Supporting Information

# Rh-Catalyzed 1,2-Sulfur Migration/aza-Diels-Alder Cascade Initiated by aza-Vinyl Carbenoids from Sulfur-Tethered *N*-Sulfonyl-1,2,3-triazoles

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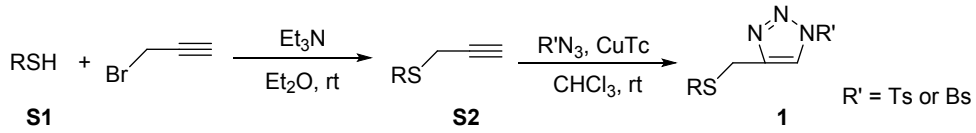
**CONTENTS**

**General Remarks**: $^{1}H$ NMR spectra were recorded on a Bruker AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in $cm^{-1}$. THF, toluene and $Et_2O$ were distilled from sodium (Na) under argon (Ar) atmosphere. $CH_3CN$, 1,2-dichloroethane and dichloromethane were distilled from $CaH_2$ under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

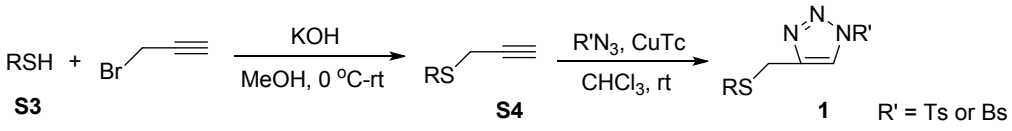
**General procedure for the synthesis of compounds 1a-1m, 1t:**




A mixture of corresponding **S1** (5.0 mmol), propargyl bromide (1.5 eq), $Et_3N$ (1.5 eq) in THF (30 mL) was stirred at room temperature for an appropriate time. After completion of the reaction as indicated by TLC, the solvent was removed under reduced pressure. The resulting product **S2** was used in the next step without further purification.

In another flask, a solution of compound **S2** (2.0 mmol) and CuTc (40 mg, 0.2 mmol) in $CHCl_3$ (5 mL) was stirred at room temperature under $N_2$. Afterwards compound $R'N_3$ (2.0 mmol) was added and the reaction solution was stirred until compound **S2** was consumed completely. The mixture was filtered through a celite and the filtrate was concentrated under reduced pressure and the residue was purified by silica gel column flash chromatography (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the product **1** in moderate yield.

**General procedure for the synthesis of compounds 1n-1s, 1u-1w:**



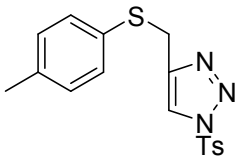

Thiol (RSH, **S3**, 5.0 mmol) was dissolved in a degassed methanol (0.5 M) at 0 °C and solid KOH was added (1.5 equiv). After 5 min, propargyl bromide (1.5 equiv) was added and the reaction mixture was allowed to warm to room temperature. After completion of the reaction as indicated by TLC, the methanol was removed under vacuum and the residue was extracted from water with ethyl acetate or dichloromethane, then the solvent was removed under reduced pressure. The resulting product **S4** was used in the next step without further purification.

In another flask, a solution of compound **S4** (2.0 mmol) and CuTc (40 mg, 0.2 mmol) in $CHCl_3$ (5 mL) was stirred at room temperature under $N_2$. Afterwards compound $R'N_3$ (2.0 mmol) was

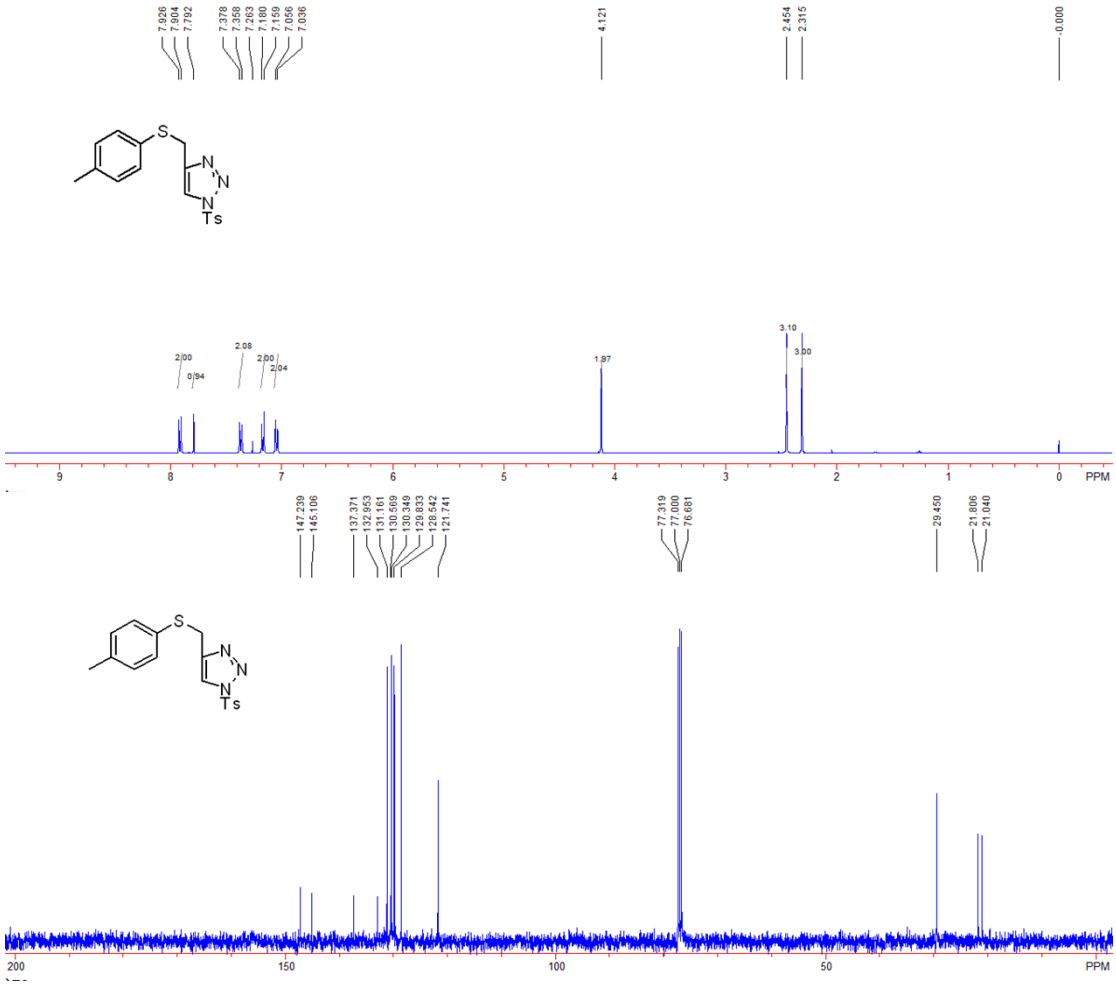
added and the reaction solution was stirred until compound **S4** was consumed completely. The mixture was filtered through a celite and the filtrate was concentrated under reduced pressure and the residue was purified by silica gel column flash chromatography (eluent: petroleum ether / ethyl acetate = 4 / 1) to afford the product **1** in moderate yield.

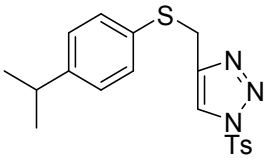
For the substrate **1v**, phenyl propargyl selenide was prepared according to the previous literature.[3]

**Spectroscopic Data of Substrates 1**

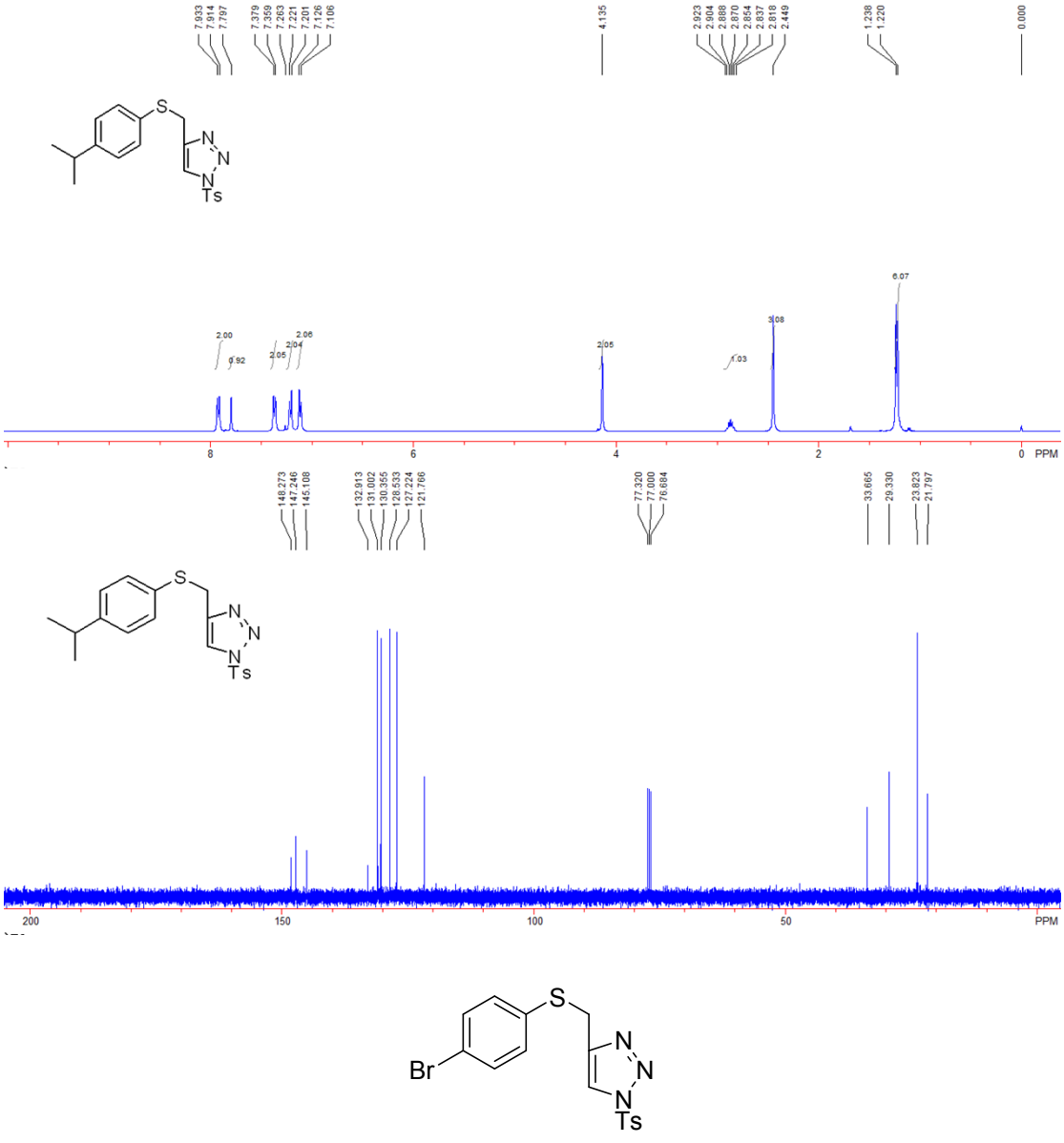



4-(*p*-tolylthiomethyl)-1-tosyl-1*H*-1,2,3-triazole **1a**: a white solid; Mp: 106-108 °C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.32 (s, 3H), 2.45 (s, 3H), 4.12 (s, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.79 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 21.8, 29.5, 121.7, 128.5, 129.8, 130.3, 130.6, 131.2, 133.0, 137.4, 145.1, 147.2; IR ($CH_2Cl_2$) ν 3146, 2923, 1595, 1493, 1393, 1308, 1241, 1195, 1180, 1122, 1091, 1010, 969, 810, 670 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{17}H_{18}N_3O_2S_2$ $(M+H)^+$: 360.0835, found: 360.0848.

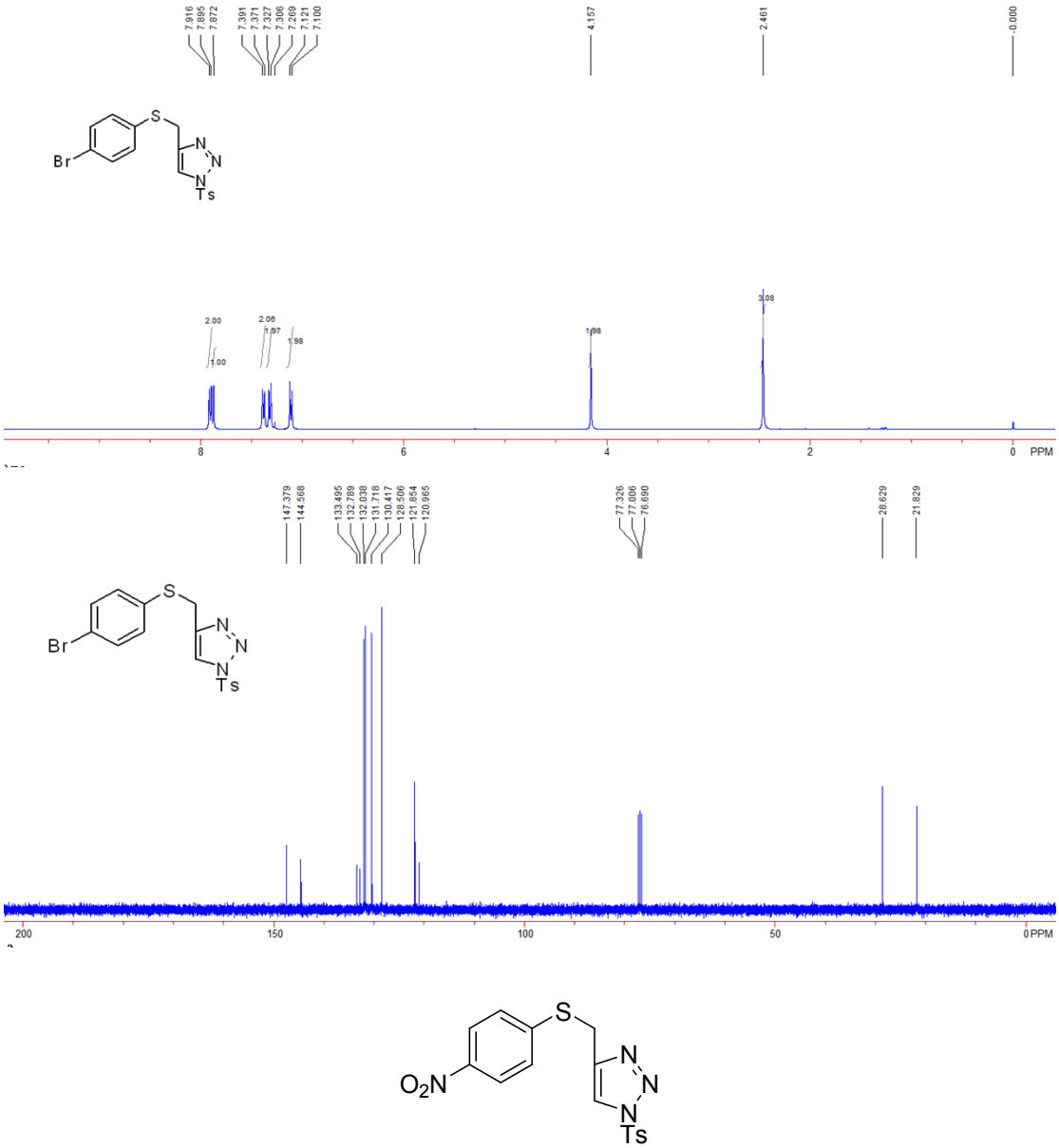





4-((4-isopropylphenylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1b**: a white solid; Mp: 106-108 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (d, *J* = 7.2 Hz, 6H), 2.45 (s, 3H), 2.81-2.93 (m, 1H), 4.14 (s, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.80 (s, 1H), 7.92 (d, *J* = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 23.8, 29.3, 33.7, 121.8, 127.2, 128.5, 130.4, 131.0, 132.9, 145.1, 147.2, 148.3; IR ($CH_2Cl_2$) ν 3146, 2960, 2869, 2127, 1594, 1554, 1495, 1392, 1194, 1179, 1091, 1009, 968, 813, 668 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{19}H_{22}N_3O_2S_2$ $(M+H)^+$: 388.1148, found: 388.1148.

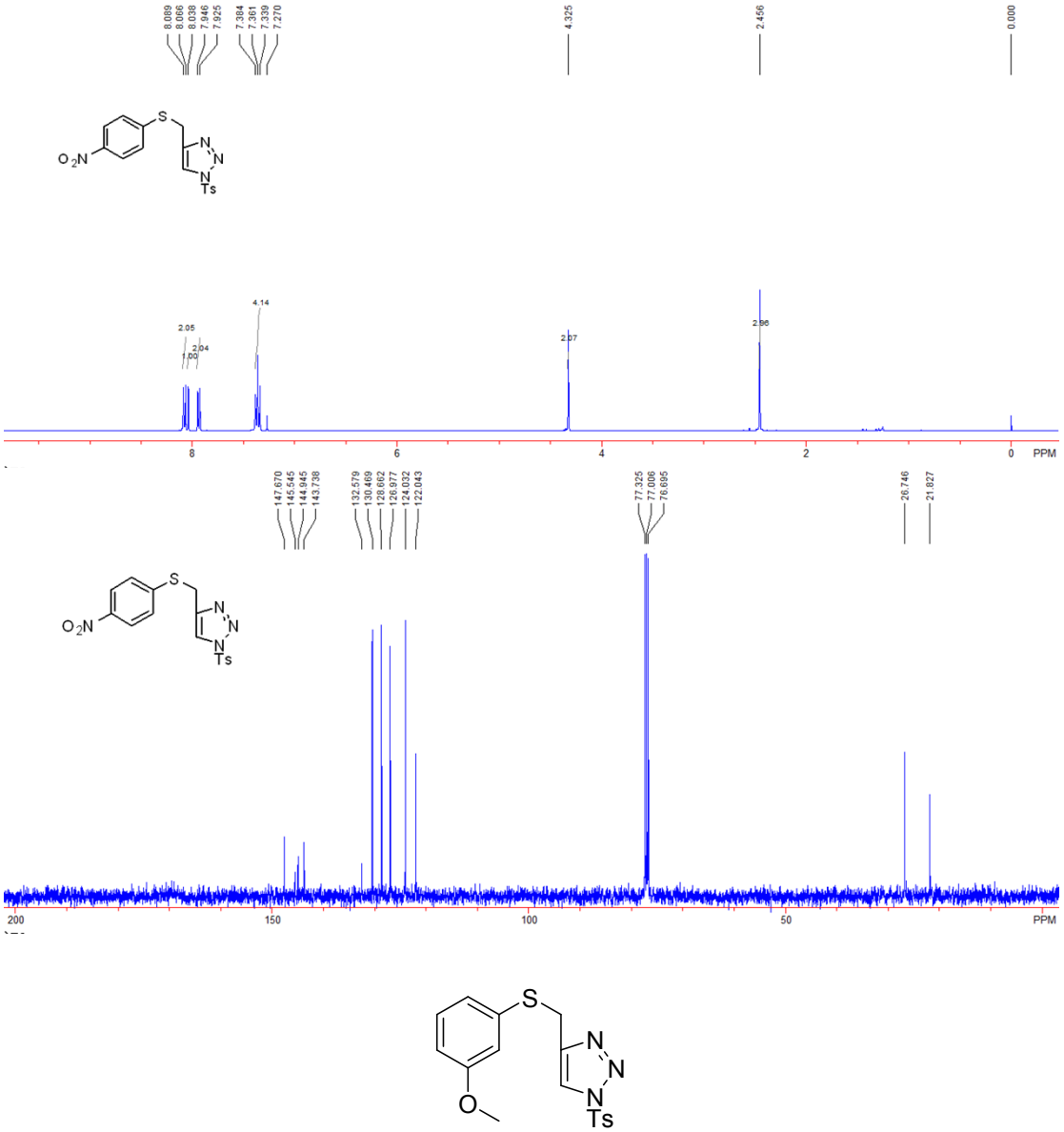


4-((4-bromophenylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1c**: a white solid; Mp: 113-115 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H), 4.16 (s, 2H), 7.11 (d, $J$ = 8.4 Hz, 2H), 7.32 (d, $J$ = 8.4 Hz, 2H), 7.38 (d, $J$ = 8.0 Hz, 2H), 7.87 (s, 1H), 7.91 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 28.6, 121.0, 121.9, 128.5, 130.4, 131.7, 132.0, 132.8, 133.5, 144.6, 147.4; IR ($CH_2Cl_2$) ν 3145, 1594, 1474, 1389, 1309, 1242, 1194, 1179, 1090, 1008, 970, 811, 668 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{16}H_{15}BrN_3O_2S_2$ $(M+H)^+$: 423.9784, found: 423.9777.




4-((4-nitrophenylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1d**: a white solid; Mp: 153-155 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H), 4.33 (s, 2H), 7.33-7.39 (m, 4H), 7.94 (d, $J$ = 8.4 Hz, 2H), 8.04 (s, 1H), 8.08 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 26.7, 122.0, 124.0, 127.0, 128.7, 130.5, 132.6, 143.7, 144.9, 145.5, 147.7; IR ($CH_2Cl_2$) ν 3146, 2924,

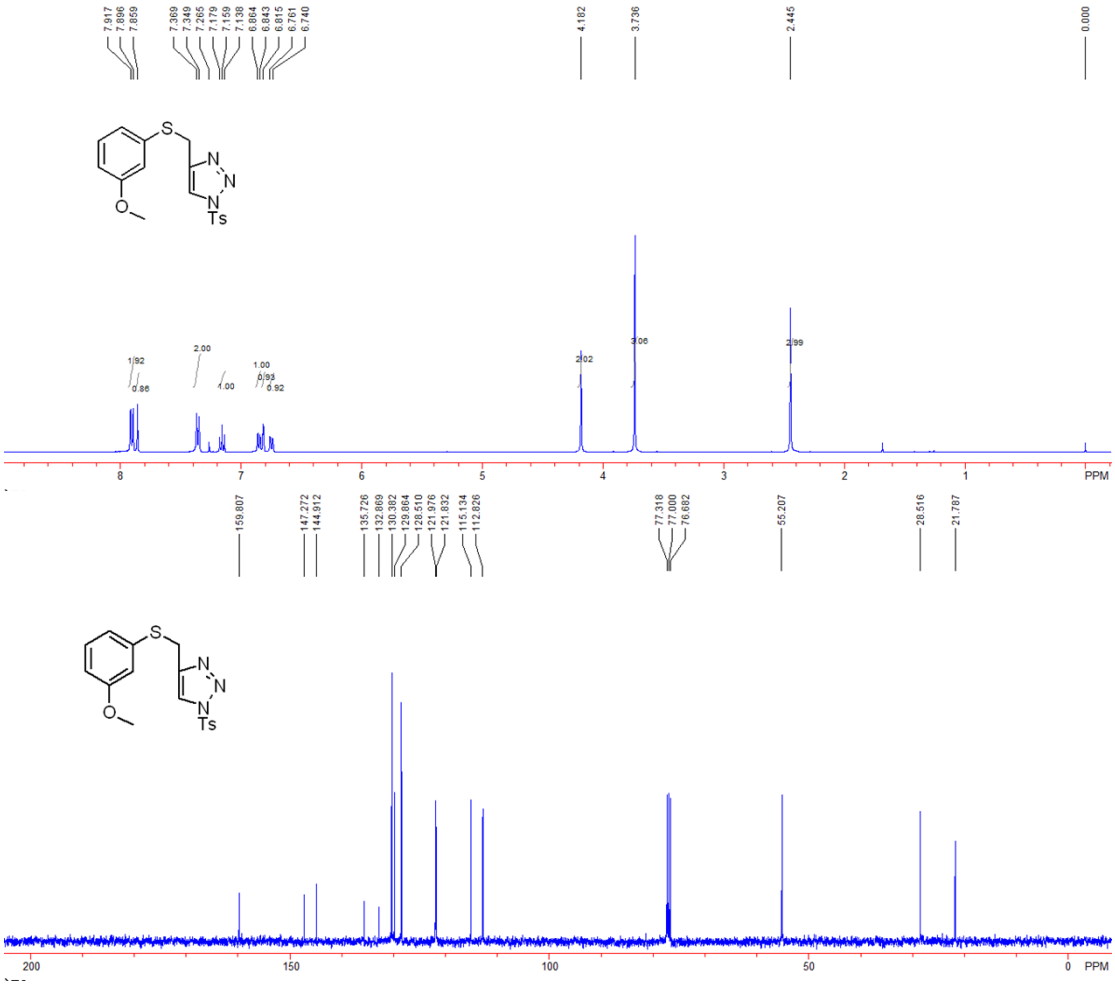
1594, 1578, 1511, 1393, 1338, 1309, 1195, 1180, 1191, 1010, 973, 854, 670 $cm^{-1}$; HRMS (ESI) Calcd. for $C_{16}H_{15}N_4O_4S_2$ $(M+H)^+$: 391.0529, found: 391.0521.

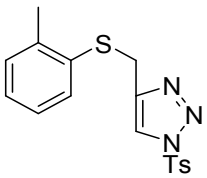




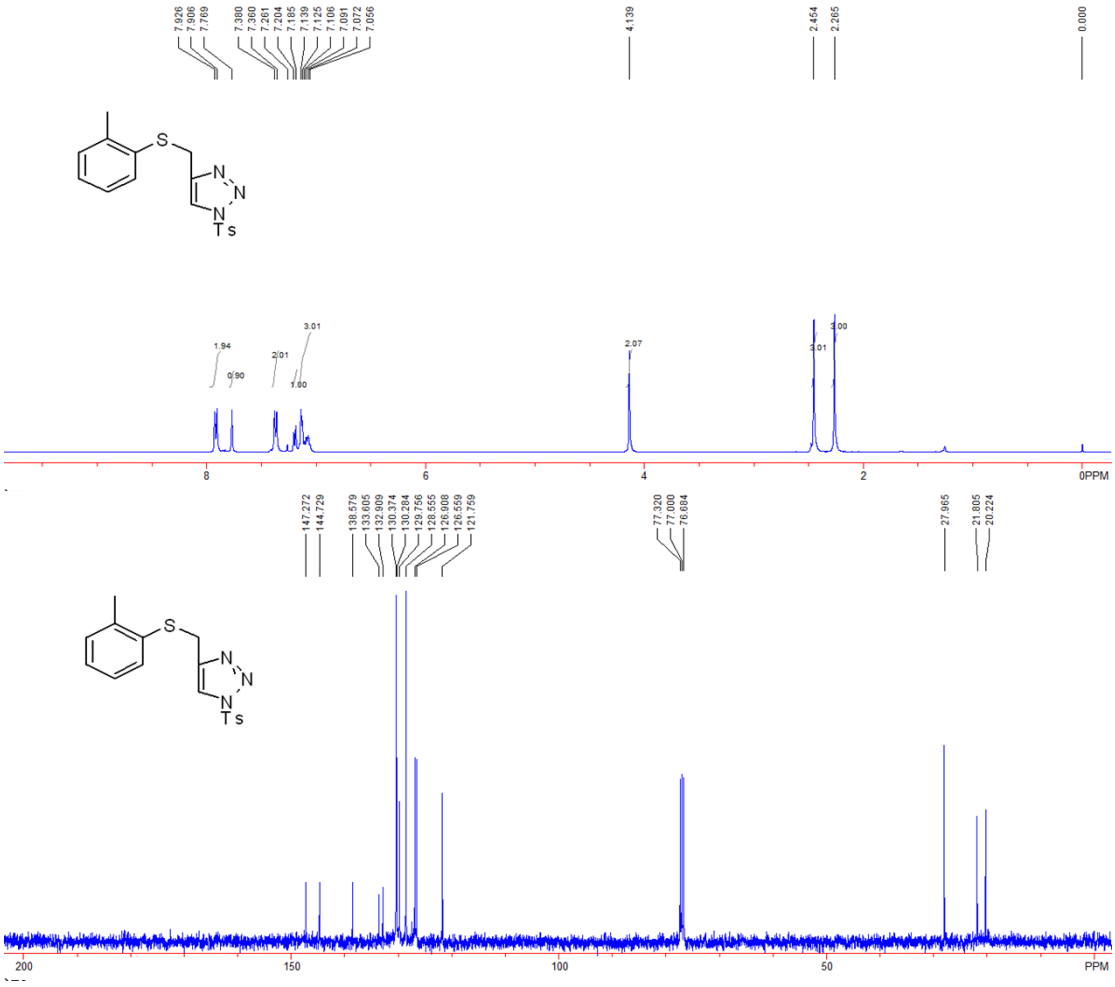


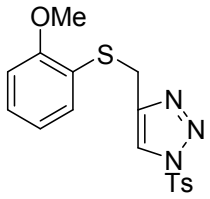
4-((3-methoxyphenylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1e**: a white solid; Mp: 75-77 $^oC$; $^1H$ NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H), 3.74 (s, 3H), 4.18 (s, 2H), 6.75 (d, $J$ = 8.4 Hz, 1H), 6.82 (s, 1H), 6.85 (d, $J$ = 8.4 Hz, 1H), 7.16 (t, $J$ = 8.4 Hz, 1H), 7.36 (d, $J$ = 8.4 Hz, 2H), 7.86 (s, 1H), 7.91 (d, $J$ = 8.4 Hz, 2H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 28.5, 55.2, 112.8, 115.1, 121.8, 122.0, 128.5, 129.9, 130.4, 132.9, 135.7, 144.9, 147.3, 159.8; IR ($CH_2Cl_2$) ν 3146, 2938, 1589, 1575, 1479, 1391, 1194, 1179, 1091, 1035, 1009, 969, 812, 734, 668 $cm^{-1}$; HRMS (ESI) Calcd. for $C_{17}H_{18}N_3O_3S_2$ $(M+H)^+$: 376.0784, found: 376.0796.



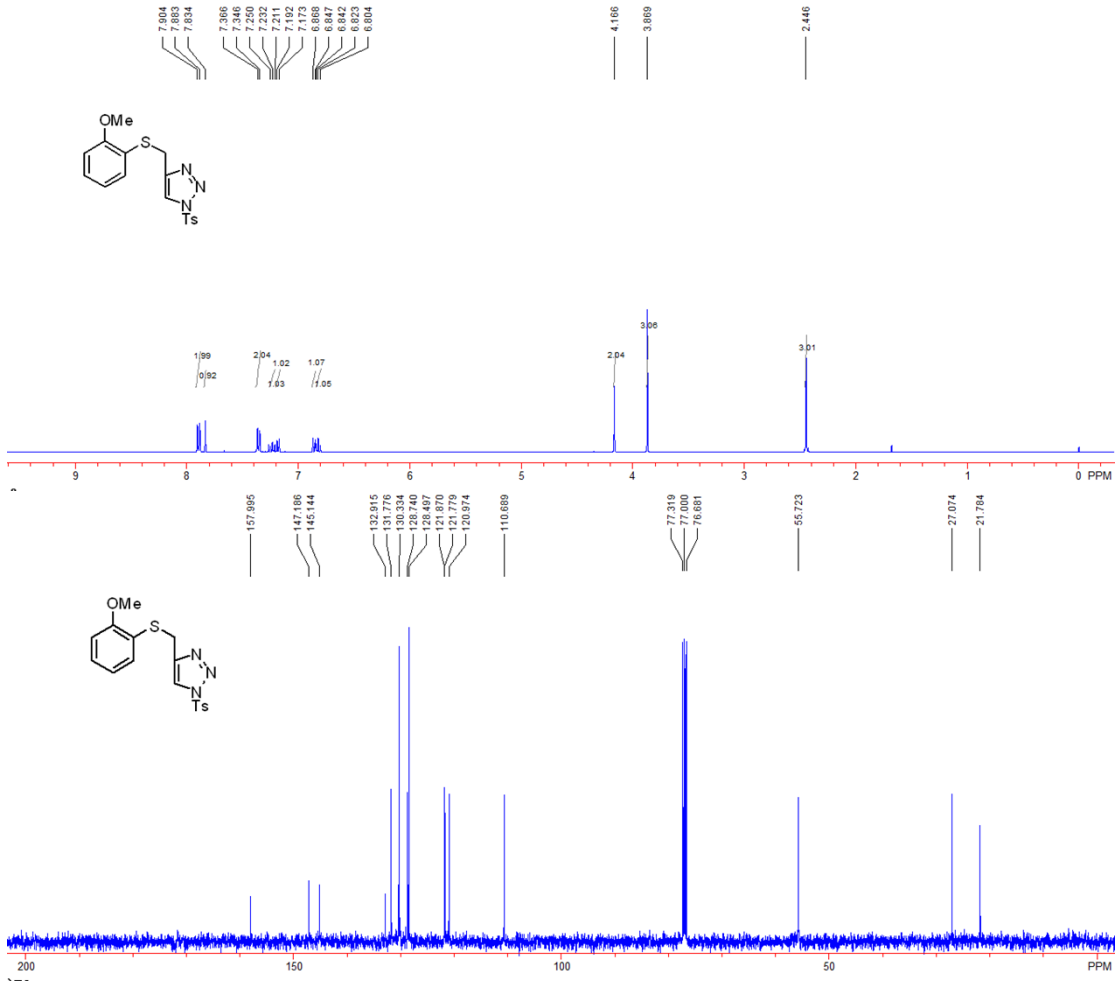


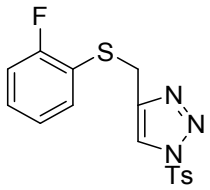
4-(o-tolylthiomethyl)-1-tosyl-1*H*-1,2,3-triazole **1f**: a white solid; Mp: 123-125 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.27 (s, 3H), 2.45 (s, 3H), 4.14 (s, 2H), 7.05-7.21 (m, 4H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.77 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.2, 21.8, 28.0, 121.8, 126.6, 126.9, 128.6, 129.8, 130.3, 130.4, 132.9, 133.6, 138.6, 144.7, 147.3; IR ($CH_2Cl_2$) ν 3145, 2925, 1594, 1470, 1392, 1308, 1194, 1179, 1091, 1010, 969, 813, 747, 669 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{17}H_{18}N_3O_2S_2$ $(M+H)^+$: 360.0835, found: 360.0838.



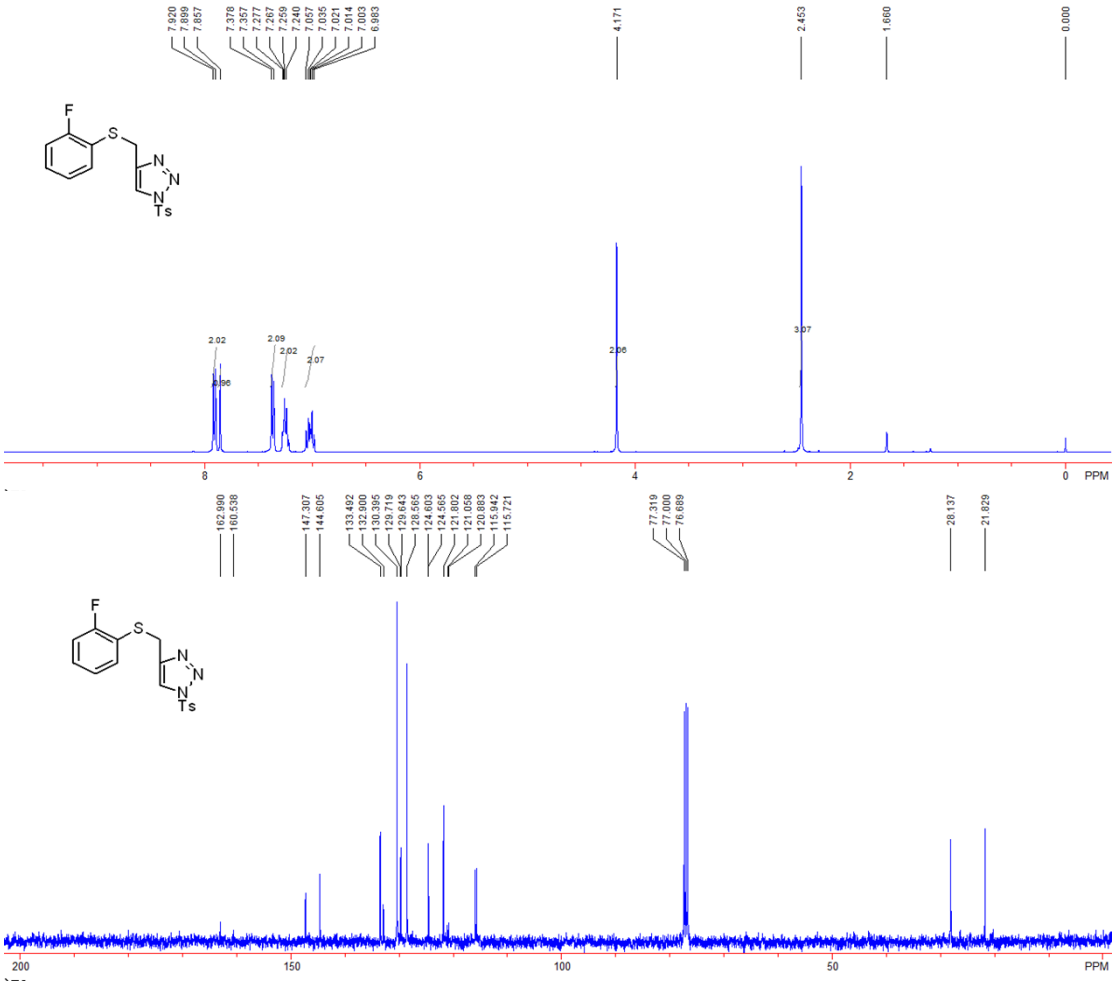



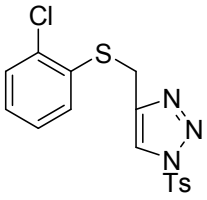

4-((2-methoxyphenylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1g**: a white solid; Mp: 85-86 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H), 3.87 (s, 3H), 4.17 (s, 2H), 6.82 (t, $J$ = 8.0 Hz, 1H), 6.86 (d, $J$ = 8.0 Hz, 1H), 7.18 (d, $J$ = 8.0 Hz, 1H), 7.23 (t, $J$ = 8.0 Hz, 1H), 7.36 (d, $J$ = 8.0 Hz, 2H), 7.83 (s, 1H), 7.89 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 27.1, 55.7, 110.7, 121.0, 121.8, 121.9, 128.5, 128.7, 130.3, 131.8, 132.9, 145.1, 147.2, 158.0; IR ($CH_2Cl_2$) ν 3144, 2938, 1594, 1580, 1477, 1391, 1307, 1243, 1194, 1179, 1091, 1009, 969, 813, 669 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{17}H_{18}N_3O_3S_2$ $(M+H)^+$: 376.0784, found: 376.0785.



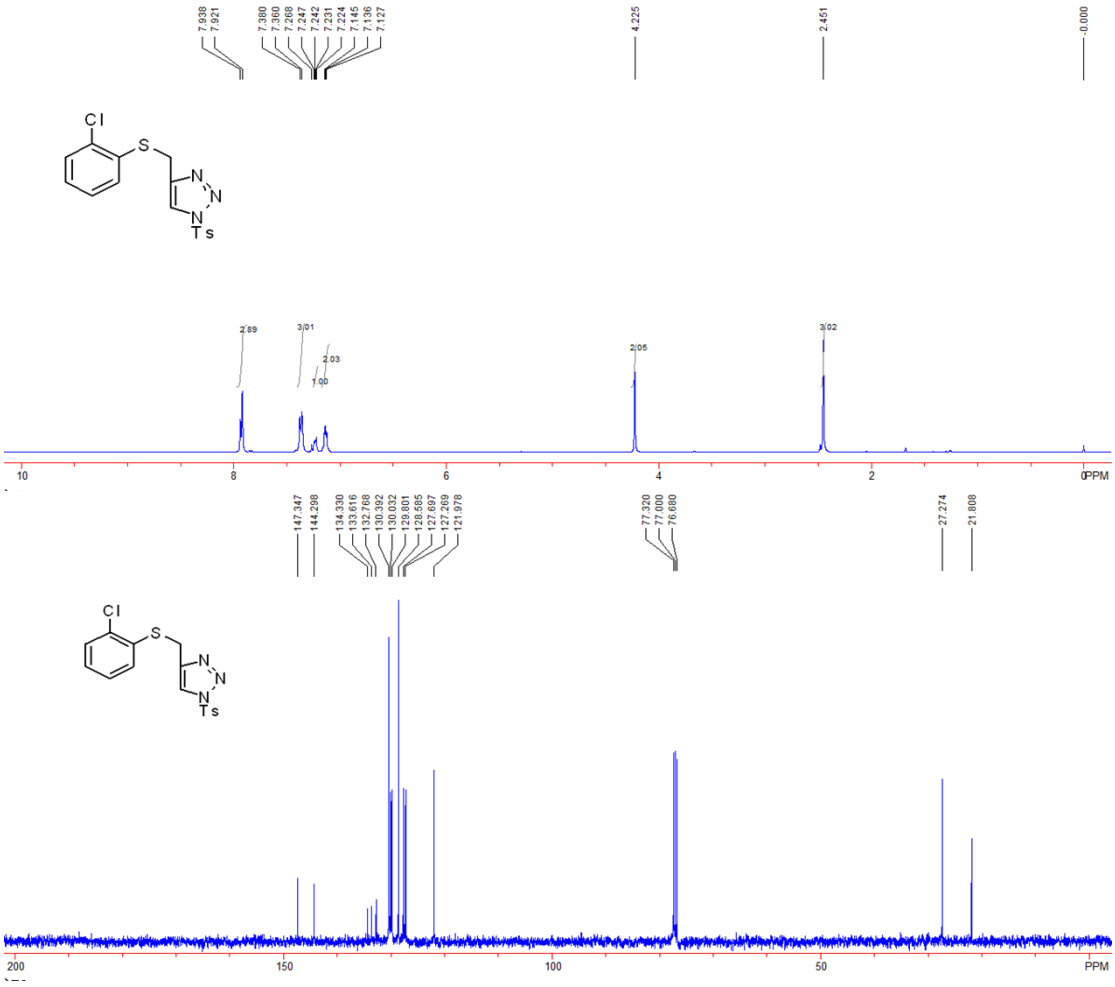



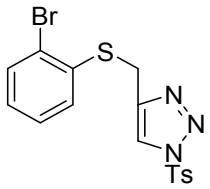

4-((2-fluorophenylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1h**: a white solid; Mp: 98-100 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H), 4.17 (s, 2H), 6.98-7.06 (m, 2H), 7.24-7.28 (m, 2H), 7.37 (d, $J$ = 8.4 Hz, 2H), 7.86 (s, 1H), 7.91 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 28.1, 115.8 (d, $J$ = 22.1 Hz), 121.0 (d, $J$ = 17.5 Hz), 121.8, 124.6 (d, $J$ = 3.8 Hz), 128.6, 129.7 (d, $J$ = 7.6 Hz), 130.4, 132.9, 133.5, 144.6, 147.3, 161.8 (d, $J$ = 245.2 Hz); IR ($CH_2Cl_2$) ν 3146, 2927, 1594, 1473, 1391, 1194, 1179, 1091, 1010, 969, 813, 669 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{16}H_{15}FN_3O_2S_2$ $(M+H)^+$: 364.0584, found: 364.0584.



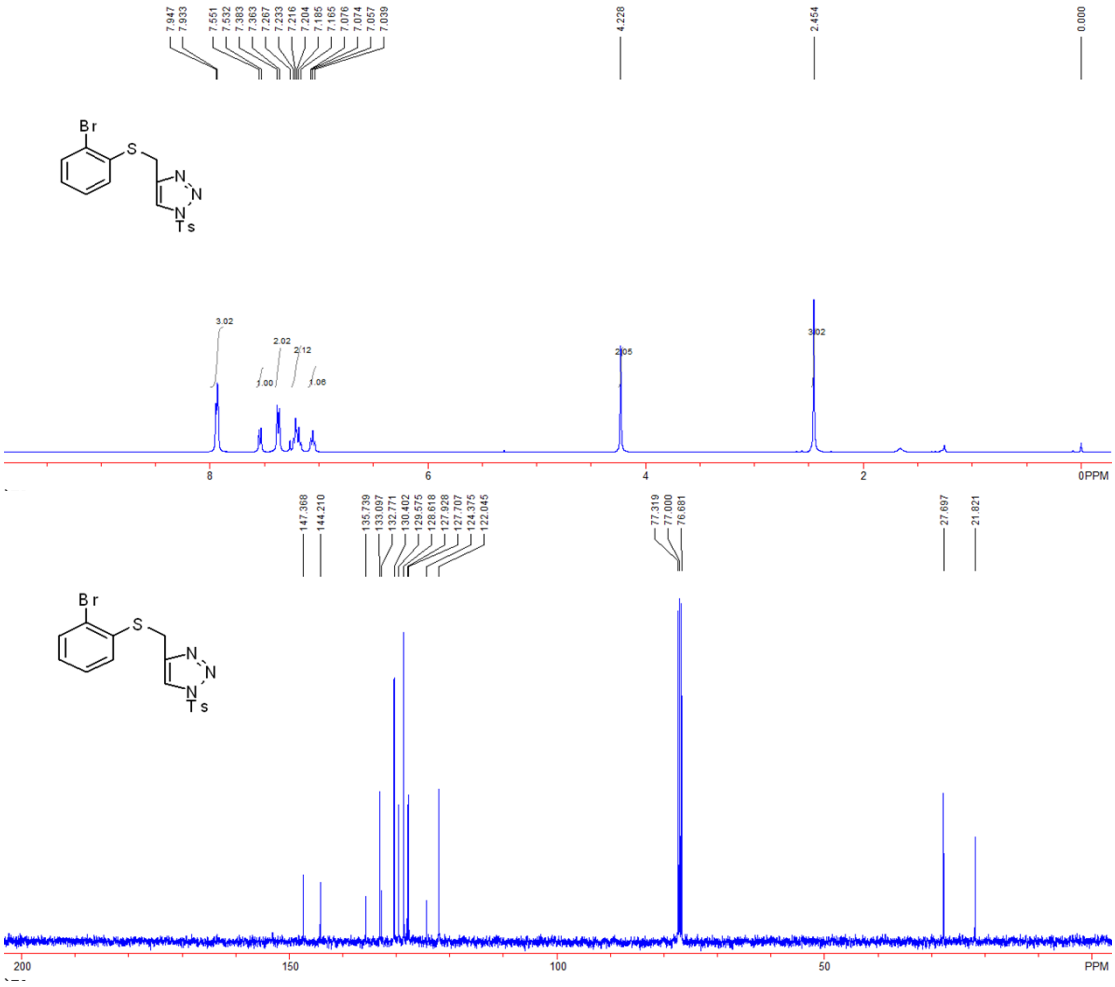


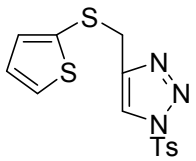
4-((2-chlorophenylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1i**: a white solid; Mp: 120-121 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H), 4.23 (s, 2H), 7.12-7.25 (m, 3H), 7.36-7.38 (m, 3H), 7.92-7.94 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 27.3, 122.0, 127.3, 127.7, 128.6, 129.8, 130.0, 130.4, 132.8, 133.6, 134.3, 144.3, 147.3; IR ($CH_2Cl_2$) ν 3145, 2925, 1594, 1452, 1391, 1193, 1178, 1090, 1009, 969, 812, 666 $cm^{-1}$; HRMS (ESI) Calcd. for $C_{16}H_{15}ClN_3O_2S_2$ $(M+H)^+$: 380.0289, found: 380.0286.



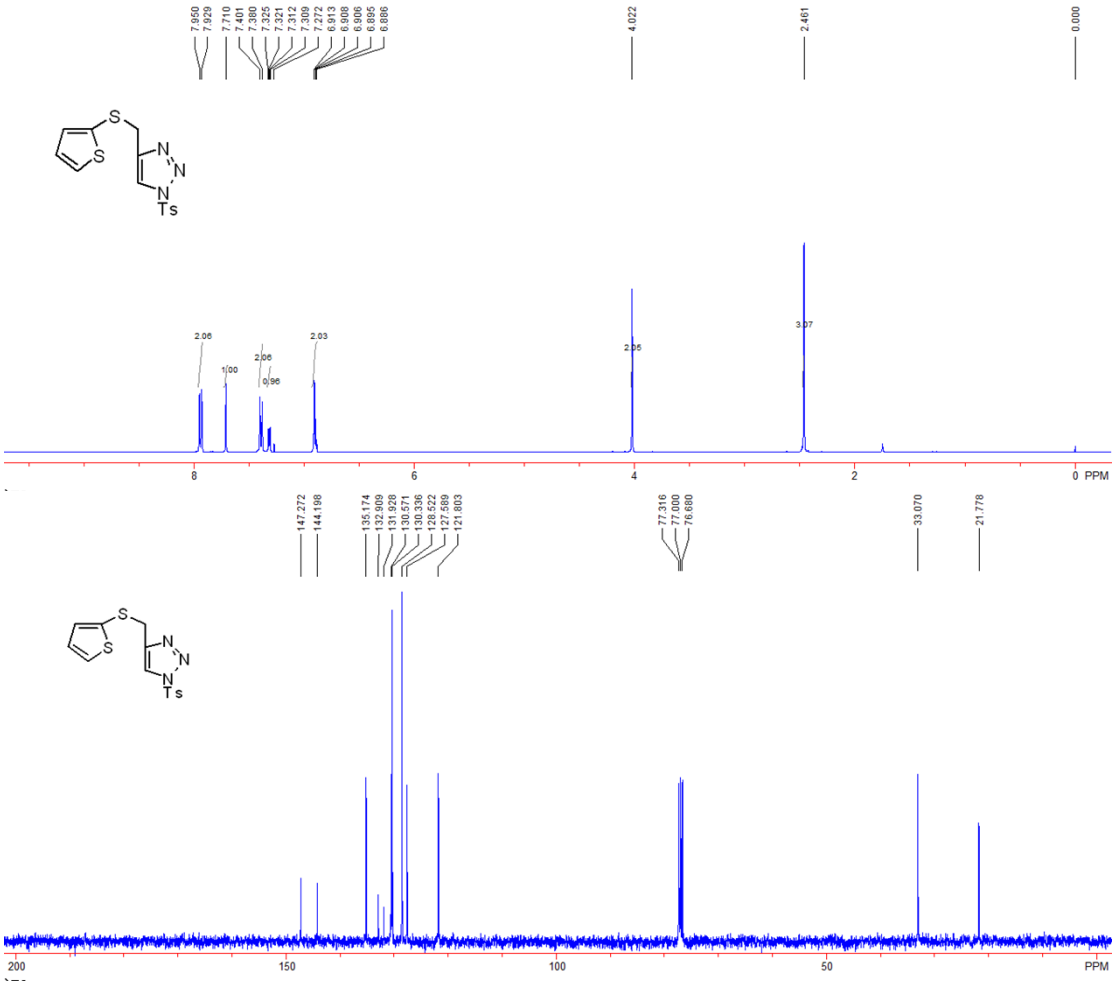



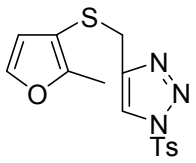

4-((2-bromophenylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1j**: a white solid; Mp: 139-141 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H), 4.23 (s, 2H), 7.06 (t, $J$ = 7.6 Hz, 1H), 7.16-7.24 (m, 2H), 7.37 (d, $J$ = 8.0 Hz, 2H), 7.54 (d, $J$ = 7.6 Hz, 1H), 7.93-7.95 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 27.7, 122.0, 124.4, 127.7, 128.0, 128.6, 129.6, 130.4, 132.8, 133.1, 135.7, 144.2, 147.4; IR ($CH_2Cl_2$) ν 3145, 2925, 1594, 1449, 1392, 1309, 1194, 1179, 1091, 1010, 971, 813, 747, 669 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{16}H_{15}BrN_3O_2S_2$ $(M+H)^+$: 423.9784, found: 423.9776.



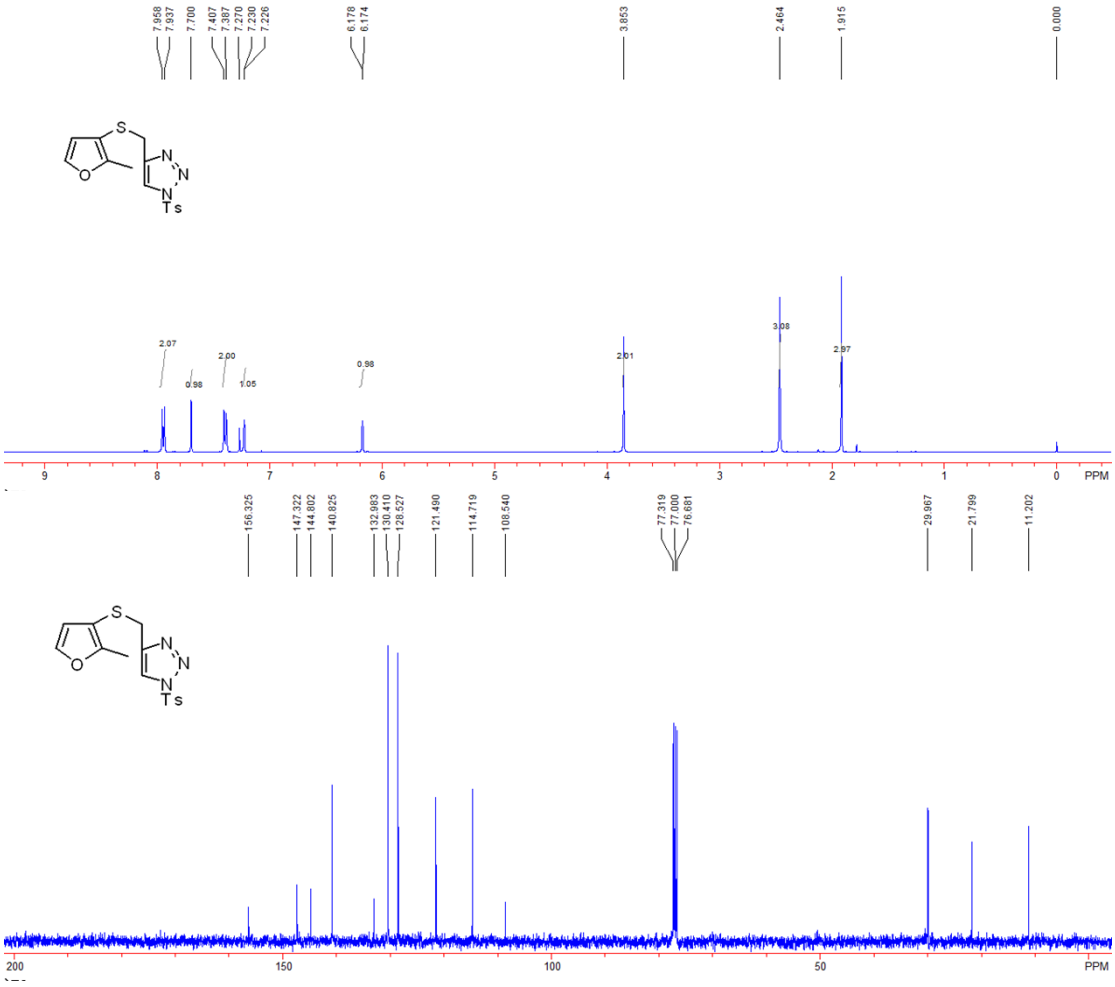


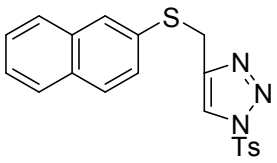
4-((thiophen-2-ylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1k**: a white solid; Mp: 103-104 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H), 4.02 (s, 2H), 6.88-6.92 (m, 2H), 7.32 (dd, $J_1$ = 1.6 Hz, $J_2$ = 4.8 Hz, 1H), 7.39 (d, $J$ = 8.4 Hz, 2H), 7.71 (s, 1H), 7.94 (d, $J$ = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 33.1, 121.8, 127.6, 128.5, 130.3, 130.6, 131.9, 132.9, 135.2, 144.2, 147.3; IR ($CH_2Cl_2$) ν 3144, 2926, 2128, 1594, 1552, 1390, 1308, 1193, 1178, 1090, 1009, 967, 847, 812, 701, 668 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{14}H_{14}N_3O_2S_2$ $(M+H)^+$: 352.0243, found: 352.0243.



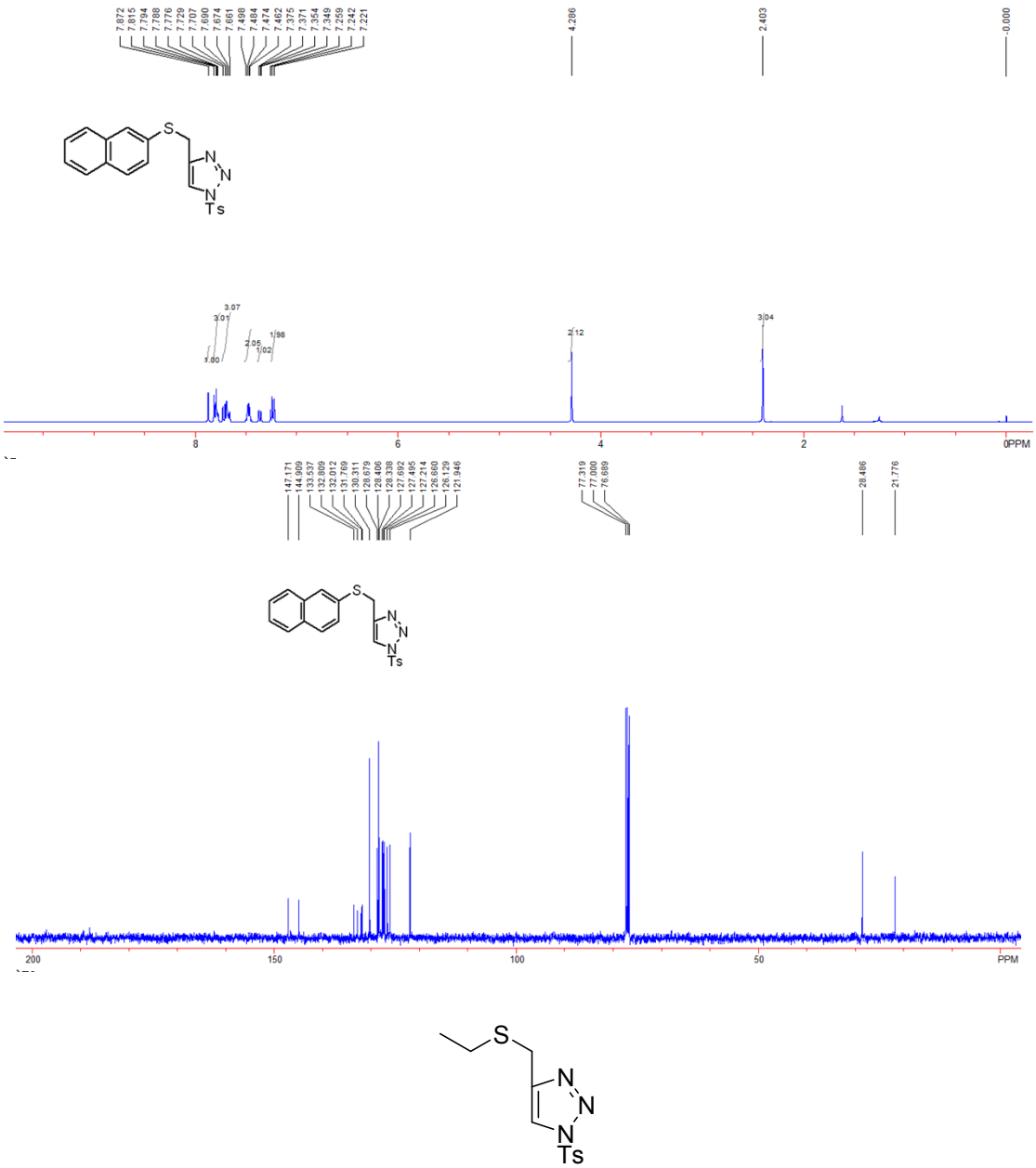


4-((2-methylfuran-3-ylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1l**: a white solid; Mp: 56-58 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.92 (s, 3H), 2.46 (s, 3H), 3.85 (s, 2H), 6.17 (d, $J$ = 1.6 Hz, 1H), 7.23 (d, $J$ = 1.6 Hz, 1H), 7.40 (d, $J$ = 8.0 Hz, 2H), 7.70 (s, 1H), 7.95 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 11.2, 21.8, 30.0, 108.5, 114.7, 121.5, 128.5, 130.4, 133.0, 140.8, 144.8, 147.3, 156.3; IR ($CH_2Cl_2$) ν 3146, 2921, 1594, 1514, 1391, 1308, 1225, 1194, 1179, 1089, 1009, 966, 813, 736, 670 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{15}H_{16}N_3O_3S_2$ $(M+H)^+$: 350.0628, found: 350.0640.





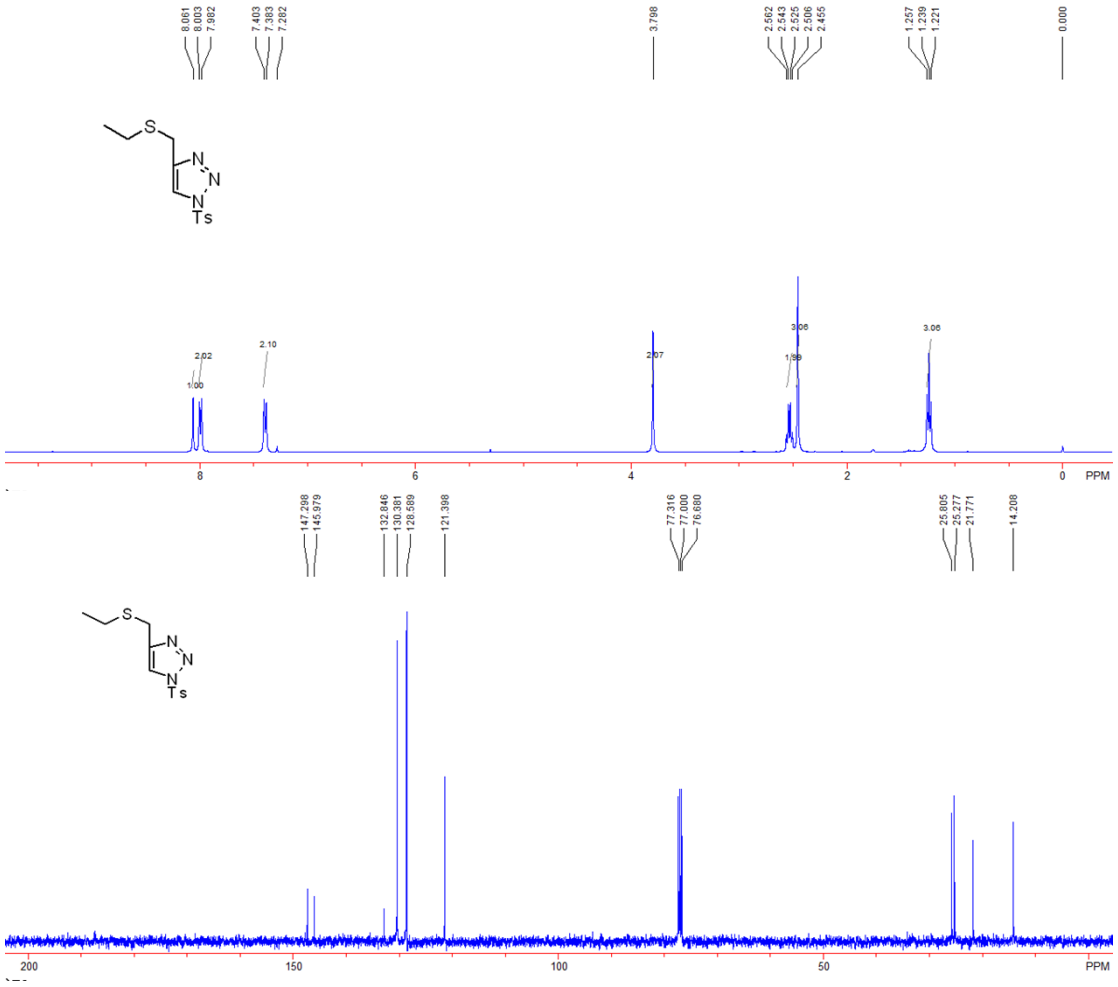
4-((naphthalen-2-ylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1m**: a white solid; Mp: 109-111 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40 (s, 3H), 4.29 (s, 2H), 7.23 (d, $J$ = 8.4 Hz, 2H), 7.36 (dd, $J_1$ = 1.6 Hz, $J_2$ = 8.4 Hz, 1H), 7.46-7.50 (m, 2H), 7.66-7.79 (m, 3H), 7.79-7.82 (m, 3H), 7.87 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 28.5, 121.9, 126.1, 126.7, 127.2, 127.5, 127.7, 128.3, 128.4, 128.7, 130.3, 131.8, 132.0, 132.8, 133.5, 144.9, 147.2; IR ($CH_2Cl_2$) ν 3145, 2925, 1593, 1392, 1308, 1194, 1179, 1091, 1010, 971, 812, 744, 669 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{20}H_{18}N_3O_2S_2$ $(M+H)^+$: 396.0835, found: 396.0835.

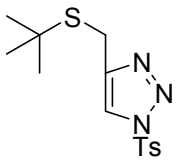




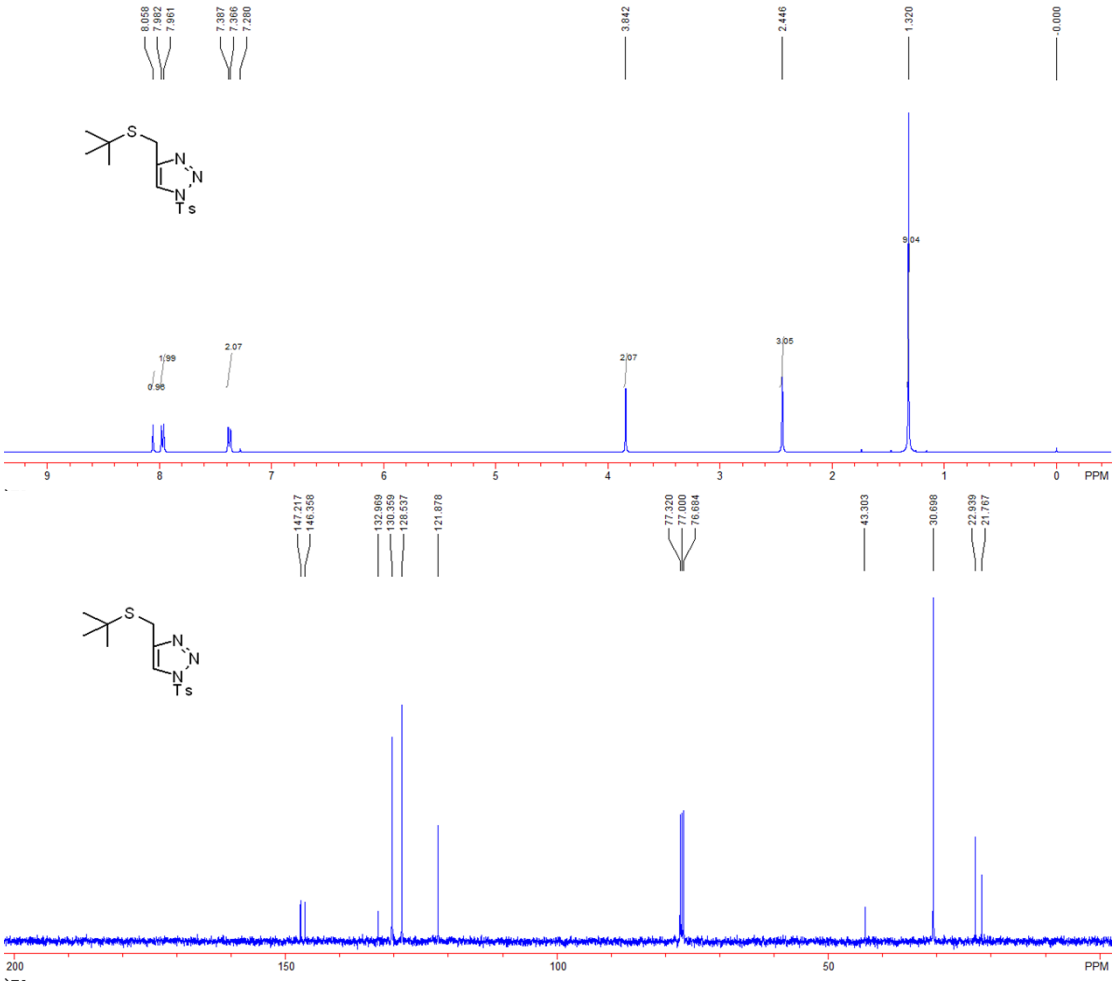


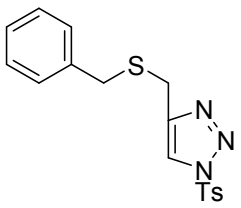
4-(ethylthiomethyl)-1-tosyl-1*H*-1,2,3-triazole **1n**: a white solid; Mp: 64-66 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, *J* = 7.2 Hz, 3H), 2.46 (s, 3H), 2.53 (q, *J* = 7.2 Hz, 2H), 3.80 (s, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 8.06 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.2, 21.8, 25.3, 25.8, 121.4, 128.6, 130.4, 132.8, 146.0, 147.3; IR ($CH_2Cl_2$) ν 3144, 2927, 2483, 1954, 1594, 1391, 1238, 1194, 1179, 1091, 1032, 1008, 968, 814, 702, 669 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{12}H_{16}N_3O_2S_2$ $(M+H)^+$: 298.0678, found: 298.0687.



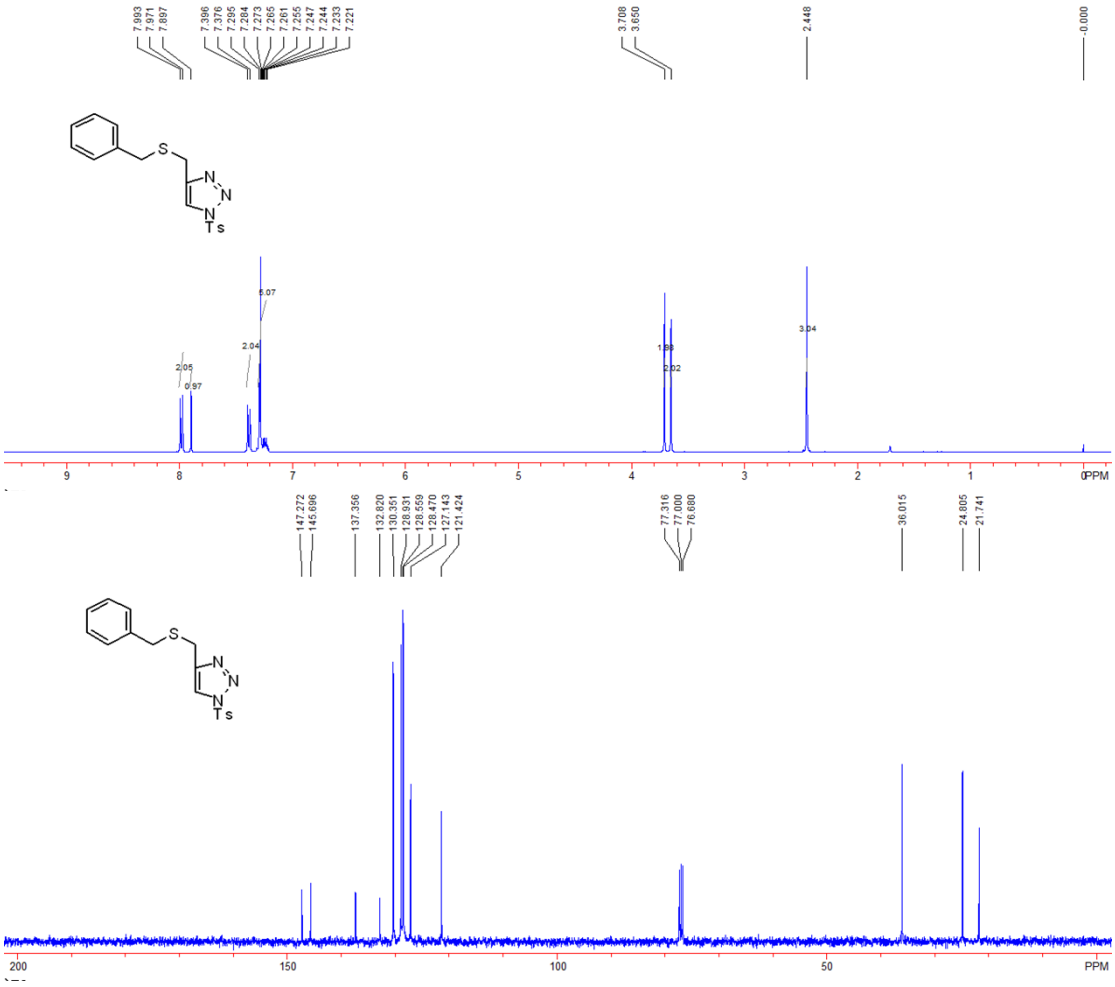


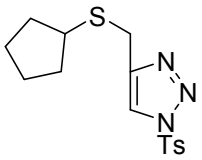
4-(tert-butylthiomethyl)-1-tosyl-1*H*-1,2,3-triazole **1o**: a white solid; Mp: 89-91 °C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.32 (s, 9H), 2.45 (s, 3H), 3.84 (s, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 8.06 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 22.9, 30.7, 43.3, 121.9, 128.5, 130.4, 133.0, 146.4, 147.2; IR ($CH_2Cl_2$) ν 3149, 2961, 1594, 1392, 1366, 1308, 1194, 1179, 1091, 1009, 969, 813, 668 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{14}H_{20}N_3O_2S_2$ $(M+H)^+$: 326.0991, found: 326.0987.



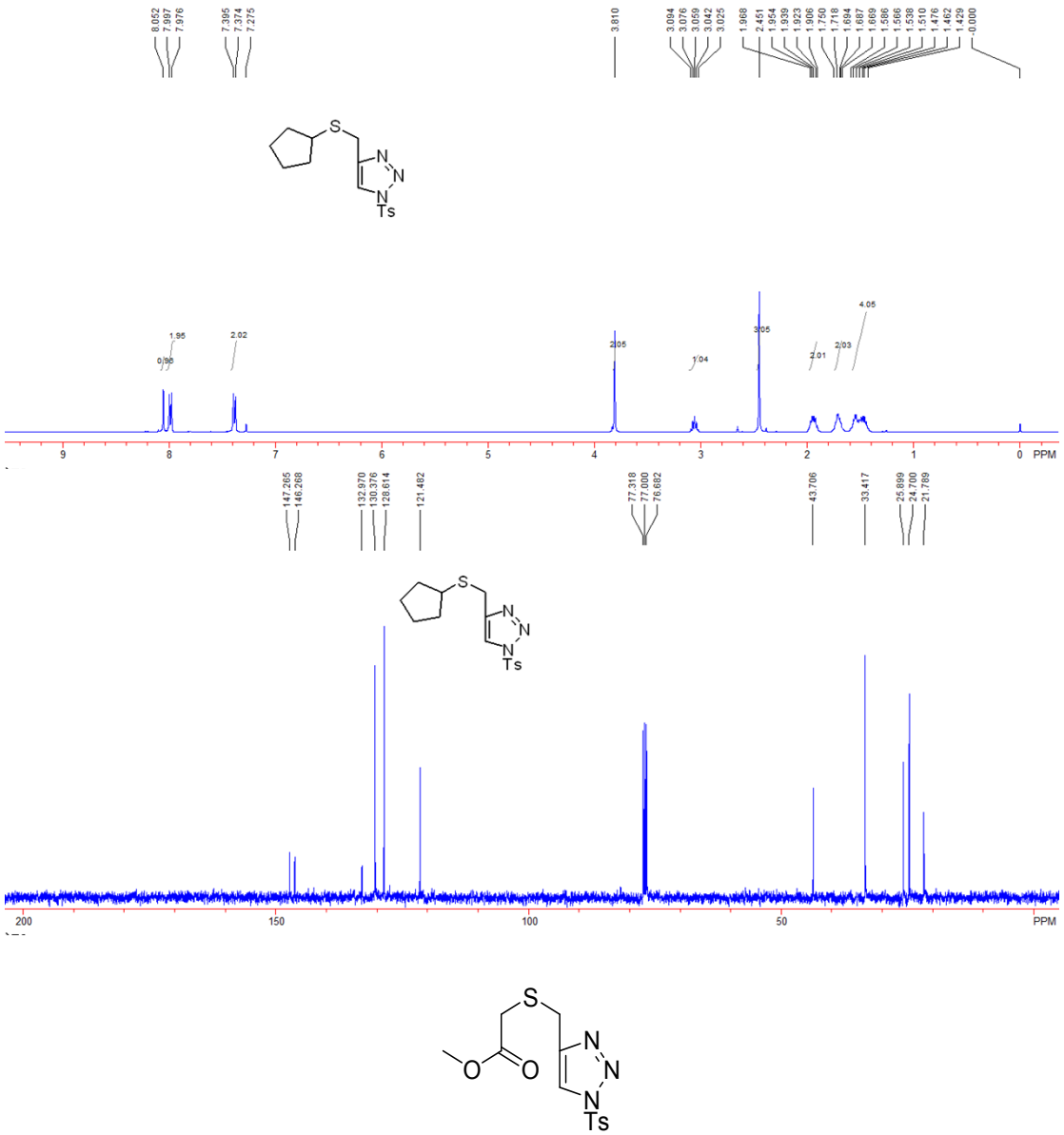



4-(benzylthiomethyl)-1-tosyl-1*H*-1,2,3-triazole **1p**: a white solid; Mp: 98-99 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H), 3.65 (s, 2H), 3.71 (s, 2H), 7.22-7.30 (m, 5H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.90 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.7, 24.8, 36.0, 121.4, 127.1, 128.5, 128.6, 128.9, 130.4, 132.8, 137.4, 145.7, 147.3; IR ($CH_2Cl_2$) ν 3144, 2921, 1594, 1494, 1390, 1193, 1178, 1090, 1009, 968, 813, 667 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{17}H_{18}N_3O_2S_2$ $(M+H)^+$: 360.0835, found: 360.0835.



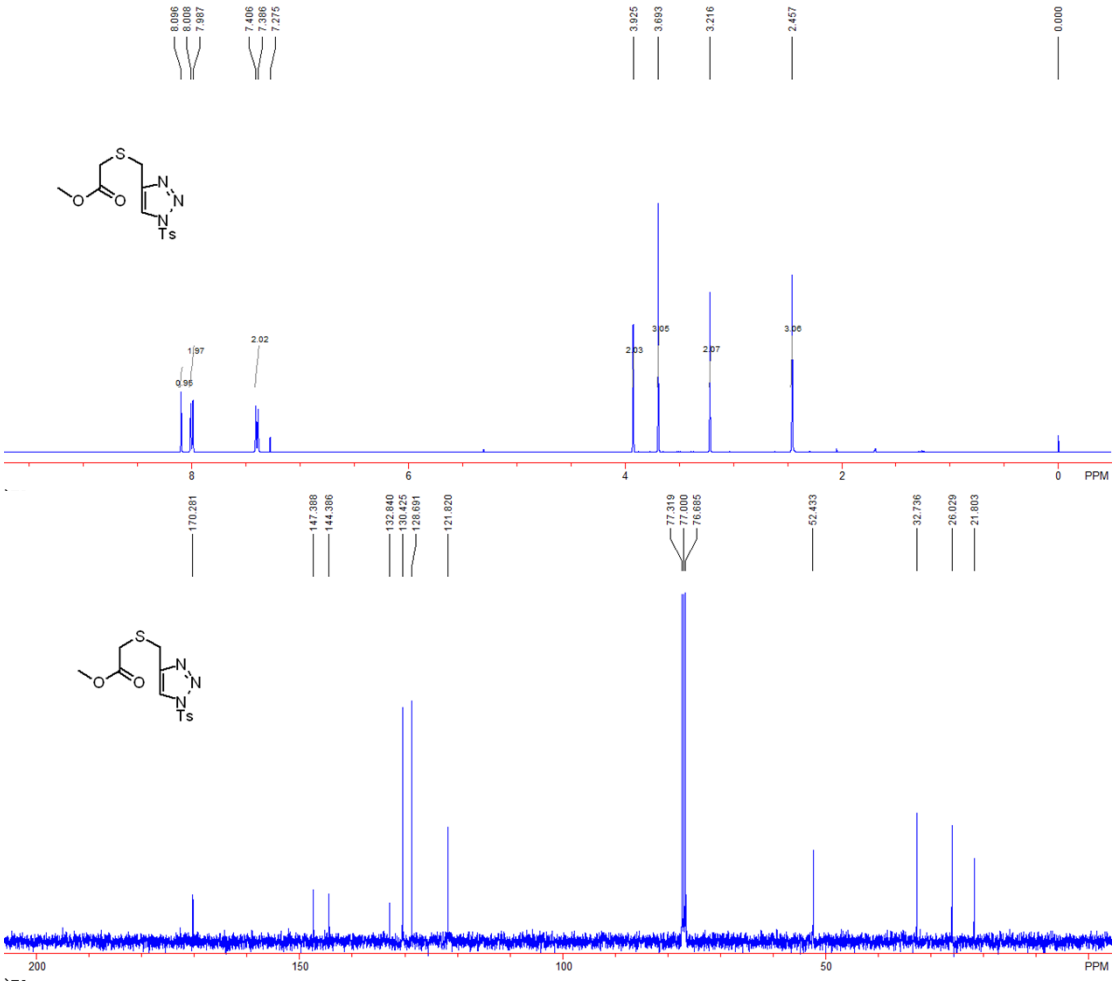


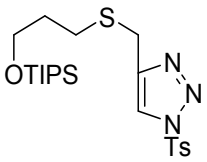
4-((cyclopentylthio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1q**: a white solid; Mp: 91-92 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.42-1.59 (m, 4H), 1.66-1.75 (m, 2H), 1.90-1.97 (m, 2H), 2.45 (s, 3H), 3.02-3.10 (m, 1H), 3.81 (s, 2H), 7.38 (d, $J$ = 8.4 Hz, 2H), 7.99 (d, $J$ = 8.4 Hz, 2H), 8.05 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 24.7, 25.9, 33.4, 43.7, 121.5, 128.6, 130.4, 133.0, 146.3, 147.3; IR ($CH_2Cl_2$) ν 3147, 2955, 2867, 1594, 1391, 1366, 1193, 1179, 1091, 1009, 968, 812, 668 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{15}H_{20}N_3O_2S_2$ $(M+H)^+$: 338.0991, found: 338.1005.



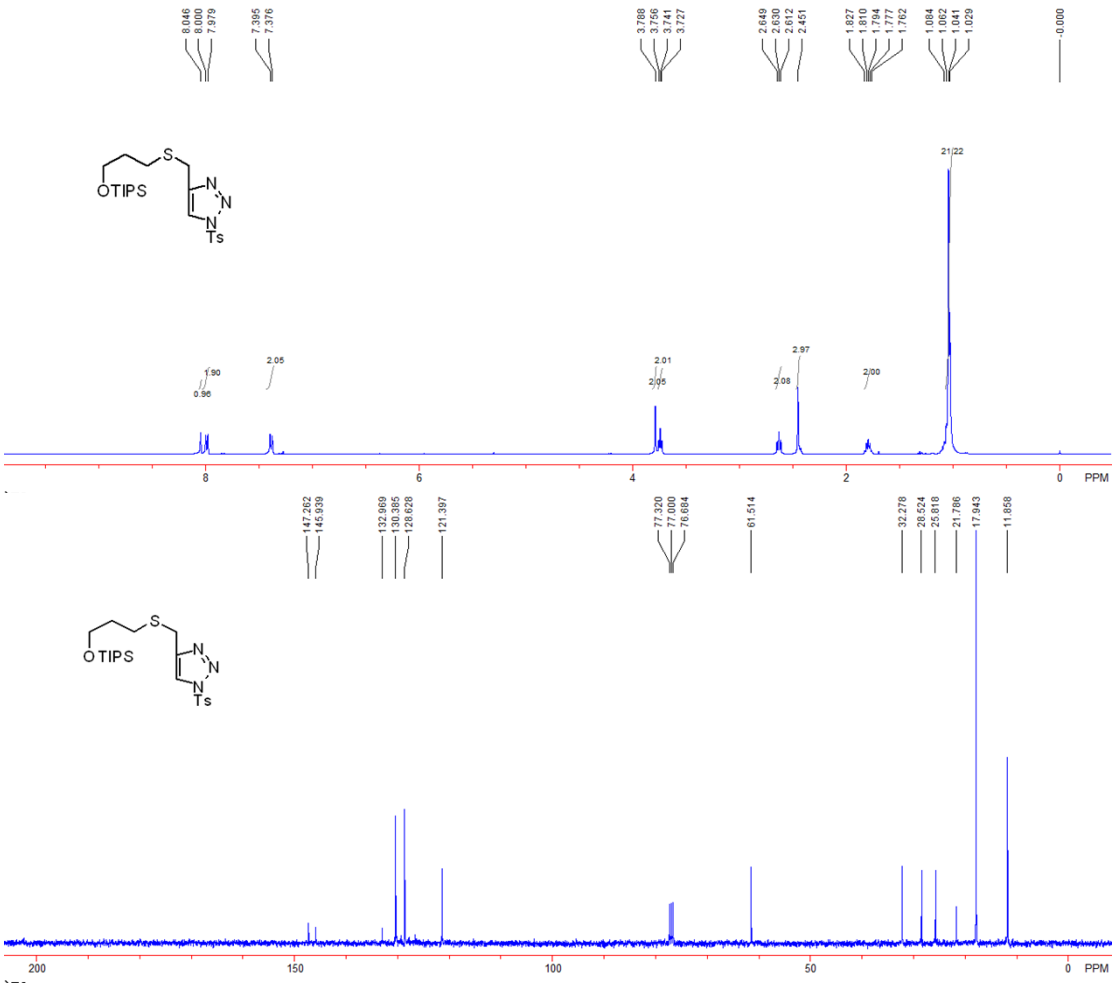


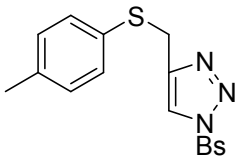
methyl 2-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methylthio)acetate **1r**: a white solid; Mp: 84-86 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H), 3.22 (s, 2H), 3.69 (s, 3H), 3.93 (s, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 2H), 8.10 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 26.0, 32.7, 52.4, 121.8, 128.7, 130.4, 132.8, 144.4, 147.4, 170.3; IR ($CH_2Cl_2$) ν 3147, 2953, 1734, 1594, 1436, 1391, 1267, 1194, 1179, 1091, 1010, 970, 918, 813, 667 cm$^{-1}$; HRMS (ESI) Canlcd. for $C_{13}H_{16}N_3O_4S_2$ $(M+H)^+$: 342.0577, found: 342.0591.



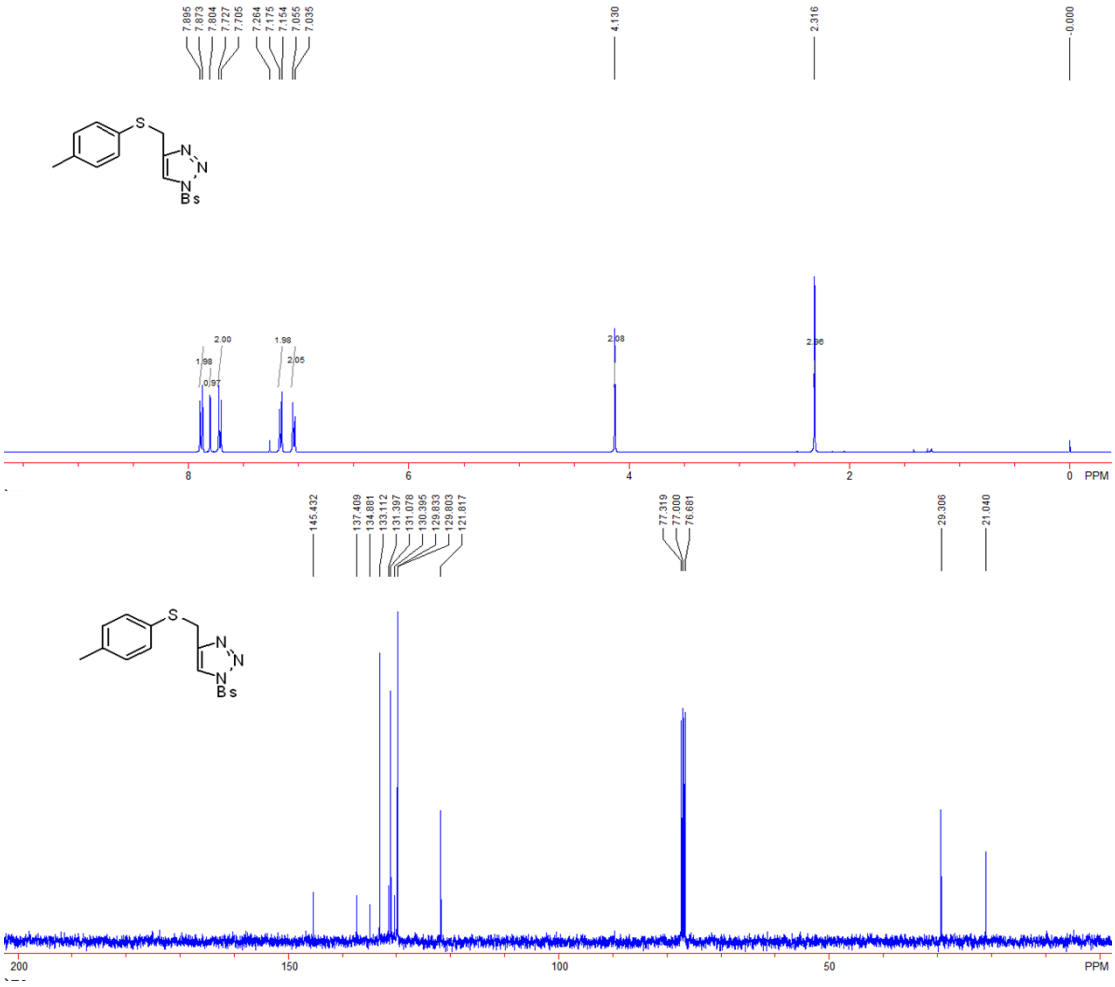



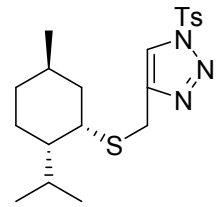

1-tosyl-4-((3-(triisopropylsilyloxy)propylthio)methyl)-1*H*-1,2,3-triazole **1s**: a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.02-1.09 (m, 21H), 1.76-1.83 (m, 2H), 2.45 (s, 3H), 2.63 (t, *J* = 7.6 Hz, 2H), 3.74 (t, *J* = 6.0 Hz, 2H), 3.79 (s, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 8.05 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 11.9, 17.9, 21.8, 25.8, 28.5, 32.3, 61.5, 121.4, 128.6, 130.4, 133.0, 145.9, 147.3; IR ($CH_2Cl_2$) ν 3120, 2924, 1702, 1586, 1388, 1186, 1179, 1090, 945, 813, 660 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{22}H_{38}N_3O_3S_2Si$ $(M+H)^+$: 484.2118, found: 484.2133.



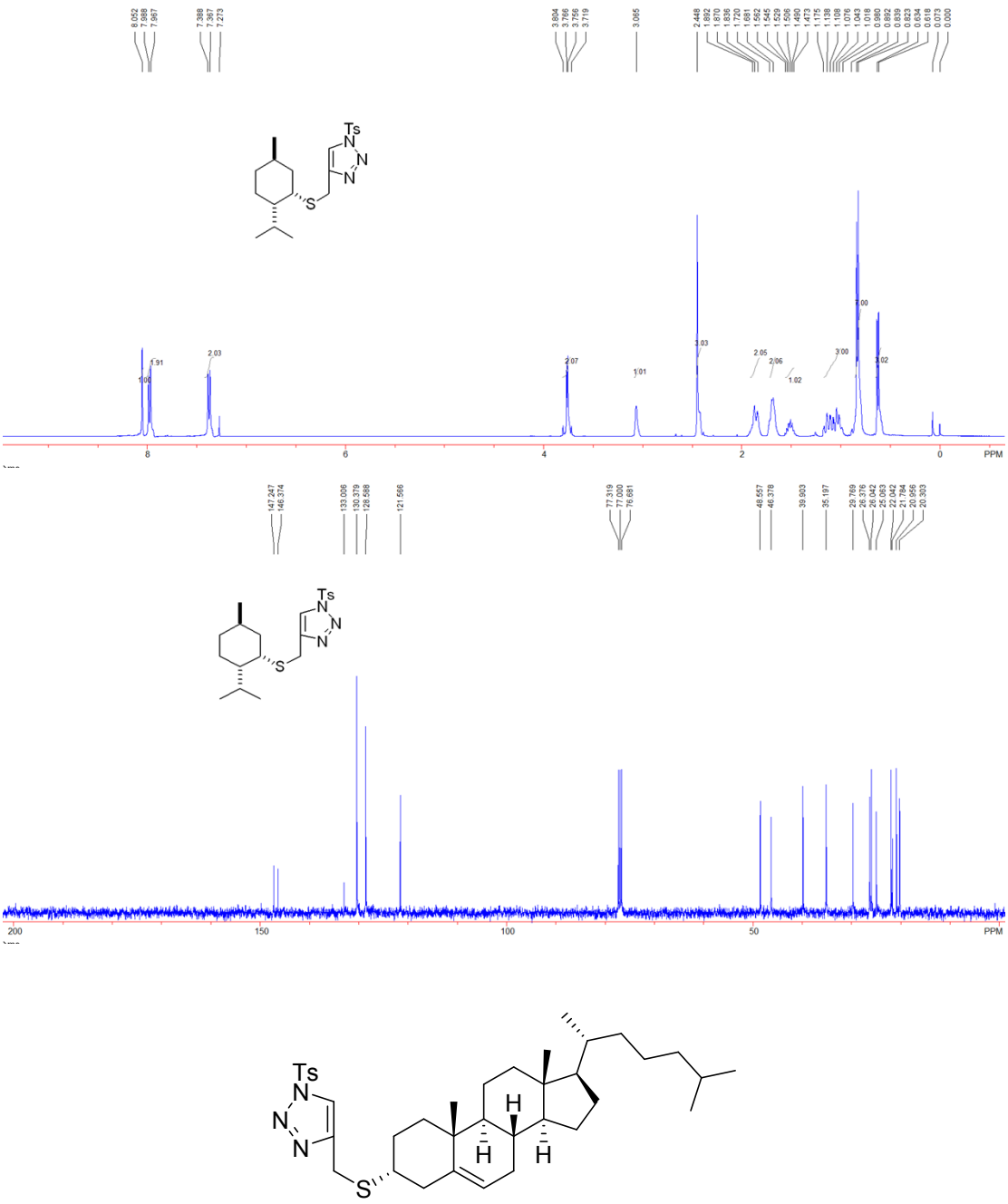




1-(4-bromophenylsulfonyl)-4-(p-tolylthiomethyl)-1*H*-1,2,3-triazole **1t**: a white solid; Mp: 147-148 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.32 (s, 3H), 4.13 (s, 2H), 7.05 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.0 Hz, 2H), 7.72 (d, $J$ = 8.8 Hz, 2H), 7.80 (s, 1H), 7.88 (d, $J$ = 8.8 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 29.3, 121.8, 129.80, 129.83, 130.4, 131.1, 131.4, 133.1, 134.9, 137.4, 145.4; IR ($CH_2Cl_2$) ν 3145, 3021, 2922, 1573, 1492, 1396, 1366, 1191, 1178, 1069, 1007, 966, 808, 846, 670 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{16}H_{15}BrN_3O_2S_2$ $(M+H)^+$: 423.9784, found: 423.9783.



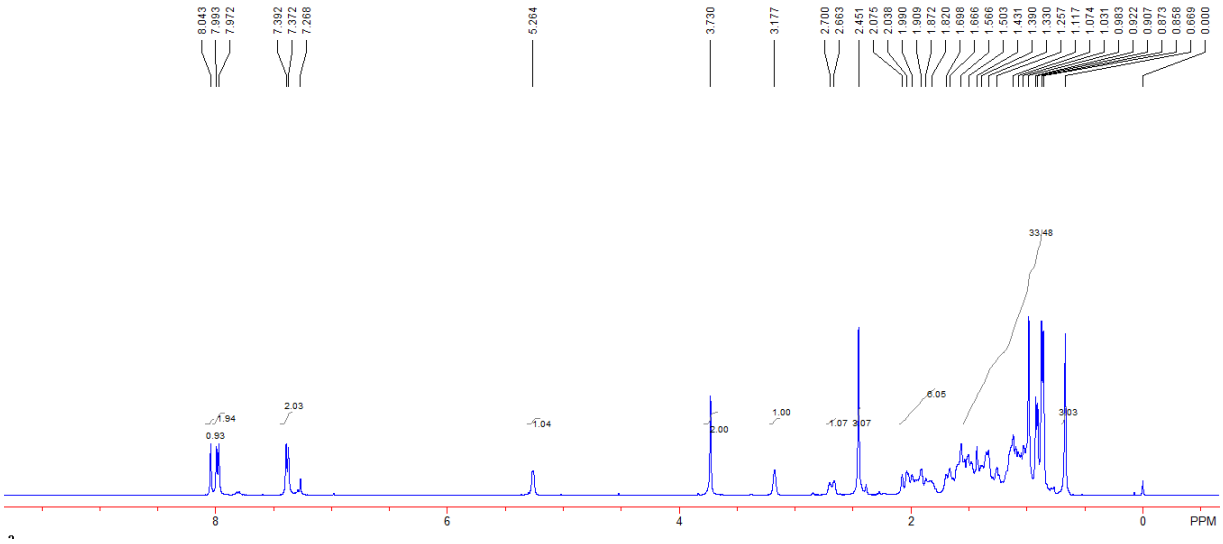


4-((((1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)thio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1u**: a white solid; Mp: 119-120 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.63 (d, *J* = 6.4 Hz, 3H), 0.82-0.90 (m, 7H), 0.98-1.18 (m, 3H), 1.47-1.57 (m, 1H), 1.68-1.72 (m, 2H), 1.83-1.90 (m, 2H), 2.45 (s, 3H), 3.07 (s, 1H), 3.74 (d, *J* = 14.8 Hz, 1H), 3.79 (d, *J* = 14.8 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.98 (d, *J* = 8.4 Hz, 2H), 8.05 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.3, 21.0, 21.8, 22.0, 25.1, 26.0, 26.4, 29.8, 35.2, 39.9, 46.4, 48.6, 121.6, 128.6, 130.4, 133.0, 146.4, 147.2; IR ($CH_2Cl_2$) ν 2947, 2917, 2868, 1595, 1394, 1276, 1261, 1195, 1092, 1010, 970, 750, 671 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{20}H_{30}N_3O_2S_2$ $(M+H)^+$: 408.1774, found: 408.1777.





4-((((3*R*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*S*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)thio)methyl)-1-tosyl-1*H*-1,2,3-triazole **1v**: a white solid; Mp: 125-126 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.67 (s, 3H), 0.85-1.70 (m, 33H), 1.82-2.08 (m, 6H), 2.45 (s, 3H), 2.68 (d, *J* = 14.8 Hz, 1H), 3.18 (s, 1H), 3.73 (s, 2H), 5.26 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 8.0 Hz, 2H), 8.04 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 11.8, 18.7, 19.2, 20.7, 21.8, 22.5, 22.8, 23.8, 24.2, 24.9, 26.3, 28.0, 28.2, 31.66, 31.69, 33.8, 35.8, 36.1, 37.1, 37.2, 39.5, 39.7, 42.2, 43.7, 49.8, 56.1, 56.6, 121.6, 122.4, 128.6, 130.4, 133.0, 138.7, 146.3, 147.2; IR ($CH_2Cl_2$) ν 3131, 2930, 2868, 1595, 1460, 1388, 1303, 1193, 1180, 1094, 1013, 816, 705, 686 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{37}H_{56}N_3O_2S_2$ $(M+H)^+$: 638.3808, found: 638.3812.


8.043
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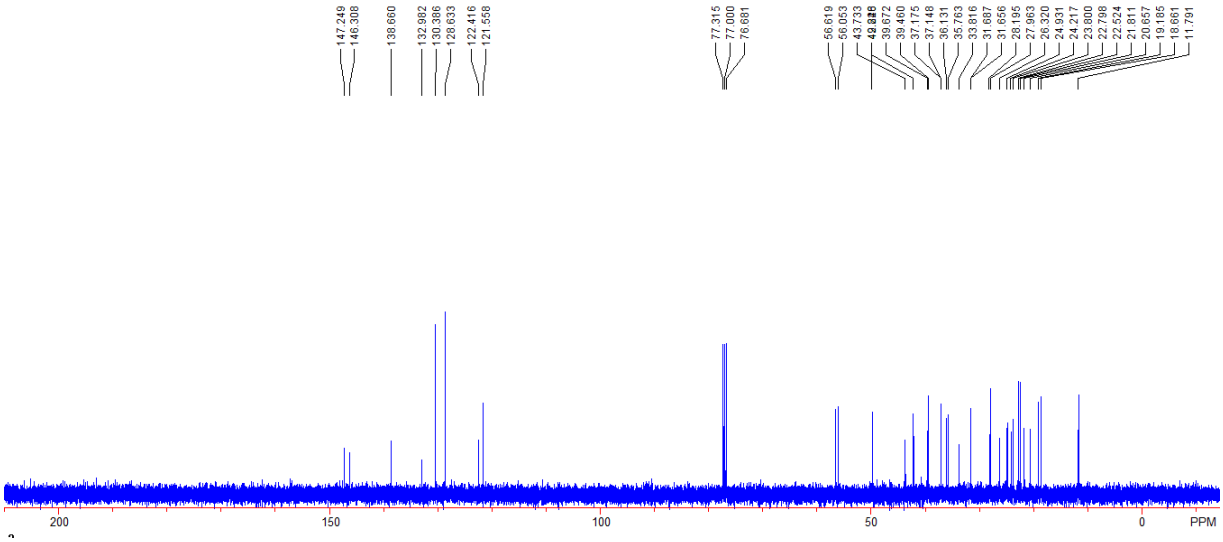
7.972
7.392
7.372
7.268
5.264
3.730
3.177
2.700
2.663
2.451
2.075
2.038
1.990
1.909
1.872
1.820
1.698
1.666
1.566
1.503
1.431
1.390
1.330
1.257
1.117
1.074
1.031
0.983
0.922
0.907
0.873
0.858
0.669
0.000
33.48
6.05
3.03
2.03
1.94
0.93
1.04
2.00
1.00
1.07
3.07
8
6
4
2
0
PPM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130.386
128.633
122.416
121.558
77.315
77.000
76.681
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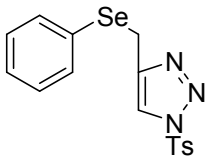
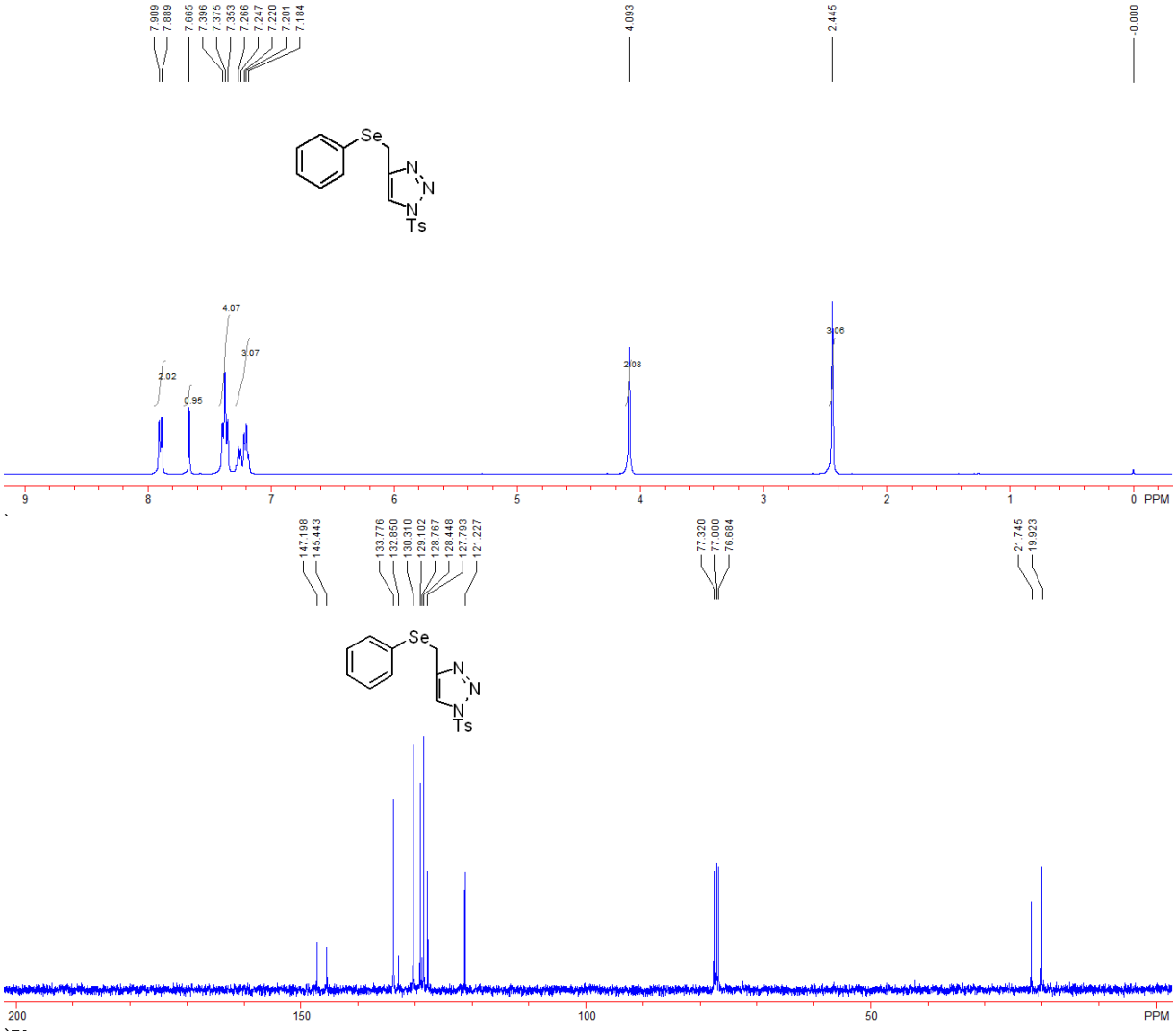
43.733
39.672
39.460
37.175
37.148
36.131
35.763
33.816
31.687
31.656
28.195
27.963
26.320
24.931
24.217
23.800
22.798
22.524
21.811
20.657
19.185
18.861
11.791
200
150
100
50
0
PPM

**Selenium-tethered triazole 1w:**

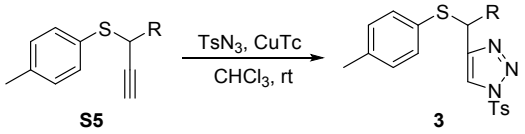
When selenium-tethered triazole (**1w**) was employed as substrate, there is no obvious product could be separated, namely complex reaction mixtures were formed.




4-((phenylselanyl)methyl)-1-tosyl-1*H*-1,2,3-triazole **1w**: a white solid; Mp: 137-138 °C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H), 4.09 (s, 2H), 7.18-7.27 (m, 3H), 7.35-7.40 (m, 4H), 7.67 (s, 1H), 7.90 (d, *J* = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.9, 21.7, 121.2, 127.8, 128.4, 128.8, 129.1, 130.3, 132.9, 133.8, 135.4, 137.2; IR ($CH_2Cl_2$) ν 3149, 3055, 2989, 1594, 1478, 1391, 1307, 1194, 1178, 1090, 1008, 967, 812, 733, 668 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{16}H_{16}N_3O_2SSe$ $(M+H)^+$: 394.0123, found: 394.0125.



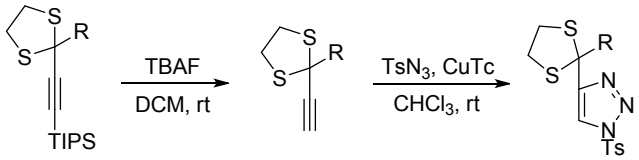
**General procedure for the synthesis of compounds 3a-3c:**




**S5** **3**

Compounds **3** were synthesized according to the similar procedure as that of **1** except using **S5**[1] instead of **S4**.

**General procedure for the synthesis of compounds 3d-3f:**

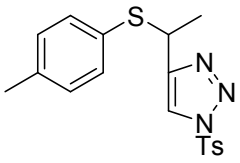



**S6** **S7** **3**

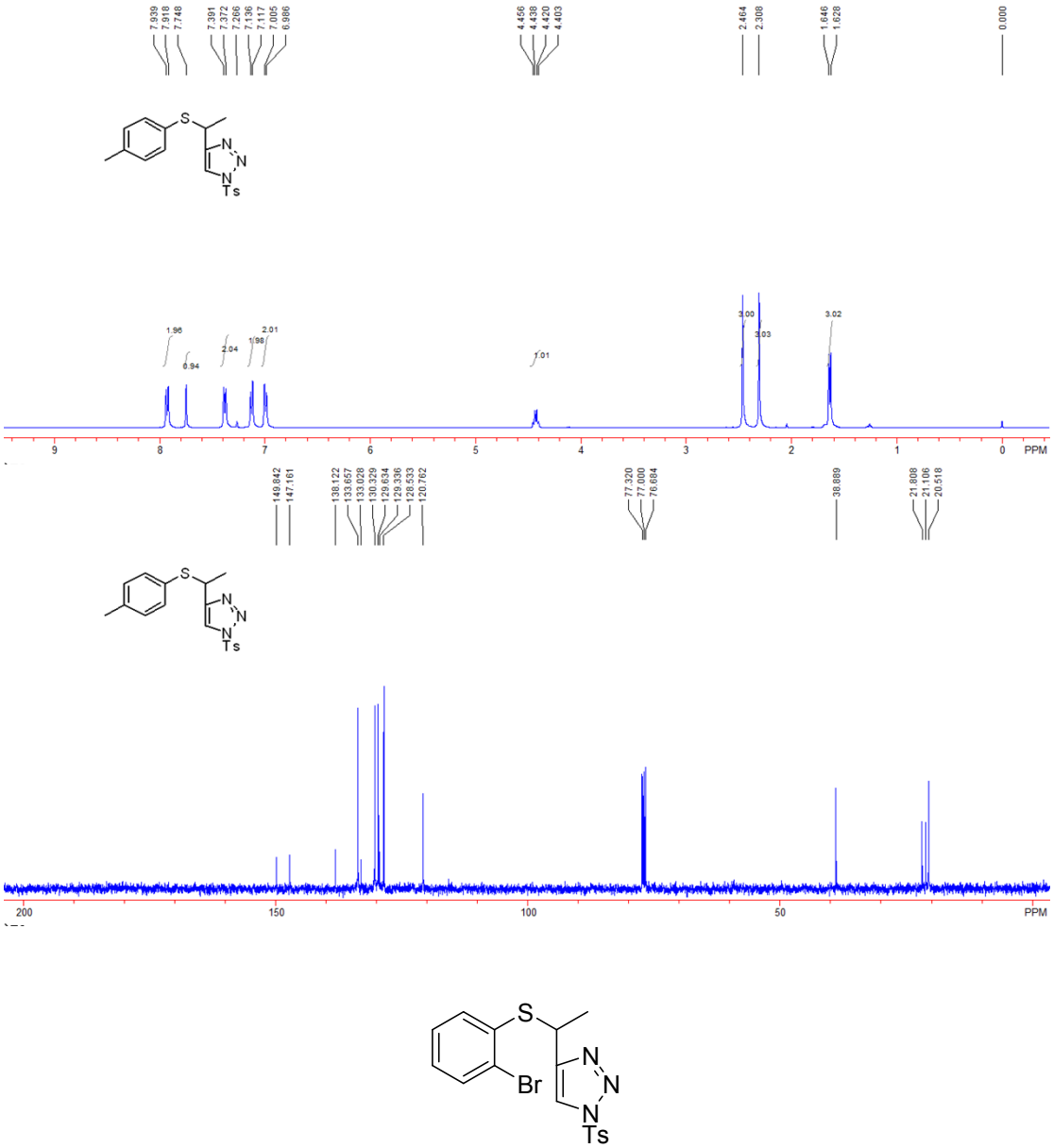
Compound **S6**[2] (5.0 mmol) was dissolved in DCM and TBAF (1.0 M in DCM, 1.0 eq) was added. After completion of the reaction as indicated by TLC, the DCM was removed under vacuum. The resulting crude product **S7** was used in the next step without further purification.

Compounds **3** were synthesized according to the similar procedure as that of **1** except using **S7** instead of **S4**.

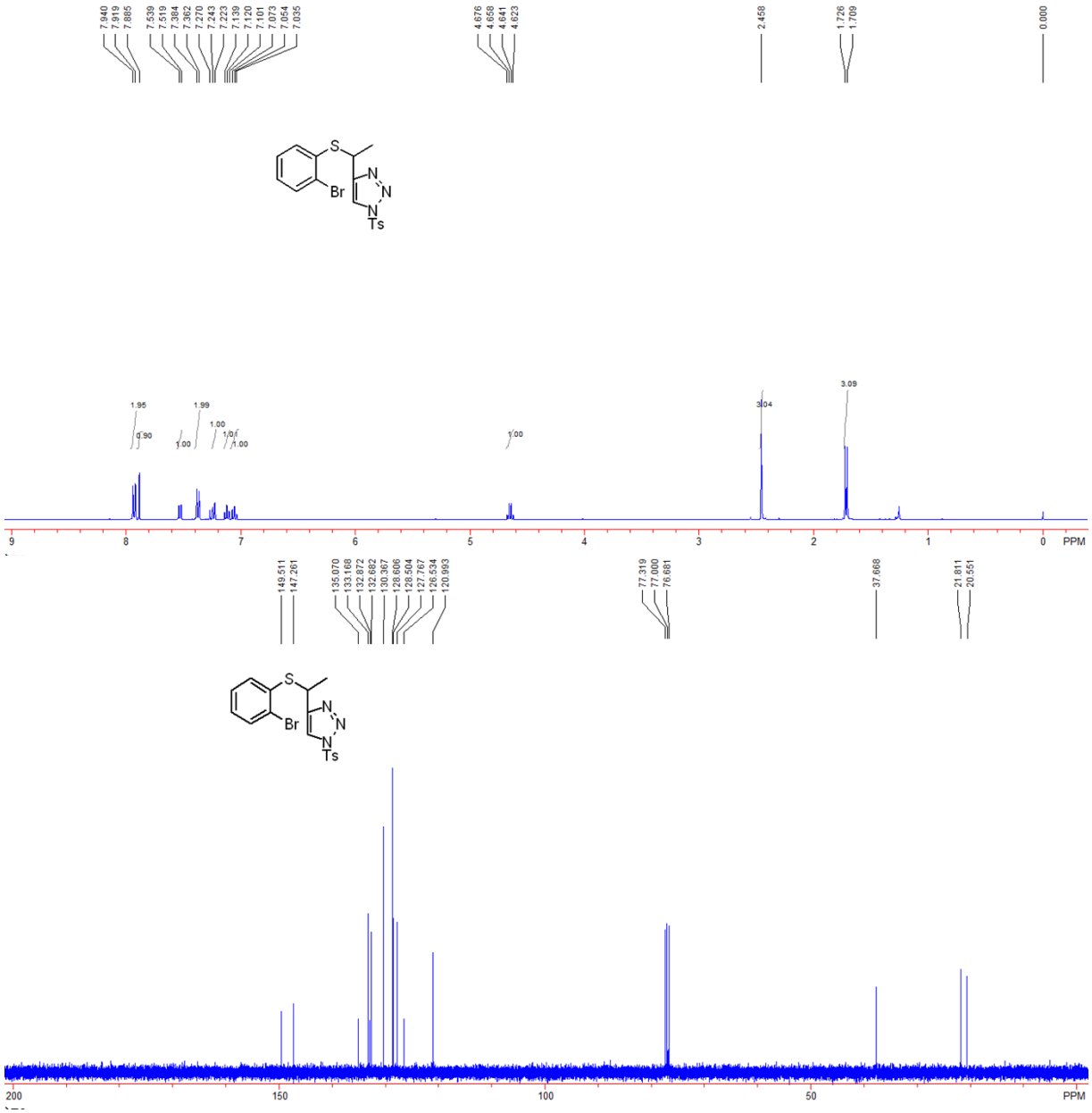
**Spectroscopic Data of Substrates 3**

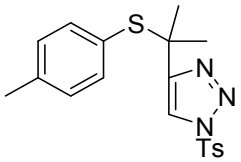



4-(1-(*p*-tolylthio)ethyl)-1-tosyl-1*H*-1,2,3-triazole **3a**: a white solid; Mp: 90-92 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.64 (d, *J* = 7.2 Hz, 3H), 2.31 (s, 3H), 2.46 (s, 3H), 4.43 (q, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.75 (s, 1H), 7.93 (d, *J* = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.5, 21.1, 21.8, 38.9, 120.8, 128.5, 129.3, 129.6, 130.3, 133.0, 133.7, 138.1, 147.2, 149.8; IR ($CH_2Cl_2$) ν 3146, 2926, 1595, 1447, 1265, 1197, 1179, 1090, 1007, 983, 813, 702, 670 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{18}H_{20}N_3O_2S_2$ $(M+H)^+$: 374.0991, found: 374.1006.

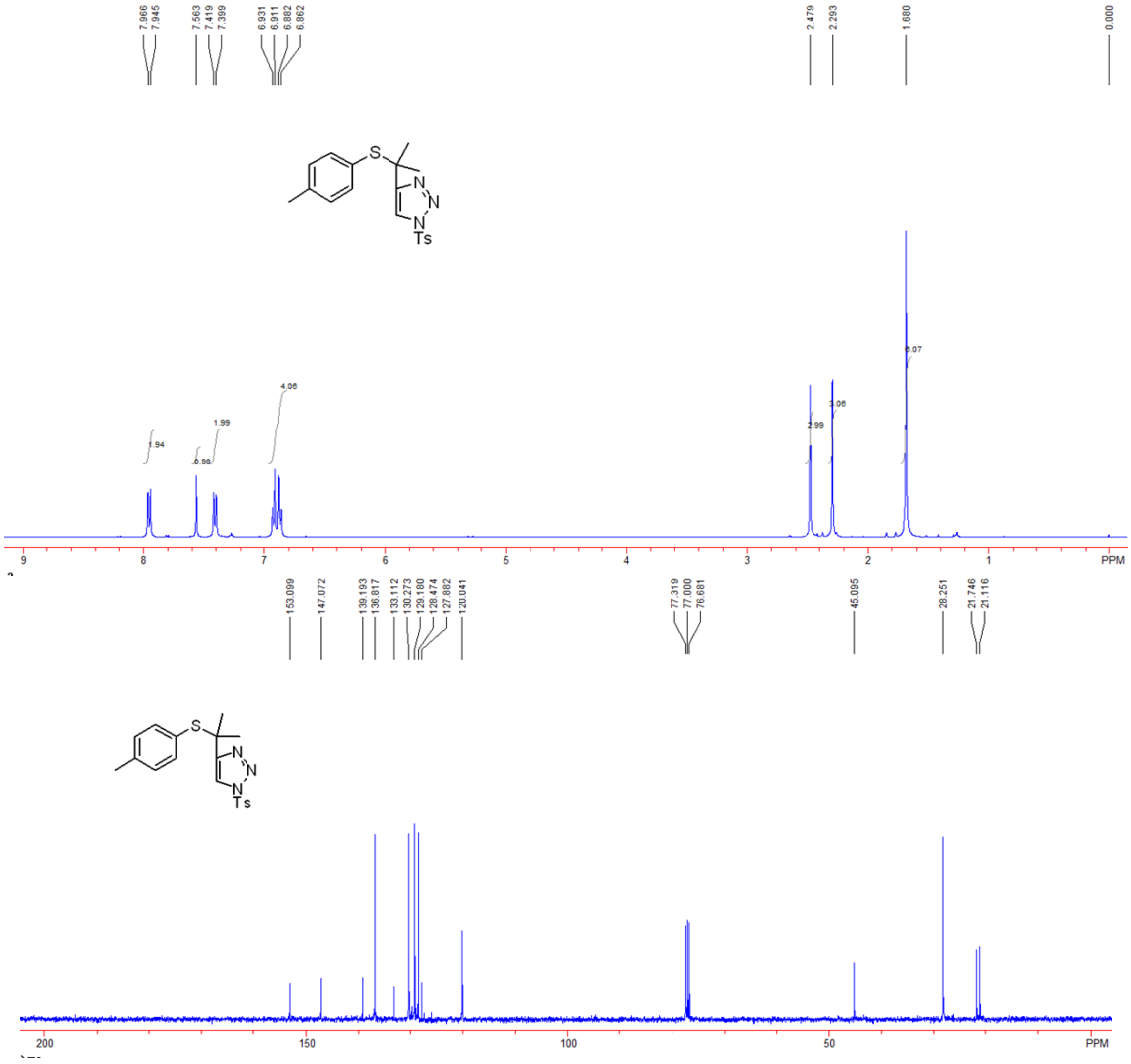


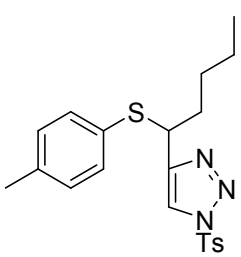
4-(1-((2-bromophenyl)thio)ethyl)-1-tosyl-1*H*-1,2,3-triazole **3b**: a white solid; Mp: 99-101 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.72 (d, *J* = 6.8 Hz, 3H), 2.46 (s, 3H), 4.65 (q, *J* = 6.8 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 1H), 7.12 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.89 (s, 1H), 7.93 (d, *J* = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.6, 21.8, 37.7, 121.0, 126.5, 127.8, 128.5, 128.6, 130.4, 132.7, 132.9, 133.2, 135.1, 147.3, 149.5; IR ($CH_2Cl_2$) ν 3056, 2926, 1753, 1595, 1448, 1265, 1195, 1180, 1091, 1007, 981, 813, 702, 671 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{17}H_{17}BrN_3O_2S_2$ $(M+H)^+$: 437.9940, found: 437.9939.



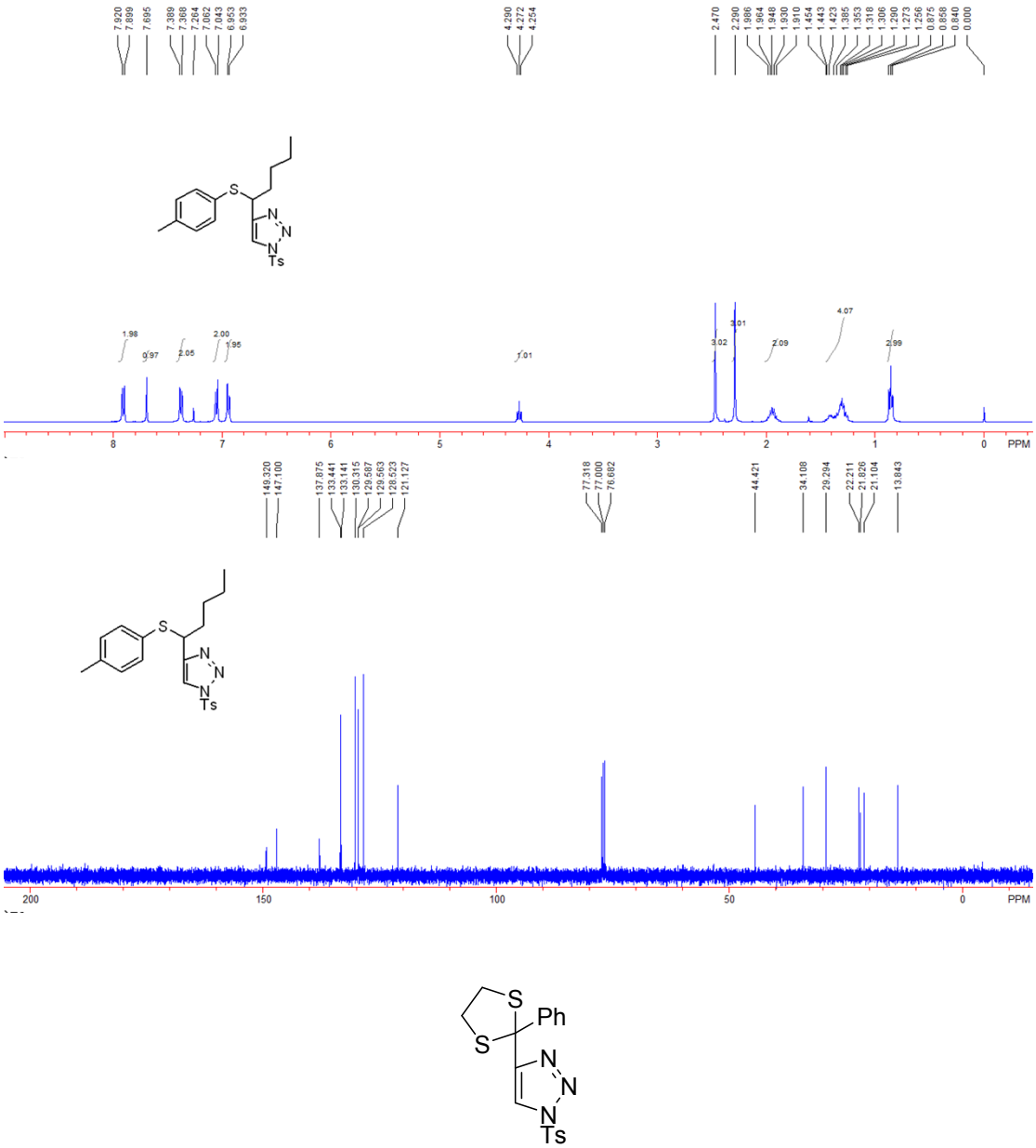


4-(2-(*p*-tolylthio)propan-2-yl)-1-tosyl-1*H*-1,2,3-triazole **3c**: a white solid; Mp: 89-90 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.68 (s, 6H), 2.29 (s, 3H), 2.48 (s, 3H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.56 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.1, 21.7, 28.3, 45.1, 120.0, 127.9, 128.5, 129.2, 130.3, 133.1, 136.8, 139.2, 147.1, 153.1; HRMS (ESI) Calcd. for $C_{19}H_{22}N_3O_2S_2$ $(M+H)^+$: 388.1148, found: 388.1150.



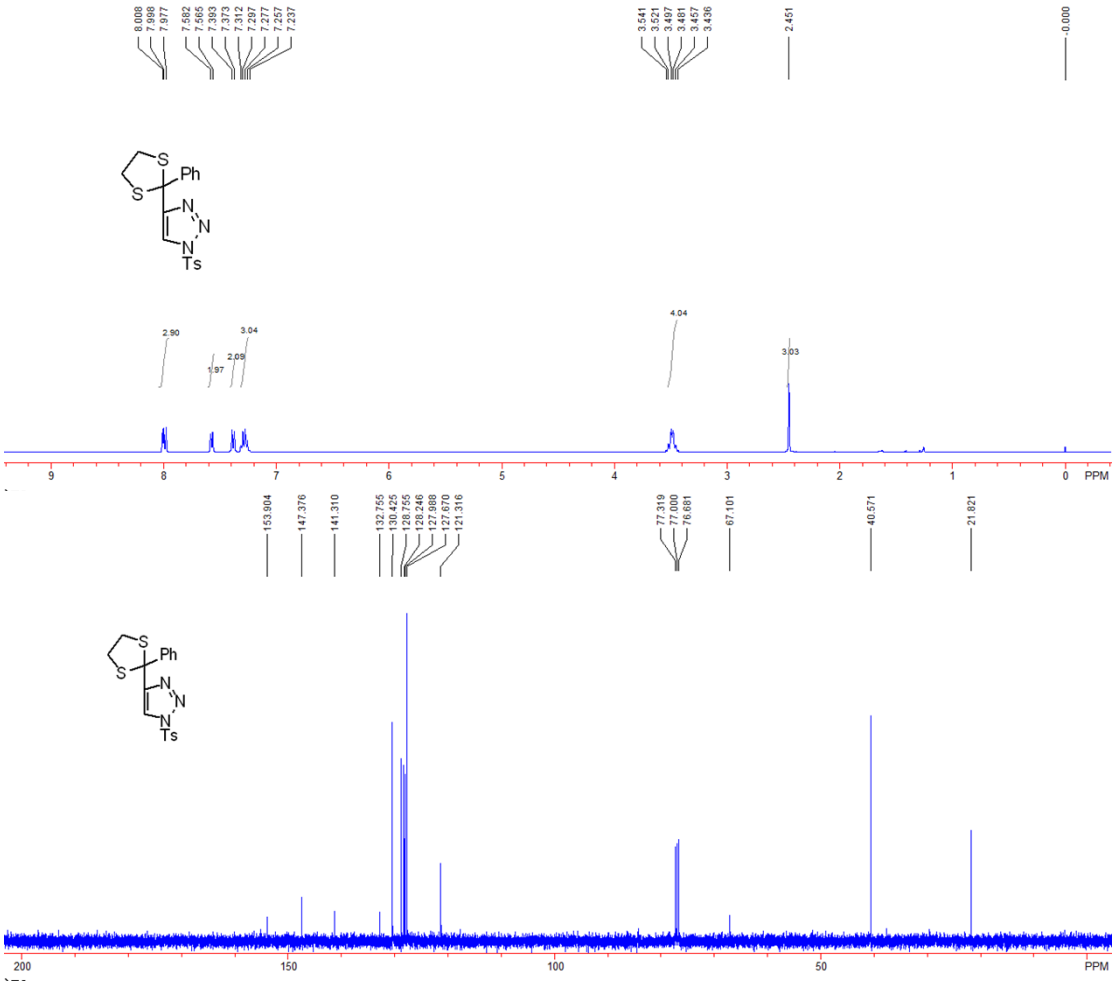



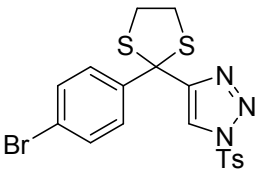
4-(1-(*p*-tolylthio)pentyl)-1-tosyl-1*H*-1,2,3-triazole **3d**: a white oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.25-1.46 (m, 4H), 1.91-1.99 (m, 2H), 2.29 (s, 3H), 2.47 (s, 3H), 4.27 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.70 (s, 1H), 7.91 (d, *J* = 8.4 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 21.1, 21.8, 22.2, 29.3, 34.1, 44.4, 121.1, 128.5, 129.56, 129.59, 130.3, 133.1, 133.4, 137.9, 147.1, 149.3; HRMS (ESI) Calcd. for $C_{21}H_{26}N_3O_2S_2$ $(M+H)^+$: 416.1461, found: 416.1462.



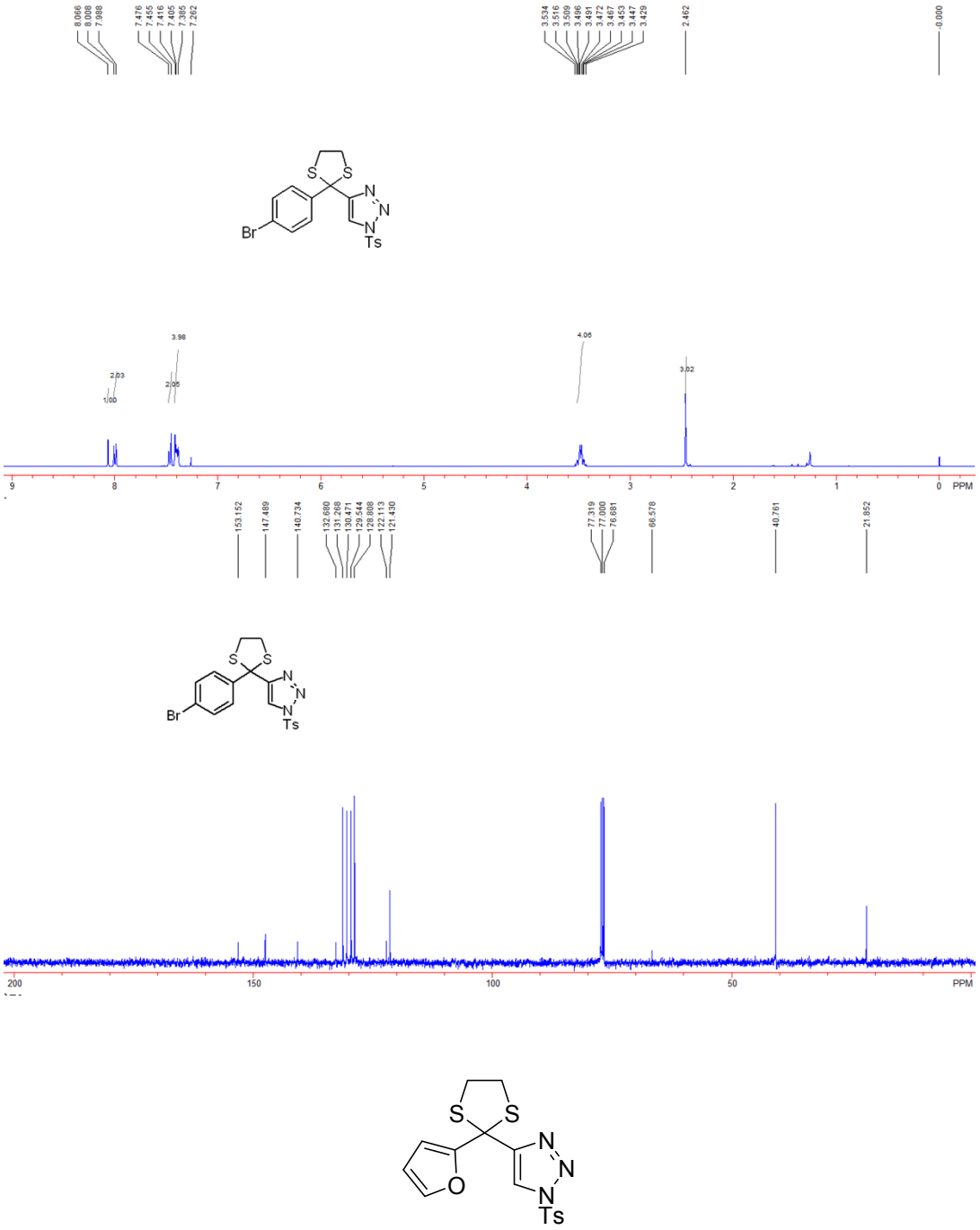


4-(2-phenyl-1,3-dithiolan-2-yl)-1-tosyl-1*H*-1,2,3-triazole **3e**: a brown solid; Mp: 169-171 °C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.45 (s, 3H), 3.43-3.55 (m, 4H), 7.23-7.32 (m, 3H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 6.8 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 8.01 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 40.6, 67.1, 121.3, 127.7, 128.0, 128.2, 128.8, 130.4, 132.8, 141.3, 147.4, 153.9; IR ($CH_2Cl_2$) ν 3159, 2922, 2853, 1592, 1488, 1389, 1210, 1195, 1173, 1089, 1009, 975, 811, 699, 669 $cm^{-1}$; HRMS (ESI) Calcd. for $C_{18}H_{18}N_3O_2S_3$ $(M+H)^+$: 404.0556, found: 404.0569.

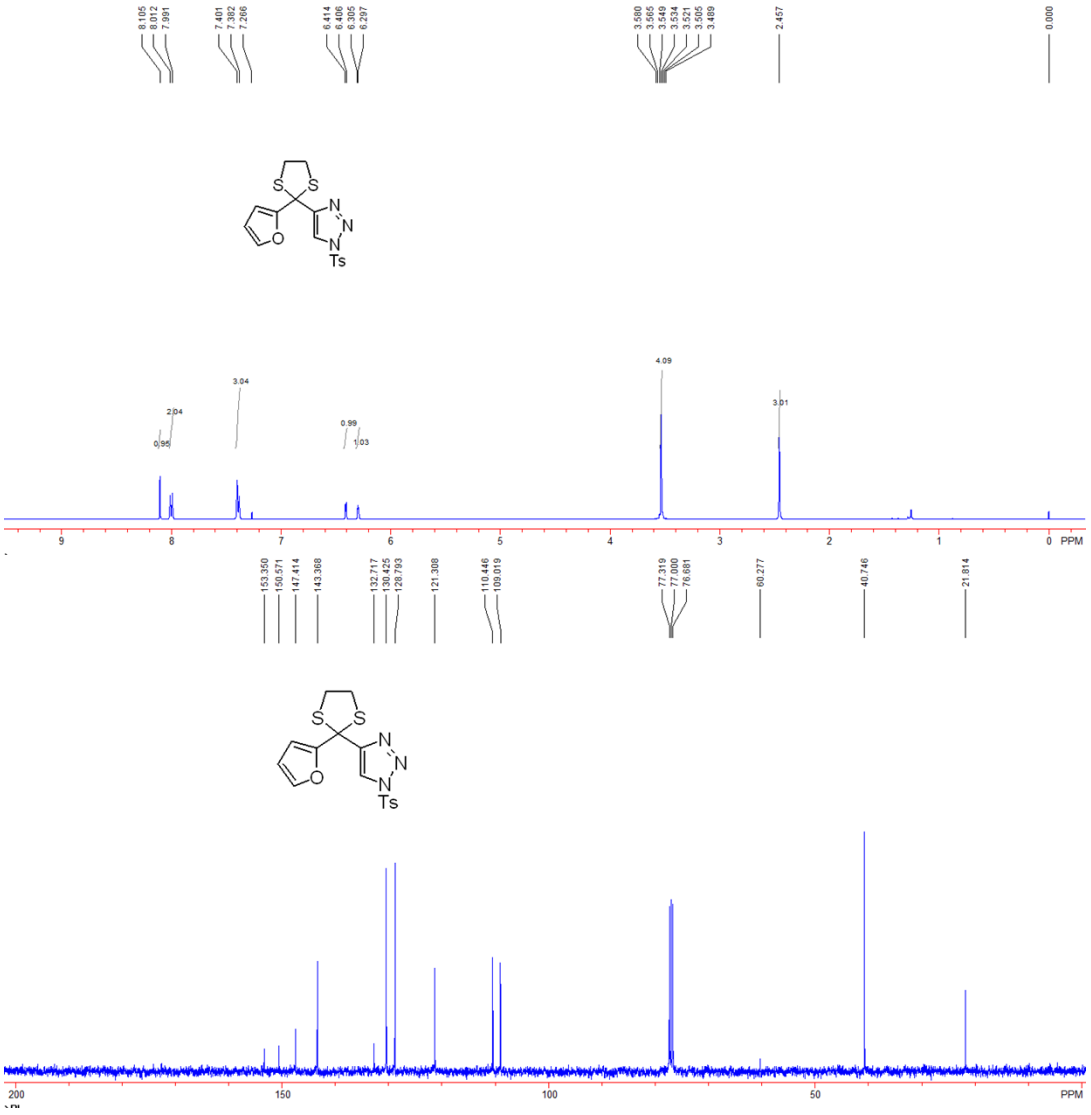




4-(2-(4-bromophenyl)-1,3-dithiolan-2-yl)-1-tosyl-1*H*-1,2,3-triazole **3f**: a white solid; Mp: 156-157 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H), 3.42-3.53 (m, 4H), 7.38-7.48 (m, 6H), 8.00 (d, $J$ = 8.0 Hz, 2H), 8.07 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.9, 40.8, 66.6, 121.4, 122.1, 128.8, 129.5, 130.5, 131.3, 132.7, 140.7, 147.5, 153.2; IR ($CH_2Cl_2$) ν 3142, 2920, 2850, 1592, 1485, 1388, 1342, 1212, 1195, 1174, 1088, 1008, 973, 810, 666 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{18}H_{17}BrN_3O_2S_3$ $(M+H)^+$: 481.9668, found: 481.9661.



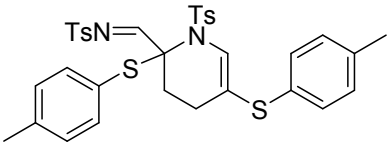

4-(2-(furan-2-yl)-1,3-dithiolan-2-yl)-1-tosyl-1*H*-1,2,3-triazole **3g**: a white solid; Mp: 166-167 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.46 (s, 3H), 3.48-3.58 (m, 4H), 6.30 (d, *J* = 3.2 Hz, 1H), 6.41 (d, *J* = 3.2 Hz, 1H), 7.38-7.41 (m, 3H), 8.00 (d, *J* = 8.4 Hz, 2H), 8.11 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.8, 40.8, 60.3, 109.0, 110.4, 121.3, 128.8, 130.4, 132.7, 143.4, 147.4, 150.6, 153.4; IR ($CH_2Cl_2$) ν 3116, 2924, 2851, 1591, 1490, 1399, 1192, 1170, 1149, 1089, 1013, 978, 849, 670 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{16}H_{16}N_3O_3S_3$ $(M+H)^+$: 394.0348, found: 394.0355.


8.105
8.012
7.991
7.401
7.382
7.266
6.414
6.406
6.305
6.297
3.580
3.565
3.549
3.534
3.521
3.505
3.489
2.457
0.000
Ts
4.09
3.04
3.01
2.04
0.99
0.95
1.03
PPM
153.350
150.571
147.414
143.368
132.717
130.425
128.793
121.308
110.446
109.019
77.319
77.000
76.681
60.277
40.746
21.814
Ts
200
150
100
50
PPM

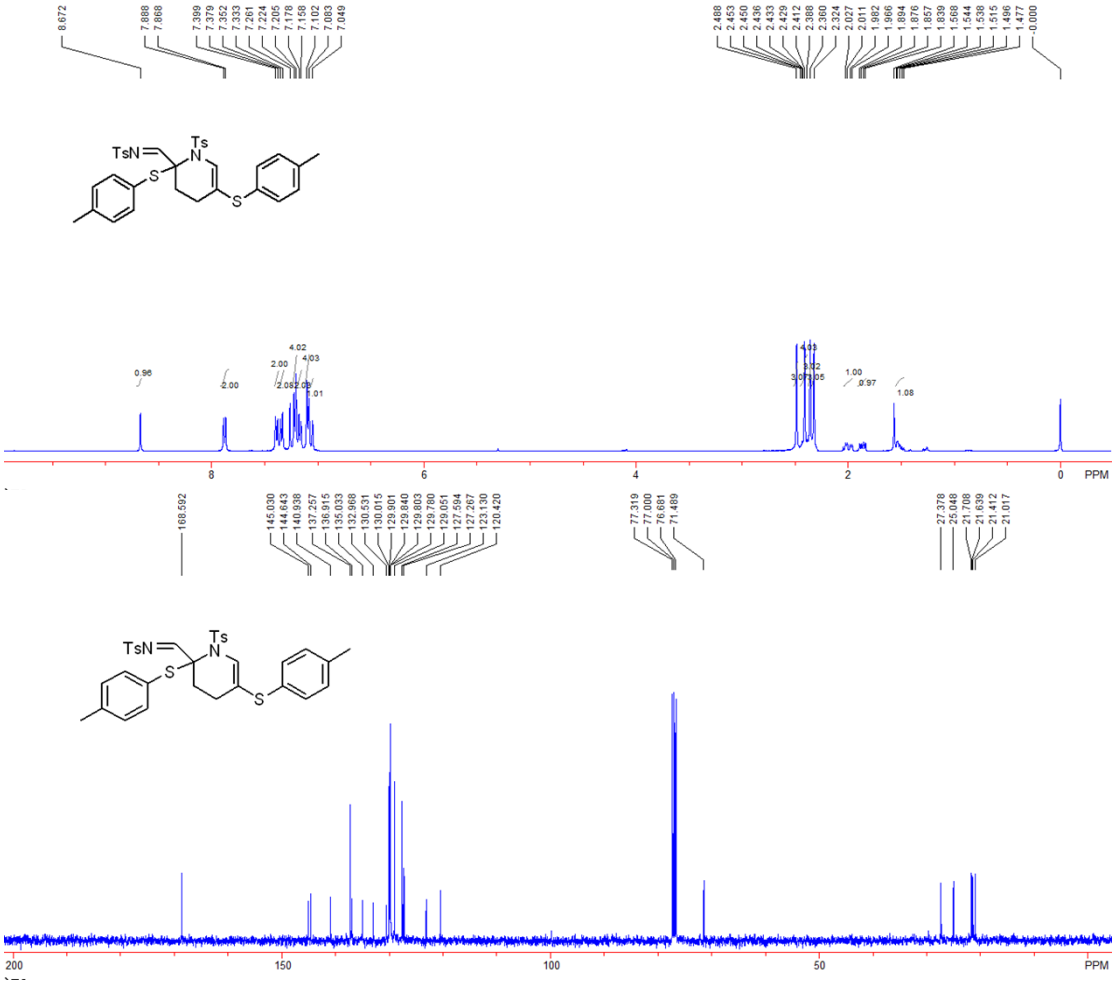
**General procedure for the synthesis of compounds 2 and 4**

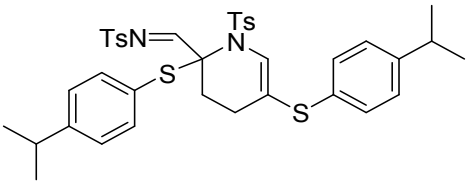
A solution of compound **1** or **3** (0.2 mmol) and $Rh_2(OAc)_4$ (1.2 mg, 0.002 mmol) in dry 1,2-dichloroethane (2 mL) was stirred at 80 $^oC$ under $N_2$ for an appropriate time. After completion of the reaction as indicated by TLC, the reaction was cooled to room temperature, and the mixture was purified by silica gel column flash chromatography (eluent: petroleum ether / ethyl acetate = 8 / 1) to afford the product **2** or **4** in good yield.

**Spectroscopic Data of Substrates 2 and 4:**

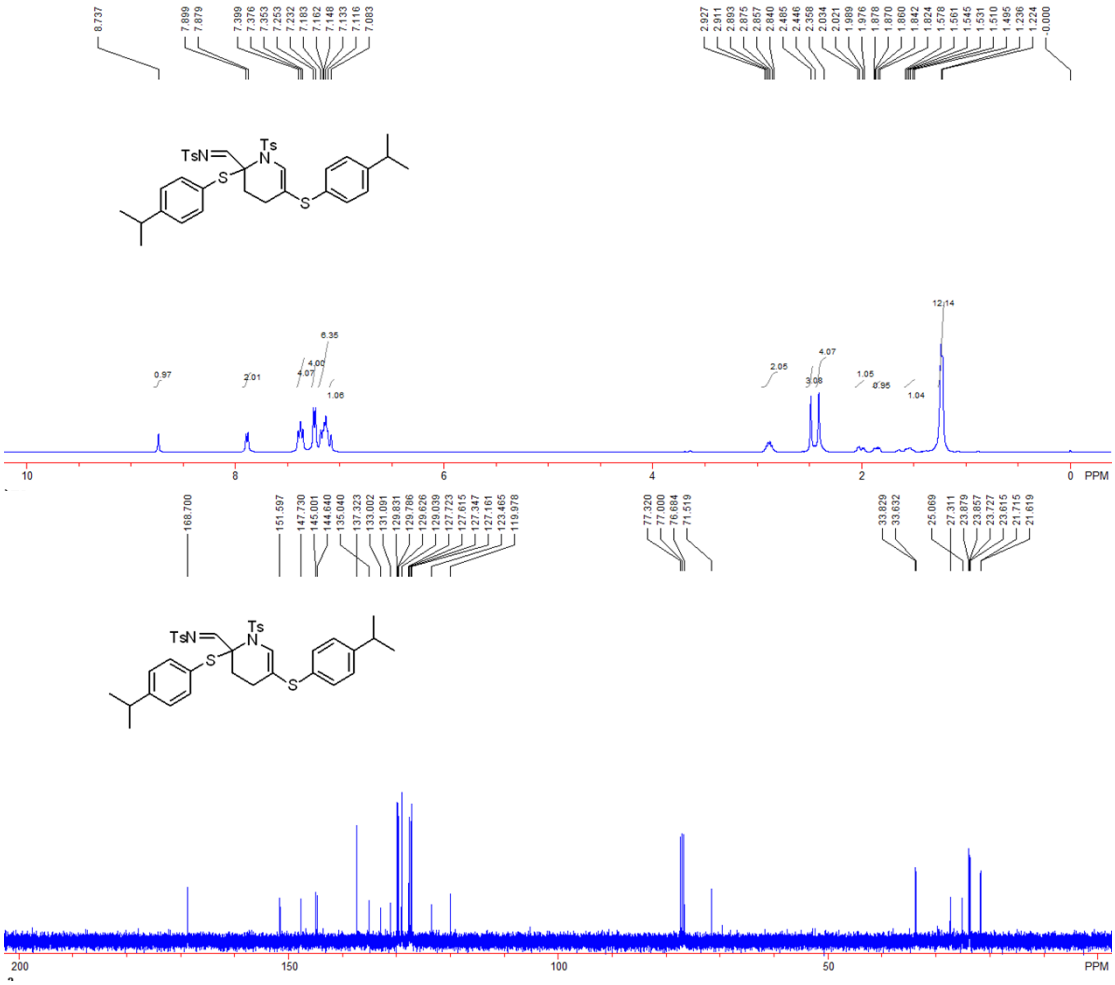


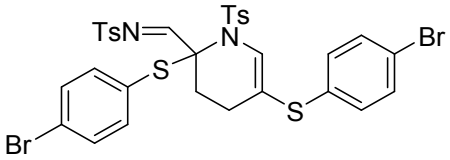

*N*-((2,5-bis(*p*-tolylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2a**: 60 mg, 91% yield, a white solid; Mp: 68-70 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.47-1.57 (m, 1H), 1.87 (dd, $J_1$ = 7.2 Hz, $J_2$ = 14.8 Hz, 1H), 1.96-2.03 (m, 1H), 2.32 (s, 3H), 2.36 (s, 3H), 2.38-2.46 (m, 4H), 2.49 (s, 3H), 7.05 (s, 1H), 7.09 (d, $J$ = 8.0 Hz, 4H), 7.17 (d, $J$ = 8.0 Hz, 2H), 7.21 (d, $J$ = 8.0 Hz, 4H), 7.34 (d, $J$ = 8.0 Hz, 2H), 7.39 (d, $J$ = 8.0 Hz, 2H), 7.88 (d, $J$ = 8.0 Hz, 2H), 8.67 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 21.4, 21.6, 21.7, 25.0, 27.4, 71.5, 120.4, 123.1, 127.3, 127.6, 129.1, 129.78, 129.80, 129.84, 129.9, 130.0, 130.5, 133.0, 135.0, 136.9, 137.3, 140.9, 144.6, 145.0, 168.6; IR ($CH_2Cl_2$) ν 3024, 2922, 2865, 1616, 1596, 1491, 1345, 1327, 1161, 1089, 1044, 965, 809, 659 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{34}H_{35}N_2O_4S_4$ $(M+H)^+$: 663.1474, found: 663.1479.



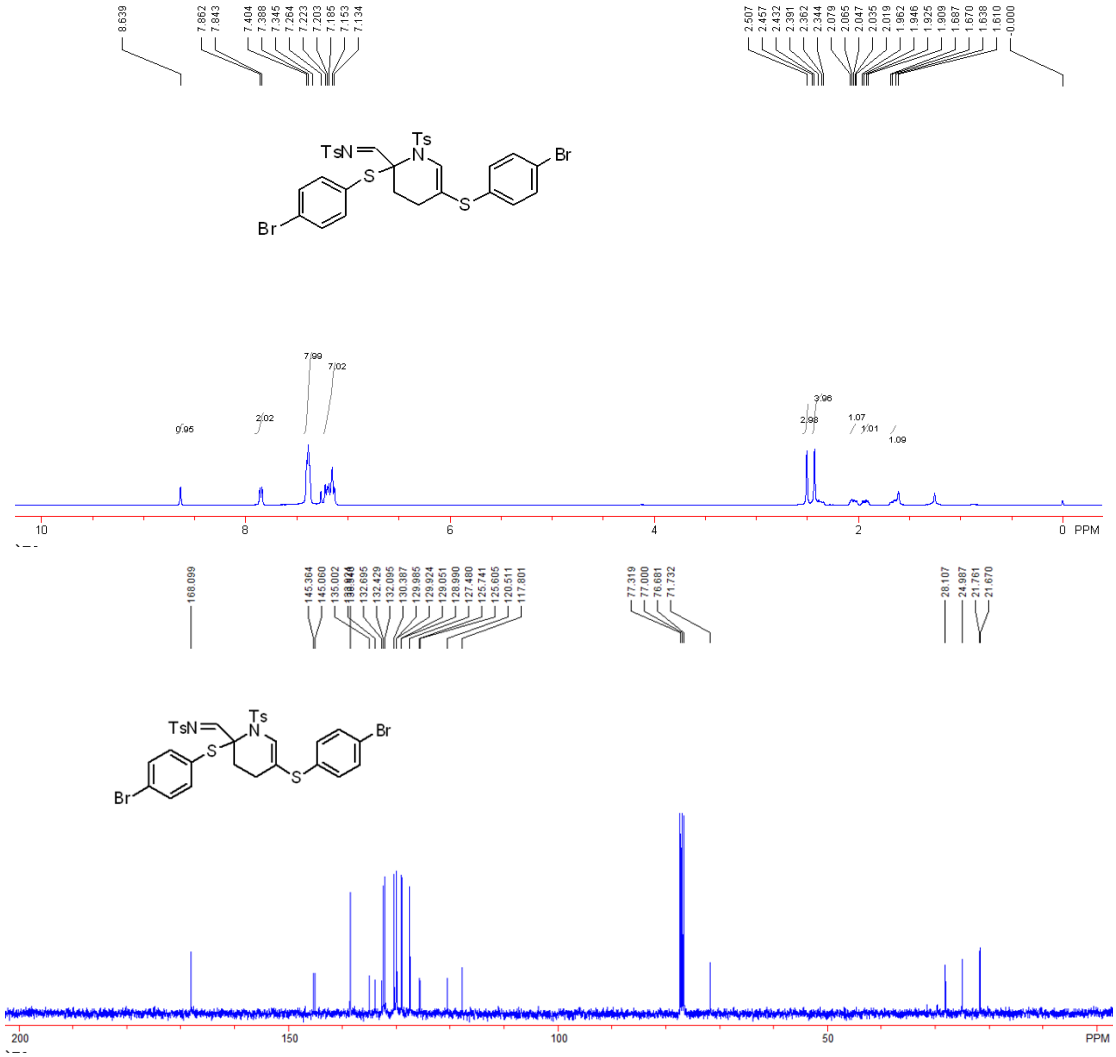


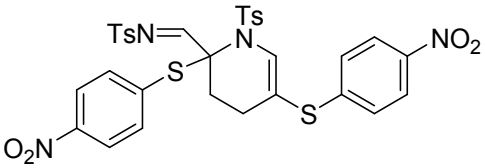

*N*-((2,5-bis(4-isopropylphenylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2b**: 68 mg, 91% yield, a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.22-1.24 (m, 12H), 1.49-1.58 (m, 1H), 1.82-1.88 (m, 1H), 1.97-2.04 (m, 1H), 2.35-2.45 (m, 4H), 2.49 (s, 3H), 2.84-2.93 (m, 2H), 7.08 (s, 1H), 7.11-7.40 (m, 14H), 7.89 (d, $J$ = 8.0 Hz, 2H), 8.74 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.7, 23.6, 23.7, 23.86, 23.88, 25.1, 27.3, 33.6, 33.8, 71.5, 120.0, 123.5, 127.2, 127.3, 127.6, 127.7, 129.0, 129.6, 129.79, 129.83, 131.1, 133.0, 135.0, 137.3, 144.6, 145.0, 147.7, 151.6, 168.7; IR ($CH_2Cl_2$) ν 3069, 2960, 2872, 1615, 1596, 1486, 1366, 1345, 1346, 1185, 1089, 1050, 813, 735, 658 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{38}H_{43}N_2O_4S_4$ $(M+H)^+$: 719.2100, found: 719.2104.



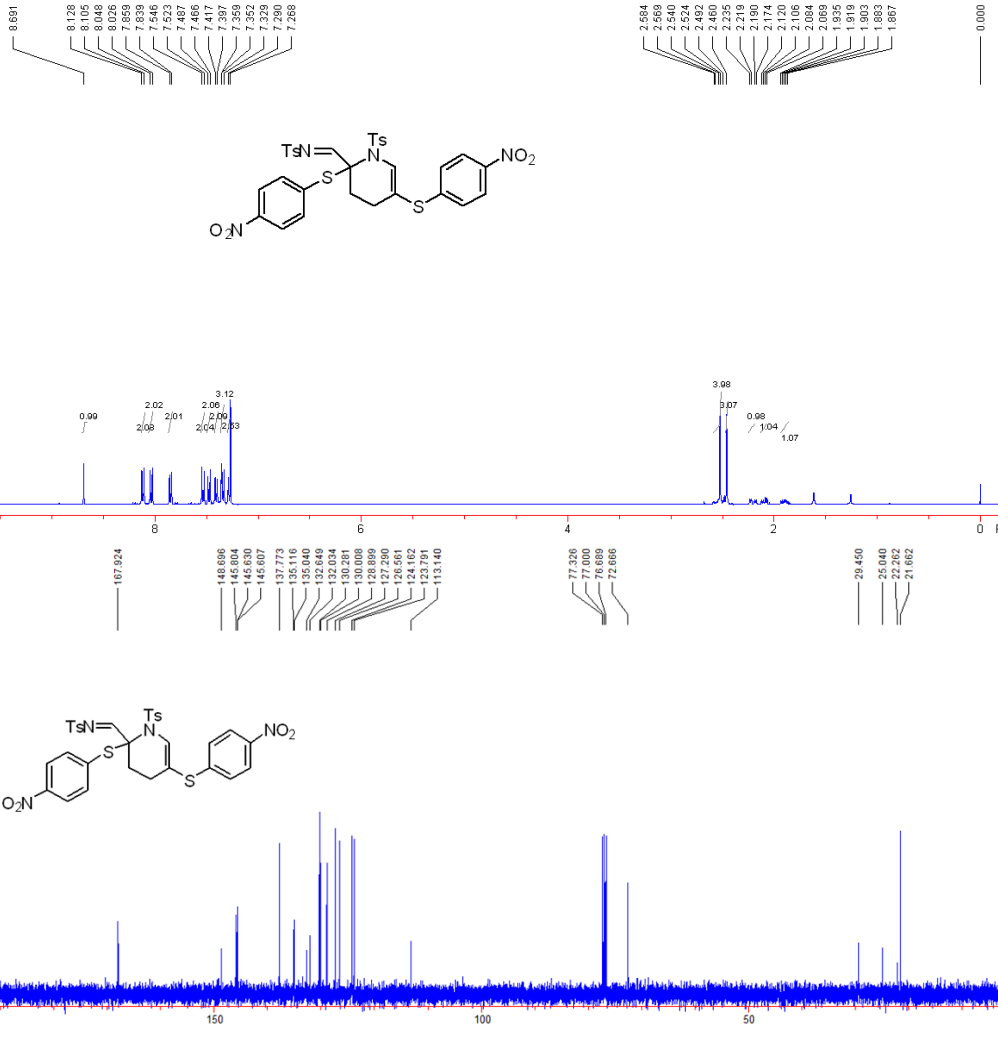


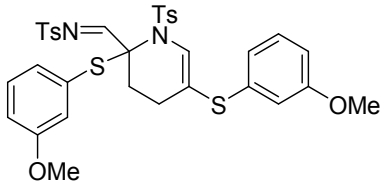

*N*-((2,5-bis(4-bromophenylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2c**: 74mg, 93% yield, a white solid; Mp: 147-148 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.61-1.69 (m, 1H), 1.91-1.97 (m, 1H), 2.01-2.08 (m, 1H), 2.34-2.46 (m, 4H), 2.51 (s, 3H), 7.13-7.27 (m, 7H), 7.34-7.41 (m, 8H), 7.85 (d, $J$ = 7.6 Hz, 2H), 8.64 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.7, 21.8, 25.0, 28.1, 71.7, 117.8, 120.5, 125.6, 125.7, 127.5, 129.0, 129.1, 129.9, 130.0, 130.4, 132.1, 132.4, 132.7, 133.9, 135.0, 138.5, 145.1, 145.4, 168.1; IR ($CH_2Cl_2$) ν 3055, 2923, 2852, 1622, 1471, 1368, 1346 1161, 1087, 1007, 811, 733, 657cm$^{-1}$; HRMS (ESI) Calcd. For $C_{32}H_{29}Br_2N_2O_4S_4$ $(M+H)^+$: 790.9371, found: 790.9376.



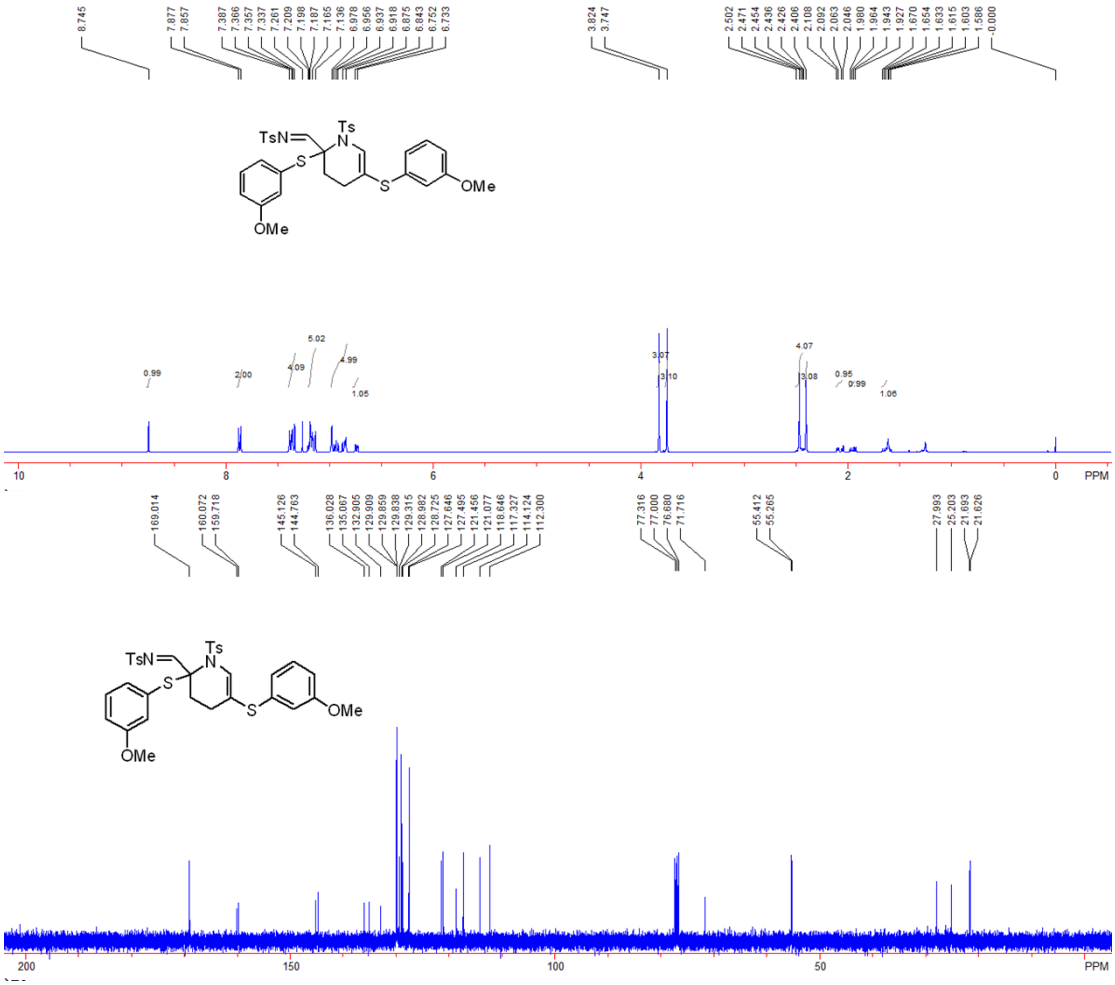


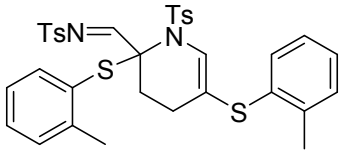

*N*-((2,5-bis(4-nitrophenylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2d**: 62mg, 86% yield, a white solid; Mp: 105-106 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.86-1.94 (m, 1H), 2.10 (dd, $J_1$ = 6.0 Hz, $J_2$ = 14.8 Hz, 1H), 2.20 (dd, $J_1$ = 6.0 Hz, $J_2$ = 18.0 Hz, 1H), 2.46 (s, 3H), 2.49-2.59 (m, 4H), 7.26-7.29 (m, 2H), 7.32-7.36 (m, 3H), 7.41 (d, $J$ = 8.0 Hz, 2H), 7.48 (d, $J$ = 8.4 Hz, 2H), 7.53 (d, $J$ = 9.2 Hz, 2H), 7.85 (d, $J$ = 8.0 Hz, 2H), 8.04 (d, $J$ = 8.8 Hz, 2H), 8.12 (d, $J$ = 9.2 Hz, 2H), 8.69 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.7, 22.3, 25.0, 29.5, 72.7, 113.1, 123.8, 124.2, 126.6, 127.3, 128.9, 130.0, 130.3, 132.0, 132.6, 135.0, 135.1, 137.8, 145.61, 145.63, 145.8, 148.7, 167.9; IR ($CH_2Cl_2$) ν 3096, 2923, 2852, 1628, 1515, 1336, 1161, 1087, 852, 731, 658 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{32}H_{29}N_4O_8S_4$ $(M+H)^+$: 725.0863, found: 725.0864.



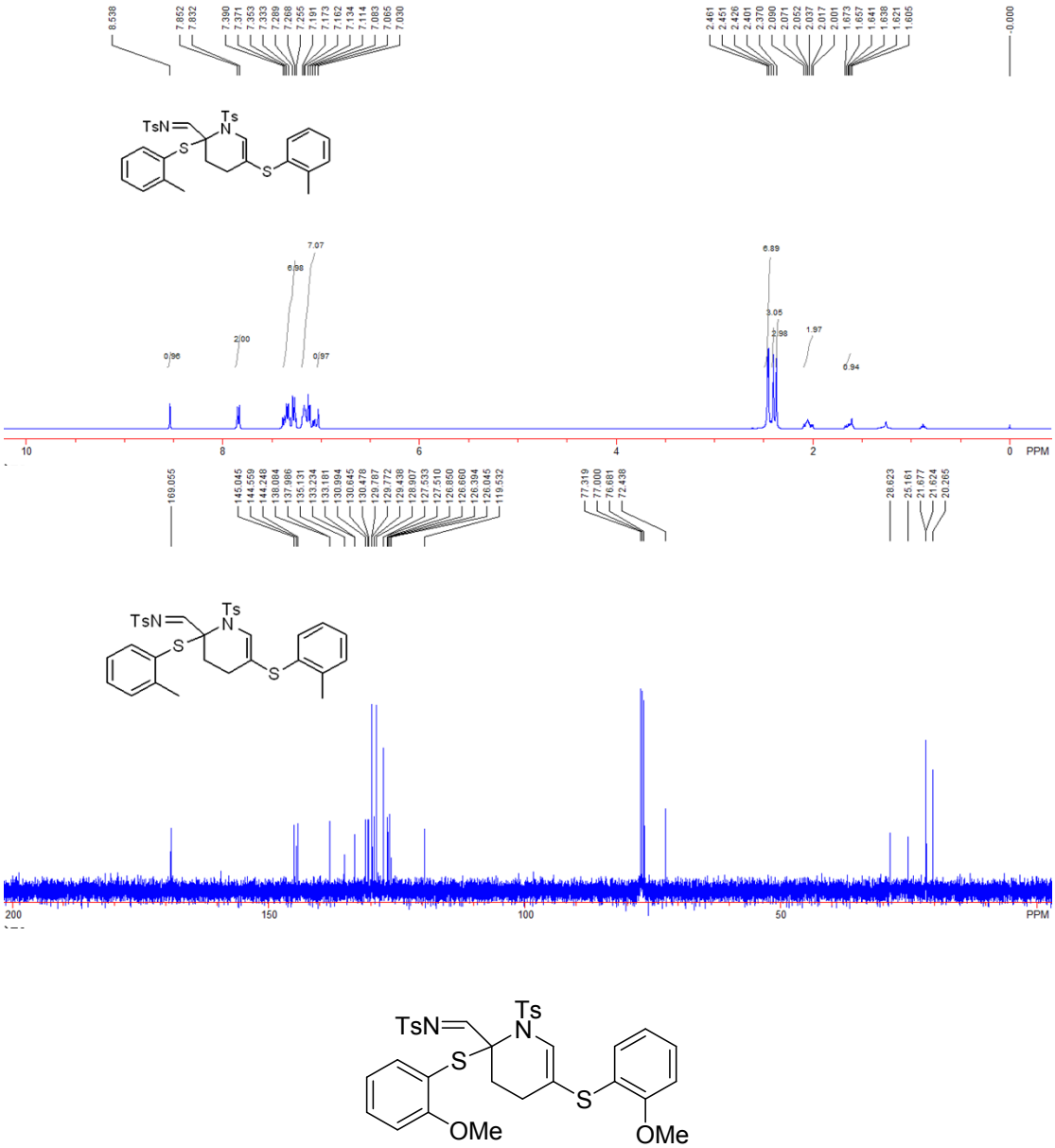



*N*-((2,5-bis((3-methoxyphenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2e**: 65 mg, 94% yield, a white solid; Mp: 150-152 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.58-1.67 (m, 1H), 1.95 (dd, $J_1$ = 6.4 Hz, $J_2$ = 14.8 Hz, 1H), 2.08 (dd, $J_1$ = 6.4 Hz, $J_2$ = 18.0 Hz, 1H), 2.41 (s, 3H), 2.42-2.51 (m, 4H), 3.75 (s, 3H), 3.82 (s, 3H), 6.74 (d, $J$ = 7.6 Hz, 1H), 6.84-6.98 (m, 5H), 7.13-7.21 (m, 5H), 7.33-7.39 (m, 4H), 7.87 (d, $J$ = 8.0 Hz, 2H), 8.75 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.7, 25.2, 28.0, 55.3, 55.4, 71.7, 112.3, 114.1, 117.3, 118.6, 121.1, 121.5, 127.5, 127.6, 128.7, 129.0, 129.3, 129.8, 129.86, 129.91, 132.9, 135.1, 136.0, 144.8, 145.1, 159.7, 160.1, 169.0; IR ($CH_2Cl_2$) ν 2961, 2925, 2838, 1620, 1589, 1479, 1164, 1090, 1039, 814, 660 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{34}H_{35}N_2O_6S_4$ $(M+H)^+$: 695.1372, found: 695.1381.

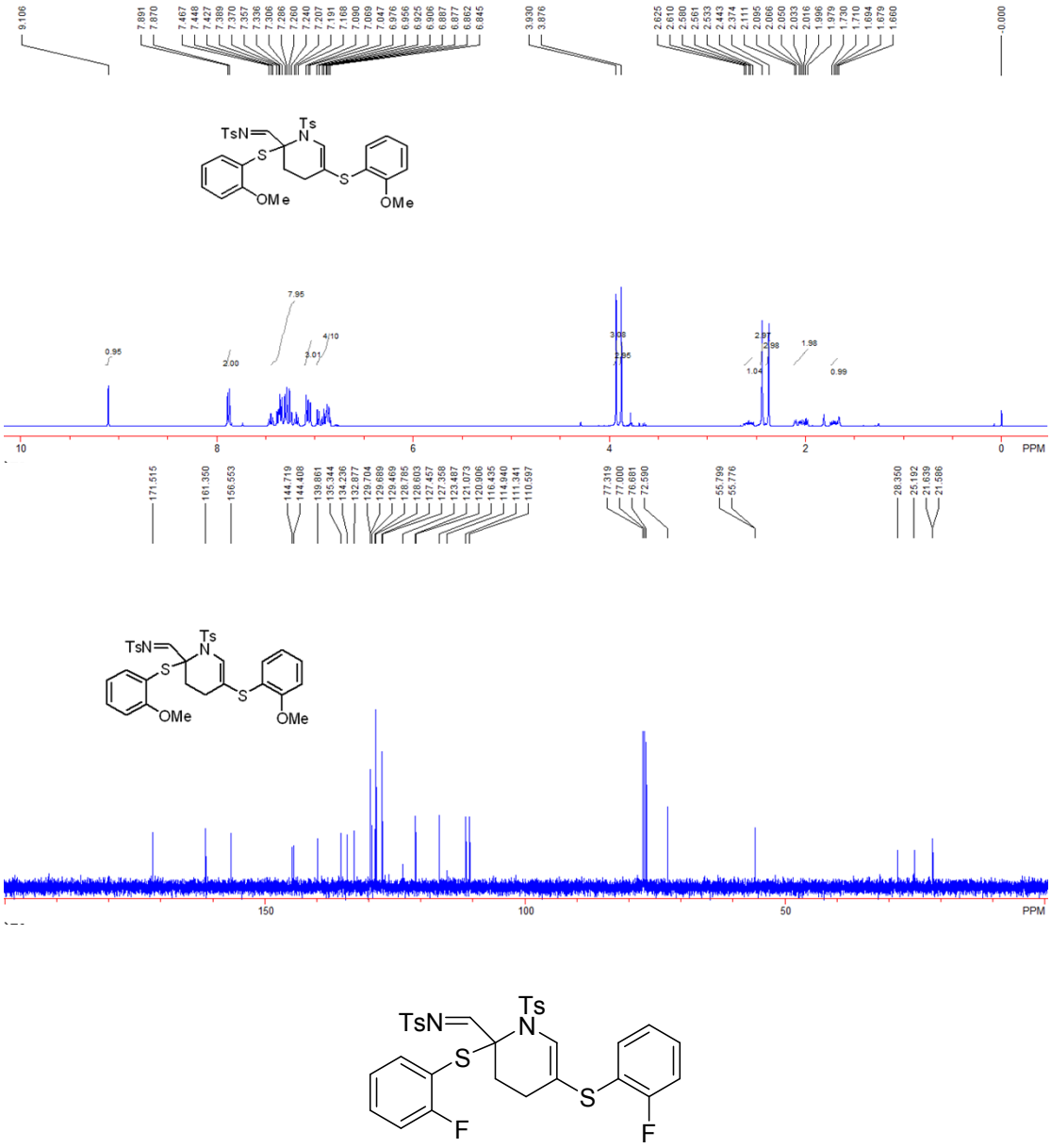





*N*-((2,5-bis(*o*-tolylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2f**: 58 mg, 88% yield, a white solid; Mp: 115-117 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.60-1.68 (m, 1H), 2.00-2.09 (m, 2H), 2.37 (s, 3H), 2.40 (s, 3H), 2.42-2.47 (m, 7H), 7.03 (s, 1H), 7.06-7.20 (m, 7H), 7.25-7.39 (m, 7H), 7.84 (d, $J$ = 8.0 Hz, 2H), 8.54 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.3, 21.6, 21.7, 25.2, 28.6, 72.4, 119.5, 126.0, 126.4, 126.7, 126.9, 127.51, 127.53, 128.9, 129.4, 129.77, 129.78, 130.5, 130.6, 131.0, 133.18, 133.23, 135.1, 138.0, 138.1, 144.2, 144.6, 145.0, 169.1; IR ($CH_2Cl_2$) ν 3060, 2924, 2855, 1615, 1596, 1469, 1345, 1327, 1161, 1090, 1043, 813, 735, 658 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{34}H_{35}N_2O_4S_4$ $(M+H)^+$: 663.1474, found: 663.1480.

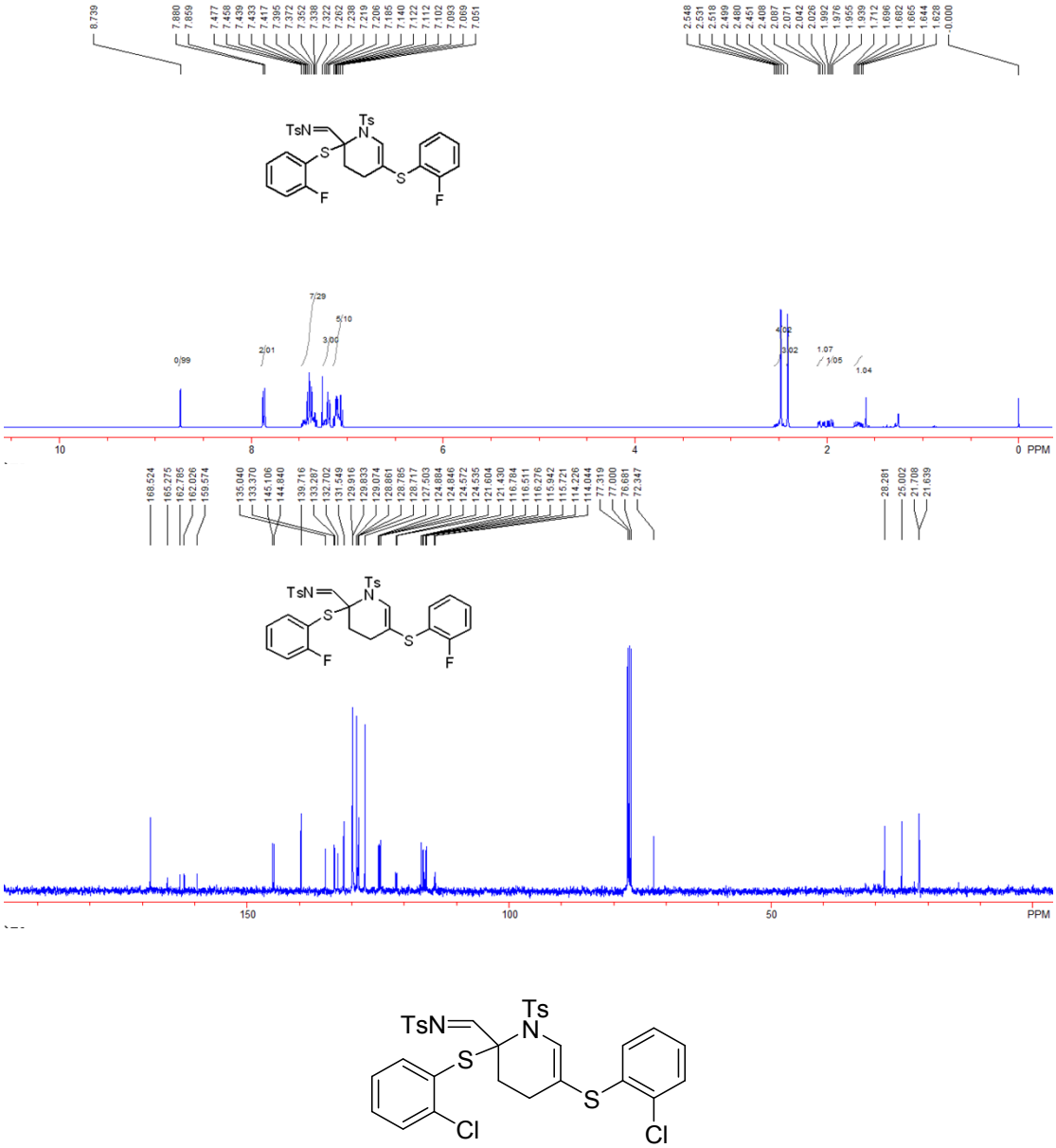


*N*-((2,5-bis((2-methoxyphenyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2g**: 51 mg, 73% yield, a white solid; Mp: 90-91 °C; $^1$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.66-1.73 (m, 1H), 1.97-2.12 (m, 2H), 2.37 (s, 3H), 2.44 (s, 3H), 2.53-2.63 (m, 1H), 3.88 (s, 3H), 3.93 (s, 3H), 6.84-6.98 (m, 4H), 7.04-7.09 (m, 3H), 7.16-7.47 (m, 8H), 7.88 (d, $J$ = 8.4 Hz, 2H), 9.11 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.59, 21.64, 25.2, 28.4, 55.78, 55.80, 72.6, 110.6, 111.3, 114.9, 116.4, 120.9, 121.1, 123.5, 127.4, 127.5, 128.6, 128.8, 129.5, 129.69, 129.70, 132.9, 134.2, 135.3, 139.9, 144.4, 144.7, 156.6, 161.4, 171.5; IR ($CH_2Cl_2$) ν 3063, 2923, 2851, 1615, 1581, 1475, 1325, 1243, 1159, 1090, 1021, 968, 814, 735, 658 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{34}H_{35}N_2O_6S_4$ $(M+H)^+$: 695.1372, found: 695.1378.




*N*-((2,5-bis(2-fluorophenylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2h**: 55 mg, 81% yield, a white solid; Mp: 75-76 °C; $^1$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.62-1.72 (m, 1H), 1.97 (dd, $J_1$ = 6.4 Hz, $J_2$ = 14.8 Hz, 1H), 2.06 (dd, $J_1$ = 6.4

Hz, $J_2$ = 18.0 Hz, 1H), 2.41 (s, 3H), 2.45-2.55 (m, 4H), 7.05-7.14 (m, 5H), 7.18-7.27 (m, 3H), 7.32-7.48 (m, 7H), 7.87 (d, $J$ = 8.4 Hz, 2H), 8.74 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.7, 25.0, 28.3, 72.3, 114.1 (d, $J$ = 18.2 Hz), 115.8 (d, $J$ = 22.1 Hz), 116.4 (d, $J$ = 23.5 Hz), 116.8, 121.5 (d, $J$ = 17.4 Hz), 124.6 (d, $J$ = 3.7 Hz), 124.9 (d, $J$ = 3.8 Hz), 127.5, 128.7, 128.8 (d, $J$ = 7.6 Hz), 129.1, 129.8, 129.9, 131.5, 132.7, 133.3 (d, $J$ = 8.3 Hz), 135.0, 139.7, 144.8, 145.1, 160.8 (d, $J$ = 245.2 Hz), 164.0 (d, $J$ = 249.0 Hz), 168.5; IR ($CH_2Cl_2$) ν 3066, 2923, 2852, 1618, 1595, 1472, 1346, 1328, 1162, 1090, 1046, 966, 814, 734, 657 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{32}H_{29}F_2N_2O_4S_4$ $(M+H)^+$: 671.0973, found: 671.0975.

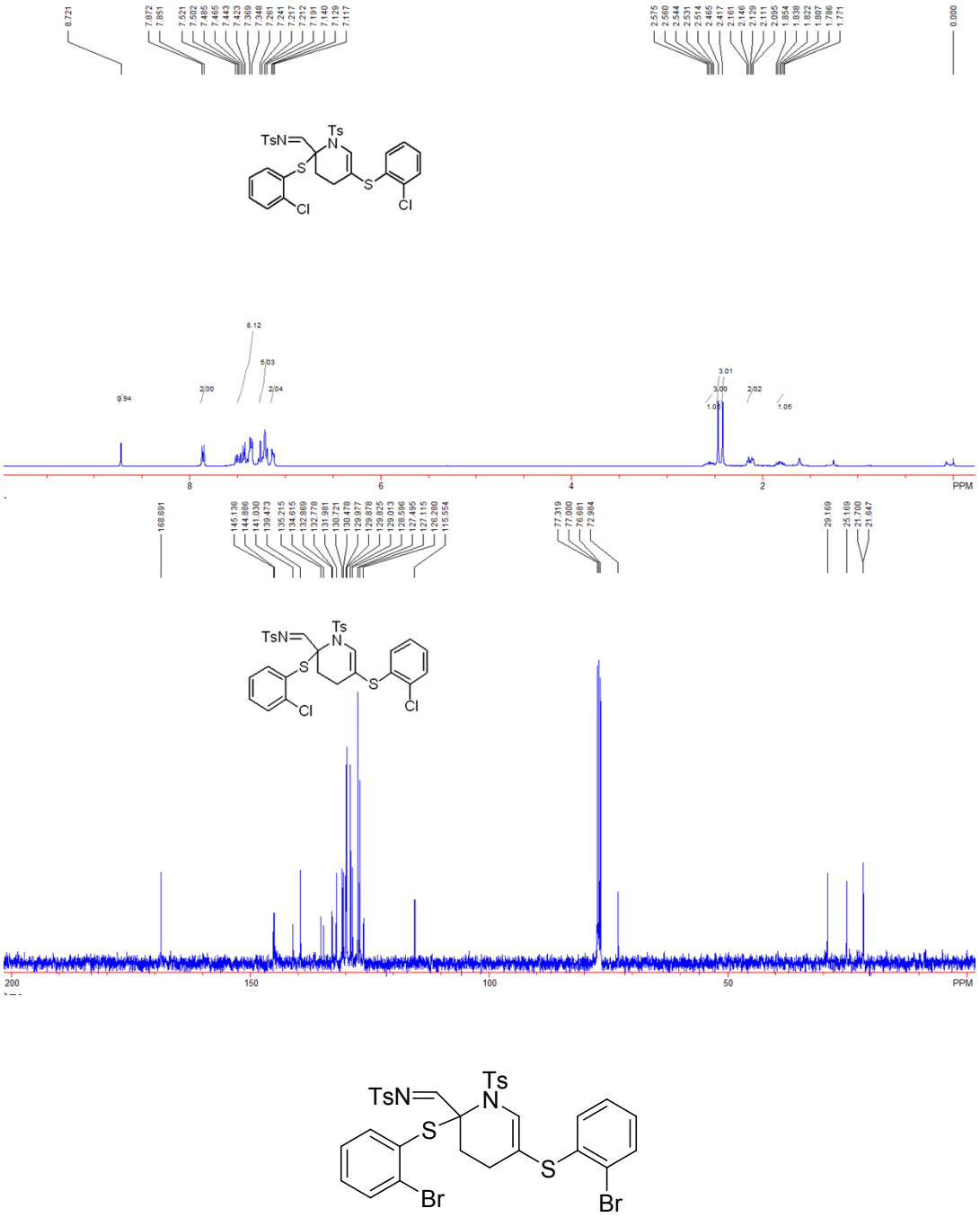






*N*-((2,5-bis(2-chlorophenylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2i**: 62 mg, 87% yield, a white solid; Mp: 150-152 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.77-1.86 (m, 1H), 2.09-2.17 (m, 2H), 2.42 (s, 3H), 2.47 (s, 3H), 2.51-2.58 (m, 1H), 7.11-7.14 (m, 2H), 7.19-7.27 (m, 5H), 7.34-7.53 (m, 8H), 7.86 (d, $J$ = 8.4 Hz,

2H), 8.72 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.7, 25.2, 29.2, 73.0, 115.6, 126.3, 127.1, 127.5, 128.6, 129.0, 129.8, 129.9, 130.0, 130.5, 130.7, 132.0, 132.8, 132.9, 134.6, 135.2, 139.5, 141.0, 144.9, 145.1, 168.7; IR ($CH_2Cl_2$) ν 3059, 2924, 2853, 1620, 1596, 1449, 1346, 1328, 1162, 1090, 1032, 813, 733, 657 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{32}H_{29}Cl_2N_2O_4S_4$ $(M+H)^+$: 703.0382, found: 703.0388.

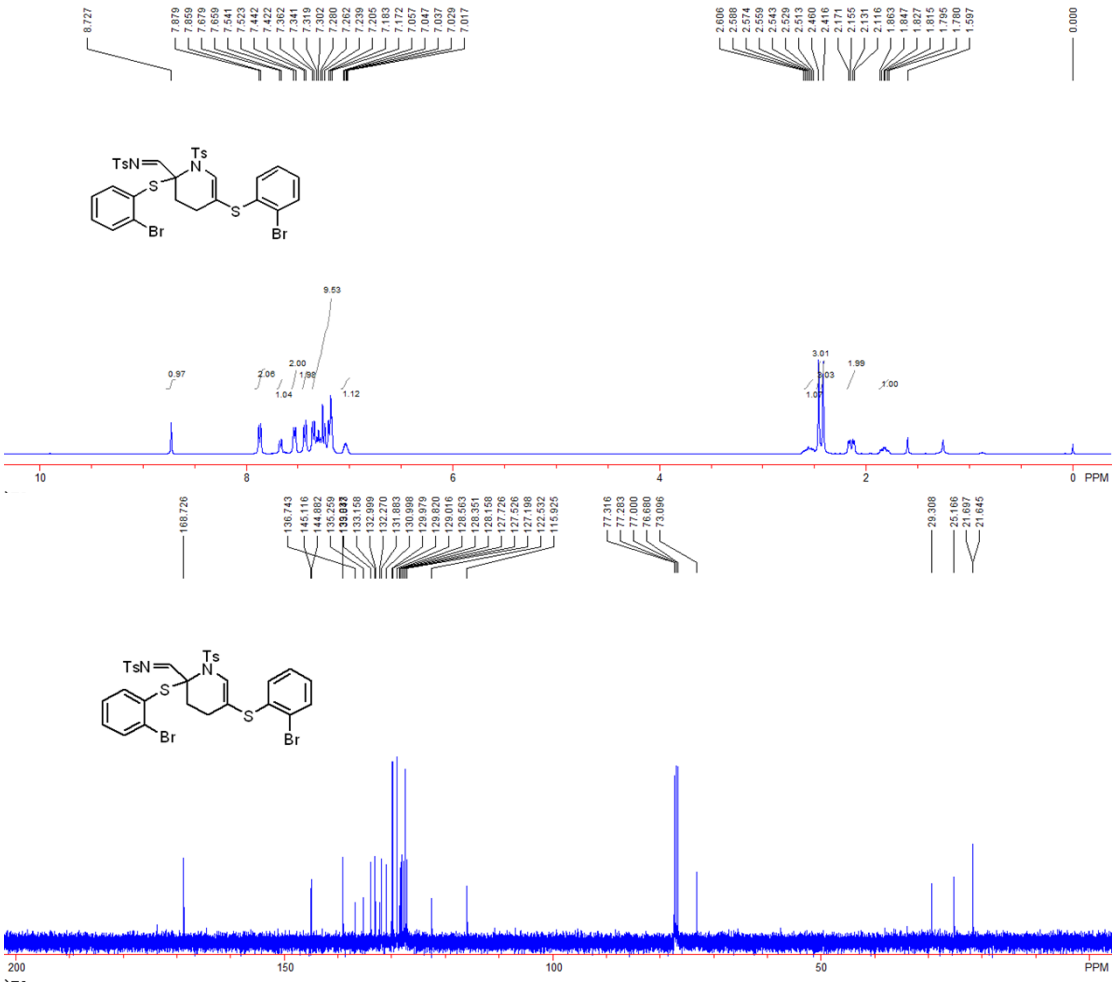


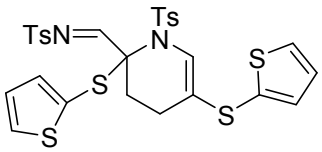




*N*-((2,5-bis(2-bromophenylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2j**: 66 mg, 81% yield, a white solid; Mp: 119-120 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.78-1.87 (m, 1H), 2.14 (dd, $J_1$ = 6.4 Hz, $J_2$ = 16.0 Hz, 2H), 2.42 (s, 3H), 2.46 (s, 3H), 2.51-2.61 (m, 1H), 7.02-7.06 (m, 1H), 7.17-7.37 (m, 9H), 7.43 (d, $J$ = 8.0 Hz,

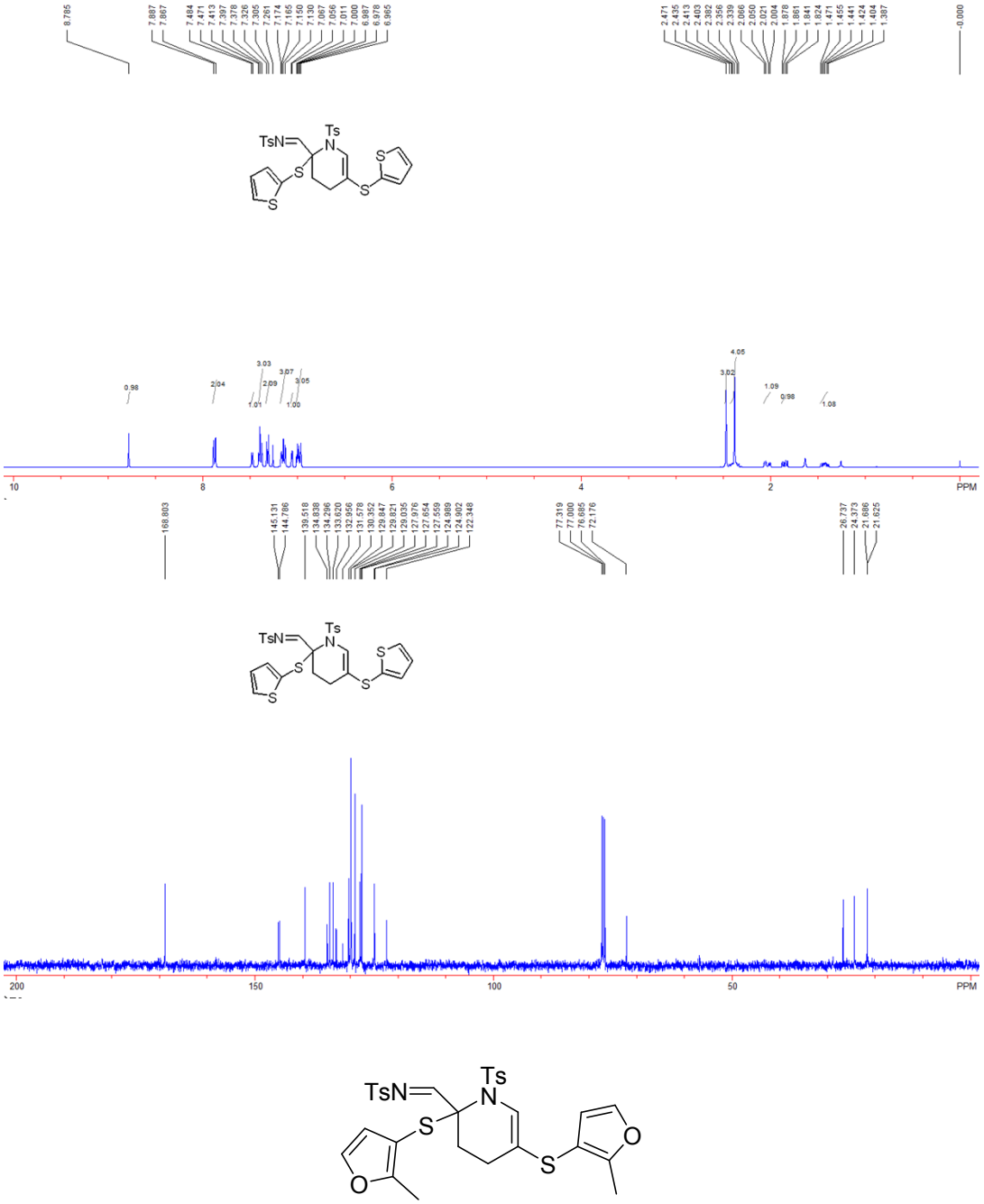
2H), 7.53 (d, $J$ = 8.0 Hz, 2H), 7.67 (d, $J$ = 8.0 Hz, 1H), 7.87 (d, $J$ = 8.0 Hz, 2H), 8.73 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.7, 25.2, 29.3, 73.1, 115.9, 122.5, 127.2, 127.5, 127.7, 128.2, 128.4, 128.6, 129.0, 129.8, 130.0, 131.0, 131.9, 132.3, 133.0, 133.2, 133.8, 135.3, 136.7, 139.0, 144.9, 145.1, 168.7; IR ($CH_2Cl_2$) ν 3060, 2923, 2852, 1620, 1596, 1445, 1346, 1328, 1160, 1090, 1019, 966, 813, 735, 658 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{32}H_{29}Br_2N_2O_4S_4$ $(M+H)^+$: 790.9371, found: 790.9368.



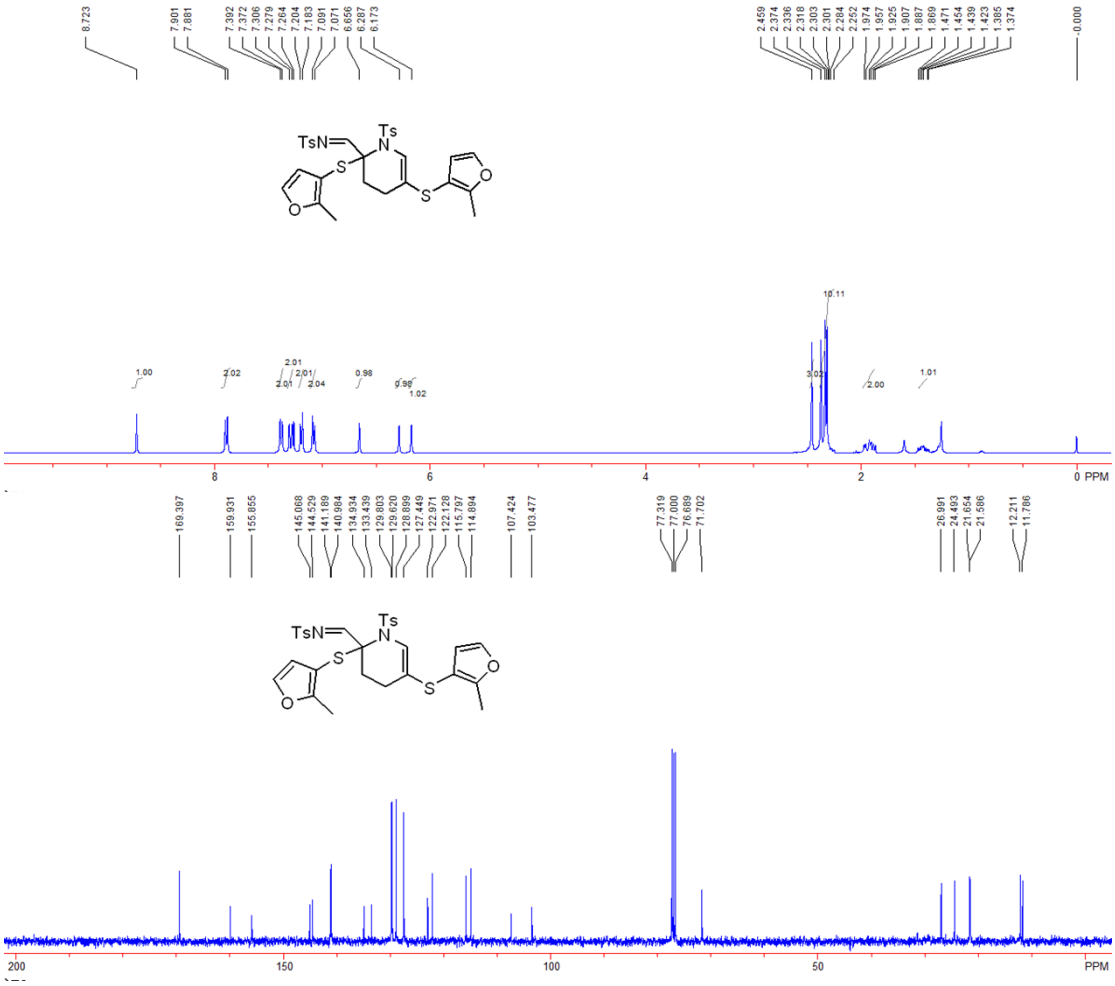

*N*-((2,5-bis(thiophen-2-ylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2k**: 58 mg, 90% yield, a white solid; Mp: 140-142 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.38-1.48 (m, 1H), 1.85 (dd, $J_1$ = 6.8 Hz, $J_2$ = 14.8 Hz, 1H), 2.04 (dd, $J_1$ = 6.8 Hz, $J_2$ = 18.4 Hz, 1H), 2.33-2.44 (m, 4H), 2.47 (s, 3H), 6.96-7.02 (m, 3H), 7.06 (d, $J$ = 4.8 Hz, 1H), 7.13-7.18 (m, 3H), 7.32 (d, $J$ = 8.0 Hz, 2H), 7.37-7.42 (m, 3H), 7.48 (d, $J$ = 4.8 Hz, 1H), 7.88 (d, $J$ = 8.0 Hz, 2H), 8.79 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.7,

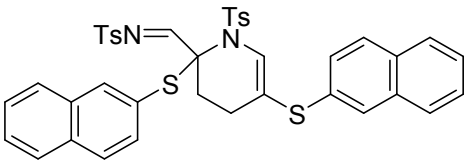
24.4, 26.7, 72.2, 122.3, 124.9, 125.0, 127.6, 127.7, 128.0, 129.0, 129.82, 129.85, 130.4, 131.6, 133.0, 133.6, 134.3, 134.8, 139.5, 144.8, 145.1, 168.8; IR ($CH_2Cl_2$) ν 3068, 2923, 2852, 1616, 1596, 1326, 1161, 1089, 1043, 965, 813, 733, 657 $cm^{-1}$; HRMS (ESI) Calcd. for $C_{28}H_{27}N_2O_4S_6$ $(M+H)^+$: 647.0290, found: 647.0292.




*N*-((2,5-bis((2-methylfuran-3-yl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2l**: 46 mg, 71% yield, a white solid; Mp: 120-121 °C; $^1H$ NMR ($CDCl_3$, 400 MHz, TMS) δ 1.37-1.48 (m, 1H), 1.86-1.98 (m, 2H), 2.25-2.38 (m, 10H), 2.46 (s, 3H), 6.17 (s, 1H), 6.29 (s, 1H), 6.66 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.27-7.31 (m, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 8.0 Hz, 2H), 8.72 (s, 1H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, TMS) δ 11.8, 12.2, 21.6, 21.7, 24.5, 27.0, 71.7, 103.5, 107.4, 114.9, 115.8,

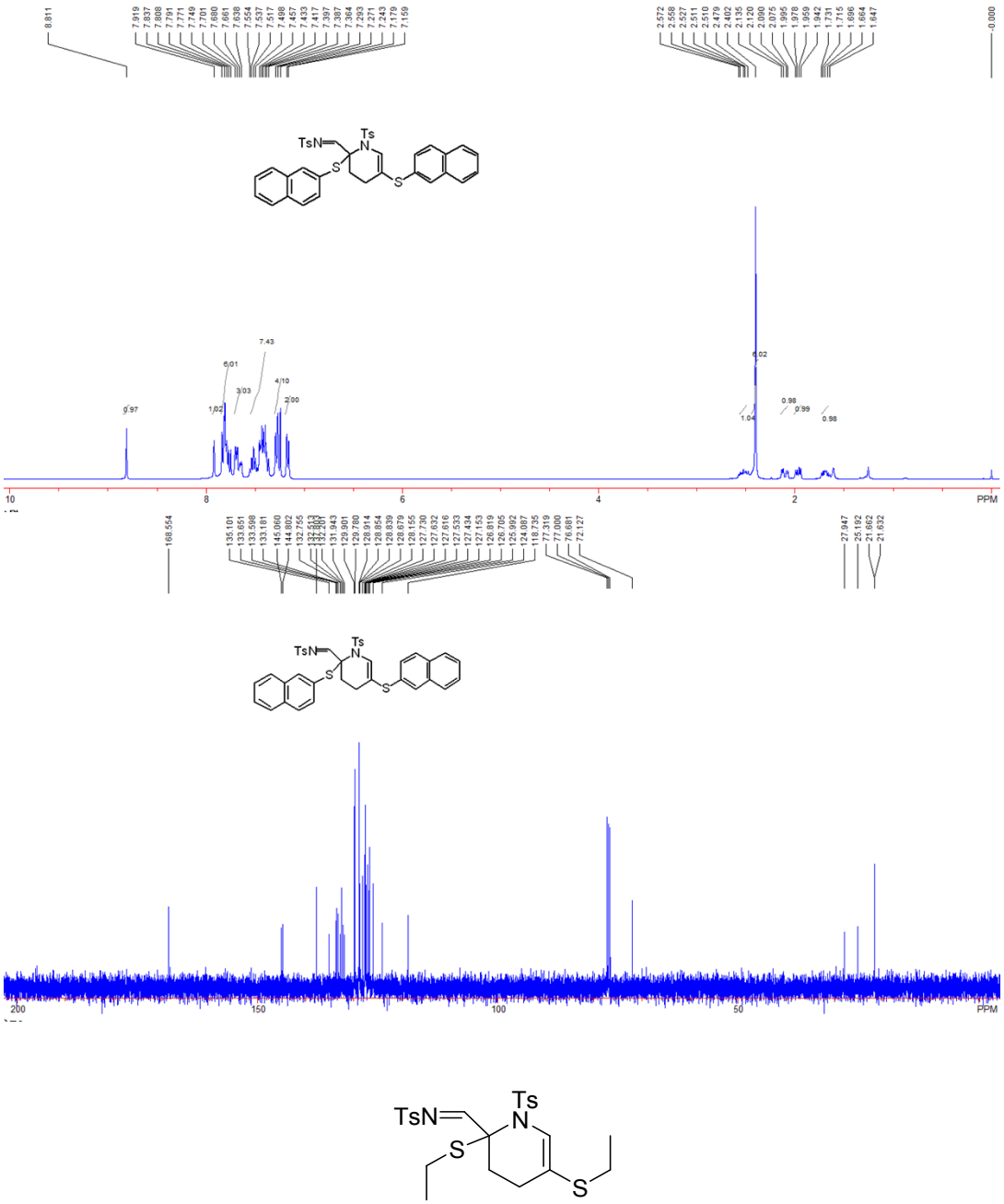
122.1, 123.0, 127.4, 128.9, 129.6, 129.8, 133.4, 134.9, 141.0, 141.2, 144.5, 145.1, 155.9, 159.9, 169.4; IR ($CH_2Cl_2$) ν 3066, 2922, 2852, 1615, 1596, 1325, 1160, 1088, 1044, 940, 814, 734, 658 $cm^{-1}$; HRMS (ESI) Calcd. for $C_{30}H_{31}N_2O_6S_4$ $(M+H)^+$: 643.1059, found: 643.1061.




*N*-((2,5-bis(naphthalen-2-ylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2m**: 65 mg, 86% yield, a white solid; Mp: 161-163 $^oC$; $^1H$ NMR ($CDCl_3$, 400 MHz, TMS) δ 1.64-1.74 (m, 1H), 1.97 (dd, $J_1$ = 6.4 Hz, $J_2$ = 14.4 Hz, 1H), 2.11 (dd, $J_1$ = 6.4 Hz, $J_2$ = 18.0 Hz, 1H), 2.40 (s, 6H), 2.47-2.58 (m, 1H), 7.17 (d, $J$ = 8.0 Hz, 2H), 7.24-7.30 (m, 4H), 7.36-7.56 (m, 7H), 7.63-7.71 (m, 3H), 7.74-7.84 (m, 6H), 7.92, (s, 1H), 8.81 (s, 1H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.7, 25.2, 27.9, 72.1, 118.7, 124.1, 126.0, 126.7, 126.8, 127.2, 127.4, 127.5, 127.62, 127.63, 127.7, 128.2, 128.7, 128.84, 128.85, 128.91, 129.8, 129.9, 131.9, 132.2, 132.5, 132.8, 133.2, 133.6, 133.7, 135.1, 137.8, 144.8, 145.1, 168.6;

IR ($CH_2Cl_2$) ν 3054, 2922, 2850, 1623, 1595, 1345, 1327, 1162, 1089, 1045, 963, 812, 733, 657 $cm^{-1}$; HRMS (ESI) Calcd. for $C_{40}H_{35}N_2O_4S_4$ $(M+H)^+$: 735.1474, found: 735.1471.

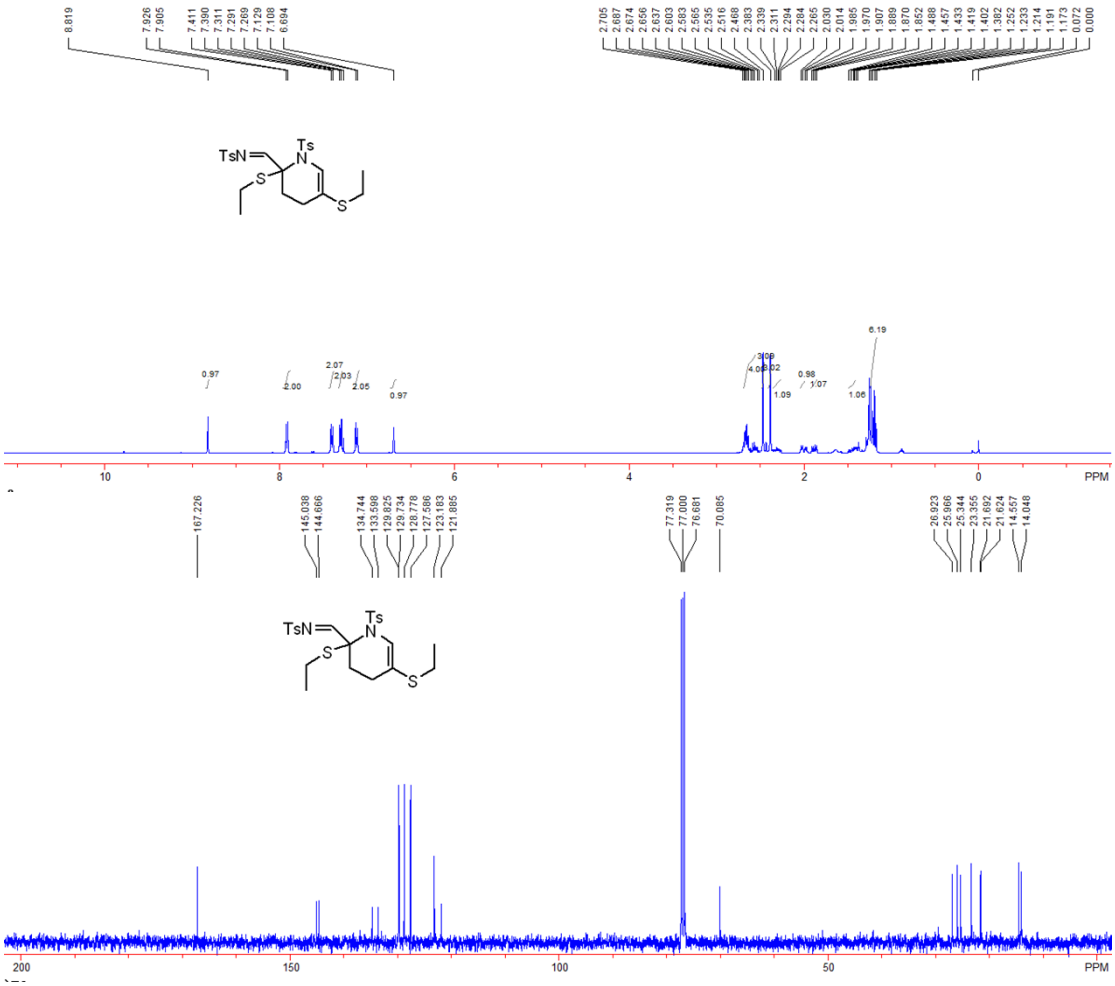


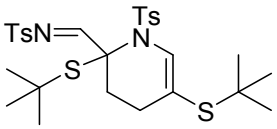




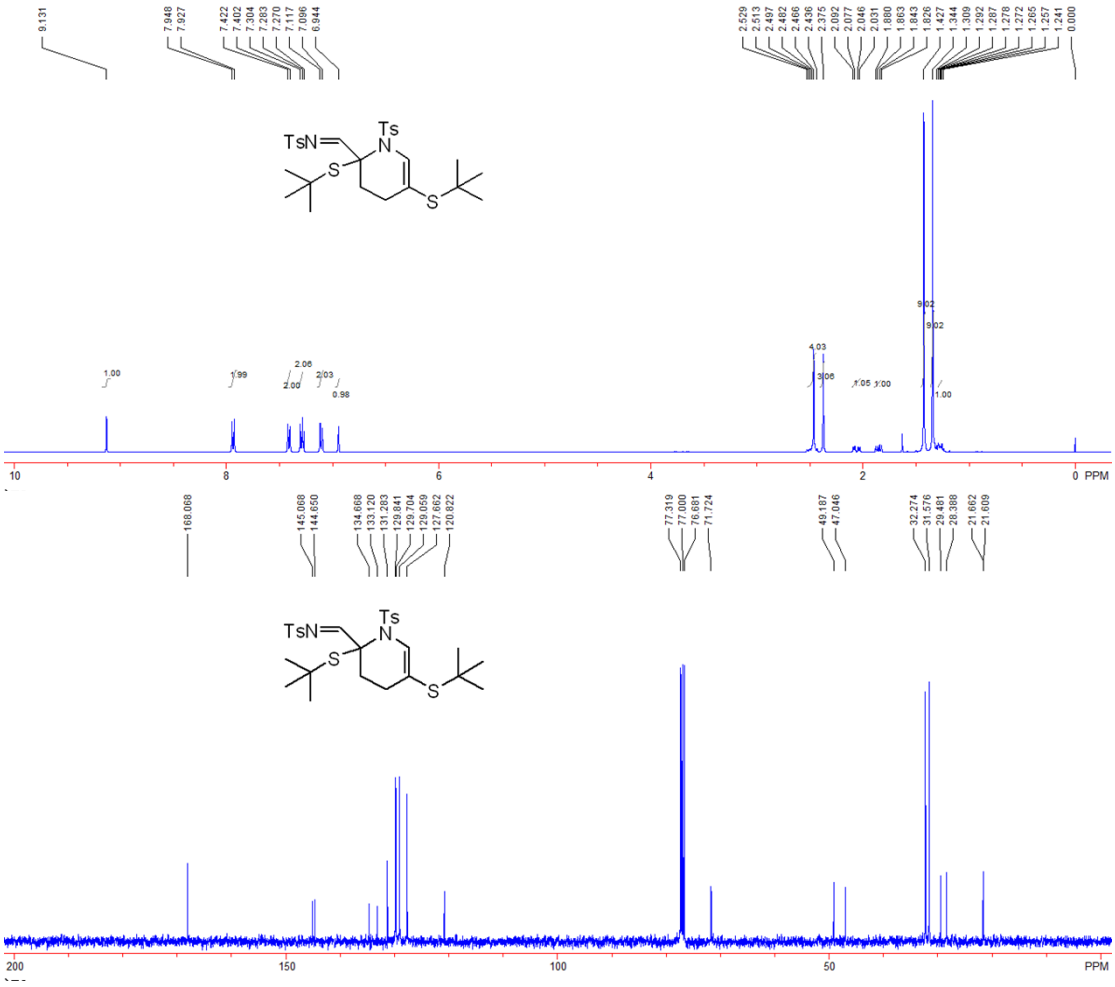
*N*-((2,5-bis(ethylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2n**: 41 mg, 76% yield, a colorless oil; $^1H$ NMR ($CDCl_3$, 400 MHz, TMS) δ 1.17-1.26 (m, 6H), 1.38-1.49 (m, 1H), 1.88 (dd, $J_1$ = 7.2 Hz, $J_2$ = 14.8 Hz, 1H), 2.00 (dd, $J_1$ = 7.2 Hz, $J_2$ = 17.6 Hz, 1H), 2.26-2.34 (m, 1H), 2.38 (s, 3H), 2.47 (s, 3H), 2.51-2.71 (m, 4H), 6.69 (s, 1H), 7.12 (d, $J$ = 8.0 Hz, 2H), 7.30 (d, $J$ = 8.0 Hz, 2H), 7.40 (d, $J$ = 8.0 Hz, 2H), 7.92 (d, $J$ = 8.0 Hz, 2H), 8.82 (s, 1H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 14.6, 21.6, 21.7, 23.4, 25.3, 26.0, 26.9, 70.1, 121.9, 123.2, 127.6, 128.8, 129.7, 129.8, 133.6, 134.7, 144.7, 145.0, 167.2;

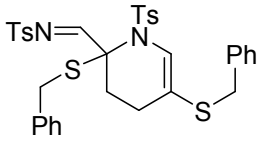
IR ($CH_2Cl_2$) ν 2964, 2924, 2852, 1614, 1596, 1449, 1326, 1160, 1090, 969, 813, 661 $cm^{-1}$; HRMS (ESI) Calcd. for $C_{24}H_{31}N_2O_4S_4$ $(M+H)^+$: 539.1161, found: 539.1168.



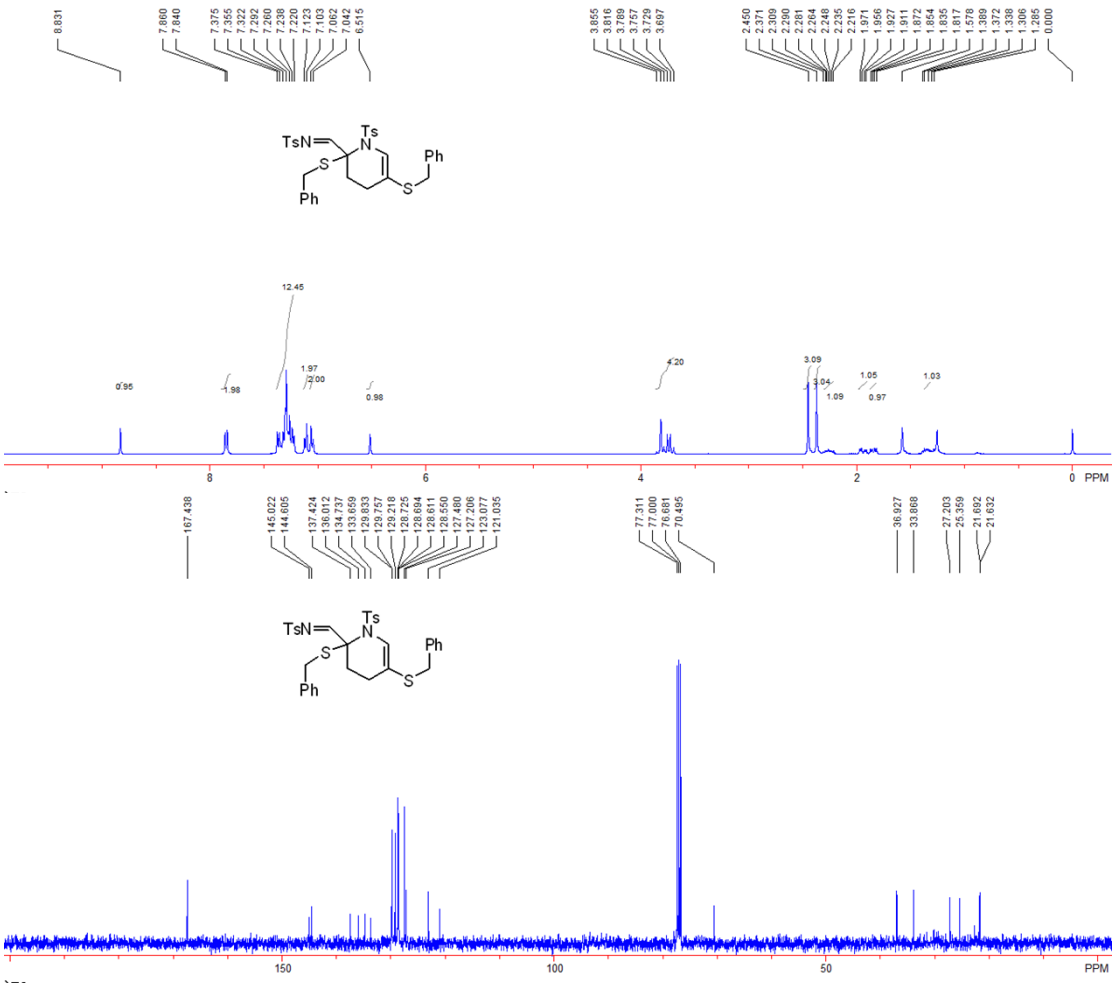



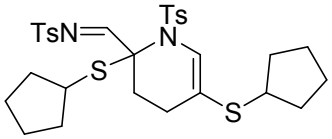

*N*-((2,5-bis(tert-butylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2o**: 55 mg, 91% yield, a white solid; Mp: 146-148 $^oC$; $^1H$ NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24-1.31 (m, 1H), 1.34 (s, 9H), 1.43 (s, 9H), 1.85 (dd, $J_1$ = 6.8 Hz, $J_2$ = 14.8 Hz, 1H), 2.06 (dd, $J_1$ = 6.8 Hz, $J_2$ = 18.4 Hz, 1H), 2.38 (s, 3H), 2.43-2.53 (m, 4H), 6.94 (s, 1H), 7.11 (d, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 8.4 Hz, 2H), 7.41 (d, $J$ = 8.4 Hz, 2H), 7.94 (d, $J$ = 8.4 Hz, 2H), 9.13 (s, 1H); $^{13}C$ NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.7, 28.4, 29.5, 31.6, 32.3, 47.0, 49.2, 71.7, 120.8, 127.7, 129.1, 129.7, 129.8, 131.3, 133.1, 134.7, 144.7, 145.1, 168.1; IR ($CH_2Cl_2$) ν 3057, 2963, 2924, 2864, 1613, 1596, 1327, 1160, 1090, 1042, 813, 734, 659 $cm^{-1}$; HRMS (ESI) Calcd. for $C_{28}H_{39}N_2O_4S_4$ $(M+H)^+$: 595.1787, found: 595.1789.



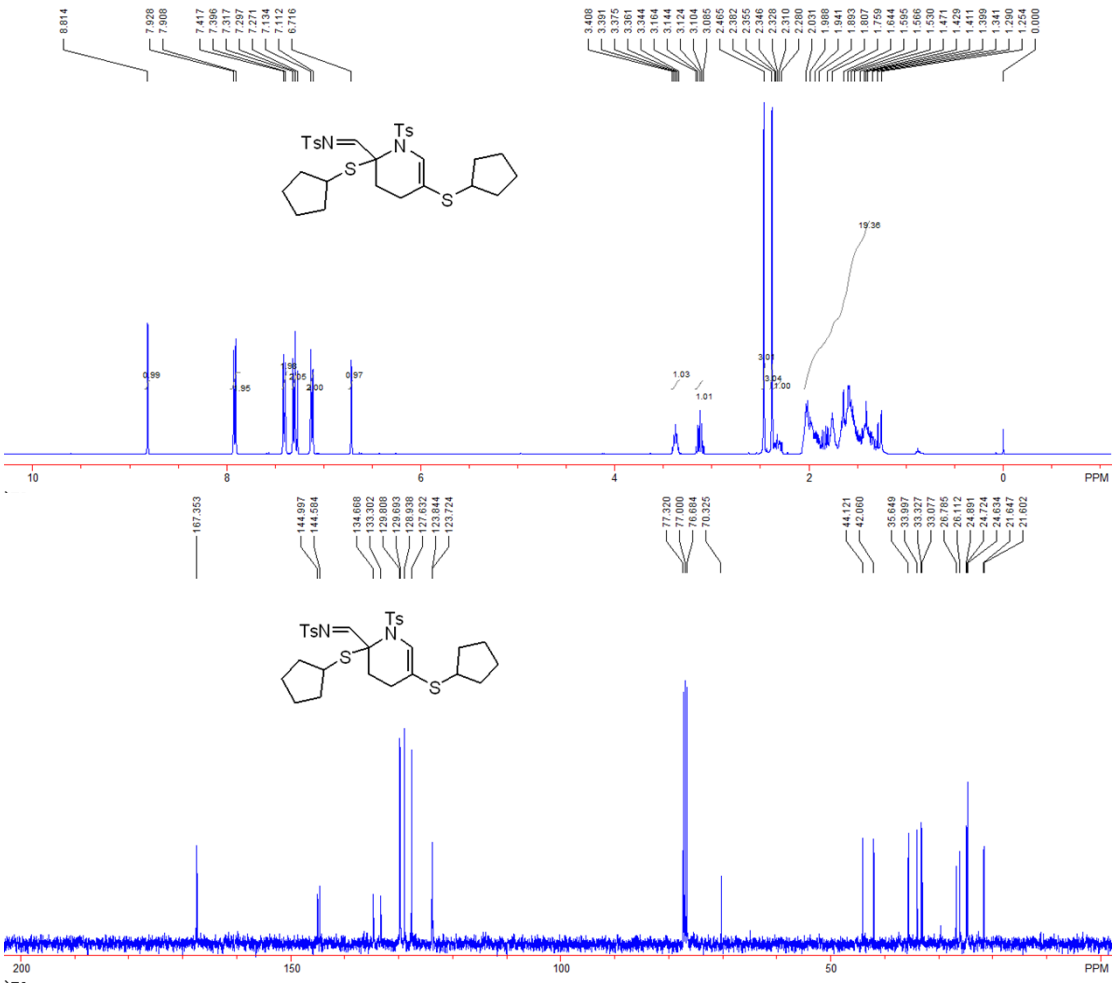



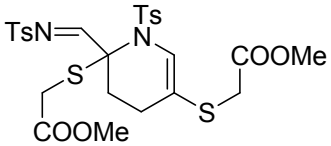

(*Z*)-*N*-((2,5-bis(benzylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2p**: 58 mg, 88% yield, a white solid; Mp: 101-102 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.28-1.58 (m, 1H), 1.84 (dd, $J_1$ = 7.2 Hz, $J_2$ = 14.8 Hz, 1H), 1.92 (dd, $J_1$ = 7.2 Hz, $J_2$ = 18.0 Hz, 1H), 2.21-2.31 (m, 1H), 2.37 (s, 3H), 2.45 (s, 3H), 3.71 (d, $J$ = 12.8 Hz, 1H), 3.77 (d, $J$ = 12.8 Hz, 1H), 3.81-3.86 (m, 2H), 6.52 (s, 1H), 7.05 (d, $J$ = 8.0 Hz, 2H), 7.11 (d, $J$ = 8.0 Hz, 2H), 7.22-7.38 (m, 12H), 7.85 (d, $J$ = 8.0 Hz, 2H), 8.83 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.7, 25.4, 27.2, 33.9, 36.9, 70.5, 121.0, 123.1, 127.2, 127.5, 128.55, 128.61, 128.69, 128.73, 129.2, 129.76, 129.83, 133.7, 134.7, 136.0, 137.4, 144.6, 145.0, 167.4; IR ($CH_2Cl_2$) ν 3054, 2927, 2854, 1614, 1597, 1329, 1264, 1163, 1091, 971, 813, 732, 660 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{34}H_{35}N_2O_4S_4$ $(M+H)^+$: 663.1474, found: 663.1479.



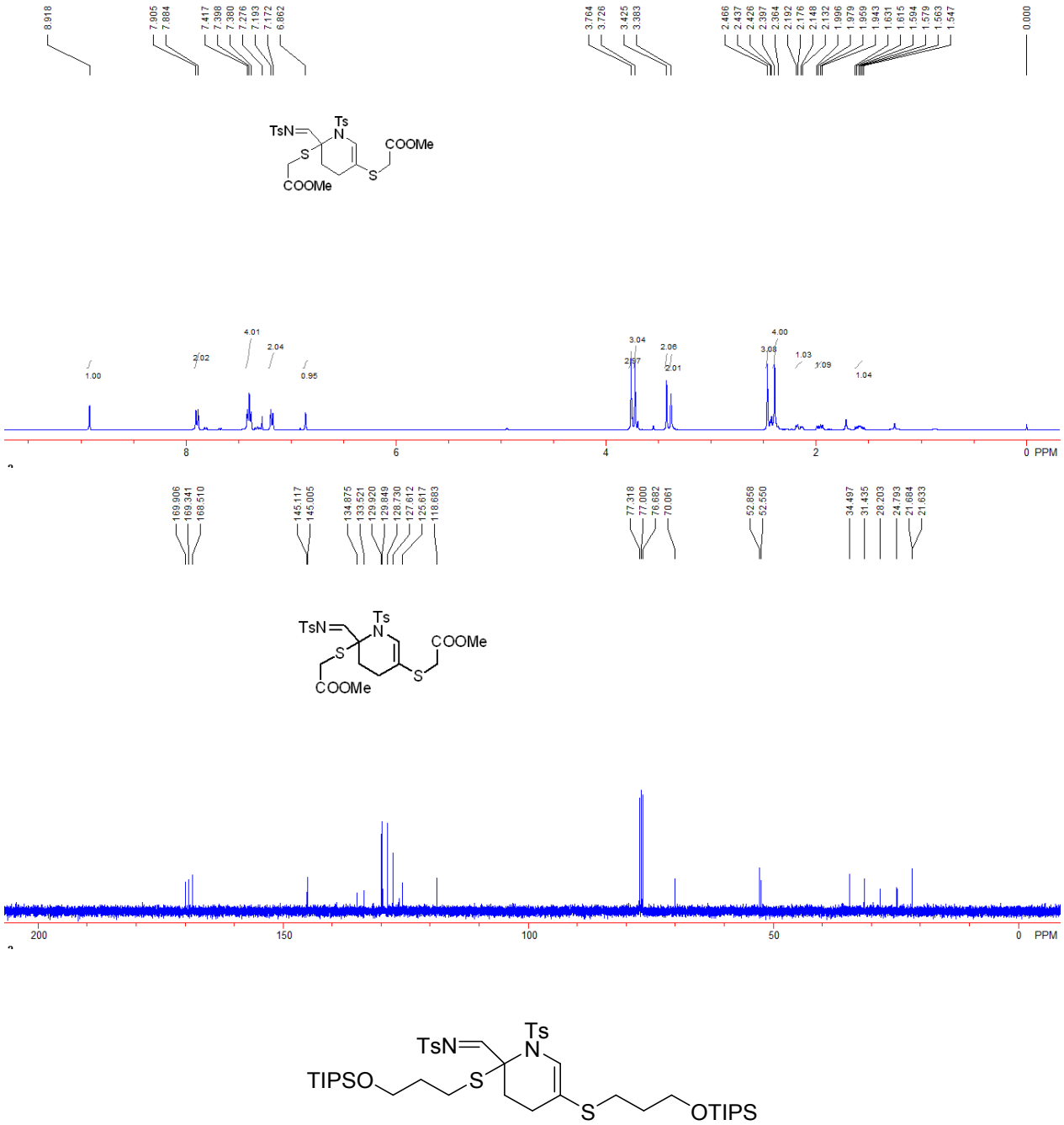

(*Z*)-*N*-((2,5-bis(cyclopentylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2q**: 56 mg, 90% yield, a white solid; Mp: 110-112 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25-2.04 (m, 19H), 2.28-2.36 (m, 1H), 2.38 (s, 3H), 2.47 (s, 3H), 3.08-3.17 (m, 1H), 3.34-3.41 (m, 1H), 6.72 (s, 1H), 7.12 (d, $J$ = 8.0 Hz, 2H), 7.31 (d, $J$ = 8.0 Hz, 2H), 7.41 (d, $J$ = 8.0 Hz, 2H), 7.92 (d, $J$ = 8.0 Hz, 2H), 8.81 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.60, 21.65, 24.6, 24.7, 24.9, 26.1, 26.8, 33.1, 33.3, 34.0, 35.6, 42.1, 44.1, 70.3, 123.7, 123.8, 127.6, 128.9, 129.7, 129.8, 133.3, 134.7, 144.6, 145.0, 167.4; IR ($CH_2Cl_2$) ν 3029, 2955, 2867, 1614, 1596, 1328, 1160, 1090, 1042, 1008, 964, 812, 735, 659 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{30}H_{39}N_2O_4S_4$ $(M+H)^+$: 619.1787, found: 619.1800.



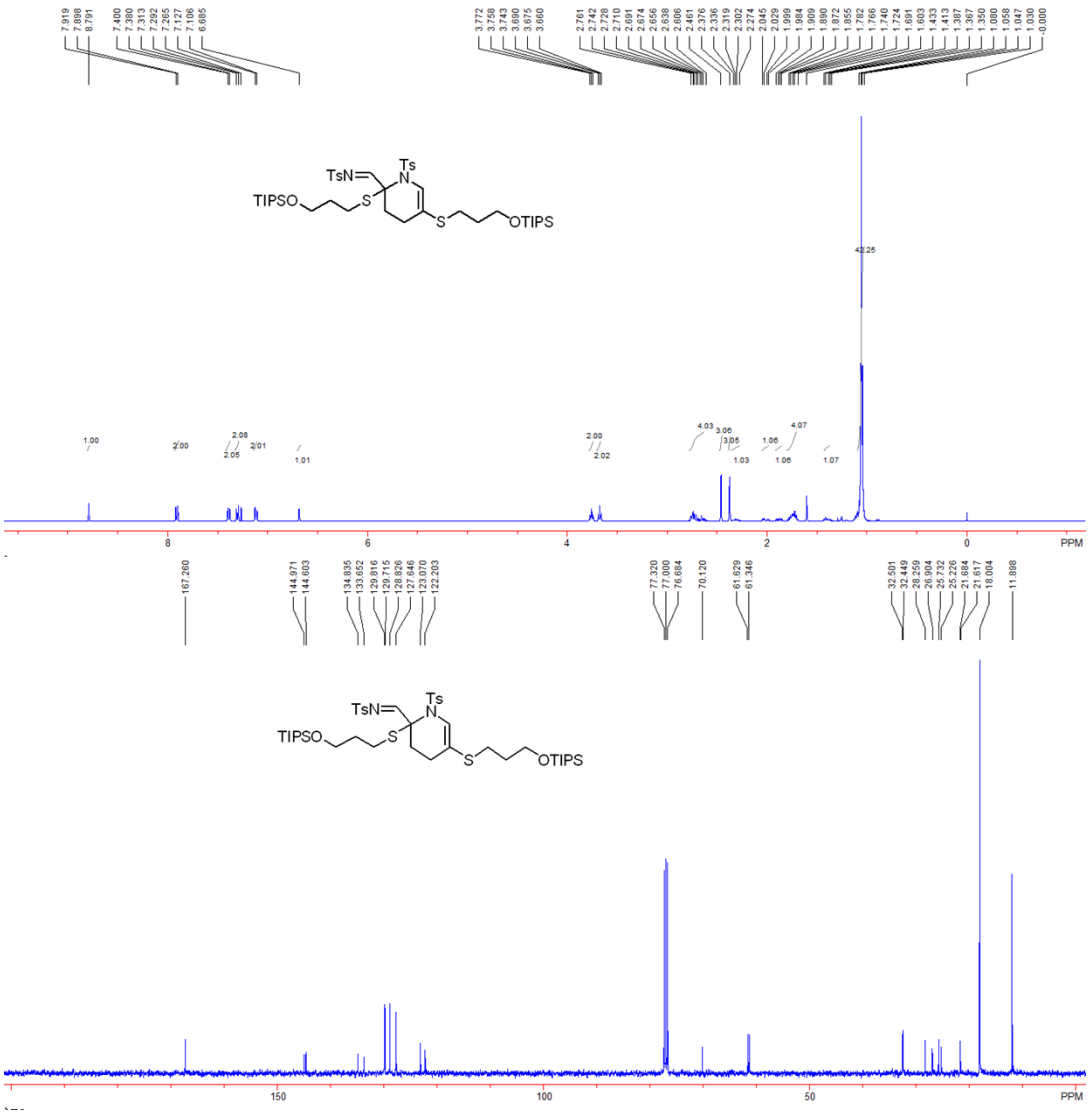



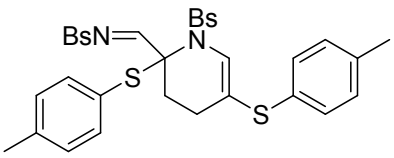

dimethyl 2,2'-((1-tosyl-2-((tosylimino)methyl)-1,2,3,4-tetrahydropyridine-2,5-diyl)bis(sulfanediyl))(*E*)-diacetate **2r**: 52 mg, 83% yield, a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.54-1.64 (m, 1H), 1.97 (dd, $J_1$ = 6.4 Hz, $J_2$ = 14.4 Hz, 1H), 2.16 (dd, $J_1$ = 6.4 Hz, $J_2$ = 14.4 Hz, 1H), 2.36-2.44 (m, 4H), 2.47 (s, 3H), 3.38 (s, 2H), 3.43 (s, 2H), 3.73 (s, 3H), 3.76 (s, 3H), 6.86 (s, 1H), 7.18 (d, $J$ = 8.4 Hz, 2H), 7.39 (d, $J$ = 8.4 Hz, 2H), 7.41 (d, $J$ = 8.4 Hz, 2H), 7.89 (d, $J$ = 8.4 Hz, 2H), 8.92 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.7, 24.8, 28.2, 31.4, 34.5, 52.6, 52.9, 70.1, 118.7, 125.6, 127.6, 128.7, 129.8, 129.9, 133.5, 134.9, 145.0, 145.1, 168.5, 169.3, 169.9; HRMS (ESI) Calcd. for $C_{26}H_{31}N_2O_8S_4$ $(M+H)^+$: 627.0958, found: 627.0960.

*On the basis of their $^{1}$H NMR and Mass spectra, the product **2r** contains trace of impurity, which can not be completely removed from the desired product by silica gel column chromatography.*

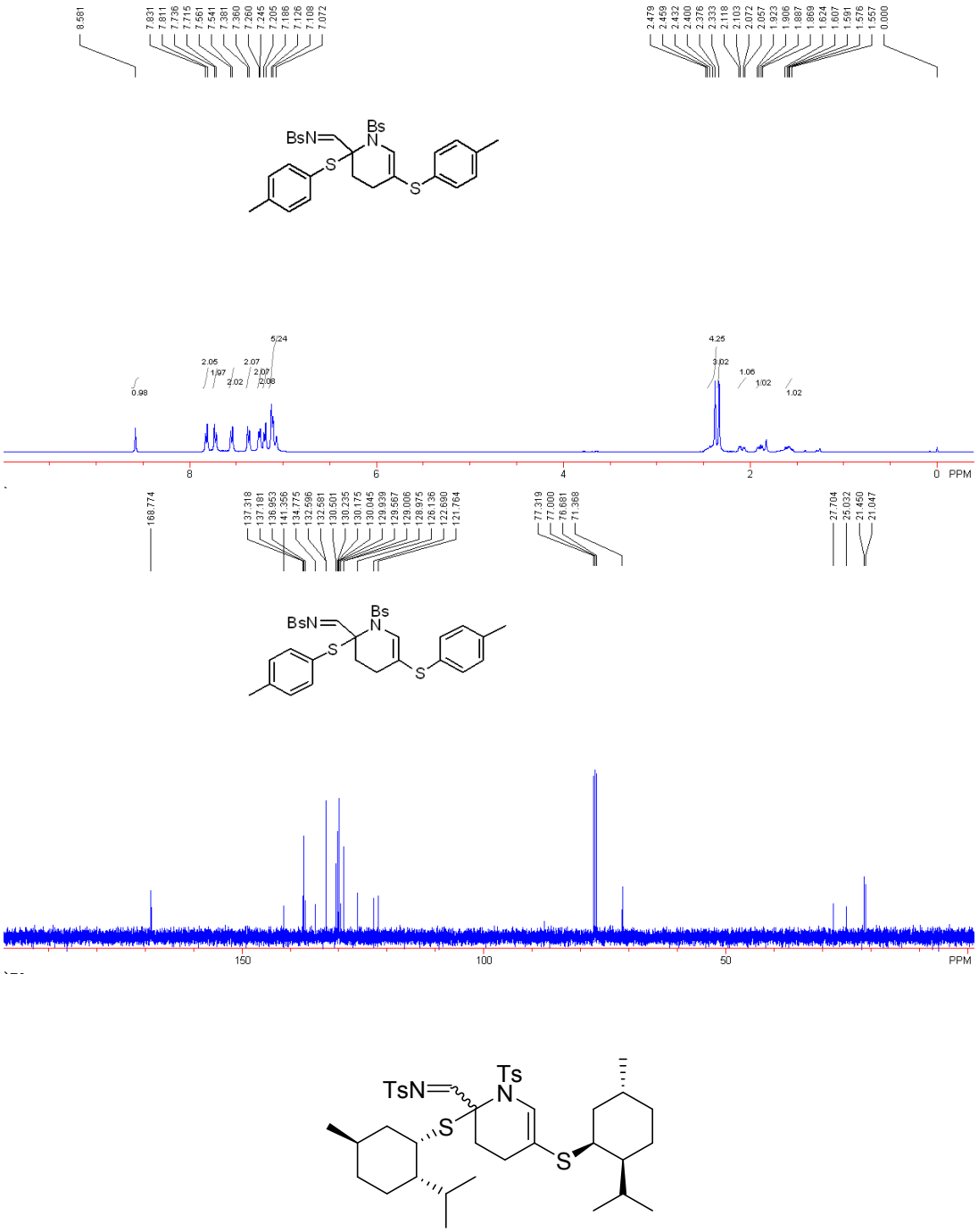



(*Z*)-4-methyl-*N*-((1-tosyl-2,5-bis((3-((triisopropylsilyl)oxy)propyl)thio)-1,2,3,4-tetrahydropyridin-2-yl)methylene)benzenesulfonamide **2s**: 56 mg, 62% yield, a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.03-1.08 (m, 42H), 1.35-1.44 (m, 1H), 1.69-1.79 (m, 4H), 1.85-1.91 (m, 1H), 2.01 (dd, $J_1$ = 6.4 Hz, $J_2$ = 18.4 Hz, 1H), 2.27-2.34 (m, 1H), 2.38 (s, 3H), 2.46 (s, 3H), 2.60-2.77 (m, 4H), 3.68 (t, $J$ = 6.0 Hz, 2H), 3.76 (t, $J$ = 6.0 Hz, 2H), 6.69 (s, 1H), 7.12 (d, $J$ = 8.4 Hz, 2H), 7.30 (d, $J$ = 8.4 Hz, 2H), 7.39 (d, $J$ = 8.4 Hz, 2H), 7.91 (d, $J$ = 8.4 Hz, 2H), 8.79 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 11.9, 18.0, 21.6, 21.7, 25.2, 25.7, 26.9, 28.3, 32.4, 32.5, 61.3, 61.6, 70.1, 122.2, 123.1, 127.6, 128.8, 129.7, 129.8, 133.7, 134.8, 144.6, 145.0, 167.3; IR ($CH_2Cl_2$) ν 2941, 2891, 2864, 1615, 1597, 1463, 1331, 1163, 1093, 1041, 948, 812, 737, 660 cm$^{-1}$; HRMS (DART) Calcd. for $C_{44}H_{75}N_2O_6S_4Si_2$ $(M+H)^+$: 911.4041, found: 911.4045.



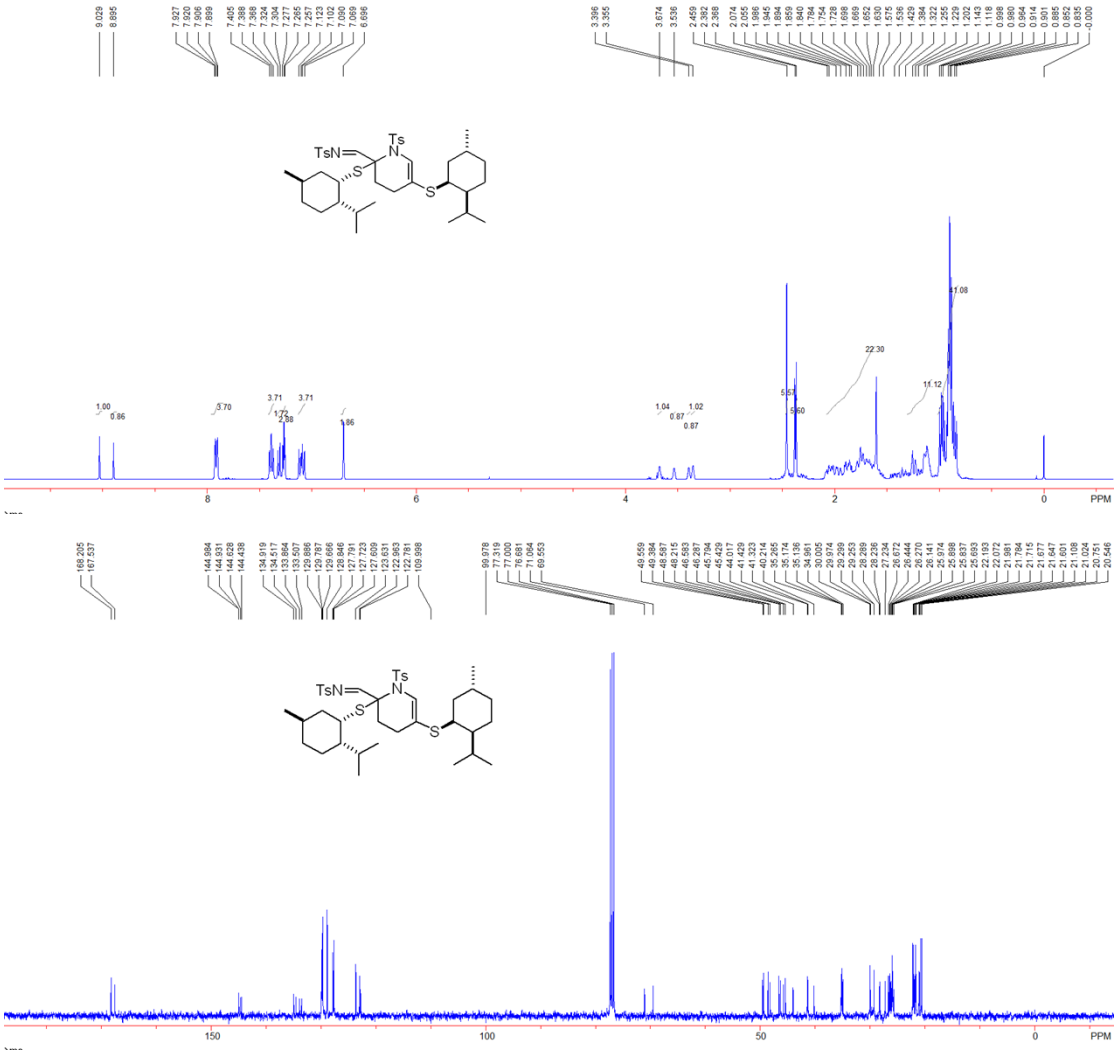



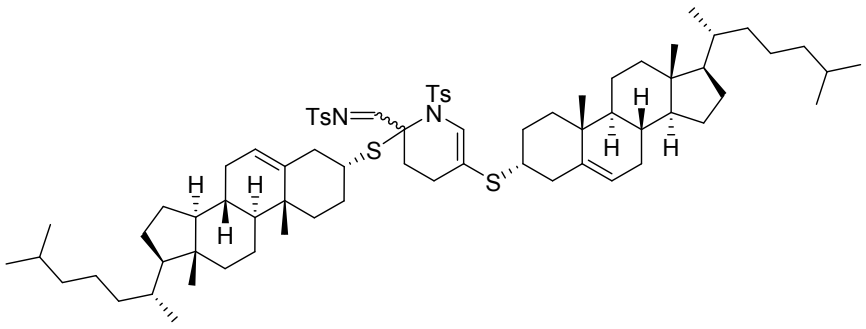

4-bromo-*N*-((1-(4-bromophenylsulfonyl)-2,5-bis(*p*-tolylthio)-1,2,3,4-tetrahydropyridin-2-yl)methylene)benzenesulfonamide **2t**: 66 mg, 83% yield, a white solid; Mp: 109-111 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.55-1.63 (m, 1H), 1.90 (dd, $J_1$ = 6.4 Hz, $J_2$ = 14.4 Hz, 1H), 2.09 (dd, $J_1$ = 6.4 Hz, $J_2$ = 18.4 Hz, 1H), 2.33 (s, 3H), 2.37-2.48 (m, 4H), 7.07-7.26 (m, 9H), 7.37 (d, $J$ = 8.0 Hz, 2H), 7.55 (d, $J$ = 8.0 Hz, 2H), 7.73 (d, $J$ = 8.0 Hz, 2H), 7.82 (d, $J$ = 8.0 Hz, 2H), 8.58 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 21.5, 25.0, 27.7, 71.4, 121.8, 122.7, 126.1, 128.98, 129.01, 129.6, 129.9, 130.0, 130.18, 130.24, 130.5, 132.58, 132.60, 134.8, 137.0, 137.2, 137.3, 141.4, 168.8; IR ($CH_2Cl_2$) ν 3089, 2922, 2852, 1615, 1573, 1349, 1163, 1087, 1010, 965, 803, 660 cm$^{-1}$; HRMS (ESI) Calcd. For $C_{32}H_{29}Br_2N_2O_4S_4$ $(M+H)^+$: 790.9371, found: 790.9371.




*N*-((*Z*)-(2,5-bis(((1*S*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2u**: 68 mg, 89% yield, **d.r.** = 1:0.86; a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.83-1.00 (m, 40.92H), 1.11-1.43 (m, 11.16H), 1.53-2.08 (m, 22.32H), 2.37 (s, 3H), 2.38 (s, 2.58H), 2.46 (s, 5.58H), 3.36 (s, 1H), 3.40 (s, 0.86H), 3.54 (s, 0.86H), 3.67 (s, 1H), 6.70 (s, 1.86H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.11(d, *J* = 8.4 Hz, 1.72H), 7.25-7.28 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 1.72H), 7.36-7.41 (m, 3.72H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.92 (d, *J* = 8.4 Hz, 1.72H), 8.90 (s, 0.86H), 9.03 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.5, 20.8, 21.0, 21.1, 21.6, 21.65, 21.68, 21.7, 21.8, 22.0, 22.1, 22.2, 25.7, 25.8, 25.9, 26.0, 26.1, 26.3, 26.4, 26.7, 27.2, 28.2, 28.3, 29.2, 29.3, 29.97, 30.01, 35.0, 35.1, 35.2, 35.3, 40.2,

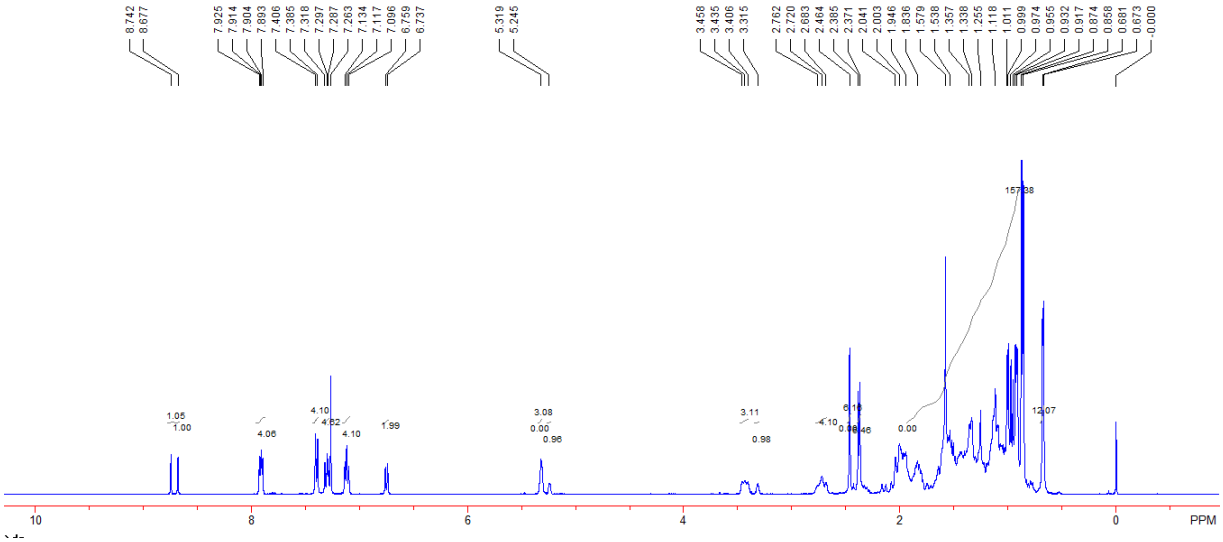
41.3, 41.4, 44.0, 45.4, 45.8, 46.3, 46.6, 48.2, 48.6, 49.4, 49.6, 69.6, 71.1, 100.0, 110.0, 122.8, 123.0, 123.6, 127.6, 127.7, 127.8, 128.8, 129.7, 129.8, 129.9, 133.5, 133.9, 134.5, 134.9, 144.4, 144.6, 144.9, 145.0, 167.5, 168.2; IR ($CH_2Cl_2$) ν 2947, 2923, 2869, 1613, 1597, 1330, 1163, 1091, 1042, 968, 812, 661 $cm^{-1}$; HRMS (ESI) Calcd. For $C_{40}H_{59}N_2O_4S_4$ $(M+H)^+$: 759.3352, found: 759.3353.

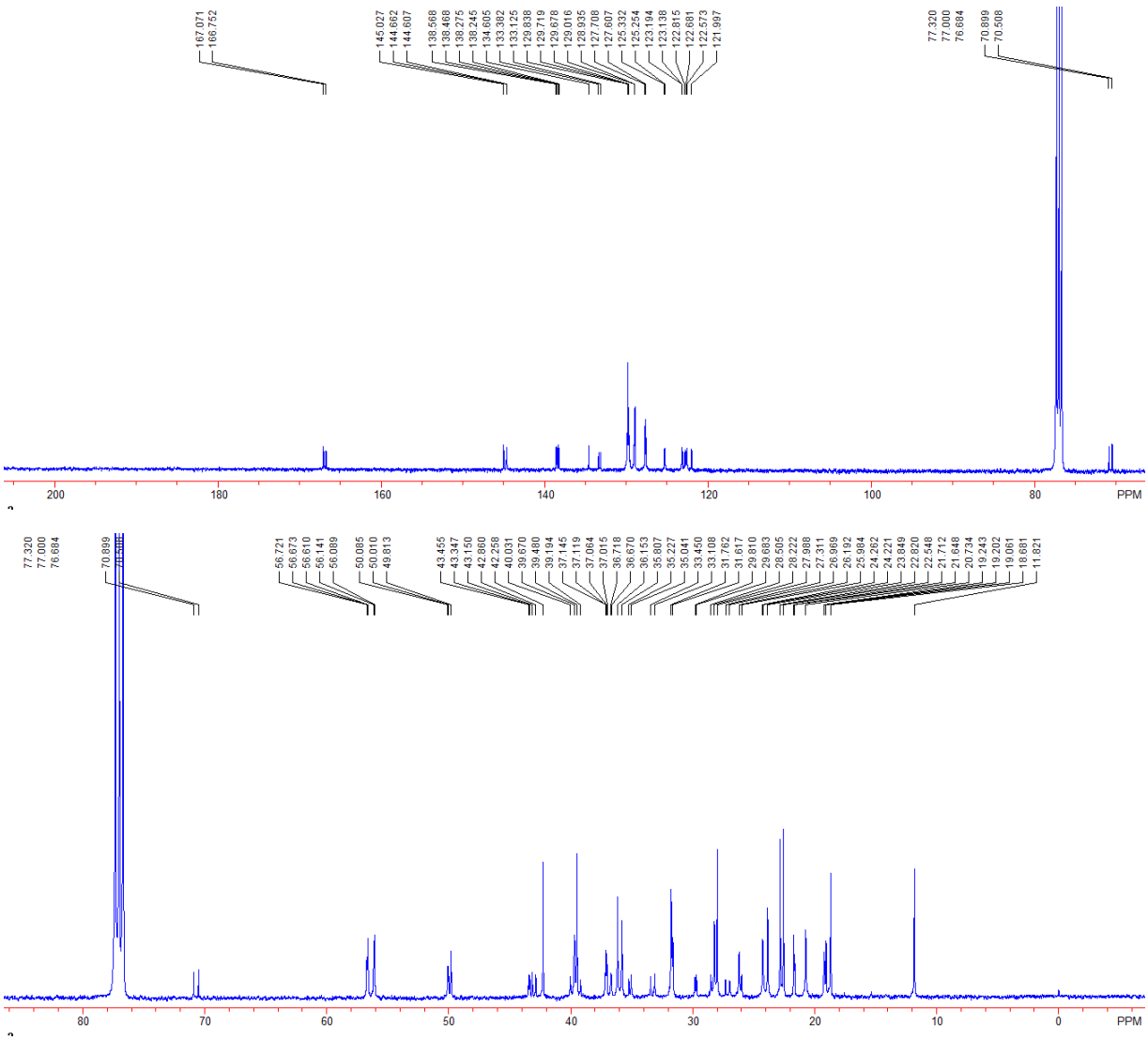


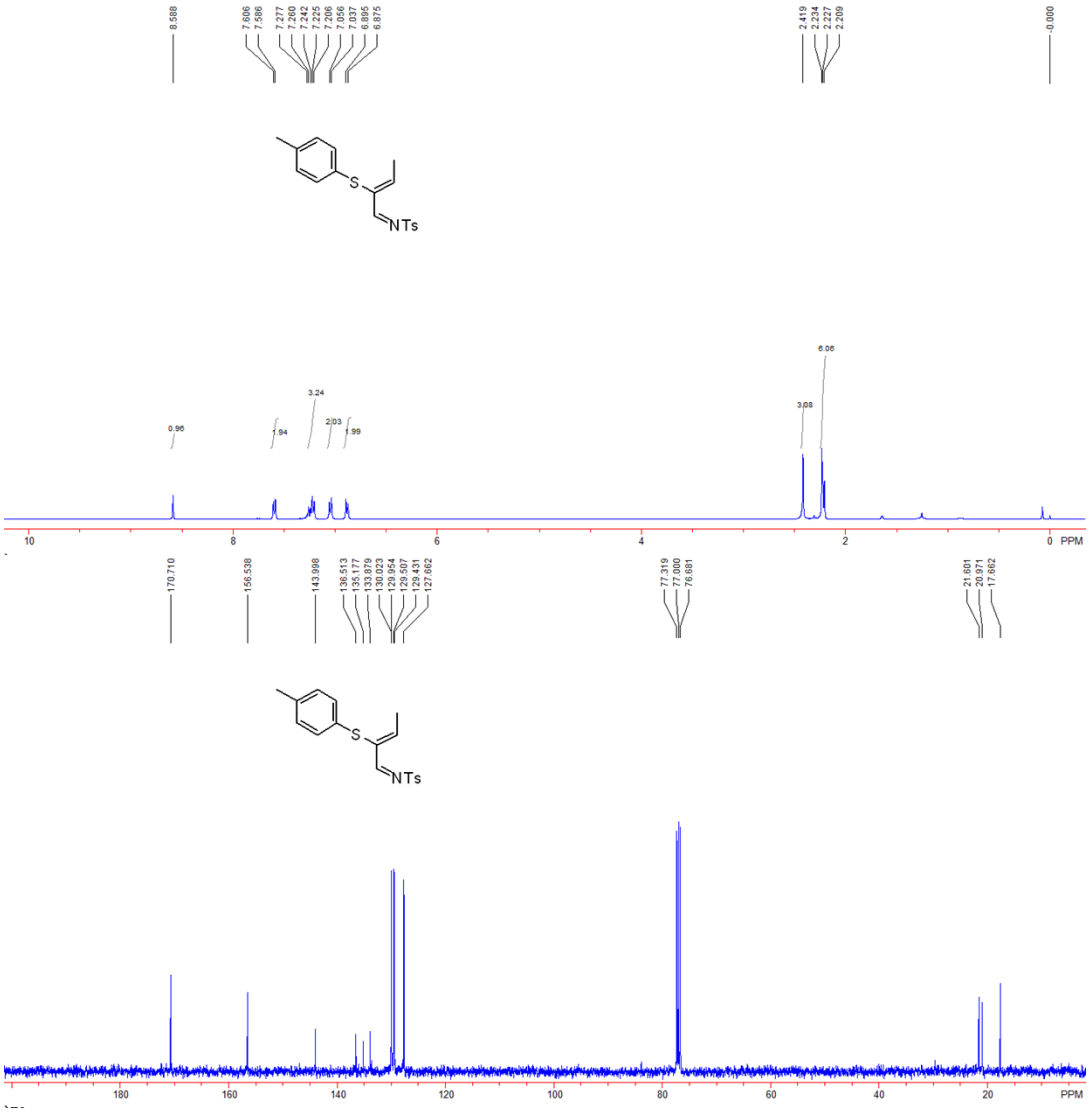

*N*-((2-(((3*R*,8*R*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*S*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)thio)-5-(((3*R*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*S*)-6-methylheptan-2-yl)-

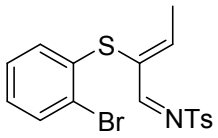
2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl)thio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)methylene)-4-methylbenzenesulfonamide **2v**: 102 mg, 84% yield, **d.r.** = 1:1; a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.67 (s, 6H), 0.68 (s, 6H), 0.85-2.05 (m, 156H), 2.37 (s, 3H), 2.39 (s, 3H), 2.46 (s, 6H), 2.68-2.76 (m, 4H), 3.32 (s, 1H), 3.40-3.46 (m, 3H), 5.25 (s, 1H), 5.32 (s, 3H), 6.74 (s, 1H), 6.76 (s, 1H), 7.09-7.14 (m, 4H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 4H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 8.68 (s, 1H), 8.74 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 11.8, 18.7, 19.1, 19.20, 19.24, 20.7, 21.6, 21.7, 22.5, 22.8, 23.8, 24.2, 24.3, 26.0, 26.2, 27.0, 27.3, 28.0, 28.2, 28.5, 29.7, 29.8, 31.6, 31.8, 33.1, 33.5, 35.0, 35.2, 35.8, 36.2, 36.67, 36.72, 37.02, 37.06, 37.12, 37.15, 39.2, 39.5, 39.7, 40.0, 42.3, 42.9, 43.2, 43.3, 43.5, 49.8, 50.0, 50.1, 56.09, 56.14, 56.61, 56.67, 56.72, 70.5, 70.9, 122.0, 122.6, 122.7, 122.8, 123.1, 123.2, 125.25, 125.33, 127.6, 127.7, 128.9, 129.0, 129.68, 129.72, 129.8, 133.1, 133.4, 134.6, 138.2, 138.3, 138.5, 138.6, 144.6, 144.7, 145.0, 166.8, 167.1; IR ($CH_2Cl_2$) ν 2932, 2867, 1613, 1597, 1347, 1163, 1091, 909, 812, 734, 660 cm$^{-1}$; HRMS (ESI) Calcd. For $C_{74}H_{111}N_2O_4S_4$ $(M+H)^+$: 1219.7421, found: 1219.7430.



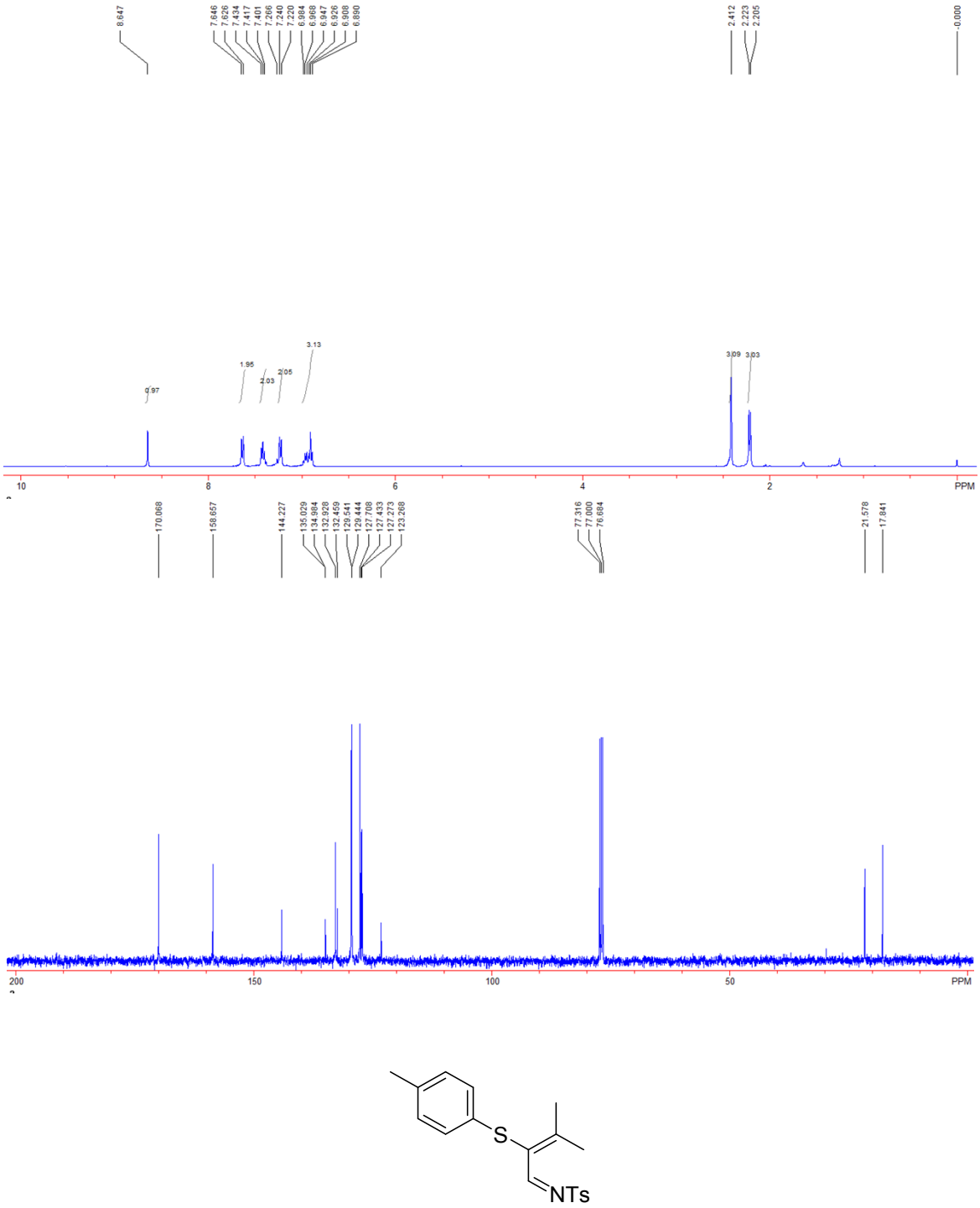



4-methyl-*N*-((1*E*,2*Z*)-2-(*p*-tolylthio)but-2-en-1-ylidene)benzenesulfonamide **4a**: 56 mg, 81% yield, a yellow solid; Mp: 94-96 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.22 (d, $J$ = 7.2 Hz, 3H), 2.23 (s, 3H), 2.42 (s, 3H), 6.89 (d, $J$ = 8.0 Hz, 2H), 7.05 (d, $J$ = 8.0 Hz, 2H), 7.22 (d, $J$ = 8.0 Hz, 2H), 7.26 (t, $J$ = 7.2 Hz, 1H), 7.60 (d, $J$ = 8.0 Hz, 2H), 8.59 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 17.7, 21.0, 21.6, 127.7, 129.4, 129.5, 129.95, 130.02, 133.9, 135.2, 136.5, 144.0, 156.5, 170.7; IR ($CH_2Cl_2$) ν 3023, 2922, 2867, 1594, 1571, 1320, 1305, 1156, 1118, 968, 805, 709, 660 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{18}H_{20}NO_2S_2$ $(M+H)^+$: 346.0930, found: 346.0941.



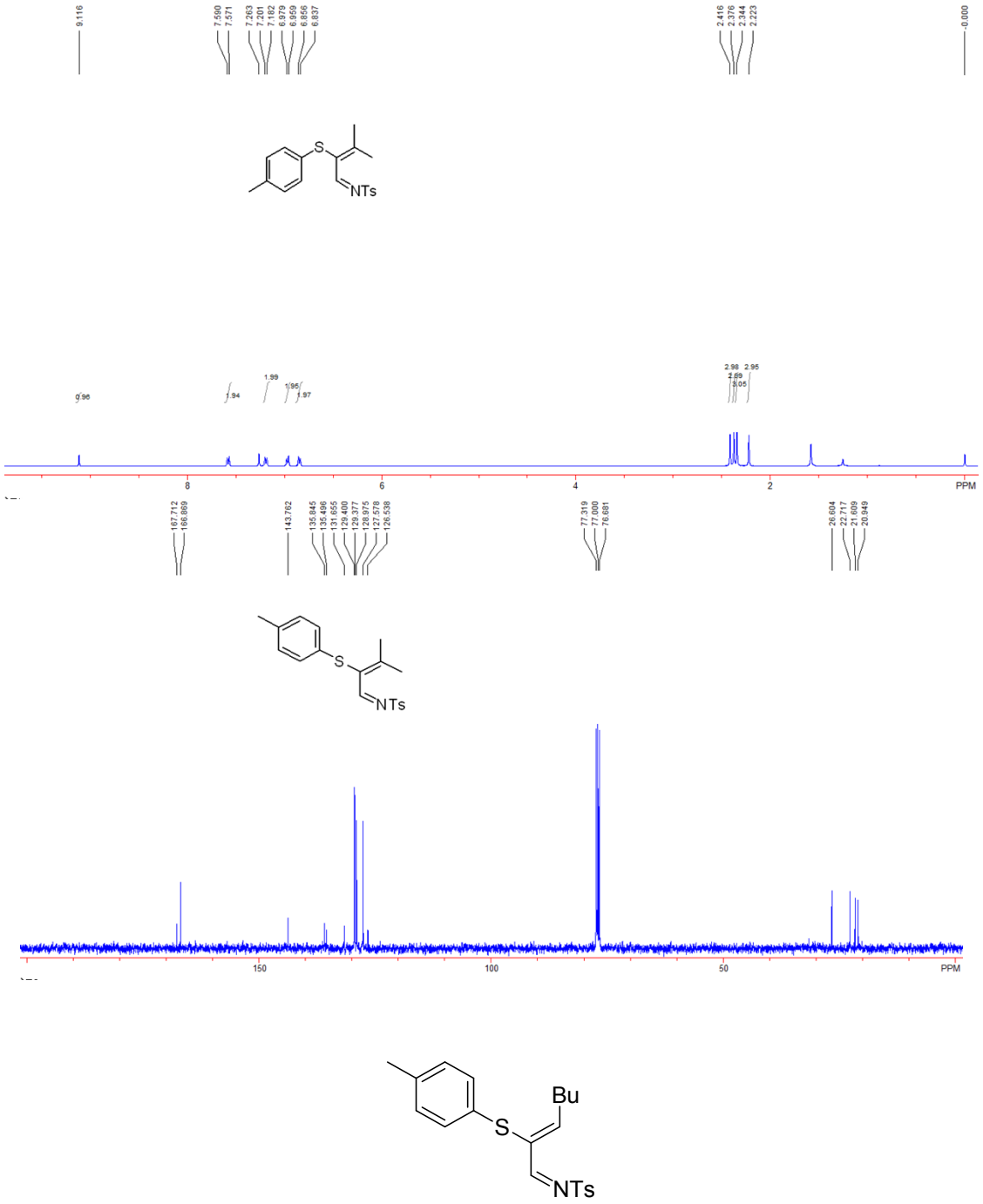

2-((2-bromophenyl)thio)but-2-en-1-ylidene)-4-methylbenzenesulfonamide **4b**: 70 mg, 85% yield, a yellow solid; Mp: 88-90 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.21 (d, $J$ = 7.2 Hz, 3H), 2.41 (s, 3H), 6.89-6.99 (m, 3H), 7.23 (d, $J$ = 8.0 Hz, 2H), 7.42 (t, $J$ = 7.2 Hz, 2H), 7.64 (d, $J$ = 8.0 Hz, 2H), 8.65 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 17.8, 21.6, 123.3, 127.3, 127.4, 127.7, 129.4, 129.5, 132.5, 132.9, 134.98, 135.03, 144.2, 158.7, 170.1; IR ($CH_2Cl_2$) ν 3059, 2922, 2850, 1594, 1573, 1320, 1155, 1088, 1018, 964, 787, 746, 658 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{17}H_{17}BrNO_2S_2$ $(M+H)^+$: 409.9879, found: 409.9882.



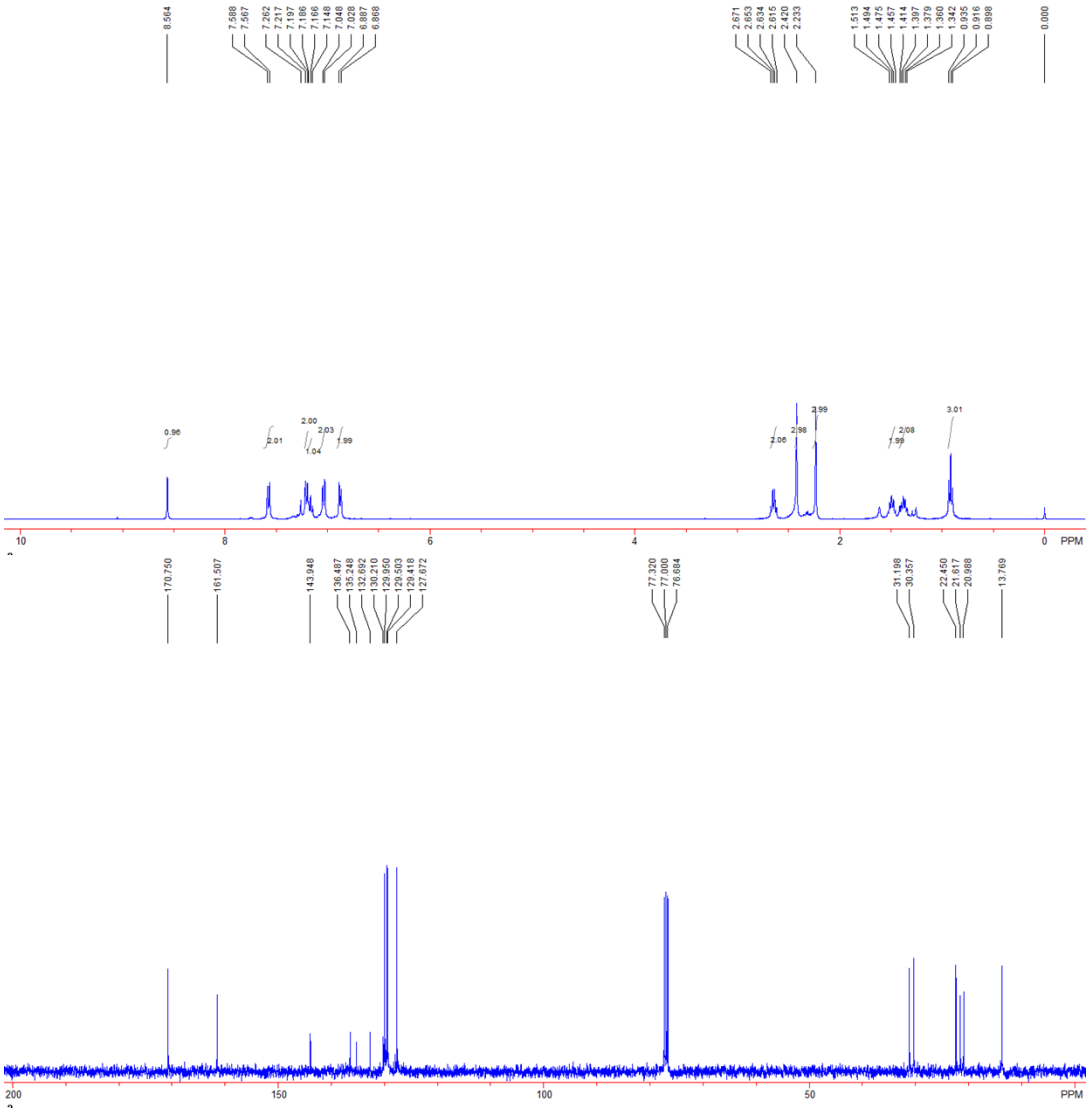




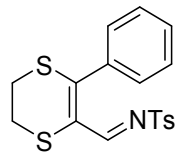
4-methyl-*N*-(3-methyl-2-(*p*-tolylthio)but-2-en-1-ylidene)benzenesulfonamide **4c**: 60 mg, 84% yield, a yellow solid; Mp: 94-96 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.22 (s, 3H), 2.34 (s, 3H), 2.38 (s, 3H), 2.42 (s, 3H), 6.85 (d, $J$ = 8.0 Hz, 2H), 6.97 (d, $J$ = 8.0 Hz, 2H), 7.19 (d, $J$ = 8.0 Hz, 2H), 7.58 (d, $J$ = 8.0 Hz, 2H), 9.12 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 20.9, 21.6, 22.7, 26.6, 126.5, 127.6, 129.0, 129.38, 129.40, 131.7, 135.5, 135.8, 143.8, 166.9, 167.7; IR ($CH_2Cl_2$) ν 3019, 2923, 2854, 1579, 1319, 1156, 1089, 887, 805, 776, 658 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{19}H_{22}NO_2S_2$ $(M+H)^+$: 360.1086, found: 360.1104.



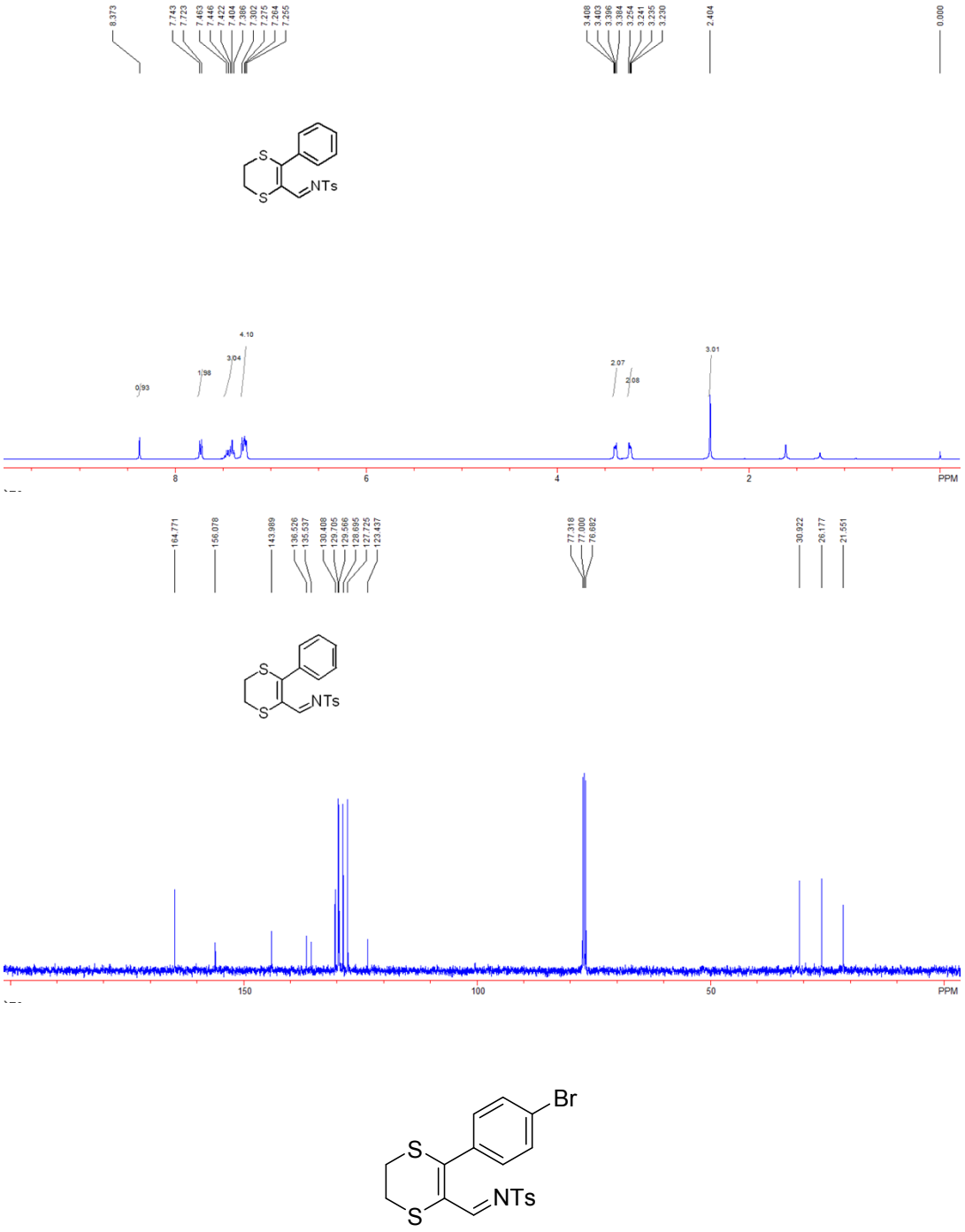

4-methyl-*N*-((1*E*,2*Z*)-2-(p-tolylthio)hept-2-en-1-ylidene)benzenesulfonamide **4d**: 58 mg, 75% yield, a yellow solid; Mp: 79-81 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.34-1.42 (m, 2H), 1.46-1.51 (m, 2H), 2.23 (s, 3H), 2.42 (s, 3H), 2.61-2.68 (m, 2H), 6.88 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 8.56 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 21.0, 21.6, 22.5, 30.4, 31.2, 127.7, 129.4, 129.5, 130.0, 130.2, 132.7, 135.2, 136.5, 143.9, 161.5, 170.8; IR ($CH_2Cl_2$) ν 2956, 2924, 2859, 1589, 1491, 1319, 1156, 1088, 954, 805, 660 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{21}H_{26}NO_2S_2$ $(M+H)^+$: 388.1399, found: 388.1407.







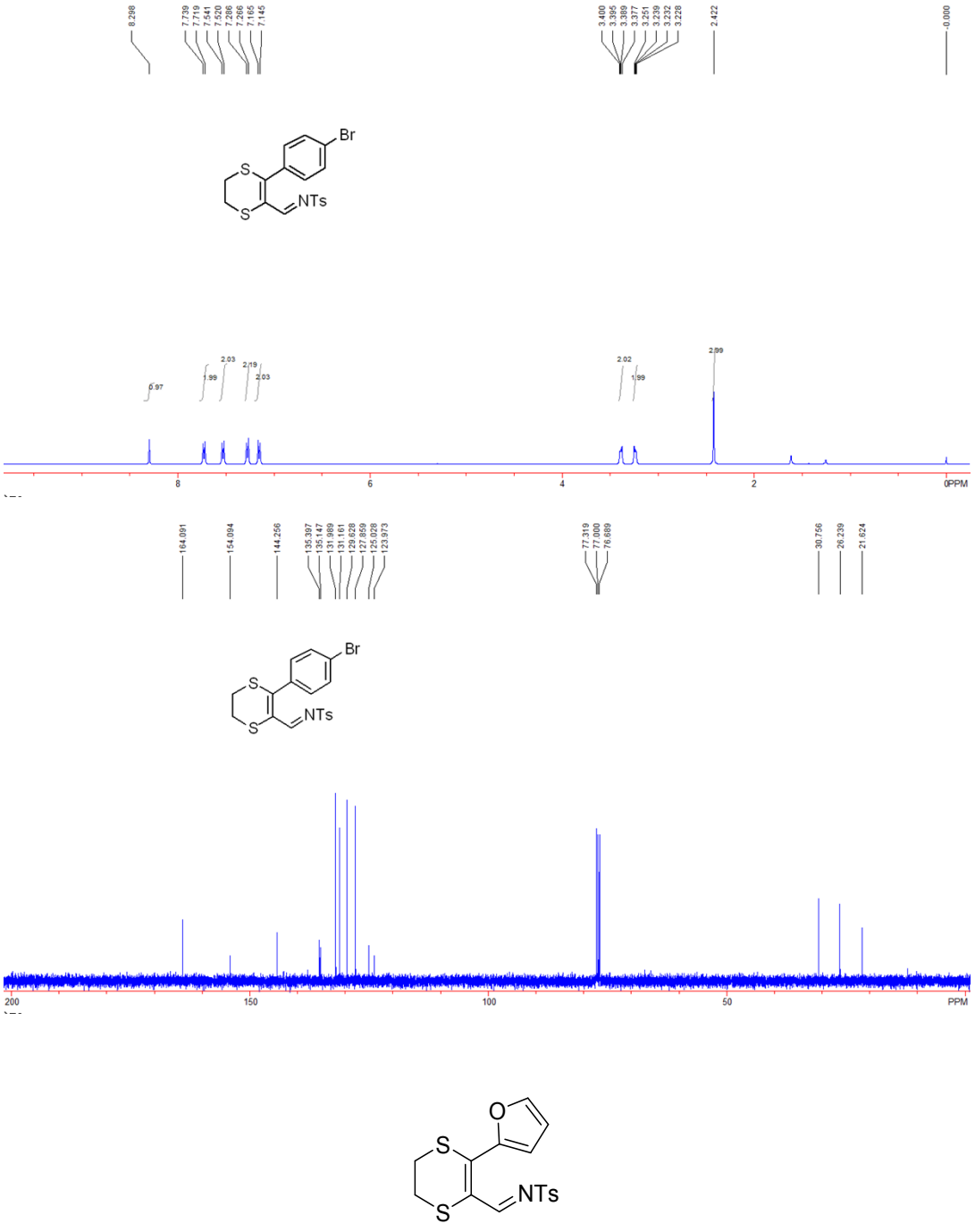

4-methyl-*N*-((3-phenyl-5,6-dihydro-1,4-dithiin-2-yl)methylene)benzenesulfonamide **4e**: 62 mg, 82% yield, a yellow solid; Mp: 181-183 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.40 (s, 3H), 3.23-3.26 (m, 2H), 3.38-3.41 (m, 2H), 7.25-7.31 (m, 4H), 7.38-7.47 (m, 3H), 7.73 (d, $J$ = 8.0 Hz, 2H), 8.37 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 26.2, 30.9, 123.4, 127.7, 128.7, 129.6, 129.7, 130.4, 135.5, 136.5, 144.0, 156.1, 164.8; IR ($CH_2Cl_2$) ν 3358, 1537, 1510, 1315, 1150, 1086, 954, 834, 770, 660 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{18}H_{18}NO_2S_3$ $(M+H)^+$: 376.0494, found: 376.0504.



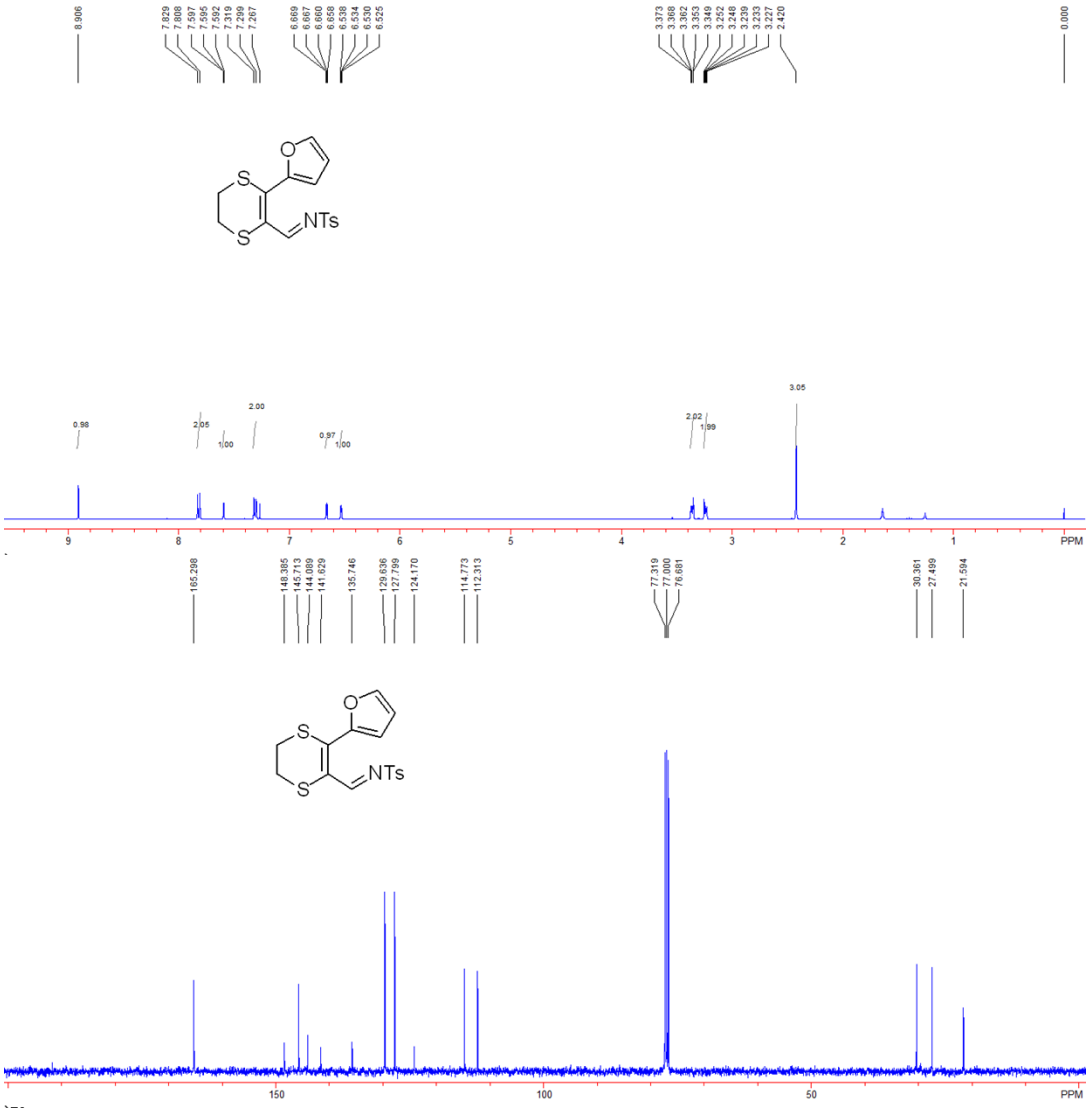




*N*-((3-(4-bromophenyl)-5,6-dihydro-1,4-dithiin-2-yl)methylene)-4-methylbenzenesulfonamide **4f**: 74 mg, 82% yield, a yellow solid; Mp: 182-184 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.42 (s, 3H), 3.22-3.36 (m, 2H), 3.37-3.40 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 8.30 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 26.2, 30.8, 124.0, 125.0, 127.9, 129.6, 131.2, 132.0, 135.1, 135.4, 144.3, 154.1, 164.1; IR ($CH_2Cl_2$) ν 3062, 2923, 2849, 1547, 1511, 1317, 1232, 1152, 1086, 1010, 814, 765, 687 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{18}H_{17}BrNO_2S_3$ $(M+H)^+$: 453.9599, found: 453.9611.




*N*-((3-(furan-2-yl)-5,6-dihydro-1,4-dithiin-2-yl)methylene)-4-methylbenzenesulfonamide **4g**: 56 mg, 77% yield, a yellow solid; Mp: 158-160 $^{o}$C; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.42 (s, 3H), 3.23-3.36 (m, 2H), 3.34-3.38 (m, 2H), 6.53 (dd, $J_1$ = 2.0 Hz, $J_2$ = 3.6 Hz, 1H), 6.66 (dd, $J_1$ = 0.8 Hz, $J_2$ = 3.6 Hz, 1H), 7.31 (d, $J$ = 8.0 Hz, 2H), 7.60 (dd, $J_1$ = 0.8 Hz, $J_2$ = 2.0 Hz, 1H), 7.82 (d, $J$ = 8.0 Hz, 2H), 8.91 (s, 1H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 27.5, 30.4, 112.3, 114.8, 124.2, 127.8, 129.6, 135.7, 141.6, 144.1, 145.7, 148.4, 165.3; IR ($CH_2Cl_2$) ν 3121, 2923, 2849, 1738, 1532, 1499, 1314, 1250, 1153, 1083, 805, 740, 683 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{16}H_{16}NO_3S_3$ $(M+H)^+$: 366.0287, found: 366.0299.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7.829
7.808
7.597
7.595
7.592
7.319
7.299
7.267
6.669
6.667
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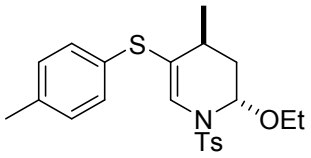
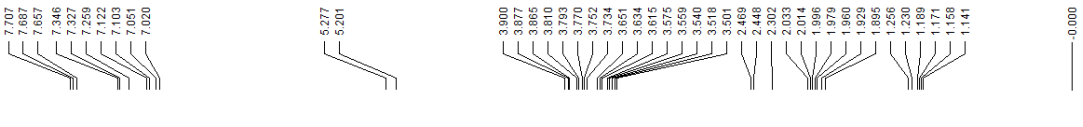
6.538
6.534
6.530
6.525
3.373
3.368
3.362
3.353
3.349
3.252
3.246
3.239
3.233
3.227
2.420
0.000
O
S
S
NTs
0.98
2.05
1.00
2.00
0.97
1.00
2.02
1.99
3.05
9
8
7
6
5
4
3
2
1
PPM
165.298
148.365
145.773
144.089
141.629
135.746
129.636
127.799
124.170
114.773
112.313
77.319
77.000
76.681
30.361
27.499
21.594
O
S
S
NTs
150
100
50
PPM

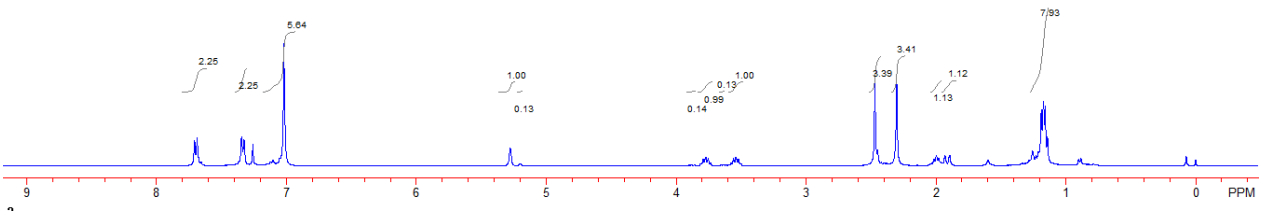
**General procedure and spectroscopic data of 5a:**

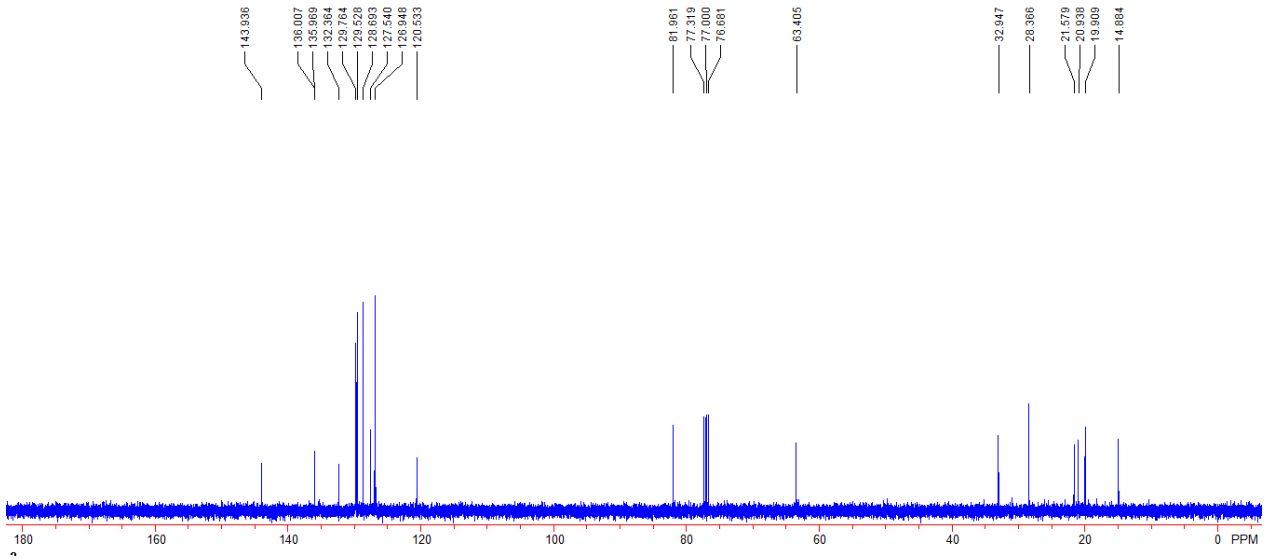
To a solution of 4-methyl-*N*-((1*E*,2*Z*)-2-(p-tolylthio)but-2-en-1-ylidene)benzenesulfonamide **4a** (0.10 mmol) in 1.0 mL of 1,2-dichloroethane was added ethoxyethene (0.30 mmol), the resulting solution was stirred at 120 °C for 6 hours and then the mixture was concentrated in vacuo. The residue was purified by flash column chromatography on silica gel chromatography (eluent: petroleum ether:EtOAc = 12:1) to give compound **5a** (1:0.13 d.r.). Its spectra include the very small signals of another diastereoisomer at the aromatic region, 5.2 ppm, 3.9 ppm and 2.4-2.5 ppm.




2-ethoxy-4-methyl-5-(*p*-tolylthio)-1-tosyl-1,2,3,4-tetrahydropyridine **5a**: 68 mg, 82% yield, **d.r.** = 1:0.13; a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.14-1.26 (m, 7.91H), 1.89-1.93 (m, 1.13H), 1.96-2.04 (m, 1.13H), 2.30 (s, 3.39H), 2.45 (s, 0.39H), 2.47 (s, 3H), 3.50-3.58 (m, 1H), 3.61-3.66 (m, 0.13H), 3.73-3.81 (m, 1H), 3.86-3.90 (m, 0.13H), 5.20 (s, 0.13H), 5.28 (s, 1H), 7.02-7.13 (m, 5.65H), 7.34 (d, *J* = 8.0 Hz, 2.26H), 7.65-7.71 (m, 2.26H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.9, 19.9, 20.9, 21.6, 28.4, 32.9, 63.4, 82.0, 120.5, 126.9, 127.5, 128.7, 129.5, 129.8, 132.4, 135.97, 136.01, 143.9; IR ($CH_2Cl_2$) ν 2972, 2927, 2874, 1625, 1361, 1169, 1106, 940, 807, 667 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{22}H_{28}NO_3S_2$ $(M+H)^+$: 418.1505, found: 418.1502.

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136.007
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132.364
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81.961
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77.000
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63.405
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120
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60
40
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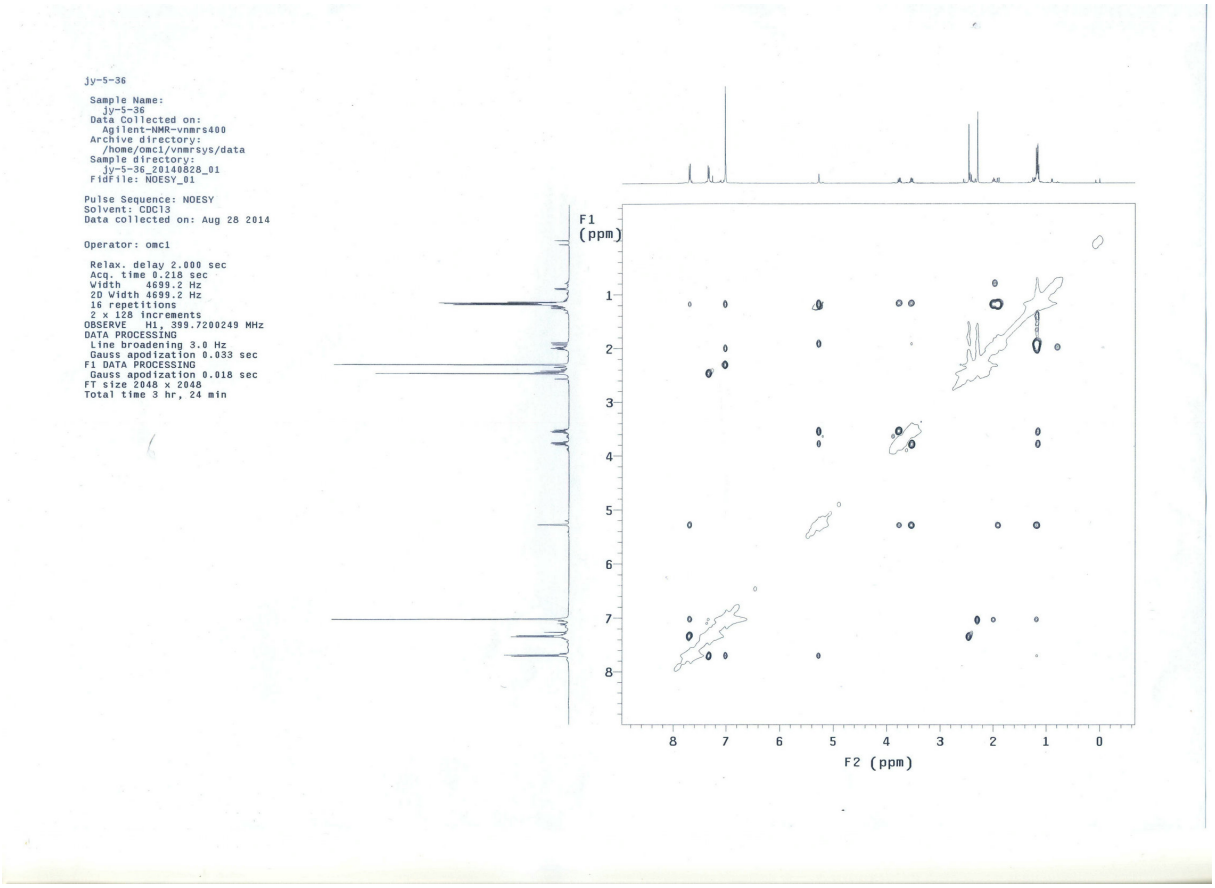
0 PPM


jy-5-36
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jy-5-36
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/omc1/vnmrsys/data
Sample directory:
jy-5-36_20140828_01
FidFile: NOESY_01
Pulse Sequence: NOESY
Solvent: CDCl3
Data collected on: Aug 28 2014
Operator: omc1
Relax. delay 2.000 sec
Acq. time 0.218 sec
Width 4699.2 Hz
2D Width 4699.2 Hz
16 repetitions
2 x 128 increments
OBSERVE H1, 399.7200249 MHz
DATA PROCESSING
Line broadening 3.0 Hz
Gauss apodization 0.033 sec
F1 DATA PROCESSING
Gauss apodization 0.018 sec
FT size 2048 x 2048
Total time 3 hr, 24 min
F1 (ppm)
F2 (ppm)

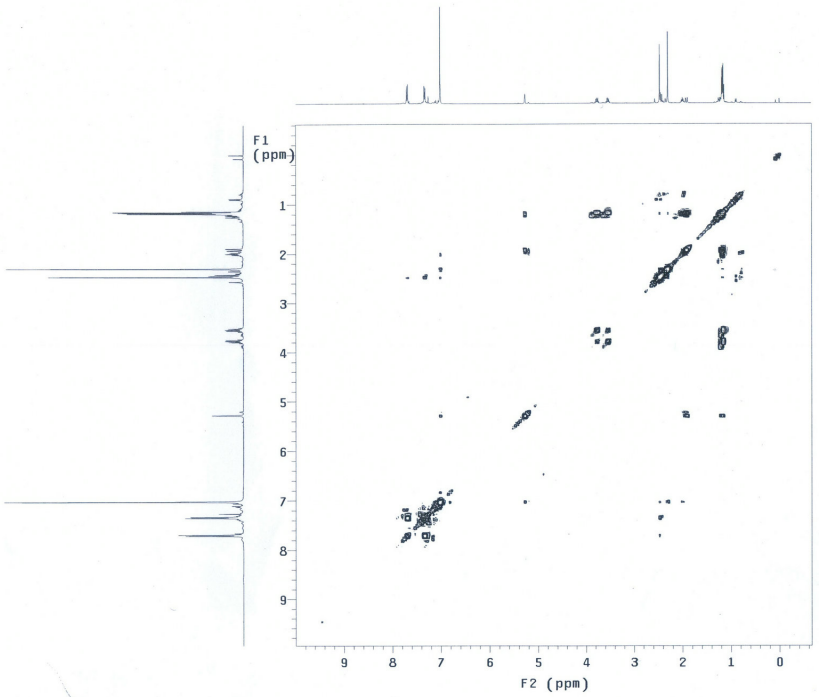
jy-5-36

Sample Name:
jy-5-36
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/omc1/vnmrsys/data
Sample directory:
jy-5-36_20140828_01
FidFile: gCOSY_01

Pulse Sequence: gCOSY
Solvent: CDCl3
Data collected on: Aug 28 2014

Operator: omc1

Relax. delay 1.000 sec
Acq. time 0.218 sec
Width 4699.2 Hz
2D Width 4699.2 Hz
2 repetitions
128 increments
OBSERVE H1, 399.7200249 MHz
DATA PROCESSING
Sq. sine bell 0.080 sec
F1 DATA PROCESSING
Sq. sine bell 0.027 sec
FT size 2048 x 2048
Total time 5 min 45 sec




jy-5-36

Sample Name:
jy-5-36
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/omc1/vnmrsys/data
Sample directory:
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FidFile: gHSQCAD_01

Pulse Sequence: gHSQCAD
Solvent: CDCl3
Data collected on: Aug 29 2014

Operator: omc1

Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 20100.5 Hz
16 repetitions
2 x 128 increments
OBSERVE H1, 399.7200249 MHz
DECOUPLE C13, 100.5187261 MHz
Power 36 dB
on during acquisition
off during delay
W40_4nuc modulated
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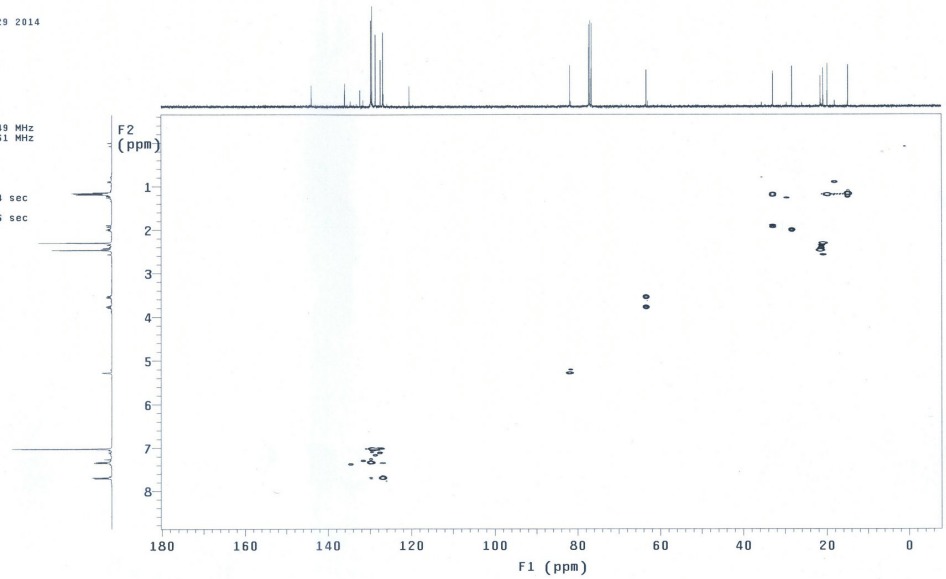
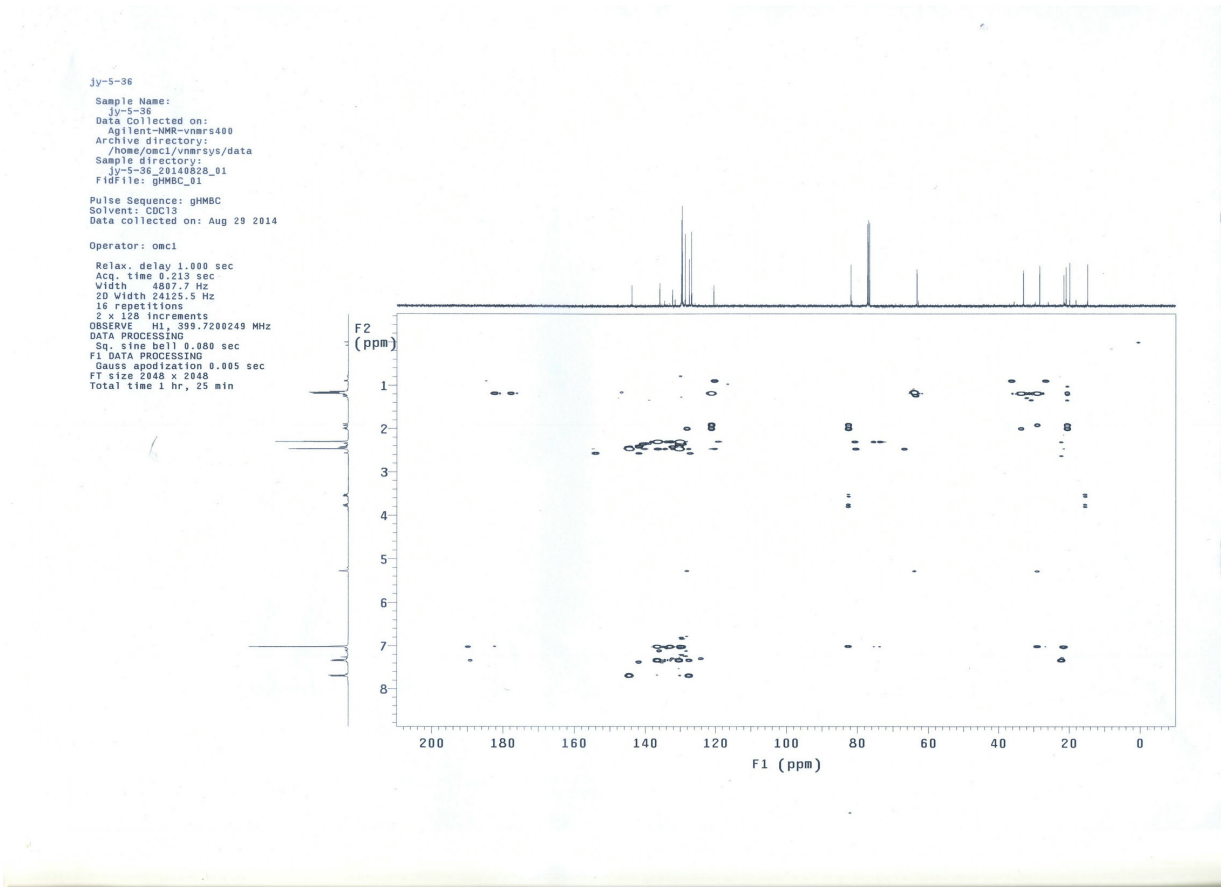
Gauss apodization 0.074 sec
F1 DATA PROCESSING
Gauss apodization 0.006 sec
FT size 2048 x 2048
Total time 1 hr, 23 min




jy-5-36
Sample Name:
jy-5-36
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/omc1/vnmrsys/data
Sample directory:
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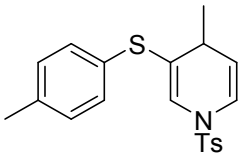
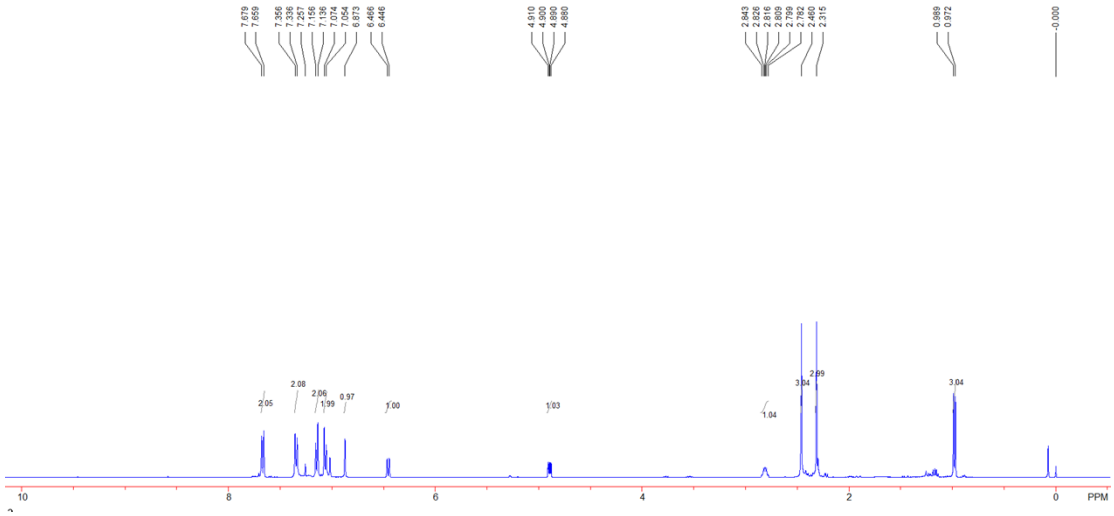
FidFile: gHMBC_01
Pulse Sequence: gHMBC
Solvent: CDCl3
Data collected on: Aug 29 2014
Operator: omc1
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 24125.5 Hz
16 repetitions
2 x 128 increments
OBSERVE H1, 399.7200249 MHz
DATA PROCESSING
Sq. sine bell 0.080 sec
F1 DATA PROCESSING
Gauss apodization 0.005 sec
FT size 2048 x 2048
Total time 1 hr, 25 min
F2 (ppm)
1
2
3
4
5
6
7
8
200
180
160
140
120
100
80
60
40
20
0
F1 (ppm)

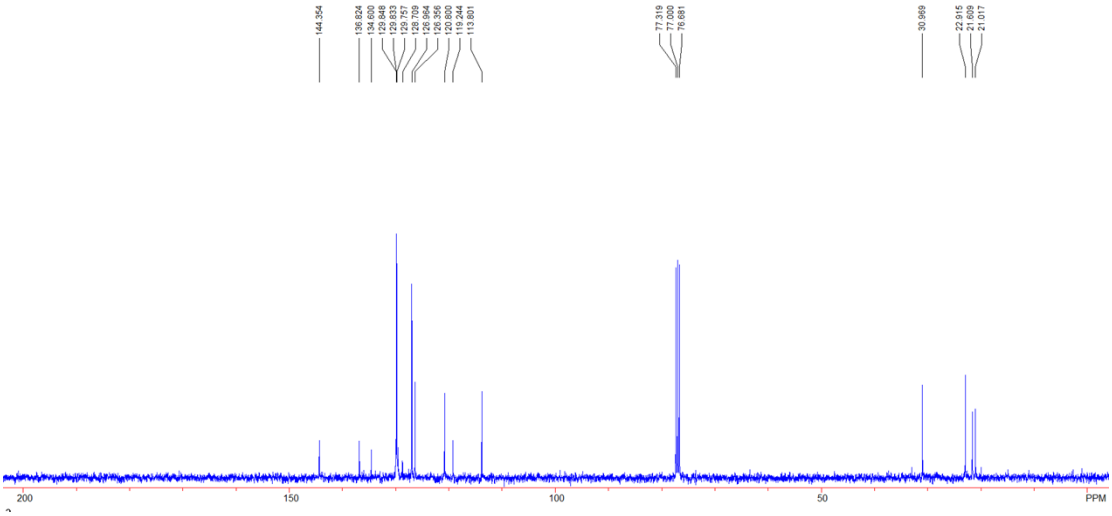
**General procedure and spectroscopic data of 6a:**

To a solution of 4-methyl-*N*-((1*E*,2*Z*)-2-(*p*-tolylthio)but-2-en-1-ylidene)benzenesulfonamide **4a** (0.10 mmol) in 1.0 mL of 1,2-dichloroethane was added ethoxyethene (0.12 mmol), the resulting solution was stirred at 120 °C for 6 hours and then the reaction mixture was concentrated in *vacuo*. The residue was purified by a flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 12:1) to give the corresponding compound **6a**.




4-methyl-3-(*p*-tolylthio)-1-tosyl-1,4-dihydropyridine **6a**: 40 mg, 54% yield, a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.98 (d, $J$ = 6.8 Hz, 3H), 2.32 (s, 3H), 2.46 (s, 3H), 2.78-2.85 (m, 1H), 4.90 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz, 1H), 6.46 (d, $J$ = 8.0 Hz, 1H), 6.87 (s, 1H), 7.06 (d, $J$ = 8.0 Hz, 2H), 7.15 (d, $J$ = 8.0 Hz, 2H), 7.35 (d, $J$ = 8.0 Hz, 2H), 7.67 (d, $J$ = 8.0 Hz, 2H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.0, 21.6, 22.9, 31.0, 113.8, 119.2, 120.8, 126.4, 127.0, 128.7, 129.76, 129.83, 129.85, 134.6, 136.8, 144.4; IR ($CH_2Cl_2$) ν 2963, 2923, 2867, 1596, 1491, 1368, 1263, 1167, 1104, 982, 805, 668 cm$^{-1}$; HRMS (ESI) Calcd. for $C_{20}H_{22}NO_2S_2$ $(M+H)^+$: 372.1086, found: 372.1087.




144.354
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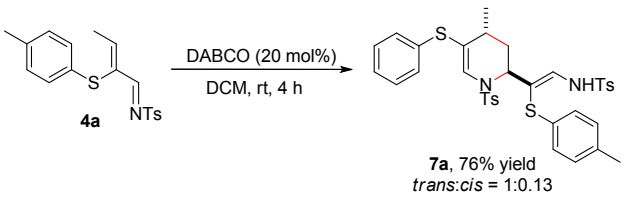
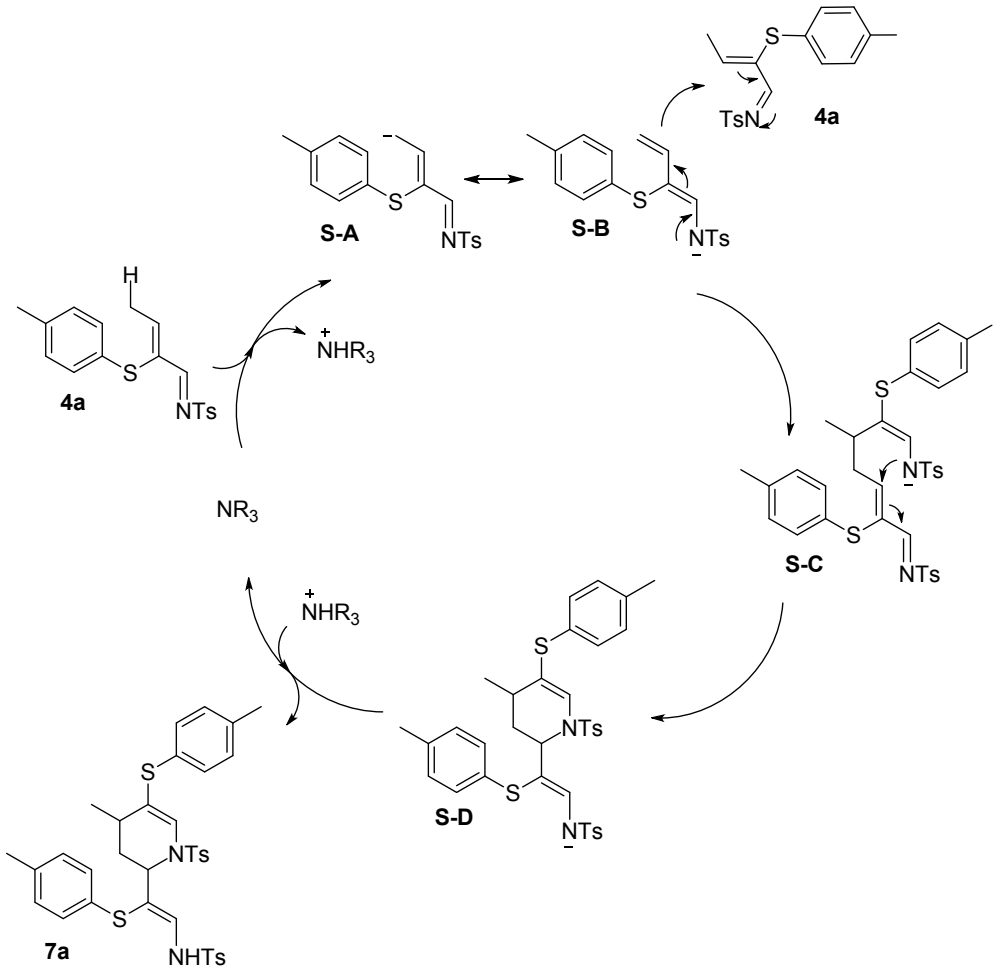
134.600
129.848
129.533
128.972
128.709
126.964
126.356
120.888
119.244
113.891
77.319
77.000
76.681
30.969
22.915
21.609
21.017
200
150
100
50
PPM

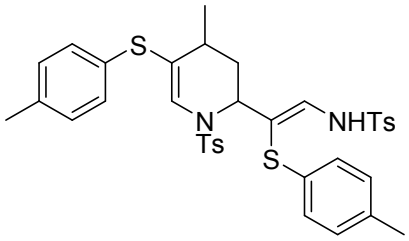
**General Procedure, Spectroscopic Data and a Plausible Mechanism for the Formation of 7a**:



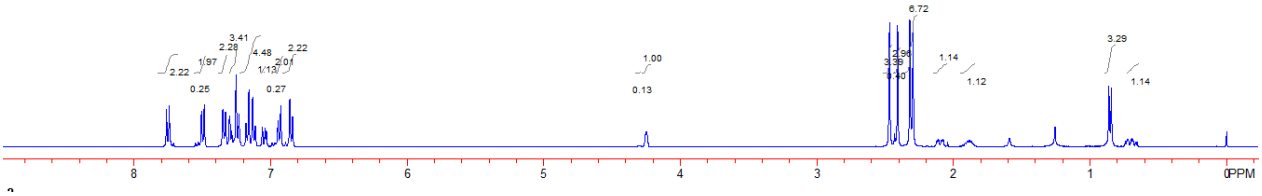

To a solution of 4-methyl-*N*-((1*E*,2*Z*)-2-(*p*-tolylthio)but-2-en-1-ylidene)benzenesulfonamide **4a** (0.10 mmol) in 1.0 mL of dichloromethane was added 1,4-diaza[2.2.2]bicyclooctane (DABCO) (0.02 mmol, 20 mol%), the resulting solution was stirred at rt for 4 hours and then the reaction mixture was concentrated in vacuo. The residue was purified by a flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 12:1) to give the corresponding compound **7a** (1:0.13 d.r.). Its spectra include the very small signals of another diastereoisomer at the aromatic region.

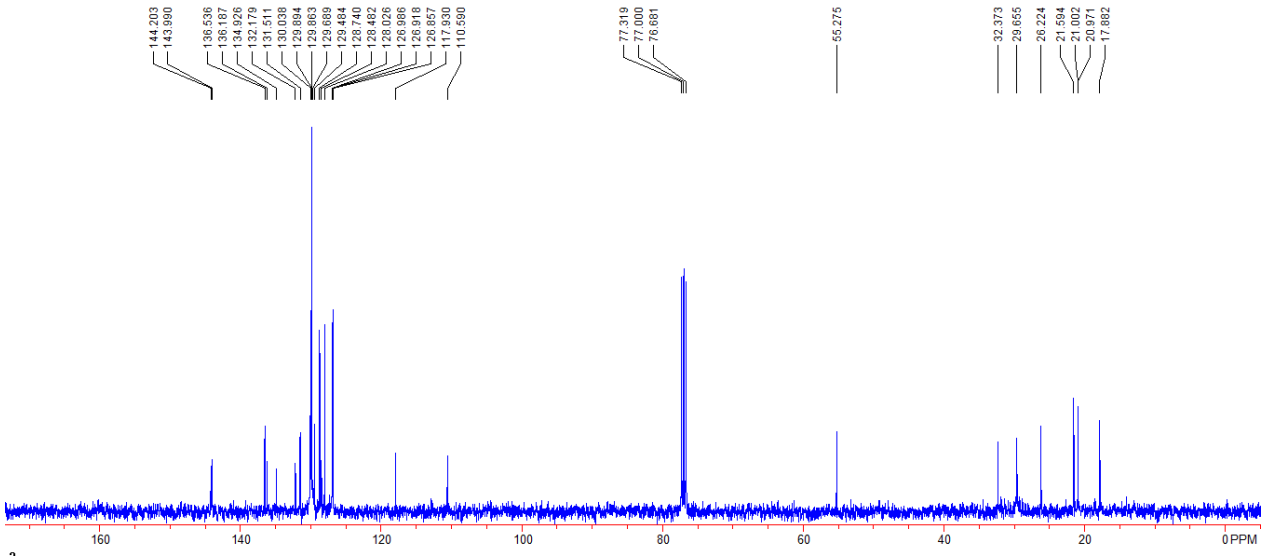



***Scheme S1***. A Plausible Mechanism for the Formation of Compound **7a**

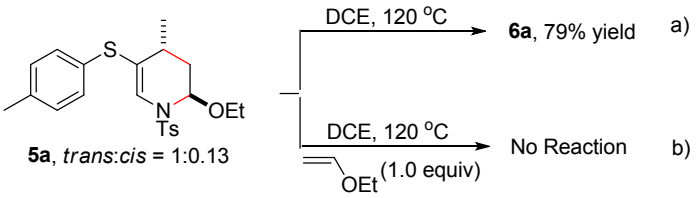



4-methyl-*N*-((*Z*)-2-((2*R*,4*S*)-4-methyl-5-(*p*-tolylthio)-1-tosyl-1,2,3,4-tetrahydropyridin-2-yl)-2-(*p*-tolylthio)vinyl)benzenesulfonamide **7a**: 108 mg, 76% yield, **d.r.** = 1:0.13; a colorless oil; $^{1}$H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.65-0.75 (m, 1.13H), 0.85 (d, *J* = 6.8 Hz, 3.39H), 1.85-1.92 (m, 1.13H), 2.07-2.13 (m, 1.13H), 2.30 (s, 3.39H), 2.32 (s, 3.39H), 2.41 (s, 3H), 2.43 (s, 0.39H), 2.47 (s, 3.39H), 4.25 (s, 1H), 4.30 (s, 0.13H), 6.85 (d, *J* = 8.0 Hz, 2.26H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 0.26H), 7.03-7.07 (m, 1.13H), 7.12 (d, *J* = 8.0 Hz, 2.26H), 7.17 (d, *J* = 8.0 Hz, 2.26H), 7.23-7.31 (m, 3.39H), 7.34 (d, *J* = 8.0 Hz, 2.26H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 0.26H), 7.75 (d, *J* = 8.0 Hz, 2.26H); $^{13}$C NMR ($CDCl_3$, 100 MHz, TMS) δ 17.9, 20.97, 21.00, 21.6, 26.2, 29.7, 32.4, 55.3, 110.6, 117.9, 126.86, 126.92, 127.0, 128.0, 128.5, 128.7, 129.5, 129.7, 129.86, 129.89, 130.0, 131.5, 132.2, 134.9, 136.2, 136.5, 144.0, 144.2; IR ($CH_2Cl_2$) ν 3263, 2961, 2923, 2868, 1644, 1597, 1491, 1362, 1338, 1165, 1089, 1017, 951, 808, 737, 667 $cm^{-1}$; HRMS (ESI) Calcd. for $C_{36}H_{42}N_3O_4S_4$ $(M+H)^+$: 708.2053, found: 708.2072.


144.203
143.990
136.536
136.187
134.926
132.179
131.511
130.038
129.894
129.863
129.689
129.484
128.740
128.462
128.026
126.986
126.918
126.857
117.930
110.590
77.319
77.000
76.681
55.275
32.373
29.655
26.224
21.594
21.002
20.971
17.882
160
140
120
100
80
60
40
20
0 PPM

**Control Experiments and Decomposition of Ethoxyethene**:



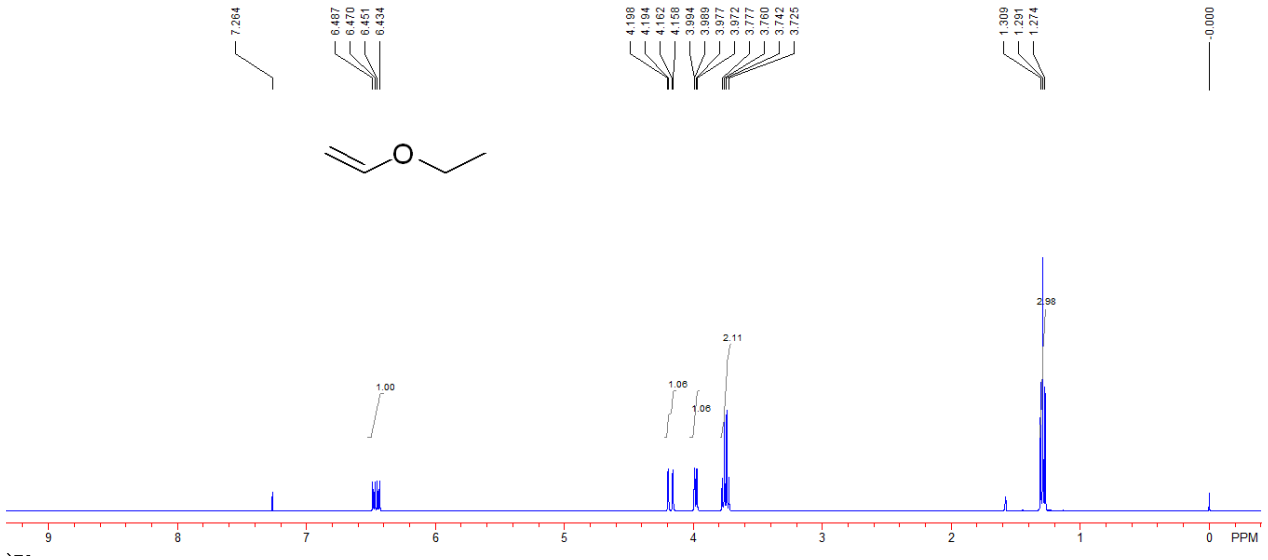

**Control Experiments**:

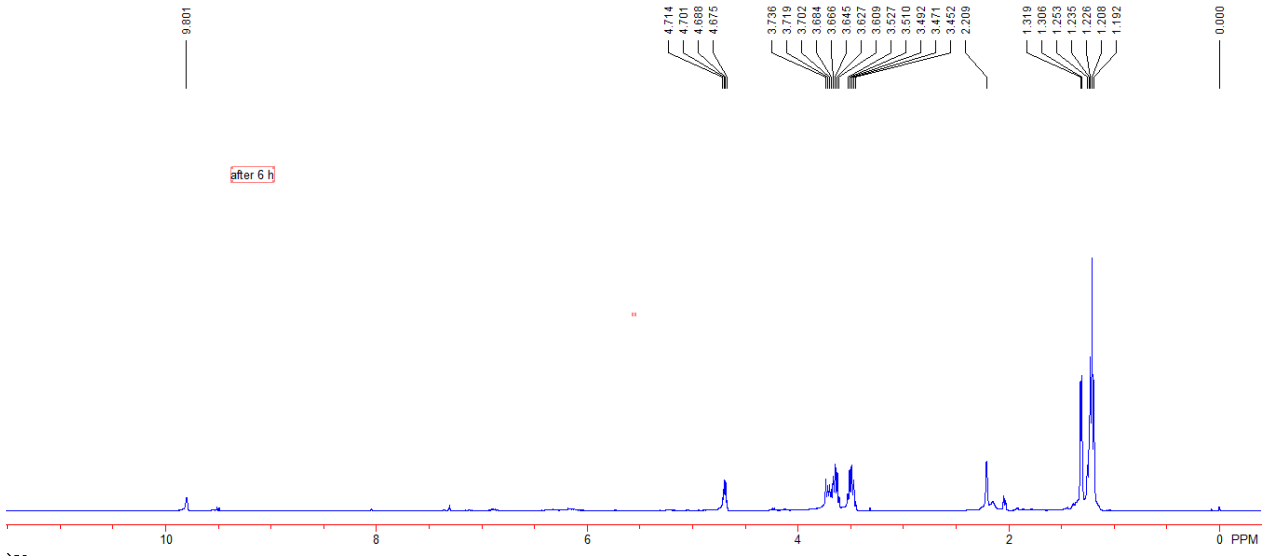
a) 0.1 mmol of 2-ethoxy-4-methyl-5-(*p*-tolylthio)-1-tosyl-1,2,3,4-tetrahydropyridine **5a** (0.10 mmol) was added to 1.0 mL of 1,2-dichloroethane, the resulting solution was stirred at 120 °C for 6 hours and then the reaction mixture was concentrated in vacuo. The residue was purified by a flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 12:1) to give the corresponding compound **6a.**

b) To a solution of 2-ethoxy-4-methyl-5-(*p*-tolylthio)-1-tosyl-1,2,3,4-tetrahydropyridine **5a** (0.10 mmol) in 1.0 mL of 1,2-dichloroethane was added ethoxyethene (0.10 mmol), the resulting solution was stirred at 120 °C for 6 hours and then the mixture was detected by NMR spectroscopy, and there is no reaction of **5a**.

**Decomposition of Ethoxyethene**:

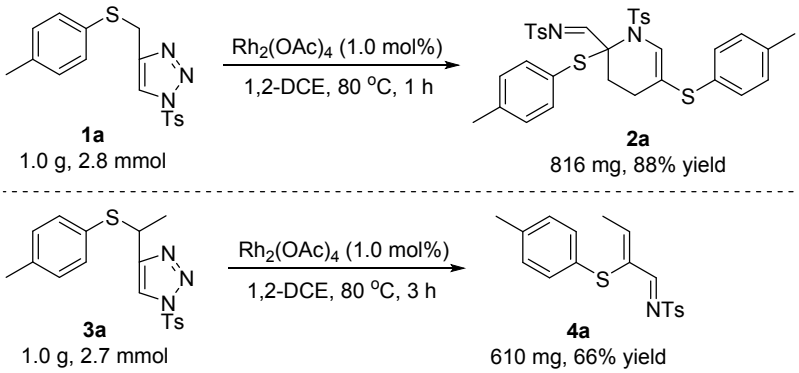
Ethoxyethene (1.0 mmol, 96 μL) and water (5.0 % mmol, 1.0 μL) were added into 1.0 mL $CDCl_3$ and the resulted solution was warmed to 120 °C. After 6 h, the $^1H$ NMR of the solution was recorded. The $^1H$ NMR showed that the ethoxyethene was decomposed after 6 h.

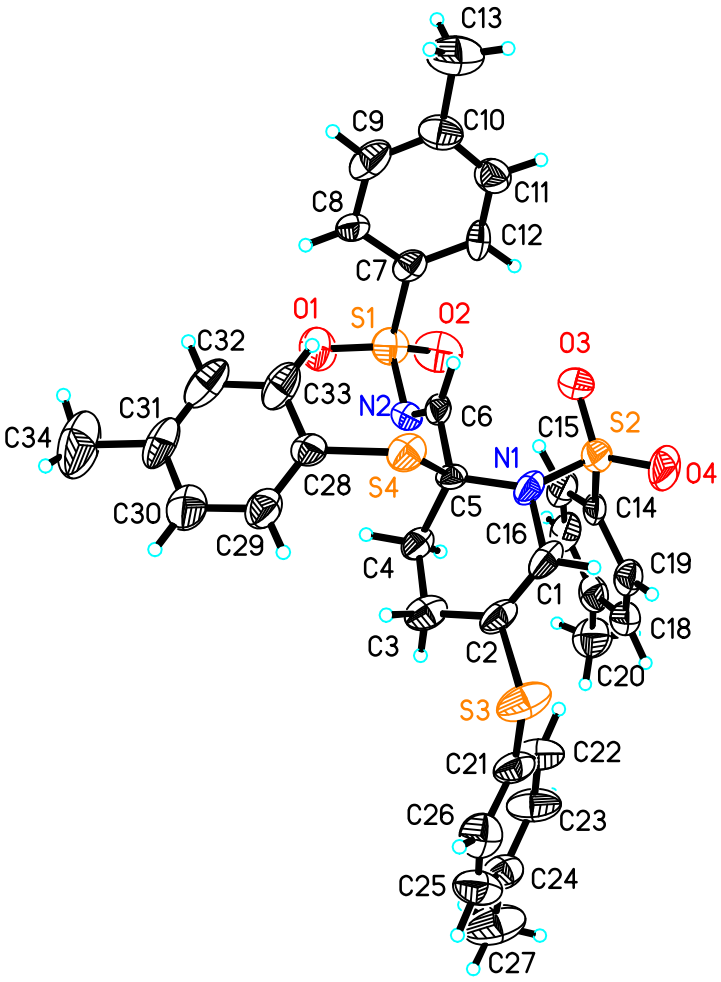

7.264
6.487
6.470
6.451
6.434
4.198
4.194
4.162
4.158
3.994
3.989
3.977
3.972
3.777
3.760
3.742
3.725
1.309
1.291
1.274
0.000
O
1.00
1.06
1.06
2.11
2.98
9
8
7
6
5
4
3
2
1
0
PPM


9.801
4.714
4.701
4.688
4.675
3.736
3.719
3.702
3.684
3.666
3.645
3.627
3.609
3.527
3.510
3.492
3.471
3.452
2.209
1.319
1.306
1.253
1.235
1.226
1.208
1.192
0.000
after 6 h
10
8
6
4
2
0
PPM

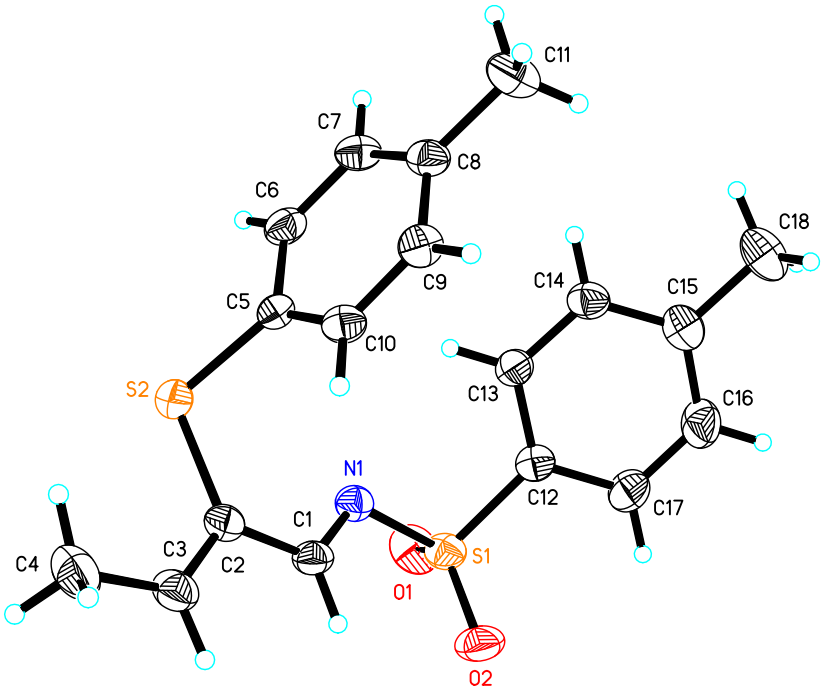
**Gram scale synthesis of 1a and 3a**

For the potential utility of this protocol, the reaction has been also carried out on a 1.0 g scale. As for triazole substrate **1a**, the reaction proceeded smoothly to give the desired product **2a** in 88% yield. Carrying out the reaction of **3a** on a 1.0 g scale under the standard conditions produced **4a** in 66% yield presumably due to the partial decomposition of this imine product in silica gel column chromatography during the purification.

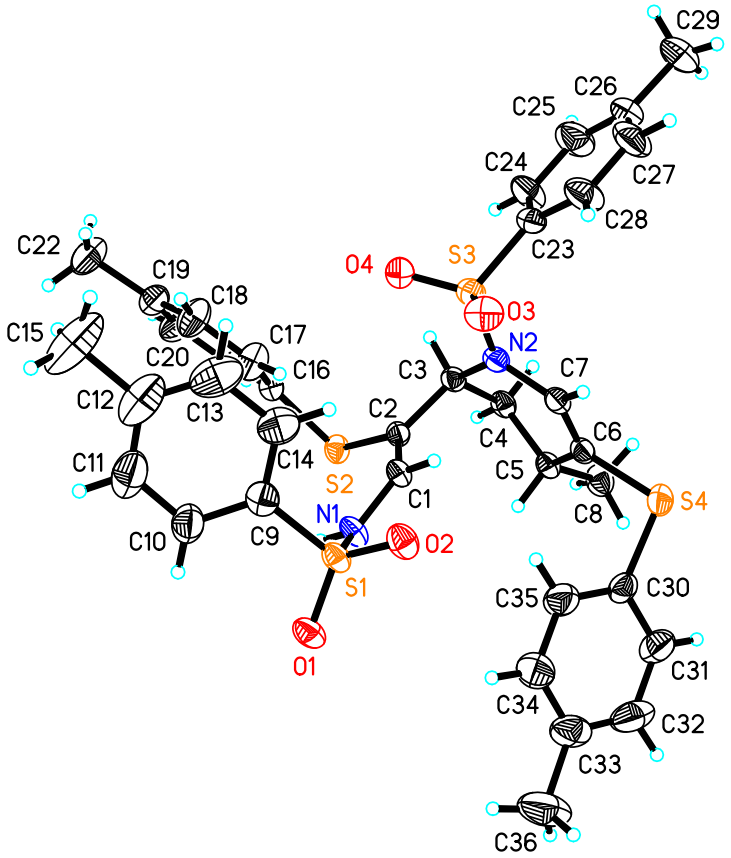





The crystal data of **2a** have been deposited in CCDC with number 996223. Empirical Formula: $C_{34}H_{34}N_2O_4S_4$; Formula Weight: 662.87; Crystal Color, Habit: colorless, Crystal Dimensions: 0.102 x 0.089 x 0.045 mm; Crystal System: Orthorhombic; Lattice Parameters: a = 28.621(7)Å, b = 26.533(8)Å, c = 9.756(3)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 7409(3)Å$^3$; Space group: A ba2; Z = 8; $D_{calc}$ = 1.189 g/cm$^3$; $F_{000}$ = 1368; Final R indices [I>2sigma(I)] R1 = 0.0887, wR2 = 0.1676.




The crystal data of **4a** have been deposited in CCDC with number 1021015. Empirical Formula: $C_{18}H_{19}NO_2S_2$; Formula Weight: 345.46; Crystal Color, Habit: colorless, Crystal Dimensions: 0.211 x 0.165 x 0.112 mm; Crystal System: Monoclinic; Lattice Parameters: a = 9.6224(10)Å, b = 14.3505(14)Å, c = 13.0206(13)Å, $\alpha = 90^{o}$, $\beta = 102.158(2)^{o}$, $\gamma = 90^{o}$, V = 1757.6(3)Å$^3$; Space group: P 21/c; Z = 4; Dcalc = 1.306 g/cm$^3$; F000 = 728; Final R indices [I>2sigma(I)] R1 = 0.0414, wR2 = 0.1103.




The crystal data of **7a** have been deposited in CCDC with number 1013188. Empirical Formula: $C_{36}H_{38}N_2O_4S_4$; Formula Weight: 690.92; Crystal Color, Habit: colorless, Crystal Dimensions: 0.212 x 0.175 x 0.123 mm; Crystal System: Triclinic; Lattice Parameters: a = 9.5970(13)Å, b = 13.9714(19)Å, c = 14.765(2)Å, α = 105.066(3)°, β = 107.053(3)°, γ = 97.126(3)°, V = 1784.1(4)Å$^3$; Space group: P-1; Z = 2; $D_{calc}$ = 1.286 g/cm$^3$; $F_{000}$ = 728; Final R indices [I>2sigma(I)] R1 = 0.0614, wR2 = 0.1678.

**Reference**

[1] (a) A. L. Moure, P. Mauleon, R. G. Arrayas, J. C. Carretero, *Org. Lett.* **2013**, *15*, 2054-2057; (b) Z.-P. Zhan, J.-L. Yu, H.-J. Liu, Y.-Y. Cui, R.-F. Yang, W.-Z. Yang, J.-P. Li, *J. Org. Chem.* **2006**, *71*, 8298-8301; (c) A. S. Dudnik, A. W. Sromek, M. Rubina, J. T. Kim, A. V. Kel'in, V. Gevorgyan, *J. Am. Chem. Soc.* **2008**, *130*, 1440-1452.

[2] L. Peng, X. Zhang, S. Zhang, J. Wang, *J. Org. Chem.* **2007**, *72*, 1192-1197.

[3] H. J. Reich, S. K. Shah, P. M. Gold, R. E. Olson, *J. Am. Chem. Soc.* **1981**, *103*, 3112-3120.