Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

Catalyst-controlled divergence in cycloisomerization reactions of *N*-propargyl-*N*-vinyl sulfonamides: Gold-catalyzed synthesis of 2-sulfonylmethyl pyrroles and dihydropyridines

Sridhar Undeela, Srinivas Thadkapally, Jagadeesh Babu Nanubolu, Kiran Kumar Singarapu and Rajeev S. Menon*

Table of Contents

1.	General Information	page 3
2.	Substrate Preparation	page 4
2.1.	Preparation of 1-(2-bromoallyl)sulfonylbenzene or 1-(2-bromoallyl)sulfonyl-4-methylbenzene	page 4
2.2.	Sonogashira coupling	page 5
3.	Formation of allenyl sulfone **6** and propargyl sulfone **11** from the bromoallyl sulfone **5a**	page 6
4.	CS_2CO_3-mediated reaction of 2-bromoallyl sulfones **5a-b** with sulfonamides **4a-g**	page 7
5.	NaH-mediated reaction of **4h** with **5b** to afford the aza-enyne **1hb**	page 14
6.	Gold-catalyzed pyrrole synthesis	page 15
7.	Bromination of pyrrole **2aa**	page 22
8.	Gold-catalyzed synthesis of dihydropyridines **3aa-3gb**	page 23
9.	Catalytic hydrogenation of the dihydropyridine **3ab**	page 29
10.	Conversion of the dihydropyridine **3ab** into 2-tosylmethylpyridine **10**	page 30
11.	1D and 2D NMR experiments on **8**	page 31
12.	Crystallographic data for **2da**	page 34
13.	Copies of NMR spectra of new compounds	page 36

1. General Information

All ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solvent on Varian Bruker 300 MHz, a Varian Unity 400 MHz and Avance 500 MHz spectrometer at ambient temperature, chemical shift δ are given in ppm on a scale downfield from TMS, and the coupling constant *J* are in Hz. The signal patterns are indicated as follows: s, Singlet; d, doublet; t, triplet; dd, doublet of doublet; m, multiplet. FTIR spectra were recorded as neat. Mass spectra were obtained on a Finnegan Mat1020B, a micromass VG 70-70H or an Agilent technologies LC/MSD treapSL spectrometer operating at 70eV using the direct inlet system and high resolution mass spectra (HRMS) were recorded on a QSTAR XL Hybrid MS/MS mass spectrometer. Melting points were recorded on an electrothermal apparatus and are uncorrected. All the reagents and solvents were used without further purification unless specified otherwise. Technical grade ethyl acetate and petroleum ether used for column chromatography were distilled prior to use. Anhydrous solvents were prepared from locally purchased LR grade solvents by standard methods. Column chromatography was carried out using silica gel (60-120 mesh and 100-200 mesh) packed in glass columns. All reactions were performed in oven-dried glassware with magnetic stirring. The catalysts were purchased from Sigma Aldrich and were used as received. 2-Bromoallylsulfones **5a**,[1] N-(3-phenylprop-2-ynyl)methanesulfonamide **4d**,[2] allenyl sulfone **6**,[3] propargyl sulfone **11**[4] and 2-tosylmethylpyridine **10**[5] are previously described and were characterized by comparison of their spectroscopic data with reported values.

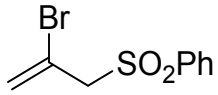
[1] S. Ma, Q. Wei, *J. Org. Chem.,* 1999, **64,** 1026.
[2] C. Zheng, Y. Wang, R. Fan, *Org. Lett*., 2015, **17**, 916.
[3] S. H. Watterson, Z. Ni, S. S. Murphree, A. Padwa, *Org. Synth*., 1997, **74**, 115.
[4] T. Achard, A. Lepronier, Y. Gimbert, H. Clavier, L. Giordano, A. Tenaglia, G. Buono, *Angew. Chem. Int. Ed*., 2011, **50**, 3552.
[5] H. Richter, S. Beckendorf, O. G. Mancheňo, *Adv. Synth. Catal*., 2011, **353**, 295.

2. Substrate Preparation

2.1. Preparation of 1-(2-bromoallyl)sulfonylbenzene or 1-(2-bromoallyl)sulfonyl-4-methylbenzene

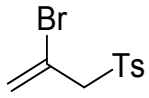
R = Ph, **5a**, 58%
R = *p*-tolyl, **5b**, 57%

Sodium benzene sulfinate or sodium-p-toluene sulfinate (10 mmol) was added to DMF (10 mL) in a round bottom flask and left to stir for 20 minute. To this suspension, 2,3-dibromopropene (10 mmol) was added and stirred at room temperature under nitrogen for 12 hrs. After the completion of the reaction, ice and ethylacetate (20 mL) were added and stirred for 15 minutes. Water (20 mL) was added and the organic layer was separated in a separatory funnel. The aqueous layer was extracted with ethyl acetate (2 X 10 mL), the organic layers were combined and the solvent was removed on a rotavapor. The residue obtained was purified by column chromatography on silica gel using ethyl acetate and hexane mixtures as eluent to obtain pure samples of **5a** or **5b**.



5a, (2-Bromoallylsulfonyl)benzene[1]

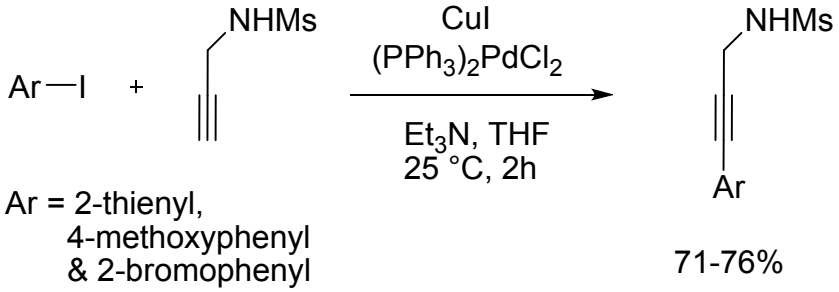
White solid, 1.51 g, 58%
R_f = 0.6 (30% ethyl acetate in hexanes)
Melting point: 77-79 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3423, 2981, 2919, 1622, 1584, 1447, 1393, 1307, 1256, 1141, 907 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.71-7.68 (m, 1H), 7.60-7.57 (m, 2H), 5.84 (d, *J* = 2.1 Hz, 1H), 5.77 (d, *J* = 2.1 Hz, 1H), 4.16 (s, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 134.1, 129.1, 128.7, 126.5, 117.1, 66.2.



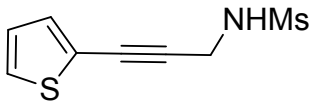
White solid, 1.56 g, 57%
R_f = 0.6 (30% ethyl acetate in hexanes)
Melting point: 89-91 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 2920, 1623, 1467, 1393, 1308, 1256, 1141, 1084, 908 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.60-7.57 (m, 2H), 5.83 (d, *J* = 2.1 Hz, 1H), 5.77 (d, *J* = 2.1 Hz, 1H), 4.14 (s, 2H), 2.46 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 134.8, 129.7, 128.7, 126.3, 117.3, 66.3, 21.6.
HRMS (ESI) calcd for $C_{10}H_{11}BrO_2SNa$ (M+Na) 296.9561; found 296.9568.

2.2. Sonogashira coupling

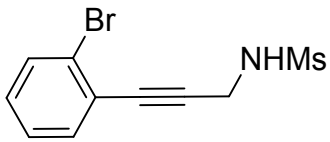


To a solution of the *N*-methanesulfinyl propargy amine (2 mmol) and aryl iodide (2.4 mmol) in THF (10mL) kept under argon, $Pd(PPh_3)_2Cl_2$ (28 mg, 0.04 mmol), CuI (15 mg, 0.08 mmol) and triethylamine (0.85 mL, 6 mmol) were sequentially added at 25 °C and stirred for 2h. The solvent was removed on a rotavapor and water (20 mL) was added. The aqueous solution was extracted with ethyl acetate (3X15 mL). The combined organic extracts was washed with brine, dried over anhydrous sodium sulfate and concentrated on a rotavapor. The residue on column chromatography on silica gel using petroleum ether-ethyl acetate as eluent afforded analytically pure samples of the products.



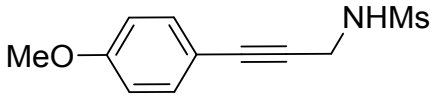
4e, N-(3-(thiophen-2-yl)prop-2-ynyl)methanesulfonamide

Brown solid, 305 mg, 71%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 82-84 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3255, 2362, 1437, 1425, 1308, 1157, 1135, 1051, 1041, 998, 725, 521 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 1.1, 5.2 Hz, 1H), 7.22 (dd, *J* = 1.1, 3.7 Hz, 1H), 6.99 (dd, *J* = 3.7, 5.2 Hz, 1H), 4.66 (brs, 1H), 4.22 (d, *J* = 6.3 Hz, 2H), 3.12 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 132.5, 127.6, 127.0, 121.6, 87.8, 78.3, 41.4, 33.6.
HRMS (ESI) calcd for $C_8H_9NO_2S_2Na$ (M+Na) 237.9972; found 237.9969.



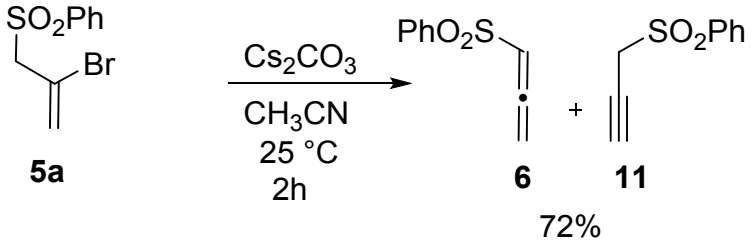
4f, N-(3-(2-bromophenyl)prop-2-ynyl)methanesulfonamide

Brown solid, 436 mg, 76%
R_f = 0.5 (30% ethyl acetate in hexanes)
Melting point: 98-100 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3280, 3062, 3009, 2955, 2926, 2853, 1469, 1435, 1312, 1151, 1064, 970, 760, 521 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, J = 7.9 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.30-7.26 (m, 1H), 7.22-7.19 (m, 1H), 4.27 (d, J = 6.1 Hz, 2H), 3.18 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 133.5, 132.4, 130.0, 127.1, 125.3, 124.0, 88.6, 83.3, 41.6, 33.5.
HRMS (ESI) calcd for $C_{10}H_{10}BrNNaO_2S$(M+Na) 309.9513; found 309.9509



4g, N-(3-(4-methoxyphenyl)prop-2-ynyl)methanesulfonamide
Brown solid, 359 mg, 75%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 96-98 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3292, 3014, 2966, 2930, 2840, 1606, 1511, 1439, 1318, 1149, 1138, 836 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 4.72 (brs, 1H), 4.18 (d, *J* = 6.1 Hz, 2H), 3.81 (s, 3H), 3.13 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 133.0, 114.0, 113.8, 84.9, 82.5, 55.2, 41.3, 33.5.
HRMS (ESI) calcd for $C_{11}H_{13}NO_3SNa$ (M+Na) 262.0514; found 262.0507.

3. Formation of allenyl sulfone 6 and propargyl sulfone 11 from the bromoallyl sulfone 5a



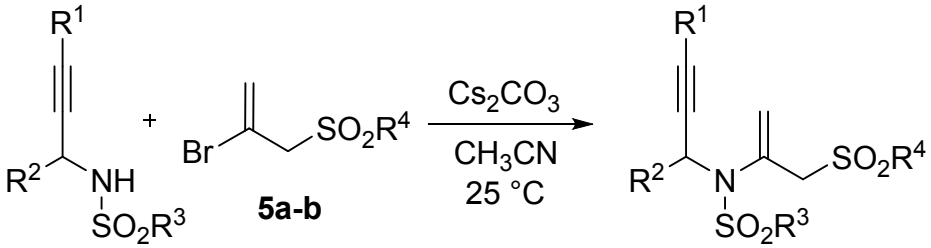
(5:1 mixture, by ^{1}H NMR)

Cesium carbonate (391 mg, 1.2 mmol) was added to a solution of the bromoallyl sulfone **5a** (260 mg, 1.0 mmol) in acetonitrile (2 mL) at room temperature and stirred for 2h. The solvent was removed on a rotavapor, deionized water (10 mL) was added and the aqueous solution was extracted with ethyl acetate (3 X 10 mL). The combined organic extracts was washed with brine, dried over anhydrous sodium sulfate and concentrated on a rotavapor. The residue on column

chromatography on silica gel using petroleum ether-ethyl acetate as eluent afforded 130 mg of a oil which was identified as a 5:1 mixture of the allenyl sulfone **6**[3] and the propargyl sulfone **11**.[4]

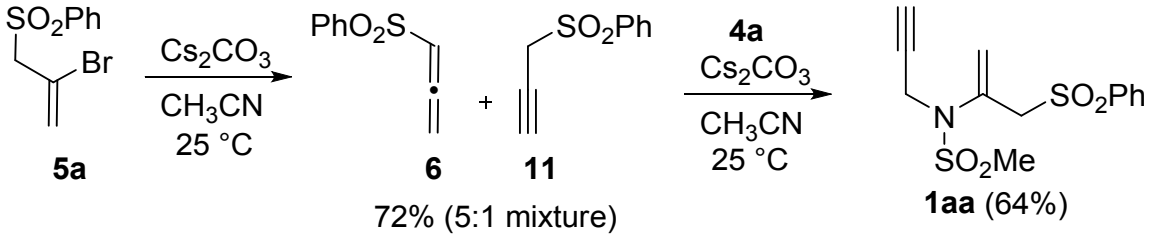
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00-7.98 (m, 0.4H), 7.93-7.91(m, 2H), 7.72-7.69 (m, 0.2H), 7.66-7.62 (m, 1H), 7.61-7.59 (m, 0.4H), 7.58-7.54 (m, 2H), 6.26 (t, *J* = 6.4 Hz, 1H), 5.45 (d, *J* = 6.4 Hz, 2H), 3.97 (d, J = 2.7 Hz, 0.4H), 2.39 (t, J = 0.2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 209.3, 141.1, 134.3, 133.5, 129.1 (2), 128.8, 128.7, 127.5, 127.3, 100.9, 84.1, 76.2, 71.5, 48.3.

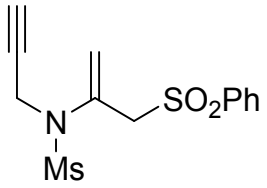
4. CS_2CO_3-mediated reaction of 2-bromoallyl sulfones 5a-b with sulfonamides 4a-g



Typical procedure: Cesium carbonate (717 mg, 2.2 mmol) was added to a solution of the propargyl sulfonamide **4** (1 mmol) and the bromoallyl sulfone **5** (1.2 mmol) in acetonitrile (5 mL) at room temperature and stirred for 4 hours. The solvent was removed on a rotavapor, deionized water (10 mL) was added and the aqueous solution was extracted with ethyl acetate (3 X 10 mL). The combined organic extracts was washed with brine, dried over anhydrous sodium sulfate and concentrated on a rotavapor. The residue on column chromatography on silica gel using petroleum ether-ethyl acetate as eluent afforded analytically pure samples of the products. (Cesium carbonate-mediated reaction of **4a** with the mixture of allenyl sulfone **6** and propargyl sulfone **7** was also carried out in the above-described manner to afford **1aa**)

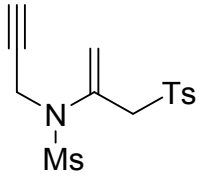
Similarly, treatment of the pre-formed mixture of the allenyl sulfone **5a** and propargyl sulfone **11** with **4aa** under the above-described conditions afforded the product **1aa** in 64% yield.





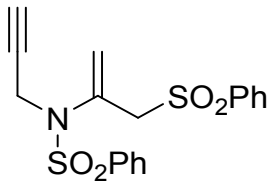
1aa, N-(3-(phenylsulfonyl)prop-1-en-2-yl)-N-(prop-2-ynyl)methanesulfonamide

White solid, 294 mg, 94%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 110-112 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3288, 3261, 2990, 2933, 2119, 1637, 1448, 1333, 1263, 1147, 1081, 939, 689, 533 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.91 (m, 2H), 7.71-7.66 (m, 1H), 7.61-7.57 (m, 2H), 5.98 (s, 1H), 5.45 (s, 1H), 4.22 (d, *J* = 2.4 Hz, 2H), 4.19 (s, 2H), 3.07 (s, 3H), 2.46 (t, *J* = 2.4 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.7, 136.9, 133.9, 129.2, 128.1, 121.1, 78.8, 74.4, 63.4, 40.9, 38.1.
HRMS calcd for $C_{13}H_{16}NO_4S_2$(M+H) 314.0521; found 314.0514.



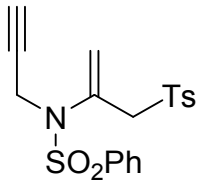
1ab, N-(prop-2-ynyl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide

White solid, 291 mg, 89%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 120-122 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3282, 2946, 1633, 1594, 1402, 1337, 1315, 1302, 1153, 1135, 1085, 1052, 963, 522 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 5.96 (s, 1H), 5.42 (s, 1H), 4.24 (d, *J* = 2.4 Hz, 2H), 4.16 (s, 2H), 3.07 (s, 3H), 2.46-2.45 (m, 4H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 136.9, 135.8, 129.8, 128.1, 121.1, 78.9, 74.5, 63.4, 40.8, 38.1, 21.6.
HRMS (ESI) calcd for $C_{14}H_{21}N_2O_4S_2$(M+NH_4) 345.0943; found 345.0932.



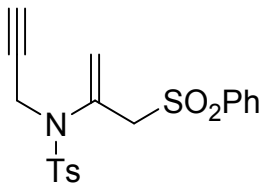
1ba, N-(3-(phenylsulfonyl)prop-1-en-2-yl)-N-(prop-2-ynyl)benzenesulfonamide

White solid, 360 mg, 96%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 179-181 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3445, 3249, 3062, 2939, 1733, 1657, 1491, 1447, 1350, 1307, 1142, 1085, 743, 685, 536 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.4 Hz, 2H), 7.81 (d, *J* = 7.4 Hz, 2H), 7.72-7.67 (m, 1H), 7.62-7.56 (m, 3H), 7.50-7.45 (m, 2H), 5.42 (s, 1H), 5.37 (s, 1H), 4.28 (d, *J* = 2.5 Hz, 2H), 4.25 (s, 2H), 2.05 (t, *J* = 2.5 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 137.5, 135.6, 134.0, 133.2, 129.2, 128.5, 128.3, 1282, 123.2, 77.9, 74.0, 63.6, 40.6.
HRMS (ESI) calcd for $C_{18}H_{17}O_4NNaS_2$(M+Na) 398.0497; found 398.0489.



1bb N-(prop-2-ynyl)-N-(3-tosylprop-1-en-2-yl)benzenesulfonamide

White solid, 358 mg, 92%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 128-130 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3270, 3060, 3003, 2949, 2117, 1631, 1595, 1446, 1417, 1339, 1265, 1169, 1085, 819, 677, 517 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.79 (m, 4H), 7.61-7.56 (m, 1H), 7.50-7.45 (m, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 5.41 (s, 1H), 5.36 (s, 1H), 4.30 (d, *J* = 2.5 Hz, 2H), 4.21 (s, 2H), 2.47 (s, 3H), 2.05 (t, *J* = 2.5 Hz, 1H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 137.5, 135.8, 135.6, 133.2, 129.8, 128.5, 128.3, 128.2, 123.3, 78.0, 73.9, 63.7, 40.6, 21.6.
HRMS calcd for $C_{19}H_{19}NO_4S_2$(M+Na) 412.0653; found 412.0638.



1ca, 4-methyl-N-(3-(phenylsulfonyl)prop-1-en-2-yl)-N-(prop-2-ynyl)benzenesulfonamide

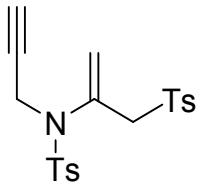
White solid, 361 mg, 93%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 140-142 ˚C (CH_2Cl_2-hexanes)

IR (KBr) ν_{max}: 3427, 3267, 2999, 2924, 2360, 1637, 1447, 1339, 1299, 1269, 1156, 1095, 1082, 645, 549 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.70-7.67 (m, 3H), 7.61-7.57 (m, 2H), 7.27-7.25 (m, 2H), 5.41 (d, J = 1.0 Hz, 1H), 5.38 (d, J = 1.0 Hz, 1H), 4.25 (d, J = 2.4 Hz, 2H), 4.24 (s, 2H), 2,42 (s, 3H), 2.06 (t, J = 2.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 138.8, 135.6, 134.5, 133.9, 129.2, 129.1, 128.4, 128.3, 123.1, 78.0, 73.9, 63.6, 40.5, 21.5.

HRMS (ESI) calcd for $C_{19}H_{20}NO_4S_2$(M+H) 390.0834; found 390.0830.



1cb, 4-methyl-N-(prop-2-ynyl)-N-(3-tosylprop-1-en-2-yl)benzenesulfonamide

White solid, 363 mg, 90%

R_f = 0.4 (30% ethyl acetate in hexanes)

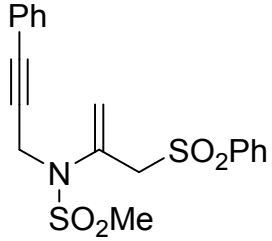
Melting point: 133-135 ˚C (CH_2Cl_2-hexanes)

IR (KBr) ν_{max}: 3303, 2997, 2974, 2939, 1633, 1596, 1495, 1343, 1302, 1270, 1159, 1083, 811, 615, 514 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 5.40 (s, 1H), 5.35 (s, 1H), 4.27 (d, *J* = 2.4 Hz, 2H), 4.20 (s, 2H), 2.46 (s, 3H), 2.42 (s, 3H), 2.07 (t, *J* = 2.4 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 144.1, 135.8, 135.7, 134.5, 129.8, 129.1, 128.4, 128.3, 123.2, 78.1, 73.9, 63.7, 40.5, 21.6(2).

HRMS calcd for $C_{20}H_{21}NNaO_4S_2$(M+Na) 426.0810; found 426.0788.



1da, N-(3-phenylprop-2-ynyl)-N-(3-(phenylsulfonyl)prop-1-en-2-yl)methanesulfonamide

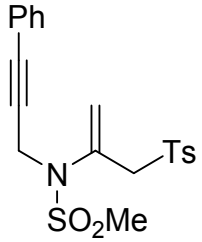
Pale yellow solid, 370 mg, 95%

R_f = 0.4 (30% ethyl acetate in hexanes)

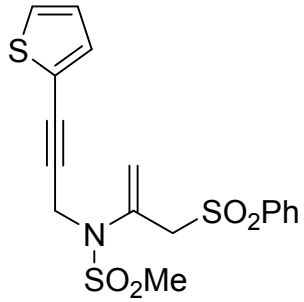
Melting point: 104-106 ˚C (CH_2Cl_2-hexanes)

IR (KBr) ν_{max}: 3439, 3023, 2986, 2925, 2242, 1629, 1597, 1584, 1490, 1446, 1336, 1242, 1155, 1127, 685, 526 cm^{-1}

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.72-7.67 (m, 1H), 7.62-7.57 (m, 2H), 7.43-7.31 (m, 5H), 6.04 (s, 1H), 5.49 (s, 1H), 4.42 (s, 2H), 4.23 (s, 2H), 3.10 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 137.1, 134.0, 131.5, 129.3, 129.0, 128.5, 128.2, 121.7, 121.0, 86.1, 83.9, 63.5, 41.8, 38.1.
HRMS (ESI) calcd for $C_{19}H_{20}NO_4S_2$(M+H) 390.0834; found 390.0834.

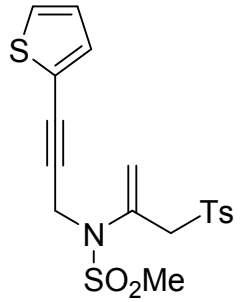


1db, N-(3-phenylprop-2-ynyl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide
Brown solid, 364 mg, 90%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 135-137 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3432, 3012, 2929, 2362, 1718, 1631, 1595, 1490, 1442, 1342, 1314, 1153, 1082, 689, 528 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.38-7.32 (m, 5H), 6.03 (s, 1H), 5.47 (s, 1H), 4.44 (s, 2H), 4.20 (s, 2H), 3.10 (s, 3H), 2.46 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 137.1, 135.8, 131.5, 129.8, 128.9, 128.4, 128.1, 121.7, 120.9, 86.0, 83.9, 63.5, 41.7, 38.1, 21.6.
HRMS (ESI) calcd for $C_{20}H_{22}NO_4S_2$(M+H) 404.0990; found 404.0989



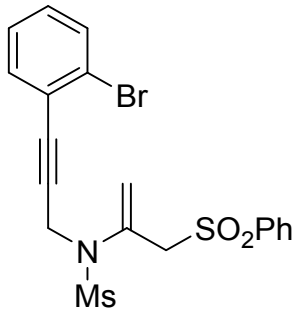
1ea, N-(3-(phenylsulfonyl)prop-1-en-2-yl)-N-(3-(thiophen-2-yl)prop-2-ynyl)methanesulfonamide
White solid, 324 mg, 82%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 162-164 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3448, 3086, 3025, 2997, 2948, 2926, 2221, 1624, 1448, 1415, 1339, 1317, 1307, 1153, 1133, 1082, 965, 621 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.70-7.67 (m, 1H), 7.61-7.58 (m, 2H), 7.30 (d, *J* = 5.0 Hz, 1H), 7.23 (d, *J* = 3.2 Hz, 1H), 7.00-6.99 (m, 1H), 5.99 (s, 1H), 5.49 (s, 1H), 4.44 (s, 2H), 4.22 (s, 2H), 3.07 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9, 137.0, 134.0, 132.7, 129.3, 128.2, 127.9, 127.2, 121.5, 121.2, 87.9, 79.5, 63.6, 42.0, 38.1.
HRMS (ESI) calcd for $C_{17}H_{18}NO_4S_3$(M+H) 396.0398; found 396.0397.



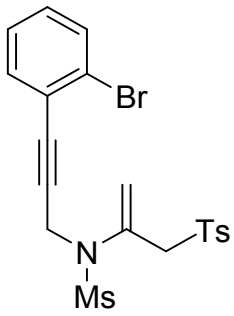
1eb, N-(3-(thiophen-2-yl)prop-2-ynyl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide

White solid, 385 mg, 94%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 117-119 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3101, 3019, 2933, 2223, 1631, 1594, 1427, 1313, 1266, 1154, 1082, 1055, 677, 524 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 4.9 Hz, 1H), 7.23 (d, *J* = 3.1 Hz, 1H), 7.00-6.99 (m, 1H), 5.97 (s, 1H), 5.47 (s, 1H), 4.46 (s, 2H), 4.19 (s, 2H), 3.08 (s, 3H), 2.46 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 137.0, 135.8, 132.6, 129.8, 128.1, 127.8, 127.1, 121.4, 121.2, 87.9, 79.4, 63.5, 41.9, 38.1, 21.6.
HRMS (ESI) calcd for $C_{18}H_{20}NO_4S_3$(M+H) 410.0554; found 410.0551.

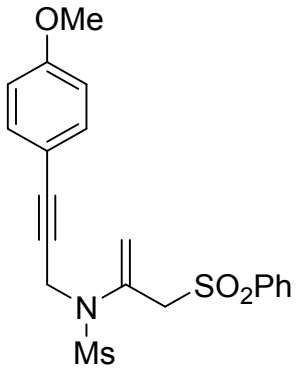


1fa, N-(3-(2-bromophenyl)prop-2-ynyl)-N-(3-(phenylsulfonyl)prop-1-en-2-yl)methanesulfonamide
White solid, 434 mg, 93%
R_f = 0.5 (30% ethyl acetate in hexanes)

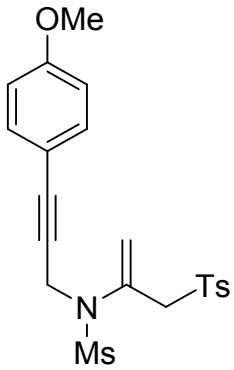
Melting point: 121-123˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3410, 2931, 2345, 1636, 1585, 1469, 1446, 1345, 1319, 1152, 1083, 1050, 755, 519 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.71-7.66 (m, 1H), 7.62-7.57 (m, 3H), 7.47 (dd, *J* = 1.7, 7.6 Hz, 1H), 7.32-7.27 (m, 1H), 7.25-7.19 (m, 1H), 6.21 (d, *J* = 0.9 Hz, 1H), 5.50 (d, *J* = 0.9 Hz, 1H), 4.49 (s, 2H), 4.24 (s, 2H), 3.13 (s, 3H),
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 136.8, 133.9, 133.7, 132.4, 130.1, 129.2, 128.1, 127.2, 125.2, 123.9, 121.6, 88.3, 84.4, 63.5, 41.8, 38.3.
HRMS (ESI) calcd for $C_{19}H_{19}BrNO_4S_2$(M+H) 469.9918; found 469.9914.



1fb, N-(3-(2-bromophenyl)prop-2-ynyl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide
White solid, 428 mg, 89%
R_f = 0.5 (30% ethyl acetate in hexanes)
Melting point: 110-112 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3069, 3028, 2931, 1637, 1595, 1467, 1417, 1336, 1253, 1152, 1084, 955, 763, 687, 526 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.58 (dd, *J* = 1.1, 8.1 Hz, 1H), 7.47 (dd, *J* = 1.7, 7.6 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.29 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.22 (dt, *J* = 1.7, 7.6 Hz, 1H), 6.19 (d, *J* = 1.1 Hz, 1H), 5.49 (d, *J* = 1.1 Hz, 1H), 4.51 (s, 2H), 4.21 (s, 2H), 3.13 (s, 3H), 2.46 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 136.9, 135.9, 133.7, 132.4, 130.1, 129.8, 128.1, 127.2, 125.2, 123.9, 121.6, 88.4, 84.3, 63.6, 41.7, 38.3, 21.6.
HRMS (ESI) calcd for $C_{20}H_{24}BrN_2O_4S_2$(M+NH_4) 499.0361; found 499.0360.



1ga, N-(3-(4-methoxyphenyl)prop-2-ynyl)-N-(3-(phenylsulfonyl)prop-1-en-2-yl)methanesulfonamide
White solid, 369 mg, 88%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 134-136 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3448, 2992, 2925, 2853, 1744, 1637, 1448, 1338, 1304, 1159, 1141, 956, 752, 543 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95-7.93 (m, 2H), 7.70-7.67 (m, 1H), 7.61-7.57 (m, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.04 (s, 1H), 5.47 (s, 1H), 4.39 (s, 2H), 4.23 (s, 2H), 3.82 (s, 3H), 3.08 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 138.8, 137.0, 133.9, 133.0, 129.2, 128.1, 120.8, 114.0, 113.6, 86.0, 82.4, 63.4, 55.2, 41.9, 38.0.
HRMS (ESI) calcd for $C_{20}H_{21}NNaO_5S_2$(M+Na) 442.0759; found 442.0739.



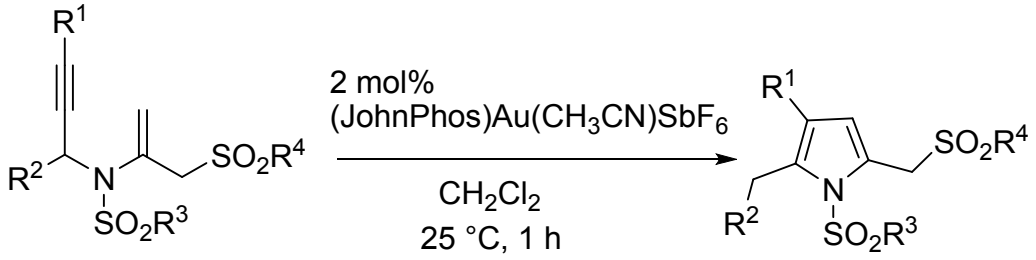
1gb, N-(3-(4-methoxyphenyl)prop-2-ynyl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide
Light yellow solid, 365 mg, 84%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 145-147 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3416, 2930, 2358, 1605, 1509, 1345, 1318, 1292, 1249, 1152, 1084, 1029, 519 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.9 Hz, 2H), 7.39-7.34 (m, 4H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.03 (s, 1H), 5.46 (s, 1H), 4.40 (s, 2H), 4.20 (s, 2H), 3.82 (s, 3H), 3.09 (s, 3H), 2.46 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 160.0, 144.9, 137.1, 135.9, 133.0, 129.8, 128.1, 120.7, 114.0, 113.6, 86.0, 82.5, 63.5, 55.2, 41.9, 38.0, 21.5.
HRMS (ESI) calcd for $C_{21}H_{24}NO_5S_2$(M+H) 434.1096; found 434.1093.

5. NaH-mediated reaction of 4h with 5b to afford the aza-enyne 1hb

To a suspension of sodium hydride (88mg, 2.2 mmol) in THF (4 mL) kept at 0 °C, propargyl sulfonamide **4h** (403 mg, 1 mmol) and the bromoallyl sulfone **5b** (323 mg, 1.2 mmol) were added in succession and the reaction mixture was stirred for 30 minutes at the same temperature. Then, ice was added to the reaction mixture and the solution was extracted with ethyl acetate (3

X 10 mL). The combined organic extracts was washed with brine, dried over anhydrous sodium sulfate and concentrated on a rotavapor. The residue on column chromatography on silica gel using petroleum ether-ethyl acetate as eluent afforded a sample of *N*-(1-phenylprop-2-ynyl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide **1hb** contaminated with unidentified impurities. This sample was directly used in the gold-catalyzed cycloisomerization and a clean reaction ensued to afford the pyrrole **2hb**.

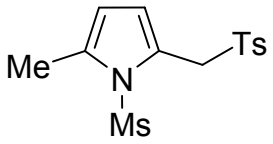
6. Gold-catalyzed pyrrole synthesis



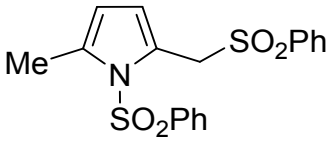
1aa-hb **2aa-hb**

To a solution of the *N*-propragyl-*N*-vinyl sulphonamide **1aa-hb** (0.3 mmol) in dichloromethane (2mL) maintained under an atmosphere of nitrgen, (acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate (5mg, 0.006 mmol) was added and the reaction was stirred for 1 h at 25 °C. The solvent was evaporated on a rotavapor and the residue was chromatographed on silica gel using petroleum ether-ethyl acetate as eluent to afford analytically pure samples of the products.

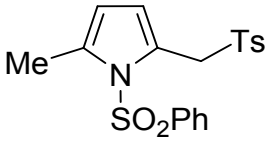
2aa, 2-Methyl-1-(methylsulfonyl)-5-(phenylsulfonylmethyl)-1H-pyrrole
White solid, 84 mg, 89%
R_f = 0.7 (40% ethyl acetate in hexane)
Melting point: 133-134 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3447, 3009, 2951, 2925, 2360, 1586, 1522, 1450, 1414, 1175, 1109, 973, 775, 654, 516 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.69-7.66 (m, 1H), 7.59-7.56 (m, 2H), 6.08 (d, *J* = 3.4 Hz, 1H), 6.01 (d, *J* = 3.4 Hz, 1H), 4.84 (s, 2H), 3.45 (s, 3H), 2.47 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 134.5, 133.9, 129.2, 128.4, 120.9, 117.6, 112.3, 55.0, 42.9, 15.4.
HRMS (ESI) calcd for $C_{13}H_{15}O_4NNaS_2$ (M+Na) 336.0340; found 336.0349.



2ab, 2-Methyl-1-(methylsulfonyl)-5-(tosylmethyl)-1H-pyrrole
White solid, 94 mg, 96%
R_f = 0.7 (40% ethyl acetate in hexane)
Melting point: 136-138 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3434, 3019, 3000, 2923, 2360, 1596, 1523, 1495, 1313, 1231, 812, 767 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 6.07 (d, *J* = 3.0 Hz, 1H), 6.01 (d, *J* = 3.0 Hz, 1H), 4.82 (s, 2H), 3.47 (s, 3H), 2.47 (s, 6H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 135.8, 134.3, 129.8, 128.4, 121.1, 117.5, 112.2, 55.0, 42.9, 21.6, 15.5.
HRMS (ESI) calcd for $C_{14}H_{17}O_4NNaS_2$ (M+Na) 350.0497; found 350.0506.

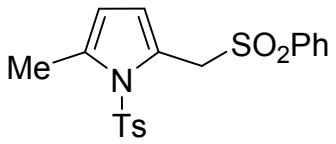


2ba, 2-Methyl-1-(phenylsulfonyl)-5-(phenylsulfonylmethyl)-1H-pyrrole
White solid, 110 mg, 98%
R_f = 0.7 (40% ethyl acetate in hexanes)
Melting point: 142-144 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3430, 3113, 3093, 3070, 3014, 2929, 2360, 2340, 1913, 1708, 1637, 1584, 1396, 1087, 769, 727, 656, 526 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.68-7.64 (m, 3H), 7.60-7.57 (m, 1H), 7.54-7.47 (m, 4H), 6.37 (d, *J* = 3.2 Hz, 1H), 5.97 (d, *J* = 3.2 Hz, 1H), 4.92 (s, 2H), 2.19 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 138.5, 135.0, 133.8, 133.7, 129.3, 128.9, 128.7, 126.4, 122.6, 118.3, 113.0, 55.3, 15.2.
HRMS (ESI) calcd for $C_{18}H_{21}O_4N_2S_2$ ($M+NH_4$) 393.0943; found 393.0925.

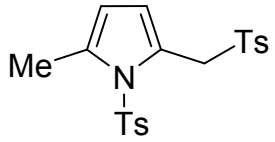


2bb, 2-Methyl-1-(phenylsulfonyl)-5-(tosylmethyl)-1H-pyrrole
White solid, 112 mg, 96%
Rf = 0.7 (40% ethyl acetate in hexane)
Melting point: 152-154 °C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3420, 3083, 3000, 2951, 2935, 2365, 2360, 1905, 1712, 1595, 1522, 1451, 1403, 1366, 1313, 1296, 1087, 800, 650, 516 cm^{-1}

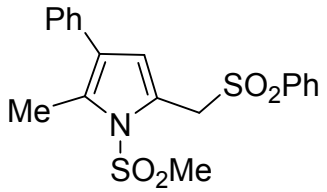
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69-7.67 (m, 4H), 7.60-7.57 (m, 1H), 7.49-7.46 (m, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 6.34 (s, 1H), 5.96 (s, 1H), 4.89 (s, 2H), 2.45 (s, 3H), 2.20 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 139.4, 135.6, 134.9, 133.8, 129.5, 129.3, 128.6, 126.3, 122.8, 118.1, 112.9, 55.3, 21.6, 15.2.
HRMS (ESI) calcd for $C_{19}H_{23}O_4N_2S_2$ (M+NH_4) 407.1099; found 407.1078.



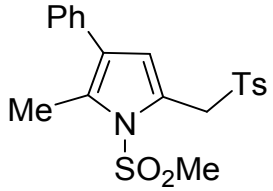
2ca, 2-Methyl-5-(phenylsulfonylmethyl)-1-tosyl-1H-pyrrole
White solid, 113 mg, 97%
R_f = 0.7 (40% ethyl acetate in hexane)
Melting point: 140-142 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3441, 3113, 3095, 3074, 3032, 3014, 2955, 2927, 2860, 2360, 1931, 1910, 1818, 1708, 1594, 1494, 1399, 1221, 1116, 1007, 865, 704 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$) 7.80 (d, *J* = 8.5 Hz, 2H), 7.67-7.62 (m, 1H), 7.57-7.49 (m, 4H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.36 (d, *J* = 3.4 Hz, 1H), 5.95 (d, *J* = 3.4 Hz, 1H), 4.91 (s, 2H), 2.39 (s, 3H), 2.19 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 138.5, 136.5, 135.0, 133.7, 129.9, 128.8, 128.7, 126.4, 122.4, 118.2, 112.8, 55.3, 21.5, 15.2.
HRMS (ESI) calcd for $C_{19}H_{23}O_4N_2S_2$ (M+NH_4) 407.1099; found 407.1077.



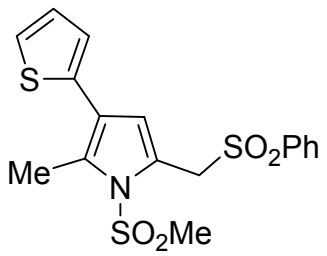
2cb, 2-Methyl-1-tosyl-5-(tosylmethyl)-1H—pyrrole
White solid, 120 mg, 99%
R_f = 0.7 (40% ethyl acetate in hexane)
Melting point: 110-113 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3433, 3110, 3045, 3013, 2950, 2922, 1927, 1739, 1595, 1524, 1493, 1439, 1318, 1249, 1177, 636 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.35 (d, *J* = 3.2 Hz, 1H), 5.95 (d, *J* = 3.2 Hz, 1H), 4.89 (s, 2H), 2.45 (s, 3H), 2.40 (s, 3H), 2.20 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 144.6, 136.5, 135.7, 134.9, 129.9, 129.5, 128.7, 126.5, 122.7, 118.0, 112.8, 55.3, 21.6, 21.5, 15.2.
HRMS (ESI) calcd for $C_{20}H_{25}O_4N_2S_2$ (M+NH_4) 421.1256; found 421.1252.



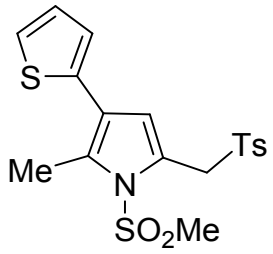
2da, 2-Methyl-1-(methylsulfonyl)-3-phenyl-5-(phenylsulfonylmethyl)-1H-pyrrole
White solid, 112 mg, 96%
R_f = 0.7 (40% ethyl acetate in hexane)
Melting point: 163-165 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3438, 3025, 3007, 2926, 2853, 2361, 1593, 1398, 1359, 1312, 1206, 1173, 1084, 835 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 2H), 7.73-7.67 (m, 1H), 7.62-7.57 (m, 2H), 7.42-7.37 (m, 2H), 7.33-7.24 (m, 3H), 6.22 (s, 1H), 4.90 (s, 2H), 3.55 (s, 3H), 2.54 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 138.6, 134.2, 133.9, 129.9, 129.1, 128.7, 128.4, 126.9, 126.2, 120.4, 118.9, 54.9, 43.0, 13.5.
HRMS (ESI) calcd $C_{19}H_{19}O_4NNaS_2$ (M+Na) 412.0653; found 412.0656.



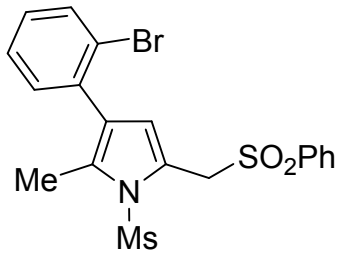
2db, 2-Methyl-1-(methylsulfonyl)-3-phenyl-5-(tosylmethyl)-1H-pyrrole
White solid, 115 mg, 95%
R_f = 0.7 (40% ethyl acetate in hexane)
Melting point: 167-169 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3438, 3025, 3007, 2853, 2361, 1593, 1432, 1359, 1312, 1243, 1173, 1147, 1084, 772, 631, 540 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.1 Hz, 2H), 7.42-7.36 (m, 4H), 7.33-7.25 (m, 3H), 6.22 (s, 1H), 4.87 (s, 2H), 3.55 (s, 3H), 2.54 (s, 3H), 2.48 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 135.8, 134.3, 129.9, 129.8, 128.7, 128.4, 126.9, 126.2, 120.6, 118.8, 55.0, 43.0, 21.6, 13.5.
HRMS (ESI) calcd for $C_{20}H_{21}O_4NNaS_2$ (M+Na) 426.0810; found 426.0808.



2ea, 2-Methyl-1-(methylsulfonyl)-5-(phenylsulfonylmethyl)-3-(thiophen-2-yl)-1H-pyrrole
White solid, 113 mg, 95%
R_f = 0.7 (40% ethyl acetate in hexane)
Melting point: 170-172 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3444, 3100, 3020, 3006, 2960, 2926, 2362, 1969, 1902, 1817, 1584, 1545, 1449, 1081, 1003, 774, 517 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.71-7.68 (m, 1H), 7.60-7.57 (m, 2H), 7.28 (dd, *J* = 1.1, 5.2 Hz, 1H), 7.06 (dd, *J* = 3.5, 5.2 Hz, 1H), 6.97 (dd, *J* = 1.1, 3.5 Hz, 1H), 6.22 (s, 1H), 4.87 (s, 2H), 3.54 (s, 3H), 2.63 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 135.8, 134.0, 130.2, 129.2, 128.4, 127.3, 125.3, 124.7, 120.7, 119.6, 118.7, 54.9, 43.1, 13.7.
HRMS (ESI) calcd $C_{17}H_{17}O_4NNaS_3$ (M+Na) 418.0217; found 418.0225.

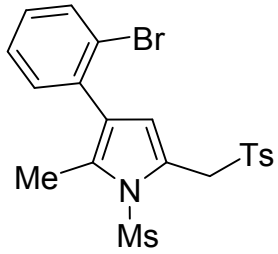


2eb, 2-Methyl-1-(methylsulfonyl)-3-(thiophen-2-yl)-5-(tosylmethyl)-1H-pyrrole
White solid, 118 mg, 96%
R_f = 0.7 (40% ethyl acetate in hexanes)
Melting point: 152-154 ˚C (CH_2Cl_2-hexane)
IR (KBr) ν_{max}: 3434, 3102, 3069, 3020, 3006, 2928, 2360, 1596, 1391, 1360, 1325, 1311, 1224, 1243, 1160, 1084, 972, 723 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 5.0 Hz, 1H), 7.06 (dd, *J* = 3.6, 5.0 Hz, 1H), 6.98 (d, *J* = 3.6 Hz, 1H), 6.22 (s, 1H), 4.85 (s, 2H), 3.55 (s, 3H), 2.63 (s, 3H), 2.48 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 135.9, 135.5, 130.1, 129.8, 128.4, 127.3, 125.3, 124.7, 120.8, 119.5, 118.6, 54.9, 43.1, 21.7, 13.7.
HRMS (ESI) calcd for $C_{18}H_{20}O_4NS_3$ (M+H) 410.0554; found 410.0552.

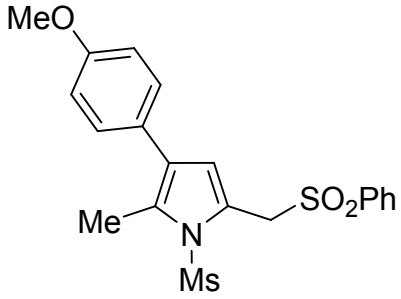


2fa, 3-(2-Bromophenyl)-2-methyl-1-(methylsulfonyl)-5-(phenylsulfonylmethyl)-1H-pyrrole

White solid, 125 mg, 89%
R_f = 0.7 (40% ethyl acetate in hexane)
Melting point: 136-138 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3448, 3114, 3052, 3026, 2958, 2939, 2858, 2329, 1905, 1819, 1712, 1603, 1584, 1523, 1469, 1445, 1429, 1397, 1243, 1003, 730, 547 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.69-7.63 (m, 2H), 7.59-7.55 (m, 2H), 7.35-7.31 (m, 1H), 7.22-7.18 (m, 2H), 6.09 (s, 1H), 4.91 (s, 2H), 3.52 (s, 3H), 2.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 135.1, 133.9, 132.8, 131.9, 131.3, 129.1, 128.5, 127.2, 125.4, 124.3, 120.2, 119.2, 54.8, 43.0, 13.6.
HRMS (ESI) calcd for $C_{19}H_{22}O_4N_2BrS_2$ (M+NH_4) 485.0204; found 485.0196.



2fb, 3-(2-Bromophenyl)-2-methyl-1-(methylsulfonyl)-5-(tosylmethyl)-1H-pyrrole
White solid, 126 mg, 87%
R_f = 0.7 (40 % ethyl acetate in hexane)
Melting point: 177-179 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3448, 3029, 2927, 2854, 2363, 2363, 1637, 1596, 1525, 1472, 1399, 1359, 1314, 1244, 1203, 1172, 1116, 964, 681, 514 cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.36-7.31 (m, 3H), 7.22-7.18 (m, 2H), 6.10 (s, 1H), 4.89 (s, 2H), 3.53 (s, 3H), 2.45 (s, 3H), 2.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 144.9, 135.6, 135.2, 132.8, 131.9, 131.3, 129.8, 129.1, 128.6, 127.2, 125.5, 124.4, 120.5, 119.2, 55.0, 43.0, 21.6, 13.7.
HRMS (ESI) calcd for $C_{20}H_{24}Br\ N_2O_4S_2$ (M+NH_4) 501.0340; found 501.0342.



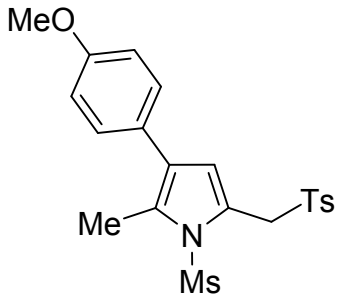
2ga, 3-(4-Methoxyphenyl)-2-methyl-1-(methylsulfonyl)-5-(phenylsulfonylmethyl)-1H-pyrrole
White solid, 114 mg, 91%
R_f = 0.7 (40% ethyl acetate in hexane)
Melting point: 139-141 ˚C (CH_2Cl_2-hexanes)

IR (KBr) ν_{max}: 3429, 3036, 2960, 2932, 2838, 2359, 2341, 1612, 1595, 1531, 1504, 1463, 1301, 1171, 813, 724, 517 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 2H), 7.71-7.68 (m, 1H), 7.61-7.58 (m, 2H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.20 (s, 1H), 4.89 (s, 2H), 3.84 (s, 3H), 3.53 (s, 3H), 2.52 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 138.7, 133.9, 129.8, 129.5, 129.2, 128.4, 126.6, 125.9, 120.1, 119.1, 113.9, 55.3, 54.9, 43.0, 13.6.

HRMS (ESI) calcd for $C_{20}H_{22}O_5NS_2$ (M+H) 420.0939; found 420.0939.



2gb, 3-(4-Methoxyphenyl)-2-methyl-1-(methylsulfonyl)-5-(tosylmethyl)-1H-pyrrole

White solid, 127 mg, 98%

R_f = 0.7 (40% ethyl acetate in hexane)

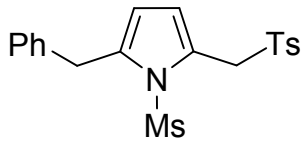
Melting point: 78-80 ˚C (CH_2Cl_2-hexanes)

IR (KBr) ν_{max}: 3430, 3037, 2957, 2930, 2836, 2302, 1611, 1341, 1247, 1161, 725, 629, 515 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.20 (s, 1H), 4.86 (s, 2H), 3.84 (s, 3H), 3.53 (s, 3H), 2.52 (s, 3H), 2.48 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 144.9, 135.9, 129.8(2), 129.4, 128.4, 126.7, 125.9, 120.4, 119.0, 113.9, 55.3, 55.0, 43.0, 21.6, 13.5.

HRMS (ESI) calcd for $C_{21}H_{24}O_5NS_2$ (M+H) 434.1096; found 434.1102.



2hb, 2-Benzyl-1-(methylsulfonyl)-5-(tosylmethyl)-1H-pyrrole

White solid, 105 mg, 87%

R_f = 0.7 (40% ethyl acetate in hexane)

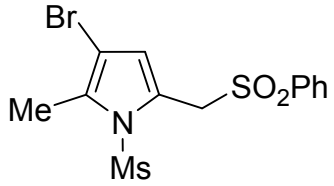
Melting point: 151-153 ˚C (CH_2Cl_2-hexanes)

IR (KBr) ν_{max}: 3432, 3013, 2924, 2852, 2362, 1735, 1595, 1496, 1455, 1356, 1317, 1169, 782, 750, 693 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.35-7.32 (m, 4H), 7.27-7.23 (m, 3H), 6.12 (d, *J* = 3.5 Hz, 1H), 5.96 (d, *J* = 3.5 Hz, 1H), 4.82 (s, 2H), 4.22 (s, 2H), 3.02 (s, 3H), 2.46 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 138.0, 137.8, 135.7, 129.8, 129.2, 128.6, 128.4, 126.8, 121.9, 117.6, 113.6, 55.1, 42.7, 34.9, 21.6.
HRMS (ESI) calcd for $C_{20}H_{25}O_4N_2S_2$ (M+NH_4) 421.1256; found 421.1231.

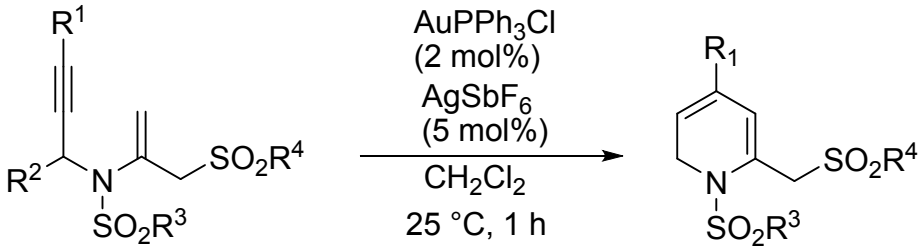
7. Bromination of pyrrole 2aa

Freshly re-crystallised *N*-bromosuccinimide (85 mg, 0.48 mmol) was added to a solution of 2-methyl-1-(methylsulfonyl)-5-(phenylsulfonylmethyl)-1H-pyrrole **2aa** (50 mg, 0.16 mmol) in anhydrous THF (3 mL) at 25 °C and the resulting solution was stirred overnight. THF was removed on a rotavapor, deionized water (10 mL) was added and the aqueous solution was extracted with ethyl acetate (3 X 10 mL). The combined organic extracts was washed with brine, dried over anhydrous sodium sulfate and concentrated on a rotavapor. The residue on column chromatography on silica gel using petroleum ether-ethyl acetate as eluent afforded the 3-bromopyrrole derivative **8** as a white solid (43 mg, 69%).



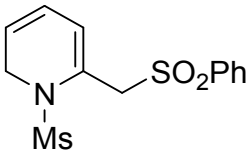
8, 3-Bromo-2-methyl-1-(methylsulfonyl)-5-(phenylsulfonylmethyl)-1H-pyrrole
White solid, 69%
R_f = 0.7 (40% ethyl acetate in hexane)
Melting point: 106-108 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3441, 3105, 3068, 3039, 3023, 2924, 2853, 1680, 1576, 1515, 1477, 1446, 1396, 1354, 1315, 1227, 1100, 612 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 2H), 7.71-7.68 (m, 1H), 7.61-7.58 (m, 2H), 6.18 (s, 1H), 4.81 (s, 2H), 3.50 (s, 3H), 2.49 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 134.1, 131.6, 129.3, 128.4, 120.9, 119.8, 102.0, 54.5, 43.0, 13.7.
HRMS (ESI) calcd for $C_{13}H_{14}O_4NBrNaS_2$ (M+Na) 413.9445; found 413.9446.

8. Gold-catalyzed synthesis of dihydropyridines 3aa-3gb

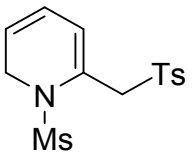


1aa-gb **3aa-gb**

PPh_3AuCl (3 mg, 0.006 mmol), silver hexafluoroantimonate (5 mg, 0.015 mmol) and *N*-propragyl-*N*-vinyl sulphonamide **1aa-gb** (0.3 mmol) were weighed out in to a round bottom flask. Dichloromethane (2mL) was added and the reaction was stirred for 1 h at 25 °C under nitrogen. The solvent was evaporated on a rotavapor and the residue was chromatographed on silica gel using petroleum ether-ethyl acetate as eluent to afford analytically pure samples of the products.

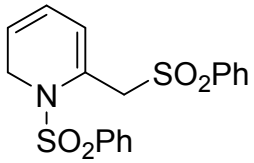


3aa, 1-(Methylsulfonyl)-6-(phenylsulfonylmethyl)-1,2-dihydropyridine
White solid, 87 mg, 92%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 132-135 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3068, 3027, 3007, 2934, 2837, 2361, 1641, 1606, 1583, 1512, 1463, 1336, 1317, 1246, 1146, 521 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 2H), 7.69-7.65 (m, 1H), 7.59-7.55 (m, 2H), 6.24 (d, *J* = 5.1 Hz, 1H), 6.13-6.10 (m, 1H), 5.81-5.77 (m, 1H), 4.38 (s, 2H), 3.98 (d, *J* = 3.1 Hz, 2H), 2.79 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4, 133.9, 129.1, 128.5, 127.7, 124.5, 123.9, 123.5, 61.6, 45.3, 39.0.
HRMS (ESI) calcd for $C_{13}H_{16}NO_4S_2$(M+H) 314.0521; found 314.0504.

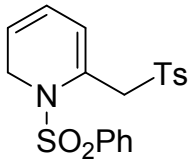


3ab, 1-(Methylsulfonyl)-6-(tosylmethyl)-1,2-dihydropyridine
White solid, 93 mg, 95%
R_f = 0.3 (30% ethyl acetate in hexanes)

Melting point: 133-135 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3474, 3026, 3010, 3000, 2944, 2931, 2850, 1595, 1335, 1317, 1158, 1146, 1086, 1054, 971, 722, 542 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 6.22 (d, *J* = 5.3 Hz, 1H), 6.12-6.10 (m, 1H), 5.81-5.77 (m, 1H), 4.35 (s, 2H), 4.00 (dd, *J* = 1.2, 4.1 Hz, 2H), 2.80 (s, 3H), 2.45 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 135.5, 129.6, 128.4, 127.7, 124.2, 123.8, 123.4, 61.5, 45.3, 39.0, 21.6.
HRMS (ESI) calcd for $C_{14}H_{17}NO_4S_2Na$(M+Na) 350.0497; found 350.0485.

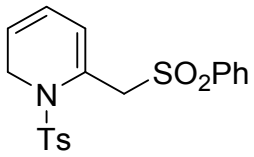


3ba, 1-(Phenylsulfonyl)-6-(phenylsulfonylmethyl)-1,2-dihydropyridine
White solid, 109 mg, 97%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 156-158 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3432, 3065, 2987, 2934, 2883, 2360, 1721, 1637, 1446, 1341, 1306, 1266, 1165, 1148, 719, 580 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.5 Hz, 2H), 7.70-7.64 (m, 3H), 7.60-7.52 (m, 3H), 7.41-7.38 (m, 2H), 6.08 (d, *J* = 5.0 Hz, 1H), 5.48-5.45 (m, 1H), 5.27-5.24 (m, 1H), 4.48 (s, 2H), 3.96-3.95 (m, 2H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 138.5, 133.9, 133.1, 129.0, 128.6 (2), 127.3, 127.0, 125.1, 123.0, 122.5, 61.8, 45.4.
HRMS (ESI) calcd for $C_{18}H_{17}NO_4S_2Na$(M+Na) 398.0497; found 398.0489.

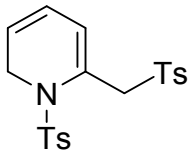


3bb, 1-(Phenylsulfonyl)-6-(tosylmethyl)-1,2-dihydropyridine
White solid, 112 mg, 96%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 182-184 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3065, 3006, 2940, 2882, 2847, 2360, 1597, 1450, 1402, 1339, 1297, 1251, 1159, 1133, 1085, 868, 815, 546 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.55-7.52 (m, 1H), 7.41-7.35 (m, 4H), 6.08 (d, *J* = 5.2 Hz, 1H), 5.48-5.45 (m, 1H), 5.28-5.25 (m, 1H), 4.44 (s, 2H), 3.98 (d, *J* = 2.7 Hz, 2H), 2.47 (s, 3H).

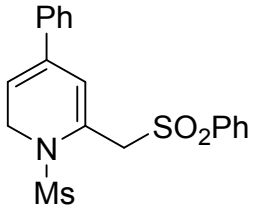
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 138.9, 135.6, 133.1, 129.6, 128.6, 128.5, 127.3, 127.2, 125.0, 122.9, 122.6, 61.9, 45.4, 21.7.
HRMS (ESI) calcd for $C_{19}H_{19}NO_4S_2Na$(M+Na) 412.0653; found 412.0639.



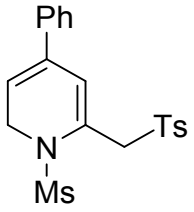
3ca, 6-(Phenylsulfonylmethyl)-1-tosyl-1,2-dihydropyridine
White solid, 114 mg, 98%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 129-131 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3414, 3068, 2969, 2926, 2877, 1723, 1636, 1596, 1446, 1401, 1303, 1161, 1084, 1047, 816, 681, 556 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.69-7.66 (m, 1H), 7.59-7.56 (m, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.08 (d, *J* = 5.3 Hz, 1H), 5.49 (dd, *J* = 5.3, 9.3 Hz, 1H), 5.29-5.25 (m, 1H), 4.47 (s, 2H), 3.94 (d, *J* = 4.0 Hz, 2H), 2.38 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 138.5, 136.0, 133.9, 129.2, 129.0, 128.6, 127.3, 127.1, 125.0, 122.9, 122.6, 61.8, 45.3, 21.5.
HRMS (ESI) calcd for $C_{19}H_{19}NO_4S_2Na$(M+Na) 412.0653; found 412.0643.



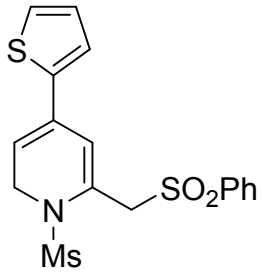
3cb, 1-Tosyl-6-(tosylmethyl)-1,2-dihydropyridine
White solid, 116 mg, 96%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 139-141 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 2985, 2930, 1718, 1597, 1457, 1402, 1341, 1302, 1271, 1159, 1134, 1084, 1049, 814, 759, 684, 513 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.07 (d, *J* = 5.3 Hz, 1H), 5.49 (dd, *J* = 5.3, 9.2 Hz, 1H), 5.30-5.25 (m, 1H), 4.44 (s, 2H), 3.97 (d, *J* = 3.5 Hz, 2H), 2.46 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 144.0, 136.0, 135.5, 130.0, 129.6, 129.2, 128.5, 127.3, 124.9, 122.8, 122.6, 61.8, 45.3, 21.6, 21.5.
HRMS (ESI) calcd for $C_{20}H_{21}NO_4S_2Na$(M+Na) 426.0810; found 426.0792.



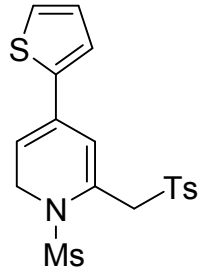
3da, 1-(Methylsulfonyl)-4-phenyl-6-(phenylsulfonylmethyl)-1,2-dihydropyridine
White solid, 109 mg, 93%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 171-173 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3448, 3058, 3021, 2998, 2944, 2921, 2844, 1647, 1446, 1334, 1305, 1152, 1084, 1064, 757, 554 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 1.0, 8.2 Hz, 2H), 7.70-7.67 (m, 1H), 7.60-7.57 (m, 2H), 7.38-7.33 (m, 5H), 6.65 (s, 1H), 5.99 (t, *J* = 4.6 Hz, 1H), 4.47 (s, 2H), 4.14 (d, *J* = 4.6 Hz, 2H), 2.80 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$ + $(CD_3)_2SO$) δ 137.9, 136.0, 135.5, 133.5, 131.0, 128.6, 128.4, 128.3, 127.9, 125.0, 124.8, 117.4, 61.1, 45.5, 38.5.
HRMS (ESI) calcd for $C_{19}H_{20}NO_4S_2$(M+H) 390.0834; found 390.0820.



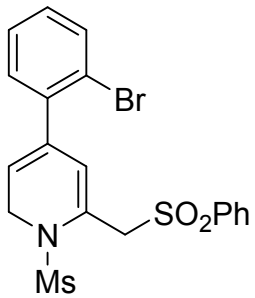
3db, 1-(Methylsulfonyl)-4-phenyl-6-(tosylmethyl)-1,2-dihydropyridine
White solid, 108 mg, 89%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 105-107˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3430, 3022, 2950, 2361, 1647, 1597, 1329, 1326, 1300, 1157, 1133, 1086, 964,758, 513 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.39-7.34 (m, 7H), 6.63 (s, 1H), 5.99 (t, *J* = 4.6 Hz, 1H), 4.44 (s, 2H), 4.16 (d, *J* = 4.6 Hz, 2H), 2.81 (s, 3H), 2.46 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 136.7, 136.3, 135.7, 129.8, 129.1, 128.8, 128.5, 128.4, 125.6, 125.3, 117.8, 61.7, 46.1, 39.1, 21.7.
HRMS (ESI) calcd for $C_{20}H_{22}NO_4S_2$(M+H) 404.0990; found 404.0981.



3ea, 1-(Methylsulfonyl)-6-(phenylsulfonylmethyl)-4-(thiophen-2-yl)-1,2-dihydropyridine
White solid, 92 mg, 78%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 168-170 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3448, 3065, 3018, 3000, 2945, 2919, 2845, 1640, 1445, 1337, 1305, 1151, 1084, 1065, 553 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.70-7.67 (m, 1H), 7.60-7.57 (m, 2H), 7.24 (d, *J* = 4.7 Hz, 1H), 7.08 (d, *J* = 3.2 Hz, 1H), 7.03-7.01 (m, 1H), 6.63 (s, 1H), 5.99 (t, *J* = 4.4 Hz, 1H), 4.47 (s, 2H), 4.08 (d, *J* = 4.4 Hz, 2H), 2.80 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 138.4, 134.0, 130.1, 129.2, 129.1, 128.5, 127.8, 125.2, 124.3, 123.9, 116.0, 61.5, 45.7, 39.1.
HRMS (ESI) calcd for $C_{17}H_{18}NO_4S_3$(M+H) 396.0398; found 396.0385.



3eb, 1-(Methylsulfonyl)-4-(thiophen-2-yl)-6-(tosylmethyl)-1,2-dihydropyridine
White solid, 118 mg, 96%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 160-162 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3448, 2926, 1636, 1595, 1327, 1314, 1151, 1084, 1067, 971, 828, 777, 526 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 5.0 Hz, 1H), 7.08 (d, *J* = 3.2 Hz, 1H), 7.02 (dd, *J* = 3.2, 5.0 Hz, 1H), 6.62 (s, 1H), 5.99 (t, *J* = 4.6 Hz, 1H), 4.44 (s, 2H), 4.10 (d, *J* = 4.6 Hz, 2H), 2.81 (s, 3H), 2.46 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 140.1, 135.5, 130.1, 129.7, 129.3, 128.5, 127.8, 125.2, 124.2, 123.9, 115.9, 61.5, 45.8, 39.1, 21.6.
HRMS calcd for $C_{18}H_{20}NO_4S_3$(M+H) 410.0554; found 410.0536.



3fa, 4-(2-bromophenyl)-1-(methylsulfonyl)-6-(phenylsulfonylmethyl)-1,2-dihydropyridine
White solid, 137 mg, 98%

R_f = 0.5 (30% ethyl acetate in hexanes)

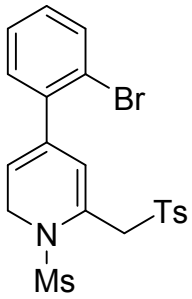
Melting point: 194-196 ˚C (CH_2Cl_2-hexanes)

IR (KBr) ν_{max}: 3448, 3018, 2927, 2361, 1644, 1580, 1467, 1444, 1334, 1317, 1152, 1082, 1049, 972, 669, 548 cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.69-7.66 (m, 1H), 7.60-7.56 (m, 3H), 7.34-7.31 (m, 1H), 7.21-7.18 (m, 2H), 6.40 (s, 1H), 5.82 (t, *J* = 4.3 Hz, 1H), 4.45 (s, 2H), 4.16 (d, *J* = 4.3 Hz, 2H), 2.97 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 138.5, 137.1, 133.9, 133.1, 130.6, 129.8, 129.1, 128.5, 127.8, 126.9 (2), 122.1, 121.7, 61.7, 45.7, 40.2.

HRMS (ESI) calcd for $C_{19}H_{22}BrN_2O_4S_2$(M+NH_4) 485.0204; found 485.0204.



3fb, 4-(2-bromophenyl)-1-(methylsulfonyl)-6-(tosylmethyl)-1,2-dihydropyridine

White solid, 140 mg, 97%

R_f = 0.5 (30% ethyl acetate in hexanes)

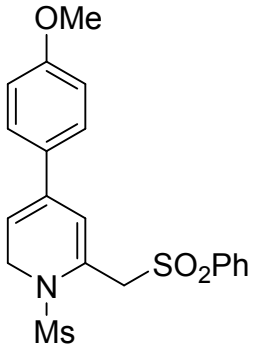
Melting point: 206-208 ˚C (CH_2Cl_2-hexanes)

IR (KBr) ν_{max}: 3448, 2992, 2939, 1594, 1466, 1435, 1403, 1343, 1316, 1177, 1149, 1132, 1085, 1045, 1024, 755, 544 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.59-7.56 (m, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.35-7.31 (m, 1H), 7.22-7.18 (m, 2H), 6.39 (s, 1H), 5.83 (t, *J* = 4.3 Hz, 1H), 4.42 (s, 2H), 4.18 (d, *J* = 4.3 Hz, 2H), 2.98 (s, 3H), 2.46 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 138.8, 137.2, 135.7, 133.1, 130.6, 129.8, 129.7, 128.5, 127.8, 127.0, 126.8, 122.1, 121.7, 61.7, 45.8, 40.2, 21.7.

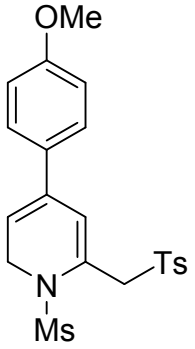
HRMS (ESI) calcd for $C_{20}H_{21}BrNO_4S_2$(M+H) 484.0075; found 484.0077.



3ga, 4-(4-methoxyphenyl)-1-(methylsulfonyl)-6-(phenylsulfonylmethyl)-1,2-dihydropyridine

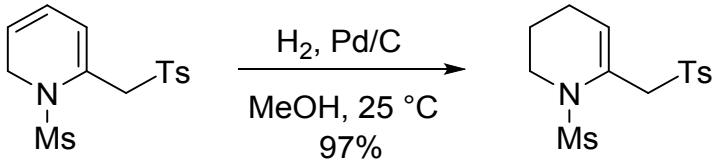
White solid, 123 mg, 98%

R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 137-139 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3438, 3007, 2934, 1606, 1446, 1246, 1182, 1146, 1114, 1083, 1034, 962, 902, 804, 767, 549 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.69-7.66 (m, 1H), 7.60-7.57 (m, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.63 (s, 1H), 5.90 (t, *J* = 4.6 Hz, 1H), 4.47 (s, 2H), 4.10 (d, *J* = 4.6 Hz, 2H), 3.82 (s, 3H), 2.79 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 138.5, 135.6, 134.0, 133.2, 129.1, 128.8, 128.5, 126.7, 125.5, 116.0, 114.2, 61.7, 55.3, 46.1, 39.0.
HRMS (ESI) calcd for $C_{20}H_{22}NO_5S_2$(M+H) 420.0939; found 420.0944.



3gb, 4-(4-methoxyphenyl)-1-(methylsulfonyl)-6-(tosylmethyl)-1,2-dihydropyridine
White solid, 126 mg, 97%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 145-147 ˚C (CH_2Cl_2-hexanes)
IR (KBr) ν_{max}: 3438, 2995, 2940, 1610, 1454, 1247, 1177, 1150, 1086, 1037, 956, 767, 556 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.62 (s, 1H), 5.90 (t, *J* = 3.8 Hz, 1H), 4.43 (s, 2H), 4.12 (d, *J* = 3.8 Hz, 2H), 3.82 (s, 3H), 2.80 (s, 3H), 2.46 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 145.0, 135.7, 129.7, 129.2, 129.0, 128.5, 126.8, 125.4, 116.0, 114.2, 61.7, 55.3, 46.1, 39.0, 21.7.
HRMS (ESI) calcd for $C_{21}H_{24}NO_5S_2$ (M+H) 434.1096; found 434.1097.

9. Catalytic hydrogenation of the dihydropyridine 3ab



3ab **9**

A suspension of the dihydropyridine **3ab** (36 mg, 0.11 mmol) and10 wt. % palladium on carbon (4 mg) in methanol (5 mL) was evacuated and filled with hydrogen from a balloon. The reaction was stirred for 3 h at 25 °C. It was filtered on a pad of celite and the residue obtained was

concentrated and purified by column chromatography on silica gel using using petroleum ether-ethyl acetate as eluent to afford the 1-(methylsulfonyl)-6-(tosylmethyl)-1,2,3,4-tetrahydropyridine **9** as a white solid (35 mg, 97%).

R_f = 0.5 (30% ethyl acetate in hexanes)

Melting point: 118-120 ˚C (CH_2Cl_2-hexanes)

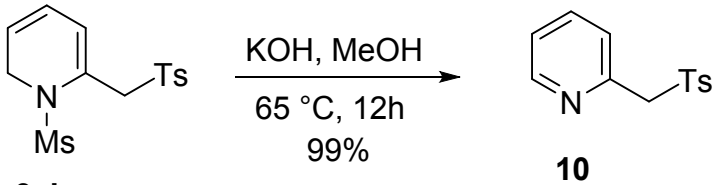
IR (KBr) ν_{max}: 3439, 3020, 2926, 2828, 2360, 1645, 1595, 1458, 1312, 1237, 1149, 1130, 1085, 1072, 970, 778, 522 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.36 (d, J = 8.3 Hz, 2H), 5.37 (t, *J* = 3.8 Hz, 1H), 4.27 (s, 2H), 3.42-3.39 (m, 2H), 3.02 (s, 3H), 2.46 (s, 3H), 2.16-2.12 (m, 2H), 1.89-1.83 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 136.0, 129.7, 128.3, 126.7, 124.5, 61.4, 46.5, 41.0, 22.8, 21.6, 21.5.

HRMS (ESI) calcd for $C_{14}H_{23}N_2O_4S_2$ ($M+NH_4$) 347.1099; found 347.1096.

10. Conversion of the dihydropyridine 3ab into 2-tosylmethylpyridine 10



3ab **10**

To a solution of the dihydropyridine **3ab** (49 mg, 0.15 mmol) in methanol (10 mL), powdered KOH (42 mg, 0.75 mmol) was added and the reaction mixture was refluxed overnight. After evaporation of the solvent on a rotavapor, water (10 mL) was added and the solution was extracted with ethyl acetate (3X10 mL). The combined organic extracts were washed with brine, dried over anhydrous sodium sulfate and concentrated on a rotavapor. The residue on column chromatography on silica gel using petroleum ether-ethyl acetate as eluent afforded 2-(tosylmethyl)pyridine **10** as a white solid (37 mg, 99%).

R_f = 0.7 (40% ethyl acetate in hexane)

Melting point: 153-155 ˚C (CH_2Cl_2-hexane) (lit. mp 154-156 ˚C)

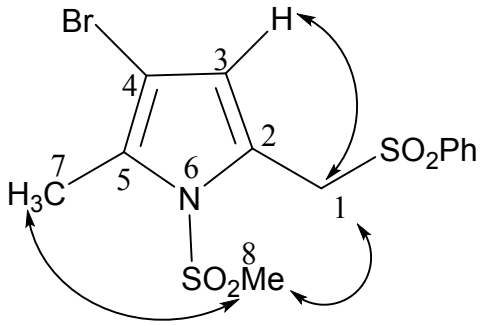
IR (KBr) ν_{max}: 3448, 3055, 2853, 2361, 1595, 1493, 1476, 1435, 1396, 1300, 1286, 1019, 993, 757, 555 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.8 Hz, 1H), 7.70 (dt, *J* = 1.7, 7.7 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.28-7.23 (m, 3H), 4.54 (s, 2H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 149.6, 149.0, 144.7, 136.7, 135.3, 129.6, 128.4, 125.7, 123.3, 64.6, 21.6.

HRMS (ESI) calcd for $C_{13}H_{14}NO_2S$ (M+H) 248.0745; found 248.0744.

11. 1D and 2D NMR experiments on 8



8

The regiochemical outcome of bromination of **3aa** to afford **8** was confirmed by means of 1D and 2D NMR experiments. The presence of strong nOe correlations of H1/H3, H7/H8 and H8/H1 confirm that the bromo substituent is on C4 as drawn above.

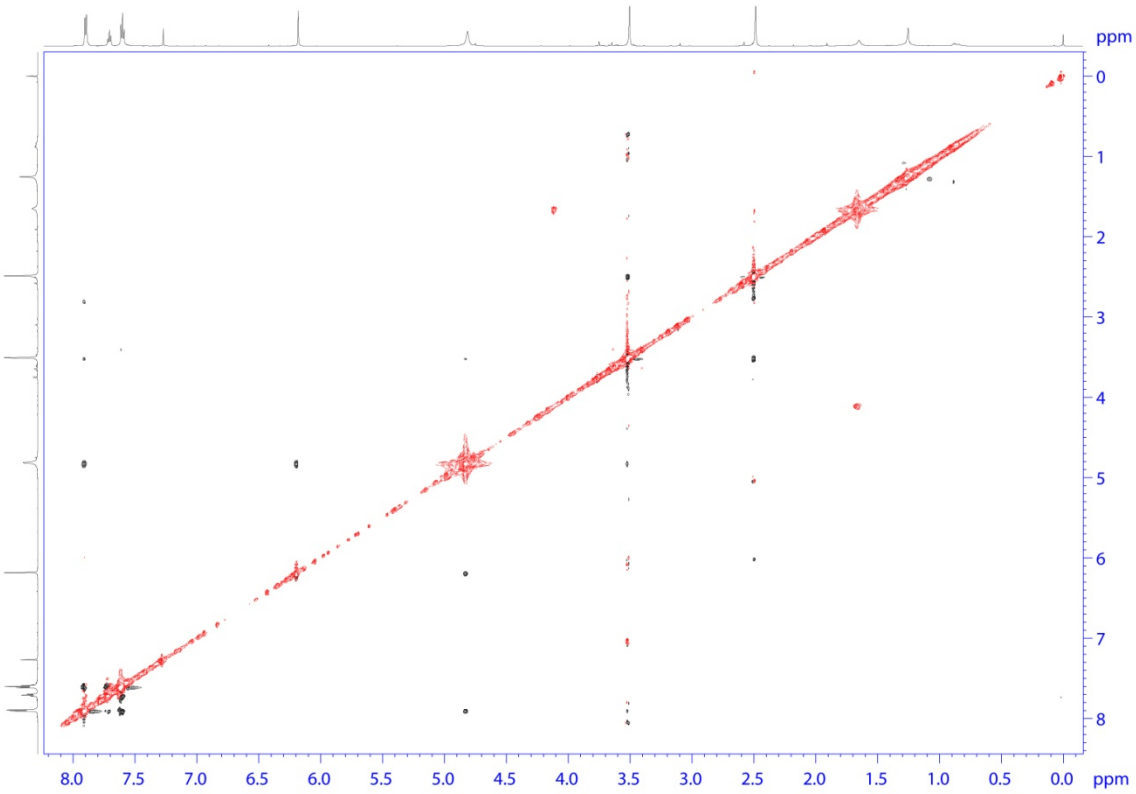


Fig. S1: 2D Nuclear Overhauser effect spectroscopy (NOESY) spectrum of compound **8** recorded at 25 °C (600 MHz)

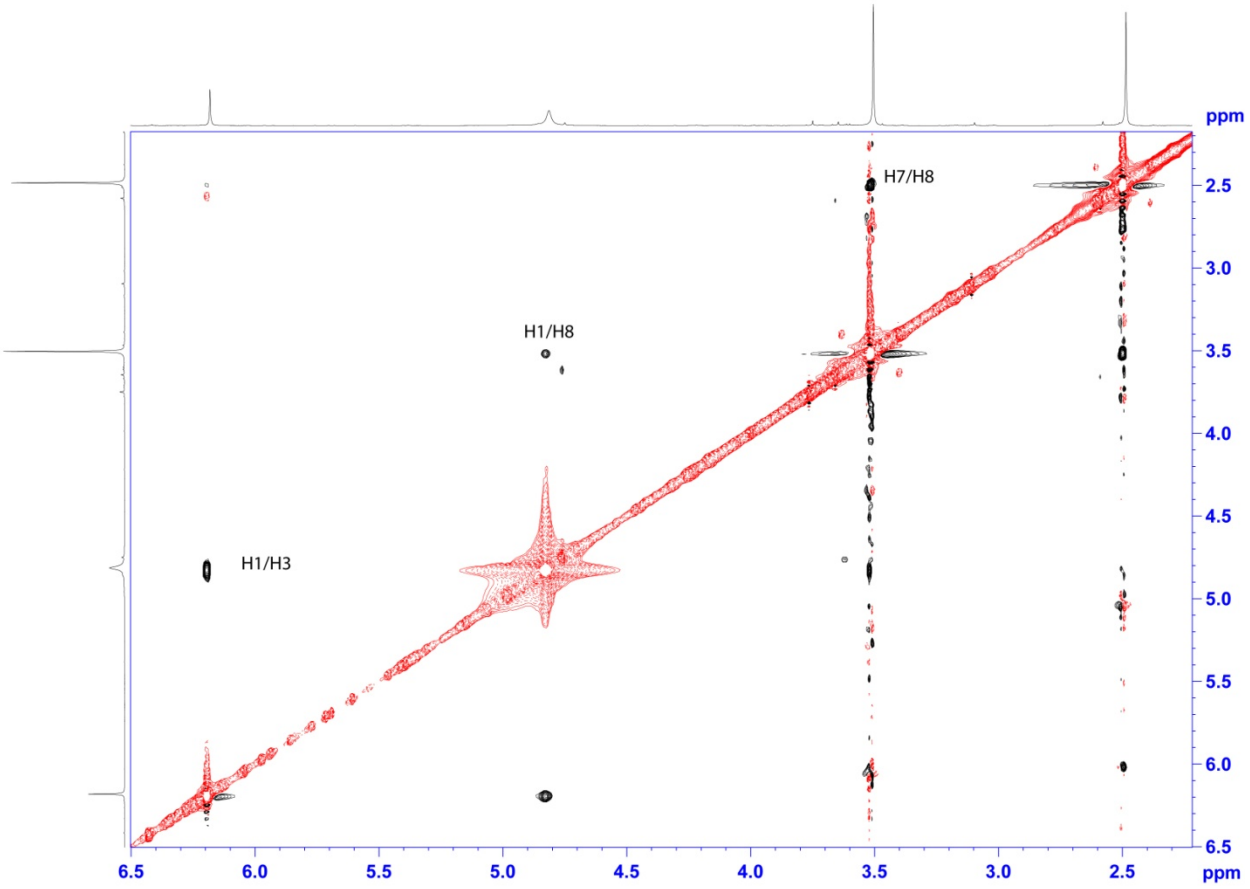


Fig. S2: Expansion of 2D Nuclear Overhauser effect spectroscopy (NOESY) spectrum of compound **8** recorded at 25 °C (600 MHz)

12. Crystallographic data for 2da

Crystallographic data for 2da: $C_{19}H_{19}NO_4S_2$, M = 389.47, colourless block, 0.49 x 0.42 x 0.33 mm^3, triclinic, space group *P***Error!**(No. 2), a = 8.0274(5), b = 8.1297(5), c = 14.6961(8) Å, α = 76.4330(10), β = 74.7090(10), γ = 85.5280(10)°, V = 899.17(9) Å^3, Z = 2, D_c = 1.439 g/cm^3, F_{000} = 408, CCD area detector, MoKα radiation, λ = 0.71073 Å, T = 293(2)K, $2\theta_{max}$ = 50.0º, 8766 reflections collected, 3160 unique (R_{int} = 0.0188), Final *GooF* = 1.049, *R1* = 0.0354, *wR2* = 0.0935, R indices based on 2916 reflections with I >2σ(I) (refinement on F^2), 237 parameters, μ = 0.321 mm^{-1}. CCDC 1063242 contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://summary.ccdc.cam.ac.uk/structure-summary-form or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk.

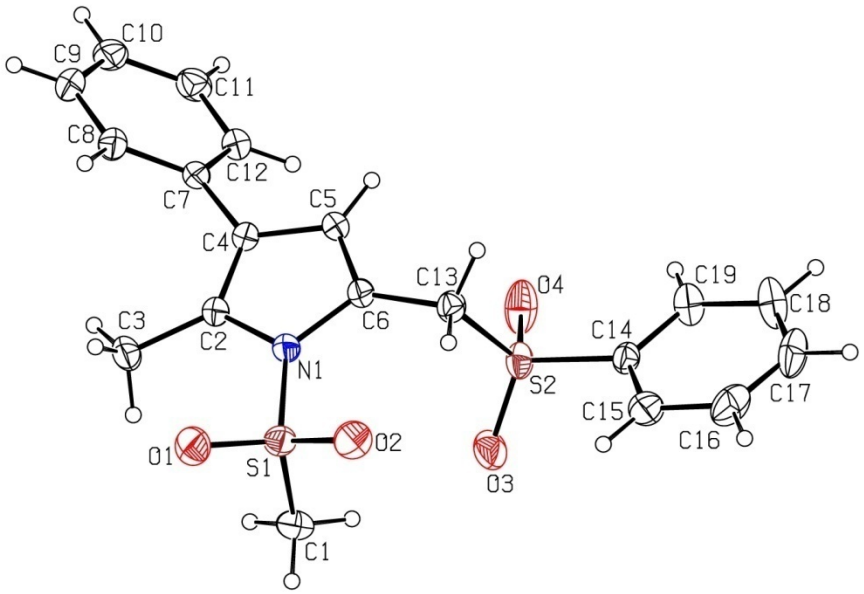
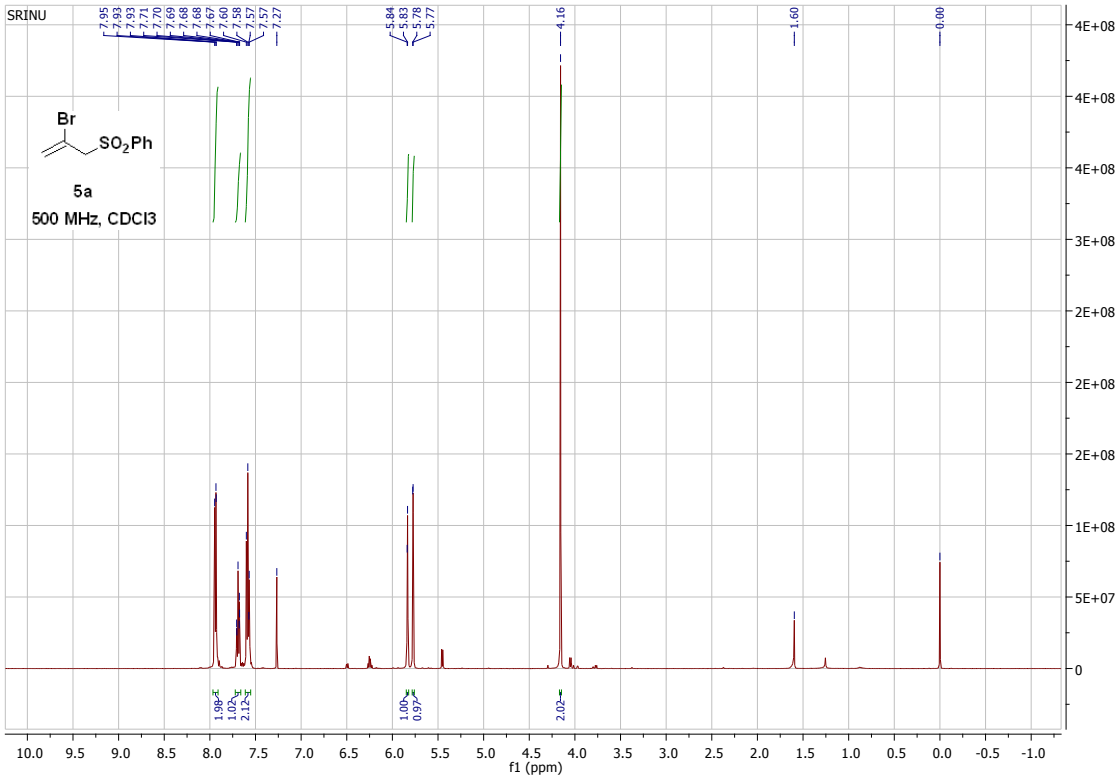


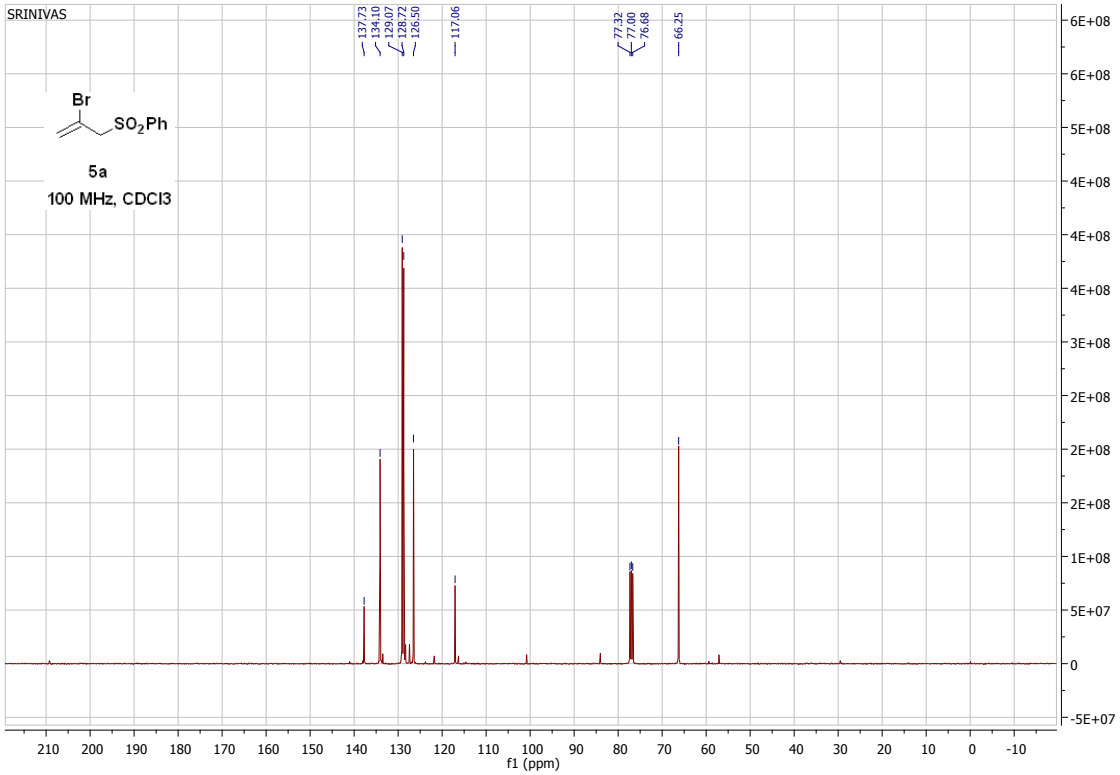
Fig. S3: The ORTEP diagram of **2da** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

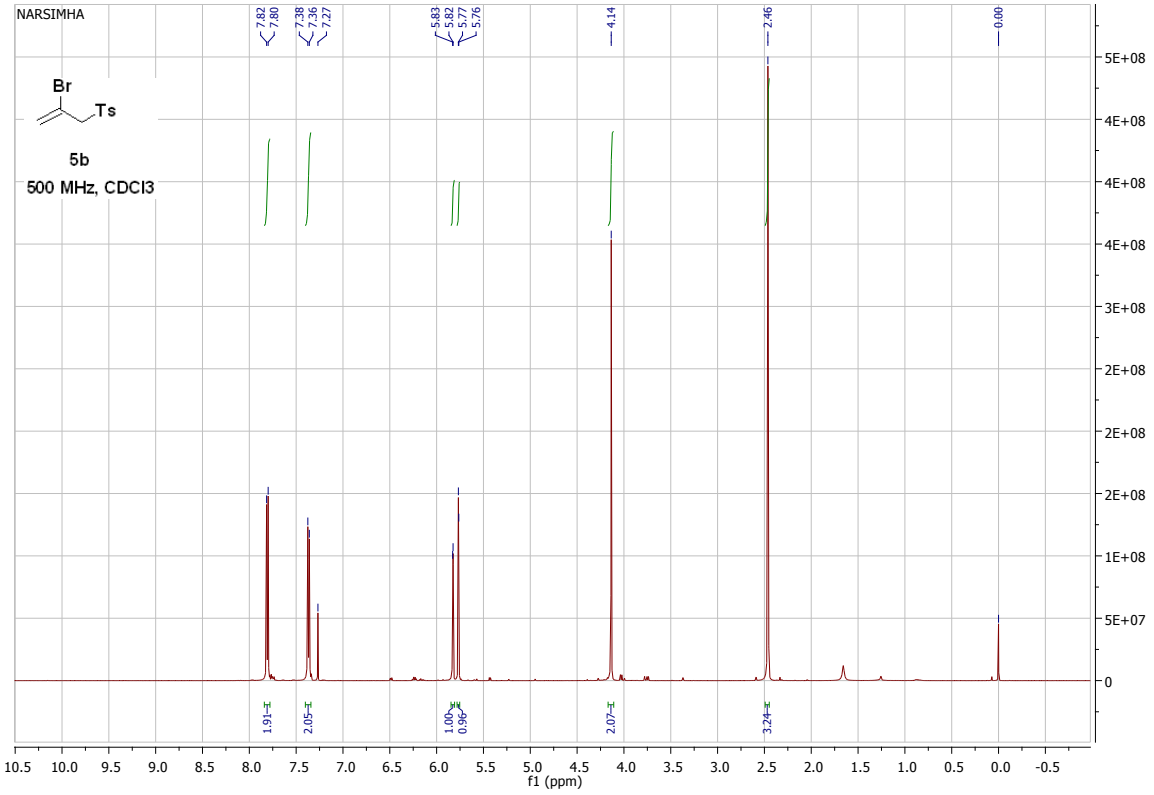
Data collection: X-ray data for the compound were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[6] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 5512 reflections for AY92 data. Integration and scaling of intensity data were accomplished using SAINT program.[6] The structure was solved by Direct Methods using SHELXS97[7] and refinement was carried out by full-matrix least-squares technique using SHELXL97.[7] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent C atoms with C-H distances of 0.93--0.97 Å, and with $U_{iso}(H) = 1.2U_{eq}$ (C) or $1.5U_{eq}$ for methyl atoms.

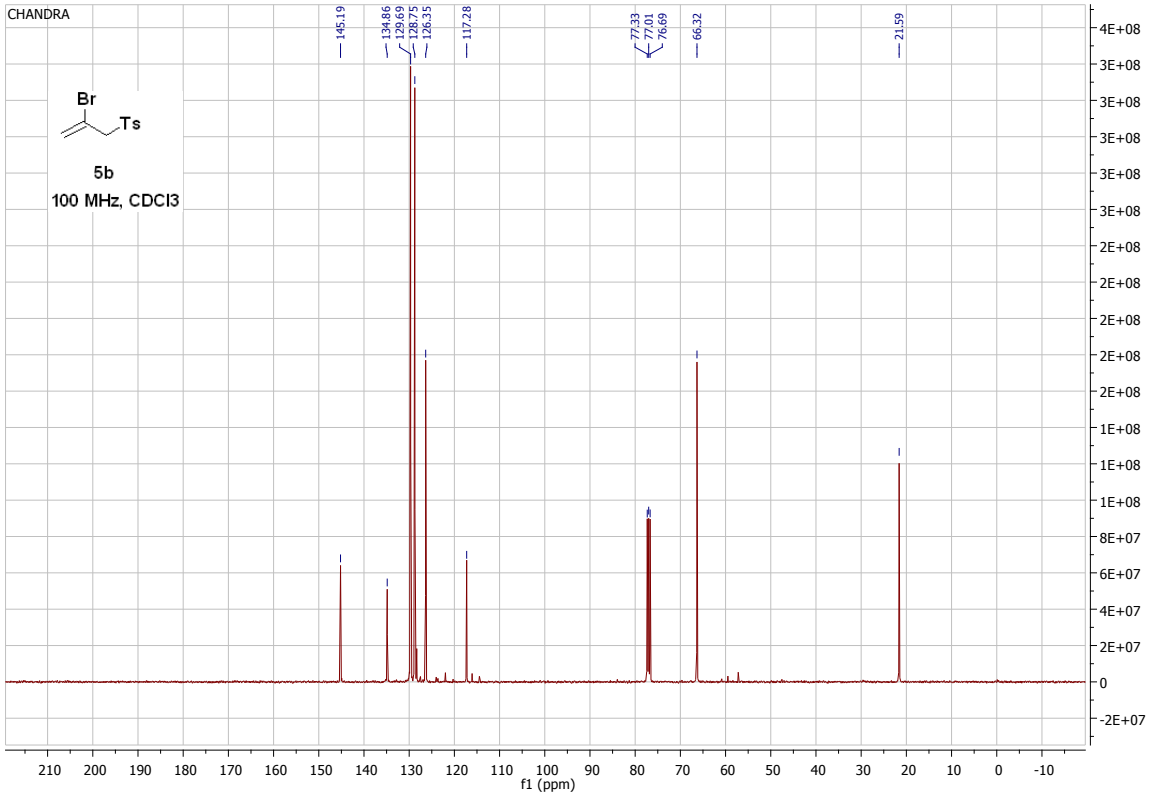
6. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
7 Sheldrick, G. M. SHELXS97 and SHELXL97, Programs for crystal structure solution and refinement; University of Gottingen: Germany, 1997.

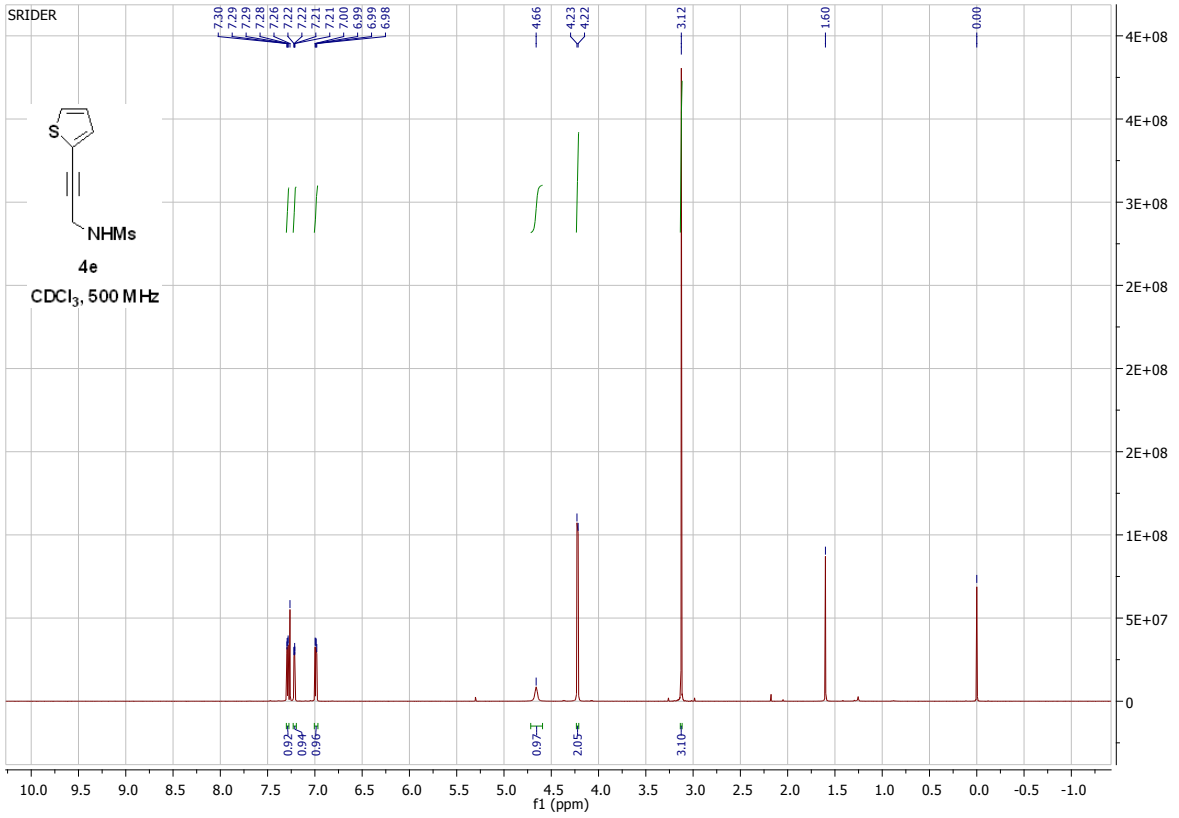
Copies of NMR spectra of new compounds

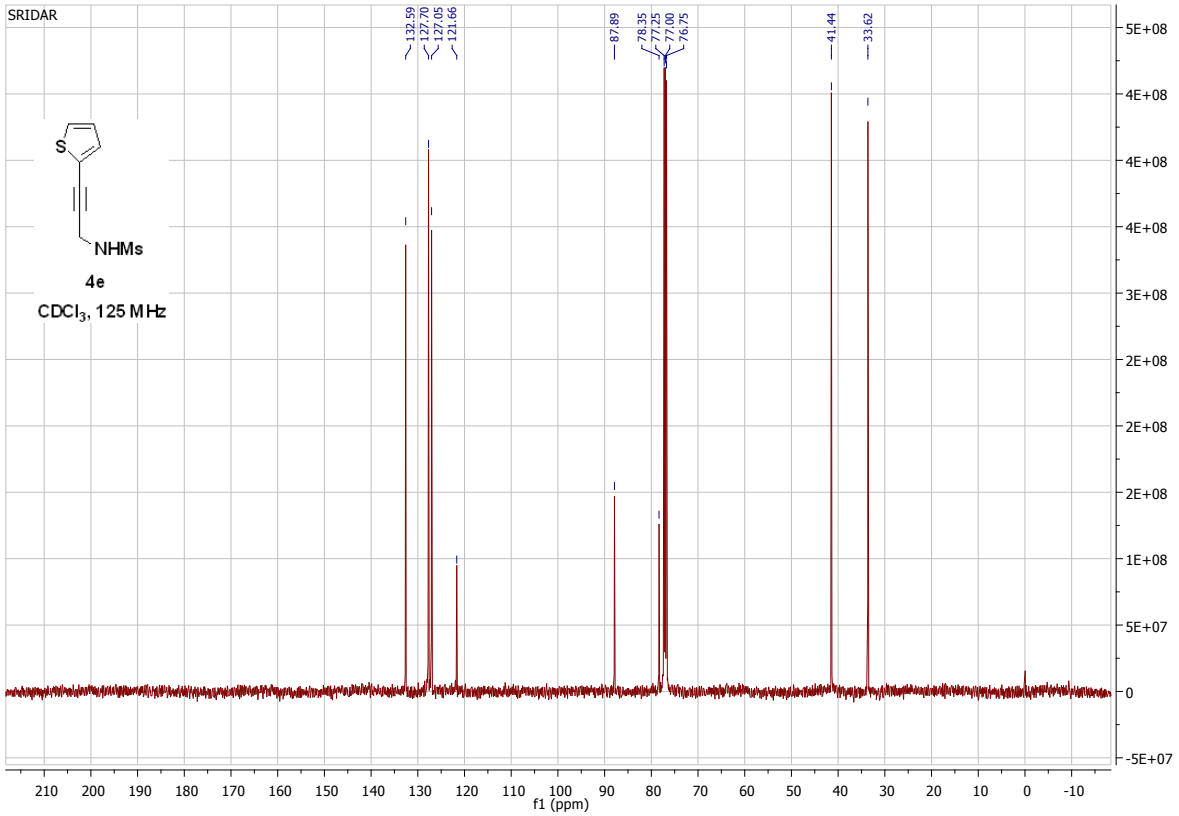


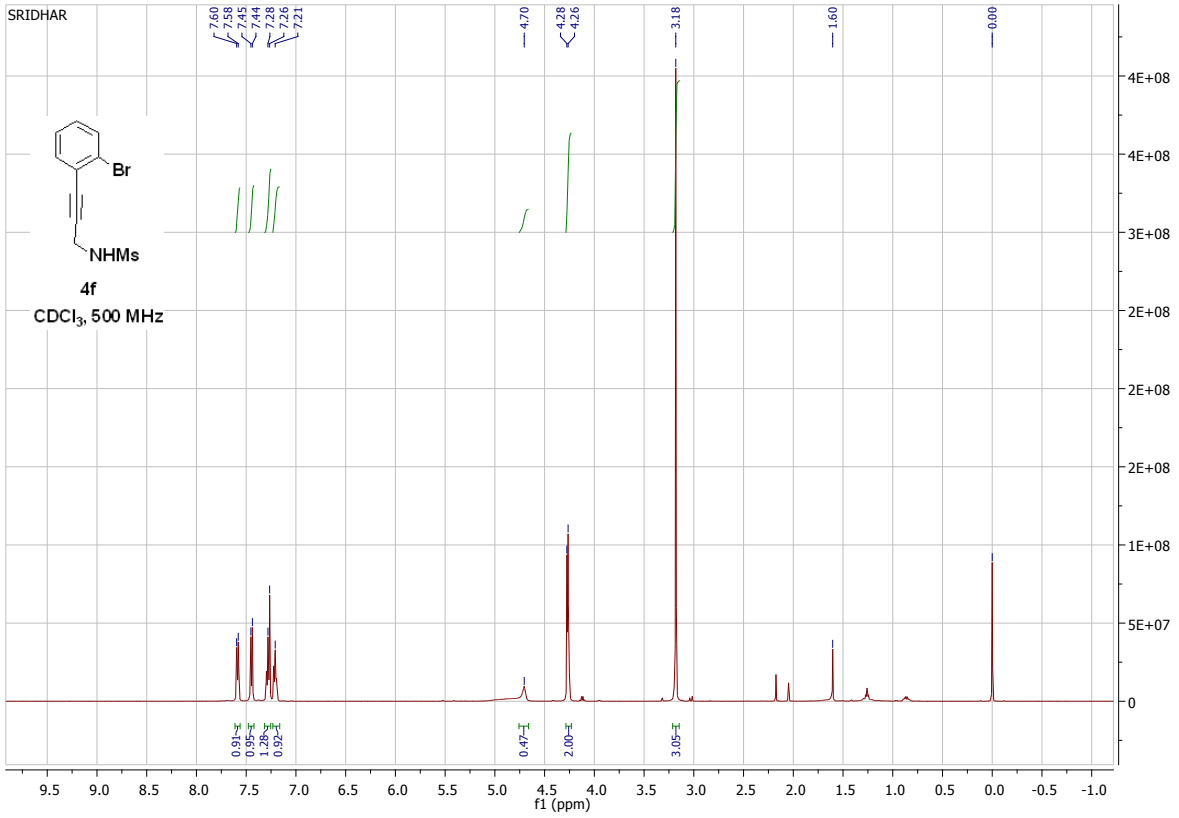


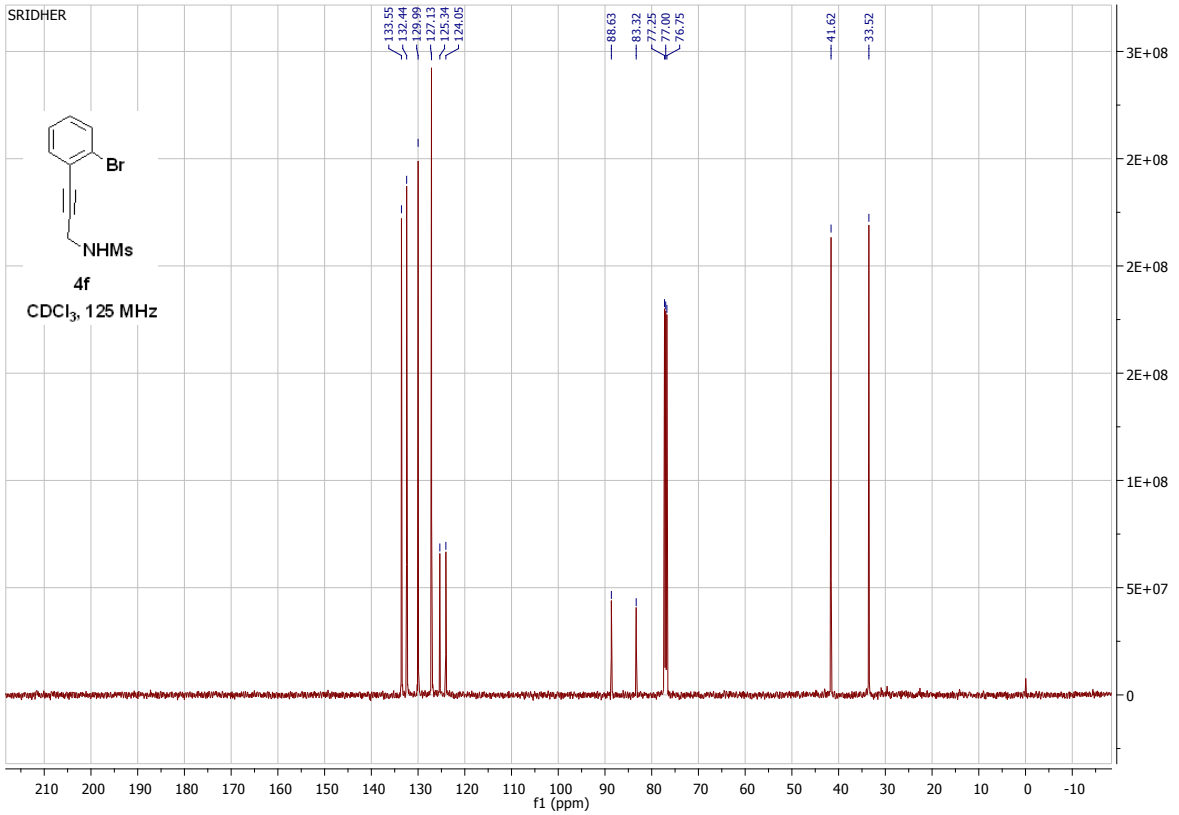

NARSIMHA
7.82
7.80
7.38
7.36
7.27
5.83
5.82
5.77
5.76
4.14
2.46
0.00
Br
Ts
5b
500 MHz, CDCl3
1.91
2.05
1.00
0.96
2.07
3.24
f1 (ppm)

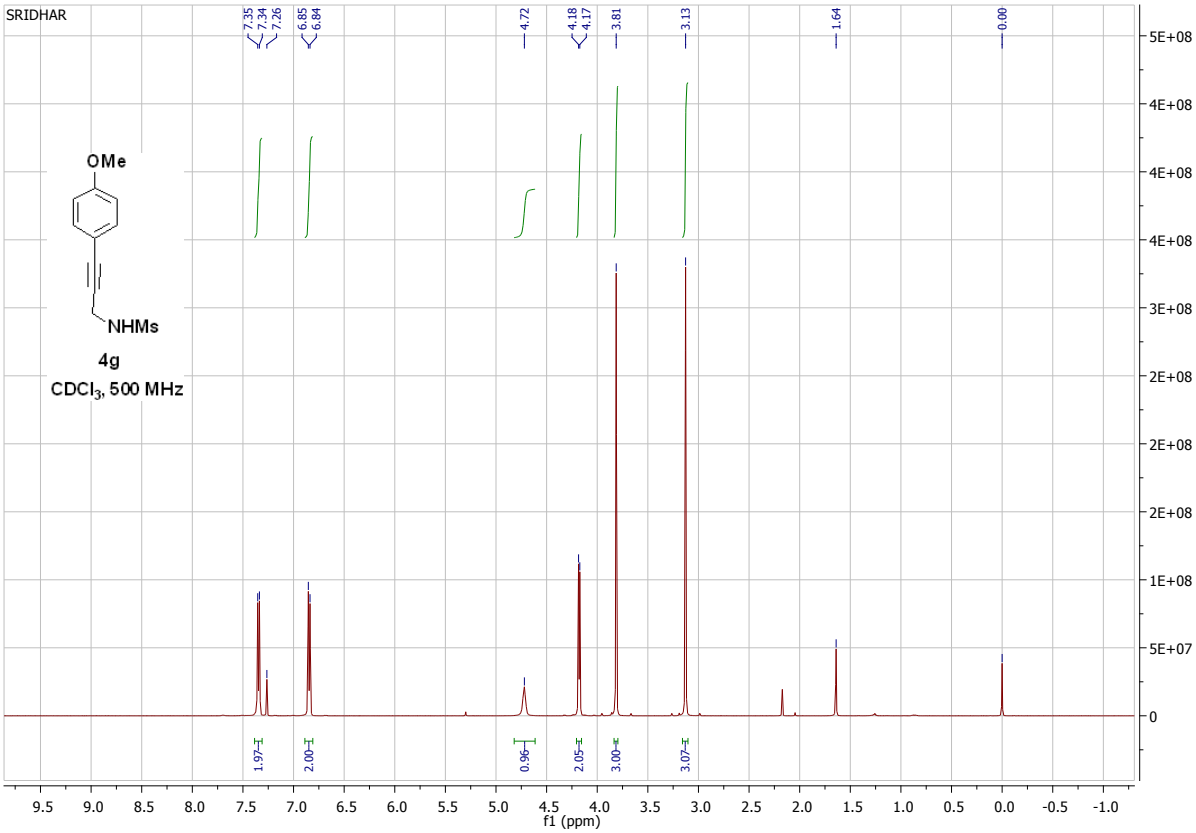

CHANDRA
145.19
134.86
129.69
128.75
126.35
117.28
77.33
77.01
76.69
66.32
21.59
Br
Ts
5b
100 MHz, CDCl3
f1 (ppm)

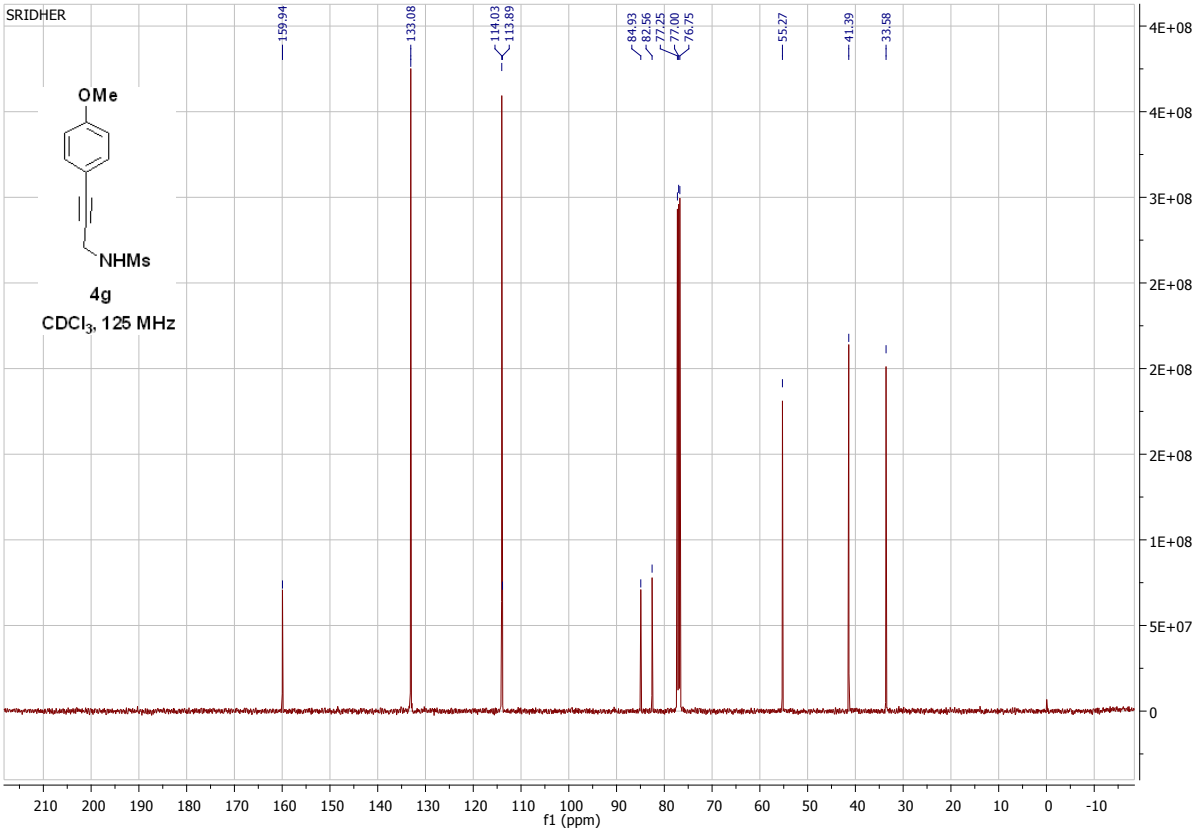

SRIDER
7.30
7.29
7.29
7.28
7.26
7.22
7.22
7.21
7.21
7.00
6.99
6.99
6.98
4.66
4.23
4.22
3.12
1.60
0.00
S
NHMs
4e
CDCl3, 500 MHz
0.92
0.94
0.96
0.97
2.05
3.10
f1 (ppm)

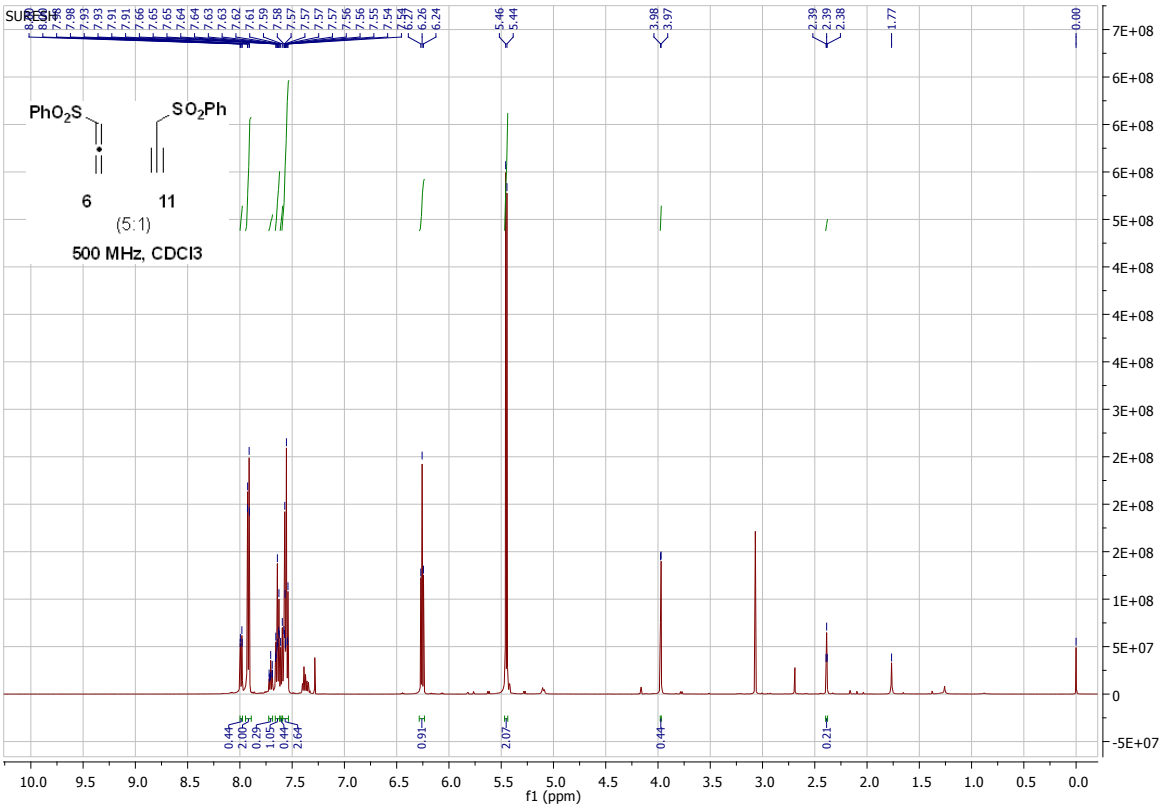

SRIDAR
132.59
127.70
127.05
121.66
87.89
78.35
77.25
77.00
76.75
41.44
33.62
S
NHMs
4e
CDCl3, 125 MHz
f1 (ppm)

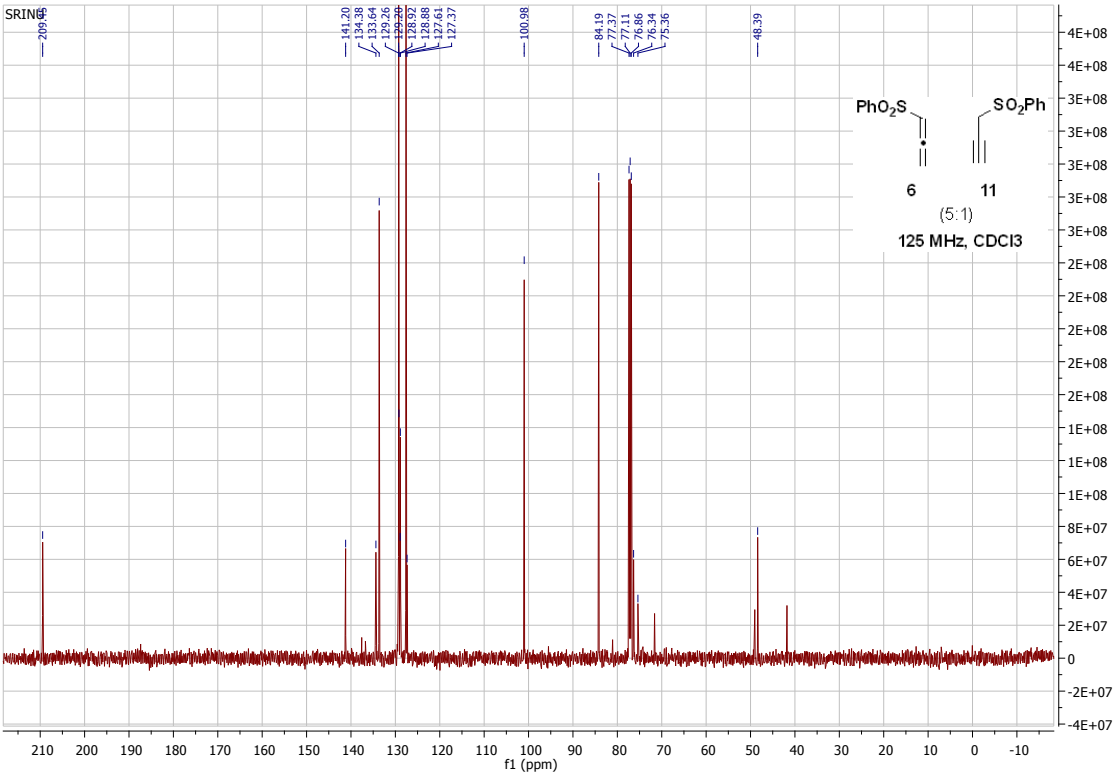

SRIDHAR
7.60
7.58
7.45
7.44
7.28
7.26
7.21
4.70
4.28
4.26
3.18
1.60
0.00
Br
NHMs
4f
CDCl3, 500 MHz
0.91
0.95
1.28
0.92
0.47
2.00
3.05
4E+08
3E+08
2E+08
1E+08
5E+07
0
f1 (ppm)

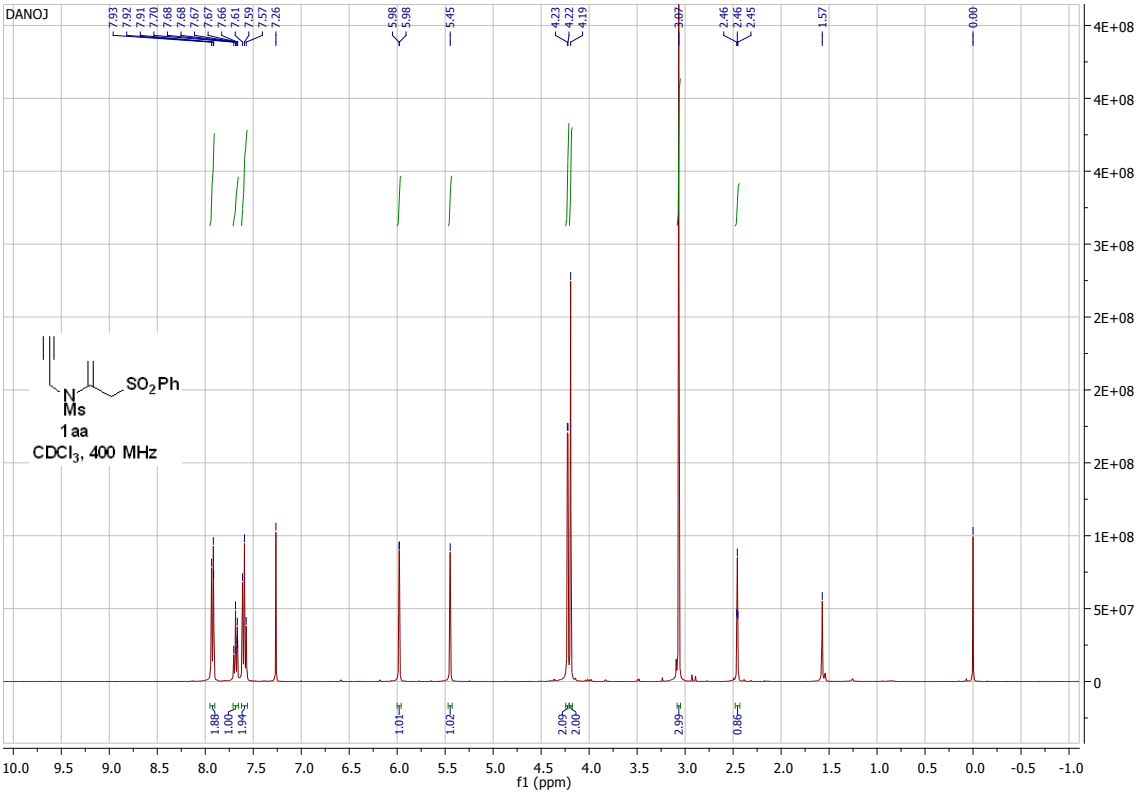

SRIDHER
133.55
132.44
129.99
127.13
125.34
124.05
88.63
83.32
77.25
77.00
76.75
41.62
33.52
Br
NHMs
4f
CDCl3, 125 MHz
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
f1 (ppm)

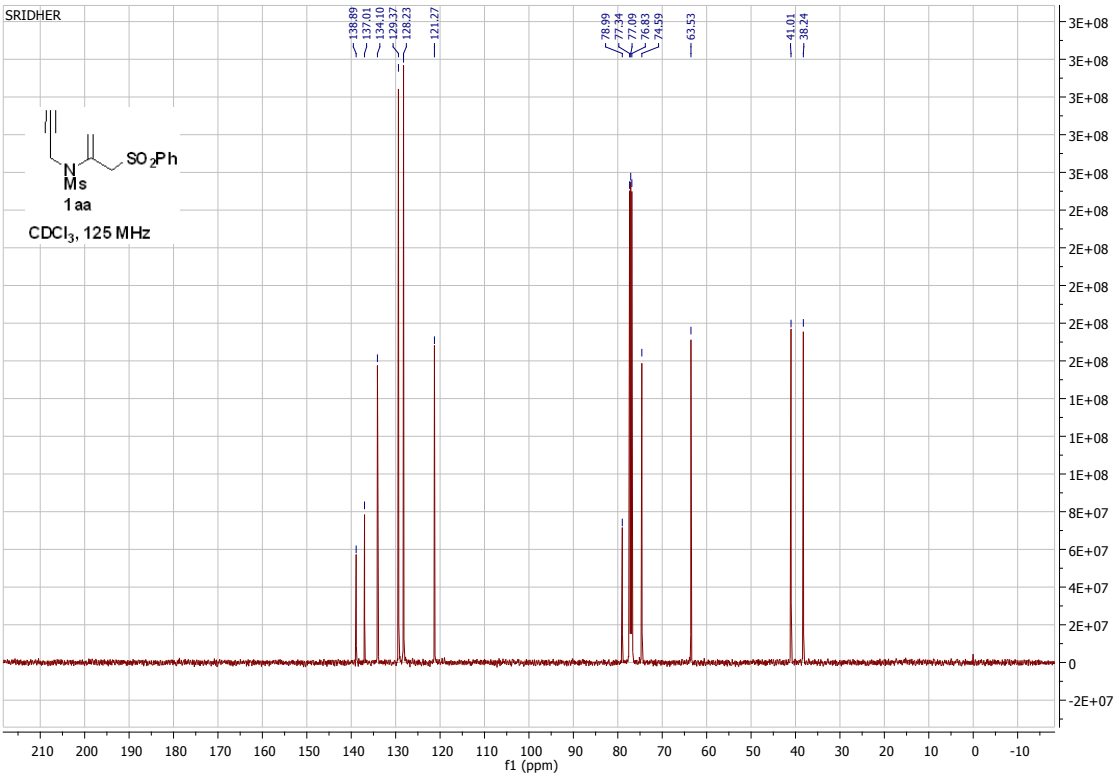

SRIDHAR
7.35
7.34
7.26
6.85
6.84
4.72
4.18
4.17
3.81
3.13
1.64
0.00
OMe
NHMs
4g
CDCl3, 500 MHz
1.97
2.00
0.96
2.05
3.00
3.07
f1 (ppm)

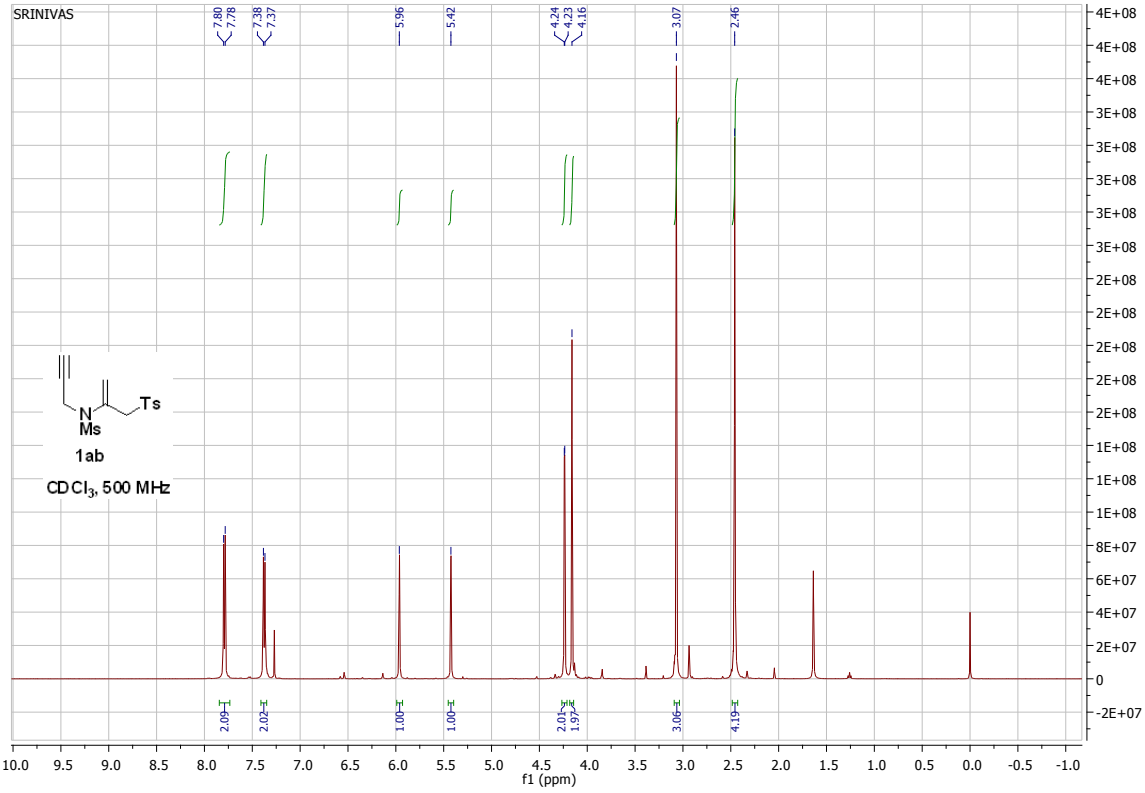

SRIDHER
159.94
133.08
114.03
113.89
84.93
82.56
77.25
77.00
76.75
55.27
41.39
33.58
OMe
NHMs
4g
CDCl3, 125 MHz
f1 (ppm)

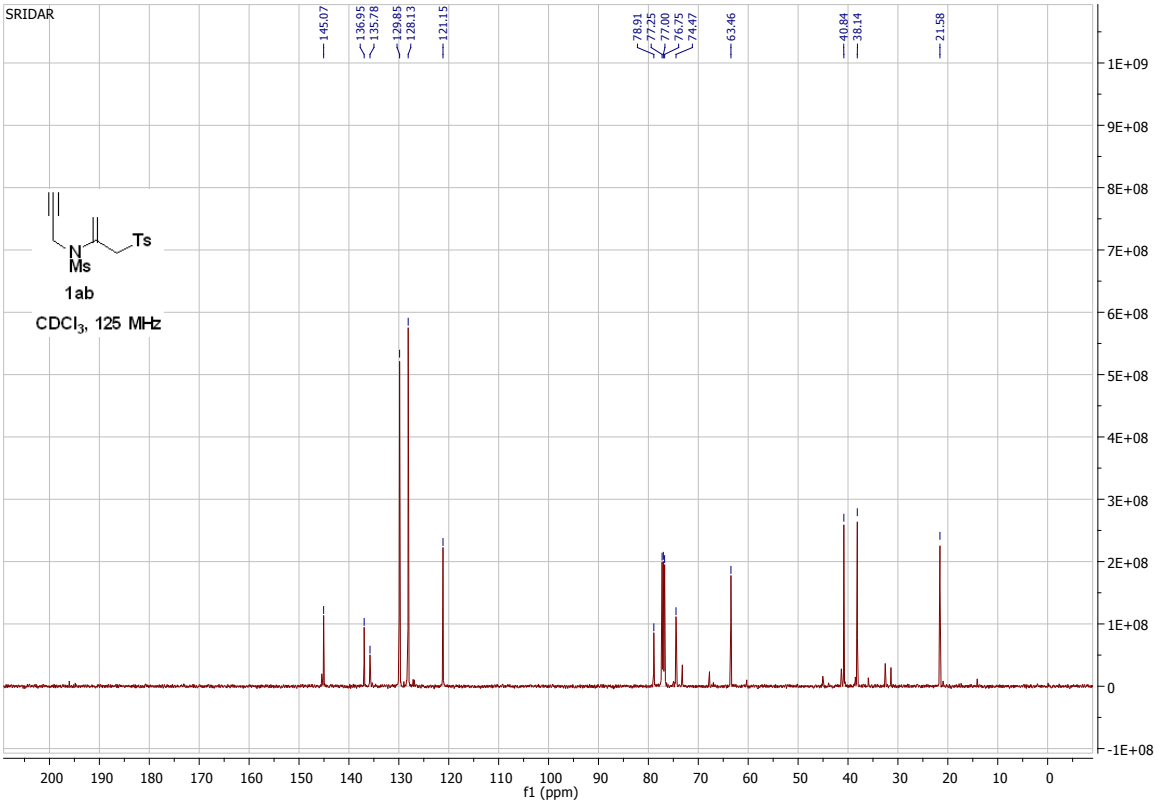

SURESH
PhO2S
SO2Ph
6
11
(5:1)
500 MHz, CDCl3
f1 (ppm)

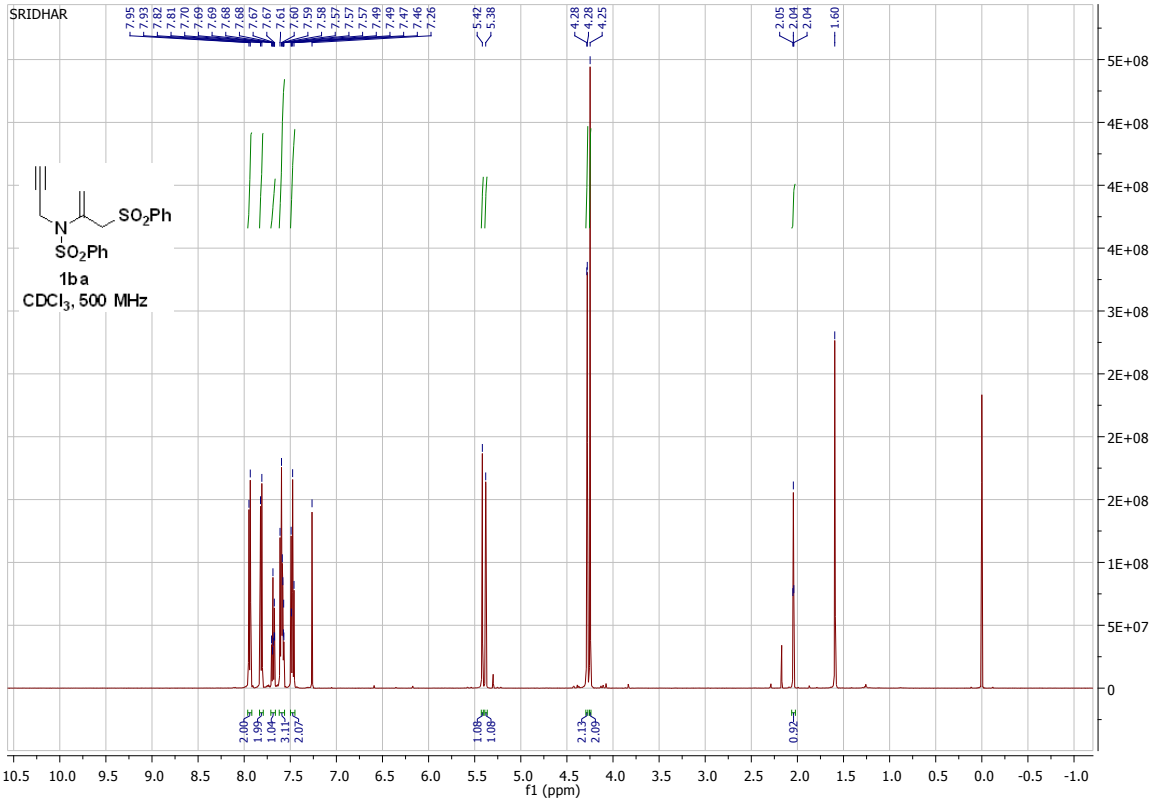

SRINU
PhO2S
SO2Ph
6
11
(5:1)
125 MHz, CDCl3
f1 (ppm)

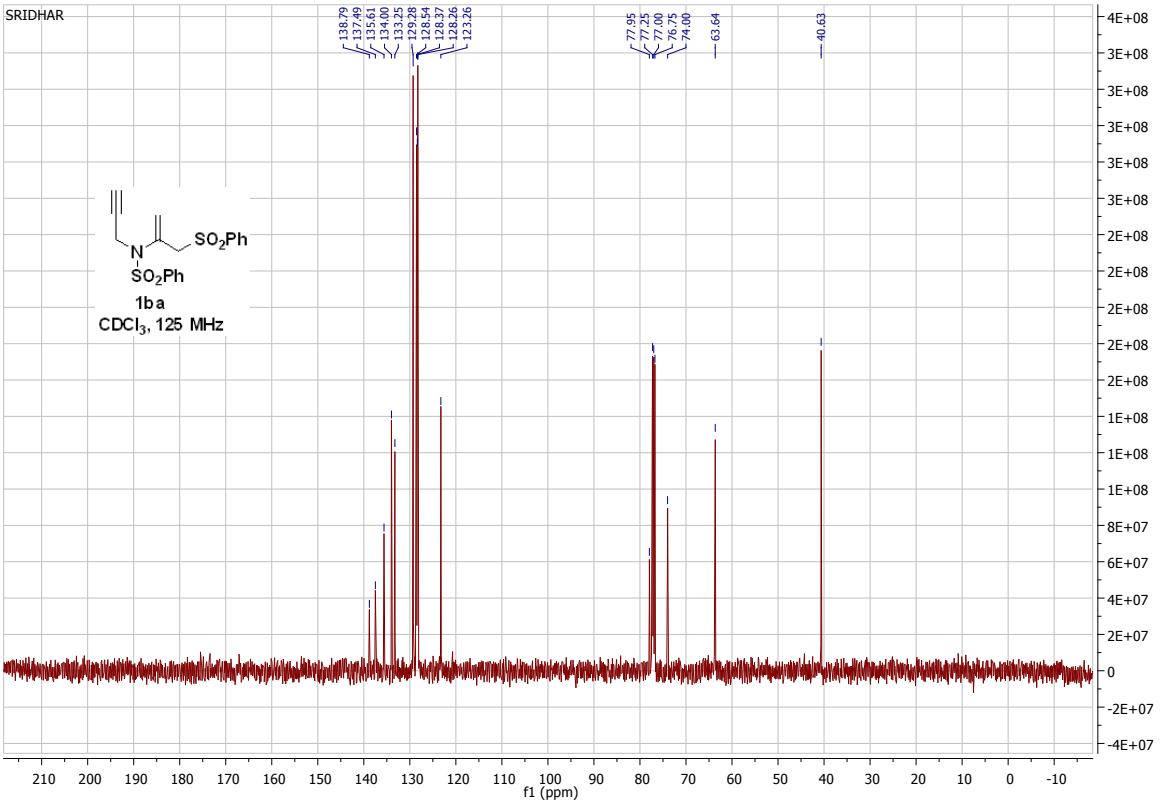

DANOJ
SO2Ph
N
Ms
1aa
CDCl3, 400 MHz
f1 (ppm)

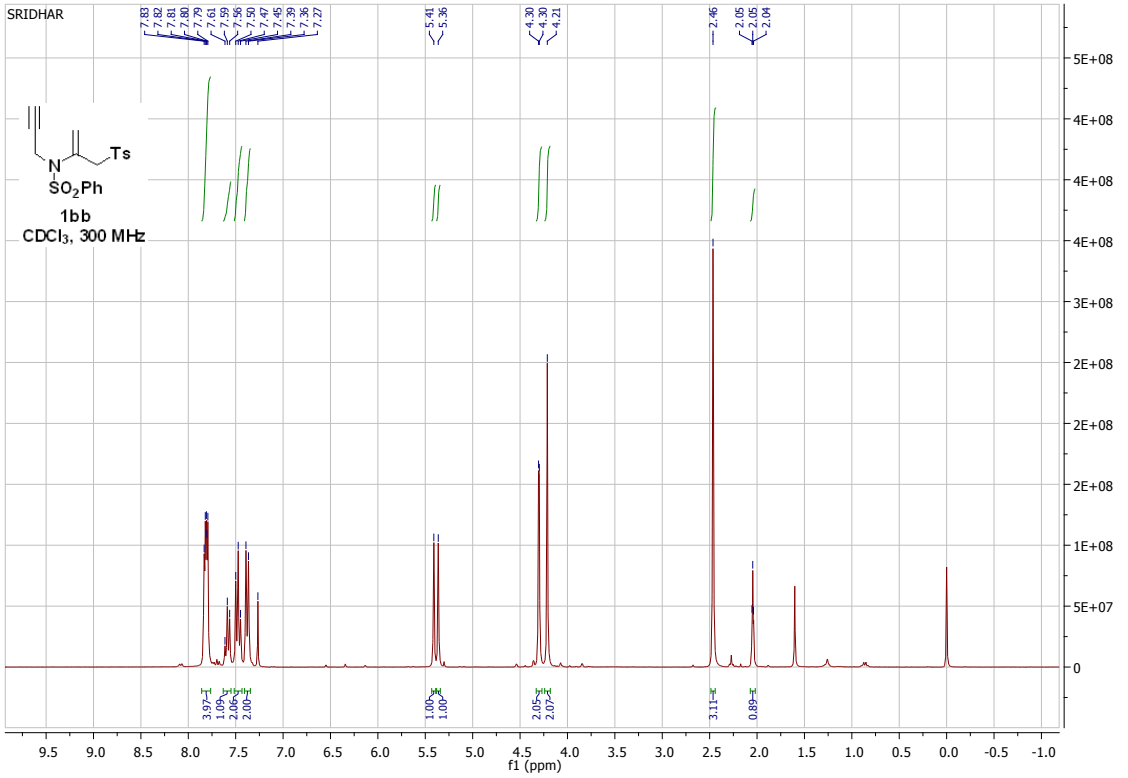

SRIDHER
SO2Ph
N
Ms
1aa
CDCl3, 125 MHz
f1 (ppm)

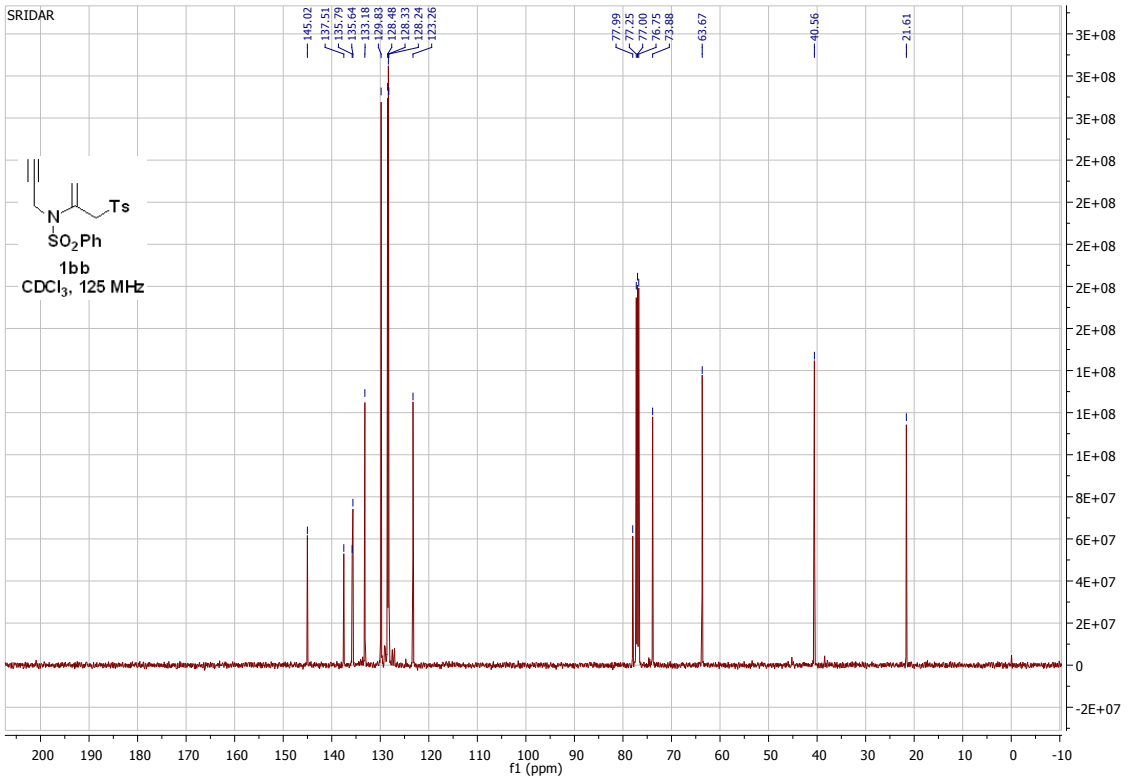

SRINIVAS
7.80
7.78
7.38
7.37
5.96
5.42
4.24
4.23
4.16
3.07
2.46
Ts
N
Ms
1ab
CDCl3, 500 MHz
2.09
2.02
1.00
1.00
2.01
1.97
3.06
4.19
f1 (ppm)

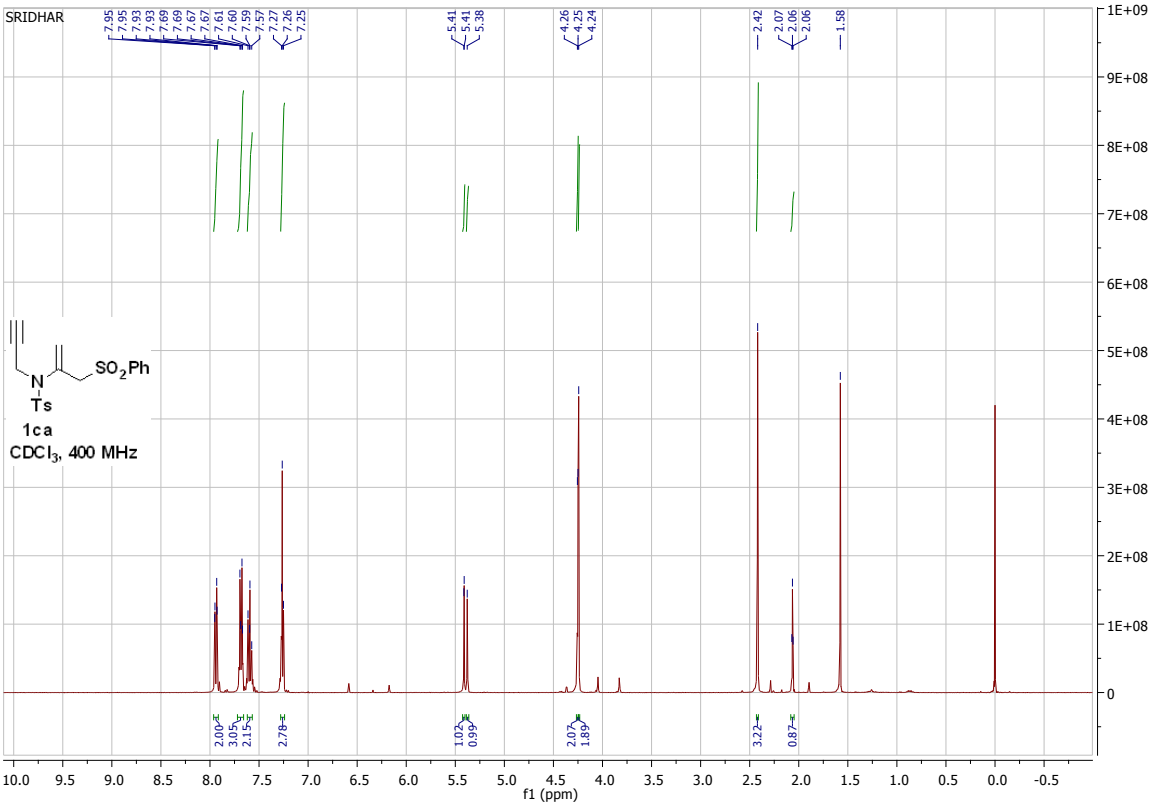

SRIDAR
145.07
136.95
135.78
129.85
128.13
121.15
78.91
77.25
77.00
76.75
74.47
63.46
40.84
38.14
21.58
Ts
N
Ms
1ab
CDCl3, 125 MHz
f1 (ppm)

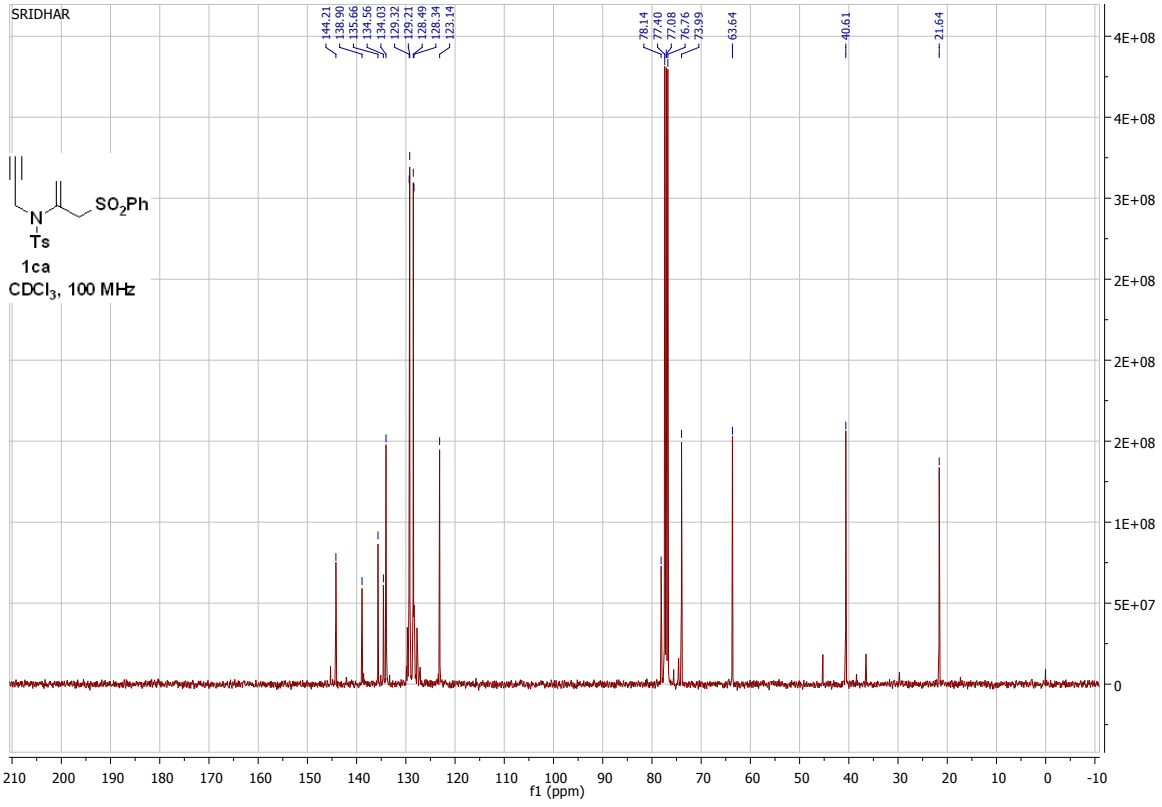

SRIDHAR
7.95 7.93 7.82 7.81 7.70 7.69 7.69 7.68 7.68 7.67 7.67 7.61 7.60 7.59 7.58 7.57 7.57 7.57 7.49 7.49 7.47 7.46 7.26
5.42 5.38
4.28 4.28 4.25
2.05 2.04 2.04
1.60
SO2Ph
N
SO2Ph
1ba
CDCl3, 500 MHz
2.00 1.99 1.04 3.11 2.07
1.05 1.08
2.13 2.09
0.92
f1 (ppm)

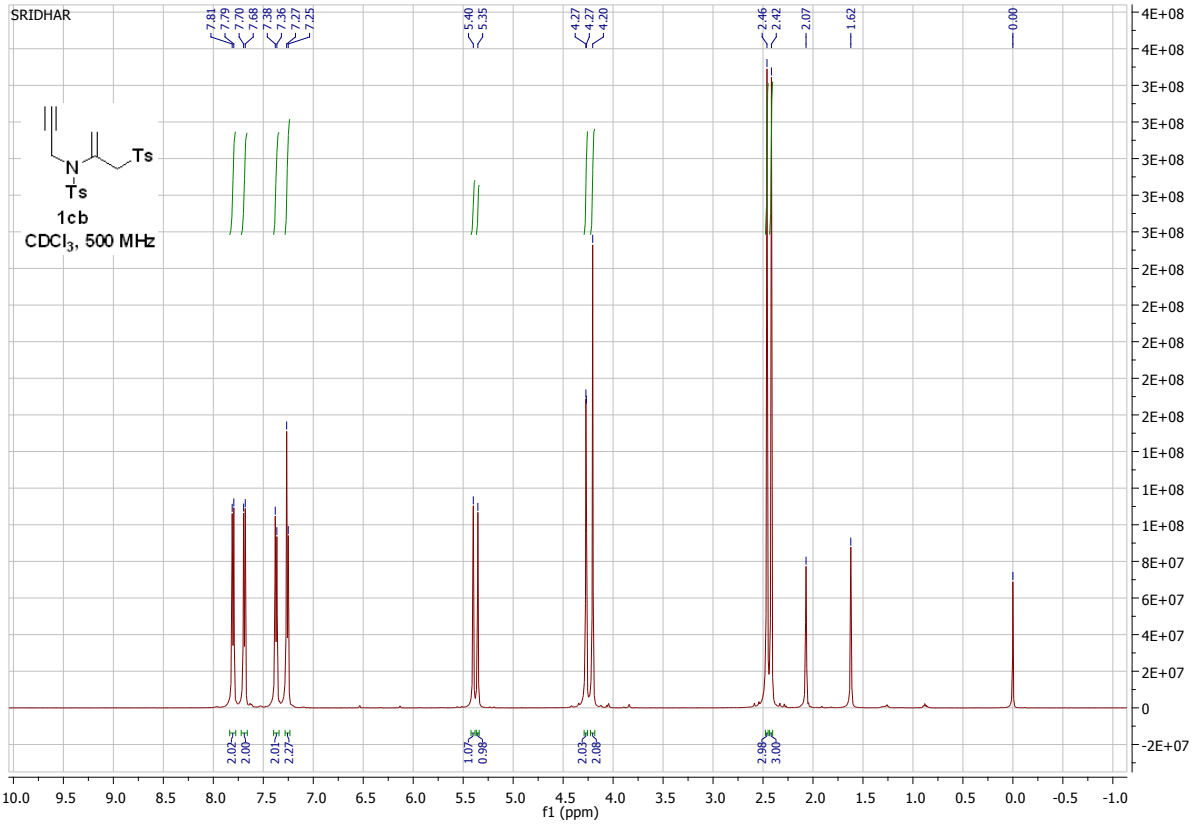

SRIDHAR
138.79 137.49 135.61 134.00 133.25 129.28 128.54 128.37 128.26 123.26
77.95 77.25 77.00 76.75 74.00
63.64
40.63
SO2Ph
N
SO2Ph
1ba
CDCl3, 125 MHz
f1 (ppm)

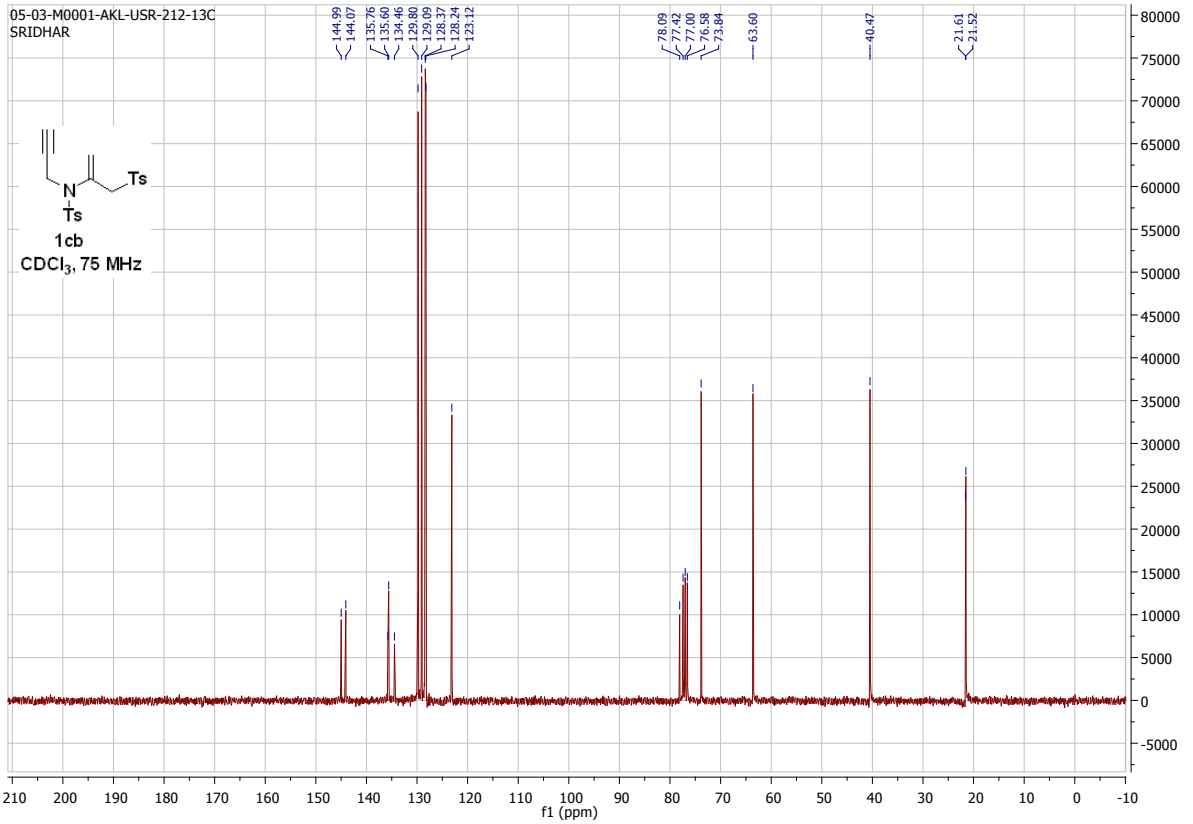

SRIDHAR
Ts
N
SO2Ph
1bb
CDCl3, 300 MHz
f1 (ppm)

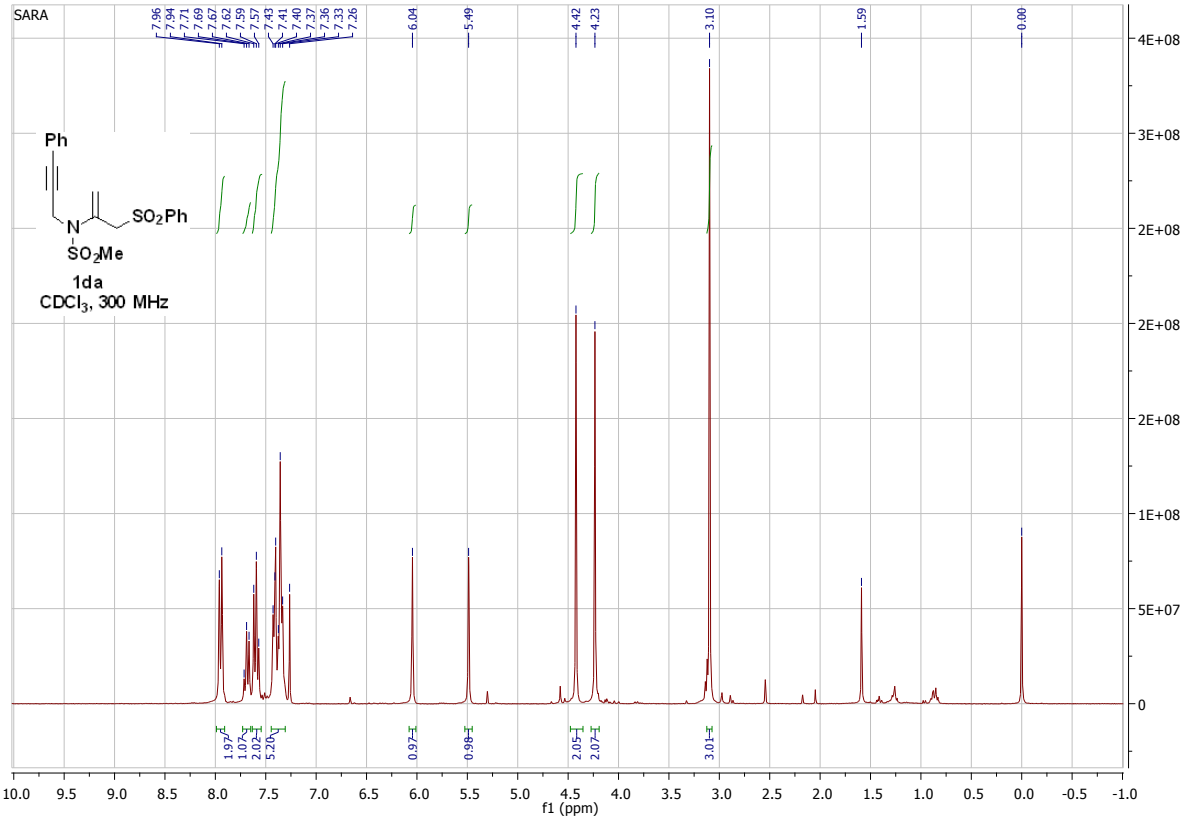

SRIDAR
Ts
N
SO2Ph
1bb
CDCl3, 125 MHz
f1 (ppm)

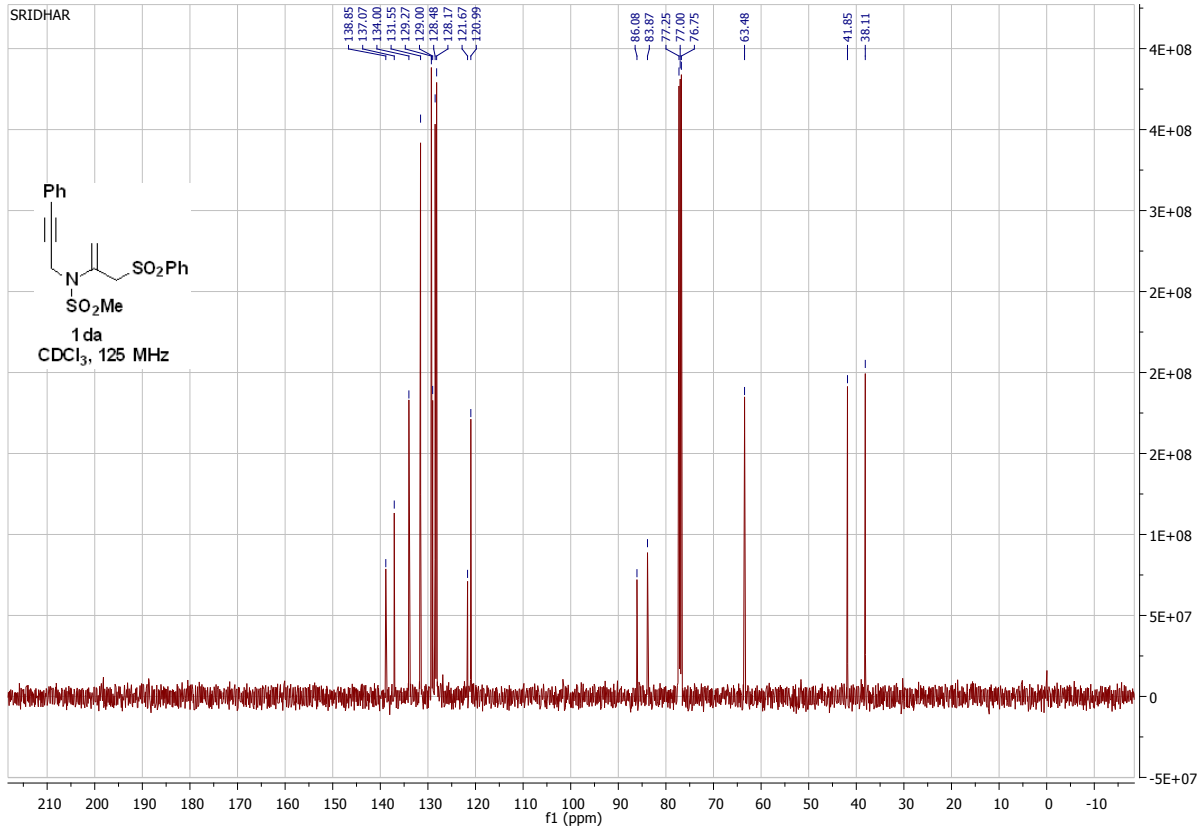

SRIDHAR
7.95
7.95
7.93
7.93
7.69
7.69
7.67
7.67
7.61
7.60
7.59
7.57
7.27
7.26
7.25
5.41
5.41
5.38
4.26
4.25
4.24
2.42
2.07
2.06
2.06
1.58
SO2Ph
N
Ts
1ca
CDCl3, 400 MHz
2.00
3.05
2.15
2.78
1.02
0.99
2.07
1.89
3.22
0.87
f1 (ppm)

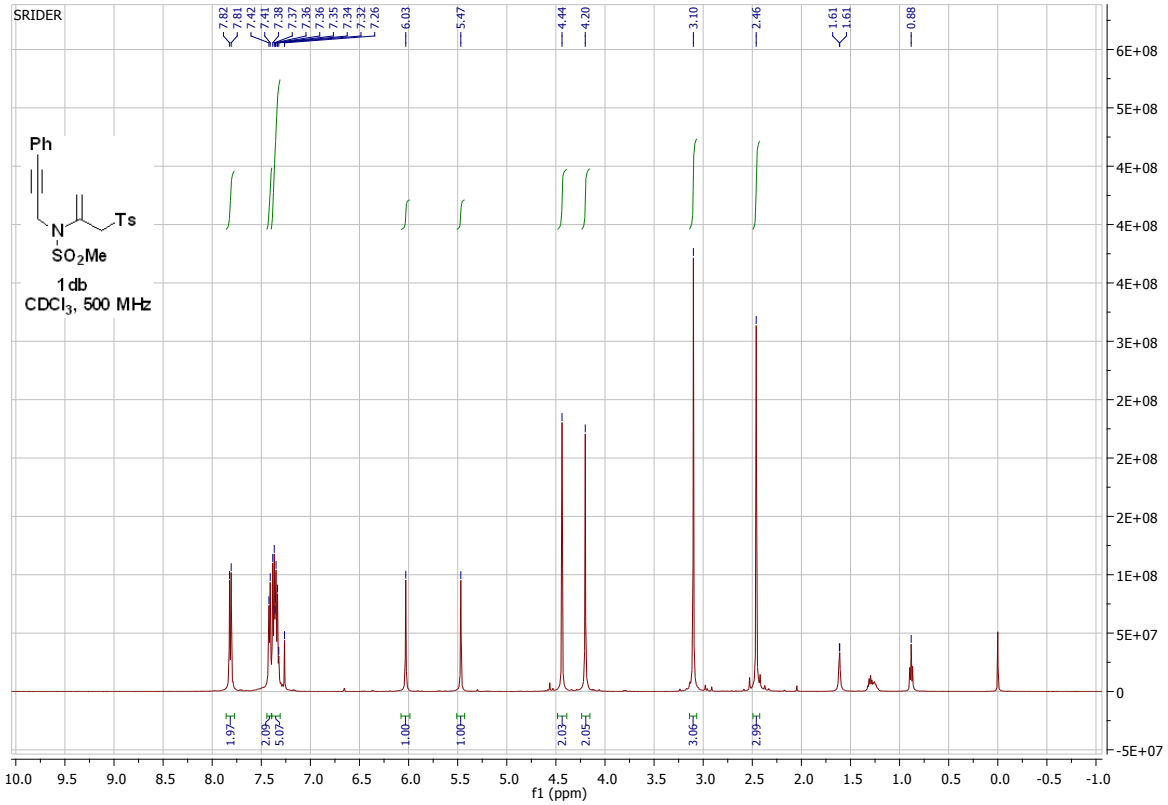

SRIDHAR
144.21
138.90
135.66
134.56
134.03
129.32
129.21
128.49
128.34
123.14
78.14
77.40
77.08
76.76
73.99
63.64
40.61
21.64
SO2Ph
N
Ts
1ca
CDCl3, 100 MHz
f1 (ppm)

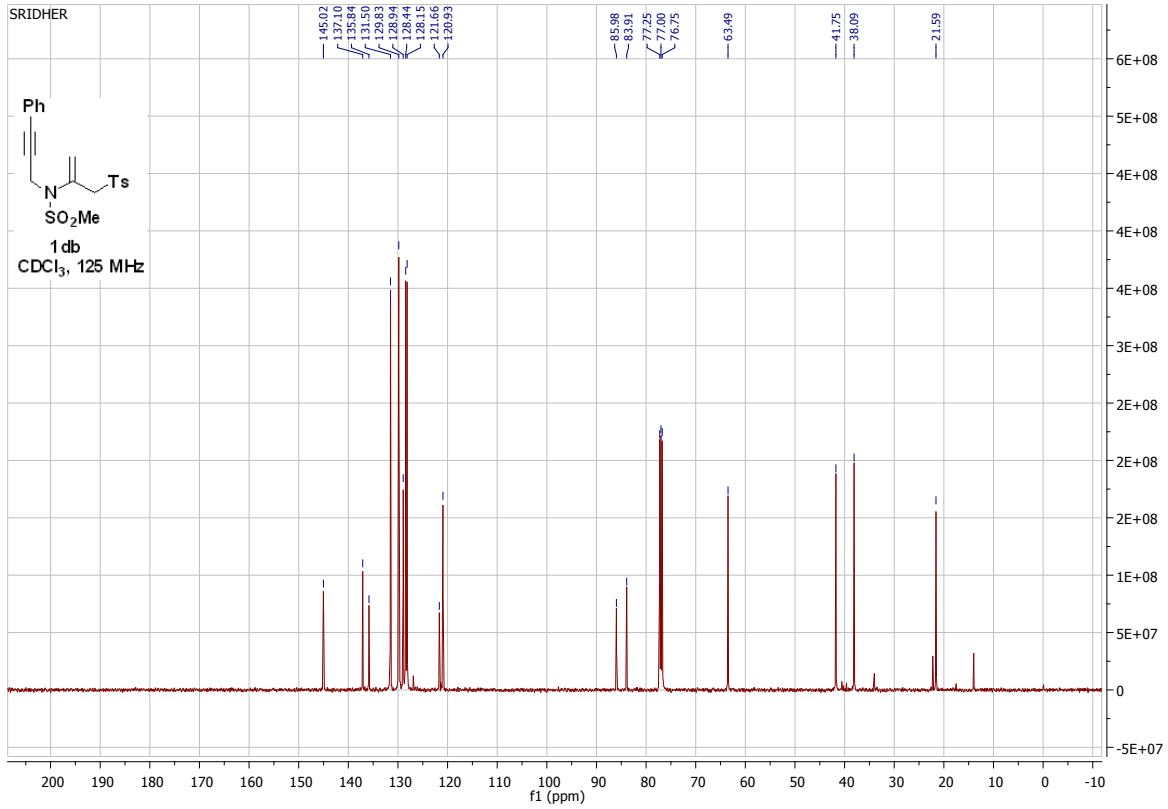

SRIDHAR
7.81
7.79
7.70
7.68
7.38
7.36
7.27
7.25
5.40
5.35
4.27
4.27
4.20
2.46
2.42
2.07
1.62
0.00
Ts
N
Ts
1cb
CDCl3, 500 MHz
2.02
2.00
2.01
2.27
1.07
0.98
2.03
2.08
2.98
3.00
f1 (ppm)

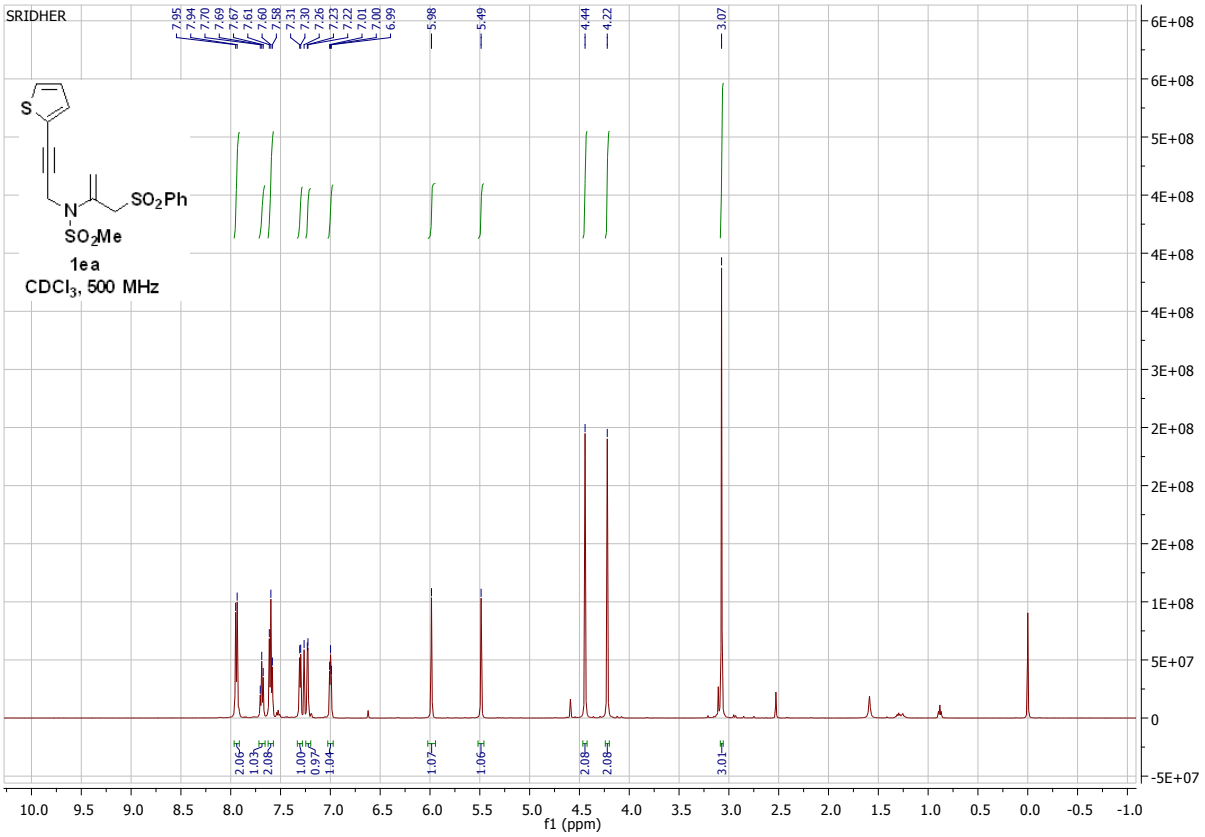

05-03-M0001-AKL-USR-212-13C
SRIDHAR
144.99
144.07
135.76
135.60
134.46
129.80
129.09
128.37
128.24
123.12
78.09
77.42
77.00
76.58
73.84
63.60
40.47
21.61
21.52
Ts
N
Ts
1cb
CDCl3, 75 MHz
f1 (ppm)

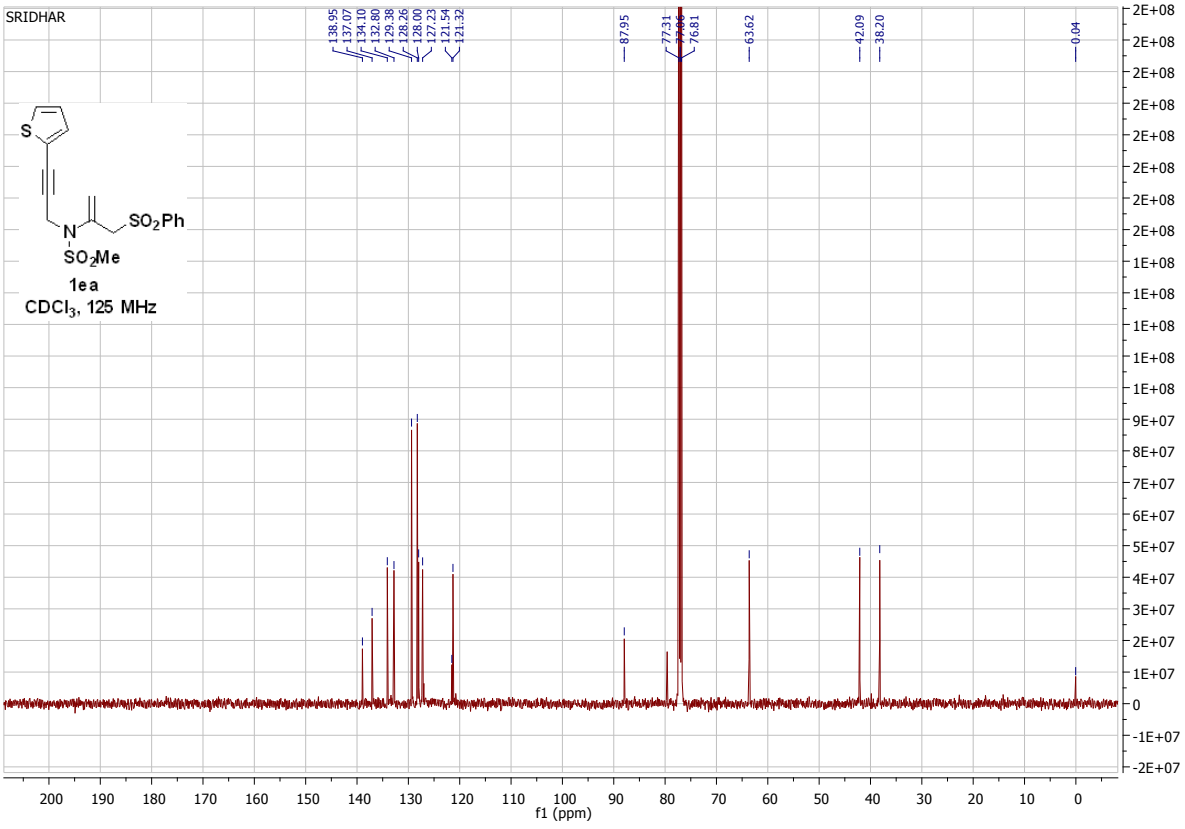

SARA
Ph
N
SO2Ph
SO2Me
1da
CDCl3, 300 MHz
f1 (ppm)

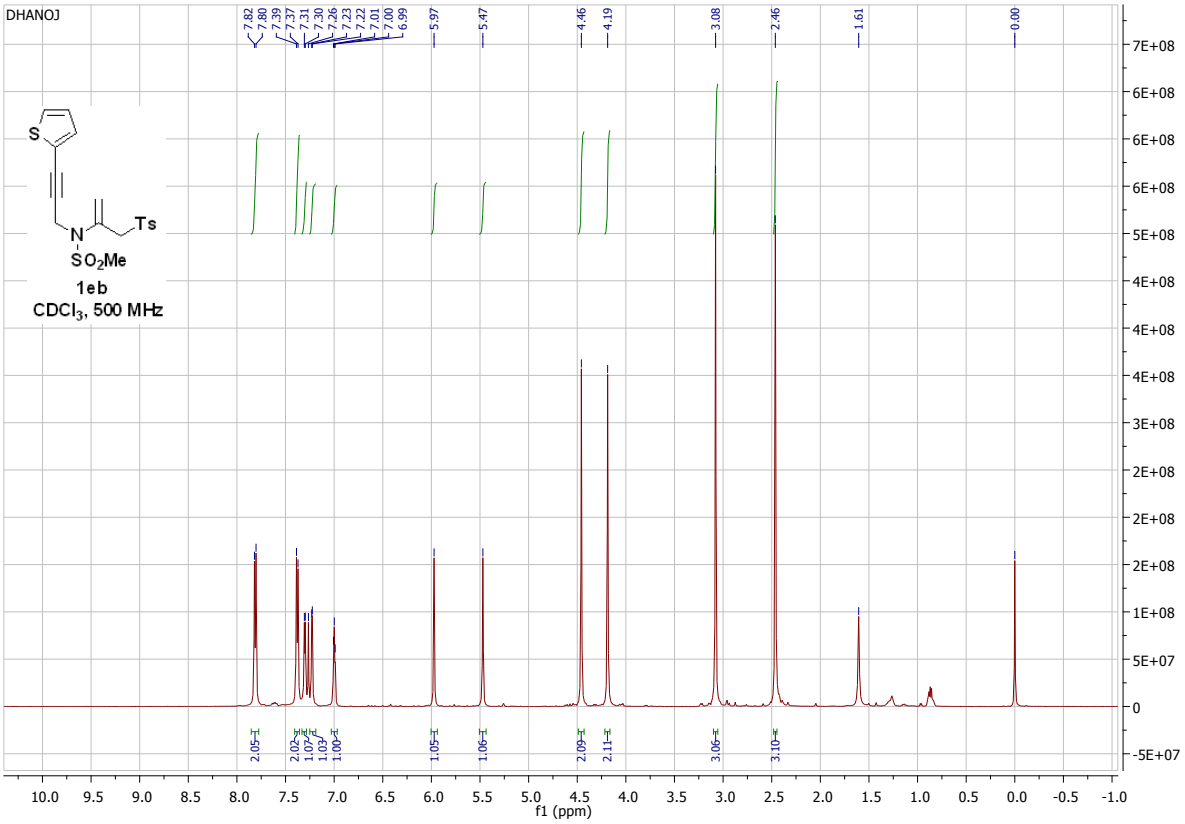

SRIDHAR
Ph
N
SO2Ph
SO2Me
1da
CDCl3, 125 MHz
f1 (ppm)

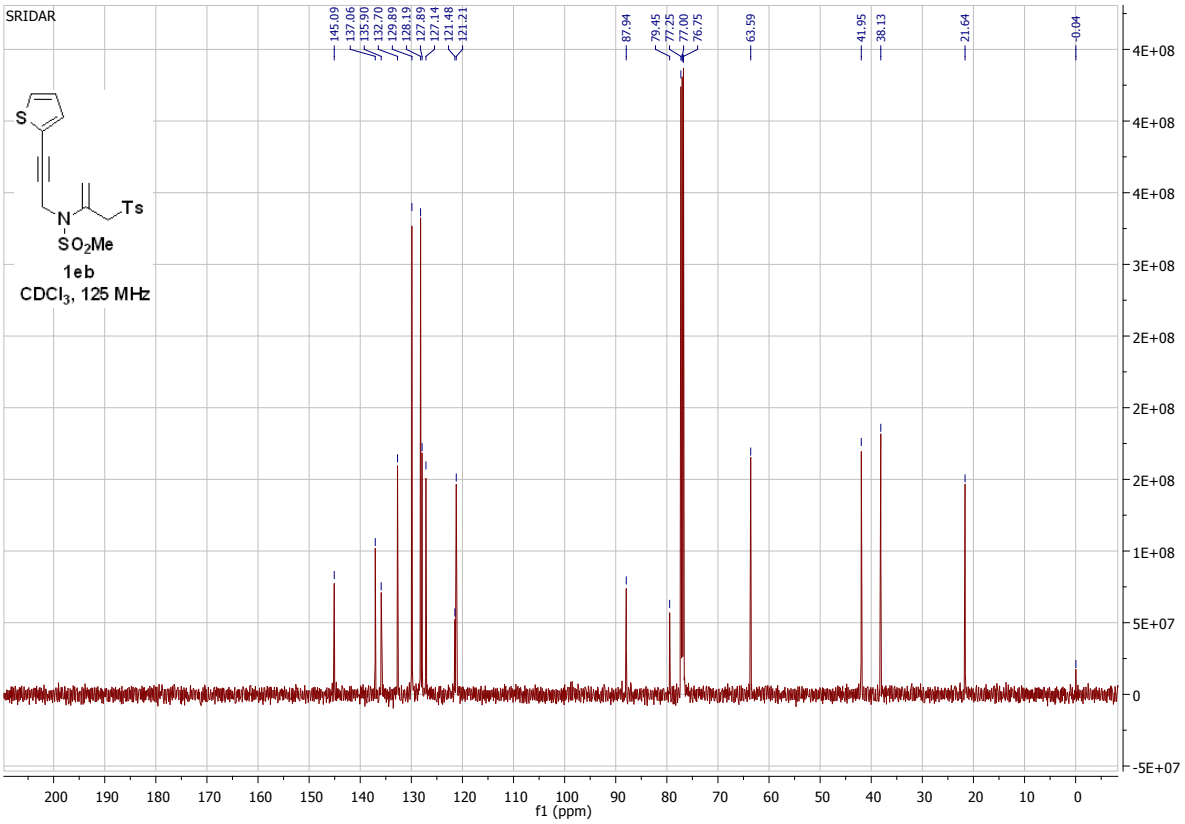

SRIDER
Ph
Ts
N
SO2Me
1 db
CDCl3, 500 MHz
f1 (ppm)

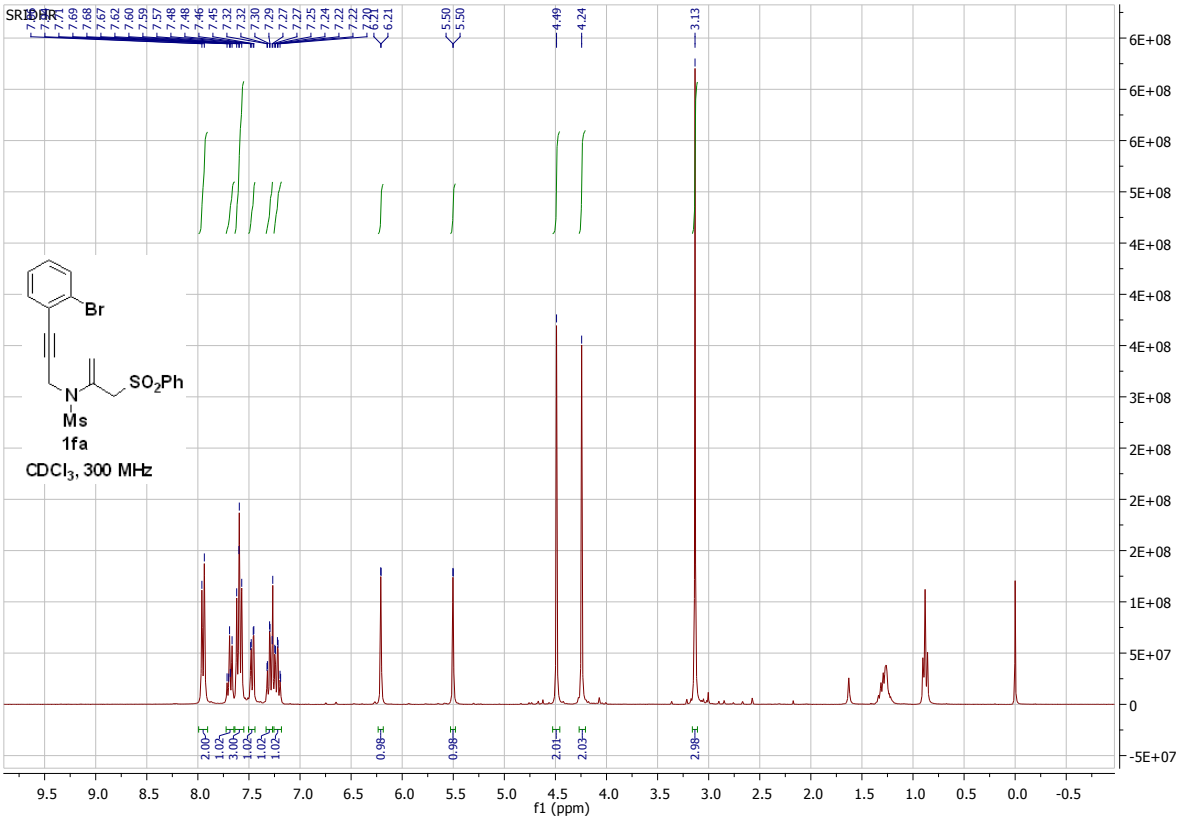

SRIDHER
Ph
Ts
N
SO2Me
1 db
CDCl3, 125 MHz
f1 (ppm)

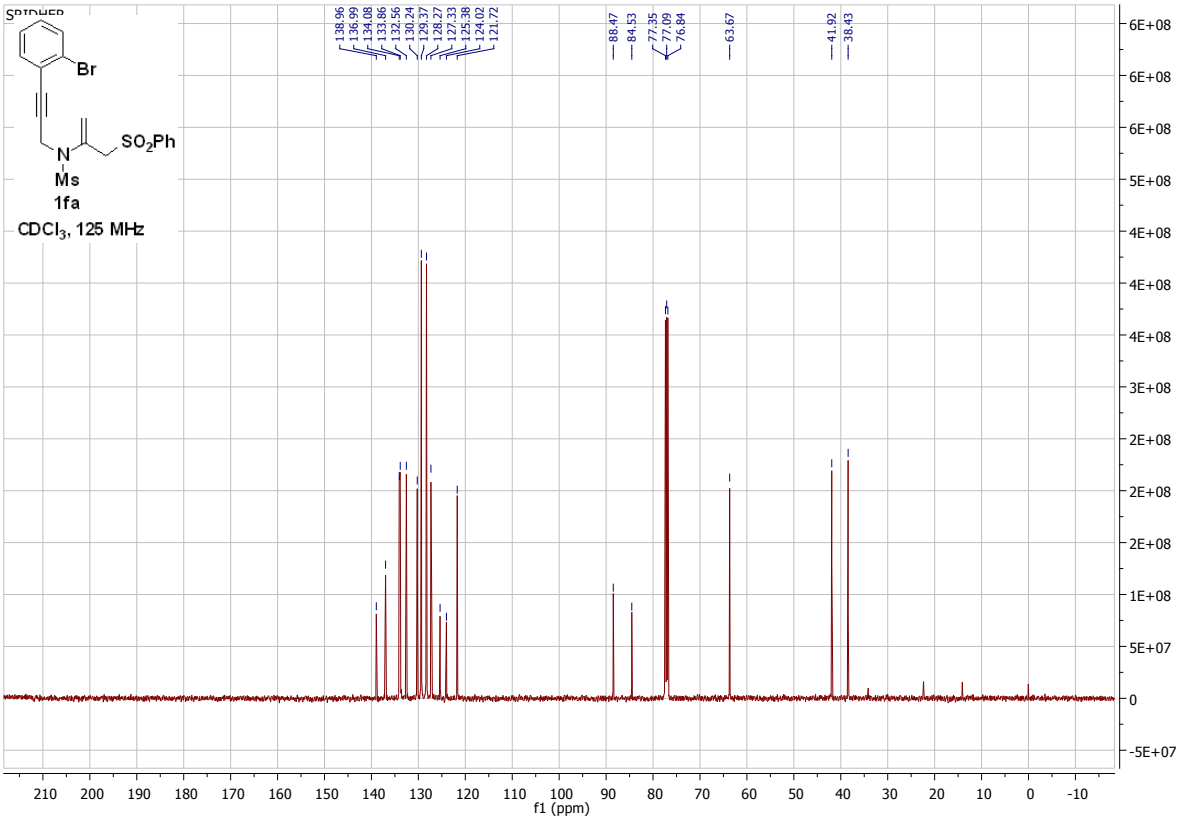

SRIDHER
7.95
7.94
7.70
7.69
7.67
7.61
7.60
7.58
7.31
7.30
7.26
7.23
7.22
7.01
7.00
6.99
5.98
5.49
4.44
4.22
3.07
S
N
SO2Ph
SO2Me
1ea
CDCl3, 500 MHz
2.06
1.03
2.08
1.00
0.97
1.04
1.07
1.06
2.08
2.08
3.01
f1 (ppm)

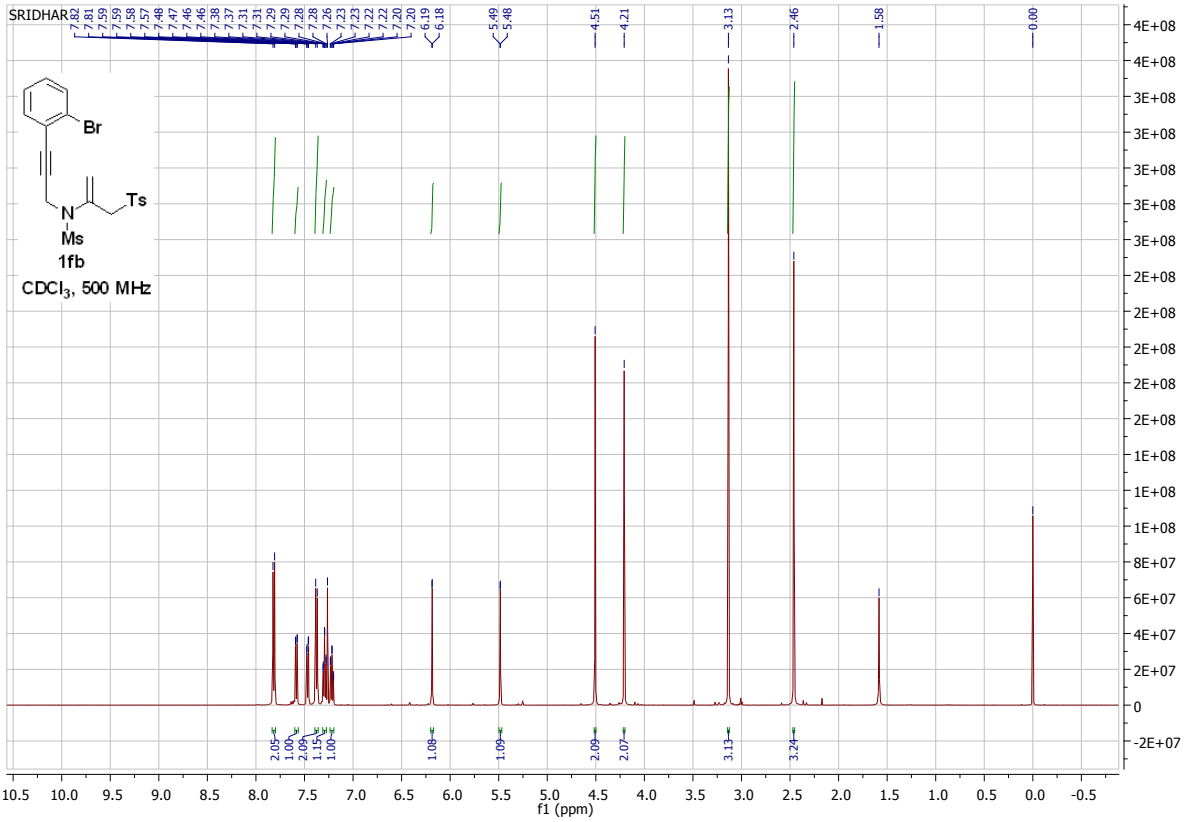

SRIDHAR
138.95
137.07
134.10
132.80
129.38
128.26
128.00
127.23
121.54
121.32
87.95
77.31
77.06
76.81
63.62
42.09
38.20
0.04
S
N
SO2Ph
SO2Me
1ea
CDCl3, 125 MHz
f1 (ppm)

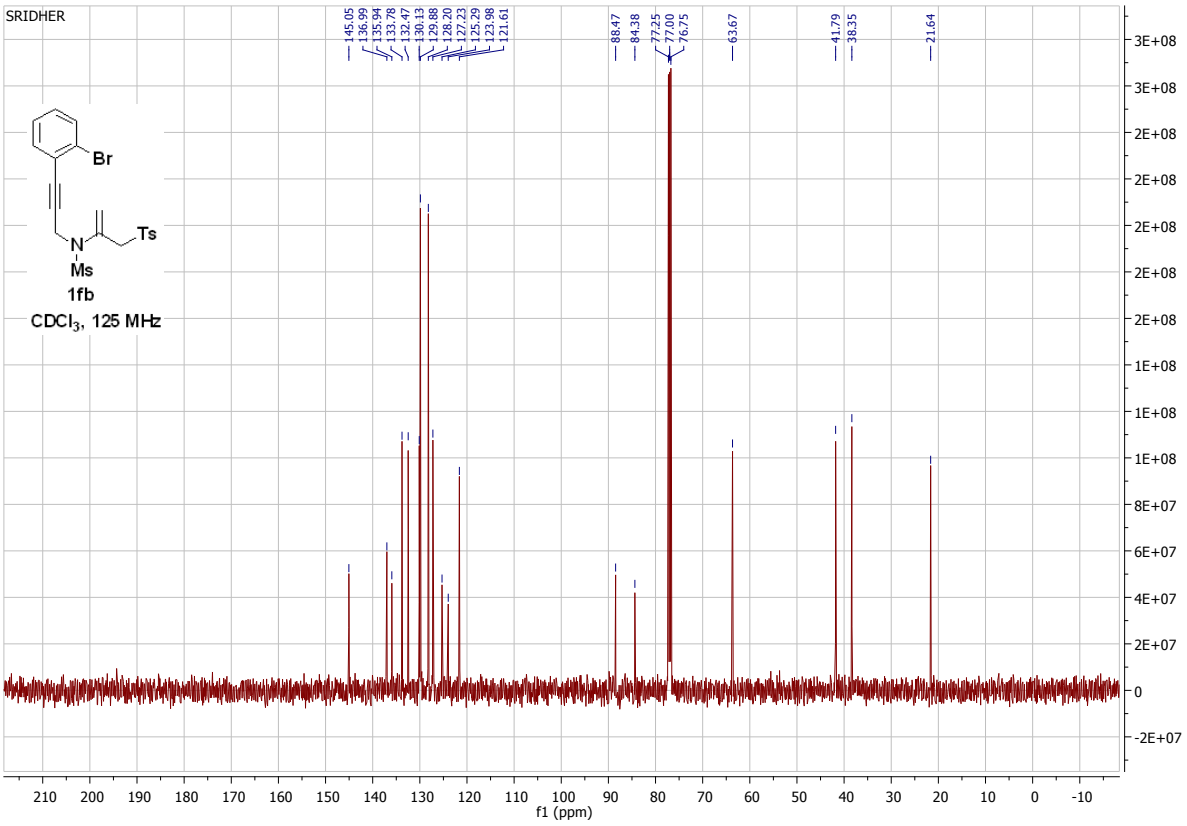

DHANOJ
7.82
7.80
7.39
7.37
7.31
7.30
7.26
7.23
7.22
7.01
7.00
6.99
5.97
5.47
4.46
4.19
3.08
2.46
1.61
0.00
S
N
Ts
SO2Me
1eb
CDCl3, 500 MHz
2.05
2.02
1.07
1.03
1.00
1.05
1.06
2.09
2.11
3.06
3.10
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

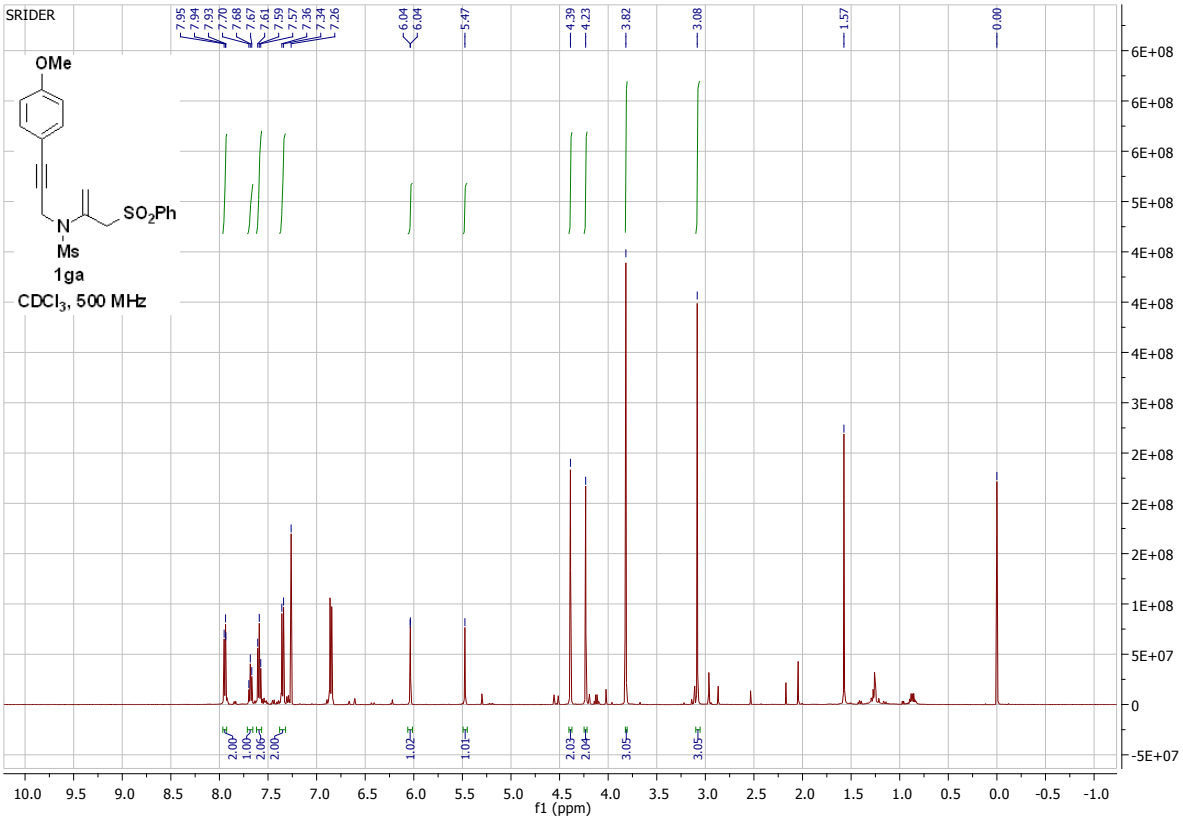

SRIDAR
145.09
137.06
135.90
132.70
129.89
128.19
127.89
127.14
121.48
121.21
87.94
79.45
77.25
77.00
76.75
63.59
41.95
38.13
21.64
-0.04
S
N
Ts
SO2Me
1eb
CDCl3, 125 MHz
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

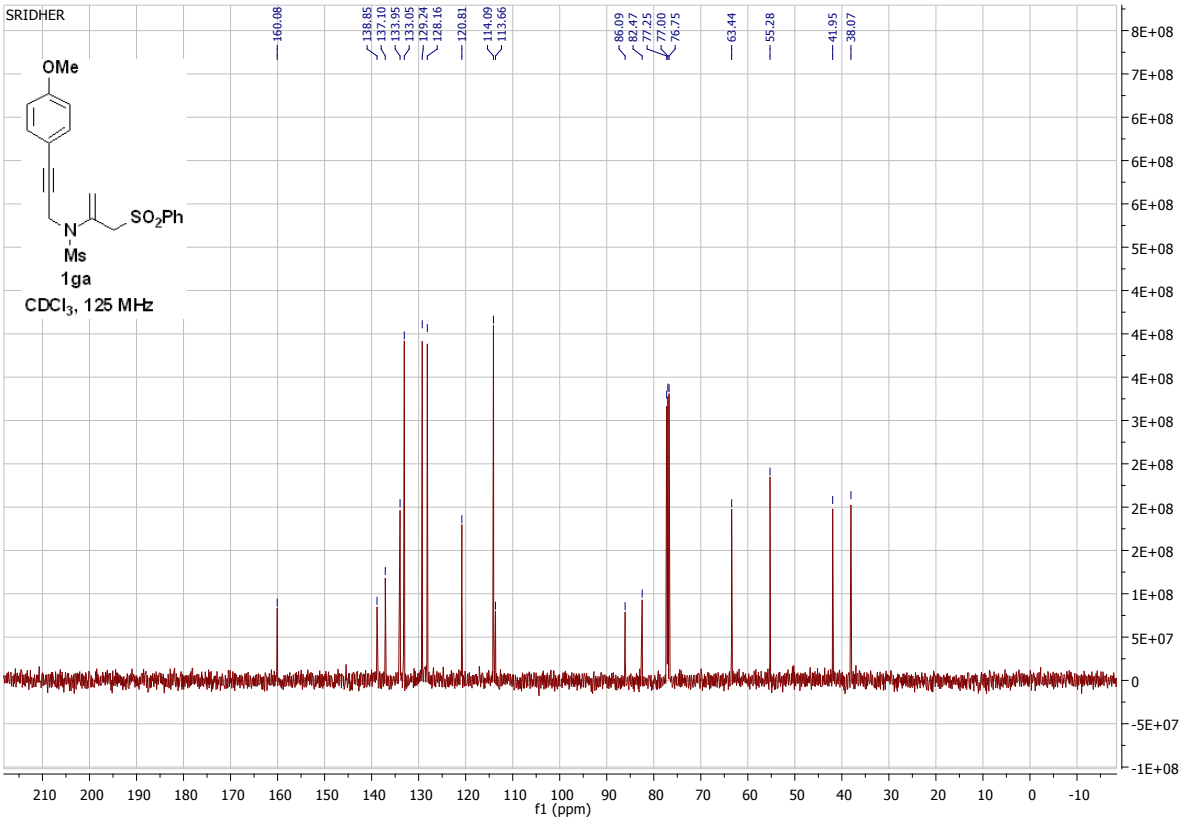

Br
SO2Ph
N
Ms
1fa
CDCl3, 300 MHz
f1 (ppm)

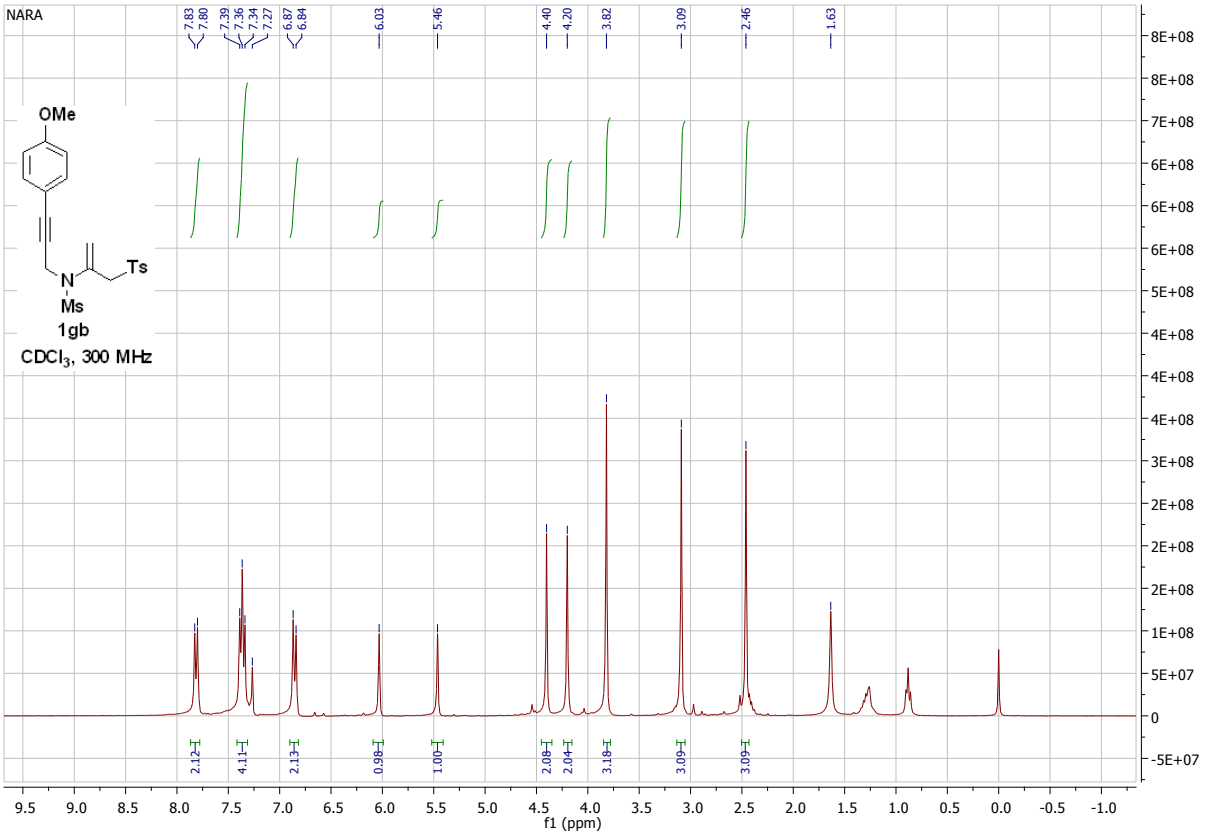

Br
SO2Ph
N
Ms
1fa
CDCl3, 125 MHz
f1 (ppm)

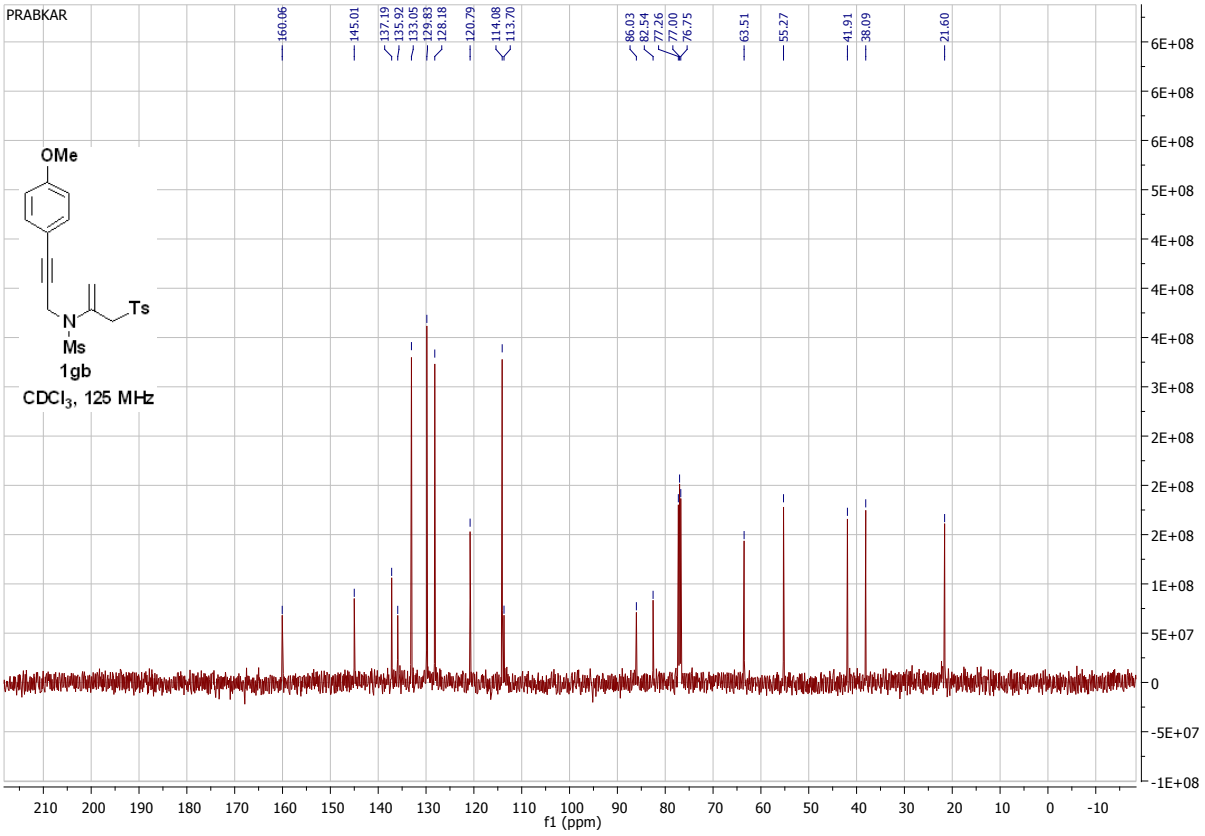

SRIDHAR
Br
Ts
N
Ms
1fb
CDCl3, 500 MHz
f1 (ppm)

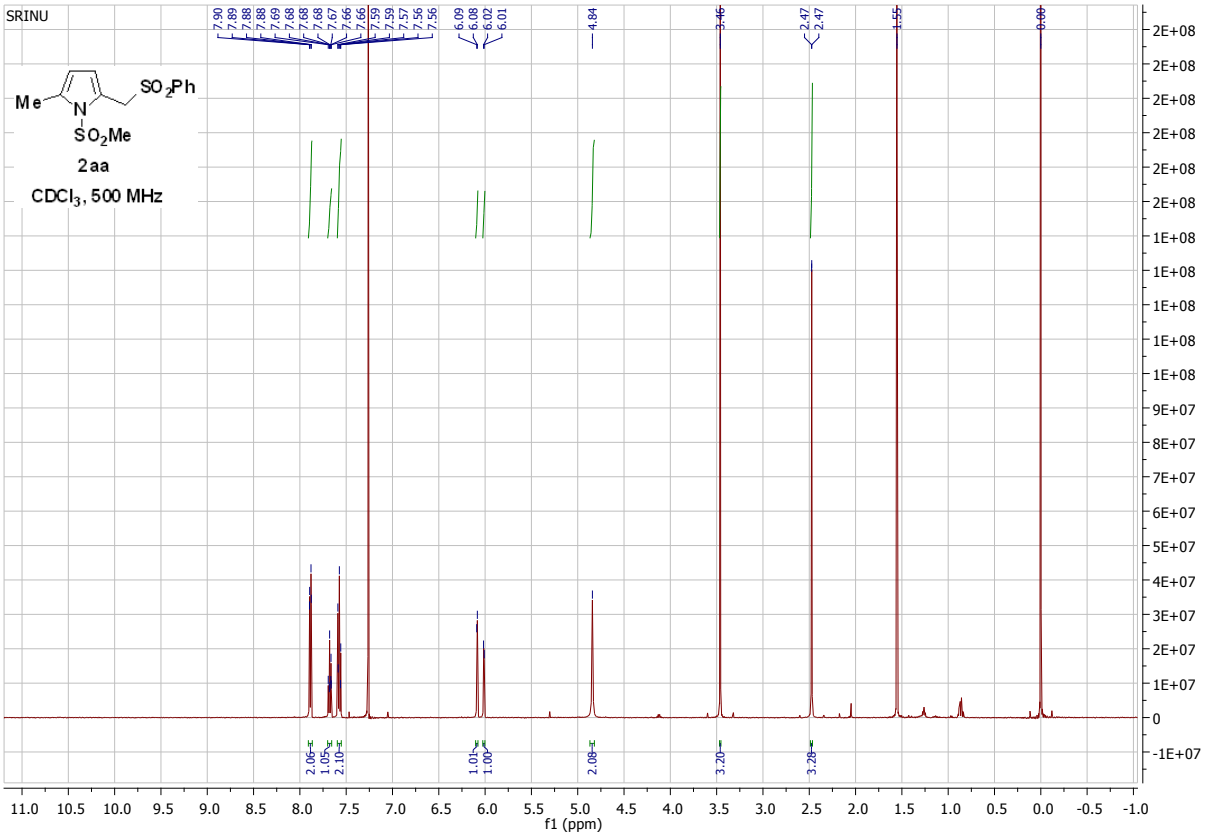

SRIDHER
Br
Ts
N
Ms
1fb
CDCl3, 125 MHz
f1 (ppm)

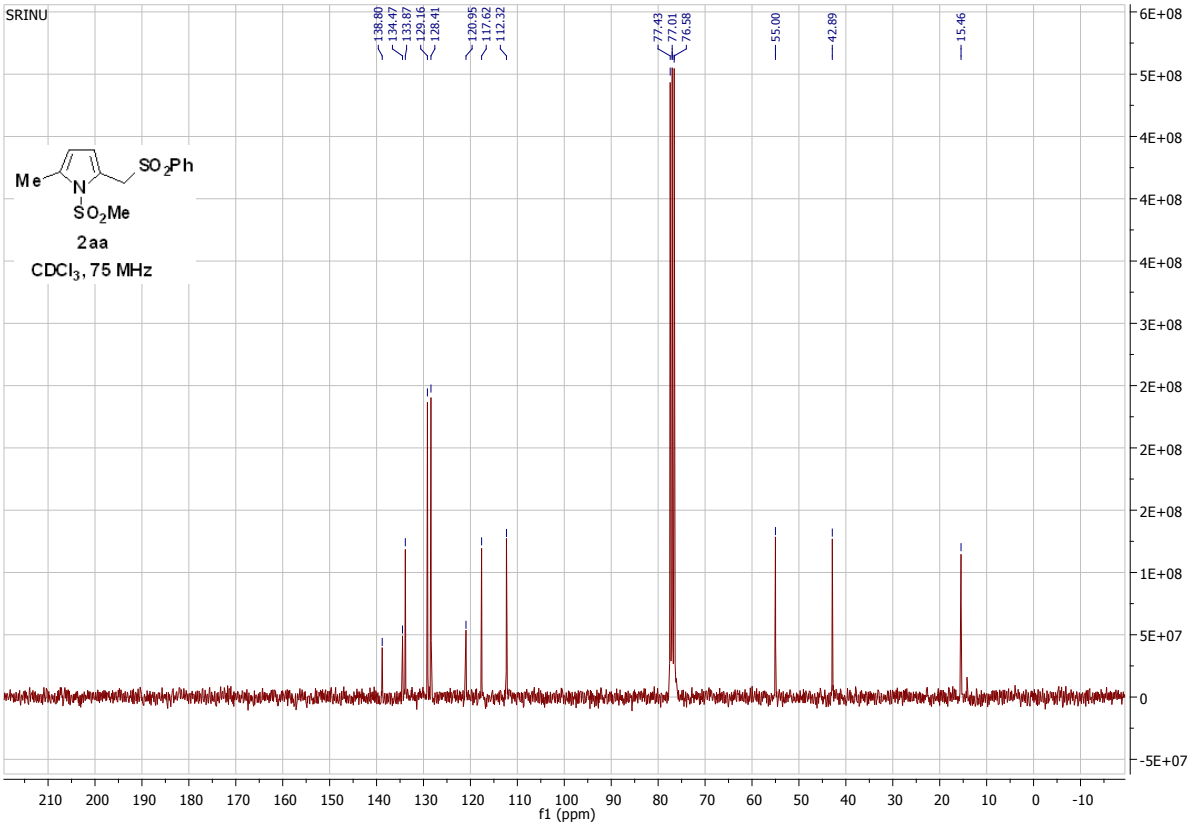

SRIDER
OMe
SO2Ph
N
Ms
1ga
CDCl3, 500 MHz
f1 (ppm)

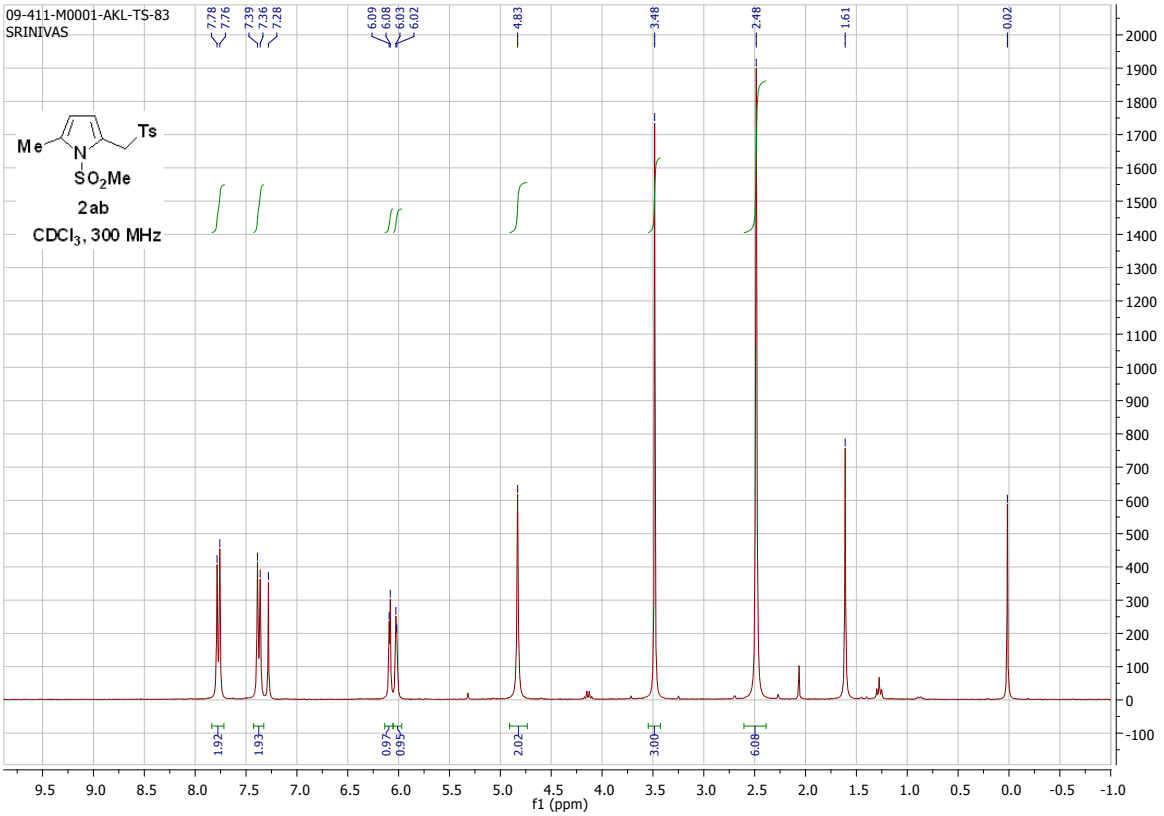

SRIDHER
OMe
SO2Ph
N
Ms
1ga
CDCl3, 125 MHz
f1 (ppm)

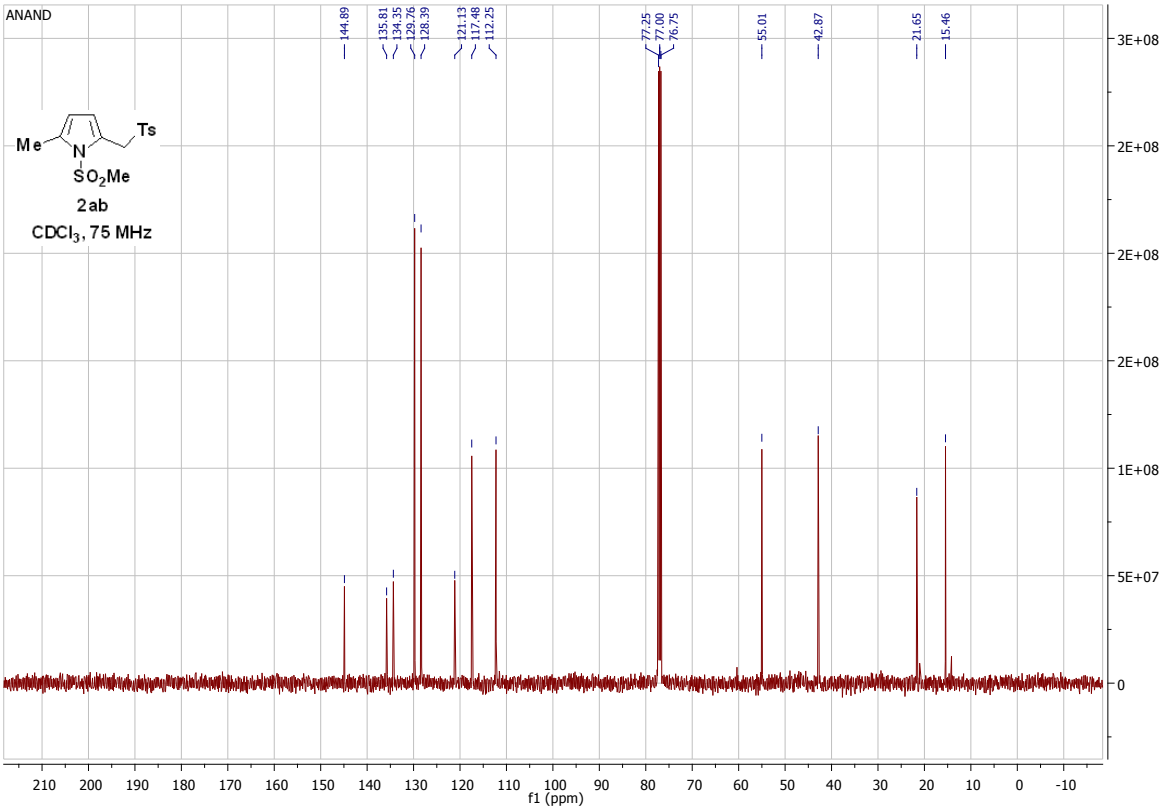

NARA
7.83
7.80
7.39
7.36
7.34
7.27
6.87
6.84
6.03
5.46
4.40
4.20
3.82
3.09
2.46
1.63
OMe
Ts
N
Ms
1gb
CDCl3, 300 MHz
2.12
4.11
2.13
0.98
1.00
2.08
2.04
3.18
3.09
3.09
f1 (ppm)

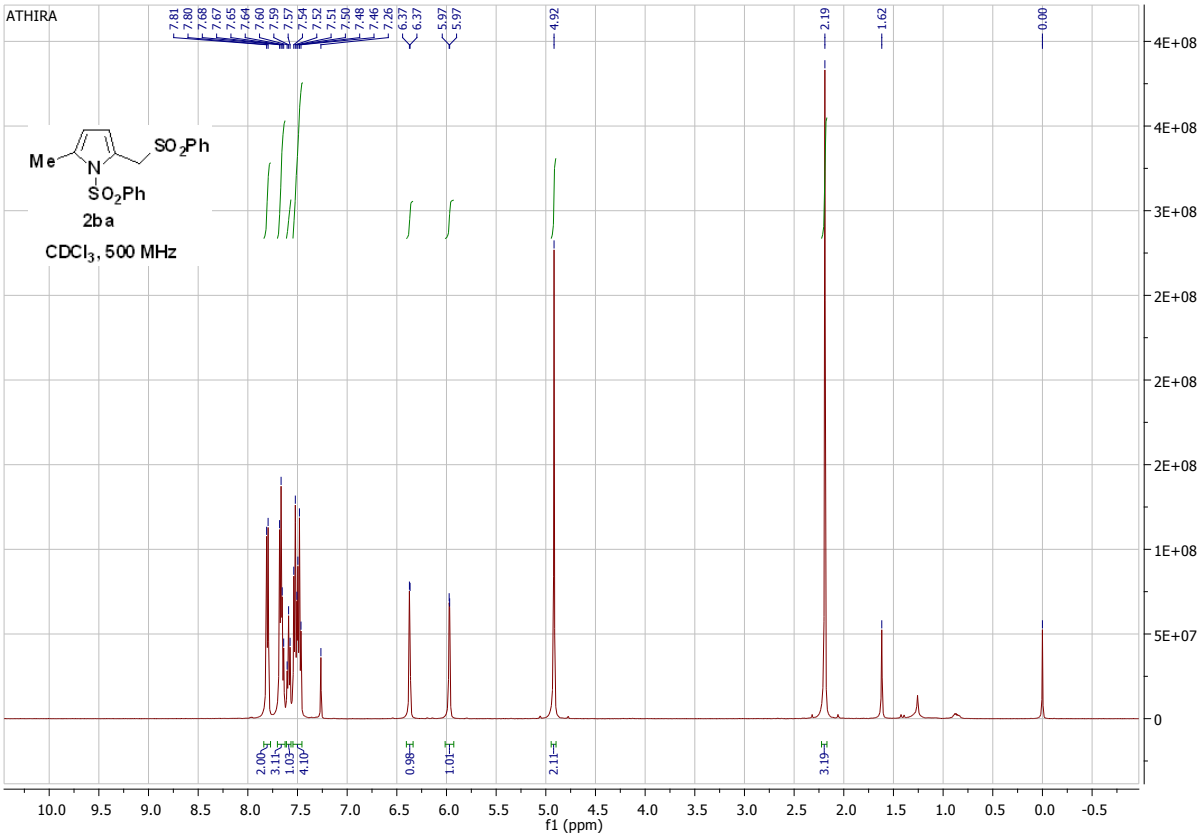

PRABKAR
160.06
145.01
137.19
135.92
133.05
129.83
128.18
120.79
114.08
113.70
86.03
82.54
77.26
77.00
76.75
63.51
55.27
41.91
38.09
21.60
OMe
Ts
N
Ms
1gb
CDCl3, 125 MHz
f1 (ppm)

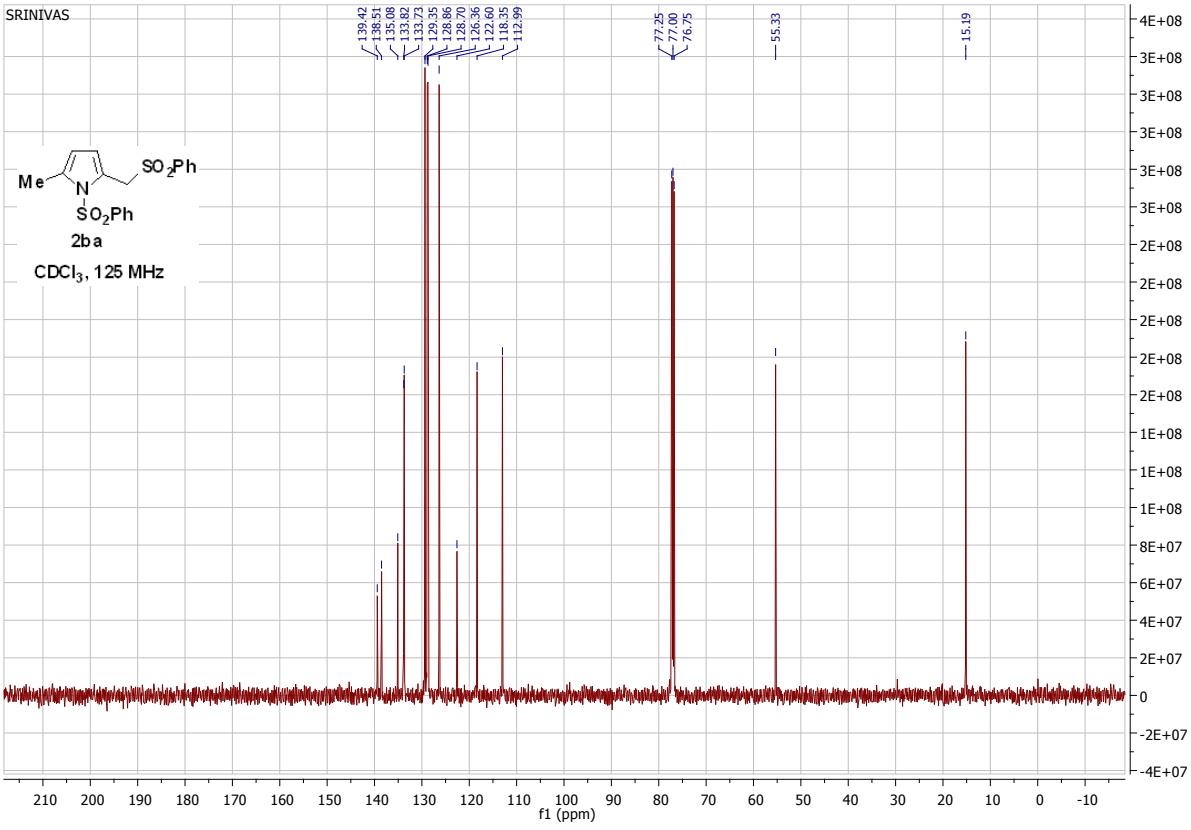

SRINU
Me
N
SO2Ph
SO2Me
2aa
CDCl3, 500 MHz
f1 (ppm)

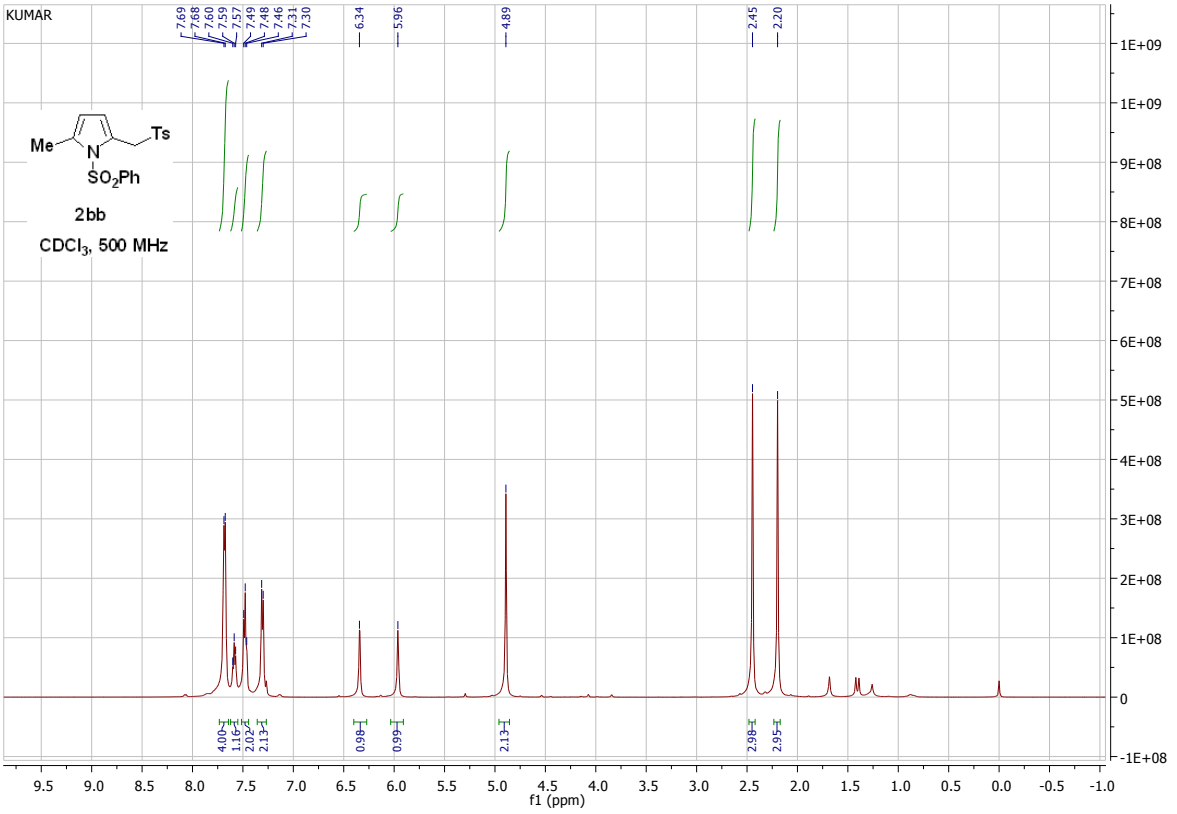

SRINU
Me
N
SO2Ph
SO2Me
2aa
CDCl3, 75 MHz
f1 (ppm)

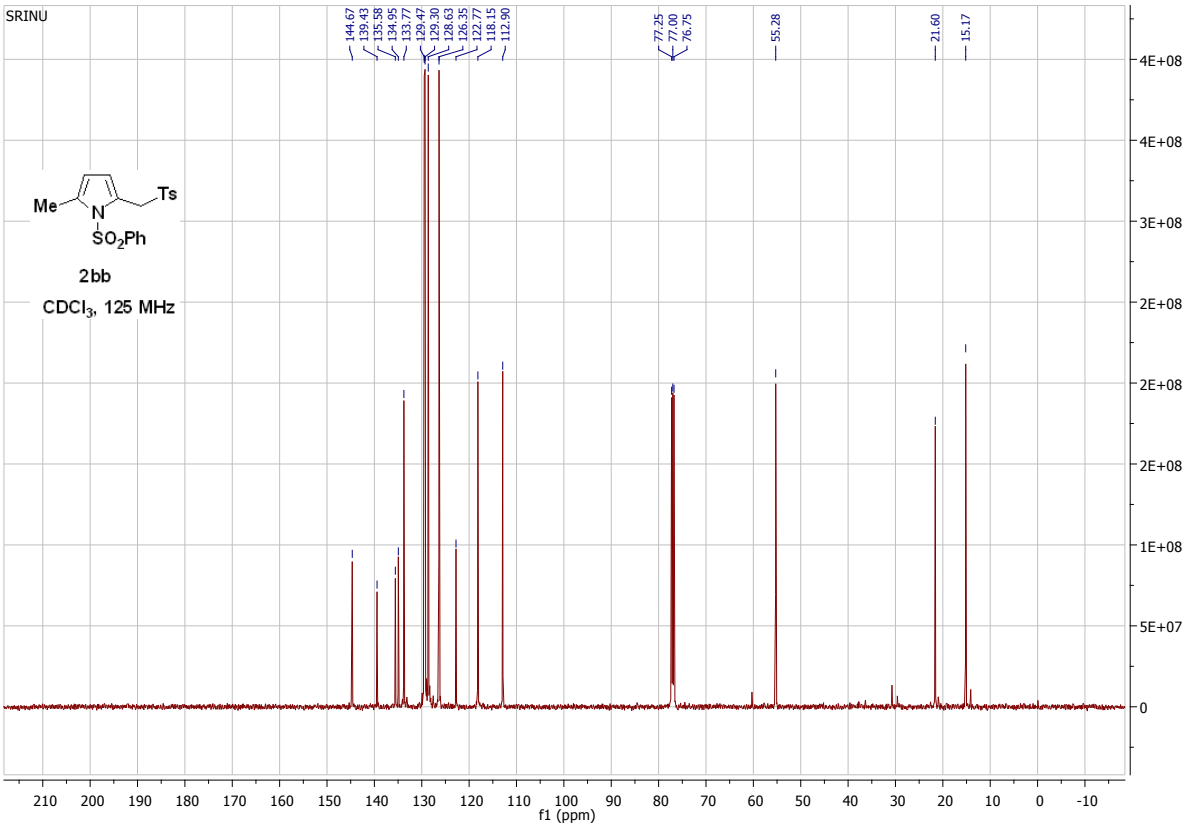

09-411-M0001-AKL-TS-83
SRINIVAS
7.78
7.76
7.39
7.36
7.28
6.09
6.08
6.03
6.02
4.83
3.48
2.48
1.61
0.02
Me
N
Ts
SO2Me
2ab
CDCl3, 300 MHz
1.92
1.93
0.97
0.95
2.02
3.00
6.08
f1 (ppm)

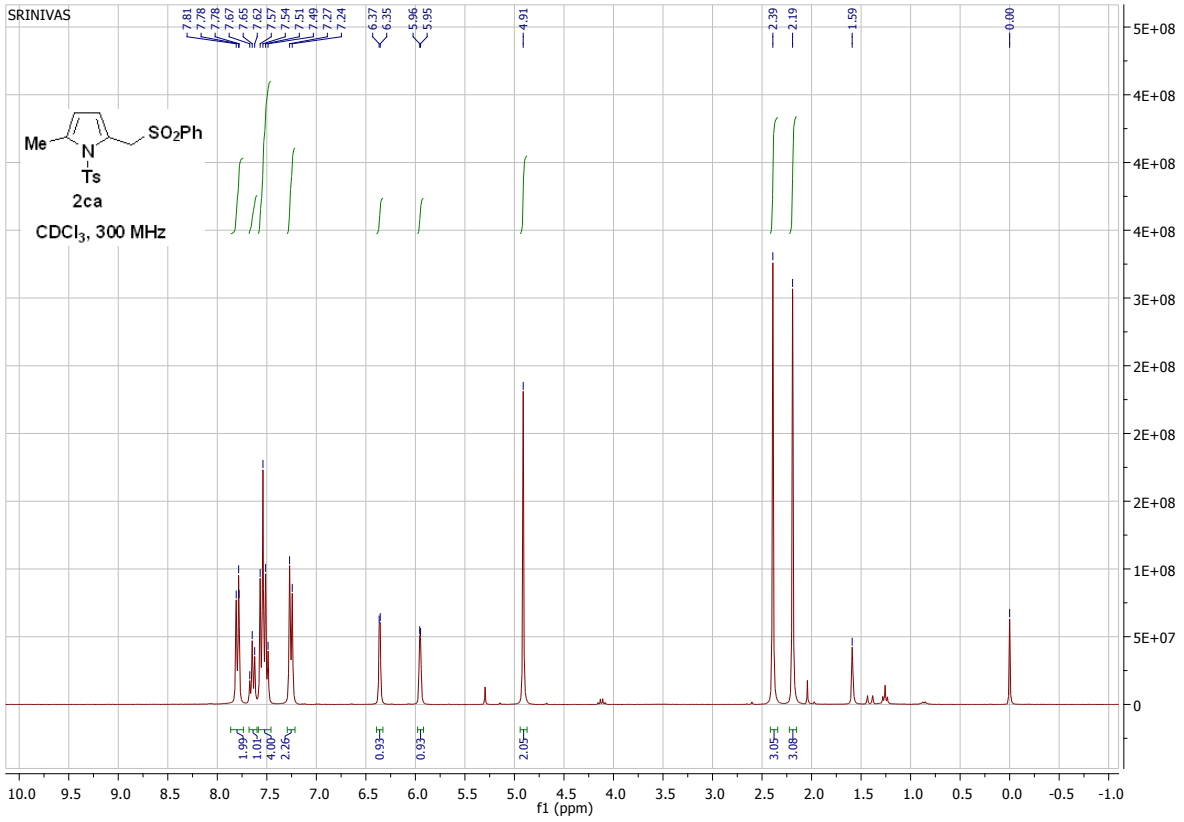

ANAND
144.89
135.81
134.35
129.76
128.39
121.13
117.48
112.25
77.25
77.00
76.75
55.01
42.87
21.65
15.46
Me
N
Ts
SO2Me
2ab
CDCl3, 75 MHz
f1 (ppm)

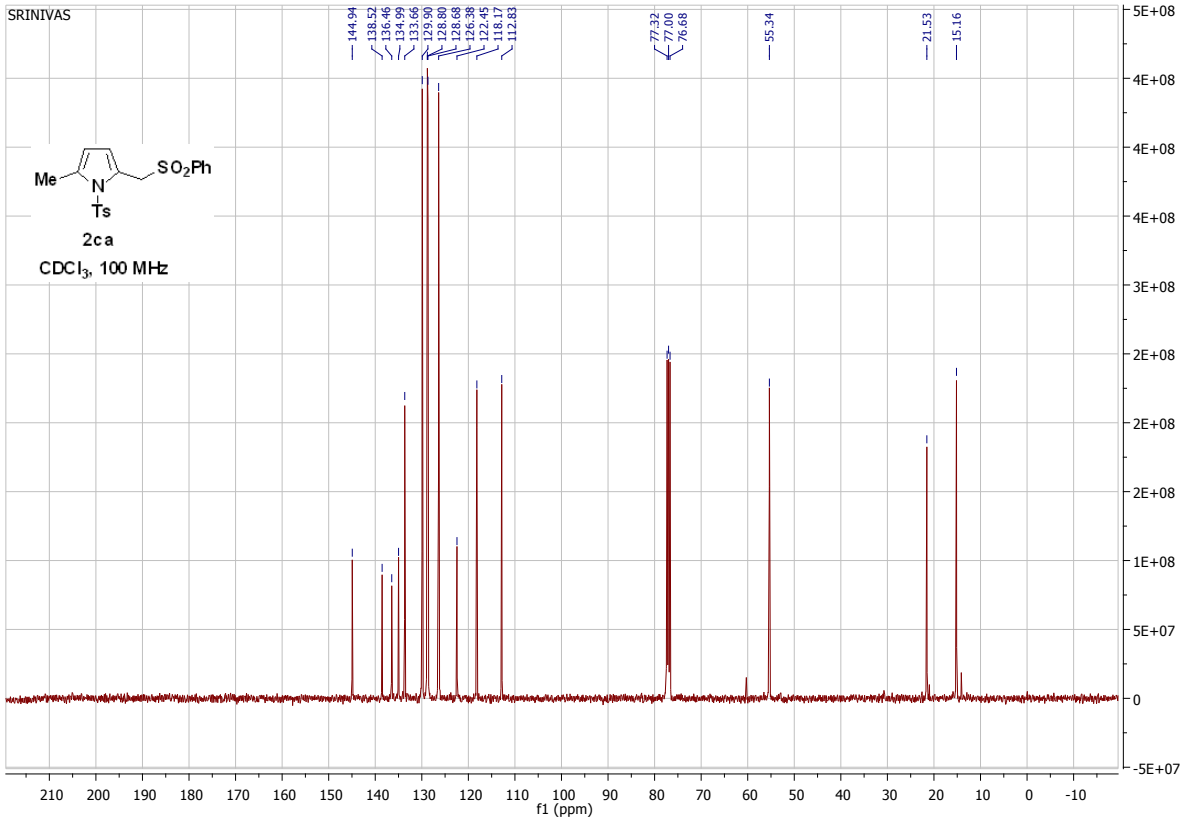

ATHIRA
7.81
7.80
7.68
7.67
7.65
7.64
7.60
7.59
7.57
7.54
7.52
7.51
7.50
7.48
7.46
7.26
6.37
6.37
5.97
5.97
4.92
2.19
1.62
0.00
Me
N
SO2Ph
SO2Ph
2ba
CDCl3, 500 MHz
2.00
3.11
1.03
4.10
0.98
1.01
2.11
3.19
4E+08
3E+08
2E+08
1E+08
5E+07
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

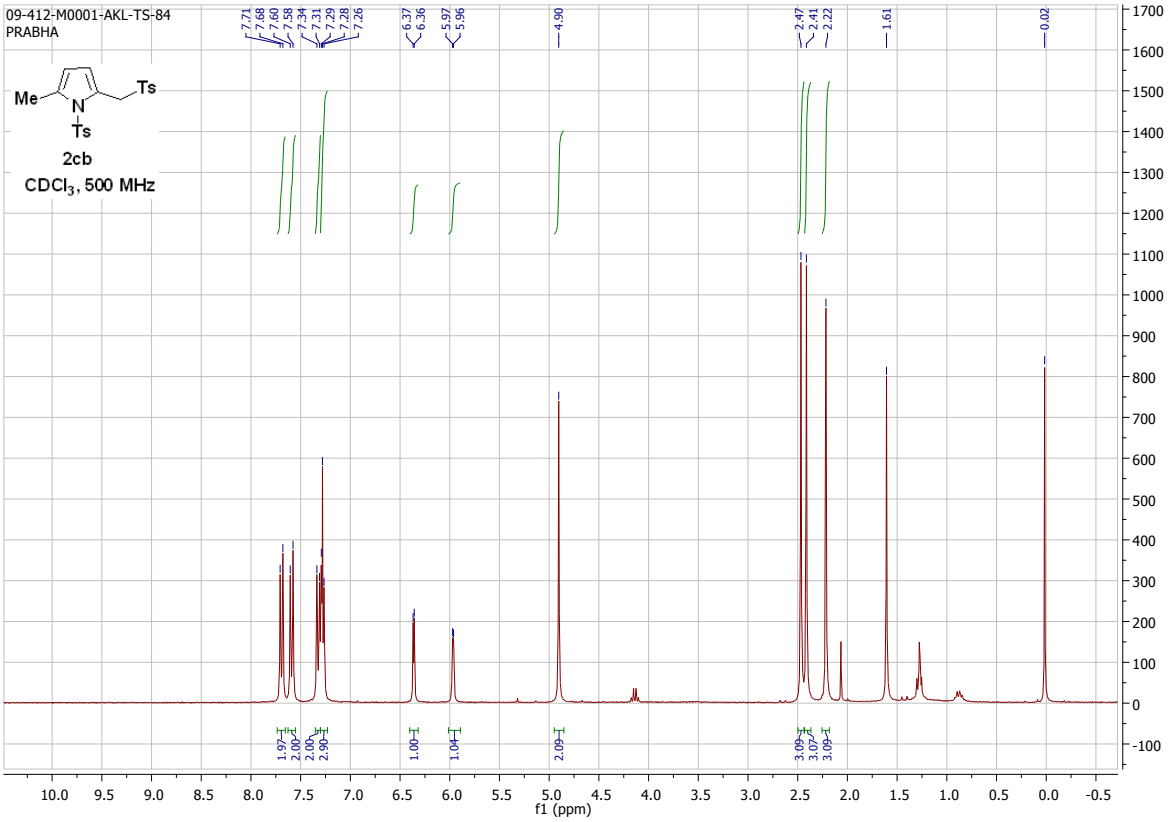

SRINIVAS
139.42
138.51
135.08
133.82
133.73
129.35
128.86
128.70
126.36
122.60
118.35
112.99
77.25
77.00
76.75
55.33
15.19
Me
N
SO2Ph
SO2Ph
2ba
CDCl3, 125 MHz
4E+08
3E+08
2E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
-4E+07
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

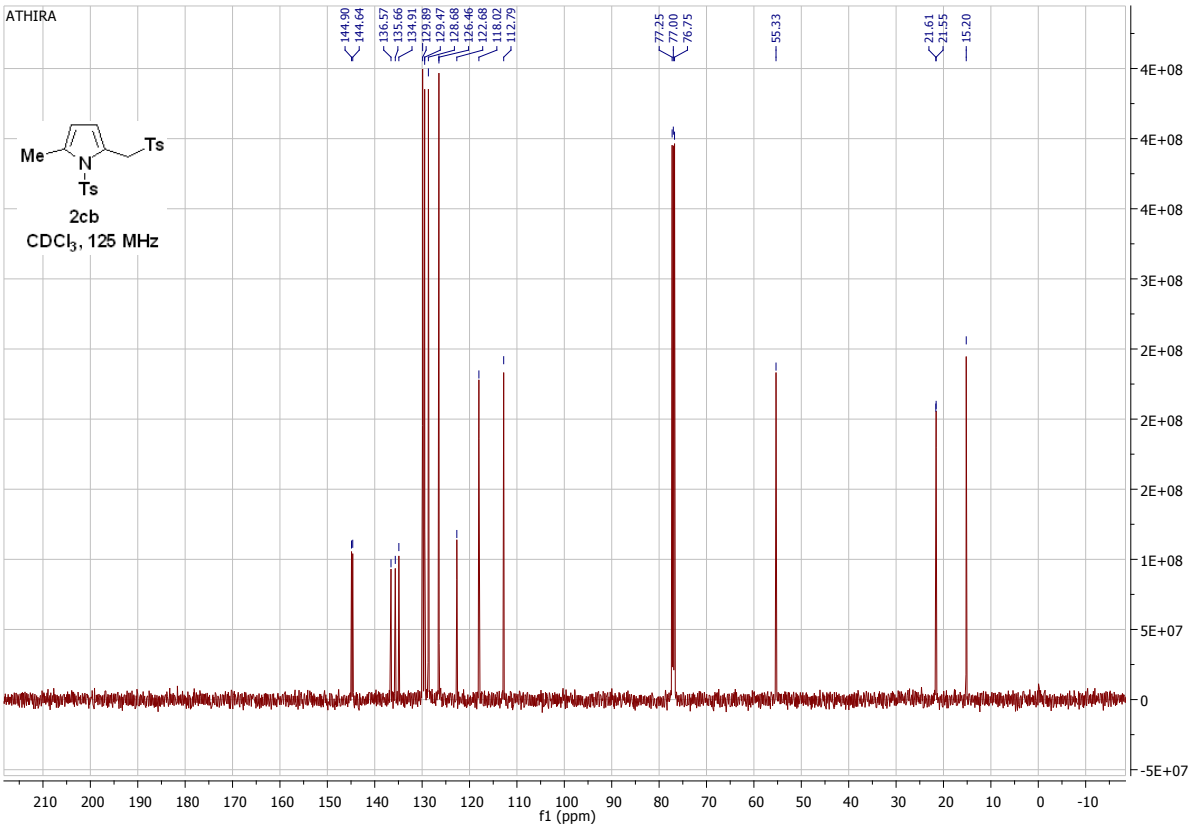

KUMAR
7.69
7.68
7.60
7.59
7.57
7.49
7.48
7.46
7.31
7.30
6.34
5.96
4.89
2.45
2.20
Me
N
Ts
SO2Ph
2bb
CDCl3, 500 MHz
4.00
1.16
2.02
2.13
0.98
0.99
2.13
2.98
2.95
f1 (ppm)

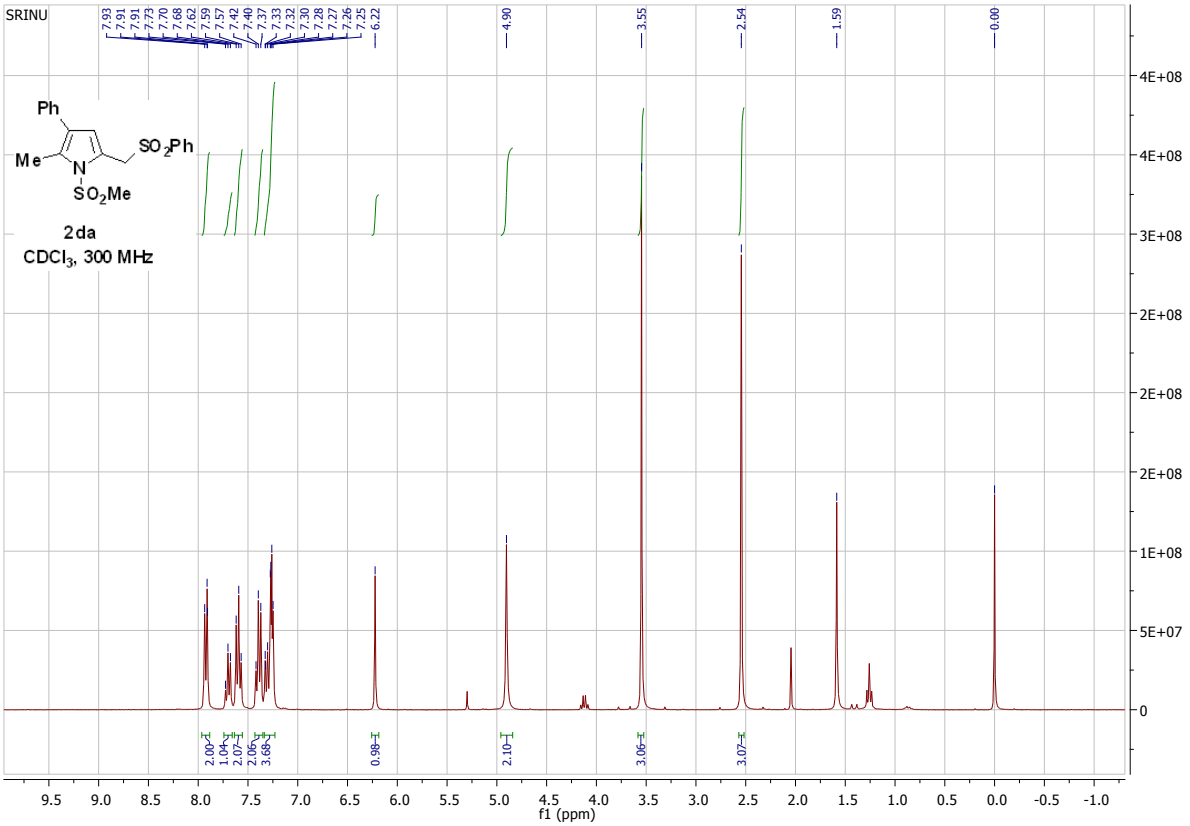

SRINU
144.67
139.43
135.58
134.95
133.77
129.47
129.30
128.63
126.35
122.77
118.15
112.90
77.25
77.00
76.75
55.28
21.60
15.17
Me
N
Ts
SO2Ph
2bb
CDCl3, 125 MHz
f1 (ppm)

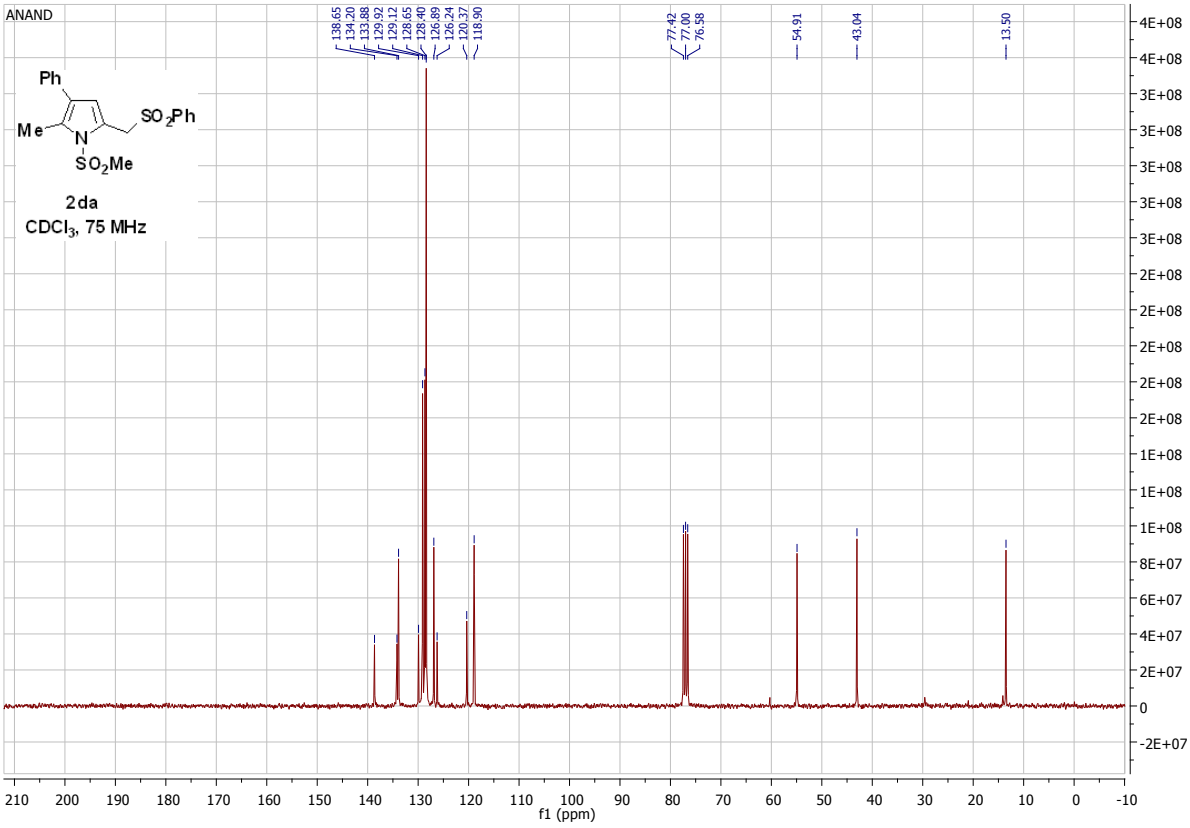

SRINIVAS
Me
N
Ts
SO2Ph
2ca
CDCl3, 300 MHz
f1 (ppm)

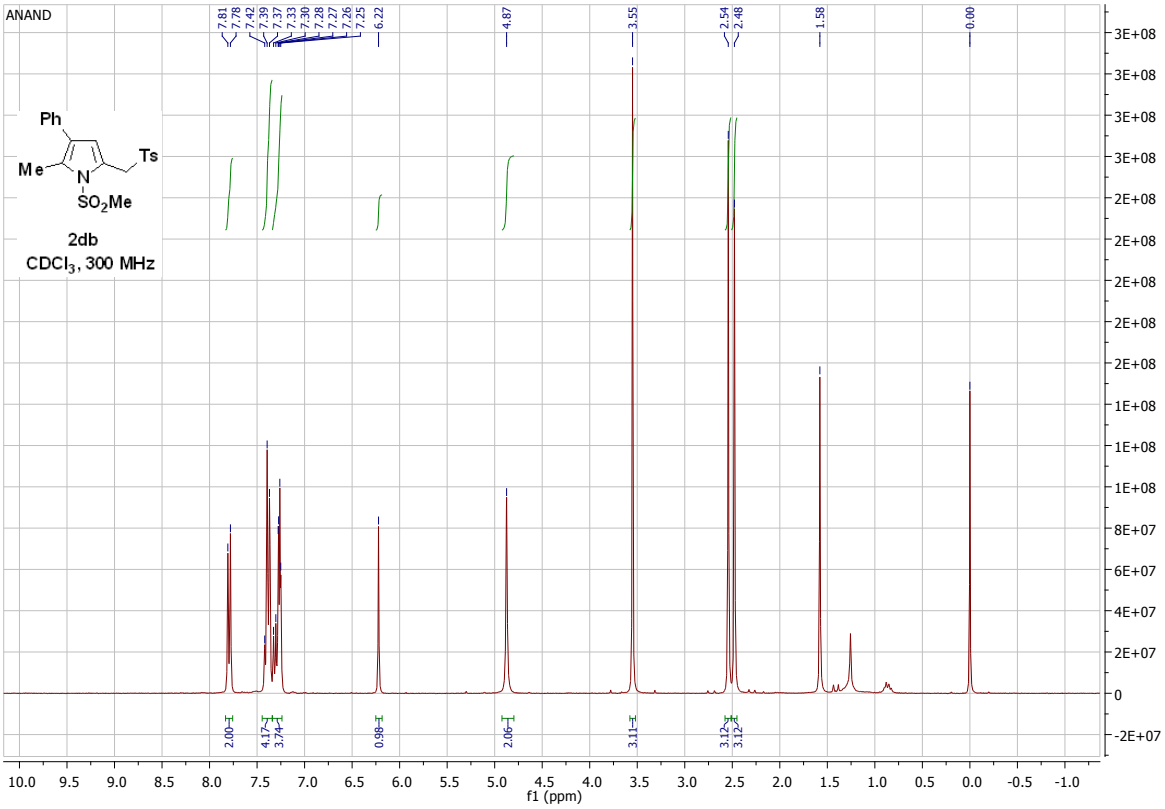

SRINIVAS
Me
N
Ts
SO2Ph
2ca
CDCl3, 100 MHz
f1 (ppm)

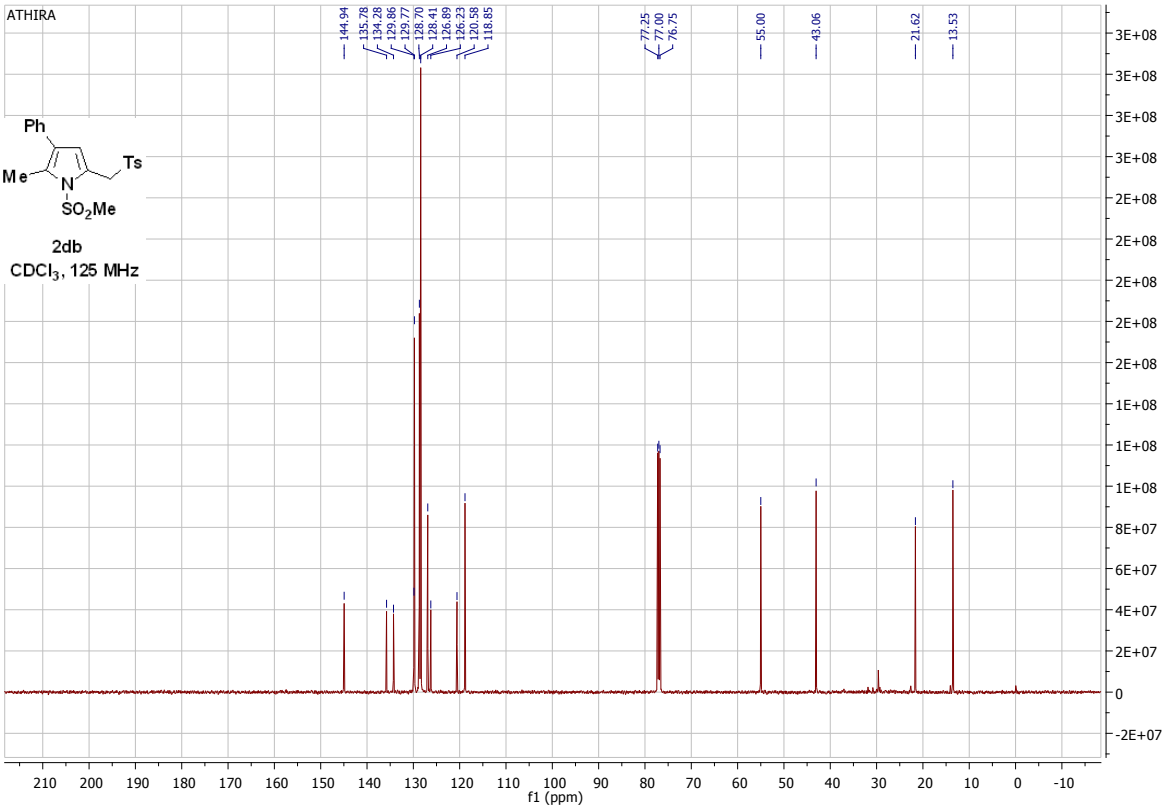

09-412-M0001-AKL-TS-84
PRABHA
Me
Ts
N
Ts
2cb
CDCl3, 500 MHz
7.71
7.68
7.60
7.58
7.34
7.31
7.29
7.28
7.26
6.37
6.36
5.97
5.96
4.90
2.47
2.41
2.22
1.61
0.02
1.97
2.00
2.00
2.90
1.00
1.04
2.09
3.09
3.07
3.09
f1 (ppm)

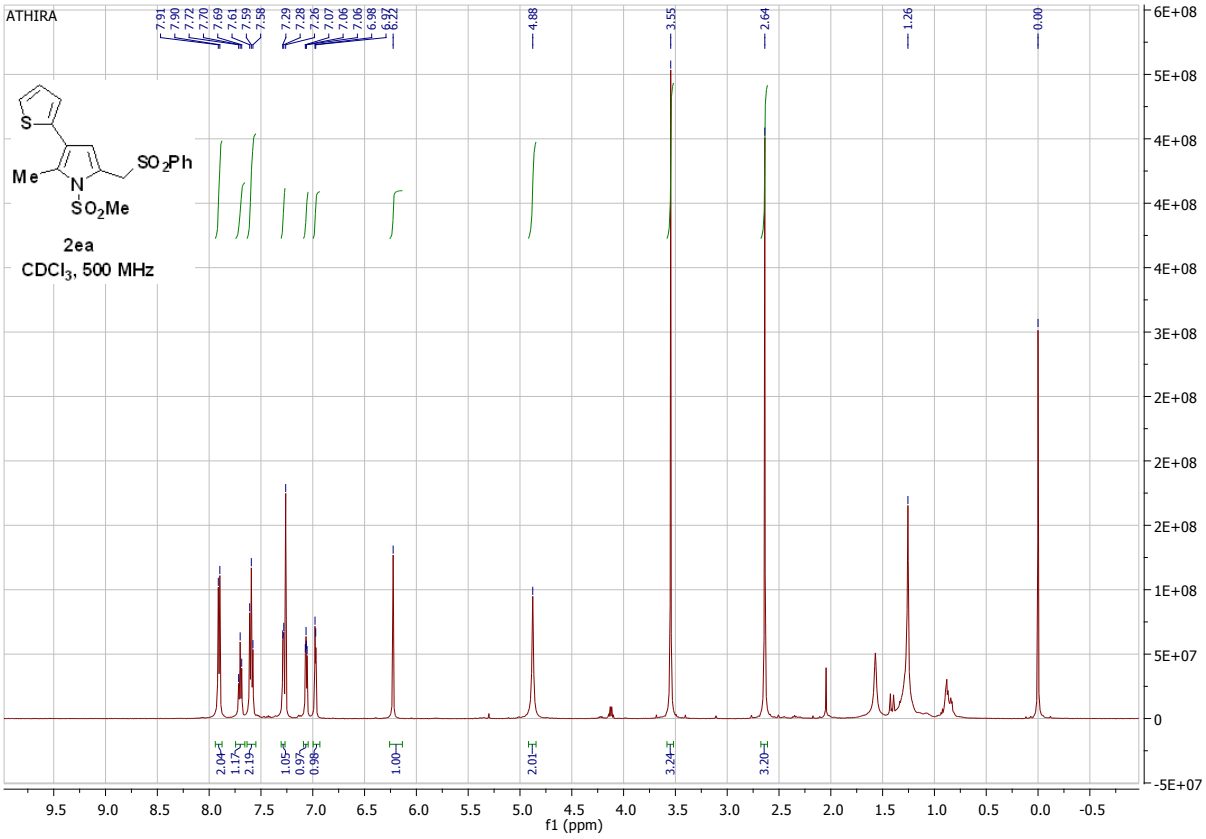

ATHIRA
Me
Ts
N
Ts
2cb
CDCl3, 125 MHz
144.90
144.64
136.57
135.66
134.91
129.89
129.47
128.68
126.46
122.68
118.02
112.79
77.25
77.00
76.75
55.33
21.61
21.55
15.20
f1 (ppm)

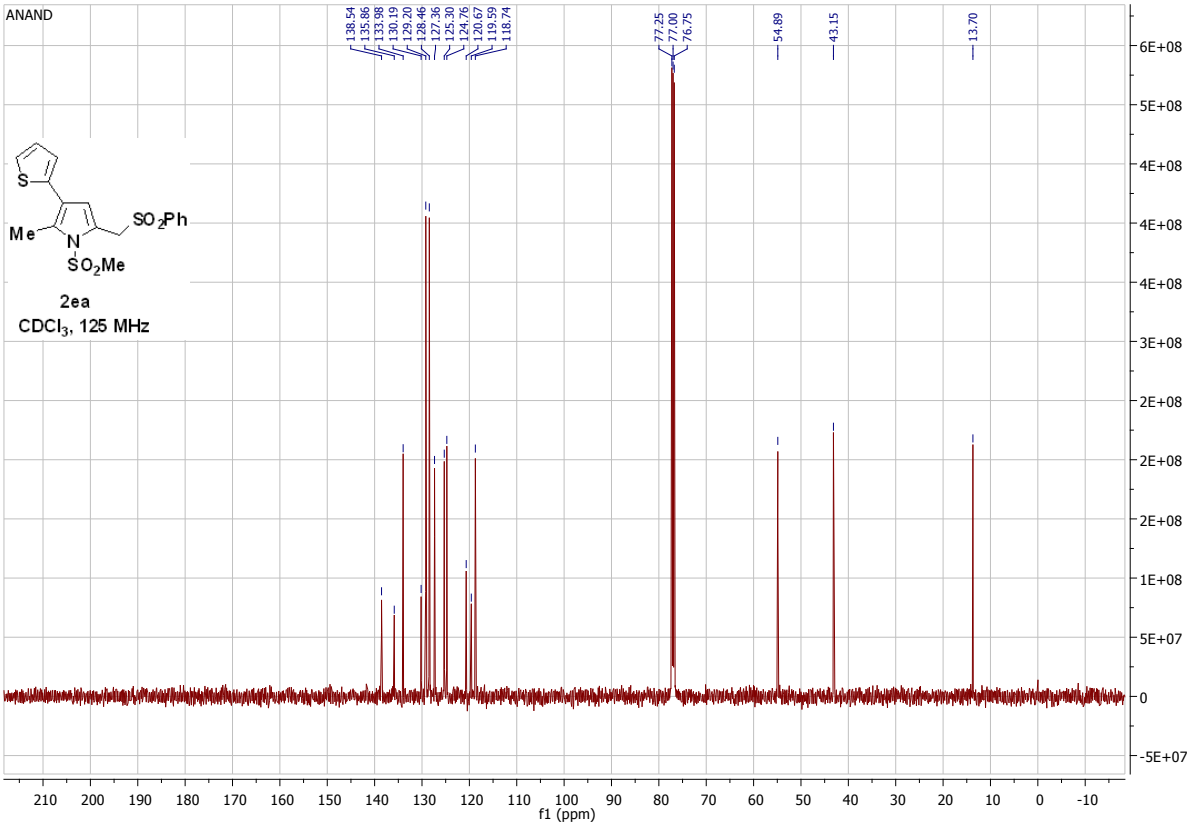

SRINU
Ph
Me
N
SO2Ph
SO2Me
2da
CDCl3, 300 MHz
f1 (ppm)

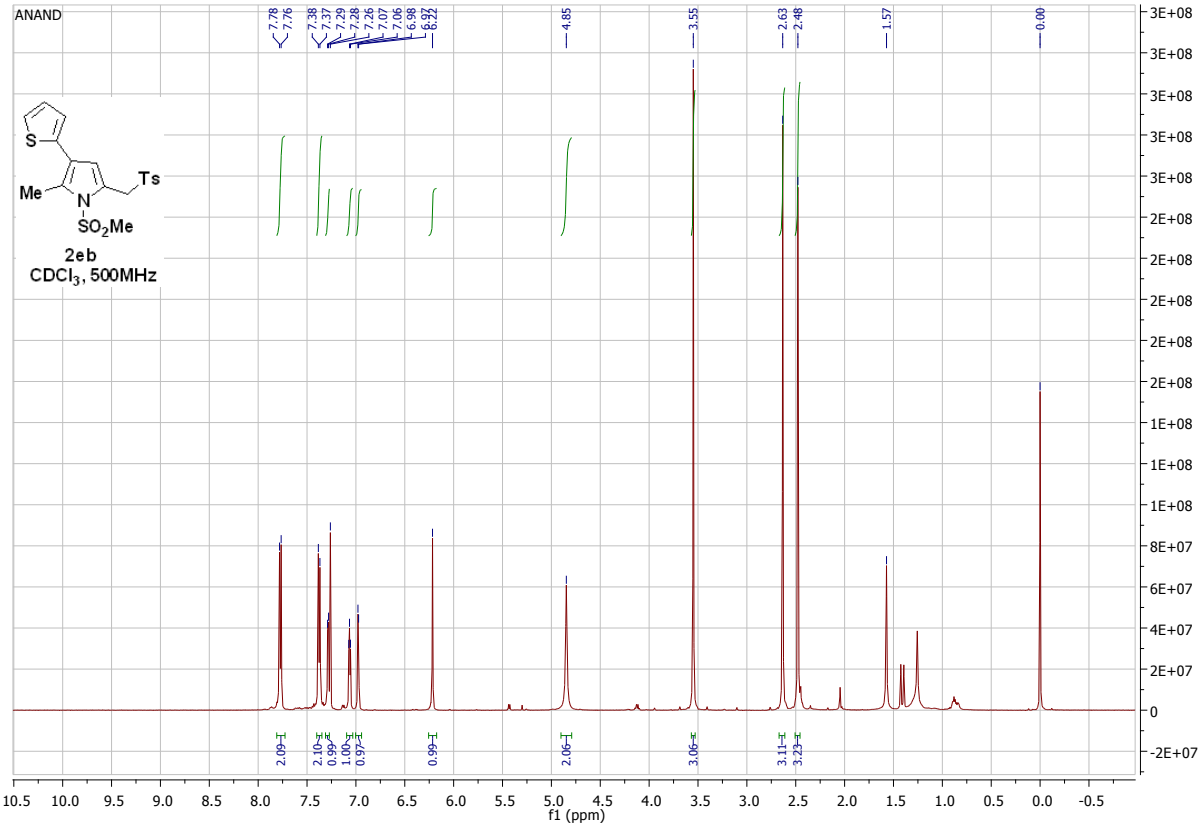

ANAND
Ph
Me
N
SO2Ph
SO2Me
2da
CDCl3, 75 MHz
f1 (ppm)

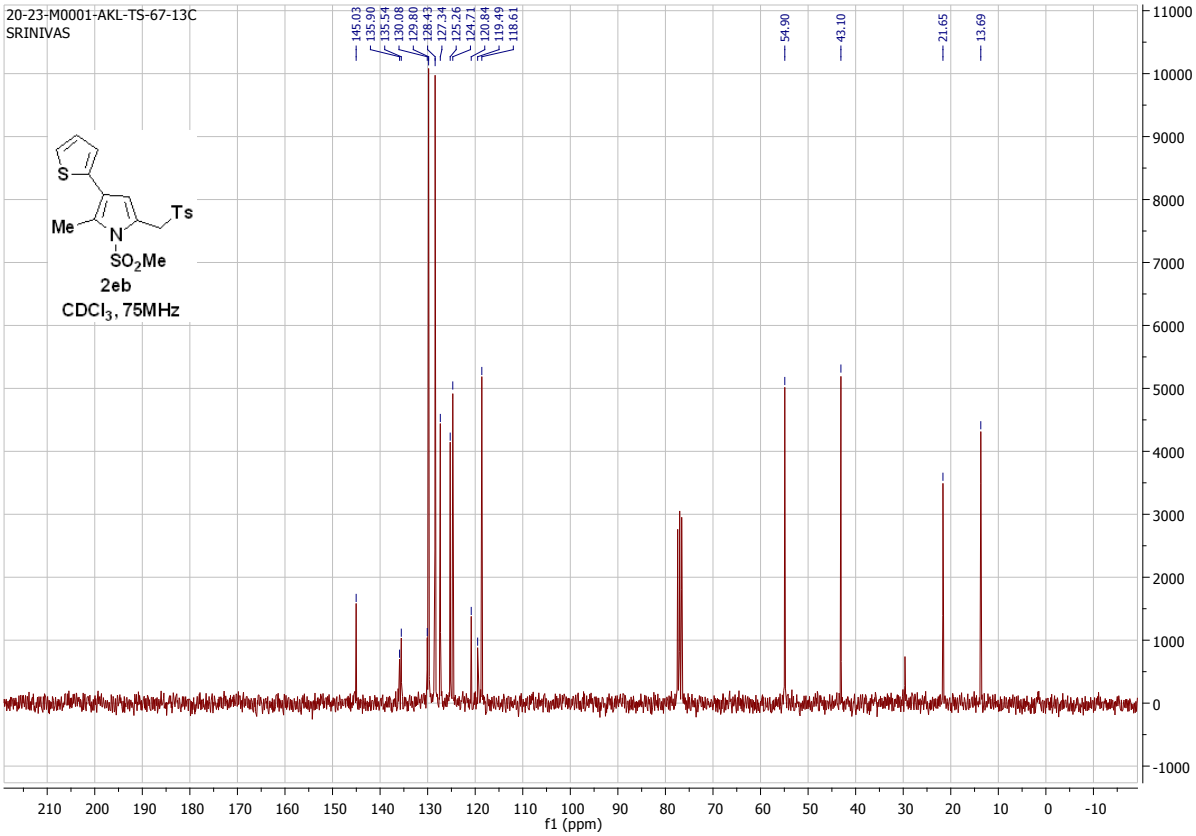

ANAND
Ph
Me
N
Ts
SO2Me
2db
CDCl3, 300 MHz
7.81
7.78
7.42
7.39
7.37
7.33
7.30
7.28
7.27
7.26
7.25
6.22
4.87
3.55
2.54
2.48
1.58
0.00
2.00
4.17
3.74
0.98
2.06
3.11
3.12
3.12
f1 (ppm)

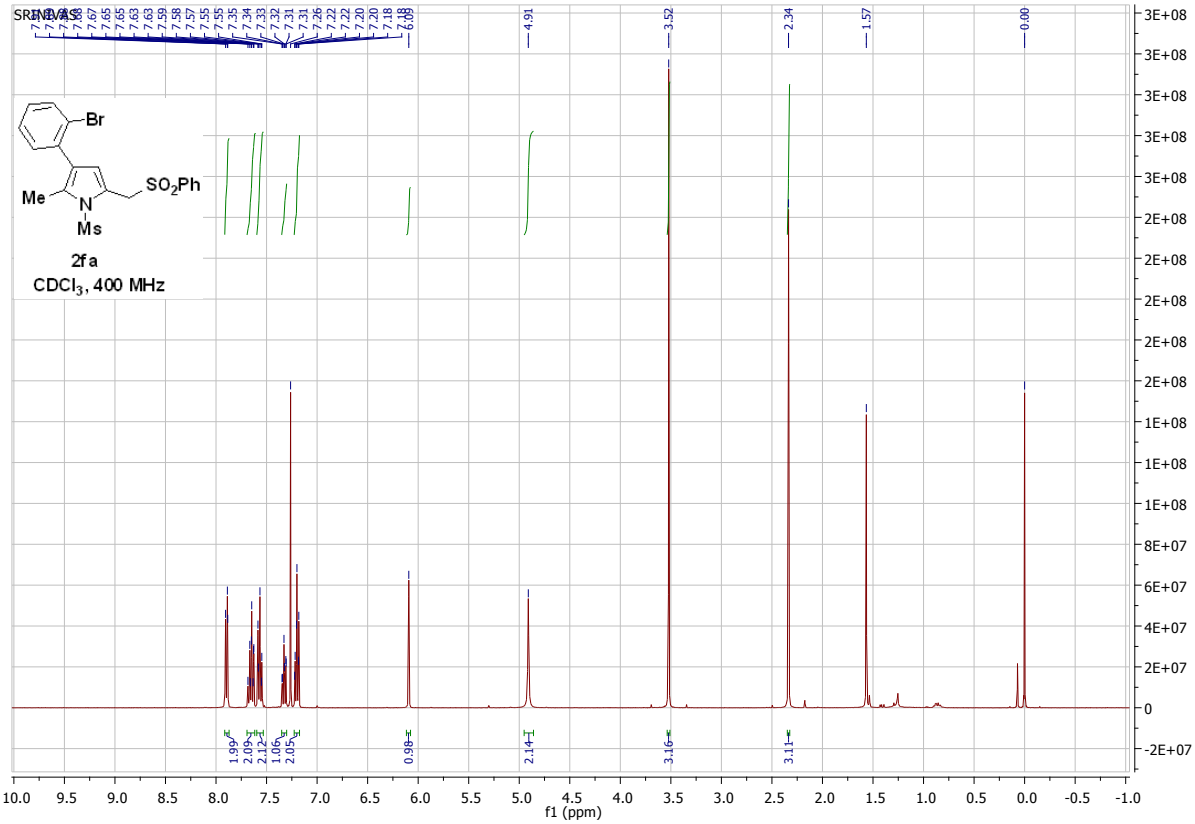

ATHIRA
Ph
Me
N
Ts
SO2Me
2db
CDCl3, 125 MHz
144.94
135.78
134.28
129.86
129.77
128.70
128.41
126.89
126.23
120.38
118.85
77.25
77.00
76.75
55.00
43.06
21.62
13.53
f1 (ppm)

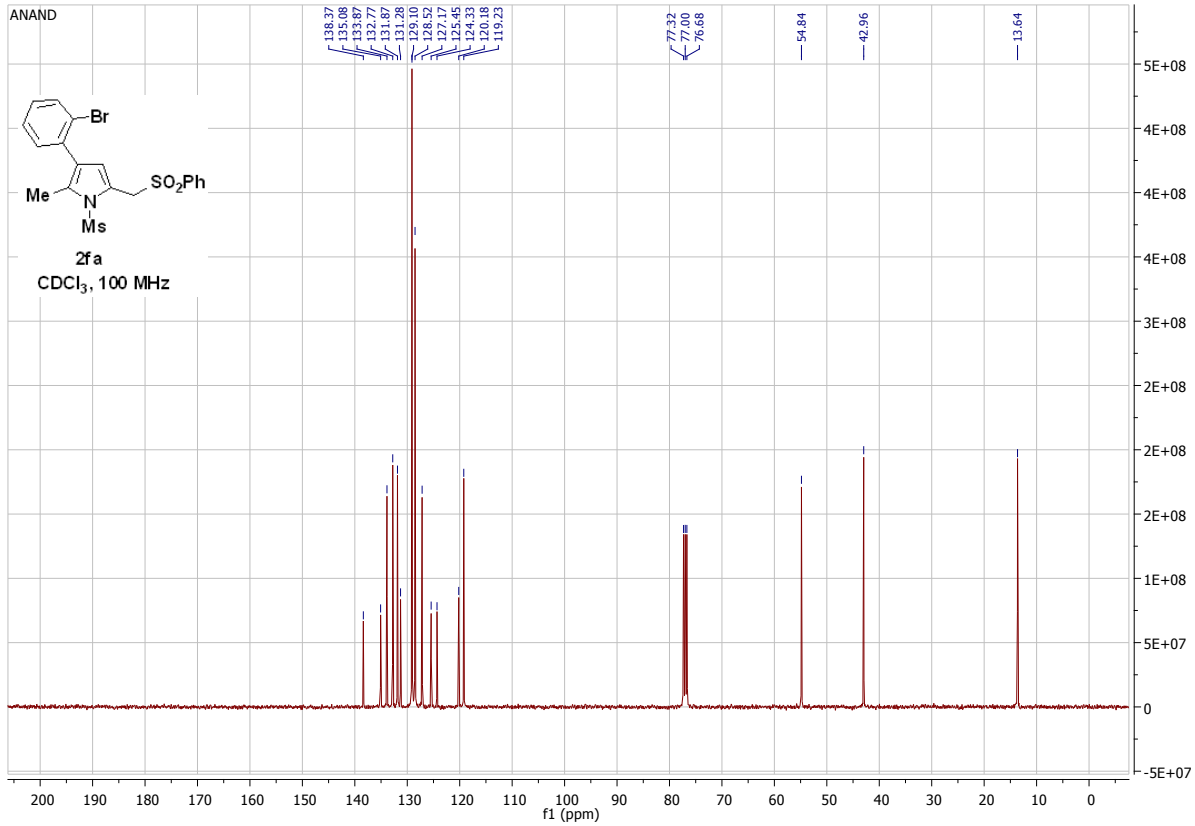

ATHIRA
7.91
7.90
7.72
7.70
7.69
7.61
7.59
7.58
7.29
7.28
7.26
7.07
7.06
7.06
6.98
6.97
6.22
4.88
3.55
2.64
1.26
0.00
S
Me
N
SO2Ph
SO2Me
2ea
CDCl3, 500 MHz
2.04
1.17
2.19
1.05
0.97
0.98
1.00
2.01
3.24
3.20
f1 (ppm)

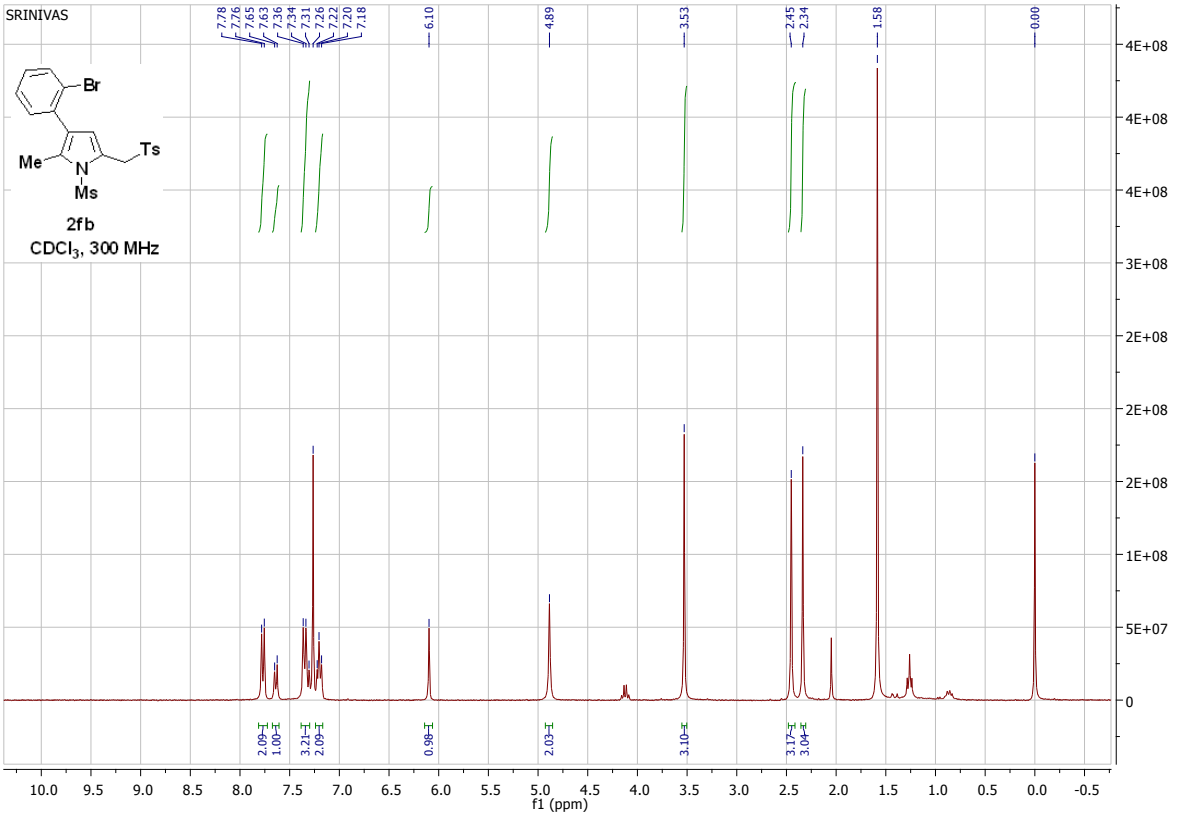

ANAND
138.54
135.86
133.98
130.19
129.20
128.46
127.36
125.30
124.76
120.67
119.59
118.74
77.25
77.00
76.75
54.89
43.15
13.70
S
Me
N
SO2Ph
SO2Me
2ea
CDCl3, 125 MHz
f1 (ppm)

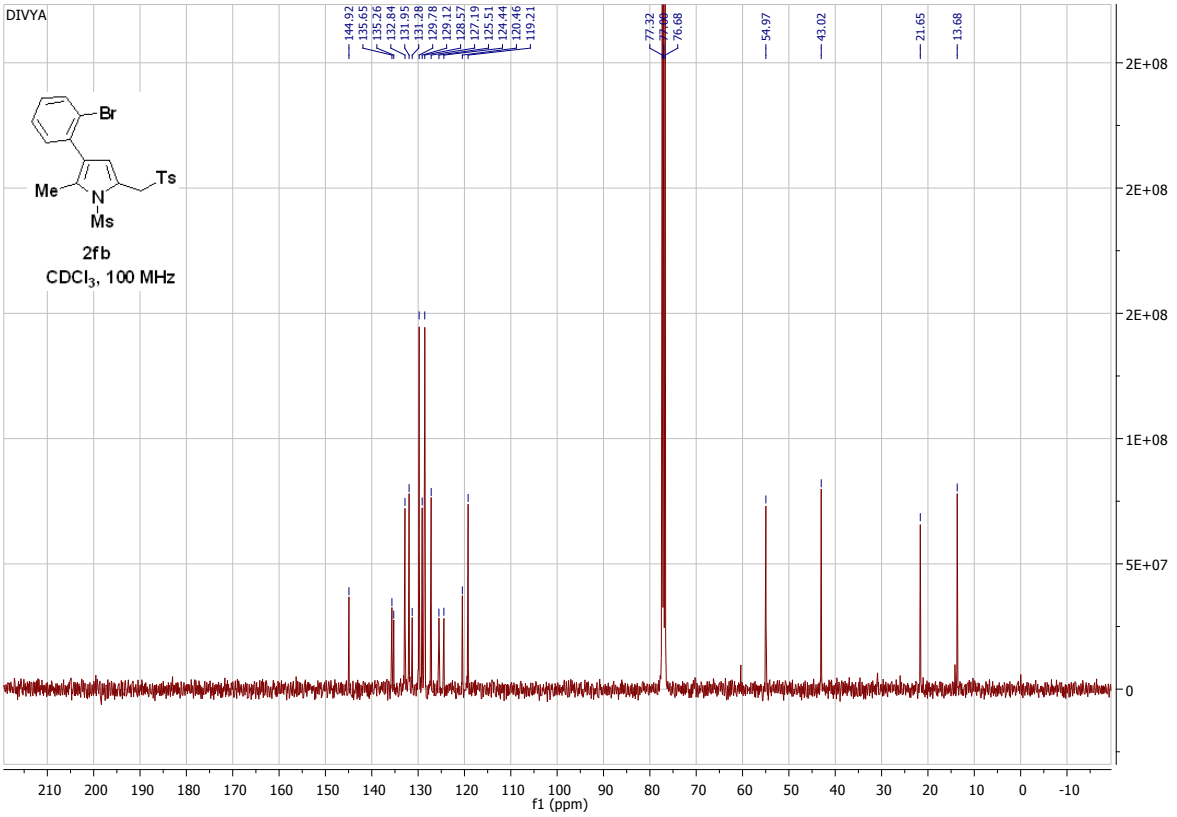

ANAND
7.78
7.76
7.38
7.37
7.29
7.28
7.26
7.07
7.06
6.98
6.92
4.85
3.55
2.63
2.48
1.57
0.00
S
Me
N
Ts
SO2Me
2eb
CDCl3, 500MHz
2.09
2.10
0.99
1.00
0.97
0.99
2.06
3.06
3.11
3.23
f1 (ppm)

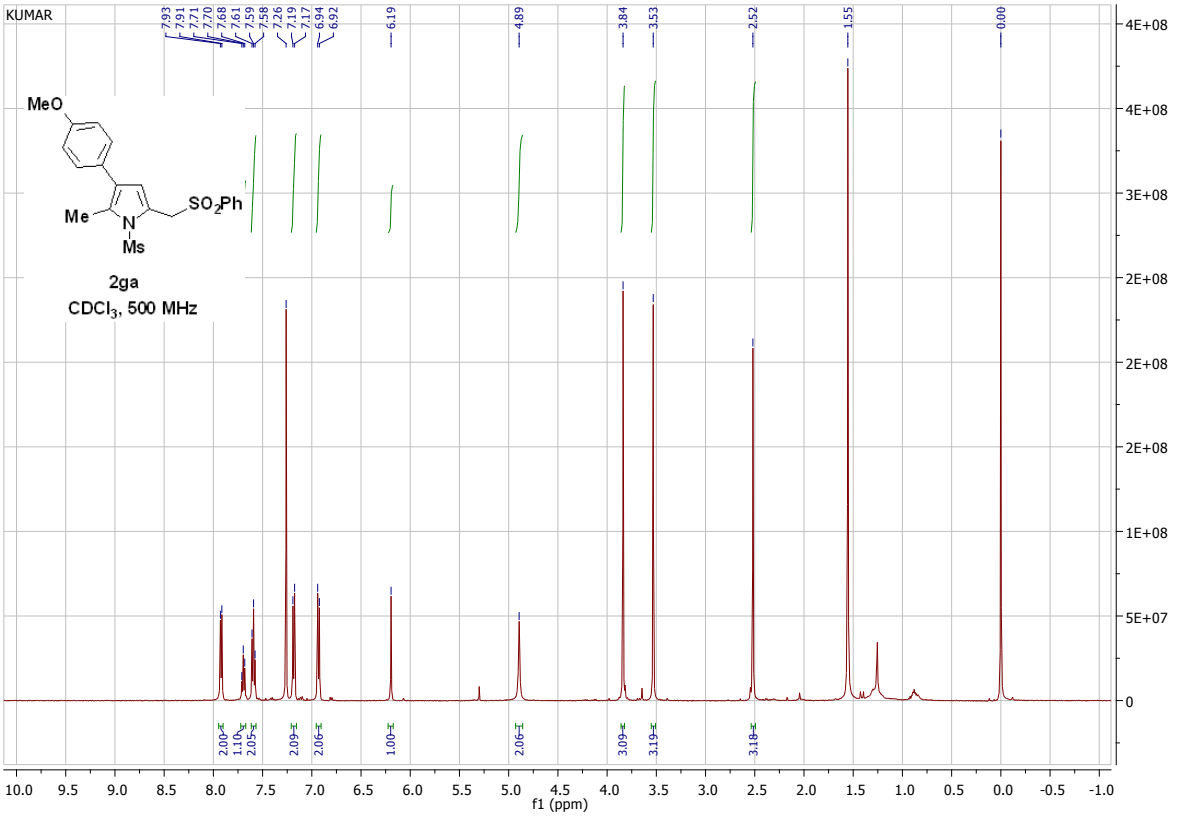

20-23-M0001-AKL-TS-67-13C
SRINIVAS
145.03
135.90
135.54
130.08
129.80
128.43
127.34
125.26
124.71
120.84
119.49
118.61
54.90
43.10
21.65
13.69
S
Me
N
Ts
SO2Me
2eb
CDCl3, 75MHz
f1 (ppm)

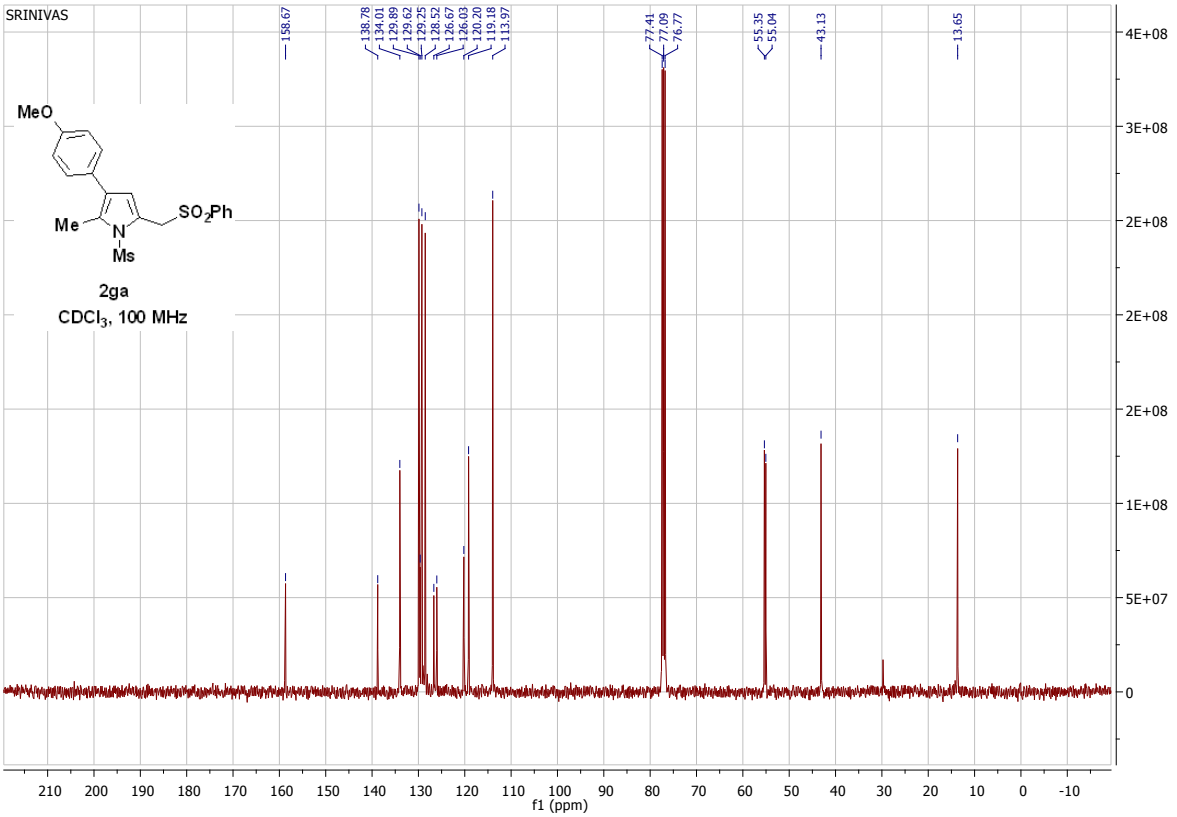

SRINIVAS
Br
Me
N
Ms
SO2Ph
2fa
CDCl3, 400 MHz
f1 (ppm)

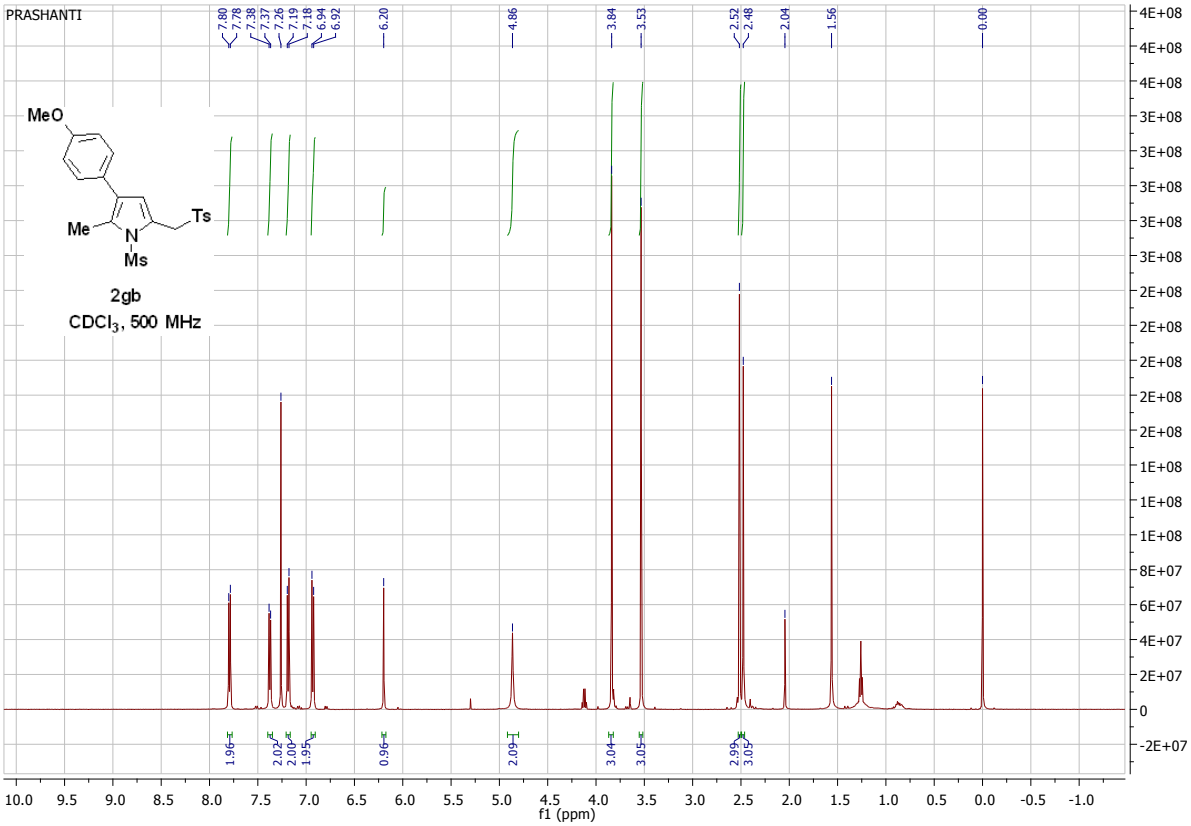

ANAND
Br
Me
N
Ms
SO2Ph
2fa
CDCl3, 100 MHz
f1 (ppm)

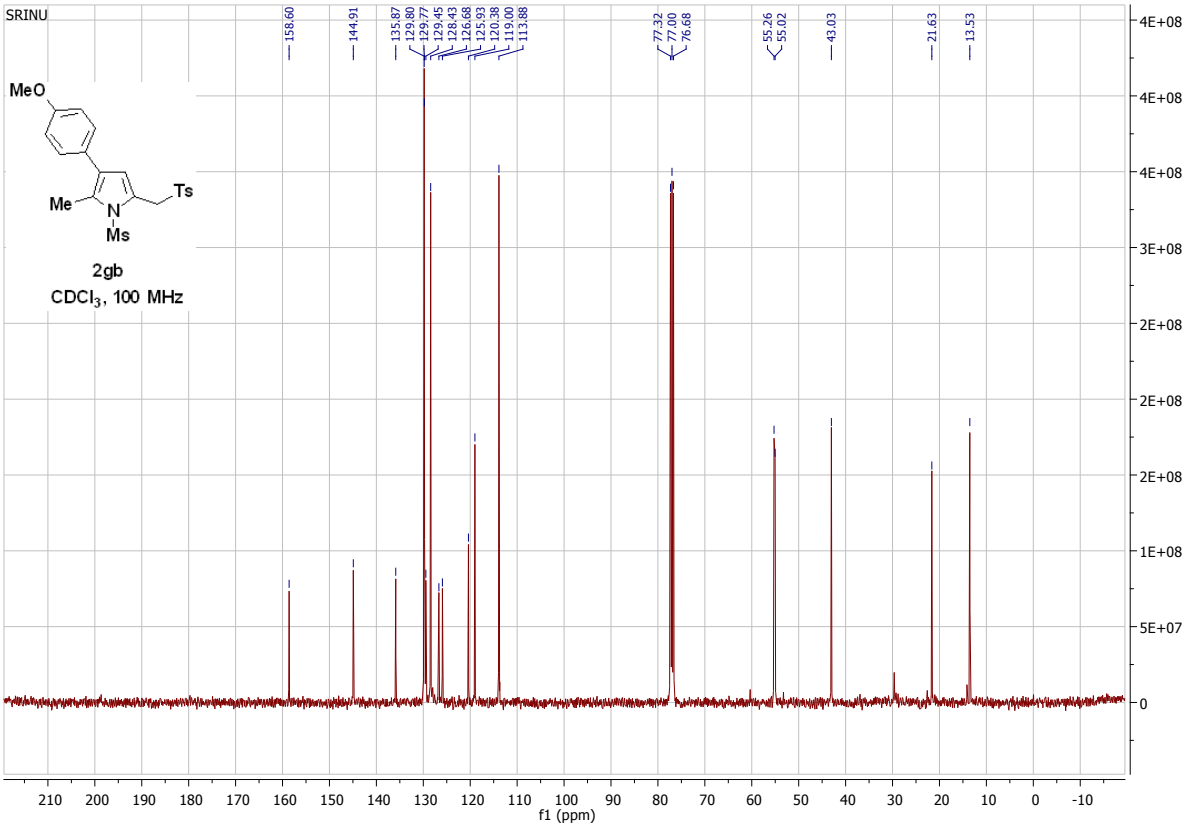

SRINIVAS
Br
Me
N
Ts
Ms
2fb
CDCl3, 300 MHz
f1 (ppm)

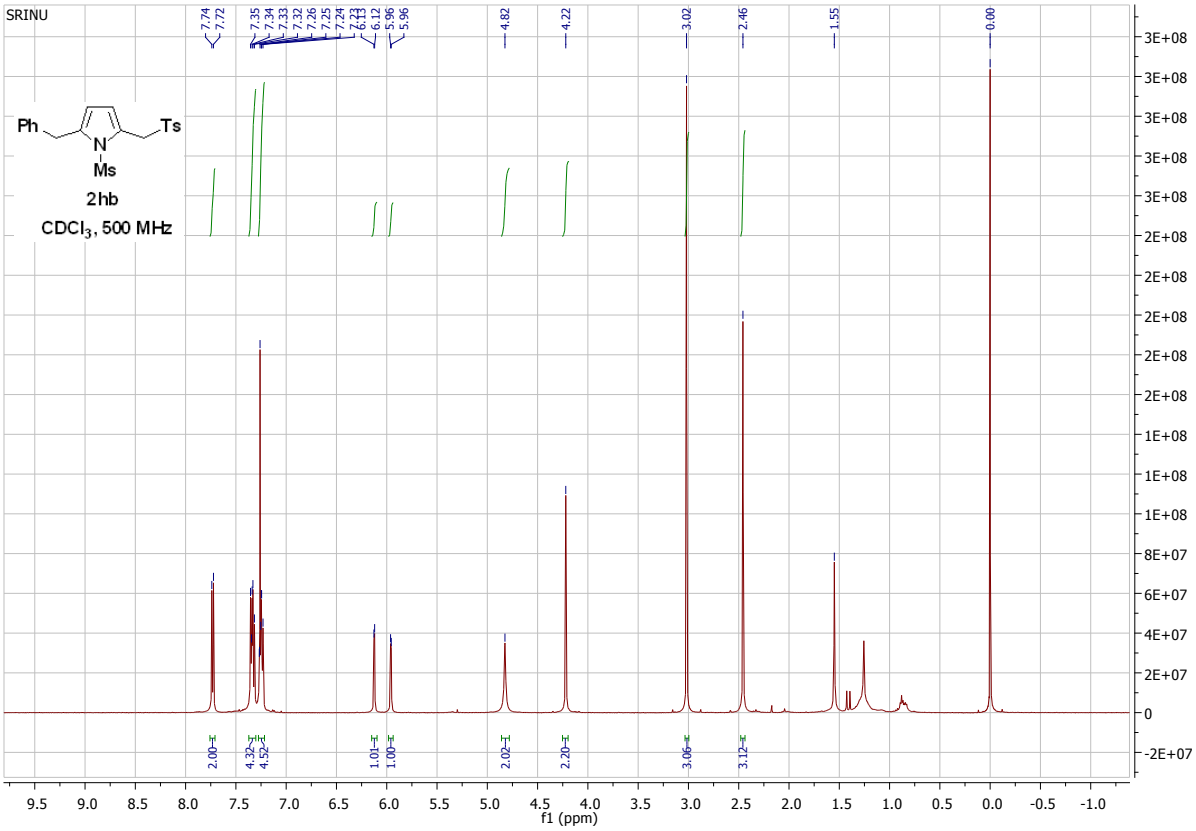

DIVYA
Br
Me
N
Ts
Ms
2fb
CDCl3, 100 MHz
f1 (ppm)

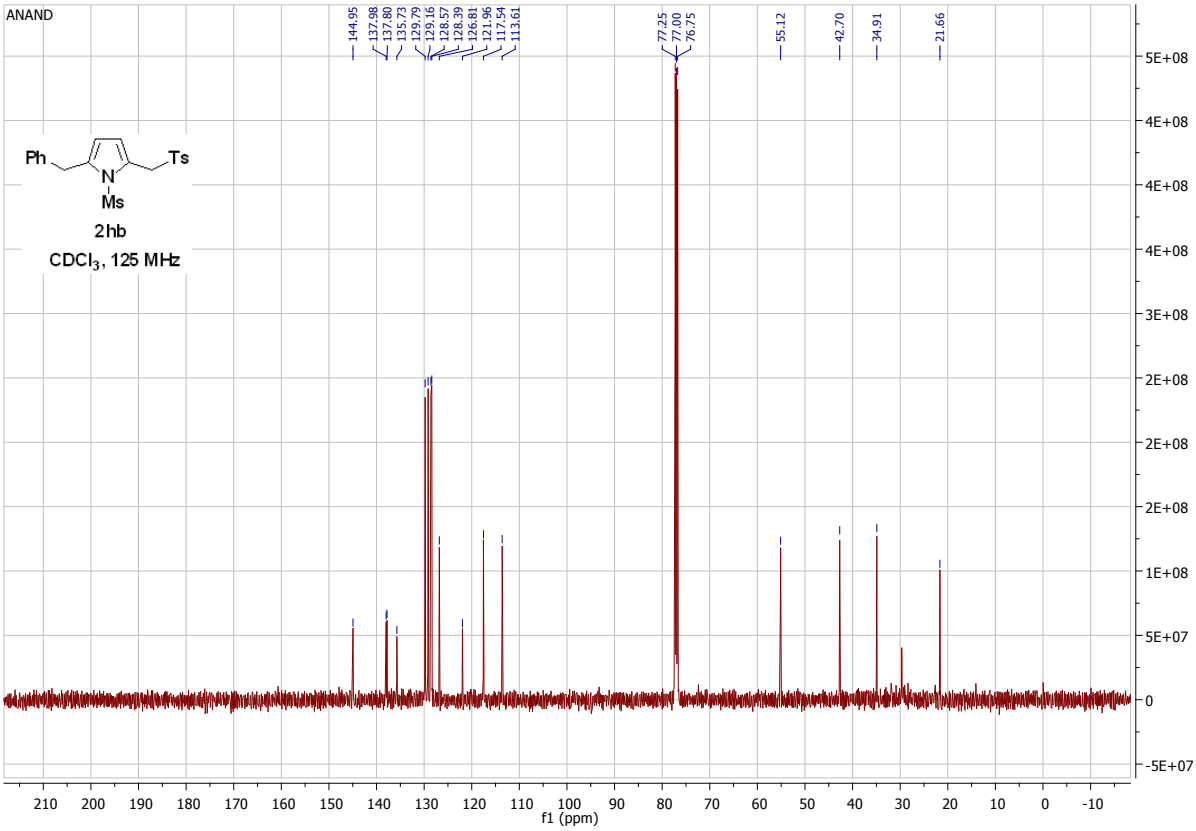

KUMAR
MeO
Me
N
Ms
SO2Ph
2ga
CDCl3, 500 MHz
f1 (ppm)

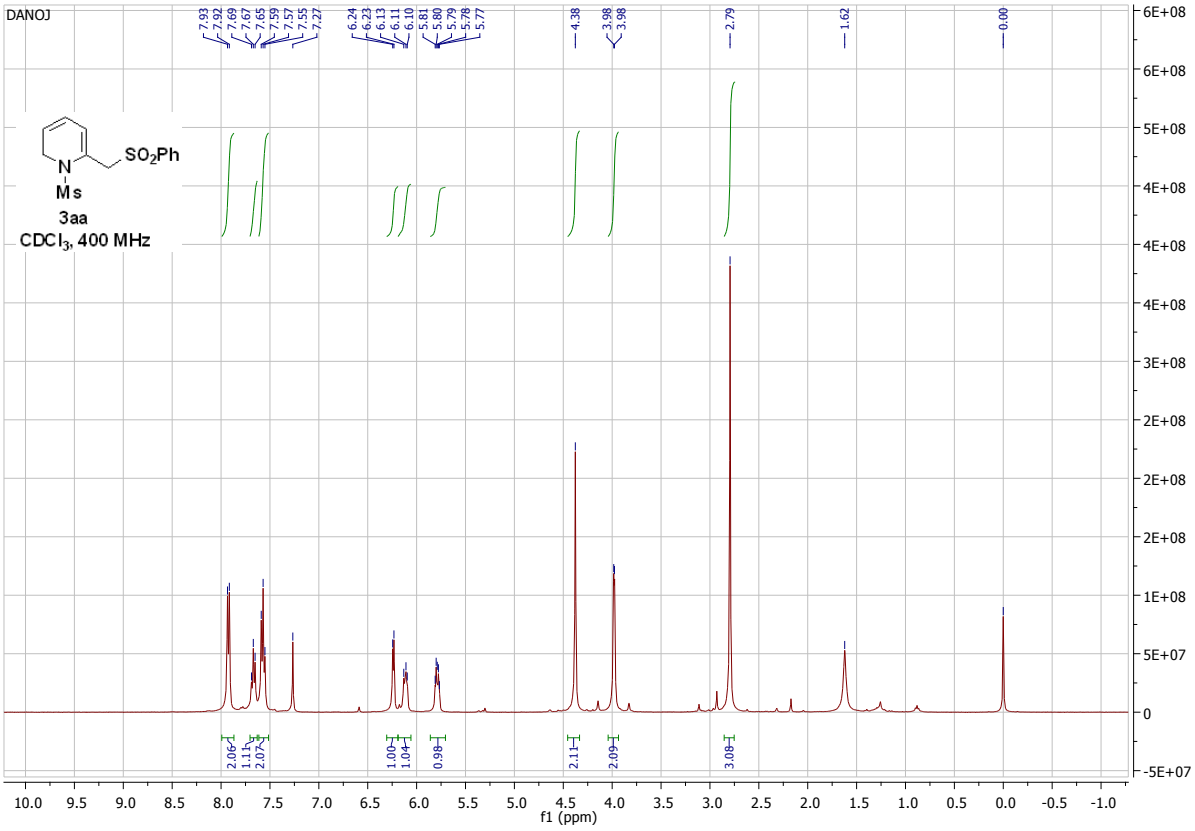

SRINIVAS
MeO
Me
N
Ms
SO2Ph
2ga
CDCl3, 100 MHz
f1 (ppm)

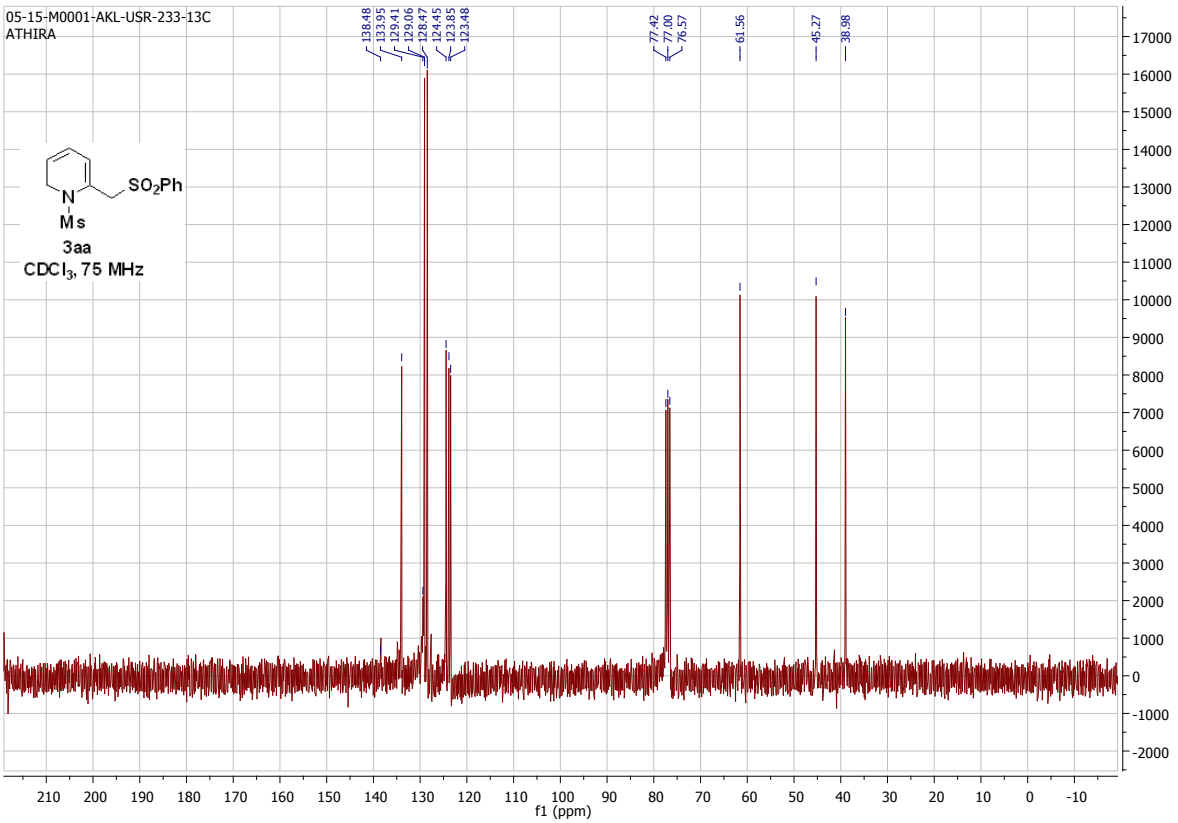

PRASHANTI
MeO
Me
N
Ts
Ms
2gb
CDCl3, 500 MHz
f1 (ppm)

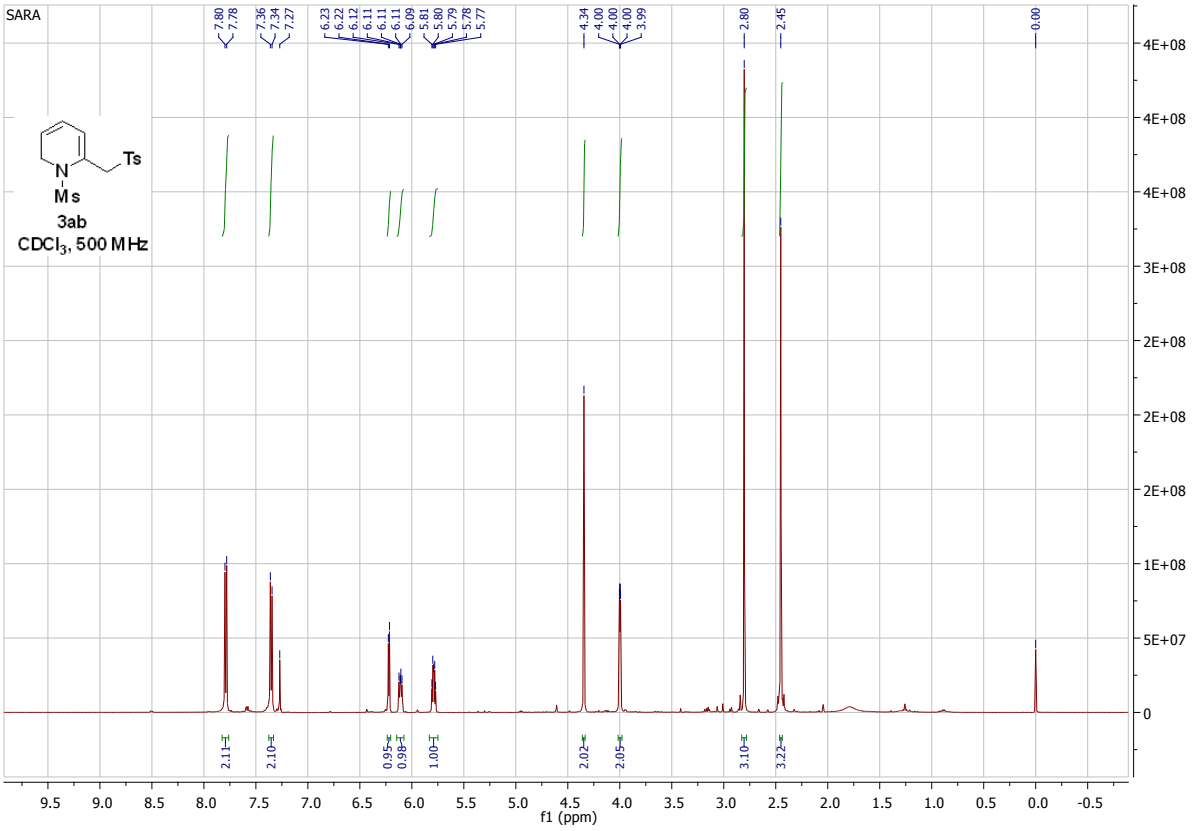

SRINU
MeO
Me
N
Ts
Ms
2gb
CDCl3, 100 MHz
f1 (ppm)

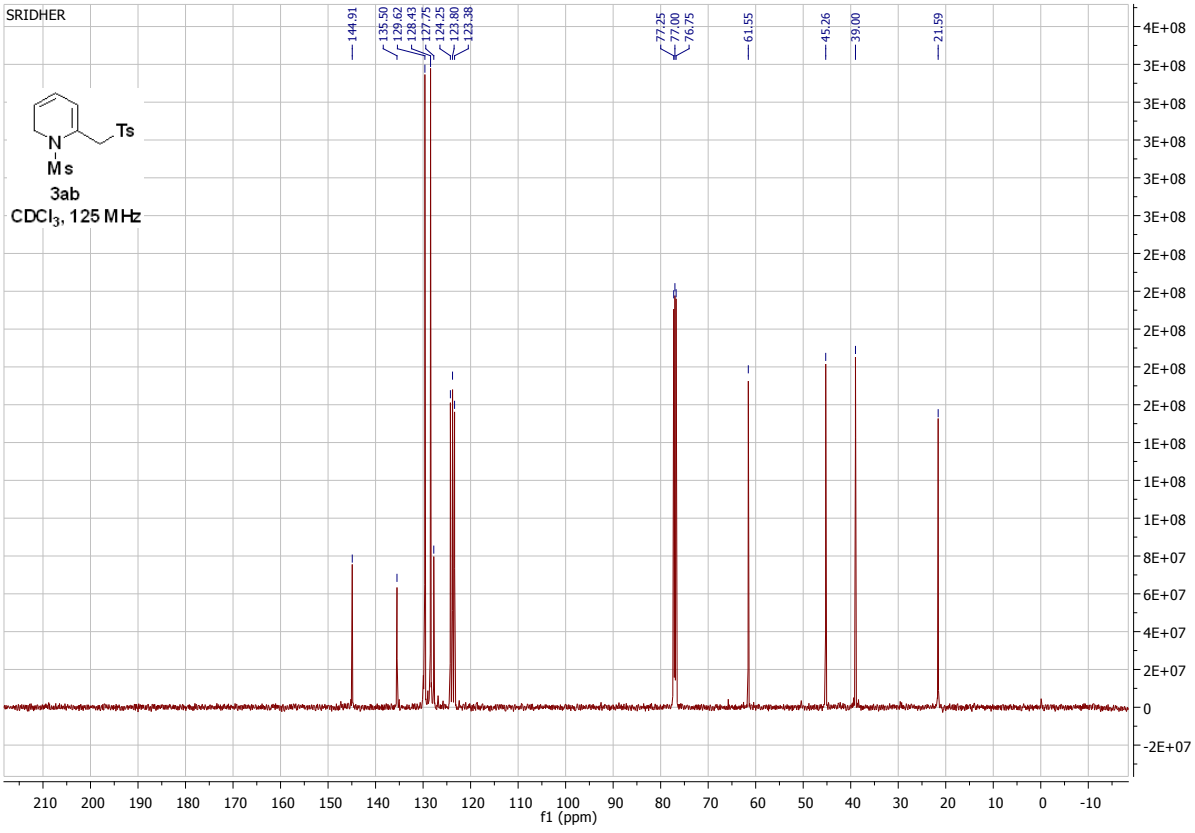

SRINU
Ph
Ts
N
Ms
2hb
CDCl3, 500 MHz
f1 (ppm)

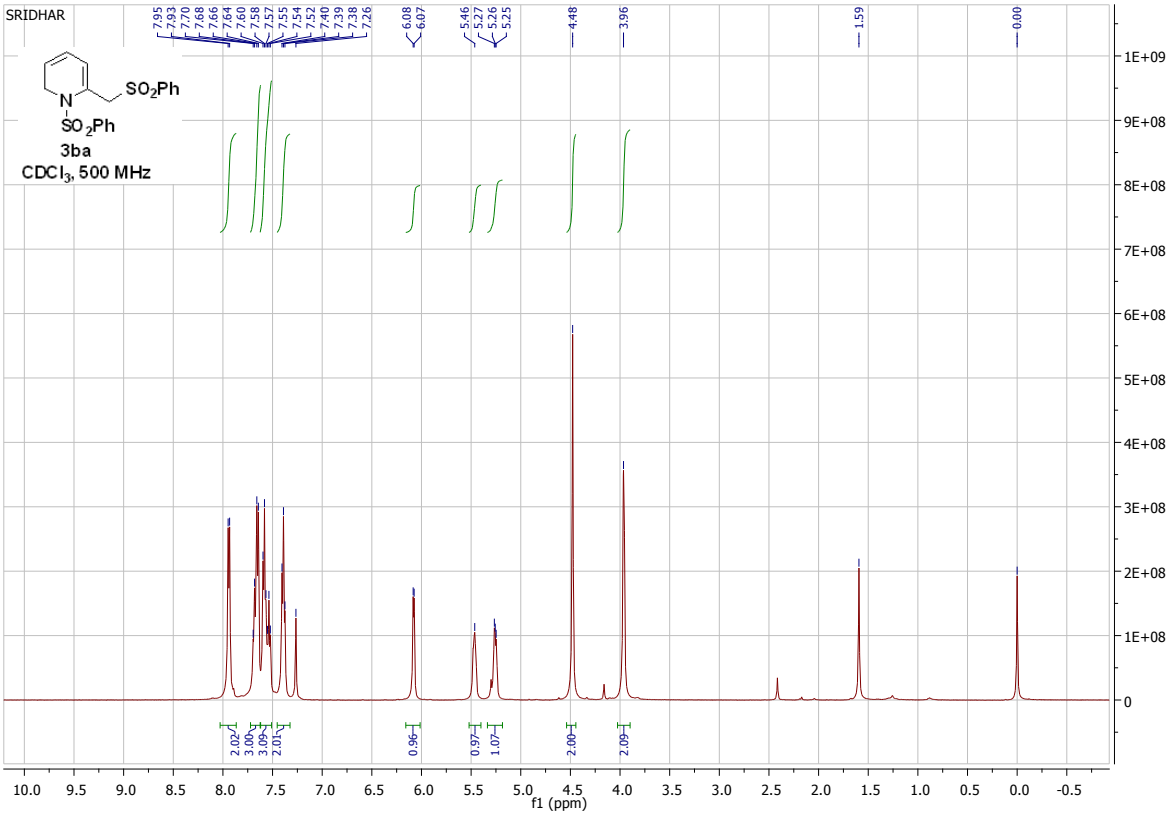

ANAND
Ph
Ts
N
Ms
2hb
CDCl3, 125 MHz
f1 (ppm)

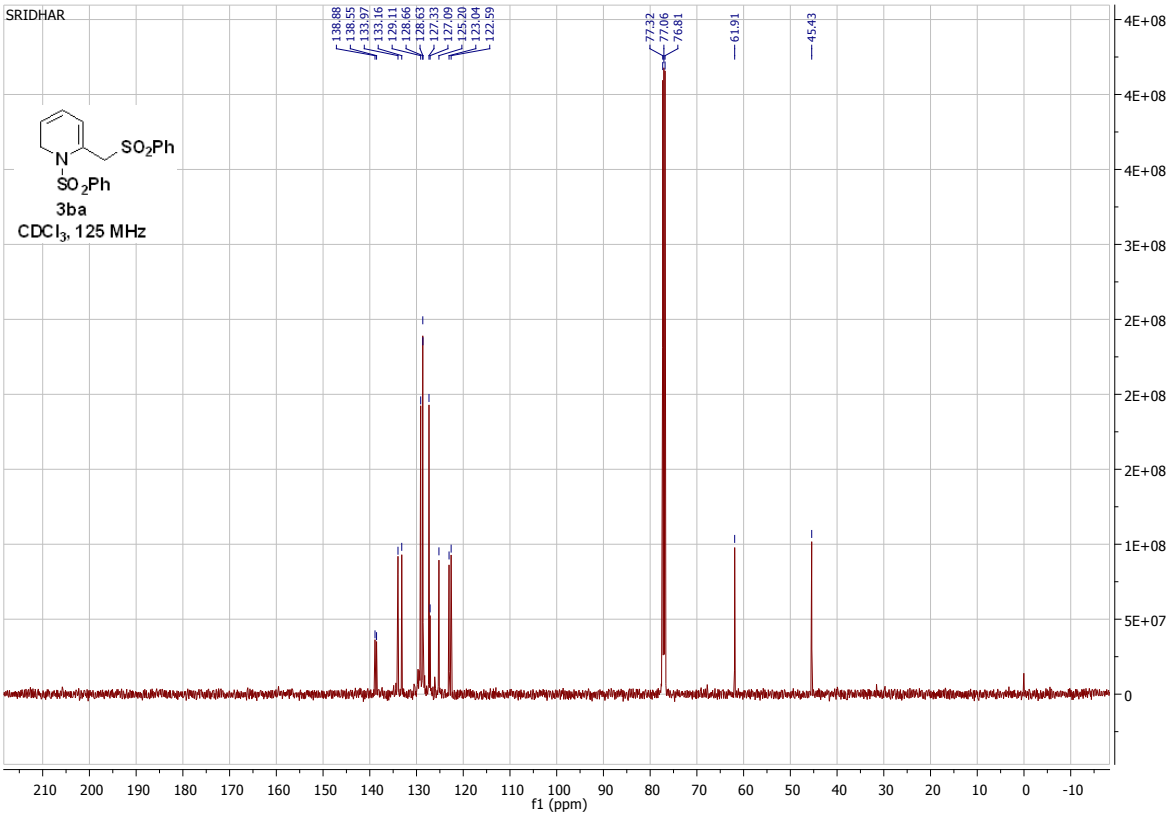

DANOJ
7.93
7.92
7.69
7.67
7.65
7.59
7.57
7.55
7.27
6.24
6.23
6.13
6.11
6.10
5.81
5.80
5.79
5.78
5.77
4.38
3.98
3.98
2.79
1.62
0.00
SO2Ph
N
Ms
3aa
CDCl3, 400 MHz
2.06
1.11
2.07
1.00
1.04
0.98
2.11
2.09
3.08
f1 (ppm)

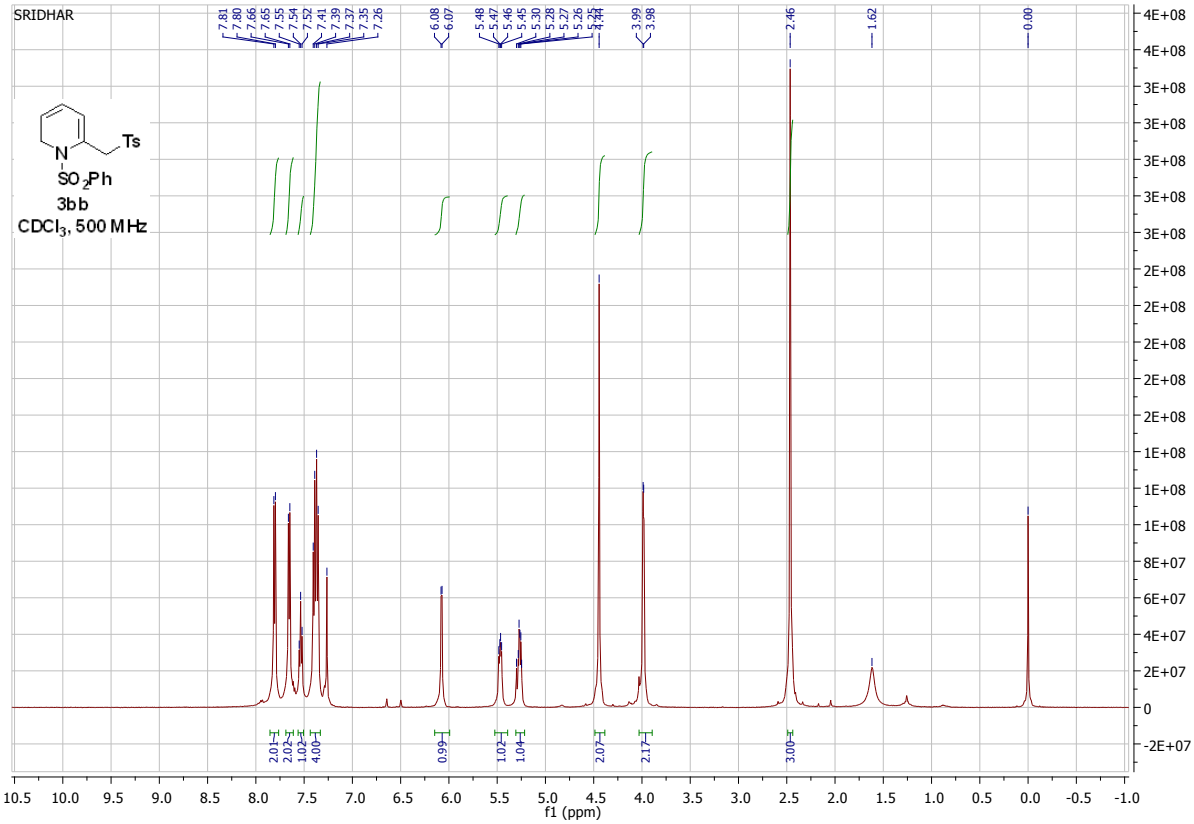

05-15-M0001-AKL-USR-233-13C
ATHIRA
138.48
133.95
129.41
129.06
128.47
124.45
123.85
123.48
77.42
77.00
76.57
61.56
45.27
38.98
SO2Ph
N
Ms
3aa
CDCl3, 75 MHz
f1 (ppm)

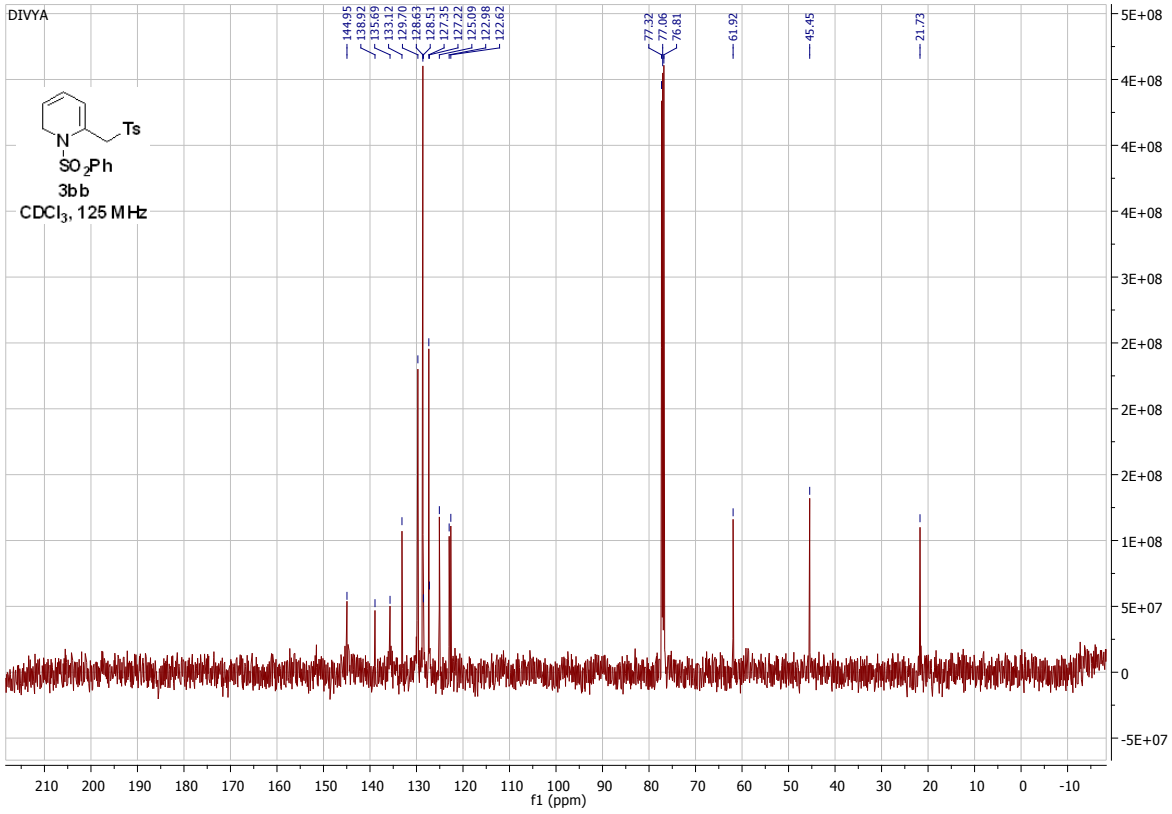

SARA
Ts
N
Ms
3ab
CDCl3, 500 MHz
f1 (ppm)

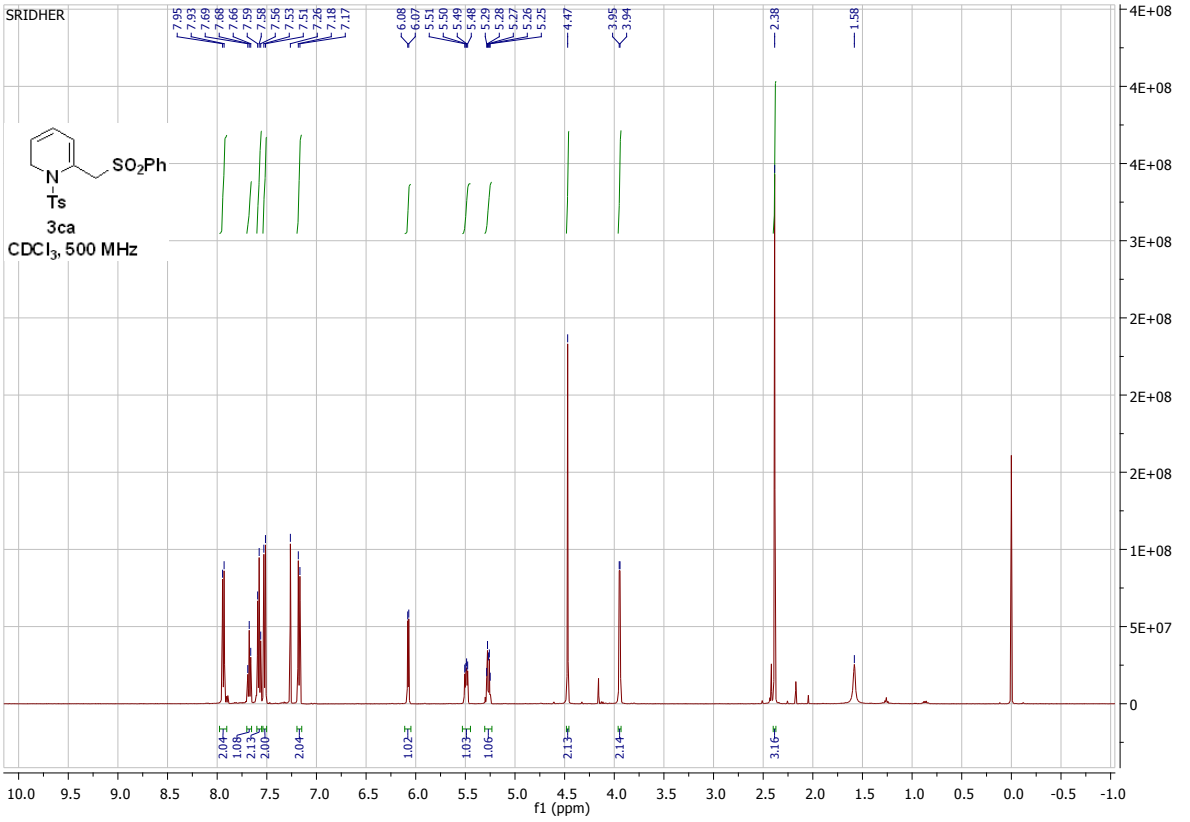

SRIDHER
Ts
N
Ms
3ab
CDCl3, 125 MHz
f1 (ppm)

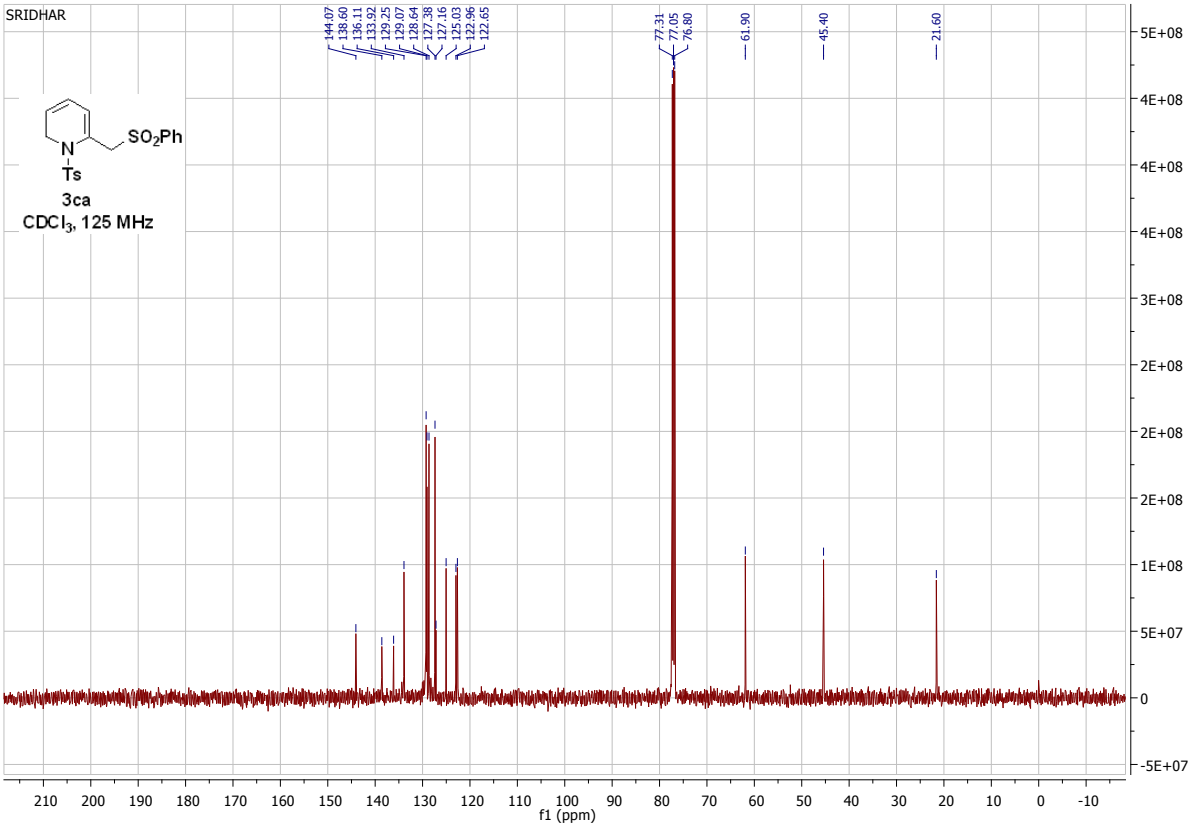

SRIDHAR
7.95
7.93
7.70
7.68
7.66
7.64
7.60
7.58
7.57
7.55
7.54
7.52
7.40
7.39
7.38
7.26
6.08
6.07
5.46
5.27
5.26
5.25
4.48
3.96
1.59
0.00
SO2Ph
N
SO2Ph
3ba
CDCl3, 500 MHz
2.02
3.00
3.09
2.01
0.96
0.97
1.07
2.00
2.09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

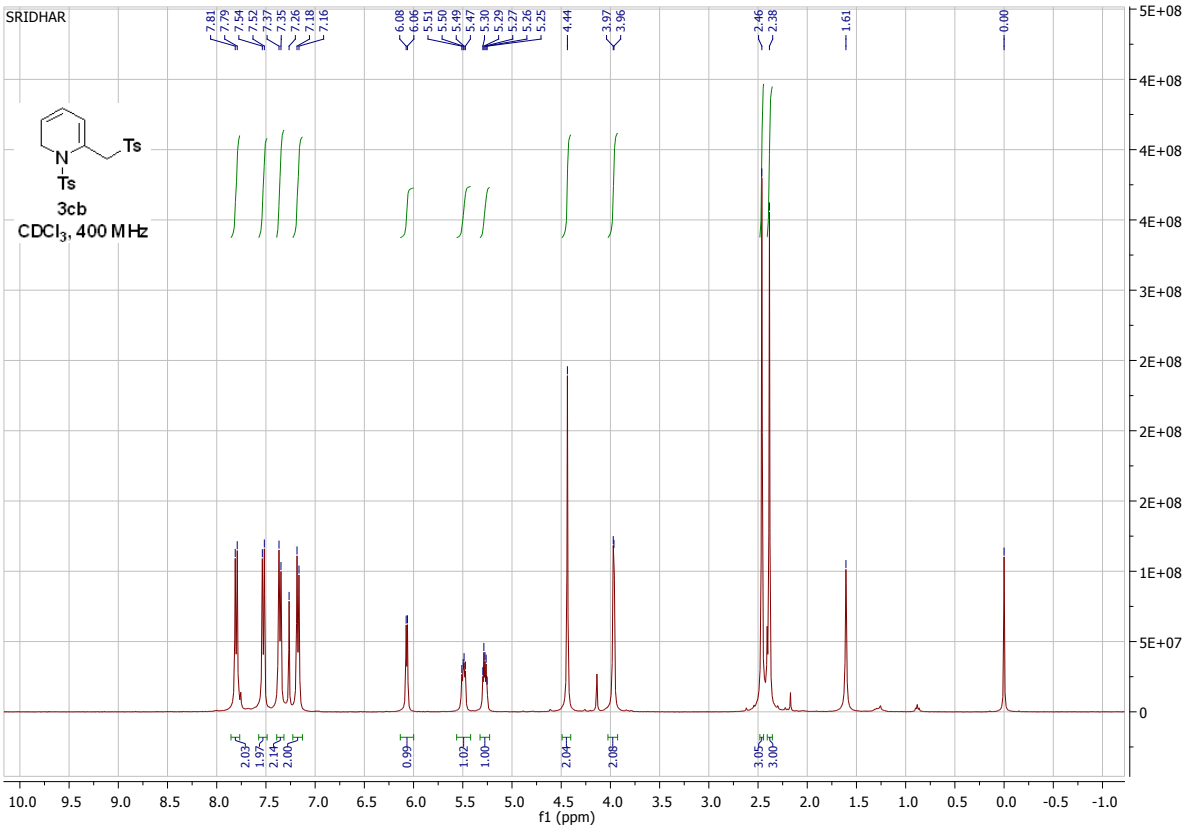

SRIDHAR
138.88
138.55
133.97
133.16
129.11
128.66
128.63
127.33
127.09
125.20
123.04
122.59
77.32
77.06
76.81
61.91
45.43
SO2Ph
N
SO2Ph
3ba
CDCl3, 125 MHz
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

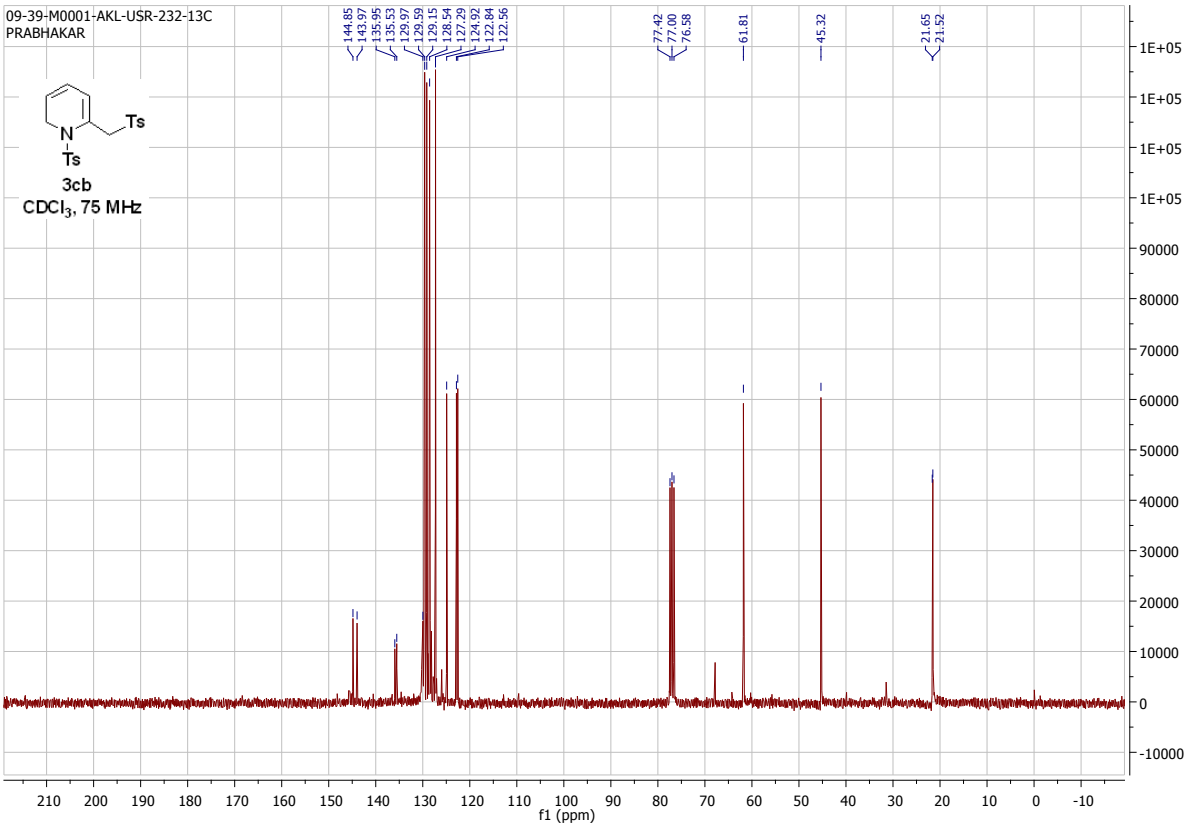

SRIDHAR
Ts
N
SO2Ph
3bb
CDCl3, 500 MHz
f1 (ppm)

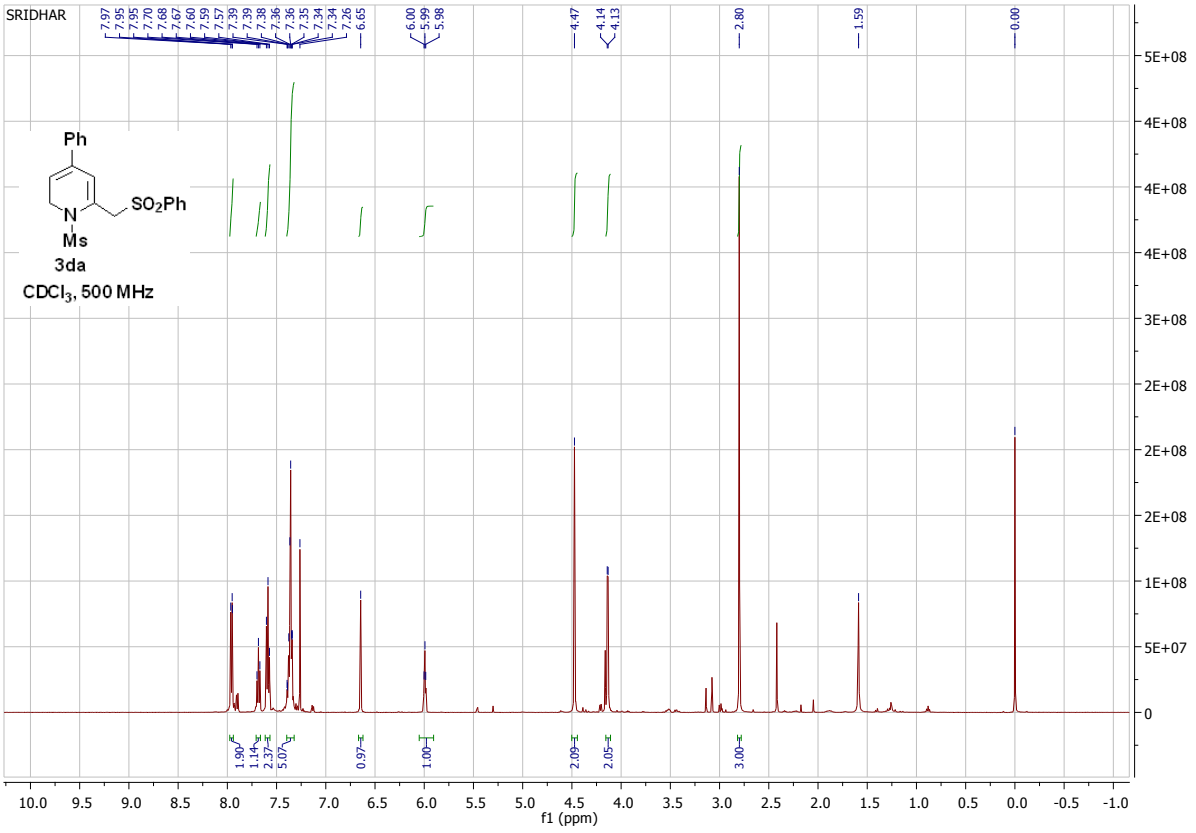

DIVYA
Ts
N
SO2Ph
3bb
CDCl3, 125 MHz
f1 (ppm)

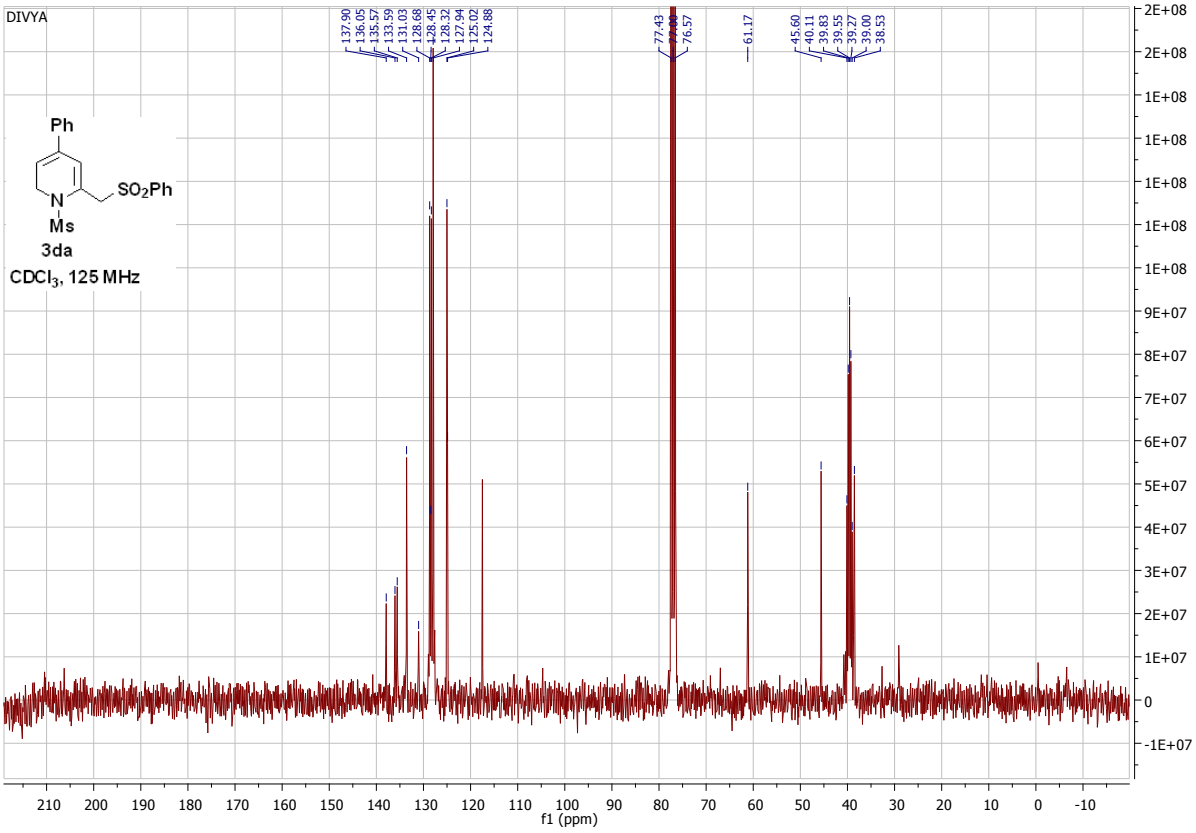

SRIDHER
SO2Ph
N
Ts
3ca
CDCl3, 500 MHz
f1 (ppm)

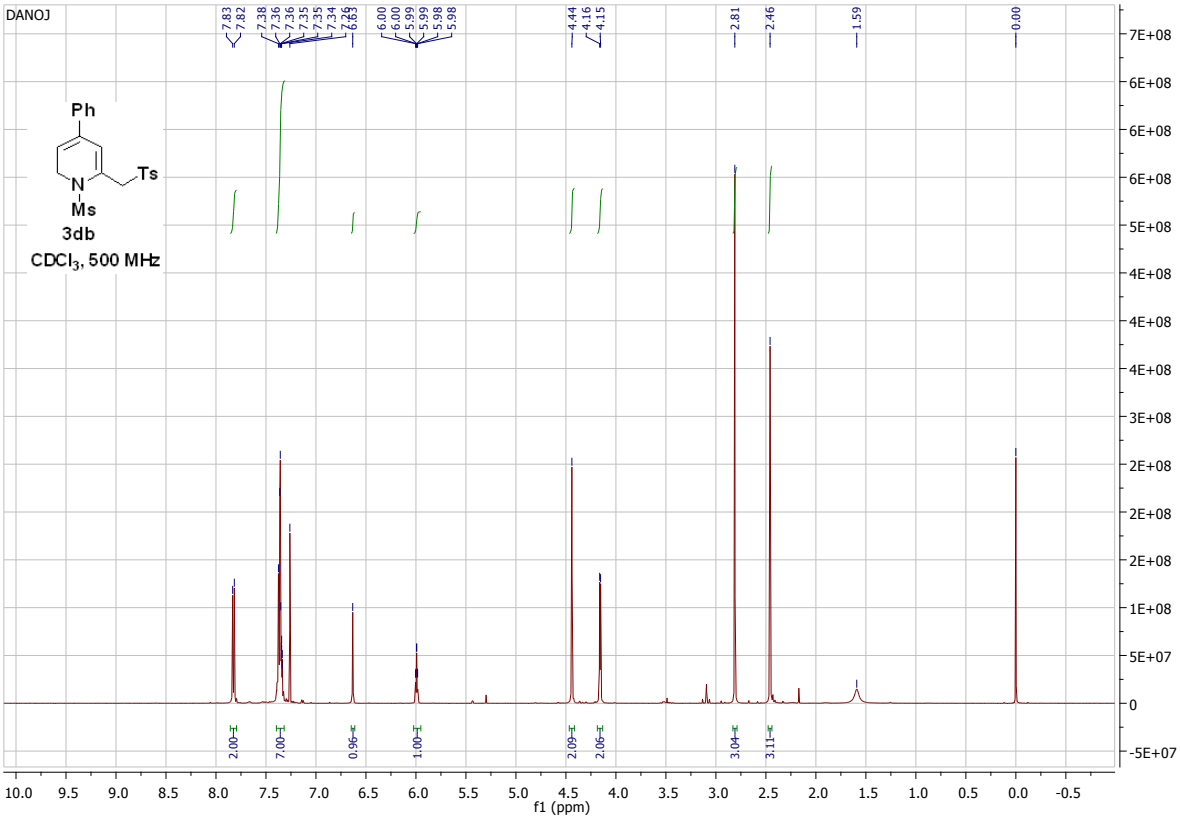

SRIDHAR
SO2Ph
N
Ts
3ca
CDCl3, 125 MHz
f1 (ppm)

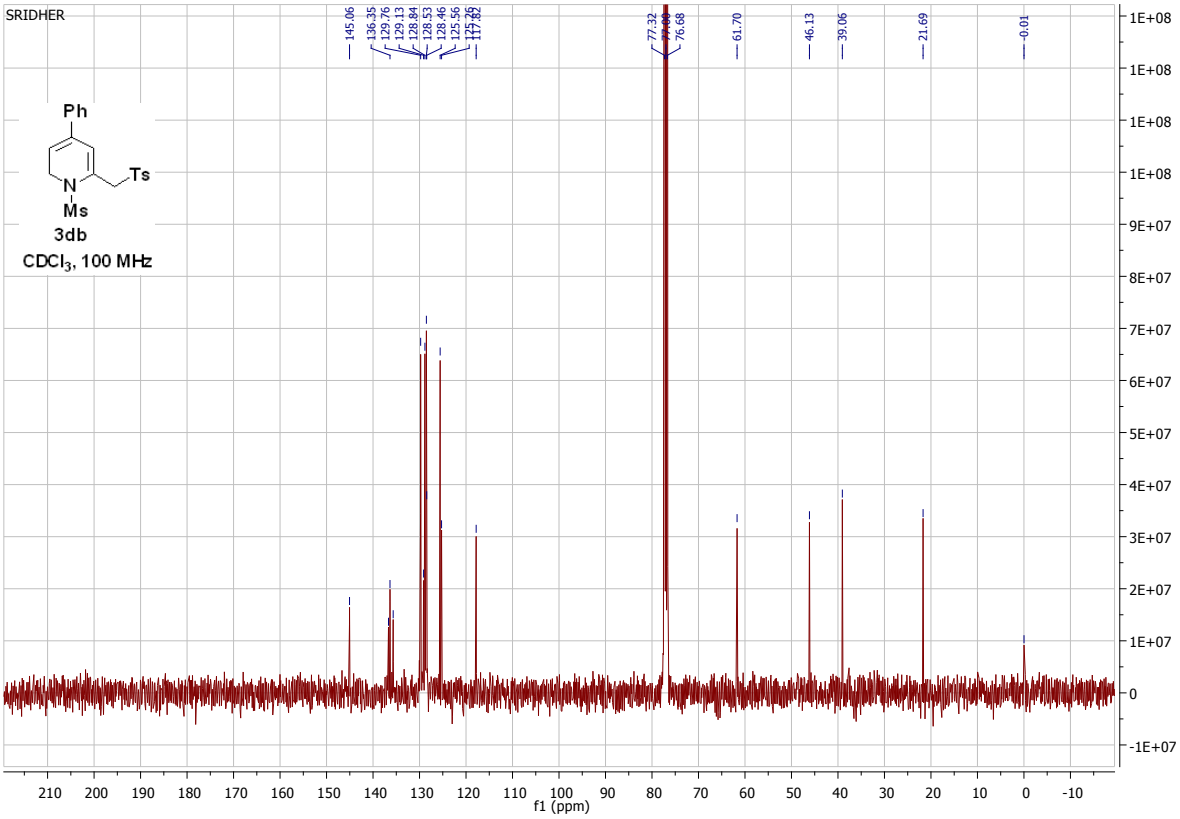

SRIDHAR
Ts
N
Ts
3cb
CDCl3, 400 MHz
f1 (ppm)

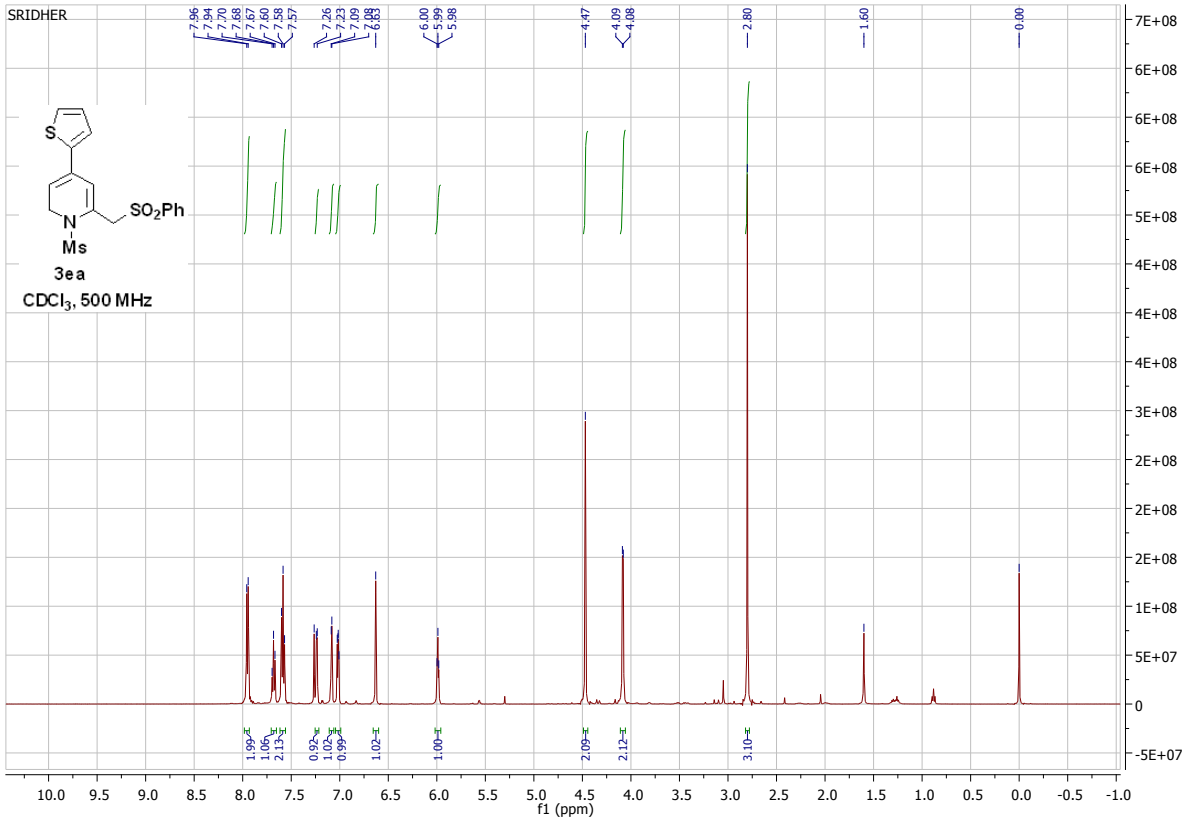

09-39-M0001-AKL-USR-232-13C
PRABHAKAR
Ts
N
Ts
3cb
CDCl3, 75 MHz
f1 (ppm)

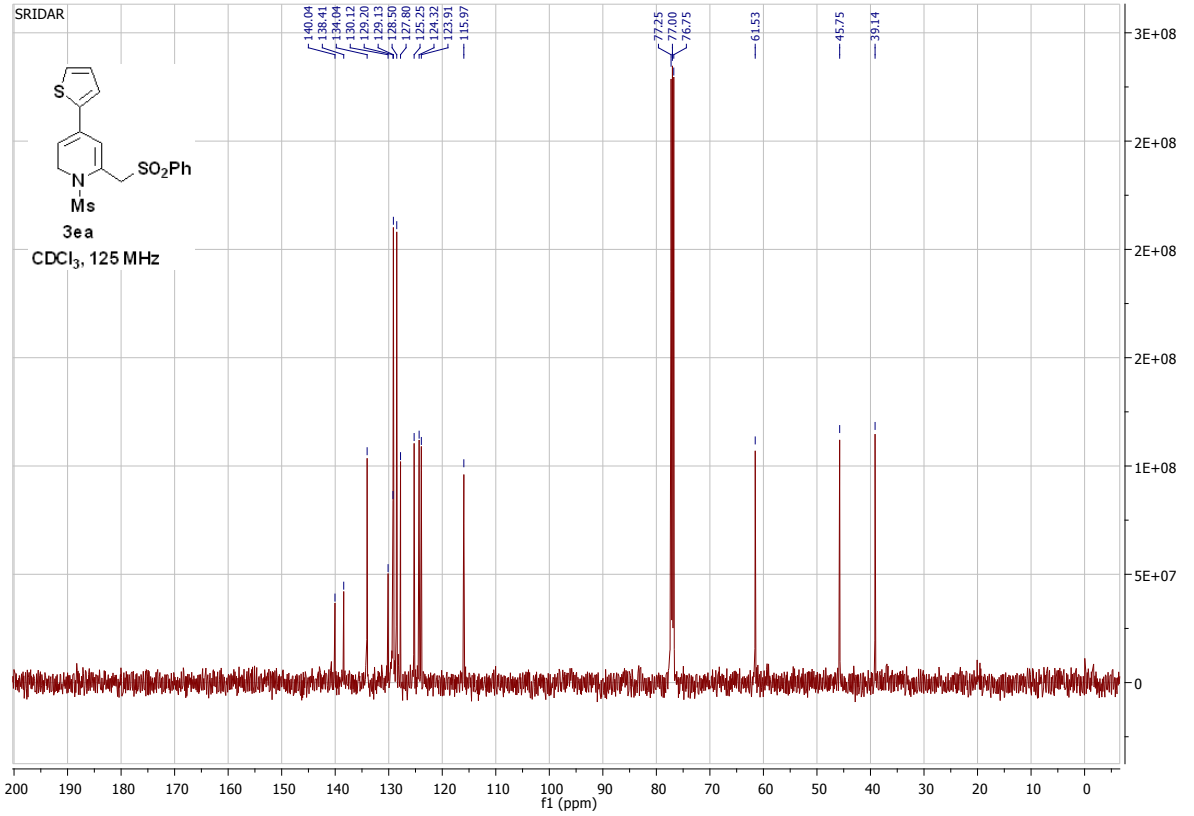

SRIDHAR
Ph
SO2Ph
N
Ms
3da
CDCl3, 500 MHz
f1 (ppm)

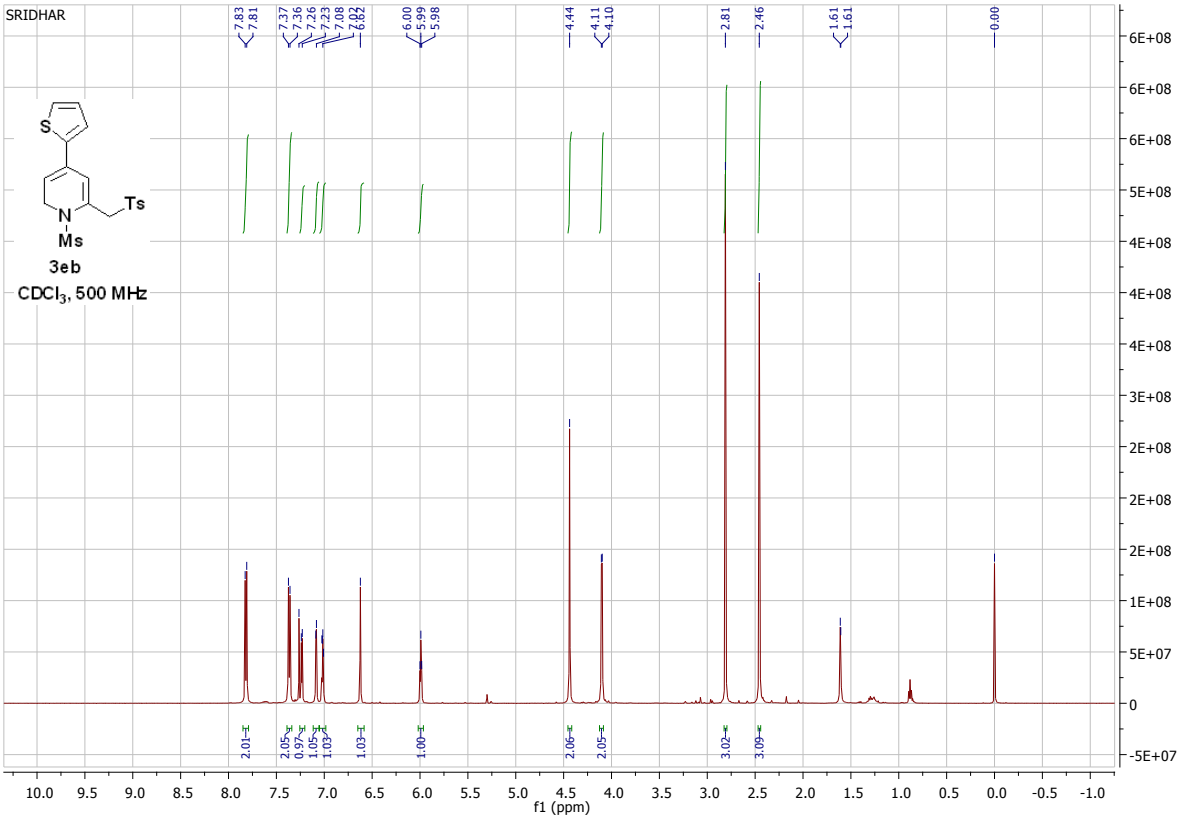

DIVYA
Ph
SO2Ph
N
Ms
3da
CDCl3, 125 MHz
f1 (ppm)

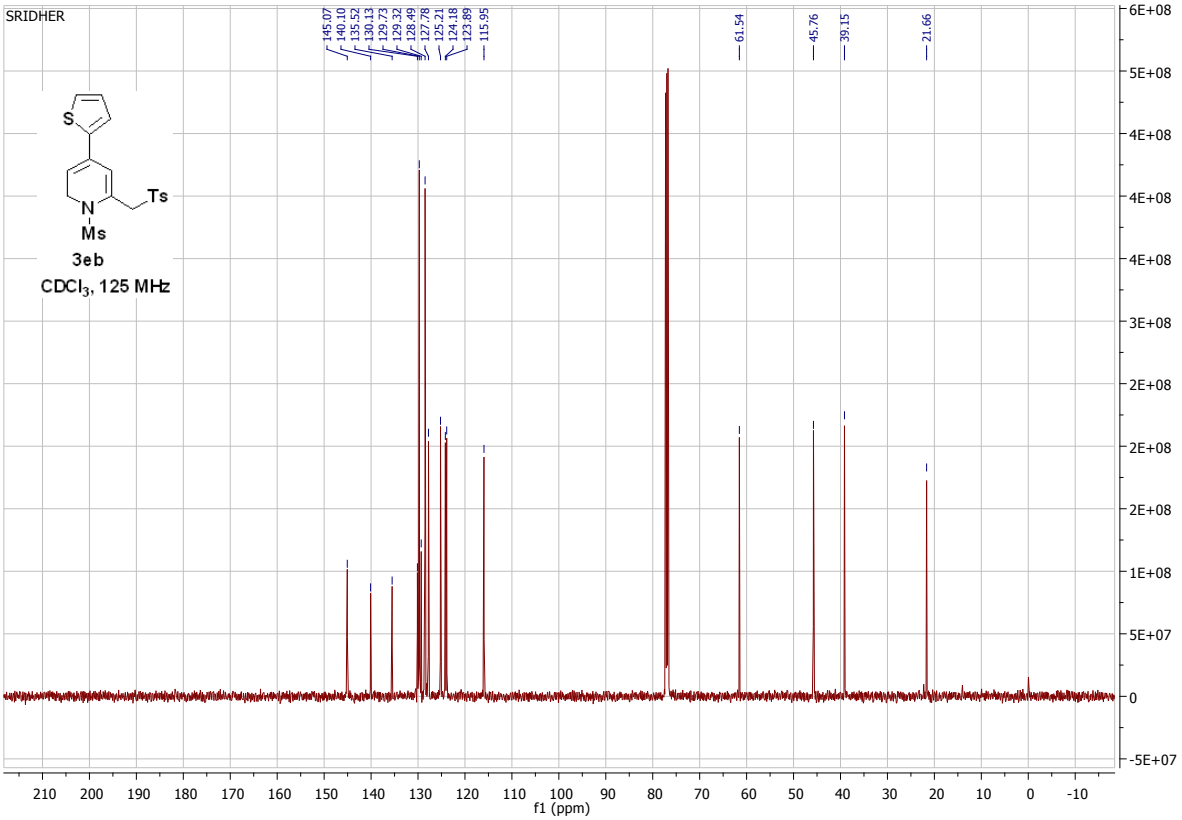

DANOJ
Ph
Ts
N
Ms
3db
CDCl3, 500 MHz
f1 (ppm)

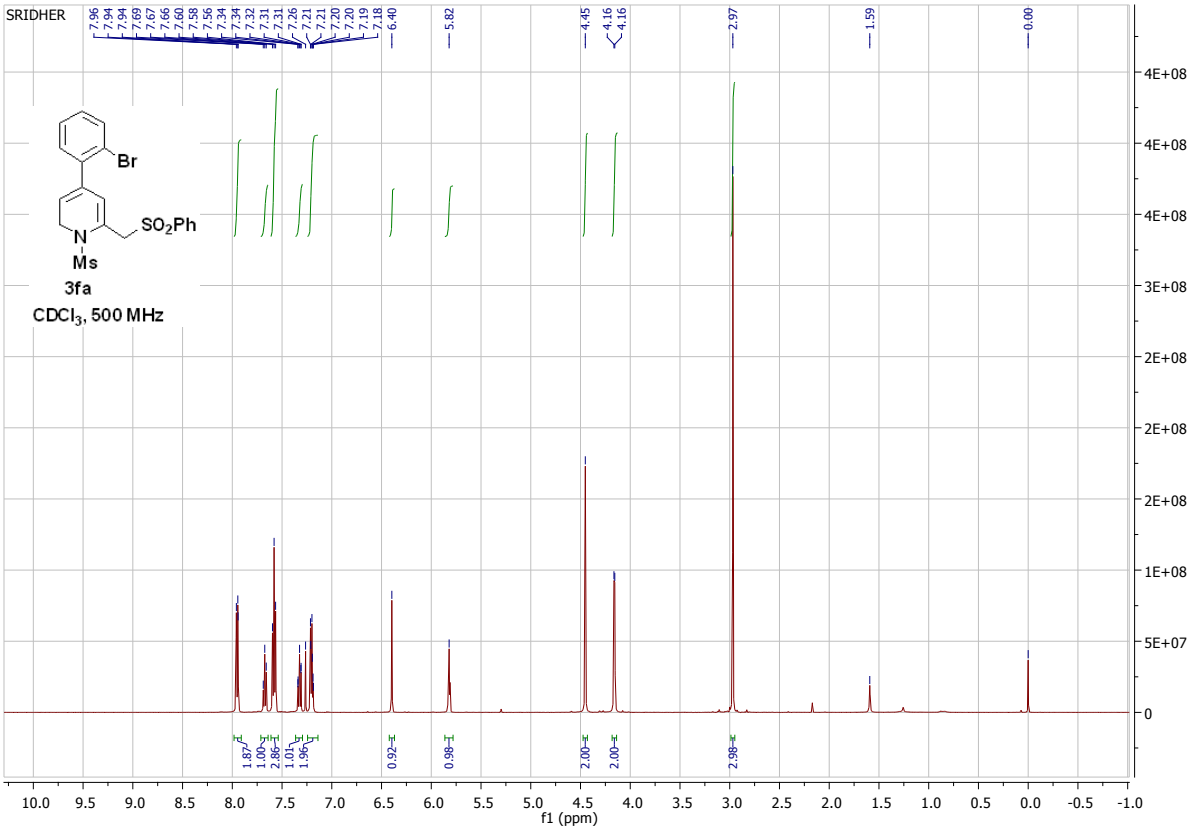

SRIDHER
Ph
Ts
N
Ms
3db
CDCl3, 100 MHz
f1 (ppm)

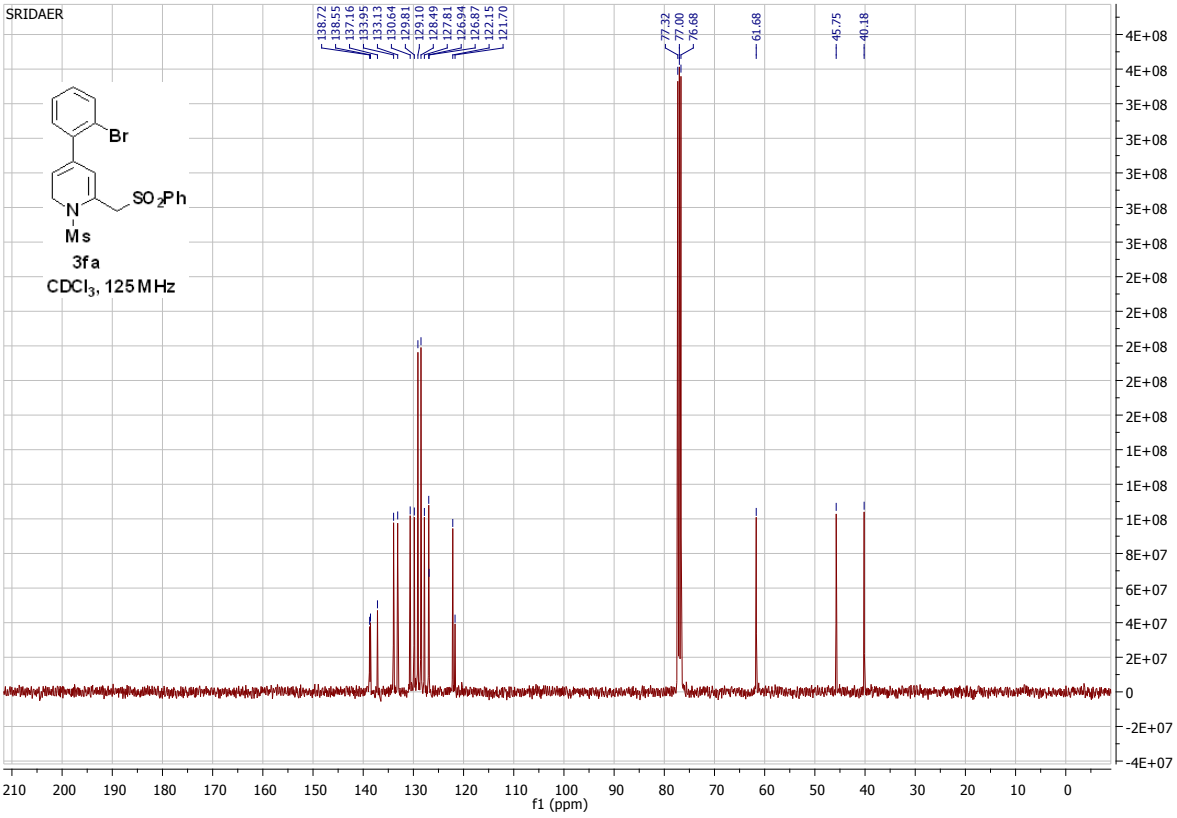

SRIDHER
7.96
7.94
7.70
7.69
7.67
7.60
7.58
7.57
7.26
7.23
7.09
7.08
6.83
6.00
5.99
5.98
4.47
4.09
4.08
2.80
1.60
0.00
S
N
Ms
SO2Ph
3ea
CDCl3, 500 MHz
1.99
1.06
2.15
0.92
1.02
0.99
1.02
1.00
2.09
2.12
3.10
f1 (ppm)

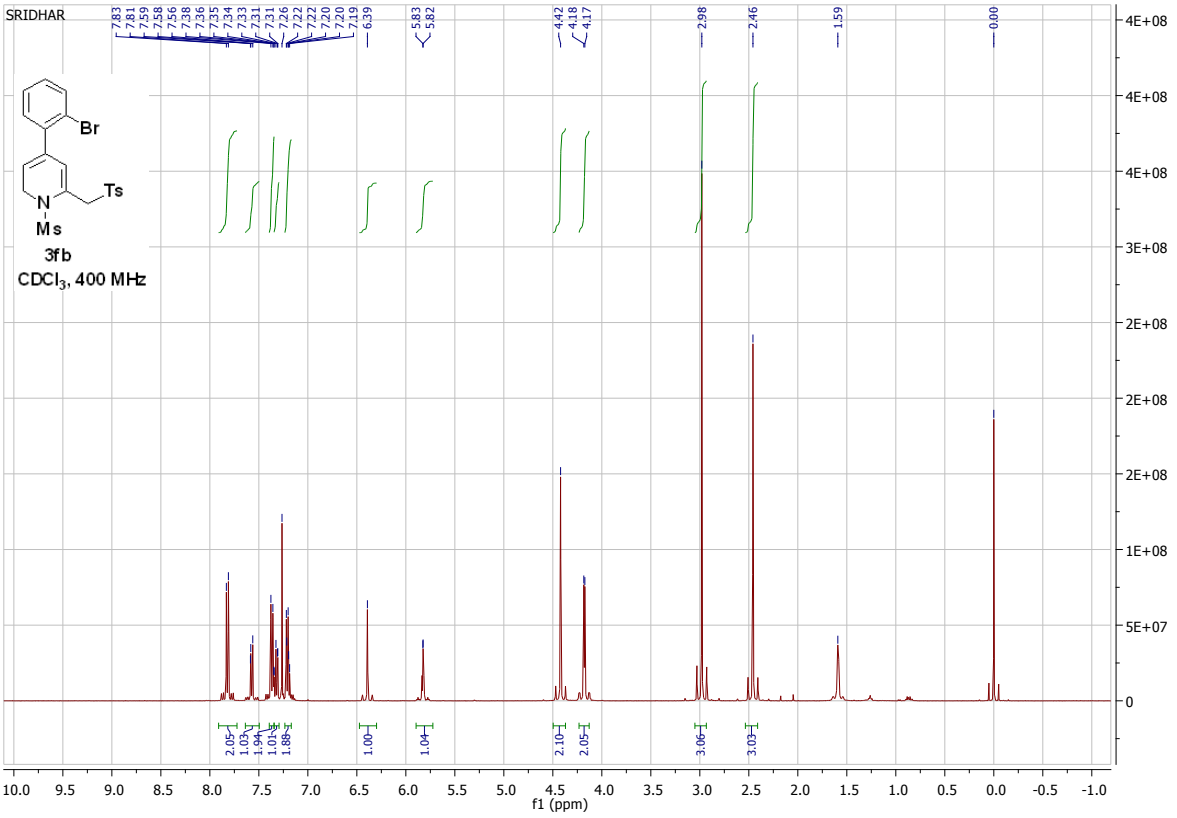

SRIDAR
140.04
138.41
134.04
130.12
129.20
129.13
128.50
127.80
125.25
124.32
123.91
115.97
77.25
77.00
76.75
61.53
45.75
39.14
S
N
Ms
SO2Ph
3ea
CDCl3, 125 MHz
f1 (ppm)

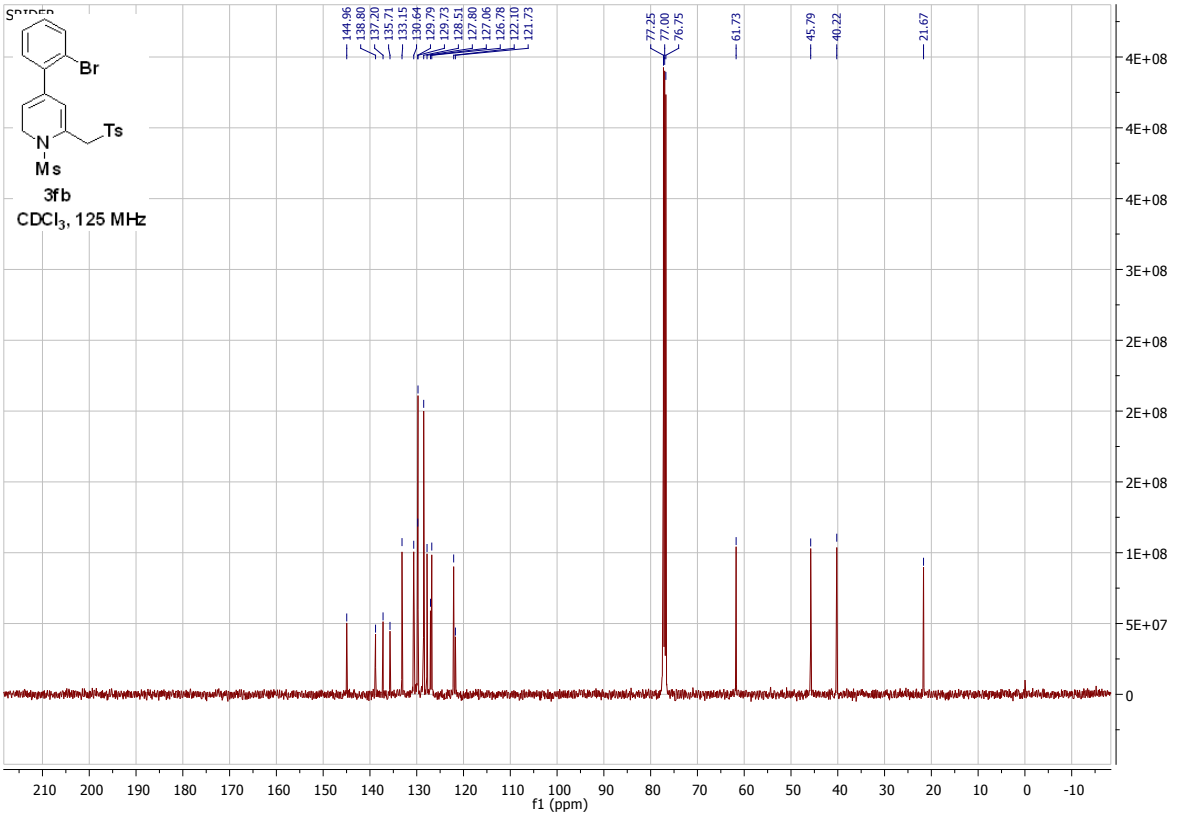

SRIDHAR
7.83
7.81
7.37
7.36
7.26
7.23
7.08
7.02
6.82
6.00
5.99
5.98
4.44
4.11
4.10
2.81
2.46
1.61
1.61
0.00
S
N
Ts
Ms
3eb
CDCl3, 500 MHz
2.01
2.05
0.97
1.05
1.03
1.03
1.00
2.06
2.05
3.02
3.09
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
5E+07
0
-5E+07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

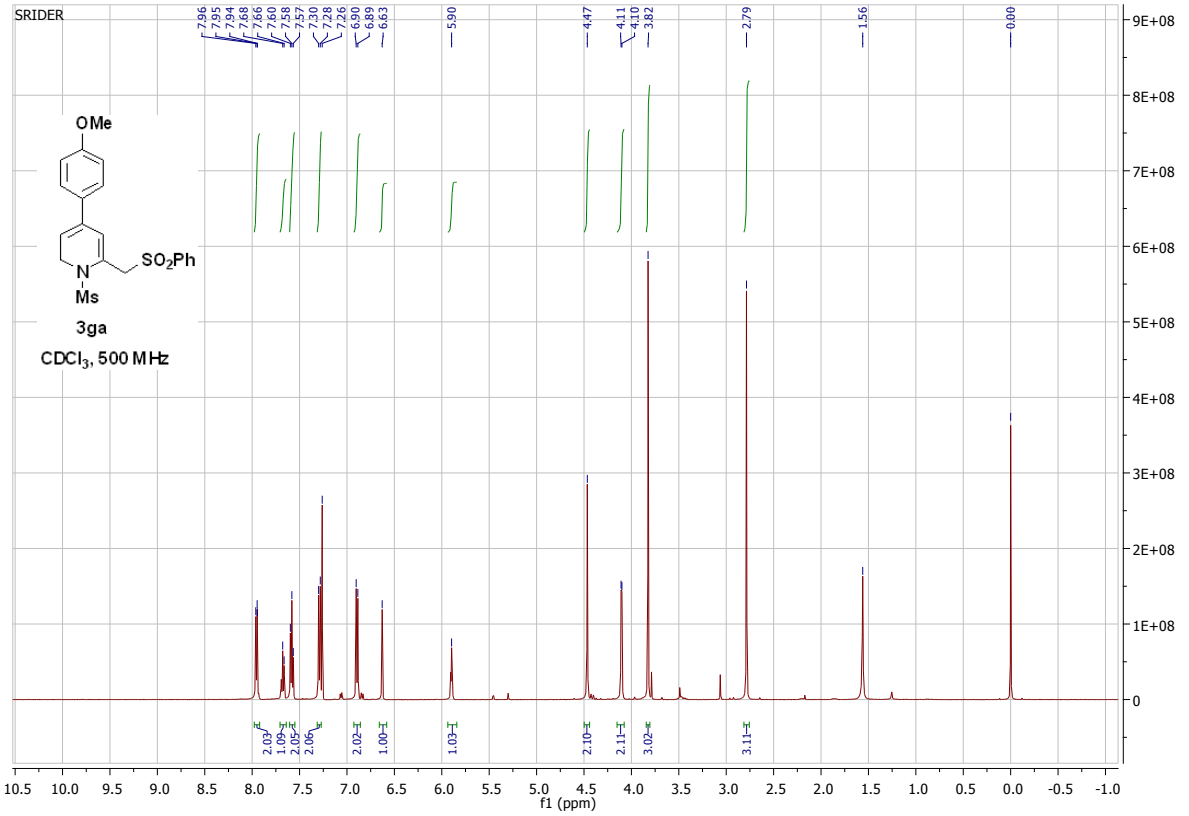

SRIDHER
145.07
140.10
135.52
130.13
129.73
129.32
128.49
127.78
125.21
124.18
123.89
115.95
61.54
45.76
39.15
21.66
S
N
Ts
Ms
3eb
CDCl3, 125 MHz
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

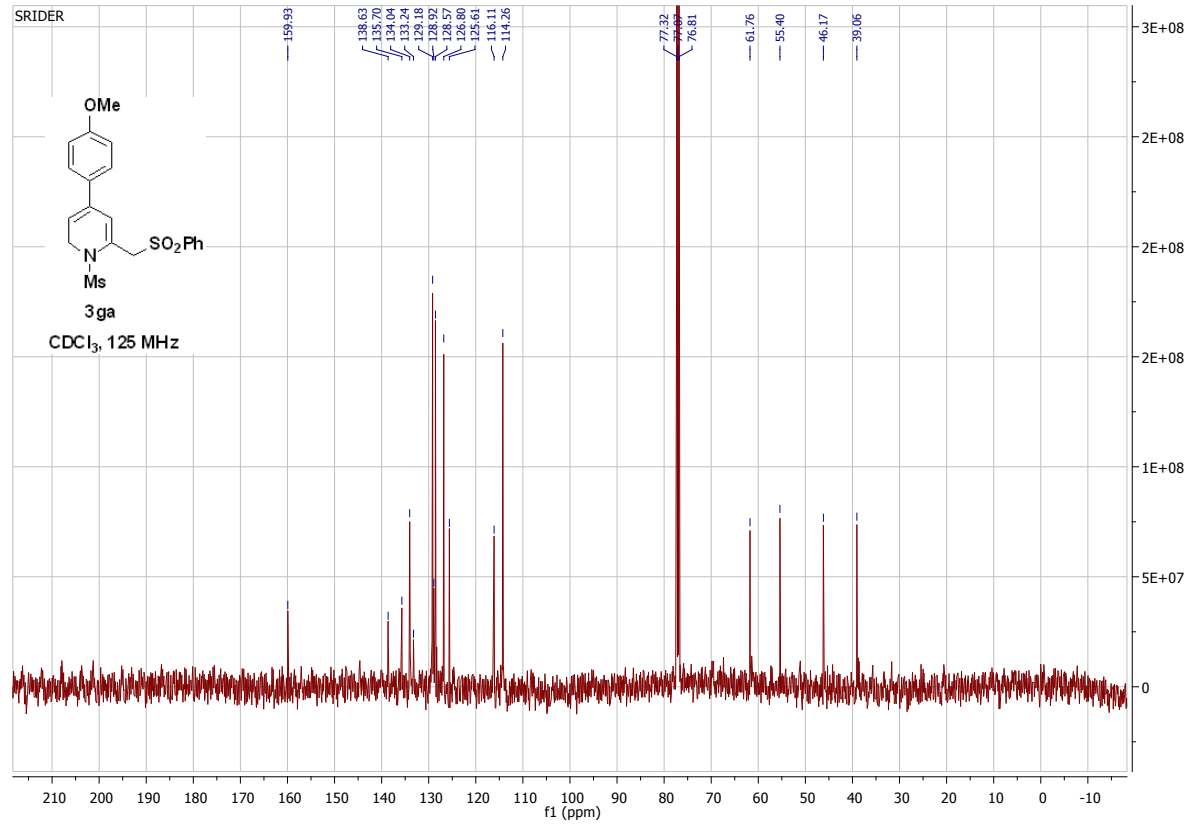

SRIDHER
Br
SO2Ph
N
Ms
3fa
CDCl3, 500 MHz
f1 (ppm)

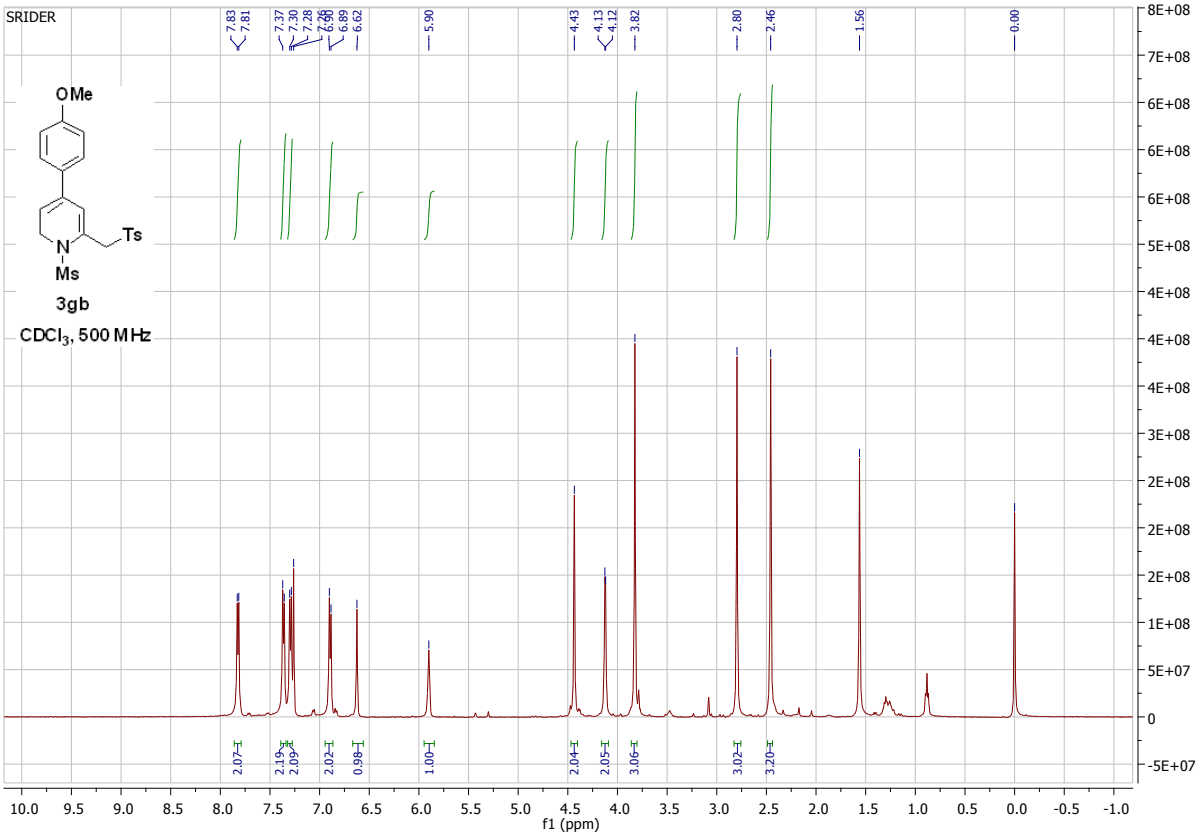

SRIDAER
Br
SO2Ph
N
Ms
3fa
CDCl3, 125 MHz
f1 (ppm)

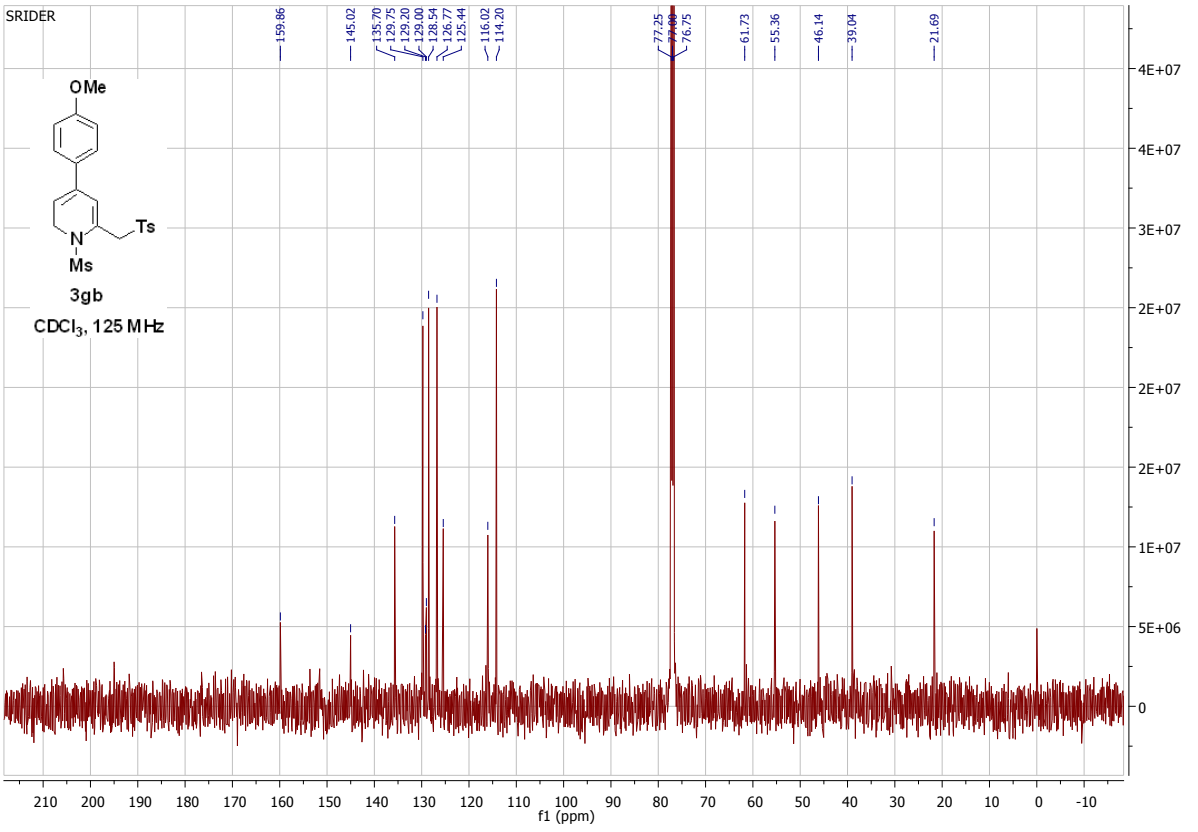

SRIDHAR
Br
Ts
N
Ms
3fb
CDCl3, 400 MHz
f1 (ppm)

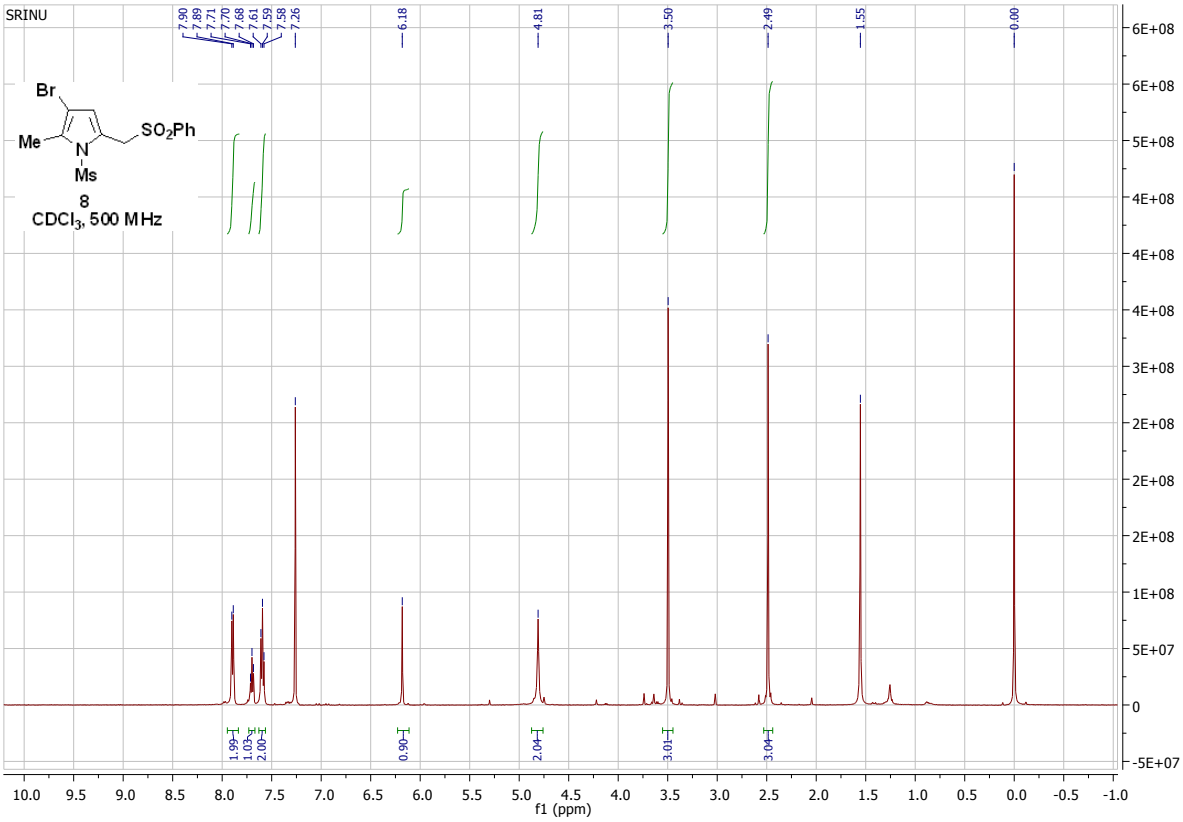

Br
Ts
N
Ms
3fb
CDCl3, 125 MHz
f1 (ppm)

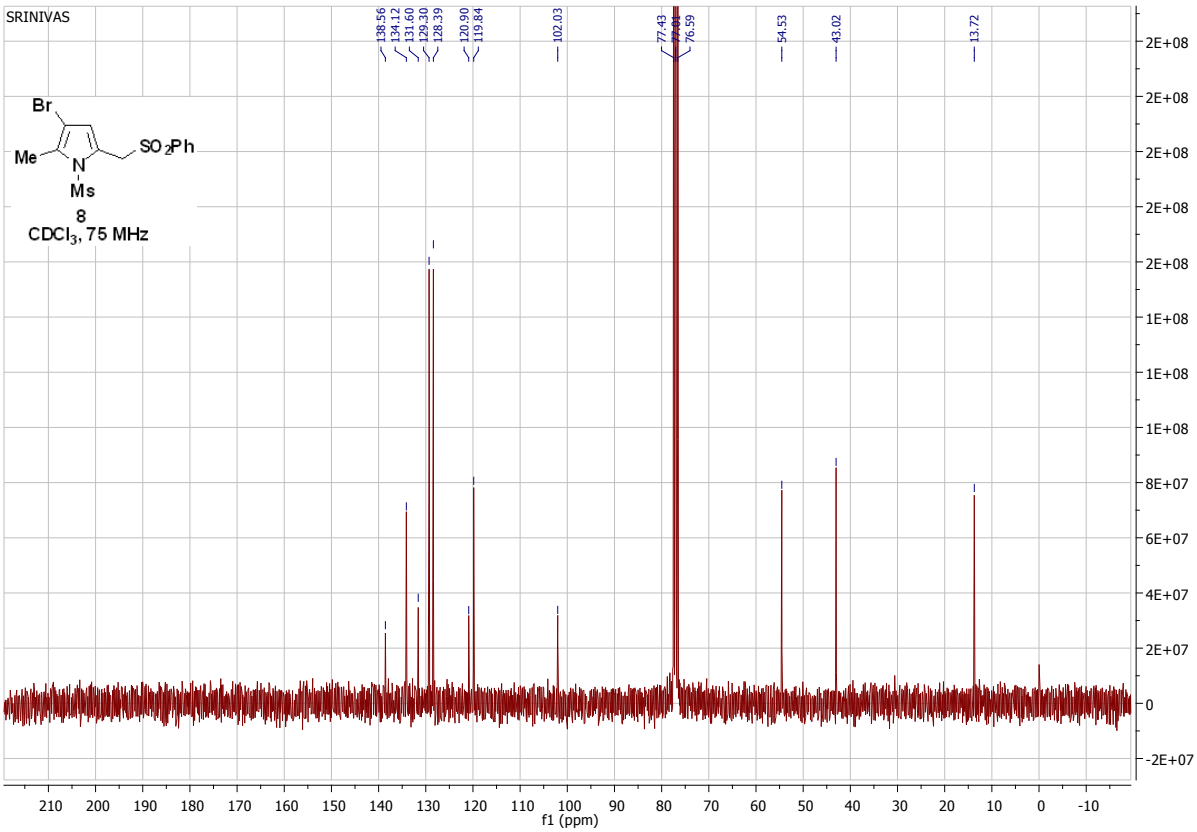

SRIDER
OMe
SO2Ph
N
Ms
3ga
CDCl3, 500 MHz
f1 (ppm)

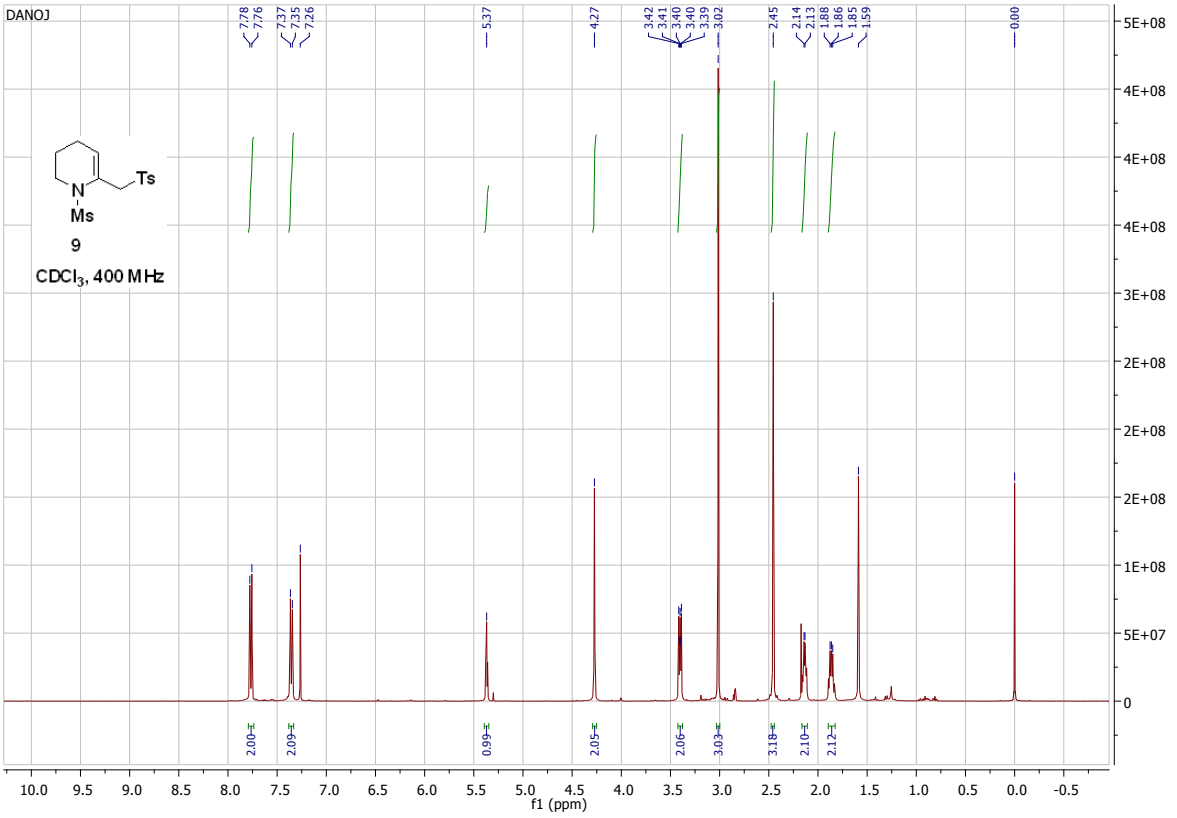

SRIDER
OMe
SO2Ph
N
Ms
3ga
CDCl3, 125 MHz
f1 (ppm)

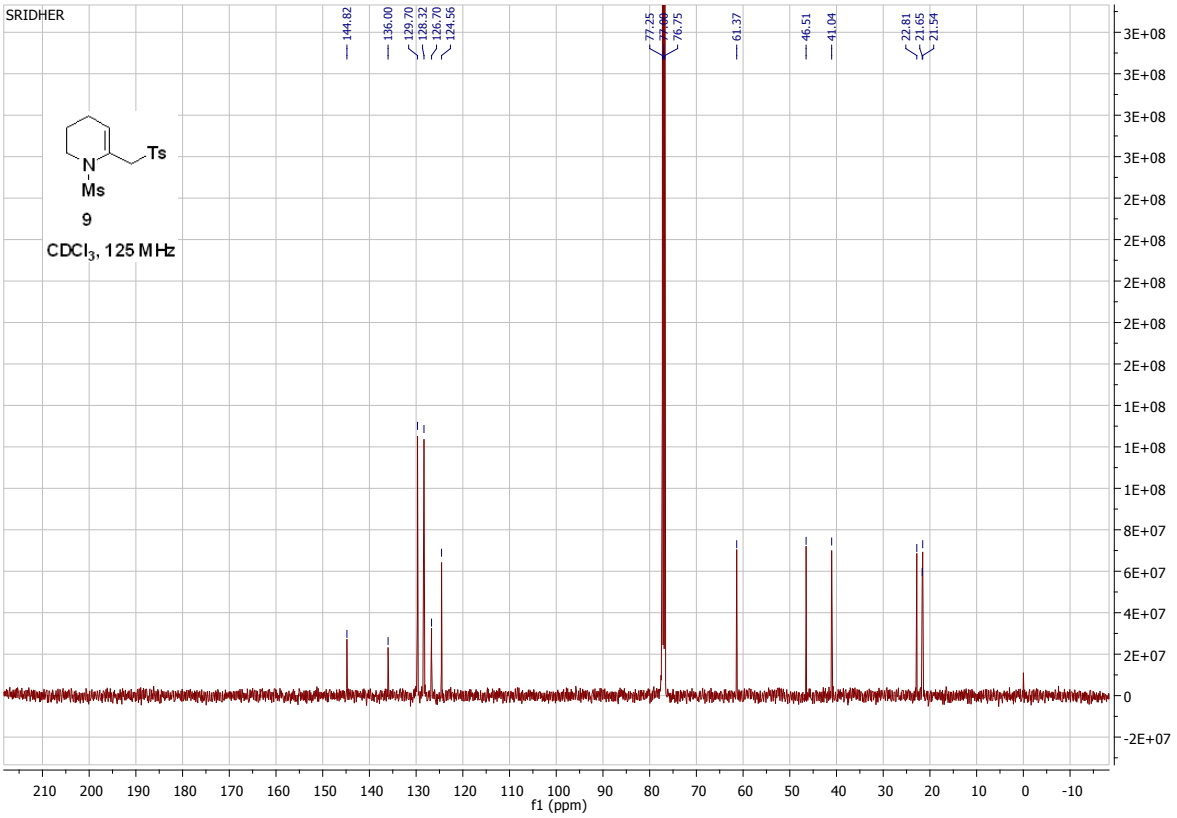

SRIDER
OMe
Ts
N
Ms
3gb
CDCl3, 500 MHz
f1 (ppm)

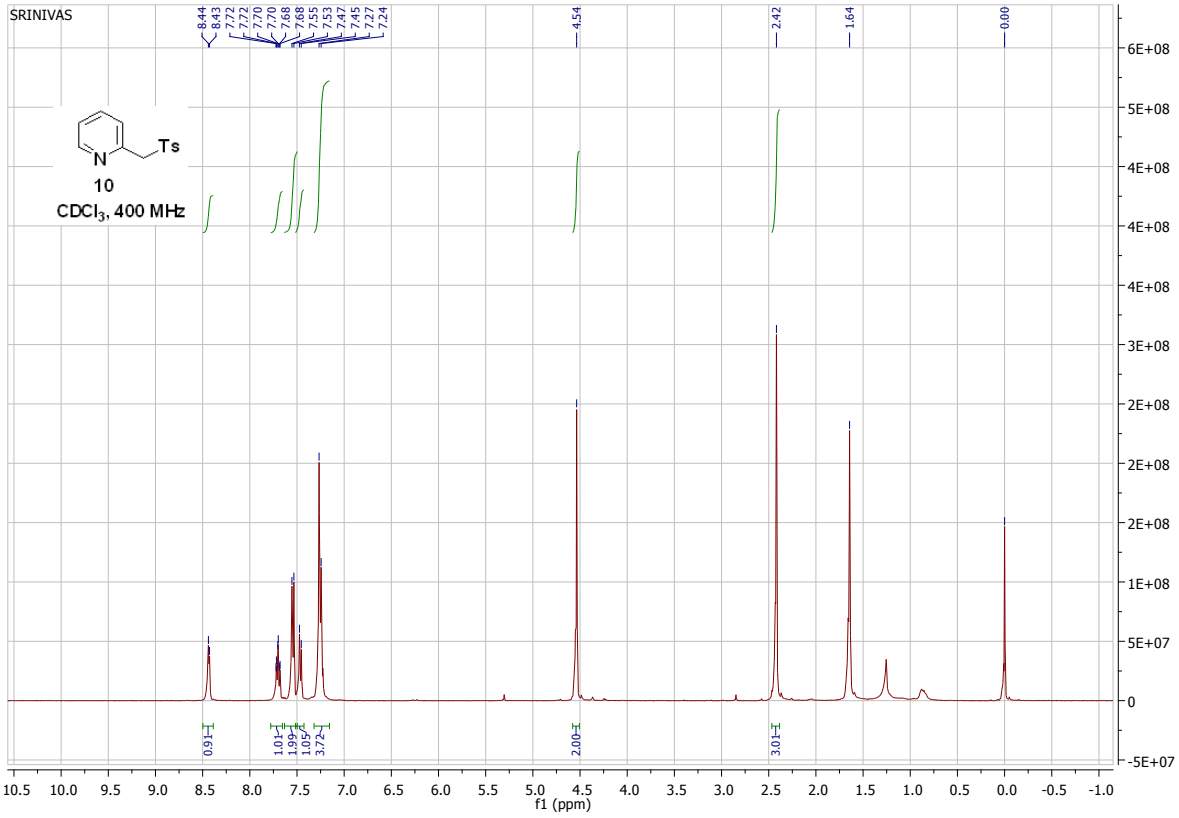

SRIDER
OMe
Ts
N
Ms
3gb
CDCl3, 125 MHz
f1 (ppm)

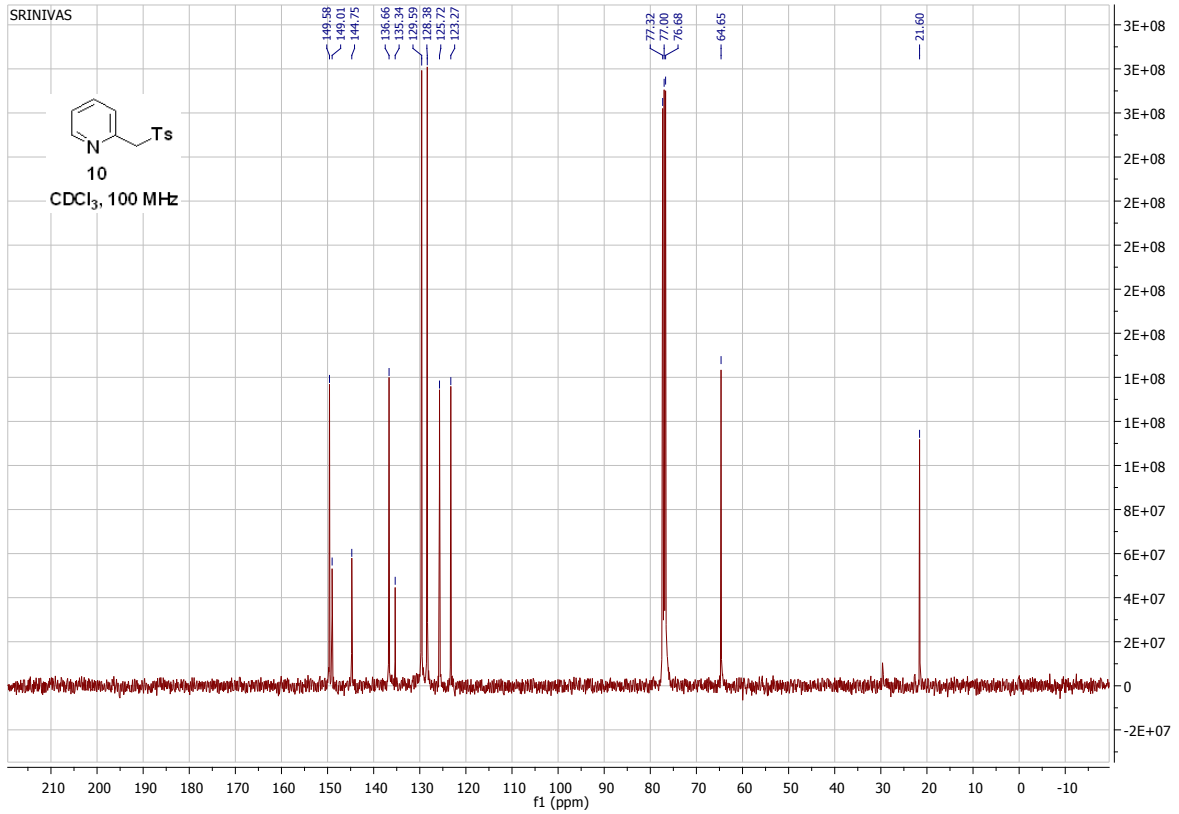

SRINU
7.90
7.89
7.71
7.70
7.68
7.61
7.59
7.58
7.26
6.18
4.81
3.50
2.49
1.55
0.00
Br
Me
N
Ms
SO2Ph
8
CDCl3, 500 MHz
1.99
1.03
2.06
0.90
2.04
3.01
3.04
f1 (ppm)


SRINIVAS
138.56
134.12
131.60
129.30
128.39
120.90
119.84
102.03
77.43
77.01
76.59
54.53
43.02
13.72
Br
Me
N
Ms
SO2Ph
8
CDCl3, 75 MHz
f1 (ppm)


DANOJ
7.78
7.76
7.37
7.35
7.26
5.37
4.27
3.42
3.41
3.40
3.40
3.39
3.02
2.45
2.14
2.13
1.88
1.86
1.85
1.59
0.00
Ts
N
Ms
9
CDCl3, 400 MHz
2.00
2.09
0.99
2.05
2.06
3.03
3.18
2.10
2.12
f1 (ppm)


SRIDHER
144.82
136.00
129.70
128.32
126.70
124.56
77.25
76.75
61.37
46.51
41.04
22.81
21.65
21.54
Ts
N
Ms
9
CDCl3, 125 MHz
f1 (ppm)


SRINIVAS
8.44
8.43
7.72
7.72
7.70
7.70
7.68
7.68
7.55
7.53
7.47
7.45
7.27
7.24
4.54
2.42
1.64
0.00
Ts
N
10
CDCl3, 400 MHz
0.91
1.01
1.99
1.05
3.72
2.00
3.01
f1 (ppm)


SRINIVAS
149.58
149.01
144.75
136.66
135.34
129.59
128.38
125.72
123.27
77.32
77.00
76.68
64.65
21.60
Ts
N
10
CDCl3, 100 MHz
f1 (ppm)