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Supplementary Material

Gold- and Silver-Catalysed Cyclisation Reactions of β-Amino Allenes

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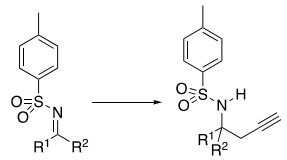
Contents:

Melting points were measured on a Gallenkamp MF-370 capillary melting point apparatus and were uncorrected. Infrared (IR) spectra were recorded as neat samples using a Shimadzu Miracle10 IRAffinity 1 Spectrometer and major bands (ν) were recorded in wavenumber (cm^{-1}). Band intensities are classified as w (weak), m (moderate) and s (strong). ^{1}H and ^{13}C NMR spectra were obtained using one of the following: 500 MHz Varian Unity Inova, 500 MHz Varian Premium Shield (VNMRS PS 54) spectrometer, 500 MHz Bruker Spectrometer (500 MHz ^{1}H, 125 MHz ^{13}C) or 400 MHs Bruker Spectrometer (400 MHz ^{1}H, 100 MHz ^{13}C in deuterochloroform ($CDCl_3$) solution. All signals which were recorded in $CDCl_3$ were relative to the tetramethylsilane (TMS) signal for ^{1}H NMR and the $CDCl_3$ signal for ^{13}C NMR, referenced at 0.00 ppm and 77.16 ppm, respectively. For this report the multiplicities are noted as: singlet (s), broad singlet (brs), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), quint (q), multiplet (m) apparent triplet (app t), apparent quartet (app q), quintet and septet (sep). coupling constants (*J*) reported in Hz. NMR assignments were based on gCOSY, gHSQC and gHMBC experiments. LRESI-MS data obtained using micromass Water Platform LCZ spectrometer. HRESI-MS data obtained using micromass Water Q-TOF Ultima spectrometer. All reactions were performed under nitrogen atmospheric conditions unless otherwise stated and were monitored by TLC analysis Analytical thin layer chromatography was carried out using aluminium backed plates coated with Merck F254 sorbent silica gel. Plates were visualized under UV light (at 254 nm), for UV active compounds or by staining with ceric ammonium molybdate or potassium permanganate solution followed by heating. Column chromatography was performed using Merck silica gel 60 or Sigma-Aldrich Aluminium Oxide 150 mesh. The solvents were purchased as analytical reagent grade. Anhydrous methanol was used as purchased from Sigma-Aldrich. Anhydrous CH_2Cl_2, THF and Et_2O were taken from a dry solvent dispenser and stored over 3Å molecular sieves.

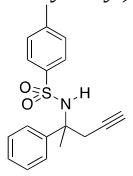
Experimental Section

General procedure for synthesis of homopropargyl-N-Ts-amines



Following the procedure of Diver[1] to a solution of known imines[2] (1 equiv) under a N_2 atmosphere in anhydrous THF (1M) was added activated zinc dust (1.2 equiv). The mixture was stirred while cooling to 0 °C before propargylbromide (1.5 equiv) was added slowly via syringe. The reaction was slowly brought up to room temperature and stirred for 2 h until or until TLC analysis indicated complete consumption of starting imine before quenching with NH_4Cl (10 mL). This was extracted with CH_2Cl_2 (3 x 10 mL), washed with saturated NaCl (3 x 5 mL), dried with $MgSO_4$ and evaporated to dryness. The product homopropargyls were recrystallised from absolute ethanol or purified by silica gel column chromatography. The product spectroscopic data matched that previously reported **α** (R^1 = Ph, R^2 = H),[1] **β** (R^1 = PhCHCH, R^2 = H),[3] and **γ** (R^1 = *i*Pr, R^2 = H).[4]

4-Methyl-N-(2-phenylpent-4-yn-2-yl)benzenesulfonamide (**δ**)



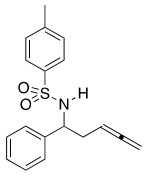
Title compound **δ** was synthesised from its corresponding imine (0.42 mmol, 114 mg) and stirred at rt for 46 h before isolation following silica gel column chromatography (80:20 *n*-hex:Et_2O) as white crystals (48 mg, 36% yield).

R_f (80:20 *n*-hex:EtOAc) = 0.24. mp 88 °C. IR (neat): ν_{max}/cm^{-1} 3283 m, 3252 m, 1437 m, 1324 s, 1151 s, 1090 s, 700 s, 665 s. δ_H (500 MHz, $CDCl_3$) 7.55 (d, *J* 8, 2H, Ar*H*), 7.32 (m, 2H, Ar*H*), 7.20 (m, 3H, Ar*H*), 7.17 (d, *J* 8 Hz, 2H, Ar*H*), 5.30 (s, 1H, N*H*), 2.93 (dd, *J* 16.5, 2, 1H, C*H*H), 2.74 (dd, *J* 16.5, 2, 1H, CH*H*), 2.39 (s, 3H, ArCH_3), 2.05 (s, 1H, C*H*), 1.69 (s, 3H, CH_3). δ_C (125 MHz, $CDCl_3$) 143.0 (Ar*C*), 142.4 (Ar*C*), 139.6 (Ar*C*), 129.4 (Ar*C*), 128.3 (Ar*C*), 127.6 (Ar*C*), 127.1 (Ar*C*), 126.2(Ar*C*), 79.9 (HC*C*CH$_2$), 72.7 (H*C*CCH$_2$), 60.3 (NH*C*), 33.2 (*C*HH), 26.7 (*C*H$_3$), 21.6 (Ar*C*H$_3$). *m*/*z* (HRESI-MS) 312.1049 $C_{18}H_{19}NSO_2H$ $[M + H]^+$; 312.1058, required.

General procedure of allene synthesis

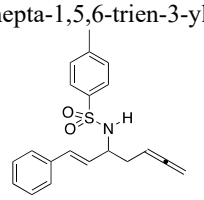
Following the method of Ma,[5] to a solution of **α** (1.76 mmol, 0.500 g, 1 equiv) in 1,4-dioxane (5 mL) was added CuI (0.176 mmol, 33.5 mg, 0.1 equiv), paraformaldehyde (2.82 mmol, 84.5 g, 1.6 equiv) and diisopropylamine (2.46 mmol, 0.374 mL, d= 0.717 g/mL, 1.4 equiv) at room temperature. The resulting mixture was heated at reflux for 19 h. The dioxane was removed *in vacuo*. Purification by column chromatography on silica gel (PE:EtOAc, 80:20) yielded a mixture of a yellow oil and white crystals. The mixture was recrystallised overnight from absolute ethanol with scratching the glass over an ice bath to induce the desired product **1a** to recrystallise. This afforded white flower shaped crystals (146.8 mg, 28%). The filtrate was recrystallised a second time from absolute ethanol to yield a further 42.6 mg (8%) for a combined yield of (36%).

4-Methyl-N-(1-phenylpenta-3,4-dien-1-yl)benzenesulfonamide (**1a**)



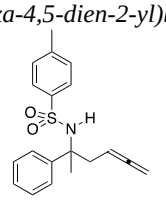
R_f (80:20 PE:EtOAc) = 0.41. mp 108 °C. IR(neat): ν_{max}/cm^{-1} 3243 m, 1952 w, 1324 m, 1157 s, 701 s, 675 s δ_H (500 MHz, $CDCl_3$) 7.56 (d, *J* 8.5, 2H, Ar*H*), 7.20-7.18 (m, 3H, ArH), 7.15 (d, *J* 8, 2H, *ArH*), 7.08-7.07 (m, 2H, Ar*H*), 4.85-4.81 (m, 2H, N*H* and CH_2CH=C=CH_2), 4.66-4.64 (m, 2H, CH=C=CH_2), 4.39 (app q, 1H, NC*H*), 2.43-2.39 (m, 2H, CHCH_2), 2.37 (s, 3H, CH_3-Ar). δ_C (125 MHz, $CDCl_3$) 209.9 (C=*C*=C), 143.3 (Ar*C*), 140.2 (Ar*C*), 137.6 (Ar*C*), 129.5 (Ar*C*), 128.6 (Ar*C*), 127.7 (Ar*C*), 127.3 (Ar*C*), 126.8 (Ar*C*), 85.1 (*C*H=C=CH_2), 75.5 (*C*H_2=C=C-), 57.6 (NH*C*H), 36.8 (CH-*C*H_2-CH=), 21.6 (*C*H_3). *m*/*z* (HRESI-MS) 336.1044 $C_{18}H_{19}NSO_2Na$ $[M + Na]^+$; 336.1034, required.

(*E*)-4-Methyl-*N*-(1-phenylhepta-1,5,6-trien-3-yl)benzenesulfonamide (**1b**)



The title compound was prepared from alkyne **β** (1.52 g, 4.70 mmol, 1 equiv) except that the mixture was heated at reflux for 24 h and filtered through a silica gel plug washing with Et_2O. Purification via silica gel column chromatography (gradient column 90:10 to 60:40 *n*-hex:EtOAc) failed to give allene in sufficient purity. Brown mixture was dissolved in EtOAc, washed with 10 mL of 5% HCl, then 10 mL H_2O and 10 mL of saturated $NaHCO_3$ solution. The final compound was dried *in vacuo* before recrystallising from absolute ethanol to yield 0.1851 g of the allene **1b** as a yellow solid (12%).
R_f (80:20 *n*-hex:EtOAc) = 0.41. mp 104-108 °C. IR(neat): ν_{max}/cm^{-1} 3330 m, 1947 w, 1441 m, 1323 m, 1154 s, 1037 m, 972 m, 750 s, 692 s δ_H (500 MHz, $CDCl_3$) 7.74 (d, *J* 8, 2H, Ar*H*), 7.14 (d, *J* 7, 2H, Ar*H*), 6.30 (d, *J* 16, 1H, ArC*H*), 5.82 (dd, *J* 7.5, 17, 1H, ArCHC*H*), 4.96 (sep, *J* 7 Hz, 1H, H_2CCCH), 4.78 (d, *J* , 1H, N*H*), 4.70 (m, 2H, HCCH_2), 4.05 (sep, *J* 6.5, 1H, NHC*H*), 2.33 (s, 3H, ArCH_3), 2.28 (m, 2H, NHCHCH_2). δ_C (125 MHz, $CDCl_3$) 210.0 (CH*C*CH_2), 143.5 (Ar*C*), 138.2 (Ar*C*), 136.4 (Ar*C*), 132.1 (Ar*C*), 129.7 (Ar*C*), 128.6 (Ar*C*), 128.3 (Ar*C*), 127.9 (Ar*C*), 127.5 (Ar*C*), 126.5 (Ar*C*), 84.9 (*C*HCCH_2), 75.5 (CHC*C*H_2), 55.7 (NH*C*H), 35.2 (NHCH*C*H_2), 21.5 (Ar*C*H_3). *m*/*z* (HRESI-MS) 362.1191 $C_{20}H_{21}NSO_2Na$ $[M + Na]^+$; 362.1191, required.

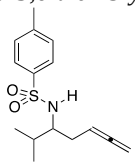
4-Methyl-N-(1-phenylhexa-4,5-dien-2-yl)benzenesulfonamide (**1c**)



The title compound was prepared from alkyne **δ** (0.742 g, 2.37 mmol, 1 equiv) except that the mixture was heated at reflux for 44 h and filtered through a silica gel plug washing wih Et_2O. Purifying via silica gel column chromatography (90:8:2 *n*-hex:EtOAc:TEA) failed to give desired allene in sufficient purity so the amber mixture was recrystallised from absolute ethanol to give 0.141 g of **3c** as white crystals (18%).

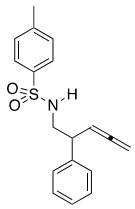
R_f (80:20 *n*-hex:EtOAc) = 0.29. mp 130 °C. IR(neat): ν_{max}/cm^{-1} 3262 m, 2989 w, 1949 w, 1441 w, 1415 w, 1317 s, 1154 s, 1095 s, 873 m, 697 m, 667 s δ_H (500 MHz, $CDCl_3$) 7.58 (d, *J* 8, 2H, Ar*H*), 7.29 (d, *J* 7.5, 2H, Ar*H*), 7.19 (m, 5H, Ar*H*), 5.08 (s, 1H, N*H*), 4.79 (sep, *J* 7, 1H, H_2CCC*H*), 4.66 (m, 2H, $HCCC$*H*$_2$), 2.65 (m, 2H, C*H*H), 2.49 (m, 2H, CH*H*), 2.39 (s, 3H, ArCH_3), 1.64 (s, 3H, C*H*$_3$). δ_C (125 MHz, $CDCl_3$) 210.5 ($CHCCH_2$), 143.6 (Ar*C*), 142.9 (Ar*C*), 140.0 (Ar*C*), 129.5 (Ar*C*), 128.3 (Ar*C*), 127.2 (Ar*C*), 127.1 (Ar*C*), 126.1 (Ar*C*), 84.5 (H_2CCCH), 74.9 ($HCCCH_2$), 61.4 (NH*C*H), 43.0 (NHCHCHH), 25.9 (*C*H$_3$), 21.6 (Ar*C*H$_3$). *m*/*z* (HRESI-MS) 350.1183 $C_{19}H_{21}NSO_2Na$ $[M + Na]^+$; 350.1191, required.

4-Methyl-N-(2-methylhepta-5,6-dien-3-yl)benzenesulfonamide **(1e)**



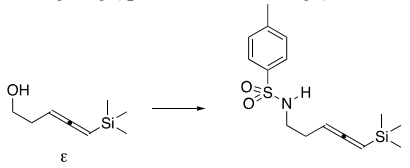
The title compound was prepared from the alkyne **γ** (2.89 g, 10.9 mmol, 1 equiv) except that the mixture was heated at reflux for 24 h and filtered through a silica gel plug washing with Et_2O. Purification via silica gel column chromatography (gradient column 95:3:2 to 70:28:2 *n*-hex:EtOAc:TEA) failed to give allene of sufficient purity, so was purified again by silica gel column chromatography (90:8:2 *n*-hex:EtOAc:TEA) to give 0.781 g of **1e** as a light brown solid (26%).
R_f (80:20 *n*-hex:EtOAc) = 0.42. mp 53 °C. IR(neat): ν_{max}/cm^{-1} 3266 m, 2967 w, 2880 w, 1957 w, 1421 m, 1319 m, 1158 s, 1052 m, 812 m, 663 s. δ_H (500 MHz, $CDCl_3$) 7.76 (d, *J* 8, 2H, Ar*H*), 7.28 (d, *J* 8, 2H, Ar*H*), 4.80 (sep, *J* 7.5, 1H, H_2CCC*H*), 7.73 (s, 1H, N*H*), 4.62 (m, 2H, $HCCC$*H*$_2$), 3.10 (m, 1H, NHC*H*), 2.42 (s, 3H, ArCH_3), 2.03 (d, *J* 3, 2H, NHCHC*HH*), 1.81 (m, 1H, NHCHC*H*), 0.82 (dd, *J* 3, 7, 6H, (C*H*$_3$)$_2$). δ_C (125 MHz, $CDCl_3$) 209.7 ($CHCCH_2$), 143.2 (Ar*C*), 138.3 (Ar*C*), 129.6 (Ar*C*), 127.2 (Ar*C*), 85.5 (H_2CCCH), 74.9 (H_2CCCH), 59.1 (NH*C*H), 31.2 (NHCH*C*H$_2$), 30.8 (NHCH*C*H), 21.6 (Ar*C*H$_3$), 18.8 (*C*H$_3$), 17.9 (*C*H$_3$). *m*/*z* (HRESI-MS) 302.1184 $C_{15}H_{21}NSO_2Na$ $[M + Na]^+$; 302.1191, required.

4-Methyl-N-(2-phenylpenta-3,4-dien-1-yl)benzenesulfonamide (**1d**)



2-Phenyl-*N*-Tosylaziridine[6] (0.36 mmol, 0.1g, 1 equiv) and propargyl-TMS (0.432 mmol, 0.753 g/mL, 64 µL, 1.2 equiv) were dissolved in CH_2Cl_2 (2.6 mL) and the temperature was lowered to -78 °C (acetone/dry ice bath). In a separate flask was dissolved $BF_3.Et_2O$ (0.432 mmol, 1.15 g/mL, 56 µL, 1.2 equiv) in 1 mL of CH_2Cl_2 which was added dropwise over the course of 1 h. The reaction mixture was quenched after 2 h by addition of ice and 1 mL of $NaHCO_3$, exctracted with CH_2Cl_2 (3 x 10 mL), washed with NaCl (5 mL) and concentrated *in vacuo*. The target allene was isolated as a yellow oil following silica gel column chromatography (90:8:2 *n*-hex : EtOAc : Et_3N) (0.0114 g, 10%).
R_f (90:10 *n*-hex:EtOAc) = 0.01. IR(neat): ν_{max}/cm^{-1} 2925 w, 1956 w, 1600 m, 1328 m, 1155 s, 813 s, 699 s, 661 s. δ_H (400 MHz, $CDCl_3$) 7.68 (d, *J* 8.3, 2H, Ar*H*), 7.31-7.23 (m, 5H, Ar*H*), 7.10 (d, *J* 8.4, Ar*H*), 5.23 (q, *J* 6.6, 1H, *H*C=C=CH_2), 4.81 (dd, *J* 3.0, 8.35, HC=C=C*H*$_2$), 4.44 (app t, 1H, N*H*), 3.45-3.39 (m, 1H, PhC*H*), 3.30-3.23 (m, 1H, NHC*H*H), 3.20-3.13 (m, 1H, NHCH*H*), 2.43 (s, 3H, ArCH_3). δ_C (125 MHz, $CDCl_3$) 208.1 (HC=*C*=CH_2), 143.6 (Ar*C*), 140.5 (Ar*C*), 137.2 (Ar*C*), 129.9 (Ar*C*), 129.0 (Ar*C*), 127.9 (Ar*C*), 127.6 (Ar*C*), 127.2 (Ar*C*), 91.5 (*C*H=C=CH_2), 77.5 (CH=C=*C*H$_2$), 47.8 (NHCH_2), 44.5 (NHCH$_2$*C*H), 21.7 (Ar*C*H$_3$). *m*/*z* (HRESI-MS) 336.1028 $C_{18}H_{19}NSO_2Na$ $[M + Na]^+$; 336.1027 required.

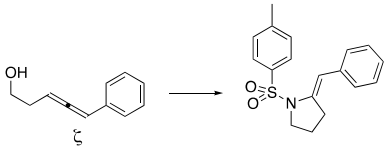
4-Methyl-N-(5-(trimethylsilyl)penta-3,4-dien-1-yl)benzenesulfonamide (**1f**)



ε

The pre-requisite TMS-substituted-homoallenyl alcohol **ε** was prepared following literature procedures [7] from its corresponding ene-yne. This allenyl alcohol was used as a crude mixture from $LiAlH_4$ reduction of the TMS-ene-yne (0.7 mmol). This crude material was then dissolved in 8.75 mL of THF and cooled to 0 °C before methanesulfonyl chloride (0.84 mmol, 65 μL, 1.2 equiv) and Et_3N (1.12 mmol, d = 0.726 g/mL, 156 μL, 1.6 equiv) were added and the solution stirred at 0 °C for 1 h before it was filtered and concentrated under reduced pressure. The crude material was then dissolved in CH_3CN (5 mL) and to this was added K_2CO_3 (1.4 mmol, 193 mg, 2 equiv) and $TsNH_2$ (1.05 mmol, 180 mg, 1.5 equiv) before being heated at reflux for 57 h. The CH_3CN was removed *in vacuo* from the green solution before being extracted with CH_2Cl_2 (3 x 10 mL), washed with H_2O (5 mL), washed with NaCl (5 mL) and dried *in vacuo*. The title allene was purified by silica gel column chromatography (80:20 *n*-hex:EtOAc) to give 17.0 mg of **1f** as a yellow oil (8%).
R_f (70:30 *n*-hex:Et_2O) = 0.35. IR(neat): ν_{max}/cm^{-1} 3282 w, 2954 w, 1937 m, 1325 m, 1247 m, 1157 s, 1094 m, 838 s, 813 s, 758 m, 664 s δ_H (400 MHz, $CDCl_3$) 7.74 (d, *J* 8.0, 2H, Ar*H*), 7.30 (d, *J* 8.0, 2H, Ar*H*), 4.95-4.92 (m, 1H, $Si(CH_3)_3CH$), 4.63 (q, *J* 6.5, 13.5, 1H, $NHCH_2CH_2CH$), 4.54 (s, 1H, N*H*), 3.00 (app q, 2H, $NHCH_2$), 2.42 (s, 3H, $ArCH_3$), 2.13-2.08 (m, 2H, $NHCH_2CH_2$), 0.06 (s, 9H, $Si(CH_3)_3$). δ_C (100 MHz, $CDCl_3$) 209.8 ($Si(CH_3)_3CHCCH$), 143.5 (Ar*C*), 137.2 (Ar*C*), 129.8 (Ar*C*), 127.3 (Ar*C*), 84.0 ($Si(CH_3)_3CH$), 79.6 ($NHCH_2CH_2CH$), 42.9 ($NHCH_2$), 28.1 ($NHCH_2CH_2$), 21.6 ($ArCH_3$), -0.9 ($Si(CH_3)_3$). *m/z* (HRESI-MS) 332.1128 $C_{15}H_{23}NSO_2SiNa$ $[M + Na]^+$; 332.1116 required.

4-Methyl-N-(5-phenylpenta-3,4-dien-1-yl)benzenesulfonamide(**1g**) *and subsequent cyclisation to (E)-2-benzylidene-1-(4-methyl-N-benzenesulfonamide)pyrrolidine* (**2g'**)



ζ

The pre-requisite phenyl-substituted-homoallenyl alcohol ζ was prepared following previous literature procedures[8] from its correspongding ene-yne. The allenyl alcohol (1.61 mmol, 0.258 g, 1 equiv) was dissolved in 11.5 mL of THF and the temperature lowered to 0 °C before methanesulfonyl chloride (1.93 mmol, 150 μL, 1.2 equiv) and Et_3N (2.58 mmol, 359 μL, 1.6 equiv) were added and stirred for 1 h. The reaction mixture was filtered and concentrated under reduced pressure. This crude reaction mixture was then dissolved in CH_3CN (6.2 mL) and to this was added K_2CO_3 (3.22 mmol, 0.445 g, 2 equiv) and $TsNH_2$ (2.415 mmol, 0.413 g, 1.5 equiv) and the solution was raised to reflux for 64 h. After 64 h the solution was cooled and the solvent removed under reduced pressure before being extracted with CH_2Cl_2 (3 x 10 mL), washed with H_2O (5 mL) and sat. NaCl (5 mL) before it was concentrated *in vacuo*. The final compounds were separated by silica gel column chromatography (97:3 *n*-hex:EtOAc) as a yellow solid (0.0103 g, 2%). The spectroscopic data of **2g'** matched that previously reported.[9]
δ_H (500 MHz, $CDCl_3$) 7.76 (d, *J* 8.4, 2H, Ar*H*), 7.32-7.27 (m, 4H, Ar*H*), 7.19-7.13 (m, 3H, Ar*H*),6.86 (s, 1H, NCC*H*), 3.66 (q, *J* 6.8, 2H,NCH_2),2.49 (td, *J* 7.2, 2.1, 2H, $NCCH_2$), 2.42 (s, 3H, $ArCH_3$), 1.79 (quint, 2H, NCH_2CH_2). δ_C (125 MHz, $CDCl_3$) 144.1, 140.2, 137.7, 134.6, 129.7, 128.4, 128.3, 127.6, 126.0, 110.7, 50.7, 30.3, 22.5, 21.7.

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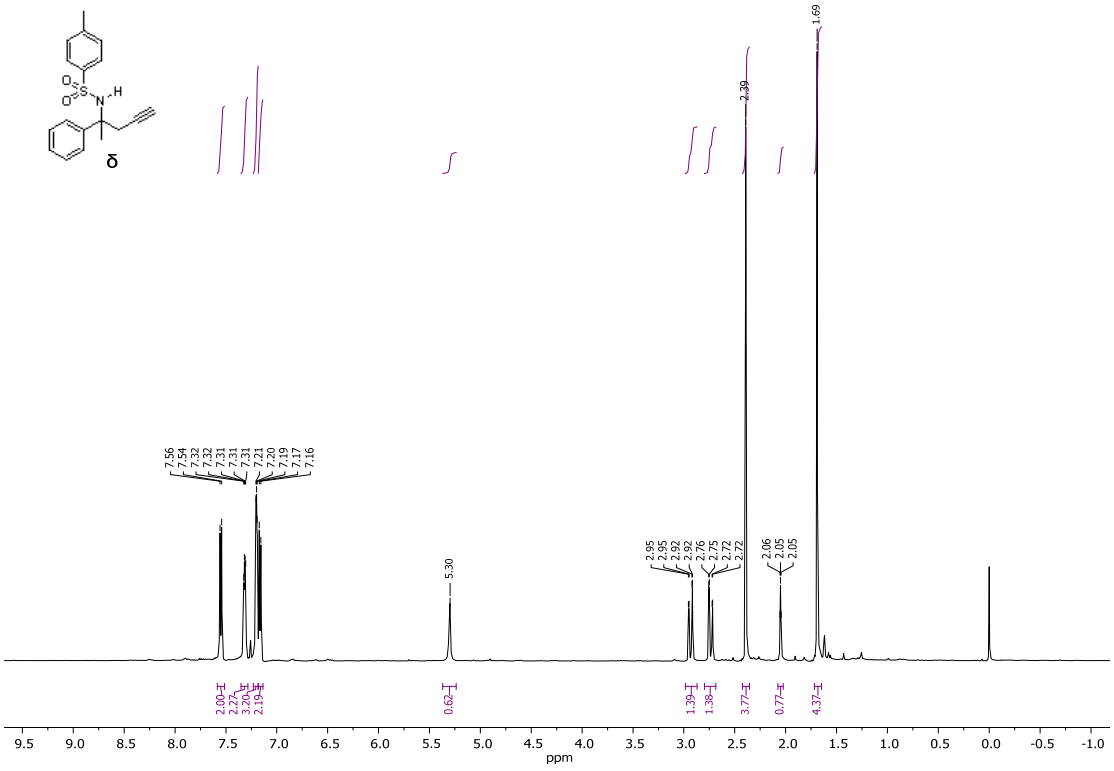
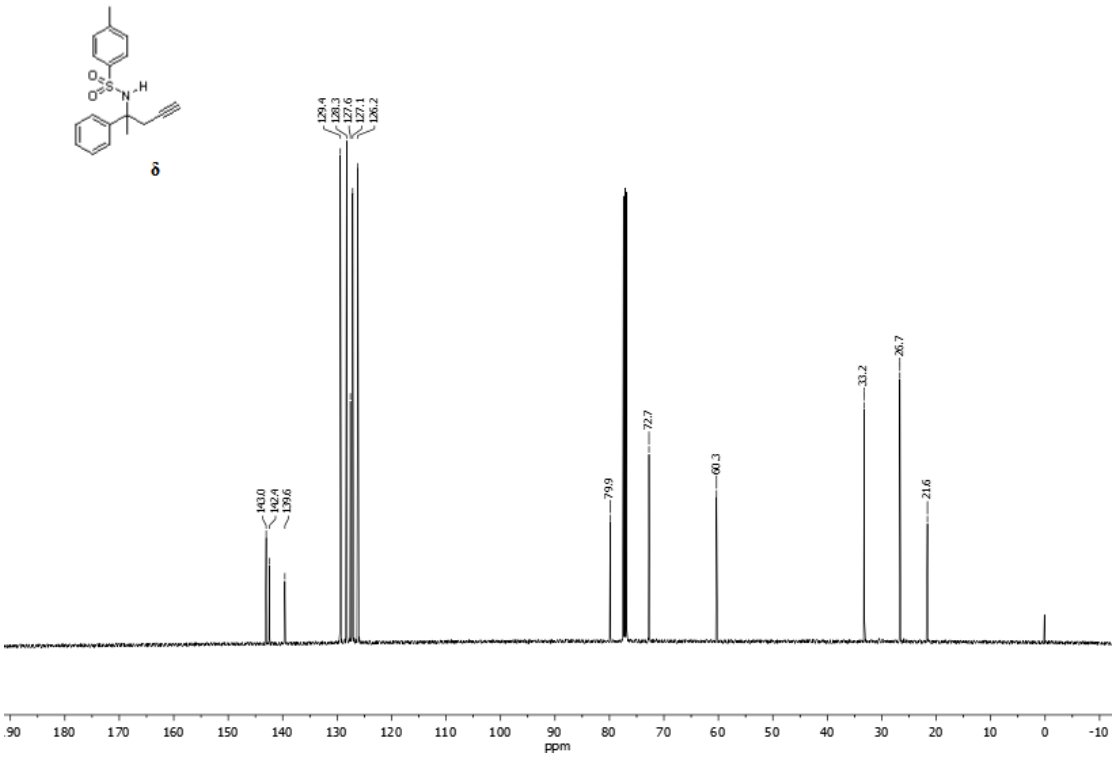
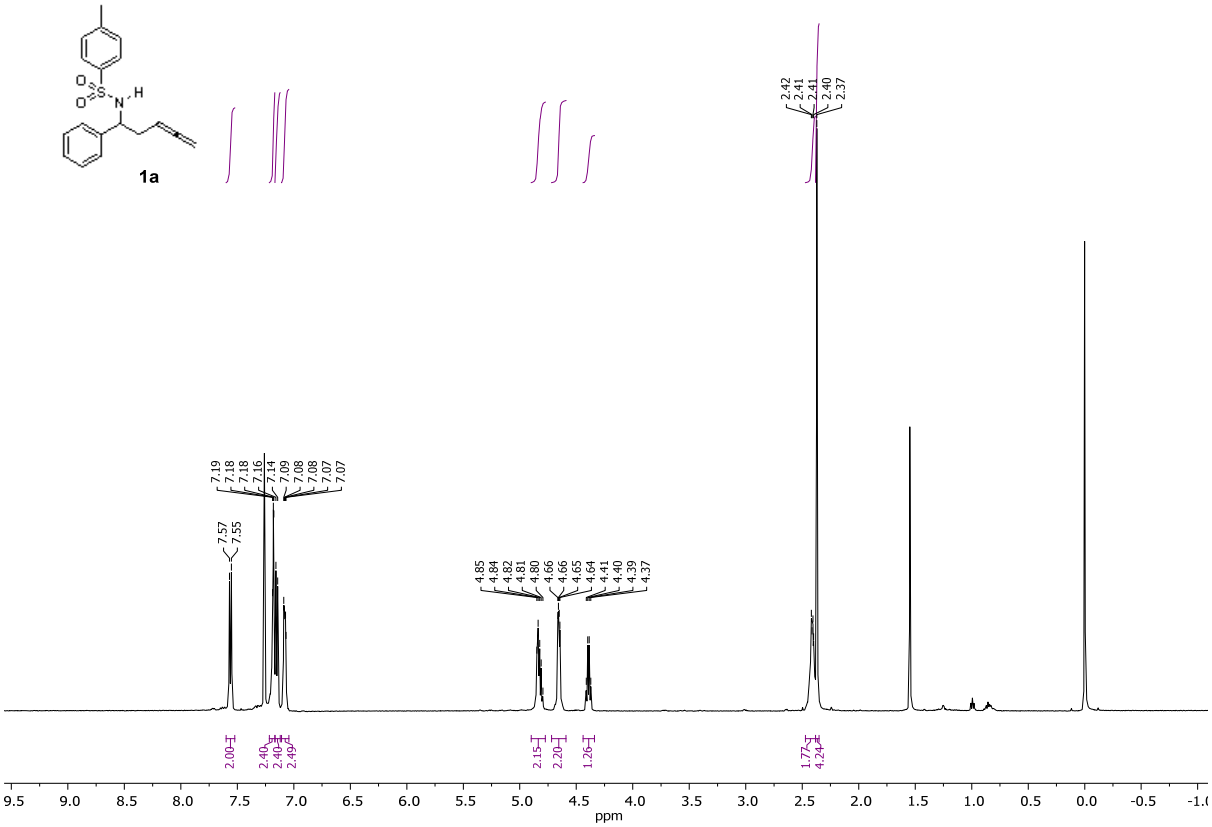
[6] H. Rubin, J. Cockrell, J. B. Morgan, *J. Org. Chem.* **2013**, *78*, 8865-8871.
[7] Following method to (*Z*)-ene-yne from R. Takeuchi, K. Tanabe, S. Tanaka, *J. Org. Chem.* **2000**, *65*, 1558-1561. $LiAlH_4$ reduction following similar procedure to P. Bovicelli, E. Mincione, P. J. Parsons *Synth. Commun.* **1988**, *18*, 1231-1239.
[8] Following method to (*Z*)-ene-yne from S. Garrais, J. Turkington, W. P. D. Goldring, *Tetrahedron* **2009**, *65*, 8418-8427. $LiAlH_4$ reduction following similar procedure to P. Bovicelli, E. Mincione, P. J. Parsons *Synth. Commun.* **1988**, *18*, 1231-1239.
[9] G. Liu, S. S. Stahl, *J. Am. Chem. Soc.* **2007**, *129*, 6328-6335.

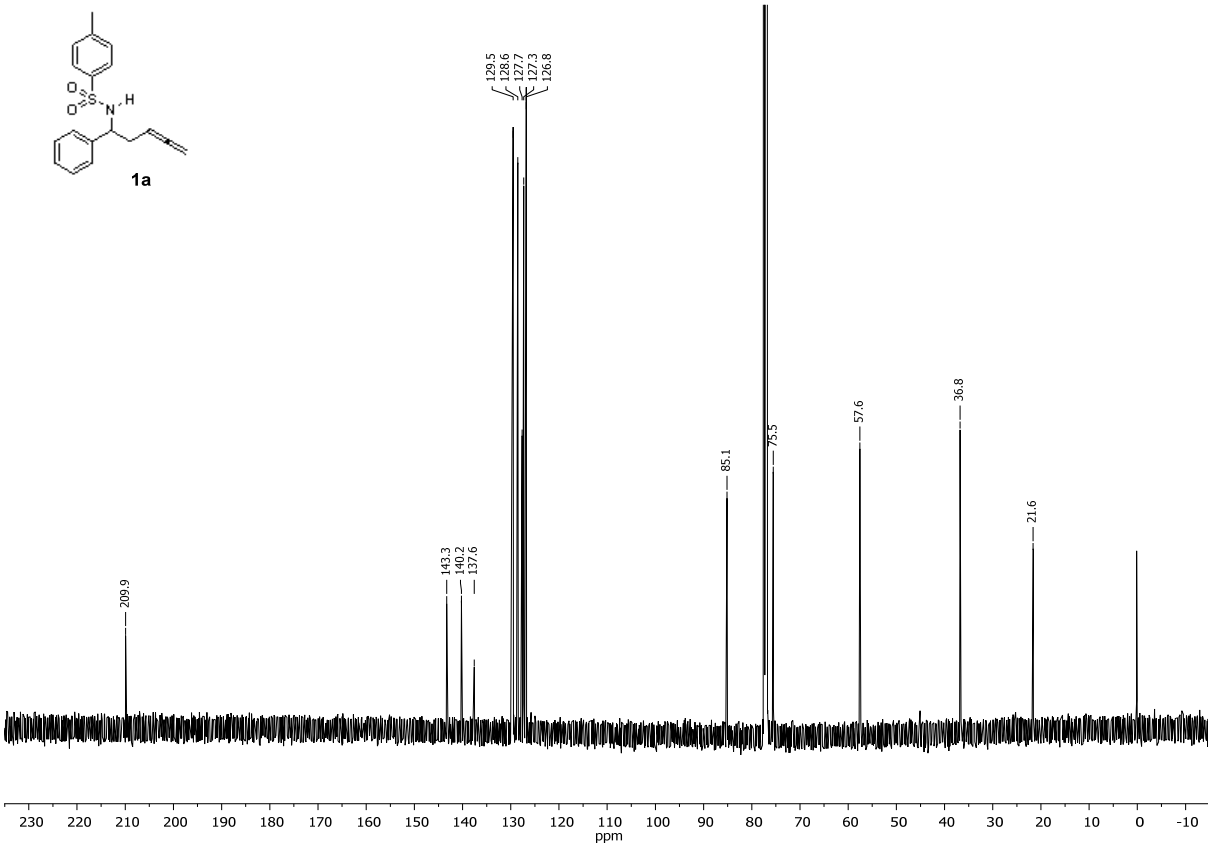
4-Methyl-N-(2-phenylpent-4-yn-2-yl)benzenesulfonamide (**δ**)



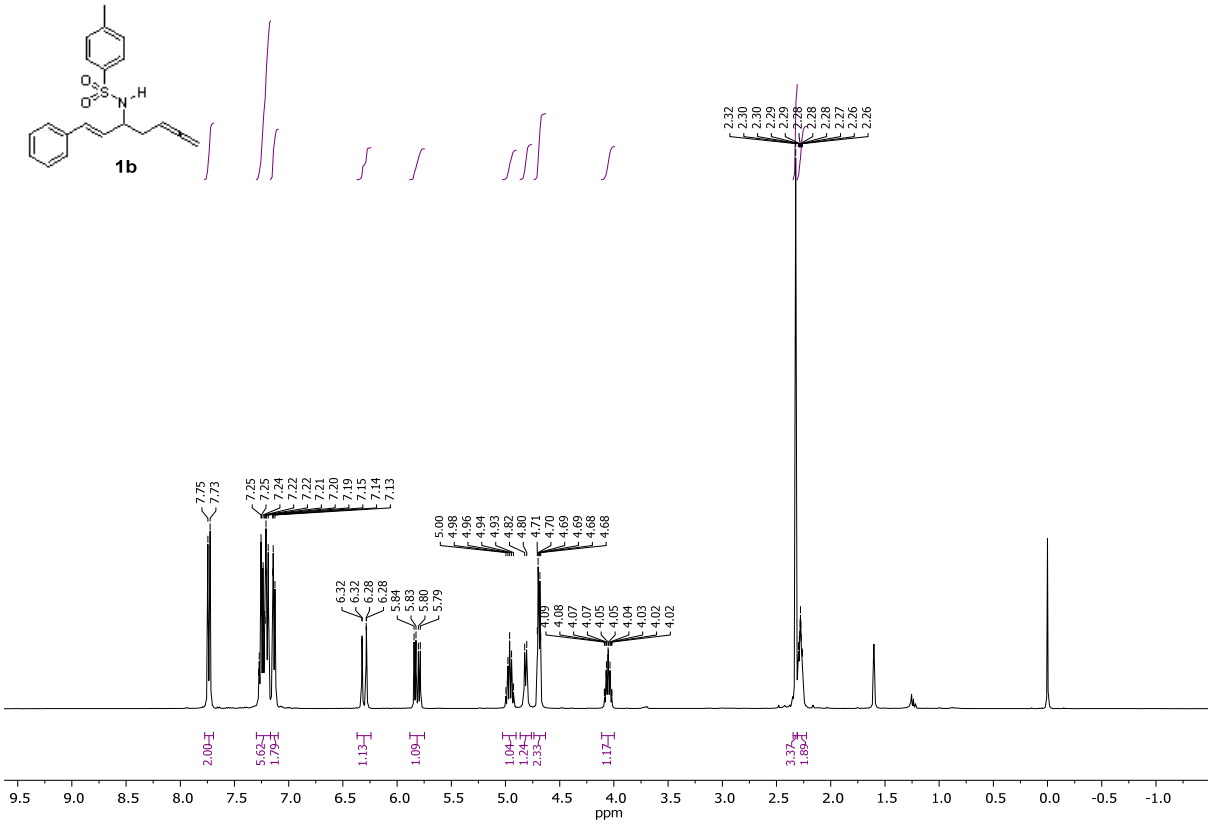


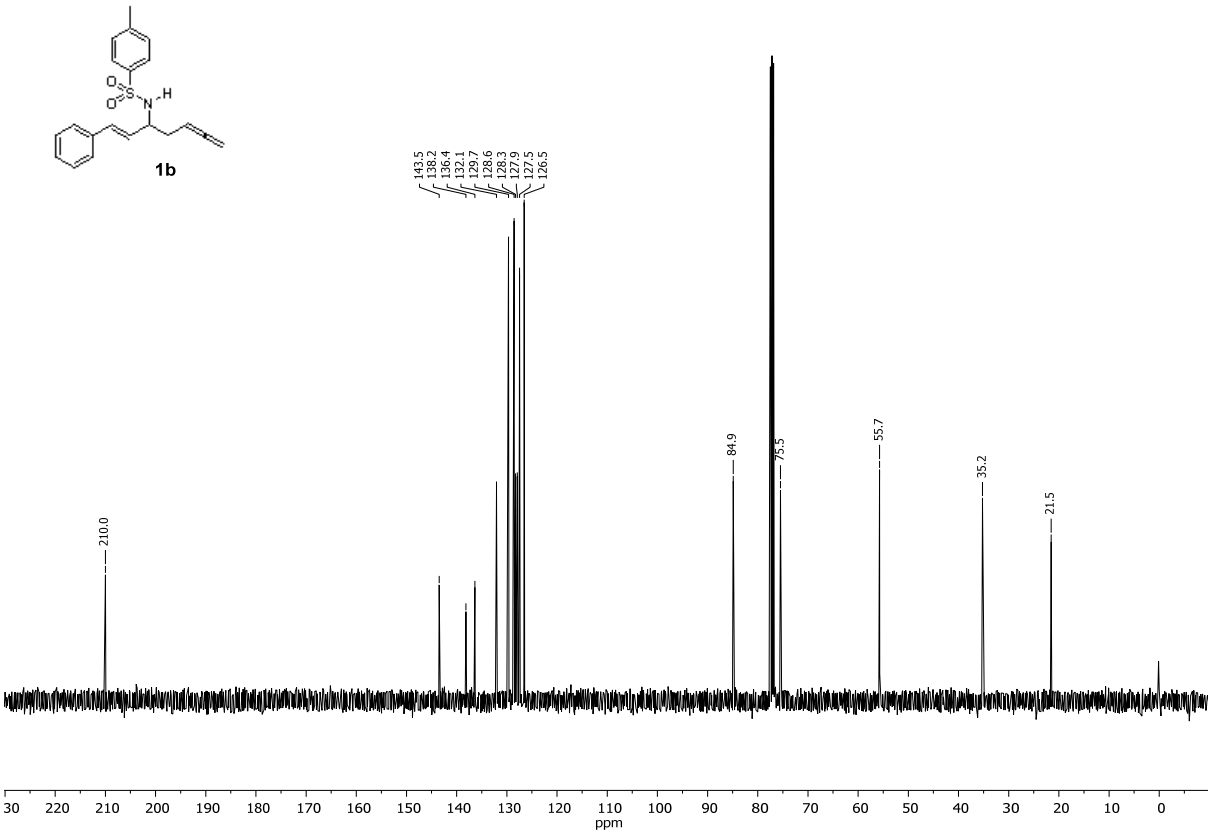
4-Methyl-N-(1-phenylpenta-3,4-dien-1-yl)benzenesulfonamide (**1a**)



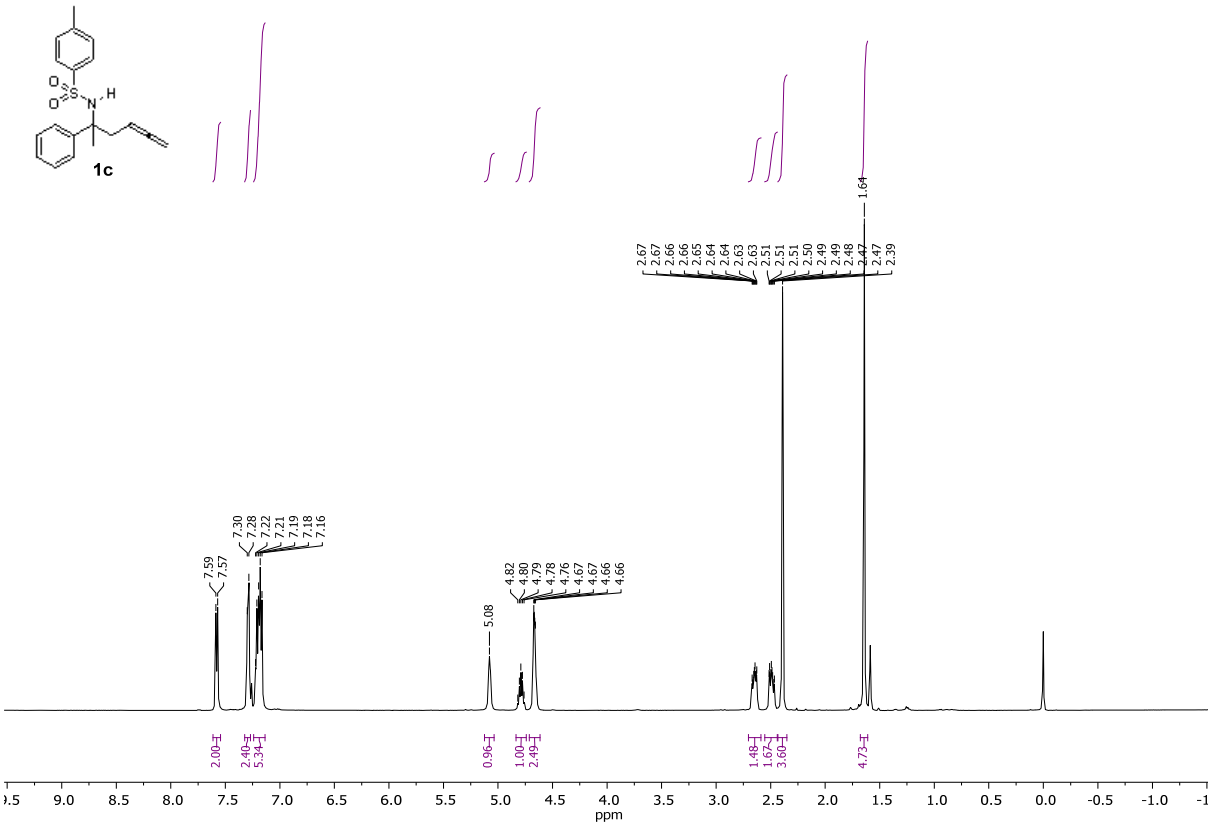


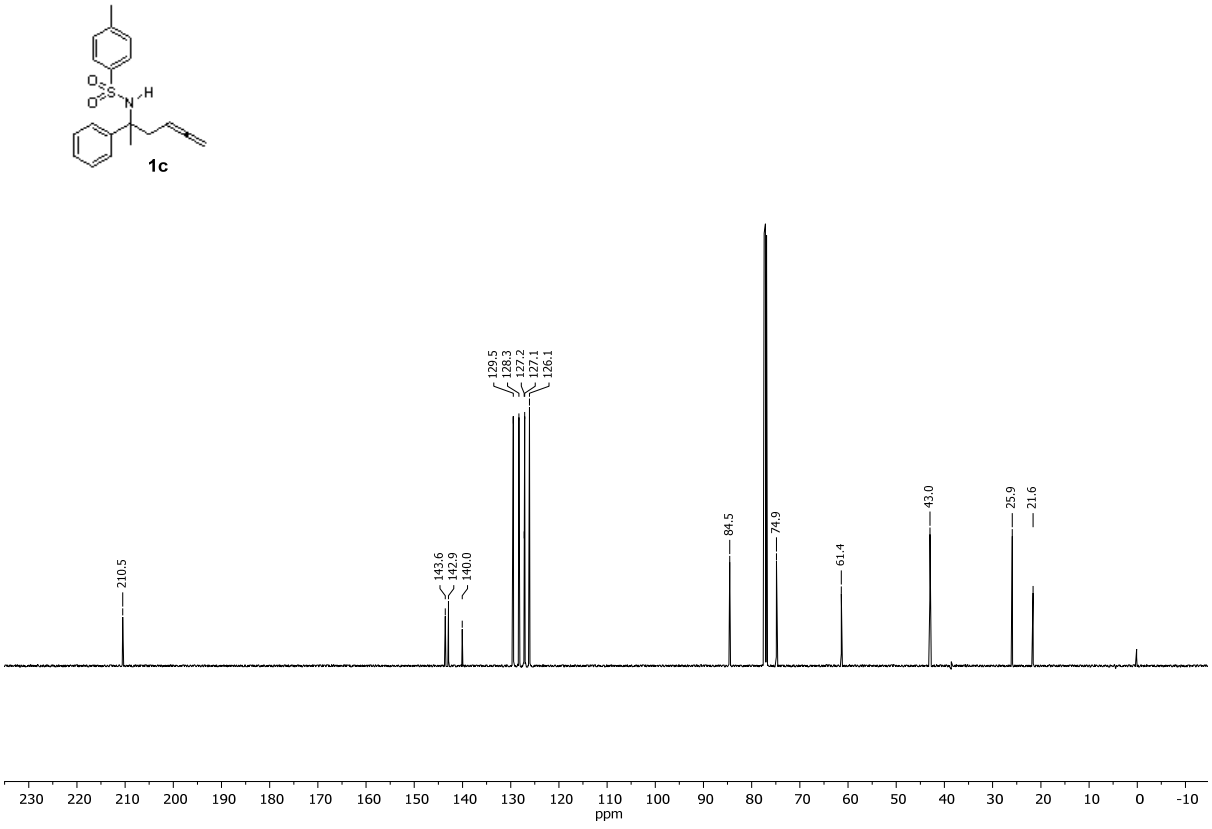
(E)-4-Methyl-N-(1-phenylhepta-1,5,6-trien-3-yl)benzenesulfonamide (**1b**)



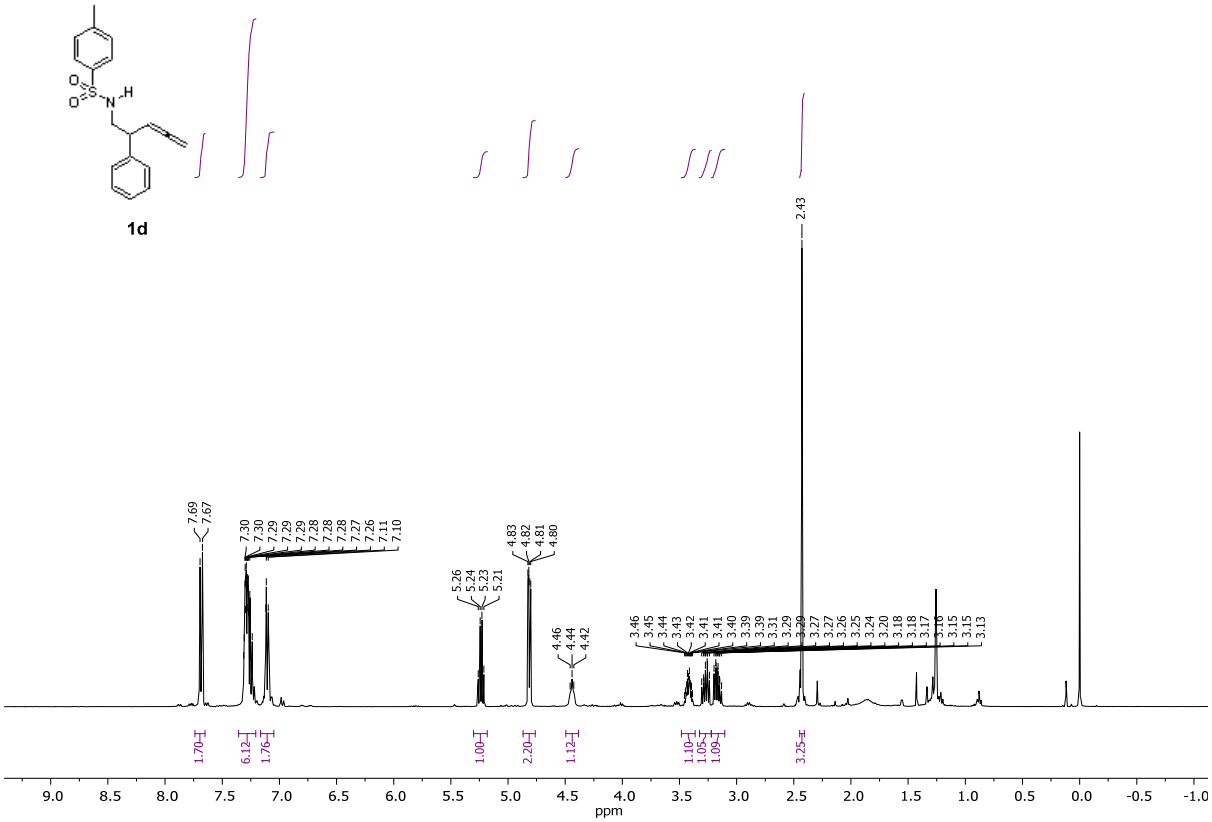


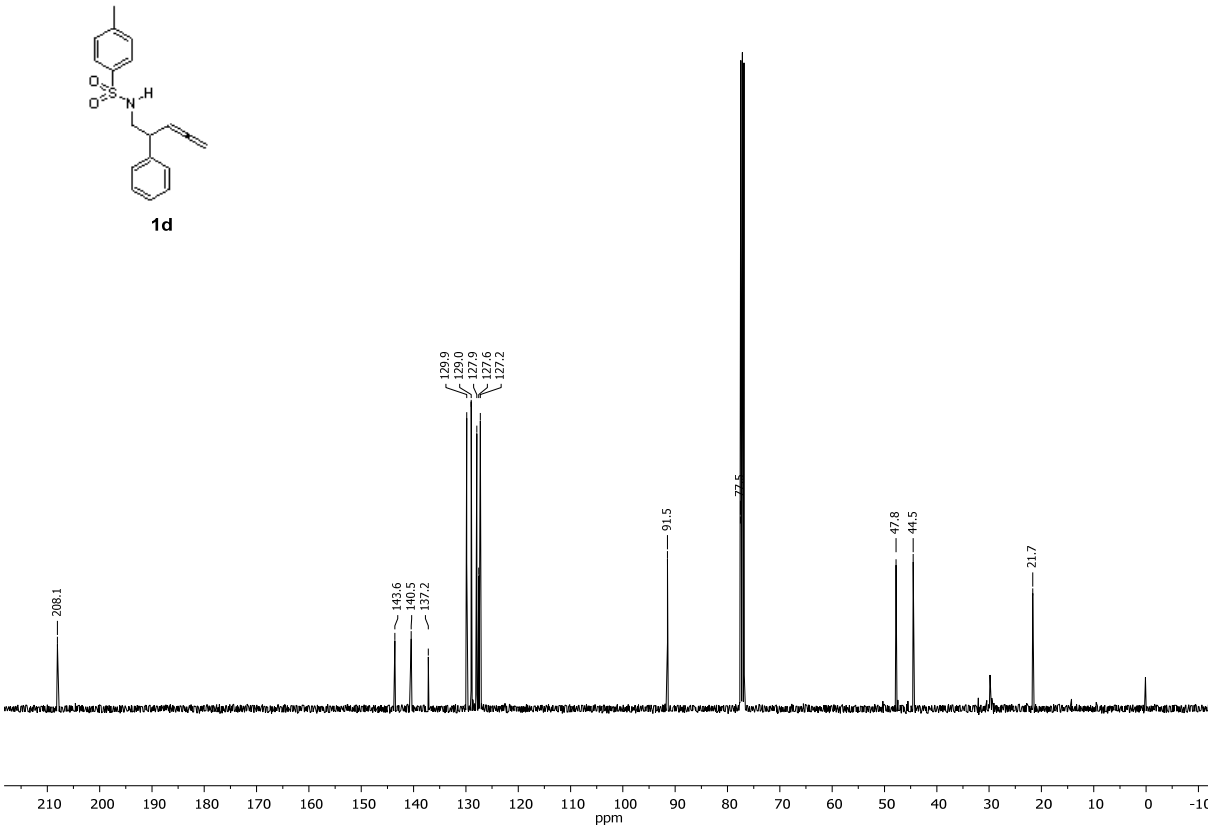
4-Methyl-N-(1-phenylhexa-4,5-dien-2-yl)benzenesulfonamide (**1c**)



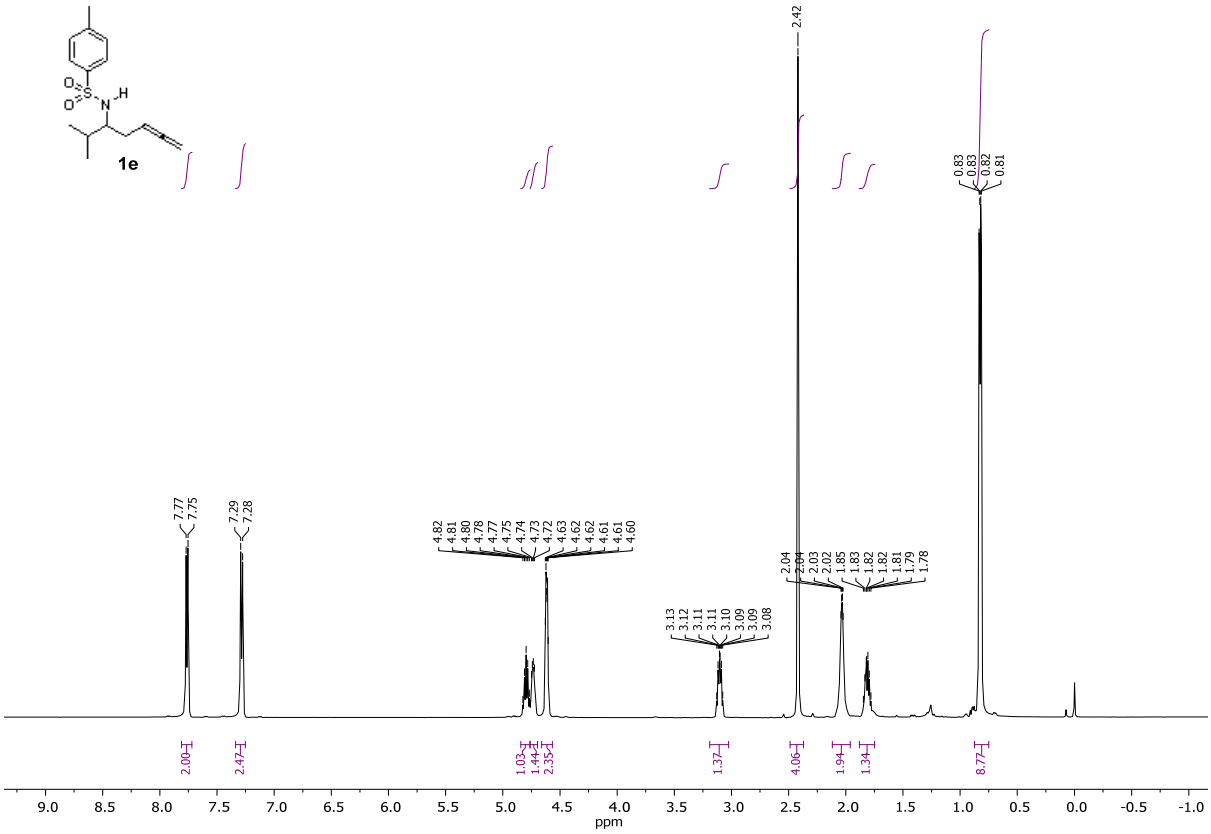


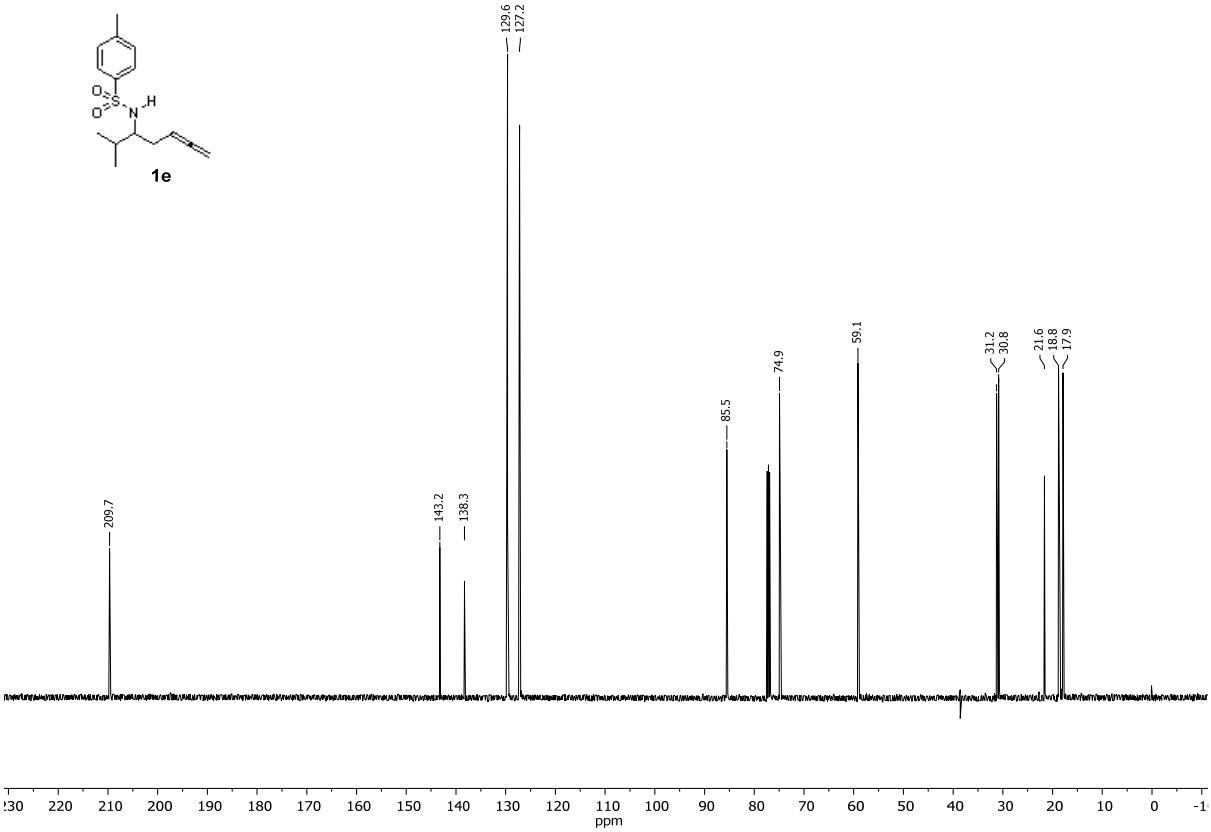
4-Methyl-N-(2-phenylpenta-3,4-dien-1-yl)benzenesulfonamide (**1d**)



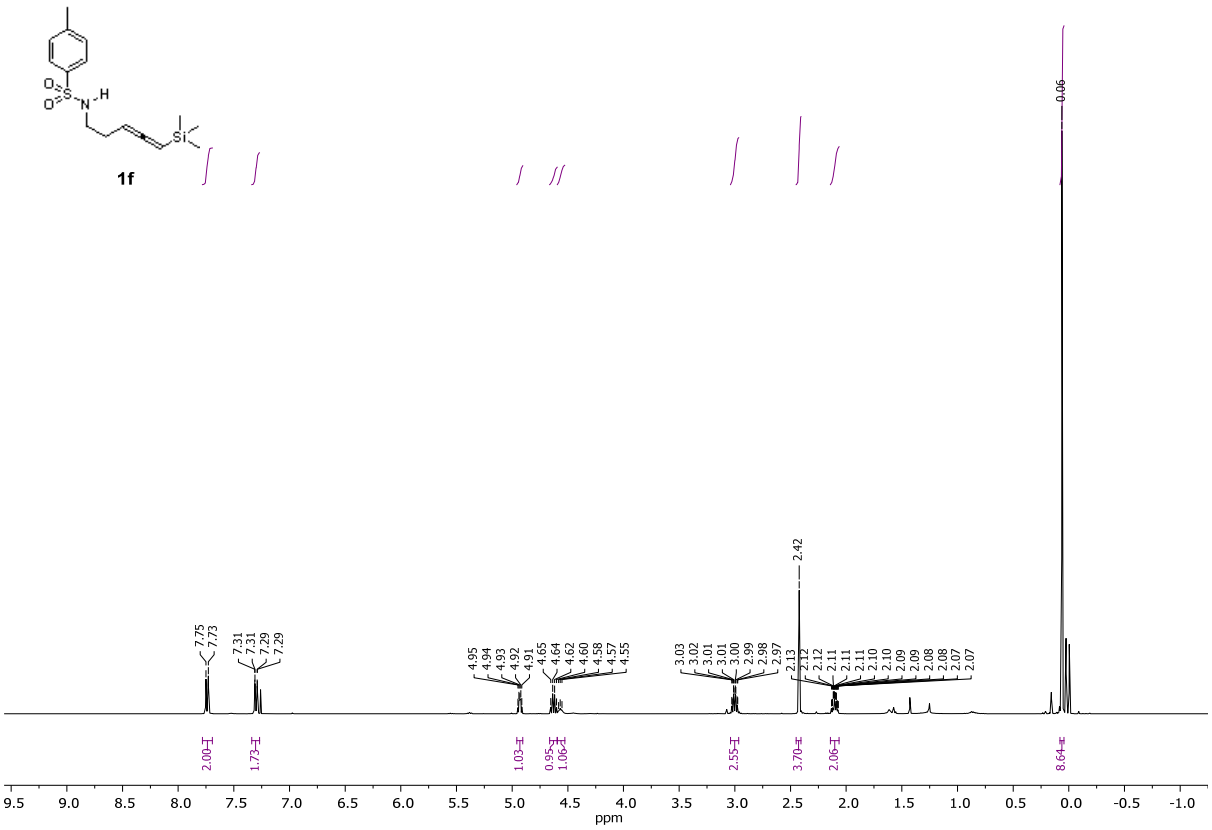


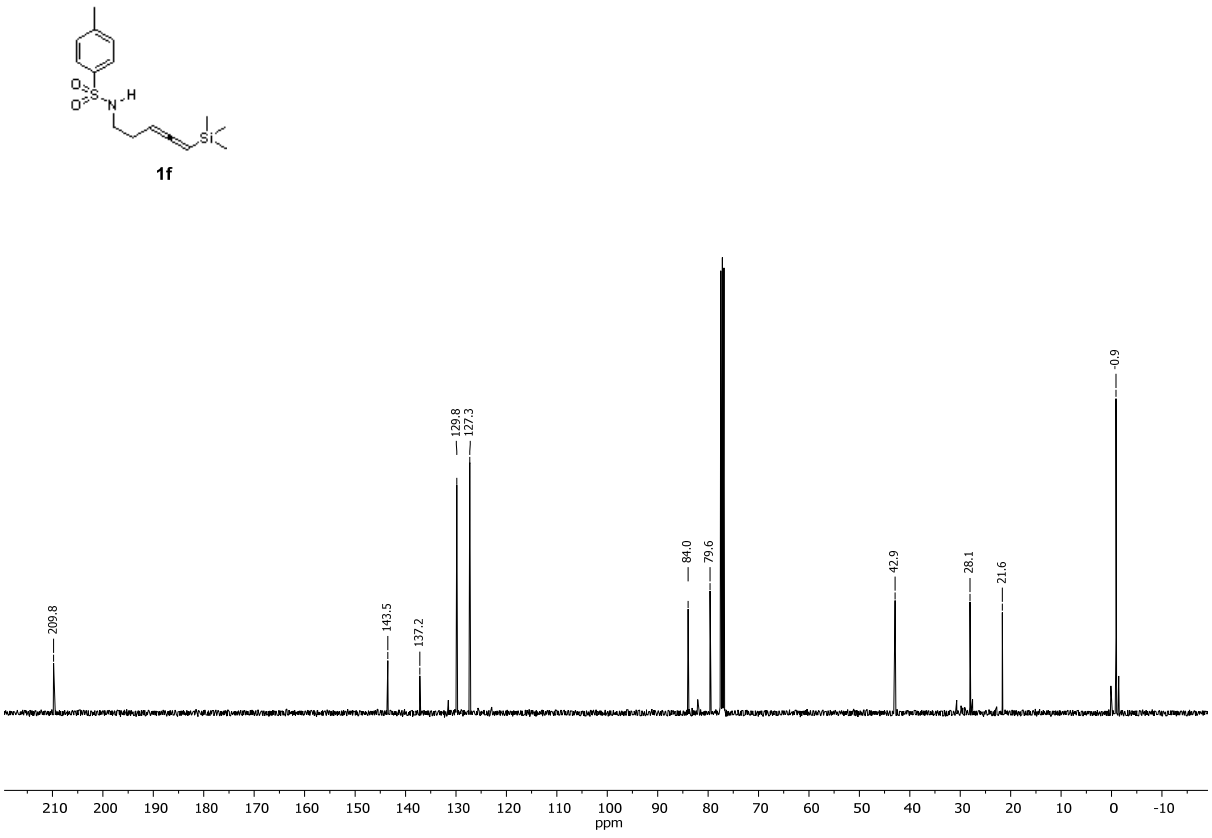
4-Methyl-N-(2-methylhepta-5,6-dien-3-yl)benzenesulfonamide **(1e)**



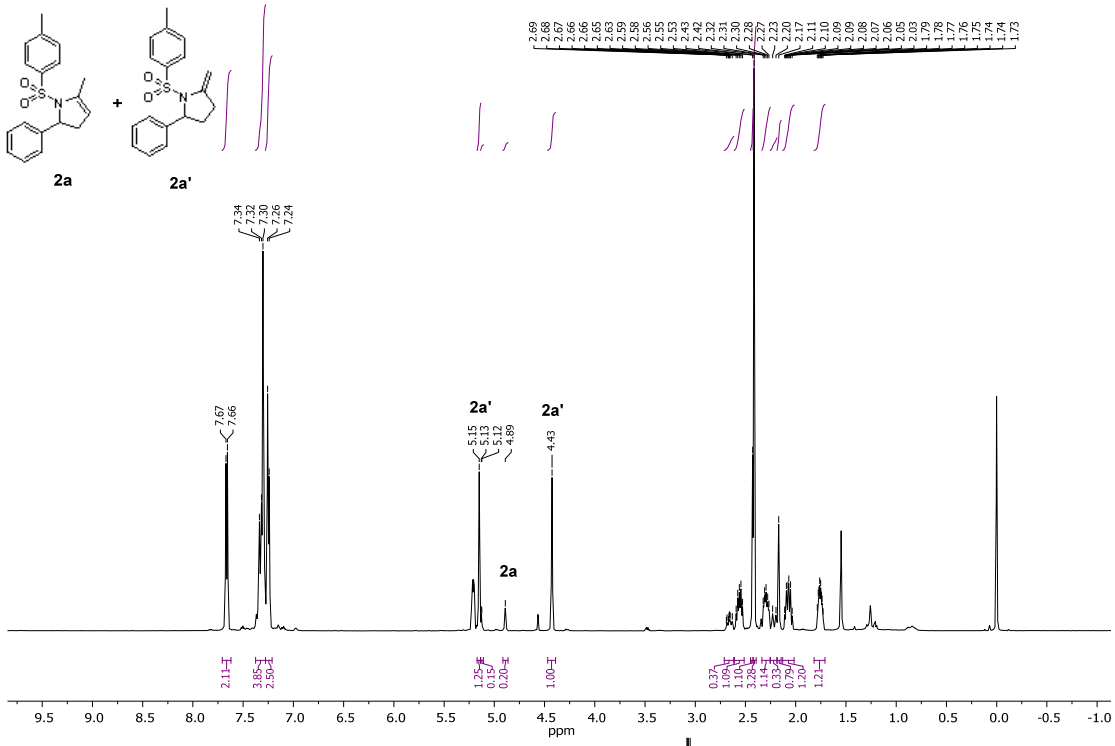


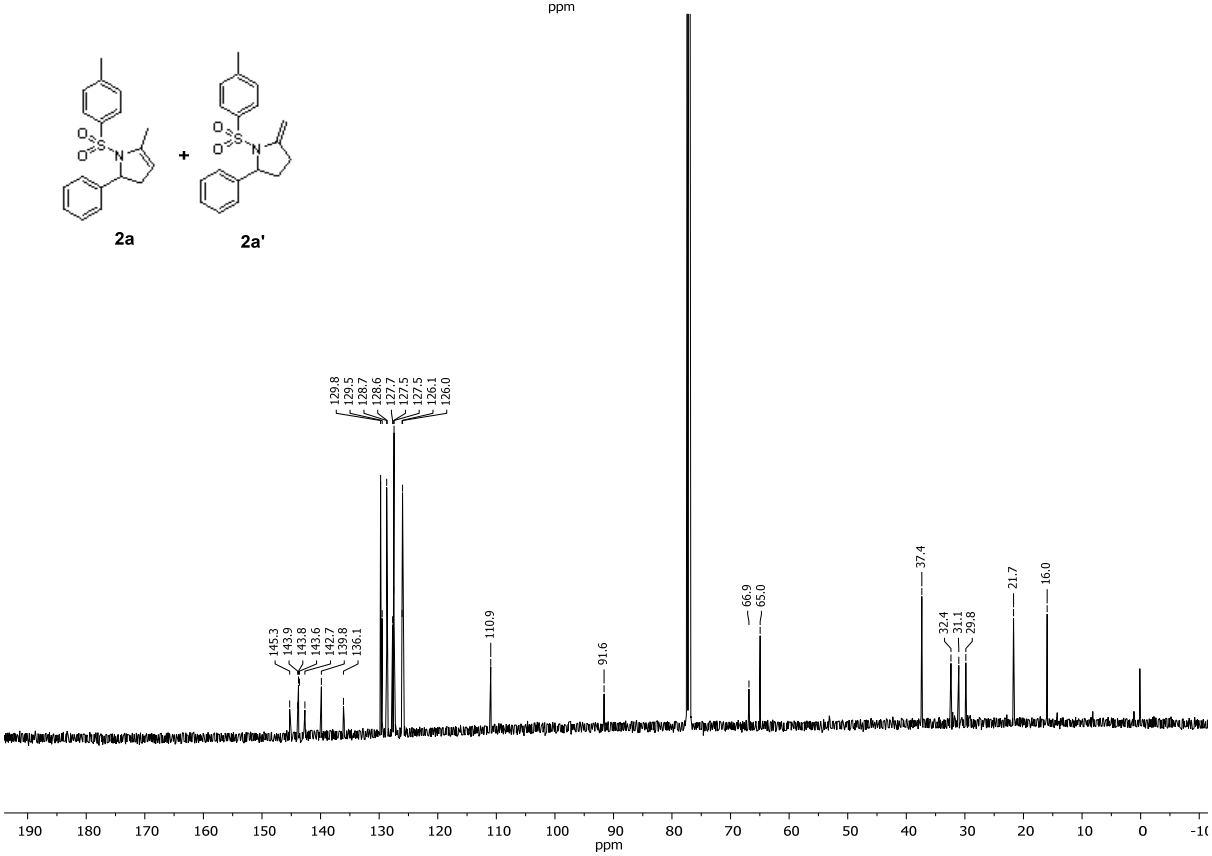
4-Methyl-N-(5-(trimethylsilyl)penta-3,4-dien-1-yl)benzenesulfonamide (**1f**)



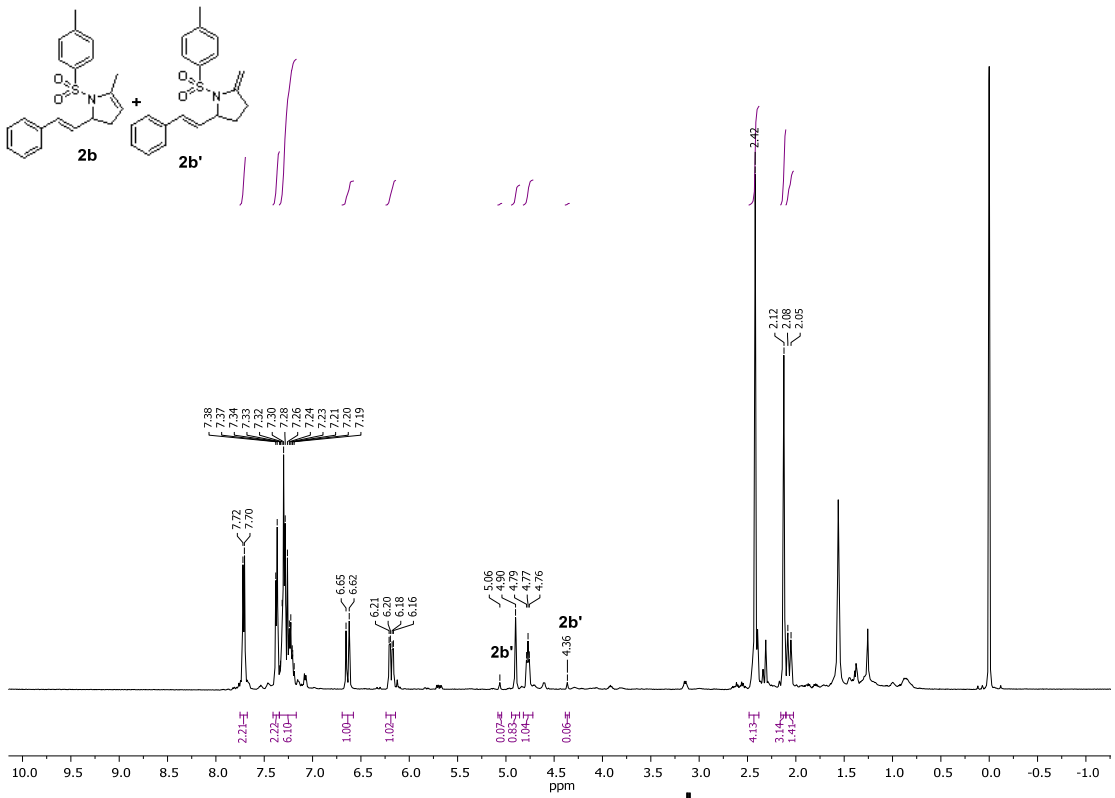


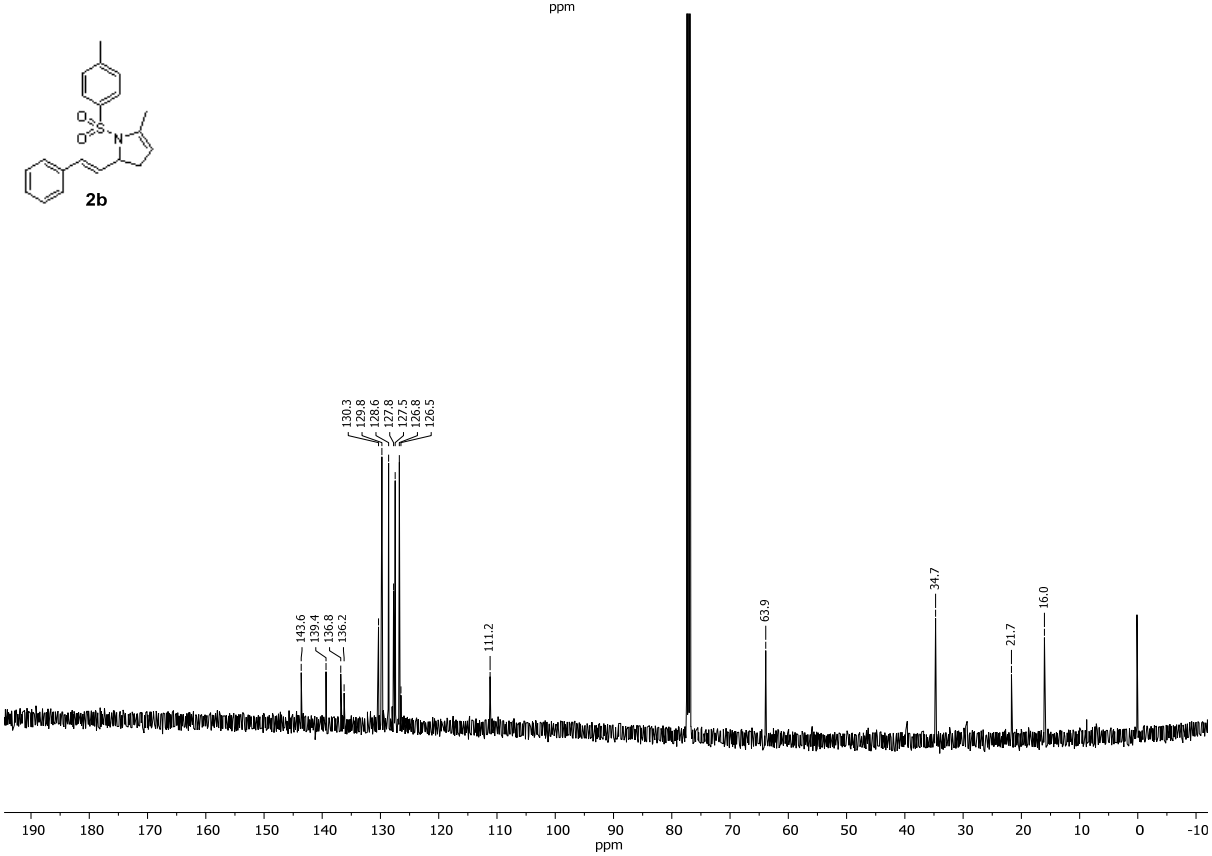
5-Methyl-2-phenyl-1-(4-methyl-N-benzenesulfonamide)-2,3-dihydro-1H-pyrrole (**2a**) and *2-methylene-5-phenyl-1-(4-methyl-N- benzenesulfonamide)pyrrolidine* (**2a'**)



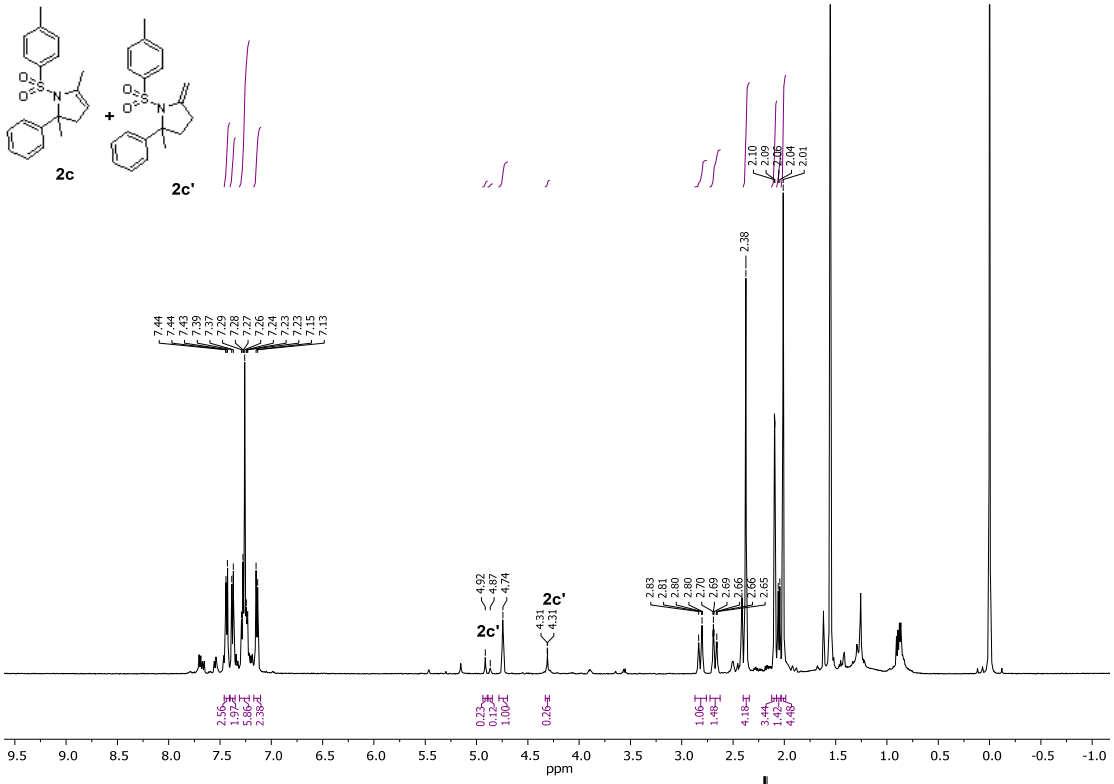


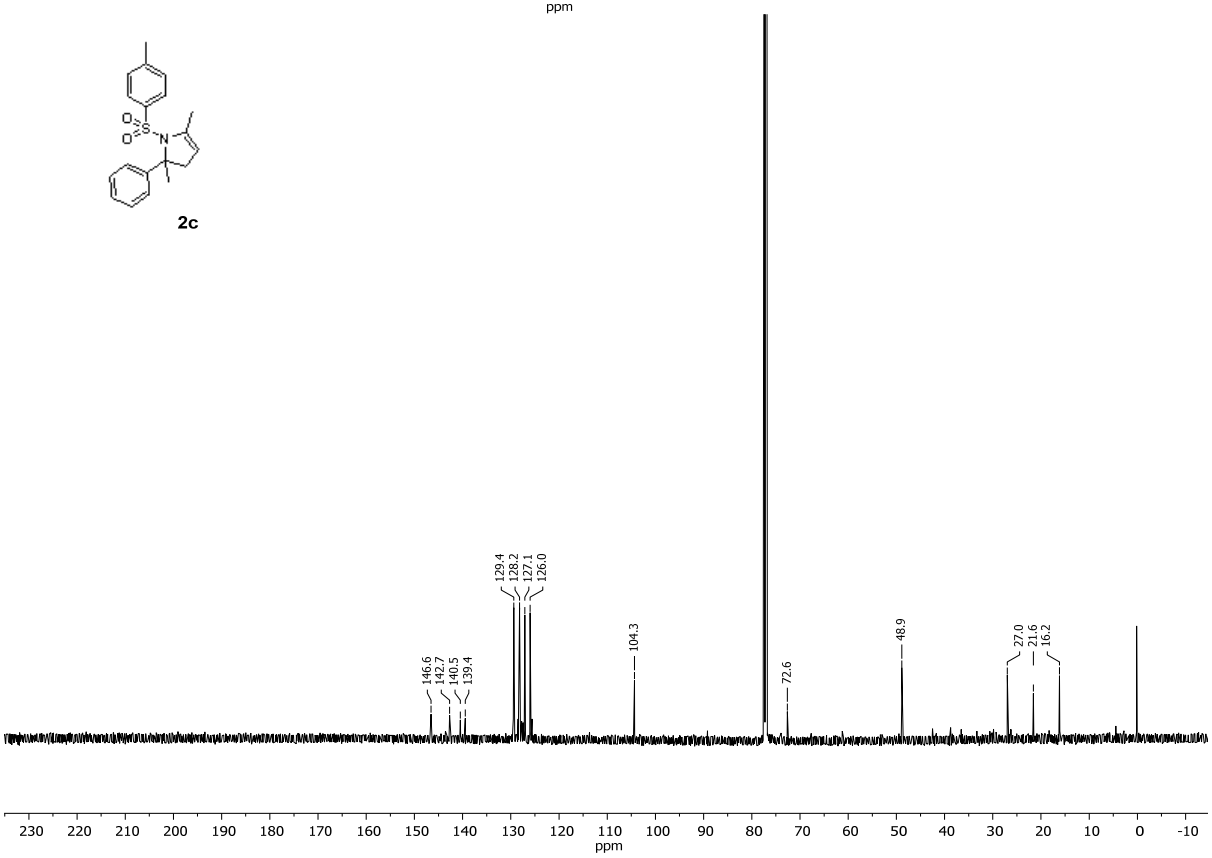
(E)-5-Methyl-2-styryl-1-(4-methyl-N-benzenesulfonamide)-2,3-dihydro-1H-pyrrole (**2b)** and *(E)-2-methylene-5-styryl-1-(4-methyl-N-benzenesulfonamide)pyrrolidine* **(2b')**



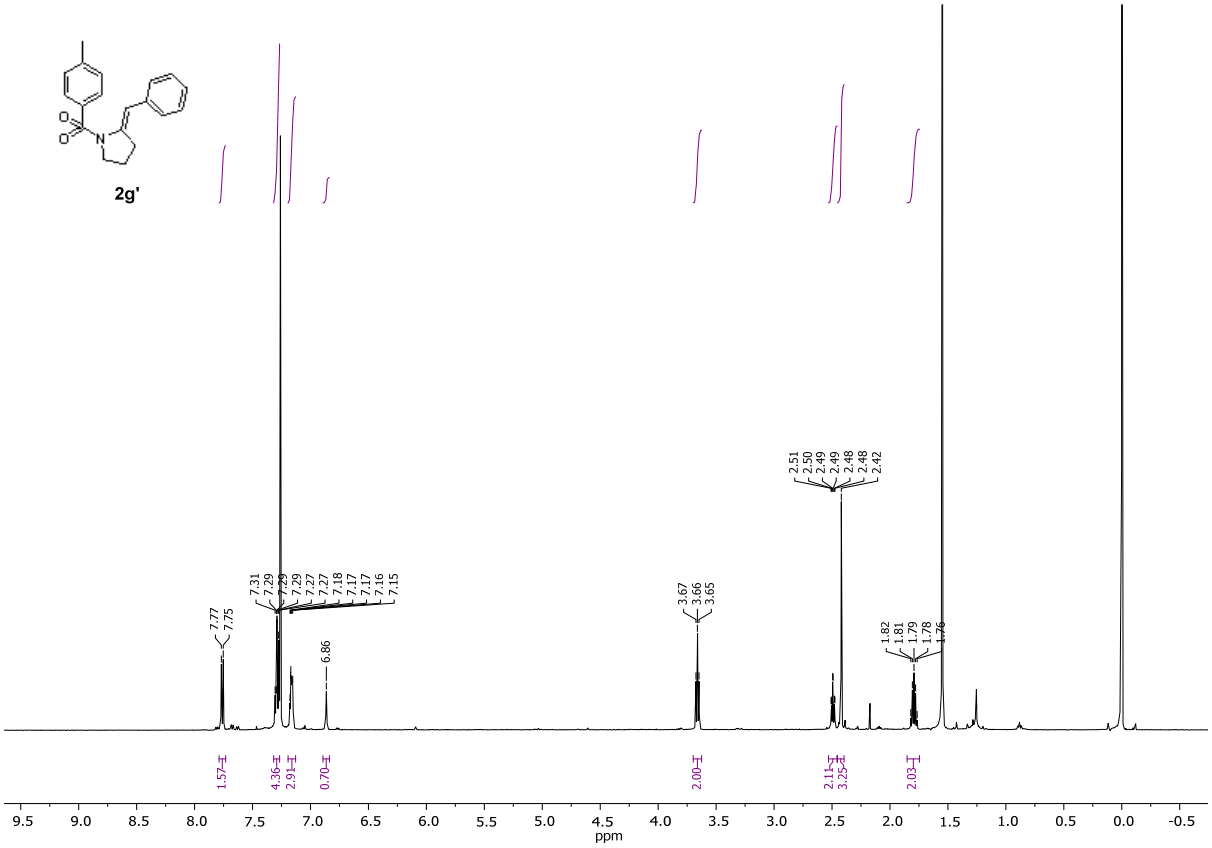


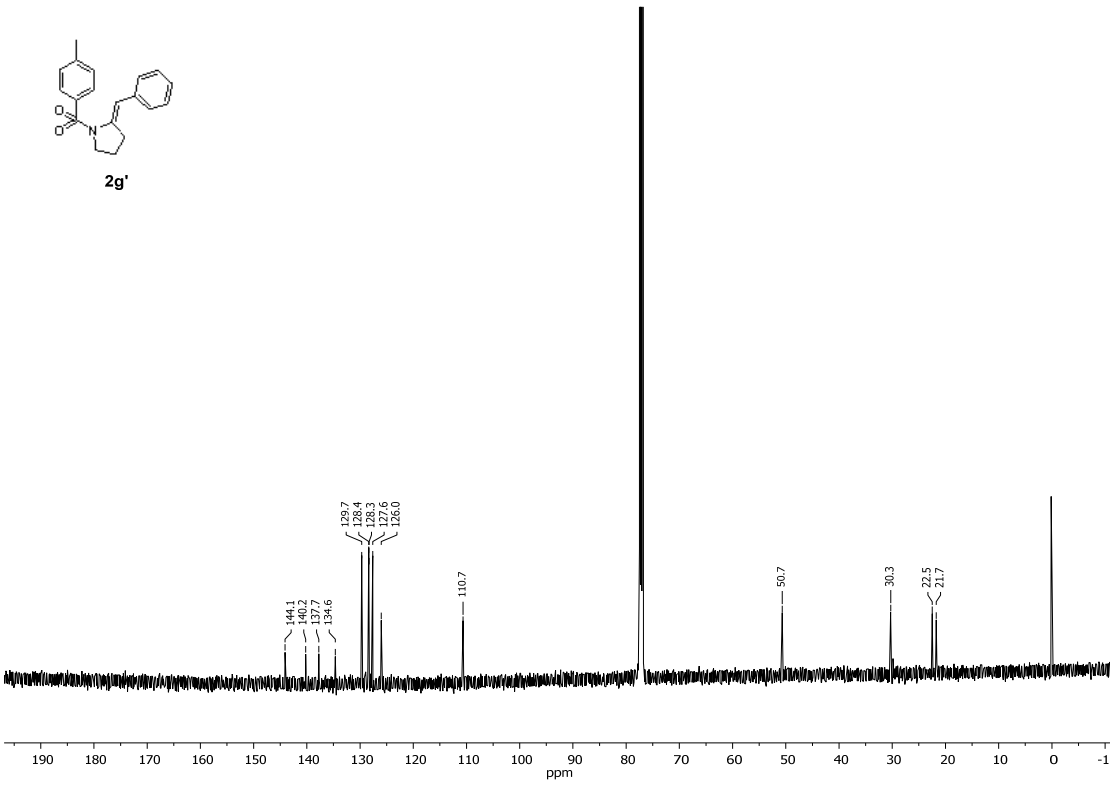
2,5-Dimethyl-2-phenyl-1-(4-methyl-N-benzenesulfonamide)-2,3-dihydro-1H-pyrrole (**2c**) and *2-methyl-5-methylene-2-phenyl-1-(4-methyl-N-benzenesulfonamide)pyrrolidine* (**2c'**)



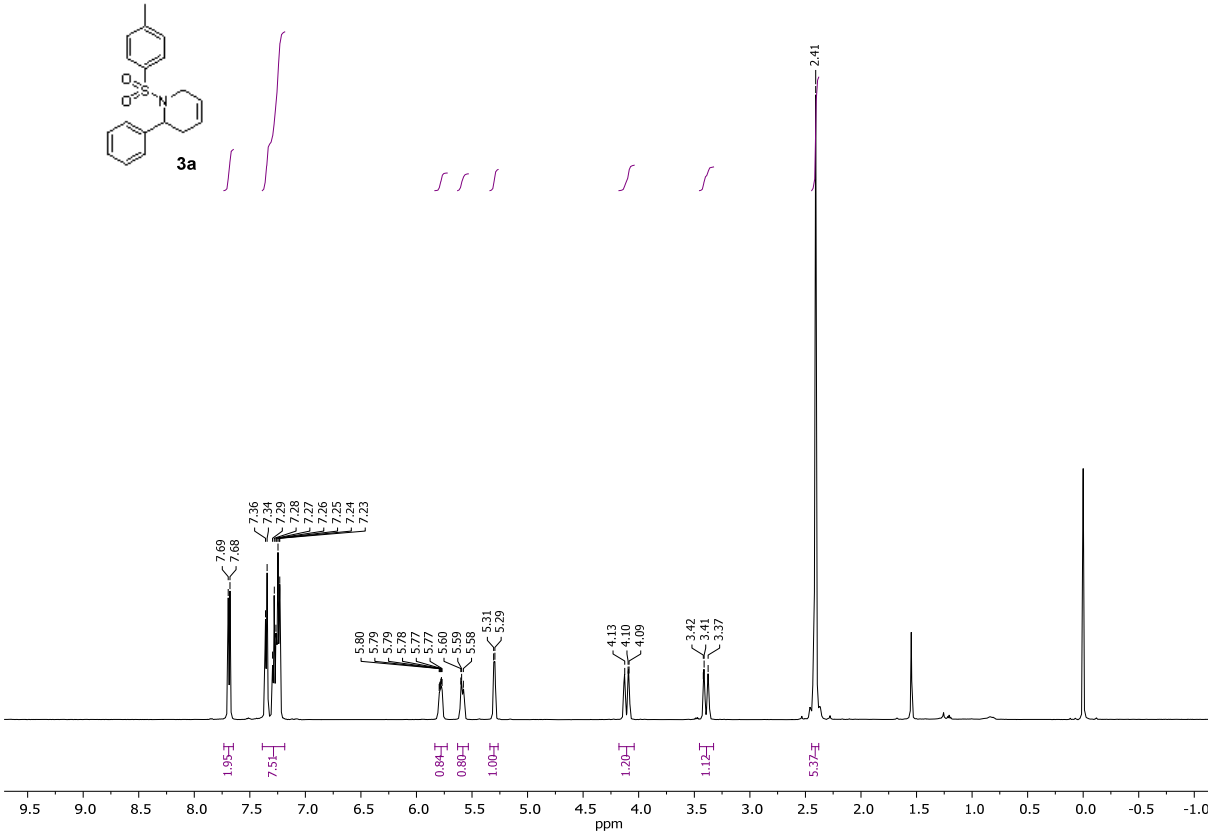


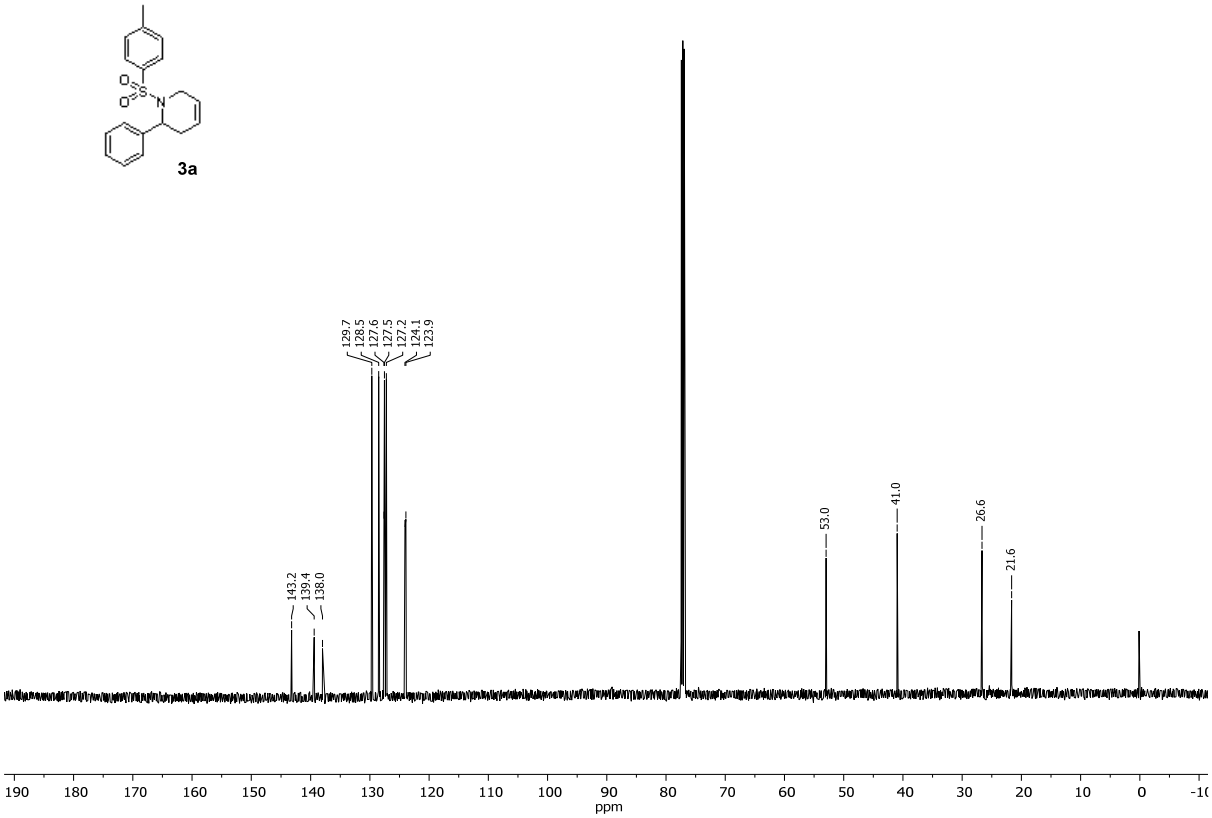
(E)-2-benzylidene-1-(4-methyl-N-benzenesulfonamide)pyrrolidine (**2g'**)



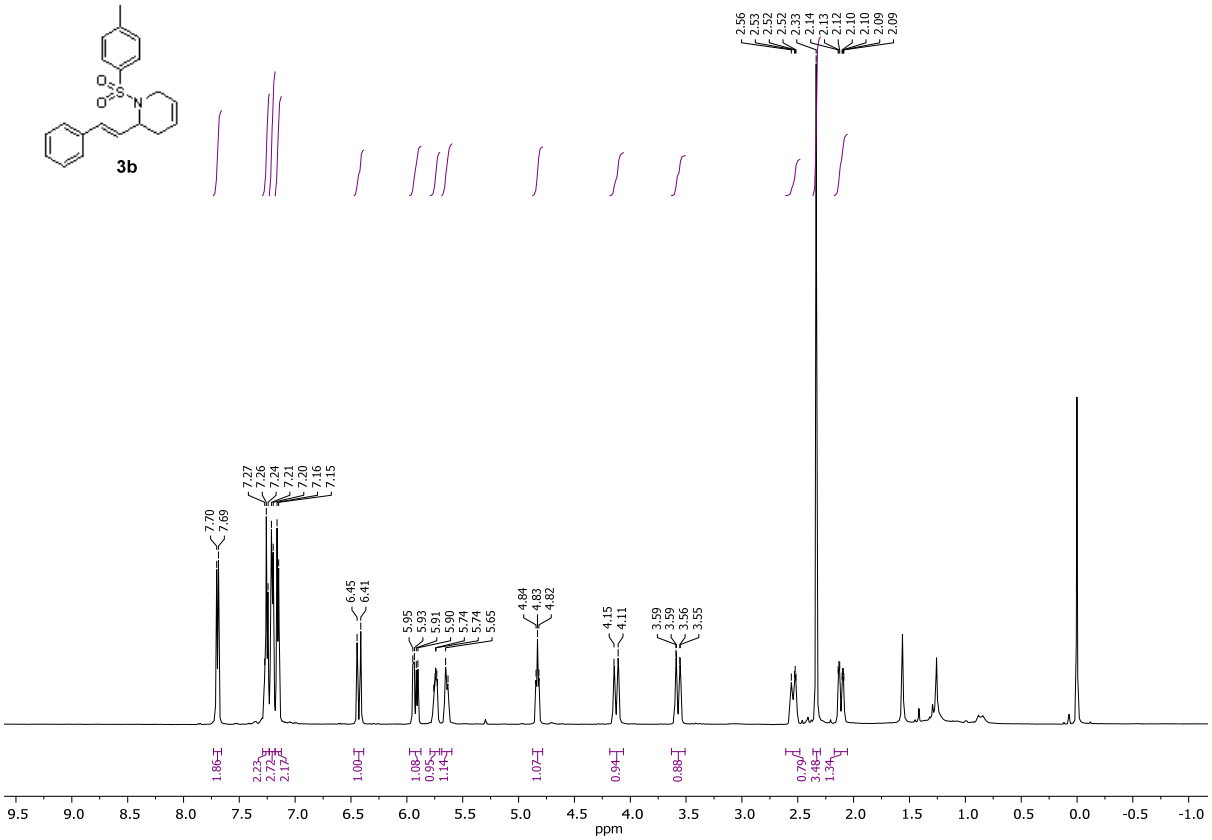


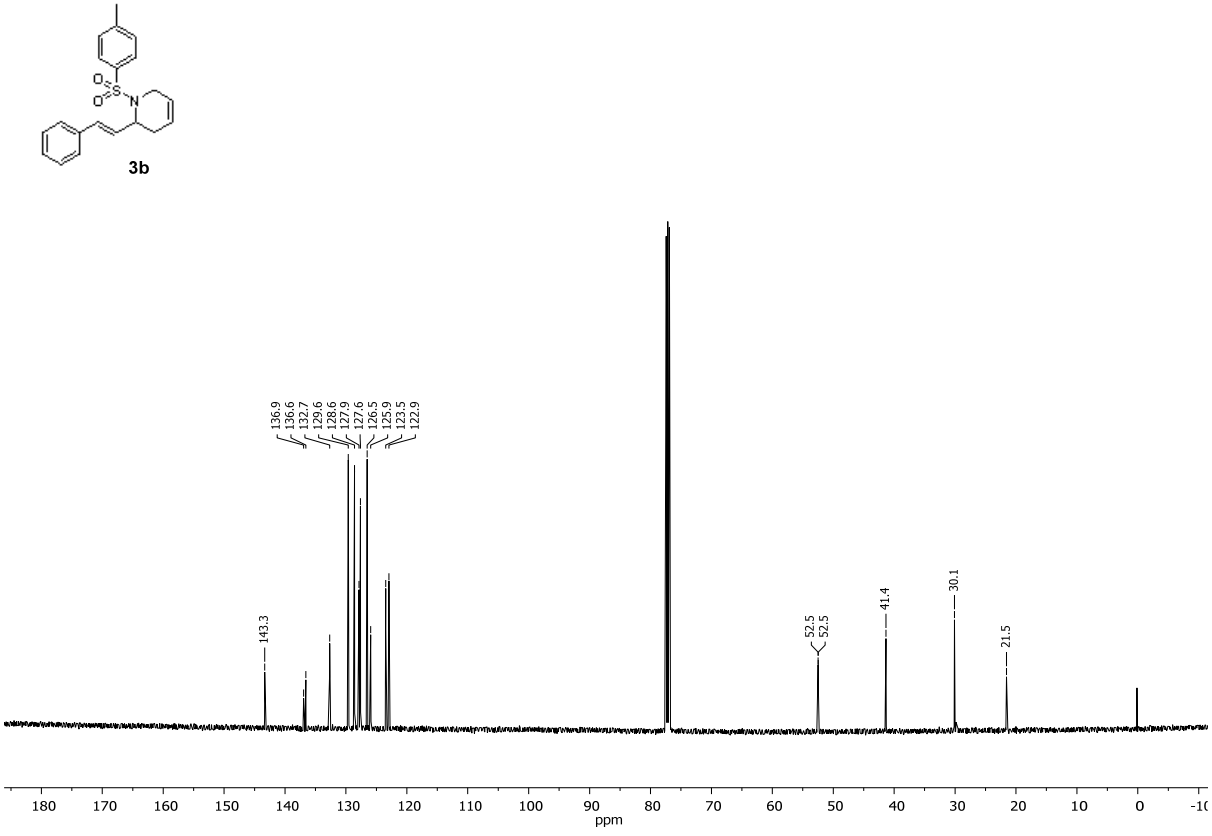
2-Phenyl-1-(4-methyl-N-benzenesulfonamide)-1,2,3,6-tetrahydropyridine (**3a**)



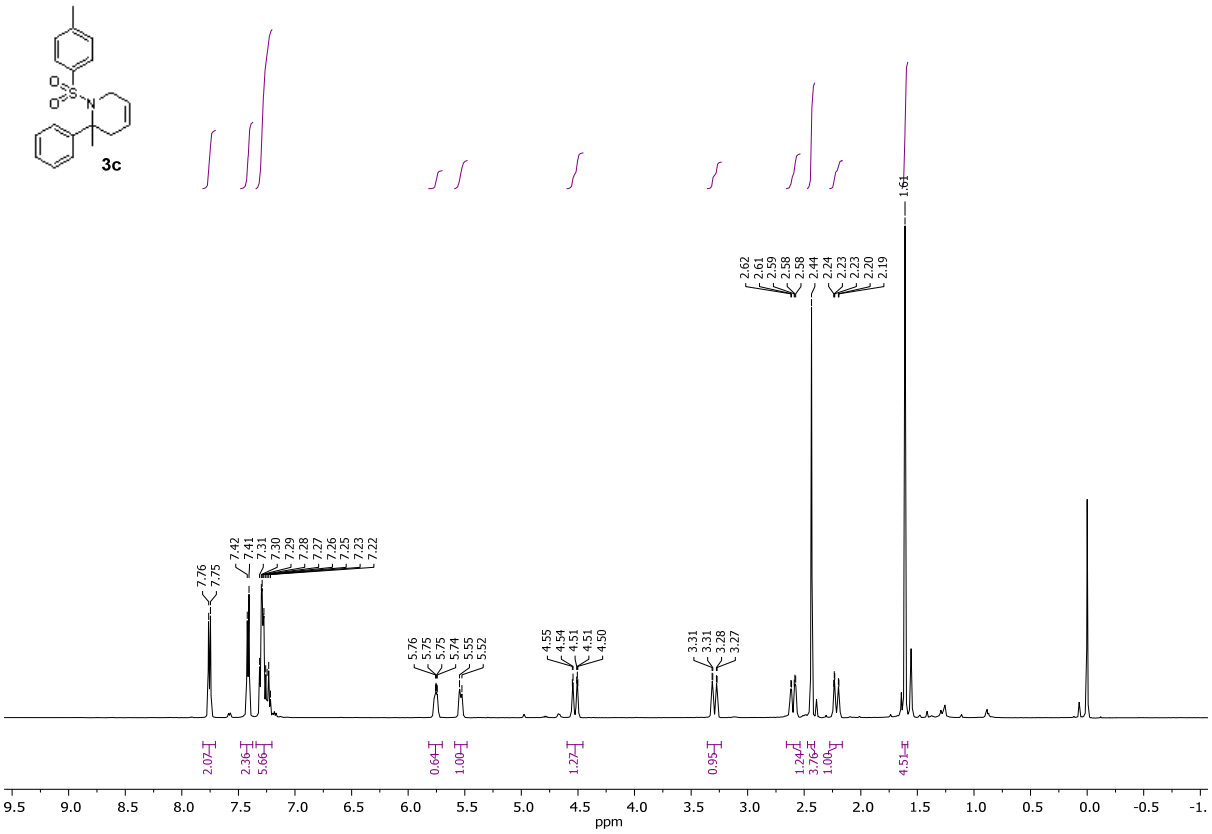


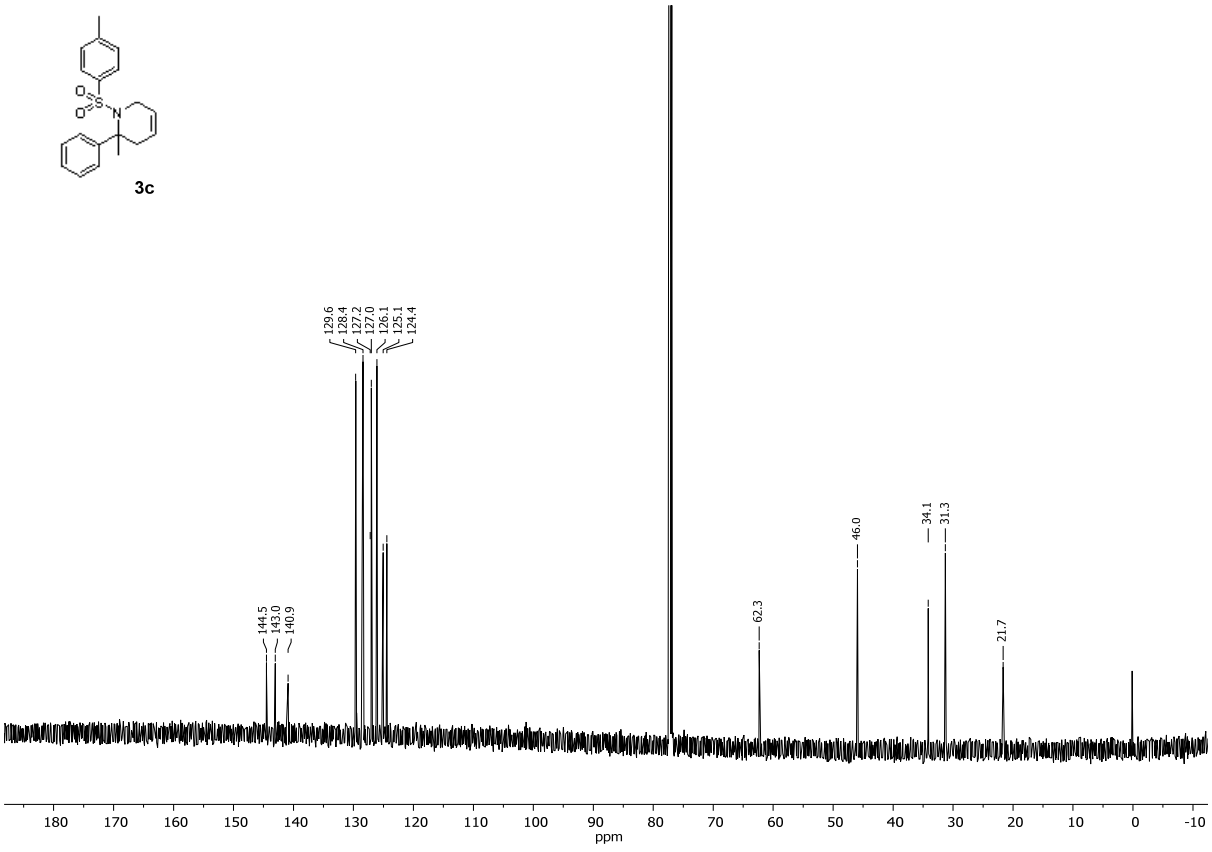
(E)-2-Styryl-1-(4-methyl-N-benzenesulfonamide)-1,2,3,6-tetrahydropyridine (**3b**)



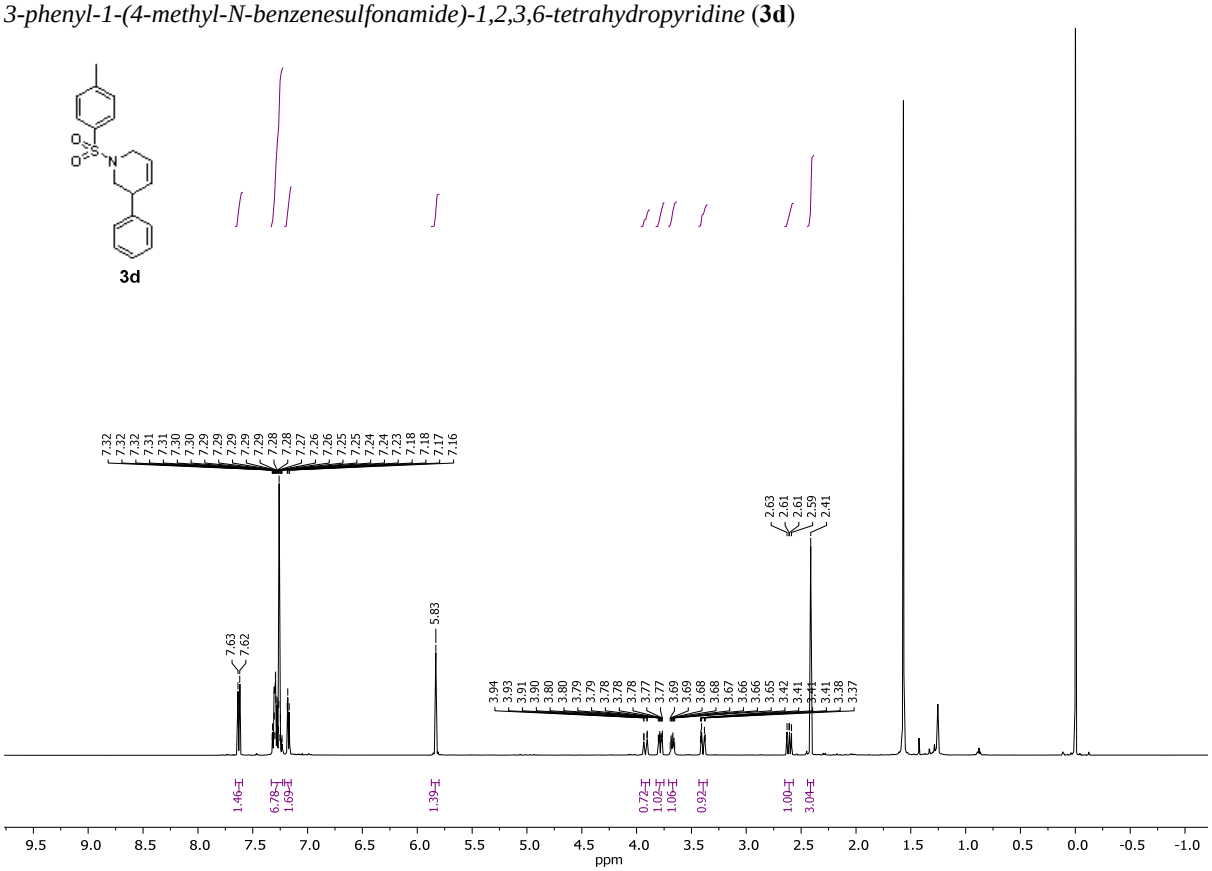


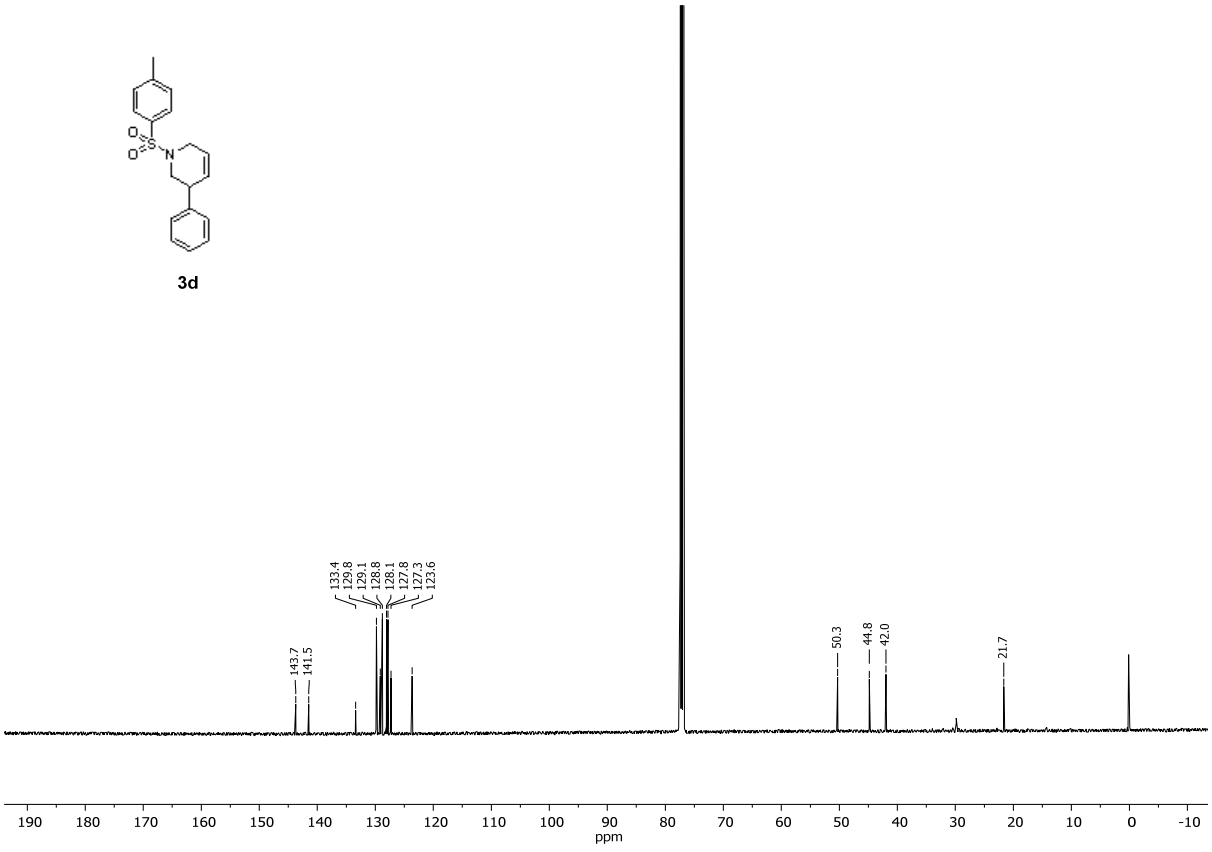
2-Methyl-2-phenyl-1-(4-methyl-N-benzenesulfonamide)-1,2,3,6-tetrahydropyridine (**3c**)



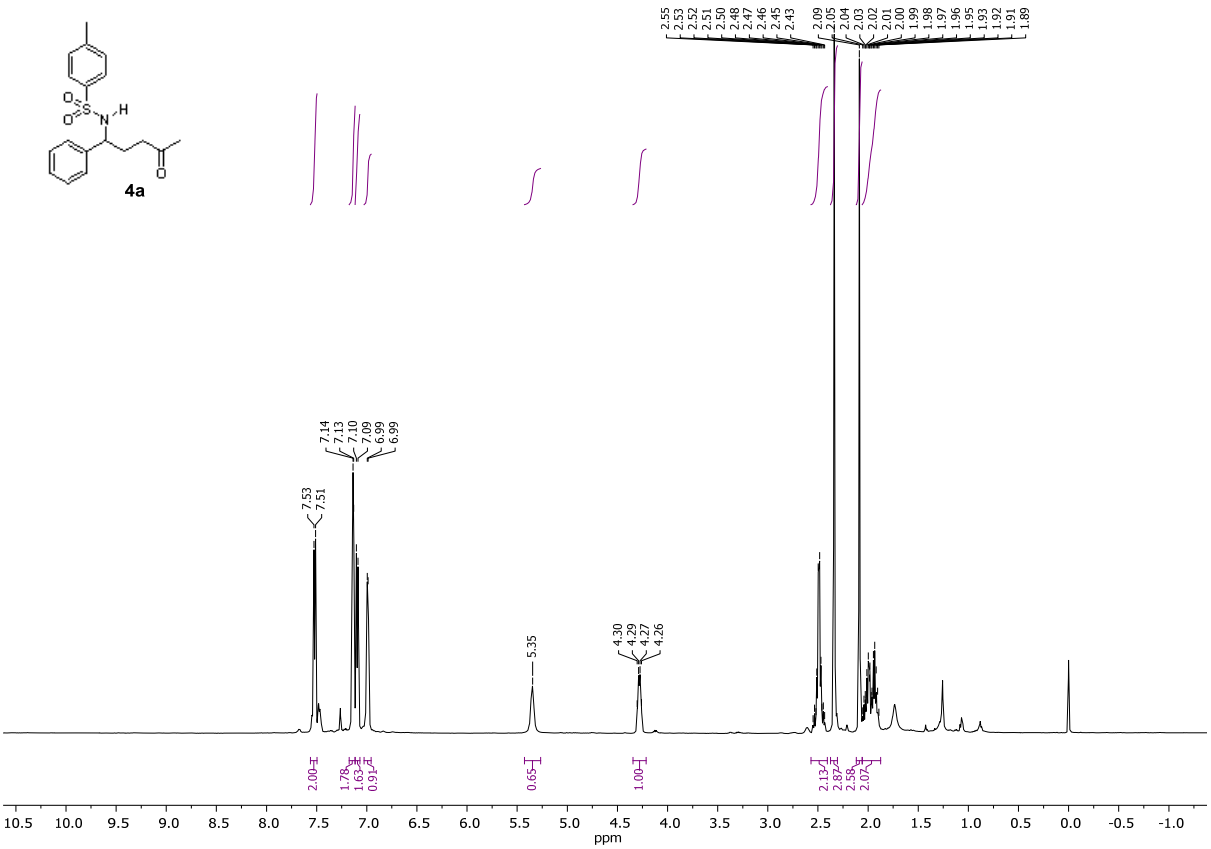


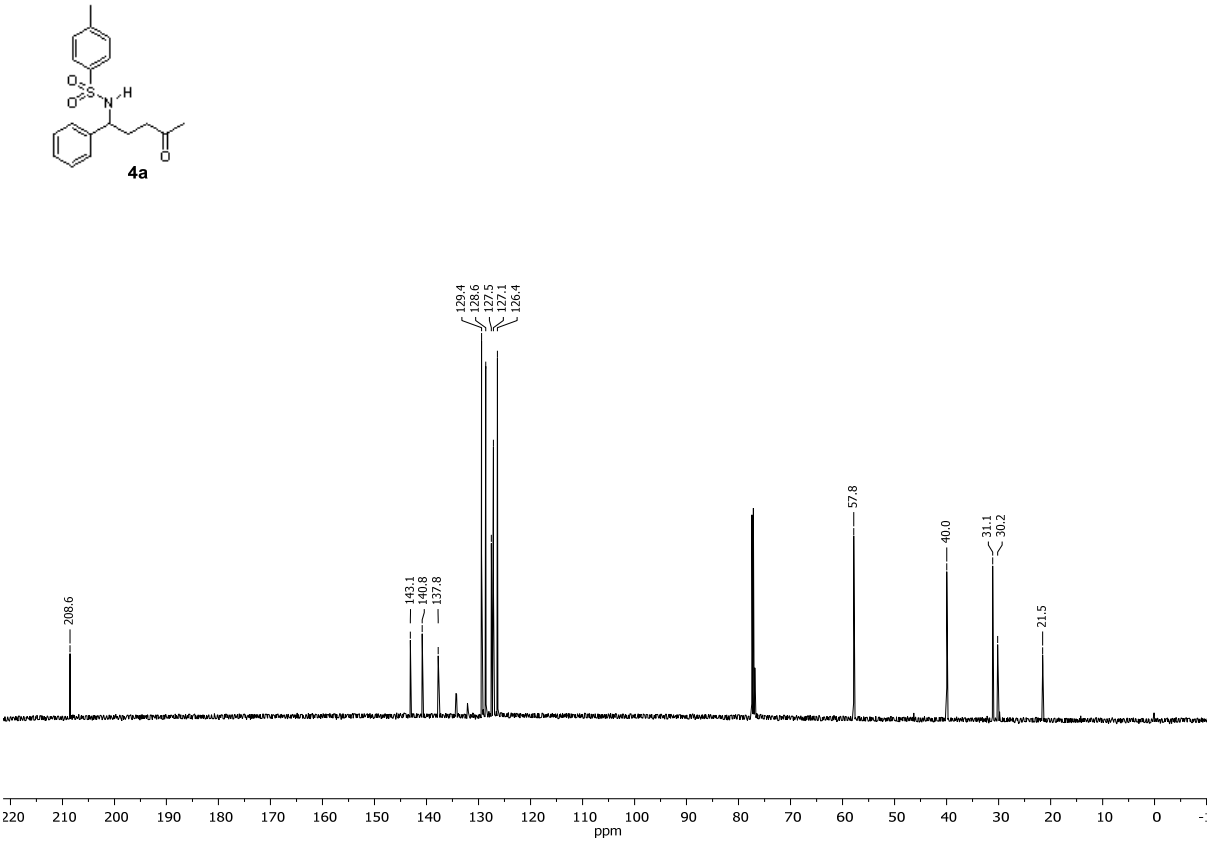
3-phenyl-1-(4-methyl-N-benzenesulfonamide)-1,2,3,6-tetrahydropyridine (**3d**)



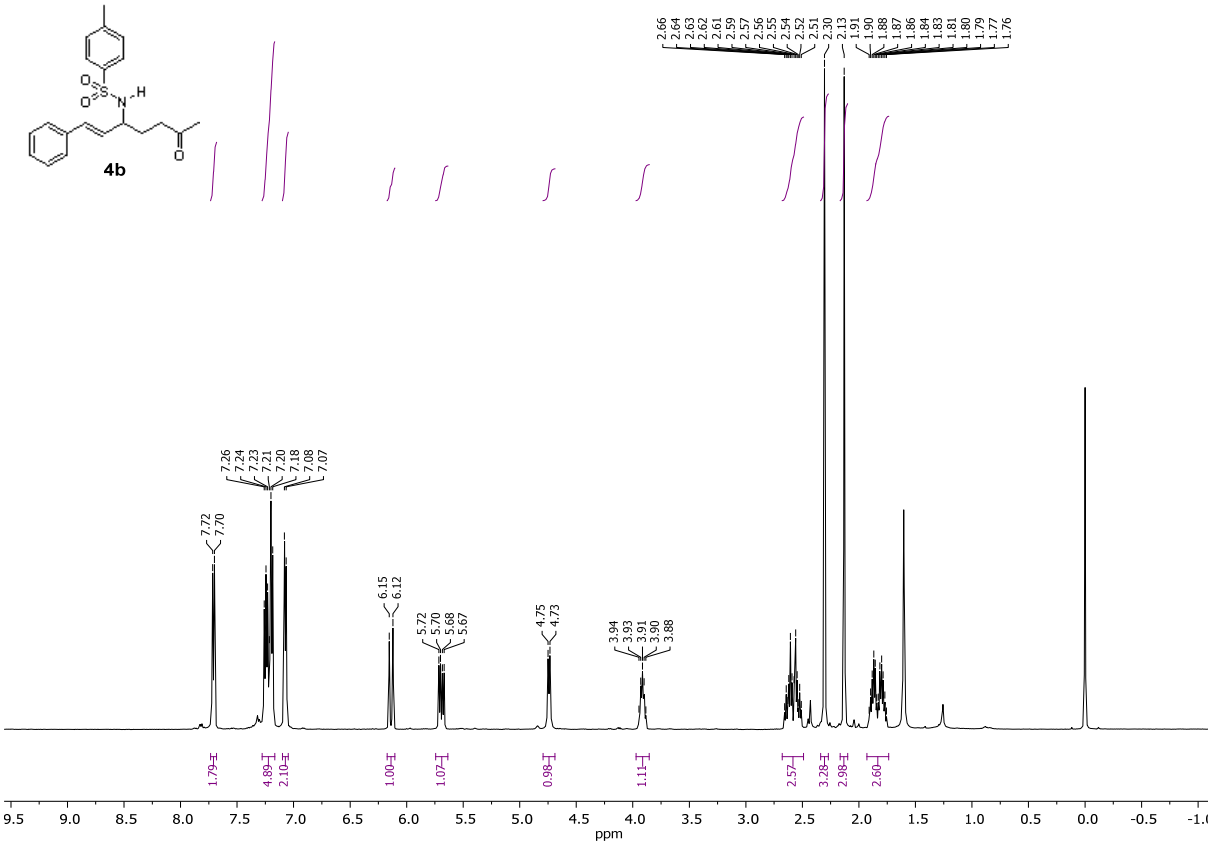


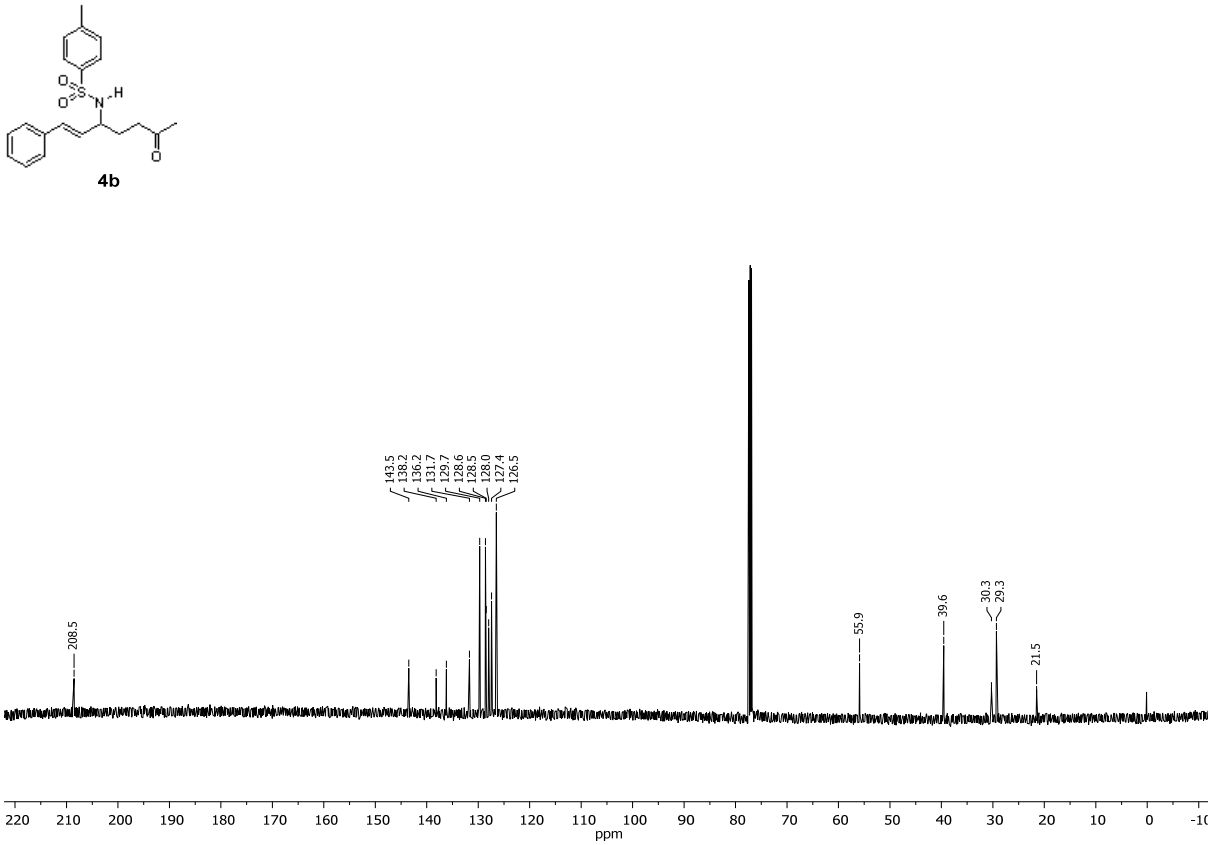
4-Methyl-N-(4-oxo-1-phenylpentyl)benzenesulfonamide **(4a)**



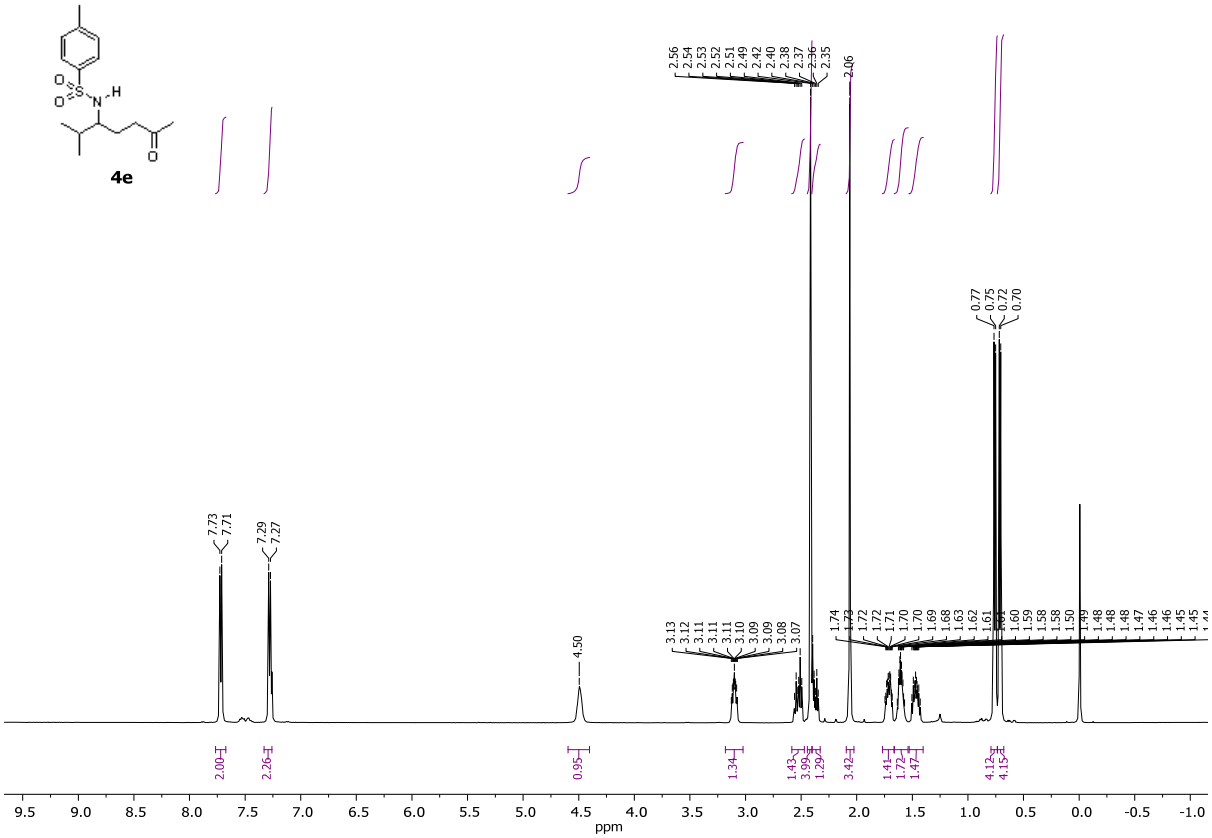


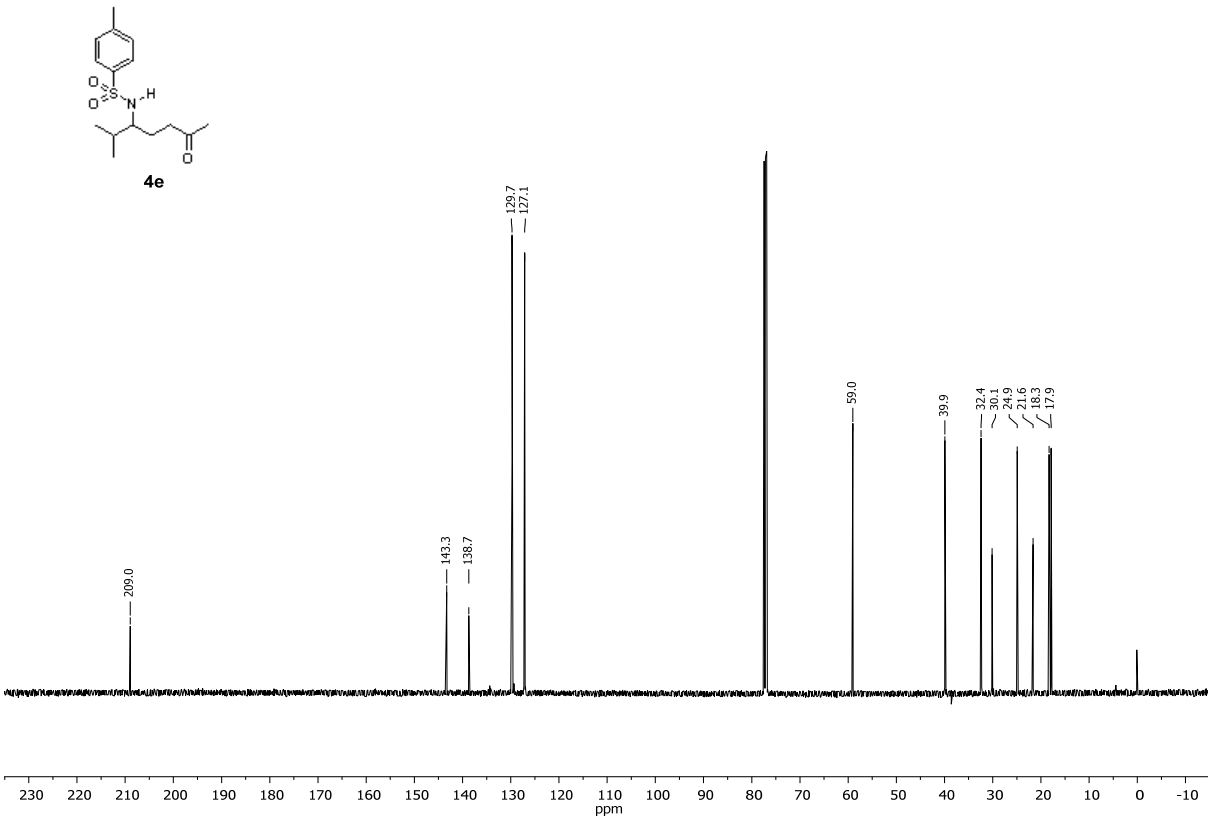
(E)-4-Methyl-N-(6-oxo-1-phenylhept-1-en-3-yl)benzenesulfonamide **(4b)**





4-Methyl-N-(2-methyl-6-oxoheptan-3-yl)benzenesulfonamide **(4e)**





Crystallographic Data

Figure 1-Crystal data for **1a**

Structure of the $C_{18}H_{19}NO_2S$ molecule with labelling of selected atoms, showing both locations of each disordered atom (C2, C3, C4 occupancy 0.865; C52, C53, C64 occupancy 0.135). Anisotropic displacement ellipsoids
display 30% probability levels. Hydrogen atoms are drawn as circles with small radii.
CCDC number - 1836512

Crystal data

$C_{18}H_{19}NO_2S$
$M_r = 313.42$
Monoclinic, $P2_1$
Hall symbol: P 2yb
$a = 10.2410\ (3)$ Å
$b = 7.3767\ (1)$ Å
$c = 11.2819\ (3)$ Å
$\beta = 111.900\ (3)°$
$V = 790.78\ (4)$ Å^3
$Z = 2$

$F(000) = 332.000$
$D_x = 1.316$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 8440 reflections
$\theta = 4–72°$
$\mu = 1.87$ mm^{-1}
$T = 150$ K
Plate, colourless
0.35 × 0.23 × 0.04 mm

Data collection

SuperNova, Dual, Cu at zero, EosS2 diffractometer
Radiation source: Supernova (Cu) X-ray Source
Mirror monochromator
ω scans

Absorption correction: multi-scan
CrysAlis PRO, Agilent Technologies, Version 1.171.37.35h (release 09-02-2015 CrysAlis171 .NET) (compiled Feb 9 2015,16:26:32) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
$T_{min} = 0.68$, $T_{max} = 0.92$
12530 measured reflections
2600 independent reflections
2570 reflections with $I > 2.0\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 72.4°$, $\theta_{min} = 4.2°$
$h = -12 \rightarrow 12$
$k = -6 \rightarrow 9$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.073$
$S = 1.00$
2600 reflections
214 parameters
9 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement
Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.31P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.008$
$\Delta\rho_{max} = 0.37$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}
Absolute structure: Flack (1983), 917 Friedel-pairs
Absolute structure parameter: 0.002 (16)

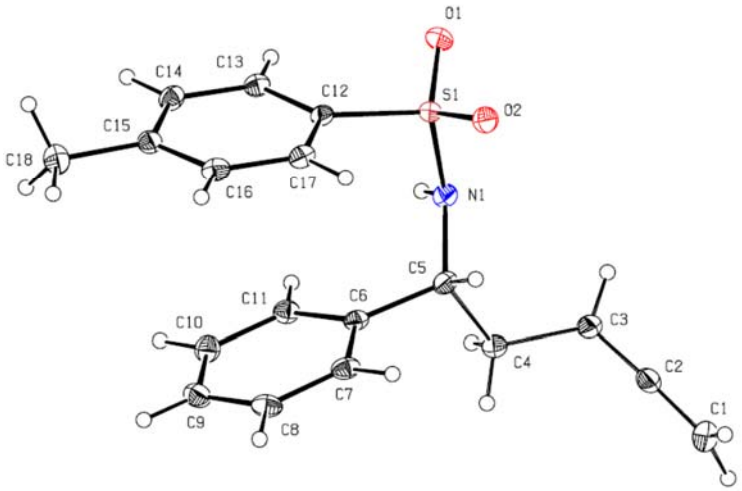


Figure 2- Crystallography data for **2a'**
Structure of the $C_{18}H_{19}NO_2S$ molecule with labelling of selected atoms. Anisotropic displacement ellipsoids display 30% probability levels. Hydrogen atoms are drawn as circles with small radii.
CCDC number - 1836513

Crystal data

$C_{18}H_{19}NO_2S$
$M_r = 313.42$
Monoclinic, *Cc*
Hall symbol: C -2yc
$a = 17.2255$ (2) Å
$b = 11.9664$ (1) Å
$c = 7.5477$ (1) Å
$\beta = 94.7454$ (10)°
$V = 1550.45$ (3) Å^3
$Z = 4$

$F(000) = 664$
$D_x = 1.343$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 9666 reflections
$\theta = 4$–72°
$\mu = 1.90$ mm^{-1}
$T = 150$ K
Block, colourless
0.30 × 0.19 × 0.07 mm

Data collection

SuperNova, Dual, Cu at zero, EosS2 diffractometer
Radiation source: Supernova (Cu) X-ray Source
Mirror monochromator
ω scans

Absorption correction: multi-scan
CrysAlis PRO, Agilent Technologies, Version 1.171.37.35h (release 09-02-2015 CrysAlis171 .NET) (compiled Feb 9 2015,16:26:32) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
$T_{min} = 0.75$, $T_{max} = 0.87$
11755 measured reflections
2488 independent reflections
2479 reflections with $I > 2.0\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 72.3°$, $\theta_{min} = 4.5°$
$h = -21 \rightarrow 21$
$k = -14 \rightarrow 14$
$l = -7 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.055$
$S = 1.01$
2488 reflections
201 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map

H-atom parameters constrained
Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.04P)^2 + 0.59P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.0002$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}
Extinction correction: Larson (1970), Equation 22
Extinction coefficient: 9.0 (16)
Absolute structure: Flack (1983), 952 Friedel-pairs
Absolute structure parameter: 0.011 (11)

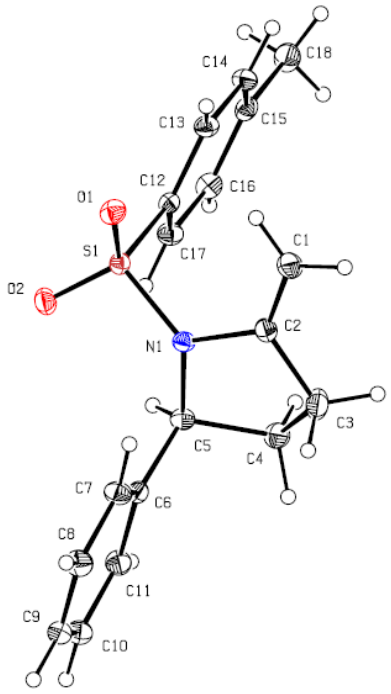


Figure 3- Crystallography data for **3a**
Structure of the $C_{18}H_{19}NO_2S$ molecule with labelling of selected atoms. Anisotropic displacement ellipsoids display 30% probability levels. Hydrogen atoms are drawn as circles with small radii.
CCDC number - 1836514

Crystal data

$C_{18}H_{19}NO_2S$
$M_r = 313.42$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 9.6292$ (1) Å
$b = 10.5065$ (1) Å
$c = 15.5004$ (1) Å
$V = 1568.16$ (2) Å^3
$Z = 4$

$F(000) = 664$
$D_x = 1.327$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 26987 reflections
$\theta = 4$–72°
$\mu = 1.88$ mm^{-1}
$T = 150$ K
Block, colourless
0.34 × 0.29 × 0.21 mm

Data collection

SuperNova, Dual, Cu at zero, EosS2 diffractometer
Radiation source: Supernova (Cu) X-ray Source
Mirror monochromator
ω scans

Absorption correction: multi-scan *CrysAlis PRO*, Agilent Technologies, Version 1.171.37.35h (release 09-02-2015 CrysAlis171 .NET) (compiled Feb 9 2015,16:26:32) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
$T_{min} = 0.60$, $T_{max} = 0.67$
30988 measured reflections
3093 independent reflections
3087 reflections with $I > 2.0\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 72.4°$, $\theta_{min} = 5.1°$
$h = -11 \rightarrow 11$
$k = -13 \rightarrow 10$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.053$
$S = 1.01$
3093 reflections
201 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map

H-atom parameters constrained
Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.36P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.0004$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Extinction correction: Larson (1970), Equation 22
Extinction coefficient: 75 (4)
Absolute structure: Flack (1983), 1309 Friedel-pairs
Absolute structure parameter: 0.009 (10)

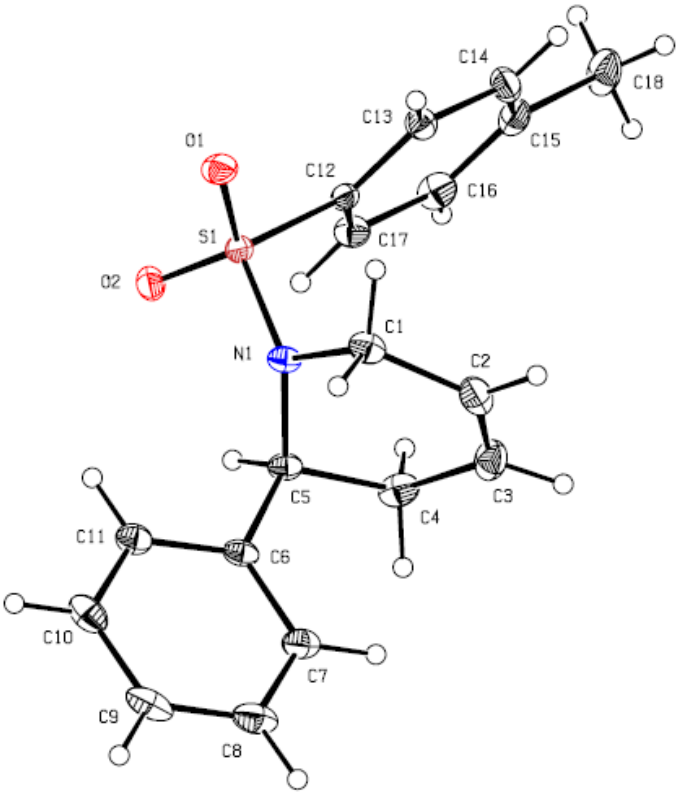


Figure 3- Crystallography data for **4a**

Structure of the $C_{18}H_{21}NO_3S$ molecule with labelling of selected atoms. Anisotropic displacement ellipsoids display 30% probability levels. Hydrogen atoms are drawn as circles with small radii.

CCDC number - 1836515

Crystal data

$C_{18}H_{21}NO_3S$
$M_r = 331.44$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 6.2364$ (2) Å
$b = 7.2255$ (2) Å
$c = 37.1584$ (15) Å
$V = 1674.40$ (10) Å^3
$Z = 4$

$F(000) = 704$
$D_x = 1.315$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
Cell parameters from 6719 reflections
$\theta = 5$–$72°$
$\mu = 1.84$ mm^{-1}
$T = 150$ K
Plate, colourless
0.14 × 0.07 × 0.02 mm

Data collection

SuperNova, Dual, Cu at zero, EosS2 diffractometer
Radiation source: Supernova (Cu) X-ray Source
Mirror monochromator
ω scans

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$T_{min} = 0.83$, $T_{max} = 0.97$
25856 measured reflections
3303 independent reflections
3187 reflections with $I > 2.0\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 72.8°$, $\theta_{min} = 4.8°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 8$
$l = -45 \rightarrow 45$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.116$
$S = 1.05$
3303 reflections
212 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement
Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.0P)^2 + 3.67P]$, where $P = (\max(F_o^2,0) + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.009$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Absolute structure: Flack (1983), 1339 Friedel-pairs
Absolute structure parameter: 0.07 (3)