**Supporting Information for**

# Facile synthesis of 1-benzoazepine derivatives *via* gold-catalyzed regioselective cycloisomerization reactions of *N*-(*o*-alkynylaryl)-*N*-vinyl sulfonamides

Sridhar Undeela,[a] Gurram Ravikumar,[a] Jagadeesh Babu Nanubolu,[b] Kiran Kumar Singarapu[c] and Rajeev S. Menon*[d]

[a]*Medicinal Chemistry and Pharmacology Division, CSIR-Indian Institute of Chemical Technology, Hyderabad, 500 007, India.*

[b]*Centre for X-ray Crystallography, CSIR-Indian Institute of Chemical Technology, Hyderabad, 500 007, India.*

[c]*Centre for Nuclear Magnetic Resonance, CSIR-Indian Institute of Chemical Technology, Hyderabad, 500 007, India.*

[d]*Department of Chemistry, Central University of Haryana, Mahendergarh, Haryana, 123 029, India. E-mail: rajeevmenon@cuh.ac.in*

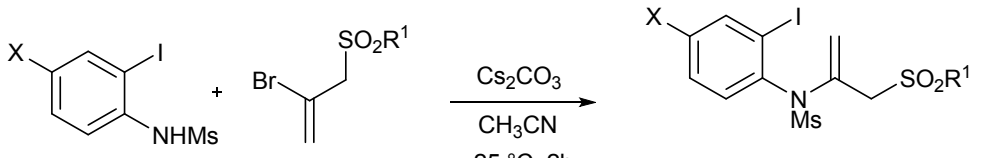
**Table of Contents**

## 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 **3a-b**,[1] *N*-(2-iodophenyl)methanesulfonamide **4a**,[2] *N*-(4-chloro-2-iodophenyl)methanesulfonamide **4b**[3] and *N*-(but-3-ynyl)-4-methylbenzenesulfonamide **9**[4] were prepared as previously described.

## 2. Substrate Preparation

### 2.1. $CS_2CO_3$-mediated reaction of 2-bromoallyl sulfones 3a-b with *N*-arylsulfonamides 4a-b




**4a**, X = H
**4b**, X = Cl

**3a**, $R^1$ = Ph
**3b**, $R^1$ = *p*-tolyl

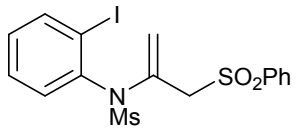
**5a**, X = H, $R^1$ = Ph, 78%
**5b**, X = H, $R^1$ = *p*-tolyl, 74%
**5c**, X = Cl, $R^1$ = Ph, 76%
**5d**, X = Cl, $R^1$ = *p*-tolyl, 79%

**Typical procedure:** Cesium carbonate (1.63 g, 5.0 mmol) was added to a solution of the *N*-arylsulfonamide **4a-b** (2.0 mmol) and the bromoallyl sulfone **3a-b** (2.8 mmol) in acetonitrile (8 mL) at ambient temperature and stirred for 2 hours. The solvent was removed on a rotavapor, deionized water (20 mL) was added and the aqueous solution was extracted with ethyl acetate (3

---

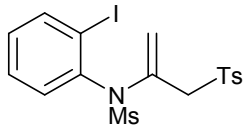
[1] S. Undeela, S. Thadkapally, J. B. Nanubolu, K. K. Singarapu and R. S. Menon, *Chem. Commun*., 2015, **51**, 13748.
[2] C. Rossy, E. Fouquet and F.-X. Felpin, *Beilstein J. Org. Chem*., 2013, **9**, 1426.
[3] M. Pal, V. Subramanian, V. R. Batchu and I. Dager, *Synlett,* 2004, 1965.
[4] Y. Yin, W. Ma, Z. Chai and G. Zhao, *J. Org. Chem.,* 2007, **72**, 5731.

X 15 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.



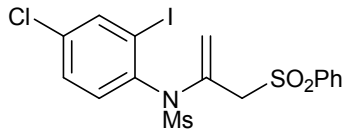

**5a**, *N*-(2-iodophenyl)-*N*-[3-(phenylsulfonyl)prop-1-en-2-yl]methanesulfonamide

White solid, 744 mg, 78%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 138-140 ˚C
**IR (KBr) $\nu_{max}$**: 3062, 2993, 2931, 1913, 1634, 1581, 1464, 1442, 1344, 1159, 967, 761, 524 $cm^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.89 (m, 3H), 7.69-7.65 (m, 1H), 7.61-7.55 (m, 3H), 7.45 (td, *J* = 7.7, 1.5 Hz, 1H), 7.10 (td, *J* = 7.7, 1.6 Hz, 1H), 5.84 (br s, 1H), 5.14 (d, *J* = 1.4 Hz, 1H), 3.77 (d, *J* = 14.6 Hz, 1H), 3.63 (d, *J* = 14.6 Hz, 1H), 3.39 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 141.0, 139.6, 138.4, 134.2, 132.6, 132.5, 130.9, 129.6, 129.4, 128.5, 117.0, 102.2, 59.6, 41.3.
**HRMS** calcd for $C_{16}H_{20}IN_2O_4S_2$ $(M+NH_4^+)$ 494.9909; found 494.9912.



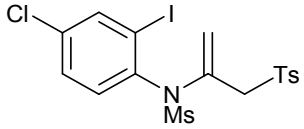

**5b**, *N*-(2-iodophenyl)-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide

White solid, 727 mg, 74%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 134-136 ˚C
**IR (KBr) $\nu_{max}$**: 3028, 2969, 2929, 1935, 1719, 1637, 1595, 1460, 1343, 1310, 1154, 1126, 765, 518 $cm^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.61 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.45 (td, *J* = 7.8, 1.2 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.10 (td, *J* = 7.8, 1.4 Hz, 1H), 5.84 (s, 1H), 5.13 (d, *J* = 0.8 Hz, 1H), 3.74 (d, *J* = 14.6 Hz, 1H), 3.61 (d, *J* = 14.6 Hz, 1H), 3.39 (s, 3H), 2.45 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.3, 141.0, 139.6, 135.4, 132.7, 132.5, 130.8, 130.0, 129.6, 128.5, 116.9, 102.3, 59.7, 41.3, 21.7.
**HRMS** calcd for $C_{17}H_{22}O_4IN_2S_2$ $(M+NH_4^+)$ 509.0060; found 509.0072.




**5c**, *N*-(4-chloro-2-iodophenyl)-*N*-[3-(phenylsulfonyl)prop-1-en-2-yl]methanesulfonamide

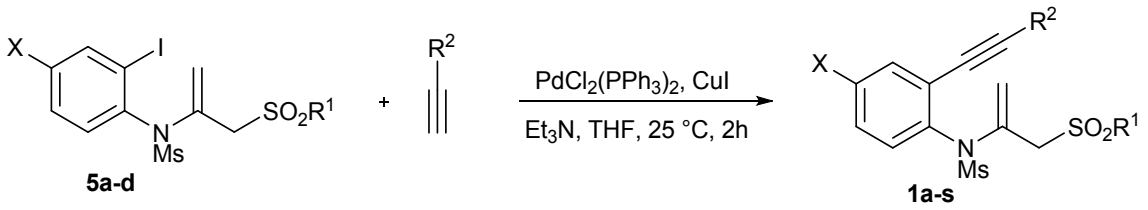
Colorless oil, 777 mg, 76%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 3022, 2932, 1629, 1569, 1462, 1347, 1321, 1157, 1084, 968, 753, 530cm$^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.92-7.86 (m, 3H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.61-7.51 (m, 3H), 7.42 (dd, *J* = 8.5, 2.3 Hz, 1H), 5.85 (s, 1H), 5.17 (d, *J* = 1.2 Hz, 1H), 3.76 (d, *J* = 14.6 Hz, 1H), 3.62 (d, *J* = 14.6 Hz, 1H), 3.38 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 140.3, 138.3, 136.0, 134.3, 132.9, 132.4, 129.8, 129.4, 128.4, 117.5, 102.5, 59.6, 41.3.
**HRMS** calcd for $C_{16}H_{16}O_4NClS_2I$ ($M+H^+$) 511.9254; found 511.9254.




**5d**, *N*-(4-chloro-2-iodophenyl)-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide

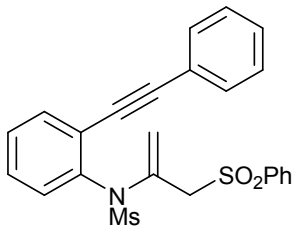
Colorless oil, 830 mg, 79%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 2926, 2854, 1726, 1630, 1597, 1462, 1348, 1320, 1156, 1085, 968, 757, 522 cm$^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.4 Hz, 1H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 1H), 7.41 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 5.85 (s, 1H), 5.16 (s, 1H), 3.73 (d, *J* = 14.6 Hz, 1H), 3.60 (d, *J* = 14.6 Hz, 1H), 3.38 (s, 3H), 2.46 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.4, 140.2, 138.4, 136.0, 135.4, 132.9, 132.5, 130.0, 129.8, 128.4, 117.4, 102.5, 59.7, 41.3, 21.7.
**HRMS** calcd for $C_{17}H_{18}O_4NClS_2I$ ($M+H^+$) 525.9410; found 525.9406.

### 2.2. Sonogashira Coupling of 5a-d with various alkynes



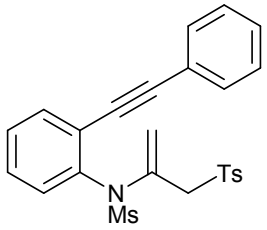

To a solution of the aryl iodide **5a-d** (0.50 mmol) and alkyne (0.60 mmol) in THF (6 mL) kept under argon, $Pd(PPh_3)_2Cl_2$ (7 mg, 0.01 mmol), CuI (4 mg, 0.04 mmol) and triethylamine (0.21 mL, 1.50 mmol) were sequentially added at 25 °C and stirred for 2h. The solvent was removed

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.



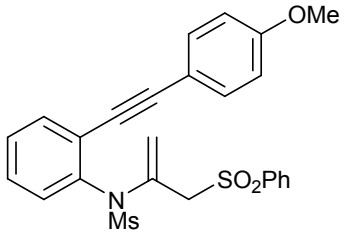

**1a**, *N*-(2-(phenylethynyl)phenyl)-*N*-[3-(phenylsulfonyl)prop-1-en-2-yl]methanesulfonamide

Colorless semisolid, 194 mg, 86%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 3283, 3061, 2989, 2929, 2853, 2223, 1721, 1672, 1633, 1495, 1447, 1347, 1311, 1160, 1127, 969, 527 $cm^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.61- 7.57 (m, 1H), 7.55- 7.50 (m, 4H), 7.46- 7.33 (m, 6H), 5.74 (s, 1H), 5.06 (d, *J* = 1.1 Hz, 1H), 3.75 (s, 2H), 3.33 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.2, 138.0, 134.0, 133.9, 133.6, 132.3, 131.6, 129.6, 129.3, 129.2, 129.0, 128.7, 128.6, 125.2, 122.5, 115.8, 95.2, 86.0, 60.1, 41.2.
**HRMS** calcd for $C_{24}H_{22}O_4NS_2$ ($M+H^+$) 452.0990; found 452.1006.



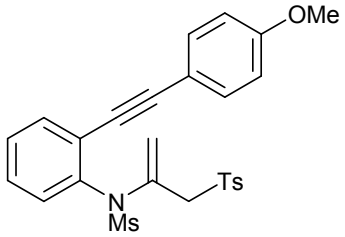

**1b**, *N*-(2-(phenylethynyl)phenyl)-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide

Colorless semisolid, 191 mg, 82%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 3026, 2929, 2218, 1629, 1597, 1495, 1346, 1322, 1156, 1087, 967, 759, 685, 515 $cm^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 2H), 7.59-7.47 (m, 4H), 7.40– 7.26 (m, 7H), 5.75 (s, 1H), 5.06 (s, 1H), 3.73 (s, 2H), 3.33 (s, 3H), 2.43 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 145.1, 138.1, 135.3, 133.8, 133.8, 132.3, 131.6, 129.8, 129.6, 129.2, 128.93 128.7, 128.5, 125.3, 122.6, 115.9, 95.2, 86.1, 60.2, 41.2, 21.7.
**HRMS** calcd for $C_{25}H_{27}O_4N_2S_2$ ($M+NH_4^+$) 483.1412; found 483.1419. \



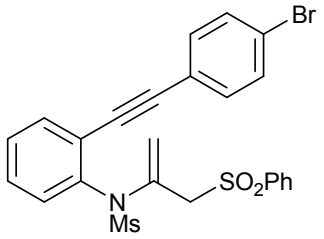

**1c**, *N*-{2-[(4-methoxyphenyl)ethynyl]phenyl}-*N*-[3-(phenylsulfonyl)prop-1-en-2-yl]-methanesulfonamide

White solid, 183 mg, 76%
**Melting point:** 132-134 ˚C
**$R_f$** = 0.3 (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 3019, 2934, 2840, 2215, 1630, 1603, 1511, 1445, 1347, 1318, 1250, 1157, 1085, 1026, 967, 757, 524 $cm^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.66-7.63 (m, 1H), 7.57-7.50 (m, 3H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.42-7.36 (m, 3H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.73 (s, 1H), 5.06 (d, *J* = 1.1 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 2H), 3.33 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 160.2, 138.3, 137.8, 134.0, 133.7, 133.6, 133.1, 132.3, 129.3, 129.2, 128.7, 125.5, 115.7, 114.6, 114.2, 95.5, 84.9, 60.1, 55.4, 41.2.
**HRMS** calcd for $C_{25}H_{27}O_5N_2S_2$ ($M+NH_4^+$) 499.1361; found 499.1373.



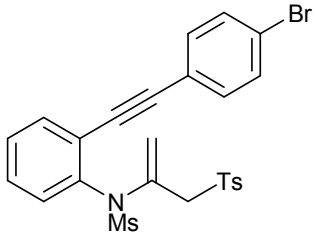

**1d**, *N*-{2-[(4-methoxyphenyl)ethynyl]phenyl}-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide

White solid, 176 mg, 71%
**Melting point:** 105-107 ˚C
**$R_f$** = 0.3 (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 3023, 2934, 2840, 2215, 1631, 1602, 1512, 1445, 1345, 1321, 1290, 1250, 1157, 1027, 760, 518 $cm^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, J = 7.8 Hz, 2H), 7.56-7.54 (m, 1H), 7.47-7.47 (m, 3H), 7.37 (br s, 2H), 7.30 (d, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 8.2 Hz, 2H), 5.74 (s, 1H), 5.05 (s,1H), 3.82 (s, 3H), 3.7(s, 2H), 3.33 (s, 3H), 2.43 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.2, 145.1, 137.9, 135.3, 133.8, 133.6, 133.1, 132.3, 129.8, 129.2, 128.7, 125.5, 115.7, 114.6, 114.2, 95.4, 84.9, 60.2, 55.4, 41.2, 21.7.
**HRMS** calcd for $C_{26}H_{29}O_5N_2S_2$ ($M+NH_4^+$) 513.1518; found 513.1529.



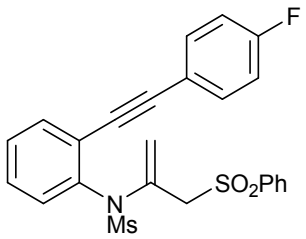

**1e**, *N*-{2-[(4-bromophenyl)ethynyl]phenyl}-*N*-[3-(phenylsulfonyl)prop-1-en-2-yl]-methanesulfonamide

Colorless semisolid, 193 mg, 73%
**$R_f$** = (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 3063, 2926, 2855, 2326, 2255, 2219, 1972, 1906, 1731, 1629, 1587, 1494, 1317, 1157, 968, 761, 516 $cm^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.59 (dd, *J* = 7.0, 2.2 Hz, 1H), 7.55-7.39 (m, 9H), 5.74 (s, 1H), 5.00 (s, 1H), 3.74 (s, 2H), 3.35 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.2, 134.1, 133.8, 133.6, 133.0, 132.1, 131.8, 129.9, 129.4, 129.3, 128.6, 125.1, 123.3, 121.5, 115.9, 94.1, 87.1, 60.1, 41.1.
**HRMS** calcd for $C_{24}H_{24}O_4N_2S_2Br$ ($M+NH_4^+$) 549.0340; found 549.0344.




**1f**, *N*-{2-[(4-bromophenyl)ethynyl]phenyl}-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide

White solid, 215 mg, 79%
**Melting point:** 113-115 ˚C
**$R_f$** = 0.7 (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 3024, 2926, 2855, 1718, 1630, 1597, 1490, 1322, 1156, 1088, 968, 818, 760, 517 $cm^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.58 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.52-7.39 (m, 7H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.74 (s, 1H), 4.99 (s, 1H), 3.72 (s, 2H), 3.35 (s, 3H), 2.43 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.2, 138.3, 135.3, 133.8, 133.0, 132.1, 131.82, 129.9, 129.3, 128.6, 125.2, 123.3, 121.6, 115.8, 94.0, 87.2, 60.2, 41.1, 21.7.
**HRMS** calcd for $C_{25}H_{23}BrNO_4S_2$ ($M+H^+$) 544.0252; found 544.0246.




**1g**, *N*-{2-[(4-fluorophenyl)ethynyl]phenyl}-*N*-[3-(phenylsulfonyl)prop-1-en-2-yl]-methanesulfonamide

White solid, 169 mg, 72%

**Melting point:** 125-127 ˚C

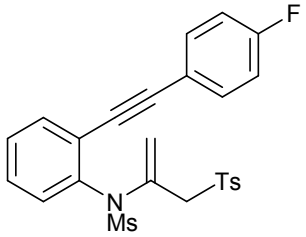
**$R_f$** = 0.5 (30% ethyl acetate in hexanes)

**IR (KBr) $\nu_{max}$**: 3065, 2983, 2930, 2227, 1633, 1509, 1448, 1354, 1312, 1232, 1160, 1017, 883, 751, 530 $cm^{-1}$

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.58 (dd, *J* = 6.9, 2.4 Hz, 1H), 7.55-7.51 (m, 4H), 7.48-7.47 (m, 1H), 7.43- 7.37 (m, 2H), 7.04 (t, *J* = 8.7 Hz, 2H), 5.74 (s, 1H), 5.01 (s, 1H), 3.75 (s, 2H), 3.35 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 162.9 (d, *J* = 250.1 Hz), 138.1 (d, J = 5.9 Hz), 134.1, 133.8, 133.6, 133.5, 132.1, 129.7, 129.4, 129.3, 128.6, 125.2, 118.6 (d, *J* = 2.7 Hz), 115.9 (d, *J* = 22.0 Hz), 115.8, 94.1, 85.7, 60.1, 41.1.

**HRMS** calcd for $C_{24}H_{24}O_4N_2FS_2$ ($M+NH_4^+$) 487.1162; found 487.1167.




**1h**, *N*-{2-[(4-fluorophenyl)ethynyl]phenyl}-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide

Colorless semisolid, 184 mg, 76%

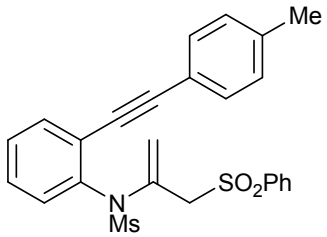
**$R_f$** = 0.5 (30% ethyl acetate in hexanes)

**IR (KBr) $\nu_{max}$**: 2926, 2854, 2220, 1725, 1631, 1597, 1508, 1346, 1321, 1291, 1229, 1157, 1087, 970, 839, 762, 514 $cm^{-1}$

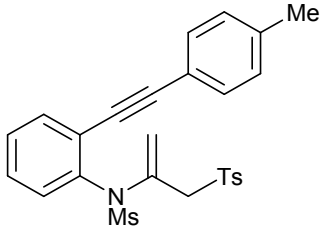
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.3 Hz, 2H), 7.58 (dd, *J* = 7.0, 2.3 Hz, 1H), 7.54-7.49 (m, 3H), 7.43-7.37 (m, 2H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.04 (t, *J* = 7.9 Hz, 2H), 5.75 (s, 1H), 5.00 (s, 1H), 3.73 (s, 2H), 3.35 (s, 3H), 2.43 (s, 3H).

**$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 162.9 (d, *J* = 250.1 Hz), 145.2, 138.2, 135.3, 133.8 (d, *J* = 8.6 Hz), 133.6, 133.6, 132.1, 129.8, 129.7, 129.3, 128.6, 125.3, 118.7 (d, *J* = 3.2 Hz), 115.9 (d, *J* = 21.8 Hz), 115.8, 94.1, 85.8, 60.2, 41.1, 21.7.

**HRMS** calcd for $C_{25}H_{26}O_4N_2FS_2$ ($M+NH_4^+$) 501.1318; found 501.1324.

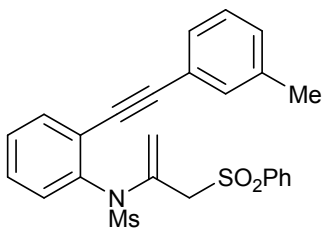



**1i**, *N*-[3-(phenylsulfonyl)prop-1-en-2-yl]-*N*-[2-(p-tolylethynyl)phenyl]methanesulfonamide
Colorless semisolid, 188 mg, 81%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 3064, 2927, 2856, 2216, 1720, 1594, 1512, 1445, 1357, 1321, 1157, 1084, 816, 760, 531 $cm^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.666-7.61 (m, 1H), 7.58-7.50 (m, 3H), 7.41- 7.37 (m, 5H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.73 (s, 1H), 5.07 (s, 1H), 3.74 (s, 2H), 3.31 (s, 3H), 2.36 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 139.3, 138.2, 137.9, 134.0, 133.8, 133.6, 132.4, 131.4, 129.4, 129.3, 129.3, 129.2, 128.7, 125.3, 119.4, 115.8, 95.6, 85. 5, 60.1, 41.2, 21.6.
**HRMS** calcd for $C_{25}H_{27}O_4N_2S_2$ ($M+NH_4^+$) 483.1412; found 483.1420.



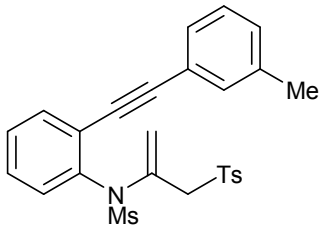

**1j**, *N*-[2-(*p*-tolylethynyl)phenyl]-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide

Colorless semisolid, 201 mg, 84%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 2924, 2856, 1720, 1597, 1512, 1396, 1326, 1155, 1086, 967, 815, 767, 518 $cm^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.56 (s, 1H), 7.44-7.38 (m, 5H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 7.1 Hz, 2H), 5.73 (s, 1H), 5.06 (s, 1H), 3.73 (s, 2H), 3.32 (s, 3H), 2.43 (s, 3H), 2.36 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.0, 139.2, 138.0, 135.3, 133.7, 132.4, 131.5, 129.8, 129.4, 129.3, 129.2, 128.7, 125.4, 119.5, 115.8, 95.5, 85.5, 60.2, 41.2, 21.7, 21.6.
**HRMS** calcd for $C_{26}H_{29}O_4N_2S_2$ ($M+NH_4^+$) 497.1569; found 497.1577.



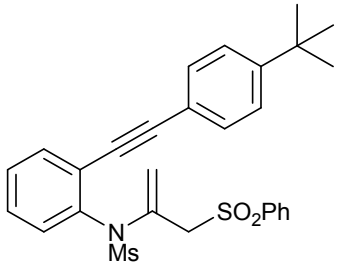
**1k**, *N*-[3-(phenylsulfonyl)prop-1-en-2-yl]-*N*-[2-(m-tolylethynyl)phenyl]methanesulfonamide

Brown solid, 188 mg, 81%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 122-124 ˚C
**IR (KBr) $\nu_{max}$**: 3025, 2927, 2211, 1629, 1590, 1484, 1446, 1347, 1312, 1158, 965, 753, 684, 537 $cm^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.58-7.56 (m, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.44-7.38 (m, 3H), 7.32-7.31 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 5.73 (s, 1H), 5.08 (s, 1H), 3.75 (s, 2H), 3.31 (s, 3H), 2.34 (s, 3H).
**$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 138.3, 137.9, 134.0, 133.8, 133.6, 132.4, 132.0, 129.9, 129.6, 129.3, 129.2, 128.8, 128.6, 128.5, 126.7, 125.1, 115.9, 114.9, 95.5, 85.6, 60.1, 41.2, 21.3.
**HRMS** calcd for $C_{25}H_{24}O_4NS_2$ ($M+H^+$) 466.1147; found 466.1140.




**1l**, *N*-[2-(*m*-tolylethynyl)phenyl]-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide

Brown solid, 192 mg, 80%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 150-152 ˚C
**IR (KBr) $\nu_{max}$**: 3060, 2922, 2207, 1718, 1640, 1594, 1489, 1387, 1341, 1321, 1233, 1159, 1125, 965, 767, 521 $cm^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.57 (dd, *J* = 6.9, 1.9 Hz, 1H), 7.46 (d, *J* = 6.9 Hz, 1H), 7.41-7.36 (m, 2H), 7.33-7.29 (m, 4H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 5.73 (s, 1H), 5.06 (s, 1H), 3.73 (s, 2H), 3.32 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.1, 138.3, 138.0, 135.3, 133.8, 133.7, 132.4, 132.0, 129.9, 129.8, 129.6, 129.2, 128.7, 128.7, 128.4, 125.3, 122.4, 115.9, 95.4, 85.7, 60.2, 41.2, 21.7, 21.3.
**HRMS** calcd for $C_{26}H_{29}O_4N_2S_2$ ($M+NH_4$) 497.1563; found 497.1575.




**1m**, *N*-{2-[(4-tert-butylphenyl)ethynyl]phenyl}-*N*-[3-(phenylsulfonyl)prop-1-en-2-yl]-methanesulfonamide

Brown solid, 188 mg, 74%

**$R_f$** = 0.4 (30% ethyl acetate in hexanes)

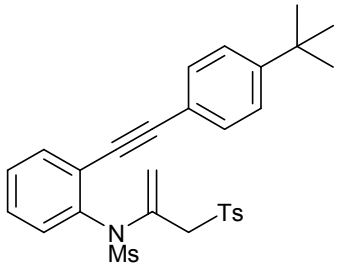
**Melting point:** 169-171 ˚C

**IR (KBr) $\nu_{max}$**: 3065, 3033, 2964, 1637, 1508, 1446, 1389, 1346, 1317, 1162, 1127, 965, 769, 527 $cm^{-1}$

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H),7.58-7.56 (m, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.40- 7.35 (m, 5H), 5.73 (s, 1H), 5.08 (s, 1H), 3.75 (s, 2H), 3.31 (s, 3H), 1.31 (s, 9H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 152.4, 138.2, 137.9, 134.0, 133.8, 133.7, 132.4, 131.3, 129.4, 129.3, 129.2, 128.8, 125.6, 125.3, 119.5, 115.8, 95.6, 85.5, 60.1, 41.3, 34.9, 31.2.

**HRMS** calcd for $C_{28}H_{33}O_4N_2S_2$ ($M+NH_4^+$) 525.1882; found 525.1876.




**1n**, *N*-{2-[(4-tert-butylphenyl)ethynyl]phenyl}-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide

Brown solid, 180 mg, 69%

**$R_f$** = 0.4 (30% ethyl acetate in hexanes)

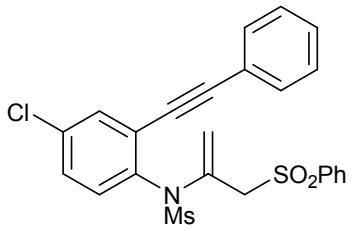
**Melting point:** 191-193 ˚C

**IR (KBr) $\nu_{max}$**: 2956, 2865, 2146, 1916, 1664, 1601, 1493, 1462, 1389, 1363, 1263, 1200, 1100, 883, 559 $cm^{-1}$

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.58-7.56 (m, 1H), 7.46-7.43 (m, 3H), 7.39-7.35 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.73 (s, 1H), 5.06 (s, 1H), 3.73 (s, 2H), 3.31 (s, 3H), 2.43 (s, 3H), 1.31 (s, 9H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.3, 145.0, 138.0, 135.3, 133.8, 132.4, 131.3, 129.8, 129.4, 129.2, 128.8, 125.6, 125.3, 119.5, 115.8, 95.5, 85.5, 60.2, 41.2, 34.9, 31.2, 21.7.

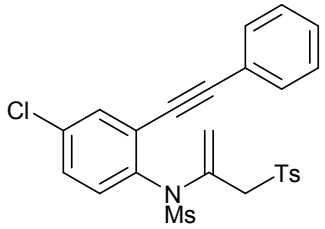
**HRMS** calcd for $C_{29}H_{32}O_4NS_2$ ($M+H^+$) 522.1773; found 522.1761.




**1o**, *N*-[4-chloro-2-(phenylethynyl)phenyl]-*N*-[3-(phenylsulfonyl)prop-1-en-2-yl]-methanesulfonamide

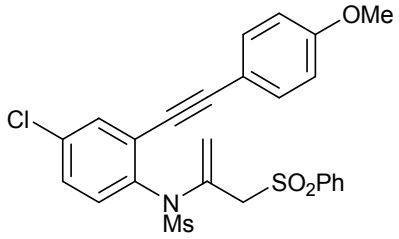
Brown solid, 177 mg, 73 %

**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 155-157 ˚C
**IR (KBr) $\nu_{max}$**: 3068, 2994, 2927, 2223, 1632, 1467, 1352, 1306, 1160, 1125, 1081, 970, 889, 766, 529 $cm^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 2.4 Hz, 1H), 7.54-7.50 (m, 4H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.38- 7.34 (m, 4H), 5.76 (s, 1H), 5.08 (s, 1H), 3.75 (s, 2H), 3.33 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 138.2, 136.6, 135.3, 134.1, 133.5, 133.4(2), 131.6, 129.8, 129.4, 129.3, 129.3, 128.6, 126.7, 122.0, 116.3, 96.4, 84.9, 60.1, 41.2.
**HRMS** calcd for $C_{24}H_{21}O_4NClS_2$ ($M+H^+$) 486.0601; found 486.0600.




**1p**, *N*-[4-chloro-2-(phenylethynyl)phenyl]-*N*-(3-tosylprop-1-en-2-yl)methanesulfonamide

Colorless semisolid, 205 mg, 82%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 2927, 2219, 1630, 1596, 1490, 1467, 1347, 1322, 1292, 1232, 1157, 1086, 760, 518 $cm^{-1}$
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.55 (s, 1H), 7.52 (d, *J* = 6.4 Hz, 2H), 7.44-7.35 (m, 5H), 7.30 (d, *J* = 7.9 Hz, 2H), 5.76 (s, 1H), 5.09 (s, 1H), 3.74 (s, 2H), 3.33 (s, 3H), 2.44 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.2, 140.2, 136.6, 135.1, 133.5, 133.3, 133.3, 131.6, 129.9, 129.8, 129.2, 128.5, 126.7, 122.0, 117.3, 116.3, 96.3, 60.1, 41.1, 21.6.
**HRMS** calcd for $C_{25}H_{23}O_4NClS_2$ ($M+H^+$) 500.0757; found 500.0760.




**1q**, *N*-{4-chloro-2-[(4-methoxyphenyl)ethynyl]phenyl}-*N*-[3-(phenylsulfonyl)prop-1-en-2-yl]-methanesulfonamide

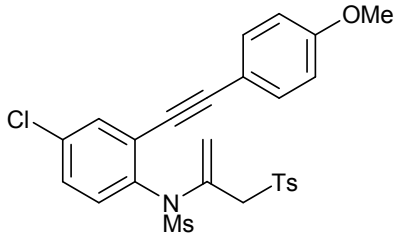
Colorless semisolid, 199 mg, 77%
**$R_f$** = 0.3 (30% ethyl acetate in hexanes)

**IR (KBr) $\nu_{max}$**: 3017, 2928, 2852, 2216, 1629, 1604, 1512, 1463, 1349, 1321, 1251, 1158, 1027, 756, 528 $cm^{-1}$

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54-7.51 (m, 3H), 7.46 (d, *J* = 8.8 Hz, 2H), 7.39-7.33 (m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.75 (s, 1H), 5.08 (s, 1H), 3.82 (s, 3H), 3.75 (s, 2H), 3.32 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.5, 138.2, 136.3, 135.2, 134.1, 133.5, 133.4, 133.2, 133.1, 129.4, 129.3, 128.6, 126.7, 116.2, 114.5, 114.3, 96.7, 83.8, 60.1, 55.4, 41.2.

**HRMS** calcd for $C_{25}H_{26}ClN_2O_5S_2$ ($M+NH_4^+$) 533.0972; found 533.0973.




**1r**, *N*-{4-chloro-2-[(4-methoxyphenyl)ethynyl]phenyl}-*N*-(3-tosylprop-1-en-2-yl)-methanesulfonamide

Colorless semisolid, 217 mg, 82%

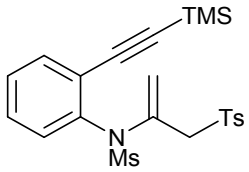
**$R_f$** = 0.3 (30% ethyl acetate in hexanes)

**IR (KBr) $\nu_{max}$**: 3020, 2929, 2216, 1632, 1602, 1511, 1462, 1398, 1347, 1321, 1290, 1250, 1157, 1027, 763, 519 $cm^{-1}$

**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 2.4 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.33-7.29 (m, 3H), 6.87 (d, *J* = 8.9 Hz, 2H), 5.76 (s, 1H), 5.08 (s, 1H), 3.82 (s, 3H), 3.74 (s, 2H), 3.32 (s, 3H), 2.44 (s, 3H).

**$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 160.4, 145.2, 136.4, 135.3, 135.1, 133.7, 133.3, 133.2, 133.1, 129.8, 129.3, 128.6, 127.1, 116.2, 114.3, 114.1, 96.7, 83.9, 60.2, 55.4, 41.2, 21. 7.

**HRMS** calcd for $C_{26}H_{25}O_5NClS_2$ ($M+H^+$) 530.0863; found 530.0860.




**1s**, *N*-(3-tosylprop-1-en-2-yl)-*N*-{2-[(trimethylsilyl)ethynyl]phenyl}methanesulfonamide

Plae brown solid, 171 mg, 74%

**$R_f$** = 0.5 (30% ethyl acetate in hexanes)

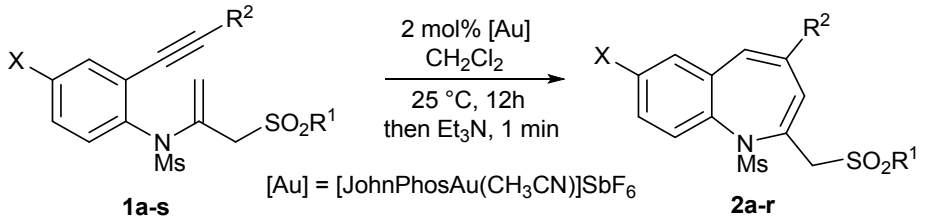
**Melting point:** 129-131 ˚C

**IR (KBr) $\nu_{max}$**: 2956, 2925, 2854, 2159, 1734, 1643, 1597, 1479, 1445, 1340, 1316, 1243, 1161, 1086, 1023, 844, 514 $cm^{-1}$

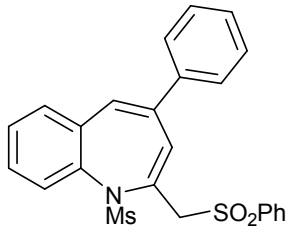
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.50 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.42-7.32 (m, 5H), 5.62 (s, 1H), 5.02 (s, 1H), 3.69 (s, 2H), 3.27 (s, 3H), 2.45 (s, 3H), 0.21 (s, 9H).

**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 145.0, 138.1, 134.3, 133.5, 132.6, 129.8, 129.7, 129.1, 128.8, 124.8, 120.8, 116.3, 60.1, 41.4, 21.7.
**HRMS** calcd for $C_{22}H_{28}O_4NSiS_2$ ($M+H^+$) 462.1229; found 462.1244.

### 2.3. Gold-catalyzed cycloisomerization reaction of aza-enynes 1a-s

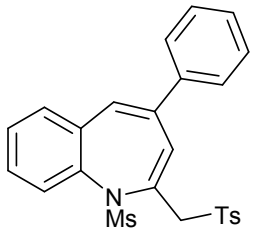



To a solution of the aza-enyne **1a-s** (0.20 mmol) in dichloromethane (2 mL) maintained at ambient temperature under an atmosphere of nitrogen, (acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate (3 mg, 0.004 mmol) was added and the reaction was stirred for 12 h at 25 °C. Triethylamine (0.06 mL, 0.40 mmol) was then added to the reaction mixture and it was stirred for a minute. Silica gel was added to the reaction mixture, the solvent was evaporated on a rotavapor and the residue was chromatographed on a silica column using petroleum ether-ethyl acetate as eluent to afford analytically pure samples of the products **2a-r**.



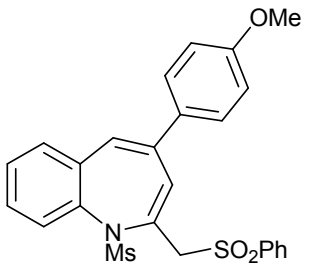

**2a**, 1-(methylsulfonyl)-4-phenyl-2-[(phenylsulfonyl)methyl]-1*H*-benzo[*b*]azepine

White solid, 80 mg, 89%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 186-188 ˚C
**IR (KBr) $\nu_{max}$**: 3053, 2997, 2924, 1637, 1591, 1485, 1446, 1405, 1337, 1310, 1156, 1134, 1082, 764, 526, 502cm$^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.44-7.32 (m, 10H), 7.24 (s, 1H), 7.20-7.17 (m, 1H), 6.49 (s, 1H), 4.56 (d, *J* = 14.5 Hz, 1H), 4.25 (d, *J* = 14.5 Hz, 1H), 2.69 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 140.1, 138.4, 137.8, 136.9, 134.8, 133.9, 132.8, 132.2, 131.7, 130.8, 130.3, 130.0, 129.1, 129.0, 128.7, 128.6, 128.3, 126.4, 64.9, 39.7.
**HRMS** calcd for $C_{24}H_{25}N_2O_4S_2$ ($M+NH_4^+$) 469.1256; found 469.1260.



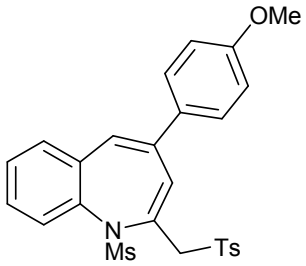

**2b**, 1-(methylsulfonyl)-4-phenyl-2-(tosylmethyl)-1*H*-benzo[*b*]azepine

White solid, 82 mg, 88%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 157-159 ˚C
**IR (KBr) $\nu_{max}$**: 3051, 2988, 2924, 1719, 1639, 1595, 1488, 1448, 1337, 1146, 1084, 965, 758, 597, 507 $cm^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.37 (m, 10H), 7.24 (s, 1H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.55 (s, 1H), 4.50 (d, *J* = 14.5 Hz, 1H), 4.25 (d, *J* = 14.5 Hz, 1H), 2.68 (s, 3H), 2.36 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 144.8, 140.1, 138.5, 136.9, 134.9, 134.7, 132.59, 132.1, 131.6, 130.5, 130.5, 130.0, 129.7, 129.0, 128.6, 128.5, 128.4, 126.4, 65.0, 39.7, 21.6.
**HRMS** calcd for $C_{25}H_{27}O_4N_2S_2$ ($M+NH_4^+$) 483.1412; found 483.1417.



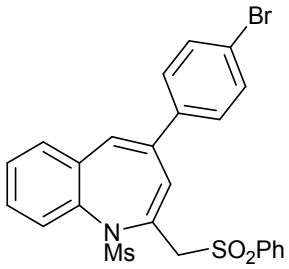

**2c**, 4-(4-methoxyphenyl)-1-(methylsulfonyl)-2-[(phenylsulfonyl)methyl]-1*H*-benzo[*b*]azepine

White solid, 85 mg, 88%
**$R_f$** = 0.3 (30% ethyl acetate in hexanes)
**Melting point:** 254-256 ˚C
**IR (KBr) $\nu_{max}$**: 3059, 2993, 2917, 2837, 1641, 1603, 1511, 1446, 1334, 1311, 1249, 1135, 1083, 957, 745, 530$cm^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.4 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.41-7.31 (m, 7H), 7.18 (s, 1H), 7.17-7.14 (m, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.47 (s, 1H), 4.54 (d, *J* = 14.5 Hz, 1H), 4.25 (d, *J* = 14.5 Hz, 1H), 3.85 (s, 3H), 2.68 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.1, 137.9, 136.8, 134.9, 133.8, 132.9, 132.5, 132.1, 130.5, 130.2, 130.1, 129.9, 129.1, 128.6, 128.3, 127.6, 114.4, 64.9, 55.5, 39.7.
**HRMS** calcd for $C_{25}H_{24}NO_5S_2$ ($M+H^+$) 482.1096; found 482.1095.



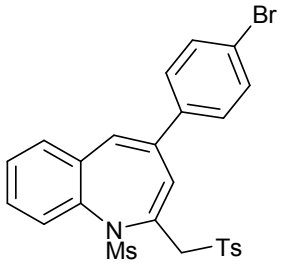

**2d**, 4-(4-methoxyphenyl)-1-(methylsulfonyl)-2-(tosylmethyl)-1*H*-benzo[*b*]azepine

White solid, 91 mg, 92%
**$R_f$** = 0.3 (30% ethyl acetate in hexanes)
**Melting point:** 231-233 ˚C
**IR (KBr) $\nu_{max}$**:3422, 2921, 1603, 1511, 1333, 1293, 1251, 1137, 1086, 1026, 959, 828, 758, 559, 509cm$^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.40-7.33 (m, 5H), 7.18 (s, 1H), 7.08 (d, *J* = 8.2 Hz, 3H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.54 (s, 1H), 4.48 (d, *J* = 14.6 Hz, 1H), 4.25 (d, *J* = 14.6 Hz, 1H), 3.85 (s, 3H), 2.67 (s, 3H), 2.36 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 160.1, 144.8, 137.9, 136.8, 134.9, 132.7, 132.5, 132.0, 130.24, 130.22, 130.1, 129.9, 129.7, 128.41, 128.38, 127.6, 114.4, 65.0, 55.5, 39.7, 21.7.
**HRMS** calcd for $C_{26}H_{26}O_5NS_2$ ($M+H^+$) 496.1252; found 496.1268.



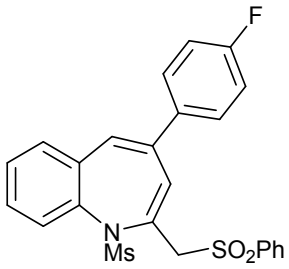

**2e**, 4-(4-bromophenyl)-1-(methylsulfonyl)-2-[(phenylsulfonyl)methyl]-1*H*-benzo[*b*]azepine

White solid, 89 mg, 84 %
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 214-216 ˚C
**IR (KBr) $\nu_{max}$**:3061, 2993, 2921, 1639, 1585, 1482, 1445, 1403, 1337, 1309, 1244, 1155, 1133, 1080, 901, 743, 529cm$^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.3 Hz, 2H), 7.56-7.52 (m, 3H), 7.45-7.33 (m, 5H), 7.31 (d, J = 8.6 Hz, 2H), 7.23 (s, 1H), 7.19-7.17 (m, 1H), 6.44 (s, 1H), 4.54 (d, *J* = 14.5 Hz, 1H), 4.24 (d, *J* = 14.5 Hz, 1H), 2.68 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 138.9, 137.9, 137.3, 136.9, 134.6, 133.9, 132.2, 131.9, 131.1, 130.8, 130.1, 129.2, 128.85, 128.3, 128.0, 122.8, 64.9, 39.8.
**HRMS** calcd for $C_{24}H_{21}BrNO_4S_2$ ($M+H^+$) 532.0075; found 532.0073.



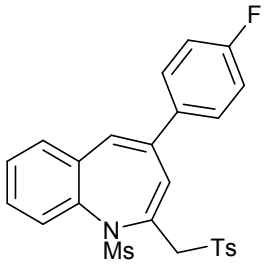

**2f**, 4-(4-bromophenyl)-1-(methylsulfonyl)-2-(tosylmethyl)-1*H*-benzo[*b*]azepine

White solid, 96 mg,88 %
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 212-214 ˚C
**IR (KBr) $\nu_{max}^{-1}$**: 3064, 2986, 2921, 1596, 1487, 1341, 1315, 1248, 1157, 1135, 1083, 1004, 785, 505cm
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.6 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.42-7.36 (m, 3H), 7.32 (d, *J* = 8.6 Hz, 2H), 7.23 (s, 1H), 7.13-7.10 (m, 3H), 6.50 (s, 1H), 4.48 (d, *J* = 14.5 Hz, 1H), 4.24 (d, *J* = 14.5 Hz, 1H), 2.68 (s, 3H), 2.37 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 144.9, 139.0, 137.3, 136.9, 135.0, 134.6, 132.2, 132.02, 131.9, 131.8, 131.0, 130.8, 130.1, 129.7, 128.6, 128.4, 128.0, 122.8, 64.9, 39.7, 21.7.
**HRMS** calcd for $C_{25}H_{23}O_4NBrS_2$ ($M+H^+$) 544.0252; found 544.0243.




**2g**, 4-(4-fluorophenyl)-1-(methylsulfonyl)-2-[(phenylsulfonyl)methyl]-1*H*-benzo[*b*]azepine

White solid, 76 mg, 81%
**$R_f$** = 0.5 (30% ethyl acetate in hexanes)
**Melting point:** 210-212 ˚C
**IR (KBr) $\nu_{max}$**: 3072, 2923, 2853, 1601, 1511, 1443, 1336, 1313, 1231, 1157, 1135, 1083, 1008, 840, 764, 520$cm^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.44-7.33 (m, 7H), 7.20 (s, 1H), 7.18-7.16 (m, 1H), 7.11 (t, *J* = 8.6 Hz, 2H), 6.46 (s, 1H), 4.54 (d, *J* = 14.5 Hz, 1H), 4.24 (d, *J* = 14.5 Hz, 1H), 2.70 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 137.9, 137.4, 136.8, 134.7, 133.9, 132.5, 132.10, 131.6, 130.9, 130.5, 130.0, 129.1, 128.7, 128.3, 128.2, 128.2, 116.0 (d, *J* = 21.8 Hz), 64.9, 39.8.
**HRMS** calcd for $C_{24}H_{21}O_4NFS_2$($M+H^+$) 470.0896; found 470.0888.




**2h**, 4-(4-fluorophenyl)-1-(methylsulfonyl)-2-(tosylmethyl)-1*H*-benzo[*b*]azepine

White solid, 79 mg,82%

**$R_f$** = 0.5 (30% ethyl acetate in hexanes)

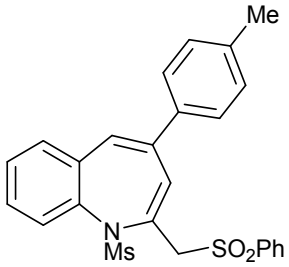
**Melting point:** 20-207 ˚C

**IR (KBr) $\nu_{max}$**: 3063, 2995, 2921, 1898, 1718, 1638, 1596, 1506, 1442, 1408, 1340, 1294, 1213, 1158, 1133, 903, 758, 505cm$^{-1}$

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.45-7.36 (m, 5H), 7.20 (s, 1H), 7.14-7.10 (m, 5H), 6.53 (s, 1H), 4.48 (d, *J* = 14.6 Hz, 1H), 4.25 (d, *J* = 14.6 Hz, 1H), 2.69 (s, 3H), 2.37 (s, 3H).

**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 163.0 (d, *J* = 249.1 Hz), 144.9, 137.4, 136.8, 136.2 (d, *J* = 3.0 Hz), 134.9, 134.7, 132.32, 132.0, 131.5, 130.7, 130.6, 130.0, 129.7, 128.5, 128.4, 128.2 (d, *J* = 8.2 Hz), 116.0 (d, *J* = 21.7 Hz) 64.9, 39.8, 21.7.

**HRMS** calcd for $C_{25}H_{22}O_4NFNaS_2$ ($M+Na^+$) 506.0872; found 506.0883.




**2i**, 1-(methylsulfonyl)-2-[(phenylsulfonyl) methyl]-4-(p-tolyl)-1*H*-benzo[*b*]azepine

White solid, 73 mg, 78%

**$R_f$** = 0.4 (30% ethyl acetate in hexanes)

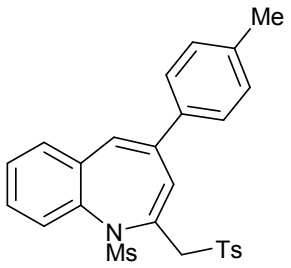
**Melting point:** 163-165 ˚C

**IR (KBr) $\nu_{max}$**: 3062, 2987, 2922, 1717, 1589, 1482, 1446, 1337, 1310, 1248, 1156, 1134, 962, 746, 524cm$^{-1}$

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.52 (t, *J* = 7.5Hz, 1H), 7.42-7.31 (m, 7H), 7.24-7.22 (m, 3H), 7.18-7.16 (m, 1H), 6.47 (s, 1H), 4.55 (d, *J* = 14.5 Hz, 1H), 4.25 (d, *J* = 14.5 Hz, 1H), 2.67 (s, 3H), 2.39 (s, 3H).

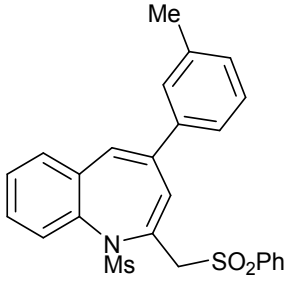
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 138.7, 138.2, 137.8, 137.2, 136.8, 134.8, 133.9, 132.9, 132.2, 131.0, 130.6, 130.2, 130.0, 129.7, 129.1, 128.6, 128.3, 126.3, 64.9, 39.7, 21.2.

**HRMS** calcd for $C_{25}H_{23}O_4NNaS_2$ ($M+Na^+$) 488.0966; found 488.0979.



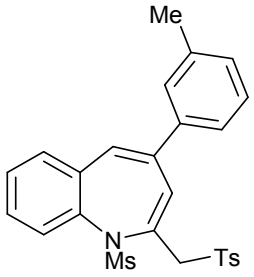

**2j**, 1-(methylsulfonyl)-4-(p-tolyl)-2-(tosylmethyl)-1*H*-benzo[*b*]azepine

White solid, 76 mg, 84%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 186-188 ˚C
**IR (KBr) $\nu_{max}$**: 3023, 2921, 1641, 1596, 1446, 1335, 1156, 1012, 964, 814, 761, 513cm$^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.41-7.33 (m, 5H), 7.24-7.22 (m, 3H), 7.11-7.07 (m, 3H), 6.54 (s, 1H), 4.49 (d, *J* = 14.5 Hz, 1H), 4.25 (d, *J* = 14.8 Hz, 1H), 2.67 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 144.8, 138.7, 138.3, 137.2, 136.8, 134.9, 134.8, 132.7, 132.1, 130.8, 130.4, 129.9, 129.7, 128.4, 128.4, 126.3, 65.0, 39.7, 21.7, 21.2.
**HRMS** calcd for $C_{26}H_{26}O_4NS_2$ ($M+H^+$) 480.1303; found 480.1313.



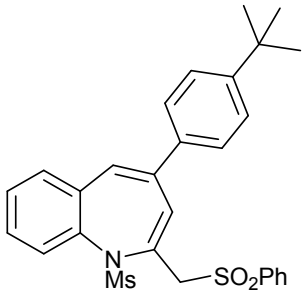

**2k**, 1-(methylsulfonyl)-2-[(phenylsulfonyl)methyl]-4-(m-tolyl)-1*H*-benzo[*b*]azepine

White solid, 79 mg, 85%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 211-213 ˚C
**IR (KBr) $\nu_{max}$**: 3053, 2996, 2920, 1641, 1586, 1483, 1446, 1339, 1308, 1248, 1156, 1135, 1083, 1007, 957, 788, 745, 506 cm$^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.43-7.37 (m, 3H), 7.34- 7.29 (m, 3H), 7.22 (d, *J* = 6.42 Hz, 2H), 7.20-7.17 (m, 2H), 6.47 (s, 1H), 4.55 (d, *J* = 14.5 Hz, 1H), 4.25 (d, *J* = 14.5 Hz, 1H), 2.69 (s, 3H), 2.41 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 140.1, 138.8, 138.5, 137.9, 136.9, 134.8, 133.8, 132.9, 132.2, 131.5, 130.7, 130.2, 130.0, 129.4, 129.1, 128.9, 128.6, 128.4, 127.1, 123.5, 65.0, 39.8, 21.5.
**HRMS** calcd for $C_{25}H_{24}O_4NS_2$ ($M+H^+$) 466.1147; found 466.1141.



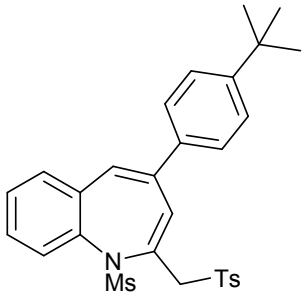

**2l**, 1-(methylsulfonyl)-4-(*m*-tolyl)-2-(tosylmethyl)-1*H*-benzo[*b*]azepine

White solid, 81mg, 90%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 198-200 ˚C
**IR (KBr) $\nu_{max}$**:2923, 1719, 1631, 1596, 1461, 1407, 1335, 1153, 1085, 1015, 920, 816, 760, 667, 517cm$^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.41-7.36 (m, 3H), 7.31-7.30 (m, 1H), 7.25-7.23 (m, 3H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.12-7.08 (m, 3H), 6.54 (s, 1H), 4.50 (d, *J* = 14.5 Hz, 1H), 4.25 (d, *J* = 14.5 Hz, 1H), 2.68 (s, 3H), 2.41 (s, 3H), 2.36 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 144.8, 140.1, 138.8, 138.5, 136.8, 134.9, 134.8, 132.7, 132.1, 131.4, 130.5, 130.4, 130.0, 129.7, 129.4, 128.9, 128.5, 128.4, 127.1, 123.5, 65.0, 39.7, 21.7, 21.5.
**HRMS** calcd for $C_{26}H_{25}O_4NNaS_2$ ($M+Na^+$) 502.1123; found 502.1142.



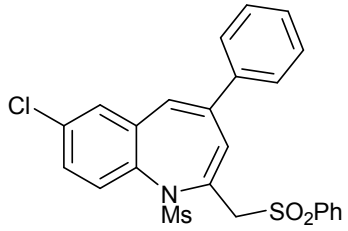

**2m**, 4-[4-(*tert*-butyl)phenyl]-1-(methylsulfonyl)-2-[(phenylsulfonyl)methyl]-1*H*-benzo[*b*]azepine

White solid, 87mg,86%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 172-174 ˚C
**IR (KBr) $\nu_{max}$**: 3062, 3028, 2961, 2930, 2868, 1721, 1631, 1482, 1444, 1406, 1338, 1317, 1152, 1082, 960, 762, 532cm$^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.9 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.45-7.31 (m, 9H), 7.22 (s, 1H), 7.20-7.17 (m, 1H), 6.47 (s, 1H), 4.56 (d, *J* = 14.5 Hz, 1H), 4.24 (d, *J* = 14.5 Hz, 1H), 2.68 (s, 3H), 1.34 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 151.9, 138.2, 137.8, 137.1, 136.8, 134.8, 133.8, 132.9, 132.2, 131.1, 130.6, 130.1, 130.0, 129.1, 128.6, 128.4, 126.1, 126.0, 65.0, 39.7, 34.7, 31.3.
**HRMS** calcd for $C_{28}H_{30}NO_4S_2$ ($M+H^+$) 508.1616; found 508.1615.



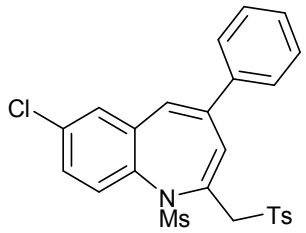

**2n**, 4-[4-(*tert*-butyl) phenyl]-1-(methylsulfonyl)-2-(tosylmethyl)-1*H*-benzo[*b*]azepine

White solid, 89 mg, 85%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 235-237 ˚C
**IR (KBr) $\nu_{max}$**: 3051, 2997, 2962, 2928, 2866, 1926, 1644, 1596, 1510, 1483, 1441, 1402, 1338, 1315, 1286, 1168, 1140, 1007, 967, 764, 549cm$^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 9H), 7.22 (s, 1H), 7.12 (d, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.53 (s, 1H), 4.50 (d, *J* = 14.5 Hz, 1H), 4.24 (d, *J* = 14.5 Hz, 1H), 2.67 (s, 3H), 2.36 (s, 3H), 1.35 (s, 9H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 151.9, 144.8, 138.2, 137.2, 136.8, 134.8, 132.7, 132.1, 131.0, 130.4, 130.3, 130.0, 129.7, 128.4, 128.4, 126.1, 126.0, 65.0, 39.7, 34.7, 31.3, 21.7.
**HRMS** calcd for $C_{29}H_{32}O_4NS_2$ ($M+H^+$) 522.1773; found 522.1754.



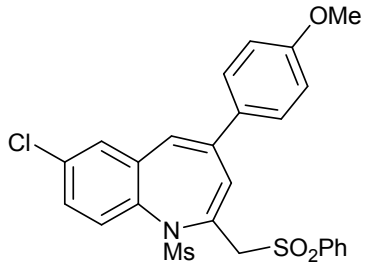

**2o**, 7-chloro-1-(methylsulfonyl)-4-phenyl-2-[(phenylsulfonyl)methyl]-1*H*-benzo[*b*]azepine

White solid, 83mg, 86%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 201-203 ˚C
**IR (KBr) $\nu_{max}$**: 3056, 3004, 2926, 1635, 1587, 1478, 1444, 1344, 1305, 1165, 1083, 1002, 895, 766, 609, 511cm$^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 2H), 7.60-7.56 (m, 1H), 7.42-7.37 (m, 9H), 7.16-7.15 (m, 2H), 6.50 (s, 1H), 4.54 (d, *J* = 14.4 Hz, 1H), 4.23 (d, *J* = 14.4 Hz, 1H), 2.70 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 139.8, 139.7, 137.9, 136.2, 135.4, 134.6, 134.0, 133.5, 132.8, 130.9, 130.7, 130.2, 129.4, 129.2, 129.1, 129.0, 128.3, 126.5, 64.7, 39.9.
**HRMS** calcd for $C_{24}H_{21}ClNO_4S_2$(M+H) 486.0601; found 486.0600.



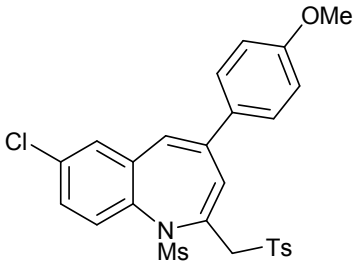

**2p**, 7-chloro-1-(methylsulfonyl)-4-phenyl-2-(tosylmethyl)-1*H*-benzo[*b*]azepine

White solid, 82mg, 82%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 223-225 ˚C
**IR (KBr) $\nu_{max}$**: 3053, 3003, 2926, 1637, 1592, 1482, 1347, 1309, 1164, 1144, 1084, 767, 511 $cm^{-1}$
**$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.3 Hz, 2H), 7.43- 7.39 (m, 5H), 7.36 (d, *J* = 2.4 Hz, 1H), 7.32 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.15-7.14 (m, 3H), 7.05 (d, *J* = 8.6 Hz, 1H), 6.59 (s, 1H), 4.46 (d, *J* = 14.5 Hz, 1H), 4.24 (d, *J* = 14.6 Hz, 1H), 2.69 (s, 3H), 2.40 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 145.1, 139.8, 139.6, 136.1, 135.4, 134.4, 133.2, 132.5, 131.0, 130.4, 129.9, 129.7, 129.3, 129.1, 128.9, 128.3, 126.4, 64.8, 39.8, 21.6.
**HRMS** calcd for $C_{25}H_{23}O_4NClS_2$ ($M+H^+$) 500.0757; found 500.0751.




**2q**, 7-chloro-4-(4-methoxyphenyl)-1-(methylsulfonyl)-2-[(phenylsulfonyl)methyl]-1*H*-benzo[*b*]-azepine

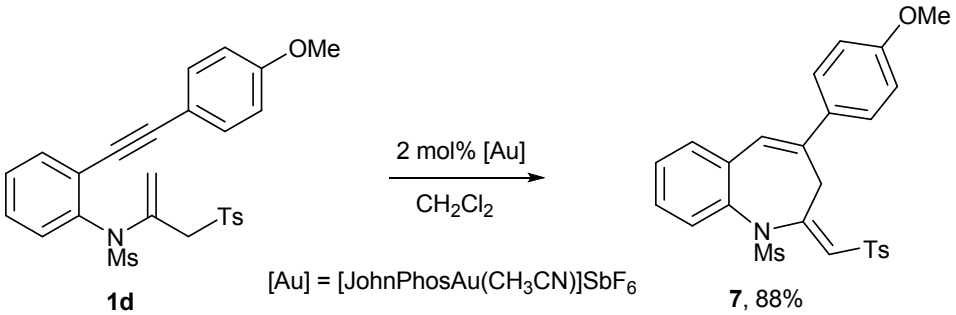
White solid, 86mg, 83%
**$R_f$** = 0.3 (30% ethyl acetate in hexanes)
**Melting point:** 215-217 ˚C
**IR (KBr) $\nu_{max}$**: 3283, 3008, 2926, 2849, 1669, 1634, 1605, 1509, 1480, 1455, 1348, 1305, 1248, 1155, 1021, 740, 523$cm^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.41-7.33 (m, 6H), 7.12 (d, *J* = 9.2 Hz, 1H), 7.08 (s, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.48 (s, 1H), 4.52 (d, *J* = 14.4 Hz, 1H), 4.23 (d, *J* = 14.4 Hz, 1H), 3.85 (s, 3H), 2.68 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.3, 139.2, 137.9, 136.3, 135.3, 134.5, 134.0, 133.4, 132.9, 132.0, 130.6, 130.3, 129.2, 128.6, 128.3, 127.7, 114.5, 64.8, 55.5, 39.9.
**HRMS** calcd for $C_{25}H_{26}N_2O_5ClS_2$($M+NH_4^+$) 533.0972; found 533.0975.



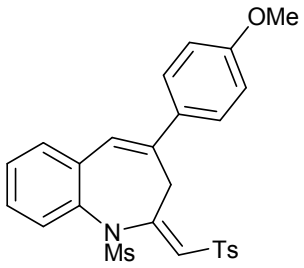

**2r**, 7-chloro-4-(4-methoxyphenyl)-1-(methylsulfonyl)-2-(tosylmethyl)-1*H*-benzo[*b*]azepine

White solid, 92mg, 87%
**$R_f$** = 0.3 (30% ethyl acetate in hexanes)
**Melting point:** 243-245 ˚C
**IR (KBr) $\nu_{max}$**: 2999, 2960, 2921, 2836, 1884, 1643, 1605, 1512, 1475, 1344, 1319, 1255, 1157, 1085, 818, 748, 514cm$^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 2.4 Hz, 1H), 7.28 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 1H), 7.01 (d, *J* = 8.6 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.58 (s, 1H), 4.44 (d, *J* = 14.6 Hz, 1H), 4.24 (d, *J* = 14.6 Hz, 1H), 3.85 (s, 3H), 2.67 (s, 3H), 2.39 (s, 3H).
**$^{13}$C NMR** (126 MHz, $CDCl_3$) δ 160.3, 145.1, 139.3, 136.2, 135.3, 134.9, 134.34, 133.1, 132.7, 132.0, 130.7, 130.1, 129.7, 129.2, 128.4, 128.4, 127.7, 114.5, 64.9, 55.5, 39.8, 21.7.
**HRMS** calcd for $C_{26}H_{25}O_5NClS_2$ ($M+H^+$) 530.0863; found 530.0888.

### 2.4. Isolation of the labile intermediate 7 and its conversion to benzoazepine 2d

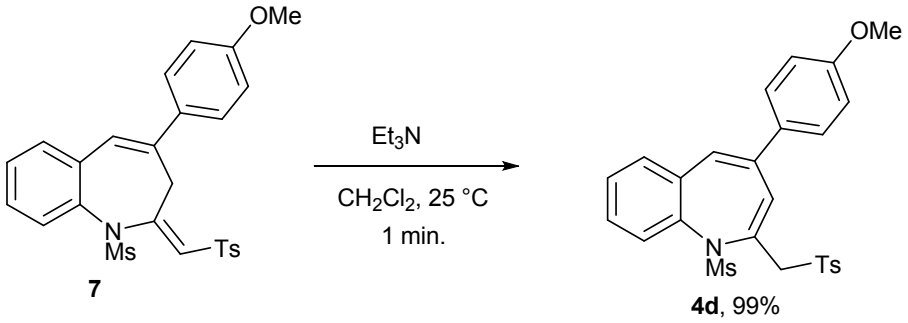



A solution of the aza-enyne **1d** (99mg, 0.20 mmol) in dichloromethane (2 mL) was treated with (acetonitrile)[(2-biphenyl)di-*tert*-butylphosphine]gold(I) hexafluoroantimonate (3 mg, 0.004 mmol) for 12 h at 25 °C. The solvent was evaporated and the residue was chromatographed on a silica column using petroleum ether-ethyl acetate as eluent to afford the exocyclic benzoazepine **7** as a white solid.




**7**, (*E*)-4-(4-methoxyphenyl)-1-(methylsulfonyl)-2-(tosylmethylene)-2,3-dihydro-1*H*-benzo[*b*]-azepine

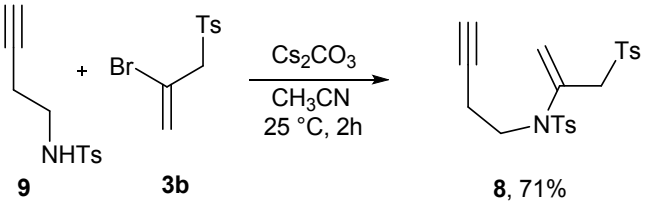
White solid, 87 mg, 88%
**$R_f$** = 0.4 (30% ethyl acetate in hexanes)
**Melting point:** 164-166 ˚C
**IR (KBr) $\nu_{max}$**: 3048, 2920, 1601, 1511, 1483, 1337, 1293, 1250, 1153, 1136, 1084, 1024, 956, 756, 506cm$^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.45- 7.40 (m, 2H), 7.34-7.30 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 3.6 Hz, 2H), 3.87 (s, 3H), 2.77 (s, 3H), 2.39 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.1, 156.7, 144.1, 141.0, 139.3, 137.0, 135.6, 131.8, 130.1, 129.9, 129.7, 129.4, 128.3, 127.8, 127.0, 125.2, 117.8, 114.3, 55.5, 39.2, 30.9, 21.6.
**HRMS** calcd for $C_{26}H_{26}O_5NS_2$ ($M+H^+$) 496.1252; found 496.1253.




**7** **4d**, 99%

Benzoazepine **7** (50 mg, 0.10 mmol) was dissolved in dichloromethane (1 mL) and triethylamine (0.03 mL, 0.20 mmol) was added to the reaction mixture and it was stirred for a minute. Silica gel was added to the reaction mixture, the solvent was evaporated on a rotavapor and the residue was chromatographed on a silica column using petroleum ether-ethyl acetate as eluent to afford the benzoazepine **2d** (49 mg, 99%) as a white solid. It was identical in all respects with to the sample obtained in the one-pot procedure.

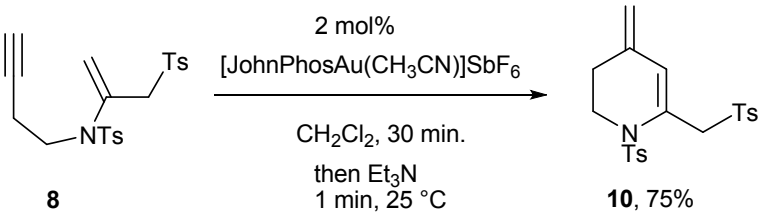
## 2.5. Preparation and cycloisomerization of the aliphatic 3-aza-1,6-enyne 8




Cesium carbonate (408 mg, 1.25 mmol)-mediated union of *N*-(but-3-ynyl)-4-methylbenzenesulfonamide **9** (112 mg, 0.50 mmol) with bromoallyl sulfone **3b** (192 mg, 0.70 mmol) was carried out as described earlier (Section 2.1). The aliphatic enyne *N*-(but-3-ynyl)-4-methyl-N-(3-tosylprop-1-en-2-yl)benzenesulfonamide **8** was obtained in 71% yield as a colorless liquid after chromatography.

**8**, *N*-(but-3-ynyl)-4-methyl-*N*-(3-tosylprop-1-en-2-yl)benzenesulfonamide

Colorless liquid, 148 mg, 71%
**$R_f$** = 0.5 (30% ethyl acetate in hexanes)
**IR (KBr) $\nu_{max}$**: 3286, 2925, 1923, 1630, 1597, 1451, 1348, 1319, 1160, 1087, 965, 816, 652, 549 $cm^{-1}$
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.53 (d, *J* = 1.2 Hz, 1H), 4.89 (d, *J* = 1.2 Hz, 1H), 4.17 (s, 2H), 3.39 (t, *J* = 7.94 Hz, 2H), 2.47-2.46 (m, 5H), 2.42 (s, 3H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 145.2, 144.3, 136.1, 135.7, 133.2, 130.0, 129.5, 128.3, 128.0, 121.2, 80.8, 70.2, 62.8, 49.6, 21.7, 21.6, 18.7.
**HRMS** calcd for $C_{21}H_{24}NO_4S_2$ ($M+H^+$) 418.1147; found 418.1149.




Gold-catalyzed cycloisomerization of **8** (83 mg, 0.2 mmol) was carried out in the presence of the catalyst (3 mg, 0.004 mmol) in 2 mL dichloromethane as described for the aromatic analogues. Exposure to triethylamine (0.06 mL, 0.40 mmol) and chromatography afforded the 4-methylene tetrahydropyridine derivative **10** as a white solid (63 mg, 75%).

**10**, 4-methylene-1-tosyl-6-(tosylmethyl)-1,2,3,4-tetrahydropyridine

White solid, 63 mg, 75%
**$R_f$** = 0.5 (30% ethyl acetate in hexanes)
**Melting point:** 121-123 ˚C
**IR (KBr) $\nu_{max}$**: 3286, 2926, 1628, 1597, 1350, 1319, 1159, 1087, 815, 755, 549 $cm^{-1}$

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.29-7.26 (m, 2H), 6.06 (s, 1H), 4.93 (s, 1H), 4.74 (s, 1H), 4.52 (s, 2H), 3.31-3.28 (m, 2H), 2.45 (s, 3H), 2.42 (s, 3H), 1.97-1.94 (m,2H).
**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 144.8, 144.3, 136.7, 136.1, 136.1, 129.9, 129.7, 128.6, 127.4, 126.8, 126.6, 115.5, 61.7, 46.7, 27.3, 21.7, 21.7.
**HRMS** calcd for $C_{21}H_{24}O_4NS_2$ (M+H) 418.1147; found 418.1138.

**3. Crystallographic data for 7 and 2r**

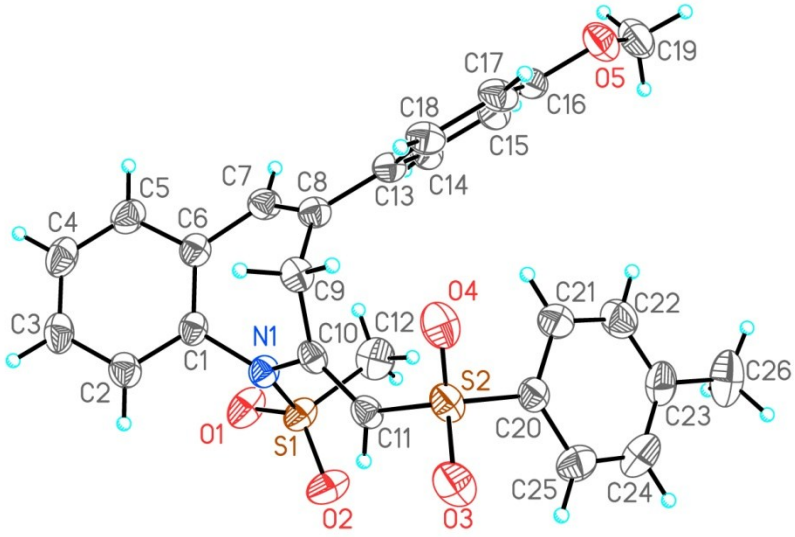



**Figure 1:** The ORTEP diagram of **7** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

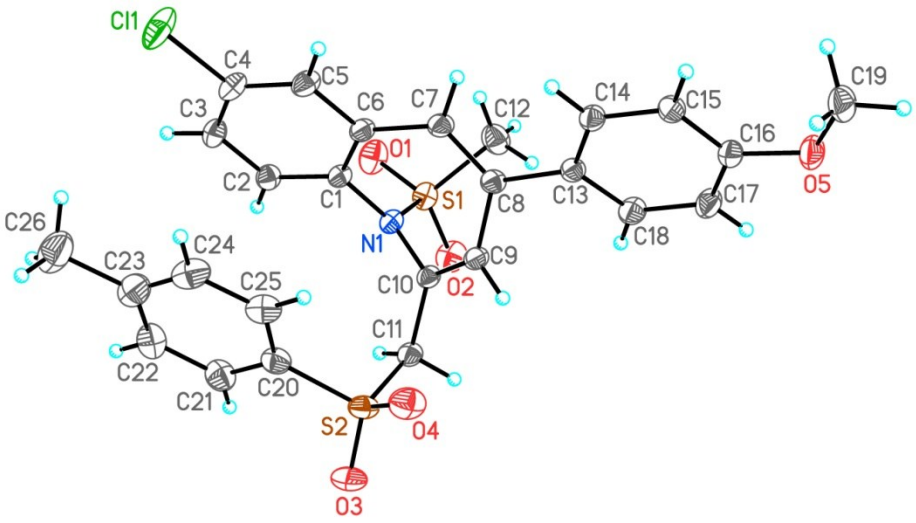



**Figure 2:** The ORTEP diagram of **2r** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

**Data collection:** X-ray data for the two compounds were collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[1] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Unit cell dimensions were determined using 9568 reflections for **7** and 7113 reflections for **2r** compounds data. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97[2] and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7.[2] 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.

1. SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.
2. G. M. Sheldrick, SHELXS97 and SHELXL Version 2014/7, http://shelx.uni-ac.gwdg.de/SHELX/index.php

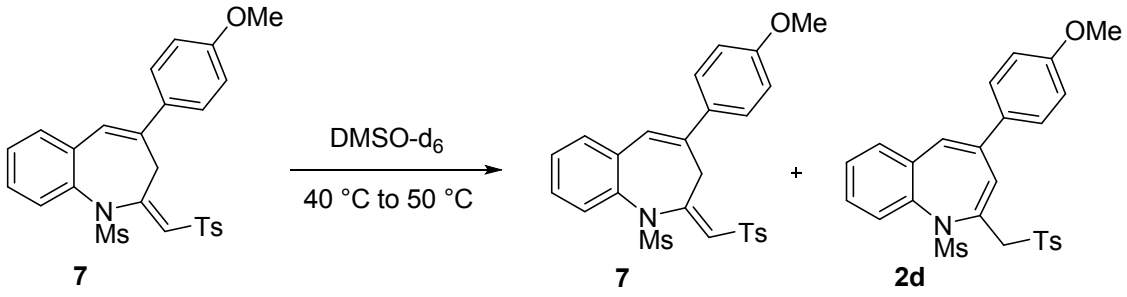
| Compound reference | **7** | **2r** |
|---|---|---|
| Chemical formula | $C_{26}H_{25}NO_5S_2$ | $C_{26}H_{24}ClNO_5S_2$ |
| Formula Mass | 495.59 | 530.03 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | *P***Error!** |
| *a*/Å | 13.9256(9) | 9.7246(6) |
| *b*/Å | 10.3322(7) | 11.0418(6) |
| *c*/Å | 17.0868(11) | 12.8181(7) |
| *α*/° | 90 | 70.8320(10) |
| *β*/° | 94.6470(10) | 71.9300(10) |
| *γ*/° | 90 | 88.3310(10) |
| Unit cell volume/Å$^3$ | 2450.4(3) | 1231.88(12) |
| Temperature/K | 293(2) | 293(2) |
| No. of formula units per unit cell, *Z* | 4 | 2 |
| Radiation type | MoKα | MoKα |
| Absorption coefficient, $\mu$/mm$^{-1}$ | 0.255 | 0.363 |
| No. of reflections measured | 22843 | 14559 |
| No. of independent reflections | 4319 | 5780 |
| $R_{int}$ | 0.0207 | 0.0183 |
| Final $R_1$ values ($I > 2\sigma(I)$) | 0.0469 | 0.0404 |
| Final $wR(F^2)$ values ($I > 2\sigma(I)$) | 0.1193 | 0.1035 |
| Final $R_1$ values (all data) | 0.0529 | 0.0463 |
| Final $wR(F^2)$ values (all data) | 0.1243 | 0.1075 |
| Goodness of fit on $F^2$ | 1.084 | 1.026 |
| CCDC number | 1446305 | 1446306 |

CCDC 1446305 (**7**) and CCDC 1446306 (**2r**) contain 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.

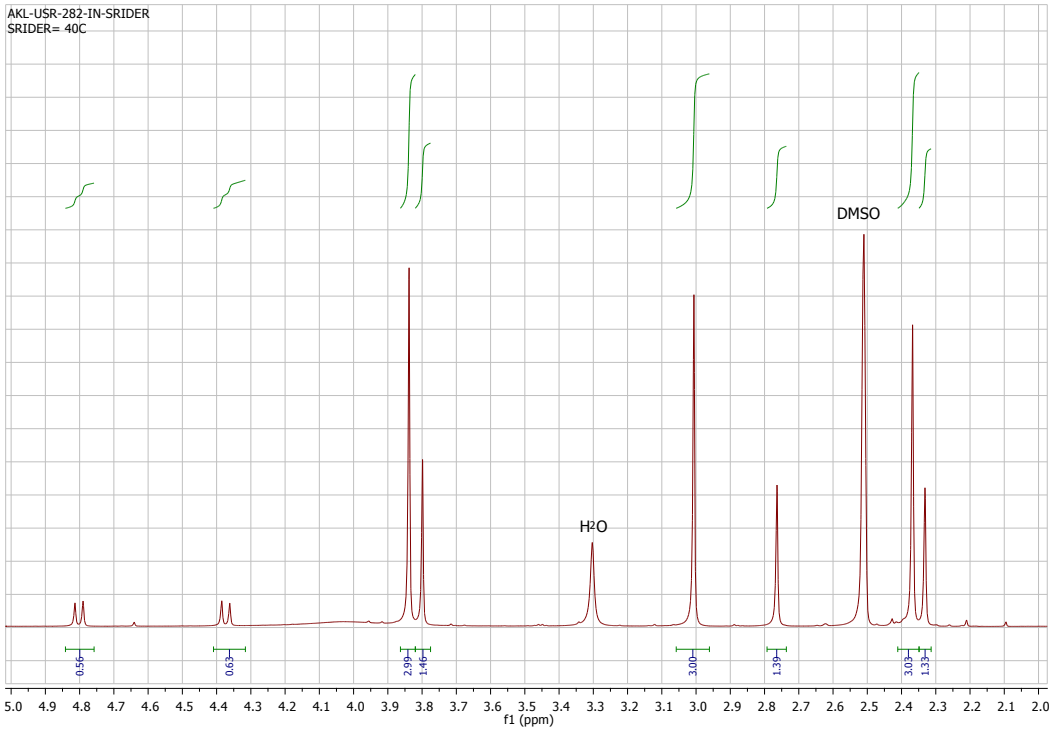
**4. Variable temperature NMR study of the isomerization of 7 into 2d**

It may be recalled that the structure of **7** has been unambiguously established by single crystal X-ray analysis. Surprisingly, resonance corresponding to the endocyclic methylene group was not visible in the $^{1}$H NMR spectrum of **7** whereas the $^{13}$C NMR and all other analytical data completely agreed with the assigned structure. A similar phenomenon was recently reported in closely related 2,3-dihydro-1*H*-azepine and 1*H*-azepin-2(3*H*)-one derivatives.[5] This anomaly was explained by invoking the presence of rapidly inter-converting conformers in solution.[5] To examine this further, variable temperature $^{1}$H NMR of a sample of **7** was investigated in DMSO-d6. However, rapid and partial isomerization of **7** to the more stable endocyclic isomer **2d** was observed in DMSO. Warming of the NMR sample up to 50 °C resulted in the increase of the ratio of **2d**. The isomerization does not proceed to completion in DMSO at 50 °C even after 1h. The relevant portions of selected $^{1}$H NMR spectra are given in Figure 1. As described earlier (see section 2.4) isolated sample of **7** could be completely converted to the endocyclic benzoazepine 2d by treating with triethylamine. The variable temperature NMR studies lend additional support to this observation.

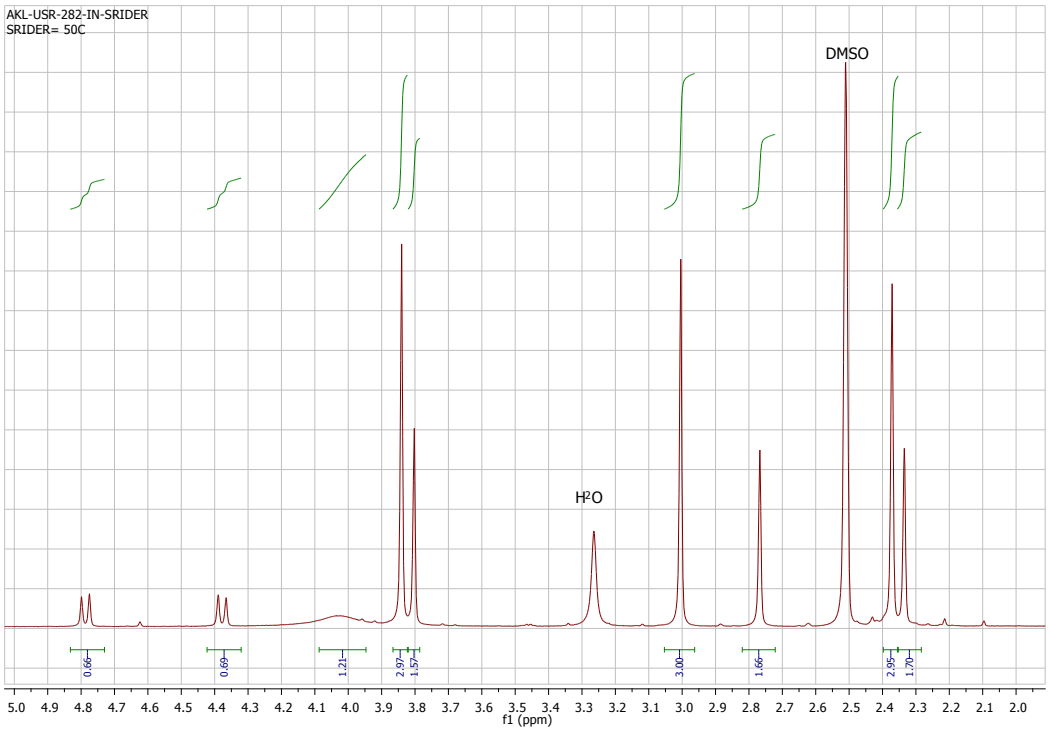



[5] W. Zhu, L. Zhao and M.-X. Wang, *J. Org. Chem*., 2015, **80**, 12047.

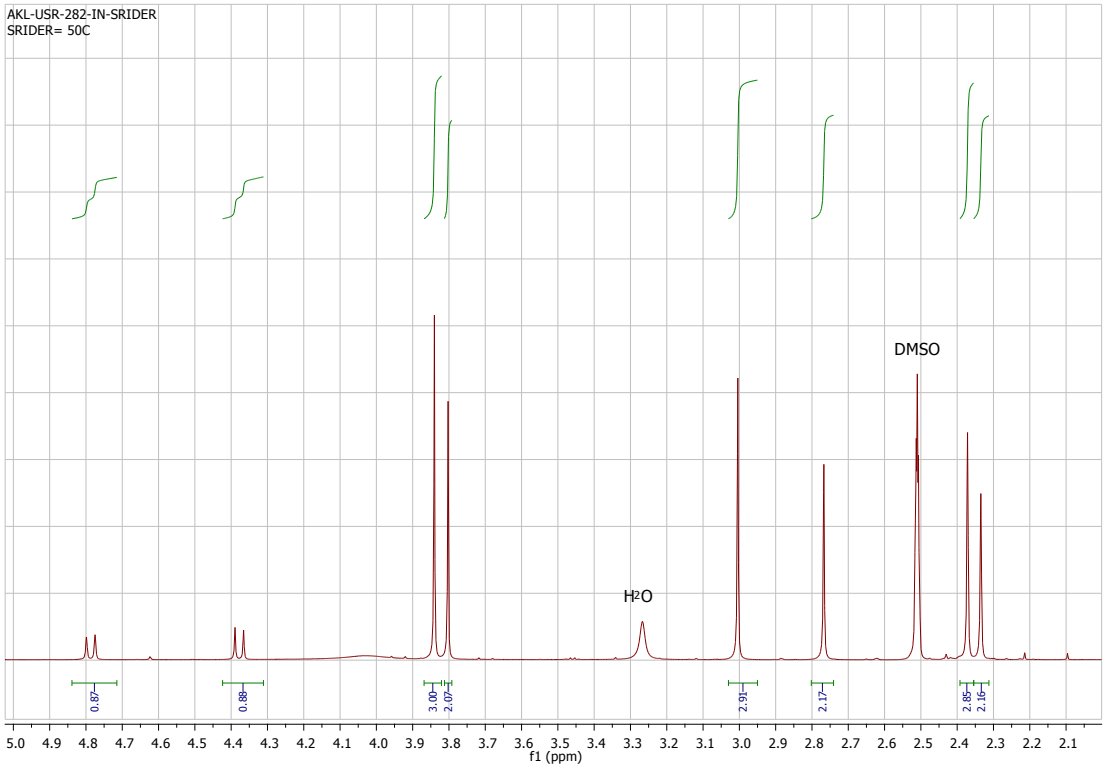
$^{1}$H NMR in DMSO at 40 °C (600 MHz): Mixture of 7 + 2d (appr. 1: 0.2): Exocyclic methylene resonances (*dd*) at d 4.80 and 4.38 of 2d begin to appear.



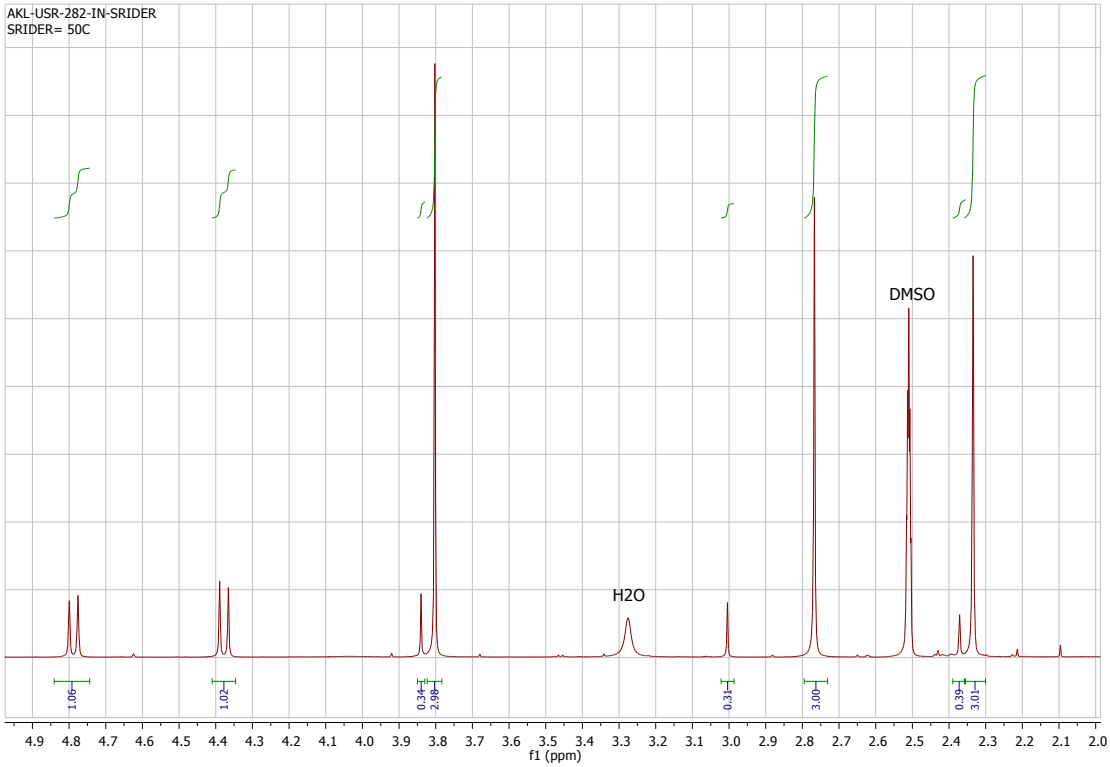

**After 10 minutes at 50 °C. 7: 2d = 3:0.7**




**After 20 minutes at 50 °C. 7: 2d = 1:0.3**

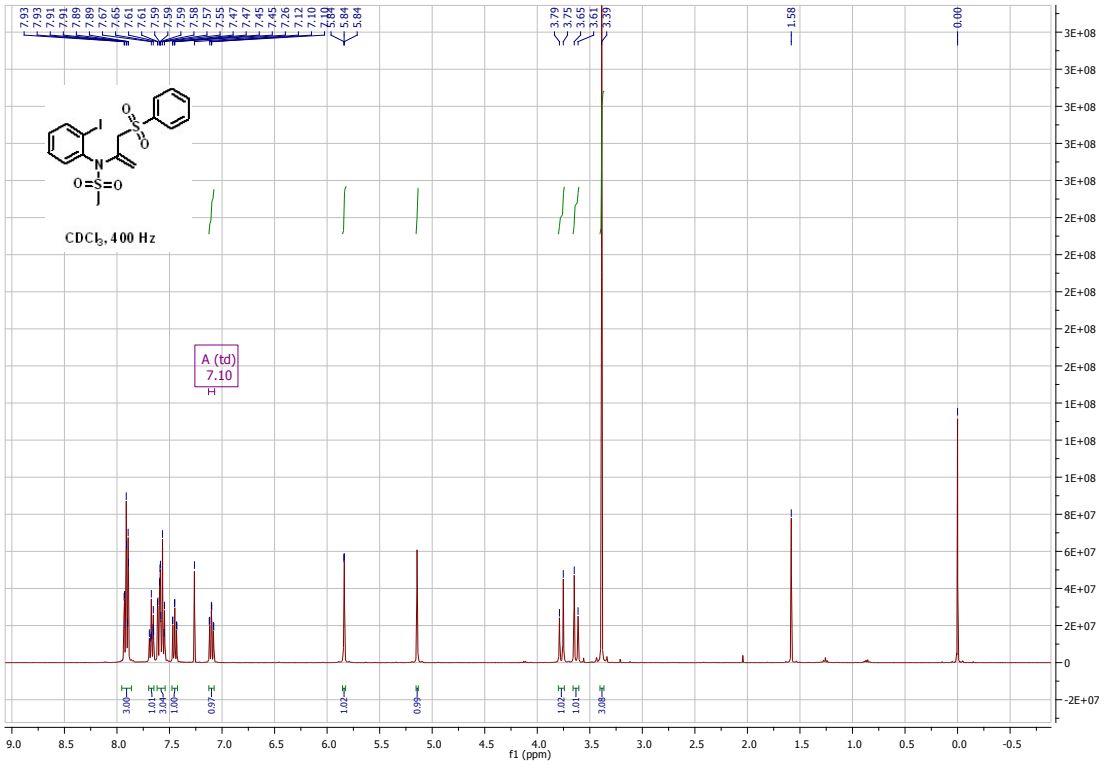



**After 1 h at 50 °C: 7: 2d = 3:1**

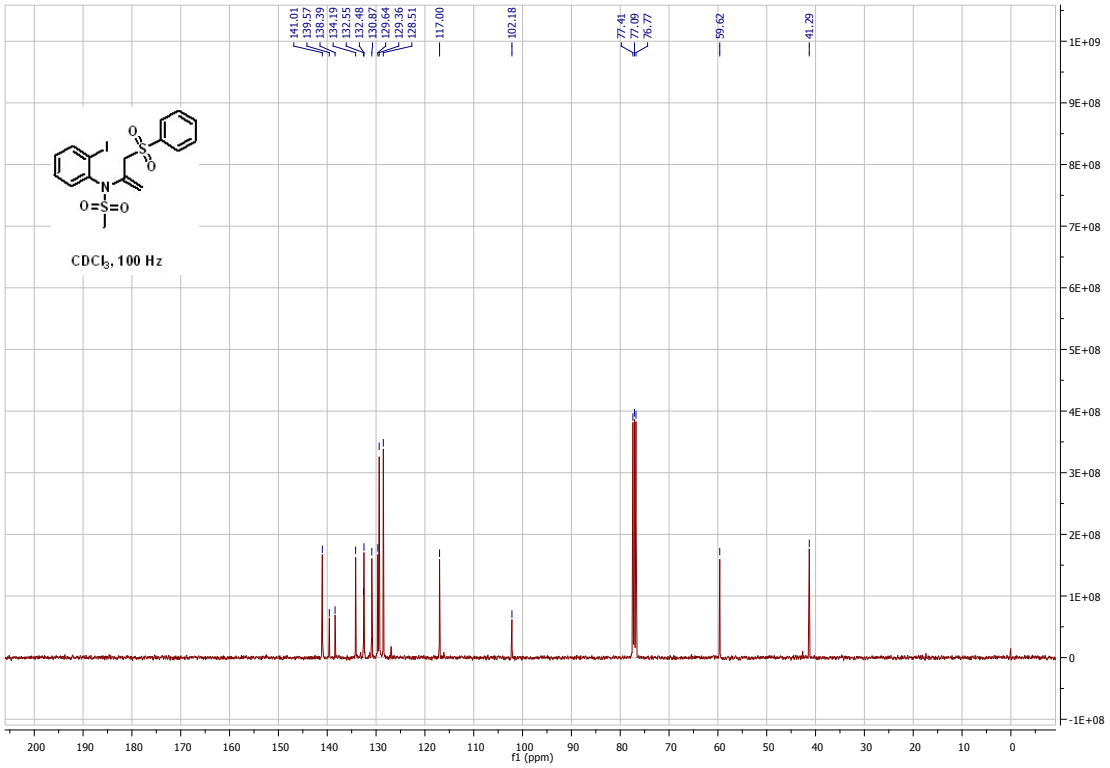



## 5. NMR spectra of new compounds

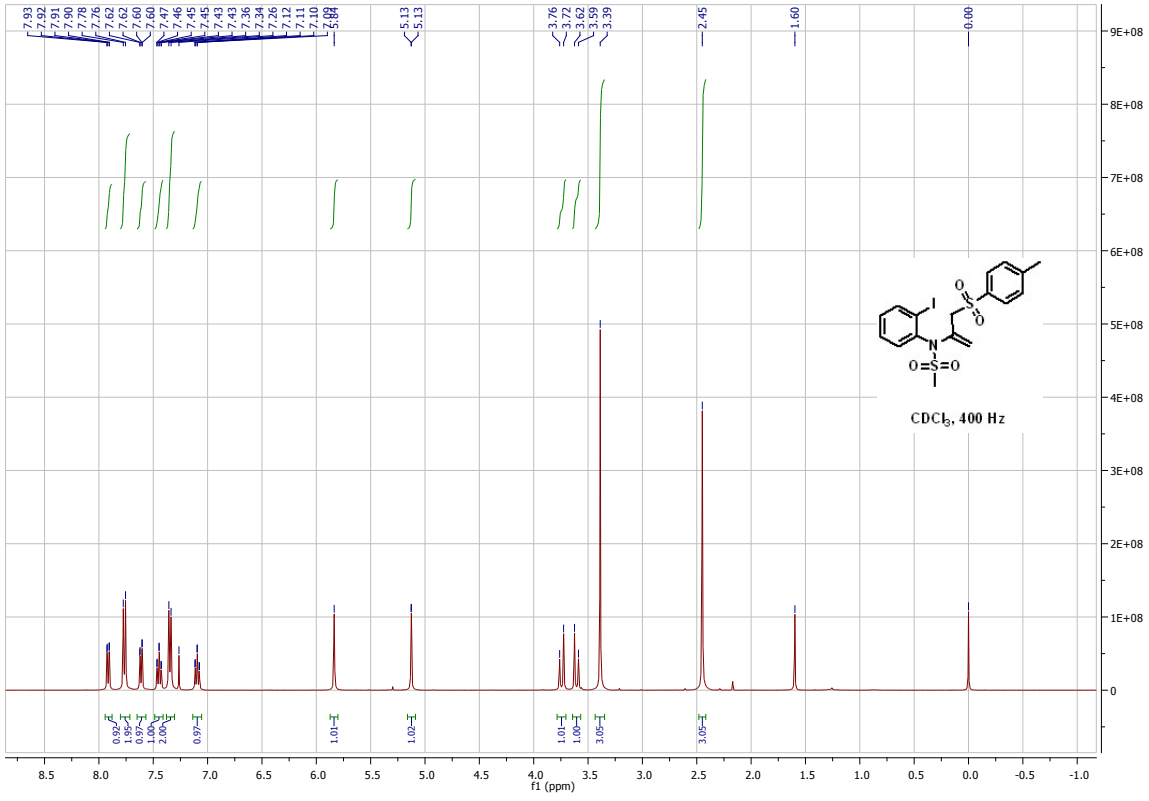
### $^{1}$H NMR spectrum of 5a



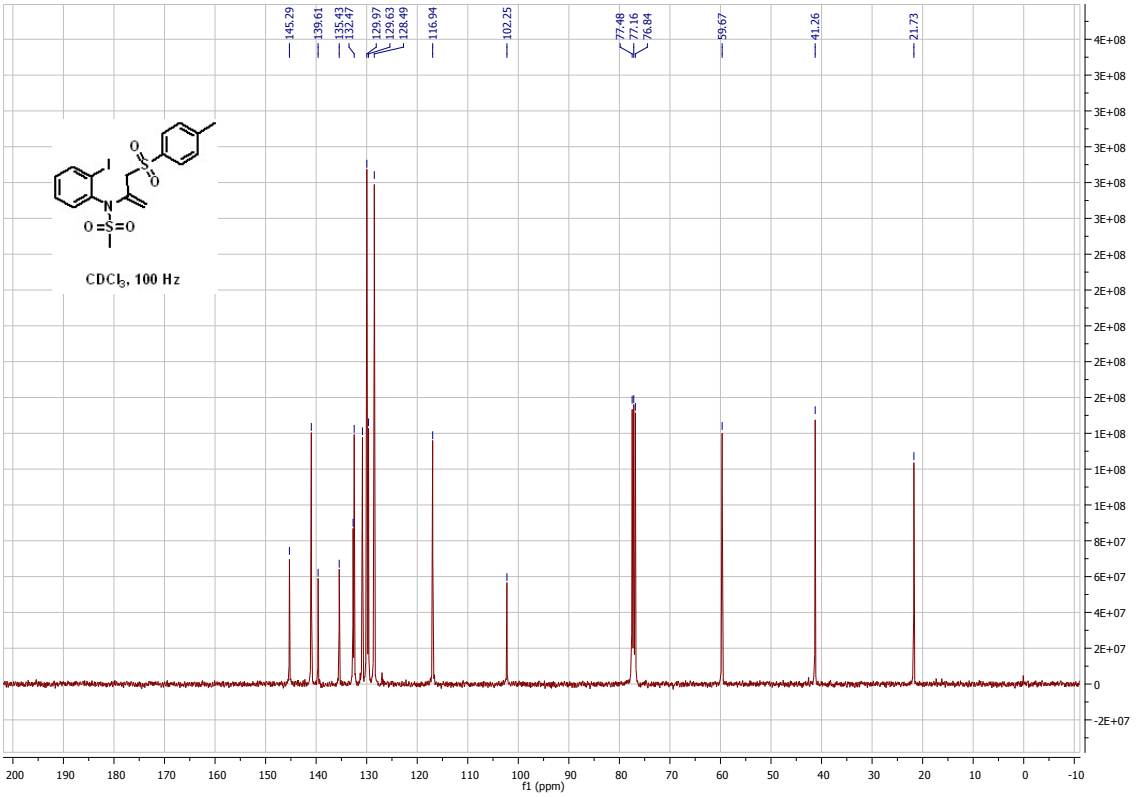

### $^{13}$C NMR spectrum of 5a



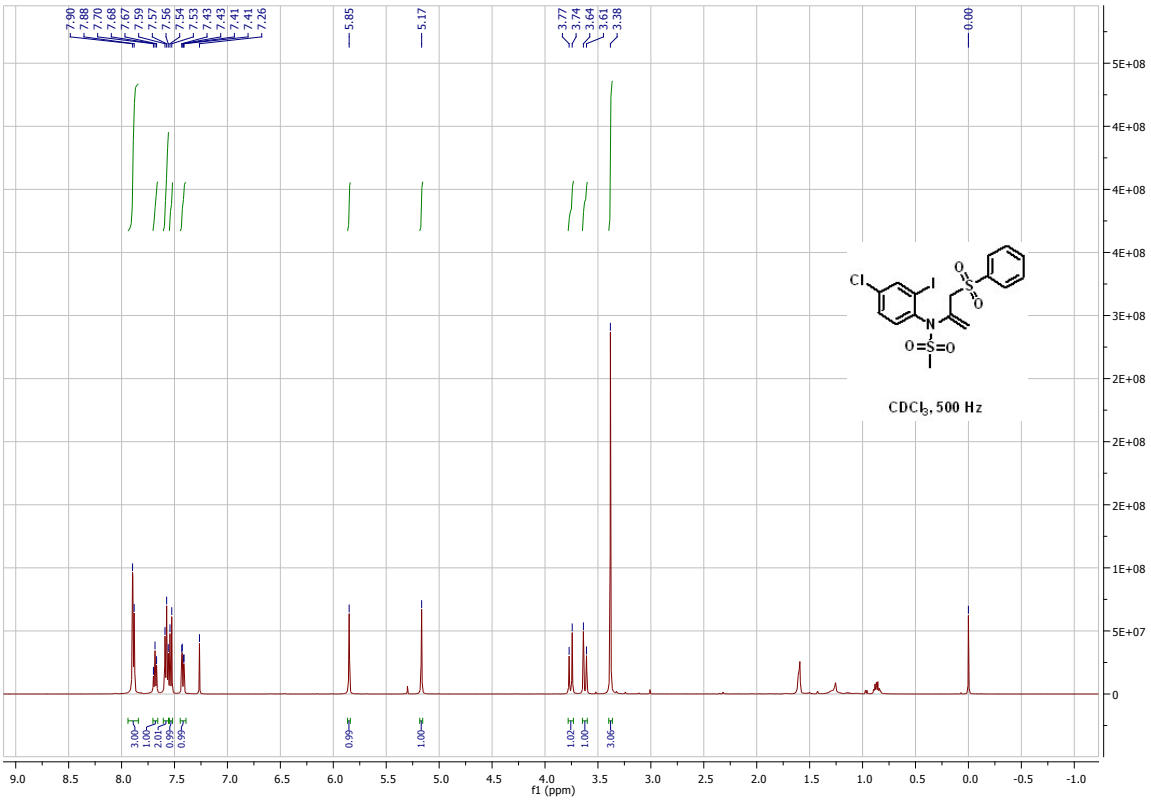

**$^{1}$H NMR spectrum of 5b**



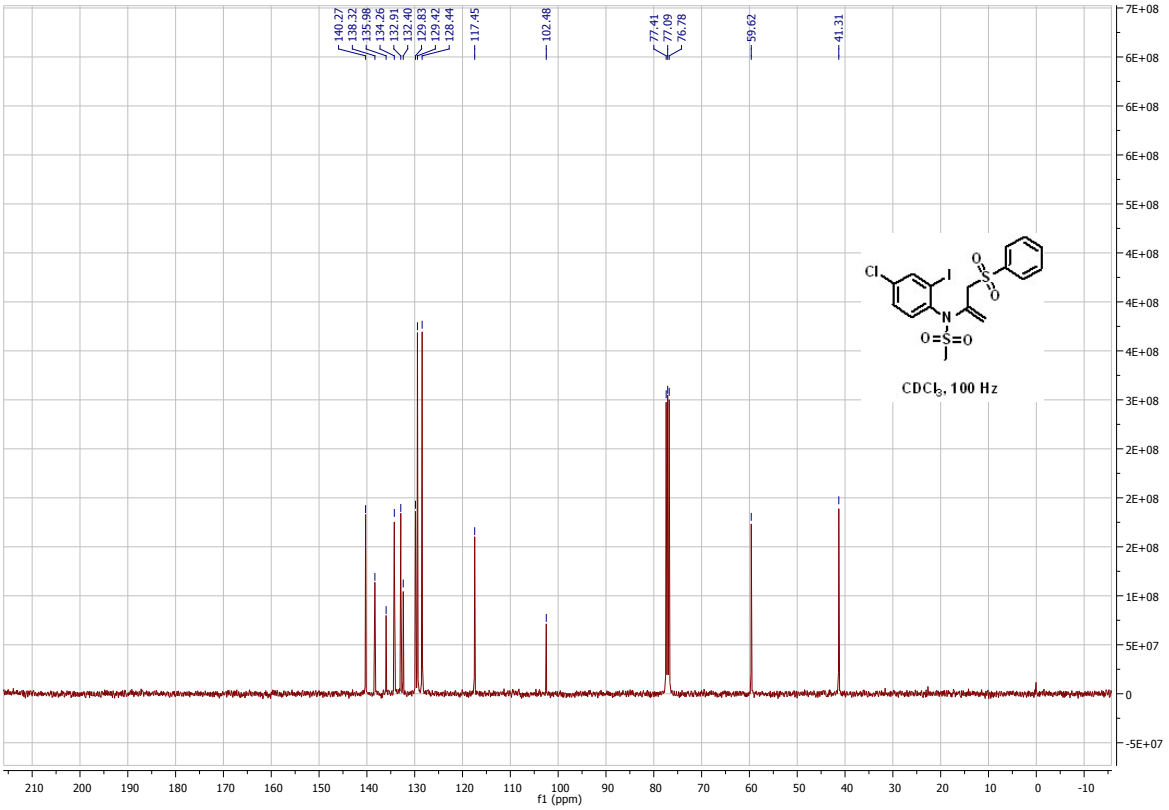

**$^{13}$C NMR spectrum of 5b**



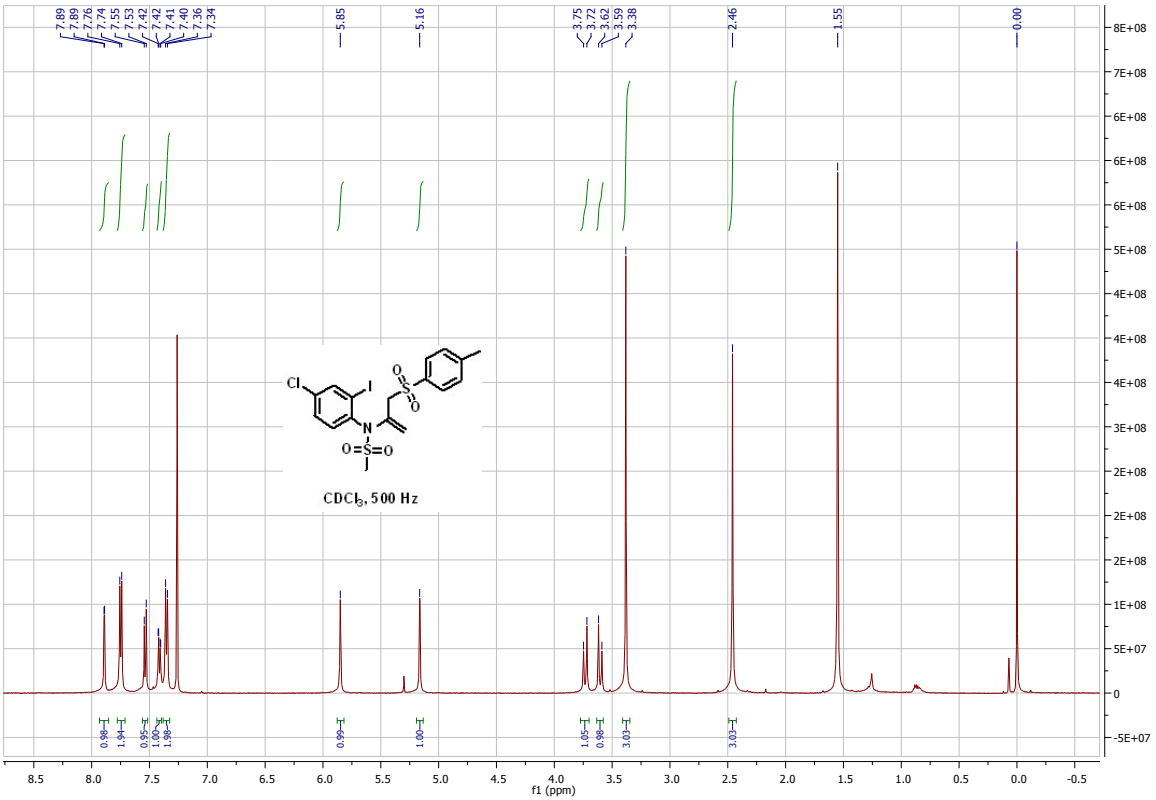

**$^{1}$H NMR spectrum of 5c**



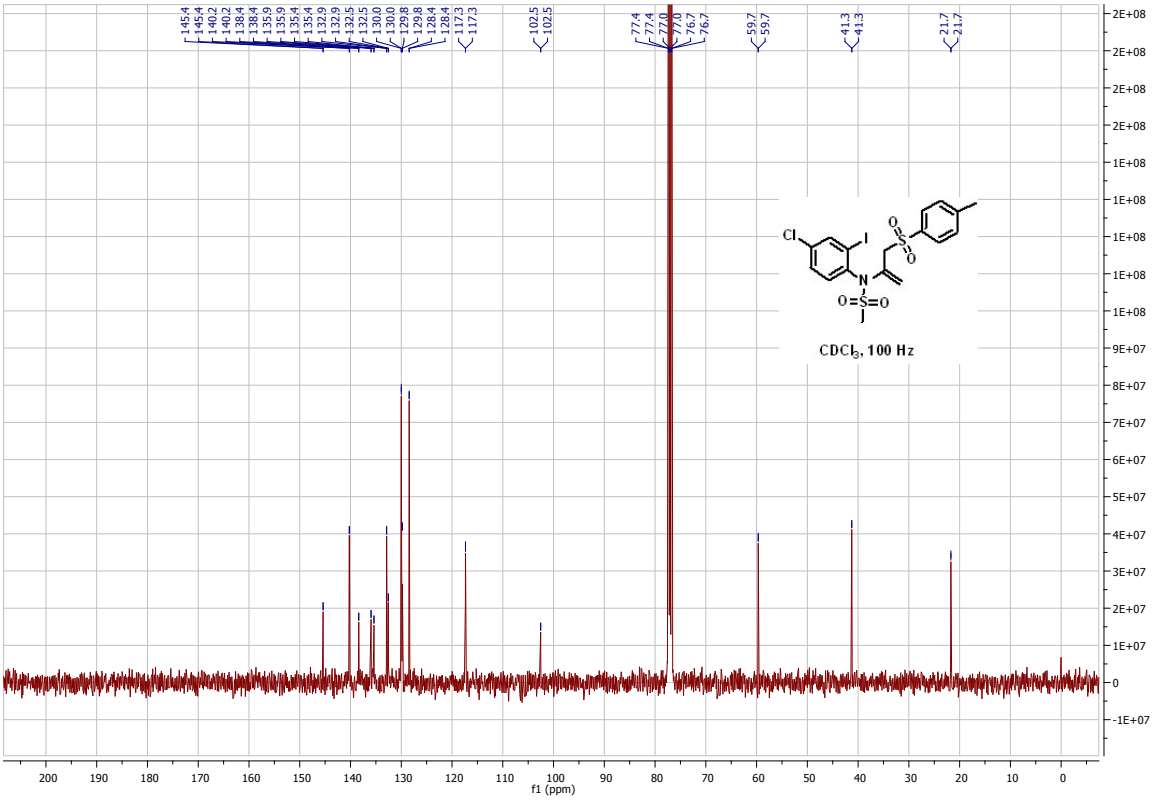

**$^{13}$C NMR spectrum of 5c**



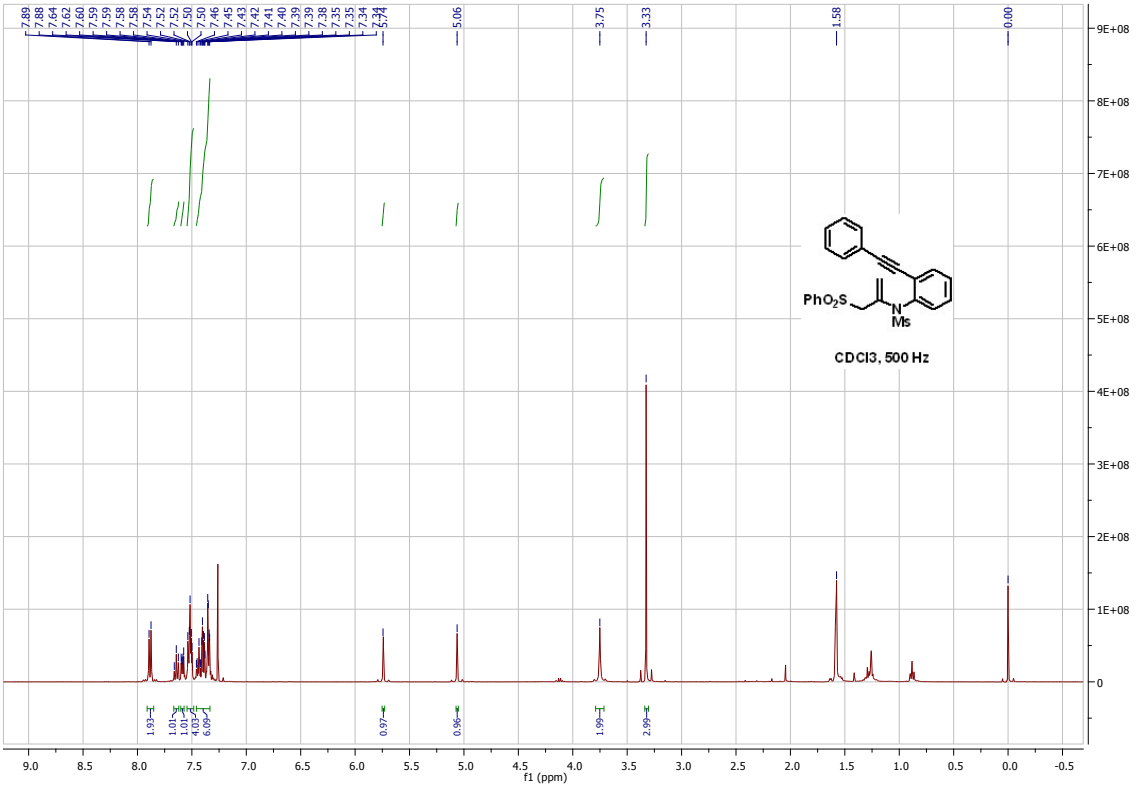

**$^{1}$H NMR spectrum of 5d**



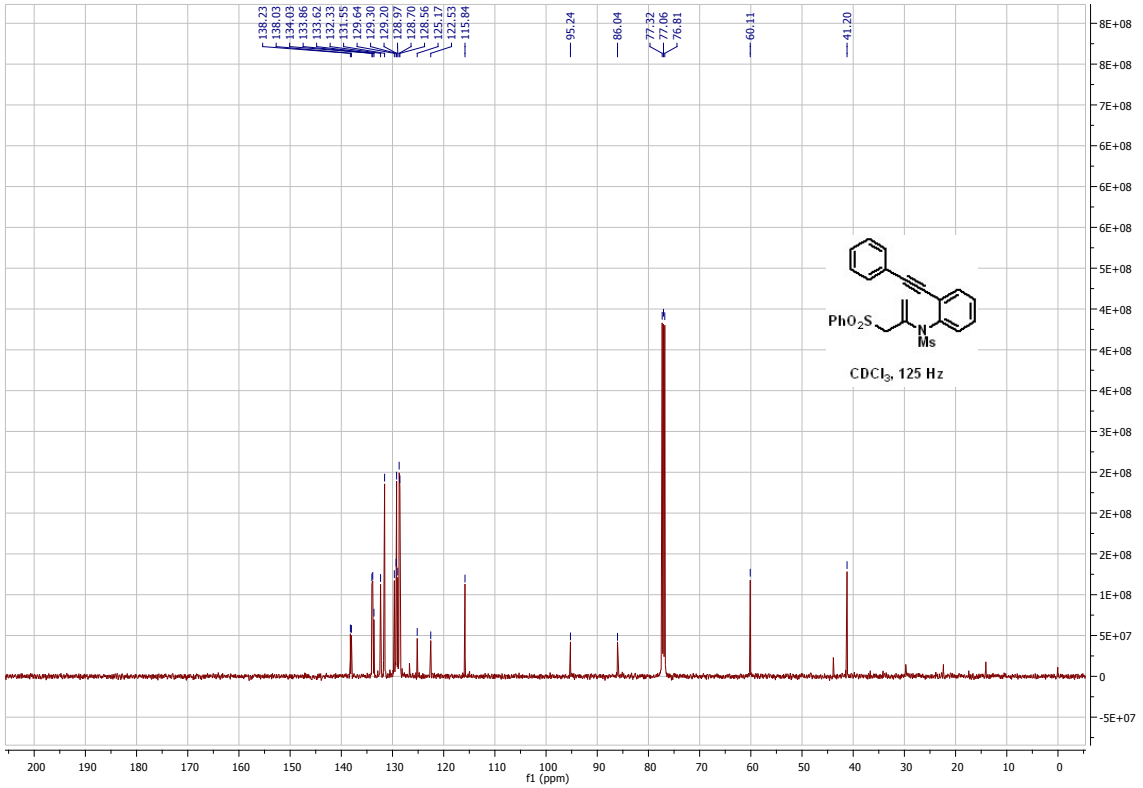

**$^{13}$C NMR spectrum of 5d**



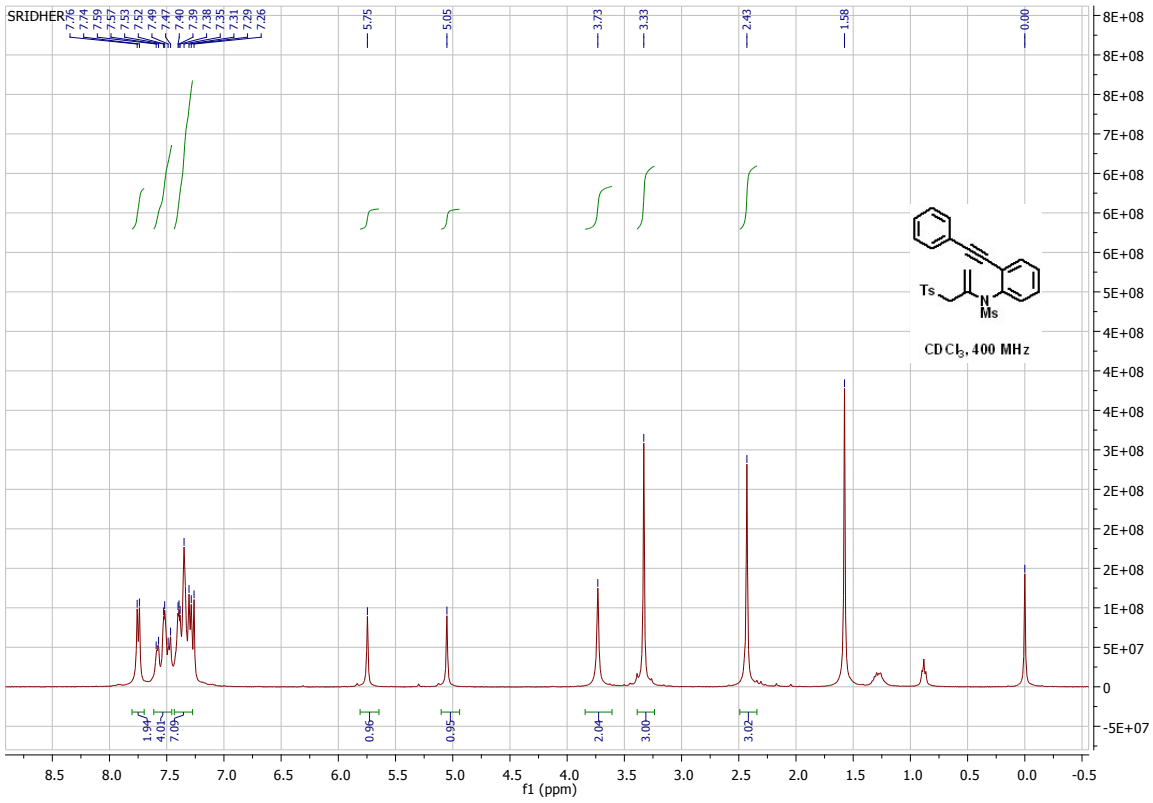

**$^{1}$H NMR spectrum of 1a**



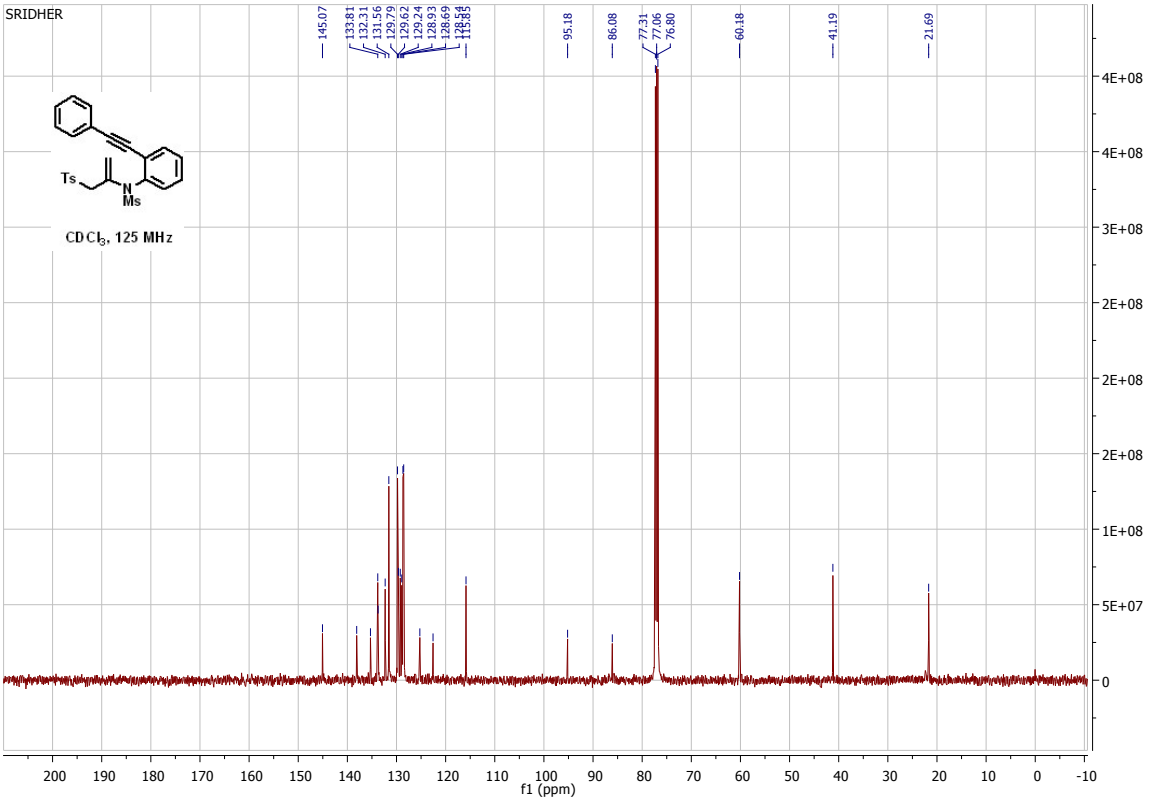

**$^{13}$C NMR spectrum of 1a**



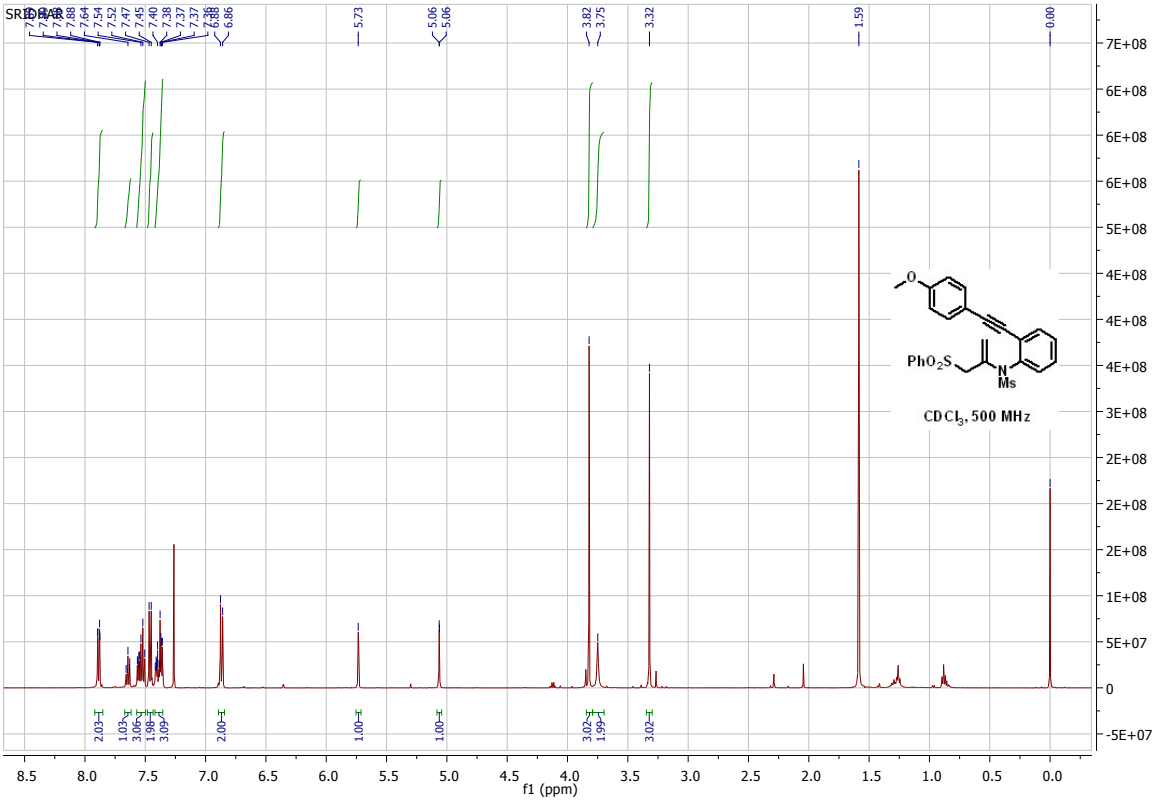

**$^{1}$H NMR spectrum of 1b**



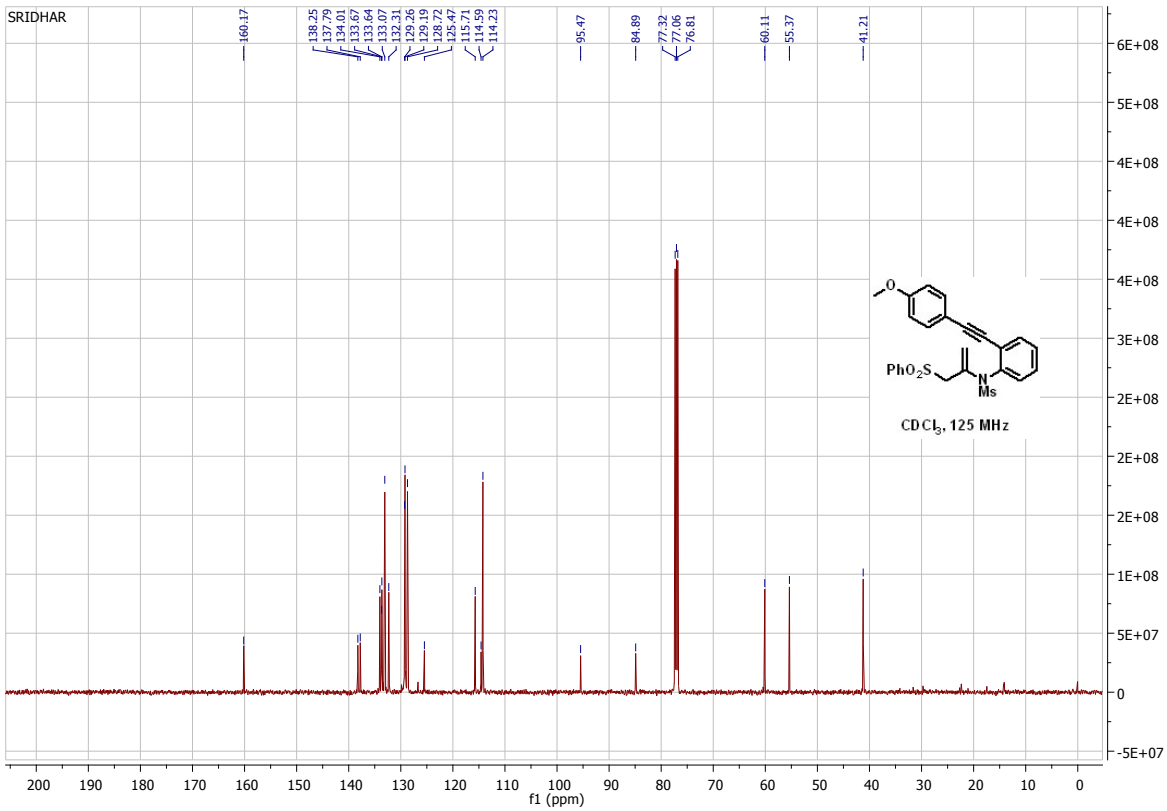

**$^{13}$C NMR spectrum of 1b**



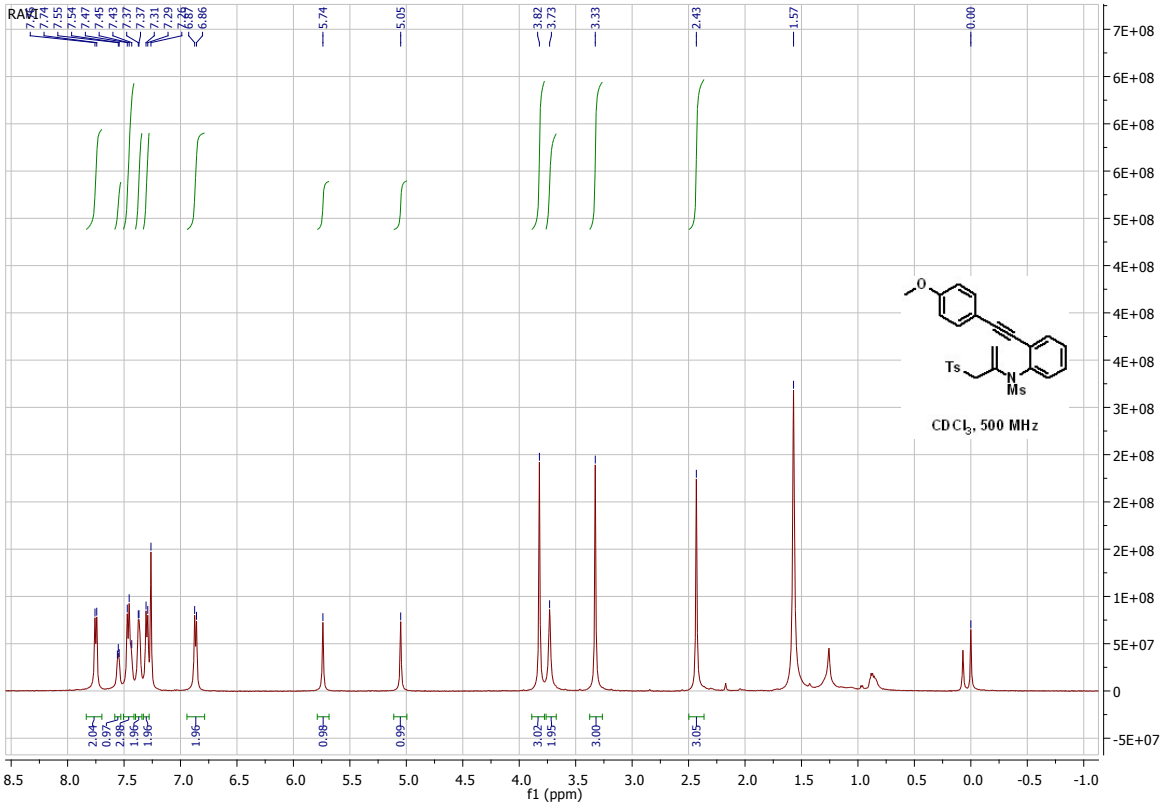

**$^{1}$H NMR spectrum of 1c**



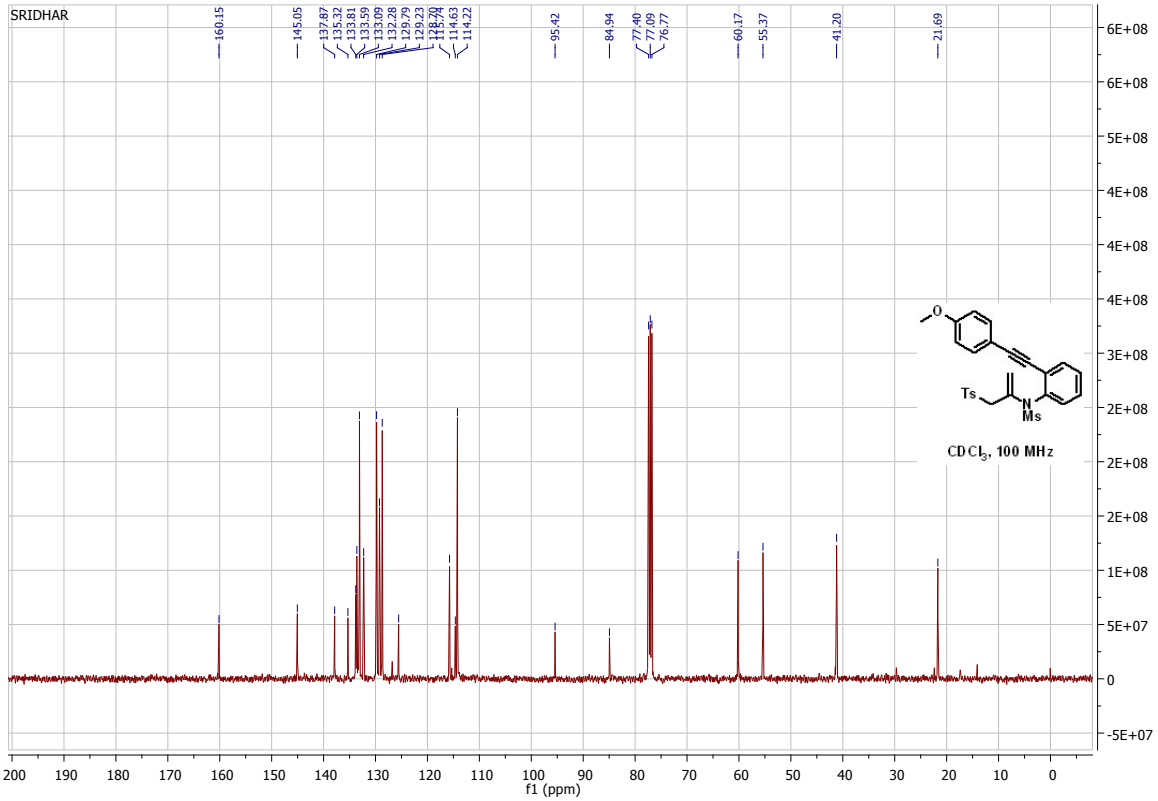

**$^{13}$C NMR spectrum of 1c**



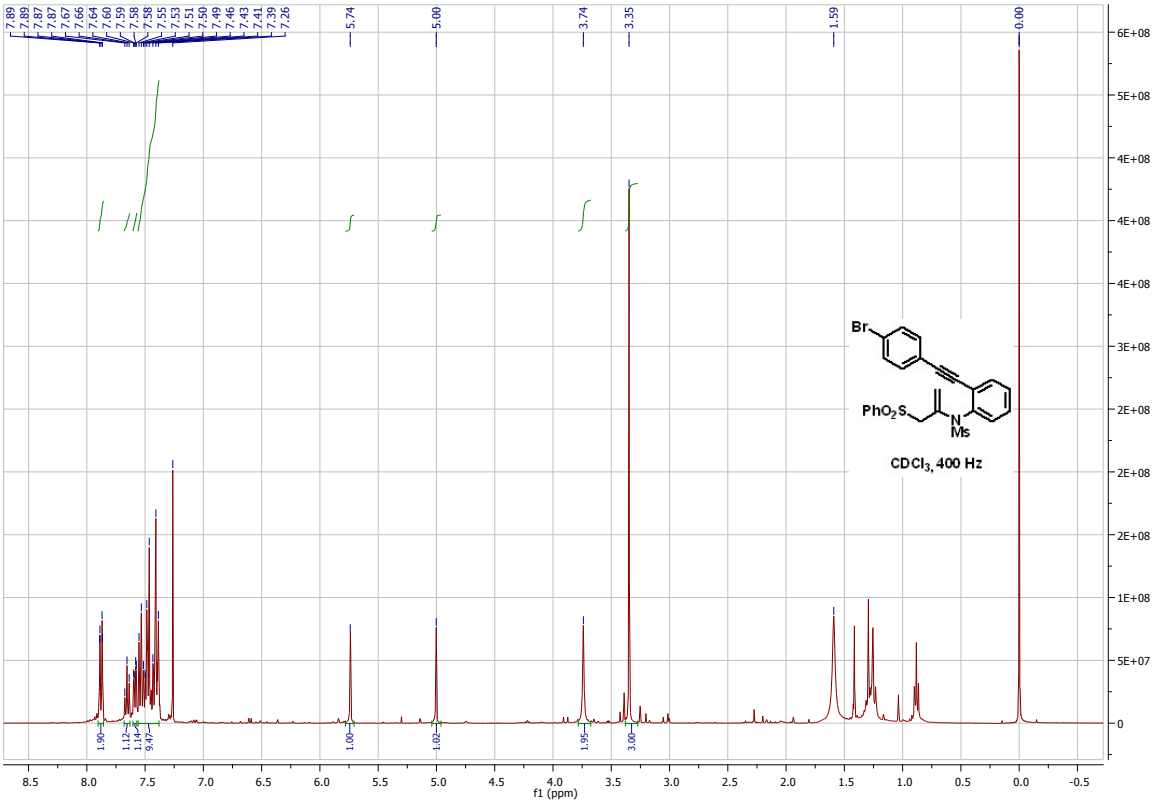

**$^{1}$H NMR spectrum of 1d**



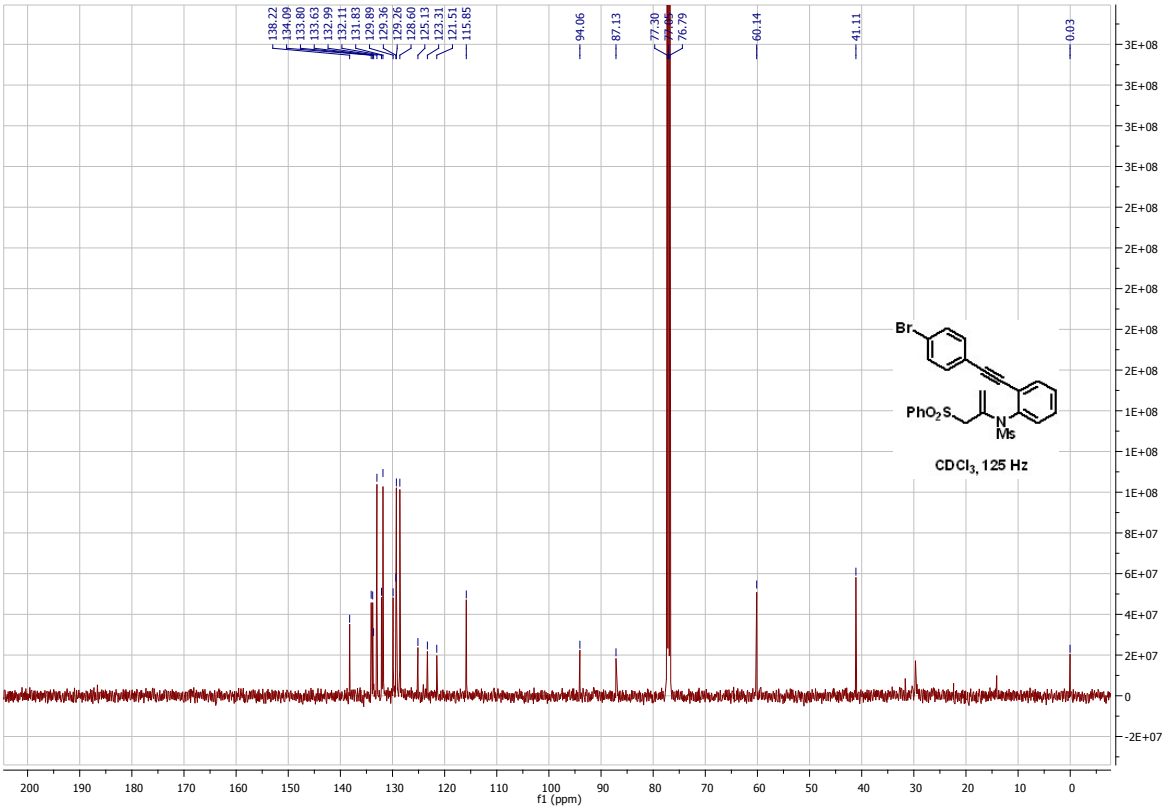
## $^{13}$C NMR spectrum of 1d



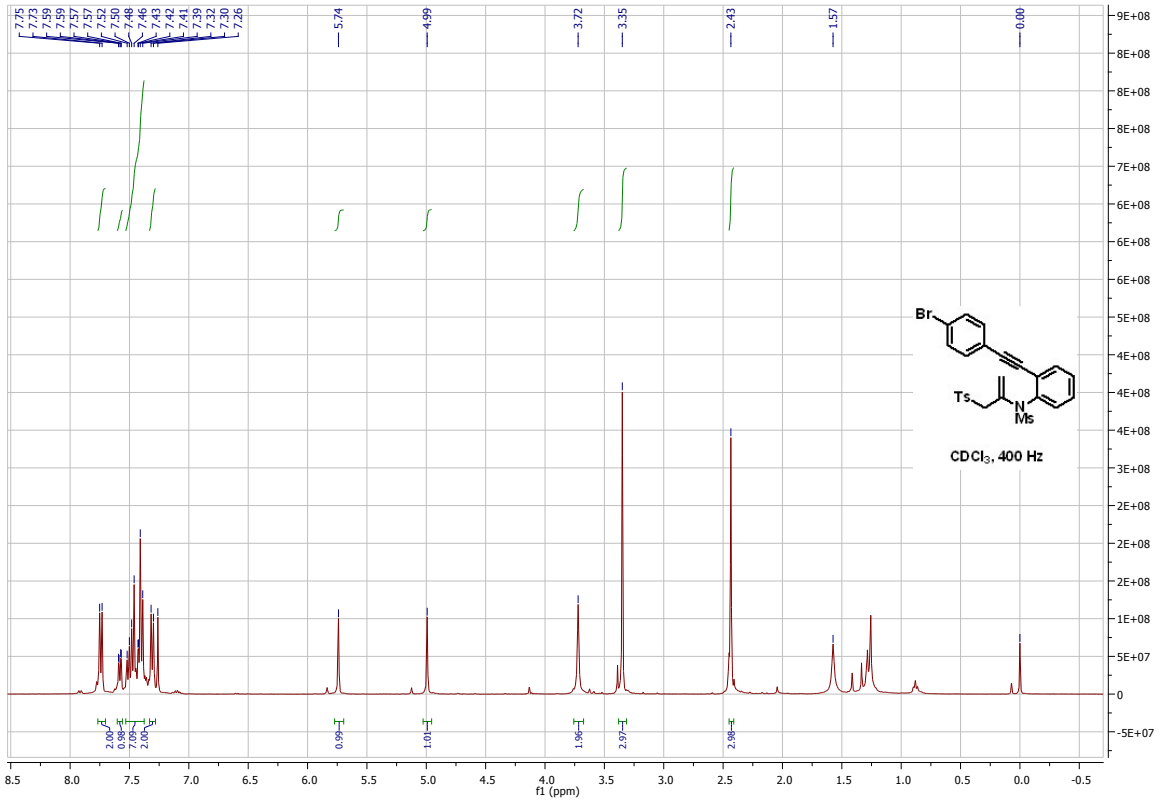

## $^{1}$H NMR spectrum of 1e



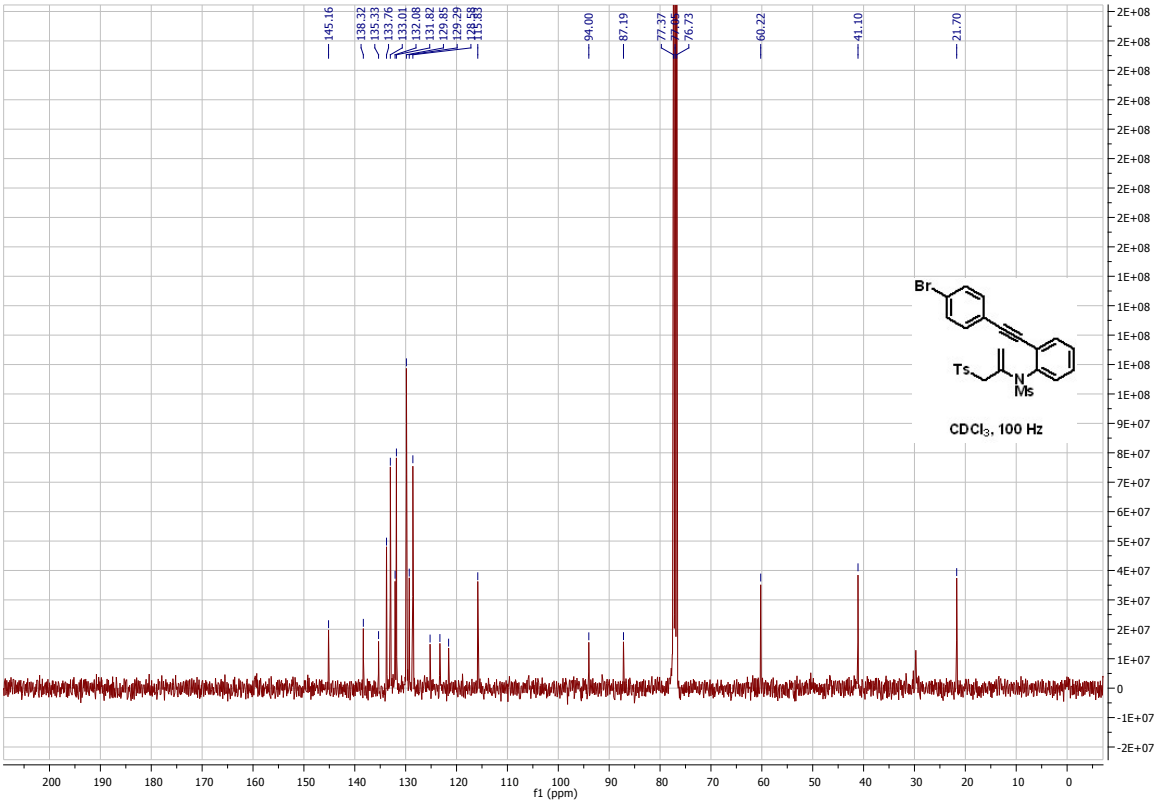
## $^{13}$C NMR spectrum of 1e



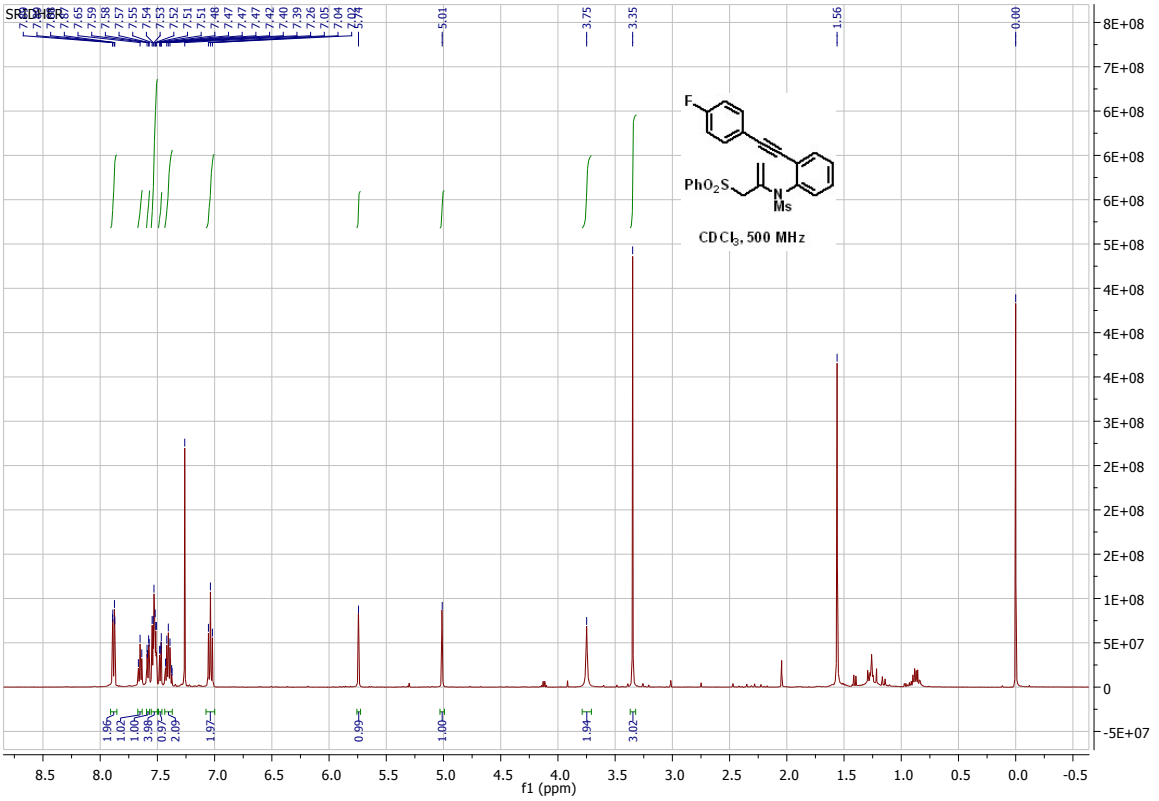

## $^{1}$H NMR spectrum of 1f



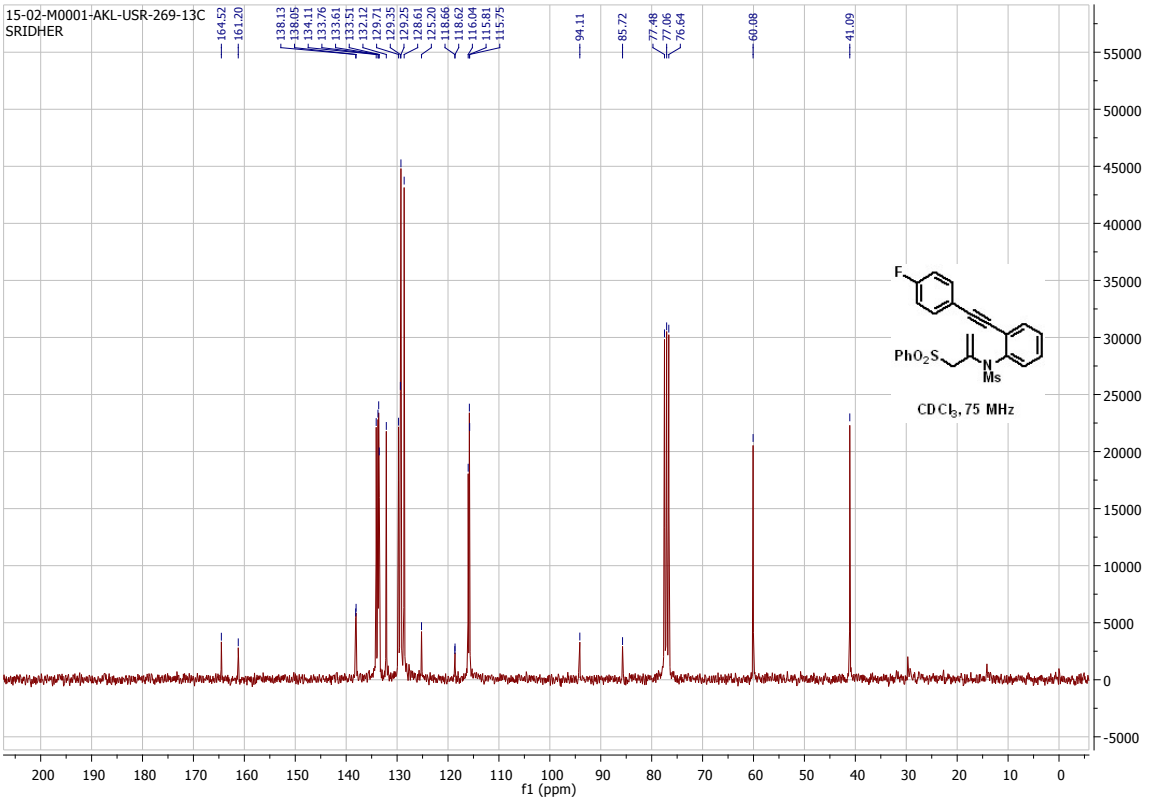
## $^{13}$C NMR spectrum of 1f



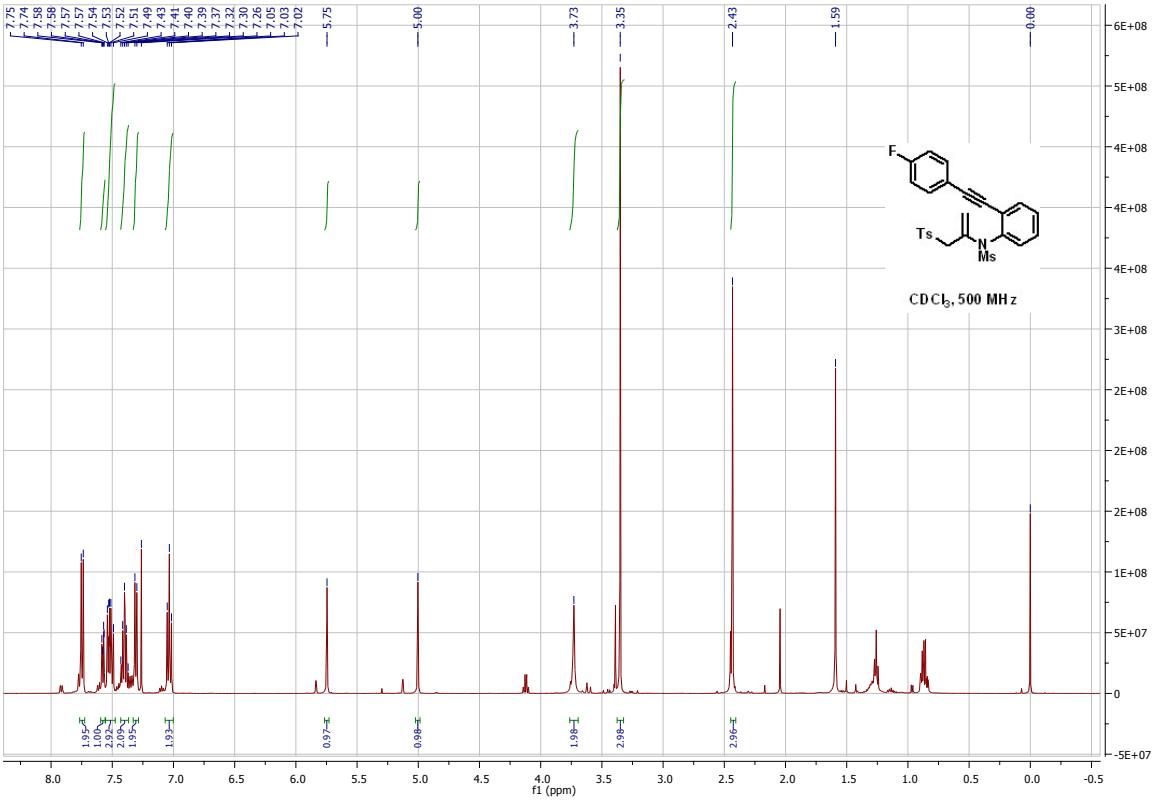

## $^{1}$H NMR spectrum of 1g



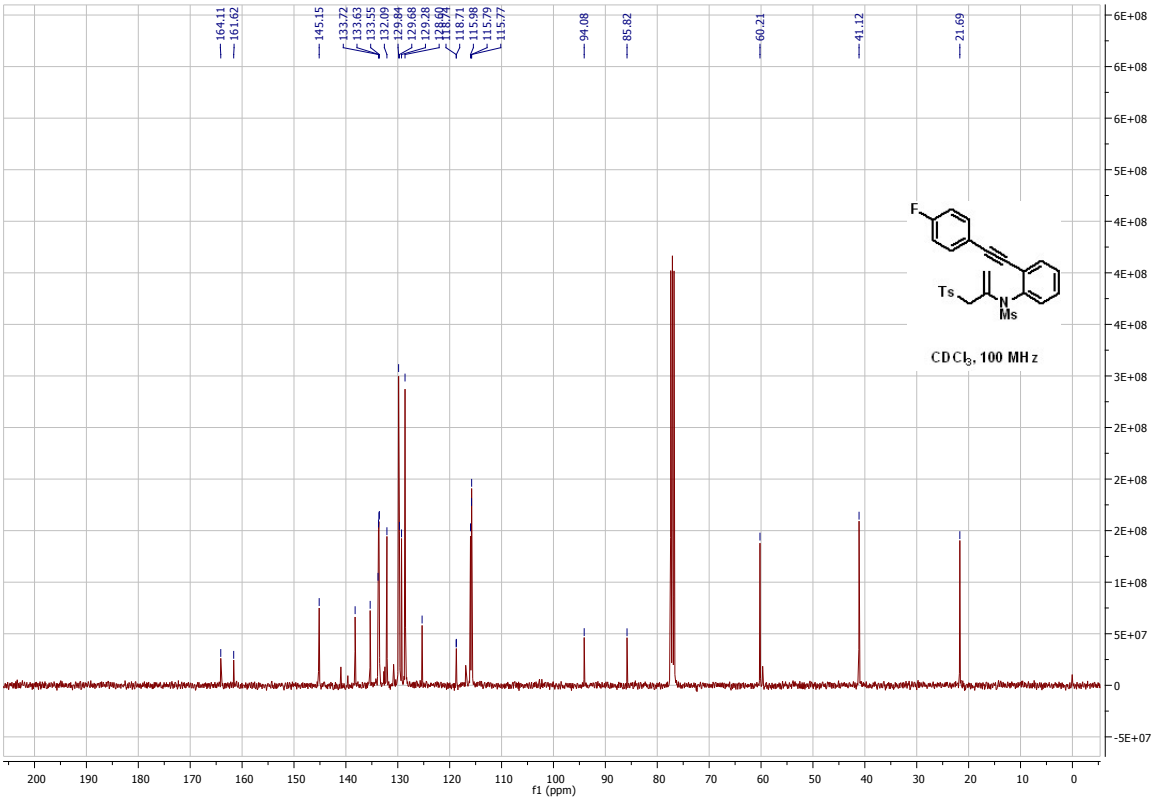
## $^{13}$C NMR spectrum of 1g



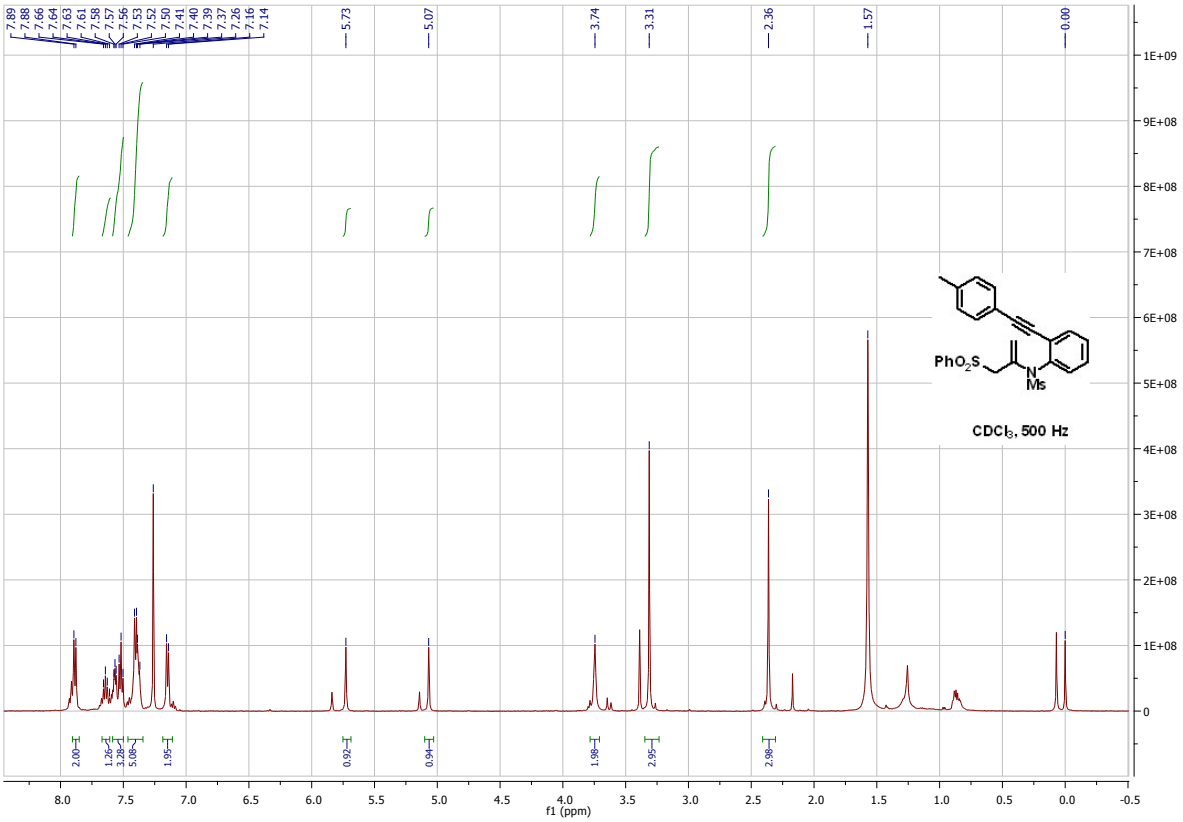

## $^{1}$H NMR spectrum of 1h



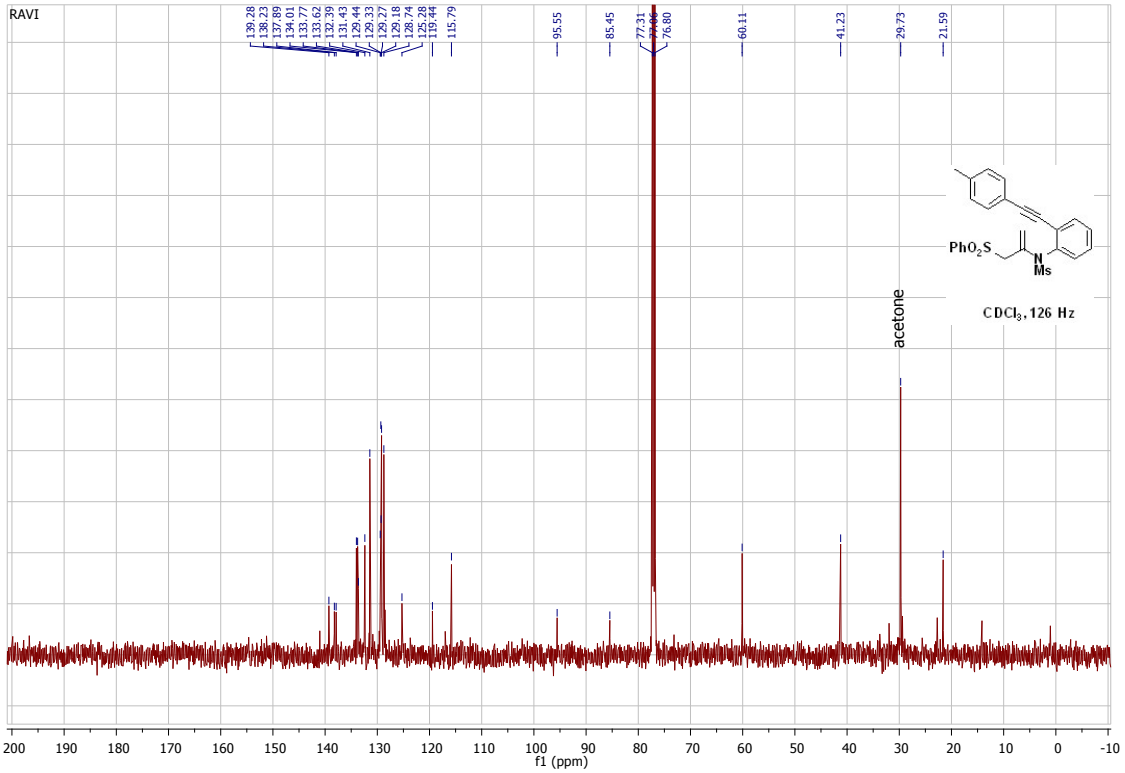
## $^{13}$C NMR spectrum of 1h



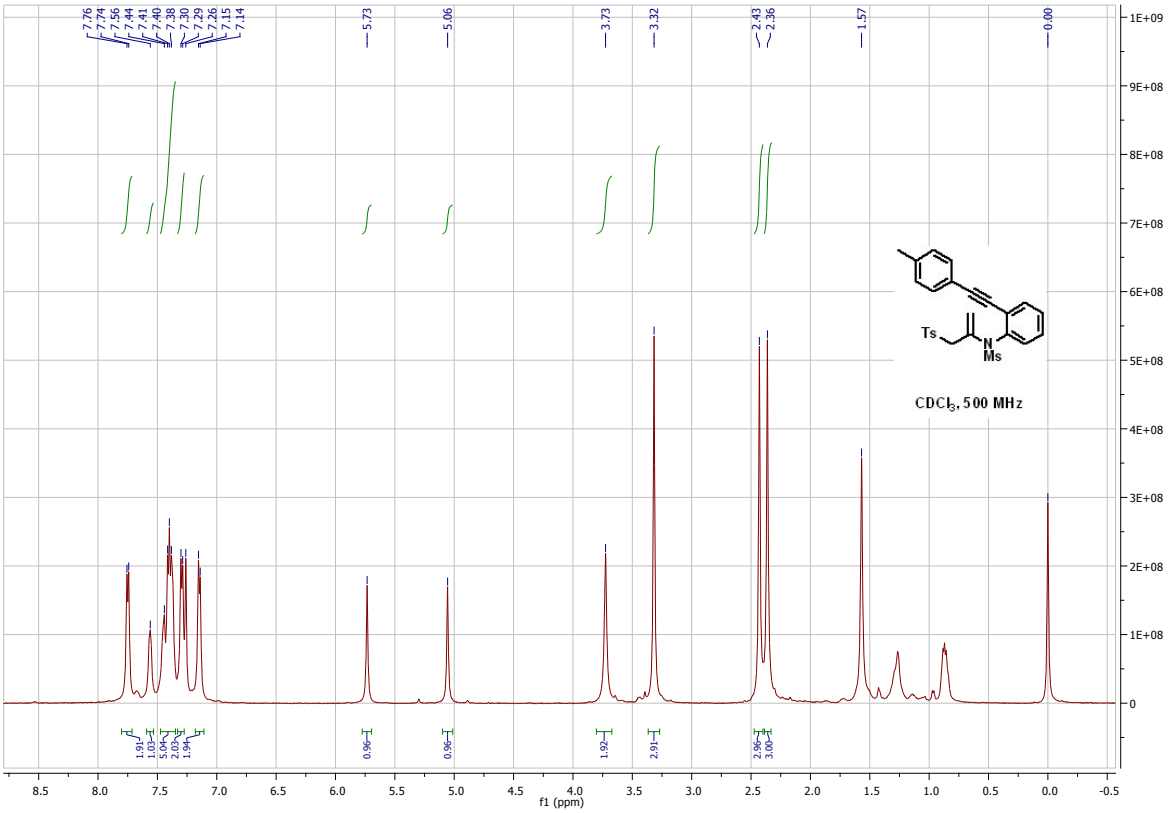
## $^{1}$H NMR spectrum of 1i



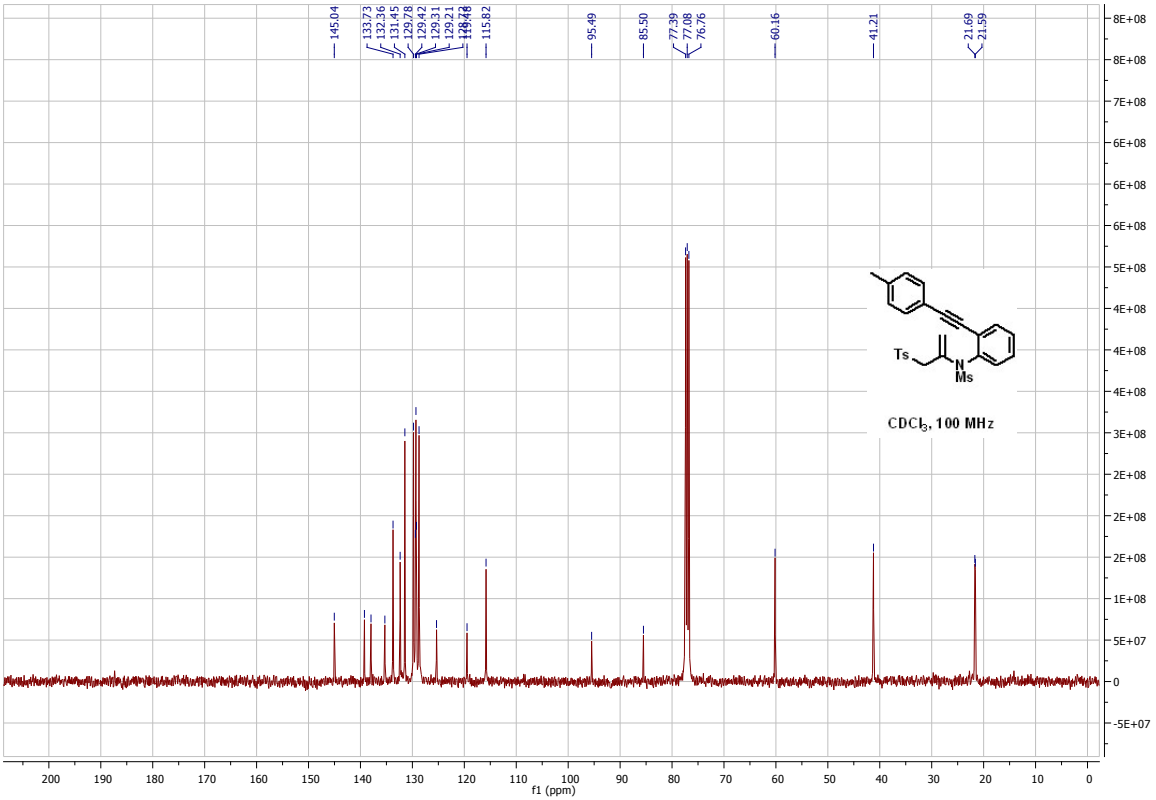

## $^{13}$C NMR spectrum of 1i



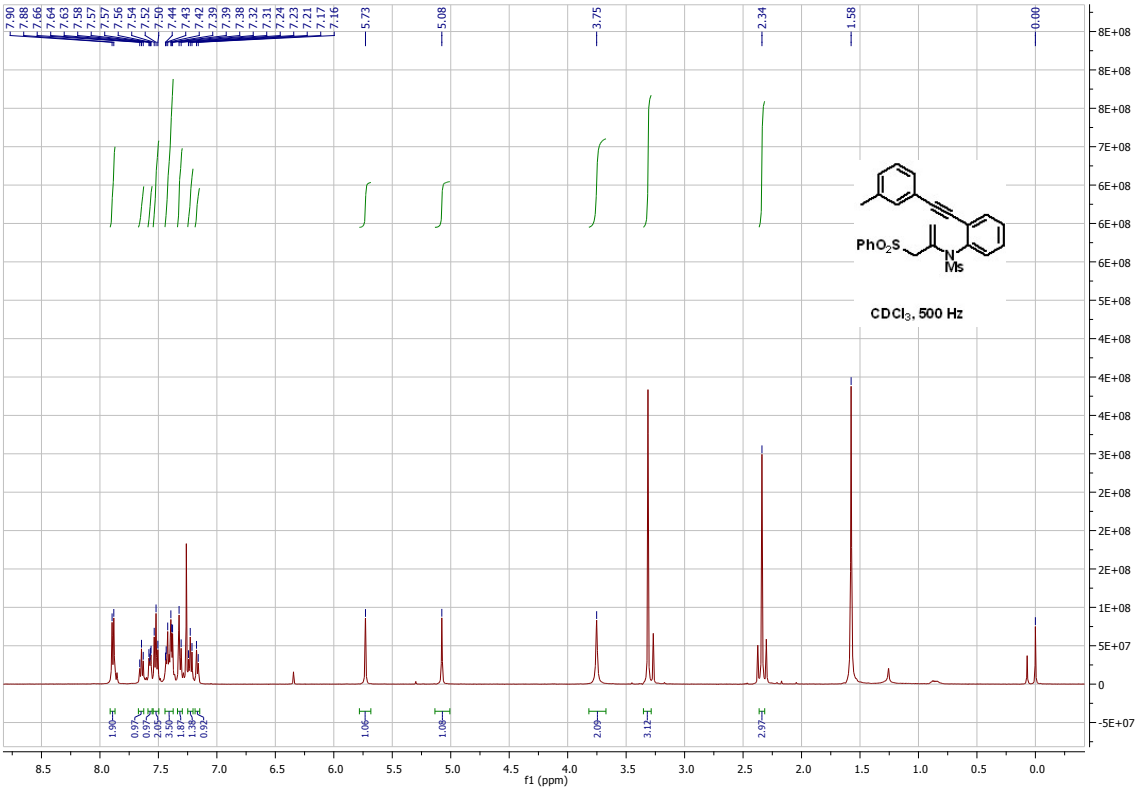
## $^{1}$H NMR spectrum of 1j



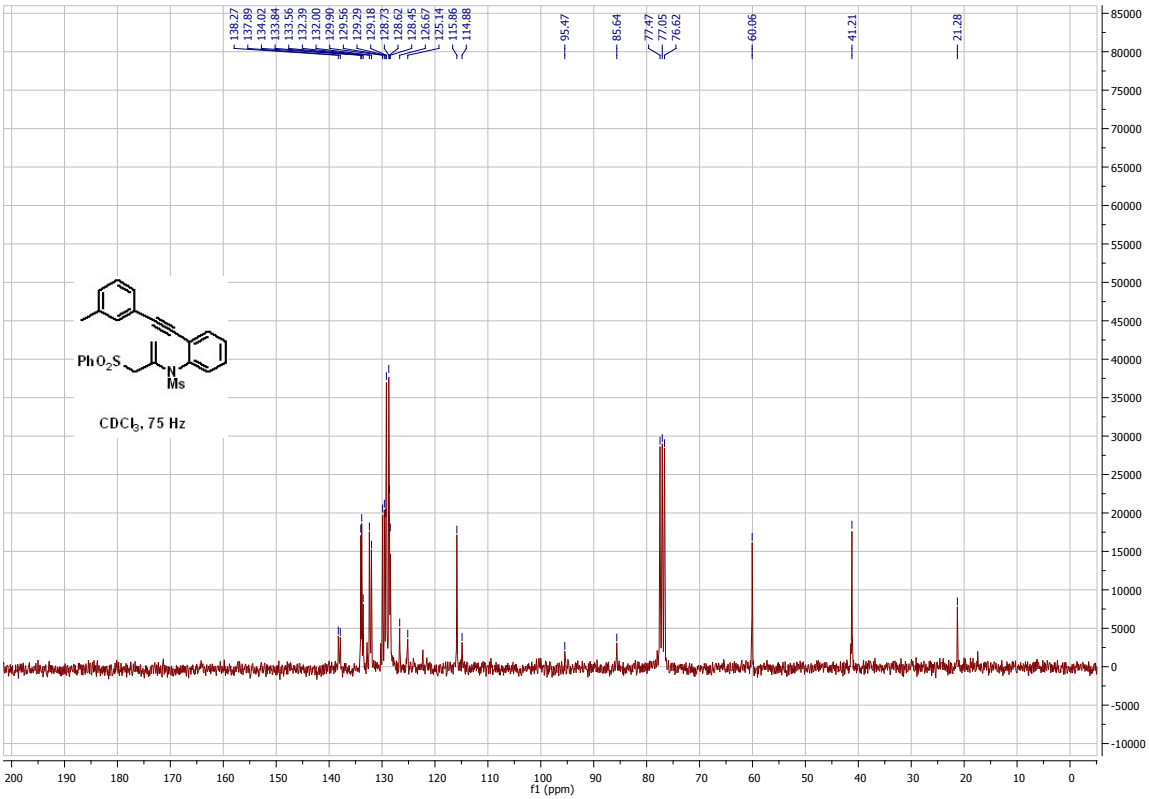

## $^{13}$C NMR spectrum of 1j



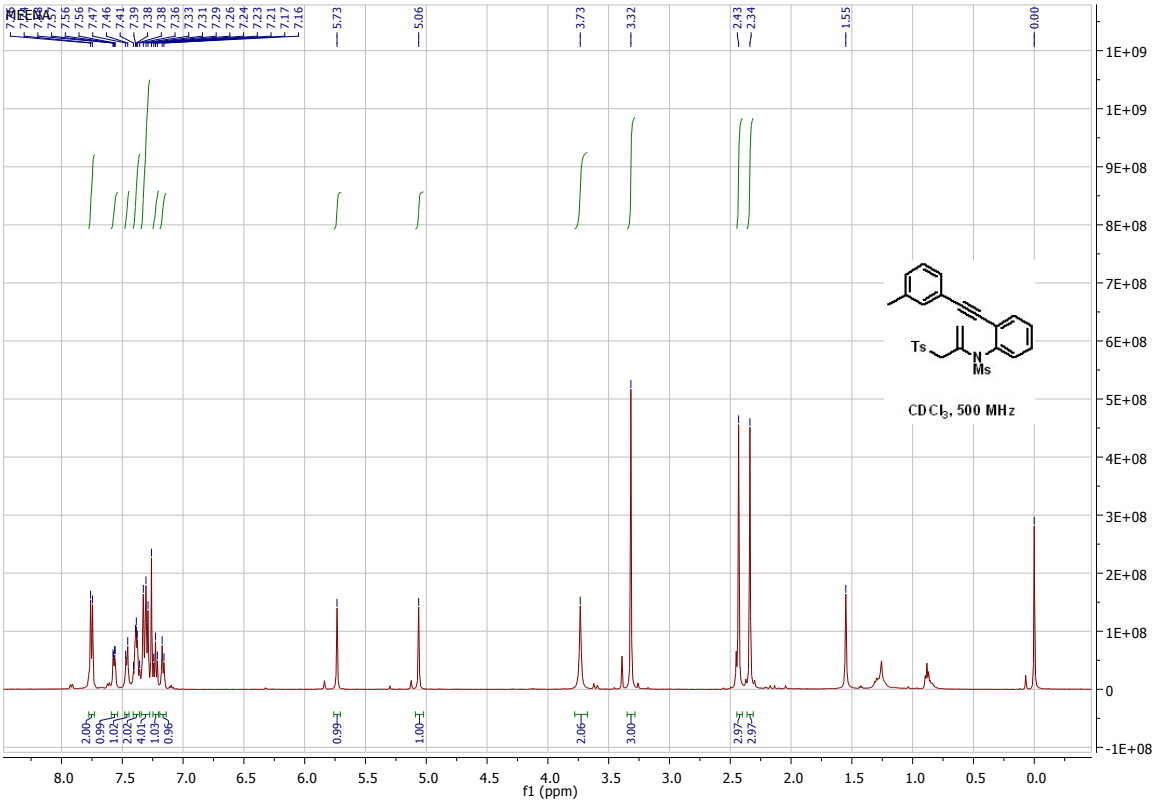
## $^{1}$H NMR spectrum of 1k



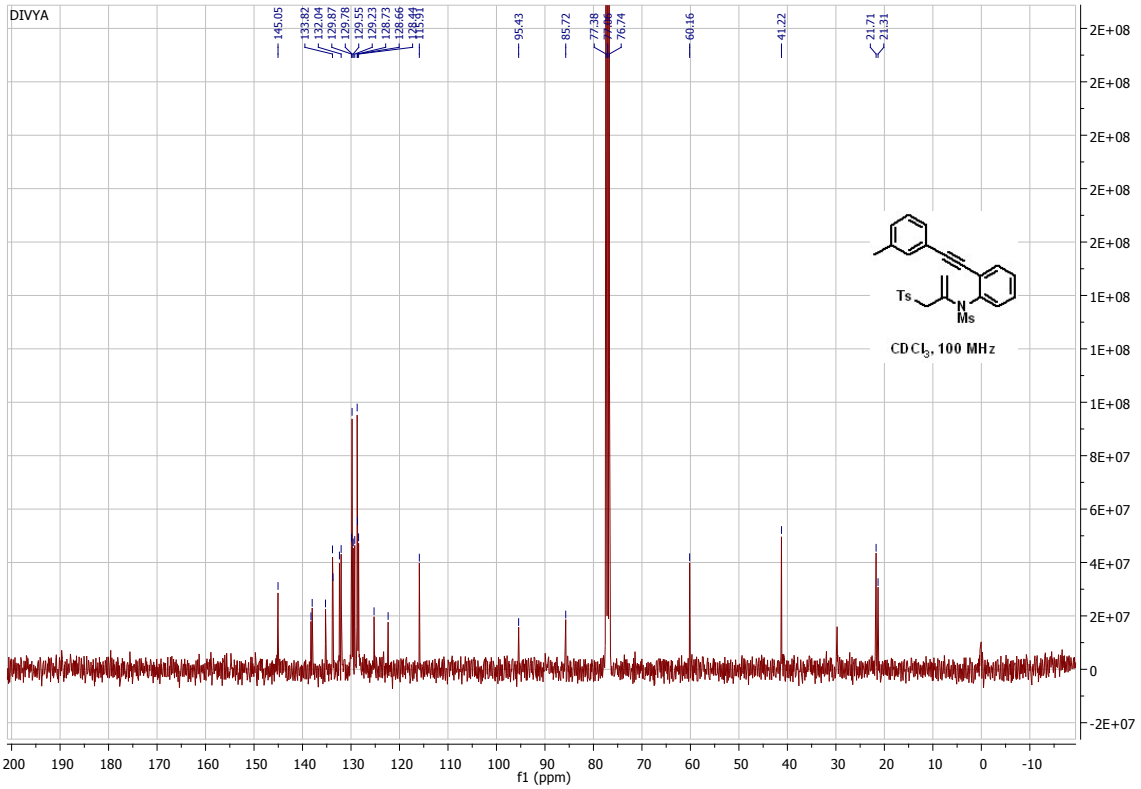

## $^{13}$C NMR spectrum of 1k



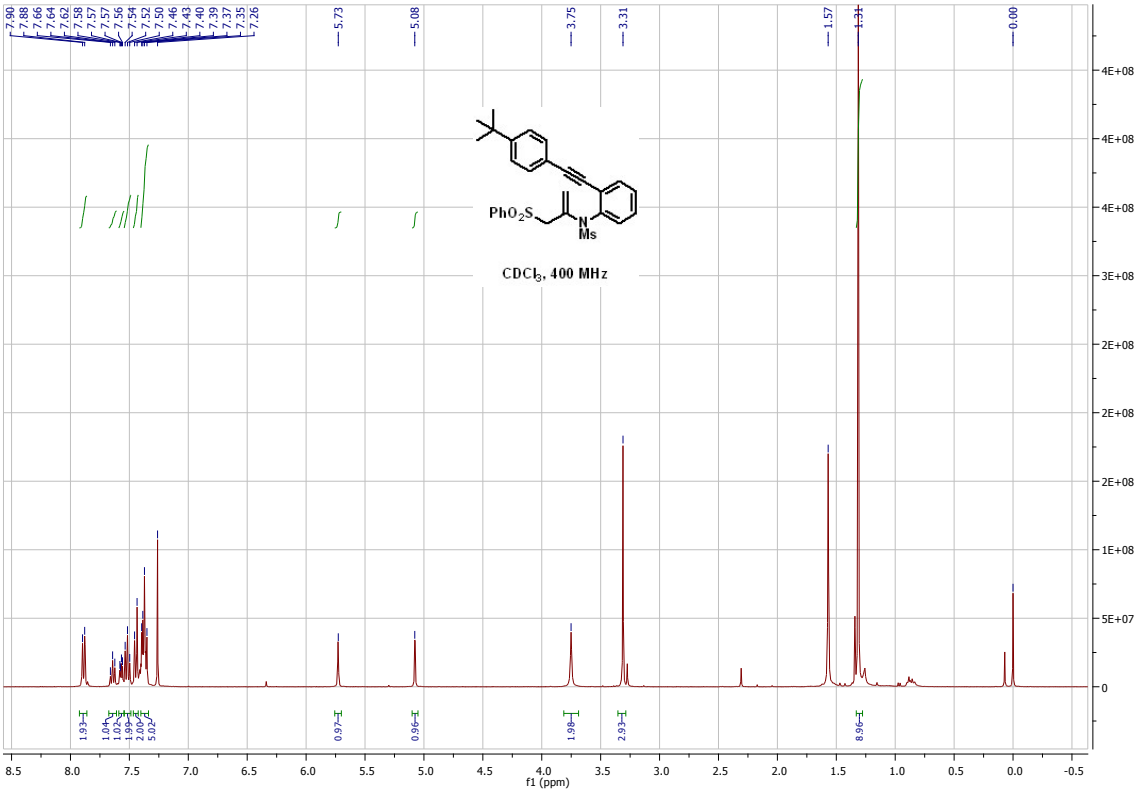
## $^{1}$H NMR spectrum of 1l



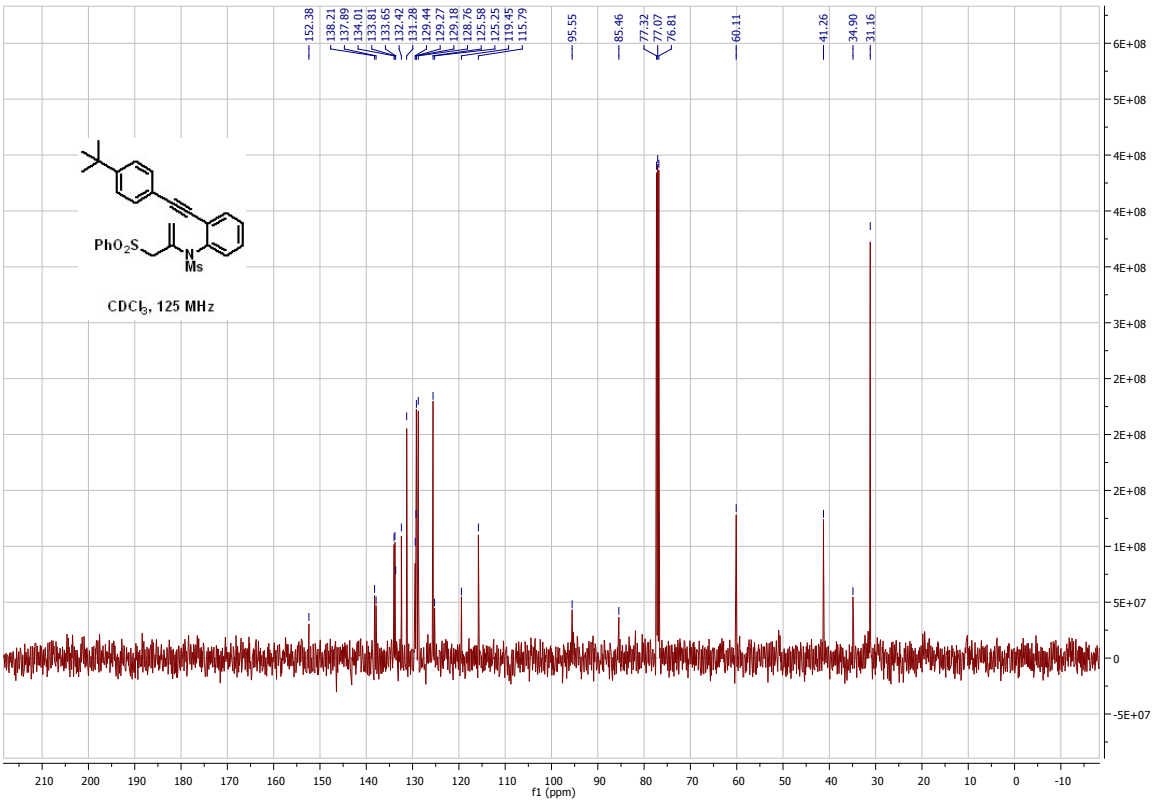

## $^{13}$C NMR spectrum of 1l



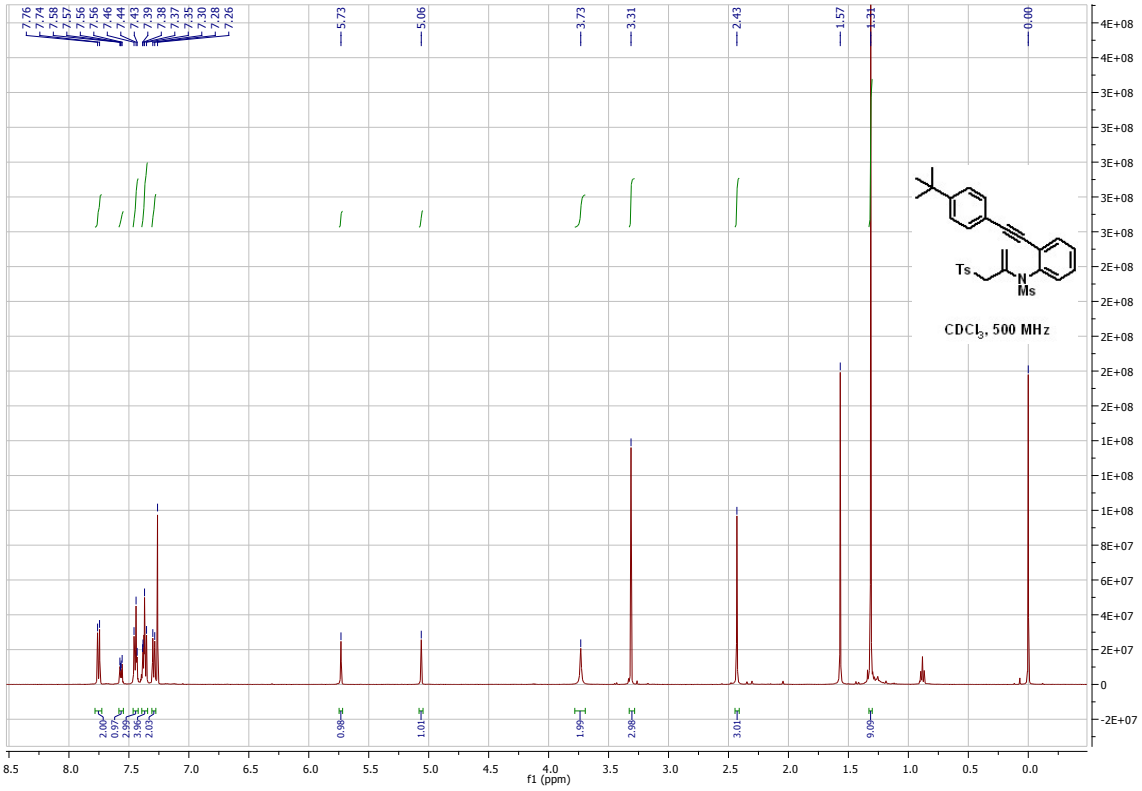
## $^{1}$H NMR spectrum of 1m



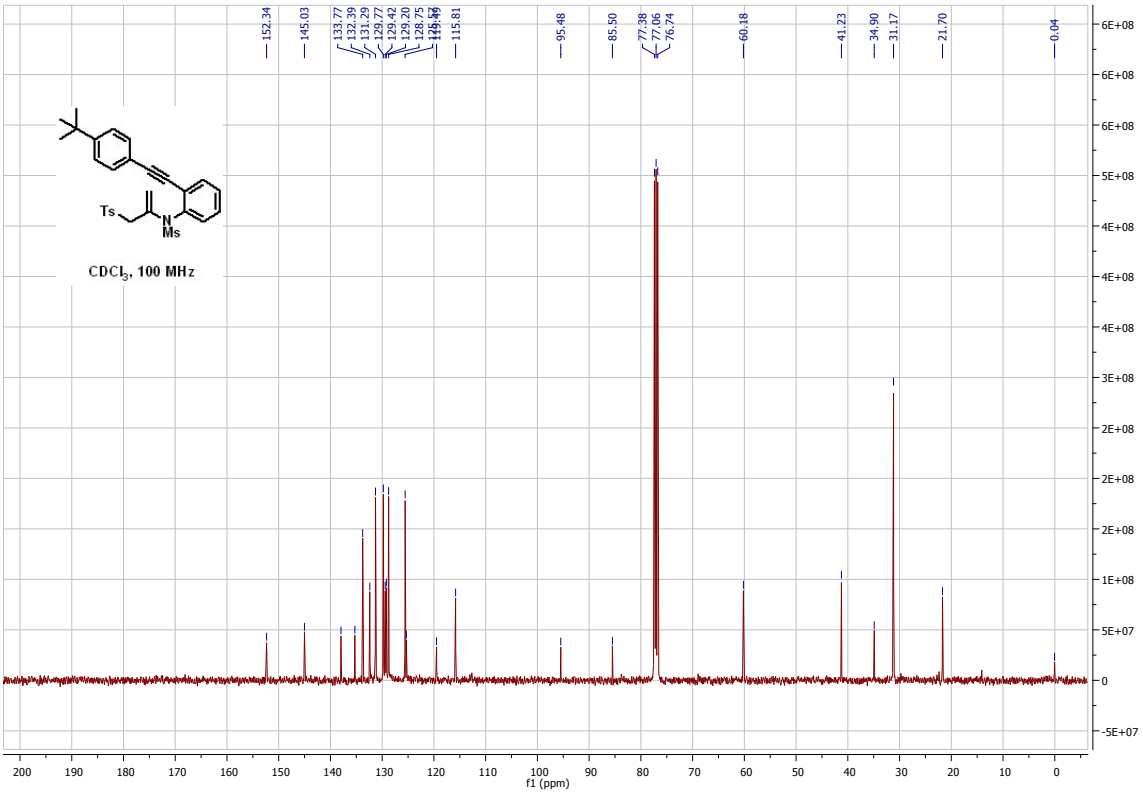

## $^{13}$C NMR spectrum of 1m



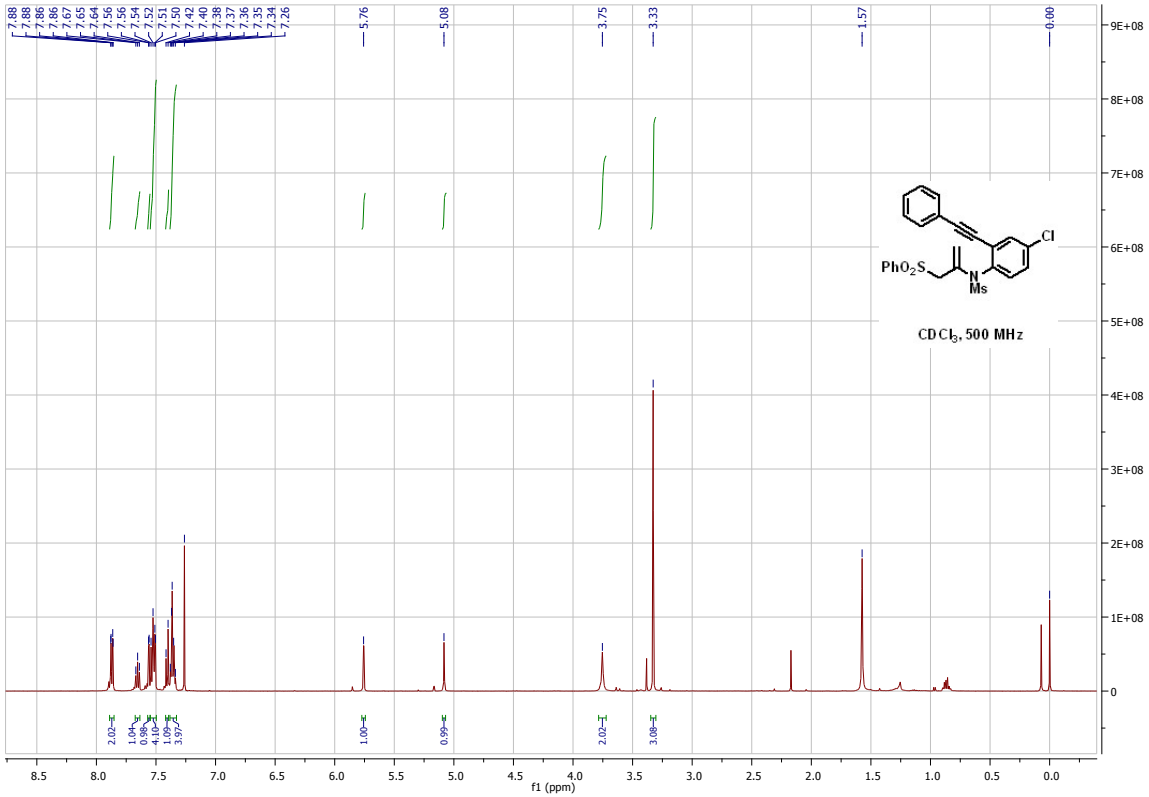
## $^{1}$H NMR spectrum of 1n



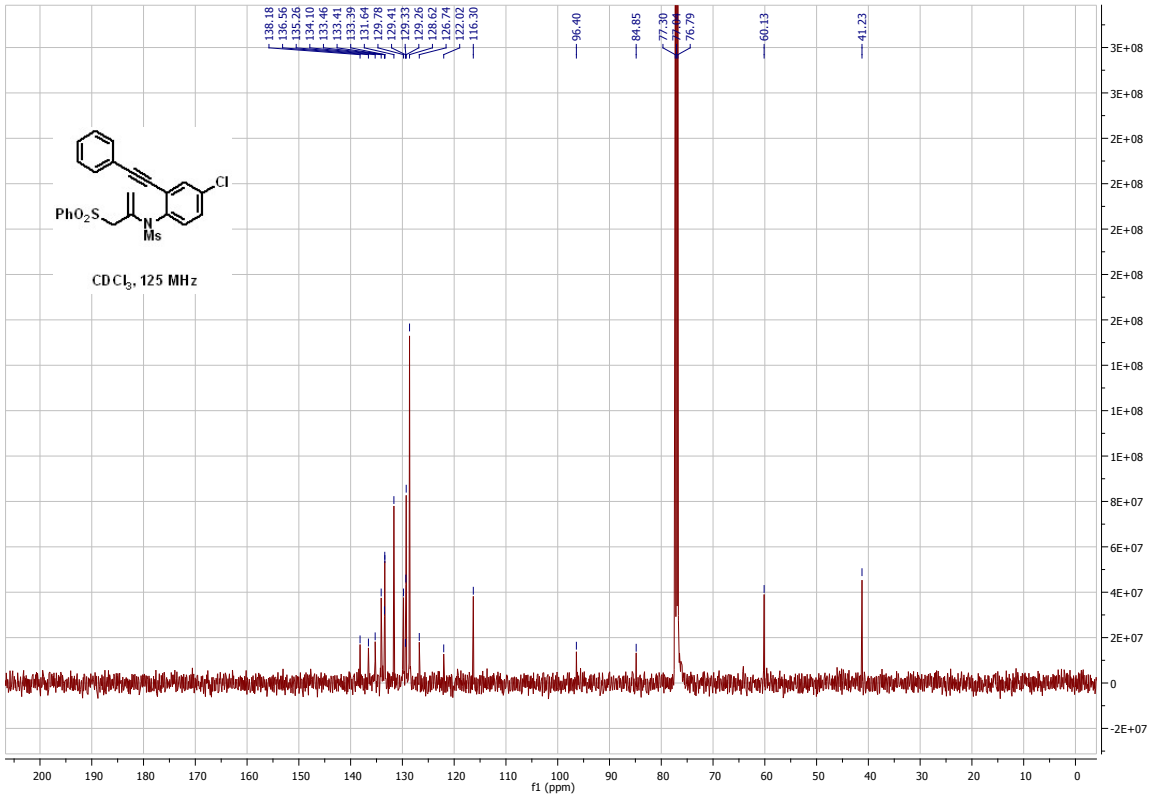

## $^{13}$C NMR spectrum of 1n



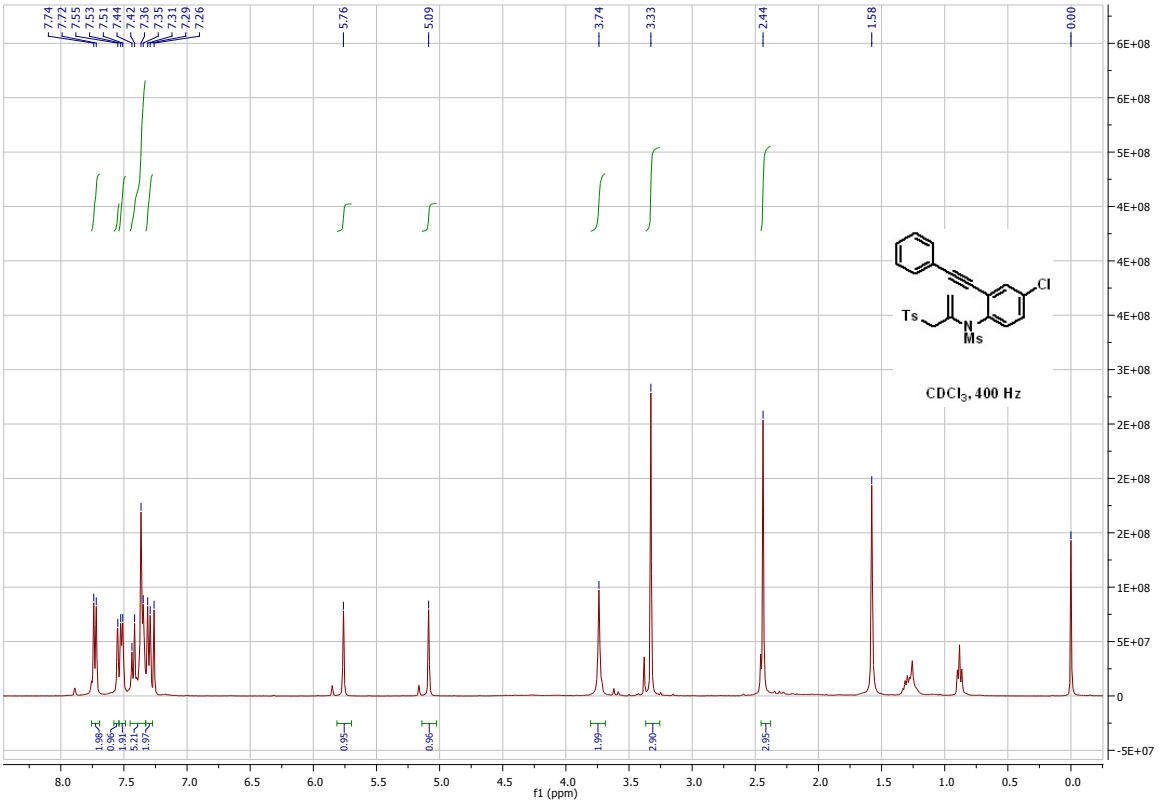
## $^{1}$H NMR spectrum of 1o



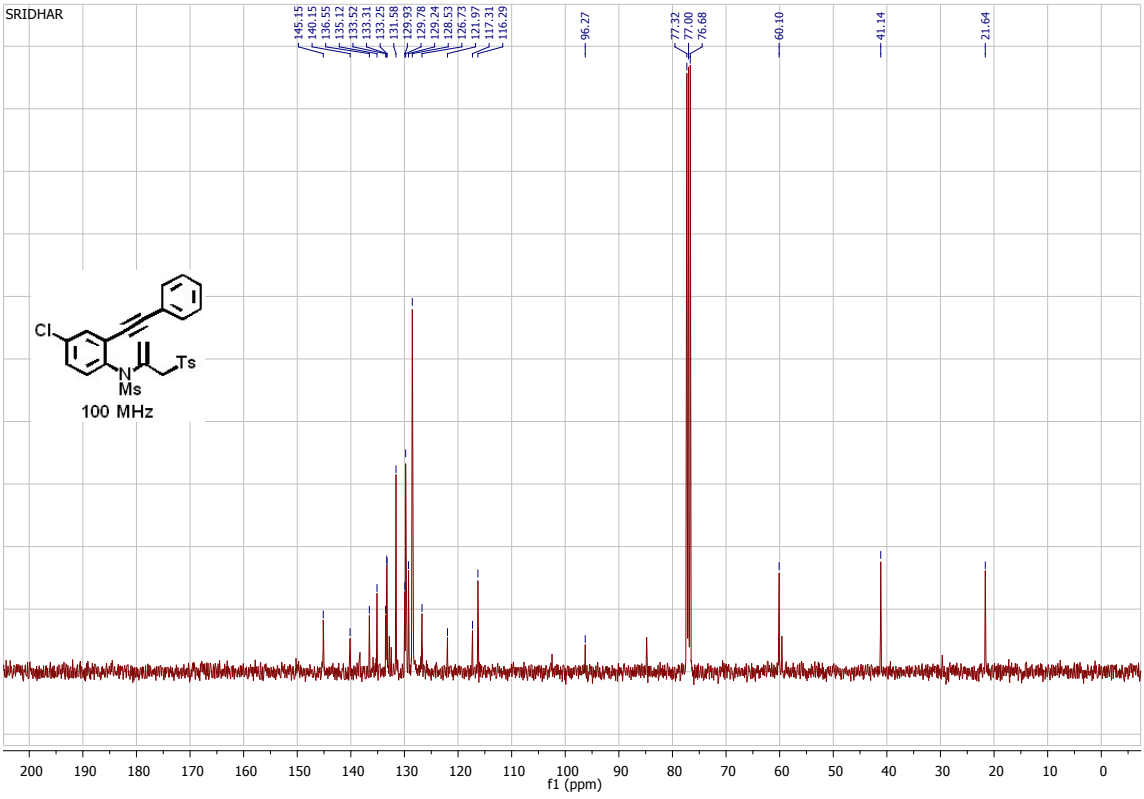

## $^{13}$C NMR spectrum of 1o



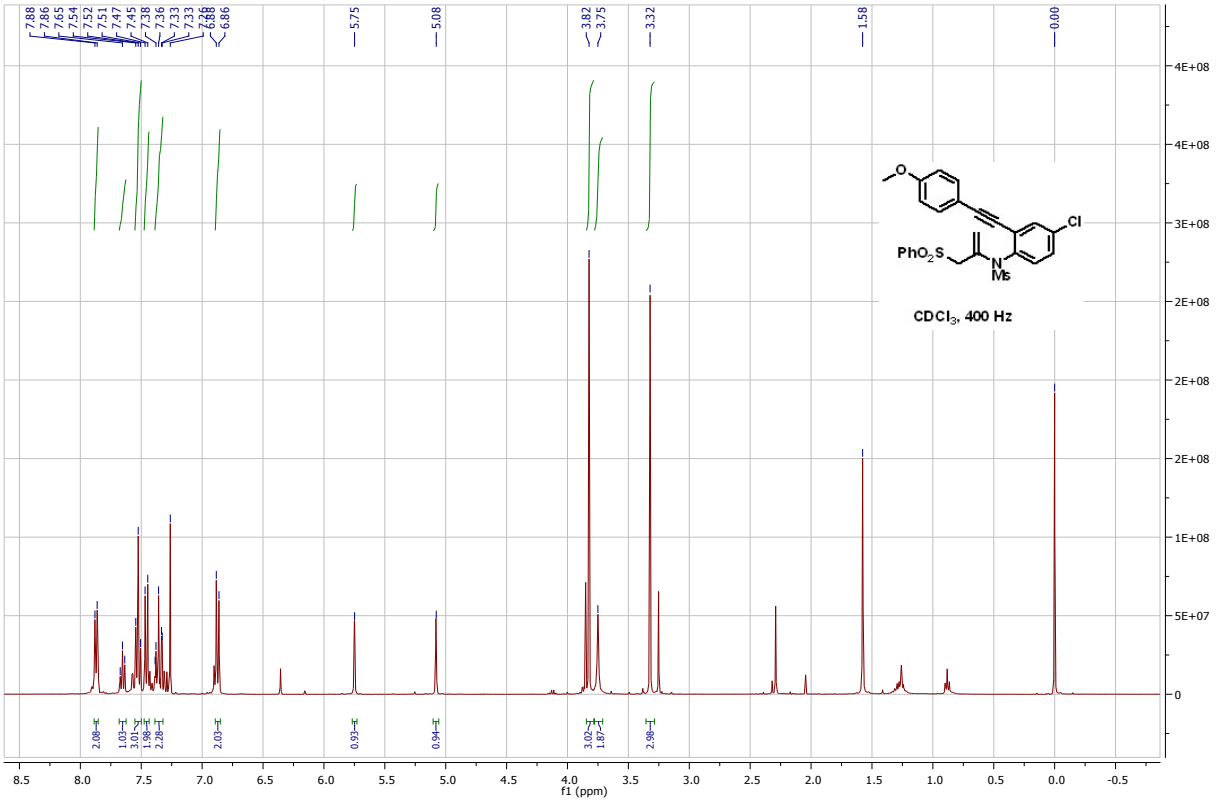
## $^{1}$H NMR spectrum of 1p



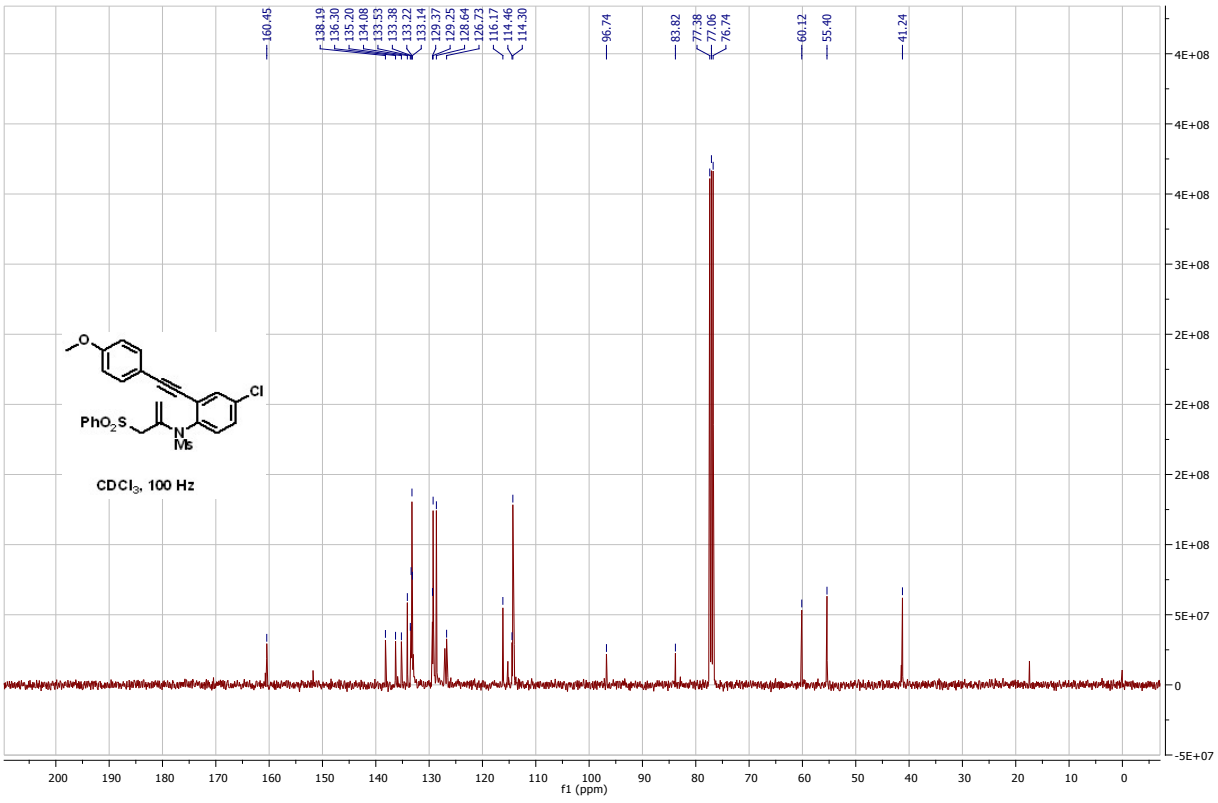

## $^{13}$C NMR spectrum of 1p



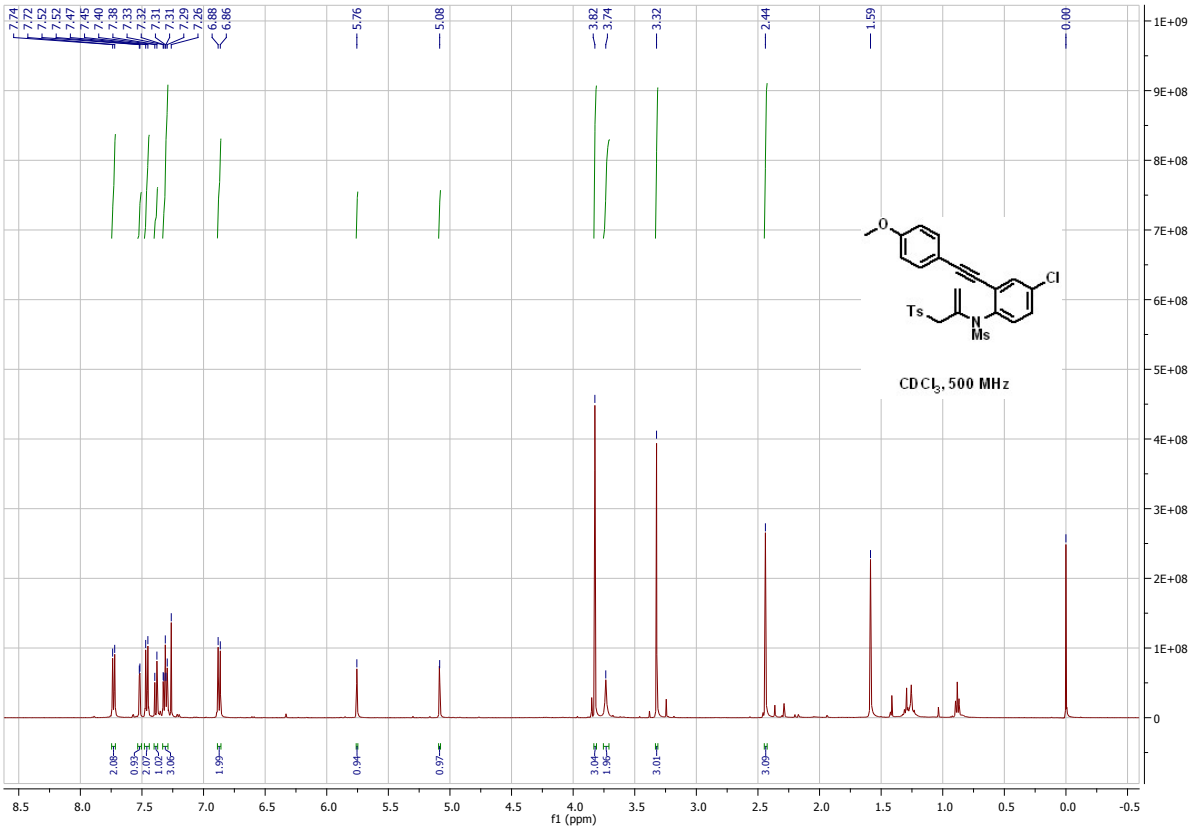
## $^{1}$H NMR spectrum of 1q



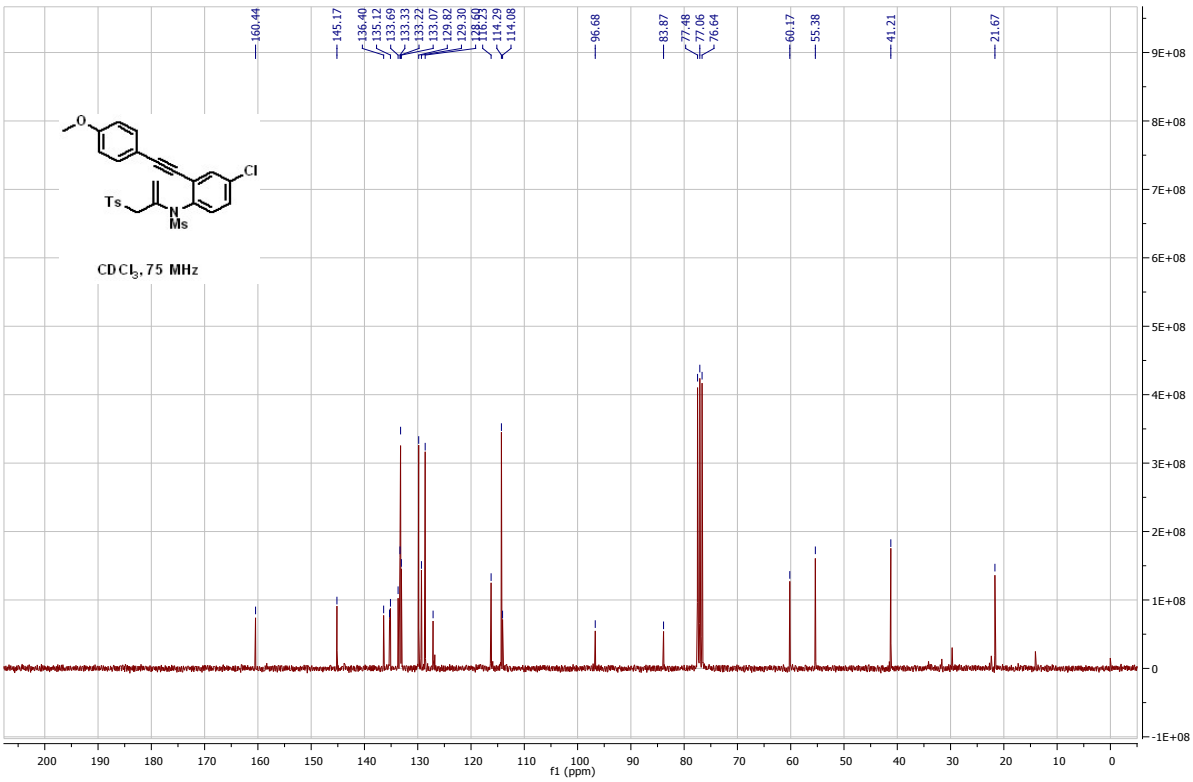

## $^{13}$C NMR spectrum of 1q



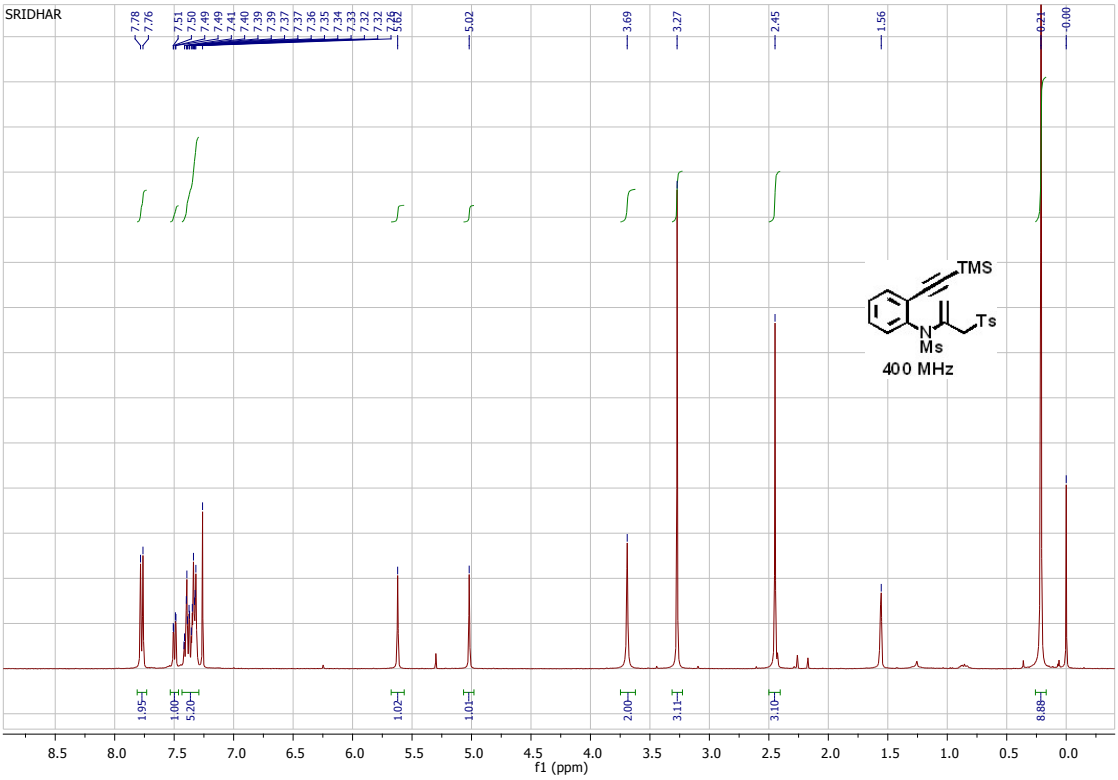
## $^{1}$H NMR spectrum of 1r



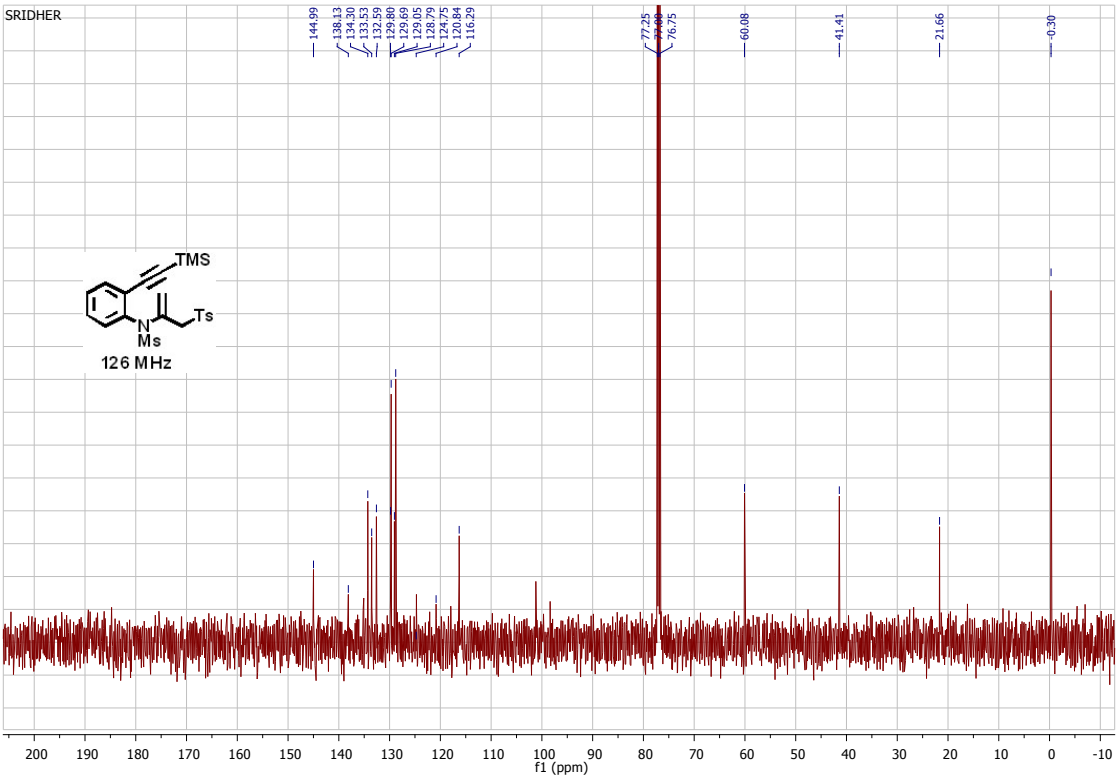

## $^{13}$C NMR spectrum of 1r



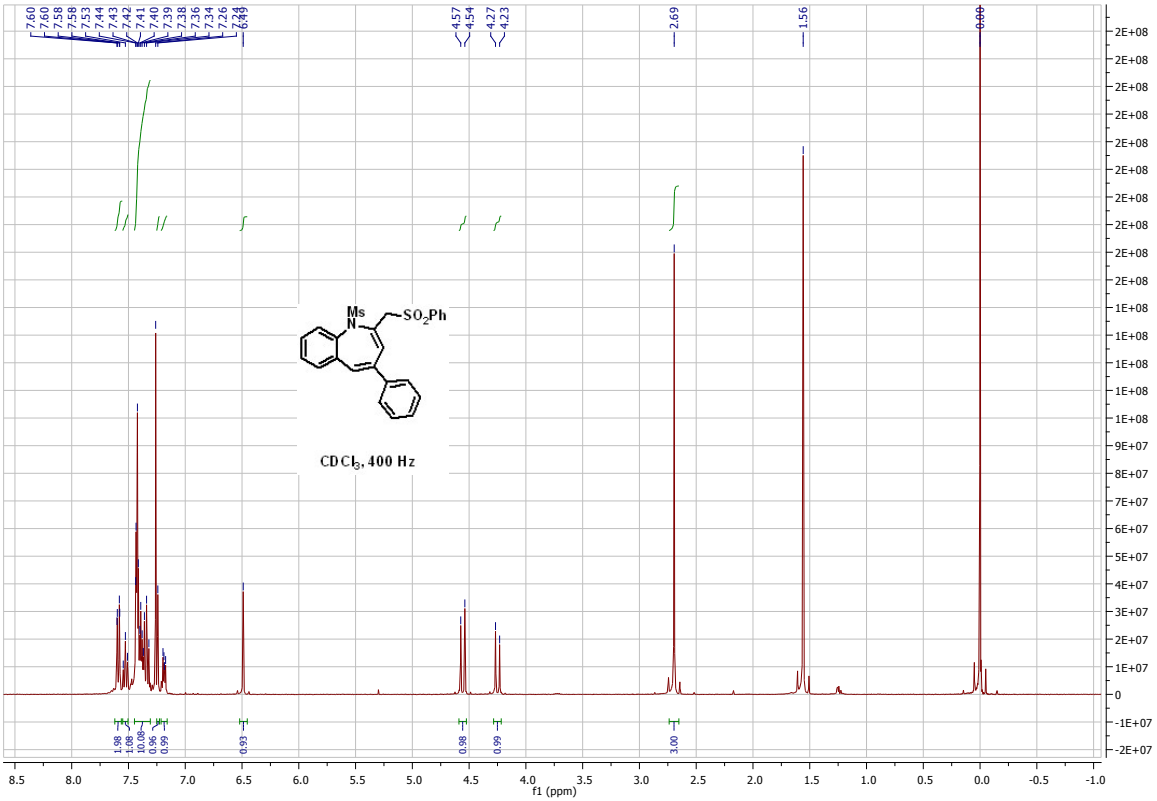
## $^{1}$H NMR spectrum of 1s



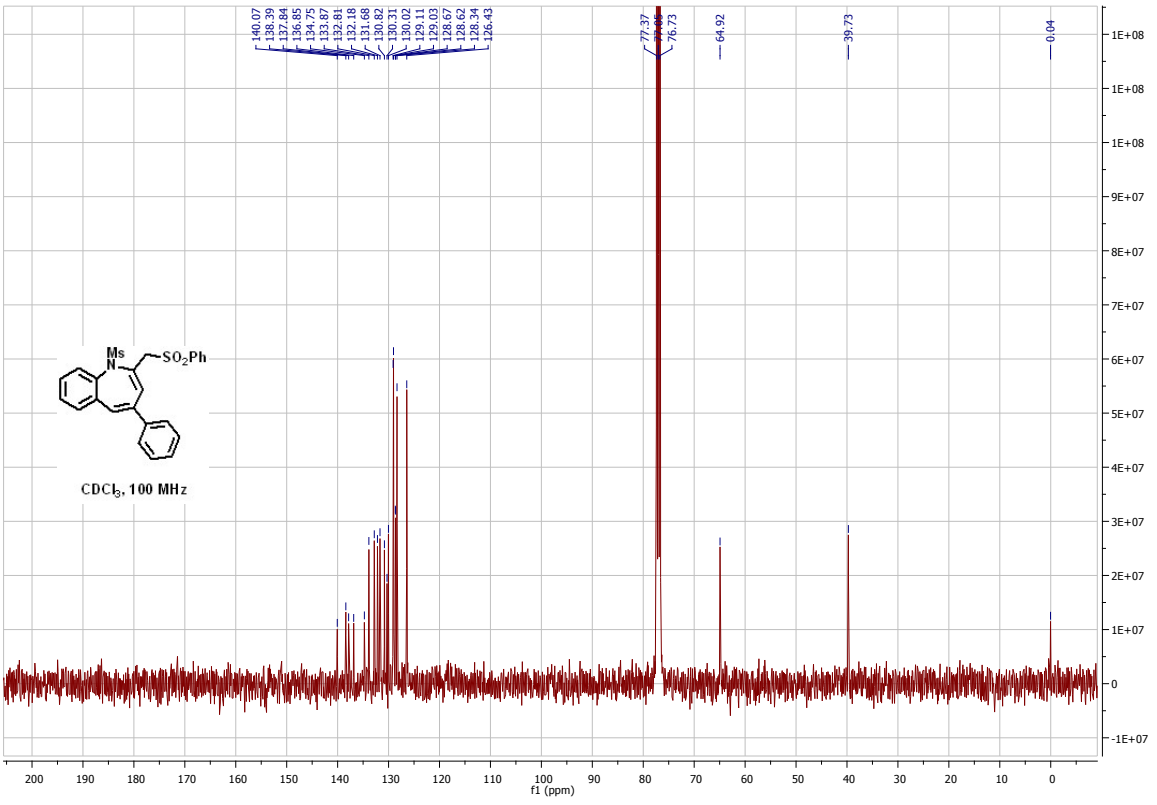

## $^{13}$C NMR spectrum of 1s



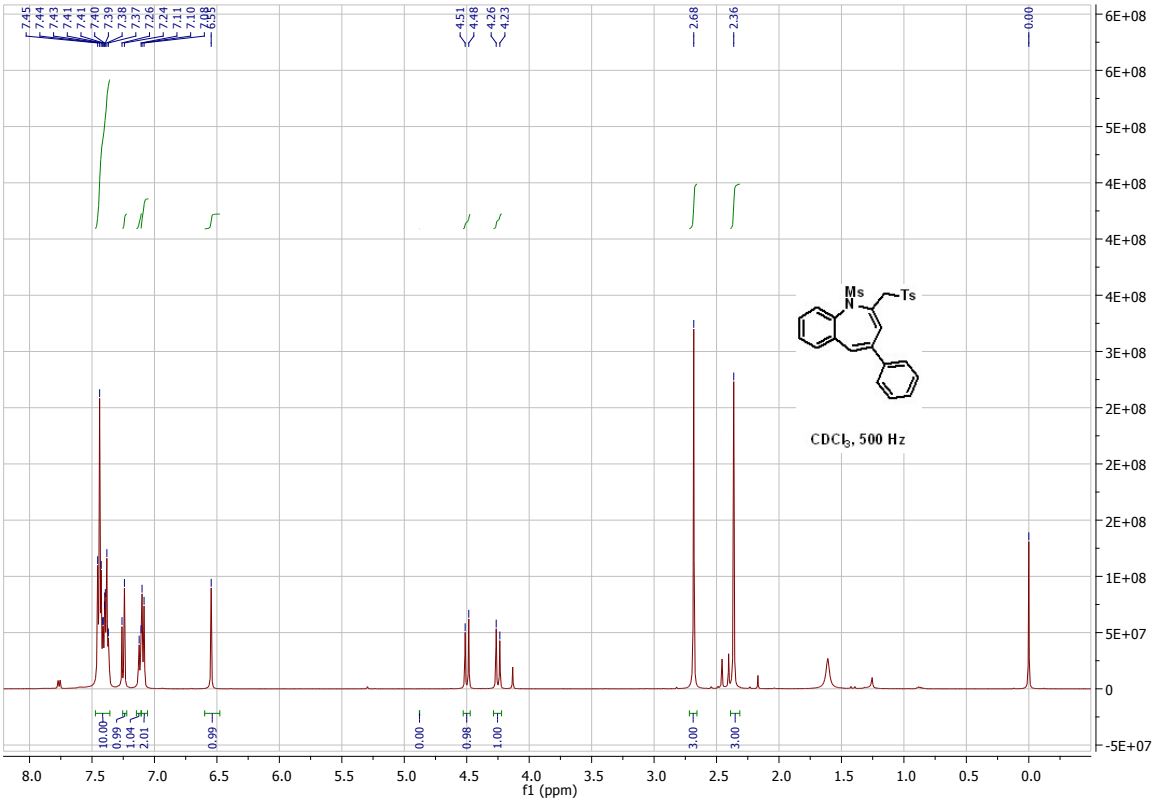
## $^{1}$H NMR spectrum of 2a



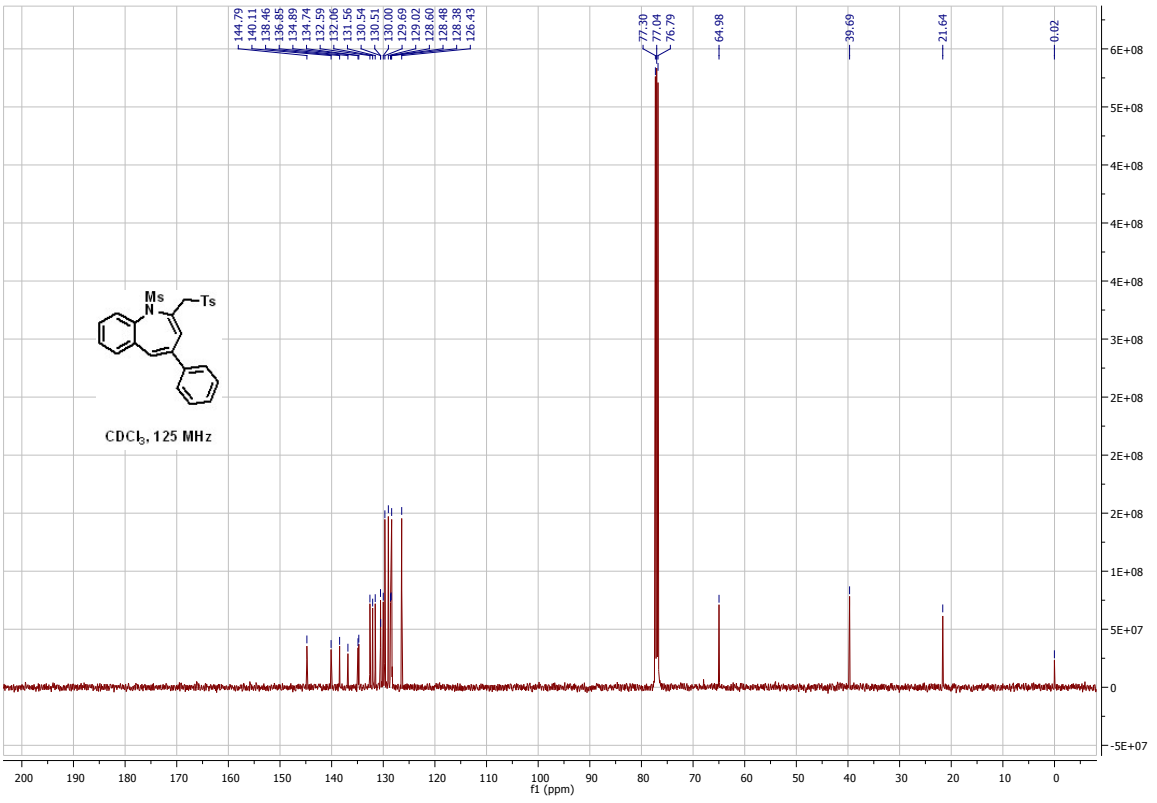

## $^{13}$C NMR spectrum of 2a



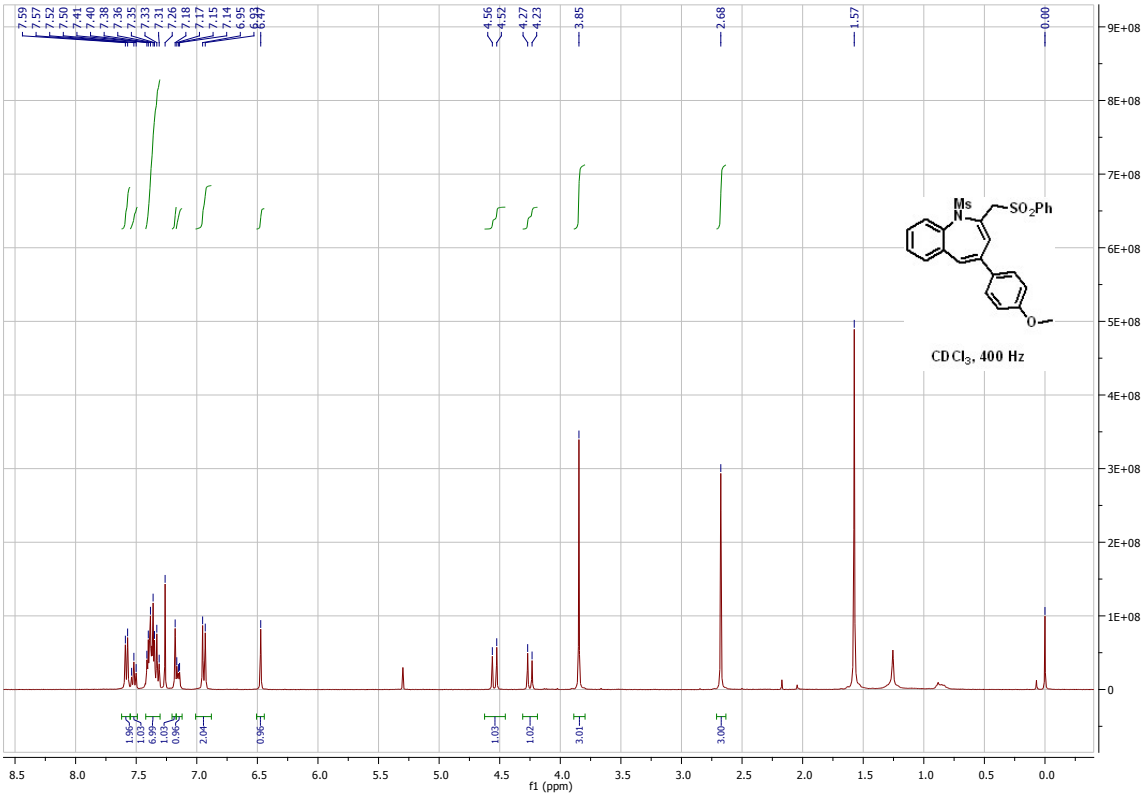
## $^{1}$H NMR spectrum of 2b



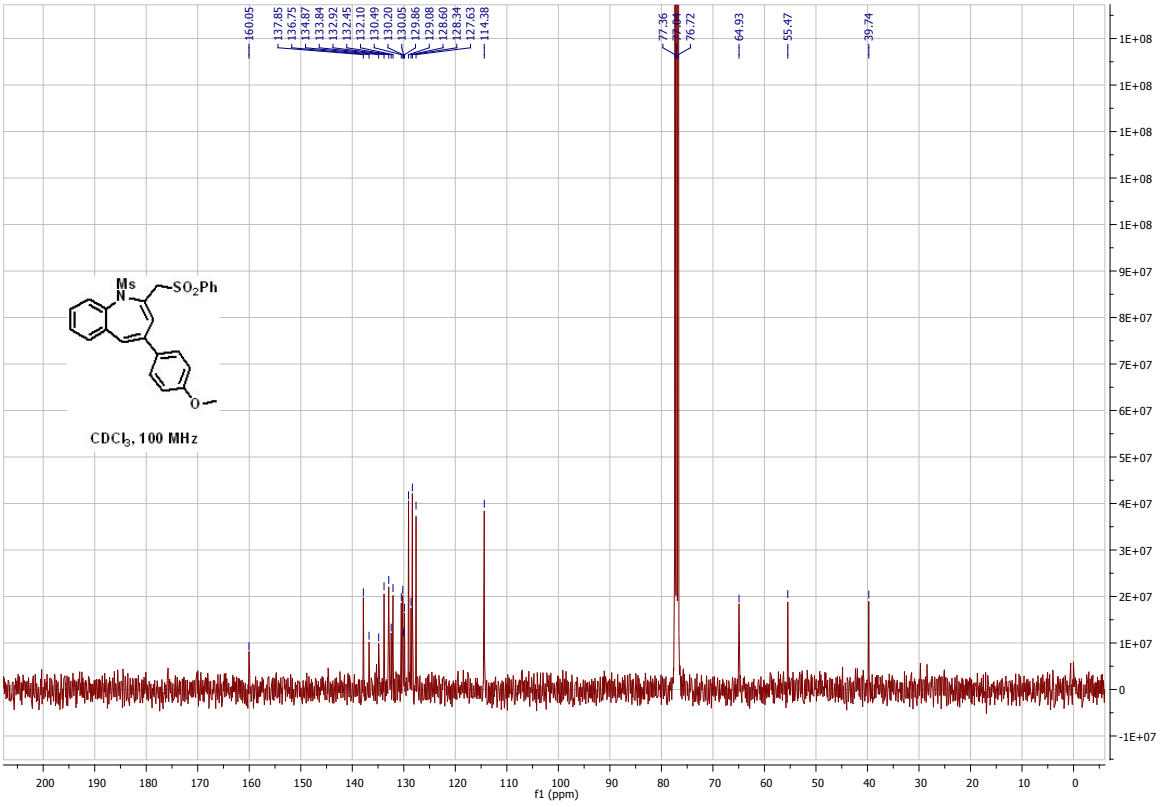

## $^{13}$C NMR spectrum of 2b



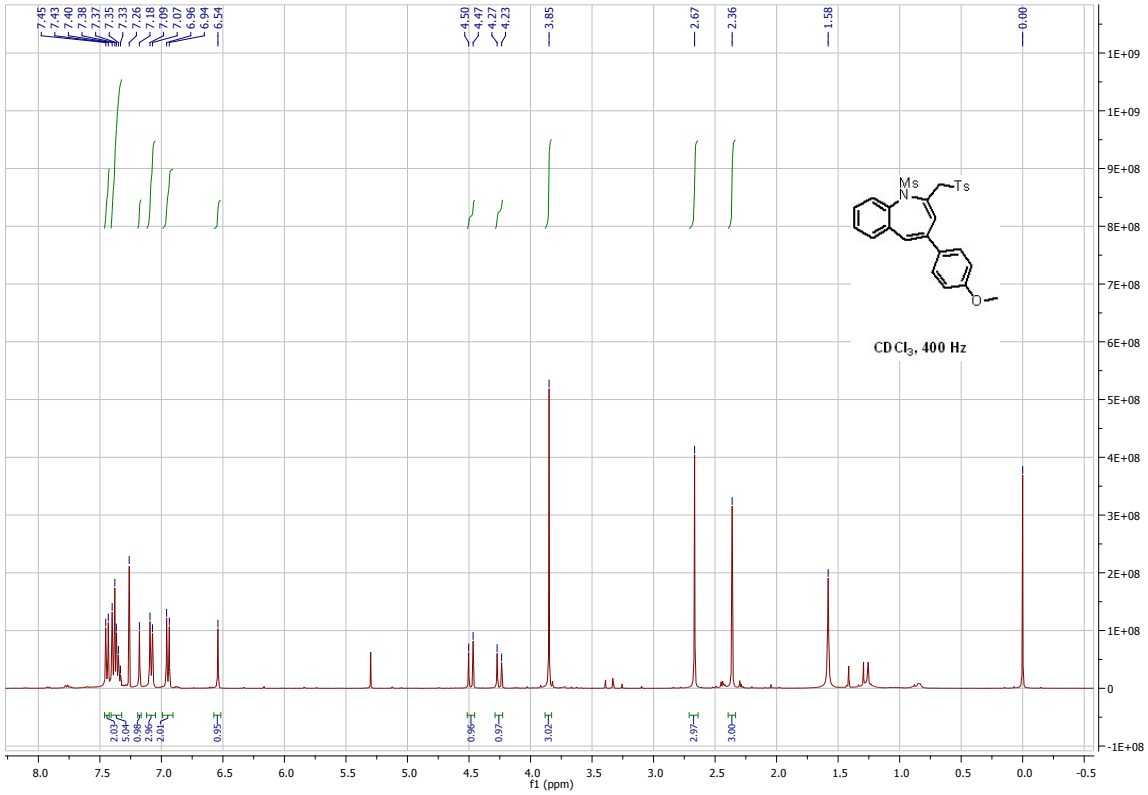
## $^{1}$H NMR spectrum of 2c



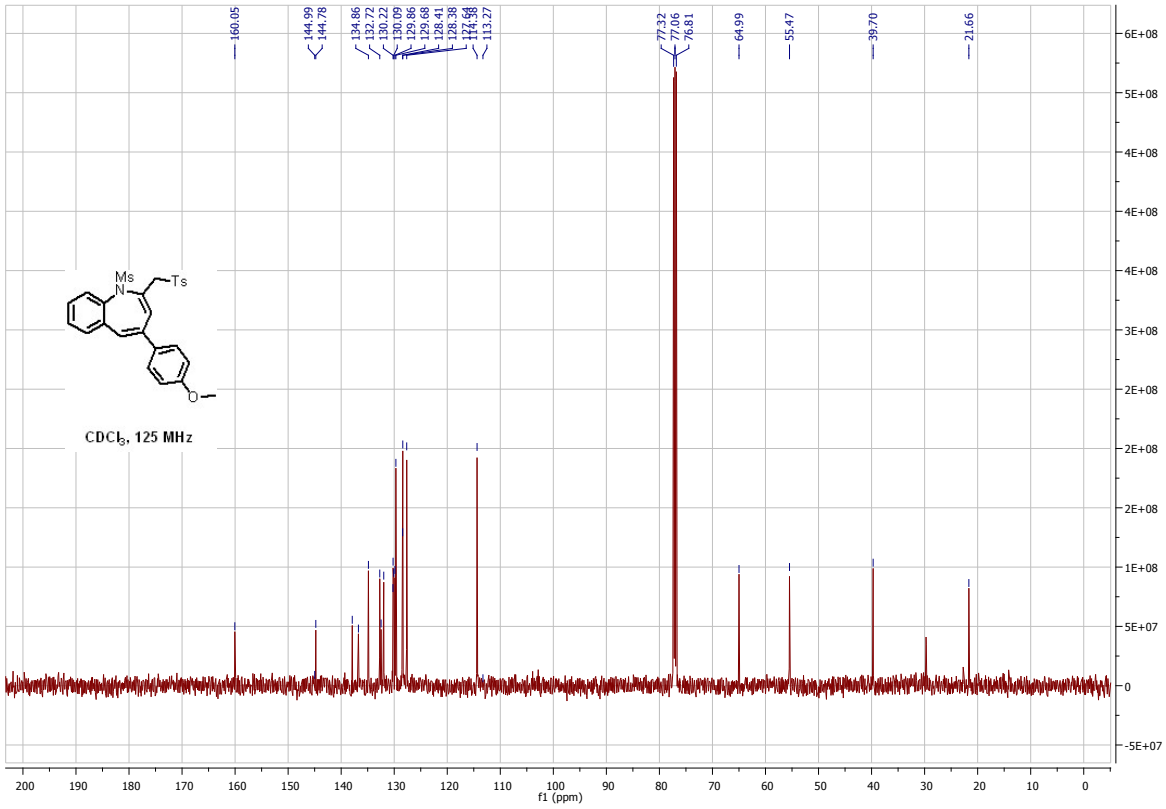

## $^{13}$C NMR spectrum of 2c



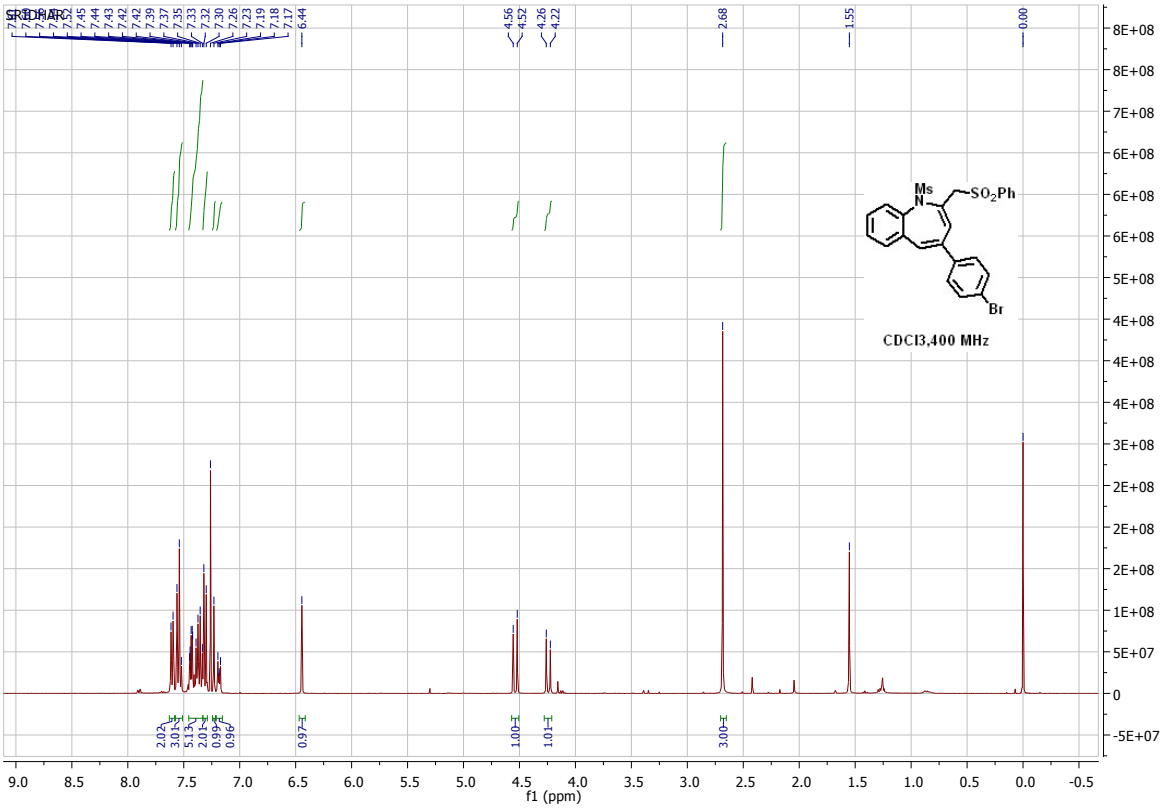
## $^{1}$H NMR spectrum of 2d



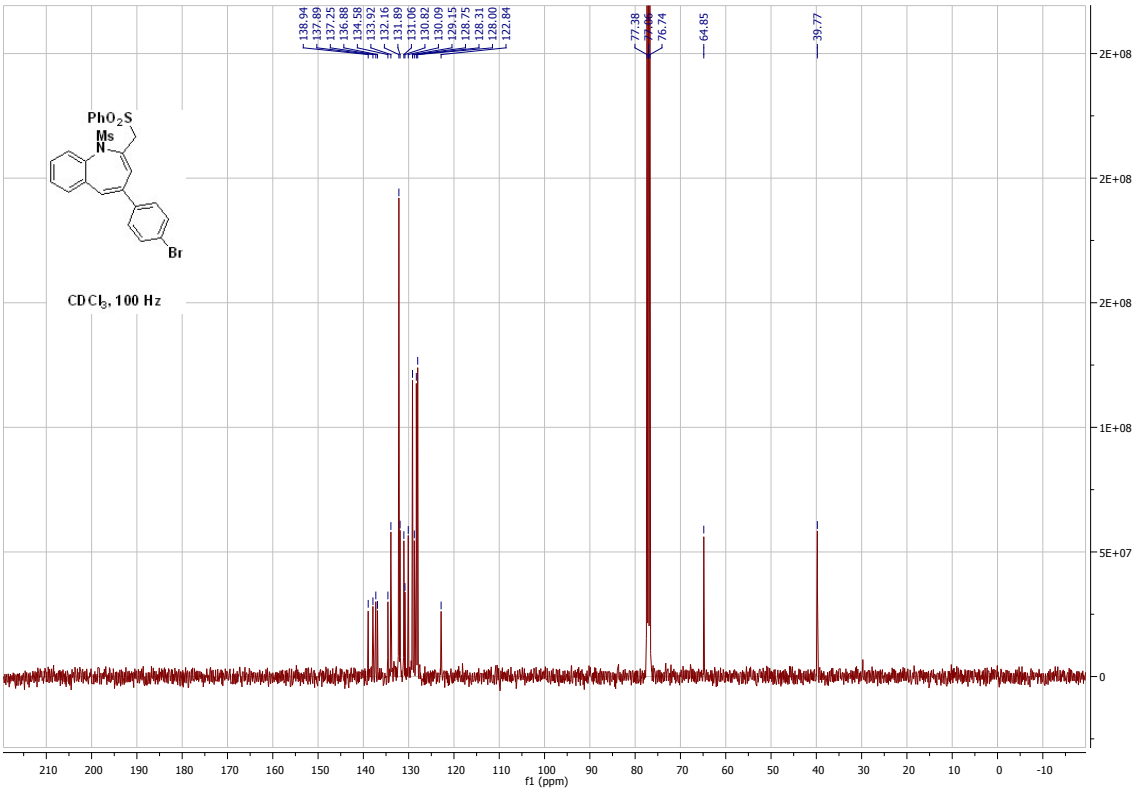

## $^{13}$C NMR spectrum of 2d



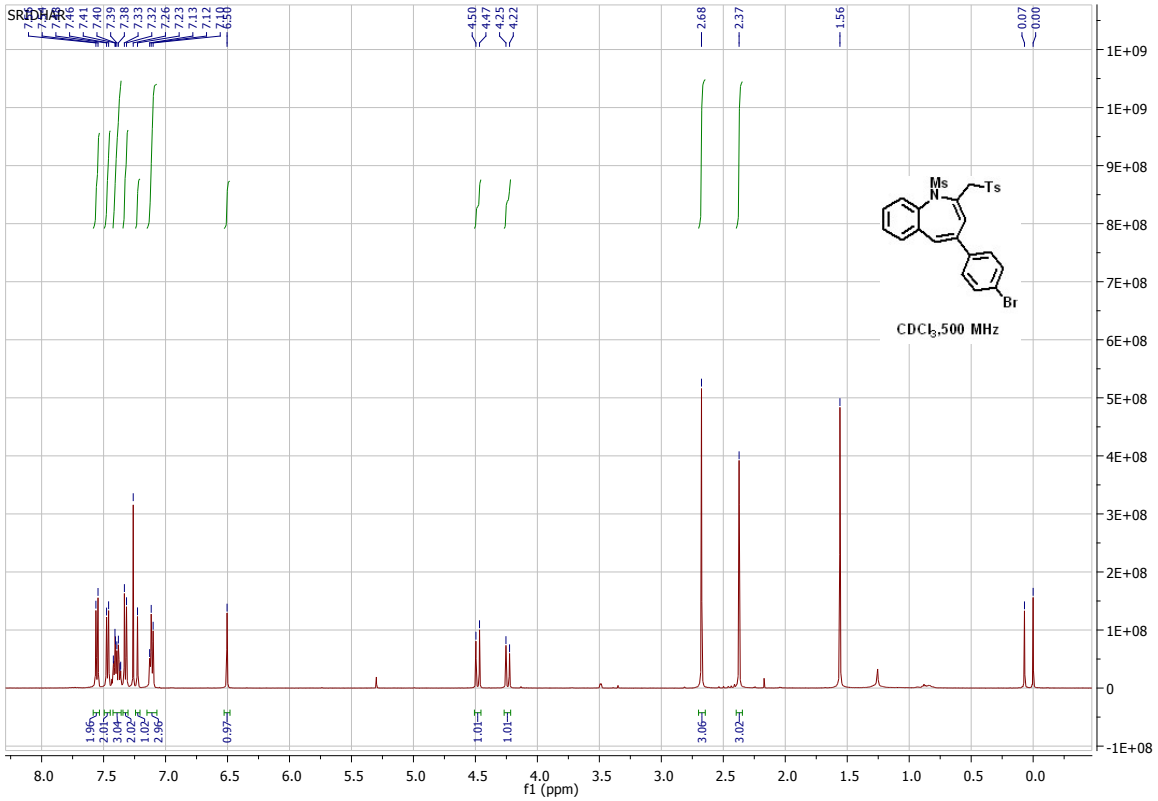
## $^{1}$H NMR spectrum of 2e



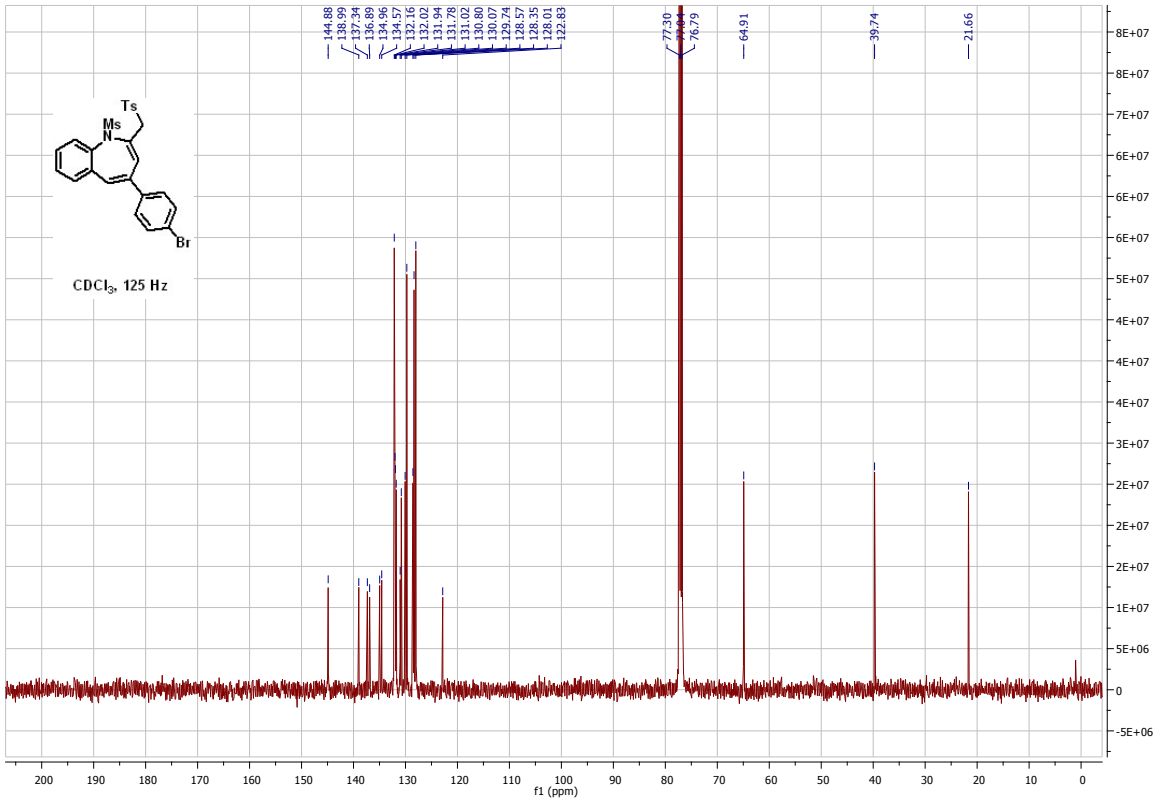

## $^{13}$C NMR spectrum of 2e



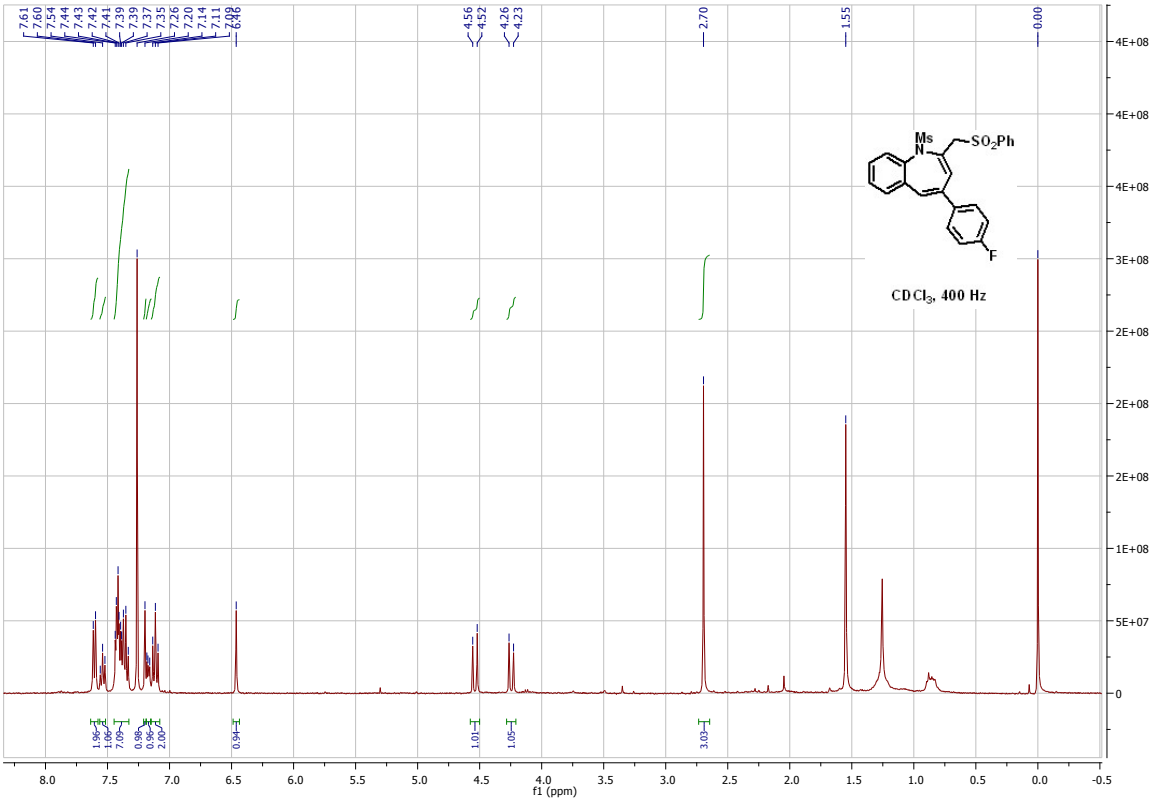
## $^{1}$H NMR spectrum of 2f



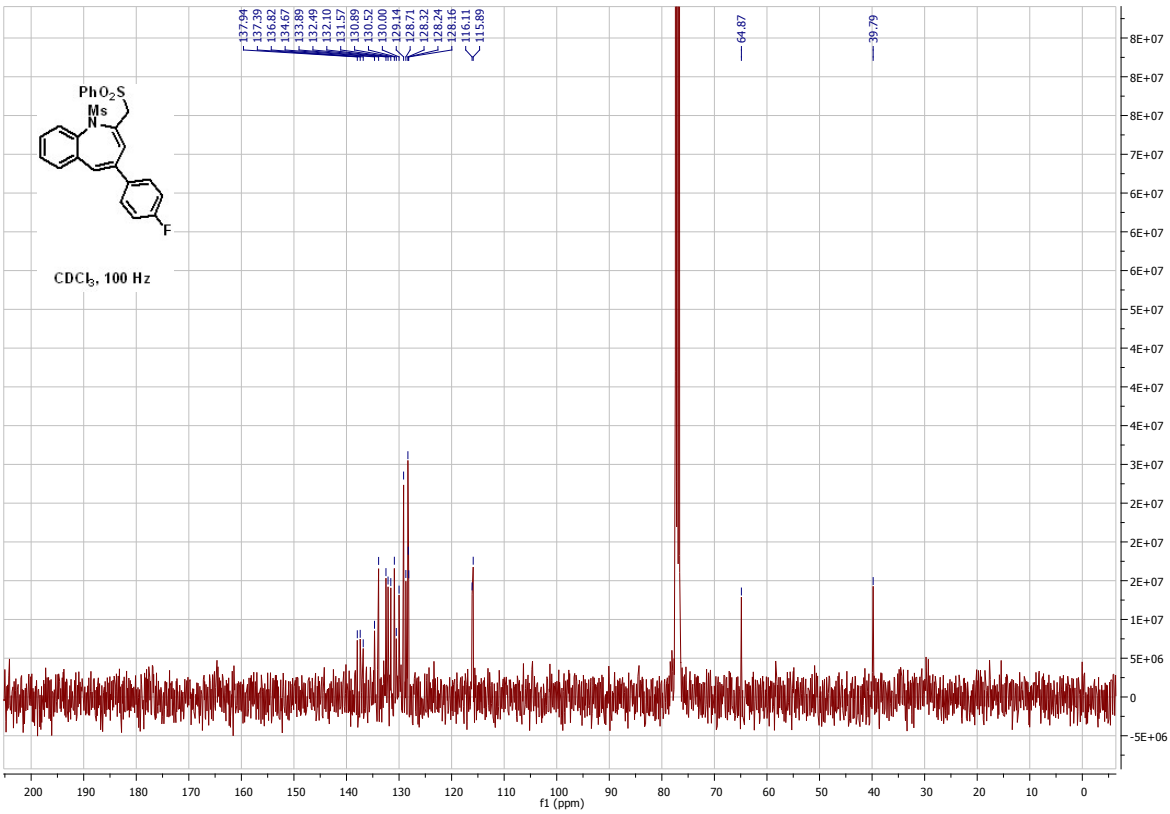

## $^{13}$C NMR spectrum of 2f



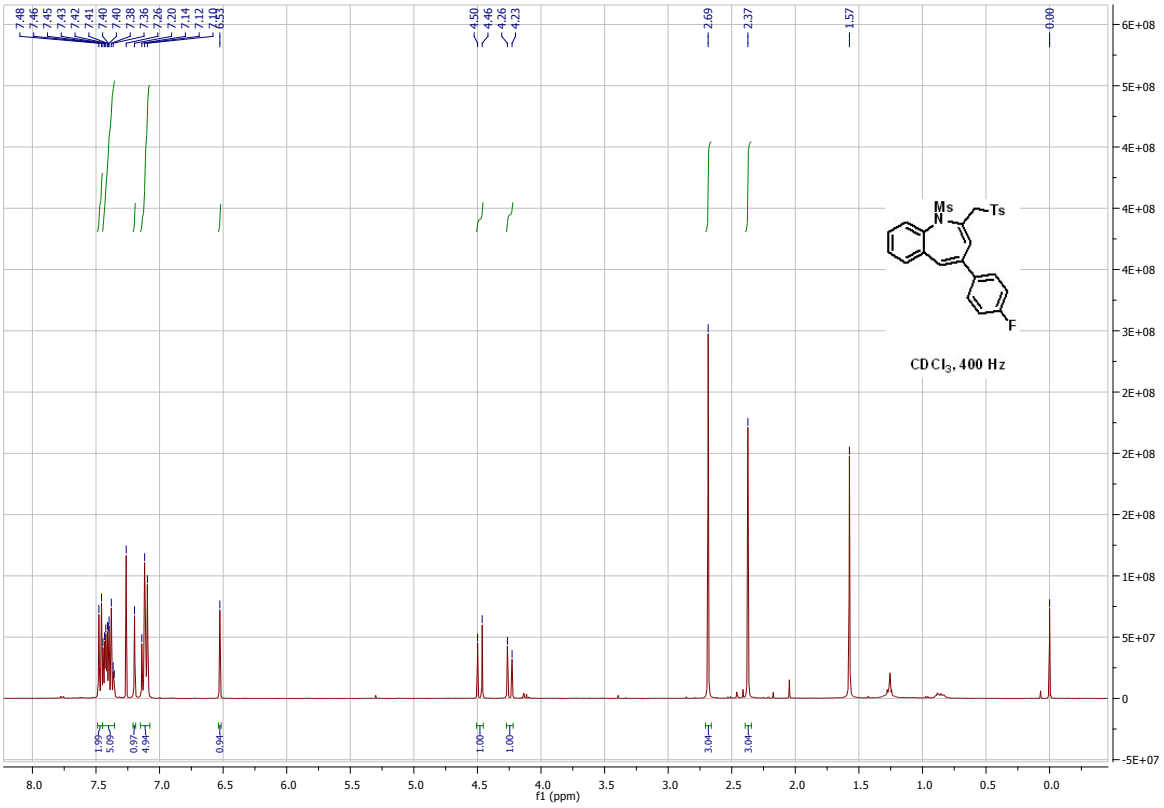
## $^{1}$H NMR spectrum of 2g



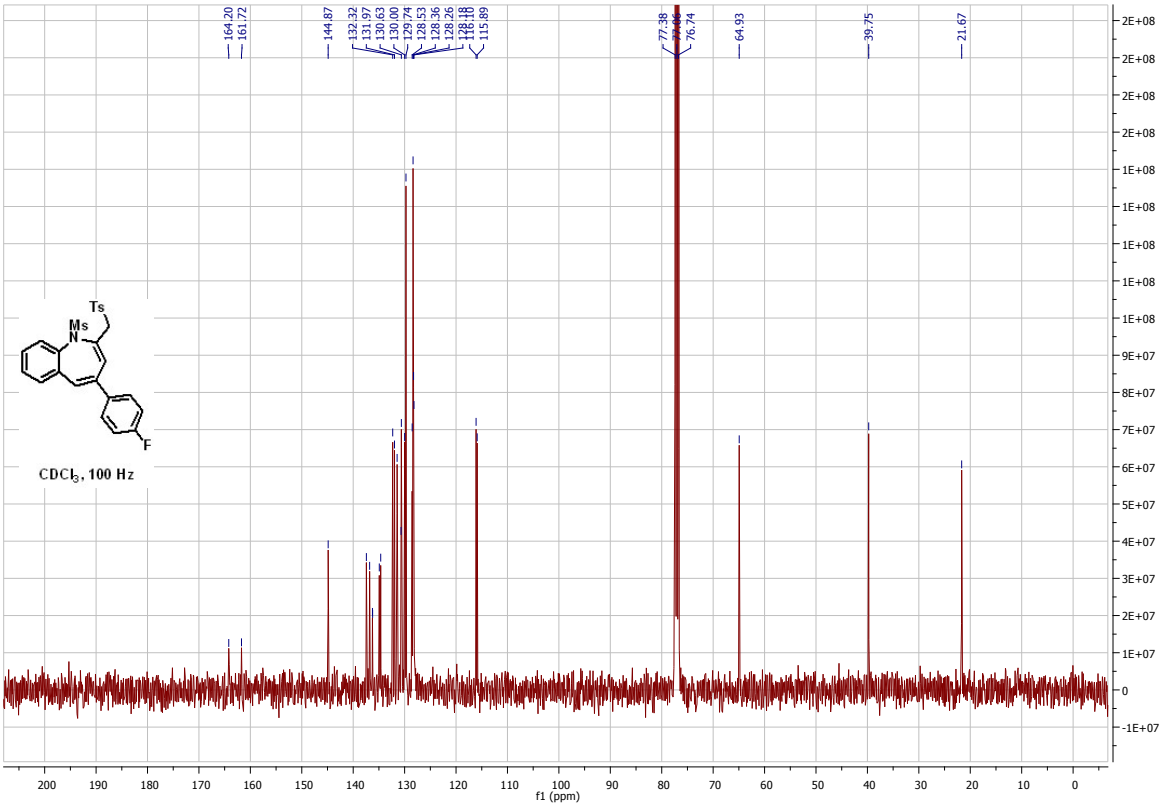

## $^{13}$C NMR spectrum of 2g



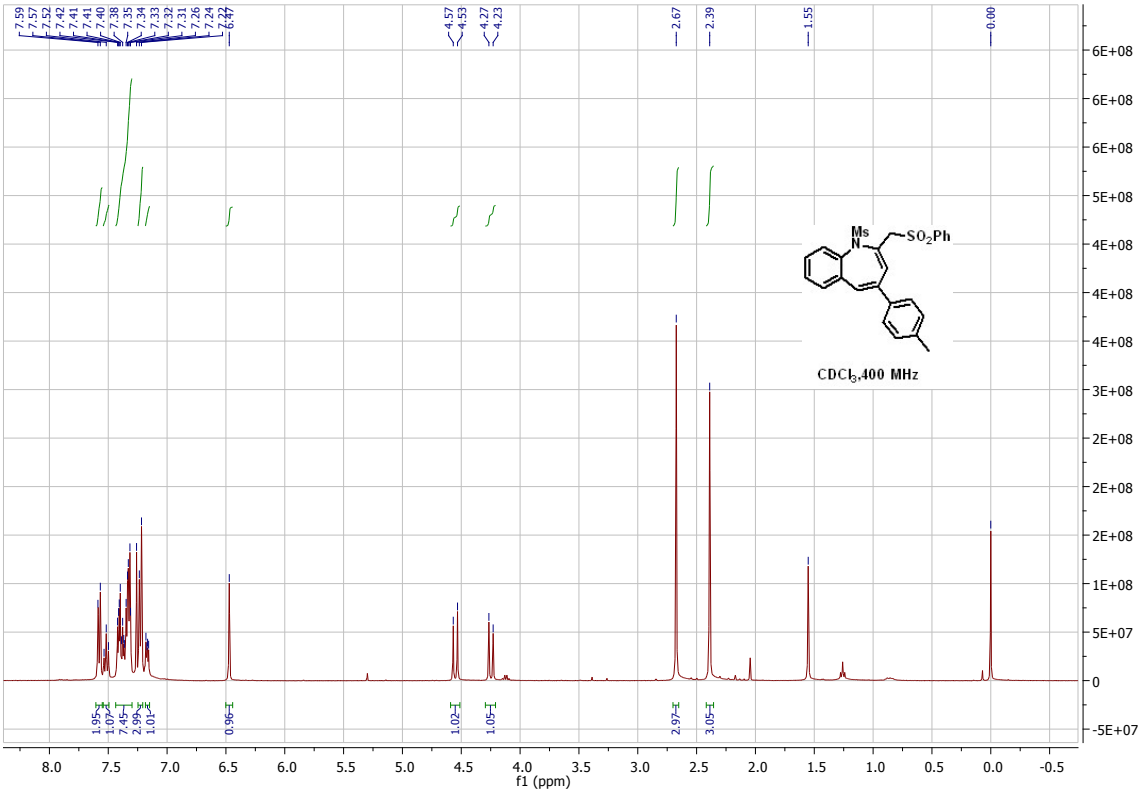
## $^{1}$H NMR spectrum of 2h



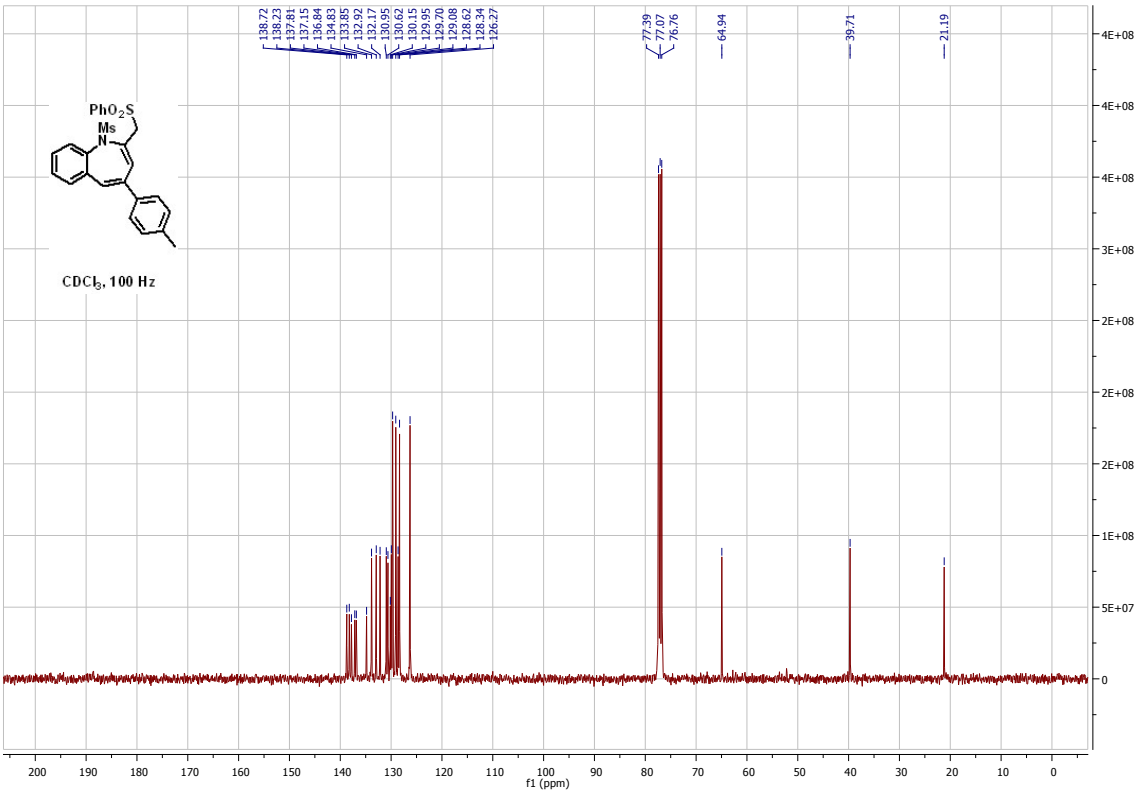

## $^{13}$C NMR spectrum of 2h



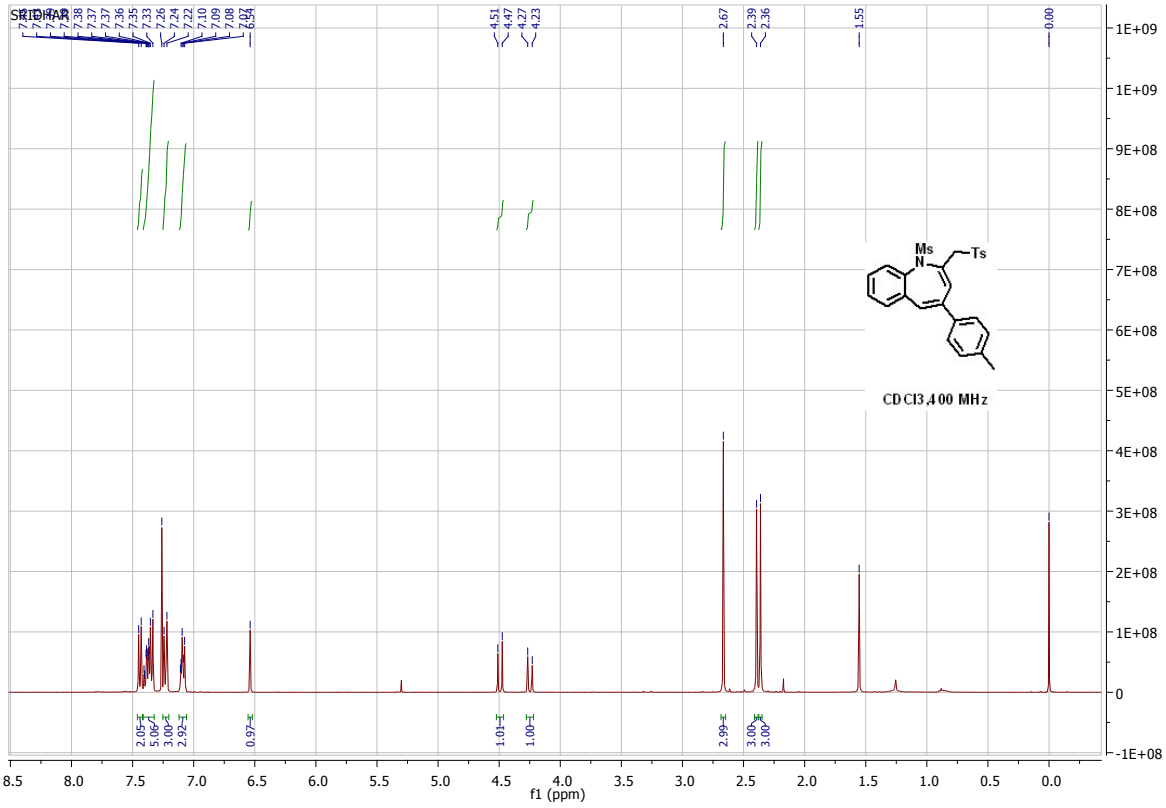
## $^{1}$H NMR spectrum of 2i



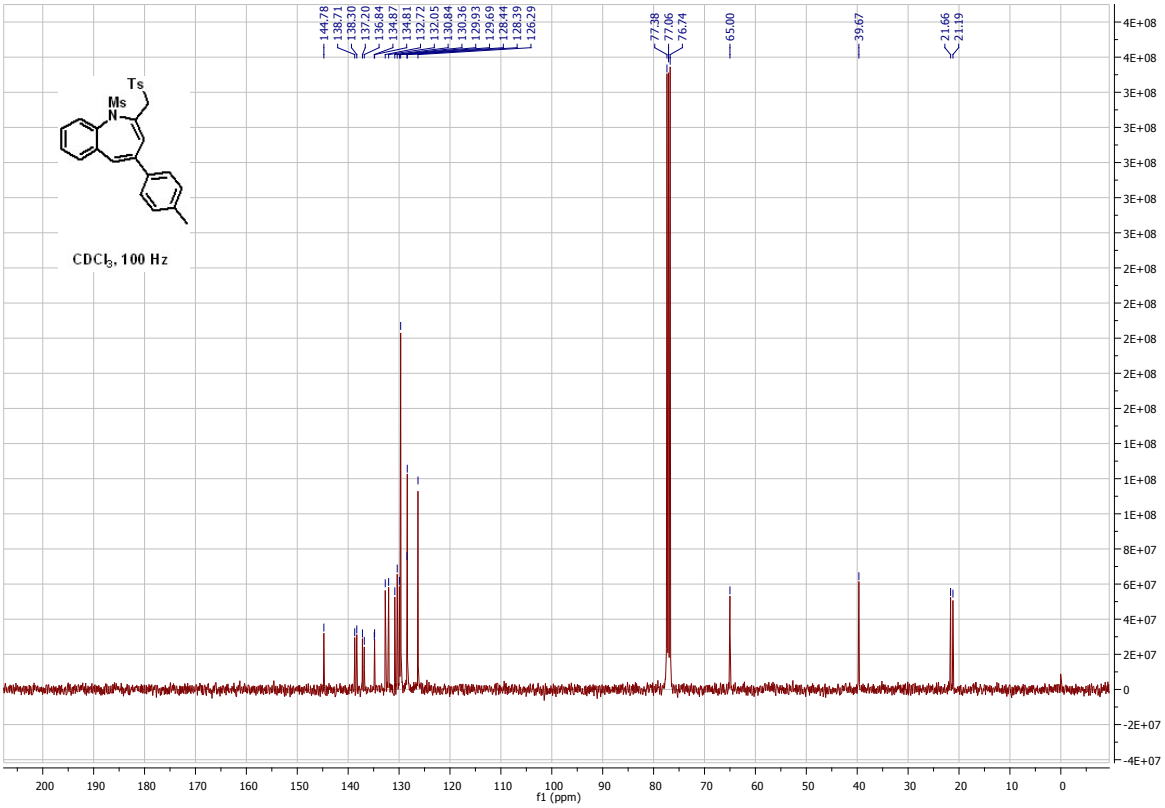

## $^{13}$C NMR spectrum of 2i



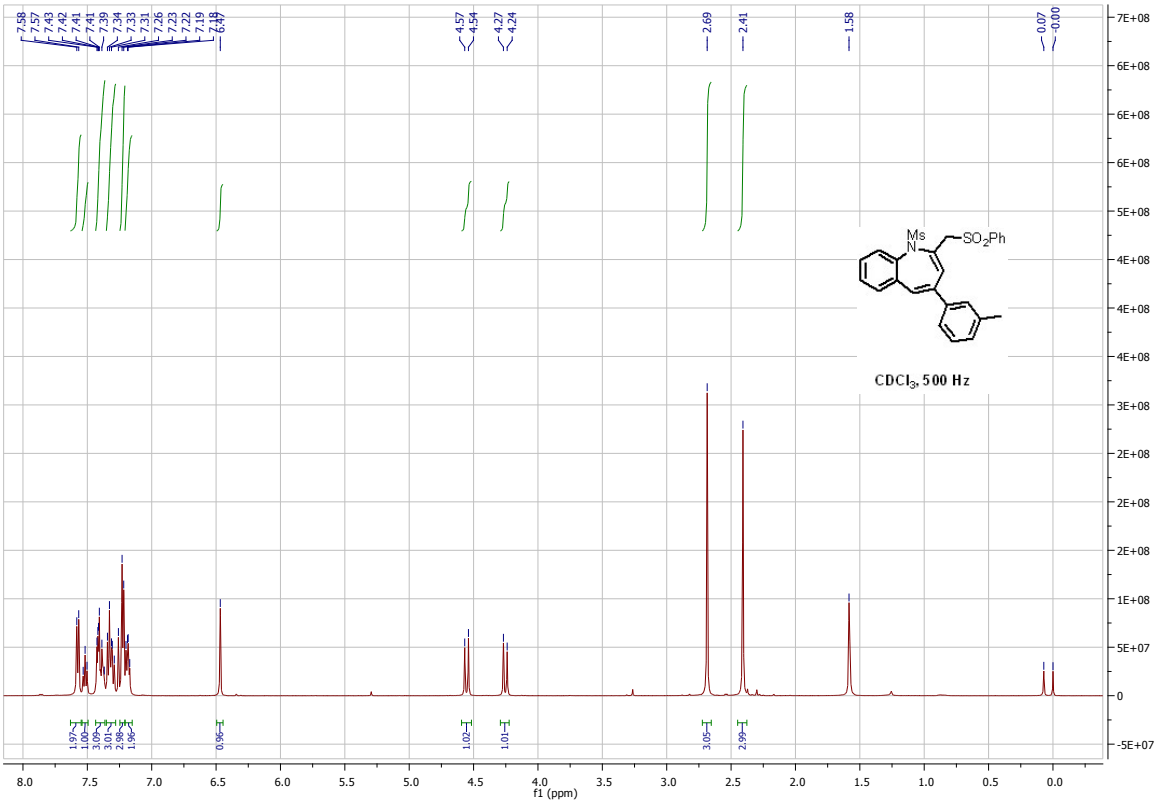
## $^{1}$H NMR spectrum of 2j



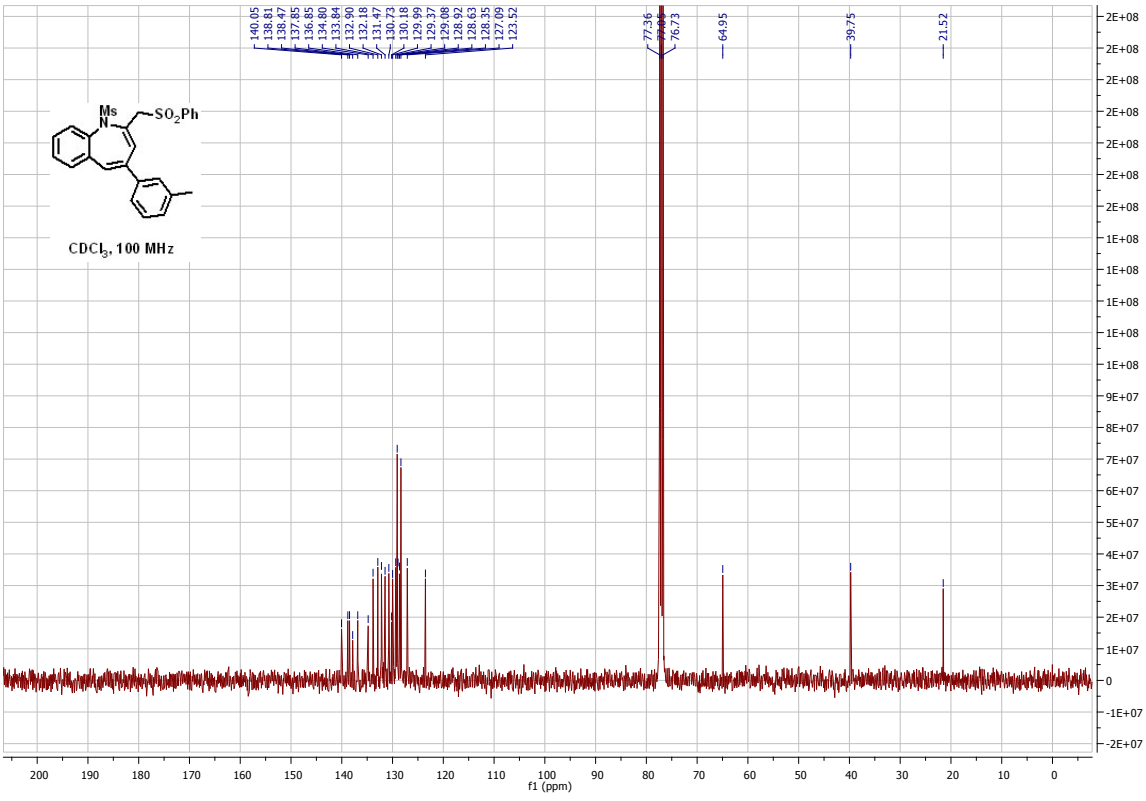

## $^{13}$C NMR spectrum of 2j



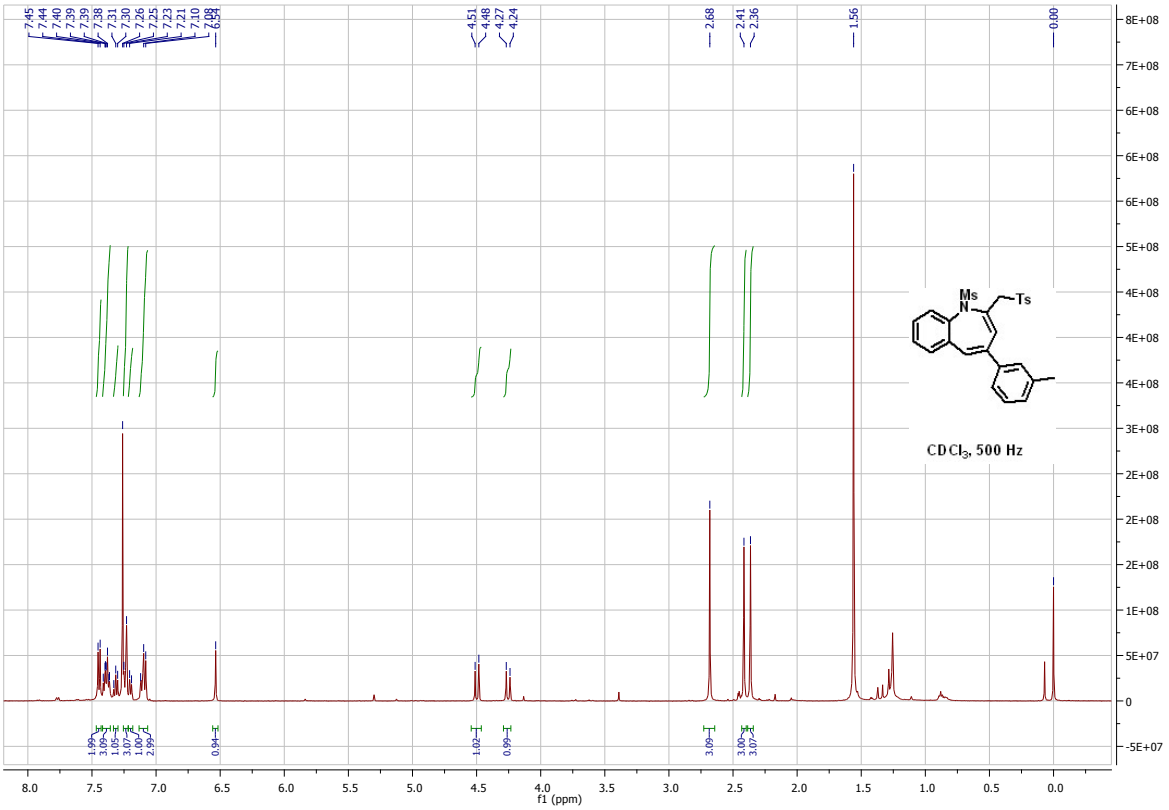
## $^{1}$H NMR spectrum of 2k



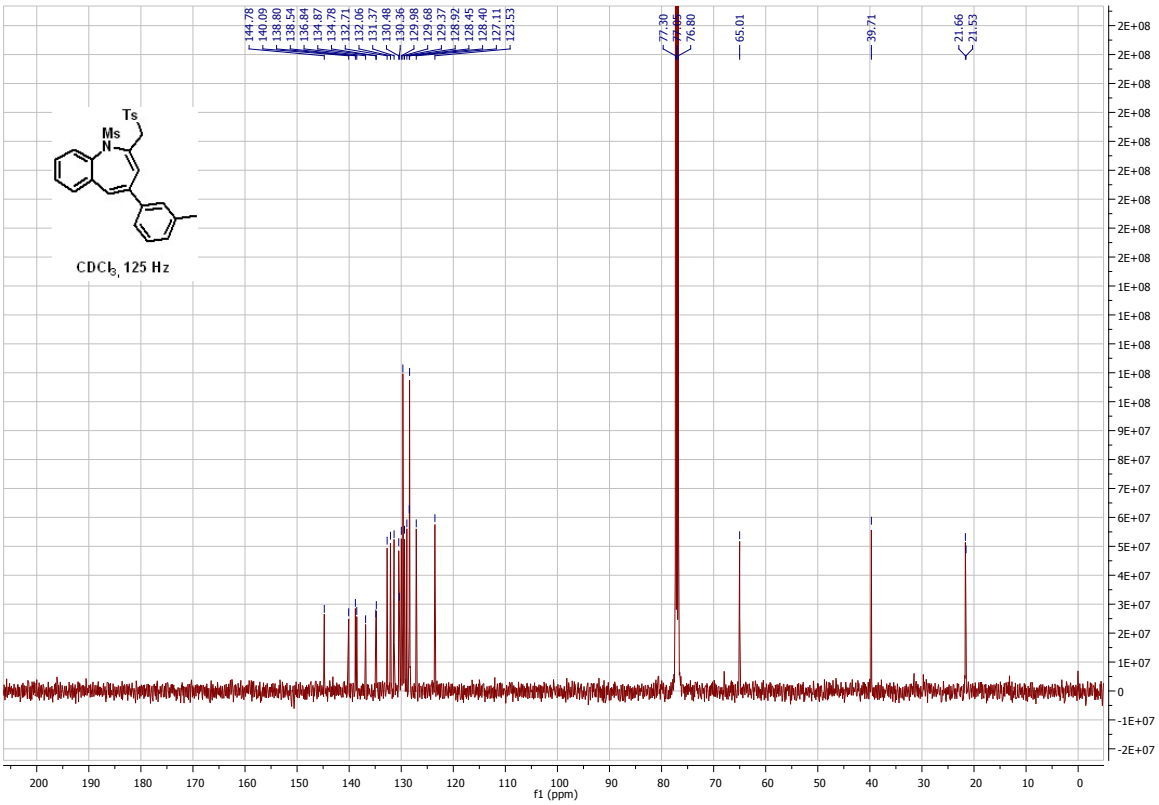

## $^{13}$C NMR spectrum of 2k



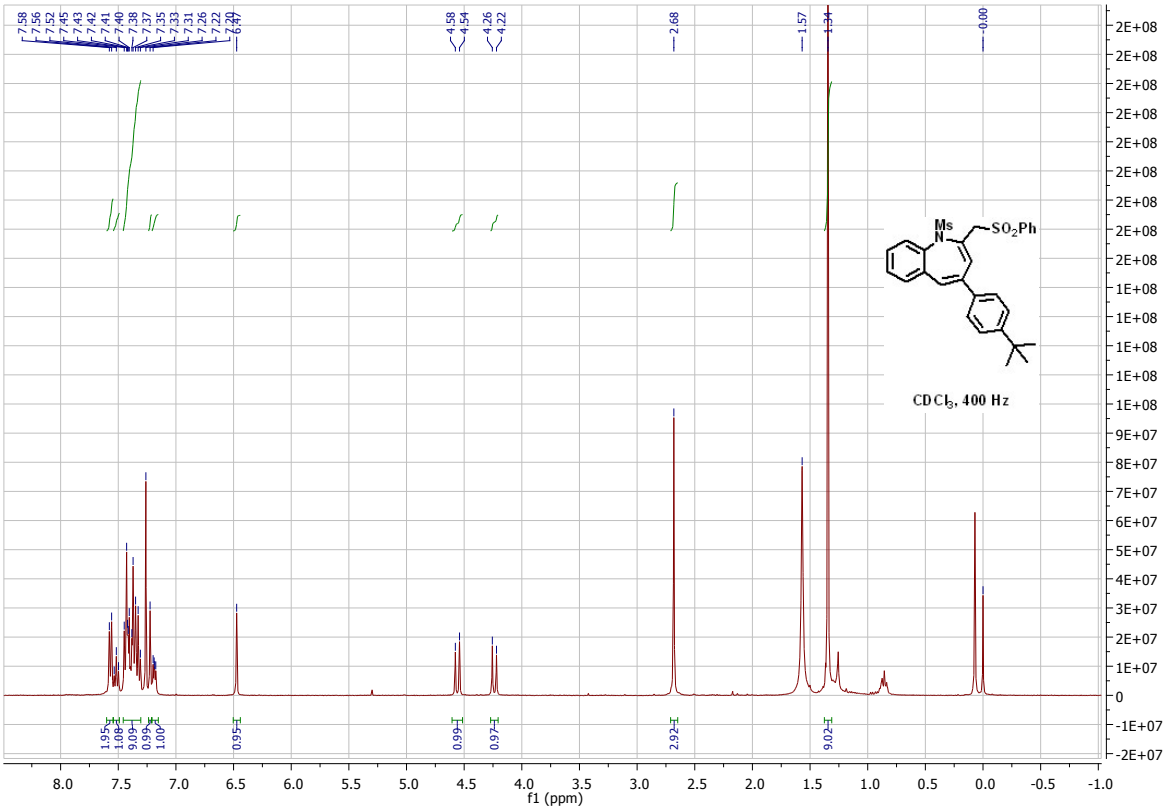
## $^{1}$H NMR spectrum of 2l



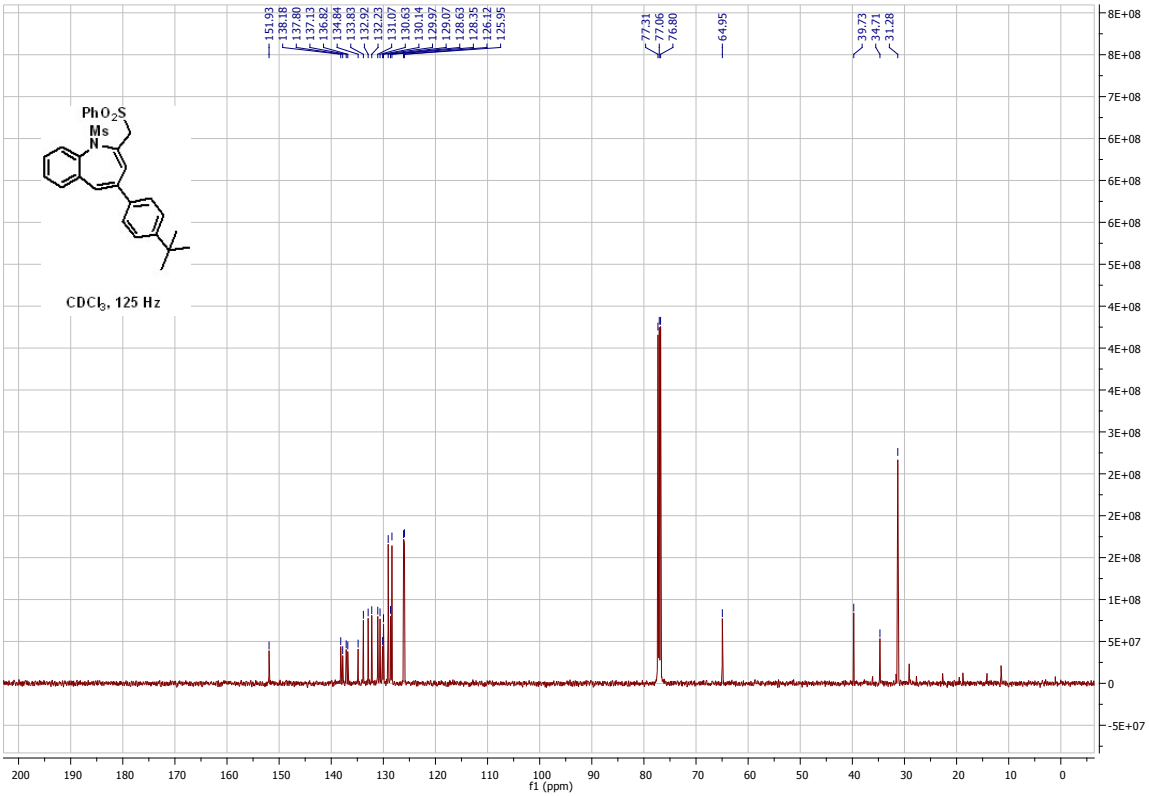

## $^{13}$C NMR spectrum of 2l



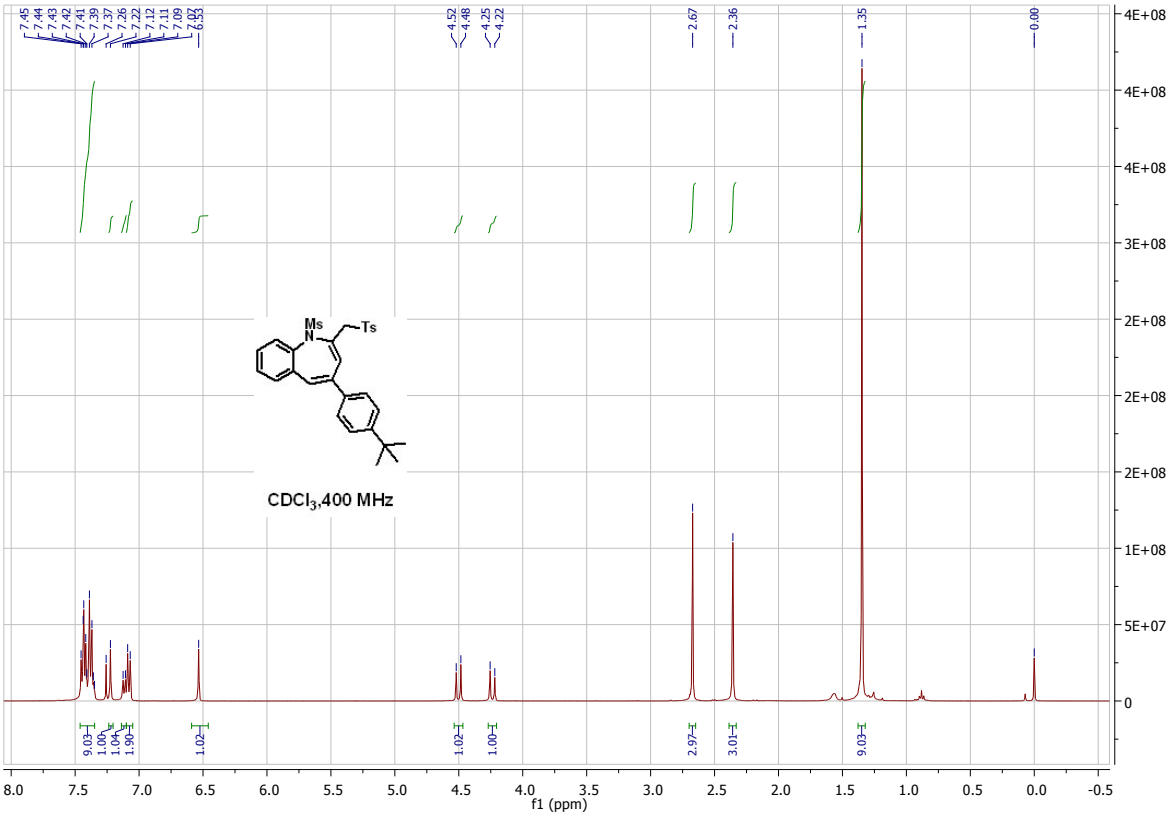
## $^{1}$H NMR spectrum of 2m



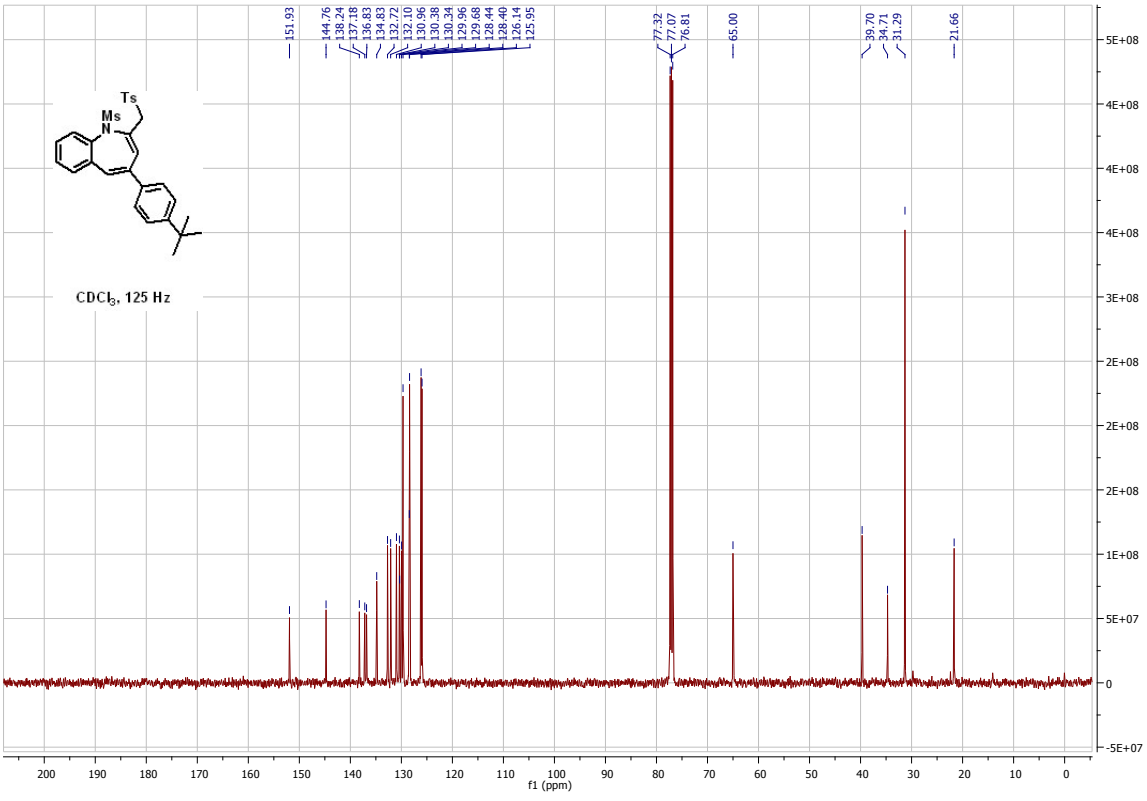

## $^{13}$C NMR spectrum of 2m



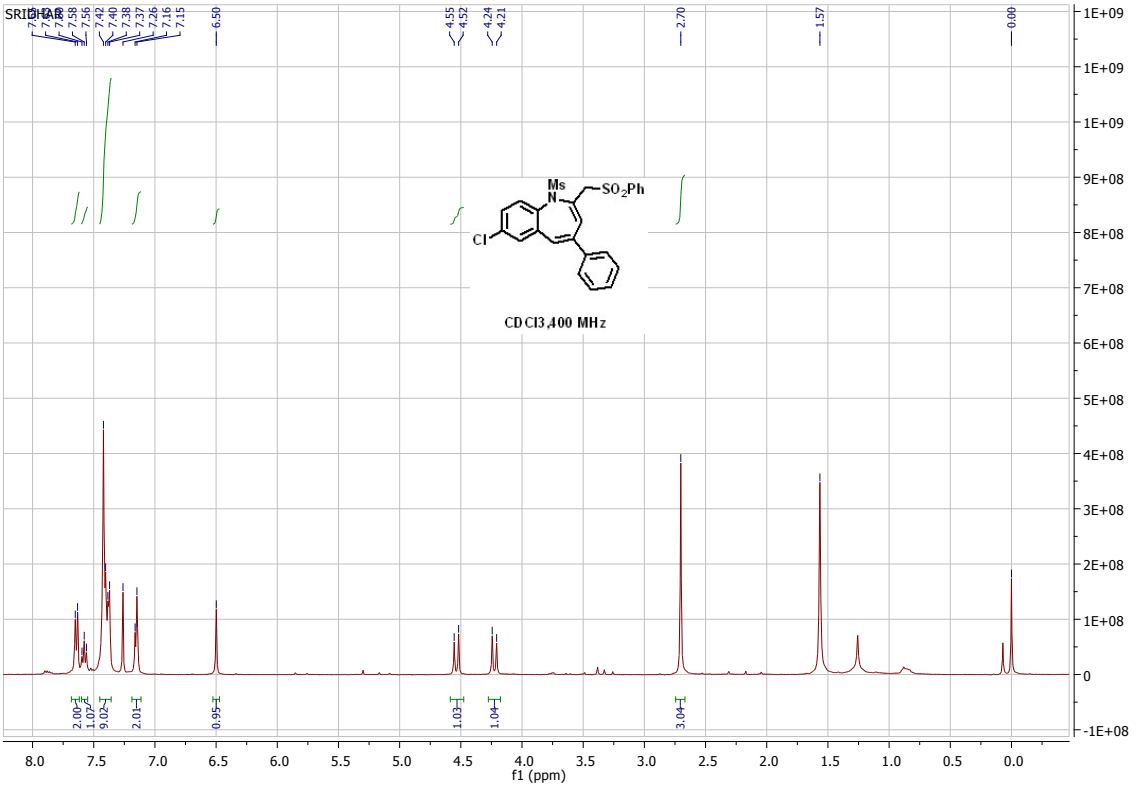
## $^{1}$H NMR spectrum of 2n



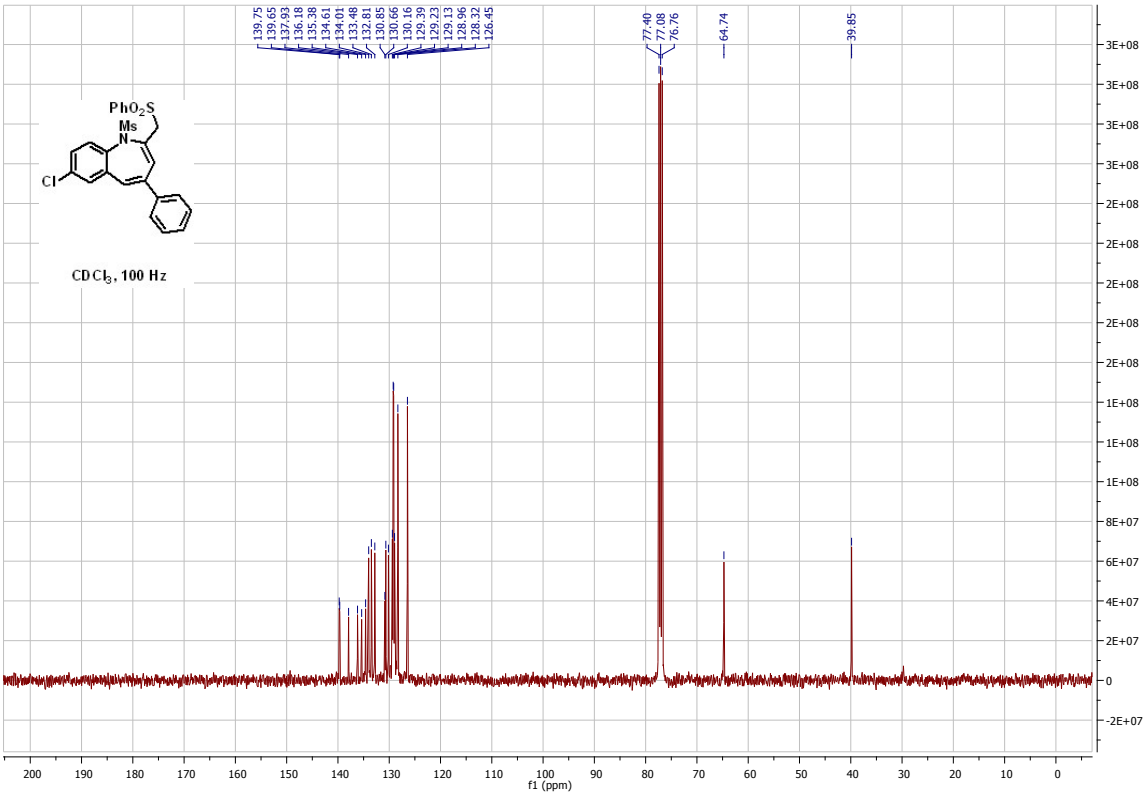

## $^{13}$C NMR spectrum of 2n



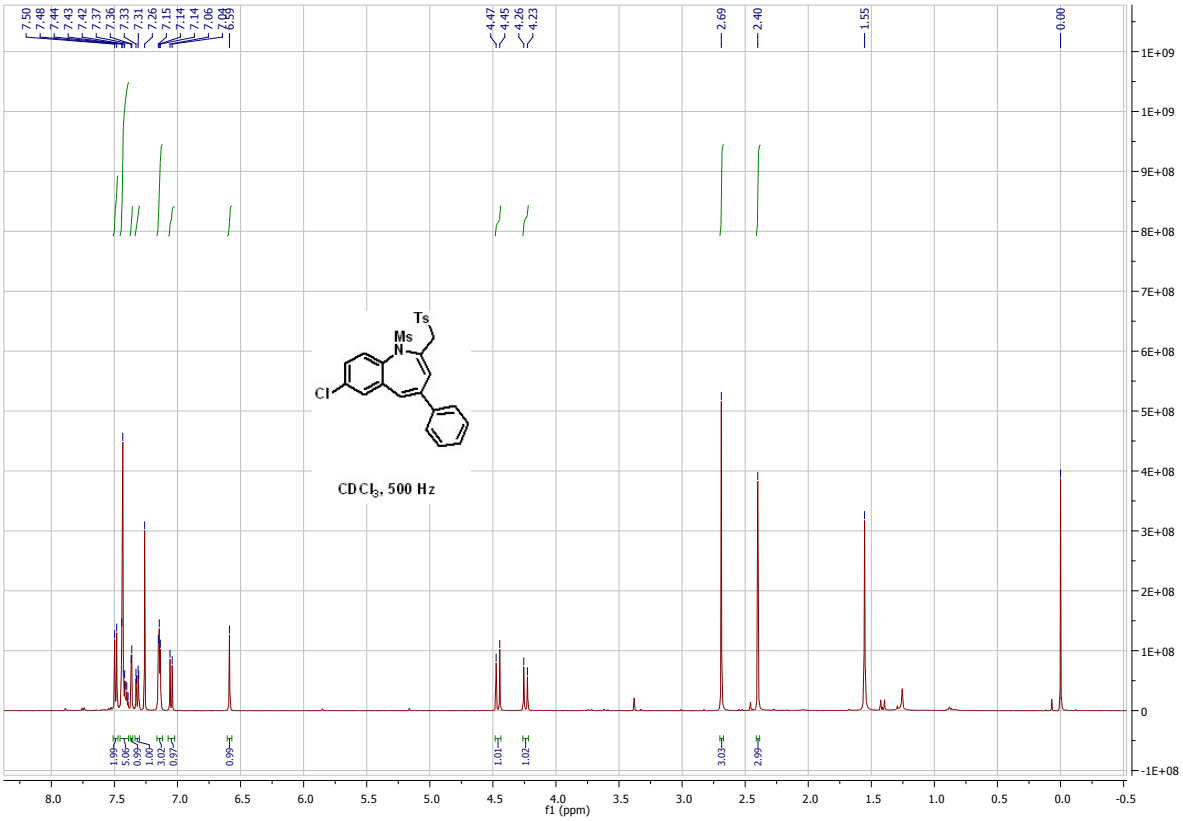
## $^{1}$H NMR spectrum of 2o



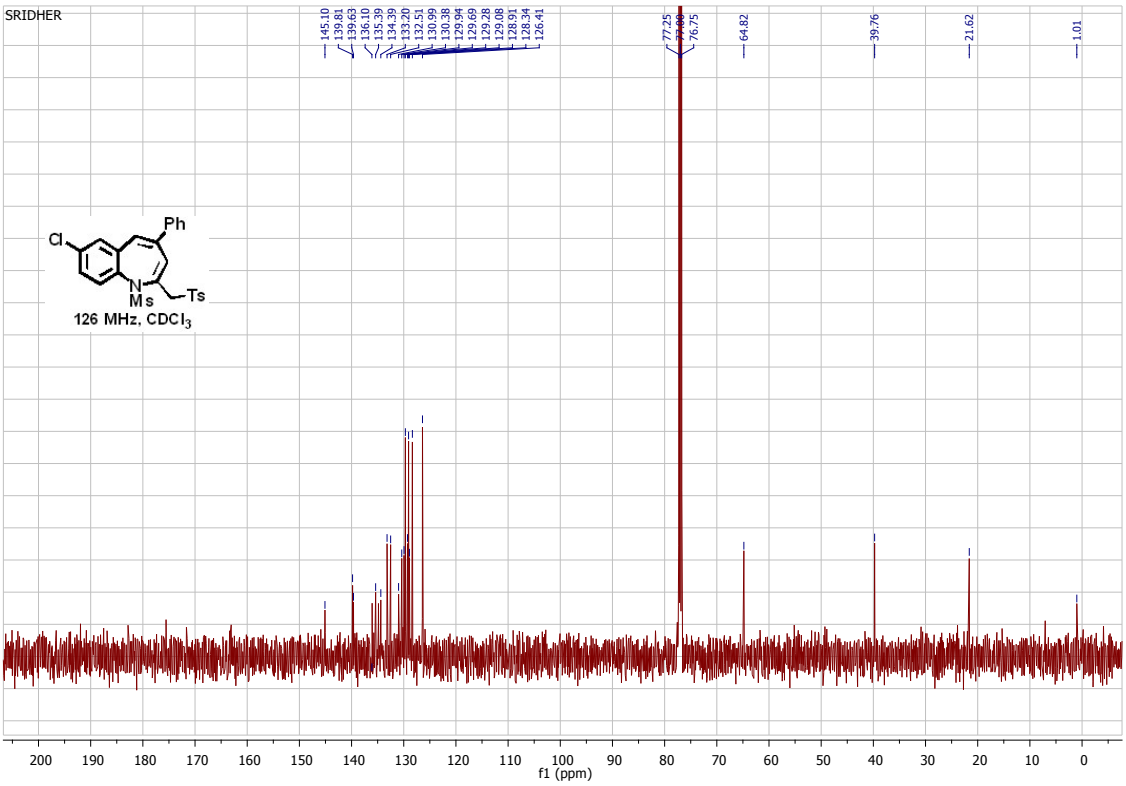

## $^{13}$C NMR spectrum of 2o



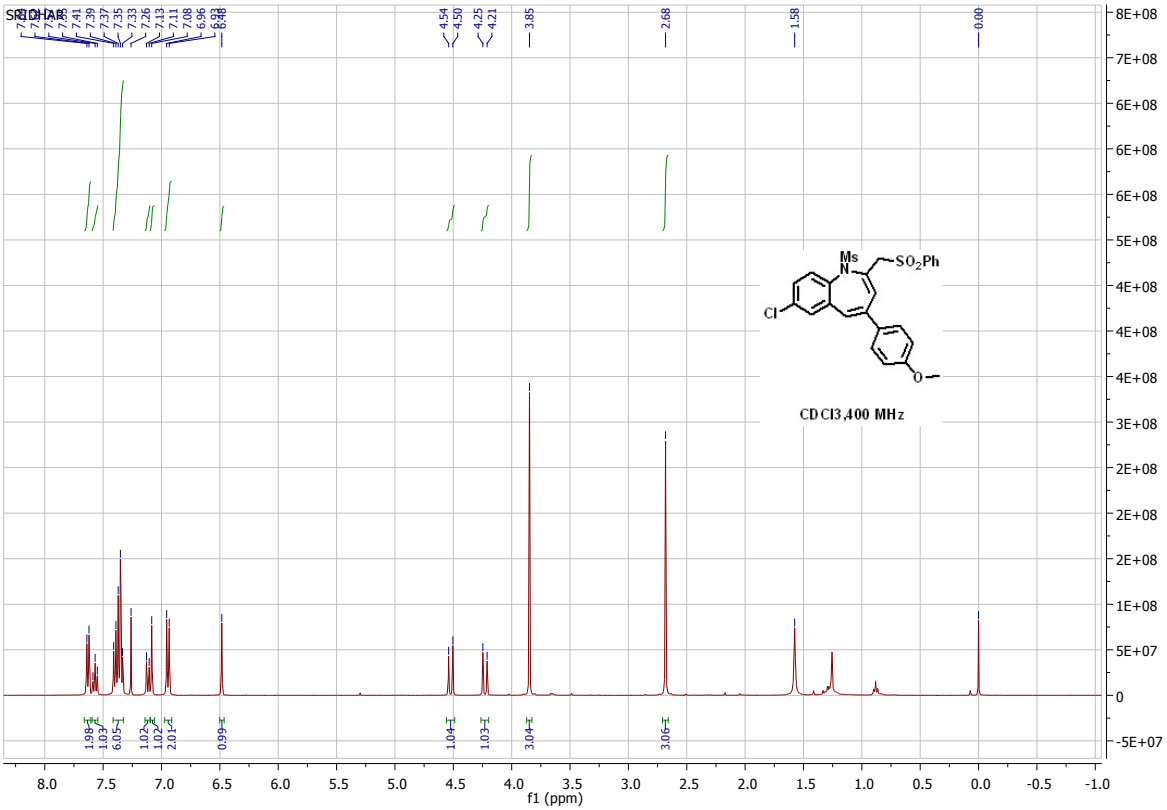
## $^{1}$H NMR spectrum of 2p



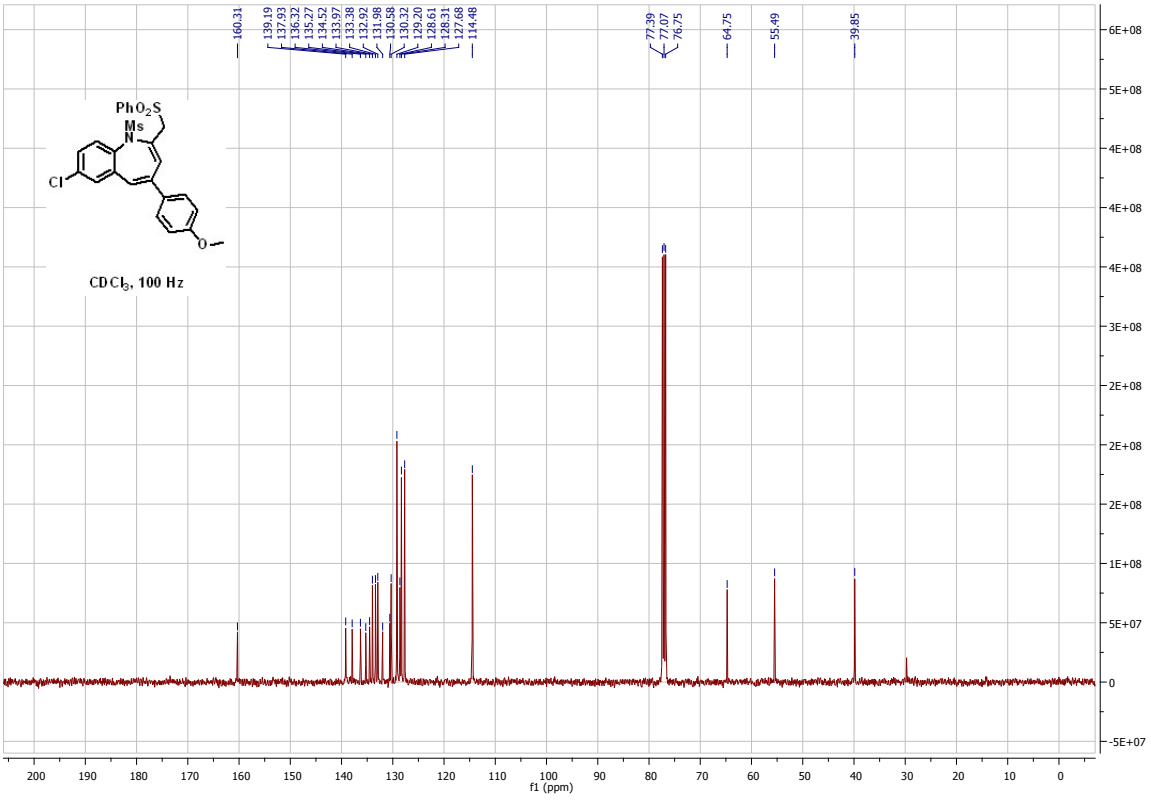

## $^{13}$C NMR spectrum of 2p



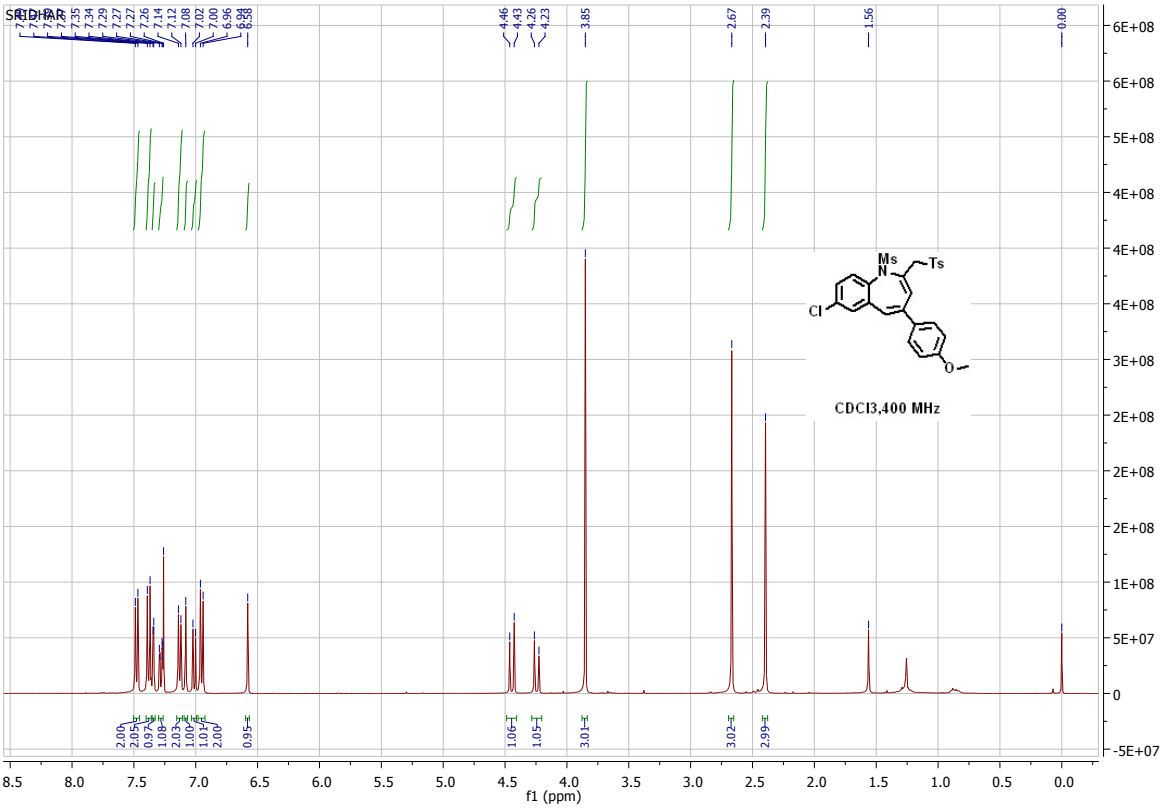
## $^{1}$H NMR spectrum of 2q



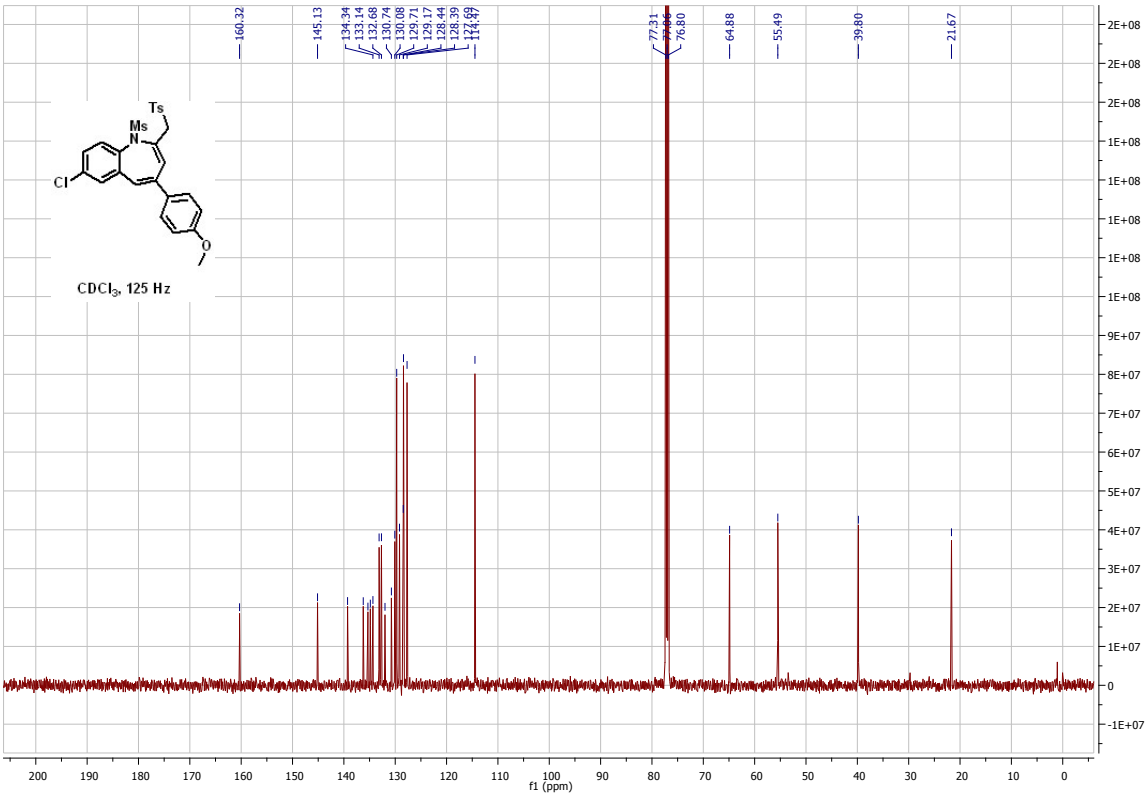

## $^{13}$C NMR spectrum of 2q



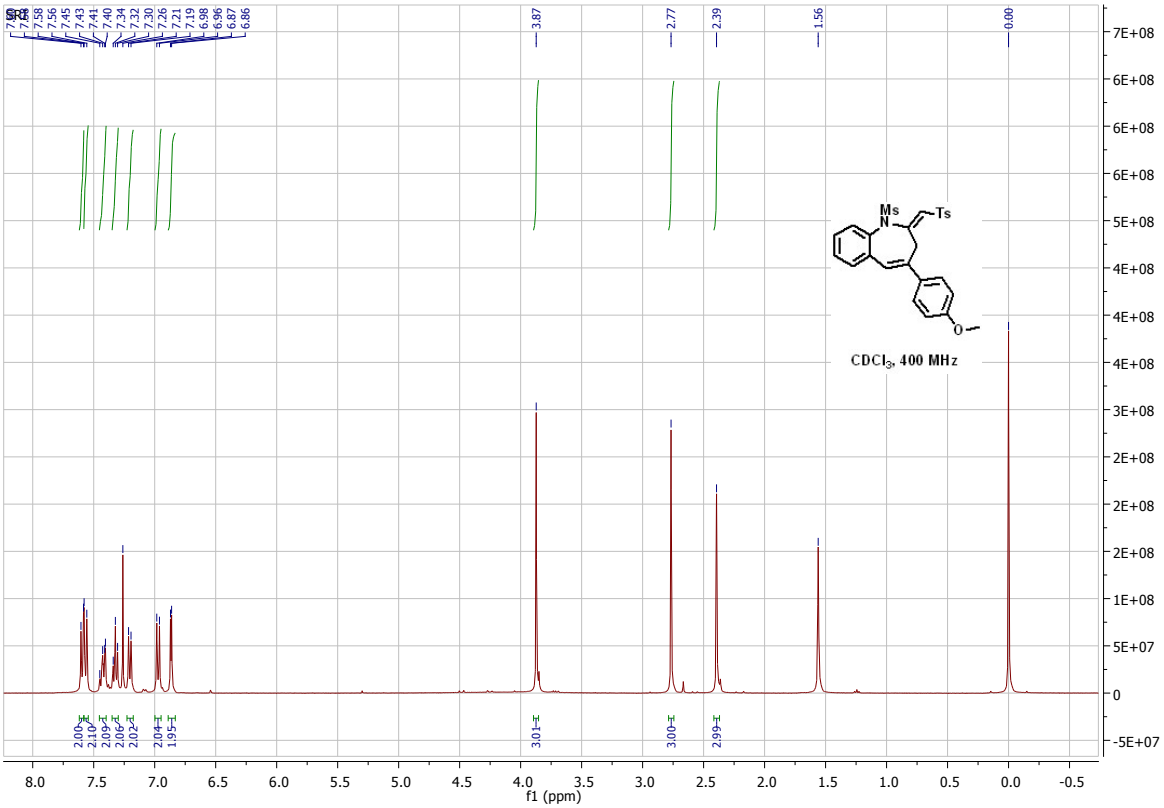
## $^{1}$H NMR spectrum of 2r



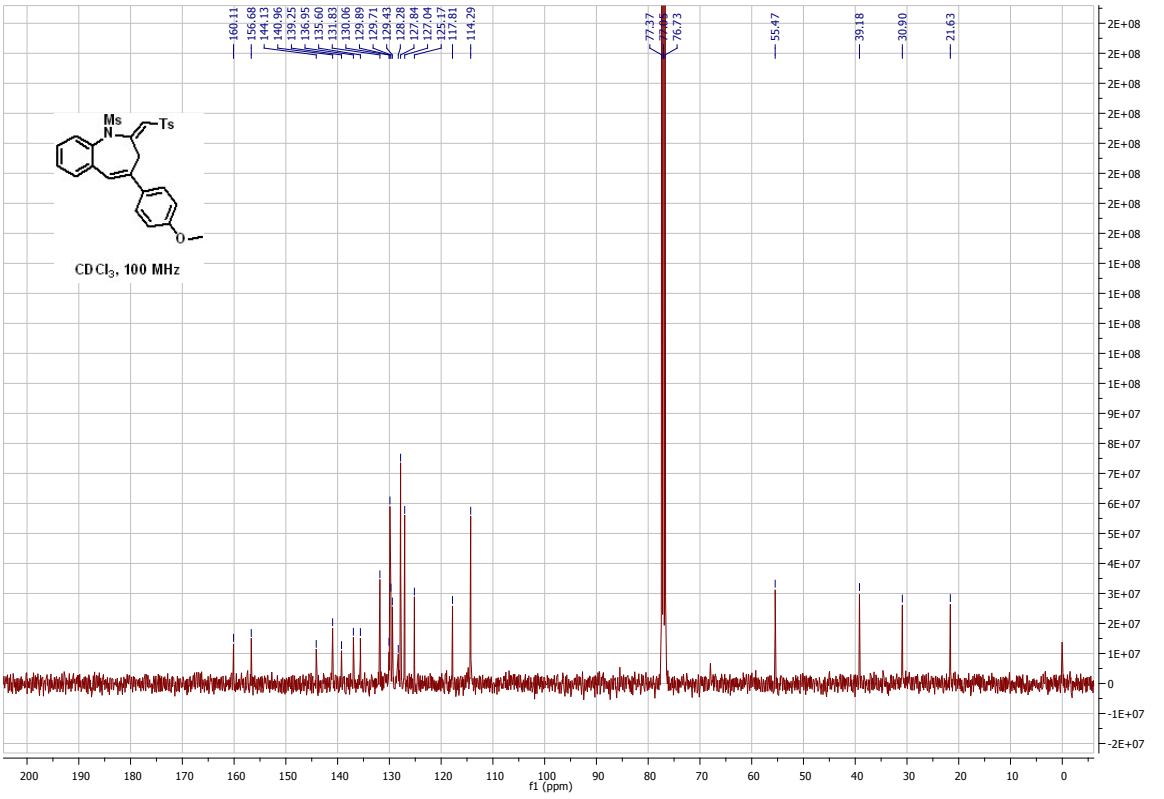

## $^{13}$C NMR spectrum of 2r



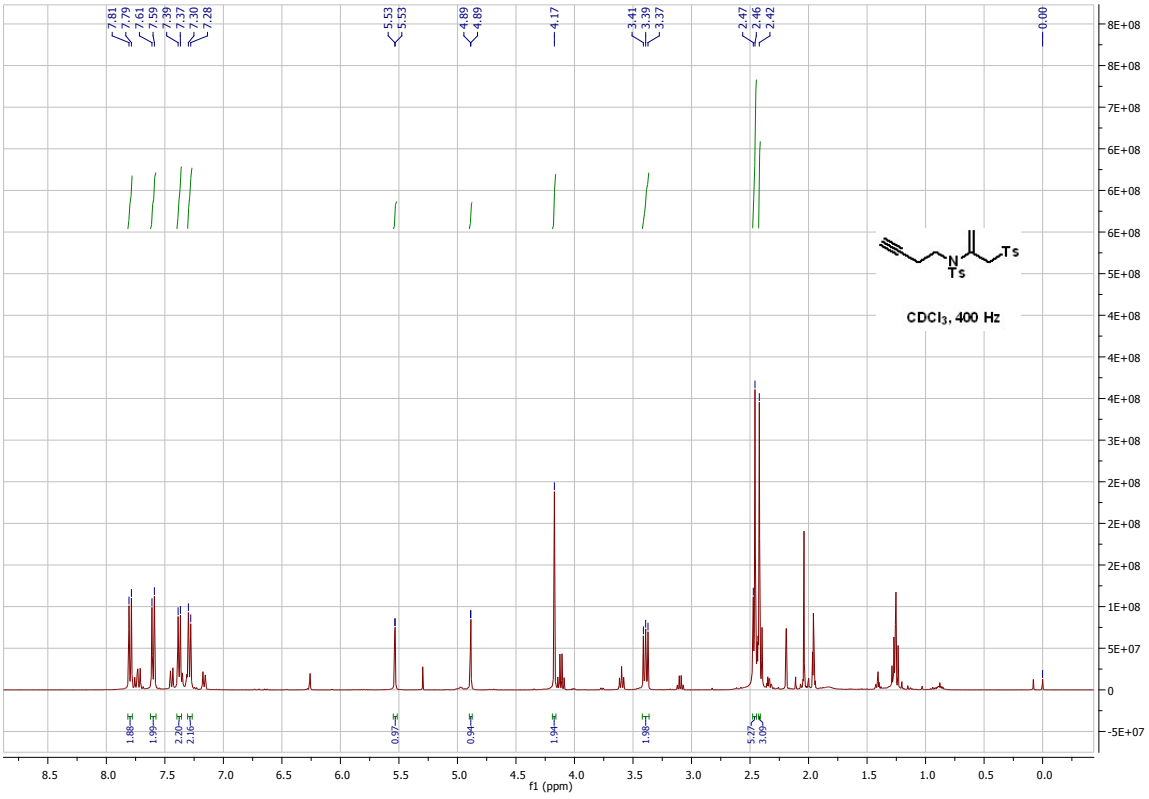
## $^{1}$H NMR spectrum of 7



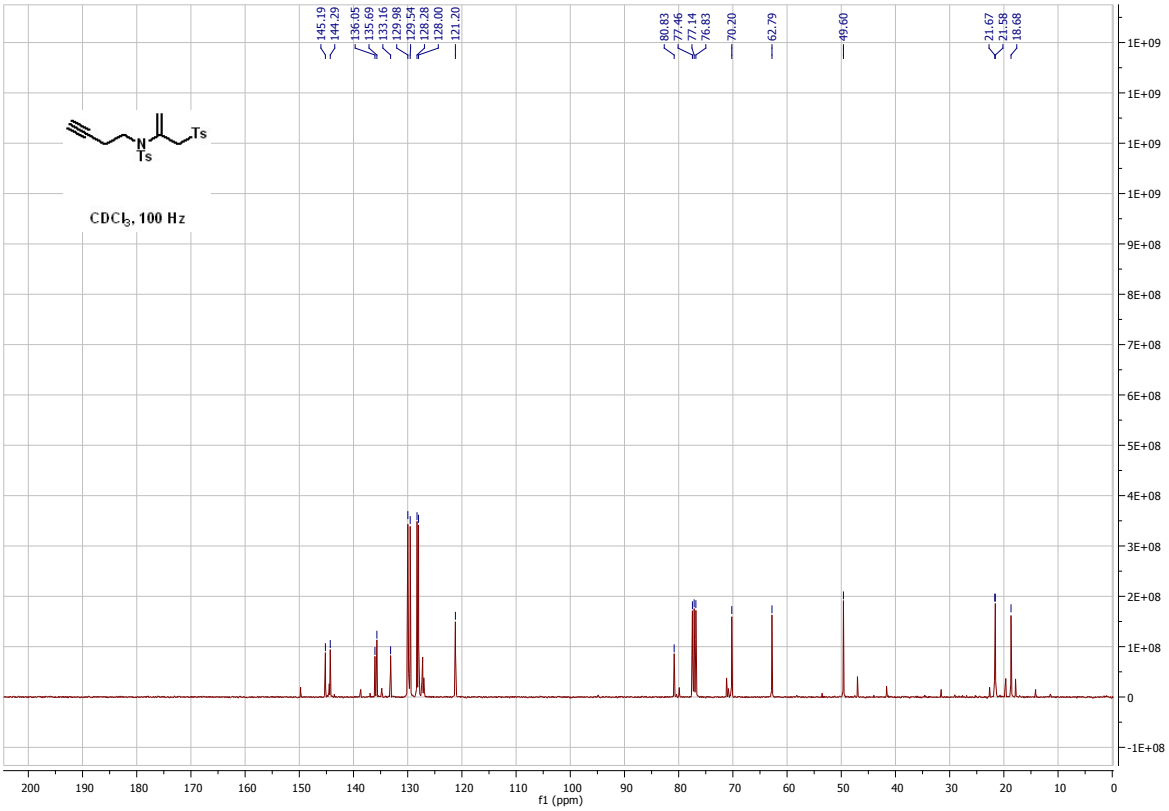

## $^{13}$C NMR spectrum of 7



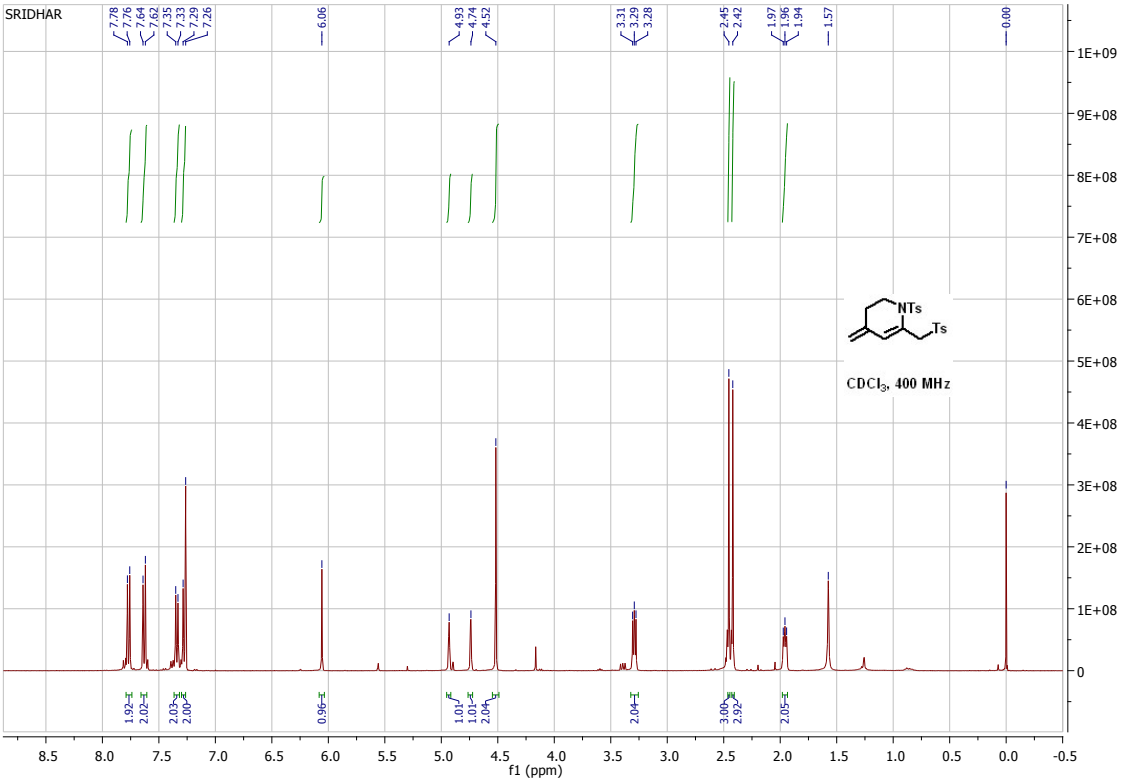
## $^{1}$H NMR spectrum of 8




## $^{13}$C NMR spectrum of 8



## $^{1}$H NMR spectrum of 10




## $^{13}$C NMR spectrum of 10