Supporting Information for

Silver-Mediated Synthesis of 1,4-Dihydropyridine Sulfones *via* [4+2] Cyclization of *N*-Allenylsulfonamides and Enaminones with 1,3-Sulfonyl Shift

Shuguang Zhou[a], Shuang-Feng Dong[a], Xin Zhang[a], Shen-Yuan Zhang[c], Teck-Peng Loh[b,d]* and Jie-Sheng Tian[a]*

[a]School of Chemistry and Chemical Engineering, Northwestern Polytechnical University (NPU), Xi'an 710072, China. E-mail: tjs@nwpu.edu.cn

[b]College of Advanced Interdisciplinary Science and Technology, Henan University of Technology, Zhenzhou, 450001, China.

[c]School of Chemistry and Molecular Engineering, Nanjing Tech University (NanjingTech), Nanjing 211816, China.

[d]School of Chemistry, Chemical Engineering and Biotechnology (CCEB), Nanyang Technological University, Singapore 637371. E-mail: teckpeng@ntu.edu.sg

Table of Contents

1. General Information

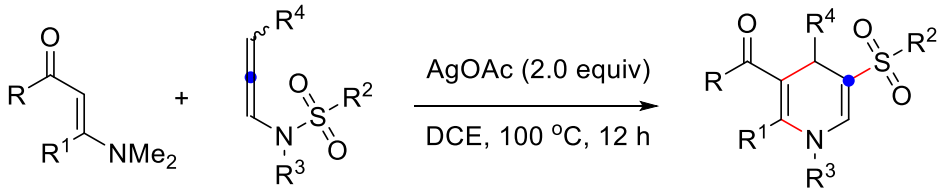
Materials:

All reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated. All chemicals were obtained from local suppliers or synthesized. The preparation of enaminones[1] and *N*-allenylsulfonamides[2-3] according to the previous procedures.

Methods:

All reactions beyond room temperature (r.t.) were run in oil baths with the temperature calibrated with a thermometer. Prior to an experiment, the oil bath was allowed to equilibrate to the desired temperature for 15 min. ^{1}H, ^{13}C, spectra were recorded in $CDCl_3$ (with tetramethylsilane as internal standard) solution on Bruker AVANCE 400 MHz spectrometer or Bruker AVANCE 500 MHz spectrometer. The following notations were used: br-broad, s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet, dd-doublet of doublet, dt-doublet of triplet, td-triplet of doublet, ddd-doublet of doublet of doublet. HRMS spectra were recorded on a waters Q-TOF permier spectrometer.

2. General Experimental Procedure for [4+2] Cyclization of *N*-Allenylsulfonamides and Enaminones with 1,3-Sulfonyl Shift towards 1,4-Dihydropyridine Sulfones

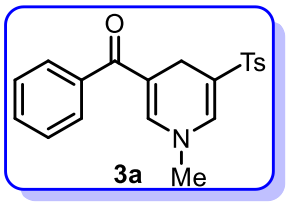


To a 10 mL Schlenk flask equipped with magnetic stir bar was added enaminones (0.5

mmol), *N*-tosylallenamides (0.75 mmol, 1.5 equiv), AgOAc (1.0 mmol, 2.0 equiv). After the DCE (2 mL) was injected into the test tube *via* syringe. The reaction mixture was allowed to stir at 100 °C for 24 h, during which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc as the eluent to afford the yellow solid.

3. <u>Characterization Data for 1,4-Dihydropyridine Sulfones</u>

(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)(phenyl)methanone (3a)



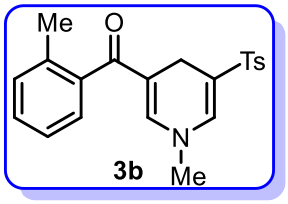
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a yellow solid, Yield = 88% (155.81 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 7.6 Hz, 2H), 7.47 – 7.42 (m, 3H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.01 (s, 1H), 6.57 (s, 1H), 3.23 (s, 2H), 3.09 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.25, 144.78, 144.38, 139.21, 136.87, 135.91, 130.96, 130.06, 128.55, 128.46, 128.27, 115.79, 113.42, 41.73, 21.83, 20.88.

HRMS (ESI, m/z): Calcd. for $C_{20}H_{19}NO_3S$: $[M+H]^+$, 354.1164. Found: *m/z* 354.1162.

(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)(o-tolyl)methanone (3b):



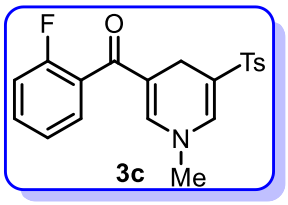
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (4:1)

The title compound was obtained as a yellow solid, Yield = 69% (127.01 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.81 – 7.76 (m, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.22 – 7.13 (m, 1H), 7.07 (s, 1H), 7.00 (s, 1H), 6.35 (s, 1H), 3.24 (s, 1H), 3.05 (s, 1H), 2.46 – 2.44 (m, 1H), 2.21 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 195.94, 145.10, 144.45, 139.09, 136.75, 135.87, 135.79, 130.99, 130.10, 129.48, 128.33, 127.37, 125.40, 116.25, 114.65, 41.71, 21.88, 20.42, 19.57.

HRMS (ESI, m/z): Calcd. for $C_{21}H_{21}FNO_3S$: $[M+H]^+$, 368.1320. Found: *m/z* 368.1319.

(2-fluorophenyl)(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)methanone (3c):



This compound was prepared by the general procedure described above.

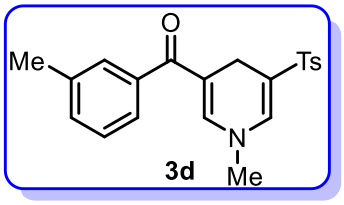
Flash chromatography: PE/EA (4:1)

The title compound was obtained as a yellow solid, Yield = 53% (98.61 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.43 – 7.37 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.17 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.07 (dd, *J* = 13.2, 4.7 Hz, 1H), 7.00 (s, 1H), 6.45 (s, 1H), 3.23 (s, 2H), 3.09 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.96, 159.1(d, *J* = 249.7 Hz), 145.45, 144.50, 136.68, 135.62, 131.87 (d, *J* = 7.9 Hz), 130.08, 129.93, 128.27, 124.48, 116.51, 116.31 (d, *J* = 21.9 Hz), 114.23, 41.81, 21.85, 20.51.

HRMS (ESI, m/z): Calcd. for $C_{20}H_{18}FNO_3S$: $[M+H]^+$, 372.1070. Found: *m/z* 372.1068.

(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)(m-tolyl)methanone (3d):



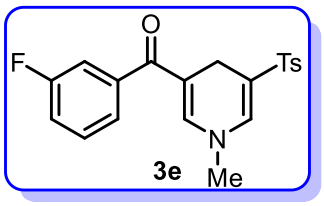
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (3:1)

The title compound was obtained as a yellow solid, Yield = 62% (114.12 mg) . **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.23 (m, 3H), 7.23 – 7.17 (m, 1H), 7.02 (s, 1H), 6.58 (s, 1H), 3.23 (s, 2H), 3.09 (s, 3H), 2.43 (s, 3H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.49, 144.74, 144.33, 139.19, 138.48, 136.91, 135.84, 131.66, 130.01, 128.93, 128.25, 128.21, 125.50, 115.60, 113.38, 41.70, 21.81, 21.57, 20.81.

HRMS (ESI, m/z): Calcd. for $C_{21}H_{21}NO_3S$: $[M+H]^+$, 368.1320. Found: *m/z* 368.1318.

(3-fluorophenyl)(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)methanone (3e):

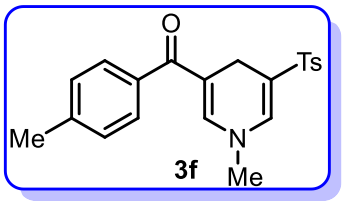


This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (4:1)

The title compound was obtained as a yellow solid, Yield = 71% (132.10 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.35 (ddd, *J* = 14.0, 8.7, 4.3 Hz, 3H), 7.21 (dt, *J* = 7.5, 1.1 Hz, 1H), 7.17 – 7.10 (m, 2H), 7.01 (d, *J* = 0.8 Hz, 1H), 6.57 (d, *J* = 0.7 Hz, 1H), 3.21 (s, 2H), 3.11 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.57 (d, *J* = 2.1 Hz), 163.83, 161.36, 145.06, 144.47, 141.20 (d, *J* = 6.4 Hz), 136.73, 135.72, 130.42, 129.97 , 128.26, 124.11 (d, *J* = 3.1 Hz), 118.02, 117.80, 116.13, 115.57, 115.35, 113.02, 41.81, 21.83, 20.79. **HRMS (ESI, m/z):** Calcd. for $C_{20}H_{18}FNO_3S$: $[M+H]^+$, 372.1069. Found: *m/z* 372.1066.

(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)(p-tolyl)methanone (3f):



3f

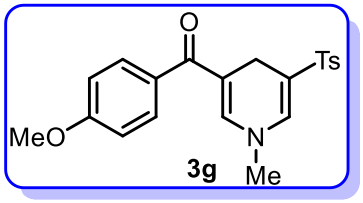
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (4:1)

The title compound was obtained as a yellow solid, Yield = 85% (156.46 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.34 (dd, *J* = 12.5, 8.1 Hz, 4H), 7.18 (d, *J* = 7.9 Hz, 2H), 7.01 (s, 1H), 6.58 (s, 1H), 3.22 (s, 2H), 3.08 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.92, 144.26, 141.02, 137.09, 135.82, 129.96, 128.10, 115.03, 114.02, 41.63, 24.75, 21.78, 20.37.

HRMS (ESI, m/z): Calcd. for $C_{21}H_{21}NO_3S$: $[M+H]^+$, 368.1320. Found: *m/z* 368.1319.

(4-methoxyphenyl)(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)methanone (3g):



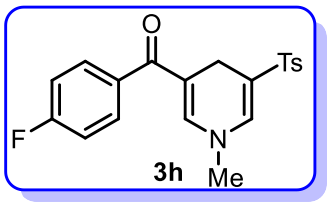
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (3:1)

The title compound was obtained as a yellow solid, Yield = 92% (176.70 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.01 (s, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.58 (s, 1H), 3.83 (s, 3H), 3.22 (s, 2H), 3.10 (s, 3H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 193.29, 162.12, 144.33, 143.81, 137.01, 135.93, 131.57, 130.67, 130.05, 128.26, 115.26, 113.83, 113.44, 55.64, 41.69, 21.85, 21.09.

HRMS (ESI, m/z): Calcd. for $C_{21}H_{21}NO_4S$: $[M+H]^+$, 384.1269. Found: *m/z* 384.1267.

(4-fluorophenyl)(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)methanone (3h):



This compound was prepared by the general procedure described above.

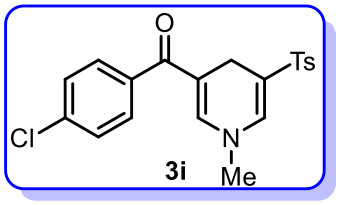
Flash chromatography: PE/EA (4:1)

The title compound was obtained as a yellow solid, Yield = 76% (141.40 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.45 (dd, *J* = 8.2, 5.6 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.05 (t, *J* = 8.5 Hz, 2H), 7.00 (s, 1H), 6.55 (s, 1H), 3.20 (s, 2H), 3.10 (s, 3H), 2.41 (s,

3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.79, 165.62, 163.12, 144.63, 144.39, 136.87, 135.77, 135.23, 135.19, 130.77, 130.68, 130.01, 128.17, 115.70, 115.66, 115.49, 113.11, 41.72, 21.78, 20.86.

HRMS (ESI, m/z): Calcd. for $C_{20}H_{18}FNO_3S$: $[M+H]^+$, 372.1069. Found: *m/z* 372.1069.

(4-chlorophenyl)(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)methanone (3i):



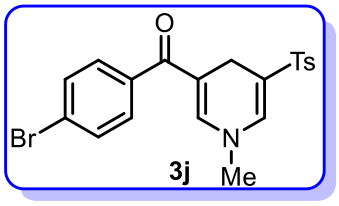
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (4:1)

The title compound was obtained as a yellow solid, Yield = 81% (157.17 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.41 – 7.34 (m, 4H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.01 (s, 1H), 6.54 (s, 1H), 3.21 (s, 2H), 3.11 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.89, 144.79, 144.45, 137.45, 137.15, 136.77, 135.76, 130.06, 129.88, 128.83, 128.25, 115.99, 113.19, 41.78, 21.83, 20.84.

HRMS (ESI, m/z): Calcd. for $C_{20}H_{18}ClNO_3S$: $[M+H]^+$, 388.0774. Found: *m/z* 388.0772.

(4-bromophenyl)(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)methanone (3j):



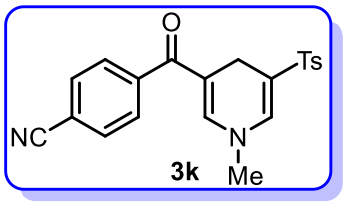
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (3:1)

The title compound was obtained as a yellow solid, Yield = 63% (136.09 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.53 (d, *J* = 8.3 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 4H), 7.01 (s, 1H), 6.54 (s, 1H), 3.21 (s, 2H), 3.11 (s, 3H), 2.43 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.97, 144.82, 144.46, 137.91, 136.73, 135.75, 131.80, 130.07, 130.06, 128.26, 125.54, 116.07, 113.20, 41.79, 21.84, 20.84.

HRMS (ESI, m/z): Calcd. for $C_{20}H_{18}NO_3BrS$: $[M+H]^+$, 432.0269. Found: *m/z* 432.0268.

4-(1-methyl-5-tosyl-1,4-dihydropyridine-3-carbonyl)benzonitrile (3k):



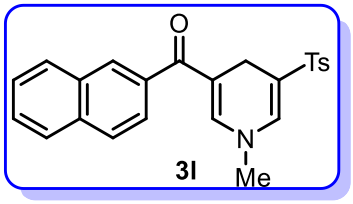
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (2:1)

The title compound was obtained as a yellow solid, Yield = 48% (90.99 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.02 (s, 1H), 6.49 (s, 1H), 3.22 (s, 2H), 3.12 (s, 3H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 192.21, 145.50, 144.65, 143.16, 136.46, 135.49, 132.48, 130.13, 128.93, 128.32, 118.30, 116.78, 114.43, 113.04, 41.92, 21.89, 20.71.

HRMS (ESI, m/z): Calcd. for $C_{21}H_{18}N_2O_3$: $[M+H]^+$, 379.1116. Found: *m/z* 379.1113.

(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)(naphthalen-2-yl)methanone (3l):



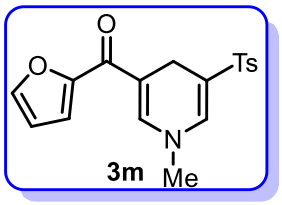
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (4:1)

The title compound was obtained as a yellow solid, Yield =81% (163.67 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.93 – 7.85 (m, 4H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.58 – 7.52 (m, 3H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.04 (s, 1H), 6.64 (s, 1H), 3.30 (s, 2H), 3.09 (s, 3H), 2.45 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** ^{13}C NMR (101 MHz,) δ 194.28, 144.90, 144.43, 136.88, 136.50, 135.87, 134.56, 132.55, 130.10, 128.98, 128.66, 128.61, 128.33, 128.04, 127.76, 127.03, 125.49, 115.90, 113.70, 41.76, 21.88, 20.99.

HRMS (ESI, m/z): Calcd. for $C_{24}H_{21}NO_3S$: $[M+H]^+$, 404.1320. Found: *m/z* 404.1317.

Furan-2-yl(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)methanone (3m):



This compound was prepared by the general procedure described above.

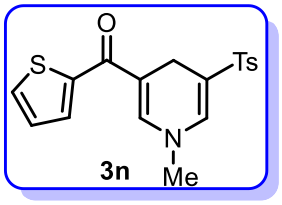
Flash chromatography: PE/EA (5:1)

The title compound was obtained as a yellow solid, Yield =54% (92.91 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.77 – 7.76 (m, 2H), 7.54 – 7.53 (m, 1H), 7.41 (dd, *J* = 3.7, 1.2 Hz, 1H), 7.34 – 7.32 (m, 2H), 7.08 – 7.05 (m, 1H), 7.02 (d, *J* = 0.8, 1H), 6.96 – 6.95 (m, 1H), 3.24 (s, 1H), 3.17 (s, 1H), 2.43 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 184.79, 144.41, 142.90,

137.01, 135.86, 131.47, 130.93, 130.07, 128.24, 127.51, 115.36, 113.34, 99.74, 41.79, 21.85, 21.27.

HRMS (ESI, m/z): Calcd. for $C_{18}H_{17}NO_4S$: $[M+H]^+$, 344.0956. Found: *m/z* 344.0955.

(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)(thiophen-2-yl)methanone (3n):



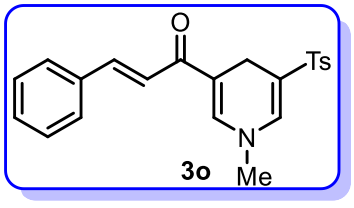
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (4:1)

The title compound was obtained as a yellow solid, Yield = 69% (124.22 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.51-7.50 (m, 1H), 7.46-7.45 (m, 1H), 7.33-7.30 (m, 2H), 7.08-7.06 (m, 1H), 7.02 (s, 1H), 3.22 (s, 3H), 3.21 (s, 2H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 178.66, 153.26, 145.05, 144.34, 143.10, 136.84, 135.86, 130.02, 128.20, 117.06, 115.52, 112.33, 112.02, 41.92, 21.82, 20.84.

HRMS (ESI, m/z): Calcd. for $C_{18}H_{17}NO_3S_2$: $[M+H]^+$, 360.0728. Found: *m/z* 360.0727.

(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)(naphthalen-2-yl)methanone (3o)



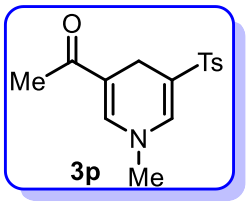
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (6:1)

The title compound was obtained as a yellow solid, Yield = 43% (81.73 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 7.4 Hz, 2H), 7.62 – 7.51 (m, 3H), 7.37 (s, 3H), 7.32 (d, *J* = 7.3 Hz, 2H), 7.02 (t, *J* = 16.2 Hz, 3H), 3.21 (s, 5H), 2.42 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 186.58, 144.32, 141.85, 140.58, 137.05, 135.85, 135.28, 130.19, 130.01, 129.03, 128.28, 128.15, 120.32, 115.40, 114.93, 41.78, 21.80, 20.85.

HRMS (ESI, m/z): Calcd. for $C_{22}H_{21}NO_3S$: $[M+H]^+$, 380.1320. Found: *m/z* 380.1320.

1-(1-methyl-5-tosyl-1,4-dihydropyridin-3-yl)ethan-1-one (3p):



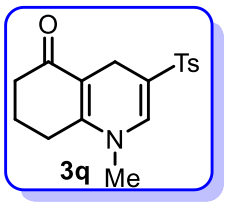
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a yellow solid, Yield = 52% (75.95 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 6.98 (s, 1H), 6.79 (s, 1H), 3.16 (s, 3H), 3.02 (s, 2H), 2.40 (s, 3H), 2.15 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.91, 144.29, 140.93, 137.08, 135.88, 130.00, 128.17, 115.20, 114.13, 41.66, 24.79, 21.82, 20.44.

HRMS (ESI, m/z): Calcd. for $C_{15}H_{17}NO_3S$: $[M+H]^+$, 292.1007. Found: *m/z* 292.1003.

1-methyl-3-tosyl-4,6,7,8-tetrahydroquinolin-5(1H)-one (3q):



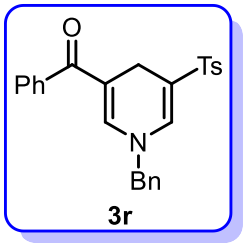
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a yellow solid, Yield =40% (63.62 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.01 (s, 1H), 3.18 (s, 3H), 3.05 (s, 2H), 2.43 (t, *J* = 6.1 Hz, 2H), 2.41 (s, 3H), 2.35 – 2.28 (m, 2H), 1.99 – 1.91 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 196.11, 153.26, 144.19, 138.65, 135.99, 129.95, 128.17, 114.92, 109.82, 38.94, 36.02, 25.77, 21.82, 21.08, 20.17.

HRMS (ESI, m/z): Calcd. for $C_{17}H_{19}NO_3S$: $[M+H]^+$, 318.1164. Found: *m/z* 318.1161.

(1-benzyl-5-tosyl-1,4-dihydropyridin-3-yl)(phenyl)methanone (3r):



3r

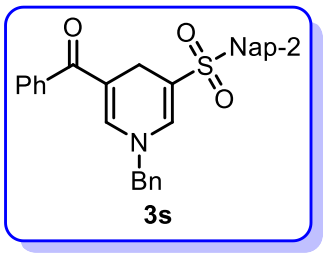
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (6:1)

The title compound was obtained as a yellow solid, Yield = 73% (157.00 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.43 – 7.29 (m, 10H), 7.20 – 7.15 (m, 2H), 7.13 (s, 1H), 6.67 (s, 1H), 4.42 (s, 2H), 3.27 (s, 2H), 2.44 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.26, 144.42, 144.07, 138.92, 136.33, 135.77, 135.41, 131.11, 130.07, 129.51, 128.86, 128.59, 128.49, 128.32, 127.44, 127.43, 127.41, 116.13, 113.56, 58.28, 21.86, 21.22.

HRMS (ESI, m/z): Calcd. for $C_{26}H_{23}NO_3S$: $[M+H]^+$, 430.1477. Found: *m/z* 430.1476.

(1-benzyl-5-(naphthalen-2-ylsulfonyl)-1,4-dihydropyridin-3-yl)(phenyl)methanone (3s):



3s

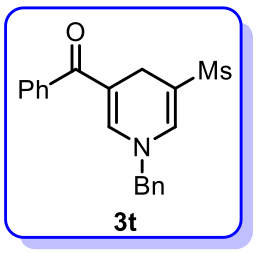
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a yellow solid, Yield = 78% (181.80 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 (d, *J* = 1.6, 1H), 8.01 – 7.96 (m, 2H), 7.91 (d, *J* = 8.0, 1H), 7.81-7.79 (m, 1H), 7.67-7.60 (m, 2H), 7.42-7.28 (m, 8H), 7.23 (s, 1H), 7.19-7.17 (m, 2H), 6.67 (d, *J* = 1.2, 1H), 4.44 (s, 2H), 3.32 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.16, 143.97, 138.83, 136.99, 135.60, 135.39, 135.30, 132.36, 131.06, 130.10, 129.74, 129.65, 129.46, 128.81, 128.51, 128.43, 128.07, 127.77, 127.40, 122.84, 115.67, 113.60, 58.25, 21.23.

HRMS (ESI, m/z): Calcd. for $C_{29}H_{23}NO_3S$: $[M+H]^+$,466.1477. Found: *m/z* 466.1474.

(1-benzyl-5-(methylsulfonyl)-1,4-dihydropyridin-3-yl)(phenyl)methanone (3t):



3t

This compound was prepared by the general procedure described above.

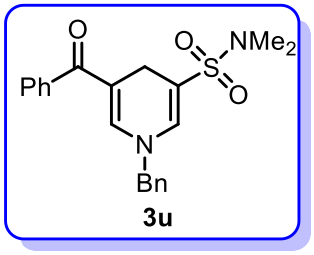
Flash chromatography: PE/EA (5:1)

The title compound was obtained as a yellow solid, Yield = 70% (123.94 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 – 7.43 (m, 3H), 7.40 – 7.35 (m, 5H), 7.19-7.17 (m, 2H), 6.98 (d, *J* = 1.2 Hz, 1H), 6.75 (t, *J* = 0.8 Hz, 1H), 4.42 (s, 2H), 3.55 (s, 2H), 2.93 (s, 2H). **^{13}C NMR (101**

MHz, $CDCl_3$) δ 194.23, 144.21, 138.83, 137.38, 135.27, 131.29, 129.56, 128.96, 128.66, 128.59, 127.52, 115.02, 113.55, 58.34, 40.11, 21.75.

HRMS (ESI, m/z): Calcd. for $C_{20}H_{19}NO_3S$: $[M+H]^+$, 354.1164. Found: *m/z* 354.1163.

5-benzoyl-1-benzyl-*N*,*N*-dimethyl-1,4-dihydropyridine-3-sulfonamide (3u):



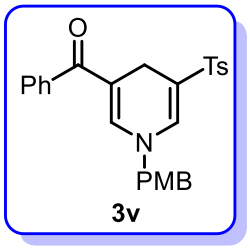
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (3:1)

The title compound was obtained as a yellow solid, Yield = 56% (107.28 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 – 7.43 (m, 3H), 7.39 – 7.34 (m, 5H), 7.19-7.16 (m, 2H), 6.85 (s, 1H), 6.75 (s, 1H), 4.40 (s, 2H), 3.42 (s, 2H), 2.86 (s, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.29, 144.62, 139.03, 136.86, 135.52, 131.10, 129.47, 128.80, 128.62, 128.52, 127.34, 113.28, 113.10, 58.20, 37.63, 21.96.

HRMS (ESI, m/z): Calcd. for $C_{21}H_{22}N_2O_3S$: $[M+H]^+$, 383.1429. Found: *m/z* 383.1427.

(1-(4-methoxybenzyl)-5-tosyl-1,4-dihydropyridin-3-yl)(phenyl)methanone (3v)：



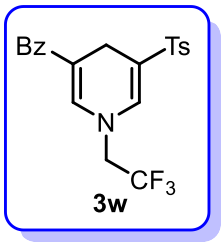
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (4:1)

The title compound was obtained as a yellow solid, Yield = 66% (151.52mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.46-7.41 (m, 1H), 7.38-7.31 (m, 6H), 7.13 -7.07 (m, 3H), 6.93-6.88 (m, 2H), 6.66 (d, *J* = 1.1 Hz, 1H), 4.35 (s, 2H), 3.83 (s, 3H), 3.26 (s, 2H), 2.44 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 194.22, 160.11, 144.38, 143.99, 139.04, 136.23, 135.90, 131.06, 130.07, 129.05, 128.61, 128.48, 128.33, 127.24, 116.07, 114.89, 113.48, 57.91, 55.64, 21.85, 21.31.

HRMS (ESI, m/z): Calcd. for $C_{27}H_{25}NO_4S$: $[M+H]^+$, 460.1577. Found: *m/z* 460.1557.

Phenyl(5-tosyl-1-(2,2,2-trifluoroethyl)-1,4-dihydropyridin-3-yl)methanone (3w):



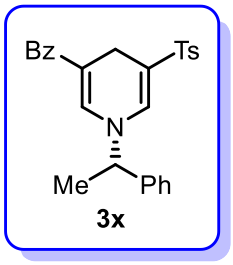
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (4:1)

The title compound was obtained as a yellow solid, Yield = 67% (141.40 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.49 – 7.46 (m, 3H), 7.43 – 7.39 (m, 3H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.08 (s, 1H), 6.61 (s, 1H), 3.77 (q, *J* = 8.4 Hz, 2H), 3.24 (s, 2H), 2.45 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.26, 144.78, 142.80, 138.48, 135.65, 135.39, 131.54, 130.20, 128.70, 128.63, 128.39, 117.73, 115.05, 21.88, 20.80.

HRMS (ESI, m/z): Calcd. for $C_{21}H_{18}F_3NO_3S$: $[M+H]^+$, 422.1038/. Found: *m/z* 422.1034.

(S)-phenyl(1-(1-phenylethyl)-5-tosyl-1,4-dihydropyridin-3-yl)methanone (3x):



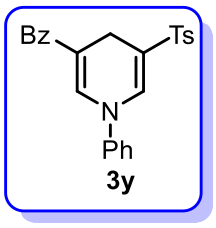
This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (5:1)

The title compound was obtained as a yellow solid, Yield = 80% (177.67 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.37 (m, 4H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.29 (m, 4H), 7.22 – 7.19 (m, 3H), 6.69 (s, 1H), 4.62 – 4.57 (q, *J* = 6.8 Hz, 1H), 3.27 (s, 2H), 2.43 (s, 3H), 1.61 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 194.23, 144.35, 142.65, 139.46, 138.92, 135.86, 134.95, 131.06, 130.06, 129.42, 128.76, 128.59, 128.44, 128.32, 126.69, 126.68, 115.89, 113.38, 62.45, 21.86, 21.66, 19.83.

HRMS (ESI, m/z): Calcd. for $C_{27}H_{25}NO_3S$: $[M+H]^+$, 444.1633. Found: *m/z* 444.1633.

Phenyl(1-phenyl-5-tosyl-1,4-dihydropyridin-3-yl)methanone (3y):



This compound was prepared by the general procedure described above.

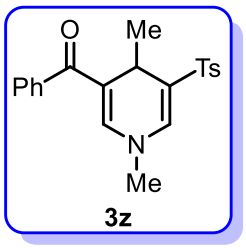
Flash chromatography: PE/EA (3:1)

The title compound was obtained as a yellow solid, Yield = 71% (147.73 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.51 (dd, *J* = 6.7, 1.5 Hz, 3H), 7.48 – 7.45 (m, 1H), 7.42 – 7.35 (m, 6H), 7.29 – 7.24 (m, 1H), 7.13 – 7.08 (m, 3H), 3.37 (s, 2H), 2.45 (s, 3H). **^{13}C**

NMR (101 MHz, $CDCl_3$) δ 194.62, 144.61, 142.74, 142.09, 138.77, 135.55, 134.78, 131.32, 130.25, 130.12, 128.65, 128.54, 128.37, 127.06, 120.94, 118.01, 115.10, 21.85, 21.38.

HRMS (ESI, m/z): Calcd. for $C_{25}H_{21}NO_3S$: $[M+H]^+$,416.1320. Found: *m/z*416.1319.

(1,4-dimethyl-5-tosyl-1,4-dihydropyridin-3-yl)(phenyl)methanone (3z):



This compound was prepared by the general procedure described above.

Flash chromatography: PE/EA (6:1)

The title compound was obtained as a yellow solid, Yield = 21% (38.65 mg). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 3H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.16 (s, 1H), 6.60 (s, 1H), 3.85 (q, *J* = 6.4 Hz, 1H), 3.18 (s, 3H), 2.42 (s, 3H), 1.08 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 194.13, 144.19, 143.39, 139.56, 137.98, 137.80, 130.99, 130.05, 128.45, 128.43, 128.03, 119.88, 118.82, 41.96, 26.19, 23.38, 21.83.

HRMS (ESI, m/z): Calcd. for $C_{21}H_{21}NO_3S$: $[M+H]^+$, 368.1320. Found: *m/z* 368.1317.

4. <u>X-Ray Diffraction Analysis of 3a</u>

Empirical formula	$C_{20}H_{19}NO_3S$	
Formula weight	353.42	

Temperature	298(2)	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a= 27.711(2)Å	Alpha=90.00°
	b=9.4240(9)Å	Beta=123.253(3)°
	c=16.1661(14)Å	Gamma=90.00°
Volume	3530.4(5)	
Z	8	
Density (calculated)	1.330 mg/m^3	
Absorption coefficient	0.202 mm^{-1}	
F(000)	1488	
Crystal size	0.43 x 0.28 x 0.21 mm^3	
Theta range for data collection	2.33 to 25.02°	
Index ranges	-26<=h<=32,-11<=k<=9, -19<=l<=13	
Absorption correction	multi-scan	
Max. and min. transmission	0.9588 and 0.9182	
Data / restraints / parameters	3118 /0 / 228	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1=0.0417	wR2=0.0923
R indices (all data)	R1=0.0788	wR2=0.1092

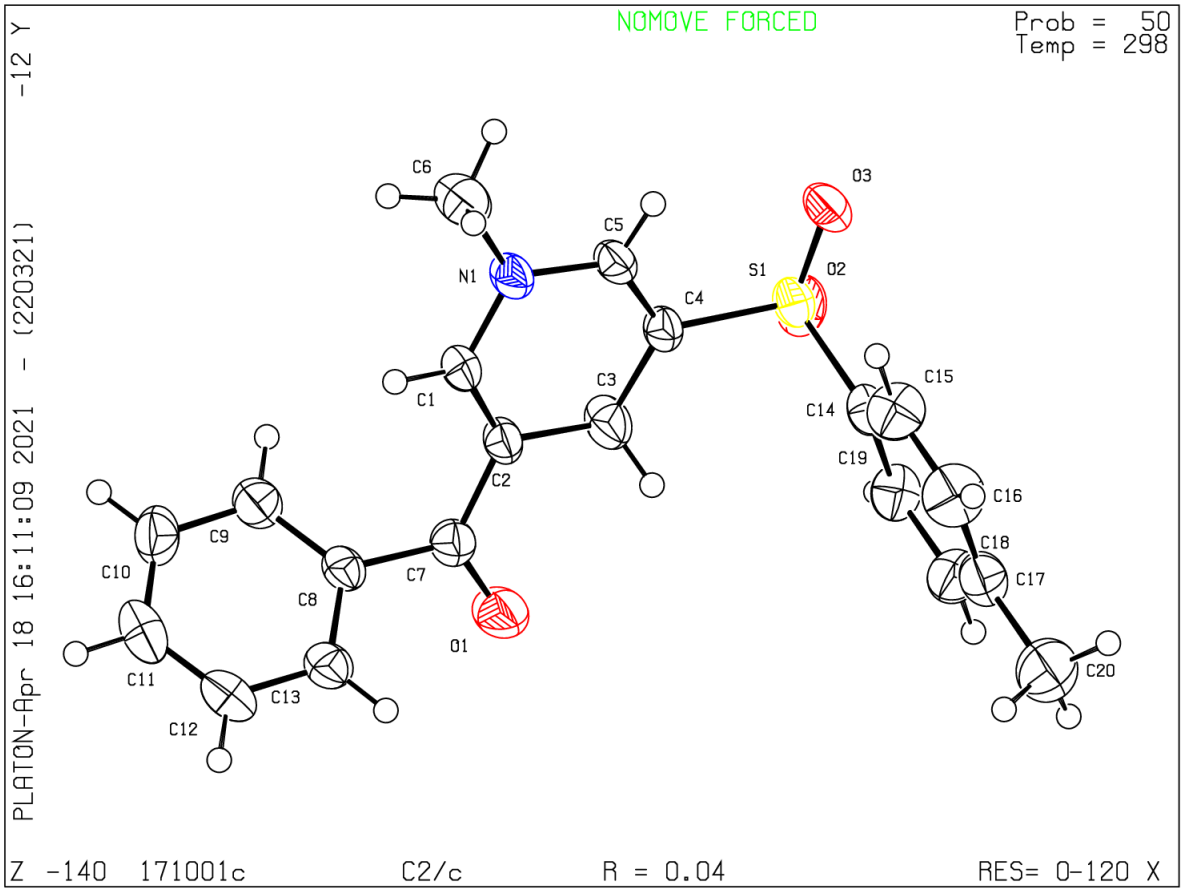
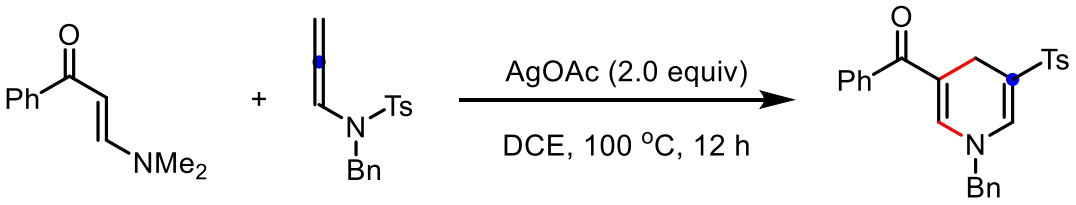


Figure S1. ORTEP drawing of **3a** showing 30% probability thermal ellipsoids.

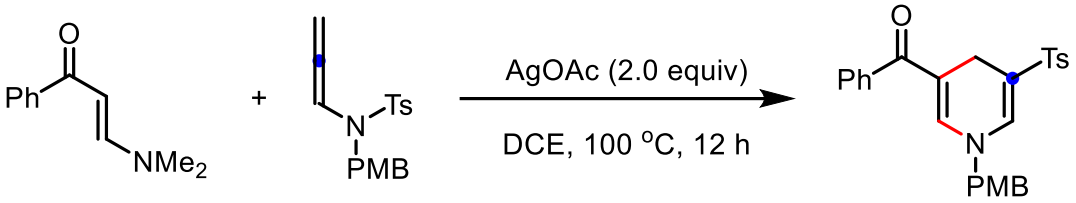
5. <u>Practical Utilities</u>

5.1 3.0 mmol scale reaction for 3r and 3v



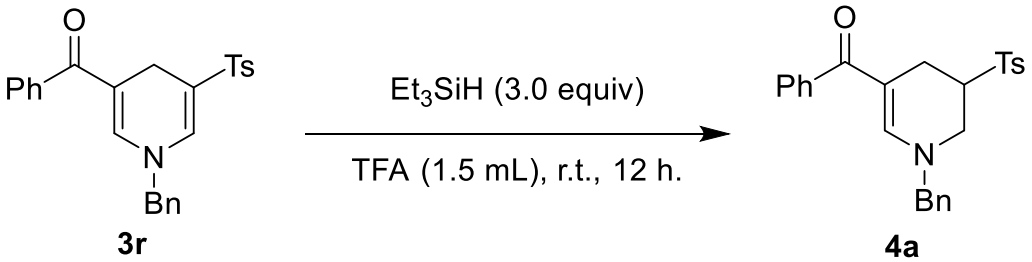
To a 25 mL Schlenk flask equipped with magnetic stir bar was added (*E*)-3-(dimethylamino)-1- phenylprop-2-en-1-one **1a** (3.0 mmol, 0.53 g), *N*-benzyl-4-methyl-*N*-(propa-1,2-dien-1-yl) benzenesulfonamide **3r** (4.5 mmol, 1.34 g, 1.5 equiv), AgOAc (6.0 mmol, 1.0 g, 2.0 equiv). After the DCE (10 mL) was injected into the test tube *via* syringe.

The reaction mixture was allowed to stir at 100 °C for 24 h, during which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc as the eluent to afford the yellow solid **3r**.



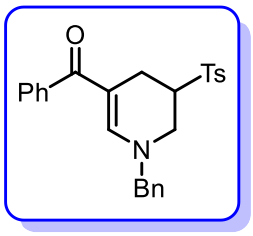
To a 25 mL Schlenk flask equipped with magnetic stir bar was added (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (3.0 mmol, 0.53 g), *N*-(4-methoxy-benzyl)-4-methyl-*N*-(propa-1,2-dien-1-yl) benzenesulfonamide **3v** (4.5 mmol, 1.48 g, 1.5 equiv), AgOAc (6.0 mmol, 1.0 g, 2.0 equiv). After the DCE (10 mL) was injected into the test tube via syringe. The reaction mixture was allowed to stir at 100 °C for 24 h, during which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc as the eluent to afford the yellow solid **3v**.

5.2 Diversification of 3r and 3v [4-7]

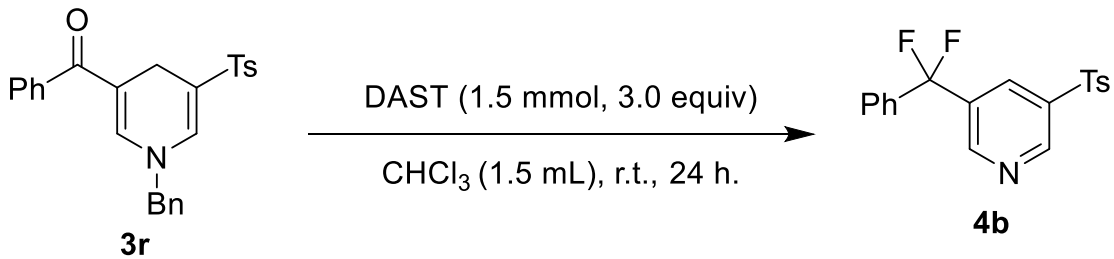


Typical procedure for the transformation of **3r** to **4a**: To a 10 mL Schlenk flask equipped with magnetic stir bar was added **3r** (0.5 mmol, 214.5 mg), Et_3SiH (3.0 equiv). After the TFA (1.5 mL) was injected into the test tube via syringe. The reaction mixture was allowed to stir at r.t. for 12 h, during which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc as the eluent to afford the yellow solid **4a**.

(1-benzyl-5-tosyl-1,4,5,6-tetrahydropyridin-3-yl)(phenyl)methanone (4a):



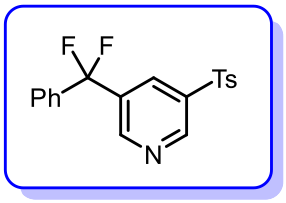
The title compound was obtained as a yellow solid in 82% yield. Flash chromatography: PE/EA (6:1). **H NMR (500 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.28 (m, 10H), 7.14 – 7.06 (m, 3H), 4.25 (q, *J* = 15.0 Hz, 2H), 3.58 – 3.46 (m, 1H), 3.42 – 3.28 (m, 2H), 2.93 – 2.83 (m, 1H), 2.58 – 2.47 (m, 1H), 2.41 (s, 3H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 192.76, 151.08, 145.38, 140.23, 135.09, 133.95, 130.05, 129.86, 129.11, 128.91, 128.45, 128.22, 128.10, 127.59, 105.54, 60.16, 57.54, 44.14, 21.68, 20.79.



Typical procedure for the transformation of **3r** to **4b**: To a 10 mL Schlenk flask equipped with magnetic stir bar was added **3r** (0.5 mmol, 214.5 mg), DAST (1.5 mmol, 3.0 equiv) via a syringe in $CHCl_3$ (1.5 mL) . The reaction mixture was allowed to stir at r.t. for 24 h, during

which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc as the eluent to afford the yellow solid **4b**.

3-(difluoro(phenyl)methyl)-5-tosylpyridine (4b):

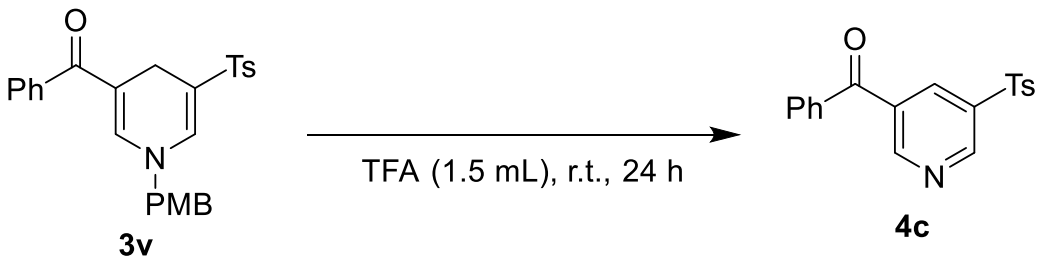


The title compound was obtained as a yellow solid in 56% yield. Flash chromatography: PE/EA (15:1). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.14 (d, *J* = 2.0 Hz, 1H), 8.88 -8.79 (m, 1H), 8.35 (t, *J* = 2.1 Hz, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.50-7.41 (m, 5H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.20 (t, *J* = 5.4 Hz), 149.96, 145.63, 138.94, 137.43, 135.89, 135.67 , 135.45, 134.75 134.51, 134.26, 132.59 (t, *J* = 5.2 Hz), 131.03 , 130.60, 129.15, 128.18, 125.74 (t, *J* = 5.6 Hz), 121.22, 119.28, 117.34, 21.86 .

^{19}F NMR (471 MHz, $CDCl_3$) δ -89.60.

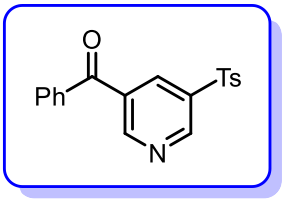
HRMS (ESI, m/z): Calcd. for $C_{19}H_{15}F_2NO_2S$: $[M+H]^+$, 360.0864. Found: *m/z* 360.0853.



Typical procedure for the transformation of **3v** to **4c**: To a 10 mL Schlenk flask equipped with magnetic stir bar was added **3v** (0.5 mmol, 229.6 mg), TFA (1.5 mL)，the reaction mixture was allowed to stir at r.t. for 24 h, during which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction

mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica gel with PE/EtOAc as the eluent to afford the yellow solid **4c**.

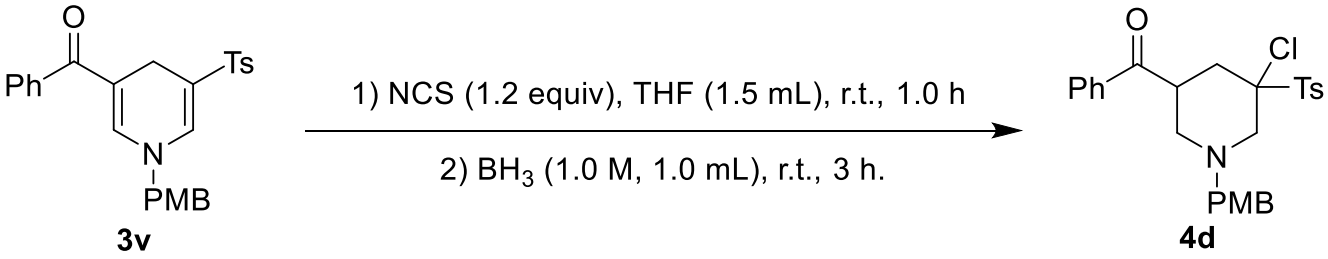
Phenyl(5-tosylpyridin-3-yl)methanone(4c):



The title compound was obtained as a yellow solid in 79% yield. Flash chromatography: PE/EA (10:1). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 9.27 (d, *J* = 1.9 Hz, 1H), 9.08 (s, 1H), 8.55 (t, *J* = 2.1 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.79-7.72 (m, 2H), 7.69-7.58 (m, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 193.07, 154.07, 151.10, 145.64, 139.05, 137.40, 136.20, 135.96, 134.05, 133.56, 130.59, 130.19, 129.11, 128.19, 21.84.

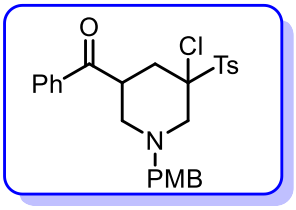
HRMS (ESI, m/z): Calcd. for $C_{19}H_{15}NO_3S$: $[M+H]^+$, 338.0845. Found: *m/z* 338.0835.



Typical procedure for the transformation of **3v** to **4d**: To a 10 mL Schlenk flask equipped with magnetic stir bar was added **3v** (0.5 mmol, 229.6 mg), NCS (0.6 mmol, 1.2 equiv) in THF (1.5 mL) in air at r.t. for 1.0 h, then BH_3 (1.0 M, 1.0 mL) in air at r.t. for 3 h, during which time a constant checking by TLC was performed. Once the reaction proceeded to a desired degree, the resulting reaction mixture was mixed with a small amount of silica gel and concentrated. The crude product was purified by flash column chromatography on silica

gel with PE/EtOAc as the eluent to afford the yellow solid **4d**.

(5-chloro-1-(4-methoxybenzyl)-5-tosylpiperidin-3-yl)(phenyl)methanone(4d)：

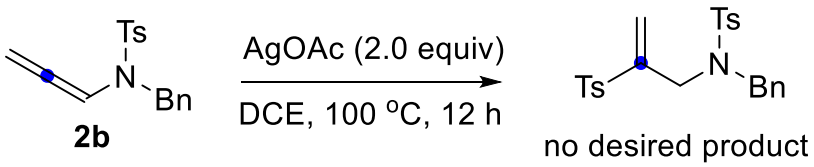


The title compound was obtained as a yellow solid in 67% yield. Flash chromatography: PE/EA (10:1). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.59 (dd, *J* = 10.7, 4.1 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.94-6.87 (m, 2H), 4.63 (ddd, *J* = 11.7, 7.9, 4.1 Hz, 1H), 3.84 (s, 3H), 3.62 (d, *J* = 13.0 Hz, 1H), 3.42 (dd, *J* = 18.3, 13.2 Hz, 2H), 3.22 (d, *J* = 9.1 Hz, 1H), 3.00 (dd, *J* = 14.7, 1.8 Hz, 1H), 2.50 (d, *J* = 13.1 Hz, 1H), 2.43 (d, *J* = 12.7 Hz, 3H), 2.29 (dt, *J* = 22.7, 12.8 Hz, 2H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 199.97, 159.33, 145.66, 135.65, 133.82, 131.46, 131.22, 130.71, 129.50, 129.11, 128.77, 114.03, 81.94, 61.85, 60.78, 55.51, 55.19, 42.56, 36.63, 21.92.

HRMS (ESI, m/z): Calcd. for $C_{27}H_{28}NO_4ClS$: $[M+H]^+$, 498.1500. Found: *m/z* 498.1486.

6. <u>Control Experiment</u>



To a 10 mL schlenk flask equipped with magnetic stir bar was added *N*-benzyl-4-methyl-*N*-(propa-1,2-dien-1-yl) benzenesulfonamide **3r** (0.5 mmol, 0.15 g), AgOAc (1.0 mmol, 0.17 g, 2.0 equiv). After the DCE (1.0 mL) was injected into the test tube *via* syringe. The

reaction mixture was allowed to stir at 100 ºC for 12 h, during which time a constant checking by TLC was performed.

7. References

[1] S. Zhou, J. Wang, L. Wang, C. Song, K. Chen, J. Zhu, *Angew. Chem. Int. Ed. 2***016**, *55*, 9384-9388.

[2] A. Ballesteros, P. Morán-Poladuraa, J. M. González, *Chem. Commun*. **2016**, *52*, 2905-2908.

[3] Y. Wang, P. Zhang, X. Di, Q. Dai, Z.-M. Zhang, J. Zhang, *Angew. Chem. Int. Ed*. **2017**, *56*, 15905-15909.

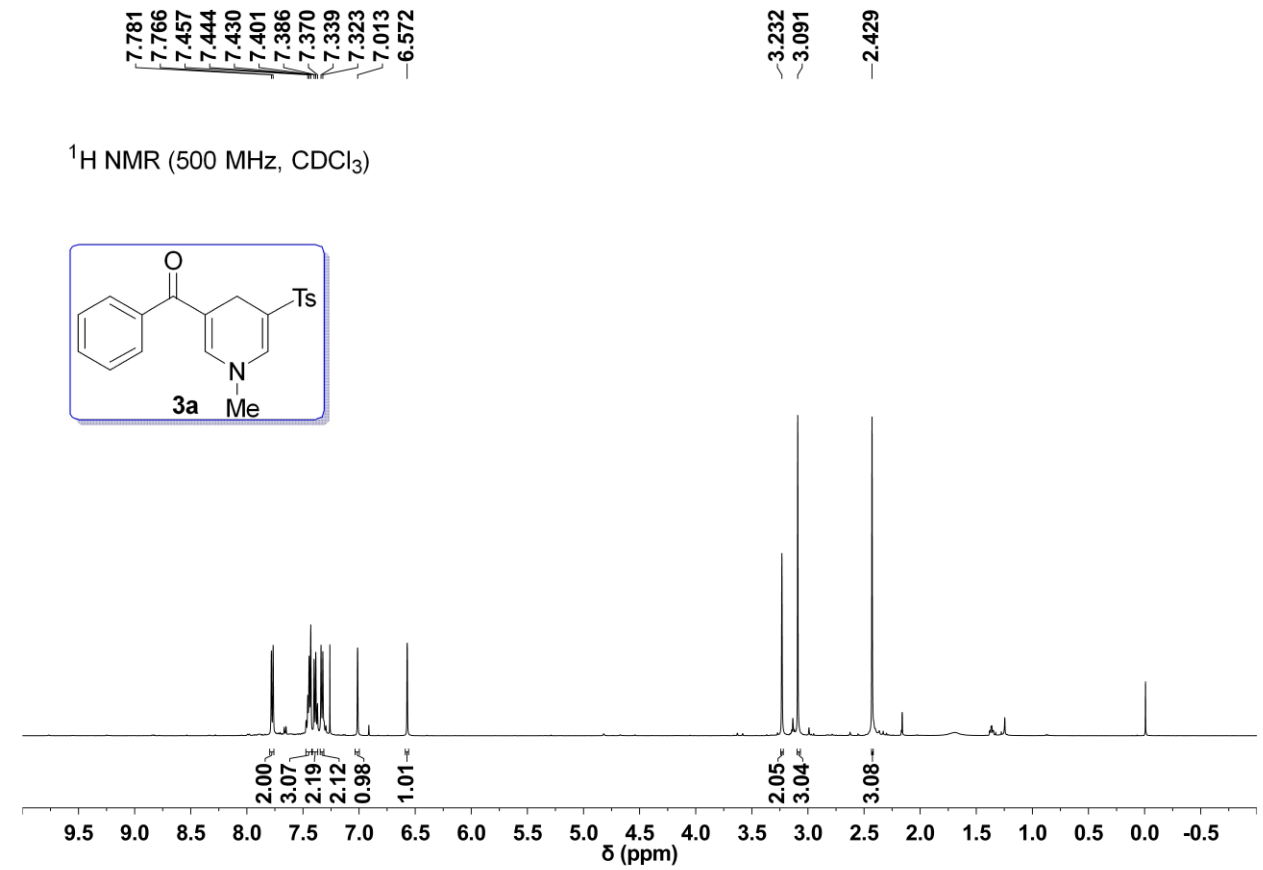
[4] G. S. Lal, G. P. Pez, R. J. Pesaresi, F. M. Prozonic, H. Cheng, *J. Org. Chem*. **1999**, *64*, 7048-7054.

[5] D. Behera, S. Thiyagarajan, P. K. Anjalikrishna, C. H. Suresh, C. Gunanathan, *ACS Catal*. **2021**, *11*, 5885-5893.

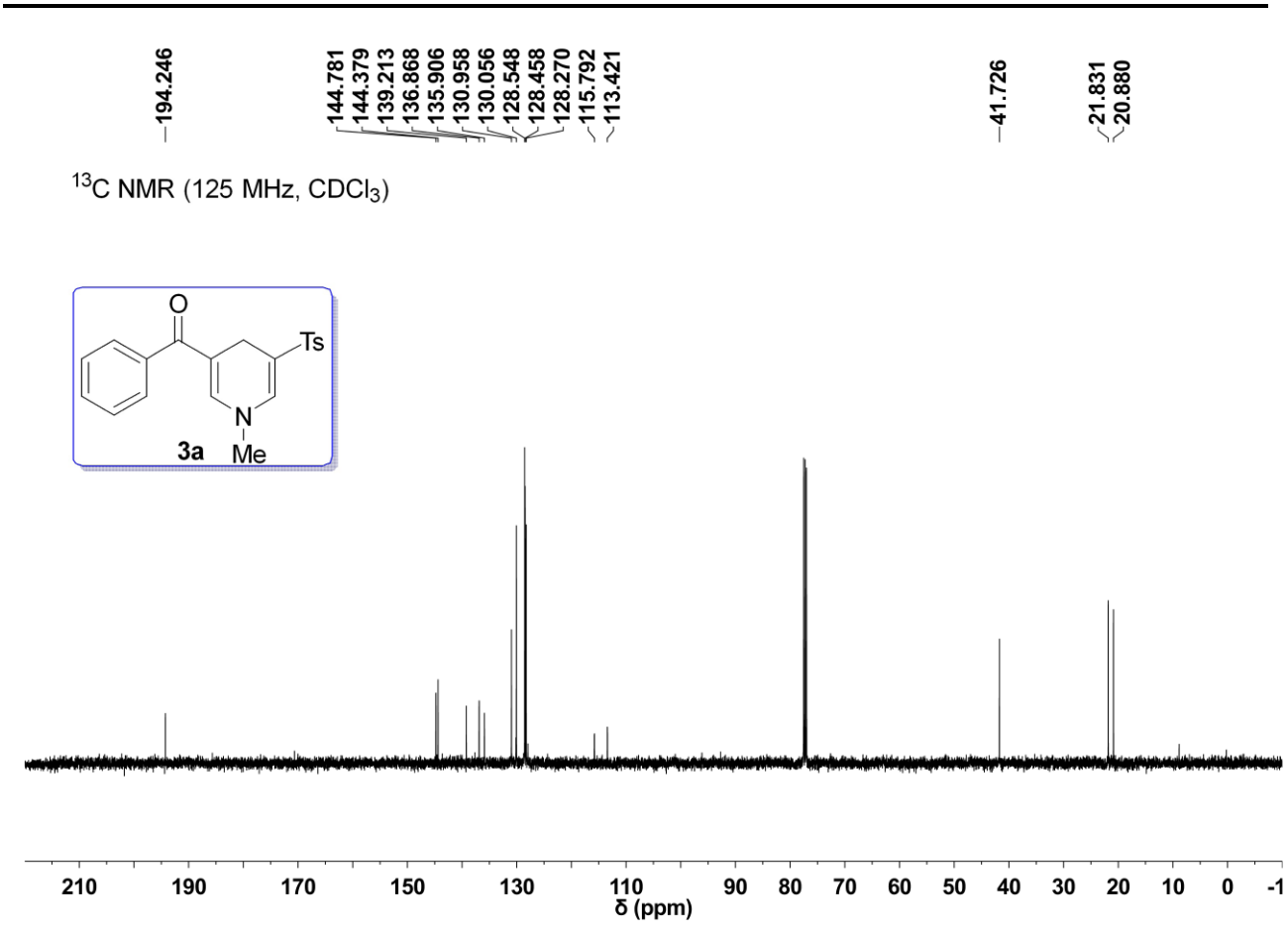
[6] M. M. Hinman, T. A. Rosenberg, D. Balli, C. Black-Schaefer, L. E. Chovan, D. Kalvin, P. J. Merta, A. M. Nilius, S. D. Pratt, N. B. Soni, F. L. Wagenaar, M. Weitzberg, R. Wagner, B. A. Beutel. *J. Med. Chem.* **2006**, *49*, 4842-4856.

[7] R. J. Griffiths, W. C. Kong, S. A. Richards, G. A. Burley, M. C. Willis, E. P. A. Talbot, *Chem. Sci*. **2018**, *9*, 2295-2300.

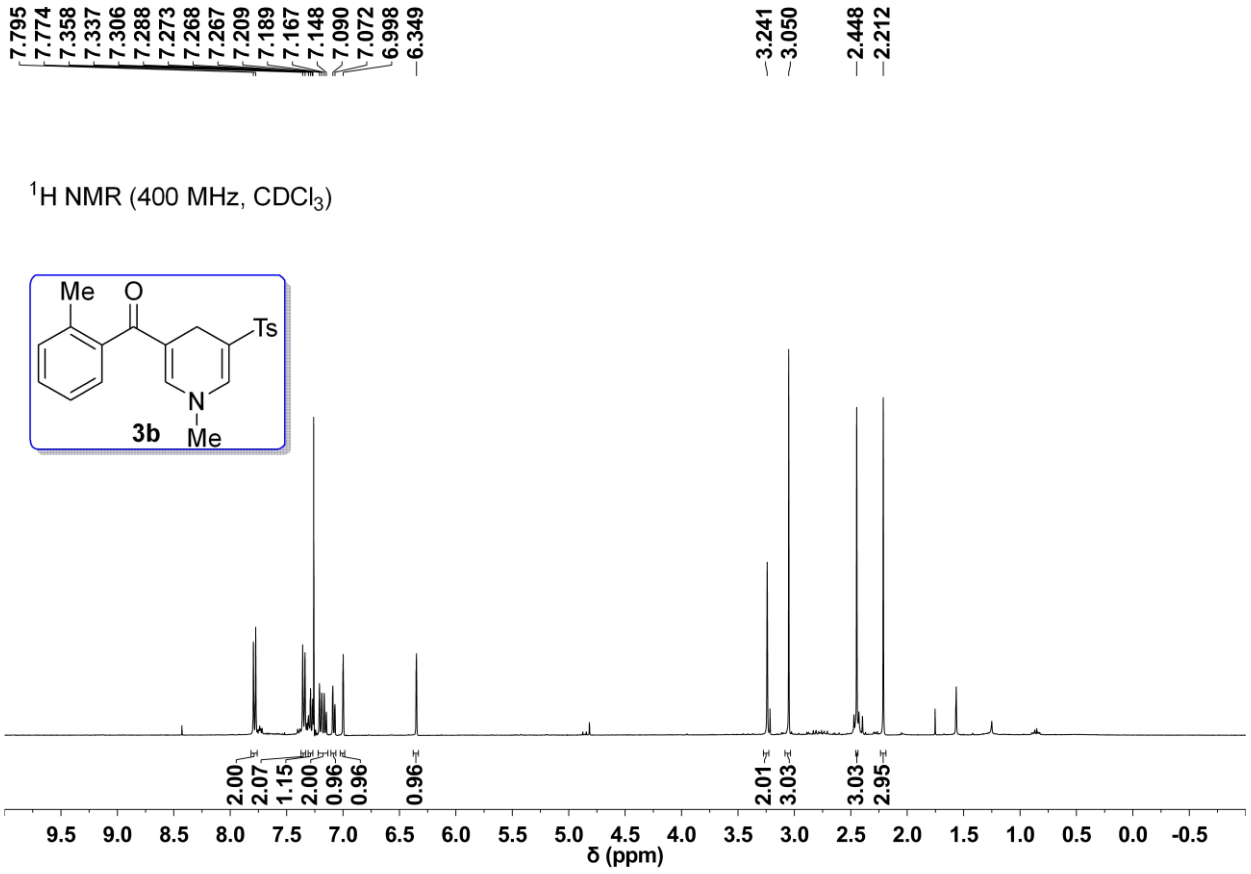
8. ^{1}H and ^{13}C NMR spectra

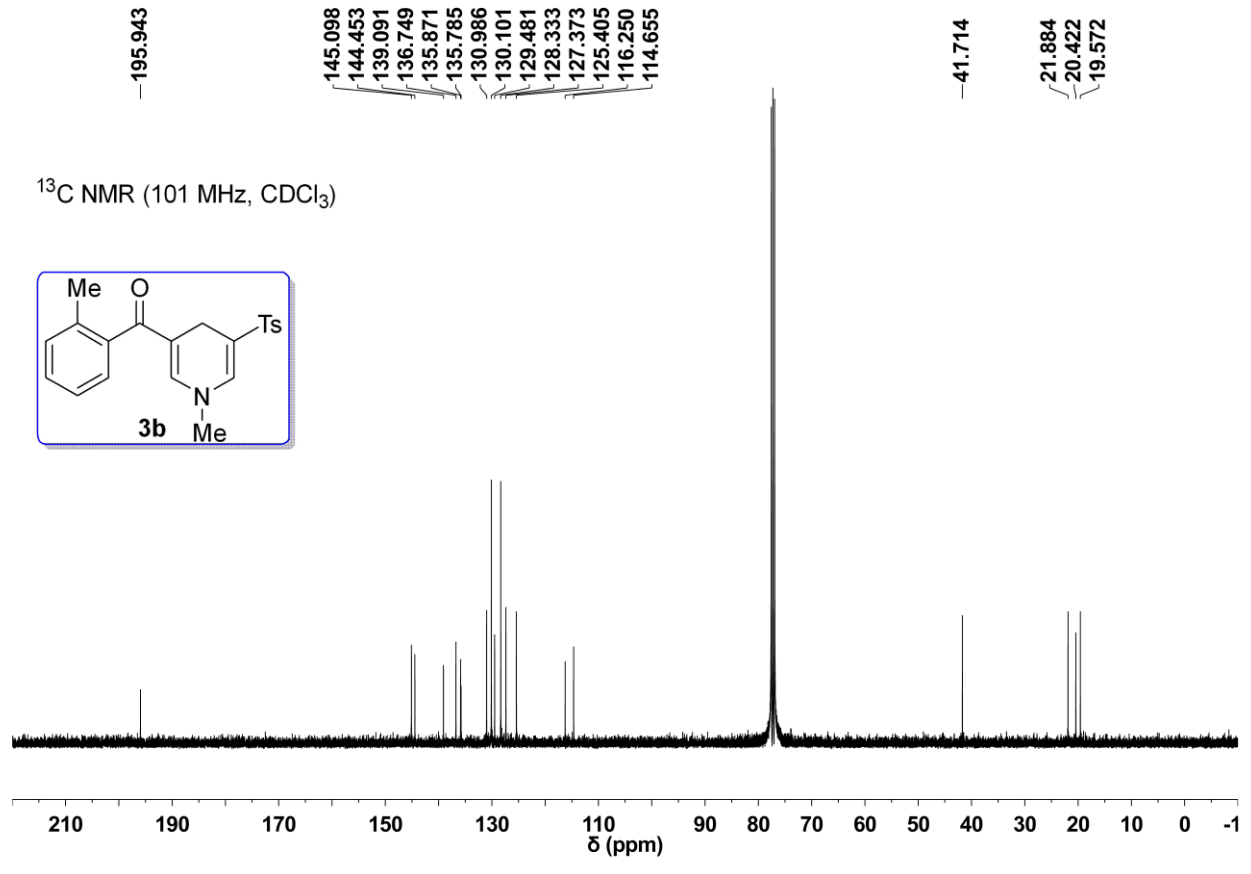


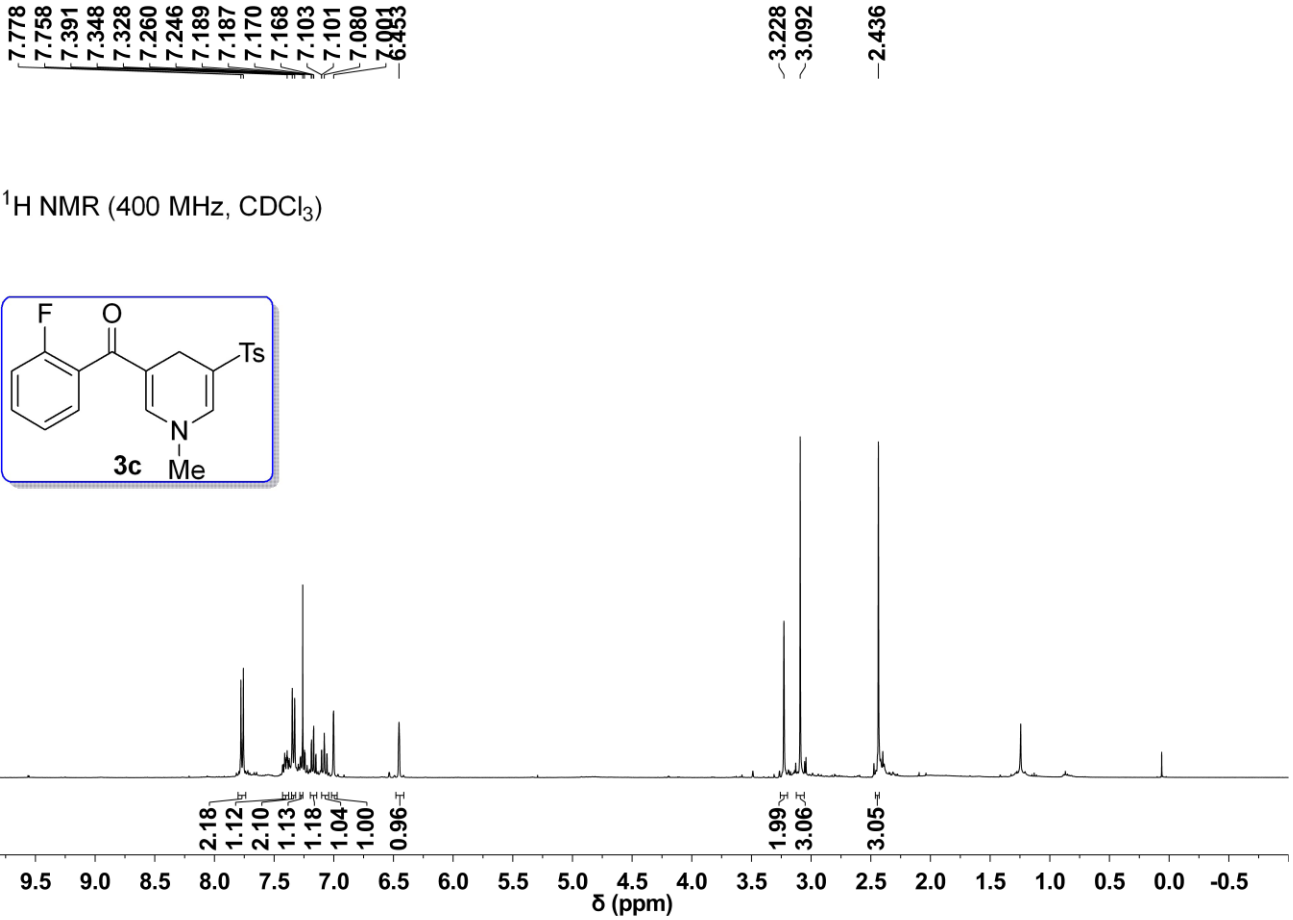
^{1}H NMR (500 MHz, $CDCl_3$)

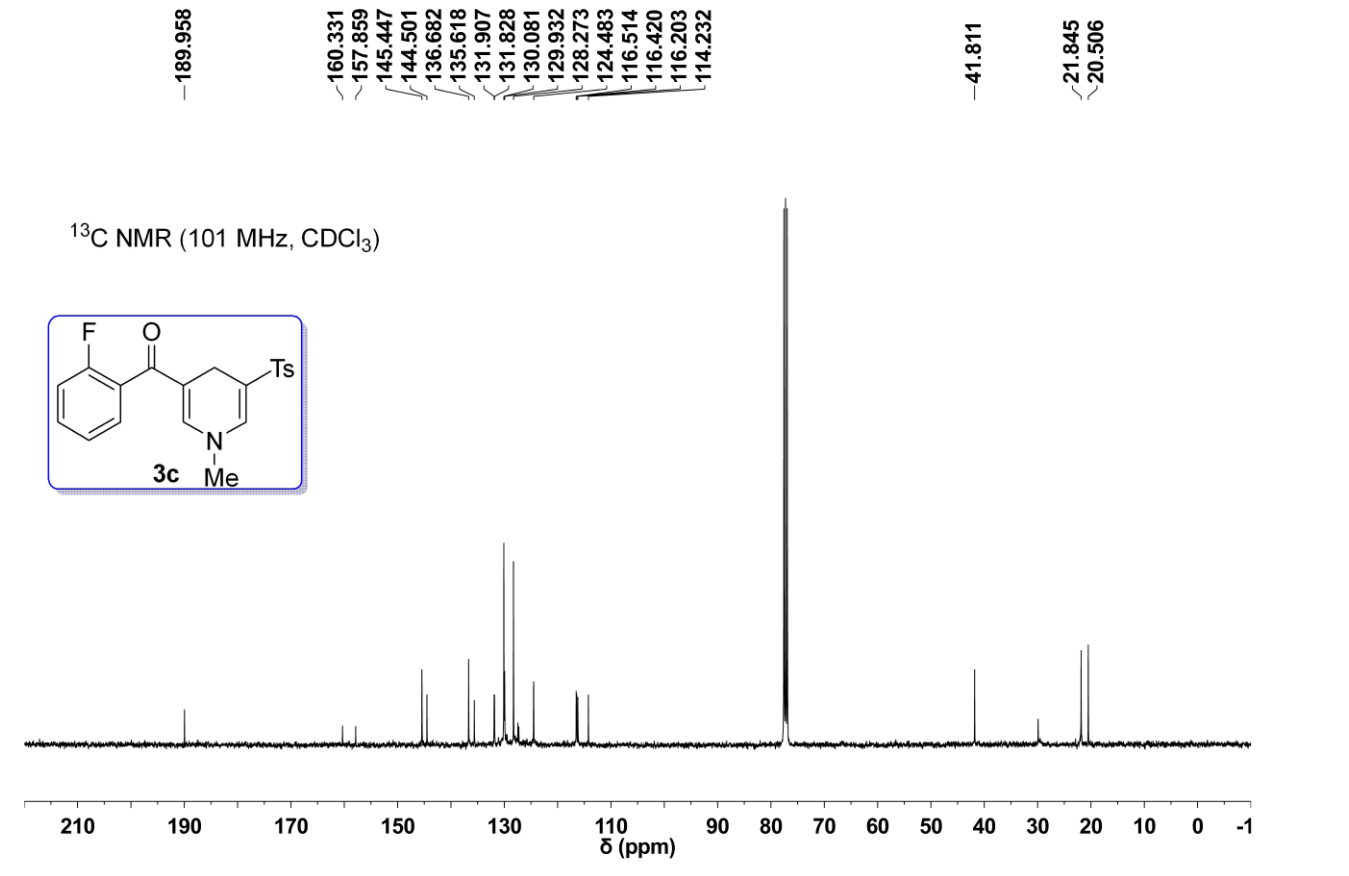


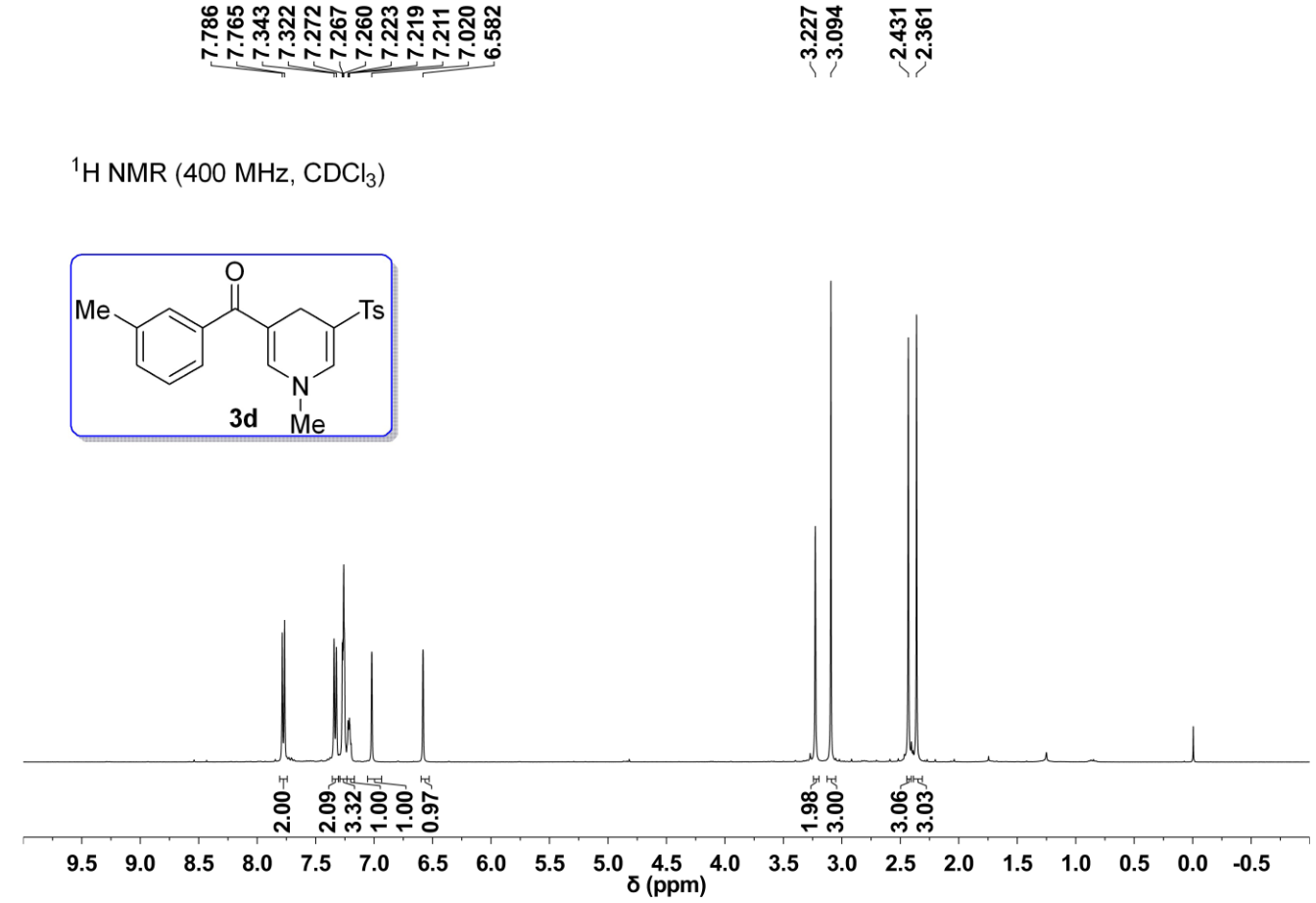
^{13}C NMR (125 MHz, $CDCl_3$)

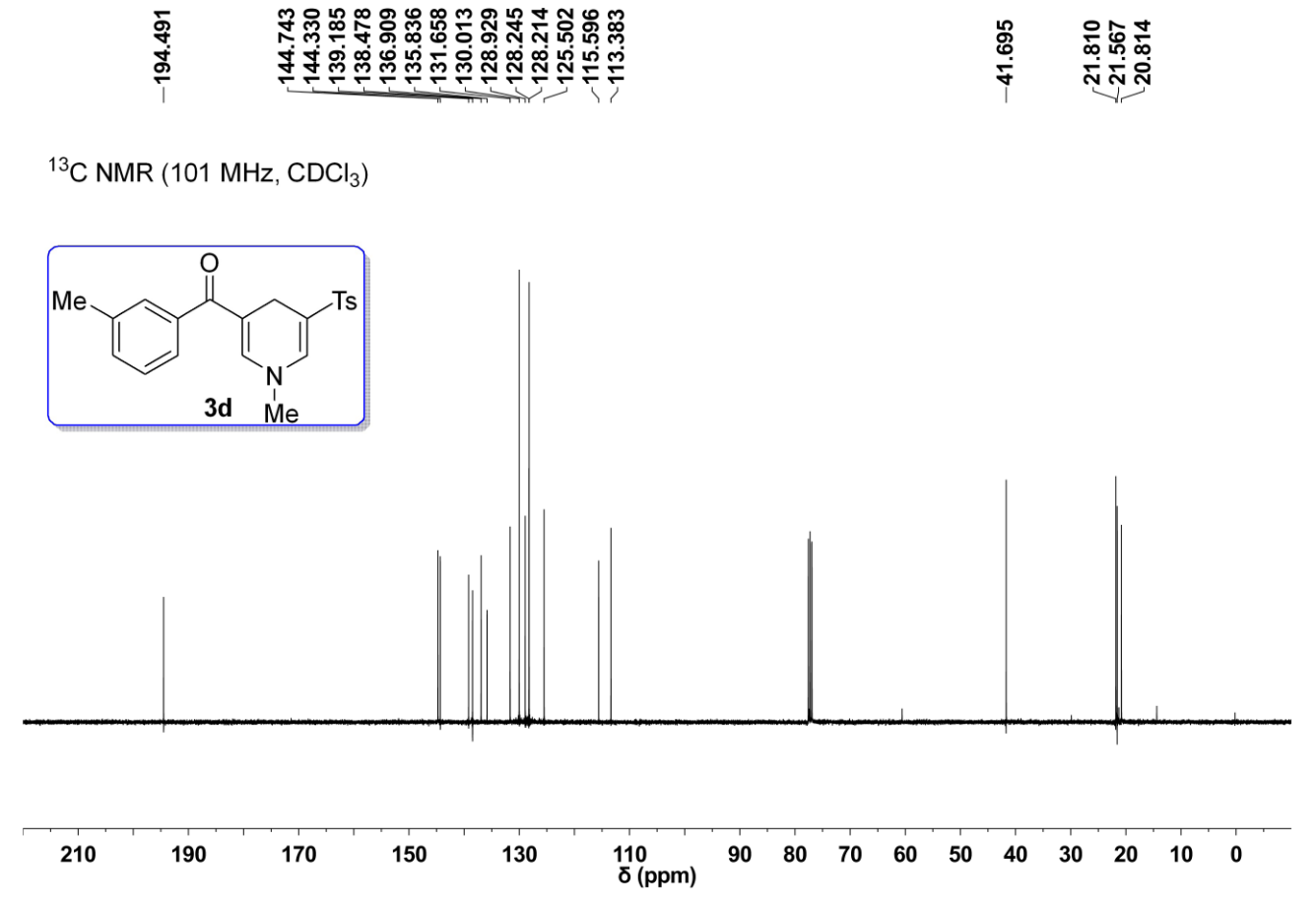

7.795
7.774
7.358
7.337
7.306
7.288
7.273
7.268
7.267
7.209
7.189
7.167
7.148
7.090
7.072
6.998
6.349
3.241
3.050
2.448
2.212
1H NMR (400 MHz, CDCl3)
Me
O
Ts
N
Me
3b
2.00
2.07
1.15
2.00
0.96
0.96
0.96
2.01
3.03
3.03
2.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

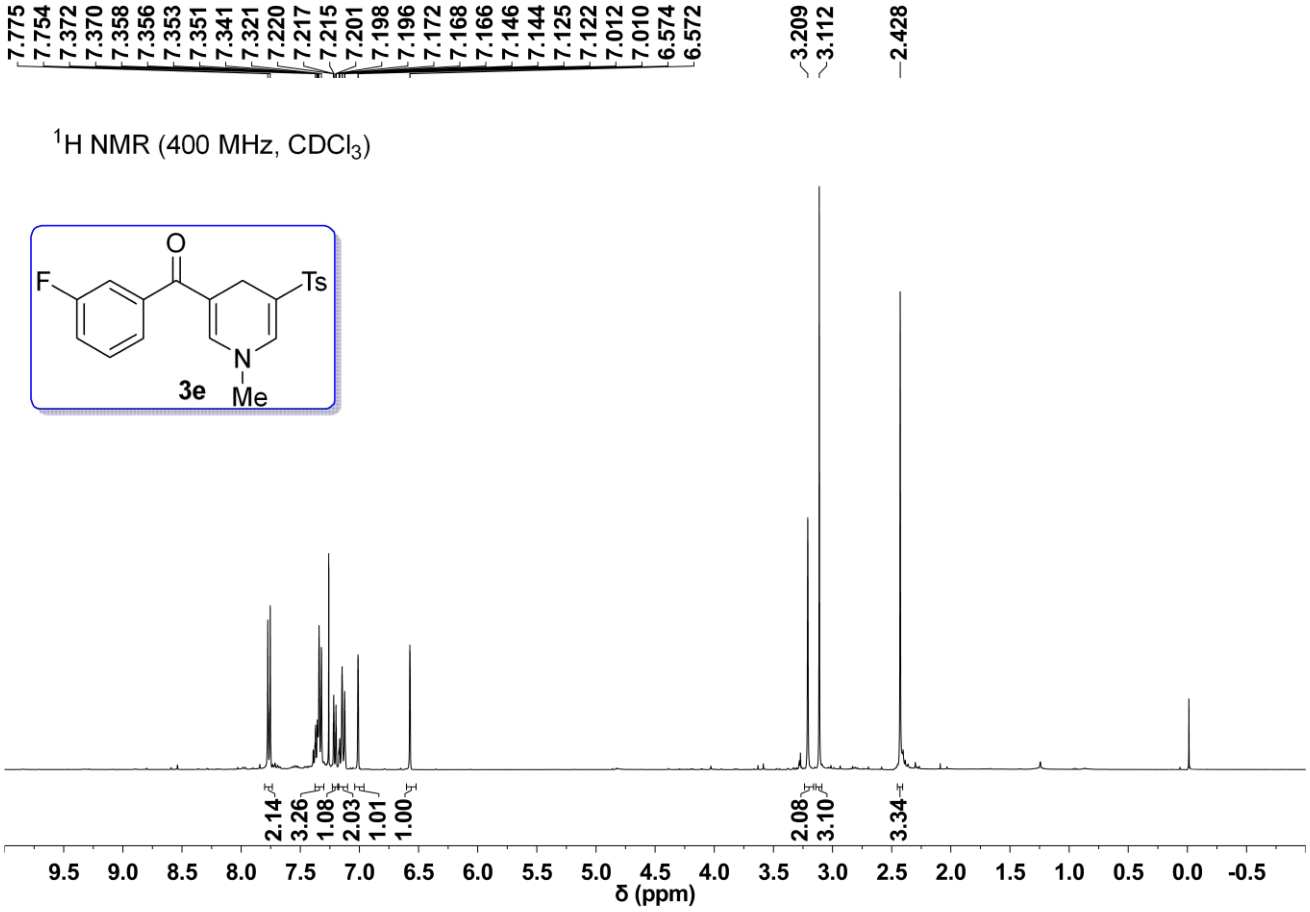

195.943
145.098
144.453
139.091
136.749
135.871
135.785
130.986
130.101
129.481
128.333
127.373
125.405
116.250
114.655
41.714
21.884
20.422
19.572
13C NMR (101 MHz, CDCl3)
Me
O
Ts
N
Me
3b
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

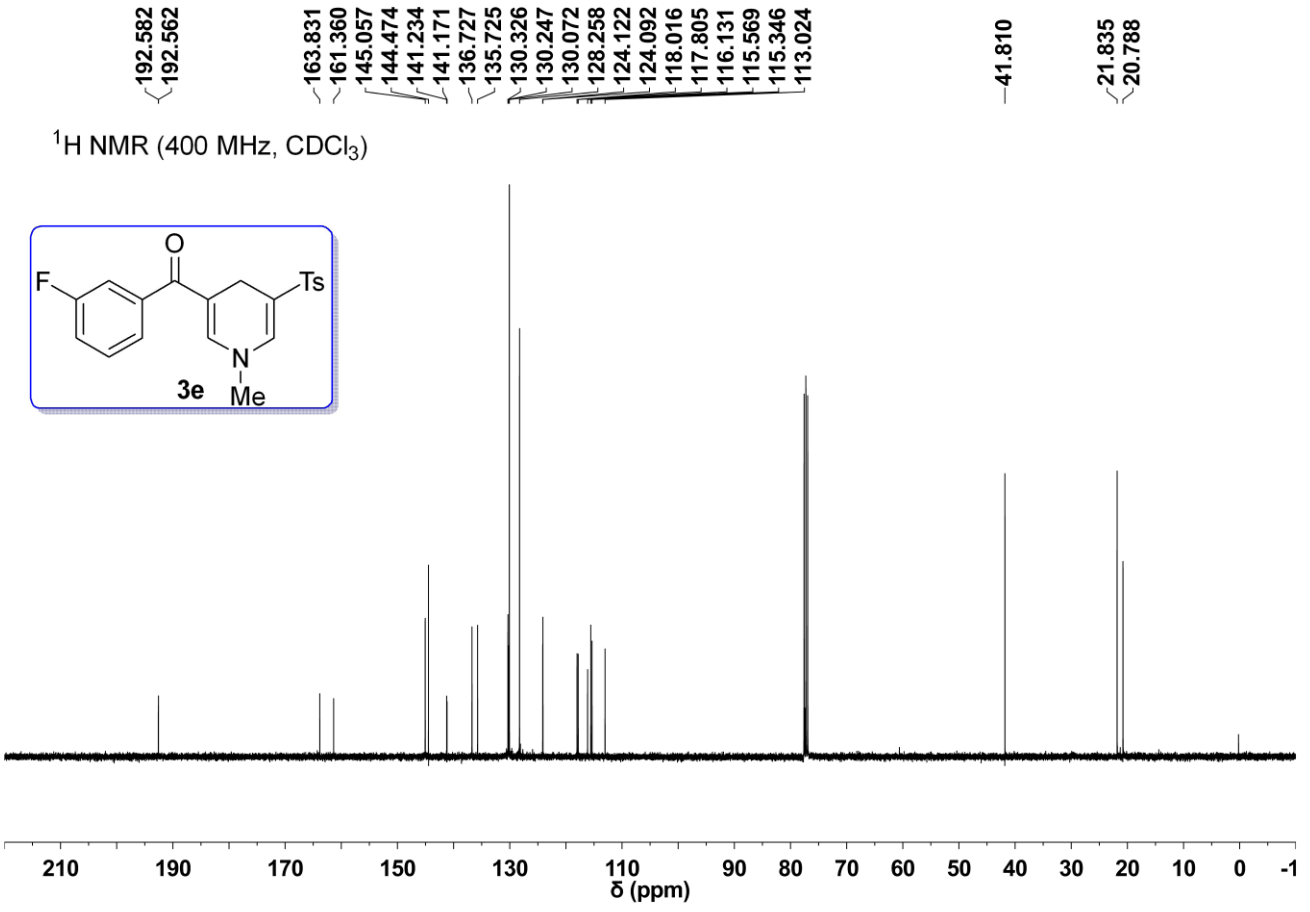

7.778
7.758
7.391
7.348
7.328
7.260
7.246
7.189
7.187
7.170
7.168
7.103
7.101
7.080
7.001
6.453
3.228
3.092
2.436
1H NMR (400 MHz, CDCl3)
F
O
Ts
N
Me
3c
2.18
1.12
2.10
1.13
1.18
1.04
1.00
0.96
1.99
3.06
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

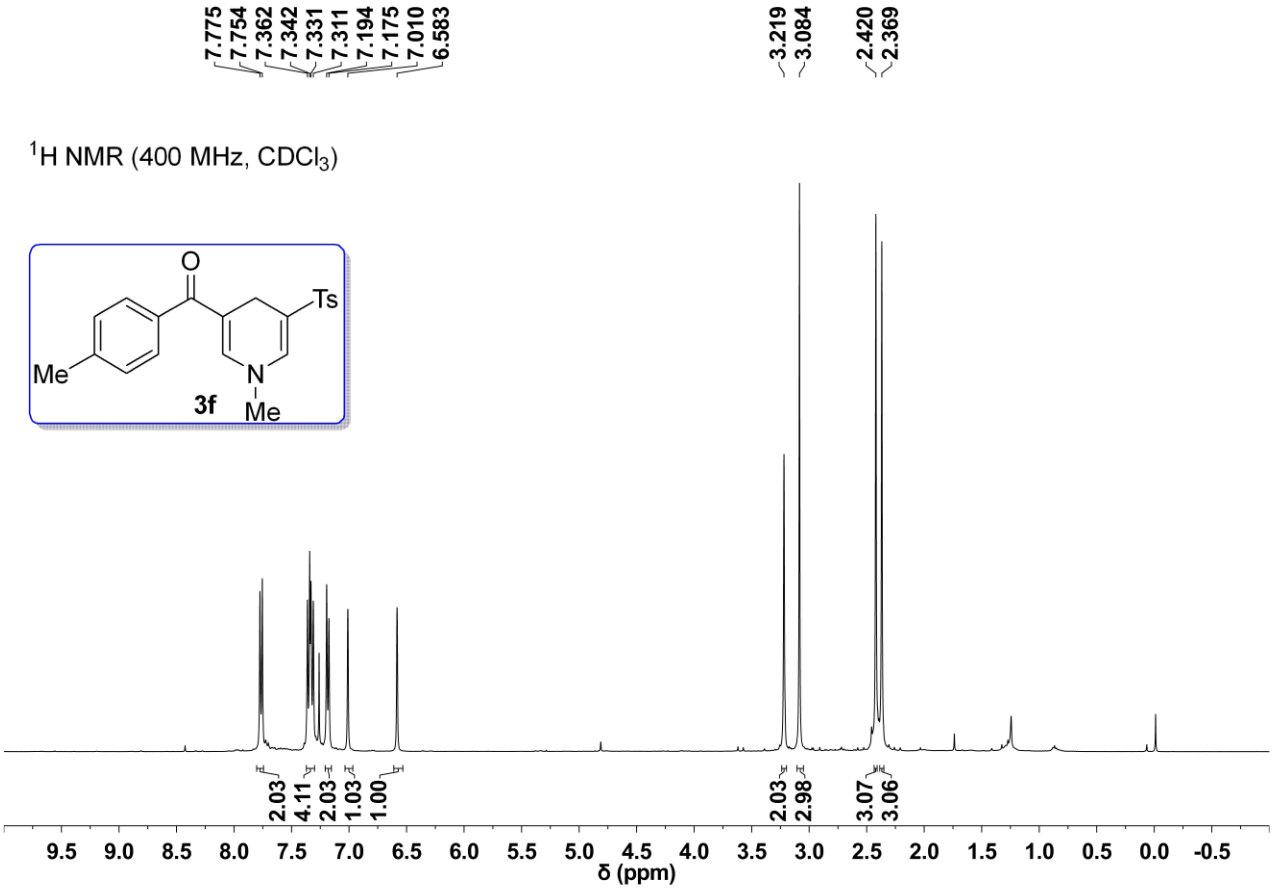

189.958
160.331
157.859
145.447
144.501
136.682
135.618
131.907
131.828
130.081
129.932
128.273
124.483
116.514
116.420
116.203
114.232
41.811
21.845
20.506
13C NMR (101 MHz, CDCl3)
F
O
Ts
N
Me
3c
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

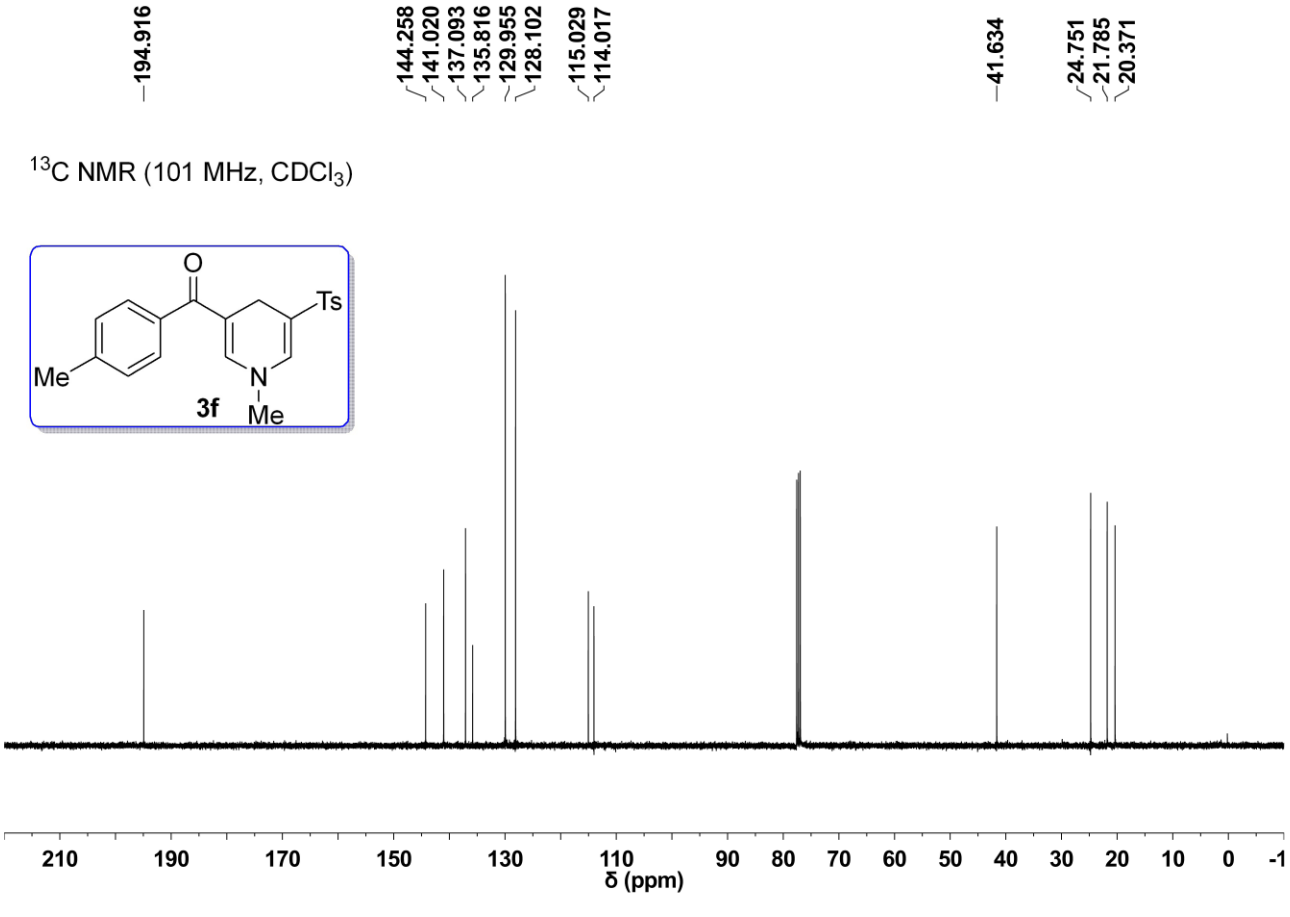

7.786
7.765
7.343
7.322
7.272
7.267
7.260
7.223
7.219
7.211
7.020
6.582
3.227
3.094
2.431
2.361
1H NMR (400 MHz, CDCl3)
O
Me
Ts
N
Me
3d
2.00
2.09
3.32
1.00
1.00
0.97
1.98
3.00
3.06
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

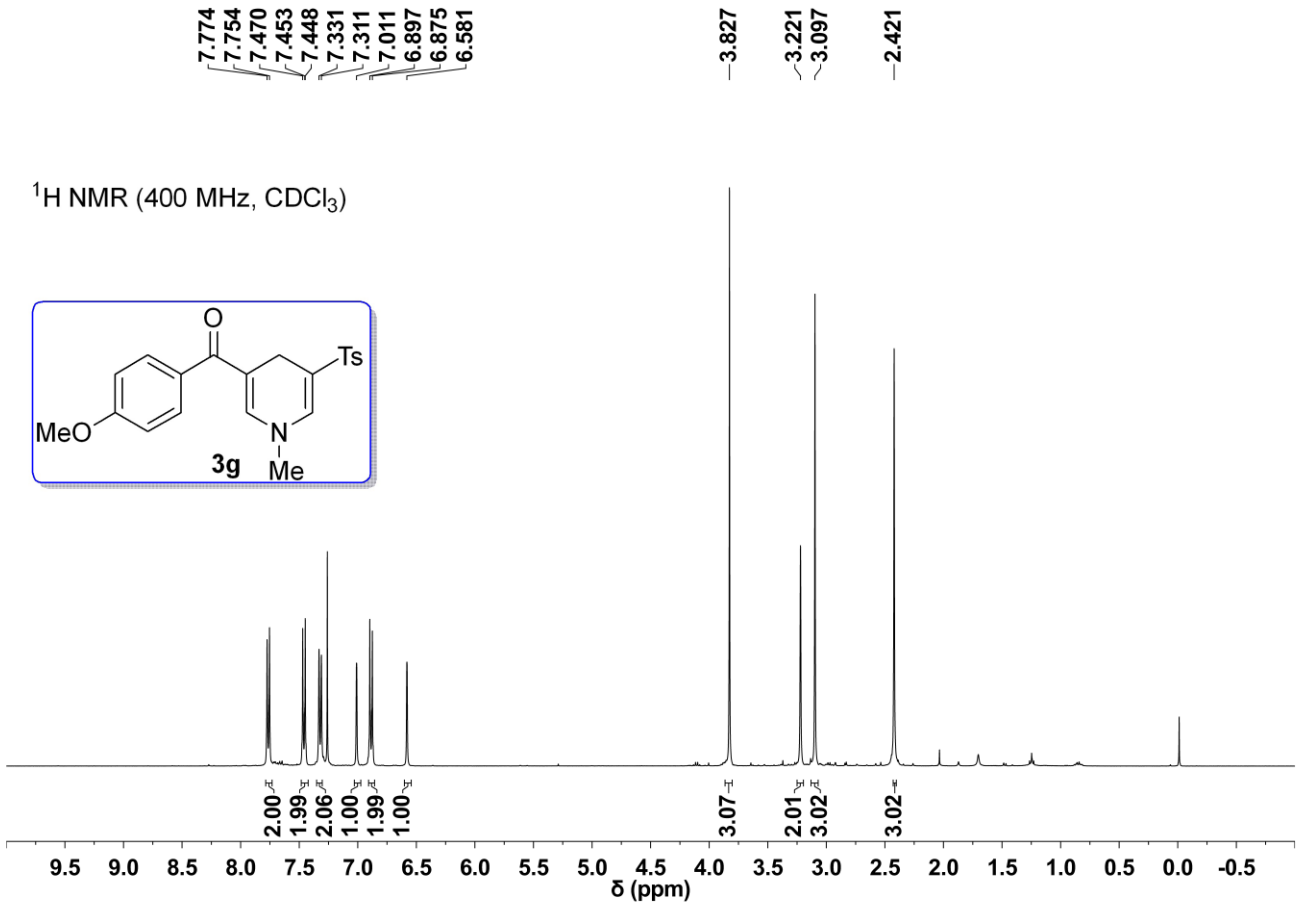

194.491
144.743
144.330
139.185
138.478
136.909
135.836
131.658
130.013
128.929
128.245
128.214
125.502
115.596
113.383
41.695
21.810
21.567
20.814
13C NMR (101 MHz, CDCl3)
O
Me
Ts
N
Me
3d
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
δ (ppm)

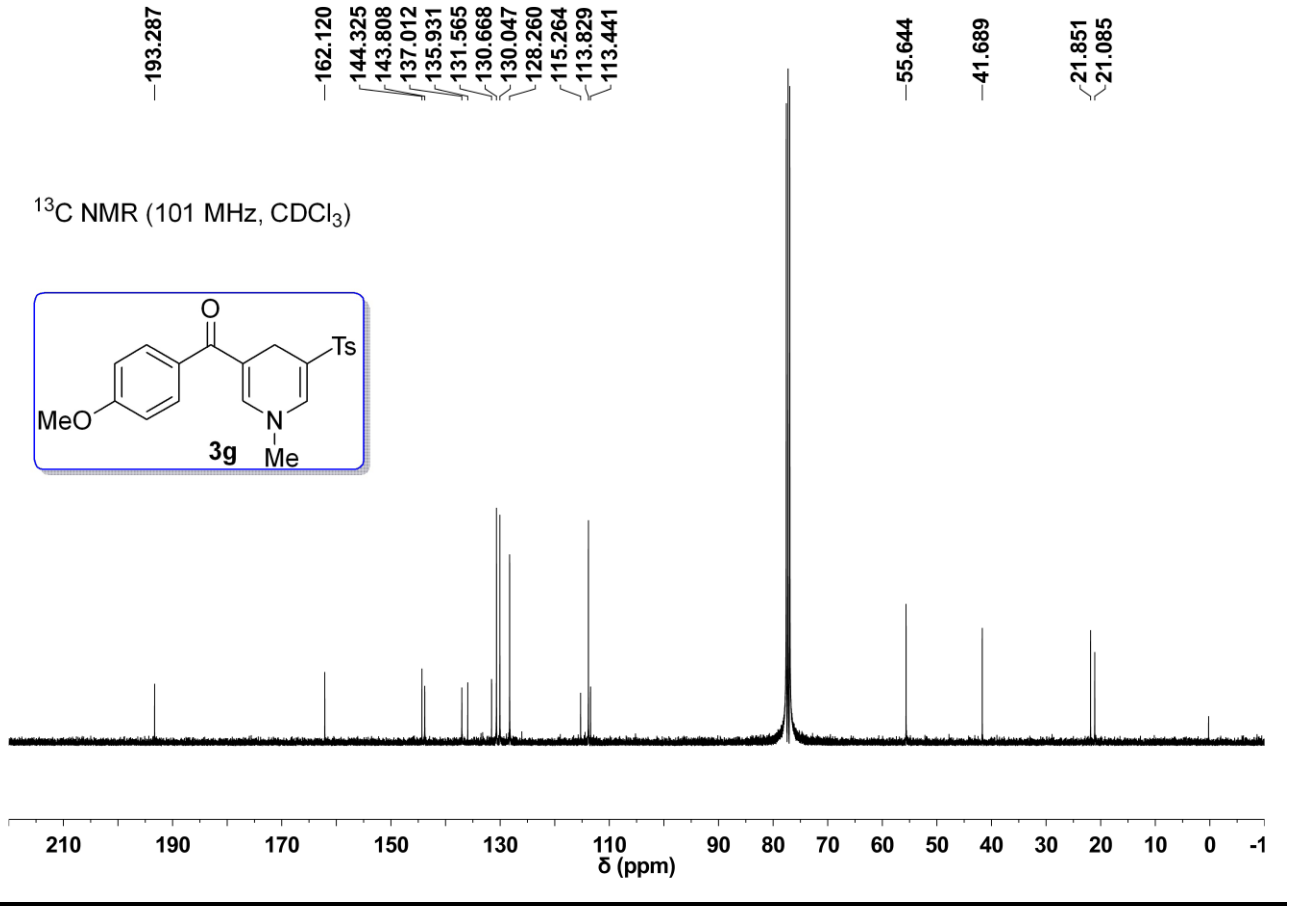

7.775
7.754
7.372
7.370
7.358
7.356
7.353
7.351
7.341
7.321
7.220
7.217
7.215
7.201
7.198
7.196
7.172
7.168
7.166
7.146
7.144
7.125
7.122
7.012
7.010
6.574
6.572
3.209
3.112
2.428
1H NMR (400 MHz, CDCl3)
O
F
Ts
N
Me
3e
2.14
3.26
1.08
2.03
1.01
1.00
2.08
3.10
3.34
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

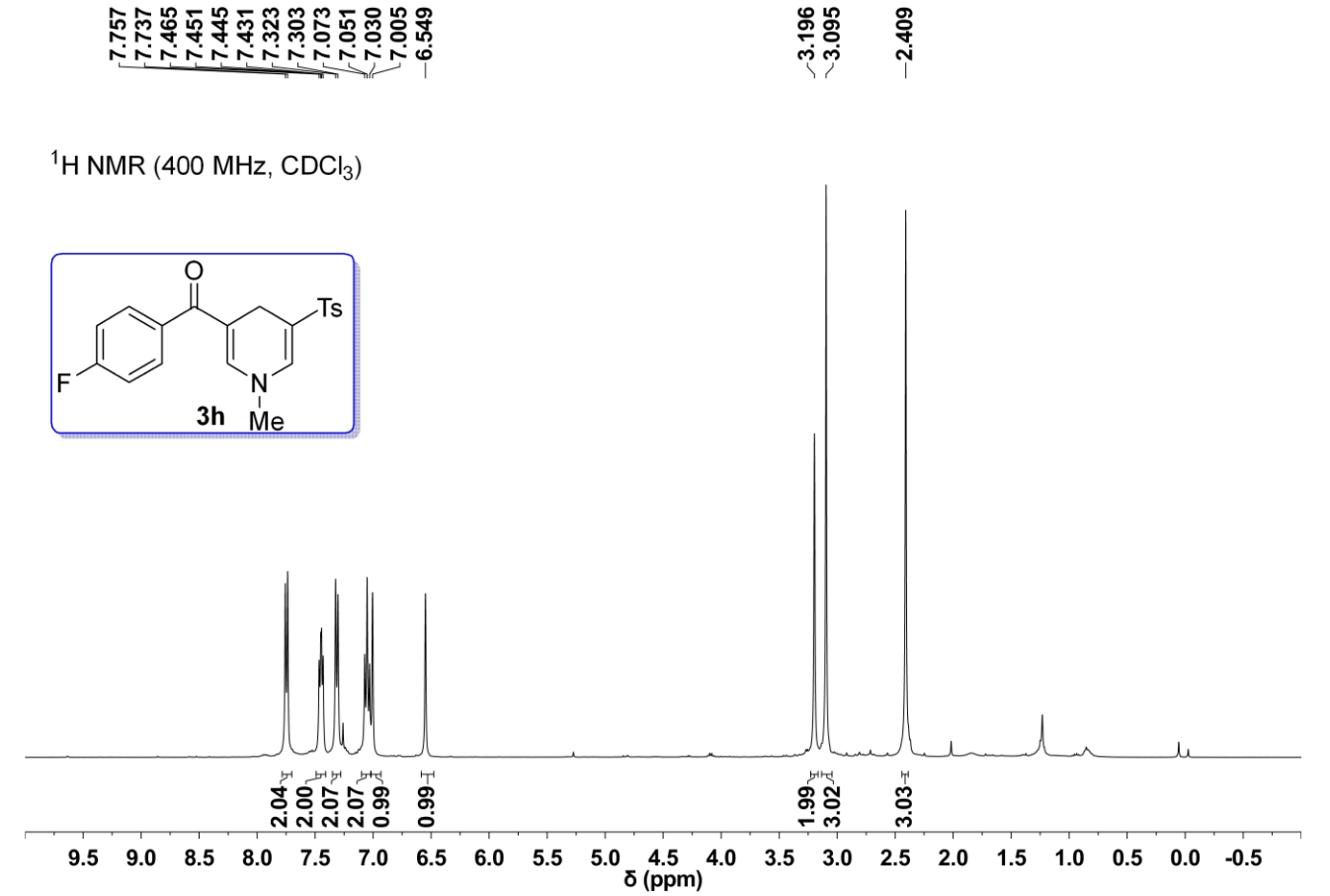

192.582
192.562
163.831
161.360
145.057
144.474
141.234
141.171
136.727
135.725
130.326
130.247
130.072
128.258
124.122
124.092
118.016
117.805
116.131
115.569
115.346
113.024
41.810
21.835
20.788
1H NMR (400 MHz, CDCl3)
O
F
Ts
N
Me
3e
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

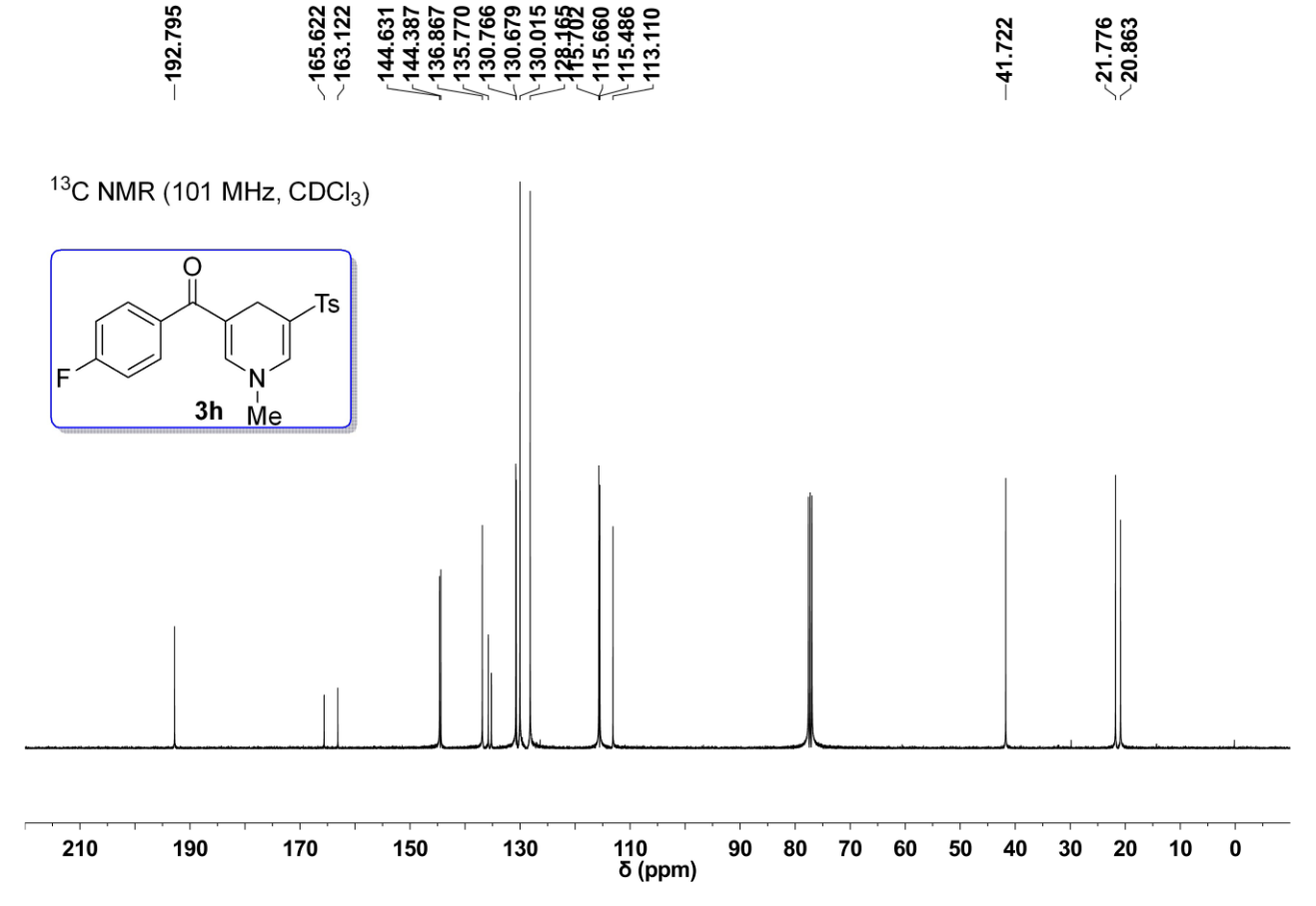

7.775
7.754
7.362
7.342
7.331
7.311
7.194
7.175
7.010
6.583
3.219
3.084
2.420
2.369
1H NMR (400 MHz, CDCl3)
O
Ts
Me
N
Me
3f
2.03
4.11
2.03
1.03
1.00
2.03
2.98
3.07
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

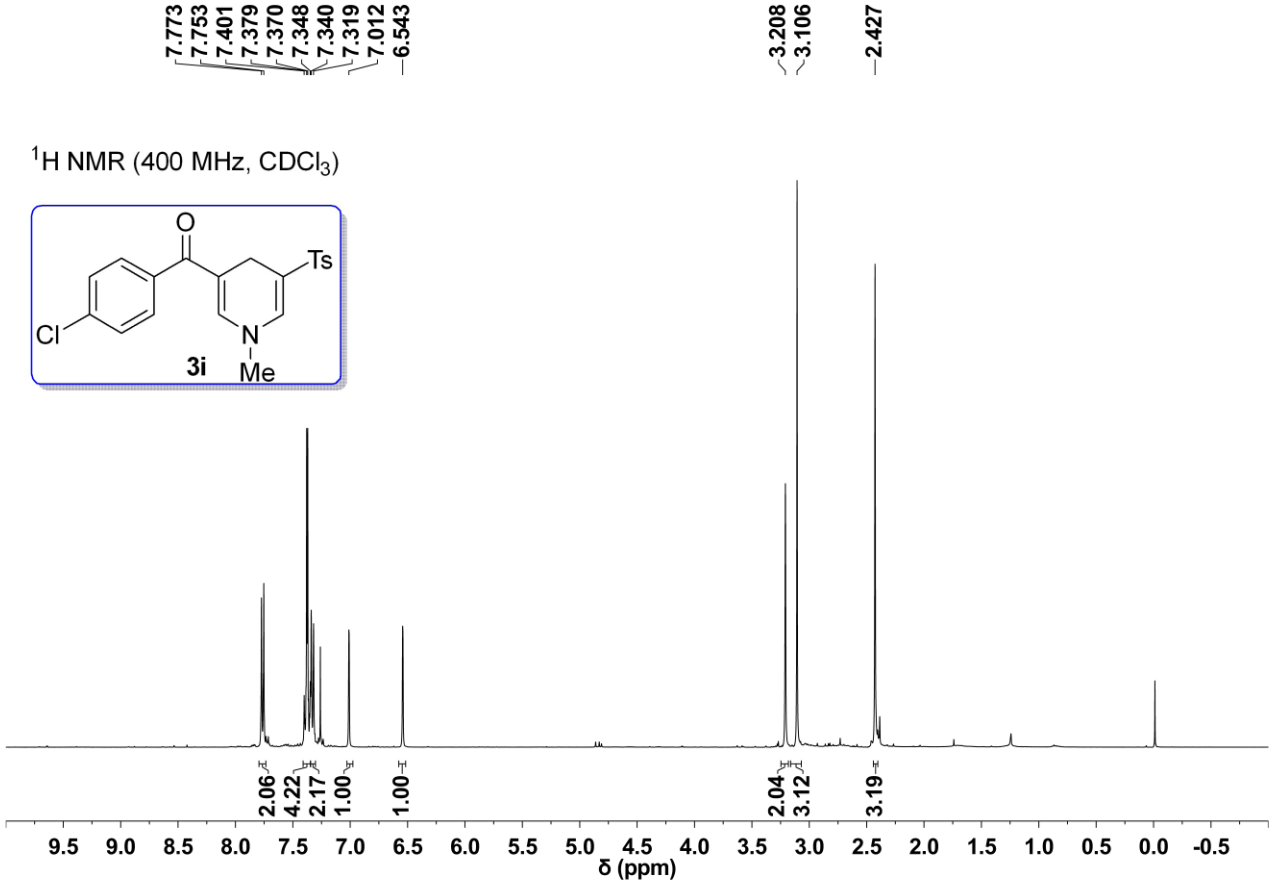

194.916
144.258
141.020
137.093
135.816
129.955
128.102
115.029
114.017
41.634
24.751
21.785
20.371
13C NMR (101 MHz, CDCl3)
O
Ts
Me
N
Me
3f
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

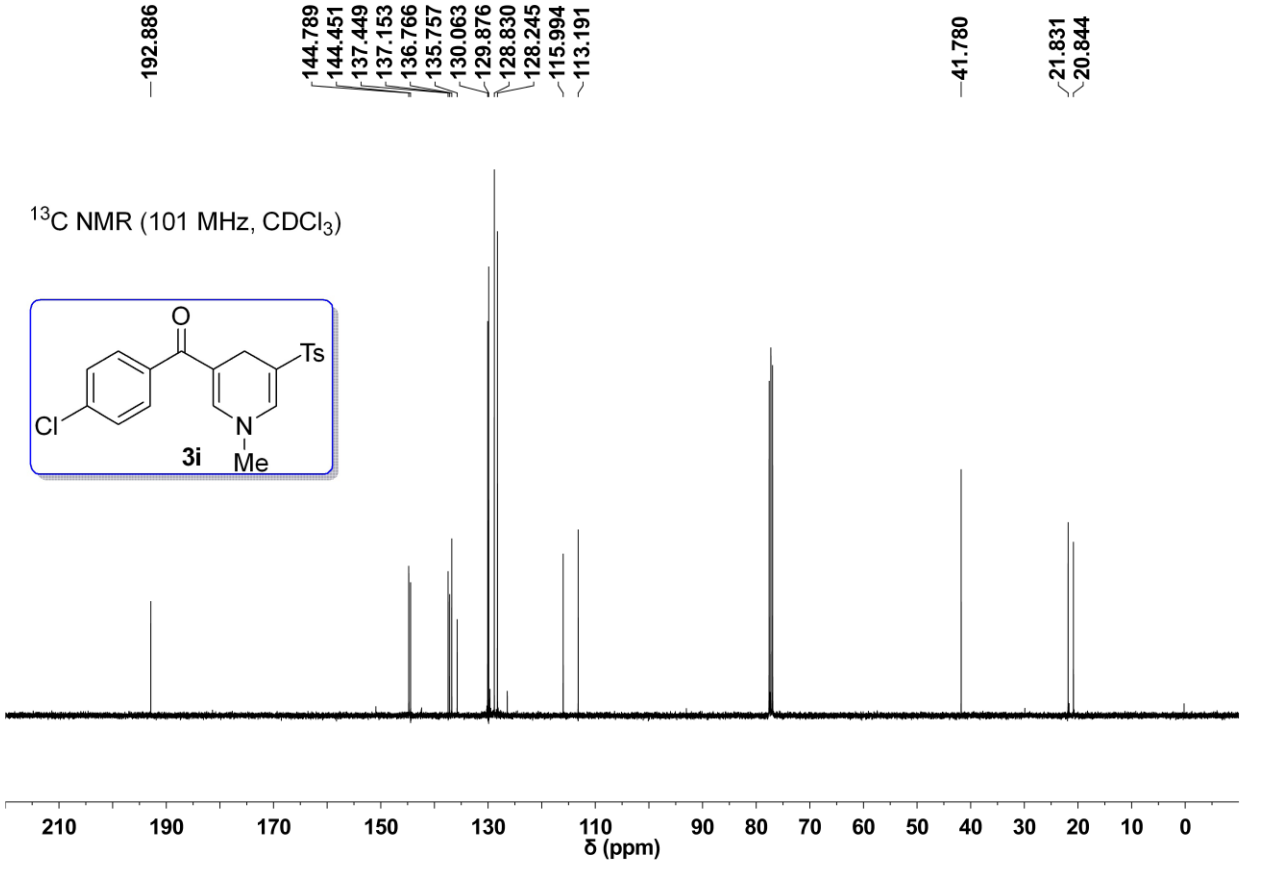

7.774
7.754
7.470
7.453
7.448
7.331
7.311
7.011
6.897
6.875
6.581
3.827
3.221
3.097
2.421
1H NMR (400 MHz, CDCl3)
O
Ts
MeO
N
Me
3g
2.00
1.99
2.06
1.00
1.99
1.00
3.07
2.01
3.02
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

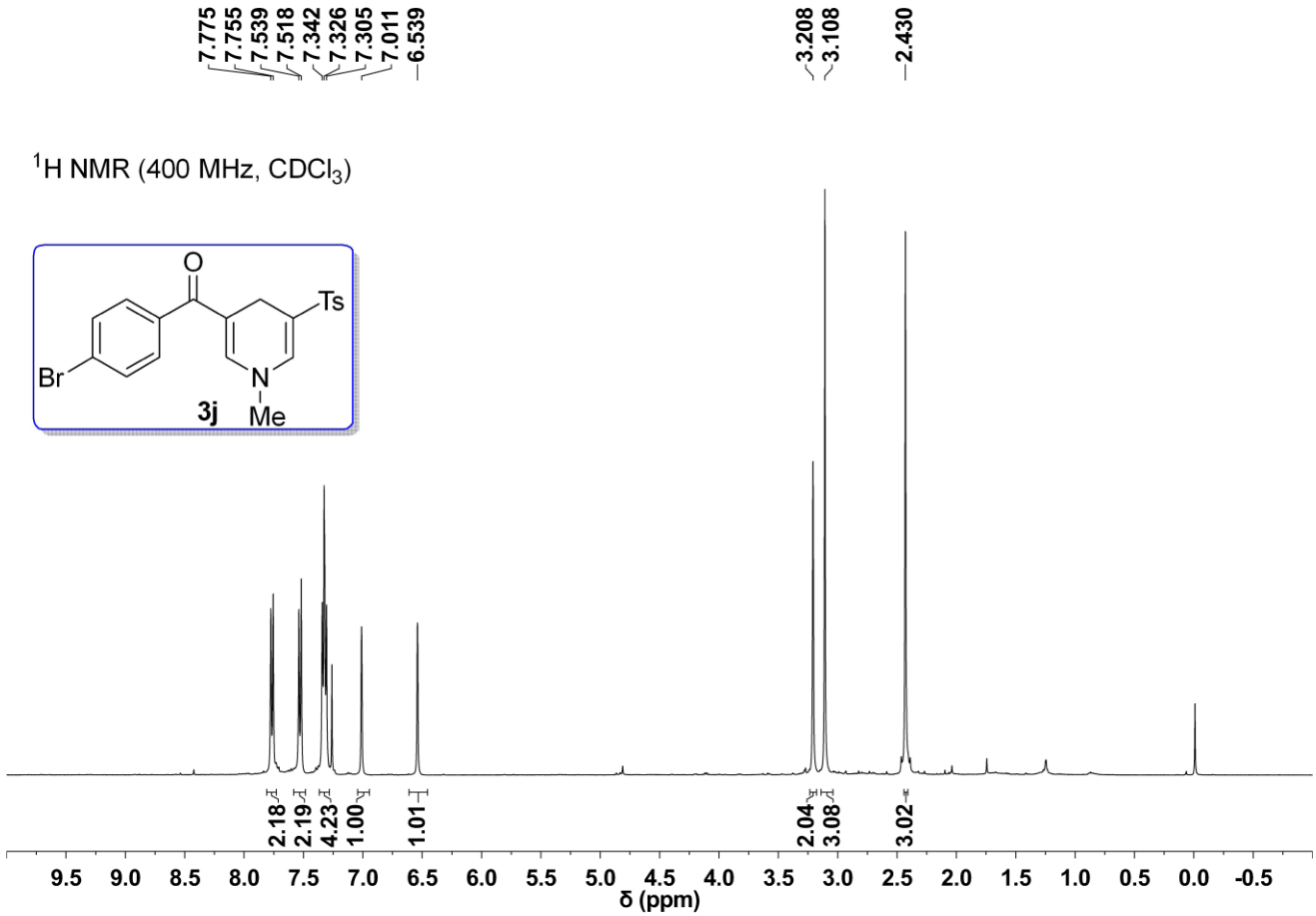

193.287
162.120
144.325
143.808
137.012
135.931
131.565
130.668
130.047
128.260
115.264
113.829
113.441
55.644
41.689
21.851
21.085
13C NMR (101 MHz, CDCl3)
O
Ts
MeO
N
Me
3g
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

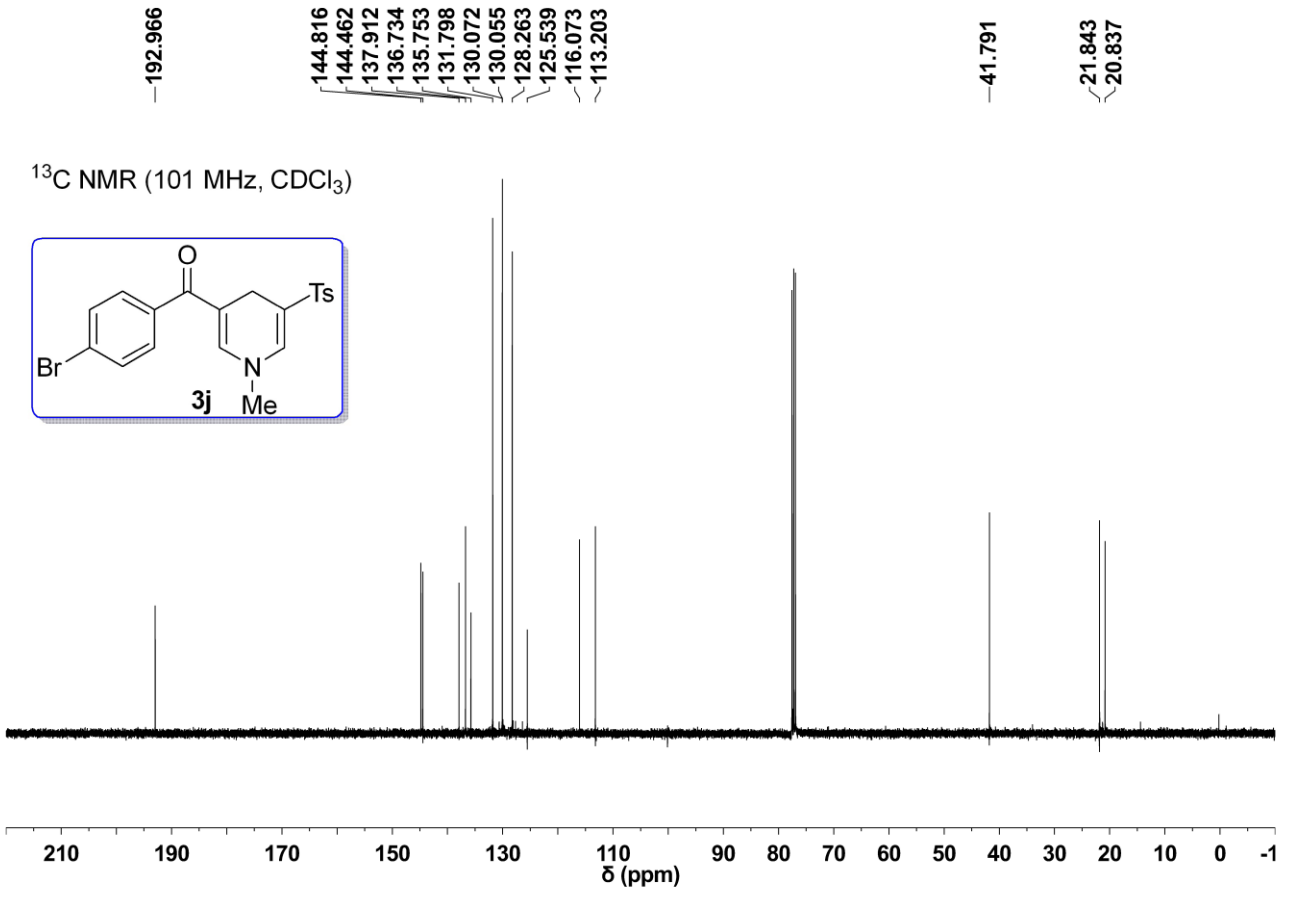

7.757
7.737
7.465
7.451
7.445
7.431
7.323
7.303
7.073
7.051
7.030
7.005
6.549
3.196
3.095
2.409
1H NMR (400 MHz, CDCl3)
O
Ts
F
N
Me
3h
2.04
2.00
2.07
2.07
0.99
0.99
1.99
3.02
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

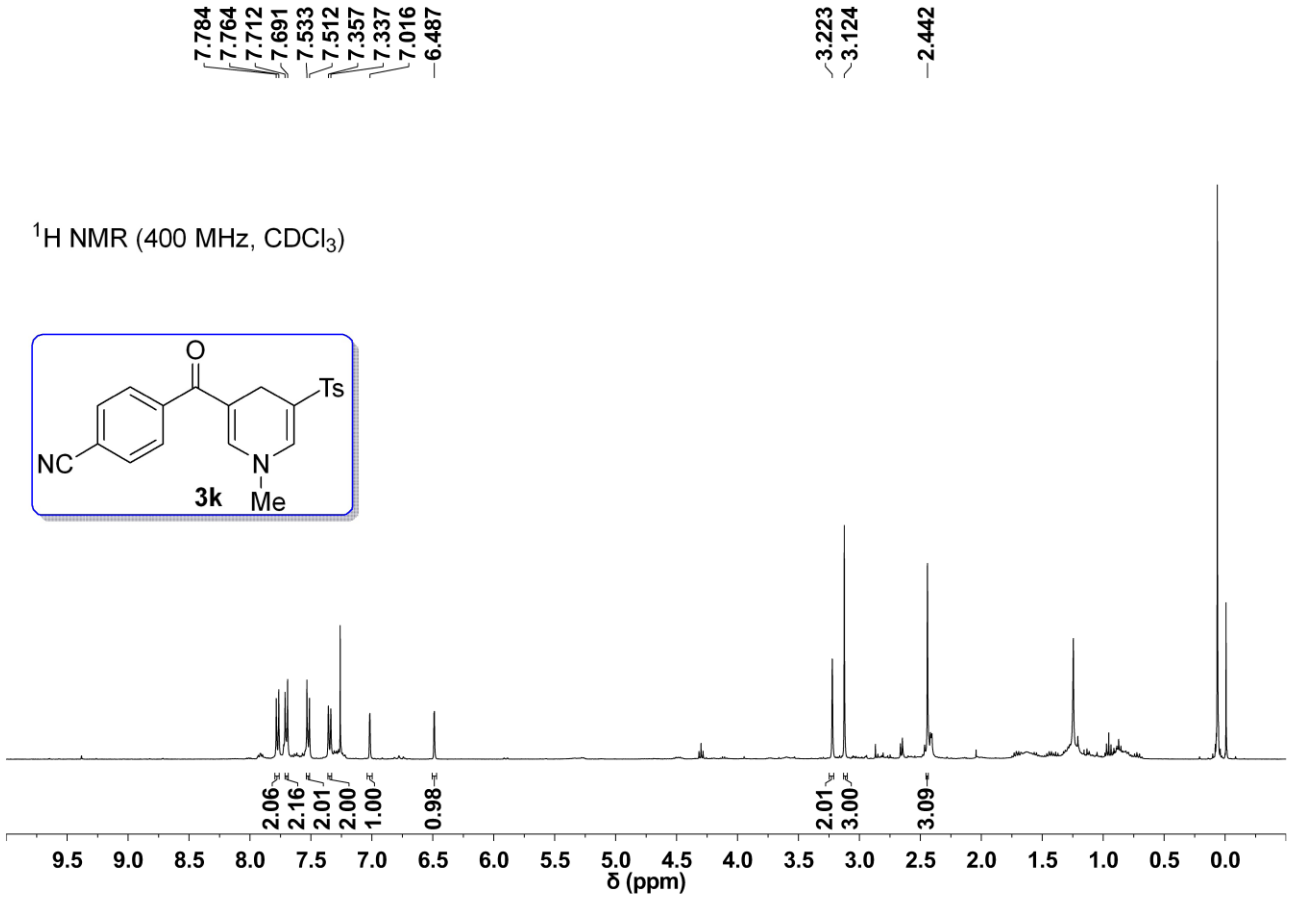

192.795
165.622
163.122
144.631
144.387
136.867
135.770
130.766
130.679
130.015
128.165
115.702
115.660
115.486
113.110
41.722
21.776
20.863
13C NMR (101 MHz, CDCl3)
O
Ts
F
N
Me
3h
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
δ (ppm)

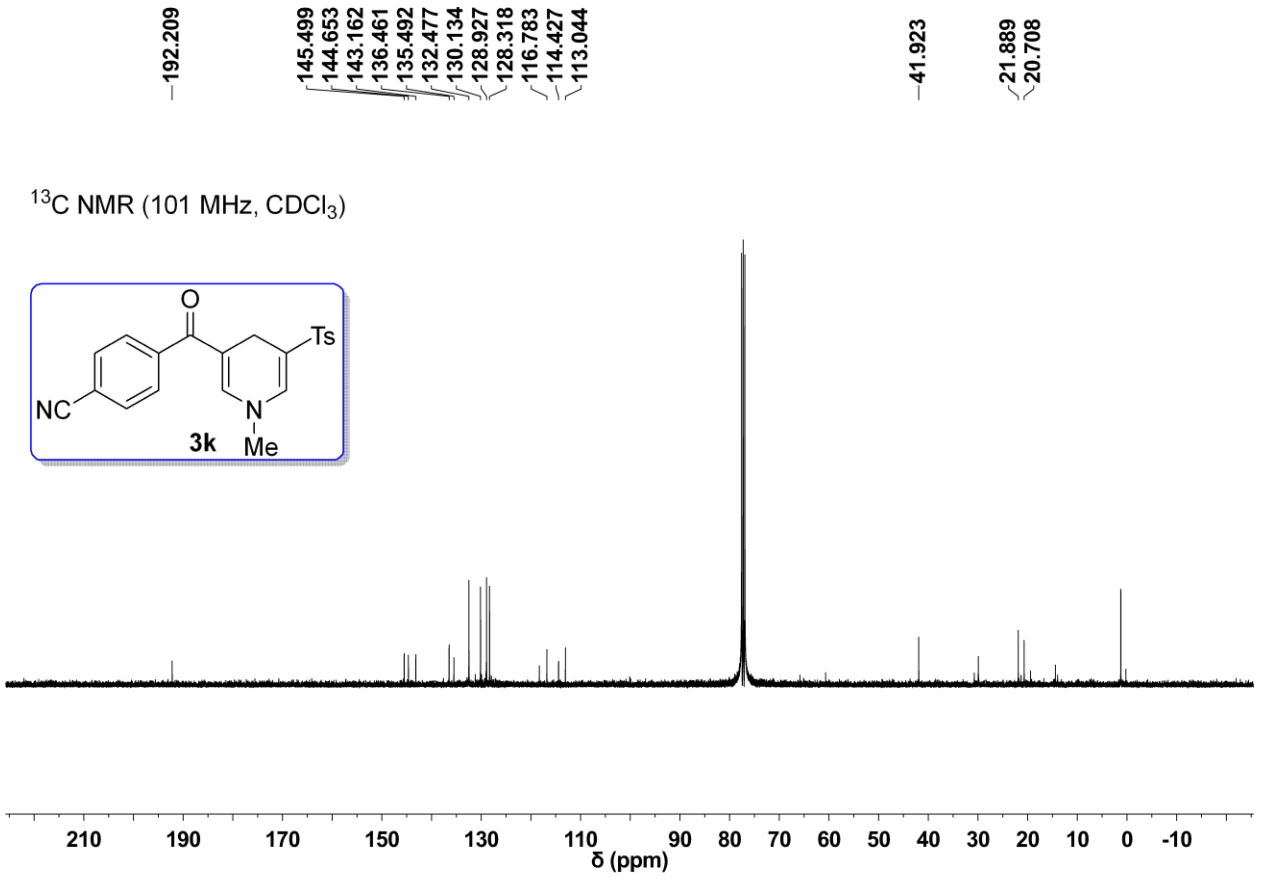

7.773
7.753
7.401
7.379
7.370
7.348
7.340
7.319
7.012
6.543
3.208
3.106
2.427
1H NMR (400 MHz, CDCl3)
O
Ts
Cl
N
Me
3i
2.06
4.22
2.17
1.00
1.00
2.04
3.12
3.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)


192.886
144.789
144.451
137.449
137.153
136.766
135.757
130.063
129.876
128.830
128.245
115.994
113.191
41.780
21.831
20.844
13C NMR (101 MHz, CDCl3)
O
Ts
Cl
N
Me
3i
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
δ (ppm)

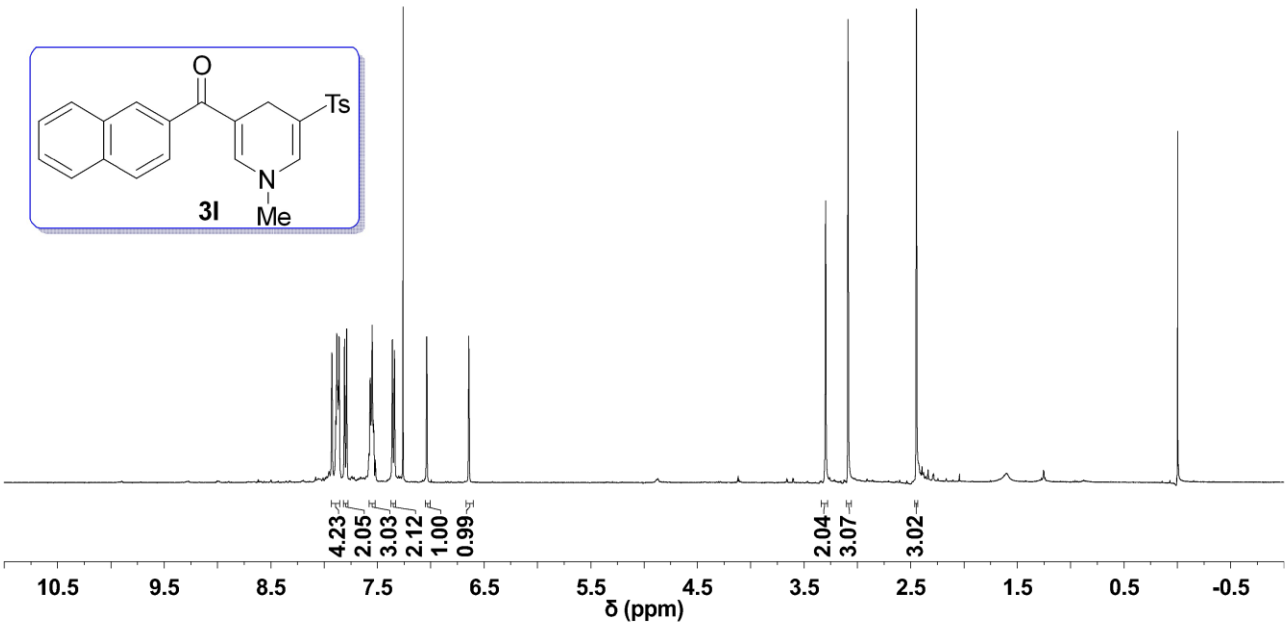

7.775
7.755
7.539
7.518
7.342
7.326
7.305
7.011
6.539
3.208
3.108
2.430
1H NMR (400 MHz, CDCl3)
O
Ts
Br
N
Me
3j
2.18
2.19
4.23
1.00
1.01
2.04
3.08
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

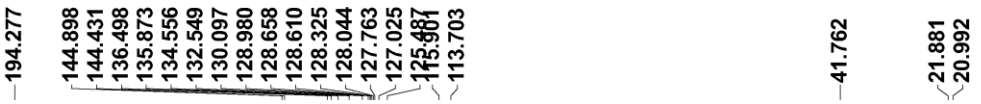

192.966
144.816
144.462
137.912
136.734
135.753
131.798
130.072
130.055
128.263
125.539
116.073
113.203
41.791
21.843
20.837
13C NMR (101 MHz, CDCl3)
O
Ts
Br
N
Me
3j
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)


7.784
7.764
7.712
7.691
7.533
7.512
7.357
7.337
7.016
6.487
3.223
3.124
2.442
1H NMR (400 MHz, CDCl3)
O
Ts
NC
N
Me
3k
2.06
2.16
2.01
2.00
1.00
0.98
2.01
3.00
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
δ (ppm)

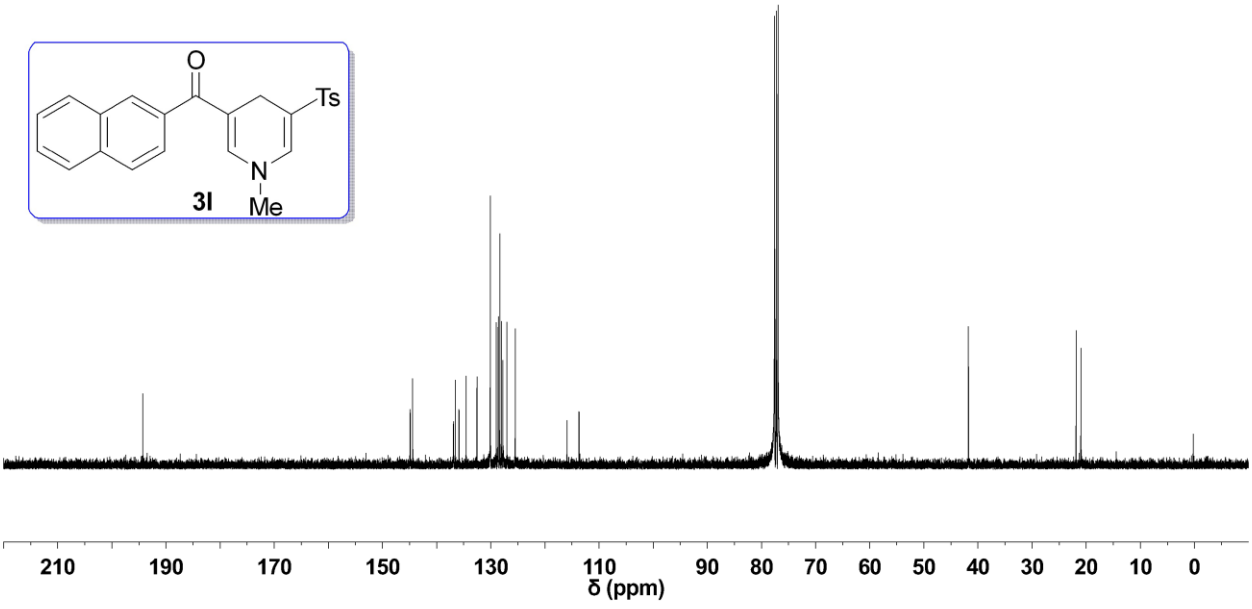

192.209
145.499
144.653
143.162
136.461
135.492
132.477
130.134
128.927
128.318
116.783
114.427
113.044
41.923
21.889
20.708
13C NMR (101 MHz, CDCl3)
O
Ts
NC
N
Me
3k
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

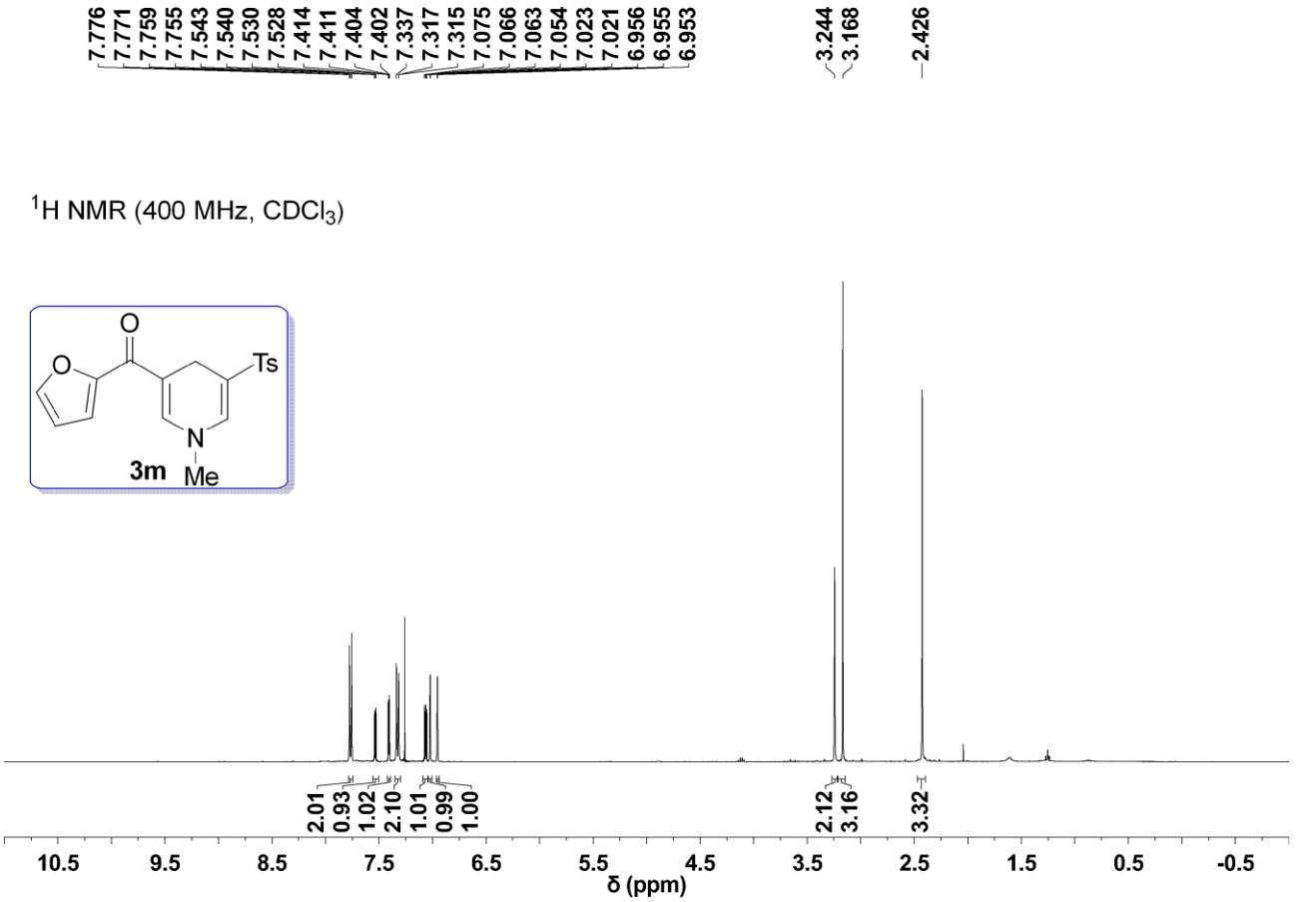
^{1}H NMR (400 MHz, $CDCl_3$)

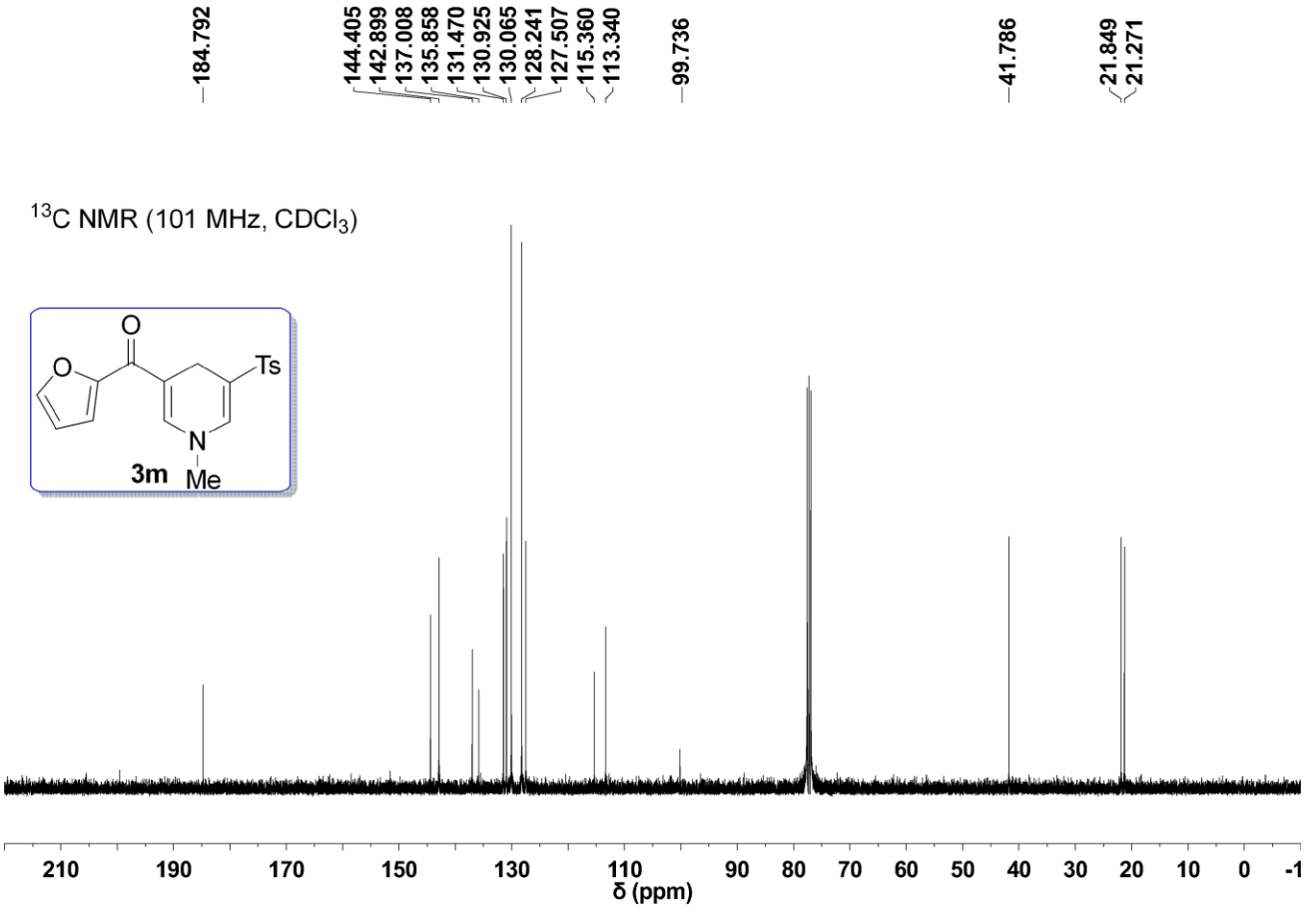


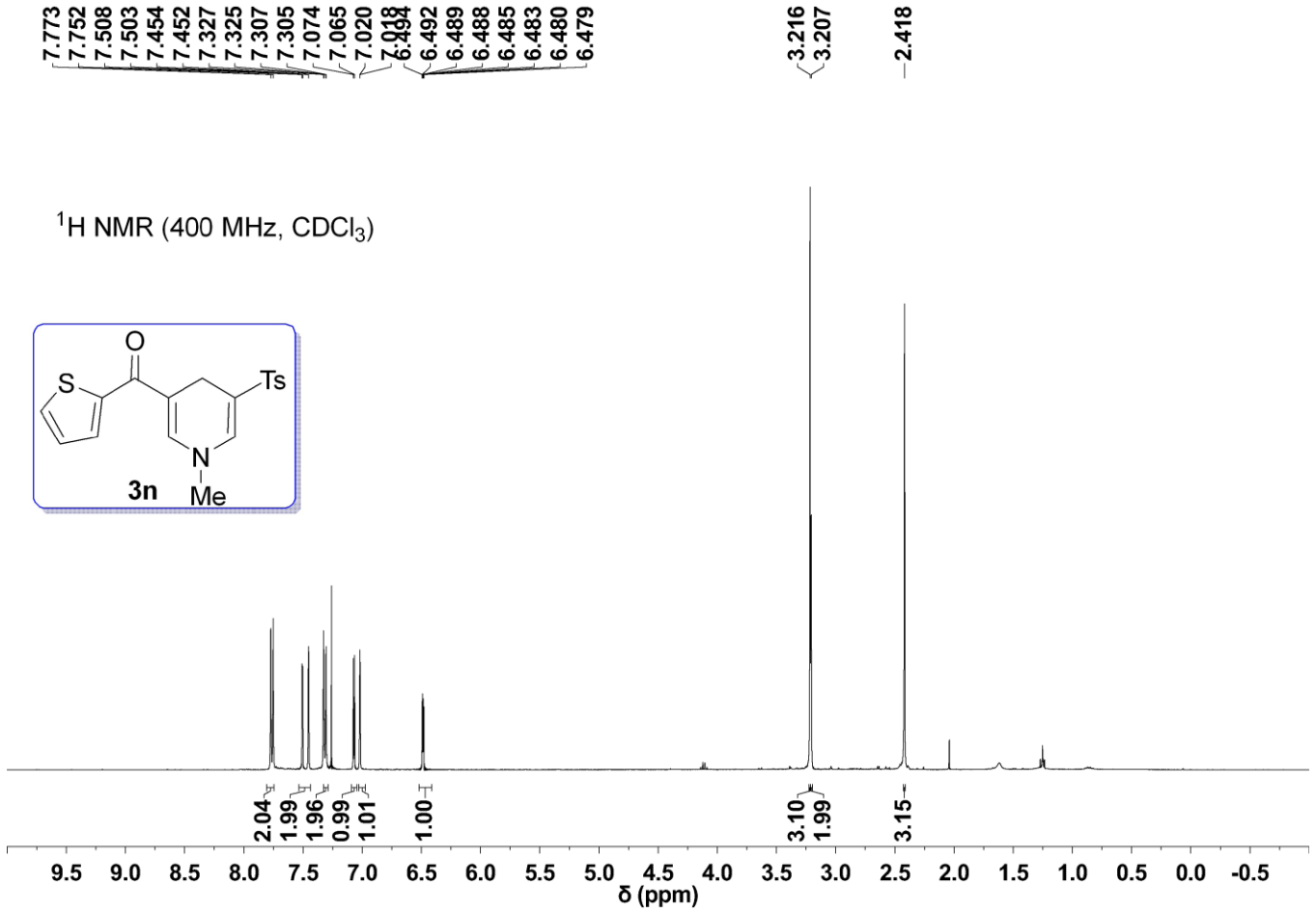


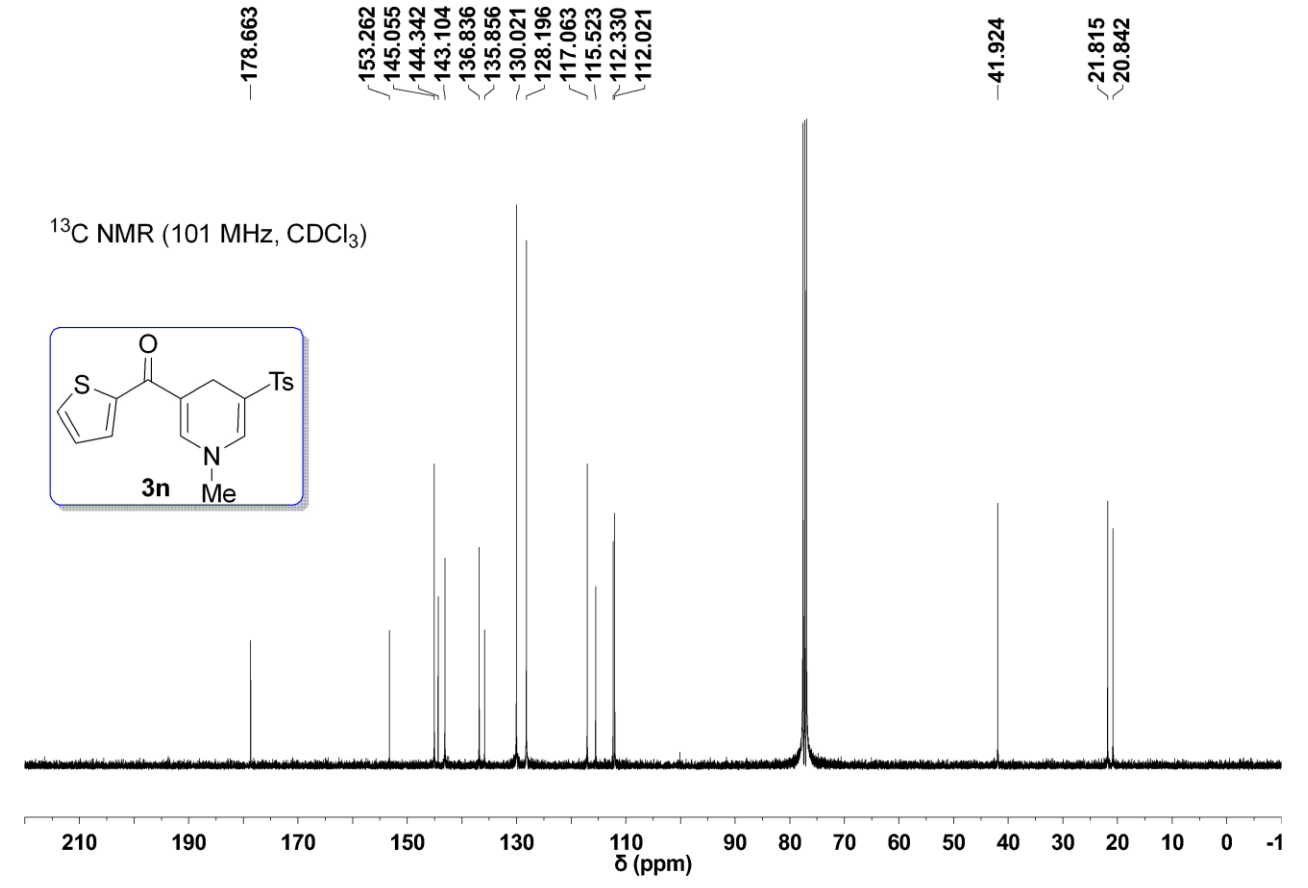
^{13}C NMR (101 MHz, $CDCl_3$)

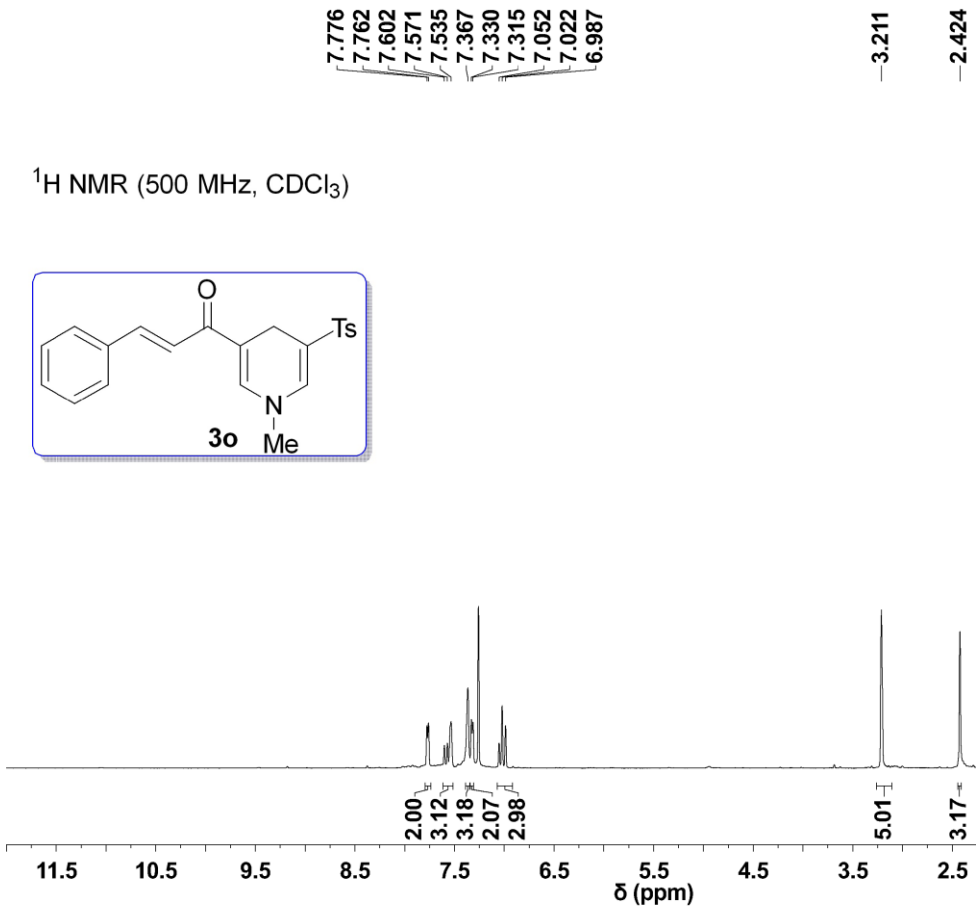



7.776
7.771
7.759
7.755
7.543
7.540
7.530
7.528
7.414
7.411
7.404
7.402
7.337
7.317
7.315
7.075
7.066
7.063
7.054
7.023
7.021
6.956
6.955
6.953
3.244
3.168
2.426
1H NMR (400 MHz, CDCl3)
O
O
Ts
N
Me
3m
2.01
0.93
1.02
2.10
1.01
0.99
1.00
2.12
3.16
3.32
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

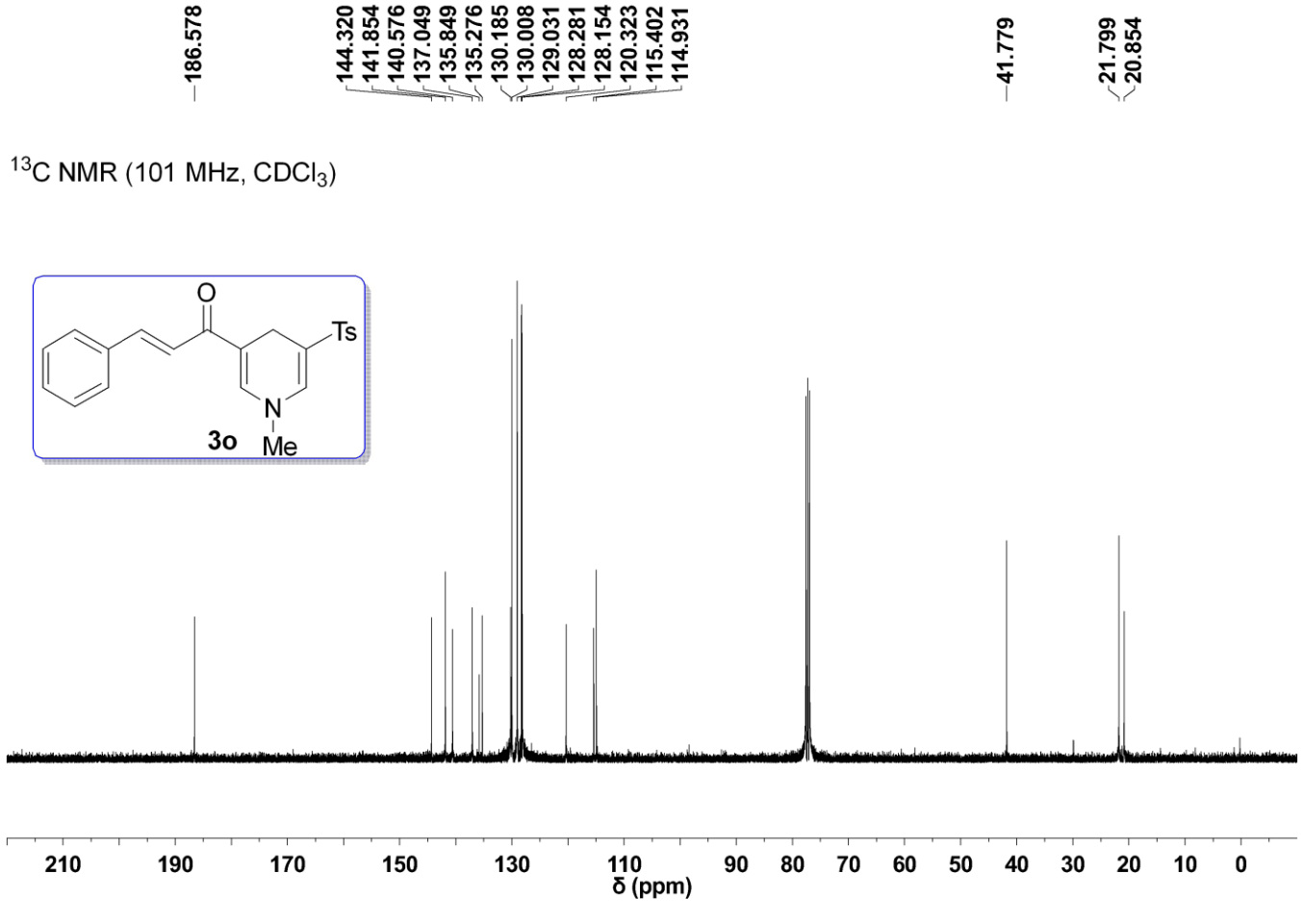

184.792
144.405
142.899
137.008
135.858
131.470
130.925
130.065
128.241
127.507
115.360
113.340
99.736
41.786
21.849
21.271
13C NMR (101 MHz, CDCl3)
O
O
Ts
N
Me
3m
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)


7.773
7.752
7.508
7.503
7.454
7.452
7.327
7.325
7.307
7.305
7.074
7.065
7.020
7.018
6.494
6.492
6.489
6.488
6.485
6.483
6.480
6.479
3.216
3.207
2.418
1H NMR (400 MHz, CDCl3)
O
S
Ts
N
Me
3n
2.04
1.99
1.96
0.99
1.01
1.00
3.10
1.99
3.15
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

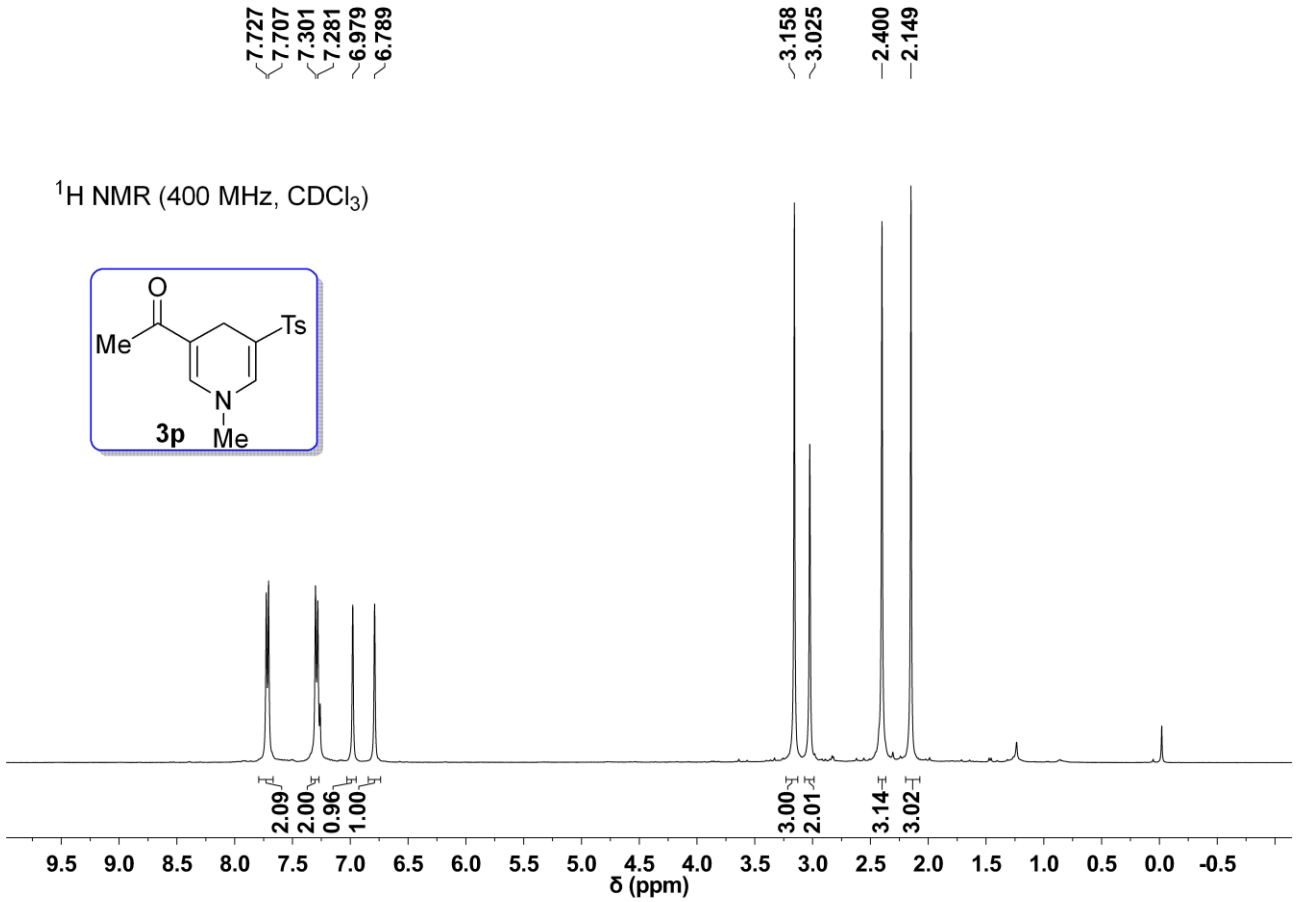

178.663
153.262
145.055
144.342
143.104
136.836
135.856
130.021
128.196
117.063
115.523
112.330
112.021
41.924
21.815
20.842
13C NMR (101 MHz, CDCl3)
O
S
Ts
N
Me
3n
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

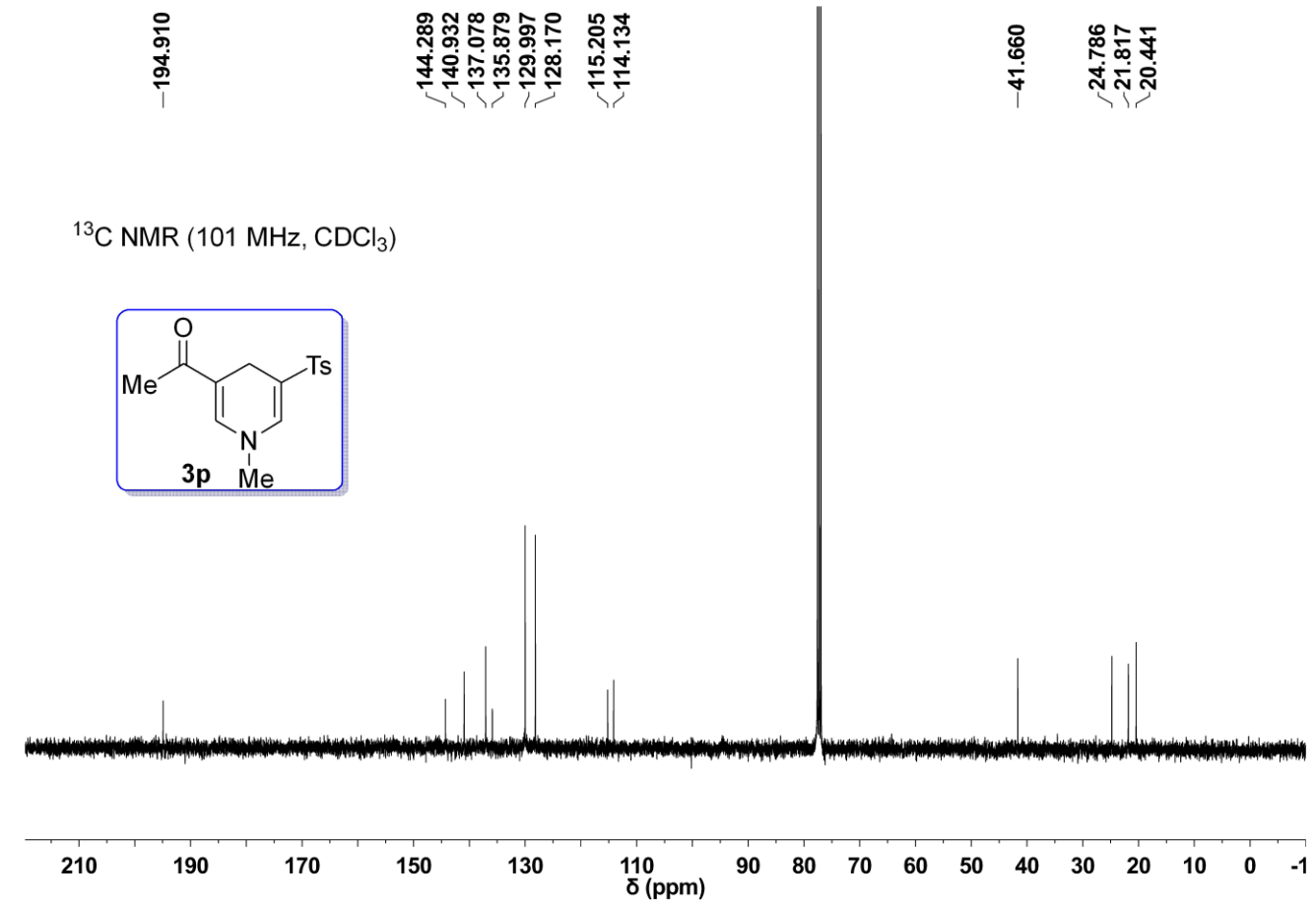


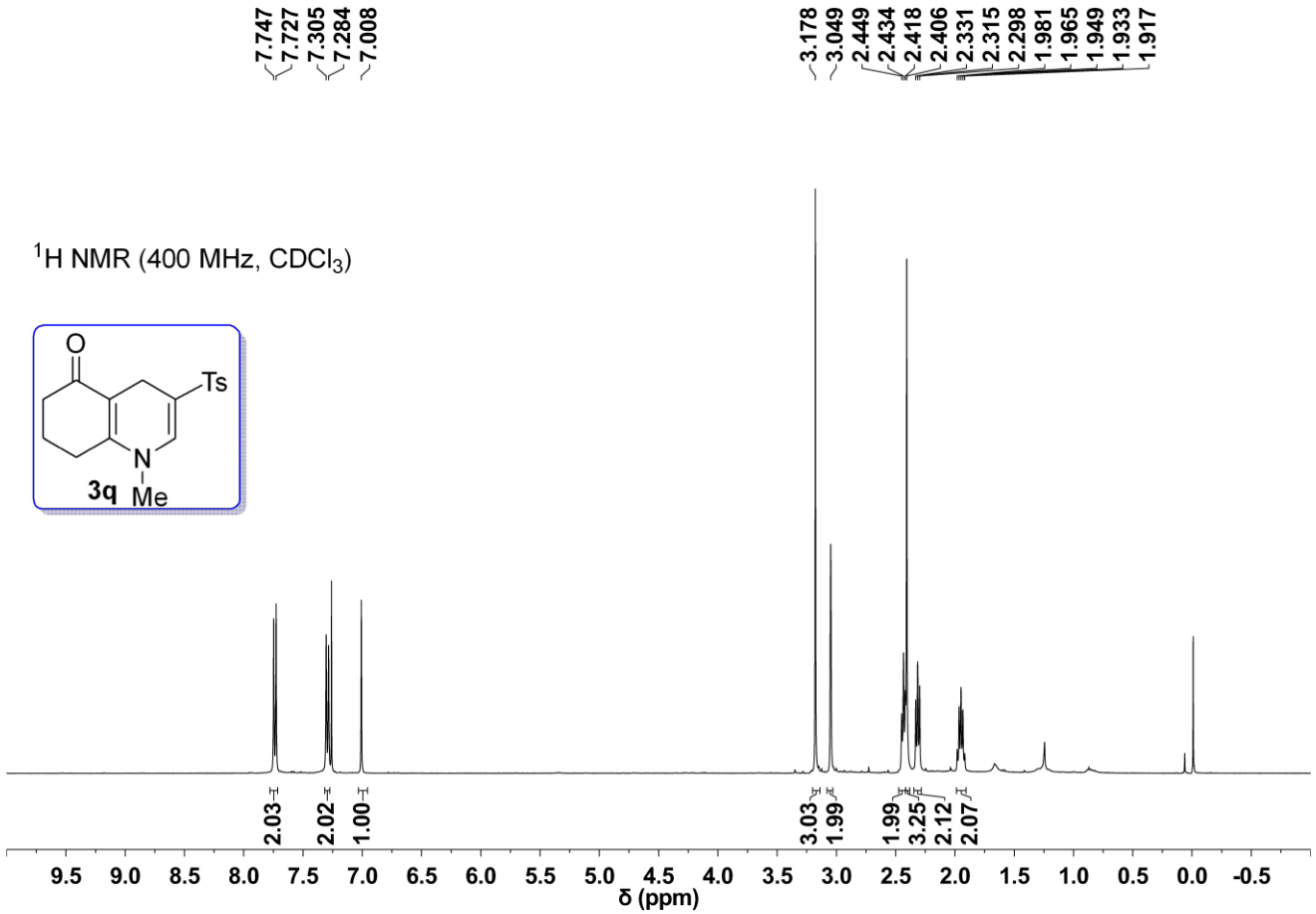
^{1}H NMR (500 MHz, $CDCl_3$)

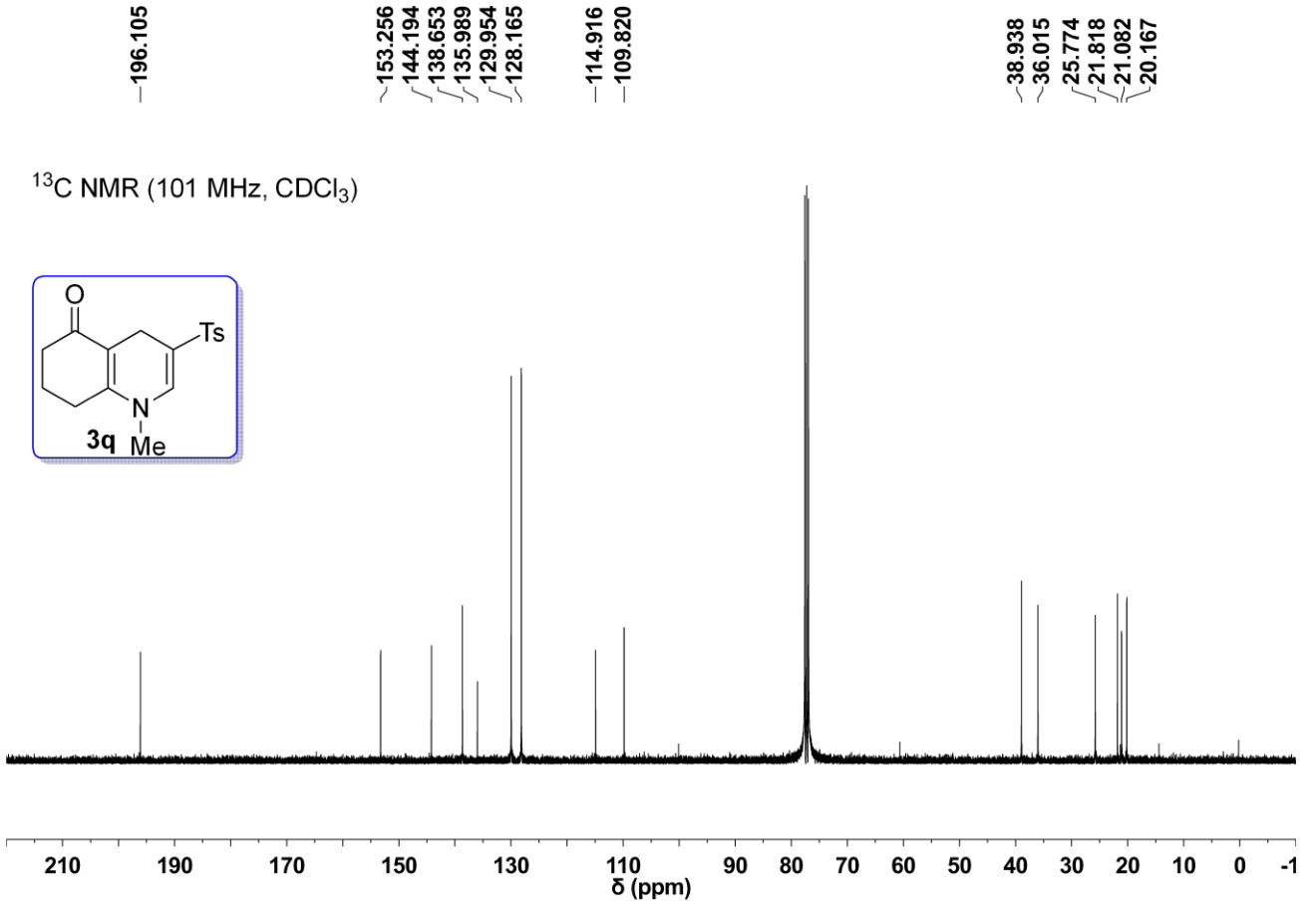


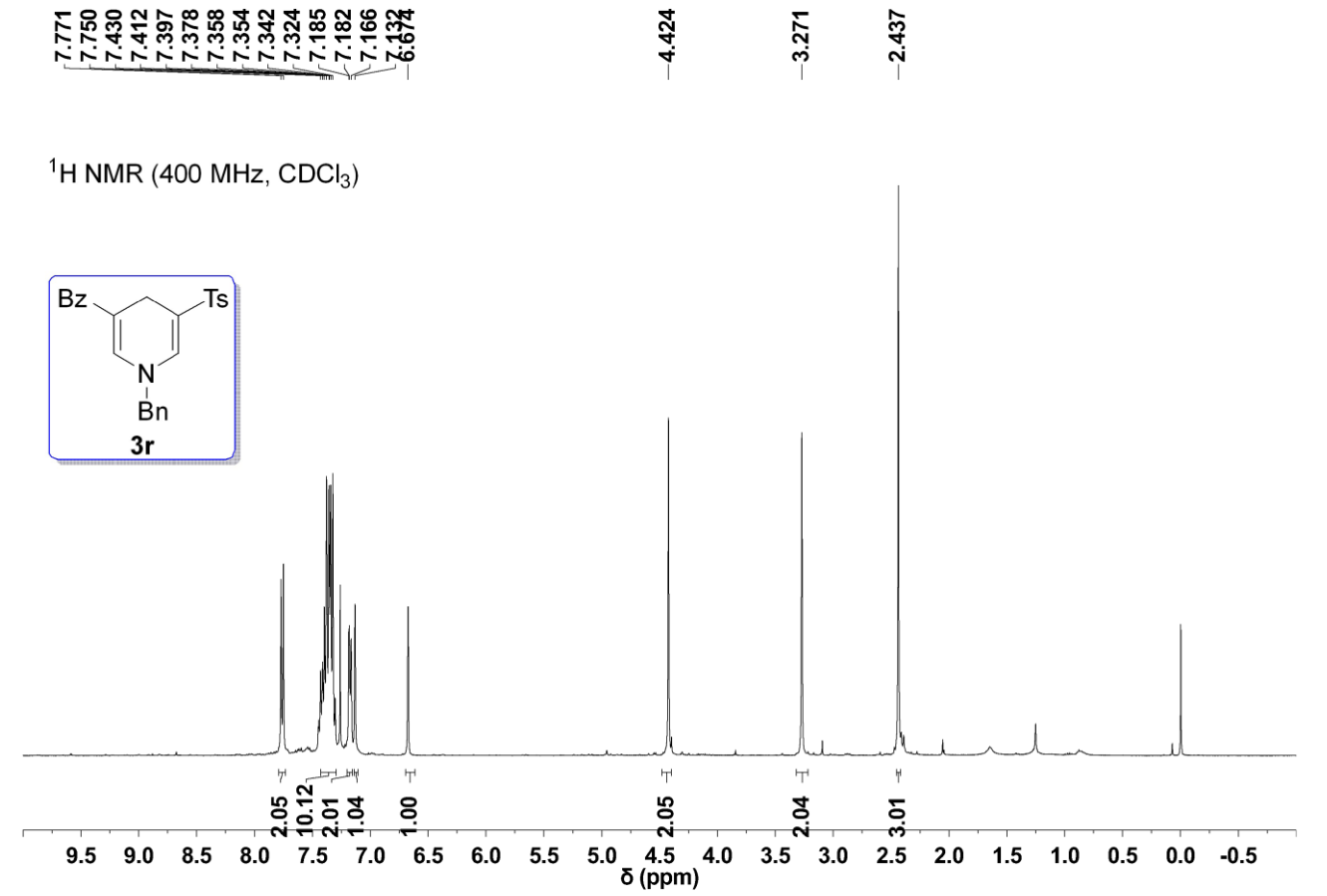
^{13}C NMR (101 MHz, $CDCl_3$)

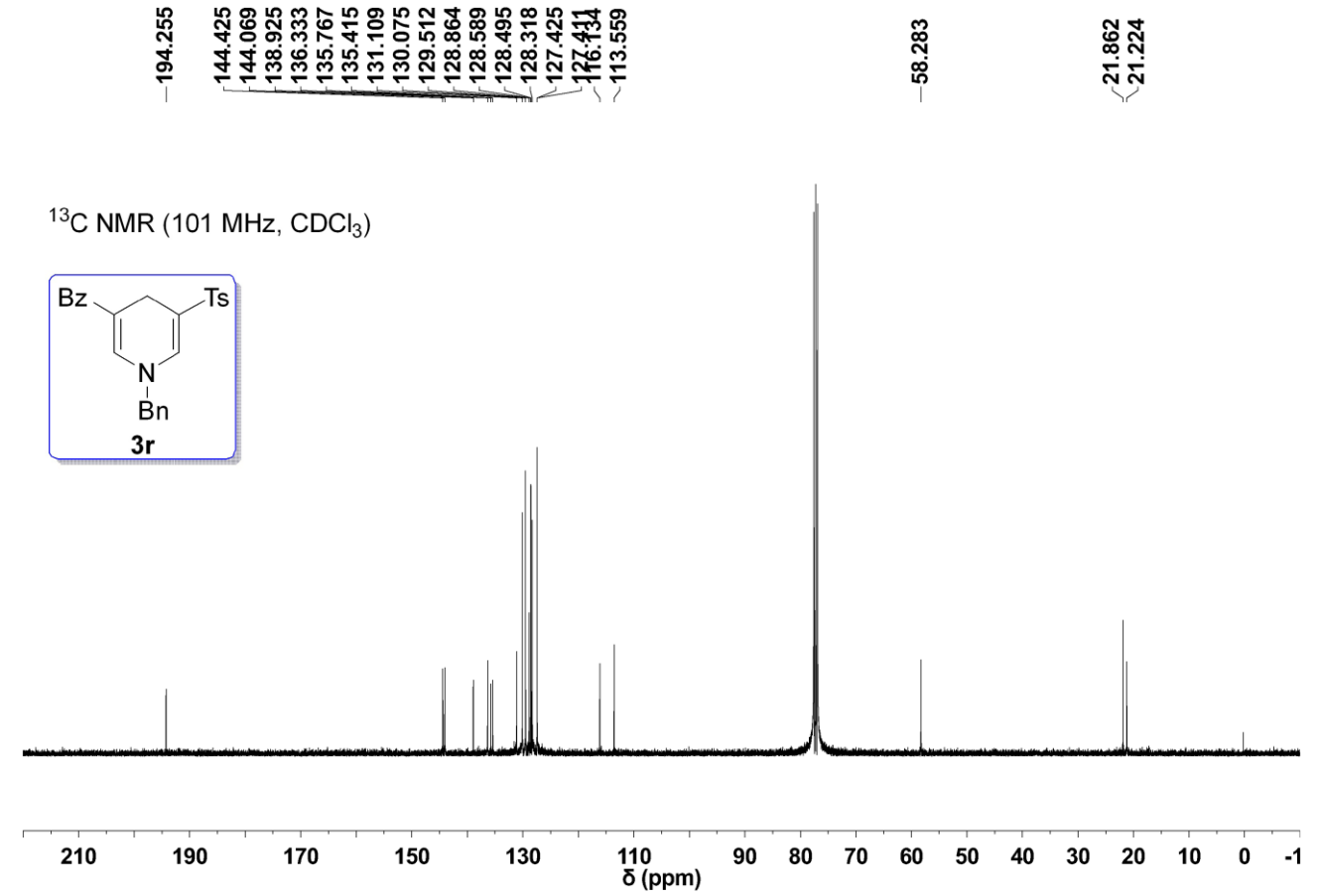

7.727
7.707
7.301
7.281
6.979
6.789
3.158
3.025
2.400
2.149
1H NMR (400 MHz, CDCl3)
O
Me
Ts
N
Me
3p
2.09
2.00
0.96
1.00
3.00
2.01
3.14
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

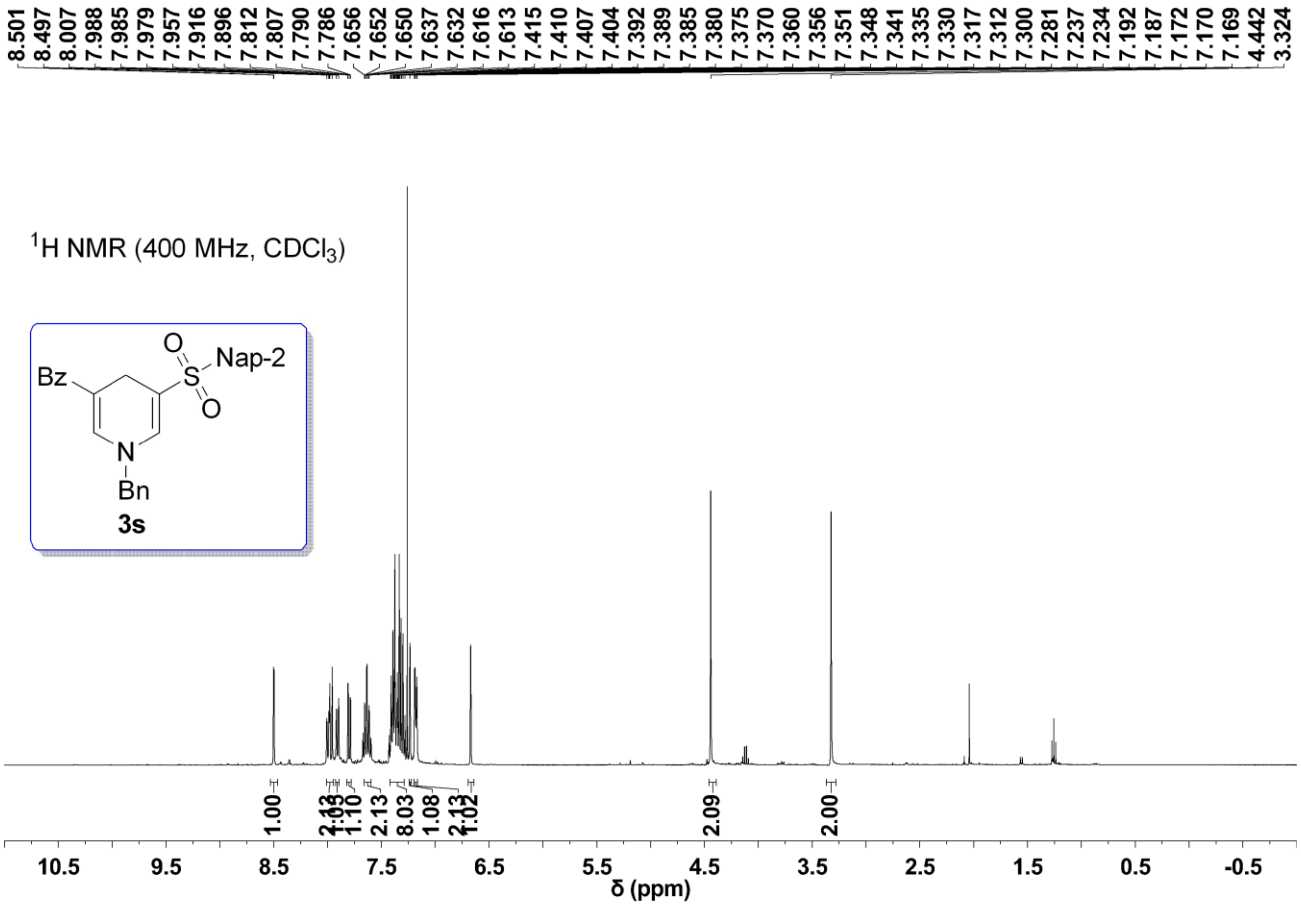

194.910
144.289
140.932
137.078
135.879
129.997
128.170
115.205
114.134
41.660
24.786
21.817
20.441
13C NMR (101 MHz, CDCl3)
O
Me
Ts
N
Me
3p
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

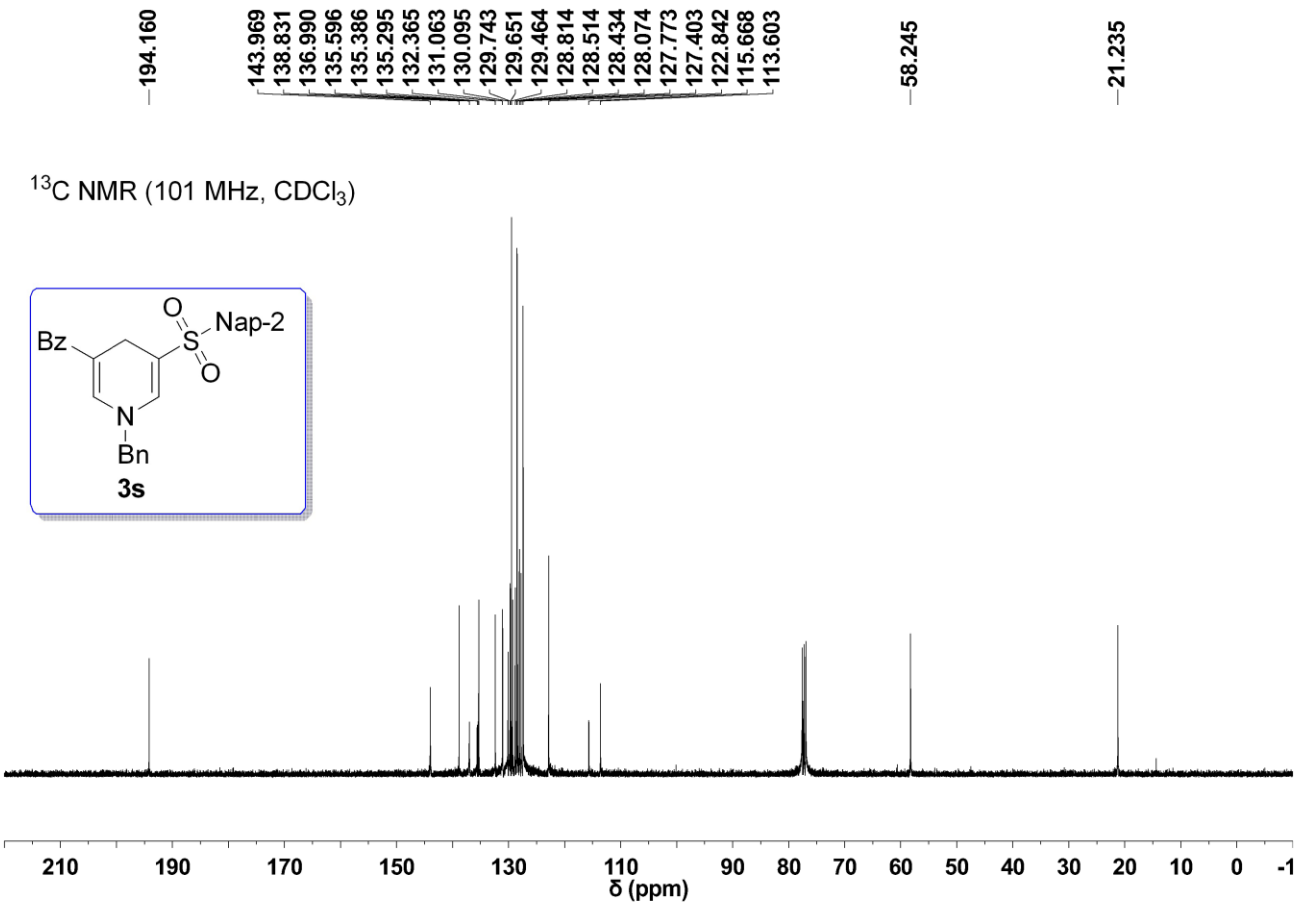

7.747
7.727
7.305
7.284
7.008
3.178
3.049
2.449
2.434
2.418
2.406
2.331
2.315
2.298
1.981
1.965
1.949
1.933
1.917
1H NMR (400 MHz, CDCl3)
O
Ts
N
Me
3q
2.03
2.02
1.00
3.03
1.99
1.99
3.25
2.12
2.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

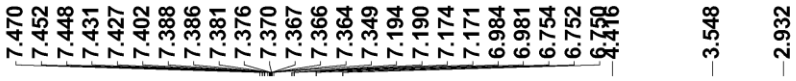

196.105
153.256
144.194
138.653
135.989
129.954
128.165
114.916
109.820
38.938
36.015
25.774
21.818
21.082
20.167
13C NMR (101 MHz, CDCl3)
O
Ts
N
Me
3q
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)


7.771
7.750
7.430
7.412
7.397
7.378
7.358
7.354
7.342
7.324
7.185
7.182
7.166
7.132
6.674
4.424
3.271
2.437
1H NMR (400 MHz, CDCl3)
Bz
Ts
N
Bn
3r
2.05
10.12
2.01
1.04
1.00
2.05
2.04
3.01
δ (ppm)

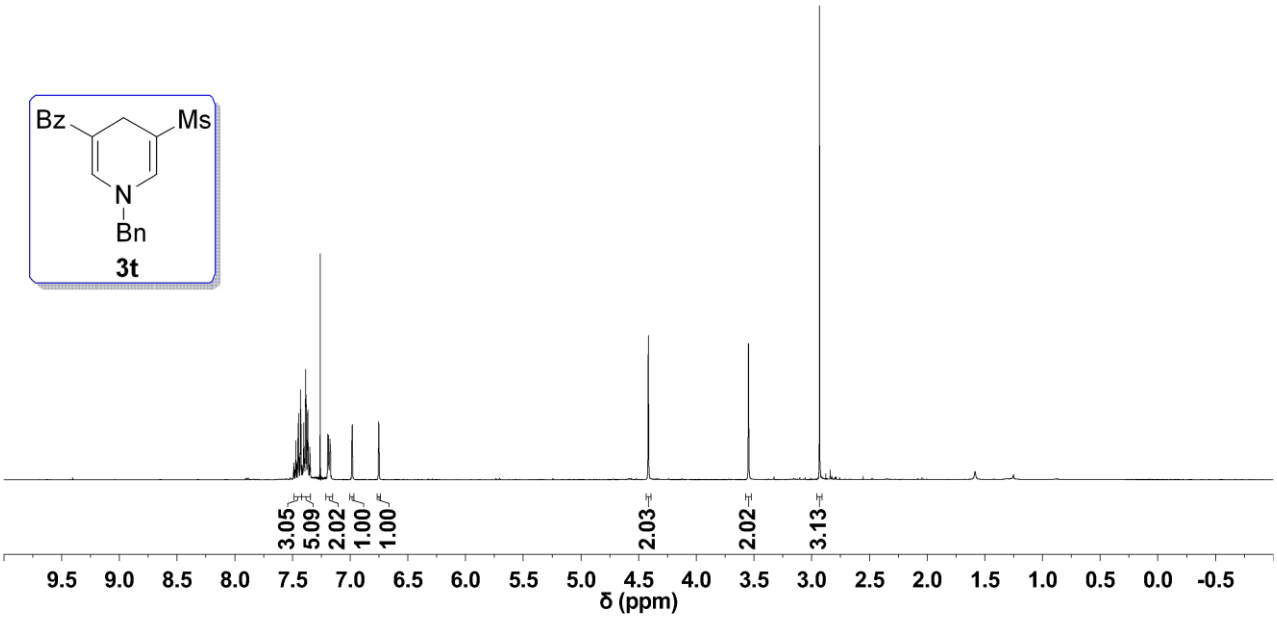

194.255
144.425
144.069
138.925
136.333
135.767
135.415
131.109
130.075
129.512
128.864
128.589
128.495
128.318
127.425
113.559
58.283
21.862
21.224
13C NMR (101 MHz, CDCl3)
Bz
Ts
N
Bn
3r
δ (ppm)

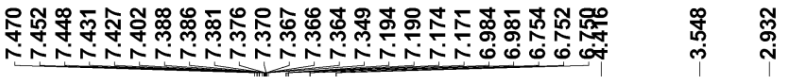

8.501
8.497
8.007
7.988
7.985
7.979
7.957
7.916
7.896
7.812
7.807
7.790
7.786
7.656
7.652
7.650
7.637
7.632
7.616
7.613
7.415
7.410
7.407
7.404
7.392
7.389
7.385
7.380
7.375
7.370
7.360
7.356
7.351
7.348
7.341
7.335
7.330
7.317
7.312
7.300
7.281
7.237
7.234
7.192
7.187
7.172
7.170
7.169
4.442
3.324
1H NMR (400 MHz, CDCl3)
Bz
Nap-2
N
Bn
3s
1.00
2.13
1.10
2.13
8.03
1.08
2.13
1.02
2.09
2.00
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)


194.160
143.969
138.831
136.990
135.596
135.386
135.295
132.365
131.063
130.095
129.743
129.651
129.464
128.814
128.514
128.434
128.074
127.773
127.403
122.842
115.668
113.603
58.245
21.235
13C NMR (101 MHz, CDCl3)
Bz
Nap-2
N
Bn
3s
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)

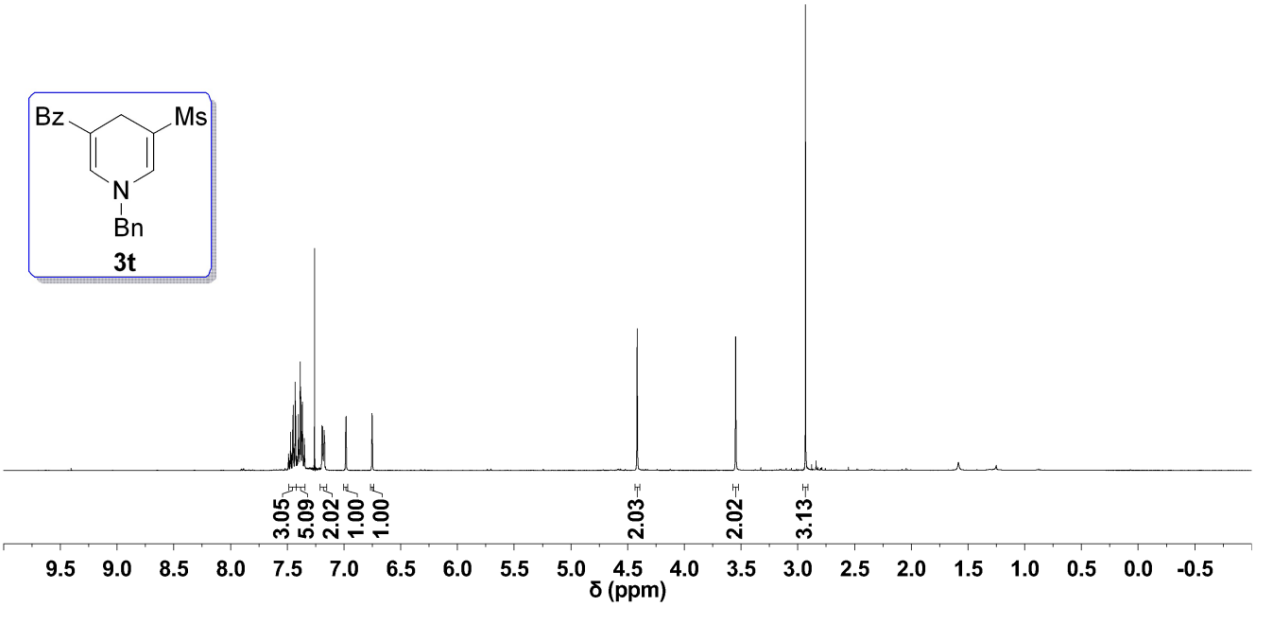


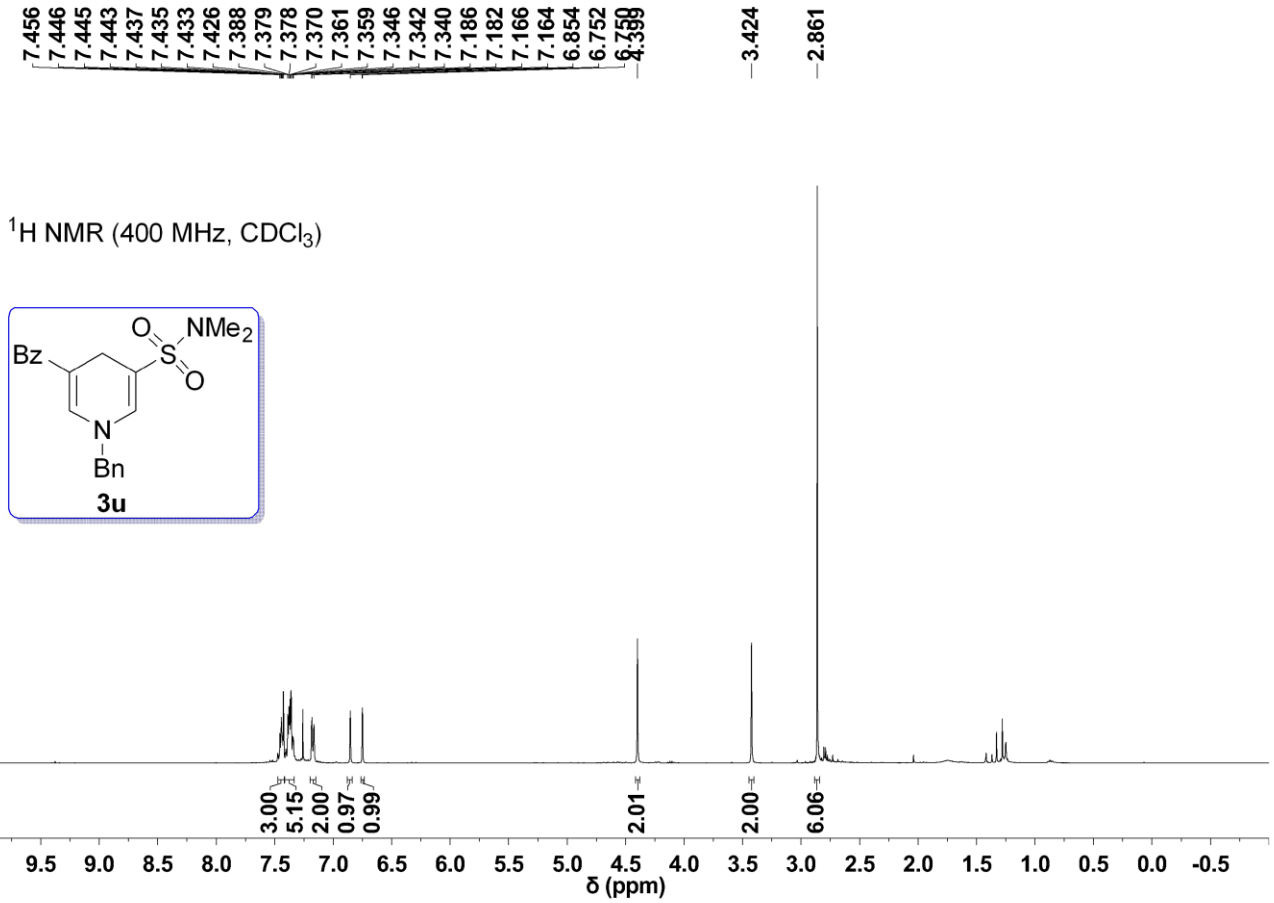
^{1}H NMR (400 MHz, $CDCl_3$)

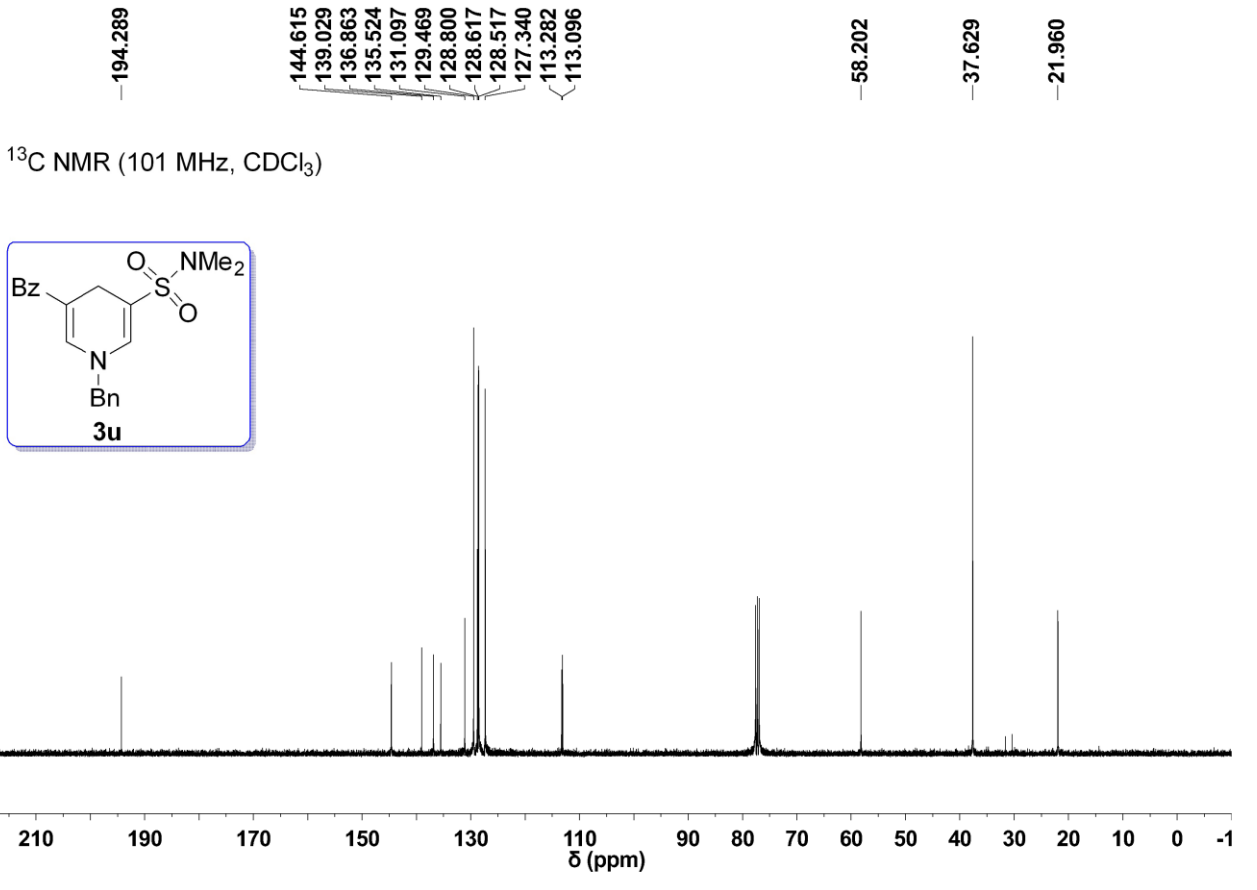


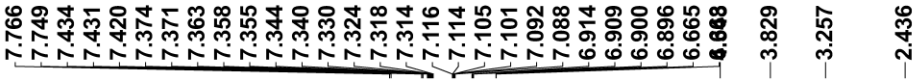


^{1}H NMR (400 MHz, $CDCl_3$)

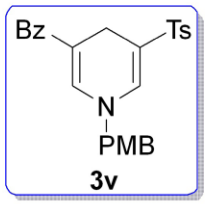


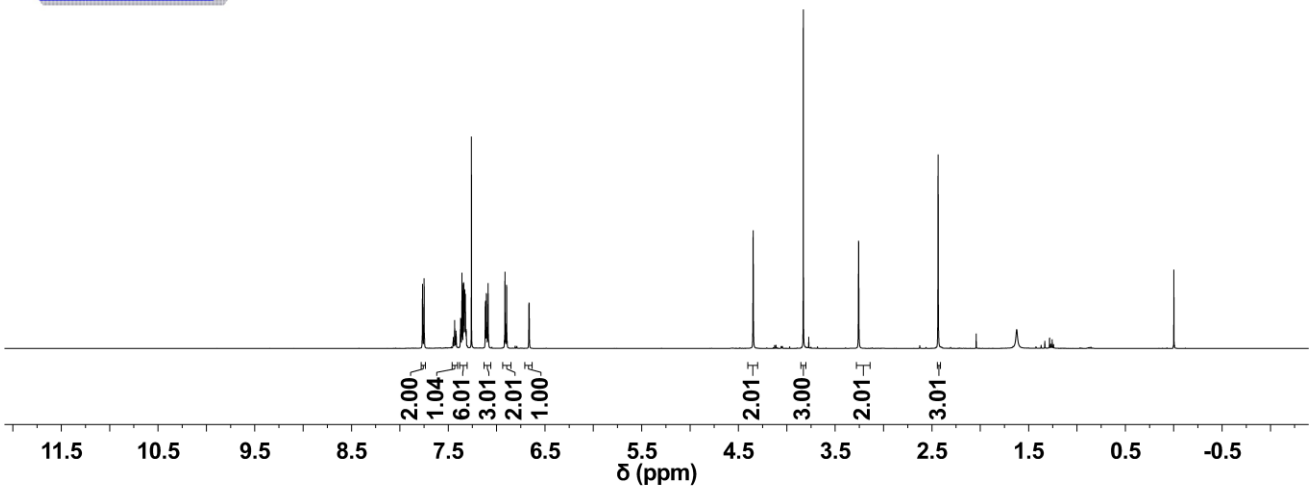

7.456
7.446
7.445
7.443
7.437
7.435
7.433
7.426
7.388
7.379
7.378
7.370
7.361
7.359
7.346
7.342
7.340
7.186
7.182
7.166
7.164
6.854
6.752
3.424
2.861
1H NMR (400 MHz, CDCl3)
Bz
NMe2
O
S
O
N
Bn
3u
3.00
5.15
2.00
0.97
0.99
2.01
2.00
6.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)

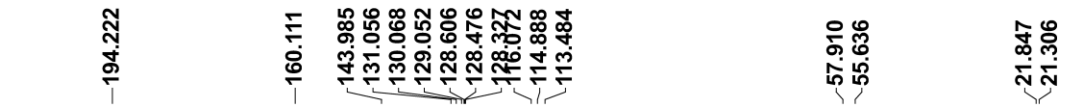

194.289
144.615
139.029
136.863
135.524
131.097
129.469
128.800
128.617
128.517
127.340
113.282
113.096
58.202
37.629
21.960
13C NMR (101 MHz, CDCl3)
Bz
NMe2
O
S
O
N
Bn
3u
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)



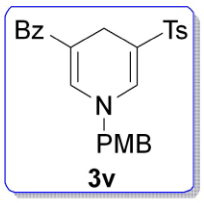
^{1}H NMR (500 MHz, $CDCl_3$)

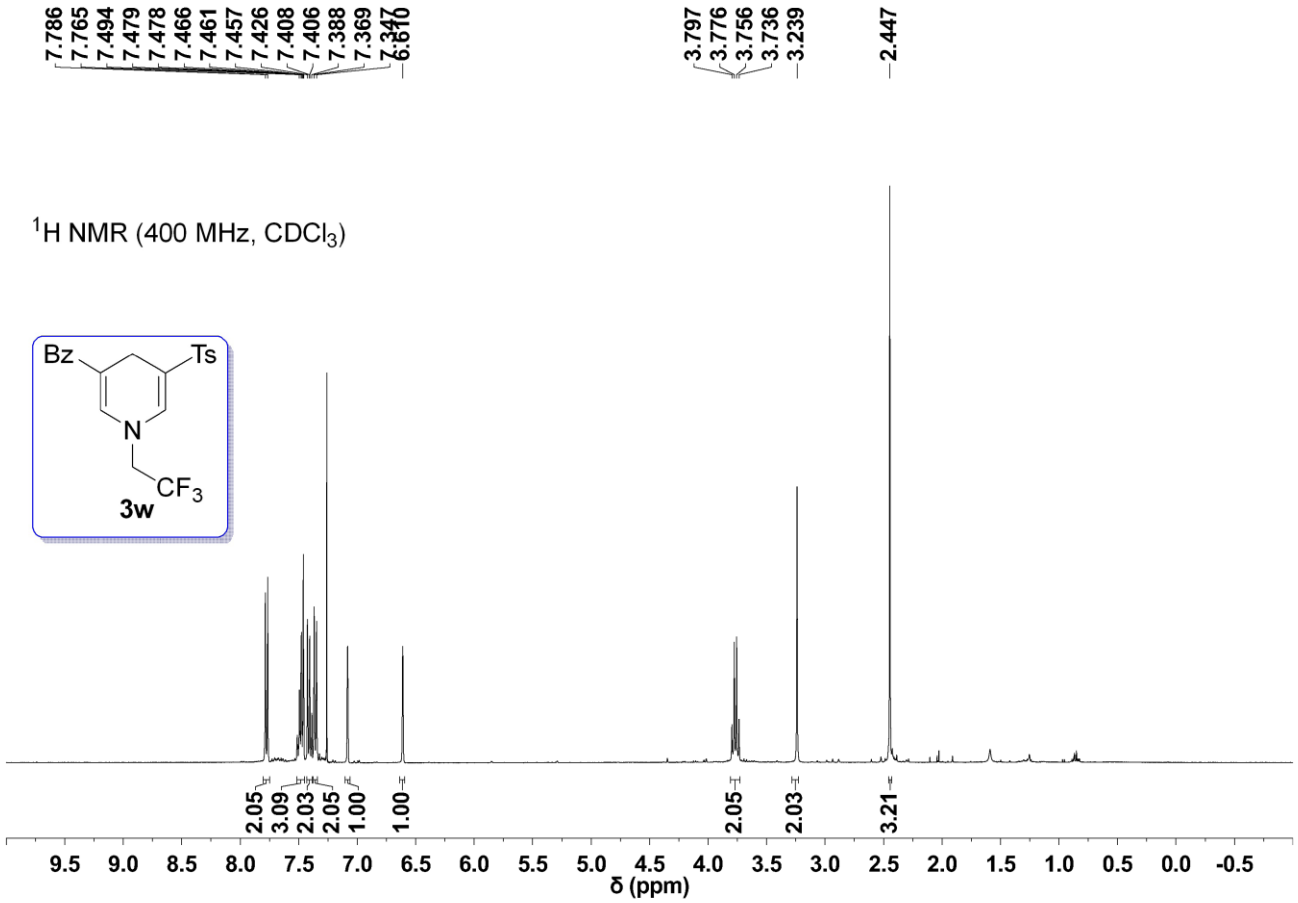


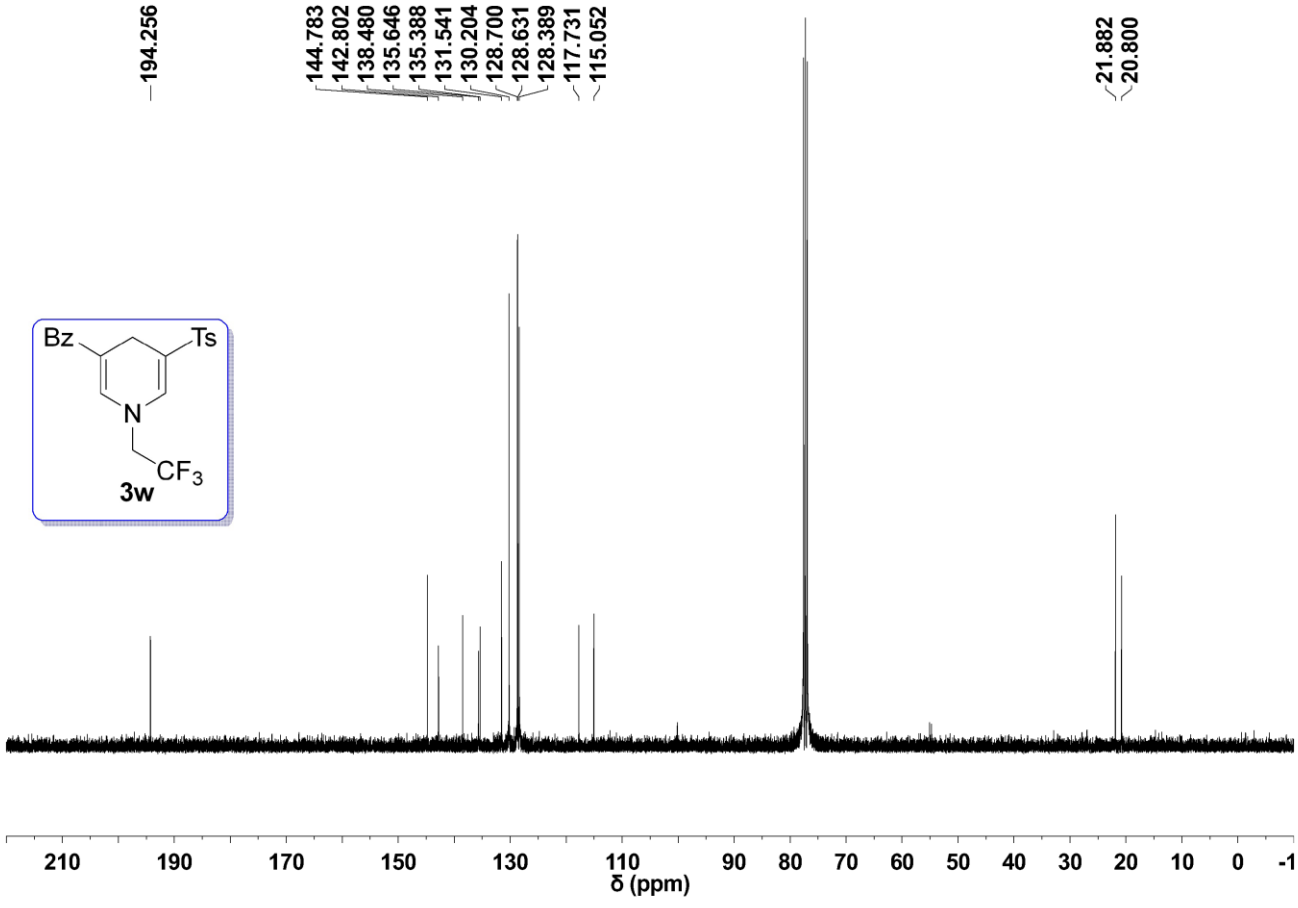


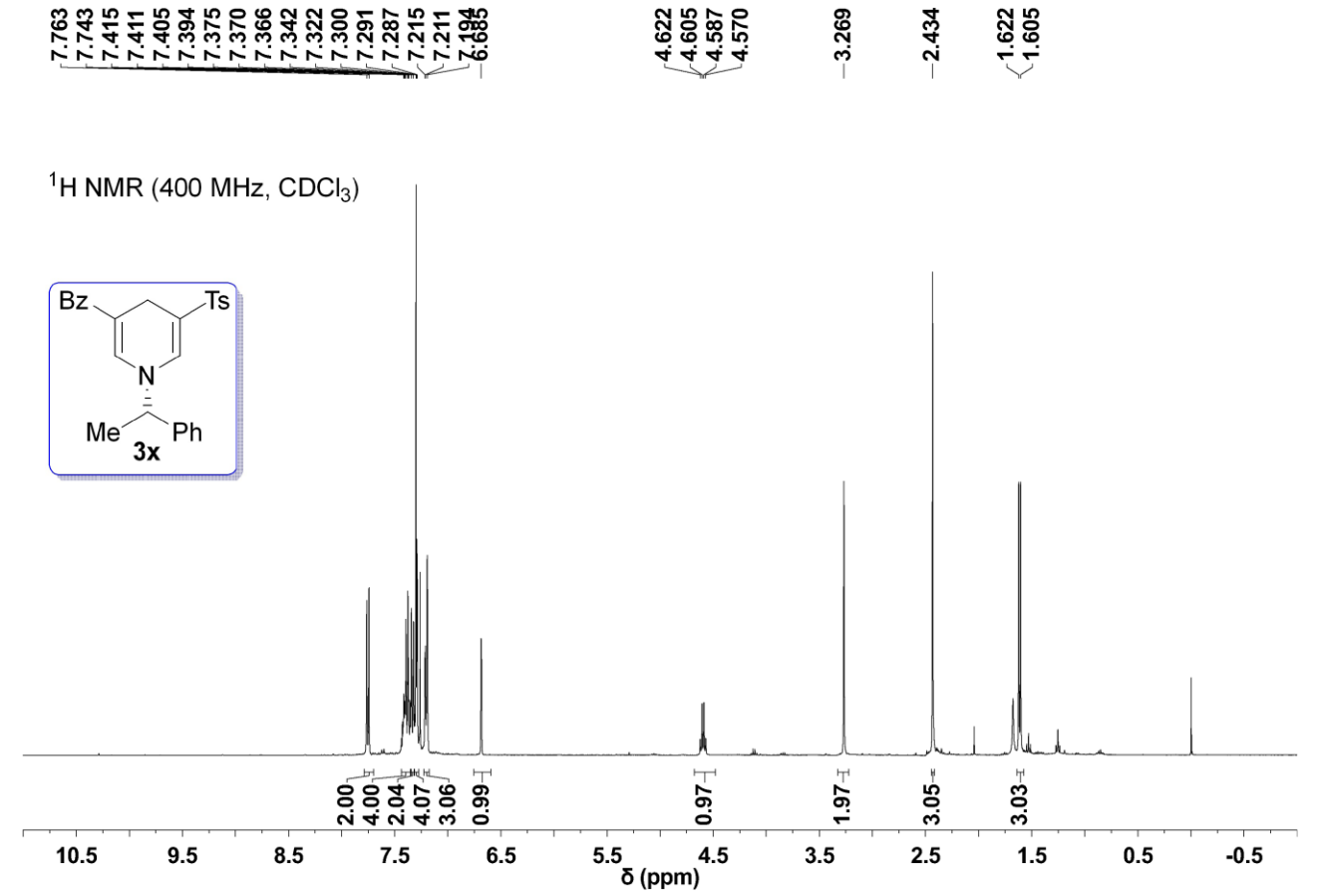


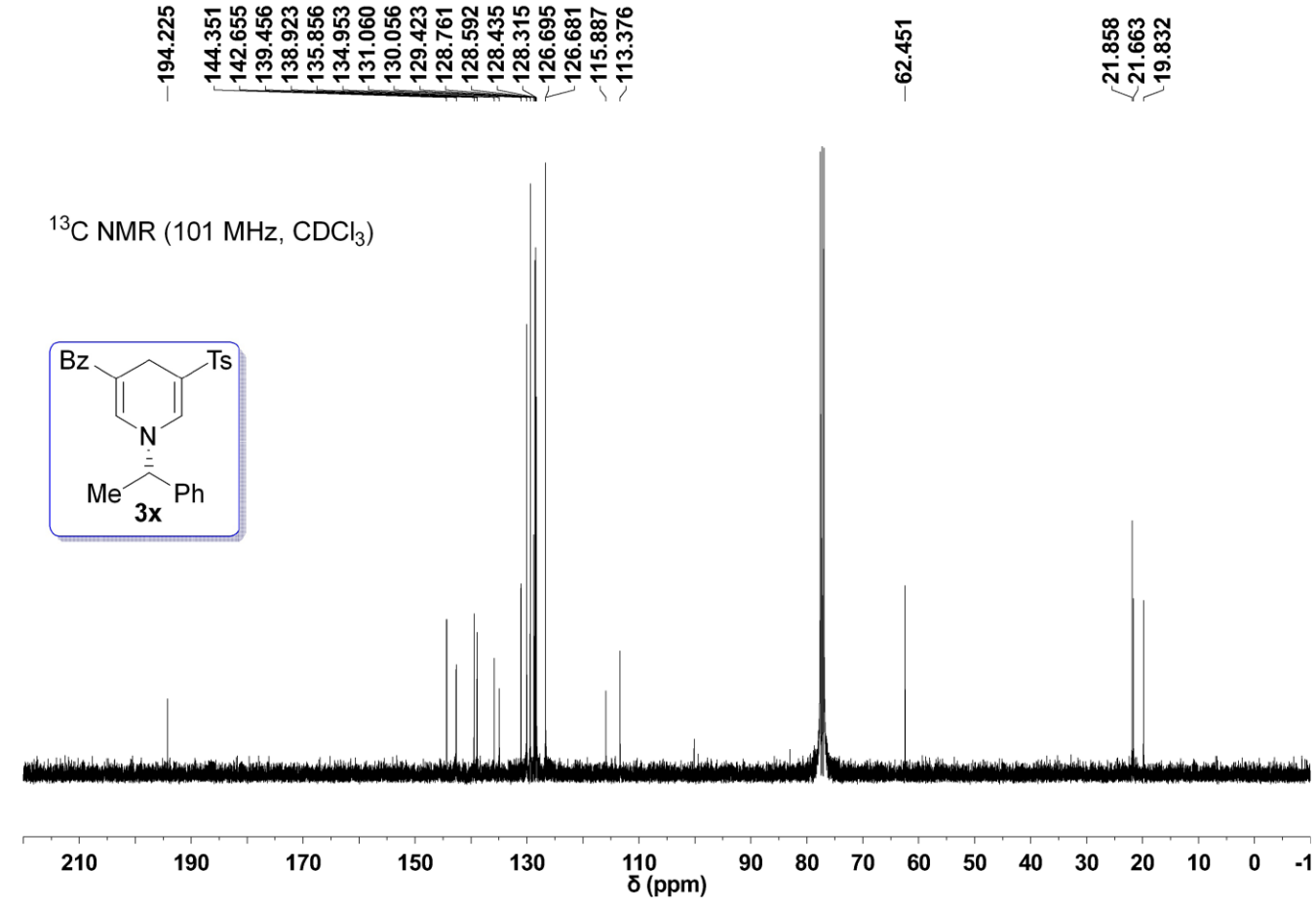
^{13}C NMR (126 MHz, $CDCl_3$)

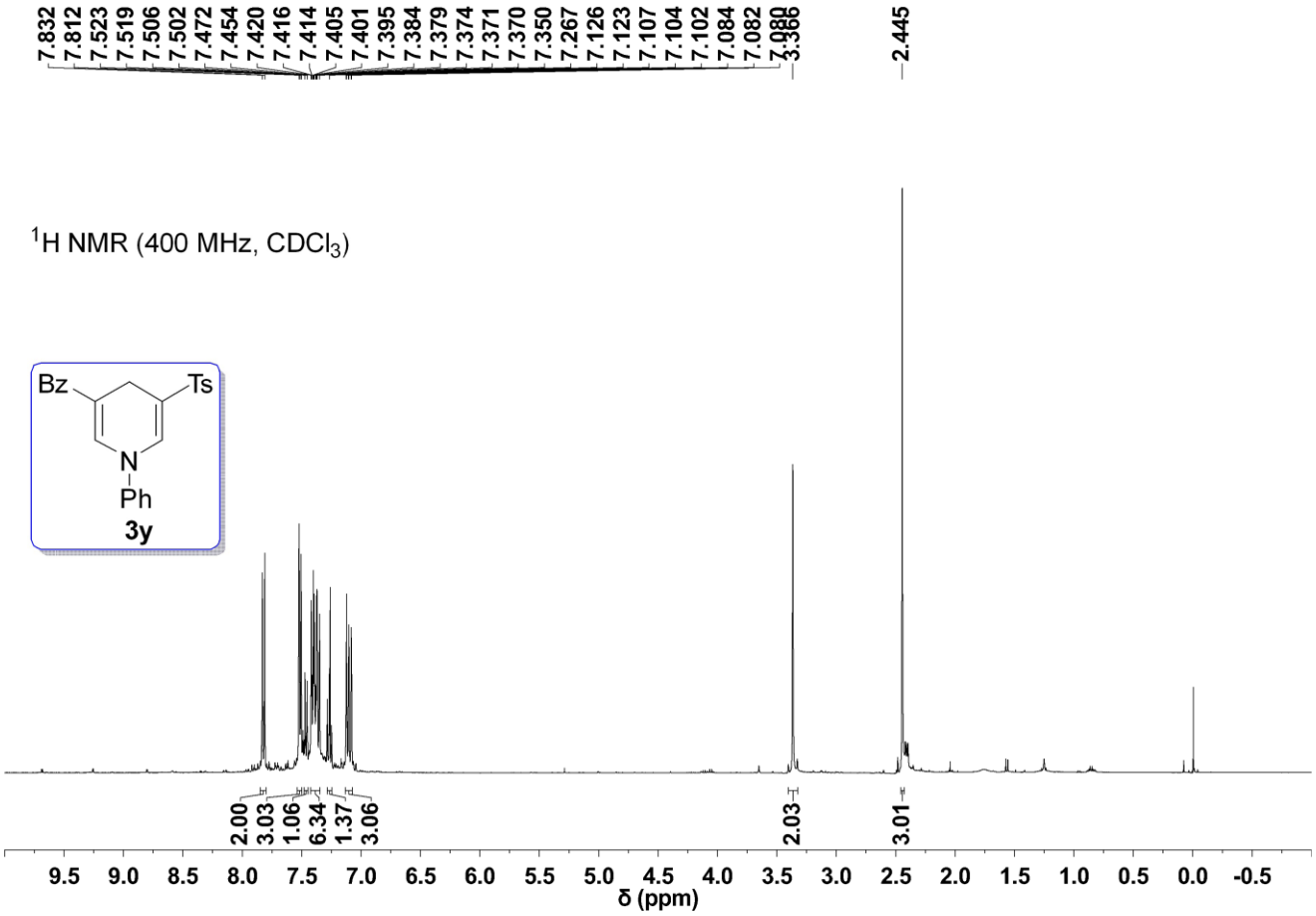


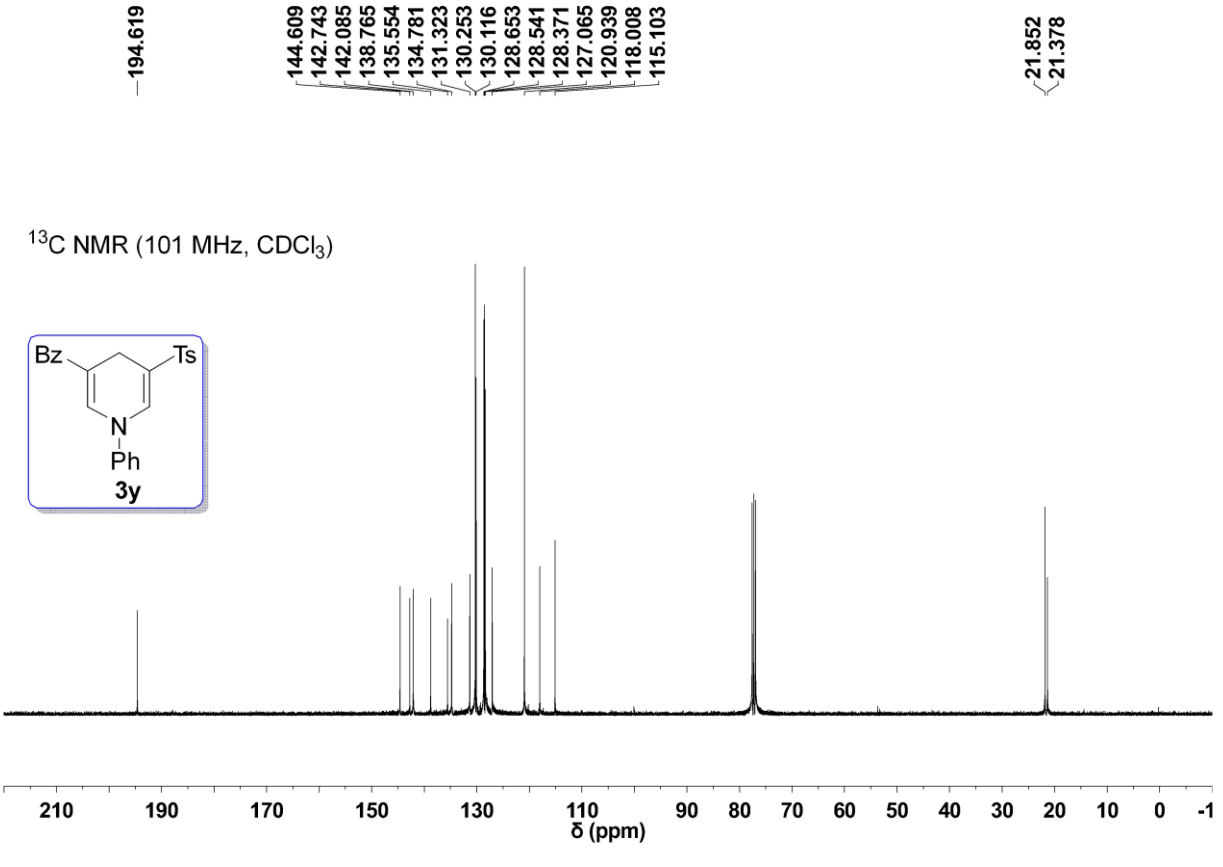

7.786
7.765
7.494
7.479
7.478
7.466
7.461
7.457
7.426
7.408
7.406
7.388
7.369
7.347
6.610
3.797
3.776
3.756
3.736
3.239
2.447
1H NMR (400 MHz, CDCl3)
Bz
Ts
N
CF3
3w
2.05
3.09
2.03
2.05
1.00
1.00
2.05
2.03
3.21
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)


194.256
144.783
142.802
138.480
135.646
135.388
131.541
130.204
128.700
128.631
128.389
117.731
115.052
21.882
20.800
Bz
Ts
N
CF3
3w
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -1
δ (ppm)

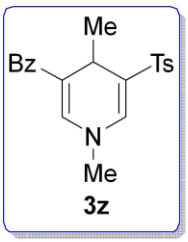

7.763
7.743
7.415
7.411
7.405
7.394
7.375
7.370
7.366
7.342
7.322
7.300
7.291
7.287
7.215
7.211
7.194
6.685
4.622
4.605
4.587
4.570
3.269
2.434
1.622
1.605
1H NMR (400 MHz, CDCl3)
Bz
Ts
N
Me
Ph
3x
2.00
4.00
2.04
4.07
3.06
0.99
0.97
1.97
3.05
3.03
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)

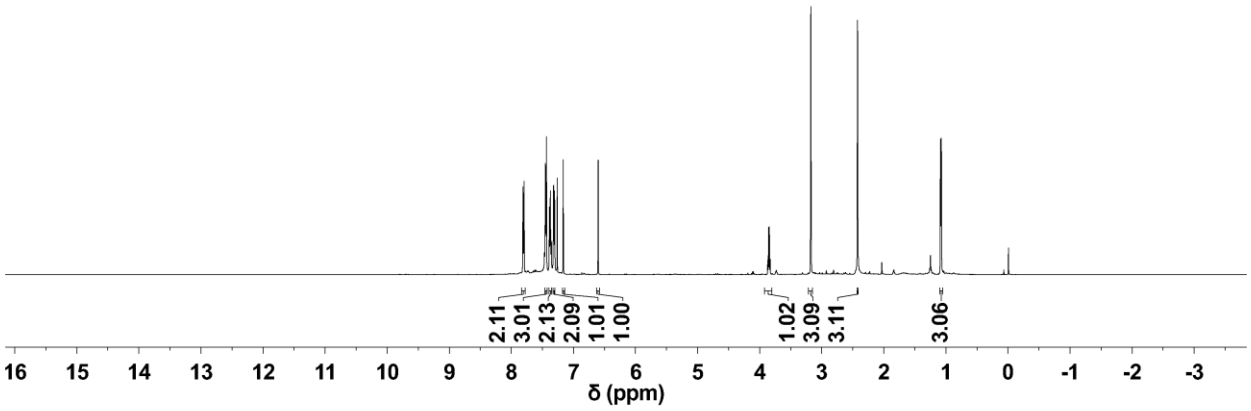

194.225
144.351
142.655
139.456
138.923
135.856
134.953
131.060
130.056
129.423
128.761
128.592
128.435
128.315
126.695
126.681
115.887
113.376
62.451
21.858
21.663
19.832
13C NMR (101 MHz, CDCl3)
Bz
Ts
N
Me
Ph
3x
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
δ (ppm)


7.832
7.812
7.523
7.519
7.506
7.502
7.472
7.454
7.420
7.416
7.414
7.405
7.401
7.395
7.384
7.379
7.374
7.371
7.370
7.350
7.267
7.126
7.123
7.107
7.104
7.102
7.084
7.082
2.445
1H NMR (400 MHz, CDCl3)
Bz
Ts
N
Ph
3y
2.00
3.03
1.06
6.34
1.37
3.06
2.03
3.01
δ (ppm)

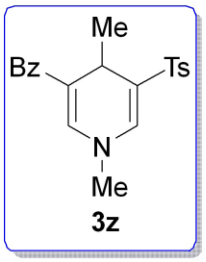

194.619
144.609
142.743
142.085
138.765
135.554
134.781
131.323
130.253
130.116
128.653
128.541
128.371
127.065
120.939
118.008
115.103
21.852
21.378
13C NMR (101 MHz, CDCl3)
Bz
Ts
N
Ph
3y
δ (ppm)

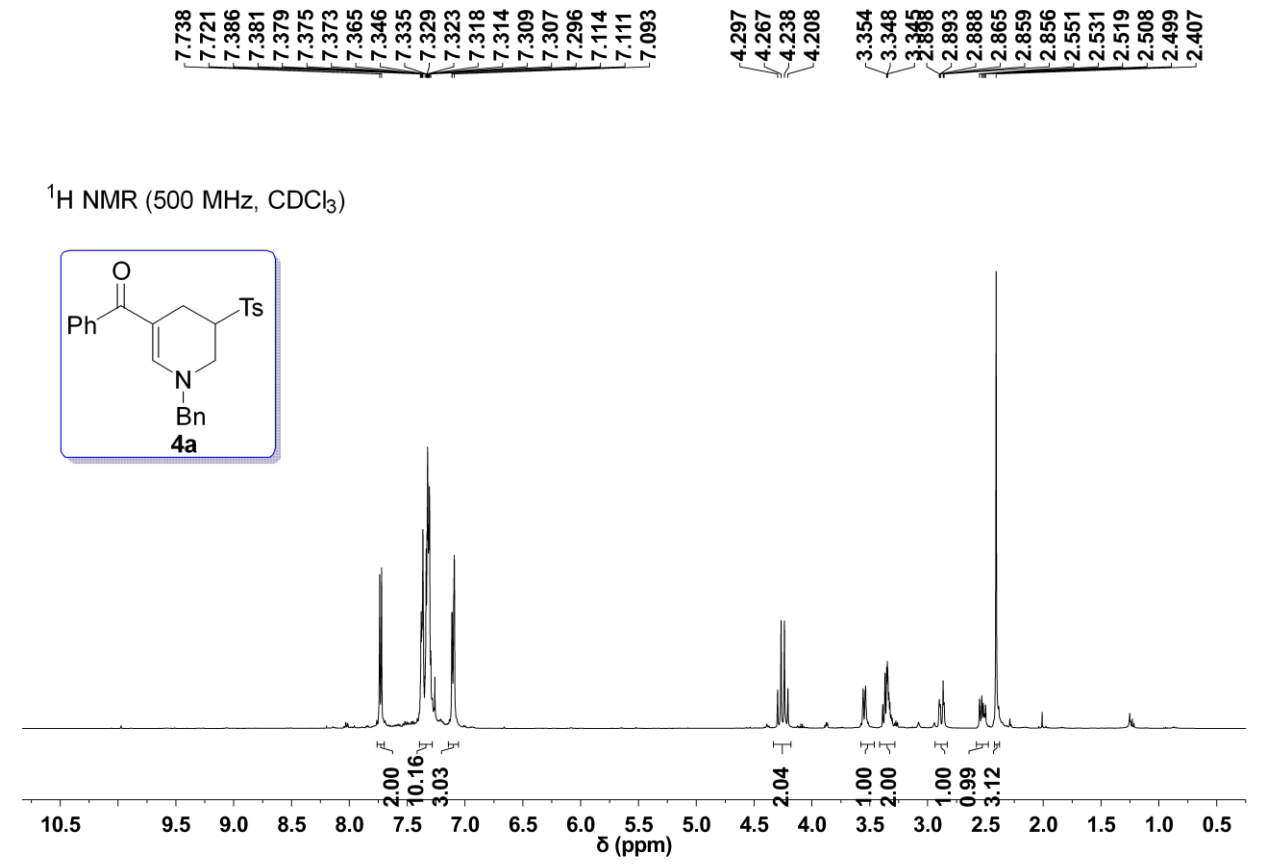
^{1}H NMR (500 MHz, $CDCl_3$)

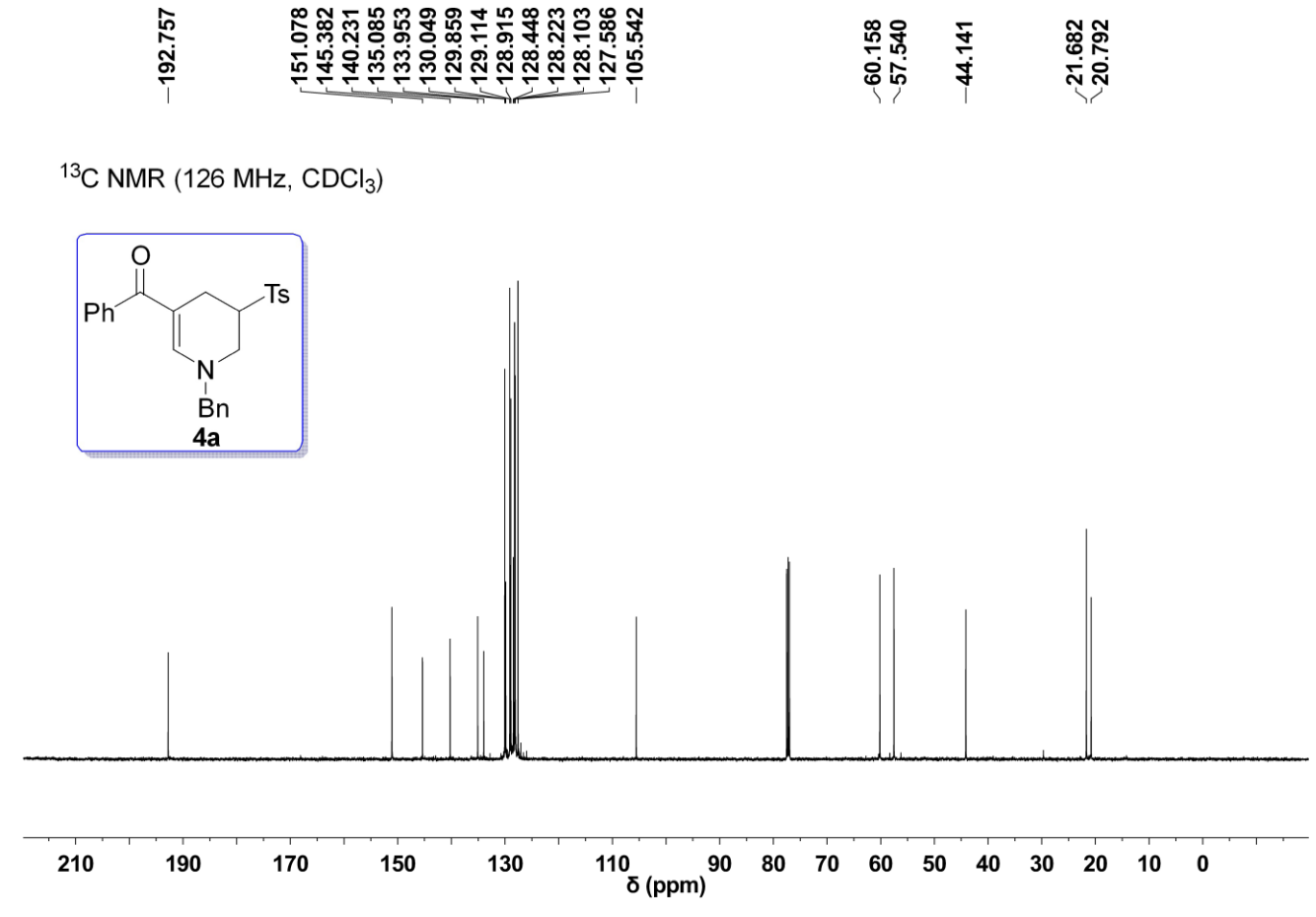


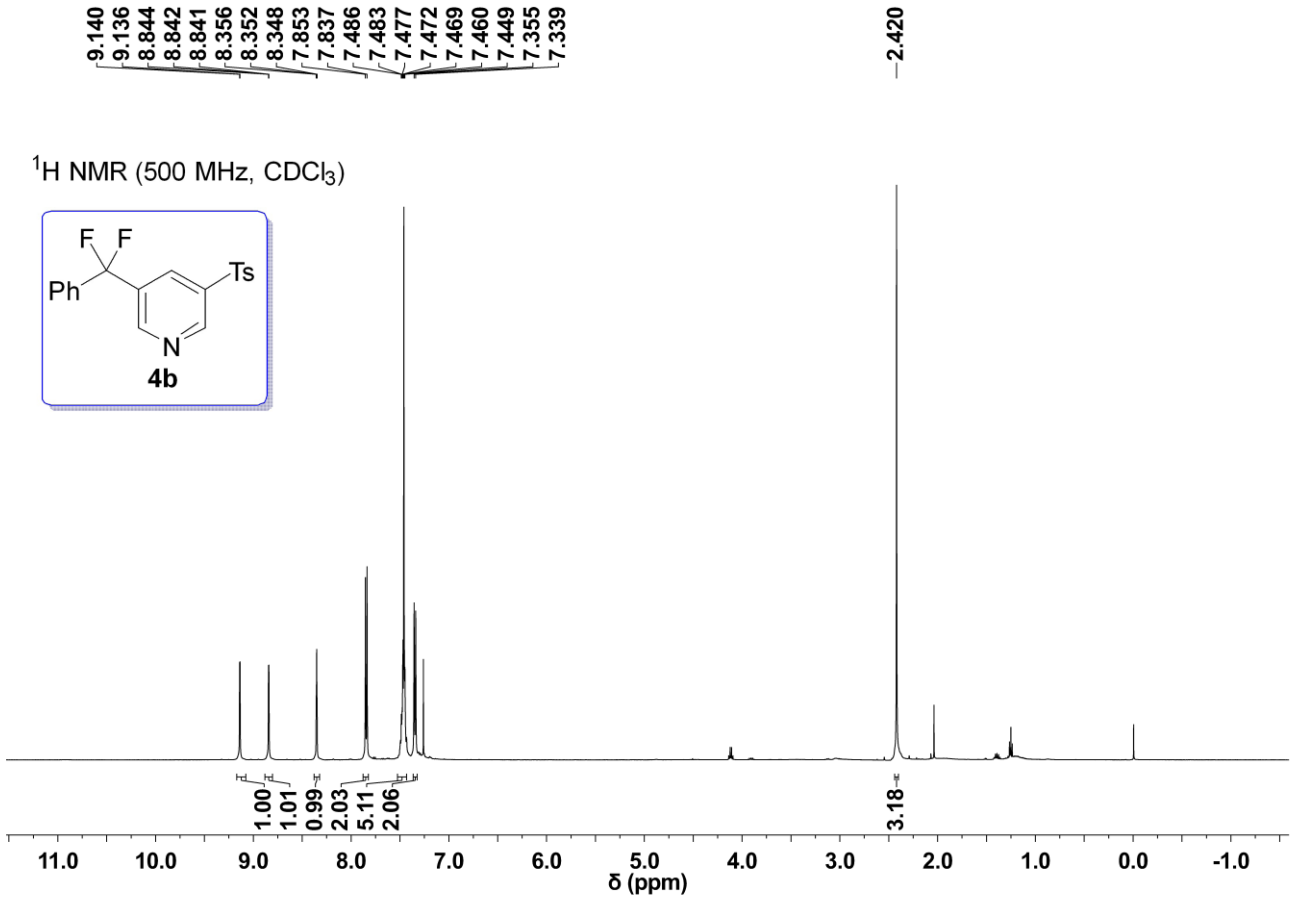


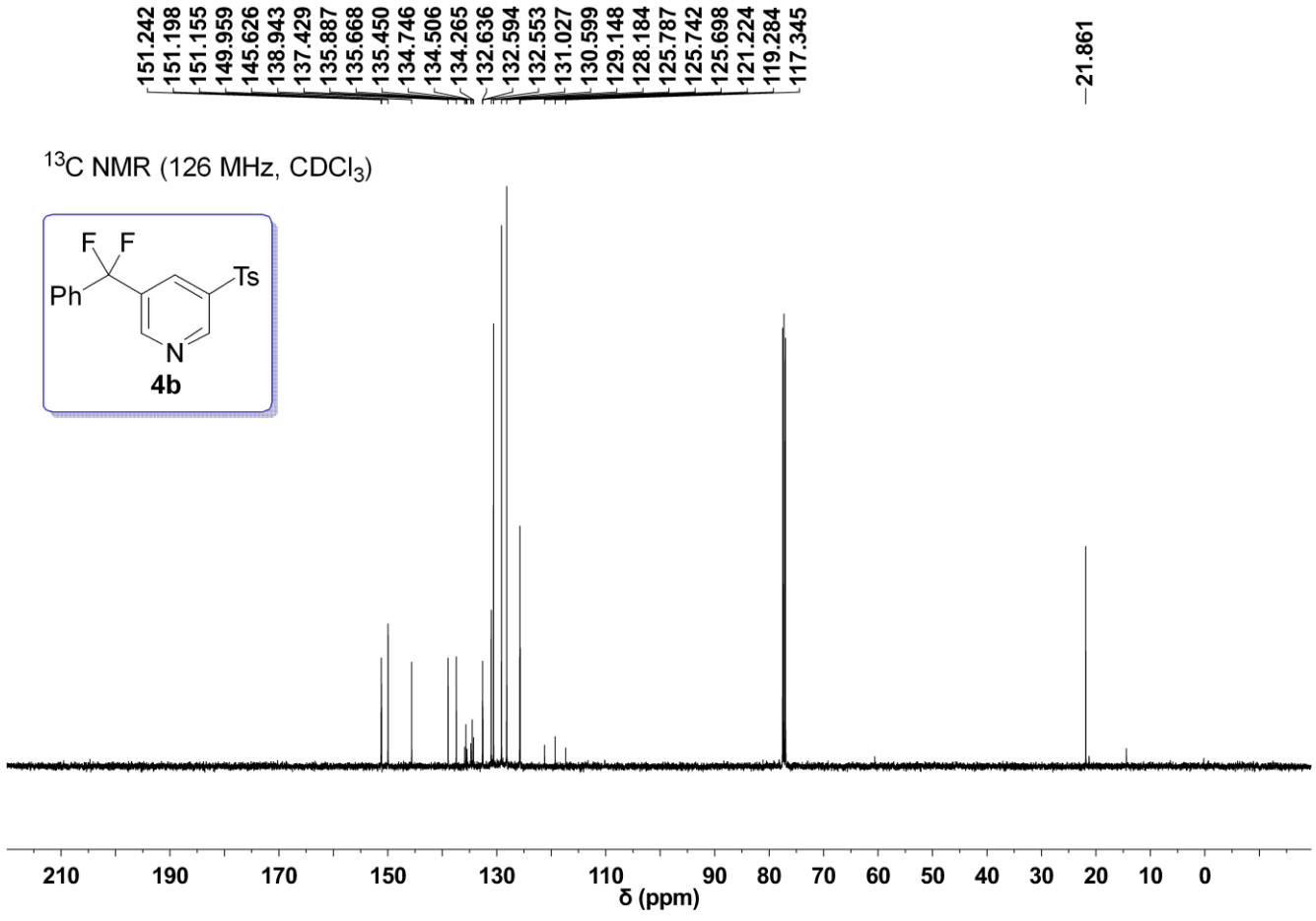
^{13}C NMR (126 MHz, $CDCl_3$)

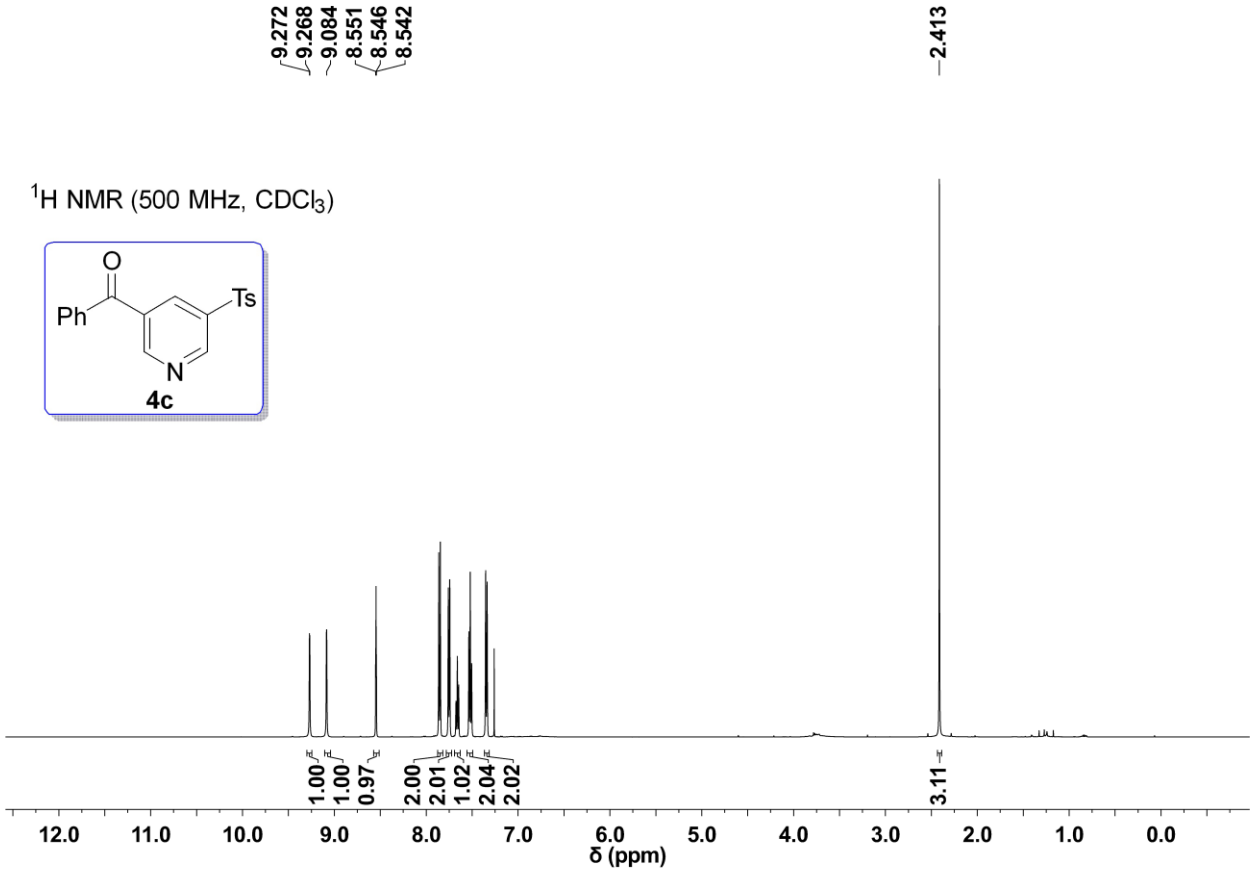


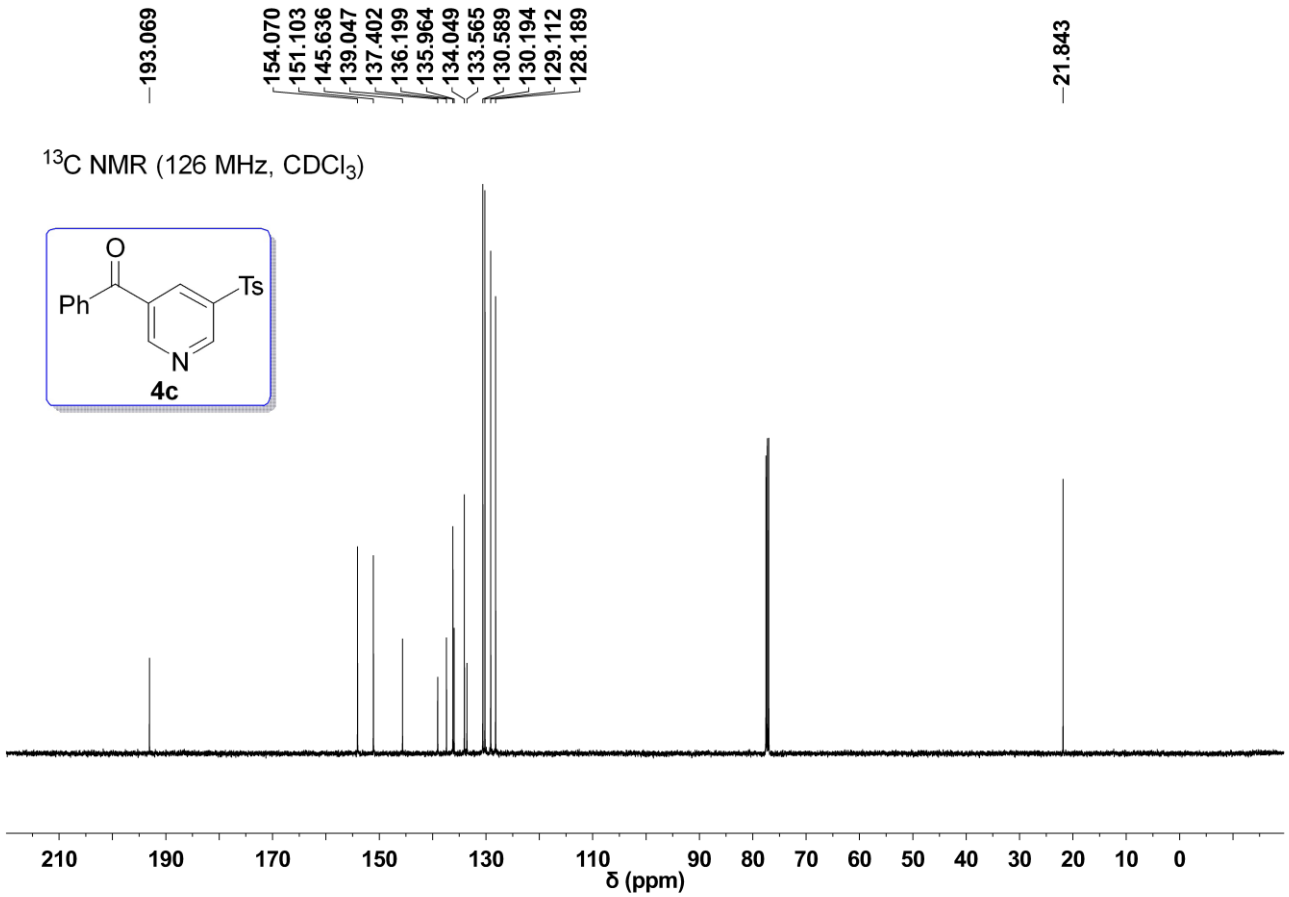

7.738
7.721
7.386
7.381
7.379
7.375
7.373
7.365
7.346
7.335
7.329
7.323
7.318
7.314
7.309
7.307
7.296
7.114
7.111
7.093
4.297
4.267
4.238
4.208
3.354
3.348
2.893
2.888
2.865
2.859
2.856
2.551
2.531
2.519
2.508
2.499
2.407
1H NMR (500 MHz, CDCl3)
O
Ph
Ts
N
Bn
4a
2.00
10.16
3.03
2.04
1.00
2.00
1.00
0.99
3.12
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
δ (ppm)

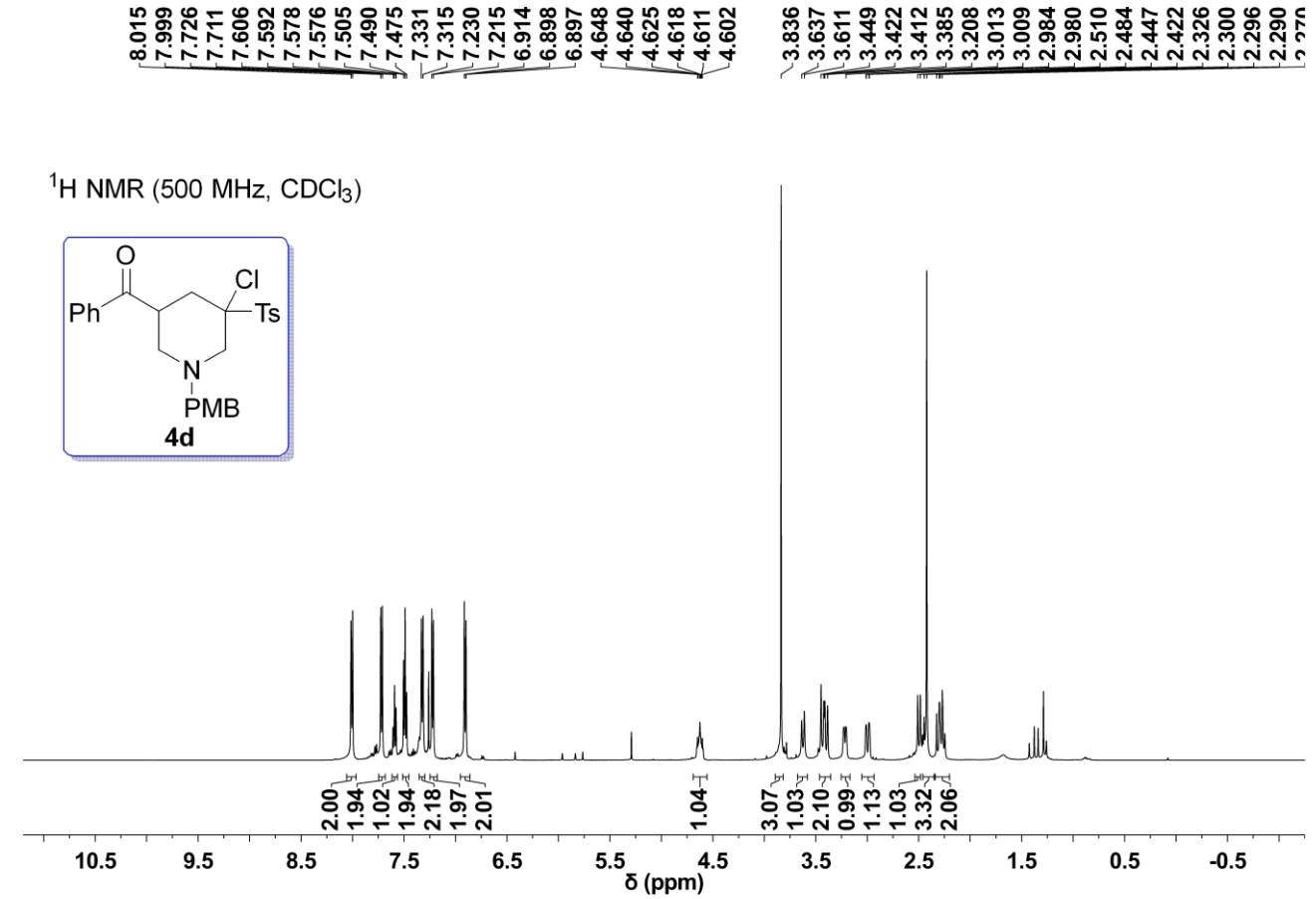

192.757
151.078
145.382
140.231
135.085
133.953
130.049
129.859
129.114
128.915
128.448
128.223
128.103
127.586
105.542
60.158
57.540
44.141
21.682
20.792
13C NMR (126 MHz, CDCl3)
O
Ph
Ts
N
Bn
4a
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)

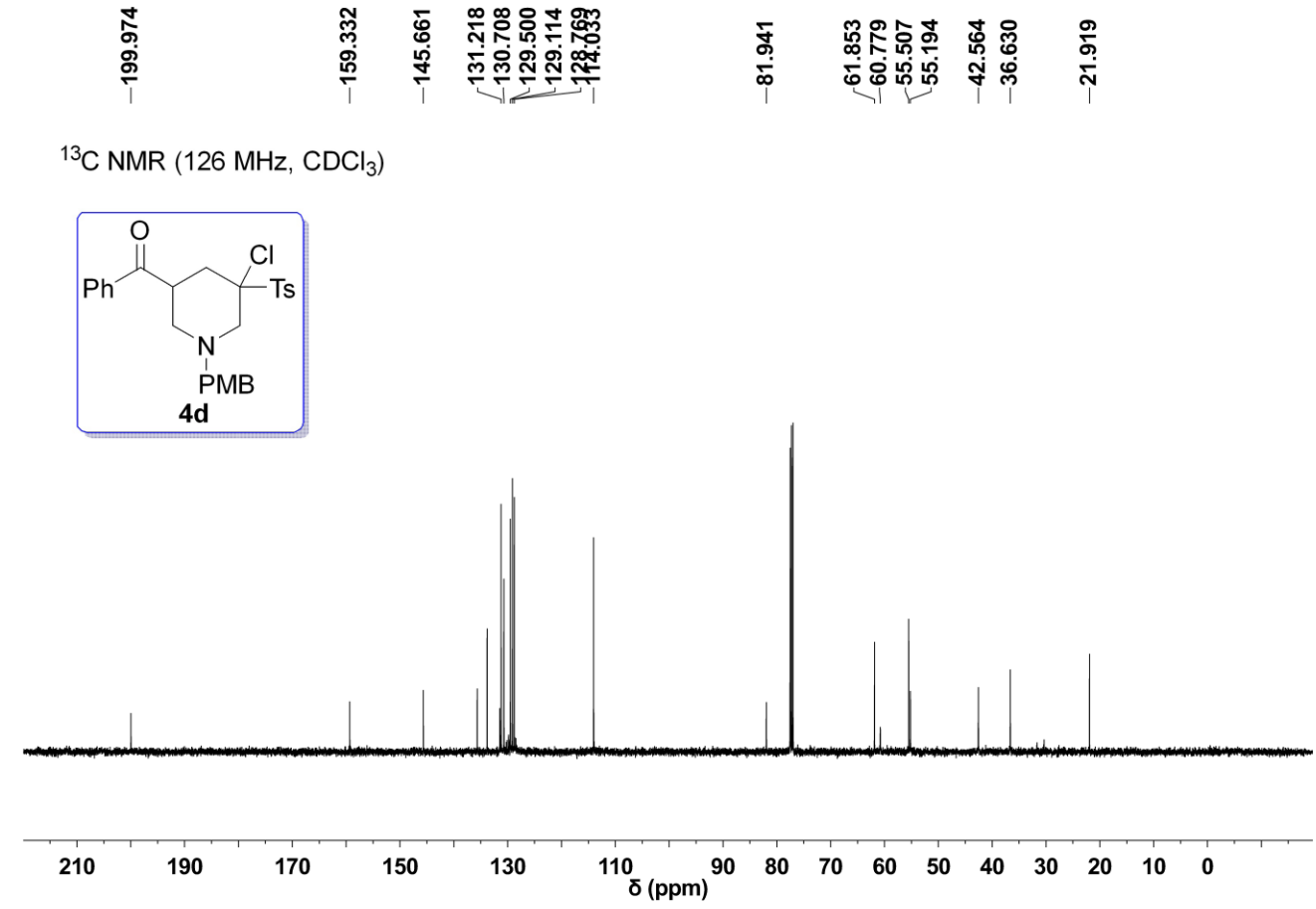

9.140
9.136
8.844
8.842
8.841
8.356
8.352
8.348
7.853
7.837
7.486
7.483
7.477
7.472
7.469
7.460
7.449
7.355
7.339
2.420
1H NMR (500 MHz, CDCl3)
F F
Ph
Ts
N
4b
1.00
1.01
0.99
2.03
5.11
2.06
3.18
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
δ (ppm)


151.242
151.198
151.155
149.959
145.626
138.943
137.429
135.887
135.668
135.450
134.746
134.506
134.265
132.636
132.594
132.553
131.027
130.599
129.148
128.184
125.787
125.742
125.698
121.224
119.284
117.345
21.861
13C NMR (126 MHz, CDCl3)
F F
Ph
Ts
N
4b
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)


9.272
9.268
9.084
8.551
8.546
8.542
2.413
1H NMR (500 MHz, CDCl3)
O
Ph
Ts
N
4c
1.00
1.00
0.97
2.00
2.01
1.02
2.04
2.02
3.11
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
δ (ppm)


193.069
154.070
151.103
145.636
139.047
137.402
136.199
135.964
134.049
133.565
130.589
130.194
129.112
128.189
21.843
13C NMR (126 MHz, CDCl3)
O
Ph
Ts
N
4c
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)


8.015
7.999
7.726
7.711
7.606
7.592
7.578
7.576
7.505
7.490
7.475
7.331
7.315
7.230
7.215
6.914
6.898
6.897
4.648
4.640
4.625
4.618
4.611
4.602
3.836
3.637
3.611
3.449
3.422
3.412
3.385
3.208
3.013
3.009
2.984
2.980
2.510
2.484
2.447
2.422
2.326
2.300
2.296
2.290
1H NMR (500 MHz, CDCl3)
O
Cl
Ph
Ts
N
PMB
4d
2.00
1.94
1.02
1.94
2.18
1.97
2.01
1.04
3.07
1.03
2.10
0.99
1.13
1.03
3.32
2.06
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
δ (ppm)


199.974
159.332
145.661
131.218
130.708
129.500
129.114
128.769
114.033
81.941
61.853
60.779
55.507
55.194
42.564
36.630
21.919
13C NMR (126 MHz, CDCl3)
O
Cl
Ph
Ts
N
PMB
4d
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)