

Supporting Information

Synthesis of 3-Arylsulfonyl-3-Pyrrolines from Allenyl Sulfonamides by Silver Ion Catalysis

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I. General Information

Isovaleraldehyde, cyclohexyl carbaldehyde, benzaldehyde, p-Methyl, p-Cl, p-OMe, p-NO₂ benzaldehydes, cinnamaldehyde, benzenesulfonamide, 5A^o molecular sieves, amberlyst 15 ion-exchange resin, nBuLi (2.5 M in Hexanes), LiHMDS (1.0 M in THF) and AgF were purchased from sigma aldrich. All reactions were carried out in oven-dried glassware under an argon atmosphere. Tetrahydrofuran and toluene were ordered from Sigma Aldrich and were distilled under a nitrogen atmosphere over sodium metal with benzophenone ketyl as an indicator. Acetonitrile was ordered from Fisher and was distilled under a nitrogen atmosphere over calcium hydride. Analytical thin layer chromatography was performed on silica gel plates with UV indicator. Flash chromatography was carried out using 230-400 mesh silica gel with HPLC grade solvents. ¹H NMR spectra were recorded on either a Bruker DRX-500 (500 MHz) or a DRX-600 (600 MHz) spectrometer with chemical shifts reported in δ ppm with tetramethylsilane as an internal reference (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, etc). ¹³C NMR spectra were obtained on the same instruments at 125 and 150 MHz, respectively, in CDCl₃ solution with CDCl₃ (77.0 ppm) as an internal reference. Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin Elmer 1600 series FT-IR spectrometer. High-resolution mass spectra were performed by College of Science Major Instrumentation Center, Old Dominion University, on a Bruker 12 Tesla APEX -Qe FTICR-MS with an Apollo II ion source.

Single crystal X-ray diffraction (SCXRD) data were collected on a Bruker D8 Venture X-ray diffractometer (Bruker AXS, Inc., Madison, WI) equipped with a Photon 100 CMOS area detector using Mo-K α (λ = 0.71073 Å) from a microfocus source (50 kV, 1.0 mA). The crystals were cooled to 100 K during collection under a cold stream of N₂ using a Cryostream 800 cryostat (Oxford Cryosystems, Oxford, UK). A hemisphere of unique data was collected for each crystal using strategies of scans about the omega and phi axes. Unit cell determination, data collection, data reduction, scaling, and absorption correction were done using the Bruker Apex3 software suite.¹

The crystal structures were solved by direct methods and refined by full matrix least squares refinement against F² using SHELXL v.2014² as implemented on Olex2 v.1.2.10.³ Non-hydrogen atoms were located from the difference map and refined anisotropically. The structure of **6d** showed difference map peaks corresponding to disorder of the tosyl phenyl ring over two positions for one of the symmetry inequivalent molecules; both conformers were refined with their occupancies fixed at 50% each. Hydrogen atoms bonded to carbon were placed in calculated positions, while the N-H hydrogen atom in **7l** was located from the difference map. Hydrogen atoms in **6d** were constrained to have idealized bond distances and angles with their coordinates and thermal parameters riding on the carrier atoms. Hydrogen atoms bonded to methyl groups were refined using a riding rotating model. The coordinates of hydrogen atoms in **7l** were freely refined, while the thermal parameters were constrained to ride on the carrier atom.

II. General procedure for the synthesis of N-Sulfonylimines.

The starting materials allenic sulfones (**5a**, **5b**, **5c**, **5d**, **5e**, **5f**)⁴ and N-sulfonylimines were synthesized according to literatures procedures.

Method A for Aromatic Substituted N-Sulfonylimines (6a, 6d, 6e, 6f, 6g, 6h and 6i):⁵ To a stirred solution of benzaldehyde (1.0 g, 9.42 mmol, 1.0 eq) in toluene (11 mL) was added benzenesulfonamide (1.48 g, 9.42 mmol, 1.0 eq) under argon atmosphere at room temperature. Then 5A° molecular sieves (1.0 g) and 13 mg of amberlyst 15 ion-exchange resin were added at rt. The reaction mixture was refluxed under dean-stark conditions for 16h. The reaction progress was monitored by TLC. After completion of the reaction, the reaction mixture was cooled to rt. Then the reaction mixture was filtered through sintered-glass funnel to remove the powdered molecular sieves and ion-exchange resin. The filtrate was evaporated by rotary evaporator. The obtained oily residue was triturated with 20 mL of pentane and the solid crashed out immediately. The solid was filtered through sintered-glass funnel and wash the solid with 20 mL of pentane to remove the unreacted traces of aldehyde. The product N-sulfonylimine **6a** was obtained as a white solid in (2.013 g) 87% yield. (Note- 5A° molecular sieves were activated in the oven (100 °C) for 7 days, aldehydes were distilled or recrystallized, toluene was distilled).

Method B for Aliphatic Substituted N-Sulfonylimines (6b and 6c):⁵ To a mixture of 15 mL of formic acid: H₂O (1:1) was added cyclohexanecarboxaldehyde (0.5g, 4.45 mmol) at room temperature. Then benzenesulfonamide (0.71g, 4.45 mmol) and sodium p-toluenesulfinate (.794g, 4.45 mmol) were added at room temperature. The white precipitate was slowly formed during the reaction. The reaction mixture was stirred at rt for 12h. The resulting white precipitate was filtered through sintered-glass funnel and washed with H₂O (2 x 5 mL) and 20 mL of pentane. The obtained white solid was dissolved in CH₂Cl₂ (50 mL) and then add sat. NaHCO₃ (35 mL). The mixture was stirred vigorously at rt for 2h. The organic phase was separated and the aqueous phase was extracted with CH₂Cl₂ (3 x 20 mL). The combined organic layers were dried over Na₂SO₄, filtered, and evaporated by rotary evaporator. The product N-sulfonylimine **6b** was obtained as a white solid in (0.7g) 62% yield.

References:

1. Apex3, AXScale and SAINT, version
2. Sheldrick, G. M. *Acta Crys. Sec. C. Struc. Chem.* **2015**, 71, 3-8.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Cryst.* **2009**, 42, 339-341.
4. (a) Tata, R. R.; Hampton, C. S.; Harmata, M. *Adv. Synth. Catal.* **2017**, 359, 1232-124. (b) Hampton, C. S.; Harmata, M. *Tetrahedron Lett.* **2015**, 56, 3243-3245. (c) Tata, R. R.; Hampton, C. S.; Altenhofer, E. F.; Topinka, M.; Ying, W.; Gao, X.; Harmata, M. *Chem. Eur. J.* **2014**, 20, 13547-13550. (d) Tata, R. R.; Harmata, M. *J. Org. Chem.* **2015**, 80, 6839-6845.
5. (a) Chemla, F.; Hebbe, V.; Normant, J-F.; *Synthesis*, **2000**, 75-77. (b) Cui, Z.; Yu, H-J.; Yang, R-F.; Gao, W-Y.; Feng, W-Y.; Lin, G-Q. *J. Am. Chem. Soc.* **2011**, 133, 12394-12397. (c) Vishwakarma, L. C.; Stringer, O. D.; Davis, F. A. *Org. Synth*, **1993**, Coll. Vol

8, 546, **1988**, *Vol* 66, 203. (d) Tokimizu, Y.; Wietek, M.; Rudolph, M.; Oishi, S.; Fujii, N.; Hashmi, S. K.; Ohno, H. *Org. Lett.* **2015**, *17*, 604-607.

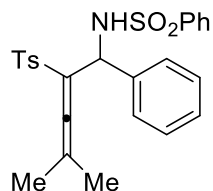
III. General procedure for the synthesis of Allenyl Sulfonamides.

General Procedure A: An oven dried round bottom flask was charged with an allenic sulfone **5a** (0.5 g, 2.25 mmol) in dry THF (22.5 mL) under an argon atmosphere at room temperature. Then the reaction flask was cooled to -78 °C. A solution of lithium bis(trimethylsilyl) amide (LiHMDS) (1.0 M in THF, 2.5 mL, 2.5 mmol) was added dropwise at -78 °C and was stirred for 10 min. Then a solution of N-sulfonylimine **6b** (0.61 g, 2.47 mmol) in dry THF (1.5 mL) was added slowly to the reaction mixture at -78 °C and stirred for 1h. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched with saturated ammonium chloride (15 mL) and extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, concentrated by rotary evaporation, and purified by flash column chromatography over silica gel. The compound eluted with 35-40% EtOAc in Hexane. The product allenyl sulfonamide **7b** was isolated as a white solid (1.02 g) in 97% yield.

General Procedure B: An oven dried round bottom flask was charged with an allenic sulfone **5a** (0.4 g, 1.8 mmol) in dry THF (18 mL) under an argon atmosphere at room temperature. Then the reaction flask was cooled to -78 °C. A solution of *n*BuLi (2.21 M in THF, 0.98 mL, 2.1 mmol) was added dropwise at -78 °C and was stirred for 10 min. Then a solution of N-sulfonylimine **6f** (0.55 g, 1.98 mmol) in dry THF (1.0 mL) was added slowly to the reaction mixture at -78 °C and stirred for 1h. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched with saturated ammonium chloride (10 mL) and extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, concentrated by rotary evaporation, and purified by flash column chromatography over silica gel. The compound eluted with 35-40% EtOAc in Hexane. The product allenyl sulfonamide **7f** was isolated as a white solid (0.87 g) in 97% yield.

IV. Characterization Data of Allenyl Sulfonamides.

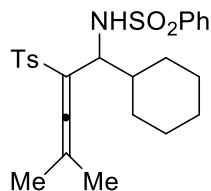
N-(4-methyl-1-phenyl-2-tosylpenta-2,3-dien-1-yl)benzenesulfonamide (**7a**).



Product was isolated as a white solid (mp = 153-155 °C) in 86% (0.09 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.79-7.77 (m, 2H), 7.55-7.53 (m, 1H), 7.47-7.44 (m, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 7.16-7.10 (m, 5H), 7.05-7.03 (m, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 5.34 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 3H), 1.65 (s, 3H), 1.60 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 203.3, 143.9, 140.3,

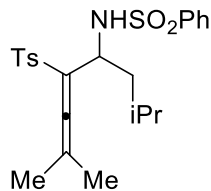
138.0, 137.5, 132.5, 129.3, 129.1, 128.9, 128.3, 127.7, 127.5, 127.1, 126.8, 126.4, 111.8, 109.4, 56.4, 21.5, 19.2, 19.1; IR (cm⁻¹) 3352, 3275, 3056, 2987, 2303, 1597, 1493, 1447, 1421, 1384, 1330, 1266, 1164, 1151, 1088, 896, 813, 787, 704, 672; HRMS m/z calcd for (C₂₅H₂₅NO₄S₂)Na⁺ 490.1117, found 490.1121.

N-(1-cyclohexyl-4-methyl-2-tosylpenta-2,3-dien-1-yl)benzenesulfonamide (7b).



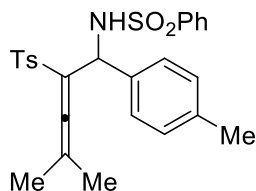
Product was isolated as a white solid (mp = 183-185 °C) in 93% (0.296 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.81-7.79 (m, 2H), 7.59-7.58 (m, 3H), 7.56-7.52 (m, 1H), 7.48-7.44 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.30 (d, *J* = 10.0 Hz, 1H), 4.01 (dd, *J* = 10.5 Hz, *J* = 7.0 Hz, 1H), 2.43 (s, 3H), 1.86-1.70 (m, 3H), 1.64-1.61 (m, 2H), 1.53-1.50 (m, 1H), 1.428 (s, 3H), 1.422 (s, 3H), 1.16-1.04 (m, 3H), 0.99-0.92 (m, 1H), 0.89-0.77 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 202.4, 144.2, 141.0, 138.0, 132.3, 129.4, 128.9, 127.8, 127.1, 110.3, 108.0, 59.0, 41.0, 30.3, 27.8, 26.0, 25.75, 25.74, 21.6, 19.1, 19.0; IR (cm⁻¹) 3346, 3284, 3056, 2982, 2925, 2851, 2300, 1593, 1446, 1425, 1331, 1262, 1164, 1139, 1078, 739, 698, 579; HRMS m/z calcd for (C₂₅H₃₁NO₄S₂)Na⁺ 496.1586, found 496.1589.

N-(2,7-dimethyl-5-tosylocta-5,6-dien-4-yl)benzenesulfonamide (7c).



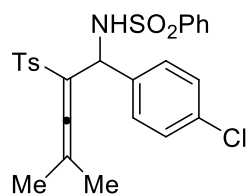
Product was isolated as a white solid (mp = 110-112 °C) in 82% (0.247 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.81-7.79 (m, 2H), 7.60-7.54 (m, 3H), 7.49-7.46 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.23 (d, *J* = 8.0 Hz, 1H), 4.19-4.14 (m, 1H), 2.43 (s, 3H), 1.69 (septet, *J* = 7.0 Hz, 1H), 1.52 (s, 3H), 1.49 (s, 3H), 1.54-1.44 (m, 2H), 0.78 (d, *J* = 6.5 Hz, 3H), 0.75 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 201.7, 144.2, 140.7, 137.9, 132.4, 129.4, 128.9, 127.8, 127.1, 111.8, 108.6, 52.4, 45.2, 24.7, 22.0, 21.7, 21.5, 19.13, 19.11; IR (cm⁻¹) 3366, 3051, 2958, 2886, 2300, 1597, 1442, 1413, 1258, 1160, 1143, 1090, 898; HRMS m/z calcd for (C₂₃H₂₉NO₄S₂)Na⁺ 470.1430, found 470.1434.

N-(4-methyl-1-(p-tolyl)-2-tosylpenta-2,3-dien-1-yl)benzenesulfonamide (7d).



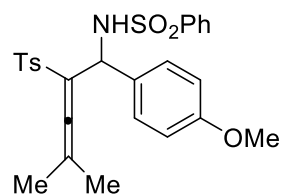
Product was isolated as a white solid (mp = 145-147 °C) in 97% (0.146 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.78-7.76 (m, 2H), 7.56-7.52 (m, 1H), 7.46-7.43 (m, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.11(d, *J* = 8.5 Hz, 2H), 6.91 (s, 4H), 5.52 (d, *J* = 8.0 Hz, 1H), 5.29 (d, *J* = 8.0 Hz, 1H), 2.37 (s, 3H), 2.25 (s, 3H), 1.65 (s, 3H), 1.61 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 203.0, 143.8, 140.3, 138.1, 137.7, 134.6, 132.5, 129.2, 129.0, 128.9, 127.6, 127.2, 126.8, 112.0, 109.4, 56.1, 21.5, 21.0, 19.3, 19.2; IR (cm⁻¹) 3358, 3272, 3047, 2986, 2917, 2251, 1601, 1446, 1413, 1327, 1270, 1164, 1143, 1086, 910, 722; HRMS *m/z* calcd for (C₂₆H₂₇NO₄S₂)Na⁺ 504.1273, found 504.1276.

***N*-(1-(4-chlorophenyl)-4-methyl-2-tosylpenta-2,3-dien-1-yl)benzenesulfonamide (7e).**



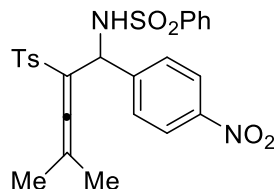
Product was isolated as a white solid (mp = 134-136 °C) in 53% (0.238 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.77 (dd, *J* = 8.3 Hz, *J* = 1.1 Hz, 2H), 7.56 (tt, *J* = 7.5 Hz, *J* = 1.2 Hz, 1H), 7.45 (t, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 5.79 (d, *J* = 8.0 Hz, 1H), 5.32 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 3H), 1.65 (s, 3H), 1.58 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 203.2, 144.4, 140.4, 136.4, 134.0, 132.9, 129.6, 129.2, 128.6, 128.5, 127.7, 127.3, 126.5, 111.6, 110.0, 56.0, 21.7, 19.5, 19.4; IR (cm⁻¹) 3364, 2974, 2929, 1917, 1687, 1601, 1511, 1303, 1262, 1176, 1151, 1082; HRMS *m/z* calcd for (C₂₅H₂₄ClNO₄S₂)Na⁺: 524.0727, found: 524.0721.

***N*-(1-(4-methoxyphenyl)-4-methyl-2-tosylpenta-2,3-dien-1-yl)benzenesulfonamide (7f).**



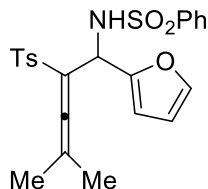
Product was isolated as a white solid (mp = 124-127 °C) in 97% (0.719 g) yield. ¹H NMR (600 MHz, CDCl₃) δ 7.76 (dt, *J* = 7.8 Hz, *J* = 0.6 Hz, 2H), 7.54 (tt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.94 (dddd, *J* = 9.6 Hz, *J* = 4.8 Hz, *J* = 3.0 Hz, 2H), 6.62 (dddd, *J* = 10.2 Hz, *J* = 5.4 Hz, *J* = 3.0 Hz, 2H), 5.59 (d, *J* = 8.4 Hz, 1H), 5.30 (d, *J* = 7.8 Hz, 1H), 3.74 (s, 3H), 2.37 (s, 3H), 1.63 (s, 3H), 1.62 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 202.9, 159.3, 143.8, 140.4, 138.1, 132.5, 129.7, 129.3, 128.9, 128.2, 127.6, 127.2, 113.7, 112.2, 109.6, 55.8, 55.2, 21.5, 19.4, 19.2; IR (cm⁻¹) 3271, 3062, 2977, 2950, 2908, 2838, 1958, 1611, 1511, 1445, 1383, 1326, 1248, 1163, 1144, 1082, 1032, 808; HRMS *m/z* calcd for (C₂₆H₂₇NO₅S₂)Na⁺: 520.1228, found: 520.1227.

***N*-(4-methyl-1-(4-nitrophenyl)-2-tosylpenta-2,3-dien-1-yl)benzenesulfonamide (7g).**



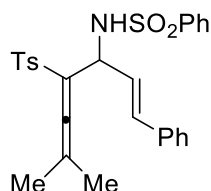
Product was isolated as a yellow solid (mp = 134-135 °C) in 72% (0.47 g) yield. ¹H NMR (600 MHz, CDCl₃) δ 7.98 (dddd, *J* = 11.4 Hz, *J* = 4.2 Hz, *J* = 2.4 Hz, 2H), 7.80 (dddd, *J* = 8.4 Hz, *J* = 3.4 Hz, 1.1 Hz, 2H), 7.59 (tt, *J* = 7.5 Hz, *J* = 1.1 Hz, 1H), 7.34 (dddd, *J* = 8.5 Hz, *J* = 3.6 Hz, 1.9 Hz, 2H), 7.28 (dddd, *J* = 10.8 Hz, *J* = 4.2 Hz, *J* = 2.4 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 5.93 (d, *J* = 7.6 Hz, 1H), 5.41 (d, *J* = 7.6 Hz, 1H), 2.38 (s, 3H), 1.67 (s, 3H), 1.53 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 203.3, 147.4, 145.1, 144.8, 139.9, 137.4, 133.0, 129.6, 129.2, 127.9, 127.6, 127.2, 123.5, 110.8, 110.3, 56.1, 21.6, 19.3, 19.2; IR (cm⁻¹) 3352, 3061, 2985, 1520, 1415, 1351, 1252, 1164, 1141, 896; HRMS *m/z* calcd for (C₂₅H₂₄N₂O₆S₂)Na⁺: 535.0968, found: 535.0966.

***N*-(1-(furan-2-yl)-4-methyl-2-tosylpenta-2,3-dien-1-yl)benzenesulfonamide (7h).**



Product was isolated as a white solid (mp = 114-117 °C) in 61% (0.253 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.79 (dd, *J* = 8.6 Hz, *J* = 1.3 Hz, 2H), 7.53 (dddd, *J* = 21.4 Hz, *J* = 13.9 Hz, *J* = 6.5 Hz, 1H), 7.46 (dddd, *J* = 21.0 Hz, *J* = 13.0 Hz, *J* = 4.6 Hz, 4H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.01 (dd, *J* = 1.4 Hz, *J* = 0.9 Hz, 1H), 6.13 (dddd, *J* = 6.8, 5.1, 3.2 Hz, 2H), 5.75 (d, *J* = 9.3 Hz, 1H), 5.45 (d, *J* = 9.3 Hz, 1H), 2.38 (s, 3H), 1.64 (s, 3H), 1.61 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 203.3, 149.8, 143.9, 142.5, 140.3, 138.0, 132.6, 129.4, 128.9, 127.5, 127.0, 110.4, 110.0, 109.9, 108.6, 50.7, 21.5, 19.3, 19.0; IR (cm⁻¹) *v*_{max} = 3269, 3060, 2983, 2909, 1958, 1593, 1450, 1328, 1164, 1144, 1086; HRMS *m/z* calcd for (C₂₃H₂₃NO₅S₂)Na⁺: 480.0910, found: 480.0911.

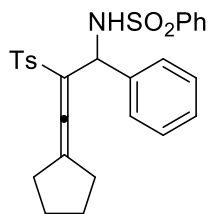
***(E)*-N-(6-methyl-1-phenyl-4-tosylhepta-1,4,5-trien-3-yl)benzenesulfonamide (7i).**



Product was isolated as a yellow solid (mp = 109-122 °C) in 64% (0.283 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, *J* = 7.4 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.24 (d, *J* = 7.3 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.09 (dd, *J* = 7.9 Hz, *J* =

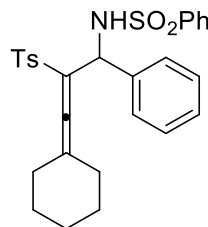
1.5 Hz, 2H), 6.40 (d, $J = 15.8$ Hz, 1H), 5.83 (dd, $J = 15.8$ Hz, $J = 6.3$ Hz, 2H), 5.58 (d, $J = 8.6$ Hz, 1H), 4.97 (t, $J = 6.9$ Hz, 1H), 2.35 (s, 3H), 1.64 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 202.5, 144.3, 140.8, 138.2, 135.7, 132.6, 132.4, 129.6, 129.0, 128.4, 128.0, 127.9, 127.2, 126.6, 126.1, 111.0, 109.5, 55.0, 21.5, 19.4, 19.3; IR (cm^{-1}) 3358, 3271, 3052, 2987, 1958, 1319, 1266, 1164, 1143, 1086; HRMS m/z calcd for $(\text{C}_{27}\text{H}_{27}\text{NO}_4\text{S}_2)\text{Na}^+$: 516.1279, found: 516.1275.

N-(3-cyclopentylidene-1-phenyl-2-tosylallyl)benzenesulfonamide (7j).



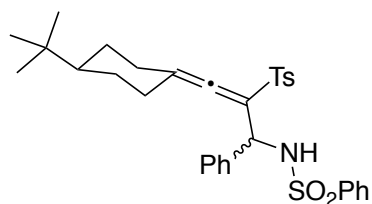
Product was isolated as a white solid (mp = 160-162 °C) in 86% (0.12 g) yield. ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, $J = 8.5$ Hz, 2H), 7.56-7.53 (m, 1H), 7.45 (dd, $J = 8.0$ Hz, $J = 8.0$, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 7.15-7.10 (m, 5H), 7.05 (d, $J = 7.0$ Hz, 2H), 5.65 (d, $J = 8.0$ Hz, 1H), 5.36 (d, $J = 8.5$ Hz, 1H), 2.37 (s, 3H), 2.33-2.18 (m, 4H), 1.65-1.63 (m, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.0, 143.9, 140.2, 138.1, 137.6, 132.5, 129.3, 128.9, 128.3, 127.8, 127.6, 127.2, 126.9, 117.4, 113.8, 56.1, 31.46, 31.42, 26.9, 26.8, 21.5; IR (cm^{-1}) 3628, 3538, 3162, 3007, 2937, 2251, 1450, 1372, 1172, 1143, 1037, 914, 730; HRMS m/z calcd for $(\text{C}_{27}\text{H}_{27}\text{NO}_4\text{S}_2)\text{Na}^+$ 516.1273, found 516.1275.

N-(3-cyclohexylidene-1-phenyl-2-tosylallyl)benzenesulfonamide (7k).



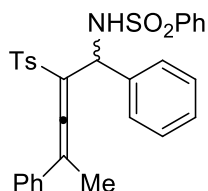
Product was isolated as a white solid (mp = 158-160 °C) in 92% (0.125 g) yield. ^1H NMR (500 MHz, CDCl_3) δ 7.79-7.77 (m, 2H), 7.56-7.53 (m, 1H), 7.46-7.43 (m, 2H), 7.38-7.37 (m, 2H), 7.14-7.12 (m, 5H), 7.07-7.06 (m, 2H), 5.58 (d, $J = 7.5$ Hz, 1H), 5.34 (d, $J = 7.5$ Hz, 1H), 2.38 (s, 3H), 2.04-1.86 (m, 4H), 1.46-1.45 (m, 5H), 1.39-1.38 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 200.1, 143.9, 140.2, 138.0, 137.7, 132.5, 129.3, 128.9, 128.3, 127.8, 127.7, 127.2, 126.9, 115.7, 111.6, 56.4, 29.88, 29.82, 26.5, 25.2, 21.5; IR (cm^{-1}) 3366, 3056, 2986, 2263, 1458, 1425, 1266, 1168, 1143, 1086, 910, 739; HRMS m/z calcd for $(\text{C}_{28}\text{H}_{29}\text{NO}_4\text{S}_2)\text{Na}^+$ 530.1430, found 530.1435.

N-(3-(4-(tert-butyl)cyclohexylidene)-1-phenyl-2-tosylallyl)benzenesulfonamide (7l).



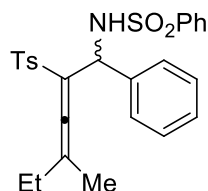
Product was isolated as a white solid (mp = 155-158 °C) in 82% yield (0.146 g). ^1H NMR (500 MHz, CDCl_3) δ 7.83 (dd, J = 8.5 Hz, J = 1.3 Hz, 2H), 7.57 (tt, J = 7.4 Hz, J = 1.2 Hz, 1H), 7.47 (tt, J = 8.0 Hz, J = 1.7 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 7.19-7.14 (m, 7H), 5.60 (d, J = 8.1 Hz, 1H), 5.45 (d, J = 8.1 Hz, 1H), 5.45 (d, J = 8.1 Hz, 1H), 2.38 (s, 3H), 2.12-2.04 (m, 2H), 1.90-1.76 (m, 4H), 0.98 (tt, J = 12.0 Hz, J = 2.7 Hz, 1H), 0.81 (s, 9H), 0.78-0.72 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.0, 144.2, 140.5, 138.1, 138.0, 132.7, 129.4, 129.1, 128.6, 128.2, 128.1, 127.5, 127.2, 115.8, 112.2, 56.4, 47.2, 32.6, 30.3, 30.2, 27.6, 27.4, 21.7; IR (cm^{-1}) 3364, 3049, 2985, 1427, 1269, 896, 762, 698; HRMS m/z calcd for $(\text{C}_{32}\text{H}_{37}\text{NO}_4\text{S}_2)\text{Na}^+$: 586.2056, found: 586.2053.

N-(4-methyl-1-phenyl-2-tosylhexa-2,3-dien-1-yl)benzenesulfonamide (7m).



Product was isolated as a white solid (mp = 140-142 °C) in 87% (0.113 g) yield. ^1H NMR (500 MHz, CDCl_3) δ 7.77-7.74 (m, 4H), 7.53-7.50 (m, 3H), 7.45-7.38 (m, 9H), 7.31-7.28 (m, 6H), 7.19-7.08 (m, 19H), 5.69 (d, J = 8.0 Hz, 1H), 5.50 (d, J = 8.0 Hz, 1H), 5.46 (d, J = 5.5 Hz, 2H), 2.37 (s, 3H), 2.35 (s, 3H), 2.00 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 206.3, 206.0, 144.2, 140.19, 140.11, 137.8, 137.5, 133.1, 132.7, 132.6, 132.5, 129.4, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.1, 127.9, 127.7, 127.1, 127.08, 127.04, 126.8, 126.3, 126.2, 116.1, 115.8, 114.1, 113.6, 56.8, 56.6, 22.5, 21.52, 21.51, 16.0; IR (cm^{-1}) 3360, 3158, 3051, 2990, 2251, 1446, 1421, 1462, 1160, 1080, 918, 726, 702, 647; HRMS m/z calcd for $(\text{C}_{30}\text{H}_{27}\text{NO}_4\text{S}_2)\text{Na}^+$ 552.1273, found 552.1274.

N-(1,4-diphenyl-2-tosylpenta-2,3-dien-1-yl)benzenesulfonamide (7n).



Product was isolated as a white solid (mp = 128-130 °C) in 96% (0.136 g) yield. ^1H NMR (500 MHz, CDCl_3) δ 7.78-7.75 (m, 3H), 7.55-7.52 (m, 3H), 7.45-7.35 (m, 8H), 7.16-7.09 (m, 10H), 7.05-7.02 (m, 4H), 5.61 (d, J = 7.5 Hz, 1H), 5.53 (d, J = 7.5 Hz, 1H), 5.34 (d, J = 7.5 Hz, 1H),

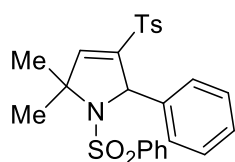
5.33 (d, $J = 7.0$ Hz, 1H), 2.39 (s, 3H), 2.31 (s, 3H), 1.99 (q, $J = 7.5$ Hz, 2H), 1.94-1.83 (m, 2H), 1.64 (s, 3H), 1.54 (s, 3H), 0.90 (t, $J = 7.5$ Hz, 3H), 0.73 (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 203.0, 202.9, 144.06, 144.0, 140.3, 140.1, 137.9, 137.8, 137.6, 132.7, 129.37, 129.31, 129.1, 128.9, 128.8, 18.28, 128.25, 127.85, 127.8, 127.7, 127.6, 127.2, 127.1, 126.9, 126.8, 126.4, 115.9, 115.6, 113.9, 113.7, 56.5, 56.3, 26.97, 26.91, 21.54, 21.52, 17.6, 17.5, 11.7, 11.4; IR (cm^{-1}) 3366, 3051, 2990, 2255, 1601, 1446, 1417, 1327, 1262, 1168, 1147, 1078, 902, 739; HRMS m/z calcd for $(\text{C}_{26}\text{H}_{27}\text{NO}_4\text{S}_2)\text{Na}^+$ 504.1273, found 504.1274.

V. General procedure for the synthesis of 3-Sulfonyl-3-Pyrrolines.

General Procedure: To a stirred solution of an allenyl sulfonamide **7b** (0.720 g, 1.52 mmol) in acetonitrile (15.2 mL, 0.1 M) under an argon atmosphere was added silver fluoride (3.8 mg, 2 mol%) at room temperature. Then the reaction mixture was stirred at 85 °C for 40 min. The reaction progress was monitored by TLC. After completion of the reaction, the reaction mixture was cooled down to room temperature. Then the solvent was evaporated by rotary evaporation, and the obtained crude product was purified by flash column chromatography over silica gel. The compound was eluted with 12-15% EtOAc in Hexane. The compound 3-sulfonyl-3-pyrroline **8b** was obtained as a white solid (0.690 g) in 96% yield.

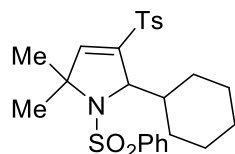
VI. Characterization Data of 3-Sulfonyl-3-Pyrrolines.

2,2-dimethyl-5-phenyl-1-(phenylsulfonyl)-4-tosyl-2,5-dihydro-1H-pyrrole (8a).



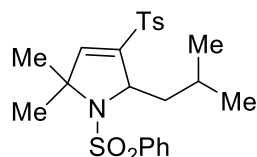
Product was isolated as a white solid (mp = 157-159 °C) in 97% (0.097 g) yield. ^1H NMR (500 MHz, CDCl_3) δ 7.31-7.27 (m, 3H), 7.14-7.10 (m, 4H), 7.01-6.98 (m, 1H), 6.94 (d, $J = 8.0$ Hz, 2H), 6.85-6.79 (m, 4H), 6.70 (d, $J = 1.5$ Hz, 1H), 5.71 (d, $J = 1.5$ Hz, 1H), 2.30 (s, 3H), 1.806 (s, 3H), 1.802 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.2, 144.0, 141.0, 140.3, 135.0, 131.8, 129.3, 128.9, 128.2, 128.0, 127.9, 127.6, 127.1, 71.9, 69.4, 28.2, 27.6, 21.4; IR (cm^{-1}) 3049, 2981, 2910, 1621, 1637, 1560, 1510, 1440, 1310, 1268, 1142, 1078, 1042, 803, 729, 660; HRMS m/z calcd for $(\text{C}_{25}\text{H}_{25}\text{NO}_4\text{S}_2)\text{Na}^+$ 490.1117, found 490.1121.

5-cyclohexyl-2,2-dimethyl-1-(phenylsulfonyl)-4-tosyl-2,5-dihydro-1H-pyrrole (8b).



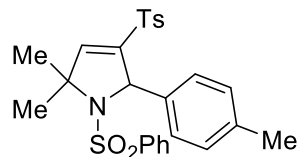
Product was isolated as a white solid (mp = 142-144 °C) in 96% (0.690 g) yield. ^1H NMR (500 MHz, CDCl_3) δ 7.69-7.66 (m, 4H), 7.54-7.50 (m, 1H), 7.41-7.37 (m, 2H), 7.33 (d, J = 8.0 Hz, 2H), 6.30 (d, J = 1.0 Hz, 1H), 4.54 (s, 1H), 2.47 (s, 3H), 1.98-1.93 (m, 1H), 1.74-1.63 (m, 3H), 1.62 (s, 3H), 1.55-1.48 (m, 4H), 1.41 (s, 3H), 1.39-1.30 (m, 1H), 1.11-0.95 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 147.8, 144.9, 142.1, 139.7, 136.3, 132.2, 129.9, 128.8, 128.1, 127.0, 72.6, 70.7, 42.7, 28.9, 28.5, 27.9, 26.8, 26.6, 26.4, 25.8, 21.6; IR (cm^{-1}) 3068, 2925, 2855, 1629, 1597, 1450, 1343, 1168, 1147, 1086, 1037, 836, 722, 698, 661; HRMS m/z calcd for $(\text{C}_{25}\text{H}_{31}\text{NO}_4\text{S}_2)\text{Na}^+$ 496.1586, found 496.1587.

5-isobutyl-2,2-dimethyl-1-(phenylsulfonyl)-4-tosyl-2,5-dihydro-1H-pyrrole (8c).



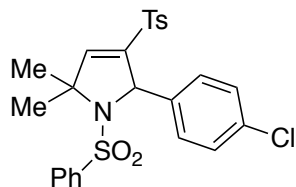
Product was isolated as a white solid (mp = 117-119 °C) in 95% (0.095 g) yield. ^1H NMR (500 MHz, CDCl_3) δ 7.72-7.70 (m, 2H), 7.63-7.61 (m, 2H), 7.52-7.49 (m, 1H), 7.38-7.34 (m, 4H), 6.38 (d, J = 1.0 Hz, 1H), 4.70 (ddd, J = 5.0 Hz, J = 4.5 Hz, J = 1.0 Hz, 1H), 2.48 (s, 3H), 1.95-1.91 (m, 2H), 1.84 (septet, J = 3.5 Hz, 1H), 1.61 (s, 3H), 1.36 (s, 3H), 0.89 (d, J = 6.0 Hz, 3H), 0.83 (d, J = 6.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 146.4, 145.1, 142.1, 141.4, 136.2, 132.2, 130.0, 128.8, 128.0, 126.8, 70.6, 66.0, 44.3, 29.4, 25.4, 24.0, 23.4, 22.9, 21.7; IR (cm^{-1}) 3068, 2953, 2868, 1642, 1601, 1470, 1450, 1343, 1168, 1147, 1094, 1041, 914, 726, 661; HRMS m/z calcd for $(\text{C}_{23}\text{H}_{29}\text{NO}_4\text{S}_2)\text{Na}^+$ 470.1430, found 470.1437.

2,2-dimethyl-1-(phenylsulfonyl)-5-(p-tolyl)-4-tosyl-2,5-dihydro-1H-pyrrole (8d).



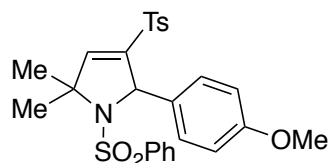
Product was isolated as a white solid (mp = 153-155 °C) in 98% (0.062 g) yield. ^1H NMR (500 MHz, CDCl_3) δ 7.33-7.29 (m, 3H), 7.15-7.12 (m, 4H), 6.95 (d, J = 8.0 Hz, 2H), 6.68 (d, J = 1.5 Hz, 1H), 6.67 (d, J = 8.5 Hz, 2H), 6.61 (d, J = 7.5 Hz, 2H), 5.65 (d, J = 2.0 Hz, 1H), 2.32 (s, 3H), 2.18 (s, 3H), 1.76 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 145.9, 143.9, 141.1, 140.4, 137.9, 136.1, 132.2, 131.6, 129.1, 128.7, 128.5, 128.1, 127.7, 127.2, 71.7, 69.0, 28.2, 27.5, 21.4, 20.9; IR (cm^{-1}) 3051, 2982, 2917, 1634, 1597, 1515, 1446, 1327, 1270, 1147, 1082, 1045, 812, 735, 698, 661; HRMS m/z calcd for $(\text{C}_{26}\text{H}_{27}\text{NO}_4\text{S}_2)\text{Na}^+$ 504.1273, found 504.1274.

5-(4-chlorophenyl)-2,2-dimethyl-1-(phenylsulfonyl)-4-tosyl-2,5-dihydro-1H-pyrrole (8e).



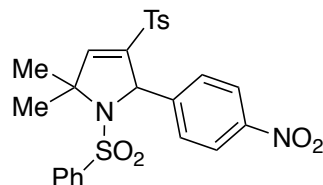
Product was isolated as a white solid (mp = 149-152 °C) in 78% (0.062g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.35 (d, *J* = 7.1 Hz, 2H), 7.18 (t, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 6.99 (d, *J* = 8.2 Hz, 2H), 6.74 (d, *J* = 8.3 Hz, 3H), 6.69 (d, *J* = 8.4 Hz, 3H), 5.67 (t, *J* = 1.4 Hz, 1H), 2.34 (s, 3H), 1.82 (s, 3H), 1.79 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 146.4, 144.5, 140.9, 140.0, 135.9, 134.2, 133.8, 132.0, 130.0, 129.4, 128.3, 128.0, 127.6, 127.2, 72.0, 68.4, 28.3, 27.4, 21.5; IR (cm⁻¹) 3072, 2978, 2921, 1650, 1491, 1324, 1148, 1086; HRMS *m/z* calcd for (C₂₅H₂₄ClNO₄S₂)Na⁺: 524.0727, found: 524.0728.

5-(4-methoxyphenyl)-2,2-dimethyl-1-(phenylsulfonyl)-4-tosyl-2,5-dihydro-1H-pyrrole (8f).



Product was isolated as a white solid (mp = 151-154 °C) in 99% yield (0.100 g). ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.29 (m, 3H), 7.16-7.13 (m, 4H), 6.97 (d, *J* = 8.1 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 3H), 6.33 (d, *J* = 8.6 Hz, 2H), 5.67 (d, *J* = 1.3 Hz, 1H), 3.70 (s, 3H), 2.32 (s, 3H), 1.79 (s, 3H), 1.79 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 159.6, 145.9, 144.0, 141.3, 140.5, 136.3, 131.7, 130.0, 129.2, 128.2, 127.8, 127.2, 127.1, 113.3, 71.6, 68.8, 55.2, 28.2, 27.6, 21.4; IR (cm⁻¹) 3066, 2929, 1610, 1507, 1446, 1315, 1160, 1086, 1042, 805; HRMS *m/z* calcd for (C₂₆H₂₇NO₅S₂)Na⁺: 520.1228, found: 520.1224.

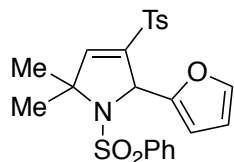
2,2-dimethyl-5-(4-nitrophenyl)-1-(phenylsulfonyl)-4-tosyl-2,5-dihydro-1H-pyrrole (8g).



Product was isolated as a white solid (mp = 163-164 °C) in 99% (0.095 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 6.78 (d, *J* = 1.4 Hz, 1H), 5.75 (d, *J* = 1.4 Hz, 1H), 2.31 (s, 3H), 1.88 (s, 3H), 1.78 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 147.5, 147.1, 145.1, 142.9, 140.4, 139.5, 135.8, 132.6, 129.5, 129.5,

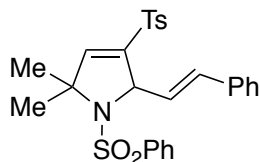
128.6, 127.6, 127.3, 122.9, 72.6, 68.3, 28.6, 27.0, 21.4; IR (cm⁻¹) 3077, 2983, 2929, 1597, 1524, 1340, 1144, 1086, 813; HRMS m/z calcd for (C₂₅H₂₄N₂O₆S₂)Na⁺: 535.0968, found: 535.0968.

5-(furan-2-yl)-2,2-dimethyl-1-(phenylsulfonyl)-4-tosyl-2,5-dihydro-1H-pyrrole (8h).



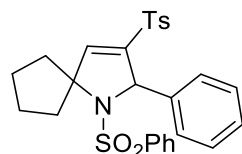
Product was isolated as a white solid (mp = 145-146 °C) in 83% (0.083 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.46 (d, *J* = 7.4 Hz, 2H), 7.40-7.37 (m, 3H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.1 Hz, 2H), 6.71 (d, *J* = 1.4 Hz, 1H), 6.67 (s, 1H), 6.21 (d, *J* = 3.2 Hz, 1H), 6.00 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.81 (d, *J* = 1.2 Hz, 1H), 2.36 (s, 3H), 1.75 (s, 3H), 1.66 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 147.4, 147.4, 144.3, 142.9, 141.0, 137.7, 135.6, 132.0, 129.5, 128.4, 127.8, 127.0, 111.6, 110.2, , 71.4, 61.9, 27.4, 27.3, 21.5; IR (cm⁻¹) 3068, 2983, 2929, 1597, 1446, 1324, 1152, 1091; HRMS m/z calcd for (C₂₃H₂₃NO₅S₂)Na⁺: 480.0910, found: 480.0912.

(E)-2,2-dimethyl-1-(phenylsulfonyl)-5-styryl-4-tosyl-2,5-dihydro-1H-pyrrole (8i).



Product was isolated as a white solid, (mp = 120-123 °C) in 78% (0.66 g) yield; ¹H NMR (500 MHz, CDCl₃) δ 7.71 (dd, *J* = 8.2, 0.9 Hz, 2H), 7.54 (dd, *J* = 8.3 Hz, 2H), 7.36 (tt, *J* = 8.4, 1.0 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.22-7.21 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.92-6.90 (m, 2H), 6.69 (d, *J* = 1.5 Hz, 1H), 6.37 (d, *J* = 15.6 Hz, 1H), 5.24 (dd, *J* = 9.4, 0.9 Hz, 1H), 5.07 (dd, *J* = 15.6, 9.4 Hz, 1H), 2.25 (s, 3H), 1.72 (s, 3H), 1.72 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 146.6, 144.8, 141.7, 139.2, 136.1, 135.4, 134.7, 132.3, 129.7, 128.6, 128.4, 128.2, 128.2, 127.7, 126.7, 125.9, 71.6, 68.0, 28.6, 26.9, 21.4; IR (cm⁻¹) 3084, 3060, 2978, 2929, 1654, 1319, 1148, 1086; HRMS m/z calcd for (C₂₇H₂₇NO₄S₂)Na⁺: 516.1274, found: 516.1272.

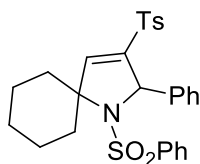
2-phenyl-1-(phenylsulfonyl)-3-tosyl-1-azaspiro[4.4]non-3-ene (8j).



Product was isolated as a white solid (mp = 152-154 °C) in 99% (0.049 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.33 (m, 3H), 7.01-6.98 (m, 1H), 7.19-7.16 (m, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.02-6.98 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.85-6.81 (m, 5H), 5.69 (d, *J* = 1.5 Hz, 1H),

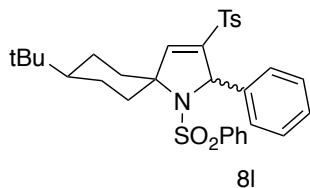
2.91-2.85 (m, 1H), 2.58-2.55 (m, 1H), 2.30 (s, 3H), 2.06-1.97 (m, 3H), 1.85-1.71 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.9, 143.9, 141.0, 139.2, 136.2, 135.9, 131.9, 129.3, 128.6, 128.3, 128.0, 127.9, 127.6, 127.1, 69.3, 80.5, 39.0, 36.5, 24.7, 24.2, 21.4; IR (cm^{-1}) 3047, 2986, 1597, 1446, 1421, 1319, 1262, 1155, 1094, 898, 747; HRMS m/z calcd for $(\text{C}_{27}\text{H}_{27}\text{NO}_4\text{S}_2)\text{Na}^+$ 516.1273, found 516.1275.

2-phenyl-1-(phenylsulfonyl)-3-tosyl-1-azaspiro[4.5]dec-3-ene (8k)



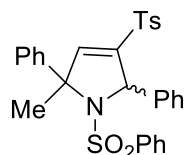
Product was isolated as a white solid (mp = 168-170 °C) in 98% (0.039 g) yield. ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.34 (m, 2H), 7.31-7.28 (m, 2H), 7.16-7.10 (m, 4H), 6.99-6.96 (m, 1H), 6.94 (d, J = 8.5 Hz, J = 1.0 Hz, 2H), 6.82-6.81 (m, 4H), 5.70 (d, J = 2.0 Hz, 1H), 2.93-2.87 (m, 1H), 2.66-2.60 (m, 1H), 2.30 (s, 3H), 2.05-2.02 (m, 1H), 1.90-1.80 (m, 4H), 1.58-1.38 (m, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.9, 142.7, 141.4, 141.1, 136.1, 135.3, 131.7, 129.2, 128.9, 128., 127.9, 127.8, 127.6, 127.1, 69.2, 37.9, 36.6, 24.9, 24.7, 24.5, 21.4; IR (cm^{-1}) 3051, 2986, 232, 1450, 1421, 1315, 1274, 1151, 1090, 1045, 898, 743, 702; HRMS m/z calcd for $(\text{C}_{28}\text{H}_{29}\text{NO}_4\text{S}_2)\text{Na}^+$ 530.1430, found 530.1432.

(5s,8s)-8-(tert-butyl)-2-phenyl-1-(phenylsulfonyl)-3-tosyl-1-azaspiro[4.5]dec-3-ene (8l).



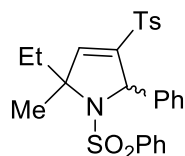
Product was isolated as a white solid (mp = 237-240 °C) in 99% (0.038 g) yield. ^1H NMR (500 MHz, CDCl_3) δ 7.36 (dd, J = 8.4, 1.1 Hz, 2H), 7.30 (tt, J = 7.5, 1.1 Hz, 1H), 7.26 (d, J = 1.9 Hz, 1H), 7.15 (dddd, J = 9.9, 9.1, 1.6 Hz, 2H), 7.12 (dt, J = 8.3, 1.7 Hz, 2H), 6.97 (d, J = 7.9 Hz, 1H), 6.94 (d, J = 7.9 Hz, 2H), 6.84-6.80 (m, 4H), 5.70 (d, J = 1.7 Hz, 1H), 2.94 (ddd, J = 25.4, 12.7, 3.9 Hz, 1H), 2.67 (ddd, J = 25.5, 12.8, 4.0 Hz, 1H), 2.30 (s, 3H), 2.08 (dd, J = 12.6, 2.5 Hz, 1H), 1.94-1.88 (m, 3H), 1.36-1.23 (m, 3H), 0.93 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.1, 142.9, 141.6, 141.3, 136.3, 135.5, 131.9, 129.5, 129.1, 128.4, 128.1, 128.0, 127.8, 127.3, 77.1, 69.4, 47.0, 38.2, 36.7, 32.5, 27.7, 25.8, 25.6, 21.6; IR (cm^{-1}) 3055, 2985, 1450, 1427, 1269, 1147, 1083, 896; HRMS m/z calcd for $(\text{C}_{32}\text{H}_{37}\text{NO}_4\text{S}_2)\text{H}^+$: 564.2237, found: 564.2239.

2-methyl-2,5-diphenyl-1-(phenylsulfonyl)-4-tosyl-2,5-dihydro-1H-pyrrole (8m).



Product was isolated as a white solid (mp = 199-201 °C) in 98% (0.062 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.58-7.56 (m, 2H), 7.44-7.42 (m, 3H), 7.32-7.27 (m, 6H), 7.17-7.16 (m, 4H), 7.11-7.03 (m, 6H), 7.00-6.96 (m, 9H), 6.83-6.79 (m, 7H), 6.66 (d, *J* = 1.5 Hz, 1H), 6.46 (d, *J* = 2.0 Hz, 1H), 6.44 (d, *J* = 1.5 Hz, 1H), 5.84 (d, *J* = 1.5 Hz, 2H), 2.34 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.9, 139.3, 136.15, 136.13, 136.1, 133.9, 131.6, 131.3, 129.5, 129.47, 129.4, 128.64, 128.6, 128.5, 128.4, 128.3, 128.28, 128.2, 128.1, 127.8, 127.78, 127.74, 127.73, 127.5, 127.0, 126.8, 126.6, 74.7, 74.6, 70.8, 68.5, 31.5, 25.8, 24.8, 22.6, 21.5; IR (cm⁻¹) 3060, 3031, 2978, 2917, 1638, 1597, 1507, 1442, 1372, 1160, 1086, 1041, 874, 808, 764, 739, 669; HRMS *m/z* calcd for (C₃₀H₂₇NO₄S₂)Na⁺ 552.1273, found 552.1272.

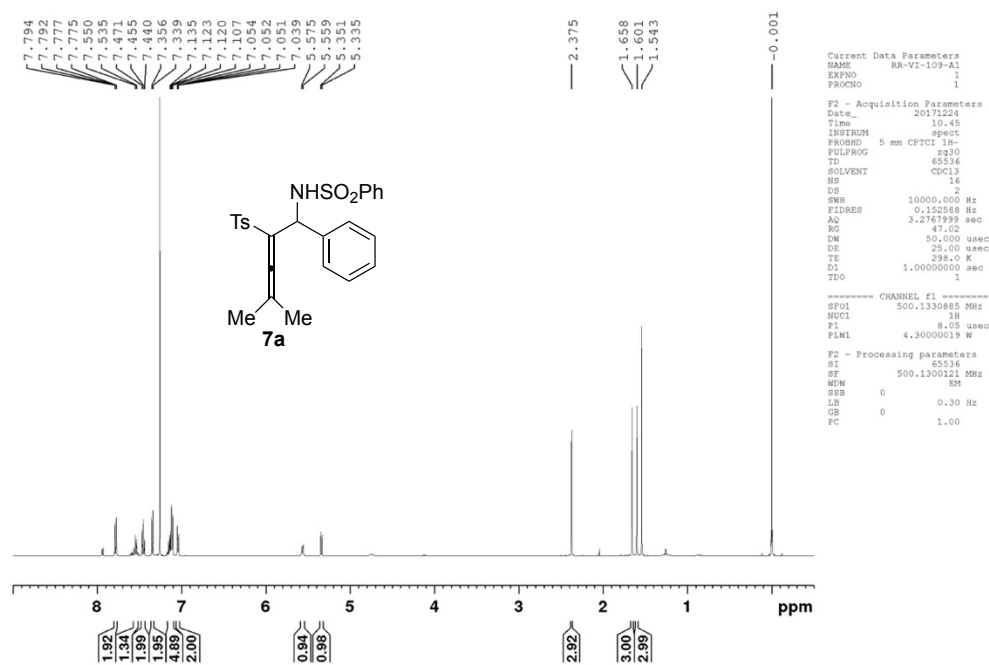
2-ethyl-2-methyl-5-phenyl-1-(phenylsulfonyl)-4-tosyl-2,5-dihydro-1H-pyrrole (8n)



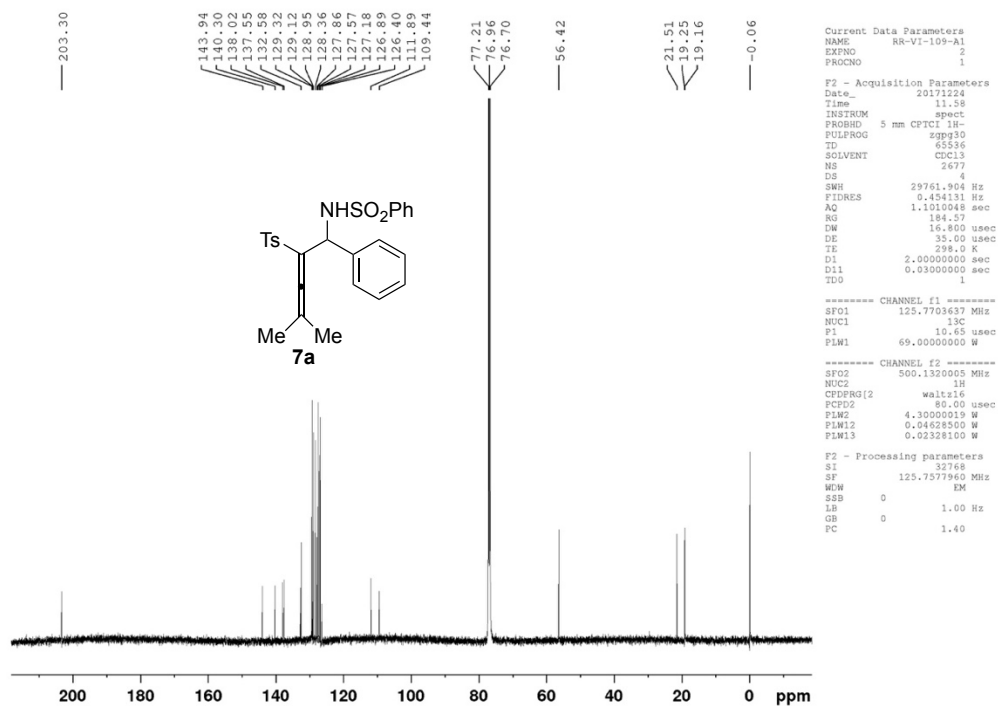
Product was isolated as a white solid (mp = 158-160 °C) in 99% (0.075 g) yield. ¹H NMR (500 MHz, CDCl₃) δ 7.29-7.27 (m, 1H), 7.25-7.20 (m, 3H), 7.19-7.17 (m, 2H), 7.13-7.08 (m, 6H), 7.02-6.97 (m, 6H), 6.95-6.93 (m, 2H), 6.83-6.76 (m, 9H), 6.62 (d, *J* = 2.0 Hz, 1H), 5.71 (d, *J* = 2.0 Hz, 2H), 2.64-2.56 (m, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.29-2.27 (m, 1H), 2.21-2.13 (m, 1H), 1.84-1.80 (m, 1H), 1.79 (s, 3H), 1.77 (s, 3H), 1.05-1.00 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 141.8, 141.6, 140.93, 140.9, 136.2, 136.1, 134.8, 131.8, 129.4, 129.3, 129.28, 129.24, 128.16, 128.15, 128.10, 127.9, 127.8, 127.7, 127.5, 127.1, 126.8, 70.7, 68.9, 33.9, 33.1, 27.0, 25.8, 21.48, 21.46, 10.4, 8.7; IR (cm⁻¹) 3064, 2970, 2933, 2872, 1634, 1597, 1458, 1450, 1339, 1323, 1160, 1080, 1041, 812, 771, 726, 690; HRMS *m/z* calcd for (C₂₆H₂₇NO₄S₂)Na⁺ 504.1273, found 504.1272.

VII. Spectral data of ¹H NMR Spectra and ¹³C NMR

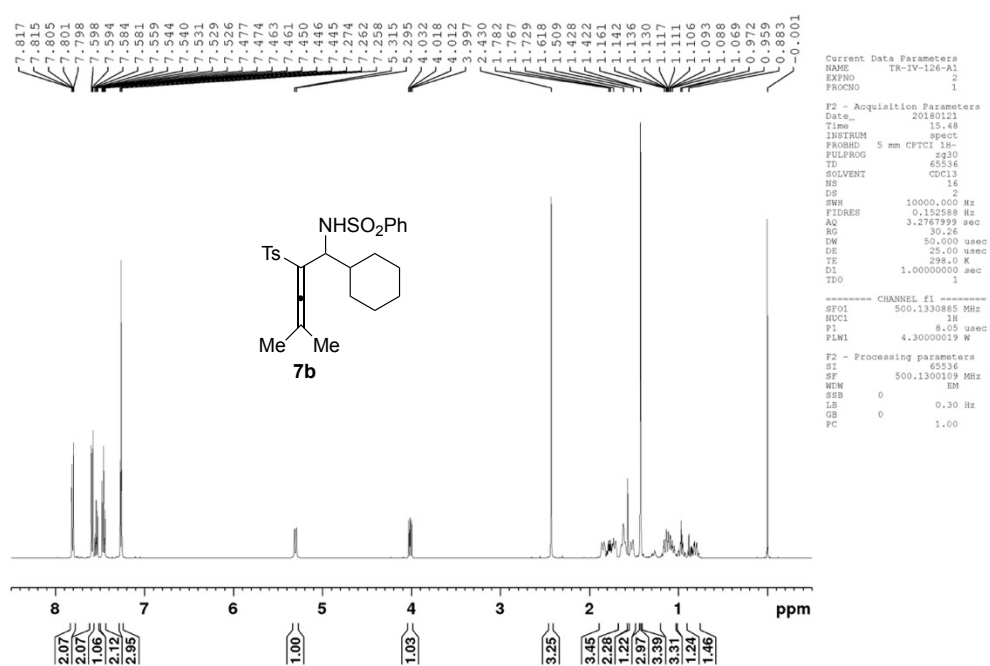
RR-VI-109-A1



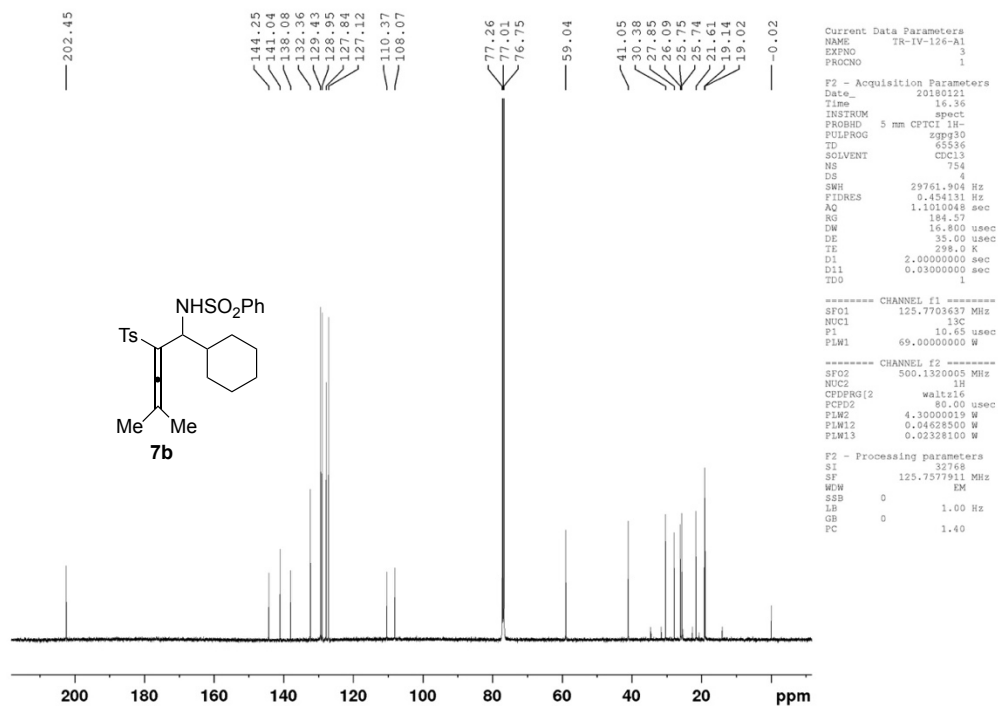
RR-VI-109-A1



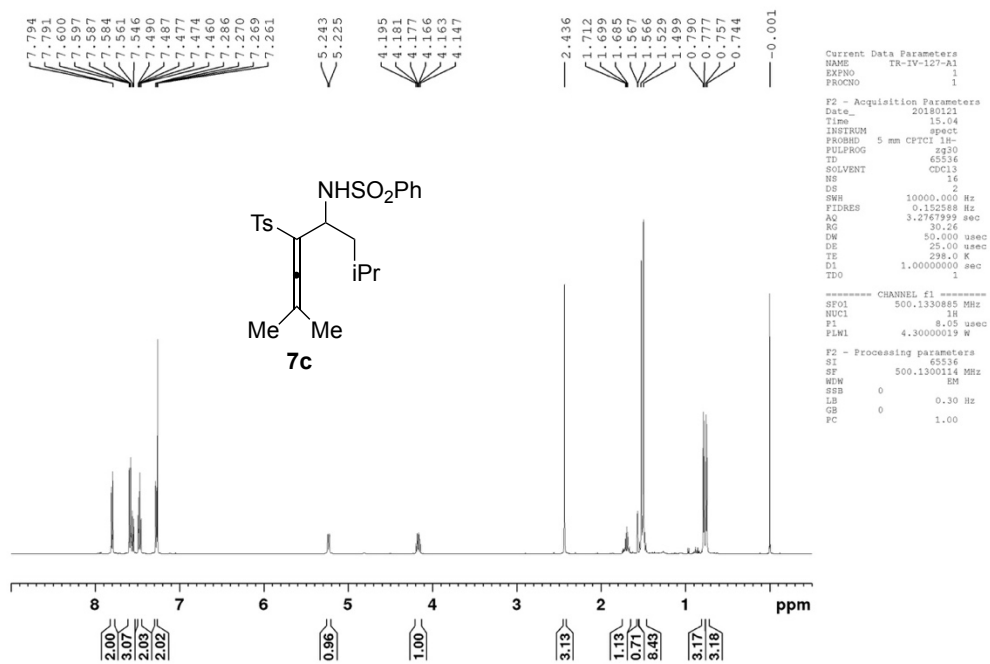
TR-IV-126-A1



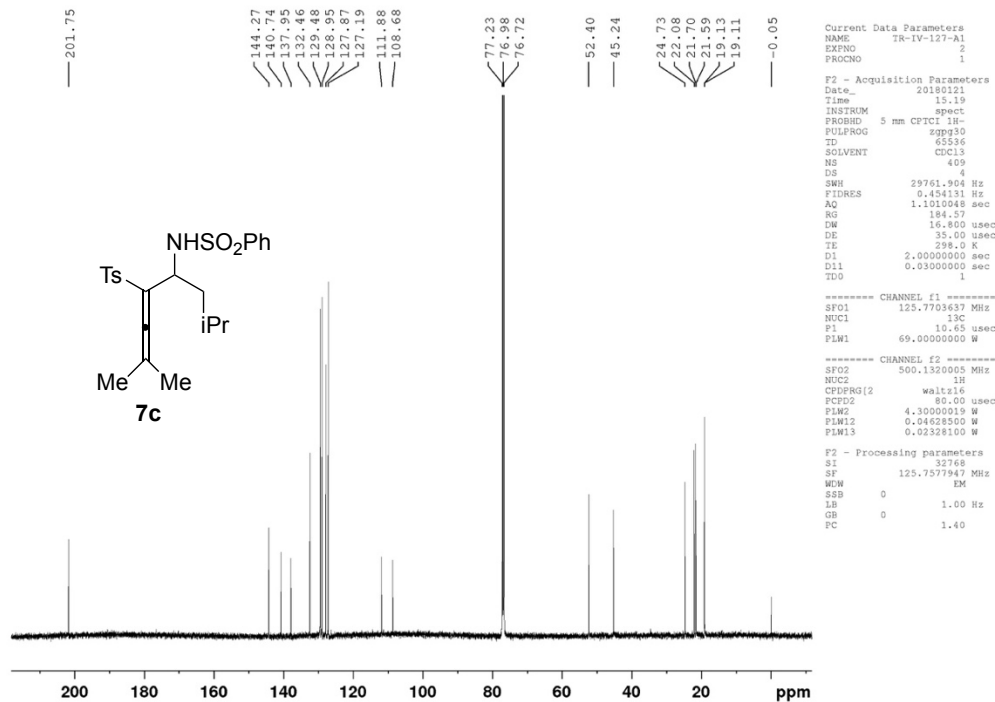
TR-IV-126-A1



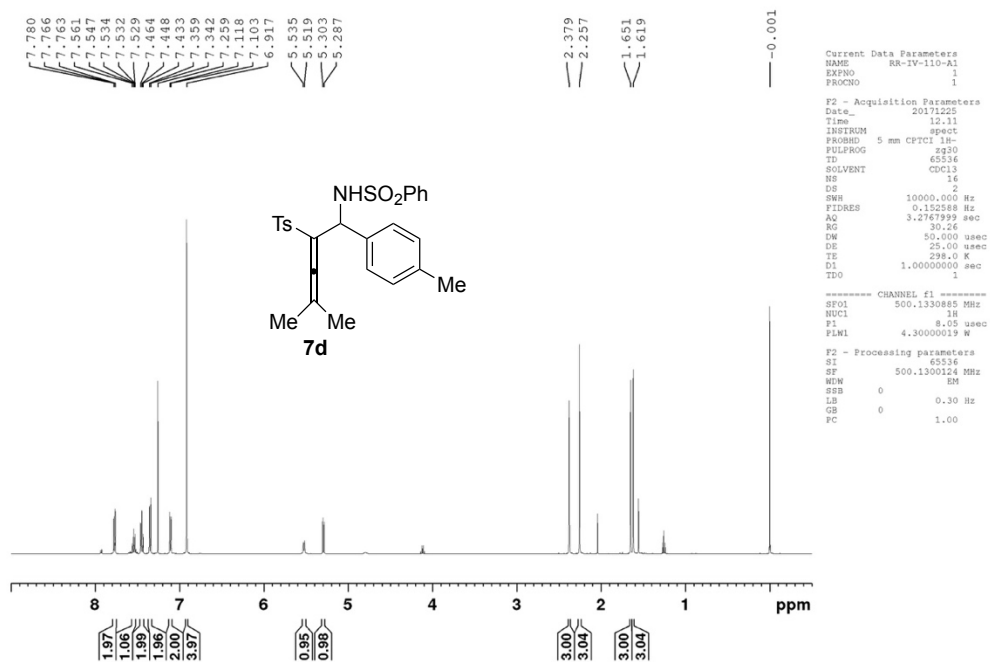
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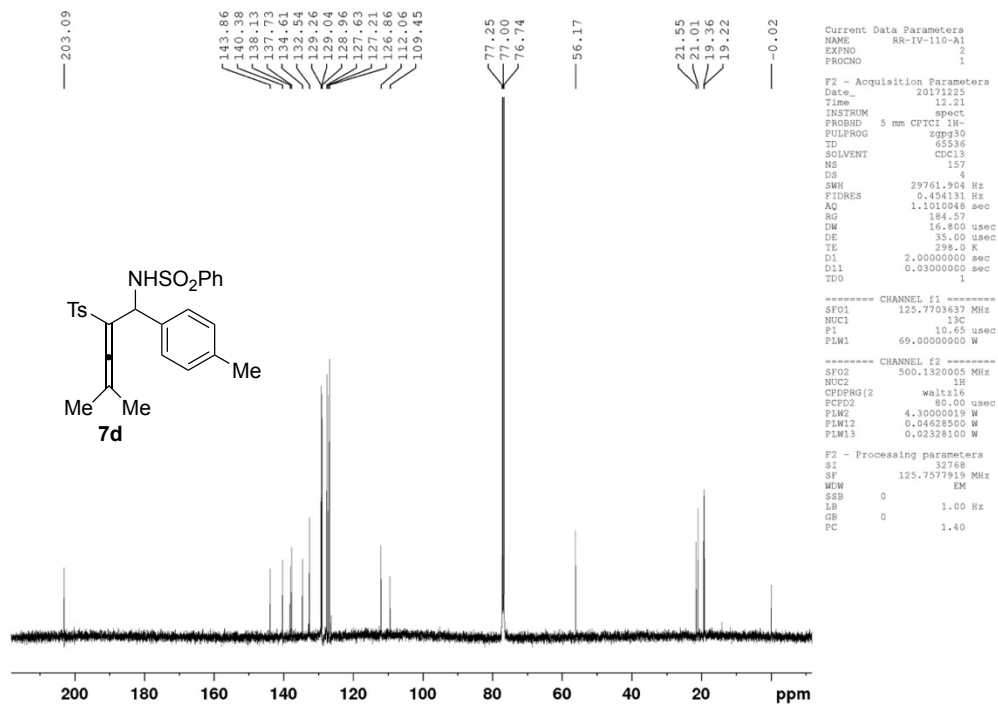
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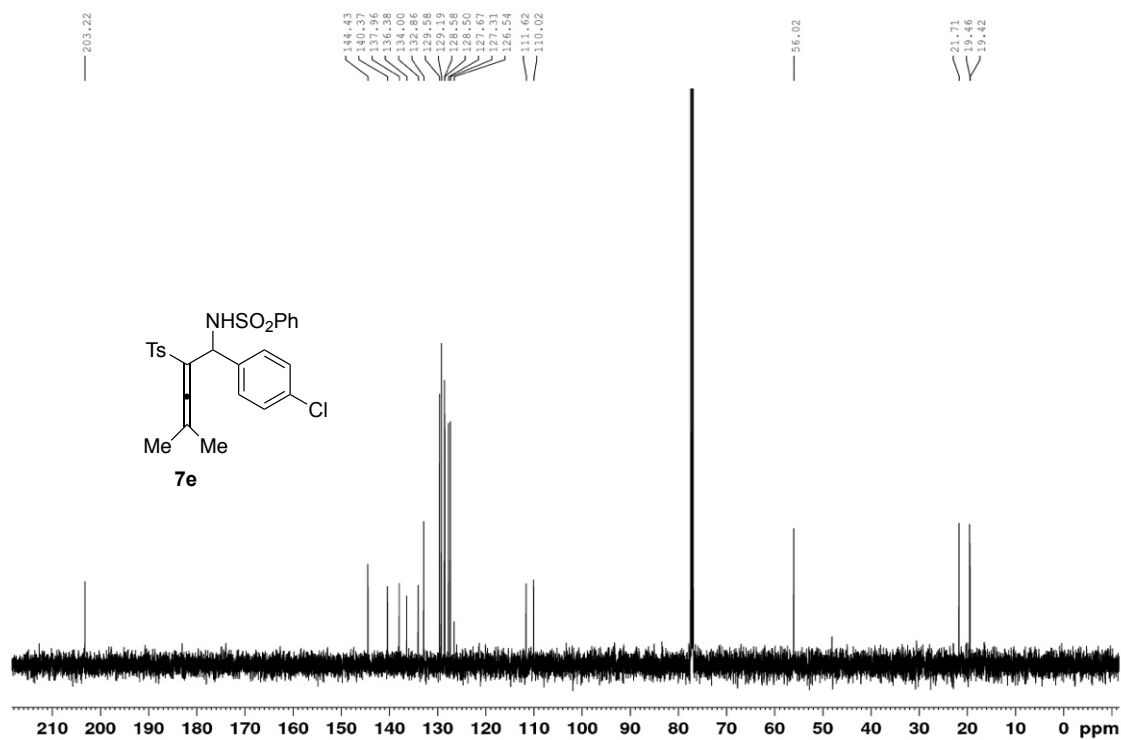
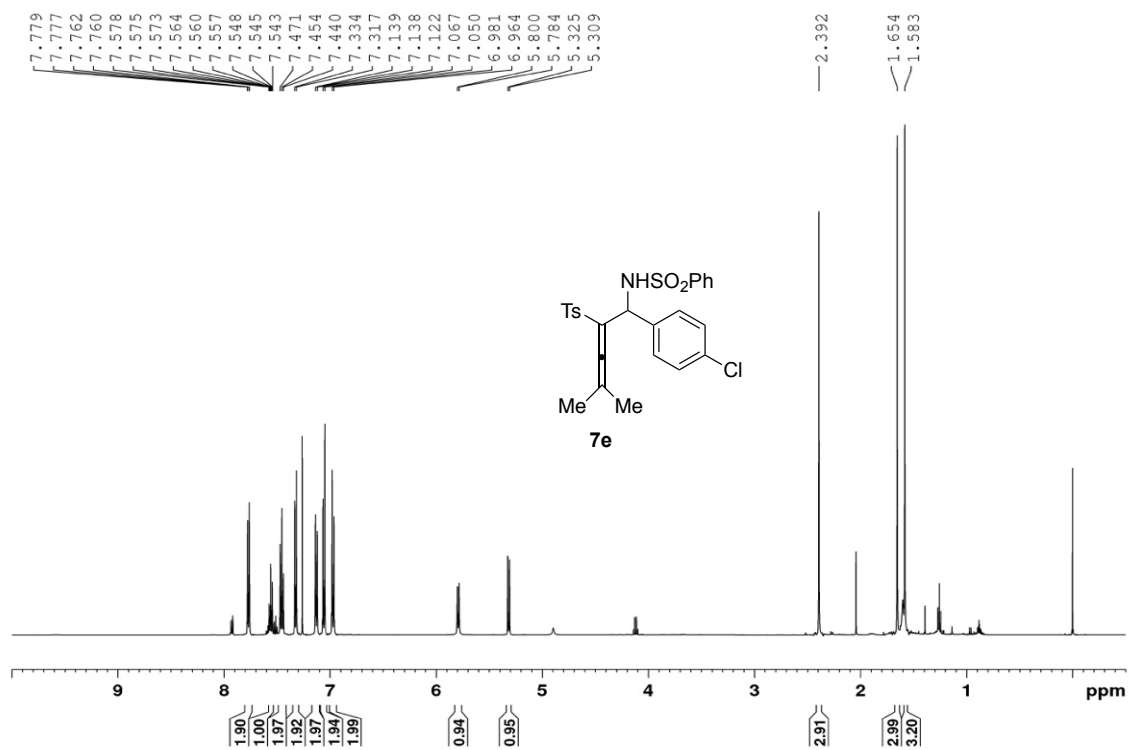


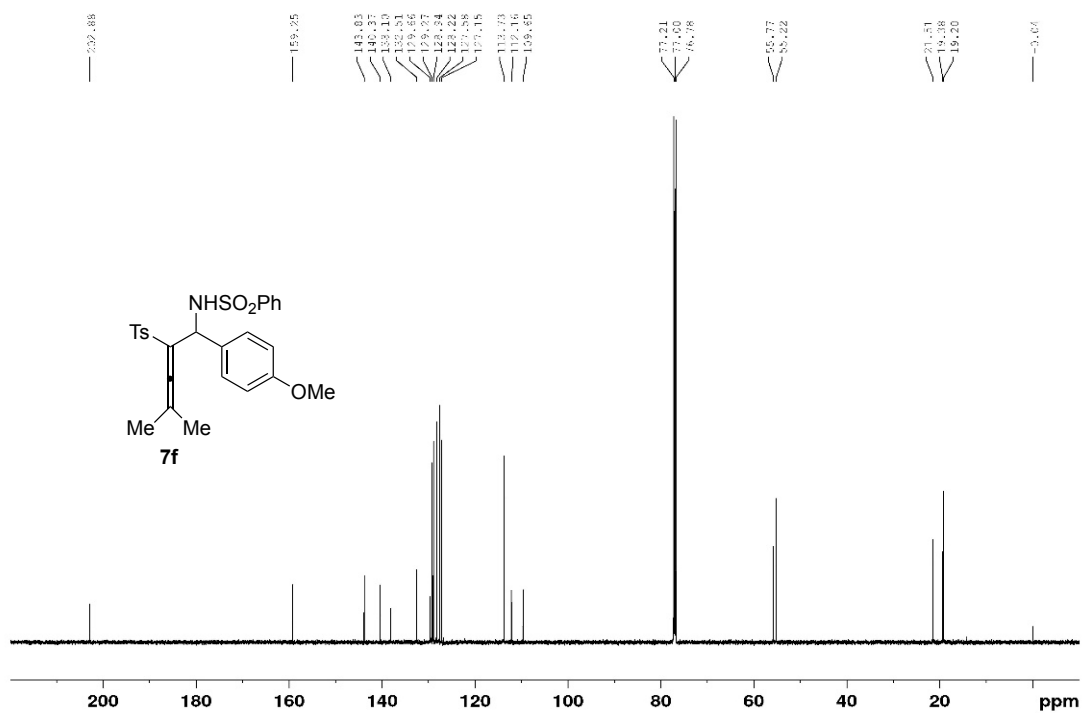
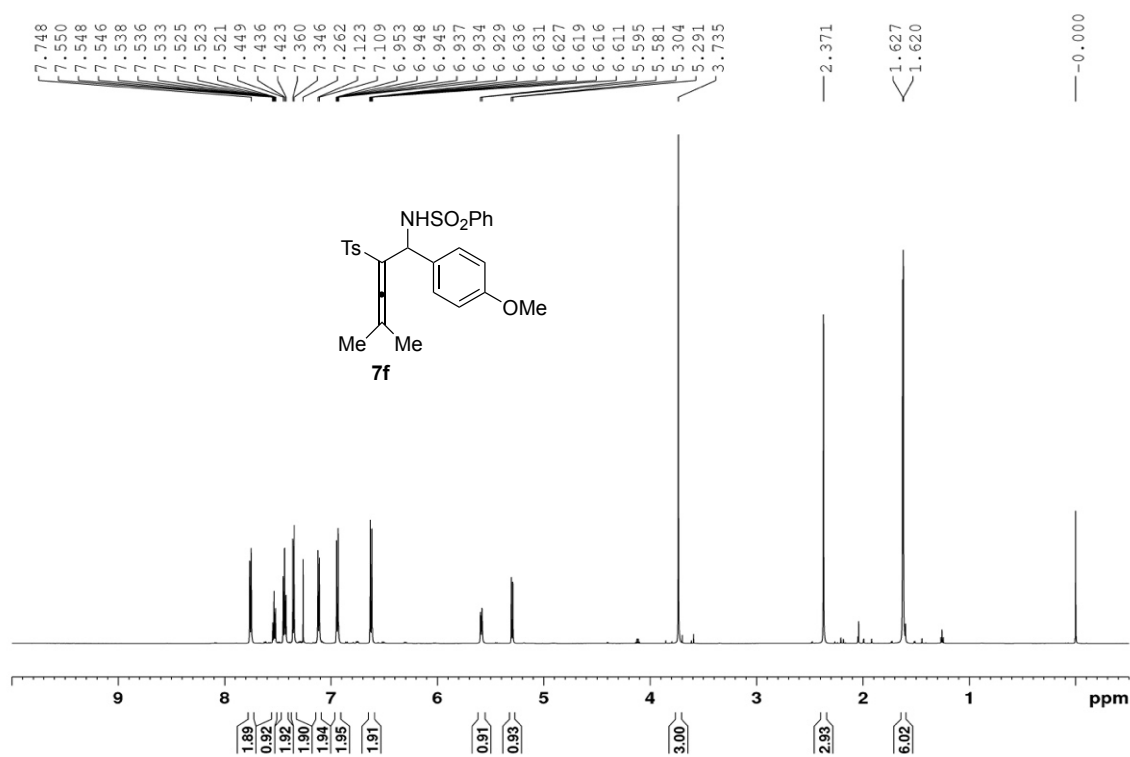
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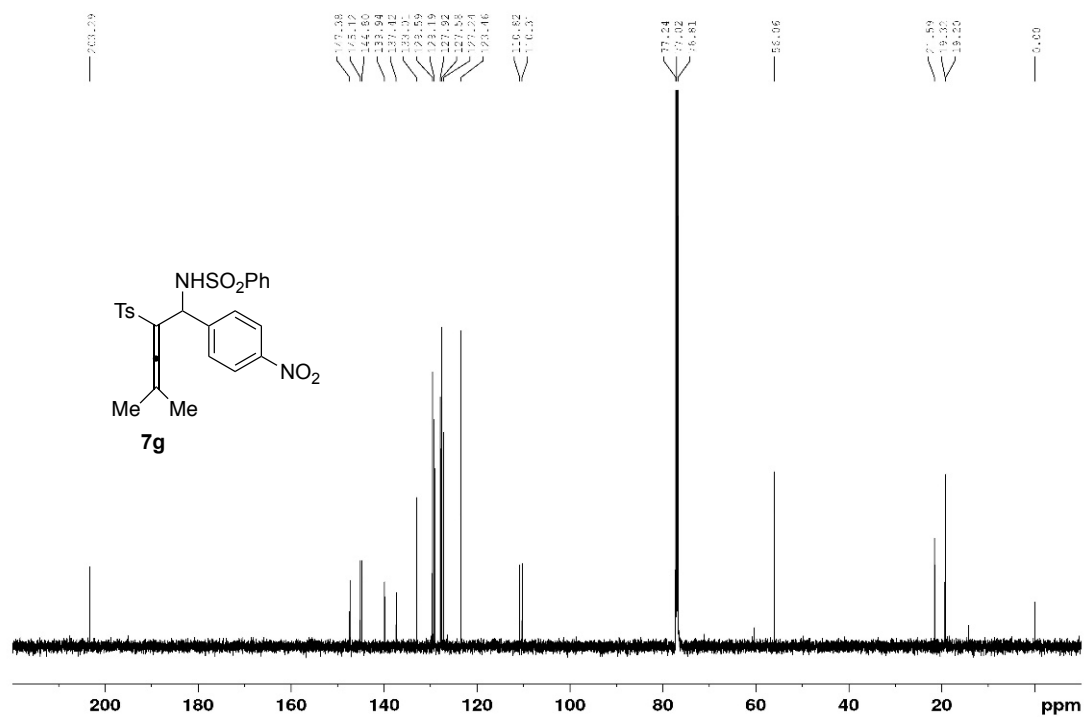
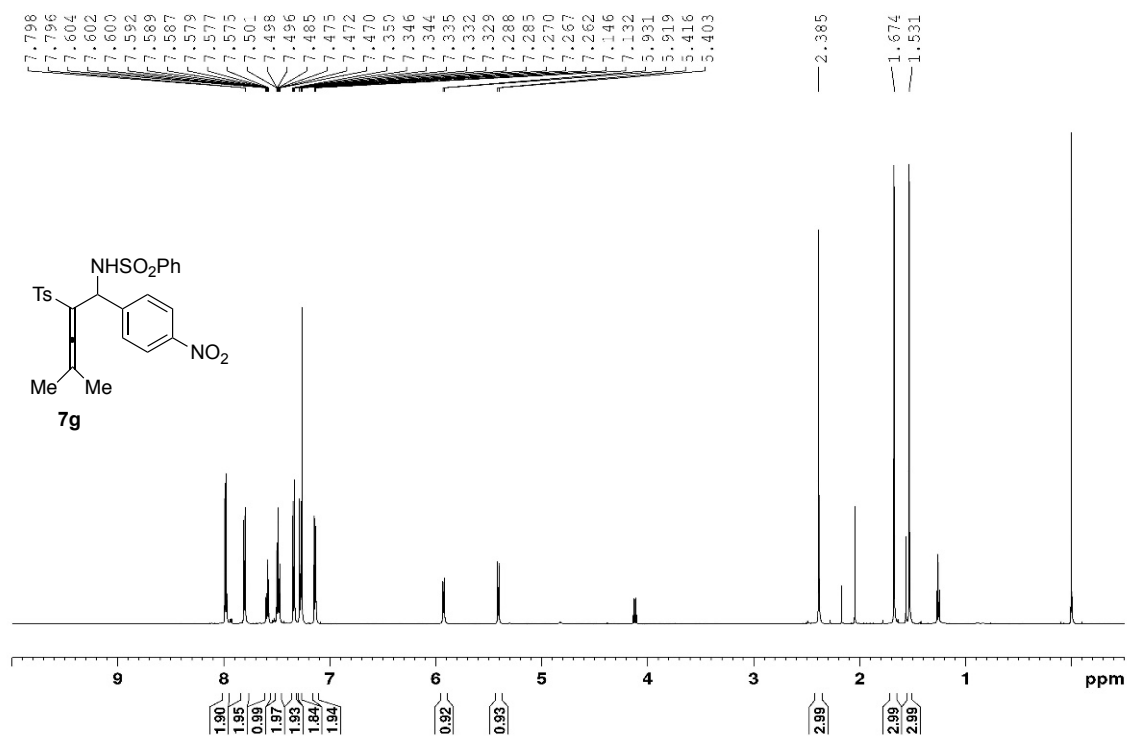


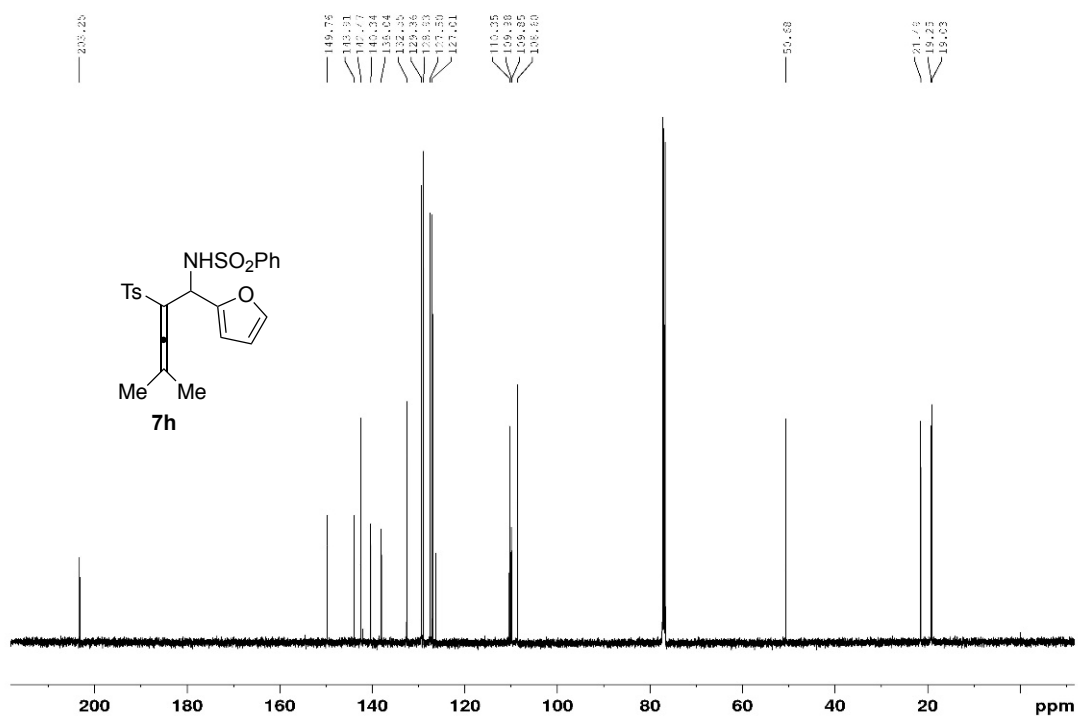
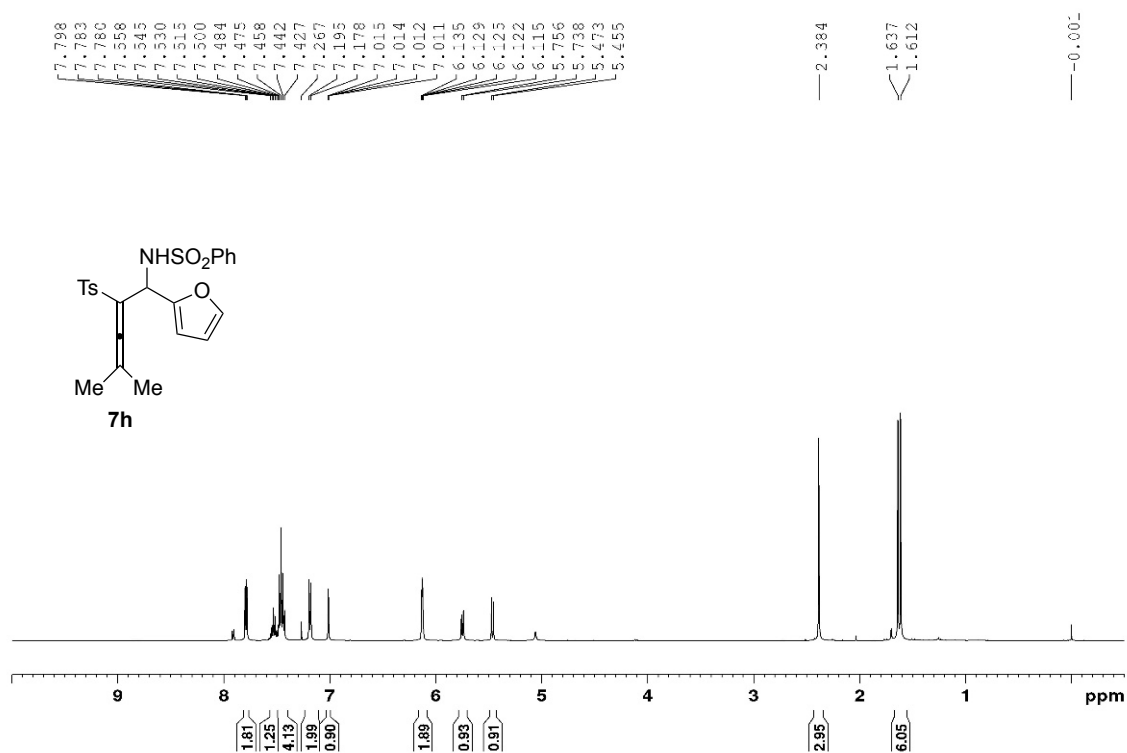
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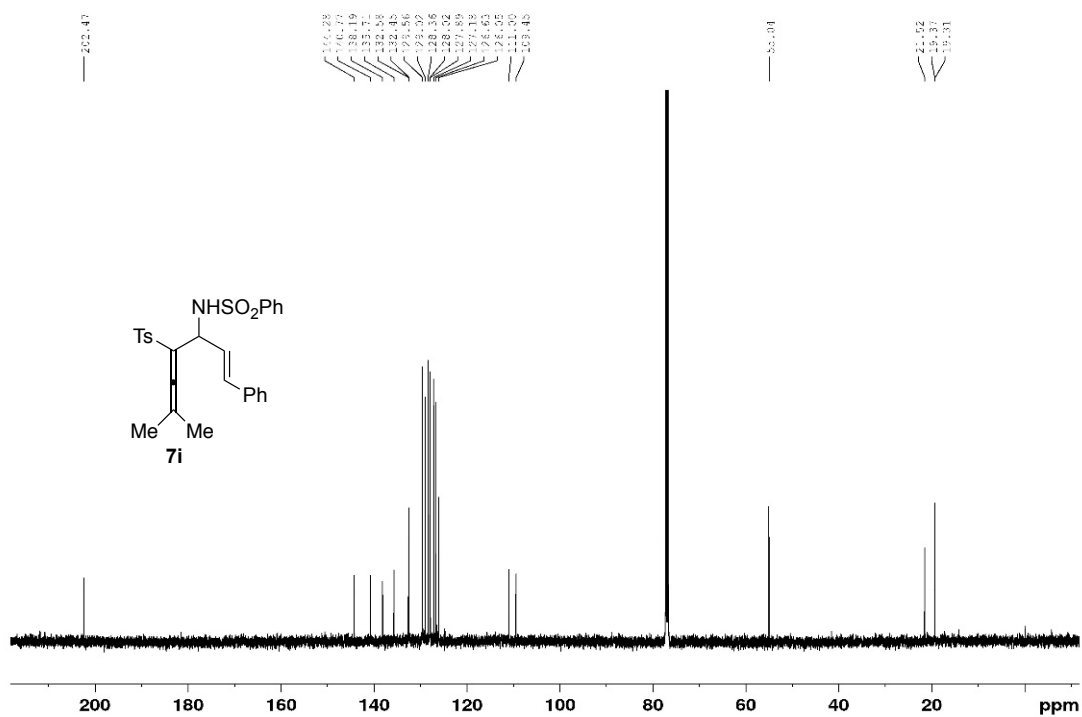
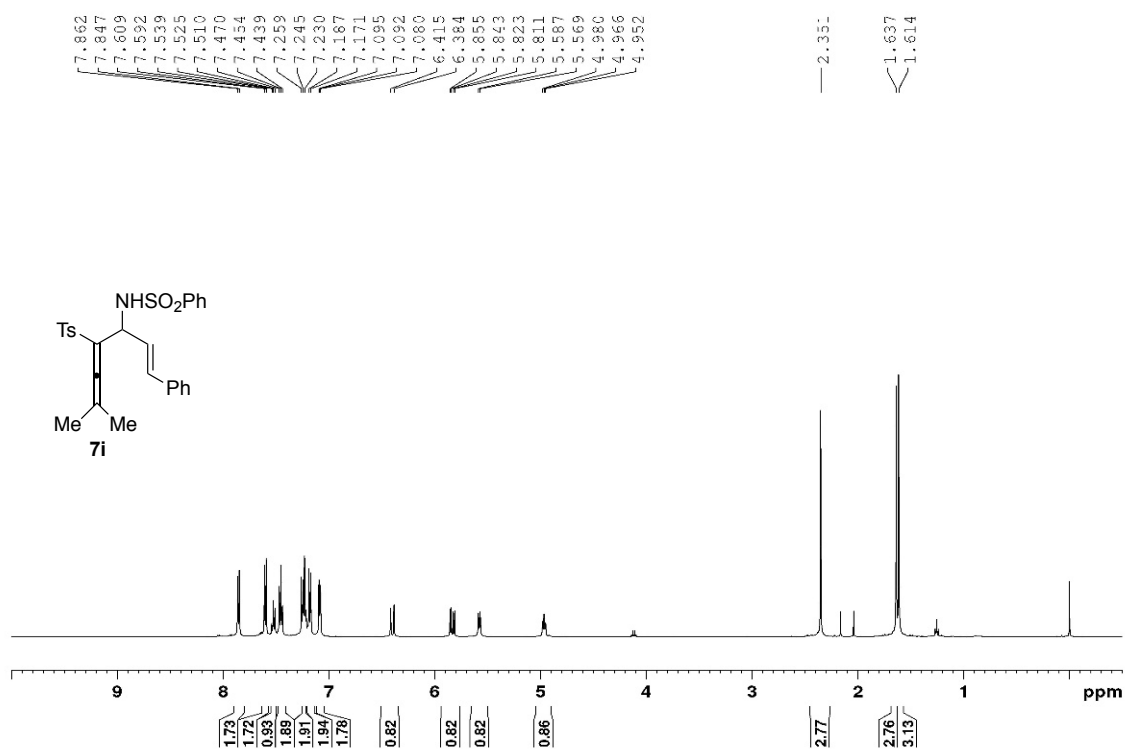




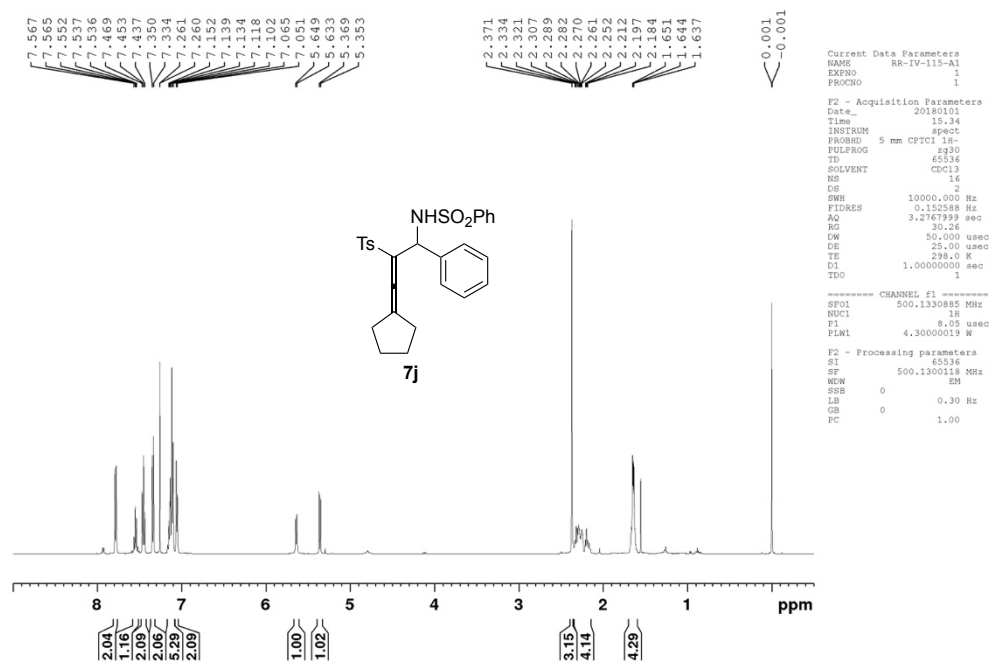




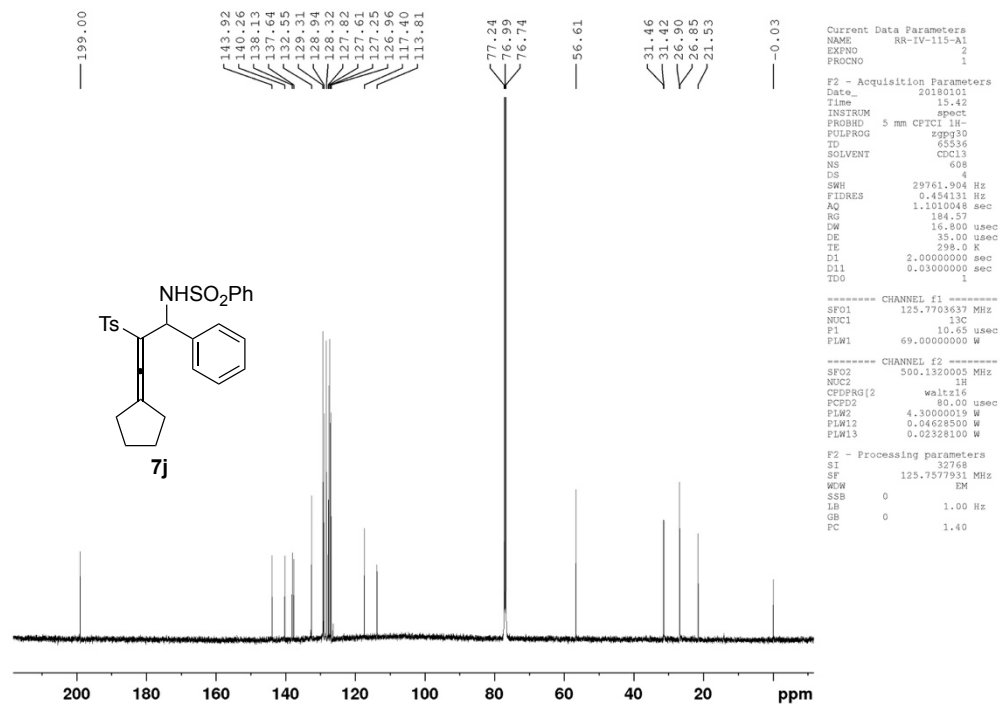




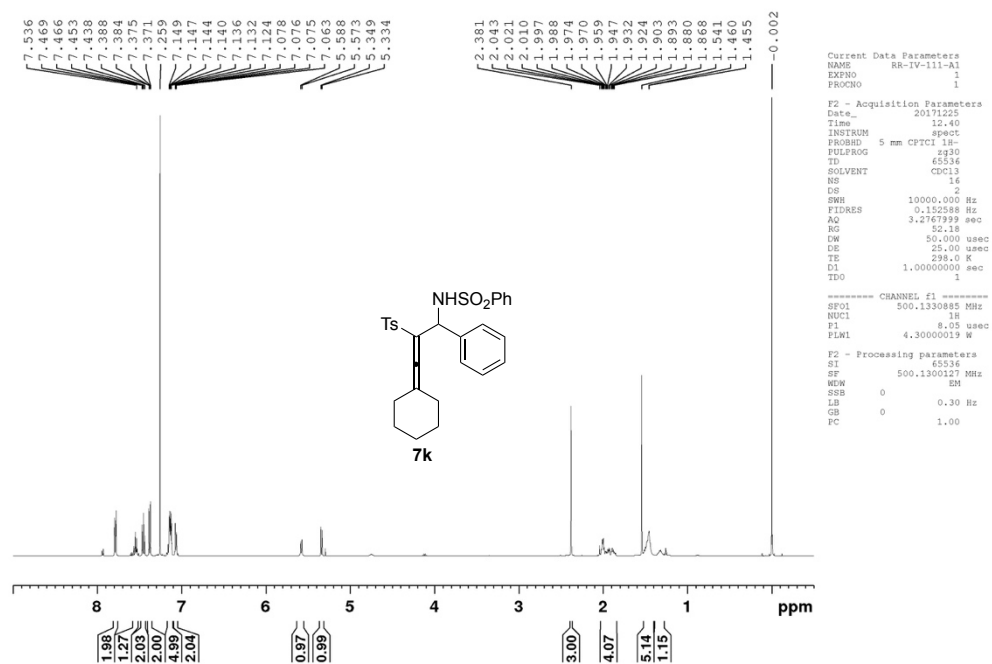
RR-IV-115-A1



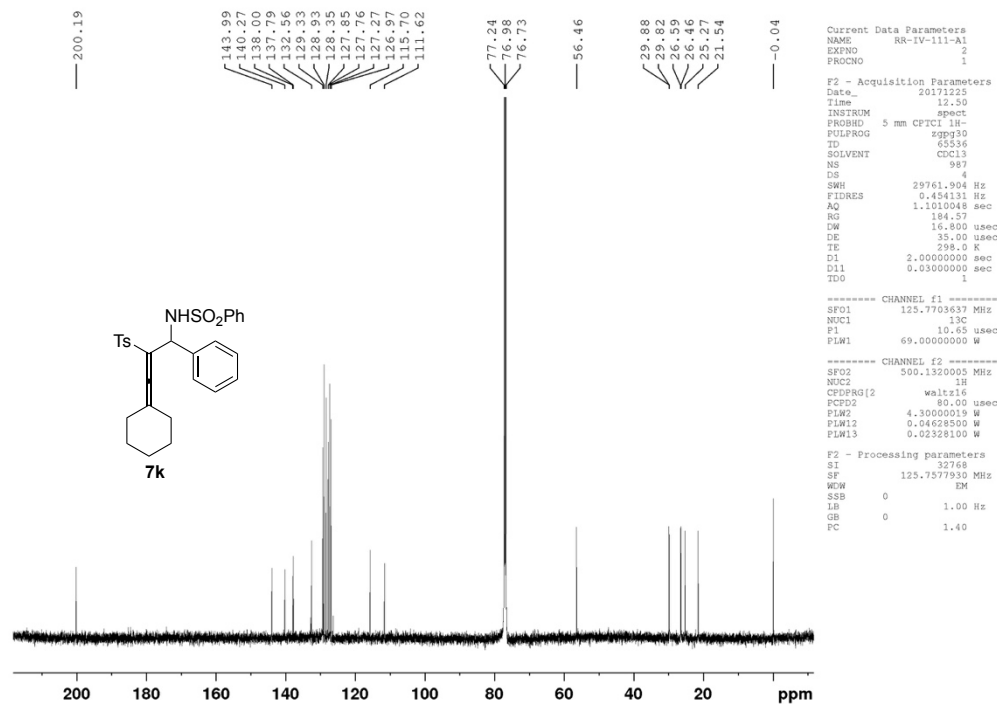
RR-IV-115-A1

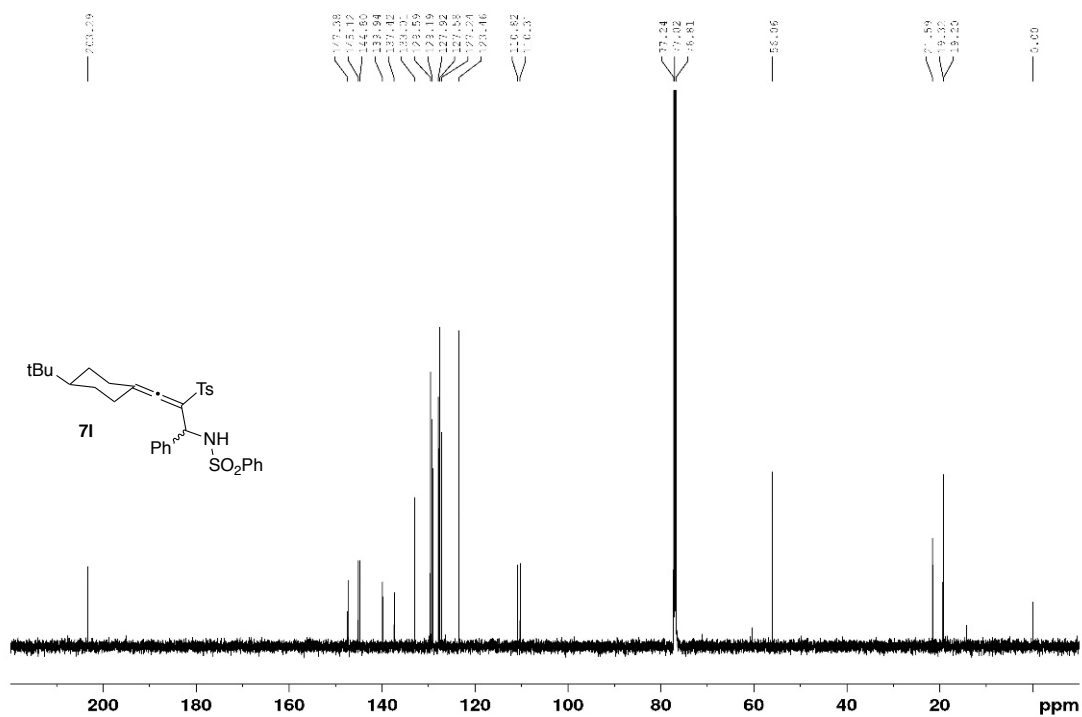
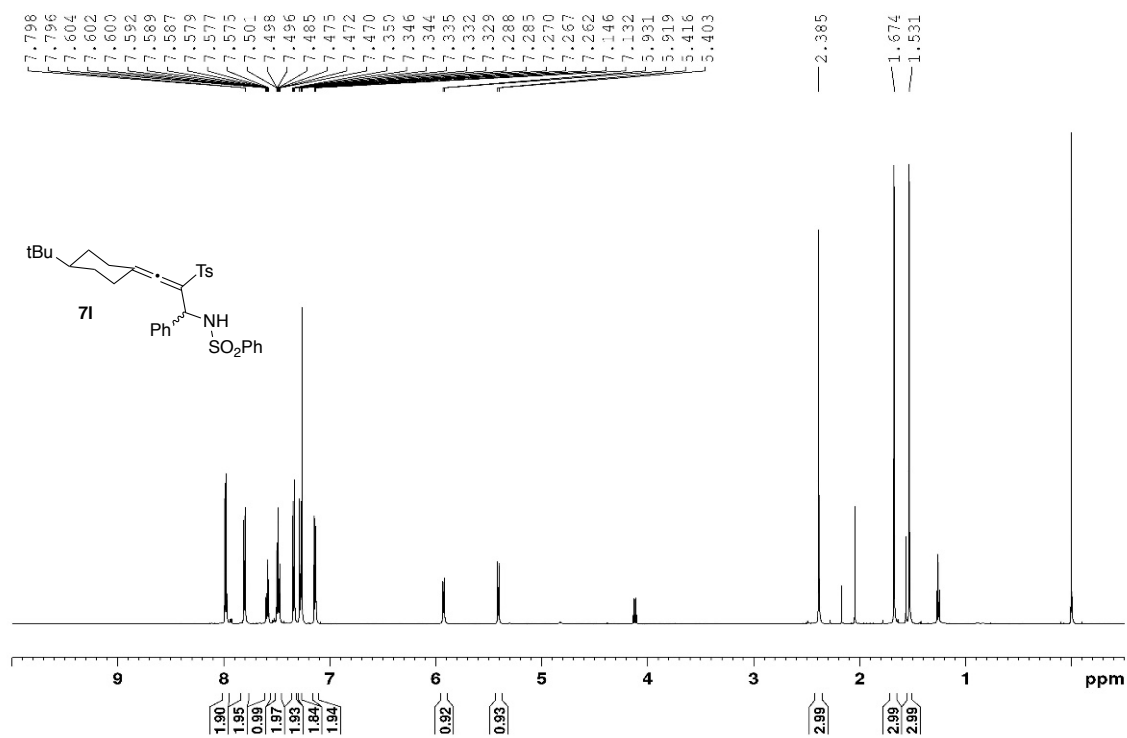


RR-IV-111-A1

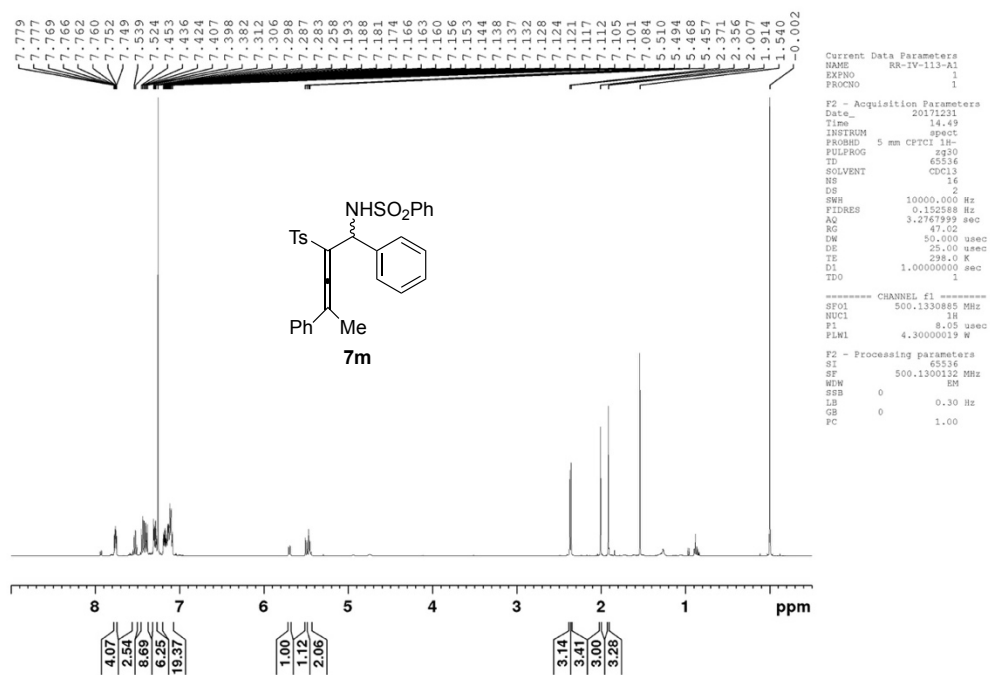


RR-IV-111-A1

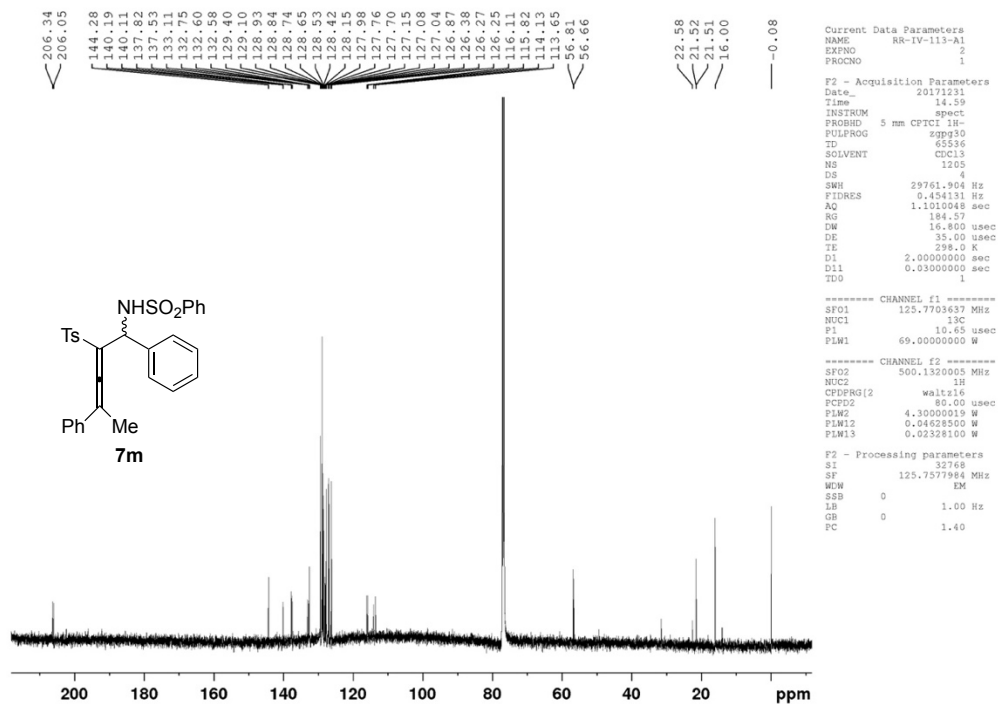




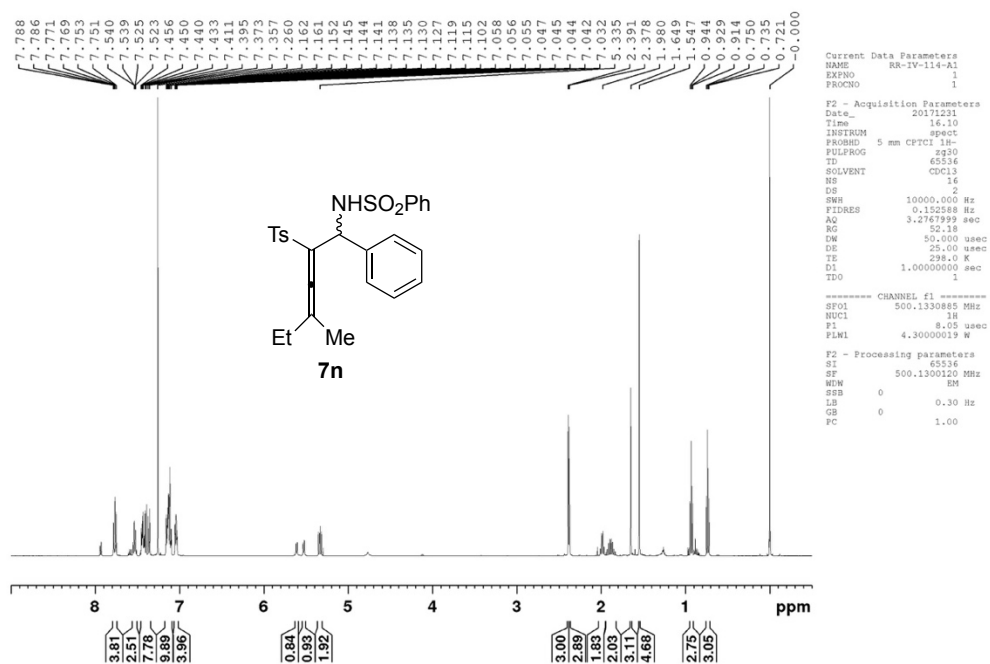
RR-IV-113-A1



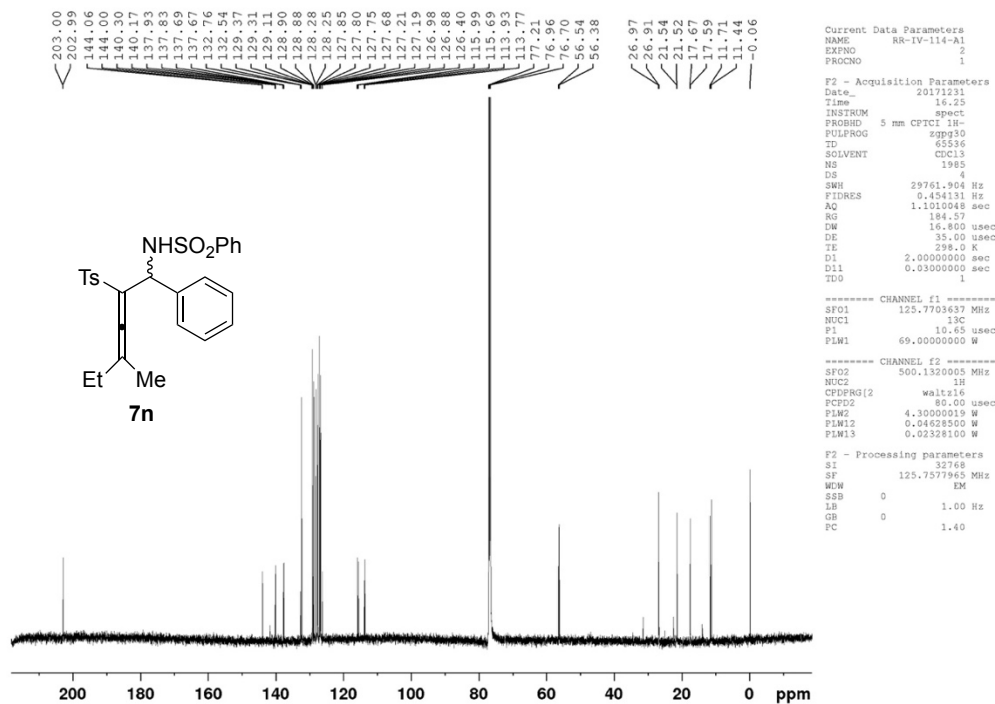
RR-IV-113-A1



RR-IV-114-A1



RR-IV-114-A1



Chemical Structure of 8a: COC1=C(C(=C(C=C1)C2=CC=CC=C2)S(=O)(=O)C3=CC=CC=C3)C

¹H NMR Spectrum (CDCl₃):

- Chemical Shifts (ppm):** 7.295, 7.281, 7.279, 7.261, 7.146, 7.130, 7.113, 7.114, 7.109, 7.010, 6.996, 6.982, 6.954, 6.938, 6.855, 6.835, 6.821, 6.812, 6.799, 6.786, 6.773, 6.753, 6.714, 2.305, 1.806, 1.802, 1.562, 0.000.
- Integration Values:** 3.26, 4.06, 1.17, 2.02, 4.07, 1.03, 1.00, 3.00, 6.03.

Current Data Parameters:

NAME	TR-IX-113-A1
EXPNO	1
PROCNO	1

F2 - Acquisition Parameters:

Date_	20130612
Time	13.42
INSTRUM	DRX500
PROBHD	5 mm CPTCI 1H-
PULPROG	zg30
TD	65536
SOLVENT	CDCl3
NS	8
DS	2
SWH	10330.578 Hz
FIDRES	0.157632 Hz
AQ	3.1719923 sec
RG	20.2
DW	48.400 usec
DE	6.00 usec
TE	300.0 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRR	0.01500000 sec

CHANNEL f1:

NUC1	1H
F1	8.00 usec
PL1	4.30 dB
SFO1	500.1335009 MHz

F2 - Processing parameters:

SI	32768
SF	500.13303131 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Chemical structure of **8a**: Cc1cc(C)c2c(c1)sc(c22)S(=O)(=O)c3ccccc3

¹H NMR spectrum (CDCl₃) of compound **8a**. The x-axis represents the chemical shift in ppm, ranging from 0 to 15. The spectrum shows several peaks corresponding to the protons in the molecule. Key peaks are labeled with their chemical shifts: 156.20, 144.05, 141.09, 140.37, 139.89, 131.68, 129.34, 128.92, 128.09, 127.95, 127.68, 127.17, 77.25, 77.00, 76.75, 76.50, 76.25, 69.41, 28.23, 27.63, and 21.46 ppm. The structure of **8a** is shown above the spectrum.

Current Data Parameters

NAME	TR-IX-113-A1
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20130612
Time	13.58
INSTRUM	DMX500
PROBHD	5 mm CPTCI 1H-
PULPROG	zgpg30
TD	71424
SOLVENT	CDCl3
NS	524
DS	4
SWH	35211.270 Hz
FIDRES	0.492989 Hz
AQ	1.0142708 sec
RG	4096
DW	14.200 usec
DE	35.00 usec
TE	300.0 K
d1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
MCORET	0.00000000 sec
MCNMR	0.01500000 sec

===== CHANNEL f1 =====

NUC1	13C
PL1	12.00 usec
PL1	0.30 dB
SFO1	125.7716224 MHz

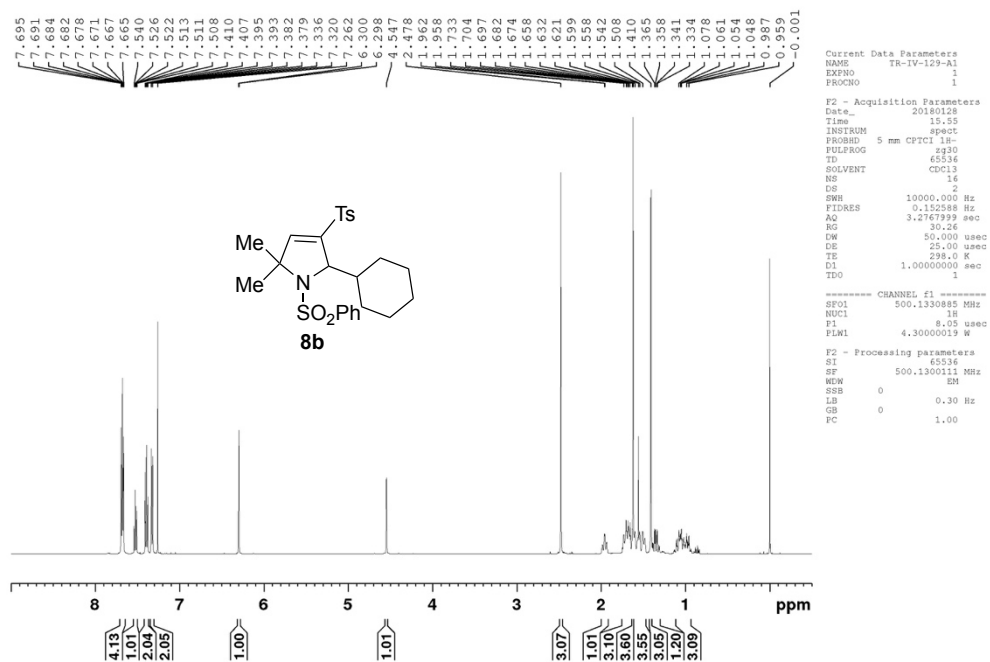
===== CHANNEL f2 =====

CFPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	5.00 dB
PL12	22.00 dB
PL13	27.40 dB
SFO2	500.1320005 MHz

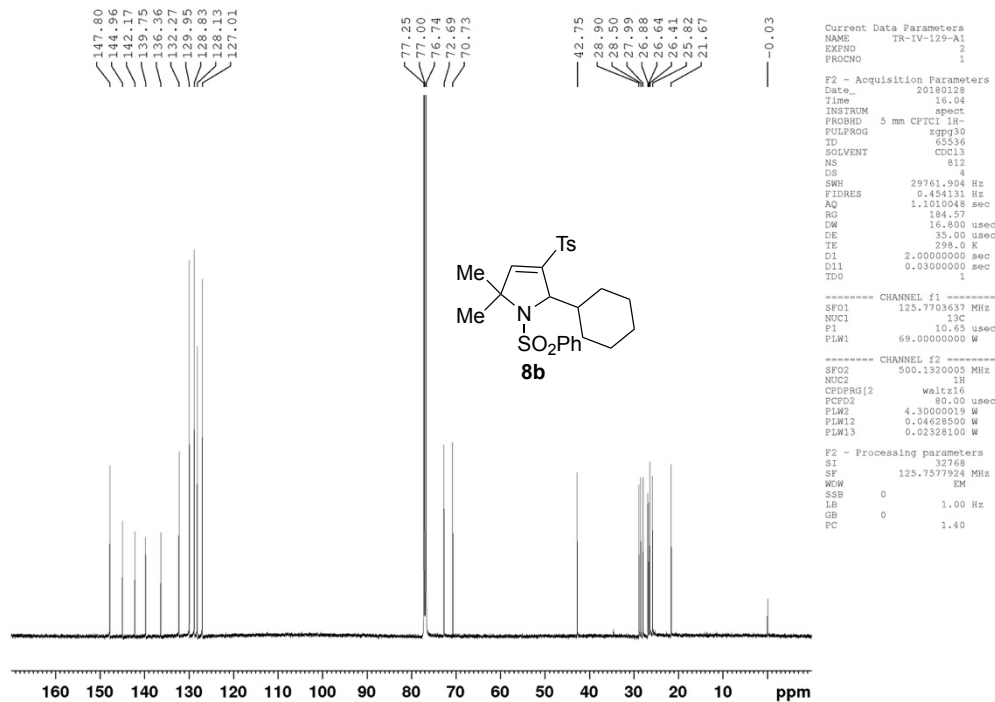
F2 - Processing parameters

SI	65536
SF	125.75777928 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
FC	1.40

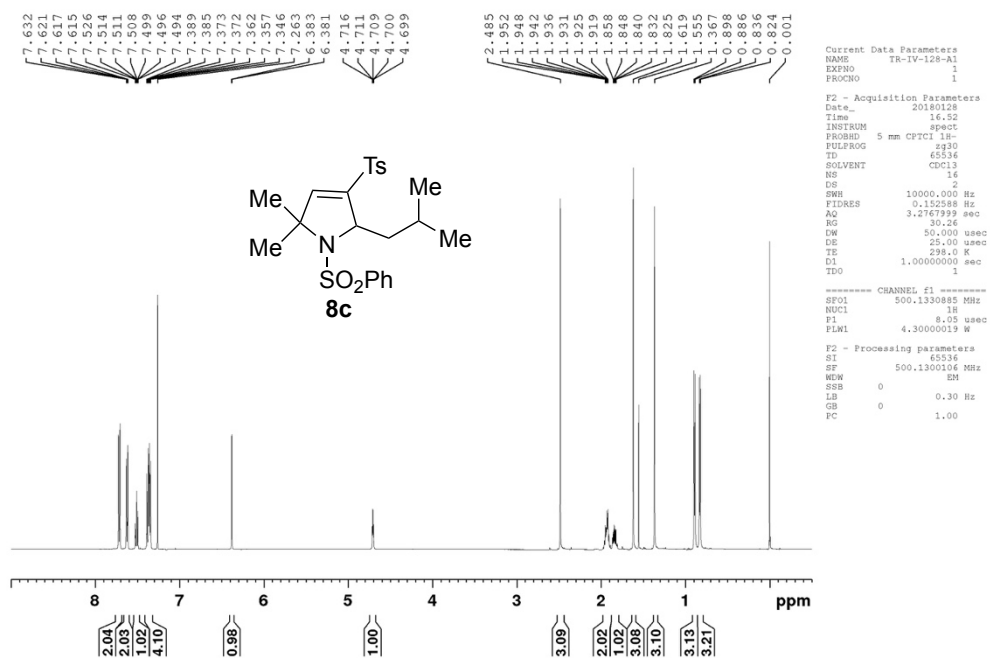
TR-IV-129-A1



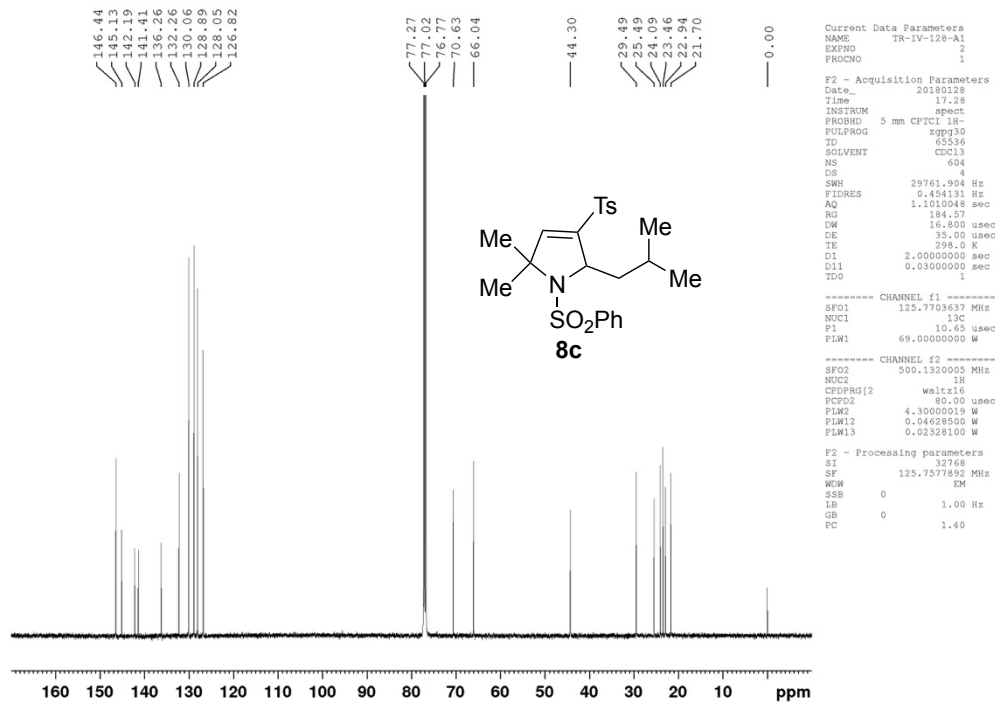
TR-IV-129-A1



TR-IV-128-A1



TR-IV-128-A1



Chemical structure of **8d** is shown above the spectrum. The structure is a 2,2-dimethyl-3-(4-methylphenyl)-4-(methylsulfonyl)pyrrole derivative.

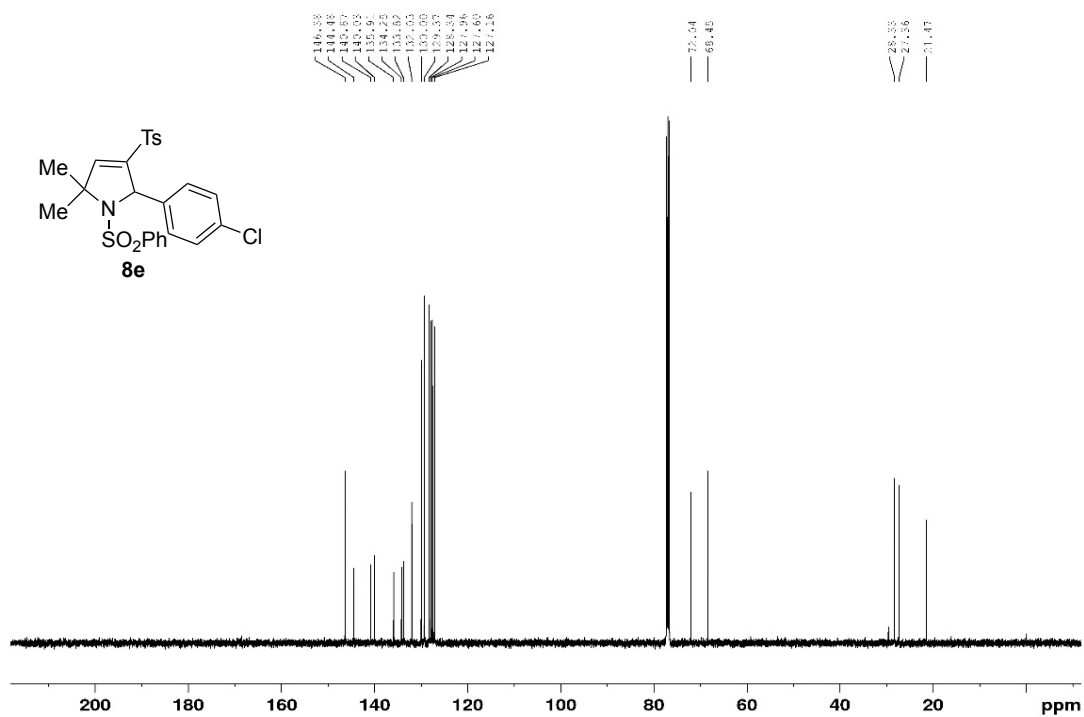
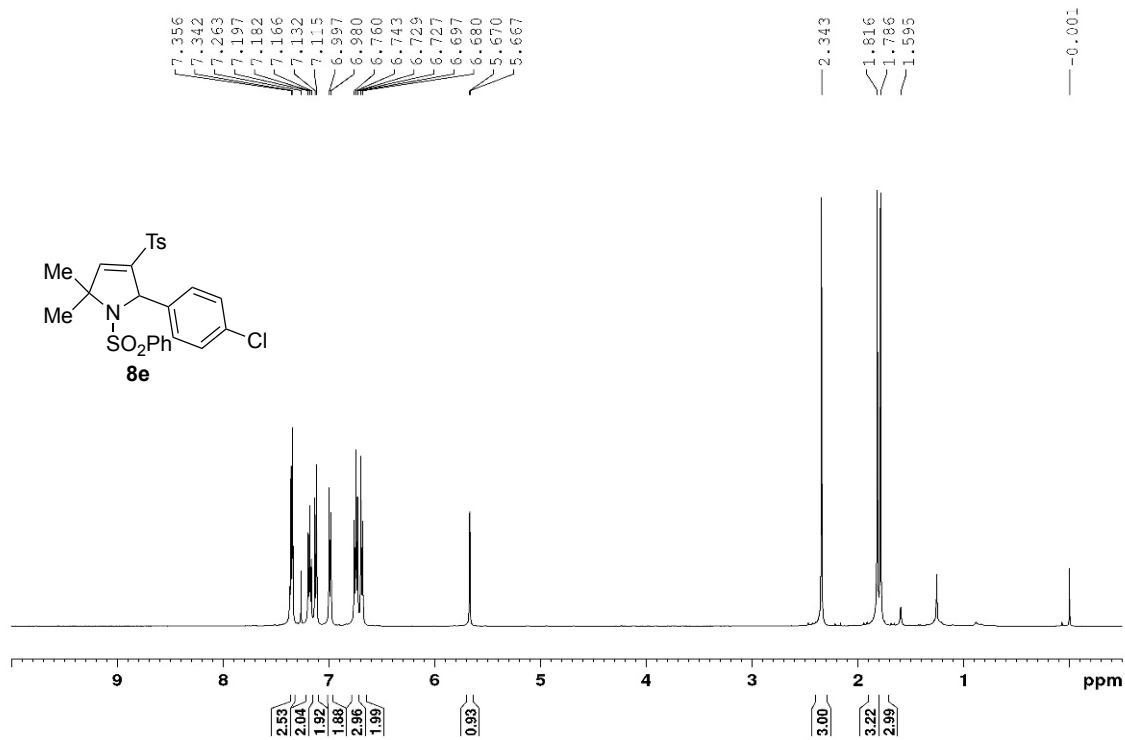
¹H NMR spectrum (CDCl₃) of **8d** is shown below the structure. The x-axis represents chemical shift in ppm, ranging from 0 to 8. Integration values are provided below the peaks.

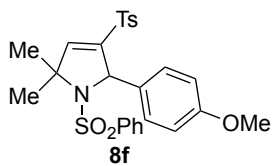
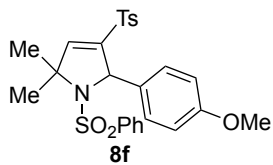
Peak list (ppm): 7.312, 7.310, 7.298, 7.295, 7.259, 7.153, 7.140, 7.138, 7.136, 7.129, 7.123, 6.957, 6.956, 6.940, 6.689, 6.686, 6.677, 6.660, 6.622, 6.607, 5.651, 5.647, 2.321, 2.186, 1.799, 1.779, 1.548, -0.001.

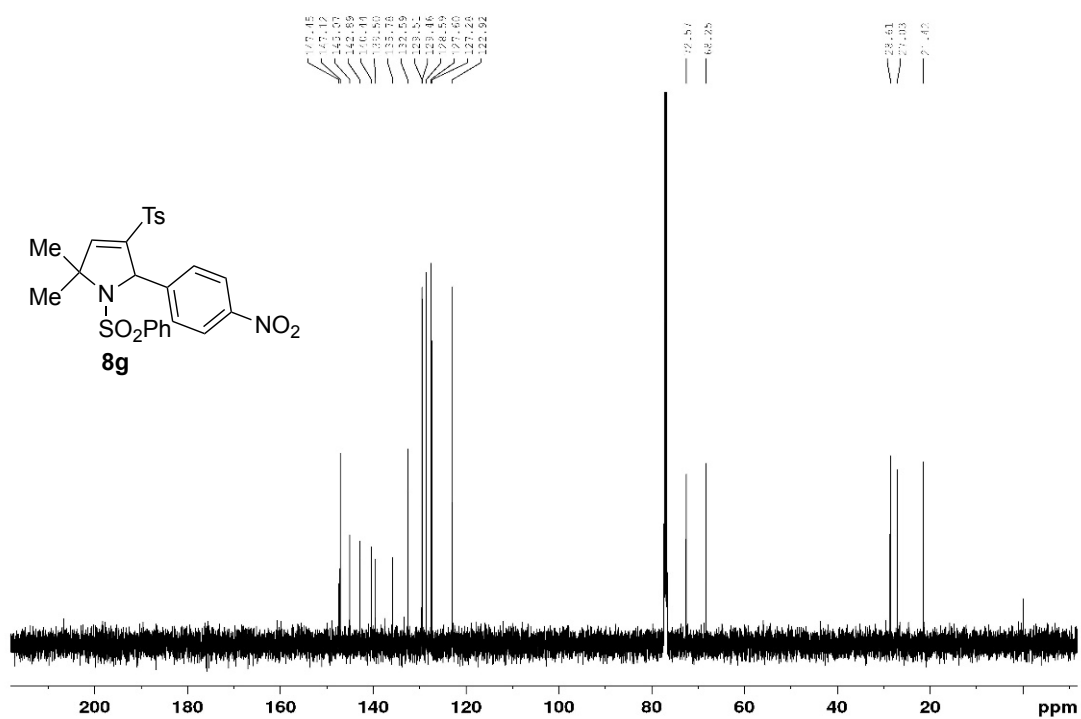
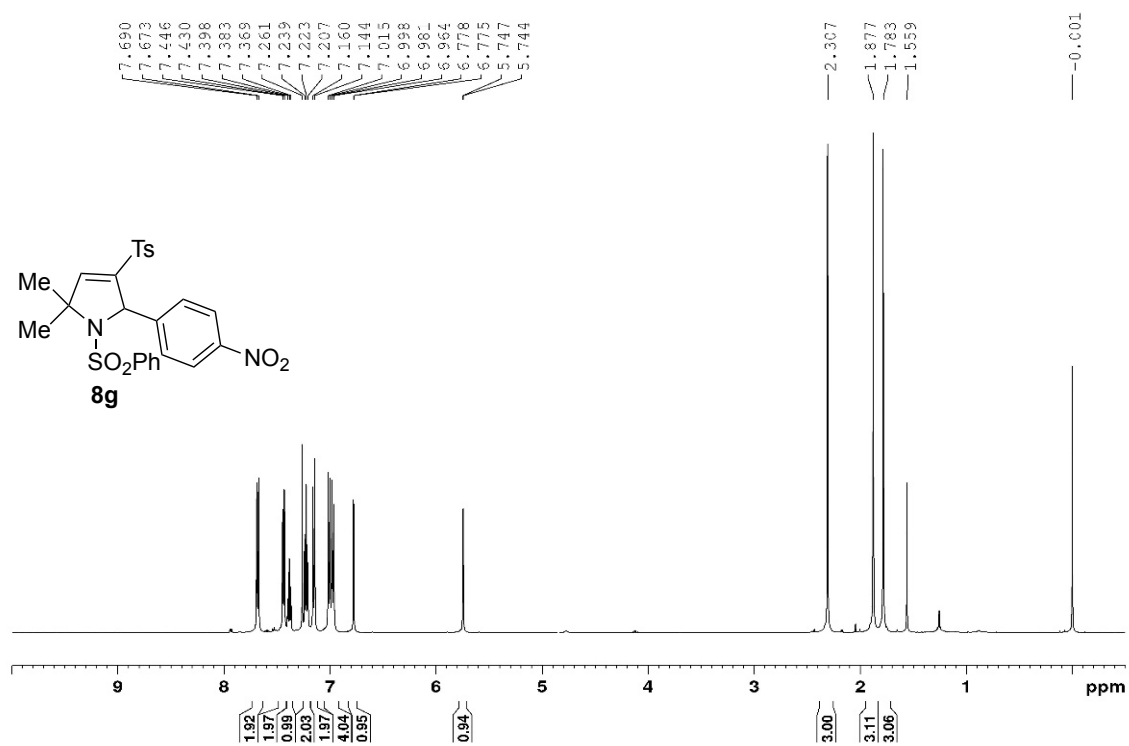
Integration values (from left to right): 3.06, 4.06, 2.04, 1.04, 2.06, 2.02, 1.00, 3.03, 3.06, 3.04, 3.12.

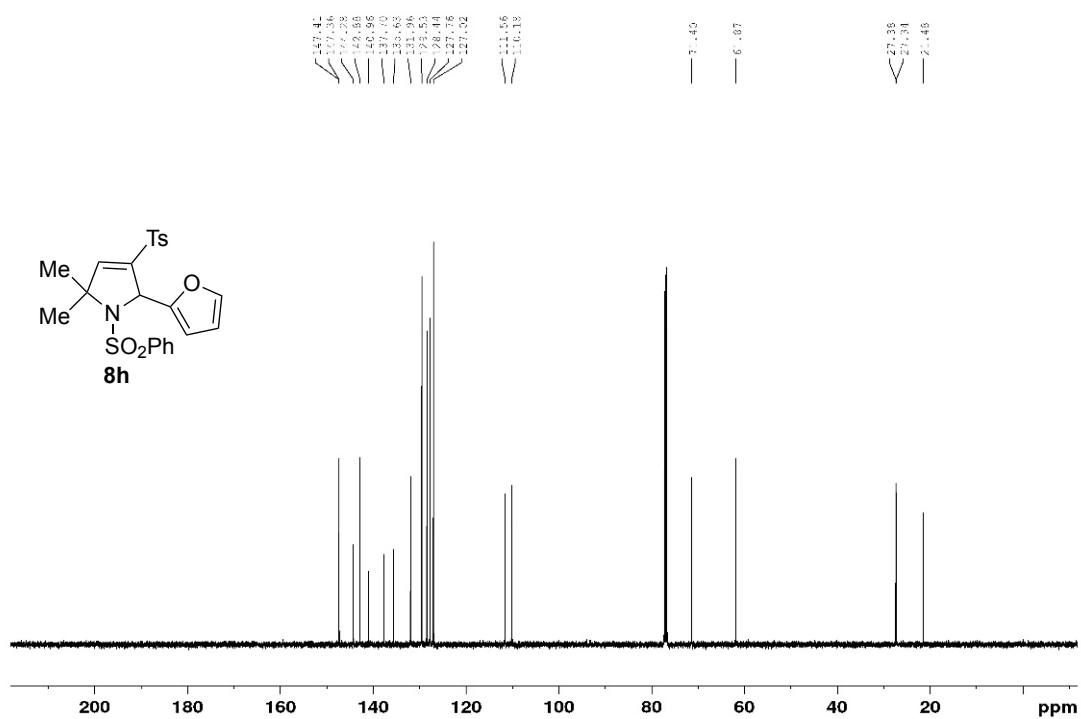
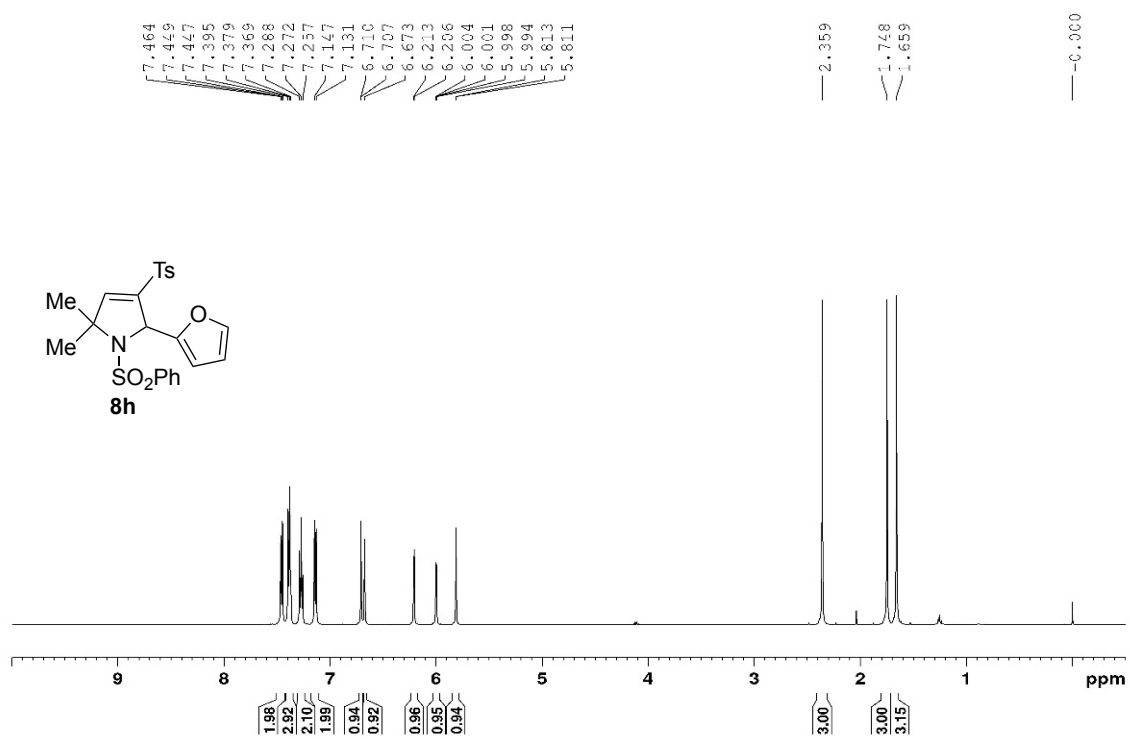
Chemical structure of **8d** is shown: 2,2-dimethyl-3-(4-methylphenyl)-4-(p-toluenesulfonyl)isoxazole.

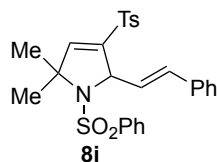
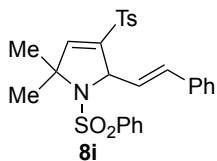
¹³C NMR spectrum (CDCl₃) peaks (ppm): 145.93, 143.93, 141.15, 139.48, 137.99, 136.18, 132.20, 131.63, 129.17, 128.74, 128.52, 128.14, 127.76, 127.23, 77.24, 76.59, 76.74, 71.74, 69.09, 28.29, 27.54, 21.48, 20.99, -0.03.



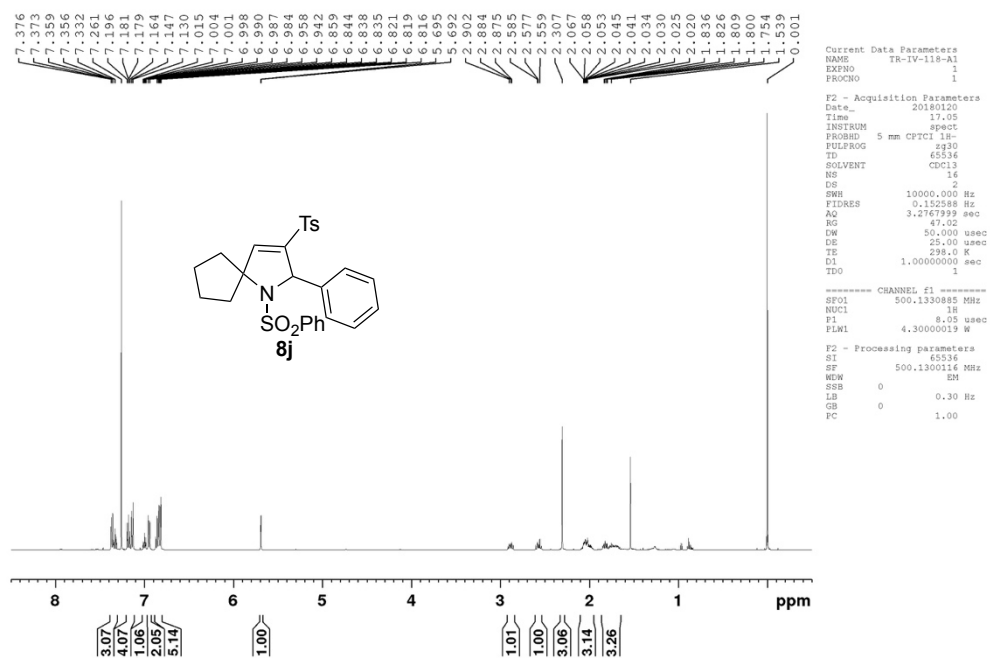




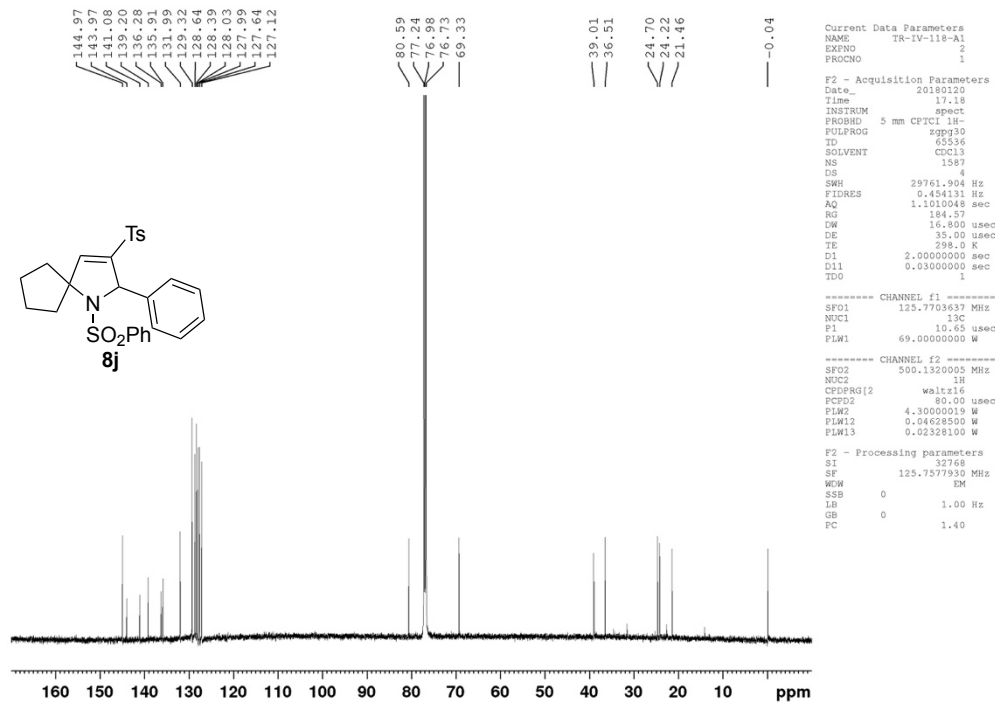




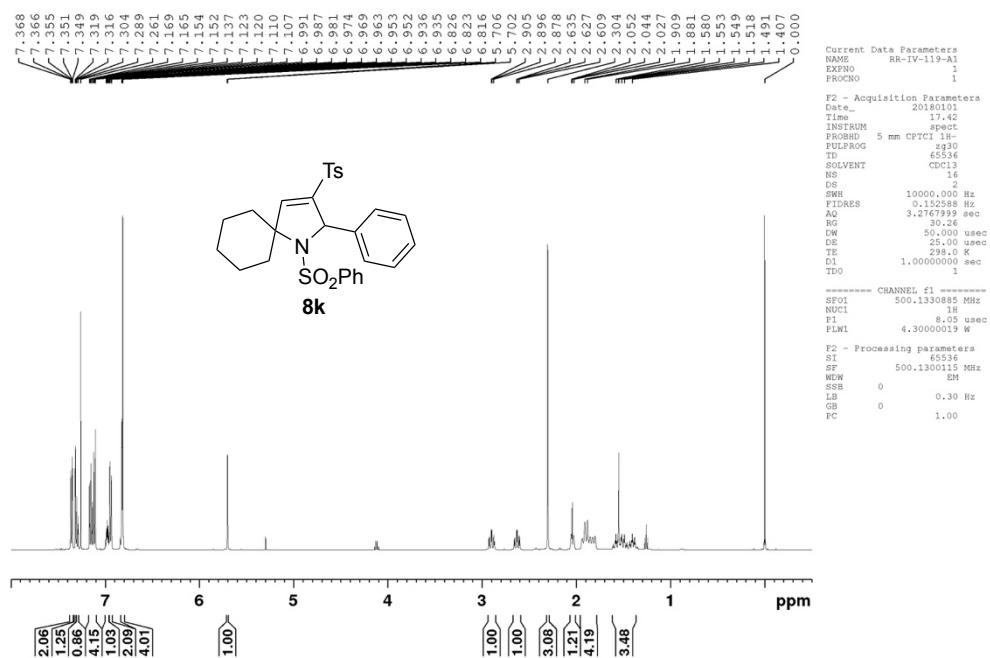
TR-IV-118-A1



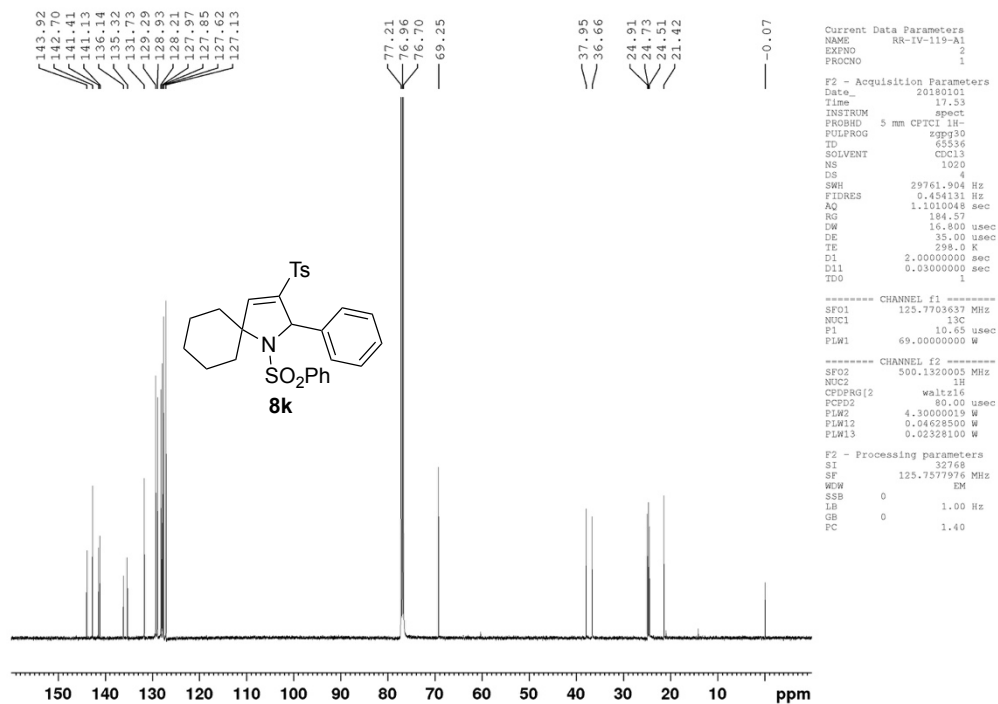
TR-IV-118-A1

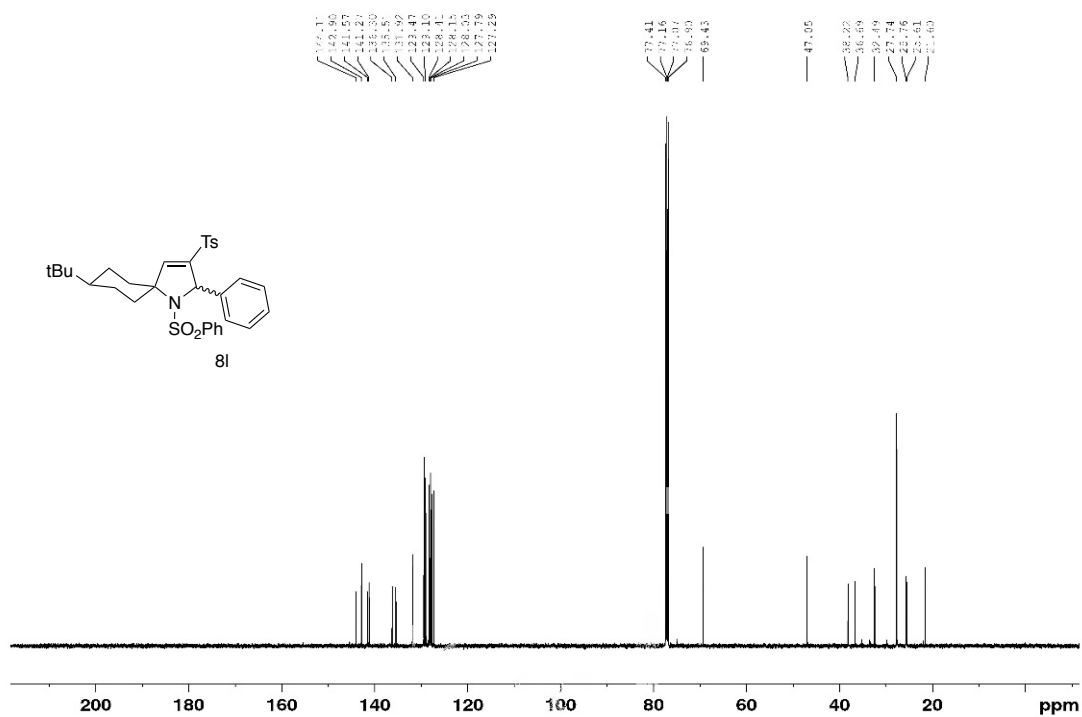
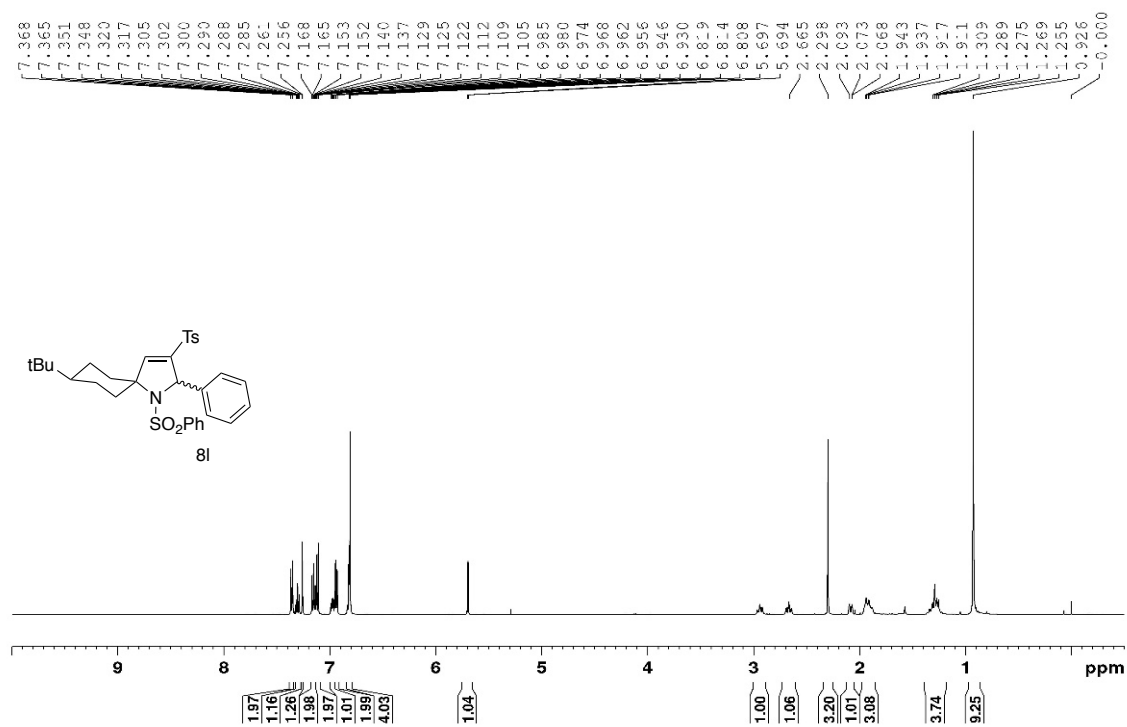


RR-IV-119-A1



RR-IV-119-A1





Chemical structure of **8m** is shown above the spectrum. The structure is a pyrrolidine derivative with a phenyl group (Ph), a methyl group (Me), a tosyl group (Ts), and a (benzenesulfonyl)methyl group (SO_2Ph) attached to the nitrogen.

¹H NMR spectrum (CDCl₃) of **8m** is shown below the structure. The x-axis represents chemical shift in ppm, ranging from 0 to 8. The spectrum displays several peaks, with integration values provided below the baseline.

Integration values (from left to right): 1.85, 2.88, 6.34, 3.92, 6.45, 8.95, 6.47, 0.98, 1.78, 1.91, 2.97, 2.87, 3.00, 2.77.

```

Current Data Name
NAME TR-IV-120-A1
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180120
Time 18.50
INSTRUM 5 mm CPTCI zgpg
PULPROG zg30
PC 18.5
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 MHz
FIDRES 0.152588 Hz
AQ 3.2767399 sec
RG 62.18
CW 50.000 usec
DE 25.00 usec
TE 298.0 K
D1 1.0000000 sec
T2 1
TD 1

===== CHANNEL f1 =====
NUC1 500.133088 MHz
NUC2 8.05 usec
P1 4.30000019 W

F2 - Processing parameters
F2 65535
SF 500.1330228 MHz
WDW EM
GB 0
LB 0 0.30 Hz
GB 0 0.10 Hz

```

Chemical structure of **8m** is shown above the spectrum:

CC1(C(=C(C=C1)C(=O)O)N(S(=O)(=O)c2ccccc2)Cc3ccccc3)C4=CC=CC=C4

8m

¹³C NMR spectrum (CDCl₃) peaks (ppm):

- 139.52, 139.37, 139.15, 136.15, 136.10, 136.10, 133.92, 133.92, 131.65, 131.35, 129.57, 129.47, 129.40, 128.64, 128.60, 128.56, 128.41, 128.30, 128.30, 128.28, 128.14, 128.14, 127.83, 127.78, 127.74, 127.73, 127.59, 127.06, 126.89, 126.63, 77.24, 76.98, 76.73, 76.52, 74.22, 74.22, 70.34, 68.51, 31.56, 25.89, 24.85, 22.63, 21.50, -0.03.

```

Current Data Parameters
NAME          TR-IV-120-A1
PROB          1
F2 - Acquisition
Time          20181020
Time          19.01
SOLVENT       DIMETHYL SULFONE
PULPROG       FM05
PROBHD         5 mm CPTCI 1H
PULPROG        zgpg30
NUC1           13
NUC2           13
SOLVENT        CDCl3
NS             3853
DS             4
SWH            29761.904 HZ
FIDRES         0.4554131 HZ
AQ             1.1018186 sec
RG             184.57
WDW             16.00
SSB             0
GB              35.00 uSec
DE              298.4 K
TE              0.00000000 sec
D1              2.00000000 sec
T1              1
TDO            1

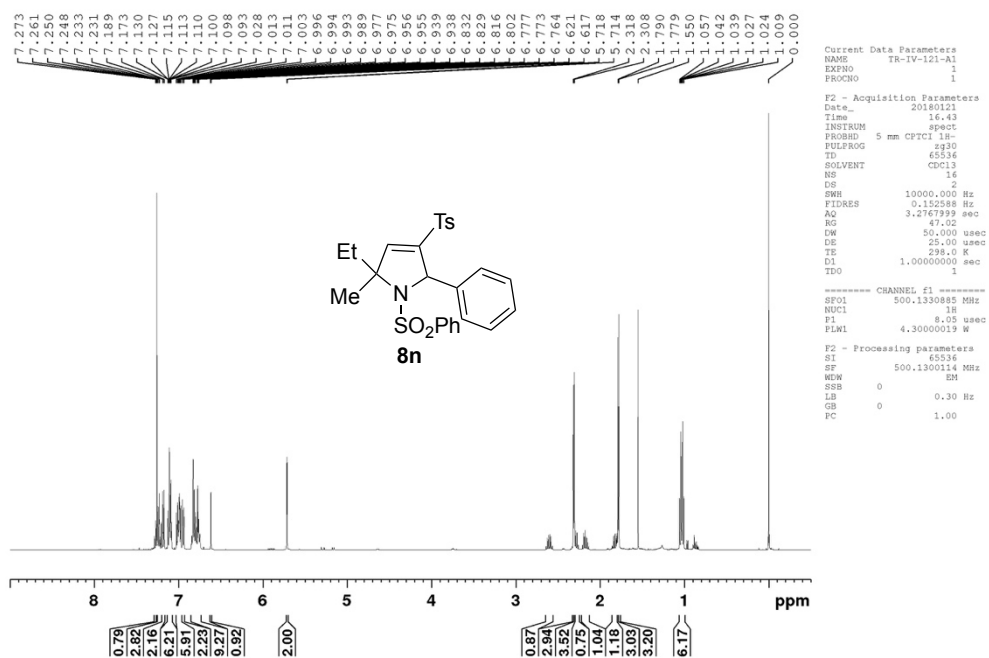
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PC1           10.00 uSec
PL1           16.05 uSec
PLW1          69.0000000 W

===== CHANNEL f2 =====
SFO2          500.1320005 MHz
PC2           10.00 uSec
PL2           16.05 uSec
PLW2          69.0000000 W
PLW12         0.04628500 W
PLW13         0.02328100 W

F1 - Processing parameters
NAME          TR-IV-120-A1
SFO           125.777930 MHz
WDW            EM
GB              0
LB              1.00 HZ
GB              0
LB              1.40

```

TR-IV-121-A1



TR-IV-121-A1

