Supporting Information

Nucleophile Dependent Formation of 6- and 7-Membered *N*-Heterocycles by Platinum-Catalysed Cyclisation of 1,5-Bisallenes

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1) General experimental details

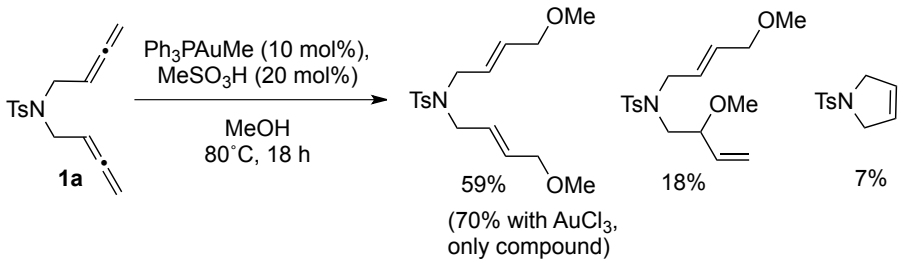
All reagents were purchased from commercial sources and used without further purification, unless noted otherwise. Solvents were dried using nitrogen atmosphere and used fresh every day for reaction. Deuterated solvents were acquired from Apollo Scientific Limited or Fluorochem and stored over molecular sieves. All the preparative procedures were carried out in the absence of moisture and air under a nitrogen atmosphere, unless stated otherwise. Glassware, standard Schlenk tubes, and Schlenk tubes from Carousel 12 Plus Reaction Station from Radleys were flame-dried and flushed with nitrogen. Thin layer chromatography was performed on Aluminium oxide TLC-Cards with Fluorescent indicator 254 nm over aluminium oxide matrix from Sigma-Aldrich, and on Silica TLC-plates (60 F_{254} Merck). Components were visualized by illumination with UV light (λ = 254 nm), or by staining using potassium permanganate solution or phosphomolibdic acid solution in EtOH. Purification was performed by flash column chromatography using silica gel from Macherey-Nagel GmbH & Co. KG (particle size of 40 to 63 μm) as stationary phase, silica gel from Sigma-Aldrich (high purity grade (Merck grade 9385), pore size 60 Å, 230 - 400 mesh particle size), or Aluminium Oxide activated (basic, Brockmann I of pore size 58 Å, pH 9.5 ± 0.5 in H_2O). Preparative TLC purifications were performed over pre-coated TLC plates from Macherey-Nagel. GmbH & Co, Sil. G-25, 0.25 mm layer. Accurate weights were obtained with a Denver Instrument SI-234. Reactions under microwave irradiation were carried out in a Biotage Initiator^{+} Microwave system. ^{1}H, ^{2}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on a Bruker Avance III 500 MHz NMR spectrometer, fitted with a 5mm broadband observed, BBFO^{plus} Z-gradient SmartProbe^{TM} probe. ^{13}C NMR was recorded using broadband proton decoupling. Calibration was made using the deuterated solvent residual peak in the case of the ^{1}H (δH = 7.26 ppm for $CDCl_3$, δH = 6.0 ppm for $CDCl_2CDCl_2$ and δH = 3.58 ppm for THF-d^8) and ^{13}C NMR (δC = 77.16 ppm for $CDCl_3$).[1] Chemical shifts (δ) are given in parts per million (ppm) and coupling constants values (*J*) are given in Hertz (Hz). Abbreviations for multiplicities are as follows: (s) singlet, (d) doublet, (dd) doublet doublet, (t) triplet, (q) quartet, (m) multiplet, (b) broad. Low resolution mass spectra were recorded using electrospray (ESI) technique in the positive and negative ion mode with a Shimadzu LCMS spectrometer. Phenomenex pre-column filter (Security Guard, ODS C18, 4 x 3 mm i.d.) was used to prevent rapid deterioration of the pre-column. Elution was carried out using a mobile phase comprising methanol, at a flow rate of 0.2

1 H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512-7515.

mL min^{-1}. All solvents were HPLC grade. High-resolution mass spectra were obtained from the EPSRC Mass Spectrometry Service at the University of Swansea by EI, NSI, ESI, APCI or ASAP techniques, using a Waters XEVO G2-S or Thermo Scientific LTQ Orbitrap XL. Melting points were measured with a BÜCHI Melting Point B-545. Infrared spectra were acquired using a Perkin Elmer System 400 FT-IR spectrophotometer. Solid samples were run as thin films of their solution in DCM. Liquid samples were run neat.

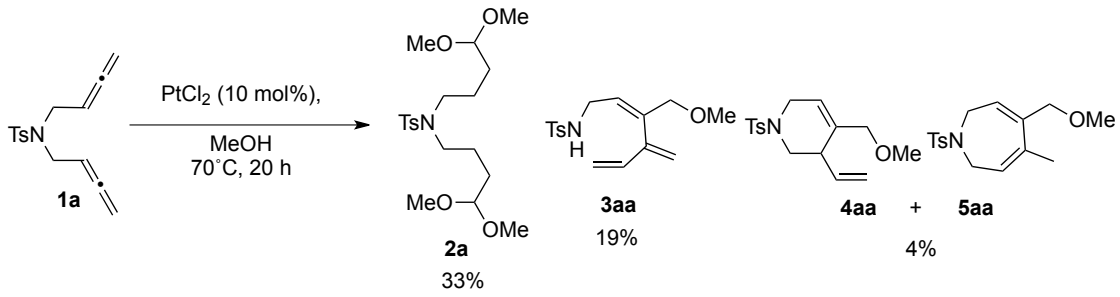
2) Screening and optimization of reaction conditions

1,5-Bisallene **1a** was used as model substrate in the reaction with different metals in MeOH. Complexes tested were: $Fe(CO)_5$ (10 mol%); $FeCl_3 \cdot H_2O$ (10 mol%); $Fe(NO_3)_3 \cdot 9H_20$ (10 mol%); $NiCl_2$ (10 mol%); $PdCl_2$ (10 mol%); $[RhCl(cod)]_2$ (10 mol%); $AgNO_3$ (10 mol%); CuCl (10 mol%); $Hg(NO_3)_2$ (excess). Unreacted starting material or complex mixtures were obtained in all cases. Gold complexes gave products of the attack of methanol to one or both allenes following reported reactivity, but no cyclization with incorporation of the alcohol in the final skeleton was observed (Scheme 2.1).



Scheme 2.1. Reaction of bisallene **1a** in MeOH with cationic gold catalysts.

Platinum was the only metal that gave cyclization products (Scheme 2.2) and therefore was selected for further screening.



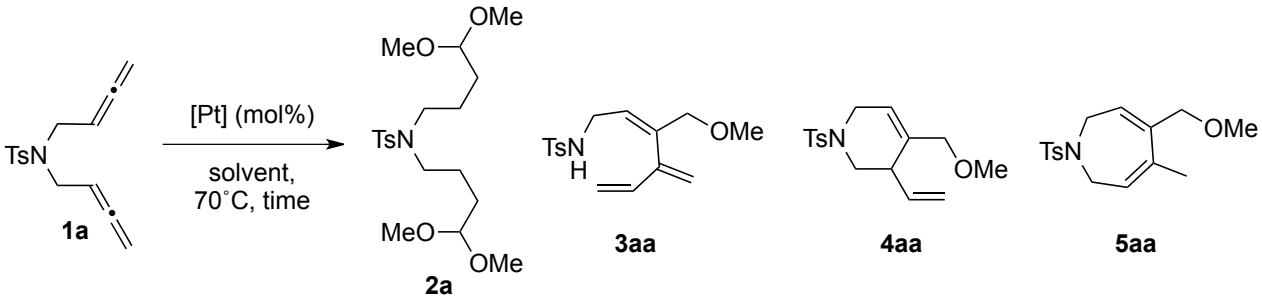
Scheme 2.2. Reaction of bisallene **1a** in MeOH with $PtCl_2$.

Supporting Information

In order to optimise the formation of the cyclic products in the platinum-catalyzed reaction, we perfomed a wide screening of platinum-complexes with different silver salts, as halogen abstractors, to preform *in situ* the cationic complexes with different counterions, in MeOH as solvent or in mixtures MeOH:THF at 70 ^{o}C. Table 2.1 shows a small selection with the representative results obtained from this screening.

Platinum complexes bearing phosphines and nitrogen ligands were also tested. In most cases bisallene was recovered unreacted or less successful results were obtained.

Table 2.1. Screening of platinum catalysts and solvent mixtures.



Entry	[Pt] (mol%)	Additives (mol%)	Solvent	Time (h)	Products Ratio 2a:3aa:4aa:5aa before purification (% isolated yield)
1	$PtCl_2$ (5)	---	MeOH	20	1:1:0.2:0.2 **2a** (33); **3aa** (19); **4aa+5aa** (4)
2	$PtCl_2(MeCN)_2$ (5)	---	MeOH	20	**2a** (14); **3aa** (36); **5aa** (5)
3	$PtCl_4$ (5)	---	MeOH	20	**2a** (74)
4	$PtCl_2(MeCN)_2$ (5)	$AgSbF_6$ (10)	MeOH	20	0:1:0.1:0.3 **3aa** (25); **4aa** (11); **5aa** (13)
5	$PtCl_2$ (5)		Toluene, MeOH (3 equiv)	20	**2a** (66)
6	$PtCl_2(MeCN)_2$ (5)	$AgSbF_6$ (10)	MeCN: MeOH (18:1)	26	**3aa** (20); 20% conversion
7	$PtCl_2(MeCN)_2$ (5)	$AgSbF_6$ (10)	THF: MeOH (1:5)	1.5	0:1:0.8:0 **3aa** (22); **4aa** (18)
8	$PtCl_2(MeCN)_2$ (5)	$AgSbF_6$ (10)	THF: MeOH (1:1)	1.5	0:1:0.7:0 **3aa** + **4aa** (58)
9	$PtCl_2(MeCN)_2$ (5)	$AgSbF_6$ (10)	THF: MeOH	4	0:1:1.4:0

			(5:1)		**3aa** + **4aa** (39)
10	$PtCl_2(MeCN)_2$ (5)	$AgSbF_6$ (10)	THF: MeOH (10:1)	4	0:1:1.2:0 **3aa** (24)+ **4aa** (35)

In order to optimise the reaction in the presence of water towards formation of the seven membered rings as the only products of the reaction a new optimization study was carried out. The best catalyst and temperature were the same than when using methanol. However, an improvement was observed when the ratio of the solvents was changed. Using a mixture of THF:H_2O 1:3, the seven membered cycles were formed as the only products, without traces of the triene, and being the cycle **6ad** the major product in the reaction.

Table 2.2. Optimization of the reaction with water.

Entry	**Solvent:H_2O (ratio)**	**t (h)**	**NMR Yields (%)[a],[b]**		
			3ad	**5ad**	**6ad**
1	THF:H_2O (18:1)	5 h 45 min	2	7	33
2	THF, H_2O (3 equiv)	26 h	31	-	-
3	Toluene:H_2O (18:1)	> 48 h	Complex mixture		
4	1,4-dioxane:H_2O (18:1)	4 h	6	1	1
5	THF:H_2O (9:1)	5 h 30 min	2	16	21
6	THF:H_2O (3:1)	12 h	2	7	33
7	THF:H_2O (1:1)	20 h	2	7	47
8	THF:H_2O (1:3)	12 h	**5ad**:**6ad** 1:9.8 (43)[c]		

[a] 100% conversion of starting material. **[b]** NMR yield using 3,4,5-trichloropyridine as internal standard added to the crude of reaction. **[c]** The products were isolated as inseparable mixture and the ratio was measured after purification.

We observed an increase in cycle **6ad** formation as the amount of H_2O in the media increases in a linear correlation for the TsN-derivative, which supports protodemetallation of intermediate **17** assisted by an external molecule of H_2O (Entries 5 to 8 in Table 2.2, Scheme 5 in main text).

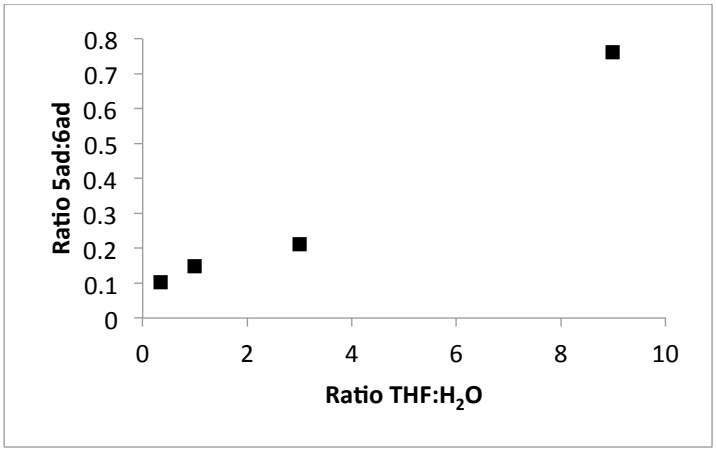
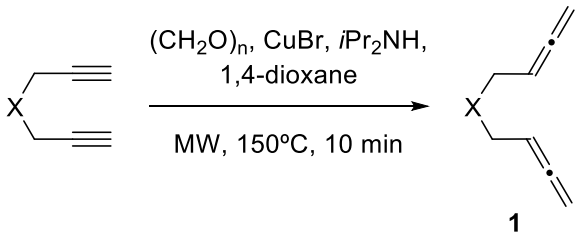


Figure 2.1. Correlation of ratio of cycles **5ad:6ad** with the amount of water present.

3) Experimental details and characterization of 1,5-bisallenes and products

3a) General procedure for the synthesis of 1,5-bisallenes 1a-1f by microwave-assisted Crabbé homologation from bispropargyl derivatives[2]



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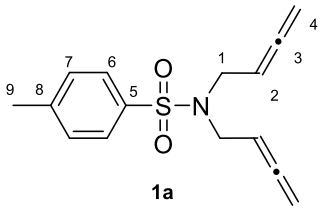
CuBr (0.6 eq) and paraformaldehyde (5.0 eq) were added into a oven-dried microwave vial under N_2. Then the corresponding bispropargylic derivative (1.0 eq, 0.5 M – absolute concentration) was added dissolved in dry 1,4-dioxane, followed by the addition of *i*Pr_2NH (4.0 eq) dropwise under inert atmosphere. The reaction mixture was heated at 150 ^oC under microwave irradiation during 10 – 20 min until complete conversion, followed by TLC. The crude of the reaction was purified by column chromatography over silica gel using Hex or PET / Et_2O or EtOAc as eluent.

2 H. Nakamura, T. Sugiishi and Y. Tanaka, *Tetrahedron Lett*., 2008, **49**, 7230-7233.

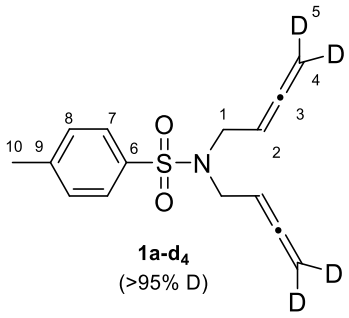
Supporting Information

Synthesis of N,N-di-buta-2,3-dienyl-4-methyl-benzenesulfonamide **(1a)** [3]



From the corresponding bispropargyl derivative (1.6 g, 6.38 mmol), CuBr (549 mg, 3.83 mmol), paraformaldehyde (958 mg, 31.88 mmol), *i*Pr_2NH (3.6 mL, 25.51 mmol) and 13.0 mL of dry 1,4-dioxane. Obtained after column chromatography, PET / EtOAc, (7:1), **1a**, 1.2 g, 4.46 mmol (70%): yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.72 – 7.68 (m, 2H; H_{Ar}-6), 7.29 (d, J = 8.2 Hz, 2H; H_{Ar}-7), 4.97 – 4.90 (m, 2H; H-2), 4.71 (dt, J = 6.6, 2.4 Hz, 4H; H-4), 3.90 (dt, J = 7.0, 2.4 Hz, 4H; H-1), 2.42 (s, 3H; H-9). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 209.8 (2 x C_q; C-3), 143.4 (C_q; C-8), 137.7 (C_q; C-5), 129.8 (2 x CH_{Ar}; C-7), 127.3 (2 x CH_{Ar}; C-6), 85.8 (2 x CH; C-2), 76.3 (2 x CH_2; C-4), 45.8 (2 x CH_2; C-1), 21.7 (CH_3; C-9). HRMS (ESI+): Calc. for $C_{15}H_{18}NO_2S$ $[M+H]^+$: 276.1053. Found: 276.1054.

Synthesis of d_4-N,N-di-buta-2,3-dienyl-4-methyl-benzenesulfonamide **(1a-d_4)**

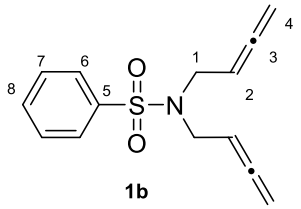


From the corresponding bispropargyl derivative (410 mg, 1.66 mmol), CuBr (143 mg, 0.99 mmol), paraformaldehyde-d_2 (265 mg, 8.28 mmol, 98% D), *i*Pr_2NH (928 µl, 6.62 mmol) and 3.3 mL of dry 1,4-dioxane. Obtained after column chromatography, PET / EtOAc, (20:1) then (7:1) then (4:1): **1a-*d*$_4$**, 284 mg, 1.02 mmol (61%): white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.73 – 7.68 (m, 2H; H_{Ar}-8), 7.29 (d, J = 8.2 Hz, 2H; H_{Ar}-7), 4.94 (t, J = 7.1 Hz, 2H; H-2), 4.73 – 4.68 (m, D-5, >90 %D), 3.90 (d, J = 7.1 Hz, 4H; H-1), 2.42 (s, 3H; H-10). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 209.9 (2 x C_q; C-3), 143.4 (C_q; C-9), 137.7 (C_q; C-6), 129.8 (2 x CH_{Ar}; C-8),

3 (a) S.-K. Kang, Y.-H. Ha, D.-H. Kim, Y. Lim and J. Jung, *Chem. Commun.,* 2001, 1306-1307; (b) T.-G. B. Suk-Ku Kang, A. N. Kulak, Y.-H. Ha, Y. Lim and J. Park, *J. Am. Chem. Soc,.* 2000, **122**, 11529-11530.

127.3 (2 x CH_{Ar}; C-7), 86.0 (2 x CH; C-2), 45.8 (2 x CH_2; C-1), 21.7 (CH_3; C-10). *C_q; C-4 could not be found due to deuteration.* ^{2}H NMR (77 MHz, $CDCl_3$, 25 ^{o}C), δ = 4.74 (s, 4D; D-5). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3079 (C-H_{Ar}), 2924 (C-H_{Alkane}), 2865 (C-H_{Alkane}), 1938 (C=C=C), 1597 (C=C_{Ar}), 1345 (S=O), 1161 (S=O), 1095 (C-N), 941, 814. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{15}H_{14}D_4NO_2S$ $[M+H]^+$: 280.1304. Found: 280.1300. M.P. = 49 – 50 ^{o}C.

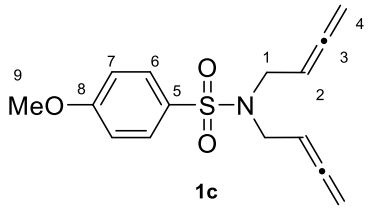
Synthesis of N,N-di-buta-2,3-dienyl-benzenesulfonamide **(1b)**



1b

From the corresponding bispropargyl derivative (1.0 g, 4.32 mmol), CuBr (372 mg, 2.59 mmol), paraformaldehyde (649 mg, 21.61 mmol), *i*Pr_2NH (2.4 mL, 17.29 mmol) and 9.0 mL of dry 1,4-dioxane. Obtained after column chromatography, Hex / EtOAc (12:1): **1b**, 707 mg, 2.71 mmol (63%): yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.84 – 7.80 (m, 2H; H_{Ar}-6), 7.60 – 7.54 (m, 1H; H_{Ar}-8), 7.53 – 7.48 (m, 2H; H_{Ar}-7), 4.99 – 4.89 (m, 2H; H-2), 4.71 (dt, *J* = 6.6, 2.4 Hz, 4H; H-4), 3.92 (dt, *J* = 6.9, 2.4 Hz, 4H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 209.8 (2 x C_q; C-3), 140.7 (C_q; C-5), 132.7 (CH_{Ar}; C-8), 129.2 (2 x CH_{Ar}; C-7), 127.3 (2 x CH_{Ar}; C-6), 85.7 (2 x CH; C-2), 76.4 (2 x CH_2; C-4), 45.8 (2 x CH_2; C-1). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3065 (C-H_{Ar}), 2991, 2924 (C-H_{Alkane}), 2862 (C-H_{Alkane}), 1954 (C=C=C), 1342 (S=O), 1160 (S=O), 1095 (C-N), 851, 749. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{14}H_{16}NO_2S$ $[M+H]^+$: 262.0896. Found: 262.0897. M.P. = 38 – 40 ^{o}C.

Synthesis of N,N-di-buta-2,3-dienyl-4-methoxy-benzenesulfonamide **(1c)**

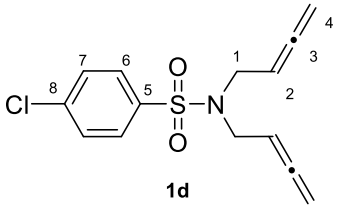


1c

From the corresponding bispropargyl derivative (596 mg, 2.26 mmol), CuBr (195 mg, 1.36 mmol), paraformaldehyde (340 mg, 11.31 mmol), *i*Pr_2NH (1.3 mL, 9.04 mmol) and 4.5 mL of dry 1,4-dioxane. Obtained after column chromatography, Hex / EtOAc, (5:1): **1c**, 342 mg, 1.17 mmol

(52%): brown oil. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.78 – 7.72 (m, 2H; H_{Ar}-6), 6.99 – 6.93 (m, 2H; H_{Ar}-7), 4.98 – 4.91 (m, 2H; H-2), 4.72 (dt, J = 6.8, 2.4 Hz, 4H; H-4), 3.89 (dt, J = 6.8, 2.4 Hz, 4H; H-1), 3.87 (s, 3H; H-9). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 209.8 (2 x C_q; C-3), 162.9 (C_q; C-8), 132.3 (C_q; C-5), 129.4 (2 x CH_{Ar}; C-7), 114.3 (2 x CH_{Ar}; C-6), 85.8 (2 x CH; C-2), 76.3 (2 x CH_2; C-4), 55.7 (CH_3; C-9), 45.8 (2 x CH_2; C-1). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3066 (C-H_{Ar}), 2941 (C-H_{Alkane}), 2840 (C-H_{Alkane}), 1954 (C=C=C), 1596 (C=C_{Ar}), 1498, 1341 (S=O), 1260 (C-O), 1156 (S=O), 1095 (C-N), 836, 756. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{15}H_{18}NO_3S$ $[M+H]^+$: 292.1002. Found: 292.0997.

Synthesis of N,N-di-buta-2,3-dienyl-4-chloro-benzenesulfonamide **(1d)**

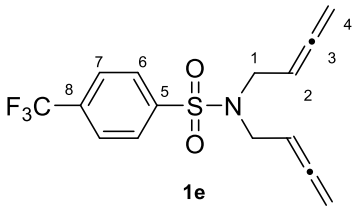


1d

From the corresponding bispropargyl derivative (575 mg, 2.07 mmol), CuBr (178 mg, 1.24 mmol), paraformaldehyde (310 mg, 10.34 mmol), *i*Pr_2NH (1.2 mL, 8.27 mmol) and 4.0 mL of dry 1,4-dioxane. Obtained after column chromatography, Hex / EtOAc, (6:1): **1d**, 318 mg, 1.07 mmol (52%): white solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.79 – 7.73 (m, 2H; H_{Ar}-6), 7.50 – 7.45 (m, 2H; H_{Ar}-7), 4.95 (p, J = 6.8 Hz, 2H; H-2), 4.73 (dt, J = 6.8, 2.5 Hz, 4H; H-4), 3.91 (dt, J = 6.8, 2.5 Hz, 4H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 209.9 (2 x C_q; C-3), 139.3 (C_q; C-8), 139.1 (C_q; C-5), 129.5 (2 x CH_{Ar}; C-7), 128.8 (2 x CH_{Ar}; C-6), 85.6 (2 x CH; C-2), 76.6 (2 x CH_2; C-4), 45.8 (2 x CH_2; C-1). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3090 (C-H_{Ar}), 2991 (C-H_{Alkane}), 2925 (C-H_{Alkane}), 2862 (C-H_{Alkane}), 1954 (C=C=C), 1585 (C=C_{Ar}), 1476, 1344 (S=O), 1161 (S=O), 1086 (C-N), 849, 617. HRMS (FTMS + p APCI (DCM)): Calc. for $C_{14}H_{15}NO_2S^{35}Cl$ $[M+H]^+$: 296.0507 Found: 296.0504. Calc. for $C_{14}H_{15}NO_2S^{37}Cl$ $[M+H]^+$: 298.0476 Found: 298.0471. M. P. = 37 – 39 ^{o}C.

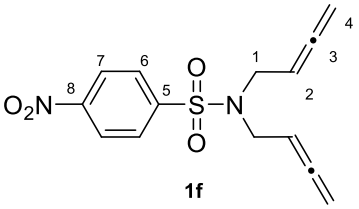
Supporting Information

Synthesis of N,N-di-buta-2,3-dienyl-4-trifluoromethyl-benzenesulfonamide **(1e)**



From the corresponding bispropargyl derivative (461 mg, 1.53 mmol), CuBr (132 mg, 0.92 mmol), paraformaldehyde (230 mg, 7.66 mmol), *i*Pr_2NH (860 µl, 6.13 mmol) and 3.1 mL of dry 1,4-dioxane. Obtained after column chromatography, PET / EtOAc, (20:1): **1e**, 319 mg, 0.97 mmol (63%): yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.95 (d, J = 8.2 Hz, 2H; H_{Ar}-6), 7.77 (d, J = 8.2 Hz, 2H; H_{Ar}-7), 4.96 (p, J = 6.7 Hz, 2H; H-2), 4.72 (dt, J = 6.7, 2.4 Hz, 4H; H-4), 3.94 (dt, J = 6.7, 2.4 Hz, 4H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 209.8 (2 x C_q; C-3), 144.4 (C_q; C-5), 134.3 (q, J_{C-F} = 33.2 Hz, C_q; C-8), 127.8 (2 x CH_{Ar}; C-6), 126.4 (q, J_{C-F} = 3.6 Hz, 2 x CH_{Ar}-7), 85.5 (2 x CH; C-2), 76.7 (2 x CH_2; C-4), 45.8 (2 x CH_2; C-1). *The signal of C_q; CF_3 could not be extracted from the spectra.* ^{19}F NMR (471 MHz, $CDCl_3$, 25 ^{o}C) δ = - 63.04 (CF_3). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3107 (C-H_{Ar}), 3073 (C-H_{Ar}), 2927 (C-H_{Alkane}), 2860 (C-H_{Alkane}), 1956 (C=C=C), 1348 (S=O), 1166 (S=O), 1134 (C-F), 1063 (C-N), 1017, 846. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{15}H_{15}F_3NO_2S$ $[M+H]^+$: 330.0770. Found: 330.0771.

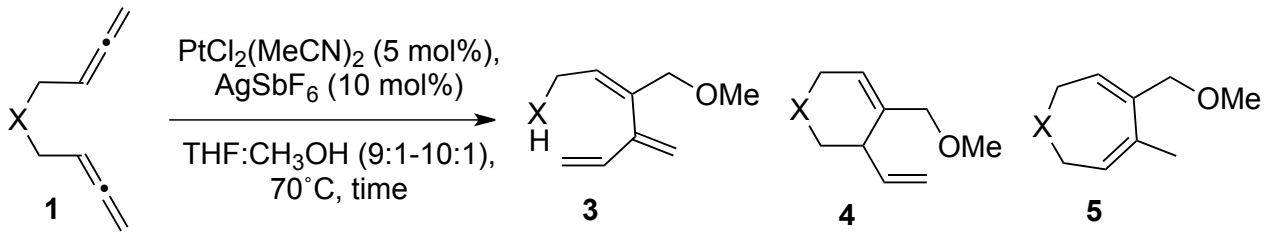
Synthesis of N,N-di-buta-2,3-dienyl-4-nitro-benzenesulfonamide **(1f)**



From the corresponding bispropargyl derivative (524 mg, 1.88 mmol), CuBr (162 mg, 1.13 mmol), paraformaldehyde (283 mg, 9.43 mmol), *i*Pr_2NH (1.1 mL, 7.54 mmol) and 3.8 mL of dry 1,4-dioxane. Obtained after column chromatography, PET / EtOAc, (30:1) then (7:1) then (4:1): **1f**, 423 mg, 1.38 mmol (73%): yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 8.35 (d, J = 8.9 Hz, 2H; H_{Ar}-6), 8.01 (d, J = 8.9 Hz, 2H; H_{Ar}-7), 4.96 (p, J = 6.8 Hz, 2H; H-2), 4.74 (dt, J = 6.8, 2.4 Hz, 4H; H-4), 3.96 (dt, J = 6.8, 2.4 Hz, 4H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 209.9 (2 x C_q; C-3), 150.1 (C_q; C-8), 146.8 (C_q; C-5), 128.5 (2 x CH_{Ar}; C-7), 124.5 (2 x CH_{Ar}; C-6), 85.4 (2 x CH; C-2), 76.9 (2 x CH_2; C-4), 45.9 (2 x CH_2; C-1). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3108 (C-

H_{Ar}), 2933 (C-H_{Alkane}), 1954 (C=C=C), 1528 (N-O), 1348 (S=O), 1157 (S=O), 1062 (C-N), 855. HRMS (FTMS + p APCI (DCM)): Calc. for $C_{14}H_{15}N_2O_4S$ $[M+H]^+$: 307.0747. Found: 301.0748. M.P. = 68 – 69 °C.

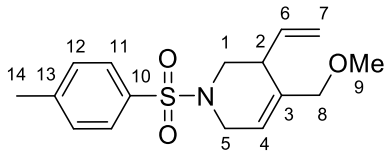
3b) General procedure for platinum-catalyzed alkoxycyclization of 1,5-bisallenes using MeOH



To a microwave vial were added $PtCl_2(MeCN)_2$ (0.05 eq.) and $AgSbF_6$ (0.1 eq.). Then the vial was closed with a stopper and flushed with N_2 during 3 min. A small amount of dry THF was added and the solution was stirred at room temperature for a few minutes to preform the cationic complex. The corresponding 1,5-bisallene **1** (1.0 eq., 0.09 M – absolute concentration) dissolved in dry THF and dry MeOH (THF:MeOH 9:1-10:1) were added sequentially under N_2. Then the vial was sealed under N_2 and placed in a pre-heated oil bath at 70 °C until completed conversion, following the reaction by TLC. The crude was filtered through celite, washed with dichloromethane and concentrated under vacuum. The mixture was purified by column chromatography using silica gel and PET, Hex / Et_2O, EtOAc as eluents.

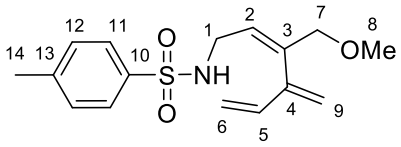
***Synthesis of N-(3-Methoxymethyl-4-methylene-hexa-2,5-dienyl)-4-methyl benzenesulfonamide* (3aa) *and 4-Methoxymethyl-1-(toluene-4-sulfonyl)-3-vinyl-1,2,3,6-tetrahydro-pyridine* (4aa)**

From 1,5-bisallene **1a** (50 mg, 0.18 mmol), $PtCl_2(MeCN)_2$ (3 mg, 0.01 mmol), silver hexafluoroantimonate (6 mg, 0.02 mmol), dry MeOH (180 µl, 4.94 mmol) and 1.8 mL of dry THF. Obtained after column chromatography using Hex / EtOAc (6:1) as eluent: **4aa**, 13.4 mg, 0.044 mmol (24%): yellow oil, and **3aa**, 19.6 mg, 0.064 mmol (35%): yellow oil.



4aa

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.59 (d, J = 8.2 Hz, 2H; H_{Ar}-11), 7.25 (d, J = 8.2 Hz, 2H; H_{Ar}-12), 5.73 (ddd, J = 17.1, 10.2, 8.5 Hz, 1H; H-6), 5.62 – 5.58 (m, 1H; H-4), 5.11 – 5.05 (m, 2H; H-7), 3.82 – 3.78 (m, 1H; H-8), 3.78 – 3.72 (m, 1H; H-5), 3.60 (dd, J = 12.3, 0.8 Hz, 1H; H-8), 3.35 (dd, J = 11.4, 3.6 Hz, 1H; H-1), 3.32 – 3.26 (m, 1H; H-5), 3.19 (s, 3H; H-9), 2.89 – 2.83 (m, 1H; H-2), 2.80 (dd, J = 11.4, 4.1 Hz, 1H; H-1) 2.36 (s, 3H; H-14). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.7 (C_q; C-13), 137.0 (CH; C-6), 135.3 (C_q; C-10), 133.3 (C_q; C-3), 129.8 (2 x CH_{Ar}; C-12), 127.9 (2 x CH_{Ar}; C-11), 120.1 (CH; C-4), 117.3 (CH_2; C-7), 73.5 (CH_2; C-8), 58.1 (CH_3; C-9), 47.8 (CH_2; C-1), 44.9 (CH_2; C-5), 40.5 (CH; C-2), 21.7 (CH_3; C-14). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3097 (C-H_{Alkene}), 3072 (C-H_{Ar}), 2924 (C-H_{Alkane}), 2858 (C-H_{Alkane}), 1737 (C=C), 1640 (C=CH_2), 1597 (C=C_{Ar}), 1456 (C-H_{Alkane}), 1344 (S=O), 1210 (C-O), 1165 (S=O), 1093 (C-N), 958, 820. HRMS (FTMS + APCI (DCM + NH_4OAc)): Calc. For $C_9H_{18}ON$ $[M+H]^+$: 325.1589. Found: 325.1580.



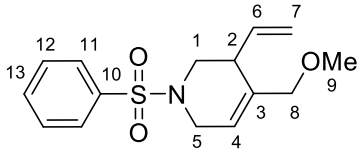
3aa

^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.72 (d, J = 8.2 Hz, 2H; H_{Ar}-11), 7.29 (d, J = 8.2 Hz, 2H; H_{Ar}-12), 6.29 (dd, J = 17.4, 10.4 Hz, 1H; H-5), 5.62 (t, J = 7.0 Hz, 1H; H-2), 5.17 (s, 1H; H-9), 5.05 (d, J = 10.4 Hz, 1H; H-6), 5.03 (d, J = 17.4 Hz, 1H; H-6), 4.89 (s, 1H; H-9), 4.56 (bt, J = 5.9 Hz, 1H; NH), 3.85 – 3.77 (s, 2H; H-7), 3.54 – 3.43 (m, 2H; H-1), 3.28 (s, 3H; H-8), 2.42 (s, 3H; H-14). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.6 (C_q; C-13), 143.5 (C_q; C-10), 139.8 (C_q; C-3 or C-4), 137.1 (CH; C-5), 129.8 (2 x CH_{Ar}; C-12), 127.3 (2 x CH_{Ar}; C-11), 123.6 (CH; C-2), 118.8 (CH_2; C-9), 116.4 (CH_2; C-6), 75.1 (CH_2; C-7), 58.3 (CH_3; C-8), 41.6 (CH_2; C-1), 21.6 (CH_3; C-14). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3282 (N-H), 3098 (C-H_{Alkene}), 3082, 3061 (C-H_{Ar}), 2925 (C-H_{Alkane}), 2855 (C-H_{Alkane}), 1727 (C=C), 1598 (C=C_{Ar}), 1450 (C-H_{Alkane}), 1310 (S=O), 1240 (C-O), 1161 (S=O), 1094 (C-N), 911. HRMS (ESI-HRMS): Calc. for $C_{16}H_{25}O_3N_2S$ $[M+NH_4]^+$: 325.1589 Found: 325.1580.

Synthesis of 1-Benzenesulfonyl-4-methoxymethyl-5-methyl-2,7-dihydro-1H-azepine **(3ba)** ***and 1-Benzenesulfonyl-4-methoxymethyl-3-vinyl-1,2,3,6-tetrahydro-pyridine*** **(4ba)**

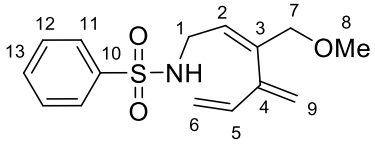
From 1,5-bisallene **1b** (50 mg, 0.19 mmol), $PtCl_2(MeCN)_2$ (3.3 mg, 0.01 mmol), silver hexafluoroantimonate (6 mg, 0.019 mmol), dry MeOH (190 µl, 4.7 mmol) and 1.9 mL of dry

THF. Obtained after column chromatography using PET / EtOAc (9:1) then (4:1) as eluent: **4ba**, 10.1 mg, 0.034 mmol (18%): colourless oil; and **3ba,** 11.8 mg, 0.04 mmol (21%): yellow oil.



4ba

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.81 – 7.77 (m, 2H; H_{Ar}-11), 7.62 – 7.57 (m, 1H; H_{Ar}-13), 7.56 – 7.51 (m, 2H; H_{Ar}-12), 5.80 (ddd, J = 17.1, 10.2, 8.4 Hz, 1H; H-6), 5.69 – 5.66 (m, 1H; H-4), 5.18 – 5.12 (m, 2H; H-7), 3.89 – 3.85 (m, 1H; H-8), 3.85 – 3.81 (m, 1H; H-5), 3.70 – 3.65 (m, 1H; H-8), 3.45 (dd, J = 11.4, 3.4 Hz, 1H; H-1), 3.42 – 3.35 (m, 1H; H-5), 3.26 (s, 3H; H-9), 2.97 – 2.91 (m, 1H; H-2), 2.89 (dd, J = 11.4, 4.1 Hz, 1H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 136.9 (CH; C-6), 136.4 (C_q; C-3), 135.3 ($C_{q;}$ C-10), 132.9 (CH_{Ar}; C-13), 129.2 (2 x CH_{Ar}; C-12), 127.8 (2 x CH_{Ar}; C-11), 120.0 (CH; C-4), 117.4 (CH_2; C-7), 73.5 (CH_2; C-8), 58.2 (CH_3; C-9), 47.8 (CH_2; C-1), 44.8 (CH_2; C-5), 40.5 (CH; C-2). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3097 (C-H_{Alkene}), 3065 (C-H_{Ar}), 2963 (C-H_{Alkane}), 2923 (C-H_{Alkane}), 2852 (C-H_{Alkane}), 1710 (C=C), 1607 (C=C_{Ar}), 1457 (C-H_{Alkane}), 1321 (S=O), 1150 (C-O), 1133 (S=O), 1081 (C-N), 961. HRMS (FTMS + p NSI (DCM) / MeOH + NH_4OAc)): Calc. for $C_{15}H_{20}O_3NS$ $[M+H]^+$: 294.1158. Found: 294.1161.



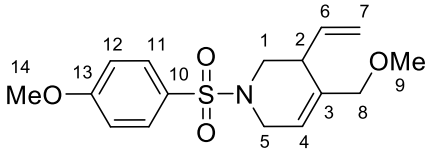
3ba

^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.84 (m, 2H; H_{Ar}-11), 7.58 (m, 1H; H_{Ar}-13), 7.51 (m, 2H, H_{Ar}-12), 6.30 (dd, J = 17.4, 10.5 Hz, 1H; H-5), 5.63 (tt, J = 7.0, 1.5 Hz, 1H; H-2), 5.17 (s, 1H; H-9), 5.06 (d, J = 11.9 Hz, 1H; H-6), 5.03 (d, J = 17.9 Hz, 1H; H-6), 4.89 (s, 1H; H-9), 4.33 (bt, J = 5.7 Hz, 1H; NH), 3.82 (d, J = 1.5 Hz, 2H; H-7), 3.52 (dd, J = 7.0, 5.7 Hz, 2H; H-1), 3.30 (s, 3H; H-8). ^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.7 (C_q; C-3), 143.5 (C_q; C-10), 140.2 (C_q; C-4), 137.2 (CH; C-5), 132.8 (CH; C-13), 129.2 (2 x CH_{Ar}; C-12), 127.3 (2 x CH_{Ar}; C-11), 123.3 (CH; C-2), 118.9 (CH_2; C-9), 116.4 (CH_2; C-6), 75.2 (CH_2; C-7), 58.4 (CH_3; C-8), 41.6 (CH_2; C-1). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3282 (N-H), 3098 (C-H_{Alkene}), 3070 (C-H_{Ar}), 2920 (C-H_{Alkane}), 2850 (C-H_{Alkane}), 2825 (C-H_{Alkane}), 1732 (C=C), 1447 (C-H_{Alkane}), 1335 (S=O), 1231 (C-O), 1164 (S=O), 1091 (C-N), 746. HRMS (FTMS+ p NSI ((DCM) / MeOH + NH_4OAc)): Calc. for $C_{15}H_{18}NO_3S$ $[M-2H+H]^+$: 292.1002. Found: 292.1000.

Supporting Information

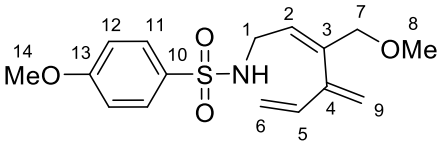
***Synthesis of 4-Methoxy-N-(3-methoxymethyl-4-methylene-hexa-2,5-dienyl)-benzenesulfonamide* (3ca) *and 1-(4-Methoxy-benzenesulfonyl)-4-methoxymethyl-3-vinyl-1,2,3,6-tetrahydro-pyridine* (4ca)**

From 1,5-bisallene **1c** (50 mg, 0.17 mmol), $PtCl_2(MeCN)_2$ (3 mg, 0.009 mmol), silver hexafluoroantimonate (5.3 mg, 0.017 mmol), dry MeOH (180 µl, 4.94 mmol) and 1.8 mL of dry THF. Obtained after column chromatography using Hex / EtOAc (5:1) as eluent: **4ca**, 17.5 mg, 0.05 mmol (31%): yellow oil; and **3ca**, 18.4 mg, 0.06 mmol (33%): yellow oil.



4ca

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.74 – 7.69 (m, 2H; H_{Ar}-11), 7.01 – 6.97 (m, 2H; H_{Ar}-12), 5.80 (ddd, *J* = 17.1, 10.1, 8.5 Hz, 1H; H-6), 5.70 – 5.64 (m, 1H; H-4), 5.17 – 5.14 (m, 1H; H-7), 5.14 – 5.11 (m, 1H; H-7), 3.87 (s, 3H; H-14), 3.89 – 3.84 (m, 1H; H-8), 3.84 – 3.77 (m, 1H; H-5), 3.68 (dd, *J* = 12.3, 0.7 Hz, 1H; H-8), 3.41 (dd, *J* = 11.4, 3.6 Hz, 1H; H-1), 3.41 – 3.34 (m, 1H; H-5), 3.26 (s, 3H; H-9), 2.96 – 2.90 (m, 1H; H-2), 2.87 (dd, *J* = 11.4, 4.1 Hz, 1H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 163.2 (C_q; C-13), 137.0 (CH; C-6), 135.3 (C_q; C-10), 129.9 (2 x CH_{Ar}; C-11), 128.0 (C_q; C-3), 120.1 (CH; C-4), 117.3 (CH_2; C-7), 114.3 (2 x CH_{Ar}; C-12), 73.5 (CH_2; C-8), 58.2 (CH_3; C-9), 55.8 (CH_3; C-14), 47.8 (CH_2; C-1), 44.9 (CH_2; C-5), 40.5 (CH; C-2). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3095 (C-H_{Alkene}), 3054 (C-H_{Ar}), 2921 (C-H_{Alkane}), 2856 (C-H_{Alkane}), 2820 (C-H_{Alkane}), 1732 (C=C), 1594 (C=C_{Ar}), 1460 (C-H_{Alkane}), 1344 (S=O), 1257 (C-O), 1153 (S=O), 1091 (C-N), 960. HRMS (FTMS + p NSI ((DCM) / MeOH + NH_4OAc)): Calc. for $C_{16}H_{22}O_4NS$ $[M+H]^+$: 324.1264. Found: 324.1265.



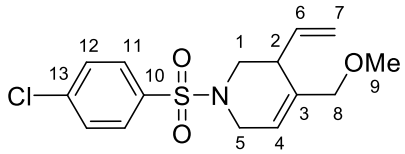
3ca

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ =7.77 (d, *J* = 8.8 Hz, 2H; H_{Ar}-11), 6.96 (d, *J* = 8.8 Hz, 2H; H_{Ar}-12), 6.31 (dd, *J* = 17.3, 10.5 Hz, 1H; H-5), 5.63 (t, *J* = 6.6 Hz, 1H; H-2), 5.18 (s, 1H; H-9), 5.09 – 5.00 (m, 2H; H-6), 4.89 (s, 1H; H-9), 4.34 – 4.30 (m, 1H; NH), 3.87 (s, 3H; H-14), 3.82 (s, 2H; H-7), 3.48 (t, *J* = 6.6 Hz, 2H; H-1), 3.30 (s, 3H; H-8). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 163.0 (C_q; C-13), 143.7 (C_q; C-3 or C-4), 139.9 (C_q; C-10), 137.2 (CH; C-5), 131.7 (C_q; C-3 or C-

4), 129.4 (2 x CH_{Ar}; C-11), 123.5 (CH; C-2), 118.9 (CH_2; C-9), 116.4 (CH_2; C-6), 114.3 (2 x CH_{Ar}; C-12), 75.2 (CH_2; C-7), 58.4 (CH_3; C-8), 55.8 (CH_3; C-14), 41.6 (CH_2; C-1). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3540 (N-H), 2964 (C-H_{Alkane}), 2920 (C-H_{Alkane}), 2852 (C-H_{Alkane}), 1744 (C=C), 1712, 1632 (C=C_{Ar}), 1596, 1448 (C-H_{Alkane}), 1312 (S=O), 1260 (C-O), 1156 (S=O), 1100 (C-N). HRMS (FTMS + p NSI ((DCM) / MeOH + NH_4OAc)): Calc. for $C_{16}H_{22}O_4NS$ $[M+H]^+$: 324.1264. Found: 324.1266.

***Synthesis of 4-Chloro-N-(3-methoxymethyl-4-methylene-hexa-2,5-dienyl)-benzenesulfonamide* (3da) *and 1-(4-Chloro-benzenesulfonyl)-4-methoxymethyl-3-vinyl-1,2,3,6-tetrahydro-pyridine* (4da)**

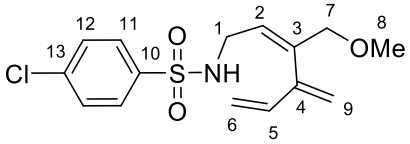
From 1,5-bisallene **1d** (50 mg, 0.17 mmol), $PtCl_2(MeCN)_2$ (3 mg, 0.009 mmol), silver hexafluoroantimonate (5.2 mg, 0.017 mmol), dry MeOH (170 µl, 4.2 mmol), 1.7 mL of dry THF. Obtained after column chromatography using Hex/EtOAc (8:1) as eluent: **4da**, 10.2 mg, 0.03 mmol (19%): yellow oil; **3da**, 22.7 mg, 0.072 mmol (43%): yellow oil.



4da

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.74 – 7.70 (m, 2H; H_{Ar}-11 or H_{Ar}-12), 7.53 – 7.48 (m, 2H; H_{Ar}-11 or H_{Ar}-12), 5.83 – 5.73 (m, 1H; H-6), 5.68 (m, 1H; H-4), 5.17 – 5.15 (m, 1H; H-7), 5.16 – 5.12 (m, 1H; H-7), 3.86 (d, *J* = 12.1 Hz, 1H; H-8), 3.85 – 3.81 (m, 1H; H-5), 3.68 (d, *J* = 12.1 Hz, 1H; H-8), 3.44 (dd, *J* = 11.3, 3.4 Hz, 1H; H-1), 3.41 – 3.35 (m, 1H; H-5), 3.26 (s, 3H; H-9), 2.96 – 2.92 (m, 1H; H-2), 2.90 (dd, *J* = 11.3, 4.1 Hz, 1H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 139.5 (C_q), 136.7 (CH; C-6), 135.4 (C_q), 135.0 (C_q), 129.5 (2 x CH_{Ar}; C-11 or C-12), 129.2 (2 x CH_{Ar}; C-11 or C-12), 119.8 (CH; C-4), 117.5 (CH_2; C-7), 73.5 (CH_2; C-8), 58.2 (CH_3; C-9), 47.8 (CH_2; C-1), 44.8 (CH_2; C-5), 40.4 (CH; C-2). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3086 (C-H_{Alkene}), 2922 (C-H_{Alkane}), 2850 (C-H_{Alkane}), 2828 (C-H_{Alkane}), 1714 (C=C), 1585 (C=C_{Ar}), 1476 (C-H_{Alkane}), 1349 (S=O), 1200 (C-O), 1165 (S=O), 1091 (C-N), 962, 828. HRMS (FTMS + p NSI ((DCM) / MeOH + NH_4OAc)): Calc. for $C_{15}H_{19}O_3NS^{35}Cl$ $[M+H]^+$: 328.0769. Found: 328.0769. Calc. For $C_{15}H_{19}O_3NS^{37}Cl$ $[M+H]^+$: 330.0738. Found: 330.0736.

Supporting Information

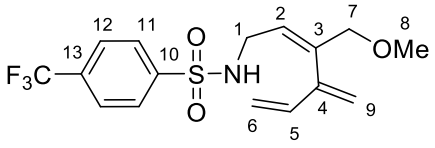


3da

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.79 – 7.76 (m, 2H; H_{Ar}-11 or H_{Ar}-12), 7.49 – 7.46 (m, 2H; H_{Ar}-11 or H_{Ar}-12), 6.32 (dd, J = 17.4, 10.4 Hz, 1H; H-5), 5.63 (tt, J = 7.0, 1.5 Hz, 1H; H-2), 5.20 (s, 1H; H-9), 5.08 (d, J = 10.4 Hz, 1H; H-6), 5.03 (d, J = 17.4 Hz, 1H; H-6), 4.90 (s, 1H; H-9), 4.35 (bt, J = 5.8 Hz, 1H; NH), 3.83 (s, 2H; H-7), 3.54 – 3.50 (m, 2H; H-1), 3.31 (s, 3H; H-8). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.6 (C_q), 140.4 (C_q), 139.3 (C_q), 138.7 (C_q), 137.2 (CH; C-5), 129.5 (2 x CH_{Ar}; C-11 or C-12), 128.7 (2 x CH_{Ar}; C-11 or C-12), 122.8 (CH; C-2), 119.0 (CH_2; C-9), 116.4 (CH_2; C-6), 75.1 (CH_2; C-7), 58.5 (CH_3; C-8), 41.6 (CH_2; C-1). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3286 (N-H), 3097 (C-H_{Alkene}), 2925 (C-H_{Alkane}), 2859 (C-H_{Alkane}), 2826 (C-H_{Alkane}), 1717 (C=C), 1586, 1476 (C-H_{Alkane}), 1395 (S=O), 1337 (C-O), 1163 (S=O), 1093 (C-N), 1013 (C-O). HRMS (FTMS + p NSI ((DCM) / MeOH + NH_4OAc)): Calc. for $C_{15}H_{22}{}^{35}ClO_3N_2S$ $[M+NH_4]^+$: 345.1034. Found: 345.1040. Calc. for $C_{15}H_{22}{}^{37}ClO_3N_2S$ $[M+NH_4]^+$: 347.1003. Found: 345.1003.

Synthesis of N-(3-Methoxymethyl-4-methylene-hexa-2,5-dienyl)-4-trifluoromethyl-benzenesulfonamide **(3ea),** ***4-Methoxymethyl-1-(4-trifluoromethyl-benzenesulfonyl)-3-vinyl-1,2,3,6-tetrahydro-pyridine*** **(4ea)** ***and 4-Methoxymethyl-5-methyl-1-(4-trifluoromethyl-benzenesulfonyl)-2,7-dihydro-1H-azepine*** **(5ea)**

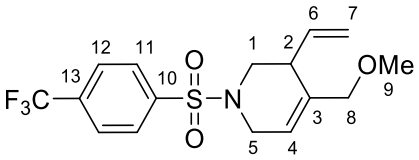
From 1,5-bisallene **1e** (50 mg, 0.15 mmol), $PtCl_2(MeCN)_2$ (2.6 mg, 0.076 mmol), silver hexafluoroantimonate (5 mg, 0.015 mmol), dry MeOH (150 µl, 3.7 mmol) and 1.5 mL of dry THF. Obtained after column chromatography using PET / EtOAc (8:1) then (4:1) as eluent: **3ea**, 19.7 mg, 0.055 mmol (36%): yellow oil; **4ea** 3.6 mg, 0.01 mmol (7%): yellow oil; and **5ea**, 3.3 mg, 0.009 mmol (6%): colourless oil.



3ea

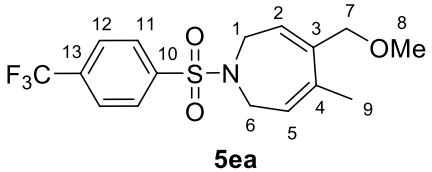
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.97 (d, J = 8.3 Hz, 2H; H_{Ar}-11), 7.78 (d, J = 8.3 Hz, 2H; H_{Ar}-12), 6.31 (dd, J = 17.4, 10.5 Hz, 1H; H-5), 5.62 (tt, J = 7.0, 1.4 Hz, 1H; H-2), 5.19 (d, J = 0.7 Hz, 1H; H-9), 5.07 (d, J = 10.5 Hz, 1H; H-6), 5.03 (d, J = 17.4 Hz, 1H; H-6), 4.90 (s, 1H; H-9),

4.41 (bt, J = 5.8 Hz, 1H; NH), 3.82 (d, J = 1.4 Hz, 2H; H-7), 3.58 – 3.53 (m, 2H; H-1), 3.30 (s, 3H; H-8). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.6 (C_q; C-10), 140.7 (C_q; C-3 or C-4), 137.2 (CH; C-5), 134.5 (q, $J_{C\text{-}F}$ = 32.9 Hz; C_q; C-13), 127.8 (2 x CH_{Ar}; C-11), 127.2 (q, $J_{C\text{-}F}$ = 231.7 Hz; CF_3), 126.3 (q, $J_{C\text{-}F}$ = 3.8 Hz; 2 x CH_{Ar}; C-12), 122.5 (CH; C-2), 119.0 (CH_2; C-9), 116.4 (CH_2; C-6), 75.0 (CH_2; C-7), 58.5 (CH_3; C-8), 41.7 (CH_2; C-1). ^{19}F NMR (471 MHz, $CDCl_3$, 25 ^{o}C) δ = -63.11. IR (Film, cm^{-1}): $\tilde{\nu}$ = 3282 (N-H), 3097 (C-H_{Alkene}), 2960 (C-H_{Alkane}), 2924 (C-H_{Alkane}), 2853 (C-H_{Alkane}), 1713 (C=C), 1456 (C-H_{Alkane}), 1404, 1322 (S=O), 1167 (S=O), 1132 (C-F), 1062 (C-O), 917, 843. HRMS (FTMS + p NSI ((DCM) / MeOH + NH_4OAc)): Calc. for $C_{16}H_{19}F_3O_3NS$ $[M+H]^+$: 362.1032 Found: 362.1036.



4ea

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.92 (d, J = 8.2 Hz, 2H; H_{Ar}-11), 7.80 (d, J = 8.2 Hz, 2H; H_{Ar}-12), 5.82 – 5.72 (m, 1H; H-6), 5.70 – 5.66 (m, 1H; H-4), 5.18 – 5.16 (m, 1H; H-7), 5.14 – 5.11 (m, 1H; H-7), 3.91 – 3.87 (m, 1H; H-5), 3.88 – 3.83 (m, 1H; H-8), 3.68 (d, J = 12.3 Hz, 1H; H-8), 3.51 – 3.45 (m, 1H; H-1), 3.45 – 3.38 (m, 1H; H-5), 3.26 (s, 3H; H-9), 2.98 – 2.94 (m, 1H; H-2), 2.94 – 2.91 (m, 1H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 136.6 (CH; C-6), 135.5 (C_q; C-10), 132.9 (C_q; C-3), 128.2 (2 x CH_{Ar}; C-11), 126.4 (q, $J_{C\text{-}F}$ = 3.7 Hz; 2 x CH_{Ar}; C-12), 119.6 (CH; C-4), 117.7 (CH_2; C-7), 73.5 (CH_2; C-8), 58.2 (CH_3; C-9), 47.8 (CH_2; C-1), 44.8 (CH_2; C-5), 40.3 (CH; C-2). *(C_q; C-13), (C_q; CF_3) could not be identified.* ^{19}F NMR (471 MHz, $CDCl_3$, 25 ^{o}C) δ = - 63.11. IR (Film, cm^{-1}): $\tilde{\nu}$ = 3095 (C-H_{Alkene}), 2963 (C-H_{Alkane}), 2923 (C-H_{Alkane}), 2852 (C-H_{Alkane}), 1607 (C=C), 1457, 1322 (S=O), 1302 (C-O), 1170 (S=O), 1133 (C-F), 961. HRMS (FTMS + p NSI ((DCM) / MeOH + NH_4OAc)): Calc. for $C_{16}H_{19}F_3NO_3S$ $[M+H]^+$: 362.1032 Found: 362.1035.



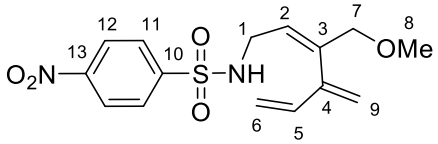
5ea

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.94 (d, J = 8.2 Hz, 2H; H_{Ar}-11), 7.79 (d, J = 8.2 Hz, 2H; H_{Ar}-12), 5.86 (t, J = 7.0 Hz, 1H; H-2), 5.76 (tq, J = 7.1, 1.4 Hz, 1H; H-5), 3.91 (s, 2H; H-7), 3.64 (d, J = 7.0 Hz, 2H; H-1), 3.60 (d, J = 7.1 Hz, 2H; H-6), 3.17 (s, 3H; H-8), 1.79 (s, 3H; H-9). ^{13}C

NMR (126 MHz, $CDCl_3$, 25 °C) δ = 145.7 (C_q), 143.0 (C_q), 128.1 (2 x CH_{Ar}; C-11), 127.2 (q, J_{C-F} = 262.3 Hz; CF_3), 126.2 (q, J_{C-F} = 3.6 Hz; 2 x CH_{Ar}-C-12), 123.8 (CH; C-5), 123.6 (CH; C-2), 73.4 (CH_2; C-7), 58.1 (CH_3; C-8), 43.9 (CH_2; C-6), 43.7 (CH_2; C-1), 19.8 (CH_3; C-9). *(C_q; C-13) could not be identified.* ^{19}F NMR (471 MHz, $CDCl_3$, 25 °C) δ = - 63.07. IR (Film, cm^{-1}): $\tilde{\nu}$ = 3118, 3052 (C-H_{Alkene}), 2924 (C-H_{Alkane}), 2852 (C-H_{Alkane}), 2826 (C-H_{Alkane}), 1738 (C=C), 1456 (C-H_{Alkane}), 1323 (S=O), 1167 (S=O), 1110 (C-O), 1062 (C-N), 1015, 845. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{16}H_{19}F_3O_3NS$ $[M+H]^+$: 362.1032 Found: 362.1036.

***Synthesis of N-(3-Methoxymethyl-4-methylene-hexa-2,5-dienyl)-4-nitro-benzenesulfonamide* (3fa), *4-Methoxymethyl-1-(4-nitrobenzenesulfonyl)-3-vinyl-1,2,3,6-tetrahydro-pyridine* (4fa) *and 4-Methoxymethyl-5-methyl-1-(4-nitro-benzenesulfonyl)-2,7-dihydro-1H-azepine* (5fa)**

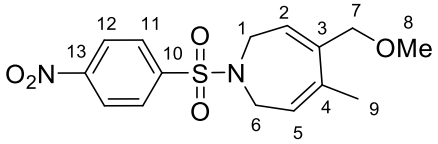
From 1,5-bisallene **1f** (50 mg, 0.16 mmol), $PtCl_2(MeCN)_2$ (3 mg, 0.008 mmol), silver hexafluoroantimonate (5 mg, 0.016 mmol), dry MeOH (160 µl, 4 mmol) and 1.6 mL of dry THF. Obtained after column chromatography using Hex / EtOAc (8:1) as eluent: **3fa**, 18.5 mg, 0.055 mmol (34%): yellow solid; **5fa**, 3.4 mg, 0.062 (6%): yellow oil and **4fa** as inseparable mixture, 3 mg, 0.05 mmol (5%): yellow oil.



3fa

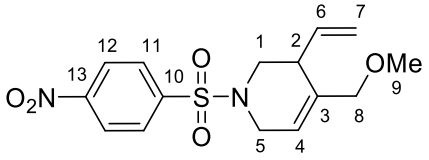
^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ = 8.35 (d, J = 8.8 Hz, 2H; H_{Ar}-11 or H_{Ar}-12), 8.02 (d, J = 8.8 Hz, 2H; H_{Ar}-11 or H_{Ar}-12), 6.32 (dd, J = 17.4, 10.5 Hz, 1H; H-5), 5.63 (t, J = 7.0 Hz, 1H; H-2), 5.21 (s, 1H; H-9), 5.09 (d, J = 10.5 Hz, 1H; H-6), 5.04 (d, J = 17.4 Hz, 1H; H-6), 4.91 (s, 1H; H-9), 4.53 (bt, J = 5.7 Hz, 1H; NH), 3.82 (s, 2H; H-7), 3.60 – 3.55 (m, 2H; H-1), 3.31 (s, 3H; H-8). ^{13}C NMR (126 MHz, $CDCl_3$, 25 °C) δ = 150.2 (C_q; C-10 or C-13), 146.2 (C_q; C-10 or C-13), 143.6 (C_q; C-3 or C-4), 140.9 (C_q; C-3 or C-4), 137.2 (CH; C-5), 128.5 (2 x CH_{Ar}; C-11 or C-12), 124.5 (2 x CH_{Ar}; C-11 or C-12), 122.2 (CH; C-2), 119.1 (CH_2; C-9), 116.5 (CH_2; C-6), 74.9 (CH_2; C-7), 58.6 (CH_3; C-8), 41.7 (CH_2; C-1). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3508 (N-H), 3110 (C-H_{Alkene}), 2925 (C-H_{Alkane}), 2855 (C-H_{Alkane}), 1716 (C=C), 1611 (C=C_{Ar}), 1531 (N-O), 1454 (C-H_{Alkane}), 1350 (S=O), 1210 (C-O), 1164 (S=O), 1094 (C-N), 918, 859, 742.0. HRMS (FTMS + p NSI (DCM)): Calc. for $C_{15}H_{19}O_5N_2S$ $[M+H]^+$: 339.1009 Found: 339.1008. M.P. = 83 – 85 °C.

Supporting Information



5fa

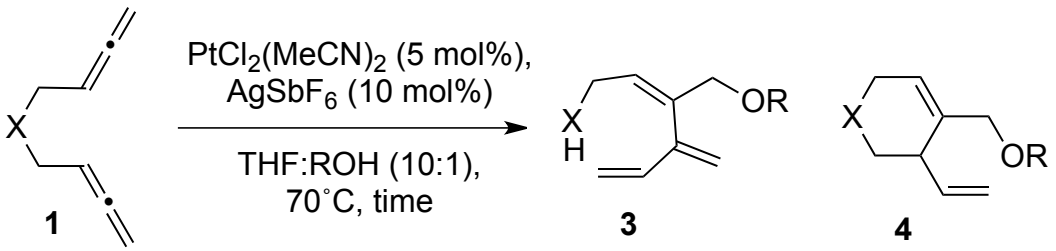
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 8.38 – 8.35 (m, 2H; H_{Ar}-11 or H_{Ar}-12), 8.01 – 7.98 (m, 2H; H_{Ar}-11 or H_{Ar}-12), 5.89 (t, J = 7.0 Hz, 1H; H-2), 5.75 (tq, J = 7.0, 1.3 Hz, 1H; H-5), 3.92 (s, 2H; H-7), 3.64 (d, J = 7.0 Hz, 2H; H-1), 3.63 (d, J = 7.0 Hz, 2H; H-6), 3.22 (s, 3H; H-8), 1.80 (s, 3H; H-9). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 150.2 (C_q; C-10 or C-13) 146.0 (C_q; C-10 or C-13), 145.3 (C_q; C-3 or C-4), 143.3 (C_q; C-3 or C-4), 128.7 (2 x CH_{Ar}; C-11), 124.5 (2 x CH_{Ar}; C-12), 123.5 (CH; C-5), 123.2 (CH; C-2), 73.4 (CH_2; C-7), 58.3 (CH_3; C-8), 43.9 (CH_2; C-6), 43.6 (CH_2; C-1), 19.8 (CH_3; C-9). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3111 (C-H_{Alkene}), 3070 (C-H_{Alkene}), 3032 (C-H_{Ar}), 2924 (C-H_{Alkane}), 2854 (C-H_{Alkane}), 1741 (C=C), 1531 (N-O), 1350 (S=O), 1164 (S=O), 1091 (C-N), 1011 (C-O), 920, 855. HRMS (FTMS + p NSI (DCM)) Calc. for $C_{15}H_{18}O_5N_2S$ $[M+H]^+$: 339.1009. Found: 339.1005.



4fa

This compound couldn't be isolated from the mixture with **3fa** *and* **5fa**. ^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 8.40 – 8.36 (m, 2H; H_{Ar}-11), 8.01 – 7.94 (m, 2H; H_{Ar}-12), 5.80 – 5.71 (m, 1H; H-6), 5.70 – 5.66 (m, 1H; H-4), 5.18 – 5.12 (m, 2H; H-7), 4.20 – 4.00 (m, 2H; H-5), 3.88 – 3.83 (m, 1H; H-8), 3.69 (d, J = 12.5 Hz, 1H; H-8), 3.51 – 3.45 (m, 1H; H-1), 3.26 (s, 3H; H-9), 3.00 – 2.9 (m, 2H; H-2+H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 146.3 (C_q; C-13) 136.4 (CH; C-6), 135.9 (C_q; C-10), 132.9 (C_q; C-3), 128.9 (2 x CH_{Ar}; C-11), 124.5 (2 x CH_{Ar}; C-12), 119.4 (CH; C-4), 117.8 (CH_2; C-7), 73.4 (CH_2; C-8), 58.3 (CH_3; C-9), 47.8 (CH_2; C-1), 44.7 (CH_2; C-5), 40.3 (CH; C-2).

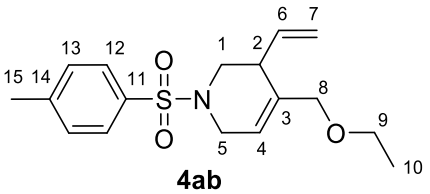
3c) General procedure for platinum-catalyzed alkoxycyclization of 1,5-bisallenes using other alcohols



To a microwave vial were added $PtCl_2(MeCN)_2$ (0.05 eq.) and $AgSbF_6$ (0.1 eq.). Then the vial was closed with a stopper and flushed with N_2 during 3 min. A small amount of dry THF was added and the solution was stirred at room temperature for a few minutes to preform the cationic complex. The corresponding 1,5-bisallene **1** (1.0 eq., 0.09 M – absolute concentration) dissolved in dry THF and the corresponding alcohol (THF:ROH 10:1) were added sequentially under N_2. Then the vial was sealed under N_2 and placed in a pre-heated oil bath at 70 ^oC until completed conversion, following the reaction by TLC. The crude was filtered through celite, washed with dichloromethane and concentrated under vacuum. The mixture was purified by column chromatography using silica gel and PET, Hex / Et_2O, EtOAc as eluents.

Synthesis of N-(3-Ethoxymethyl-4-methylene-hexa-2,5-dienyl)-4-methyl-benzenesulfonamide* (3ab) *and 4-Ethoxymethyl-1-(toluene-4-sulfonyl)-3-vinyl-1,2,3,6-tetrahydro-pyridine* (4ab) *using EtOH as nucleophile

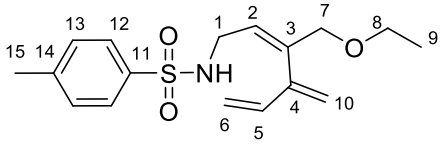
From 1,5-bisallene **1a** (50 mg, 0.18 mmol), $PtCl_2(MeCN)_2$ (3 mg, 0.01 mmol), silver hexafluoroantimonate (6 mg, 0.02 mmol), dry EtOH (288 µl, 4.94 mmol) and 1.8 mL of dry THF. Obtained after column chromatography using PET / EtOAc (4:1) as eluent: **4ab**, 14 mg, 0.04 mmol (23%): colourless oil; and **3ab**, 12 mg, 0.04 mmol (20%): colourless oil.



4ab

^1H NMR (500 MHz, $CDCl_3$, 25 ^oC) δ = 7.66 (d, J = 8.2 Hz, 2H; H_{Ar}-12), 7.31 (d, J = 8.2 Hz, 2H; H_{Ar}-13), 5.80 (ddd, J = 17.1, 10.1, 8.5 Hz, 1H; H-6), 5.68 – 5.65 (m, 1H; H-4), 3.87 (dd, J = 12.3, 2.0 Hz, 1H; H-8), 3.84 – 3.79 (m, 1H; H-5), 3.75 (dd, J = 12.3, 0.8 Hz, 1H; H-8), 3.45 – 3.40 (m,

2H; H-9), 3.45 – 3.35 (m, 1H; H-1), 3.37 – 3.32 (m, 1H; H-5), 2.96 – 2.92 (m, 1H; H-2), 2.87 (dd, *J* = 11.4, 4.1 Hz, 1H; H-1), 2.43 (s, 3H; H-15), 1.16 (t, *J* = 7.0 Hz, 3H; H-10). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.7 (C_q), 137.1 (CH; C-6), 135.6 (C_q), 133.3 (C_q), 129.8 (2 x CH_{Ar}; C-13), 127.9 (2 x CH_{Ar}; C-12), 119.7 (CH; C-4), 117.2 (CH_2; C-7), 71.5 (CH_2; C-8), 65.9 (CH_2; C-9), 47.8 (CH_2; C-1), 44.9 (CH_2; C-5), 40.6 (CH; C-2), 21.7 (CH_3; C-15), 15.3 (CH_3; C-10). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3090 (C-H_{Alkene}), 3066 (C-H_{Ar}), 3039 (C-H_{Ar}), 2966 (C-H_{Alkane}), 2919 (C-H_{Alkane}), 2850 (C-H_{Alkane}), 1648 (C=C), 1598, 1456 (C-H_{Alkane}), 1331 (S=O), 1161 (S=O), 1094 (C-N), 1042 (C-O), 908, 814. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{18}H_{26}O_3NS$ $[M+H]^+$: 322.1471. Found: 322.1472.



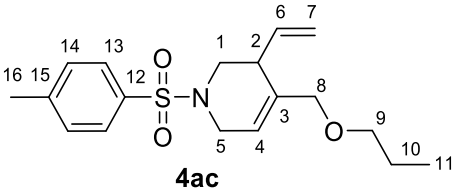
3ab

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.72 (d, *J* = 8.2 Hz, 2H; H_{Ar}-12), 7.29 (d, *J* = 8.2 Hz, 2H; H_{Ar}-13), 6.30 (dd, *J* = 17.3, 10.5 Hz, 1H; H-5), 5.62 (tt, *J* = 7.0, 1.5 Hz, 1H; H-2), 5.17 (d, *J* = 0.8 Hz, 1H; H-10), 5.08 – 5.04 (m, 1H; H-6), 5.03 (d, *J* = 17.3 Hz, 1H; H-6), 4.88 (s, 1H; H-10), 4.28 (bt, *J* = 5.9 Hz, 1H; NH), 3.86 (d, *J* = 1.5 Hz, 2H; H-7), 3.52 – 3.47 (m, 2H; H-1), 3.44 (q, *J* = 7.0 Hz, 2H; H-8), 2.43 (s, 3H; H-15), 1.17 (t, *J* = 7.0 Hz, 3H; H-9). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.8 (C_q), 143.5 (C_q), 140.4 (C_q), 137.2 (CH; C-5), 137.2 (C_q), 129.8 (2 x CH_{Ar}; C-13), 127.3 (2 x CH_{Ar}; C-12), 122.7 (CH; C-2), 118.8 (CH_2; C-10), 116.3 (CH_2; C-6), 73.0 (CH_2; C-7), 66.1 (CH_2; C-8), 41.6 (CH_2; C-1), 21.7 (CH_3; C-15), 15.2 (CH_3 C-9). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3286 (N-H), 3094 (C-H_{Alkene}), 3028 (C-H_{Ar}), 2977 (C-H_{Alkane}), 2925 (C-H_{Alkane}), 2857 (C-H_{Alkane}), 1720 (C=C), 1598, 1442 (C-H_{Alkane}), 1352 (S=O), 1336, 1161 (S=O), 1094 (C-O), 1051, 912, 815. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{18}H_{26}O_3NS$ [M + H]+: 322.1471. Found: 322.1474.

Synthesis of 4-Methyl-N-(4-methylene-3-propoxymethyl-hexa-2,5-dienyl)-benzenesulfonamide* (3ac) *and 4-Propoxymethyl-1-(toluene-4-sulfonyl)-3-vinyl-1,2,3,6-tetrahydro-pyridine* (4ac) *using 1-propanol as nucleophile

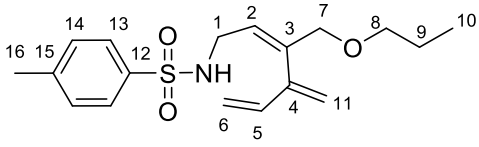
From 1,5-bisallene **1a** (53 mg, 0.19 mmol), $PtCl_2(MeCN)_2$ (3 mg, 0.01 mmol), silver hexafluoroantimonate (7 mg, 0.02 mmol), 1-Propanol (393 µl, 5.27 mmol) and 1.9 mL of dry

THF. Obtained after column chromatography using PET / EtOAc (7:1) as eluent: **4ac**, 13 mg, 0.04 mmol (20%): colourless oil; and **3ac**, 15 mg, 0.05 mmol (24%): colourless oil.



4ac

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.66 (d, J = 8.2 Hz, 2H; H_{Ar}-13), 7.31 (d, J = 8.2 Hz, 2H; H_{Ar}-14), 5.80 (ddd, J = 17.1, 10.1, 8.5 Hz, 1H; H-6), 5.69 – 5.64 (m, 1H; H-4), 5.18 – 5.10 (m, 2H; H-7), 3.87 (d, J = 12.3 Hz, 1H; H-8), 3.84 – 3.78 (m, 1H; H-5), 3.74 (d, J = 12.3 Hz, 1H; H-8), 3.42 (dd, J = 11.4, 3.6 Hz, 1H; H-1), 3.38 – 3.34 (m, 1H; H-5), 3.33 – 3.23 (m, 2H; H-9), 2.97 – 2.93 (m, 1H; H-2), 2.87 (dd, J = 11.4, 4.1 Hz, 1H; H-1), 2.43 (s, 3H; H-16), 1.55 (sex, J = 7.3 Hz, 1H; H-10), 0.89 (t, J = 7.3 Hz, 3H; H-11). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.7 (C_q), 137.1 (CH; C-6), 135.7 (C_q), 133.3 (C_q), 129.8 (2 x CH_{Ar}; C-14), 127.9 (2 x CH_{Ar}; C-13), 119.6 (CH; C-4), 117.2 (CH_2; C-7), 72.3 (CH_2; C-9), 71.7 (CH_2; C-8), 47.8 (CH_2; C-1), 44.9 (CH_2; C-5), 40.6 (CH; C-2), 23.0 (CH_2; C-10), 21.7 (CH_3; C-16), 10.8 (CH_3; C-11). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3083 (C-H_{Alkene}), 3069 (C-H_{Alkene}), 3035 (C-H_{Ar}), 2961 (C-H_{Alkane}), 2924 (C-H_{Alkane}), 2852 (C-H_{Alkane}), 1637 (C=C), 1597, 1457 (C-H_{Alkane}), 1347 (S=O), 1163 (S=O), 1120 (C-O), 1093 (C-N), 955, 815. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{14}H_{17}O_5N_2S$ $[M-H+O]^+$: 350.1421. Found: 350.1425.

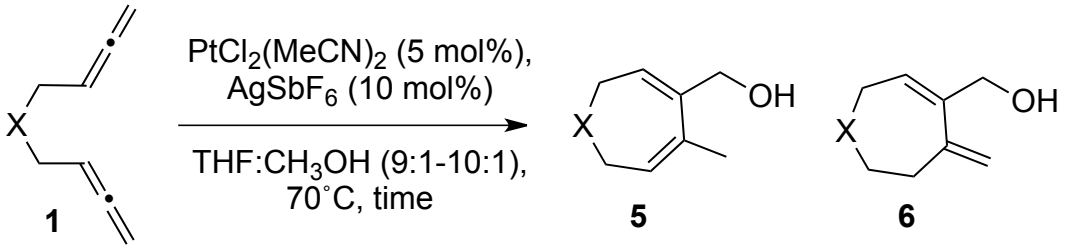


3ac

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.72 (d, J = 8.2 Hz, 2H; H_{Ar}-13), 7.29 (d, J = 8.2 Hz, 2H; H_{Ar}-14), 6.30 (dd, J = 17.3, 10.5 Hz, 1H; H-5), 5.62 (tt, J = 7.0, 1.5 Hz, 1H; H-2), 5.17 (d, J = 0.8 Hz, 1H; H-11), 5.07 (d, J = 10.5 Hz, 1H; H-6), 5.04 (d, J = 17.3 Hz, 1H; H-6), 4.88 (s, 1H; H-11), 4.26 (bt, J = 5.9 Hz, 1H; NH), 3.86 (d, J = 1.5 Hz, 2H; H-7), 3.53 – 3.47 (m, 2H; H-1), 3.34 (t, J = 6.9 Hz, 2H; H-8), 2.43 (s, 3H; H-16), 1.61 – 1.52 (m, 2H; H-9), 0.90 (t, J = 7.2 Hz, 3H; H-10). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.8 (C_q), 143.5 (C_q), 140.5 (C_q), 137.3 (CH; C-5), 137.2 (C_q), 129.8 (2 x CH_{Ar}; C-14), 127.3 (2 x CH_{Ar}; C-13), 122.6 (CH; C-2), 118.8 (CH_2; C-11), 116.3 (CH_2; C-6), 73.2 (CH_2; C-7 or C-8), 72.5 (CH_2; C-7 or C-8), 41.6 (CH_2; C-1), 23.0 (CH_3; C-16), 21.7 (CH_2; C-9), 10.8 (CH_3; C-10). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3291 (N-H), 3090 (C-H_{Alkene}), 3066 (C-

H_{Alkene}), 3039 (C-H_{Ar}), 2966 (C-H_{Alkane}), 2929 (C-H_{Alkane}), 2850 (C-H_{Alkane}), 1648 (C=C), 1598, 1456 (C-H_{Alkane}), 1331 (S=O), 1161 (S=O), 1094 (C-N), 1042 (C-O), 908, 814. HRMS (FTMS + p APCI (OIL)): Calc. for $C_{18}H_{26}O_3NS$ $[M+H]^+$: 336.1628. Found: 336.1624.

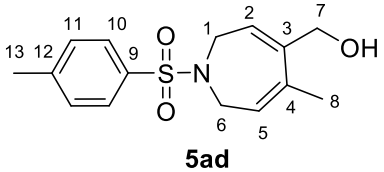
3d) General procedure for platinum-catalyzed hydroxycyclization of 1,5-bisallenes



To a microwave vial were added $PtCl_2(MeCN)_2$ (0.05 eq.) and $AgSbF_6$ (0.12 eq.). Then the vial was closed with a stopper and flushed with N_2 during 3 min. A small amount of dry THF was added and the solution was stirred at room temperature for a few min to preform the cationic complex. The corresponding 1,5-bisallene **1** (1.0 eq., 0.09 M – absolute concentration) dissolved in dry THF was added, then distilled H_2O (THF:H_2O, 1:3) was added. The vial was sealed under N_2 and placed in a pre-heated oil bath at 70 ^oC or under microwave irradiation until completed conversion, following the reaction by TLC. The crude was filtered through a pad of celite / $MgSO_4$ anhydrous (1:2), washed with acetonitrile and concentrated under vacuum. The mixture was purified by column chromatography using (Sigma-Aldrich Silica gel) and PET, Hex / Et_2O, EtOAc as eluents.

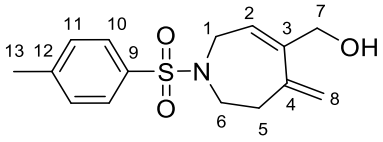
***Synthesis of [5-Methyl-1-(toluene-4-sulfonyl)-2,7-dihydro-1H-azepin-4-yl]-methanol* (5ad) *and [5-methylene-1-(toluene-4-sulfonyl)-2,5,6,7-tetrahydro-1H-azepin-4-yl]-methanol* (6ad)**

From 1,5-bisallene **1a** (100 mg, 0.36 mmol), $PtCl_2(MeCN)_2$ (6 mg, 0.02 mmol), silver hexafluoroantimonate (15 mg, 0.04 mmol), distilled water (3.0 mL, 0.17 mmol) and 1.0 mL of dry THF. Obtained as inseparable mixture after column chromatography using PET / EtOAc (5:1) then (1:1) as eluent: **5ad**:**6ad** (1:9.8), 46 mg, 0.16 mmol (43%): yellow oil.



5ad

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.68 (d, J = 8.2 Hz, 2H; H_{Ar}-11), 7.30 (d, J = 8.2 Hz, 2H; H_{Ar}-10), 5.88 (t, J = 7.0 Hz, 1H; H-2), 5.73 (tq, J = 7.0, 1.2 Hz, 1H; H-5), 4.13 (s, 2H; H-7), 3.58 (d, J = 7.0 Hz, 2H; H-1), 3.57 (d, J = 7.0 Hz, 2H; H-6), 2.42 (s, 3H; H-13), 1.79 (s, 3H; H-8). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 147.6 (C_q), 143.4 (C_q), 142.0 (C_q), 136.2 (C_q), 129.8 (2 x CH_{Ar}; C-11), 127.6 (2 x CH_{Ar}; C-10), 124.5 (CH; C-5), 122.5 (CH; C-2), 63.8 (CH_2; C-7), 43.8 (CH_2; C-6), 43.5 (CH_2; C-1), 21.7 (CH_3; C-13), 19.8 (CH_3; C-8).



6ad

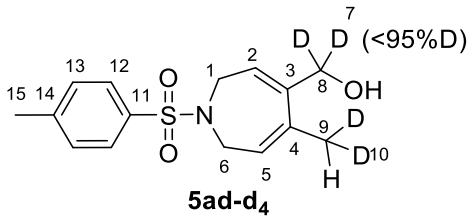
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.63 (d, J = 8.2 Hz, 2H; H_{Ar}-10), 7.25 (d, J = 8.2 Hz, 2H; H_{Ar}-11), 5.80 (t, J = 5.3 Hz, 1H; H-2), 5.00 (s, 1H; H-8), 4.95 (s, 1H; H-8), 4.11 (s, 2H; H-7), 3.95 (d, J = 5.3 Hz, 2H; H-1), 3.44 (t, J = 6.4 Hz, 2H; H-6), 2.49 (t, J = 6.4 Hz, 2H; H-5), 2.40 (s, 3H; H-13). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.3 (C_q), 142.8 (C_q), 142.6 (C_q), 136.3 (C_q), 129.5 (2 x CH_{Ar}; C-11), 127.5 (2 x CH_{Ar}; C-10), 124.8 (CH; C-2), 115.1 (CH_2; C-8), 65.3 (CH_2; C-7), 48.8 (CH_2; C-6), 45.0 (CH_2; C-1), 36.3 (CH_2; C-5), 21.6 (CH_3; C-13). M.P. = 79 – 81 ^{o}C.

9a and **10a** as inseparable mixture. IR (Film, cm^{-1}): $\tilde{\nu}$ = 3521 (O-H), 3296 (N-H), 3087 (C-H_{Alkene}), 3063 (C-H_{Alkene}), 3035 (C-H_{Ar}), 2925 (C-H_{Alkane}), 2857 (C-H_{Alkane}), 1725 (C=C), 1598, 1455 (C-H_{Alkane}), 1333 (S=O), 1159 (S=O), 1094 (C-N), 1070 (C-O), 904, 816. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{15}H_{20}O_3NS$ $[M+H]^+$: 294.1158. Found: 294.1154.

***Synthesis of products [5-Methyl-1-(toluene-4-sulfonyl)-2,7-dihydro-1H-azepin-4-yl]-methanol-d^4* (5ad-d_4) *and [5-methylene-1-(toluene-4-sulfonyl)-2,5,6,7-tetrahydro-1H-azepin-4-yl]-methanol-d^4* (6ad-d_4)**

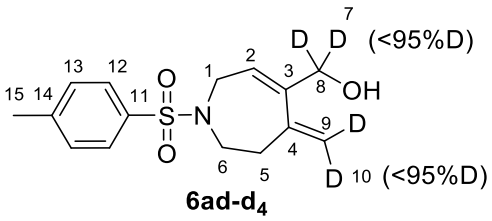
From 1,5-bisallene **1a**-d_4 (150 mg, 0.54 mmol), $PtCl_2(MeCN)_2$ (9 mg, 0.03 mmol), silver hexafluoroantimonate (22 mg, 0.06 mmol), distilled water (4.5 mL, 0.25 mmol) and 1.5 mL of dry THF. Obtained as inseparable mixture after column chromatography using PET / EtOAc (2:1) as eluent: **5ad**-d_4:**6ad**-d_4 (1:10), 63 mg, 0.21 mmol (40%): white solid.

Supporting Information



5ad-d$_4$

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.61 (d, J = 8.2 Hz, 2H; H_{Ar}-12), 7.23 (d, J = 8.2 Hz, 2H; H_{Ar}-13), 5.81 (t, J = 7.0 Hz, 1H; H-2), 5.66 (t, J = 7.0 Hz, 1H; H-5), 4.07 (s, 2H; H-7, 5 % H), 3.51 (d, J = 7.0 Hz, 2H; H-1), 3.51 (d, J = 7.0 Hz, 2H; H-6), 2.36 (s, 3H; H-15), 1.70 (m, 1H; H-10). *The deuterium incorporation in C-9, could not be accurately determine due to overlapping with other signals.* ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 147.5 (C_q), 143.4 (C_q), 142.7 (C_q), 136.1 (C_q), 129.8 (2 x CH_{Ar}; C-13), 127.5 (2 x CH_{Ar}; C-12), 124.4 (CH; C-5), 122.5 (CH; C-2), 43.8 (CH_2; C-6), 43.5 (CH_2; C-1), 21.6 (CH_3; C-15). *C-8 and C-9 could not be assigned due to the high deuterium incorporation*. ^{2}H NMR (77 MHz, $CDCl_3$, 25 ^{o}C) δ = 4.11 (bs, 2^{2}H; ^{2}H-7), 1.81 (bs, 1^{2}H; ^{2}H-10), 1.79 (bs, 1^{2}H; ^{2}H-10).



6ad-d$_4$

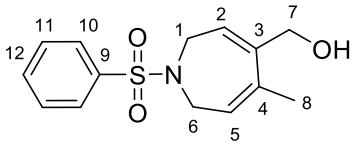
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.57 (d, J = 8.2 Hz, 2H; H_{Ar}-12), 7.19 (d, J = 8.2 Hz, 2H; H_{Ar}-13), 5.73 (t, J = 5.3 Hz, 1H; H-2), 4.92 (s, 1H; H-10, 5 % H), 4.87 (s, 1H; H-10, 5 % H), 4.05 (s, 2H; H-7, < 5 % H), 3.88 (d, J = 5.3 Hz, 2H; H-1), 3.37 (t, J = 6.4 Hz, 2H; H-6), 2.42 (t, J = 6.4 Hz, 2H; H-5), 2.34 (s, 3H; H-15). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.3 (C_q), 142.6 (C_q), 142.5 (C_q), 136.2 (C_q), 129.5 (2 x CH_{Ar}; C-13), 127.5 (2 x CH_{Ar}; C-12), 48.8 (CH_2; C-6), 45.0 (CH_2; C-1), 36.2 (CH_2; C-5), 21.6 (CH_3; C-15). *C-8 and C-9 could not be assigned due to the high deuterium incorporation*. ^{2}H NMR (77 MHz, $CDCl_3$, 25 ^{o}C) δ = 5.06 (bs, 1^{2}H; ^{2}H-10), 5.01 (bs, 1^{2}H; ^{2}H-10), 4.11 (bs, 2^{2}H; ^{2}H-7).

5ad-*d*^{4} and **6ad-*d*^{4}** as inseparable mixture. IR (Film, cm^{-1}): $\tilde{\nu}$ = 3514 (O-H), 2954 (C-H_{Alkane}), 2853 (C-H_{Alkane}), 1644 (C=C), 1454 (C-H_{Alkane}), 1332 (S=O), 1157 (S=O), 1096 (C-N), 1062 (C-O), 907. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{15}H_{16}D_4O_3NS$ $[M+H]^+$: 298.1409. Found: 298.1409. M.P. = 106 – 108 ^{o}C.

Supporting Information

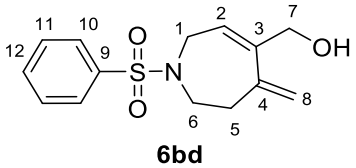
***Synthesis of (1-Benzenesulfonyl-5-methylene-2,5,6,7-tetrahydro-1H-azepin-4-yl)-methanol* (5bd) *and (1-Benzenesulfonyl-5-methyl-2,7-dihydro-1H-azepin-4-yl)-methanol* (6bd)**

From 1,5-bisallene **1b** (154 mg, 0.59 mmol), $PtCl_2(MeCN)_2$ (10 mg, 0.03 mmol), silver hexafluoroantimonate (24 mg, 0.07 mmol), distilled water (4.9 mL, 0.27 mmol) and 1.6 mL of dry THF. Obtained as inseparable mixture after column chromatography using PET / EtOAc (5:1) then (1:1) as eluent: **5bd**:**6bd** (1:7.8), 86 mg, 0.31 mmol (52%): colourless oil.



5bd

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.82 – 7.79 (m, 2H; H_{Ar}-10), 7.60 – 7.49 (m, 1H; H_{Ar}-12), 7.48 – 7.46 (m, 2H; H_{Ar}-11), 5.87 (t, J = 7.0 Hz, 1H; H-2), 5.71 (tq, J = 7.0, 1.4 Hz, 1H; H-5), 4.13 (s, 2H; H-7), 3.59 (d, J = 7.0 Hz, 2H; H-1), 3.58 (d, J = 7.0 Hz, 2H; H-6), 1.78 (s, 3H; H-8). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 147.7 (C_q; C-3 or C-4), 142.1 (C_q; C-3 or C-4), 139.1 (C_q; C-9), 132.7 (CH_{Ar}; C-12), 129.2 (2 x CH_{Ar}; C-11), 127.5 (2 x CH_{Ar}; C-10), 124.3 (CH; C-5), 122.3 (CH; C-2), 63.7 (CH_2; C-7), 43.9 (CH_2; C-6), 43.6 (CH_2; C-1), 19.8 (CH_3; C-8).



6bd

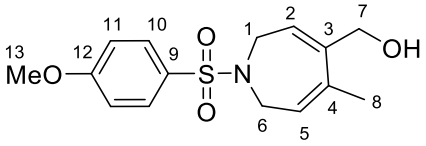
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.78 – 7.73 (m, 2H; H_{Ar}-10), 7.59 – 7.56 (m, 1H; H_{Ar}-12), 7.49 – 7.43 (m, 2H; H_{Ar}-11), 5.80 (tt, J = 5.0, 0.9 Hz, 1H; H-2), 4.99 (s, 1H; H-8), 4.91 (s, 1H; H-8), 4.08 (d, J = 0.9 Hz, 2H; H-7), 3.99 (d, J = 5.0 Hz, 2H; H-1), 3.47 (t, J = 6.4 Hz, 2H; H-6), 2.49 (t, J = 6.4 Hz, 2H; H-5). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 142.7 (C_q; C-3 or C-4), 142.6 (C_q; C-3 or C-4), 139.3 (C_q; C-9), 132.5 (CH_{Ar}; C-12), 128.9 (2 x CH_{Ar}; C-11), 127.5 (2 x CH_{Ar}; C-10), 124.6 (CH; C-2), 115.2 (CH_2; C-8), 65.1 (CH_2; C-7), 48.8 (CH_2; C-6), 45.0 (CH_2; C-1), 36.3 (CH_2; C-5).

5bd and **6bd** as inseparable mixture. IR (Film, cm^{-1}): $\tilde{\nu}$ = 3518 (O-H), 3064 (C-H_{Alkene}), 2924 (C-H_{Alkane}), 2864 (C-H_{Alkane}), 1606 (C=C), 1447 (C-H_{Alkane}), 1329 (S=O), 1159 (S=O), 1095 (C-N), 1061 (C-O), 903. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{14}H_{18}O_3NS$ $[M+H]^+$: 280.1002. Found: 280.1003.

Supporting Information

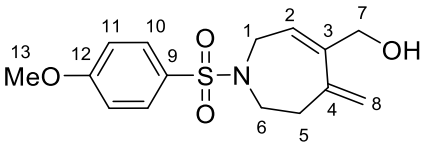
***Synthesis of [1-(4-Methoxy-benzenesulfonyl)-5-methyl-2,7-dihydro-1H-azepin-4-yl]-methanol* (5cd) *and [1-(4-methoxy-benzenesulfonyl)-5-methylene-2,5,6,7-tetrahydro-1H-azepin-4-yl]-methanol* (6cd)**

From 1,5-bisallene **1c** (160 mg, 0.55 mmol), $PtCl_2(MeCN)_2$ (9 mg, 0.03 mmol), silver hexafluoroantimonate (23 mg, 0.07 mmol), distilled H_2O (4.5 mL, 0.25 mmol) and 1.5 mL of dry THF. Obtained as inseparable mixture after column chromatography using PET / EtOAc (1:1) then (1:1) as eluent: **5cd**:**6cd** (1:10), 71 mg, 0.23 mmol (42%): yellow oil.



5cd

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.74 – 7.70 (m, 2H; H_{Ar}-10), 6.99 – 6.95 (m, 2H; H_{Ar}-11), 5.88 (t, J = 7.0 Hz, 1H; H-2), 5.73 (tq, J = 7.0, 1.4 Hz, 1H; H-5), 4.13 (s, 2H; H-7), 3.86 (s, 3H; H-13), 3.56 (d, J = 7.0 Hz, 2H; H-1), 3.55 (d, J = 7.0 Hz, 2H; H-6), 1.79 (s, 3H; H-8). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 162.9 (C_q; C-12), 147.7 (C_q; C-3), 142.1 (C_q; C-4), 130.7 (C_q; C-9), 129.6 (2 x CH_{Ar}; C-10), 124.5 (CH; C-5), 122.5 (CH; C-2), 114.4 (2 x CH_{Ar}; C-11), 63.7 (CH_2; C-7), 55.8 (CH_3; C-13), 43.8 (CH_2; C-6), 43.5 (CH_2; C-1), 19.8 (CH_3; C-8).



6cd

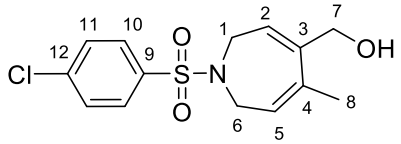
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.70 – 7.66 (m, 2H; H_{Ar}-10), 6.94 – 6.90 (m, 2H; H_{Ar}-11), 5.80 (t, J = 5.0 Hz, 1H; H-2), 4.99 (s, 1H; H-8), 4.94 (s, 1H; H-8), 4.11 (s, 2H; H-7), 3.94 (d, J = 5.0 Hz, 2H; H-1), 3.84 (s, 3H; H-13), 3.42 (t, J = 6.4 Hz, 2H; H-6), 2.48 (t, J = 6.4 Hz, 2H; H-5). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 162.9 (C_q; C-12), 142.8 (C_q; C-3 or C-4), 142.6 (C_q; C-3 or C-4), 130.9 (C_q; C-9), 129.6 (2 x CH_{Ar}; C-10), 124.6 (CH; C-2), 115.0 (CH_2; C-8), 114.1 (2 x CH_{Ar}; C-11), 65.2 (CH_2; C-7), 55.7 (CH_3; C-13), 48.7 (CH_2; C-6), 45.0 (CH_2; C-1), 36.3 (CH_2; C-5).

5cd and **6cd** as inseparable mixture. IR (Film, cm^{-1}): $\tilde{\nu}$ = 3520 (O-H), 3096 (C-H_{Alkene}), 3076 (C-H_{Alkene}), 2927 (C-H_{Alkane}), 2845 (C-H_{Alkane}), 1596 (C=C), 1498, 1332 (S=O), 1260 (C-O), 1154 (S=O), 1096 (C-N), 1063 (C-O), 899. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{15}H_{20}O_4NS$ $[M+H]^+$: 310.1108. Found: 310.1112.

Supporting Information

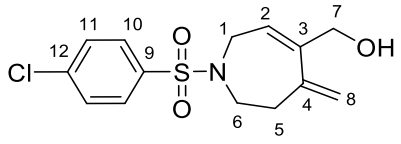
***Synthesis of [1-(4-Chloro-benzenesulfonyl)-5-methyl-2,7-dihydro-1H-azepin-4-yl]-methanol* (5dd) *and [1-(4-chloro-benzenesulfonyl)-5-methylene-2,5,6,7-tetrahydro-1H-azepin-4-yl]-methanol* (6dd)**

From 1,5-bisallene **1d** (161 mg, 0.59 mmol), $PtCl_2(MeCN)_2$ (10 mg, 0.03 mmol), silver hexafluoroantimonate (23 mg, 0.07 mmol), distilled H_2O (4.5 mL, 0.25 mmol) and 1.5 mL of dry THF. Obtained as inseparable mixture after column chromatography using PET / EtOAc (2:1) then (1:1) as eluent: **5dd**:**6dd** (1:7.6), 77 mg, 0.25 mmol (46%): yellow oil.



5dd

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.74 (d, J = 8.7 Hz, 2H; H_{Ar}-10), 7.49 (d, J = 8.7 Hz, 2H; H_{Ar}-11), 5.91 (t, J = 7.2 Hz, 1H; H-2), 5.75 (tq, J = 7.3, 1.4 Hz, 1H; H-5), 4.16 (s, 2H; H-7), 3.60 (d, J = 7.2 Hz, 2H; H-1), 3.58 (d, J = 7.3 Hz, 2H; H-6), 1.81 (bs, 3H; H-8). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 147.9 (C_q), 142.4 (C_q), 139.2 (C_q), 129.5 (2 x CH_{Ar}; C-11), 128.9 (2 x CH_{Ar}; C-10), 124.2 (CH; C-5), 122.1 (CH; C-2), 63.8 (CH_2; C-7), 43.8 (CH_2; C-6), 43.6 (CH_2; C-1), 19.8 (CH_3; C-8). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3494 (O-H), 3097 (C-H_{Alkene}), 2923 (C-H_{Alkane}), 2860 (C-H_{Alkane}), 1727 (C=C), 1586, 1336 (S=O), 1162 (S=O), 1093 (C-N), 1064 (C-O), 913, 828. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{14}H_{17}{}^{35}ClO_3NS$ $[M+H]^+$: 314.0612. Found: 314.0616. Calc. for $C_{14}H_{17}{}^{37}ClO_3NS$ $[M+H]^+$: 316.0581. Found: 316.0585.



6dd

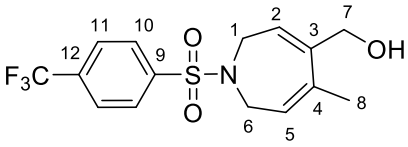
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.69 (d, J = 8.7 Hz, 2H; H_{Ar}-10), 7.43 (d, J = 8.7 Hz, 2H; H_{Ar}-11), 5.81 (tt, J = 5.2, 1.0 Hz, 1H; H-2), 5.00 (s, 1H; H-8), 4.91 (s, 1H; H-8), 4.11 (d, J = 1.0 Hz, 2H; H-7), 4.01 (d, J = 5.2 Hz, 2H; H-1), 3.46 (t, J = 6.4 Hz, 2H; H-6), 2.50 (t, J = 6.4 Hz, 2H; H-5). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 142.7 (C_q), 142.6 (C_q), 139.0 (C_q), 138.0 (C_q), 129.2 (2 x CH_{Ar}; C-11), 129.0 (2 x CH_{Ar}; C-10), 124.4 (CH; C-2), 115.3 (CH_2; C-8), 65.0 (CH_2; C-7), 48.8 (CH_2; C-6), 45.0 (CH_2; C-1), 36.3 (CH_2; C-5).

5dd:6dd as inseparable mixture. IR (Film, cm^{-1}): $\tilde{\nu}$ = 3498 (O-H), 3350 (N-H), 3090 (C-H_{Alkene}), 2924 (C-H_{Alkane}), 2854 (C-H_{Alkane}), 1648 (C=C), 1585, 1335 (S=O), 1161 (S=O), 1093 (C-N),

1052 (C-O), 903, 828. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{14}H_{17}{}^{35}ClO_3NS$ $[M+H]^+$: 314.0612. Found: 314.0616. Calc. for $C_{14}H_{17}{}^{37}ClO_3NS$ $[M+H]^+$: 316.0581. Found: 316.0585.

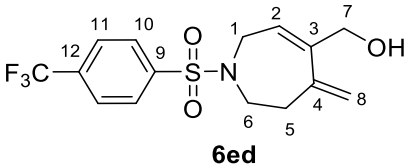
***Synthesis of [5-Methyl-1-(4-trifluoromethyl-benzenesulfonyl)-2,7-dihydro-1H-azepin-4-yl]-methanol* (5ed) *and [5-Methylene-1-(4-trifluoromethyl-benzenesulfonyl)-2,5,6,7-tetrahydro-1H-azepin-4-yl]-methanol* (6ed)**

From 1,5-bisallene **1e** (149 mg, 0.45 mmol), $PtCl_2(MeCN)_2$ (8 mg, 0.02 mmol), silver hexafluoroantimonate (19 mg, 0.05 mmol), distilled water (3.8 mL, 0.21 mmol) and 1.3 mL of dry THF. Obtained after column chromatography using PET / EtOAc (1:1) as eluent: **5ed**, 8.5 mg, 0.024 mmol (5%): yellow oil; **6ed,** 72.5 mg, 0.206 mmol (47%): yellow solid.



5ed

^1H NMR (500 MHz, $CDCl_3$, 25 ^oC) δ = 7.94 (d, J = 8.2 Hz, 2H; H_{Ar}-10), 7.79 (d, J = 8.2 Hz, 2H; H_{Ar}-11), 5.92 (t, J = 7.0 Hz, 1H; H-2), 5.76 (tq, J = 7.1, 1.5 Hz, 1H; H-5), 4.18 (s, 2H; H-7), 3.64 (d, J = 7.0 Hz, 2H; H-1), 3.62 (d, J = 7.1 Hz, 2H; H-6), 1.82 (s, 3H; H-8). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^oC) δ = 147.9 (C_q), 143.0 (C_q), 142.5 (C_q), 128.0 (2 x CH_{Ar}; C-10), 127.3 (q, J_{C-F} = 238.0 Hz, C_q; CF_3), 126.4 (q, J_{C-F} = 3.7 Hz, 2 x CH_{Ar}; C-11), 124.1 (CH; C-5), 122.0 (CH; C-2), 63.8 (CH_2; C-7), 43.8 (CH_2; C-1), 43.6 (CH_2; C-6), 19.9 (CH_3; C-8). *C_q-12 could not be identified.* ^{19}F NMR (471 MHz, CDCl3, 25 ^oC) δ = - 63.00. IR (Film, cm^{-1}): $\tilde{\nu}$ = 3522 (O-H), 3104 (C-H_{Alkene}), 3059 (C-H_{Alkene}), 2924 (C-H_{Alkane}), 2860 (C-H_{Alkane}), 1727 (C=C), 1323 (S=O), 1165 (S=O), 1132 (C-F), 1058 (C-O), 920, 844. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{15}H_{17}O_3NSF_3$ $[M+H]^+$: 348.0876. Found: 348.0876.



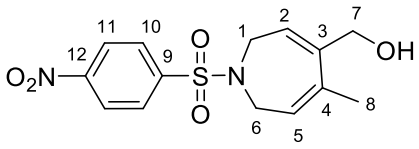
6ed

^1H NMR (500 MHz, $CDCl_3$, 25 ^oC) δ = 7.87 (d, J = 8.2 Hz, 2H; H_{Ar}-10), 7.70 (d, J = 8.2 Hz, 2H; H_{Ar}-11), 5.80 (t, J = 4.6 Hz, 1H; H-2), 4.94 (s, 1H; H-8), 4.82 (s, 1H; H-8), $4.05_{(Overlap)}$ (s, 2H; H-7), $4.04_{(overlap)}$ (d, 2H; H-1), 3.48 (t, J = 6.4 Hz, 2H; H-6), 2.49 (t, J = 6.4 Hz, 2H; H-5). *J coupling*

from the doublet at 4.04 ppm could not be obtained as it is overlapping with H-7. ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.0 (C_q), 142.7 (C_q), 142.4 (C_q), 134.1 (q, $J_{C\text{-}F}$ = 33.0 Hz, C_q; C-12), 128.0 (2 x CH_{Ar}; C-10), 126.0 (q, $J_{C\text{-}F}$ = 3.7 Hz, 2 x CH_{Ar}; C-11), 124.1 (CH; C-2), 123.4 (q, $J_{C\text{-}F}$ = 272.9 Hz, C_q; CF_3), 115.3 (CH_2; C-8), 64.7 (CH_2; C-7), 48.8 (CH_2; C-6), 45.0 (CH_2; C-1), 36.3 (CH_2; C-5). ^{19}F NMR (471 MHz, $CDCl_3$, 25 ^{o}C) δ = - 63.07. IR (Film, cm^{-1}): $\tilde{\nu}$ = 3522 (O-H), 3107 (C-H_{Alkene}), 3063 (C-H_{Alkene}), 2926 (C-H_{Alkane}), 2860 (C-H_{Alkane}), 1720 (C=C), 1404, 1324 (S=O), 1165 (S=O), 1133 (C-F), 1063 (C-O), 905, 844. HRMS (FTMS + p NSI ((DCM)/MeOH + NH_4OAc)): Calc. for $C_{15}H_{20}O_3N_2SF_3$ $[M+NH_4]$+: 365.1141. Found: 365.1146. M.P = 104 – 106 ^{o}C.

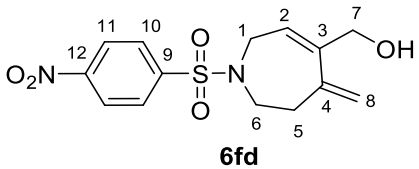
***Synthesis of [5-Methyl-1-(4-nitro-benzenesulfonyl)-2,7-dihydro-1H-azepin-4-yl]-methanol* (9fd), *[5-methylene-1-(4-nitro-benzenesulfonyl)-2,5,6,7-tetrahydro-1H-azepin-4-yl]-methanol* (6fd) *and 6,7-Dimethylene-3-(4-nitro-benzenesulfonyl)-3-aza-bicyclo[3.2.0]heptane* (18f)**

From 1,5-bisallene **1f** (204 mg, 0.67 mmol), $PtCl_2(MeCN)_2$ (12 mg, 0.03 mmol), silver hexafluoroantimonate (28 mg, 0.08 mmol), distilled water (5.5 mL, 0.30 mmol) and 1.8 mL of dry THF. Obtained after column chromatography using PET / EtOAc (2:1) as eluent: **5fd**:**6fd** (1:5.9) as inseparable mixture, 75 mg, 0.23 mmol (35%): yellow solid; and **18f,** 6 mg, 0.02 mmol (3%): yellow solid.



5fd

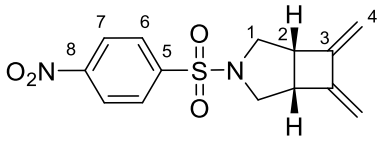
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 8.37 (d, J = 8.8 Hz, 2H; H_{Ar}-11), 7.99 (d, J = 8.8 Hz, 2H; H_{Ar}-10), 5.93 (t, J = 7.1 Hz, 1H; H-2), 5.77 (tq, J = 7.2, 1.3 Hz, 1H; H-5), 4.18 (s, 2H; H-7), 3.65 (d, J = 7.1 Hz, 2H; H-1), 3.63 (d, J = 7.2 Hz, 2H; H-6), 1.82 (s, 3H; H-8). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 150.2 (C_q; C-12), 148.2 (C_q; C-3), 145.3 (C_q; C-9), 142.8 (C_q; C-4), 128.6 (2 x CH_{Ar}; C-10), 124.5 (2 x CH_{Ar}; C-11), 123.8 (CH; C-5), 121.6 (CH; C-2), 63.6 (CH_2; C-7), 43.8 (CH_2; C-6), 43.6 (CH_2; C-1), 19.9 (CH_3; C-8).



6fd

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 8.29 (d, J = 9.0 Hz, 2H; H_{Ar}-11), 7.95 (d, J = 9.0 Hz, 2H; H_{Ar}-10), 5.84 (t, J = 4.3 Hz, 1H; H-2), 4.99 (s, 1H; H-8), 4.86 (s, 1H; H-8), 4.14 – 4.10 (m, 2H; H-1), 4.09 (s, 2H; H-7), 3.53 (t, J = 6.4 Hz, 2H; H-6), 2.53 (t, J = 6.4 Hz, 2H; H-5), 1.56 (bs, 1H; OH). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 150.0 (C_q; C-12), 145.5 (C_q; C-9), 142.8 (C_q; C-4), 142.4 (C_q; C-3), 128.7 (2 x CH_{Ar}; C-10), 124.2 (2 x CH_{Ar}; C-11), 124.1 (CH; C-2), 115.6 (CH_2; C-8), 64.8 (CH_2; C-7), 49.0 (CH_2; C-6), 45.0 (CH_2; C-1), 36.3 (CH_2; C-5).

5fd and **6fd** as inseparable mixture. IR (Film, cm^{-1}): $\tilde{\nu}$ = 3543 (O-H), 3104 (C-H_{Alkene}), 3031 (C-H_{Alkene}), 2926 (C-H_{Alkane}), 2863 (C-H_{Alkane}), 1606 (C=C), 1531 (N-O), 1351 (S=O), 1309, 1161 (S=O), 1094 (C-N), 1061 (C-O), 910. HRMS (FTMS + p APCI (Solid)): Calc. for $C_{14}H_{17}O_5N_2S$ $[M+H]^+$: 325.0853. Found: 325.0854. M.P. = 141 – 143 ^{o}C.

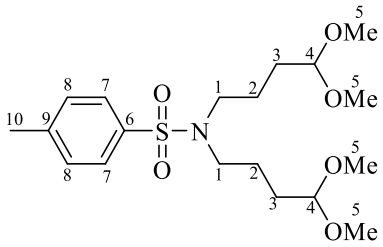


18f

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 8.35 (d, J = 8.8 Hz, 2H; H_{Ar}-7), 7.99 (d, J = 8.8 Hz, 2H; H_{Ar}-6), 5.18 (s, 2H; H-4), 4.80 (s, 2H; H-4), 3.70 (d, J = 10.2 Hz, 2H; H-1), 3.40 – 3.35 (m, 2H; H-2), 2.95 (dd, J = 10.2, 6.1 Hz, 2H; H-1). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 150.3 (C_q; C-8), 148.8 (2 x C_q; C-3), 142.4 (C_q; C-5), 129.1 (2 x CH_{Ar}; C-6), 124.2 (2 x CH_{Ar}; C-7), 106.2 (2 x CH_2; C-4), 53.6 (2 x CH_2; C-1), 44.9 (2 x CH; C-2). IR (Film, cm^{-1}): $\tilde{\nu}$ = 3110 (C-H_{Alkene}), 2969 (C-H_{Alkane}), 2923 (C-H_{Alkane}), 2853 (C-H_{Alkane}), 1527 (N-O), 1347 (S=O), 1168 (S=O), 1089 (C-N), 1015 (C-O), 897. HRMS (FTMS + p APCI (Solid)): Calc. for $C_{14}H_{15}O_4N_2S$ $[M+H]^+$: 307.0747. Found: 307.0749. M.P. = 156 – 158 ^{o}C.

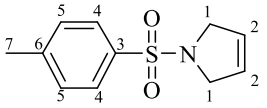
3e) Other products obtained during the optimization of reaction conditions

N,N-Bis-(4,4-dimethoxy-butyl)-4-methyl-benzenesulfonamide



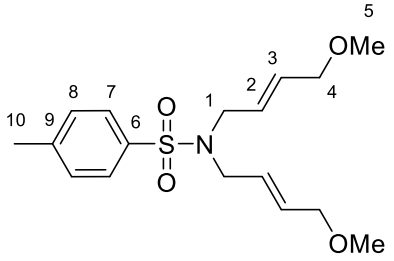
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.66 (d, *J* = 8.2 Hz, 2H; H_{Ar}-8), 7.27 (d, *J* = 8.2 Hz, 2H; H_{Ar}-7), 4.32 (t, *J* = 5.0 Hz, 2H; H-4), 3.28 (s, 12H; H-5), 3.10 (t, *J* = 7.0 Hz, 4H; H-1), 2.40 (s, 3H; H-10), 1.61 – 1.52 (m, 8H; H-3 and H-2). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.17 (C_q), 137.03 (C_q), 129.73 (CH-Ar), 127.25 (CH-Ar), 104.31 (2 x CH), 53.10 (4 x CH_3O), 48.07 (2 x CH_2), 29.84 (2 x CH_2), 23.85 (2 x CH_2), 21.59 (CH_3). IR (Film, cm^{-1}): $\tilde{\nu}$ = 2926 (C-H_{Alkane}), 2870 (C-H_{Alkane}), 1719, 1682, 1335 (S=O), 1158 (S=O), 1091 (C-N), 1015 (C-O), 815. HRMS (+ESI): Calc. for $C_{19}H_{33}O_6NSNa$ $[M+Na]^+$: 426.1921. Found: 426.1924. M.P. = 115 – 117 ^{o}C.

1-(Toluene-4-sulfonyl)-2,5-dihydro-1H-pyrrole[4]



^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C) δ = 7.74 – 7.70 (m, 2H; H_{Ar}-4), 7.32 (d, *J* = 8.2 Hz, 2H; H_{Ar}-5), 5.65 (s, 2H; H-2), 4.12 (s, 4H; H-1), 2.43 (s, 3H; H-7). ^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C) δ = 143.6 (C_q; C-6), 134.5 (C_q; C-3), 129.9 (2 x CH_{Ar}; C-3), 127.6 (2 x CH; C-2), 125.6 (2 x CH_{Ar}; C-4), 55.0 (2 x CH_2; C-1), 21.7 (CH_3; C-7). HRMS (+ESI): Calc. for $C_{11}H_{14}O_2NS$ $[M+H]^+$: 224.0740. Found: 224.0739.

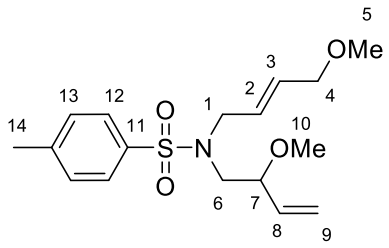
N,N-bis((E)-4-methoxybut-2-en-1-yl)-4-methylbenzenesulfonamide



^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.0, 2H-7), 7.22 (d, *J* = 8.0, 2H-8), 5.66 – 5.53 (m, 2H-2), 5.51 – 5.33 (m, 2H-3), 3.77 (dd, *J* = 5.4, 1.2, 4H-4), 3.73 (dd, *J* = 6.1, 1.2, 4H-1), 3.21 (s, 6H-5), 2.36 (s, 3H-10). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.37 (C_q-9), 137.41 (C_q-6), 131.19 (2 x CH-3), 129.76 (2 x CH_{Ar}-8), 127.35 (2 x CH_{Ar}-7), 127.31 (2 x CH-2), 72.21 (2 x CH_2-4), 58.09 (2 x CH_3O-5), 48.30 (2 x CH_2-1), 21.60 (CH_3-10). HRMS (+ESI): Calc. for $C_{17}H_{26}O_4NS$ $[M+H]^+$: 340.1577. Found: 340.1571.

4 J. A. Varela, C. González-Rodríguez, S. G. Rubín, L. Castedo, C. Saá, *J. Am. Chem. Soc*. **2006**, *128*, 9576-9577.

(*E*)-*N*-(4-methoxybut-2-en-1-yl)-*N*-(2-methoxybut-3-en-1-yl)-4-methylbenzenesulfonamide

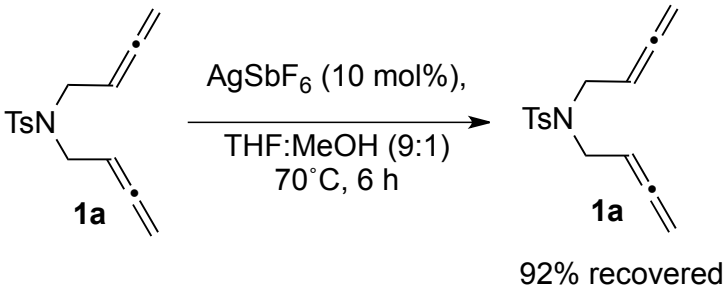


^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.3, 2H-12), 7.29 (d, *J* = 8.3, 2H-13), 5.75 – 5.42 (m, 3H, H8+H2+H3), 5.27 (ddd, *J* = 14.0, 2.8, 1.7, 2H-9), 4.12 (q, *J* = 7.1, 2H-4), 3.98 – 3.79 (m, 2H-1), 3.82 – 3.73 (m, 1H-7), 3.28 (s, 3H-5), 3.24 – 3.16 (m, 2H-6), 3.19 (s, 3H-10), 2.42 (s, 3H-14). HRMS (+ESI): Calc. for $C_{17}H_{26}O_4NS$ $[M+H]^+$: 340.1577. Found: 340.1584.

4) Decomposition experiments

It has been reported before that 1,5-bisallenes decompose in the presence of transition metals under certain reaction conditions. In order to explore this possibility in our system and explain the low yields obtained in some cases we performed a series of experiments testing the stability of our substrate under the platinum catalysis.

1. The reaction of 1,5-bisallene **1a** was performed in absence of the platinum complex but in the presence of silver salt. After 6 hours, the NMR yield was measured using as internal reference an accurate volume of a stock solution of 3,4,5-trichloropyridine in $CDCl_3$ added to the crude of the reaction, 92% of the bisallene was recovered.



2. We performed an experiment measuring the concentration of 1,5-bisallene **1a** with time in the presence of the cationic catalytic complex at 50ºC (Figure 4.1). We found out that the bisallene

decomposed with time to a complex mixture. After 2h in the presence of the platinum complex, the amount of bisallene had decreased in an 8%, which could partially explain the low yields encountered in the process. The same experiment at 70 ^{o}C showed much rapid decomposition with no signals of **1a** after 3 h. It should be noted that the signals corresponding to the allenic skeleton disappeared under reaction conditions, while signals of a tosyl group could still be identified. We were not able to isolate any characterizable product from these experiments.

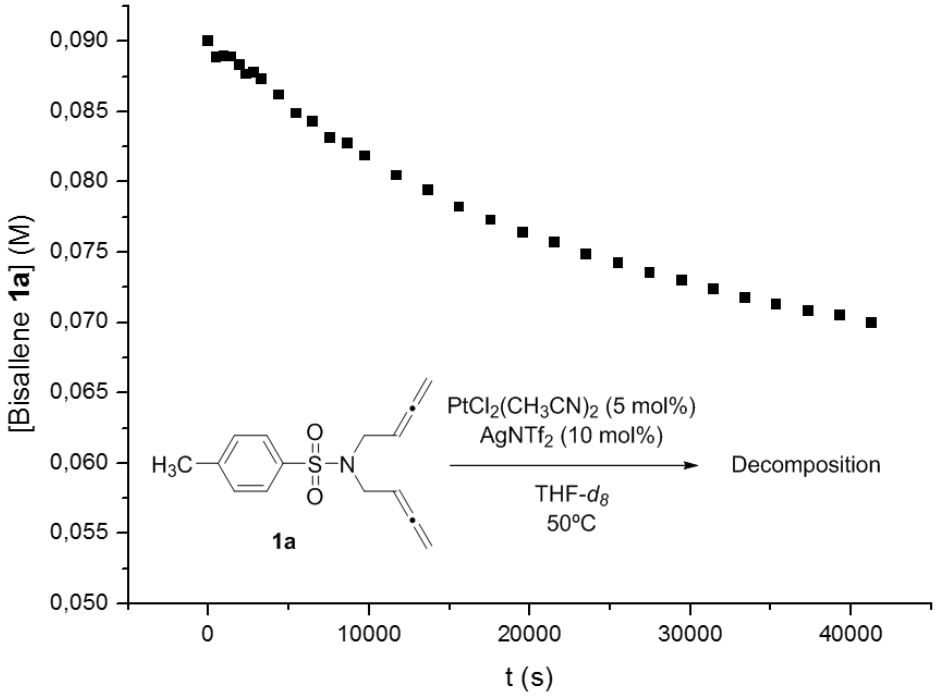


Figure 4.1. Plot of the concentration of bisallene **1a** versus time, showing the decomposition of this compound in the presence of the cationic complex.

However, this decomposition doesn't completely explain the low yields, and experiments were carried out to test the decomposition of the products formed under the reaction conditions. The cycles didn't decompose under the reaction conditions, but an experiment measuring the concentration of triene **3aa** with time under the optimized reaction conditions, in the presence of CD_3OD and at 50ºC, showed that the concentration of the compound decreased with time. After 2h the concentration of triene in the reaction mixture was 10% lower (Figure 4.2).

In addition, we found out that sometimes the purified yields were slightly lower than the NMR yields obtained from the ^{1}H NMR of the crude with a reference (dimethylsulfone), which point out

to decomposition of the products (cycles and triene) in the column. We tried other purification methods, but they turned out to be less effective than the chromatography in silica gel.

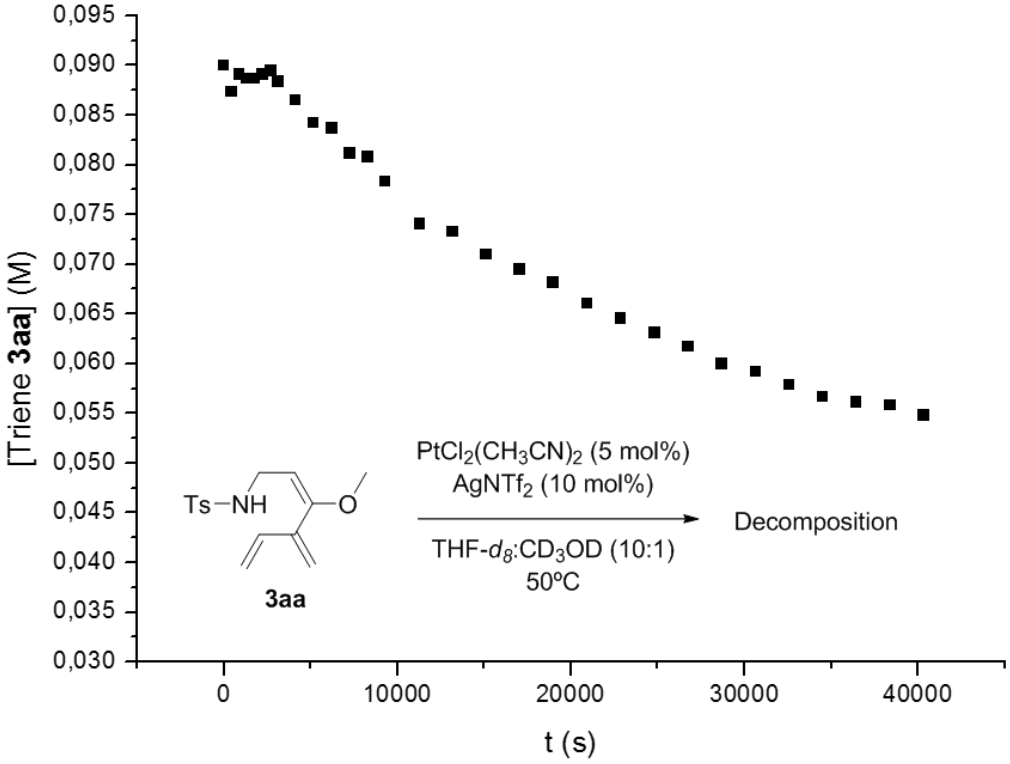


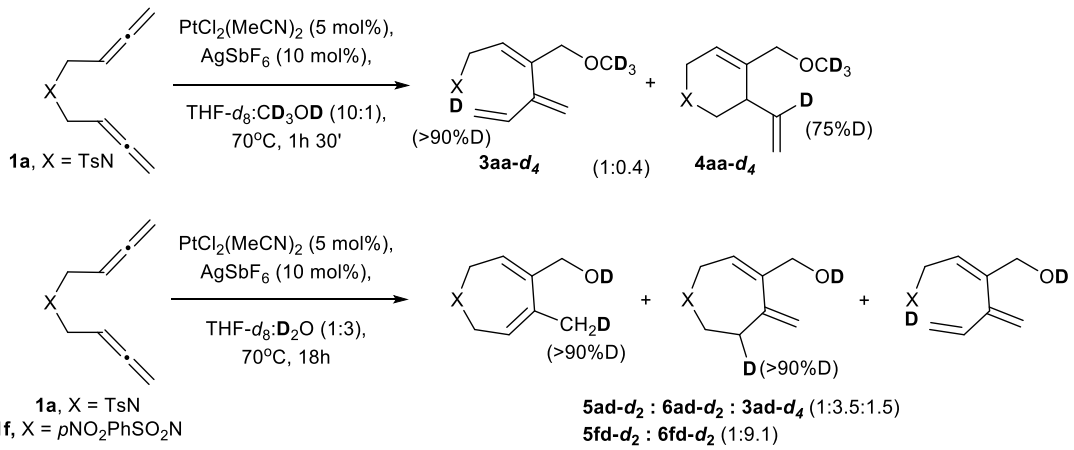
Figure 4.2. Plot of the concentration of triene **3aa** versus time, showing the decomposition of this compound in the optimized reaction conditions.

Similar results were obtained in experiments with water as the nucleophile.

Supporting Information

5) Deuteration experiments and KIEs

We carried out deuterium labelling studies using CD_3OD and D_2O. The positions where the deuterium was incorporated are shown in Scheme 5.1.



Scheme 5.1. Deuteration experiments. Ratios where obtained from the reaction crude.

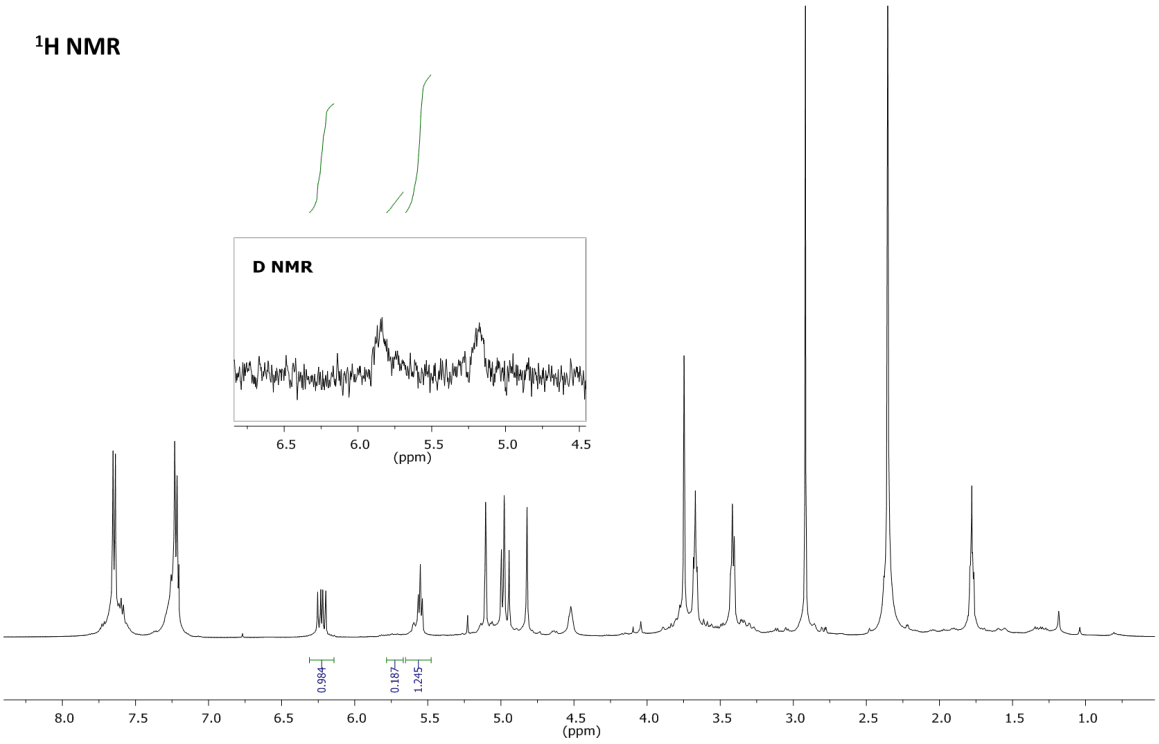


Figure 5.1. ^1H and ^2H NMR for the reaction of bisallene **1a** with CD_3OD in $CDCl_3$.

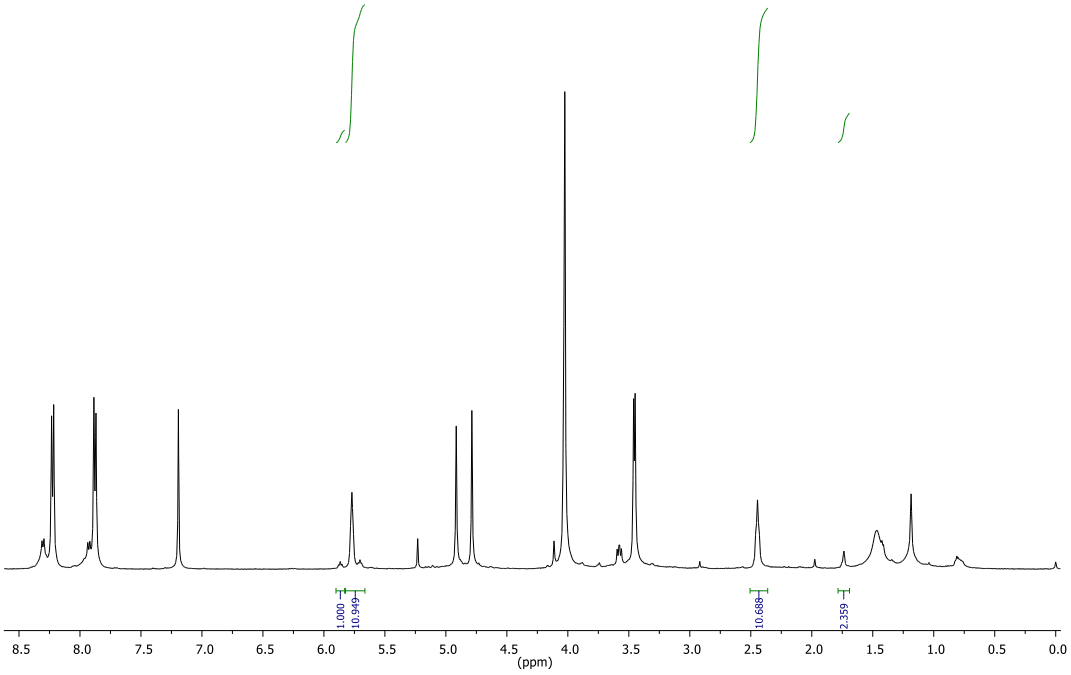


Figure 5.2. ^{1}H NMR for the reaction of bisallene **1f** with D_2O in $CDCl_3$.

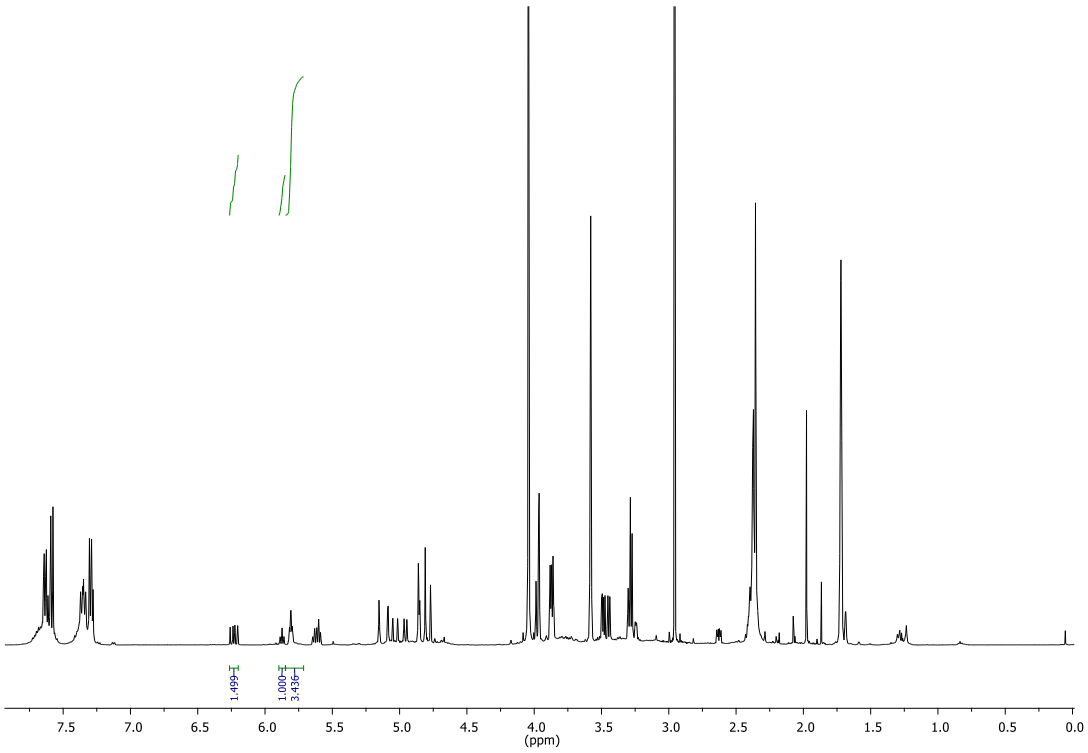
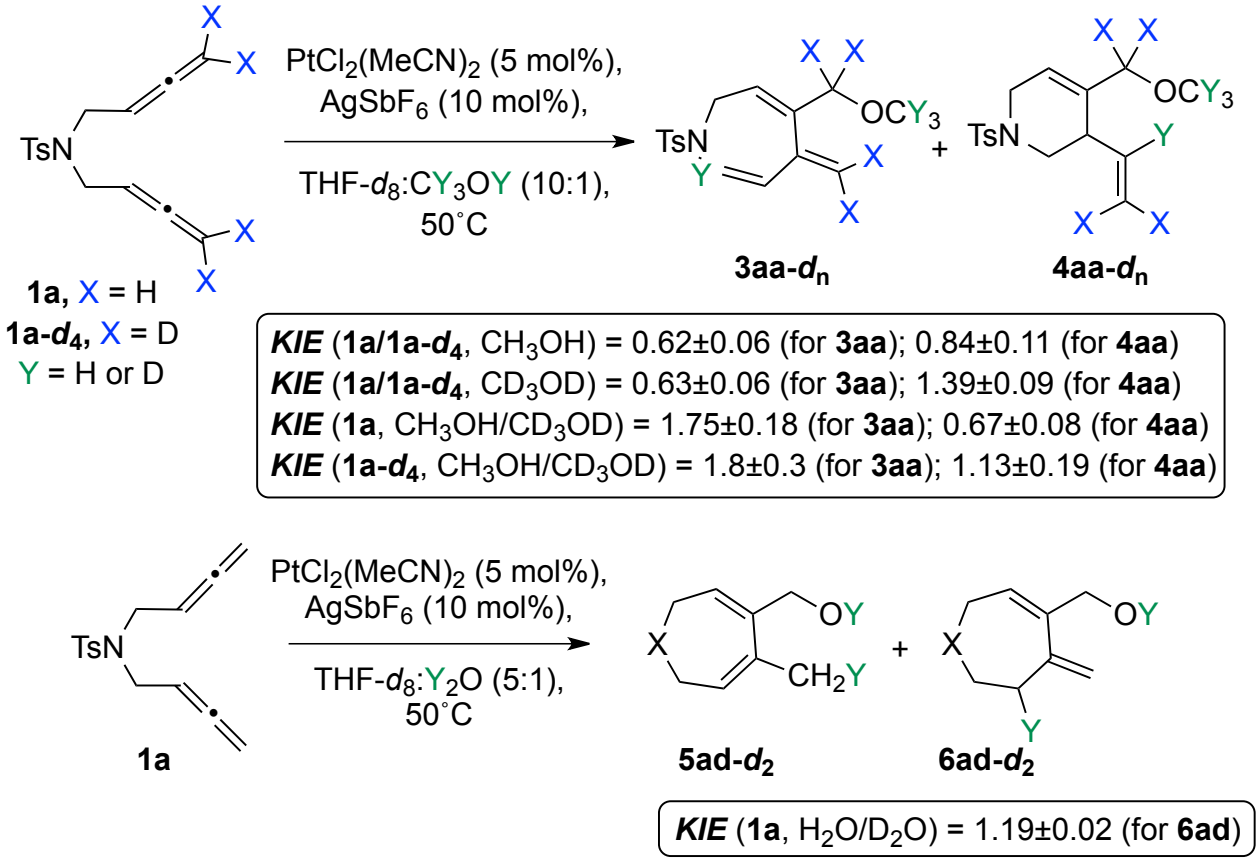


Figure 5.3. ^{1}H NMR for the reaction of bisallene **1a** with D_2O in THF-d_8.

Supporting Information

- Values for the KIEs with methanol and water

Initial rate method was used to calculate the initial rates and KIEs in methanol and water in all cases. An induction period when protonated nucleophiles were used was observed, which could indicate that these nucleophiles are participating in an out-of-cycle process, supporting the formation of Pt-H. The initial rates were calculated after the induction period. The final values of the KIEs were calculated as the average value of a series of experiments (between 2 and 5), with the errors calculated as the standard deviations (Scheme 5.2). Representative examples of the obtained *k* values along with the calculated KIEs, and representative "concentration *vs* time" graphs are shown in the tables and figures below.



Scheme 5.2. Labeling experiments and average values of KIEs with deuterated analogues.

Supporting Information

- KIEs in methanol

We carried out the reaction in the presence of methanol and deuterated methanol under the optimized reaction conditions with bisallenes **1a** (Figure 5.4) and **1a-*d*$_4$** (Figure 5.5), in which the terminal positions of the bisallene were deuterated.

Table 5.1. Representative examples of initial rates and KIEs in methanol for the reaction of bisallenes **1a** and **1a-*d*$_4$** using CH_3OH and CD_3OD.

		Initial rates		***Primary KIE*** k_{CH3OH}/k_{CD3OD}	
Bisallene	**CX_3OX**	***k*(4aa)**	***k*(3aa)**	**k_H/k_D (4aa)**	**k_H/k_D (3aa)**
1a	CH_3OH	$9.30\ 10^{-7}$	$2.87\ 10^{-6}$	0.80	1.92
1a	CD_3OD	$1.24\ 10^{-6}$	$1.49\ 10^{-6}$		
1a-*d*$_4$	CH_3OH	$1.01\ 10^{-6}$	$4.24\ 10^{-6}$	1.12	1.80
1a-*d*$_4$	CD_3OD	$8.92\ 10^{-7}$	$2.36\ 10^{-6}$		

A clear primary KIE in the formation of the cycle **4aa** could not be detected (KIE ~ 1) when deuterated methanol was used. However, a primary KIE ~ 2 was measured in the formation of the triene **3a**. Similar values were obtained in the reaction of **1a-*d*$_4$** in CH_3OH and CD_3OD.

- KIEs in water

No primary KIE was found in the formation of the major cycle **6ad** when the reaction was carried out with D_2O (Figure 5.4). Data obtained for the formation of cycle **5ad** in the reaction with H_2O could not be analysed, due to the low concentration of this cycle.

Table 5.2. Example of initial rates and KIE for the reaction of bisallene **1a** using H_2O and D_2O.

Bisallene	**Nucleophile**	***k*(6ad)**	**k_H/k_D (6ad)**
1a	H_2O	$9.31\ 10^{-7}$	1.21
1a	D_2O	$7.64\ 10^{-7}$	

Supporting Information

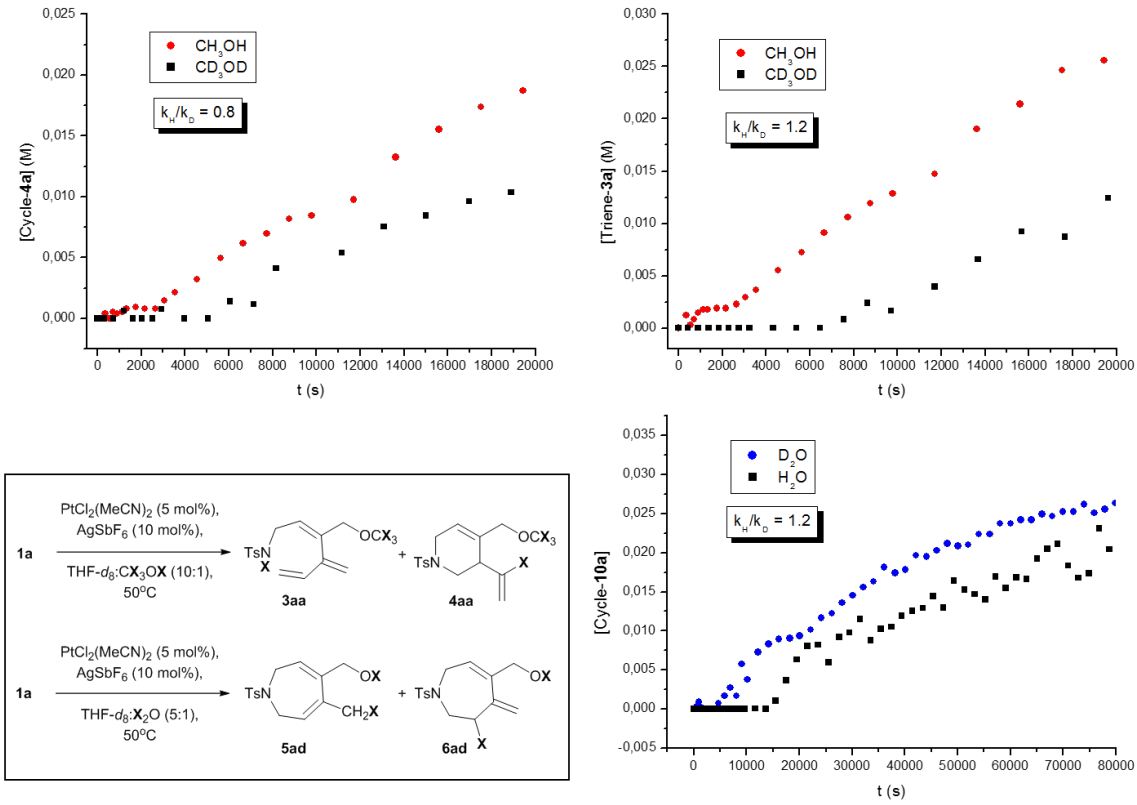


Figure 5.4. Examples of kinetic measurements and KIE in nucleophile for the reaction of bisallene **1a** with protonated and deuterated nucleophiles.

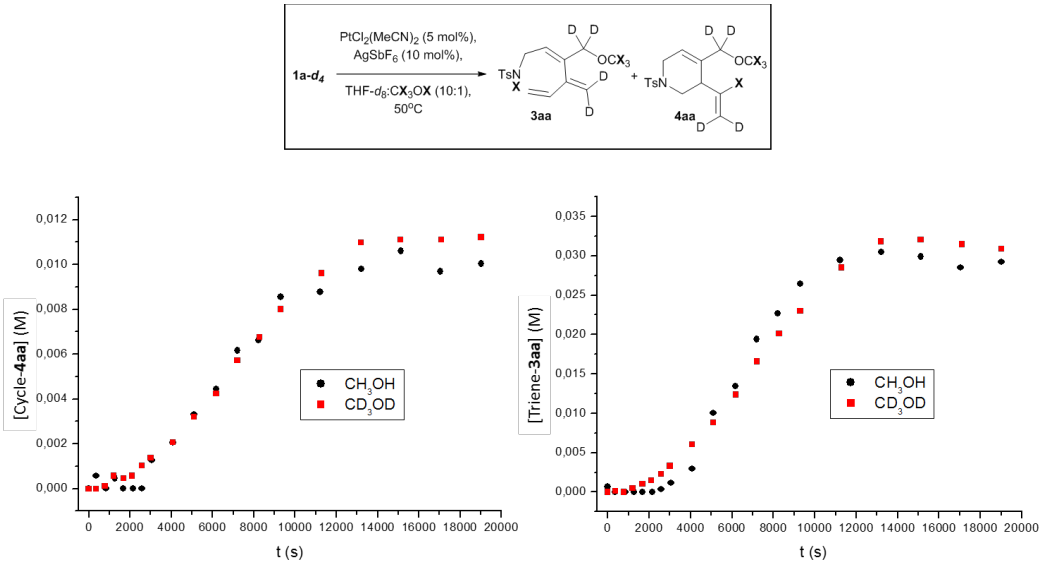


Figure 5.5. Examples of kinetic measurements and KIE in methanol for the reaction of bisallene **1a-*d*$_4$** with protonated and deuterated methanol.

Supporting Information

- Secondary KIE using deuterated bisallene

The KIEs using deuterated bisallene were also calculated using both CH_3OH (Figure 5.6) and CD_3OD (Figure 5.7). No clear secondary KIE ($k_H/k_D \sim 1$) for the formation of the cycle was observed (similar values obtained in CH_3OH and CD_3OD). However, inverse secondary KIE ($k_H/k_D \sim 0.65$) was observed for the formation of the triene **3aa-*d*$_4$** when **1a-*d*$_4$**, was used, suggesting a change in the hybridization of the terminal carbon of the allene from sp^2 to sp^3 in the rate limiting step of the formation of the triene.[5]

Table 5.3. Examples of initial rates and KIEs in bisallene for the reaction of bisallenes **1a** and **1a-*d*$_4$** using CH_3OH and CD_3OD.

		Initial rates		***Secondary KIE*** $k_{1a}/k_{1a\text{-}d4}$	
Bisallene	**CX_3OX**	***k*(4aa)**	***k*(3aa)**	k_H/k_D **(4aa)**	k_H/k_D **(3aa)**
1a	CH_3OH	$9.30\ 10^{-7}$	$2.87\ 10^{-6}$	0.93	0.68
1a-*d*$_4$	CH_3OH	$1.01\ 10^{-6}$	$4.24\ 10^{-6}$		
1a	CD_3OD	$1.24\ 10^{-6}$	$1.49\ 10^{-6}$	1.38	0.63
1a-*d*$_4$	CD_3OD	$8.92\ 10^{-7}$	$2.36\ 10^{-6}$		

5 M. Gomez-Gallego and M. A. Sierra, *Chem. Rev.*, 2011, **111**, 4857-4963.

Supporting Information

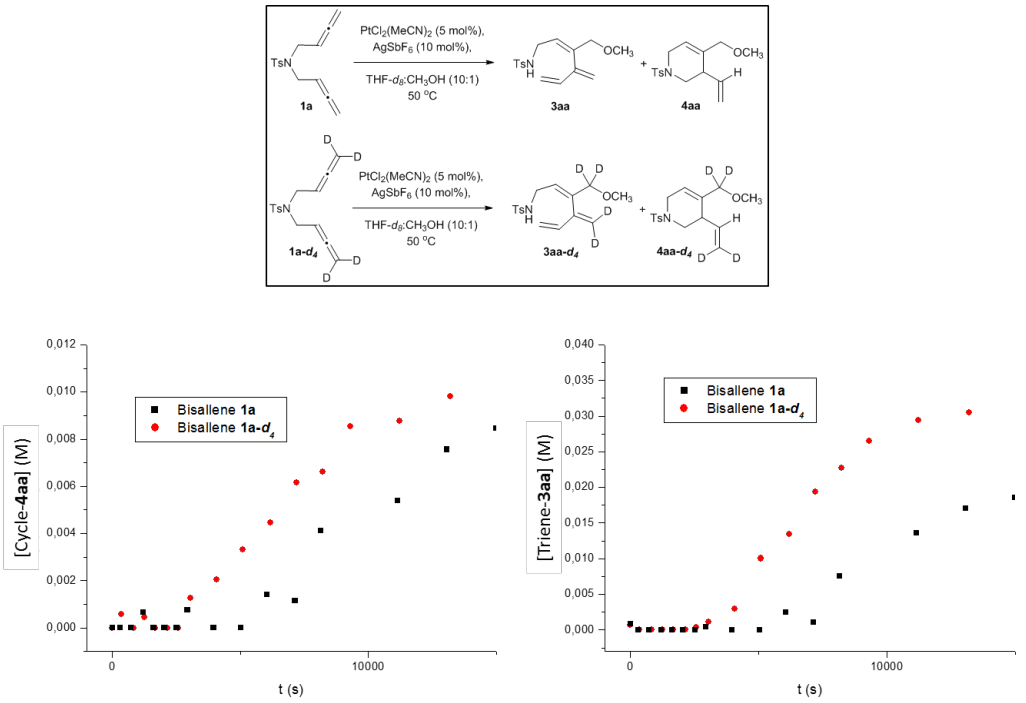


Figure 5.6. Examples of deuteration experiments and KIE in bisallene with protonated and deuterated bisallenes using CH_3OH (**1a** and **1a-*d*$_4$**).

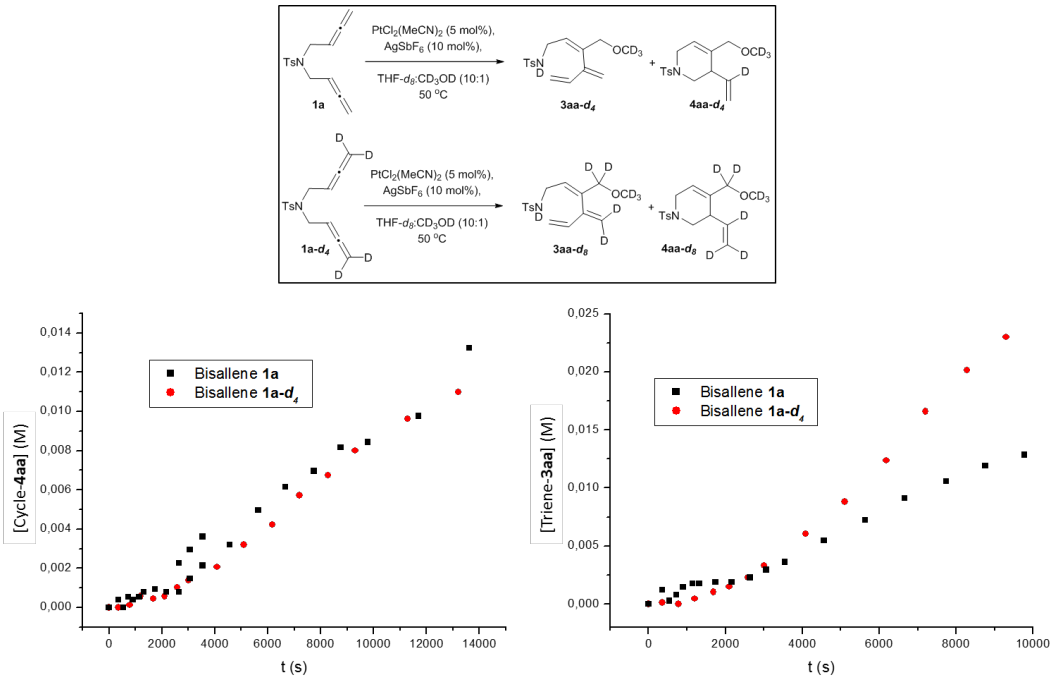


Figure 5.7. Examples of deuteration experiments and KIE in bisallene with protonated and deuterated bisallenes using CD_3OD (**1a** and **1a-*d*$_4$**).

Supporting Information

6) Kinetic Analysis

All the kinetic experiments were carried out measuring ^{1}H NMR spectra at different times. The boiling point of THF-d_8 limited the temperature of the experiments carried out in the magnet to 50ºC. The order of the different components was measured by the initial rates method and/or the graphical method.[6]

- Order in bisallene in methanol and water

The bisallene decay in methanol followed pseudo-zero order kinetics, with the graph of [bisallene] *versus* time being a straight line after the induction period. This behaviour was observed with allene **1a** and its deuterated version **1a-*d*$_4$** in CH_3OH and in CD_3OD. Interestingly the rate observed with the deuterated analogue was twice faster than with the protonated one in both solvents, suggesting a change in hybridization from sp^2 to sp^3 in the terminal carbon of the bisallene in the catalytic cycle (Figure 6.1).

Table 6.1. Pseudo-zero order rate constanst for the decay of bisallene in methanol.

Bisallene	Solvent	*k* (M/s)
1a	CH_3OH	4×10^{-6}
1a	CD_3OD	4×10^{-6}
1a-*d*$_4$	CH_3OH	7.5×10^{-6}
1a-*d*$_4$	CD_3OD	7.5×10^{-6}

Primary $KIE_{CH_3OH/CD_3OD} = 1$ for both allenes

Inverse Secondary $KIE_{allene/d\text{-}allene} = 0.5$ in both methanols

[6] J. Bures, *Angew. Chem. Int. Ed.,* 2016, **55**, 2028-2031.

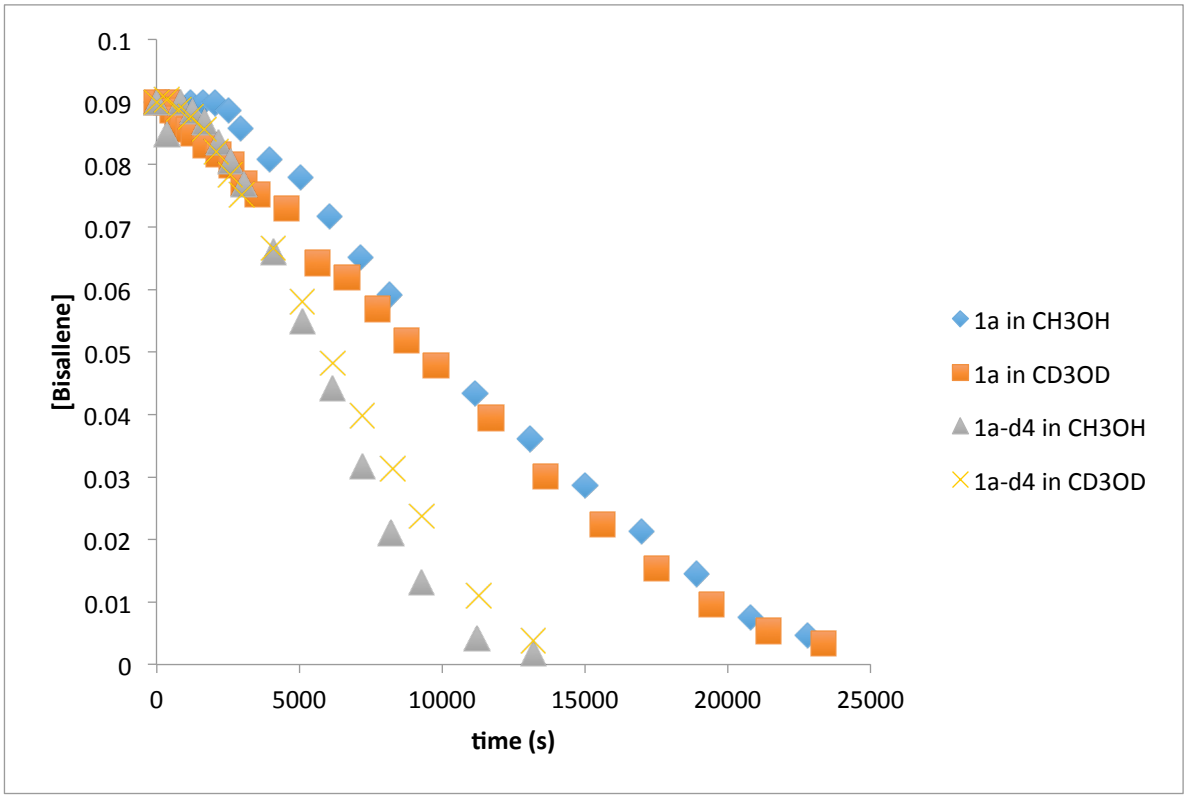


Figure 6.1. Analysis of the decay of bisallene **1a** in methanol

In contrast, the bisallene decay in water showed first order kinetics after the induction period, with the graph of ln[bisallene] *versus* time being a straight line. Similar behaviour was observed in D_2O (Figure 6.2).

$k_{H2O} = 2 \times 10^{-5}\ s^{-1}$

$k_{D2O} = 2 \times 10^{-5}\ s^{-1}$

$KIE_{H2O/D2O} = 1$

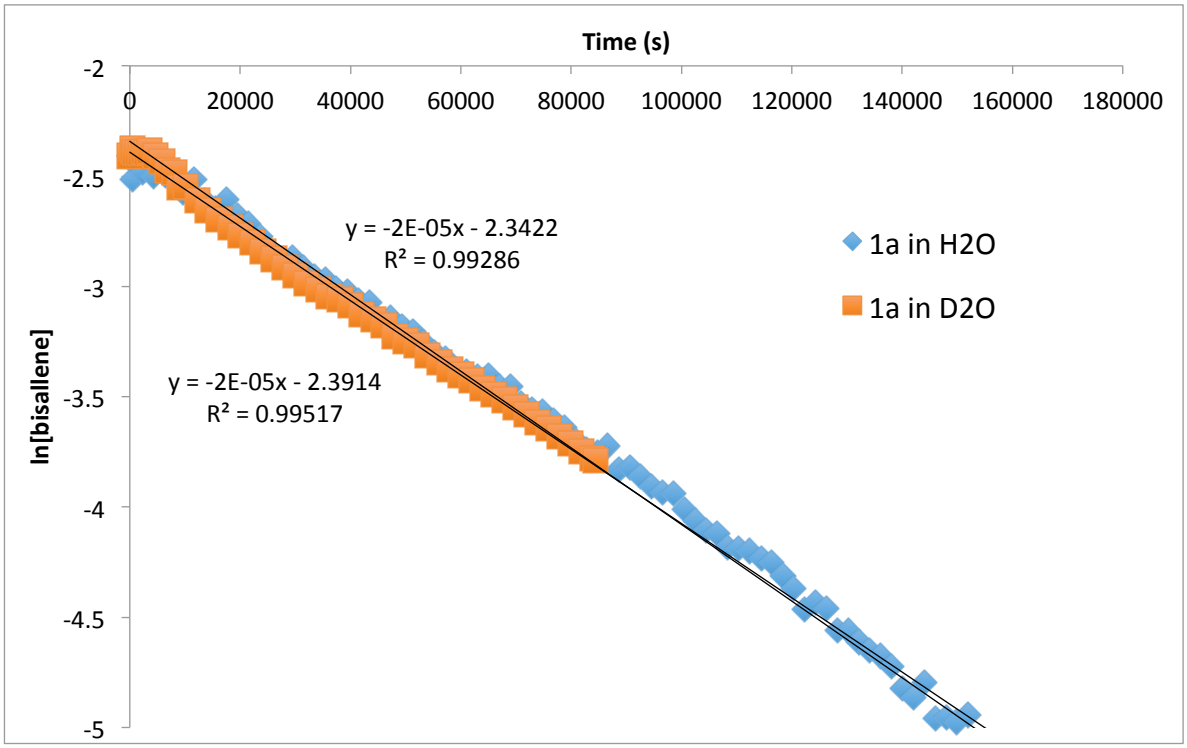


Figure 6.2. Analysis of the decay of bisallene **1a** in water

- Order in methanol

The order in methanol calculated using the intial rates was 1 for both products, triene **3aa** and cycle **4aa** (Figure 6.3).

Table 6.3. Initial rates for cycle **4aa** and triene **3aa** with different concentrations of CD_3OD.

[CD_3OD] (M)	*k*(4aa)	*k*(3aa)
4.09	$1.63\ 10^{-6}$	$3.54\ 10^{-6}$
2.045	$1.24\ 10^{-6}$	$1.49\ 10^{-6}$
1.543	$6.63\ 10^{-7}$	$1.05\ 10^{-6}$
1.23	$5.28\ 10^{-7}$	$9.57\ 10^{-7}$

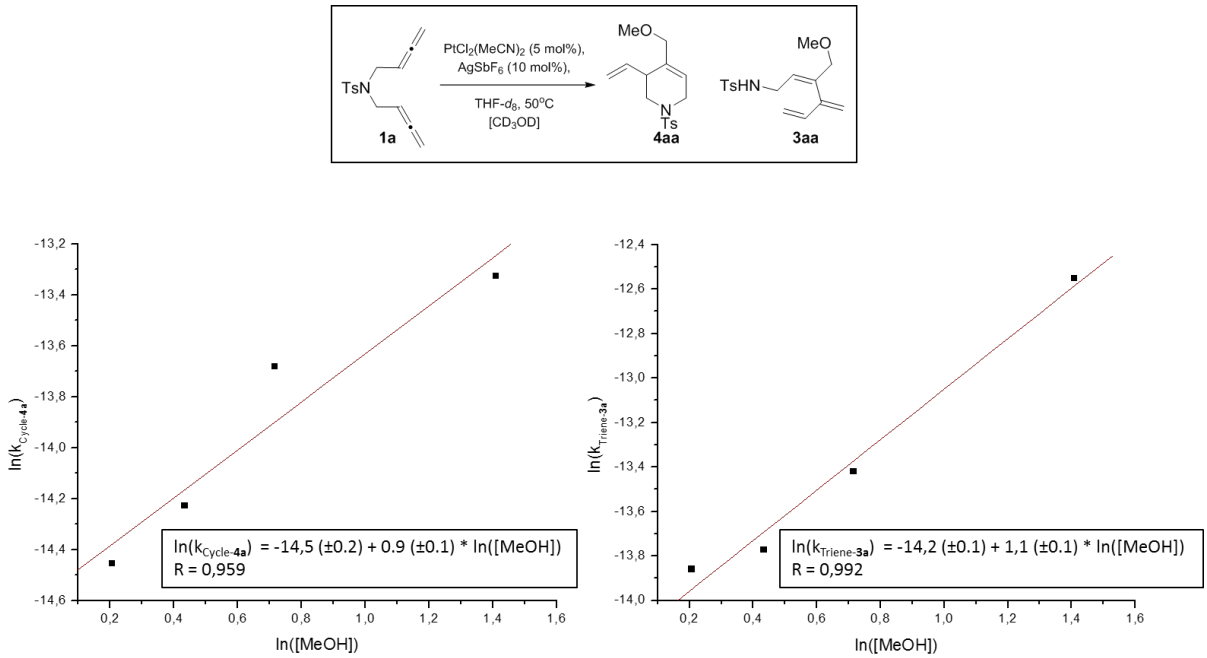


Figure 6.3. Order 1 in methanol for the different products formed in the platinum-catalyzed reaction of bisallene **1a** with CD_3OD.

- Order in platinum in methanol and in water

In the reaction with methanol as nucleophile, the order in platinum calculated using the intial rates after the induction period, was 1 for cycle **4aa**, but could not be determined for the formation of triene **3aa** (Table 6.4 and Figure 6.4a). Analysis of the order in platinum in the formation of triene **3aa** using the graphical method (with and without the induction period) did not give better results and non of the graphs plotting [triene] *versus* $[cat]_x$time, $[cat]^{0.5}{}_x$time or $[cat]^2{}_x$time gave a good fit, suggesting changes in the catalytic species in unknown ways or a fast catalysts deactivation process. This could also being explained by the complex equilibrium between the cationic platinum complexes, platinum-alkoxides, platinum-hydrides and platinum-di-hydrides as mentioned in the main text in reference 24. Several species might be catalytically active in the reaction. Therefore, assuming that the same concentration of active catalytis is formed in each condition has to be done with caution.

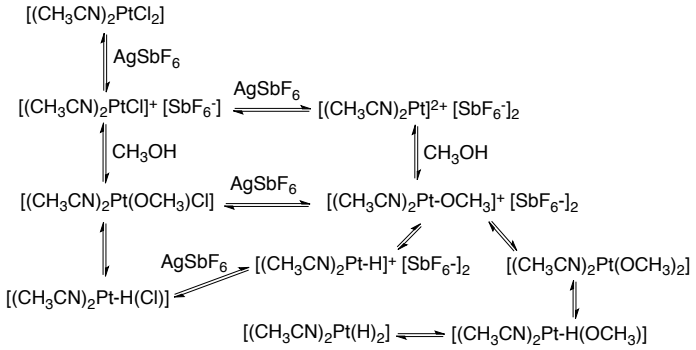
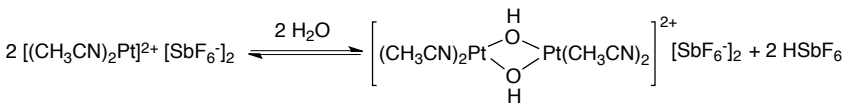


Table 6.4. Initial rates for the cycle **4aa** and the triene **3aa** with diferent concentrations of platinum

[Pt] (M)	*k*(4aa)	*k*(3aa)
$2.27\ 10^{-3}$	$6.15\ 10^{-7}$	$5.13\ 10^{-6}$
$4.55\ 10^{-3}$	$1.24\ 10^{-6}$	$1.49\ 10^{-6}$
$9.10\ 10^{-3}$	$2.73\ 10^{-6}$	$3.90\ 10^{-6}$
0.0182	$5.51\ 10^{-6}$	$2.19\ 10^{-6}$

In order to get good enough resolution in the ^{1}H NMR spectra, the kinetic measurements using H_2O were performed using THF-d_8:D_2O 5:1 at 50ºC. In these conditions we observed formation of a small amount of triene **3ad**. Data obtained for the formation of cycle **5ad** in the reaction with H_2O could not be analysed, due to the low concentration of this cycle.

In the reaction with water, the order in platinum was calculated using the initial rates method (Table 6.5 and Figure 6.4b) and the graphical method. Values obtained with the initial rates were lower than 1 for all the products, which suggests that the platinum could be involved in more than one process in a complex mechanism, supporting the involvement of an out-of-cycle process and different competing pathways as described in the main text. The order of platinum for the formation of cycle **6ad** was calculated to be 0.5 by the initial rates method and this also fitted the graphical method, which would indicate that the catalysts exists as an inactive dimmer as mentioned in reference 18 in the main text.[7]



7 G. W. Bushnell, K. R. Dixon, R. G. Hunter and J. J. McFarland, *Can. J. Chem.*, 1972, **50**, 3694.

Table 6.5. Initial rates for cycle **6ad** with diferent concentrations of platinum

[Pt] (M)	*k*(6ad)
$4.55\ 10^{-3}$	$8.70\ 10^{-7}$
$9.10\ 10^{-3}$	$1.07\ 10^{-6}$
0.0137	$1.21\ 10^{-6}$
0.0182	$1.51\ 10^{-6}$
0.0455	$2.76\ 10^{-6}$

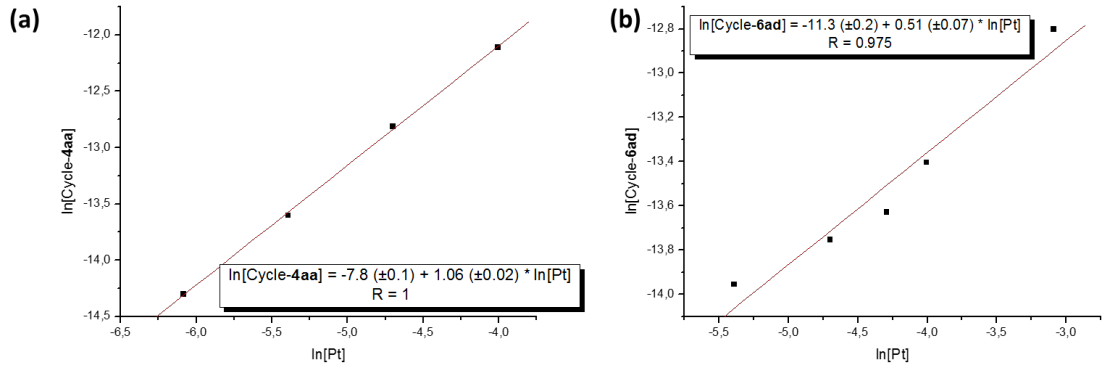


Figure 6.4. Order in platinum for the different products formed in the platinum catalyzed reaction of bisallene **1a** with MeOH (a) and water (b).

7) Hammett analysis

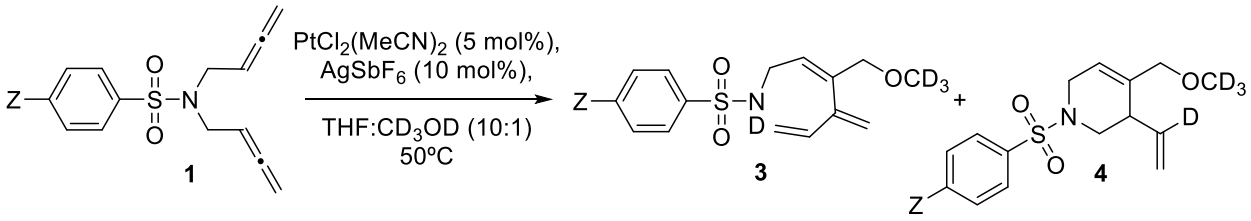
- Reaction in methanol

We performed a Hammett analysis for the products of the reactions of 1,5-bisallenes in CD_3OD with substituents with different electronic properties in the *para*- position of the $PhSO_2N$- group (Figure 7.1). The Hammett plot showed a change of the sign of the slope, with a concave shape, when going from EDG to EWG. This suggests that different mechanisms are operating depending on the electronic properties of the tethers in bisallenes **1**.[8]

8 a) J. O. Schreck, *J. Chem. Ed.*, 1971, **48**, 103; b) H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191; c) L. P. Hammett, *J. Am. Chem. Soc.*, 1937, **59**, 96.

Supporting Information

Table 7.1. Initial rates for trienes **3** and cycles **4** with bisallenes **1** with different *para*-substituents.



Bisallene 1, Z	k(3)	k(4)	σ(para)	Log(k_Z/k_H) Triene 3	Log(k_Z/k_H) Cycle 4
1c, OCH_3	$1.86\ 10^{-6}$	$2.36\ 10^{-6}$	-0,27	0,768	0,27
1a, CH_3	$1.24\ 10^{-6}$	$1.48\ 10^{-6}$	-0,17	0,591	0,069
1b, H	$3.17\ 10^{-7}$	$1.27\ 10^{-6}$	0	0	0
1d, Cl	$5.22\ 10^{-7}$	$1.65\ 10^{-6}$	0,23	0,216	0,116
1e, CF_3	--	$2.08\ 10^{-6}$	0,54	--	0,215
1f, NO_2	--	$4.00\ 10^{-6}$	0,78	--	0,5

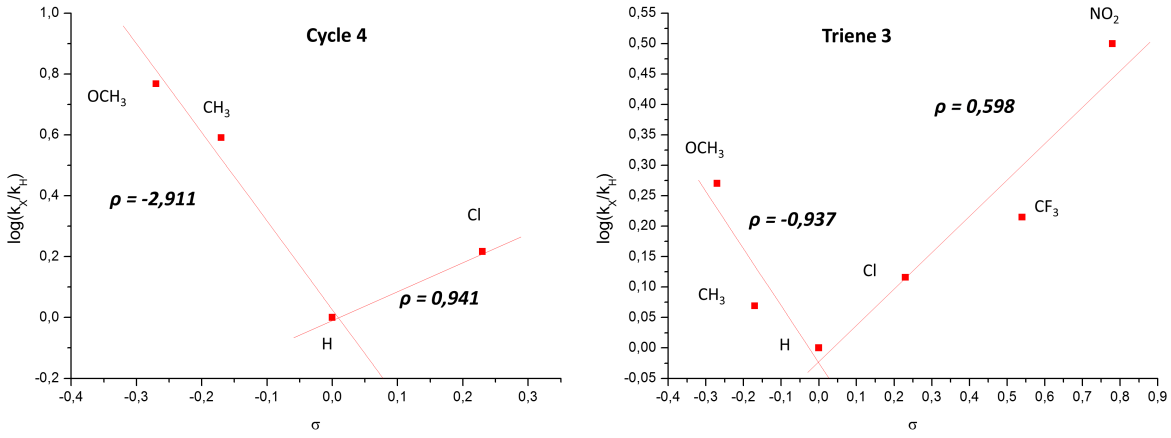


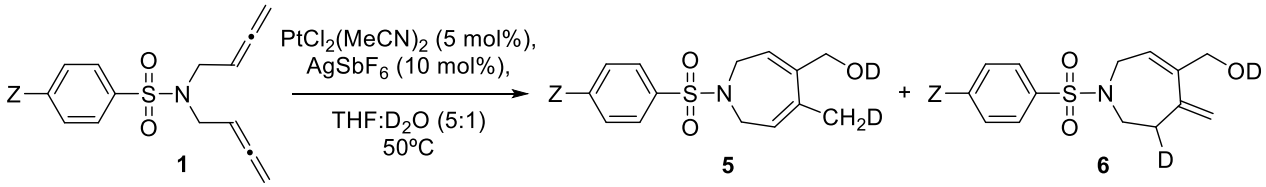
Figure 7.1. Hammett plots for the reaction with CD_3OD.

- Reaction in water

The Hammett plot also showed a change of the sign of the slope, with a concave shape, when going from EDG to EWG in the reactions of 1,5-bisallenes in D_2O (Figure 7.2).

Supporting Information

Table 7.2. Initial rates for cycles **5** and **6** with bisallenes **1** with different para-substituents.



Bisallene 1, Z	k(9)	k(10)	σ(para)	Log(k_Z/k_H) Cycle 5	Log(k_Z/k_H) Cycle 6
1c, CH_3O	$2{,}53\ 10^{-7}$	$1{,}03\ 10^{-6}$	-0,27	0,529	0,410
1a, CH_3	$2{,}13\ 10^{-7}$	$7{,}00\ 10^{-7}$	-0,17	0,454	0,243
1b, H	$7{,}48\ 10^{-8}$	$4{,}00\ 10^{-7}$	0	0	0
1d, Cl	$9{,}25\ 10^{-8}$	$6{,}39\ 10^{-7}$	0,23	0,092	0,204
1e, CF_3	$2{,}14\ 10^{-7}$	$7{,}24\ 10^{-7}$	0,54	0,457	0,258
1f, NO_2	$2{,}49\ 10^{-7}$	$8{,}56\ 10^{-7}$	0,78	0,521	0,330

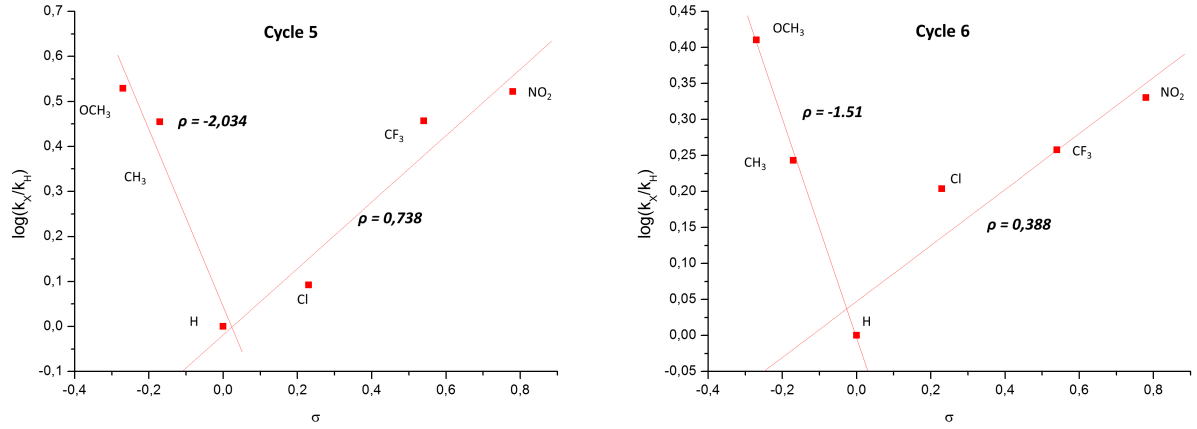


Figure 7.2. Hammett plots for the reaction with D_2O.

- Analysis of the ratio of cycles 6 and 5

Analysis of the ratio of cycles **6** and **5** during the reaction and after complete consumption of the bisallene showed no change, suggesting that these two cycles do not intercovert between them once formed. Besides, deuterium experiments did not show deuterium scramble between the allylic positions, suggesting irreversible protodemetalation and that, if an equilibrium takes place, it has to be between the intermediates, and not the final products. The analysis of Hammett constants *vs* log(ratio **6**:**5**) was linear with a slight negative slope ($\rho = -0.17$),[9] which supports this equilibrium between the π-allyl Pt intermediates **17** and **16** (see Scheme 5 in main text), and indicates the equilibrium is favoured toward intermediate **17** with EDG and toward **16** with EWG.

Table 7.3. Data of log(ratio **6:5**) with bisallenes **1** with different para-substituents.

Bisallene 1, Z	σ	ratio 6:5	log(ratio 6:5)
1b, H	0	7.8	0.892094603
1a, CH_3	-0.17	9.8	0.991226076
1d, Cl	0.23	7.6	0.880813592
1c, CH_3O	-0.27	10	1
1f, NO_2	0.78	5.9	0.770852012
1e, CF_3	0.54	8.5	0.929418926

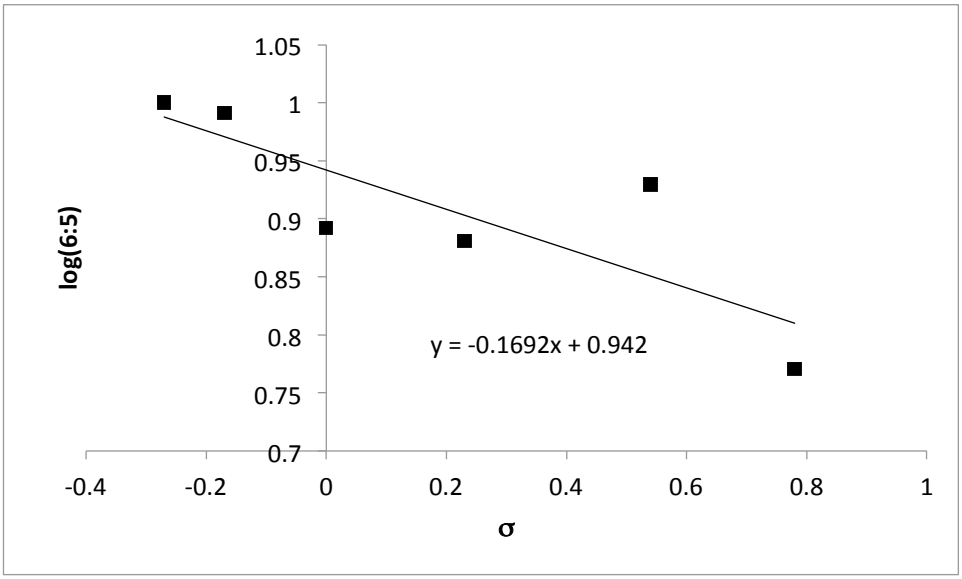


Figure 7.3. Plots of log(ratio **6:5**) versus the Hammett constants for the different biallenes **1**.

9 Q. Qiao, S.-S. So, R. A. Goodnow, Jr., *Org. Lett.* **2001**, *3*, 3655.

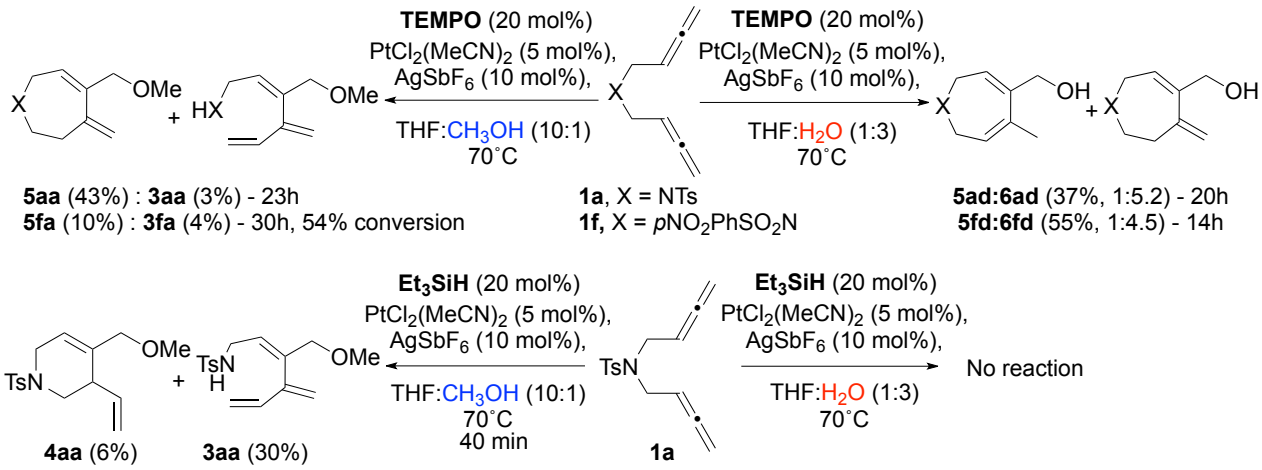
Supporting Information

8) Experiments with TEMPO and Et_3SiH

We performed the reaction in the presence of 20 mol% of TEMPO, which has been reported to inhibit the formation of metal hydrides (Scheme 8.1).

The reaction of bisallene **1a** with water in the presence of TEMPO led to the seven membered cycles in a similar way than when no TEMPO was present, ruling out Pt-H as the active species in the formation of the cycloheptadienes. On the contrary, the reaction of the same bisallene with methanol in the presence of TEMPO led to the formation of triene **3aa** and the seven membered cycle **5fa**, which wasn't observed with the normal reaction conditions, inhibiting the formation of 6-membered cycles **4**.

On the other hand, experiments in the presence of a silane, which favours the formation of metal hydrides, were performed. In the experiment using water as a nucleophile we recovered the starting material with no traces of other products. However, the experiment with methanol led to the formation of triene **3aa** and cycle **4aa**, as in the normal reaction conditions, although with different yields. These results suggest that platinum hydrides could be indeed active species in the reaction with methanol.



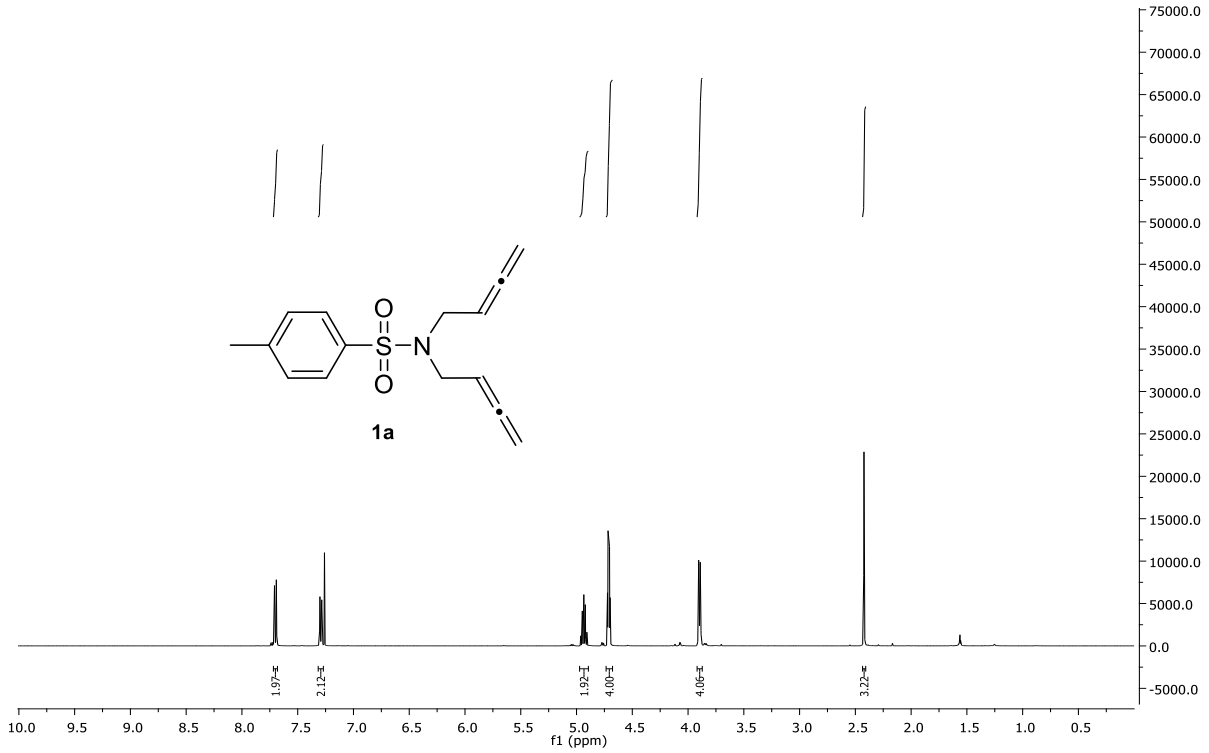
Scheme 8.1. Experiments with TEMPO and Et_3SiH to study the presence of platinum hydrides in the reaction.

Supporting Information

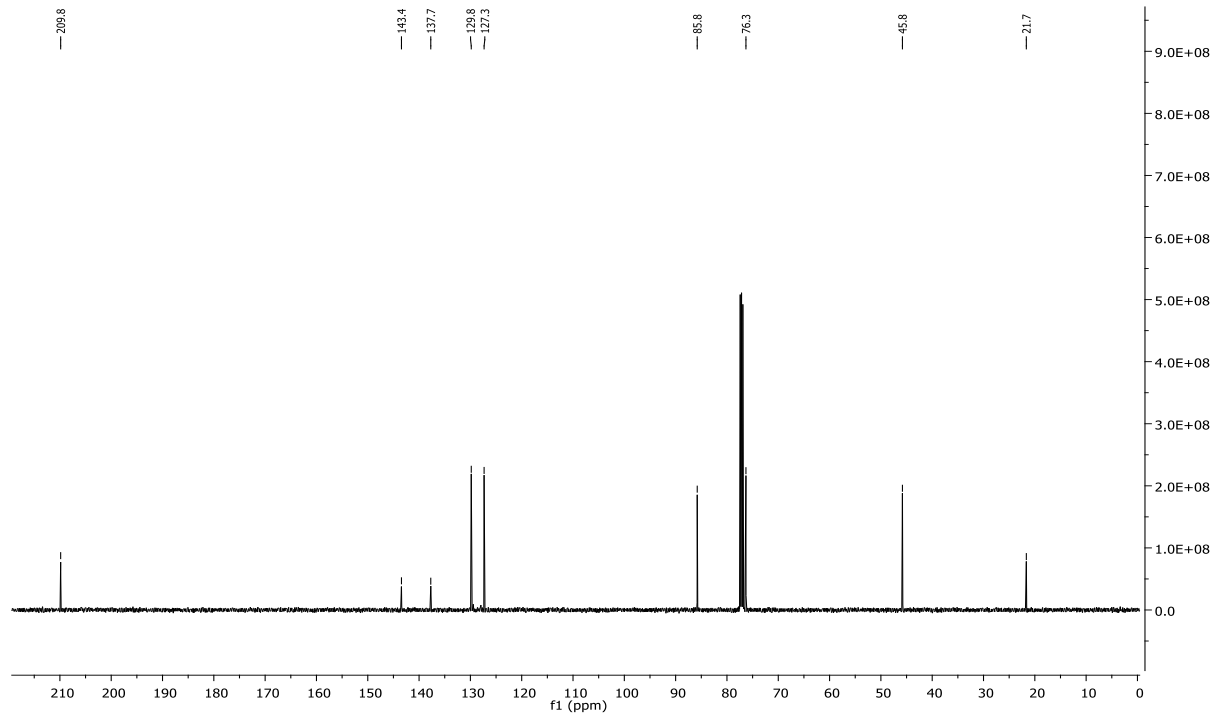
9) NMR Spectra

N,*N*-Di-buta-2,3-dienyl-4-methyl-benzenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

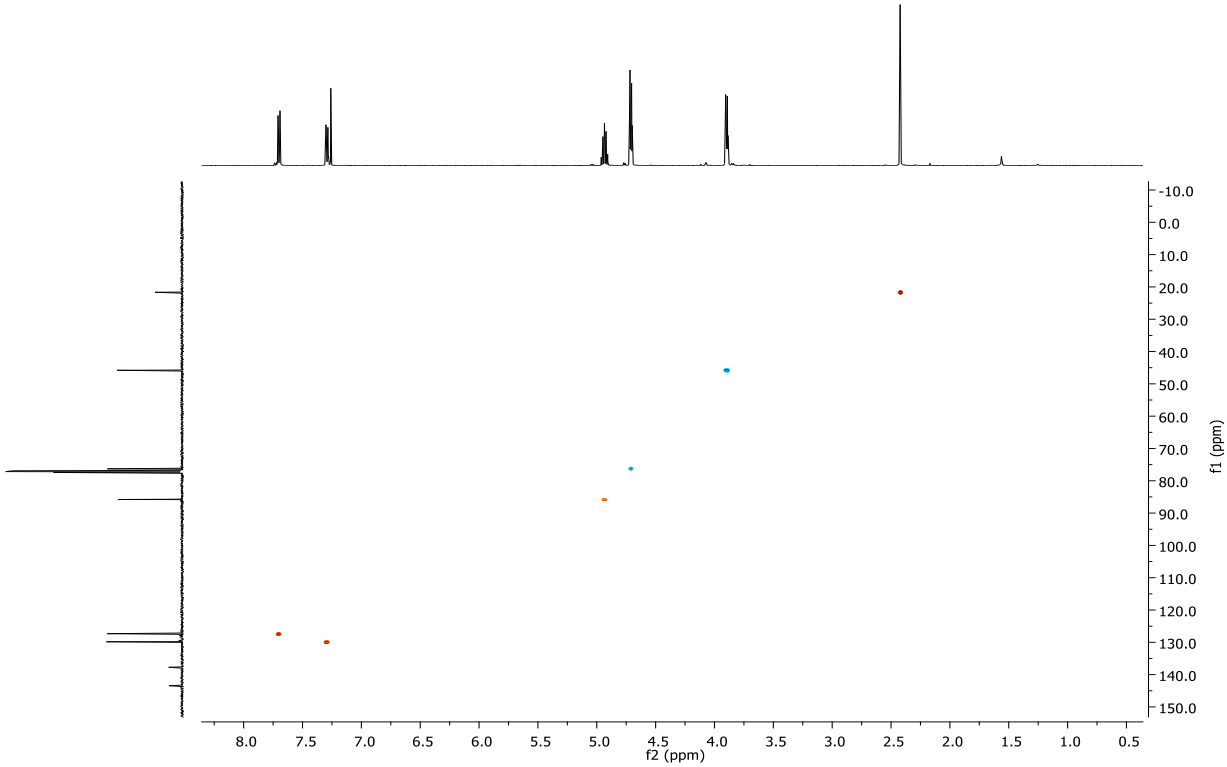


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

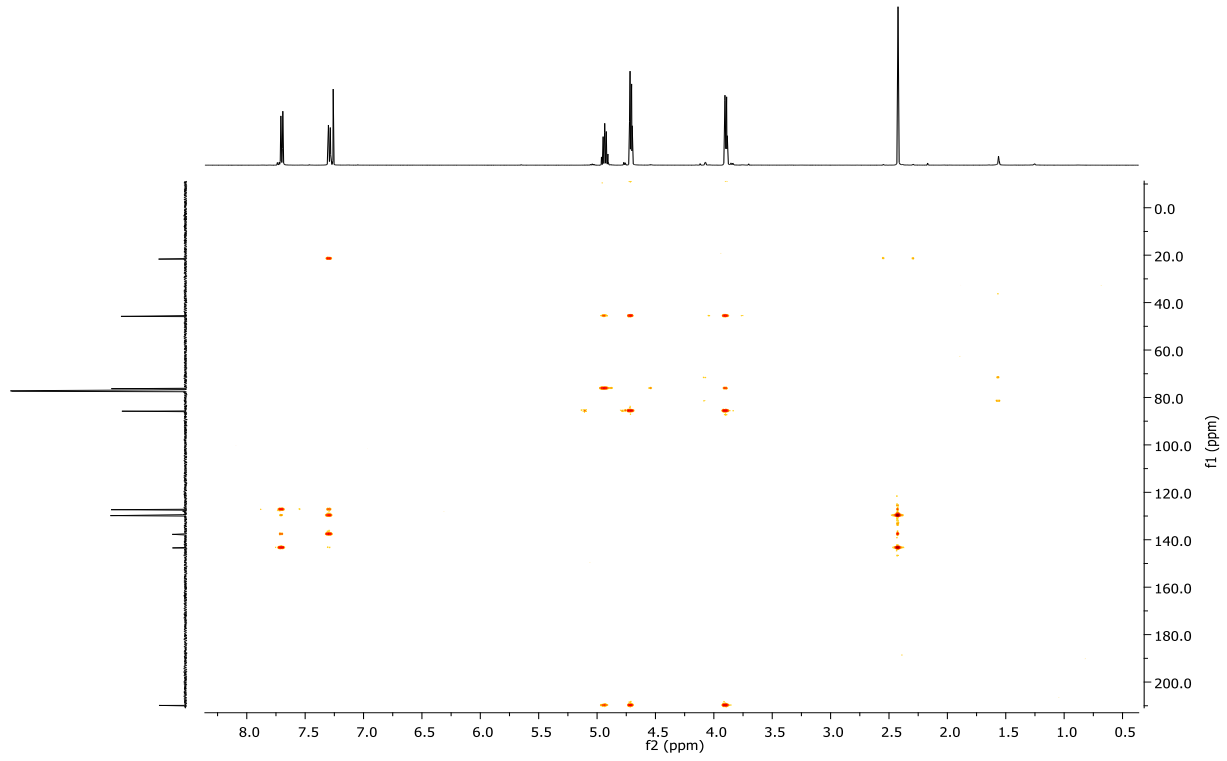


Supporting Information

2D HSQC ($CDCl_3$)



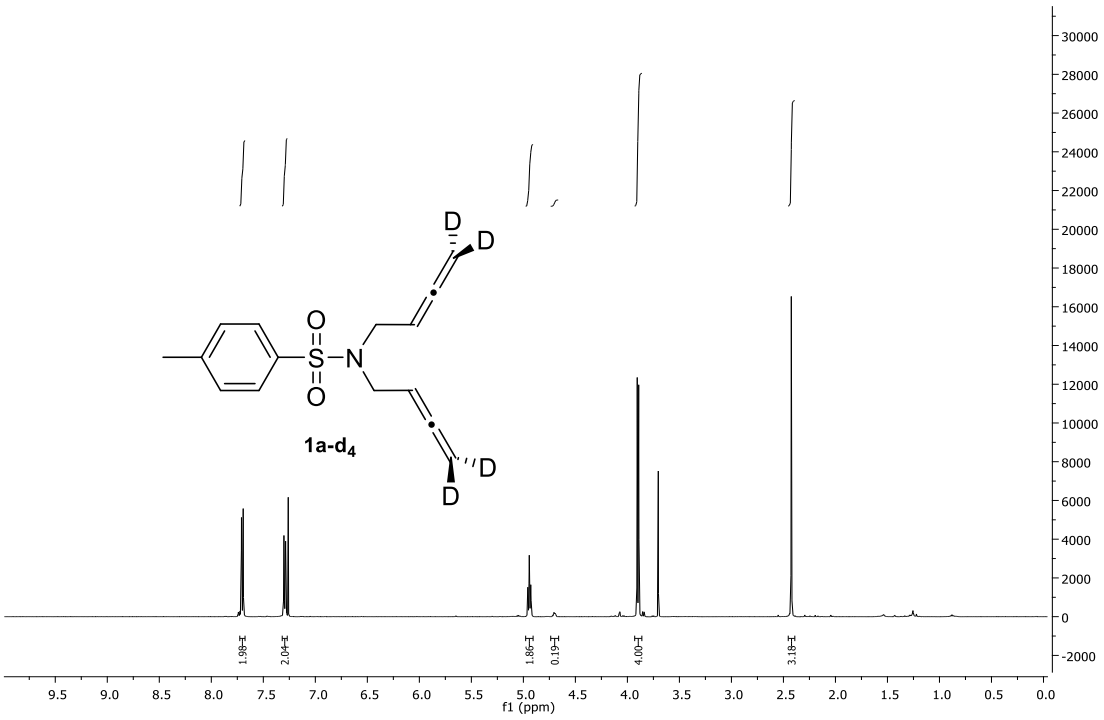
2D HMBC ($CDCl_3$)



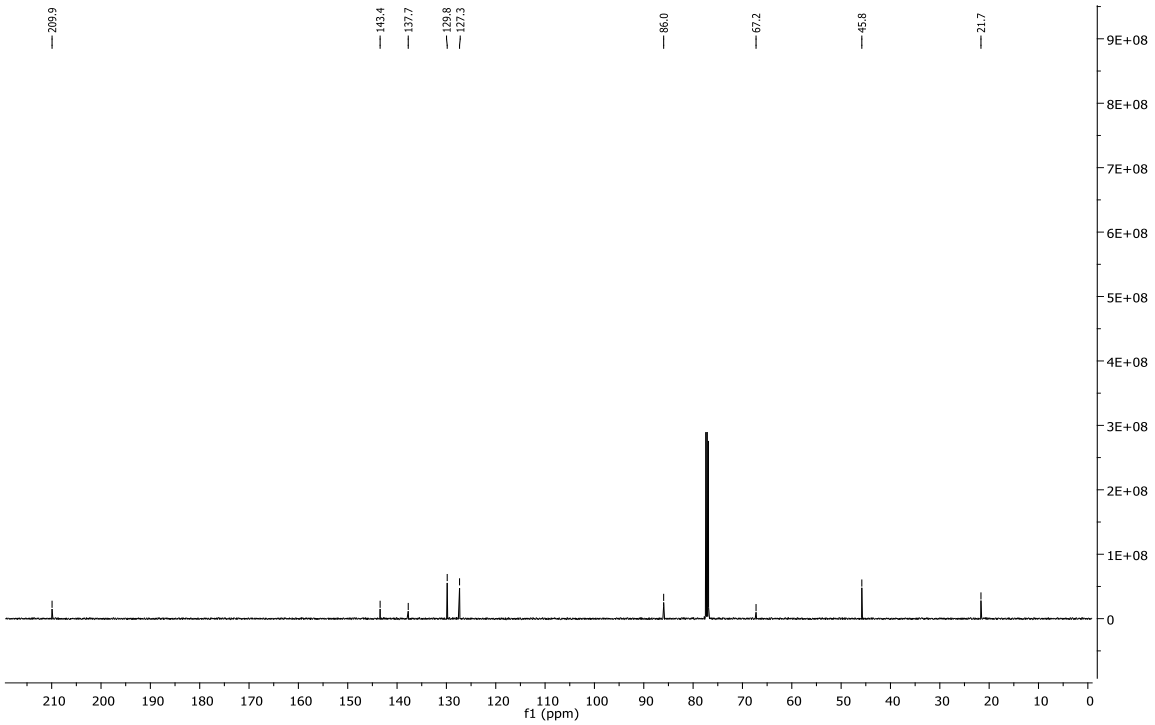
Supporting Information

N,*N*-Di-buta-2,3-dienyl-4-methyl-benzenesulfonamide-d^4

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

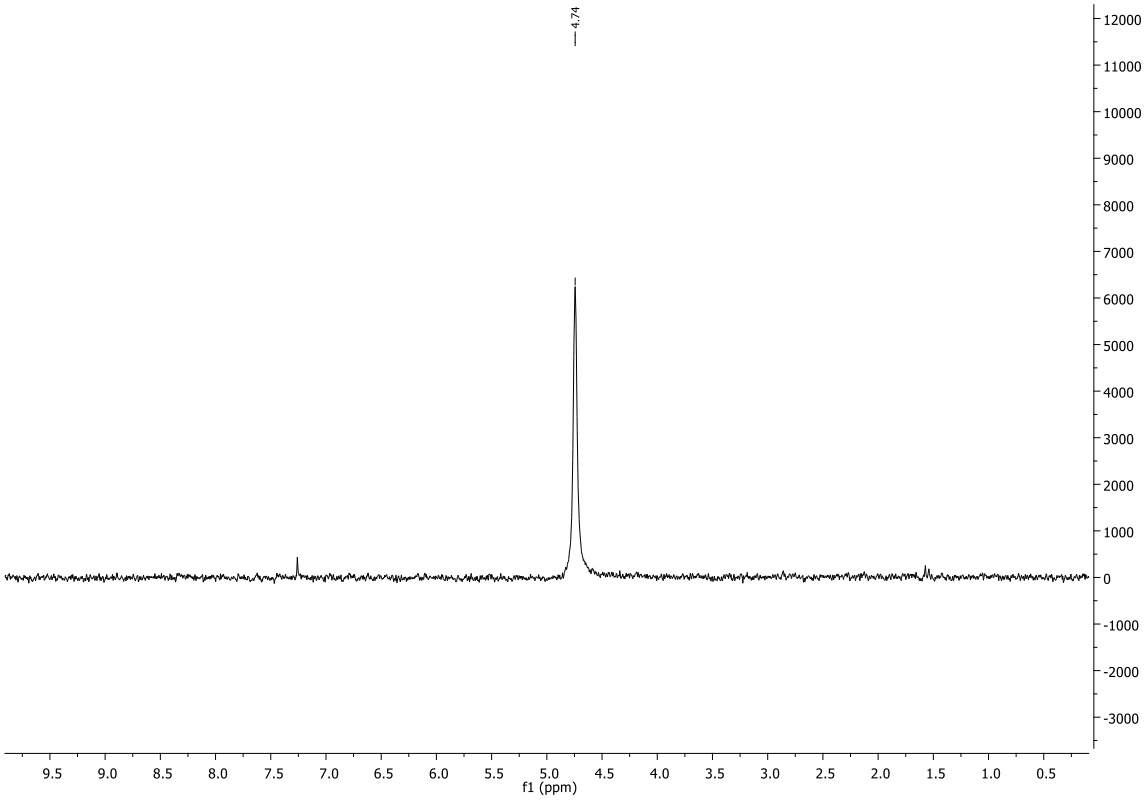


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

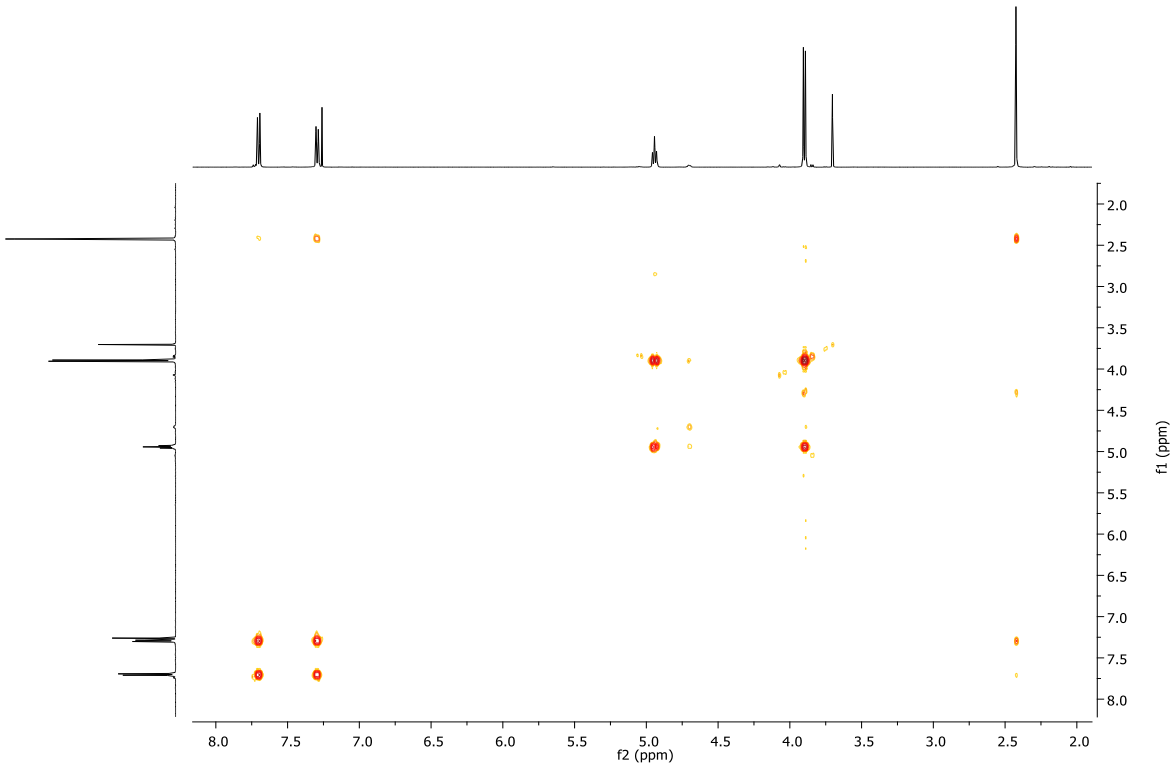


Supporting Information

^{2}H NMR (77 MHz, $CDCl_3$)



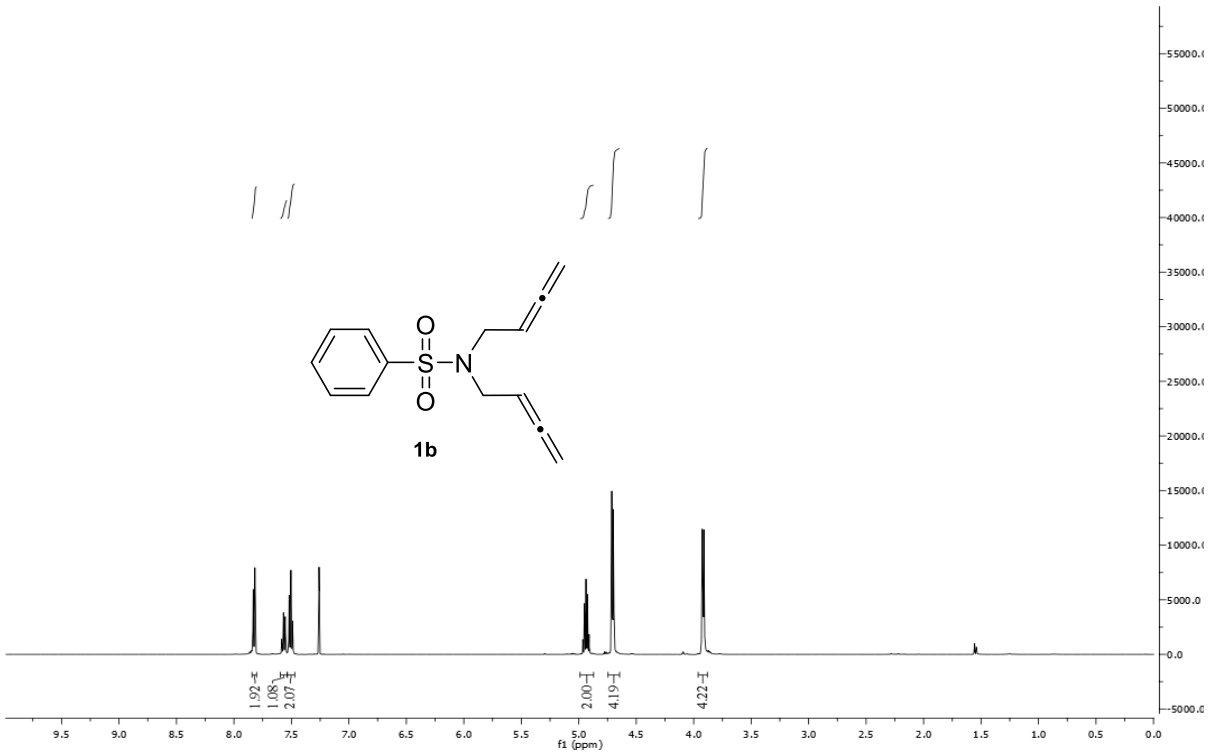
2D gCOSY ($CDCl_3$):



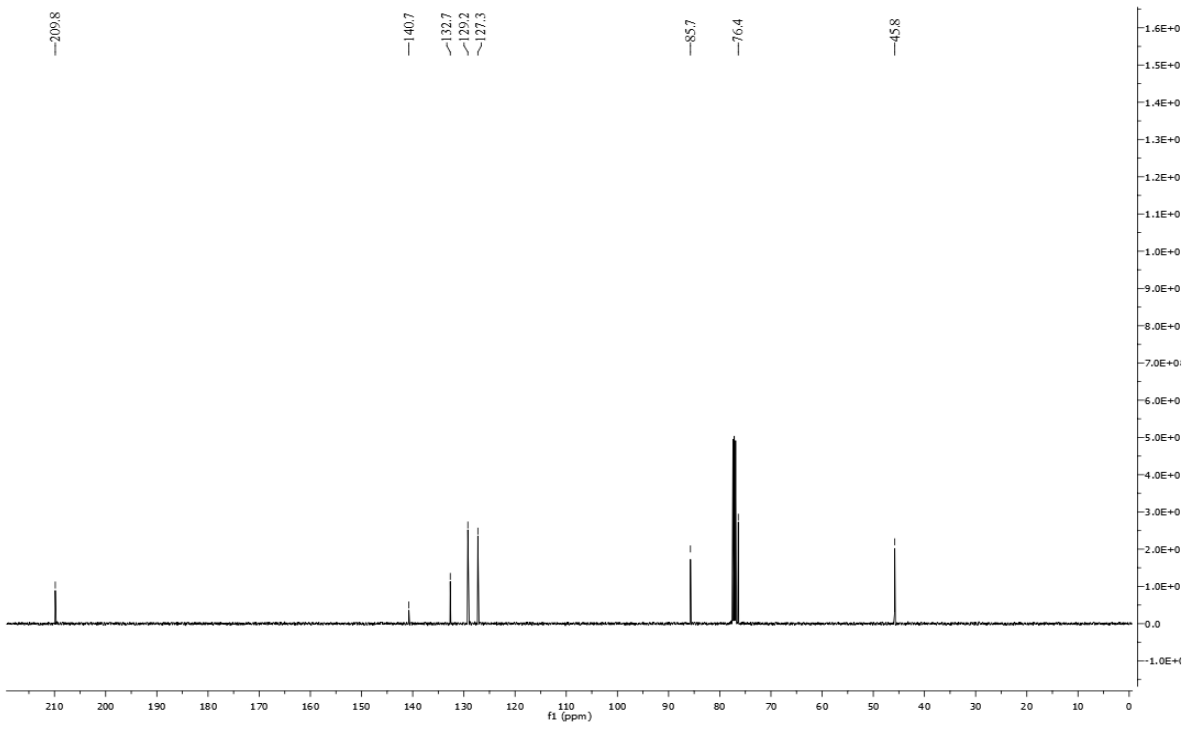
Supporting Information

N,*N*-Di-buta-2,3-dienyl-benzenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)



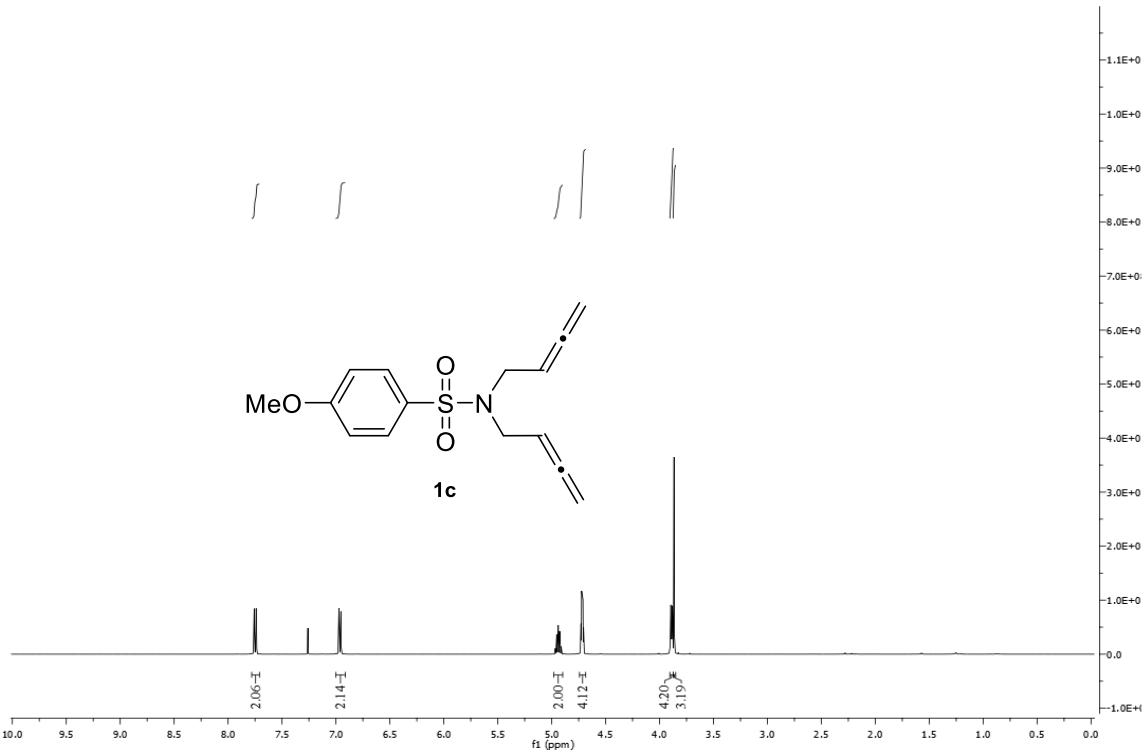
^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



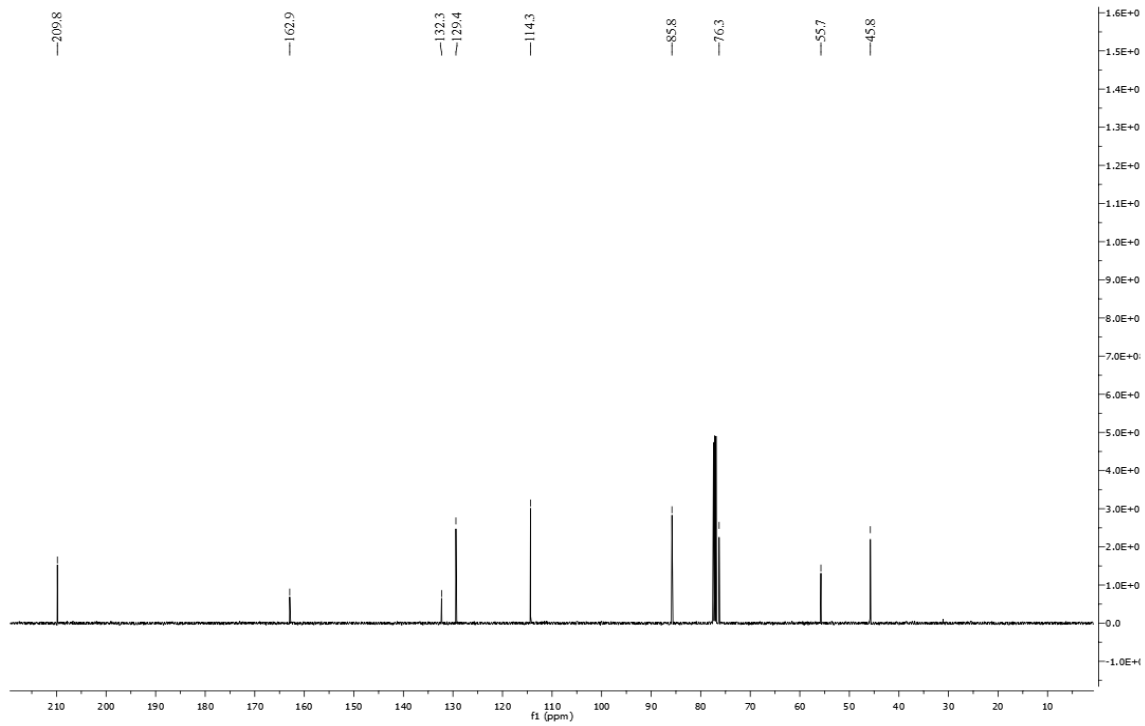
Supporting Information

N,*N*-Di-buta-2,3-dienyl-4-methoxy-benzenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)



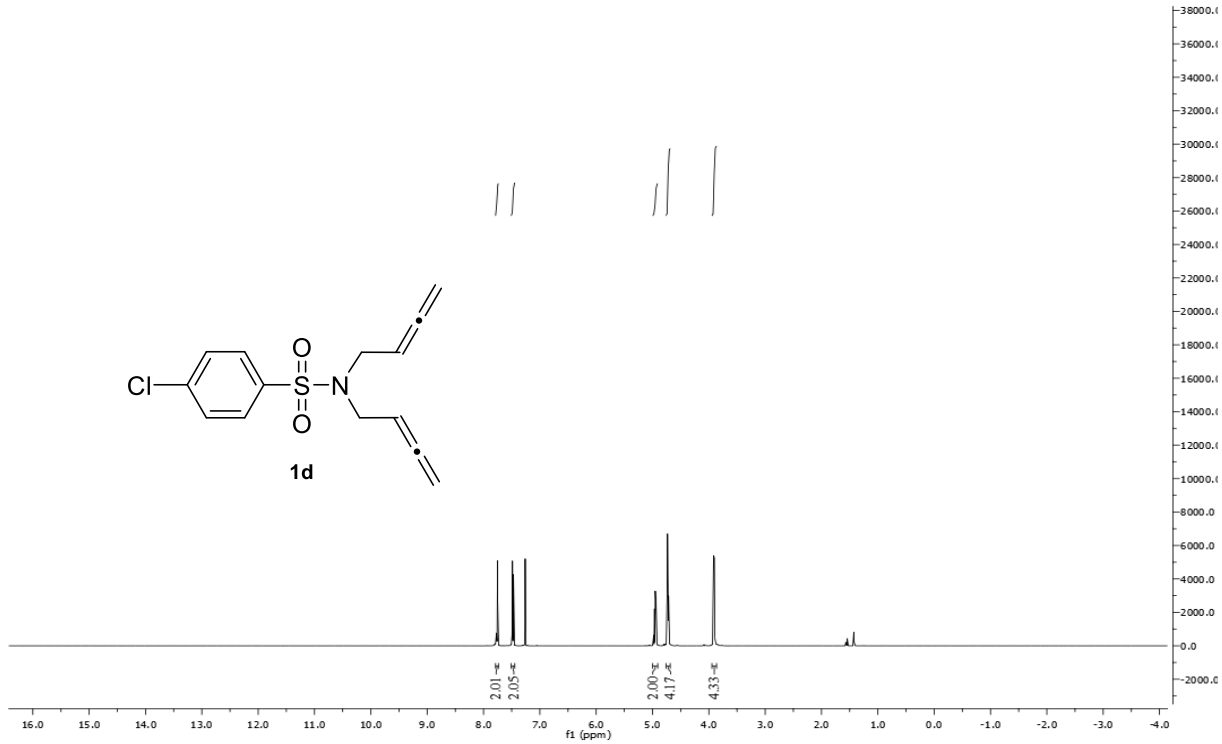
^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



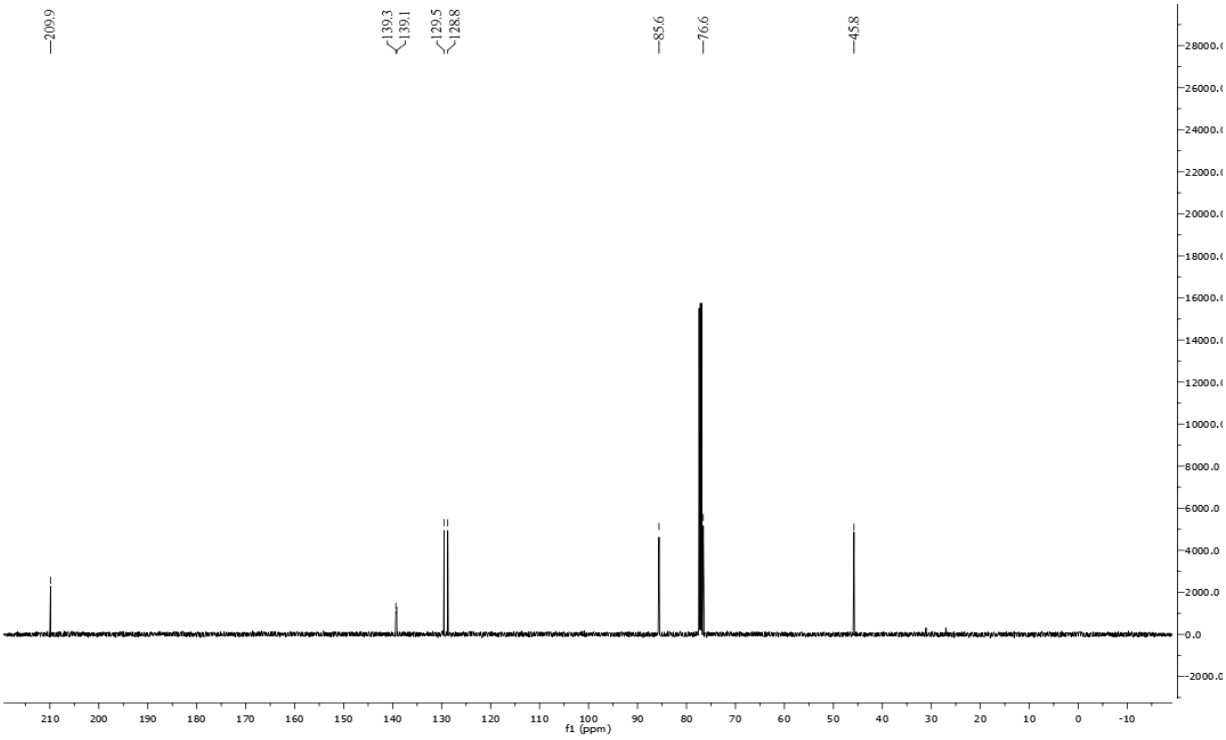
Supporting Information

N,*N*-Di-buta-2,3-dienyl-4-chloro-benzenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)



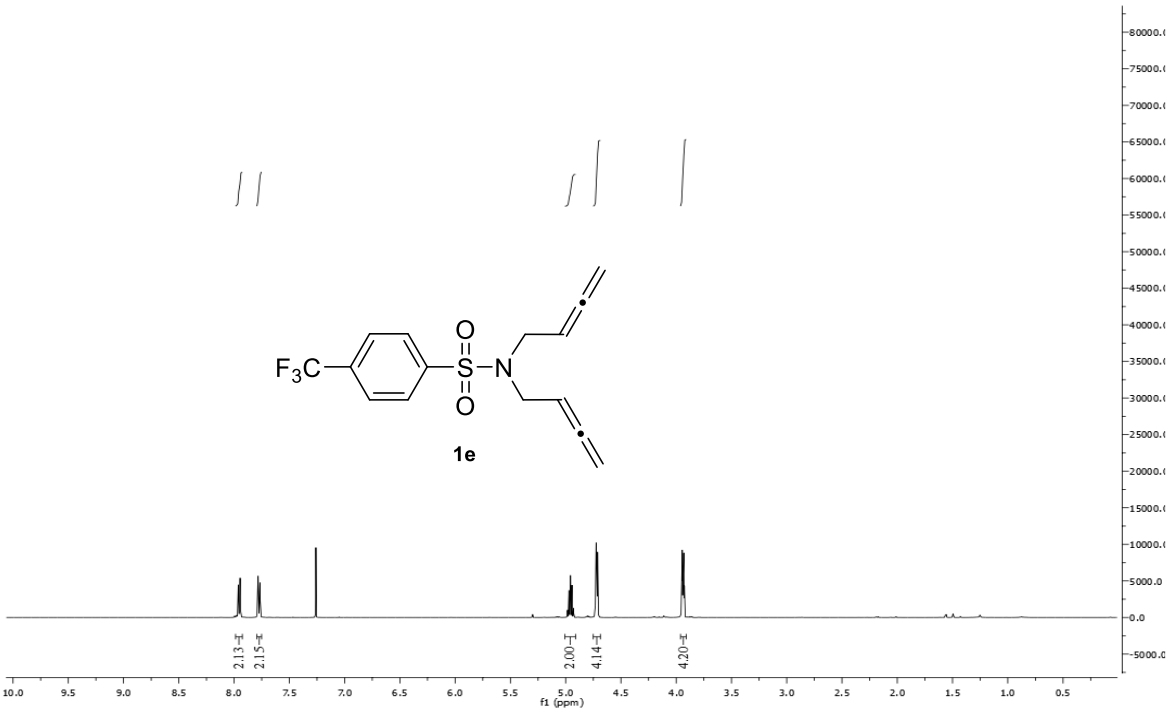
^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



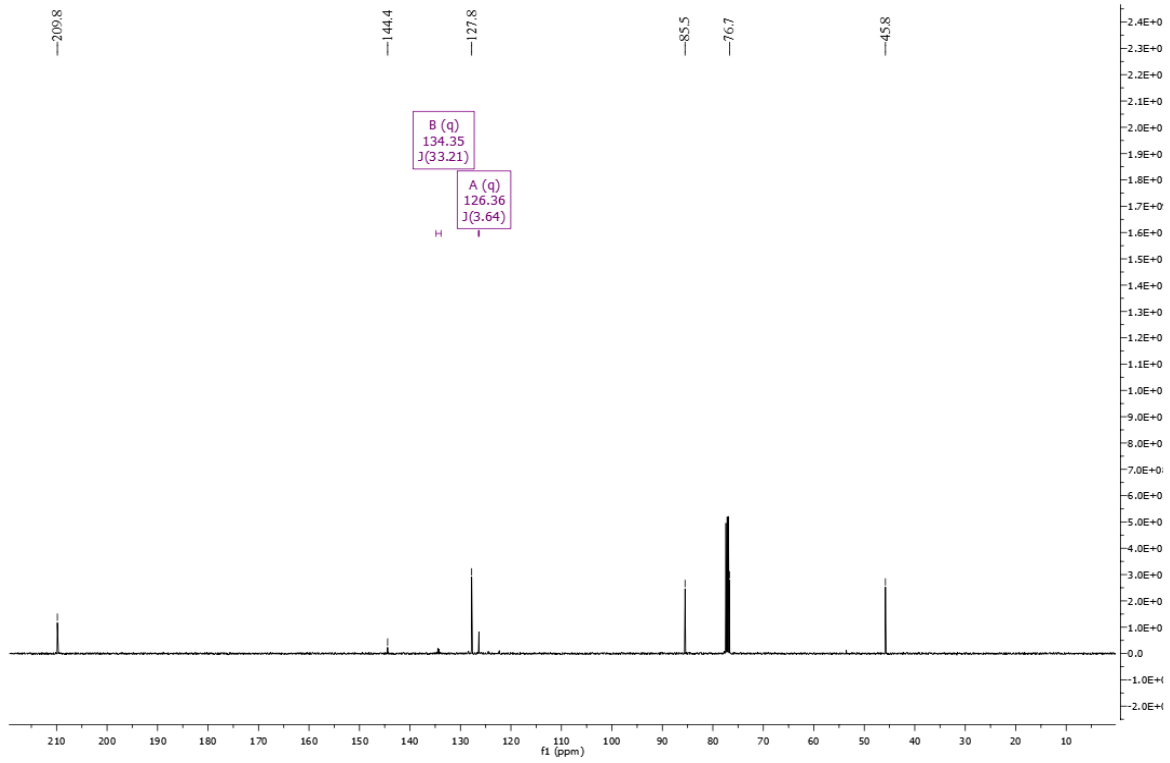
Supporting Information

N,*N*-Di-buta-2,3-dienyl-4-trifluoromethyl-benzenesulfonamide

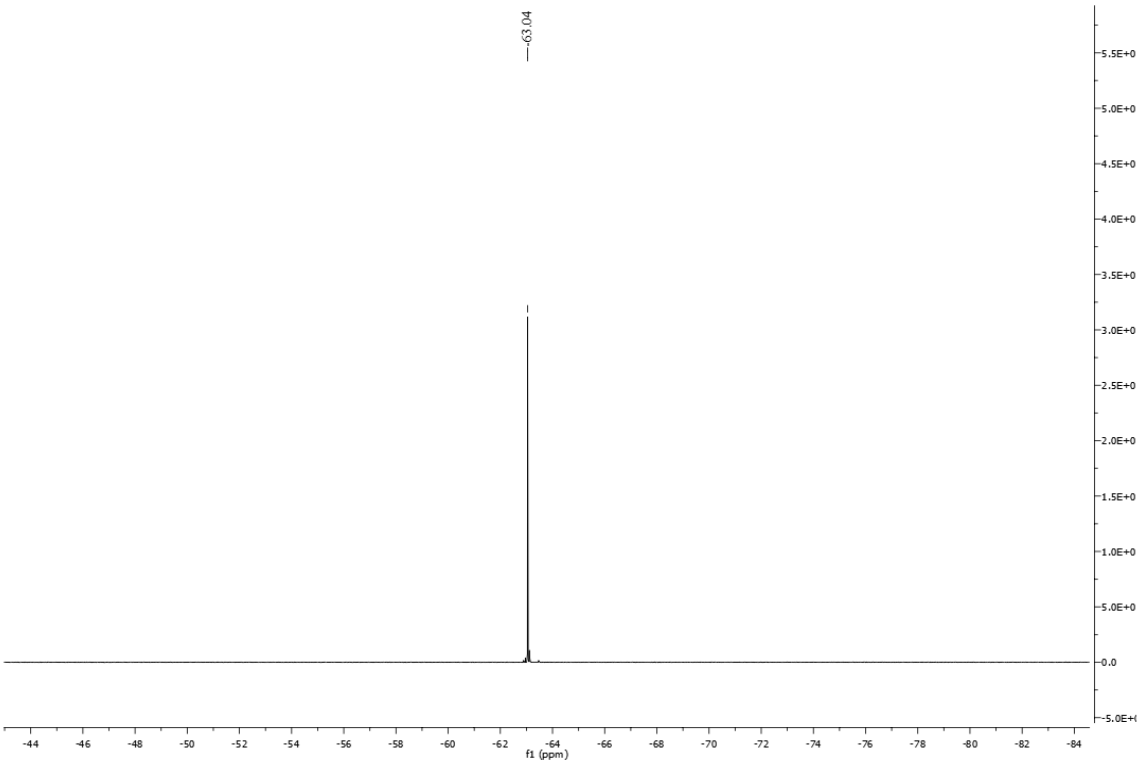
^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)



^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



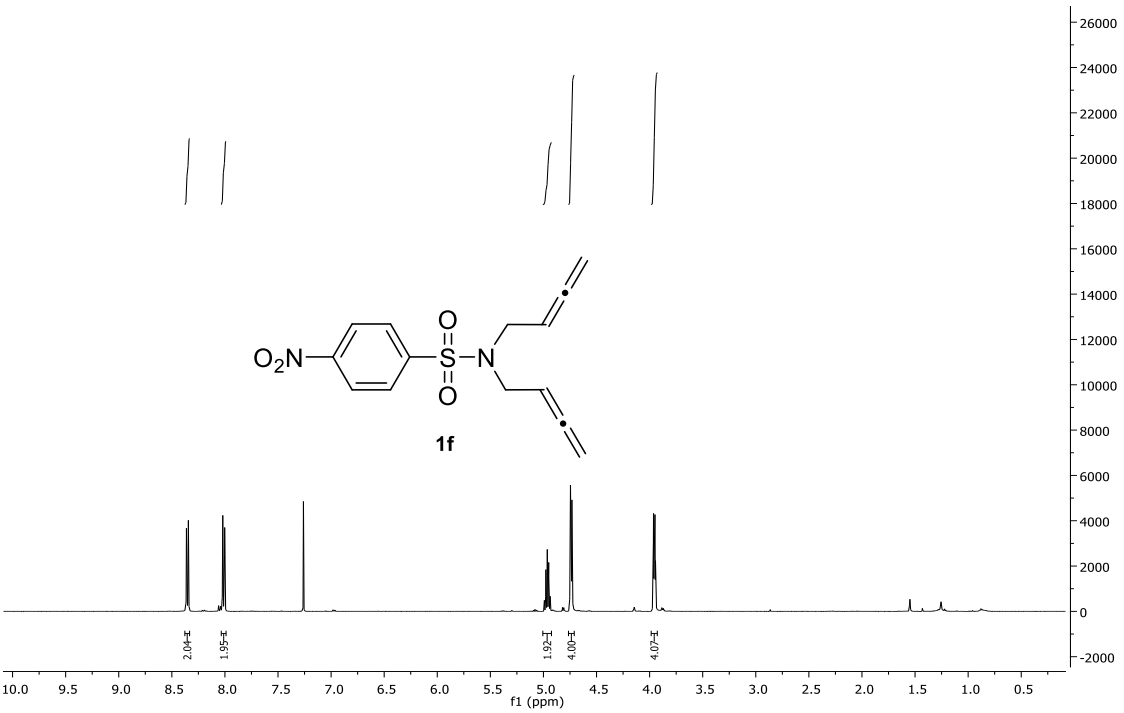
^{19}F NMR (471 MHz, $CDCl_3$)



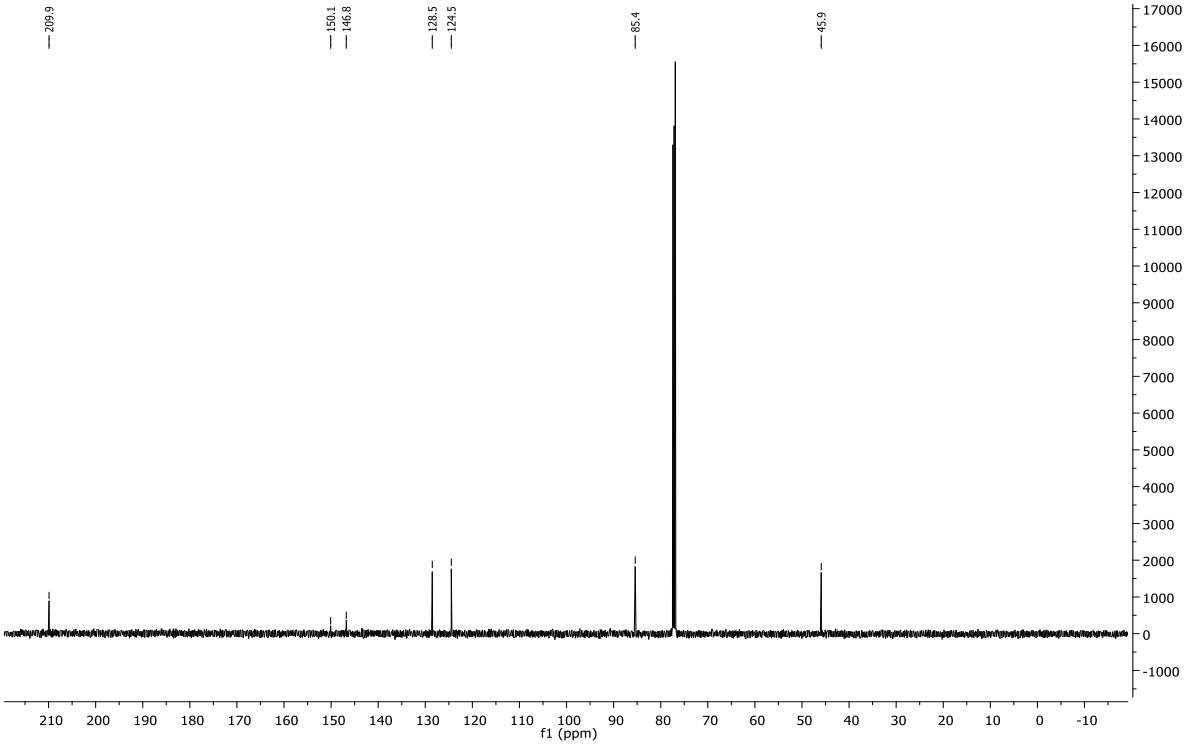
Supporting Information

N,*N*-Di-buta-2,3-dienyl-4-nitro-benzenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)



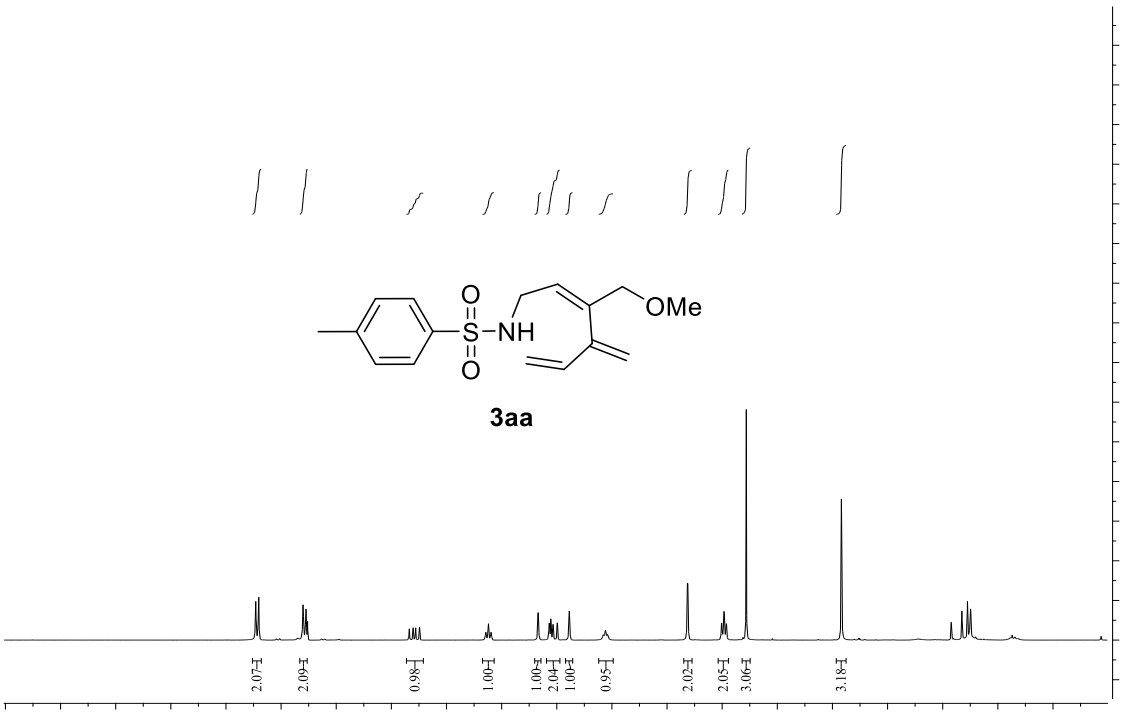
^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



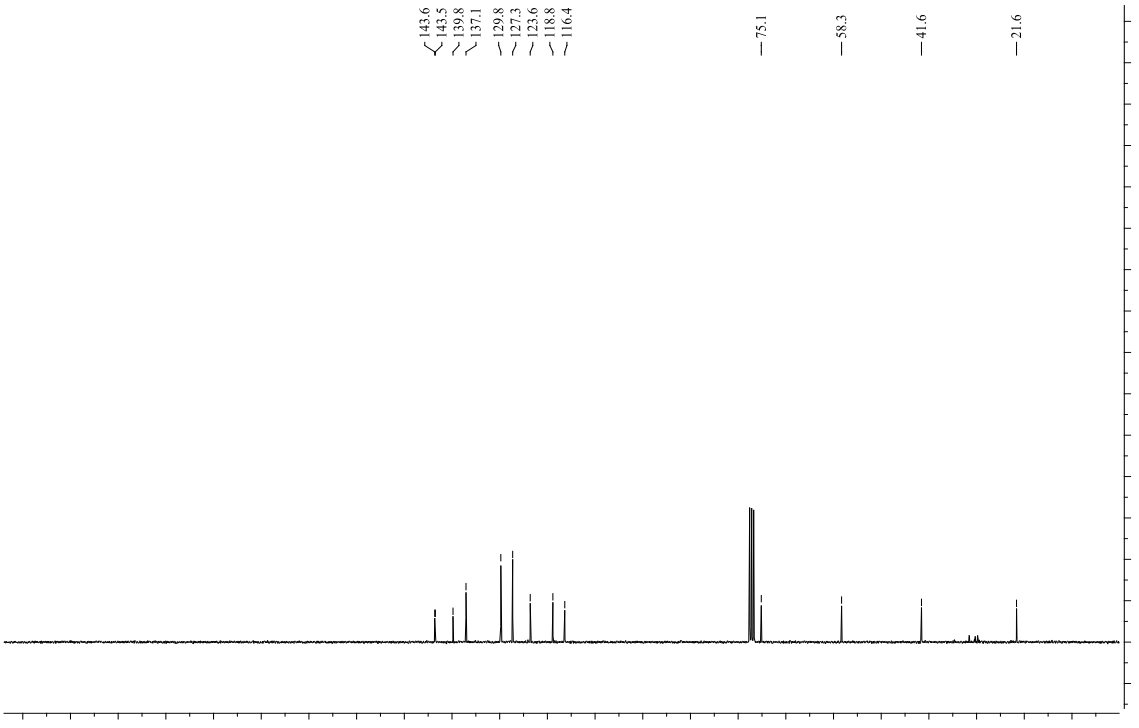
Supporting Information

***N*-(3-Methoxymethyl-4-methylene-hexa-2,5-dienyl)-4-methyl benzenesulfonamide**

^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C)

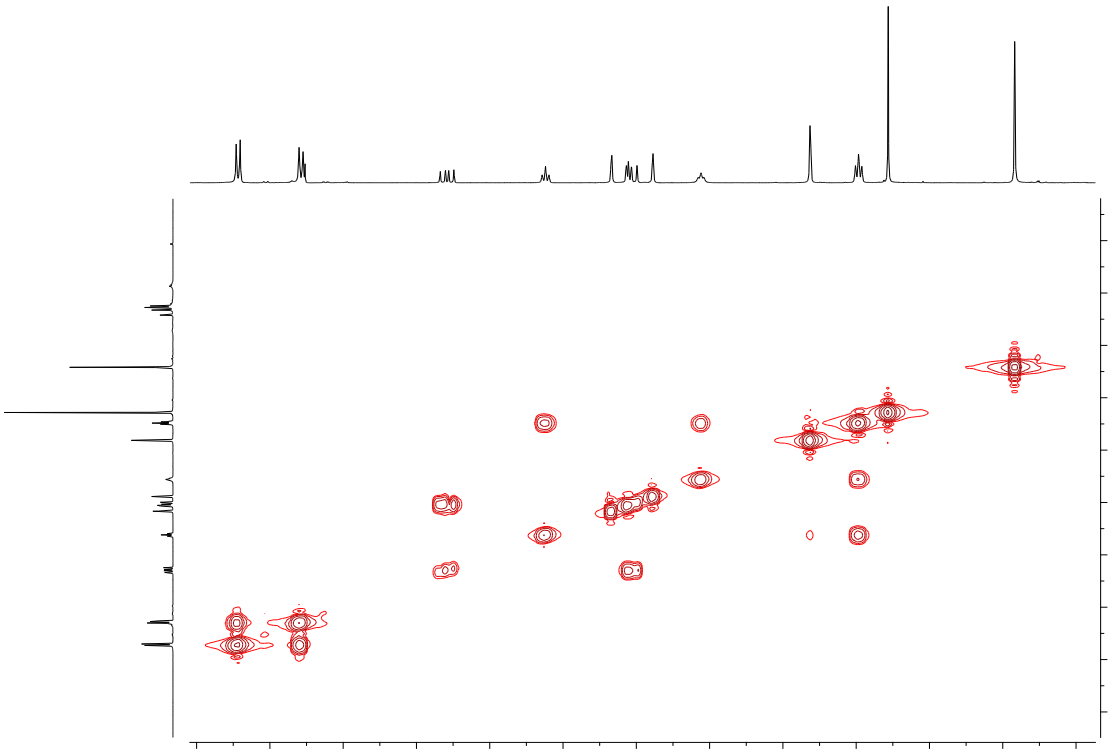


^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C)

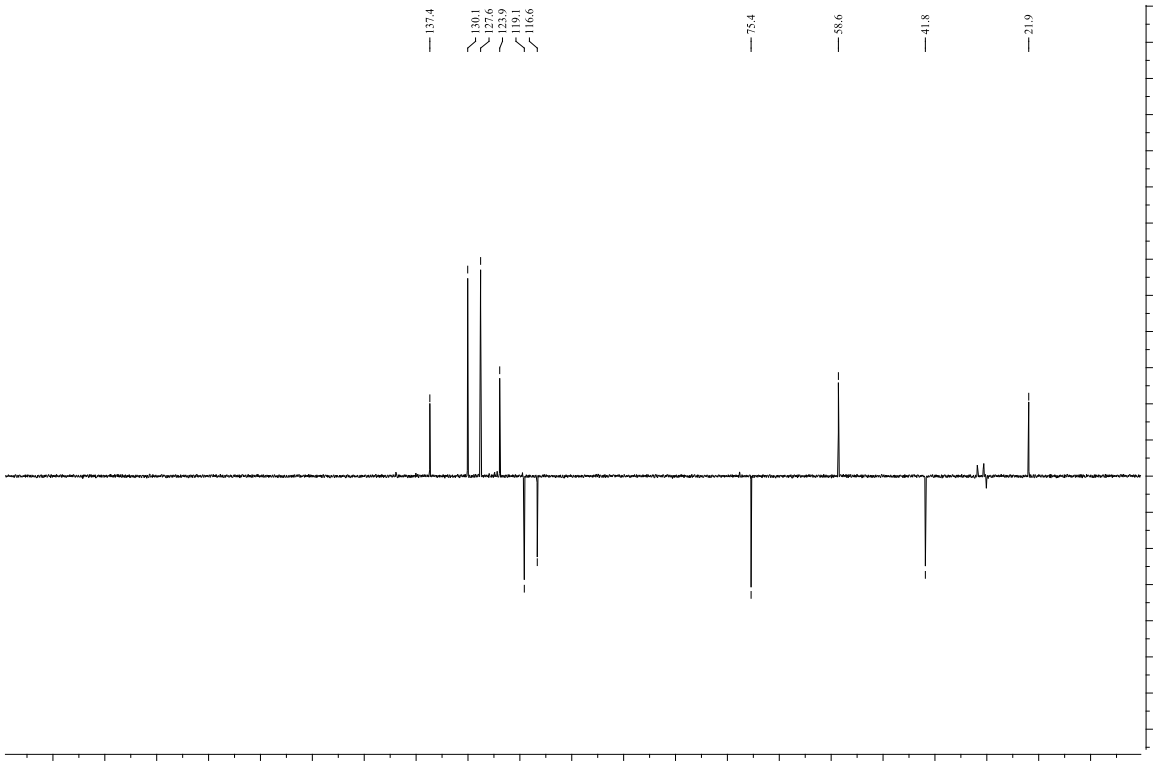


Supporting Information

2D gCOSY ($CDCl_3$)

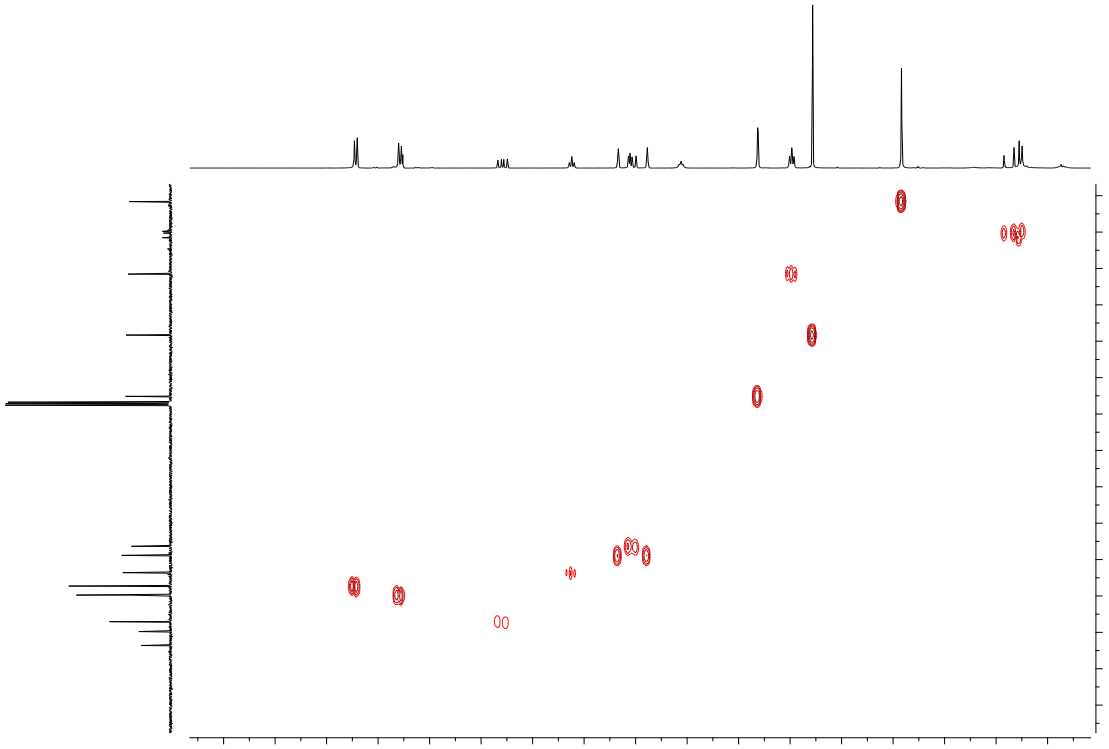


^{13}C DEPT (75 MHz, $CDCl_3$, 25 ^{o}C)

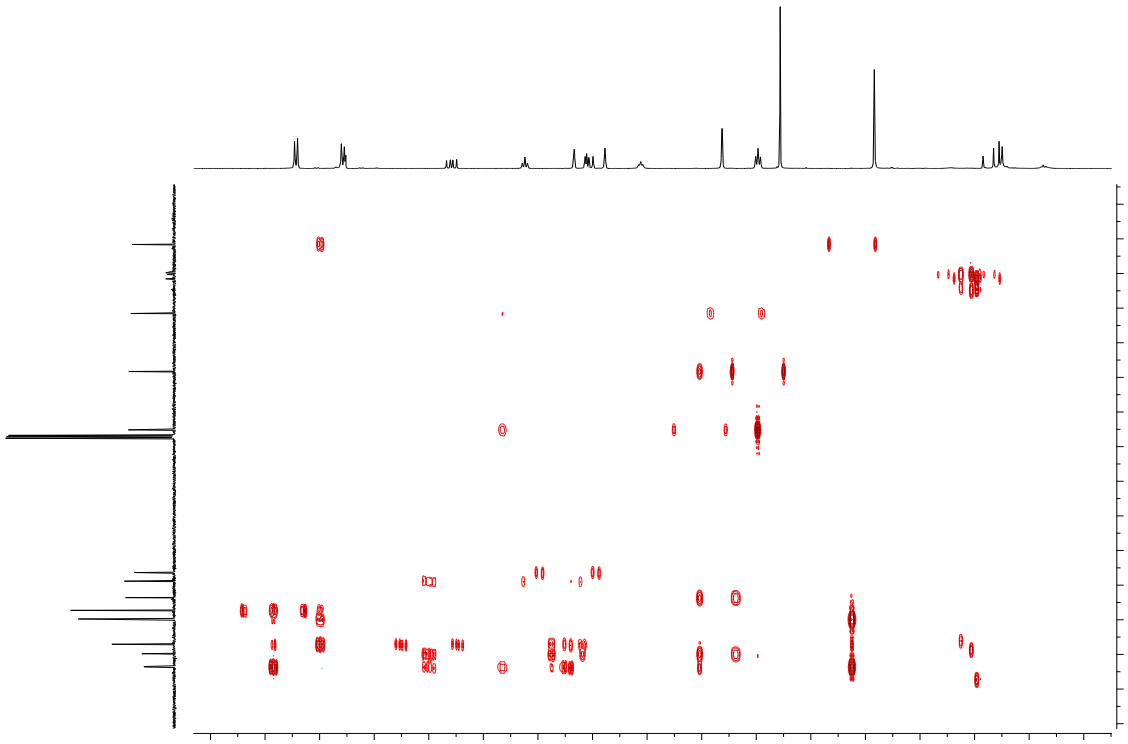


Supporting Information

2D HSQC ($CDCl_3$)



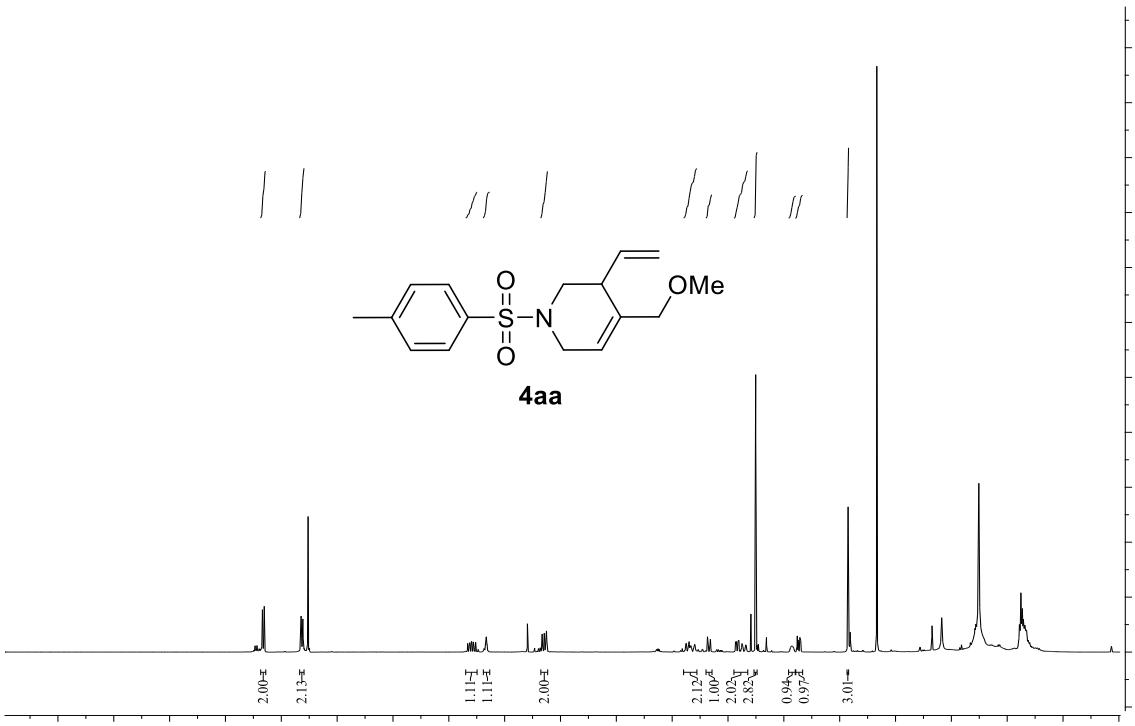
2D HMBC ($CDCl_3$)



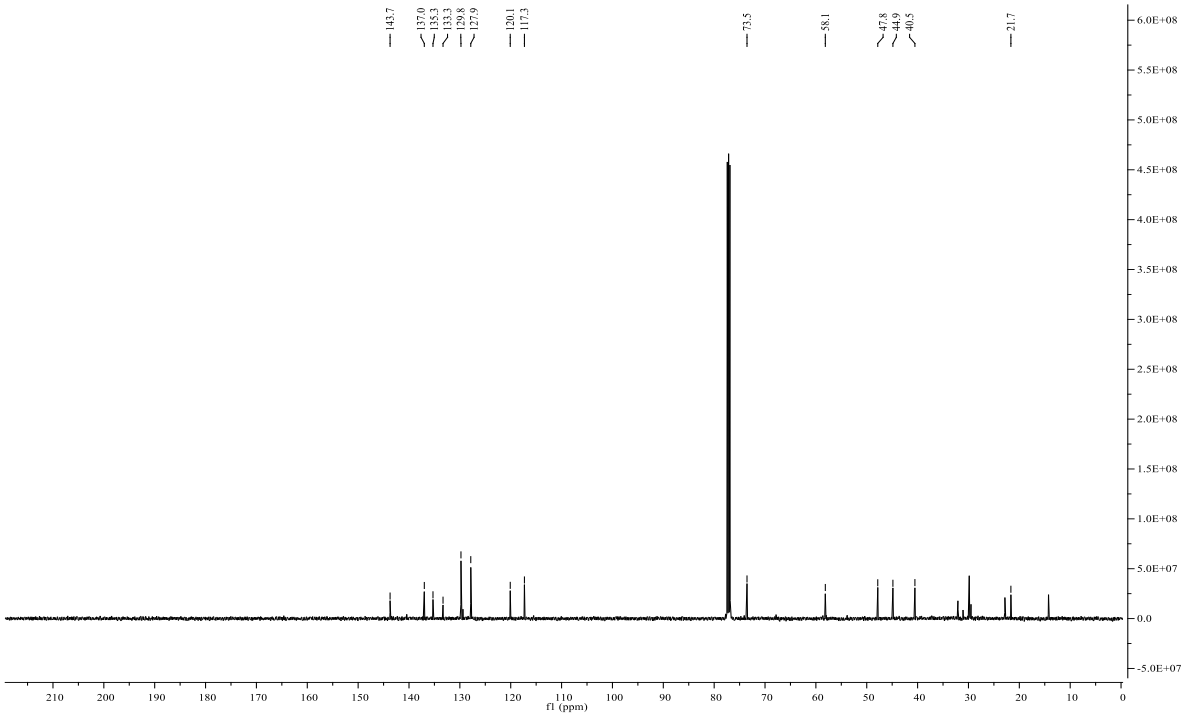
Supporting Information

4-Methoxymethyl-1-(toluene-4-sulfonyl)-3-vinyl-1,2,3,6-tetrahydro-pyridine

^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C)

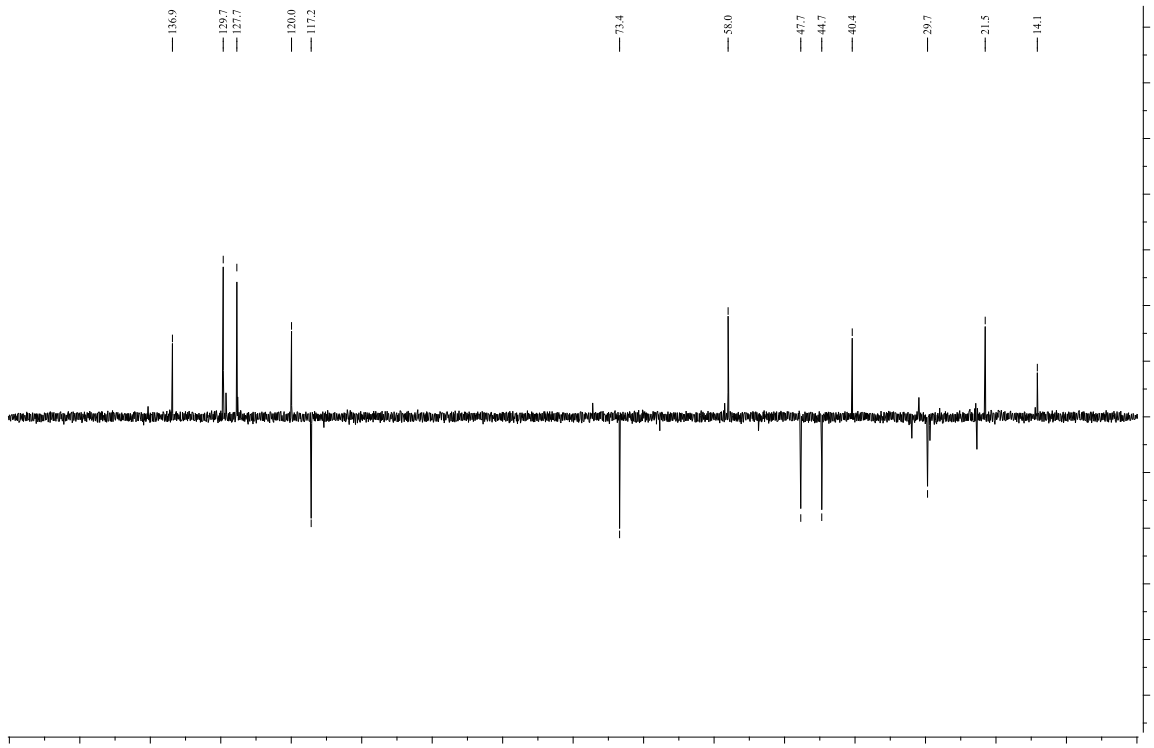


^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C)

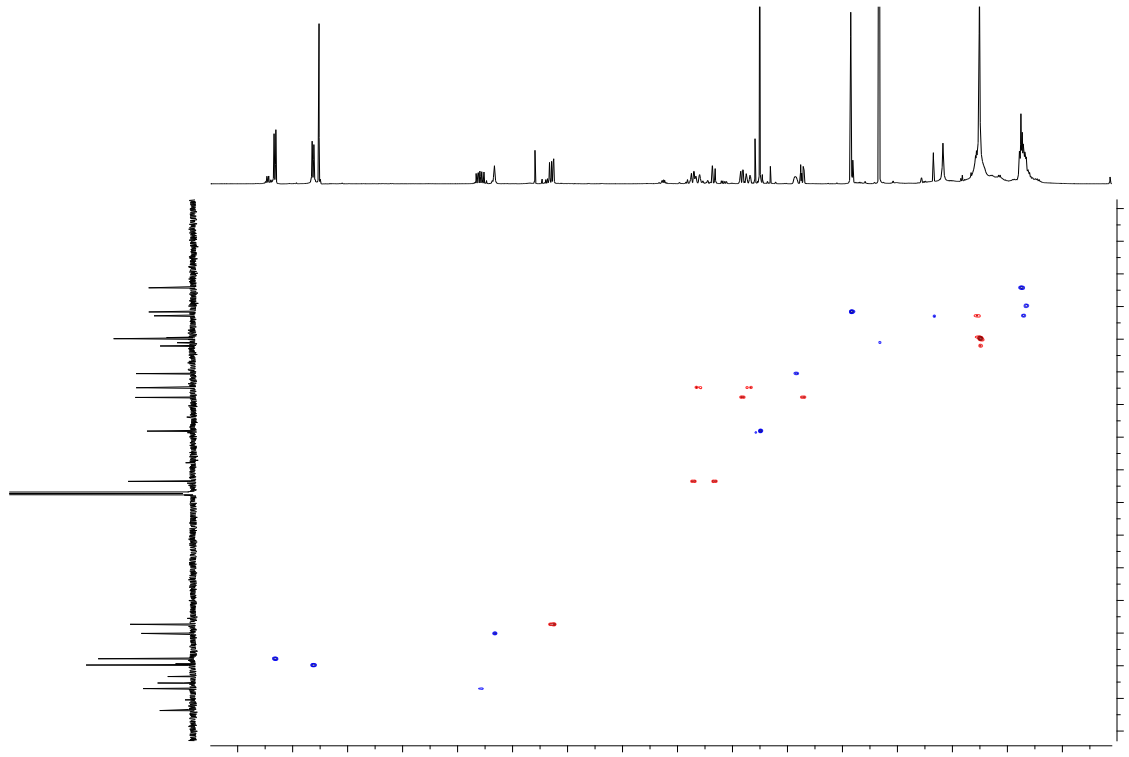


Supporting Information

^{13}C DEPT (75 MHz, $CDCl_3$, 25 ^oC)



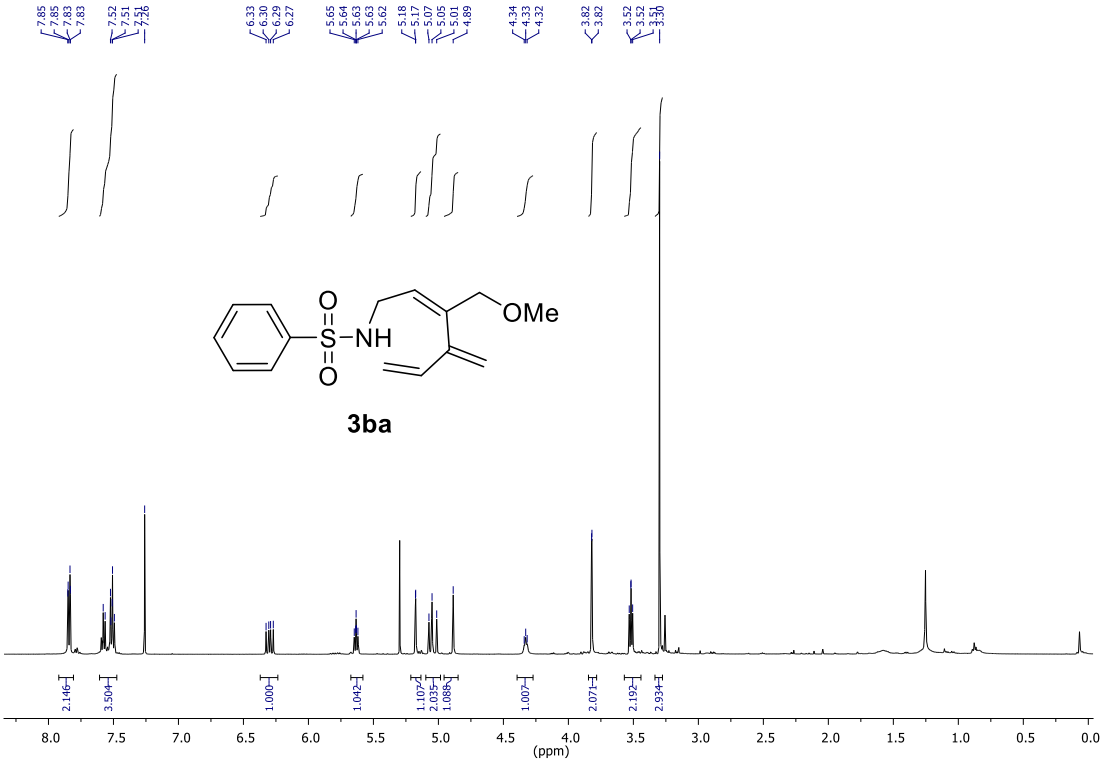
2D HSQC ($CDCl_3$)



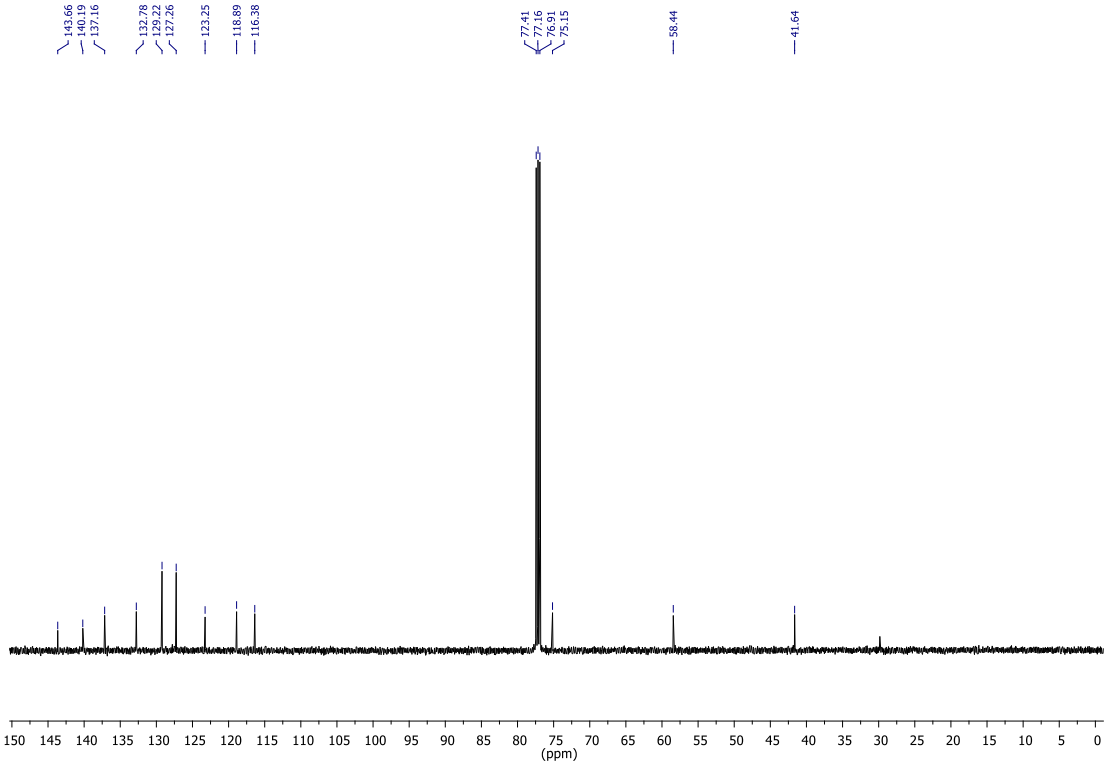
Supporting Information

1-Benzenesulfonyl-4-methoxymethyl-5-methyl-2,7-dihydro-1H-azepine

^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C)



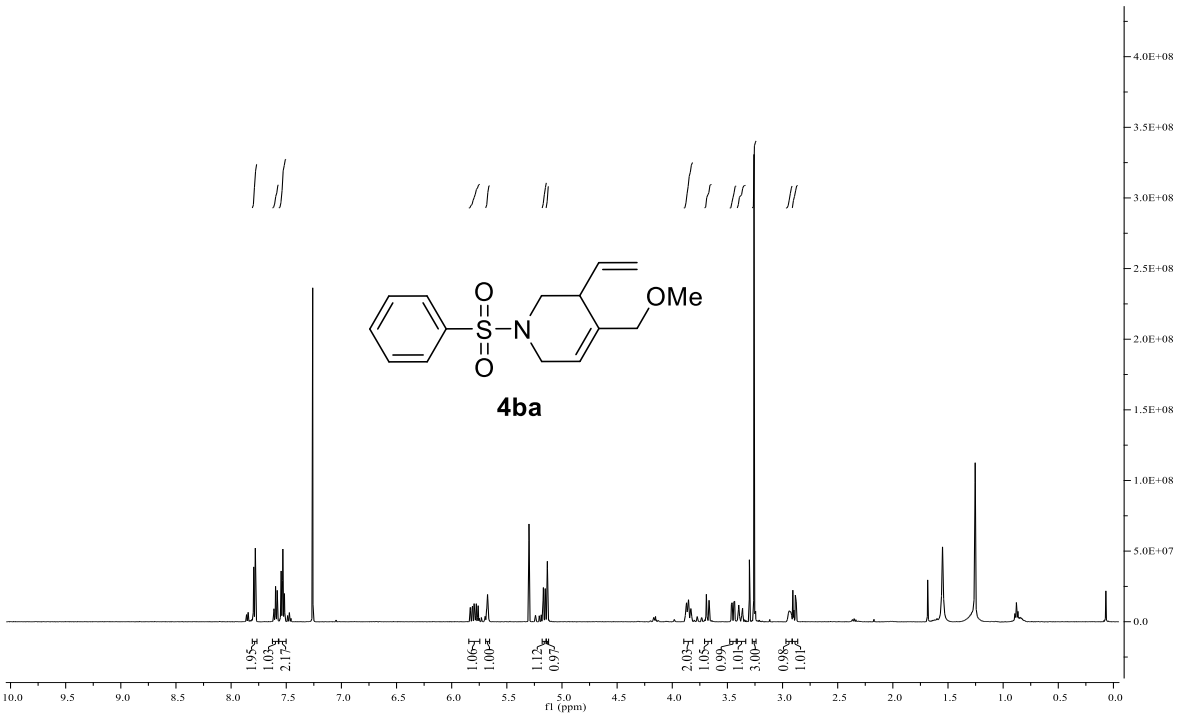
^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C)



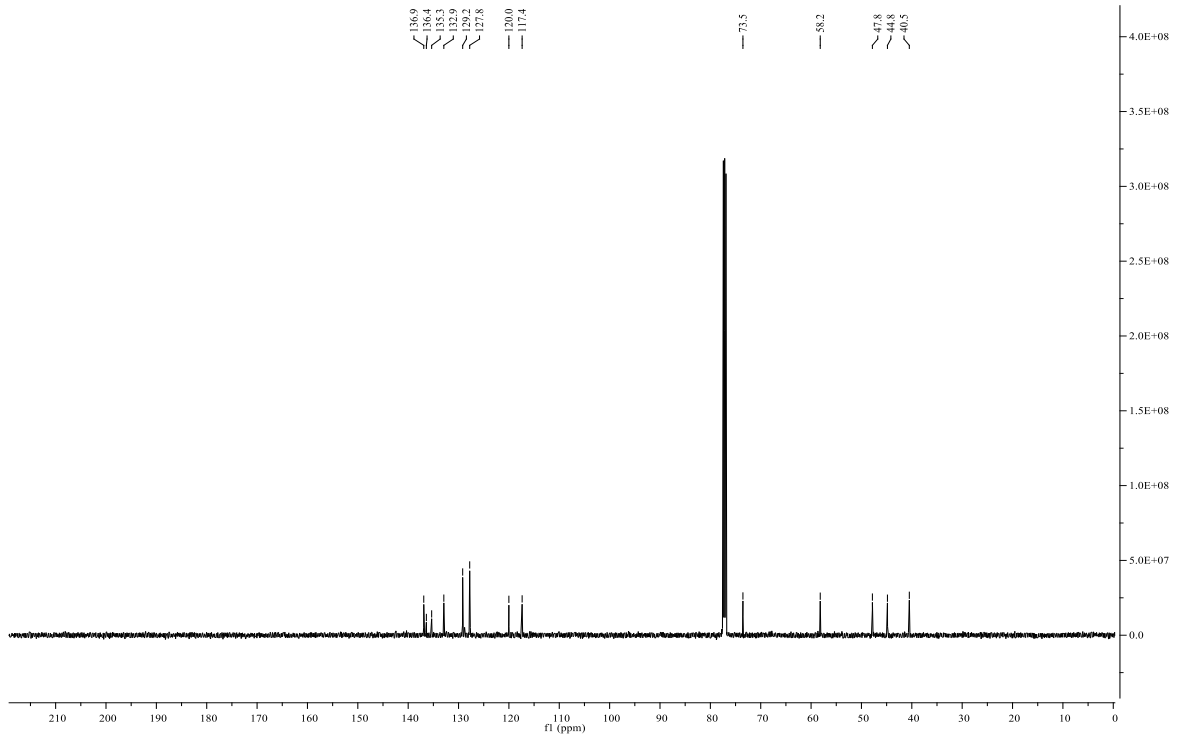
Supporting Information

1-Benzenesulfonyl-4-methoxymethyl-3-vinyl-1,2,3,6-tetrahydro-pyridine

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

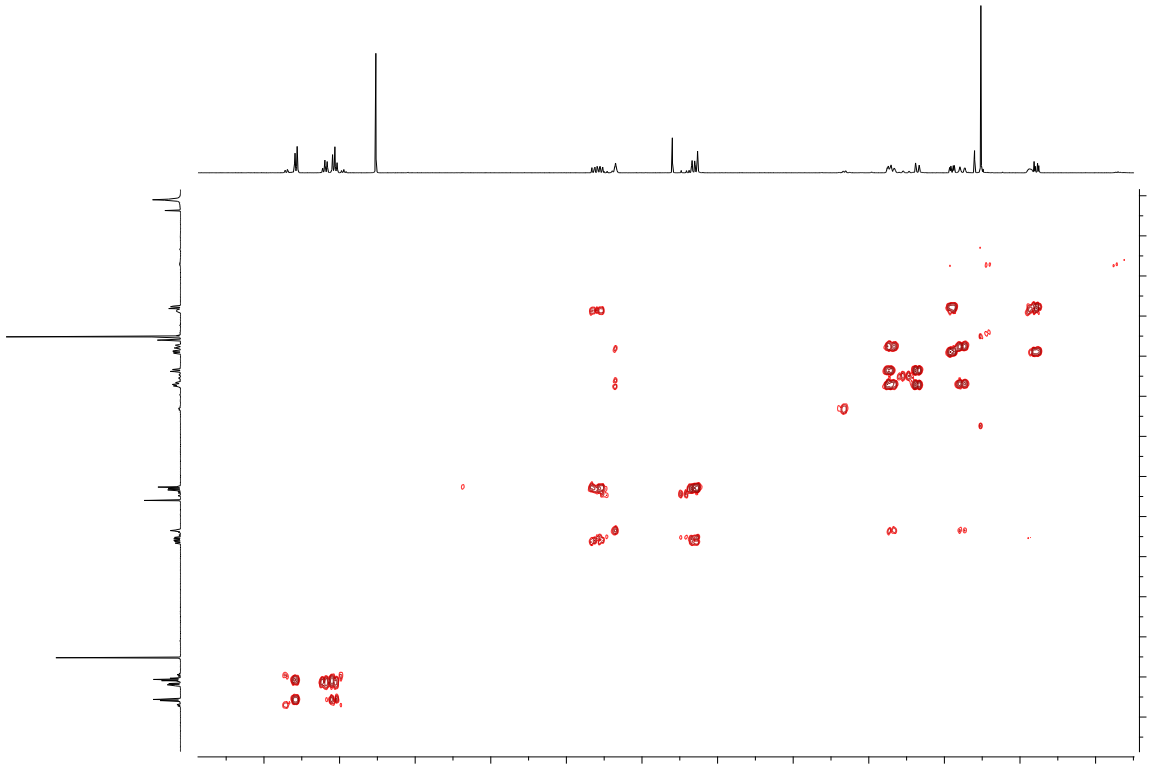


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

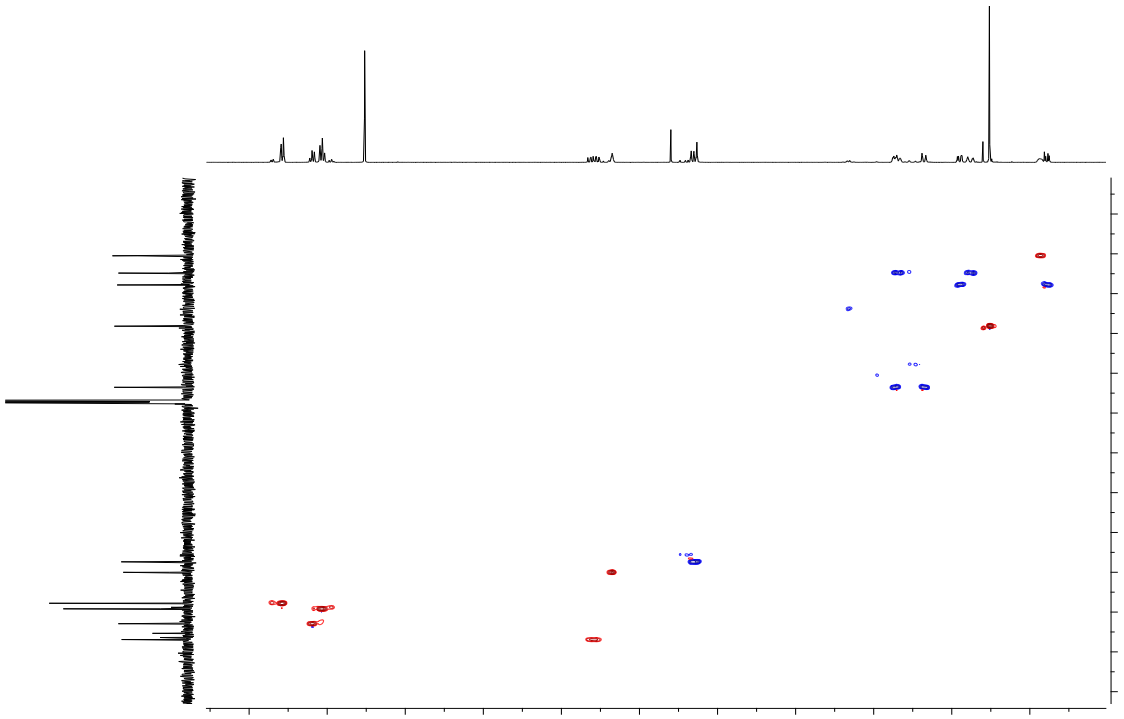


Supporting Information

2D gCOSY ($CDCl_3$)



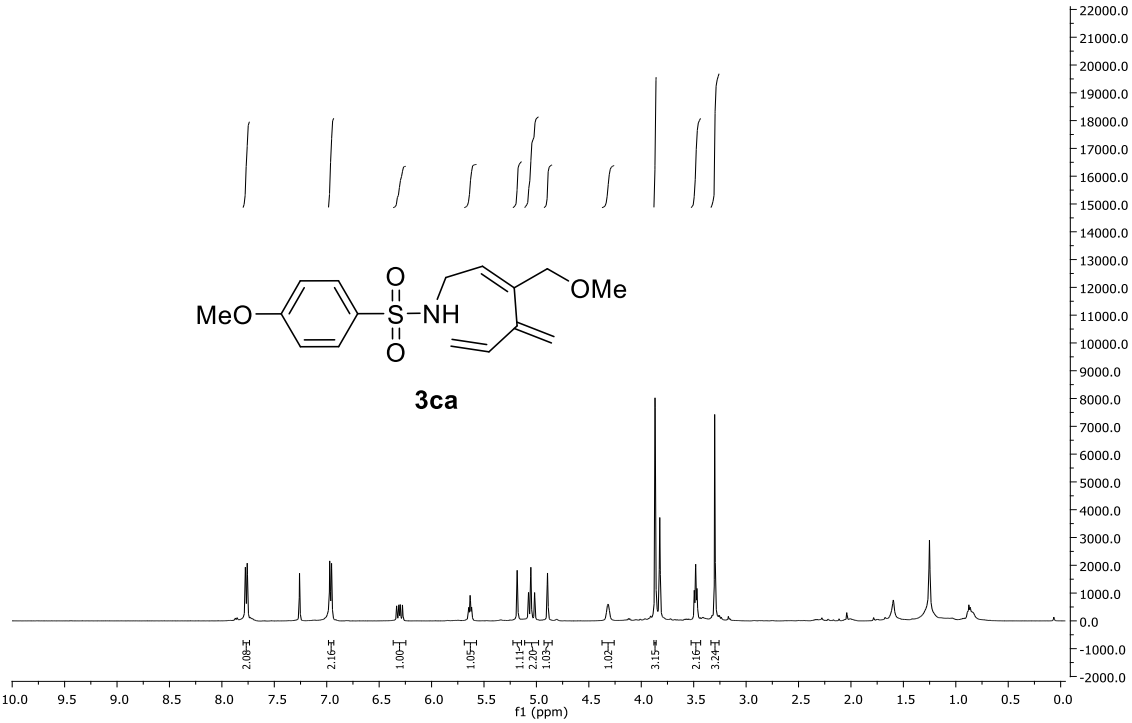
2D HSQC ($CDCl_3$)



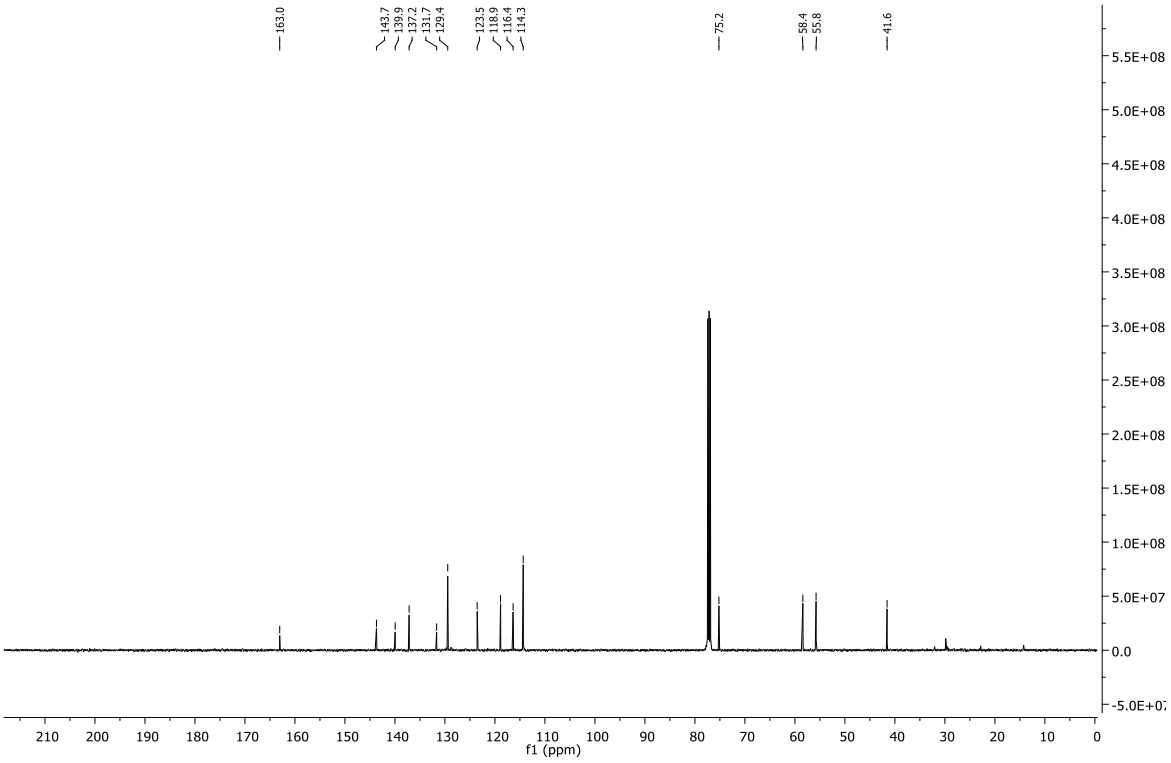
Supporting Information

4-Methoxy-*N*-(3-methoxymethyl-4-methylene-hexa-2,5-dienyl)-benzenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

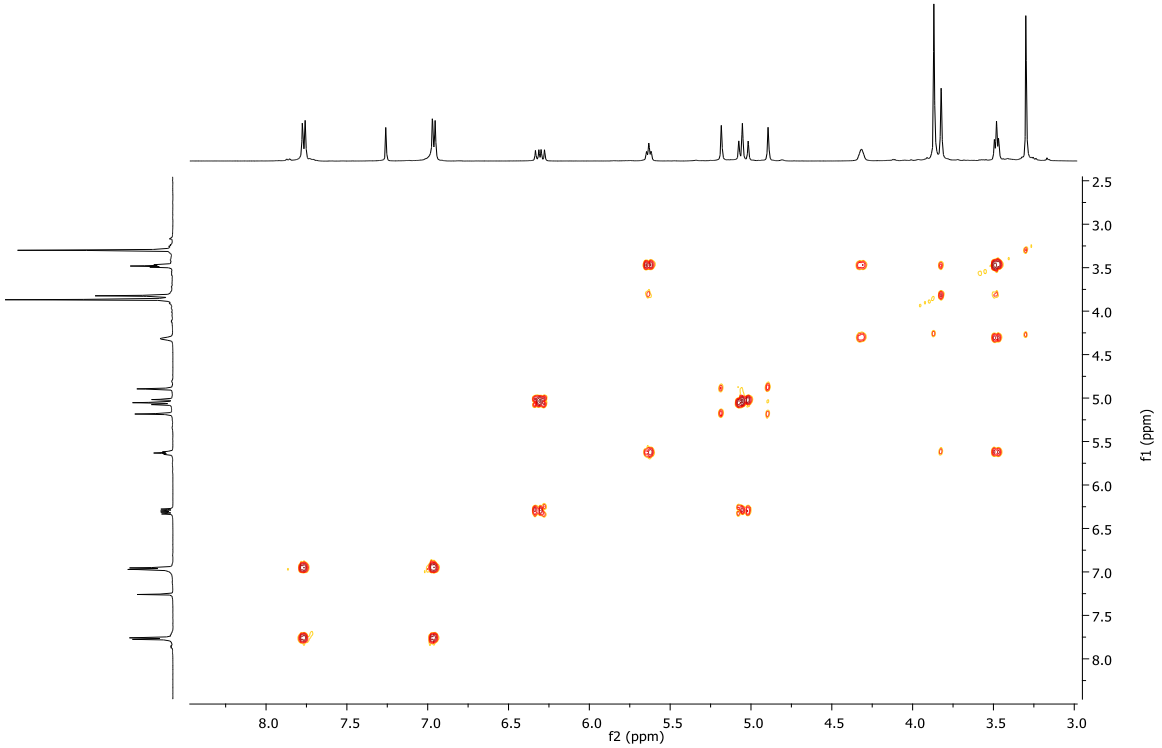


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

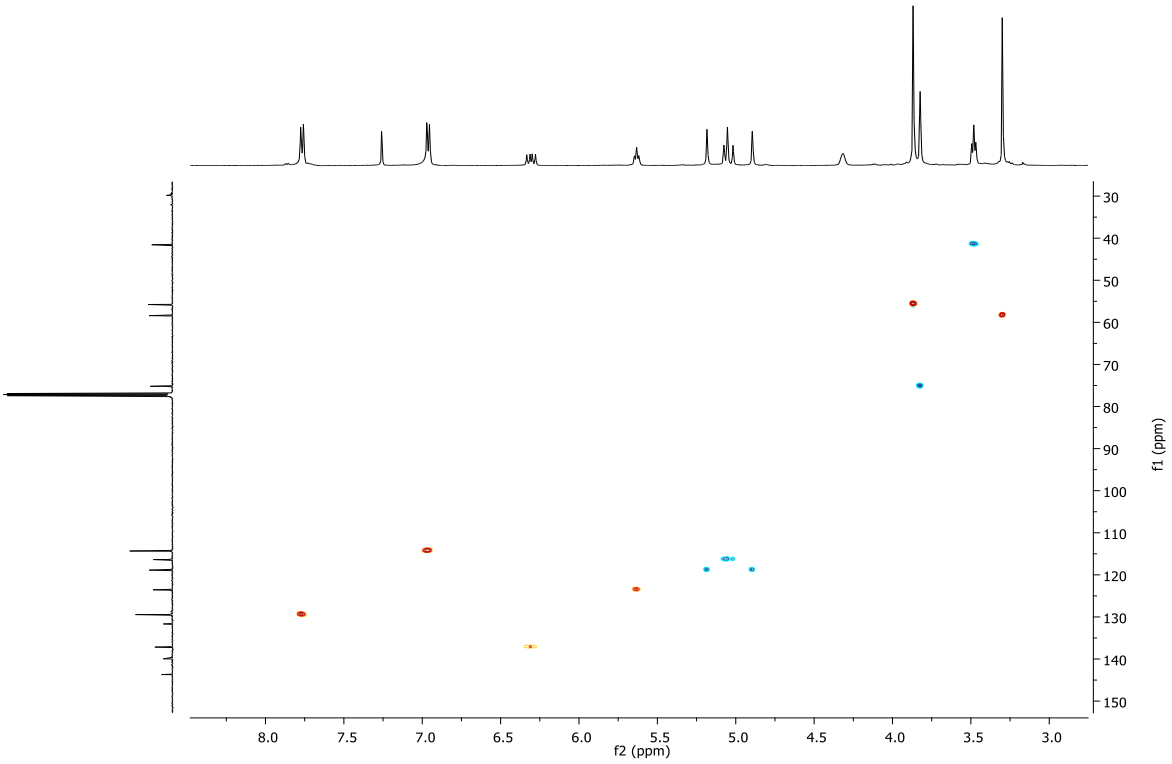


Supporting Information

2D gCOSY ($CDCl_3$)



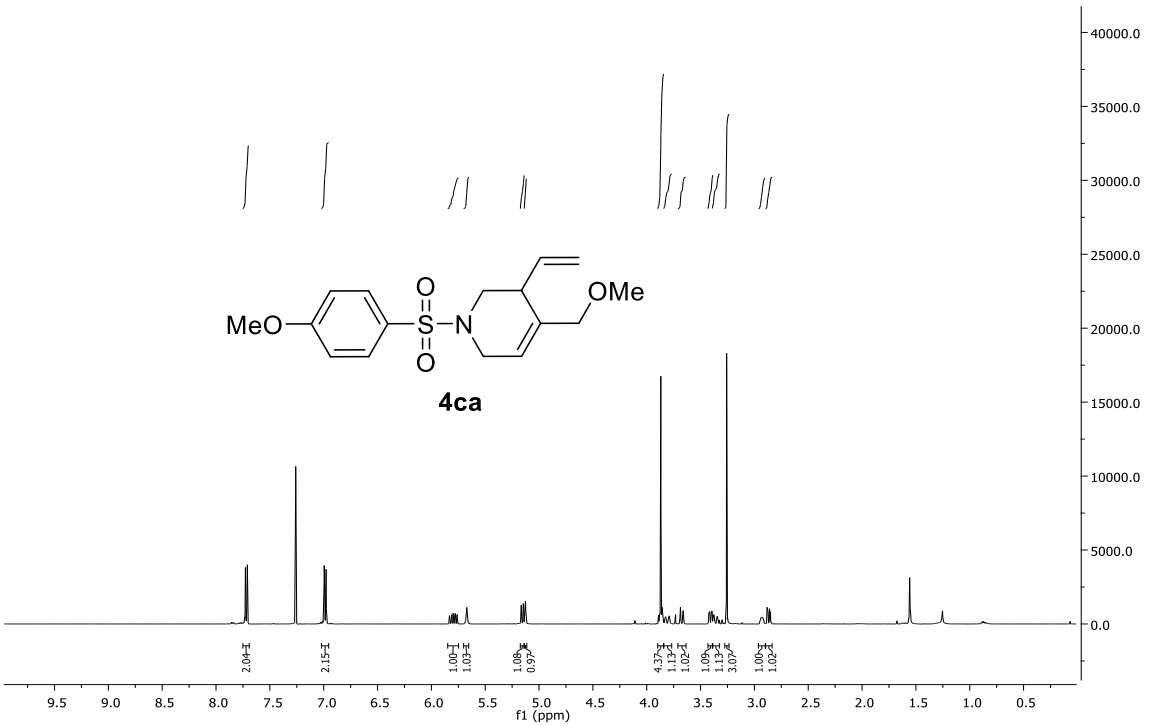
2D HSQC ($CDCl_3$)



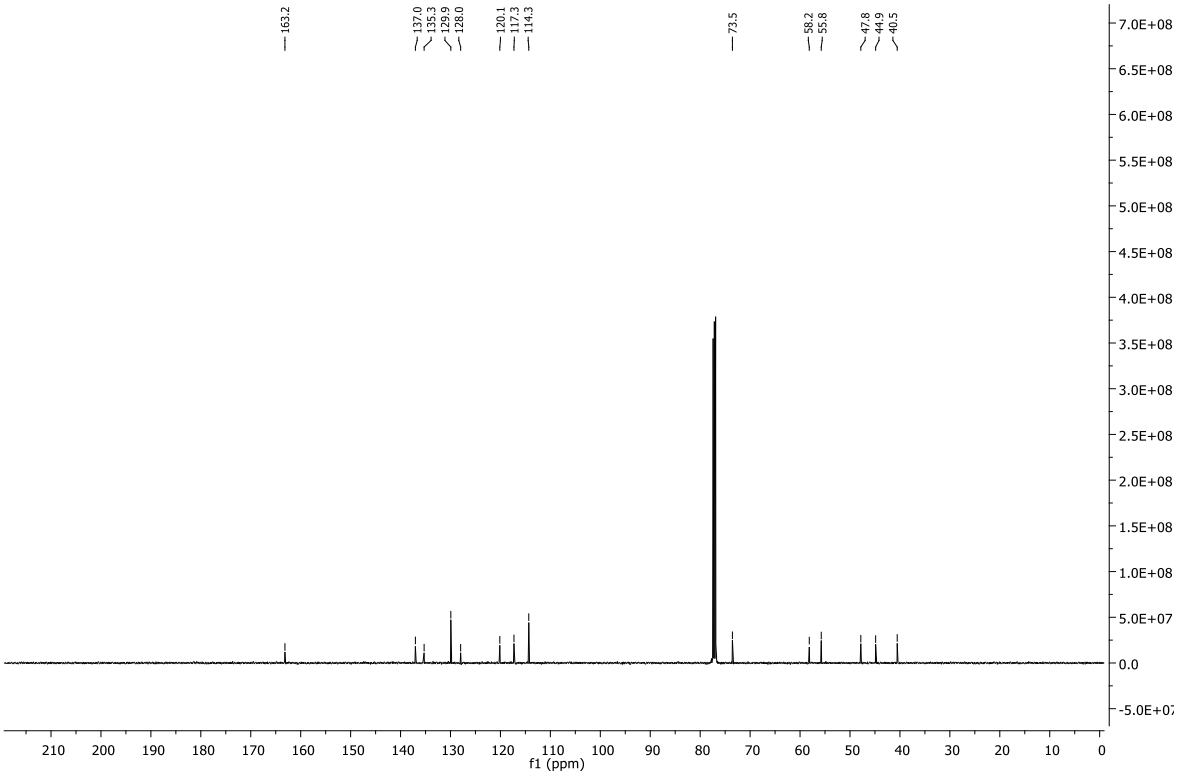
Supporting Information

1-(4-Methoxy-benzenesulfonyl)-4-methoxymethyl-3-vinyl-1,2,3,6-tetrahydro-pyridine

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

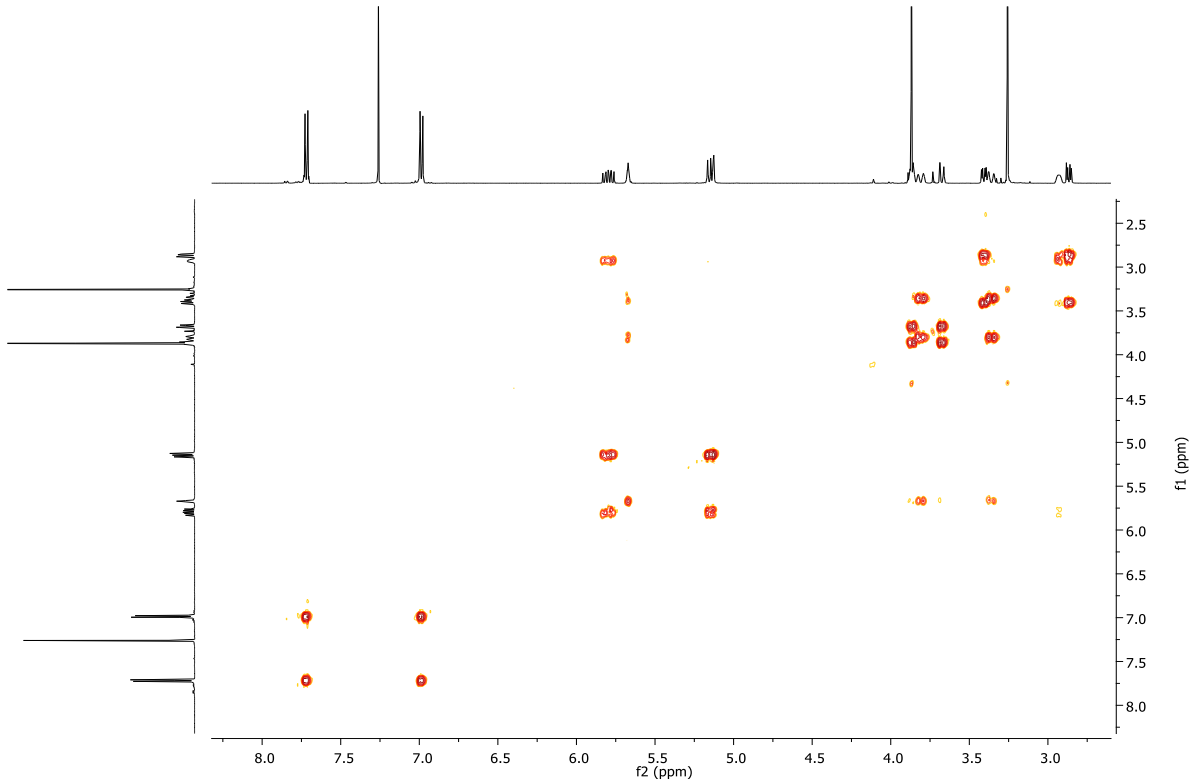


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

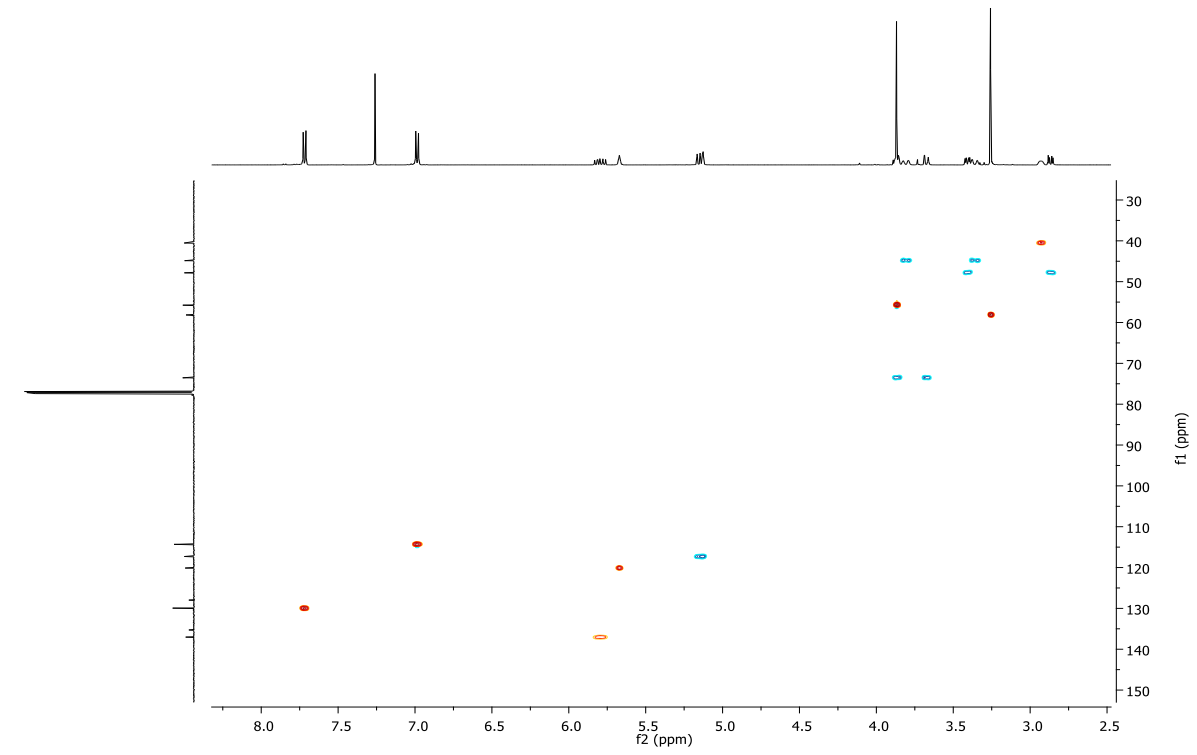


Supporting Information

2D gCOSY ($CDCl_3$)



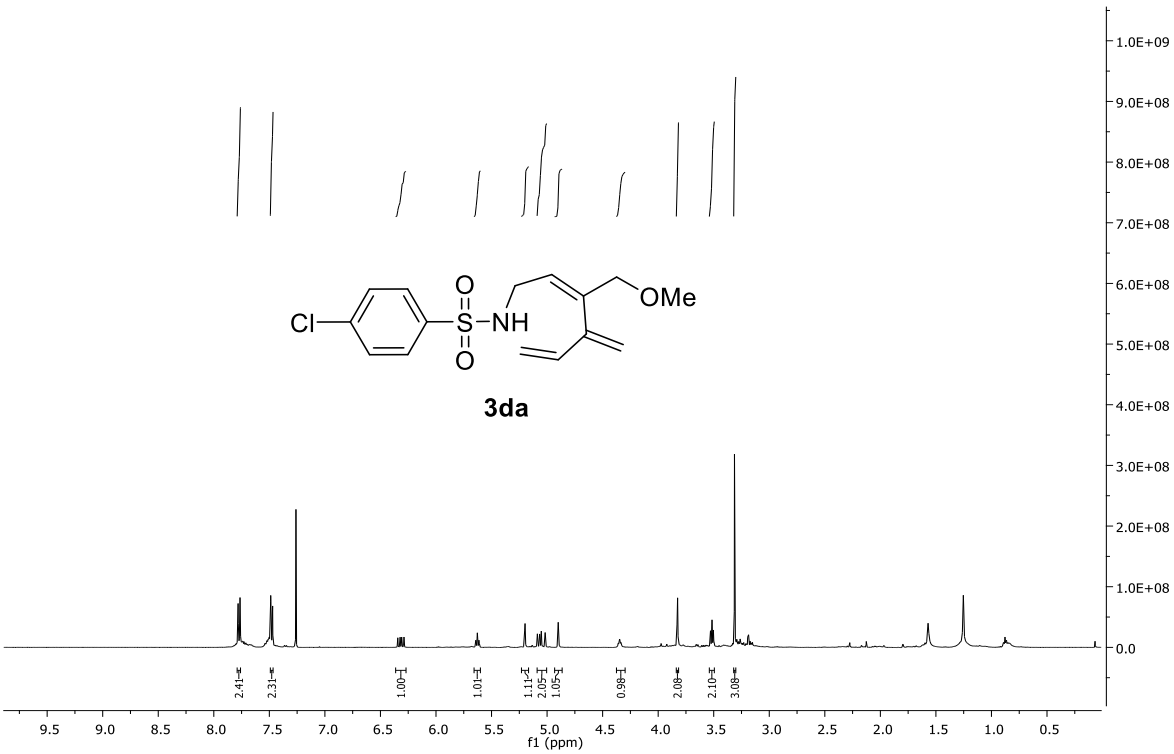
2D HSQC ($CDCl_3$)



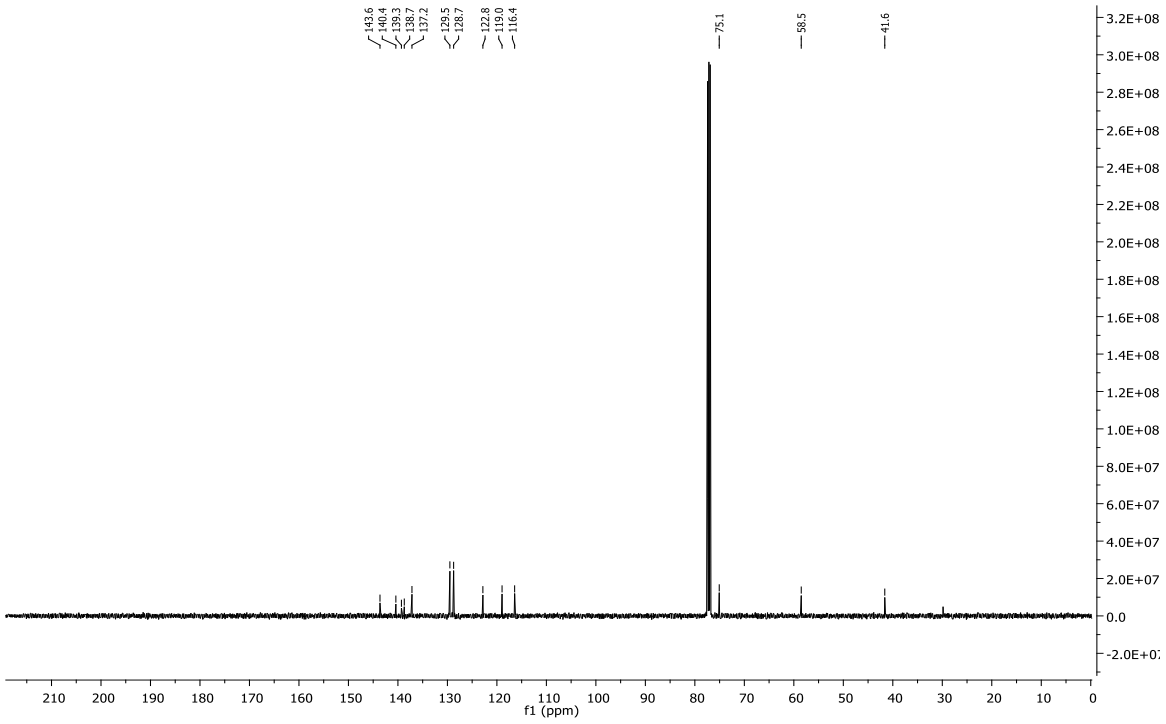
Supporting Information

4-Chloro-*N*-(3-methoxymethyl-4-methylene-hexa-2,5-dienyl)-benzenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

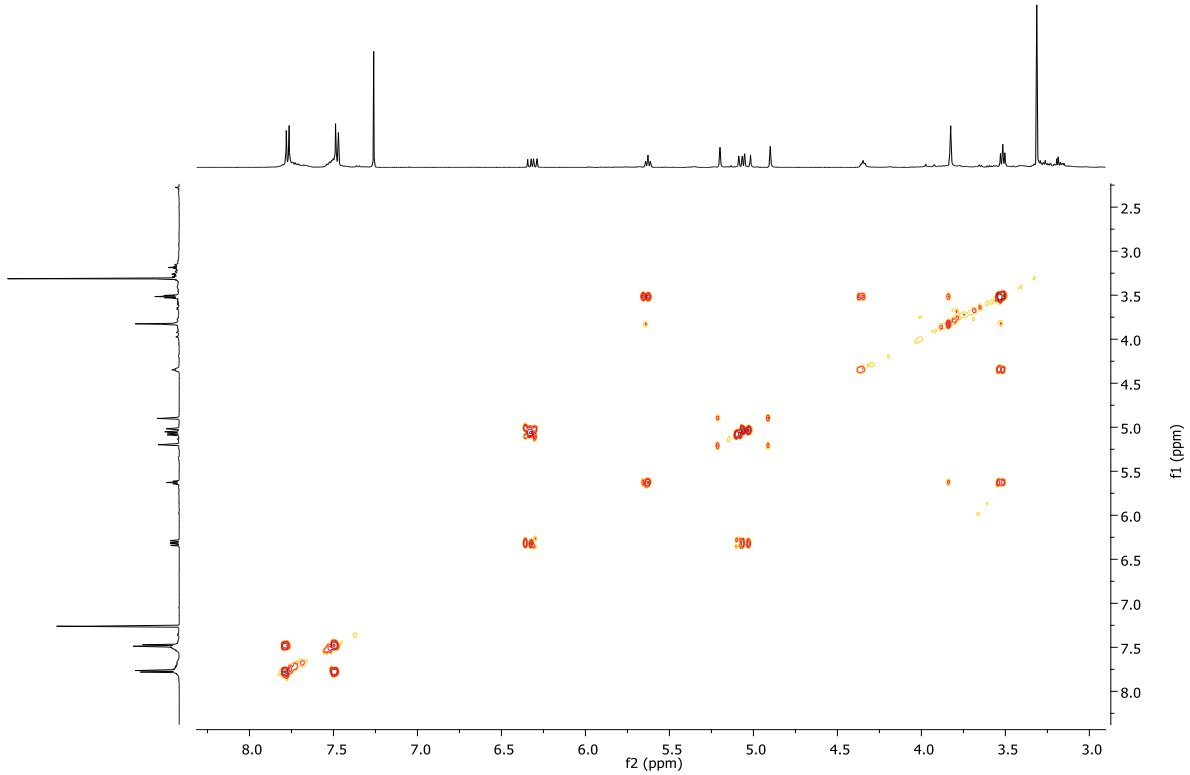


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

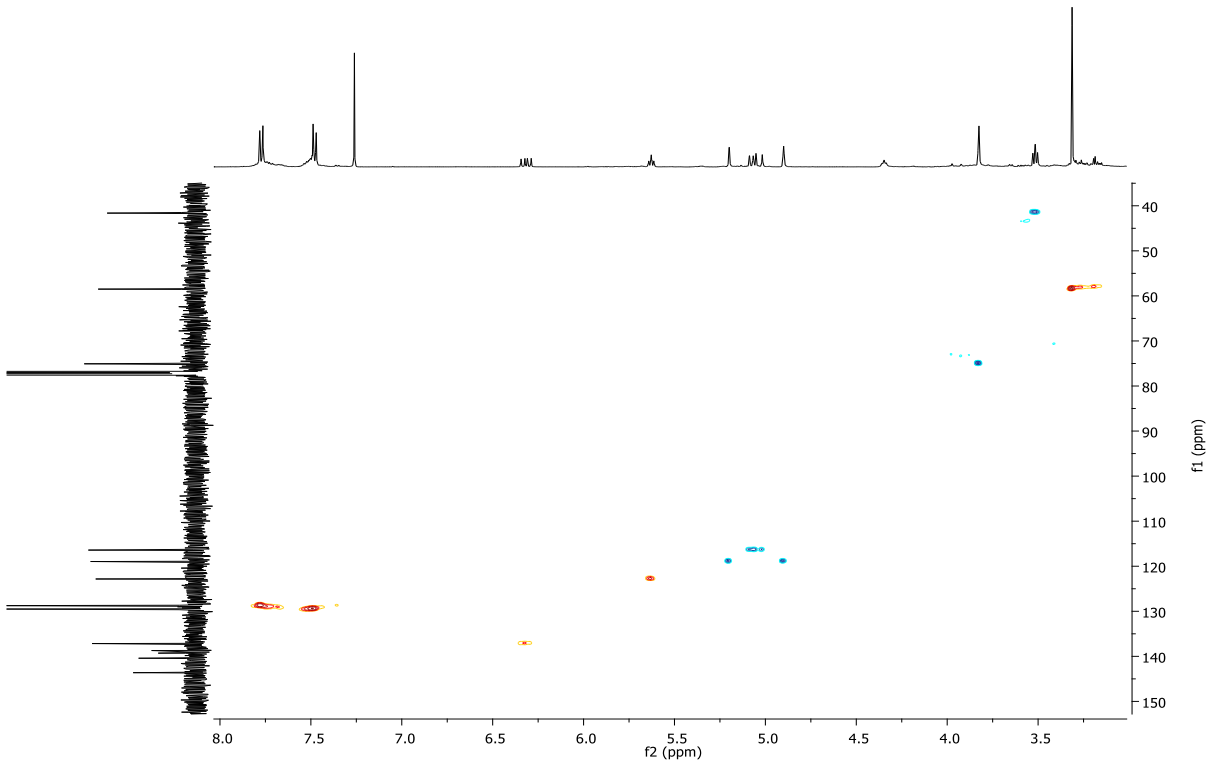


Supporting Information

2D gCOSY ($CDCl_3$)



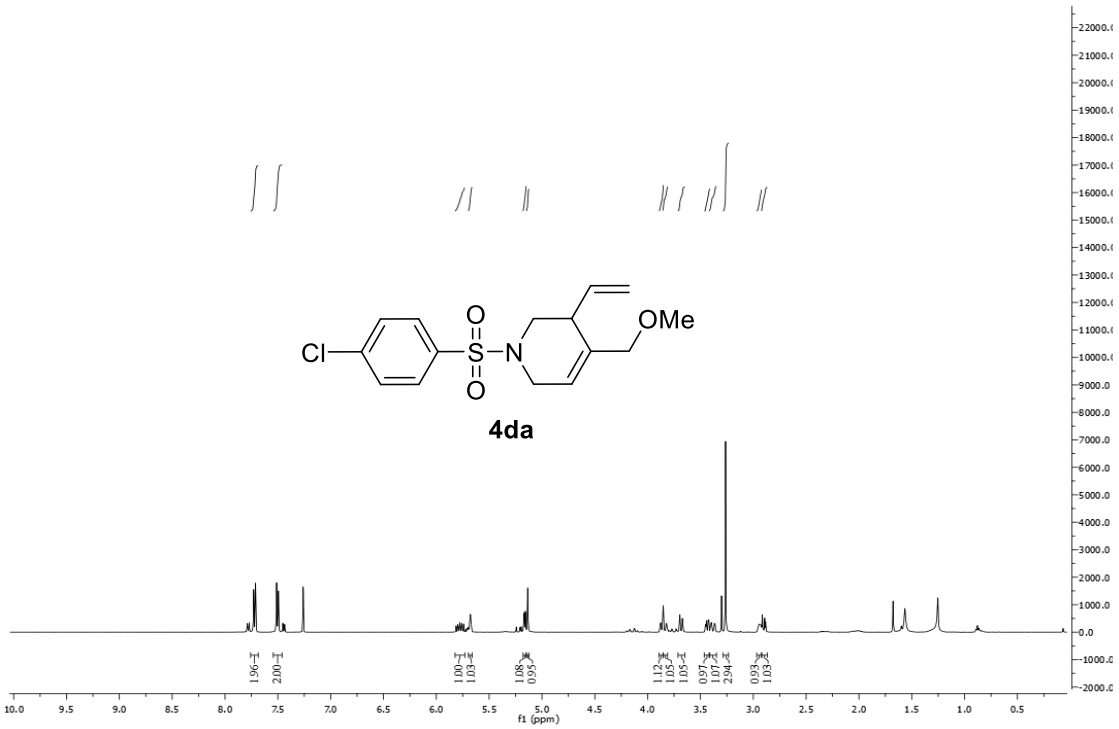
2D HSQC ($CDCl_3$)



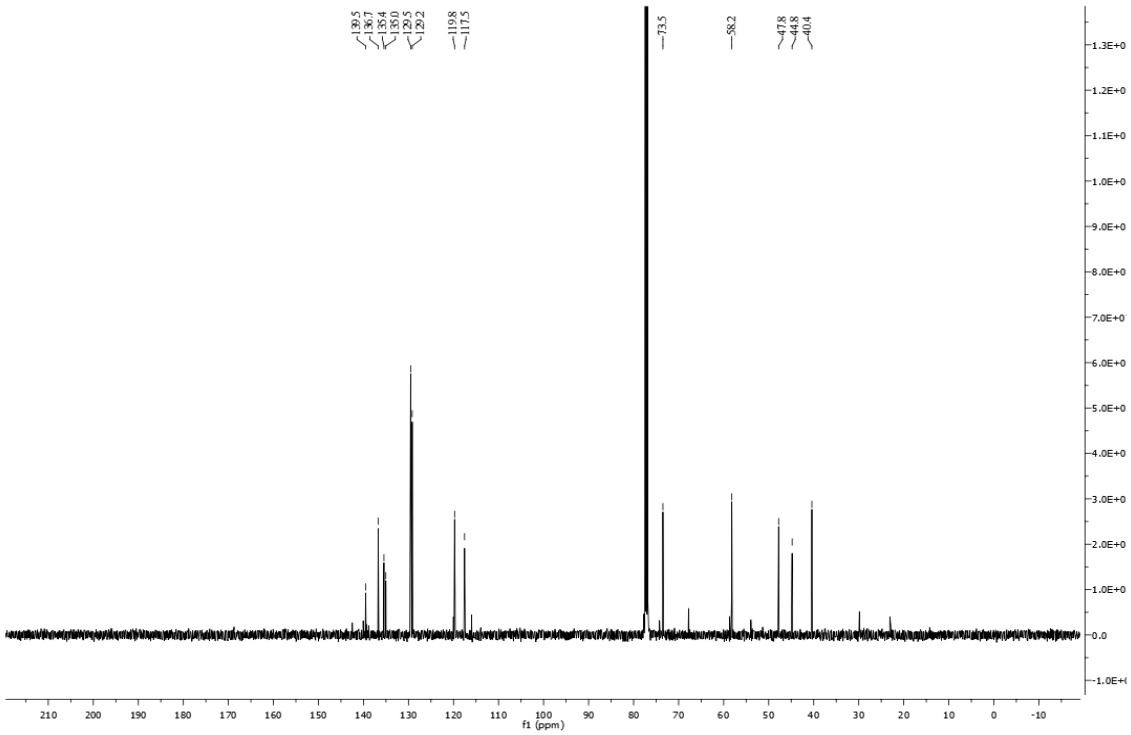
Supporting Information

1-(4-Chloro-benzenesulfonyl)-4-methoxymethyl-3-vinyl-1,2,3,6-tetrahydro-pyridine

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

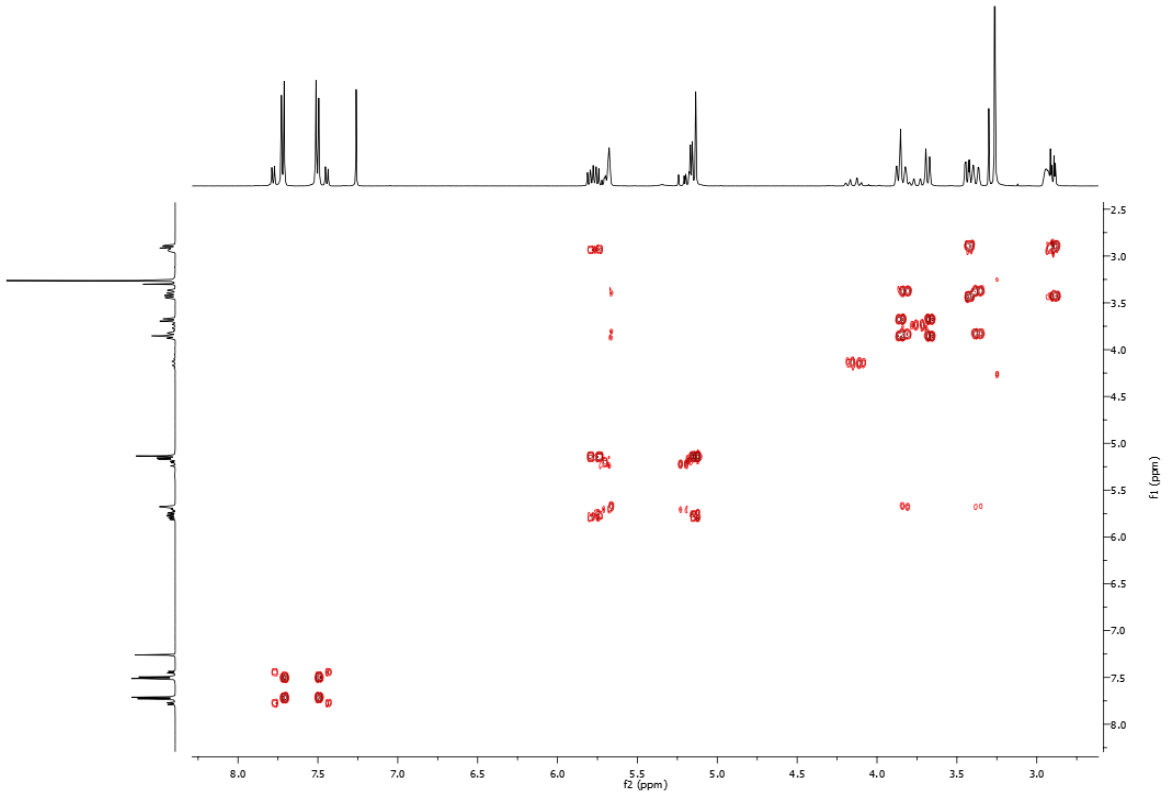


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

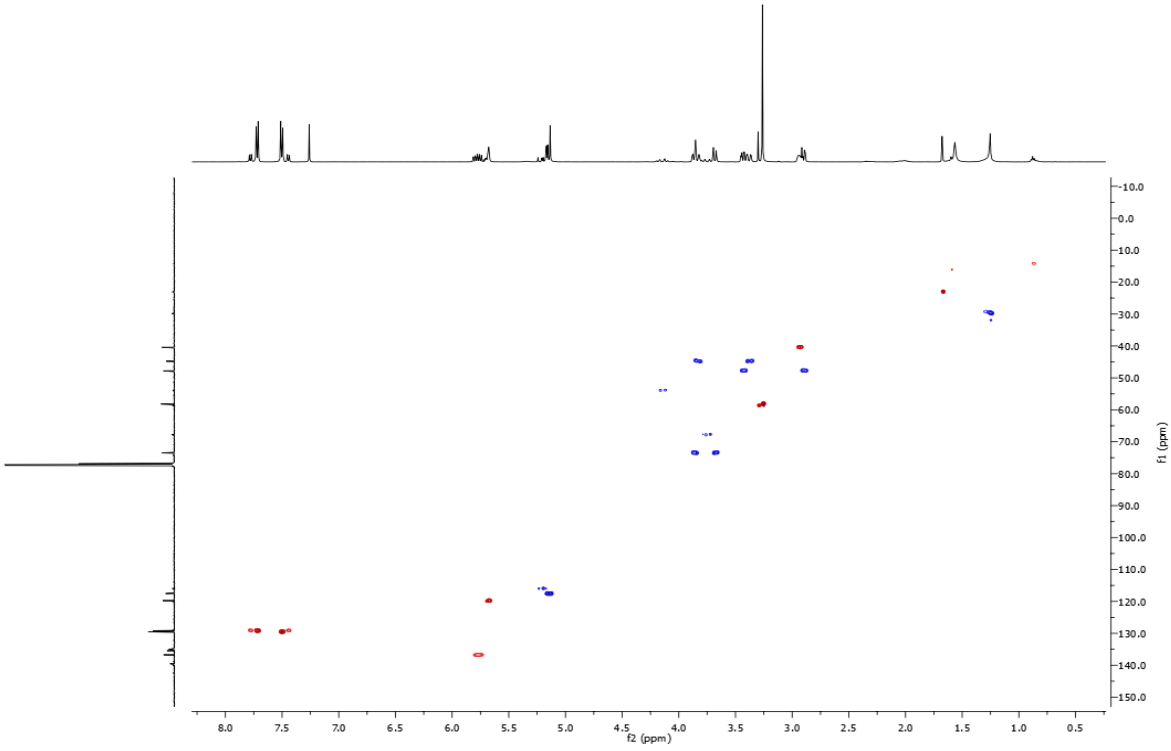


Supporting Information

2D gCOSY ($CDCl_3$)



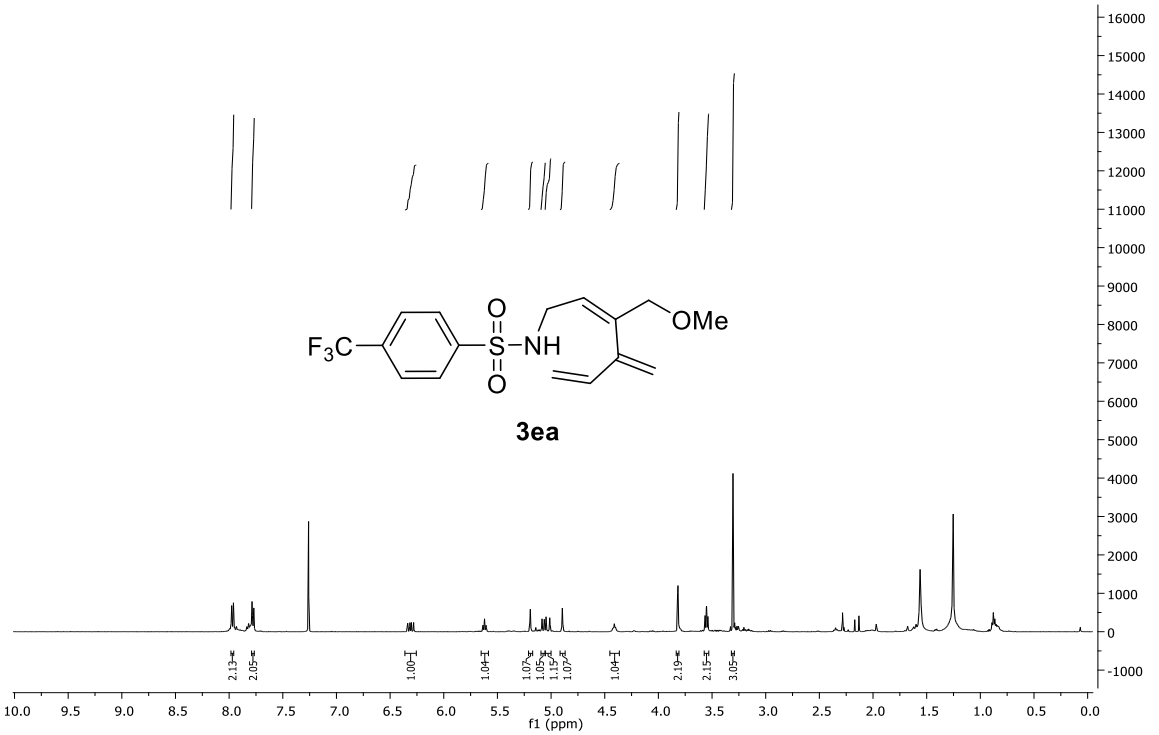
2D HSQC ($CDCl_3$)



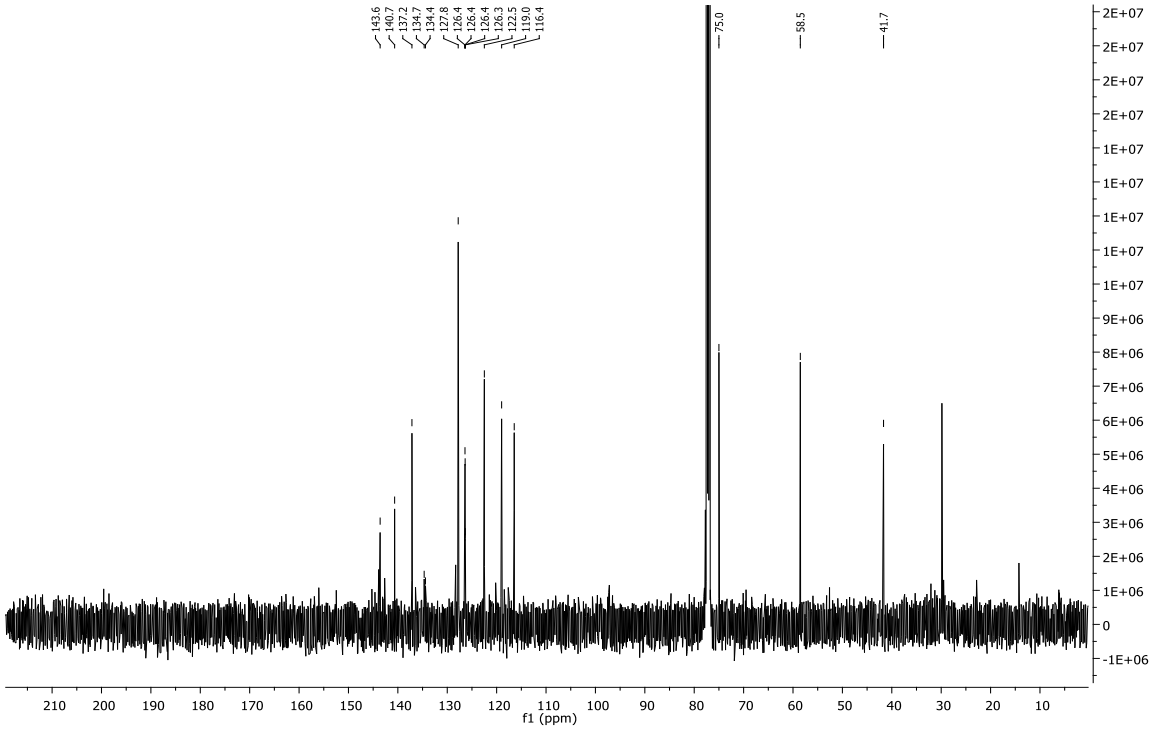
Supporting Information

***N*-(3-Methoxymethyl-4-methylene-hexa-2,5-dienyl)-4-trifluoromethyl-benzenesulfonamide**

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

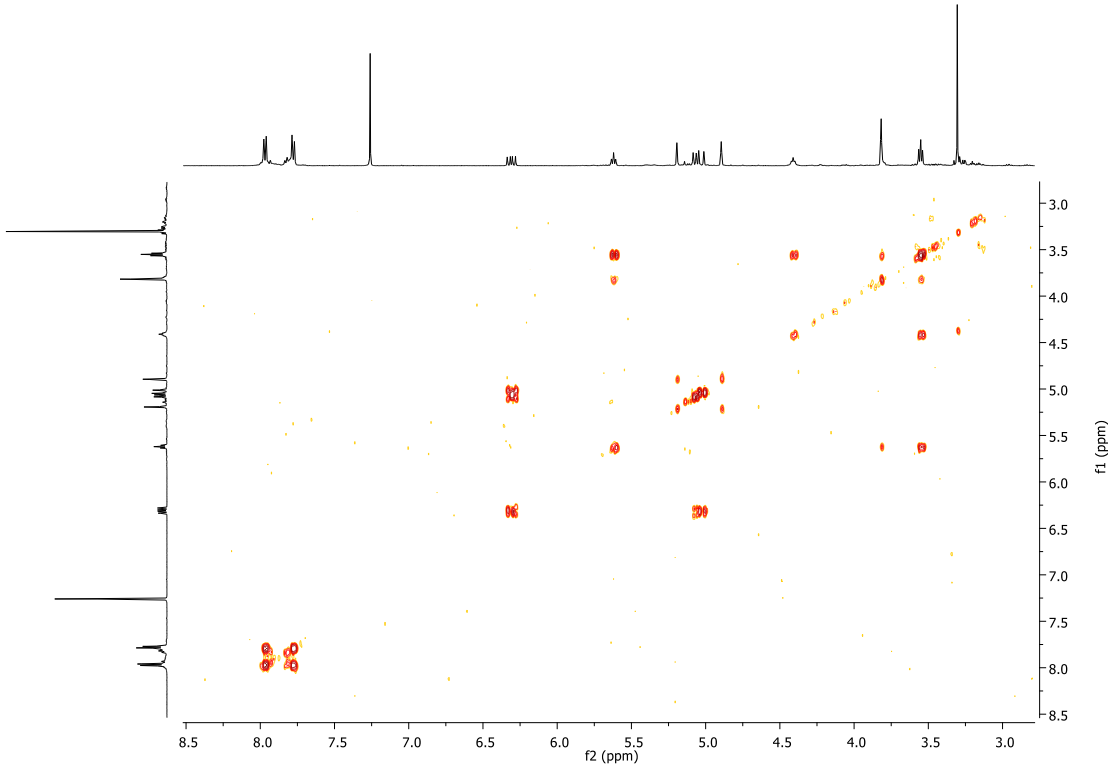


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

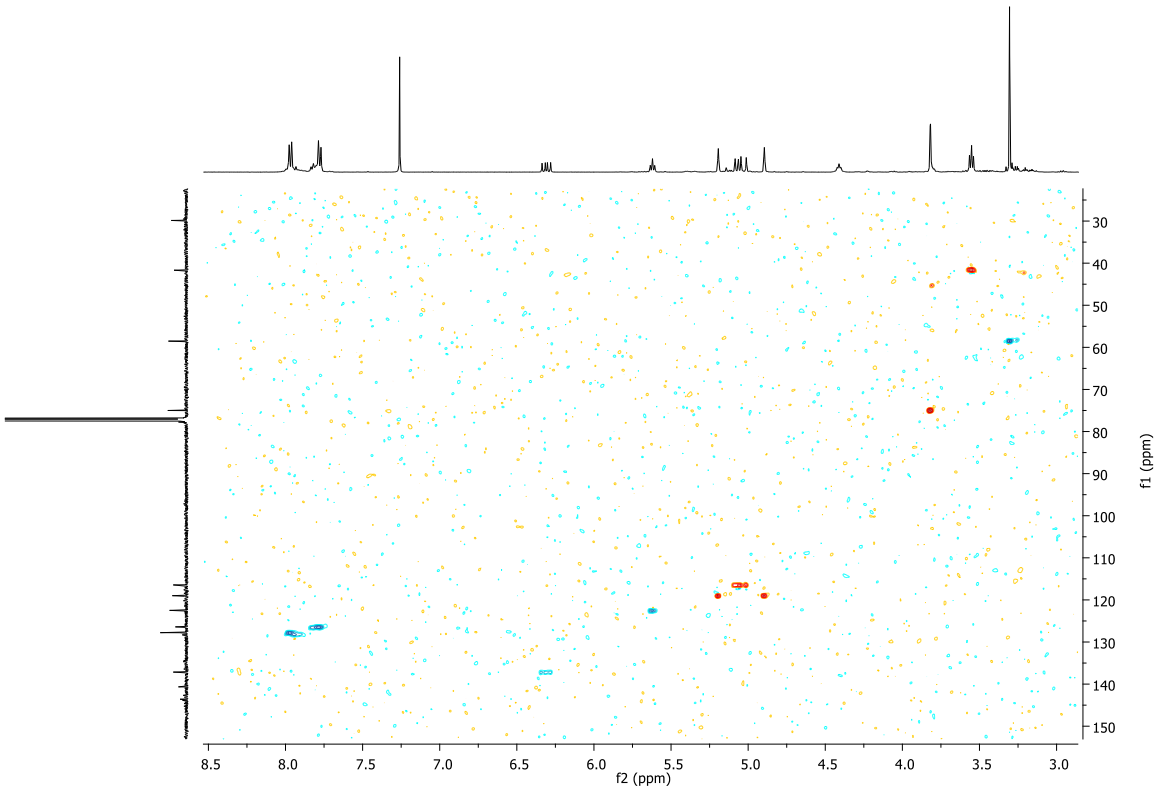


Supporting Information

2D gCOSY ($CDCl_3$)

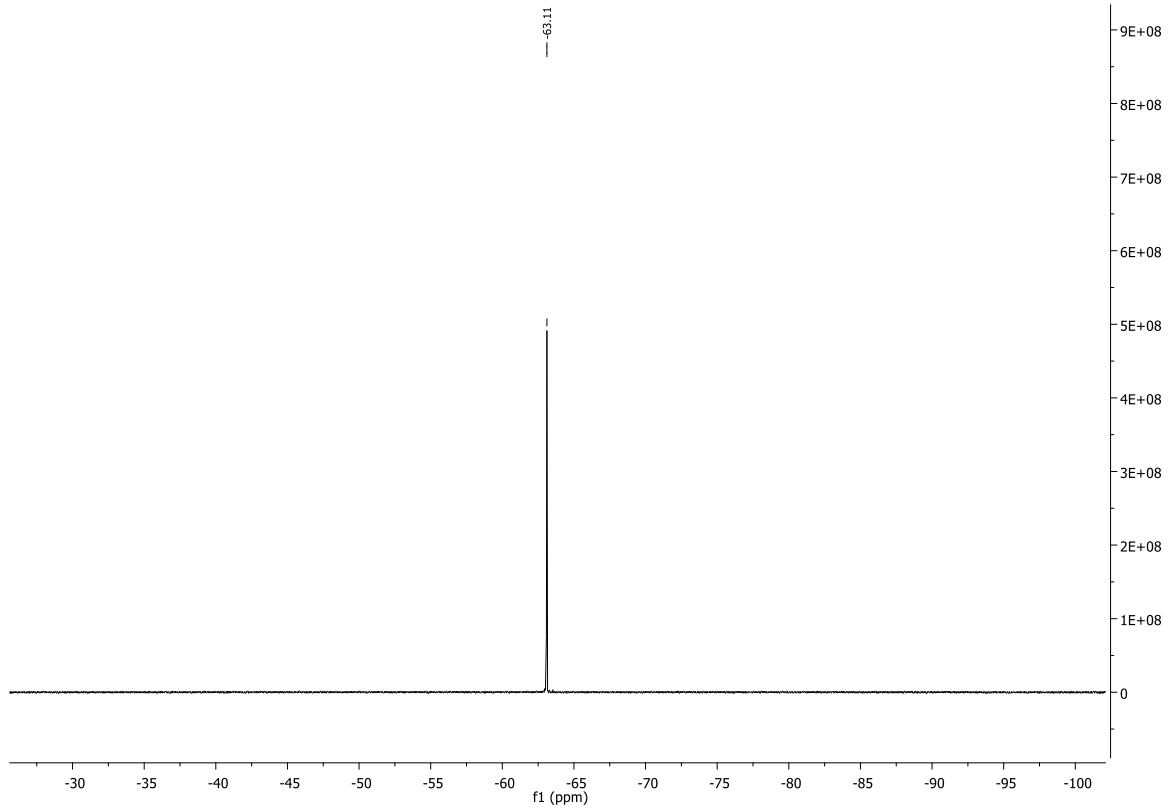


2D HSQC ($CDCl_3$)



Supporting Information

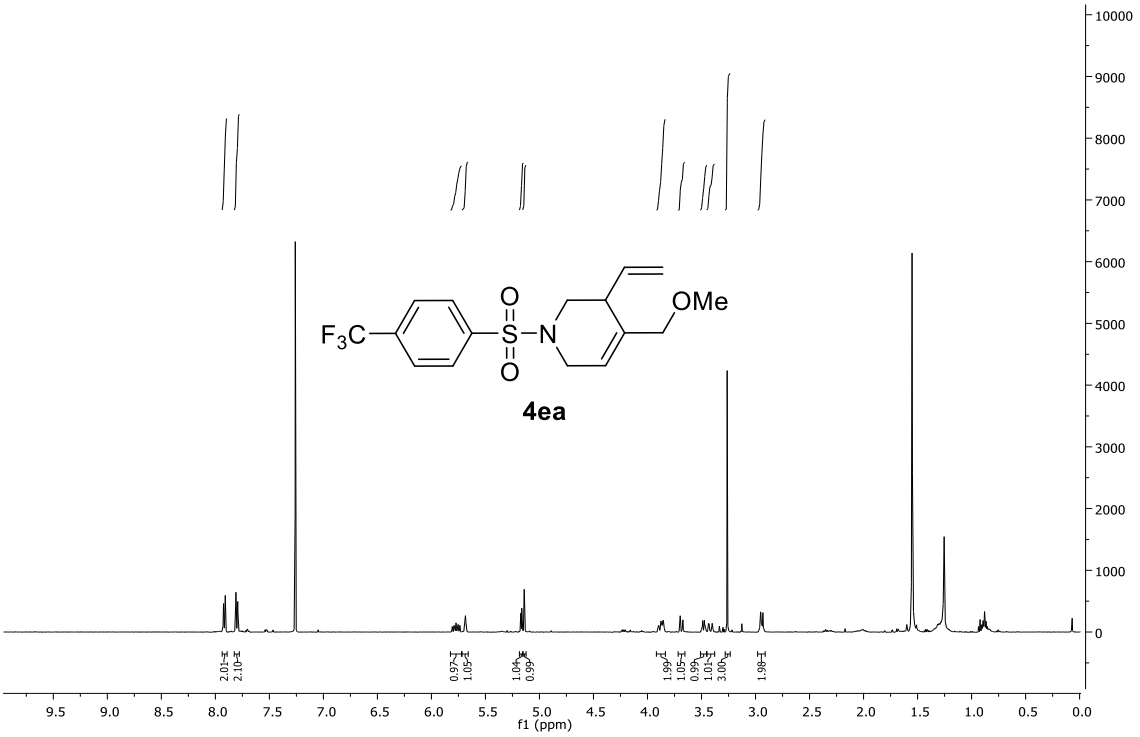
^{19}F NMR (471 MHz, $CDCl_3$)



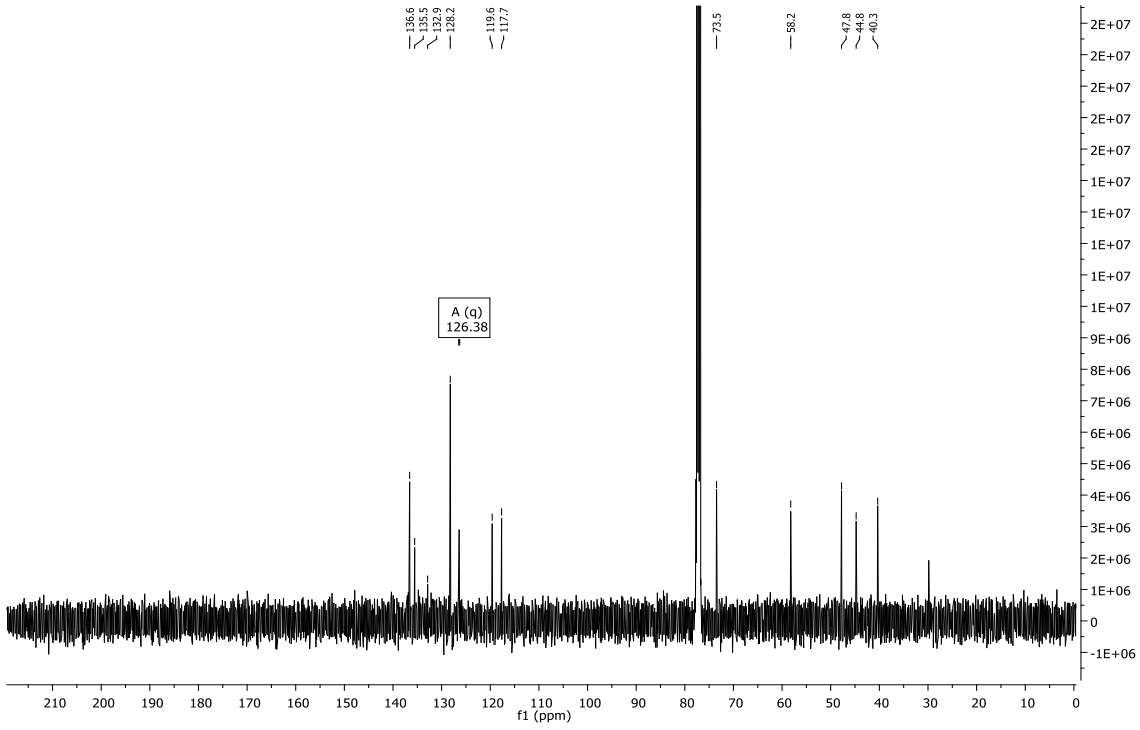
Supporting Information

4-Methoxymethyl-1-(4-trifluoromethyl-benzenesulfonyl)-3-vinyl-1,2,3,6-tetrahydro-pyridine

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

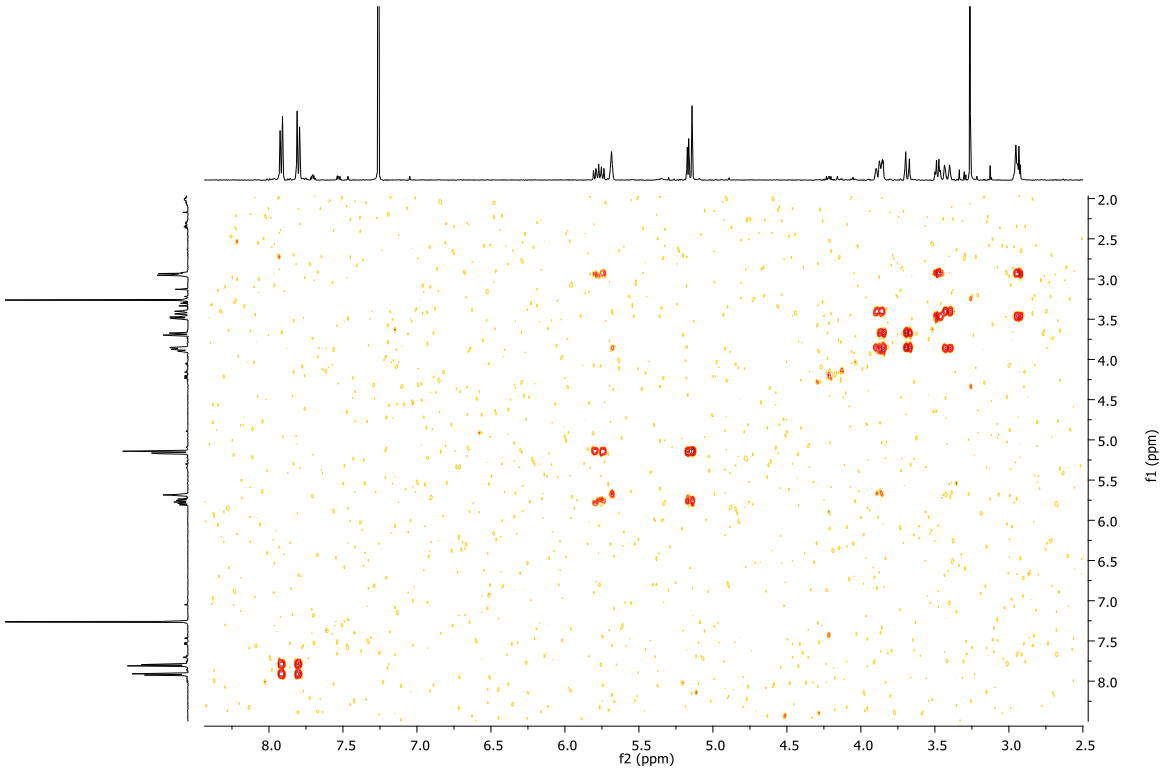


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

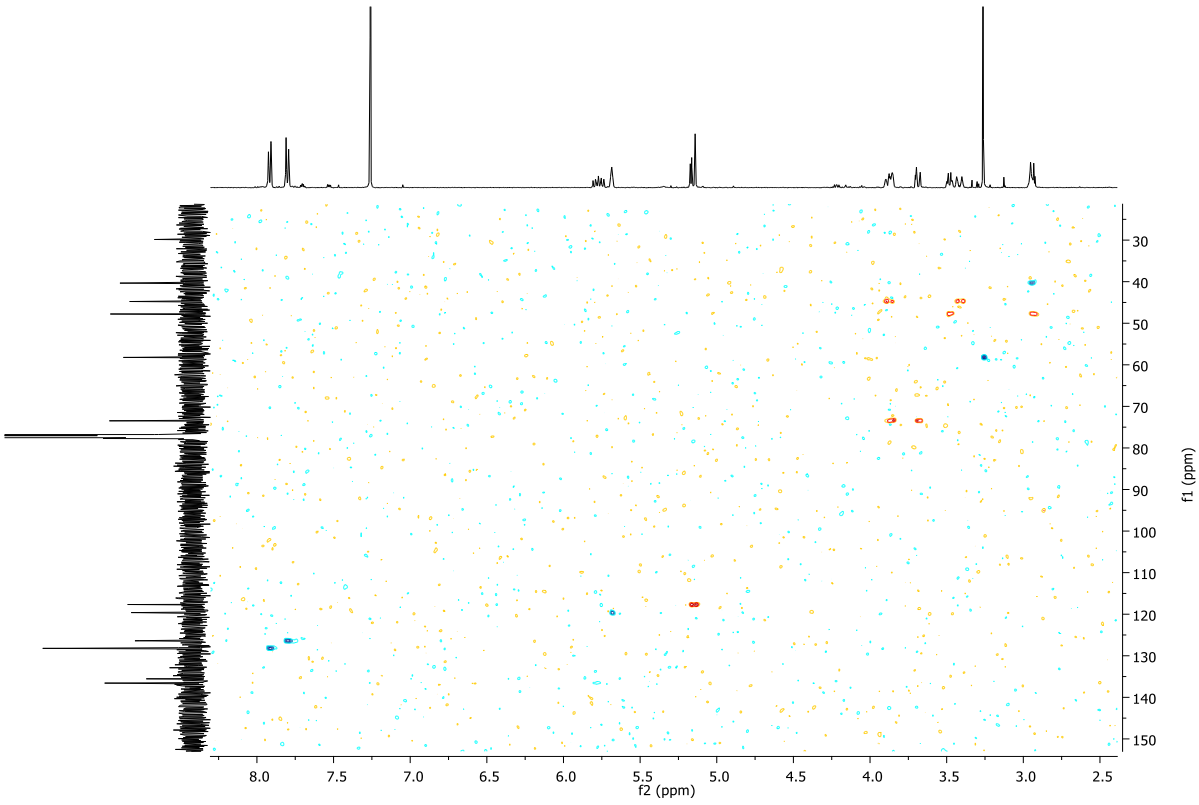


Supporting Information

2D gCOSY ($CDCl_3$)

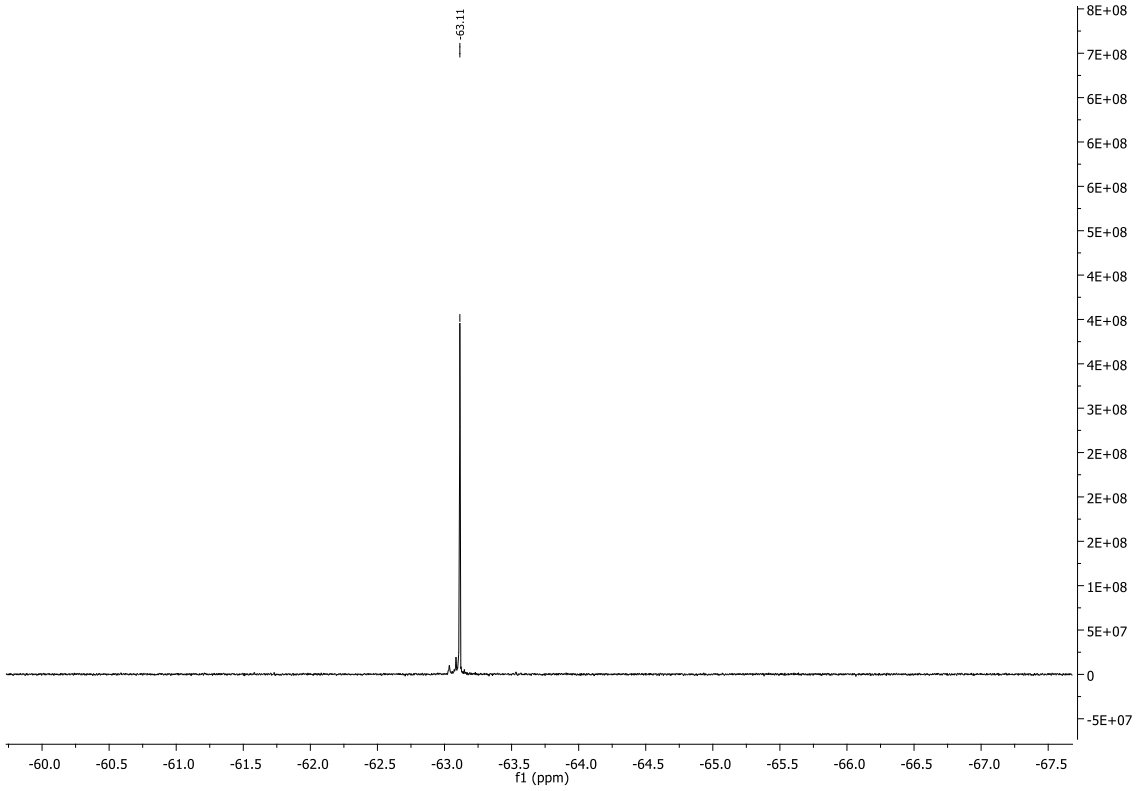


2D HSQC ($CDCl_3$)



Supporting Information

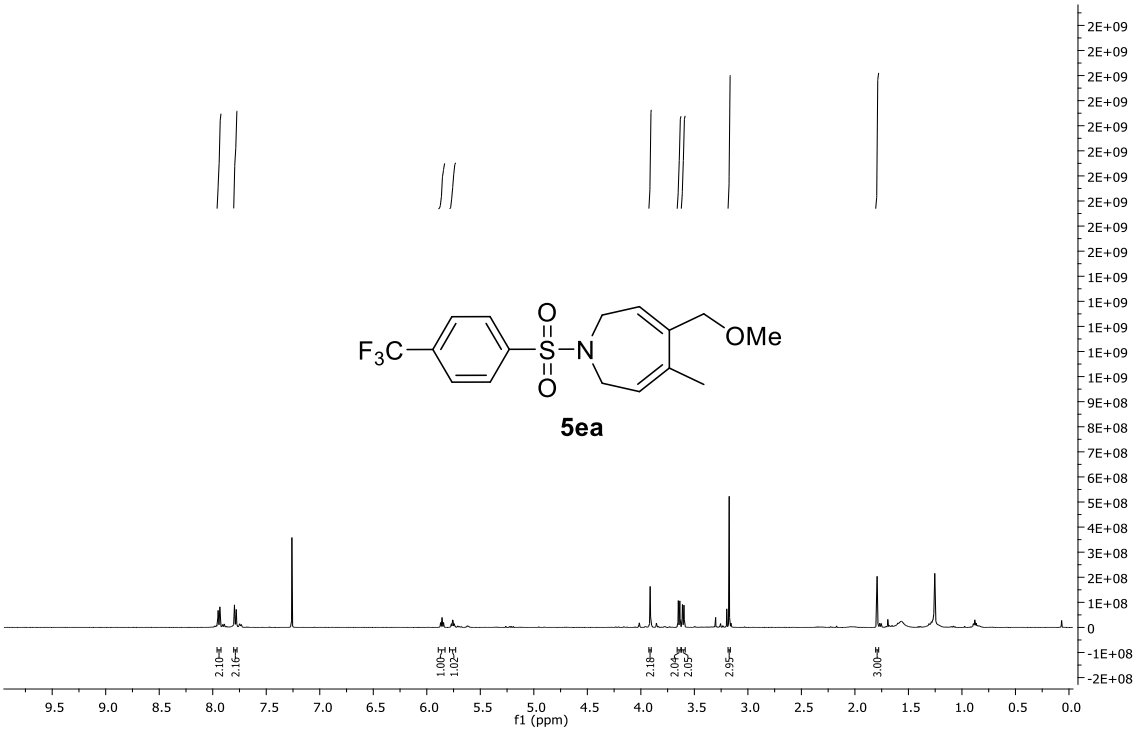
^{19}F NMR (471 MHz, $CDCl_3$)



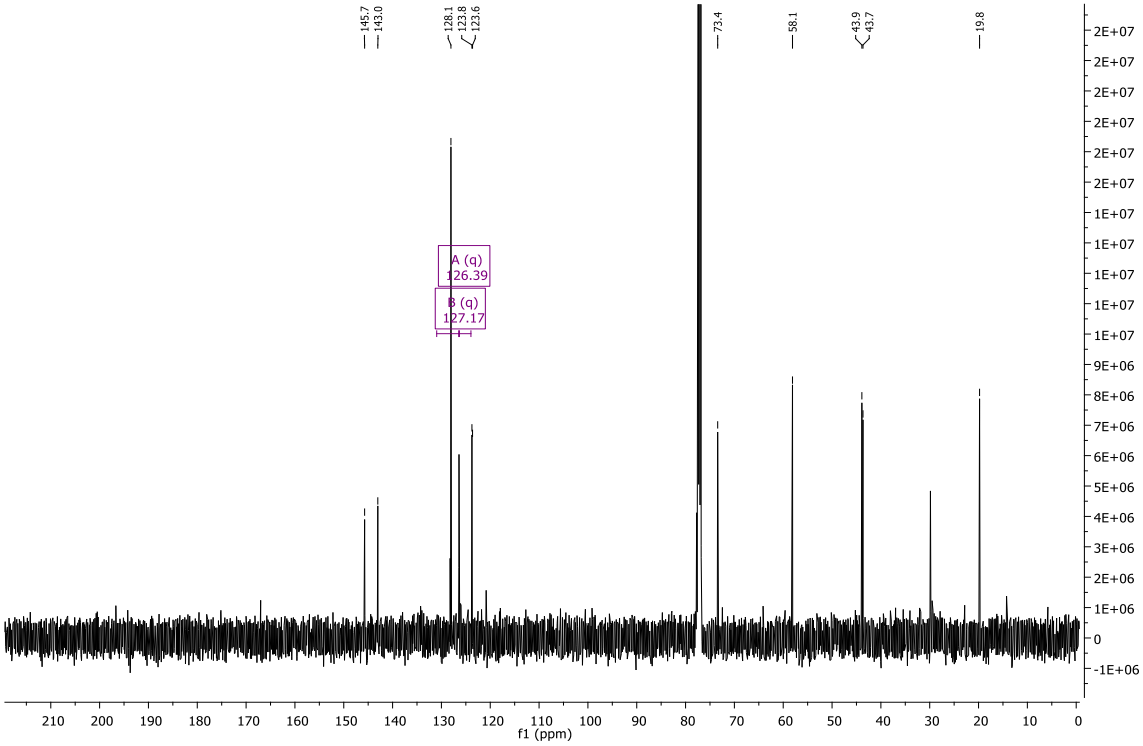
Supporting Information

***N*-(3-Methoxymethyl-4-methylene-hexa-2,5-dienyl)-4-trifluoromethyl-benzenesulfonamide**

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

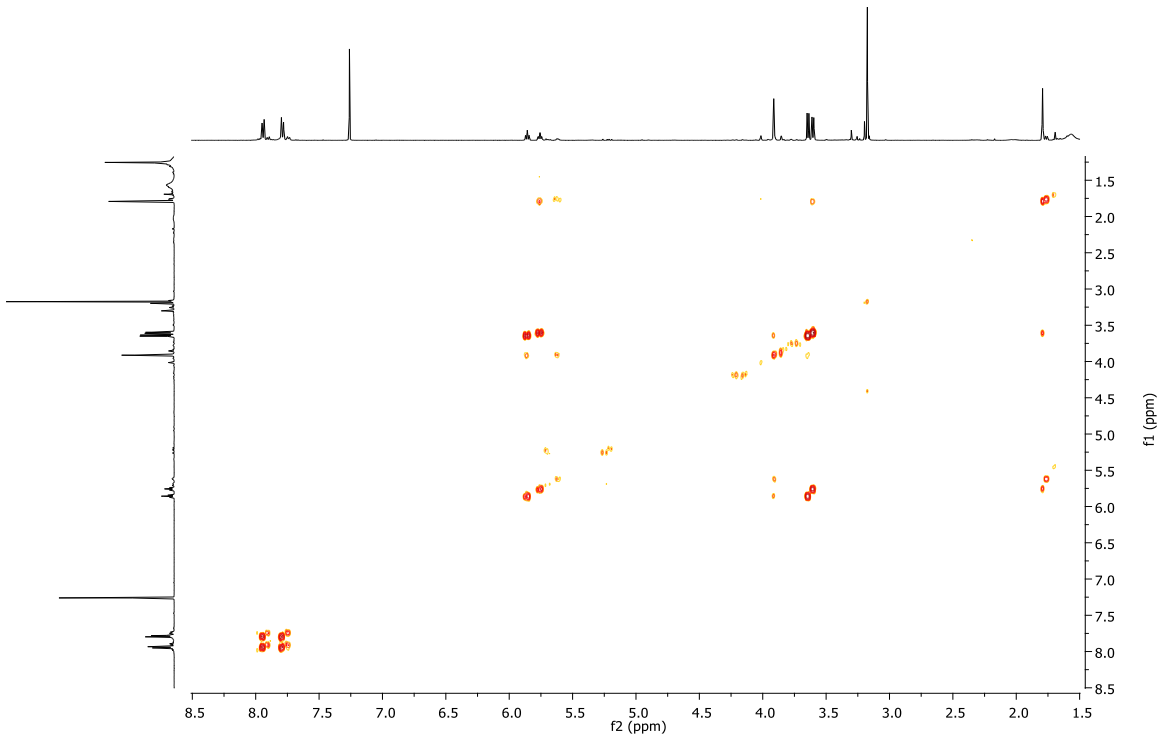


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

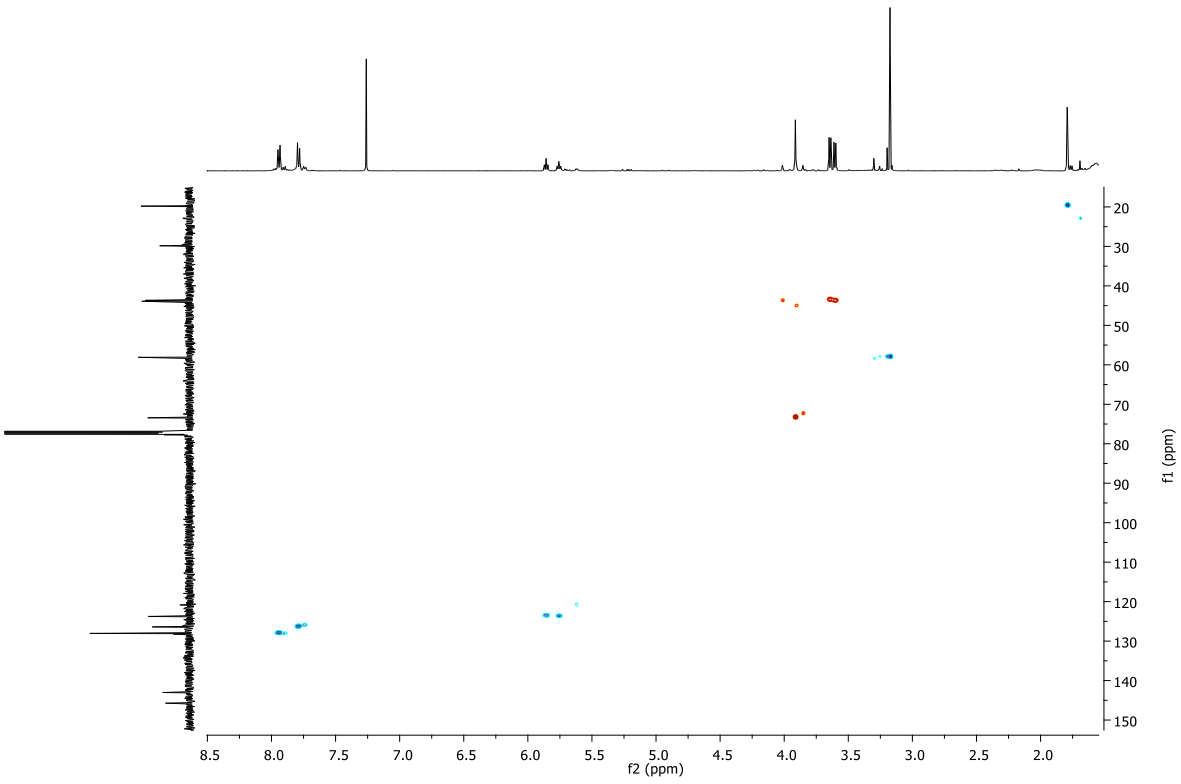


Supporting Information

2D gCOSY ($CDCl_3$)

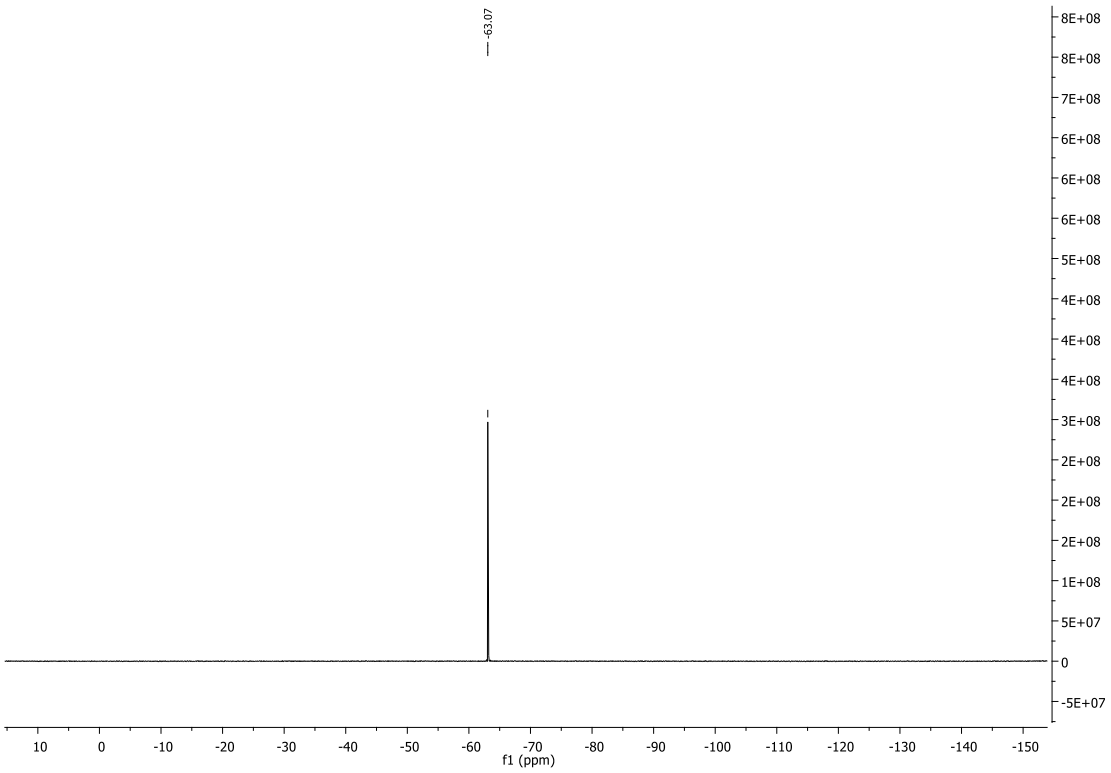


2D HSQC ($CDCl_3$)



Supporting Information

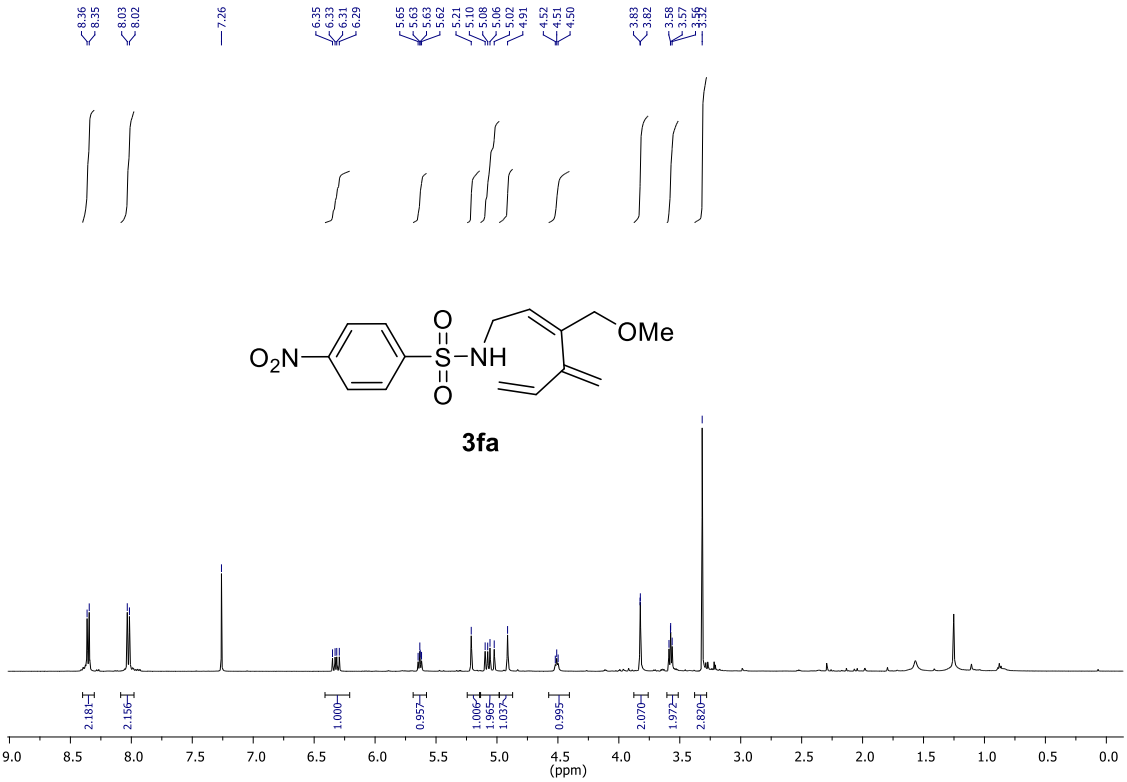
^{19}F NMR (471 MHz, $CDCl_3$)



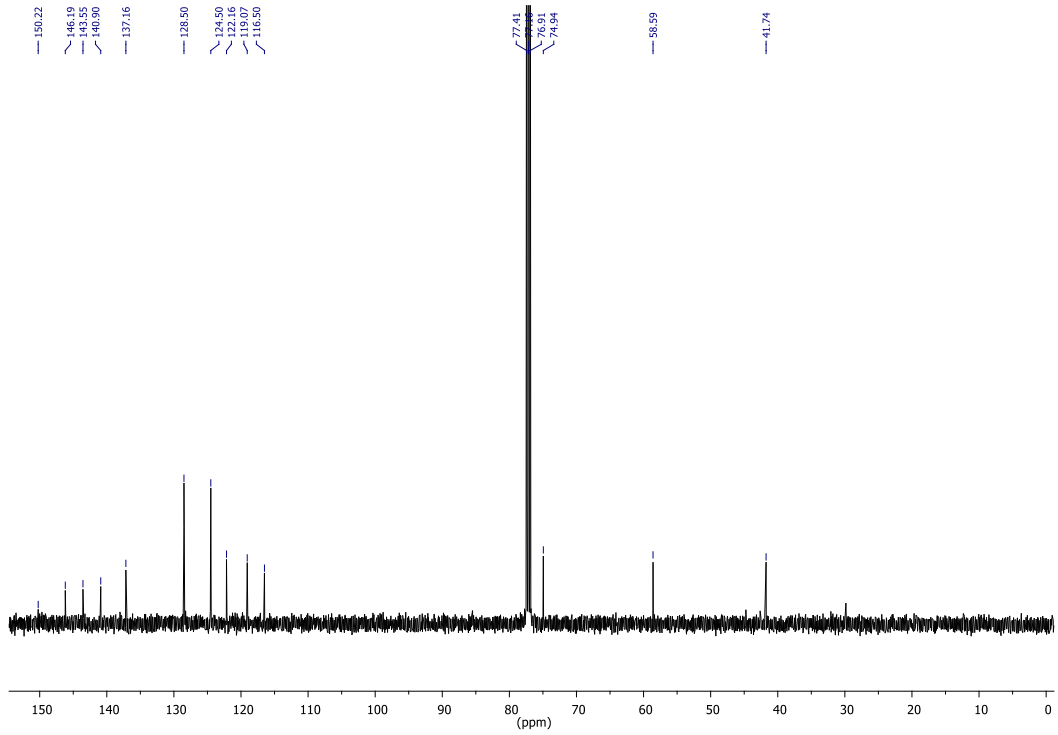
Supporting Information

N-(3-Methoxymethyl-4-methylene-hexa-2,5-dienyl)-4-nitro-benzenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

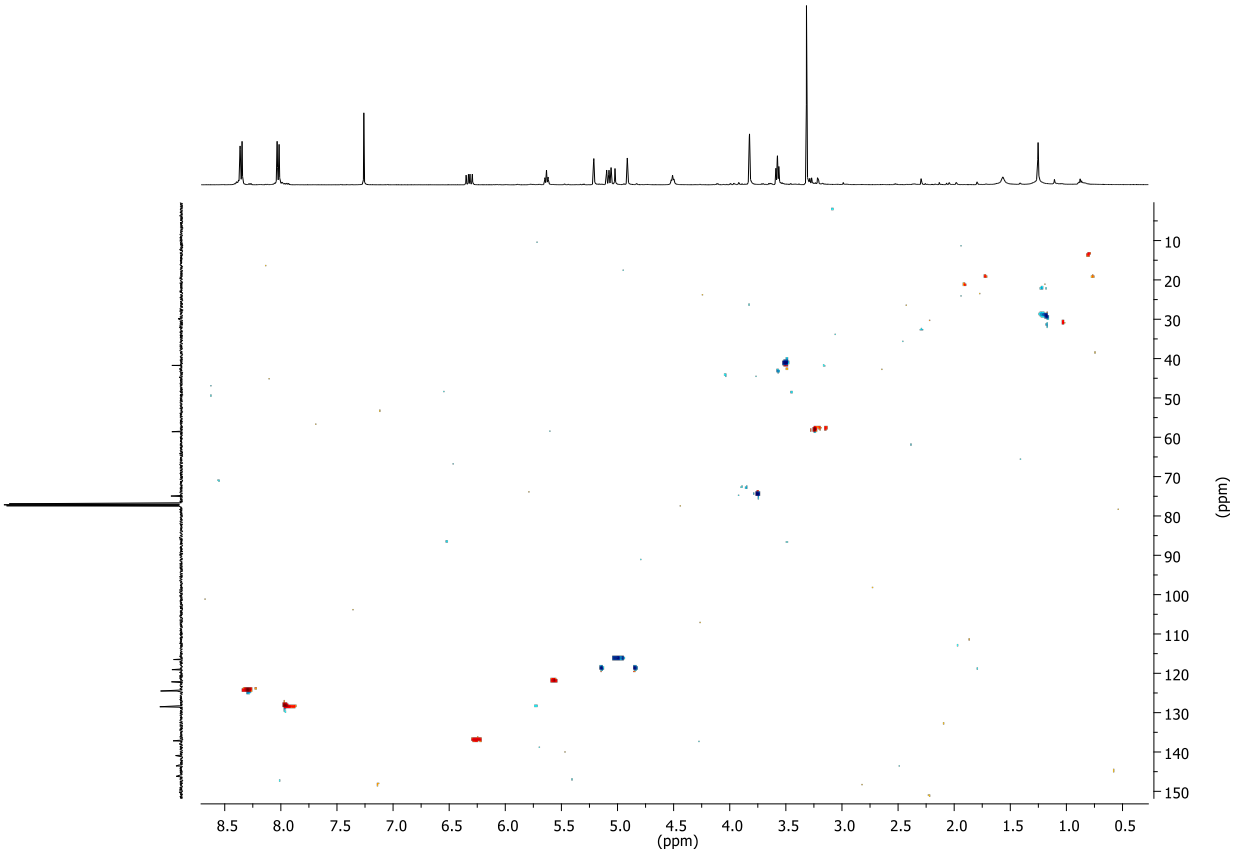


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



Supporting Information

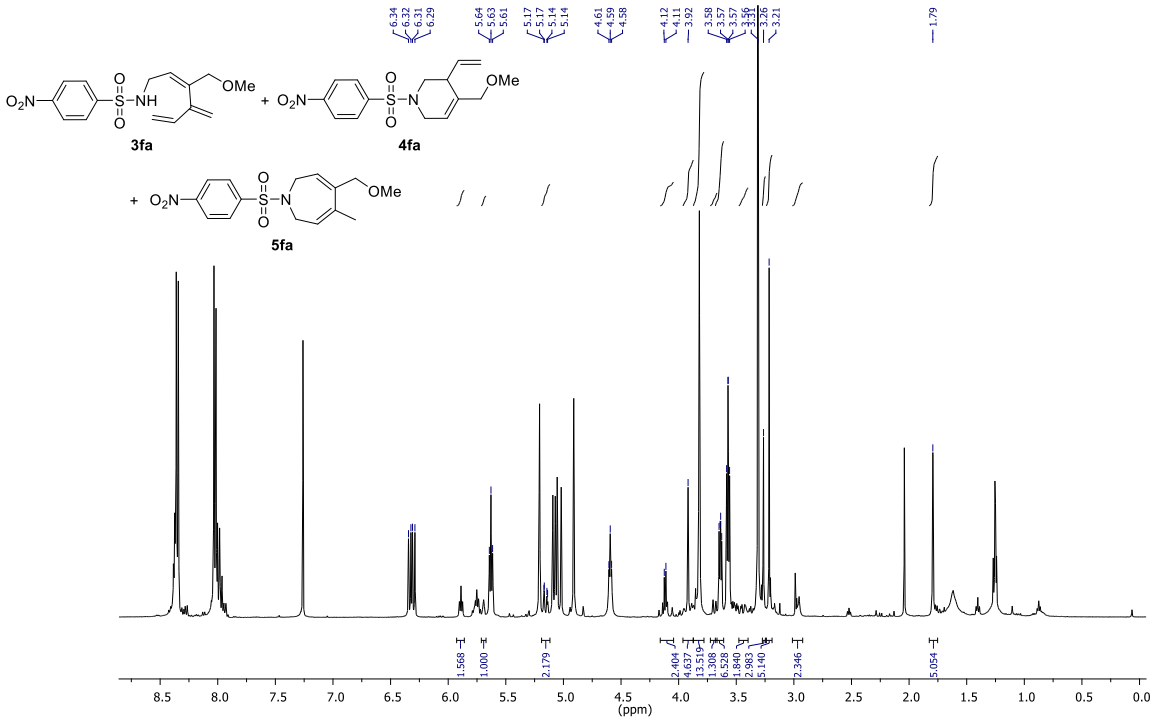
2D HSQC ($CDCl_3$)



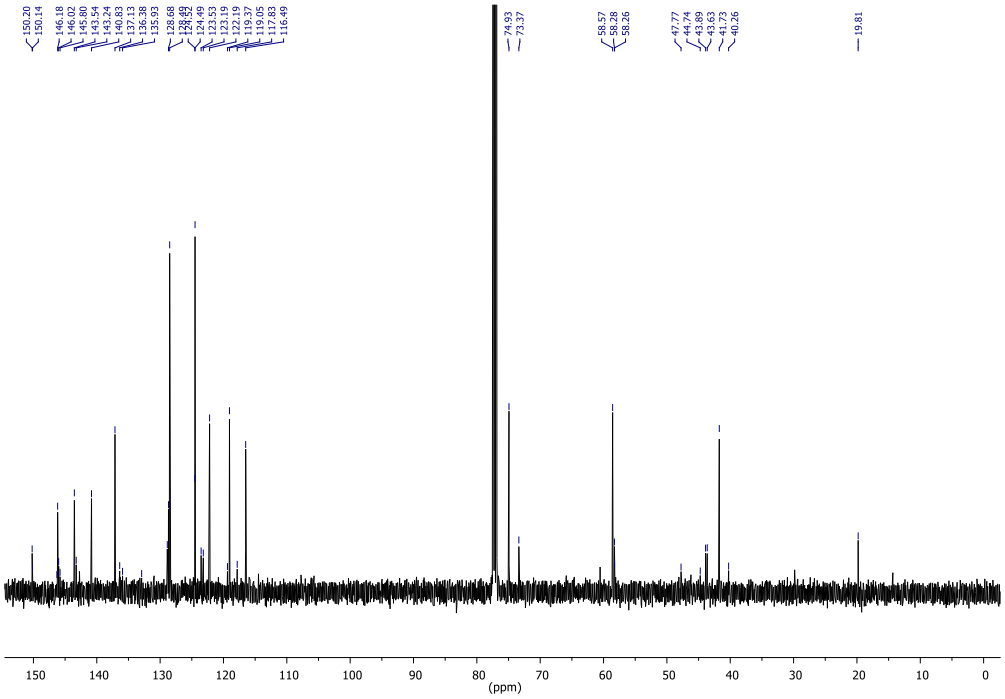
Supporting Information

N-(3-Methoxymethyl-4-methylene-hexa-2,5-dienyl)-4-nitro-benzenesulfonamide (3fa), 4-Methoxymethyl-1-(4-nitrobenzenesulfonyl)-3-vinyl-1,2,3,6-tetrahydro-pyridine (4fa) and 4-Methoxymethyl-5-methyl-1-(4-nitro-benzenesulfonyl)-2,7-dihydro-1H-azepine (5fa)

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)



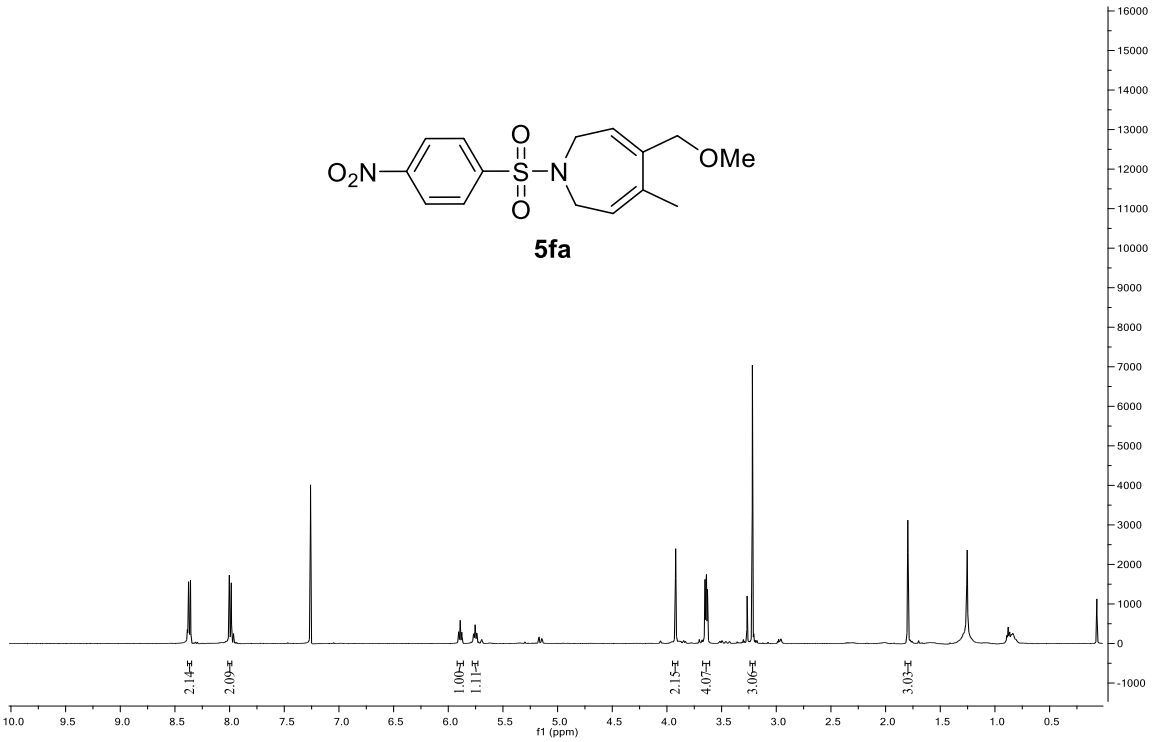
^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



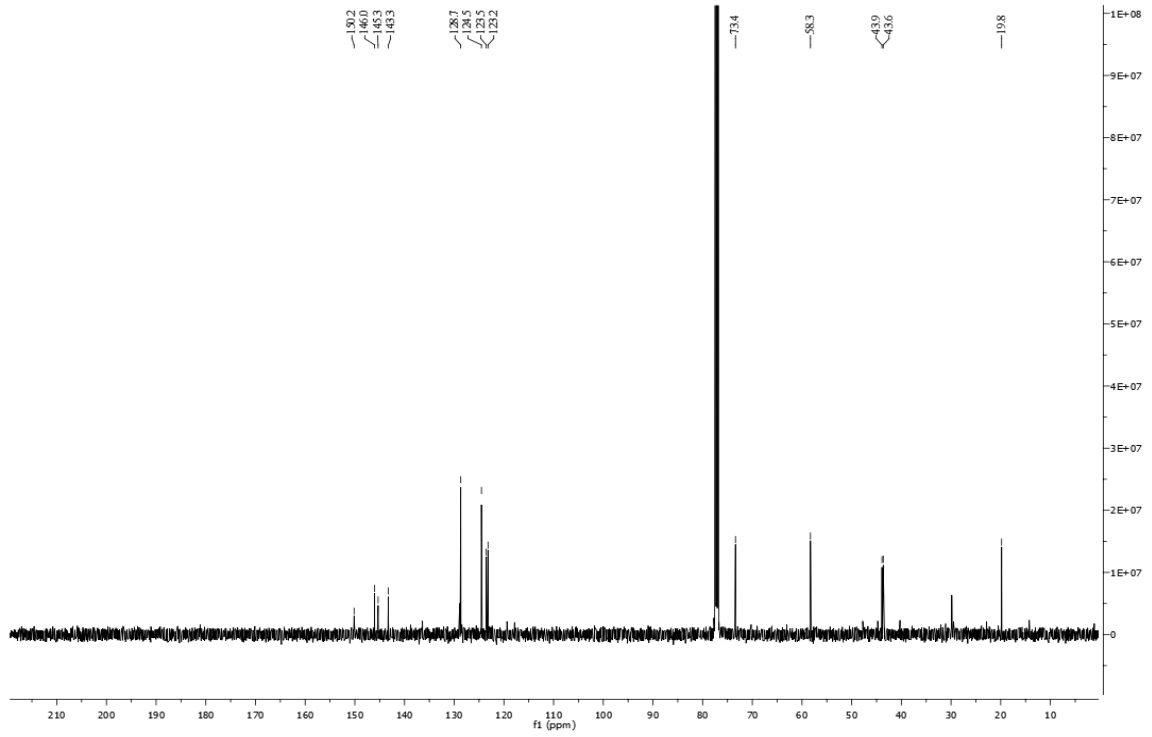
Supporting Information

4-Methoxymethyl-5-methyl-1-(4-nitro-benzenesulfonyl)-2,7-dihydro-1*H*-azepine

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

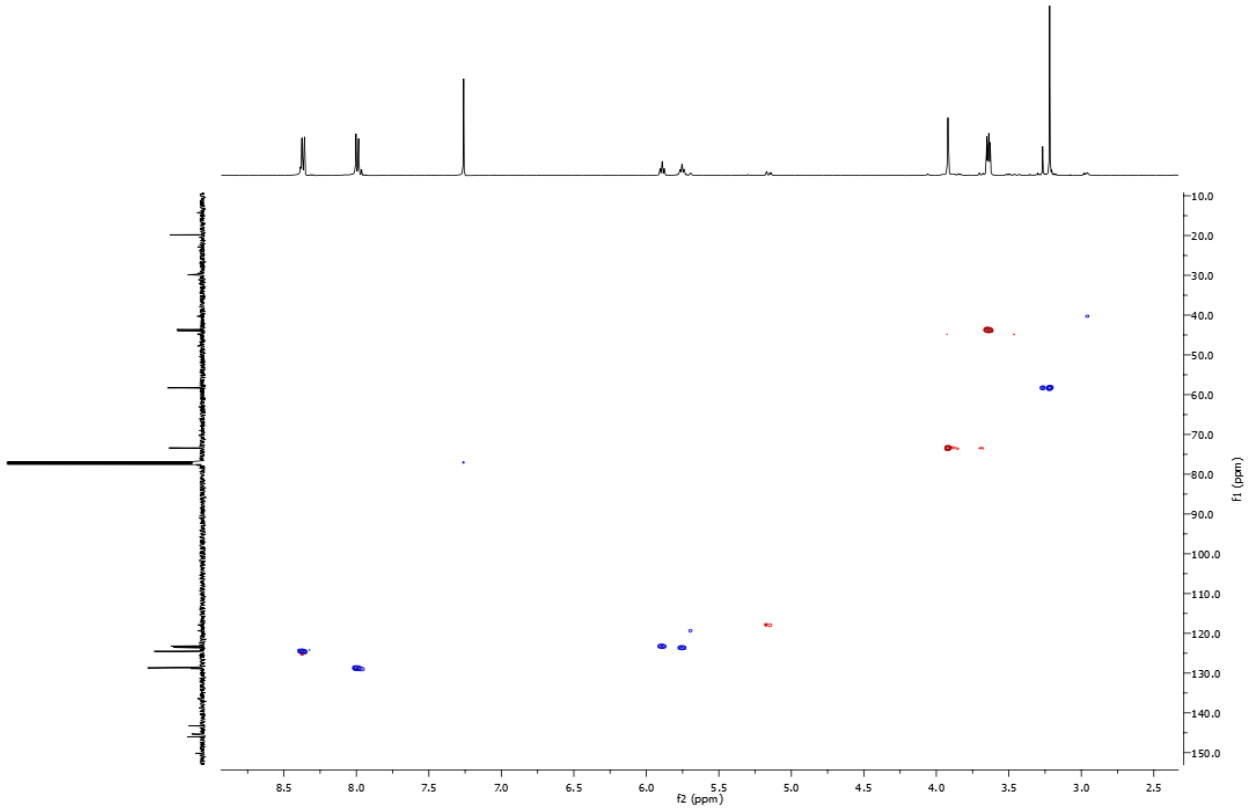


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



Supporting Information

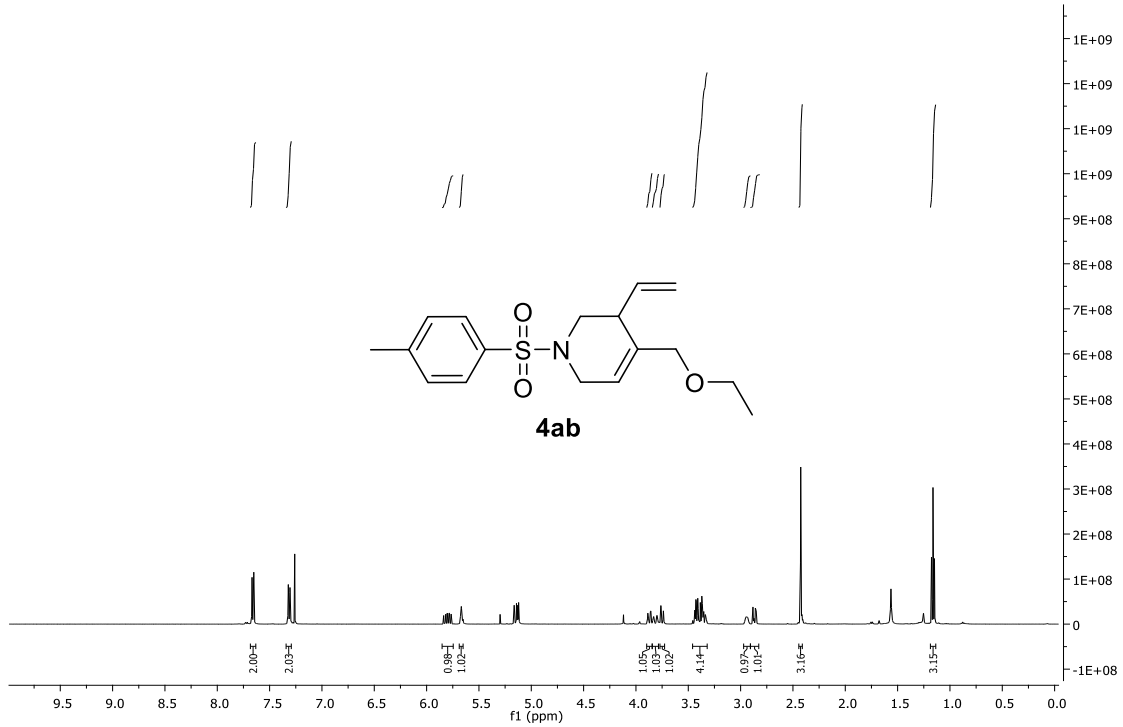
2D HSQC ($CDCl_3$)



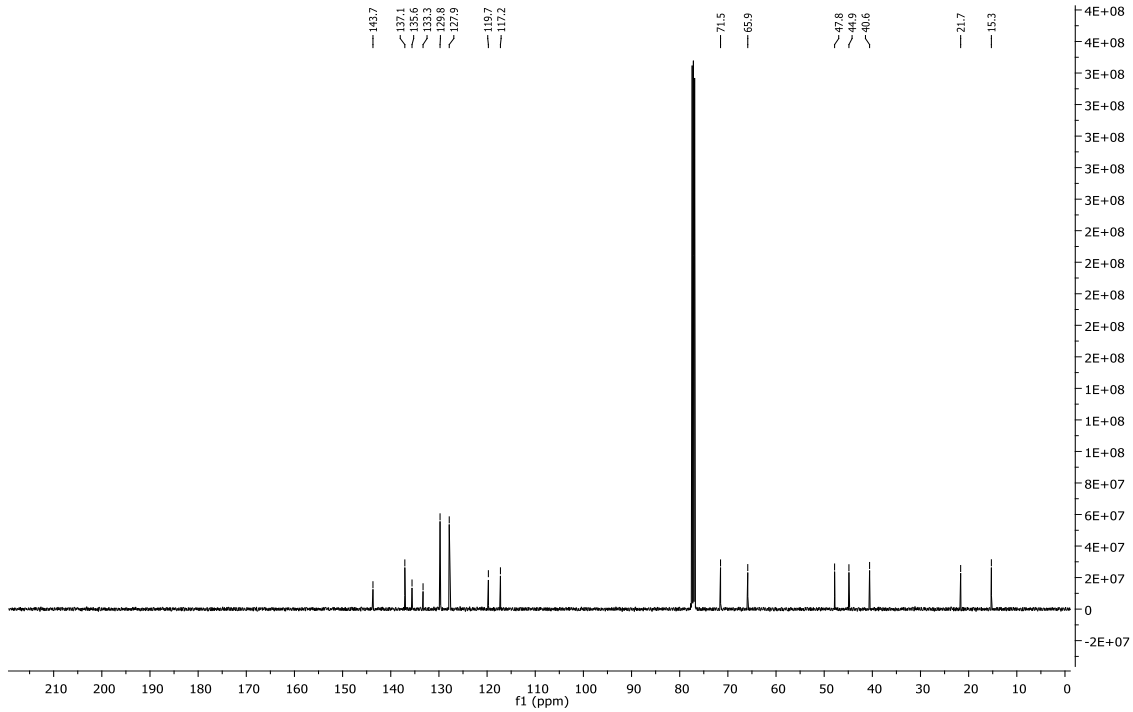
Supporting Information

4-Ethoxymethyl-1-(toluene-4-sulfonyl)-3-vinyl-1,2,3,6-tetrahydro-pyridine

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

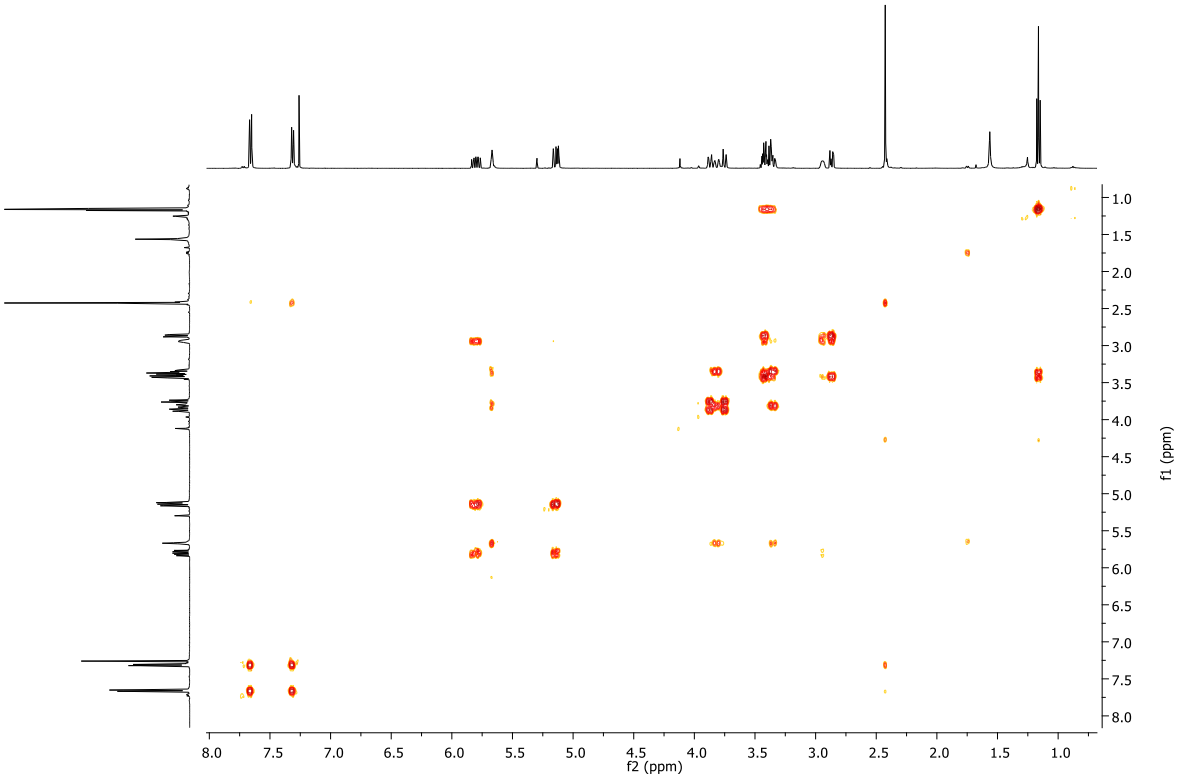


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

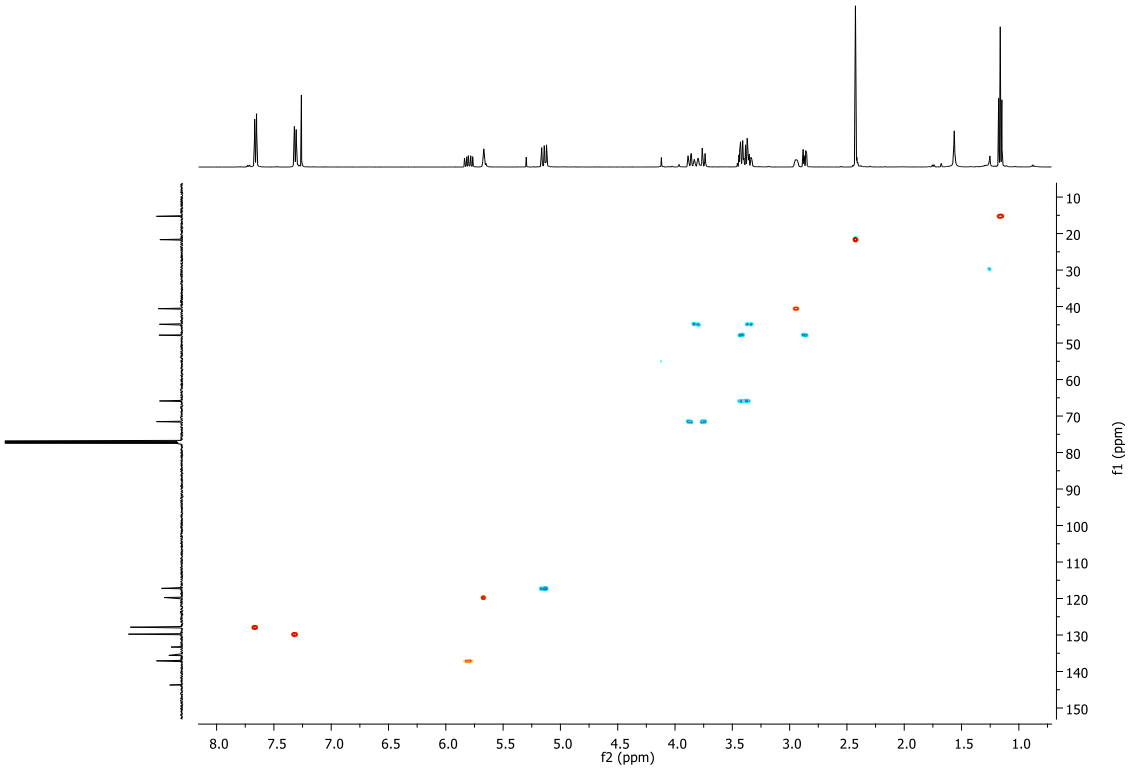


Supporting Information

2D gCOSY ($CDCl_3$)



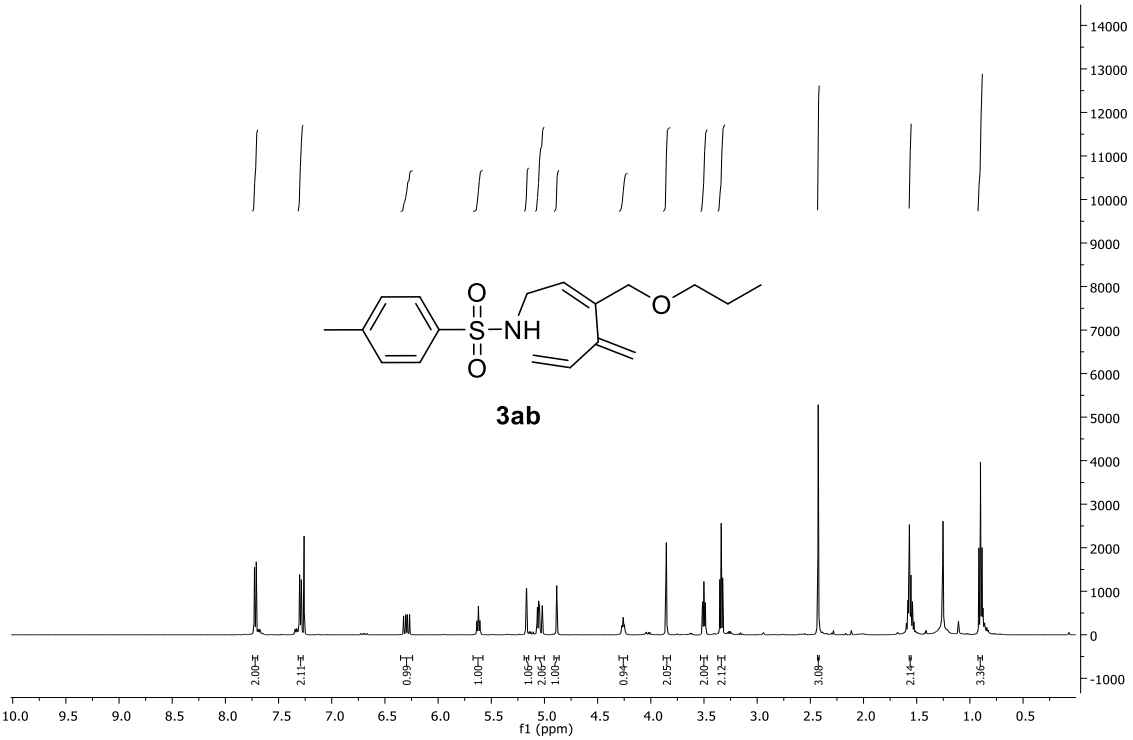
2D HSQC ($CDCl_3$)



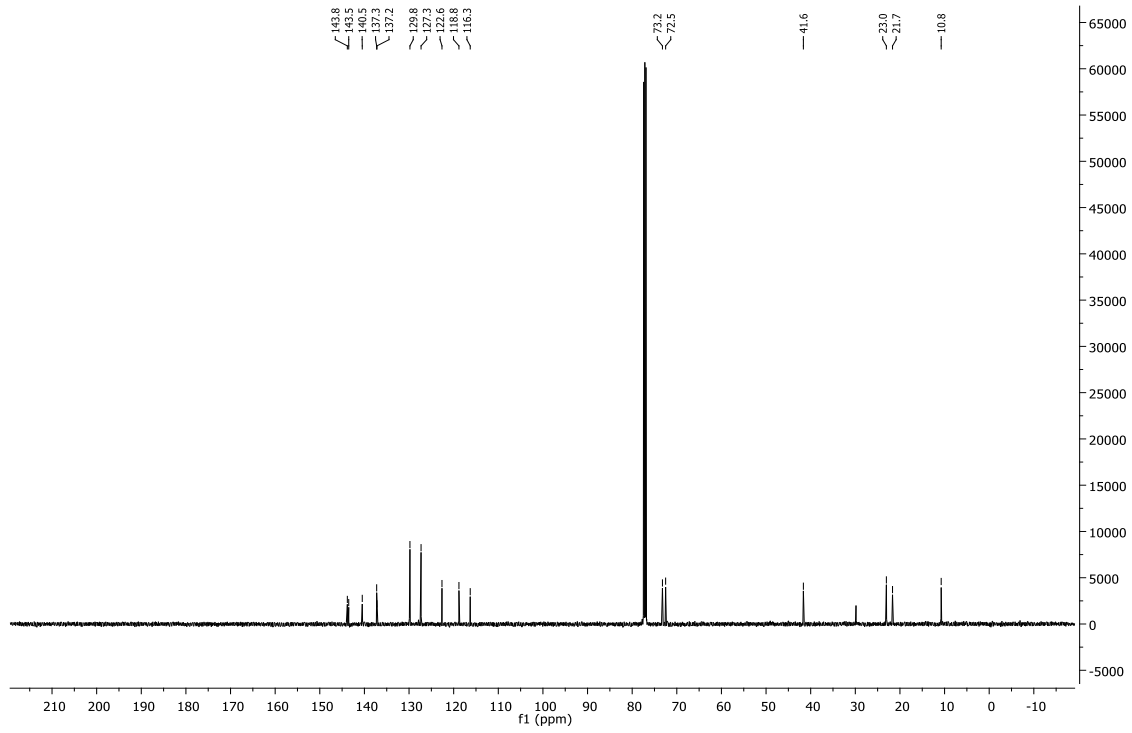
Supporting Information

4-Methyl-*N*-(4-methylene-3-propoxymethyl-hexa-2,5-dienyl)-benzenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)



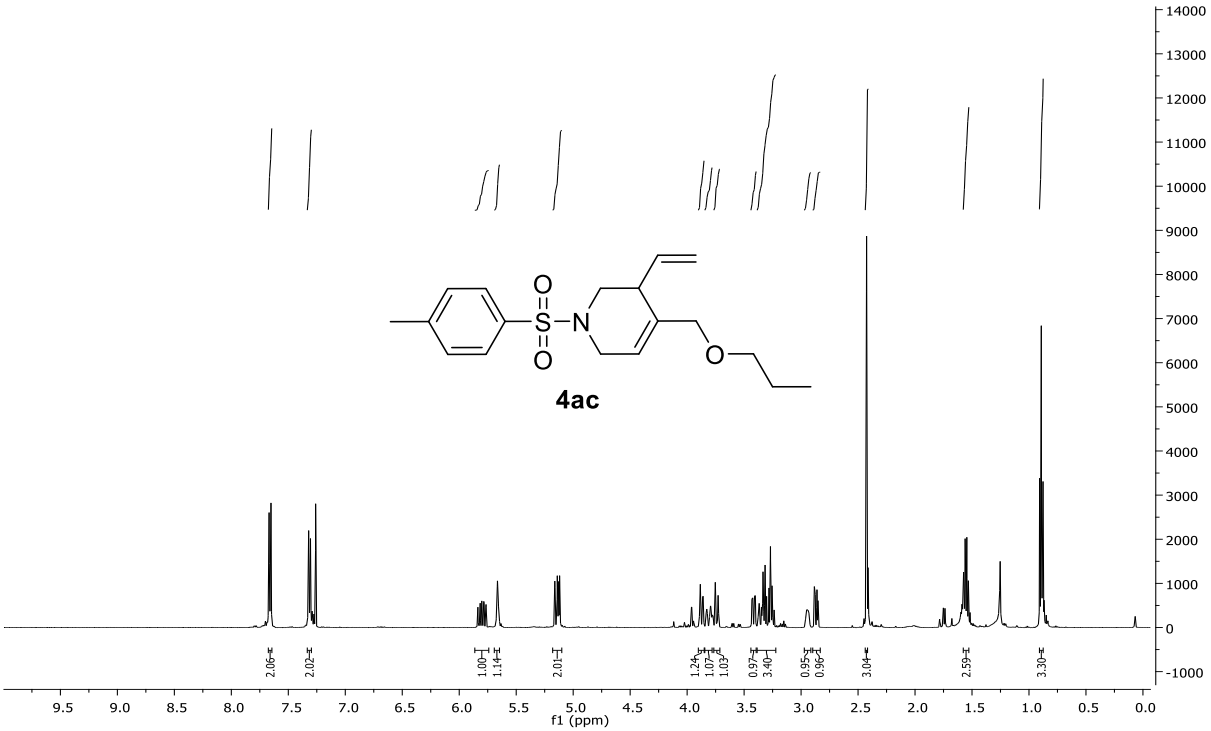
^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



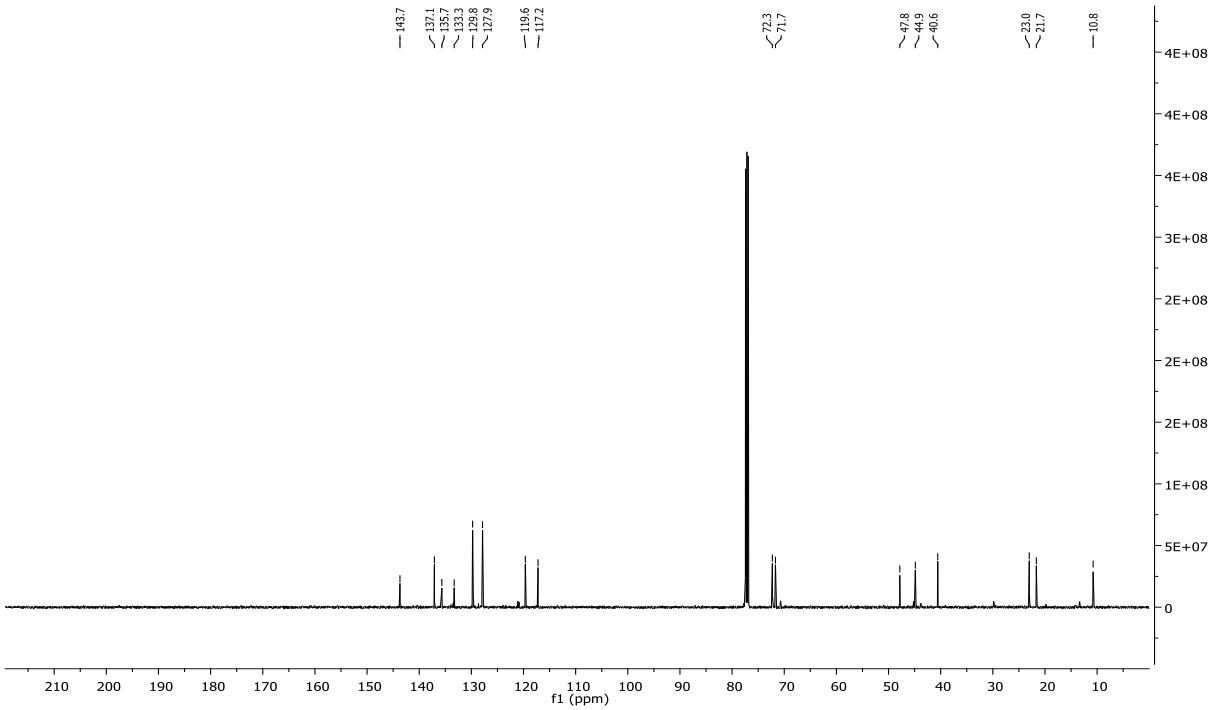
Supporting Information

4-Propoxymethyl-1-(toluene-4-sulfonyl)-3-vinyl-1,2,3,6-tetrahydro-pyridine

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

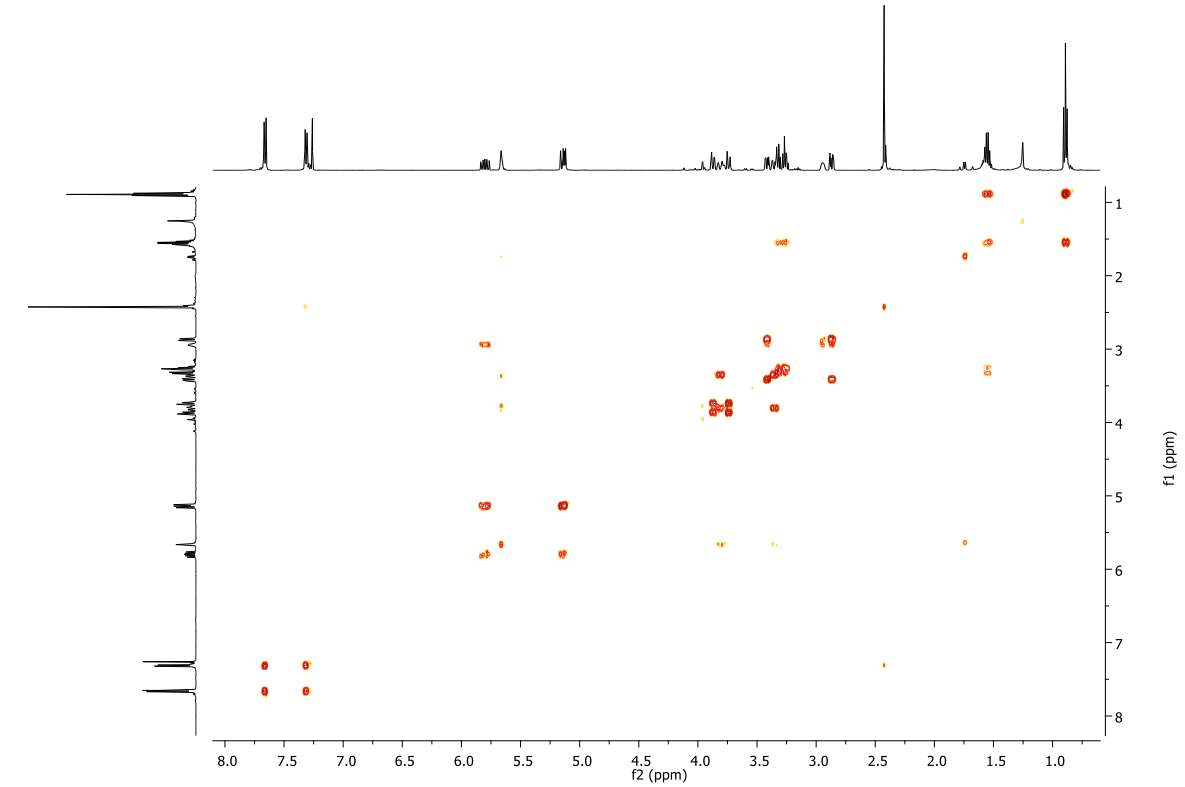


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

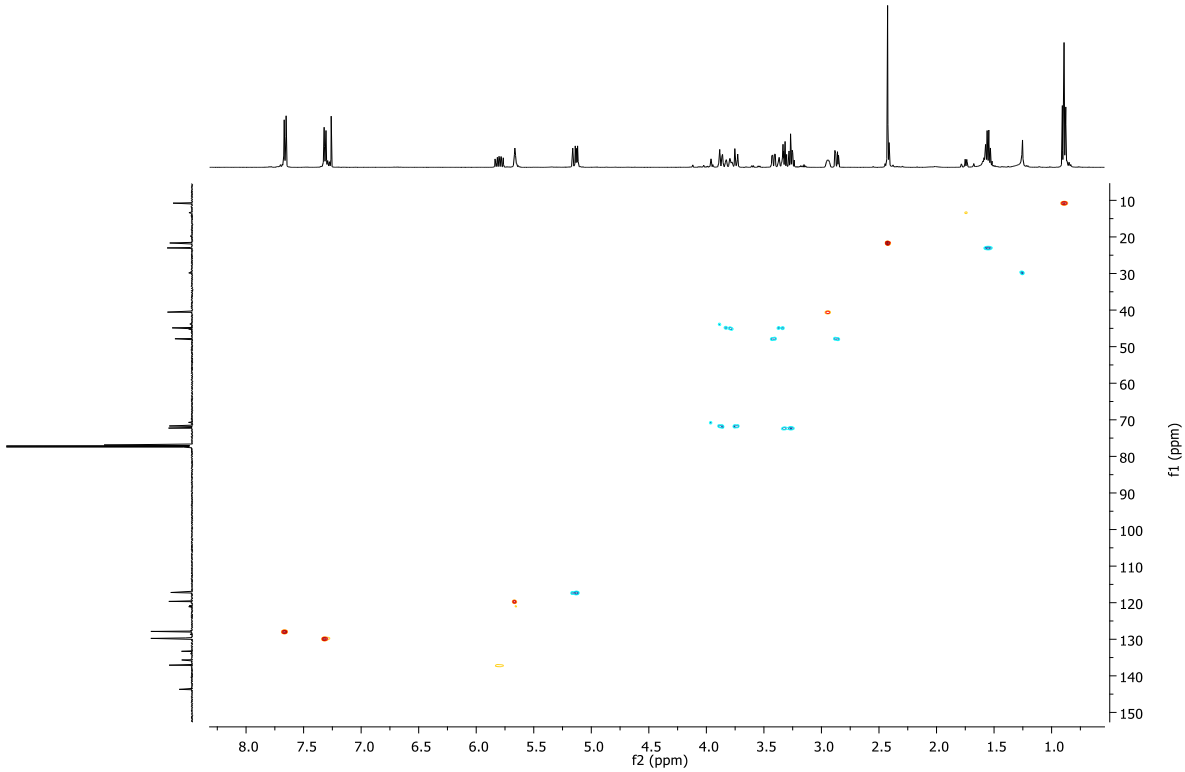


Supporting Information

2D gCOSY ($CDCl_3$)



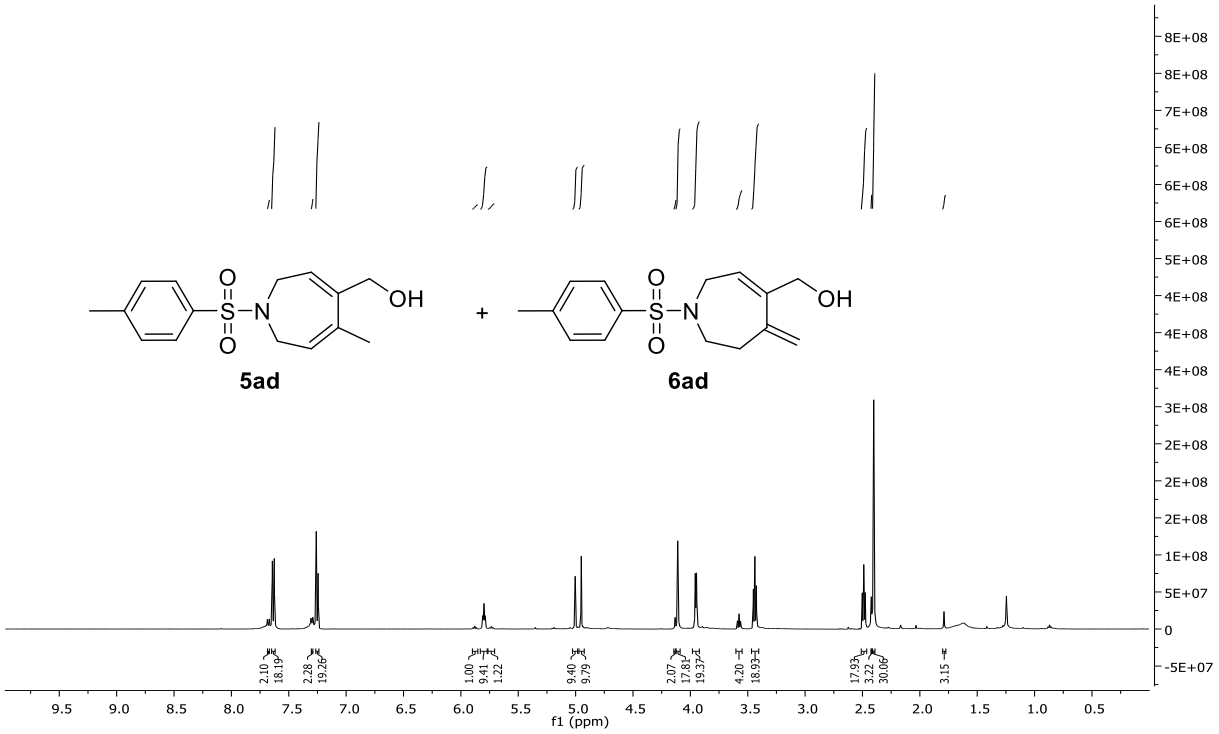
2D HSQC ($CDCl_3$)



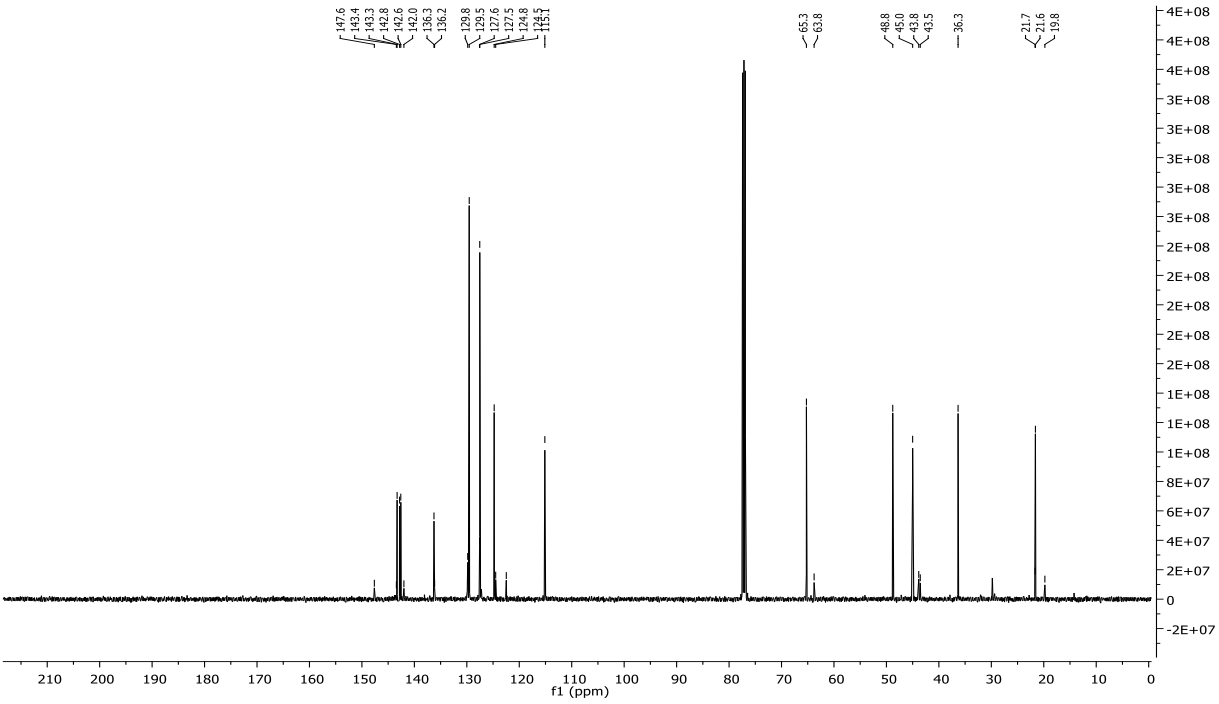
Supporting Information

[5-Methyl-1-(toluene-4-sulfonyl)-2,7-dihydro-1*H*-azepin-4-yl]-methanol and [5-Methylene-1-(toluene-4-sulfonyl)-2,5,6,7-tetrahydro-1*H*-azepin-4-yl]-methanol. (1:9.8)

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

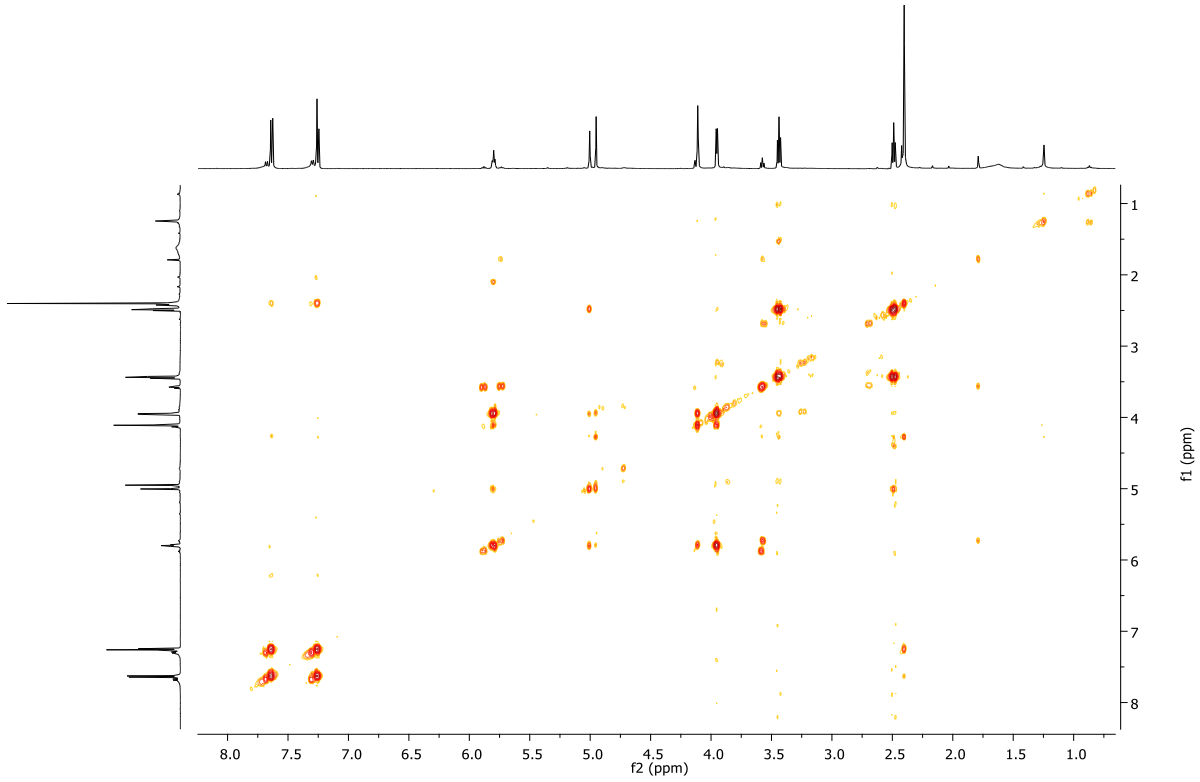


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

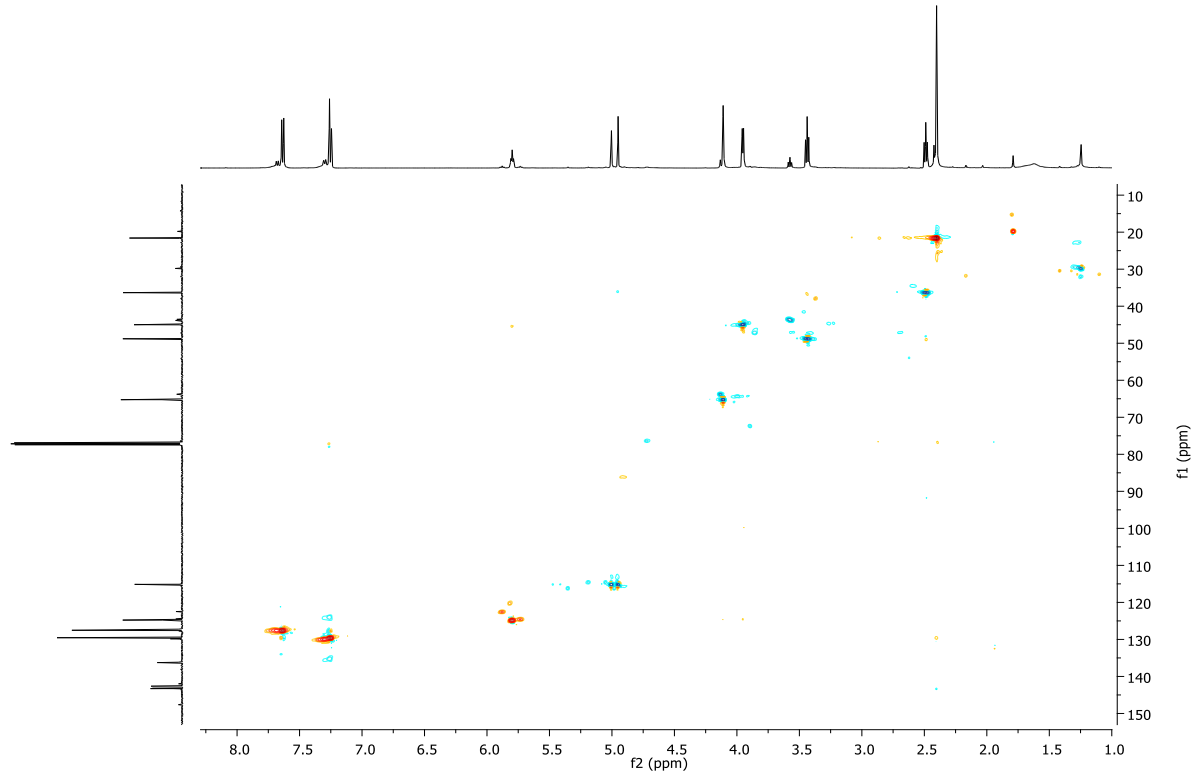


Supporting Information

2D gCOSY ($CDCl_3$)



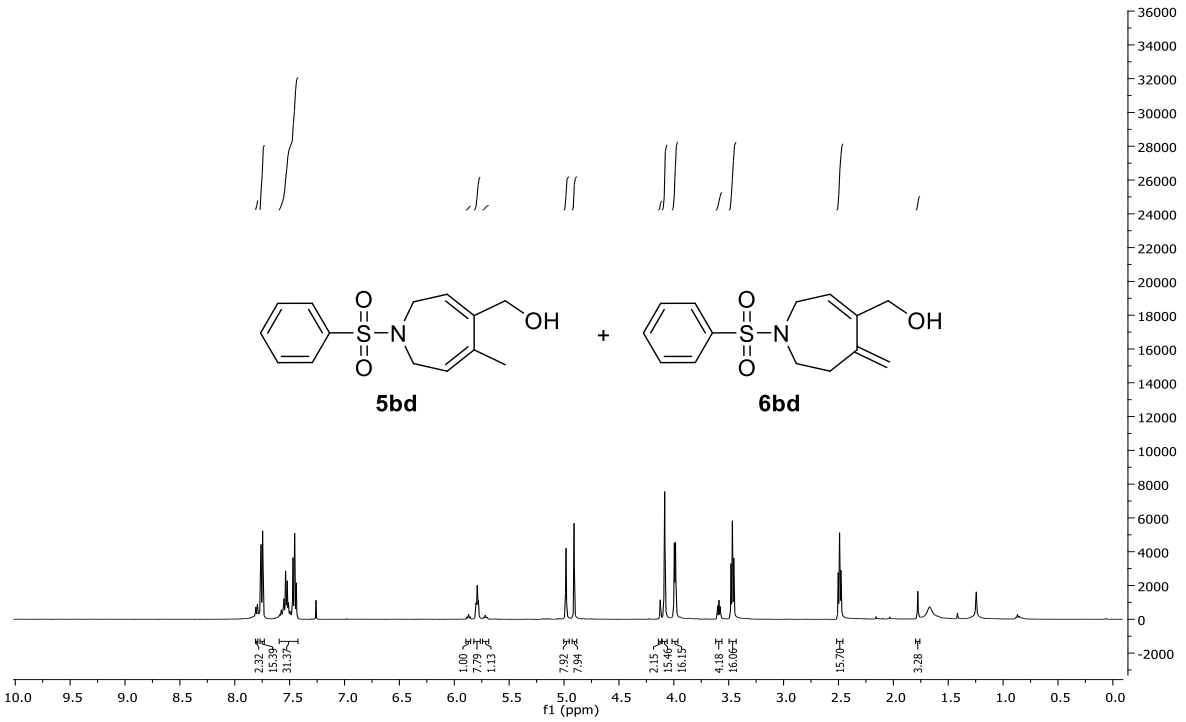
2D HSQC ($CDCl_3$)



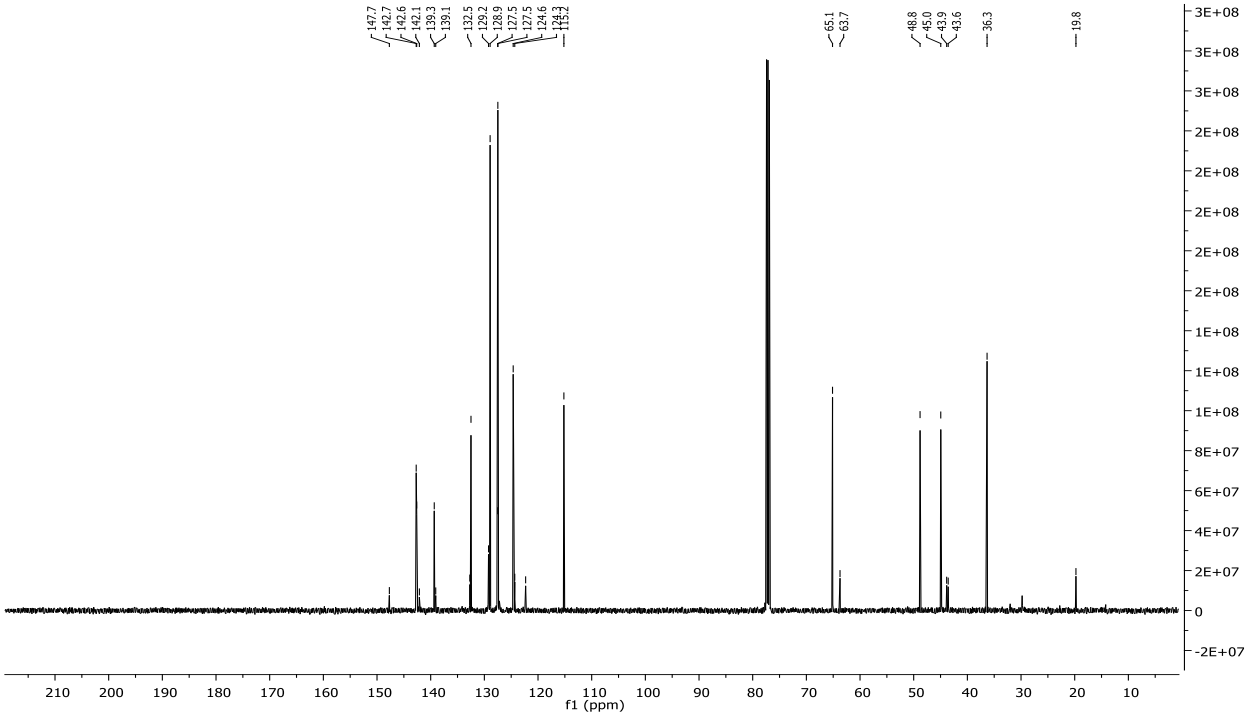
Supporting Information

(1-Benzenesulfonyl-5-methyl-2,7-dihydro-1*H*-azepin-4-yl)-methanol and (1-Benzenesulfonyl-5-methylene-2,5,6,7-tetrahydro-1*H*-azepin-4-yl)-methanol. (1:7.8)

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

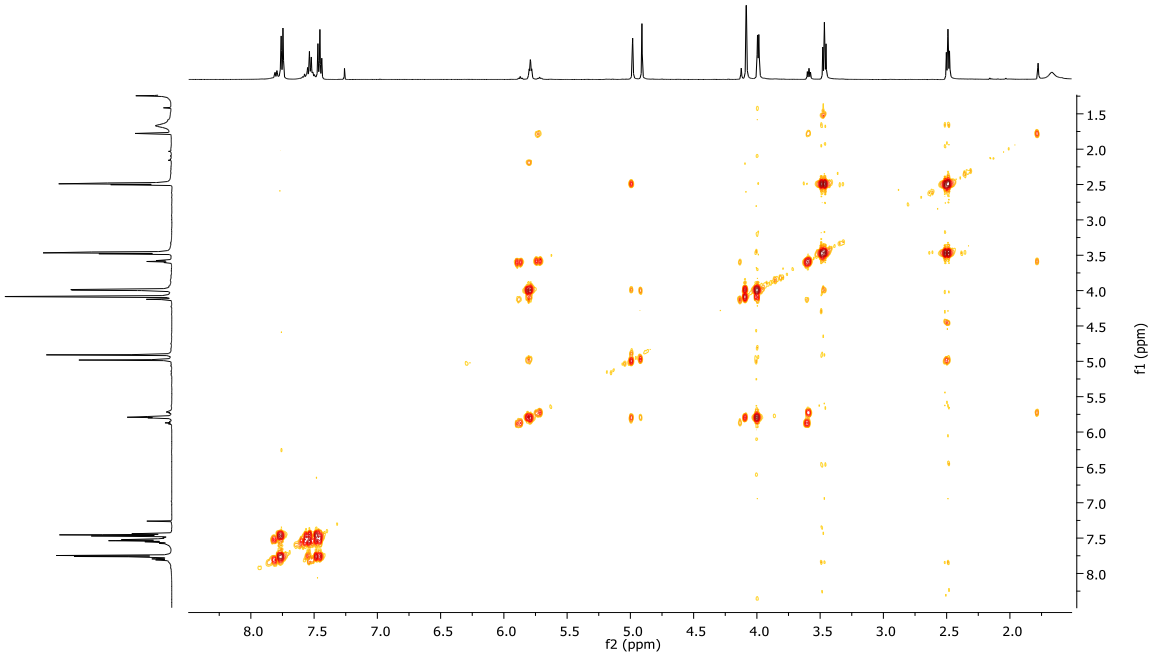


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

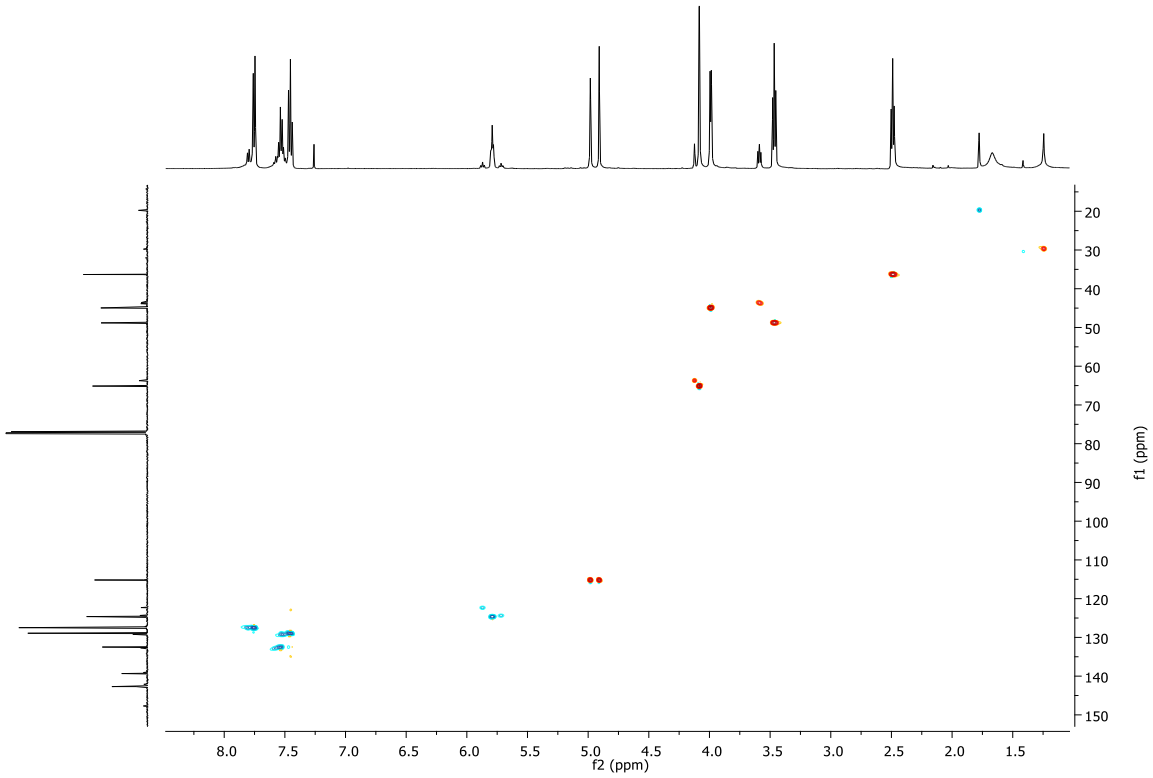


Supporting Information

2D gCOSY ($CDCl_3$)



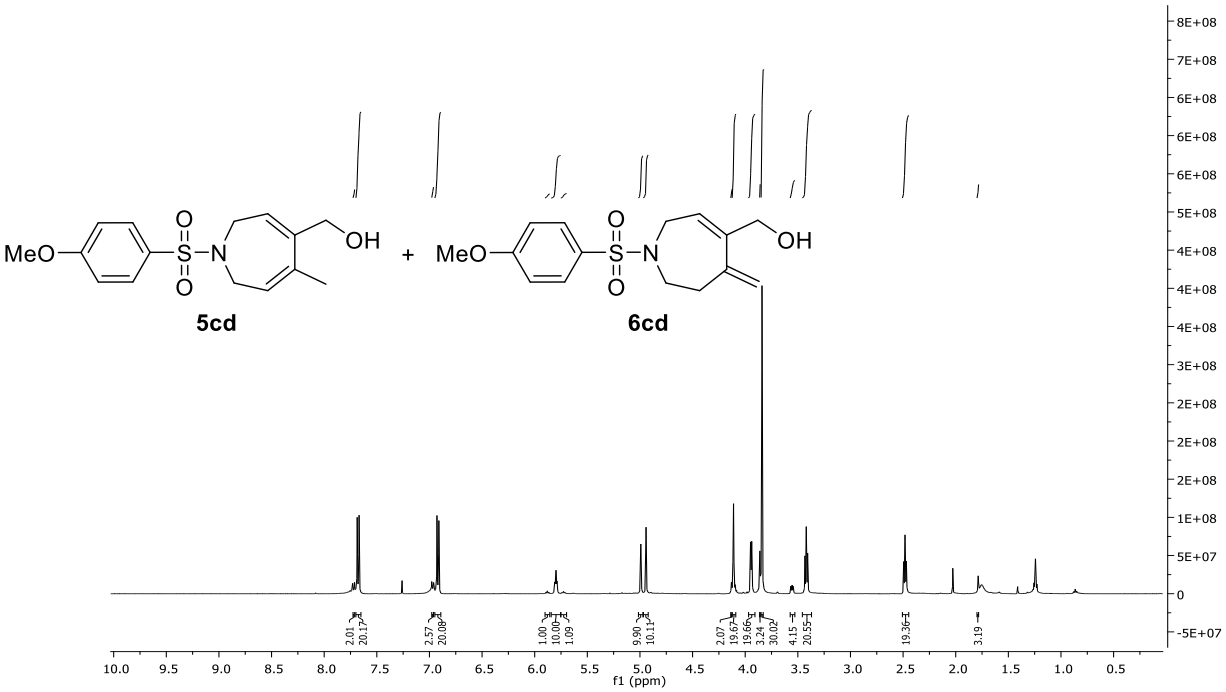
2D HSQC ($CDCl_3$)



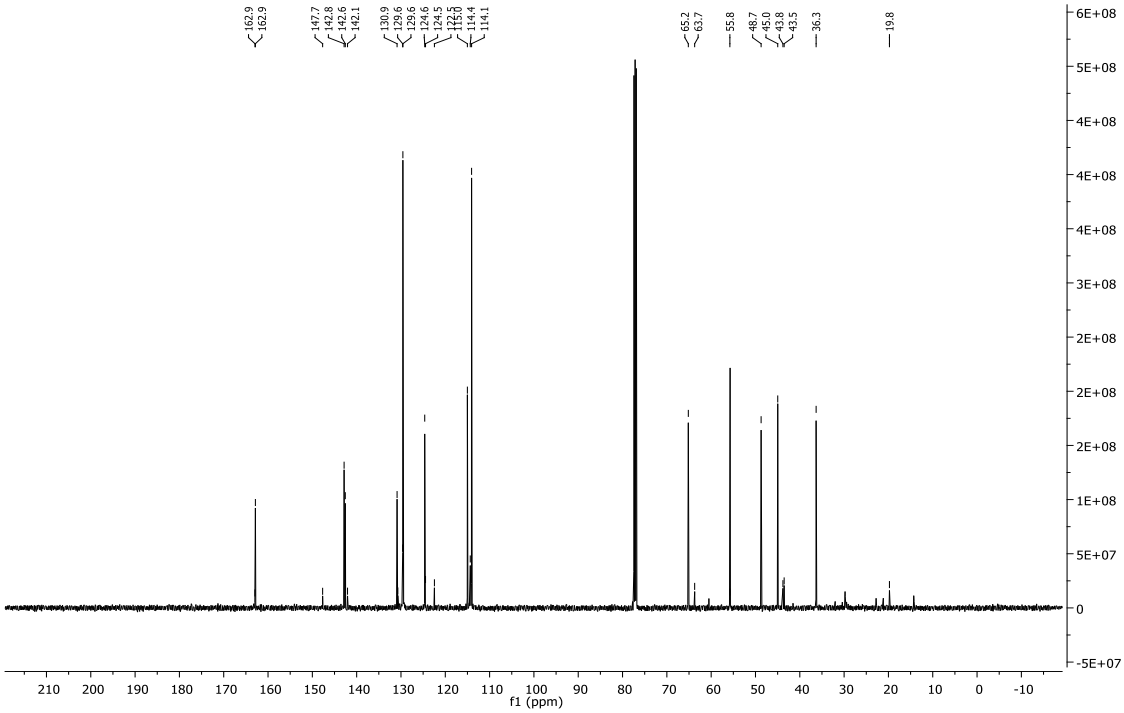
Supporting Information

[1-(4-Methoxy-benzenesulfonyl)-5-methyl-2,7-dihydro-1*H*-azepin-4-yl]-methanol and [1-(4-Methoxy-benzenesulfonyl)-5-methylene-2,5,6,7-tetrahydro-1*H*-azepin-4-yl]-methanol. (1:10)

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

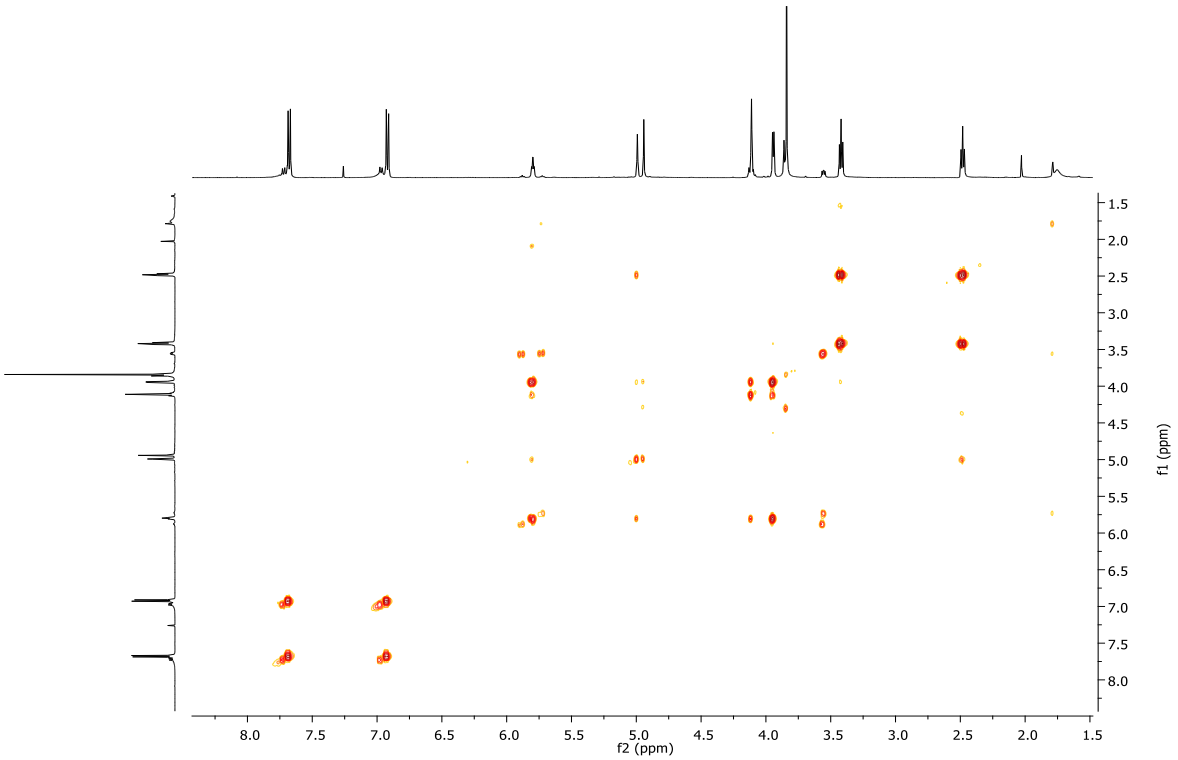


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

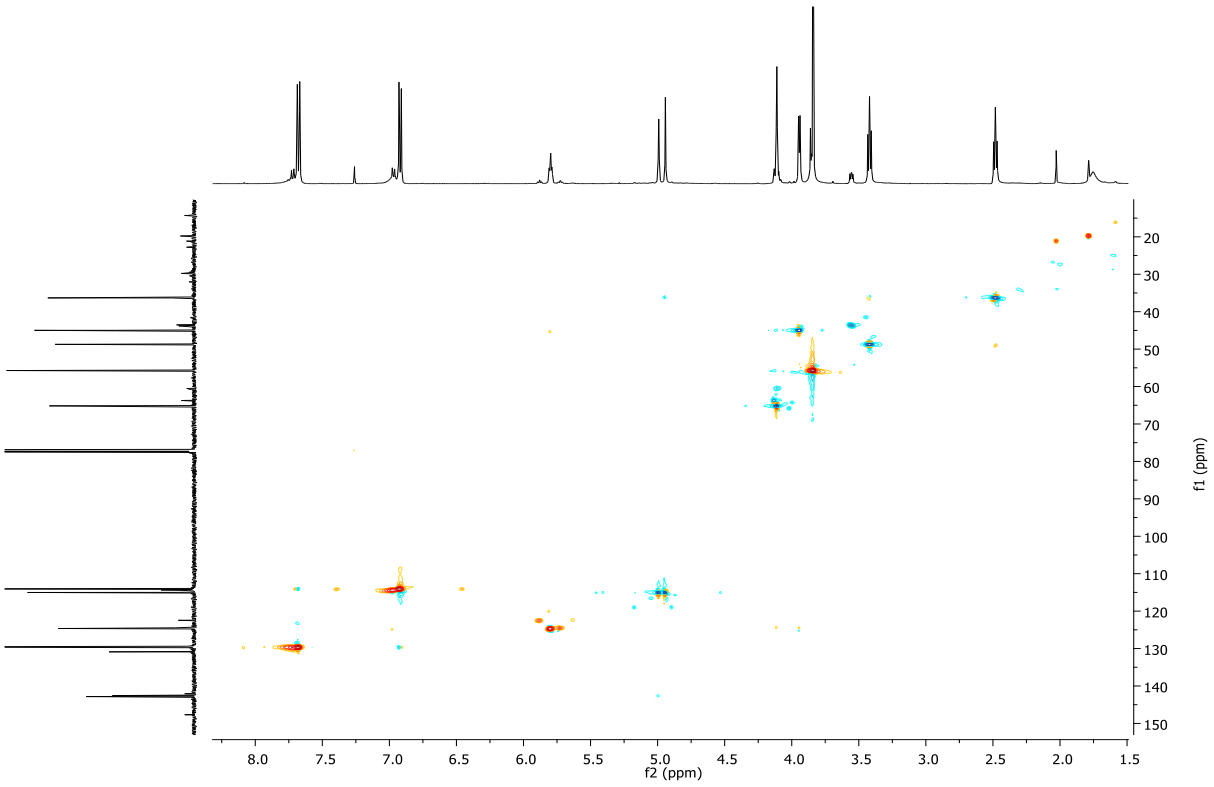


Supporting Information

2D gCOSY ($CDCl_3$)



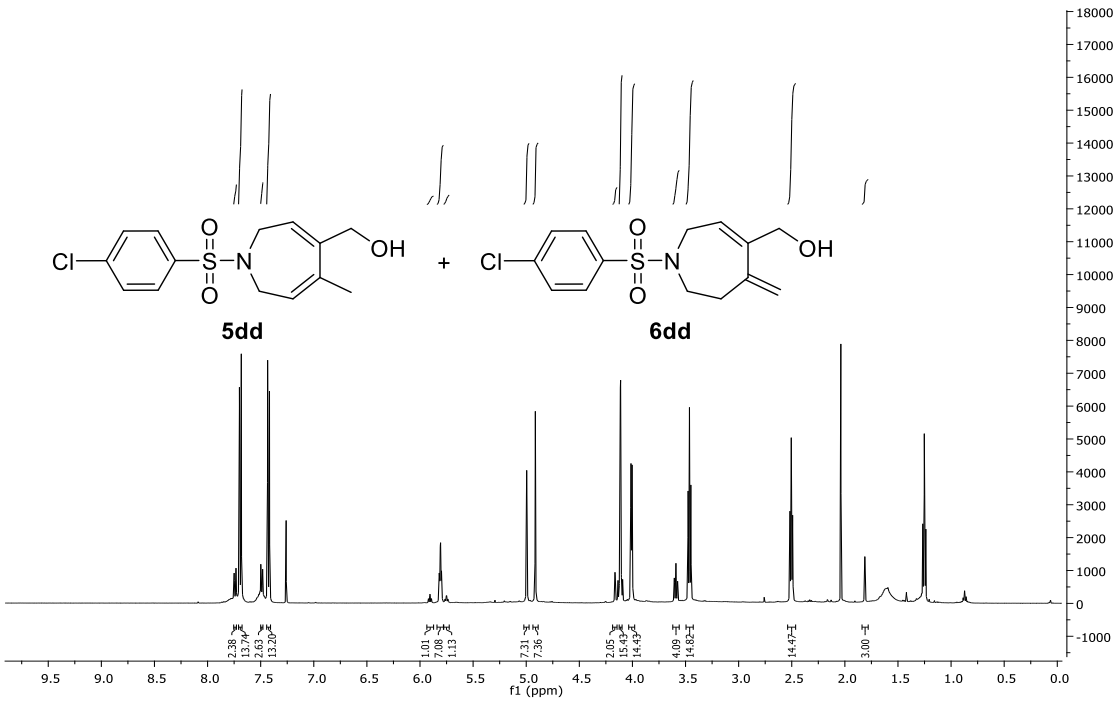
2D HSQC ($CDCl_3$)



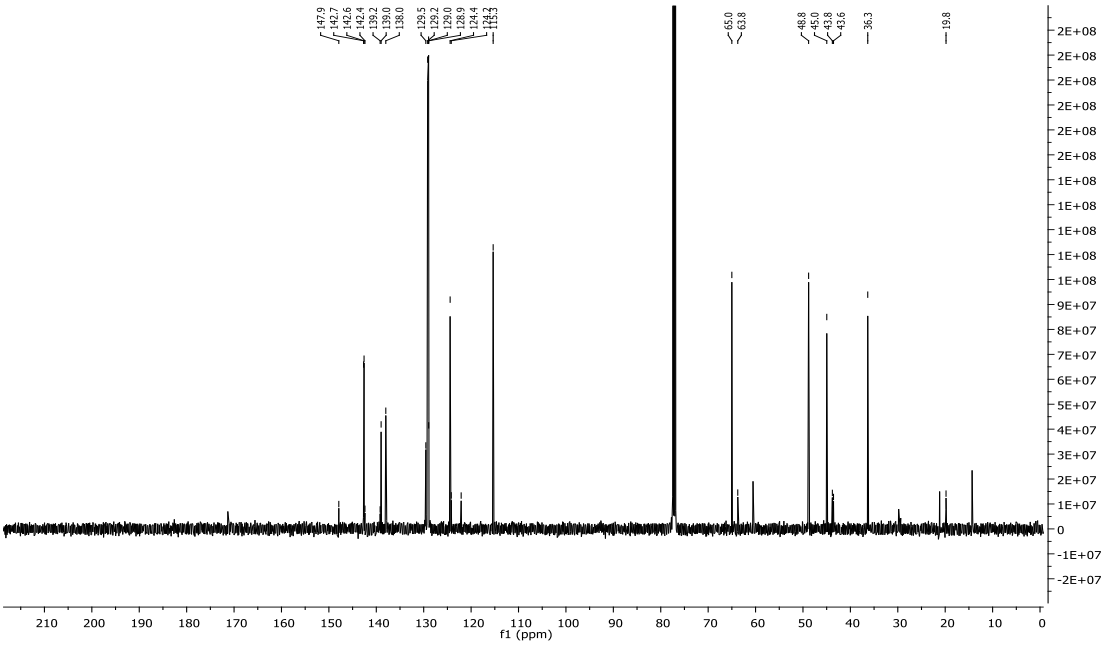
Supporting Information

[1-(4-Chloro-benzenesulfonyl)-5-methyl-2,7-dihydro-1*H*-azepin-4-yl]-methanol and [1-(4-Chloro-benzenesulfonyl)-5-methylene-2,5,6,7-tetrahydro-1*H*-azepin-4-yl]-methanol. (1:7.6)

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

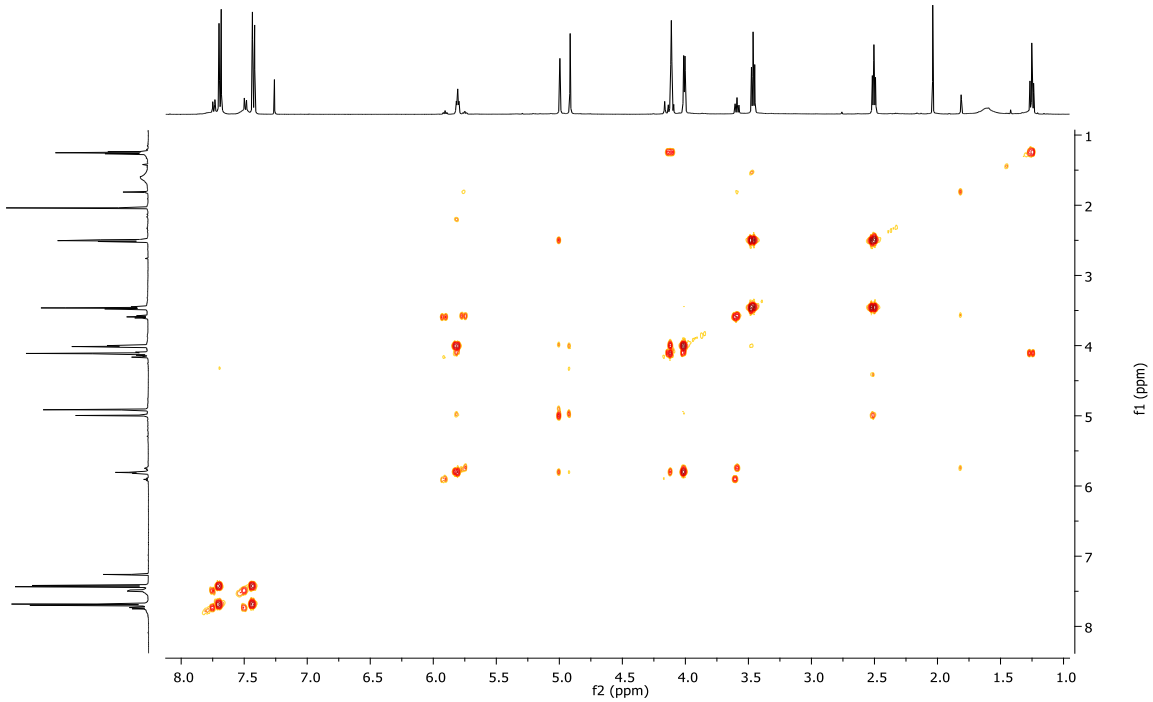


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

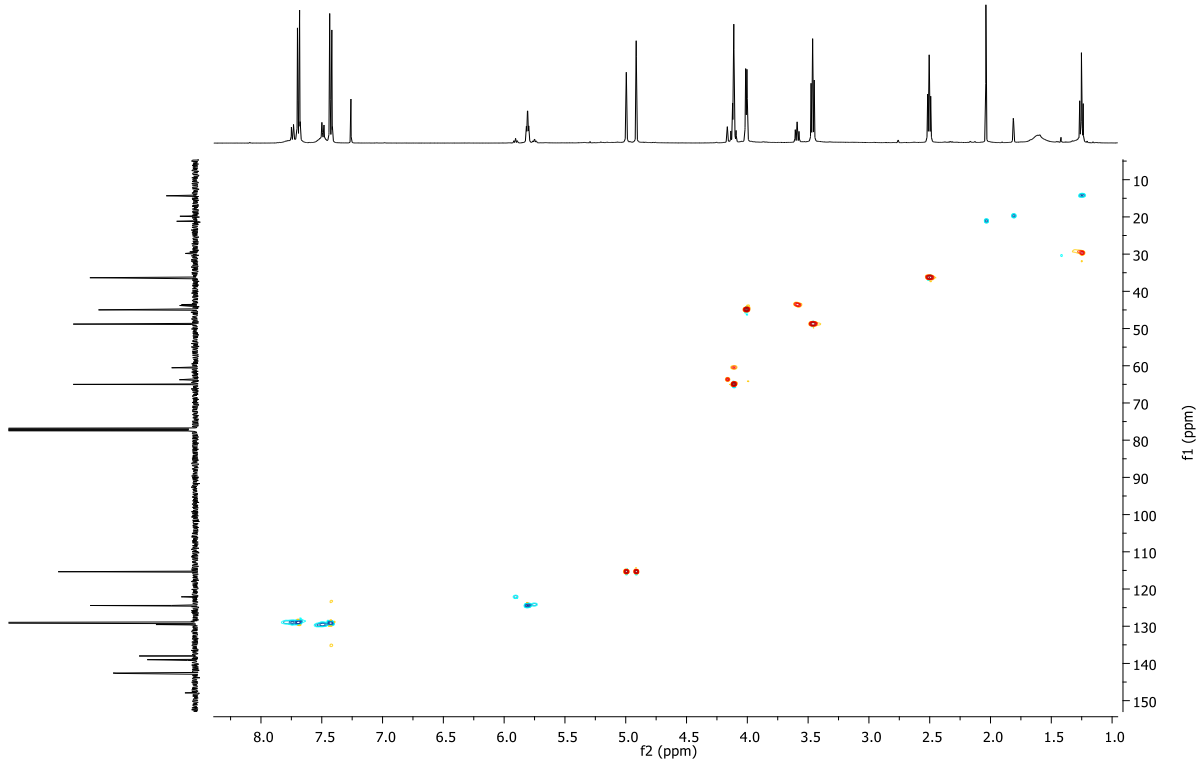


Supporting Information

2D gCOSY ($CDCl_3$)



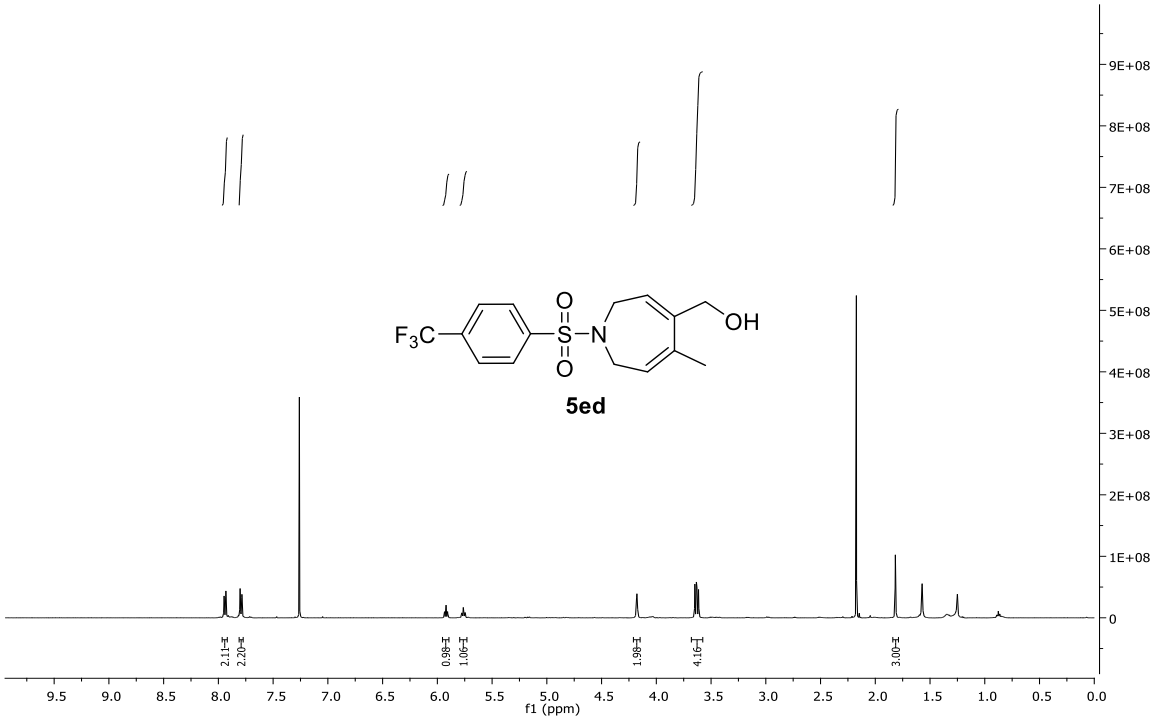
2D HSQC ($CDCl_3$)



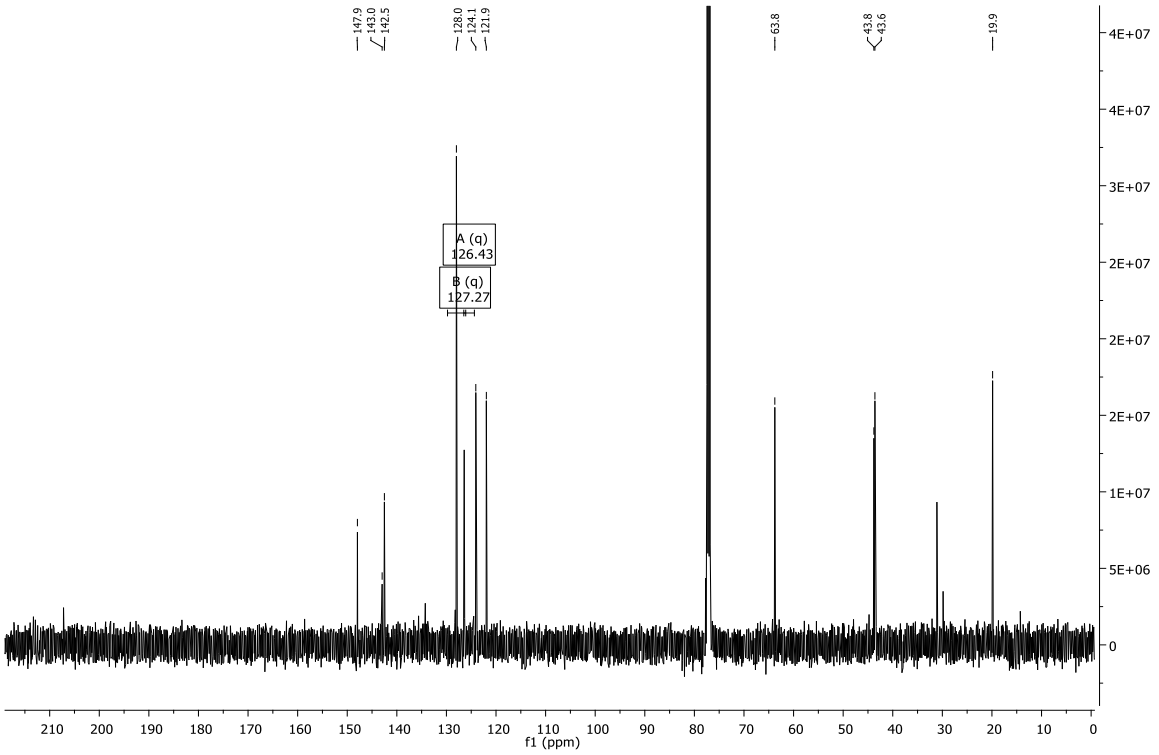
Supporting Information

[5-Methyl-1-(4-trifluoromethyl-benzenesulfonyl)-2,7-dihydro-1*H*-azepin-4-yl]-methanol

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

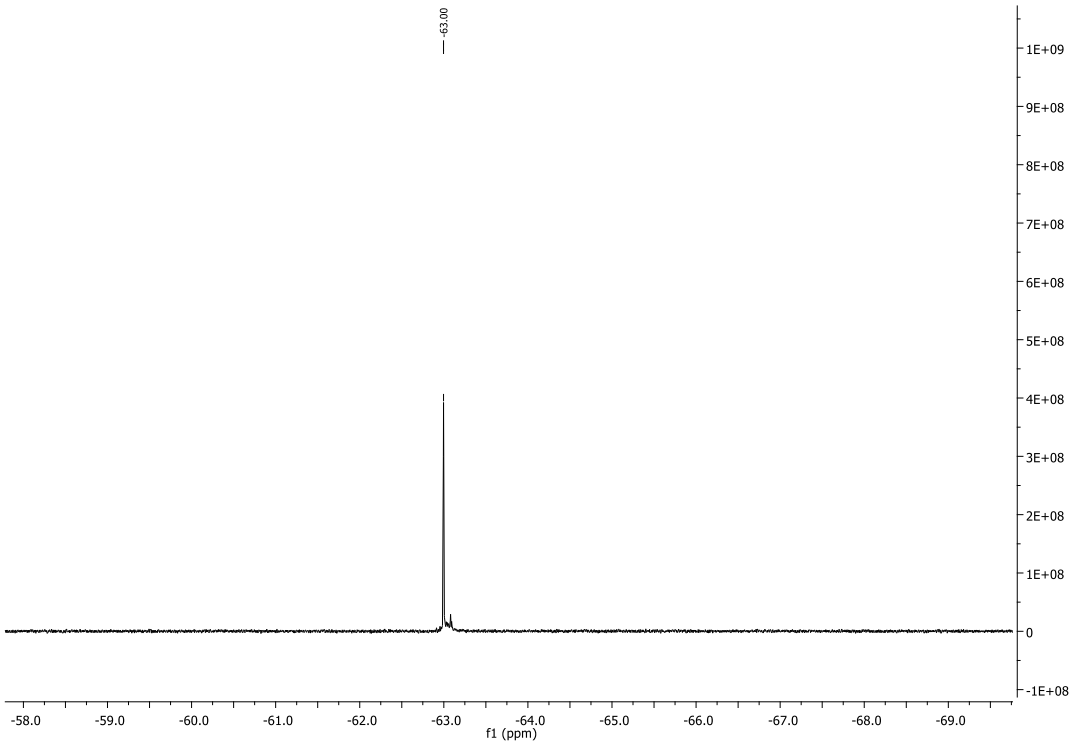


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

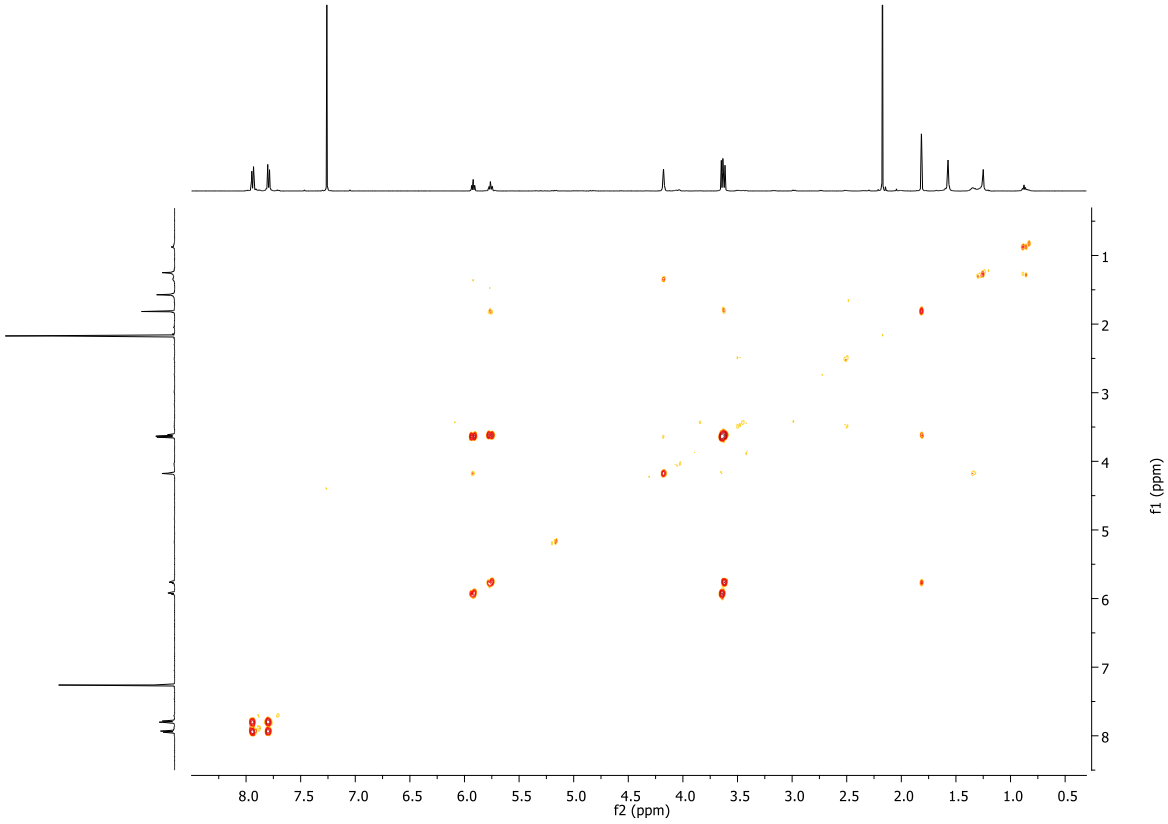


Supporting Information

^{19}F NMR (471 MHz, $CDCl_3$, 25 ^oC)

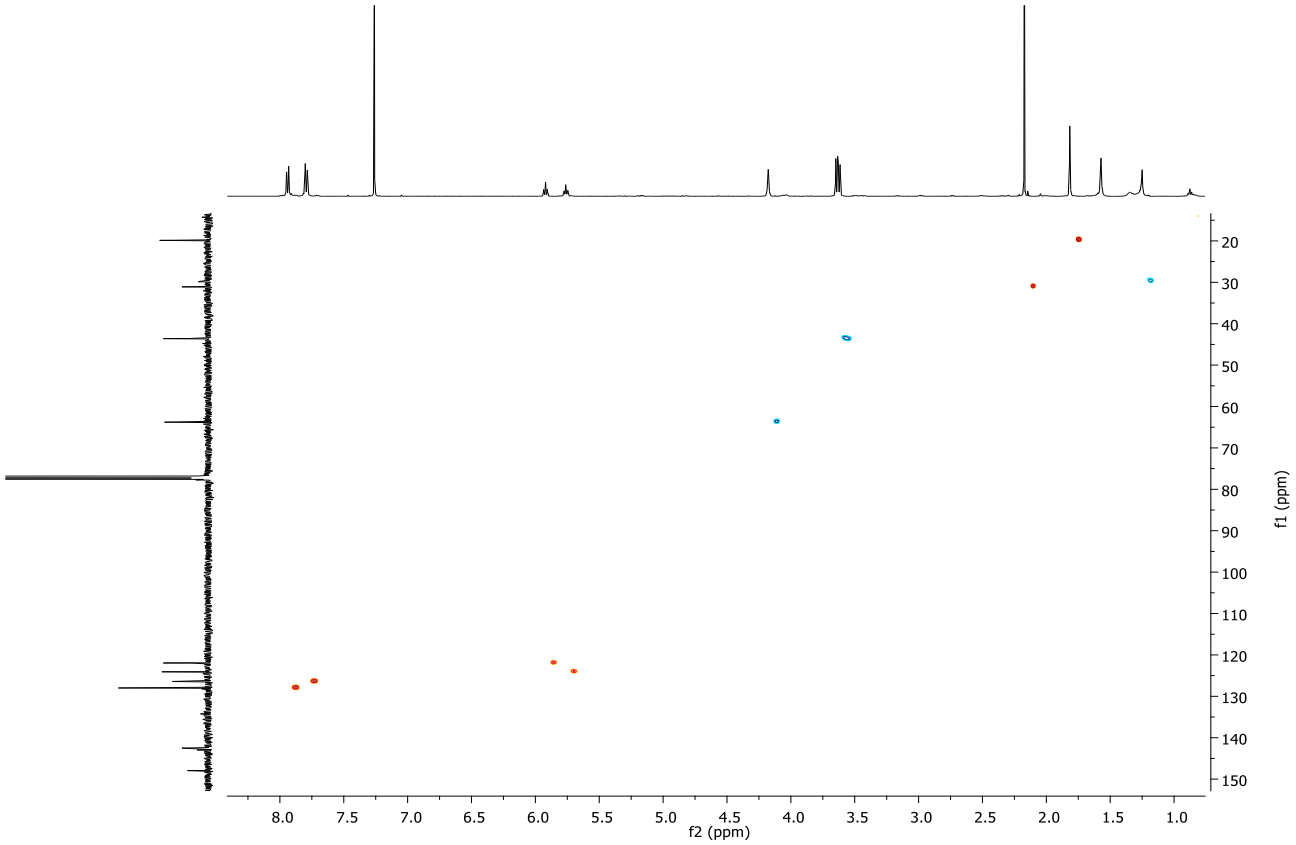


2D gCOSY ($CDCl_3$)



Supporting Information

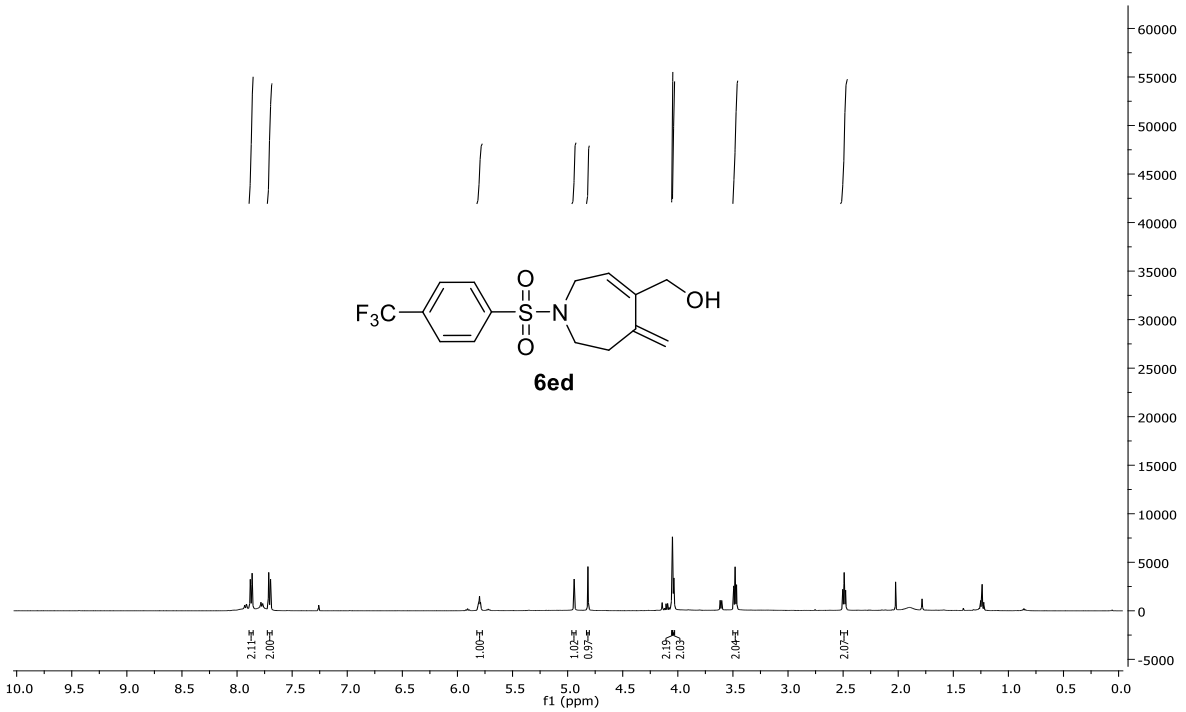
2D HSQC ($CDCl_3$)



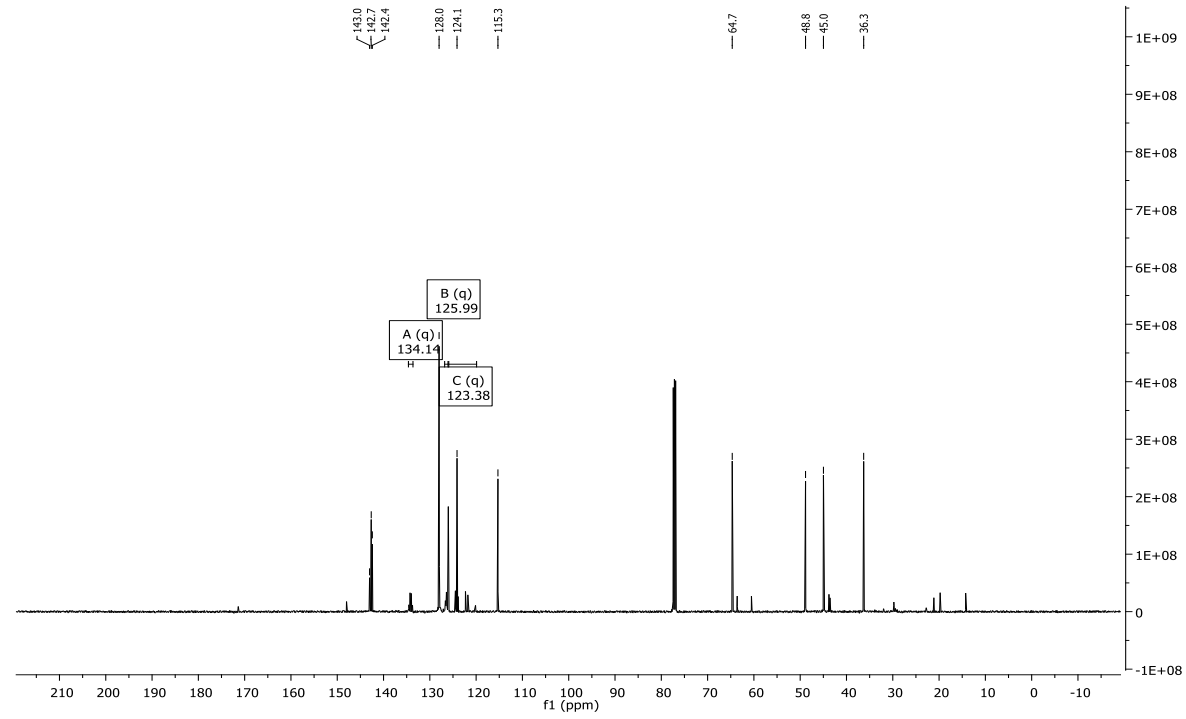
Supporting Information

[5-Methylene-1-(4-trifluoromethyl-benzenesulfonyl)-2,5,6,7-tetrahydro-1*H*-azepin-4-yl]-methanol

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

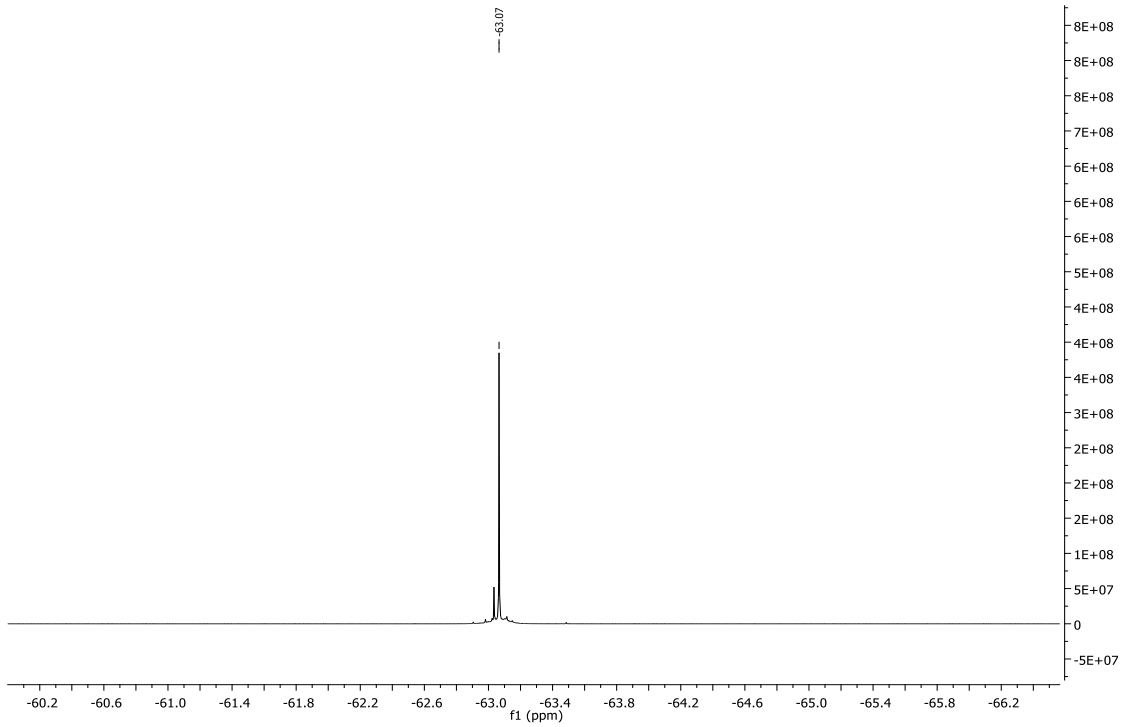


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

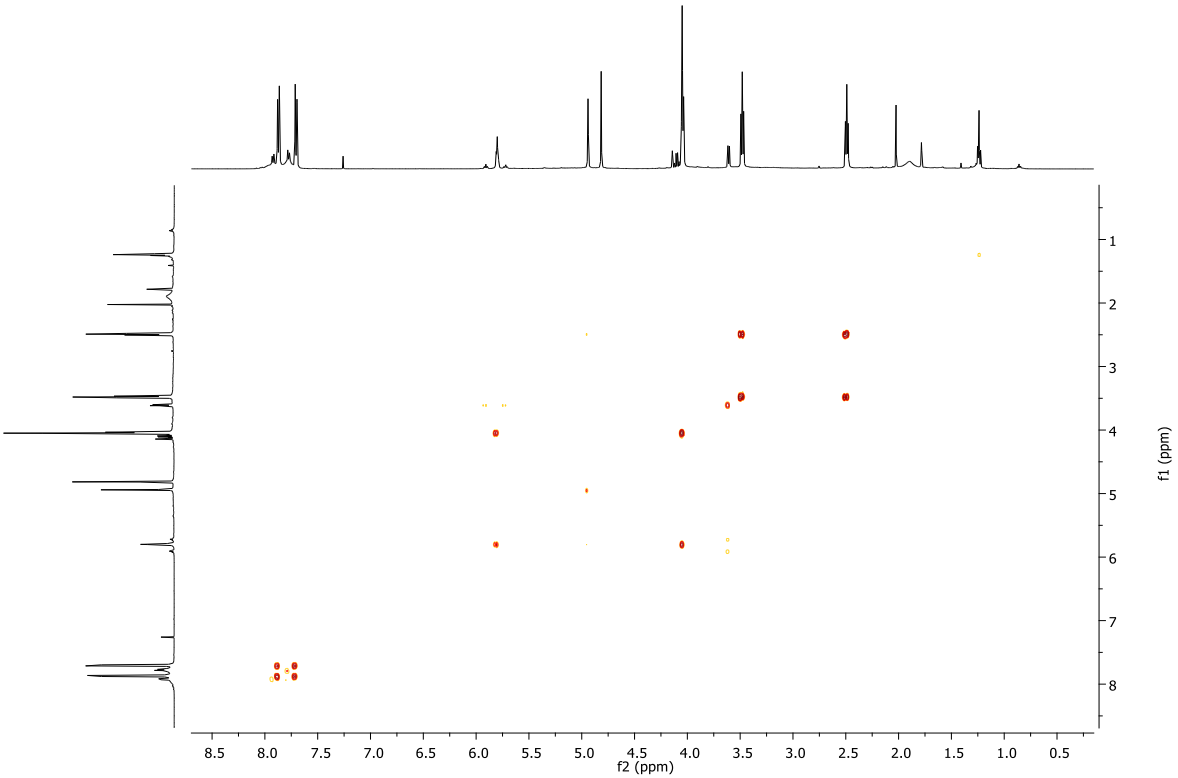


Supporting Information

^{19}F NMR (471 MHz, $CDCl_3$, 25 ^oC)

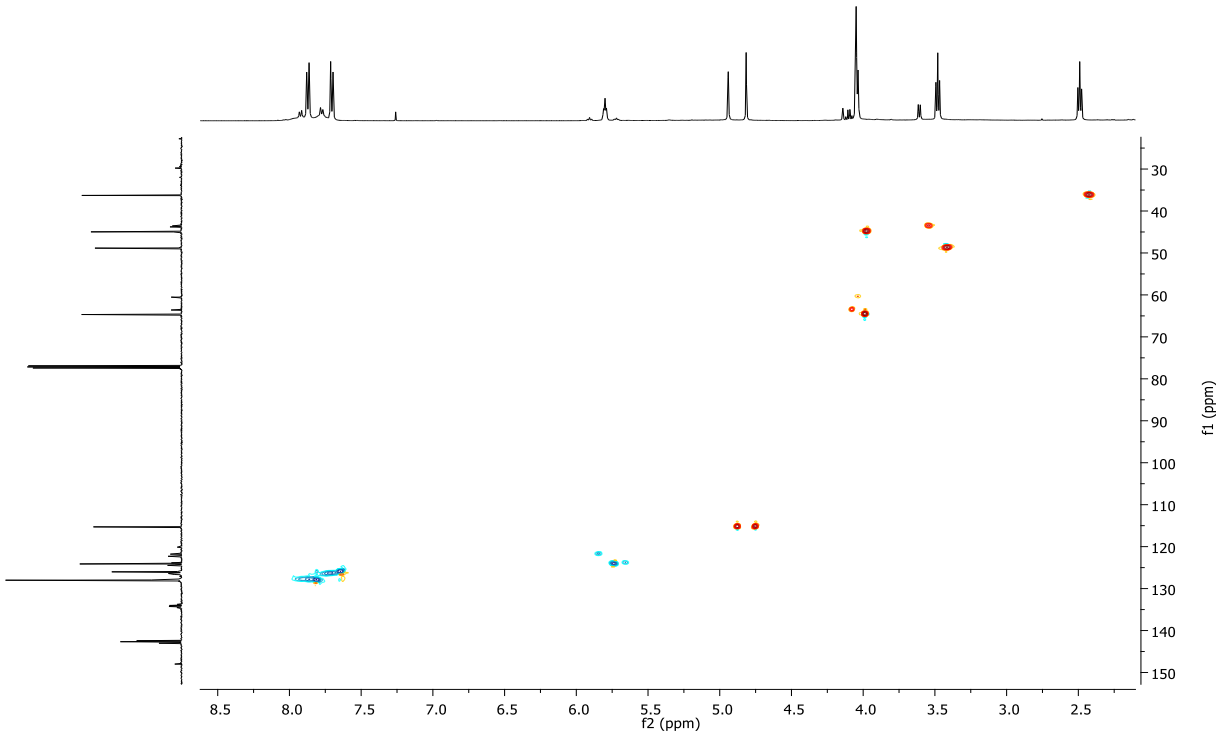


2D gCOSY ($CDCl_3$)



Supporting Information

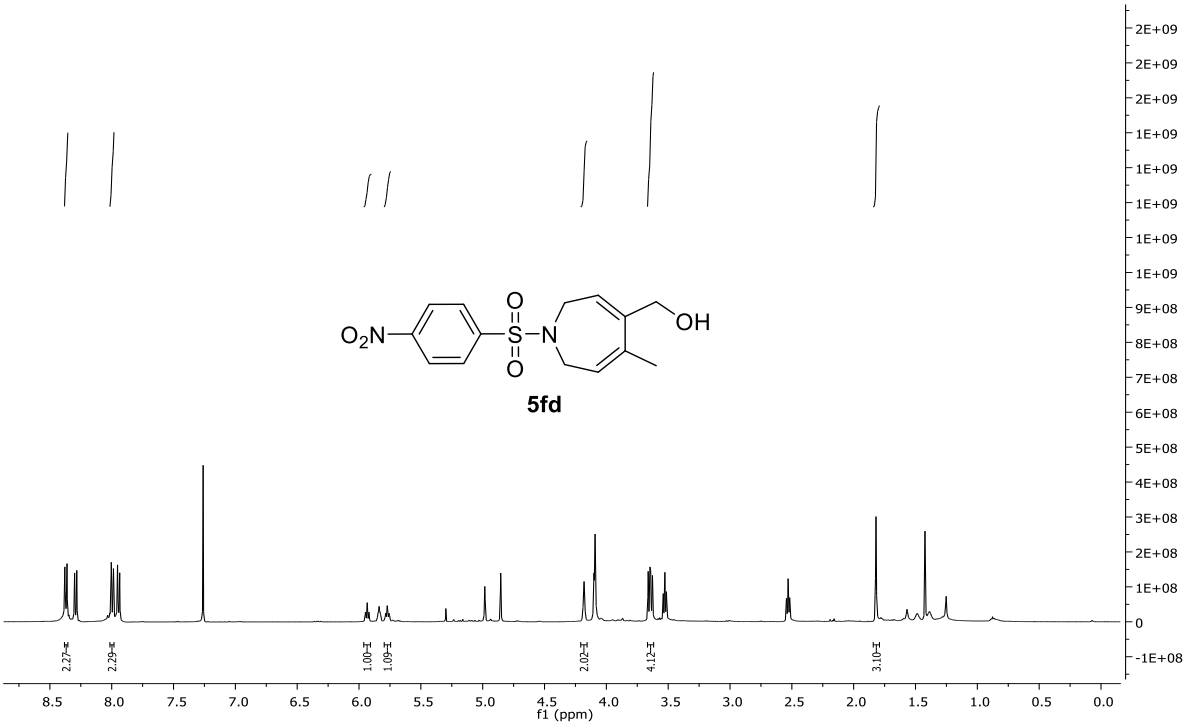
2D HSQC ($CDCl_3$)



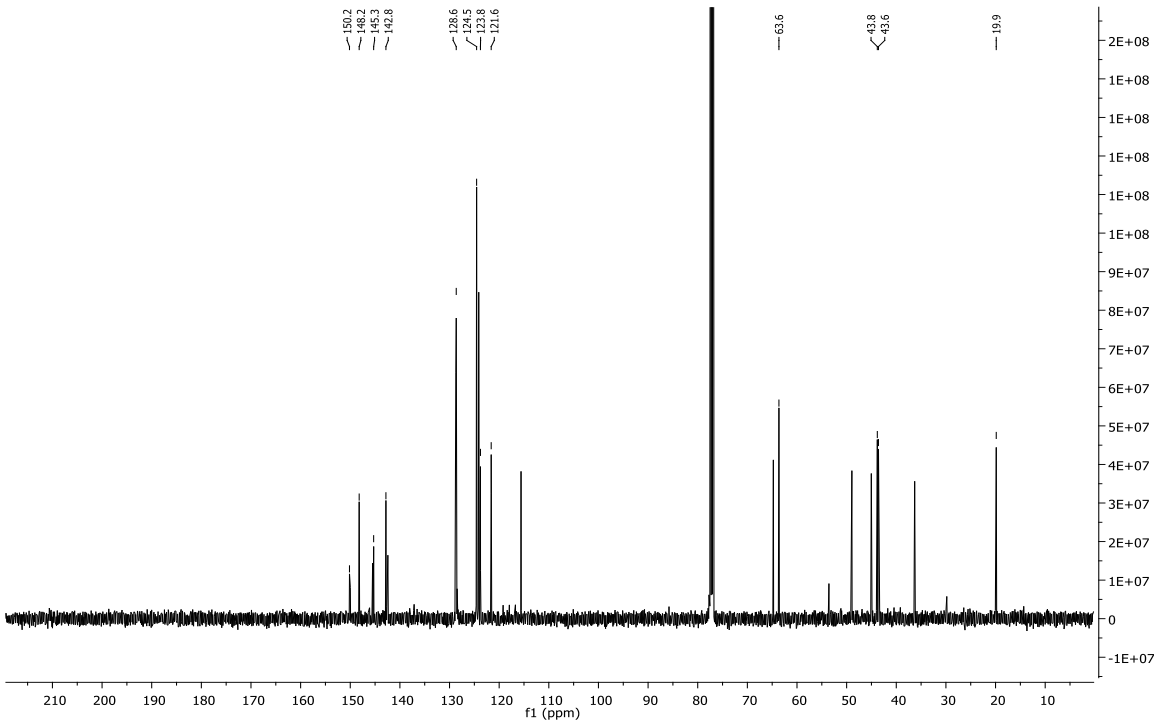
Supporting Information

[5-Methyl-1-(4-nitro-benzenesulfonyl)-2,7-dihydro-1*H*-azepin-4-yl]-methanol

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

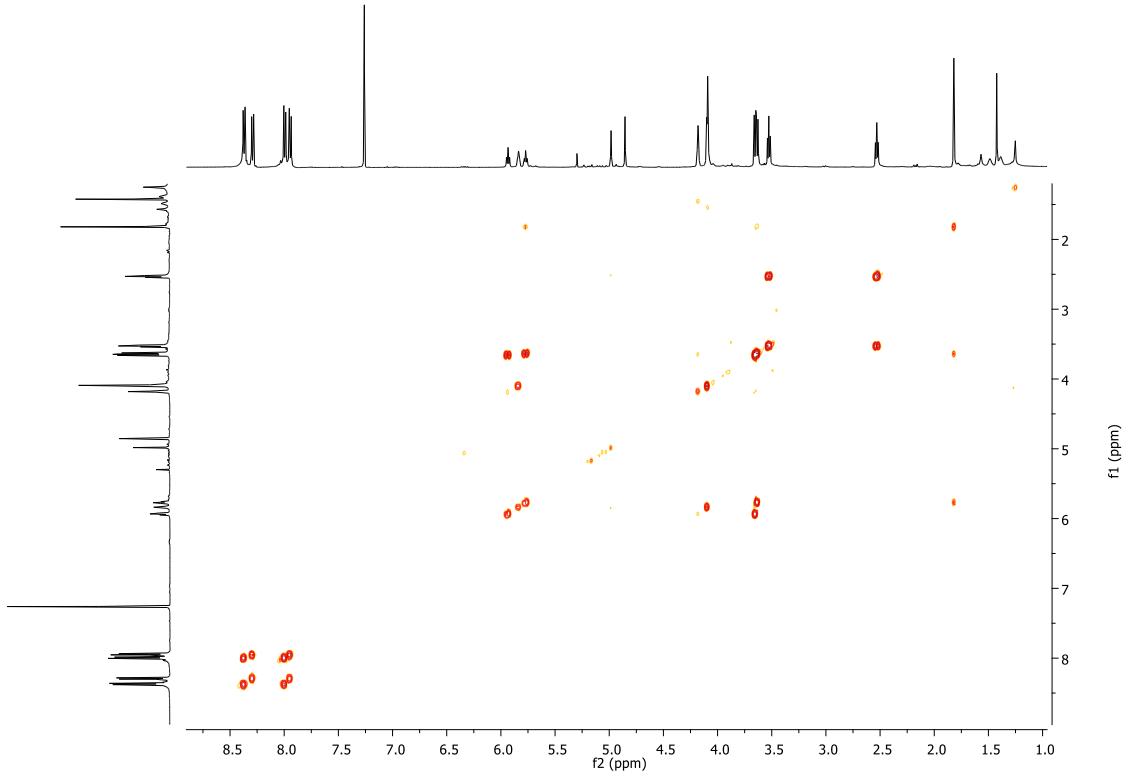


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

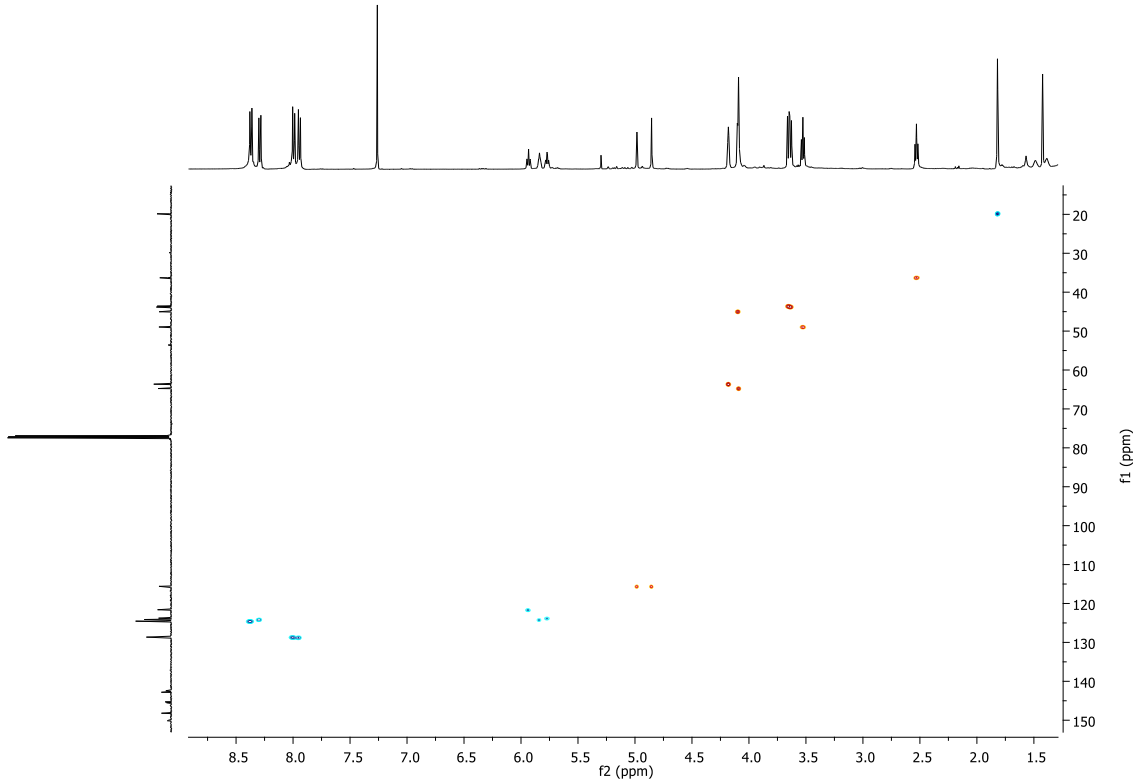


Supporting Information

2D gCOSY ($CDCl_3$)

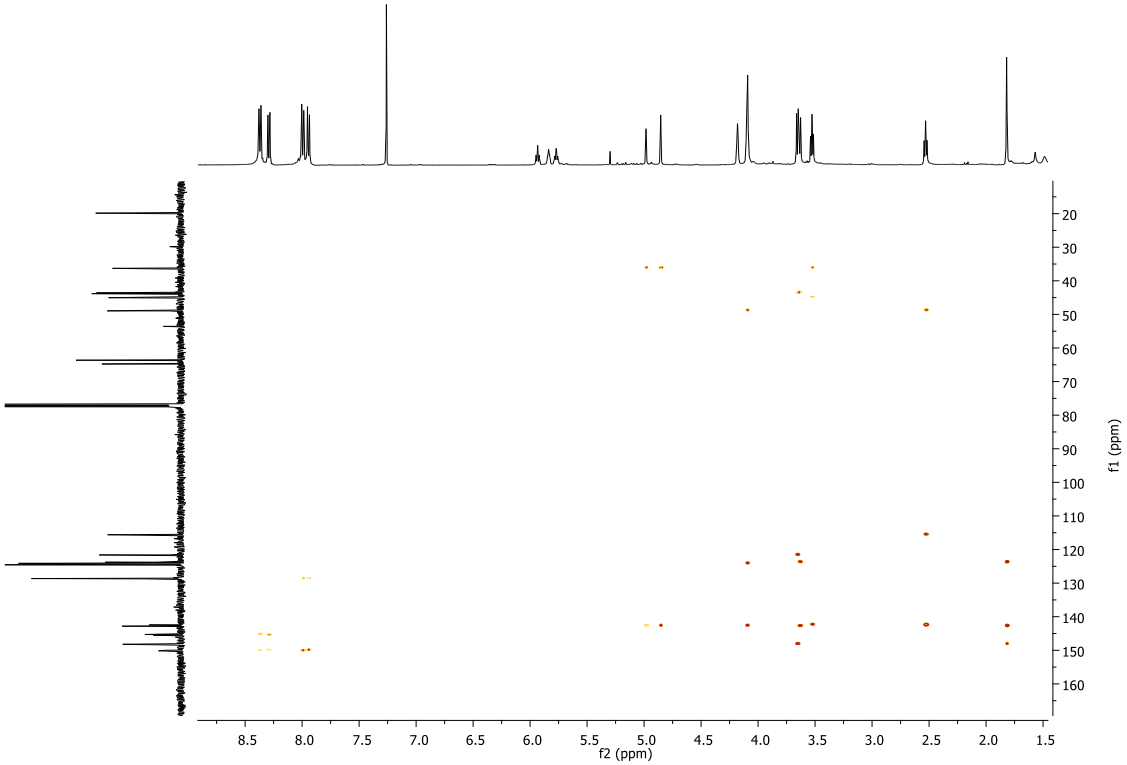


2D HSQC ($CDCl_3$)



Supporting Information

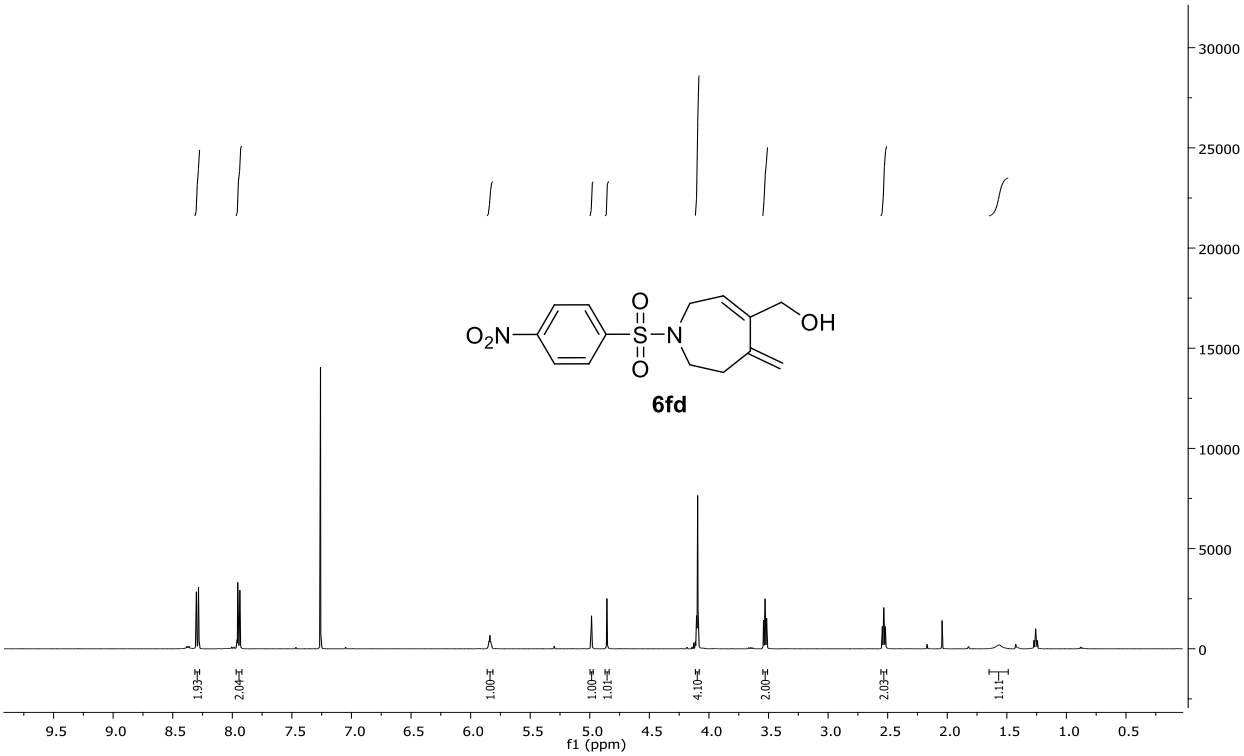
2D HMBC ($CDCl_3$)



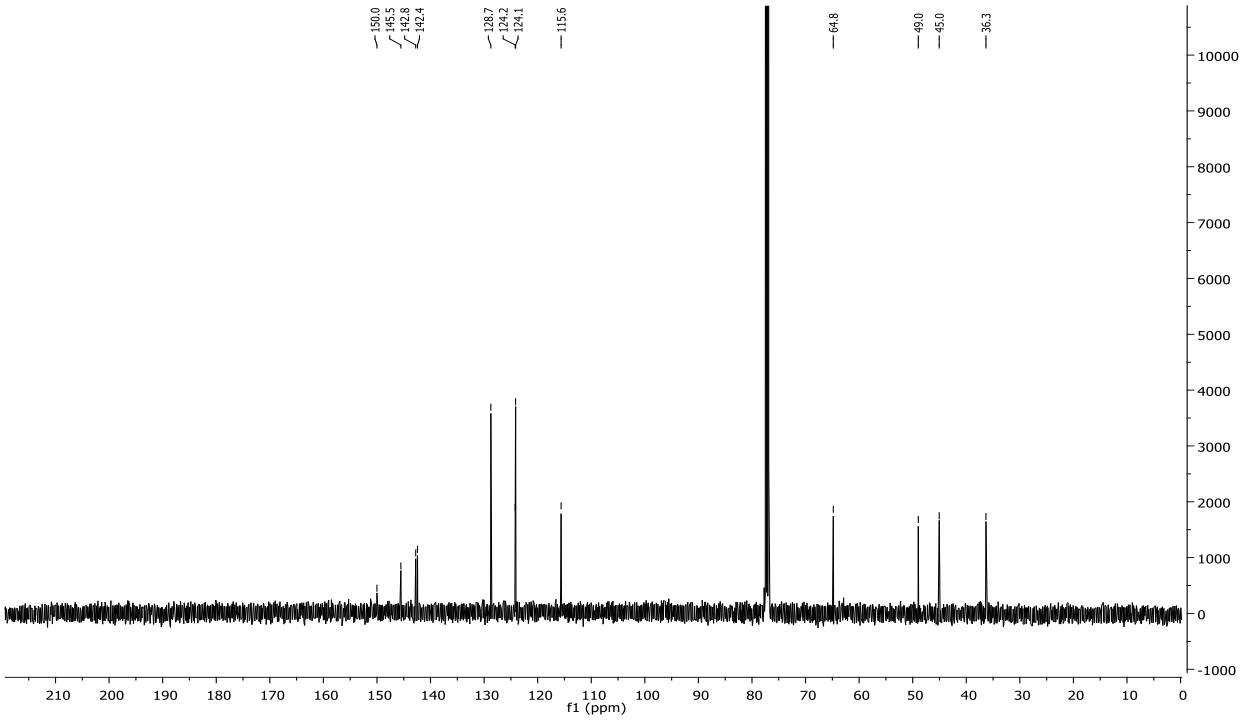
Supporting Information

[5-Methylene-1-(4-nitro-benzenesulfonyl)-2,5,6,7-tetrahydro-1*H*-azepin-4-yl]-methanol

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)



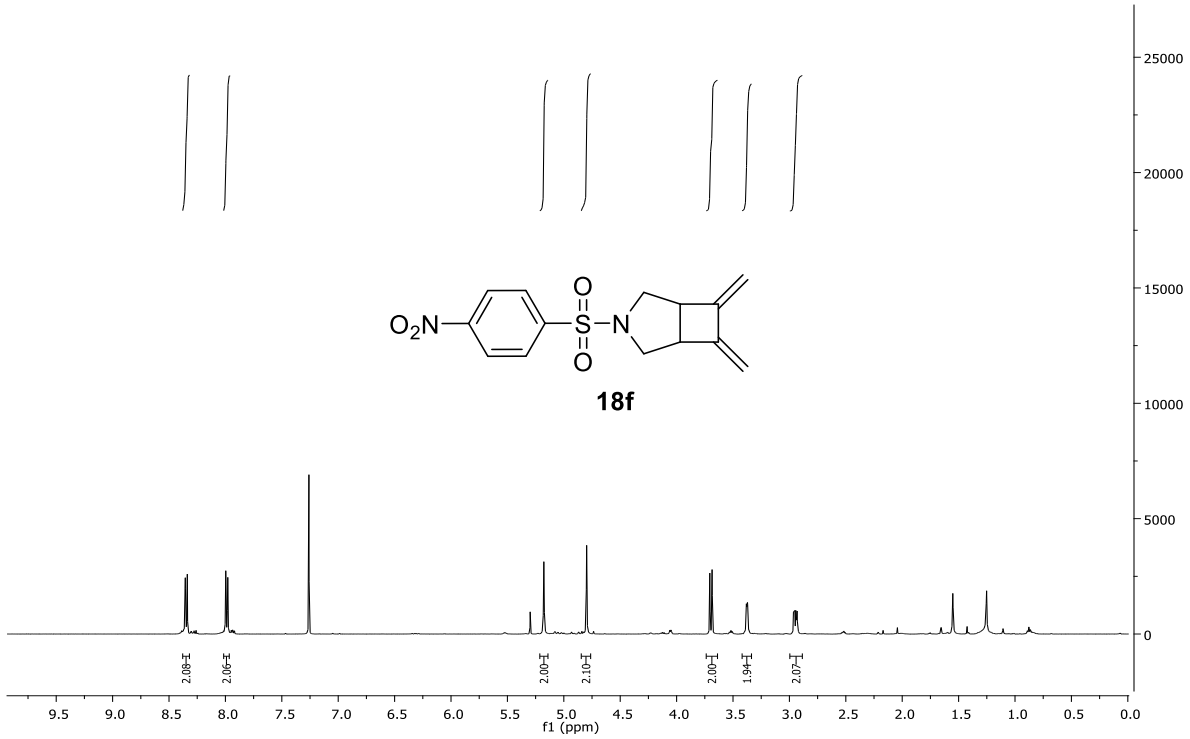
^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



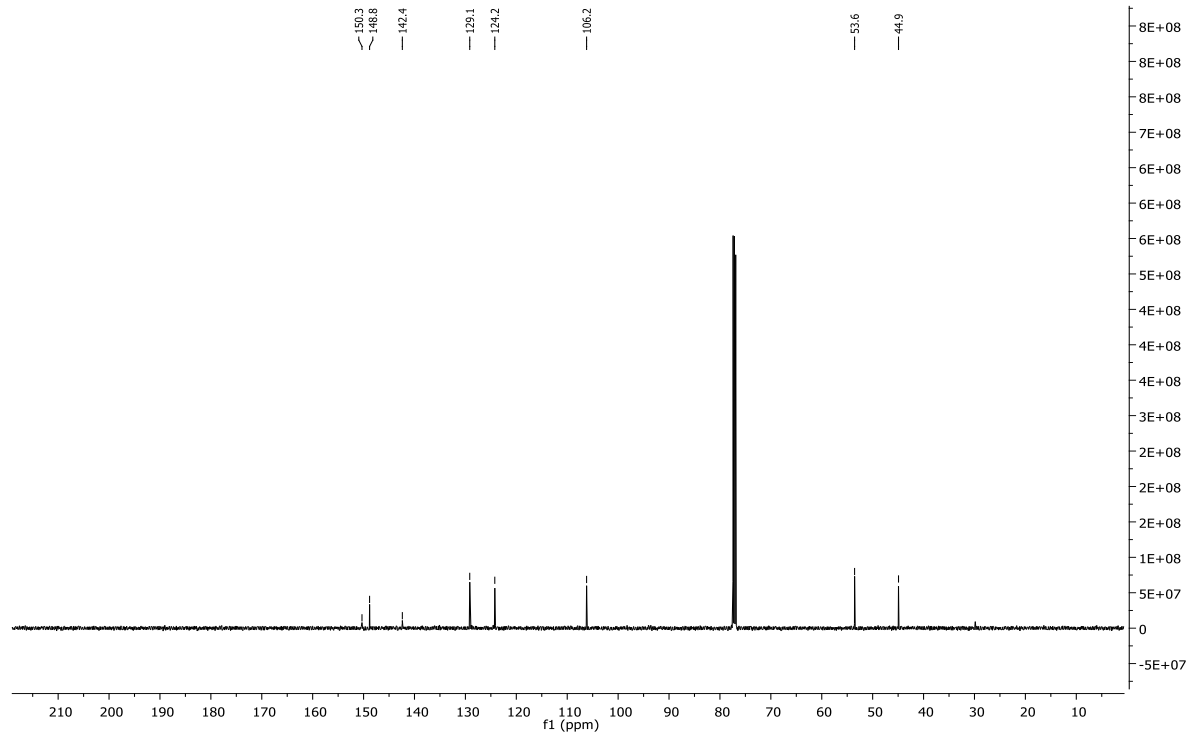
Supporting Information

6,7-Dimethylene-3-(4-nitro-benzenesulfonyl)-3-aza-bicyclo[3.2.0]heptane

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

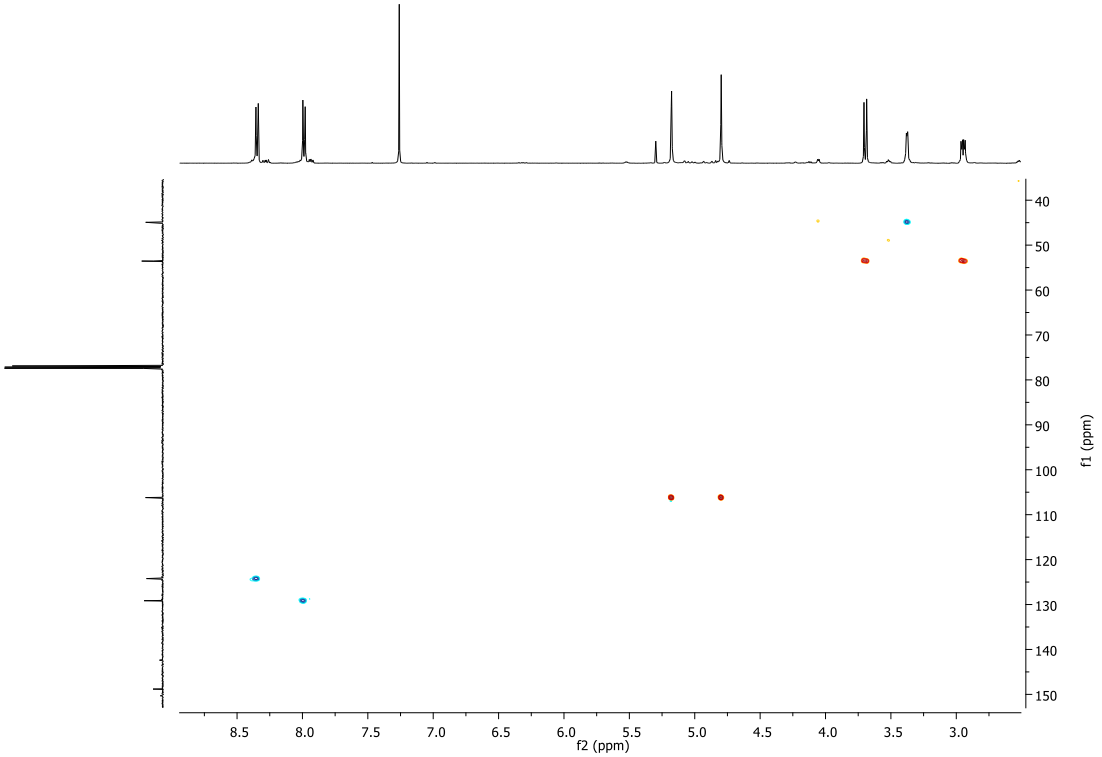


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



Supporting Information

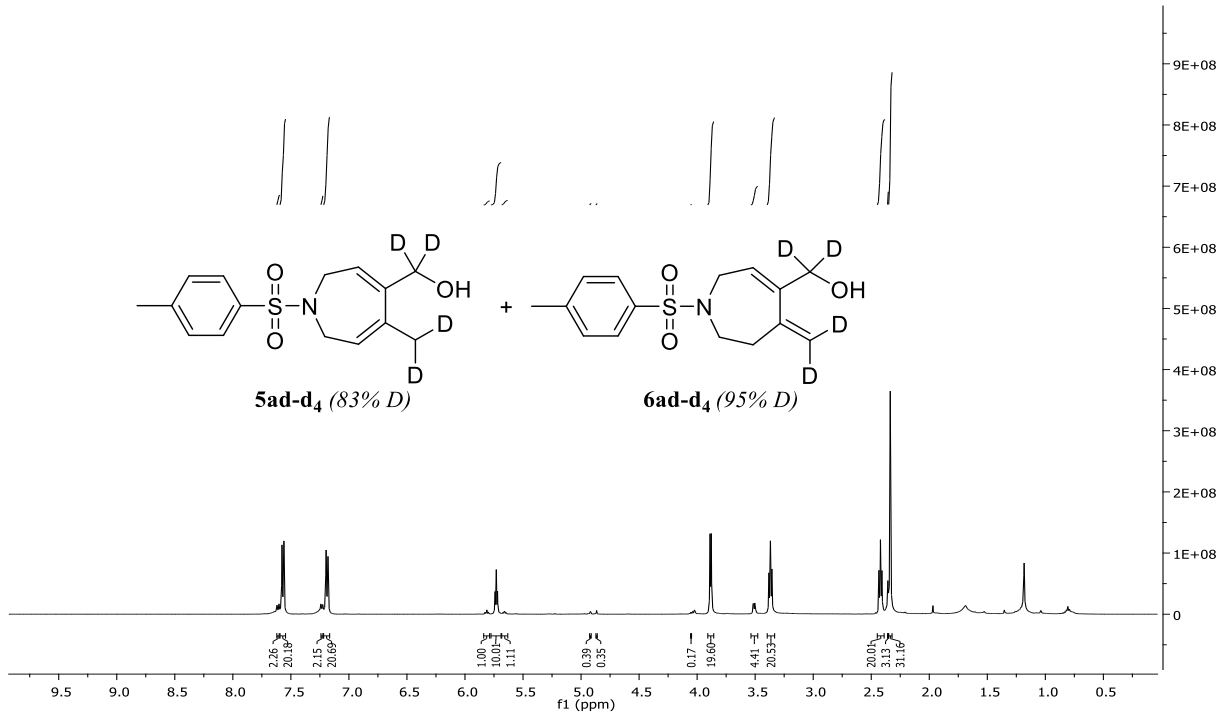
2D HSQC ($CDCl_3$)



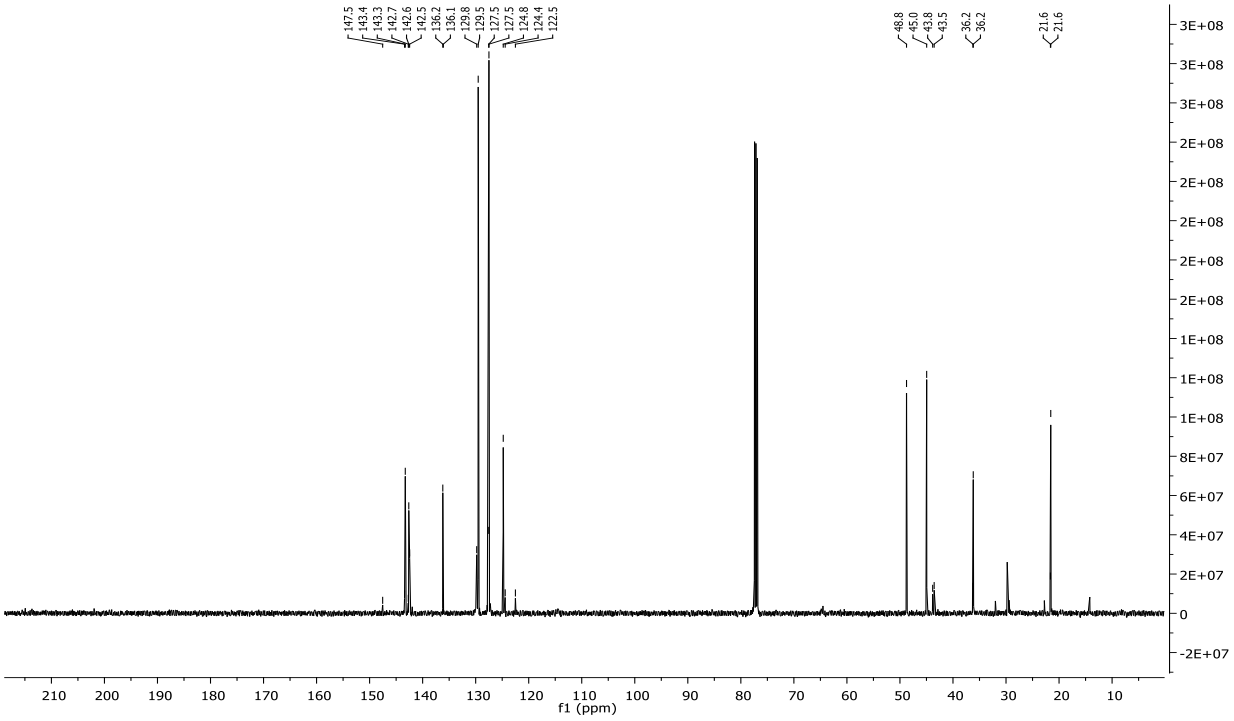
Supporting Information

[5-Methyl-1-(toluene-4-sulfonyl)-2,7-dihydro-1*H*-azepin-4-yl]-methanol-d^4 and [5-Methylene-1-(toluene-4-sulfonyl)-2,5,6,7-tetrahydro-1*H*-azepin-4-yl]-methanol- d^4 (1:10)

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)

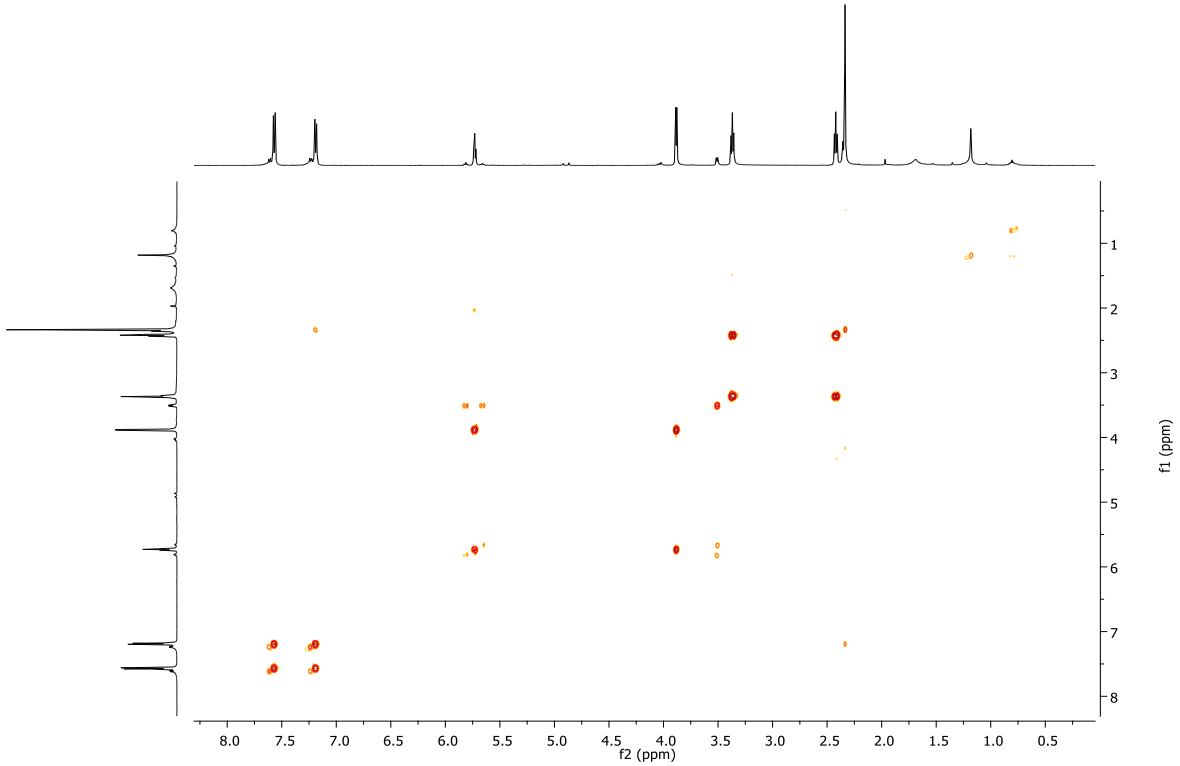


^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)

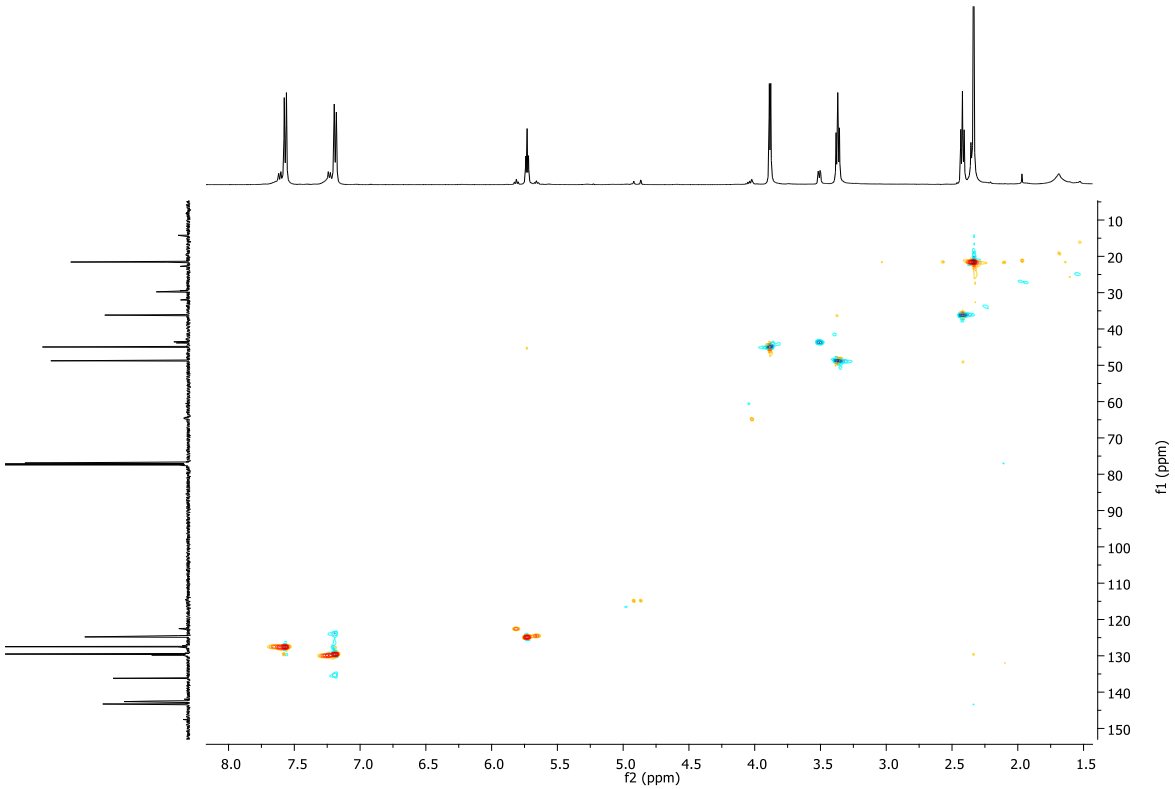


Supporting Information

2D gCOSY ($CDCl_3$)

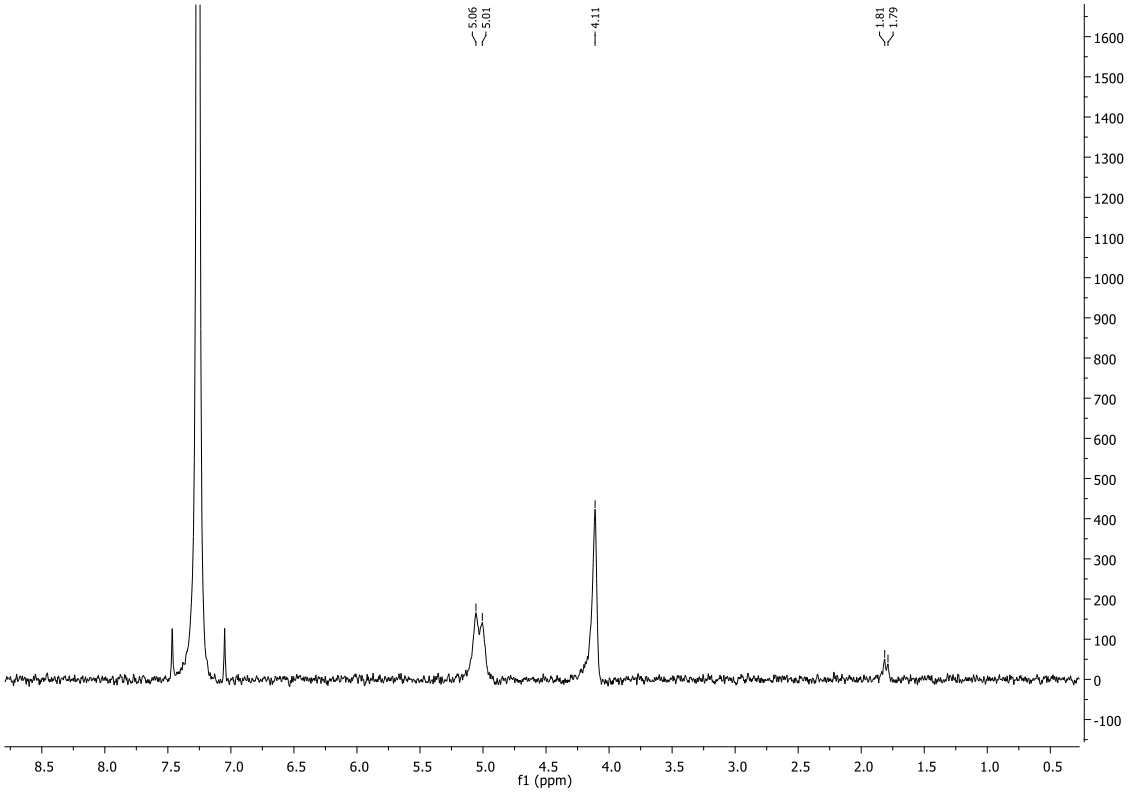


2D HSQC ($CDCl_3$)



Supporting Information

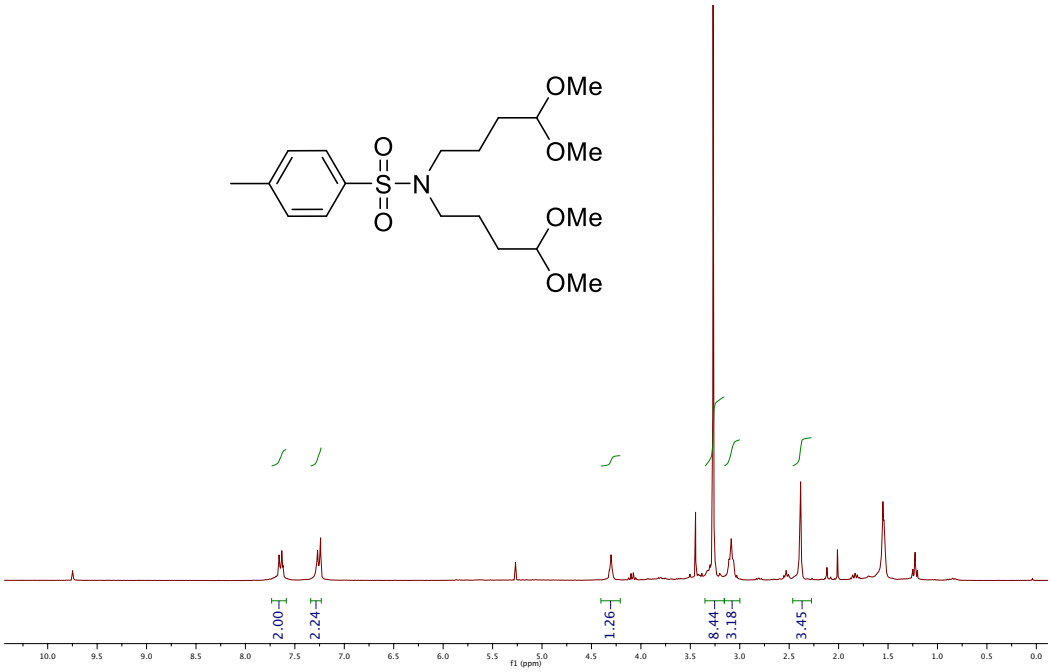
^{2}H NMR (77 MHz, $CDCl_3$, 25 ^{o}C)



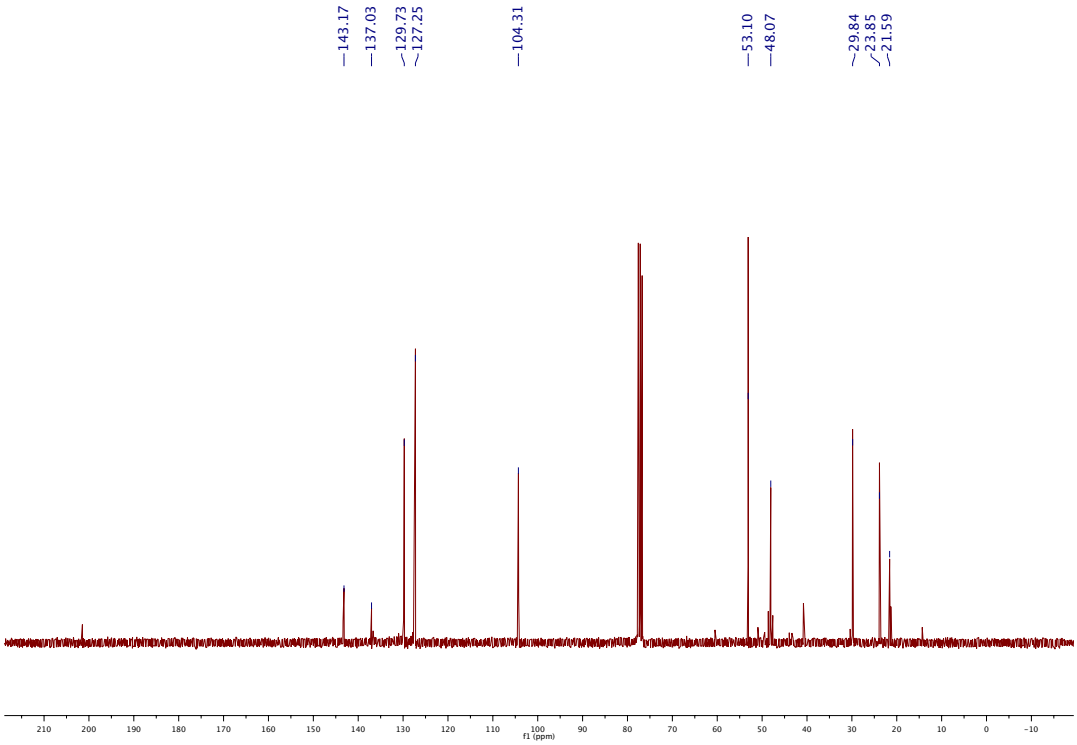
Supporting Information

_N_,_N_-Bis-(4,4-dimethoxy-butyl)-4-methyl-benzenesulfonamide

^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C)



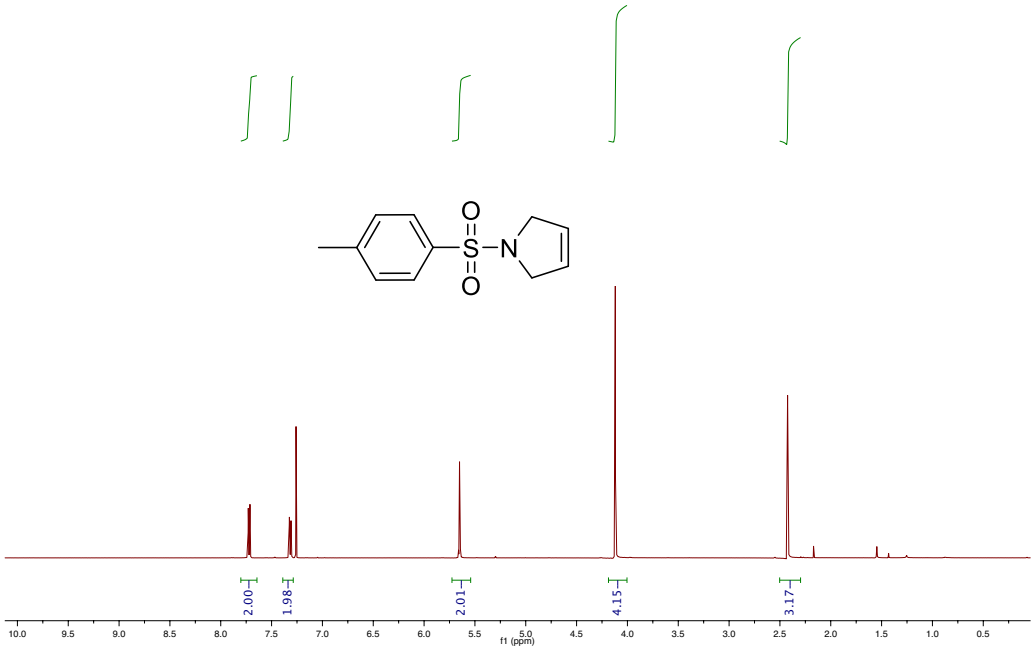
^{13}C NMR (75 MHz, $CDCl_3$, 25 ^{o}C)



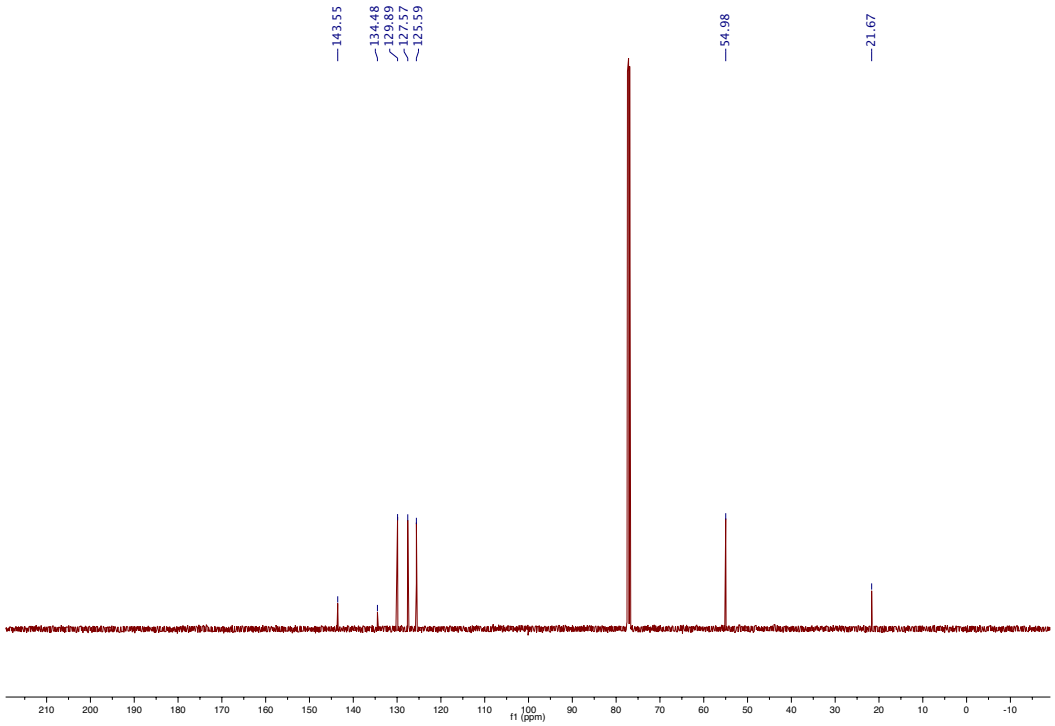
Supporting Information

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)



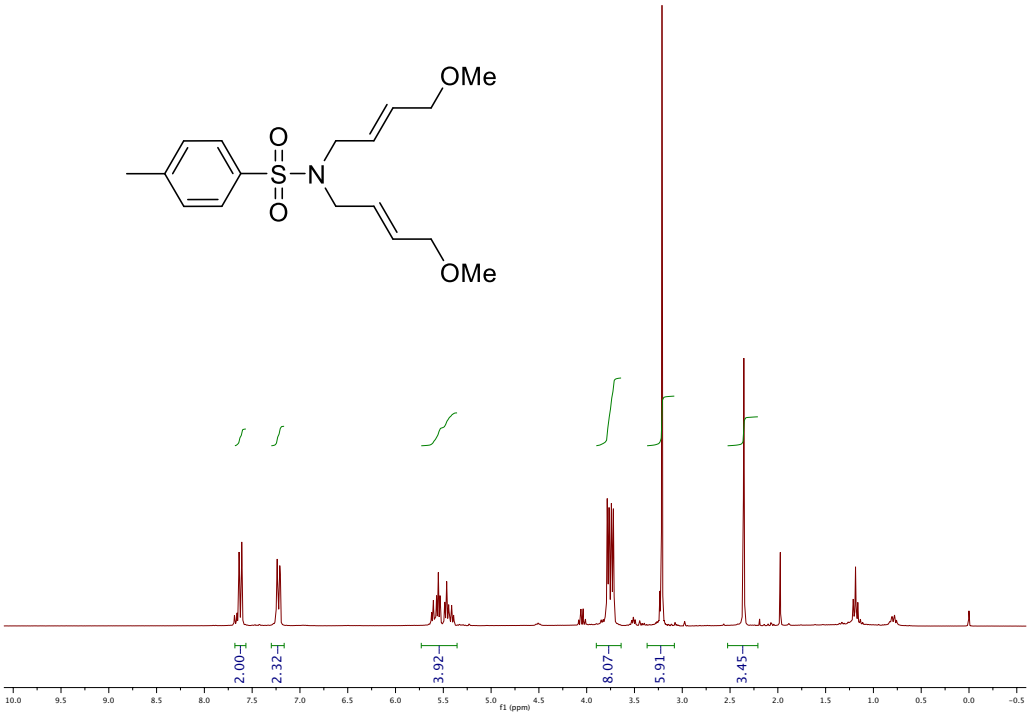
^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



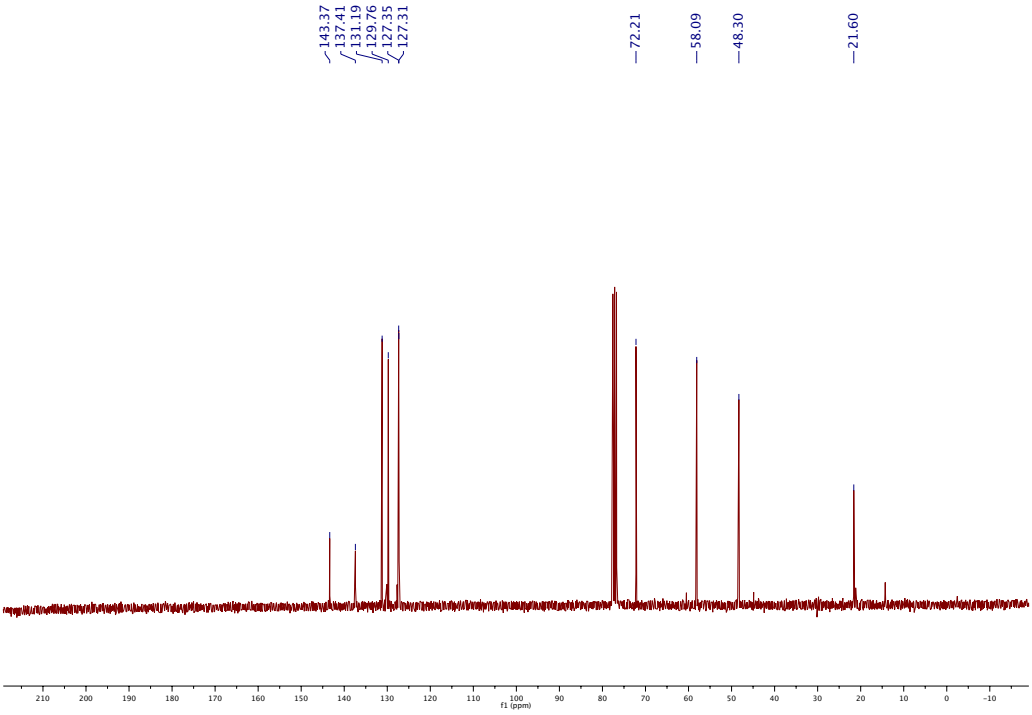
Supporting Information

***N*,*N*-bis((*E*)-4-methoxybut-2-en-1-yl)-4-methylbenzenesulfonamide**

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)



^{13}C NMR (126 MHz, $CDCl_3$, 25 ^{o}C)



Supporting Information

(*E*)-*N*-(4-methoxybut-2-en-1-yl)-*N*-(2-methoxybut-3-en-1-yl)-4-methylbenzenesulfonamide

^{1}H NMR (500 MHz, $CDCl_3$, 25 ^{o}C)