 mL) was added $[Ru(bpy)_3](PF6)_2$ (2 mol %). The reaction mixture was stirred at room temperature for ten minutes under irradiation of LED light source (LED light bulb installed in a tool box). After this time, a solution of the allene **1** (0.5 mmol) in acetonitrile (3.5 mL) was added via syringe. The progress of the reaction was monitored using TLC analysis. The resulting mixture was concentrated in vacuo and the crude residue was purified using silica gel column flash chromatography. Spectroscopic and analytical data for pure forms of compounds **3**, **5** and **6** follows.



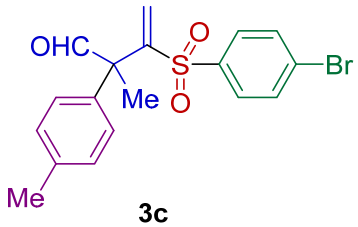
3a

Aldehyde-3a. From 68 mg (0.28 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (6:1→3:1) as eluent, gave compound **3a** (76 mg, 59%) as a pale yellow oil; *Rf* = 0.20 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.88 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.76 (d, *J* = 2.3 Hz, 1H), 6.27 (d, *J* = 2.3 Hz, 1H), 1.65 (s, 4H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.2, 153.9, 141.3, 137.7, 133.6 (2C), 132.7, 132.5, 131.4 (2C), 130.3 (2C), 129.1 (2C), 123.0, 58.0, 23.3; IR ($CHCl_3$, cm^{-1}): ν 1725, 1144, 1600, 747. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{14}Br_2NaO_3S$ 478.89226; Found 478.89089.



3b

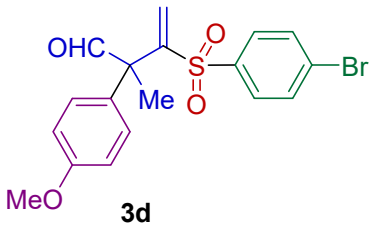
Aldehyde-3b. From 64.6 mg (0.40 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3b** (75 mg, 49%) as a yellow oil; *Rf* = 0.46 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.92 (s, 1H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.25 – 7.14 (m, 5H), 6.67 (d, *J* = 2.3 Hz, 1H), 6.15 (d, *J* = 2.3 Hz, 1H), 1.66 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.1, 154.6, 141.1, 138.4, 133.2 (2C), 132.0, 130.2 (2C), 129.6 (2C), 128.9 (2C), 128.8, 128.7, 58.4, 22.7; IR ($CHCl_3$, cm^{-1}): ν 1727, 1142, 1597, 754. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}BrNaO_3S$ 400.98175; Found 400.97999.



3c

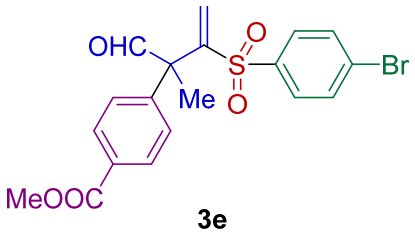
Aldehyde-3c. From 68 mg (0.39 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent, gave compound **3c** (90.6 mg, 59%) as a pale yellow oil; *Rf* = 0.38 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN,

25 ºC) δ 9.89 (s, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.00 (m, 4H), 6.69 (d, *J* = 2.2 Hz, 1H), 6.17 (d, *J* = 2.1 Hz, 1H), 2.28 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.2, 154.4, 141.0, 138.8, 134.8, 133.6, 133.0 (2C), 131.6, 130.0 (2C), 129.9 (2C), 128.8 (2C), 57.8, 22.6, 20.9; IR ($CHCl_3$, cm^{-1}): ν 1729, 1144, 1647, 747. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{17}BrNaO_3S$ 414.99740; Found 414.99560.



3d

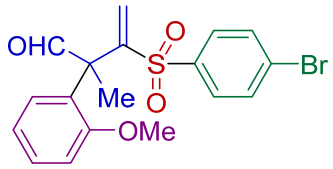
Aldehyde-3d. From 95 mg (0.5 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **3d** (147 mg, 72%) as a yellow oil; *Rf* = 0.34 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.85 (s, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 6.69 (m, 3H), 6.18 (d, *J* = 2.1 Hz, 1H), 3.75 (s, 3H), 1.65 (s, 4H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.4, 160.6, 155.0, 141.6, 133.5 (2C), 131.9, 130.7 (2C), 130.4 (2C), 129.7, 128.9, 115.2 (2C), 57.9, 56.4, 23.1; IR ($CHCl_3$, cm^{-1}): ν 1726, 1313, 1144, 752. HRMS (ESI-TOF) m/z: $[M + Na + 2]^+$ Calcd for $C_{18}H_{17}BrNaO_4S$ 432.99039; Found 432.99069.



3e

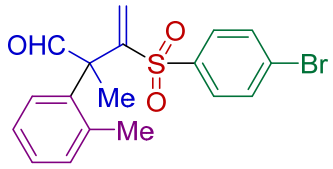
Aldehyde-3e. From 110 mg (0.5 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **3e** (134 mg, 61%) as a pale yellow oil; *Rf* = 0.25 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.93 (s, 1H), 7.74 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 6.76 (d, *J* = 2.4 Hz, 1H), 6.27 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.2, 167.5, 154.0, 143.7, 141.3, 133.7 (2C), 132.8, 130.9, 130.6

(2C), 130.5 (2C), 129.6 (2C), 129.3, 58.6, 53.2, 23.4; IR ($CHCl_3$, cm^{-1}): ν 1738, 1725, 1601, 1144. HRMS (ESI-TOF) m/z: $[M + Na + 2]^+$ Calcd for $C_{19}H_{17}BrNaO_5S$ 460.98533; Found 460.98552.



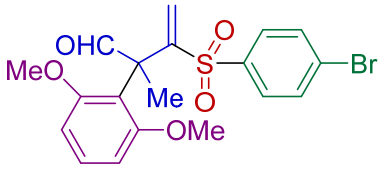
3f

Aldehyde-3f. From 50 mg (0.26 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent, gave compound **3g** (65.7 mg, 61%) as a yellow oil; *Rf* = 0.30 (hexanes/ethyl acetate 4:1); ^1H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.84 (s, 1H), 7.55 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.24 (m, 2H), 6.95 (td, *J* = 7.6, 1.1 Hz, 1H), 6.67 (d, *J* = 1.8 Hz, 1H), 6.58 (dd, *J* = 8.5, 0.6 Hz, 1H), 6.29 (d, *J* = 1.8 Hz, 1H), 3.42 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 200.5, 157.9, 153.5, 141.2, 133.4 (2C), 131.3, 131.1, 130.4 (2C), 130.3, 128.8, 128.1, 122.2, 112.5, 56.4, 55.9, 23.2; IR ($CHCl_3$, cm^{-1}): ν 1726, 1600, 1141, 755. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{17}BrNaO_4S$ 430.99231; Found 430.99115.



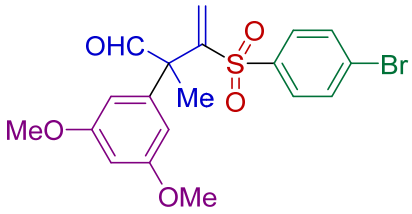
3g

Aldehyde-3g. From 65 mg (0.37 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent, gave compound **3g** (93 mg, 64%) as a yellow oil; *Rf* = 0.49 (hexanes/ethyl acetate 4:1); ^1H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.79 (s, 1H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.33 – 7.16 (m, 5H), 6.86 (m, 1H), 6.72 (d, *J* = 1.9 Hz, 1H), 6.37 (d, *J* = 1.9 Hz, 1H), 1.83 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.5, 152.9, 140.6, 138.9, 136.9, 133.6, 133.5 (2C), 132.2, 130.6 (2C), 130.0, 129.7, 129.2, 127.6, 58.7, 23.4, 21.9; IR ($CHCl_3$, cm^{-1}): ν 1726, 1600, 1140, 755. HRMS (ESI-TOF) m/z: $[M + Na + 2]^+$ Calcd for $C_{18}H_{17}BrNaO_3S$ 416.99546; Found 416.99394.



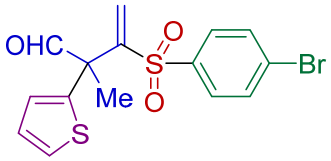
3h

Aldehyde-3h. From 42 mg (2 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (12:1) as eluent, gave compound **3h** (44.4 mg, 53%) as a yellow oil; *Rf* = 0.33 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC) δ 9.85 (s, 1H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.18 (t, *J* = 8.3 Hz, 1H), 6.66 (d, *J* = 1.5 Hz, 1H), 6.42 (d, *J* = 8.3 Hz, 2H), 6.00 (d, *J* = 1.5 Hz, 1H), 3.58 (s, 6H), 1.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.8, 157.7 (2C), 152.1, 140.3, 131.7 (2C), 129.6 (2C), 129.5, 129.1, 127.9, 117.9, 105.5 (2C), 55.9, 55.6 (2C), 19.6; IR ($CHCl_3$, cm^{-1}): ν 1725, 1597, 1140, 830. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{19}BrNaO_5S$ 461.00288; Found 461.00458.



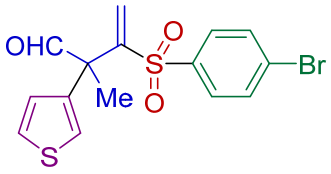
3i

Aldehyde-3i. From 45 mg (0.2 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **3i** (55 mg, 61%) as a yellow oil; *Rf* = 0.18 (hexanes/ethyl acetate 4:1); ^{1}H NMR (500 MHz, CD_3CN, 25 ºC) δ 9.92 (s, 1H), 7.54 (d, *J* = 8.9 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.74 (d, *J* = 2.1 Hz, 1H), 6.31 (t, *J* = 2.2 Hz, 1H), 6.24 (d, *J* = 2.1 Hz, 1H), 6.22 (d, *J* = 2.3 Hz, 2H), 3.67 (s, 6H), 1.63 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 199.1, 161.9 (2C), 154.0, 141.3, 140.1, 133.0 (2C), 131.9, 130.0 (2C), 128.7, 107.4 (2C), 99.8, 58.0, 55.9 (2C), 22.9; IR ($CHCl_3$, cm^{-1}): ν 1725, 1597, 1140, 824. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{19}BrNaO_5S$ 461.00288; Found 461.00382.



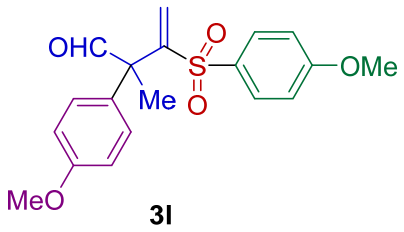
3j

Aldehyde-3j. From 36 mg (0.22 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (3:1) as eluent, gave compound **3j** (51.5 mg, 62%) as a yellow oil; *Rf* = 0.27 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.74 (s, 1H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.29 (dd, *J* = 5.1, 1.3 Hz, 1H), 6.80 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.75 (dd, *J* = 3.7, 1.3 Hz, 1H), 6.69 (d, *J* = 2.3 Hz, 1H), 6.25 (d, *J* = 2.3 Hz, 1H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 197.1, 154.5, 141.4, 141.4, 133.6 (2C), 132.3, 130.4 (2C), 129.3, 129.0, 128.1, 127.8, 56.6, 25.0; IR ($CHCl_3$, cm^{-1}): ν 3096, 1713, 1573, 1145, 826. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{13}BrNaO_3S_2$ 406.93817; Found 406.93702.



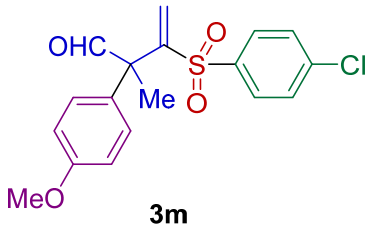
3k

Aldehyde-3k.From 41 mg (0.25 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (4:1) as eluent, gave compound **3k** (57 mg, 60%) as a yellow oil; *Rf* = 0.35 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.83 (s, 1H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 2H), 7.28 (dd, *J* = 2.9, 1.5 Hz, 1H), 7.18 (dd, *J* = 5.1, 2.9 Hz, 1H), 6.73 (dd, *J* = 5.1, 1.4 Hz, 1H), 6.65 (d, *J* = 2.1 Hz, 1H), 6.14 (d, *J* = 2.1 Hz, 1H), 1.63 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 198.2, 154.1, 141.0, 138.8, 133.2 (2C), 131.7, 130.0 (2C), 128.8, 128.0, 127.2, 124.7, 56.1, 22.9; IR ($CHCl_3$, cm^{-1}): ν 3095, 1715, 1573, 1140, 824. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{15}H_{14}BrO_3S_2$ 384.95623; Found 384.95743.



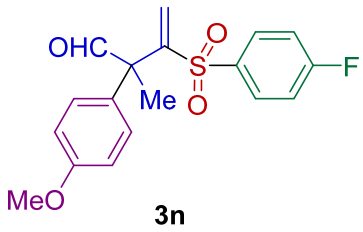
3l

Aldehyde-3l. From 43 mg (0.23 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (6:1→4:1→2:1) as eluent, gave compound **3l** (41.5 mg, 51%) as a yellow oil; *Rf* = 0.29 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.86 (s, 1H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.07 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 9.0 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 6.54 (d, *J* = 1.9 Hz, 1H), 5.99 (d, *J* = 1.9 Hz, 1H), 3.84 (s, 3H), 3.75 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.4, 164.8, 160.4, 156.4, 133.7, 131.2 (2C), 130.5, 130.5 (2C), 115.7 (2C), 115.3 (2C), 110.4, 58.2, 57.0, 56.3, 22.9; IR ($CHCl_3$, cm^{-1}): ν 1727, 1596, 1140, 833. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}NaO_5S$ 383.09237; Found 383.09176.



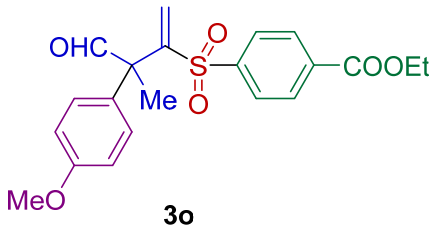
3m

Aldehyde-3m. From 49.5 mg (0.26 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (7:1) as eluent, gave compound **3m** (41 mg, 43%) as a yellow oil; *Rf* = 0.52 (hexanes/ethyl acetate 3:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.85 (s, 1H), 7.38 (m, 4H), 7.03 (d, *J* = 9.0 Hz, 2H), 6.68 (m, 3H), 6.17 (d, *J* = 2.1 Hz, 1H), 3.74 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.4, 160.5, 155.0, 141.1, 140.3, 131.9, 130.7 (2C), 130.5 (2C), 130.3 (2C), 129.7, 115.2 (2C), 57.9, 56.3, 23.0; IR ($CHCl_3$, cm^{-1}): ν 1724, 1142, 1598, 828. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{17}ClNaO_4S$ 387.04283; Found 387.04304.



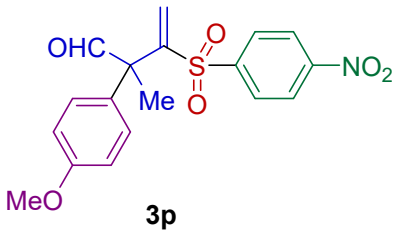
3n

Aldehyde-3n.From 59 mg (0.31 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (6:1→5:1) as eluent, gave compound **3n** (75 mg, 69%) as a yellow oil; *Rf* = 0.25 (hexanes/ethyl acetate 2:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) 9.86 (s, 1H), 7.52 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 9.0 Hz, 1H), 7.13 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 2.1 Hz, 1H), 6.12 (d, *J* = 2.1 Hz, 1H), 3.75 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.4, 166.6 (d, *J* = 253.1 Hz), 160.5, 155.4, 138.7 (d, *J* = 3.0 Hz), 131.8 (d, *J* = 9.9 Hz, 2C), 131.6, 130.6 (2C), 130.0, 117.5 (d, *J* = 22.9 Hz, 2C), 115.3 (2C), 58.0, 56.3, 23.0; ^{19}F NMR (282 MHz, $CDCl_3$, 25 ºC): –99.03 (s, 1F, C–F); IR ($CHCl_3$, cm^{-1}): ν 1726, 1589, 1140, 832. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{17}FNaO_4S$ 371.07238; Found 371.07382.



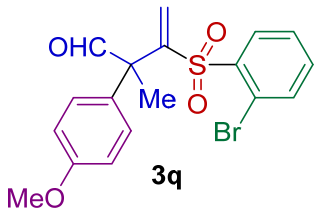
3o

Aldehyde-3o.From 40 mg (0.21 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent, gave compound **3o** (32 mg, 38%) as a yellow oil; *Rf* = 0.26 (hexanes/ethyl acetate 3:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.85 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 9.0 Hz, 2H), 6.74 (d, *J* = 2.2 Hz, 1H), 6.63 (d, *J* = 9.0 Hz, 2H), 6.22 (d, *J* = 2.2 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.69 (s, 3H), 1.65 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.4, 166.3, 160.5, 154.7, 146.1, 135.6, 132.3, 131.0 (2C), 130.7 (2C), 129.5, 128.7 (2C), 115.2 (2C), 62.9, 57.8, 56.2, 23.0, 14.9; IR ($CHCl_3$, cm^{-1}): 1736, 1725, 1601, 1144. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{22}NaO_6S$ 425.10293; Found 425.10137.



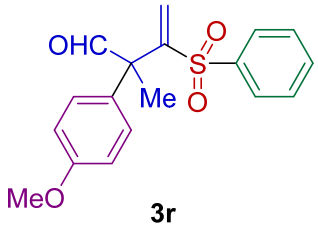
3p

Aldehyde-3p. From 42 mg (0.22 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (8∶1→6∶1) as eluent, gave compound **3p** (35 mg,42%) as a yellow oil; *Rf* = 0.23 (hexanes/ethyl acetate 2:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.85 (s, 1H), 8.11 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 9.0 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 2.3 Hz, 1H), 6.62 (d, *J* = 8.9 Hz, 2H), 6.33 (d, *J* = 2.3 Hz, 1H), 3.69 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.3, 160.6 (2C), 154.1, 147.7, 133.1, 130.9 (2C), 129.8 (2C), 129.2, 125.3 (2C), 115.2 (2C), 57.7, 56.2, 23.1; IR ($CHCl_3$, cm^{-1}): ν 1727, 1604, 1138, 853. HRMS (ESI-TOF) m/z: [*M* + Na]$^+$ Calcd for $C_{18}H_{17}NNaO_6S$ 398.06688; Found 398.06557.



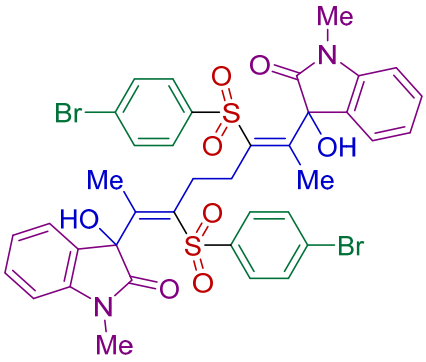
3q

Aldehyde-3q. From 59 mg (0.31 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, gave compound **3q** (75 mg, 59%) as as a yellow oil; *Rf* = 0.46 (hexanes/ethyl acetate 2:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.84 (s, 1H), 7.67 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.54 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.39 (td, *J* = 7.7, 1.8 Hz, 1H), 7.29 (td, *J* = 7.7, 1.3 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 2H), 6.85 (d, *J* = 2.0 Hz, 1H), 6.61 (d, *J* = 9.0 Hz, 2H), 6.36 (d, *J* = 2.0 Hz, 1H), 3.69 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 198.4, 160.1, 152.1, 139.9, 136.3, 135.5, 133.8, 132.6, 130.0 (2C), 129.4, 129.1, 121.1, 114.8 (2C), 57.3, 55.8, 22.9; IR ($CHCl_3$, cm^{-1}): ν 1726, 1602, 1142, 755. HRMS (ESI-TOF) m/z: [*M* + Na]$^+$ Calcd for $C_{18}H_{17}BrNaO_4S$ 430.99231; Found 430.99346.



3r

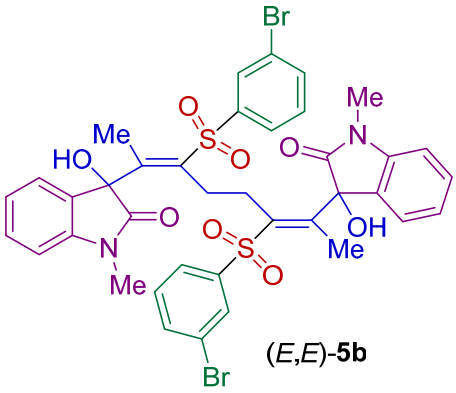
Aldehyde-3r. From 52 mg (0.27 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (8:1) as eluent, gave compound **3r** (47 mg, 52%) as a pale yellow oil; *Rf* = 0.47 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.86 (s, 1H), 7.62–7.41 (m, 5H), 7.07 (d, *J* = 9.0 Hz, 2H), 6.73 (d, *J* = 9.0 Hz, 2H), 6.60 (d, *J* = 2.0 Hz, 1H), 6.07 (d, *J* = 2.0 Hz, 1H), 3.75 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 199.4, 160.5, 155.8, 143.2, 142.4, 134.6, 131.6, 130.6 (2C), 130.5 (2C), 128.8 (2C), 115.3 (2C), 58.2, 56.3, 22.9; IR ($CHCl_3$, cm^{-1}): ν 1726, 1595, 1140, 826. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{18}NaO_4S$ 353.08180; Found 353.08210.



(*Z*,*Z*)-**5a**

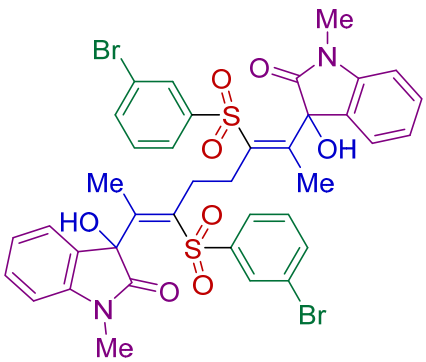
Bis(indolin-2-one)-(*Z*,*Z*)-5a. From 68 mg (0.32 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent, gave compound **(*Z*,*Z*)-5a** (77 mg, 28%) as a yellow oil; *Rf* = 0.08 (hexanes/ethyl acetate 1:1); ^{1}H NMR (700 MHz, CD_3CN, 25 ºC) δ 7.77 (d, *J* = 8.6 Hz, 4H), 7.71 (d, *J* = 8.6 Hz, 4H), 7.40 (td, *J* = 7.8, 1.3 Hz, 2H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 5.49 (s, 2H), 3.93 (m, 2H), 3.49 (m, 2H), 3.13 (s, 6H), 1.50 (s, 6H); ^{13}C NMR (175 MHz, CD_3CN) δ 175.7 (2C), 148.0 (2C), 145.6 (2C), 143.8 (2C), 143.0 (2C), 133.8 (4C), 132.1 (2C), 130.4 (2C), 129.8 (4C), 128.9 (2C), 125.4 (2C), 124.7 (2C), 110.8 (2C), 82.8 (2C), 31.5 (2C), 27.2 (2C), 18.9 (2C); IR ($CHCl_3$, cm^{-1}): ν 1719,

1611, 1142, 753. HRMS (ESI-TOF) m/z: $[M + Na + 2]^+$ Calcd for $C_{38}H_{34}Br_2N_2NaO_8S_2$ 892.99983; Found 893.00072.



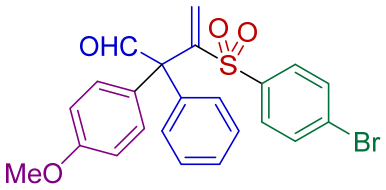
(*E*,*E*)-**5b**

Bis(indolin-2-one)-(*E*,*E*)-5b. From 68 mg (0.32 mmol) of the corresponding α-Allenic Alcohol, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent, gave compound **(*E*,*E*)-5b** (82.6 mg, 30%) as a pale yellow solid; mp 174–176 ºC; *Rf* = 0.15 (hexanes/ethyl acetate 1:1); ^{1}H NMR (700 MHz, CD_3CN, 25 ºC) δ 7.99 (t, *J* = 1.7 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 2H), 7.79 (m, 2H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.39 (td, *J* = 7.7, 1.2 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 2H), 7.09 (td, *J* = 7.7, 0.7 Hz, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 5.29 (s, 2H), 3.77 (d, *J* = 9.0 Hz, 2H), 3.44 (m, 2H), 3.15 (s, 6H), 1.52 (s, 6H); ^{13}C NMR (175 MHz, CD_3CN) δ 175.8 (2C), 148.9 (2C), 145.7 (2C), 145.5 (2C), 143.7 (2C), 137.6 (2C), 132.6 (2C), 132.0 (2C), 130.7 (2C), 130.3 (2C), 126.7 (2C), 125.4 (2C), 124.7 (2C), 123.9 (2C), 110.8 (2C), 82.7 (2C), 31.5 (2C), 27.3 (2C), 19.3 (2C); IR ($CHCl_3$, cm^{-1}): ν 1718, 1612, 1140, 753. HRMS (ESI-TOF) m/z: $[M + Na + 2]^+$ Calcd for $C_{38}H_{34}Br_2N_2NaO_8S_2$ 892.99983; Found 893.00109.



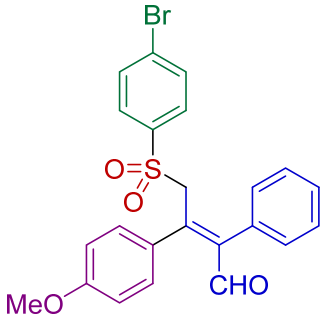
(*Z*,*Z*)-**5b**

Bis(indolin-2-one)-(*Z*,*Z*)-5b.From 68 mg (0.32 mmol) of the corresponding α-Allenic Alcohol, and after chromatography of the residue using hexanes/ethyl acetate (2:1) as eluent, gave compound **(*Z*,*Z*)-5b** (69 mg, 25%) as a yellow oil; *Rf* = 0.09 (hexanes/ethyl acetate 1:1); ^{1}H NMR (700 MHz, CD_3CN, 25 ºC) δ 8.00 (t, *J* = 1.8 Hz, 2H), 7.85 (m, 2H), 7.78 (ddd, *J* = 8.0, 1.8, 0.8 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 2H), 7.39 (td, *J* = 7.7, 1.2 Hz, 2H), 7.29 (dd, *J* = 7.3, 1.1 Hz, 2H), 7.10 (m, 2H), 6.96 (d, *J* = 7.8 Hz, 2H), 5.52 (s, 2H), 3.97 (br.s, 2H), 3.50 (m, 2H), 3.13 (s, 6H), 1.50 (s, 6H); ^{13}C NMR (175 MHz, CD_3CN) δ 175.7 (2C), 148.3 (2C), 145.7 (2C), 145.6(2C), 143.6 (2C), 137.6 (2C), 132.6 (2C), 132.1 (2C), 130.4 (2C), 130.3 (2C), 126.7 (2C), 125.5 (2C), 124.8 (2C), 123.9 (2C), 110.8 (2C), 82.9 (2C), 31.5 (2C), 27.2 (2C), 18.9 (2C); IR ($CHCl_3$, cm^{-1}): ν 1721, 1611, 1141, 755. HRMS (ESI-TOF) m/z: $[M + Na + 2]^+$ Calcd for $C_{38}H_{34}Br_2N_2NaO_8S_2$ 892.99983; Found 892.99776.



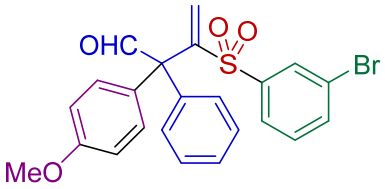
6a (major product)

Aldehyde-6a (major product). From 51.6 mg (0.2 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, gave compound **6a** (27 mg, 28%) as a yellow oil; *Rf* = 0.45 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 10.14 (s, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.35 (m, 3H), 7.20 (m, 2H), 7.02 (d, *J* = 9.1 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.75 (d, *J* = 2.3 Hz, 1H), 6.00 (d, *J* = 2.3 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 197.3, 160.8, 156.2, 142.2, 138.3, 135.2, 133.5 (2C), 132.8 (2C), 131.3 (2C), 130.6 (2C), 129.9 (2C), 129.5, 129.2, 129.1, 115.2 (2C), 68.6, 56.4; IR ($CHCl_3$, cm^{-1}): ν 1721, 1606, 1105, 763. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{19}BrNaO_4S$ 493.00796; Found 493.00806.



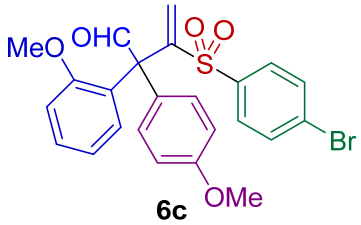
7a (minor product)

Aldehyde-7a (minor product). From 51.6 mg (0.2 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (5:1) as eluent, gave compound **7a** (9.6 mg, 10%) as a yellow oil; *Rf* = 0.36 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.78 (s, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.22 (m, 1H), 7.12 (m, 2H), 7.03 (d, *J* = 8.9 Hz, 2H), 6.86 (m, 4H), 3.77 (s, 2H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 200.4, 161.6, 157.2, 141.4, 140.1, 136.7, 133.8, 133.1 (2C), 130.7 (2C), 130.6 (4C), 129.6, 129.0 (2C), 128.6, 115.3 (2C), 56.4, 46.1; IR ($CHCl_3$, cm^{-1}): ν 1611, 1509, 1169, 835. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}BrO_4S$ 471.02602; Found 471.02602.



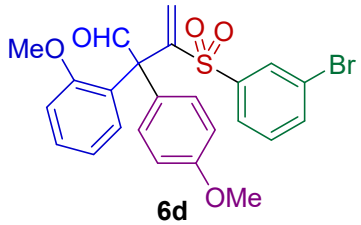
6b

Aldehyde-6b. From 83 mg (0.33 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (6:1) as eluent, gave compound **6b** (63 mg, 41%) as a yellow oil; *Rf* = 0.31 (hexanes/ethyl acetate 3:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 10.12 (s, 1H), 7.70 (m, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 1.8 Hz, 1H), 7.35 (m, 4H), 7.20 (m, 2H), 7.05 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.80 (d, *J* = 2.2 Hz, 1H), 6.08 (d, *J* = 2.2 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) 197.0, 160.8, 155.9, 145.0, 138.0, 137.5, 135.4, 132.9 (2C), 132.2, 131.4 (2C), 131.4, 129.9 (2C), 129.6, 128.8, 127.6, 123.6, 115.2 (2C), 68.5, 56.4; IR ($CHCl_3$, cm^{-1}): ν 1728, 1607, 1145, 833. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{20}BrO_4S$ 471.02602; Found 471.02597.



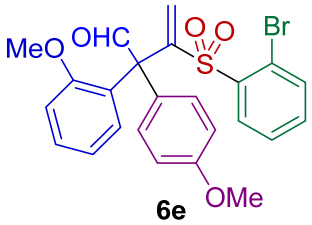
6c

Aldehyde-6c. From 39 mg (0.14 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent, gave compound **6c** (36 mg, 52%) a yellow oil; *Rf* = 0.27 (hexanes/ethyl acetate 4:1, eluted two times); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.91 (s, 1H), 7.53 (d, *J* = 8.7 Hz, 2H), 7.29 (m, 1H), 7.28 (d, *J* = 8.8 Hz, 2H), 7.10 (d, *J* = 9.0 Hz, 2H), 7.01 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.94 (m, 1H), 6.90 (d, *J* = 1.7 Hz, 1H), 6.87 (d, *J* = 9.1 Hz, 2H), 6.73 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.35 (d, *J* = 1.7 Hz, 1H), 3.79 (s, 3H), 3.46 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 197.1, 160.7, 158.2, 141.8, 134.8, 133.3 (2C), 133.2, 132.3 (2C), 131.6, 130.1 (2C), 128.7, 128.6, 121.9, 115.0 (2C), 112.9, 56.4, 56.2; IR ($CHCl_3$, cm^{-1}): ν 1728, 1602, 1139, 756. HRMS (ESI-TOF) m/z: [*M* + H]$^+$ Calcd for $C_{24}H_{22}BrO_5S$ 501.03658; Found 501.03802.



6d

Aldehyde-6d. From 50 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 **6d** (41 mg, 46%) as a yellow oil; *Rf* = 0.23 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.84 (s, 1H), 7.65 (ddd, *J* = 8.0, 2.0, 1.1 Hz, 1H), 7.42 (ddd, *J* = 8.0, 1.8, 1.1 Hz, 1H), 7.28 (m, 3H), 7.14 (d, *J* = 9.2 Hz, 2H), 7.05 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.00 (d, *J* = 1.7 Hz, 1H), 6.95 (m, 1H), 6.88 (d, *J* = 9.2 Hz, 2H), 6.66 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.55 (d, *J* = 1.7 Hz, 1H), 3.80 (s, 3H), 3.45 (s, 3H); ^{13}C NMR (75 MHz, CD_3CN) δ 196.8, 160.7, 158.3, 151.5, 144.4, 137.1, 135.2, 133.4, 132.4 (2C), 132.0, 131.9, 130.7, 128.5, 127.9, 127.0, 123.4, 121.7, 115.1 (2C), 112.7, 66.0, 56.4, 56.1; IR ($CHCl_3$, cm^{-1}): ν 1727, 1603, 1138, 755. HRMS (ESI-TOF) m/z: [*M* + H]$^+$ Calcd for $C_{24}H_{22}BrO_5S$ 501.03658; Found 501.03663.



6e

Aldehyde-6e. From 46 mg (0.16 mmol) of the corresponding α-allenic alcohol, and after chromatography of the residue using hexanes/ethyl acetate (9:1) as eluent, gave compound **6e** (37 mg, 45%) as a yellow oil; *Rf* = 0.43 (hexanes/ethyl acetate 4:1); ^{1}H NMR (300 MHz, CD_3CN, 25 ºC) δ 9.92 (s, 1H), 7.68 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.36 (m, 1H), 7.32 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.19 (m, 2H), 7.15 (d, *J* = 9.2 Hz, 2H), 6.94 (dd, *J* = 7.8, 1.9 Hz, 1H), 6.89 (m, 1H), 6.84 (d, *J* = 9.2 Hz, 2H), 6.73 (d, *J* = 1.6 Hz, 1H), 6.56 (dd, *J* = 8.2, 0.9 Hz, 1H), 3.78 (s, 3H), 3.47 (s, 3H); ^{13}C NMR (125 MHz, CD_3CN) δ 197.3, 160.6, 158.2, 149.3, 140.4, 138.1, 136.5, 135.50, 133.5, 132.7, 132.4 (2C), 131.5, 129.7, 129.5, 129.3, 121.7, 121.3, 114.9 (2C), 112.3, 64.9, 56.4, 55.9; IR ($CHCl_3$, cm^{-1}): ν 1728, 1604, 1139, 755. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}BrO_5S$ 501.03658; Found 501.03690.

Radical inhibition experiment with TEMPO.

To a solution of diazonium salt **2a** (68 mg, 0.25 mmol), [DABCO·$(SO_2)_2$] (0.33 mmol) in acetonitrile (1.2 mL) was added $[Ru(bpy)_3](PF6)_2$ (2 mol %). The reaction mixture was stirred at room temperature for ten minutes under irradiation of LED light source (LED light bulb installed in a tool box). After this time, a solution of the allene **1a** (32 mg, 0.166 mmol) and TEMPO (0.33 mmol) in acetonitrile (3.0 mL) was added via syringe. The resulting mixture was stirred at rt for 20 h. Then, the solution was concentrated in vacuo and the crude residue was purified using silica gel column flash chromatography eluting with hexanes/ethyl acetate (3:1) to give 29 mg (91% recovered) of unreacted allenol **1a**.

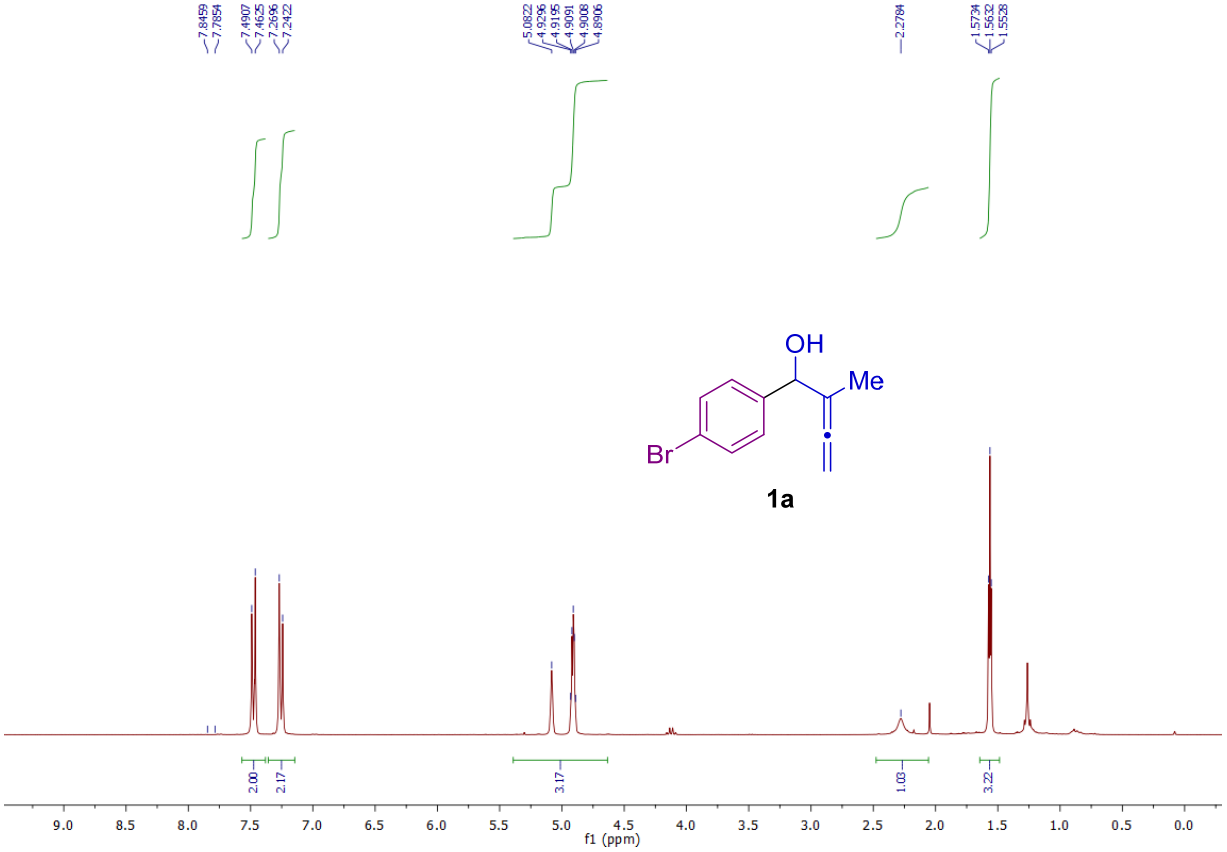
Synthetic procedure for scale-up reaction of 3-(arylsulfonyl)but-3-enal 3a

To a solution of diazonium salt **2a** (660 mg, 2.44 mmol), [DABCO·$(SO_2)_2$] (3.25 mmol) in acetonitrile (11.3 mL) was added $[Ru(bpy)_3](PF6)_2$ (2 mol %). The reaction mixture was stirred at room temperature for ten minutes under irradiation of LED light source (LED light bulb installed in

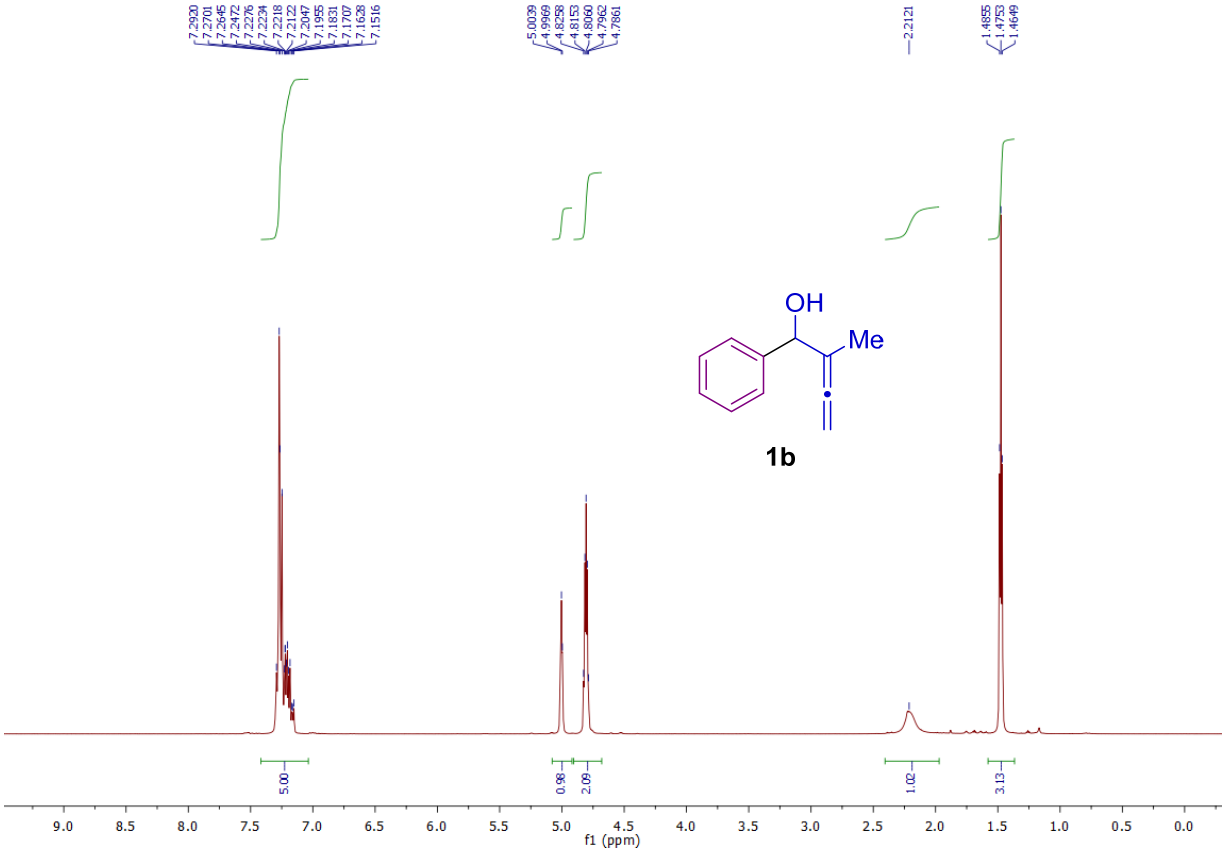
a tool box). After this time, a solution of allenol **1a** (309 mg, 1.62 mmol) in acetonitrile (11.5 mL) was added via syringe and the reaction was stirred at rt for 20 h. The resulting mixture was concentrated in vacuo and the crude residue was purified using silica gel column flash chromatography eluting with hexanes/ethyl acetate (3:1) to get the target product as a pale yellow oil (243 mg, 58% yield; which is comparable to the experiment on a lesser scale in Table 1, entry 2).

7. NMR Spectra

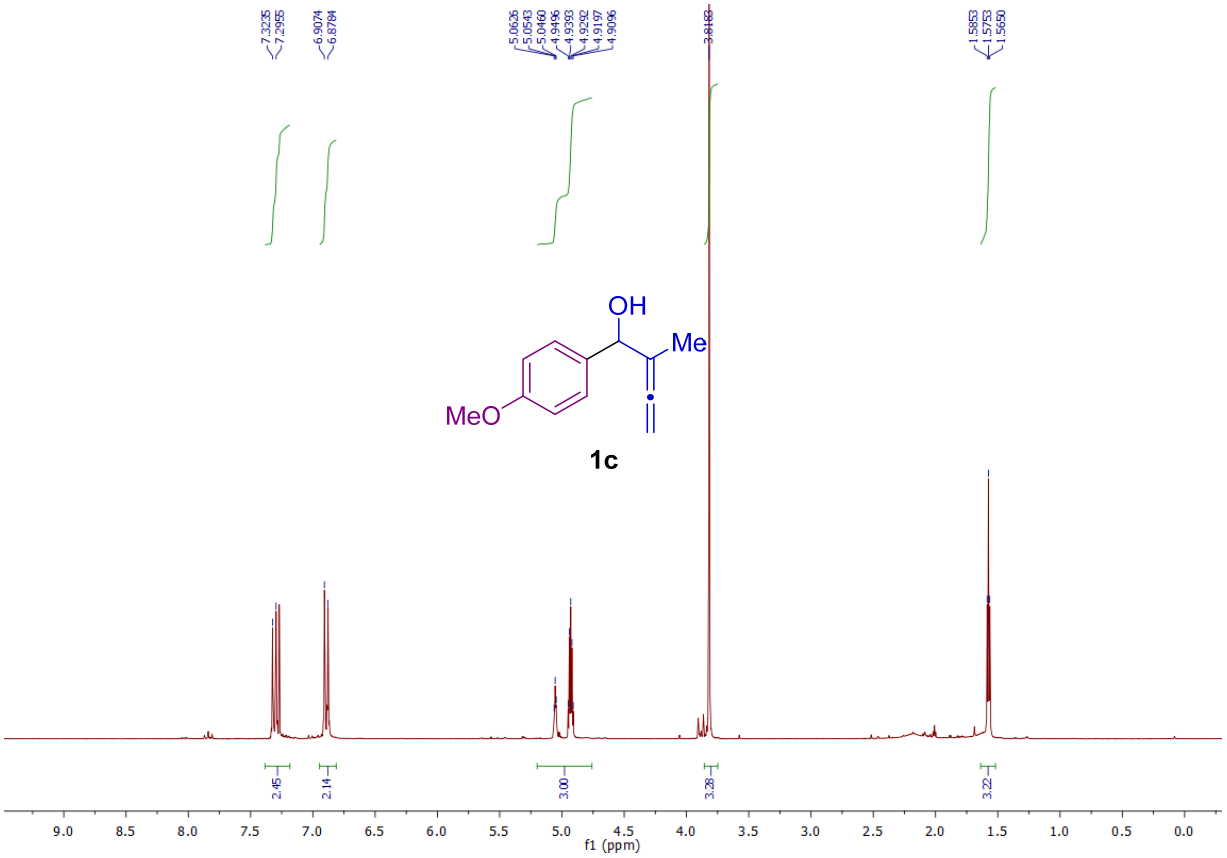
^{1}H NMR spectrum of **1a** in $CDCl_3$ at 300 MHz



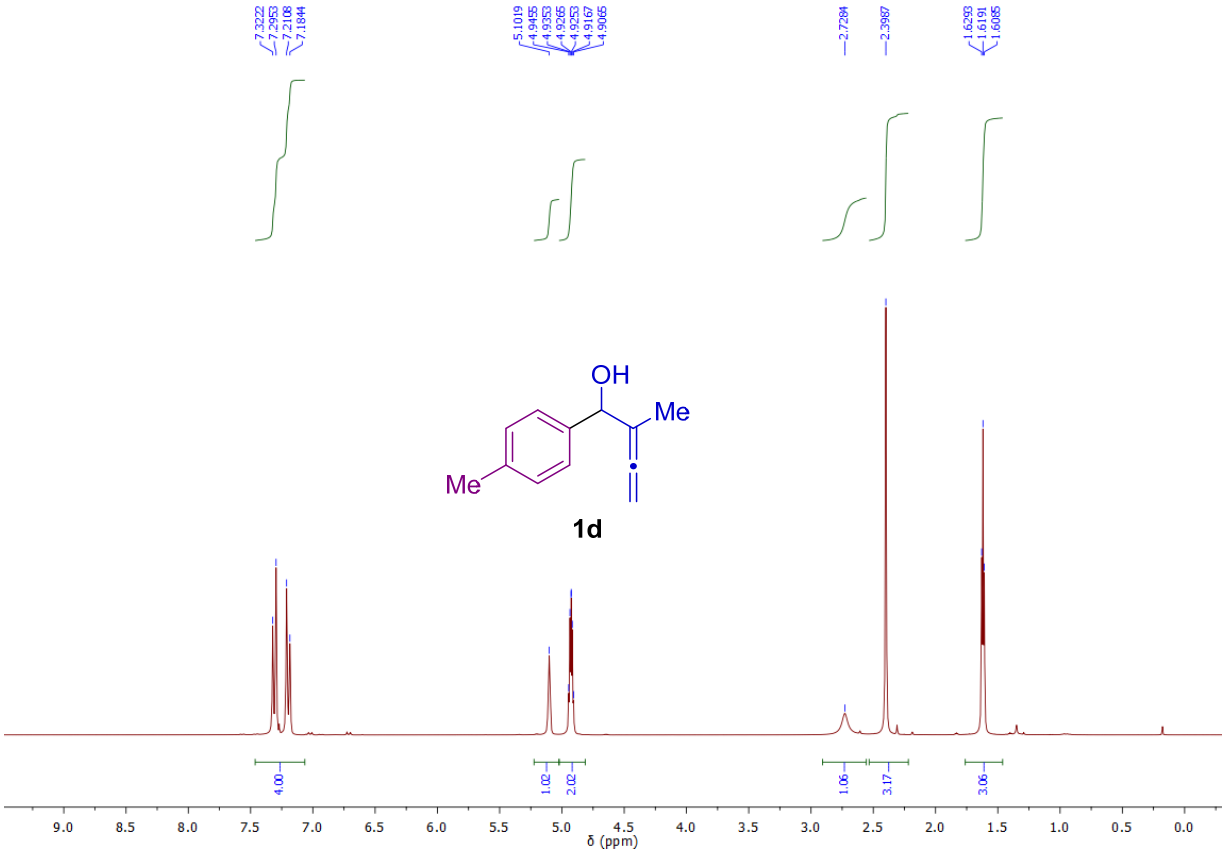
^{1}H NMR spectrum of **1b** in $CDCl_3$ at 300 MHz



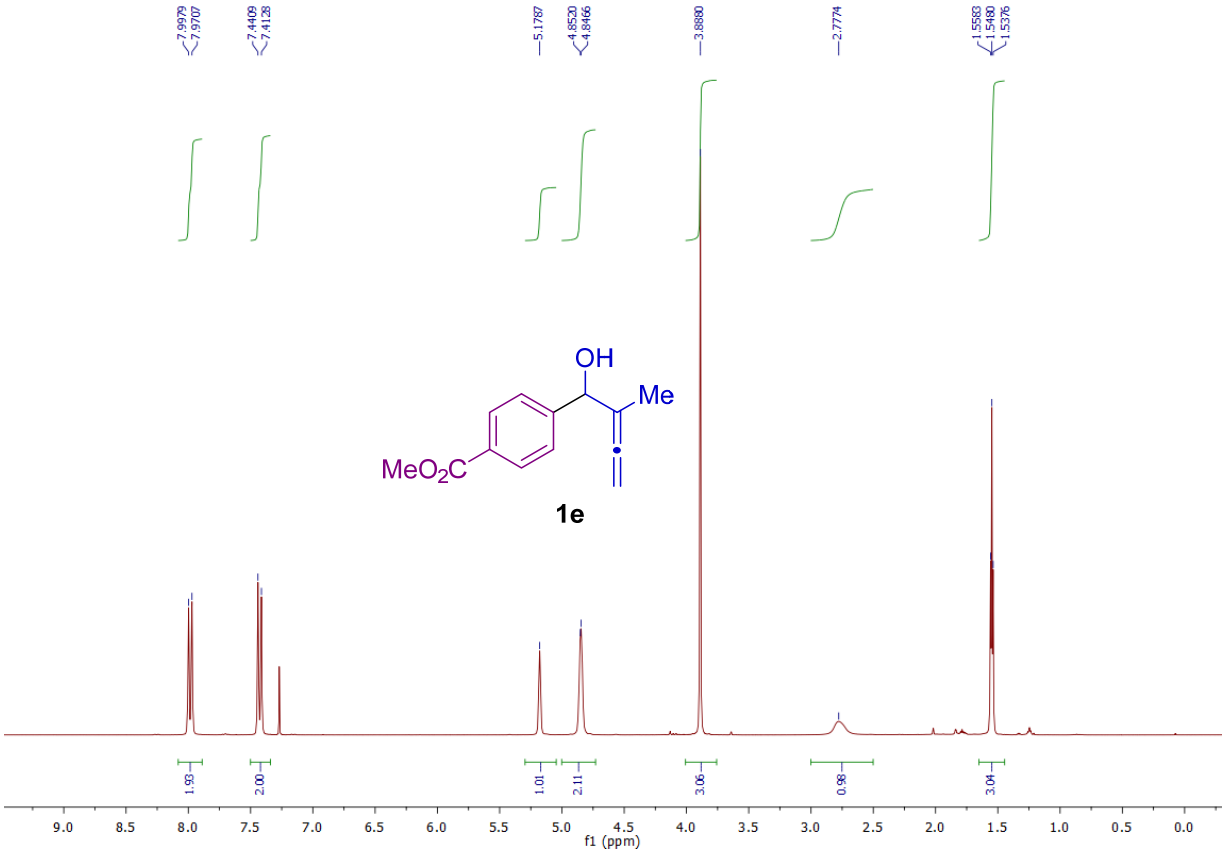
^{1}H NMR spectrum of **1c** in $CDCl_3$ at 300 MHz



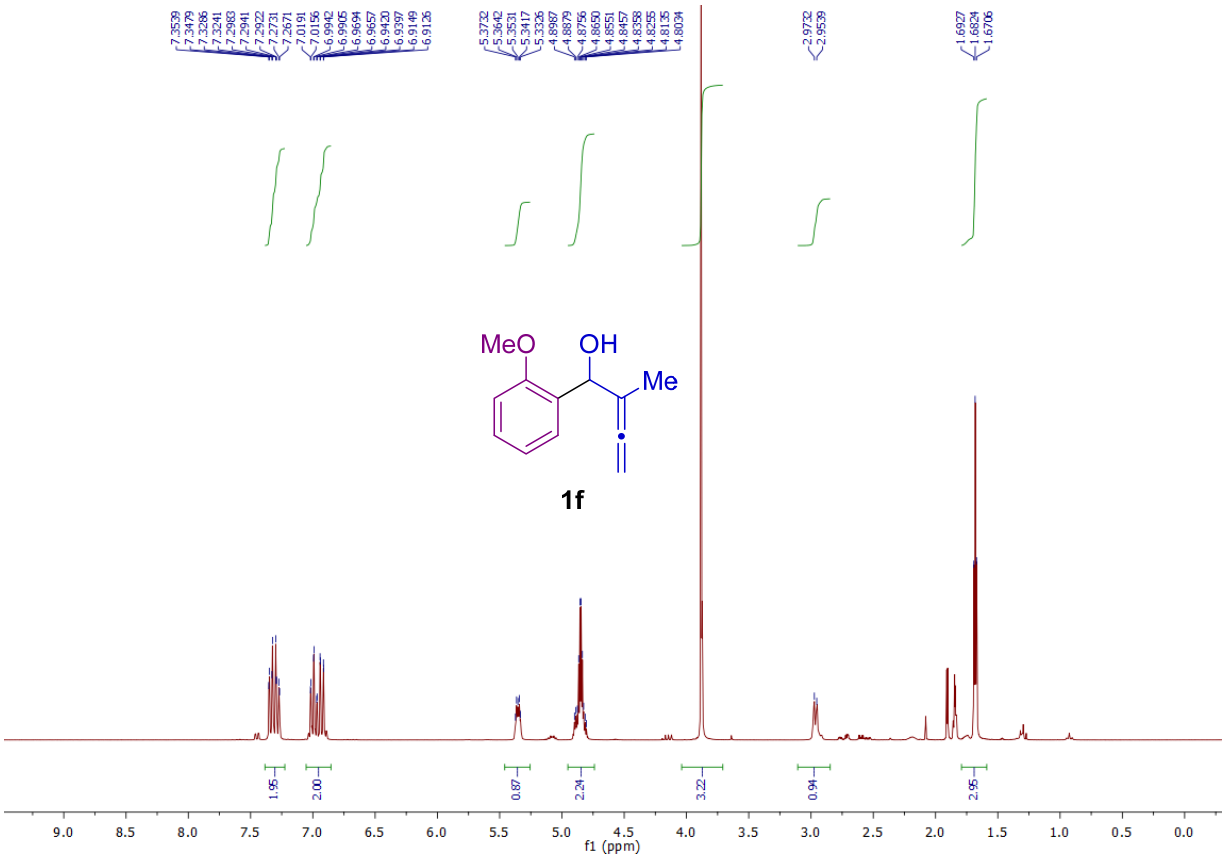
^{1}H NMR spectrum of **1d** in $CDCl_3$ at 300 MHz



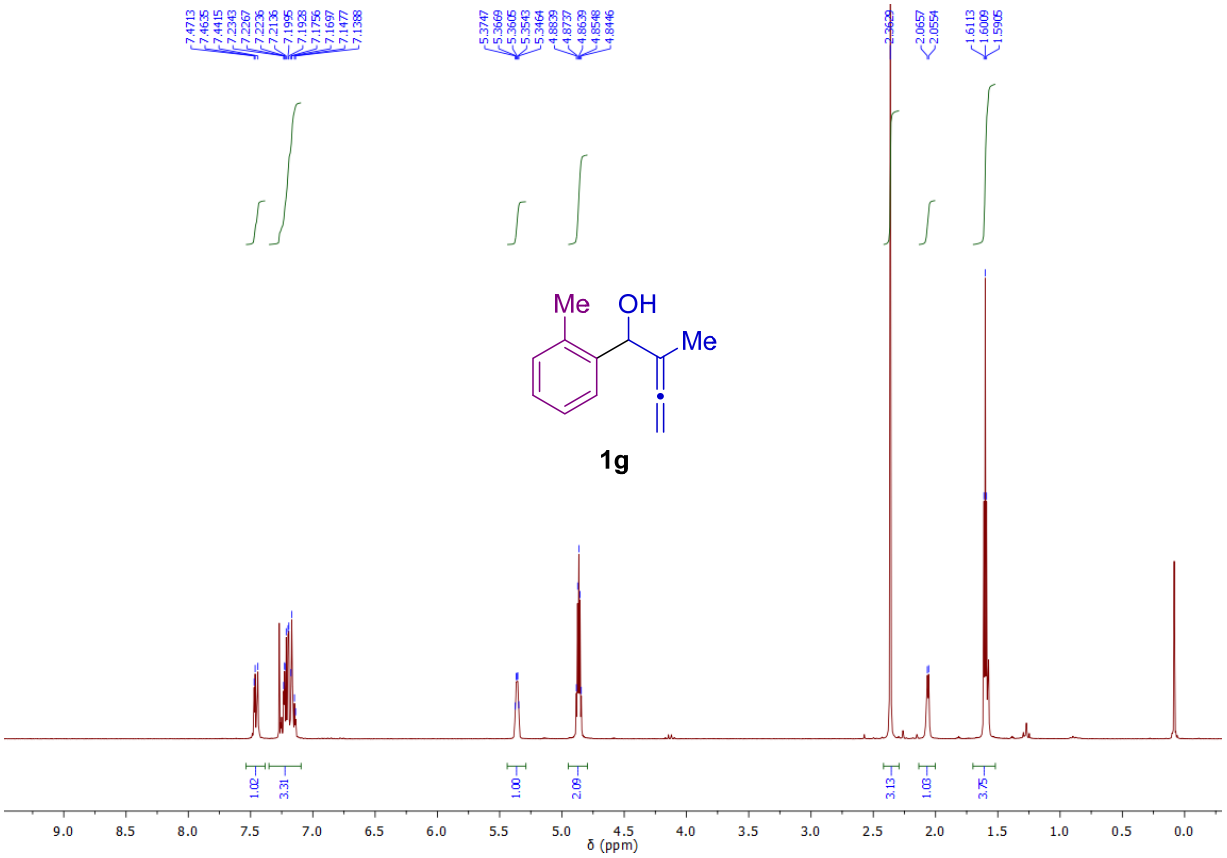
^{1}H NMR spectrum of **1e** in $CDCl_3$ at 300 MHz



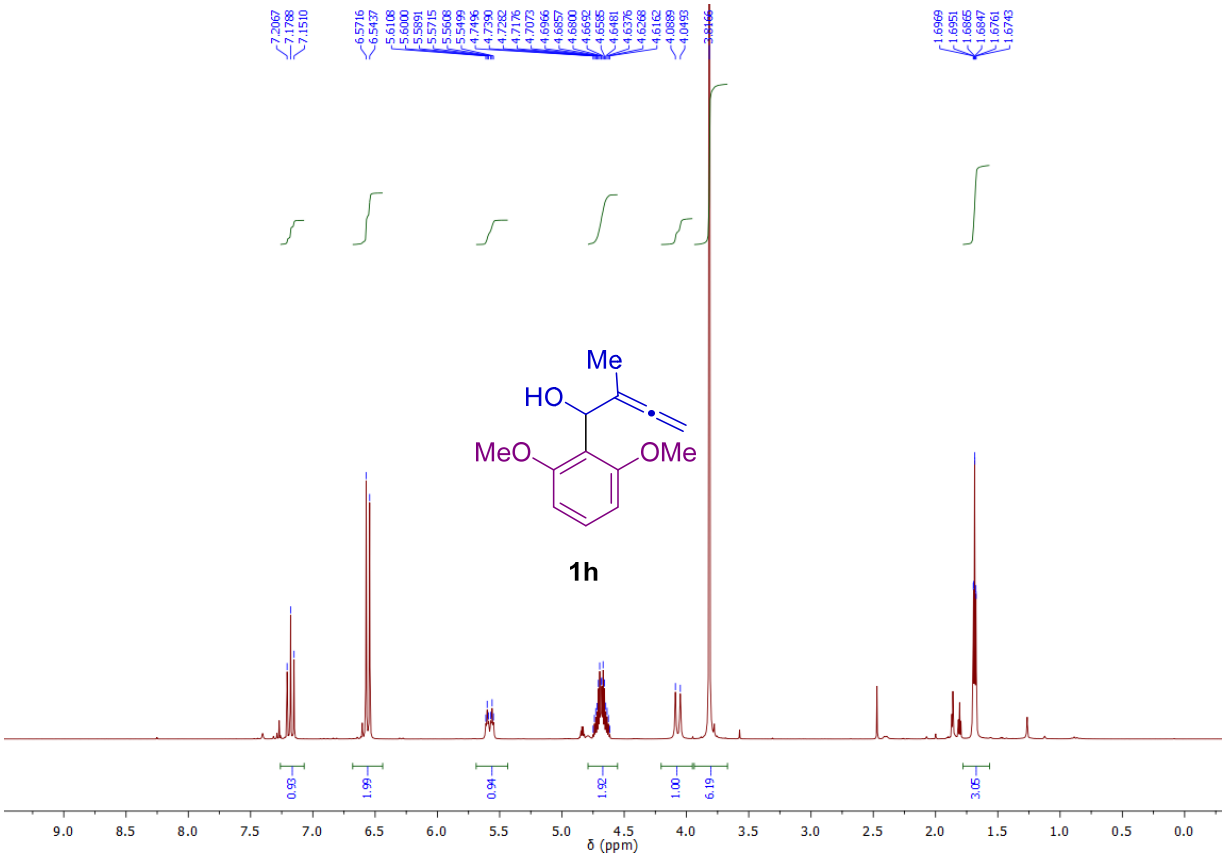
^{1}H NMR spectrum of **1f** in $CDCl_3$ at 300 MHz



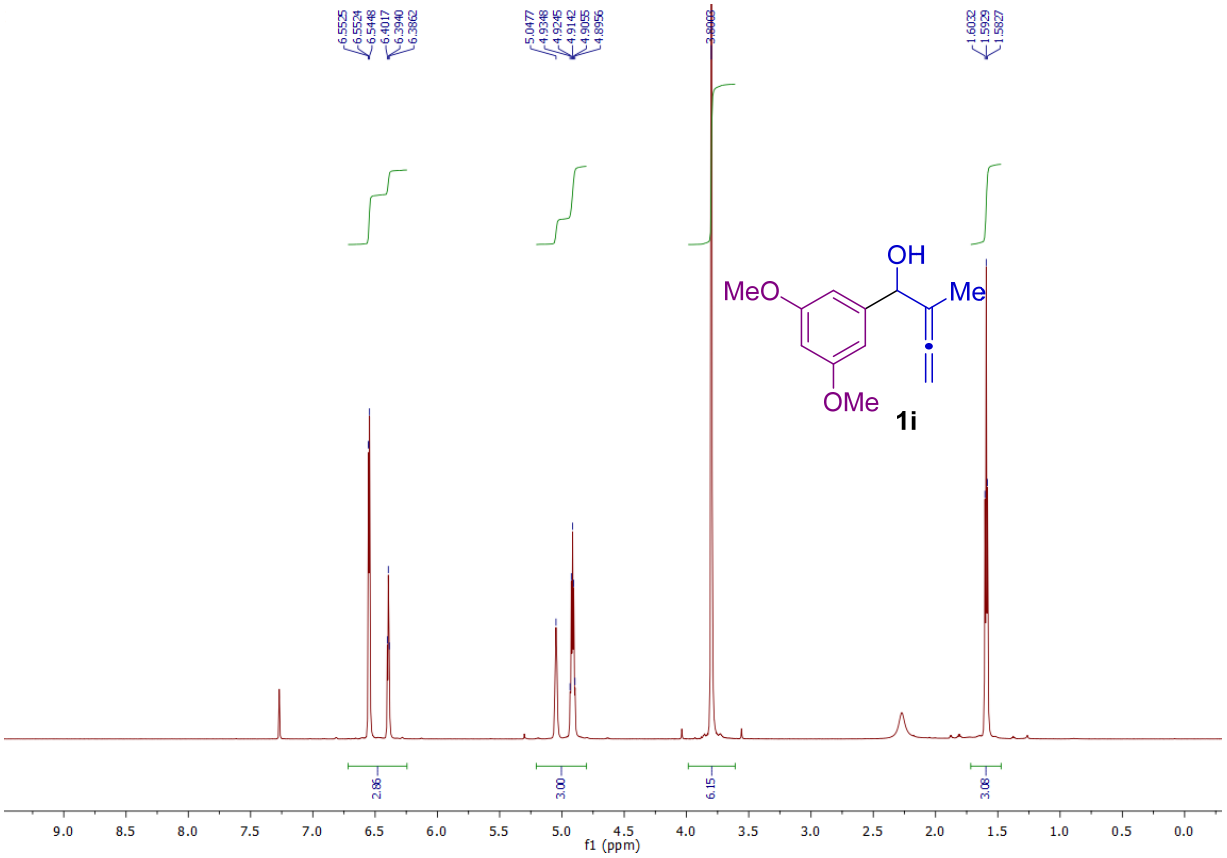
^{1}H NMR spectrum of **1g** in $CDCl_3$ at 300 MHz



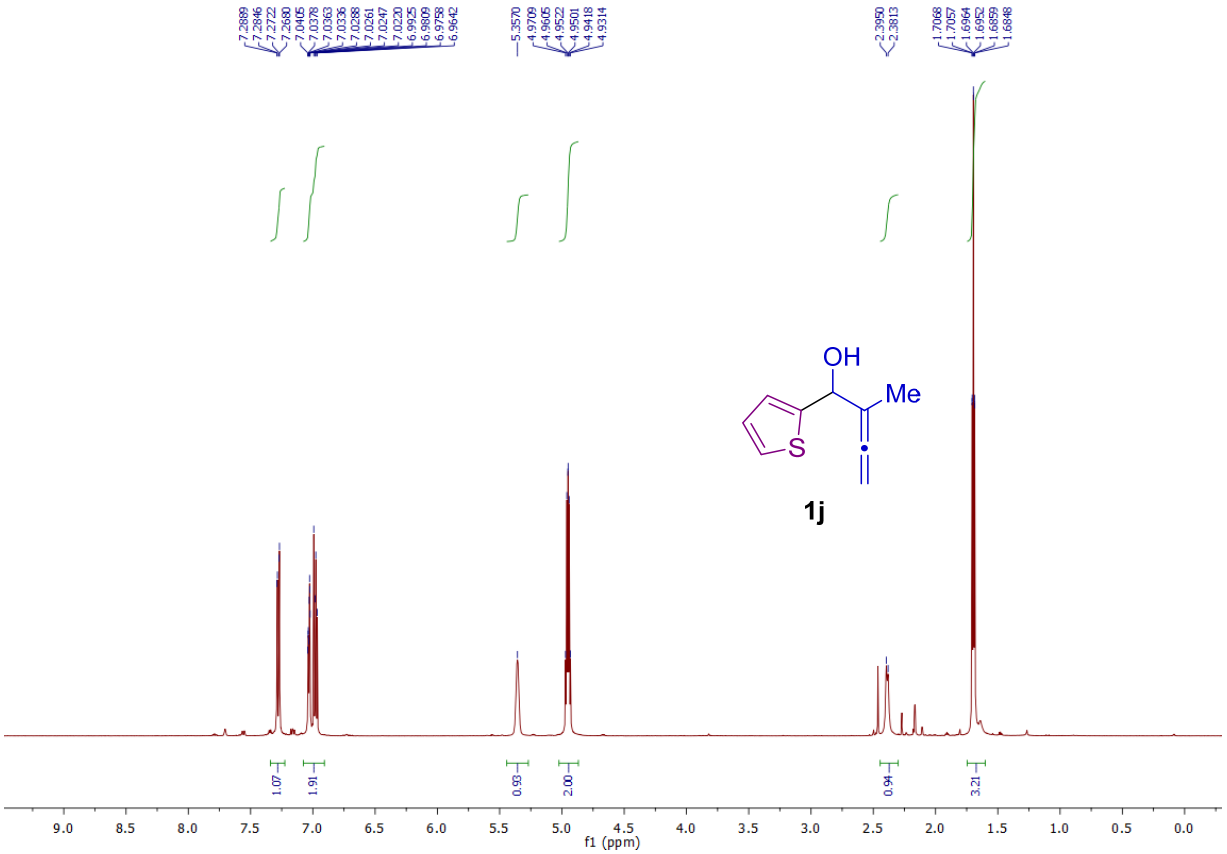
^{1}H NMR spectrum of **1h** in $CDCl_3$ at 300 MHz



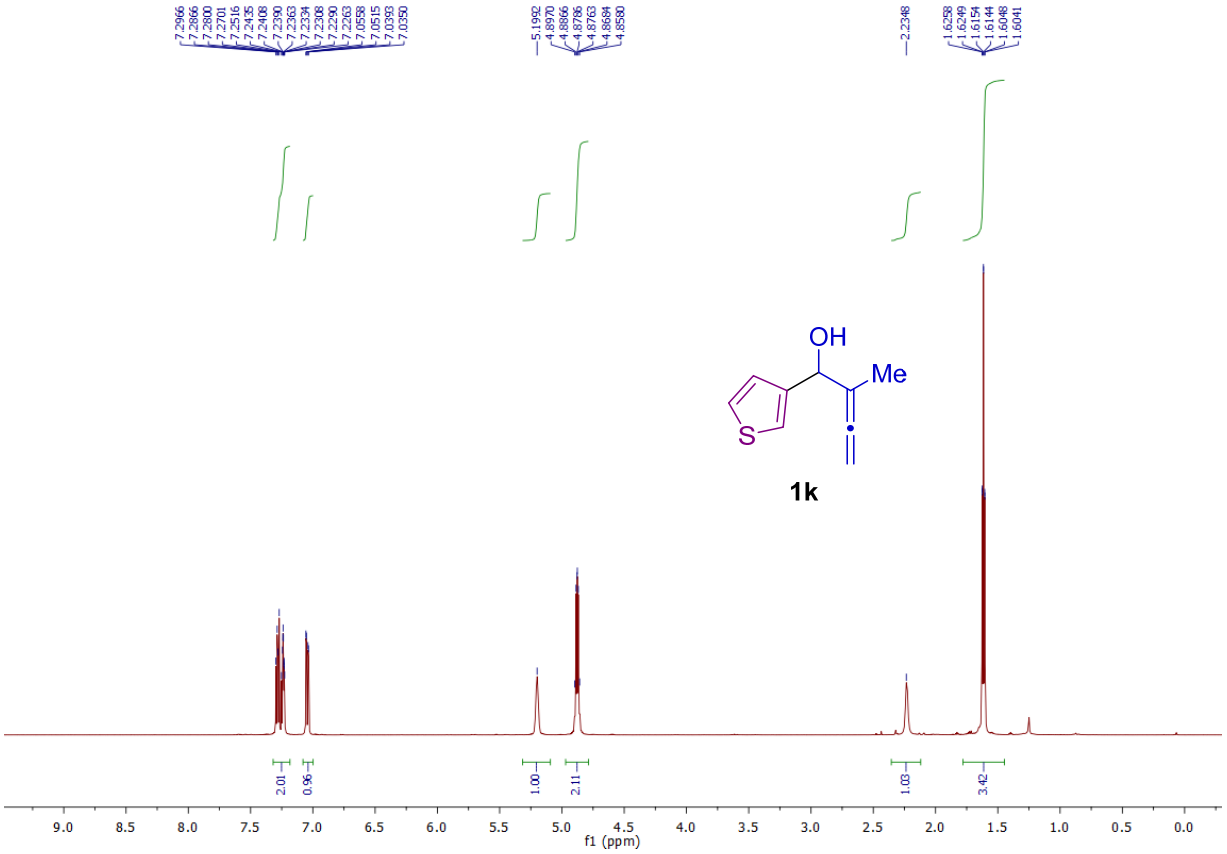
^{1}H NMR spectrum of **1i** in $CDCl_3$ at 300 MHz



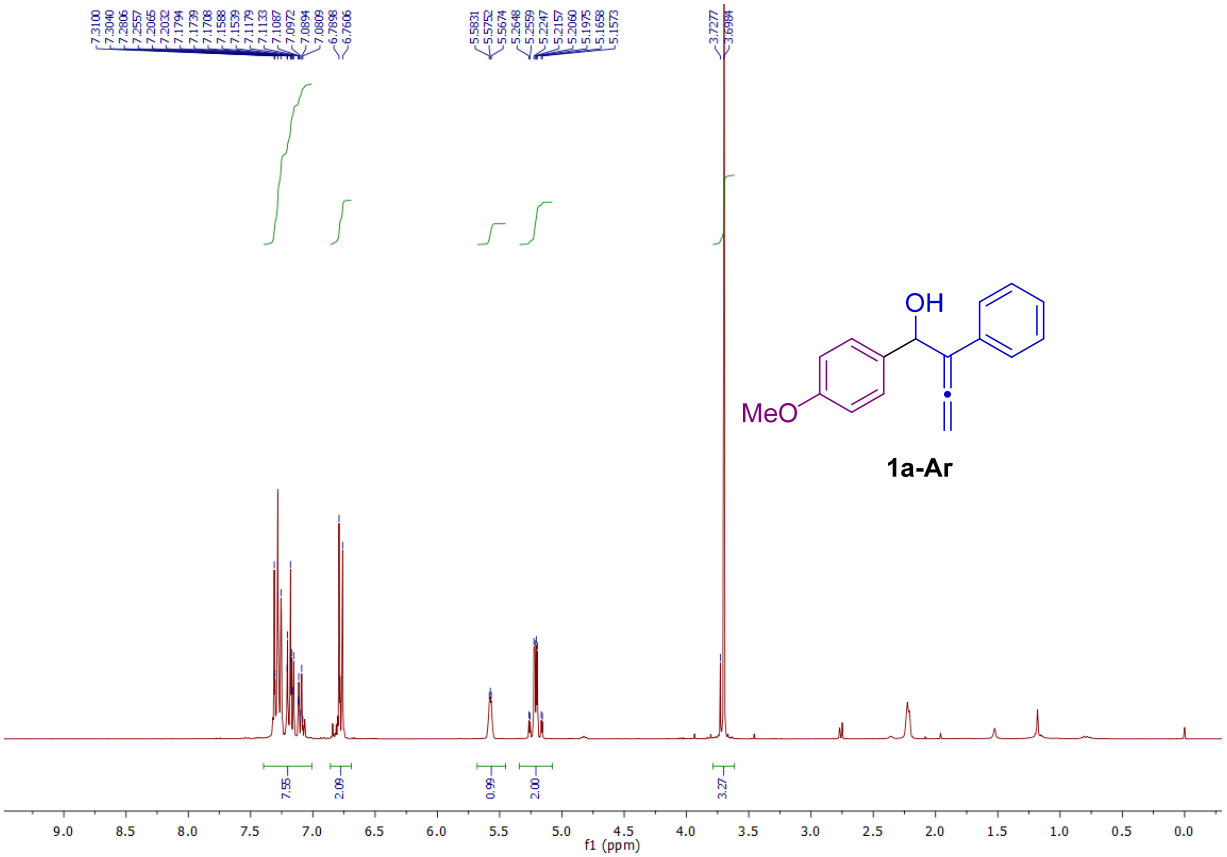
^{1}H NMR spectrum of **1j** in $CDCl_3$ at 300 MHz



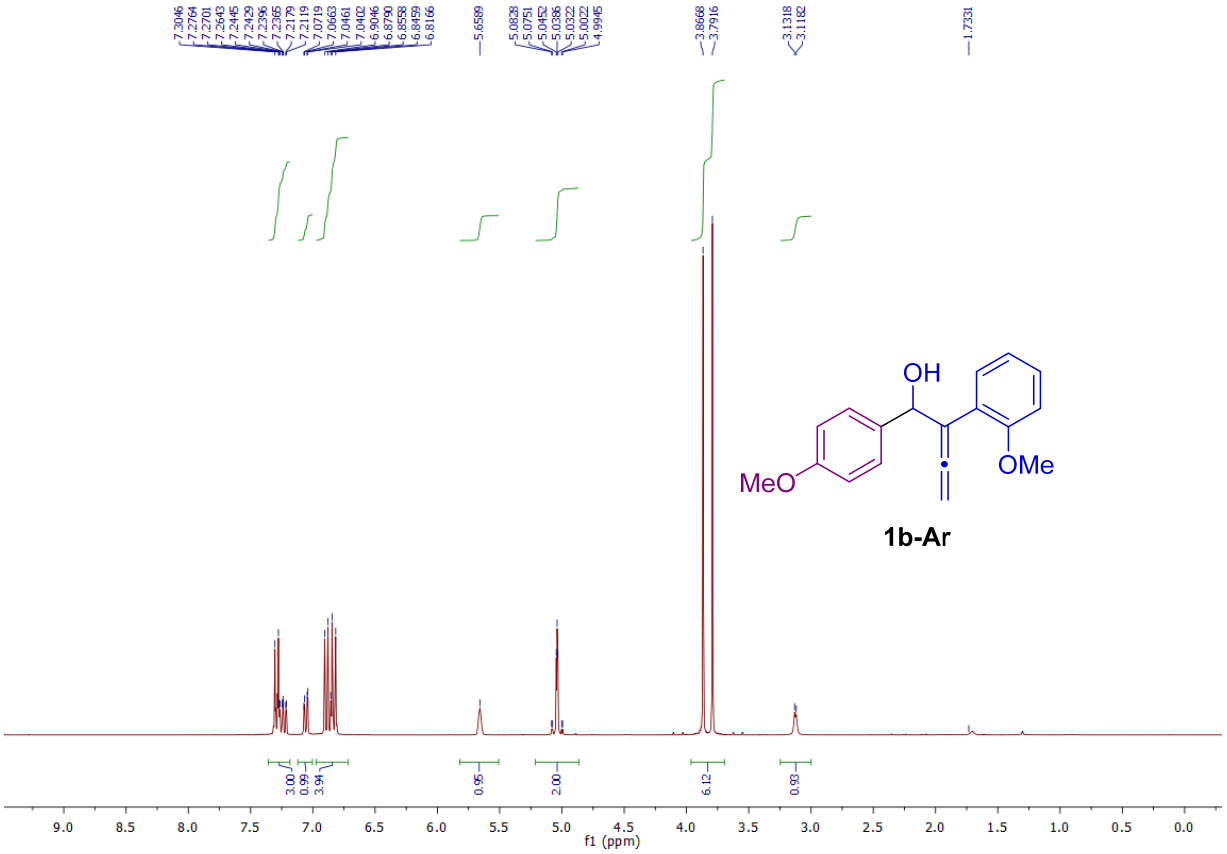
^{1}H NMR spectrum of **1k** in $CDCl_3$ at 300 MHz



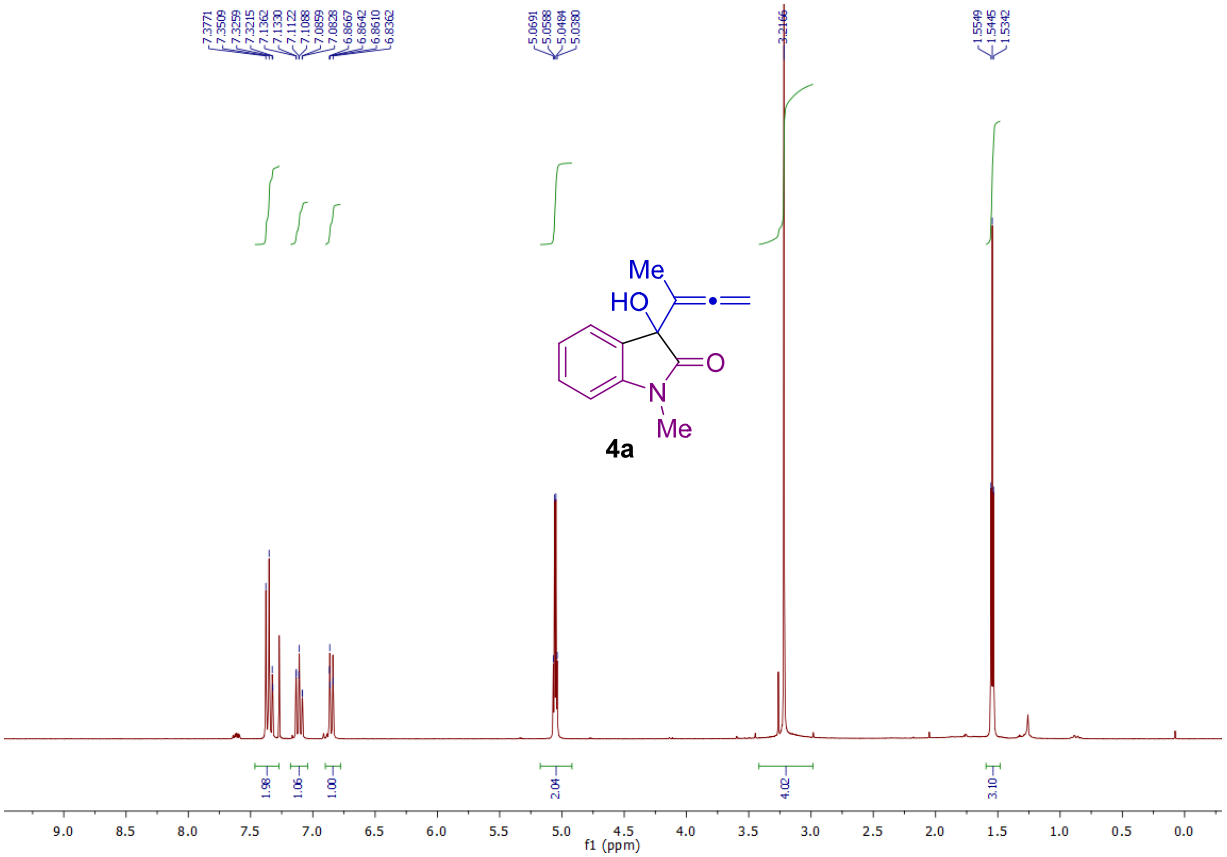
^{1}H NMR spectrum of **1a-Ar** in $CDCl_3$ at 300 MHz



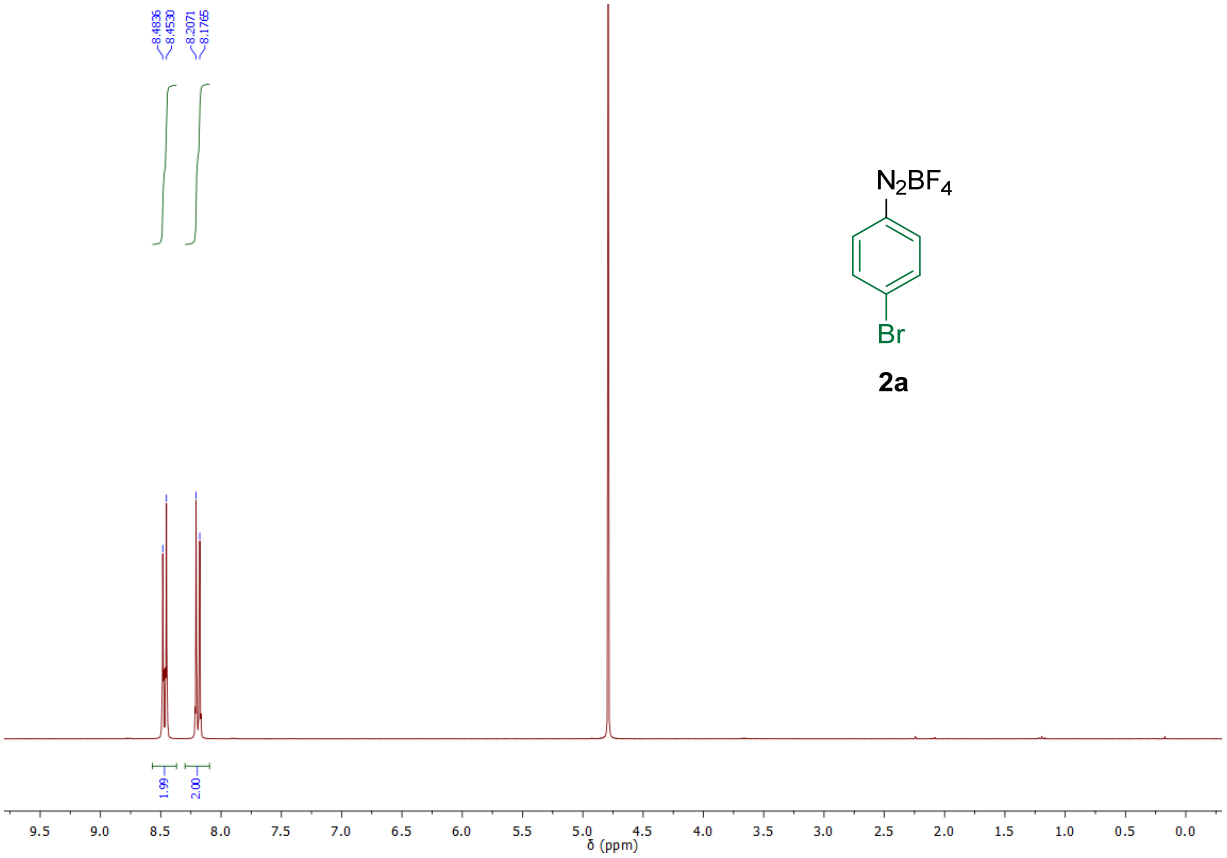
^{1}H NMR spectrum of **1b-Ar** in $CDCl_3$ at 300 MHz



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



^{1}H NMR spectrum of **2a** in D_2O at 300 MHz

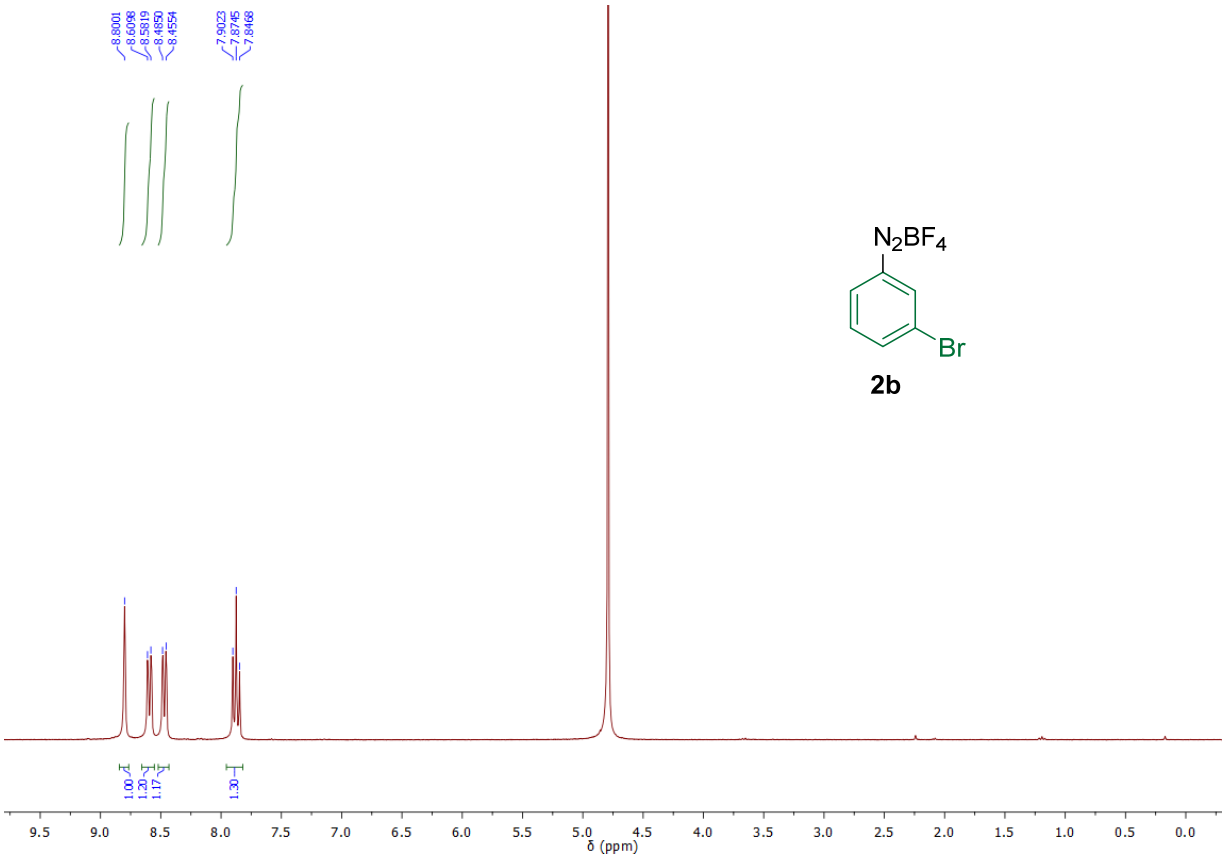


N_2BF_4

Br

2a

^{1}H NMR spectrum of **2b** in D_2O at 300 MHz

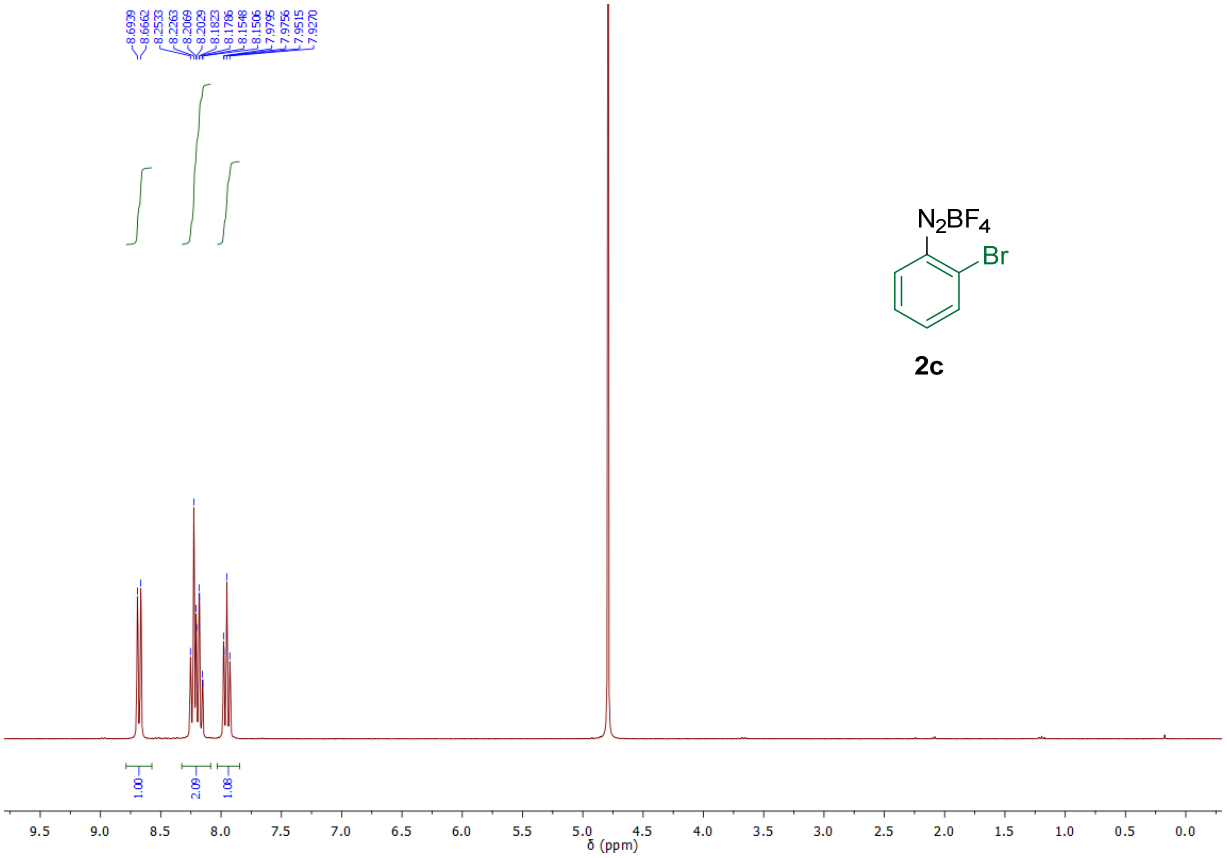


N_2BF_4

Br

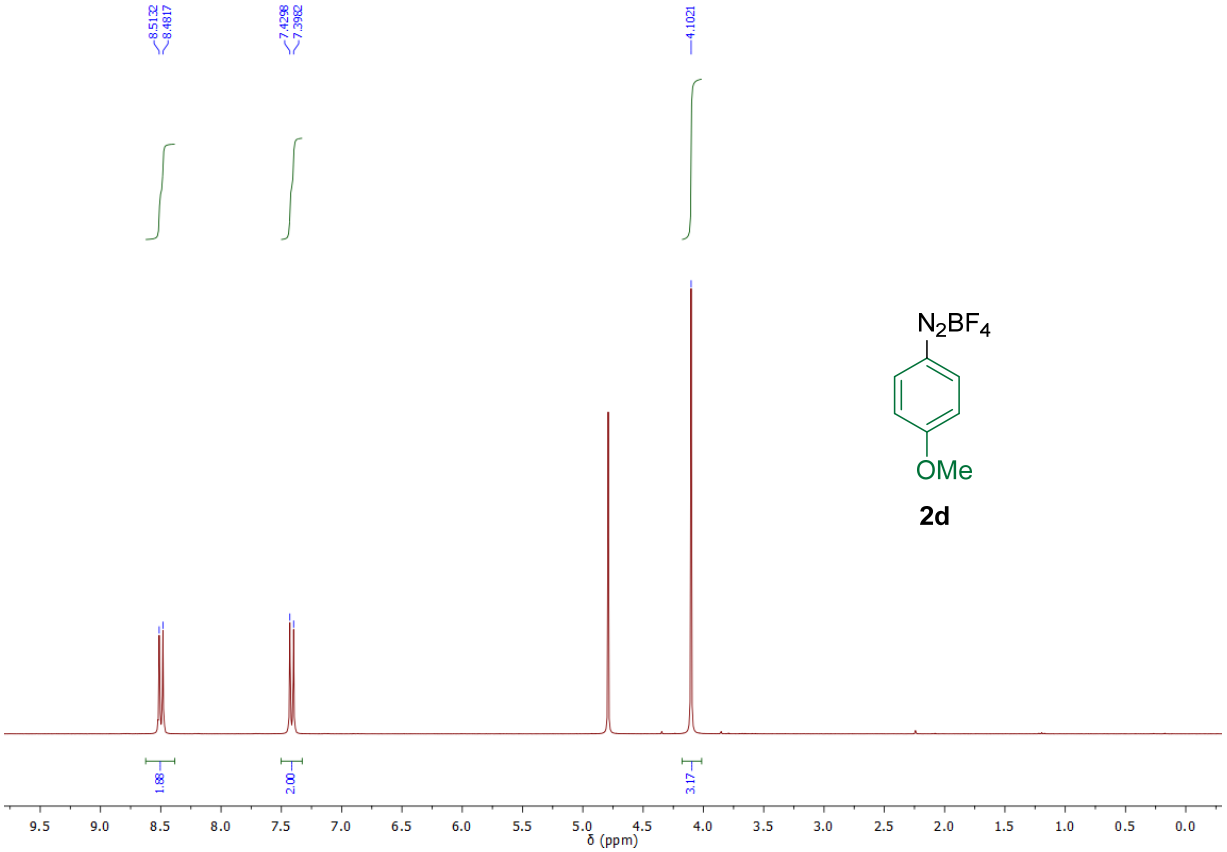
2b

^{1}H NMR spectrum of **2c** in D_2O at 300 MHz



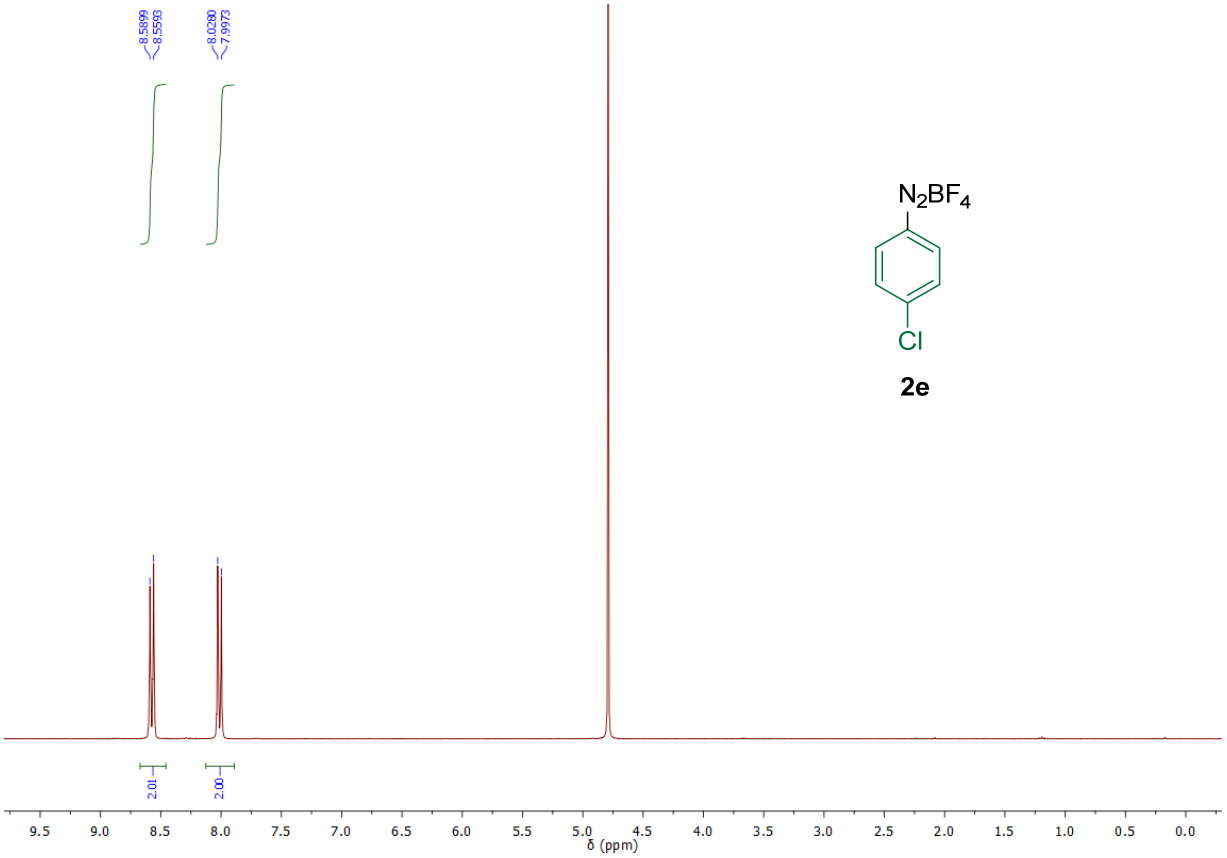
2c

^{1}H NMR spectrum of **2d** in D_2O at 300 MHz



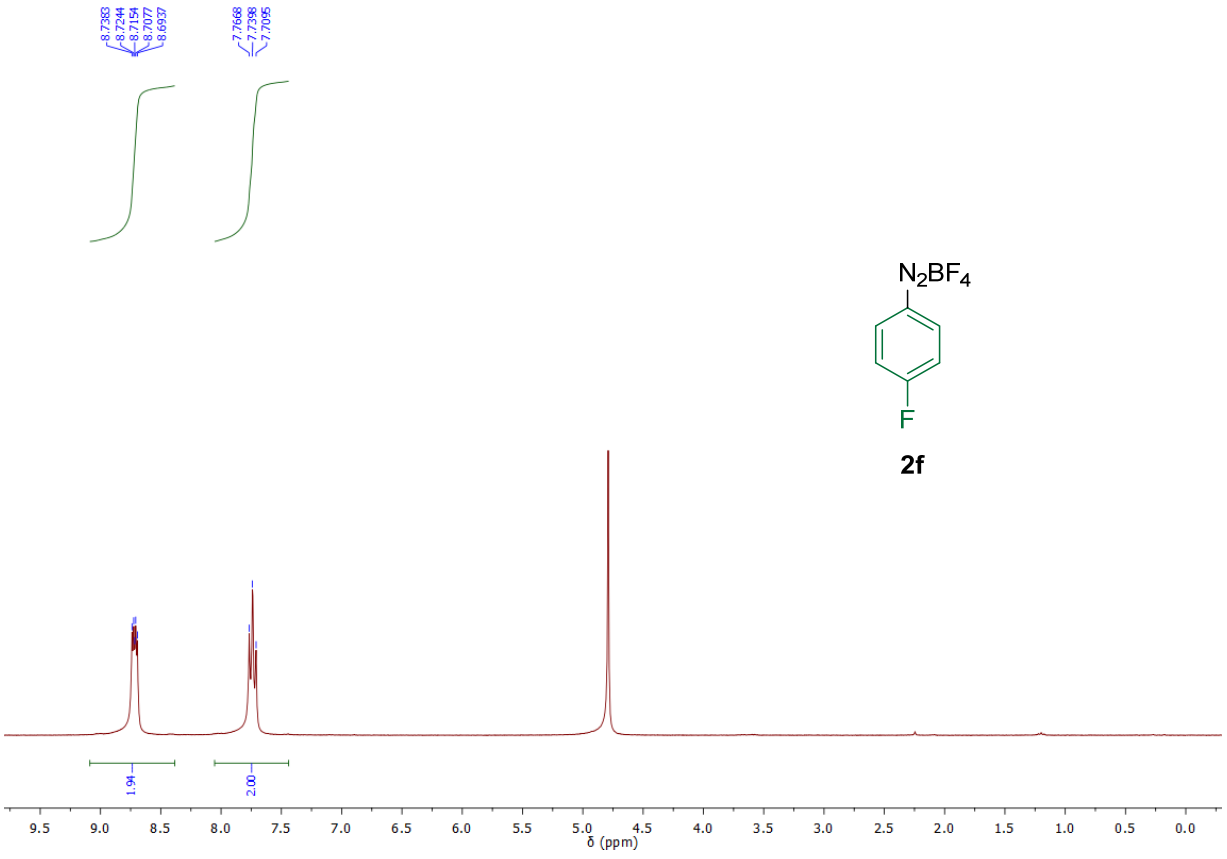
2d

^{1}H NMR spectrum of **2e** in D_2O at 300 MHz



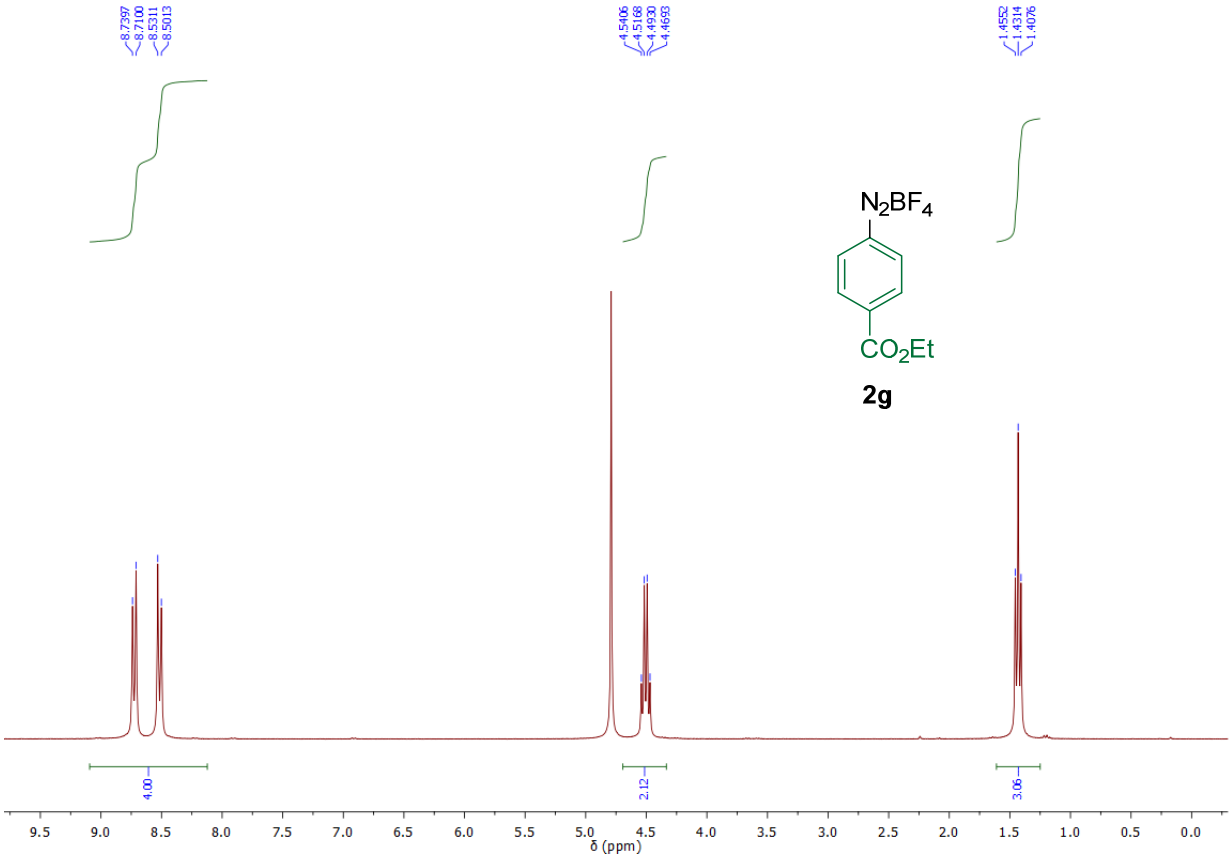
2e

^{1}H NMR spectrum of **2f** in D_2O at 300 MHz

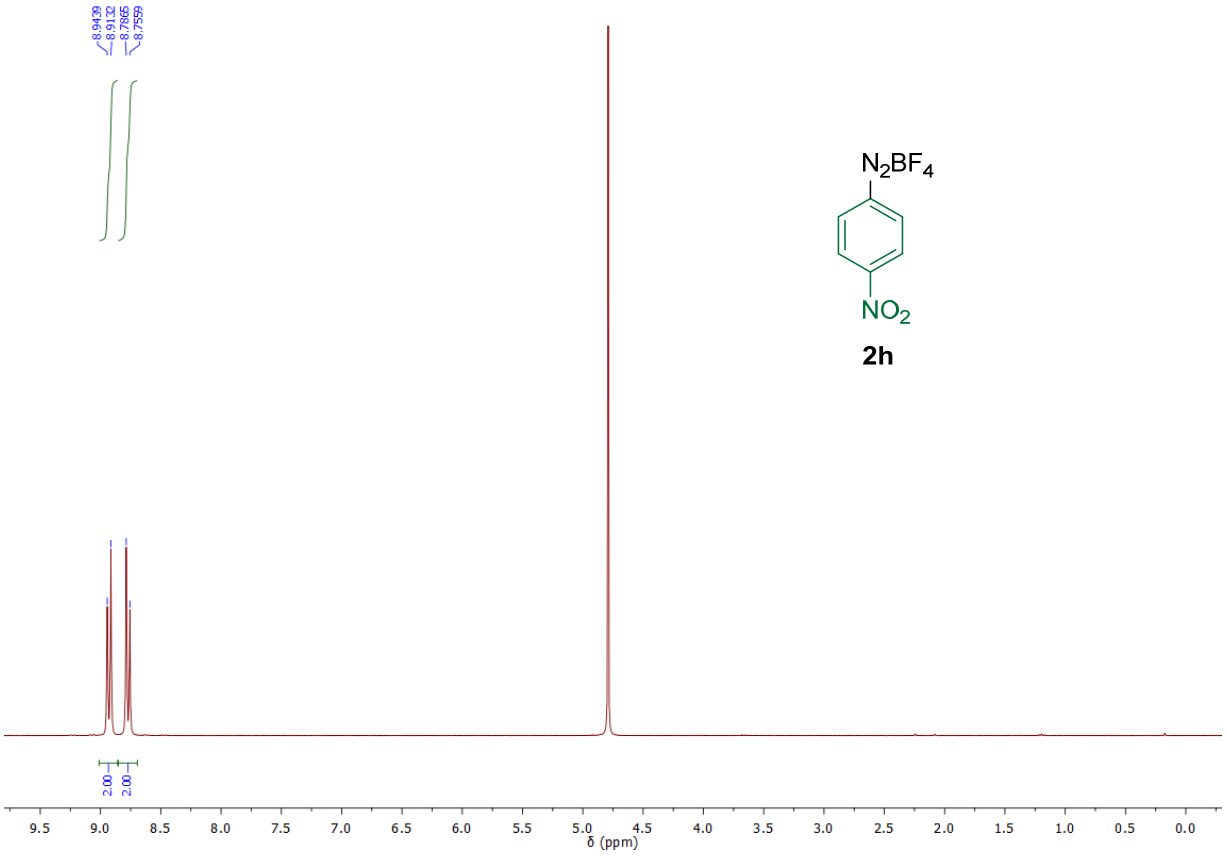


2f

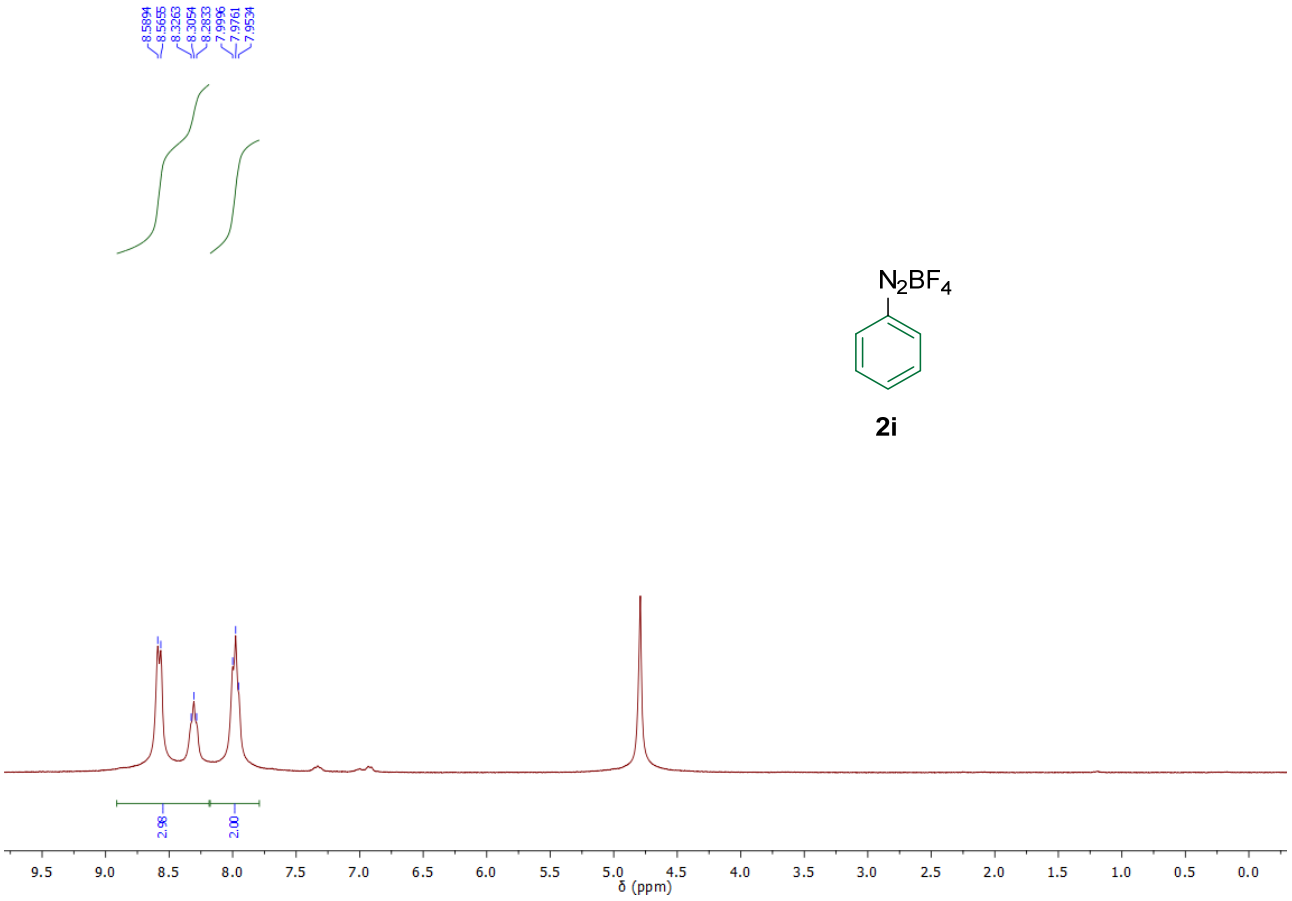
^{1}H NMR spectrum of **2g** in D_2O at 300 MHz



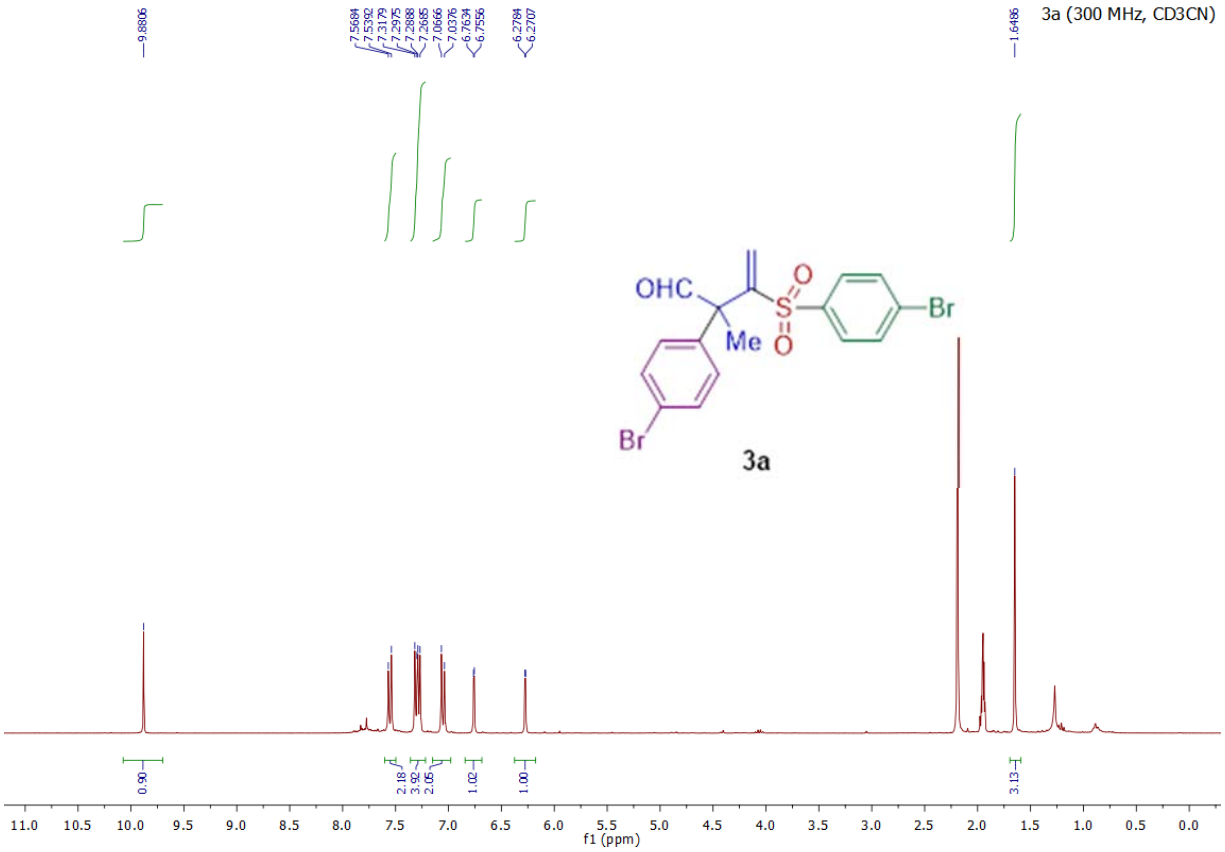
^{1}H NMR spectrum of **2h** in D_2O at 300 MHz



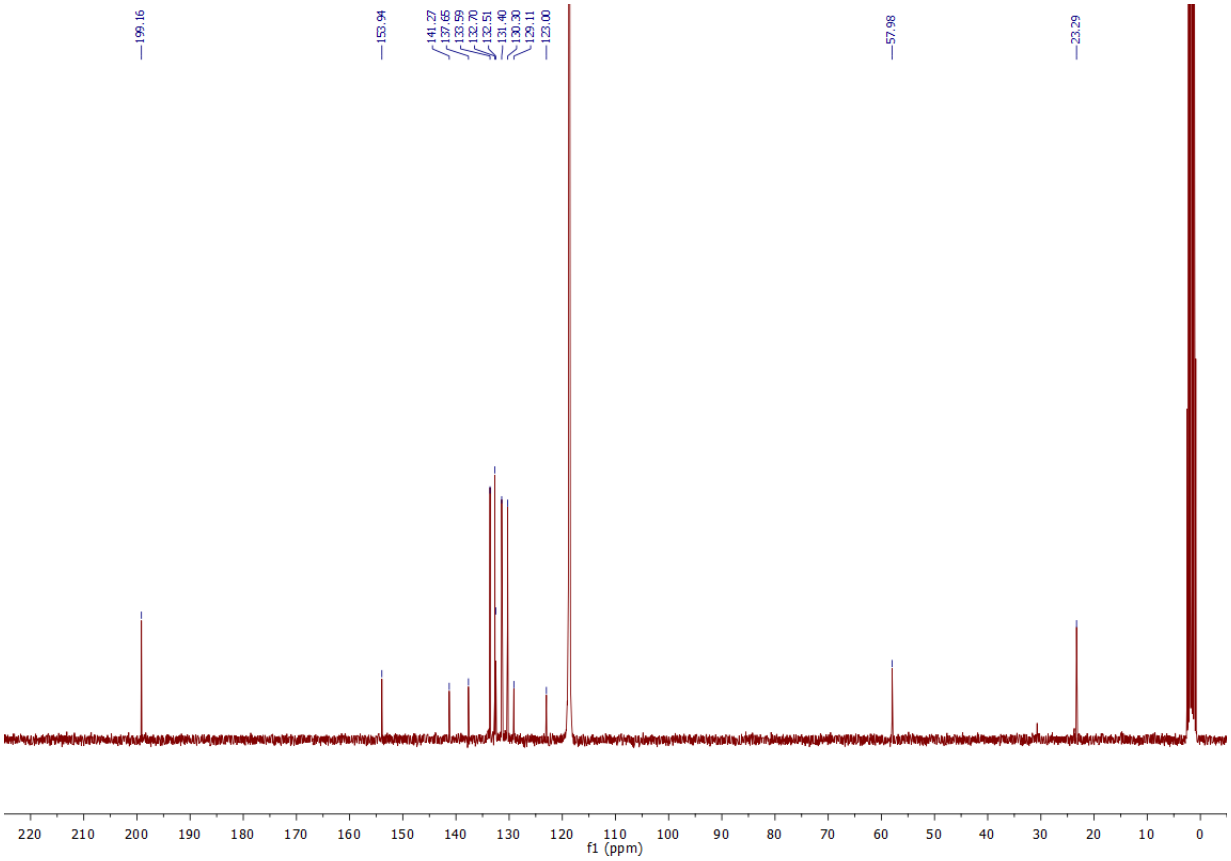
^{1}H NMR spectrum of **2i** in D_2O at 300 MHz



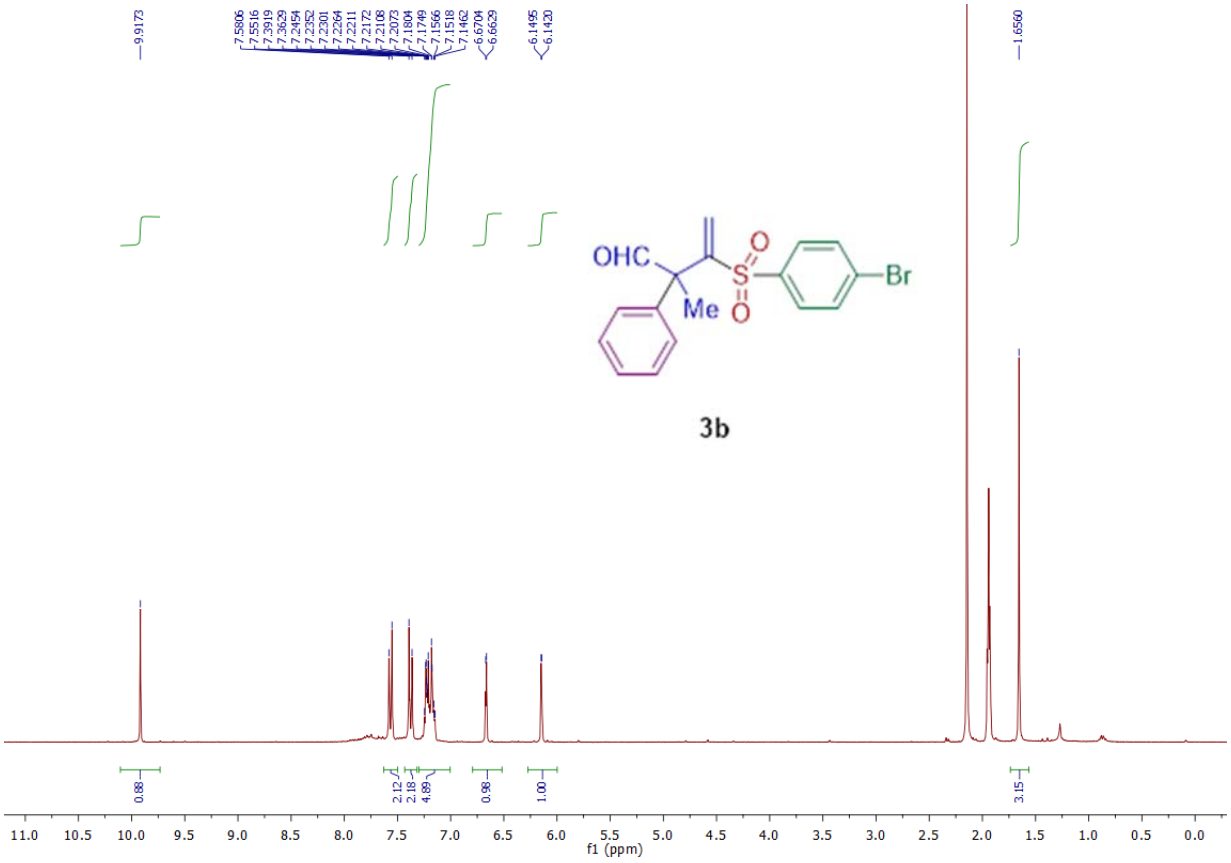
^{1}H NMR spectrum of **3a** in CD_3CN at 300 MHz



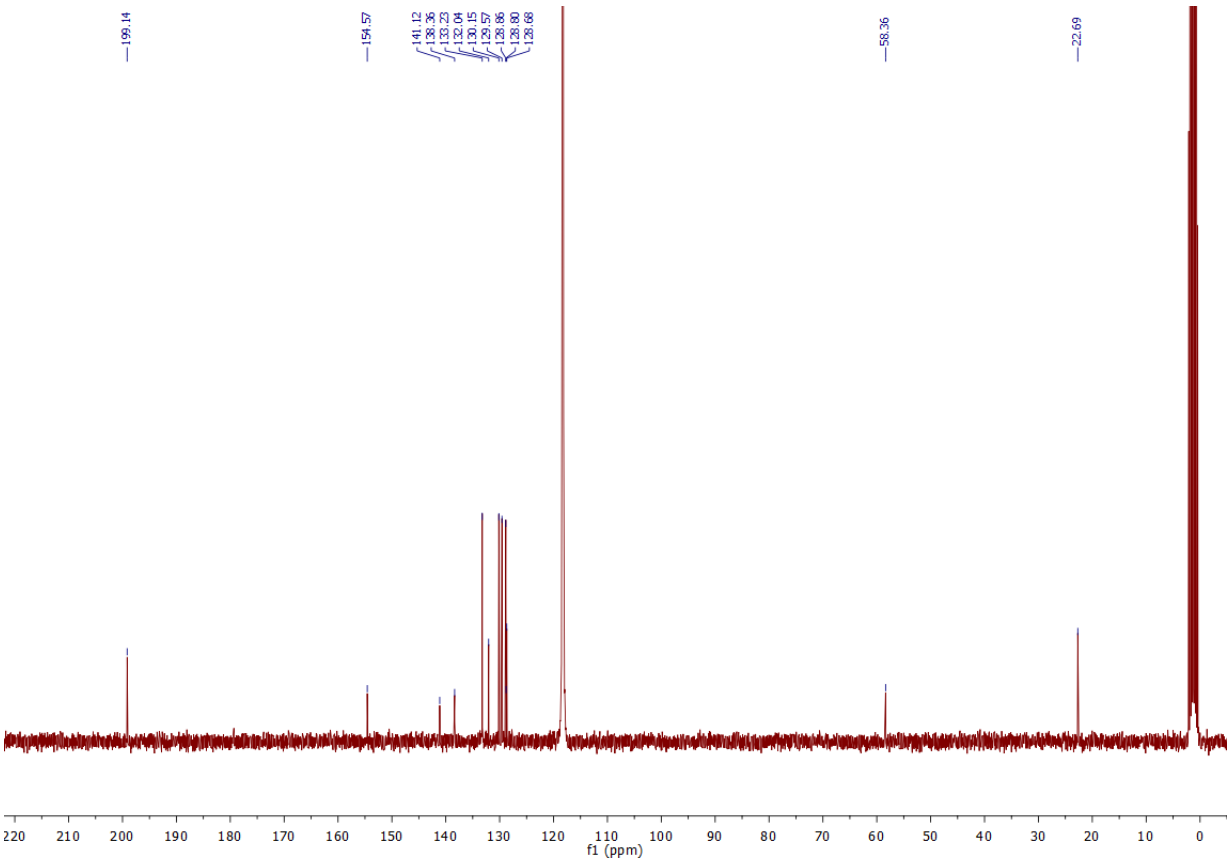
^{13}C NMR spectrum of **3a** in CD_3CN at 75 MHz



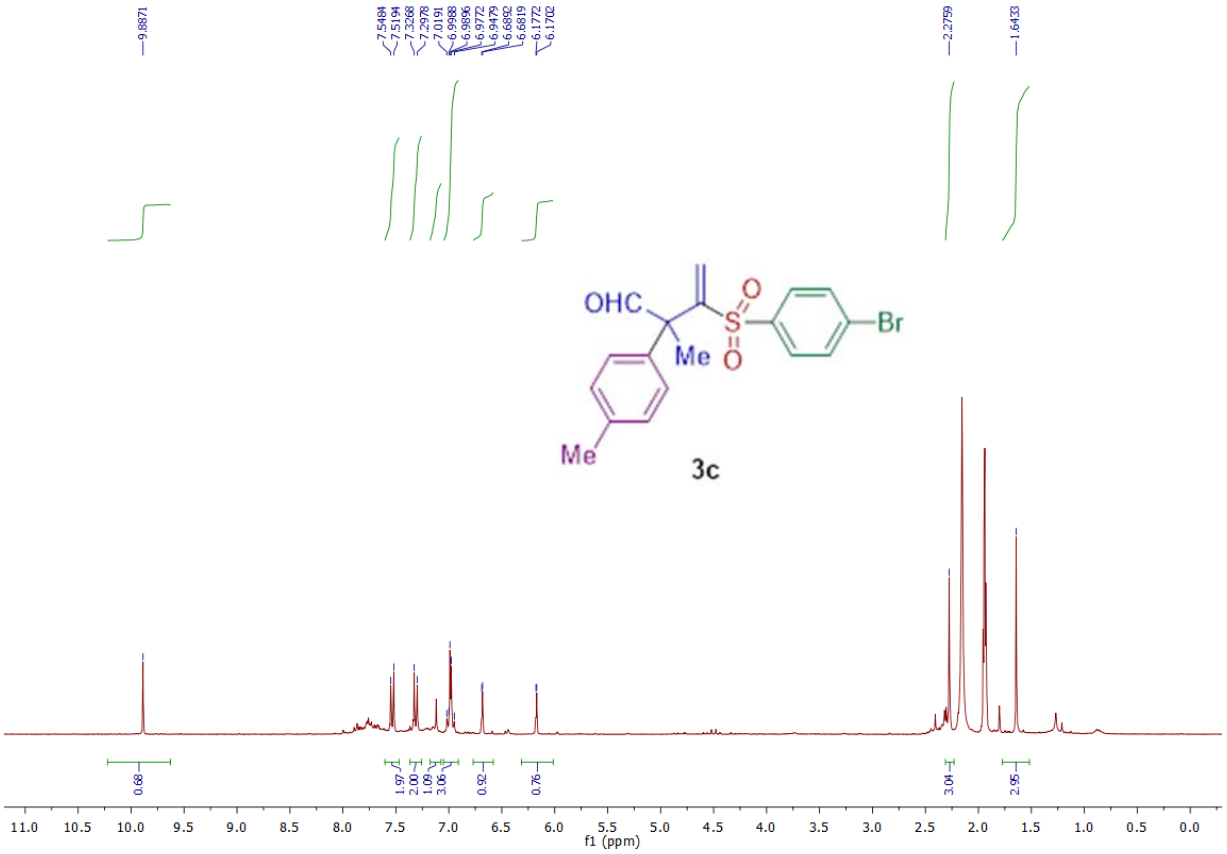
^{1}H NMR spectrum of **3b** in CD_3CN at 300 MHz



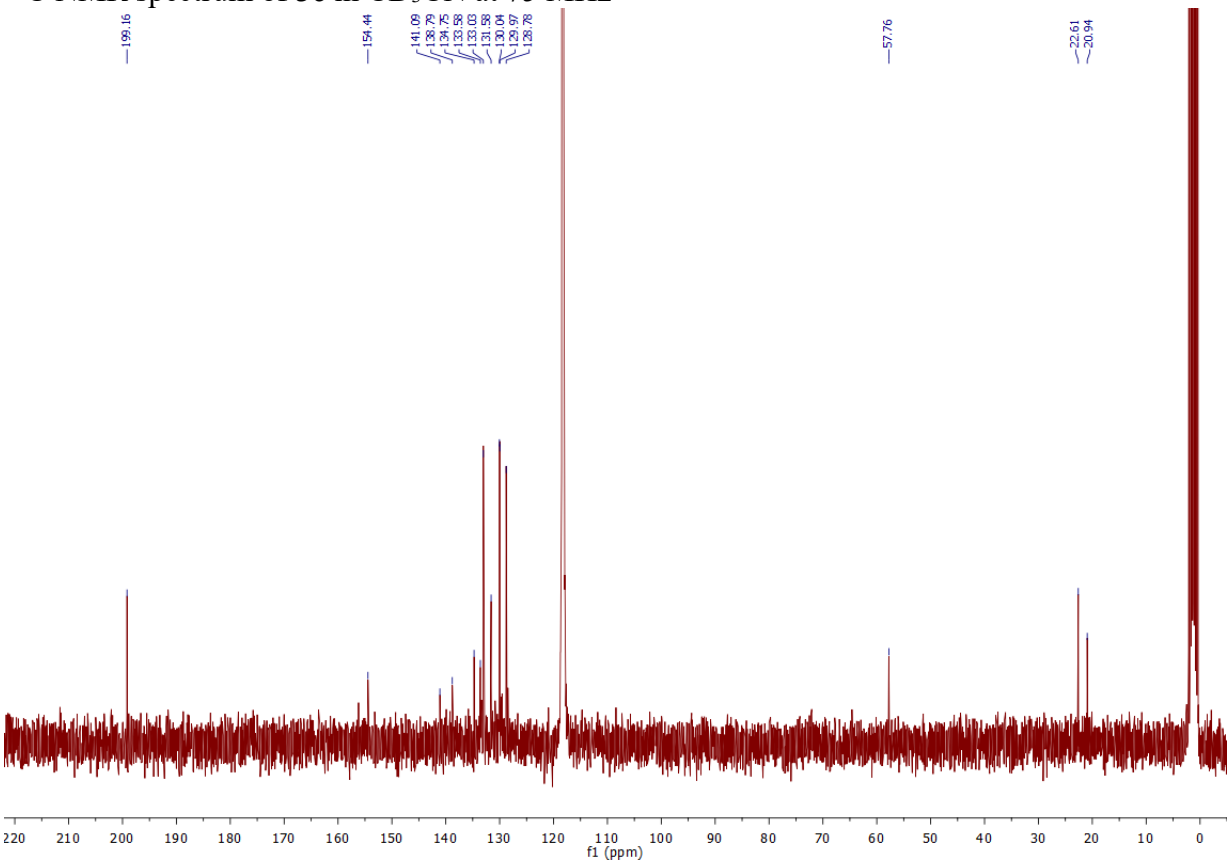
^{13}C NMR spectrum of **3b** in CD_3CN at 75 MHz



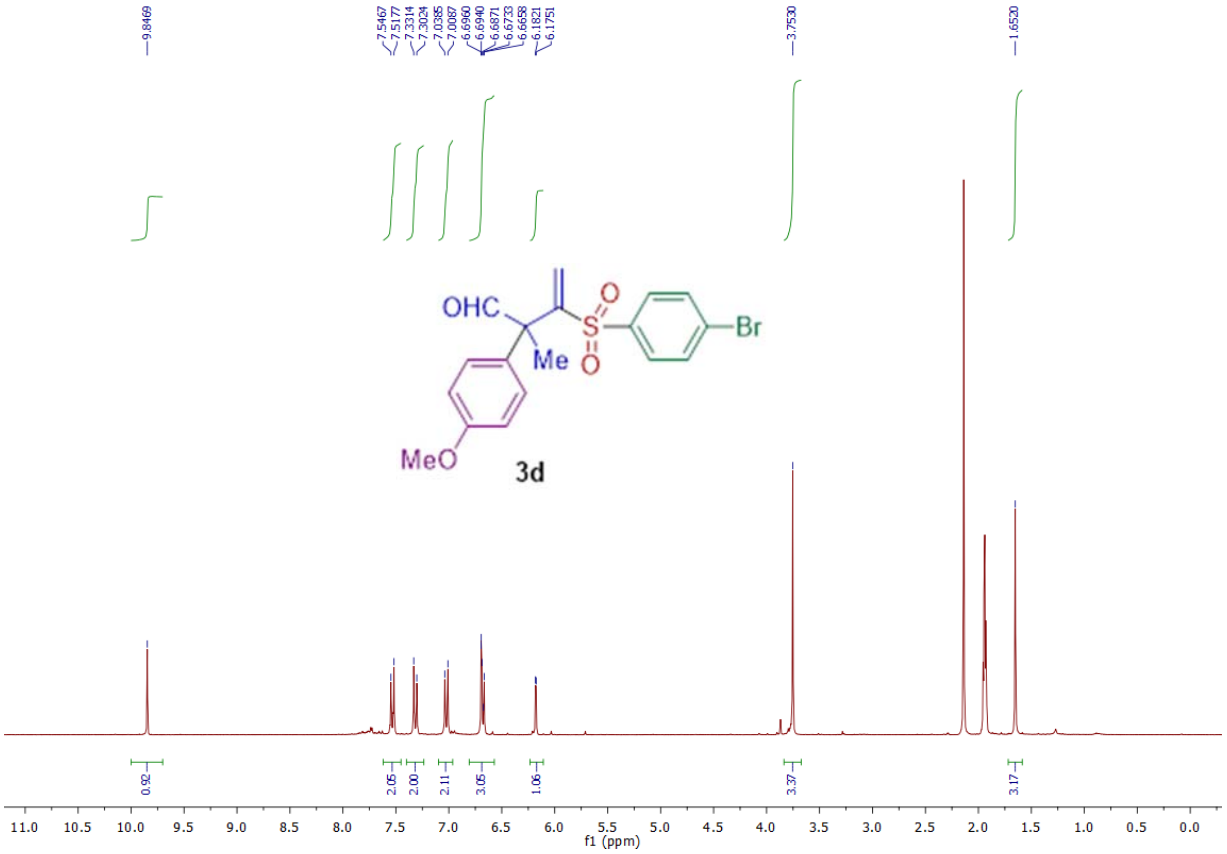
^{1}H NMR spectrum of **3c** in CD_3CN at 300 MHz



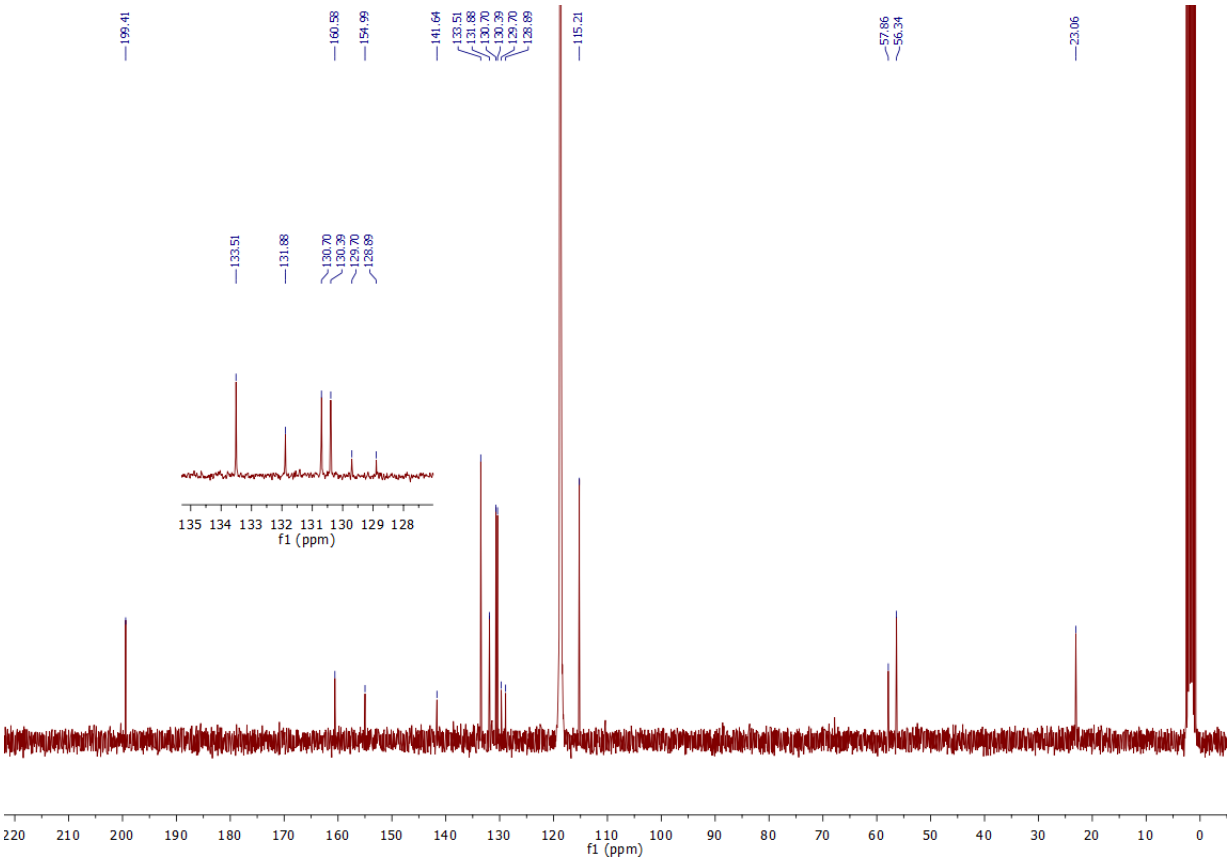
^{13}C NMR spectrum of **3c** in CD_3CN at 75 MHz



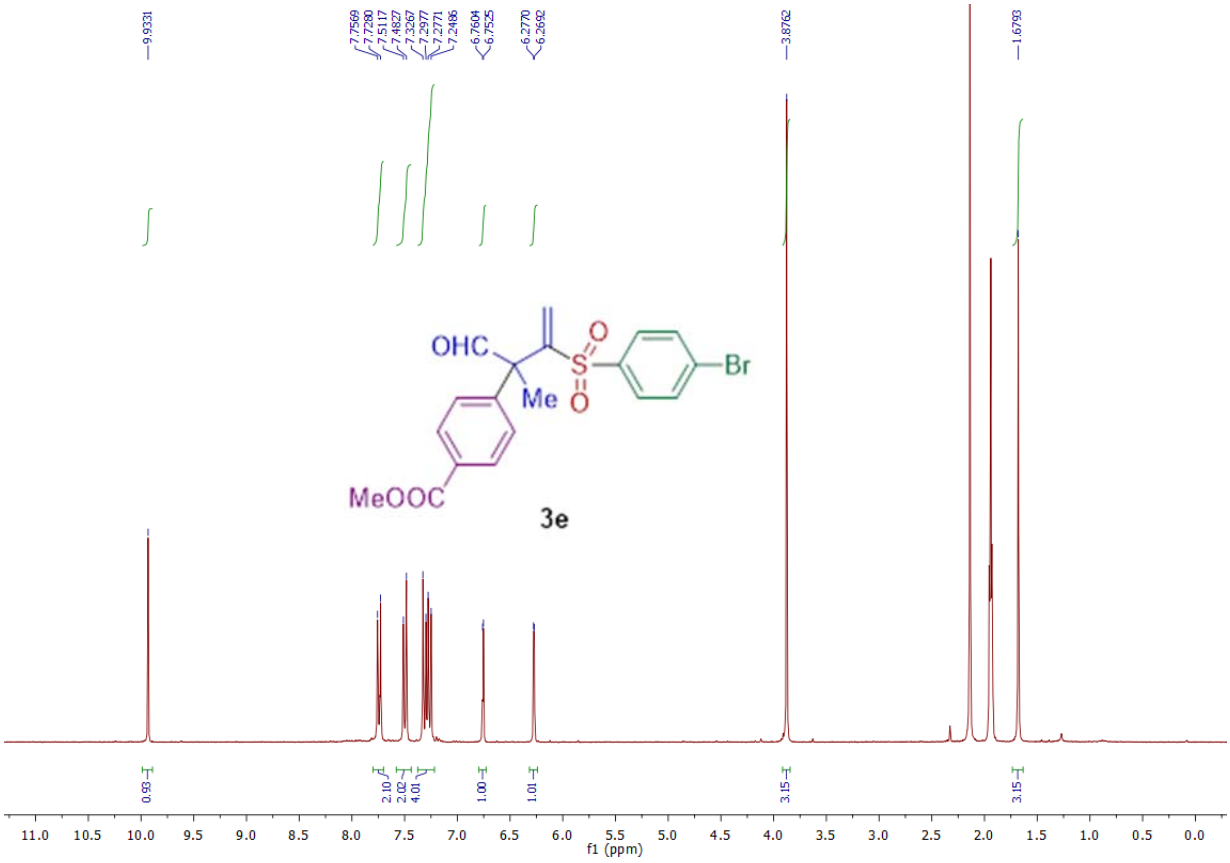
^{1}H NMR spectrum of **3d** in CD_3CN at 300 MHz



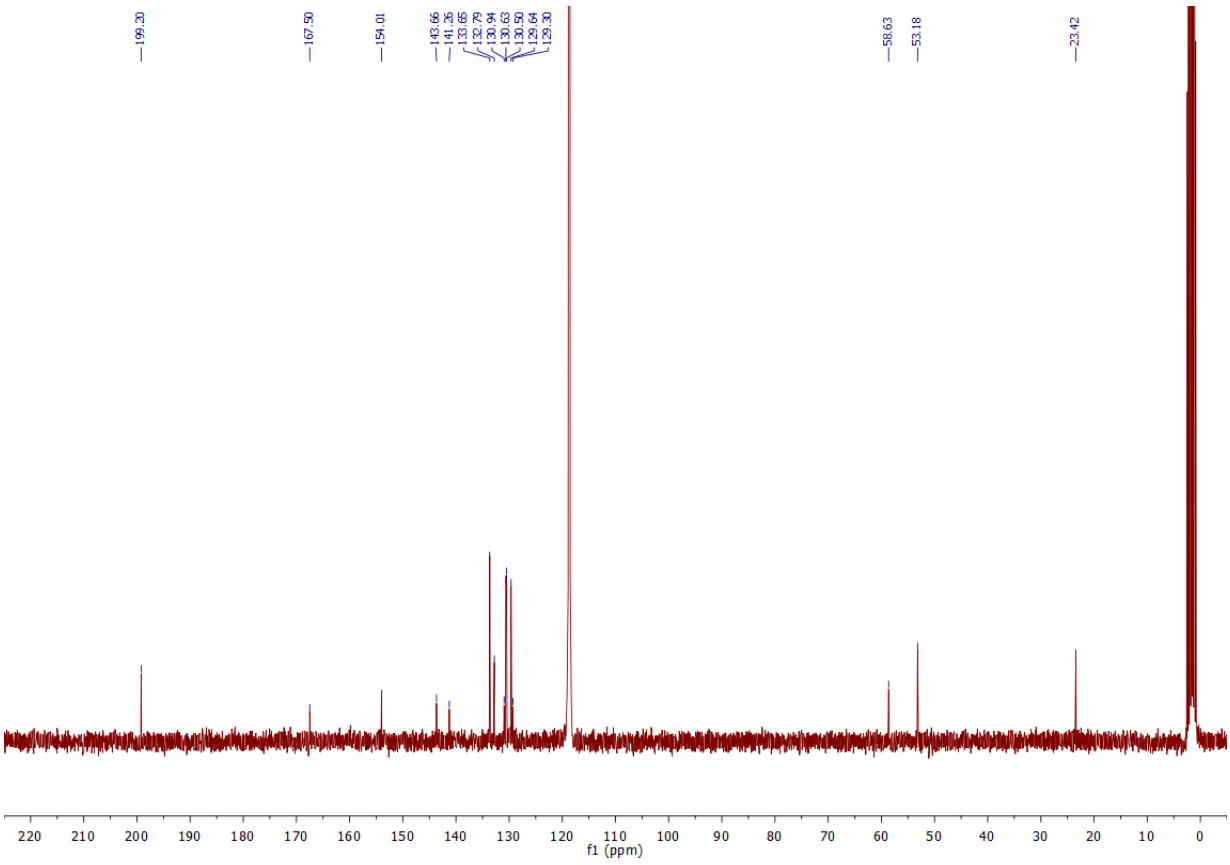
^{13}C NMR spectrum of **3d** in CD_3CN at 75 MHz



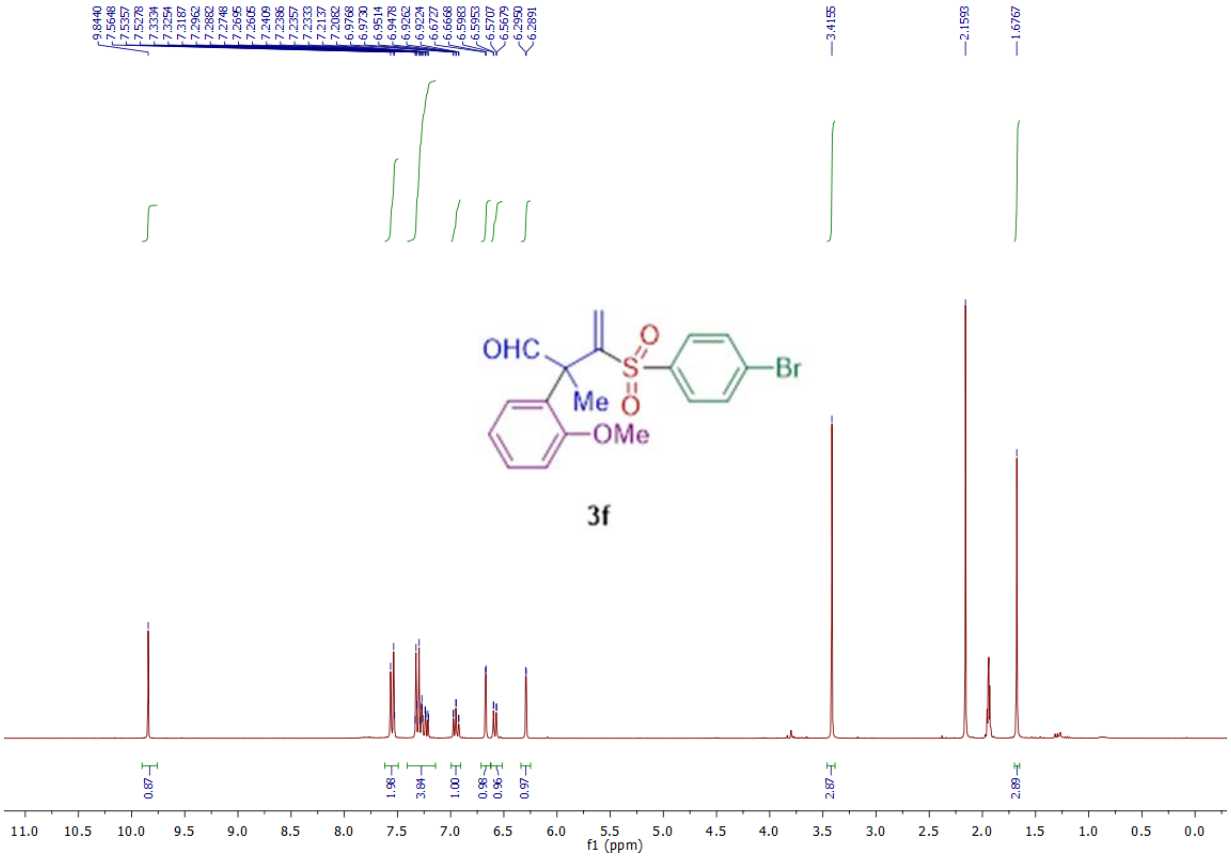
^{1}H NMR spectrum of **3e** in CD_3CN at 300 MHz



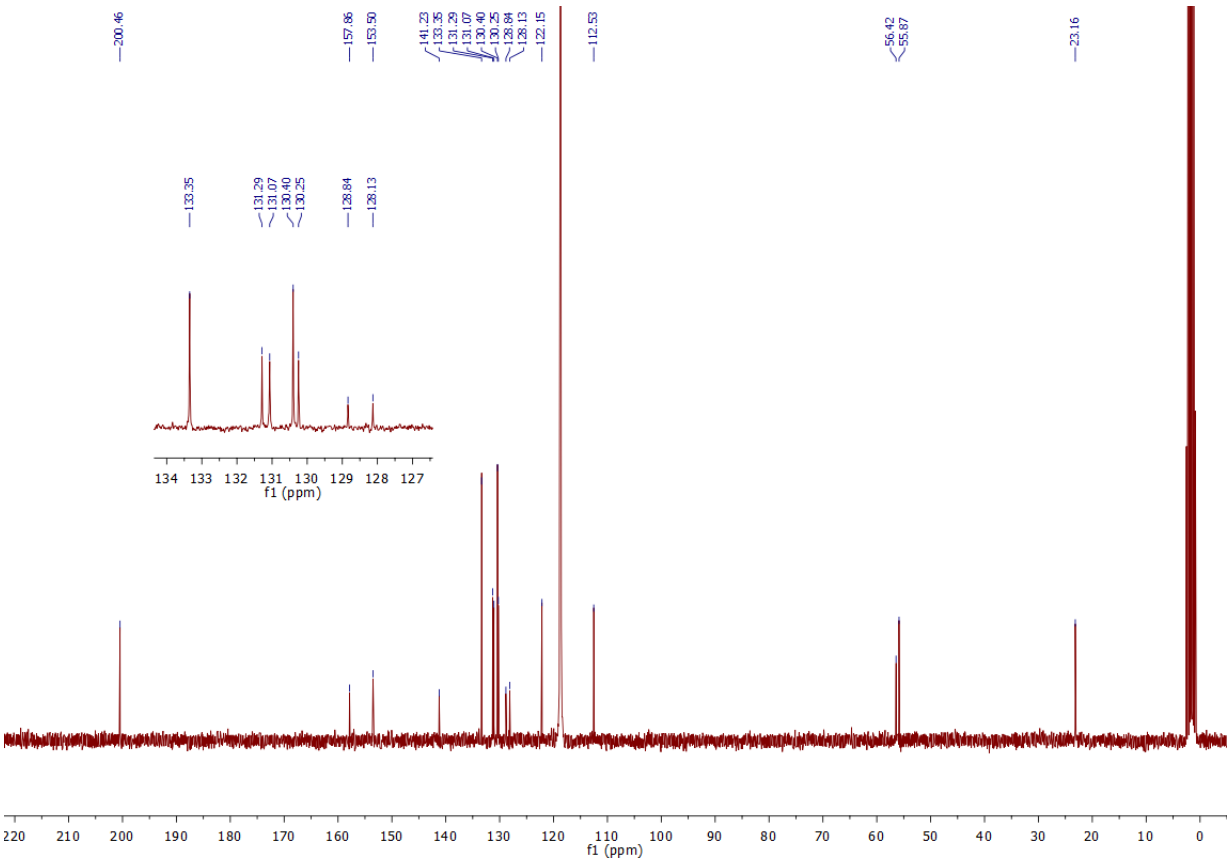
^{13}C NMR spectrum of **3e** in CD_3CN at 75 MHz



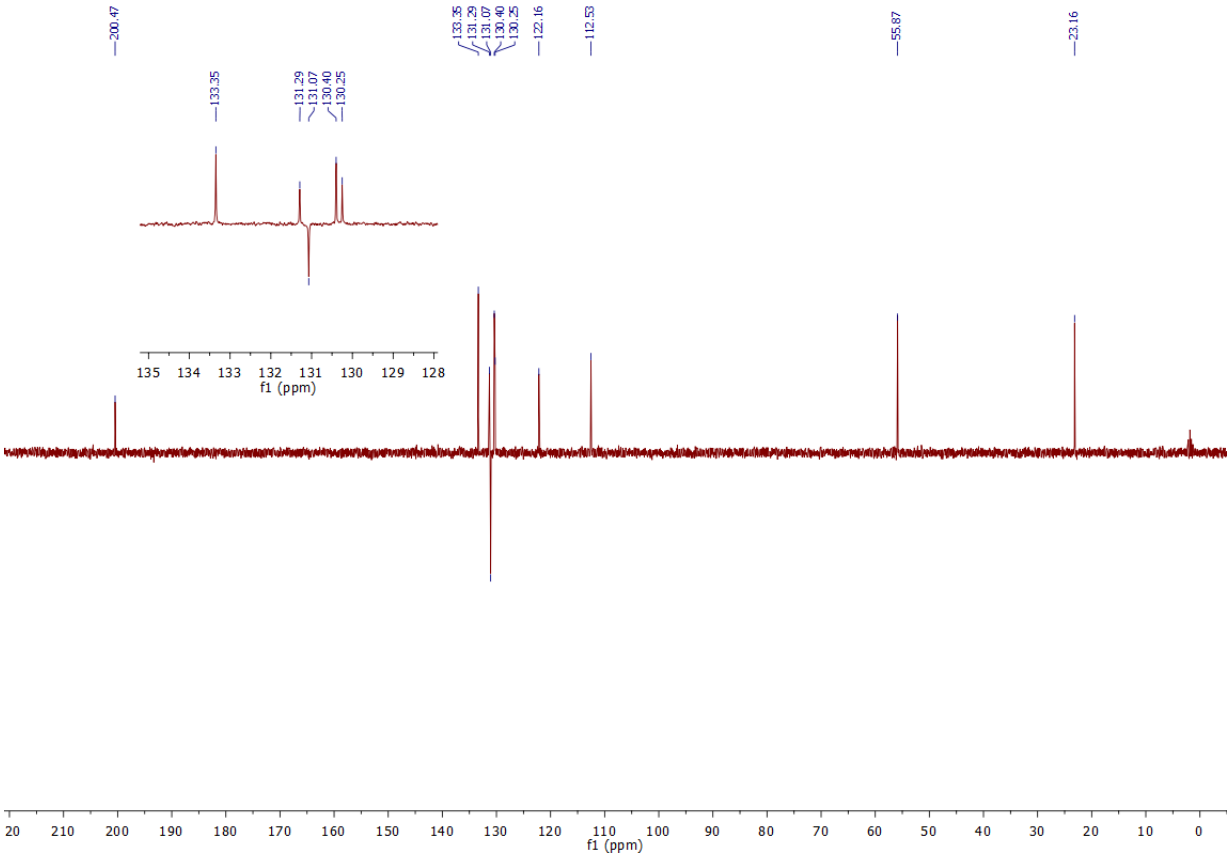
^{1}H NMR spectrum of **3f** in CD_3CN at 300 MHz



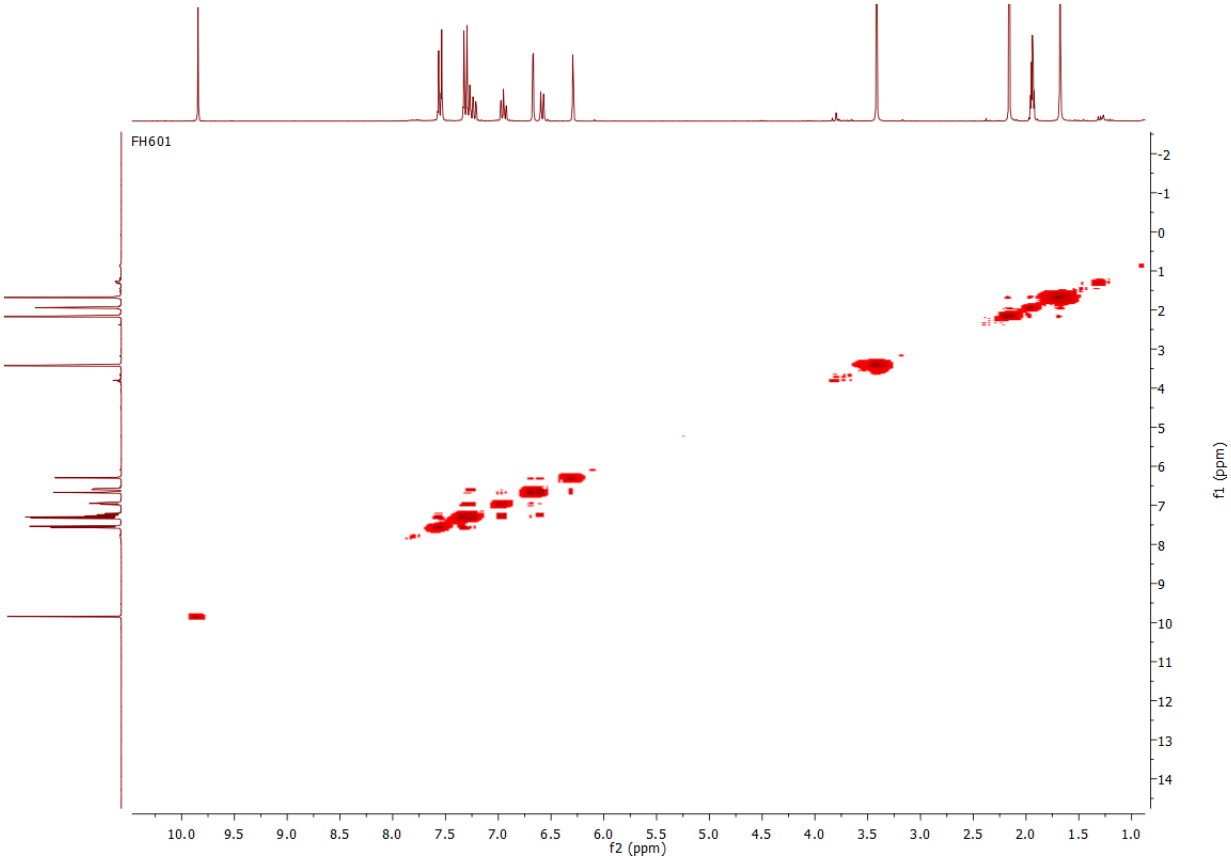
^{13}C NMR spectrum of **3f** in CD_3CN at 75 MHz



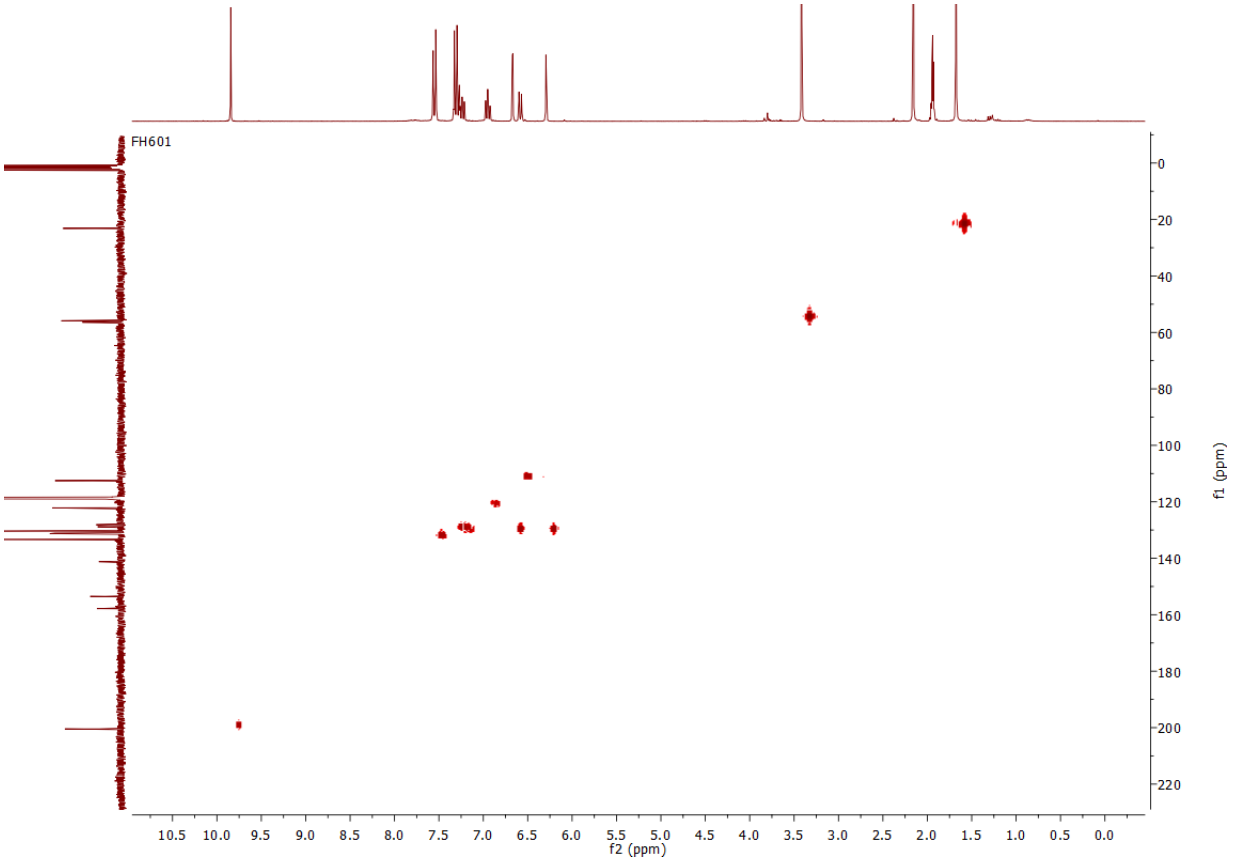
DEPT NMR spectrum of **3f** in CD_3CN at 75 MHz



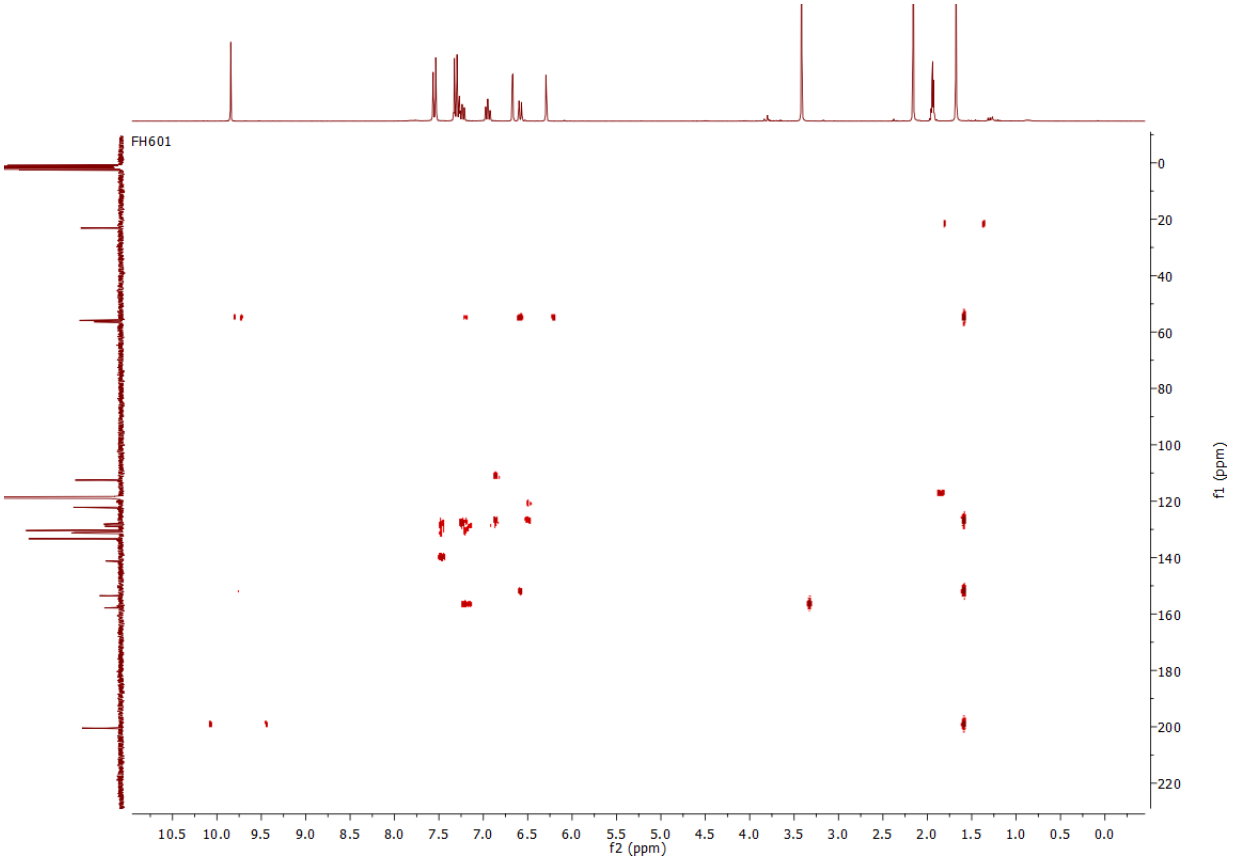
Two-dimensional COSY NMR spectrum ^1H-^1H of **3f** in CD_3CN at 300 MHz



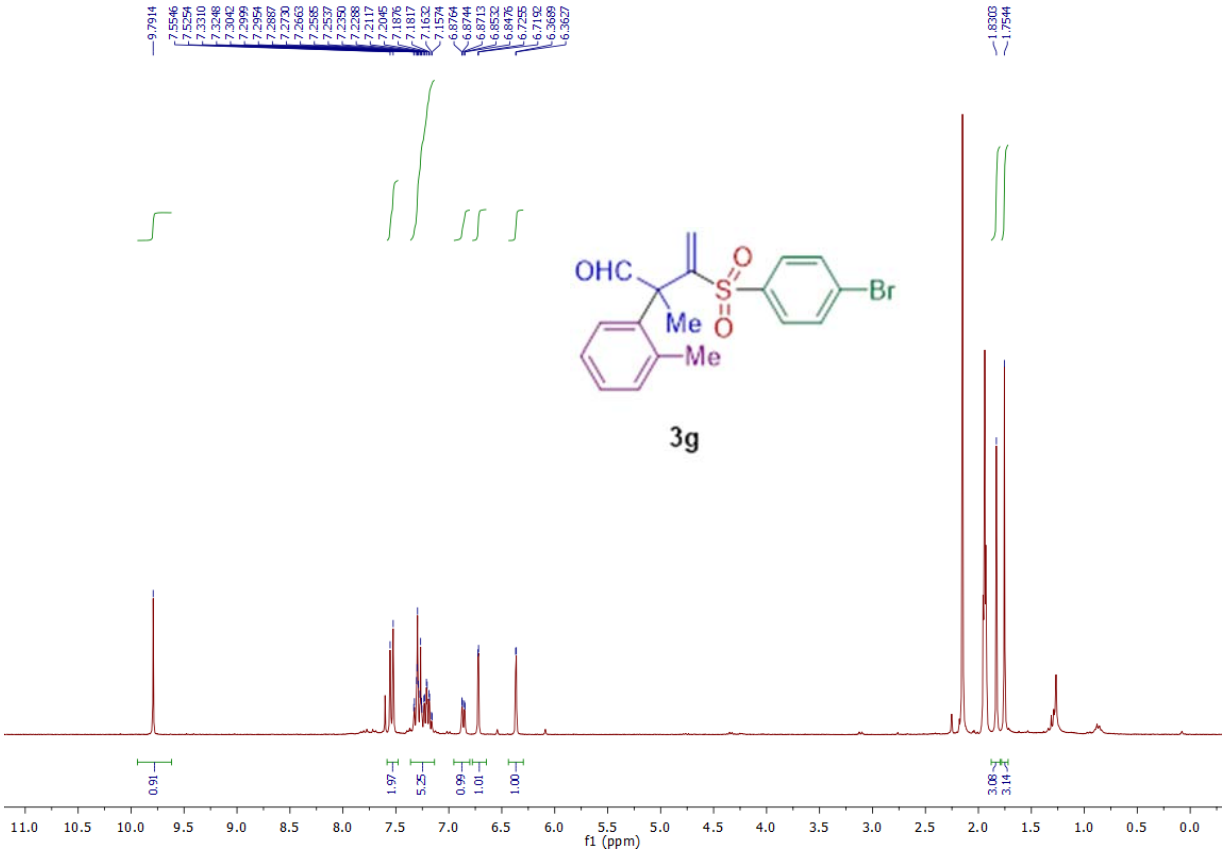
Two-dimensional HMQC NMR spectrum ^{1}H-^{13}C of **3f** in CD_3CN



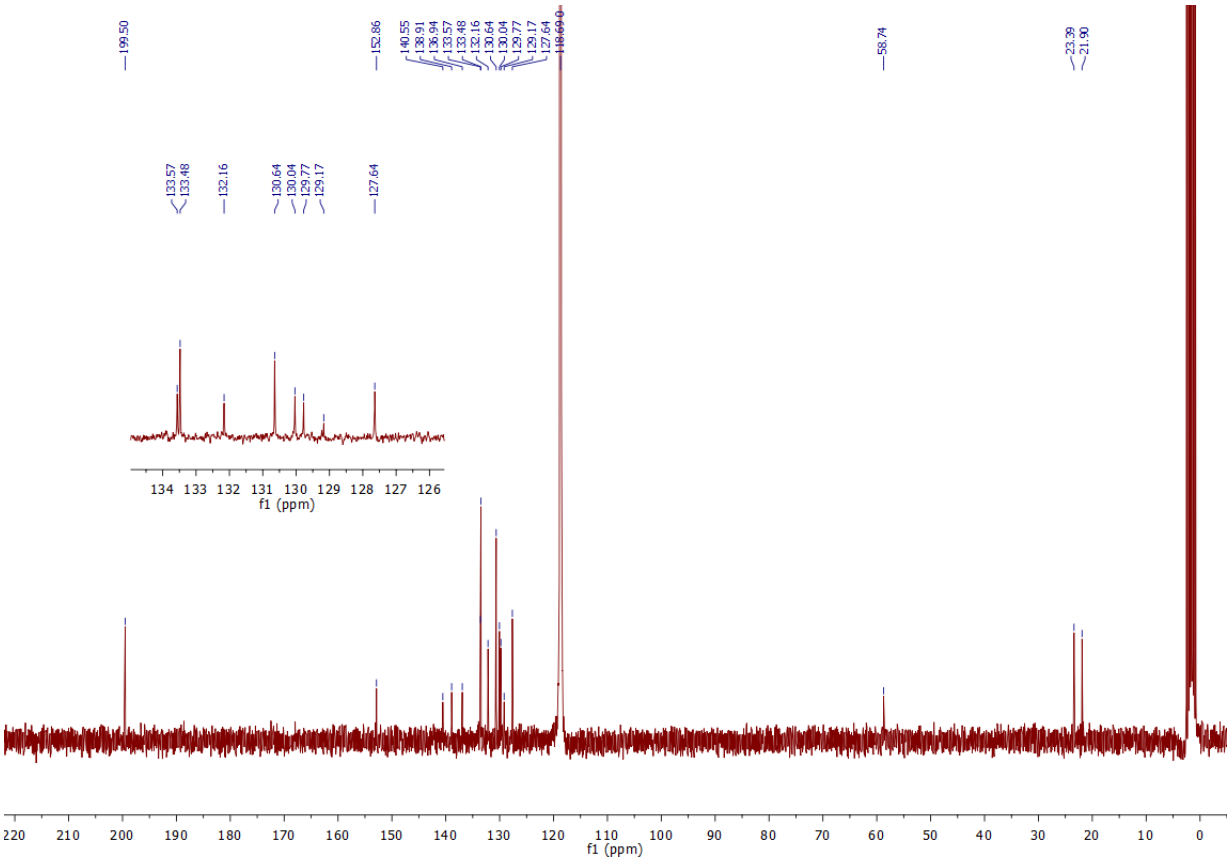
Two-dimensional HMBC NMR spectrum ^{1}H-^{13}C of **3f** in CD_3CN



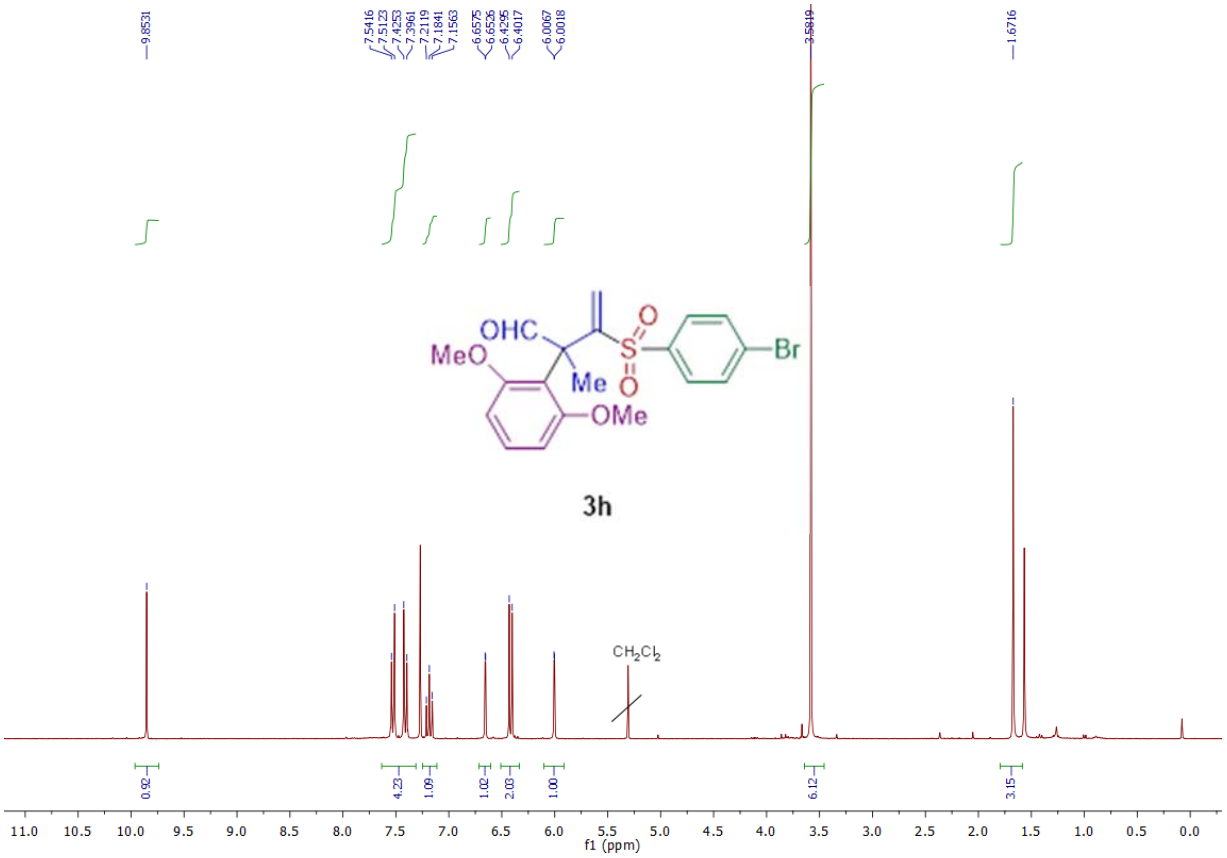
^{1}H NMR spectrum of **3g** in CD_3CN at 300 MHz



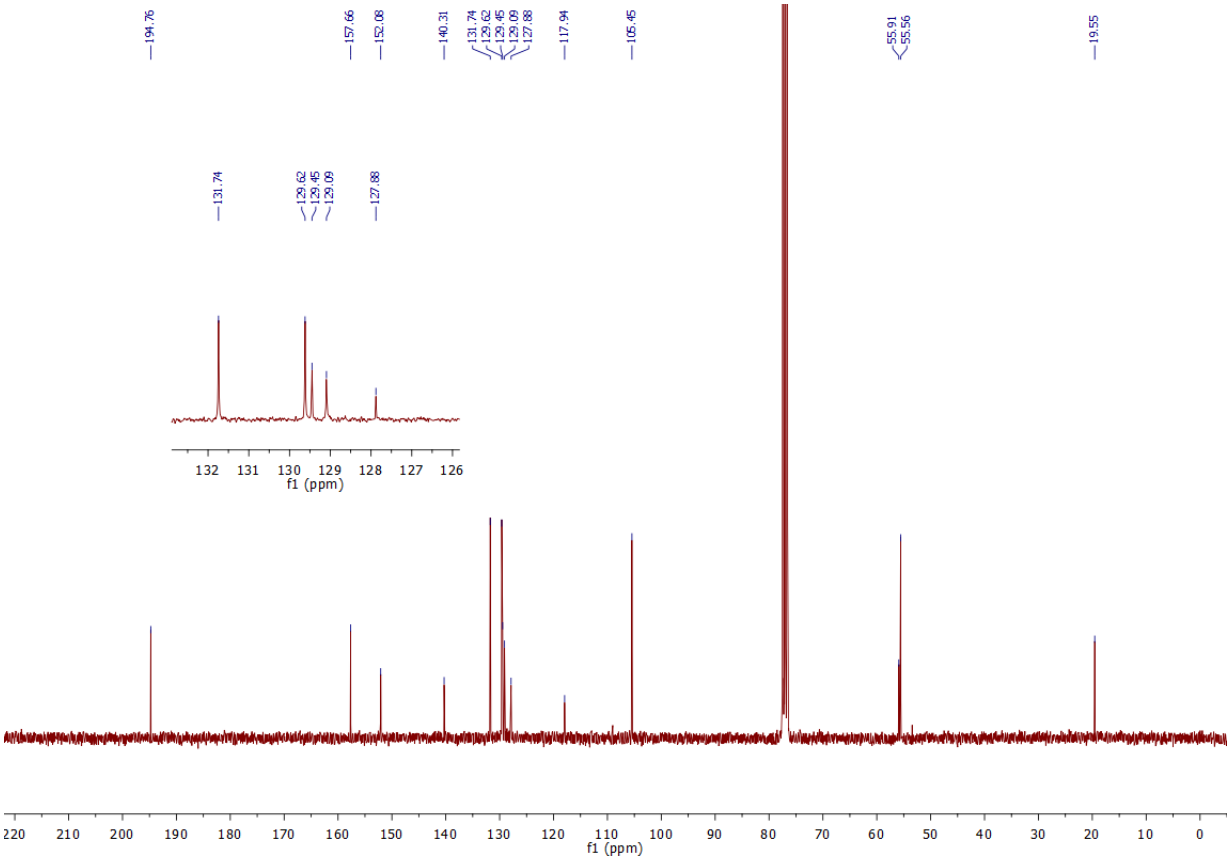
^{13}C NMR spectrum of **3g** in CD_3CN at 75 MHz



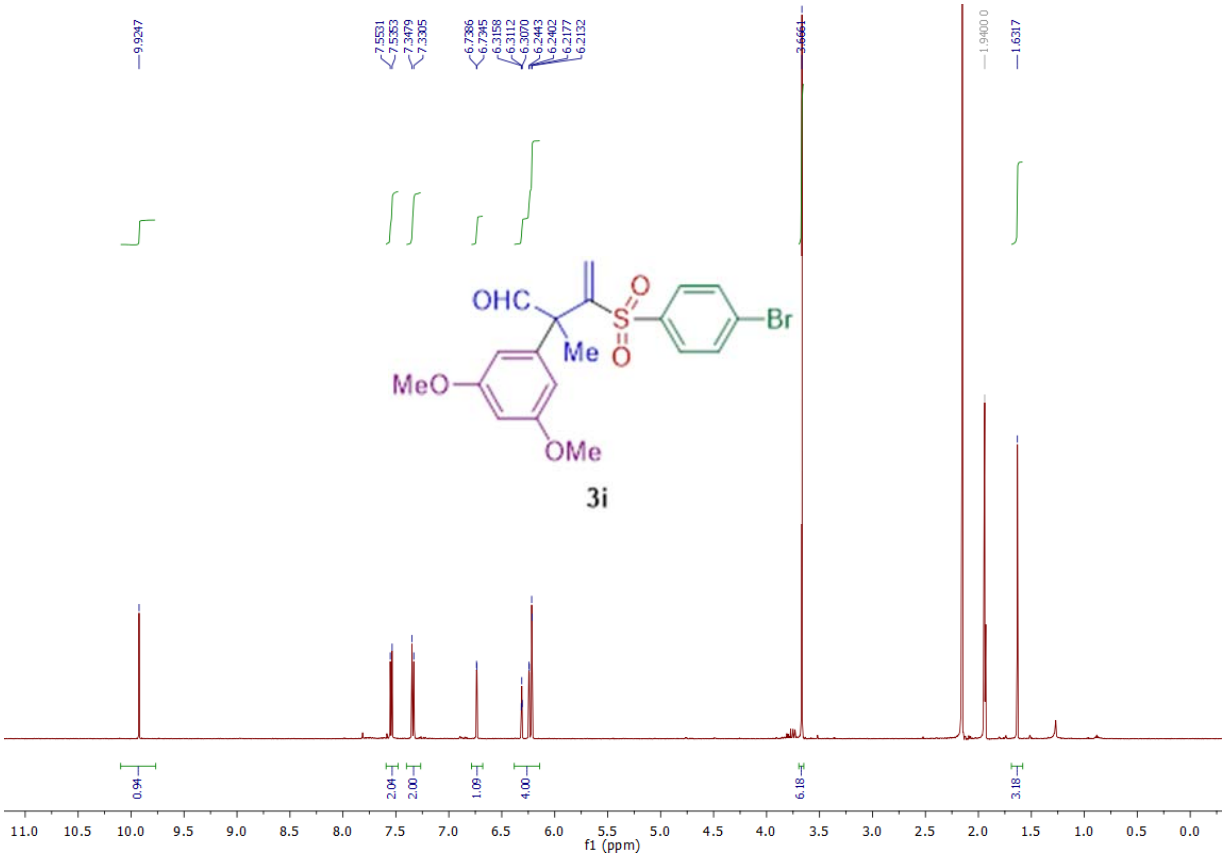
^{1}H NMR spectrum of **3h** in $CDCl_3$ at 300 MHz



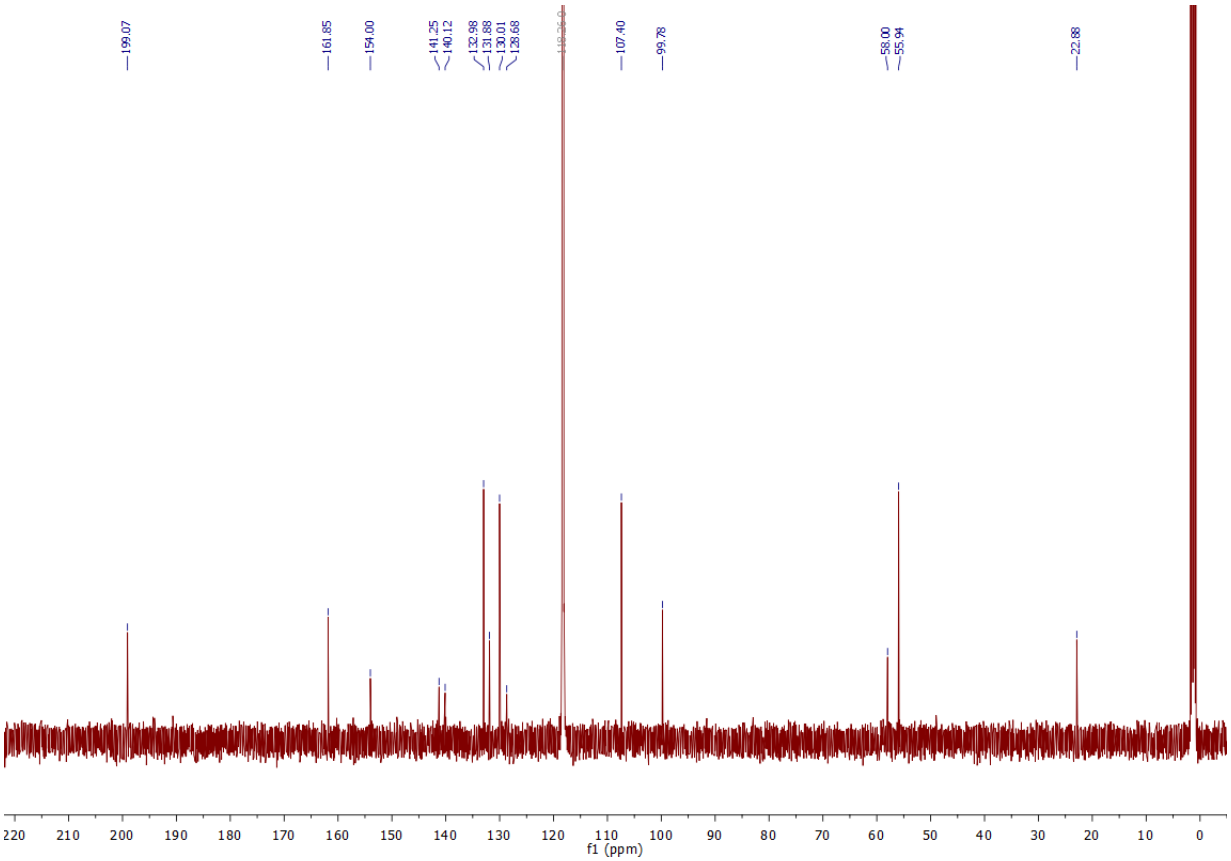
^{13}C NMR spectrum of **3h** in $CDCl_3$ at 75 MHz



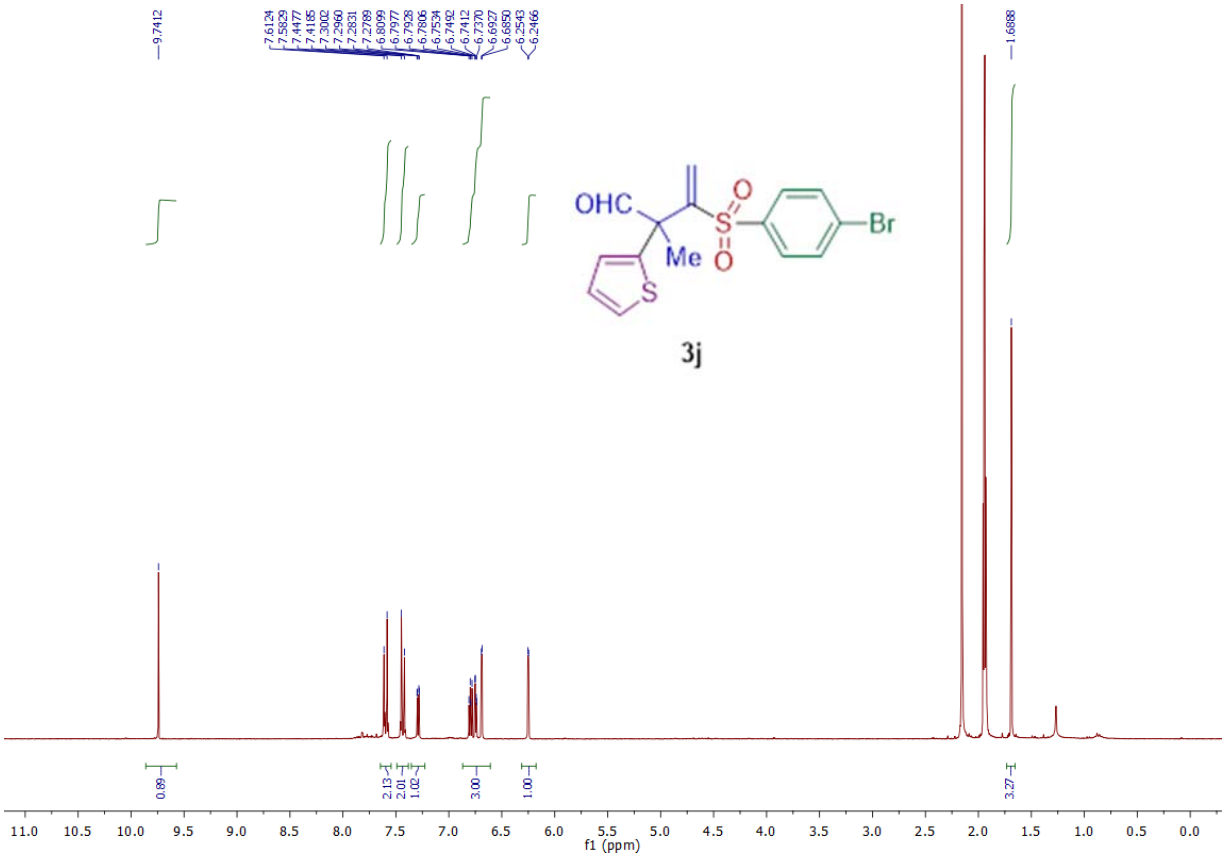
^{1}H NMR spectrum of **3i** in CD_3CN at 500 MHz



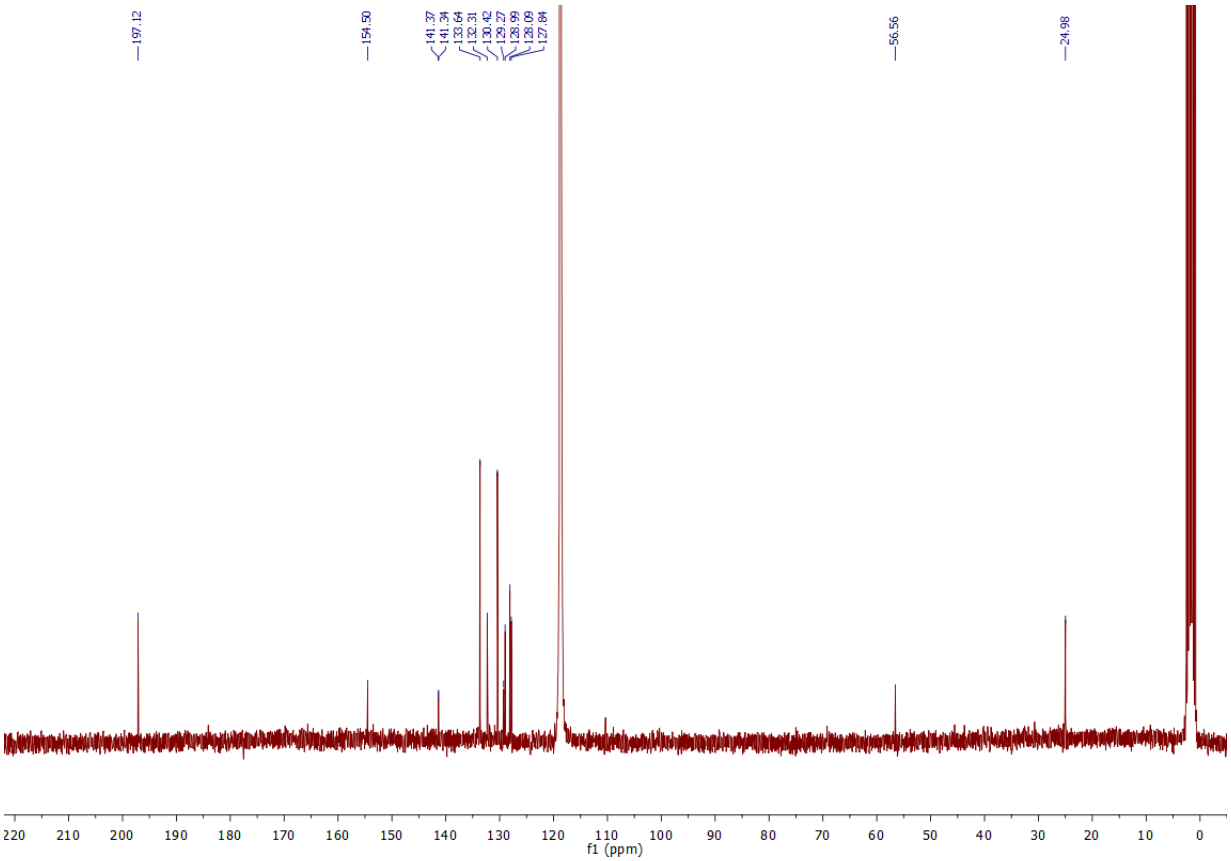
^{13}C NMR spectrum of **3i** in CD_3CN at 125 MHz



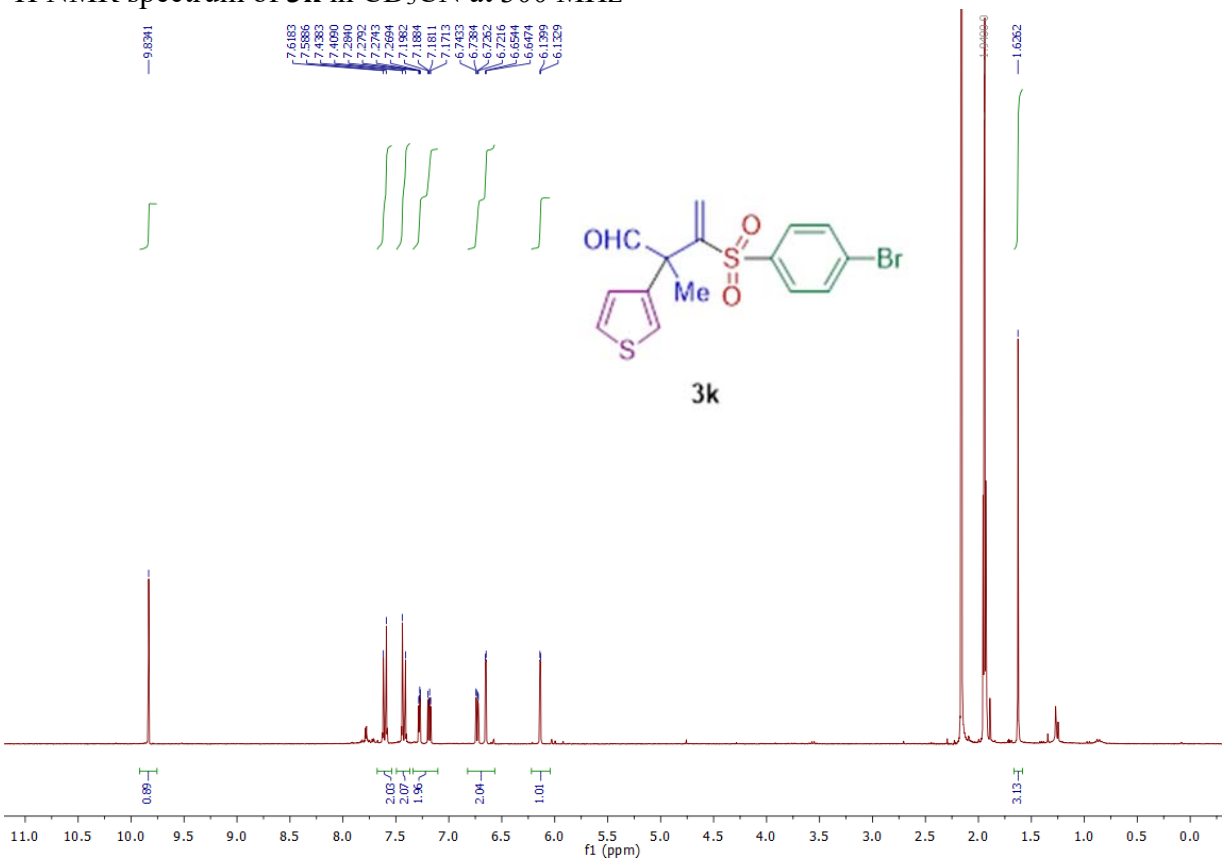
^{1}H NMR spectrum of **3j** in CD_3CN at 300 MHz



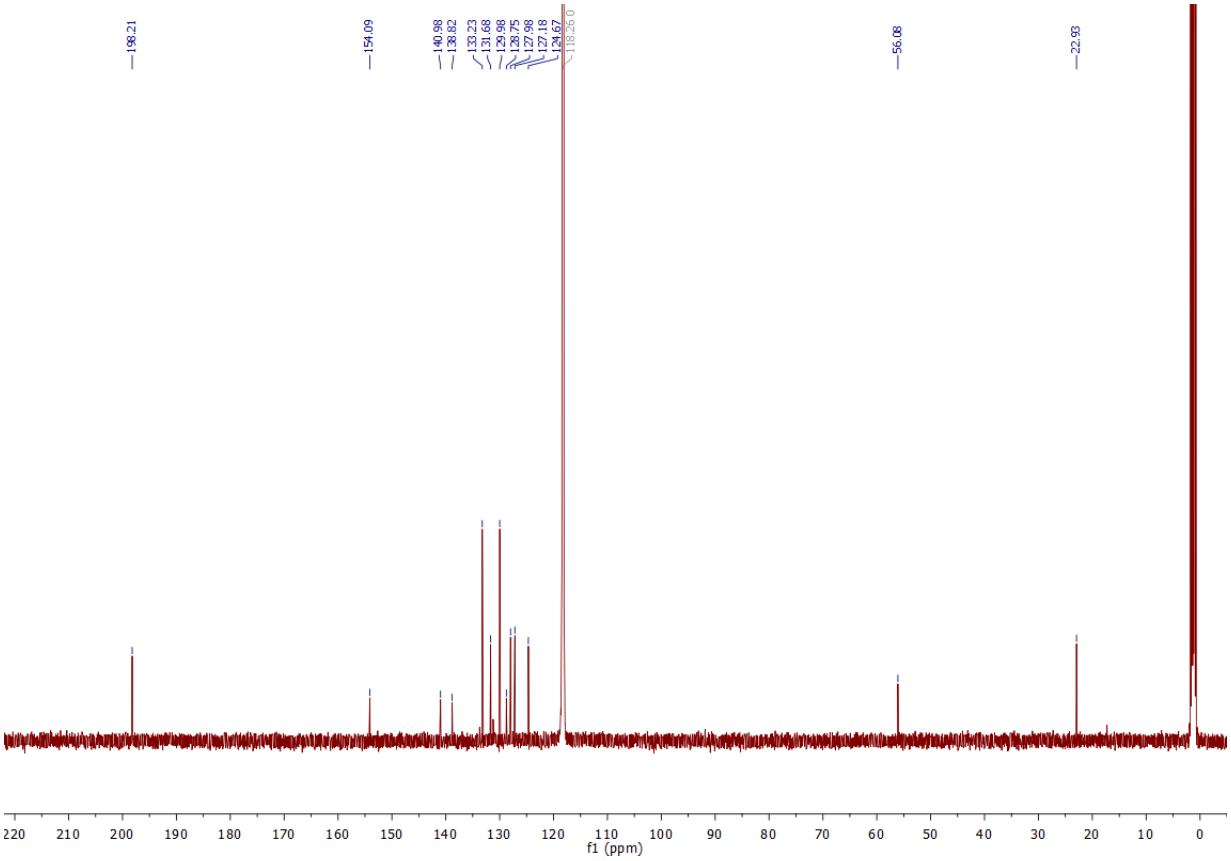
^{13}C NMR spectrum of **3j** in CD_3CN at 75 MHz



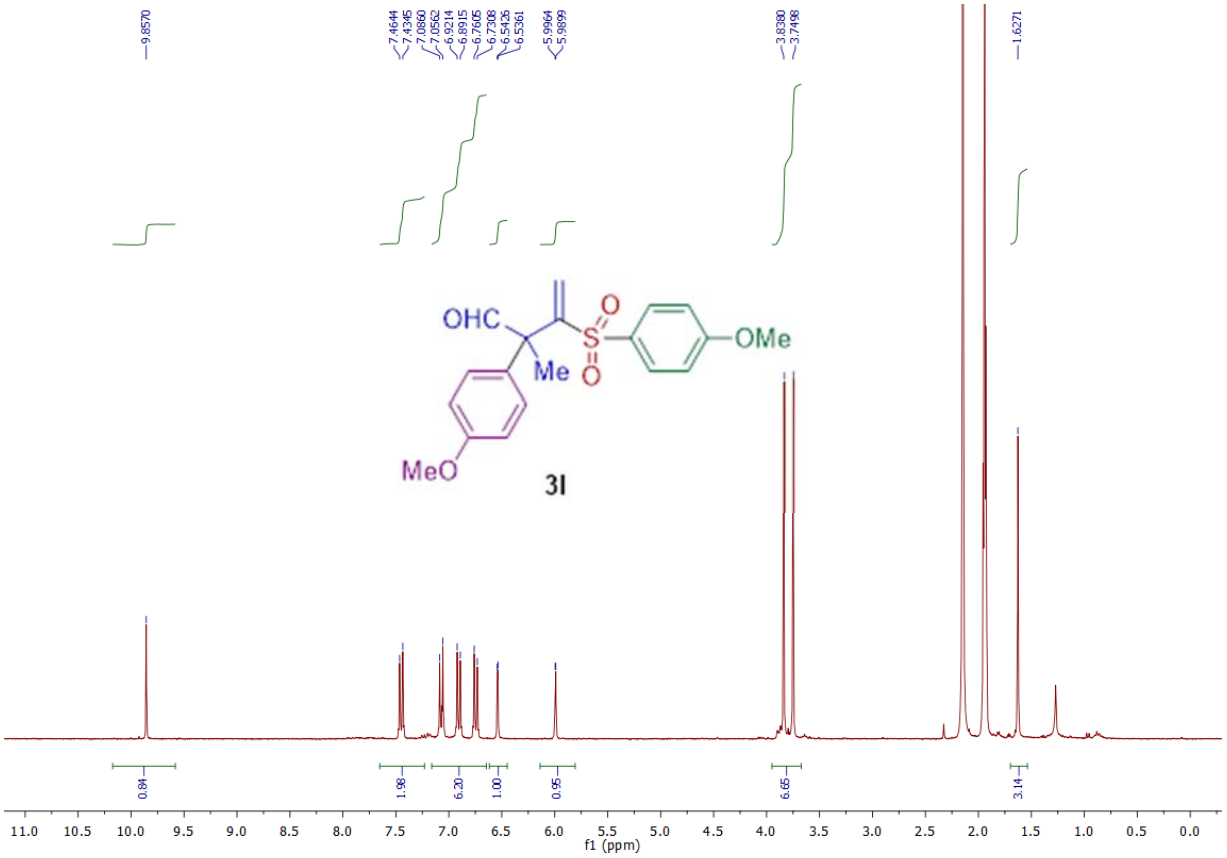
^{1}H NMR spectrum of **3k** in CD_3CN at 300 MHz



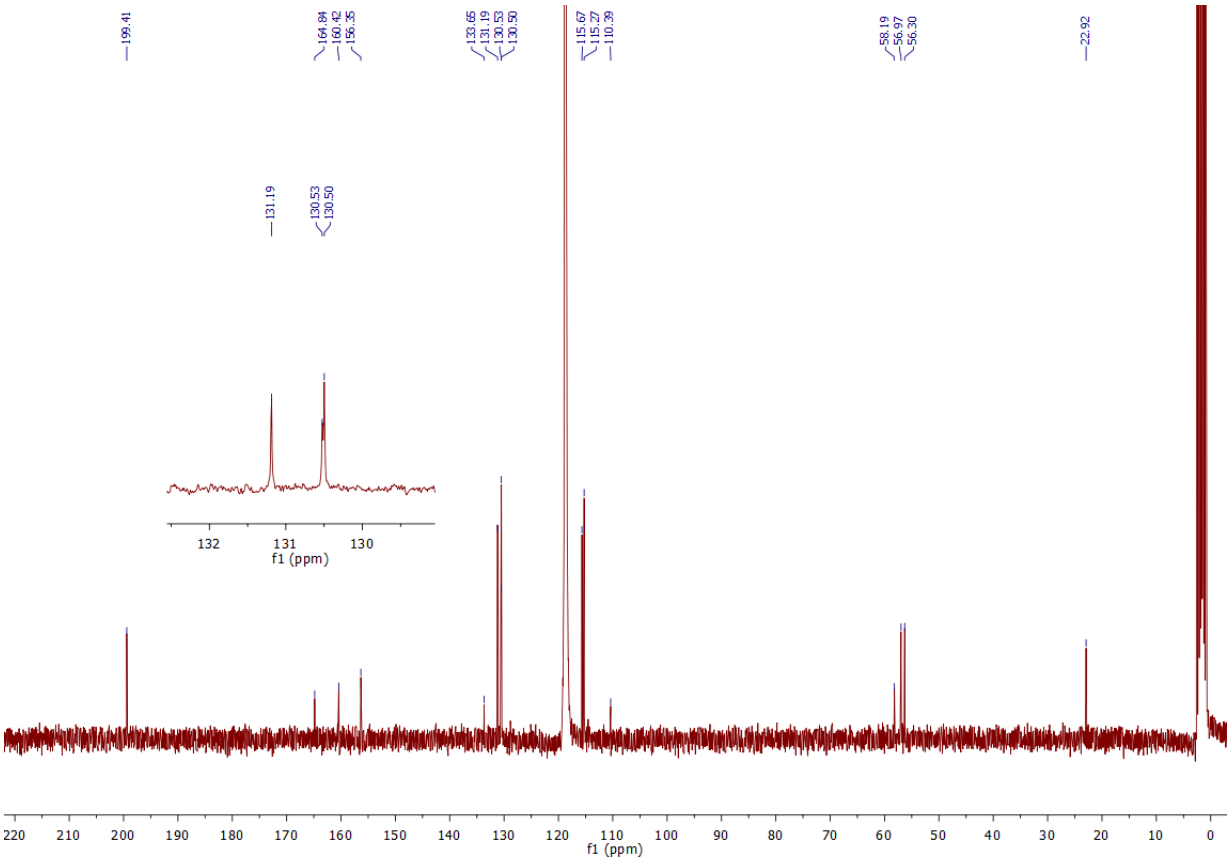
^{13}C NMR spectrum of **3k** in CD_3CN at 125 MHz



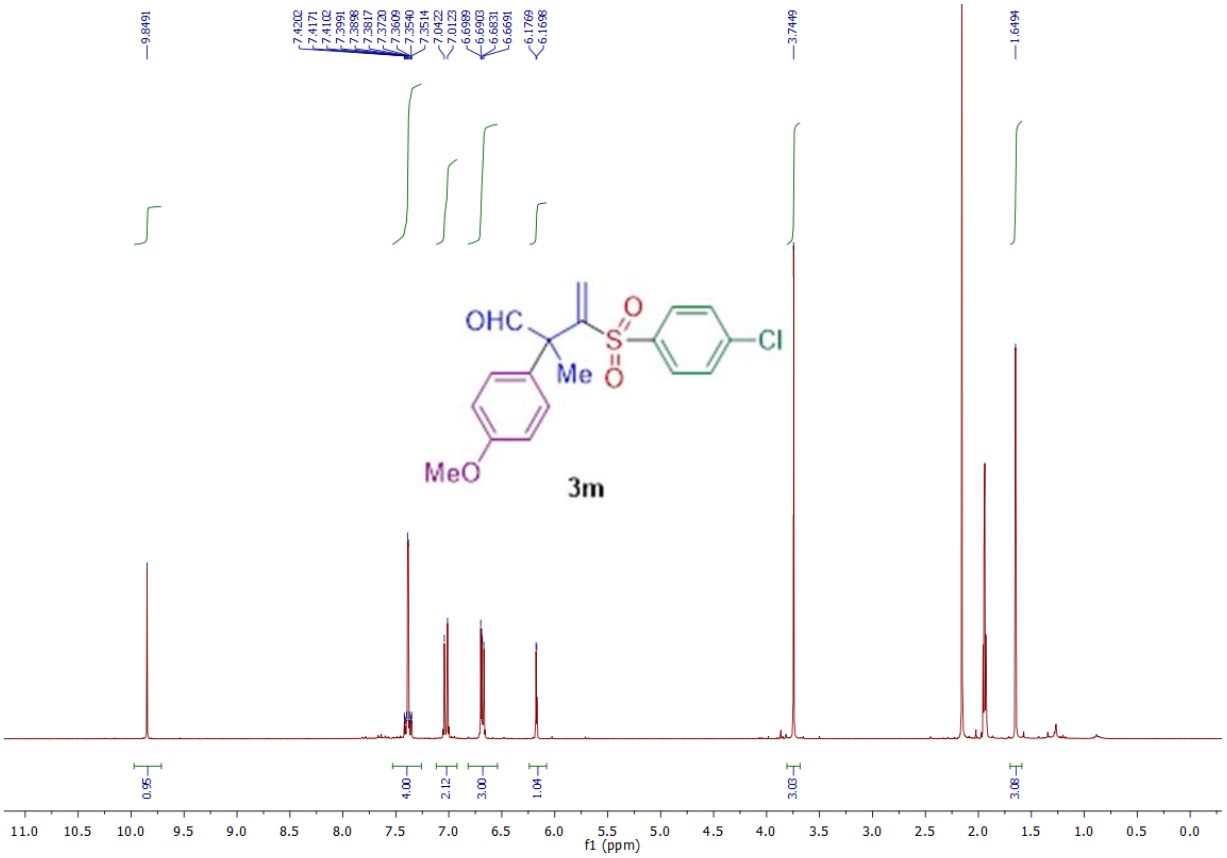
^{1}H NMR spectrum of **3l** in CD_3CN at 300 MHz



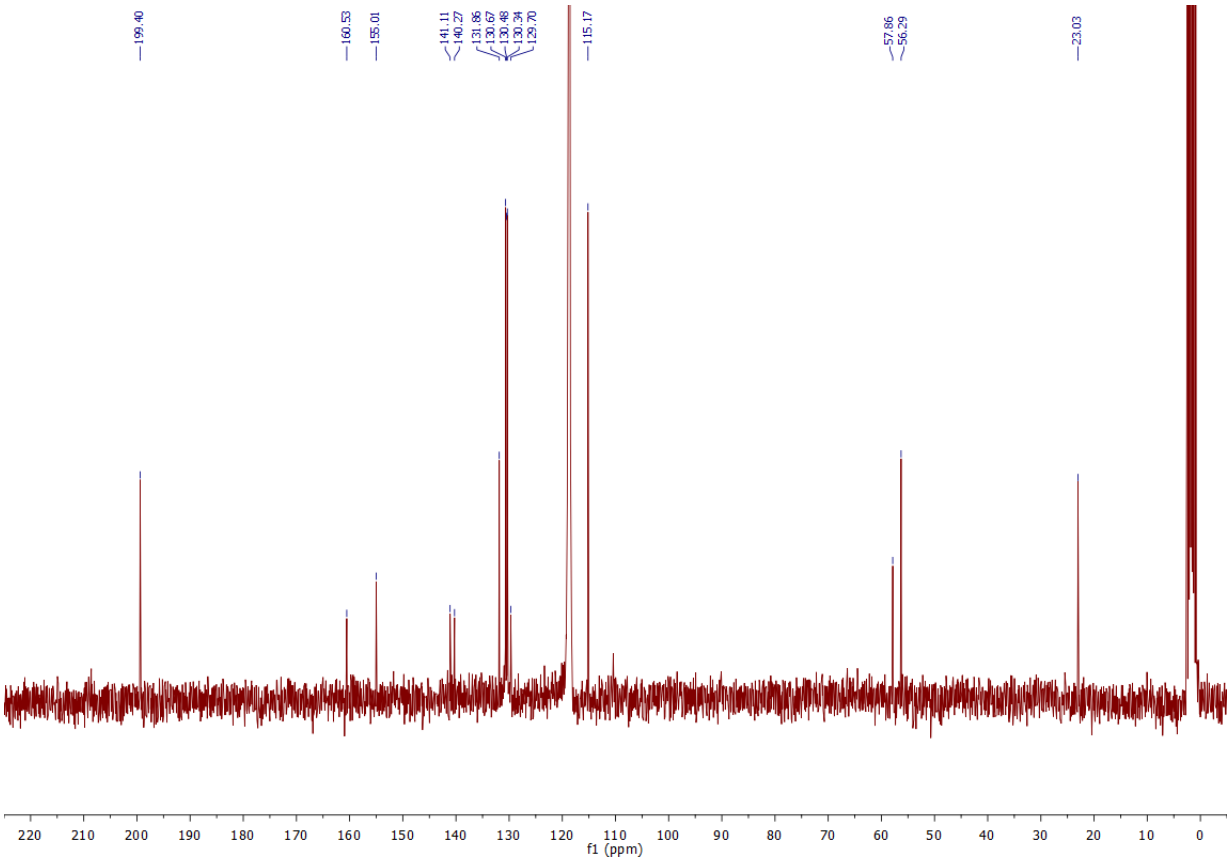
^{13}C NMR spectrum of **3l** in CD_3CN at 75 MHz



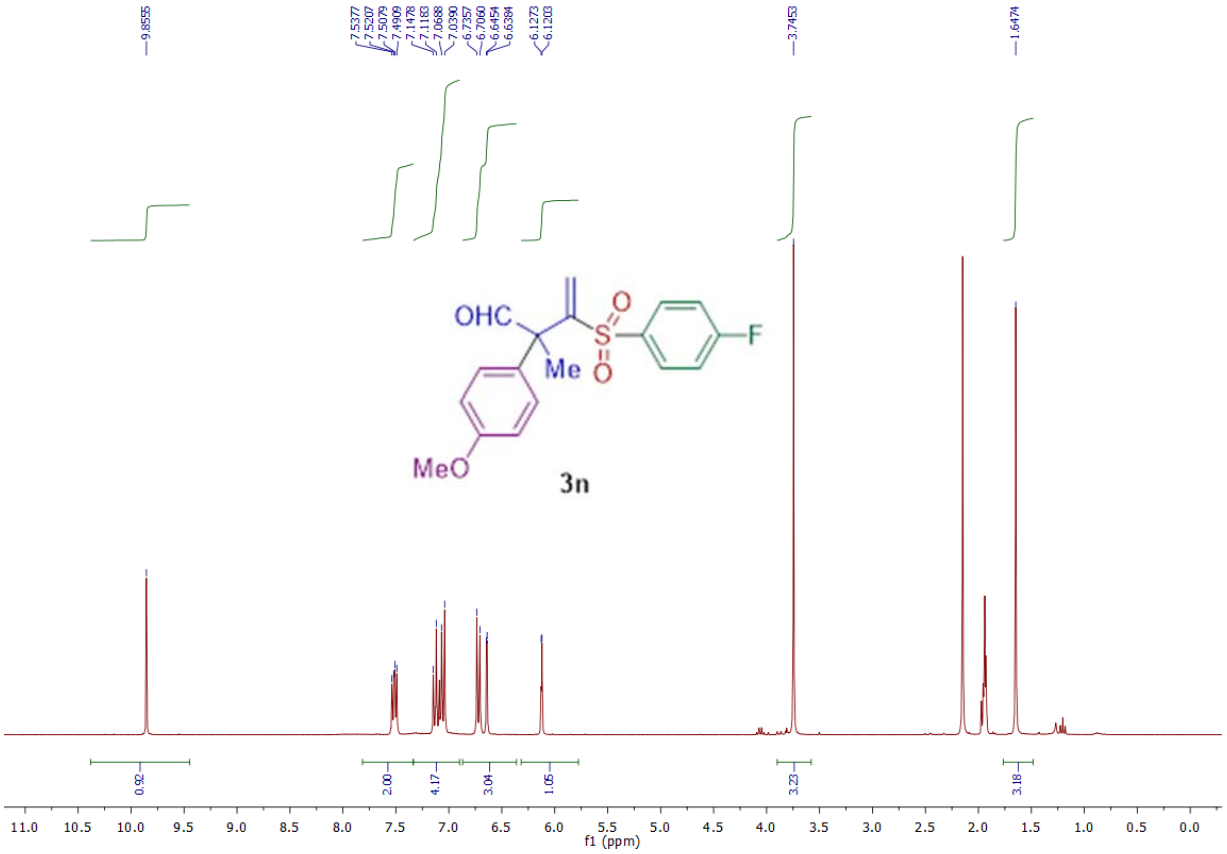
^{1}H NMR spectrum of **3m** in CD_3CN at 300 MHz



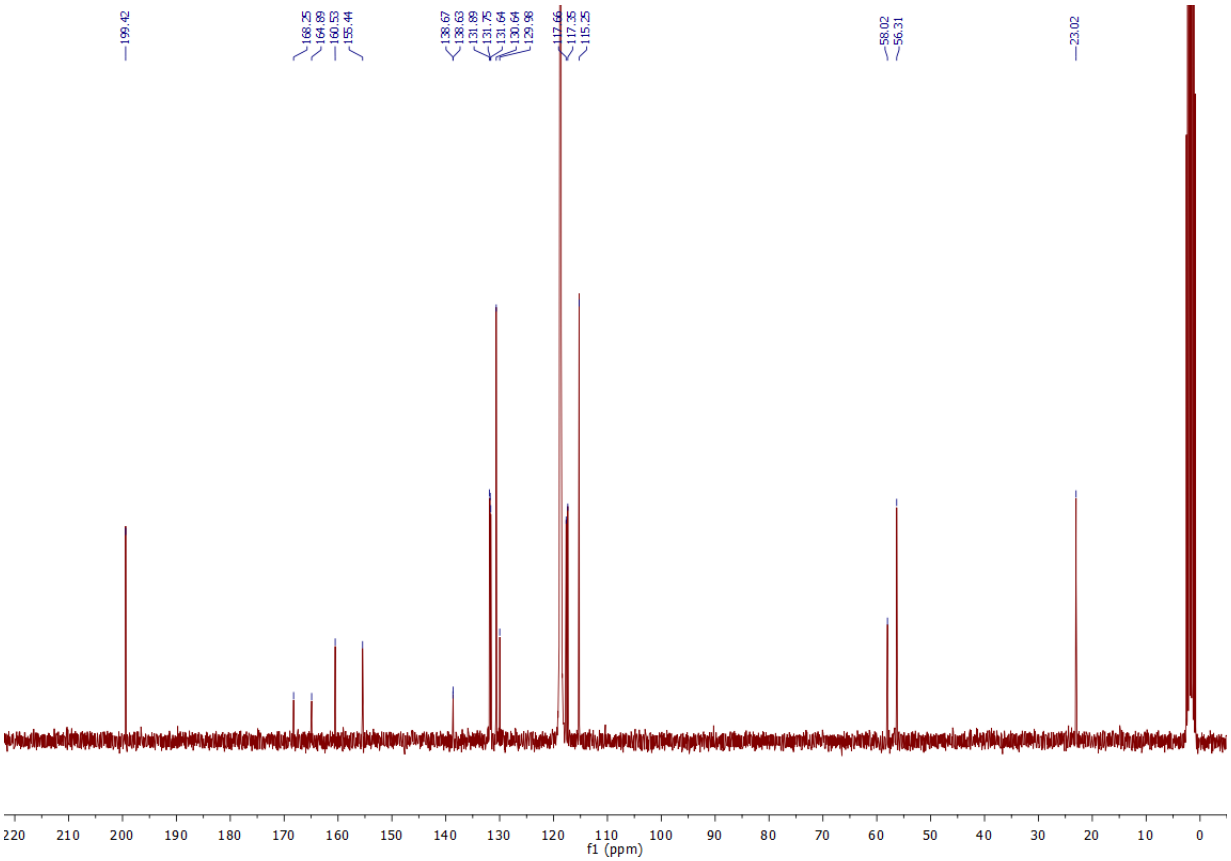
^{13}C NMR spectrum of **3m** in CD_3CN at 75 MHz



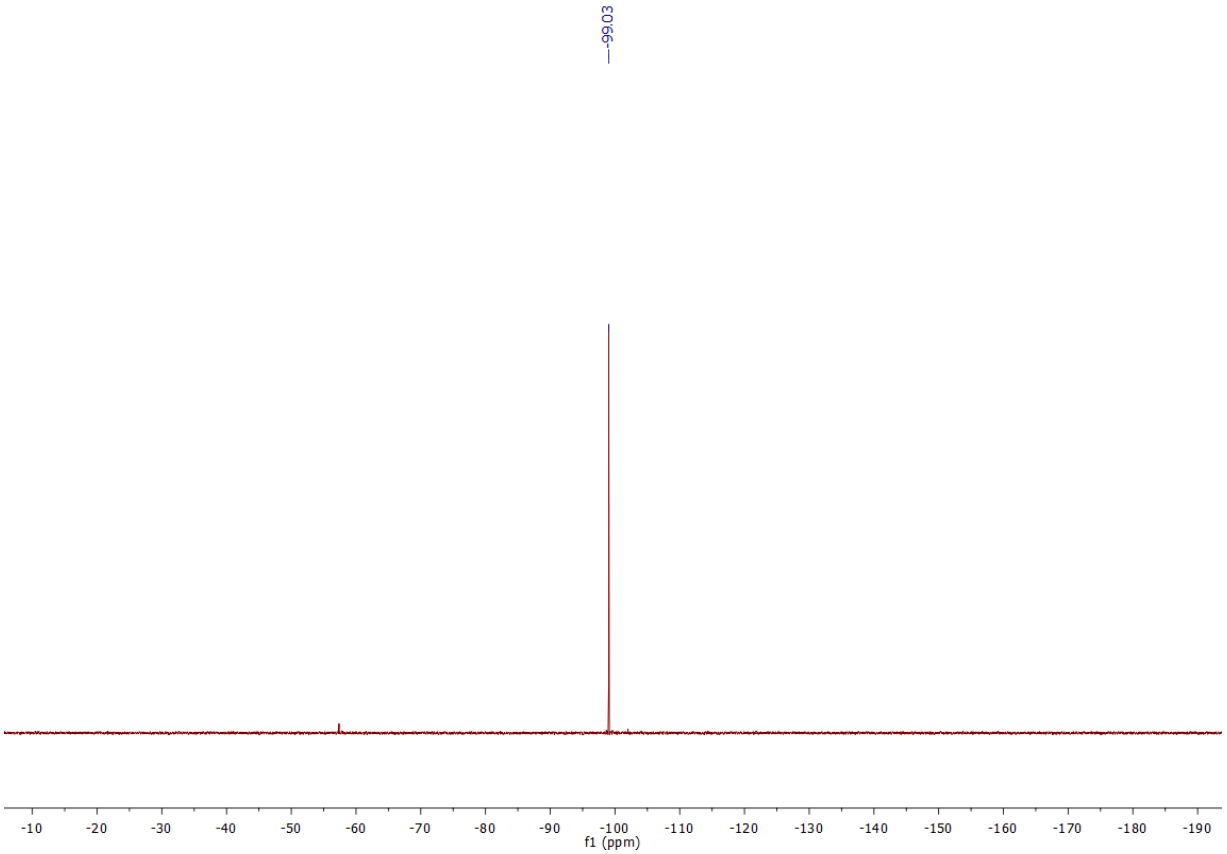
^{1}H NMR spectrum of **3n** in CD_3CN at 300 MHz



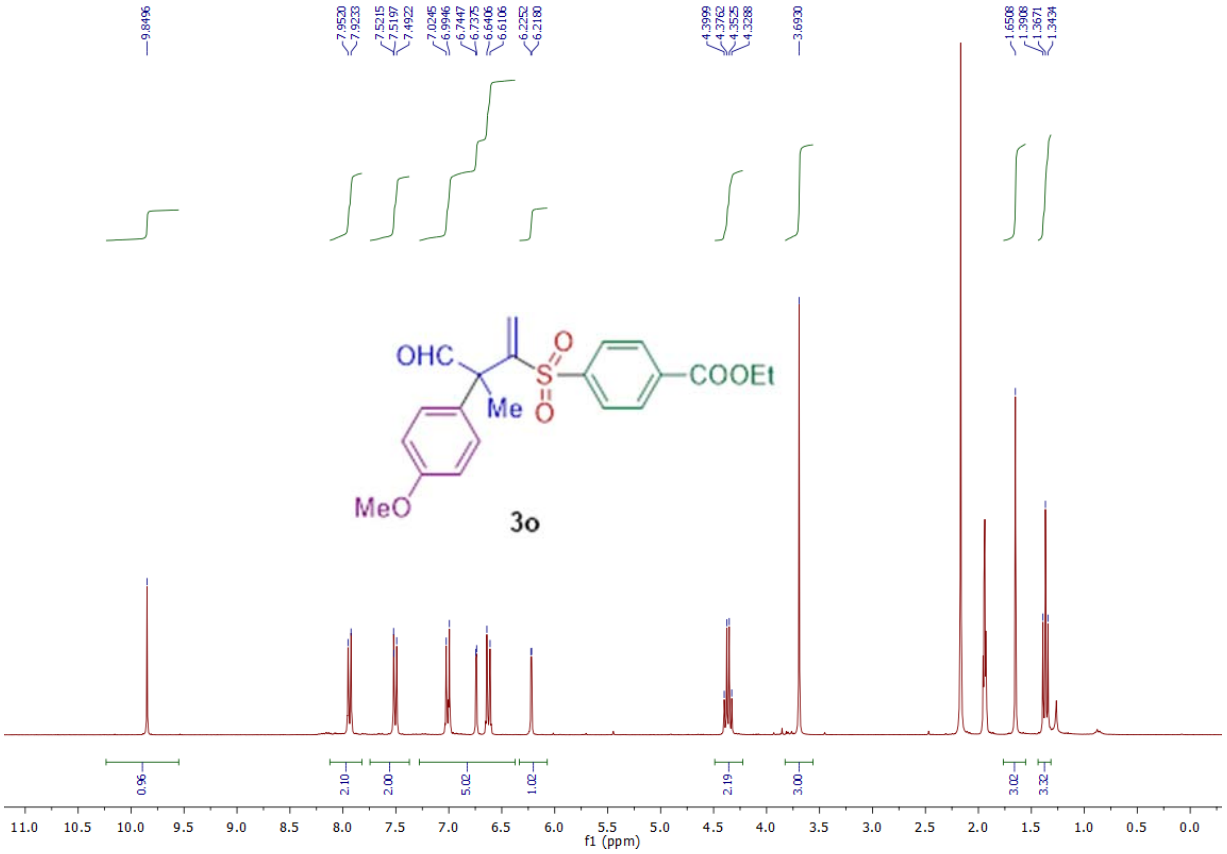
^{13}C NMR spectrum of **3n** in CD_3CN at 75 MHz



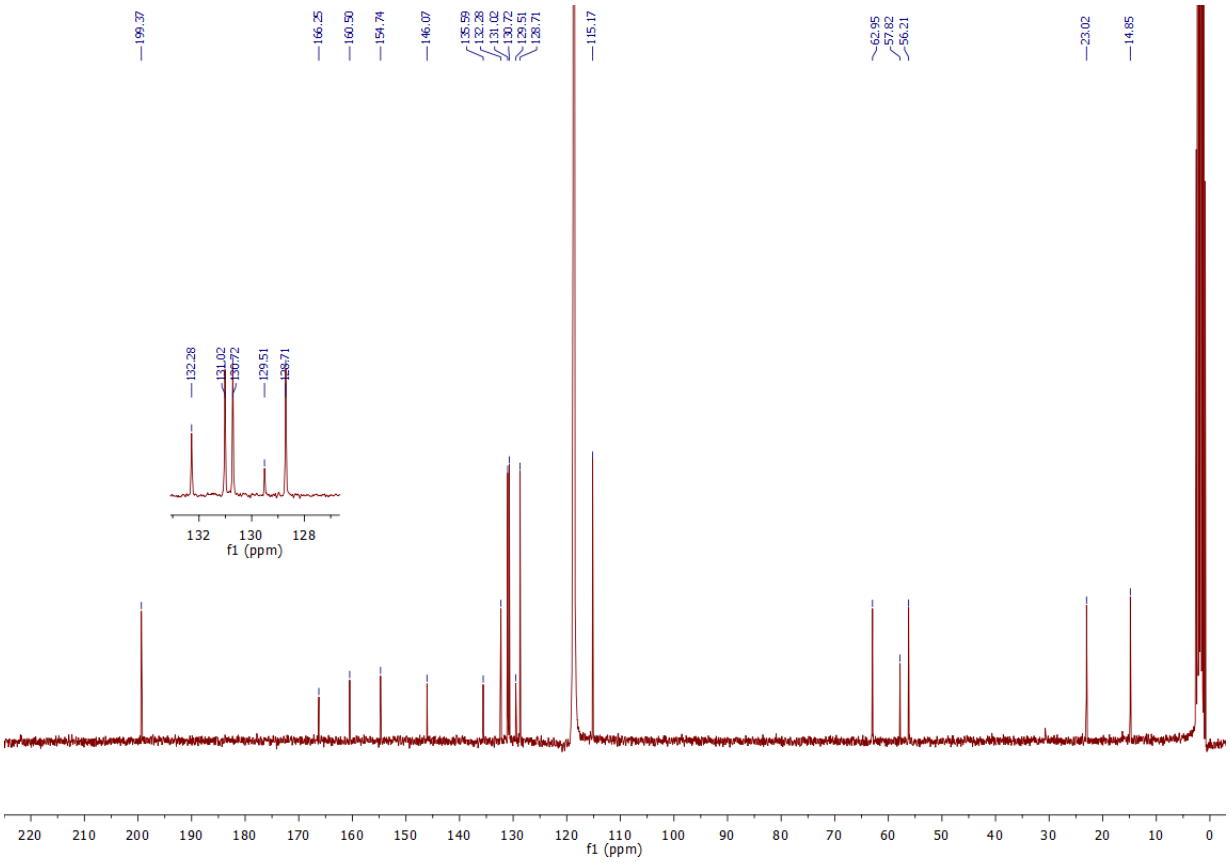
^{19}F NMR spectrum of **3n** in CD_3CN



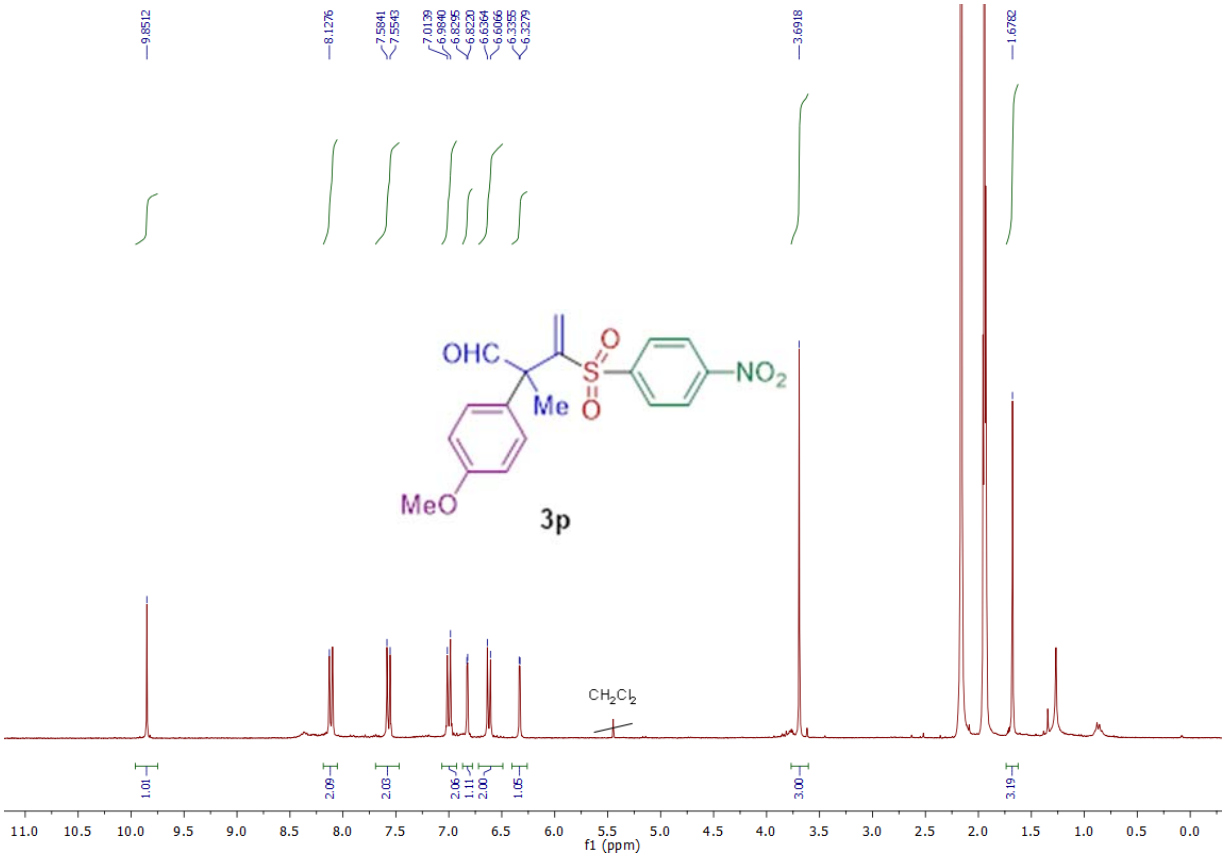
^{1}H NMR spectrum of **3o** in CD_3CN at 300 MHz



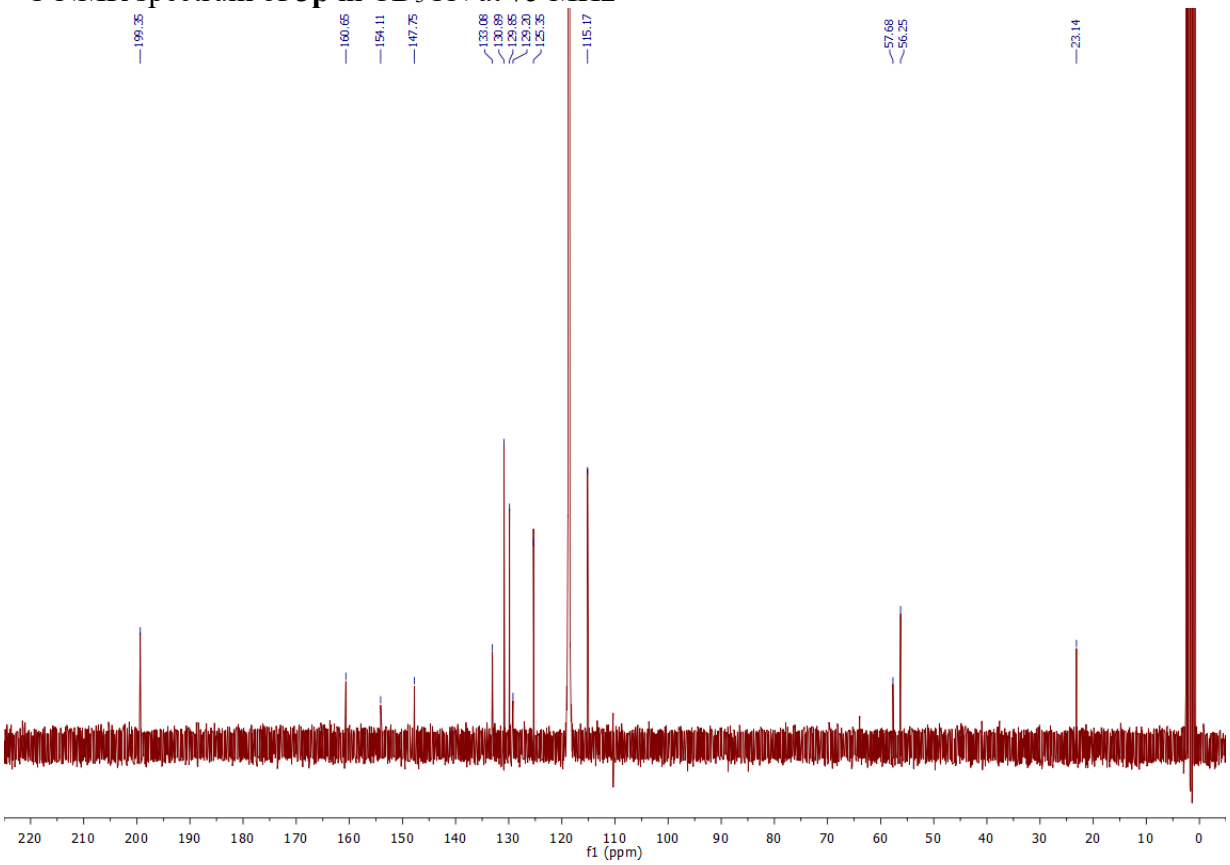
^{13}C NMR spectrum of **3o** in CD_3CN at 75 MHz



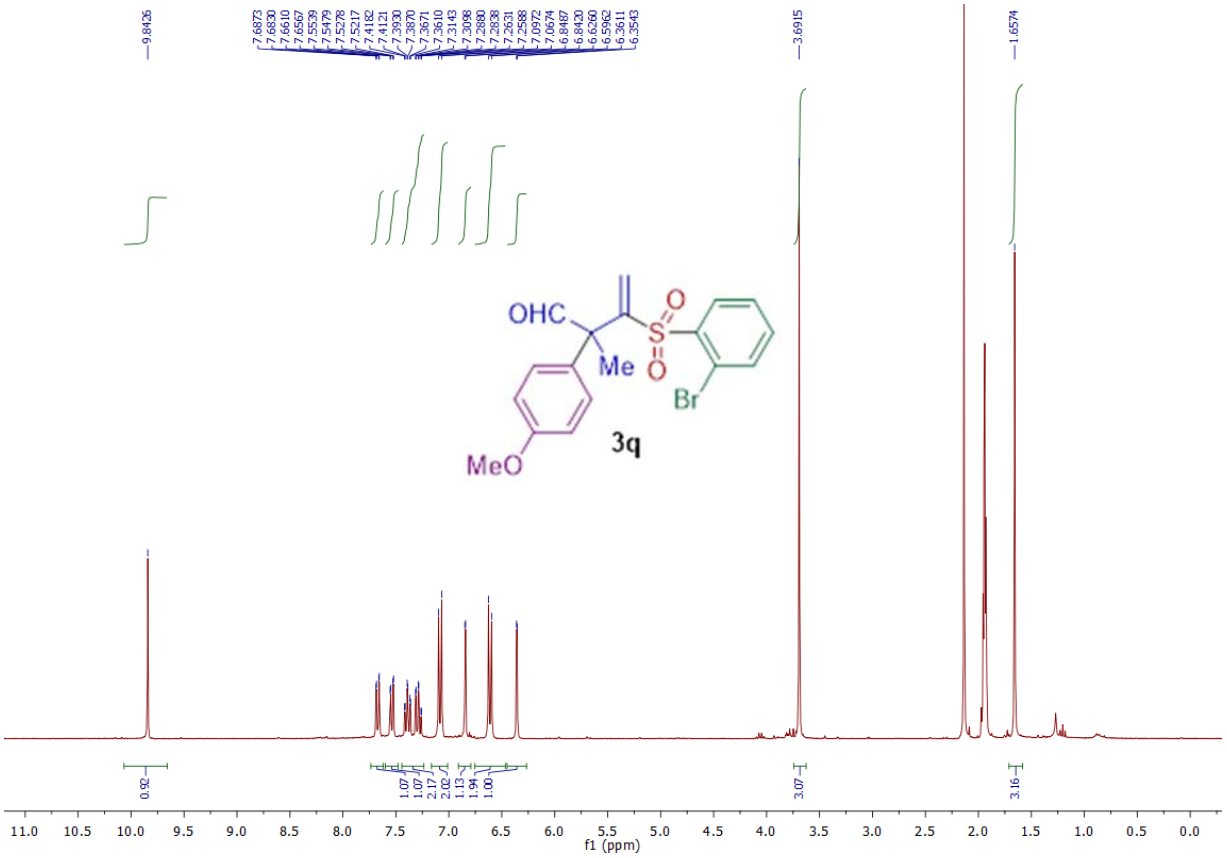
^{1}H NMR spectrum of **3p** in CD_3CN at 300 MHz



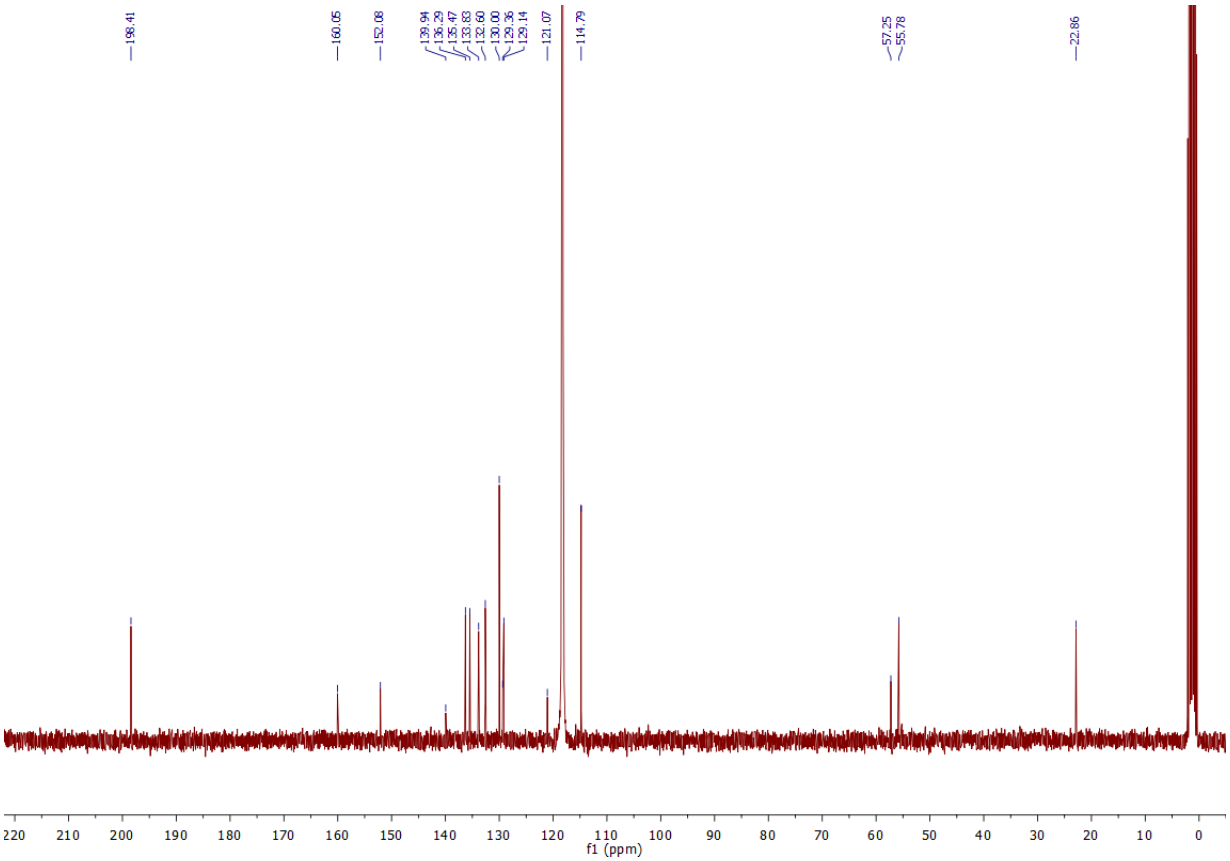
^{13}C NMR spectrum of **3p** in CD_3CN at 75 MHz



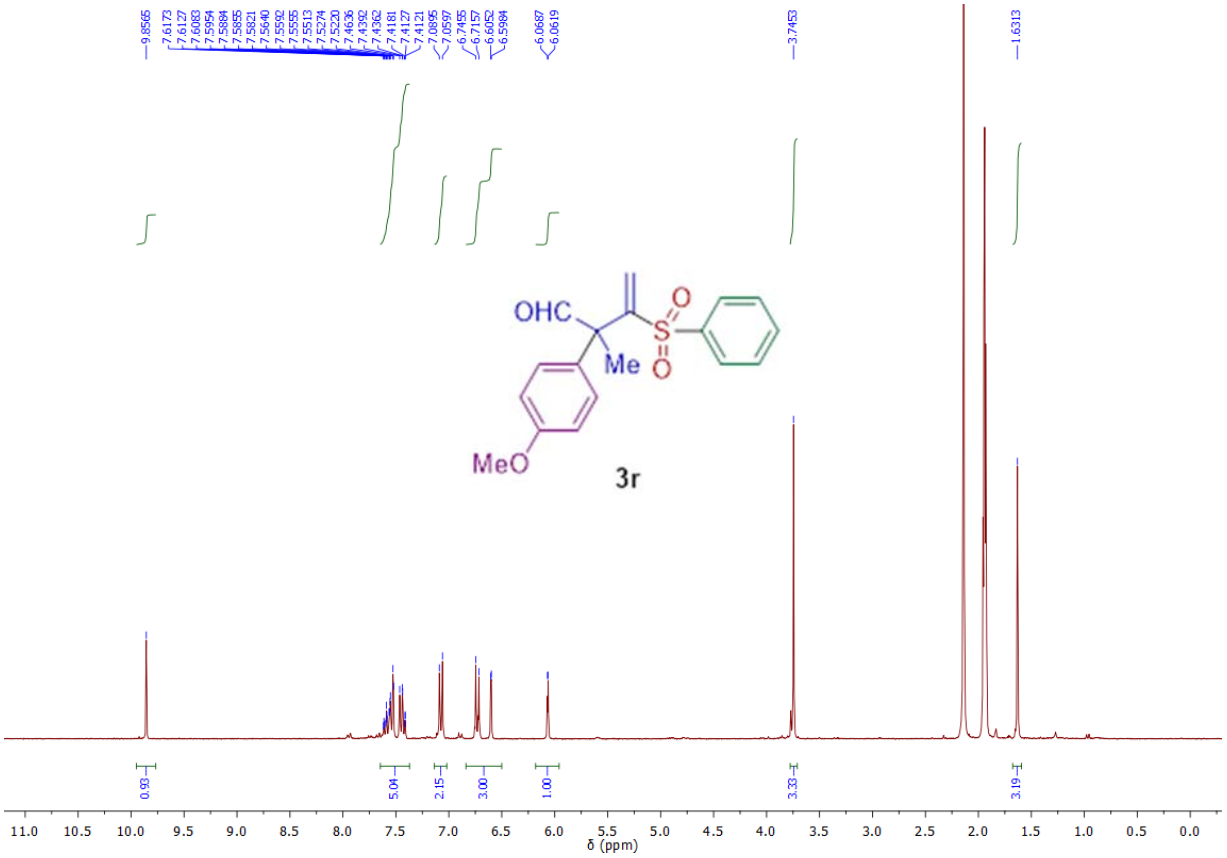
^{1}H NMR spectrum of **3q** in CD_3CN at 300 MHz



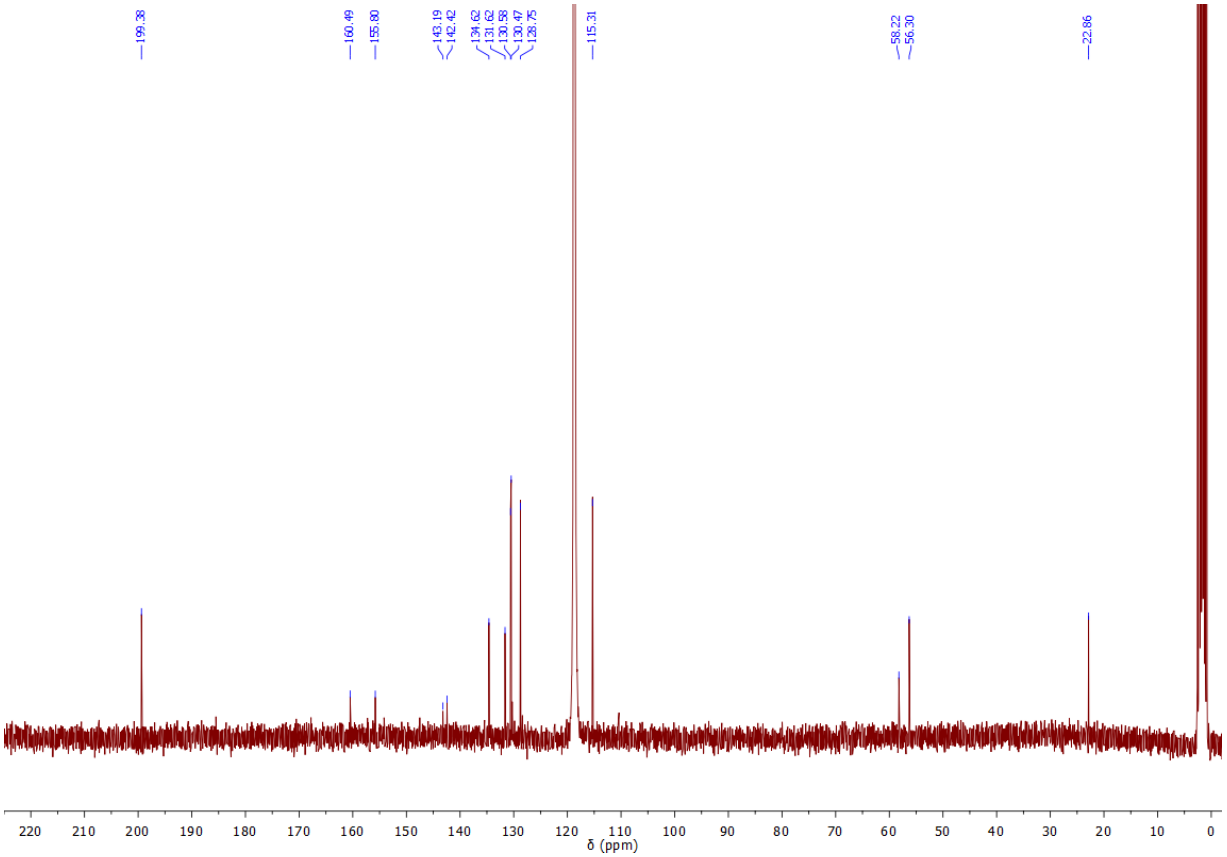
^{13}C NMR spectrum of **3q** in CD_3CN at 75 MHz



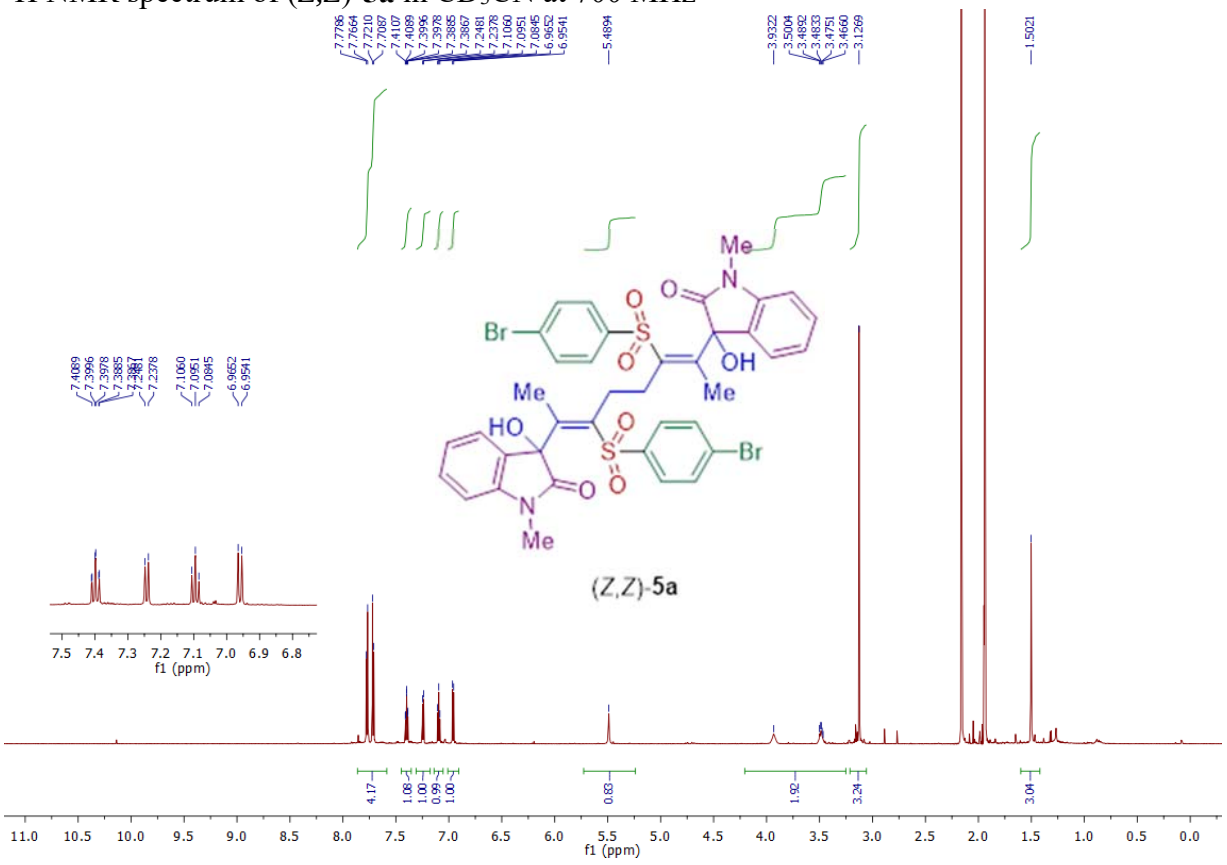
^{1}H NMR spectrum of **3r** in CD_3CN at 300 MHz



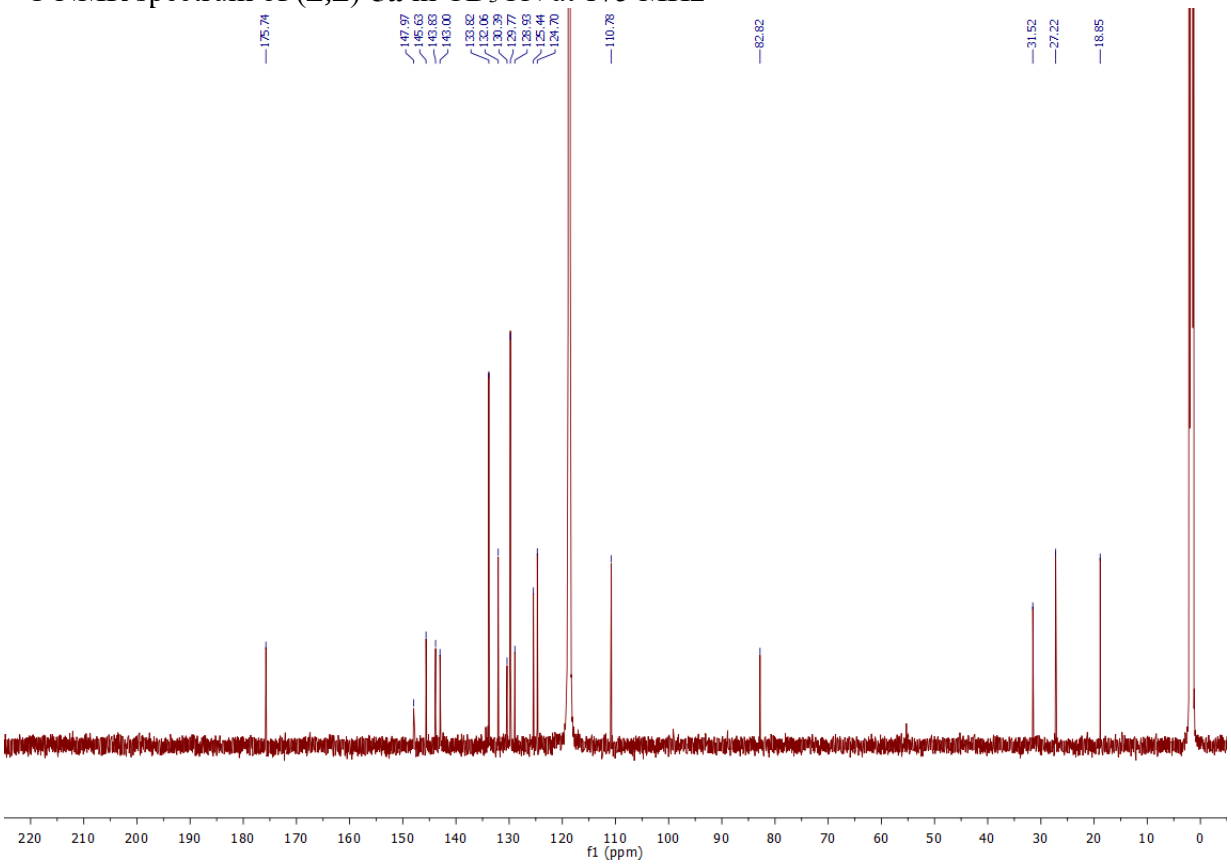
^{13}C NMR spectrum of **3r** in CD_3CN at 75 MHz



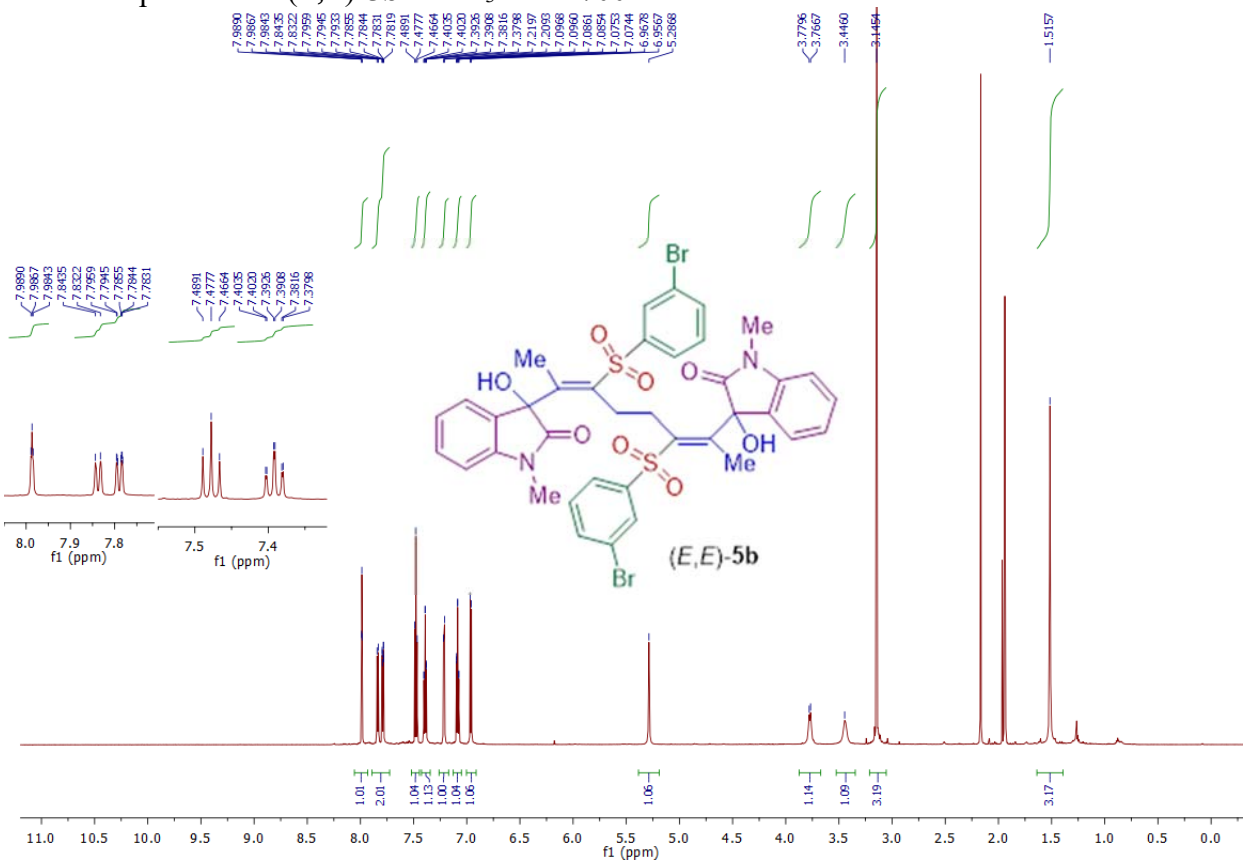
^{1}H NMR spectrum of (*Z*,*Z*)-**5a** in CD_3CN at 700 MHz



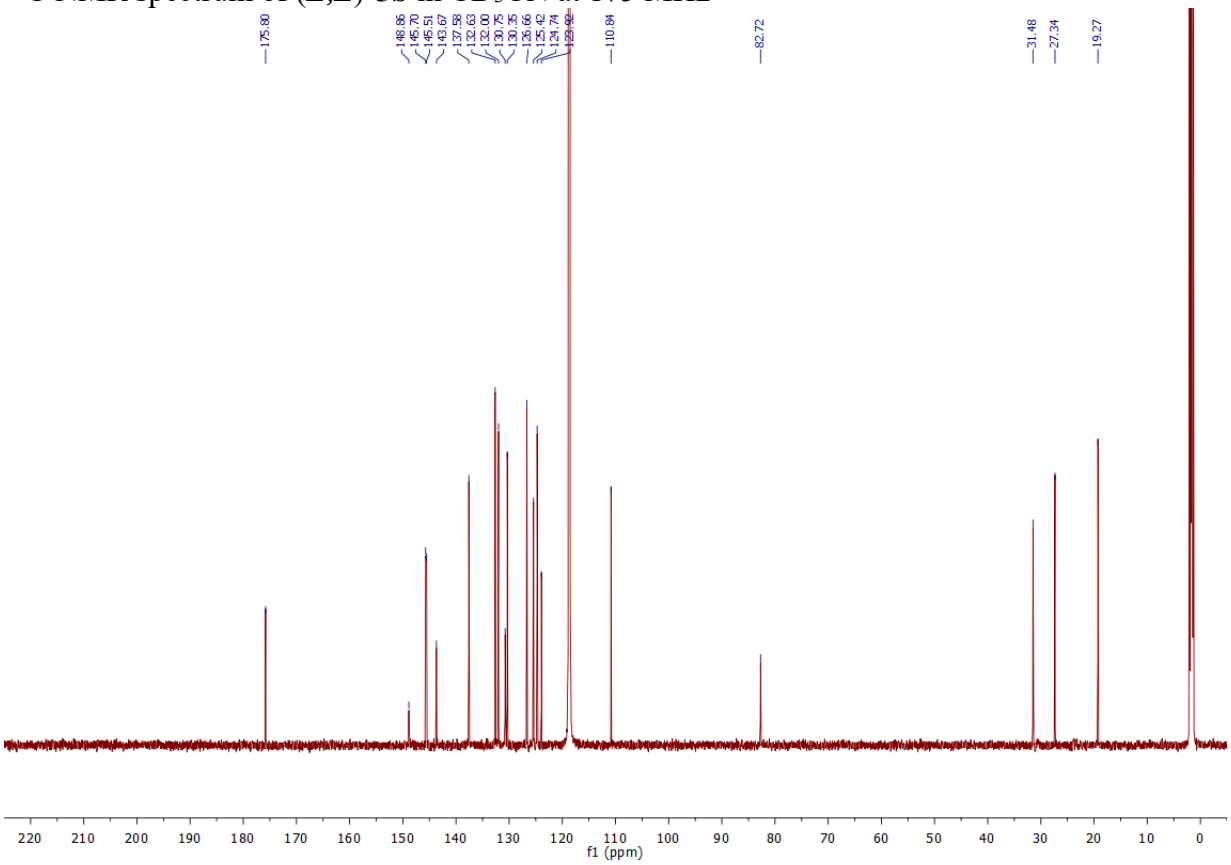
^{13}C NMR spectrum of (*Z*,*Z*)-**5a** in CD_3CN at 175 MHz



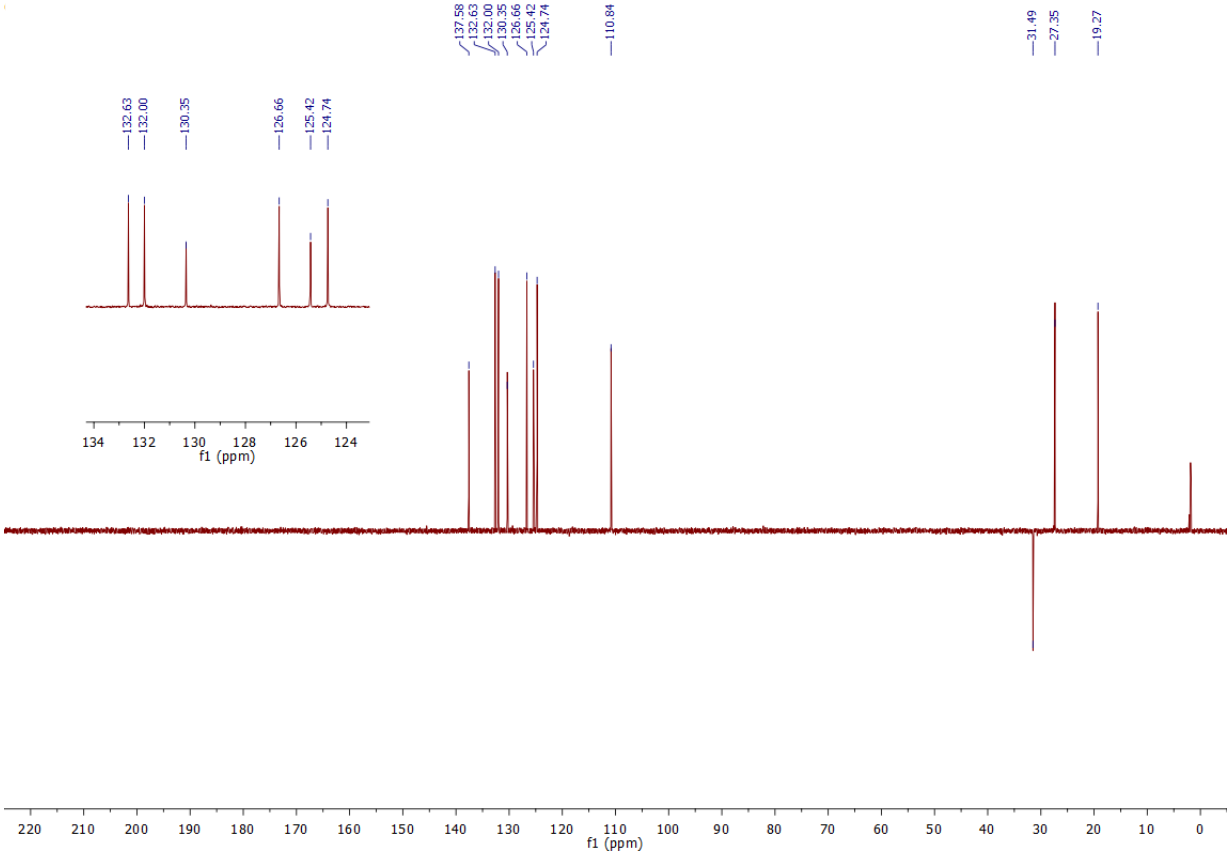
^{1}H NMR spectrum of (*E*,*E*)-**5b** in CD_3CN at 700 MHz



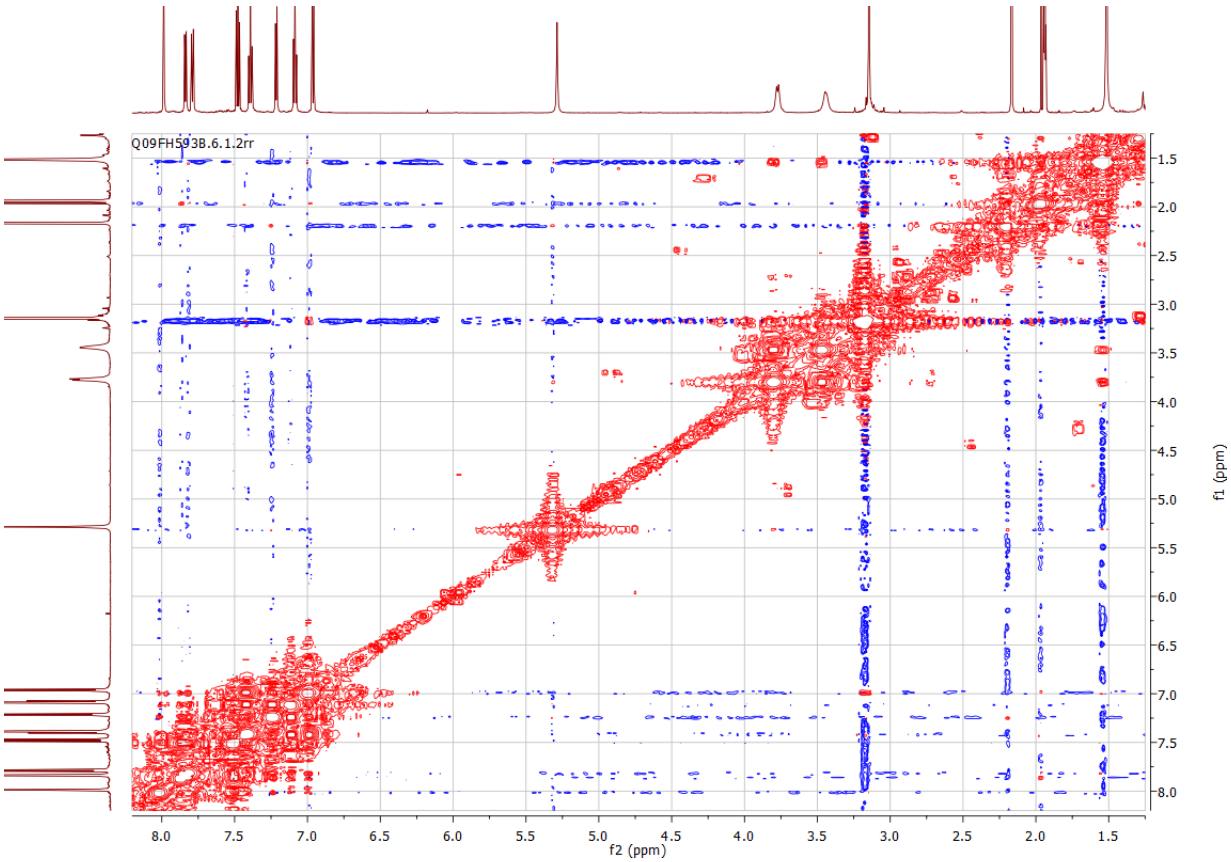
^{13}C NMR spectrum of (*E*,*E*)-**5b** in CD_3CN at 175 MHz



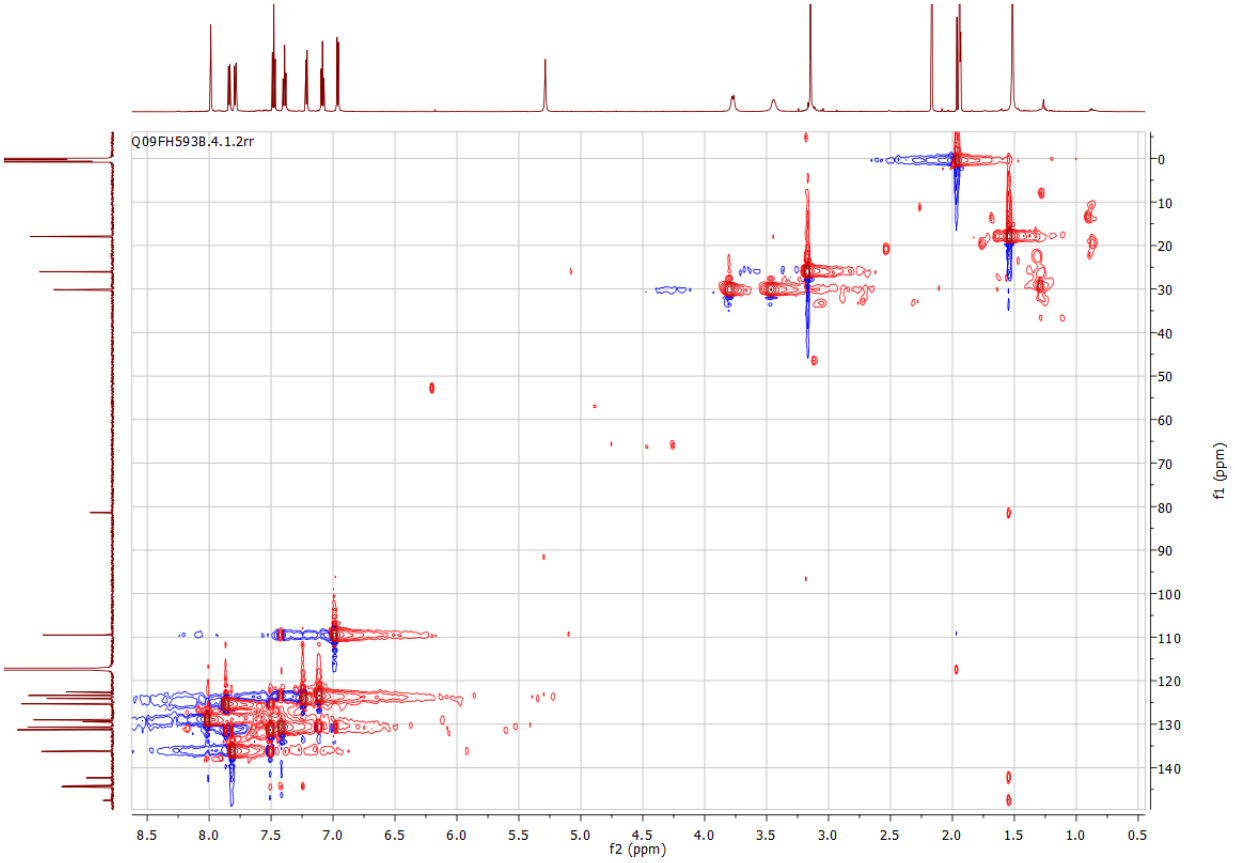
DEPT NMR spectrum of (*E*,*E*)-**5b** in CD_3CN at 175 MHz



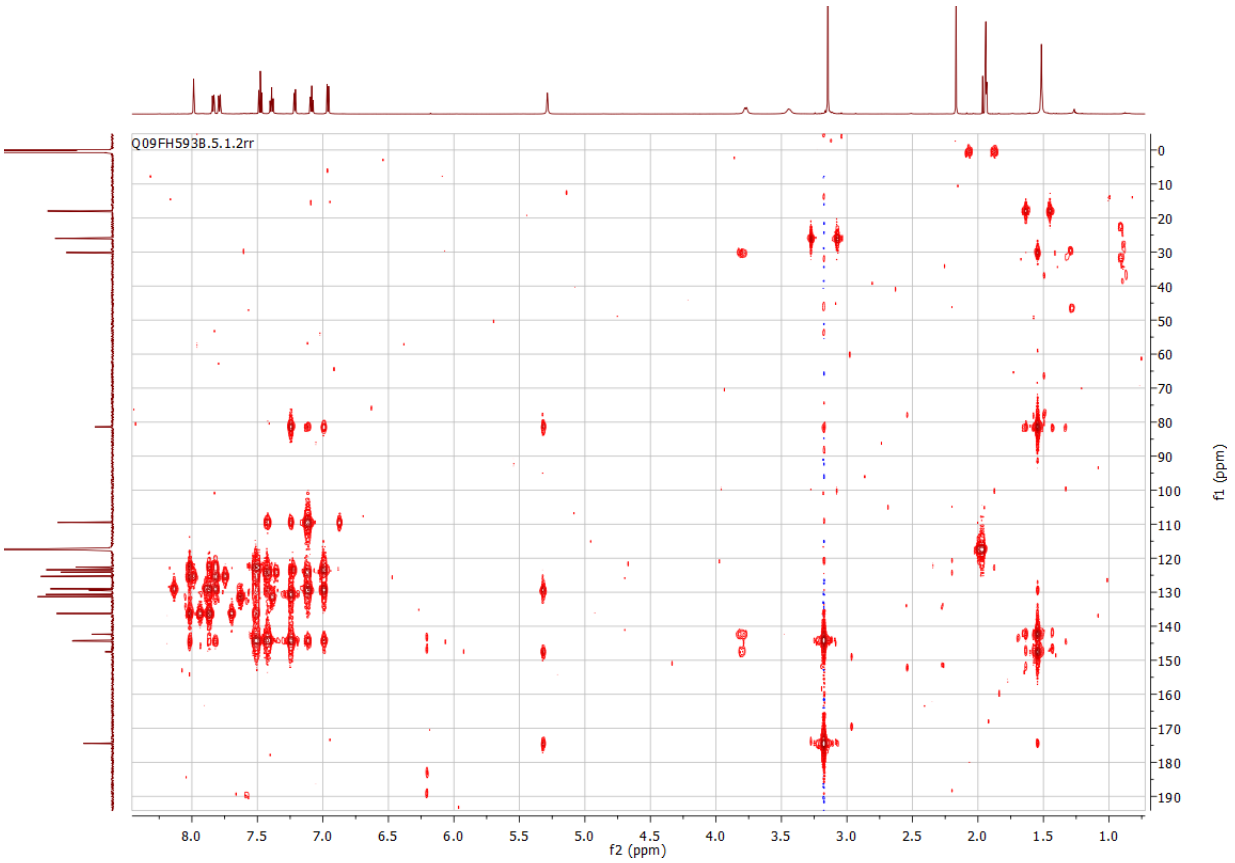
Two-dimensional COSY NMR spectrum ^1H-^1H of (*E*,*E*)-**5b** in CD_3CN at 700 MHz



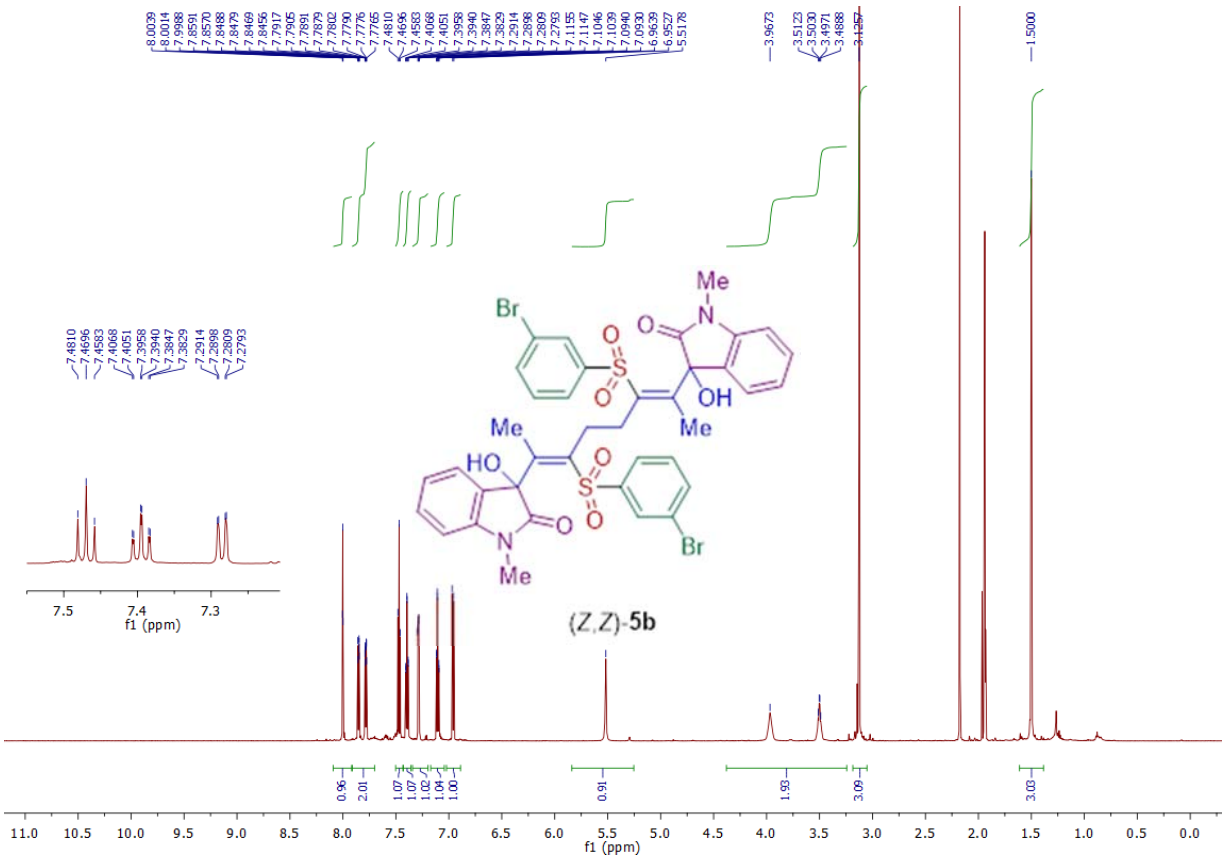
Two-dimensional HSQC NMR spectrum ^{1}H-^{13}C of (*E*,*E*)-**5b** in CD_3CN



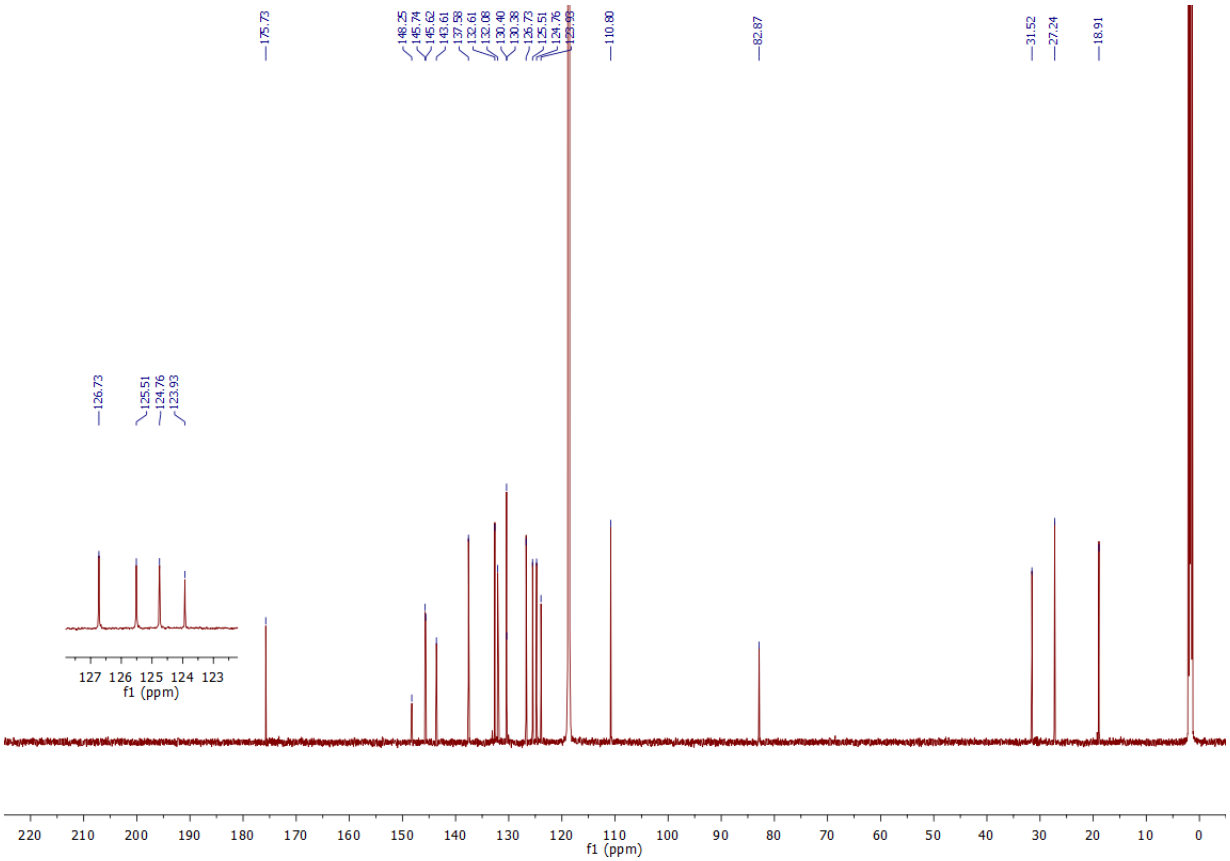
Two-dimensional HMBC NMR spectrum ^{1}H-^{13}C of (*E*,*E*)-**5b** in CD_3CN



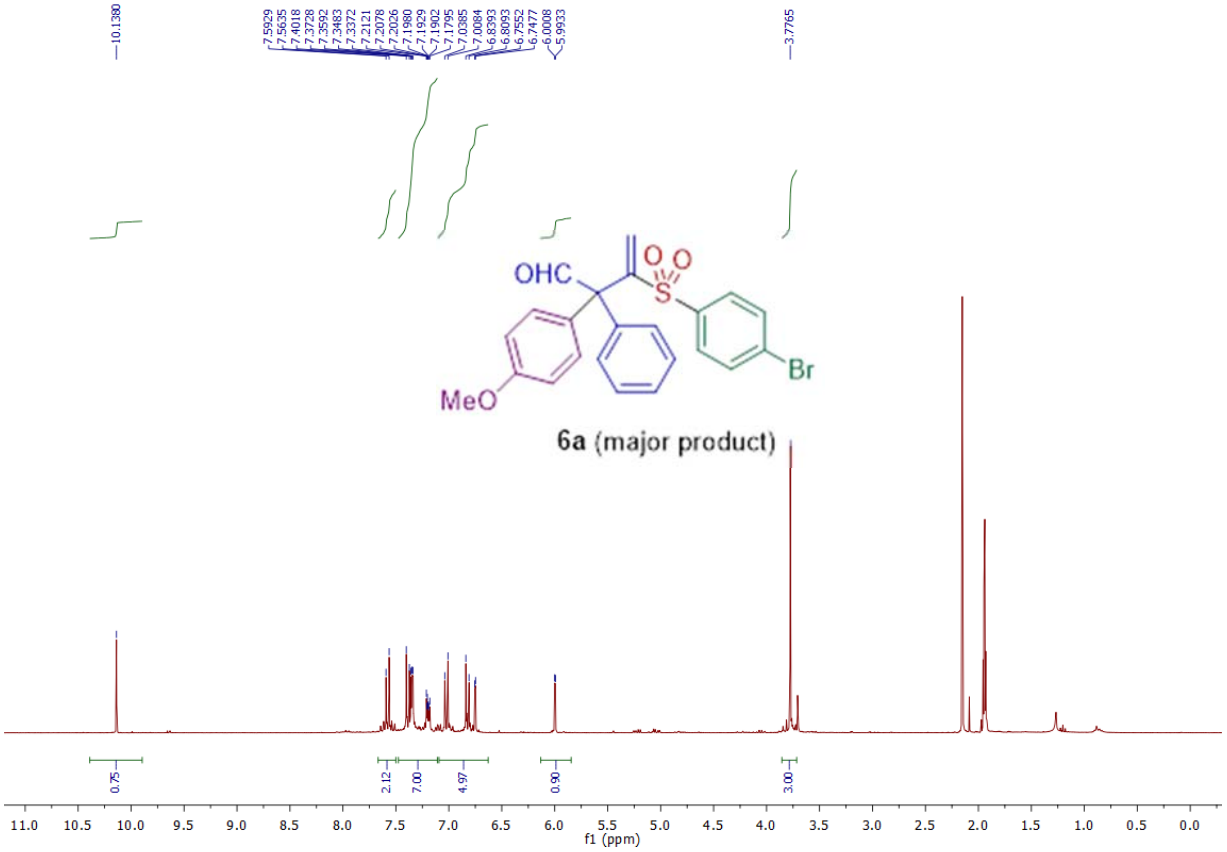
^{1}H NMR spectrum of (*Z*,*Z*)-**5b** in CD_3CN at 700 MHz



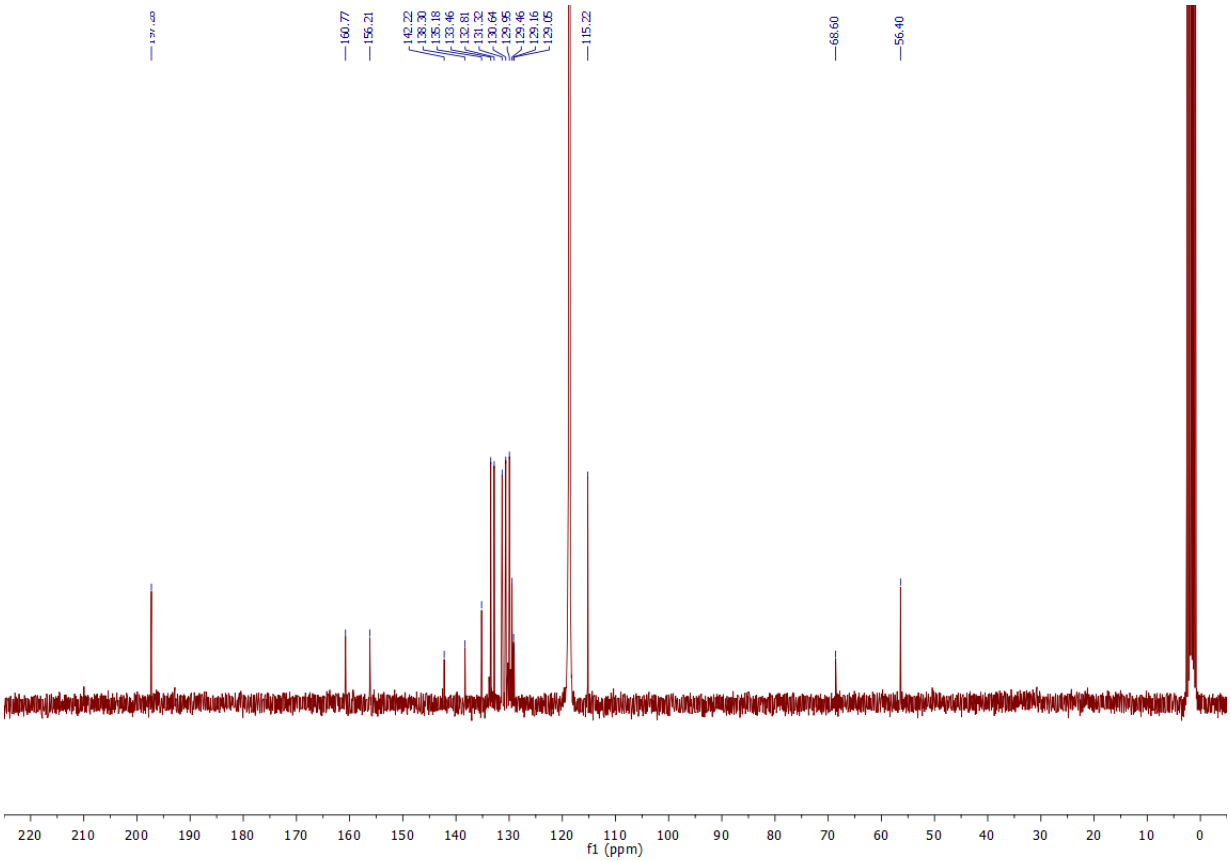
^{13}C NMR spectrum of (*Z*,*Z*)-**5b** in CD_3CN at 175 MHz



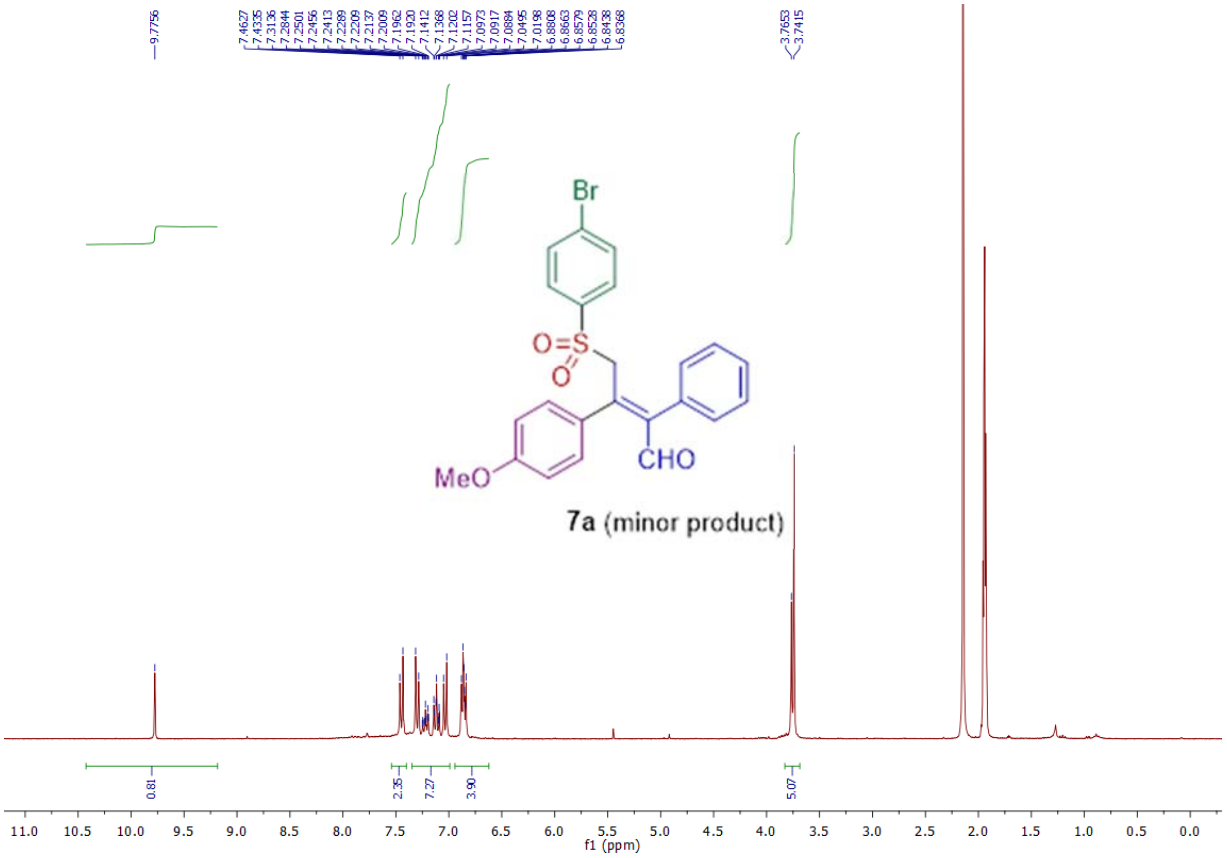
^{1}H NMR spectrum of **6a** in CD_3CN at 300 MHz



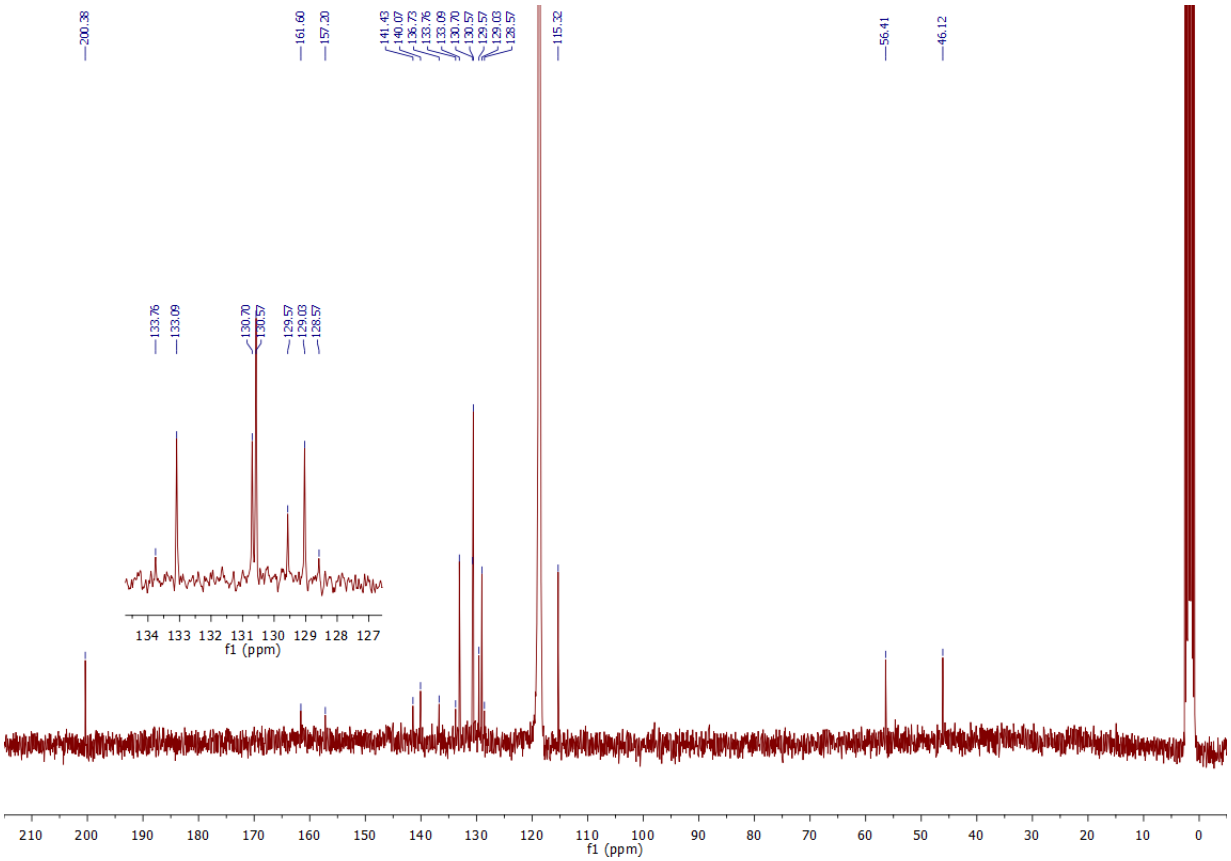
^{13}C NMR spectrum of **6a** in CD_3CN at 75 MHz



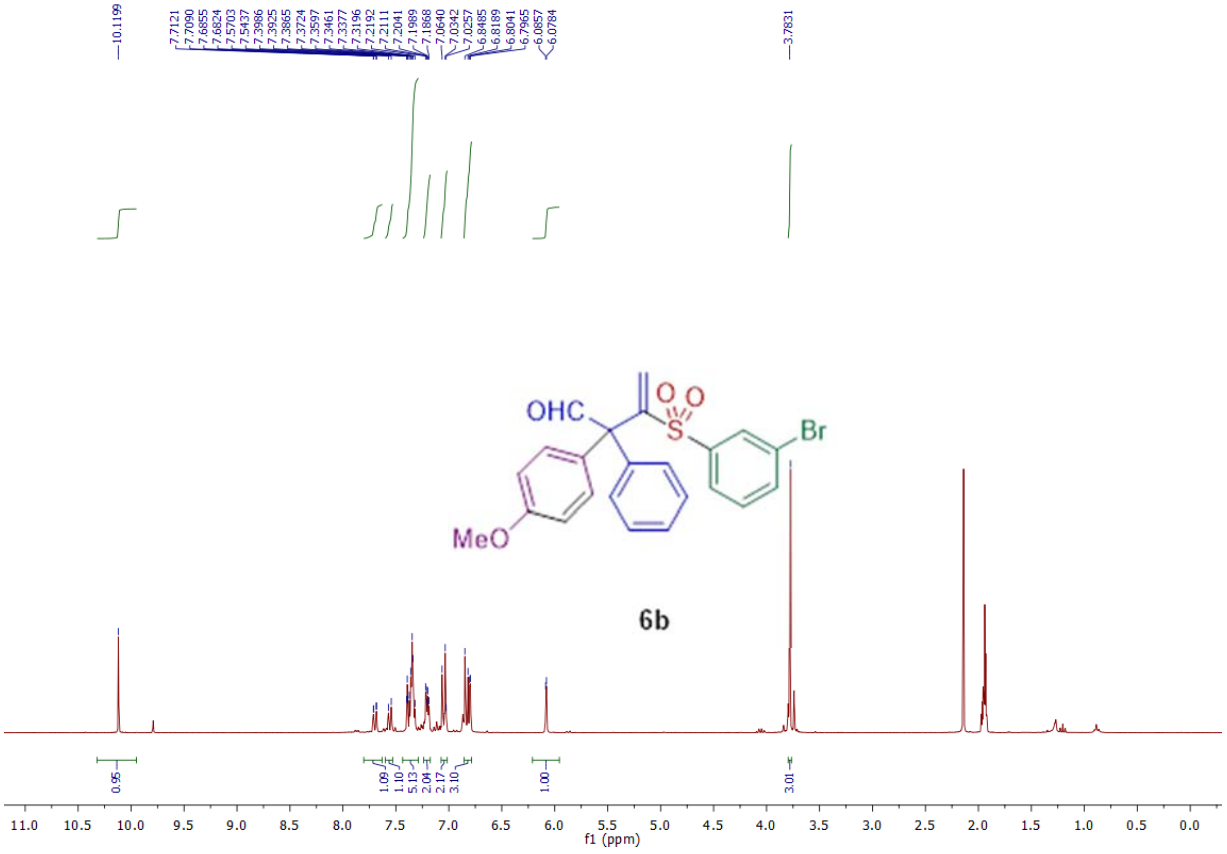
^{1}H NMR spectrum of **7a** in CD_3CN at 300 MHz



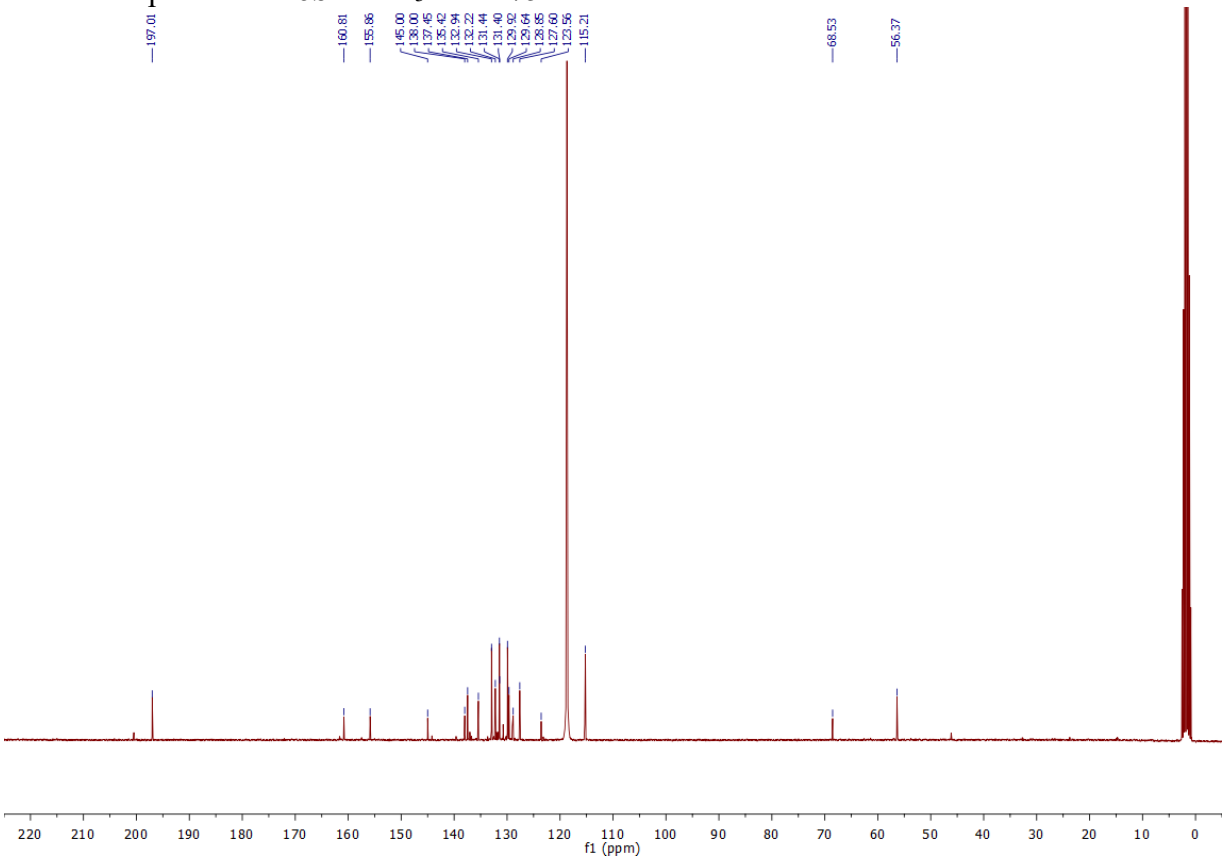
^{13}C NMR spectrum of **7a** in CD_3CN at 75 MHz



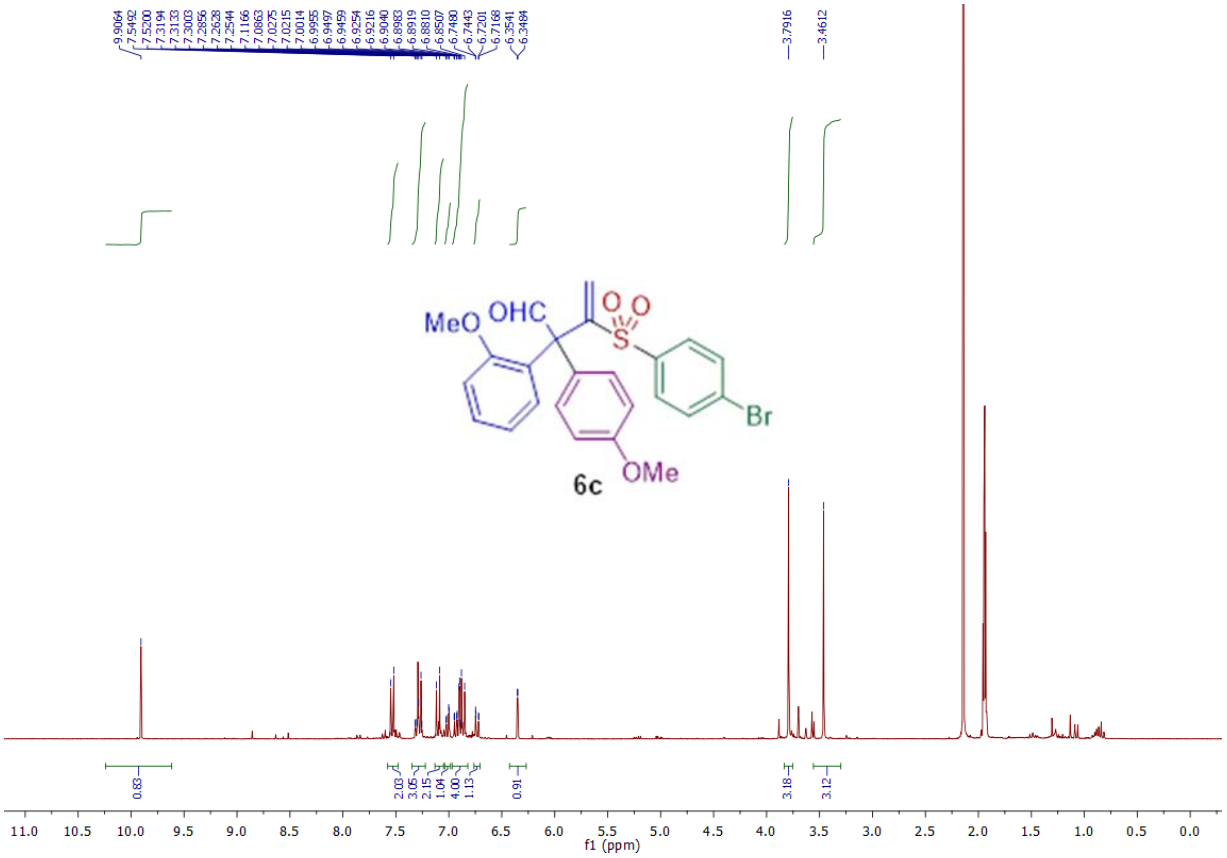
^{1}H NMR spectrum of **6b** in CD_3CN at 300 MHz. This spectrum contains traces of the isomer **7b**.



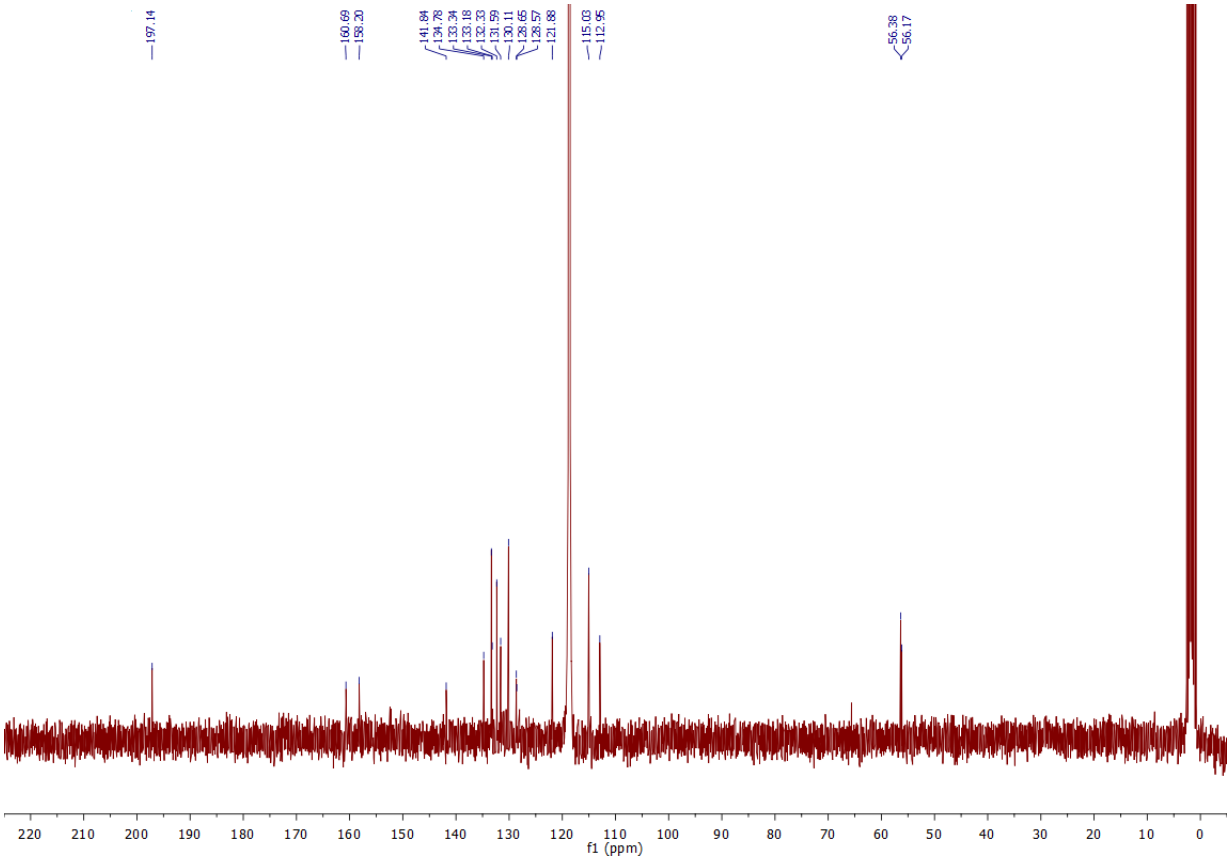
^{13}C NMR spectrum of **6b** in CD_3CN at 75 MHz



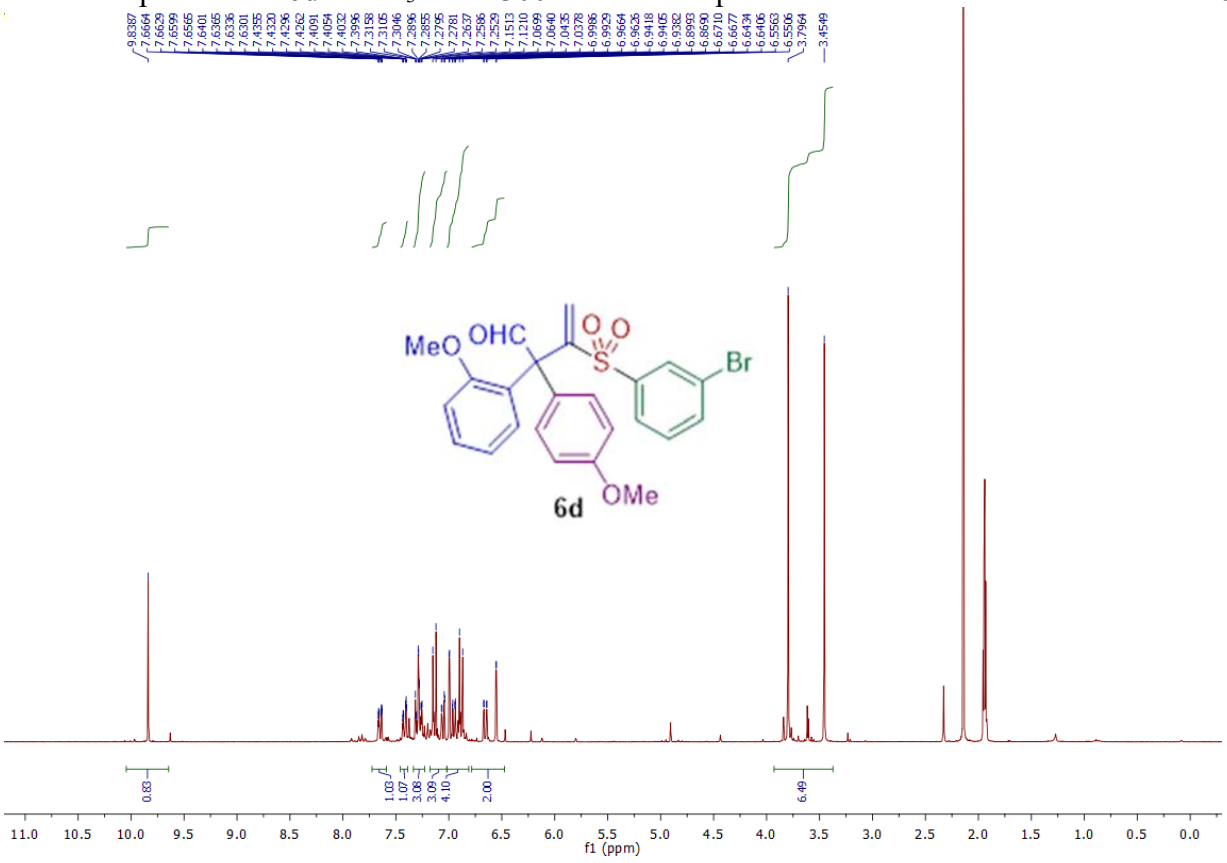
^{1}H NMR spectrum of **6c** in CD_3CN at 300 MHz



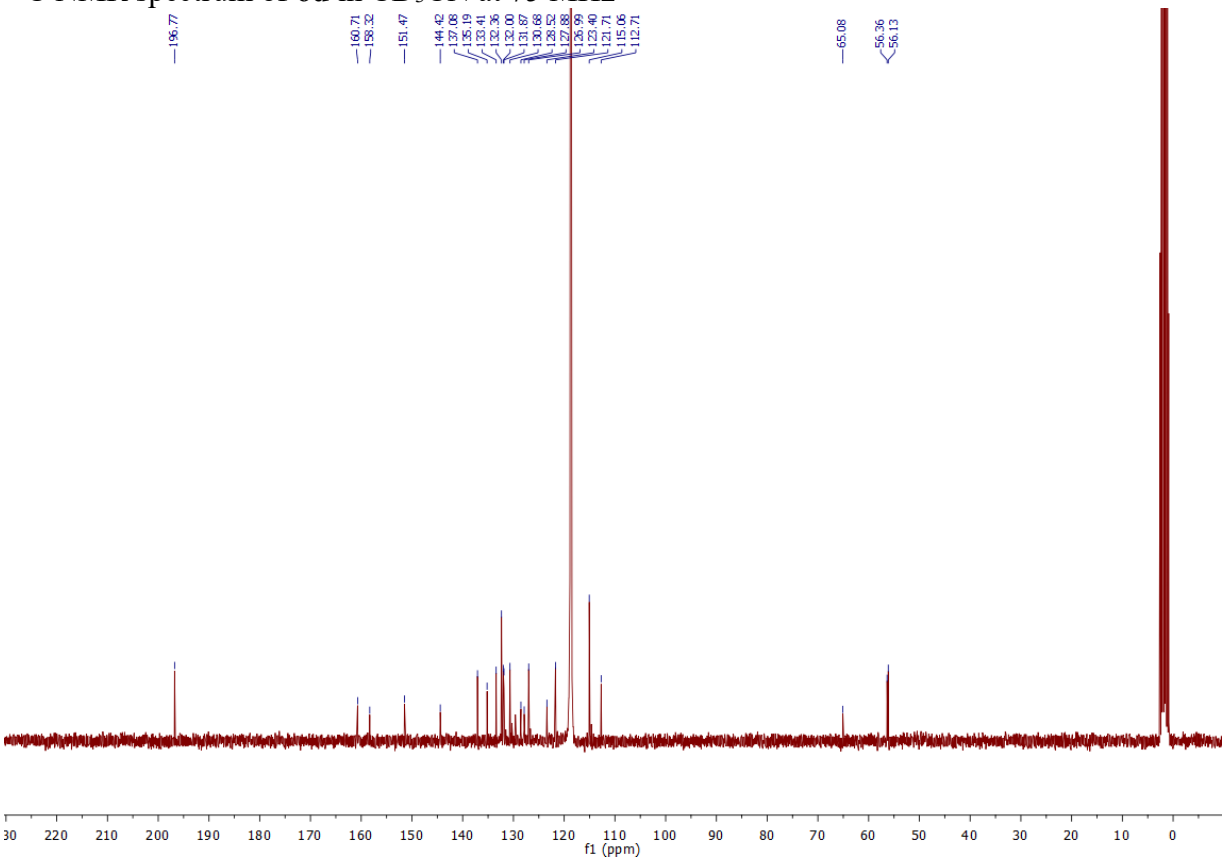
^{13}C NMR spectrum of **6c** in CD_3CN at 75 MHz



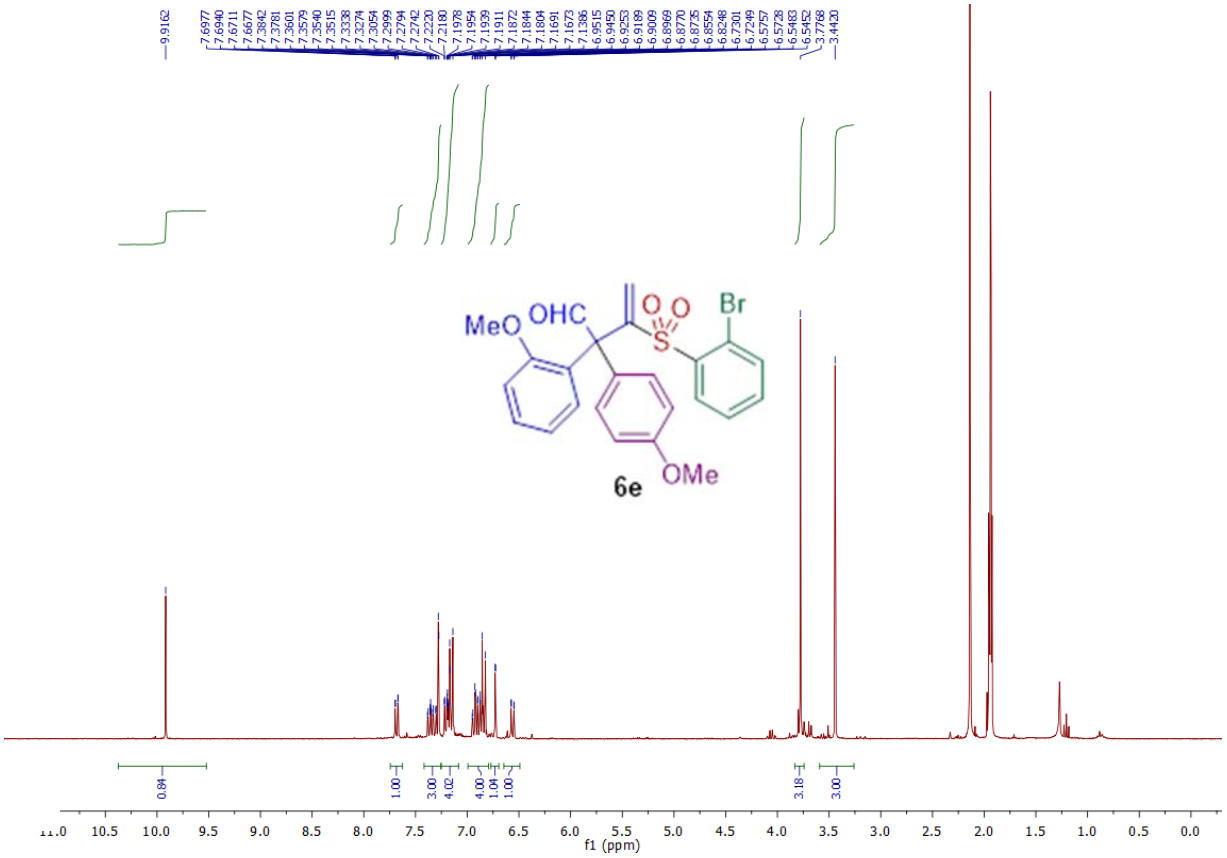
^{1}H NMR spectrum of **6d** in CD_3CN at 300 MHz. This spectrum contains traces of the isomer **7d**.



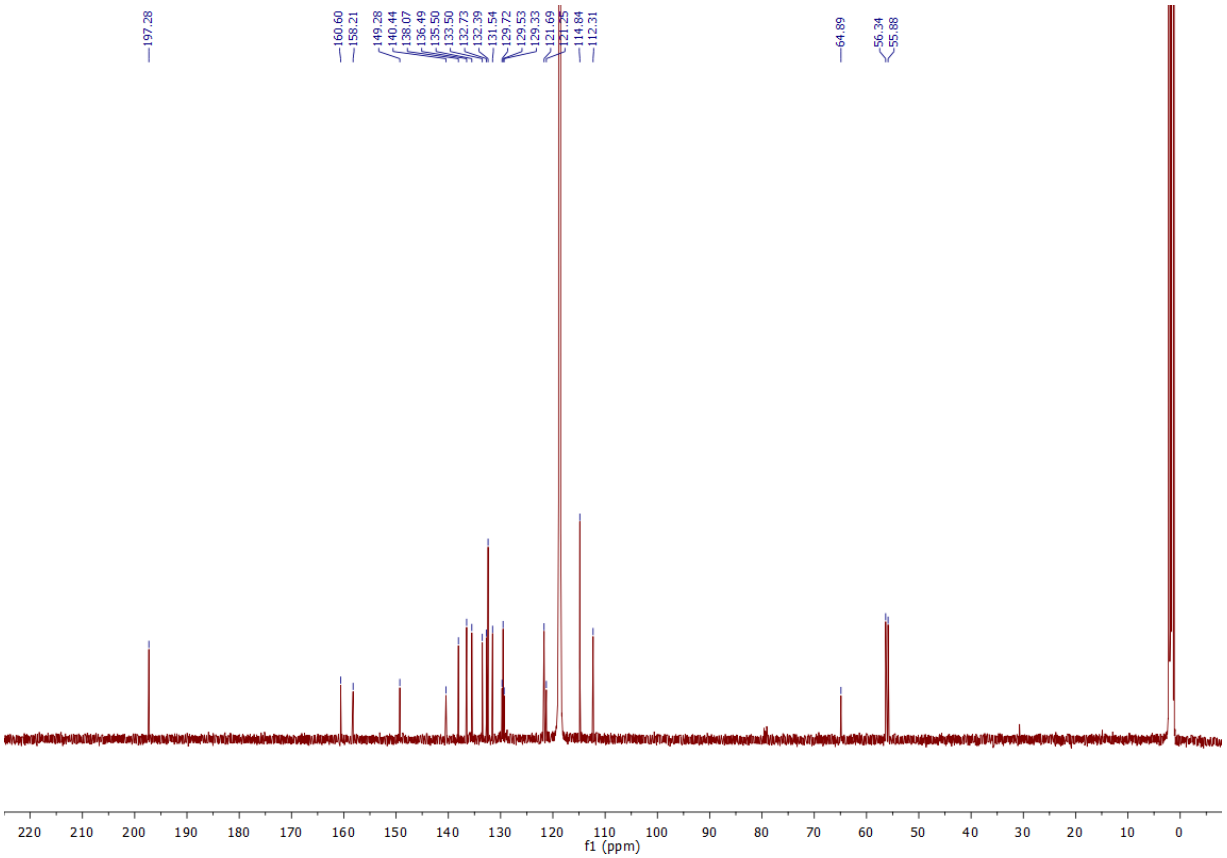
^{13}C NMR spectrum of **6d** in CD_3CN at 75 MHz



^{1}H NMR spectrum of **6e** in CD_3CN at 300 MHz



^{13}C NMR spectrum of **6e** in CD_3CN at 125 MHz



4. ORTEP drawing of Compound (*E,E*)-5b (CCDC 1900824)

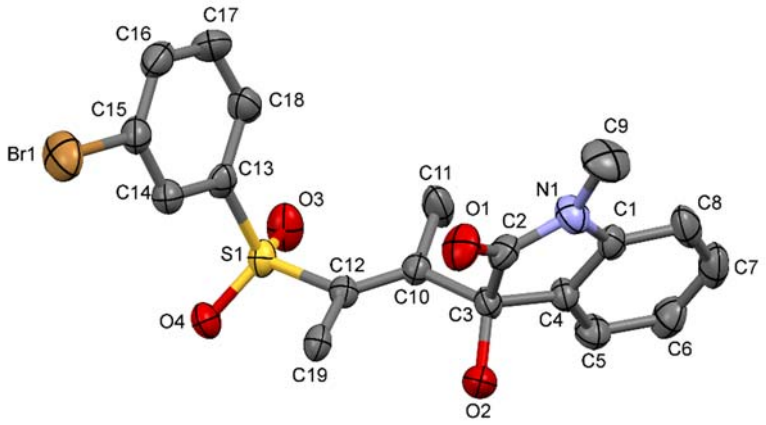


Figure S2. ORTEP drawing of the asymmetric unit of the compound **(*E,E*)-5b**. C, gray; N, blue; Br, brown; O, red; S, yellow. Hydrogen atoms were removed for clarity. Thermal ellipsoids shown at 50% probability.

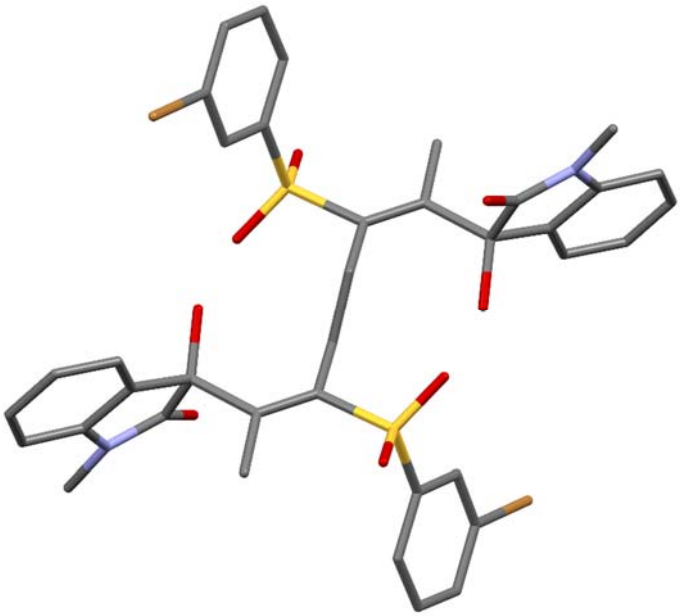


Figure S3. X-ray crystal structure of dimer **(*E,E*)-5b** in the solid state. C, gray; N, blue; Br, brown; O, red; S, yellow. Hydrogen atoms were removed for clarity.

fh-539b

Table 1 Crystal data and structure refinement for fh-539b.

Identification code	fh-539b
Empirical formula	$C_{19}H_{17}BrNO_4S$
Formula weight	435.30
Temperature/K	296.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.8918(7)
b/Å	12.0084(8)
c/Å	14.8327(10)
α/°	90
β/°	110.4070(10)
γ/°	90
Volume/Å^3	1818.3(2)
Z	4
ρ_{calc}g/cm^3	1.590
μ/mm^{-1}	2.400
F(000)	884.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.99 to 57.83
Index ranges	$-14 \leq h \leq 14$, $-16 \leq k \leq 16$, $-19 \leq l \leq 19$
Reflections collected	18748
Independent reflections	4510 [R_{int} = 0.0948, R_{sigma} = 0.1100]
Data/restraints/parameters	4510/0/238
Goodness-of-fit on F^2	0.989
Final R indexes [I>=2σ (I)]	R_1 = 0.0546, wR_2 = 0.1081
Final R indexes [all data]	R_1 = 0.1721, wR_2 = 0.1550
Largest diff. peak/hole / e Å^{-3}	0.42/-0.49

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for fh-539b. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br(1)	9206.3(7)	-2738.2(6)	-924.9(5)	66.8(3)
C(1)	6595(5)	4555(4)	1031(4)	33.8(11)
C(2)	6559(5)	3111(4)	11(4)	36.3(12)
C(3)	5944(5)	2666(4)	747(3)	31.8(11)
C(4)	5961(5)	3703(4)	1331(4)	33.9(12)
C(5)	5428(5)	3924(4)	2029(4)	41.9(13)
C(6)	5495(6)	5001(5)	2382(4)	49.0(15)
C(7)	6130(6)	5817(5)	2083(4)	53.5(16)
C(8)	6691(6)	5617(4)	1392(4)	47.3(15)
C(9)	7654(7)	4835(5)	-228(5)	65.3(18)
C(10)	6811(5)	1694(4)	1314(4)	32.4(11)
C(11)	7913(5)	2091(4)	2193(4)	50.1(15)
C(12)	6597(5)	633(4)	993(3)	29.3(11)
C(13)	8764(5)	-787(4)	1232(3)	32.4(11)
C(14)	8526(5)	-1522(4)	472(4)	37.3(12)
C(15)	9533(5)	-1751(4)	128(4)	42.5(13)
C(16)	10754(5)	-1270(5)	541(4)	47.1(14)
C(17)	10964(5)	-550(5)	1296(4)	49.9(15)
C(18)	9984(5)	-291(4)	1647(4)	44.0(14)
C(19)	5669(5)	217(4)	14(3)	31.9(11)
N(1)	7000(4)	4158(3)	271(3)	42.9(11)
O(1)	6630(4)	2594(3)	-672(3)	52.8(10)
O(2)	4615(3)	2363(3)	270(3)	40.0(9)
O(3)	8131(4)	-180(3)	2692(2)	47.8(10)
O(4)	6652(3)	-1445(3)	1509(2)	37.9(8)
S(1)	7513.8(13)	-490.2(10)	1705.7(9)	33.4(3)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for fh-539b. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	86.7(5)	55.7(4)	74.5(5)	-19.8(4)	49.0(4)	-3.6(4)
C(1)	37(3)	26(3)	36(3)	7(2)	10(2)	4(2)
C(2)	38(3)	36(3)	40(3)	4(2)	20(3)	9(2)
C(3)	36(3)	23(2)	38(3)	0(2)	15(2)	-3(2)
C(4)	39(3)	26(3)	38(3)	-1(2)	17(2)	-1(2)
C(5)	44(3)	39(3)	48(3)	-1(3)	24(3)	-4(3)
C(6)	53(4)	47(4)	49(4)	-9(3)	20(3)	10(3)
C(7)	62(4)	33(3)	57(4)	-12(3)	11(3)	8(3)
C(8)	55(4)	25(3)	52(4)	4(3)	6(3)	-3(3)
C(9)	69(4)	68(4)	71(5)	20(4)	39(4)	-12(4)
C(10)	34(3)	28(3)	38(3)	1(2)	15(2)	3(2)
C(11)	52(4)	30(3)	53(4)	-5(3)	-1(3)	-3(3)
C(12)	34(3)	27(3)	30(3)	1(2)	14(2)	2(2)
C(13)	33(3)	29(3)	29(3)	3(2)	3(2)	7(2)
C(14)	38(3)	30(3)	44(3)	1(2)	15(3)	1(2)
C(15)	48(3)	29(3)	54(4)	1(3)	22(3)	3(3)
C(16)	43(3)	40(3)	64(4)	10(3)	26(3)	11(3)
C(17)	30(3)	52(4)	62(4)	0(3)	8(3)	1(3)
C(18)	40(3)	36(3)	49(4)	1(3)	6(3)	0(3)
C(19)	40(3)	27(3)	32(3)	1(2)	16(2)	7(2)
N(1)	51(3)	35(2)	48(3)	3(2)	24(2)	-7(2)
O(1)	70(3)	52(2)	50(2)	-2.8(19)	37(2)	10(2)
O(2)	34(2)	36(2)	49(2)	-2.2(18)	13.2(17)	-1.3(16)
O(3)	67(3)	42(2)	30(2)	-0.7(17)	10.6(19)	5.4(19)
O(4)	43(2)	26.7(18)	45(2)	5.8(16)	16.6(17)	-2.6(16)
S(1)	42.7(8)	27.7(6)	30.5(7)	2.5(5)	13.6(6)	4.1(6)

Table 4 Bond Lengths for fh-539b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br(1)	C(15)	1.893(5)	C(10)	C(11)	1.508(7)
C(1)	C(4)	1.391(7)	C(10)	C(12)	1.352(6)
C(1)	C(8)	1.372(7)	C(12)	C(19)	1.536(6)
C(1)	N(1)	1.428(6)	C(12)	S(1)	1.788(5)
C(2)	C(3)	1.562(7)	C(13)	C(14)	1.384(7)
C(2)	N(1)	1.354(6)	C(13)	C(18)	1.389(7)
C(2)	O(1)	1.213(6)	C(13)	S(1)	1.772(5)
C(3)	C(4)	1.514(6)	C(14)	C(15)	1.389(7)
C(3)	C(10)	1.551(6)	C(15)	C(16)	1.382(7)
C(3)	O(2)	1.419(6)	C(16)	C(17)	1.369(8)
C(4)	C(5)	1.378(7)	C(17)	C(18)	1.376(7)
C(5)	C(6)	1.387(7)	C(19)	C(19)[1]	1.535(9)
C(6)	C(7)	1.360(8)	O(3)	S(1)	1.430(4)
C(7)	C(8)	1.386(8)	O(4)	S(1)	1.446(3)
C(9)	N(1)	1.445(6)			

[1]1-X,-Y,-Z

Table 5 Bond Angles for fh-539b.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(4)	C(1)	N(1)	109.4(4)	C(10)	C(12)	S(1)	120.7(4)
C(8)	C(1)	C(4)	122.5(5)	C(19)	C(12)	S(1)	111.2(3)
C(8)	C(1)	N(1)	127.9(5)	C(14)	C(13)	C(18)	120.8(5)
N(1)	C(2)	C(3)	108.3(4)	C(14)	C(13)	S(1)	120.0(4)
O(1)	C(2)	C(3)	125.2(5)	C(18)	C(13)	S(1)	119.2(4)
O(1)	C(2)	N(1)	126.5(5)	C(13)	C(14)	C(15)	118.6(5)
C(4)	C(3)	C(2)	101.3(4)	C(14)	C(15)	Br(1)	118.8(4)
C(4)	C(3)	C(10)	115.1(4)	C(16)	C(15)	Br(1)	120.2(4)
C(10)	C(3)	C(2)	107.9(4)	C(16)	C(15)	C(14)	121.0(5)
O(2)	C(3)	C(2)	110.5(4)	C(17)	C(16)	C(15)	119.2(5)
O(2)	C(3)	C(4)	107.7(4)	C(16)	C(17)	C(18)	121.4(5)
O(2)	C(3)	C(10)	113.6(4)	C(17)	C(18)	C(13)	119.0(5)
C(1)	C(4)	C(3)	109.3(4)	C(19)[1]	C(19)	C(12)	116.2(5)
C(5)	C(4)	C(1)	119.0(5)	C(1)	N(1)	C(9)	124.1(4)
C(5)	C(4)	C(3)	131.6(4)	C(2)	N(1)	C(1)	111.0(4)
C(4)	C(5)	C(6)	118.9(5)	C(2)	N(1)	C(9)	124.4(5)
C(7)	C(6)	C(5)	120.9(5)	C(13)	S(1)	C(12)	105.4(2)
C(6)	C(7)	C(8)	121.5(5)	O(3)	S(1)	C(12)	112.0(2)
C(1)	C(8)	C(7)	117.1(5)	O(3)	S(1)	C(13)	107.8(2)
C(11)	C(10)	C(3)	112.4(4)	O(3)	S(1)	O(4)	117.0(2)
C(12)	C(10)	C(3)	121.4(4)	O(4)	S(1)	C(12)	106.8(2)
C(12)	C(10)	C(11)	126.1(4)	O(4)	S(1)	C(13)	107.1(2)
C(10)	C(12)	C(19)	128.0(4)				

[1]1-X,-Y,-Z

Table 6 Torsion Angles for fh-539b.

A	B	C	D	Angle/°
Br(1)	C(15)	C(16)	C(17)	179.4(4)
C(1)	C(4)	C(5)	C(6)	2.5(8)
C(2)	C(3)	C(4)	C(1)	-4.9(5)
C(2)	C(3)	C(4)	C(5)	171.7(5)
C(2)	C(3)	C(10)	C(11)	88.3(5)
C(2)	C(3)	C(10)	C(12)	-88.6(5)
C(3)	C(2)	N(1)	C(1)	-8.3(6)
C(3)	C(2)	N(1)	C(9)	178.7(5)
C(3)	C(4)	C(5)	C(6)	-173.8(5)
C(3)	C(10)	C(12)	C(19)	9.3(7)
C(3)	C(10)	C(12)	S(1)	-174.6(3)
C(4)	C(1)	C(8)	C(7)	0.3(8)
C(4)	C(1)	N(1)	C(2)	5.1(6)
C(4)	C(1)	N(1)	C(9)	178.1(5)
C(4)	C(3)	C(10)	C(11)	-24.0(6)
C(4)	C(3)	C(10)	C(12)	159.1(4)
C(4)	C(5)	C(6)	C(7)	-3.2(8)
C(5)	C(6)	C(7)	C(8)	2.4(9)
C(6)	C(7)	C(8)	C(1)	-0.9(8)
C(8)	C(1)	C(4)	C(3)	176.0(5)
C(8)	C(1)	C(4)	C(5)	-1.1(8)
C(8)	C(1)	N(1)	C(2)	-170.1(5)
C(8)	C(1)	N(1)	C(9)	2.9(8)
C(10)	C(3)	C(4)	C(1)	111.2(5)
C(10)	C(3)	C(4)	C(5)	-72.1(7)
C(10)	C(12)	C(19)	C(19)[1]	-98.5(7)
C(10)	C(12)	S(1)	C(13)	-99.1(4)
C(10)	C(12)	S(1)	O(3)	17.8(5)
C(10)	C(12)	S(1)	O(4)	147.2(4)
C(11)	C(10)	C(12)	C(19)	-167.1(5)
C(11)	C(10)	C(12)	S(1)	9.0(7)
C(13)	C(14)	C(15)	Br(1)	-179.0(4)
C(13)	C(14)	C(15)	C(16)	0.9(8)
C(14)	C(13)	C(18)	C(17)	-0.7(8)
C(14)	C(13)	S(1)	C(12)	-87.2(4)
C(14)	C(13)	S(1)	O(3)	153.0(4)
C(14)	C(13)	S(1)	O(4)	26.3(4)
C(14)	C(15)	C(16)	C(17)	-0.6(8)
C(15)	C(16)	C(17)	C(18)	-0.4(9)
C(16)	C(17)	C(18)	C(13)	1.0(8)
C(18)	C(13)	C(14)	C(15)	-0.3(7)
C(18)	C(13)	S(1)	C(12)	94.0(4)
C(18)	C(13)	S(1)	O(3)	-25.7(5)
C(18)	C(13)	S(1)	O(4)	-152.4(4)
C(19)	C(12)	S(1)	C(13)	77.6(4)
C(19)	C(12)	S(1)	O(3)	-165.4(3)
C(19)	C(12)	S(1)	O(4)	-36.1(4)
N(1)	C(1)	C(4)	C(3)	0.4(6)
N(1)	C(1)	C(4)	C(5)	-176.7(5)
N(1)	C(1)	C(8)	C(7)	174.9(5)
N(1)	C(2)	C(3)	C(4)	7.9(5)
N(1)	C(2)	C(3)	C(10)	-113.4(4)
N(1)	C(2)	C(3)	O(2)	121.8(4)
O(1)	C(2)	C(3)	C(4)	-172.5(5)
O(1)	C(2)	C(3)	C(10)	66.1(6)
O(1)	C(2)	C(3)	O(2)	-58.6(6)
O(1)	C(2)	N(1)	C(1)	172.2(5)
O(1)	C(2)	N(1)	C(9)	-0.8(9)
O(2)	C(3)	C(4)	C(1)	-120.9(4)
O(2)	C(3)	C(4)	C(5)	55.7(7)
O(2)	C(3)	C(10)	C(11)	-148.8(4)
O(2)	C(3)	C(10)	C(12)	34.3(6)
S(1)	C(12)	C(19)	C(19)[1]	85.1(5)
S(1)	C(13)	C(14)	C(15)	-179.0(4)
S(1)	C(13)	C(18)	C(17)	178.1(4)

[1] 1-X,-Y,-Z

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for fh-539b.

Atom	*x*	*y*	*z*	U(eq)
H(5)	5030	3361	2259	50
H(6)	5099	5167	2830	59
H(7)	6188	6525	2349	64
H(8)	7115	6177	1181	57
H(9A)	7149	5495	-469	98
H(9B)	7742	4420	-756	98
H(9C)	8507	5040	207	98
H(11A)	7596	2180	2717	75
H(11B)	8234	2792	2057	75
H(11C)	8609	1554	2365	75
H(14)	7710	-1856	198	45
H(16)	11425	-1433	310	57
H(17)	11787	-229	1578	60
H(18)	10137	208	2154	53
H(19A)	5522	823	-445	38
H(19B)	6106	-375	-202	38
H(2)	4509	2176	-284	60

Experimental

Single crystals of $C_{19}H_{17}BrNO_4S$ **[fh-539b]** were obtained after crystallization from ethyl acetate/n-hexane at 20 oC. A suitable crystal was selected and placed on a diffractometer. The crystal was kept at 296.15 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [fh-539b]

Crystal Data for $C_{19}H_{17}BrNO_4S$ (M =435.30 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 10.8918(7) Å, b = 12.0084(8) Å, c = 14.8327(10) Å, β = 110.4070(10)°, V = 1818.3(2) Å^3, Z = 4, T = 296.15 K, μ(MoKα) = 2.400 mm^{-1}, *Dcalc* = 1.590 g/cm^3, 18748 reflections measured (3.99° ≤ 2Θ ≤ 57.83°), 4510 unique (R_{int} = 0.0948, R_{sigma} = 0.1100) which were used in all calculations. The final R_1 was 0.0546 (I > 2σ(I)) and wR_2 was 0.1550 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups, All O(H) groups
2.a Secondary CH2 refined with riding coordinates:
 C19(H19A,H19B)
2.b Aromatic/amide H refined with riding coordinates:
 C5(H5), C6(H6), C7(H7), C8(H8), C14(H14), C16(H16), C17(H17), C18(H18)
2.c Idealised Me refined as rotating group:
 C9(H9A,H9B,H9C), C11(H11A,H11B,H11C)
2.d Idealised tetrahedral OH refined as rotating group:
 O2(H2)
```


This report has been created with Olex2, compiled on 2018.05.29 svn.r3508 for OlexSys. Please let us know if there are any errors or if you would like to have additional features.