Supporting Information

A facile method for the synthesis of dihydroquinoline-azide from the Lewis acid-catalyzed reaction of alkylidenecyclopropanes with $TMSN_3$

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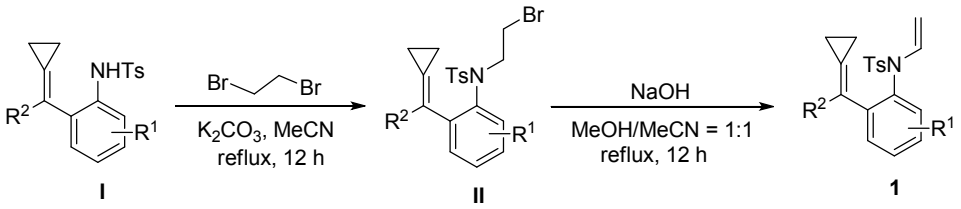
General Remarks

^{1}H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass and HRMS spectra were recorded by EI method. Organic solvents used were dried by standard methods when necessary. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates or ^{19}F NMR. Flash column chromatography was carried out using silica gel at increased pressure.

1. General procedure for the preparation of substrates 1

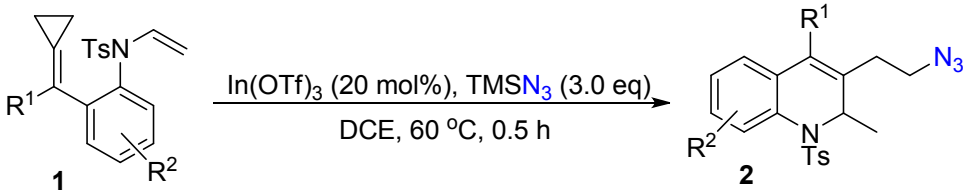
Substrates were synthesized from MCPs[1] by the procedure shown below:



To a solution of MCPs **I** (1.0 equiv, 2 mmol) in MeCN (15 mL) was added K_2CO_3 (5.0 equiv, 10 mmol) and 1,2-dibromoethane (5.0 equiv, 10 mmol). The mixture was heated and stirred for 12 h. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue, which is purified by a chromatography on silica gel (PE/EA = 10/1) to afford the corresponding product **II**.

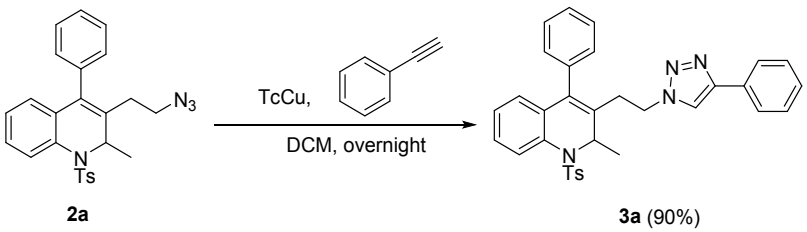
Elimination step: NaOH (5.0 equiv, 5.0 mmol) was added to solution of substrate **II** (1.0 equiv, 1.0 mmol) in MeOH/MeCN (1/1, 20 mL). The mixture was heated and stirred for 12 h. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue, which is purified by a chromatography on silica gel (PE/EA = 10/1) to afford the corresponding ***N***-vinylbenzenesulfonamide product **1**.

2. General procedure for the synthesis of the azide products 2



Substrate **1** (0.2 mmol) and $TMSN_3$ (78 μL, 0.6 mmol) were placed in a 25 mL flask and 2 mL DCE was added. Stirring in an oil bath at 60 °C, $In(OTf)_3$ (23.0 mg, 0.04 mmol) was added and the mixture was continued to stir within 30 min. When the reaction completed (confirmed by the thin layer chromatography), the mixture was directly purified by a flash silica gel chromatography (PE: EA = 20:1) to give pure product **2**.

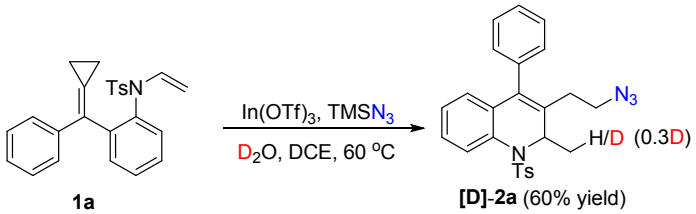
3. Procedure for the synthesis of 3a[2]



2a **3a** (90%)

Product **2a** (44.4 mg, 0.1 mmol), CuTc (1.9 mg, 0.01 mmol) and phenylacetylene (20.4 mg, 0.2 mmol) were placed in a 50 mL flask and 5 mL DCM was added. The mixture was stirred at ambient temperature overnight. When it completed, the solvent was removed under reduced pressure and the residue was purified by a flash silica gel chromatography (PE: EA = 4:1) to give pure product **3a** in a yield of 90%.

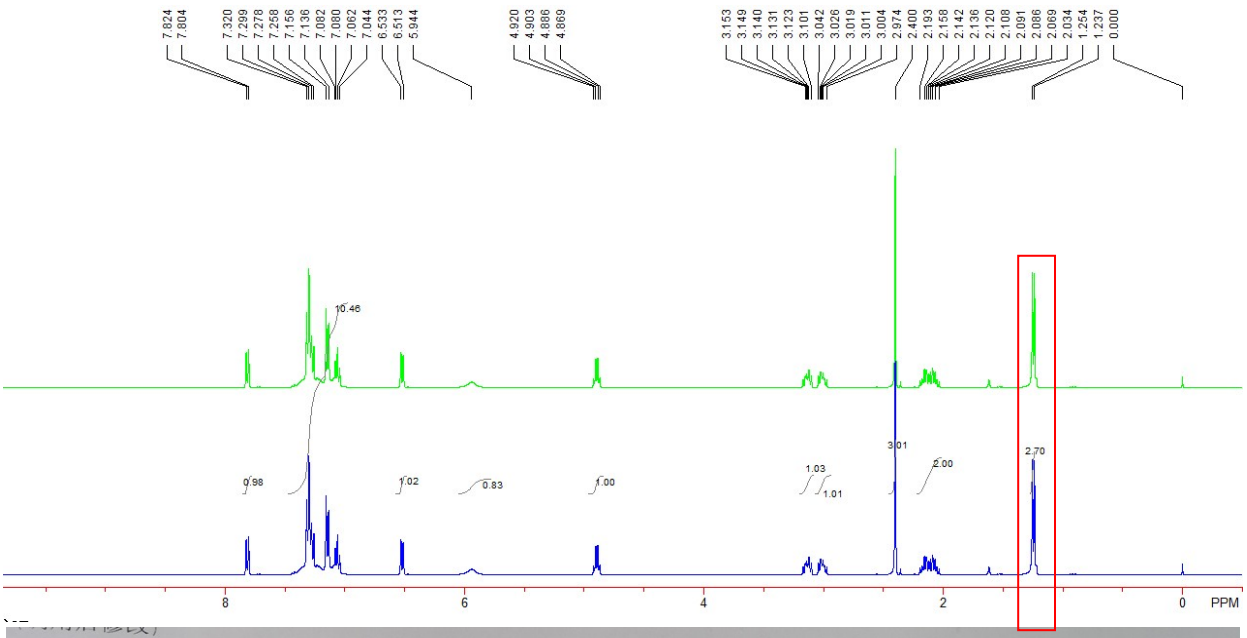
4. Procedure for the deuteration experiment



1a **[D]-2a** (60% yield)

Preparation of D_2O containing DCE: D_2O (8.0 mg, 0.4 mmol) was dropped into 4 mL DCE and the mixture was fiercely shaken. Then, the mixture was kept static overnight for the free diffusion of D_2O into DCE.

Deuteration experiment: 1a (80.3 mg, 0.2 mmol) and $TMSN_3$ (78 μL, 0.6 mmol) were placed in a 25 mL flask and 2 mL D_2O containing DCE was injected. Stirring in an oil bath at 60 °C, $In(OTf)_3$ (23.0 mg, 0.04 mmol) was added and the mixture was continued to stir until the reaction completed. Afterwards, the mixture was directly purified by a flash silica gel chromatography (PE: EA = 20:1) to give pure product **2a** in a yield of 60% along with 30% deuterium corporation (verified by ^1H NMR spectroscopic data and LRMS data).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6.513
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4.903
4.886
4.869
3.153
3.149
3.140
3.131
3.123
3.101
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3.026
3.019
3.011
3.004
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2.142
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2.091
2.086
2.069
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1.237
0.000
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1.00
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2.00
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6
4
2
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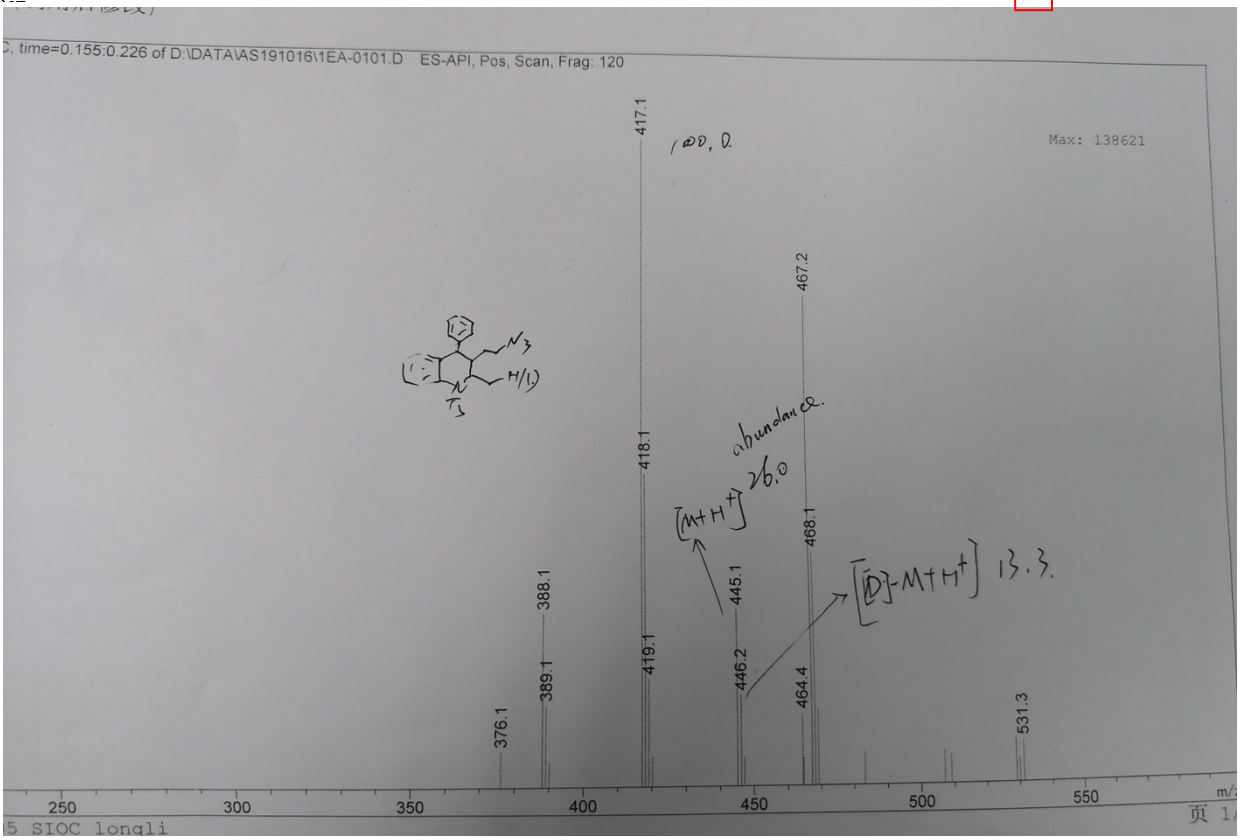
PPM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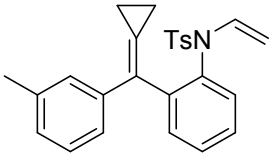
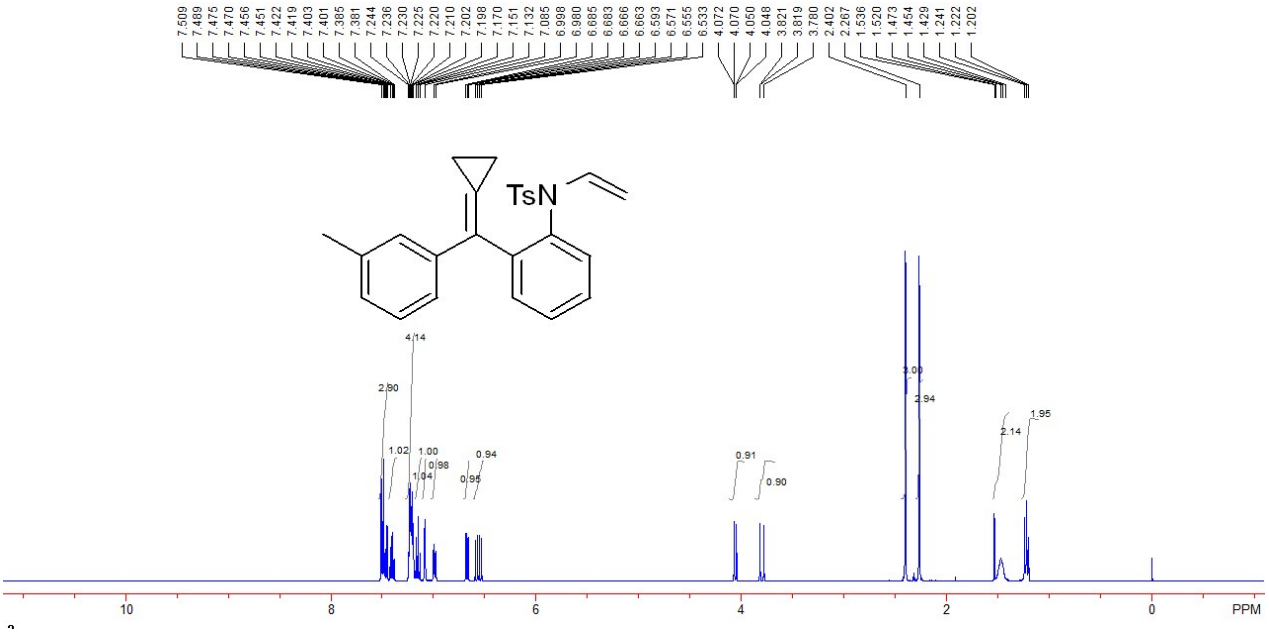
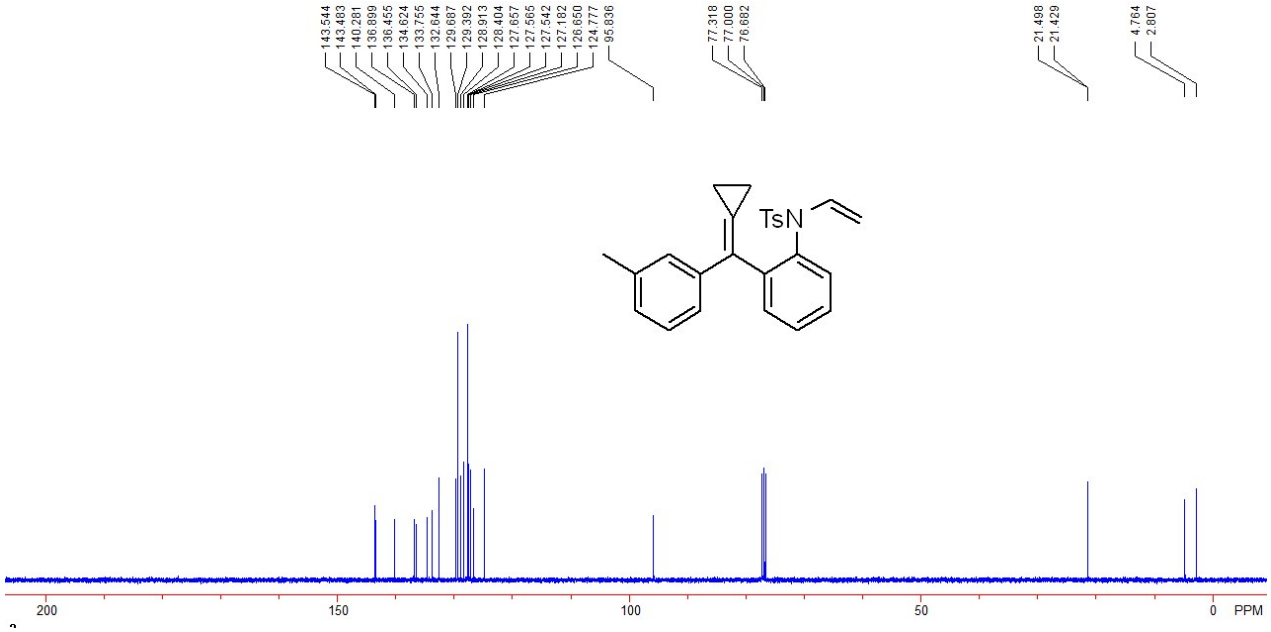
Spectroscopic Data of compound 1, 2 and 3a.[3]

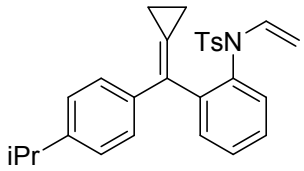


N-(2-(cyclopropylidene(m-tolyl)methyl)phenyl)-4-methyl-N-vinylbenzenesulfonamide (1h).

A white solid, 706.5 mg, 85% yield. M.p.: 129-131 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.22 (t, J = 8.0 Hz, 2H, CH_2), 1.43-1.52 (m, 2H, CH_2), 2.27 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 3.80 (dd, J = 0.8 Hz, 15.6 Hz, 1H, =CH_2), 4.06 (dd, J = 0.8 Hz, 8.8 Hz, 1H, =CH_2), 6.56 (dd, J = 8.8 Hz, 15.6 Hz, 1H, =CH), 6.67 (dd, J = 0.8 Hz, 7.6 Hz, 1H, ArH), 6.99 (d, J = 7.2 Hz, 1H, ArH), 7.08 (s, 1H, ArH), 7.15 (t, J = 7.6 Hz, 1H, ArH), 7.20-7.24 (m, 4H, ArH), 7.40 (dt, J = 1.2 Hz, 7.6 Hz, 1H, ArH), 7.46 (dd, J = 2.0 Hz, 7.6 Hz, 1H, ArH), 7.50 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 2.8, 4.8, 21.4, 21.5, 95.8, 124.8, 126.6, 127.2, 127.5, 127.6, 127.7, 128.4, 128.9, 129.4, 129.7, 132.6, 133.8, 134.6, 136.4, 136.9, 140.3, 143.4, 143.5. IR (CH_2Cl_2) ν 3045, 2974, 2911, 1625, 1364, 1167, 1089, 1043, 719, 656 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{26}O_2NS$: 416.1679, Found: 416.1682.

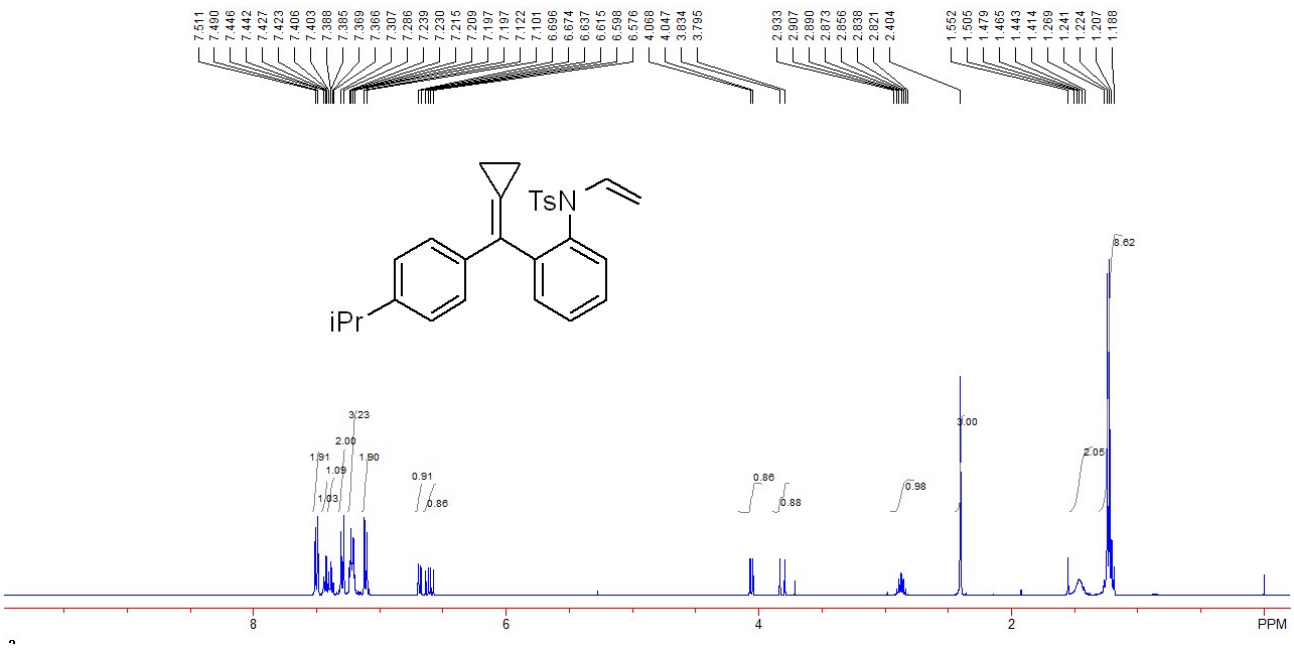


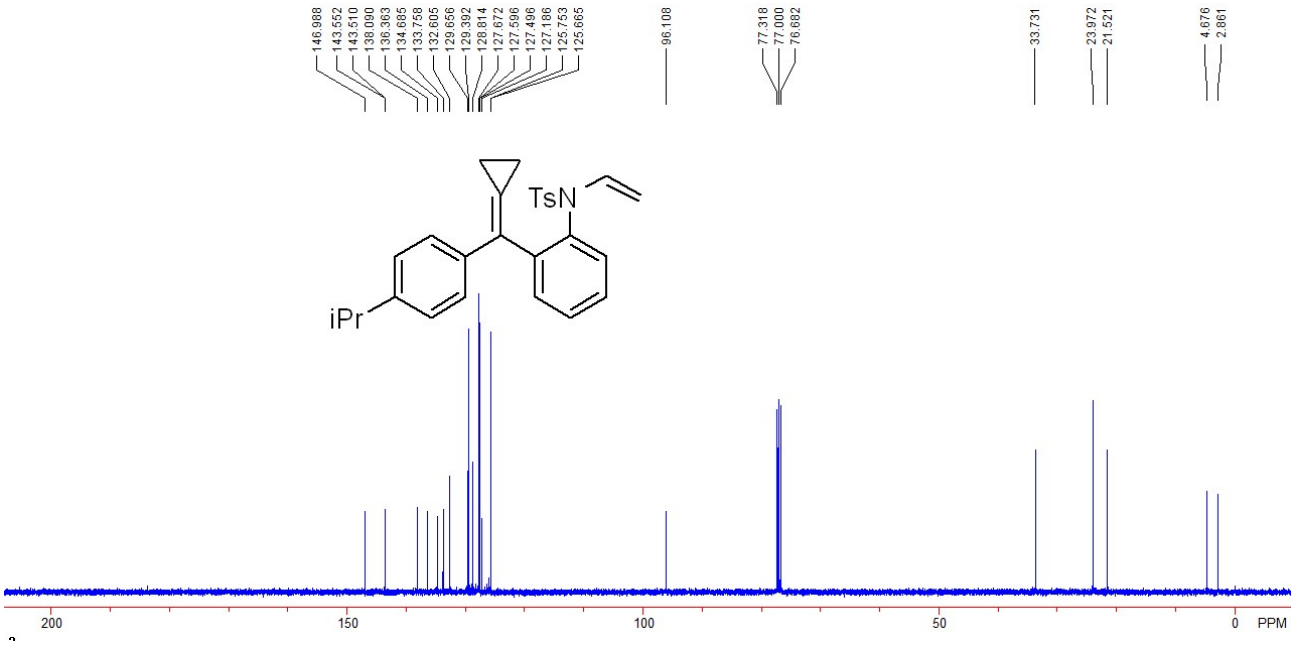


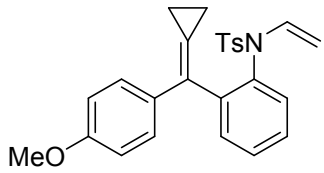


N-(2-(cyclopropylidene(4-isopropylphenyl)methyl)phenyl)-4-methyl-N-vinylbenzenesulfonamide (1i).

A white solid, 727.5 mg, 82% yield. M.p.: 131-133 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.19-1.27 (m, 2H, CH_2), 1.22 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.41-1.55 (m, 2H, CH_2), 2.40 (s, 3H, CH_3), 2.87 (sept, J = 6.8 Hz, 1H, CH), 3.81 (d, J = 15.6 Hz, 1H, =CH_2), 4.06 (d, J = 8.8 Hz, 1H, =CH_2), 6.61 (dd. J = 8.8 Hz, 15.6 Hz, 1H, =CH), 6.68 (d, J = 8.8 Hz, 1H, ArH), 7.11 (d, J = 8.4 Hz, 1H, ArH), 7.20-7.24 (m, 3H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.39 (dt, J = 1.2 Hz, 7.6 Hz, 1H, ArH), 7.43 (dd, J = 1.6 Hz, 7.6 Hz, 1H, ArH), 7.50 (d, J = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 2.9, 4.7, 21.5, 24.0, 33.7, 96.1, 125.7, 125.8, 127.2, 127.5, 127.6, 127.7, 128.8, 129.4, 129.6, 132.6, 133.8, 134.7, 136.4, 138.1, 143.5, 143.6, 147.0. IR (CH_2Cl_2) ν 2959, 2919, 2864, 1626, 1363, 1166, 1089, 660 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{28}H_{30}O_2NS$: 444.1992, Found: 444.1992.



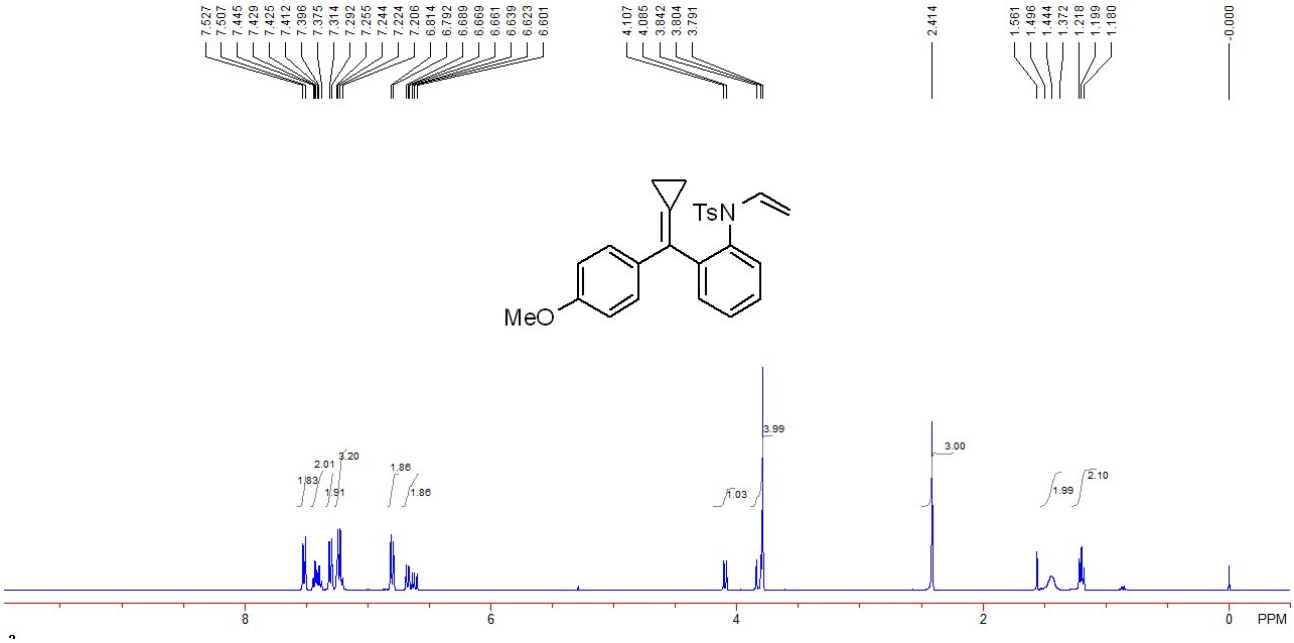


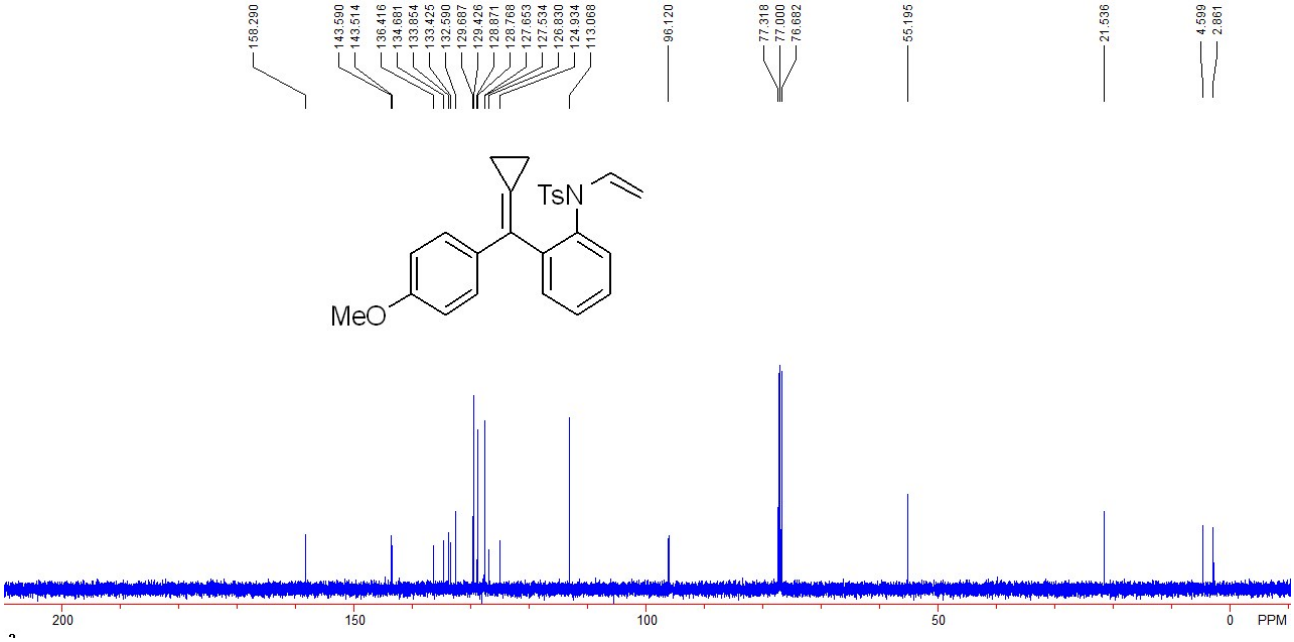


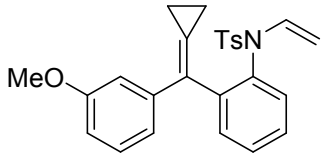
N-(2-(cyclopropylidene(4-methoxyphenyl)methyl)phenyl)-4-methyl-N-vinylbenzenesulfonamide (1k).

A white solid, 699.2 mg, 81% yield. M.p.: 107-109 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.20 (t, J = 7.6 Hz, 2H, CH_2), 1.37-1.50 (m, 2H, CH_2), 2.41 (s, 3H, CH_3), 3.79 (s, 3H, CH_3), 3.82 (d, J = 15.2 Hz, 1H, =CH_2), 4.10 (d, J = 8.8 Hz, 1H, =CH_2), 6.63 (dd. J = 0.8 Hz, 8.0 Hz, 1H, ArH), 6.68

(d, J = 8.0 Hz, 1H, ArH), 6.80 (d, J = 8.8 Hz, 2H, ArH), 7.21-7.26 (m, 3H, ArH), 7.30 (d, J = 8.8 Hz, 2H, ArH), 7.38-7.44 (m, 2H, ArH), 7.52 (d, J = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 2.9, 4.6, 21.5, 55.2, 96.1, 113.1, 124.9, 126.8, 127.5, 127.6, 128.8, 128.9, 129.4, 129.7, 132.6, 133.4, 133.8, 134.7, 136.4, 143.5, 143.6, 158.3. IR (CH_2Cl_2) ν 2972, 2830, 1608, 1509, 1354, 1249, 1158, 1090, 1027 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{26}O_3NS$: 432.1628, Found: 432.1631.

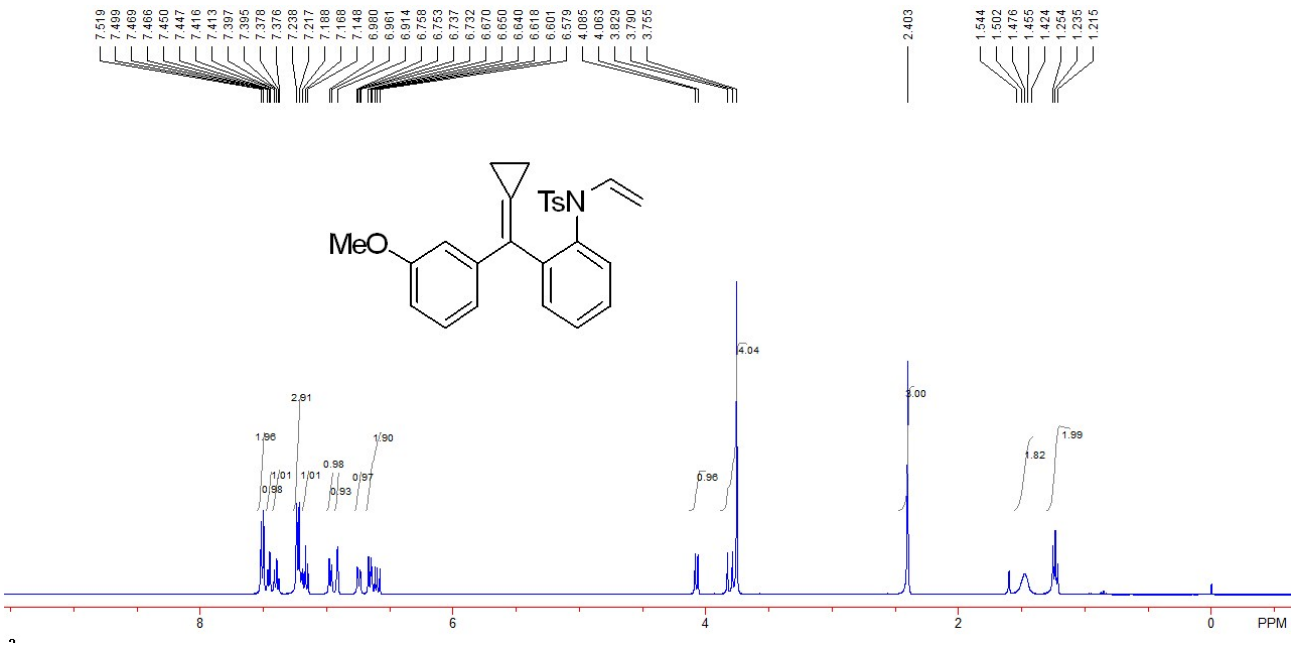


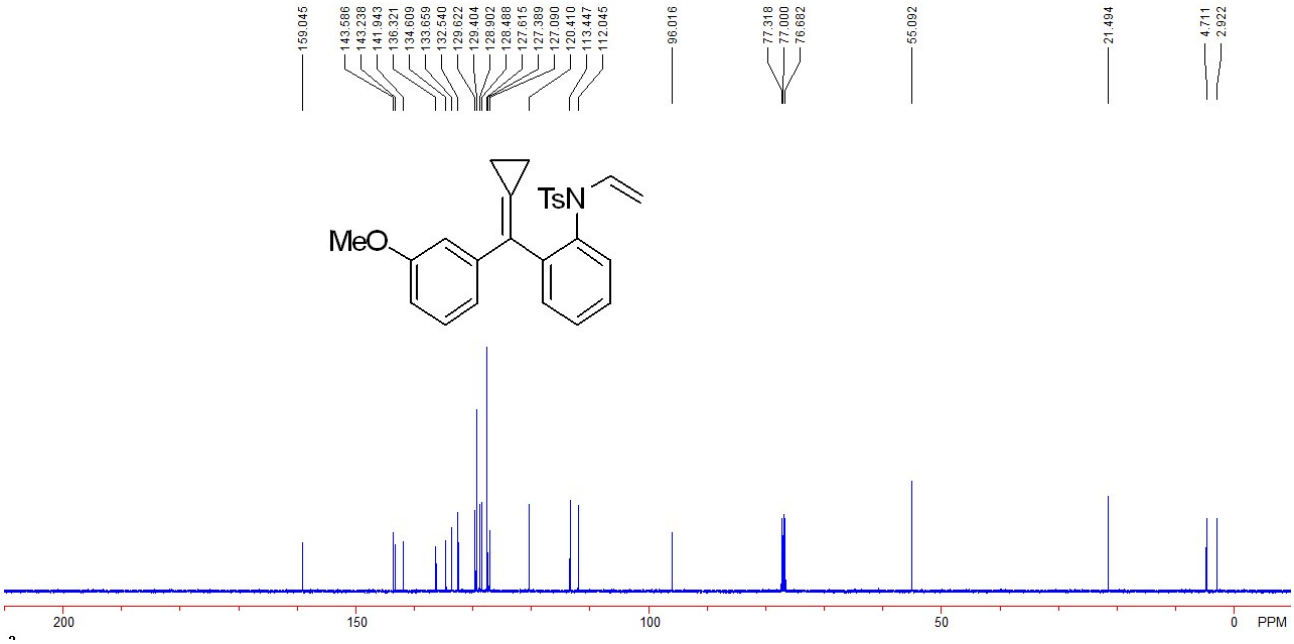


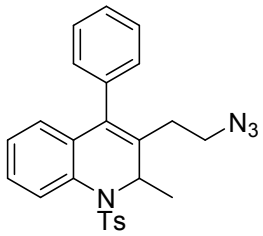


N-(2-(cyclopropylidene(3-methoxyphenyl)methyl)phenyl)-4-methyl-N-vinylbenzenesulfonamide (1l).

A white solid, 604.2 mg, 70% yield. M.p.: 111-113 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.24 (t, *J* = 8.0 Hz, 2H, CH_2), 1.42-1.50 (m, 2H, CH_2), 2.40 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 3.81 (d, *J* = 15.6 Hz, 1H, =CH_2), 4.07 (d, *J* = 8.8 Hz, 1H, =CH_2), 6.61 (dd, *J* = 8.8 Hz, 15.6 Hz, 1H, =CH), 6.66 (d, *J* = 8.0 Hz, 1H, ArH), 6.74 (dd, *J* = 2.0 Hz, 8.4 Hz, 1H, ArH), 6.91 (s, 1H, ArH), 6.97 (d, *J* = 7.6 Hz, 1H, ArH), 7.17 (t, *J* = 8.0 Hz, 1H, ArH), 7.23 (d, *J* = 8.4 Hz, 3H, ArH), 7.40 (dt, *J* = 0.8 Hz, 7.6 Hz, 1H, ArH), 7.46 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H, ArH), 7.51 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 2.9, 4.7, 21.5, 55.1, 96.0, 112.0, 113.4, 120.4, 127.1, 127.4, 127.6, 128.5, 128.9, 129.4, 129.6, 132.5, 133.6, 134.6, 136.3, 141.9, 143.2, 143.6, 159.0. IR (CH_2Cl_2) ν 2969, 1626, 1596, 1487, 1363, 1166, 1088, 1045, 655 cm^{-1}. HRMS (M+H^{+}) calcd. for $C_{26}H_{26}O_3NS$: 432.1628, Found: 432.1634.

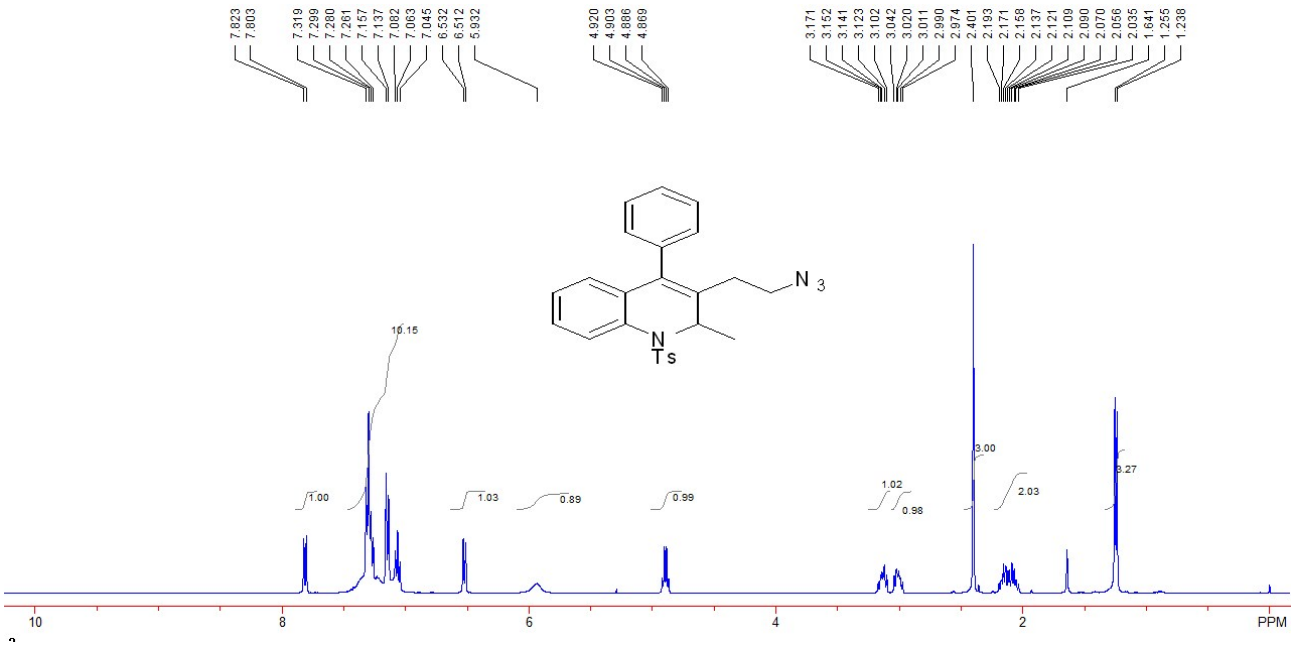


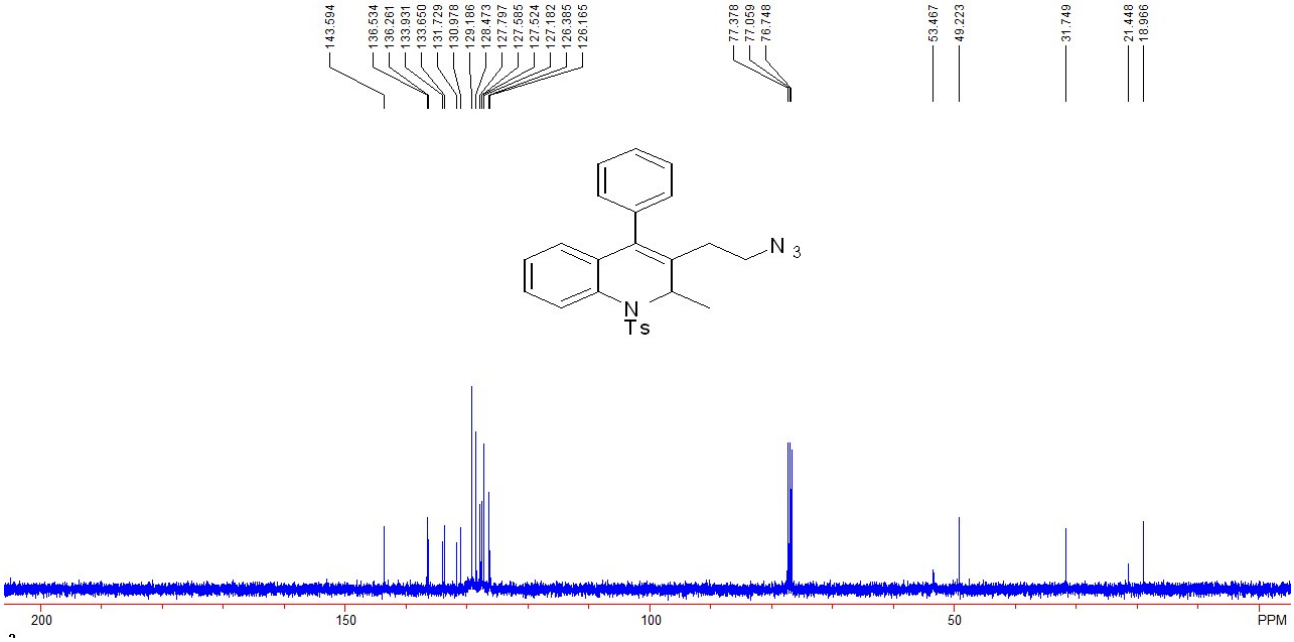


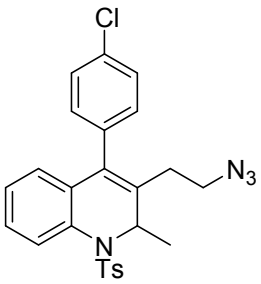


3-(2-azidoethyl)-2-methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (2a).

A white solid, 75.5 mg, 85% yield. M.p.: 139-141 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.25 (d, J = 6.8 Hz, 3H, CH_3), 1.64-2.19 (m, 2H, CH_2), 2.40 (s, 3H, CH_3), 2.97-3.04 (m, 1H, CH2), 3.10-3.17 (m, 1H, CH_2), 4.89 (q, J = 6.8 Hz, 1H, CH), 5.93 (br, 1H, ArH), 6.52 (d, J = 8.0 Hz, 1H, ArH), 7.04-7.32 (m, 10H, ArH), 7.81 (d, J = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.0, 21.4, 31.7, 49.2, 53.5, 126.2, 126.4, 127.2, 127.5, 127.6, 127.8, 128.5, 129.2, 131.0, 131.7, 133.6, 133.9, 136.3, 136.5, 143.6. IR (CH_2Cl_2) ν 3063, 2932, 2096, 2084, 1349, 1165, 1084, 762, 707 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{25}H_{25}O_2N_4S$: 445.1693, Found: 445.1699.



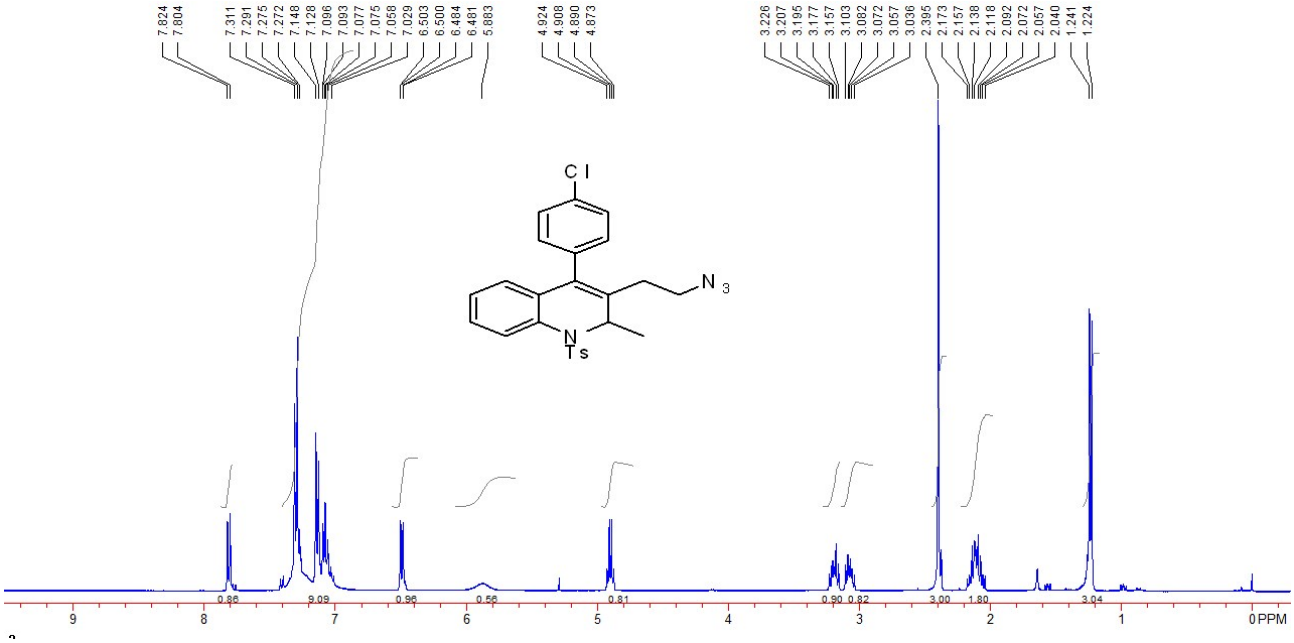


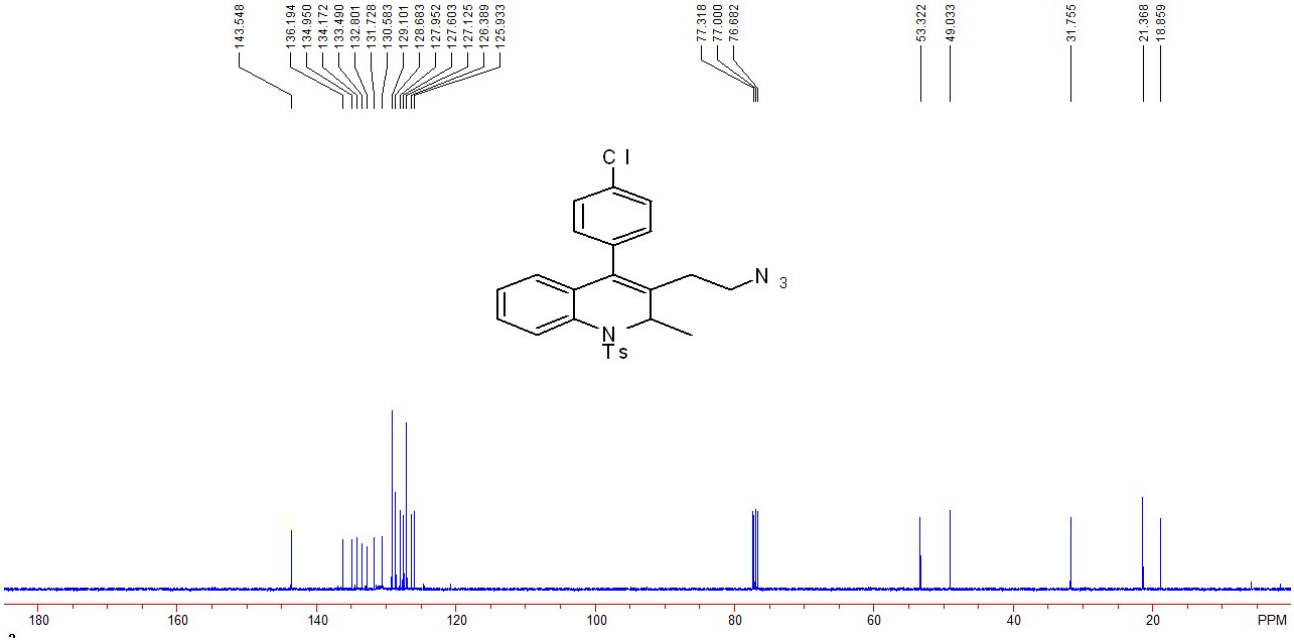


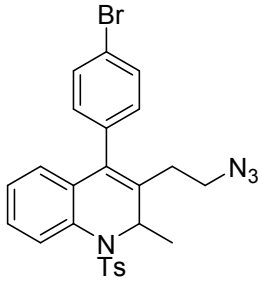
3-(2-azidoethyl)-4-(4-chlorophenyl)-2-methyl-1-tosyl-1,2-dihydroquinoline (2b).

A white solid, 69.9 mg, 73% yield. M.p.: 124-126 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.23 (d, J = 6.8 Hz, 3H, CH_3), 2.04-2.17 (m, 2H, CH2), 2.40 (s, 3H, CH_3), 3.04-3.10 (m, 1H, CH_2), 3.16-

3.23 (m, 1H, CH_2), 4.90 (q, J = 6.8 Hz, 1H, CH), 5.88 (br, 1H, ArH), 6.49 (dd, J = 1.2 Hz, 7.6 Hz, 1H, ArH), 7.03-7.31 (m, 9H, ArH), 7.81 (d, J = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 18.8, 21.4, 31.8, 49.0, 53.3, 125.9, 126.4, 127.1, 127.6, 128.0, 128.6, 129.1, 130.6, 131.7, 132.8, 133.4, 134.2, 134.9, 136.2, 143.5. IR (CH_2Cl_2) ν 2969, 2919, 1692, 1341, 1171, 1086, 1046, 880 cm^{-1}. HRMS (M+Na$^+$) calcd. for $C_{25}H_{23}O_2N_4ClNaS$: 501.1122, Found: 501.1132.

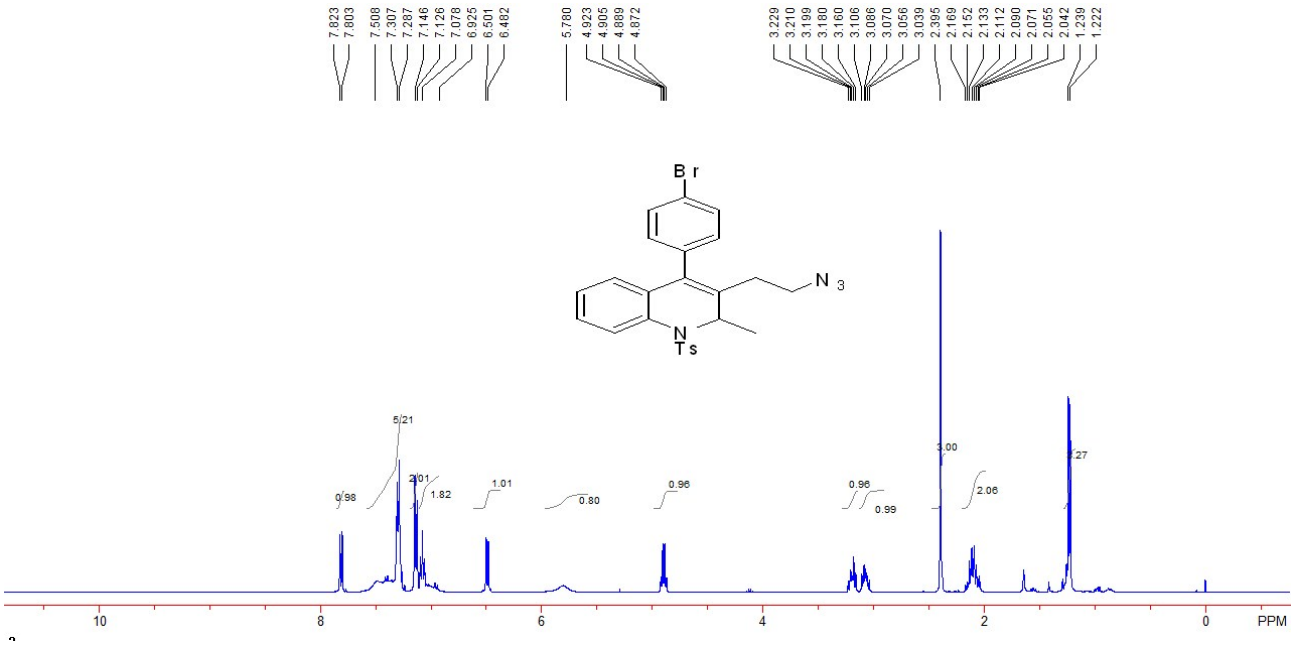


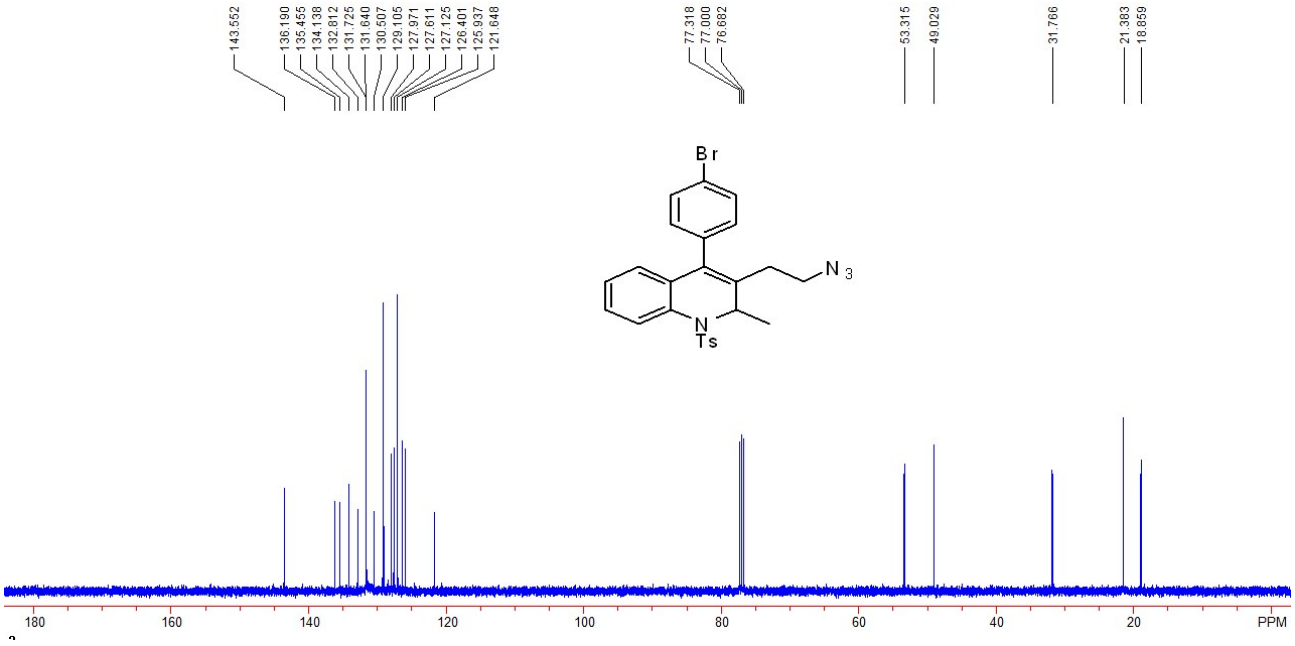


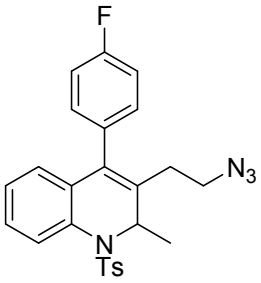


3-(2-azidoethyl)-4-(4-bromophenyl)-2-methyl-1-tosyl-1,2-dihydroquinoline (2c).

A white solid, 72.2 mg, 69% yield. M.p.: 123-125 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.23 (d, J = 6.8 Hz, 3H, CH_3), 2.04-2.17 (m, 2H, CH_2), 2.40 (s, 3H, CH_3), 3.04-3.11 (m, 1H, CH_2), 3.16-3.23 (m, 1H, CH_2), 4.90 (q, J = 6.8 Hz, 1H, CH), 5.78 (br, 1H, ArH), 6.49 (d, J = 7.6 Hz, 1H, ArH), 6.92-7.15 (m, 2H, ArH), 7.29-7.51 (m, 5H, ArH), 7.81 (d, J = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 18.8, 21.4, 31.8, 49.0, 53.3, 121.6, 125.9, 126.4, 127.1, 127.6, 128.0, 129.1, 130.5, 131.6, 131.7, 132.8, 134.1, 135.4, 136.2, 143.6. IR (CH_2Cl_2) ν 2974, 2922, 2099, 1477, 1348, 1165, 1088, 817, 668 cm^{-1}. HRMS (M+Na^{+}) calcd. for $C_{25}H_{23}O_2N_4BrNaS$: 545.0617, Found: 545.0627.

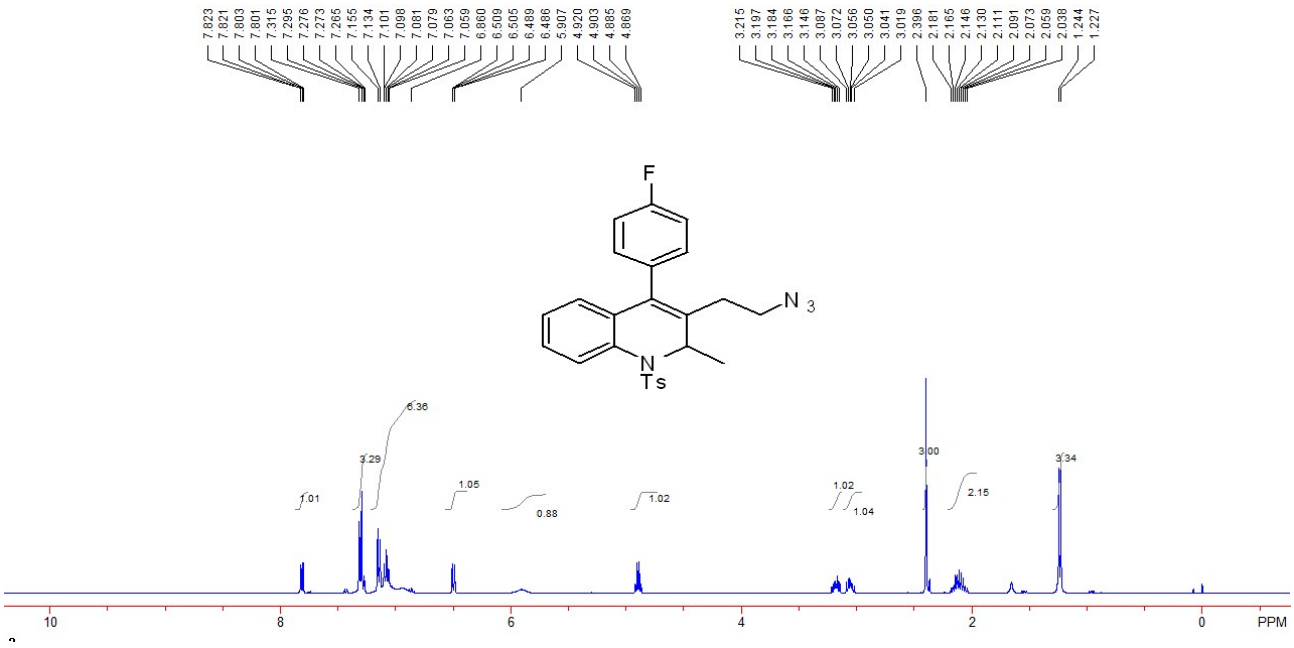






3-(2-azidoethyl)-4-(4-fluorophenyl)-2-methyl-1-tosyl-1,2-dihydroquinoline (2d).

A white solid, 50.0 mg, 64% yield. M.p.: 117-119 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.23 (d, J = 6.8 Hz, 3H, CH_3), 2.04-2.18 (m, 2H, CH_2), 2.40 (s, 3H, CH_3), 3.02-3.09 (m, 1H, CH_2), 3.15-3.22 (m, 1H, CH_2), 4.89 (q, J = 6.8 Hz, 1H, CH), 5.91 (br, 1H, ArH), 6.50 (dd, J = 2.0 Hz, 8.0 Hz, 1H, ArH), 7.06-7.16 (m, 6H, ArH), 7.26-7.32 (m, 3H, ArH), 7.81 (dd, J = 0.8 Hz, 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 375 MHz) δ 18.9, 21.4, 31.7, 49.1, 53.4, 126.0, 126.4, 127.2, 127.6, 127.9, 129.1, 130.8, 131.7, 132.3 (d, J = 3.5 Hz), 133.0, 134.2, 136.2, 143.5, 162.0 (d, J = 245.5 Hz). ^{19}F NMR ($CDCl_3$, TMS, 100 MHz) δ -114.29. IR (CH_2Cl_2) ν 2974, 2924, 2848, 2098, 1508, 1348, 1226, 1167, 1089, 810, 666 cm^{-1}. M HRMS ($M+H^+$) calcd. for $C_{25}H_{24}O_2N_4FS$: 463.1599, Found: 463.1606.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F
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N
Ts
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3.29
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3.00
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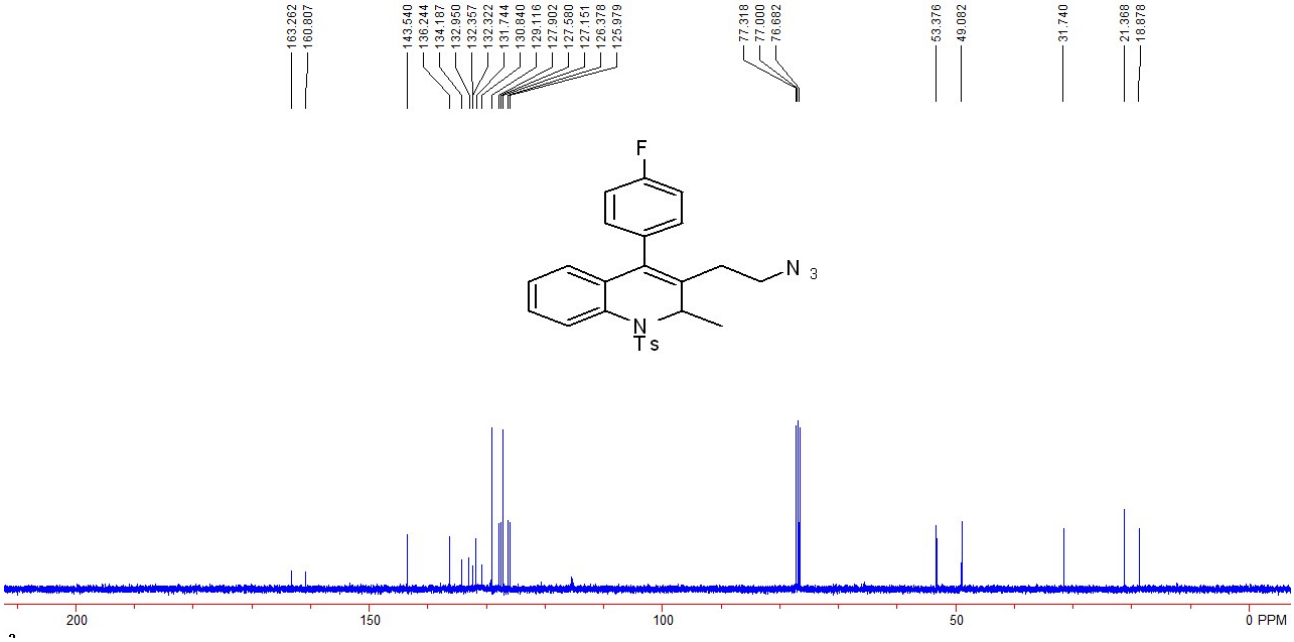
PPM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127.151
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150
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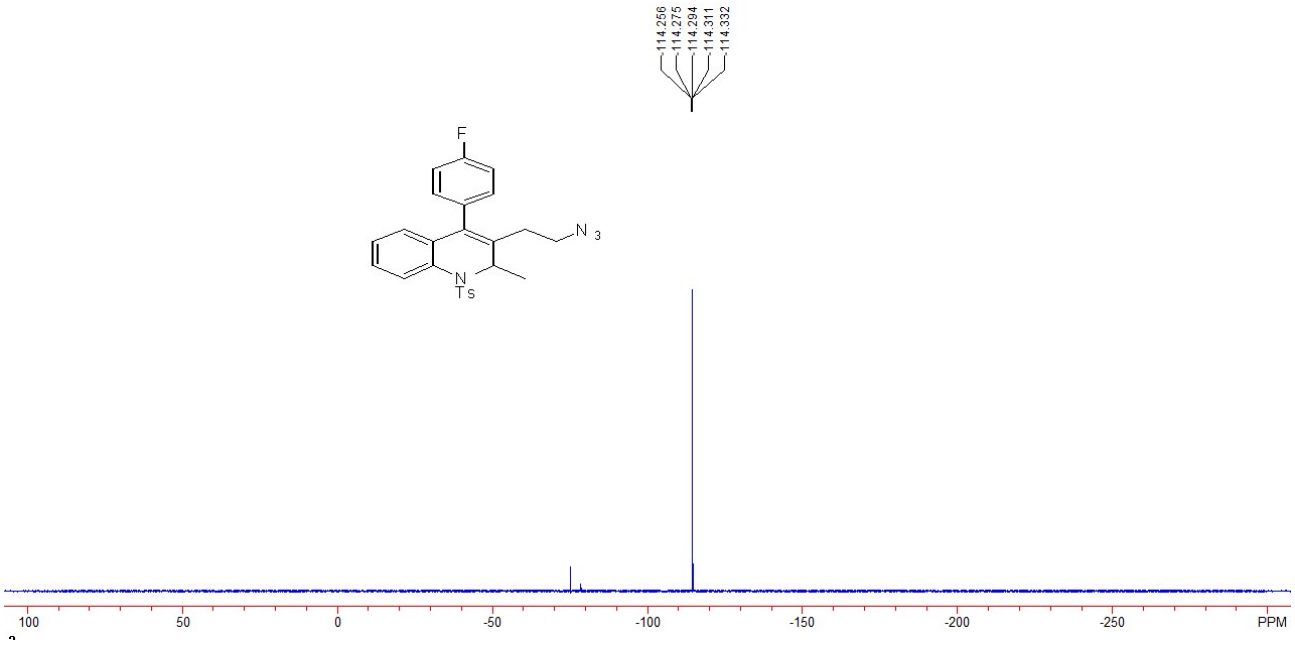
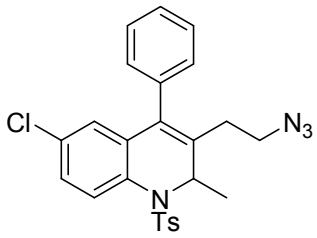
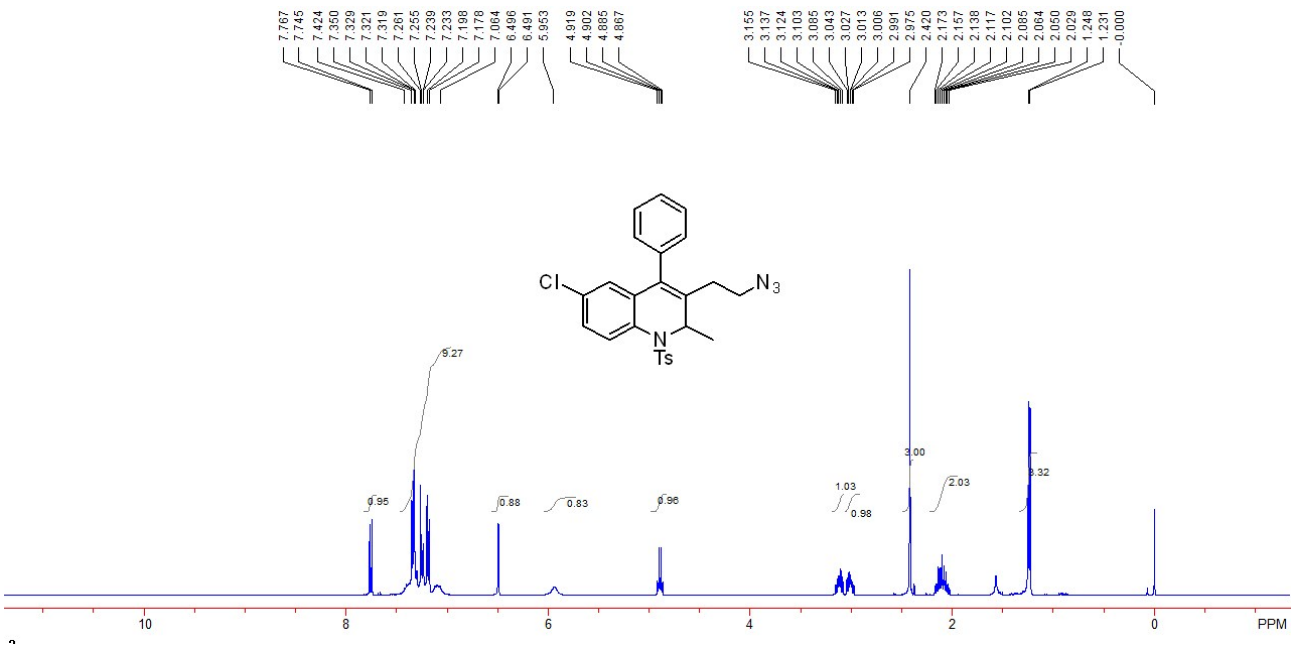
0 PPM

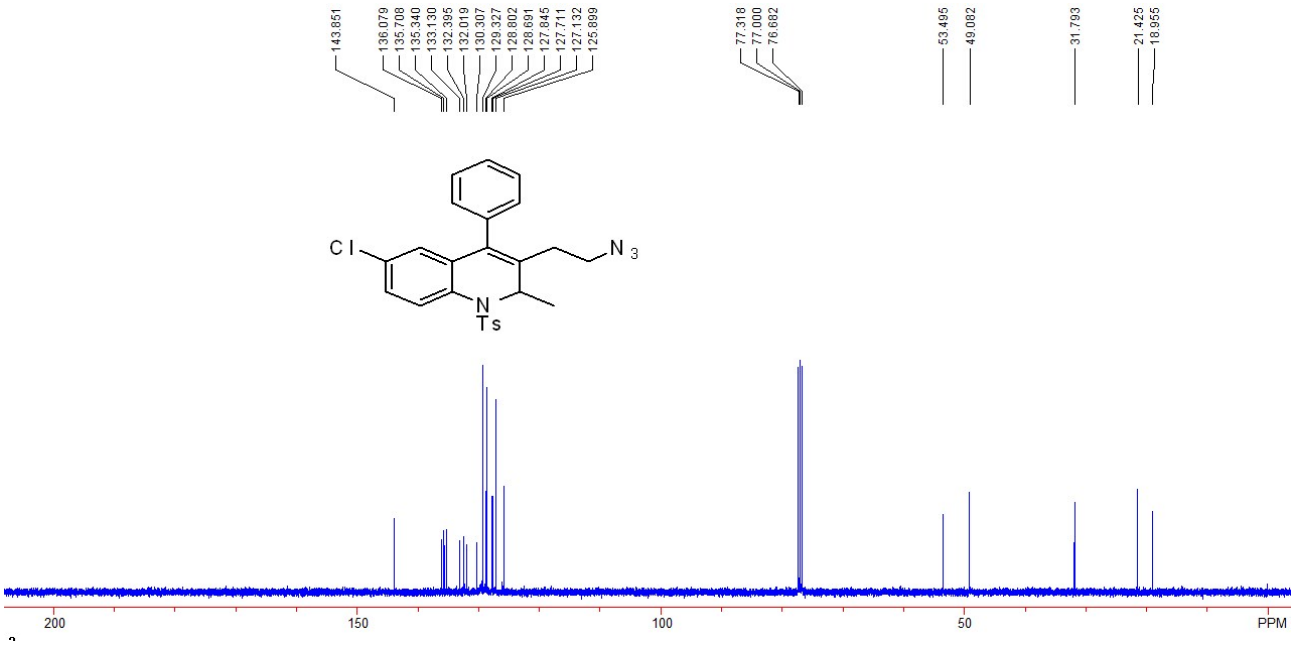


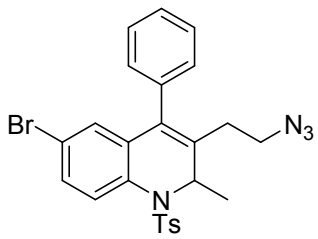


3-(2-azidoethyl)-6-chloro-2-methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (2e).

A white solid, 60.4 mg, 63% yield. M.p.: 129-131 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.24 (d, J = 6.8 Hz, 3H, CH_3), 2.03-2.17 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.98-3.04 (m, 1H, CH_3), 3.08-3.16 (m, 1H, CH_3), 4.89 (q, J = 6.8 Hz, 1H, CH), 5.95 (br, 1H, ArH), 6.49 (d, J = 2.0 Hz, 1H, ArH), 7.06-7.42 (m, 9H, ArH), 7.76 (d, J = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.0, 21.4, 31.8, 49.1, 53.5, 125.9, 127.1, 127.7, 128.7, 128.8, 129.3, 130.3, 132.0, 132.4, 133.1, 135.3, 135.7, 136.1, 143.9. IR (CH_2Cl_2) ν 2924, 2098, 1474, 1350, 1165, 1088, 705, 670 cm^{-1}. HRMS ($M+Na^+$) calcd. for $C_{25}H_{23}O_2N_4ClNaS$: 501.1122, Found: 501.1130.



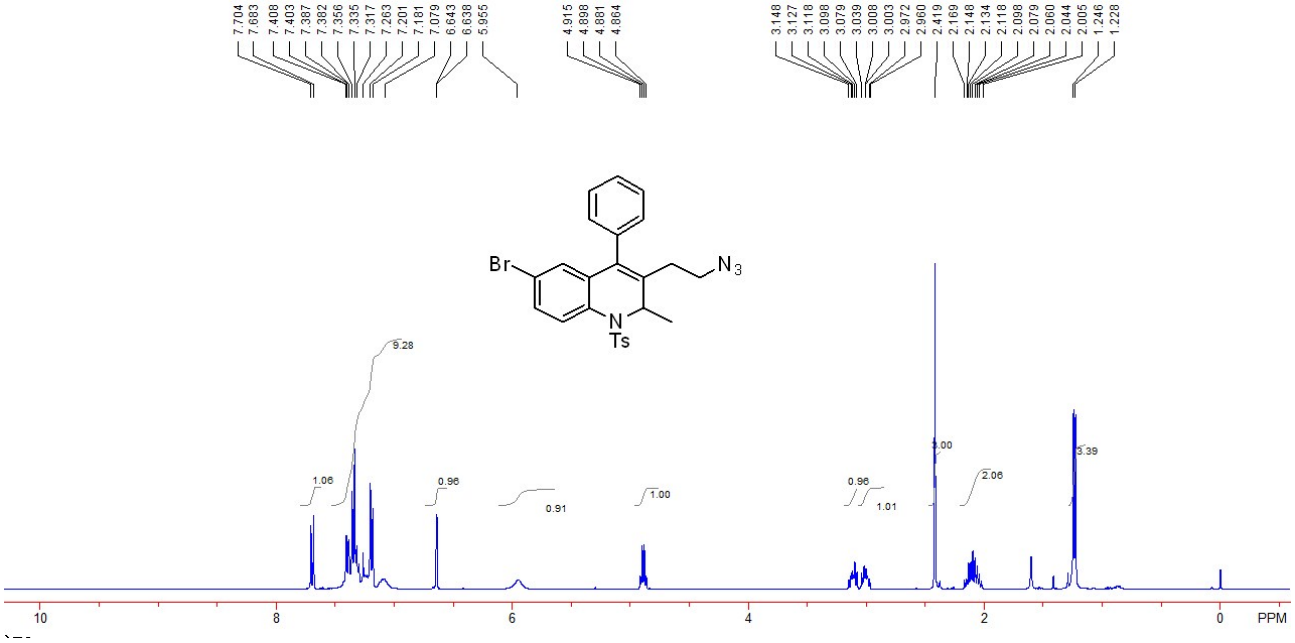


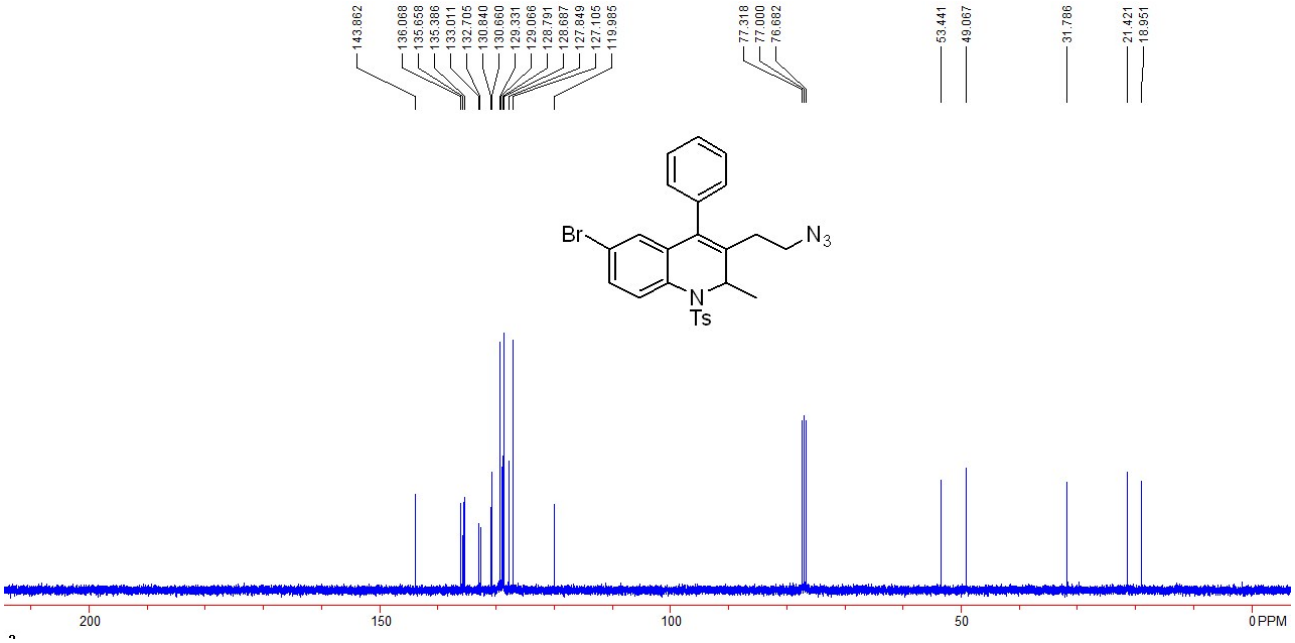


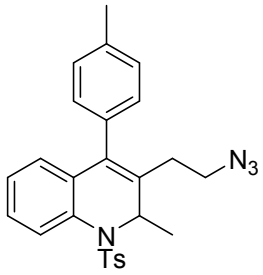
3-(2-azidoethyl)-6-bromo-2-methyl-4-phenyl-1-tosyl-1,2-dihydroquinoline (2f).

A white solid, 60.8 mg, 65% yield. M.p.: 125-127 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.24 (d, J = 7.2 Hz, 3H, CH_3), 2.00-2.17 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.96-3.04 (m, 1H, CH_2), 3.08-3.15 (m, 1H, CH2), 4.89 (q, J = 6.8 Hz, 1H, CH), 5.96 (br, 1H, ArH), 6.64 (d, J = 2.0 Hz, 1H, ArH),

7.08-7.41 (m, 9H, ArH), 7.69 (d, J = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.0, 21.4, 31.8, 49.1, 53.4, 120.0, 127.1, 127.8, 128.7, 128.8, 129.1, 130.7, 130.8, 132.7, 133.0, 135.4, 135.6, 136.1, 143.9. IR (CH_2Cl_2) ν 2922, 2097, 1480, 1349, 1165, 1087, 705, 668 cm^{-1}. HRMS ($M+Na^+$) calcd. for $C_{25}H_{23}O_2N_4BrNaS$: 545.0617, Found: 545.0628.

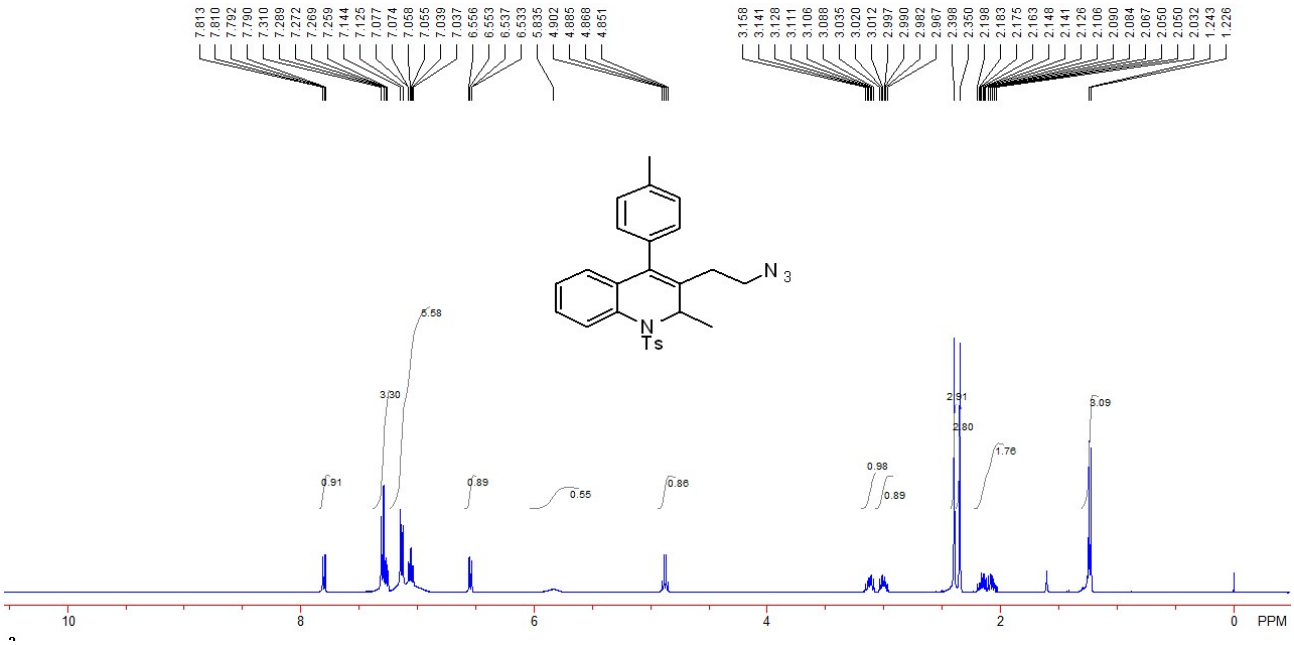


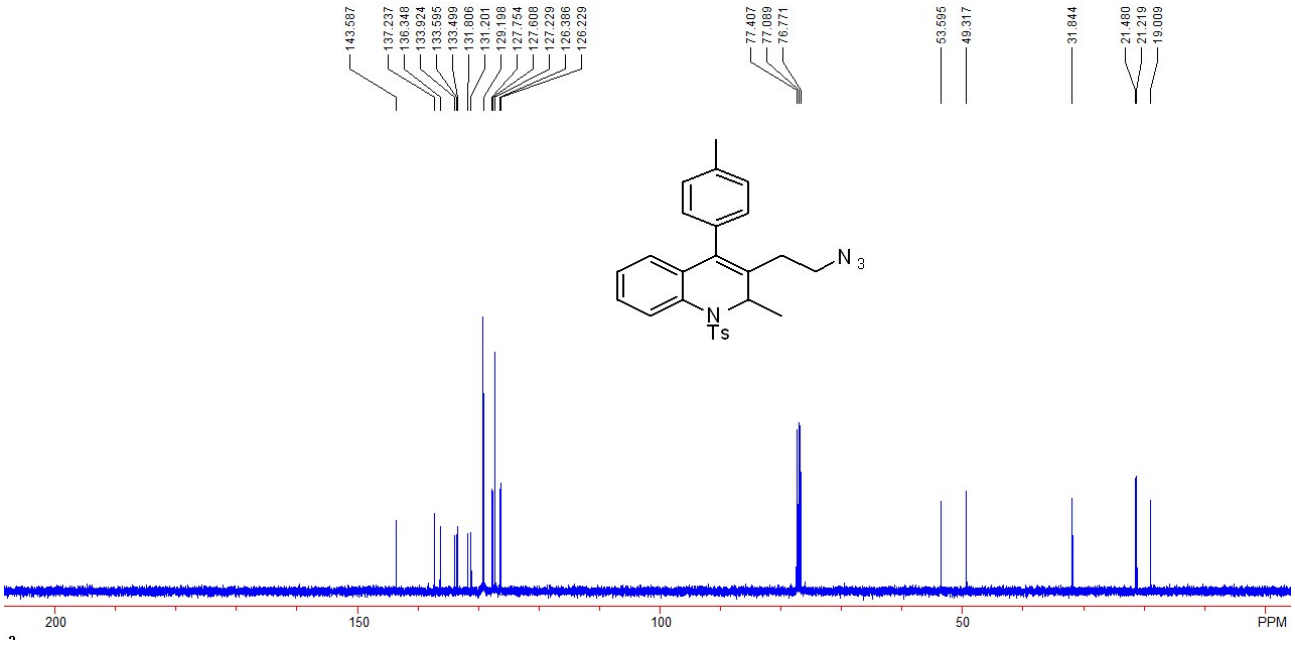


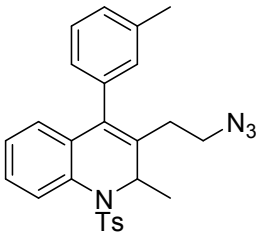


3-(2-azidoethyl)-2-methyl-4-(p-tolyl)-1-tosyl-1,2-dihydroquinoline (2g).

A white solid, 68.8 mg, 75% yield. M.p.: 131-133 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.23 (d, *J* = 6.8 Hz, 3H, CH_3), 2.03-2.20 (m, 2H, CH_2), 2.35 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.97-3.04 (m, 1H, CH_2), 3.09-3.16 (m, 1H, CH_2), 4.88 (q, *J* = 6.8 Hz, 1H, CH), 5.84 (br, 1H, ArH), 6.55 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H, ArH), 7.04-7.14 (m, 6H, ArH), 7.26-7.31 (m, 3H, ArH), 7.80 (dd, *J* = 1.2 Hz, 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.0, 21.2, 21.5, 31.8, 49.3, 53.6, 126.2, 126.4, 127.2, 127.6, 127.8, 129.2, 131.2, 131.8, 133.5, 133.6, 133.9, 136.3, 137.2, 143.6. IR (CH_2Cl_2) ν 2979, 2932, 2097, 1341, 1158, 1084, 812, 770, 666 cm^{-1}. HRMS ($M+Na^+$) calcd. for $C_{26}H_{26}O_2N_4NaS$: 481.1669, Found: 481.1668.

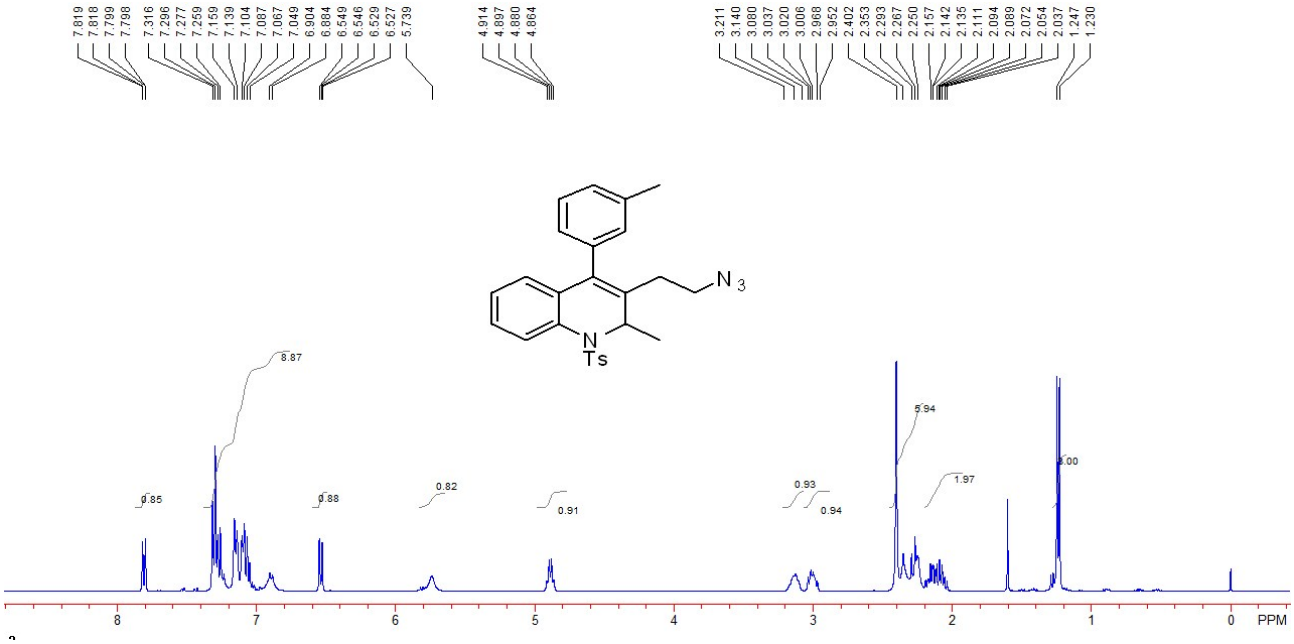


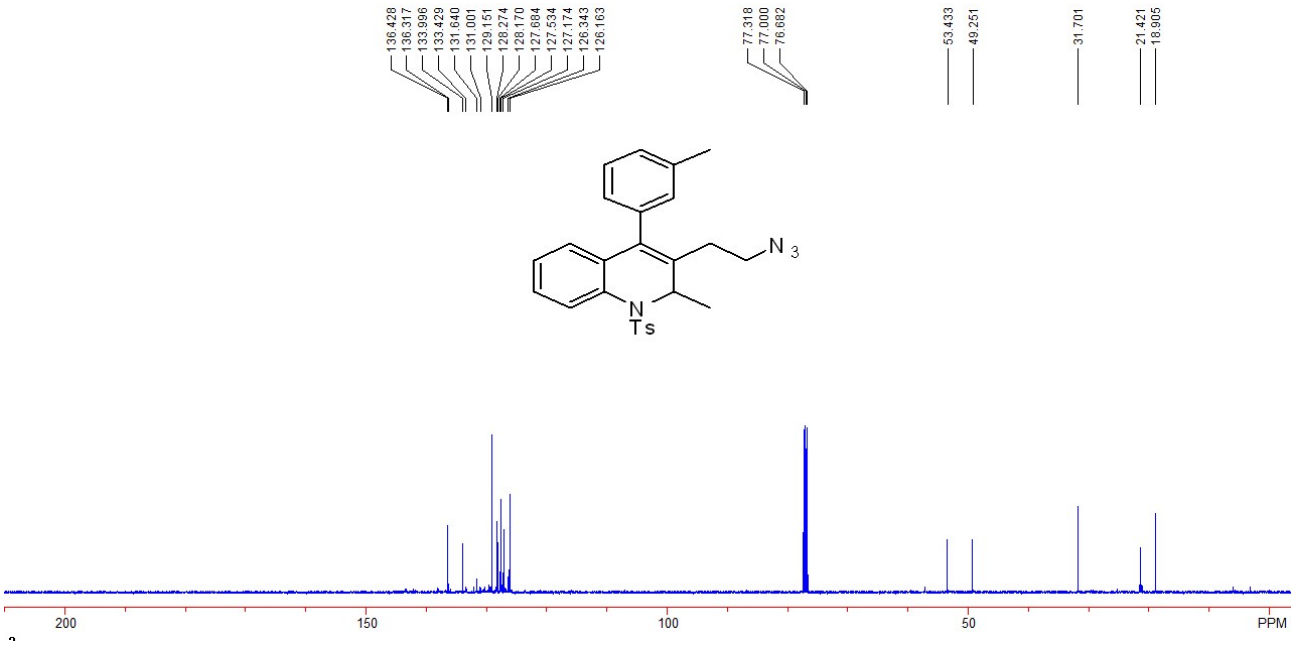


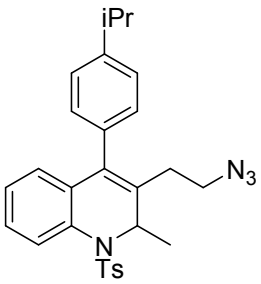


3-(2-azidoethyl)-2-methyl-4-(m-tolyl)-1-tosyl-1,2-dihydroquinoline (2h).

A colorless oil, 70.6 mg, 77% yield. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.24 (d, *J* = 6.8 Hz, 3H, CH3), 2.04-2.16 (m, 2H, CH_2), 2.25-2.40 (m, 3H, CH_3), 2.40 (s, 3H, CH_3), 2.95-3.04 (m, 1H, CH_2), 3.08-3.21 (m, 1H, CH_2), 4.89 (q, *J* = 6.8 Hz, 1H, CH), 5.74 (br, 1H, ArH), 6.54 (dd, *J* = 1.2 Hz, 8.0 Hz, 1H, ArH), 6.88-7.32 (m, 9H, ArH), 7.81 (dd, *J* = 0.4 Hz, 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 18.9, 21.4, 31.7, 49.2, 53.4, 126.2, 126.3, 127.2, 127.5, 127.7, 128.2, 128.3, 129.2, 131.0, 131.6, 133.4, 134.0, 136.3, 136.4. IR (CH_2Cl_2) ν 2972, 2924, 2867, 2098, 1347, 1164, 1090, 1037, 665 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{26}H_{27}O_2N_4S$: 459.1849, Found: 459.1855.



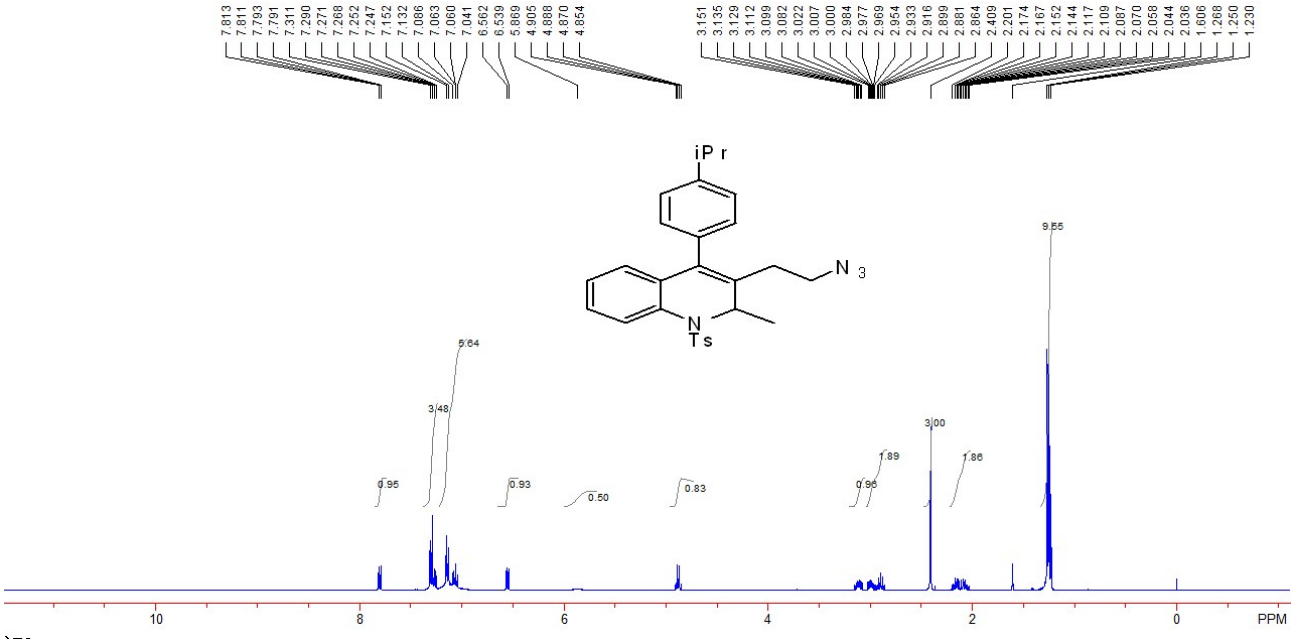


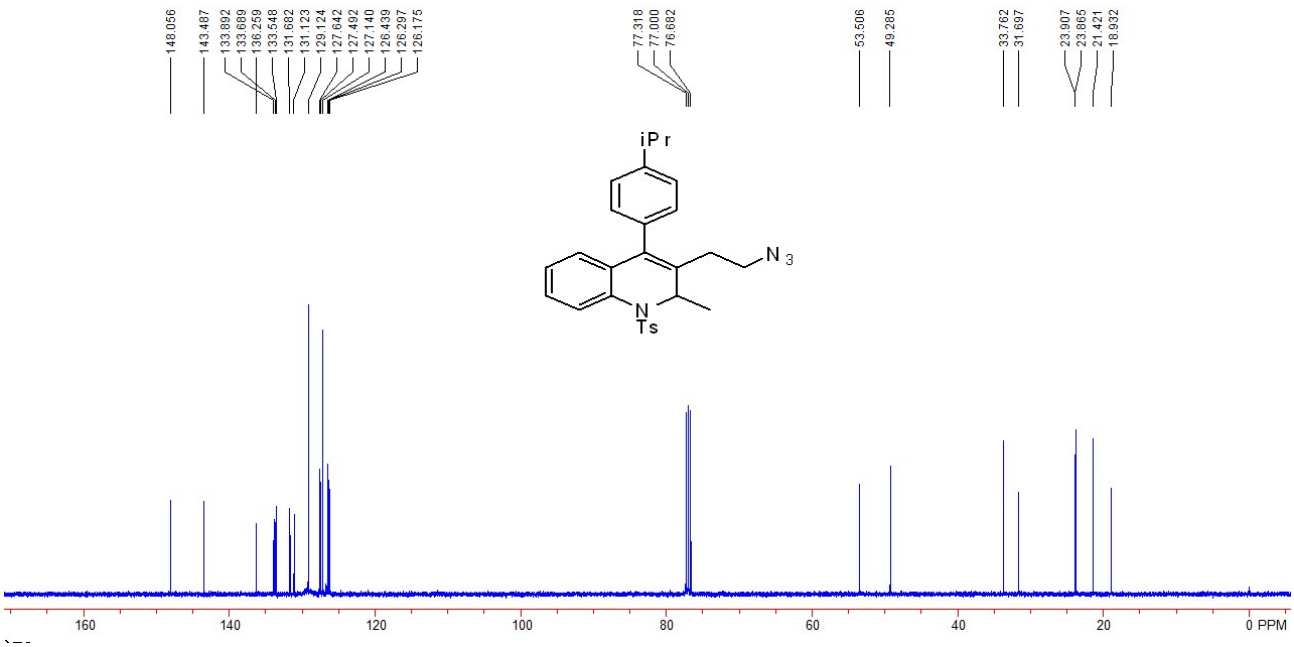


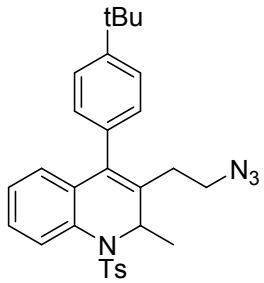
3-(2-azidoethyl)-4-(4-isopropylphenyl)-2-methyl-1-tosyl-1,2-dihydroquinoline (2i).

A white solid, 74.0 mg, 76% yield. M.p.: 114-116 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.23-1.27 (m, 9H, CH_3), 2.04-2.20 (m, 2H, CH_2), 2.41 (s, 3H, CH_3), 2.86-3.02 (m, 2H, CH_2), 3.08-3.15

(m, 1H, CH_2), 4.88 (q, J = 6.8 Hz, 1H, CH), 5.87 (br, 1H, ArH), 6.55 (d, J = 9.2 Hz, 1H, ArH), 7.04-7.15 (m, 6H, ArH), 7.25-7.31 (m, 3H, ArH), 7.80 (dd, J = 0.8 Hz, 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 18.9, 21.4, 23.8, 23.9, 31.7, 33.8, 49.3, 53.5, 126.2, 126.3 126.4, 127.1, 127.5, 127.6, 129.1, 131.1, 131.7, 133.5, 133.7, 133.9, 136.2, 143.5, 148.0. IR (CH_2Cl_2) ν 2964, 2930, 2864, 2099, 1348, 1166, 1089, 666 cm^{-1}. HRMS ($M+Na^+$) calcd. for $C_{28}H_{30}O_2N_4NaS$: 509.1982, Found: 509.1982.

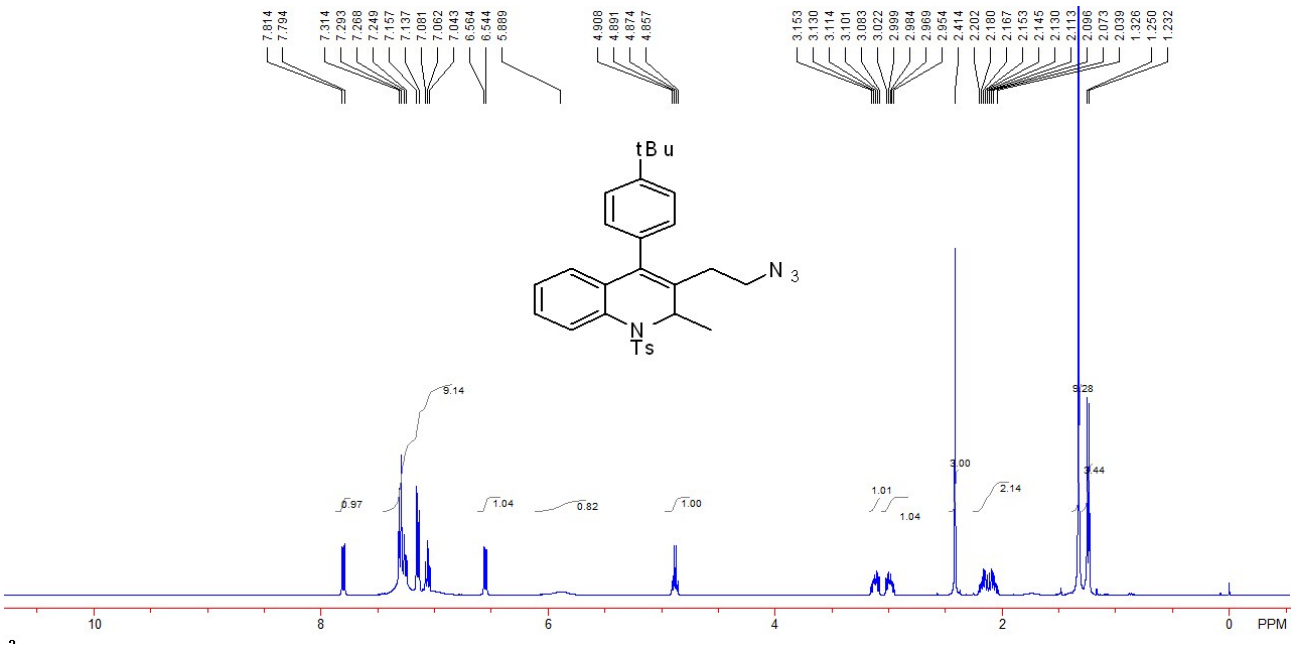


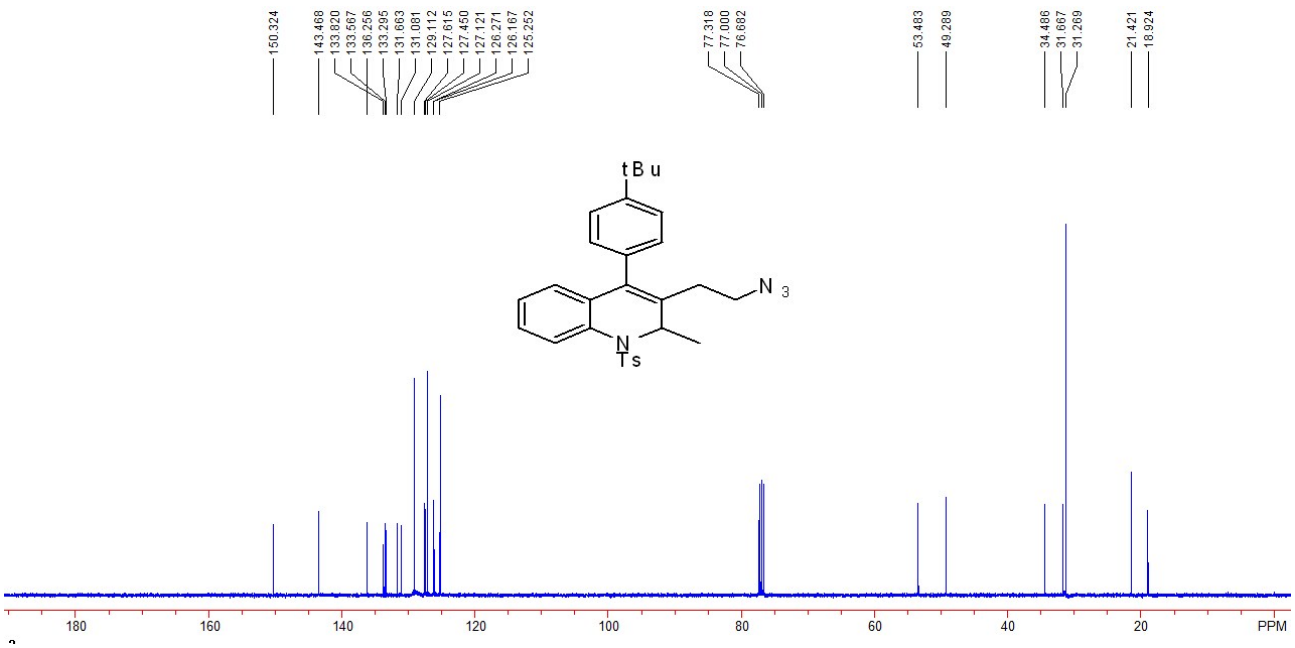


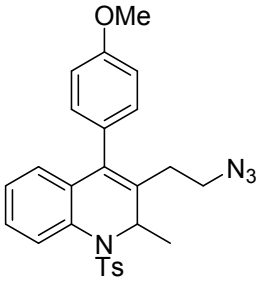


3-(2-azidoethyl)-4-(4-(tert-butyl)phenyl)-2-methyl-1-tosyl-1,2-dihydroquinoline (2j).

A white solid, 80.1 mg, 80% yield. M.p.: 109-111 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.24 (d, J = 7.2 Hz, 3H, CH_3), 1.33 (s, 9H, CH_3), 2.04-2.20 (m, 2H, CH_2), 2.41 (s, 3H, CH_3), 2.95-3.02 (m, 1H, CH_2), 3.08-3.15 (m, 1H, CH_2), 4.88 (q, J = 6.8 Hz, 1H, CH), 5.89 (br, 1H, ArH), 6.55 (d, J = 8.0 Hz, 1H, ArH), 7.04-7.31 (m, 9H, ArH), 7.80 (d, J = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 18.9, 21.4, 31.3, 31.7, 34.5, 49.3, 53.5, 125.2, 126.2, 126.3, 127.1, 127.4, 127.6, 129.1, 131.1, 131.7, 133.3, 133.6, 133.8, 136.2, 143.5, 150.3. IR (CH_2Cl_2) ν 2958, 2872, 2097, 1480, 1349, 1165, 1088, 762, 666 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{29}H_{33}O_2N_4S$: 501.2319, Found: 501.2327.

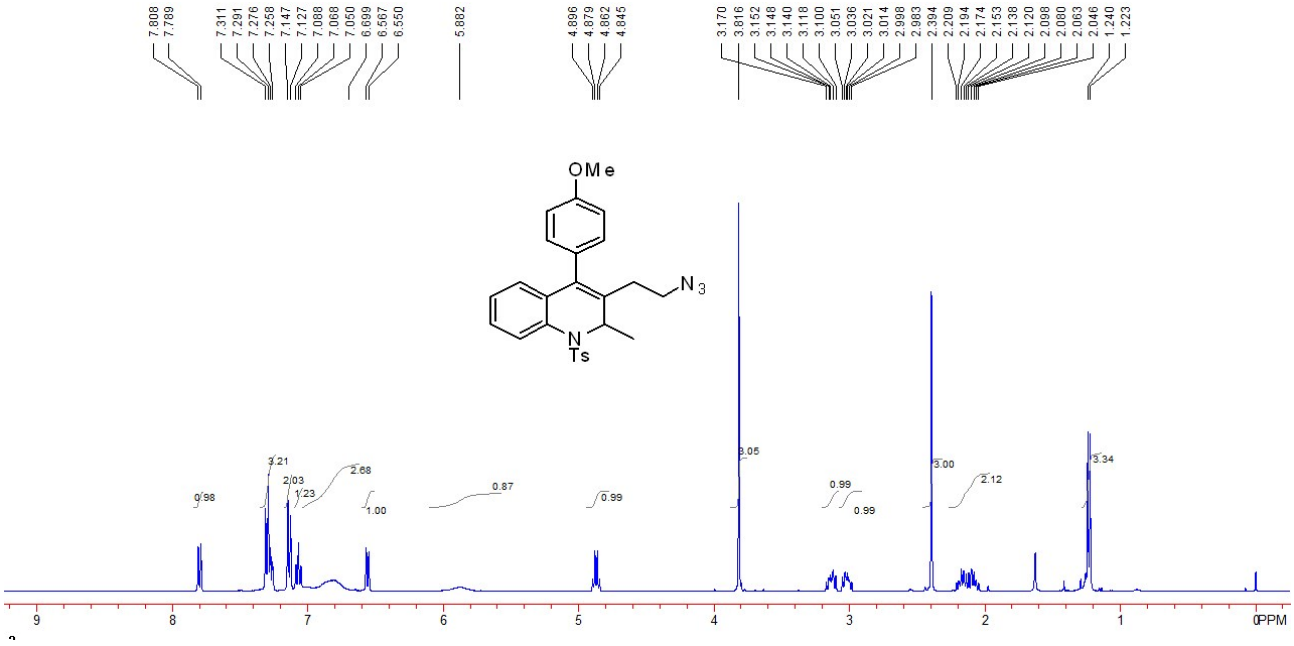


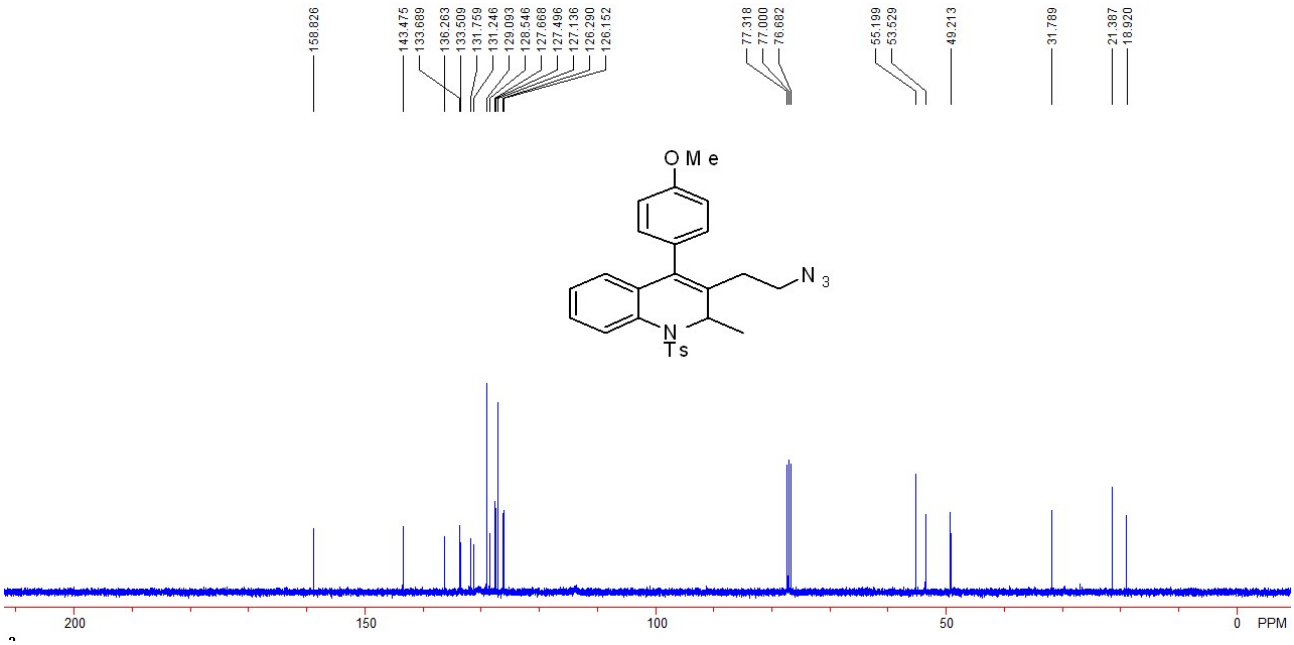


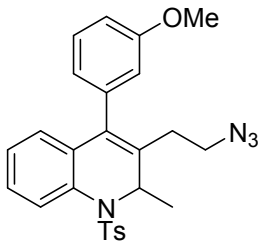


3-(2-azidoethyl)-4-(4-methoxyphenyl)-2-methyl-1-tosyl-1,2-dihydroquinoline (2k).

A white solid, 62.6 mg, 66% yield. M.p.: 118-120 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.23 (d, J = 6.8 Hz, 3H, CH_3), 2.05-2.21 (m, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.98-3.05 (m, 1H, CH_2), 3.10-3.17 (m, 1H, CH_2), 3.82 (s, 3H, ArH), 4.87 (q, J = 6.8 Hz, 1H, CH), 5.88 (br, 1H, ArH), 6.56 (d, J = 6.8 Hz, 1H, ArH), 7.00-7.05 (m, 3H, ArH), 7.07 (t, J = 8.0, 1H, ArH), 7.14 (d, J = 8.0 Hz, 2H, ArH), 7.26-7.31 (m, 3H, ArH), 7.80 (d, J = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 18.9, 21.4, 31.8, 49.2, 53.5, 55.2, 126.2, 126.3, 127.1, 127.5, 127.7, 128.5, 129.1, 131.2, 131.8, 133.5, 133.7, 136.3, 143.5, 158.8. IR (CH_2Cl_2) ν 2972, 2919, 2846, 2092, 1631, 1346, 1244, 1163, 1087, 1044, 878 cm^{-1}. HRMS (M+H^{+}) calcd. for $C_{26}H_{27}O_3N_4S$: 475.1798, Found: 475.1807.



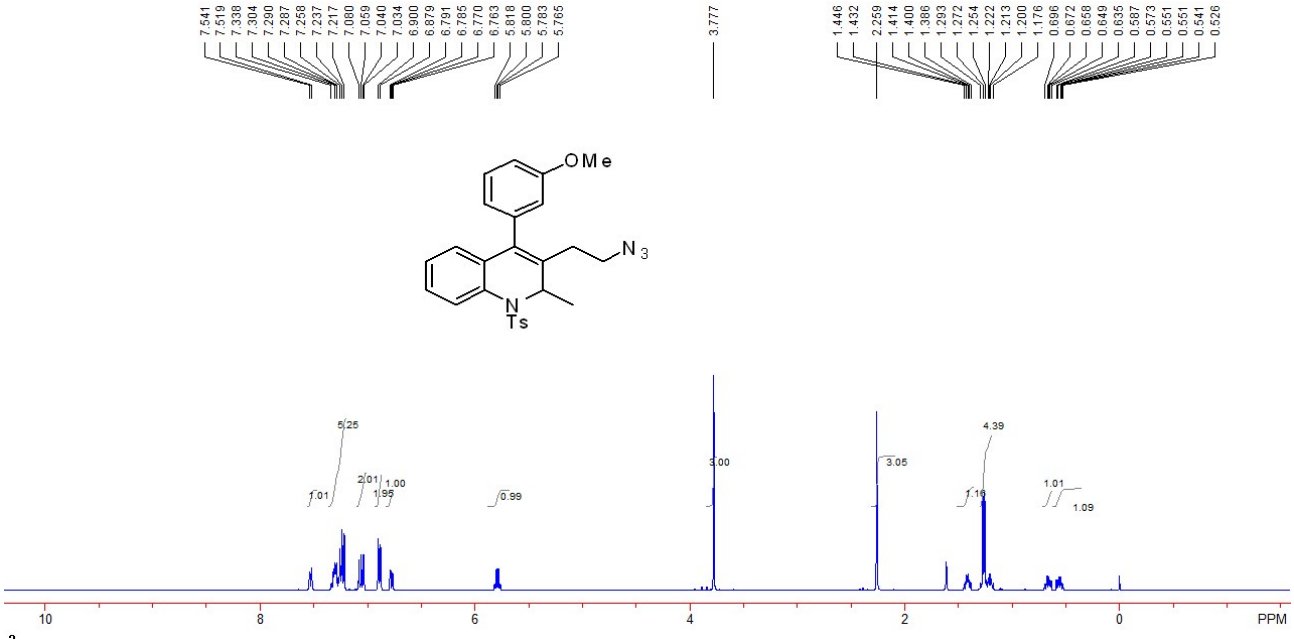


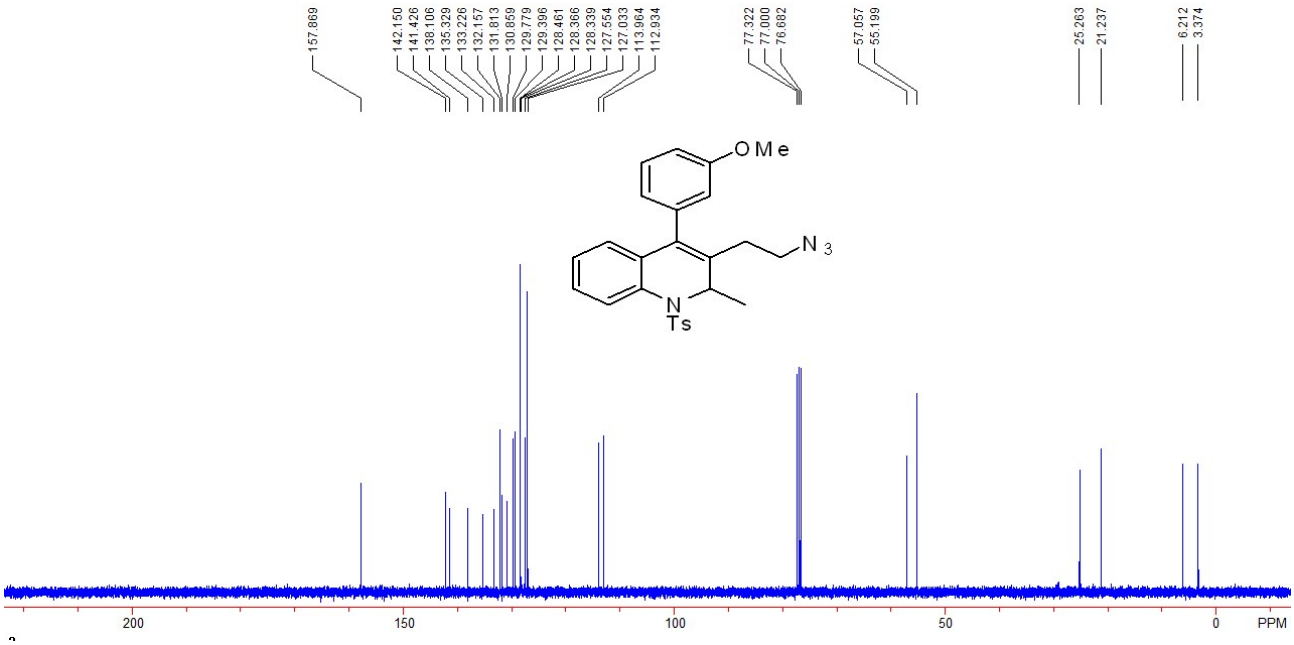


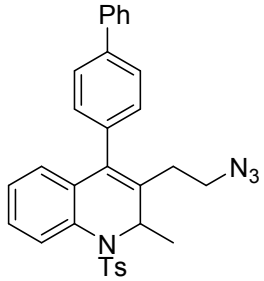
3-(2-azidoethyl)-4-(3-methoxyphenyl)-2-methyl-1-tosyl-1,2-dihydroquinoline (2l).

A white solid, 59.8 mg, 63% yield. M.p.: 176-178 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.53-0.59 (m, 1H, CH_2), 0.64-0.70 (m, 1H, CH_2), 1.18-1.29 (m, 1H, CH_2), 1.26 (d, J = 7.2 Hz, 3H, CH_3), 1.39-1.45 (m, 1H, CH_2), 2.26 (s, 3H, CH3), 3.78 (s, 3H, CH_3), 5.79 (q, J = 7.2 Hz, 1H, CH), 6.78

(dd, J = 2.4 Hz, 8.4 Hz, 1H, ArH), 6.89 (d, J = 8.4 Hz, 2H, ArH), 7.03-7.08 (m, 2H, ArH), 7.22-7.34 (m, 5H, ArH), 7.53 (d, J = 8.8 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 3.4, 6.2, 21.2, 25.3, 55.2, 57.0, 112.9, 114.0, 127.0, 127.6, 128.3, 128.4, 128.5, 129.4, 129.8, 130.8, 131.8, 132.2, 133.2, 135.3, 138.1, 141.4, 142.2, 157.9. IR (CH_2Cl_2) ν 2956, 2914, 2848, 1600, 1495, 1344, 1162, 802, 666 cm^{-1}. HRMS (M-HN_3+H^+) calcd. for $C_{26}H_{26}O_3NS$: 432.1628, Found: 432.1624.

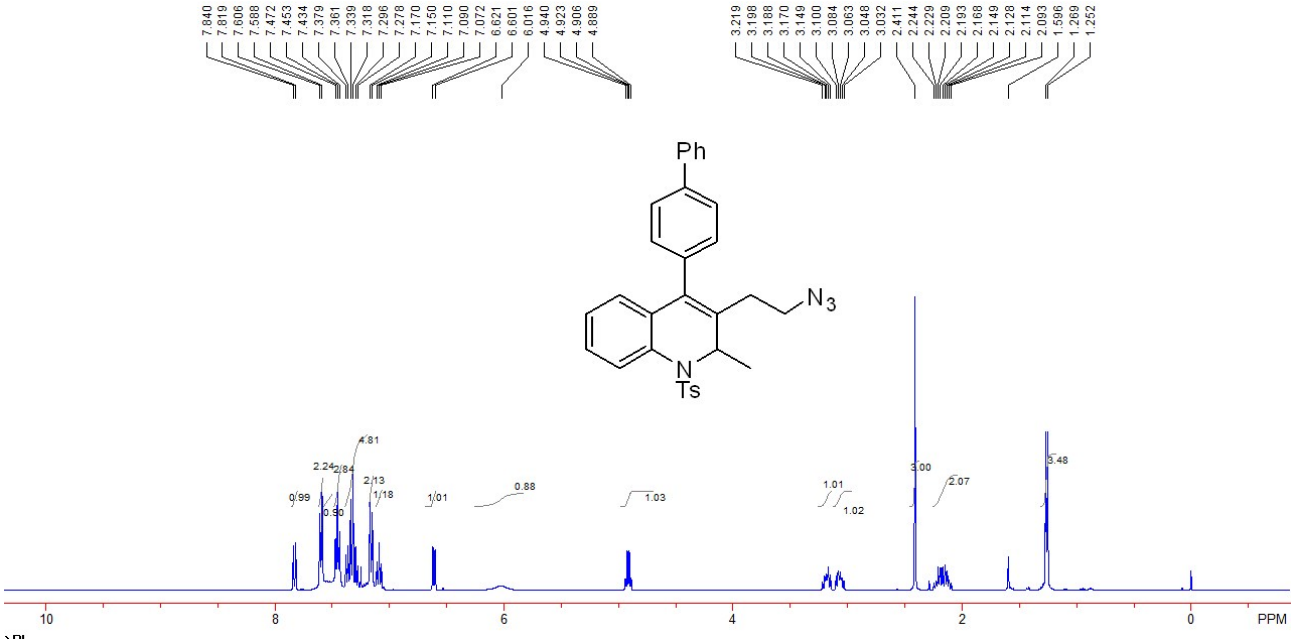


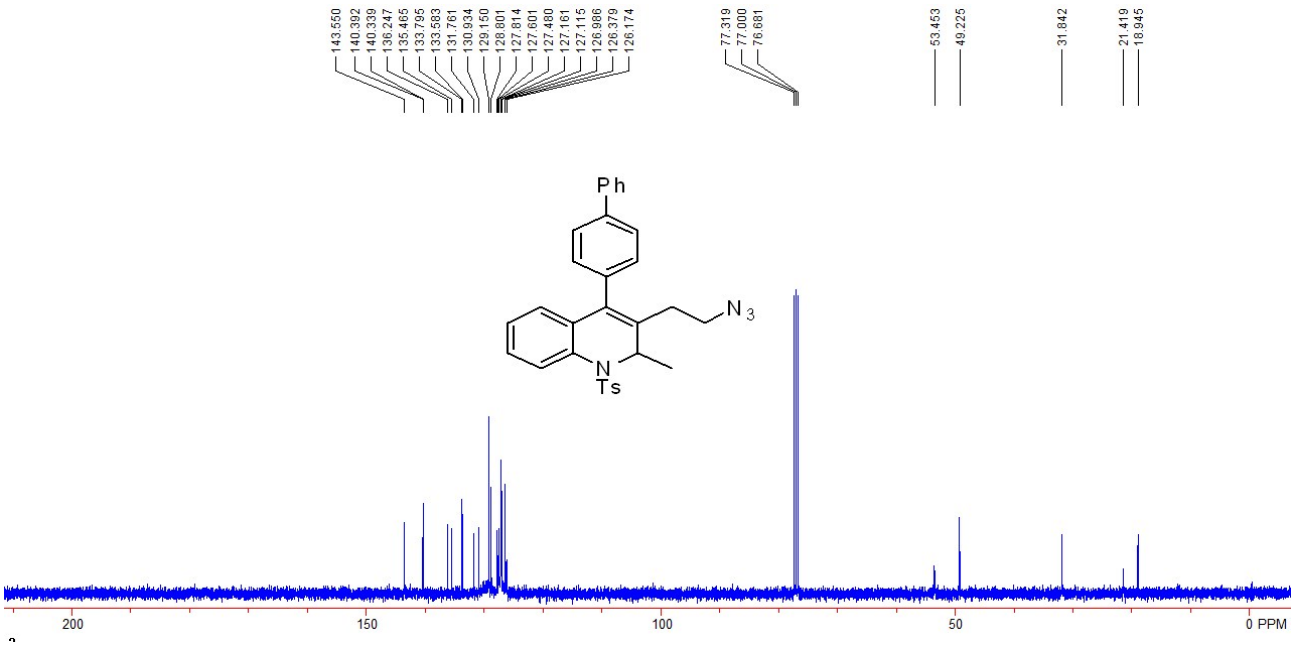


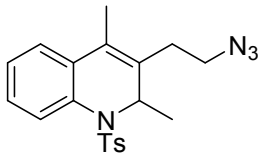


4-([1,1'-biphenyl]-4-yl)-3-(2-azidoethyl)-2-methyl-1-tosyl-1,2-dihydroquinoline (2m).

A white solid, 70.8 mg, 68% yield. M.p.: 67-69 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.26 (d, *J* = 6.8 Hz, 3H, CH_3), 2.09-2.24 (m, 2H, CH_2), 2.41 (s, 3H, CH_3), 3.03-3.10 (m, 1H, CH_2), 3.15-3.22 (m, 1H, CH_2), 4.91 (q, *J* = 6.8 Hz, 1H, CH), 6.02 (br, 1H, ArH), 6.61 (d, *J* = 8.0 Hz, 1H, ArH), 7.09 (t, *J* = 8.0 Hz, 1H, ArH), 7.16 (d, *J* = 8.0 Hz, 2H, ArH), 7.28-7.38 (m, 5H, ArH), 7.45 (t, *J* = 7.6 Hz, 3H, ArH), 7.47-7.59 (m, 1H, ArH), 7.60 (d, *J* = 7.2 Hz, 2H, ArH), 7.83 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 18.9, 21.4, 31.8, 49.2, 53.4, 126.2, 126.4, 127.0, 127.1, 127.2, 127.6, 127.8, 128.8, 129.2, 130.9, 131.8, 133.6, 133.8, 135.5, 136.2, 140.3, 140.4, 143.6. IR (CH_2Cl_2) ν 2972, 2890, 2012, 1480, 1346, 1168, 1084, 762 cm^{-1}. HRMS (M+Na^{+}) calcd. for $C_{31}H_{28}O_2N_4NaS$: 543.1825, Found: 543.1829.

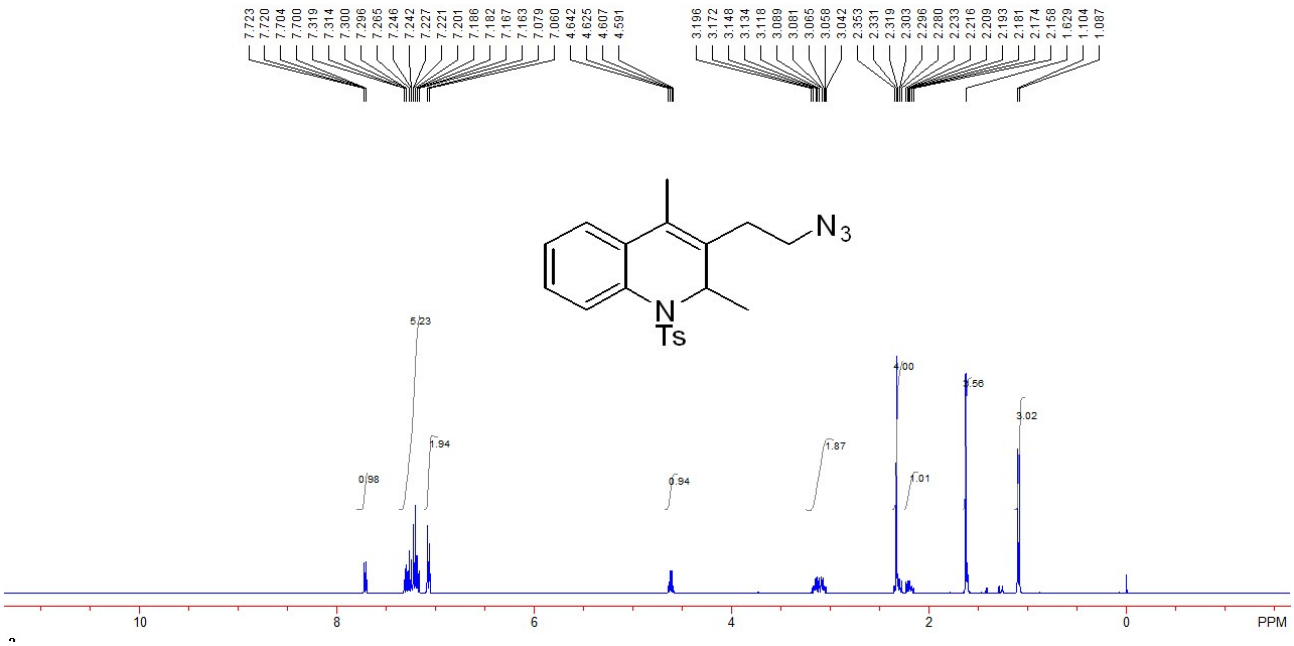


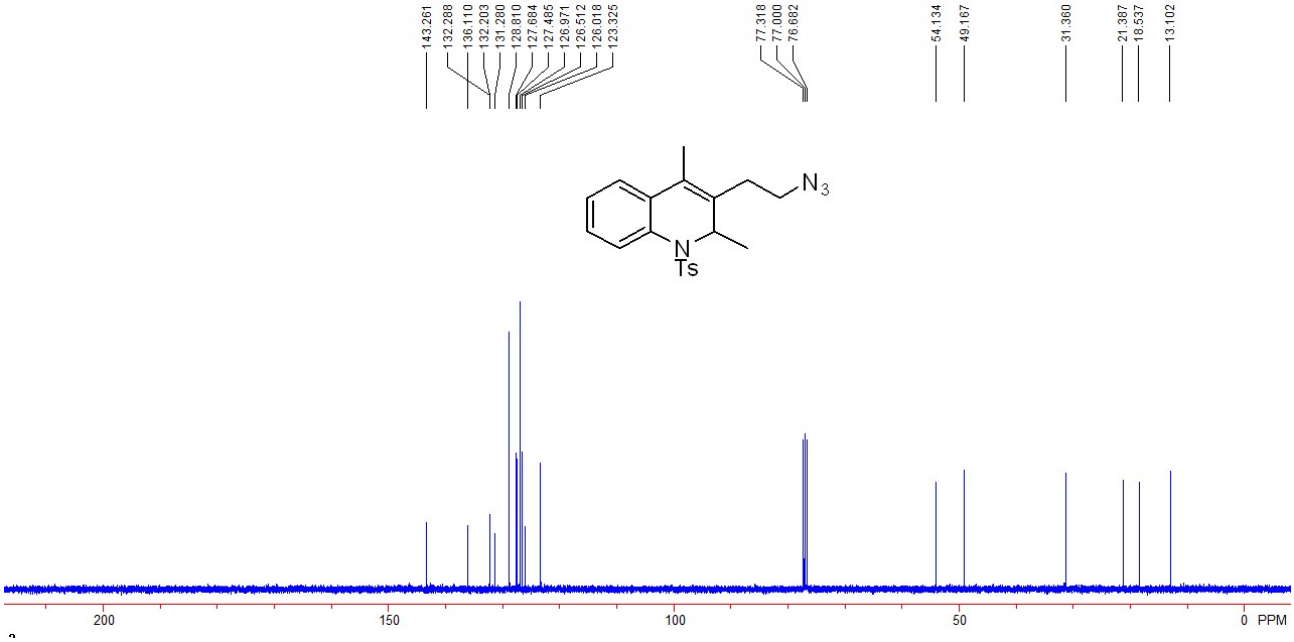


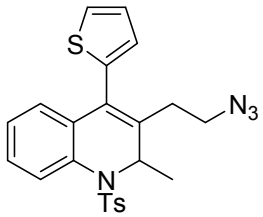


3-(2-azidoethyl)-2,4-dimethyl-1-tosyl-1,2-dihydroquinoline (2n).

A white solid, 590.0 mg, 71% yield. M.p.: 95-97 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.10 (d, *J* = 6.8 Hz, 3H, CH_3), 1.63 (s, 3H, CH_3), 2.16-2.23 (m, 2H, CH_2), 2.28-2.35 (m, 1H, CH_2), 2.33 (s, 3H, CH_3), 3.04-3.20 (m, 2H, CH_2), 4.62 (q, *J* = 6.8 Hz, 1H, CH), 7.07 (d, *J*= 7.6 Hz, 1H, ArH), 7.16-7.32 (m, 5H, ArH), 7.71 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 13.1, 18.5, 214, 31.4, 49.2, 54.1, 123.3, 126.0, 126.5, 127.0, 127.5, 127.7, 128.8, 131.3, 132.2, 132.3, 136.1, 143.3. IR (CH_2Cl_2) ν 2974, 2924, 2869, 2095, 1344, 1163, 1090, 757, 660 cm^{-1}. HRMS (M+Na^{+}) calcd. for $C_{20}H_{22}O_2N_4NaS$: 405.1356, Found: 405.1357.



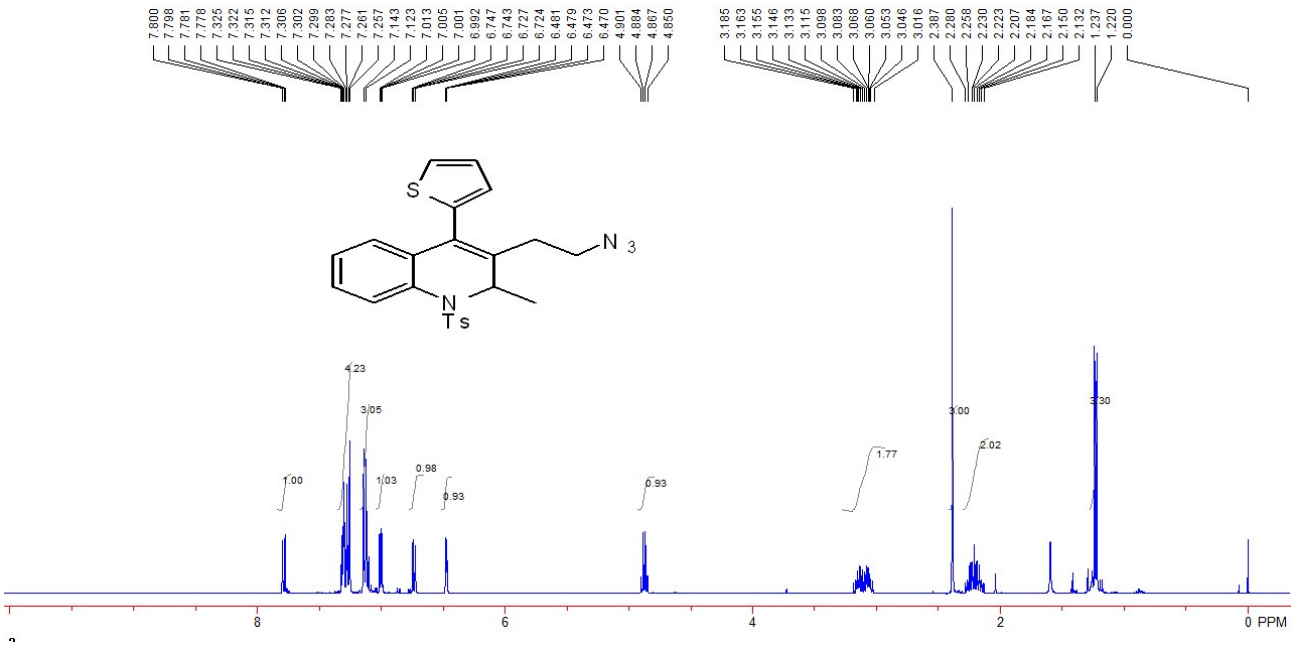


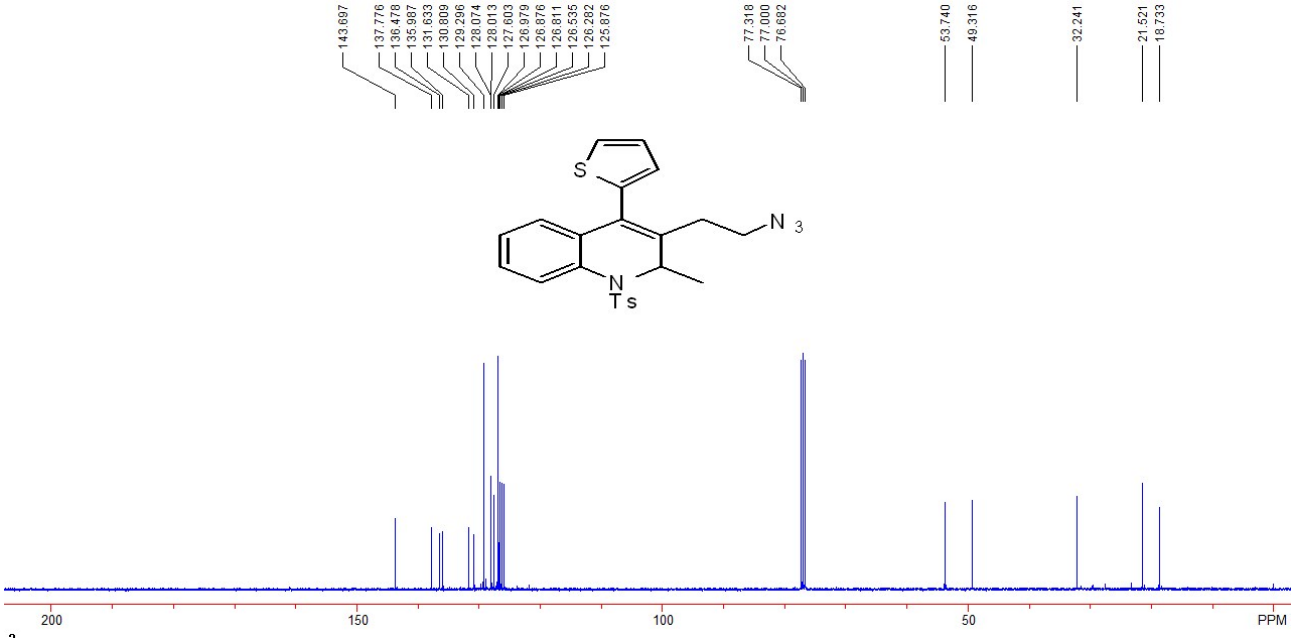


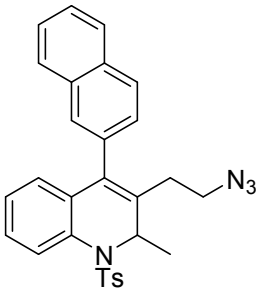
3-(2-azidoethyl)-2-methyl-4-(thiophen-2-yl)-1-tosyl-1,2-dihydroquinoline (2o).

A white solid, 54.1 mg, 60% yield. M.p.: 120-122. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.23 (d, J = 6.8 Hz, 3H, CH_3), 2.13-2.28 (m, 2H, CH_2), 2.39 (s, 3H, CH_3), 3.02-3.18 (m, 2H, CH2), 4.88 (q, J = 6.8 Hz, 1H, CH), 6.48 (dd, J = 0.8 Hz, 3.2 Hz, 1H, ArH), 6.74 (dd, J = 0.8 Hz, 8.0 Hz, 1H, ArH),

6.99-7.01 (m, 1H, ArH), 7.13 (d, J = 8.0 Hz, 3H, ArH), 7.26-7.32 (m, 4H, ArH), 7.79 (dd, J = 0.8 Hz, 8.0 Hz, 1H, Ar). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 18.7, 21.5, 32.2, 49.3, 53.7, 125.9, 126.3, 126.5, 126.8, 127.0, 127.6, 128.0, 128.1, 129.3, 130.8, 131.6, 136.0, 136.5, 137.8, 143.7. IR (CH_2Cl_2) ν 2982, 2927, 2869, 2097, 1347, 1164, 1088, 812, 707, 667 cm^{-1}. HRMS (M+Na$^+$) calcd. for $C_{23}H_{22}O_2N_4NaS_2$: 473.1076, Found: 473.1077.

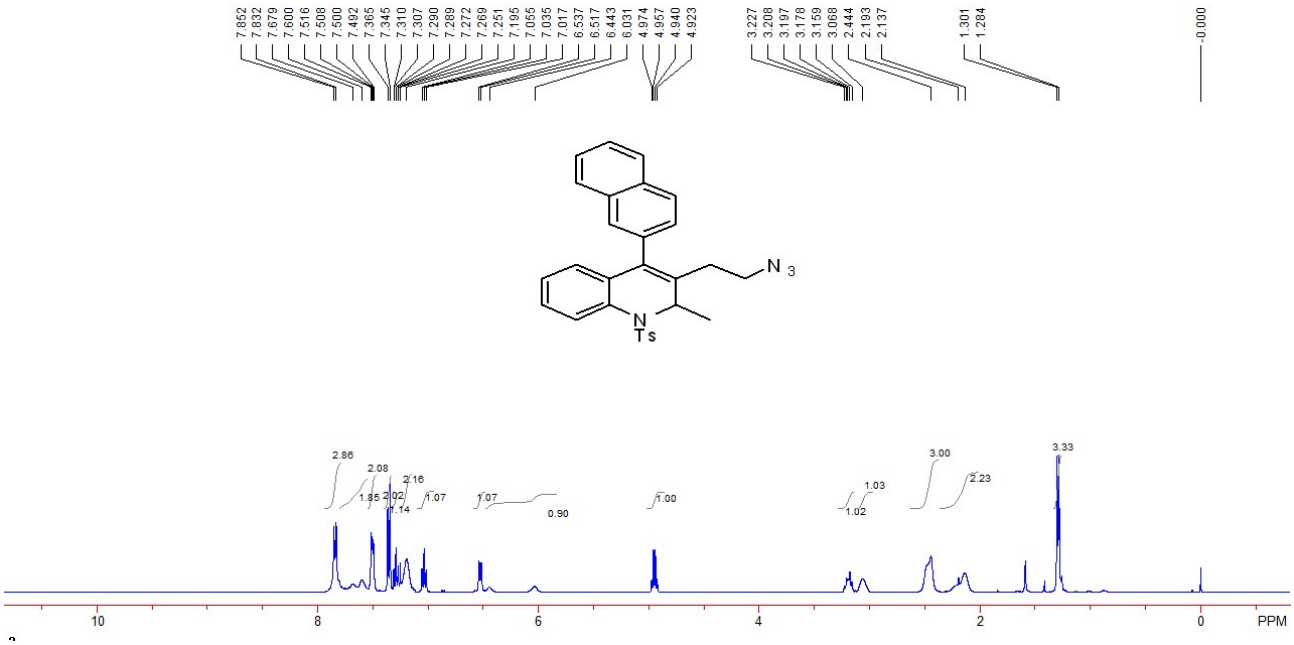


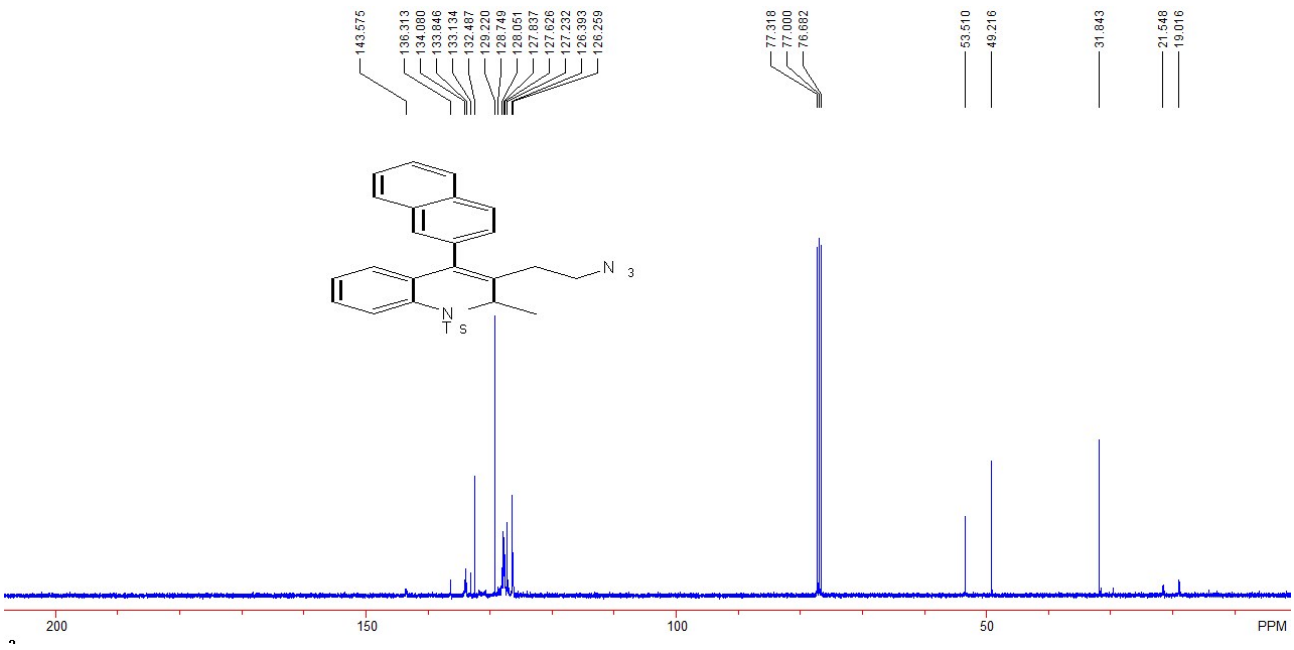


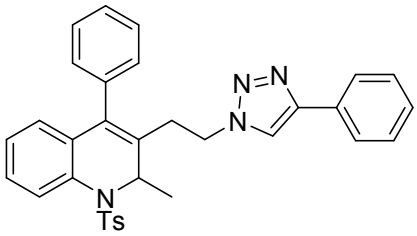


3-(2-azidoethyl)-2-methyl-4-(naphthalen-2-yl)-1-tosyl-1,2-dihydroquinoline (2p).

A white solid, 590.0 mg, 71% yield. M.p.: 142-144 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.29 (d, *J* = 6.8 Hz, 3H, CH3), 2.14 (br, 2H, CH_2), 2.44 (br, 3H, CH_3), 3.07 (br, 1H, CH2), 3.16-3.23 (m, 1H, CH2), 4.95 (q, *J* = 6.8 Hz, 1H, CH), 6.22 (d, *J* = 84.8 Hz, 1H, ArH), 6.53 (d, *J* = 8.0 Hz, 1H, ArH), 7.04 (t, 8.0 Hz, 1H, ArH), 7.20 (br, 2H, ArH), 7.29 (dt, *J* = 1.2 Hz, 8.0 Hz, 1H, ArH), 7.36 (d, *J* = 8.0 Hz, 2H, ArH), 7.49-7.52 (m, 2H, ArH), 7.60-7.68 (m, 2H, ArH), 7.84 (d, *J* = 8.0 Hz, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.0, 21.5, 31.8, 49.2, 53.5, 126.2, 126.4, 127.2, 127.6, 127.8, 128.0, 128.7, 129.2, 132.5, 133.1, 133.8, 134.1, 136.3, 143.6. IR (CH_2Cl_2) ν 2922, 2085, 1344, 1168, 1087, 820, 751, 668 cm^{-1}. HRMS (M+Na^{+}) calcd. for $C_{29}H_{26}O_2N_4NaS$: 517.1669, Found: 517.1671.

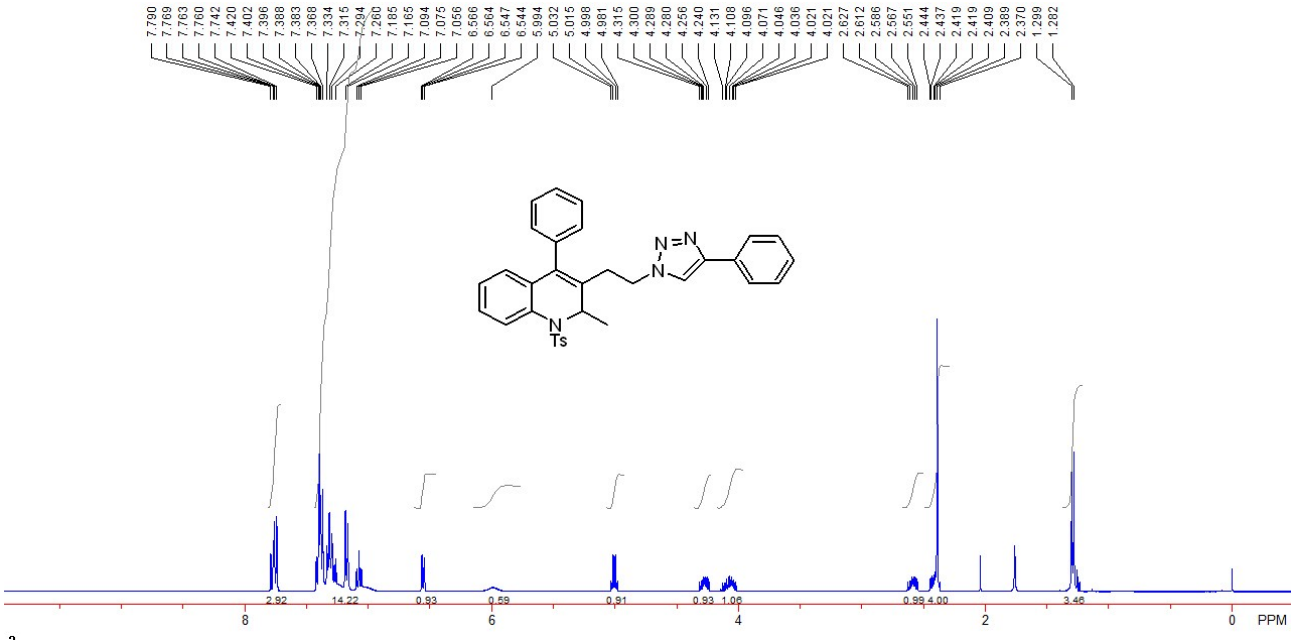






2-methyl-4-phenyl-3-(2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl)-1-tosyl-1,2-dihydroquinoline (3a).

A white solid, 98.4 mg, 90% yield. M.p.: 92-94 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.29 (d, *J* = 6.8 Hz, 3H, CH_3), 2.37-2.44 (m, 1H, CH_2), 2.39 (s, 3H, CH_3), 2.55-2.63 (m, 1H, CH_2), 4.02-4.13 (m, 1H, CH_2), 4.24-4.32 (m, 1H, CH_2), 5.01 (q, *J* = 6.8 Hz, 1H, CH), 5.99 (br, 1H, ArH), 6.56 (dd, *J* = 1.2 Hz, 7.6 Hz, 1H, ArH), 7.06-7.42 (m, 14H, ArH), 7.74-7.79 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 18.9, 21.4, 33.5, 48.1, 53.6, 119.3, 125.6, 126.2, 126.4, 127.1, 127.3, 127.7, 128.0, 128.1, 128.6, 128.8, 129.3, 130.4, 130.6, 131.8, 132.7, 134.7, 136.2, 136.4, 143.8, 147.7. IR (CH_2Cl_2) ν 2977, 2925, 1481, 1348, 1165, 1084, 764, 705, 665 cm^{-1}. HRMS ($M+H^+$) calcd. for $C_{33}H_{31}O_2N_4S$: 547.2162, Found: 547.2172.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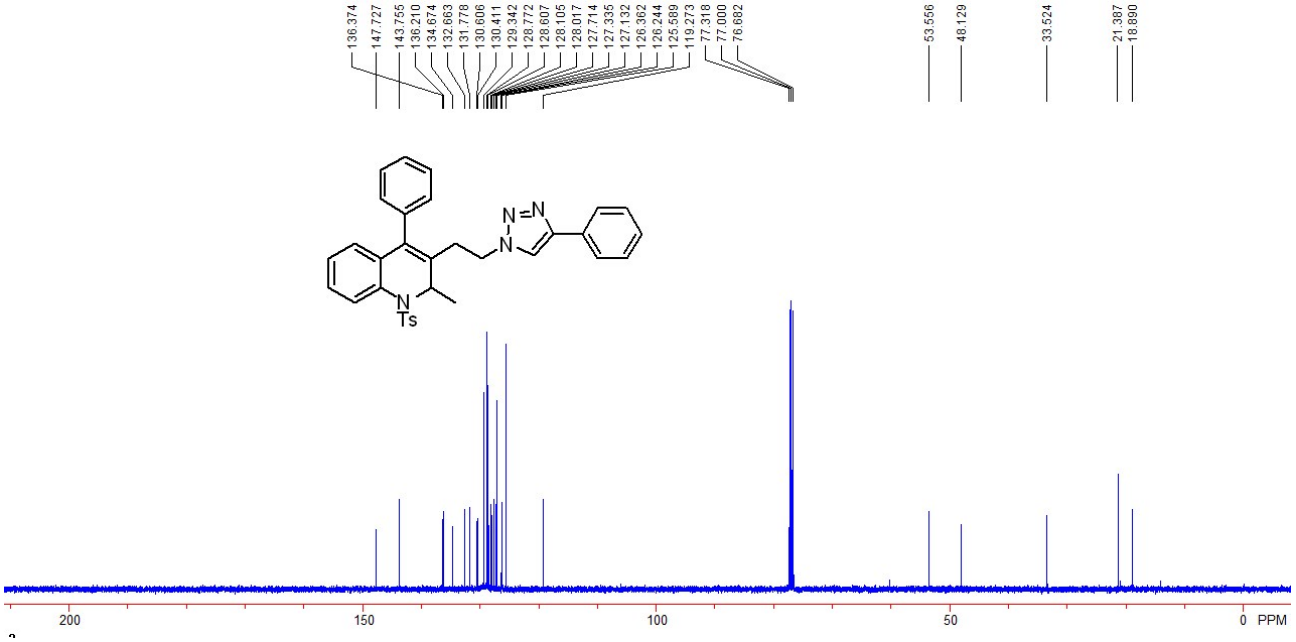
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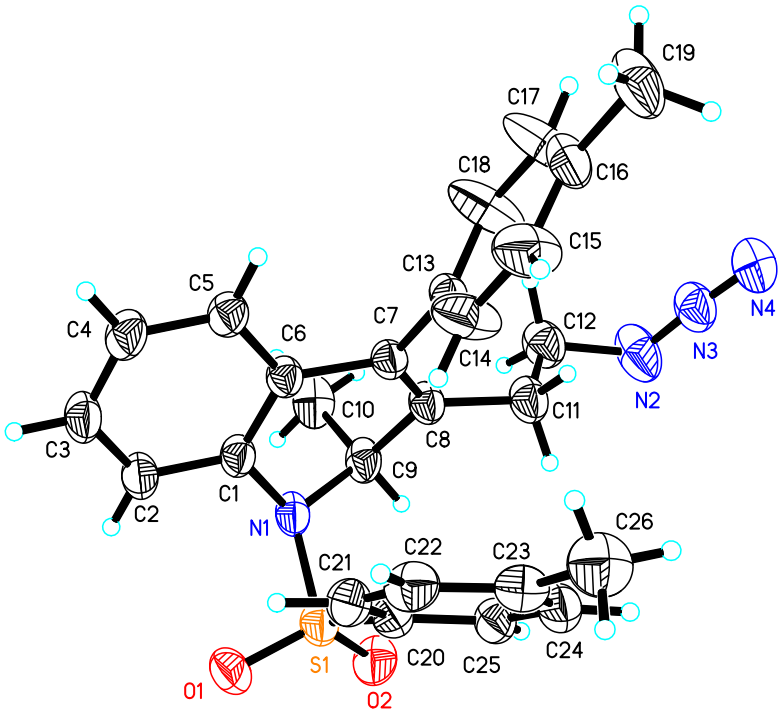
The Crystal Data of 2a



The crystal data of **2a** have been deposited in CCDC with number 1584465. Empirical formula: $C_{26}H_{26}N_4O_2S$, Formula weight: 458.57, Crystal system: Triclinic, Space group: P 21/c, Unit cell dimensions: a = 9.1784(4) Å, α = 90°; b = 15.0323(6) Å, β = 99.5730(10)°; c = 17.5468(6) Å, γ = 90°. Volume: 2387.26(16) $Å^3$, Z = 4, Density (calculated): 1.276 Mg/m^3, F(000) = 968, Crystal size: 0.200 x 0.170 x 0.130 mm^3, Final R indices [I>2sigma(I)]: R1 = 0.0678, wR2 = 0.1932.

References

1. K. Chen, R. Sun, Q. Xu, Y. Wei, M. Shi, *Org. Biomol. Chem.* 2013, **11**, 3949.

2. R.-Q. Ran, J. He, S.-D. Xiu, K.-B. Wang, C.-Y. Li. *Org. Lett.* 2014, **16**, 3704.

3. Q. Wang, B. Jiang, L.-Z. Yu, Y. Wei, M. Shi. *Org. Chem. Front.* 2017, **4**, 1294.