Gold-catalysed regioselective cascade cycloisomerisation reactions of aza-enediynes for the synthesis of substituted benzoisoquinoline derivatives

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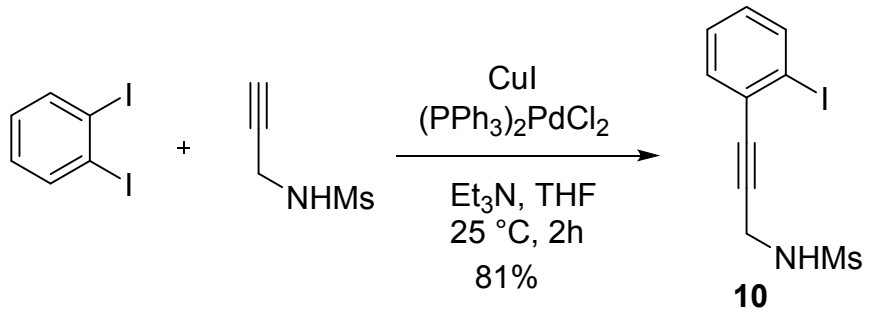
1. General Information

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. 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-b**,[1] N-(3-(2-iodophenyl)prop-2-yn-1-yl)methanesulfonamide **10**,[2] were prepared as previously described.

[1] S. Undeela, S. Thadkapally, J. B. Nanubolu, K. K. Singarapu and R. S. Menon, *Chem. Commun*., 2015, **51**, 13748.
[2] A. J. Szkotak, M. Murthy, L. J. MacVinish, M. Duszyk and A. W. Cuthbert, *Br. J. Pharmacol.* 2004, **142**, 531.

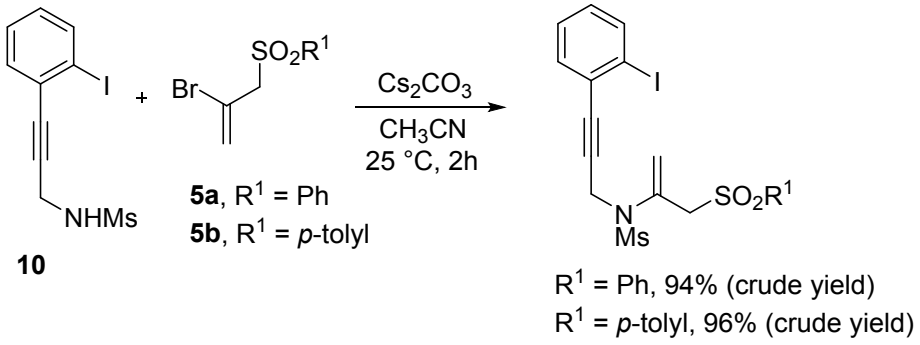
2. Substrate Preparation

2.1. Preparation of N-(3-(2-iodophenyl)prop-2-yn-1-yl)methanesulfonamide 10[2]



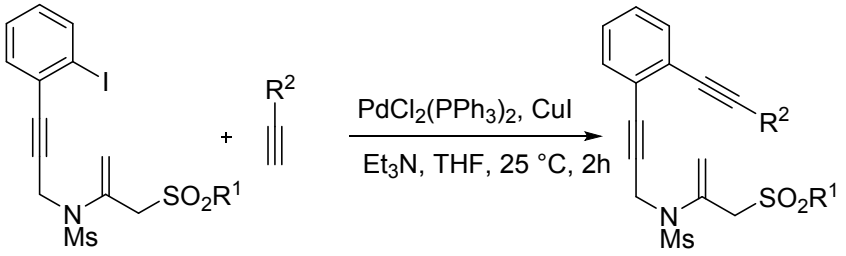
To a solution of the *N*-methanesulfonyl propargyl amine (532 mg, 4.00 mmol) and 1,2-diiodobenzene (1.58 g, 4.80 mmol) in THF (15 mL) kept under argon, $Pd(PPh_3)_2Cl_2$ (56 mg, 0.08 mmol), CuI (30 mg, 0.16 mmol) and triethylamine (1.90 mL, 12.00 mmol) were sequentially added at 25 °C and stirred for 2h. The solvent was removed on a rotavapor and water (30 mL) was added. The aqueous solution was extracted with ethyl acetate (3X25 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 product **10** (1.09 g, 81%).

2.2. Cs_2CO_3-mediated reaction of 2-bromoallyl sulfones 5a-b with N-(3-(2-iodophenyl)prop-2-yn-1-yl)methanesulfonamide 10



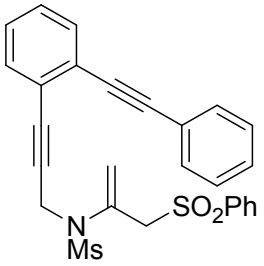
Typical procedure: Cesium carbonate (1.63 g, 5.00 mmol) was added to a solution of the N-(3-(2-iodophenyl)prop-2-yn-1-yl)methanesulfonamide **10** (670 mg, 2.00 mmol) and the bromoallyl sulfone **5a-b** (2.80 mmol) in acetonitrile (8 mL) at ambient temperature and stirred for 2 hours. The solvent was removed on a rotavapor, deionised water (20 mL) was added and the aqueous solution was extracted with ethyl acetate (3 X 15 mL). The combined organic extracts was washed with brine, dried over anhydrous sodium sulfate and concentrated on a rotavapor. The residue was filtered on a pad of celite and eluted with 30 % ethylacetate-hexane solution. The combined eluents were evaporated on a rotavapor and the residue obtained was used as such for further reactions.

2.3. Preparation of azaenediynes 8a-s



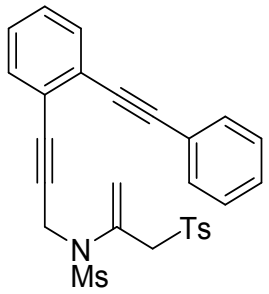
R^1 = Ph or *p*-tolyl **8a-s**

To a solution of the aryl iodide (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 **8a-s**.



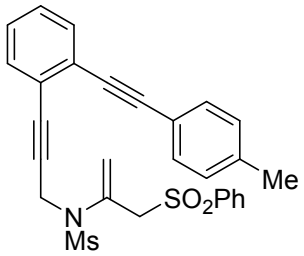
8a, N-(3-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl)-N-(3-(phenylsulfonyl)prop-1-en-2-yl)methanesulfonamide

Brown solid, 213 mg, 87%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 148-150 ˚C
IR (KBr) ν_{max}: 3708, 2925, 1627, 1440, 1343, 1294, 1141, 1078, 966, 864, 750, 728, 693, 653, 639, 621, 611 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.69 – 7.65 (m, 1H), 7.60 – 7.51 (m, 5H), 7.49 – 7.46 (m, 1H), 7.39 – 7.36 (m, 3H), 7.36 – 7.30 (m, 2H), 6.19 (d, *J* = 1.3 Hz, 1H), 5.36 (d, *J* = 1.3 Hz, 1H), 4.48 (s, 2H), 4.19 (s, 2H), 3.04 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 137.0, 133.9, 132.4, 132.3, 131.6, 129.3, 129.2, 128.8, 128.7, 128.5, 128.1, 125.7, 123.9, 122.5, 121.3, 93.3, 87.8, 87.7, 84.7, 63.6, 42.0, 37.9.
HRMS calcd for $C_{27}H_{24}O_4NS_2$ ($M+H^+$) 490.1141; found 490.1132.



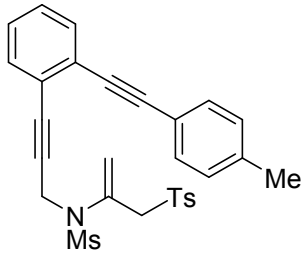
8b, N-(3-(2-(phenylethynyl)phenyl)prop-2-yn-1-yl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide

White solid, 221 mg, 88%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 116-118 ˚C
IR (KBr) ν_{max}: 3655, 1715, 1597, 1494, 1317, 1143, 1082, 968, 816, 756, 692 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.51 (m, 3H), 7.47 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.41 – 7.28 (m, 7H), 6.17 (d, *J* = 1.1 Hz, 1H), 5.35 (d, *J* = 1.0 Hz, 1H), 4.50 (s, 2H), 4.15 (s, 2H), 3.04 (s, 3H), 2.45 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 145.0, 137.1, 136.0, 132.4, 132.3, 131.6, 129.8, 128.8, 128.7, 128.5, 128.3, 128.1, 125.7, 123.9, 122.5, 121.3, 93.3, 87.8, 84.6, 63.7, 42.0, 37.9, 21.6.
HRMS calcd for $C_{28}H_{26}O_4NS_2$ ($M+H^+$) 504.1297; found 504.1288.



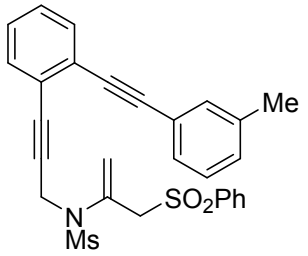
8c, N-(3-(phenylsulfonyl)prop-1-en-2-yl)-N-(3-(2-(p-tolylethynyl)phenyl)prop-2-yn-1-yl)methanesulfonamide

Brown solid, 221 mg, 88%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 115-117 ˚C
IR (KBr) ν_{max}: 3689, 3566, 2662, 1716, 1558, 1488, 1418, 1396, 1148, 748 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.70 – 7.65 (m, 1H), 7.60 – 7.52 (m, 3H), 7.48 – 7.44 (m, 1H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.29 (m, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.20 (d, *J* = 1.3 Hz, 1H), 5.37 (d, *J* = 1.2 Hz, 1H), 4.47 (s, 2H), 4.19 (s, 2H), 3.04 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 139.1, 139.0, 137.0, 133.9, 132.4, 132.3, 131.5, 129.3, 129.2, 128.7, 128.1, 128.0, 125.9, 123.8, 121.4, 119.4, 93.5, 87.6, 87.2, 84.8, 63.6, 42.0, 37.9, 21.5.
HRMS calcd for $C_{28}H_{25}O_4NNaS_2$ ($M+Na^+$) 526.1117; found 526.1111.



8d, N-(3-(2-(p-tolylethynyl)phenyl)prop-2-yn-1-yl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide

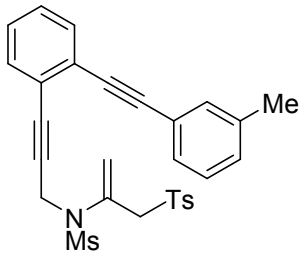
White solid, 225 mg, 87%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 136-138 ˚C
IR (KBr) ν_{max}: 3853, 3749, 3675, 3649, 1717, 1698, 1648, 1558, 1541, 1508, 1456, 1316, 1150, 1076, 961, 896, 817, 761 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.53 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.46 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.18 (s, 1H), 5.36 (s, 1H), 4.49 (s, 2H), 4.16 (s, 2H), 3.04 (s, 3H), 2.45 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 139.0, 137.1, 136.0, 132.4, 132.3, 131.5, 129.8, 129.3, 128.7, 128.1, 127.9, 125.9, 123.8, 121.3, 119.4, 93.5, 87.7, 87.2, 84.7, 63.7, 42.0, 37.9, 21.6, 21.5.
HRMS calcd for $C_{29}H_{28}O_4NS_2$ ($M+H^+$) 518.1454; found 518.1454.



8e, N-(3-(phenylsulfonyl)prop-1-en-2-yl)-N-(3-(2-(m-tolylethynyl)phenyl)prop-2-yn-1-yl)methanesulfonamide

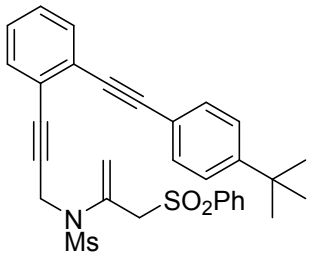
White solid, 224 mg, 89%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 134-136 ˚C
IR (KBr) ν_{max}: 3831, 3654, 1715, 1332, 1146, 1080, 945, 794, 769, 729, 686 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 8.3, 0.9 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.47 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.37 – 7.23 (m, 5H), 7.18 (d, *J* = 7.6 Hz, 1H), 6.18 (d, *J* = 0.9 Hz, 1H), 5.37 (d, *J* = 0.7 Hz, 1H), 4.48 (s, 2H), 4.19 (s, 2H), 3.04 (s, 3H), 2.37 (s, 3H).
^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 138.2, 137.0, 133.9, 132.4, 132.3, 132.2, 129.7, 129.2, 128.7, 128.7, 128.4, 128.1, 128.0, 125.8, 123.8, 122.3, 121.3, 93.5, 87.6, 87.4, 84.7, 63.6, 42.0, 37.9, 21.2.

HRMS calcd for $C_{28}H_{26}O_4NS_2$ ($M+H^+$) 504.1298; found 504.1292.



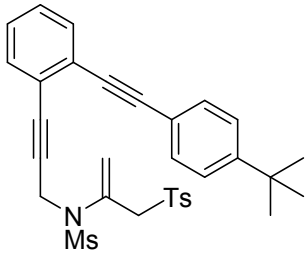
8f, N-(3-(2-(m-tolylethynyl)phenyl)prop-2-yn-1-yl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide

White solid, 222 mg, 86%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 111-113 ˚C
IR (KBr) ν_{max}: 3840, 2358, 1713, 1596, 1489, 1315, 1143, 1084, 899, 814, 753, 641 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.54 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.47 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.38 – 7.23 (m, 7H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.17 (d, *J* = 1.2 Hz, 1H), 5.36 (d, *J* = 1.1 Hz, 1H), 4.50 (s, 2H), 4.16 (s, 2H), 3.04 (s, 3H), 2.45 (s, 3H), 2.37 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 138.2, 137.1, 136.0, 132.4, 132.3, 132.2, 129.8, 129.7, 128.7, 128.4, 128.1, 128.0, 127.6, 125.8, 123.9, 122.3, 121.2, 93.5, 87.7, 87.4, 84.7, 63.7, 42.0, 37.9, 21.6, 21.1.
HRMS calcd for $C_{29}H_{27}O_4NNaS_2$ ($M+Na^+$) 540.1274; found 540.1274.



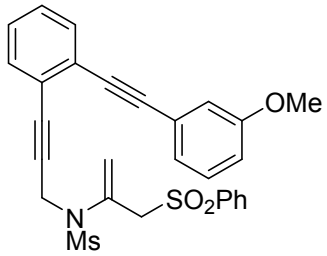
8g, N-(3-(2-((4-(tert-butyl)phenyl)ethynyl)phenyl)prop-2-yn-1-yl)-N-(3-(phenylsulfonyl)prop-1-en-2-yl)methanesulfonamide

Brown sticky solid, 229 mg, 84%
R_f = 0.4 (30% ethyl acetate in hexanes)
IR (KBr) ν_{max}: 3838, 3628, 2361, 1792, 1716, 1557, 1521, 1456, 1396, 1150, 749, 688 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.1 Hz, 2H), 7.67 (tt, *J* = 7.4 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.48 – 7.44 (m, 3H), 7.39 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.29 (m, 2H), 6.20 (d, *J* = 1.3 Hz, 1H), 5.38 (d, *J* = 1.2 Hz, 1H), 4.47 (s, 2H), 4.20 (s, 2H), 3.06 (s, 3H), 1.33 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2, 145.2, 139.0, 137.1, 133.9, 132.4, 131.4, 129.2, 128.7, 128.1, 127.9, 126.0, 125.5, 123.7, 121.3, 119.5, 93.6, 87.6, 87.2, 84.8, 77.2, 77.0, 76.7, 63.6, 42.0, 38.0, 34.8, 31.1.
HRMS calcd for $C_{31}H_{32}O_4NS_2$ ($M+H^+$) 546.1767; found 546.1754.



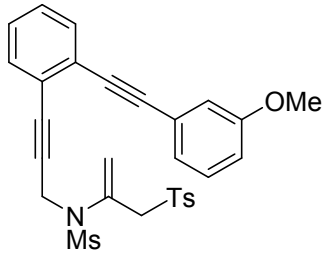
8h, N-(3-(2-((4-(tert-butyl)phenyl)ethynyl)phenyl)prop-2-yn-1-yl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide

Brown semisolid, 229 mg, 82%
R_f = 0.4 (30% ethyl acetate in hexanes)
IR (KBr) ν_{max}: 3750, 3649, 1716, 1541, 1507, 1318, 1146, 1083, 967, 815, 757, 670 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 3H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.27 (m, 2H), 6.18 (s, 1H), 5.37 (s, 1H), 4.49 (s, 2H), 4.17 (s, 2H), 3.06 (s, 3H), 2.45 (s, 3H), 1.33 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.2, 145.0, 137.2, 136.1, 132.4, 131.4, 129.8, 128.7, 128.2, 127.9, 126.0, 125.5, 123.8, 121.3, 119.5, 93.6, 87.7, 87.2, 84.8, 63.7, 42.0, 38.0, 34.8, 31.1, 21.6.
HRMS calcd for $C_{32}H_{33}NNaO_4S_2$(M+/Na^+) 582.1749; found 582.1737.



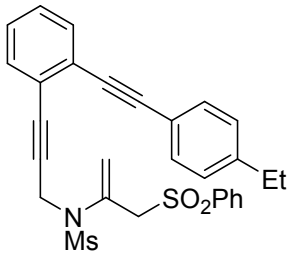
8i, N-(3-(2-((3-methoxyphenyl)ethynyl)phenyl)prop-2-yn-1-yl)-N-(3-(phenylsulfonyl)prop-1-en-2-yl)methanesulfonamide

White solid, 220 mg, 85%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 106-108 ˚C
IR (KBr) ν_{max}: 3821, 3538, 1714, 1556, 1512, 1326, 1156, 1101, 1076, 987, 767 cm^{-1}
^{1}H NMR (300 MHz, CDCl3) d 7.92 (d, J = 7.2 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.47 (dd, J = 6.8, 2.2 Hz, 1H), 7.39 – 7.27 (m, 3H), 7.11 (d, J = 7.6 Hz, 1H), 7.07 – 7.03 (m, 1H), 6.93 (ddd, J = 8.3, 2.5, 0.8 Hz, 1H), 6.18 (d, J = 1.1 Hz, 1H), 5.37 (d, J = 1.0 Hz, 1H), 4.47 (s, 2H), 4.19 (s, 2H), 3.83 (s, 3H), 3.04 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.4, 138.9, 137.1, 133.9, 132.4, 129.6, 129.2, 128.7, 128.2, 128.1, 125.6, 124.2, 123.9, 123.5, 121.2, 116.3, 115.4, 93.2, 87.7, 87.5, 84.7, 63.6, 55.3, 42.0, 38.0.
HRMS calcd for $C_{28}H_{26}O_5NS_2$ (M+H^+) 520.1246; found 520.1231.



8j, N-(3-(2-((3-methoxyphenyl)ethynyl)phenyl)prop-2-yn-1-yl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide

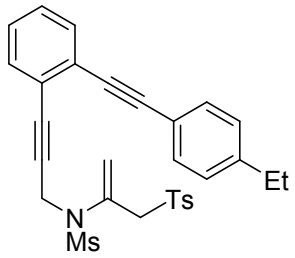
White solid, 221 mg, 83%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 116-118 ˚C
IR (KBr) ν_{max}: 3853, 3538, 1710, 1646, 1561, 1501, 1432, 1336, 1237, 1181, 1052, 873, 801, 761cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.55 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.47 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.37 – 7.27 (m, 5H), 7.13 – 7.10 (m, 1H), 7.06 – 7.04 (m, 1H), 6.93 (ddd, *J* = 8.3, 2.6, 0.8 Hz, 1H), 6.16 (d, *J* = 1.0 Hz, 1H), 5.36 (d, *J* = 1.0 Hz, 1H), 4.49 (s, 2H), 4.16 (s, 2H), 3.84 (s, 3H), 3.04 (d, *J* = 6.8 Hz, 3H), 2.45 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 144.9, 137.1, 136.0, 132.3, 132.3, 129.8, 129.5, 128.7, 128.1, 128.1, 125.6, 124.2, 123.8, 123.5, 121.1, 116.3, 115.4, 93.2, 87.7, 87.5, 84.6, 63.6, 55.3, 41.9, 37.9, 21.5.
HRMS calcd for $C_{29}H_{28}O_5NS_2$ ($M+H^+$) 534.1403; found 534.1398.



8k, N-(3-(2-((4-ethylphenyl)ethynyl)phenyl)prop-2-yn-1-yl)-N-(3-(phenylsulfonyl)prop-1-en-2-yl)methanesulfonamide

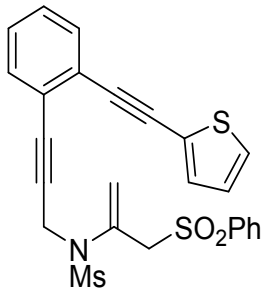
Brown solid, 222 mg, 86%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 47-49 ˚C
IR (KBr) ν_{max}: 3852, 3617, 2360, 1716, 1541, 1521, 1489, 1457, 1418, 1396, 1338, 1150, 758, 686 cm^{-1}
^{1}H NMR (500 MHz, CDCl3) d 7.93 (d, J = 7.5 Hz, 2H), 7.67 (t, J = 7.4 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.50 – 7.41 (m, 3H), 7.34 (d, J = 7.6 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.21 (d, J = 8.0 Hz, 2H), 6.20 (s, 1H), 5.37 (s, 1H), 4.47 (s, 2H), 4.19 (s, 2H), 3.04 (s, 3H), 2.68 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.6 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 139.0, 137.0, 133.9, 132.4, 132.3, 131.6, 129.2, 128.7, 128.1, 128.1, 127.9, 126.0, 123.8, 121.4, 119.7, 93.6, 87.6, 87.2, 84.8, 63.6, 42.0, 38.0, 28.8, 15.2.
HRMS calcd for $C_{29}H_{28}O_4NS_2$ ($M+H^+$) 518.1454; found 518.1446.



8l, N-(3-(2-((4-ethylphenyl)ethynyl)phenyl)prop-2-yn-1-yl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide

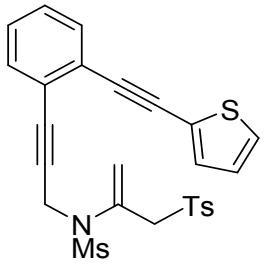
White solid, 223 mg, 84%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 158-160 ˚C
IR (KBr) ν_{max}: 3843, 3548, 2323, 1710, 1559, 1525, 1477, 1333, 1313, 1151, 1121, 1074, 958, 933, 895, 763, 646 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.53 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.38 – 7.27 (m, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.18 (d, *J* = 1.2 Hz, 1H), 5.36 (d, *J* = 1.1 Hz, 1H), 4.49 (s, 2H), 4.16 (s, 2H), 3.04 (s, 3H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.3, 144.9, 137.1, 136.0, 132.3, 132.3, 131.6, 129.8, 128.7, 128.1, 128.1, 127.9, 125.9, 123.8, 121.3, 119.7, 93.6, 87.7, 87.2, 84.7, 63.7, 42.0, 37.9, 28.8, 21.6, 15.2.
HRMS calcd for $C_{30}H_{30}O_4NS_2$ ($M+H^+$) 532.1610; found 532.1608.



8m, N-(3-(phenylsulfonyl)prop-1-en-2-yl)-N-(3-(2-(thiophen-2-ylethynyl)phenyl)prop-2-yn-1-yl)methanesulfonamide

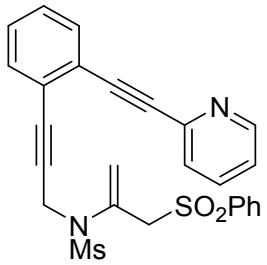
White solid, 208 mg, 84%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 134-136 ˚C

IR (KBr) ν_{max}: 3869, 3674, 3586, 2362, 1992, 1716, 1698, 1647, 1557, 1521, 1489, 1457, 1418, 1340, 1143, 1079, 749, 730, 687 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.61 – 7.56 (m, 3H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.31 (m, 3H), 7.20 (dd, *J* = 5.0, 1.1 Hz, 1H), 6.19 (s, 1H), 5.39 (s, 1H), 4.48 (s, 2H), 4.20 (s, 2H), 3.06 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 137.1, 133.9, 132.4, 132.2, 129.7, 129.4, 129.2, 128.7, 128.3, 128.1, 128.1, 125.8, 123.8, 121.6, 121.3, 88.5, 87.6, 87.3, 84.7, 63.6, 42.0, 37.9.
HRMS calcd for $C_{25}H_{22}O_4NS_3$ ($M+H^+$) 496.0705; found 496.0698.



8n, N-(3-(2-(thiophen-2-ylethynyl)phenyl)prop-2-yn-1-yl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide

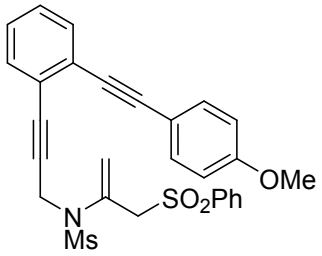
White solid, 209 mg, 82%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 108-110 ˚C
IR (KBr) ν_{max}: 3800, 3648, 2378, 1792, 1717, 1316, 1145, 1082, 967, 870, 757, 670 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.58 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.53 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.46 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.38 – 7.29 (m, 5H), 7.20 (dd, *J* = 5.0, 1.2 Hz, 1H), 6.17 (d, *J* = 1.2 Hz, 1H), 5.38 (d, *J* = 1.1 Hz, 1H), 4.50 (s, 2H), 4.17 (s, 2H), 3.05 (d, *J* = 7.6 Hz, 3H), 2.46 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 137.2, 136.0, 132.4, 132.2, 130.0, 129.8, 129.7, 129.4, 128.7, 128.3, 128.1, 128.1, 125.8, 123.8, 121.3, 88.5, 87.7, 87.3, 84.6, 63.7, 42.0, 37.9, 21.6.
HRMS calcd for $C_{26}H_{24}O_4NS_3$ ($M+H^+$) 510.0862; found 510.0859.



8o, N-(3-(phenylsulfonyl)prop-1-en-2-yl)-N-(3-(2-(pyridin-2-ylethynyl)phenyl)prop-2-yn-1-yl)methanesulfonamide

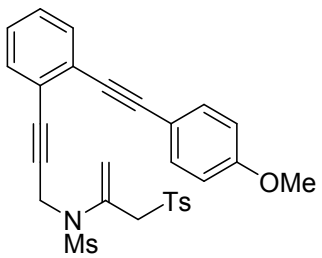
White solid, 167 mg, 68%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 108-110 ˚C

IR (KBr) ν_{max}: 3819, 3674, 2361, 1772, 1716, 1647, 1541, 1507, 1489, 1418, 1339, 1143, 729, 638 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.8 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 2H), 7.73 (td, *J* = 7.7, 1.8 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.63 – 7.60 (m, 1H), 7.61 – 7.54 (m, 3H), 7.51 – 7.46 (m, 1H), 7.39 – 7.33 (m, 2H), 7.30 – 7.27 (m, 1H), 6.22 (s, 1H), 5.37 (s, 1H), 4.50 (s, 2H), 4.20 (s, 2H), 3.13 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 142.8, 139.0, 136.6, 136.4, 133.9, 132.7, 132.4, 129.2, 128.8, 128.7, 128.1, 127.5, 124.8, 124.4, 123.2, 121.8, 92.2, 88.1, 87.3, 84.4, 63.6, 41.9, 38.2.
HRMS calcd for $C_{26}H_{23}O_4N_2S_2$ ($M+H^+$) 491.1093; found 491.1087.



8p, N-(3-(2-((4-methoxyphenyl)ethynyl)phenyl)prop-2-yn-1-yl)-N-(3-(phenylsulfonyl)prop-1-en-2-yl)methanesulfonamide

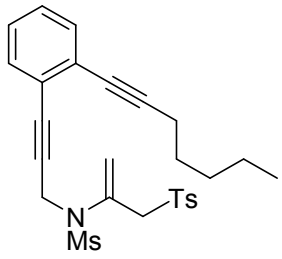
White solid, 220 mg, 85%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 57-59 ˚C
IR (KBr) ν_{max}: 3853, 3628, 2361, 1792, 1716, 1684, 1558, 1507, 1473, 1418, 1339, 727 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.69 – 7.65 (m, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.52 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.33 (td, *J* = 7.6, 1.4 Hz, 1H), 7.30 – 7.26 (m, 1H), 6.94 – 6.87 (m, 2H), 6.20 (d, *J* = 1.2 Hz, 1H), 5.38 (d, *J* = 1.0 Hz, 1H), 4.48 (s, 2H), 4.19 (s, 2H), 3.84 (s, 3H), 3.04 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 139.0, 137.0, 133.9, 133.1, 132.3, 132.2, 129.2, 128.7, 128.1, 127.8, 126.1, 123.7, 121.4, 114.5, 114.2, 93.5, 87.5, 86.5, 84.8, 63.6, 55.3, 42.0, 37.9.
HRMS calcd for $C_{28}H_{26}O_5NS_2$ ($M+H^+$) 520.1247; found 520.1233.



8q, N-(3-(2-((4-methoxyphenyl)ethynyl)phenyl)prop-2-yn-1-yl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide

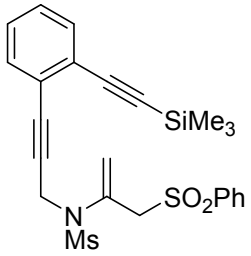
White solid, 226 mg, 85%

R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 123-125 ˚C
IR (KBr) ν_{max}: 3801, 3628, 2462, 1716, 1648, 1558, 1541, 1508, 1473, 1457, 1340, 1246, 1155, 762 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.52 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.34 – 7.27 (m, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 6.19 (d, *J* = 1.2 Hz, 1H), 5.37 (d, *J* = 1.1 Hz, 1H), 4.50 (s, 2H), 4.16 (s, 2H), 3.85 (d, *J* = 4.5 Hz, 3H), 3.05 (s, 3H), 2.45 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.0, 145.0, 137.1, 136.1, 133.1, 132.3, 132.1, 129.8, 128.7, 128.1, 127.8, 126.1, 123.7, 121.4, 114.5, 114.1, 93.5, 87.6, 86.6, 84.8, 63.7, 55.3, 42.0, 37.9, 21.6.
HRMS calcd for $C_{29}H_{28}O_5NS_2$ ($M+H^+$) 534.1403; found 534.1398.



8r, N-(3-(2-(hept-1-yn-1-yl)phenyl)prop-2-yn-1-yl)-N-(3-tosylprop-1-en-2-yl)methanesulfonamide

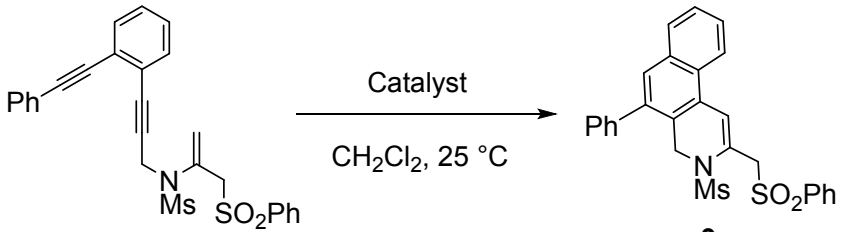
White solid, 184 mg, 74%
R_f = 0.5 (30% ethyl acetate in hexanes)
Melting point: 87-89 ˚C
IR (KBr) ν_{max}:3841, 3567, 2930, 1717, 1548, 1448, 1321, 1148, 1082, 968, 813, 762, 670 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.44 – 7.35 (m, 3H), 7.32 – 7.21 (m, 3H), 6.22 (d, *J* = 1.0 Hz, 1H), 5.48 (d, *J* = 0.9 Hz, 1H), 4.45 (s, 2H), 4.21 (s, 2H), 3.13 (s, 3H), 2.46 (s, 3H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.65 – 1.58 (m, 2H), 1.47 – 1.40 (m, 2H), 1.40 – 1.33 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 137.5, 136.0, 132.3, 132.1, 129.8, 128.6, 128.2, 127.3, 126.6, 123.7, 120.8, 94.9, 87.1, 85.0, 79.2, 63.7, 42.1, 38.0, 31.0, 28.3, 22.1, 21.6, 19.6, 13.9.
HRMS calcd for $C_{27}H_{32}O_4NS_2$ ($M+H^+$) 498.1767; found 498.1765.



8s, N-(3-(phenylsulfonyl)prop-1-en-2-yl)-N-(3-(2-((trimethylsilyl)ethynyl)phenyl)prop-2-yn-1-yl)methanesulfonamide

White solid, 184 mg, 76%
R_f = 0.59 (30% ethyl acetate in hexanes)
Melting point: 123-125 ˚C
IR (KBr) ν_{max}:3838, 3674, 2362, 1792, 1716, 1647, 1558, 1521, 1489, 1457, 1396, 1340, 1319, 1140, 1082, 847, 759 cm^{-1}
^{1}H NMR (500 MHz, D_2O) δ 7.96 – 7.68 (m, 2H), 7.70 – 7.66 (m, 1H), 7.59 (t, *J* = 7.7 Hz, 2H), 7.50 – 7.47 (m, 1H), 7.42 – 7.39 (m, 1H), 7.32 – 7.27 (m, 2H), 6.19 (d, *J* = 1.1 Hz, 1H), 5.49 (d, *J* = 1.0 Hz, 1H), 4.44 (s, 2H), 4.25 (s, 2H), 3.12 (s, 3H), 0.26 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 137.3, 133.9, 132.9, 132.2, 129.2, 128.6, 128.3, 128.1, 125.6, 124.0, 121.0, 103.2, 98.9, 87.6, 84.7, 63.6, 42.0, 38.3, -0.03.
HRMS calcd for $C_{24}H_{27}O_4NNaS_2Si$ ($M+Na^+$) 508.1043; found 508.1032.

3. Optimisation of reaction conditions for cycloisomerisation of 8a[a]



8a **9a**

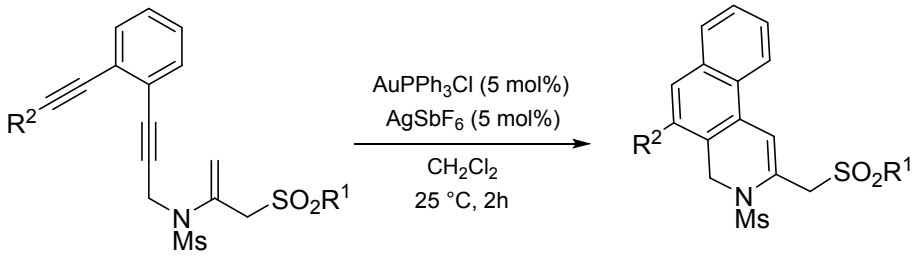
Entry	Catalysts (mol%)	Time(h)	Isolated yield of **9a**
1	JohnPhosAu(CH_3CN)SbF_6 (5 mol%)[b]	1	57%
2	**PPh_3AuCl and $AgSbF_6$ (5 mol% each)**	**2**	**91%**
3	PPh_3AuCl (5 mol%)[c]	12	-
4	$AgSbF_6$ (10 mol%)[c]	12	-
5	$AuCl_3$ (5 mol%)[d]	6	-

[a]Reaction conditions: **8a** (0.20 mmol), catalysts, CH_2Cl_2 (2 mL). [b]Another unidentified product was also obtained [c]Separation of products was not attempted as the TLC analysis indicated a non-selective reaction with multiple products. [d]**8a** was unchanged.

Procedure: The catalyst was dissolved in CH_2Cl_2 (2 mL). Aza-enediyne **8a** (98 mg, 0.20 mmol) was added to this solution and stirred at ambient temperature for the specified time. The solvent

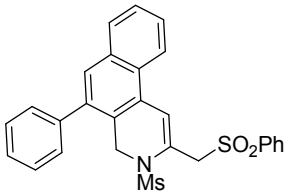
was evaporated on a rotavapor and the residue was chromatographed on silica gel using petroleum ether-ethyl acetate as eluent.

4. Gold-catalysed cascade cycloisomerisation of 8a-s



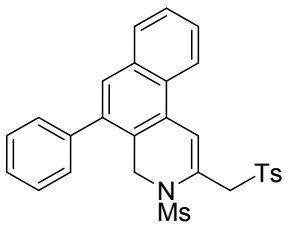
8a-s **9a-s**

PPh_3AuCl (8 mg, 0.02 mmol, 5 mol%) and silver hexafluoroantimonate (5 mg, 0.02 mmol, 5 mol%) were added to dichloromethane (2mL) in a round bottom flask and stirred for a minute. To this solution, N-vinyl N-propargyl-3-(2-ethynylphenyl methanesulfonamide **8a-s** (0.30 mmol) was added. The resulting solution was stirred for 2 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 **9a-s**.



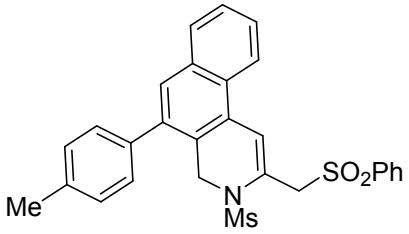
9a, 3-(methylsulfonyl)-5-phenyl-2-((phenylsulfonyl)methyl)-3,4-dihydrobenzo[*f*]isoquinoline

Light brown solid, 89 mg, 91%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 169-171 ˚C
IR (KBr) ν_{max}: 3055, 2992, 2927, 1604, 1447, 1406, 1345, 1308, 1252, 1151, 1132, 1082, 1055, 1026, 957, 872, 759, 686, 630, 514cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 7.4 Hz, 2H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.80 (s, 1H), 7.67 (m, 1H), 7.60 (m, 5H), 7.49 (d, *J* = 7.3 Hz, 3H), 7.33 (d, *J* = 6.4 Hz, 2H), 4.60 (s, 2H), 4.59 (s, 2H), 2.34 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 138.8, 137.6, 134.0, 132.7, 130.6, 129.8, 129.2, 128.9, 128.7, 128.6, 128.5, 128.4, 127.9, 127.8, 127.3, 126.7, 126.4, 123.4, 122.3, 61.9, 48.0, 38.4.
HRMS calcd for $C_{27}H_{24}O_4NS_2$ ($M+H^+$) 490.1141; found 490.1135.



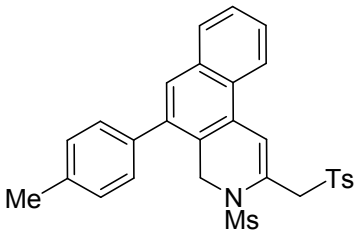
9b, 3-(methylsulfonyl)-5-phenyl-2-(tosylmethyl)-3,4-dihydrobenzo[*f*]isoquinoline

White solid, 90 mg, 90%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 189-191 ˚C
IR (KBr) ν_{max}: 2957, 2924, 2853, 1726, 1597, 1461, 1330, 1306, 1262, 1149, 1079, 1035, 971, 911, 814, 745, 698, 533, 505cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 3H), 7.79 (s, 1H), 7.63 – 7.53 (m, 3H), 7.52 – 7.44 (m, 3H), 7.39 – 7.31 (m, 4H), 4.61 (s, 2H), 4.56 (s, 2H), 2.45 (s, 3H), 2.35 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 145.0, 138.9, 137.5, 136.0, 132.7, 130.5, 129.8, 128.9, 128.7, 128.5, 127.9, 127.8, 127.3, 127.0, 126.7, 126.5, 123.2, 122.4, 62.0, 48.0, 38.4, 21.6.
HRMS calcd for $C_{28}H_{26}O_4NS_2$ ($M+Na^+$) 504.1297; found 504.1286.



9c, 3-(methylsulfonyl)-2-((phenylsulfonyl)methyl)-5-(p-tolyl)-3,4-dihydrobenzo[*f*]isoquinoline

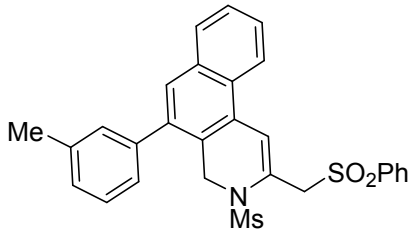
White solid, 92 mg, 92%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 165-167 ˚C
IR (KBr) ν_{max}: 2923, 2853, 1710, 1618, 1505, 1446, 1340, 1313, 1153, 1078, 1042, 958, 750, 560, 521cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 7.7 Hz, 1H), 7.78 (s, 1H), 7.70 – 7.66 (m, 1H), 7.60-7.30 (m, 5H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.60 (s, 2H), 4.59 (s, 2H), 2.44 (s, 3H), 2.32 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 137.7, 137.5, 135.9, 134.0, 132.7, 130.6, 129.4, 129.1, 128.8, 128.7, 128.5, 128.4, 127.7, 127.2, 127.0, 126.6, 126.3, 123.4, 122.3, 62.0, 47.9, 38.3, 21.2.
HRMS calcd for $C_{28}H_{26}O_4NS_2$ ($M+Na^+$) 504.1298; found 504.1302.



9d, 3-(methylsulfonyl)-5-p-tolyl-2-(tosylmethyl)-3,4-dihydrobenzo[*f*]isoquinoline

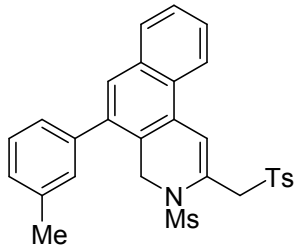
White solid, 94 mg, 91%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 216-218 ˚C

IR (KBr) ν_{max}: 3004, 2936, 1629, 1595, 1498, 1440, 1340, 1316, 1293, 1161, 1136, 1085, 1039, 952, 774, 750, 621, 512cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.83 (m, 3H), 7.78 (s, 1H), 7.62 – 7.51 (m, 3H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.60 (s, 2H), 4.56 (s, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 2.33 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 137.7, 137.6, 135.9, 132.7, 130.5, 129.8, 129.4, 128.8, 128.7, 128.5, 127.8, 127.2, 127.1, 126.6, 126.4, 123.3, 122.4, 62.0, 48.0, 38.3, 21.6, 21.2.
HRMS calcd for $C_{29}H_{28}O_4NS_2$ ($M+Na^+$) 518.1454; found 518.1451.



9e, 3-(methylsulfonyl)-2-((phenylsulfonyl)methyl)-5-(m-tolyl)-3,4-dihydrobenzo[*f*]isoquinoline

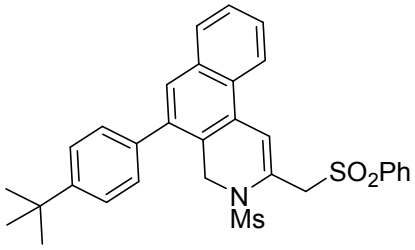
White solid, 91 mg, 91%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 115-117 ˚C
IR (KBr) ν_{max}: 2923, 2856, 1716, 1596, 1448, 1310, 1149, 1078, 1034, 959, 752, 689, 614, 518cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 8.01 – 7.98 (m, 2H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.79 (s, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.63 – 7.53 (m, 5H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.21 (m, 1H), 7.12 (d, *J* = 11.7 Hz, 2H), 4.61 (s, 2H), 4.59 (s, 2H), 2.44 (s, 3H), 2.33 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 138.8, 138.4, 137.7, 134.0, 132.7, 130.6, 129.7, 129.2, 128.7, 128.6, 128.6, 128.5, 127.8, 127.3, 127.1, 126.7, 126.4, 126.0, 123.4, 122.3, 62.0, 48.0, 38.3, 21.5.
HRMS calcd for $C_{28}H_{26}O_4NS_2$ ($M+Na^+$) 504.1297; found 504.1291.



9f, 3-(methylsulfonyl)-5-m-tolyl-2-(tosylmethyl)-3,4-dihydrobenzo[*f*]isoquinoline

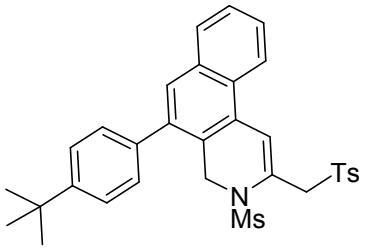
Yellow solid, 93 mg, 90%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 141-143 ˚C
IR (KBr) ν_{max}: 3047, 2924, 1594, 1488, 1449, 1342, 1314, 1290, 1243, 1154, 1083, 1039, 958, 770, 750, 627, 600, 540, 509cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.83 (m, 3H), 7.78 (s, 1H), 7.62 – 7.54 (m, 3H), 7.40 – 7.32 (m, 3H), 7.28 – 7.22 (m, 1H), 7.13 (d, *J* = 10.0 Hz, 2H), 4.61 (s, 2H), 4.56 (s, 2H), 2.45 (s, 3H), 2.44 (s, 3H), 2.34 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 138.8, 138.4, 137.7, 136.0, 132.7, 130.5, 129.8, 129.7, 128.7, 128.6, 128.5, 127.8, 127.7, 127.2, 127.1, 126.7, 126.4, 126.0, 123.3, 122.4, 62.0, 48.0, 38.3, 21.6, 21.5.
HRMS calcd for $C_{29}H_{27}O_4NS_2$ ($M+Na^+$) 540.1274; found 540.1274.



9g, 5-(4-(tert-butyl)phenyl)-3-(methylsulfonyl)-2-((phenylsulfonyl)methyl)-3,4-dihydrobenzo[*f*]isoquinoline

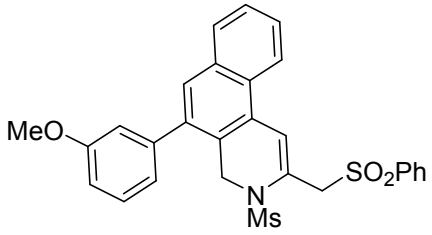
Pale yellow solid, 98 mg, 90%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 150-152 ˚C
IR (KBr) ν_{max}: 2922, 2857, 1674, 1613, 1507, 1450, 1334, 1253, 1147, 1078, 1030, 955, 884, 836, 752, 688, 612, 531cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 1H), 8.01 – 7.98 (m, 2H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.79 (s, 1H), 7.71 – 7.64 (m, 1H), 7.62 – 7.53 (m, 6H), 7.52 – 7.48 (m, 2H), 7.28 (d, *J* = 2.0 Hz, 1H), 4.65 (s, 2H), 4.59 (s, 2H), 2.33 (s, 3H), 1.40 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 138.8, 137.5, 135.8, 134.0, 132.7, 131.3, 130.8, 129.2, 128.7, 128.6, 128.4, 127.2, 127.1, 126.6, 126.3, 125.7, 125.6, 123.5, 122.3, 62.0, 48.0, 38.3, 31.3, 31.1, 29.6.
HRMS calcd for $C_{31}H_{32}O_4NS_2$ ($M+H^+$) 546.1761; found 546.1767.



9h, 5-(4-tert-butylphenyl)-3-(methylsulfonyl)-2-(tosylmethyl)-3,4-dihydrobenzo[*f*]isoquinoline

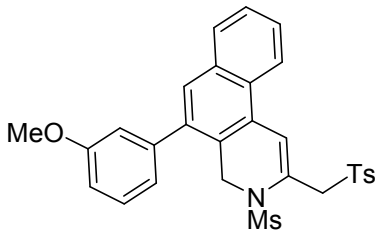
White solid, 94 mg, 85%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 120-122 ˚C
IR (KBr) ν_{max}: 2924, 2858, 1718, 1596, 1455, 1315, 1149, 1078, 1024, 963, 810, 752, 670, 630, 518, 462cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1H), 7.87-7.83 (m, 3H), 7.79 (s, 1H), 7.60 – 7.54 (m, 3H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.28-7.26 (m, 2H), 4.65 (s, 2H), 4.56 (s, 2H), 2.46 (s, 3H), 2.35 (s, 3H), 1.40 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 145.0, 137.5, 136.0, 130.7, 129.8, 128.7, 128.6, 128.5, 127.2, 127.2, 126.6, 126.4, 125.7, 123.4, 122.4, 62.0, 48.0, 38.3, 31.3, 21.6.
HRMS calcd for $C_{32}H_{33}O_4NNaS_2$ ($M+Na^+$) 582.1743; found 582.1742.



9i, 5-(3-methoxyphenyl)-3-(methylsulfonyl)-2-((phenylsulfonyl)methyl)-3,4-dihydrobenzo[*f*]isoquinoline

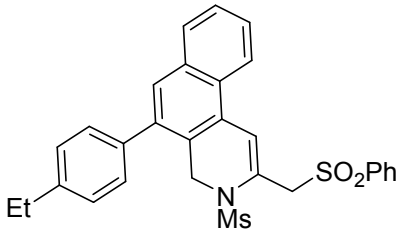
Faint yellow solid, 90 mg, 87%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 131-133 ˚C
IR (KBr) ν_{max}: 3065, 2998, 2929, 2840, 1577, 1484, 1447, 1341, 1302, 1255, 1150, 1083, 1042, 956, 908, 868, 744, 687, 625, 579, 537cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.99 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.80 (s, 1H), 7.70 – 7.65 (m, 1H), 7.63 – 7.52 (m, 5H), 7.44 – 7.36 (m, 1H), 7.01 – 6.96 (m, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.88 – 6.85 (m, 1H), 4.61 (s, 2H), 4.59 (s, 2H), 3.87 (s, 3H), 2.36 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 140.3, 138.8, 137.4, 134.0, 132.7, 130.5, 129.8, 129.2, 128.7, 128.6, 128.4, 127.8, 127.3, 126.9, 126.7, 126.4, 123.3, 122.3, 121.3, 114.7, 113.4, 61.9, 55.3, 47.9, 38.4.
HRMS calcd for $C_{28}H_{25}O_5NNaS_2$ ($M+Na^+$) 542.1066; found 542.1067.



9j, 5-(3-methoxyphenyl)-3-(methylsulfonyl)-2-(tosylmethyl)-3,4-dihydrobenzo[*f*]isoquinoline

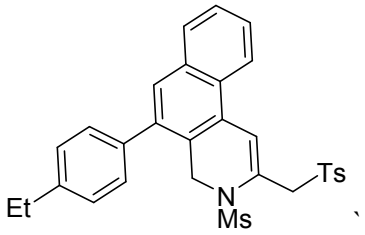
White solid, 93 mg, 88%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 202-204 ˚C
IR (KBr) ν_{max}: 2924, 2856, 1721, 1593, 1449, 1316, 1227, 1149, 1082, 1038, 809, 761, 718, 529cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 3H), 7.80 (s, 1H), 7.63 – 7.53 (m, 3H), 7.42 – 7.34 (m, 3H), 6.98 (dd, *J* = 8.3, 2.0 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 1.9 Hz, 1H), 4.61 (s, 2H), 4.56 (s, 2H), 3.87 (s, 3H), 2.45 (s, 3H), 2.37 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 145.0, 140.3, 137.4, 135.9, 132.7, 130.4, 129.8, 128.8, 128.7, 128.5, 127.9, 127.3, 126.9, 126.7, 126.5, 123.2, 122.4, 121.3, 114.8, 113.3, 62.0, 55.3, 47.9, 38.4, 21.6.
HRMS calcd for $C_{29}H_{27}O_5NNaS_2$ ($M+Na^+$) 556.1223; found 556.1217



9k, 5-(4-ethylphenyl)-3-(methylsulfonyl)-2-((phenylsulfonyl)methyl)-3,4-dihydrobenzo[*f*]isoquinoline

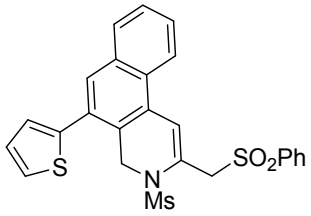
Brown solid, 90 mg, 87%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 156-158 ˚C
IR (KBr) ν_{max}: 3022, 2963, 2927, 1630, 1506, 1446, 1344, 1314, 1152, 1082, 1041, 960, 832, 753, 688, 623, 562, 527cm^{-1}
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 7.3 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.79 (s, 1H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.64 – 7.51 (m, 5H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.27 – 7.21 (m, 2H), 4.62 (s, 2H), 4.59 (s, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.32 (s, 3H), 1.32 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 138.8, 137.6, 136.1, 134.0, 132.7, 130.7, 129.2, 128.9, 128.7, 128.5, 128.5, 128.2, 127.8, 127.2, 127.1, 126.7, 126.3, 123.4, 122.3, 62.0, 48.0, 38.3, 28.5, 15.3.
HRMS calcd for $C_{29}H_{28}O_4NS_2$ ($M+Na^+$) 518.1454; found 518.1446.



9l, 5-(4-ethylphenyl)-3-(methylsulfonyl)-2-(tosylmethyl)-3,4-dihydrobenzo[*f*]isoquinoline

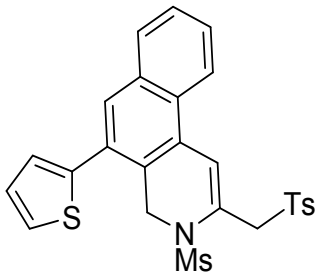
White solid, 93 mg, 88%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 199-201 ˚C
IR (KBr) ν_{max}: 2960, 2924, 2854, 1598, 1455, 1409, 1314, 1149, 1081, 1022, 961, 813, 760, 671, 627, 513cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.89 – 7.82 (m, 3H), 7.78 (s, 1H), 7.63 – 7.52 (m, 3H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.22 (m, 2H), 4.62 (s, 2H), 4.56 (s, 2H), 2.75 (q, *J* = 7.6 Hz, 2H), 2.45 (s, 3H), 2.34 (s, 3H), 1.32 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 143.9, 137.6, 136.1, 135.9, 132.7, 130.6, 129.7, 128.8, 128.6, 128.5, 128.2, 127.7, 127.1, 126.6, 126.4, 123.3, 122.3, 62.0, 48.0, 38.3, 28.5, 21.6, 15.3.
HRMS calcd for $C_{30}H_{29}O_4NNaS_2$ ($M+Na^+$) 554.1430; found 554.1422.



9m, 3-(methylsulfonyl)-2-((phenylsulfonyl)methyl)-5-(thiophen-2-yl)-3,4-dihydrobenzo[*f*]isoquinoline

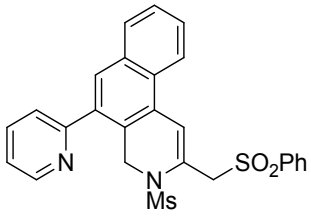
Pale yellow solid, 88 mg, 89%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 162-164 ˚C
IR (KBr) ν_{max}: 3061, 3004, 2927, 1676, 1608, 1449, 1409, 1339, 1300, 1252, 1142, 1081, 1028, 968, 874, 753, 683, 581, 515cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 7.4 Hz, 2H), 7.84 (d, *J* = 6.9 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.63 – 7.52 (m, 5H), 7.48 (dd, *J* = 4.8, 3.0 Hz, 1H), 7.31 (dd, *J* = 2.8, 1.0 Hz, 1H), 7.18 (dd, *J* = 4.9, 1.0 Hz, 1H), 4.68 (s, 2H), 4.60 (s, 2H), 2.37 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 138.8, 134.0, 132.7, 132.1, 130.5, 129.2, 128.7, 128.6, 128.4, 128.3, 127.8, 127.3, 126.9, 126.7, 126.5, 123.6, 123.3, 122.3, 61.9, 47.9, 38.4.
HRMS calcd for $C_{25}H_{22}O_4NS_3$ ($M+Na^+$) 496.0705; found 496.0699.



9n, 3-(methylsulfonyl)-5-(thiophen-2-yl)-2-(tosylmethyl)-3,4-dihydrobenzo[*f*]isoquinoline

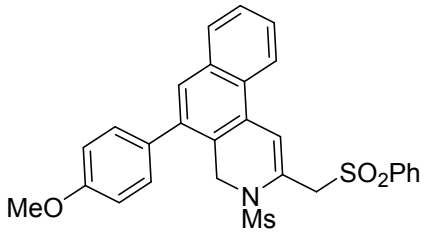
White solid, 88 mg, 87%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 115-117 ˚C
IR (KBr) ν_{max}: 2921, 2852, 1747, 1595, 1539, 1452, 1314, 1150, 1080, 1028, 962, 764, 677, 577, 515 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.82 (m, 4H), 7.62 – 7.52 (m, 3H), 7.49 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.31 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.19 (dd, *J* = 4.9, 1.3 Hz, 1H), 4.71 (s, 2H), 4.56 (s, 2H), 2.46 (s, 3H), 2.38 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 145.0, 139.3, 135.9, 132.7, 132.1, 130.4, 129.8, 128.8, 128.6, 128.4, 128.3, 127.8, 127.3, 127.0, 126.7, 126.6, 126.5, 123.6, 123.2, 122.4, 61.9, 48.0, 38.4, 21.7.
HRMS calcd for $C_{26}H_{24}O_4NS_3$ ($M+H^+$) 510.0867; found 510.0864.



9o, 3-(methylsulfonyl)-2-(phenylsulfonylmethyl)-5-(pyridin-2-yl)-3,4-dihydrobenzo[*f*]isoquinoline

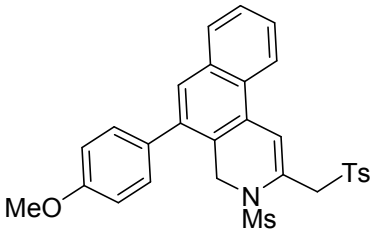
Brown solid, 56 mg, 57%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 188-190 ˚C
IR (KBr) ν_{max}: 2922, 2855, 1722, 1636, 1447, 1308, 1150, 1082, 762, 726, 689, 608, 536 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 – 8.72 (m, 1H), 7.97 (d, *J* = 7.3 Hz, 2H), 7.75 (td, *J* = 7.7, 1.7 Hz, 1H), 7.73 – 7.64 (m, 2H), 7.61 – 7.56 (m, 3H), 7.50 – 7.46 (m, 3H), 7.33 – 7.29 (m, 2H), 6.90 (s, 1H), 4.80 (s, 2H), 4.56 (s, 2H), 2.64 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 153.9, 149.9, 137.2, 136.6, 133.9, 132.0, 129.9, 129.1, 128.6, 128.5, 128.4, 128.1, 126.5, 126.3, 122.9, 120.1, 119.5, 118.3, 62.5, 47.2, 38.3.
HRMS calcd for $C_{26}H_{23}O_4N_2S_2$ ($M+H^+$) 491.1082; found 491.1093.



9p, 5-(4-methoxyphenyl)-3-(methylsulfonyl)-2-((phenylsulfonyl)methyl)-3,4-dihydrobenzo[*f*]isoquinoline

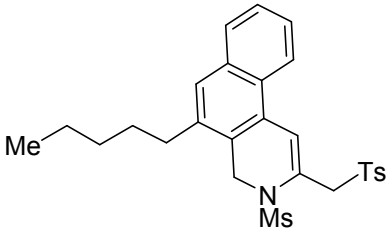
Pale yellow solid, 92 mg, 89%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 182-184 ˚C
IR (KBr) ν_{max}: 3059, 2924, 2852, 1717, 1604, 1510, 1341, 1318, 1247, 1154, 1080, 1030, 958, 830, 745, 687, 559, 511cm^{-1}

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 7.7 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.62 – 7.52 (m, 5H), 7.28 – 7.23 (m, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 4.61 (s, 2H), 4.59 (s, 2H), 3.89 (s, 3H), 2.32 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 138.8, 137.2, 134.0, 132.7, 131.2, 130.6, 130.1, 129.2, 128.6, 128.5, 128.5, 128.2, 127.7, 127.2, 126.7, 126.3, 123.4, 122.3, 114.2, 61.9, 55.3, 48.0, 38.3.
HRMS calcd for $C_{28}H_{26}O_5NS_2$ ($M+Na^+$) 520.1247; found 520.1234.



9q, 5-(4-methoxyphenyl)-3-(methylsulfonyl)-2-(tosylmethyl)-3,4-dihydrobenzo[*f*]isoquinoline

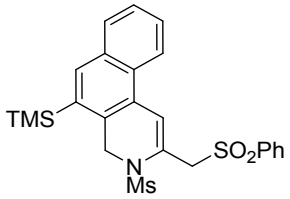
Faint yellow solid, 95 mg, 89%
R_f = 0.3 (30% ethyl acetate in hexanes)
Melting point: 163-165 ˚C
IR (KBr) ν_{max}: 2926, 1718, 1601, 1508, 1452, 1315, 1247, 1150, 1080, 1029, 959, 820, 769, 538cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.82 (m, 3H), 7.77 (s, 1H), 7.63 – 7.51 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.03 – 7.00 (m, 2H), 4.62 (s, 2H), 4.56 (s, 2H), 3.89 (s, 3H), 2.46 (s, 3H), 2.34 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 145.0, 137.3, 136.0, 132.7, 131.2, 130.5, 130.1, 129.8, 128.7, 128.6, 128.5, 127.7, 127.2, 127.1, 126.6, 126.4, 123.3, 122.4, 114.2, 62.0, 55.3, 48.0, 38.4, 21.7.
HRMS calcd for $C_{29}H_{27}O_5NNaS_2$ ($M+Na^+$) 556.1223; found 556.1216.



9r, 3-(methylsulfonyl)-5-pentyl-2-(tosylmethyl)-3,4-dihydrobenzo[*f*]isoquinoline

Pale yellow solid, 79 mg, 80%
R_f = 0.6 (30% ethyl acetate in hexanes)
Melting point: 177-179 ˚C

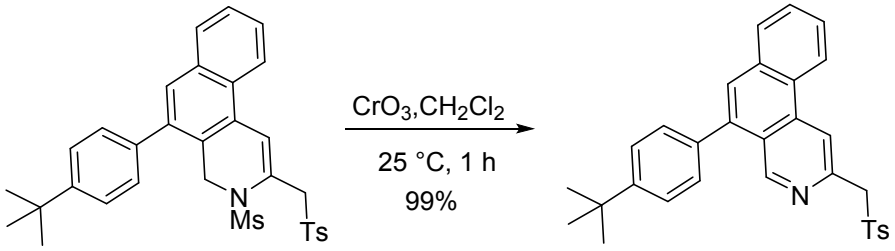
IR (KBr) ν_{max}: 3009, 2959, 2925, 2855, 1721, 1636, 1599, 1459, 1380, 1327, 1306, 1149, 1087, 1062, 973, 906, 778, 749, 538, 507 cm^{-1}
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.29-7.24 (m, 3H), 6.91 (s, 1H), 6.78-6.74 (m, 1H), 4.69 (s, 2H), 4.50 (s, 2H), 2.60 (s, 3H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 1.62-1.59 (m, 4H), 1.38-1.36 (m, 2H), 0.94-0.91 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 144.9, 137.5, 136.6, 136.0, 135.8, 130.0, 129.7, 128.8, 128.5, 127.9, 127.5, 127.2, 125.9, 120.8, 119.0, 118.0, 62.3, 46.4, 37.8, 31.5, 30.0, 29.6, 22.5, 21.6, 13.9.
HRMS calcd for $C_{27}H_{31}O_4NNaS_2$ ($M+Na^+$) 520.1587; found 520.1584.



9s, 3-(methylsulfonyl)-2-(phenylsulfonylmethyl)-5-(trimethylsilyl)-3,4-dihydrobenzo[*f*]isoquinoline

White solid, 75 mg, 77%
R_f = 0.59 (30% ethyl acetate in hexanes)
Melting point: 199-201 ˚C
IR (KBr) ν_{max}: 2956, 2924, 2853, 1719, 1601, 1452, 1348, 1307, 1250, 1149, 1083, 1025, 955, 851, 764, 687, 562, 525cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.69 – 7.65 (m, 2H), 7.61 – 7.56 (m, 2H), 7.29 – 7.27 (m, 2H), 7.24 – 7.21 (m, 1H), 6.88 (s, 1H), 6.40 (s, 1H), 4.56 (s, 2H), 4.32 (s, 2H), 2.60 (s, 3H), 0.37 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 139.4, 138.5, 136.3, 136.2, 134.6, 134.0, 131.2, 129.1, 128.7, 128.6, 128.2, 126.0, 123.5, 120.6, 118.4, 62.3, 44.0, 37.9, -0.3.
HRMS calcd for $C_{24}H_{27}O_4NNaS_2Si$ ($M+Na^+$) 508.1043; found 508.1049.

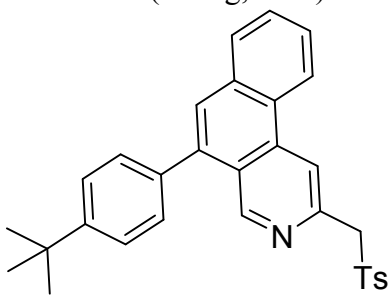
5. Chromium trioxide oxidation of dihydrobenzo[*f*]isoquinoline 9h



9h **14**

To a solution of the methylsulfonyl-3,4-dihydrobenzo[*f*]isoquinoline **9h** (84 mg, 0.15 mmol) in dichloromethane (10 mL), Chromium trioxide (75 mg, 0.75 mmol) was added and the reaction mixture was stirred for 1 hr at 25 °C. 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 5-(4-tert-butylphenyl)-2-(tosylmethyl)benzo[*f*]isoquinoline **14** as a white solid (71 mg, 99%).



14, 5-(4-tert-butylphenyl)-2-(tosylmethyl)benzo[*f*]isoquinoline

White solid, 71 mg, 99%
R_f = 0.4 (30% ethyl acetate in hexanes)
Melting point: 138-140˚C
IR (KBr) ν_{max}: 2925, 2860, 1723, 1602, 1510, 1461, 1314, 1149, 1086, 1027, 894, 758, 519 cm^{-1}
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.65 (d, J = 7.6 Hz, 1H), 8.57 (s, 1H), 7.94 (d, J = 7.0 Hz, 1H), 7.80 (s, 1H), 7.78 – 7.72 (m, 2H), 7.60 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 4.80 (s, 2H), 2.40 (s, 3H), 1.41 (d, J = 5.6 Hz, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 150.4, 144.7, 137.3, 135.5, 133.3, 131.3, 129.6, 129.6, 129.3, 129.3, 128.8, 128.5, 128.3, 127.7, 127.2, 125.6, 125.4, 125.3, 123.2, 118.3, 64.8, 34.7, 31.3, 21.6.
HRMS calcd for $C_{31}H_{30}O_2NS$ ($M+H^+$) 480.1988; found 480.1991.

6. Crystallographic data for 9j

Table 1: Crystal data and structure refinement for KA115mf.

Identification code	KA115mf
Empirical formula	$C_{29}H_{27}NO_5S_2$
Formula weight	533.63
Temperature/K	293(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	14.943(6)

b/Å	10.893(5)
c/Å	16.259(6)
α/°	90
β/°	90.199(10)
γ/°	90
Volume/Å^3	2646.5(18)
Z	4
ρ_{calc}g/cm^3	1.339
μ/mm^{-1}	0.241
F(000)	1120.0
Crystal size/mm^3	0.430 × 0.320 × 0.230
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.628 to 51.996
Index ranges	-18 ≤ h ≤ 16, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	19517
Independent reflections	5202 [R_{int} = 0.0267, R_{sigma} = 0.0243]
Data/restraints/parameters	5202/0/337
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0394, wR_2 = 0.1185
Final R indexes [all data]	R_1 = 0.0482, wR_2 = 0.1247
Largest diff. peak/hole / e Å^{-3}	0.26/-0.37

Data collection and structure solution of **KA115**: Single crystal X-ray data for two compounds were collected at room temperature on a Bruker D8 QUEST equipped with a four-circle kappa diffractometer and Photon 100 detector. An Iμs microfocus Mo source (λ=0.71073Å) supplied the multi-mirror monochromated incident beam. A combination of Phi and Omegascans were

used to collect the necessary data.Unit cell dimensions were determined using 9891 reflections. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structures were solved by Direct Methods using SHELXS97[3] and refinement was carried out by full-matrix least-squares technique using SHELXL-2014/7.[3,4] 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. CCDC 1864240 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/

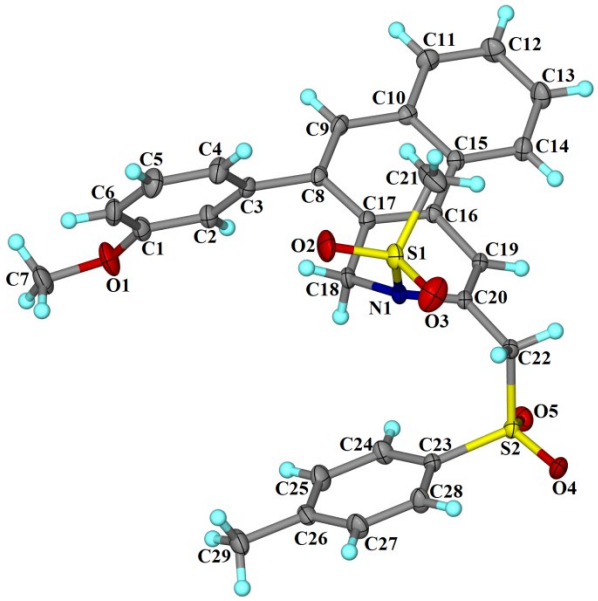
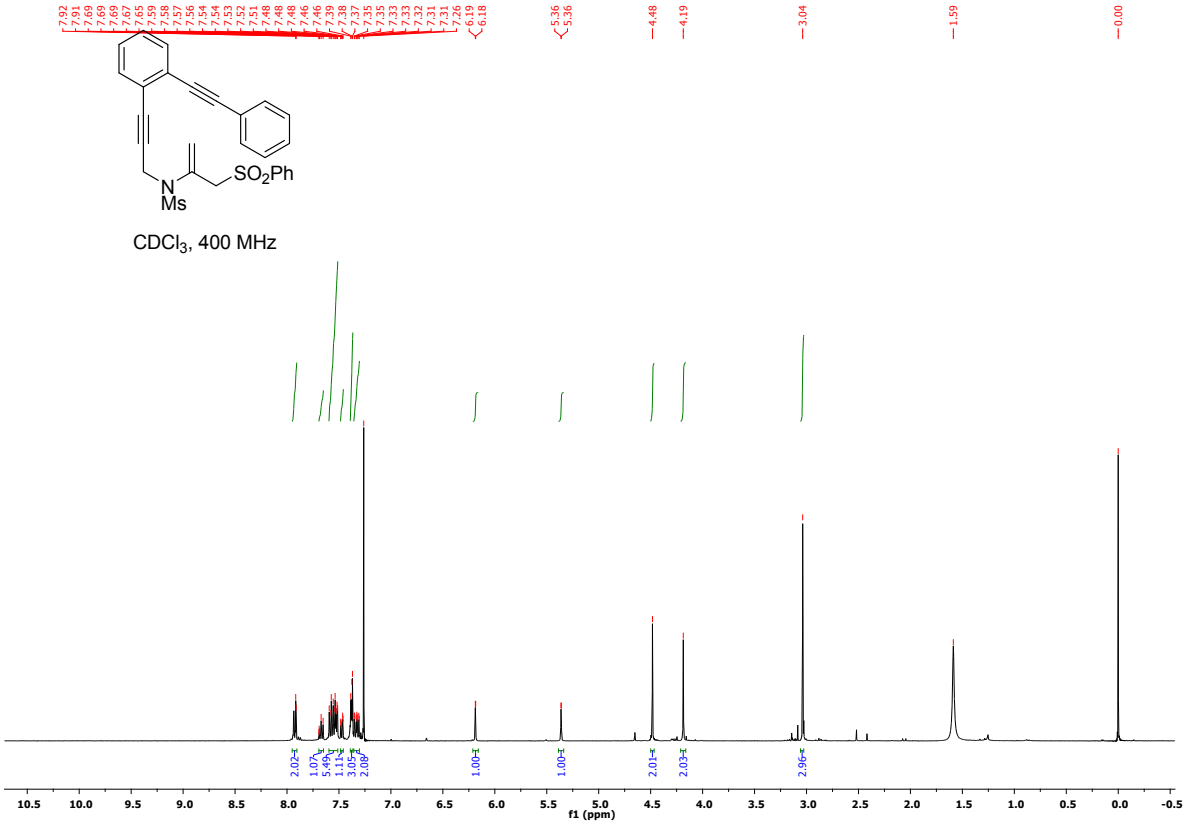


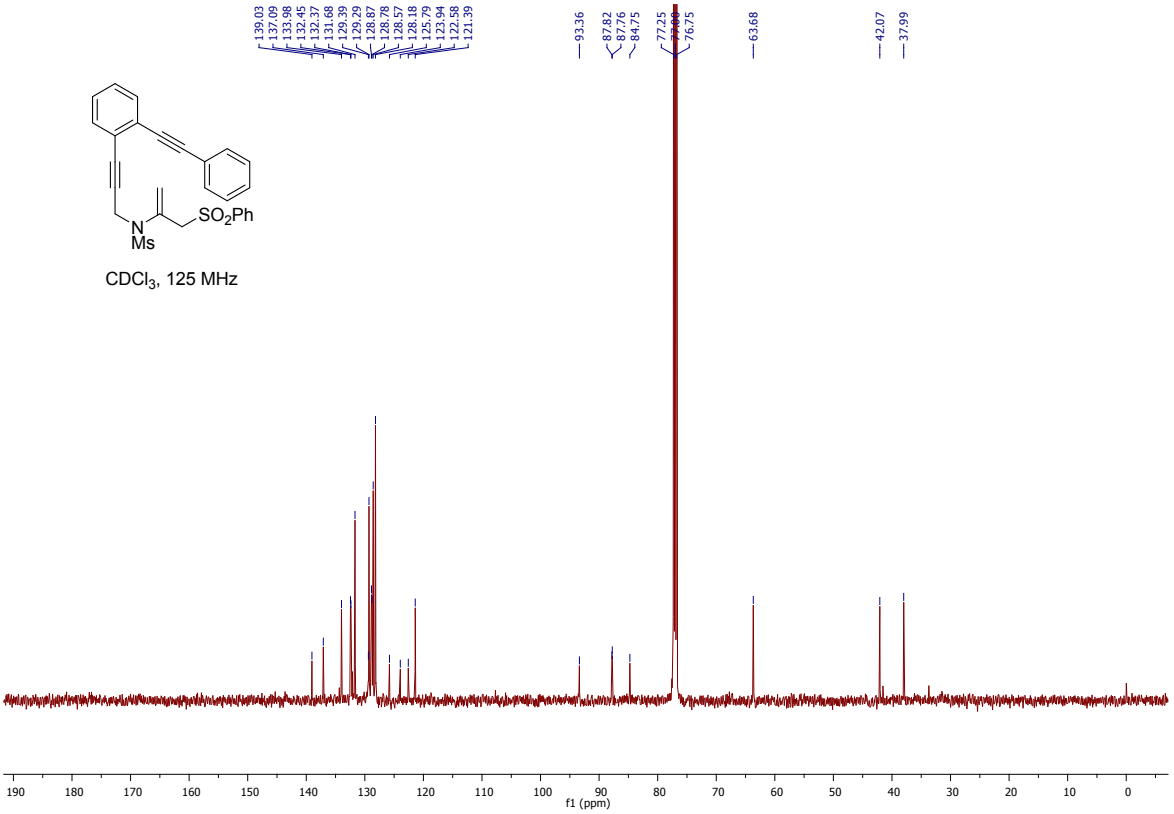
Figure 1: The molecular structure of **9j** with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius. CCDC 1864240 contains the supplementary crystallographic data.

[3] SMART & SAINT. Software Reference manuals. Versions 6.28a & 5.625, Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, U.S.A., 2001.

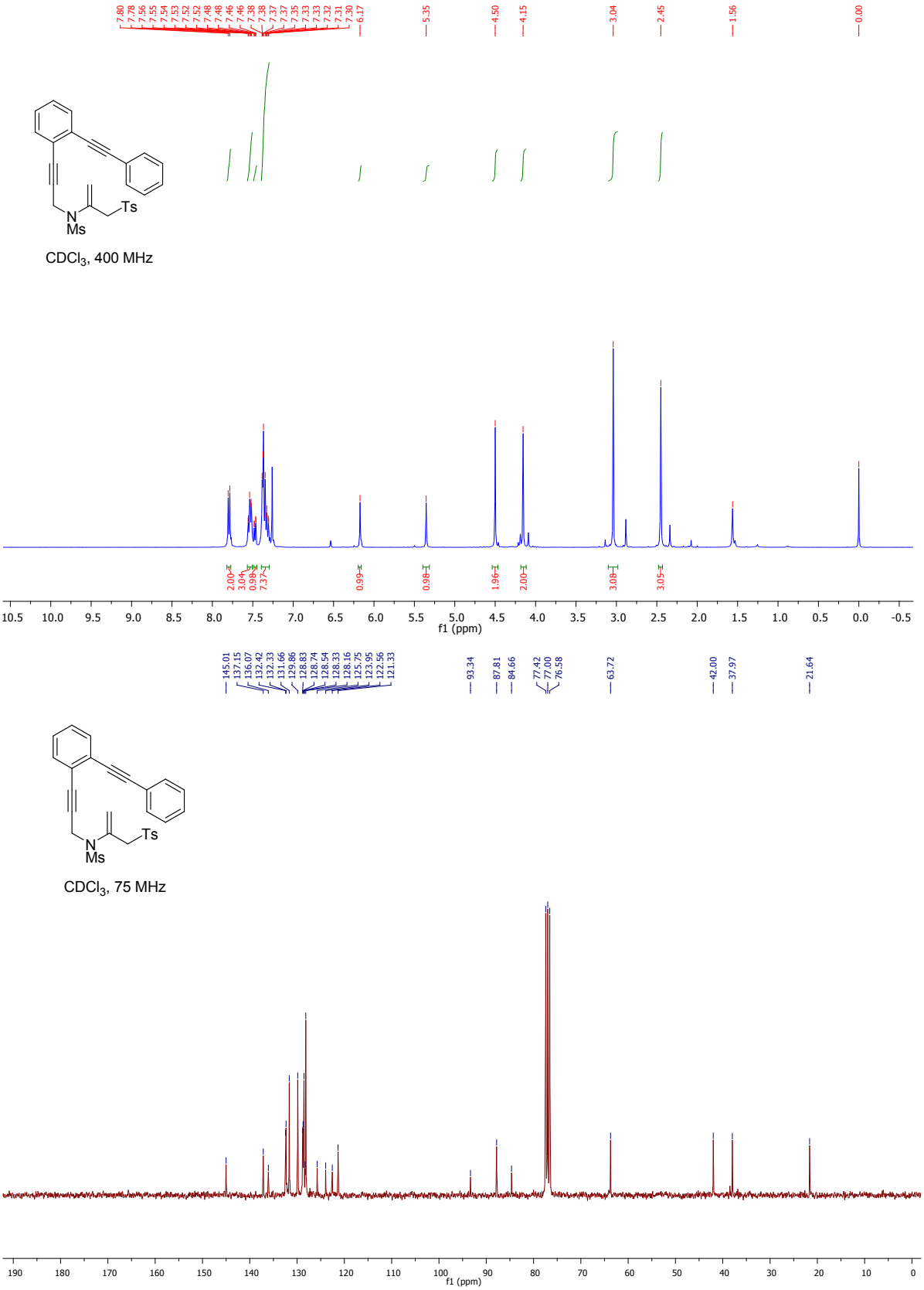
[4] Muller, P, Herbst-Imer, R, Spek, A. L, Schneider, T. R, and Sawaya, M. R. Crystal Structure Refinement: A Crystallographer's Guide to SHELXL. Muller, P. Ed. 2006 Oxford University Press: Oxford, New York, pp. 57–91.

^{1}H NMR and ^{13}C NMR of 8a

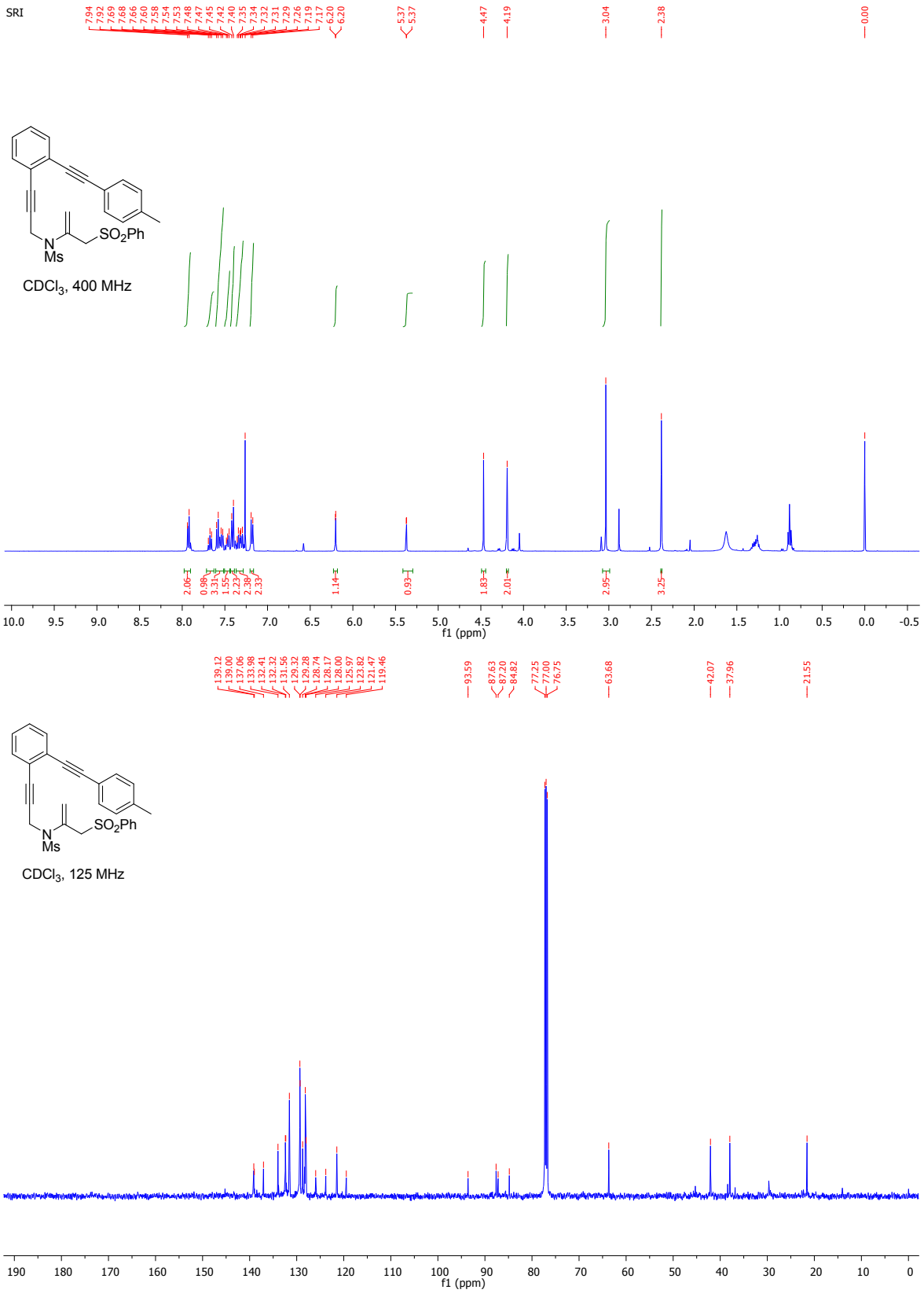




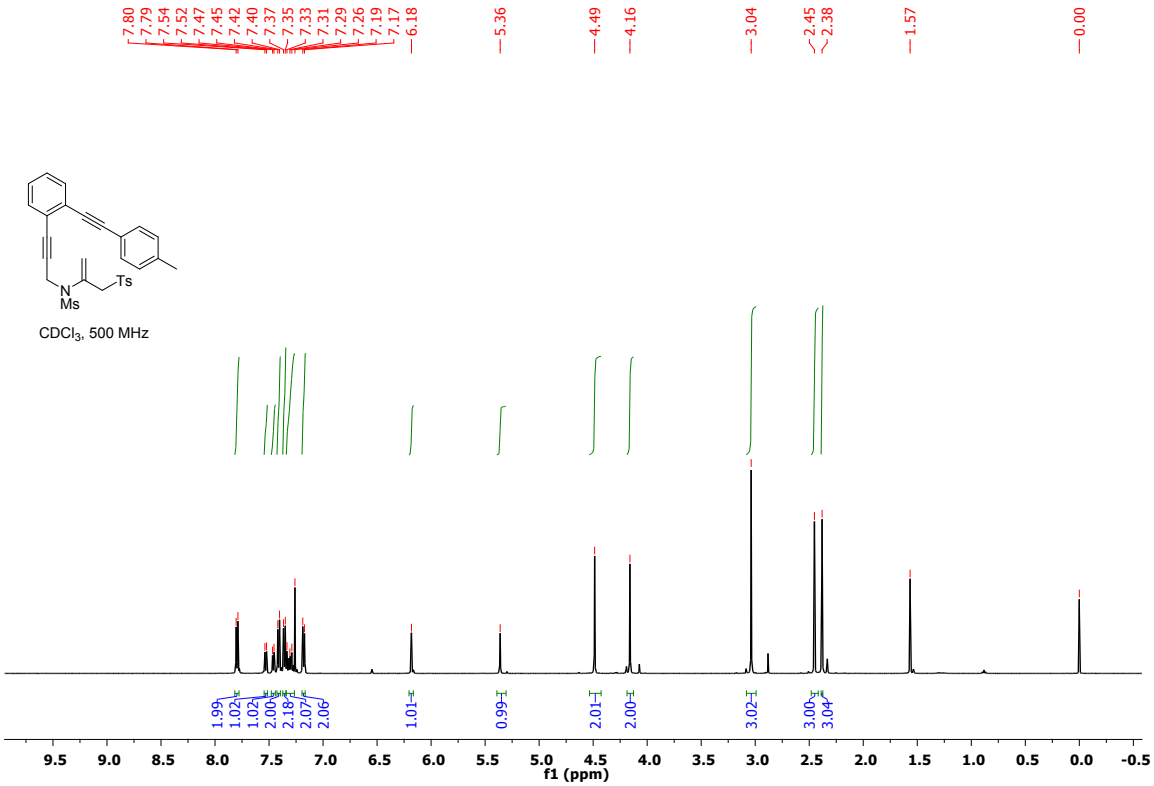
^{1}H NMR and ^{13}C NMR of 8b

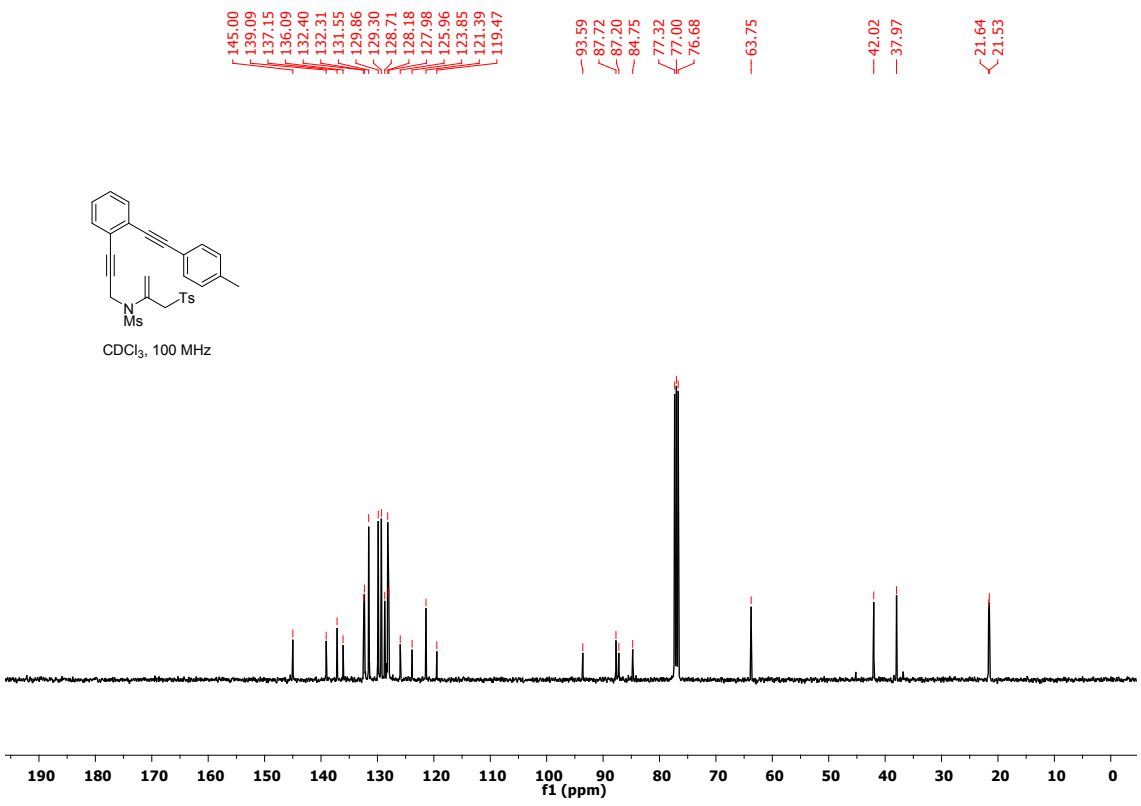


^{1}H NMR and ^{13}C NMR of 8c

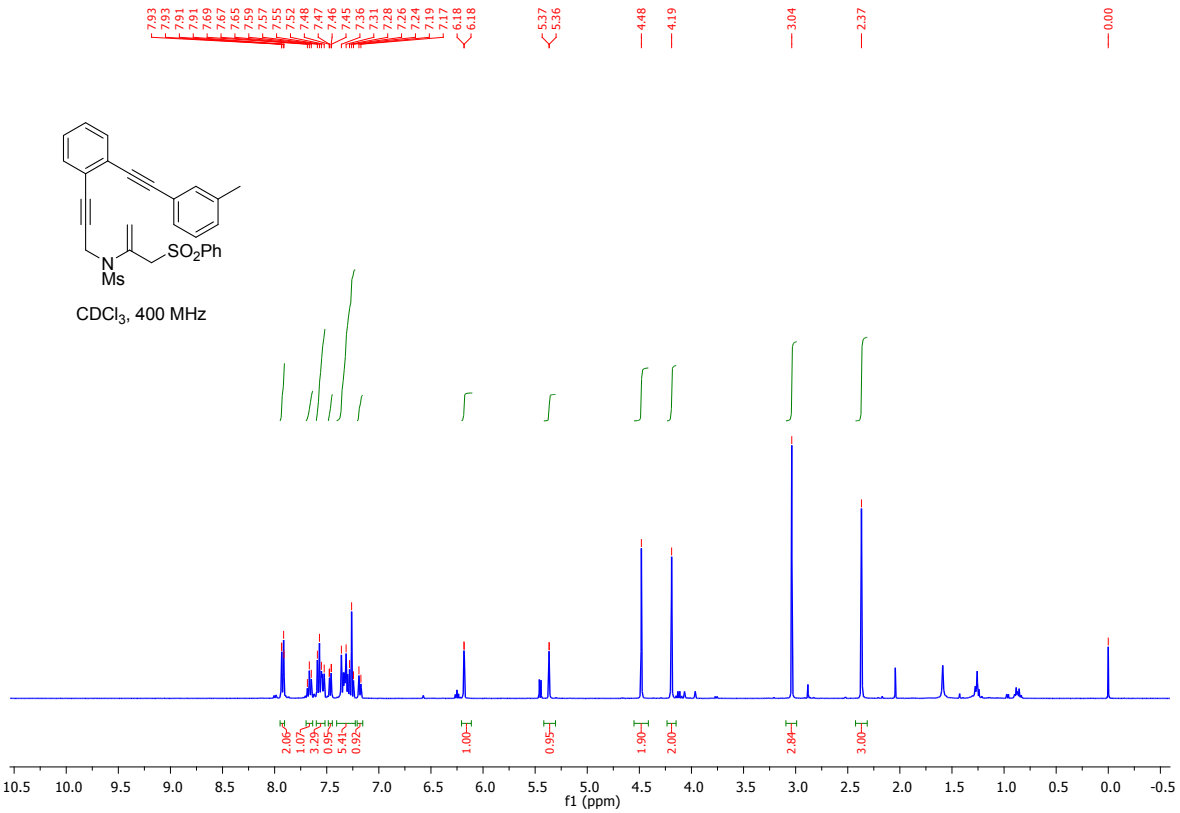


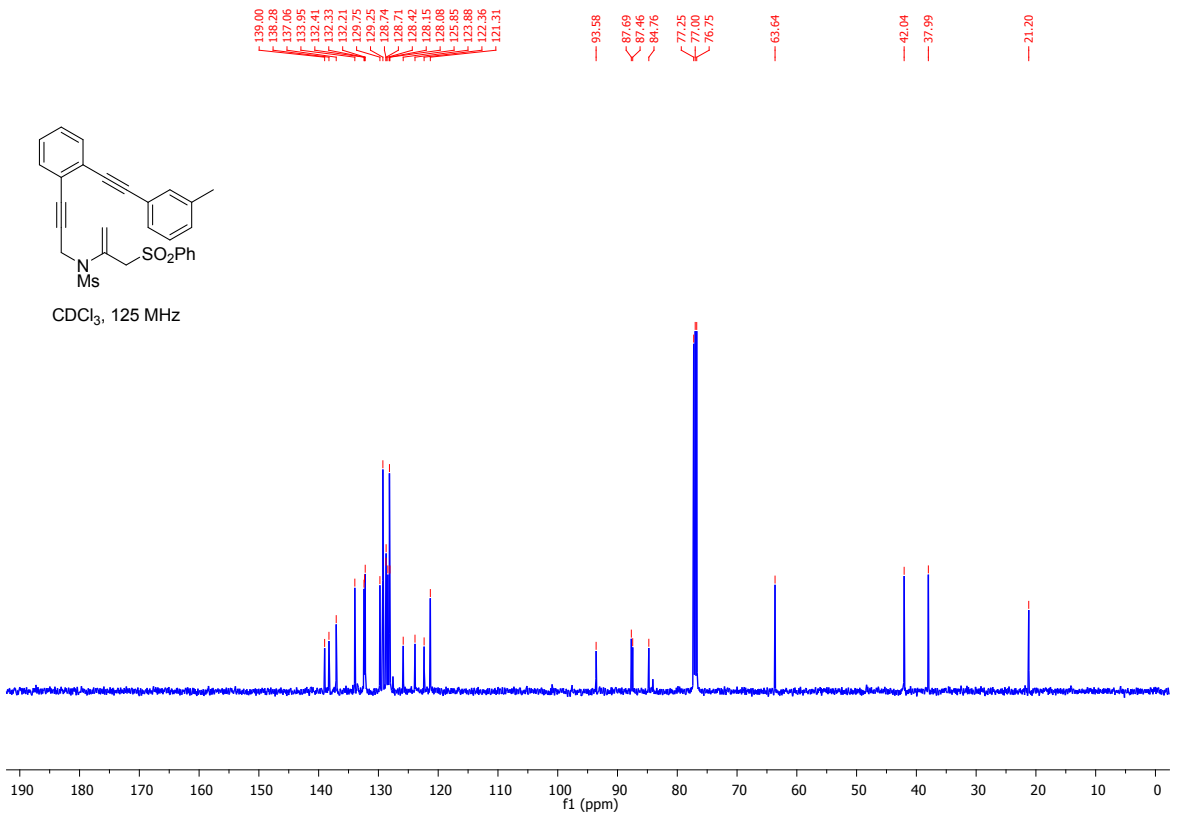
^{1}H NMR and ^{13}C NMR of 8d



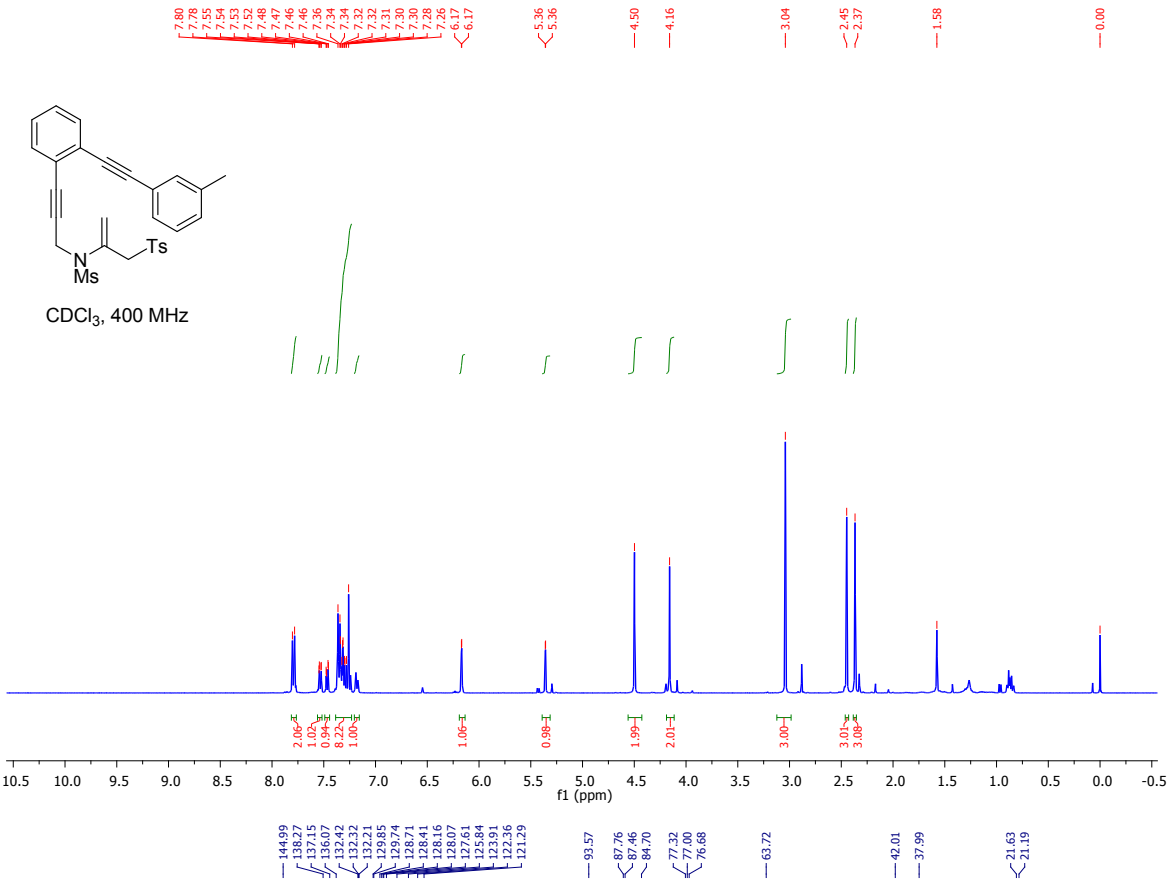


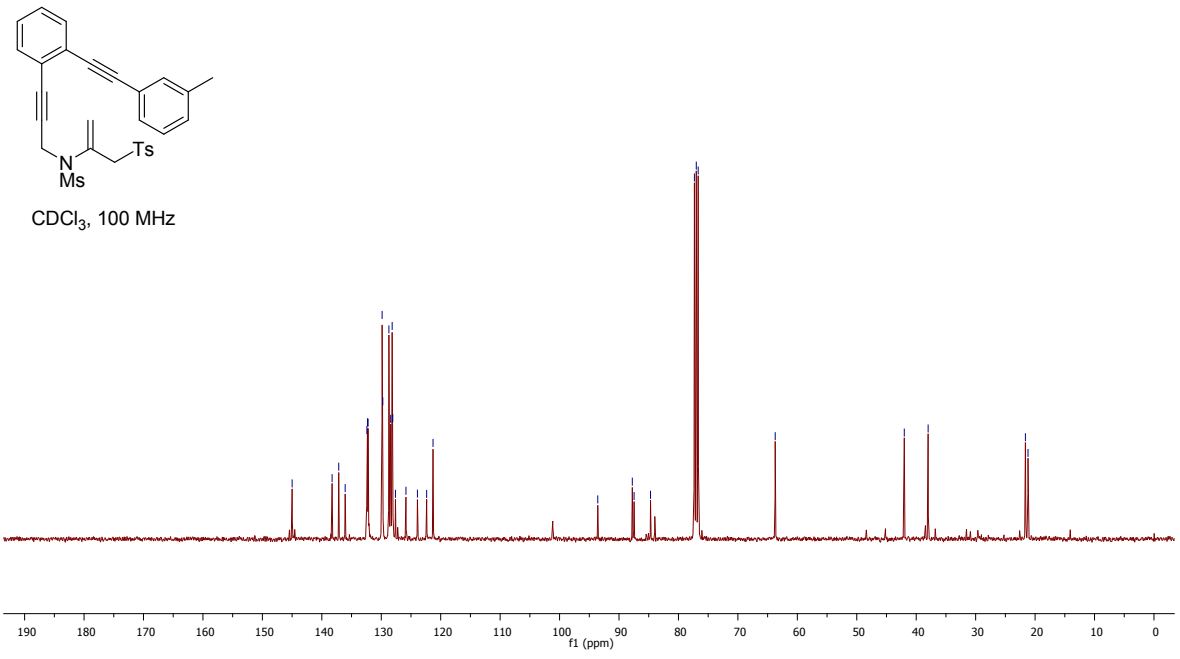
^{1}H NMR and ^{13}C NMR of 8e



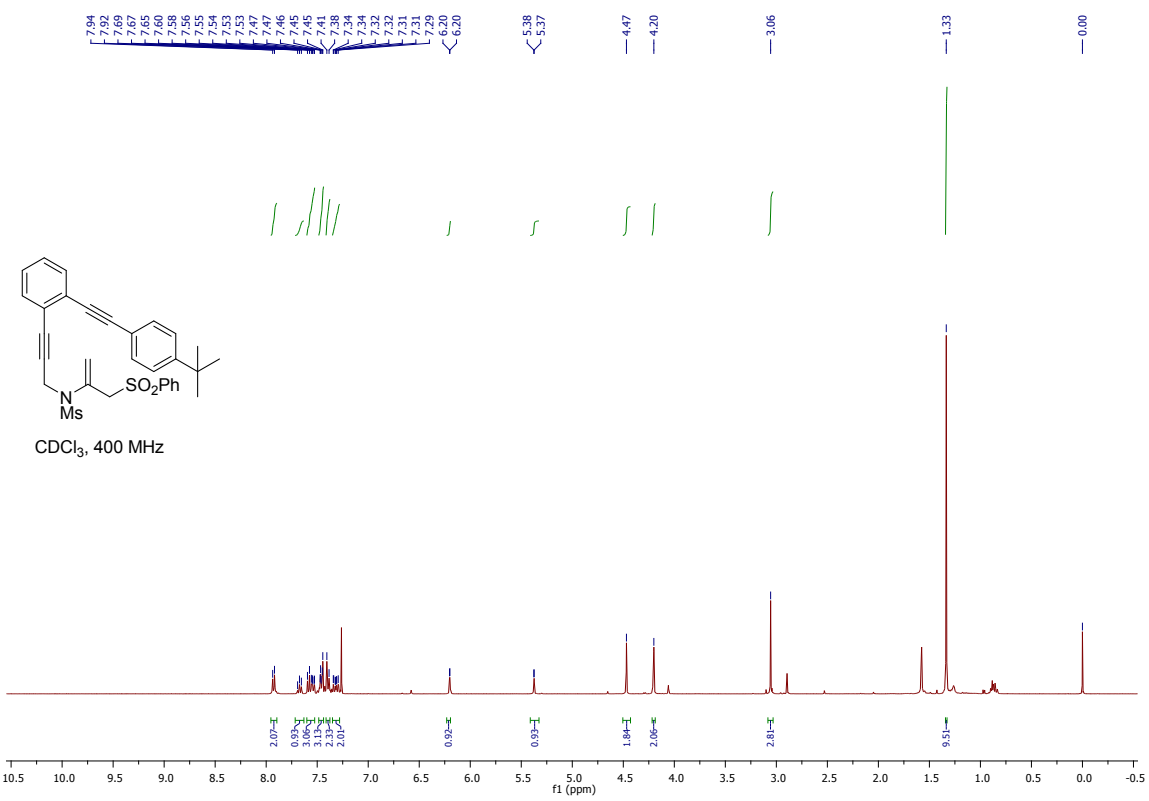


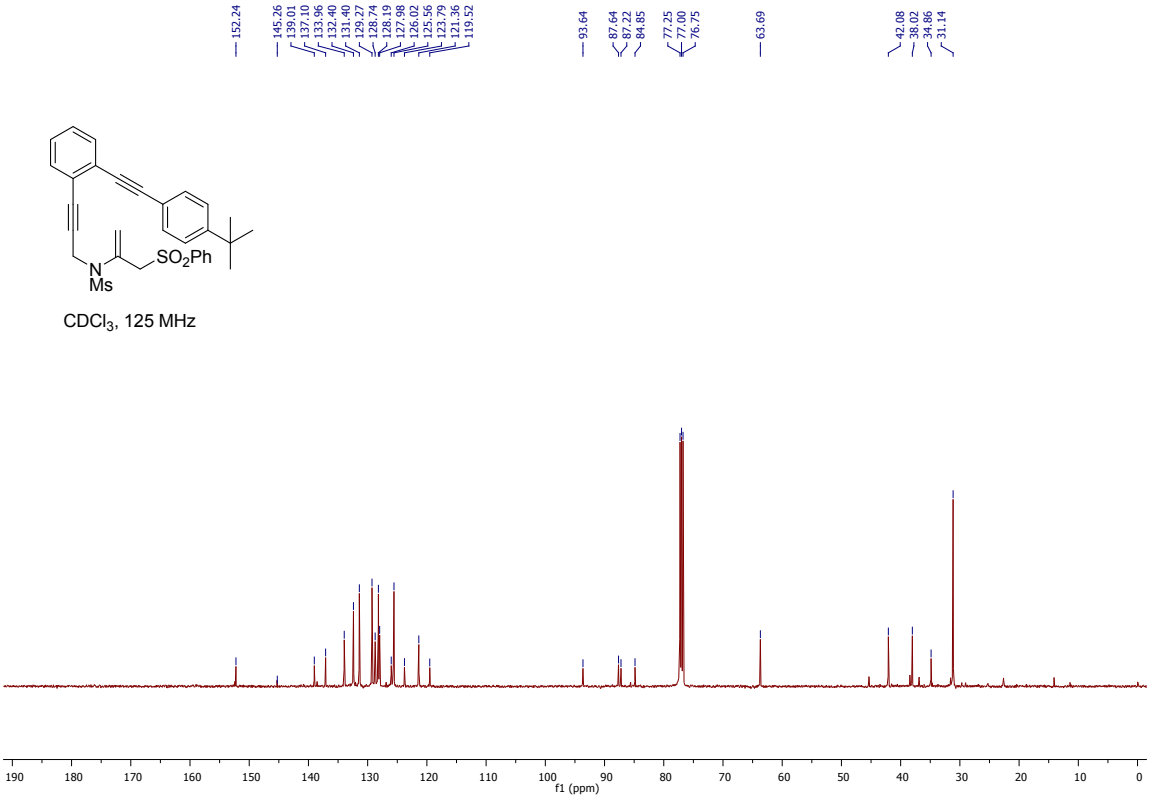
^{1}H NMR and ^{13}C NMR of 8f



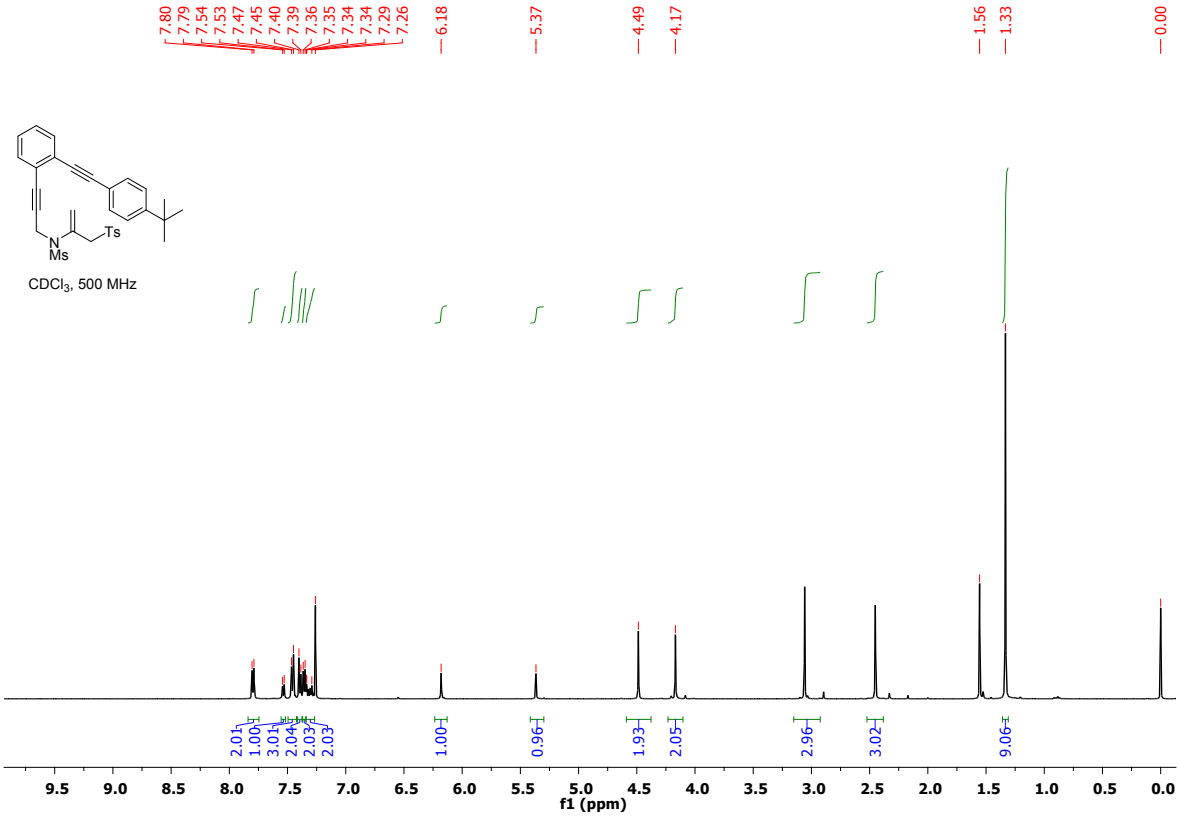


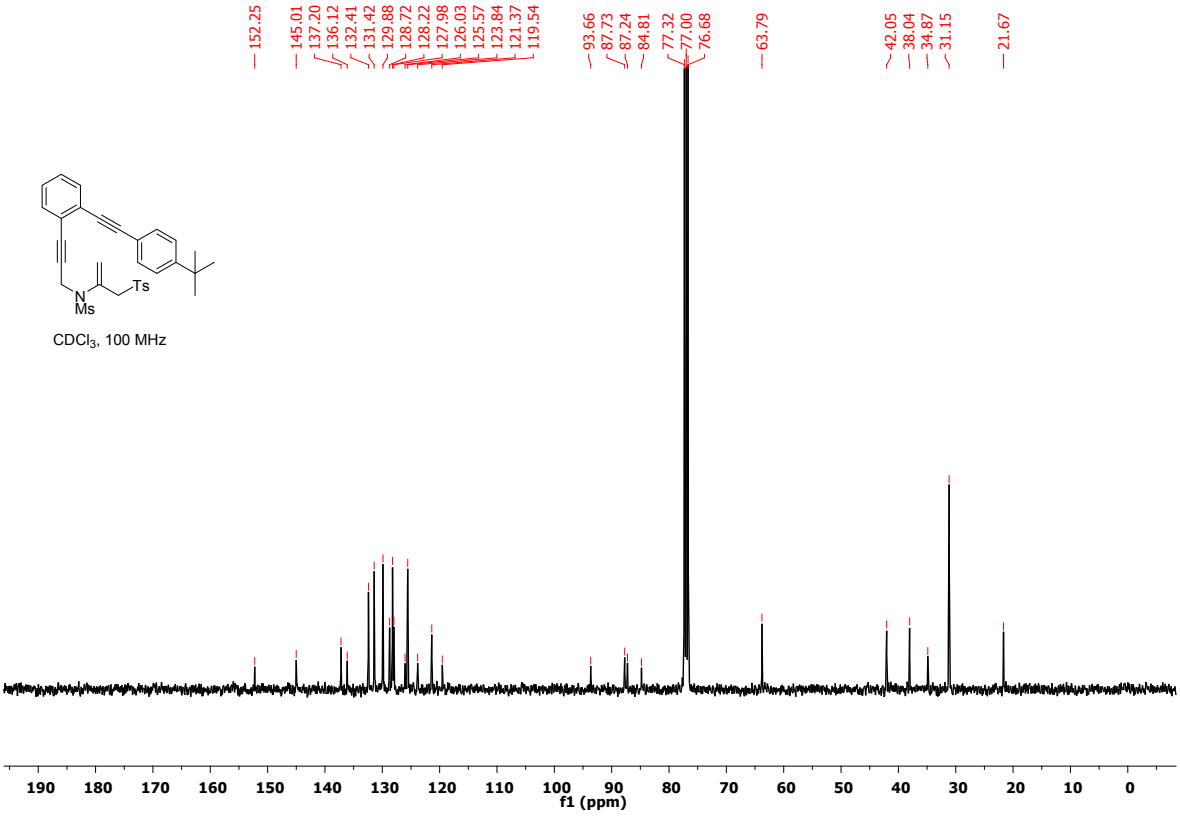
^{1}H NMR and ^{13}C NMR of 8g



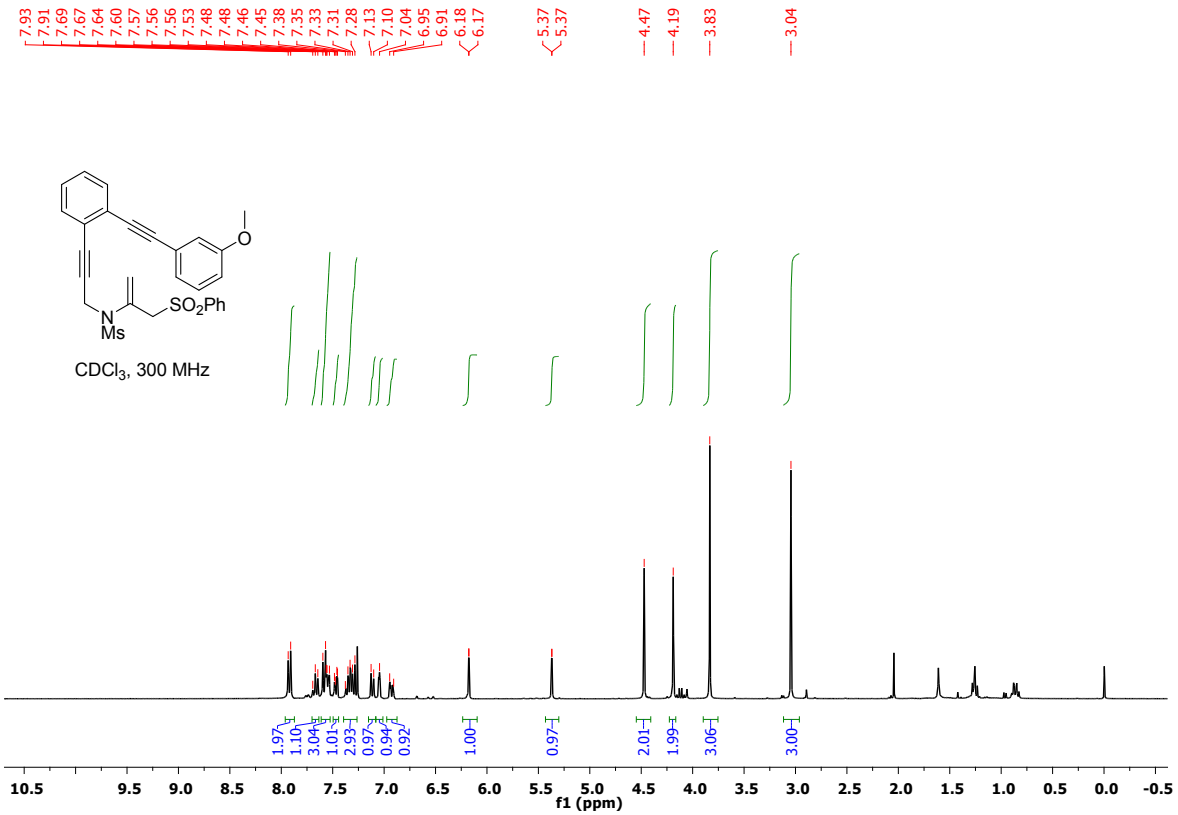


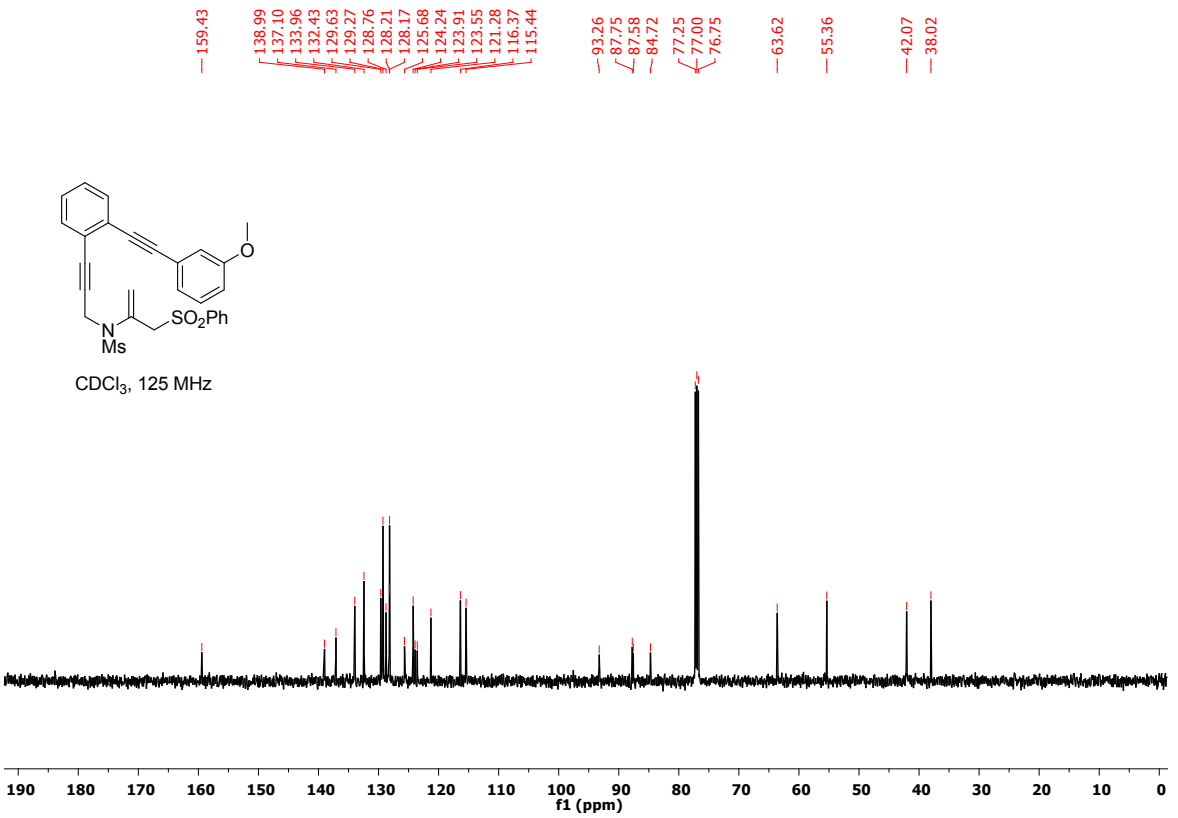
^{1}H NMR and ^{13}C NMR of 8h



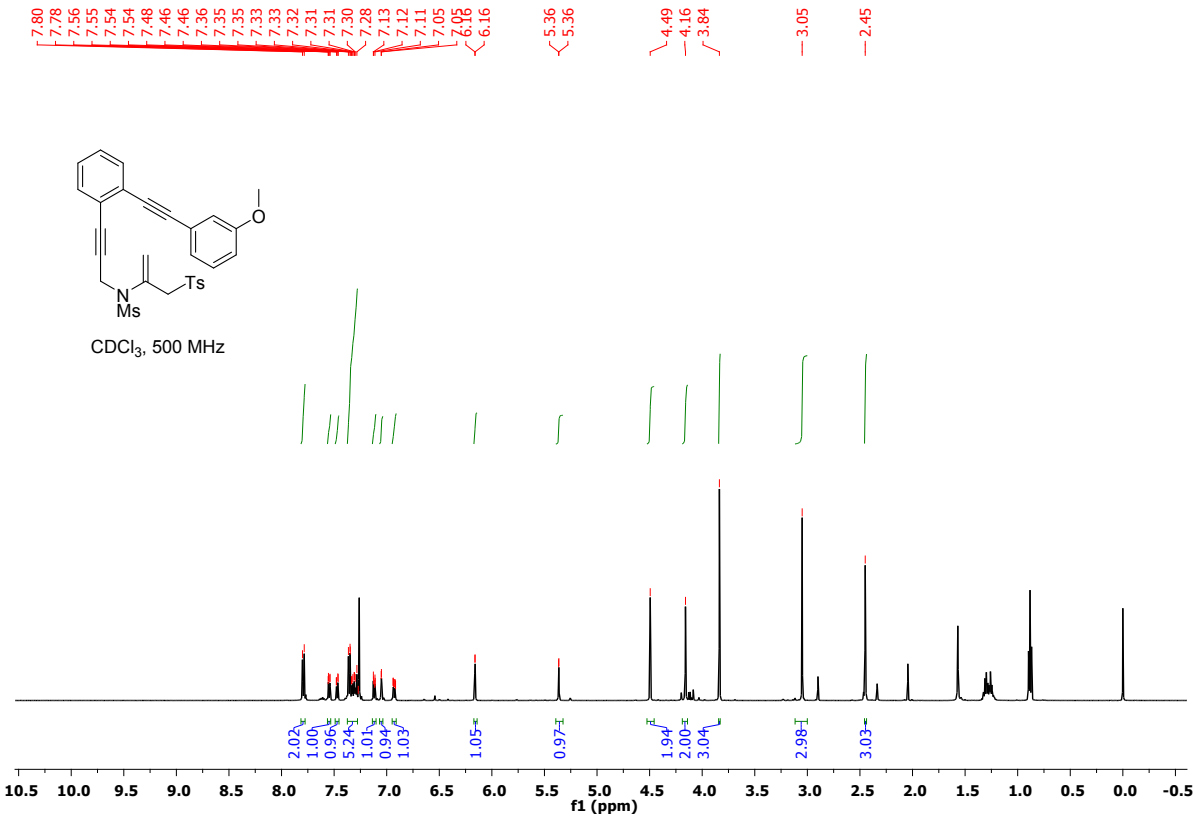


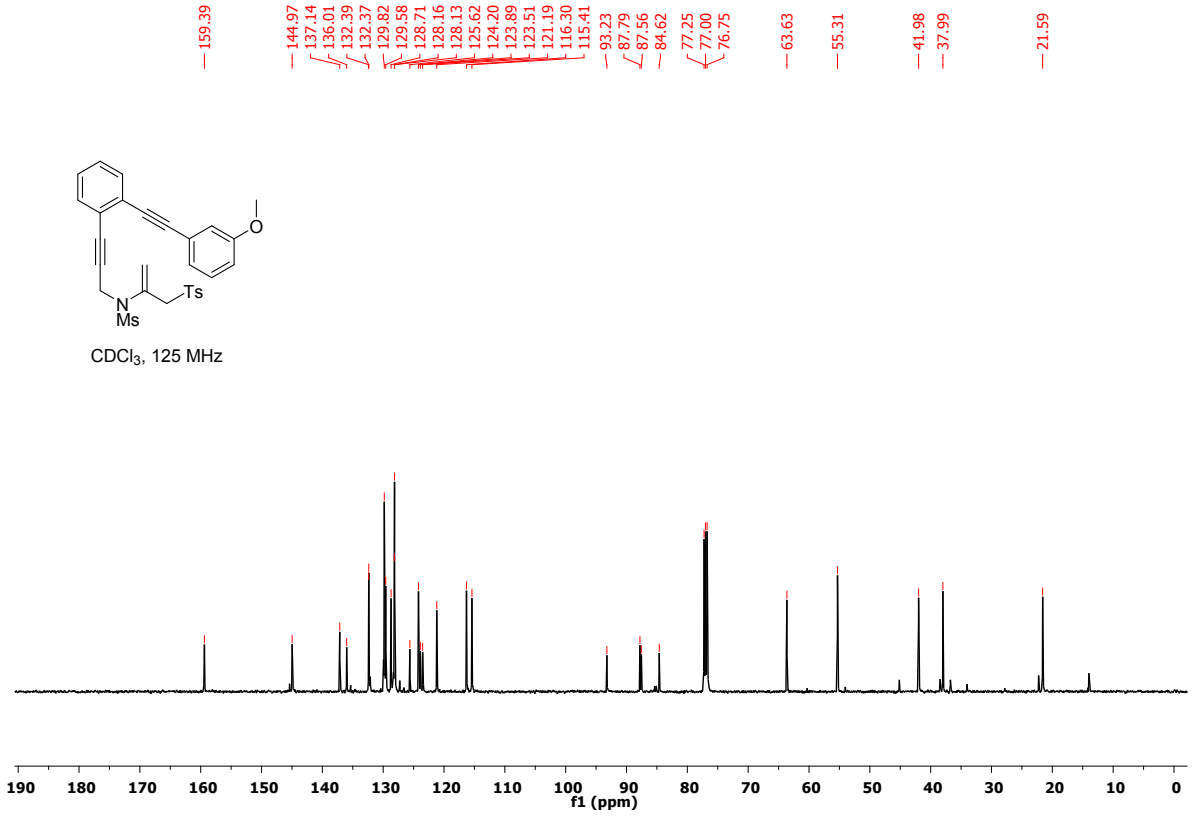
^{1}H NMR and ^{13}C NMR of 8i



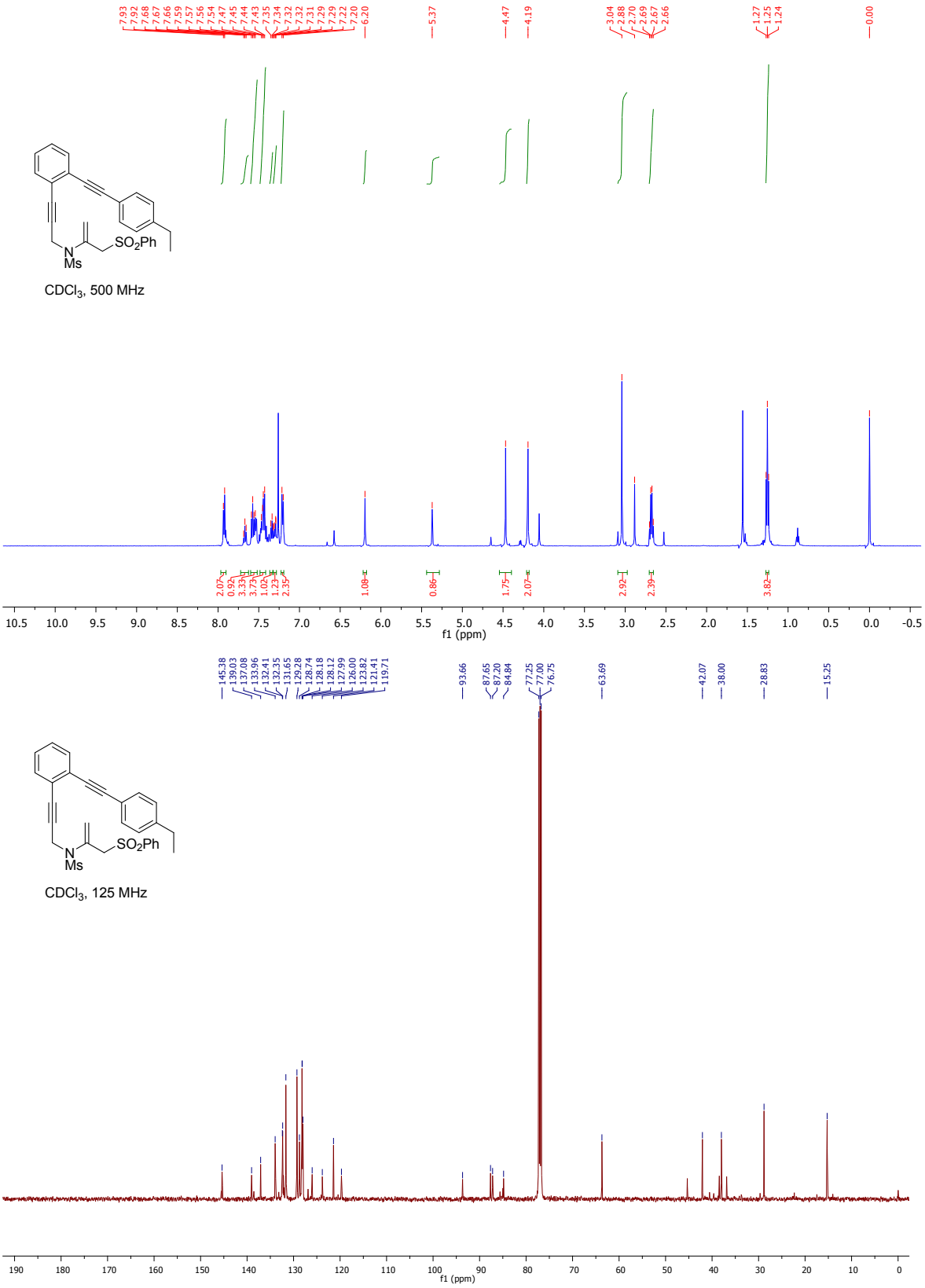


^{1}H NMR and ^{13}C NMR of 8j

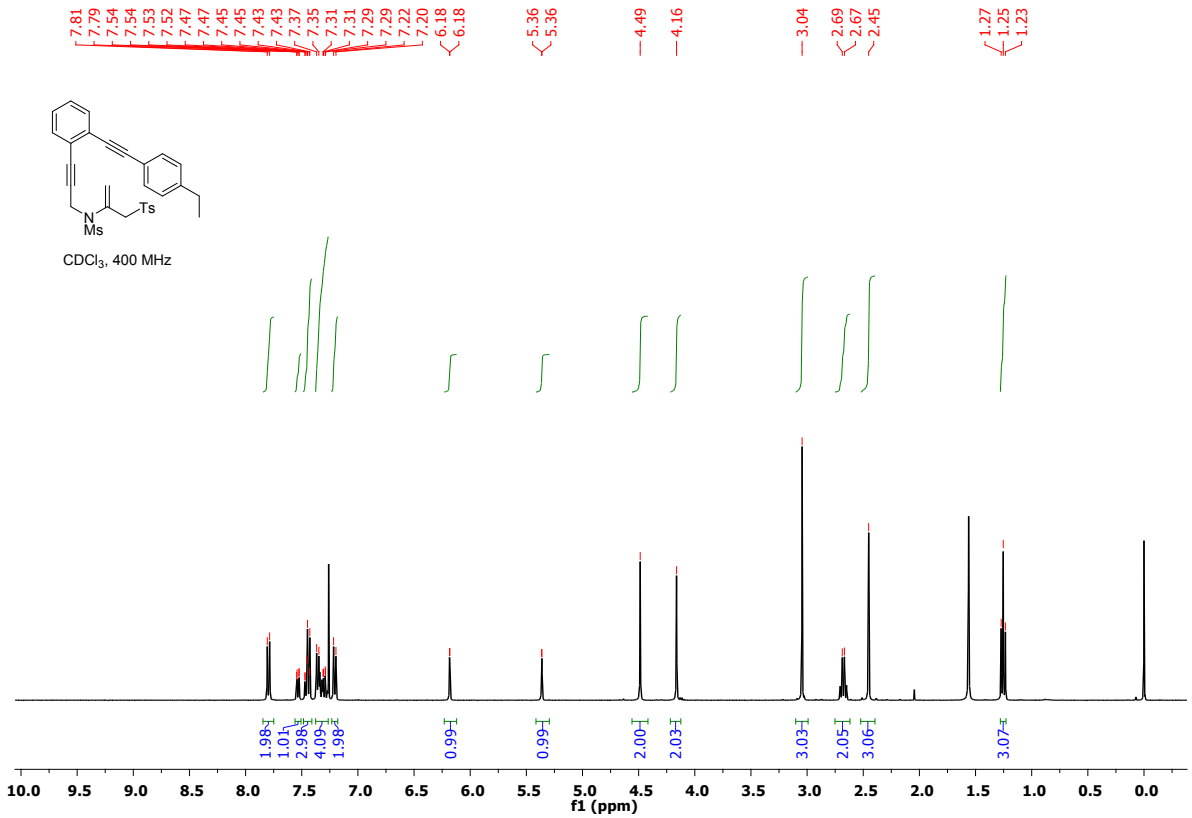


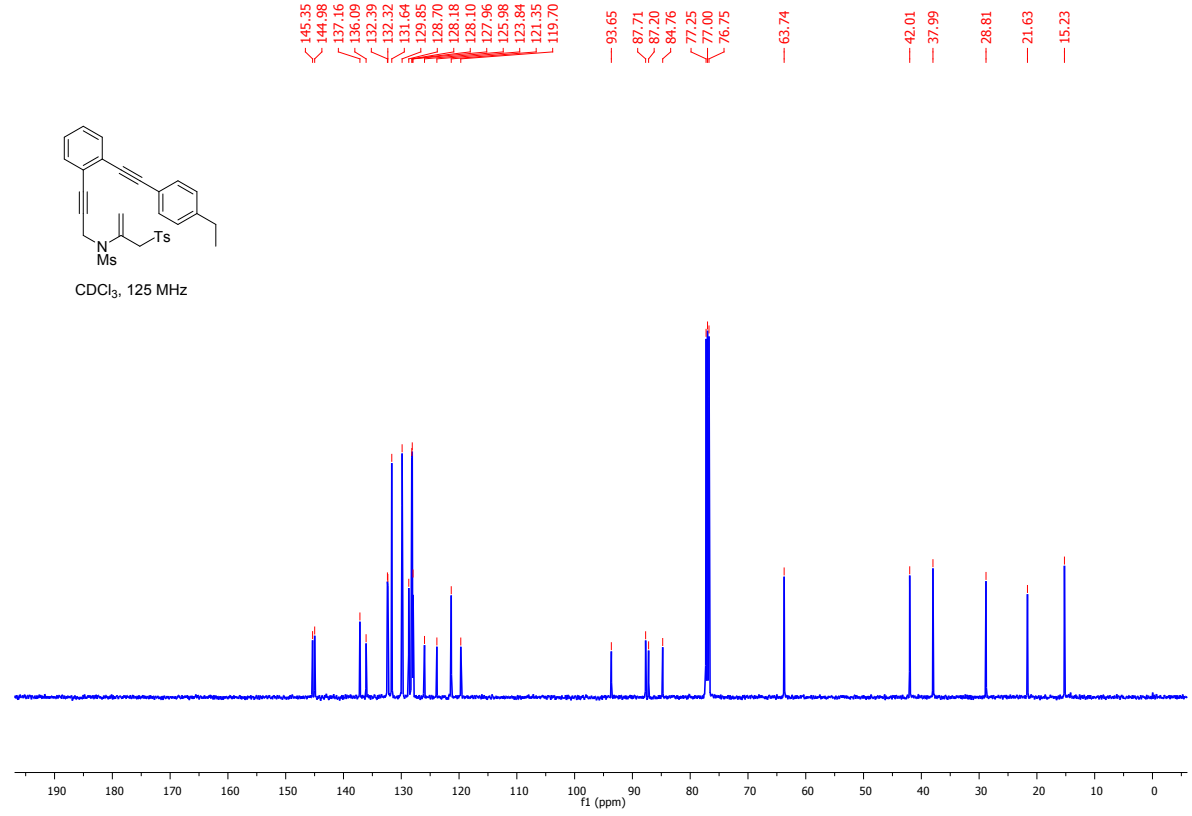


^{1}H NMR and ^{13}C NMR of 8k

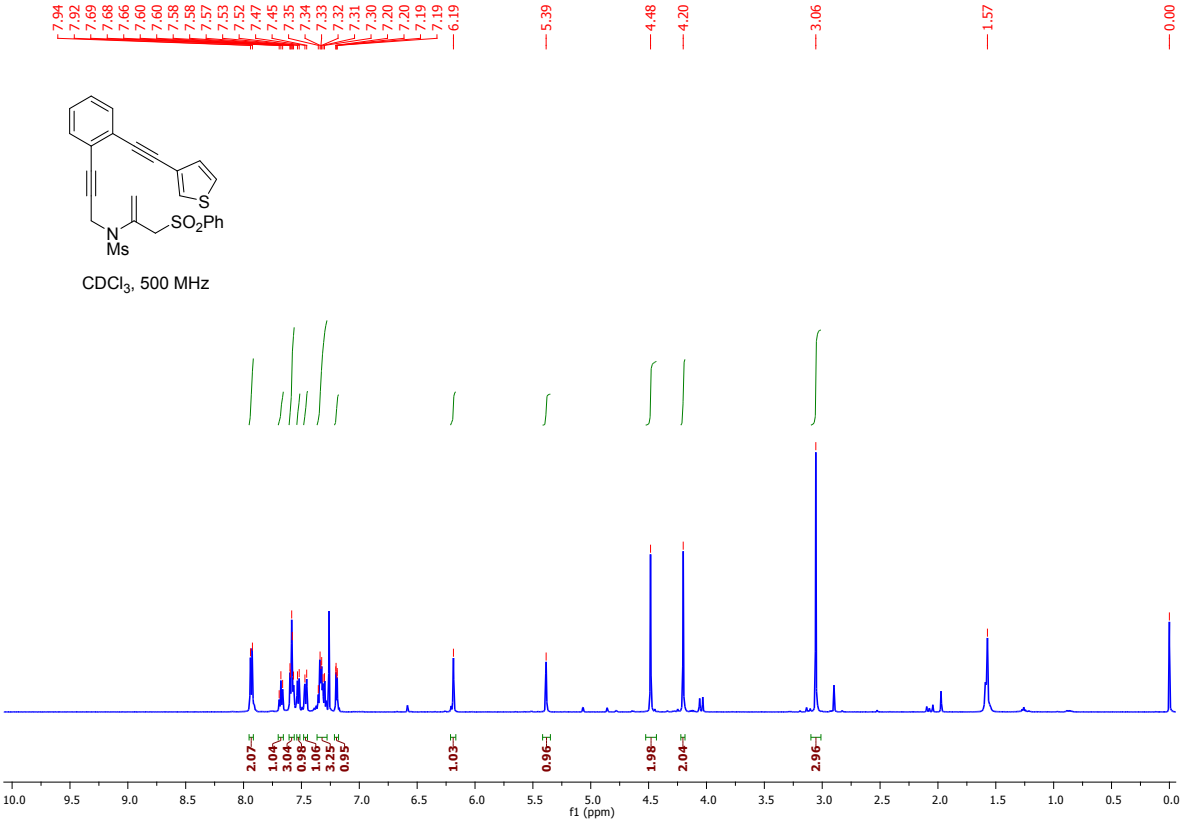


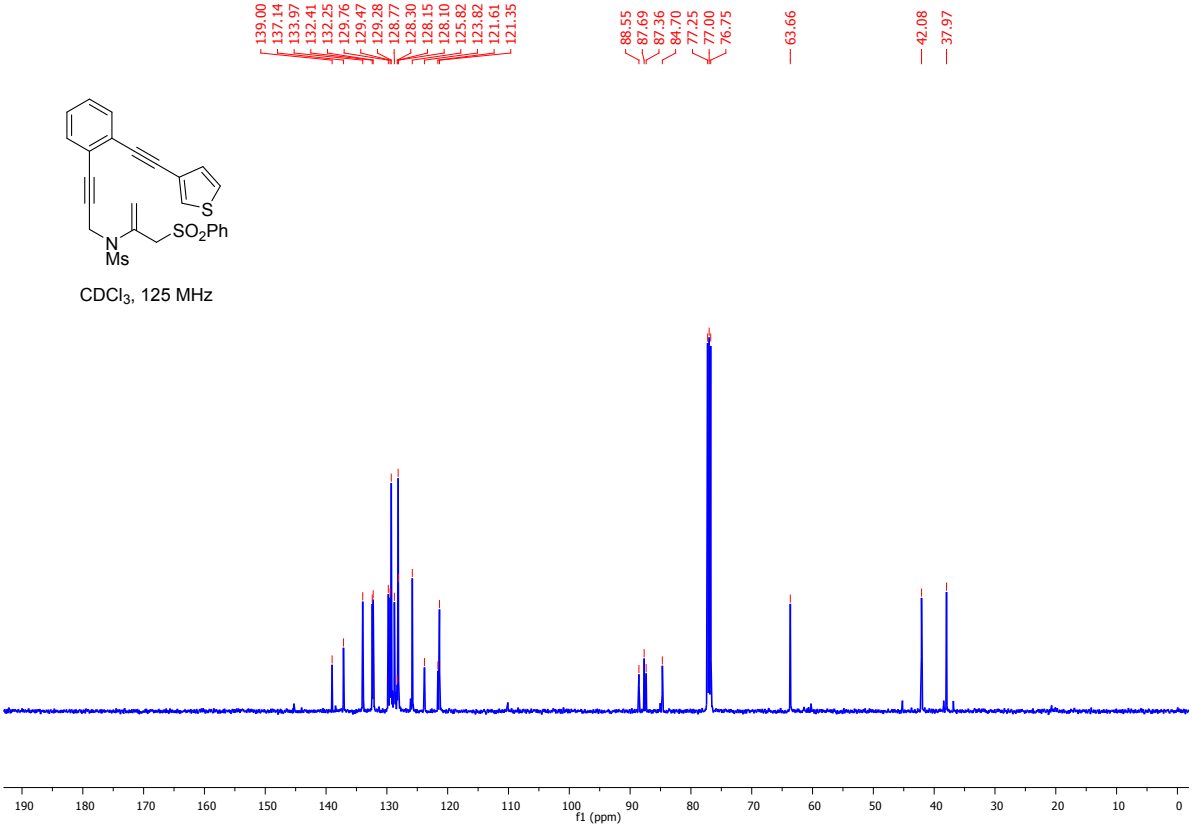
^{1}H NMR and ^{13}C NMR of 8l



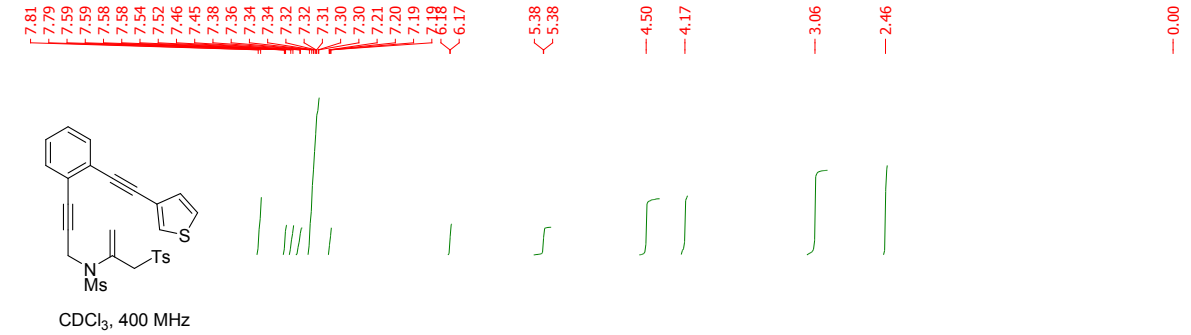


^{1}H NMR and ^{13}C NMR of 8m

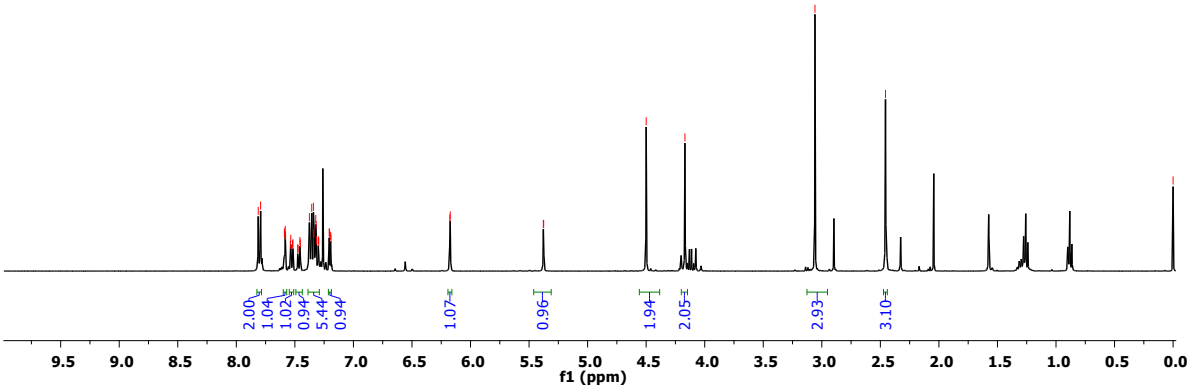


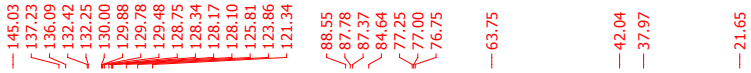


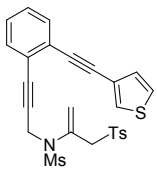
^{1}H NMR and ^{13}C NMR of 8n



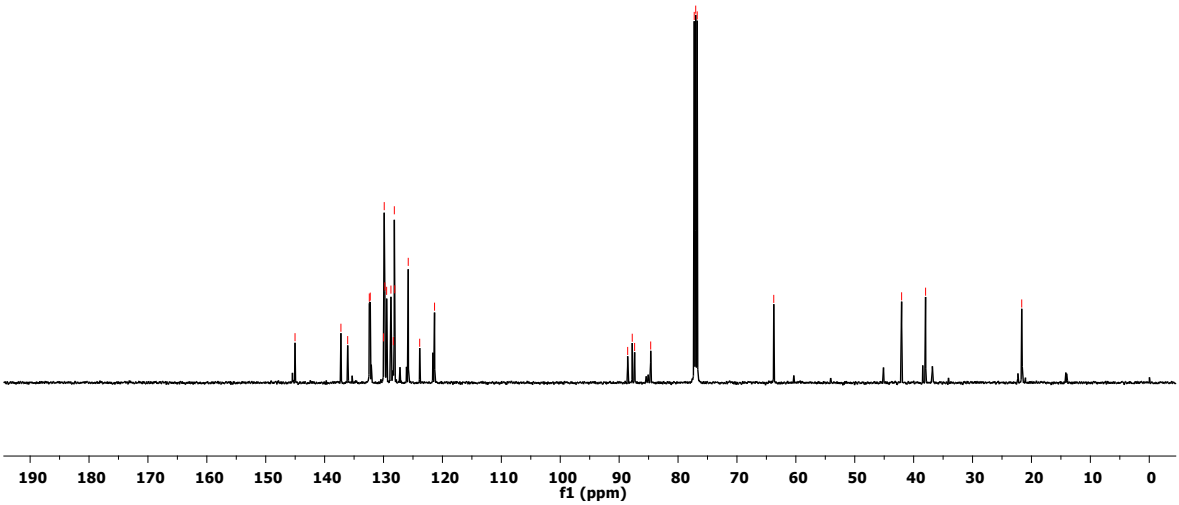
$CDCl_3$, 400 MHz



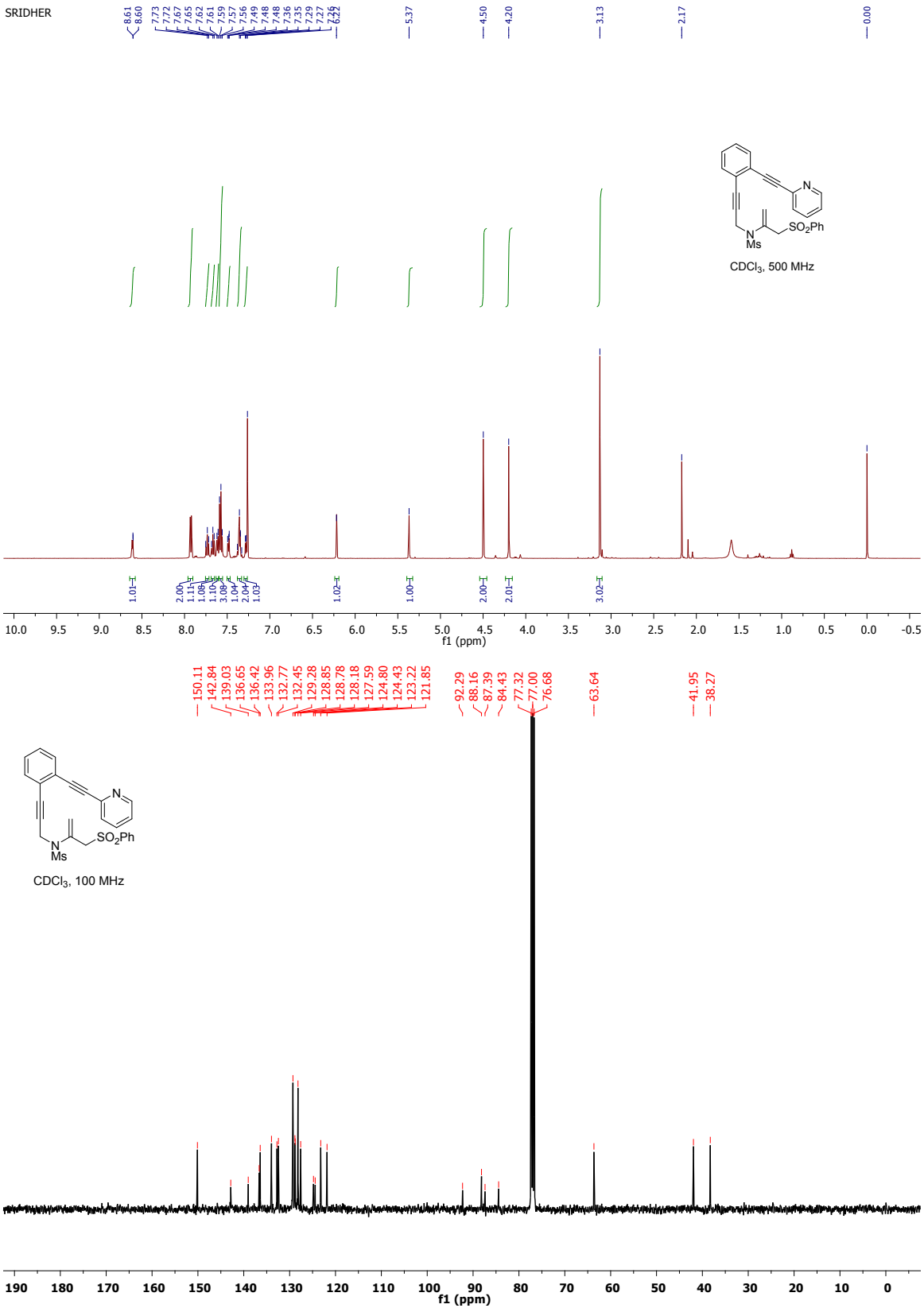




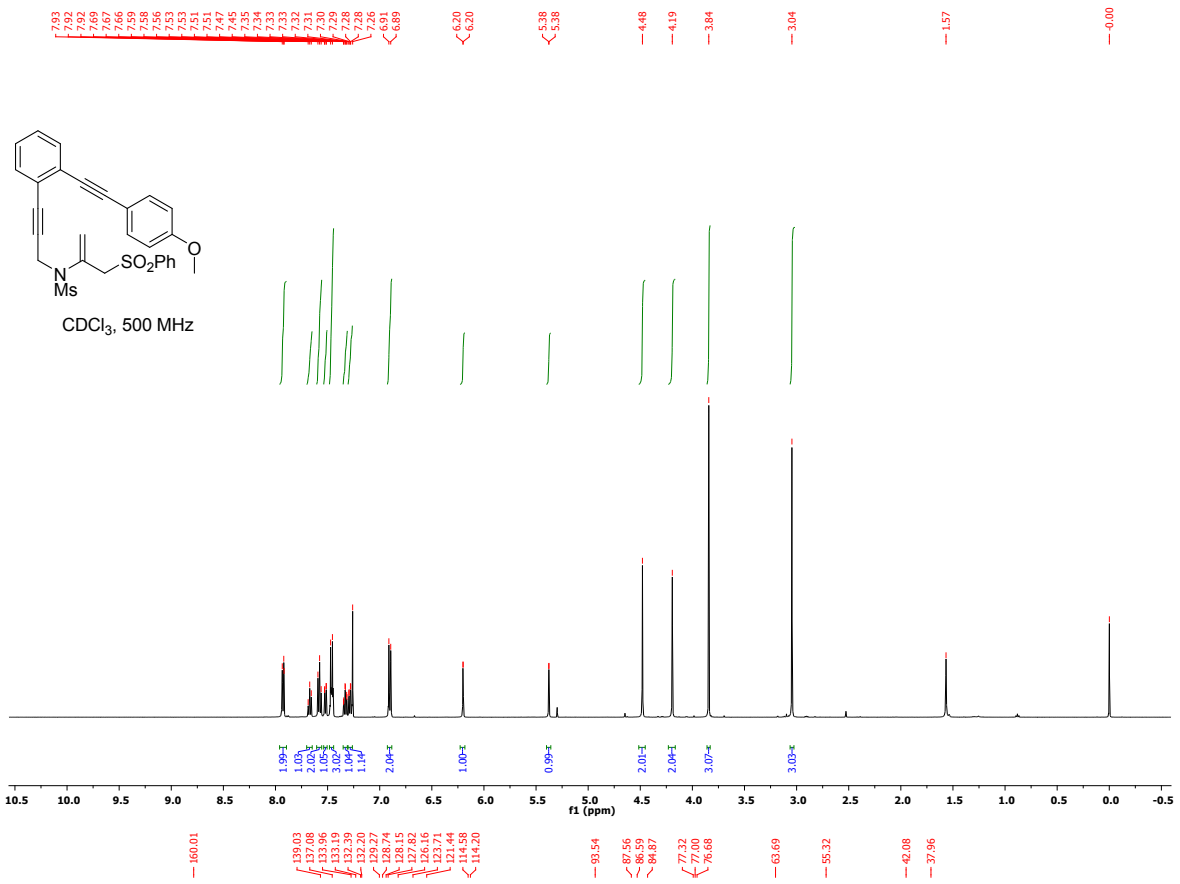
$CDCl_3$, 125 MHz

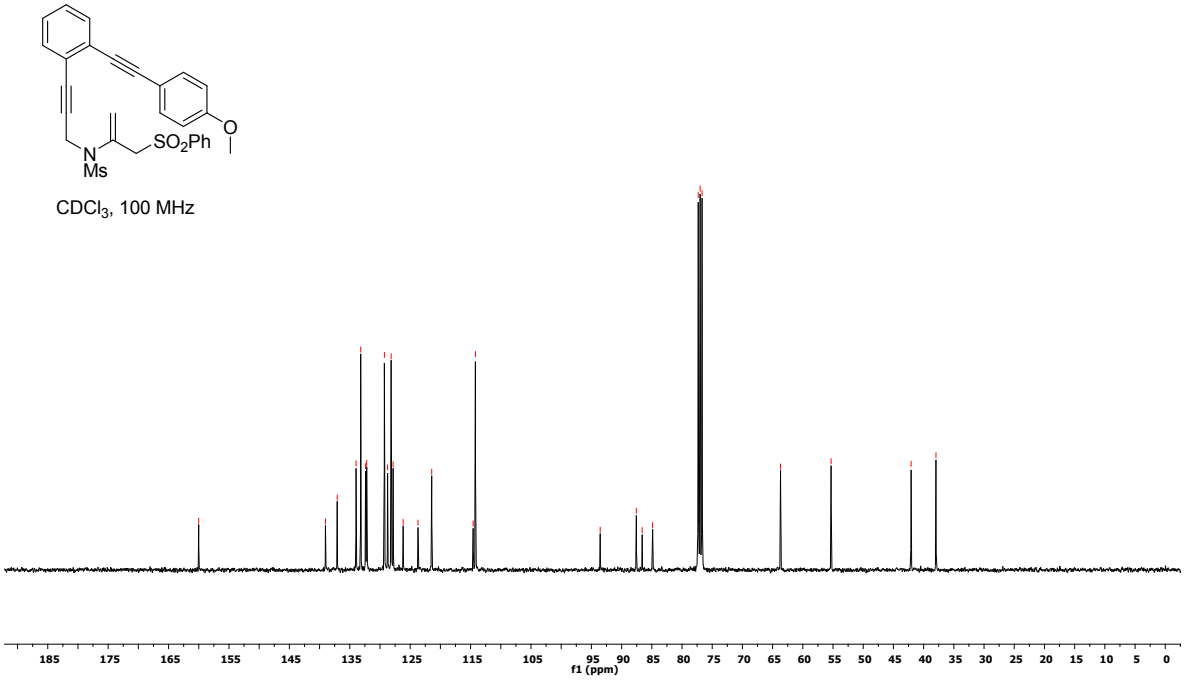


^{1}H NMR and ^{13}C NMR of 8o

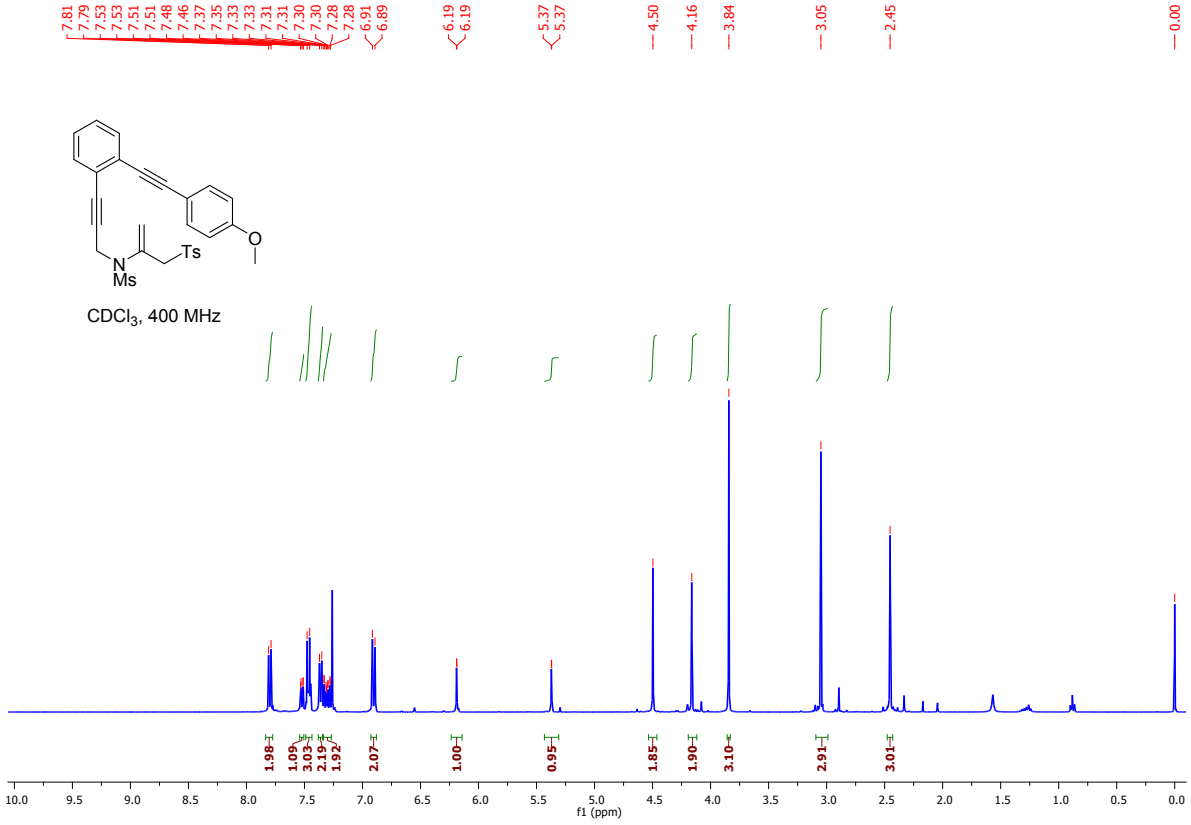


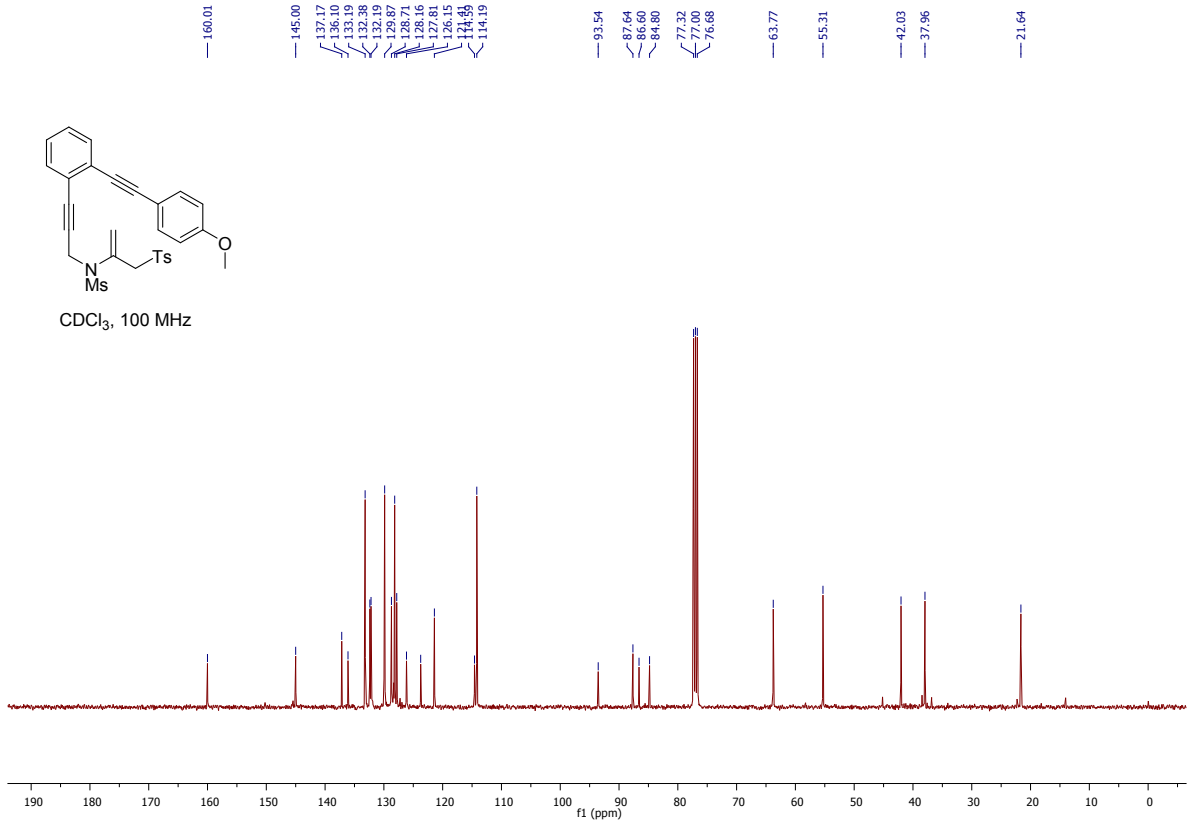
^{1}H NMR and ^{13}C NMR of 8p



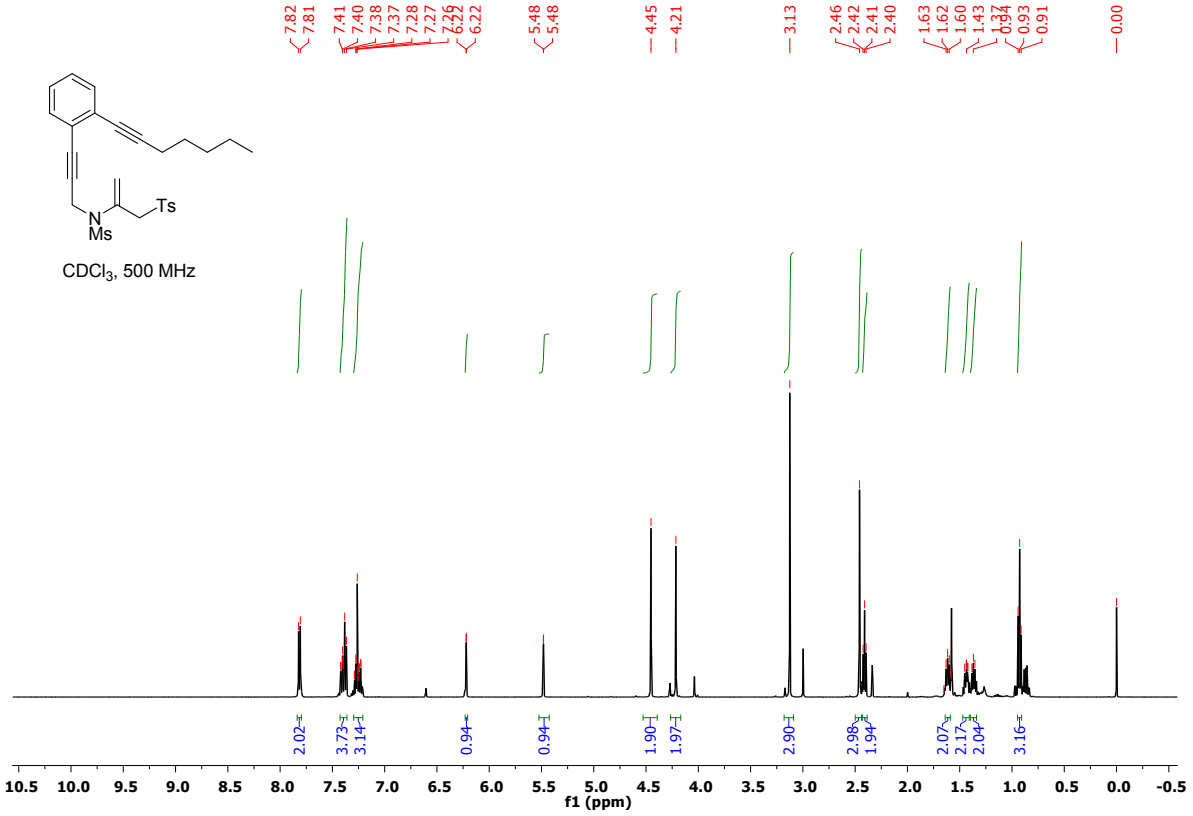


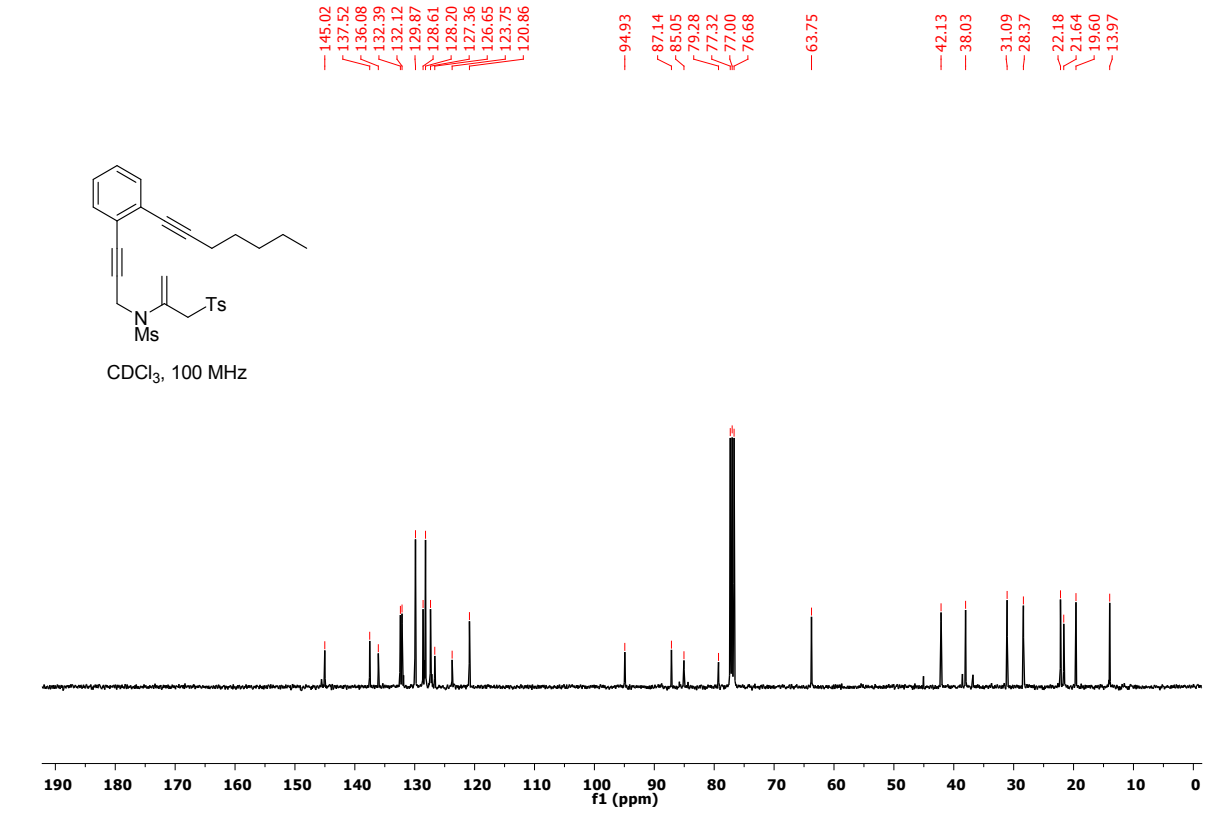
^{1}H NMR and ^{13}C NMR of 8q



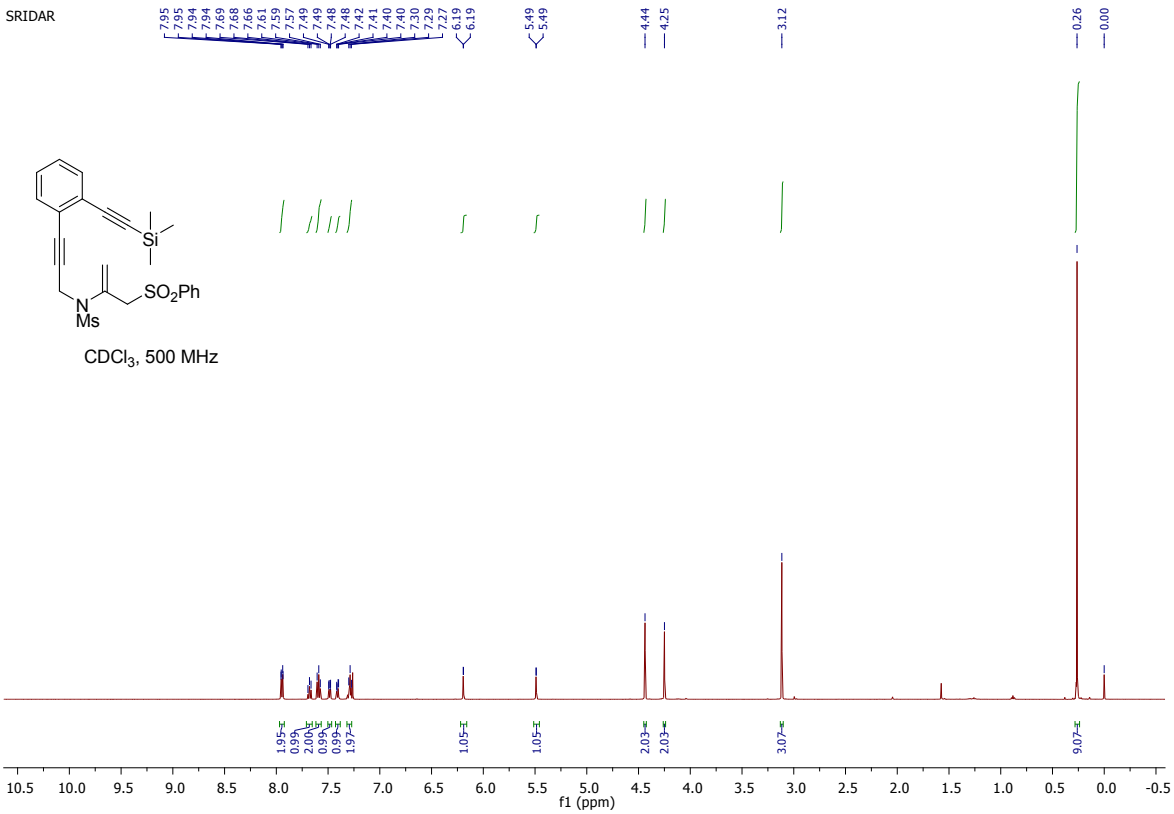


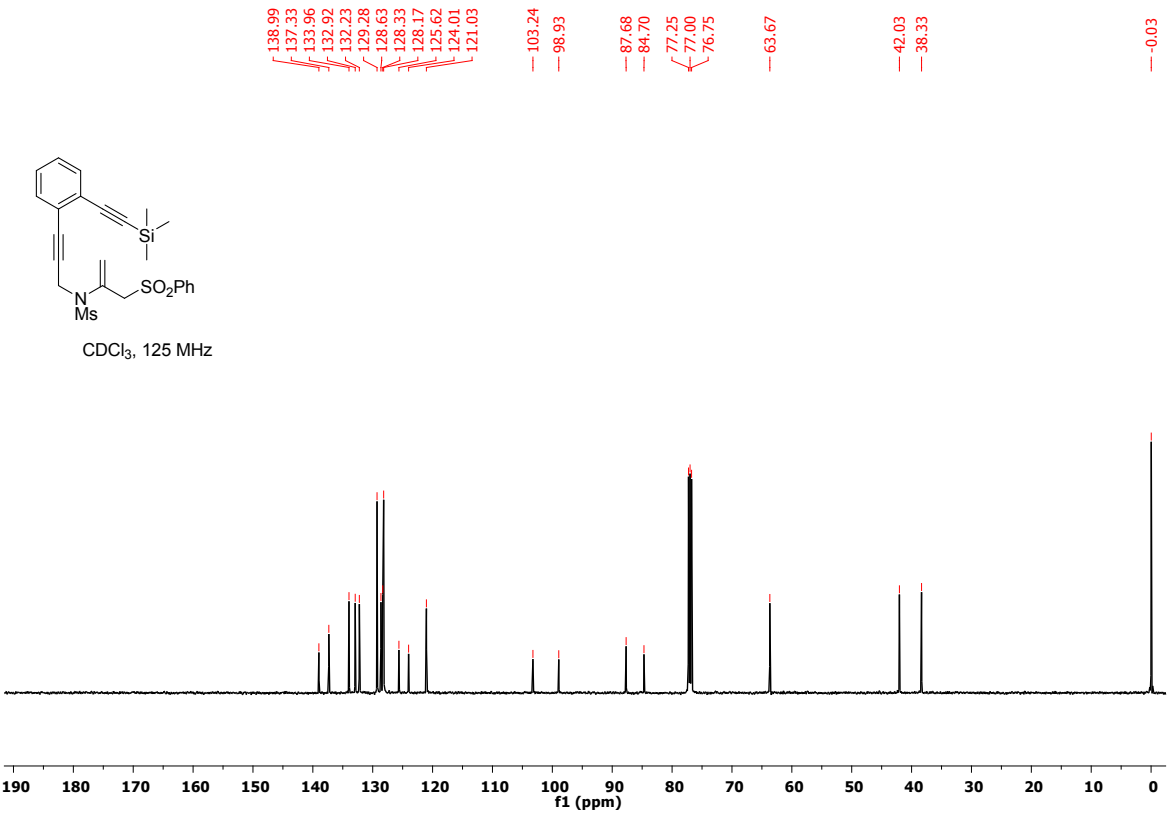
^{1}H NMR and ^{13}C NMR of 8r



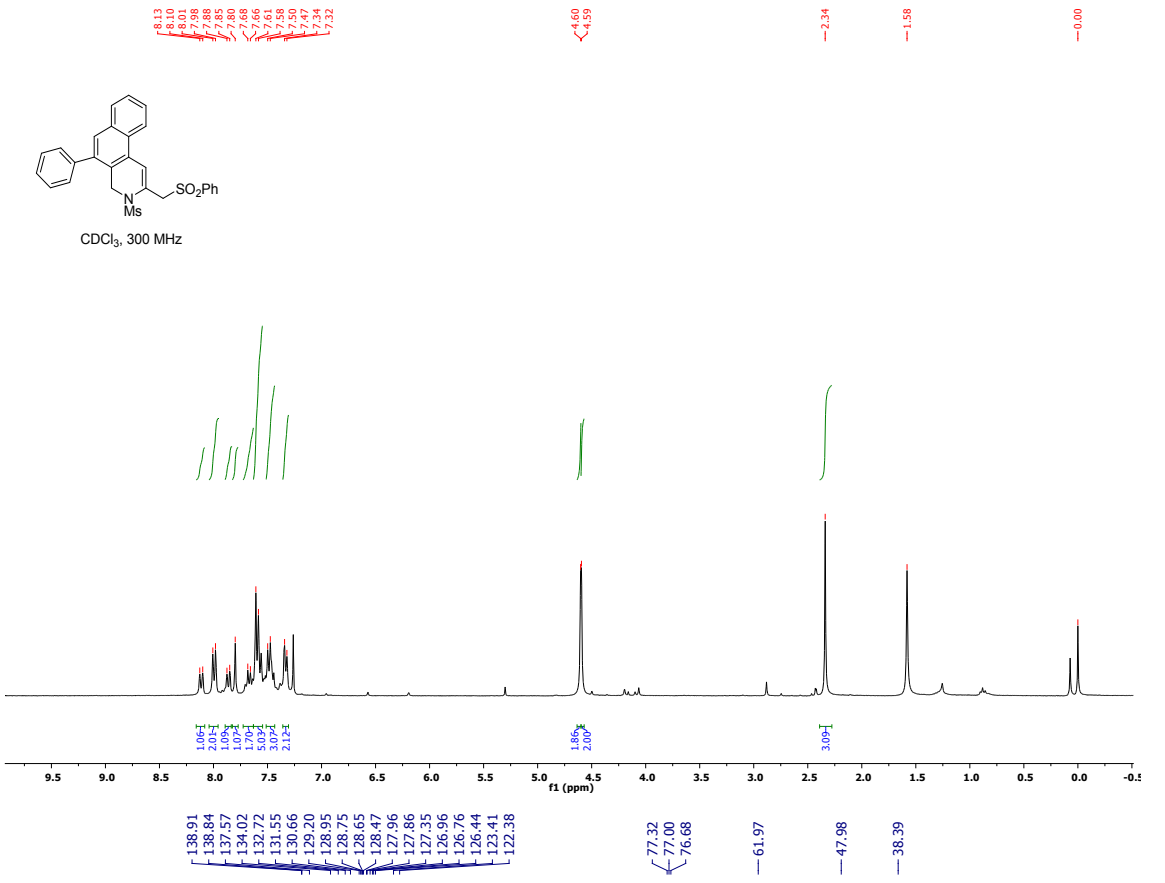


^{1}H NMR and ^{13}C NMR of 8s

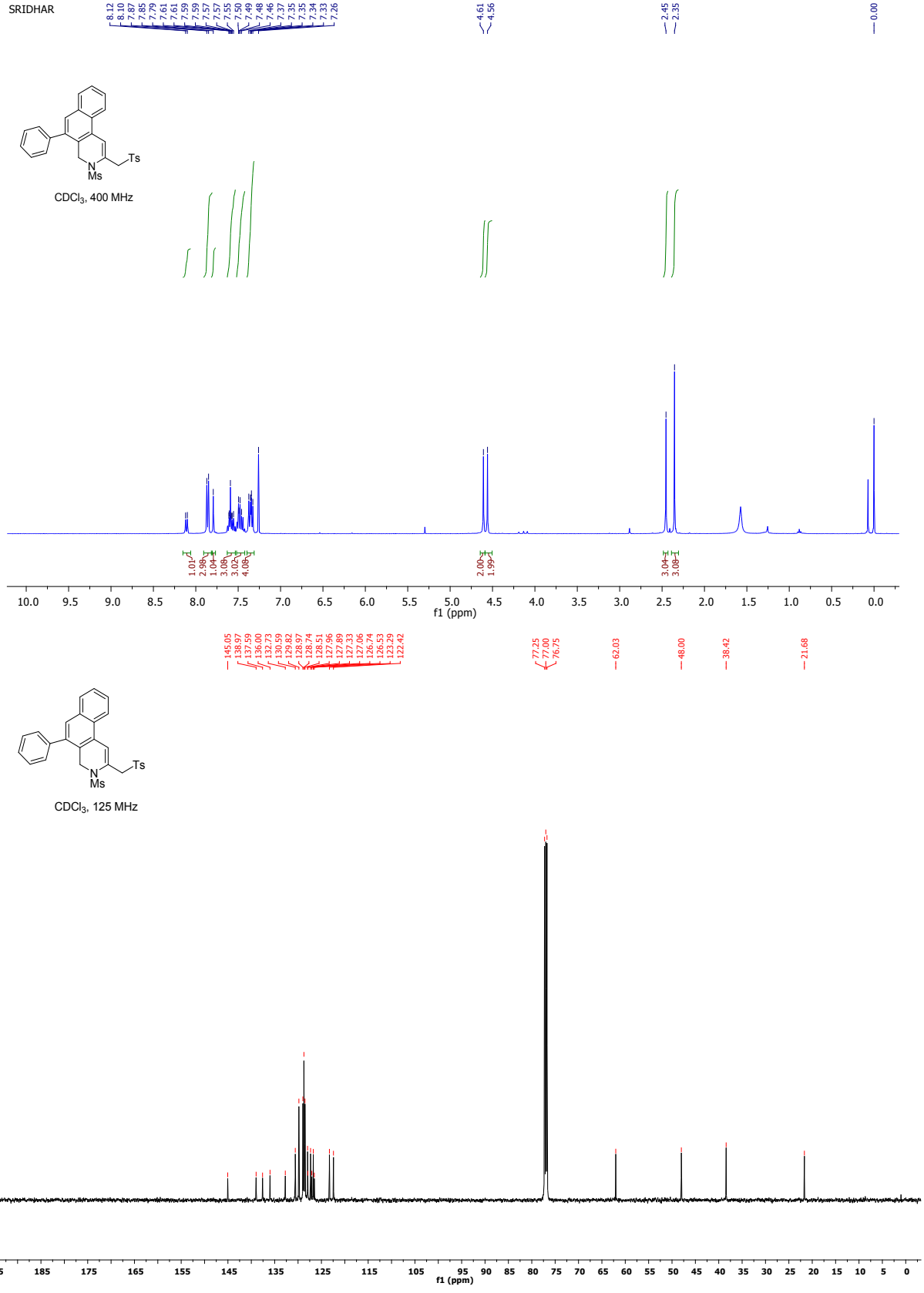




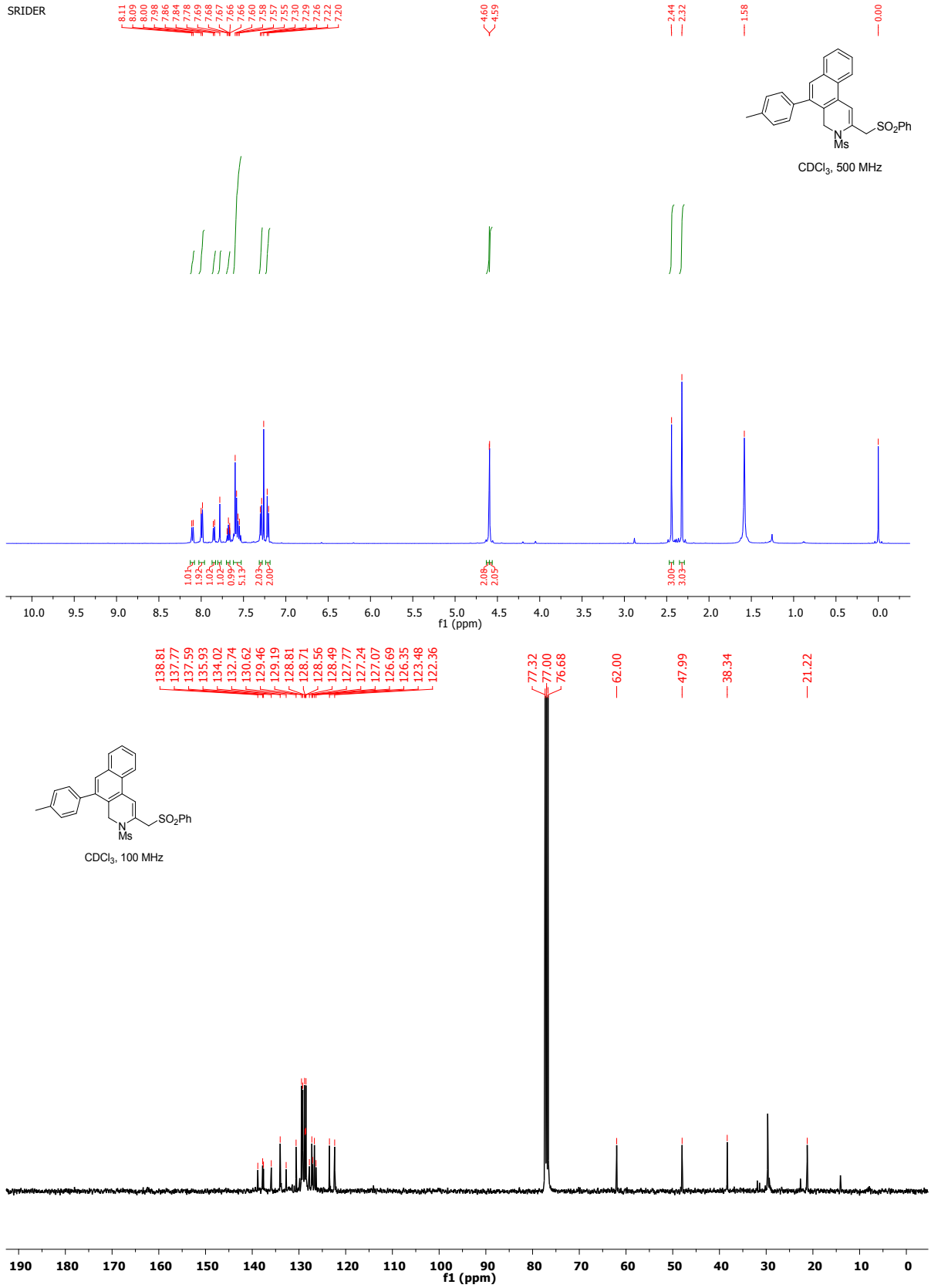
^{1}H NMR and ^{13}C NMR of 9a



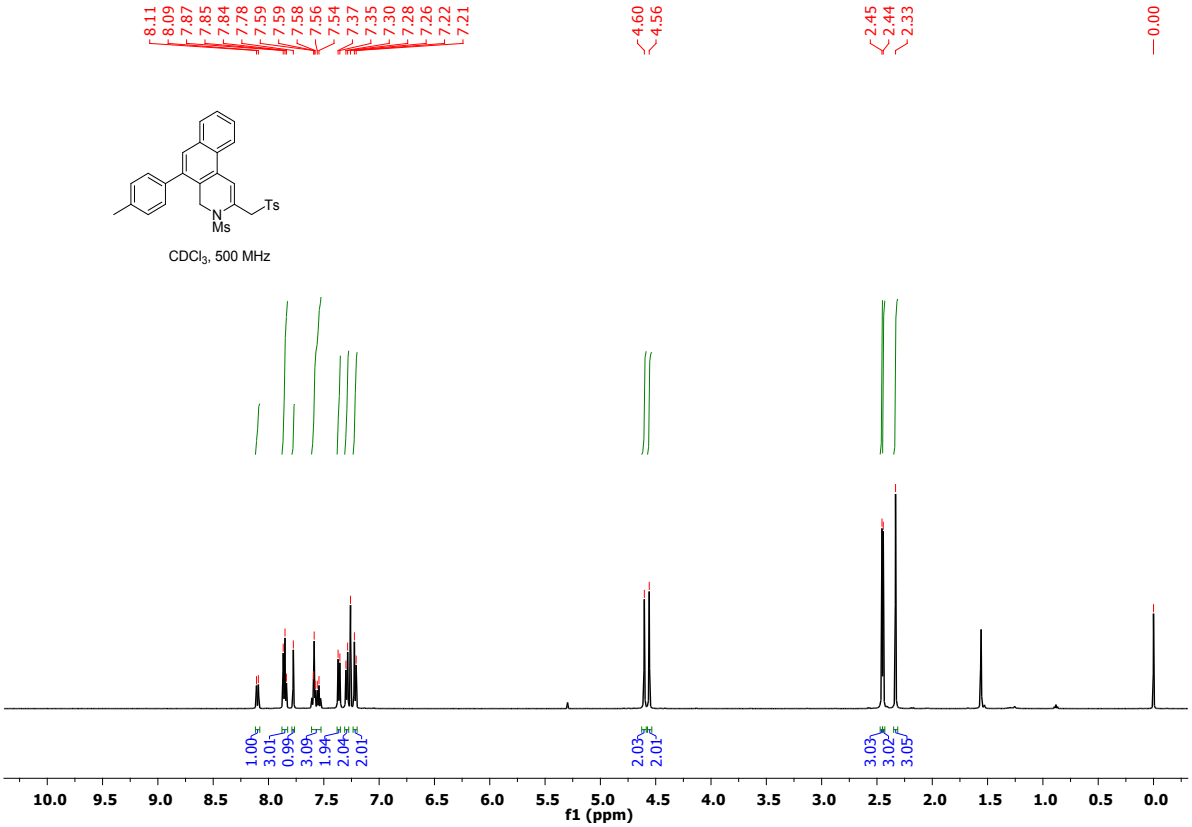
^{1}H NMR and ^{13}C NMR of 9b

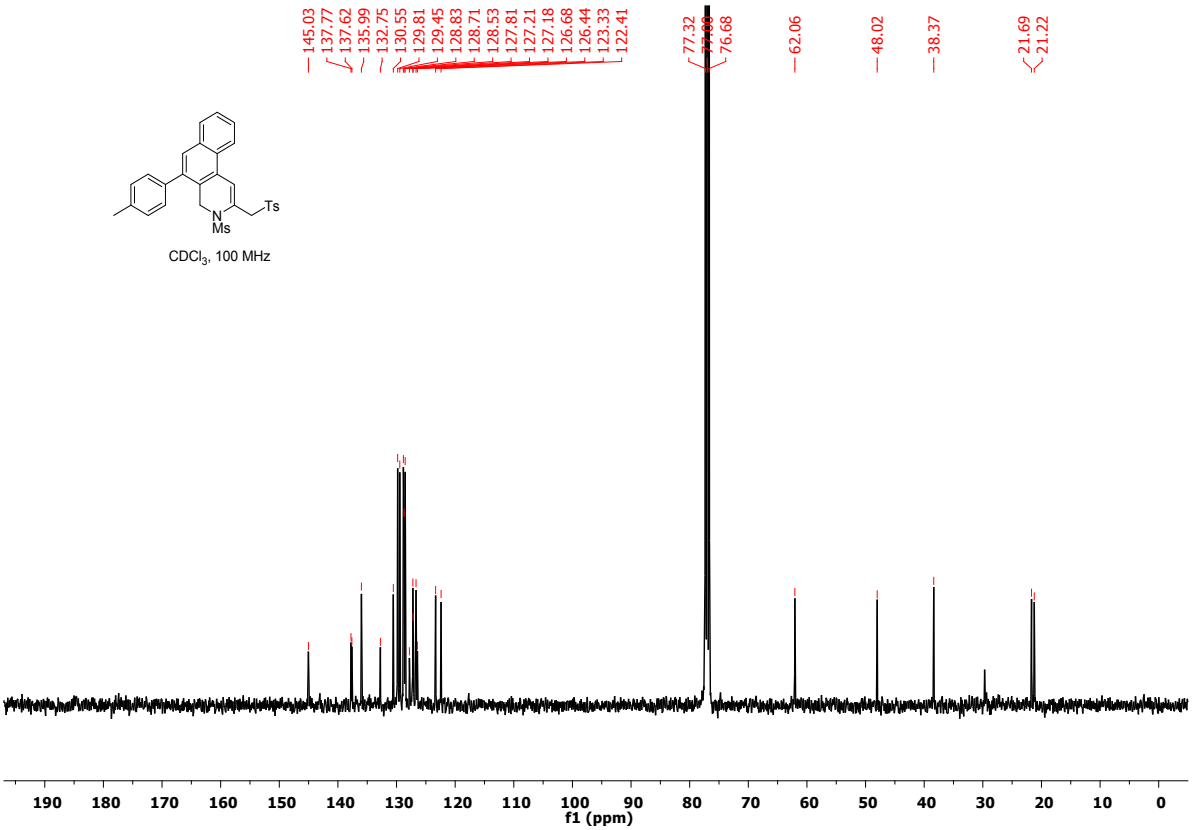


^{1}H NMR and ^{13}C NMR of 9c

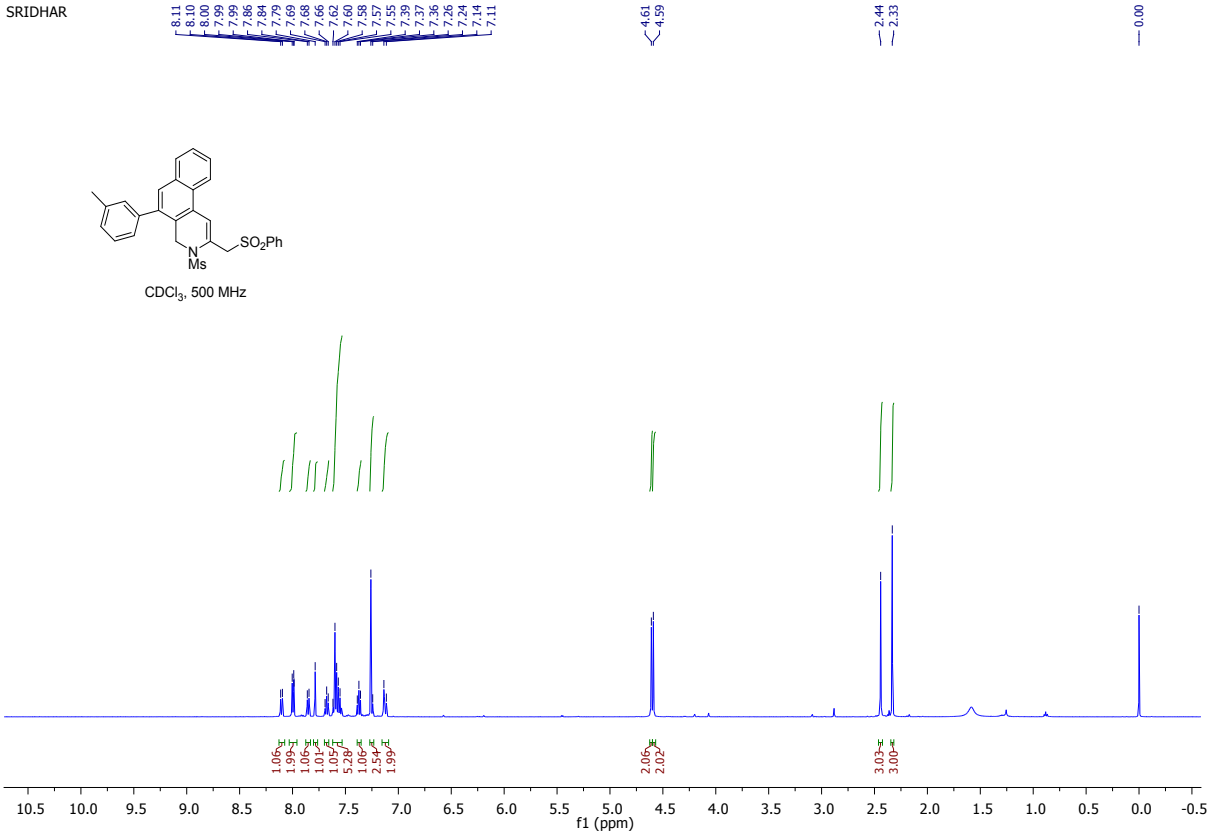


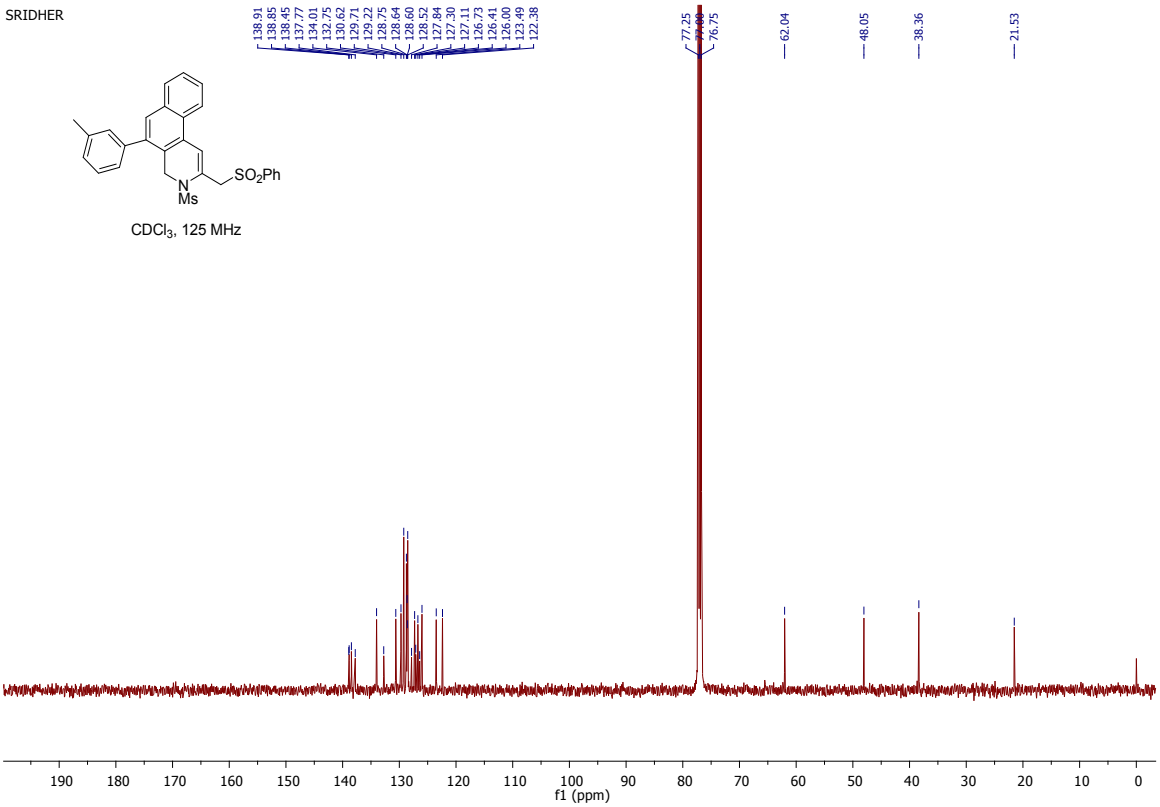
^{1}H NMR and ^{13}C NMR of 9d



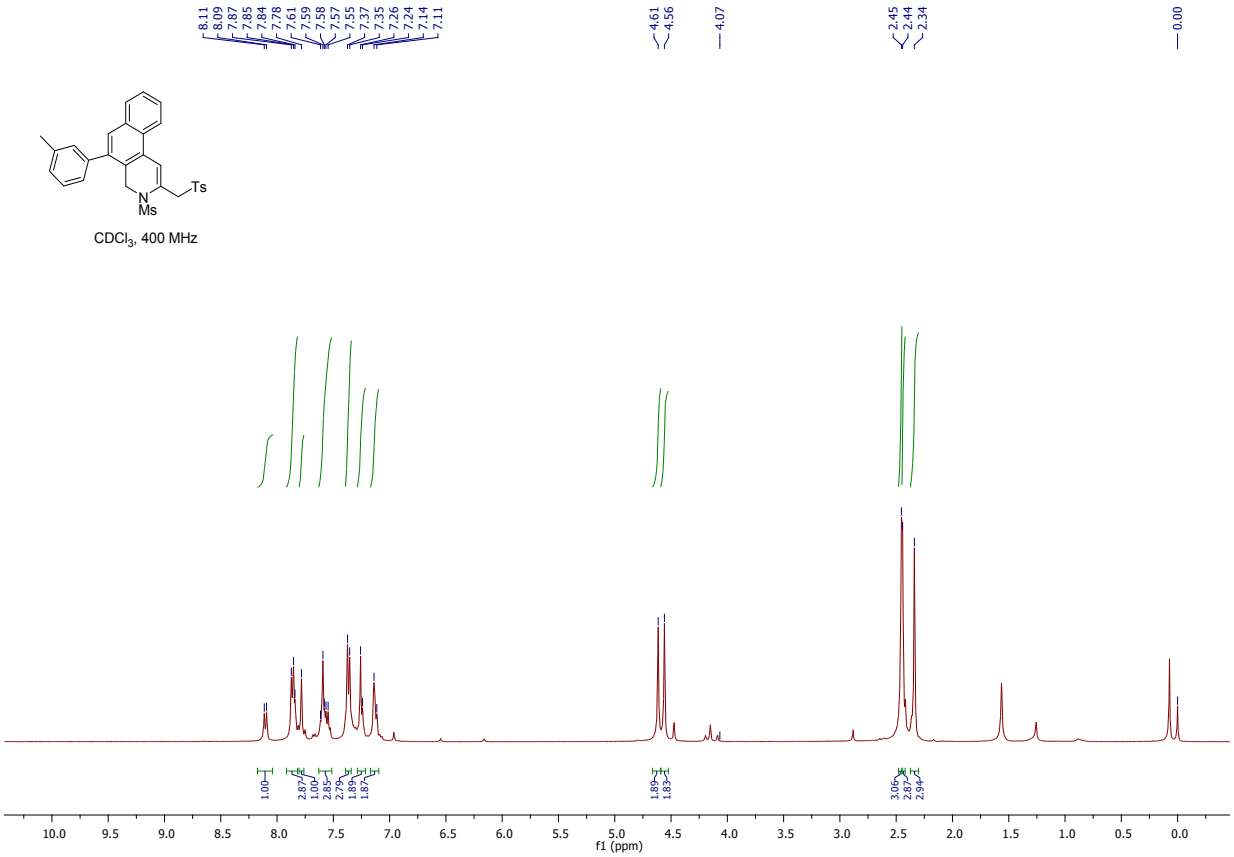


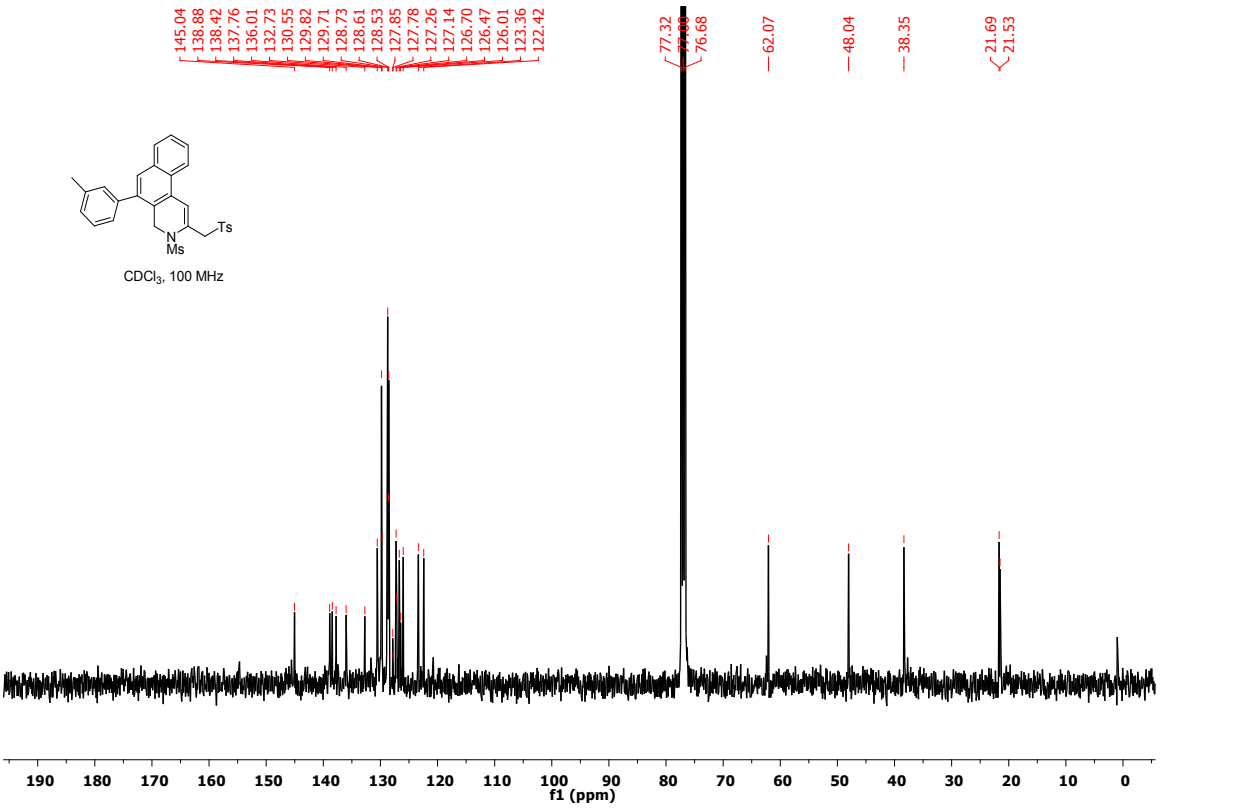
^{1}H NMR and ^{13}C NMR of 9e



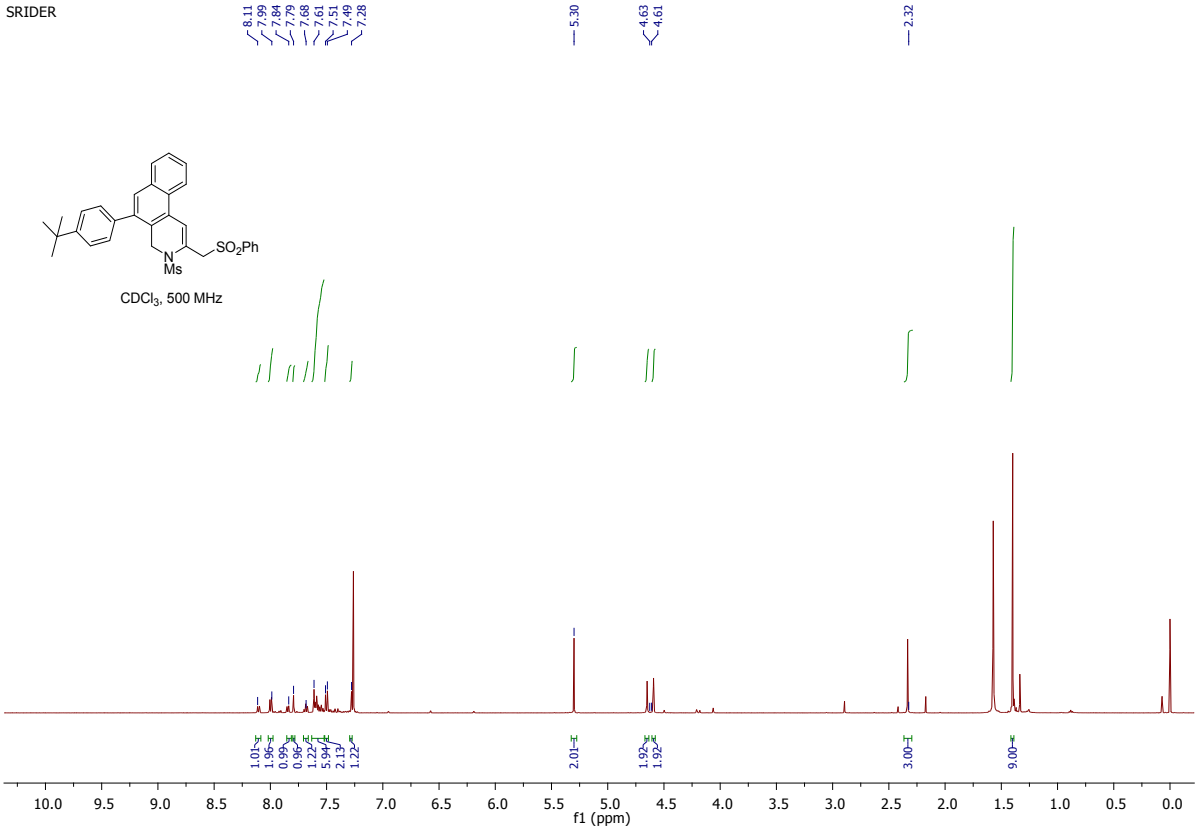


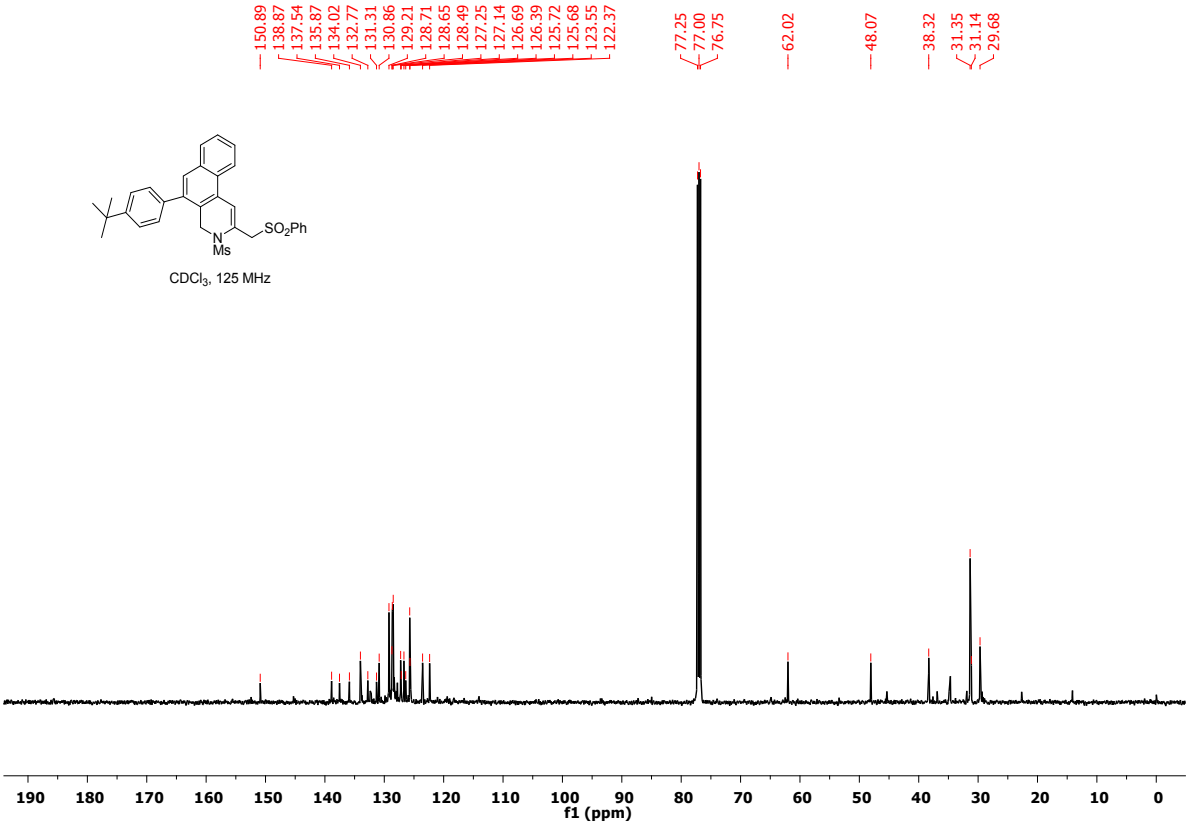
^{1}H NMR and ^{13}C NMR of 9f



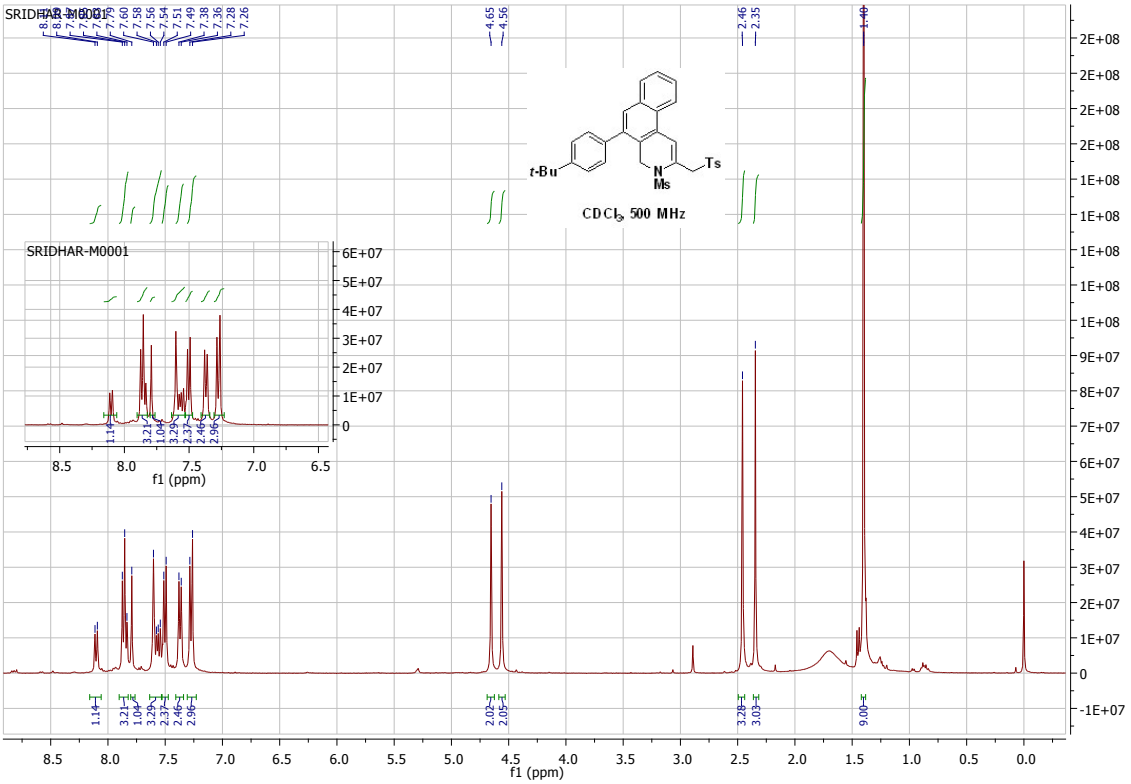


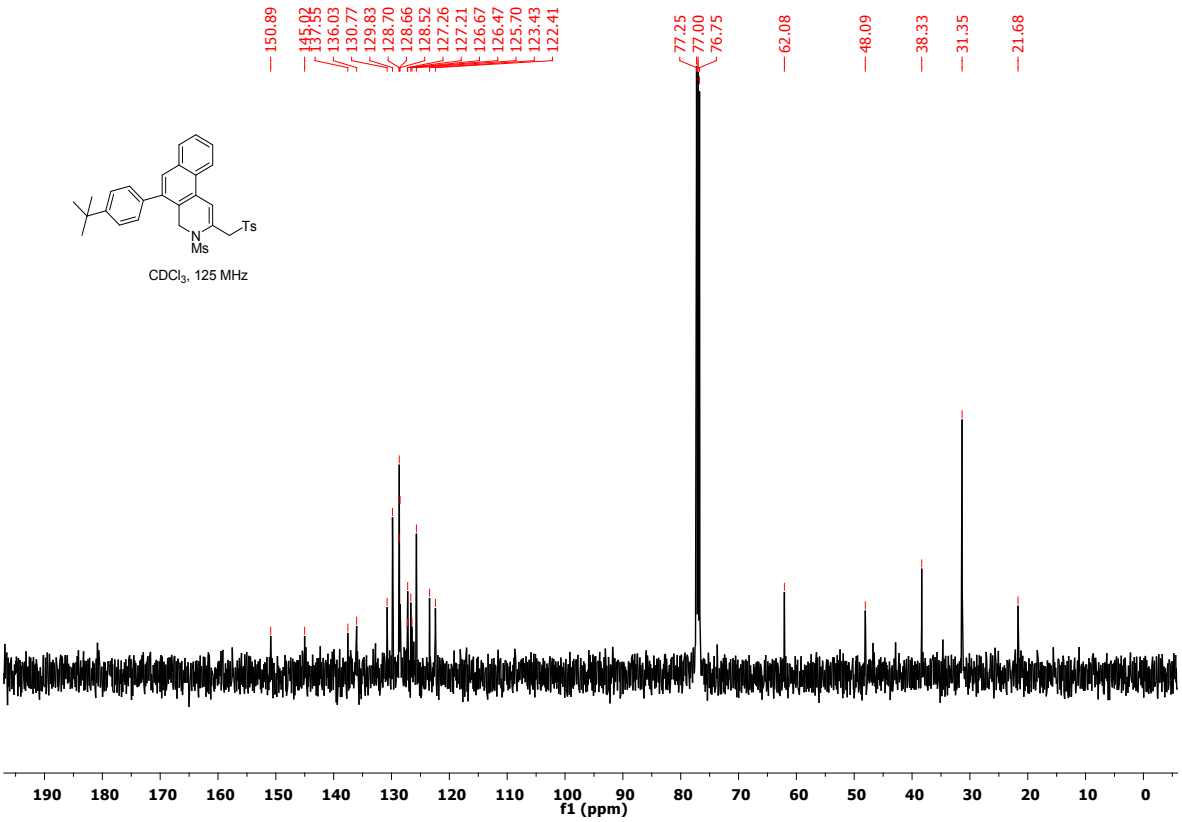
^{1}H NMR and ^{13}C NMR of 9g



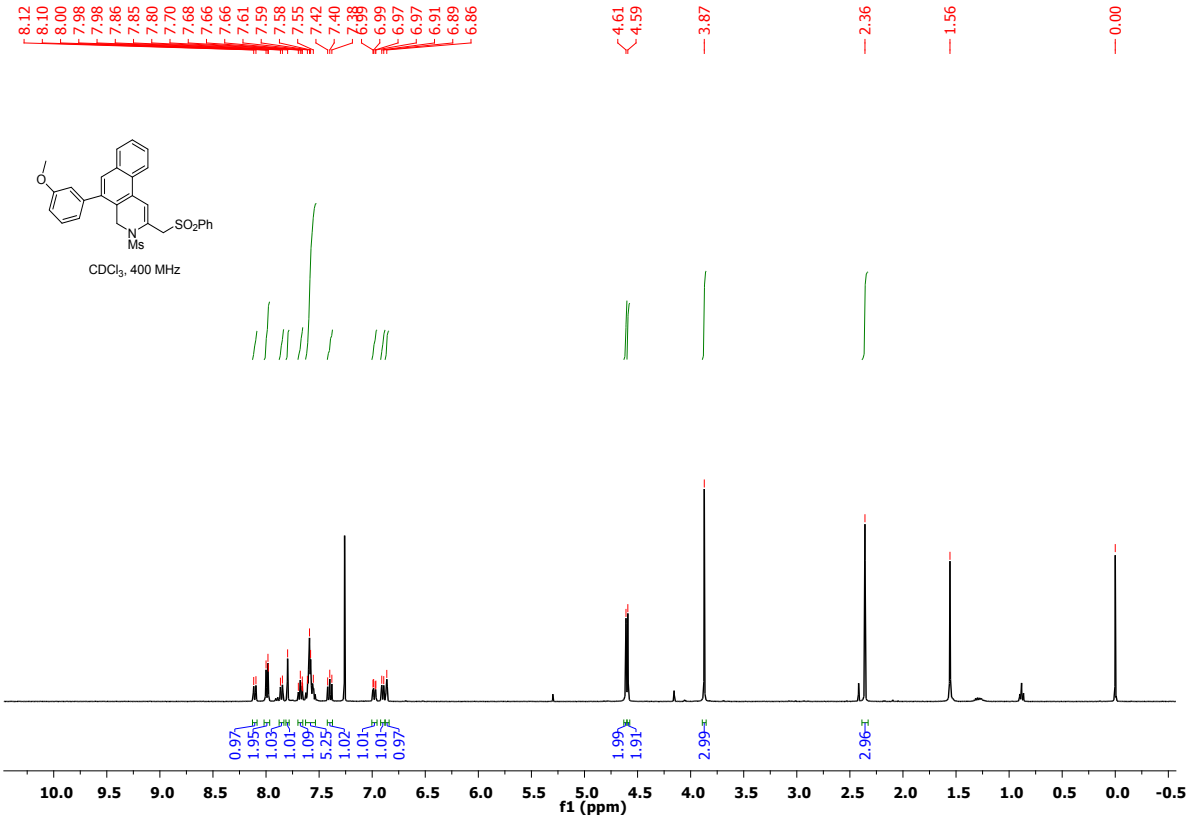


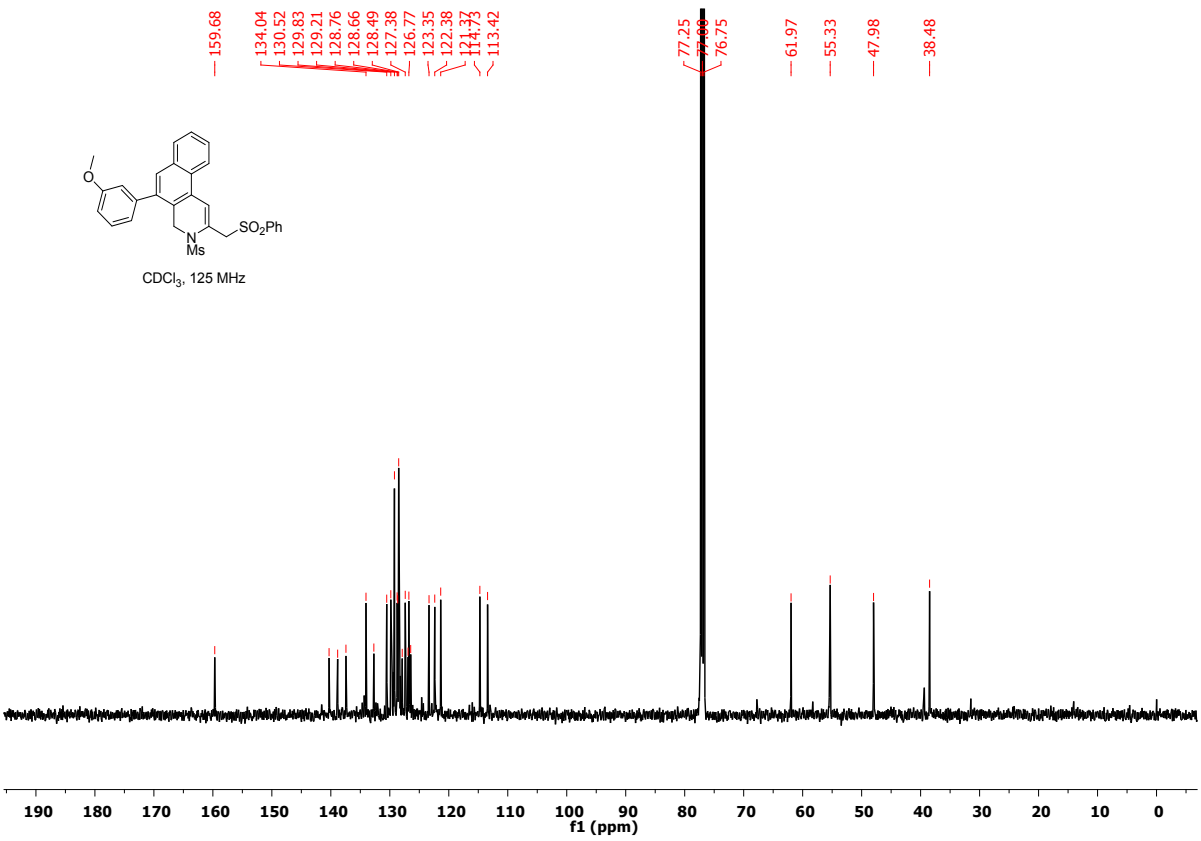
^{1}H NMR and ^{13}C NMR of 9h



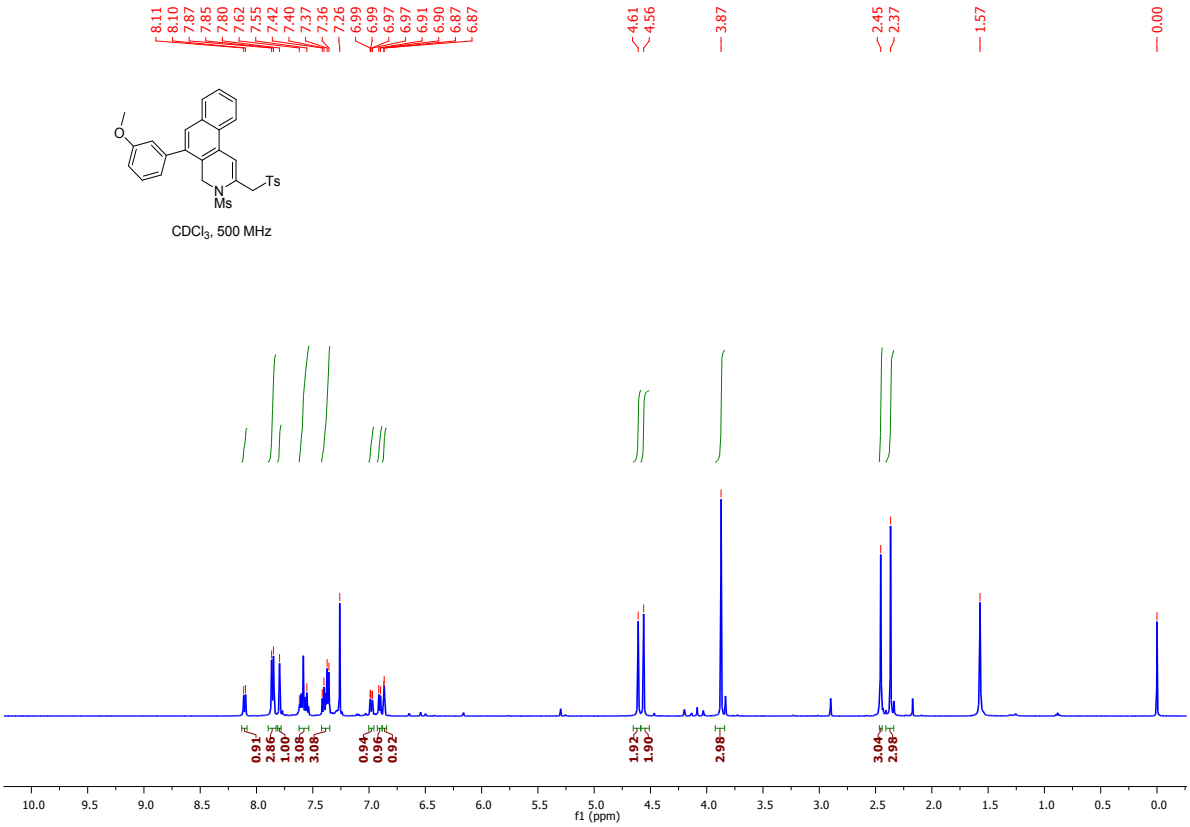


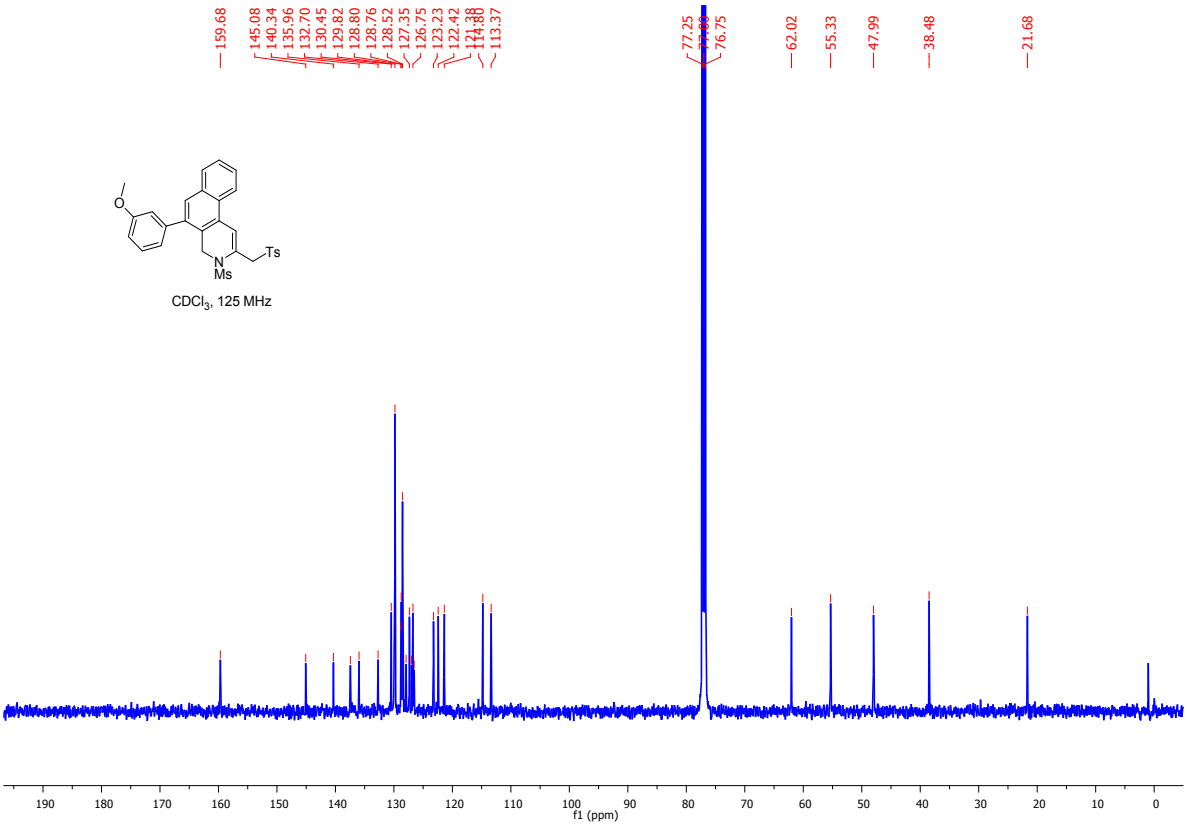
^{1}H NMR and ^{13}C NMR of 9i



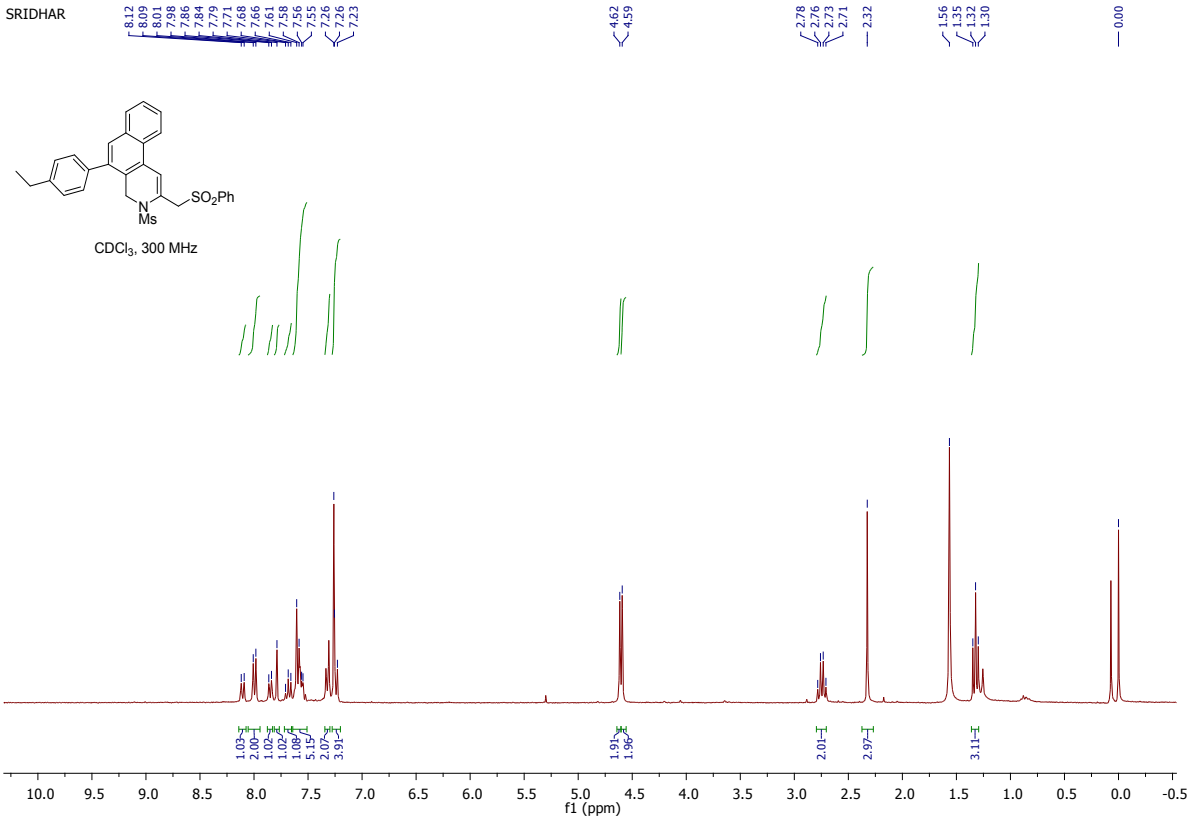


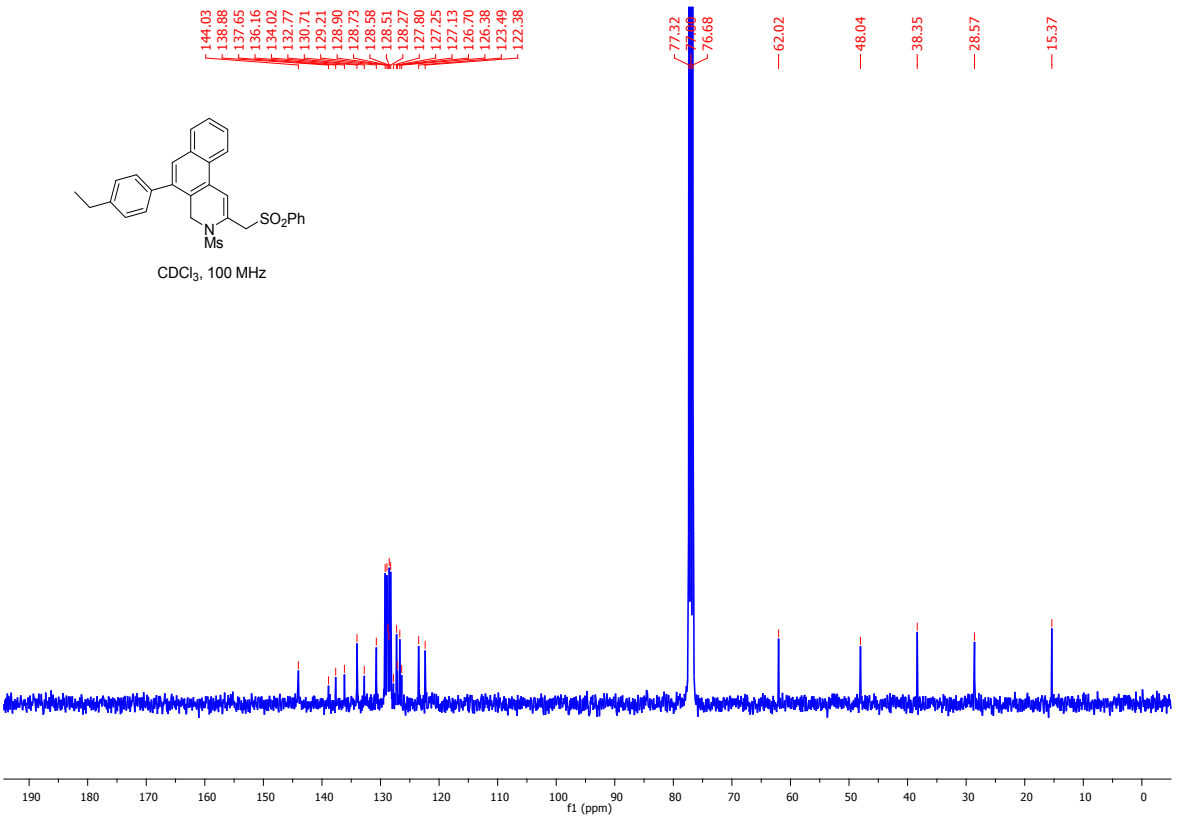
^{1}H NMR and ^{13}C NMR of 9j



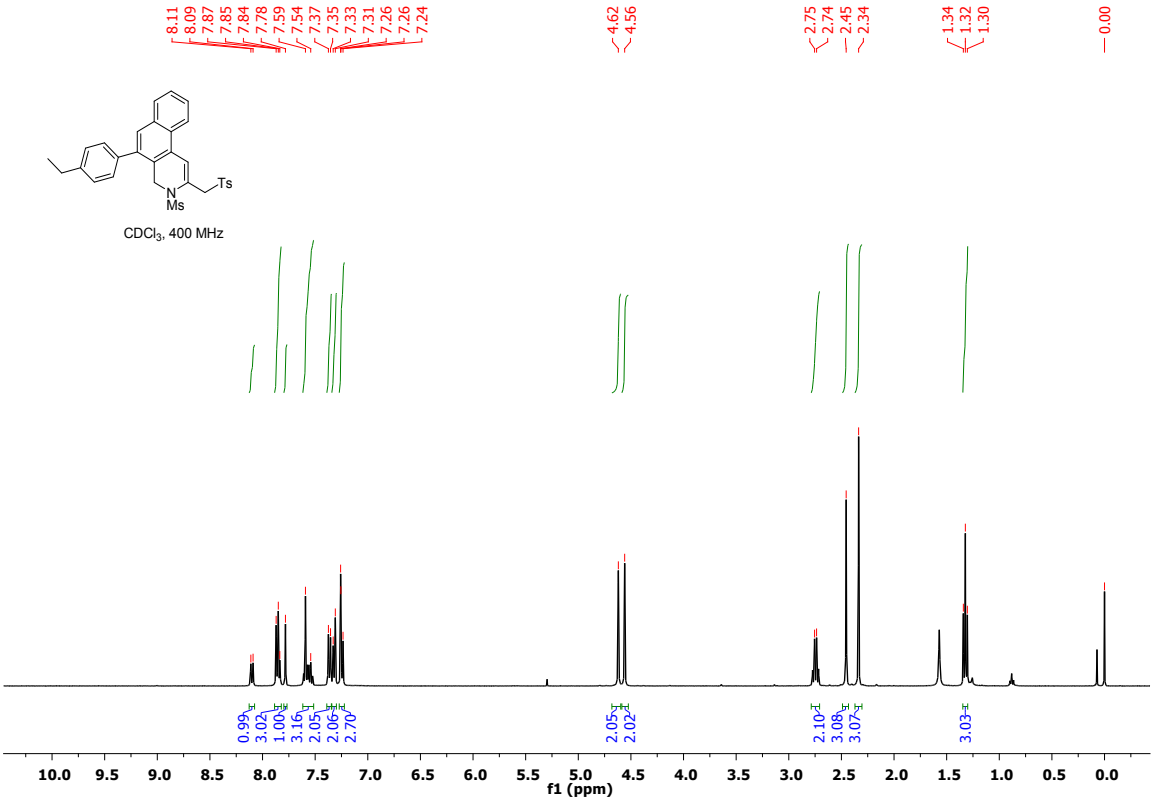


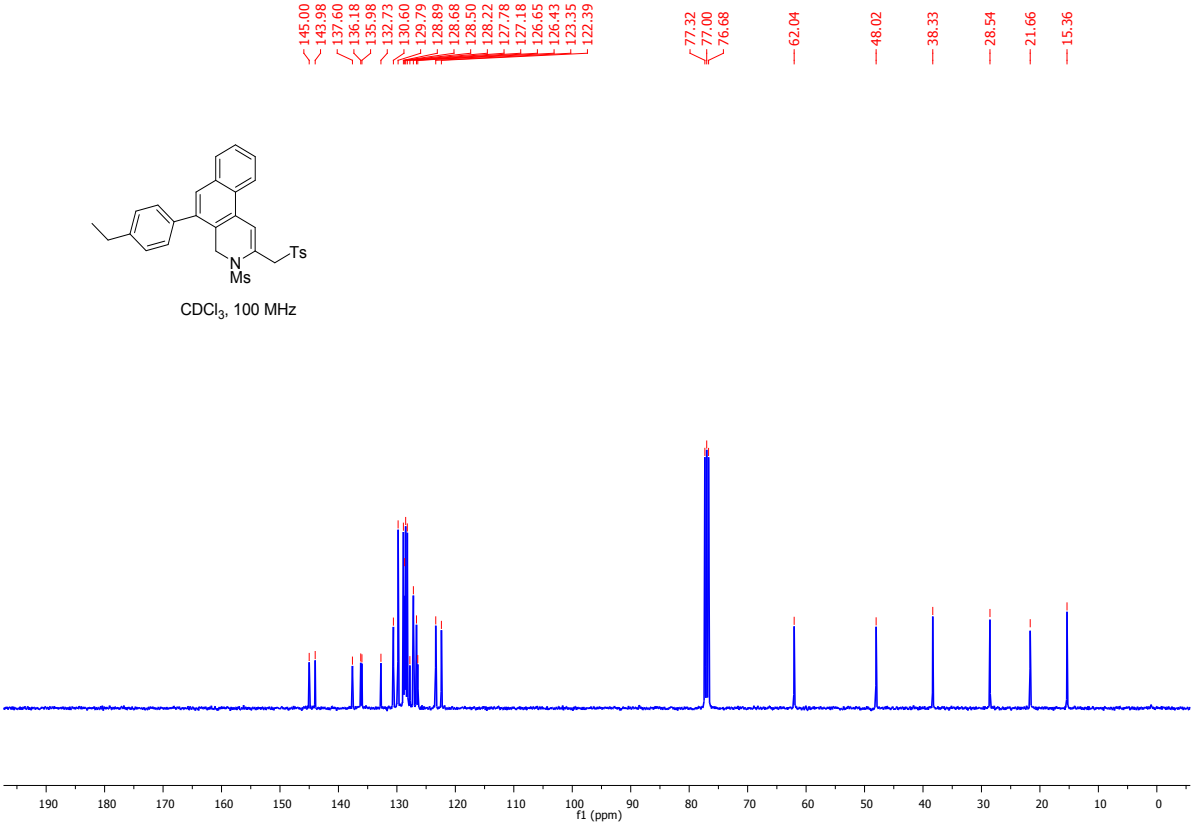
^{1}H NMR and ^{13}C NMR of 9k



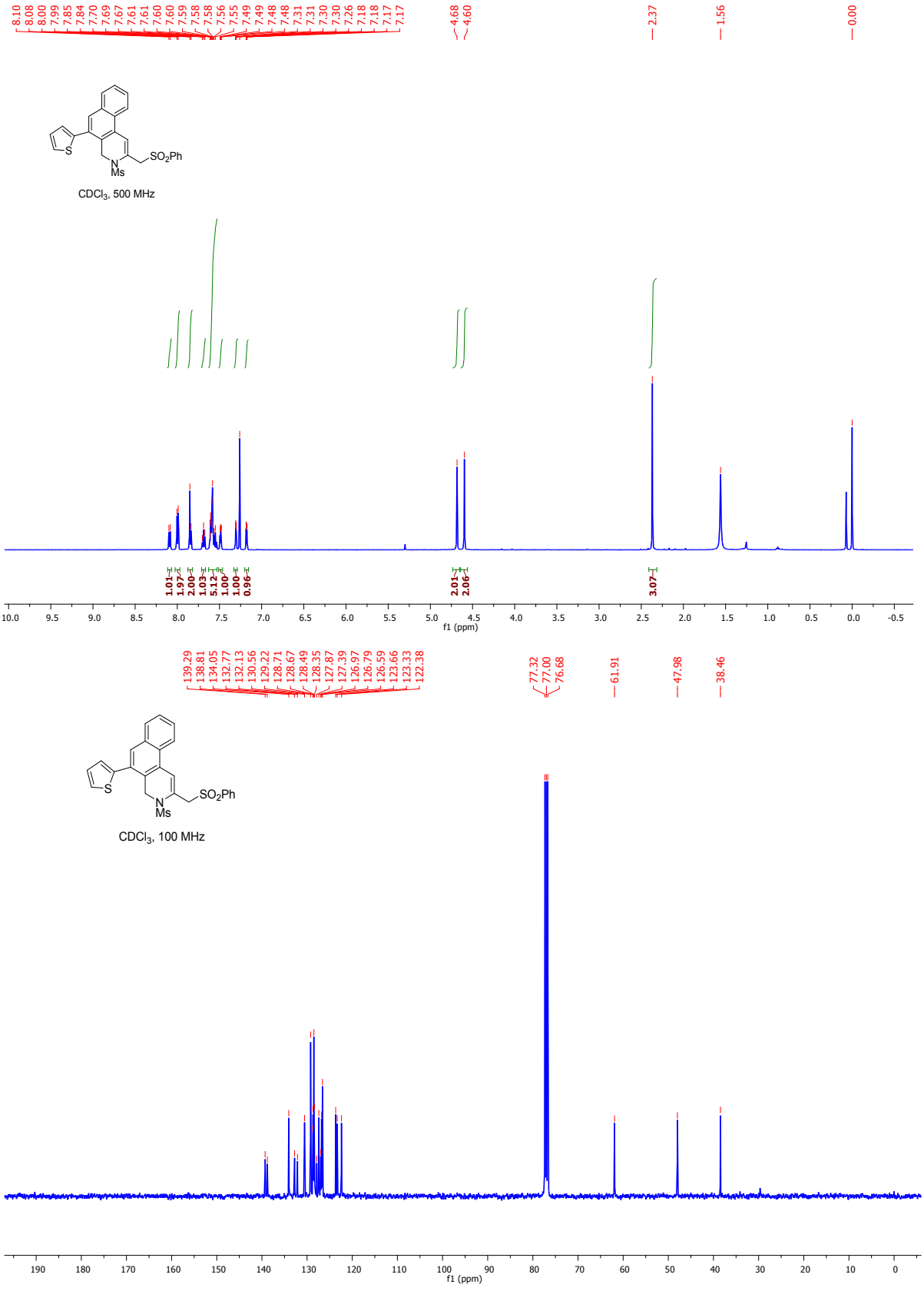


^{1}H NMR and ^{13}C NMR of 9l

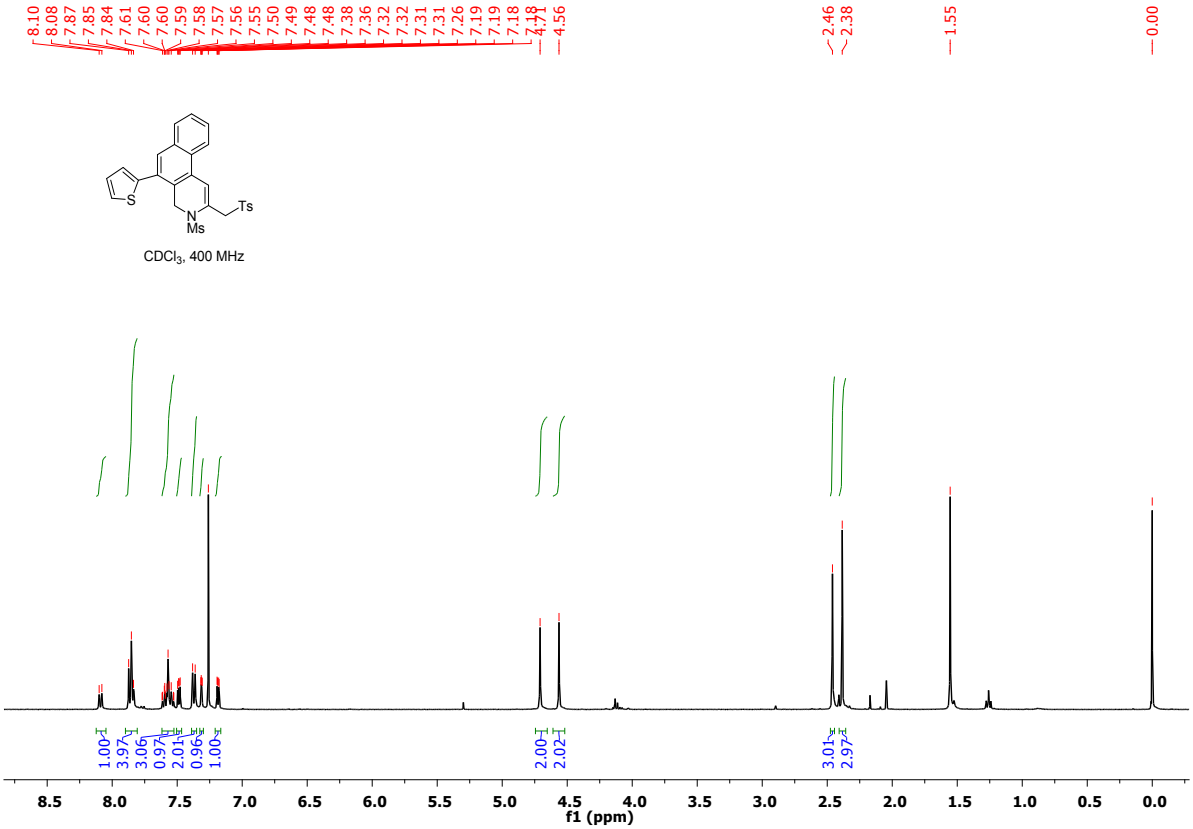


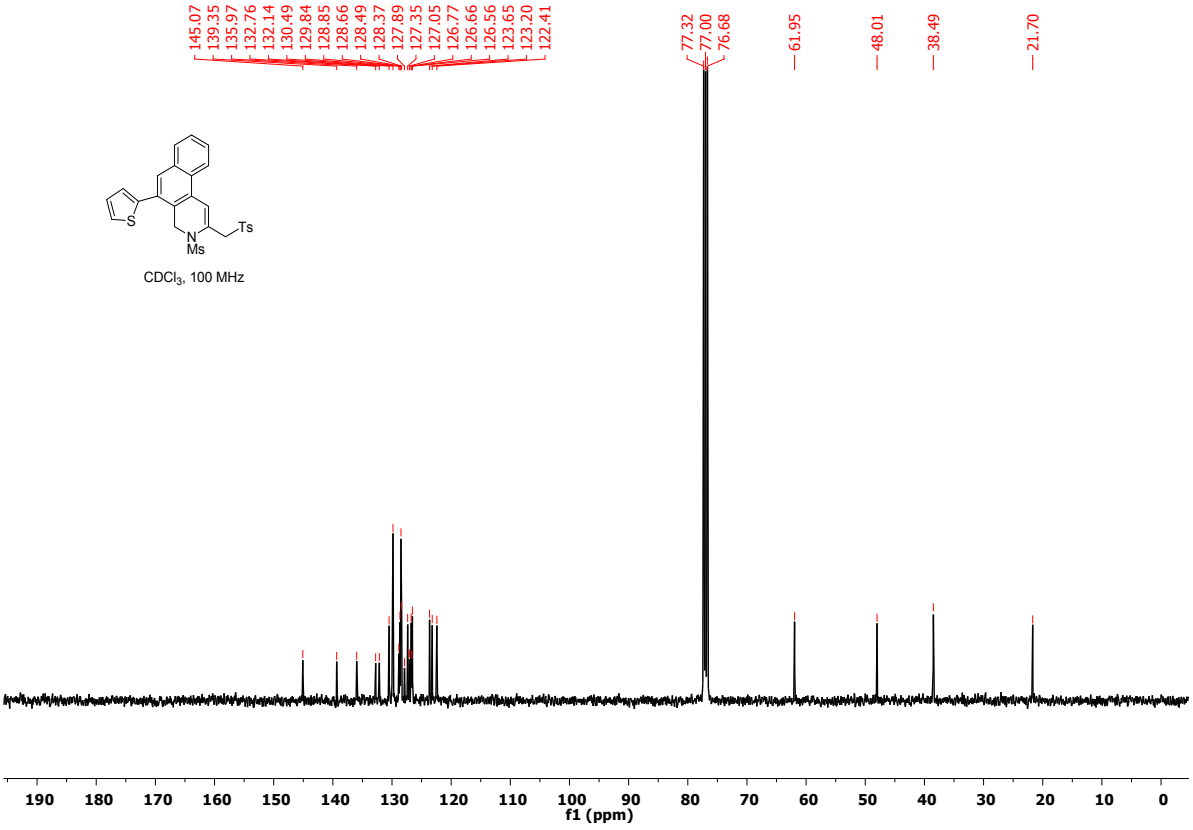


^{1}H NMR and ^{13}C NMR of 9m

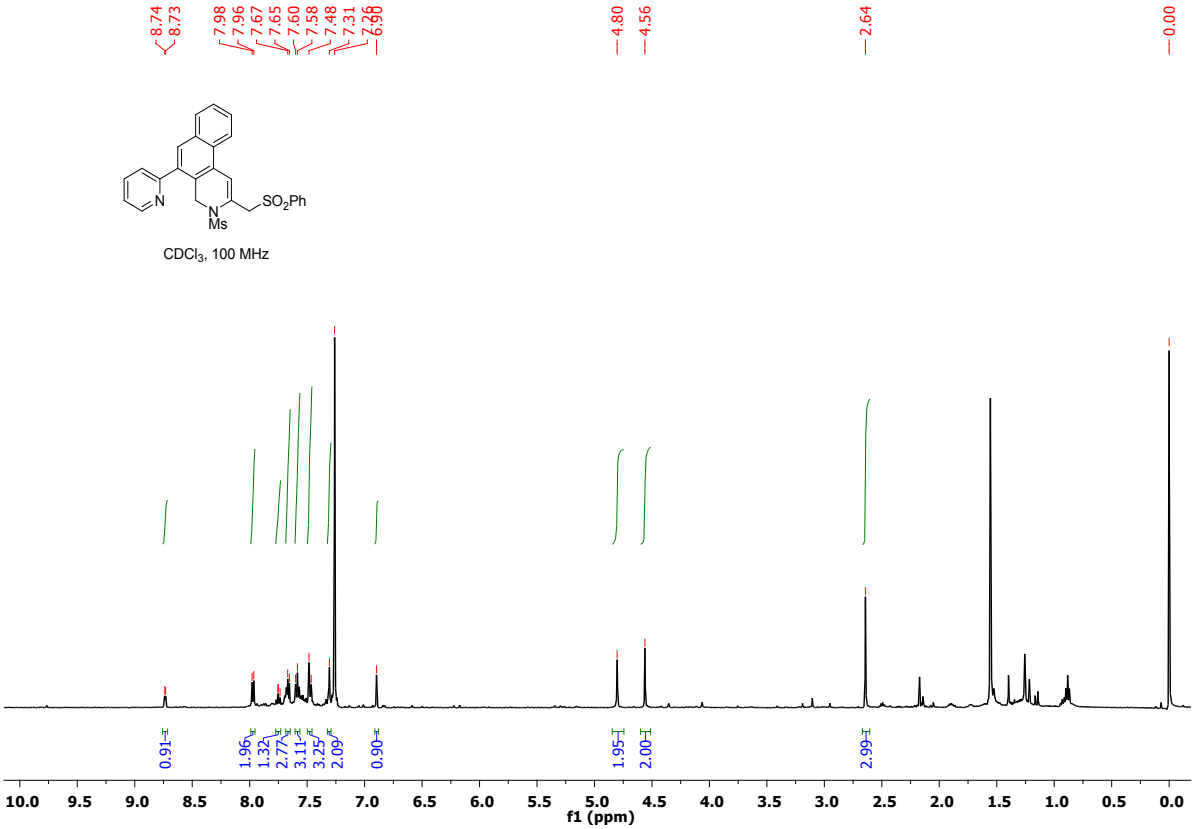


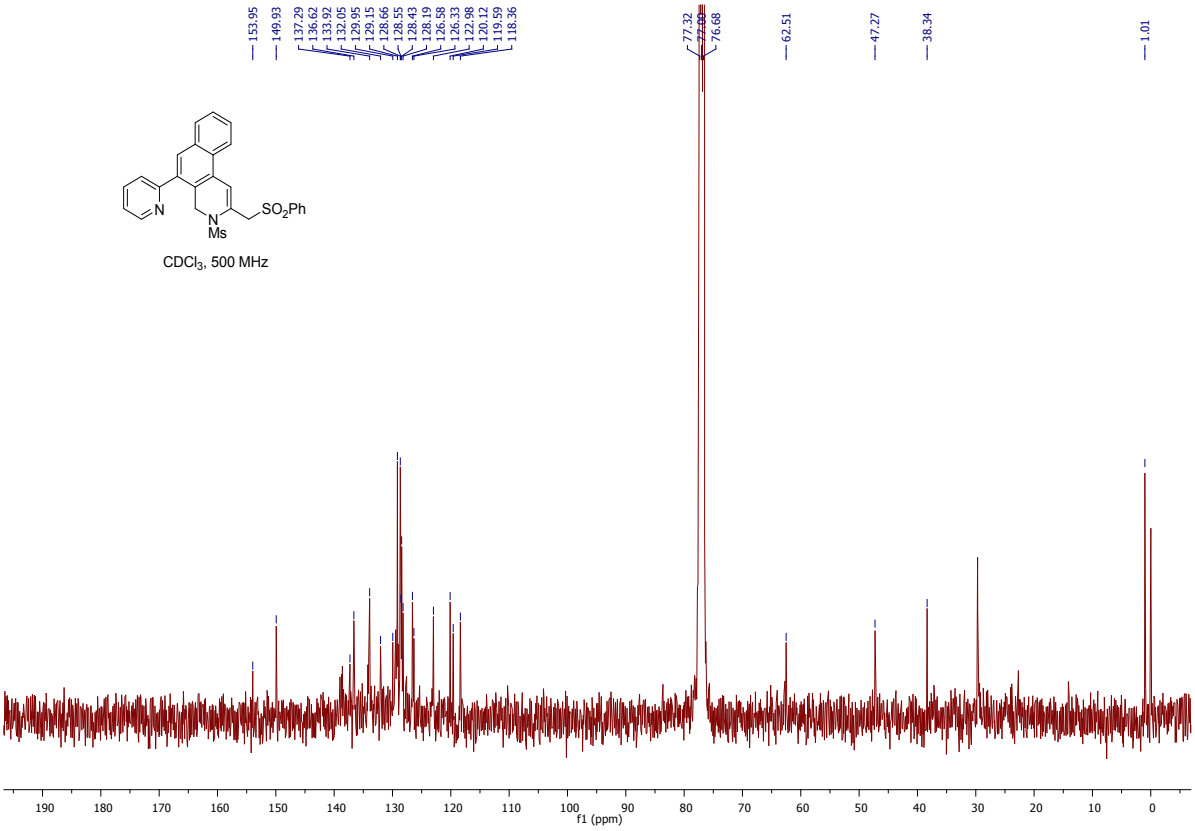
^{1}H NMR and ^{13}C NMR of 9n



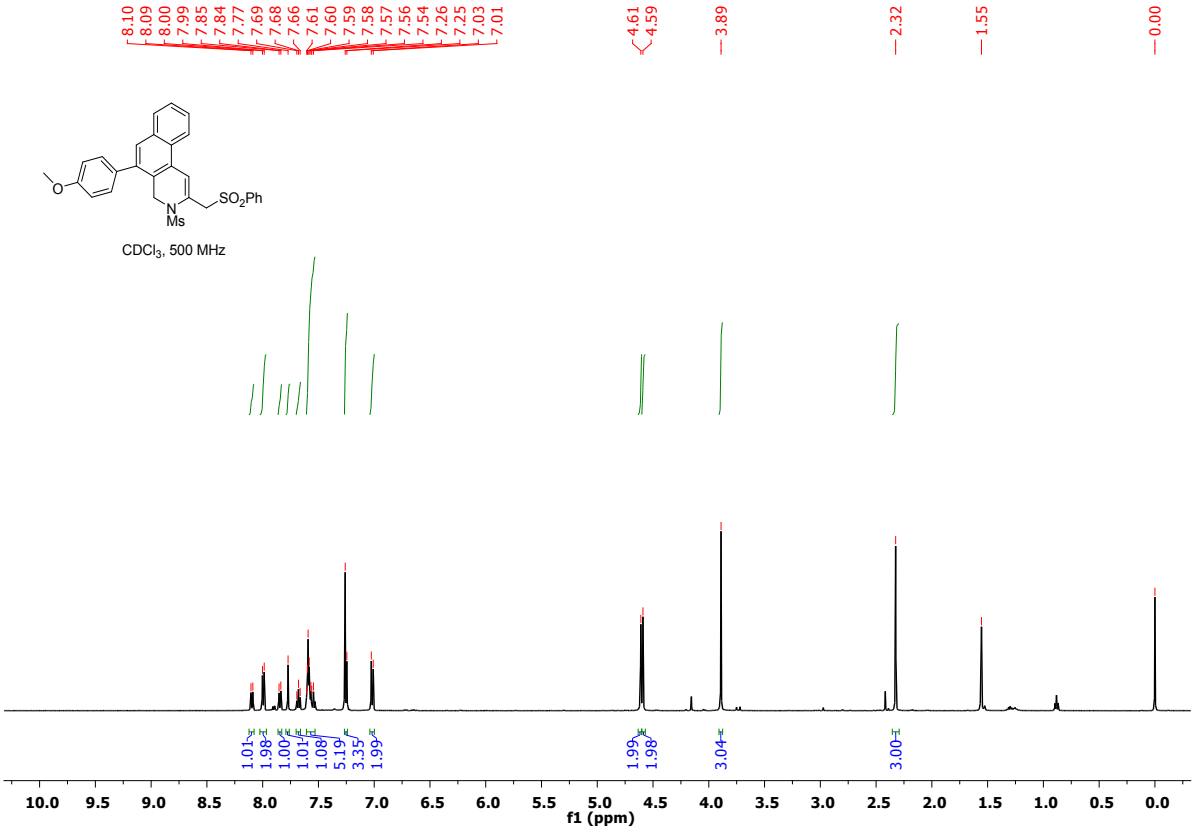


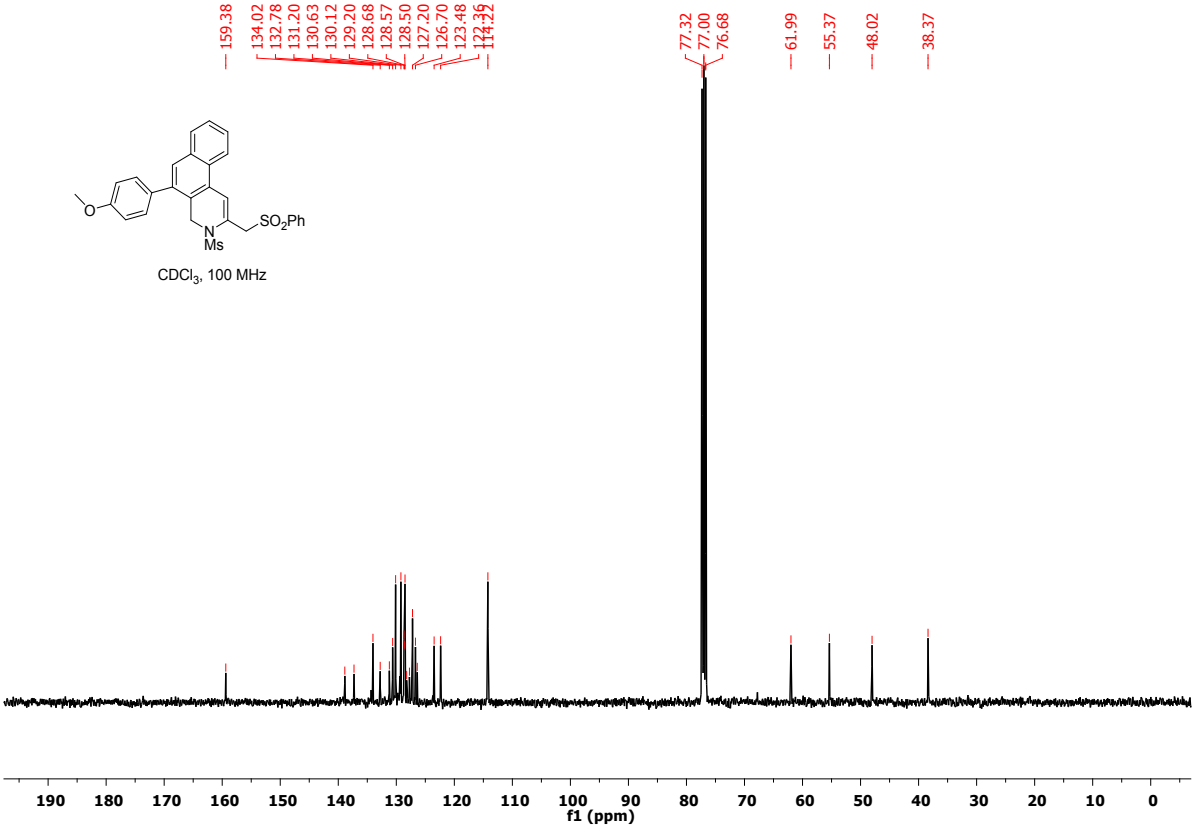
^{1}H NMR and ^{13}C NMR of 9o



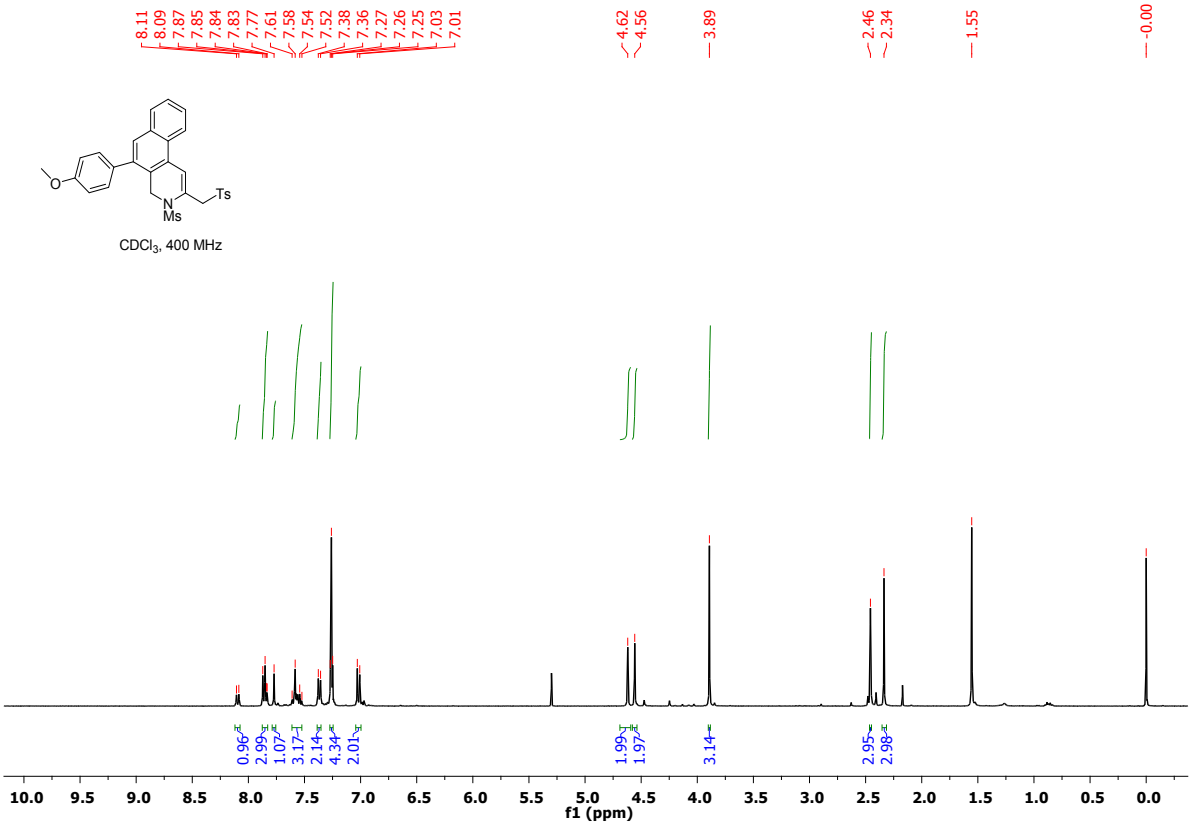


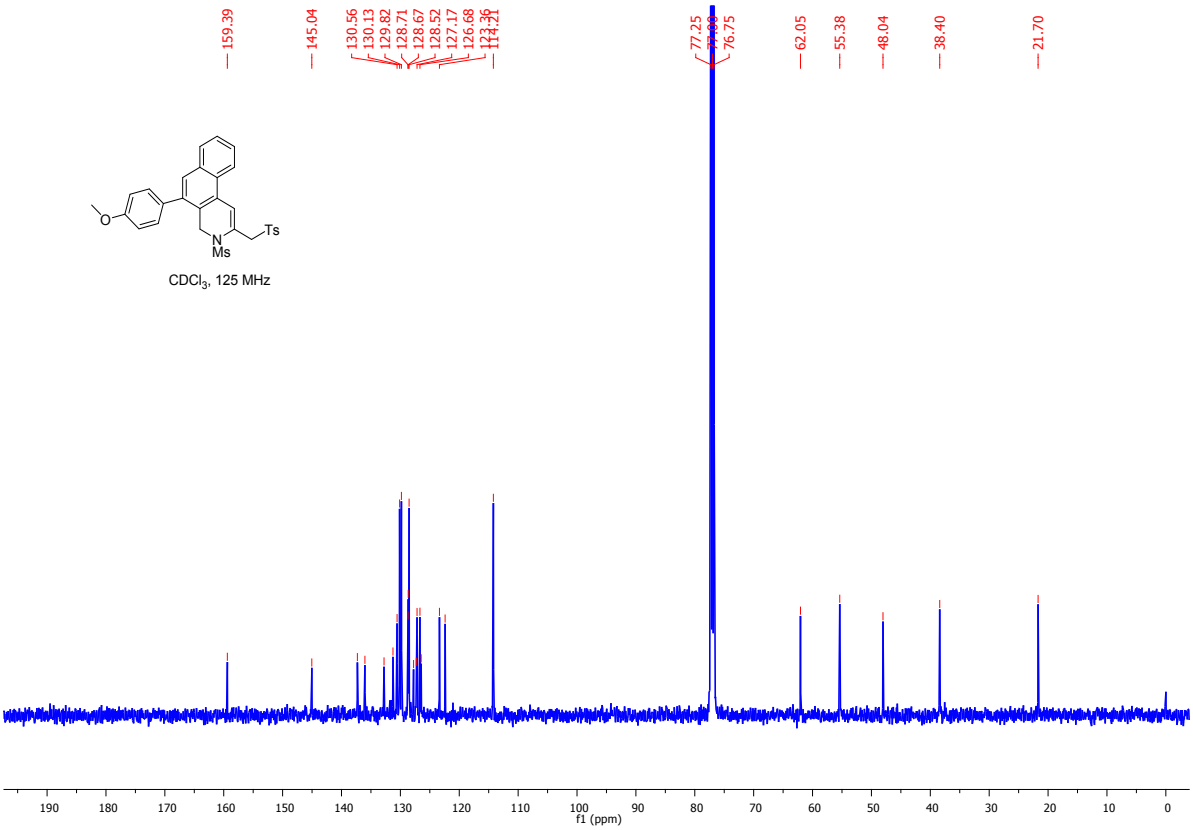
^{1}H NMR and ^{13}C NMR of 9p



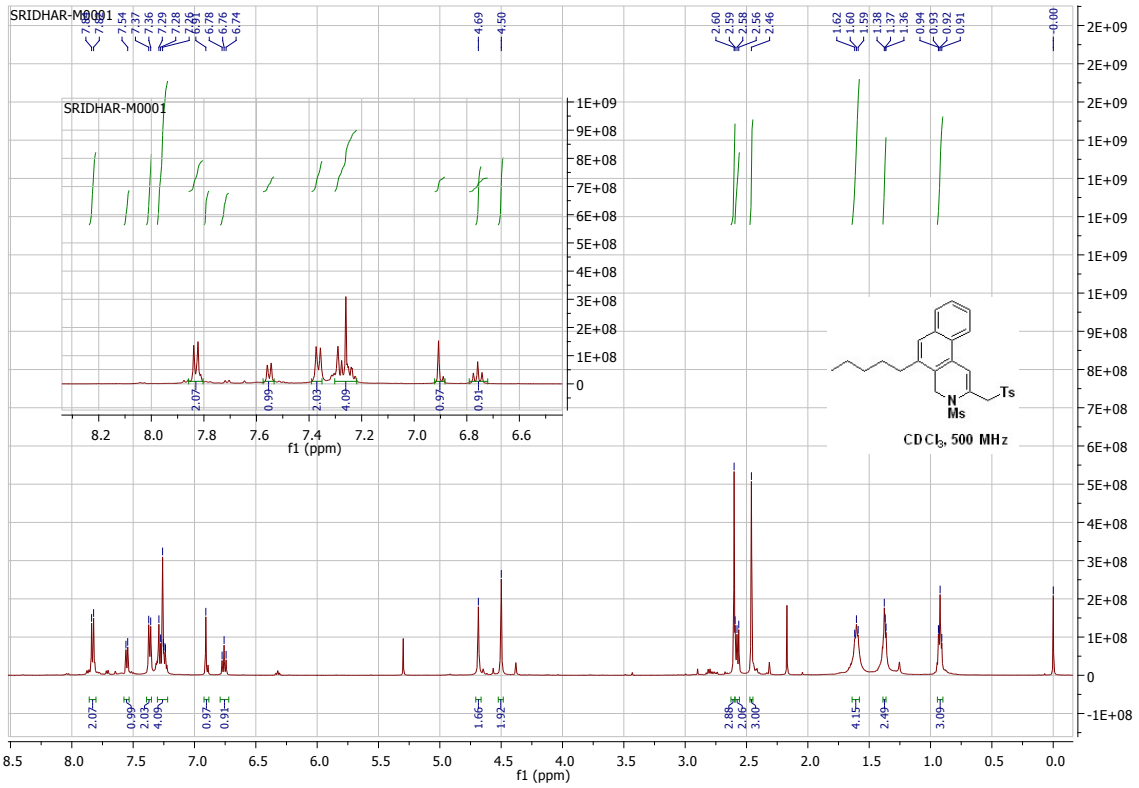


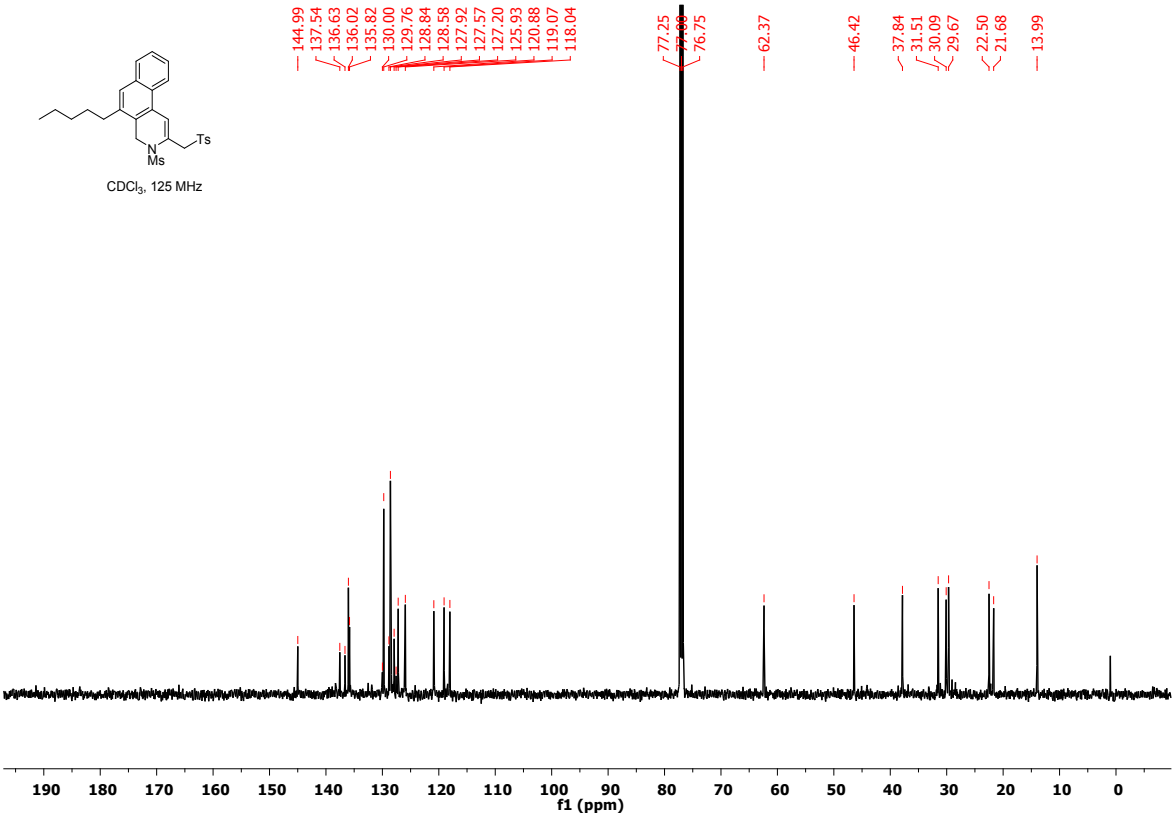
^{1}H NMR and ^{13}C NMR of 9q



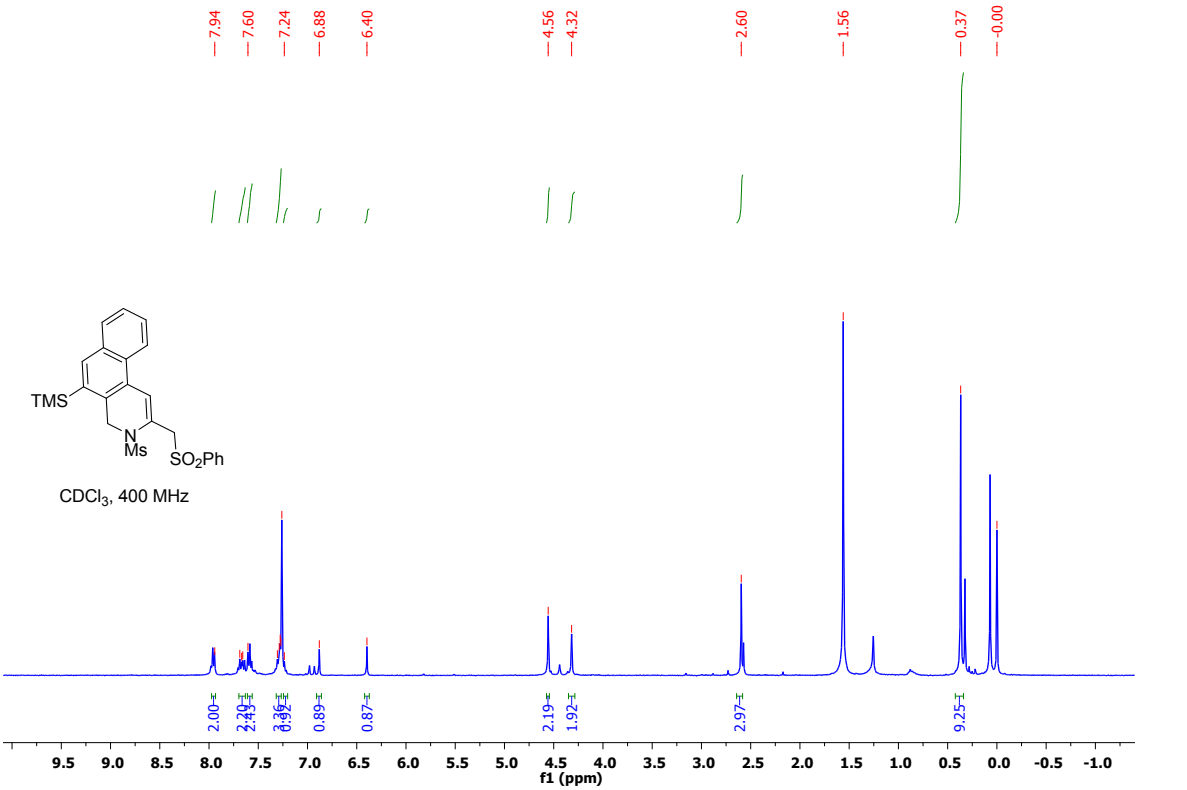


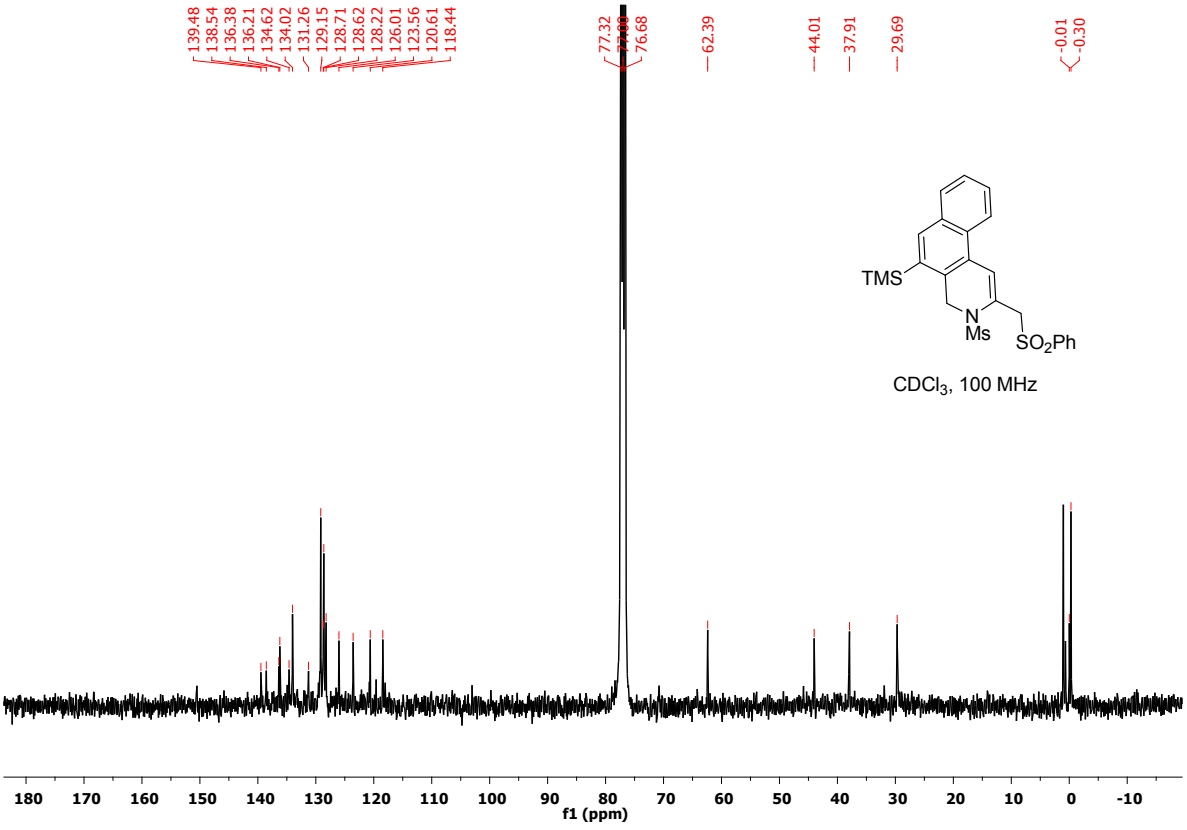
^{1}H NMR and ^{13}C NMR of 9r





^{1}H NMR and ^{13}C NMR of 9s





^{1}H NMR and ^{13}C NMR of 14