Electronic Supplementary Material (ESI) for RSC Advances.

One Pot Hydroamination/[4+3] Cycloaddition: Synthesis towards the Cyclohepta[b]indole Core of Silicine and Ervatamine

Jie Zhang, Jidong Shao, Jijun Xue*, Yongxiang Wang, and Ying Li*

State Key Laboratory of Applied Organic Chemistry & College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, P. R. China

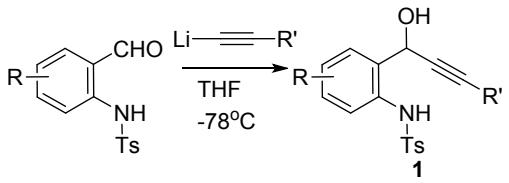
Fax: +86-931-8912582; E-mail: liying@lzu.edu.cn

Table of Contents

I. General Information

All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on GF254 plates. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petro ether was 60- 90 ^{o}C, ethyl acetate are used for product purification by flash column chromatography. CH_2Cl_2 was dried by distillation over CaH_2. THF was dried by distillation over Na/K alloy. Commercially available reagents and solvents were used without any purification. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution n on Bruker AM-400 MHz or Varian Mercury-600 MHz instruments, and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV and signals were given in m/z with relative intensity (%) in brackets.IR spectra were recorded on a Nicolet FT-170SX spectrometer. High-resolution mass spectral analysis (HRMS) data were determined on a Thermo Scientific Orbitrap Elite spectrometer. Melting points were measured on a melting point apparatus and are uncorrected.

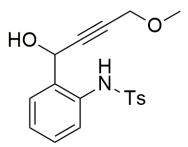
II. Experimental Procedures



1

General Experimental Procedure for the Preparation of 1a-e.[1] To a stirred solution of diisopropylamine (0.21 mL, 1.5 mmol) in anhydrous THF at −78 °C was added n-butyllithium (2.5 M in hexane solution, 0.60 mL, 1.5 mmol) dropwise, and the resulting solution was allowed to stirred at the same temperature for 30 min. The appropriate alkyne (1 mmol) was added in a dropwise manner. The resulting mixture was stirred at the same temperature for 1 h. The corresponding 2-aminobenzaldehyde (0.5 mmol) was dissolved in THF (2 mL) and added to the reaction mixture dropwise and allowed to stir for 1 h at the same temperature. The reaction mixture was slowly warmed up to room temperature and stirred for a further 1 h. Upon completion, the reaction mixture was quenched by adding saturated NH_4Cl (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (10% EtOAc/n-hexane) gave the title compound.

N-(2-(1-hydroxy-4-methoxybut-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1a):



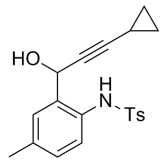
Chemical Formula: $C_{18}H_{19}NO_4S$
Molecular Weight: 345.41

N-(2-(1-hydroxy-4-methoxybut-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**1a**) was prepared following general procedure as a colorless oil (88.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.68 (d, 2H, J = 8.4 Hz), 7.50 (dd, 1H, J = 7.6, 1.2 Hz), 7.36 (dd, 1H, J = 8.0, 0.8 Hz), 7.27-7.22 (m, 3H), 7.12 (td, 1H, J = 7.6, 1.2 Hz), 5.35 (s, 1H), 4.16 (d, 2H, J = 1.6 Hz), 3.38 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 136.7, 135.4, 130.9, 129.7, 129.7, 128.2, 127.2, 125.3, 123.0,

84.3, 84.0, 62.7, 59.9, 57.9, 21.5. EI-MS *m/z* [M]: 57.1 (24.0), 65.1 (39.2), 71.1 (18.9), 77.1 (24.0), 85.1 (16.6), 89.1 (24.1), 91.1 (100), 92.1 (22.4), 115.1 (22.3), 128.1 (18.9), 129.1 (36.2), 130.1 (28.4), 139.1 (32.8), 143.2 (48.4), 144.1 (31.5), 155.0 (16.2), 157.1 (75.7), 158.1 (20.1), 172.0 (19.3), 327.0 (23.6). FTIR (neat): 3273, 3062, 2956, 2922, 2852, 2373, 1737, 1598, 1494, 1461, 1378, 1334, 1266, 1160, 1092, 1019, 931, 915, 760, 740, 662, 566 cm^{-1}. HRMS-ESI (m/z): $[M+Na]^+$ calcd 368.0927; found 368.0922.

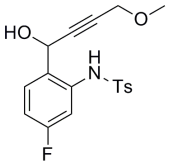
N-(2-(3-cyclopropyl-1-hydroxyprop-2-yn-1-yl)-4-methylphenyl)-4-methylbenzenesulfonamide (1b):



Chemical Formula: $C_{20}H_{21}NO_3S$
Molecular Weight: 355.45

N-(2-(3-cyclopropyl-1-hydroxyprop-2-yn-1-yl)-4-methylphenyl)-4-methylbenzenesulfonamide (**1b**) was prepared following general procedure as a white solid (96.5%), m.p. 139-140 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, 2H, J = 8.4 Hz), 7.62 (s, 1H), 7.28-7.23 (m, 5H), 7.05 (dd, 1H, J = 8.4, 1.6 Hz), 5.15 (d, 1H, J = 4.0 Hz), 2.40 (s, 3H), 2.30 (s, 3H), 1.34-1.30 (m, 1H), 0.87-0.80 (m, 2H), 0.78-0.75, (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7, 136.7, 135.2, 132.4, 132.0, 129.8, 129.6, 128.8, 127.2, 123.5, 92.4, 73.1, 63.0, 21.5, 20.9, 8.3. EI-MS m/z [M]: 65.1 (36.5), 69.1 (15.8), 77.1 (21.4), 91.1 (63.4), 106.1 (14.2), 115.1 (14.7), 127.1 (10.3), 128.1 (10.7), 134.1 (37.8), 139.1 (32.0), 142.1 (11.2), 143.1 (10.1), 144.1 (32.8), 154.1 (22.6), 155.1 (18.9), 157.1 (14.2), 158.1 (12.7), 167.1 (19.4), 172.1 (100), 173.1 (12.9), 182.1 (15.4), 200.1 (52.0). FTIR (neat): 3856, 3842, 3652, 3447, 3272, 2956, 2925, 2853, 2373, 2346, 2235, 1917, 1736, 1597, 1499, 1461, 1379, 1330, 1265, 1160, 1091, 814, 739, 666 cm^{-1}. HRMS-ESI (m/z): $[M+Na]^+$ calcd 378.1134; found 378.1127.

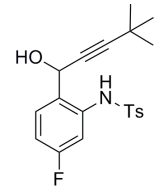
N-(5-fluoro-2-(1-hydroxy-4-methoxybut-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1c):



Chemical Formula: $C_{18}H_{18}FNO_4S$
Molecular Weight: 363.40

N-(5-fluoro-2-(1-hydroxy-4-methoxybut-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**1c**) was prepared following general procedure as a colorless oil (90.6%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.73 (d, 2H, J = 8.0 Hz), 7.41 (td, 1H, J = 6.4, 2.4 Hz), 7.27-7.20 (m, 3H), 6.77 (td, 1H, J = 8.4, 2.8 Hz), 5.32 (d, 1H, J = 5.2 Hz), 4.16 (s, 2H), 3.39 (s, 3H), 2.92 (d, 1H, J = 5.2 Hz), 2.40 (s, 3H). ^{13}C NMR (100 MHz, CDCl3) δ 163.1 (d, J = 247 Hz), 144.2, 137.5, 137.4, 136.5, 129.8, 129.6 (d, J = 9 Hz), 127.2, 111.2 (d, J = 22 Hz), 109.2 (d, J = 27 Hz), 84.6, 83.6, 62.7, 59.8, 58.0, 21.6. EI-MS *m/z* [M]-: 65.0 (20.3), 75.1 (21.3), 91.1 (100), 147.0 (14.3), 148.0 (13.6), 155.0 (30.5), 175.0 (23.9), 191.0 (12.4), 291.0 (12.7), 304.0 (18.2), 305.0 (32.9), 306.0 (12.3), 317.0 (20.2), 318.0 (17.2), 333.0 (13.7), 335.0 (13.3), 347.0 (24.0), 348.0 (26.2), 349.0 (13.8), 503.0 (17.4). FTIR (neat): 3280, 2931, 2372, 1657, 1613, 1599, 1507, 1408, 1335, 1281, 1168, 1155, 1091, 994, 905, 815, 733, 663, 569, 545 cm^{-1}. HRMS-ESI (m/z): $[M+Na]^+$ calcd 386.0833; found 386.0828.

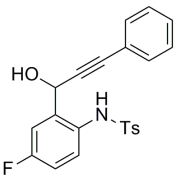
N-(5-fluoro-2-(1-hydroxy-4,4-dimethylpent-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1d):



Chemical Formula: $C_{20}H_{22}FNO_3S$
Molecular Weight: 375.46

N-(5-fluoro-2-(1-hydroxy-4,4-dimethylpent-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**1d**) was prepared following general procedure as a white solid (81.4%), m.p. 127-128 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.72 (d, 2H, J = 8.4 Hz), 7.41 (dd, 1H, J = 8.4, 6.0 Hz), 7.25 (d, 2H, J = 8.0 Hz), 7.22 (dd, 1H, J = 8.0, 2.4 Hz), 6.75 (td, 1H, J = 8.4, 2.8 Hz), 5.19 (d, 1H, J = 4.8Hz), 2.52 (t, 1H, J = 6.4 Hz), 2.39 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, J = 235 Hz),144.1, 137.4, 136.7, 129.9(d, J = 10 Hz), 129.6 (d, J = 11 Hz), 127.3, 127.1, 110.9 (d, J = 22 Hz), 108.9 (d, J = 26 Hz), 98.6, 75.9, 62.7, 30.7, 27.6, 21.5. EI-MS m/z [M]: 65.0 (14.5), 91.1 (54.4), 92.1 (5.9), 155.0 (9.2), 184.0 (4.6), 185.0 (14.4), 186.0 (6.5), 197.0 (5.6), 198.0 (35.1), 199.0 (8.4), 210.0 (9.4), 211.0 (23.7), 212.0 (100), 213.0 (34.1), 214.0 (4.6), 226.0 (53.1), 227.0 (8.3), 258.0 (95.7), 259.0 (17.47), 368.0 (15.14). FTIR (neat): 3467, 3286 2969, 2928, 2869, 2239, 1704, 1613, 1599, 1506, 1405, 1335, 1280.2, 1168, 1154, 1093, 993, 905, 852, 814, 736, 662 cm^{-1}. HRMS-ESI (m/z): $[M+Na]^+$ calcd 398.1197; found 398.1190.

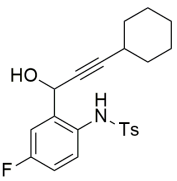
N-(4-fluoro-2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (1e):



Chemical Formula: $C_{22}H_{18}FNO_3S$
Molecular Weight: 395.45

N-(4-fluoro-2-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenyl)-4-methylbenzenesulfonamide (**1e**) was prepared following general procedure as a white solid (73.2%), m.p. 138-139 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68- 7.64 (m, 3H), 7.48 (dd, 2H, J = 7.6, 1.6, 1.2 Hz), 7.40-7.32 (m, 5H), 7.23 (d, 2h, J = 8.4 Hz), 7.01-6.96 (m, 1H), 5.45 (d, 1H, J = 4.8 Hz), 2.983 (d, 2H, J = 5.6 Hz), 2.396 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4 (d, J = 245 Hz), 144.1, 136.4, 135.0 (d, J = 7 Hz), 131.8, 130.4, 129.8, 129.1, 128.4, 127.2, 126.4 (d, J = 8 Hz), 121.6, 116.2 (d, J = 23 Hz), 115.4 (d, J = 24 Hz), 88.6, 85.8, 62.4, 21.5. EI-MS m/z [M]: 65.1 (15.3), 77.1 (10.7), 83.0 (6.0), 89.1 (5.9), 90.2 (7.4), 91.1 (100), 92.1 (8.2), 105.1 (50.2), 110.1 (8.1), 129.1 (10.4), 138.1 (24.6), 139.1 (18.4), 165.1 (7.0), 183.1 (5.8), 211.1 (6.4), 222.1 (11.8), 238.1 (10.1), 239.1 (6.6), 240.1 (29.4). FTIR (neat): 3443, 3275, 3067, 2925, 2854, 2374, 2346, 2232, 1888, 1802, 1597, 1494, 1330, 1185, 1160, 1091, 7588, 691, 666 cm^{-1}. HRMS-ESI (m/z): $[M+Na]^+$ calcd 418.0884; found 418.0876.

N-(2-(3-cyclohexyl-1-hydroxyprop-2-yn-1-yl)-4-fluorophenyl)-4-methylbenzenesulfonamide (1f):

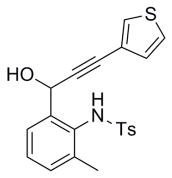


Chemical Formula: $C_{22}H_{24}FNO_3S$
Molecular Weight: 401.49

N-(2-(3-cyclohexyl-1-hydroxyprop-2-yn-1-yl)-4-fluorophenyl)-4-methylbenzenesulfonamide (**1f**) was prepared following general procedure as a white solid (87.1%), m.p. 146-147 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, 2H, J = 8.4 Hz), 7.60 (s, 1H), 7.39-7.36 (m, 1H), 7.29-7.24 (m, 5H), 6.97 (td, 1H, J = 8.4, 3.2, 2.8 Hz), 5.05 (d, 1H, J = 4.8 Hz), 2.40 (s, 3H), 2.36 (d, 1H, J = 6.4 Hz), 1.84-1.82 (m, 2H), 1.72-1.69 (m, 2H), 1.53-1.42 (m, 3H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2 (d, J = 244 Hz), 144.0, 136.6, 135.1 (d, J = 7 Hz), 131.0 (d, J = 3 Hz), 129.7, 127.1, 126.1 (d, J = 8 Hz), 115.9 (d, J = 23 Hz), 115.1 (d, J = 25 Hz), 94.2, 77.0, 62.0, 32.3, 29.1, 25.7, 24.8, 21.5. EI-MS *m/z* [M]-: 55.1 (15.4), 65.1 (11.8), 67.1 (9.1), 77.1 (6.6), 79.1 (7.2), 83.1

(16.5), 91.1 (35.0), 93.1 (6.4), 95.1 (16.8), 110.1 (6.7), 135.1 (6.2), 138.1 (35.4), 139.1 (100), 140.1 (9.1), 148.1 (15.3), 150.1 (11.6), 155.1 (6.3), 164.1 (20.9), 186.1 (6.0), 228.1 (11.9), 246.2 (13.8). FTIR (neat): 3431, 3273, 3066, 2954, 2927, 2854, 2725, 2375, 2345, 2232, 1597, 1494, 1461, 1379, 1334, 1264, 1185, 1161, 1122, 1092, 1019, 814, 664 cm^{-1}. HRMS-ESI (m/z): $[M+Na]^+$ calcd 424.1353; found 424.1347.

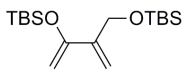
N-(2-(1-hydroxy-3-(thiophen-3-yl)prop-2-yn-1-yl)-6-methylphenyl)-4-methylbenzenesulfonamide (1g):



Chemical Formula: $C_{21}H_{19}NO_3S_2$
Molecular Weight: 397.51

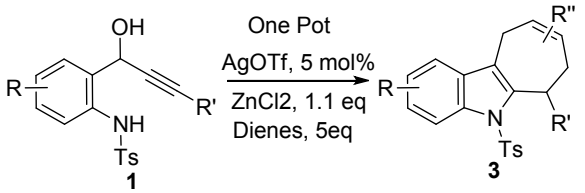
N-(2-(1-hydroxy-3-(thiophen-3-yl)prop-2-yn-1-yl)-6-methylphenyl)-4-methylbenzenesulfonamide (**1g**) was prepared following general procedure as a white solid (94.8%), m.p. 147-148 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, 1H, J = 7.6 Hz), 7.61 (d, 2H, J = 8.4 Hz), 7.48 (dd, 1H, J = 2.8, 0.8 Hz), 7.29-7.26 (m, 5H), 7.16-7.12 (m, 2H), 6.63 (s, 1H), 5.80 (s, 1H), 3.26 (b, 1H), 2.44 (s, 3H), 1.91 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ144.2, 137.8, 137.3, 136.8, 131.5, 129.9, 129.8, 129.3, 128.4, 128.4, 127.2, 127.1, 125.3, 121.4, 87.8, 82.1, 61.7, 21.6, 18.2. EI-MS *m/z* [M]-: 65.0 (14.9), 77.0 (11.6), 83.0 (7.6), 91.1 (27.3), 97.0 (39.1), 111.0 (100), 112.0 (6.7), 113.0 (6.3), 130.1 (8.7), 134.1 (21.2), 135.0 (6.9), 139.1 (5.53), 199.0 (6.4), 224.0 (6.1), 225.0 (5.8), 227.0 (20.2), 240.0 (5.4), 241.0 (7.0), 242.0 (33.0), 243.0 (5.3). FTIR (neat): 3430, 3276, 2925, 2856, 2373, 1597, 1463, 1381, 1325, 1305, 1264, 1184, 1158, 1092, 1026, 909, 787, 736, 665, 627, 568 cm^{-1}. HRMS-ESI (m/z): $[M+Na]^+$ calcd 420.0699; found 420.0695.

2,2,3,3,9,9,10,10-octamethyl-5,6-dimethylene-4,8-dioxa-3,9-disilaundecane (4b) :



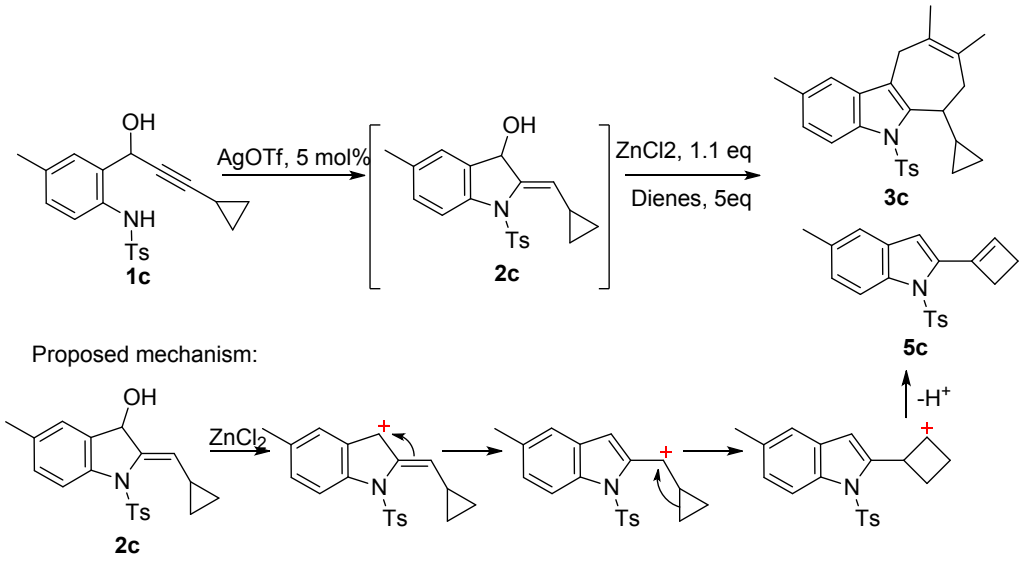
Chemical Formula: $C_{17}H_{36}O_2Si_2$
Molecular Weight: 328.64

2,2,3,3,9,9,10,10-octamethyl-5,6-dimethylene-4,8-dioxa-3,9-disilaundecane (**4b**) was prepared according to a literature procedure.[2] ^1H NMR (400 MHz, $CDCl_3$) δ 5.59 (s, 1H), 5.35 (s, 1H), 4.39 (s, 1H), 4.32 (s, 1H), 4.32 (s 2H), 1.00 (s, 9H), 0.95 (s, 9H), 0.20 (s, 6H) , 0.11 (s, 6H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 143.5, 112.1, 91.9, 62.6, 25.9, 25.8, 18.4, 18.3, -4.7, -5.4. HRMS-ESI (m/z): $[M+H]^+$ calcd 329.2327; found 329.2325.

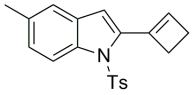


General experimental procedure for the one pot hydroamination/[4+3] cycloaddition tandem annulation. To a stirred solution of compound **1** (0.13 mmol) in anhydrous CH_2Cl_2 (2 mL) at room temperature was added AgOTf (5 mol%, 6.3 µmol, 1.0 mg), and the resulting solution was allowed to stir at the same temperature for 18 h. As soon as the completion of hydroamination, the appropriate diene (5 eq.) was added in one portion. After carefully dropwise addition of $ZnCl_2$ (1.1 eq., 0.1375 mmol, 1M solution in diethyl ether, 0.14 mL), the resulting mixture was stirred at the same temperature for another 2 h. The reaction mixture was quenched by

saturated $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layer were washed with brine (20 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (1% EtOAc/n-hexane) gave the title compound.

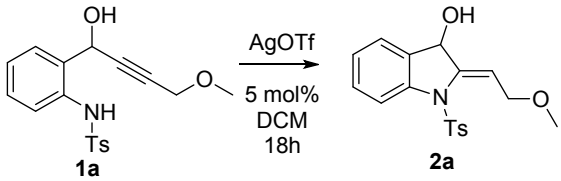


2-(cyclobut-1-en-1-yl)-5-methyl-1-tosyl-1H-indole: A main byproduct of compound **1c** under Lewis acid ($ZnCl_2$) condition.

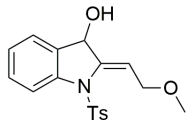


Chemical Formula: $C_{20}H_{19}NO_2S$
Molecular Weight: 337.44

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, 1H, J = 8.8 Hz), 7.66 (d, 2H, J = 8.0 Hz), 7.21-7.11 (m, 5H), 6.61 (s, 1H), 6.20-6.13 (m, 1H), 3.71 (t, 2H, J = 6.8, 6.4 Hz), 2.78 (ddd, 2H, J = 6.8, 1.6, 1.2 Hz), 2.41 (s, 3H,), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ144.6, 139.1, 135.5, 135.4, 133.5, 130.2, 129.5, 126.6, 126.0, 123.6, 120.4, 120.4, 114.8, 108.4, 44.0, 35.9, 21.5, 21.2.



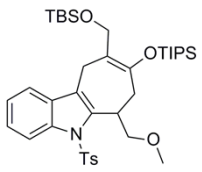
(Z)-2-(2-methoxyethylidene)-1-tosylindolin-3-ol (2a):



Chemical Formula: $C_{18}H_{19}NO_4S$
Molecular Weight: 345.41

(Z)-2-(2-methoxyethylidene)-1-tosylindolin-3-ol (**2a**) was prepared following general procedure (entry 8 in manuscript, table 1) as a light yellow oil (99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, 1H, J = 8.0 Hz), 7.37-7.35 (m, 1H), 7.32 (d, 2H, J = 8.4 Hz), 7.21-7.15 (m, 2H), 7.10 (d, 2H, J = 8.0 Hz), 5.90-5.87 (m, 1H), 4.70 (s, 1H), 4.49-4.37 (m, 2H), 3.34 (s, 3H), 2.33 (s, 3H), 1.99 (s, 2H), 1.82 (bd, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.7, 143.3, 141.9, 134.5, 133.1, 129.6, 129.3, 127.8, 126.6, 124.5, 122.4, 119.8, 72.4, 69.5, 58.3, 21.5.

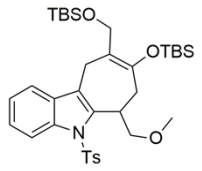
9-(((tert-butyldimethylsilyl)oxy)methyl)-6-(methoxymethyl)-5-tosyl-8-((triisopropylsilyl)oxy)-5,6,7,10-tetrahydrocyclohepta[*b*]indole (5a):



Chemical Formula: $C_{38}H_{59}NO_5SSi_2$
Molecular Weight: 698.11

9-(((tert-butyldimethylsilyl)oxy)methyl)-6-(methoxymethyl)-5-tosyl-8-((triisopropylsilyl)oxy)-5,6,7,10-tetrahydrocyclohepta[*b*]indole (**5a)** was prepared following general procedure as a colorless oil (11%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, 1H, J = 8.4, 0.8 Hz), 7.47 (d, 2H, J = 8.4 Hz), 7.36 (dd, 1H, J = 6.8, 1.2 Hz), 7.28-7.21 (m, 2H), 7.09 (d, 2H, J = 8.4 Hz), 4.37 (t, 1H, J = 2.0 Hz), 4.34 (d, 1H, J = 11.6 Hz), 4.20 (d, 1H, J = 11.6 Hz), 3.96 (s, 1H), 3.82 (dd, 1H, J = 8.8, 3.2 Hz), 3.52 (t, 1H, J = 9.2 Hz), 3.41-3.25 (m, 5H), 2.78-2.67 (m, 2H), 2.29 (s, 3H), 1.14-1.11 (m, 20H) , 0.80 (s, 8H) , -0.04 (d, 5H, J = 8.8 Hz). EI-MS *m/z* [M]-: 57.1 (4.9), 59.1 (83.3), 60.1 (6.9), 61.1 (7.2), 73.1 (78.4), 74.1 (8.0), 75.1 (100), 76.0 (7.5), 77.1 (5.0), 87.1 (36.5), 89.1 (13.2), 91.1 (18.4), 101.1 (7.4), 115.1 (35.5), 129.1 (5.2), 133.1 (9.5), 157.2 (5.9), 180.1 (8.2), 192.0 (6.4), 208.1 (7.0), 236.1 (5.6), 254.1 (6.6), 322.2 (9.4), 365.2 (5.6), 410.2 (35.4), 411.3 (11.5), 520.2 (50.9), 521.2 (20.3), 522.2 (8.3), 652.3 (4.6). FTIR (neat): 3368, 3066, 2954, 2926, 2855, 2713, 2373, 2346, 1738, 1675, 1598, 1510, 1459, 1376, 1262, 1176, 1151, 1118, 1092, 1053, 837, 742, 680 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 698.3725; found 698.3718.

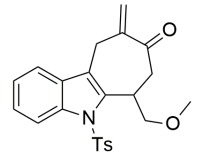
8-((tert-butyldimethylsilyl)oxy)-9-(((tert-butyldimethylsilyl)oxy)methyl)-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (5b):



Chemical Formula: $C_{35}H_{53}NO_5SSi_2$
Molecular Weight: 656.0350

8-((tert-butyldimethylsilyl)oxy)-9-(((tert-butyldimethylsilyl)oxy)methyl)-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (**5b**) was prepared following general procedure as a colorless oil (less than 3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, 1H, J = 7.6 Hz), 7.49 (d, 2H, J = 8.4 Hz), 3.79 (dd, 1H, J = 7.2, 1.2 Hz), 7.26-7.24 (m, 3H), 7.11 (d, 2H, J = 8.0 Hz), 4.32 (d, 1H, J = 12.0 Hz), 4.18 (d, 1H, J = 11.6 Hz), 3.94 (s, 1H), 3.86 (dd, 1H, J = 8.8, 3.2 Hz), 3.48 (t, 1H, J = 9.2 Hz), 3.43-3.28 (m, 5H), 2.70 (d, 2H, J = 5.6 Hz), 2.40-2.310 (m, 4H), 0.98 (s, 9H), 0.81 (s, 9H), 0.17 (d, 6H, J = 11.6 Hz), 0.01 (d, 4H, J = 3.6 Hz), -0.04 (s, 3H). No ^{13}C NMR data collected because of product unstable in deuterated solvent. EI-MS *m/z* [M]-: 65.1 (15.2), 73.1 (63.8), 75.0 (63.9), 77.1 (10.7), 89.1 (28.9), 91.1 (87.0), 119.1 (10.9), 127.1 (10.2), 154.1 (24.9), 155.1 (37.5), 156.1 (10.3), 167.1 (17.5), 168.1 (11.5), 180.1 (56.3), 181.1 (21.6), 194.0 (11.2), 208.0 (14.9), 209.0 (12.6), 222.1 (14.3), 254.1 (100), 255.1 (18.2), 284.1 (32.4), 297.1 (9.7), 328.1 (9.9), 329.1 (52.5), 330.2 (16.9), 364.1 (20.9), 478.1 (17.2), 484.2 (13.9). FTIR (neat): 3678, 3652, 3394, 3060, 2954, 2928, 2854, 2373, 2346, 1921, 1798, 1701, 1598, 1454, 1371, 1255, 1189, 1172, 1152, 1112, 1094, 836, 577 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 656.3256; found 656.3248.

6-(methoxymethyl)-9-methylene-5-tosyl-6,7,9,10-tetrahydrocyclohepta[*b*]indol-8(5H)-one (5c):

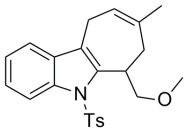


Chemical Formula: $C_{23}H_{23}NO_4S$
Molecular Weight: 409.4980

6-(methoxymethyl)-9-methylene-5-tosyl-6,7,9,10-tetrahydrocyclohepta[*b*]indol-8(5H)-one (**5c**) was prepared following general procedure as a light yellow oil (53 % from **4a**, 69 % from **4b**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, 1H, J = 8.0 Hz), 7.45 (d, 2H, J = 8.4 Hz), 7.42 (d, 1H, J = 1.2 Hz), 7.36-7.28 (m, 2H), 7.13 (d, 2H, J = 8.4 Hz), 5.99 (s, 1H), 5.30 (d, 1H, J = 1.2 Hz), 4.23-4.22 (m,

1H), 3.93-
3.83 (m, 2H), 3.73-3.61 (m, 2H), 3.36-3.30 (m, 4H), 3.08-3.04 (m, 1H), 2.31 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 144.9, 144.8, 137.2, 135.1, 134.7, 130.4, 129.7, 126.1, 125.2, 124.0, 122.2, 121.0, 118.0, 116.2, 75.7, 58.7, 42.0, 37.3, 28.4, 21.5. EI-MS *m/z* [M]-: 65.1 (13.1), 77.1 (5.1), 91.1 (60.4), 92.1 (4.8), 119.1 (12.7), 127.1 (8.5), 128.1 (7.7), 129.1 (4.8), 139.1 (5.8), 152.1 (6.1), 154.1 (20.8), 155.1 (29.9), 156.1 (5.9), 167.1 (7.2), 168.1 (4.7), 179.0 (4.3), 180.1 (52.1), 181.1 (18.3), 194.1 (12.3), 200.1 (4.7), 208.1 (12.5), 209.1 (12.5), 222.1 (12.1), 254.1 (100), 255.1 (20.1), 310.1 (5.4), 336.1 (6.5), 364.1 (21.3), 365.1 (5.1). FTIR (neat): 3373, 3062, 2923, 2851, 2374, 1798, 1697, 1618, 1597, 1453, 1370, 1307, 1189, 1171, 1152, 1111, 1029, 951, 812, 749, 706, 671, 577, 543 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 410.1421; found 410.1417.

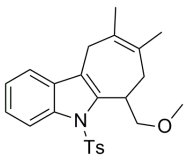
6-(methoxymethyl)-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (3a):



Chemical Formula: $C_{23}H_{25}NO_3S$
Molecular Weight: 395.51

6-(methoxymethyl)-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (**3a**) was prepared following general procedure as a colorless oil (88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, 1H, J = 8.4 Hz), 7.52 (d, 2H, J = 8.0 Hz), 7.33-7.20 (m, 3H), 7.13 (d, 2H, J = 8.4 Hz), 5.65 (t, 1H, J = 4.4 Hz), 4.07 (dd, 1H, J = 9.6, 4.4 Hz),
3.73 (dd, 1H, J = 9.2, 4.0 Hz), 3.51-3.45 (m, 1H), 3.38 (s, 3H), 3.36-3.30 (m, 2H), 2.52 (d, 2H, J = 4.8 Hz), 2.30 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 137.2, 136.7, 136.4, 136.0, 131.1, 129.6, 126.2, 124.4, 123.5, 121.4, 120.3, 117.9, 115.6, 73.7, 58.3, 35.9, 32.4, 26.4, 23.8, 21.5. EI-MS *m/z* [M]-: 65.1 (29.8), 77.1 (10.6), 89.1 (10.9), 91.1 (92.6), 115.1 (13.0), 128.1 (11.6), 130.1 (10.5), 152.1 (11.2), 155.1 (18.9), 167.1 (22.9), 168.1 (11.5), 180.1 (36.5), 192.1 (10.6), 193.1 (23.5), 194.1 (94.5), 195.1 (33.9), 208.1 (54.5), 240.2 (100), 241.2 (15.4). FTIR (neat): 3427, 3307, 3067, 3047, 2962, 2926, 2827, 2739, 2587, 2373, 2345, 2306, 2251, 1913, 1719, 1598, 1453, 1364, 1213, 1191, 1171, 1154, 1122, 1091, 754, 733, 682, 665, 581, 545 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 396.1628; found 396.1623.

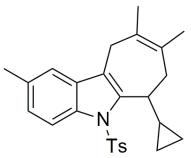
6-(methoxymethyl)-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (3b):



Chemical Formula: $C_{24}H_{27}NO_3S$
Molecular Weight: 409.54

6-(methoxymethyl)-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (**3b**) was prepared following general procedure as a colorless oil (97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, 1H, J = 8.4, 1.2 Hz), 7.44 (d, 2H, J = 8.4 Hz), 7.34 (dd, 1H, J = 8.4, 2.0 Hz), 7.27-7.19 (m, 2H), 7.07 (d, 2H, J = 8.0 Hz), 3.94-3.88 (m, 2H), 3.40 (s, 3H), 3.37-3.30 (m, 2H), 3.20 (d, 1H, J = 17.2 Hz), 2.67-2.58 (m, 2
H), 2.27 (s, 3H), 1.82 (s, 3H), 1.75(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 137.2, 136.6, 135.1, 131.7, 130.2, 129.4, 128.8, 126.1, 123.7, 121.8, 117.9, 116.0, 74.7, 58.3, 37.2, 34.2, 29.9, 21.4, 20.8, 17.7. EI-MS *m/z* [M]-: 65.0 (17.4), 91.0 (40.4), 166.0 (7.7), 167.0 (17.2), 180.0 (15.0), 181.0 (10.8), 192.0 (11.9), 193.0 (18.6), 194.0 (59.8), 195.0 (10.5), 206.0 (9.4), 207.0 (18.5), 208.1 (99.5), 209.0 (43.5), 222.1 (37.8), 254.1 (100), 255.1 (19.8), 364.0 (29.7), 365.0 (7.5), 409.0 (11.0). FTIR (neat): 3067, 3047, 2928, 2865, 2248, 1598, 1494, 1453, 1371, 1307, 1292, 1212, 1191, 1172, 1142, 1101, 1028, 992, 946, 910, 811, 732, 656, 581, 542 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 410.1784; found 410.1780.

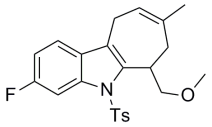
6-cyclopropyl-2,8,9-trimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (3c):



Chemical Formula: $C_{26}H_{29}NO_2S$
Molecular Weight: 419.58

6-cyclopropyl-2,8,9-trimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (**3c**) was prepared following general procedure as a light yellow oil (63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, 1H, J = 8.4 Hz), 7.33 (d, 2H, J = 8.4 Hz), 7.08-7.03 (m, 4H), 3.29-3.25 (m, 1H), 3.24 (s, 1H), 2.61 (d, 1H, J = 14.0 Hz), 2.39 (s, 3H), 2.31 (s, 1H), 2.27 (s, 3H), 1.85 (s, 3H), 1.75 (s, 1H), 1.70-1.67 (m, 1H), 1.00-0.84 (m, 3H), 0.51-0.31 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 141.7, 135.3, 134.7, 133.5, 132.7, 129.1, 128.7, 128.1, 126.3, 125.3, 121.2, 117.9, 116.6, 38.5, 38.1, 30.8, 22.2, 21.5, 21.5, 21.4, 21.2, 16.9, 4.2; EI-MS *m/z* [M]-: 65.0 (20.5), 91.1 (44.8), 133.1 (12.2), 180.0 (12.2), 181.0 (13.3), 194.0 (33.3), 195.0 (15.8), 196.0 (25.3), 207.0 (12.9), 208.0 (44.8), 209.105 (14.7), 220.0 (17.5), 221.0 (13.7), 222.1 (38.3), 234.0 (20.3), 235.1 (12.2), 248.1 (16.9), 264.1 (100), 265.1 (24.1), 419.1 (33.1). FTIR (neat): 3425, 2924, 2863, 2732, 2257, 1720, 1598, 1493, 1368, 1306, 1262, 1205, 1175, 1136, 1090, 1045, 1020, 957, 909, 810, 733, 703, 672, 651, 607, 572, 547 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 420.1992; found 420.1987.

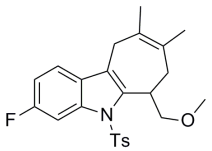
3-fluoro-6-(methoxymethyl)-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (3d):



Chemical Formula: $C_{23}H_{24}FNO_3S$
Molecular Weight: 413.50

3-fluoro-6-(methoxymethyl)-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (**3d**) was prepared following general procedure as a colorless oil (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (dd, 1H, J = 10.8, 2.0 Hz), 7.55 (d, 2H, J = 8.4 Hz), 7.26-7.21 (m, 1H), 7.17 (d, 2H, J = 8.4 Hz), 6.98 (td, 1H, J = 8.8, 2.0 Hz), 5.64 (t, 1H, J = 4.4 Hz), 4.04-4.01 (m, 1H), 3.72-3.69 (m, 1H), 3.49-3.44 (m, 1H), 3.38 (s, 3H), 3.29-3.28 (m, 2H), 2.50 (d, 2H, J = 4.0 Hz), 2.33 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, J = 239 Hz), 144.7, 137.5 (d, J = 4 Hz), 136.8, 136.5 (d, J = 12 Hz), 135.8, 129.8, 127.3, 126.2, 121.1, 119.8, 118.6 (d, J = 10 Hz), 111.6 (d, J = 24 Hz), 103.1 (d, J = 29 Hz), 73.6, 58.4, 35.9, 32.4, 26.4, 23.8, 21.5. EI-MS *m/z* [M]-: 65.1 (12.7), 91.1 (53.0), 92.1 (5.9), 155.1 (12.8), 184.0 (4.3), 185.1 (13.9), 186.1 (6.8), 197.1 (5.0), 198.1 (35.8), 199.1 (8.3), 210.1 (8.4), 211.1 (20.5), 212.1 (100), 213.1 (33.7), 214.1 (6.2), 226.1 (54.8), 227.1 (9.6), 258.2 (94.9), 259.1 (18.8), 368.1 (17.6), 369.1 (4.4). FTIR (neat): 3344, 3114, 3053, 2955, 2926, 2854, 2721, 2371, 2345, 1871, 1799, 1737, 1612, 1598, 1486, 1461, 1376, 1267, 1191, 1174, 1138, 1123, 1092, 741, 585 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 414.1534; found 414.1527.

3-fluoro-6-(methoxymethyl)-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (3e):



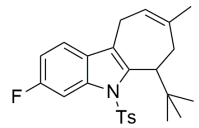
Chemical Formula: $C_{24}H_{26}FNO_3S$
Molecular Weight: 427.53

3-fluoro-6-(methoxymethyl)-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (**3e**) was prepared following general procedure as a colorless oil (79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (dd, 1H, J = 10.4, 2.0 Hz), 7.47 (d, 2H, J = 8.4 Hz), 7.29-7.24 (m, 1H), 7.12 (d, 2H, J = 8.4 Hz), 6.97 (td, 1H, J = 8.8, 2.4 Hz), 3.91-3.85 (m, 2H), 3.41 (s, 3H), 3.39-3.29 (m, 2H), 3.15 (d, 1H, J = 17.2

Hz), 2.60 (d,

2H, *J* = 6.0 Hz), 2.31 (s, 3H), 1.81 (s, 3H) , 1.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, *J* = 239Hz), 144.6, 137.4 (d, *J* = 4 Hz), 136.7 (d, *J* = 13 Hz), 134.9, 123.0, 129.5, 128.8, 127.9, 126.2, 121.3, 118.5 (d, *J* = 10 Hz), 111.8 (d, *J* = 24 Hz), 103.5 (d, *J* = 29 Hz), 74.6, 58.4, 37.1, 36.6, 34.1, 30.0, 24.6, 21.5, 20.9. EI-MS *m/z* [M]-: 65.1 (18.0), 91.1 (58.0), 185.1 (15.1), 198.1 (18.3), 199.1 (12.2), 200.1 (8.1), 210.1 (11.2), 211.1 (17.4), 212.1 (63.4), 213.1 (11.0), 224.1 (9.2), 225.1 (19.3), 226.1 (100), 227.1 (38.5), 240.1 (38.6), 272.2 (73.9), 273.2 (13.4), 382.2 (22.3), 427.2 (7.6). FTIR (neat): 3371, 2927, 2866, 2591, 2373, 2346, 2302, 1878, 1798, 1610, 1598, 1485, 1455, 1433, 1370, 1269, 1190, 1173, 1152, 1109, 659, 586 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 428.1690; found 428.1685.

6-(tert-butyl)-3-fluoro-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (3f):

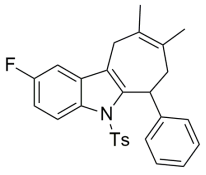


Chemical Formula: $C_{25}H_{28}FNO_2S$
Molecular Weight: 425.56

6-(tert-butyl)-3-fluoro-8-methyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (**3f**) was prepared following general procedure as a colorless oil (45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, 2H, *J* = 8.4 Hz), 7.36 (dd, 1H, *J* = 10.8, 2.4 Hz), 7.22 (d, 2H, *J* = 8.0 Hz), 6.96 (dd, 1H, *J* = 7.6, 6.0 Hz), 6.64 (td, 1H, *J* = 8.4, 2.4, 2.0 Hz), 5.53 (s, 1H), 3.58-3.55 (m, 1H), 3.00 (dd, 1H, *J* = 15.2, 5.6 Hz), 2.70

(d, 1H, *J* = 12.4 Hz), 2.43-2.38 (m, 4H), 2.18 (dd, 1H, *J* = 15.2, 5.2, 4.4 Hz), 1.86 (s, 3H), 1.63 (s, 3H), 1.57 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 247 Hz), 143.6 (d, *J* = 12 Hz), 143.4, 138.1, 135.7, 132.5, 131.6, 129.3 (d, *J* = 3 Hz), 129.0, 127.0, 124.0 (d, *J* = 10 Hz), 120.9, 108.8 (d, *J* = 23 Hz), 101.2 (d, *J* = 29 Hz), 78.9, 76.7, 49.7, 35.1, 33.6, 23.7, 22.9, 22.6, 21.5, 17.8. EI-MS *m/z* [M]-: 65.1 (21.3), 67.1 (9.6), 69.1 (9.4), 91.1 (66.8), 133.1 (8.1), 148.1 (27.4), 155.1 (8.5), 172.1 (11.7), 185.1 (15.7), 186.1 (26.5), 187.1 (19.9), 198.1 (8.0), 200.1 (15.0), 201.1 (9.9), 202.1 (100), 203.1 (15.0), 212.1 (9.6), 228.1 (8.1), 270.2 (13.3), 357.2 (63.6), 358.2 (15.08). FTIR (neat): 3405, 3034, 2925, 2857, 2730, 2588, 2370, 2346, 2258, 1878, 1800, 1599, 1491, 1454, 1432, 1356, 1274, 1259, 1162.5, 1109, 1092, 734, 706, 667, 584, 547 cm^{-1}. HRMS-ESI (m/z): $[M+Na]^+$ calcd 448.1717; found 448.1710.

2-fluoro-8,9-dimethyl-6-phenyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (3g):



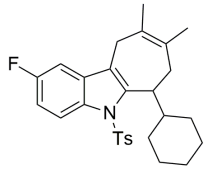
Chemical Formula: $C_{28}H_{26}FNO_2S$
Molecular Weight: 459.57

4,8,9-trimethyl-6-(thiophen-3-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (**3g**) was prepared following general procedure as a light yellow oil (29%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (dd, 1H, *J* = 9.2, 4.8 Hz), 7.17-7.09 (m, 6H), 7.02-6.94 (m, 5H), 5.10 (t, 1H, *J* = 3.2 Hz), 3.54 (d, 1H, *J* = 17.6 Hz), 3.25 (d, 1H, J = 17.2 Hz), 3.05 (d, 1H, J = 14.0 Hz), 2.48-2.43 (m, 2H), 2.28 (s, 3H), 1.76 (s, 3H), 1.10 (

s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (d, *J* = 238 Hz), 143.9, 143.0, 139.8, 135.9, 132.1, 129.6, 129.3, 128.5, 127.8, 126.3, 125.9, 116.2 (d, *J* = 9 Hz), 119 (d, *J* = 25 Hz), 103.8 (d, *J* = 24 Hz), 42.1, 41.6, 30.2, 21.4, 20.9, 20.7. EI-MS *m/z* [M]-: 65.1 (20.0), 91.1 (100), 200.0 (13.7), 212.0 (15.6), 226.0 (11.8), 235.0 (21.7), 236.0 (15.5), 248.0 (16.7), 262.0 (24.5), 272.0 (13.6), 273.0 (8.9), 274.0 (17.4), 288.0 (29.3), 289.1 (20.6), 302.0 (13.9), 303.1 (19.0), 304.1 (83.7), 305.1 (19.2), 459.0 (35.5), 460.0 (10.3). FTIR (neat): 3762, 3335, 3064, 3031, 2926, 2860, 2374, 1598, 1493,

1464, 1453, 1372, 1266, 1175, 1156, 1117, 1090, 1033, 963, 898, 856, 808, 701, 668, 576, 543, 492 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 460.1741; found 460.1737.

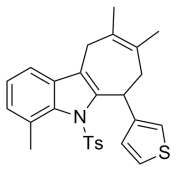
6-cyclohexyl-2-fluoro-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (3h):



Chemical Formula: $C_{28}H_{32}FNO_2S$
Molecular Weight: 465.62

6-cyclohexyl-2-fluoro-8,9-dimethyl-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (**3h**) was prepared following general procedure as a colorless oil (56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, 1H, J = 8.8, 4.4 Hz), 7.30 (d, 2H, J = 8.4 Hz), 7.04 (d, 2H, J = 8.0 Hz), 6.97-6.92 (m, 2H), 3.51 (t, 1H, J = 5.2 Hz), 3.43 (d, 1H, J = 18.0 Hz), 2.83 (d, 1H, J = 18.0 Hz), 2.60 (dd, 1H, J = 14.4, 10.4 Hz), 2.29 (s, 3H), 2.13 (d, 2H, J = 12.0 Hz), 1.78 (s, 3H), 1.75-1.64 (m, 2H), 1.55 (s, 5H), 1.37-1.29 (m, 2H), 1.17-1.13 (m, 2H), 1.06-1.03 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4 (d, J = 240 Hz), 144.2, 143.4, 134.3, 133.7 (d, J = 9 Hz), 133.1, 130.0, 129.0, 127.7, 126.2, 123.8 (d, J = 3 Hz), 117.8 (d, J = 9 Hz), 111.4 (d, J = 25 Hz), 103.5 (d, J = 24 Hz), 42.8, 41.4, 33.1, 31.3, 30.6, 29.7, 28.7, 27.0, 26.6, 21.5, 20.7, 14.1. EI-MS *m/z* [M]-: 55.0 (62.6), 56.1 (34.4), 57.0 (33.6), 59.0 (18.9), 64.0 (18.0), 65.0 (23.0), 67.0 (20.3), 69.1 (100), 70.1 (25.4), 71.1 (18.6), 73.1 (20.9), 77.1 (22.5), 85.1 (28.1), 91.0 (57.0), 92.1 (17.8), 98.1 (28.1), 99.1 (25.2), 108.1 (21.3), 112.1 (18.5), 126.0 (18.7). FTIR (neat): 3333, 2926, 2855, 2373, 1799, 1703, 1597, 1546, 1457, 1376, 1298, 1262, 1174, 1121, 1090, 906, 809, 733, 658, 571 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 466.2211; found 466.2206.

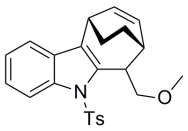
4,8,9-trimethyl-6-(thiophen-3-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (3i):



Chemical Formula: $C_{27}H_{27}NO_2S_2$
Molecular Weight: 461.64

4,8,9-trimethyl-6-(thiophen-3-yl)-5-tosyl-5,6,7,10-tetrahydrocyclohepta[*b*]indole (**3i**) was prepared following general procedure as a light yellow oil (43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.13 (m, 2H), 7.09 (dd, 2H, J = 7.6, 2.4 Hz), 7.05(d, 2H, J = 8.0 Hz), 6.95 (d, 2H, J = 8.0 Hz), 6.87 (dd, 1H, J = 2.4, 0.8 Hz), 6.83 (dd, 1H, J = 4.8, 1.6 Hz), 4.91 (dd, 1H, J = 8.4, 1.6 Hz), 3.32 (d, 1H, J = 16.8 Hz), 2.88 (d, 1H, J = 16.8 Hz), 2.67 (dd, 1H, J = 13.6, 11.4 Hz), 2.57 (s, 3H), 2.49 (dd, 1H, J = 14.0, 4.0, 3.6 Hz), 2.294 (s, 3H), 1.580 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.2, 143.6, 141.9, 139.2, 135.8, 133.1, 131.8, 130.2, 128.8, 128.4, 128.4, 127.7, 127.2, 126.5, 125.0, 124.5, 121.2, 115.6, 41.0, 38.7, 29.5, 21.5, 21.4, 20.6, 19.8. EI-MS *m/z* [M]-: 65.1 (35.6), 91.1 (84.7), 97.1 (100), 111.1 (30.4), 115.1 (10.7), 175.1 (12.4), 194.1 (13.2), 196.1 (21.2), 207.1 (9.8), 208.1 (21.2), 209.1 (13.5), 222.2 (50.9), 223.1 (14.9), 264.1 (27.7), 276.1 (16.8), 290.2 (21.4), 291.1 (12.7), 305.2 (13.1), 306.2 (78.6), 307.2 (27.5), 461.2 (9.6). FTIR (neat): 3371, 3103, 3048, 2980, 2931, 2858, 2733, 2585, 2524, 2372, 2345, 2304, 2249, 1915, 1848, 1721, 1597, 1451, 1413, 1366, 1265, 1190, 1168, 1087, 896, 809, 776, 739, 704, 693, 675, 575, 543 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 462.1556; found 462.1549.

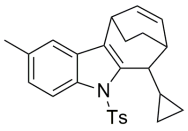
6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[*b*]indole (3j):



Chemical Formula: $C_{24}H_{25}NO_3S$
Molecular Weight: 407.53

6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[*b*]indole (**3j**) was prepared following general procedure as a colorless oil (72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, 1H, J = 6.8, 1.6 Hz), 7.43 (d, 2H, J = 8.4 Hz), 7.35 (d, 1H, J = 6.8 Hz), 7.34-7.20 (m, 2H), 7.08 (d, 2H, J = 8.0 Hz), 6.49 (t, 1H, J = 8.0 Hz), 6.07 (t, 1H, J = 8.0 Hz), 3.99 (dd, 1H, J = 9.2, 3.6 Hz), 3.83-3.79 (m, 1H), 3.47 (d, 1H, J = 2.0 Hz), 3.45 (s, 3H), 3.39-3.34 (m, 1H), 3.21-3.16 (m, 1H), 2.28 (s, 3H), 1.94-1.86 (m, 1H) 1.79-1.64 (m, 2H), 1.58-1.50 (m, 1H), 0.89-0.84 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 137.3, 136.6, 134.6, 134.6, 130.6, 130.0, 129.3, 126.9, 126.2, 124.3, 123.9, 117.7, 116.5, 73.4, 58.6, 46.1, 31.2, 31.0, 29.1, 23.3, 21.5. EI-MS *m/z* [M]-: 65.0 (16.8), 91.1 (35.9), 151.0 (6.2), 152.1 (12.5), 178.0 (13.5), 179.0 (100), 180.0 (30.3), 191.0 (6.4), 204.0 (12.0), 205.0 (7.4), 206.0 (21.4), 207.0 (8.0), 220.1 (6.4), 224.0 (7.3), 252.1 (13.5), 334.0 (86.5), 335.0 (18.8), 362.0 (50.1), 363.0 (11.7), 407.0 (17.3). FTIR (neat): 3038, 2934, 2865, 2826, 1638, 1597, 1493, 1475, 1451, 1365, 1306, 1293, 1271, 1232, 1187, 1168, 1148, 1116, 1089, 1025, 978, 968, 942, 900, 868, 832, 812, 768, 749, 726, 705, 676, 652, 577, 548 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 408.1628; found 408.1623.

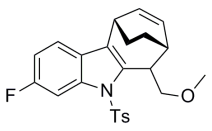
6-cyclopropyl-2-methyl-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[*b*]indole (3k):



Chemical Formula: $C_{26}H_{27}NO_2S$
Molecular Weight: 417.56

6-cyclopropyl-2-methyl-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[*b*]indole (**3k**) was prepared following general procedure as a light yellow oil (56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, 1H, J = 8.4 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.11 (s, 1H), 7.08-7.03 (m, 3H), 6.47 (t, 1H, J = 8.4 Hz), 6.18 (t, 1H, J = 8.4 Hz), 3.43-3.05 (m, 1H), 3.14-3.11 (m, 1H), 3.03-2.98 (m, 1H), 2.40 (s, 3H), 2.29 (s, 3H), 1.94-1.90 (m, 1H), 1.76-1.73 (m, 2H), 1.15-1.11 (m, 1H), 0.91-0.84 (m, 2H), 0.51-0.49 (m, 2H), 0.42-0.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 139.5, 136.2, 135.5, 133.8, 133.7, 131.7, 131.3, 128.8, 127.1, 126.4, 125.3, 117.8, 117.1, 48.4, 35.8, 30.7, 29.3, 23.6, 21.5, 21.3, 16.7, 6.0, 3.7. EI-MS *m/z* [M]-: 91.1 (59.3), 144.1 (17.0), 167.0 (28.3), 168.0 (28.5), 181.1 (18.3), 182.0 (100), 183.0 (65.2), 184.1 (15.0), 193.0 (20.1), 194.0 (23.0), 218.0 (17.2), 220.0 (30.9), 221.0 (14.8), 232.0 (17.6), 234.1 (46.5), 262.1 (38.3), 338.0 (56.6), 339.0 (18.3), 342.1 (17.1), 417.1 (32.4). FTIR (neat): 3334, 3013, 2928, 2864, 2374, 2256, 1639, 1597, 1462, 1363, 1291, 1271, 1174, 1148, 1089, 1020, 910, 810, 733, 672, 617, 571, 545 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 418.1835; found 418.1829.

3-fluoro-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[*b*]indole (3l):

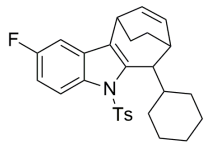


Chemical Formula: $C_{24}H_{24}FNO_3S$
Molecular Weight: 425.52

3-fluoro-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[*b*]indole (**3l**) was prepared following general procedure as a colorless oil (67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, 1H, J = 8.0, 2.0 Hz), 7.45 (d, 2H, J = 8.4 Hz), 7.26 (dd, 1H, J = 8.4, 5.6 Hz), 7.12 (d, 2H, J = 8.0 Hz), 6.98 (td, 1H, J = 7.2, 2.4 Hz), 6.49 (t, 1H, J = 8.0 Hz), 6.07 (t, 1H, J = 8.0 Hz), 3.97 (dd, 1H, J = 7.2, 3.6 Hz), 3.78-3.75 (m, 1H), 3.43 (s, 3H), 3.42-3.34 (m, 2H), 3.18-3.17 (m, 1H), 2.31 (s, 3H), 1.92-1.88 (m, 1H) , 1.76-1.63 (m, 2H) , 1.56-1.50 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8 (d, J = 240 Hz), 144.7, 137.5 (d, J = 12 Hz),

136.4, 134.8 (d, J = 4 Hz), 134.5, 130.1, 129.4, 126.8, 126.4, 126.2, 118.3 (d, J = 9 Hz), 112.0 (d, J = 24 Hz), 104.0 (d, J = 29 Hz), 73.3, 58.6, 46.1, 31.2, 31.1, 29.2, 23.2, 21.5. EI-MS *m/z* [M]-: 65.1 (8.4), 91.1 (31.2), 155.0 (10.1), 170.0 (5.0), 196.0 (6.1), 197.0 (56.0), 198.0 (17.7), 222.0 (6.1), 223.0 (5.1), 224.0 (18.5), 225.0 (6.4), 238.0 (8.2), 270.1 (7.1), 352.0 (100), 353.0 (20.5), 354.0 (7.4), 380.0 (51.9), 381.0 (12.3), 425.0 (16.1), 426.0 (5.0). FTIR (neat): 3338, 3113, 3048, 2934, 2865, 2374, 1892, 1610, 1596, 1582, 1480, 1459, 1397, 1364, 1267, 1237, 1185, 1166, 1128, 1113, 1084, 979, 908, 825, 806, 722, 701, 672, 657, 618, 586, 547 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 426.1534; found 426.1528.

6-cyclohexyl-2-fluoro-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[*b*]indole (3m):

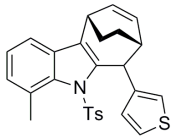


Chemical Formula: $C_{28}H_{30}FNO_2S$
Molecular Weight: 463.61

6-cyclohexyl-2-fluoro-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[*b*]indole (**3m**) was prepared following general procedure as a light yellow oil (41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, 2H, J = 9.6, 4.8 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.07 (d, 2H, J = 8.0 Hz), 6.99-6.93 (m, 2H), 6.38 (t, 1H, J = 8.0 Hz), 6.09 (t, 1H, J = 8.0 Hz),

3.56 (t, 1H, J = 4.8 Hz), 3.30-3.28 (m, 1H), 3.02 (q, 1H, J = 7.2 Hz), 2.30 (m, 4H), 1.84-1.78 (m, 2H), 1.70-1.60 (m, 2H), 1.56-1.55 (m, 3H), 1.43-1.26 (m, 2H), 1.16-1.05 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6 (d, J = 370 Hz), 135.1, 133.9, 133.7, 132.7, 132.3, 129.2, 129.0, 128.7, 126.7, 126.3, 118.4 (d, J = 9Hz), 111.4 (d, J = 24 Hz), 103.6 (d, J = 24 Hz), 51.8, 43.8, 32.3, 32.1, 31.6, 30.0, 29.4, 27.4, 27.4, 26.9, 25.1, 21.5. EI-MS *m/z* [M]-: 71.1 (28.6), 73.1 (41.2), 85.2 (27.5), 89.1 (17.8), 93.1 (17.8), 97.1 (38.1), 99.1 (27.9), 105.1 (26.2), 113.1 (17.8), 117.2 (34.8), 125.1 (18.0), 135.1 (39.3), 149.1 (28.1), 172.1 (25.2), 185.1 (41.4), 186.1 (43.8), 198.1 (25.0), 201.1 (22.4), 202.1 (23.9), 303.1 (69.6), 353.1 (100), 385.2 (18.4), 463.3 (46.7). FTIR (neat): 3039, 2930, 2854, 2666, 2590, 2258, 1912, 1796, 1638, 1597, 1493, 1465, 1363, 1307, 1263, 1175, 1149, 1137, 1089, 1063, 992, 909, 840, 810, 731, 670, 611, 569, 544, 506, 429 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 464.2054; found 464.2050.

4-methyl-6-(thiophen-3-yl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[*b*]indole (3n):



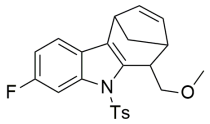
Chemical Formula: $C_{27}H_{25}NO_2S_2$
Molecular Weight: 459.62

4-methyl-6-(thiophen-3-yl)-5-tosyl-5,6,7,10-tetrahydro-7,10-ethanocyclohepta[*b*]indole (**3n**) was prepared following general procedure as a light yellow oil (40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 2H), 7.17-7.13 (m, 4H), 7.05 (d, 2H, J = 8.0 Hz), 6.79-6.77 (m, 2H), 6.39 (t, 1H, J = 8.0 Hz), 5.68 (t, 1H, J = 8.0 Hz), 4.90 (d, 1H, J = 4.8

Hz), 3.41 (t, 1H, J = 3.6 Hz), 2.96 (q, 1H, J = 6.8 Hz), 2.61 (s, 3H), 2.35 (s, 3H), 1.89-1.82 (m, 1H), 1.78-1.66 (m, 2H), 1.55-1.51 (m, 1H), 0.92-0.86 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 143.1, 139.6, 139.0, 135.8, 134.4, 134.1, 131.2, 130.4, 130.1, 128.7, 128.3, 126.2, 125.0, 123.9, 121.6, 115.5, 47.5, 38.9, 30.4, 29.0, 24.4, 21.7, 21.5. EI-MS *m/z* [M]-: 65.0 (14.8), 79.0 (6.5), 91.0 (40.1), 97.0 (45.5), 123.0 (13.2), 165.0 (7.1), 194.0 (11.4), 207.0 (7.2), 220.0 (13.4), 224.0 (9.7), 226.0 (6.3), 256.0 (6.6), 274.0 (10.9), 275.0 (6.3), 276.0 (49.5), 277.0 (10.0), 303.0 (25.4), 304.0 (100), 305.0 (22.9), 459.0 (11.7). FTIR (neat): 3394, 3042, 2934, 2864, 2254, 1917, 1596, 1493, 1452, 1412, 1365, 1305, 1291, 1262, 1233, 1189, 1167, 1112, 1089, 1061, 987, 909, 572, 837, 812, 775, 759, 773, 642, 578, 562, 528 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 460.1399;

found 460.1395.

3-fluoro-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-methanocyclohepta[*b*]indole (3o):

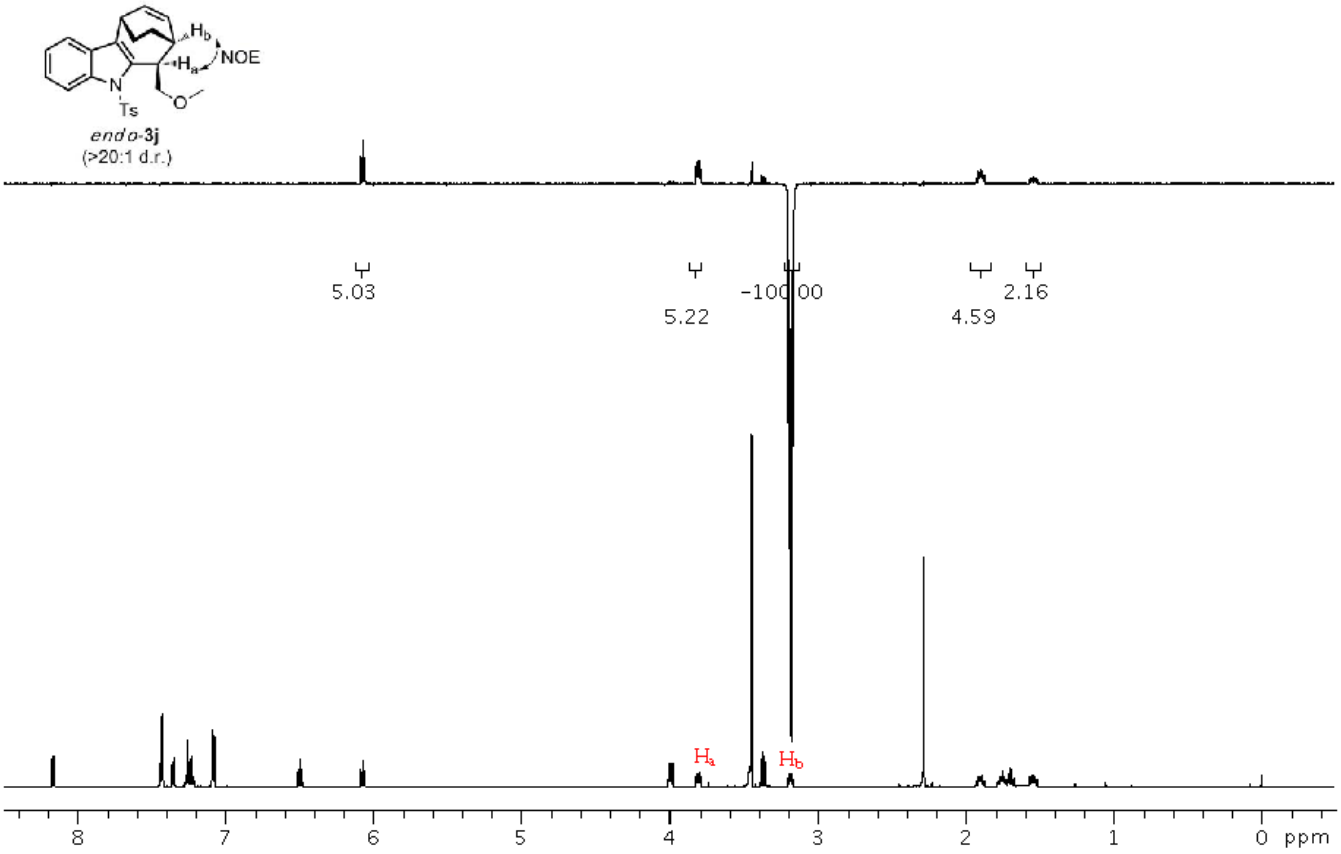


Chemical Formula: $C_{23}H_{22}FNO_3S$
Molecular Weight: 411.49

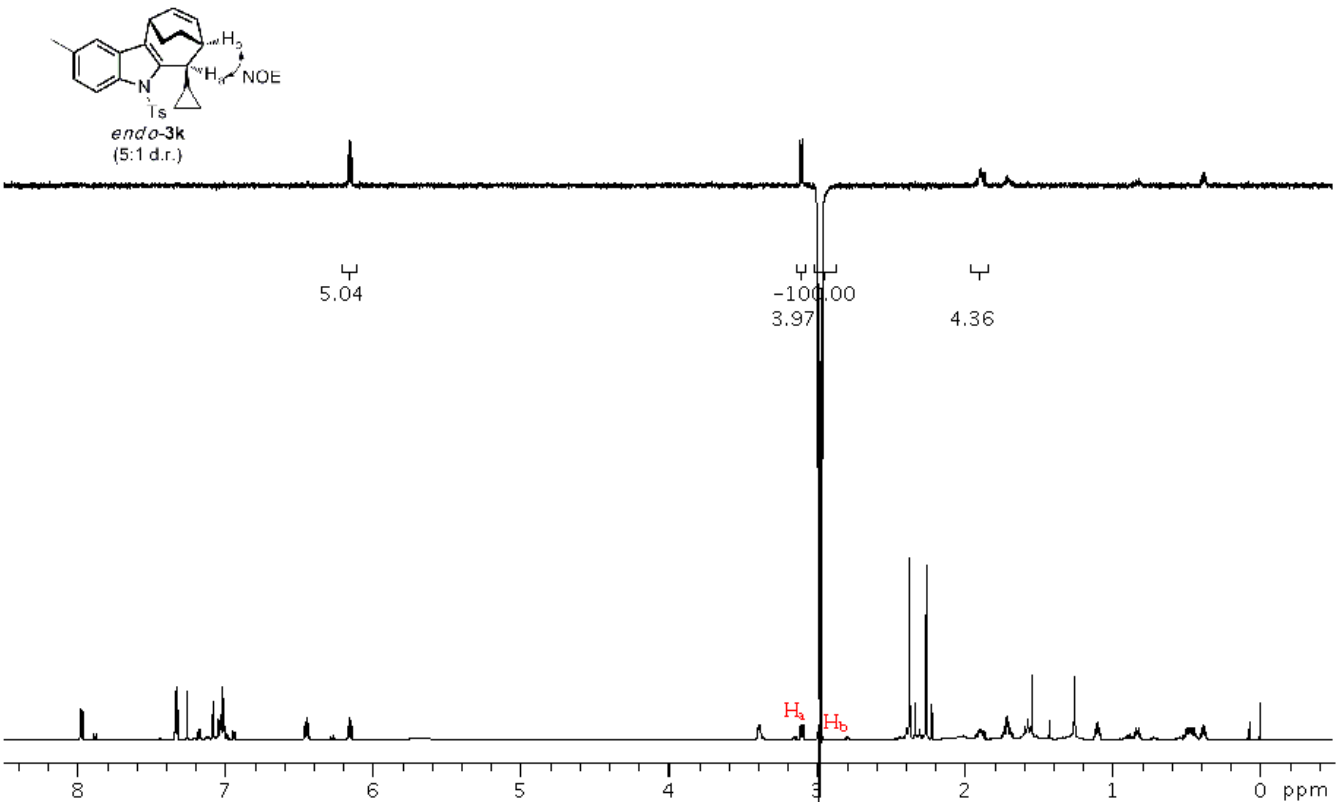
3-fluoro-6-(methoxymethyl)-5-tosyl-5,6,7,10-tetrahydro-7,10-methanocyclohepta[*b*]indole (**3o**) was prepared following general procedure as a colorless oil (65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, 1H, J = 10.0, 1.0 Hz), 7.31 (d, 2H, J = 8.4 Hz), 7.28-7.22 (m, 1H), 7.07 (t, 2H, J = 8.8 Hz), 6.97-6.92 (m, 1H), 6.33-6.29 (m, 1H), 5.88-5.85 (m, 1H), 4.28 (dd, 1H, J = 9.2, 2.8 Hz), 3.57 (t, 1H, J = 9.6 Hz), 3.47 (s, 3H), 3.43-3.40 (m, 1H), 3.30-3.29 (m, 1H), 2.28 (s, 3H), 2.01-1.94 (m, 2H). Major isomer of **3o** ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (d, J = 239 Hz), 144.5, 142.5, 139.5, 134.4, 133.0, 131.4, 130.7, 129.6, 129.4 (d, J = 3 Hz), 126.3, 118.4 (d, J = 9 Hz), 112.0 (d, J = 24 Hz), 103.7 (d, J = 29 Hz), 75.8, 58.8, 40.8, 39.9, 36.9, 36.1, 21.5. EI-MS *m/z* [M]-: 69.1 (9.9), 91.1 (43.4), 155.0 (33.5), 184.0 (16.3), 185.0 (15.4), 196.0 (8.1), 198.0 (12.0), 209.0 (11.1), 210.0 (34.5), 211.0 (19.9), 212.0 (9.6), 222.0 (8.0), 224.1 (26.1), 225.1 (6.3), 256.1 (18.8), 366.0 (100), 367.0 (22.0), 368.0 (8.9), 411.0 (35.4), 412.1 (7.9). FTIR (neat): 3366, 3054, 2952, 2927, 2865, 2589, 2370, 1795, 1613, 1596, 1482, 1448, 1427, 1366, 1265, 1232, 1186, 1169, 1113, 1088, 1031, 980, 917, 864, 825, 809, 738, 708, 666, 585, 548 cm^{-1}. HRMS-ESI (m/z): $[M+H]^+$ calcd 412.1377; found 412.1371.

III. Determination of Relative Configuration of Products.

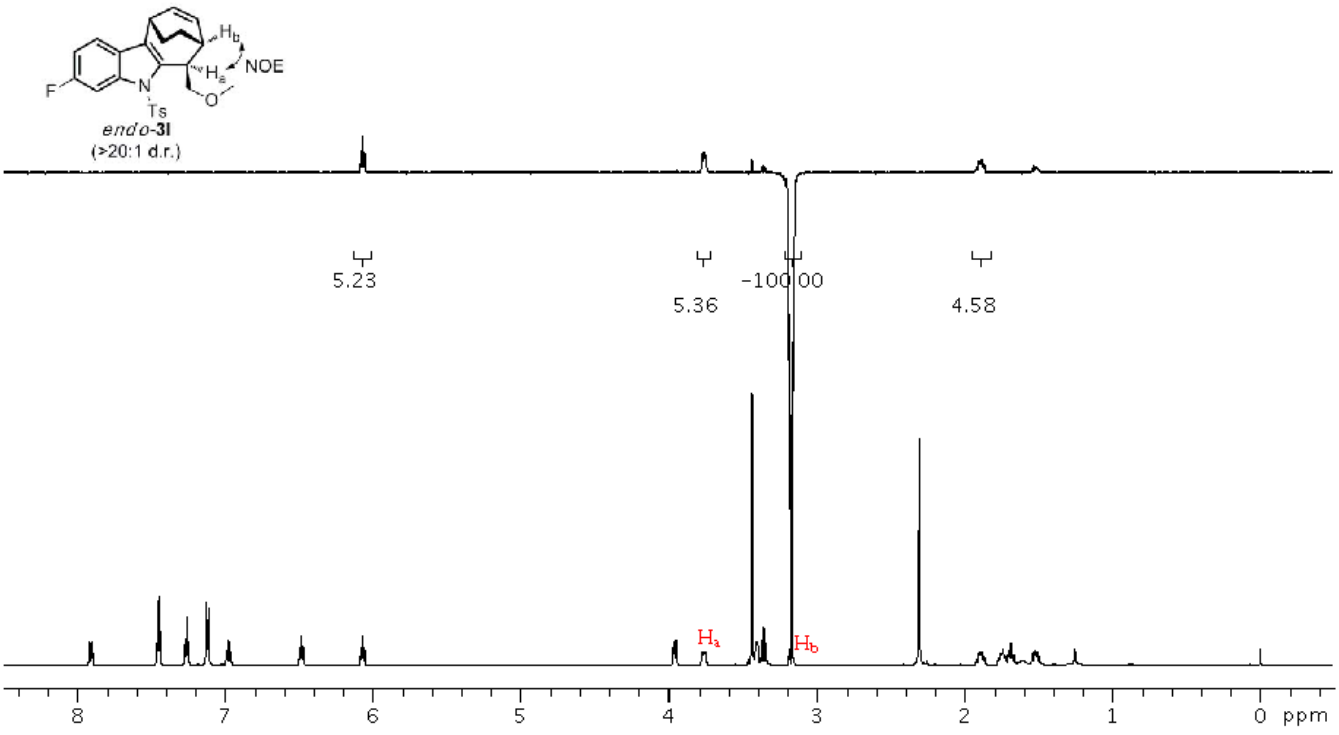
1D NOE ($CDCl_3$) spectrum of *endo*-**3j**, 600 MHz



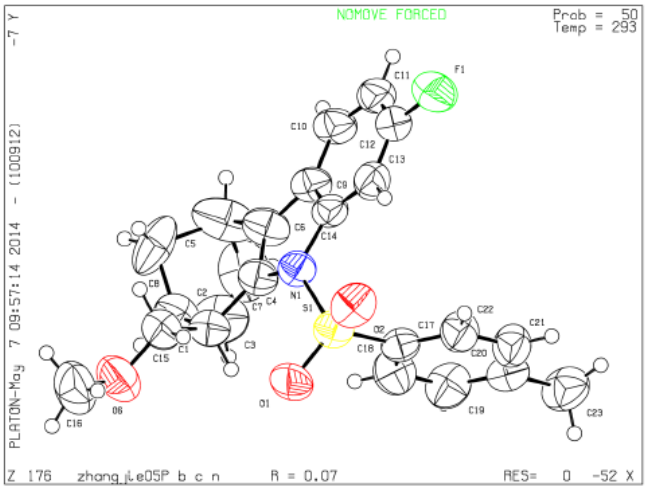
1D NOE ($CDCl_3$) spectrum of *endo*-**3k**, 600 MHz



1D NOE ($CDCl_3$) spectrum of *endo*-**3l**, 600 MHz



X-Ray Diffraction Analysis of Arylation Product *endo*-3o.



The crystallographic data of *endo*-**3o** were summarized in the following table.

```
Bond precision:   C-C = 0.0067 A          Wavelength=0.71073

Cell:             a=23.1688(16)     b=8.5376(4)     c=20.5949(12)
                  alpha=90          beta=90         gamma=90
Temperature:      293 K

                  Calculated                Reported
Volume            4073.8(4)                 4073.8(4)
Space group       P b c n                   P b c n
Hall group        -P 2n 2ab                 -P 2n 2ab
Moiety formula    C23 H22 F N O3 S          C23 H22 F N O3 S
Sum formula       C23 H22 F N O3 S          C23 H22 F N O3 S
Mr                411.49                    411.47
Dx,g cm-3         1.342                     1.342
Z                 8                         8
Mu (mm-1)         0.192                     0.192
F000              1728.0                    1728.0
F000'             1729.82
h,k,lmax          28,10,25                  28,10,25
Nref              4018                      4002
Tmin,Tmax         0.962,0.977               0.559,1.000
Tmin'             0.955

Correction method= MULTI-SCAN

Data completeness= 0.996          Theta(max)= 26.020

R(reflections)= 0.0734( 2259)     wR2(reflections)= 0.2200( 4002)

S = 1.032                 Npar= Npar = 264
```

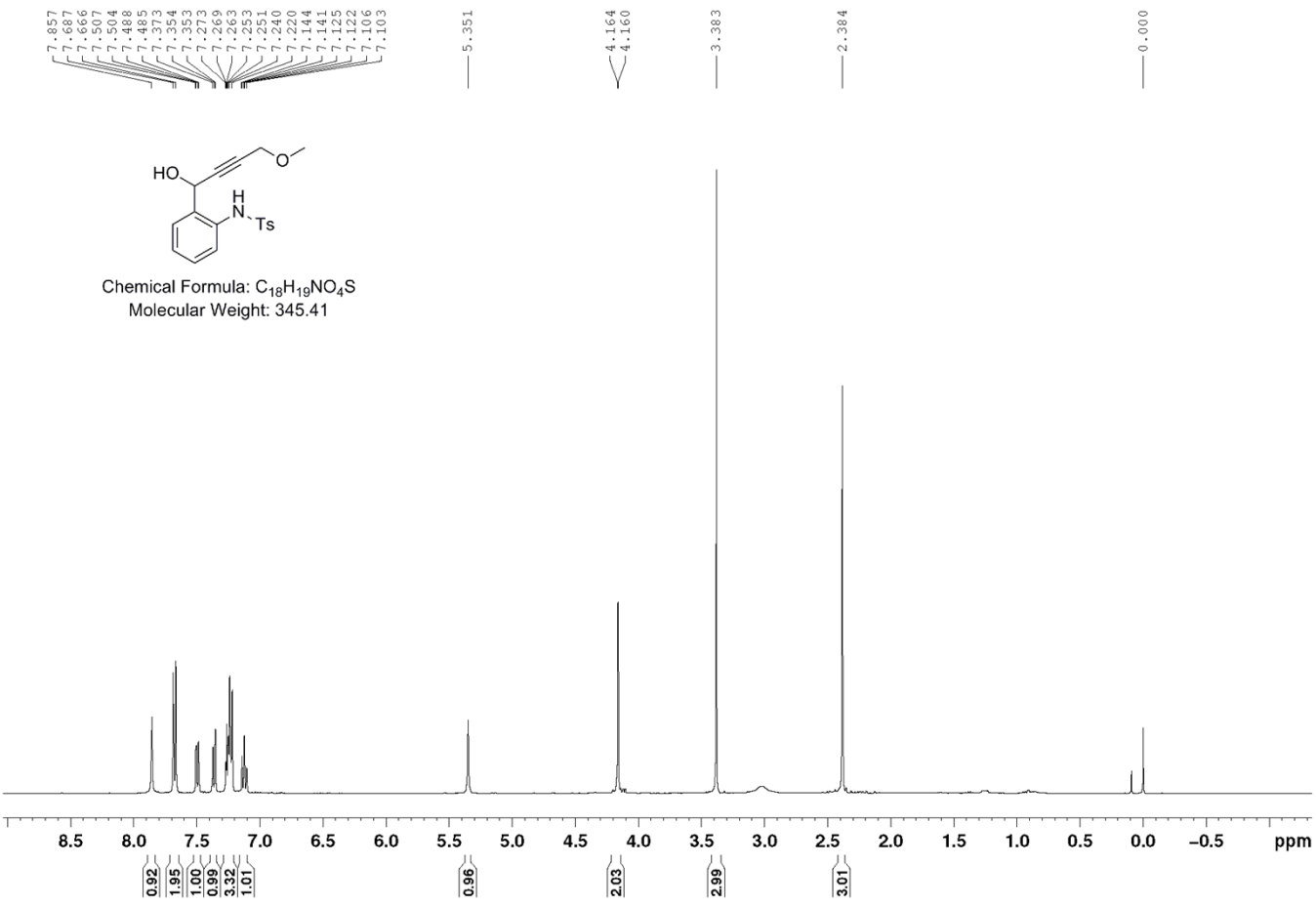
CIF file of *endo*-**3o** can be obtained from the Cambridge Crystallographic Data Centre using deposition number CCDC 1001592. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk].

[1]. D. Susanti, F. Koh, J. A. Kusuma, P. Kothandaraman, P. W. H. Chan, *J. Org. Chem.* **2012**, *77*, 7166.

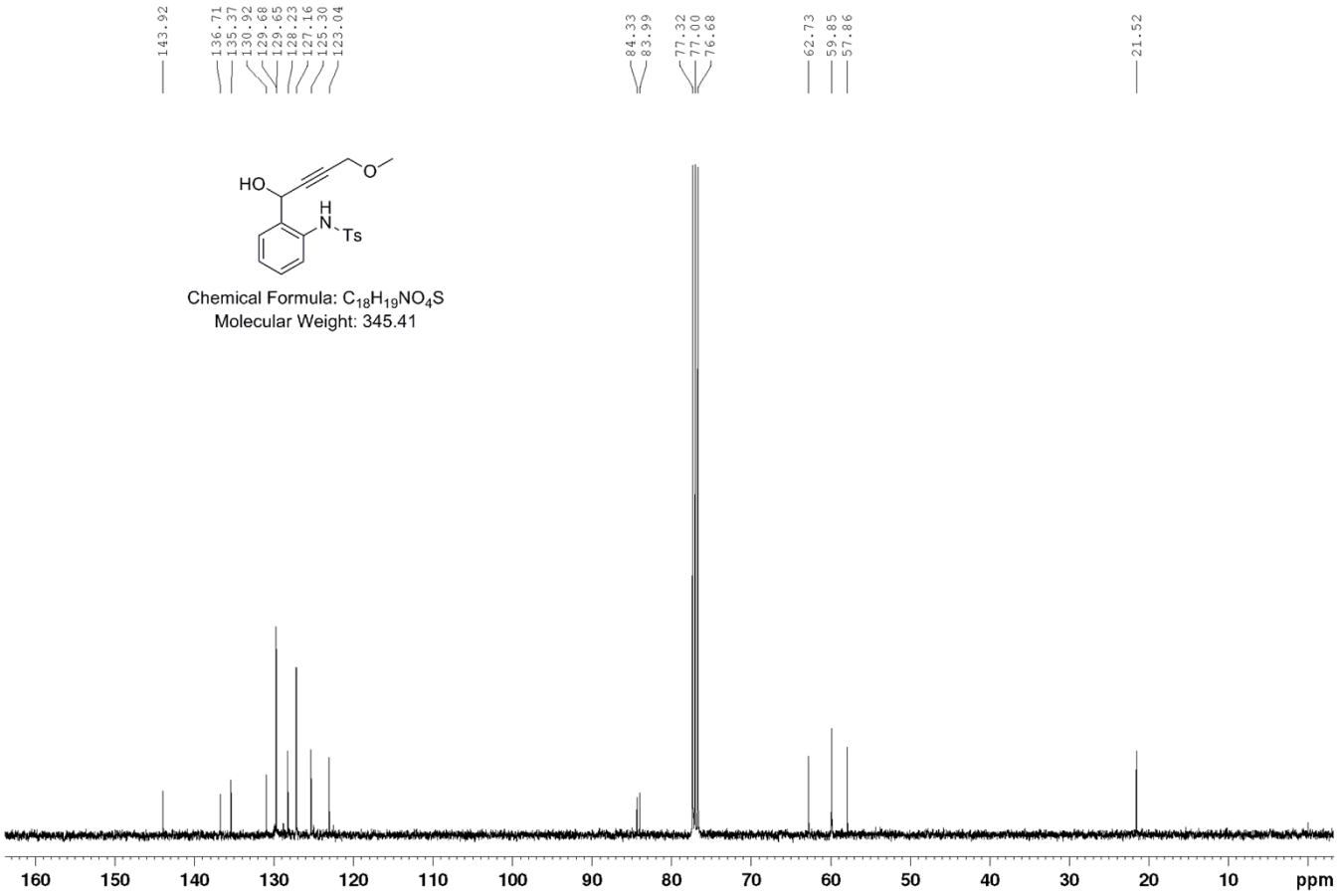
[2]. D. Shu, W. Song, X. Li, W. Tang, *Angew. Chem.* **2013**, *125*, 3319; *Angew. Chem. Int. Ed.* **2013**, *52*, 3237.

IV. NMR Spectra of Compounds

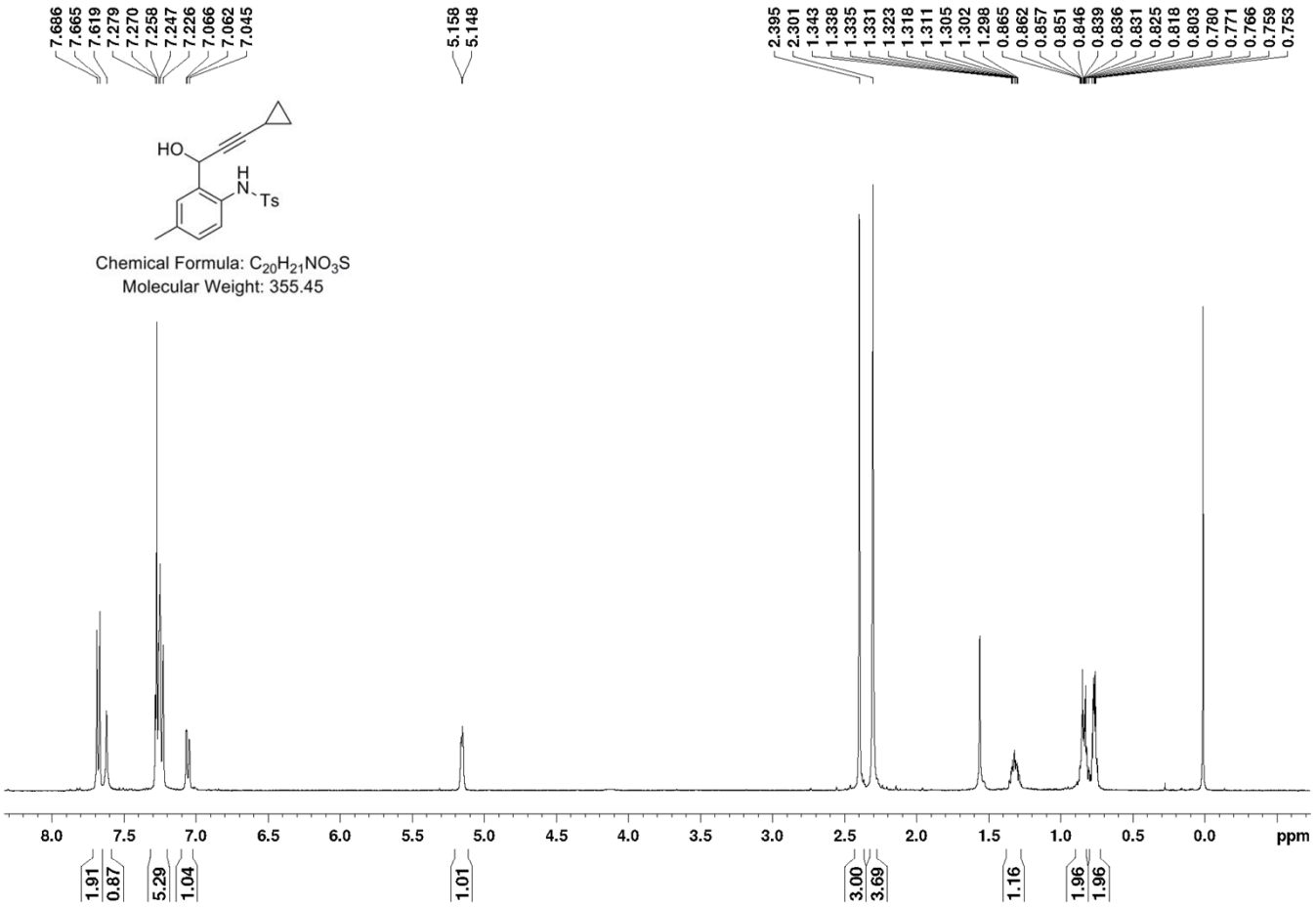
1a ^{1}H NMR, 400 MHz, $CDCl_3$



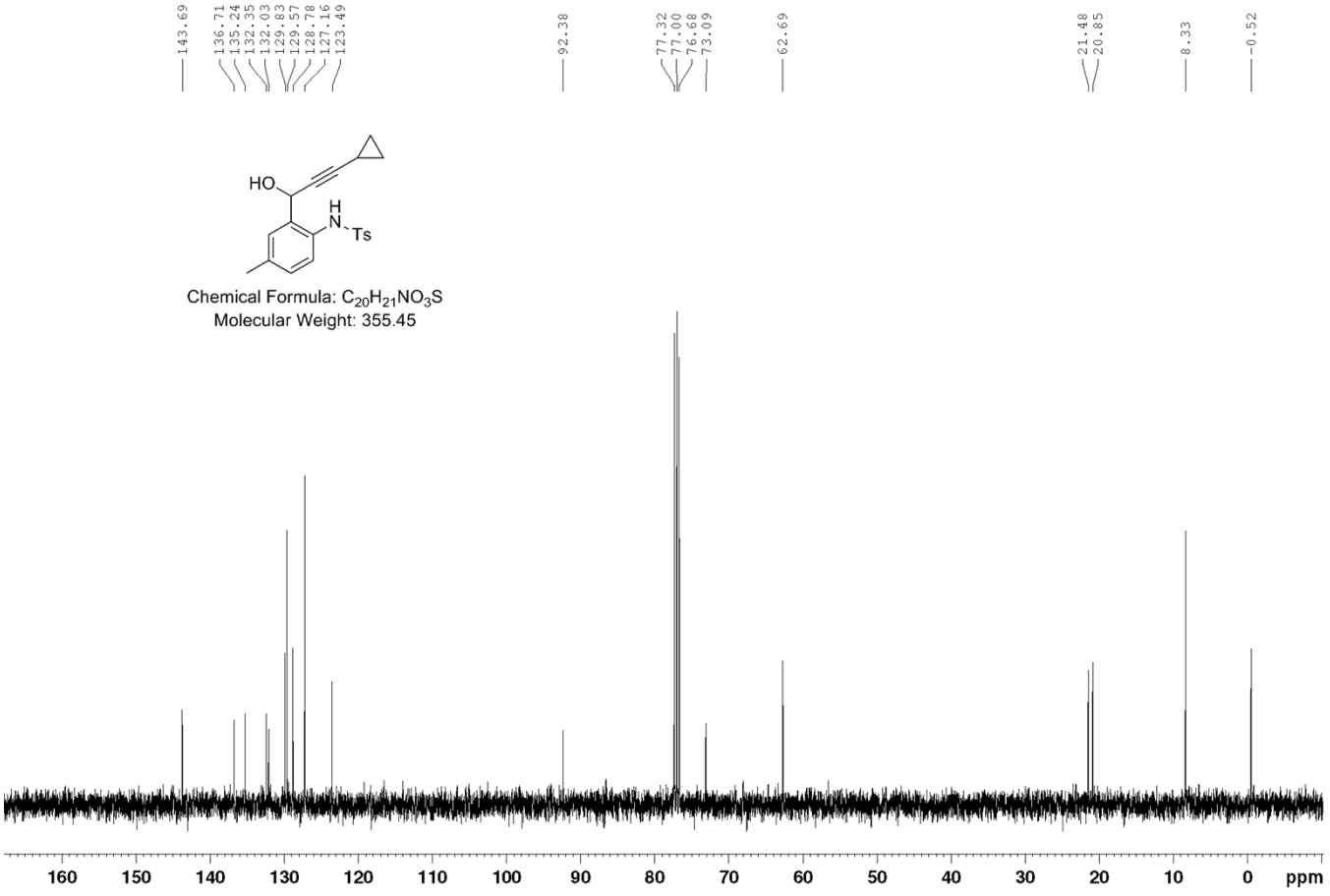
1a ^{13}C NMR, 100 MHz, $CDCl_3$



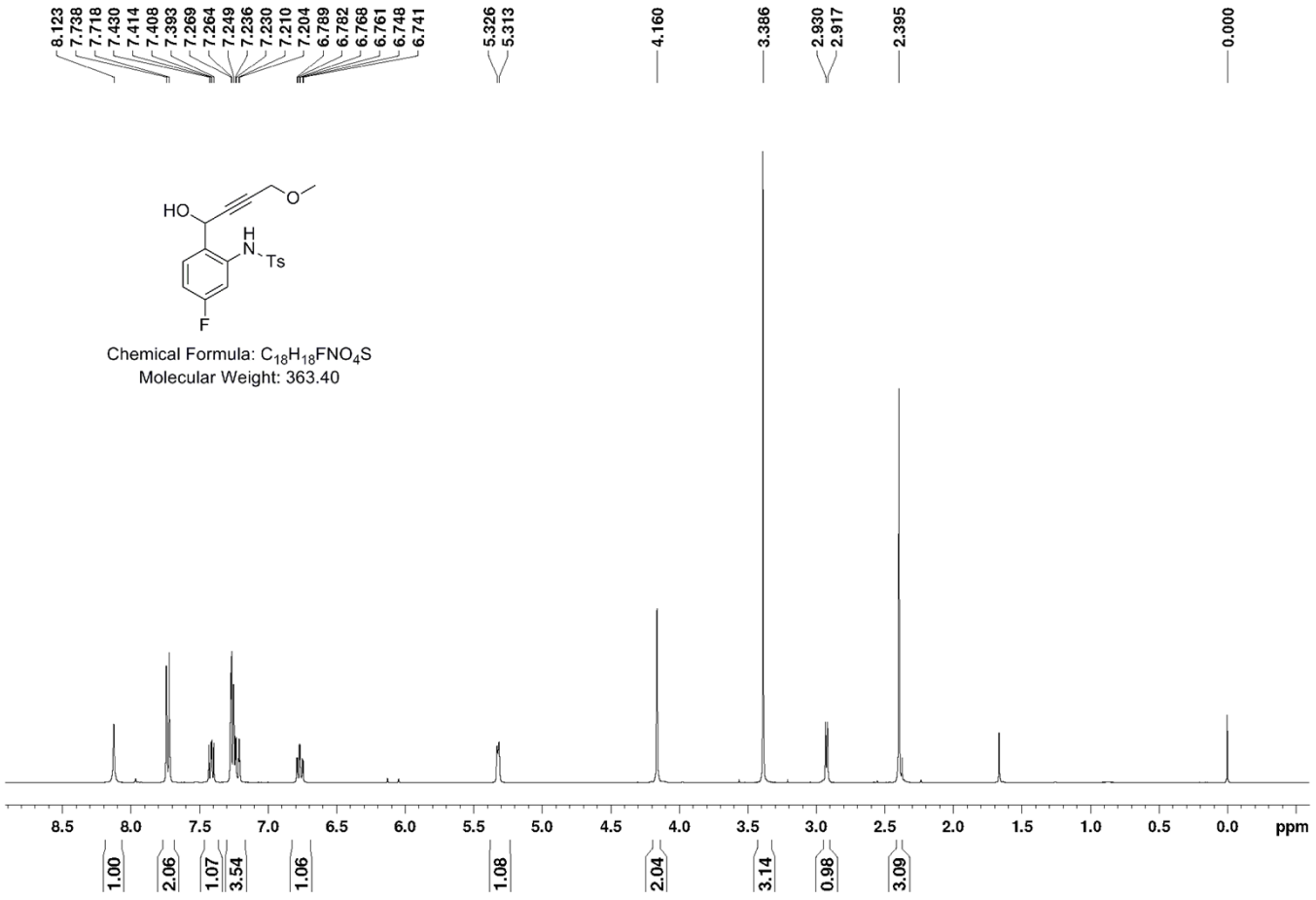
1b ^{1}H NMR, 400 MHz, $CDCl_3$



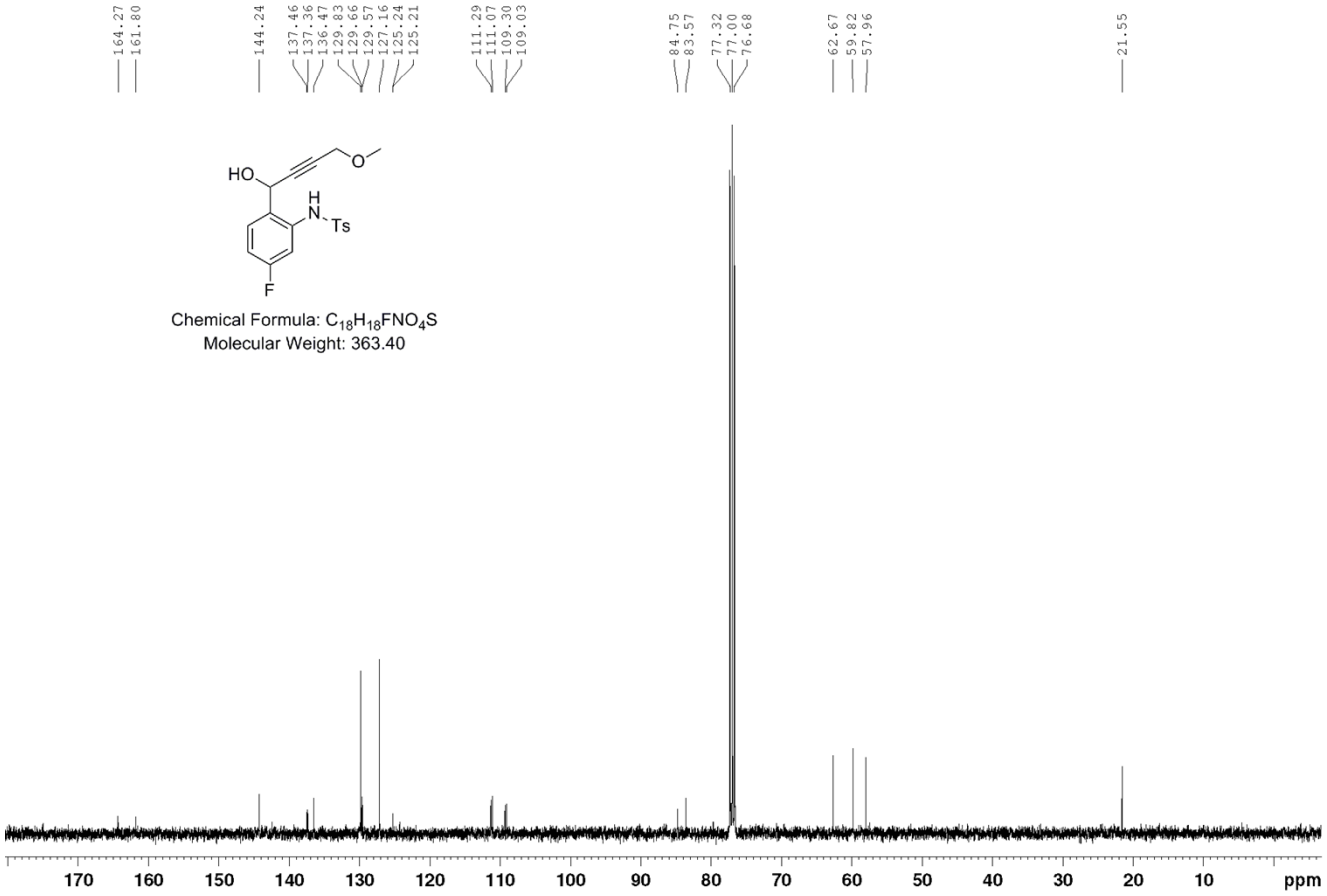
1b ^{13}C NMR, 100 MHz, $CDCl_3$



1c ^{1}H NMR, 400 MHz, $CDCl_3$

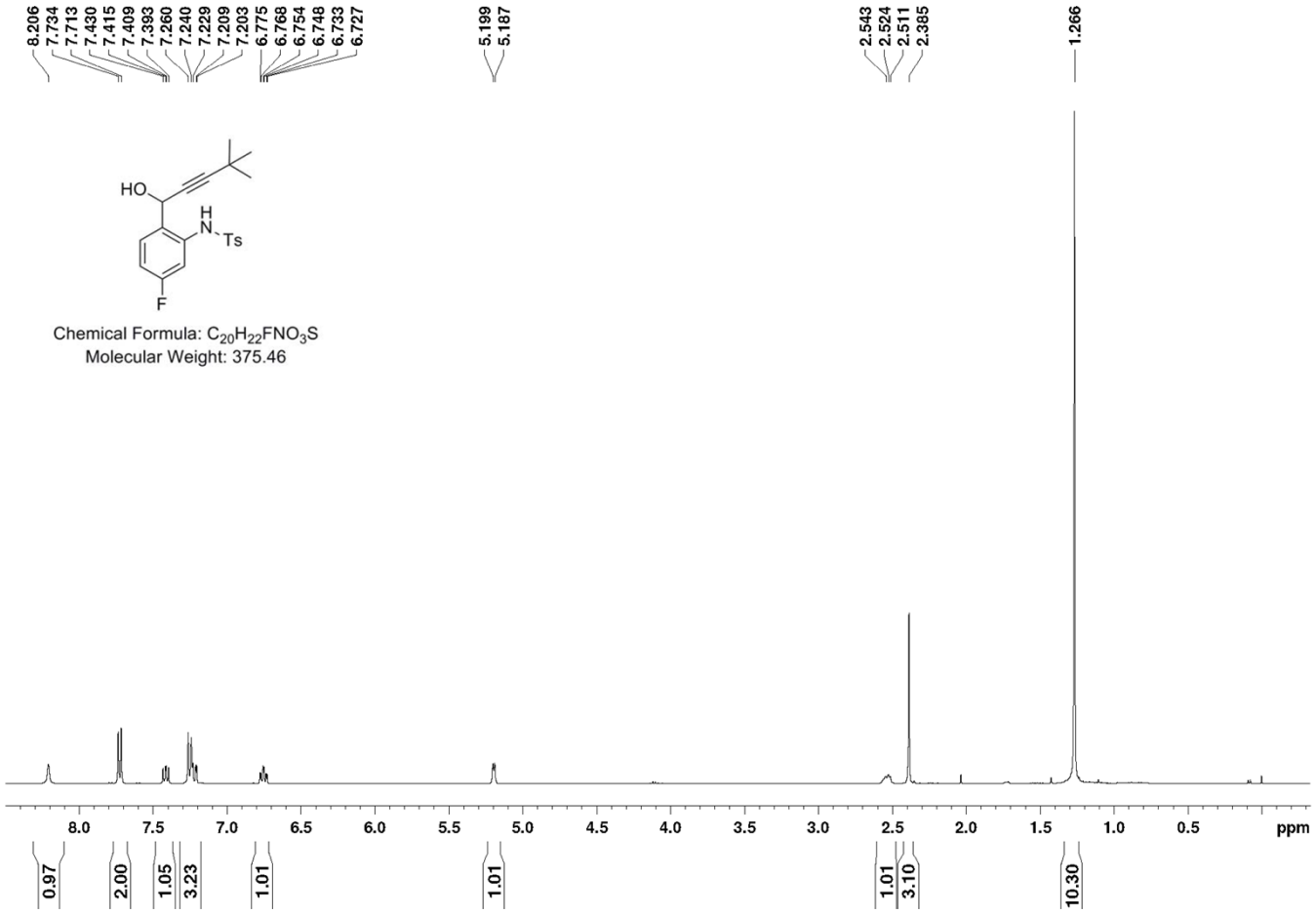


1c ^{13}C NMR, 100 MHz, $CDCl_3$



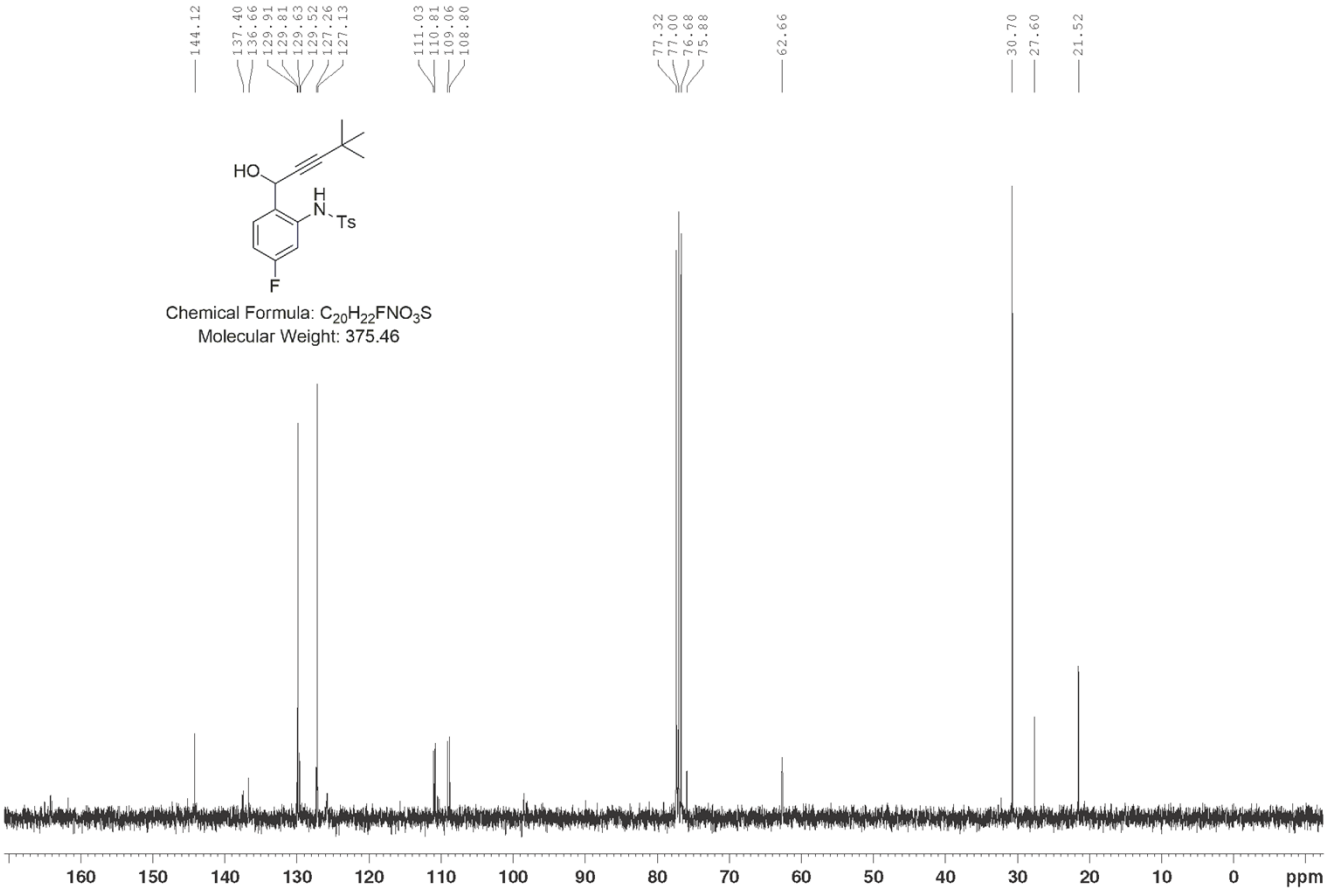
Chemical Formula: $C_{18}H_{18}FNO_4S$
Molecular Weight: 363.40

1d ^{1}H NMR, 400 MHz, $CDCl_3$

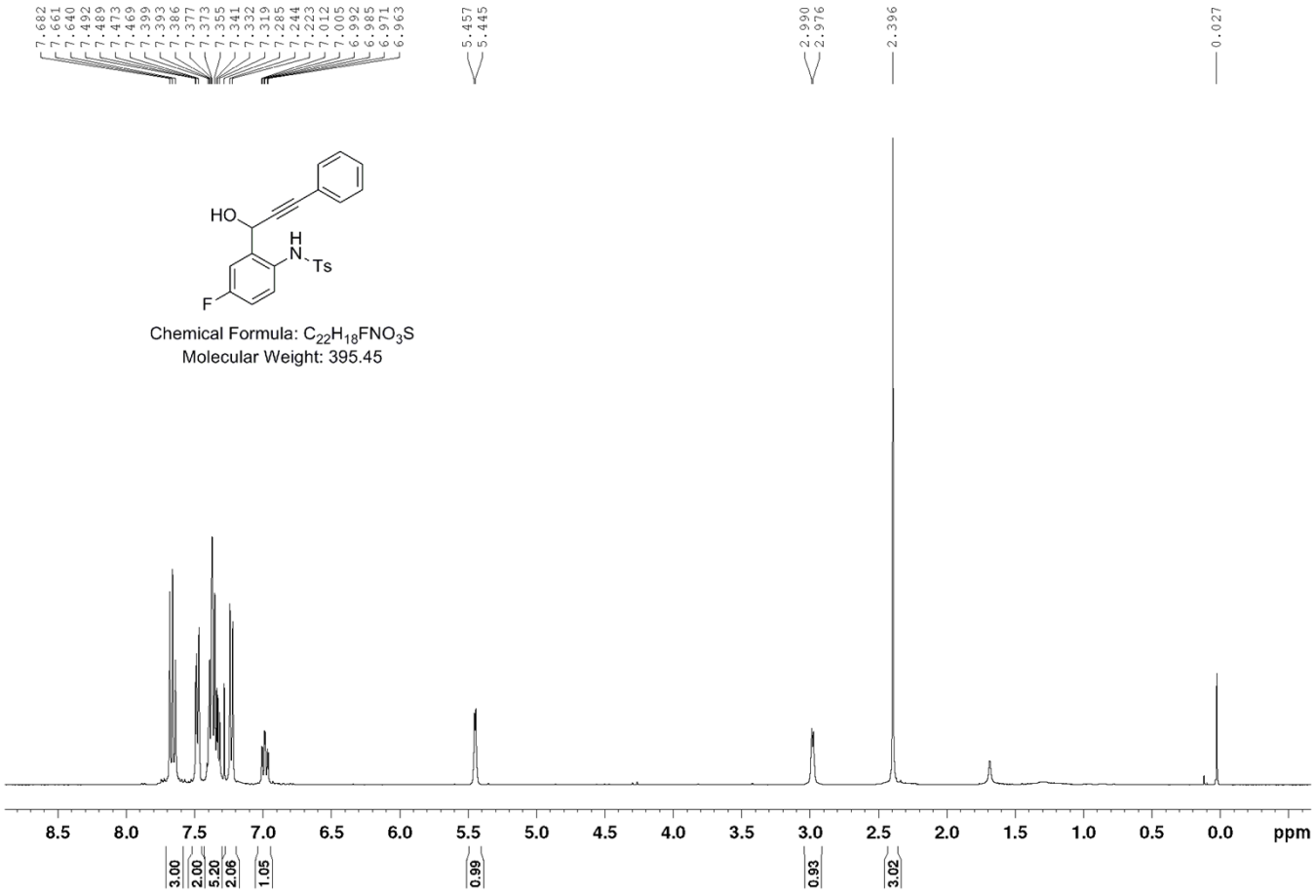


Chemical Formula: $C_{20}H_{22}FNO_3S$
Molecular Weight: 375.46

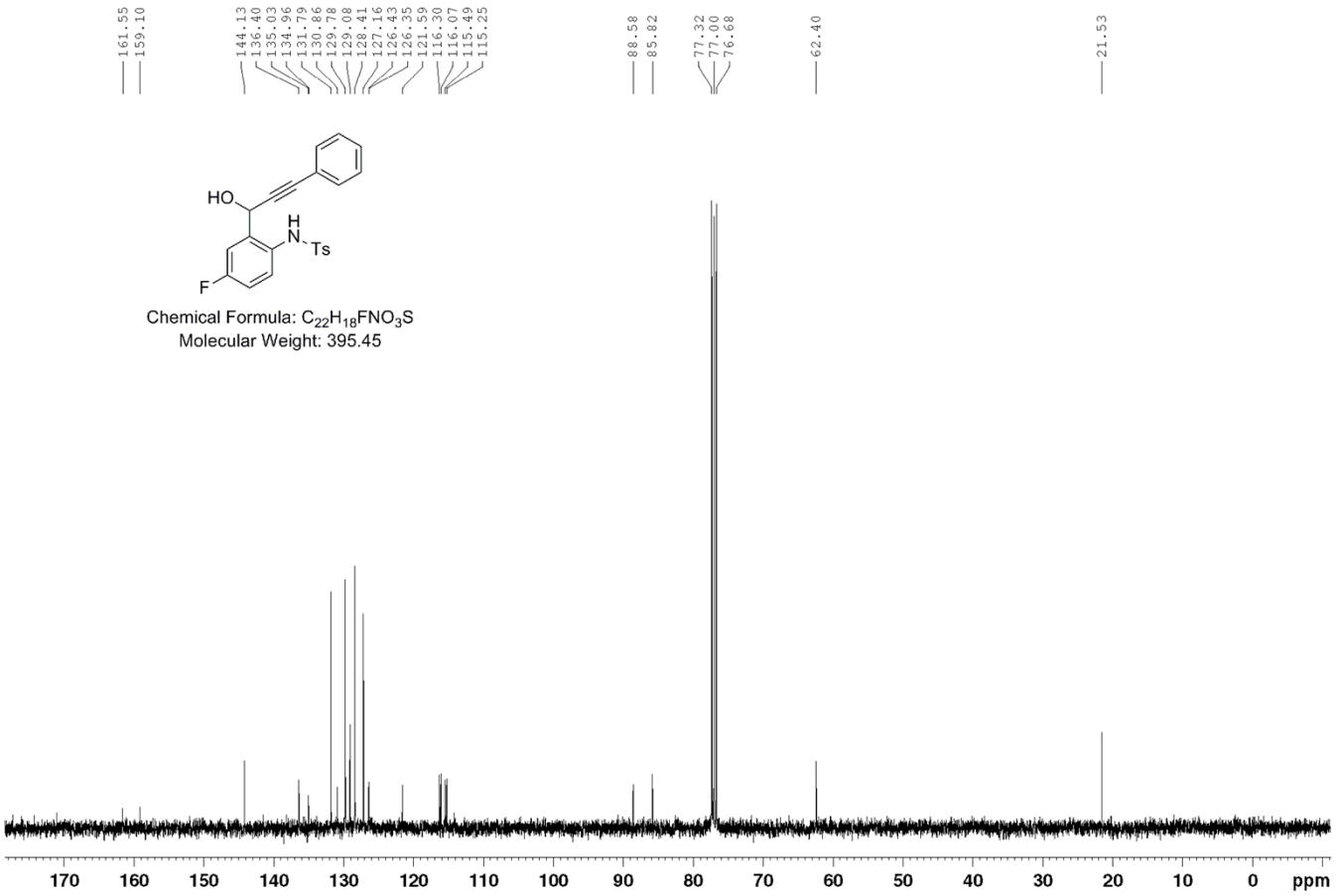
1d ^{13}C NMR, 100 MHz, $CDCl_3$



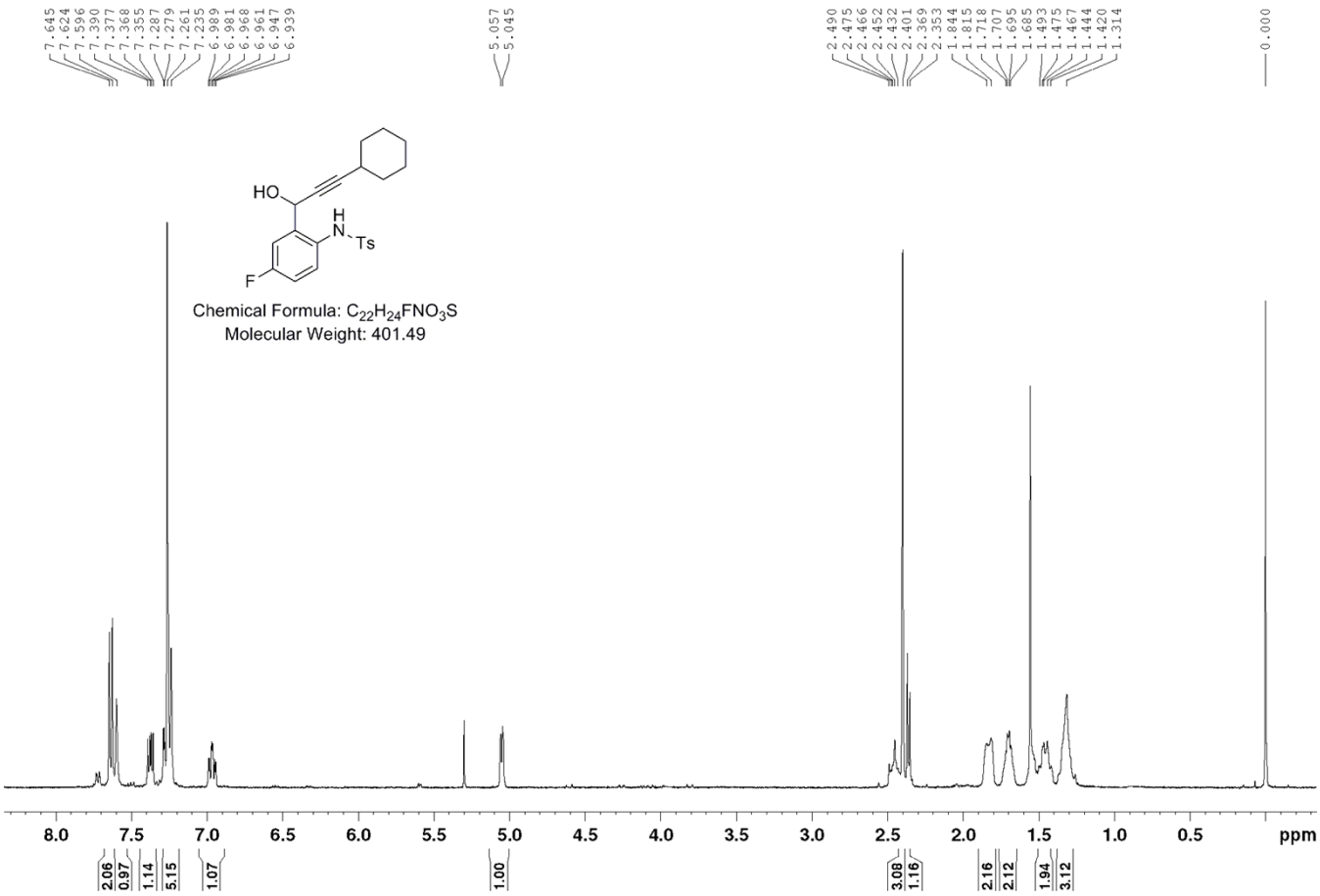
1e ^{1}H NMR, 400 MHz, $CDCl_3$



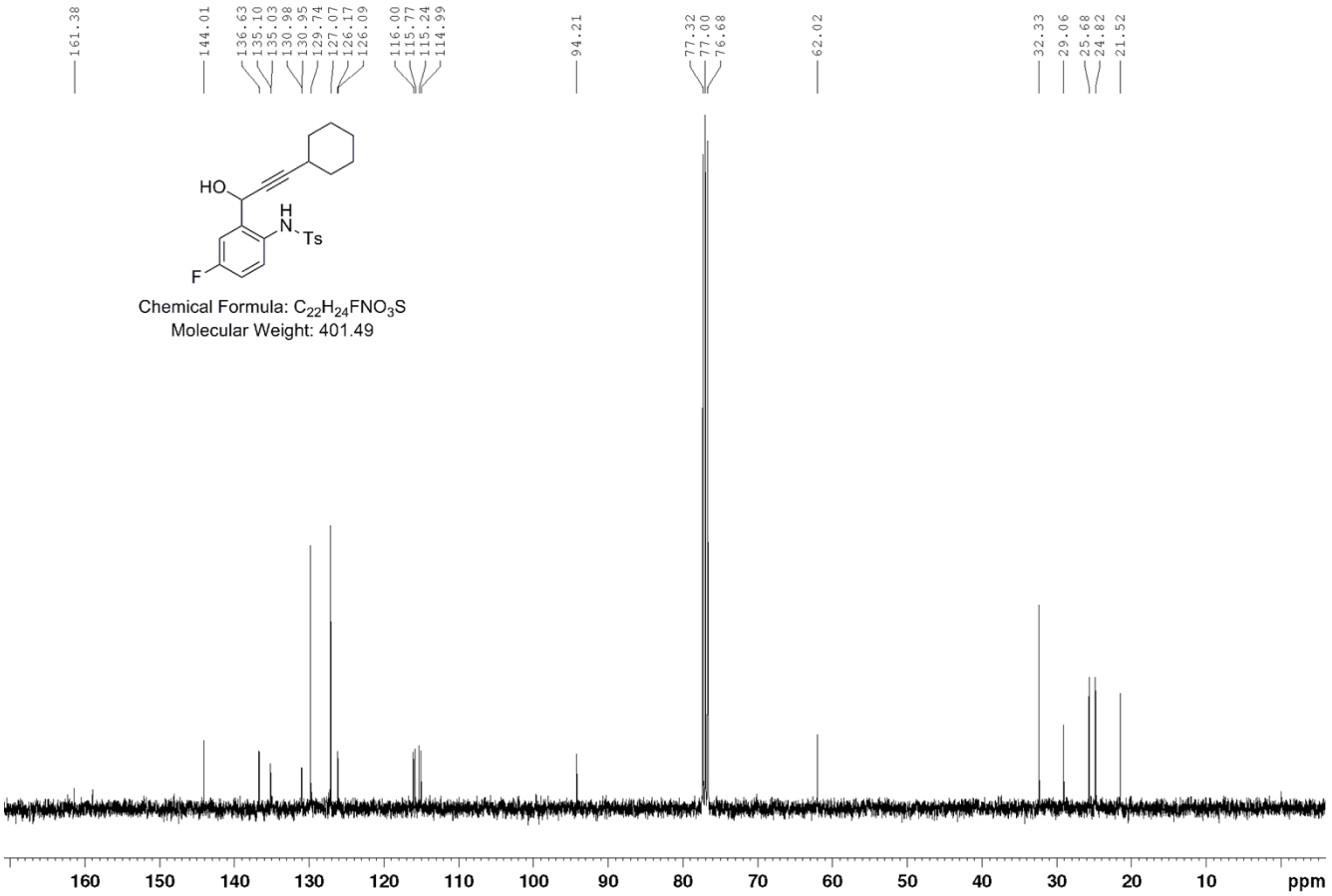
1e ^{13}C NMR, 100 MHz, $CDCl_3$



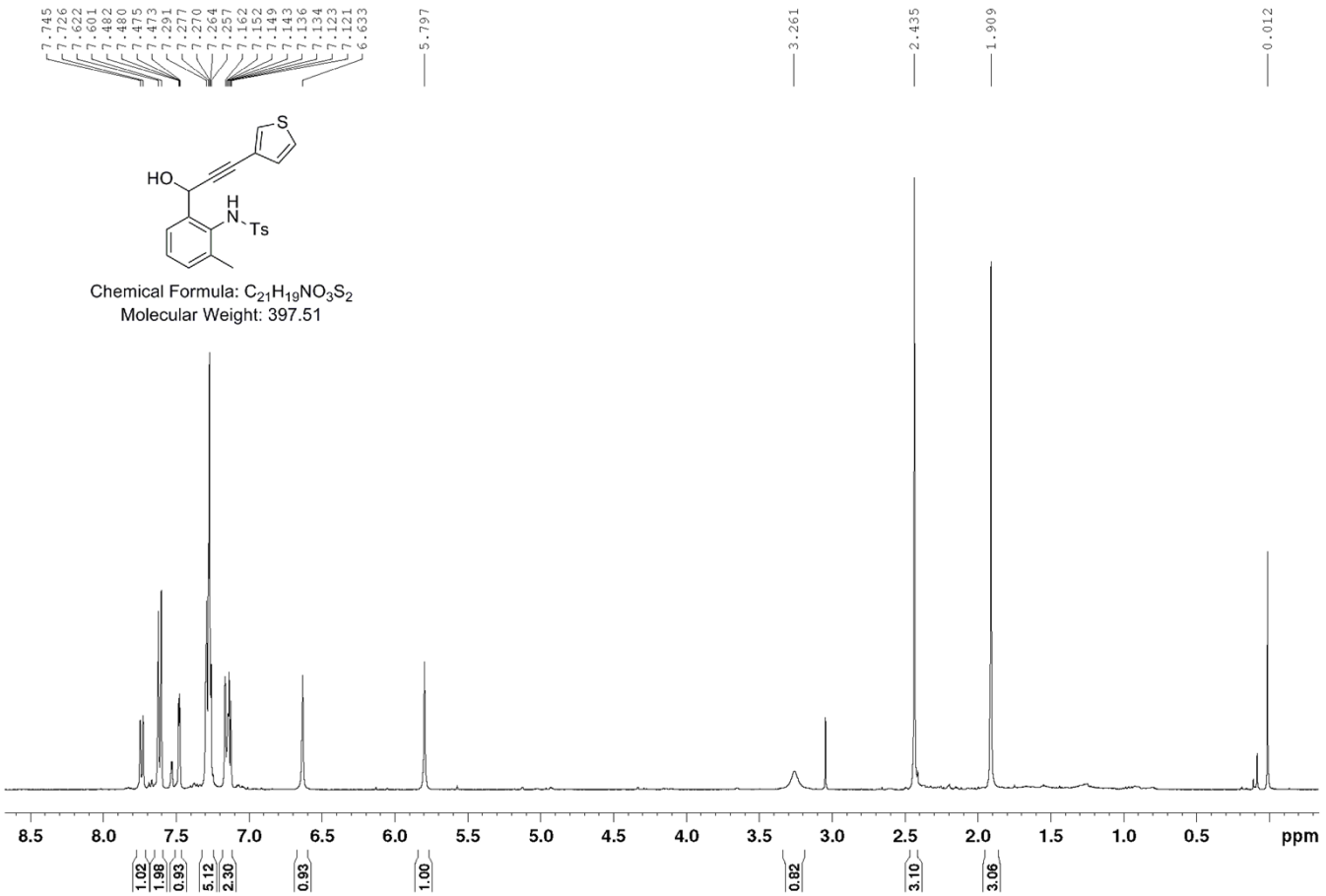
1f ^{1}H NMR, 400 MHz, $CDCl_3$



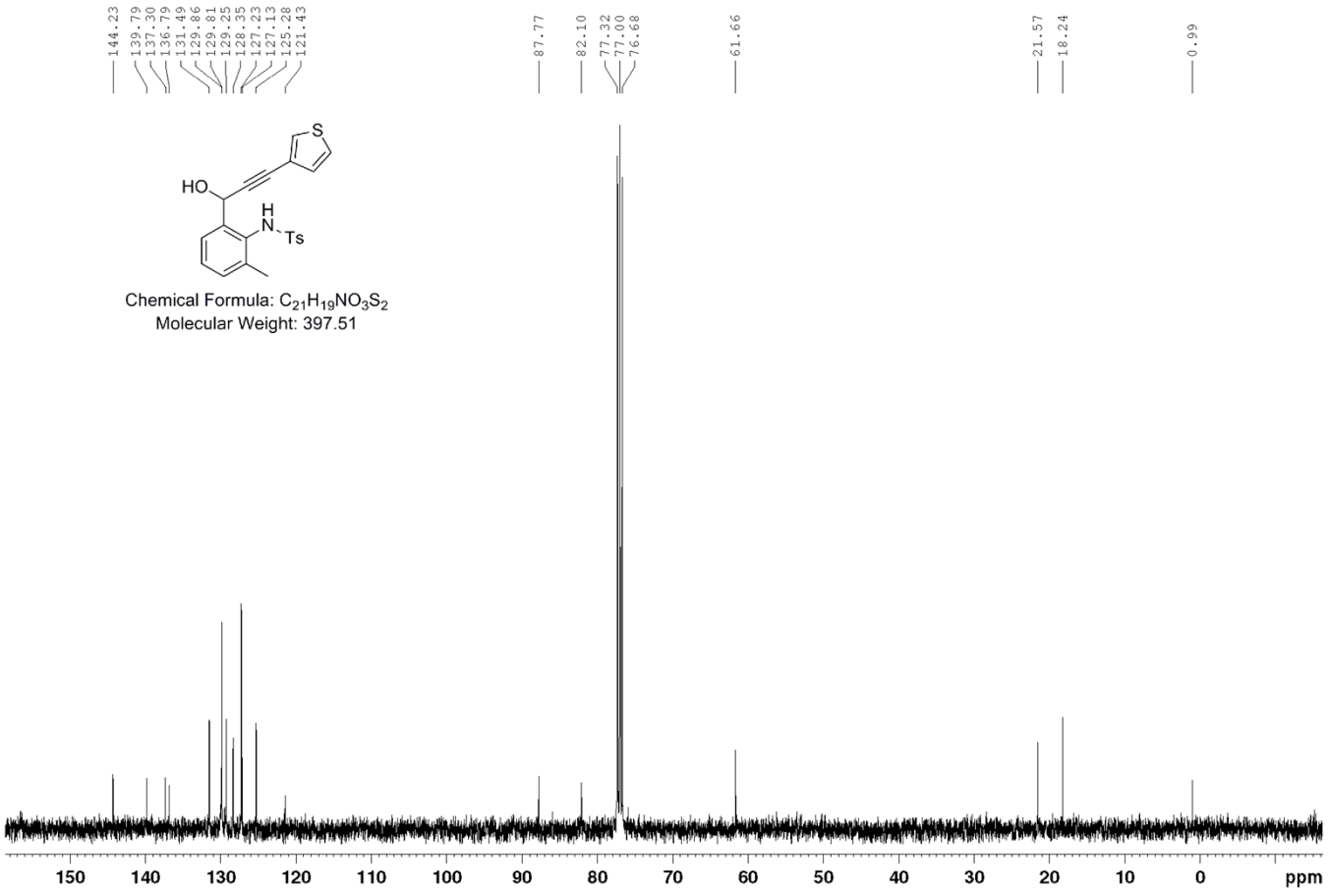
1f ^{13}C NMR, 100 MHz, $CDCl_3$



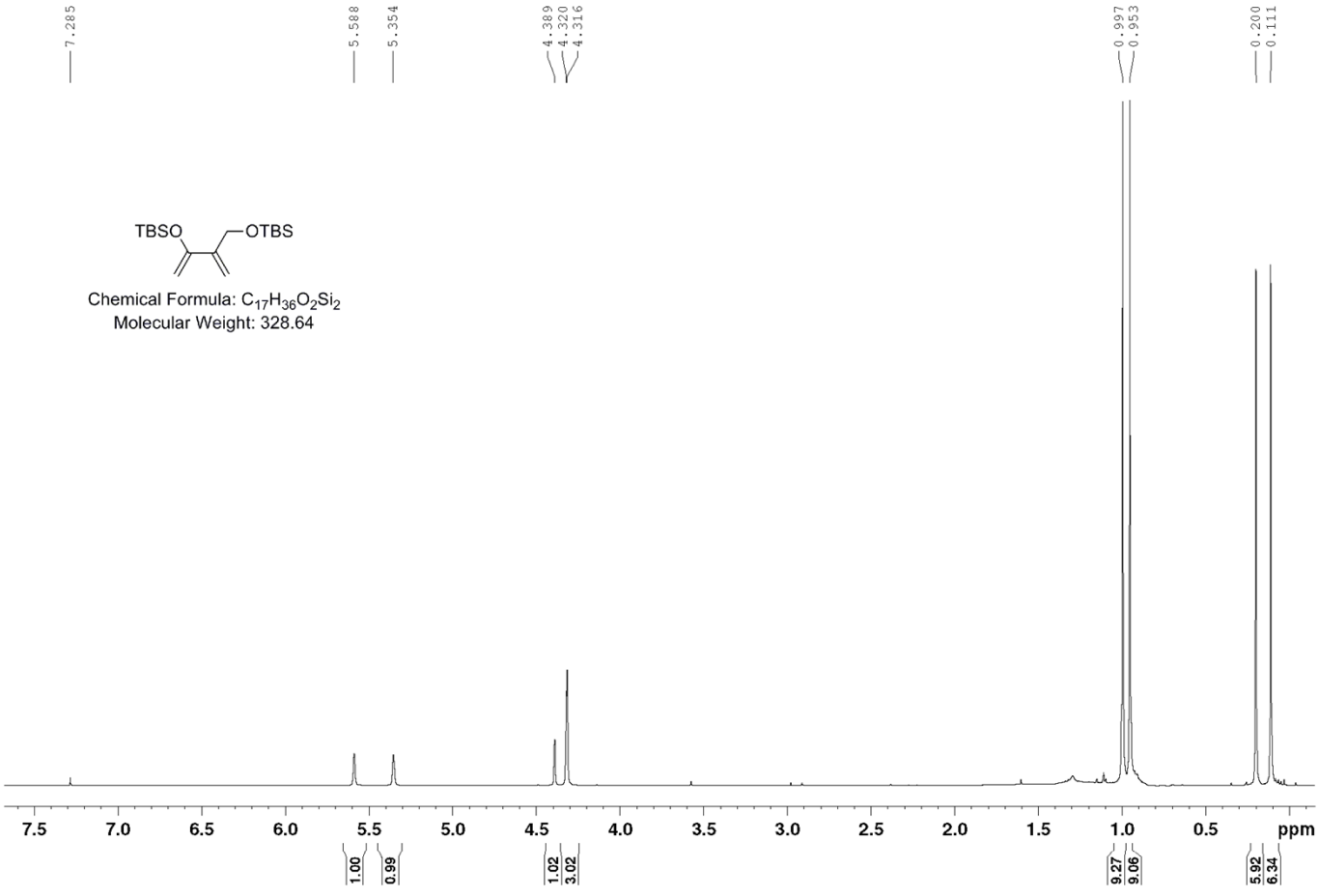
1g ^{1}H NMR, 400 MHz, $CDCl_3$



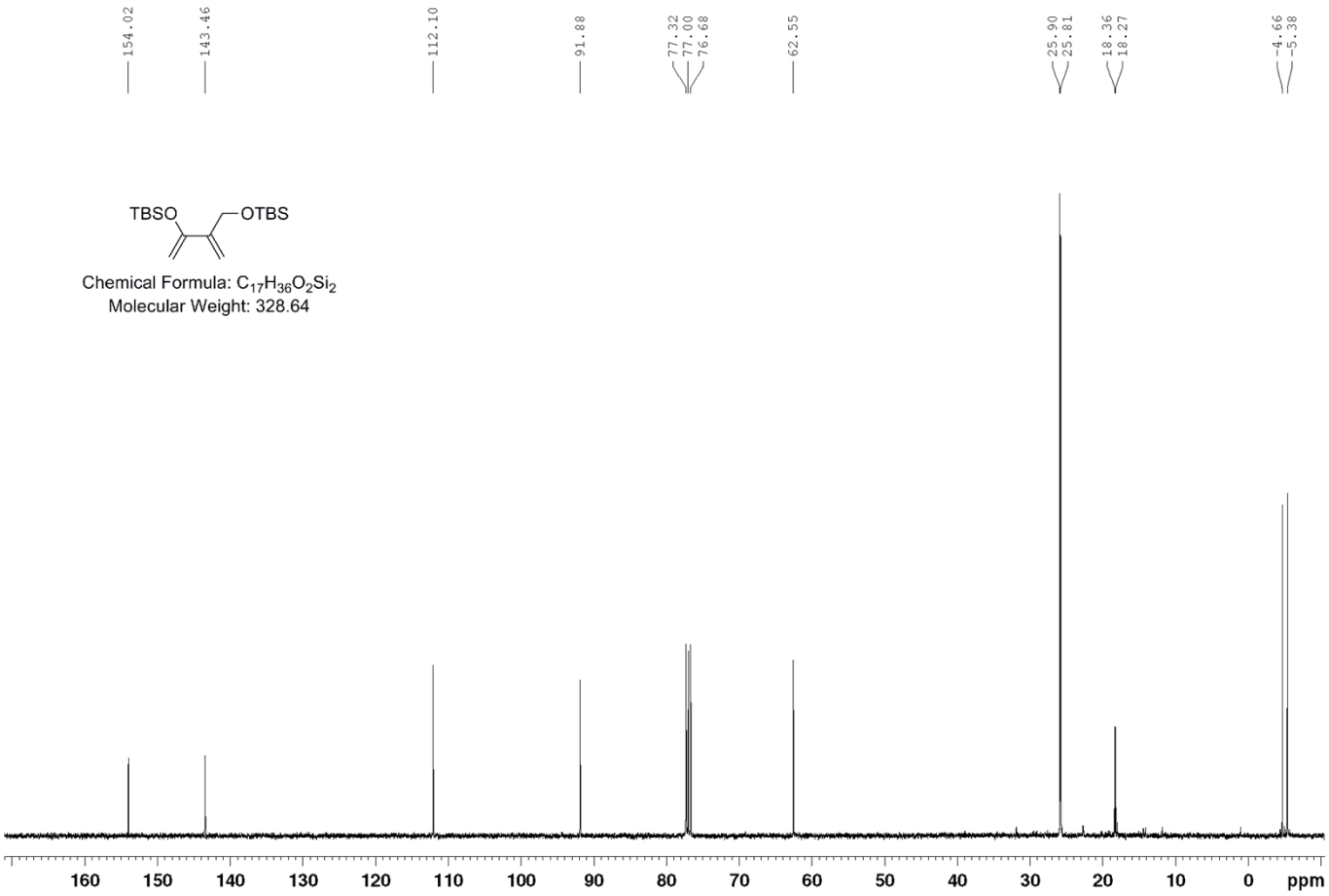
1g ^{13}C NMR, 100 MHz, $CDCl_3$



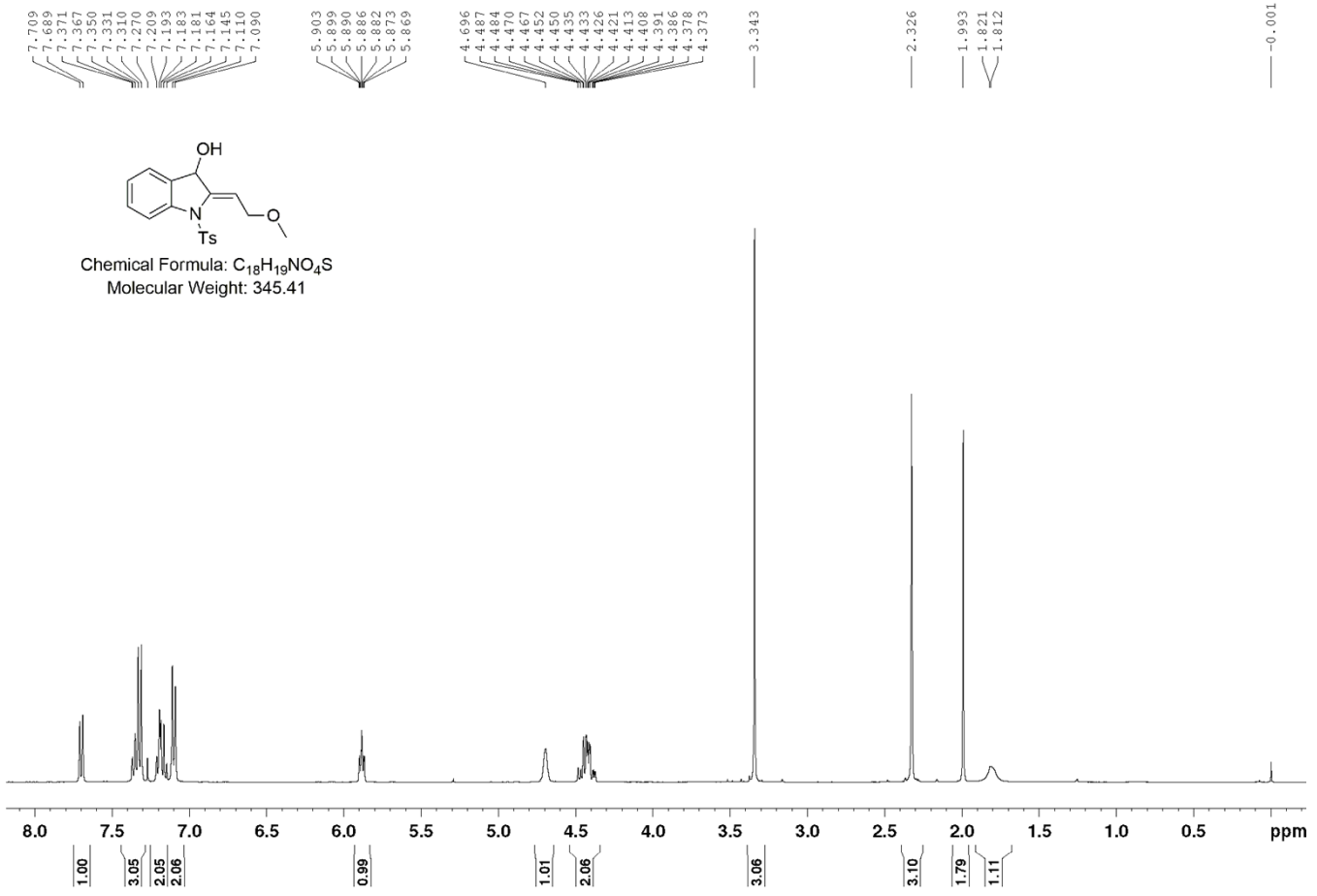
4b ^{1}H NMR, 400 MHz, $CDCl_3$



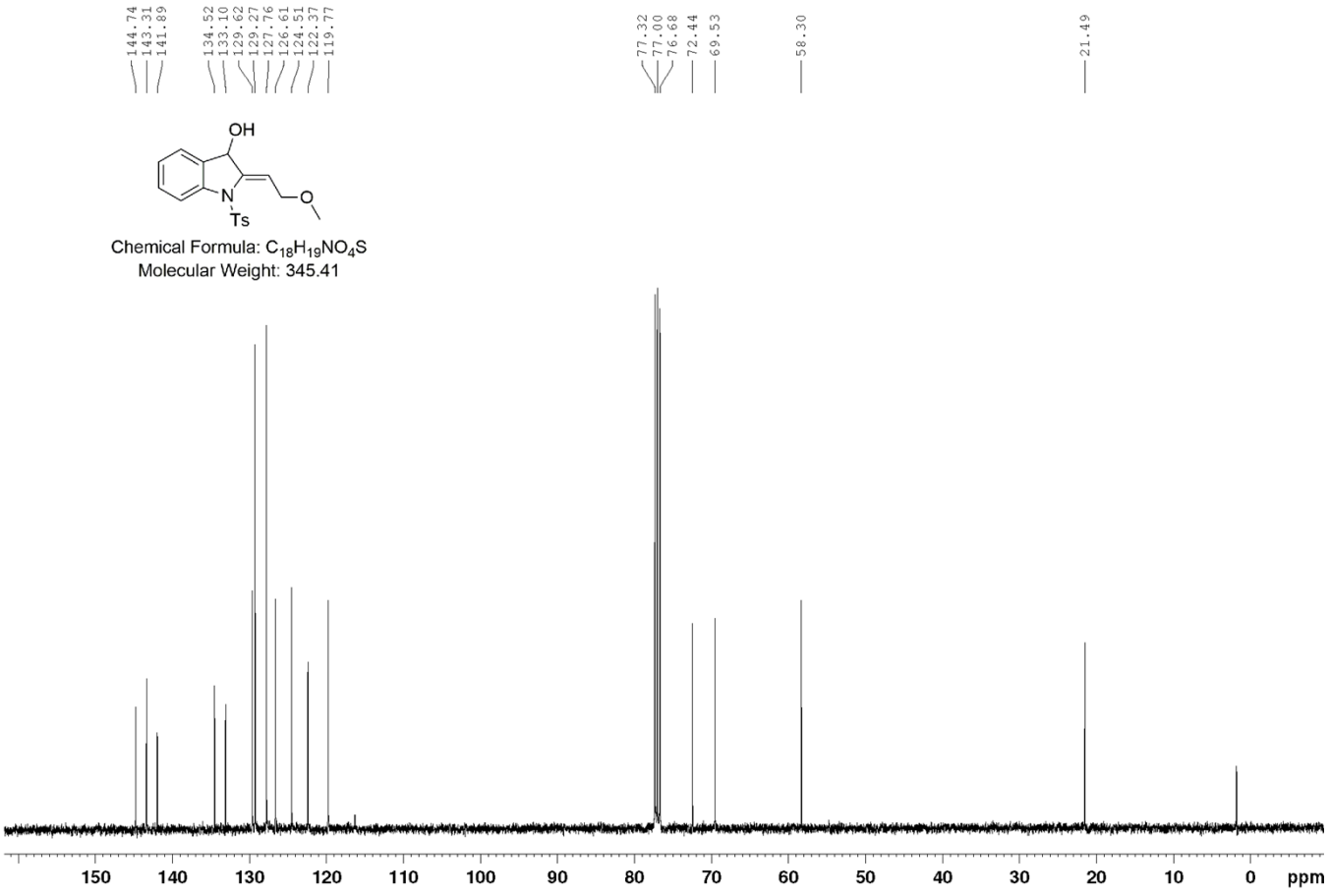
4b^{13}C NMR, 100 MHz, $CDCl_3$



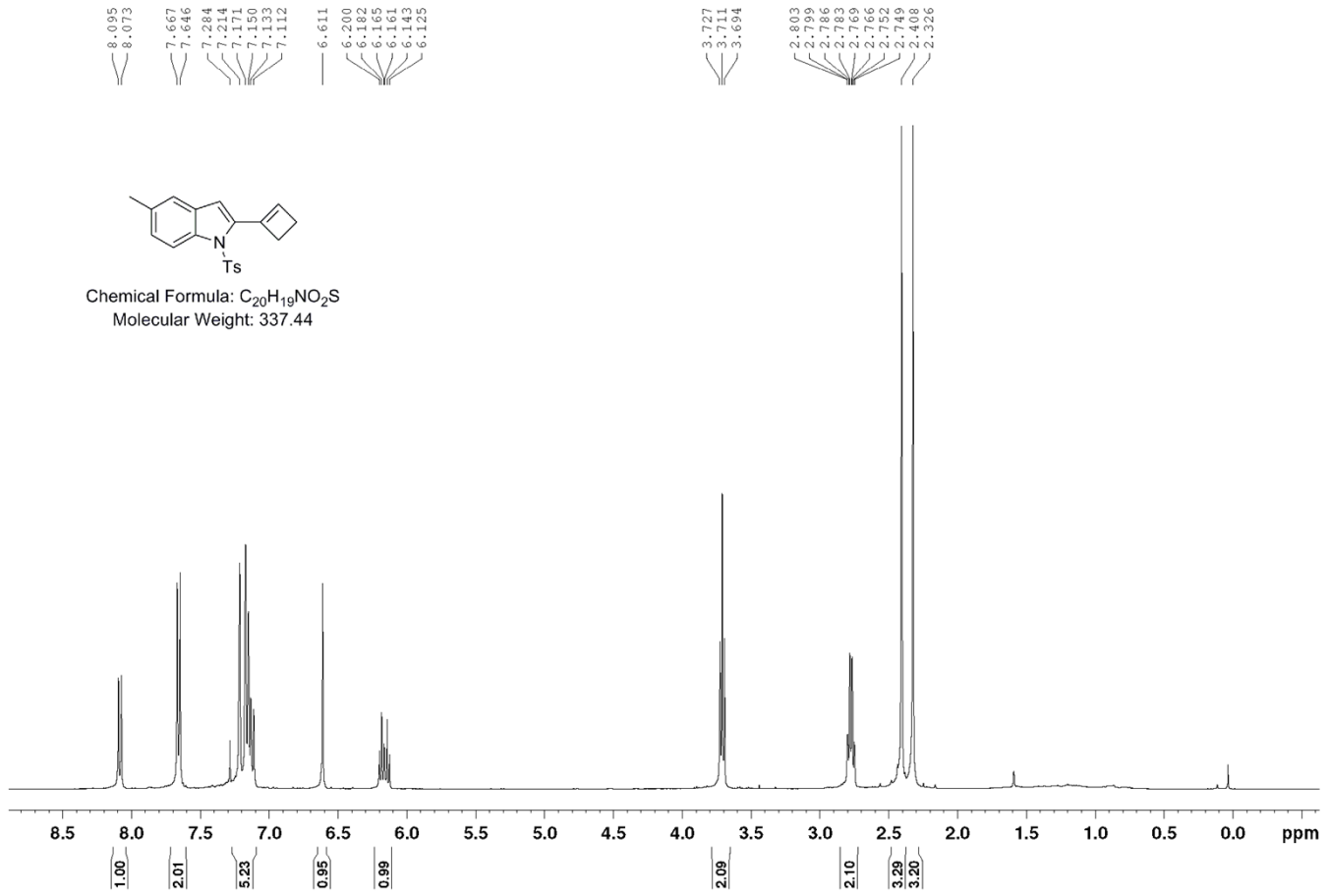
2a ^{1}H NMR, 400 MHz, $CDCl_3$



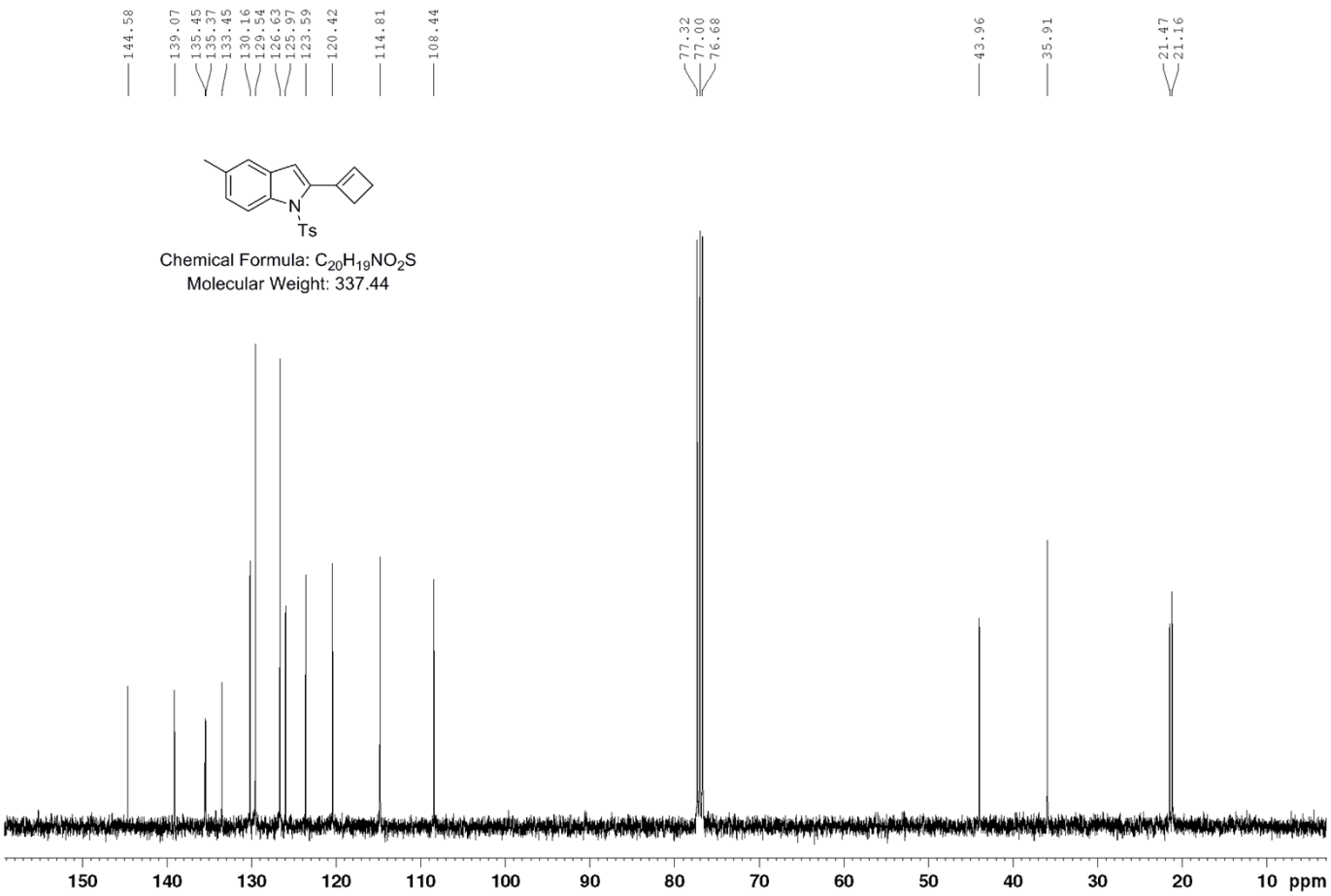
2a ^{13}C NMR, 100 MHz, $CDCl_3$



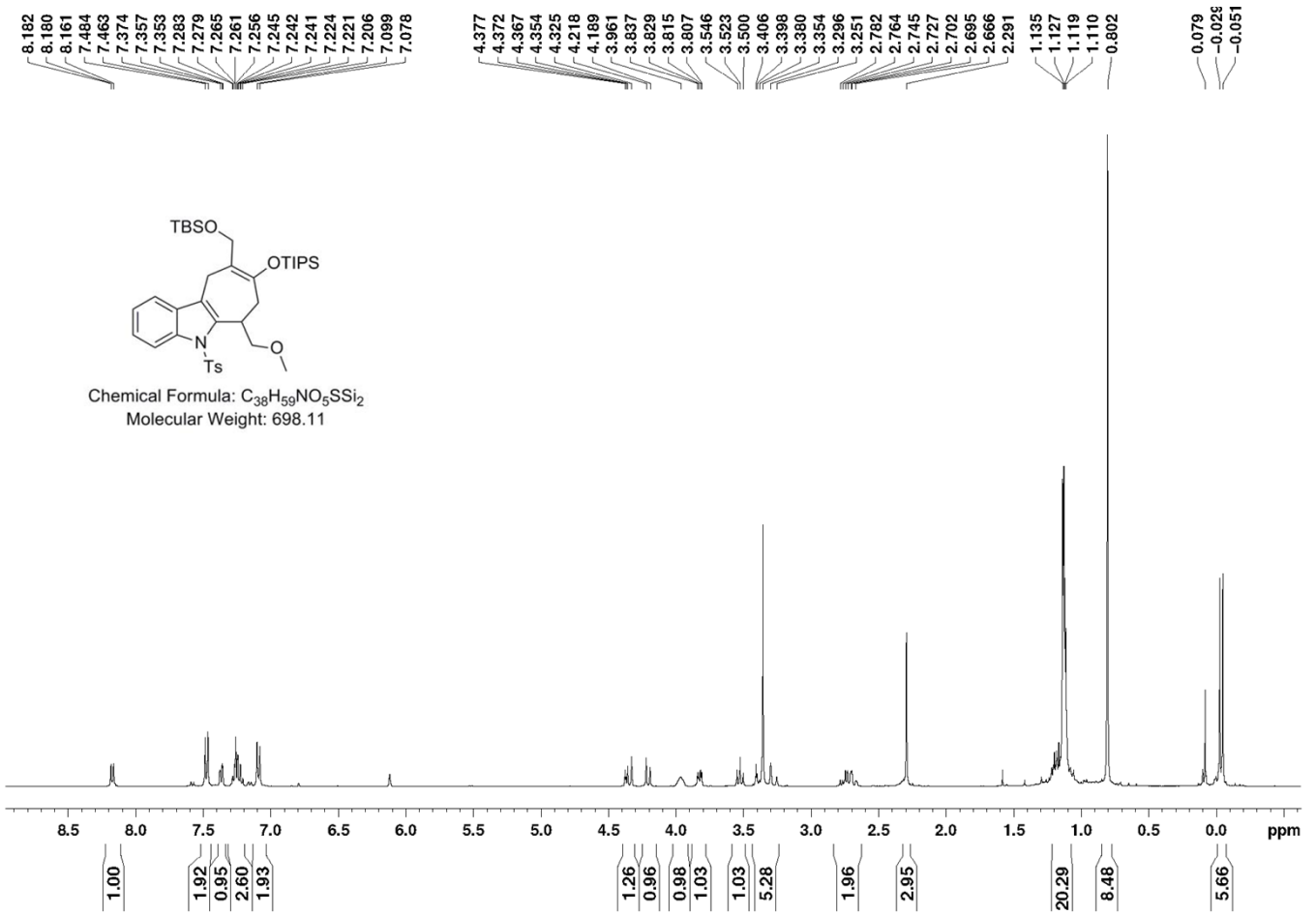
2-(cyclobut-1-en-1-yl)-5-methyl-1-tosyl-1H-indole ^{1}H NMR, 400 MHz, $CDCl_3$



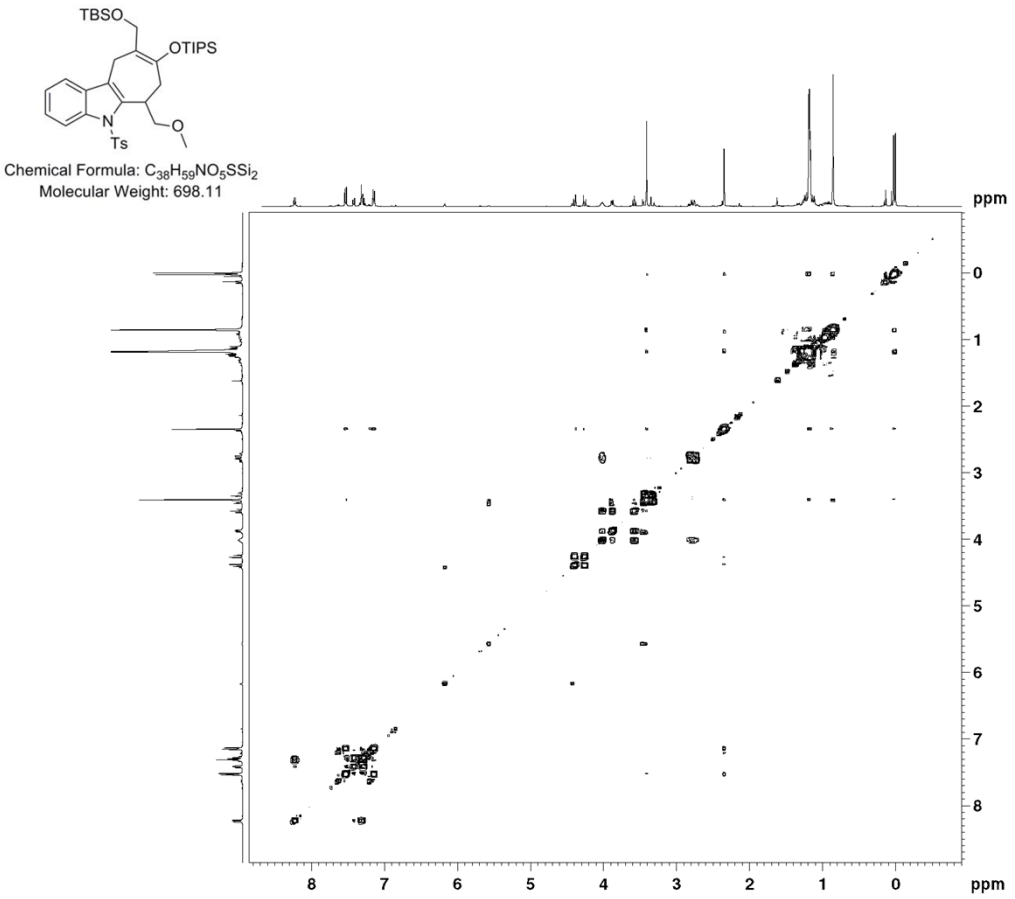
2-(cyclobut-1-en-1-yl)-5-methyl-1-tosyl-1H-indole ^{13}C NMR, 100 MHz, $CDCl_3$



5a ^{1}H NMR, 400 MHz, $CDCl_3$

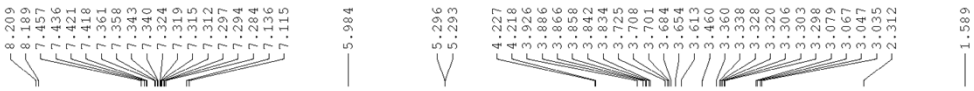


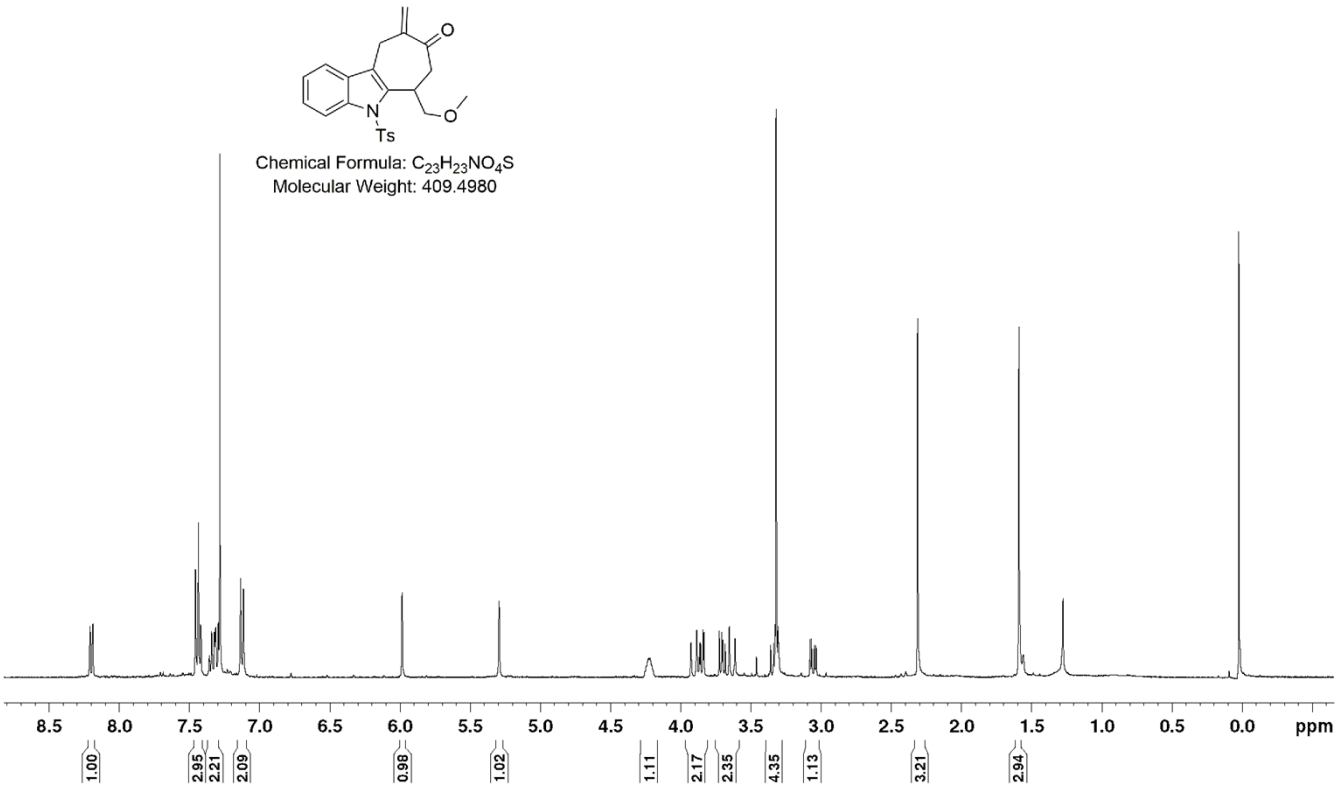
5a COSY NMR, 400 MHz, $CDCl_3$



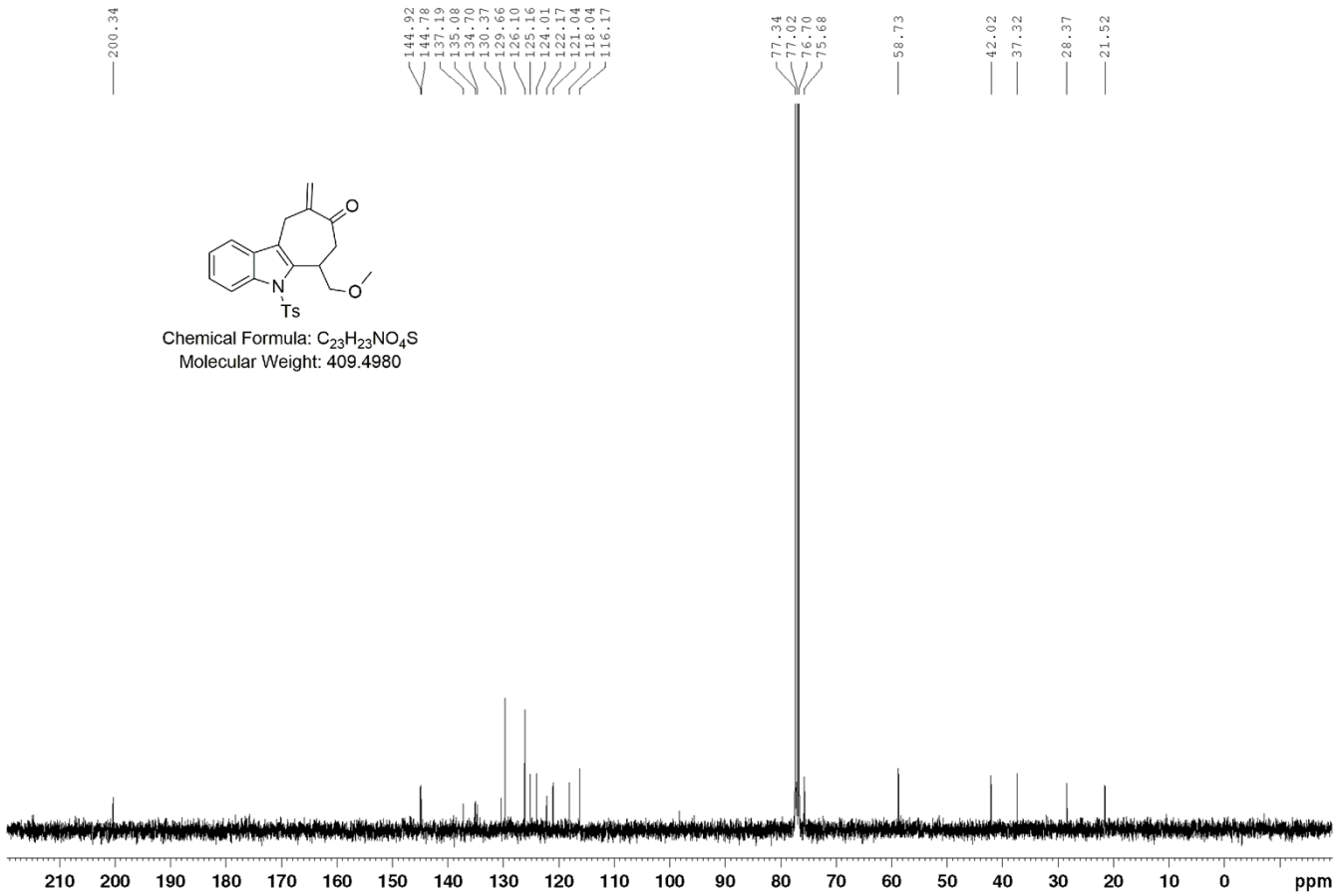

```
NAME          ZJ-140319-1
EXPNO                  21
PROCNO                  1
Date_           20140319
Time               22.57
INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG      cosygpppqf
TD                   2048
SOLVENT           CDCl3
NS                      2
DS                      8
SWH           3906.250 Hz
FIDRES        1.907349 Hz
AQ            0.2621940 sec
RG                     64
DW             128.000 usec
DE               6.50 usec
TE              295.5 K
D0            0.00000300 sec
D1            1.92954898 sec
D11           0.03000000 sec
D12           0.00002000 sec
D13           0.00000400 sec
D16           0.00020000 sec
IN0           0.00025600 sec

======== CHANNEL f1 ========
SFO1        400.1315797 MHz
NUC1                   1H
P0               14.10 usec
P1               14.10 usec
P17            2500.00 usec
ND0                    1
TD                   128
SFO1          400.1316 MHz
FIDRES         30.517578 Hz
SW              9.762 ppm
FnMODE                QF
SI                  1024
SF          400.1299896 MHz
WDW               QSINE
SSB                    0
LB                0.00 Hz
GB                     0
PC                1.40
SI                  1024
MC2                   QF
SF          400.1299896 MHz
WDW               QSINE
SSB                    0
LB                0.00 Hz
GB                     0
```

5c ^{1}H NMR, 400 MHz, $CDCl_3$

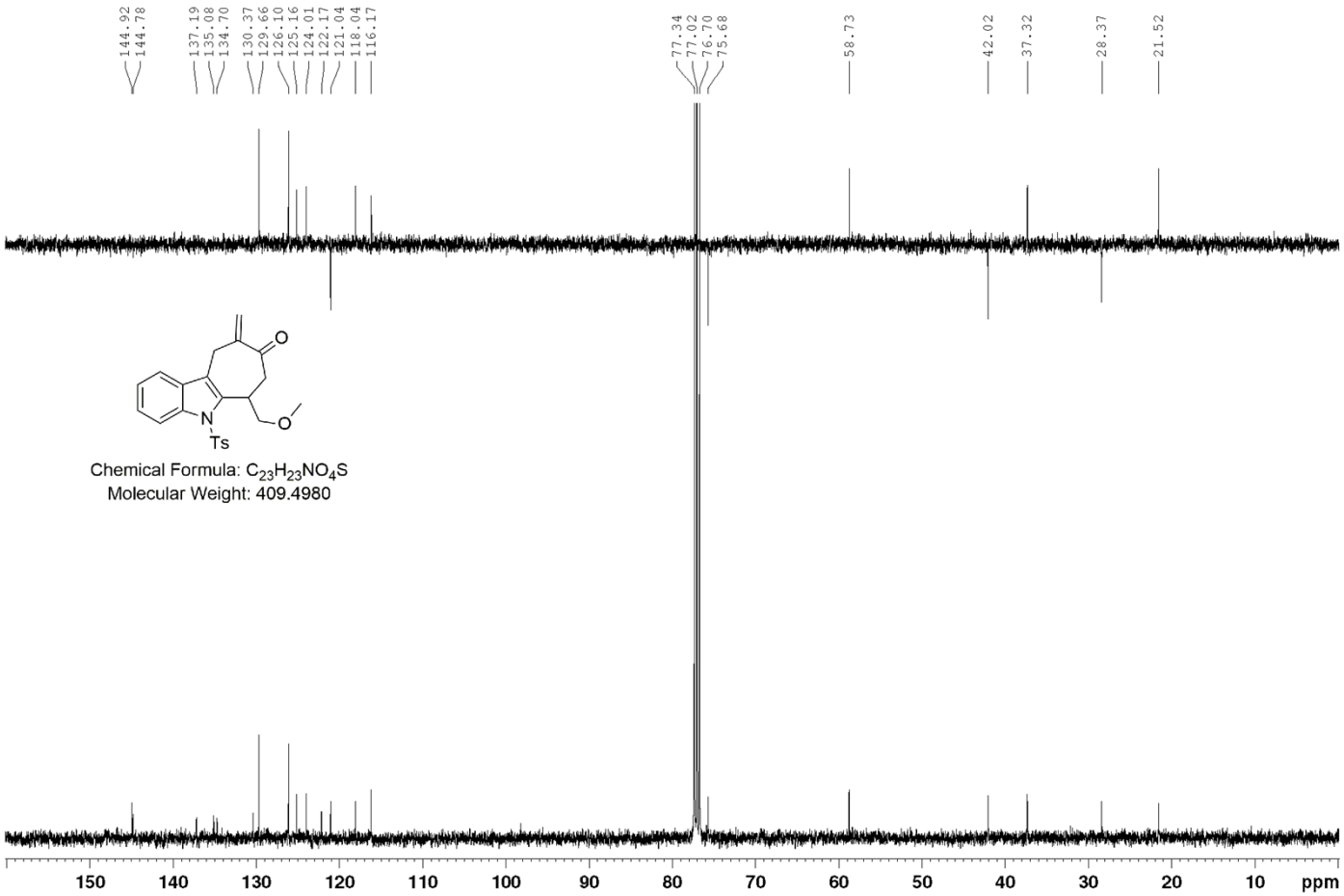




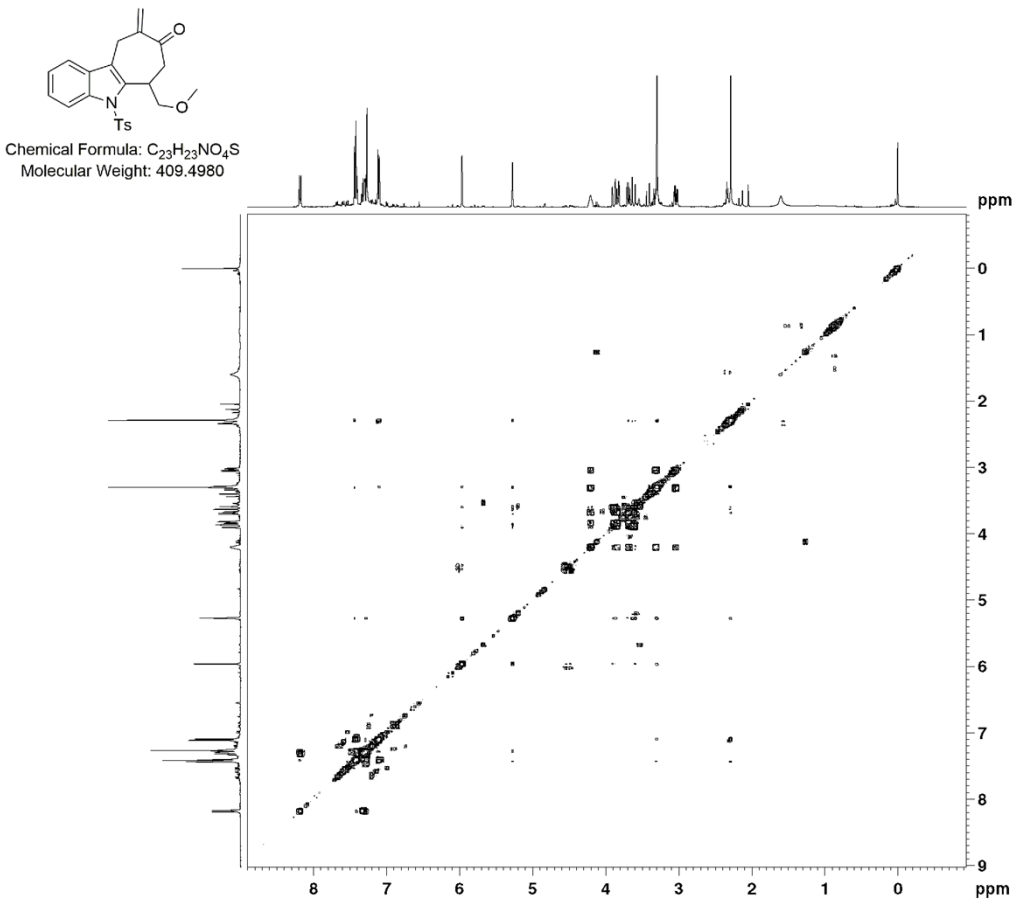
5c ^{13}C NMR, 100 MHz, $CDCl_3$



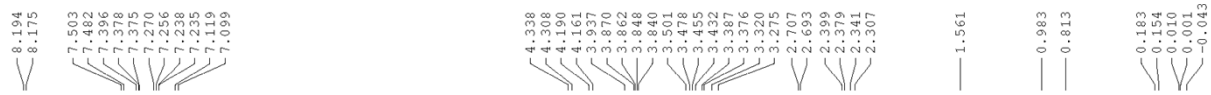
5c ^{13}C NMR, 100 MHz, $CDCl_3$

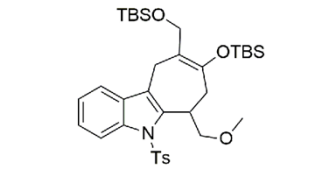


5c COSY NMR, 400 MHz, $CDCl_3$

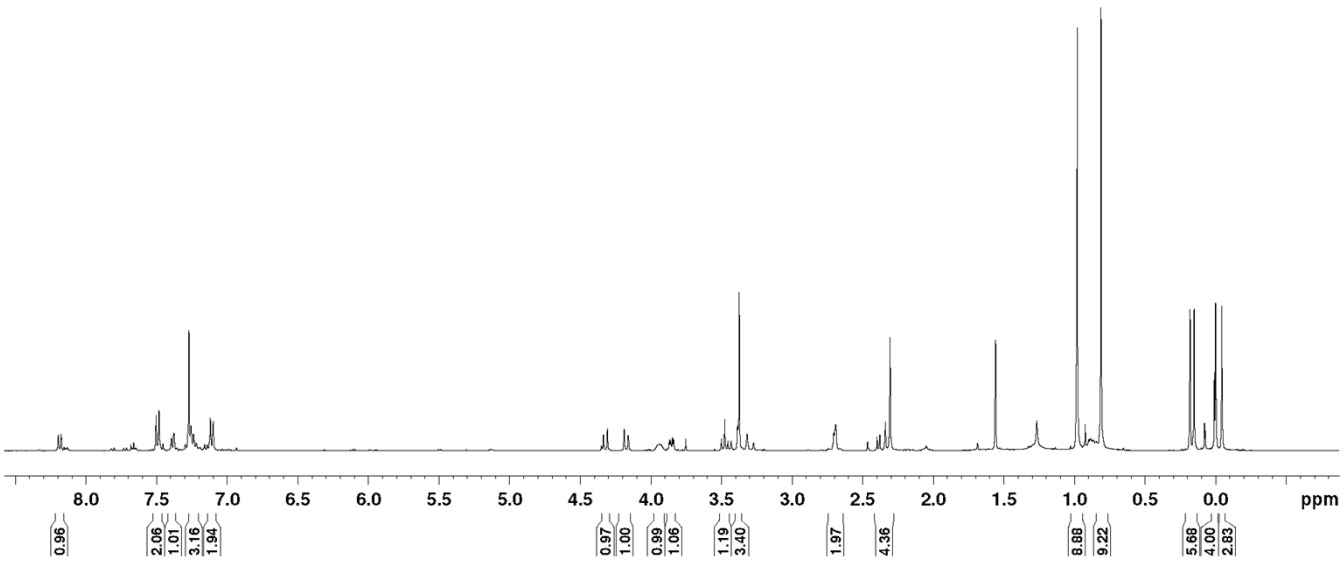


5b ^{1}H NMR, 400 MHz, $CDCl_3$

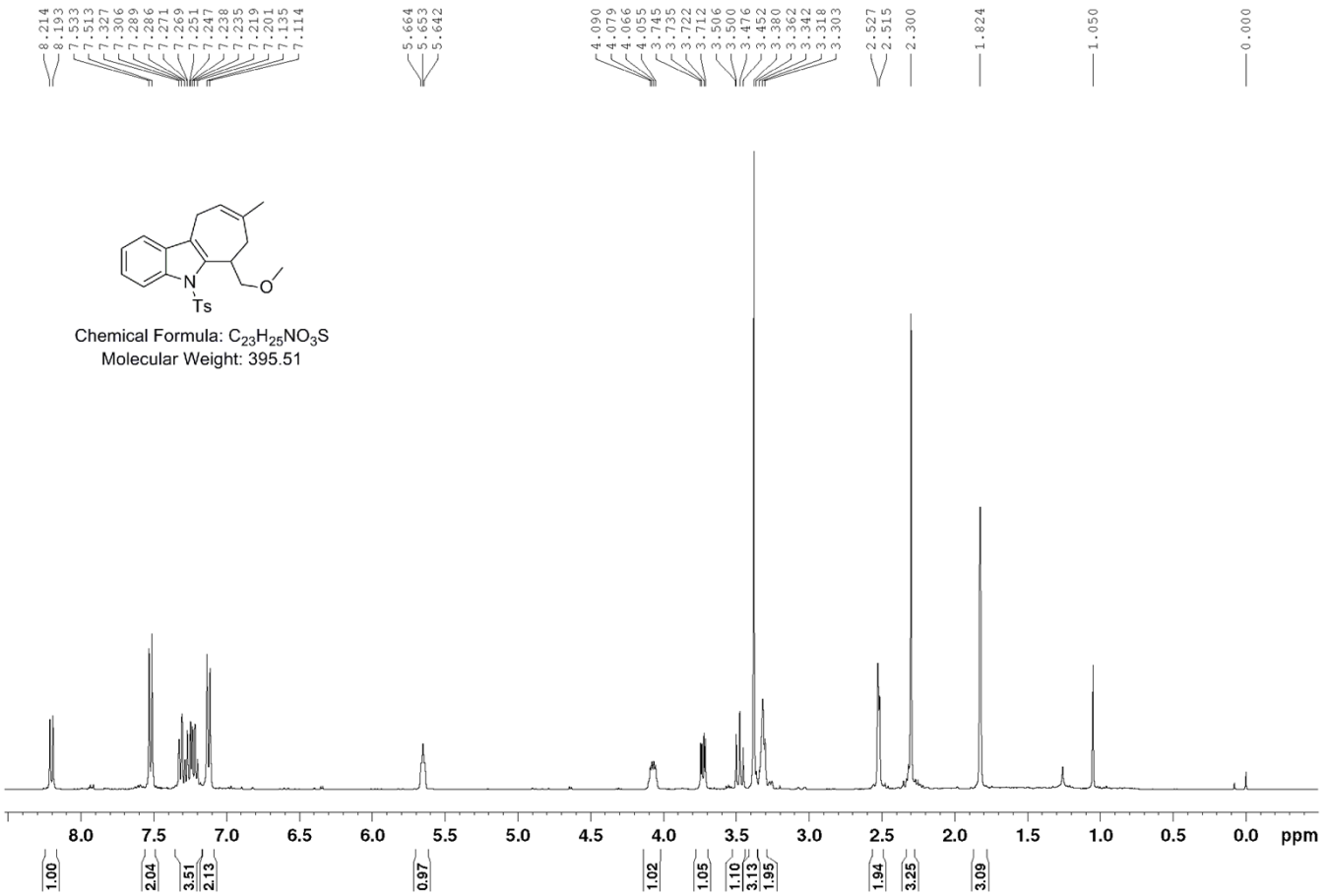




Chemical Formula: $C_{35}H_{53}NO_5SSi_2$
Molecular Weight: 656.0350

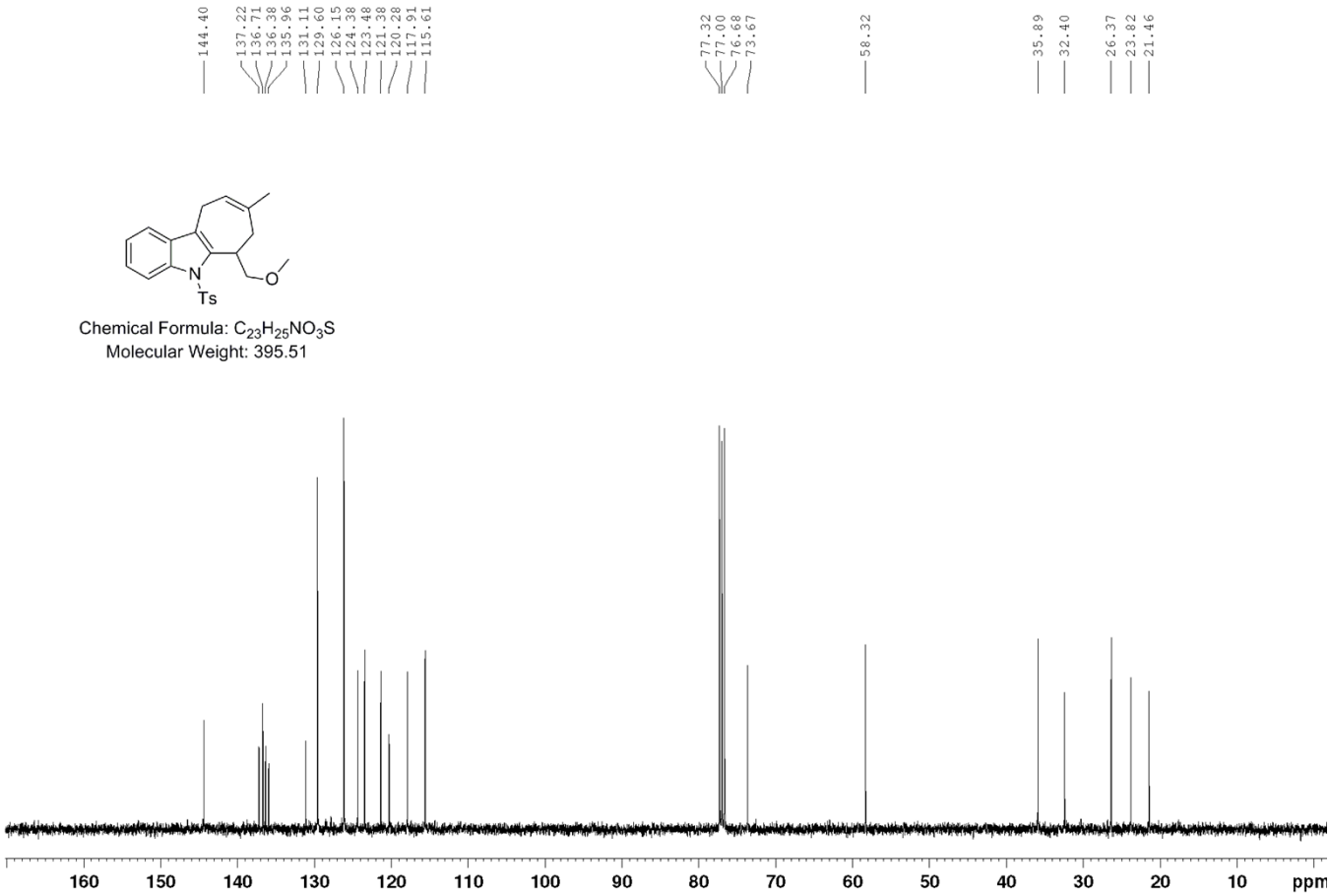


3a ^{1}H NMR, 400 MHz, $CDCl_3$



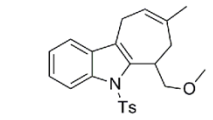
Chemical Formula: $C_{23}H_{25}NO_3S$
Molecular Weight: 395.51

3a ^{13}C NMR, 100 MHz, $CDCl_3$

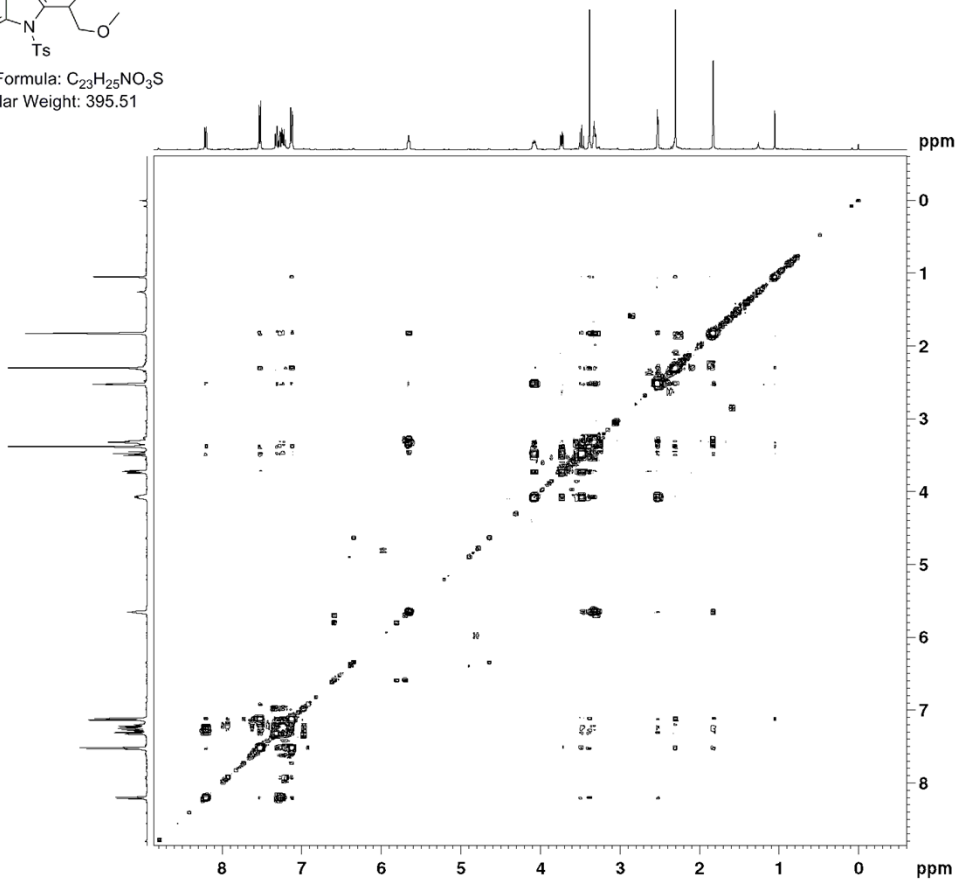


Chemical Formula: $C_{23}H_{25}NO_3S$
Molecular Weight: 395.51

3a COSY NMR, 400 MHz, $CDCl_3$

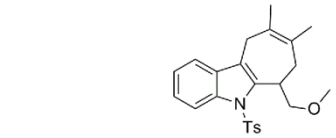


Chemical Formula: $C_{23}H_{25}NO_3S$
Molecular Weight: 395.51

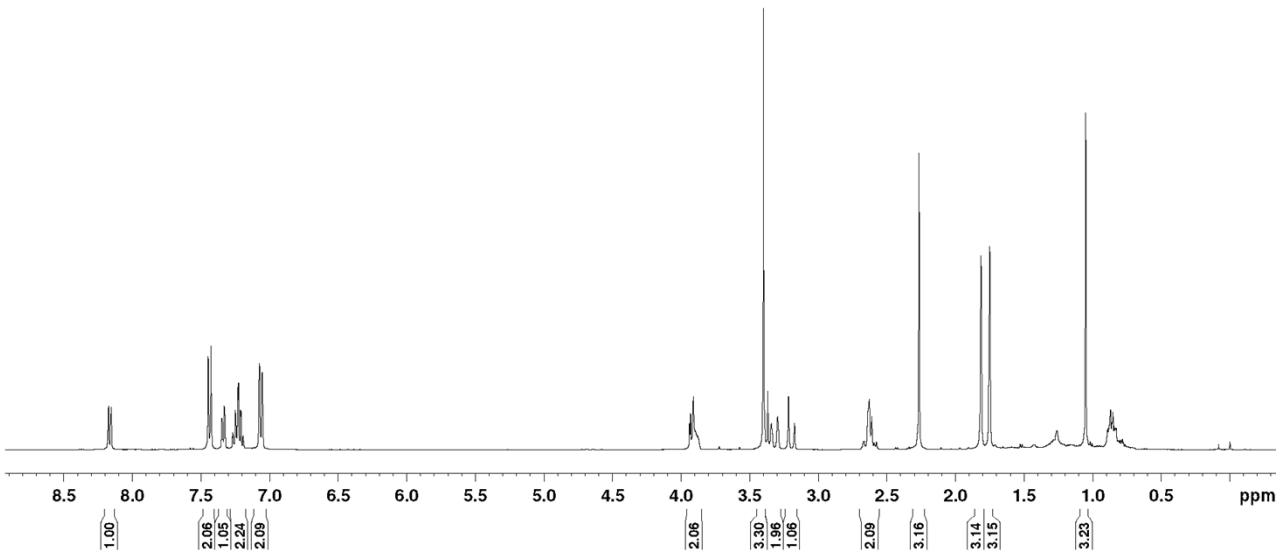



```
NAME            ZJ-140325-1A
EXPNO                     11
PROCNO                     1
Date_               20140325
Time                   22.12
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG         cosygpppqf
TD                      2048
SOLVENT              CDCl3
NS                         1
DS                         8
SWH                3787.879 Hz
FIDRES             1.849550 Hz
AQ                 0.2703860 sec
RG                        32
DW                  132.000 usec
DE                    6.50 usec
TE                   296.8 K
D0                 0.00000300 sec
D1                 1.92135704 sec
D11                0.03000000 sec
D12                0.00002000 sec
D13                0.00000400 sec
D16                0.00020000 sec
IN0                0.00026400 sec

======== CHANNEL f1 ========
SFO1            400.1316658 MHz
NUC1                    1H
P0                   14.10 usec
P1                   14.10 usec
P17                2500.00 usec
ND0                        1
TD                       128
SFO1             400.1317 MHz
FIDRES            29.592804 Hz
SW                    9.467 ppm
FnMODE                   QF
SI                     1024
SF              400.1300147 MHz
WDW                   QSINE
SSB                        0
LB                    0.00 Hz
GB                         0
PC                      1.40
SI                     1024
MC2                      QF
SF              400.1300147 MHz
WDW                   QSINE
SSB                        0
LB                    0.00 Hz
GB                         0
```

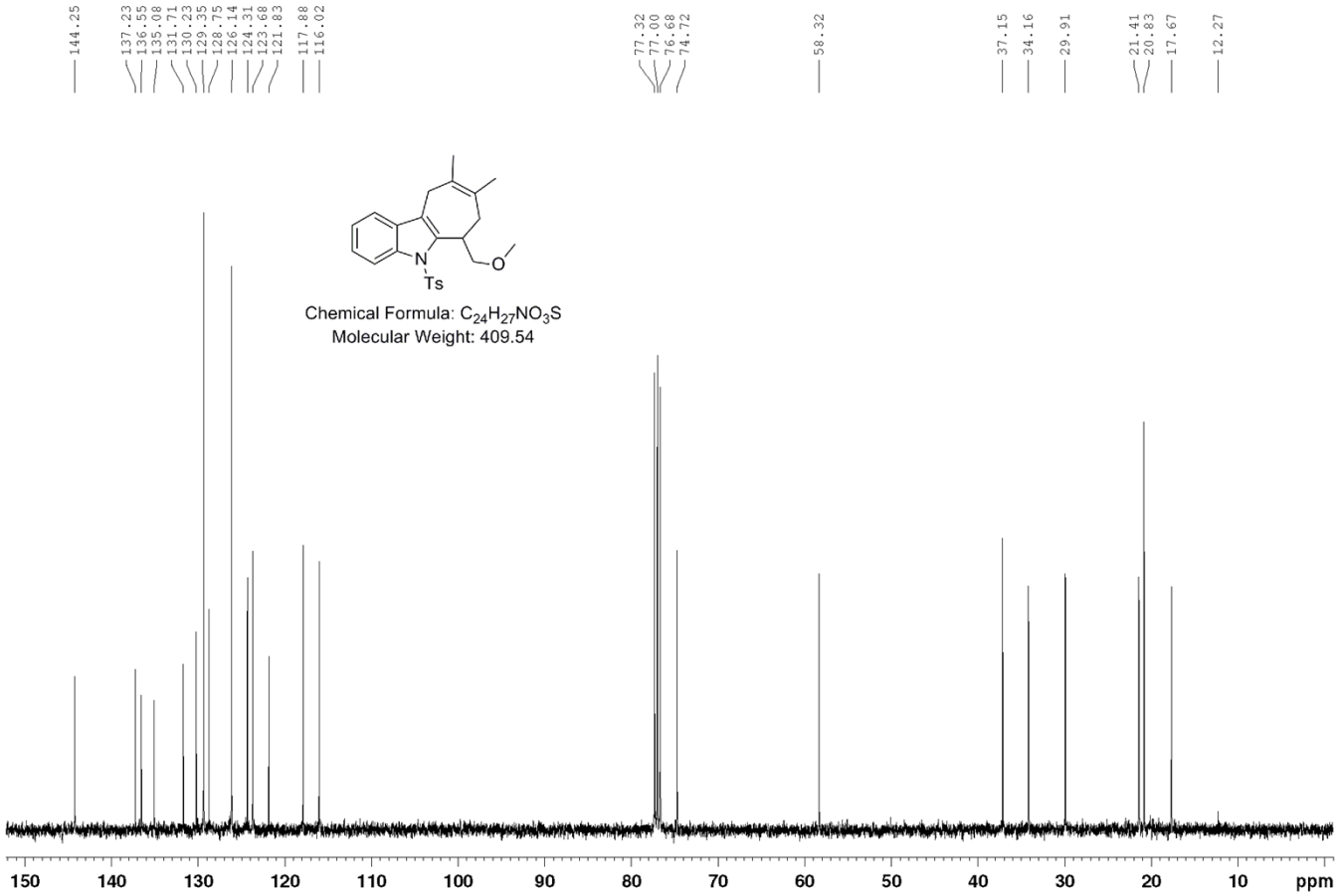
3b ^{1}H NMR, 400 MHz, $CDCl_3$



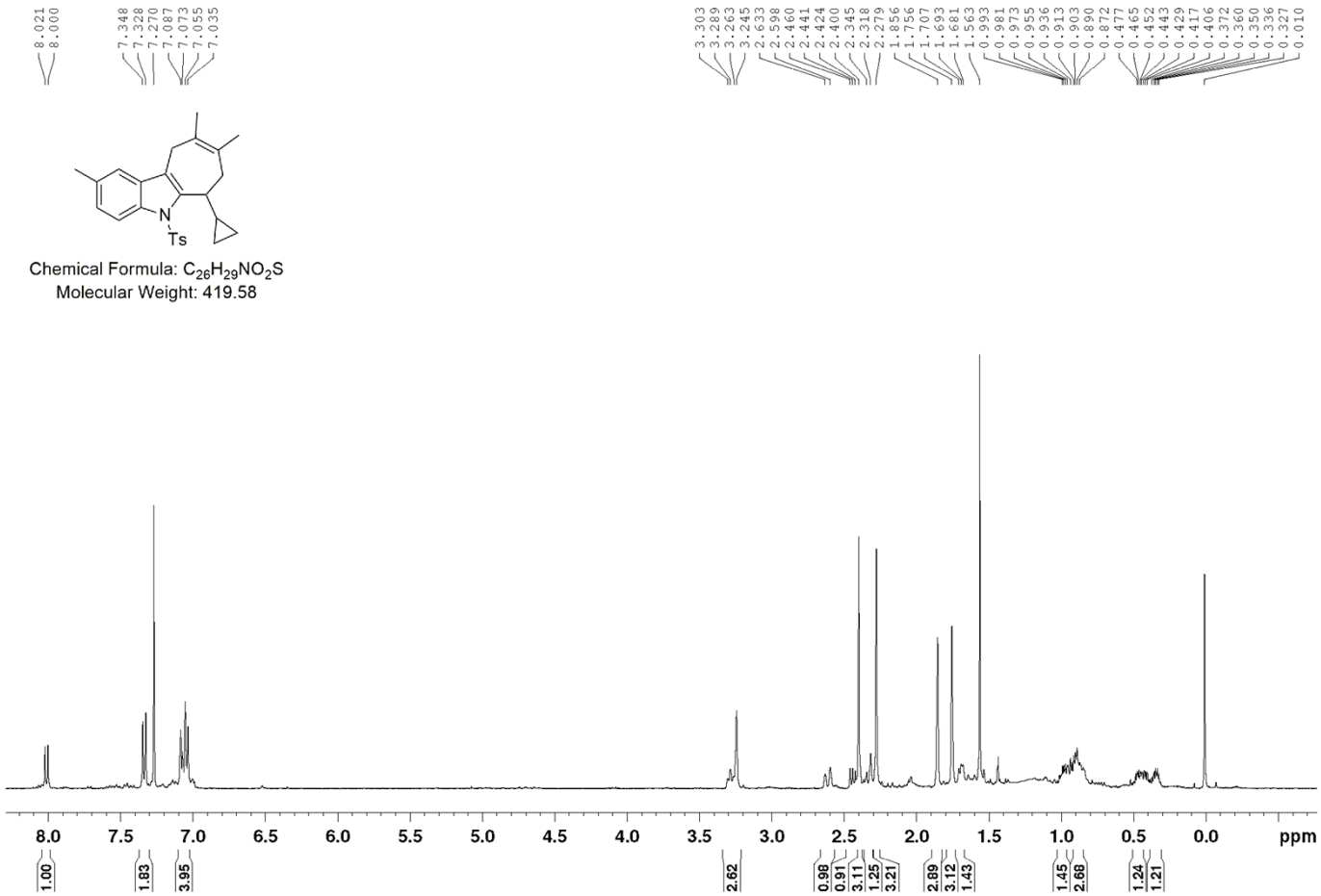
Chemical Formula: $C_{24}H_{27}NO_3S$
Molecular Weight: 409.54



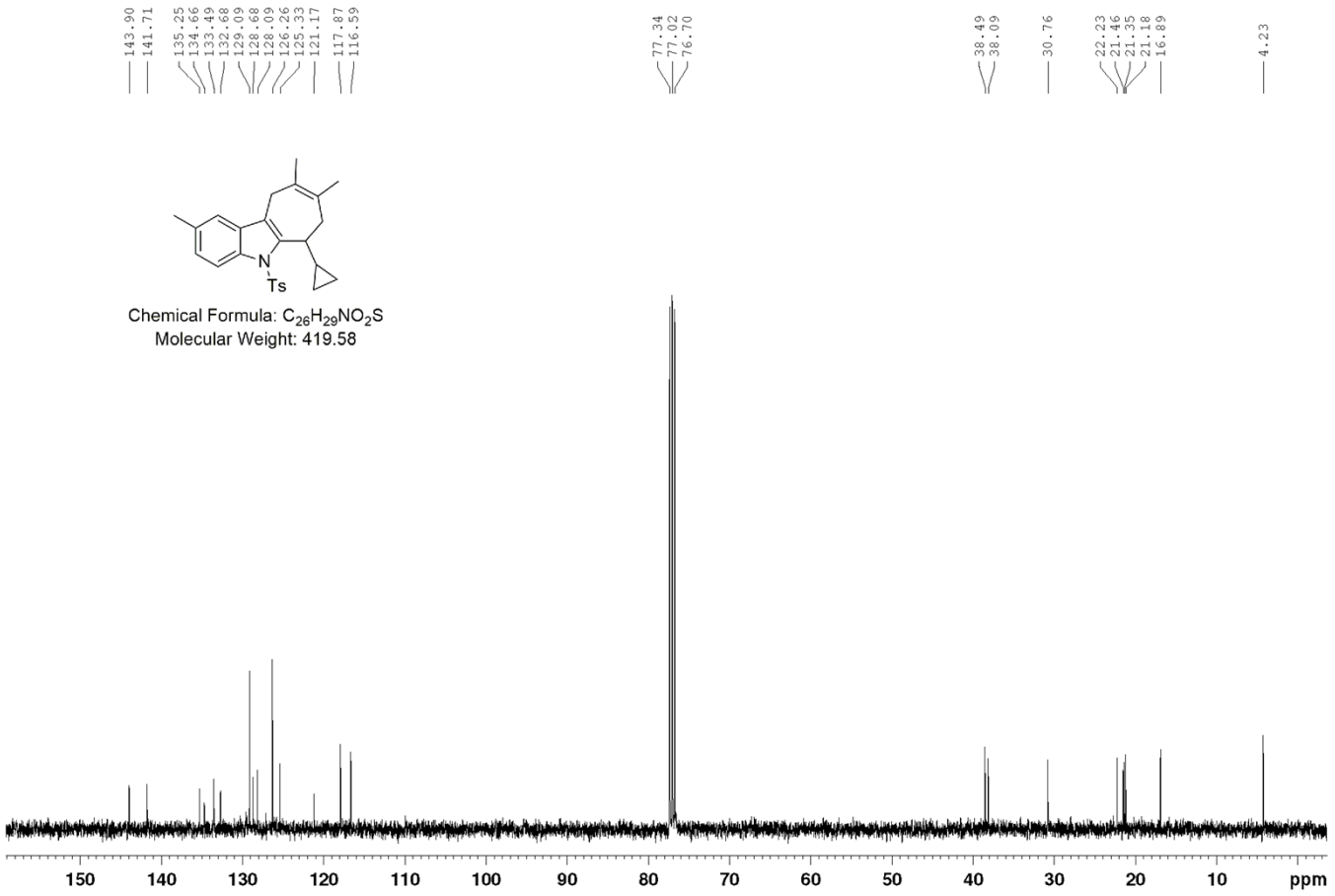
3b ^{13}C NMR, 100 MHz, $CDCl_3$



3c ^{1}H NMR, 400 MHz, $CDCl_3$

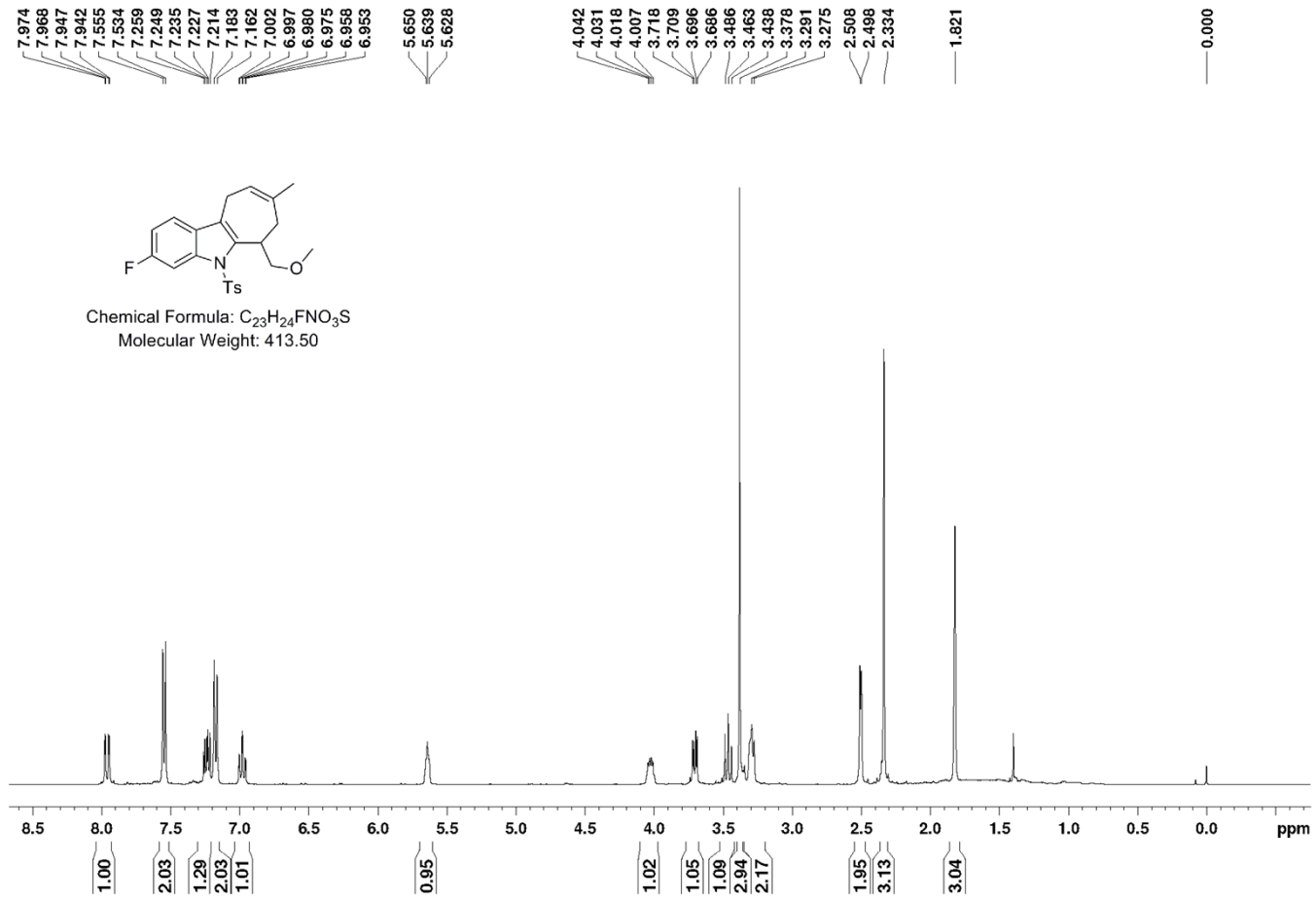


3c ^{13}C NMR, 100 MHz, $CDCl_3$



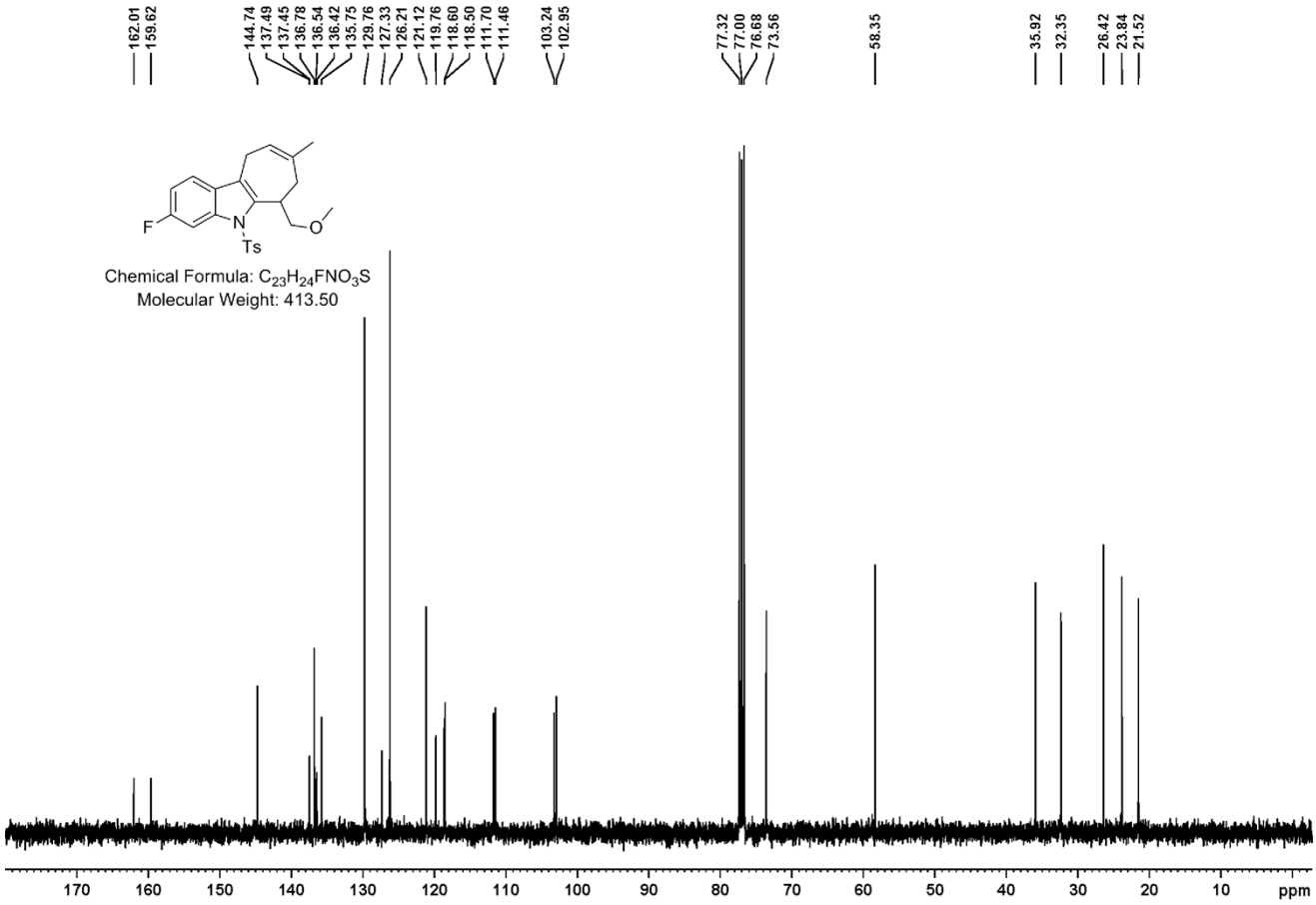
Chemical Formula: $C_{26}H_{29}NO_2S$
Molecular Weight: 419.58

3d ^{1}H NMR, 400 MHz, $CDCl_3$

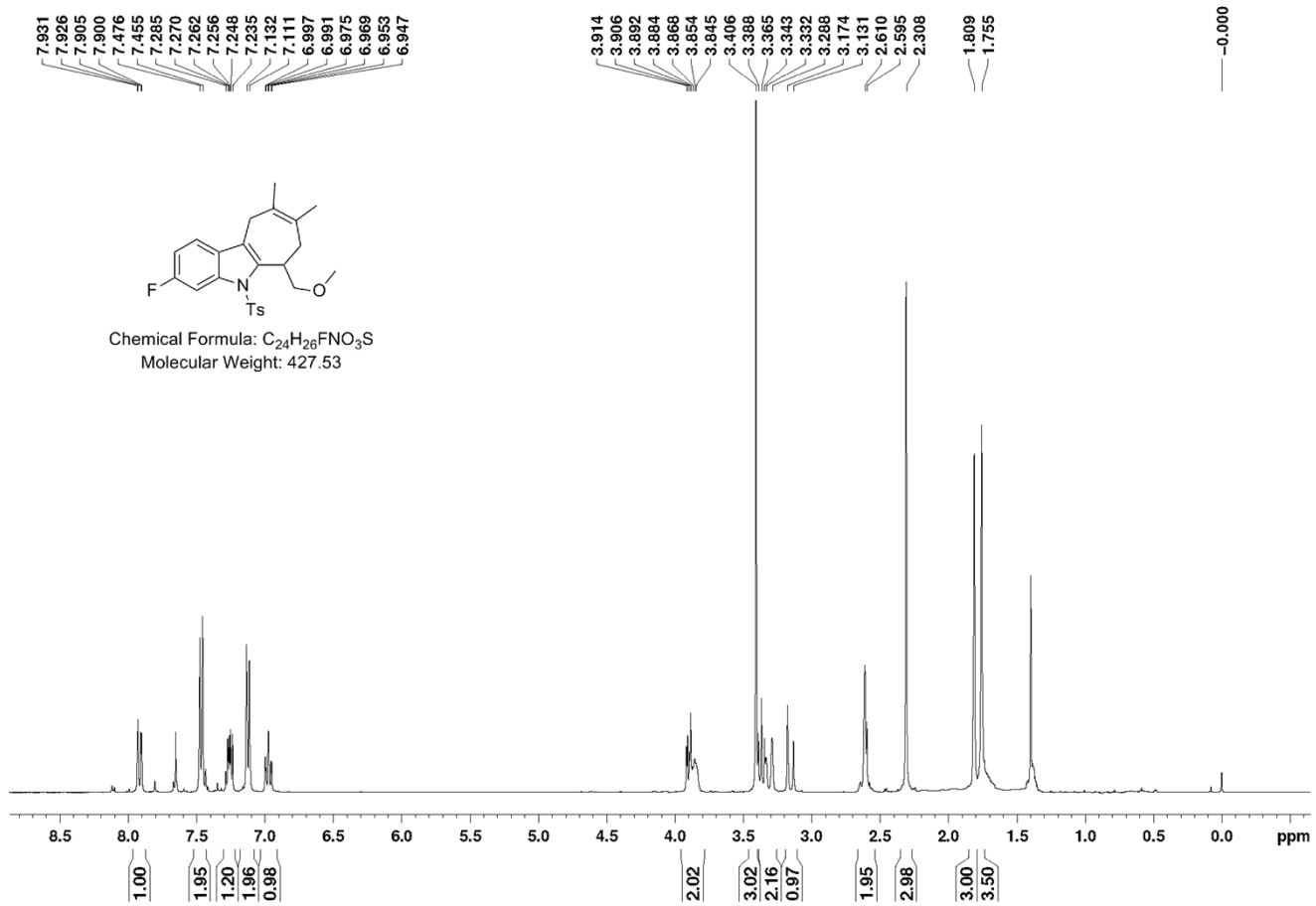


Chemical Formula: $C_{23}H_{24}FNO_3S$
Molecular Weight: 413.50

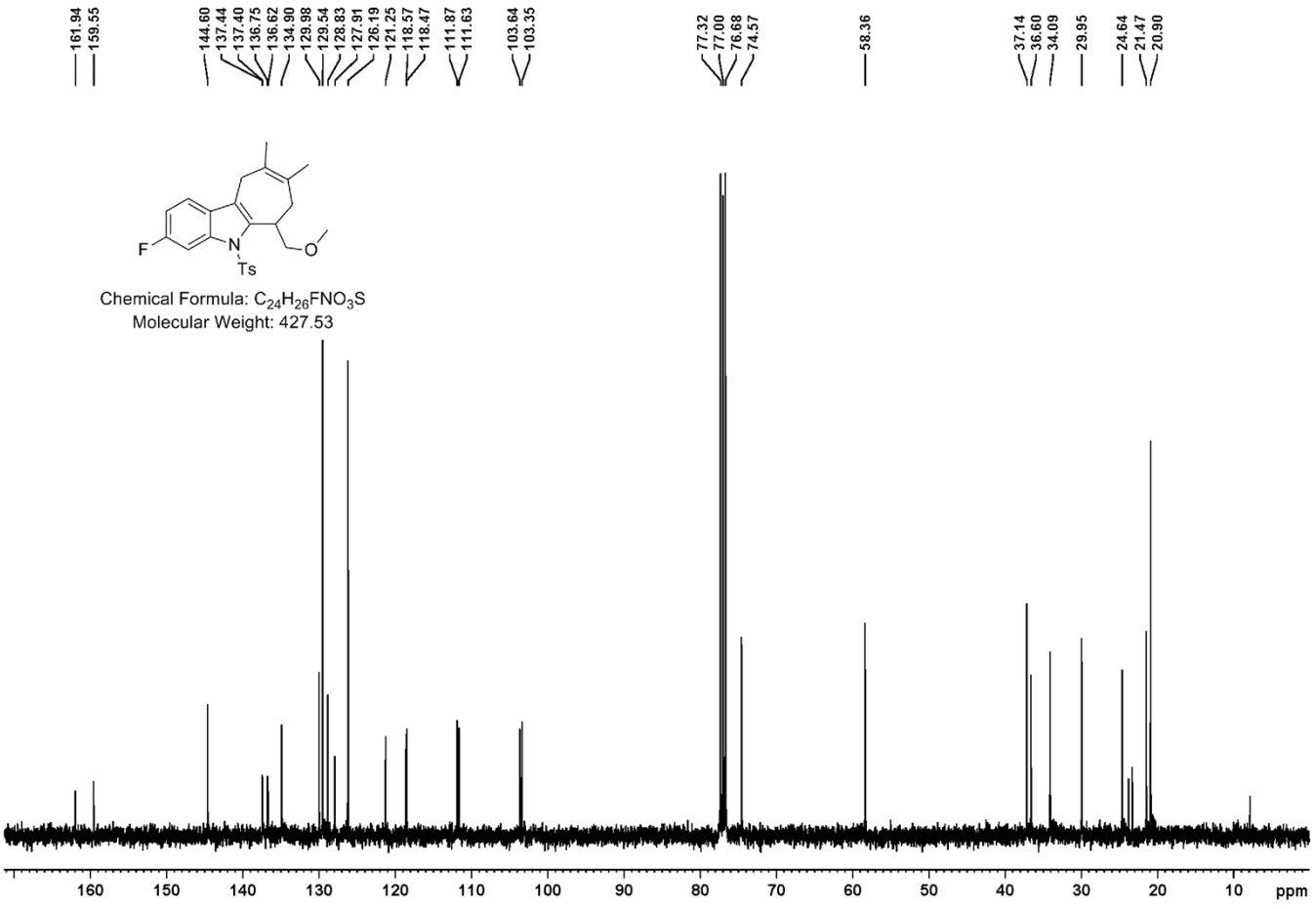
3d ^{13}C NMR, 100 MHz, $CDCl_3$



3e ^{1}H NMR, 400 MHz, $CDCl_3$

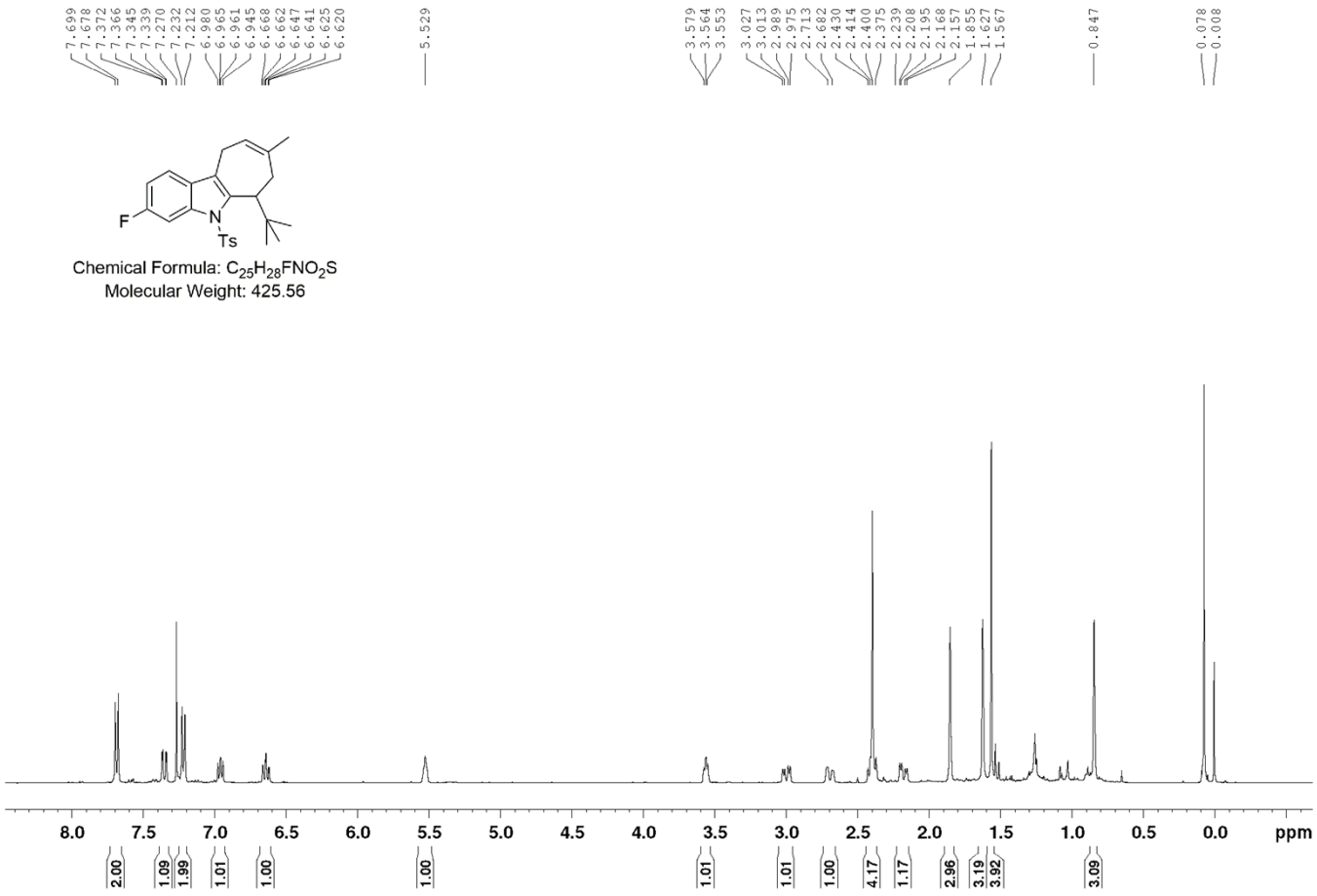


3e ^{13}C NMR, 100 MHz, $CDCl_3$



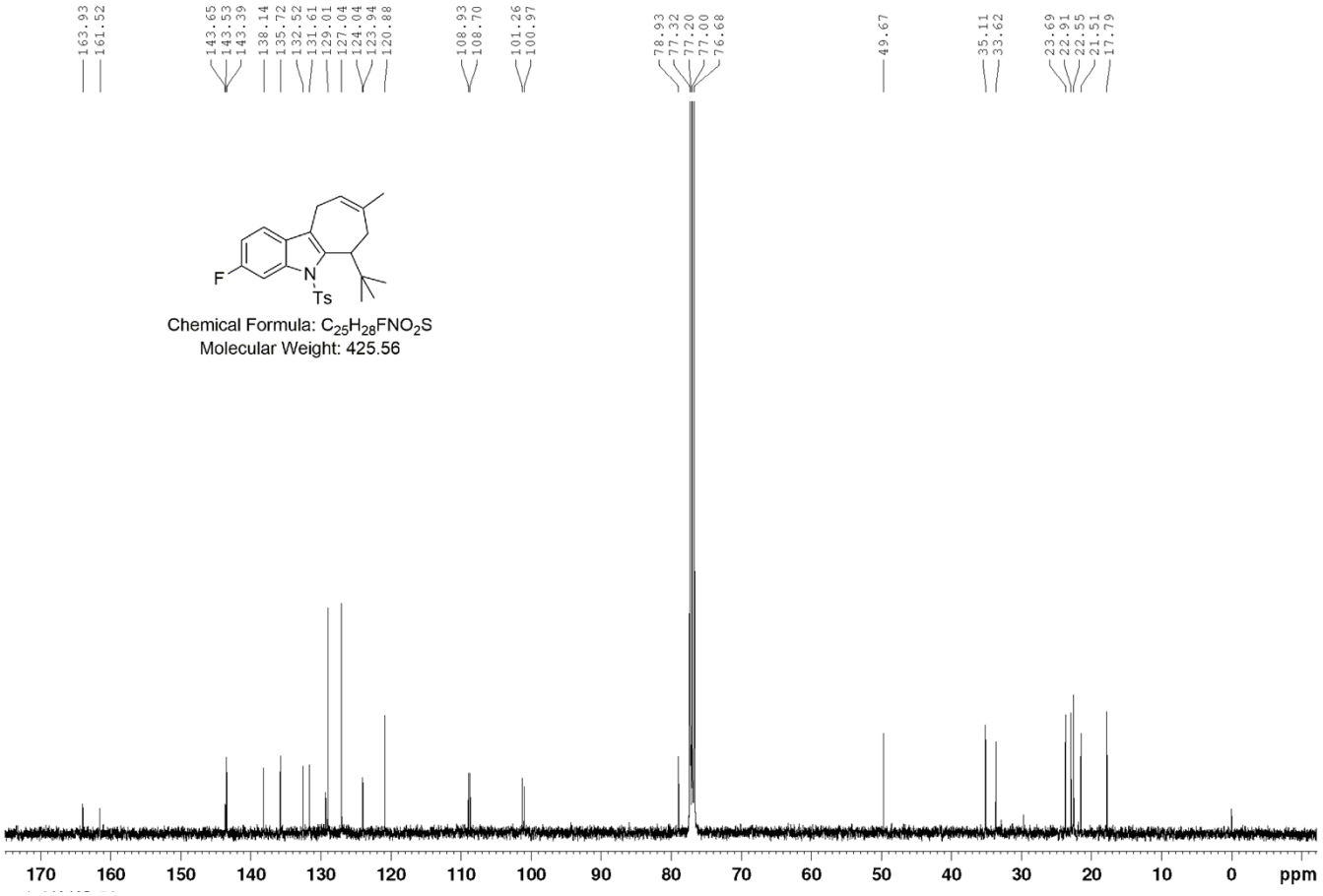
Chemical Formula: $C_{24}H_{26}FNO_3S$
Molecular Weight: 427.53

3f ^{1}H NMR, 400 MHz, $CDCl_3$

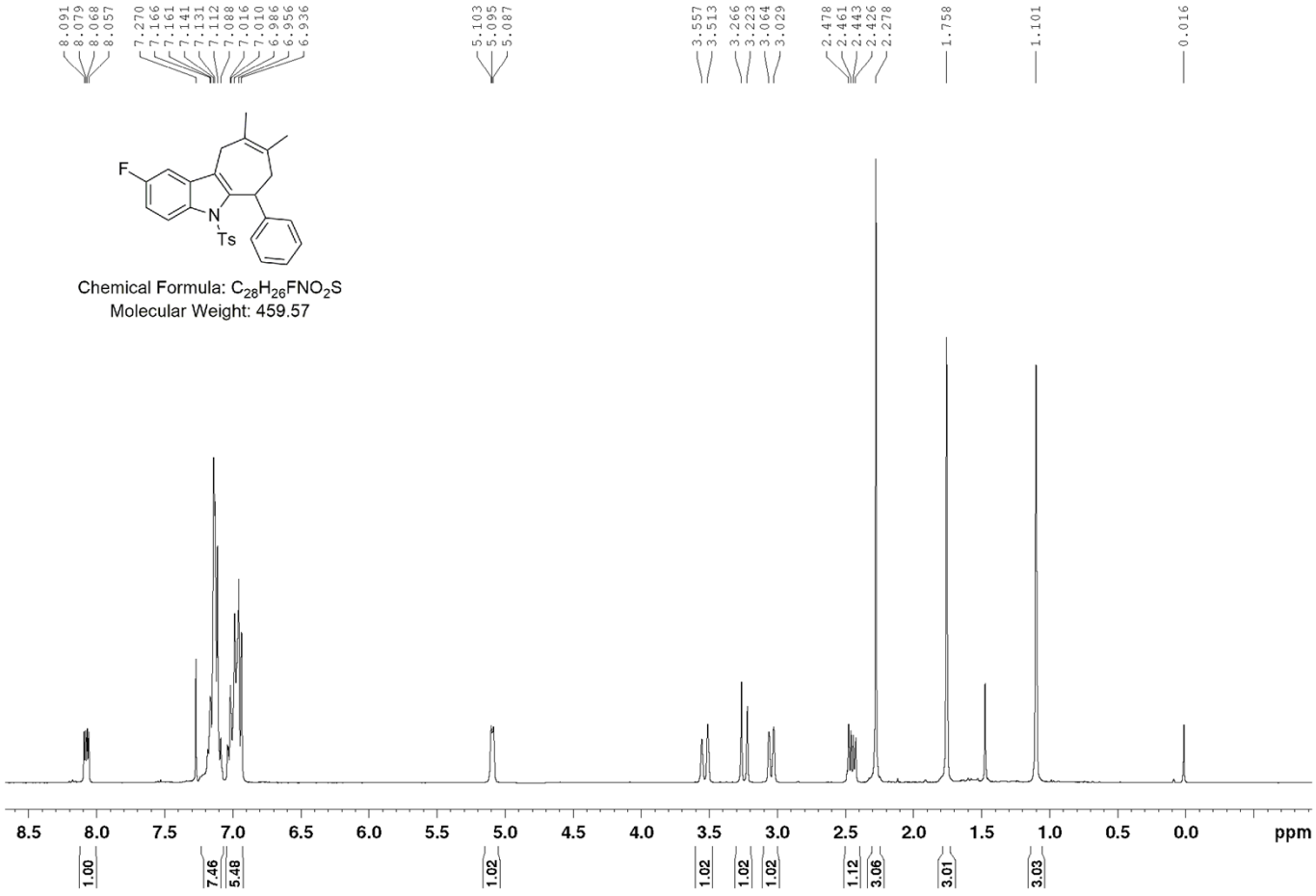


Chemical Formula: $C_{25}H_{28}FNO_2S$
Molecular Weight: 425.56

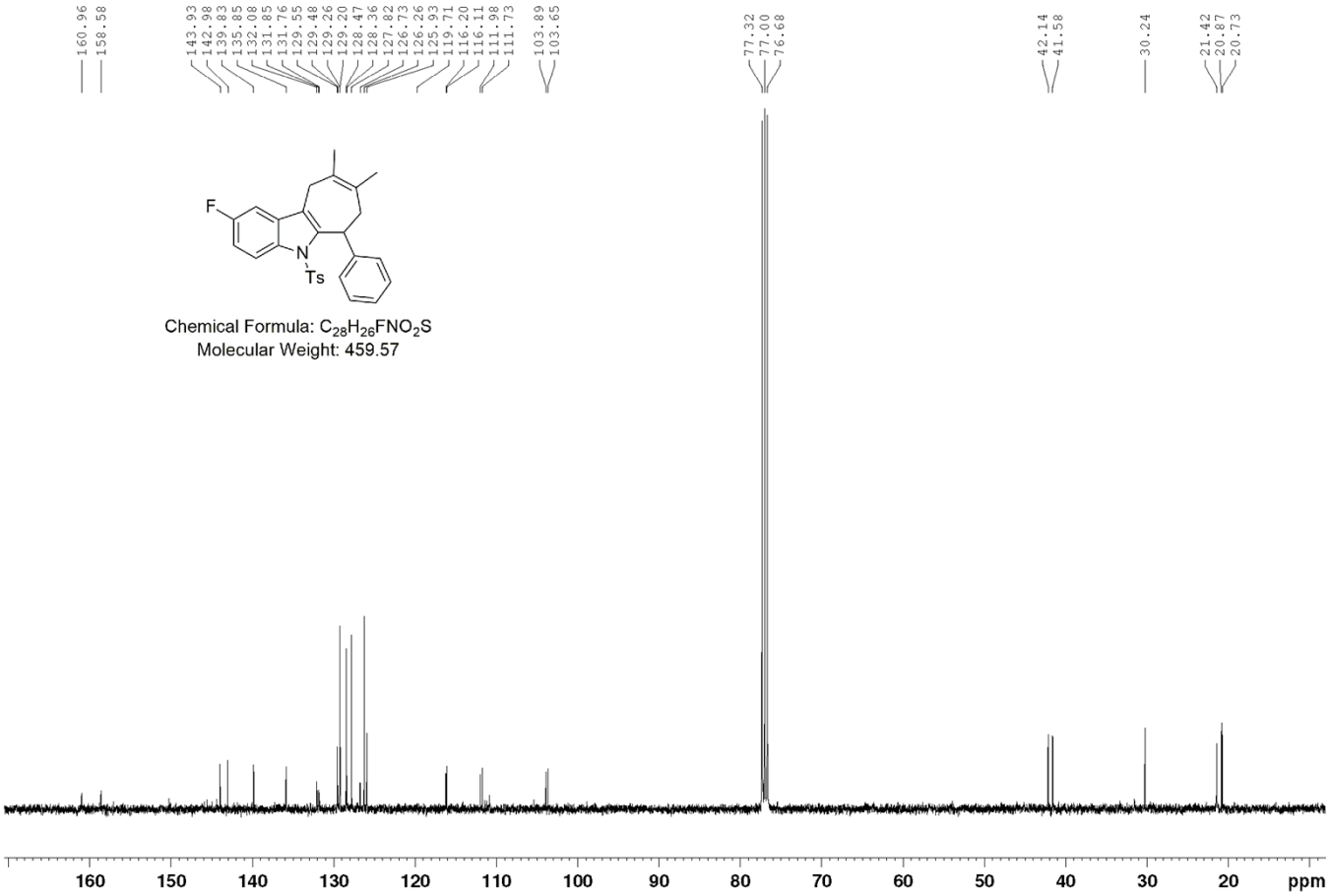
3f ^{13}C NMR, 100 MHz, $CDCl_3$



3g ^{1}H NMR, 400 MHz, $CDCl_3$

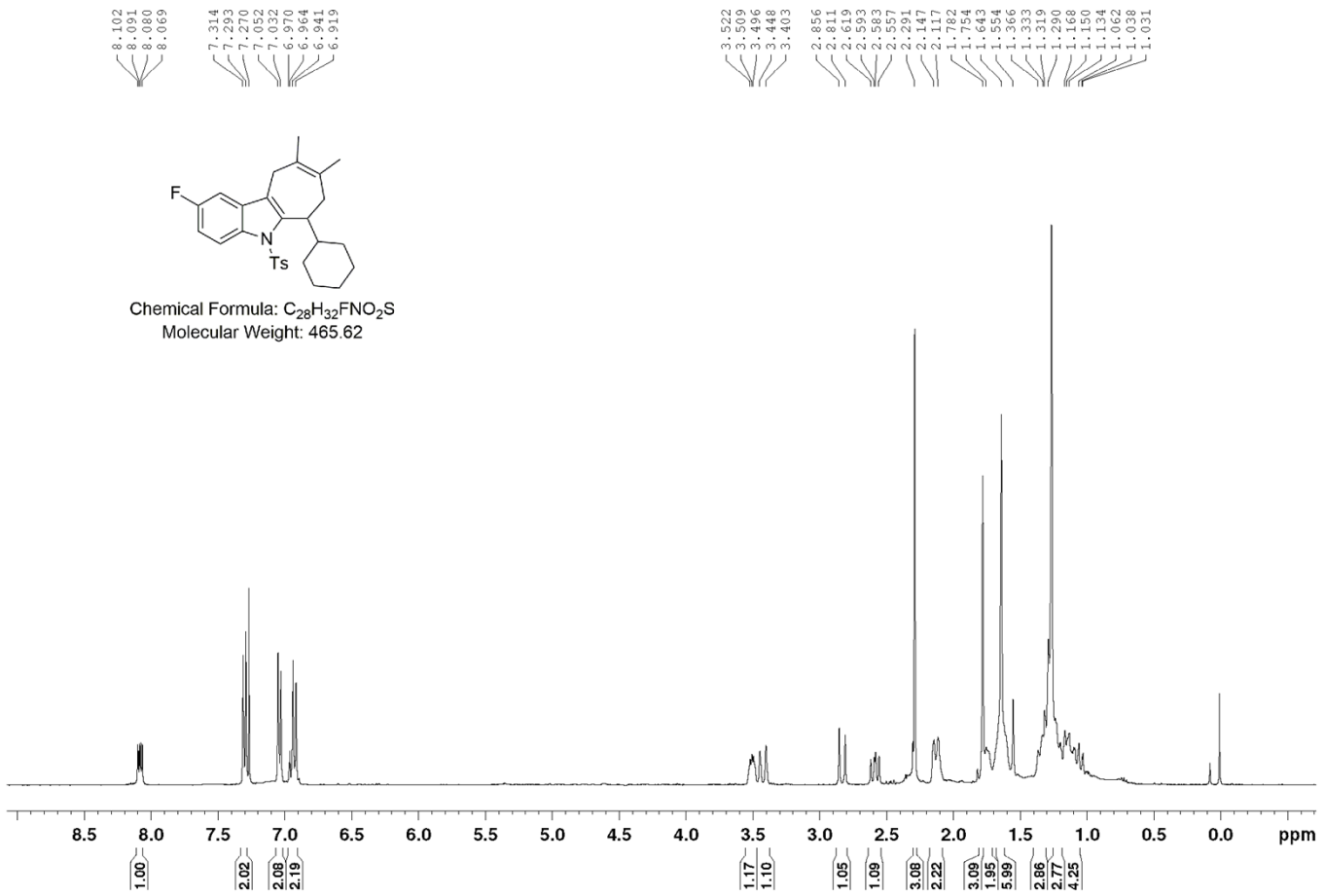


3g ^{13}C NMR, 100 MHz, $CDCl_3$



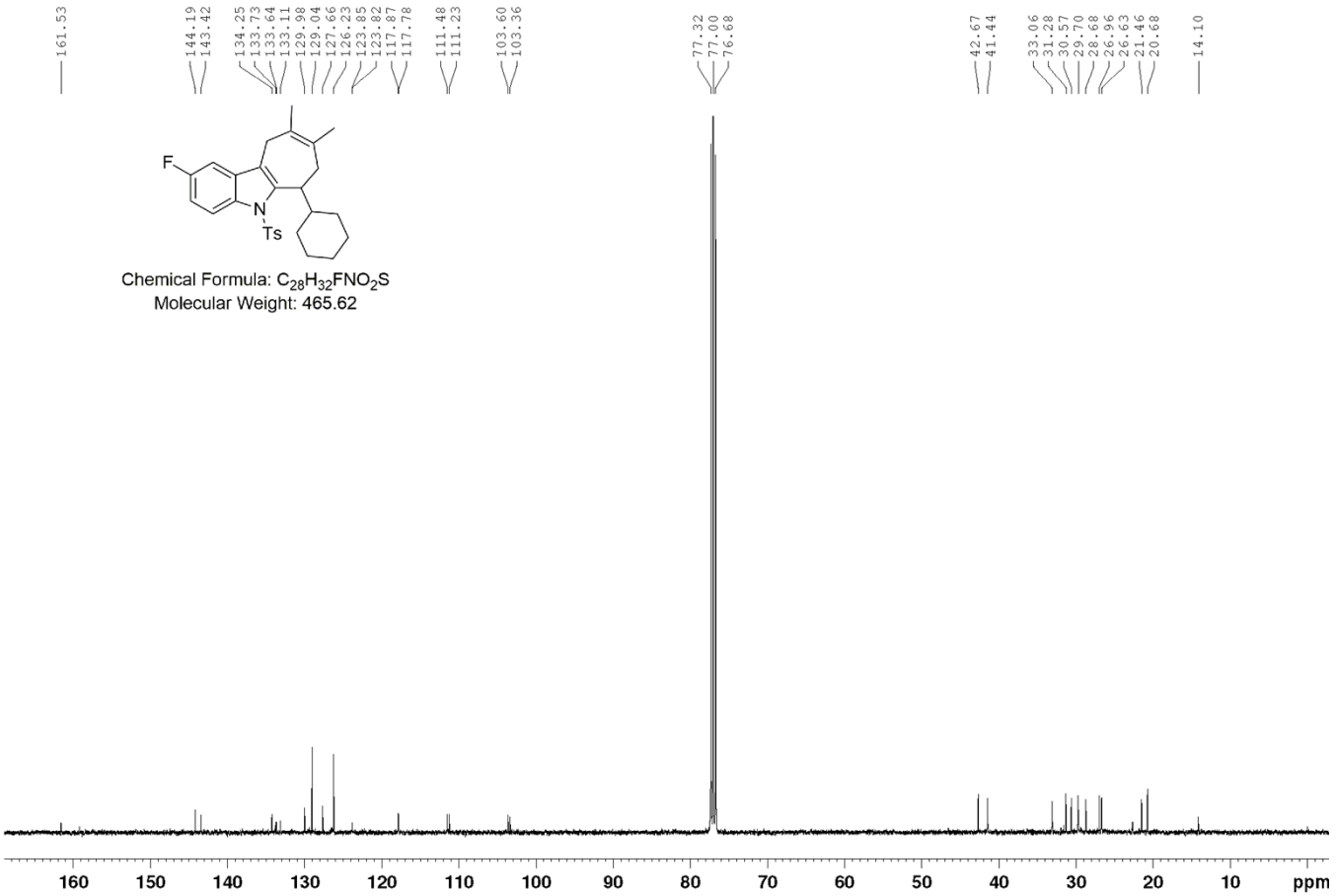
Chemical Formula: $C_{28}H_{26}FNO_2S$
Molecular Weight: 459.57

3h ^{1}H NMR, 400 MHz, $CDCl_3$



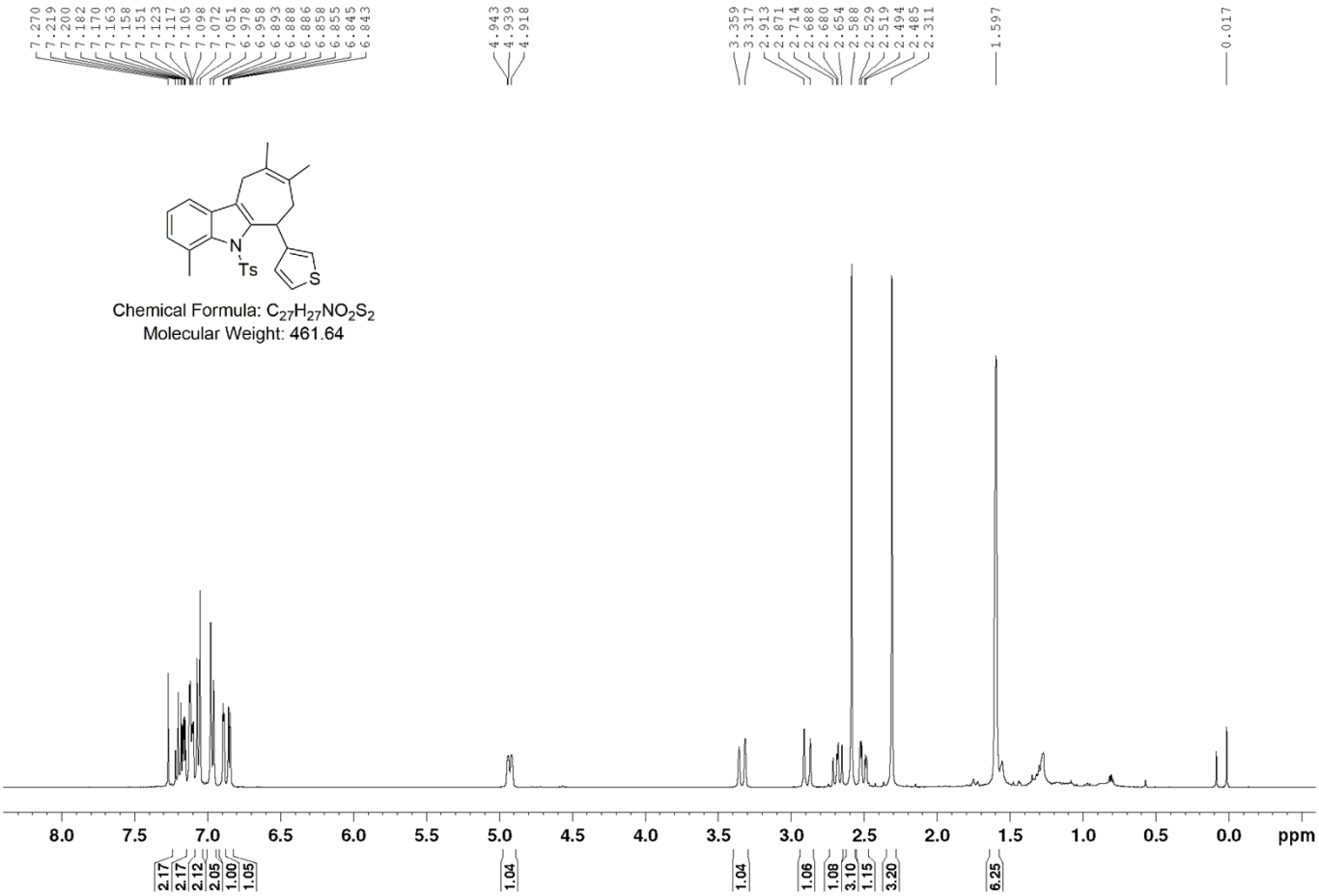
Chemical Formula: $C_{28}H_{32}FNO_2S$
Molecular Weight: 465.62

3h ^{13}C NMR, 100 MHz, $CDCl_3$



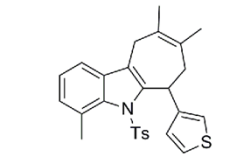
Chemical Formula: $C_{28}H_{32}FNO_2S$
Molecular Weight: 465.62

3i ^{1}H NMR, 400 MHz, $CDCl_3$



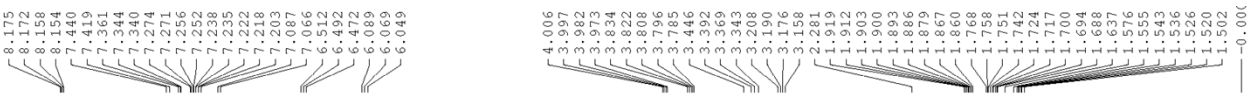
Chemical Formula: $C_{27}H_{27}NO_2S_2$
Molecular Weight: 461.64

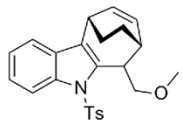
3i ^{13}C NMR, 100 MHz, $CDCl_3$



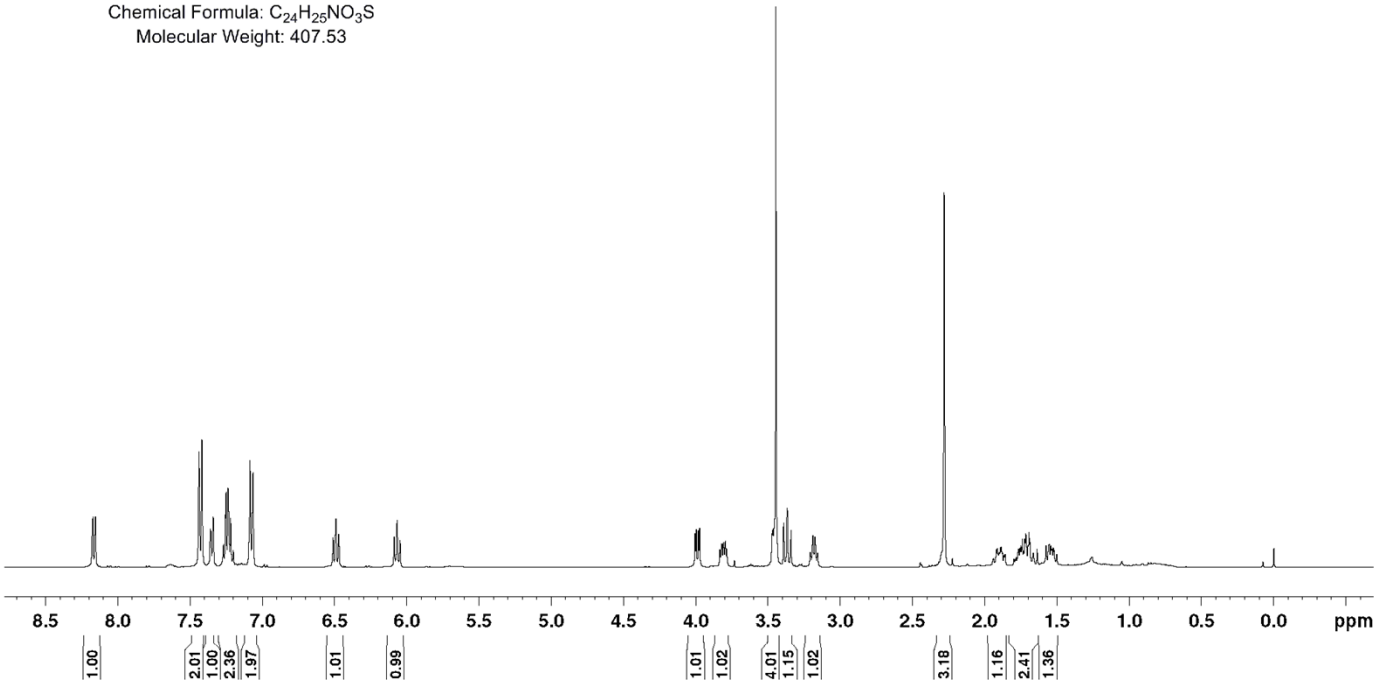
Chemical Formula: $C_{27}H_{27}NO_2S_2$
Molecular Weight: 461.64

3j ^{1}H NMR, 400 MHz, $CDCl_3$

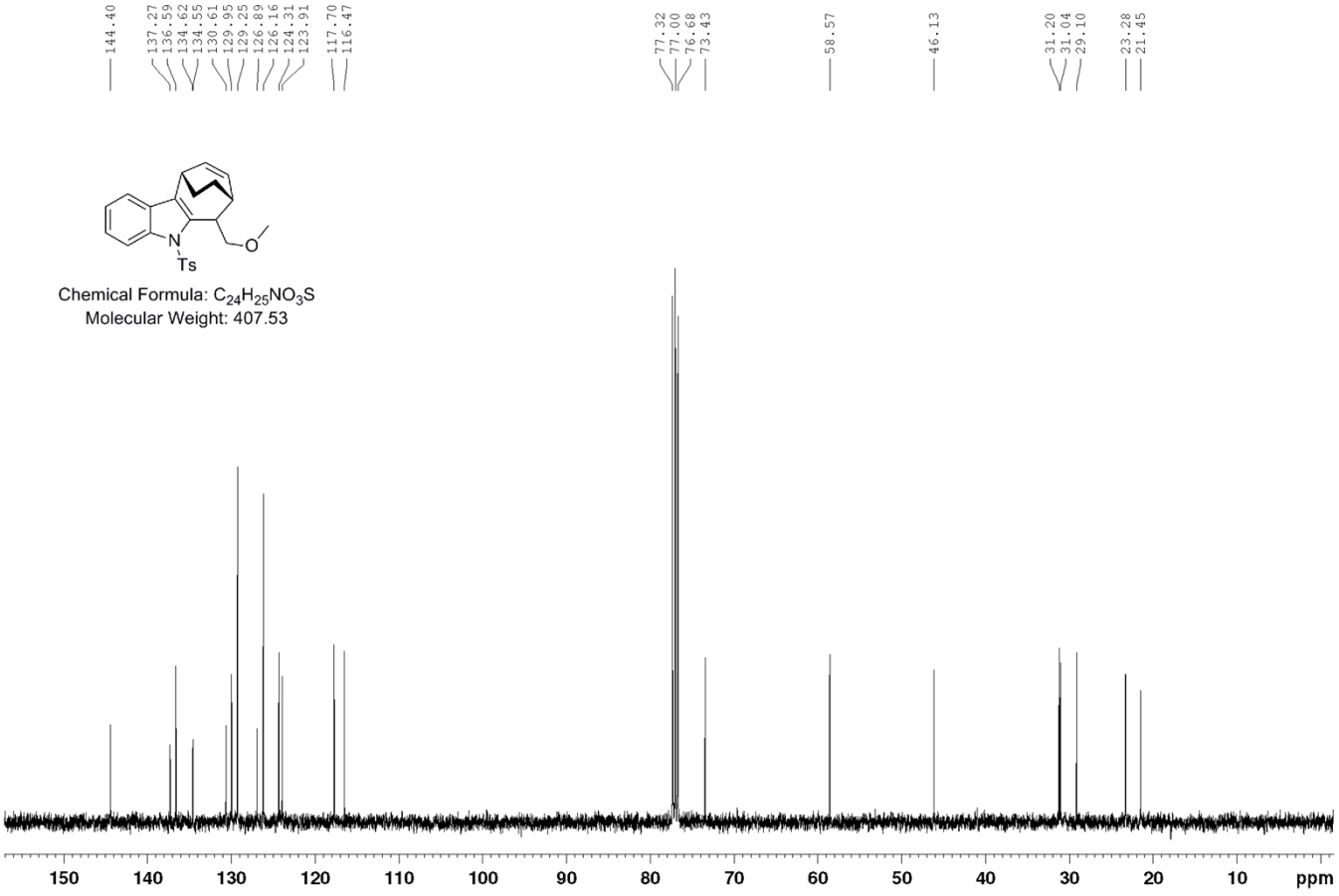




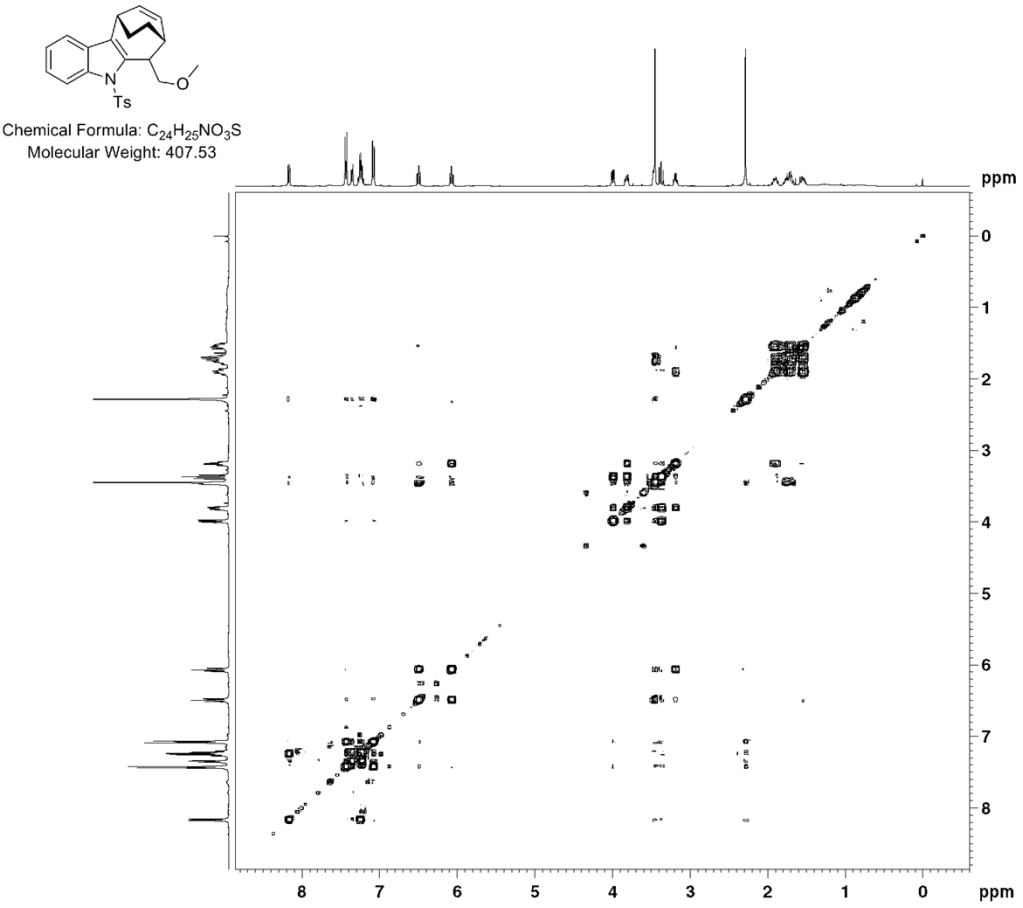
Chemical Formula: $C_{24}H_{25}NO_3S$
Molecular Weight: 407.53



3j ^{13}C NMR, 100 MHz, $CDCl_3$

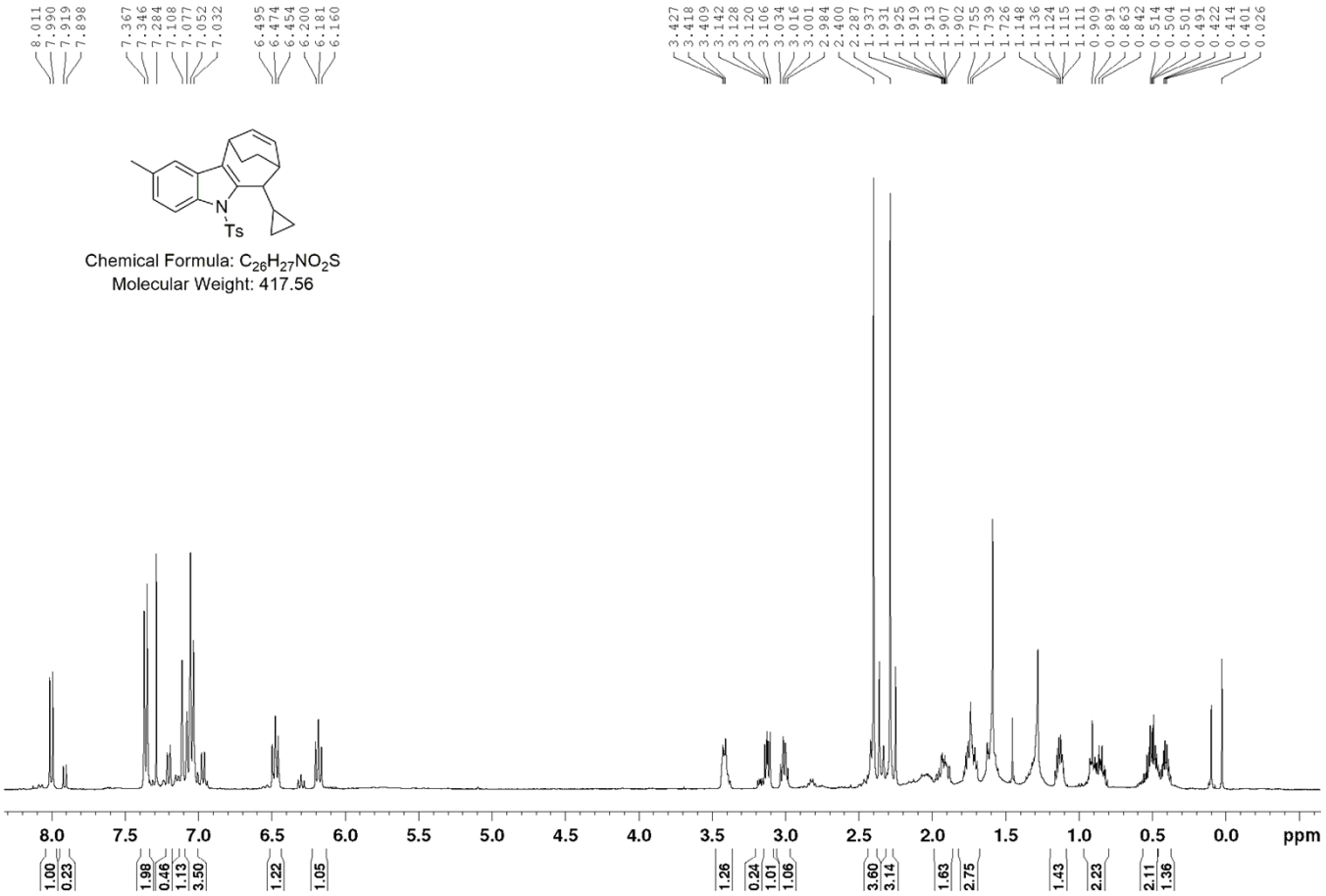


3j COSY NMR, 100 MHz, $CDCl_3$

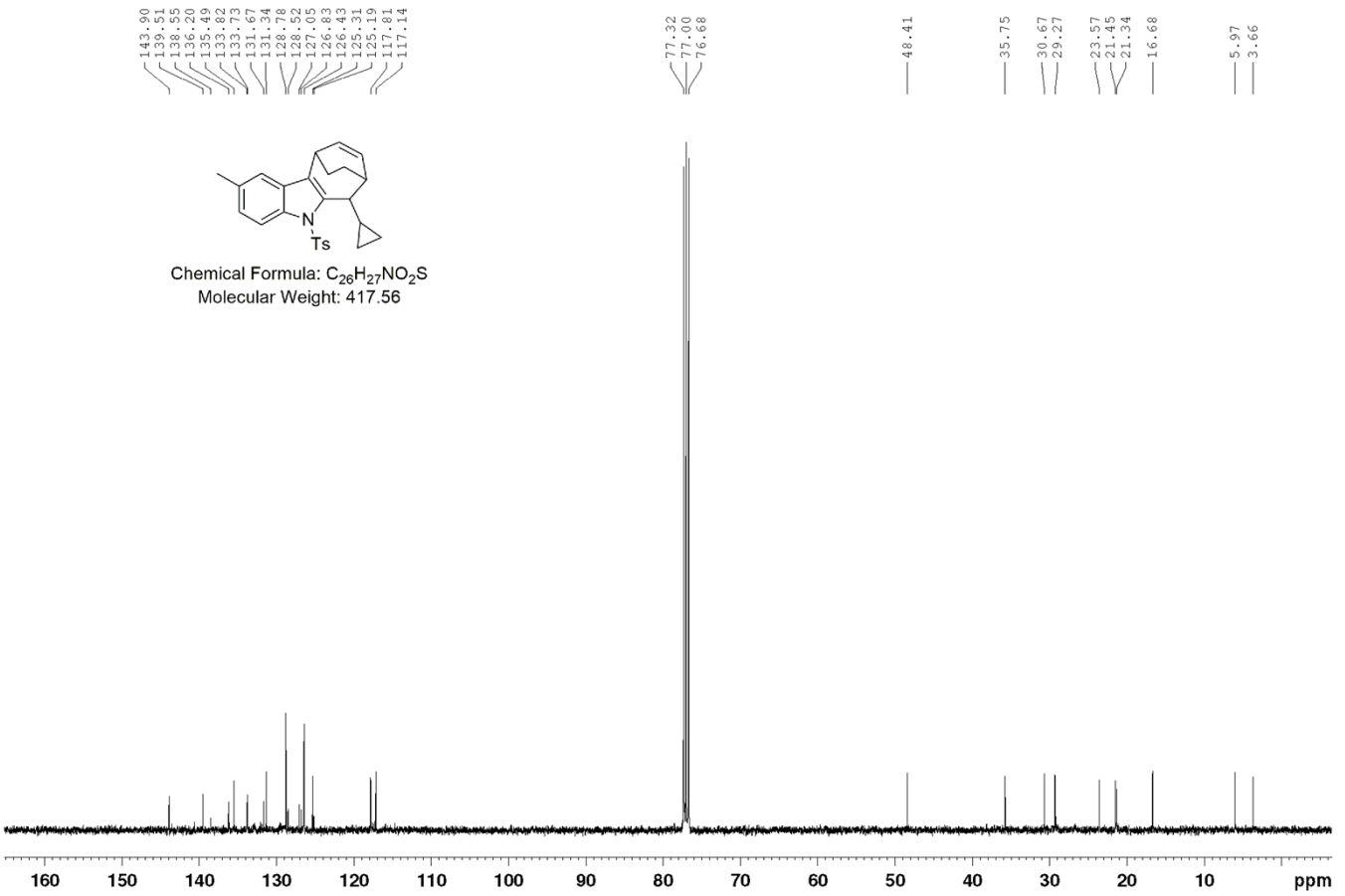



```
NAME          ZJ-140325-2B
EXPNO                   11
PROCNO                   1
Date_             20140325
Time                 22.31
INSTRUM              spect
PROBHD    5 mm PABBO BB/
PULPROG       cosygpppqf
TD                    2048
SOLVENT              CDCl3
NS                       1
DS                       8
SWH               3846.154 Hz
FIDRES            1.878005 Hz
AQ                0.2662900 sec
RG                      64
DW                 130.000 usec
DE                   6.50 usec
TE                  296.9 K
D0              0.00000300 sec
D1              1.92545295 sec
D11             0.03000000 sec
D12             0.00002000 sec
D13             0.00000400 sec
D16             0.00020000 sec
IN0             0.00026000 sec

======== CHANNEL f1 ========
SFO1          400.1316930 MHz
NUC1                    1H
P0                  14.10 usec
P1                  14.10 usec
P17               2500.00 usec
ND0                      1
TD                     128
SFO1            400.1317 MHz
FIDRES          30.048077 Hz
SW                  9.612 ppm
FnMODE                  QF
SI                    1024
SF            400.1300123 MHz
WDW                 QSINE
SSB                      0
LB                    0.00 Hz
GB                       0
PC                    1.40
SI                    1024
MC2                     QF
SP            400.1300123 MHz
WDW                 QSINE
SSB                      0
LB                    0.00 Hz
GB                       0
```

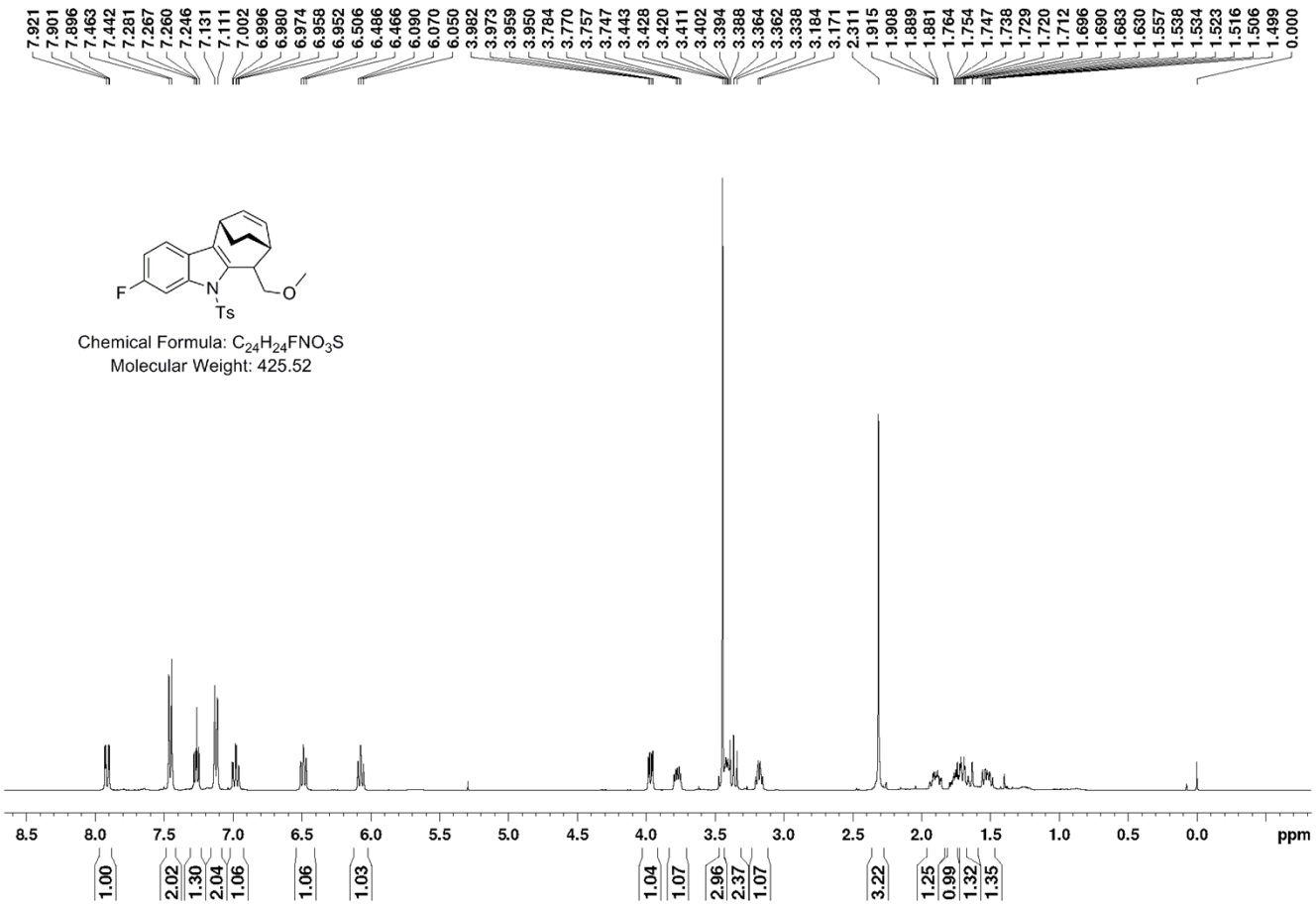
3k ^{1}H NMR, 400 MHz, $CDCl_3$



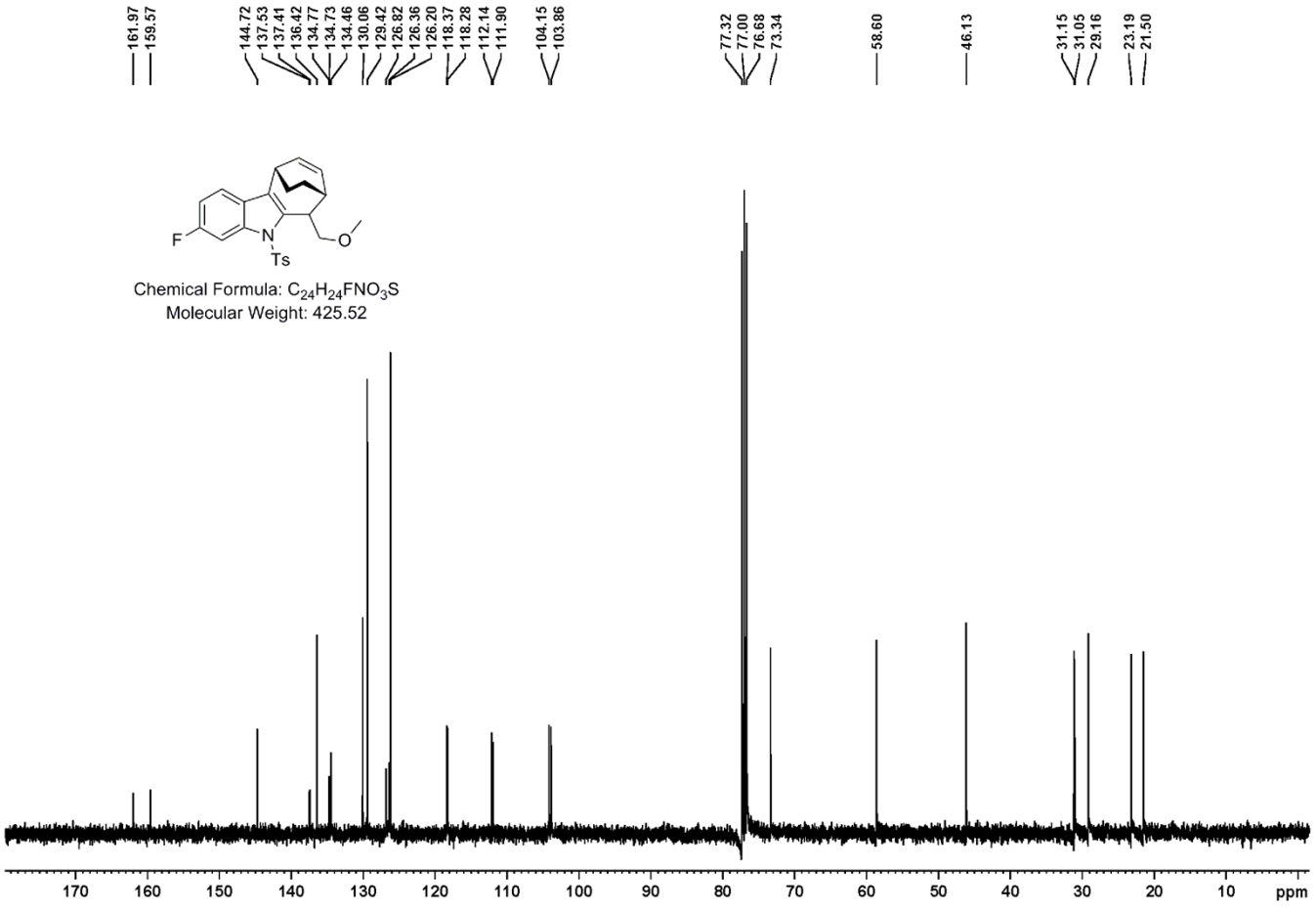
3k ^{13}C NMR, 100 MHz, $CDCl_3$



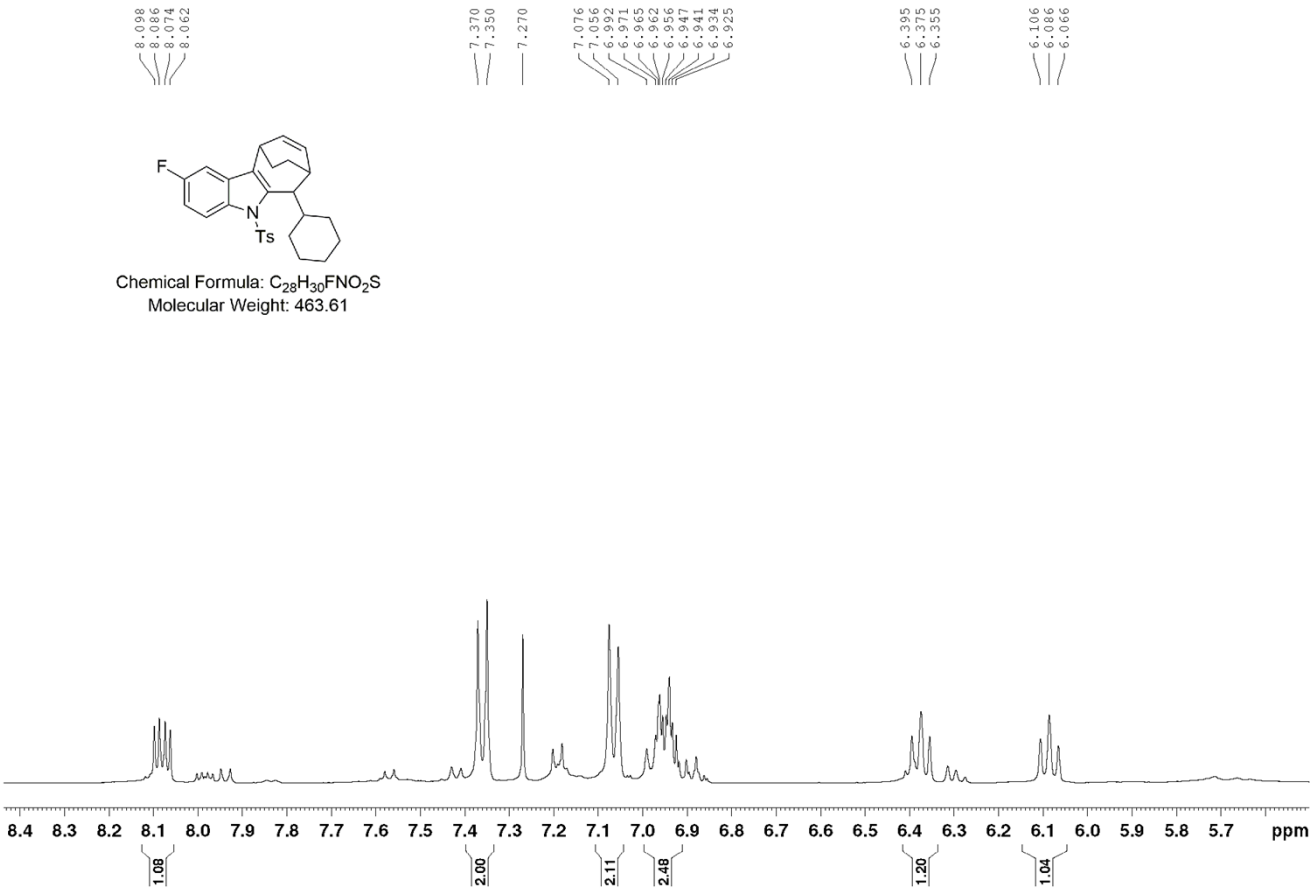
3l ^{1}H NMR, 400 MHz, $CDCl_3$



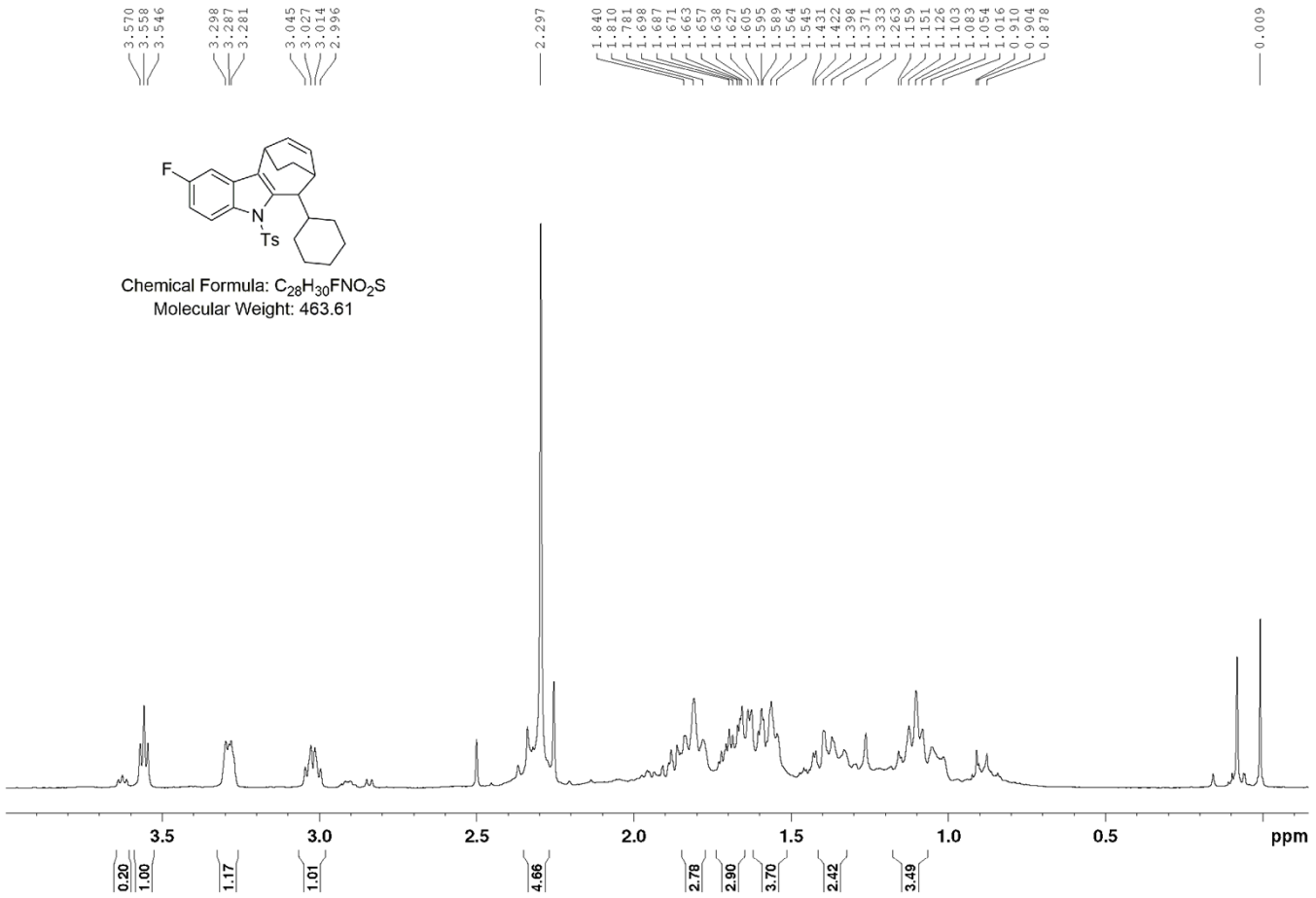
3l ^{13}C NMR, 100 MHz, $CDCl_3$



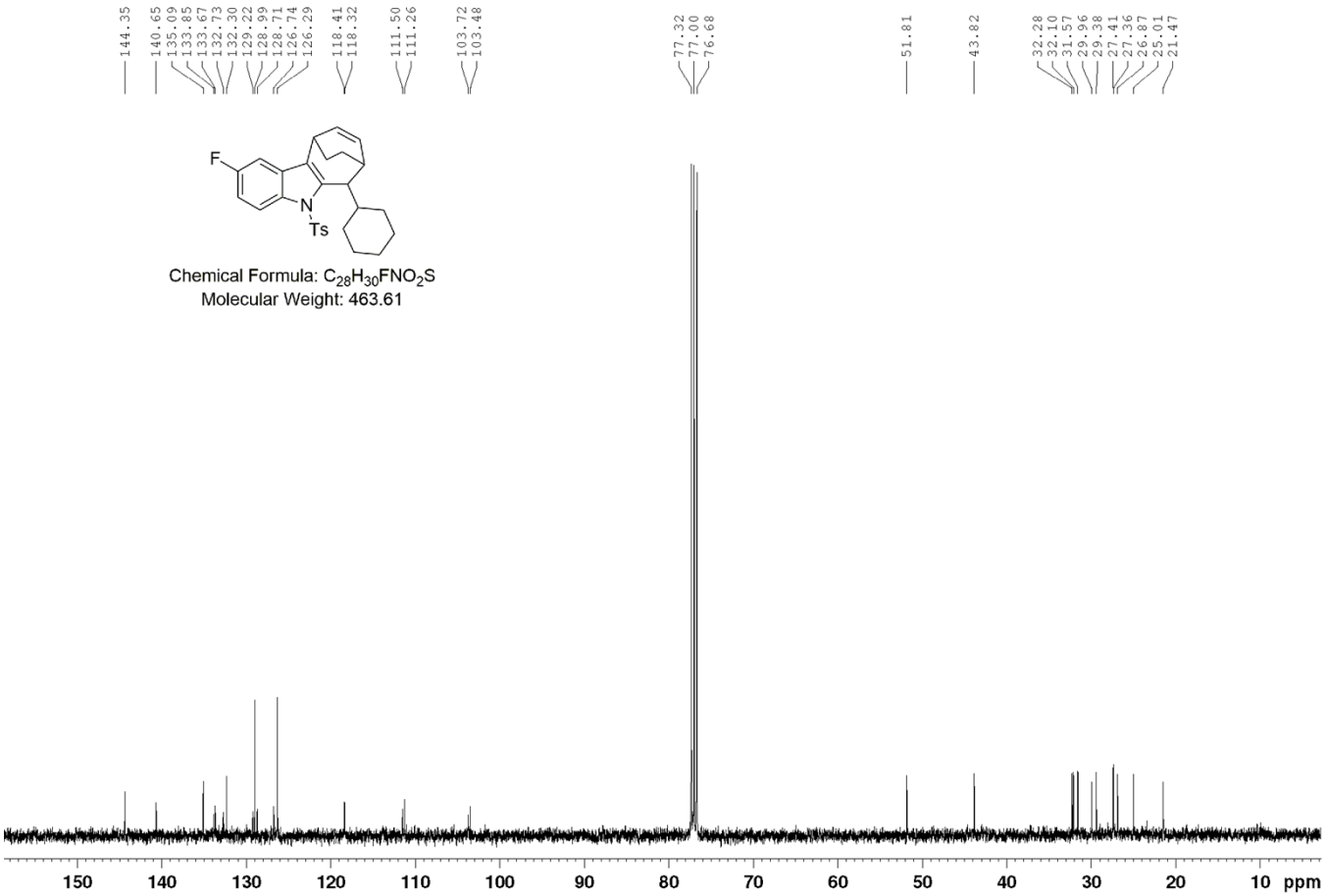
3m ^{1}H NMR, 400 MHz, $CDCl_3$ (part A)



3m ^{1}H NMR, 400 MHz, $CDCl_3$ (part B)

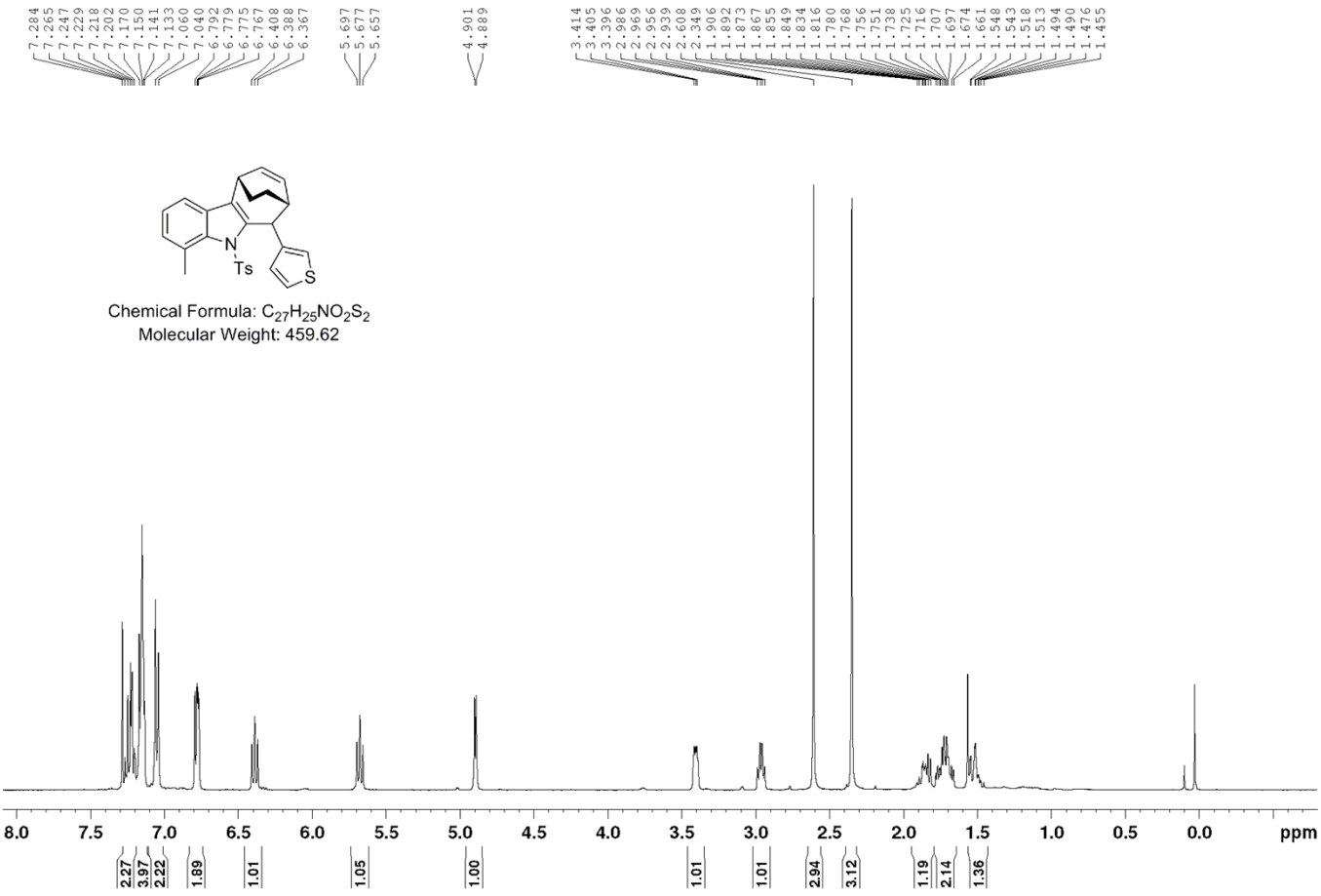


3m ^{13}C NMR, 100 MHz, $CDCl_3$



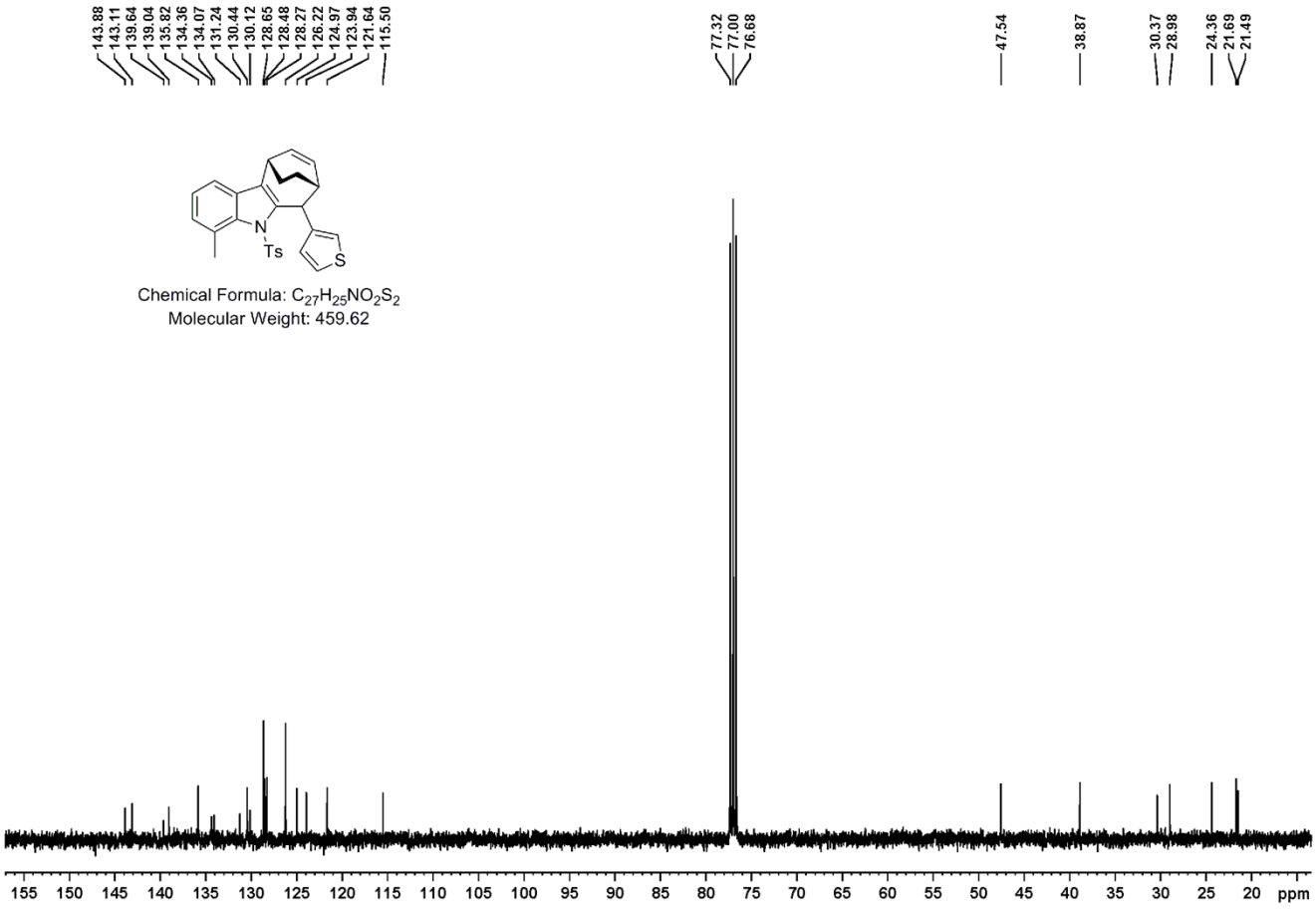
Chemical Formula: $C_{28}H_{30}FNO_2S$
Molecular Weight: 463.61

3n ^{1}H NMR, 400 MHz, $CDCl_3$



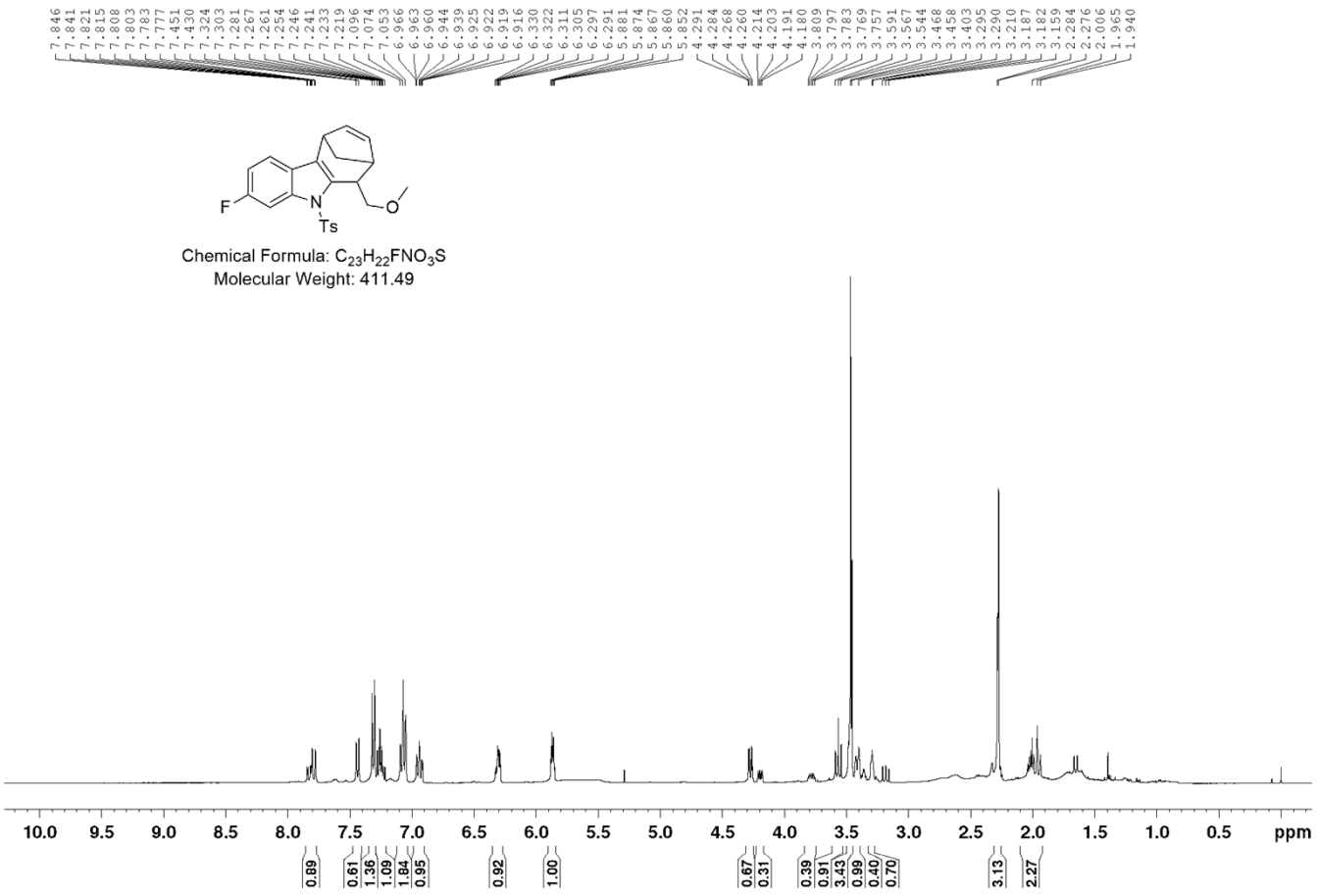
Chemical Formula: $C_{27}H_{25}NO_2S_2$
Molecular Weight: 459.62

3n ^{13}C NMR, 100 MHz, $CDCl_3$



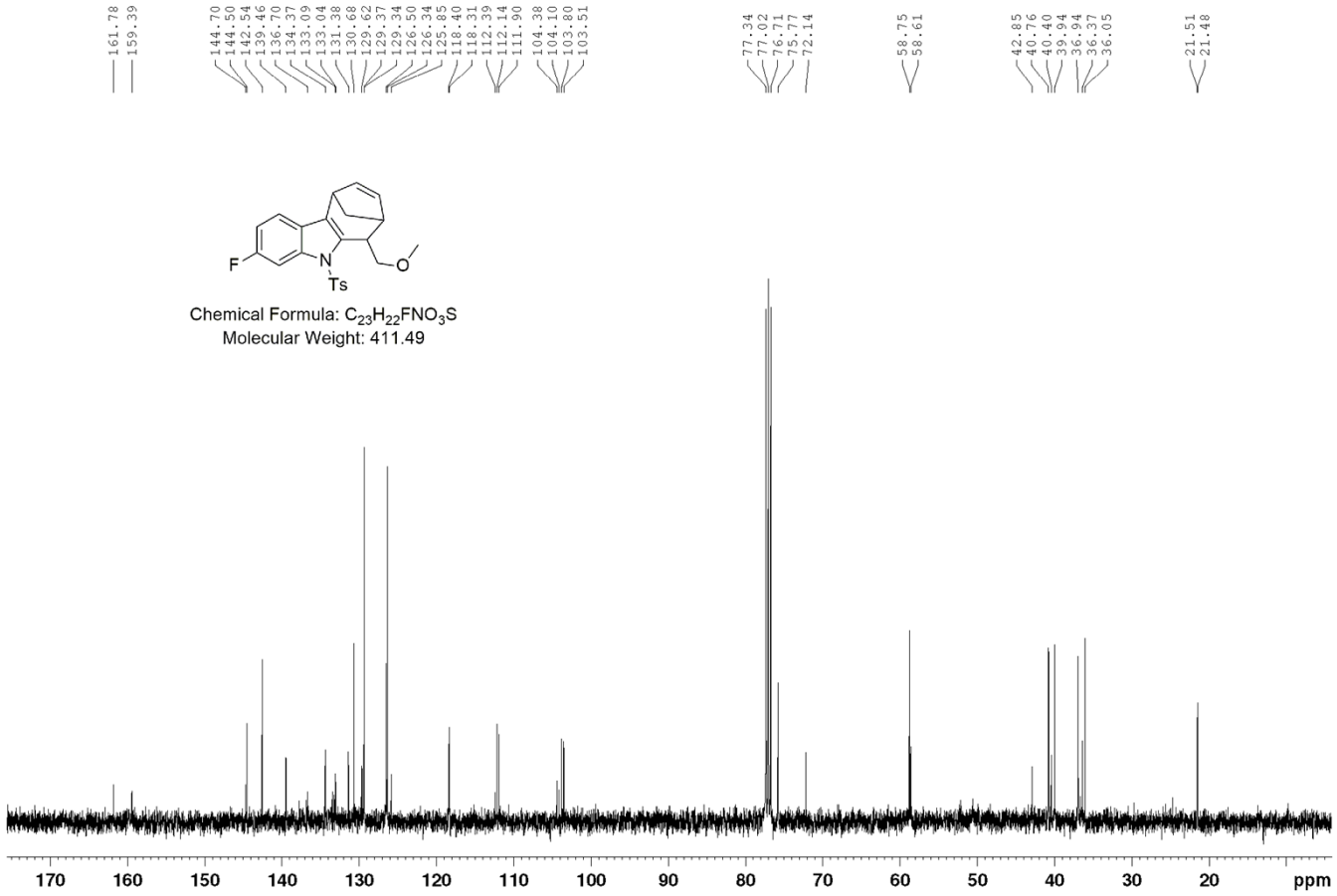
Chemical Formula: $C_{27}H_{25}NO_2S_2$
Molecular Weight: 459.62

3o ^{1}H NMR, 400 MHz, $CDCl_3$



Chemical Formula: $C_{23}H_{22}FNO_3S$
Molecular Weight: 411.49

3o ^{13}C NMR, 100 MHz, $CDCl_3$


161.78
159.39
144.70
144.50
142.54
139.46
136.70
134.37
133.09
133.04
131.38
130.68
129.62
129.37
129.34
126.50
126.34
125.85
118.40
118.31
112.39
112.14
111.90
104.38
104.10
103.80
103.51
77.34
77.02
76.71
75.77
72.14
58.75
58.61
42.85
40.76
40.40
39.94
36.94
36.37
36.05
21.51
21.48
F
N
Ts
O
Chemical Formula: C23H22FNO3S
Molecular Weight: 411.49
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm