Supporting Information

Rh(I)-Catalyzed Intramolecular [3 + 2] Cycloaddition Reactions of Yne-Vinylidenecyclopropanes

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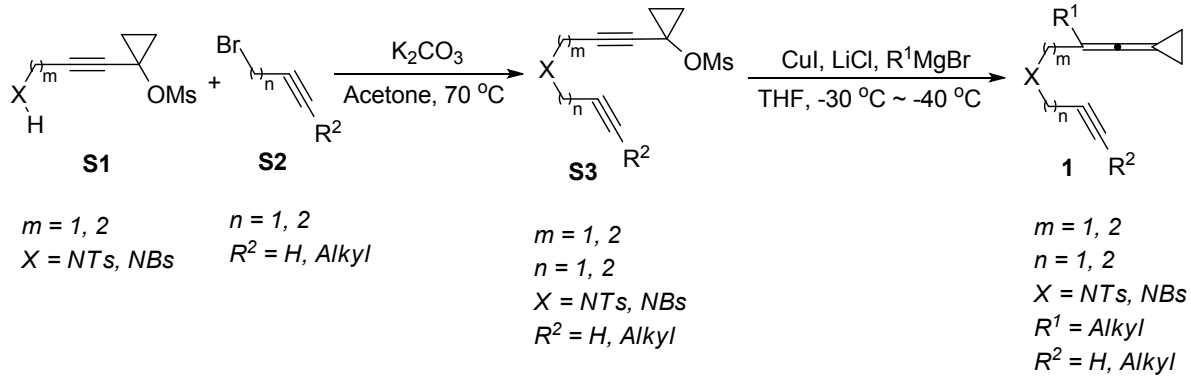
CONTENTS

1. General Remarks.

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. NMR spectra were recorded with a Bruker spectrometer at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR) in $CDCl_3$, respectively. Chemical shift were reported in ppm down field from internal TMS. Organic solvents used were dried by standard methods when necessary. Commercially available reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All reactions were performed under argon using standard Schlenk techniques. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Mass spectra were recorded by ESI and HRMS was measured on a HP-5989 instrument. Substrates **1a** (72% yield), **1b** (65% yield), **1d** (31% yield), **1f** (53% yield), **1g** (48% yield), **1h** (45% yield), **1i** (46% yield), **1j** (46% yield), **1k** (72% yield), **1u** (70% yield) and **1v** (62% yield) were prepared and characterized according to the procedure in the previous literature.[1,2] It is noteworthy that products **2a**-**2j** derived from terminal alkynes were not stable under ambient atmosphere.

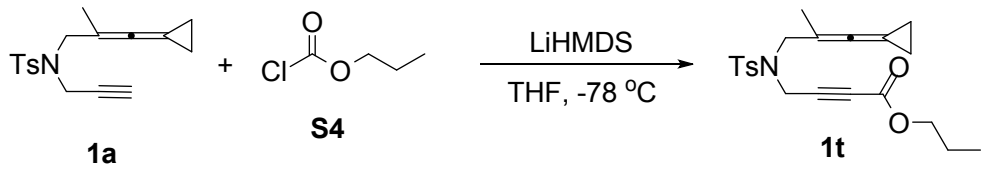
2. General Procedure for the Synthesis of Yne-vinylidenecyclopropanes 1



To the solution of **S1**[3] (1.5 mmol) and K_2CO_3 (1.8 mmol) in acetone (10 mL) was added **S2** (1.8 mmol). The resulting solution was allowed to stir at 70 °C for 8 h. Then, the reaction mixture was cooled to room temperature and the mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **S3** (PE/EA: 4:1~2:1).

Under argon atmosphere, CuI (2.2 mmol) and LiCl (2.2 mmol) in a three-necked bottle was dried upon heating. Then THF (10 mL) was added. At -15 °C, R^1MgBr (1.0 mol/L in THF, 2.0 mmol, 2.0 mL) was added to the reaction. After 10 minutes, the flask was moved into a -30 °C bath and the reaction mixture was stirred for a while before a solution of **S3** (1.0 mmol) in THF (10 mL) was added dropwise into the above flask. After stirring at -30 °C for 5 h, the reaction was quenched with a saturated NH_4Cl solution, extracted with EA (10 mL x 3), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **1** (PE/EA: 10:1).

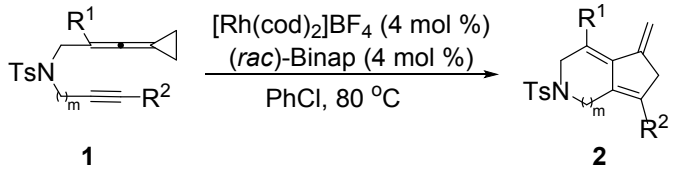
3. Typical Procedure for the Preparation of Compound 1t



1a **S4** **1t**

To the solution of compound **1a** (2.0 mmol) in THF (20 mL) was added LiHMDS (2.2 mmol, 1.0 M in THF) within 20 min at -78 °C under argon. The resulting solution was allowed to stir at -78 °C for 0.5 h before **S4** (3 mmol) was added into the above mixture. Consequently, the reaction mixture was allowed to warm up to room temperature and was stirred for 8 h. Then, a saturated NH_4Cl solution was added to quench the reaction. Extracted with ethyl ether, dried over anhydrous Na_2SO_4, filtered, the organic phase was purified by a flash column chromatography on silica gel to give the corresponding product **1t** in 52% yield (PE/EA: 8:1~10:1).

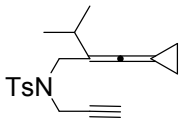
4. General Procedure for the Synthesis of 2.



1 **2**

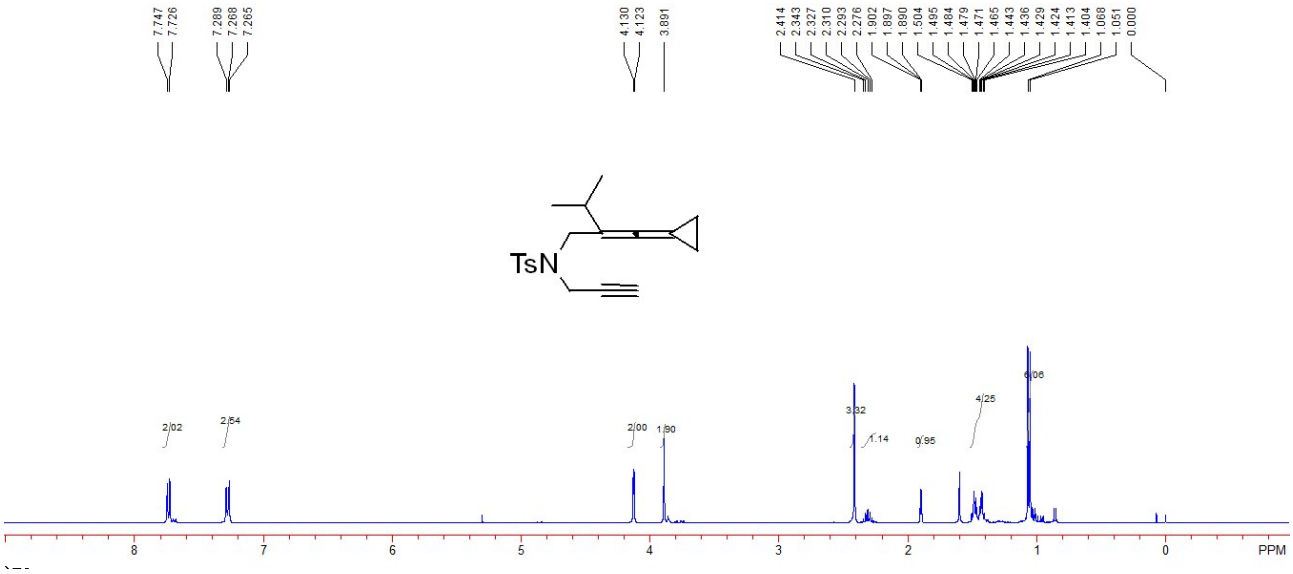
To a 10 mL dried tube was charged with yne-VDCP **1** (0.1 mmol, 1.0 equiv), $[Rh(COD)_2]BF_4$ (4.0 mol %) and (*rac*)-Binap (4.0 mol %). The reaction tube was evacuated and backfilled with argon (repeated three times). Then, PhCl (2.0 mL) was added into the tube. The reaction mixture was stirred at 80 °C for 6-8 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding product **2**.

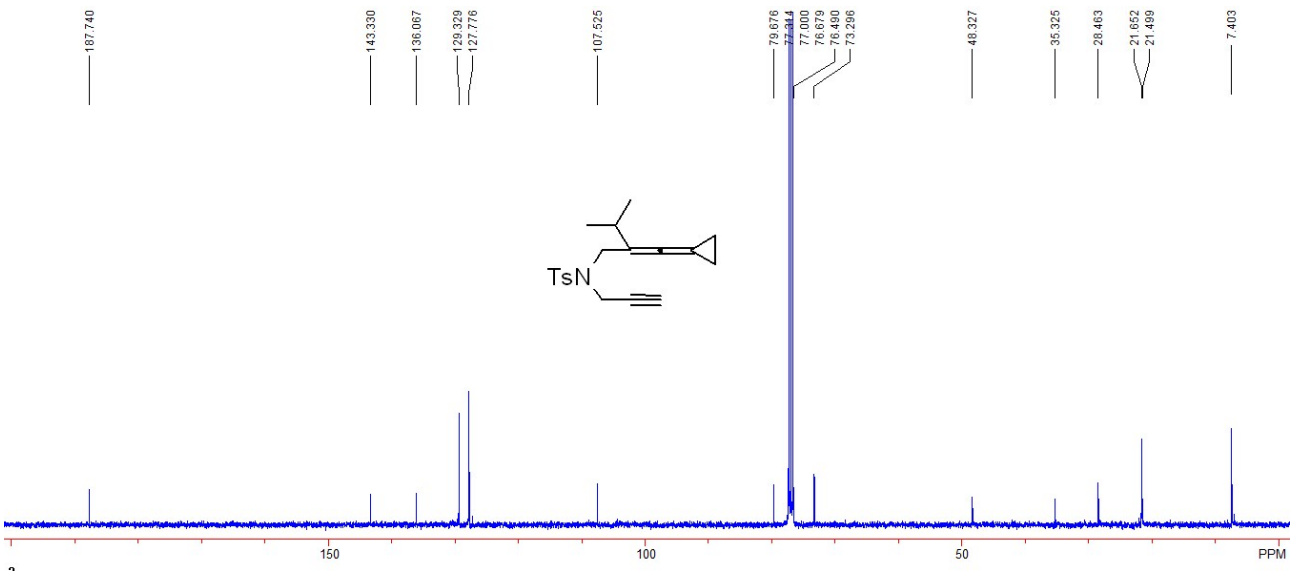
5. The characterization data of compounds 1

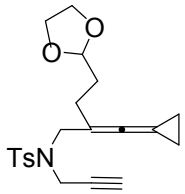


N-(2-(cyclopropylidene-λ^5-methylene)-3-methylbutyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (1c)

2.0 mmol scale, white solid, 67% yield (440 mg). M. P. 91-94 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.13 (d, *J* = 2.8 Hz, 2H), 3.89 (s, 2H), 2.41 (s, 3H), 2.28-2.34 (m, 1H), 1.90 (t, *J* = 2.8 Hz, 1H), 1.05-1.50 (m, 4H), 1.06 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 187.7, 143.3, 136.1, 129.3, 127.8, 107.5, 79.7, 76.5, 73.3, 48.3, 35.3, 28.5, 21.7, 21.5, 7.4; IR (CH_2Cl_2): ν 3285, 3063, 2985, 2909, 2024, 1651, 1599, 1435, 1335, 1088, 1050, 991, 699 cm^{-1}; HRMS (ESI) Calcd. For $C_{19}H_{24}NO_2S$ $(M+H)^+$ requires: 330.1522, Found: 330.1522.

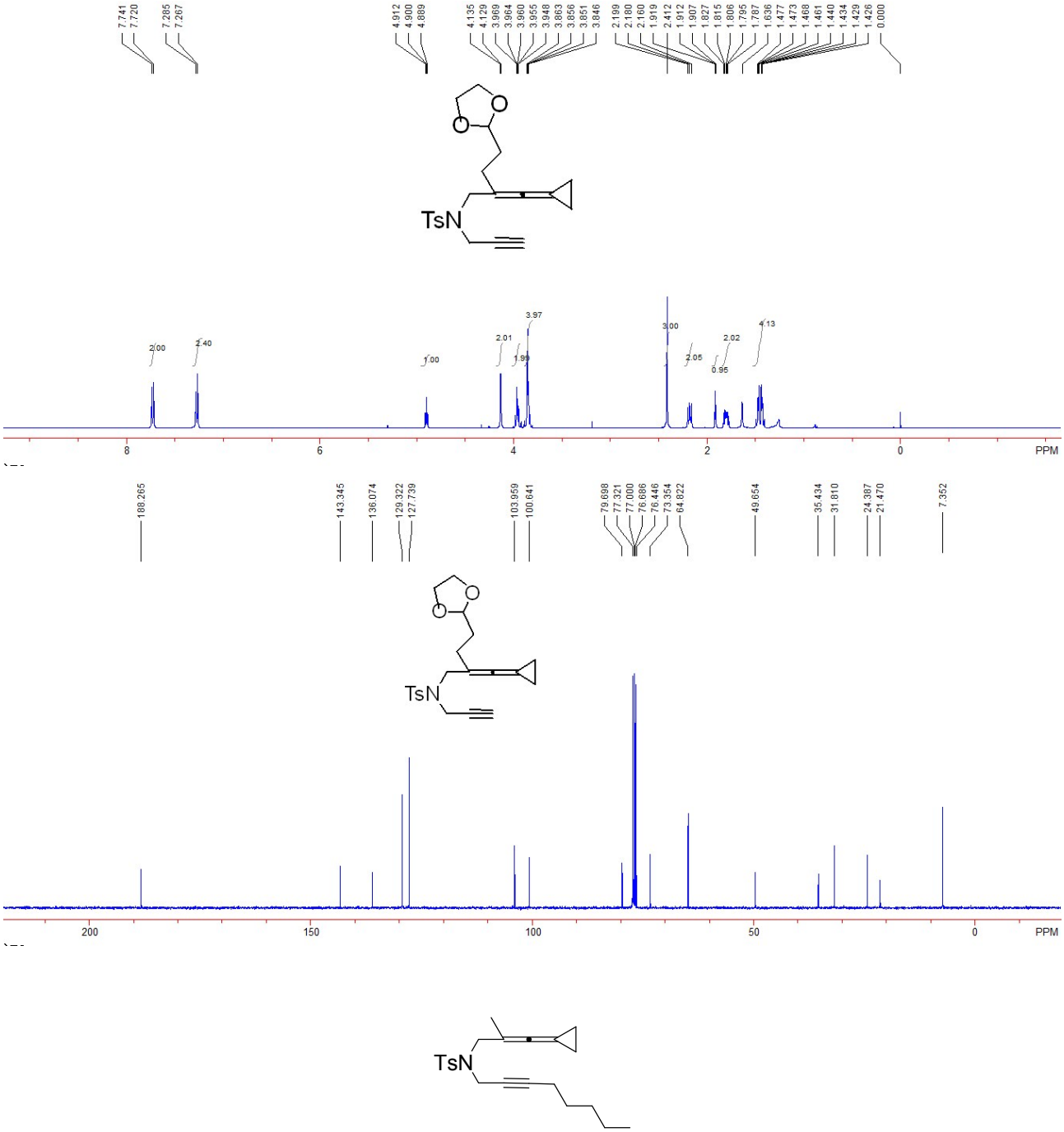






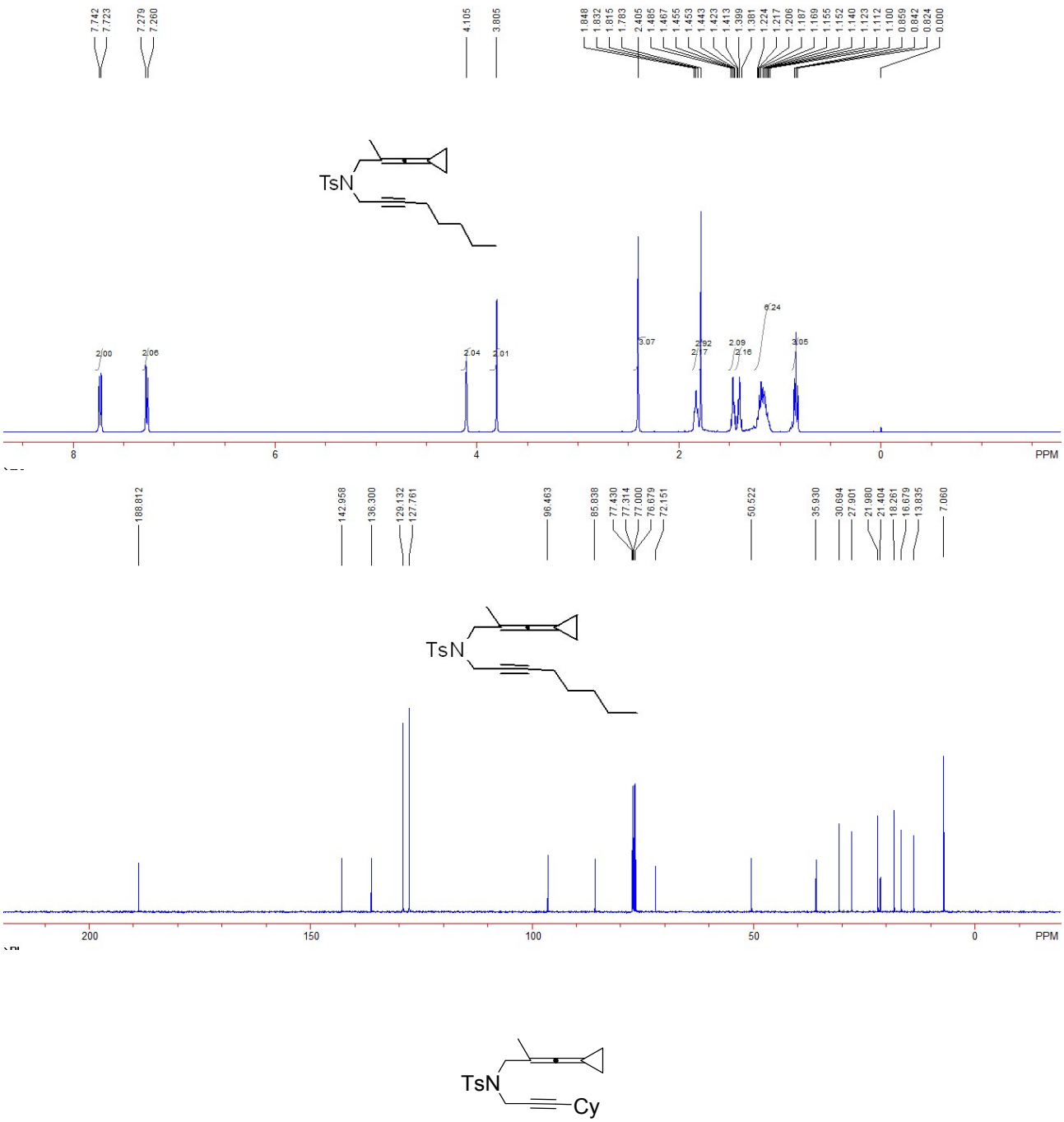
N-(2-(cyclopropylidene-λ⁵-methylene)-4-(1,3-dioxolan-2-yl)butyl)-4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (1e)

2.0 mmol scale, a light yellow oil, 58% yield (449 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 4.90 (t, *J* = 4.8 Hz, 1H), 4.13-4.14 (m, 2H), 3.95-3.97 (m, 2H), 3.85-3.86 (m, 4H), 2.41 (s, 3H), 2.16-2.20 (m, 2H), 1.91 (t, *J* = 2.0 Hz, 1H), 1.79-1.83 (m, 2H), 1.43-1.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.3, 143.3, 136.1, 129.3, 127.7, 104.0, 100.6, 79.7, 76.4, 73.4, 64.8, 49.7, 35.4, 31.8, 24.4, 21.5, 7.4; IR (CH_2Cl_2): ν 3289, 2927, 2841, 2027, 1437, 1341, 1329, 1265, 1229, 1086, 906, 813, 768 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{29}N_2O_4S$ $(M+NH_4)^+$ requires: 405.1843, Found: 405.1835.



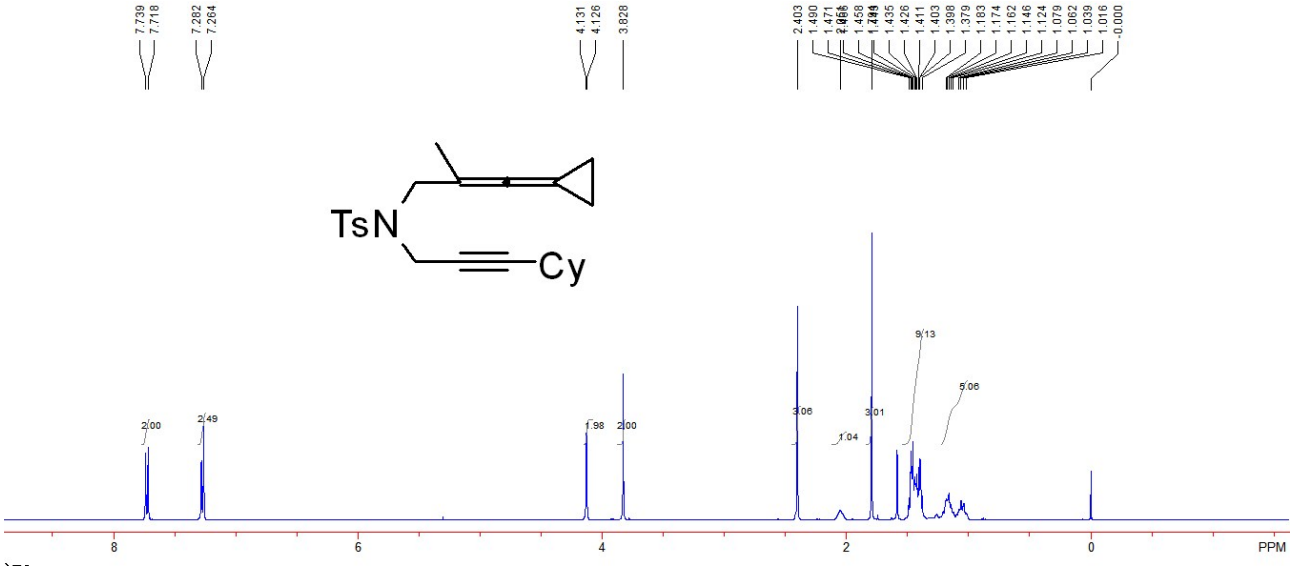
N-(3-cyclopropylidene-2-methyl-3λ⁵-allyl)-4-methyl-N-(oct-2-yn-1-yl)benzenesulfonamide (1l)

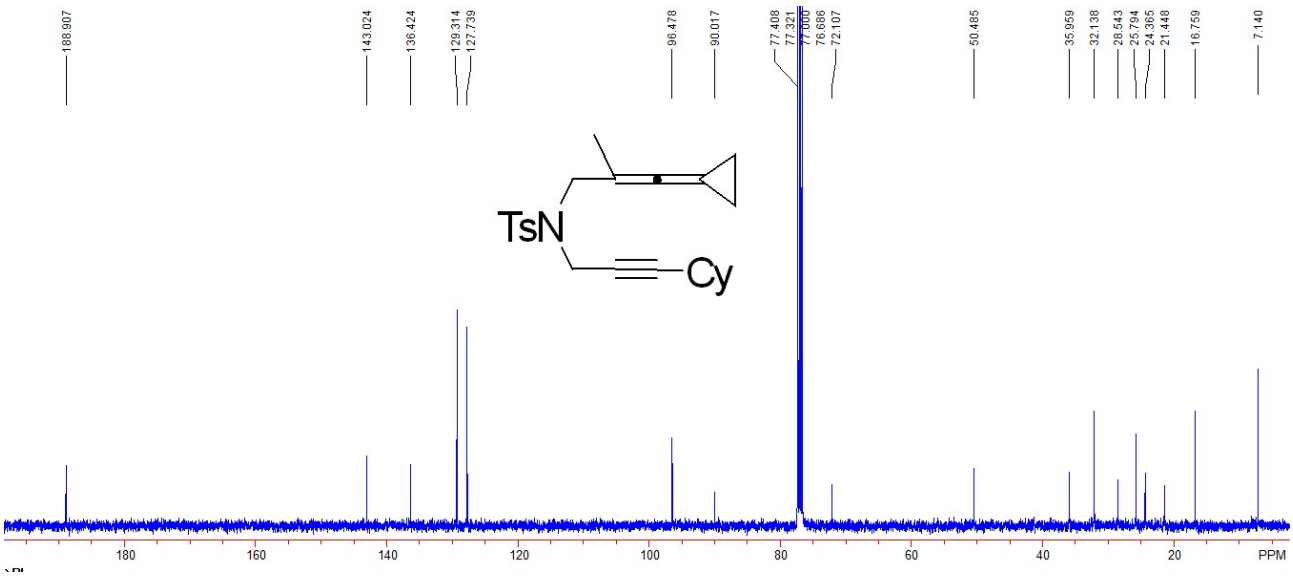
2.0 mmol scale, white solid, 68% yield (506 mg). M. P. 102-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, *J* = 7.2 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 4.11 (s, 2H), 3.81 (s, 2H), 2.40 (s, 3H), 1.83 (t, *J* = 6.0 Hz, 2H), 1.78 (s, 3H), 1.44-1.48 (m, 2H), 1.38-1.42 (m, 2H), 1.12-1.22 (m, 6H), 0.84 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.8, 143.0, 136.3, 129.1, 127.8, 96.5, 85.8, 77.4, 72.2, 50.5, 35.9, 30.7, 27.9, 22.0, 21.4, 18.3, 16.7, 13.8, 7.1; IR (CH_2Cl_2): ν 2982, 2906, 2023, 1652, 1443, 1367, 1343, 1187, 1074, 981, 897, 826 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{30}NO_2S$ $(M+H)^+$ requires: 372.1992, Found: 372.1987.

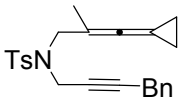


N-(3-cyclohexylprop-2-yn-1-yl)-N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methylbenzenesulfonamide (1m)

2.0 mmol scale, white solid, 73% yield (560 mg). M. P. 131-134 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, J_1 = 8.4 Hz, 2H), 7.27 (d, J = 7.2 Hz, 2H), 4.13 (d, J = 2.0 Hz, 2H), 3.83 (s, 2H), 2.40 (s, 3H), 2.05 (s, 1H), 1.79 (s, 3H), 1.38-1.49 (m, 9H), 1.02-1.18 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.9, 143.0, 136.4, 129.3, 127.7, 96.5, 90.0, 77.4, 72.1, 50.5, 36.0, 32.1, 28.5, 25.8, 24.4, 21.4, 16.8, 7.1; IR (CH_2Cl_2): ν 2987, 2914, 2846, 2017, 1623, 1599, 1435, 1156, 1088, 1050, 898, 705 cm^{-1}; HRMS (ESI) Calcd. For $C_{19}H_{24}NO_2S$ $(M+H)^+$ requires: 330.1522, Found: 330.1519.



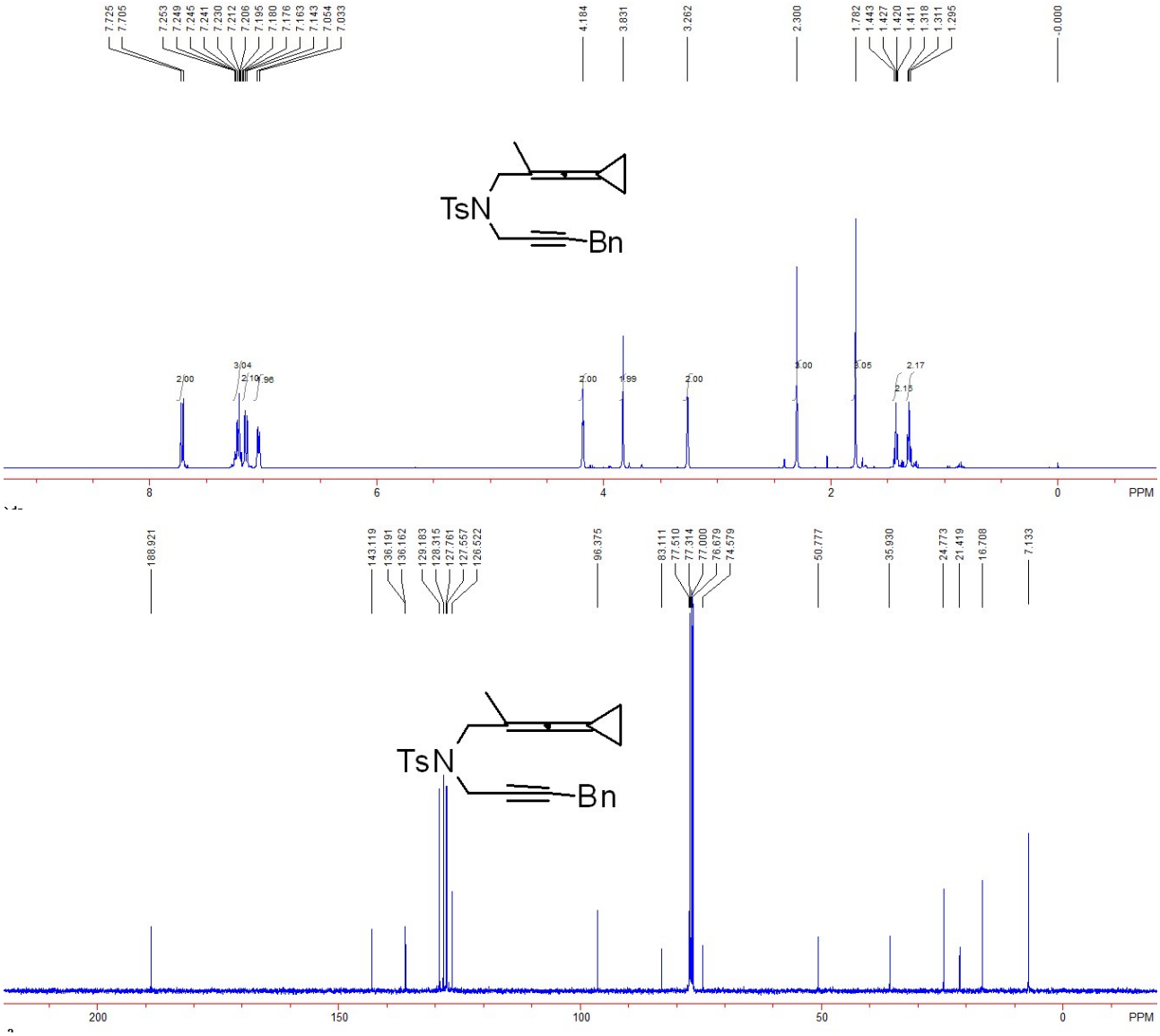




N-(3-cyclopropylidene-2-methyl-3λ⁵-allyl)-4-methyl-N-(4-phenylbut-2-yn-1-yl)benzenesulfonamide (1n)

2.0 mmol scale, a light yellow oil, 72% yield (563 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.16-7.25 (m, 3H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 4.18 (s, 2H), 3.83 (s, 2H), 3.26 (s, 2H), 2.30 (s, 3H), 1.78 (s, 3H), 1.41-1.44 (m, 2H), 1.30-1.32 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.9, 143.1, 136.19, 136.16, 129.2, 128.3, 127.8, 127.6, 126.5, 96.4, 83.1, 77.5, 74.6, 50.8, 35.9, 24.8, 21.4, 16.7, 7.1; IR (CH_2Cl_2): ν 2956, 2925, 2019, 1573, 1437, 1340, 1340, 1156, 1091, 905, 814, 707 cm^{-1}; HRMS (ESI) Calcd. For $C_{24}H_{29}N_2O_2S$

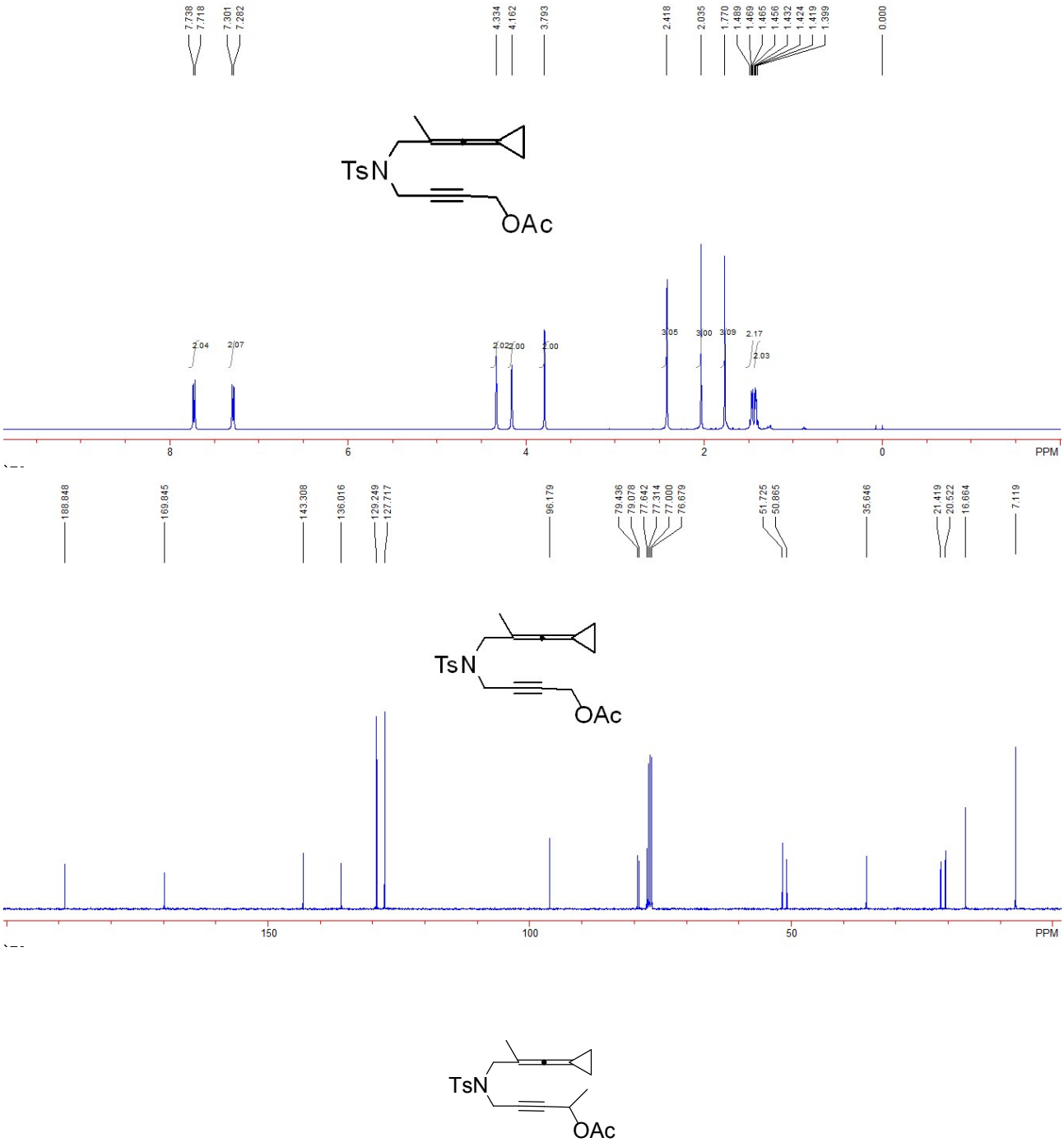
$(M+NH_4)^+$ requires: 409.1944, Found: 409.1938.



4-((N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methylphenyl)sulfonamido)but-2-yn-1-yl acetate (1o)

2.0 mmol scale, a light yellow oil, 82% yield (612 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 7.6 Hz, 2H), 4.33 (s, 2H), 4.16 (s, 2H), 3.79 (s, 2H), 2.42 (s, 3H), 2.04 (s, 3H), 1.77 (s, 3H), 1.46-1.49 (m, 2H), 1.40-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.8, 169.8, 143.3, 136.0, 129.2, 127.7, 96.2, 79.4, 79.1, 77.6, 51.7, 50.9, 35.6, 21.4, 20.5, 16.7,

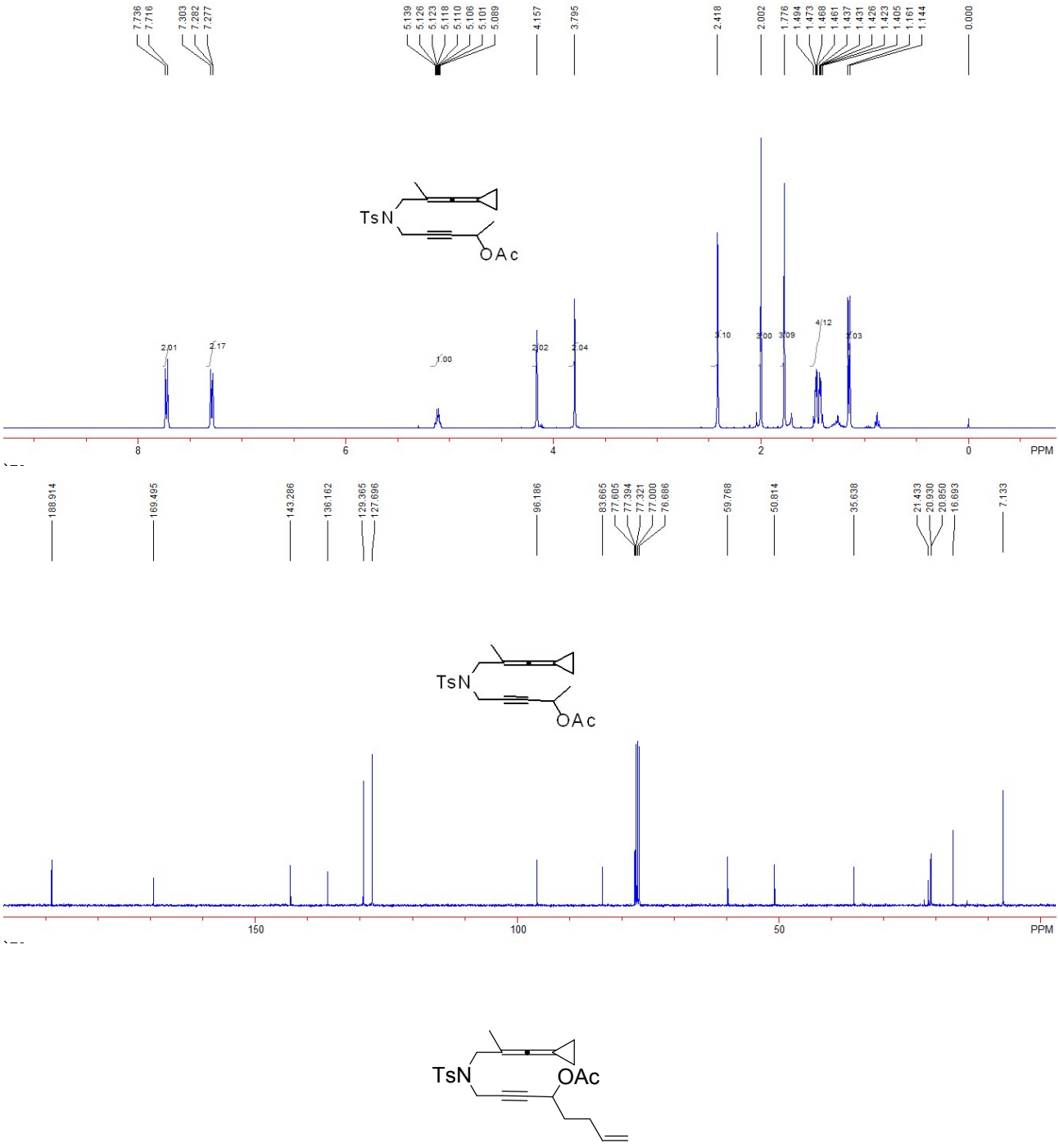
7.1; IR (CH_2Cl_2): ν 2979, 2912, 2841, 2012, 1719, 1599, 1338, 1156, 1089, 905, 767, 736, 697 cm^{-1}; HRMS (ESI) Calcd. For $C_{20}H_{27}N_2O_4S$ $(M+NH_4)^+$ requires: 391.1686, Found: 391.1680.



5-((N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methylphenyl)sulfonamido)pent-3-yn-2-yl acetate (1p)

2.0 mmol scale, white solid, 85% yield (658 mg). M. P. 102-105 ^oC. ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 5.09-5.14 (m, 1H), 4.16 (s, 2H), 3.80 (s, 2H), 2.42 (s, 3H), 2.00 (s, 3H), 1.78 (s, 3H), 1.41-1.49 (m, 4H), 1.15 (d, J = 2.8 Hz, 3H); ^{13}C NMR

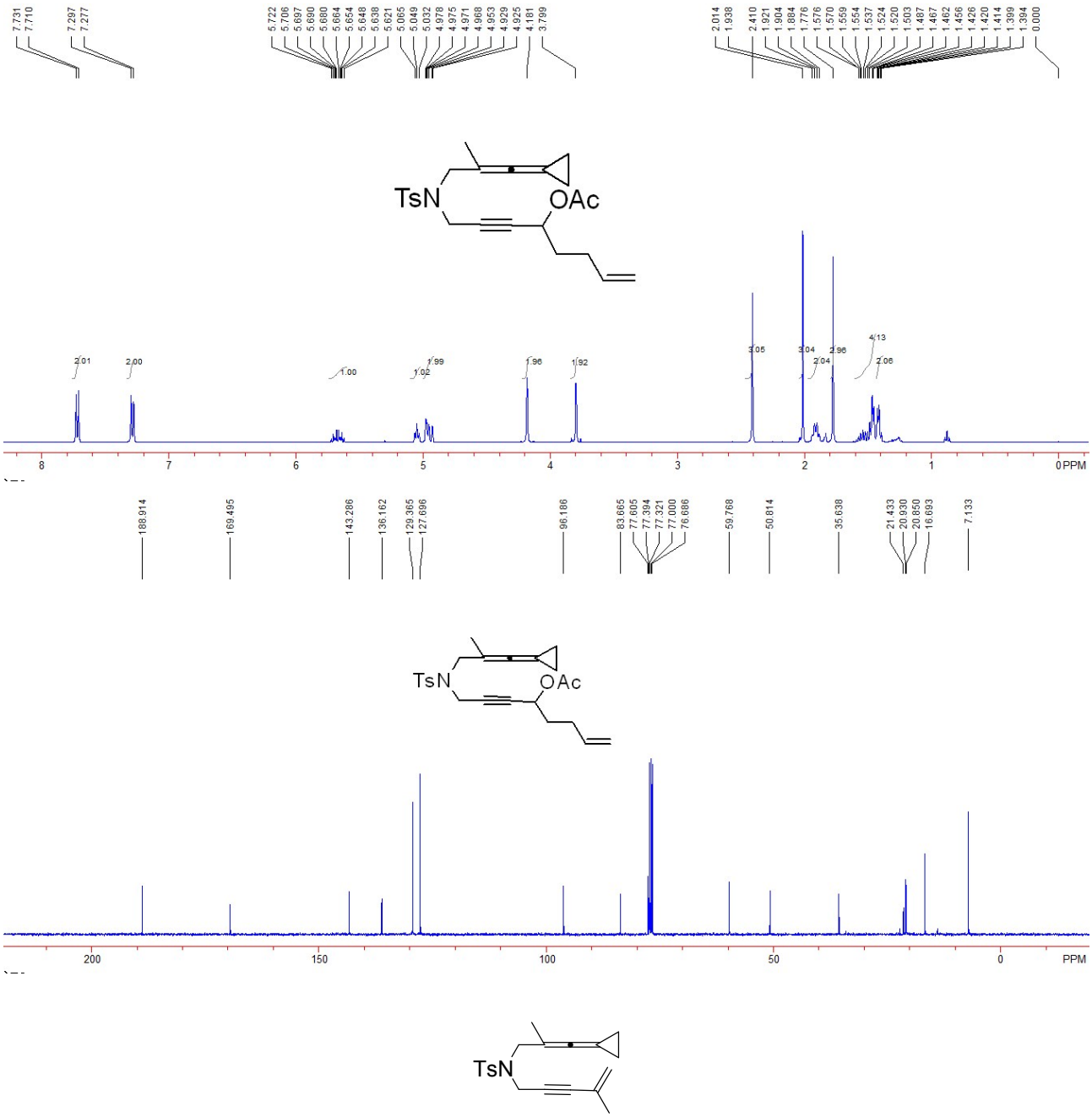
(100 MHz, $CDCl_3$, TMS) δ 188.9, 169.5, 143.3, 136.2, 129.4, 127.7, 96.2, 83.7, 77.6, 77.4, 59.8, 50.8, 35.6, 21.4, 20.93, 20.85, 16.7, 7.1; IR (CH_2Cl_2): ν 2962, 2930, 1706, 1651, 1574, 1389, 1350, 1222, 1089, 1068, 1009, 738 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{29}N_2O_4S$ $(M+NH_4)^+$ requires: 405.1843, Found: 405.1837.



1-((N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methylphenyl)sulfonamido)oct-7-en-2-yn-4-yl acetate (1q)

2.0 mmol scale, a light yellow oil, 84% yield (717 mg). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72

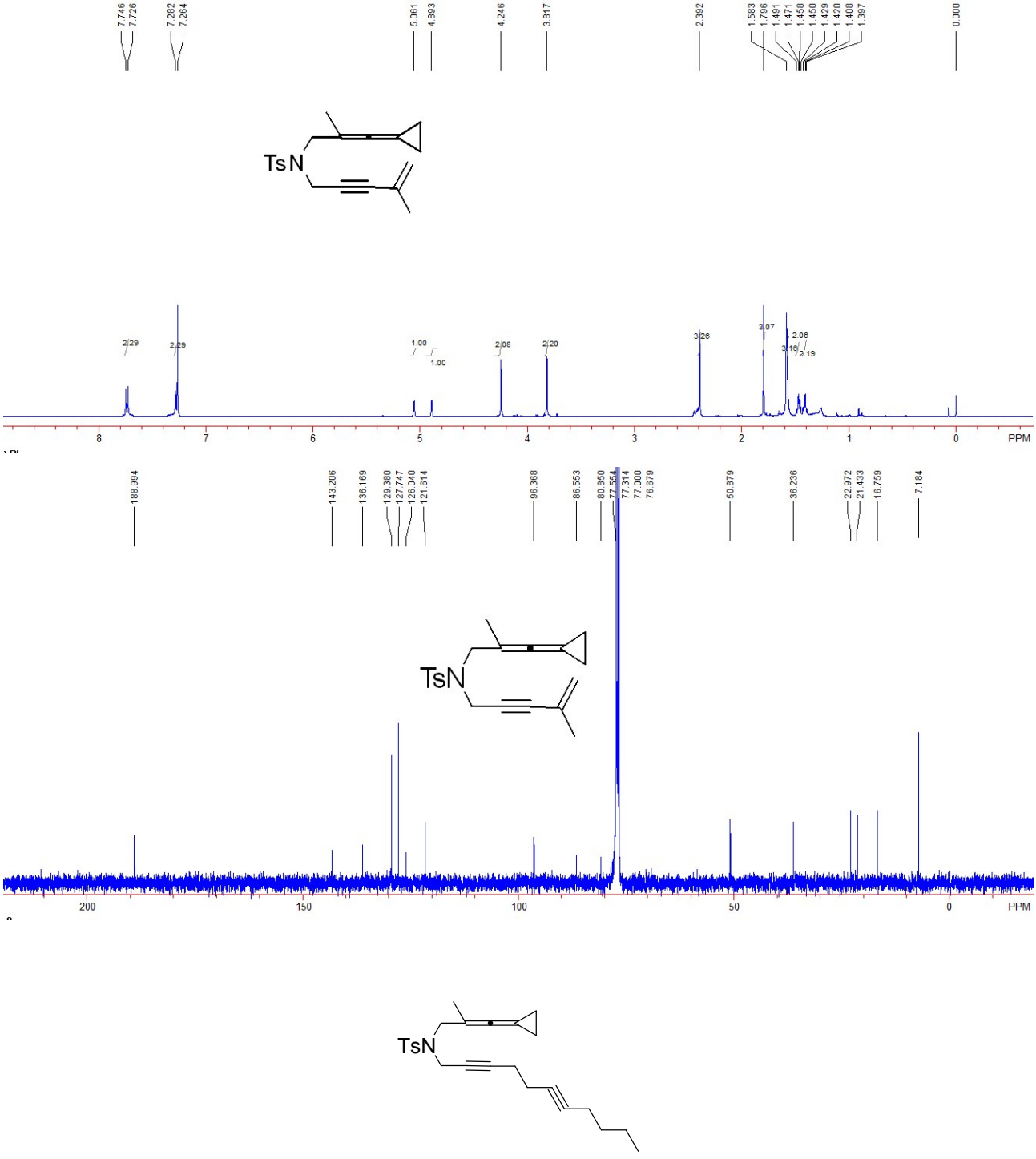
(d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.62-5.72 (m, 2H), 5.05 (t, J = 6.8 Hz, 1H), 4.93-4.98 (m, 2H), 4.18 (s, 2H), 3.80 (s, 2H), 2.41 (s, 3H), 2.01 (s, 3H), 1.91 (q, J = 6.8 Hz, 2H), 1.78 (s, 3H), 1.46-1.58 (m, 4H), 1.39-1.43 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.9, 169.5, 143.3, 136.2, 129.4, 127.7, 96.2, 83.7, 77.6, 77.4, 59.8, 50.8, 35.6, 21.4, 20.93, 20.85, 16.7, 7.1; IR (CH_2Cl_2): ν 2956, 2930, 2849, 1722, 1632, 1597, 1456, 1348, 1160, 1093, 1018, 905, 813, 651 cm^{-1}; HRMS (ESI) Calcd. For $C_{24}H_{33}N_2O_4S$ $(M+NH_4)^+$ requires: 445.2156, Found: 445.2155.



N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methyl-N-(4-methylpent-4-en-2-yn-1-yl)benzenesulfonamide (1r)

A white solid, 2.0 mmol scale, 61% yield (416 mg), M. P. 93-96 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$,

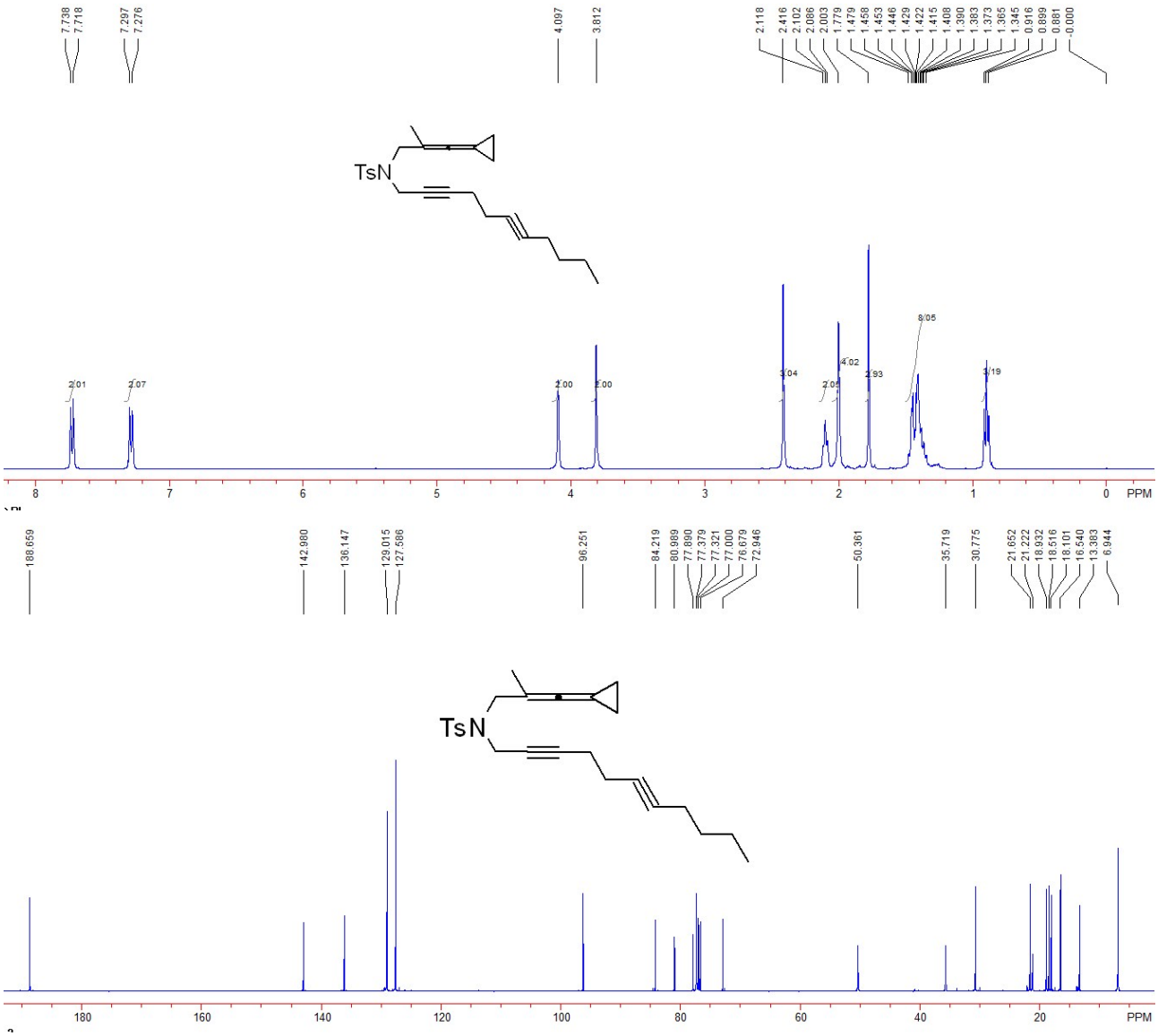
TMS) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.06 (s, 1H), 4.89 (s, 1H), 4.25 (s, 2H), 3.82 (s, 2H), 2.39 (s, 3H), 1.80 (s, 3H), 1.58 (s, 3H), 1.45-1.49 (m, 2H), 1.40-1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 190.0, 143.2, 136.2, 129.4, 127.7, 126.0, 121.6, 96.4, 86.6, 80.9, 77.6, 50.9, 36.2, 23.0, 21.4, 16.8, 7.2; IR (CH_2Cl_2): ν 2925, 2878, 2017, 1664, 1437, 1337, 1156, 1090, 1030, 967, 912, 802, 773, 736, 707, 636 cm^{-1}; HRMS (ESI) Calcd. For $C_{20}H_{24}NO_2S$ $(M+H)^+$ requires: 342.1522, Found: 342.1519.

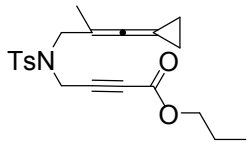


N-(3-cyclopropylidene-2-methyl-3λ⁵-allyl)-4-methyl-N-(undeca-2,6-diyn-1-

yl)benzenesulfonamide (1s)

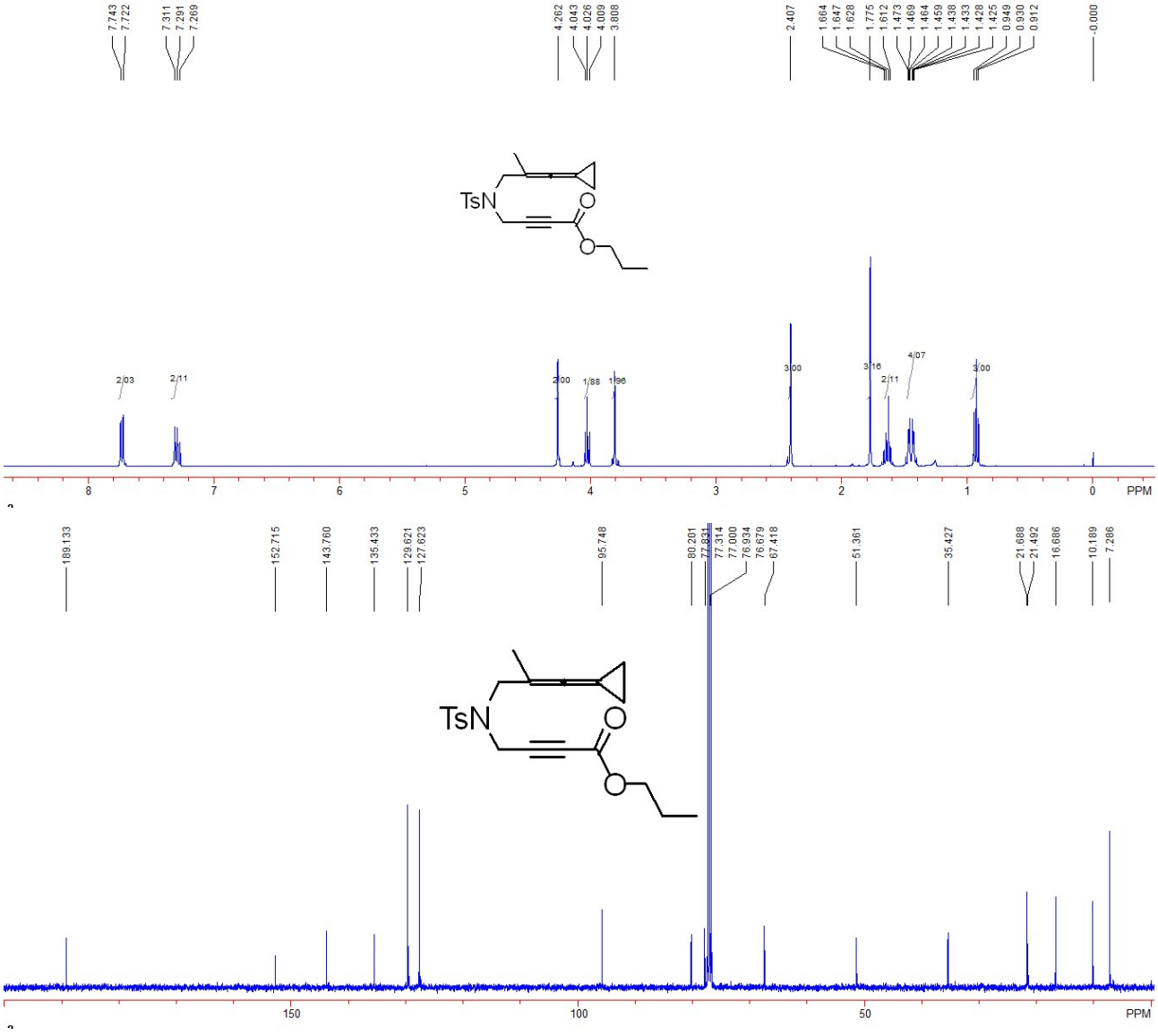
2.0 mmol scale, a light yellow oil, 78% yield (638 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.10 (s, 2H), 3.81 (s, 2H), 2.42 (s, 3H), 2.10 (t, *J* = 6.4 Hz, 2H), 2.00 (s, 4H), 1.78 (s, 3H), 1.35-1.48 (m, 8H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 188.7, 143.0, 136.1, 129.0, 127.6, 96.3, 84.2, 81.0, 77.9, 77.4, 72.9, 50.4, 35.7, 30.8, 21.7, 21.2, 18.9, 18.5, 18.1, 16.5, 13.4, 6.9; IR (CH_2Cl_2): ν 2922, 2911, 2022, 1618, 1443, 1410, 1333, 1305, 1155, 1101, 1019, 906, 815, 804, 768, 708 cm^{-1}; HRMS (ESI) Calcd. For $C_{25}H_{32}NO_2S$ $(M+H)^+$ requires: 410.2148, Found: 410.2147.



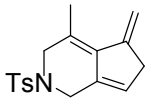


Propyl4-((N-(3-cyclopropylidene-2-methyl-3λ^5-allyl)-4-methylphenyl)sulfonamido)but-2-ynoate (1t)

2.0 mmol scale, a light yellow oil, 55% yield (426 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 4.26 (s, 2H), 4.03 (t, *J* = 6.8 Hz, 2H), 3.81 (s, 2H), 2.41 (s, 3H), 1.78 (s, 3H), 1.61-1.66 (m, 2H), 1.43-1.47 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 189.1, 152.7, 143.8, 135.4, 129.6, 127.6, 95.7, 80.2, 77.8, 76.9, 67.4, 51.4, 35.4, 21.7, 21.5, 16.7, 10.2, 7.3; IR (CH_2Cl_2): ν 2985, 2922, 2022, 1720, 1684, 1443, 1415, 1340, 1156, 1115, 1089, 1048, 1017, 905, 813, 802, 769, 646 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{29}N_2O_4S$ $(M+NH_4)^+$ requires: 405.1843, Found: 405.1843.

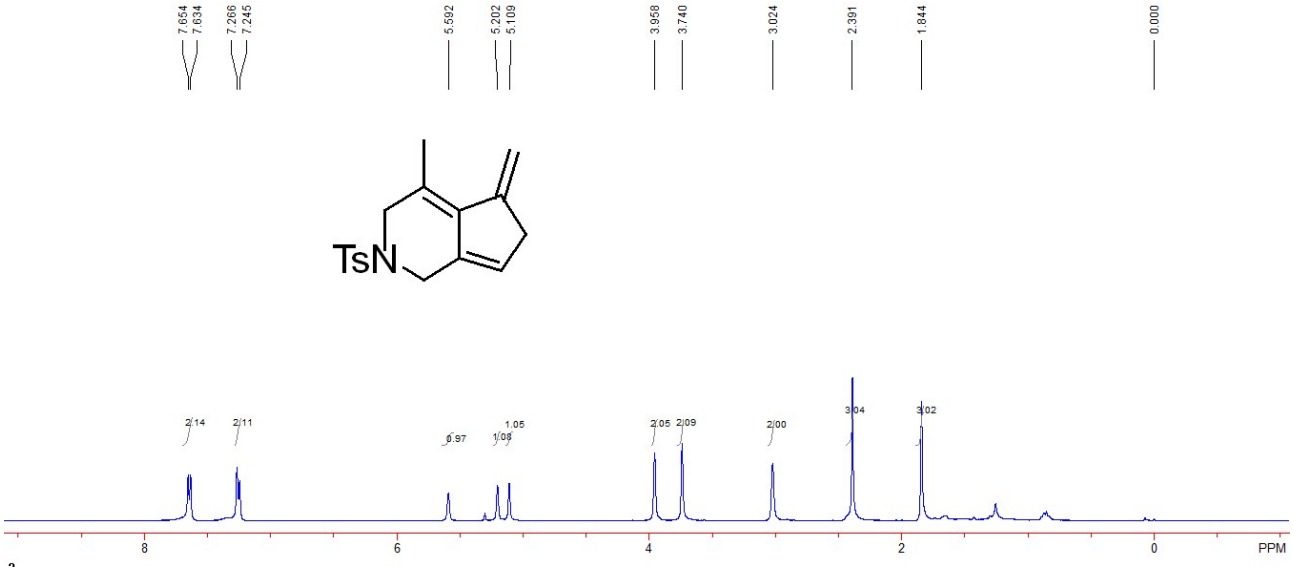


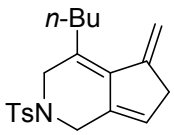
4. The characterization data of products 2



4-methyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2a)

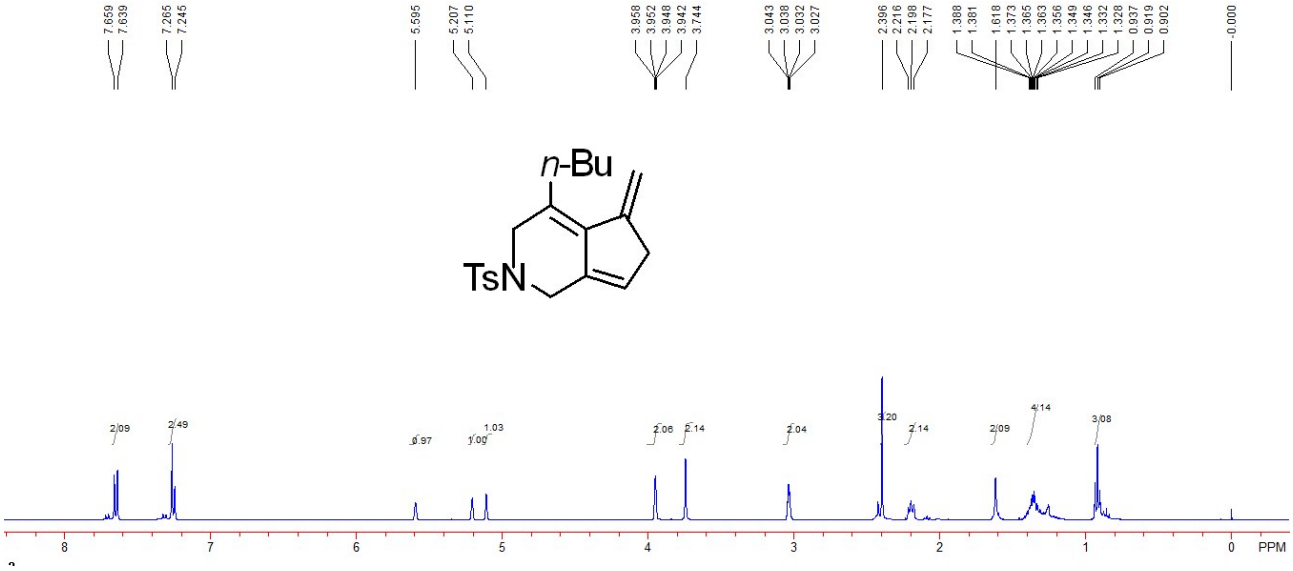
This is a known compound.[1] White solid, 83% yield (25 mg), M. P. 102-105 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.59 (s, 1H), 5.20 (s, 1H), 5.11 (s, 1H), 3.96 (s, 2H), 3.74 (s, 2H), 3.02 (s, 2H), 2.39 (s, 3H), 1.84 (s, 3H).

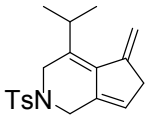




4-butyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2b)

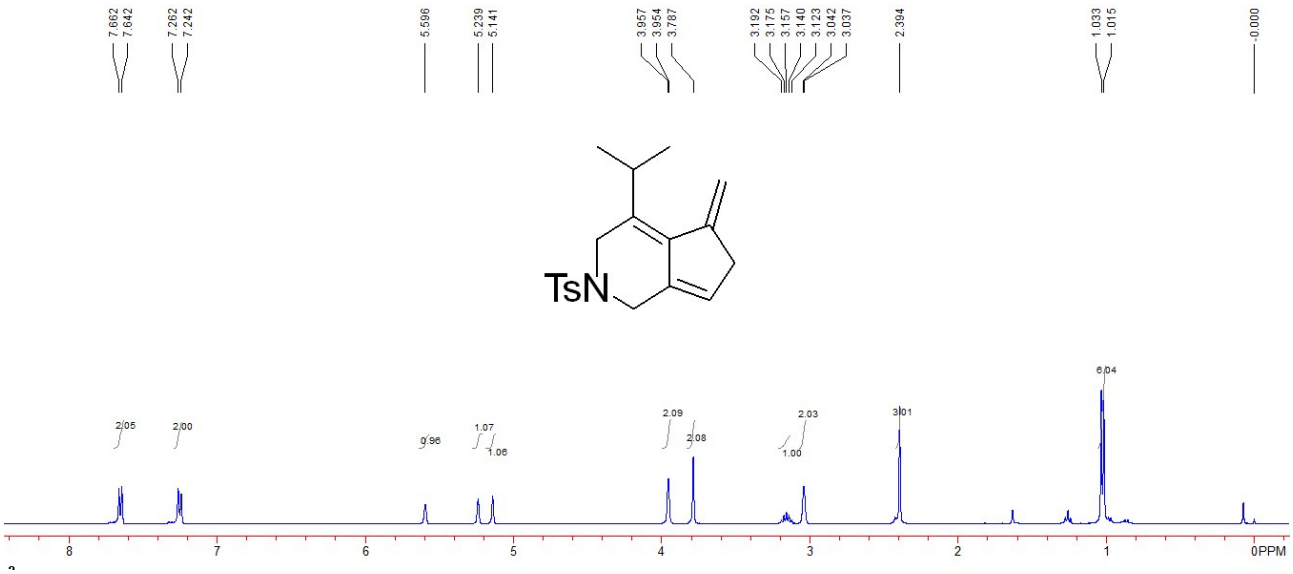
This is a known compound.[1] A light yellow oil, 76% yield (26 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.60 (s, 1H), 5.21 (s, 1H), 5.11 (s, 1H), 3.95 (q, *J* = 2.4 Hz, 2H), 3.74 (s, 2H), 3.04 (q, *J* = 2.0 Hz, 2H), 2.40 (s, 3H), 2.18-2.22 (m, 2H), 1.62 (s, 2H), 1.33-1.39 (m, 4H), 0.92 (t, *J* = 6.8 Hz, 3H).

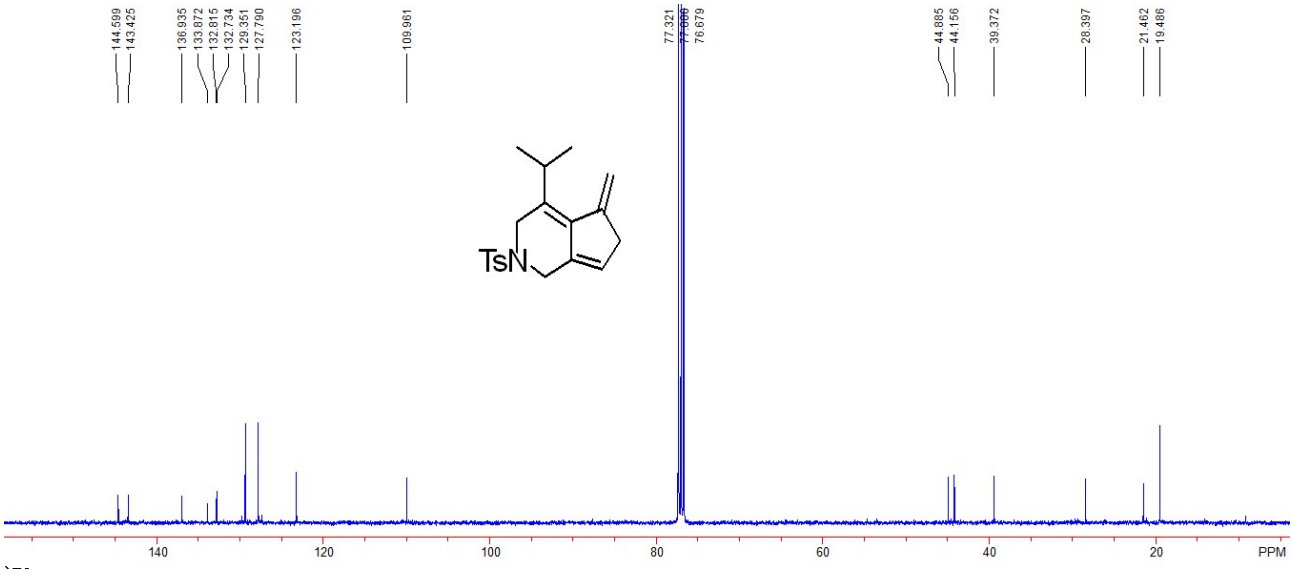


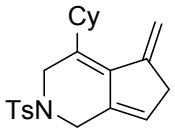


4-isopropyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2c)

A white solid, 81% yield (26 mg), M. P. 109-112 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 5.60 (s, 1H), 5.24 (s, 1H), 5.14 (s, 1H), 3.96 (d, J = 1.2 Hz, 2H), 3.79 (s, 2H), 3.12-3.19 (m, 1H), 3.04 (d, J = 2.0 Hz, 2H), 2.39 (s, 3H), 1.02 (d, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.6, 143.4, 136.9, 133.9, 132.8, 132.7, 129.4, 127.8, 123.2, 110.0, 44.9, 44.2, 39.4, 28.4, 21.5, 19.5; IR (CH_2Cl_2): ν 2959, 2923, 1607, 1584, 1495, 1452, 1349, 1328, 1161, 1090, 815, 732 cm^{-1}; HRMS (ESI) Calcd. For $C_{19}H_{24}NO_2S$ $(M+H)^+$ requires: 330.1522, Found: 330.1517.

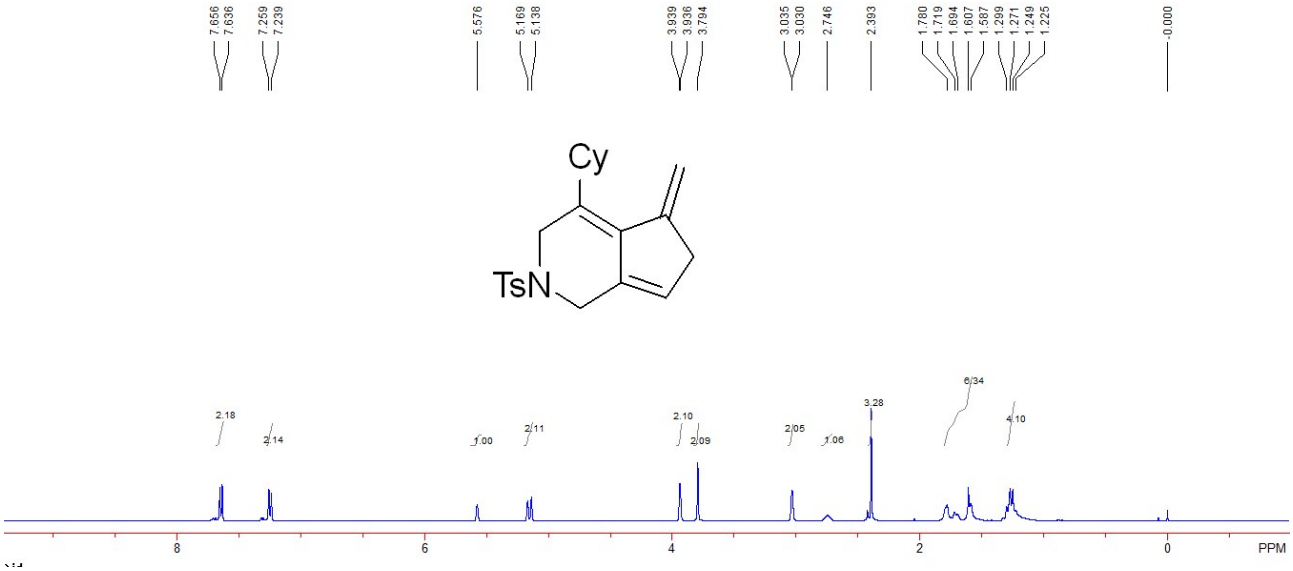


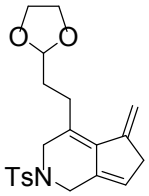




4-cyclohexyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2d)

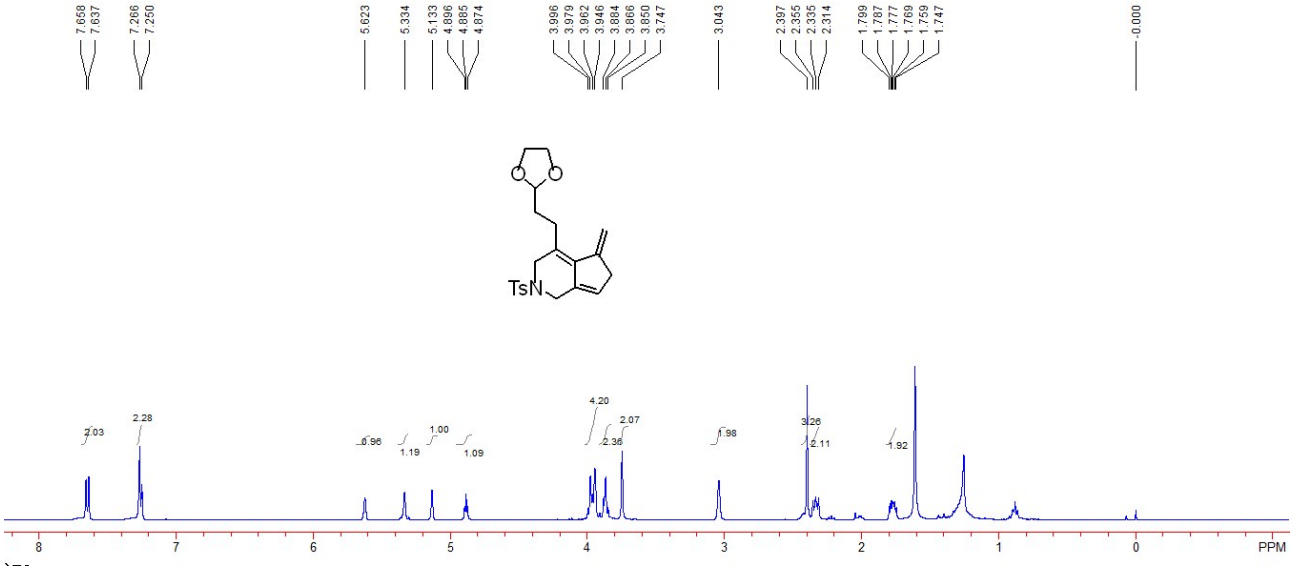
This is a known compound.[1] white solid, 88% yield (33 mg), M. P. 113-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.57 (s, 1H), 5.17 (s, 1H), 5.14 (s, 1H), 3.94 (d, *J* = 2.0 Hz, 2H), 3.79 (s, 2H), 3.03 (d, *J* = 2.4 Hz, 2H), 2.75 (s, 1H), 2.39 (s, 3H), 1.59-1.78 (m, 6H), 1.16-1.30 (m, 4H). It is noteworthy that the compound **2d** was not stable under ambient atmosphere.

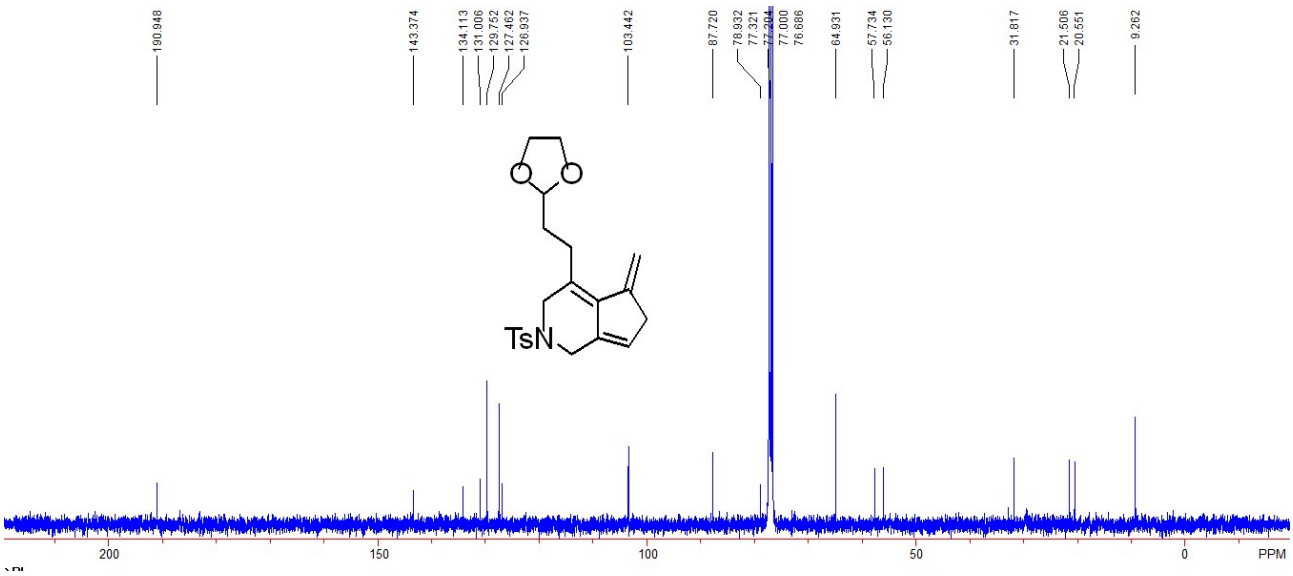


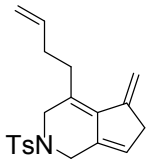


4-(2-(1,3-dioxolan-2-yl)ethyl)-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2e)

A light yellow oil, 68% yield (26 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 5.62 (s, 1H), 5.33 (s, 1H), 5.13 (s, 1H), 4.89 (d, *J* = 4.4 Hz, 1H), 3.95-4.00 (m, 4H), 3.85-3.88 (m, 2H), 3.75 (s, 2H), 3.04 (s, 2H), 2.40 (s, 3H), 2.31-2.36 (m, 2H), 1.75-1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 190.9, 143.4, 134.1, 131.0, 129.8, 127.5, 126.9, 103.4, 87.7, 78.9, 77.2, 64.9, 57.7, 56.1, 31.8, 21.5, 20.6, 9.3; IR (CH_2Cl_2): ν 2956, 2923, 2849, 1675, 1591, 1448, 1432, 1354, 1338, 1161, 1112, 1091, 1019, 958, 813, 803, 687 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{29}N_2O_4S$ $(M+H)^+$ requires: 405.1843, Found: 405.1834.

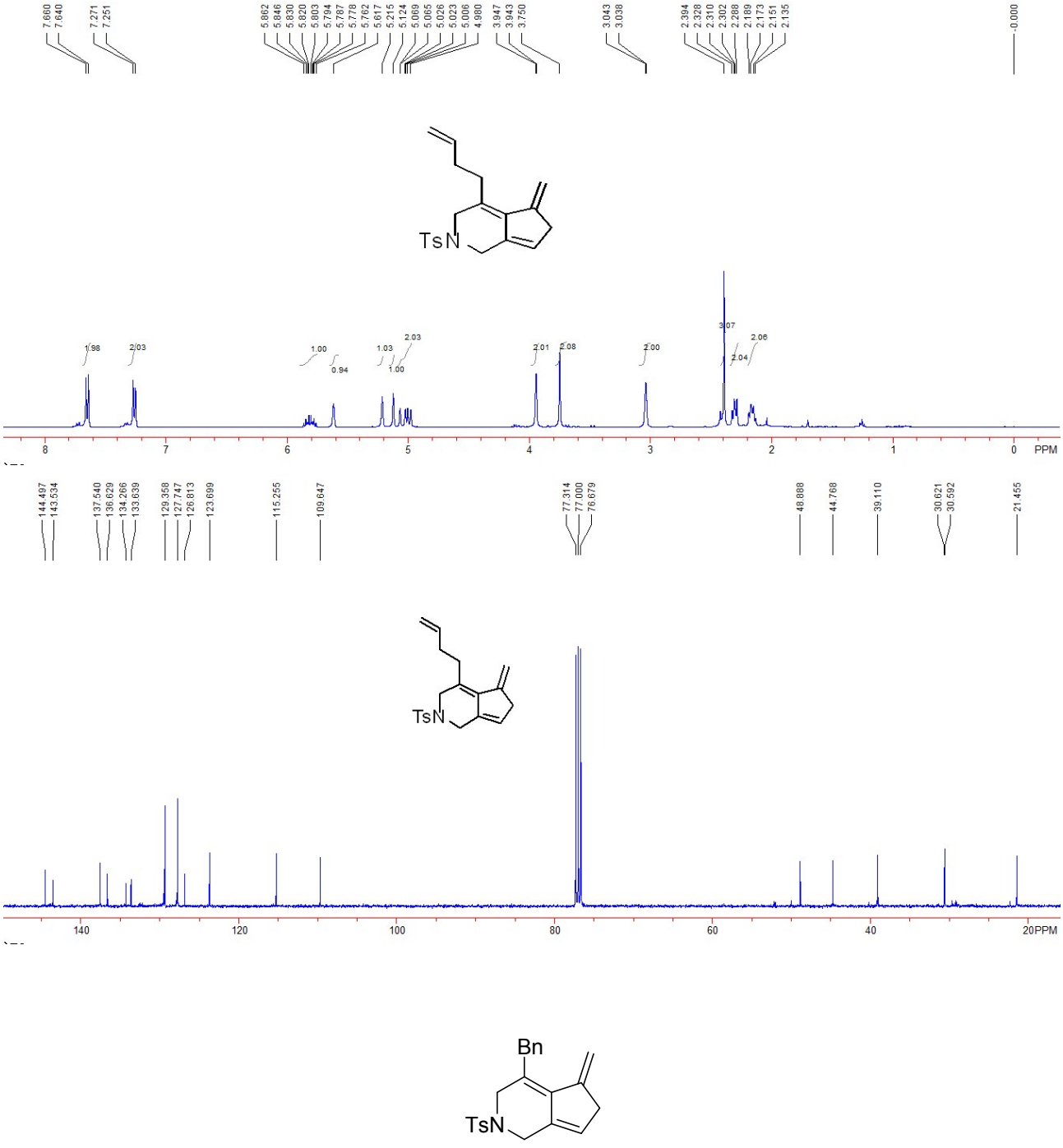






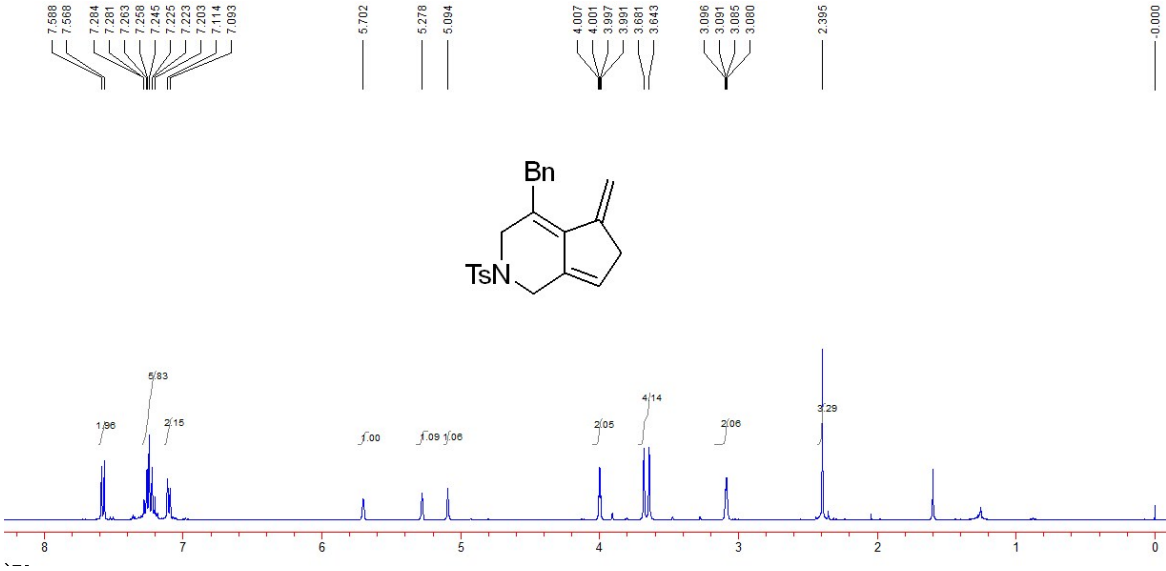
4-(but-3-en-1-yl)-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2f)

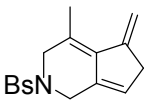
A light yellow oil, 72% yield (25 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.76-5.86 (m, 1H), 5.62 (s, 1H), 5.22 (s, 1H), 5.12 (s, 1H), 4.98-5.07 (m, 2H), 3.95 (d, *J* = 1.6 Hz, 2H), 3.75 (s, 2H), 3.04 (d, *J* = 2.0 Hz, 2H), 2.39 (s, 3H), 2.29-2.33 (m, 2H), 2.14-2.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.5, 143.5, 137.5, 136.6, 134.3, 133.6, 129.4, 127.7, 126.8, 123.7, 115.3, 109.6, 48.9, 44.8, 39.1, 30.62, 30.59, 21.5; IR (CH_2Cl_2): ν 2953, 2923, 1667, 1643, 1460, 1425, 1379, 1162, 1091, 1051, 844, 812, 745, 721, 670 cm^{-1}; HRMS (ESI) Calcd. For $C_{20}H_{27}N_2O_2S$ $(M+H)^+$ requires: 359.1788, Found: 359.1786.



4-benzyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2g)

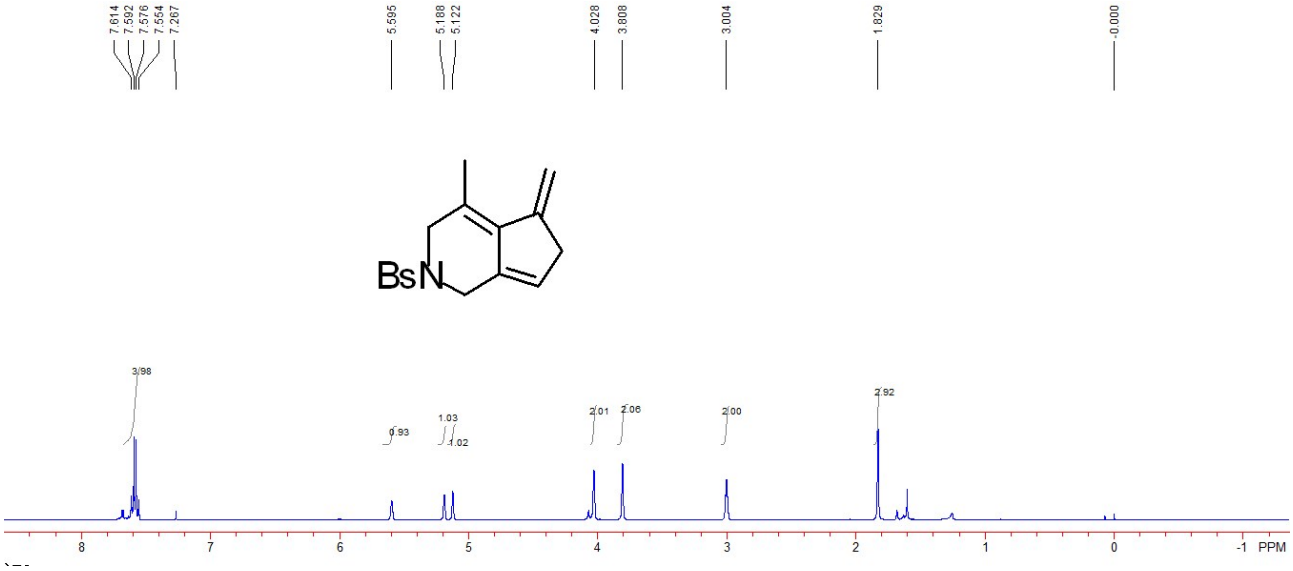
This is a known compound.[1] A light yellow oil, 78% yield (29 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.58 (d, J = 8.0 Hz, 2H), 7.20-7.28 (m, 5H), 7.10 (d, J = 8.4 Hz, 2H), 5.70 (s, 1H), 5.28 (s, 1H), 5.09 (s, 1H), 4.00 (dd, J_1 = 2.4 Hz, J_2 = 4.0 Hz, 2H), 3.68 (s, 2H), 3.64 (s, 2H), 3.09 (dd, J_1 = 2.0 Hz, J_2 = 4.0 Hz, 2H), 2.40 (s, 3H).

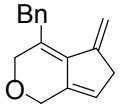




2-((4-bromophenyl)sulfonyl)-4-methyl-5-methylene-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2h)

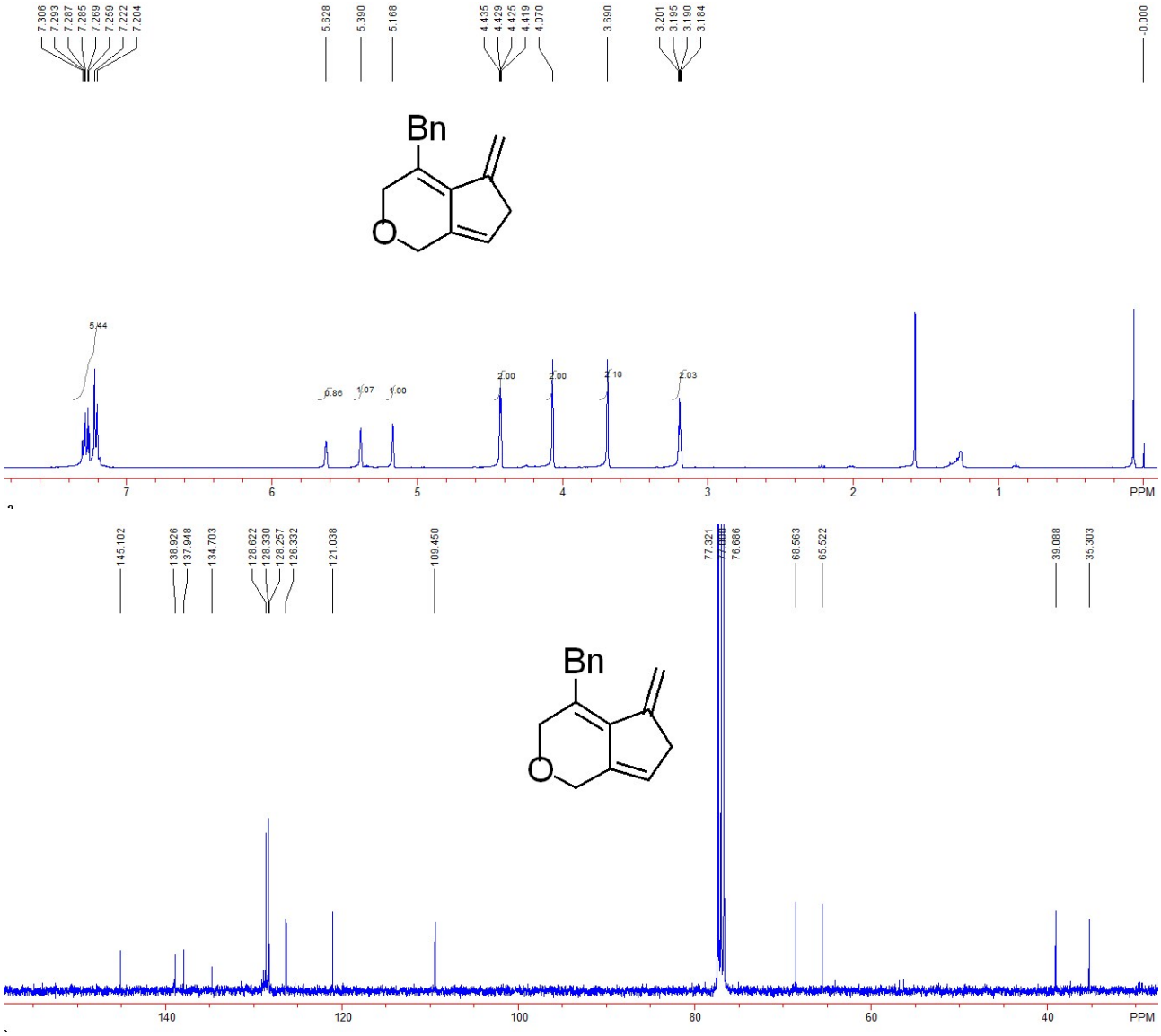
This is a known compound.[1] A light yellow oil, 82% yield (30 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.55-7.61 (m, 4H), 5.60 (s, 1H), 5.19 (s, 1H), 5.12 (s, 1H), 4.03 (s, 2H), 2.81 (s, 2H), 3.00 (s, 2H), 1.83 (s, 3H).

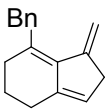




4-benzyl-5-methylene-1,3,5,6-tetrahydrocyclopenta[c]pyran (2i)

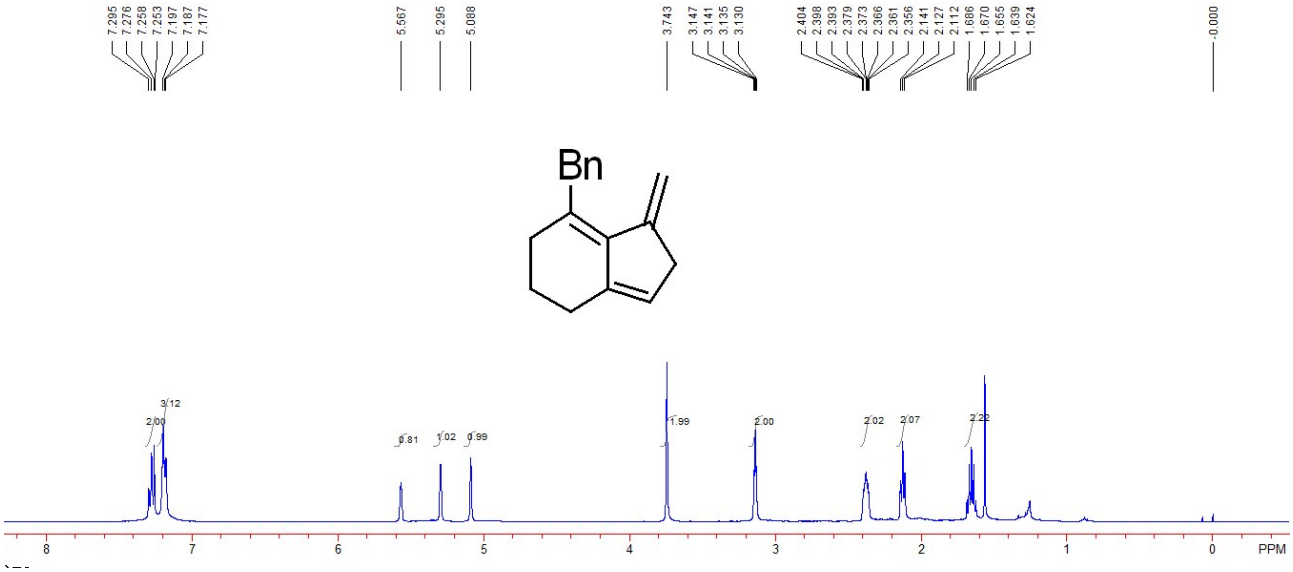
A light yellow oil, 68% yield (15 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.20-7.31 (m, 5H), 5.63 (s, 1H), 5.39 (s, 1H), 5.17 (s, 1H), 4.43 (dd, J_1 = 2.4 Hz, J_2 = 4.0 Hz, 2H), 4.07 (s, 2H), 3.69 (s, 2H), 3.19 (dd, J_1 = 2.4 Hz, J_2 = 4.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 145.1, 138.9, 137.9, 134,7, 128.6, 128.33, 128.26, 126.3, 121.0, 109.5, 68.6, 65.5, 39.1, 35.3; IR (CH_2Cl_2): ν 3012, 2961, 2926, 1699, 1597, 1459, 1337, 1316, 1255, 1118, 1090, 1037, 994, 966, 938, 782 cm^{-1}; Mass (EI) $(M)^+$: 224.2, HRMS (EI) Calcd. For $C_{16}H_{16}O$ $(M)^+$ requires: 224.1201, Found: 224.1199.

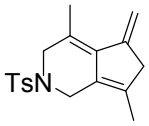




7-benzyl-1-methylene-2,4,5,6-tetrahydro-1H-indene (2j)

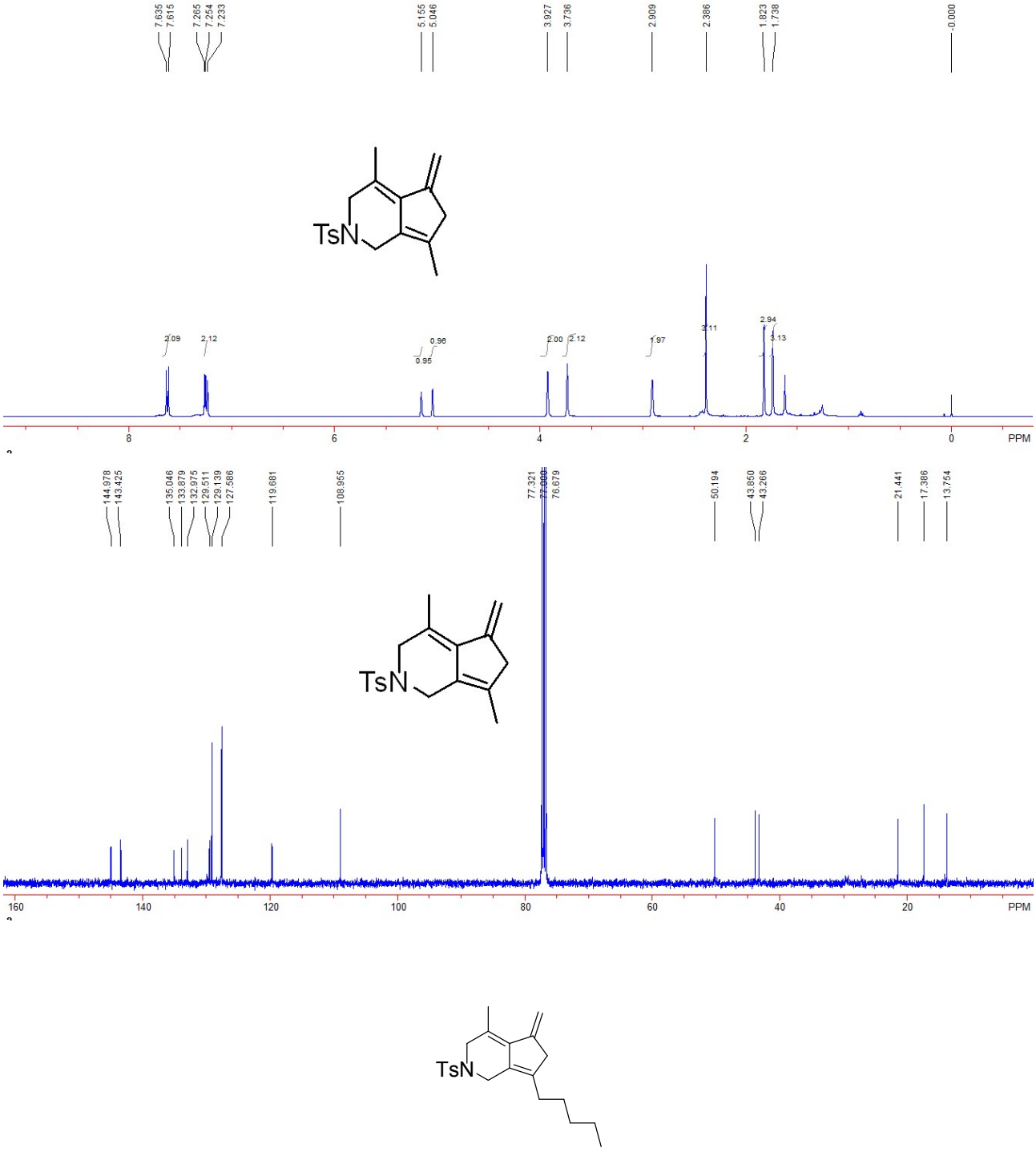
This is a known compound.[1] A light yellow oil, 75% yield (17 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.18-7.30 (m, 5H), 5.57 (s, 1H), 5.23 (s, 1H), 5.09 (s, 1H), 3.74 (s, 2H), 3.14 (q, J = 2.4 Hz, 2H), 2.36-2.40 (m, 2H), 2.13 (t, J = 6.0 Hz, 2H), 1.62-1.69 (m, 2H).





4,7-dimethyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2k)

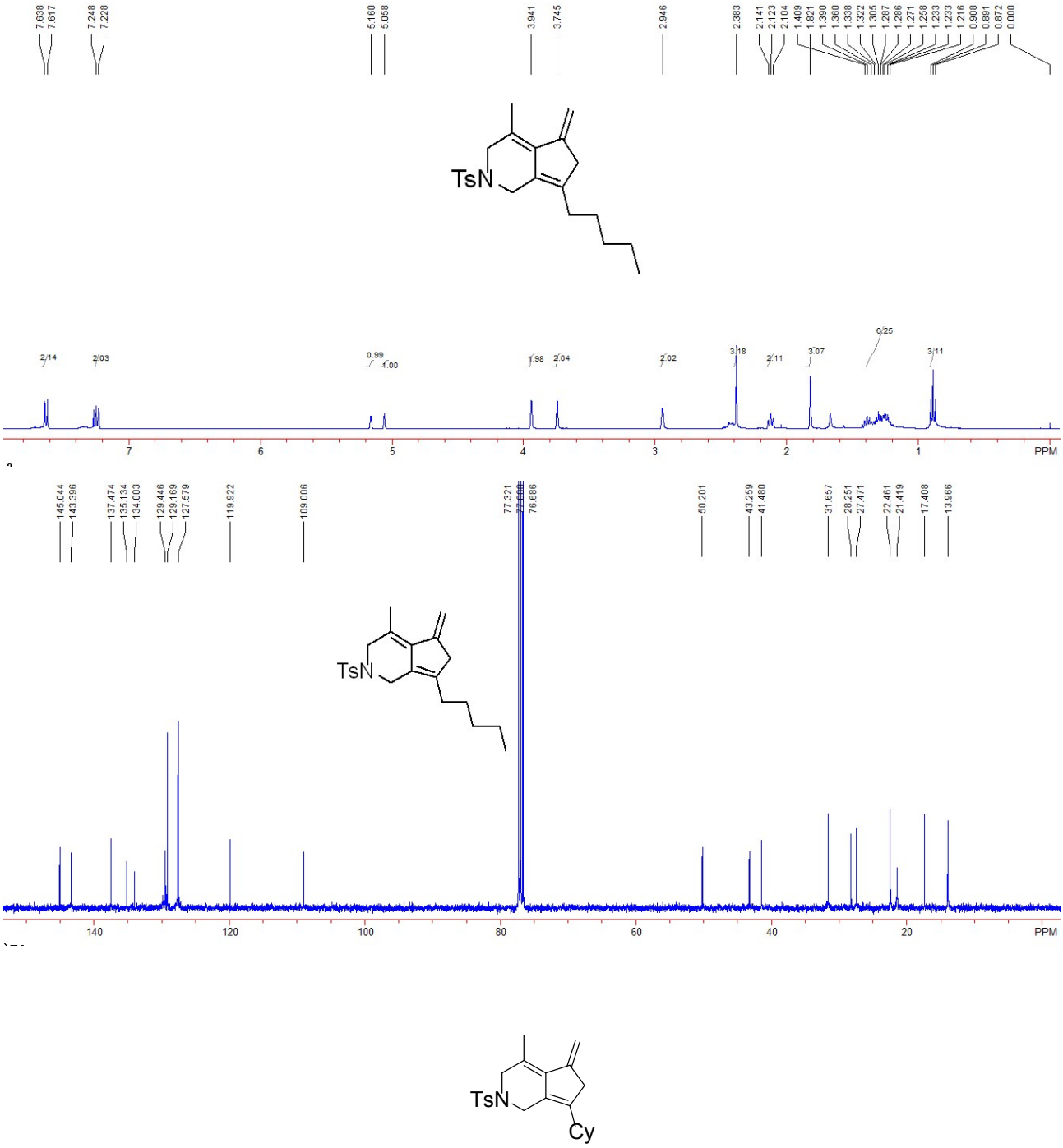
A light yellow oil, 91% yield (29 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 5.16 (s, 1H), 5.05 (s, 1H), 3.93 (s, 2H), 3.74 (s, 2H), 2.91 (s, 2H), 2.39 (s, 3H), 1,82 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 145.0, 143.4, 135.0, 133.9, 133.0, 129.5, 129.1, 127.6, 119.7, 109.0, 50.2, 43.9, 43.3, 21.4, 17.4, 13.8; IR (CH_2Cl_2): ν 3042, 2951, 2922, 1664, 1591, 1492, 1443, 1349, 1162, 1090, 959, 811, 819, 766, 700 cm^{-1}; HRMS (ESI) Calcd. For $C_{18}H_{22}NO_2S$ $(M+H)^+$ requires: 316.1366, Found: 316.1363.



4-methyl-5-methylene-7-pentyl-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2l)

A light yellow oil, 84% yield (31 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.63 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 5.16 (s, 1H), 5.06 (s, 1H), 3.94 (s, 2H), 3.75 (s, 2H), 2.95 (s, 2H), 2.38 (s, 3H), 2.12 (t, J = 8.0 Hz, 2H), 1.82 (s, 3H), 1.22-1.41 (m, 6H), 0.89 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 145.0, 143.4, 137.5, 135.1, 134.0, 129.4, 129.2, 127.6, 119.9, 109.0, 50.2, 43.3, 41.5, 31.7, 28.3, 27.5, 22.5, 21.4, 17.4, 14.0; IR (CH_2Cl_2): ν 2951, 2922, 2883, 1659, 1594, 1450, 1339, 1162, 1058, 956, 814, 630 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{30}NO_2S$

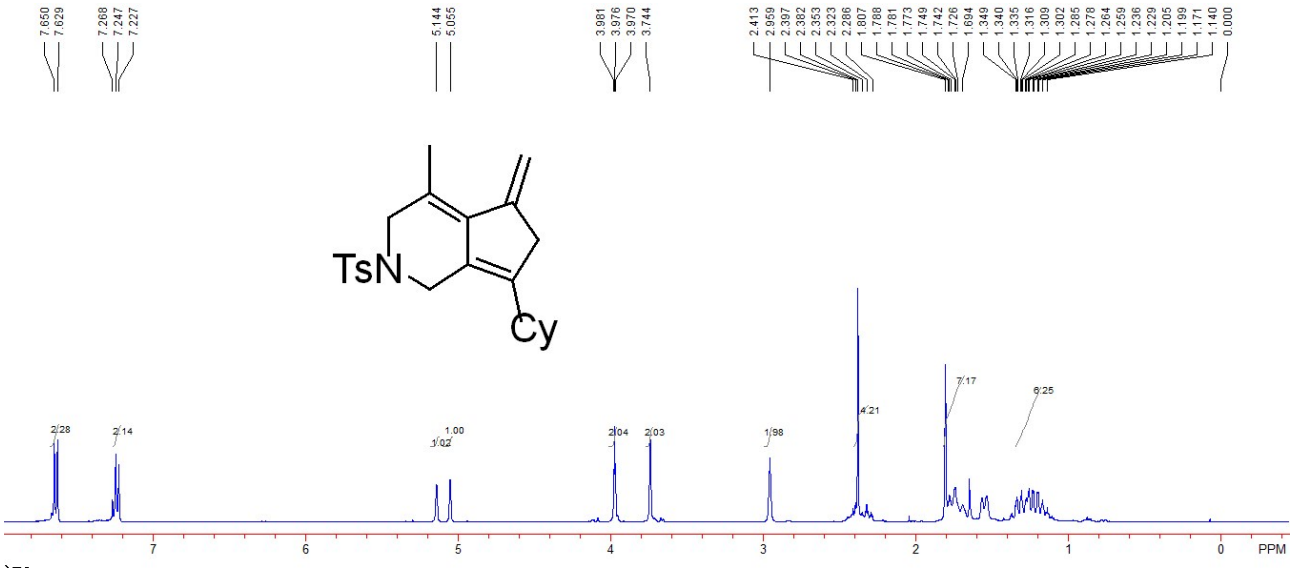
$(M+H)^+$ requires: 372.1992, Found: 372.1985.

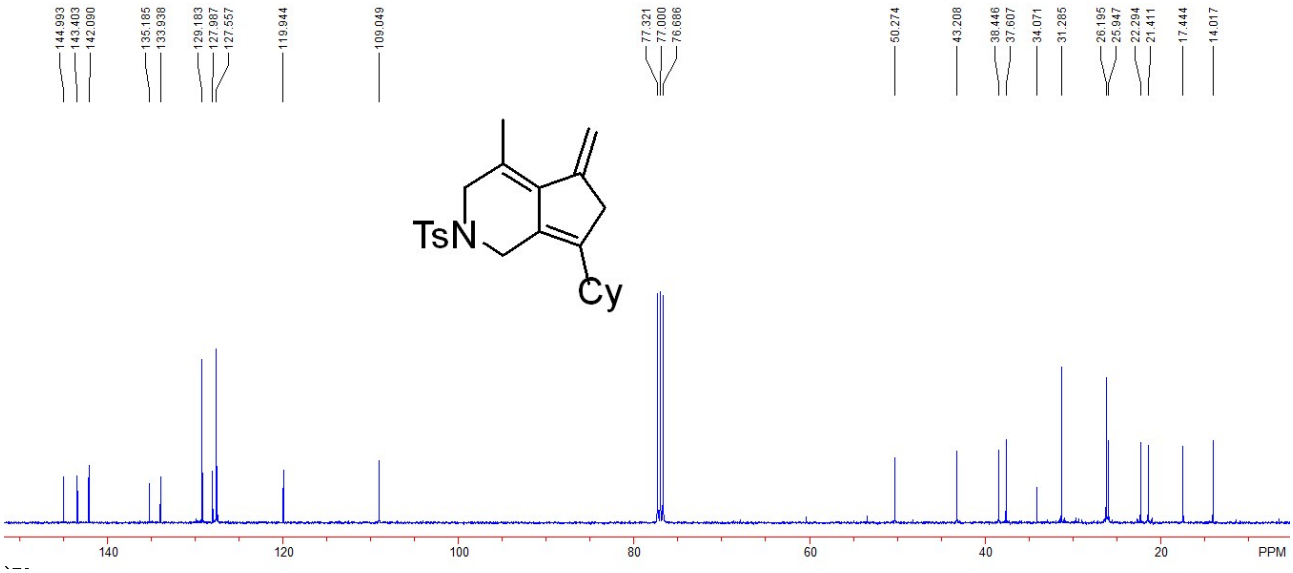


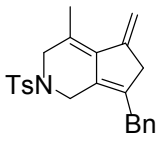
7-cyclohexyl-4-methyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2m)

A light yellow oil, 86% yield (33 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.14 (s, 1H), 5.06 (s, 1H), 3.98 (t, *J* = 2.0 Hz, 2H), 3.74 (s, 2H), 2.96 (s, 2H), 2.29-2.41 (m, 4H), 1.69-1.81 (m, 7H), 1.14-1.35 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 145.0, 143.4, 142.1, 135.2, 133.9, 129.2, 128.0, 127.6, 119.9, 109.0, 50.3, 43.2, 38.4, 37.6, 34.1, 31.3, 26.2, 25.9, 22.3, 21.4, 17.4; IR (CH_2Cl_2): ν 2953, 2923, 1642, 1589, 1456, 1336, 1159,

1090, 814, 735, 641 cm^{-1}; HRMS (ESI) Calcd. For $C_{23}H_{30}NO_2S$ $(M+H)^+$ requires: 384.1992, Found: 384.1989.



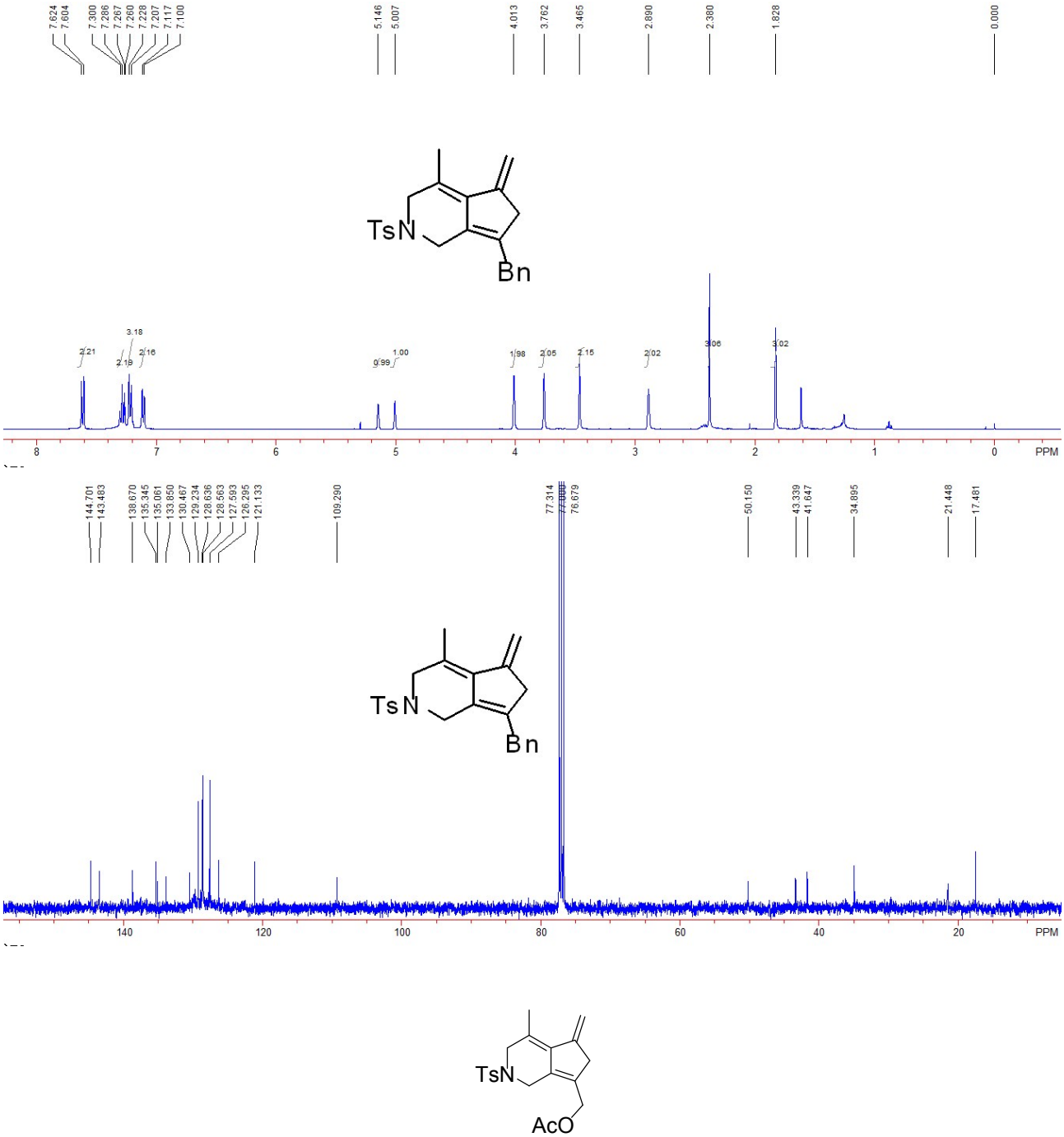




7-benzyl-4-methyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2n)

A light yellow oil, 74% yield (29 mg). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.61 (d, J = 8.0 Hz, 2H), 7.21-7.30 (m, 5H), 7.11 (d, J = 6.8 Hz, 2H), 5.15 (s, 1H), 5.01 (s, 1H), 4.01 (s, 2H), 3.76 (s, 2H), 3.47 (s, 2H), 2.89 (s, 3H), 2.38 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.7, 143.5, 138.7, 135.3, 135.1, 133.9, 130.5, 129.2, 128.64, 128.56, 127.6, 126.3, 121.1, 109.3,

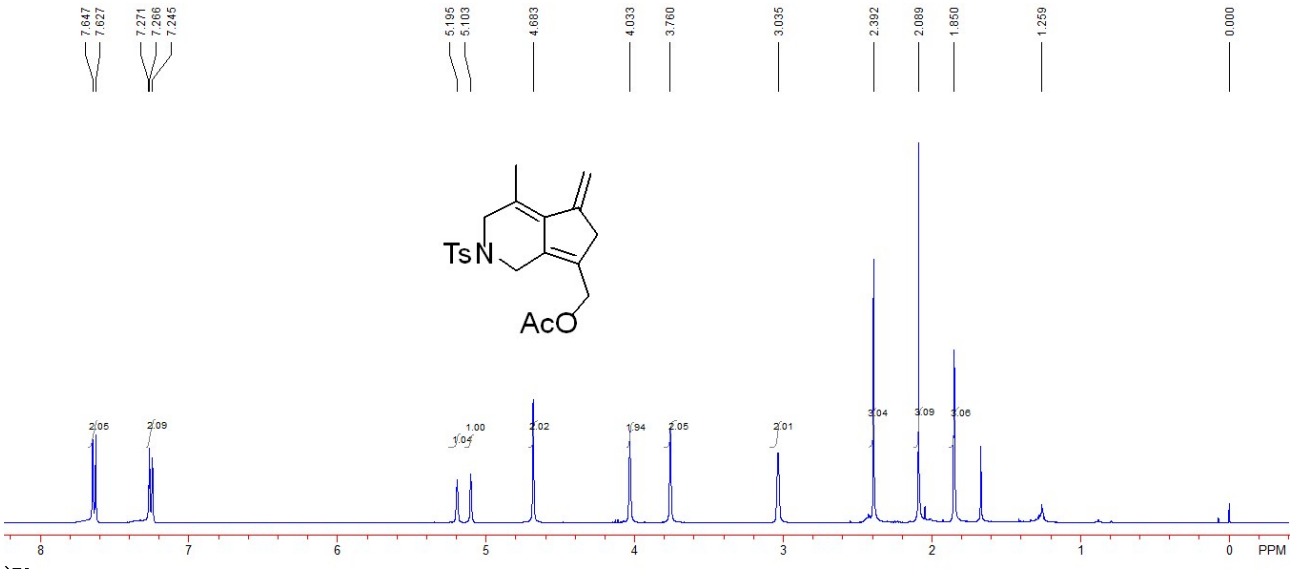
50.2, 43.3, 41.6, 34.9, 21.4, 17.5; IR (CH_2Cl_2): ν 3088, 2924, 2844, 1687, 1594, 1445, 1336, 1161, 1090, 806, 736, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{24}H_{29}N_2O_2S$ $(M+NH_4)^+$ requires: 410.1944, Found: 410.1938.

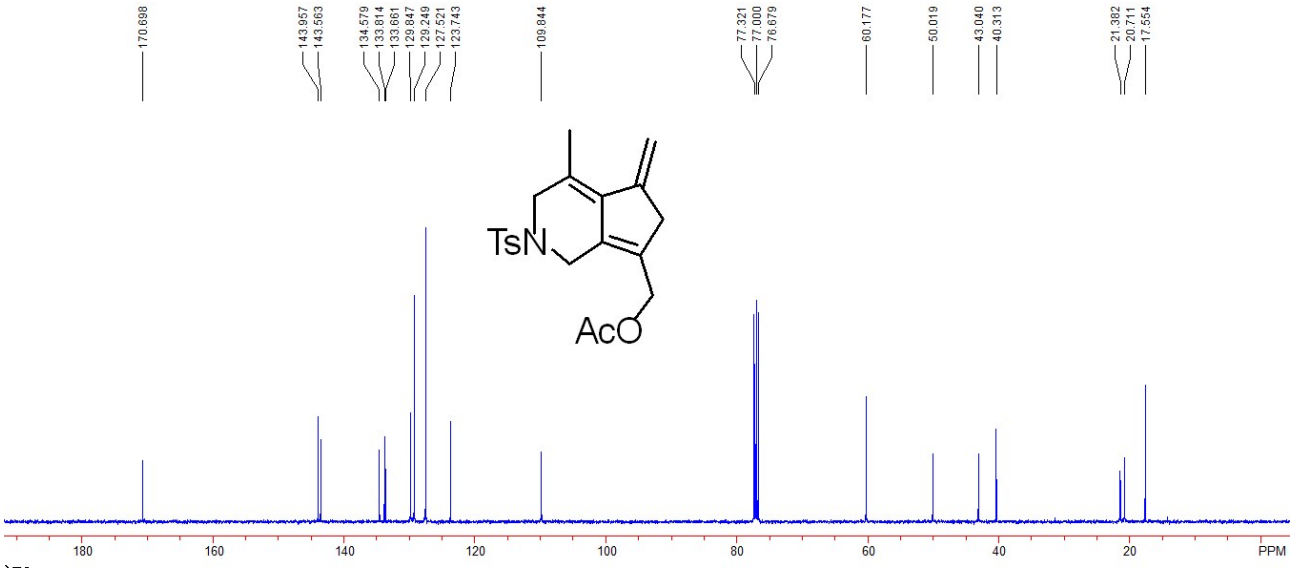


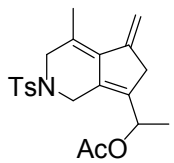
(4-methyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridin-7-yl)methyl acetate (2o)

A yellow solid, 86% yield (32 mg). M. P. 114-117 ^oC; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.64 (d, J = 8.0 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 5.20 (s, 1H), 5.10 (s, 1H), 4.68 (s, 2H), 4.03 (s, 2H), 3.76 (s, 2H), 3.04 (s, 2H), 2.39 (s, 3H), 2.09 (s, 3H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ

170.7, 144.0, 143.6, 134.6, 133.8, 133.7, 129.8, 129.2, 127.5, 123.7, 109.8, 60.2, 50.0, 43.0, 40.3, 21.3, 20.7, 17.6; IR (CH_2Cl_2): ν 2922, 2852, 1712, 1648, 1594, 1450, 1451, 1333, 1158, 1090, 816, 734, 699 cm^{-1}; HRMS (ESI) Calcd. For $C_{20}H_{27}N_2O_4S$ $(M+NH_4)^+$ requires: 391.1686, Found: 391.1681.



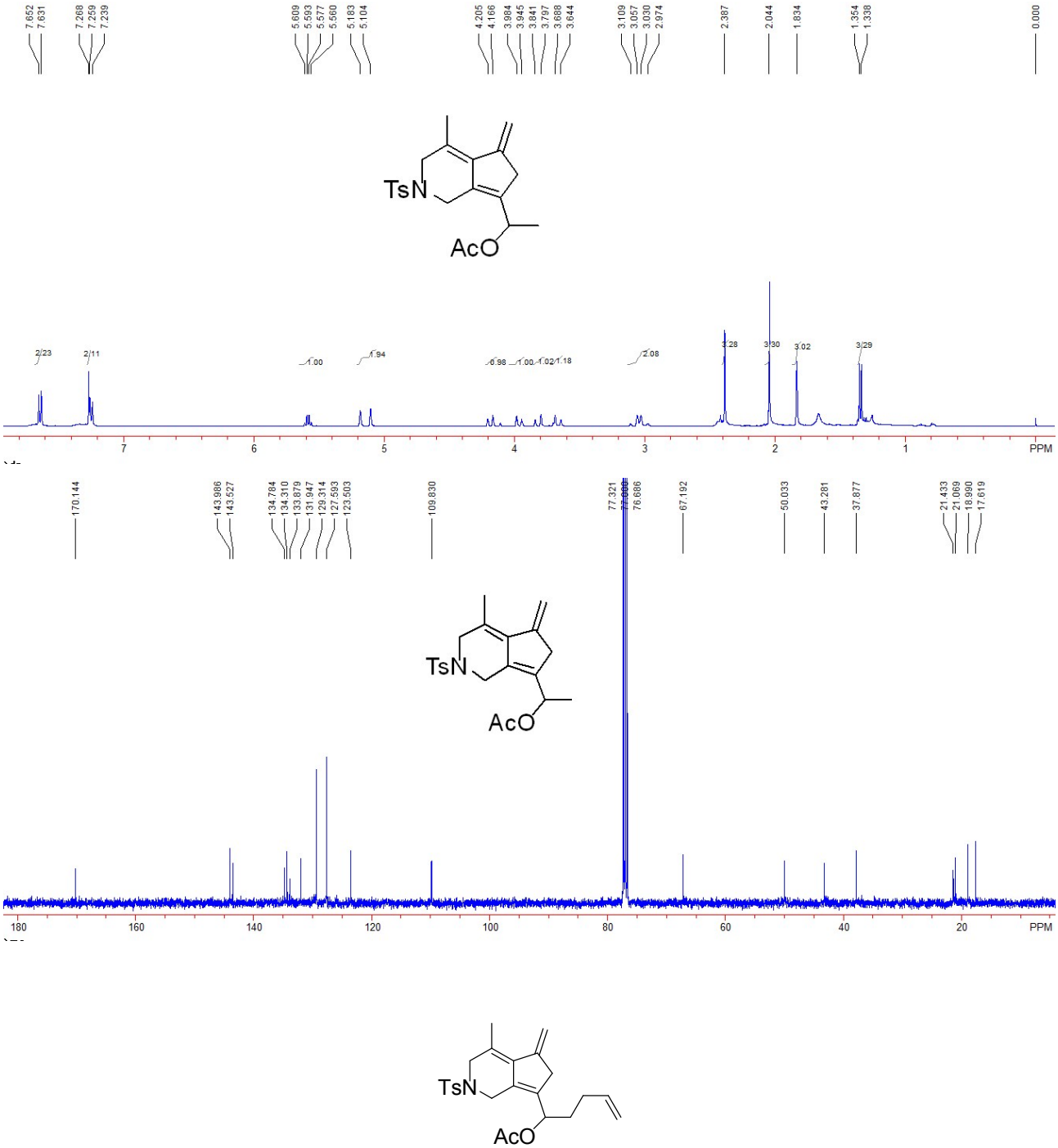




1-(4-methyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridin-7-yl)ethyl acetate (2p)

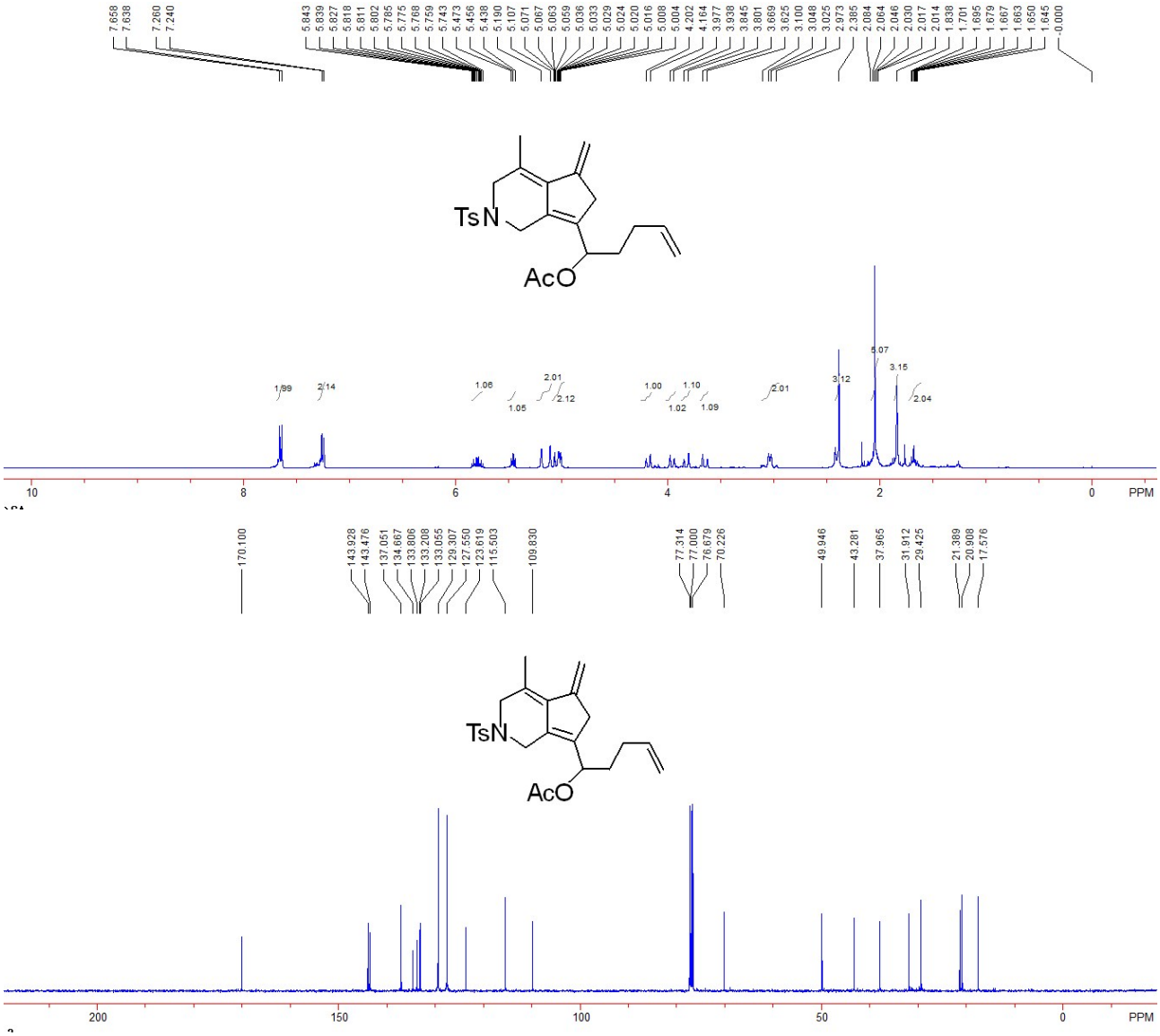
A yellow solid, 82% yield (32 mg). M. P. 120-123 ^oC; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.64 (d,

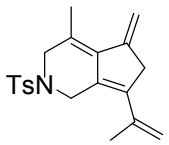
J = 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.59 (d, *J* = 15.6 Hz, 1H), 5.18 (s, 1H), 5.10 (s, 1H), 4.19 (d, *J* = 15.6 Hz, 1H), 3.96 (d, *J* = 15.6 Hz, 1H), 3.82 (d, *J* = 17.6 Hz, 1H), 3.67 (d, *J* = 17.6 Hz, 1H), 2.97-3.11 (m, 2H), 2.39 (s, 3H), 2.04 (s, 3H), 1.84 (s, 3H), 1.35 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.1, 144.0, 143.5, 134.8, 134.3, 133.9, 131.9, 129.3, 127.6, 123.5, 109.8, 67.2, 50.0, 43.3, 37.9, 21.4, 21.1, 19.0, 17.6; IR (CH_2Cl_2): ν 2959, 2922, 2862, 1709, 1638, 1599, 1453, 1335, 1159, 1090, 952, 813 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{29}N_2O_4S$ $(M+NH_4)^+$ requires: 405.1843, Found: 405.1837.



1-(4-methyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridin-7-yl)pent-4-en-1-yl acetate (2q)

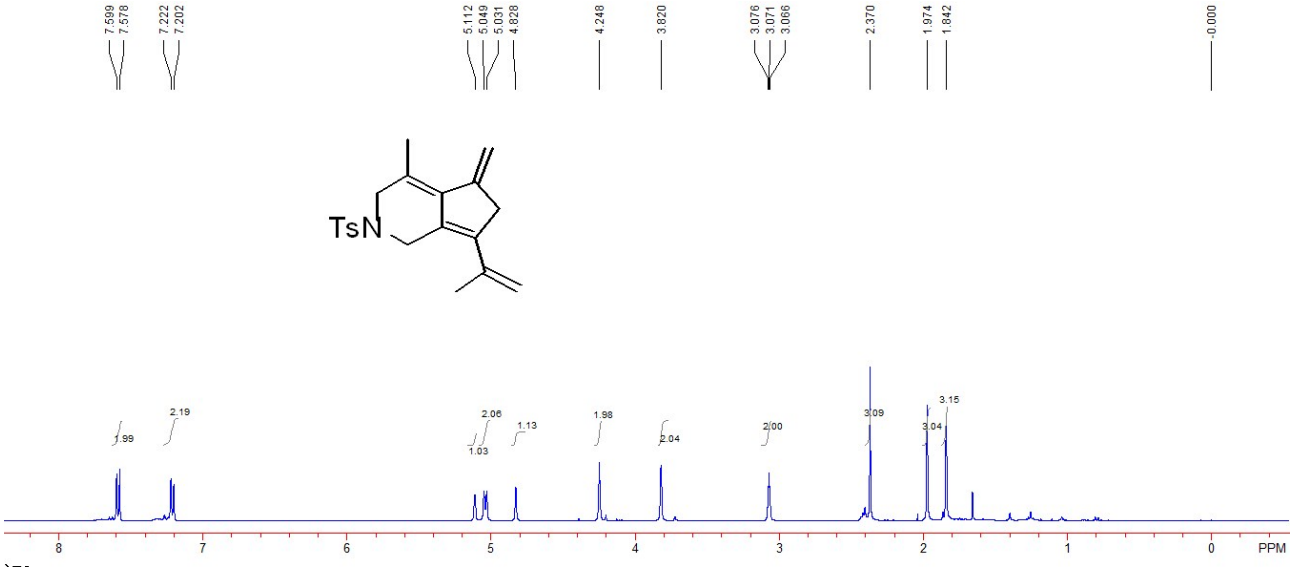
A light yellow oil, 81% yield (35 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.74-5.84 (m, 1H), 5.46 (t, *J* = 7.2 Hz, 1H), 5.19 (s, 1H), 5.11 (s, 1H), 5.00-5.07 (m, 2H), 4.18 (d, *J* = 15.3 Hz, 1H), 3.96 (d, *J* = 15.6 Hz, 1H), 3.82 (d, *J* = 17.6 Hz, 1H), 3.65 (d, *J* = 17.6 Hz, 1H), 3.07 (d, *J* = 20.8 Hz, 1H), 3.00 (d, *J* = 20.8 Hz, 1H), 2.38 (s, 3H), 2.01-2.08 (m, 5H), 1.84 (s, 3H), 1.65-1.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.1, 143.9, 143.5, 137.0, 134.7, 133.8, 133.2, 133.0, 129.3, 127.6, 123.6, 115.5, 109.8, 70.2, 49.9, 43.3, 38.0, 31.9, 29.4, 21.4, 20.9, 17.6; IR (CH_2Cl_2): ν 2961, 2927, 1706, 1591, 1453, 1336, 1160, 1090, 814, 736, 705 cm^{-1}; HRMS (ESI) Calcd. For $C_{24}H_{33}N_2O_4S$ $(M+NH_4)^+$ requires: 445.2156, Found: 445.2154.

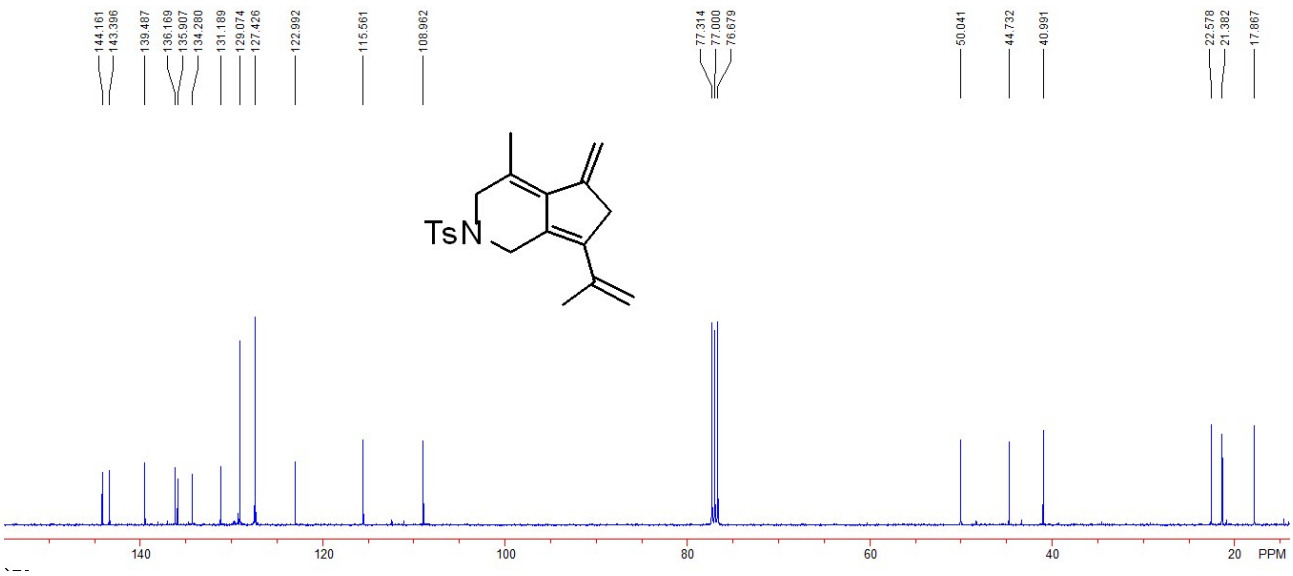


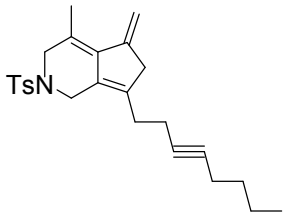


4-methyl-5-methylene-7-(prop-1-en-2-yl)-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2r)

A light yellow oil, 88% yield (30 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.11 (s, 1H), 5.05 (s, 1H), 5.03 (s, 1H), 4.83 (s, 1H), 4.25 (s, 2H), 3.82 (s, 2H), 3.07 (t, *J* = 2.0 Hz, 2H), 2.37 (s, 3H), 1.97 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.2, 143.4, 139.5, 136.2, 135.9, 134.3, 131.2, 129.1, 127.4, 123.0, 115.6, 109.0, 50.0, 44.7, 41.0, 22.6, 21.4, 17.9; IR (CH_2Cl_2): ν 2985, 2912, 1574, 1440, 1436, 1388, 1343, 1159, 1099, 1086, 1067, 1004, 903, 779, 734 cm^{-1}; HRMS (ESI) Calcd. For $C_{20}H_{24}NO_2S$ $(M+H)^+$ requires: 342.1522, Found: 342.1518.

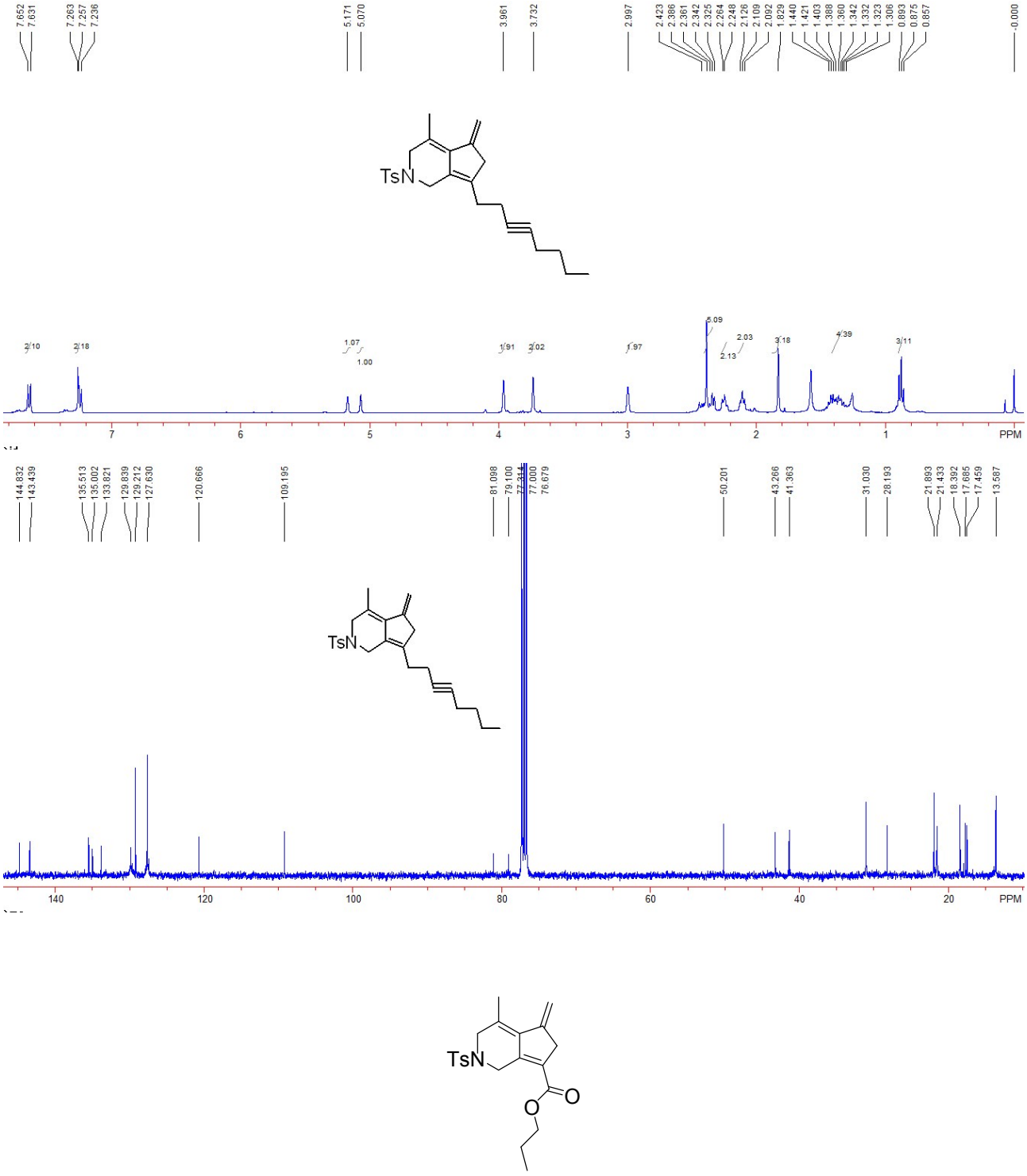






4-methyl-5-methylene-7-(oct-3-yn-1-yl)-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2s)

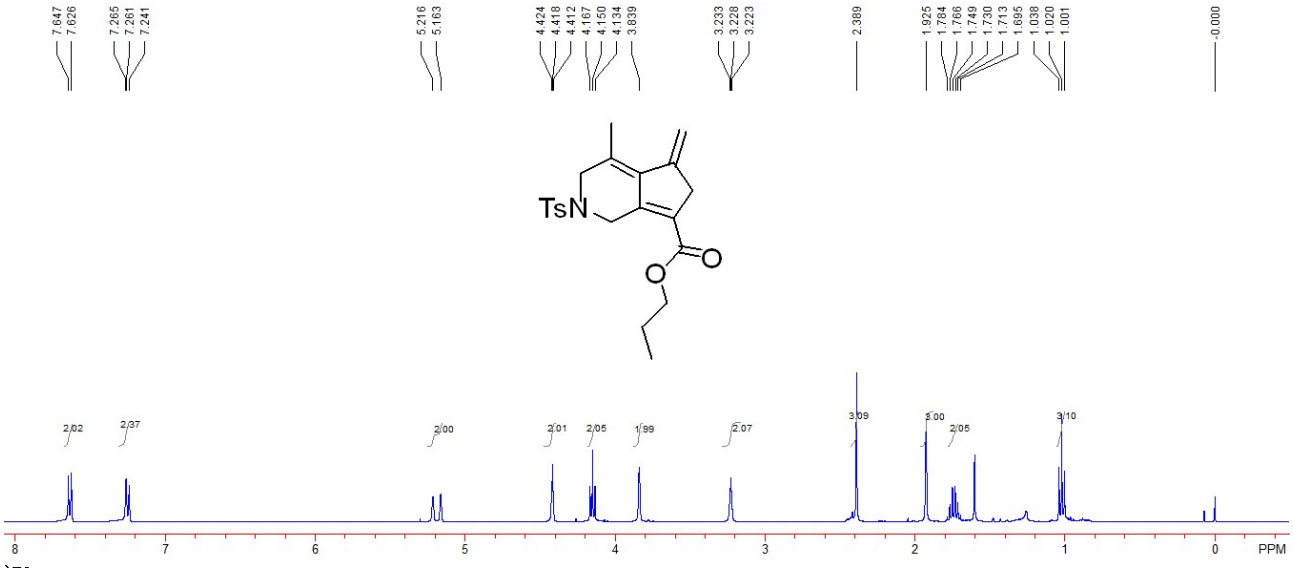
A light yellow oil, 72% yield (29 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 5.17 (s, 1H), 5.07 (s, 1H), 3.96 (s, 2H), 3.73 (s, 2H), 3.00 (s, 2H), 2.33-2.42 (m, 5H), 2.25-2.26 (m, 2H), 2.09-2.13 (m, 2H), 1.83 (s, 3H), 1.32-1.44 (m, 4H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 144.8, 143.4, 135.5, 135.0, 133.8, 129.8, 129.2, 127.6, 120.7, 109.2, 81.1, 79.1, 50.2, 43.3, 41.4, 31.0, 28.2, 21.9, 21.4, 18.4, 17.7, 17.5, 13.6; IR (CH_2Cl_2): ν 3089, 2922, 2849, 1688, 1599, 1492, 1448, 1344, 1165, 1089, 959, 814, 706, 648 cm^{-1}; HRMS (ESI) Calcd. For $C_{25}H_{32}NO_2S$ $(M+H)^+$ requires: 410.2148, Found: 410.2149.

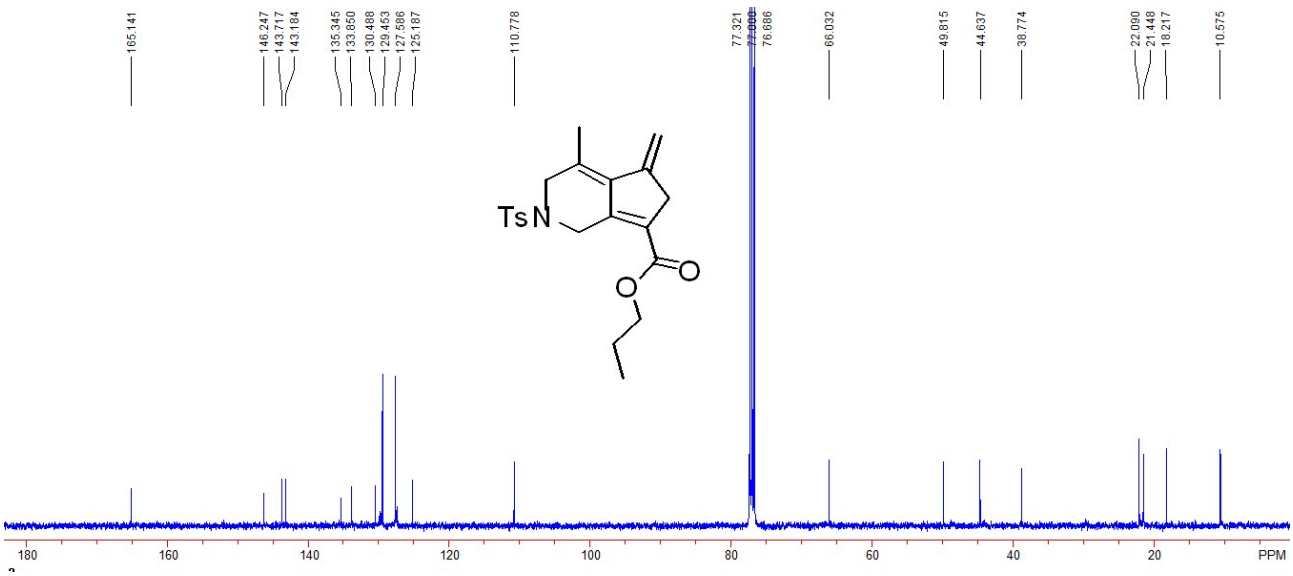


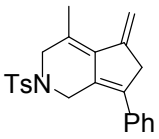
Propyl-4-methyl-5-methylene-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine-7-carboxylate (2t)

A light yellow oil, 76% yield (30 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.64 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 5.22 (s, 1H), 5.16 (s, 1H), 4.42 (t, J = 2.4 Hz, 2H), 4.15 (t, J = 6.8 Hz, 2H), 3.84 (s, 2H), 3.23 (t, J = 2.0 Hz, 2H), 2.39 (s, 3H), 1.93 (s, 3H), 1.70-1.77 (m, 2H), 1.02 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 165.1, 146.3, 143.7, 143.2, 135.3, 133.9, 130.5,

129.5, 127.6, 125.2, 110.8, 66.0, 49.8, 44.6, 38.8, 22.1, 21.4, 18.2, 10.6; IR (CH_2Cl_2): ν 2961, 2930, 1706, 1651, 1574, 1389, 1350, 1270, 1089, 1068, 1009, 946, 738 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{29}N_2O_4S$ $(M+NH_4)^+$ requires: 405.1843, Found: 405.1843.



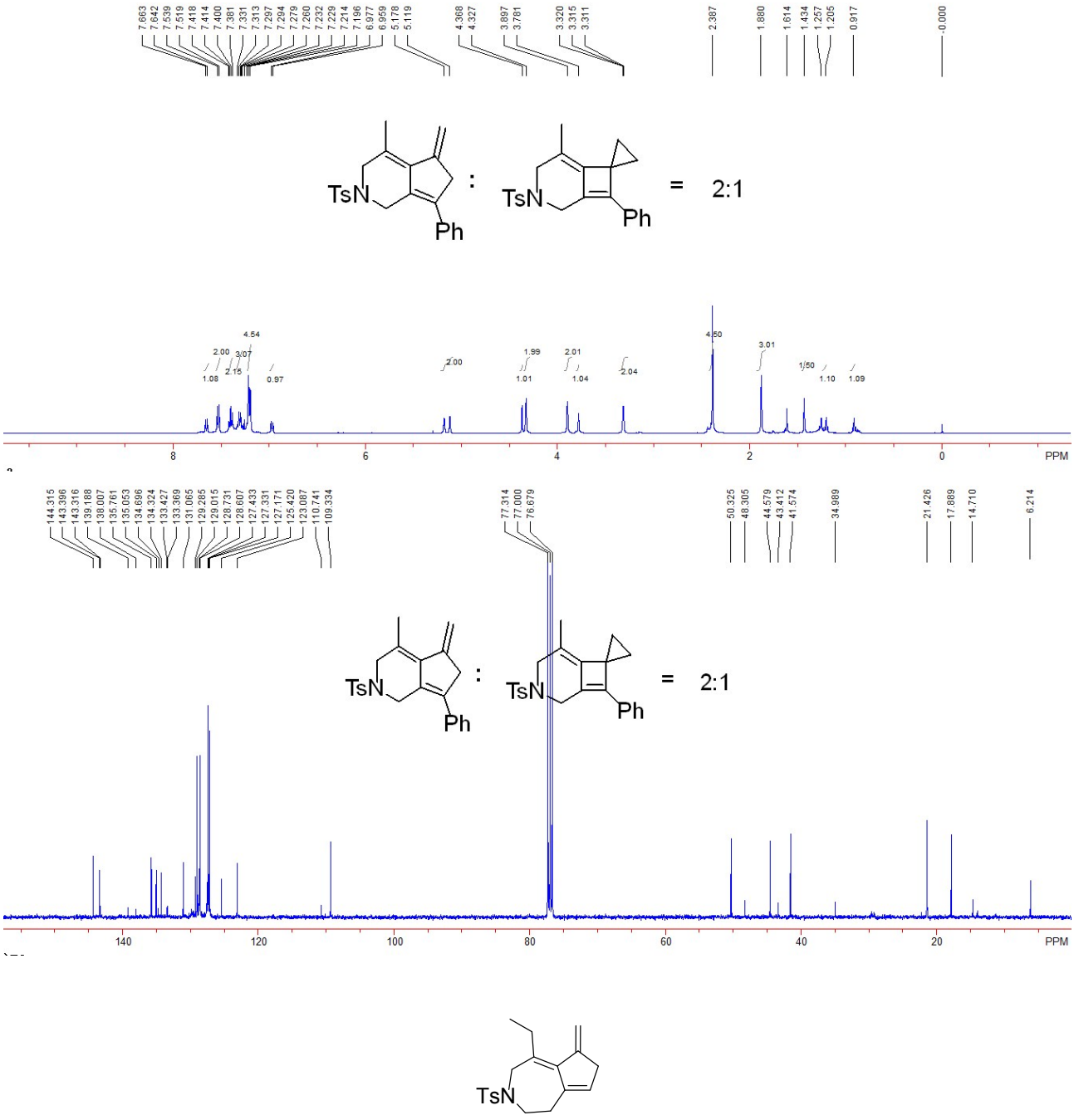




4-methyl-5-methylene-7-phenyl-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (2u)

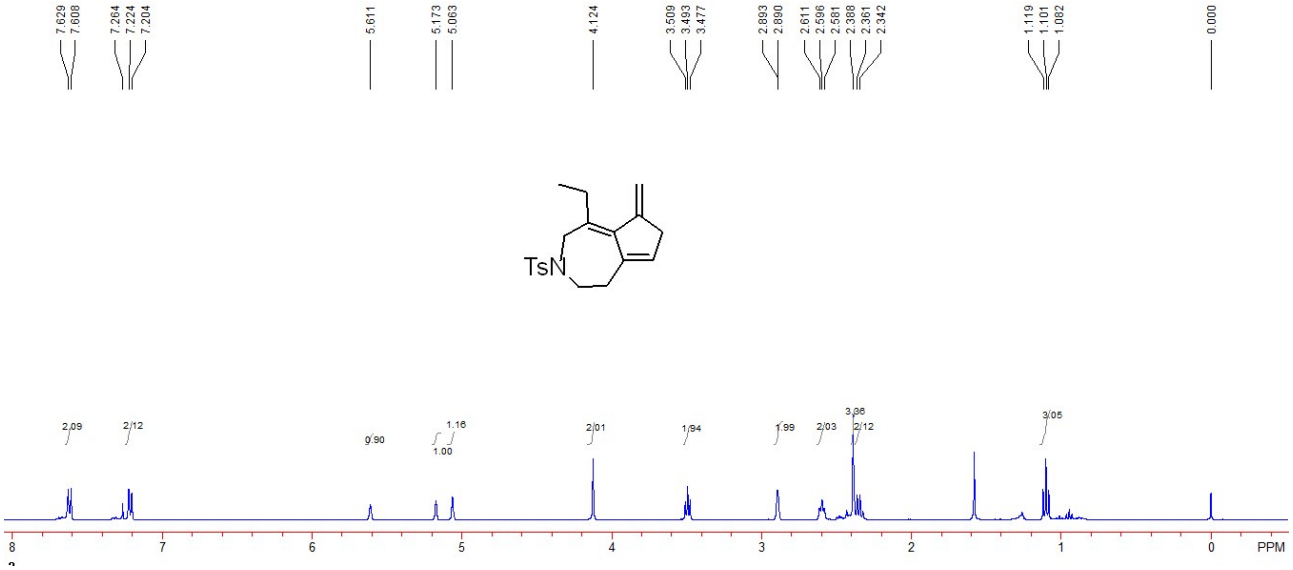
A light yellow oil, 58% yield (22 mg). ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.53 (d, J = 8.0 Hz, 2H), 7.38-7.42 (m, 2H), 7.28-7.33 (m, 2H), 7.20-7.23 (m, 3H), 5.18 (s, 1H), 5.12 (s, 1H), 4.33 (s, 2H), 3.90 (s, 2H), 3.32 (t, J = 1.6 Hz, 2H), 2.39 (s, 3H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,

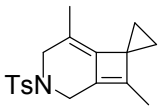
TMS) δ 144.3, 143.4, 135.8, 135.1, 134.3, 131.1, 129.0, 128.6, 127.4, 127.2, 123.1, 109.3, 50.3, 44.6, 41.6, 21.4, 17.9. The [2+2] byproduct is a known compound.[2]



5-ethyl-6-methylene-3-tosyl-1,2,3,4,6,7-hexahydrocyclopenta[d]azepine (2v)

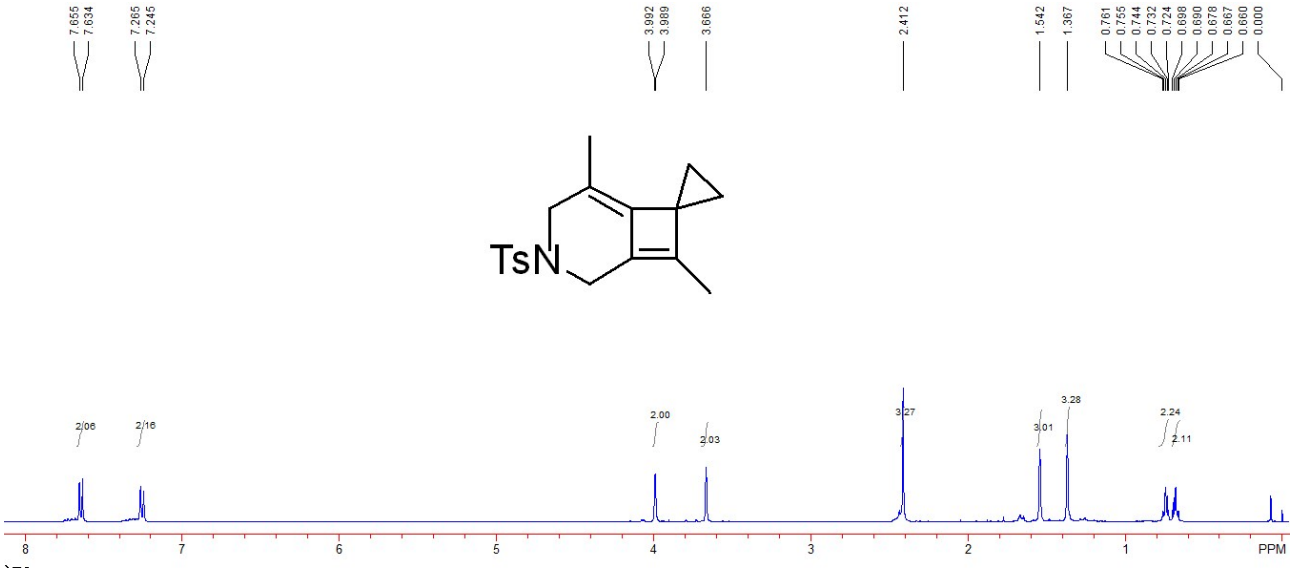
This is a known compound.[1] A light yellow oil, 41% yield (13 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.61 (s, 1H), 5.17 (s, 1H), 5.06 (s, 1H), 4.12 (s, 2H), 3.49 (t, *J* = 6.4 Hz, 2H), 2.89 (d, *J* = 1.2 Hz, 2H), 2.60 (t, *J* = 6.0 Hz, 2H), 2.34-2.37 (m, 5H), 1.10 (t, *J* = 7.2 Hz, 3H).

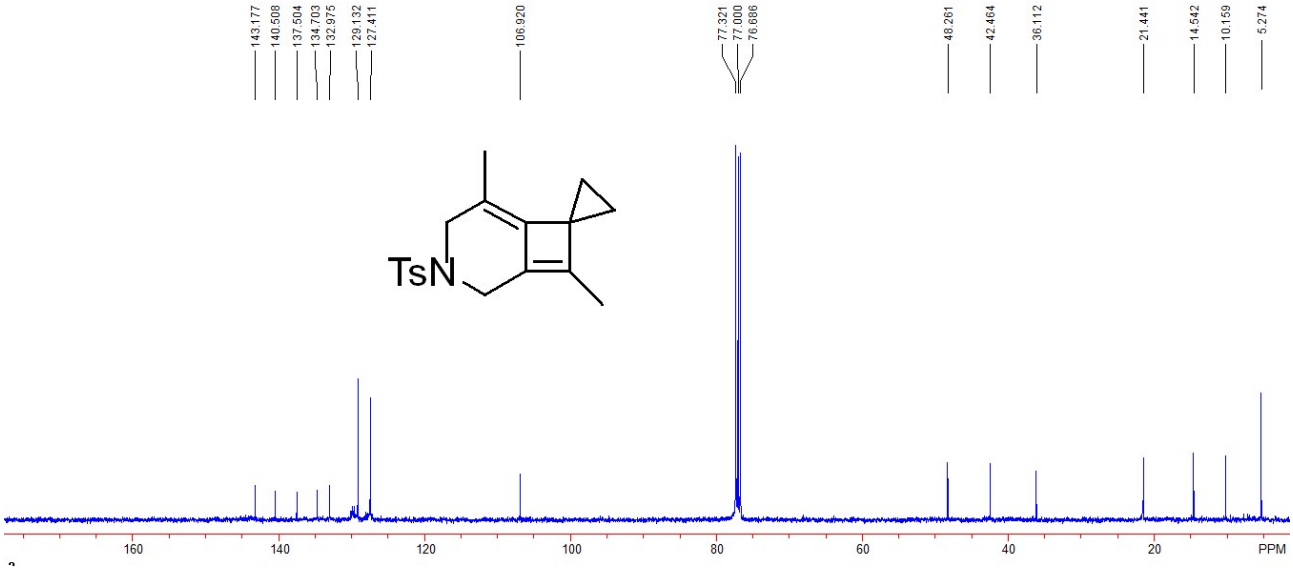


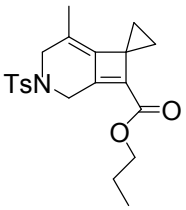


5,8-dimethyl-3-tosyl-3-azaspiro[bicyclo[4.2.0]octane-7,1'-cyclopropane]-1(8),5-diene (3k)

A light yellow oil, 38% yield (12 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 3.99 (d, *J* = 1.2 Hz, 2H), 3.67 (s, 2H), 2.41 (s, 3H), 1.54 (s, 3H), 1.37 (s, 3H), 0.72-0.76 (m, 2H), 0.66-0.70 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 143.2, 140.5, 137.5, 134.7, 133.0, 129.1, 127.4, 106.9, 66.0, 48.3, 42.5, 36.1, 21.4, 14.5, 10.2, 5.3; IR (CH_2Cl_2): ν 2964, 2925, 1597, 1457, 1160, 964, 813, 706, 661 cm^{-1}; HRMS (ESI) Calcd. For $C_{18}H_{22}NO_2S$ $(M+H)^+$ requires: 316.1366, Found: 316.1372.

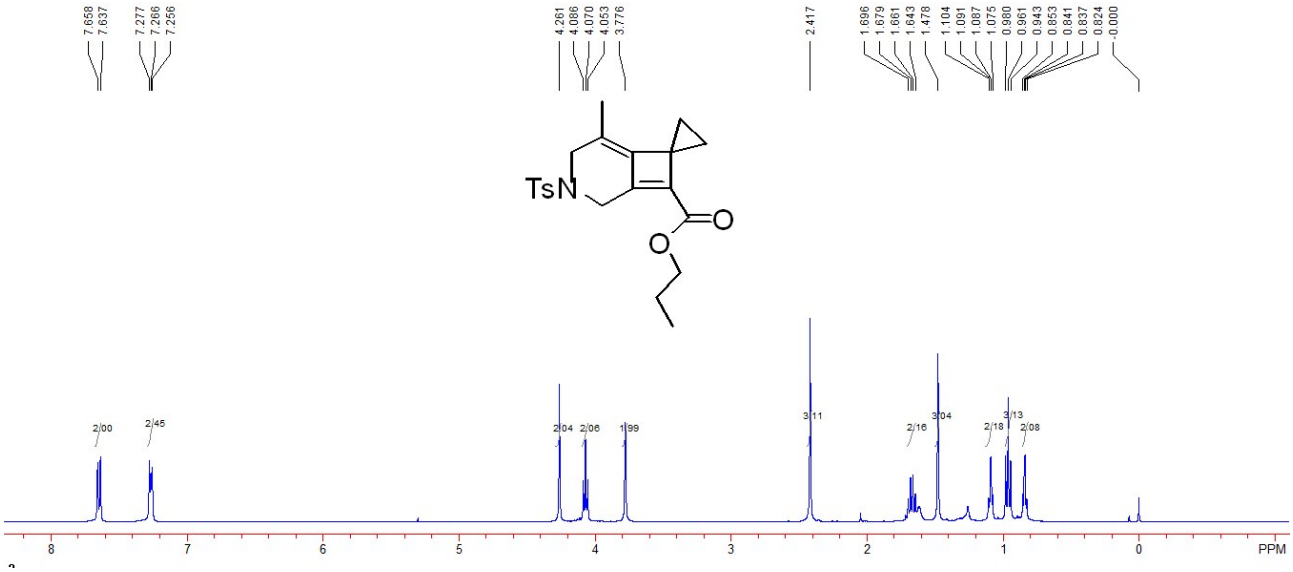


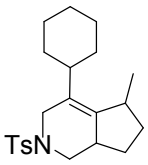




propyl5-methyl-3-tosyl-3-azaspiro[bicyclo[4.2.0]octane-7,1'-cyclopropane]-1(8),5-diene-8-carboxylate (3t)

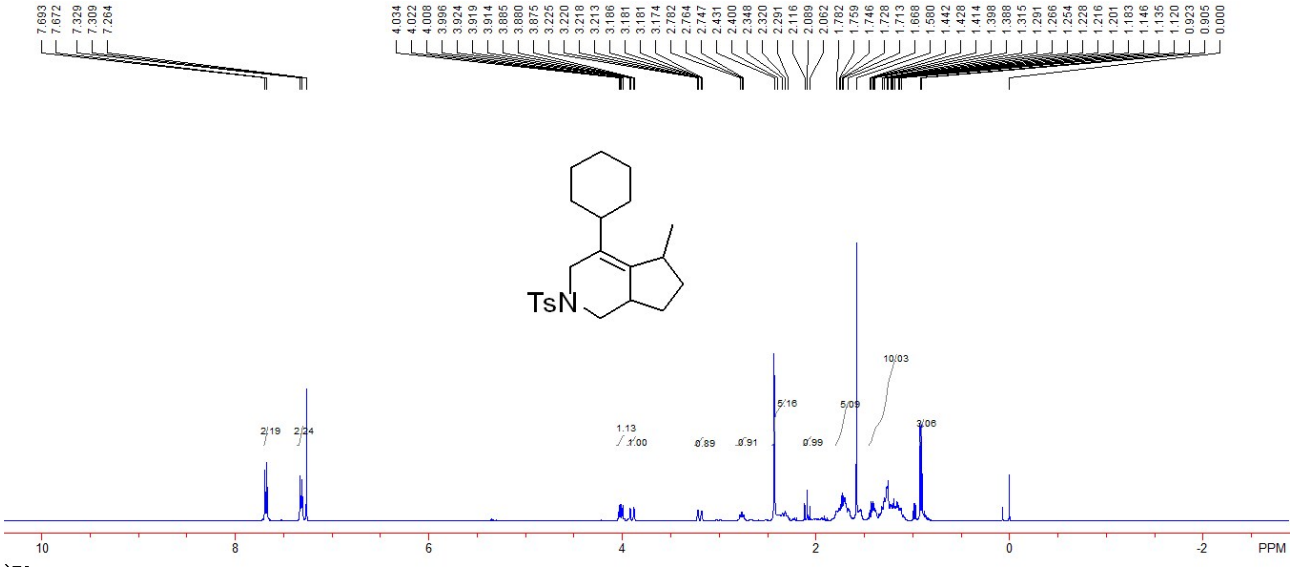
This is a thermal-induced intramolecular [2+2] cycloaddition product.[2] A light yellow oil, 20% yield (8.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.65 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 4.26 (s, 2H), 4.07 (t, J = 6.4 Hz, 2H), 3.78 (s, 2H), 2.42 (s, 3H), 1.64-1.70 (m, 2H), 1.48 (s, 3H), 1.08-1.10 (m, 2H), 0.96 (t, J = 7.2 Hz, 2H), 0.82-0.85 (m, 2H).

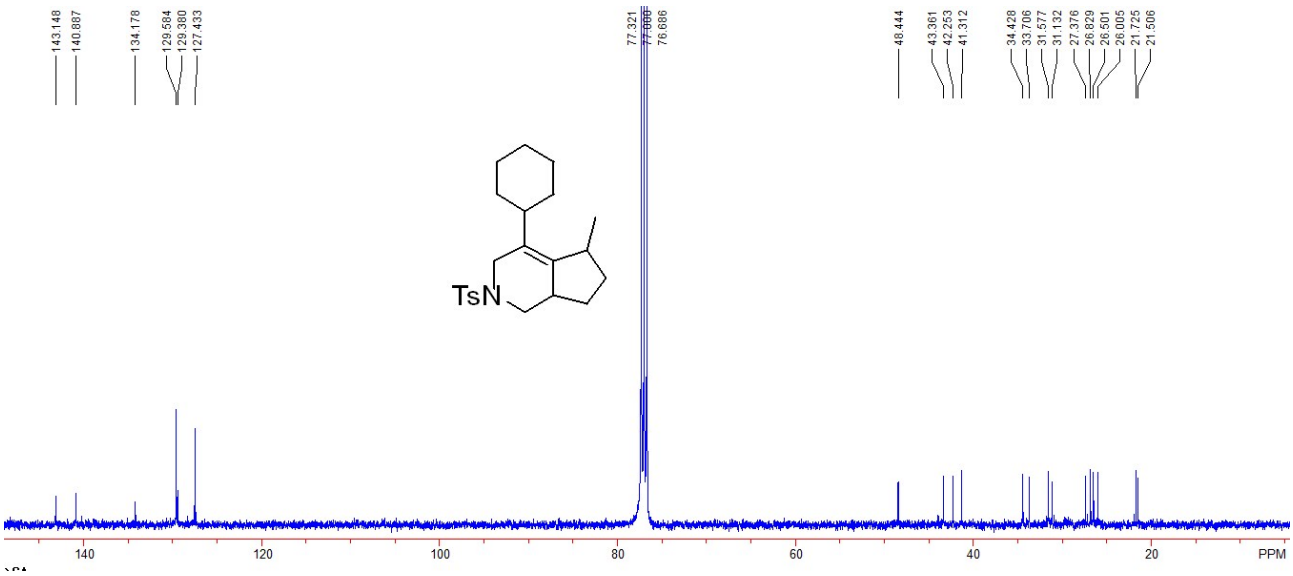


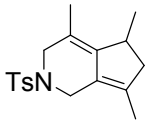


4-cyclohexyl-5-methyl-2-tosyl-2,3,5,6,7,7a-hexahydro-1H-cyclopenta[c]pyridine (4)

A light yellow oil, 61% yield (23 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.68 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.02 (dd, J_1 = 4.8 Hz, J_2 = 10.4 Hz, 1H), 3.88-3.92 (m, 1H), 3.17-3.23 (m, 1H), 2.76 (t, J = 7.2 Hz, 1H), 2.29-2.43 (m, 5H), 2.09 (t, J = 10.8 Hz, 1H), 1.67-1.78 (m, 5H), 1.12-1.44 (m, 10H), 0.91 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 143.1, 140.9, 134.2, 129.6, 129.4, 127.4, 48.4, 43.4, 42.3, 41.3, 34.4, 33.7, 31.6, 31.1, 27.4, 26.8, 26.5, 26.0, 21.7, 21.5; IR (CH_2Cl_2): ν 2919, 2852, 1599, 1506, 1443, 1349, 1161, 1089, 1015, 958, 833, 806, 790 cm^{-1}; Mass (EI) $(M)^+$: 373.3, HRMS (EI) Calcd. For $C_{22}H_{31}NO_2S$ $(M)^+$ requires: 373.2072, Found: 373.2076.

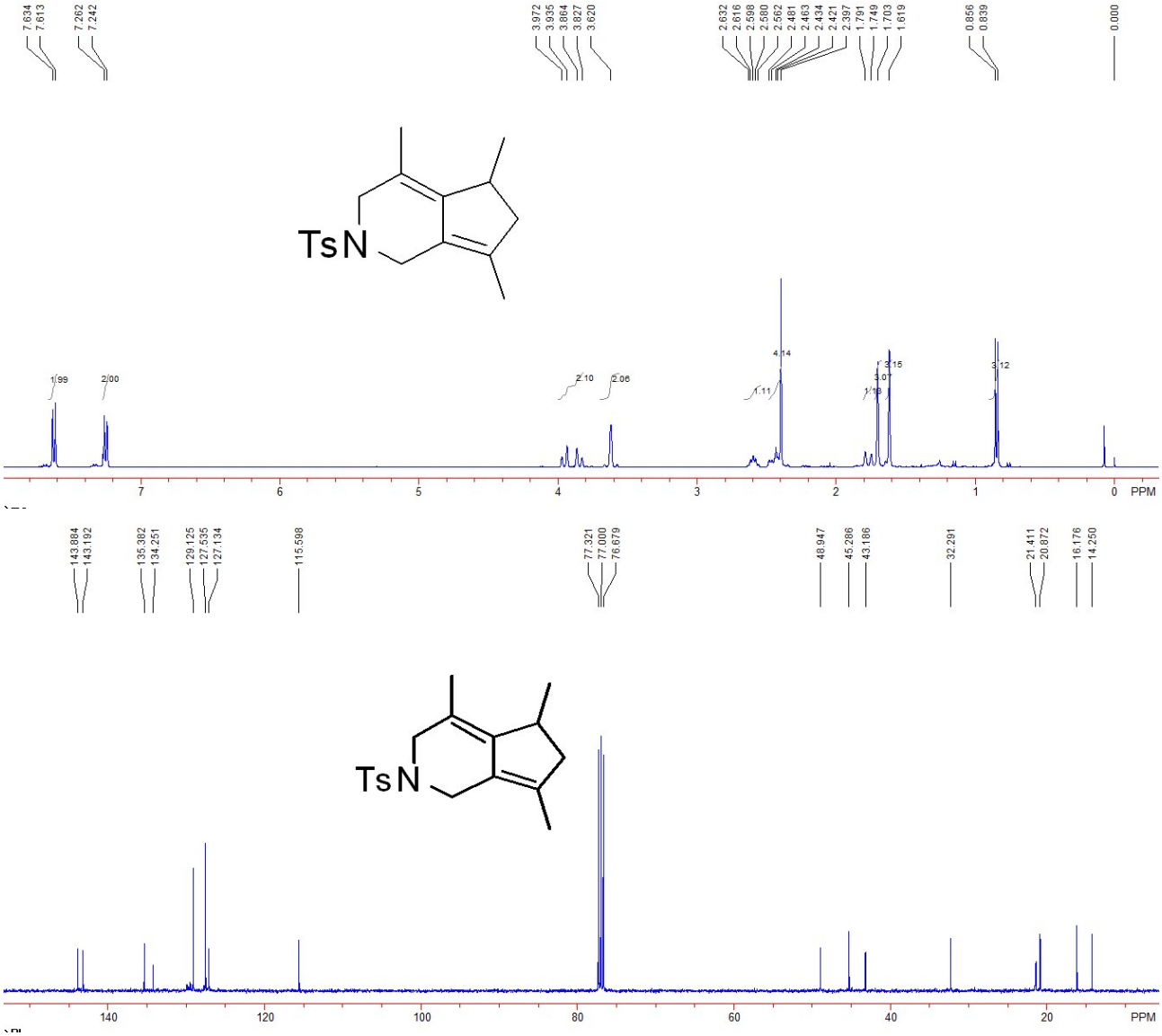






4,5,7-trimethyl-2-tosyl-2,3,5,6-tetrahydro-1H-cyclopenta[c]pyridine (5)

A light yellow oil, 72% yield (23 mg). ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 3.95 (d, *J* = 14.8 Hz, 1H), 3.85 (d, *J* = 14.8 Hz, 1H), 3.62 (s, 2H), 2.56-2.63 (m, 1H), 2.40-2.48 (m, 4H), 1.77 (d, *J* = 16.8 Hz, 1H), 1.70 (s, 3H), 1.62 (s, 3H), 0.85 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 143.9, 143.2, 135.4, 134.3, 129.1, 127.5, 127.1, 115.6, 48.9, 45.3, 43.2, 32.3, 21.4, 20.9, 16.2, 14.3; IR (CH_2Cl_2): ν 2919, 2852, 1600, 1506, 1443, 1349, 1161, 1089, 1051, 958, 833, 806, 790, 733, 634 cm^{-1}; HRMS (ESI) Calcd. For $C_{18}H_{24}NO_2S$ $(M+H)^+$ requires: 318.1513, Found: 318.1522.


7.634
7.613
7.262
7.242
3.972
3.935
3.864
3.827
3.620
2.632
2.616
2.598
2.580
2.562
2.481
2.463
2.434
2.421
2.397
1.791
1.749
1.703
1.619
0.856
0.839
0.000
TsN
1.99
2.00
2.10
2.06
4.14
1.11
3.15
3.07
1.19
3.12
7
6
5
4
3
2
1
0
PPM
143.884
143.192
135.382
134.251
129.125
127.535
127.134
115.598
77.321
77.000
76.679
48.947
45.286
43.186
32.291
21.411
20.872
16.176
14.250
TsN
140
120
100
80
60
40
20
PPM

6. References.

1) W. Yuan, X.-Y. Tang, Y. Wei and M. Shi, *Chem. Eur. J.* 2014, **20**, 3198-3204.

2) S. Yang, Q. Xu and M. Shi, *Tetrahedron* 2016, **72**, 584-591.

3) S. Yang, K.-H. Rui, X.-Y. Tang, Q. Xu and M. Shi, *J. Am. Chem. Soc.* 2017, **139**, 5957-5964.