# Rhodium/Selenium Dual Catalysis for Accessing 2-Aminopyrroles from *N*-Sulfonyl-1,2,3-triazoles

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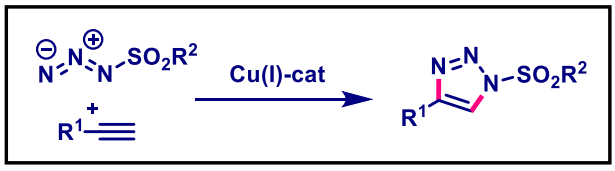
## 1. Methods

All reactions were carried out under nitrogen atmosphere in screw cap reaction tubes and the workups were performed under air. All the solvents used for the reactions were dried by following the reported procedures. Unless otherwise noted, all materials were purchased from commercial suppliers and used as received. All sulfonyl azides were prepared in house using conventional procedure. Reactions were monitored using thin-layer chromatography ($SiO_2$). A gradient elution using petroleum ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel $60F_{254}$). TLC plates were visualized with UV light (254 nm) or $KMnO_4$ stain or Anisaldehyde stain. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. NMR studies were performed on Bruker Advance DPX at 400 MHz ($^1H$) or 500 MHz ($^1H$) and at 100 MHz ($^{13}C$) or 125 MHz ($^{13}C$), respectively. Chemical shifts ($\delta$) are reported in ppm, using the residual solvent peak in $CDCl_3$ ($\delta H = 7.26$ and $\delta C = 77.16$) ppm as internal standards, and coupling constants (*J*) are given in Hz. HRMS were recorded with Bruker MaXis impact mass spectrometer using ESI-TOF techniques.

## 2. Experimental Procedures

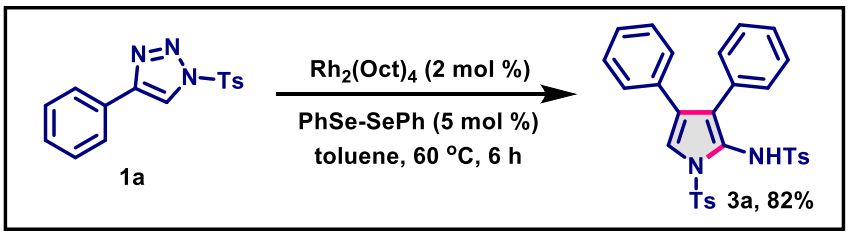
### (a) General procedure for the synthesis of *N*-sulfonyl-1, 2, 3-triazoles (1)[1]




To a solution of terminal alkyne (150 mg, 1 equiv.) in 10 mL toluene, 1 equiv. of sulphonyl azide was added dropwise while stirring the solution. To this mixture, 5 mol % of CuTc was added. The reaction was monitored by TLC. After 2-3 h, the reaction mixture was quenched with ammonium chloride ($NH_4Cl$) and the organic layer was extracted with ethyl acetate

(EtOAc). The pure product was obtained by washing the organic layer with celite-silica-sodium sulfate and concentrating it under high pressure.

**(b) Typical procedure for the synthesis of 2-aminopyrroles:** Preparation *N*-(2,4-diphenyl-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide.

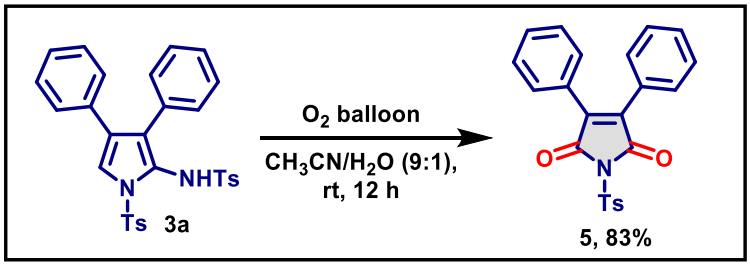



4-Phenyl-1-tosyl-1*H*-1,2,3-triazole **1a** (0.2 mmol), $Rh_2(Oct)_4$ (2 mol %) and diphenyl diselenide (5 mol %) were added to an oven-dried screw cap reaction tube equipped with a stir bar. The tube was evacuated and refilled with nitrogen three times. Then, toluene (2.0 mL) was added *via* syringe. The reaction mixture was heated to 60 °C for 6 h. After the TLC analysis, it was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was purified by flash column chromatography (silica gel, mesh 100-200; hexane: ethyl acetate; 80:20) to give the product **3a** (44 mg, 82%).

**(c) Gram scale synthesis**

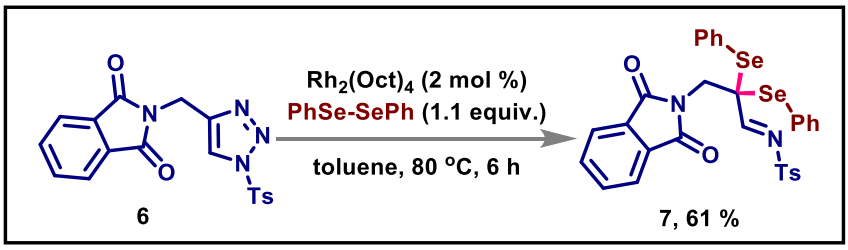
4-Phenyl-1-tosyl-1*H*-1,2,3-triazole **1a** (1.0 g), diphenyl diselenide (5 mol %) and $Rh_2(Oct)_4$ (0.5 mol %) were added to an ovendried 100 mL reaction tube equipped with a stir bar. The tube was evacuated and refilled with argon three times. Then, toluene (30 mL) was added via syringe. The reaction mixture was heated to 60 ° C for 24 h in an oil bath. Then the resulting mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. Then the solution was evaporated under reduced pressure and residue was purified by flash column chromatography (silica gel, mesh 100-200; hexane: ethyl acetate; 80:20) to give the product **3a** (0.65 g, 72%).

**(d) Functionalization**: Synthesis of 3,4-diphenyl-1-tosyl-1*H*-pyrrole-2,5-dione.



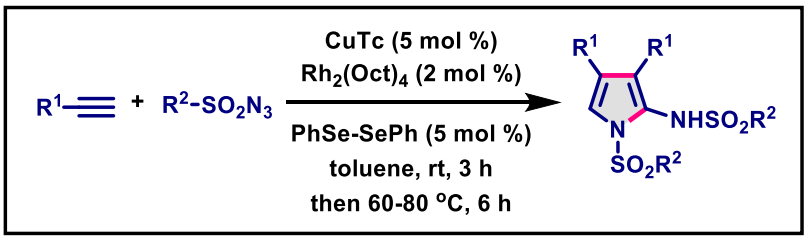
**3a** (50 mg) was taken in a clean and dry reaction tube connected with $O_2$ balloon. Then, acetonitrile:water (9:1) (2 mL) was added via syringe. Reaction tube was stoppered and the resulting reaction mixture was stirred at room tempereture for 12 h. Upon completion of the reaction as monitored by TLC, the solvent was evaporated under reduced pressure and the residue was purified by column chromatography (silica gel, mesh 100-200; hexane: ethyl acetate; 70:30) to give the spirocyclic product **5** (31 mg, 83%).

**(e) 1,1-insetion: access to selenoketals.**




2-((1-tosyl-1*H*-1,2,3-triazol-4-yl)methyl)isoindoline-1,3-dione **6** (0.2 mmol), diphenyl diselenide (1.1 equiv.), $Rh_2(Oct)_4$ ( 2 mol %) and toluene (2 mL) were added to an oven-dried culture tube equipped with a stir bar. The reaction mixture heated at 80 °C for 6 h. After the resulting mixture was cooled to room temperature, filtered through cotton wool, washed with ethyl acetate and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, mesh 100-200; hexane: ethyl acetate; 80:20) to give the product **7** (81 mg, 61%).

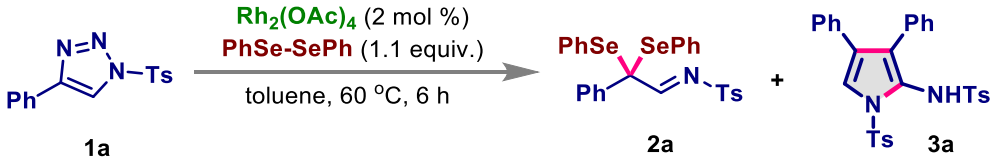
**(f) Typical procedure for the all-in-one-pot synthesis of 3a from terminal alkynes**.




Phenylacetylene (0.3 mmol), $TsN_3$ (0.3 mmol), CuTc (5 mol %), diphenyl diselenide (5 mol %), $Rh_2(Oct)_4$ (2 mol %) and toluene (3 mL) were added to an oven-dried culture tube equipped with a stir bar. The reaction mixture was stirred at room temperature for 3-4 h, and then heated at 60 °C for 6 h. After the resulting mixture was cooled to room temperature, filtered through cotton wool, washed with ethyl acetate and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, mesh 100-200;

hexane: ethyl acetate; 80:20) to give the product **3** (58 mg, 71%). The one-pot process was also examined with differently substituted phenylacetylenes with tosyl azide to produce **4** (67%), **9** (76%), **12** (52%) and **26** (59%).

## 3. Optimization of the reaction



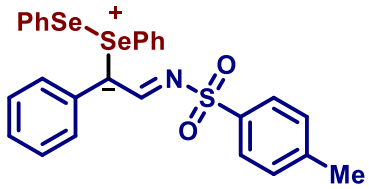

| Entry | Change in reaction conditions | Yield of **2** (%)[b] | Yield of **3** (%)[b] |
|---|---|---|---|
| 1 | None | trace | 64 |
| | ***Control studies*** | | |
| 2 | Only $Rh_2(OAc)_4$ | 0 | 0 |
| 3 | Only $(PhSe)_2$ | 0 | 0 |
| 4 | With 20 mol% $(PhSe)_2$ | 0 | 72 |
| 5 | With 10 mol% $(PhSe)_2$ | 0 | 79 |
| 6 | With 5 mol% $(PhSe)_2$ | 0 | 78 |
| | ***Change in $(PhSe)_2$*** | | |
| 7 | With 5 mol% ($p$-F-PhSe)$_2$ | 0 | 62 |
| 8 | With 5 mol% ($p$-OMe-PhSe)$_2$ | 0 | 46 |
| 9 | using 5 mol% PhSePh | - | <10 |
| 10 | With 5 mol% $(PhTe)_2$ | - | 25 |
| 11 | With 5 mol% $PPh_3$ | - | 0 |
| 12 | With 5 mol% PhSPh | - | 0 |
| 13 | With 5 mol% $(PhS)_2$ | - | 0 |
| | ***Reaction optimization with 5 mol% $(PhSe)_2$*** | | |
| 14 | at 50 °C or lower | 0 | <63 |
| 15 | at 80 °C | 0 | 70 |
| 16 | DCE instead of toluene | 0 | 68 |
| 17 | DCM instead of toluene | 0 | 63 |
| 18 | $CHCl_3$ instead of toluene | 0 | 37 |
| **19** | **using 2 mol% $Rh_2(Oct)_4$** | **0** | **86 (82)**[d] |
| 20 | using 2 mol% $Rh_2(esp)_2$ | 0 | 83 |
| 21 | using 2 mol% $Rh_2(TFA)_4$ | 0 | trace |

[a]0.1 mmol of triazole **1**, 2 mol% $Rh_2(Oct)_4$, 1.1 equiv. diphenyl diselenide and 1 mL of dry toluene under an argon atmosphere at 60 °C for 6 h. [b]NMR yield using 0.1 mmol of 1,3,5-trimethoxybenzene as an internal standard. [b]Trace amount of 1,1-insertion product was detected in crude $^1$H-NMR analysis. [c]Isolated yield of **3** with 0.2 mmol of **1**.

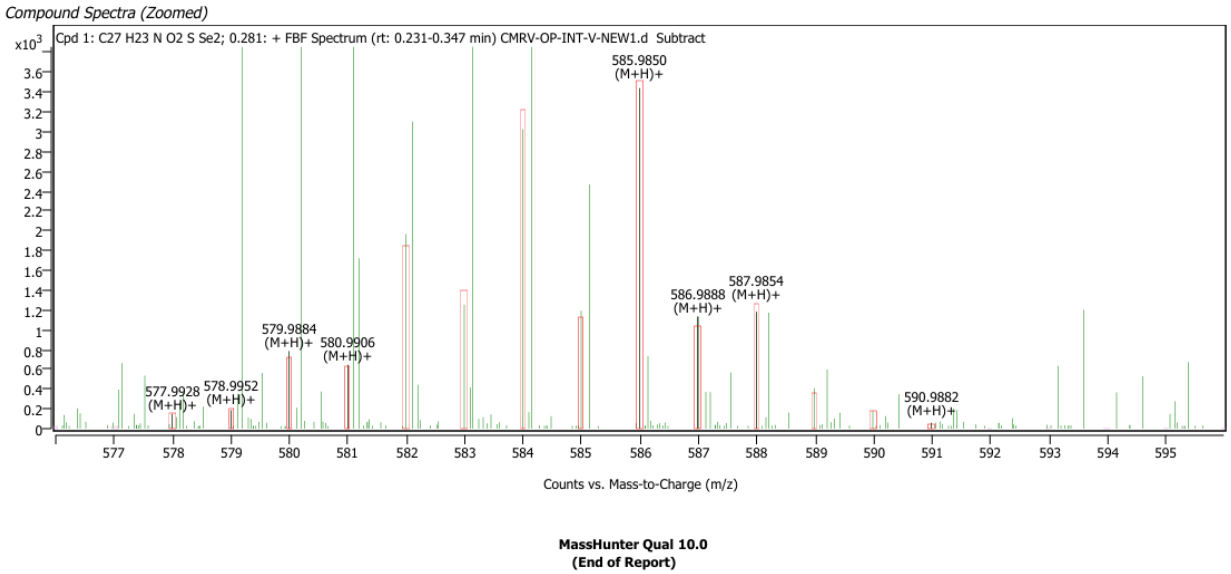
## 4. References

1.(a) Raushel, J.; Fokin, V. V. *Org. Lett*., **2010**, *12*, 4952–4955.

## 5. Mechanistic investigation

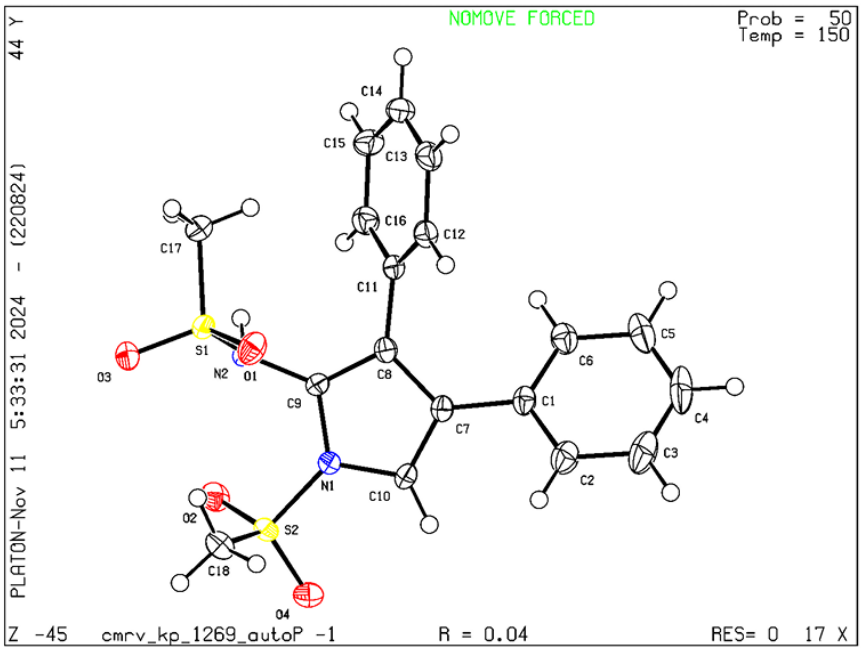



**HRMS (ESI):** $C_{27}H_{24}NO_2SSe_2$ $[M+H]^+$ calculated = 585.9853; found = 585.9850.




**6. X-ray crystallography data for the compound of 4f:** Crystal of the compound **26** was obtained after slow evaporation of chloroform solvent. Molecular structure of **4f** with 50% ellipsoid probability.

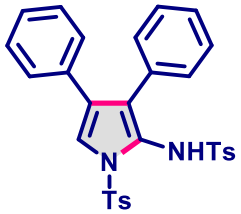
Datablock cmrv_kp_1269_autored - ellipsoid plot




| Table 1 Crystal data and structure refinement for CMRV_KP_1269_autored. | |
|---|---|
| **Identification code** | CMRV_KP_1269_autored |
| **Empirical formula** | $C_{18}H_{18}N_2O_4S_2$ |
| **Formula weight** | 390.46 |
| **Temperature/K** | 150.0 |
| **Crystal system** | triclinic |
| **Space group** | P-1 |
| **a/Å** | 9.0198(4) |
| **b/Å** | 9.8165(4) |
| **c/Å** | 11.3146(4) |
| **α/°** | 89.792(3) |
| **β/°** | 89.757(3) |
| **γ/°** | 63.581(4) |
| **Volume/Å$^3$** | 897.19(7) |
| **Z** | 2 |
| **$\rho_{calc}$g/cm$^3$** | 1.445 |
| **μ/mm$^{-1}$** | 0.324 |
| **F(000)** | 408.0 |
| **Crystal size/mm$^3$** | 0.168 × 0.142 × 0.052 |

| | |
|---|---|
| **Radiation** | MoKα (λ = 0.71073) |
| **2Θ range for data collection/°** | 4.634 to 49.99 |
| **Index ranges** | -10 ≤ h ≤ 10, -11 ≤ k ≤ 11, -13 ≤ l ≤ 13 |
| **Reflections collected** | 13911 |
| **Independent reflections** | 3145 [$R_{int}$ = 0.0319, $R_{sigma}$ = 0.0282] |
| **Data/restraints/parameters** | 3145/0/237 |
| **Goodness-of-fit on $F^2$** | 1.051 |
| **Final R indexes [I>=2σ (I)]** | $R_1$ = 0.0352, $wR_2$ = 0.0925 |
| **Final R indexes [all data]** | $R_1$ = 0.0399, $wR_2$ = 0.0966 |
| **Largest diff. peak/hole / e $Å^{-3}$** | 0.75/-0.73 |

## 7. Experimental data and spectra of final compounds




**3a, 82%**

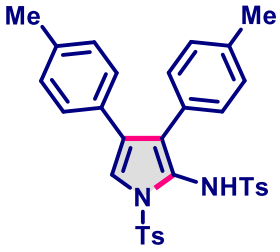
***N*-(2,4-diphenyl-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

Purified by (petroleum ether/EtOAc: 80/20), 44 mg, 82% yield, yellow sticky liquid.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.32 (s, 1H), 7.21 – 7.14 (m, 5H), 7.04 – 6.94 (m, 4H), 6.90 (t, *J* = 7.7 Hz, 2H), 6.87 – 6.80 (m, 4H), 2.45 (s, 3H), 2.28 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 145.77, 142.98, 137.67, 135.44, 133.28, 131.67, 130.20, 130.18, 129.17, 128.53, 128.32, 128.27, 127.99, 127.04, 126.88, 126.82, 126.74, 125.69, 121.83, 118.82, 21.92, 21.54.

**HRMS (ESI):** $C_{30}H_{26}N_2NaO_4S_2$ $[M+Na]^+$ calculated = 565.1226; found = 565.1225.




**3b, 80%**

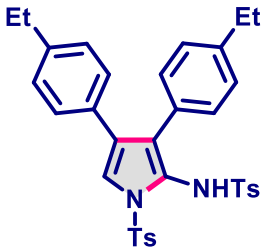
***N*-(2,4-di-*p*-tolyl-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

Purified by (petroleum ether/EtOAc: 80/20), 46 mg, 80% yield, yellow sticky liquid.

**$^{1}$H NMR (500 MHz, $CDCl_3$):** δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.29 (s, 1H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.01 – 6.95 (m, 3H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.73 (d, *J* = 7.9 Hz, 2H), 6.68 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H), 2.21 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 145.62, 142.70, 138.03, 136.66, 135.51, 130.42, 130.12, 129.96, 128.98, 128.95, 128.64, 128.61, 128.33, 128.28, 126.84, 126.63, 125.63, 121.66, 118.43, 21.89, 21.62, 21.34, 21.23.

**HRMS (ESI):** $C_{32}H_{30}N_2NaO_4S_2$ $[M+Na]^+$ calculated = 593.1539; found = 593.1532.




**3c, 76%**

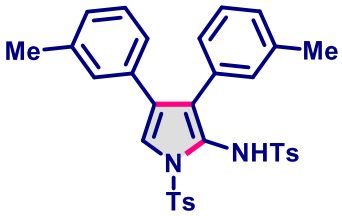
***N*-(3,4-bis(4-ethylphenyl)-1-tosyl-1*H*-pyrrol-2-yl)-4-methylbenzenesulfonamide**

Purified by (petroleum ether/EtOAc: 80/20), 45 mg, 76% yield, yellow sticky liquid.

**$^{1}$H NMR (500 MHz, $CDCl_3$)** δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.29 (s, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.03 – 6.98 (m, 3H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.81 – 6.71 (m, 4H), 2.59 (q, *J* = 7.6 Hz, 2H), 2.52 (q, *J* = 7.6 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H), 1.19 (t, *J* = 7.6 Hz, 6H).

**$^{13}$C NMR (125 MHz, $CDCl_3$)** δ 145.60, 142.97, 142.79, 142.72, 137.84, 135.57, 130.65, 130.11, 130.02, 128.99, 128.87, 128.34, 128.21, 127.74, 127.30, 126.92, 126.78, 125.93, 121.63, 118.63, 28.56, 28.49, 21.89, 21.60, 15.43, 15.07.

**HRMS (ESI):** $C_{34}H_{35}N_2O_4S_2$ $[M+H]^+$ calculated = 599.2033; found = 599.2014.




**3d, 77%**

***N*-(2,4-di-*m*-tolyl-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

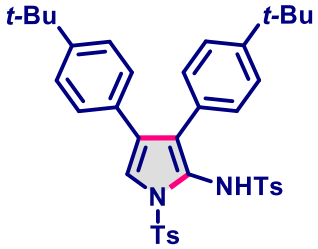
The reaction was performed at 60 ºC for 8 h.

Purified by (petroleum ether/EtOAc: 80/20), 44 mg, 77% yield, yellow sticky liquid.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.30 (s, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.04 – 6.98 (m, 2H), 6.88 – 6.79 (m, 5H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.67 (s, 1H), 6.63 (d, *J* = 7.2 Hz, 1H), 2.45 (s, 3H), 2.28 (s, 3H), 2.22 (s, 3H), 2.00 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 145.67, 142.71, 137.91, 137.81, 137.27, 135.47, 133.20, 131.58, 130.55, 130.14, 129.12, 128.97, 128.33, 128.01, 127.82, 127.70, 127.57, 126.71, 126.63, 125.70, 125.67, 121.64, 118.62, 21.92, 21.50, 21.46, 21.24.

**HRMS (ESI):** $C_{32}H_{30}N_2NaO_4S_2$ $[M+Na]^+$ calculated = 593.1539; found = 593.1527.




**3e, 77%**

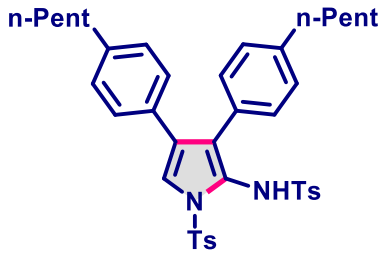
***N*-(2,4-bis(4-(*tert*-butyl) phenyl)-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

Purified by (petroleum ether/EtOAc: 95/5), 50 mg, 77% yield, yellow sticky liquid.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.30 (s, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.02 (s, 1H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.89 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 2.43 (s, 3H), 2.28 (s, 3H), 1.27 (s, 9H), 1.25 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 149.86, 149.75, 145.51, 142.74, 137.50, 135.66, 130.35, 130.10, 129.80, 129.03, 128.67, 128.09, 127.89, 127.12, 126.90, 126.29, 125.10, 124.71, 121.61, 118.99, 34.56, 34.47, 31.47, 31.40, 21.86, 21.68.

**HRMS (ESI):** $C_{38}H_{42}N_2NaO_4S_2$ $[M+H]^+$ calculated = 655.2659; found = 655.2635.




**3f, 78%**

***N*-(2,4-bis(4-pentylphenyl)-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

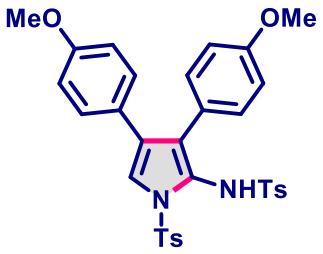
The reaction was performed at 60 °C for 7 h.

Purified by (petroleum ether/EtOAc: 80/20), 42 mg, 78% yield, yellow sticky liquid.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.29 (s, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.95 (s, 1H), 6.89 (d, *J* = 8.2 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.75 (d, *J* = 8.2 Hz, 2H), 6.72 (d, *J* = 8.2 Hz, 2H), 2.53 (t, *J* = 7.5 Hz, 2H), 2.46 (t, *J* = 7.5 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H), 1.59 – 1.53 (m, 4H), 1.34 – 1.28 (m, 8H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.87 (t, *J* = 7.1 Hz, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$):** δ 145.59, 142.75, 141.73, 141.68, 137.79, 135.57, 130.58, 130.11, 129.97, 129.01, 128.86, 128.26, 128.24, 128.20, 127.81, 126.94, 126.84, 125.96, 121.59, 118.56, 35.75, 35.68, 31.86, 31.67, 31.09, 30.89, 22.68, 22.64, 21.90, 21.63, 14.23, 14.15.

**HRMS (ESI):** $C_{40}H_{47}N_2O_4S_2$ $[M+H]^+$ calculated = 683.2972; found = 683.2957.




**3g, 88%**

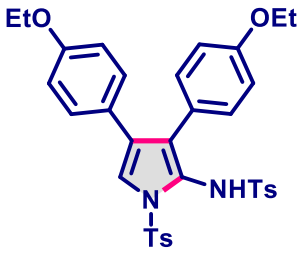
***N*-(2,4-bis(4-methoxyphenyl)-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

Purified by (petroleum ether/EtOAc: 70/30), 53 mg, 88% yield, yellow sticky liquid.

**$^{1}$H NMR (400 MHz, $CDCl_3$):** δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.26 (s, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.02 (s, 1H), 6.93 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.73 (d, *J* = 8.9 Hz, 2H), 6.41 (d, *J* = 8.8 Hz, 2H), 3.75 (s, 3H), 3.70 (s, 3H), 2.44 (s, 3H), 2.30 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 158.73, 145.60, 142.77, 138.14, 135.54, 131.22, 130.12, 129.62, 129.02, 128.28, 126.87, 126.31, 125.82, 125.33, 123.92, 121.53, 118.05, 113.74, 113.41, 55.28, 54.98, 21.89, 21.45.

**HRMS (ESI):** $C_{32}H_{31}N_2NaO_6S_2$ $[M+H]^+$ calculated = 603.1618; found = 603.1599.




**3h, 80%**

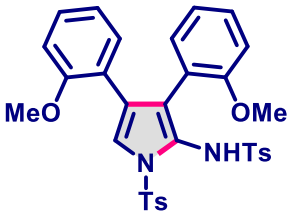
**N-(3,4-bis(4-ethoxyphenyl)-1-tosyl-1H-pyrrol-2-yl)-4-methylbenzenesulfonamide**

Purified by (petroleum ether/EtOAc: 70/30), 50 mg, 80% yield, yellow sticky liquid.

**$^{1}$H NMR (500 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.26 (s, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.04 (s, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.1 Hz, 2H), 6.73 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.38 (d, *J* = 8.8 Hz, 2H), 3.97 (q, *J* = 7.0 Hz, 2H), 3.88 (q, *J* = 7.0 Hz, 2H), 2.43 (s, 3H), 2.29 (s, 3H), 1.40 (t, *J* = 6.3 Hz, 3H), 1.37 (t, *J* = 6.3 Hz, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 158.15, 158.07, 145.55, 142.69, 138.16, 135.51, 131.16, 130.09, 129.59, 129.00, 128.26, 126.82, 126.31, 125.65, 125.41, 123.67, 121.43, 118.02, 114.21, 113.80, 63.41, 63.09, 21.87, 21.42, 15.00, 14.92.

**HRMS (ESI):** $C_{34}H_{34}N_2NaO_6S_2$ $[M+Na]^+$ calculated = 653.1750; found = 653.1757.




**3i, 61%**

***N*-(2,4-bis(2-methoxyphenyl)-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

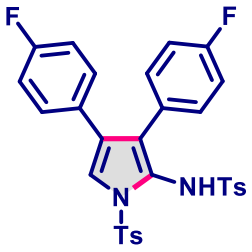
The reaction was performed at 80 °C for 10 h.

Purified by (petroleum ether/EtOAc: 70/30), 37 mg, 61% yield, yellow sticky liquid.

**$^1$H NMR (500 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.41 (s, 1H), 7.35 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 8.5 Hz, 1H), 7.01 (dd, *J* = 7.4, 1.3 Hz, 1H), 6.92 (t, *J* = 8.5 Hz, 1H), 6.85 – 6.81 (m, 2H), 6.74 (d, *J* = 8.1 Hz, 2H), 6.66 (d, *J* = 8.2 Hz, 1H), 6.48 (d, *J* = 8.2 Hz, 1H), 6.45 (t, *J* = 7.5 Hz, 1H), 6.34 (dd, *J* = 7.5, 1.2 Hz, 1H), 3.44 (s, 3H), 3.17 (s, 3H), 2.43 (s, 3H), 2.19 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 156.51, 155.23, 145.04, 142.88, 137.22, 136.15, 131.03, 129.78, 128.98, 128.68, 128.30, 127.97, 126.79, 123.69, 122.70, 122.59, 122.42, 122.13, 120.83, 120.78, 120.48, 112.25, 111.03, 56.40, 54.75, 21.85, 21.48.

**HRMS (ESI):** $C_{32}H_{31}N_2NaO_6S_2$ $[M+H]^+$ calculated = 603.1618; found = 603.1603.




**3j, 70%**

***N*-(2,4-bis(4-fluorophenyl)-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

The reaction was performed at 80 °C for 8 h.

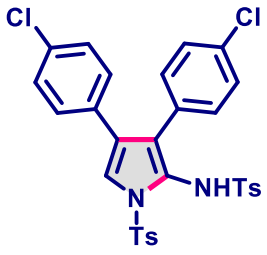
Purified by (petroleum ether/EtOAc: 80/20), 40 mg, 70% yield, yellow sticky liquid.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.28 (s, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.05 – 6.81 (m, 7H), 6.82 – 6.66 (m, 2H), 6.55 (t, *J* = 8.8 Hz, 2H), 2.46 (s, 3H), 2.33 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 162.24 (d, *J* = 246.9 Hz), 162.15 (d, *J* = 246.9 Hz), 146.00, 143.43, 138.06, 135.18, 131.75 (d, *J* = 8.5 Hz), 130.24, 130.17 (d, *J* = 7.9 Hz), 129.21, 129.13 (d, *J* = 3.2 Hz), 128.49, 127.38 (d, *J* = 3.2 Hz), 126.76, 125.45, 123.99, 122.05, 118.35, 115.39 (d, *J* = 21.7 Hz), 115.10 (d, *J* = 21.2 Hz), 21.97, 21.45.

**$^{19}$F NMR (376 MHz, $CDCl_3$)** δ -114.87, -115.08.

**HRMS (ESI):** $C_{30}H_{25}F_2N_2O_4S_2$ $[M+H]^+$ calculated = 579.1218; found = 579.1207.




**3k, 80%**

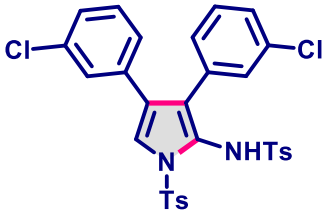
**N-(3,4-bis(4-chlorophenyl)-1-tosyl-1H-pyrrol-2-yl)-4-methylbenzenesulfonamide**

Purified by (petroleum ether/EtOAc: 80/20), 49 mg, 80% yield, yellow sticky liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.31 (s, 1H), 7.16 (dd, *J* = 8.4, 3.3 Hz, 4H), 7.00 (s, 1H), 6.91 (t, *J* = 9.0 Hz, 4H), 6.81 (d, *J* = 8.5 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 2H), 2.46 (s, 3H), 2.37 (s, 3H).

**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 146.11, 143.66, 138.08, 135.05, 133.61, 133.23, 132.05, 131.51, 131.33, 130.27, 129.77, 129.26, 128.68, 128.57, 128.28, 126.59, 125.09, 123.52, 122.30, 118.52, 21.97, 21.71.

**HRMS (ESI):** $C_{30}H_{24}Cl_2N_2NaO_4S_2$ $[M+Na]^+$calculated = 633.0447; found = 633.0458.




**3l, 78%**

***N*-(2,4-bis(3-chlorophenyl)-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

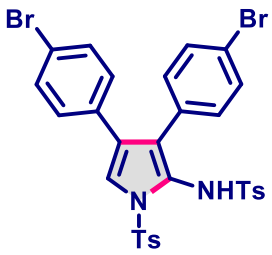
The reaction was performed at 80 °C for 8 h.

Purified by (petroleum ether/EtOAc: 80/20), 48 mg, 76% yield, yellow sticky liquid.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.33 (s, 1H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 9.2 Hz, 1H), 7.10 – 7.07 (m, 1H), 7.03 (t, *J* = 2.0 Hz, 1H), 6.98 (s, 1H), 6.94 (dd, *J* = 8.6, 1.8 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 7.9 Hz, 1H), 6.82 (t, *J* = 1.9 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 2.47 (s, 3H), 2.30 (s, 3H).

**$^{13}$C NMR (126 MHz, $CDCl_3$)** δ 146.16, 143.39, 137.69, 135.01, 134.78, 134.28, 134.00, 133.23, 130.29, 129.86, 129.58, 129.38, 129.29, 128.60, 128.57, 128.39, 127.34, 127.19, 126.78, 126.53, 124.99, 123.47, 122.36, 118.95, 21.99, 21.57.

**HRMS (ESI):** $C_{30}H_{24}Cl_2N_2NaO_4S_2$ $[M+Na]^+$calculated = 633.0447; found = 633.0448.




**3m, 83%**

***N*-(2,4-bis(4-bromophenyl)-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

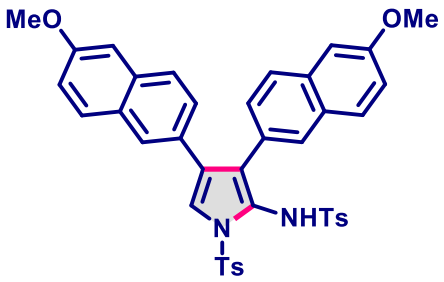
The reaction was performed at 80 °C for 8 h.

Purified by (petroleum ether/EtOAc: 80/20), 58 mg, 83% yield, yellow semi-solid.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.07 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.30 (m, 3H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.07 (s, 1H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.67 (d, *J* = 8.5 Hz, 2H), 2.45 (s, 3H), 2.40 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 146.10, 143.68, 138.05, 135.02, 131.94, 131.62, 131.19, 130.26, 130.25, 130.07, 129.28, 128.56, 126.54, 125.02, 123.55, 122.25, 121.94, 121.37, 118.55, 21.96, 21.87.

**HRMS (ESI):** $C_{30}H_{25}Br_2N_2NaO_4S_2$ $[M+Na]^+$calculated = 720.9436; found = 720.9420.




**3n, 81%**

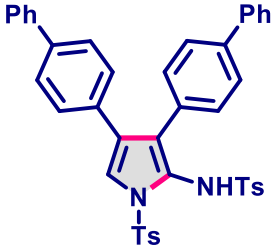
***N*-(2,4-bis(6-methoxynaphthalen-2-yl)-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

Purified by (petroleum ether/EtOAc: 70/30), 57 mg, 81% yield, yellow sticky liquid.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 8.13 (d, *J* = 8.4 Hz, 2H), 7.55 – 7.50 (m, 2H), 7.47 (s, 1H), 7.46 – 7.41 (m, 3H), 7.30 (d, *J* = 9.5 Hz, 2H), 7.23 (d, *J* = 8.5 Hz, 1H), 7.13 (s, 1H), 7.09 – 7.04 (m, 2H), 7.03 – 7.00 (m, 3H), 6.99 (t, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 2.3 Hz, 1H), 6.89 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.39 (d, *J* = 8.1 Hz, 2H), 3.90 (s, 3H), 3.87 (s, 3H), 2.46 (s, 3H), 1.86 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 157.79, 145.76, 142.51, 138.08, 135.46, 133.82, 133.54, 130.19, 129.65, 129.54, 128.95, 128.91, 128.77, 128.73, 128.63, 128.58, 128.53, 127.41, 126.97, 126.84, 126.59, 126.54, 126.39, 126.15, 125.29, 122.11, 118.97, 118.56, 118.35, 105.68, 105.42, 55.42, 55.41, 21.94, 21.25.

**HRMS (ESI):** $C_{40}H_{35}N_2O_6S_2$ $[M+H]^+$ calculated = 703.1931; found = 703.1983.




**3o, 77%**

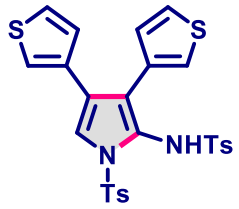
***N*-(3,4-di([1,1'-biphenyl]-4-yl)-1-tosyl-1*H*-pyrrol-2-yl)-4-methylbenzenesulfonamide**

Purified by (petroleum ether/EtOAc: 75/25), 53 mg, 77% yield, yellow sticky liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 8.6 Hz, 2H), 7.59 – 7.52 (m, 4H), 7.48 – 7.44 (m, 9H), 7.35 (dd, *J* = 5.6, 1.9 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.16 (dd, *J* = 12.9, 8.4 Hz, 4H), 7.04 (s, 1H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.81 (d, *J* = 8.2 Hz, 2H), 2.48 (s, 3H), 1.94 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 145.85, 143.07, 140.68, 140.35, 139.80, 139.47, 138.17, 135.42, 132.32, 130.64, 130.62, 130.22, 129.09, 128.93, 128.90, 128.88, 128.49, 127.54, 127.47, 127.41, 127.03, 126.80, 126.70, 126.38, 126.14, 124.93, 122.15, 118.71, 21.95, 21.23.

**HRMS (ESI):** $C_{42}H_{35}N_2O_4S_2$ $[M+H]^+$ calculated = 695.2033; found =695.2030.




**3p, 79%**

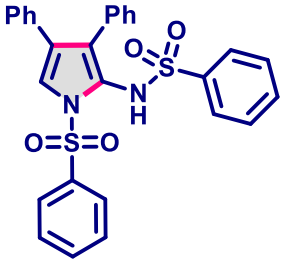
***N*-(2,4-di(thiophen-3-yl)-1-tosyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide**

Purified by (petroleum ether/EtOAc: 80/20), 44 mg, 79% yield, yellow sticky liquid.

**$^1$H NMR (400 MHz, $CDCl_3$):** δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.34 (s, 1H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.18 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.02 (s, 1H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.90 (dd, *J* = 4.9, 3.0 Hz, 1H), 6.86 – 6.77 (m, 3H), 6.62 (dd, *J* = 4.9, 1.1 Hz, 1H), 2.43 (s, 3H), 2.33 (s, 3H).

**$^{13}$C NMR (100 MHz, $CDCl_3$):** δ 145.76, 143.22, 137.86, 135.35, 133.54, 131.67, 130.17, 129.23, 128.85, 128.23, 127.51, 126.86, 125.28, 124.74, 124.68, 122.07, 122.04, 121.79, 120.89, 118.29, 21.89, 21.60.

**HRMS (ESI):** $C_{26}H_{23}N_2O_4S_4$ $[M+H]^+$ calculated = 555.0535; found = 555.0517.




**4a, 80%**

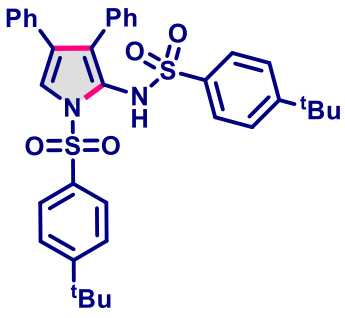
***N*-(3,4-diphenyl-1-(phenylsulfonyl)-1*H*-pyrrol-2-yl)benzenesulfonamide**

Purified by (petroleum ether/EtOAc: 80/20), 41 mg, 80% yield, yellow sticky liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.15 (d, *J* = 7.7 Hz, 2H), 7.69 (t, *J* = 7.4 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.37 (s, 1H), 7.33 – 7.26 (m, 3H), 7.21 – 7.16 (m, 3H), 7.08 (dd, *J* = 8.3, 7.5 Hz, 2H), 7.04 (s, 1H), 7.02 – 6.96 (m, 3H), 6.93 – 6.85 (m, 4H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 140.75, 138.35, 134.55, 133.12, 132.34, 131.47, 130.12, 129.57, 128.55, 128.49, 128.30, 128.24, 128.07, 127.45, 127.12, 126.89, 126.72, 126.12, 121.76, 118.88.

**HRMS (ESI):** $C_{28}H_{23}N_2NaO_4S_2$ $[M+Na]^+$ calculated = 537.0913; found = 537.0902.




**4b, 79%**

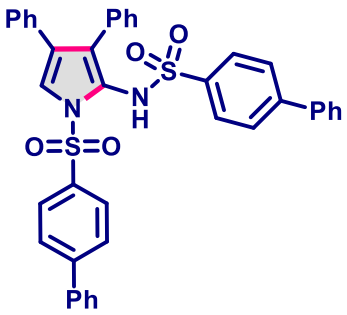
**4-(tert-butyl)-*N*-(1-((4-(tert-butyl)phenyl)sulfonyl)-3,4-diphenyl-1*H*-pyrrol-2-yl)benzenesulfonamide**

Purified by (petroleum ether/EtOAc: 80/20), 49 mg, 79% yield, yellow sticky liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.33 (s, 1H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.20 – 7.16 (m, 3H), 7.08 (d, *J* = 8.7 Hz, 2H), 7.05 (s, 1H), 7.01 – 6.98 (m, 2H), 6.98 – 6.94 (m, 1H), 6.92 – 6.86 (m, 4H), 1.35 (s, 9H), 1.27 (s, 9H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 158.58, 155.50, 137.96, 135.29, 133.32, 131.63, 130.19, 128.53, 128.26, 128.19, 127.90, 127.30, 126.99, 126.63, 126.58, 126.54, 125.52, 125.43, 121.98, 118.74, 35.50, 35.03, 31.11.

**HRMS (ESI):** $C_{36}H_{39}N_2O_4S_2$ $[M+H]^+$ calculated = 627.2346; found =627.2357.




**4c, 82%**

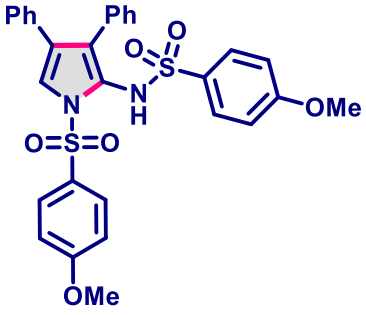
***N*-(1-([1,1'-biphenyl]-4-ylsulfonyl)-3,4-diphenyl-1*H*-pyrrol-2-yl)-[1,1'-biphenyl]-4-sulfonamide**

Purified by (petroleum ether/EtOAc: 75/25), 55 mg, 82% yield, yellow sticky liquid.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.26 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 2H), 7.51 – 7.45 (m, 6H), 7.44 – 7.37 (m, 5H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.15 (m, 4H), 7.02 (dd, *J* = 6.4, 3.1 Hz, 2H), 6.96 – 6.92 (m, 1H), 6.92 – 6.85 (m, 4H).

**$^{13}$C NMR (125 MHz, $CDCl_3$)** δ 147.42, 144.94, 139.58, 139.34, 139.05, 136.80, 133.18, 131.51, 130.19, 129.17, 129.11, 128.89, 128.88, 128.54, 128.44, 128.31, 128.13, 128.06, 127.58, 127.31, 127.30, 127.19, 127.10, 127.03, 126.83, 126.00, 121.75, 118.98.

**HRMS (ESI):** $C_{40}H_{31}N_2O_4S_2$ $[M+H]^+$ calculated = 667.1720; found = 667.1710.




**4d, 84%**

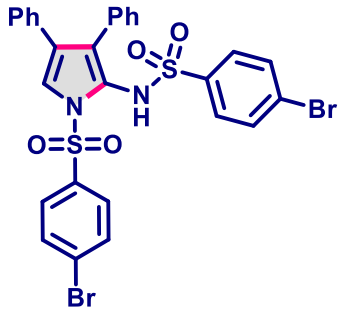
**4-methoxy-*N*-(1-((4-methoxyphenyl)sulfonyl)-3,4-diphenyl-1*H*-pyrrol-2-yl)benzenesulfonamide**

Purified by (petroleum ether/EtOAc: 70/30), 48 mg, 84% yield, yellow sticky liquid.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 8.9 Hz, 2H), 7.31 (s, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 7.20 – 7.14 (m, 3H), 7.05 (d, *J* = 8.9 Hz, 2H), 7.03 – 6.96 (m, 4H), 6.93 (t, *J* = 7.6 Hz, 2H), 6.87 (d, *J* = 7.4 Hz, 2H), 6.51 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.76 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$)** δ 164.42, 162.51, 133.36, 132.31, 131.85, 130.73, 130.22, 129.77, 129.03, 128.53, 128.26, 128.03, 127.04, 126.99, 126.58, 125.50, 121.85, 118.81, 114.75, 113.78, 55.86, 55.55.

**HRMS (ESI):** $C_{30}H_{27}N_2O_6S_2$ $[M+H]^+$ calculated = 575.1305; found = 575.1264.




**4e, 77%**

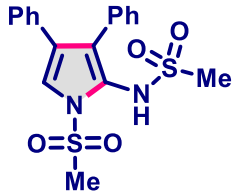
**4-bromo-*N*-(1-((4-bromophenyl)sulfonyl)-3,4-diphenyl-1*H*-pyrrol-2-yl)benzenesulfonamide**

Purified by (petroleum ether/EtOAc: 80/20), 52 mg, 77% yield, yellow sticky liquid.

**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.36 (s, 1H), 7.21 – 7.16 (m, 3H), 7.14 – 7.08 (m, 6H), 6.99 – 6.96 (m, 2H), 6.92 (t, *J* = 7.8 Hz, 2H), 6.80 (dd, *J* = 8.1, 1.1 Hz, 2H).

**$^{13}$C NMR (100 MHz, $CDCl_3$)** δ 139.52, 137.27, 132.93, 132.83, 131.84, 131.17, 130.10, 130.05, 129.89, 128.51, 128.38, 128.25, 128.22, 127.69, 127.30, 127.03, 126.41, 121.25, 118.96.

**HRMS (ESI):** $C_{28}H_{21}Br_2N_2O_4S_2$ $[M+H]^+$ calculated = 670.9304; found = 670.9288.




**4f, 72%**

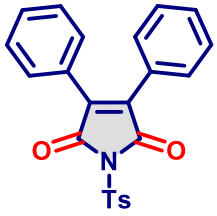
***N*-(1-(methylsulfonyl)-3,4-diphenyl-1*H*-pyrrol-2-yl)methanesulfonamide**

Purified by (petroleum ether/EtOAc: 85/15), 28 mg, 72% yield, white solid.

**$^1$H NMR (500 MHz, DMSO)** δ 9.87 (s, 1H), 7.42 – 7.36 (m, 3H), 7.36 – 7.32 (m, 1H), 7.27 – 7.20 (m, 5H), 7.13 (d, *J* = 6.8 Hz, 2H), 3.66 (s, 3H), 2.20 (s, 3H).

**$^{13}$C NMR (125 MHz, DMSO)** δ 132.97, 132.22, 130.02, 128.59, 128.39, 127.87, 127.73, 126.85, 125.25, 124.10, 122.07, 118.47, 43.22, 41.71

**HRMS (ESI):** $C_{18}H_{18}N_2NaO_4S_2$ $[M+Na]^+$ calculated = 413.0600; found = 413.0585.




**5, 83%**

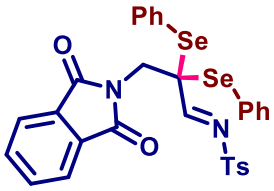
**3,4-diphenyl-1-tosyl-1*H*-pyrrole-2,5-dione**

Purified by (petroleum ether/EtOAc: 70/30), 33 mg, 83% yield, white solid.

**$^1$H NMR (500 MHz, $CDCl_3$)** δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.37 (m, 8H), 7.35 – 7.31 (m, 4H), 2.45 (s, 3H).

**$^{13}$C NMR (125 MHz, $CDCl_3$)** δ 165.40, 146.24, 137.67, 135.52, 130.72, 130.16, 130.13, 128.82, 128.64, 127.52, 21.92.

**HRMS (ESI):** $C_{23}H_{17}NNaO_4S$ $[M+H]^+$ calculated = 426.0770; found = 426.0775.




**7**, 61 %

***N*-(3-(1,3-dioxoisoindolin-2-yl)-2,2-bis(phenylselanyl)propylidene)-4-methylbenzenesulfonamide**

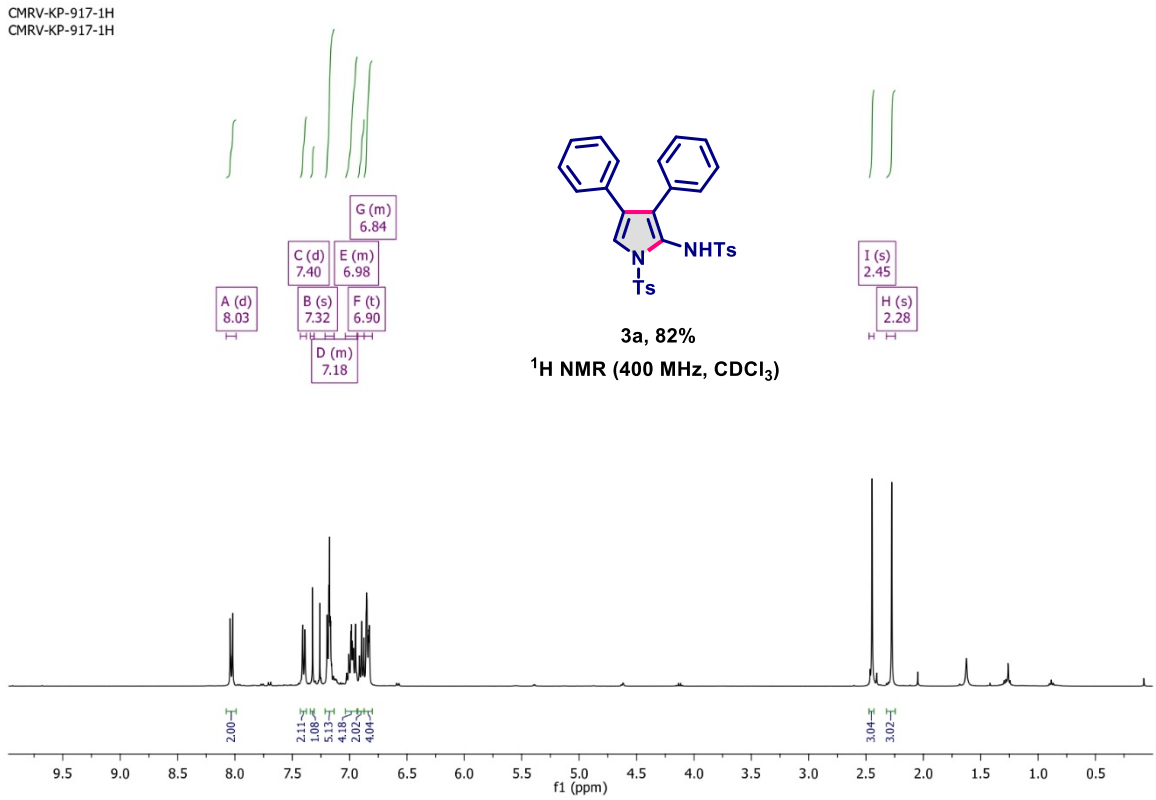
Purified by (petroleum ether/EtOAc: 75/25), 81 mg, 61% yield, yellow liquid.

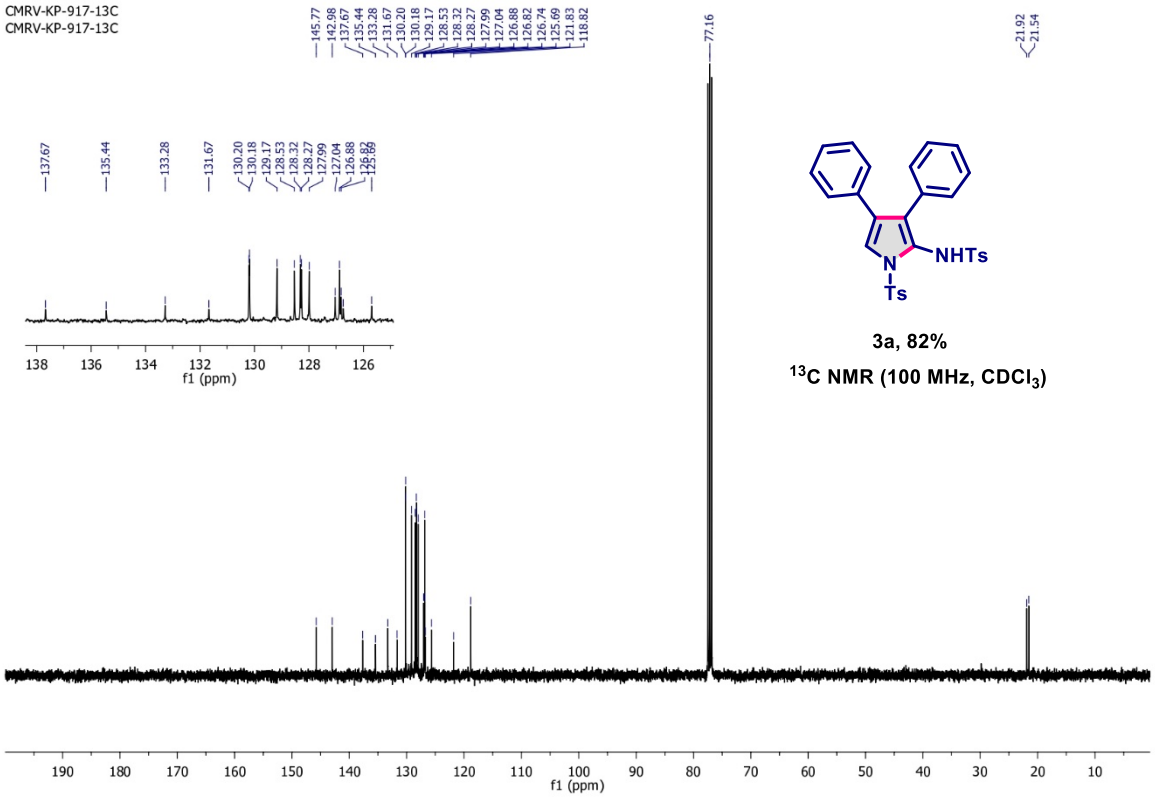
**$^1$H NMR (400 MHz, $CDCl_3$)** δ 8.42 (s, 1H), 7.86 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.77 – 7.69 (m, 6H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.27 – 7.22 (m, 6H), 4.35 (s, 2H), 2.44 (s, 3H).

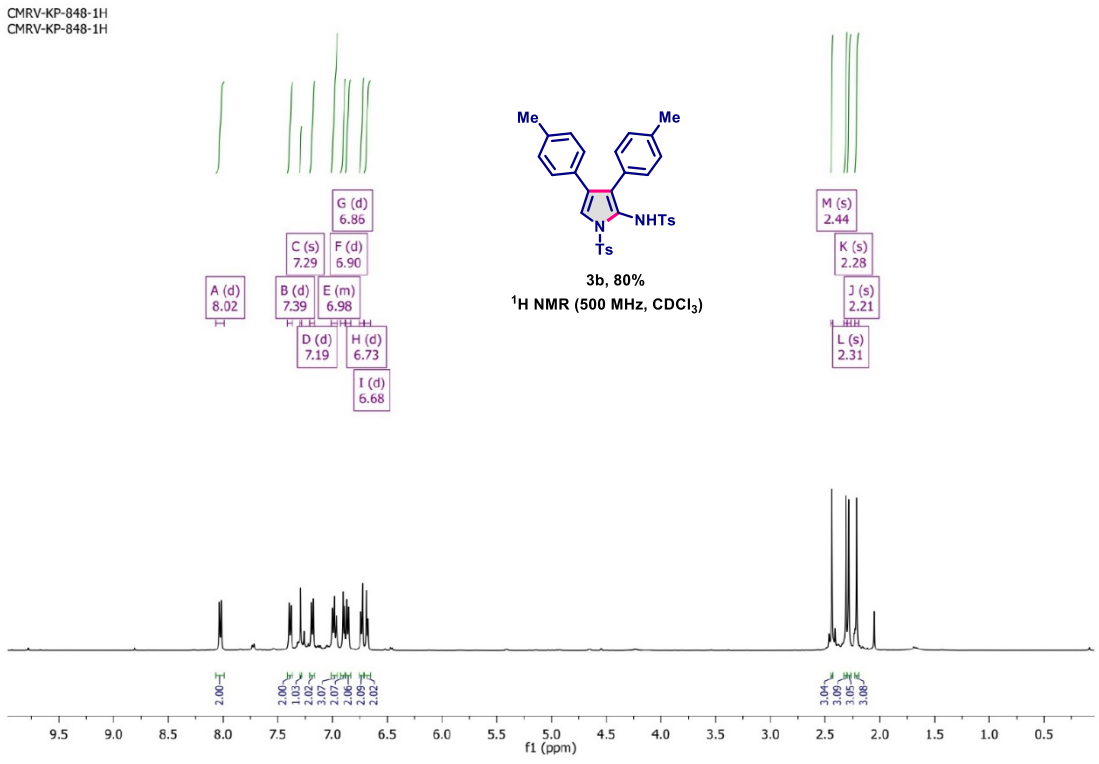
**$^{13}$C NMR (101 MHz, $CDCl_3$)** δ 172.42, 168.29, 144.51, 137.91, 134.64, 134.39, 131.90, 130.09, 129.71, 129.37, 128.38, 125.98, 123.75, 52.43, 43.41, 21.80.

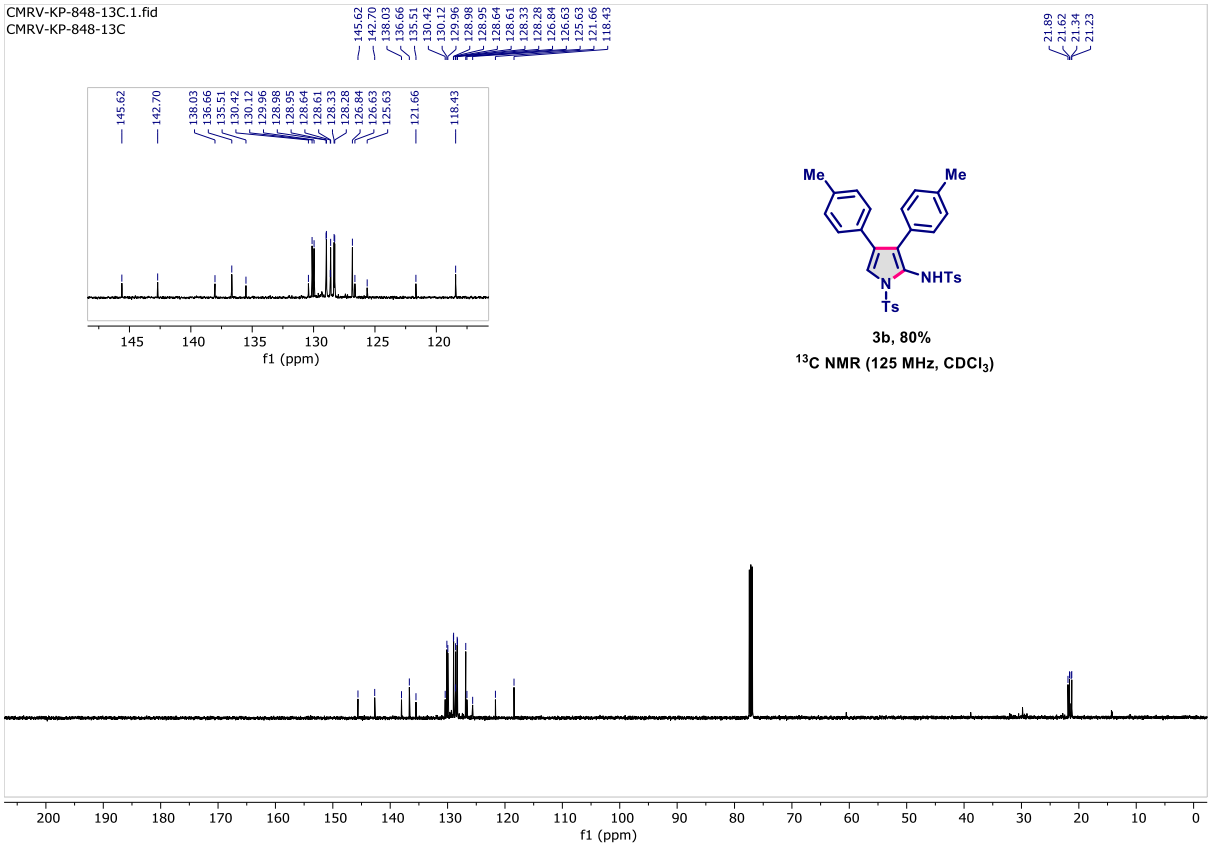
**$^{77}$Se NMR (95 MHz, $CDCl_3$)** δ 487.49.

**HRMS (ESI):** $C_{30}H_{24}KN_2O_4SSe_2$ $[M+K]^+$ calculated = 706.9419; found = 706.9370.



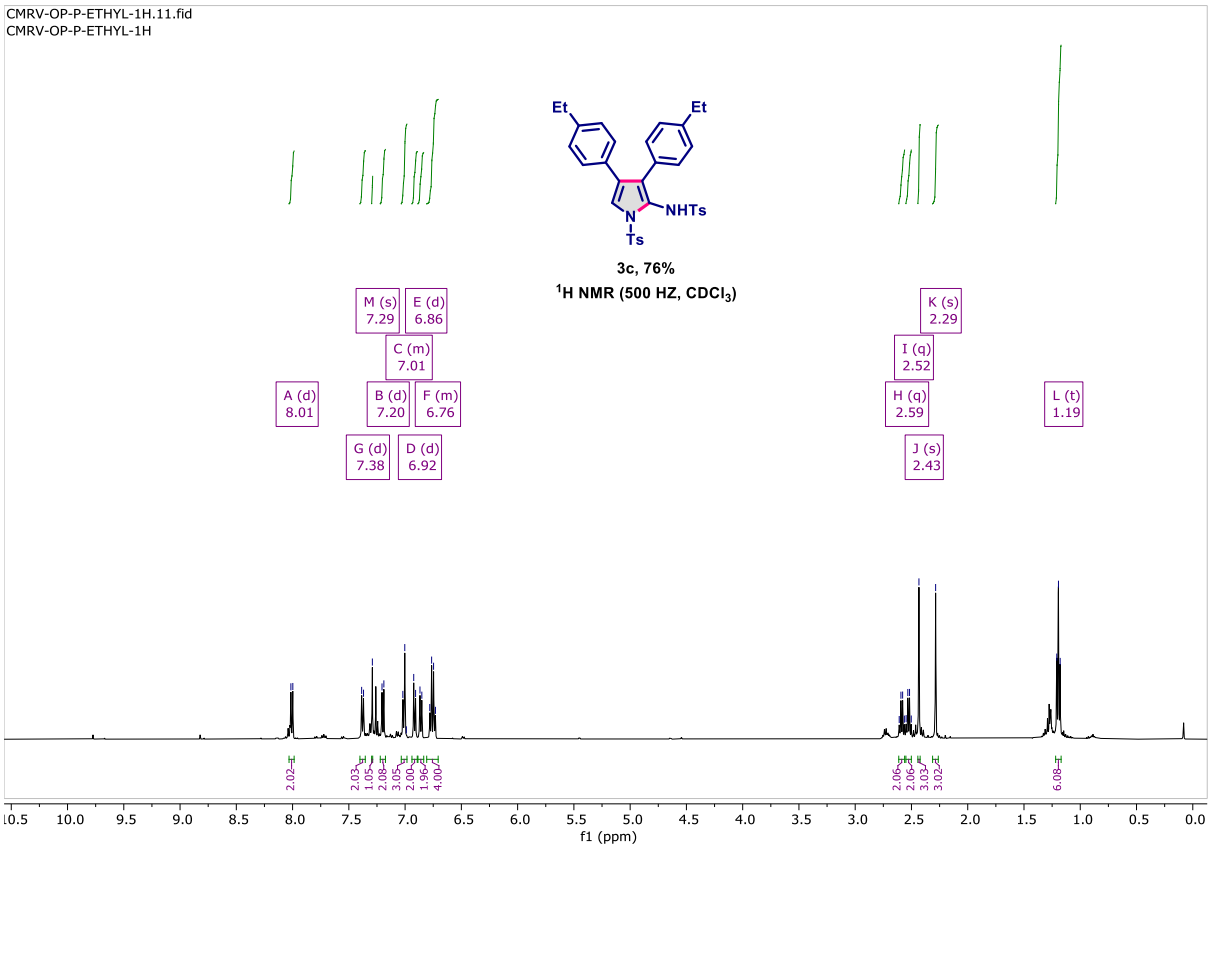

CMRV-KP-917-13C
CMRV-KP-917-13C
145.77
142.98
137.67
135.44
133.28
131.67
130.20
130.18
129.17
128.53
128.32
128.27
127.99
127.04
126.88
126.82
126.74
125.69
121.83
118.82
77.16
21.92
21.54
NHTs
N
Ts
3a, 82%
13C NMR (100 MHz, CDCl3)
f1 (ppm)


CMRV-KP-848-1H
CMRV-KP-848-1H
A (d) 8.02
B (d) 7.39
C (s) 7.29
D (d) 7.19
E (m) 6.98
F (d) 6.90
G (d) 6.86
H (d) 6.73
I (d) 6.68
J (s) 2.21
K (s) 2.28
L (s) 2.31
M (s) 2.44
Me
Me
NHTs
N
Ts
3b, 80%
1H NMR (500 MHz, CDCl3)
f1 (ppm)



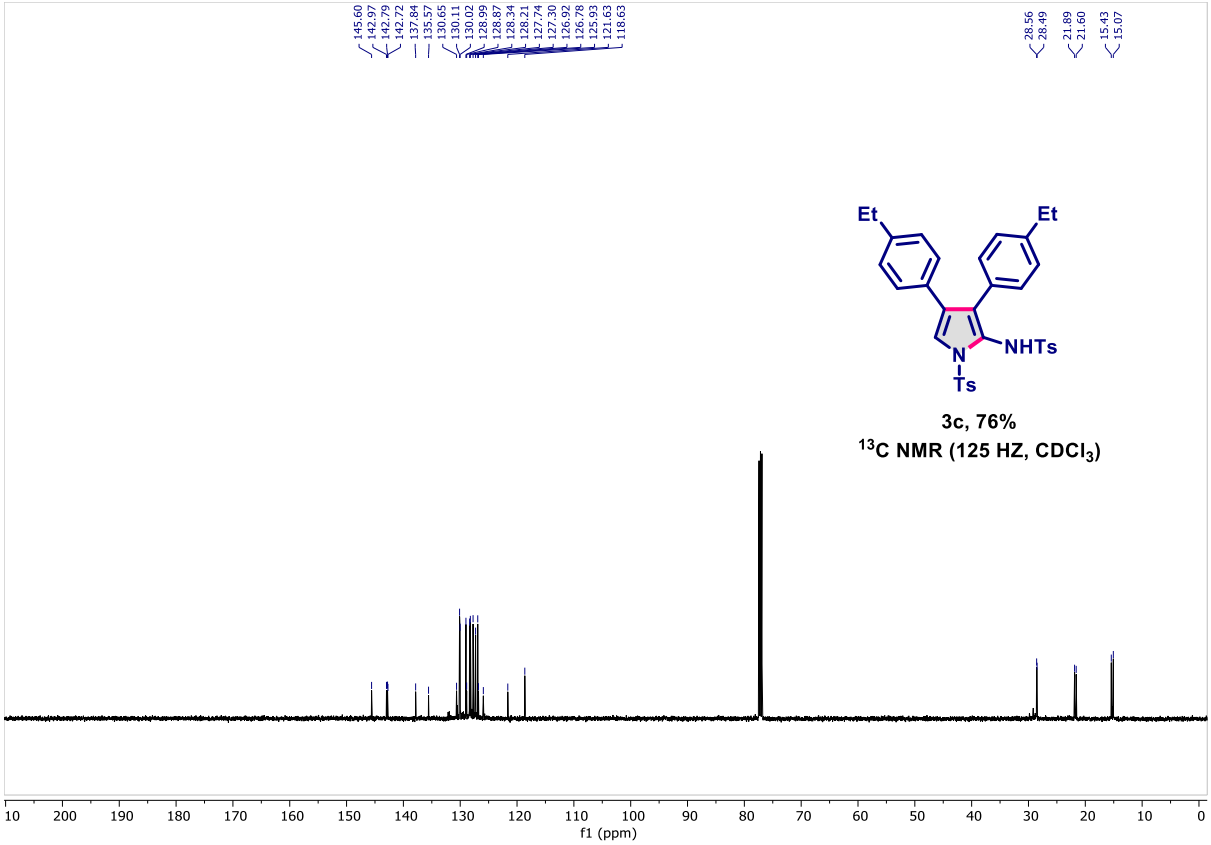

**3b, 80%**

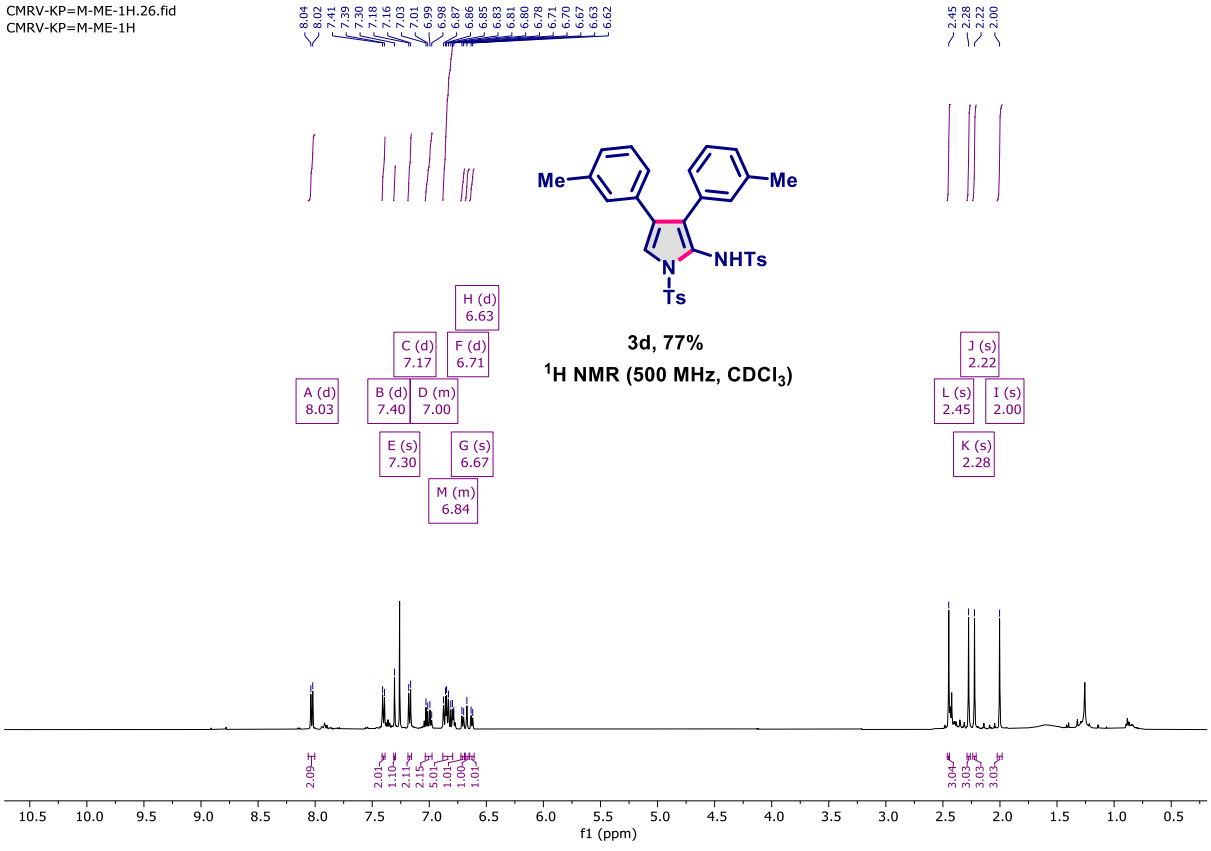
**$^{13}$C NMR (125 MHz, $CDCl_3$)**



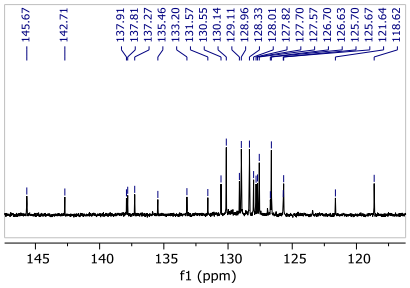

**3c, 76%**

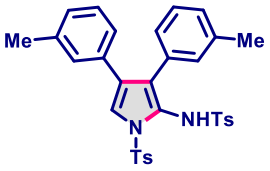
**$^{1}$H NMR (500 HZ, $CDCl_3$)**


145.60
142.97
142.79
142.72
137.84
135.57
130.65
130.11
130.02
128.99
128.87
128.34
128.21
127.74
127.30
126.92
126.78
125.93
121.63
118.63
28.56
28.49
21.89
21.60
15.43
15.07
Et
Et
NHTs
N
Ts
3c, 76%
13C NMR (125 HZ, CDCl3)
f1 (ppm)


CMRV-KP=M-ME-1H.26.fid
CMRV-KP=M-ME-1H
8.04
8.02
7.41
7.39
7.30
7.18
7.16
7.03
7.01
6.99
6.98
6.87
6.86
6.85
6.83
6.81
6.80
6.78
6.71
6.70
6.67
6.63
6.62
2.45
2.28
2.22
2.00
Me
Me
NHTs
N
Ts
H (d) 6.63
C (d) 7.17
F (d) 6.71
A (d) 8.03
B (d) 7.40
D (m) 7.00
E (s) 7.30
G (s) 6.67
M (m) 6.84
J (s) 2.22
L (s) 2.45
I (s) 2.00
K (s) 2.28
3d, 77%
1H NMR (500 MHz, CDCl3)
2.09
2.01
1.10
2.11
2.15
5.01
1.01
1.00
1.01
3.04
3.03
3.03
3.03
f1 (ppm)

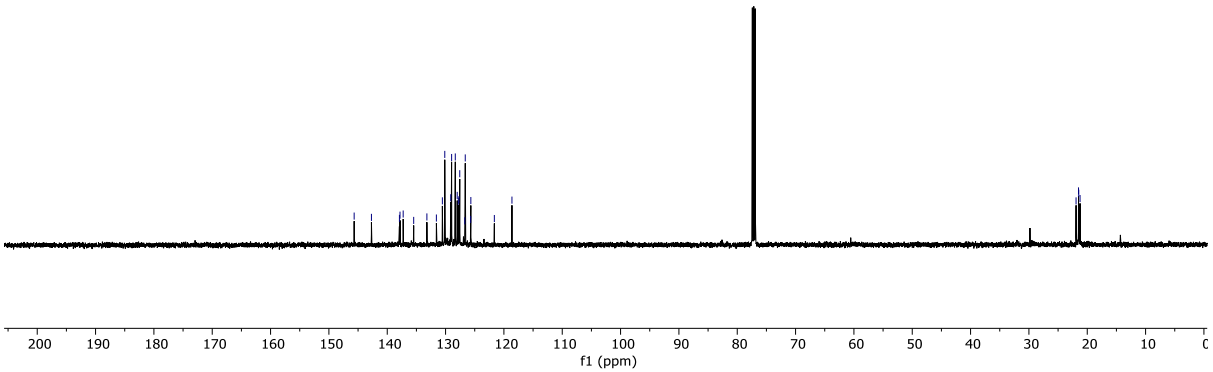




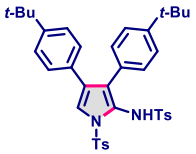




**3d, 77%**

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

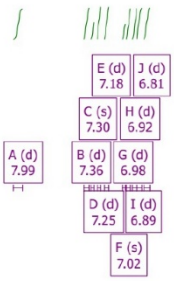


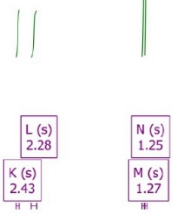

CMRV-KP-859-1H
CMRV-KP-859-1H

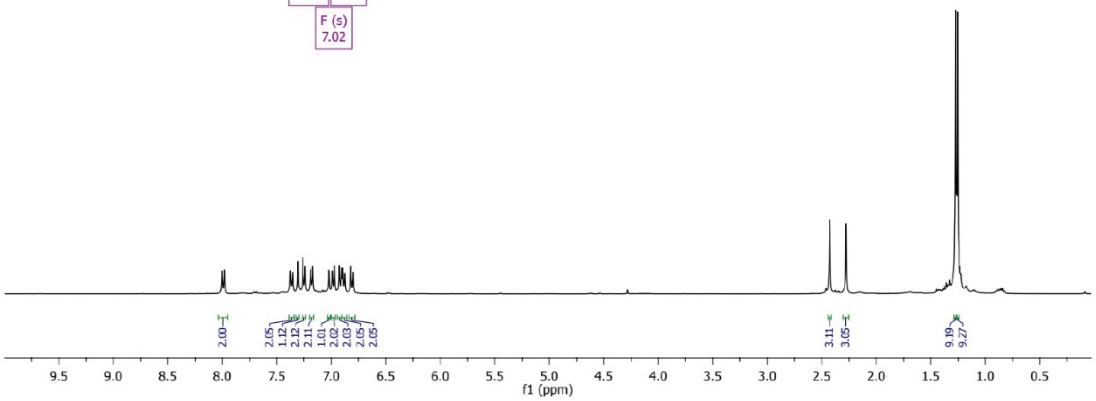


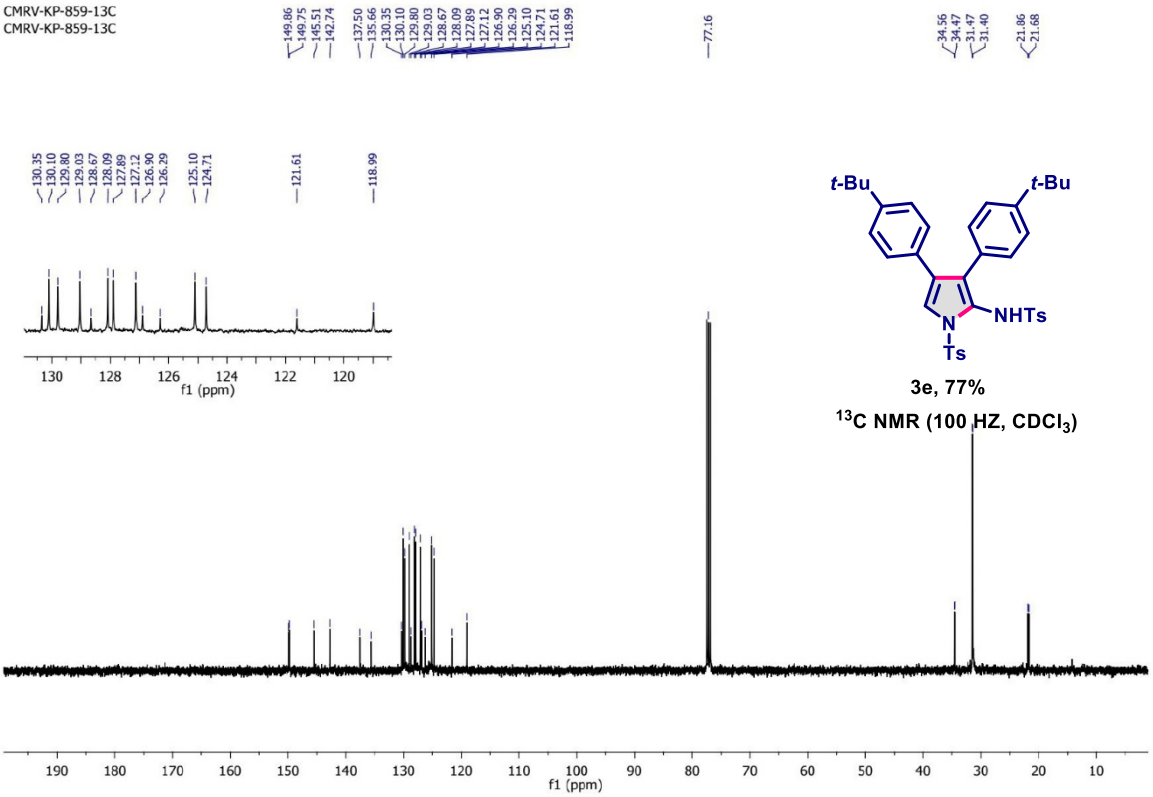

**3e, 77%**

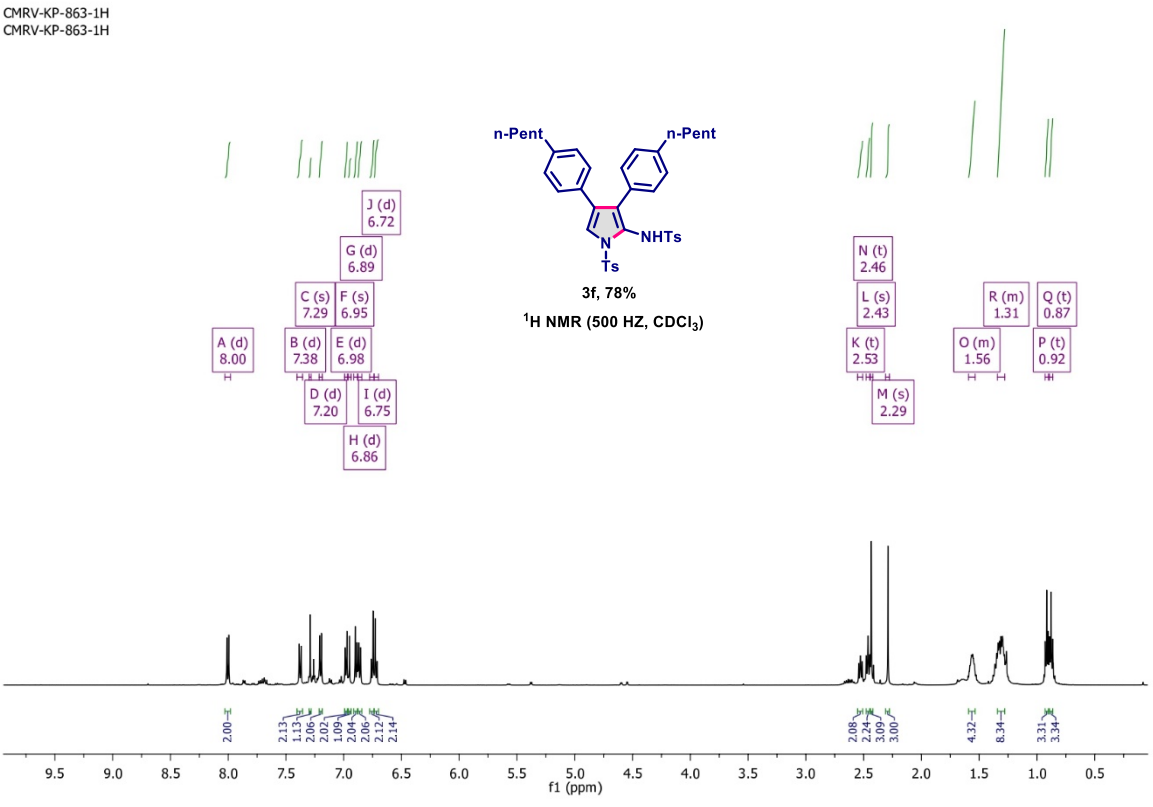
**$^{1}$H NMR (400 HZ, $CDCl_3$)**

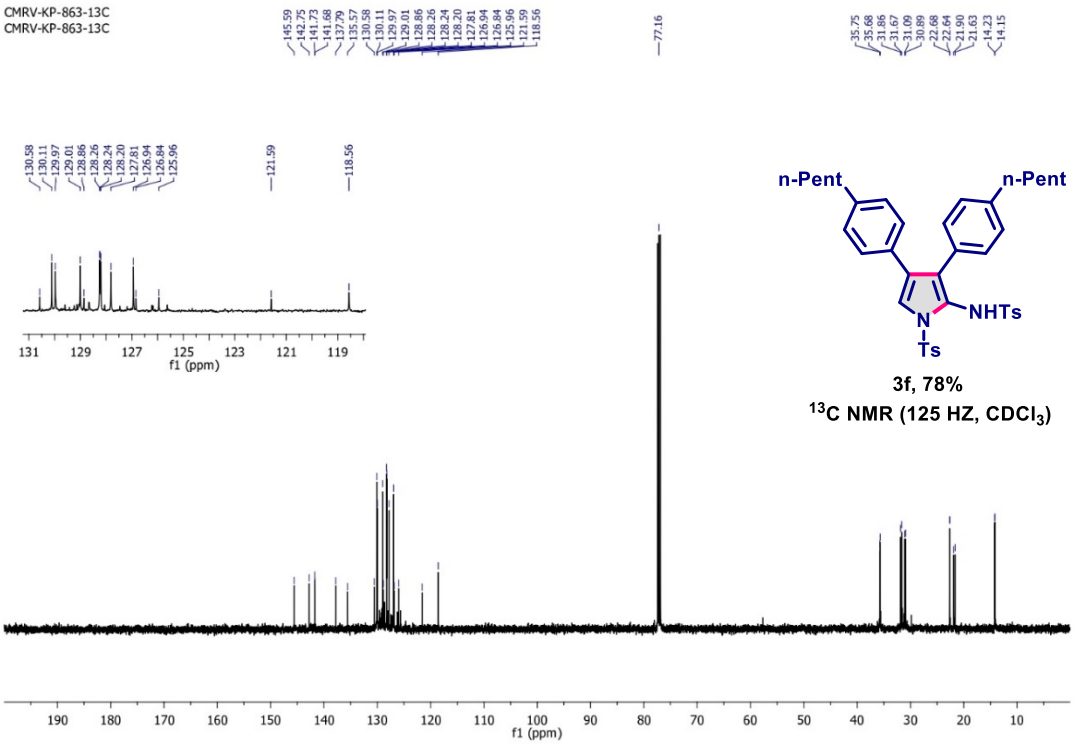


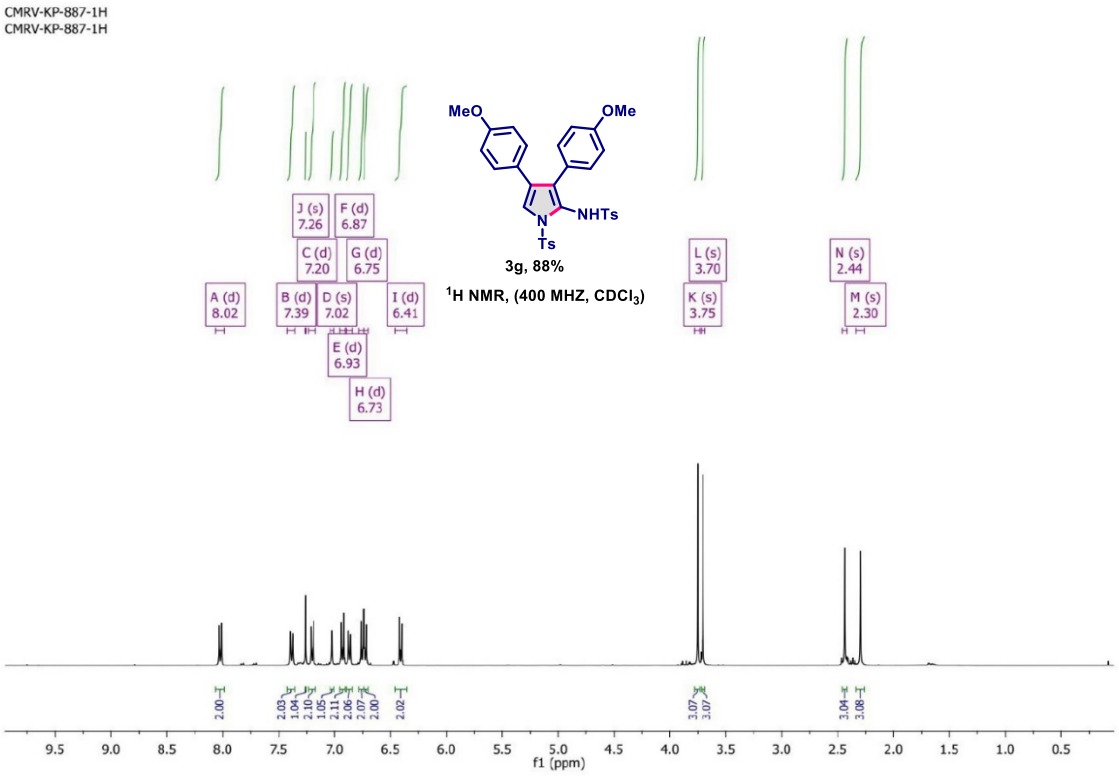



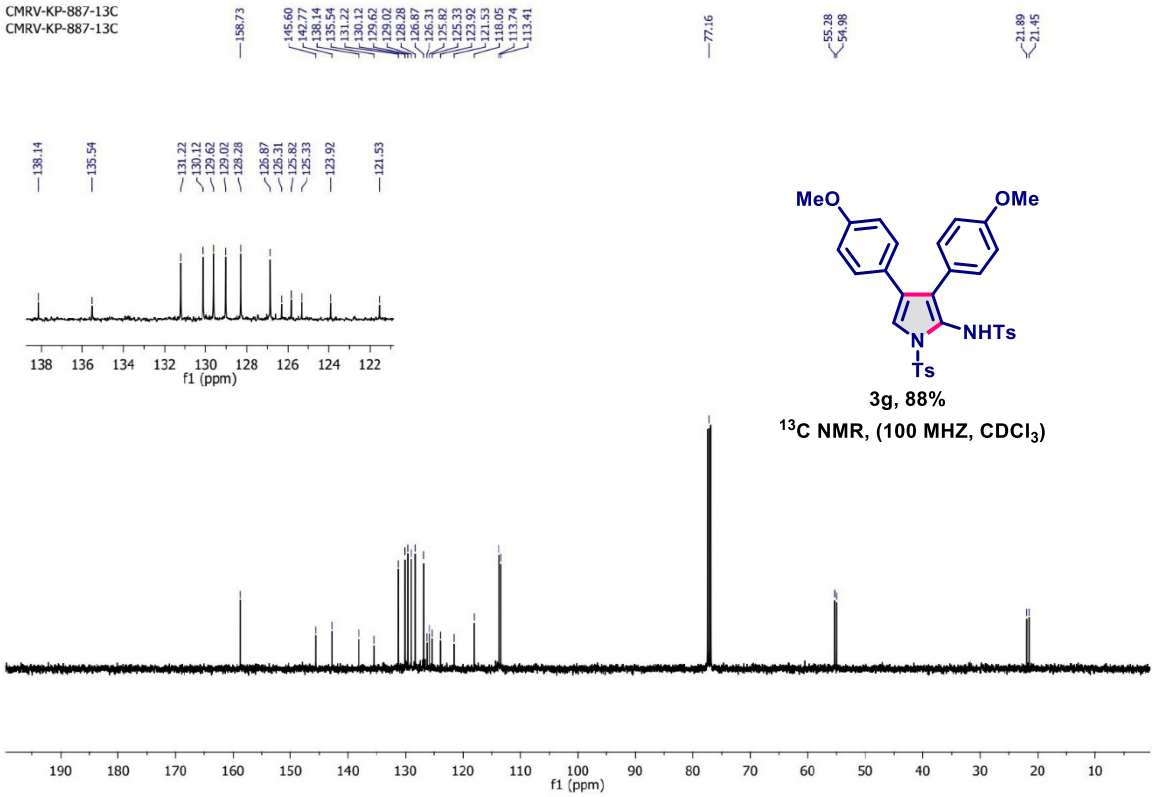



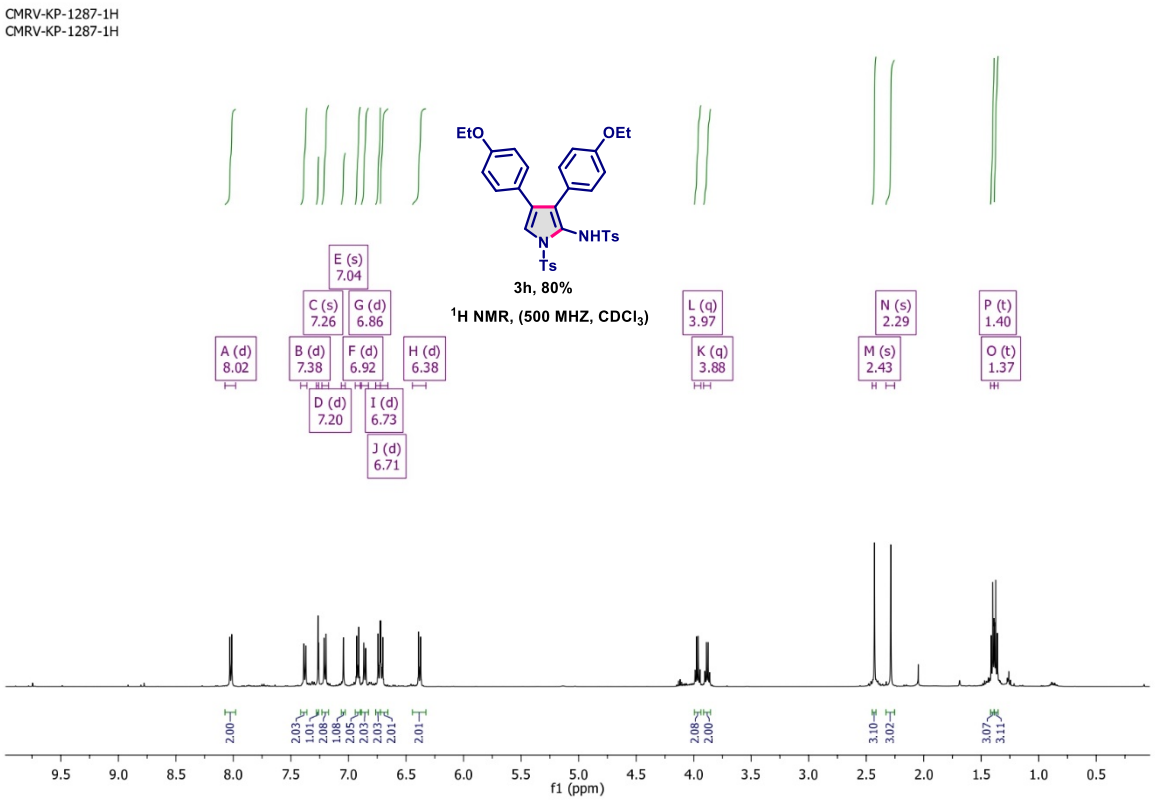

CMRV-KP-859-13C
CMRV-KP-859-13C
149.86
149.75
145.51
142.74
137.50
135.66
130.35
130.10
129.80
129.03
128.67
128.09
127.89
127.12
126.90
126.29
125.10
124.71
121.61
118.99
77.16
34.56
34.47
31.47
31.40
21.86
21.68
t-Bu
t-Bu
NHTs
N
Ts
3e, 77%
13C NMR (100 HZ, CDCl3)
f1 (ppm)

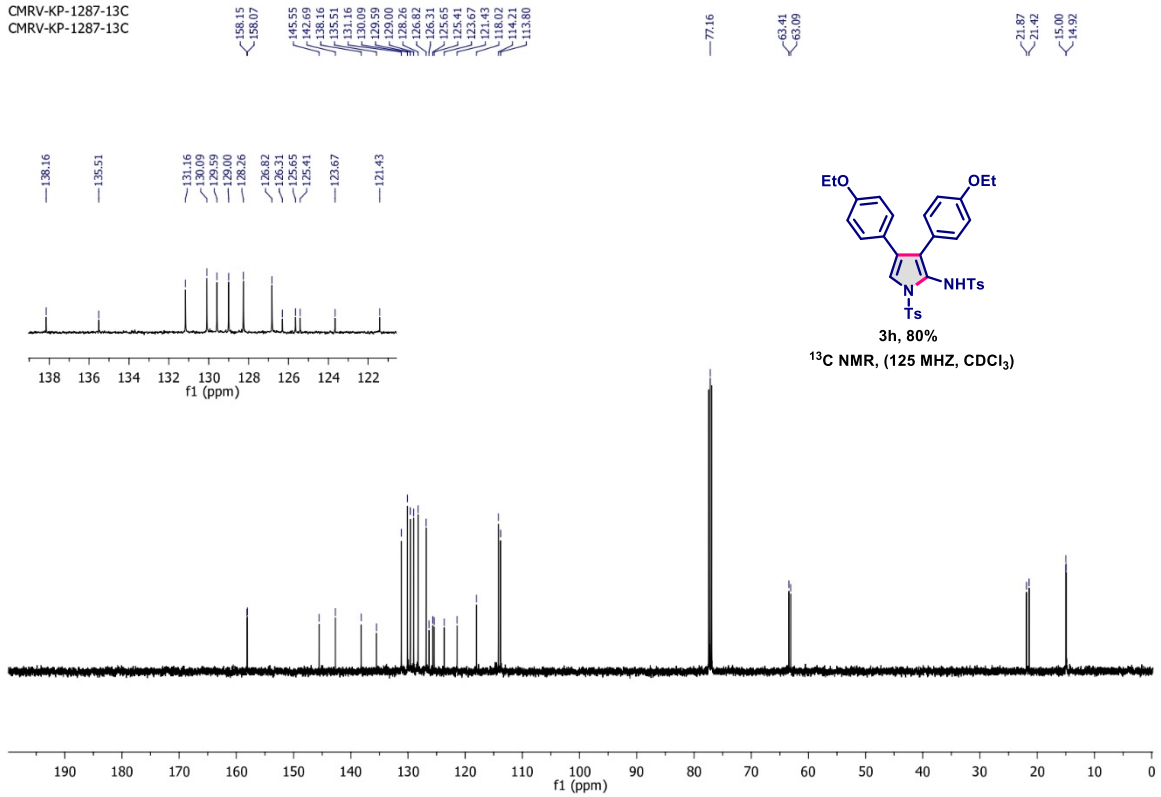

CMRV-KP-863-1H
CMRV-KP-863-1H
n-Pent
n-Pent
NHTs
N
Ts
3f, 78%
1H NMR (500 HZ, CDCl3)
J (d) 6.72
G (d) 6.89
C (s) 7.29
F (s) 6.95
A (d) 8.00
B (d) 7.38
E (d) 6.98
D (d) 7.20
I (d) 6.75
H (d) 6.86
N (t) 2.46
L (s) 2.43
K (t) 2.53
M (s) 2.29
R (m) 1.31
Q (t) 0.87
O (m) 1.56
P (t) 0.92
f1 (ppm)

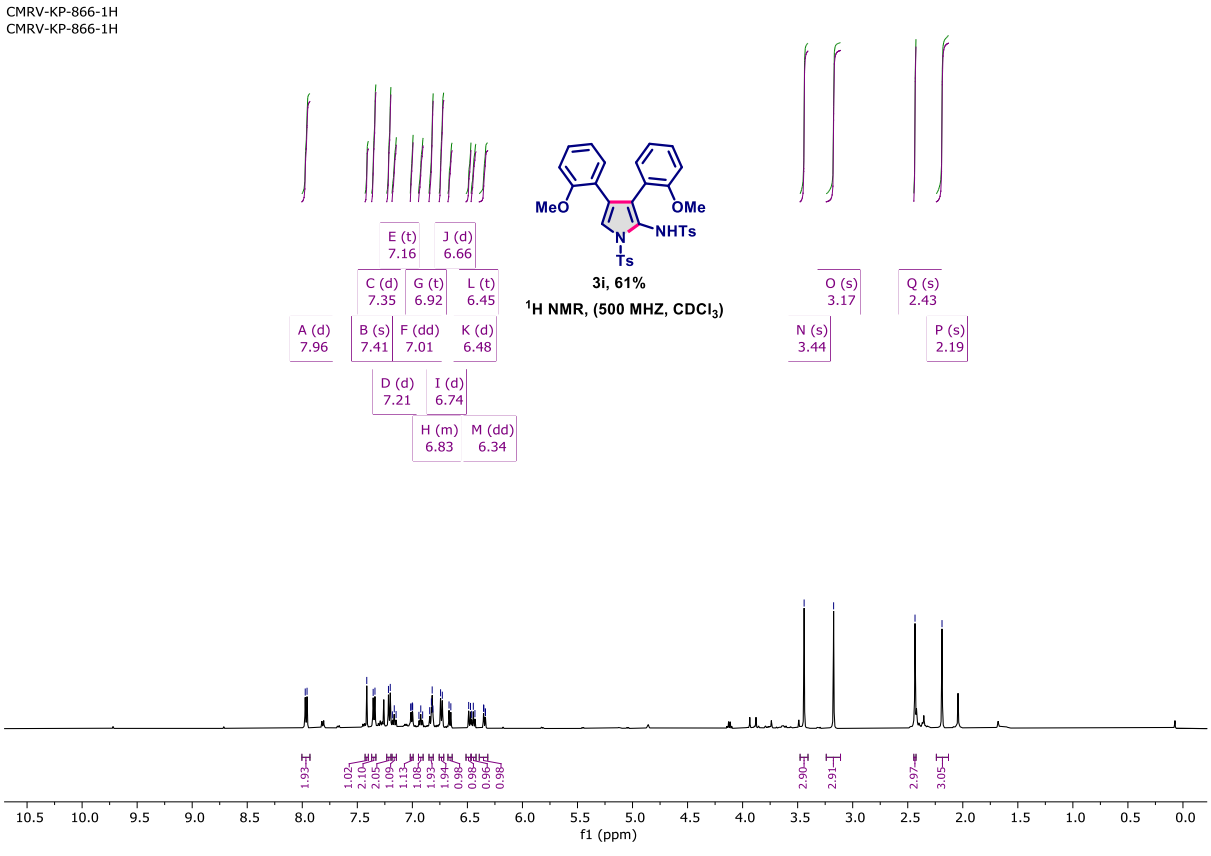

CMRV-KP-863-13C
CMRV-KP-863-13C
n-Pent
n-Pent
NHTs
N
Ts
3f, 78%
13C NMR (125 HZ, CDCl3)
f1 (ppm)

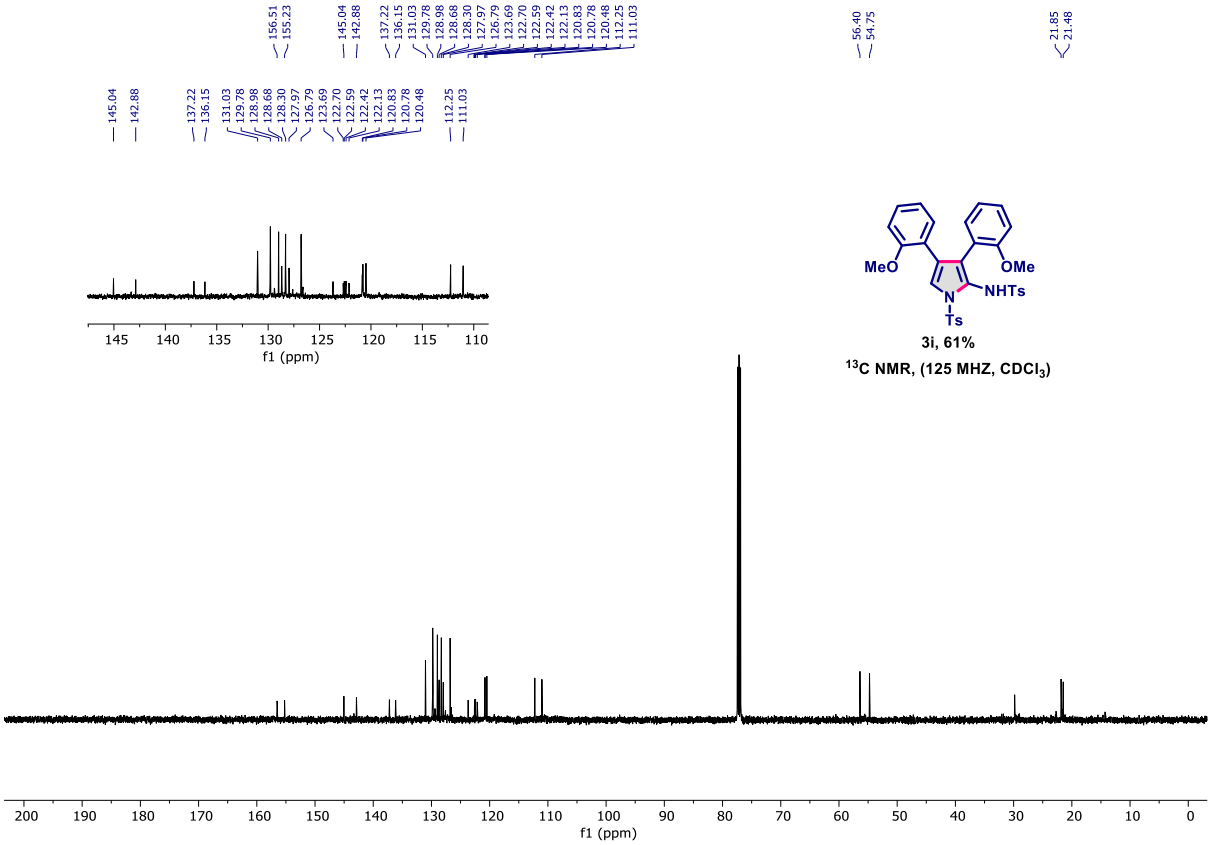

CMRV-KP-887-1H
CMRV-KP-887-1H
MeO
OMe
NHTs
N
Ts
3g, 88%
1H NMR, (400 MHZ, CDCl3)
A (d) 8.02
B (d) 7.39
C (d) 7.20
D (s) 7.02
E (d) 6.93
F (d) 6.87
G (d) 6.75
H (d) 6.73
I (d) 6.41
J (s) 7.26
K (s) 3.75
L (s) 3.70
M (s) 2.30
N (s) 2.44
f1 (ppm)


CMRV-KP-887-13C
CMRV-KP-887-13C
158.73
145.60
142.77
138.14
135.54
131.22
130.12
129.62
129.02
128.28
126.87
126.31
125.82
125.33
123.92
121.53
118.05
113.74
113.41
77.16
55.28
54.98
21.89
21.45
MeO
OMe
NHTs
N
Ts
3g, 88%
$^{13}$C NMR, (100 MHZ, CDCl$_3$)
f1 (ppm)


CMRV-KP-1287-1H
CMRV-KP-1287-1H
EtO
OEt
NHTs
N
Ts
3h, 80%
$^{1}$H NMR, (500 MHZ, CDCl$_3$)
A (d) 8.02
B (d) 7.38
C (s) 7.26
D (d) 7.20
E (s) 7.04
F (d) 6.92
G (d) 6.86
H (d) 6.38
I (d) 6.73
J (d) 6.71
K (q) 3.88
L (q) 3.97
M (s) 2.43
N (s) 2.29
O (t) 1.37
P (t) 1.40
f1 (ppm)

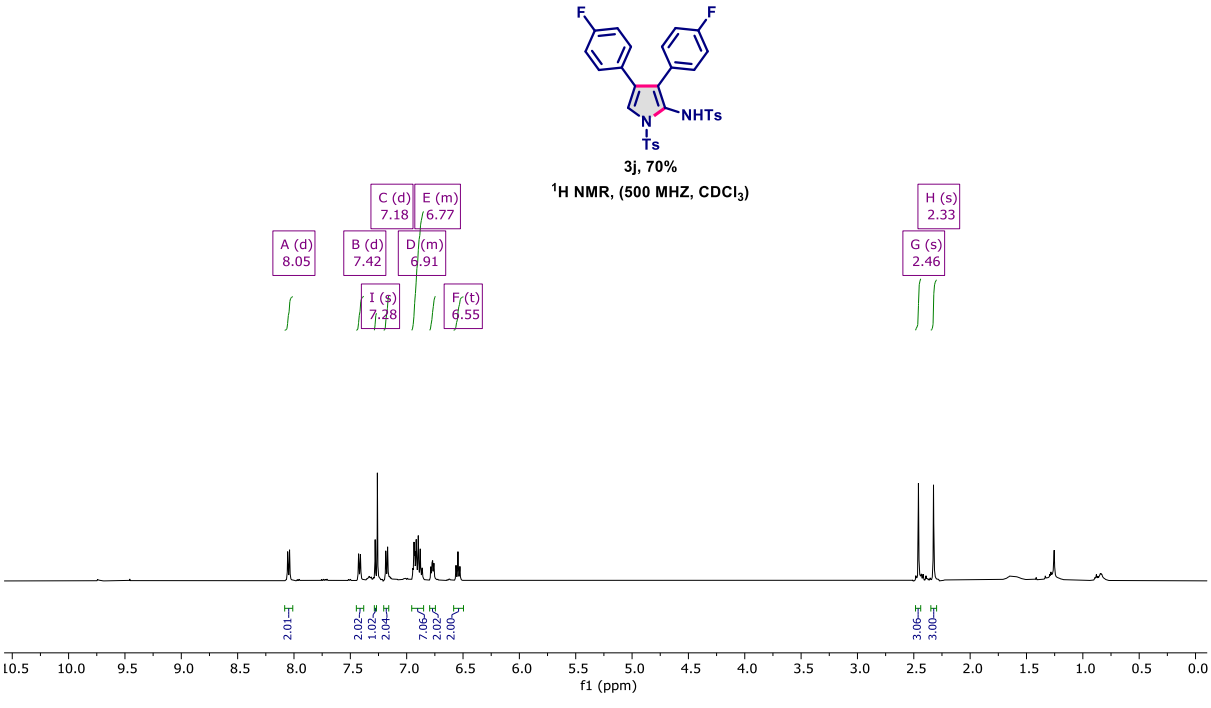

CMRV-KP-1287-13C
CMRV-KP-1287-13C
158.15
158.07
145.55
142.69
138.16
135.51
131.16
130.09
129.59
129.00
128.26
126.82
126.31
125.65
125.41
123.67
121.43
118.02
114.21
113.80
77.16
63.41
63.09
21.87
21.42
15.00
14.92
EtO
OEt
NHTs
N
Ts
3h, 80%
13C NMR, (125 MHZ, CDCl3)
f1 (ppm)


CMRV-KP-866-1H
CMRV-KP-866-1H
E (t) 7.16
J (d) 6.66
C (d) 7.35
G (t) 6.92
L (t) 6.45
A (d) 7.96
B (s) 7.41
F (dd) 7.01
K (d) 6.48
D (d) 7.21
I (d) 6.74
H (m) 6.83
M (dd) 6.34
MeO
OMe
NHTs
N
Ts
3i, 61%
1H NMR, (500 MHZ, CDCl3)
O (s) 3.17
Q (s) 2.43
N (s) 3.44
P (s) 2.19
f1 (ppm)



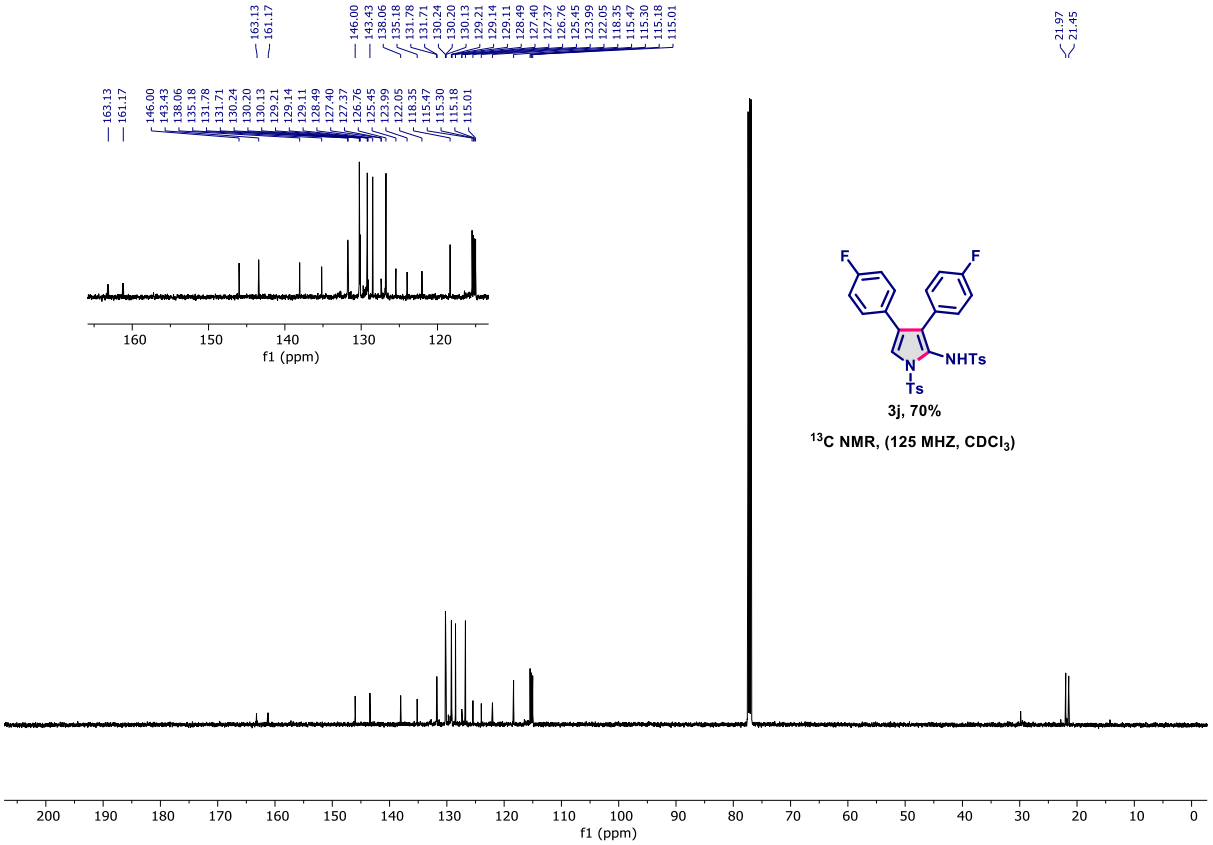

**3i, 61%**

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




**3j, 70%**

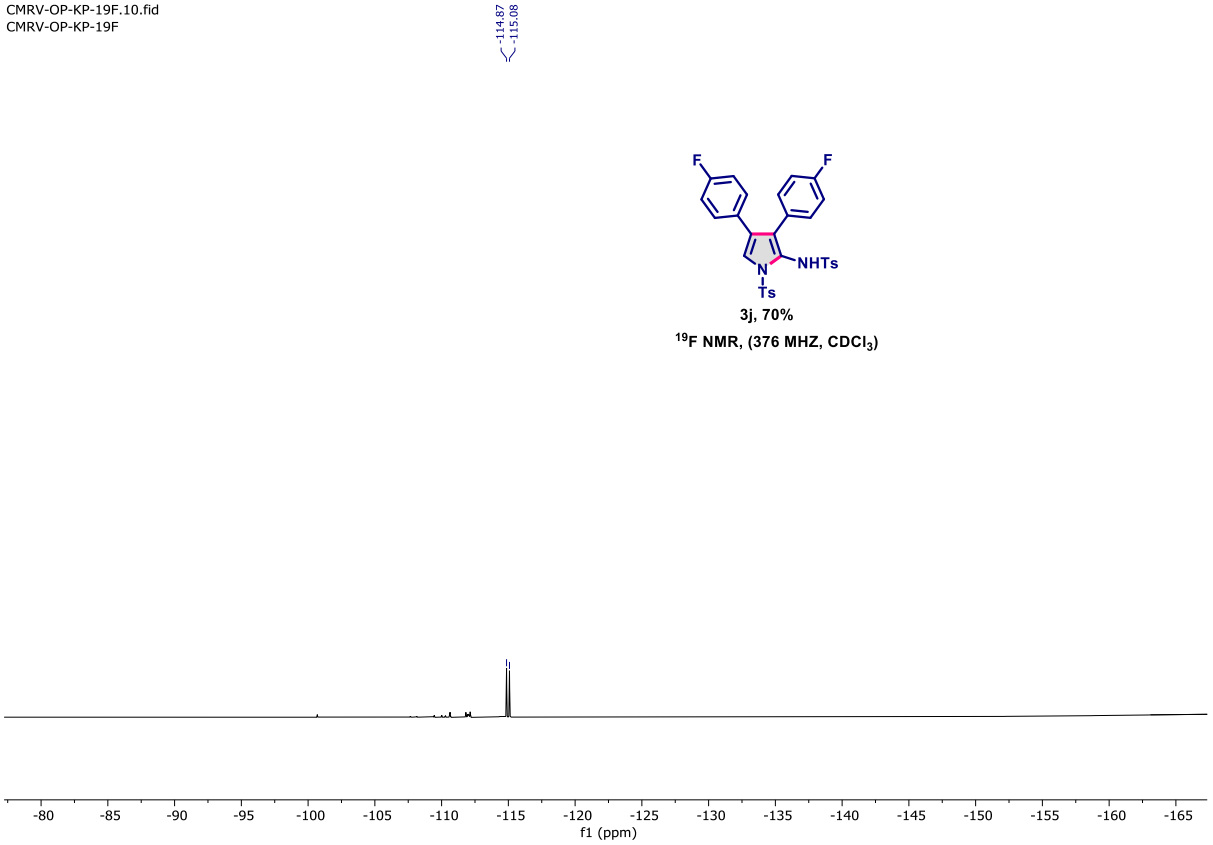
**$^{1}$H NMR, (500 MHZ, $CDCl_3$)**




**3j, 70%**

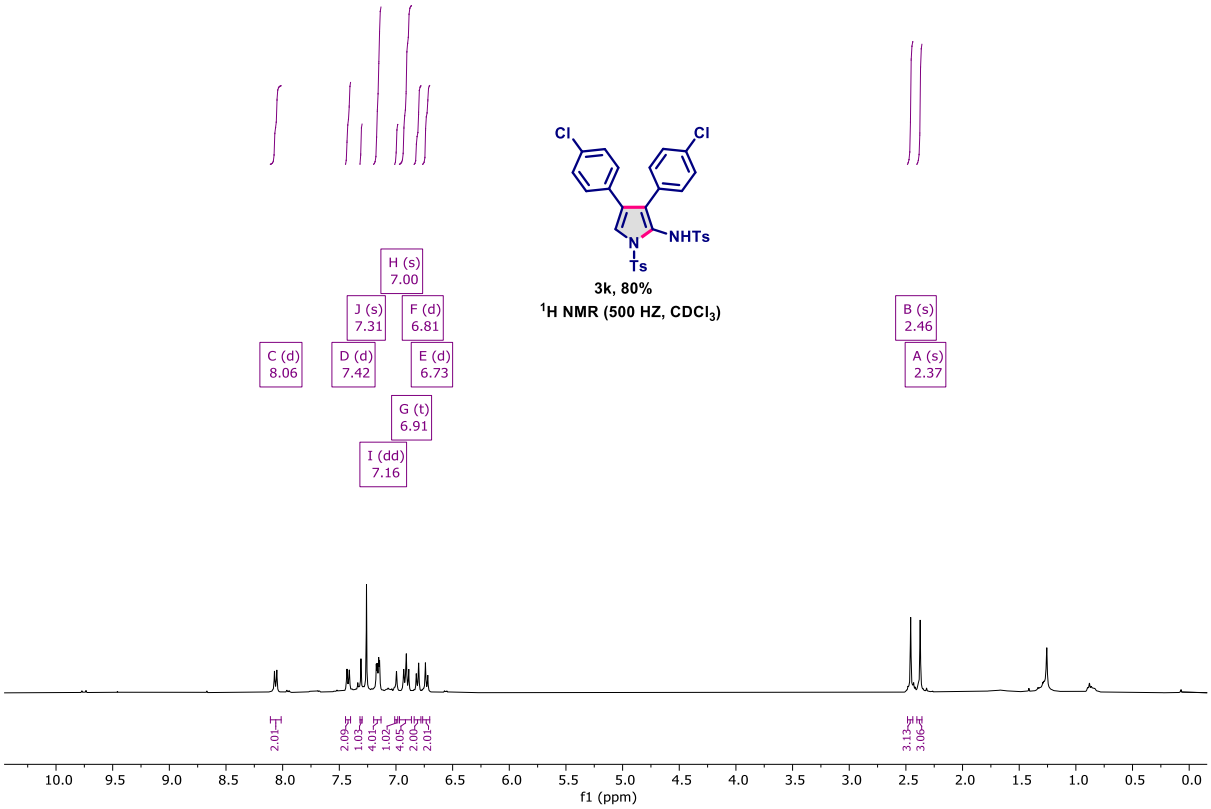
**$^{13}$C NMR, (125 MHZ, $CDCl_3$)**

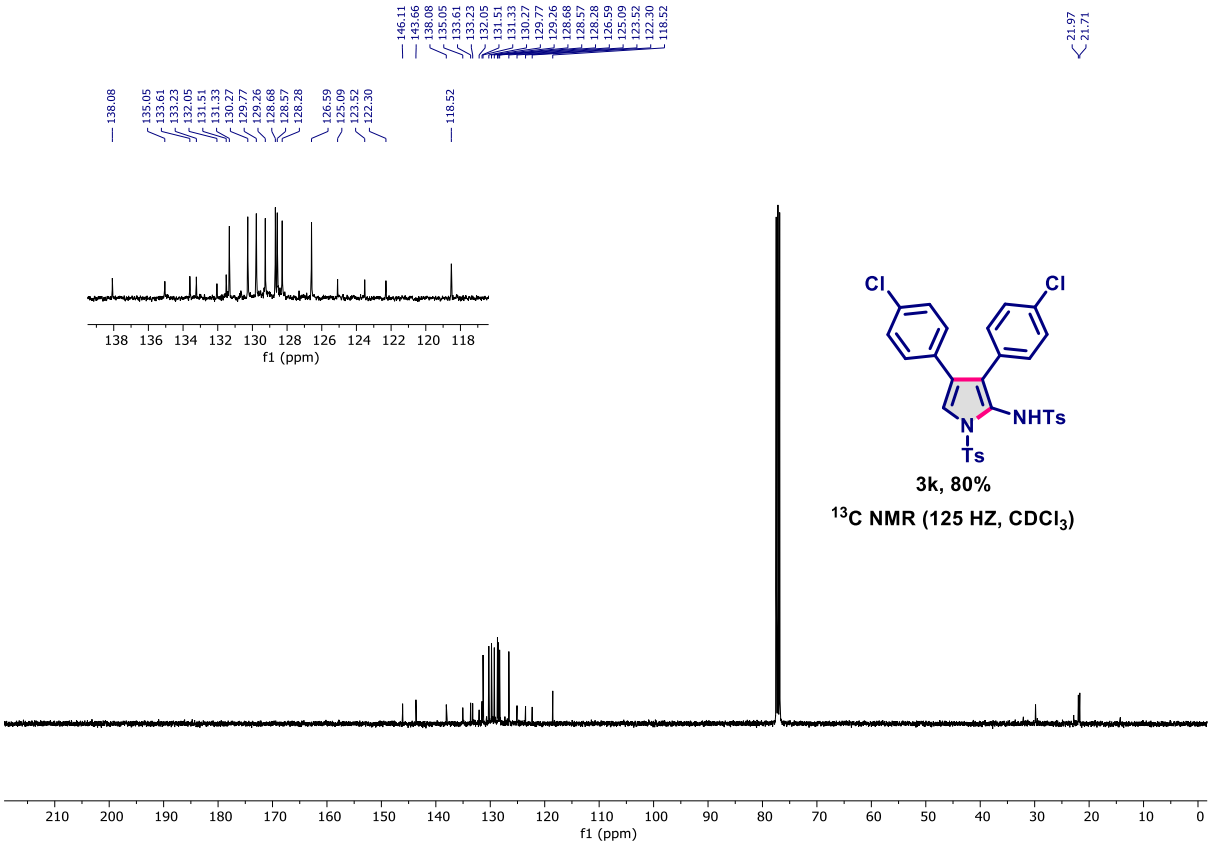
CMRV-OP-KP-19F.10.fid
CMRV-OP-KP-19F

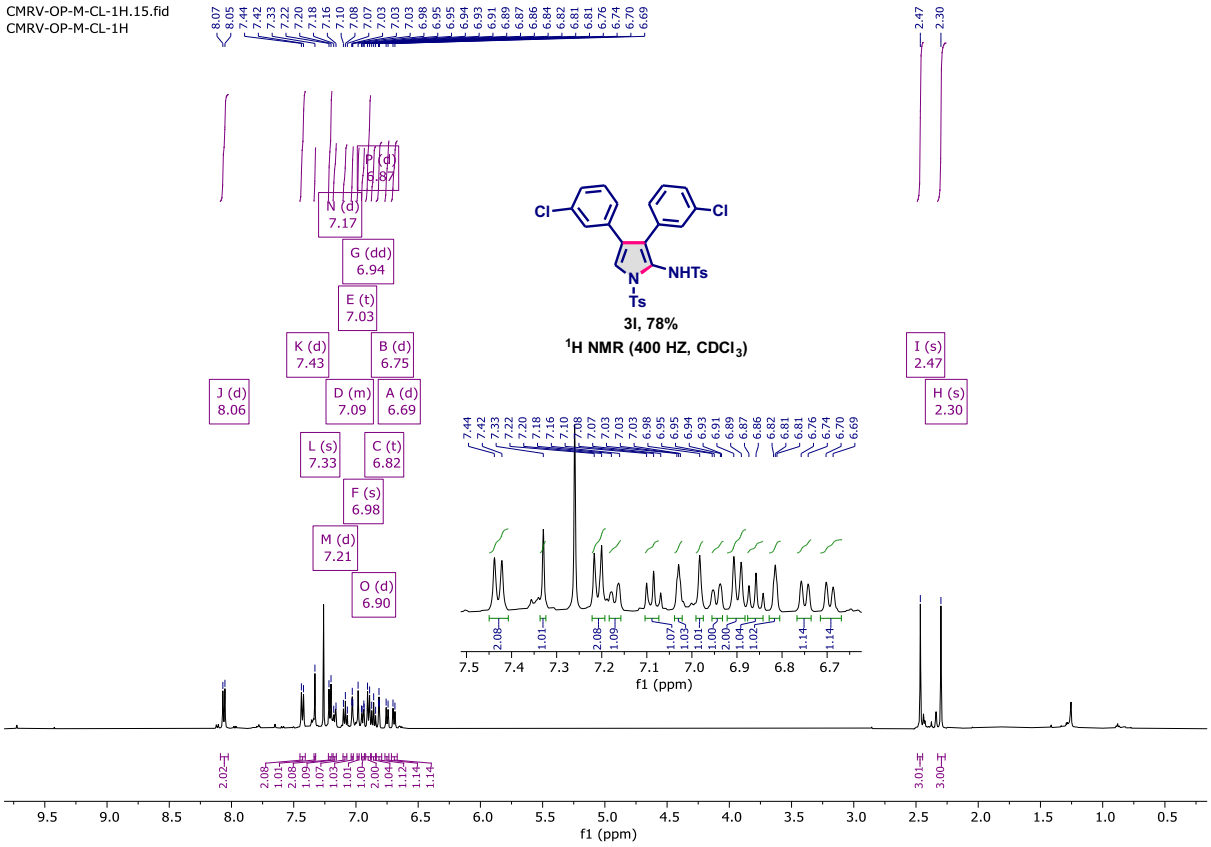


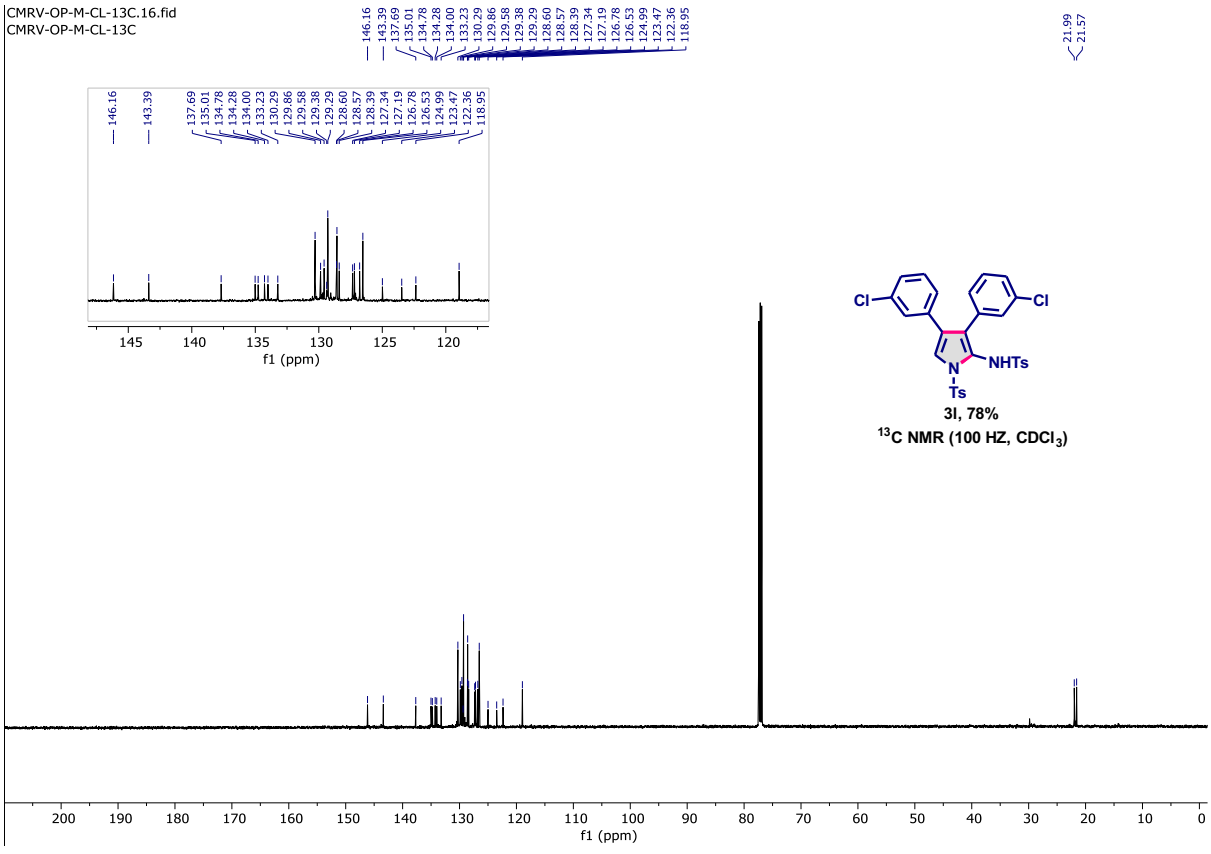

**3j, 70%**

**$^{19}$F NMR, (376 MHZ, $CDCl_3$)**

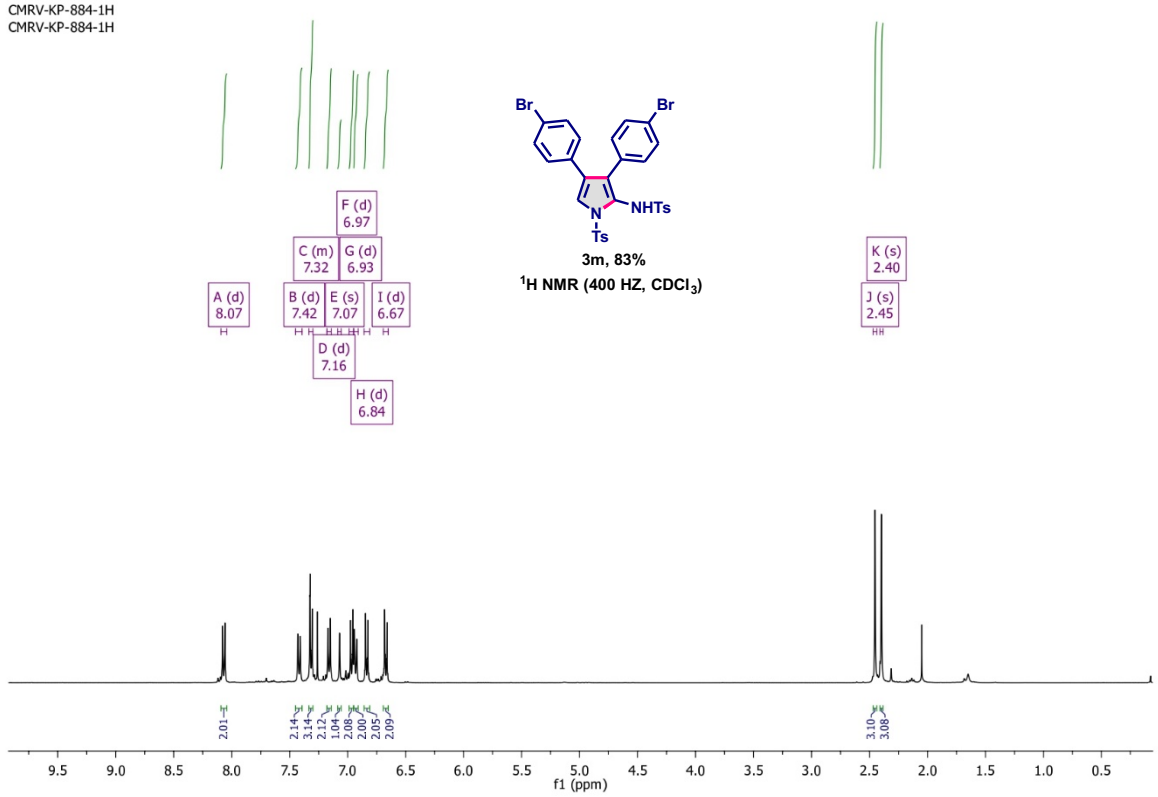

H (s) 7.00
J (s) 7.31
F (d) 6.81
C (d) 8.06
D (d) 7.42
E (d) 6.73
G (t) 6.91
I (dd) 7.16
B (s) 2.46
A (s) 2.37
Cl
Cl
NHTs
N
Ts
3k, 80%
1H NMR (500 HZ, CDCl3)
2.01
2.09
1.03
4.01
1.02
4.05
2.00
2.01
3.13
3.06
f1 (ppm)


146.11
143.66
138.08
135.05
133.61
133.23
132.05
131.51
131.33
130.27
129.77
129.26
128.68
128.57
128.28
126.59
125.09
123.52
122.30
118.52
21.97
21.71
f1 (ppm)
Cl
Cl
NHTs
N
Ts
3k, 80%
13C NMR (125 HZ, CDCl3)
f1 (ppm)


CMRV-OP-M-CL-1H.15.fid
CMRV-OP-M-CL-1H
P (d) 8.87
N (d) 7.17
G (dd) 6.94
E (t) 7.03
K (d) 7.43
B (d) 6.75
J (d) 8.06
D (m) 7.09
A (d) 6.69
L (s) 7.33
C (t) 6.82
F (s) 6.98
M (d) 7.21
O (d) 6.90
I (s) 2.47
H (s) 2.30
Cl
Cl
NHTs
N
Ts
3l, 78%
$^{1}$H NMR (400 HZ, CDCl$_3$)
f1 (ppm)


CMRV-OP-M-CL-13C.16.fid
CMRV-OP-M-CL-13C
Cl
Cl
NHTs
N
Ts
3l, 78%
$^{13}$C NMR (100 HZ, CDCl$_3$)
f1 (ppm)

CMRV-KP-884-1H
CMRV-KP-884-1H



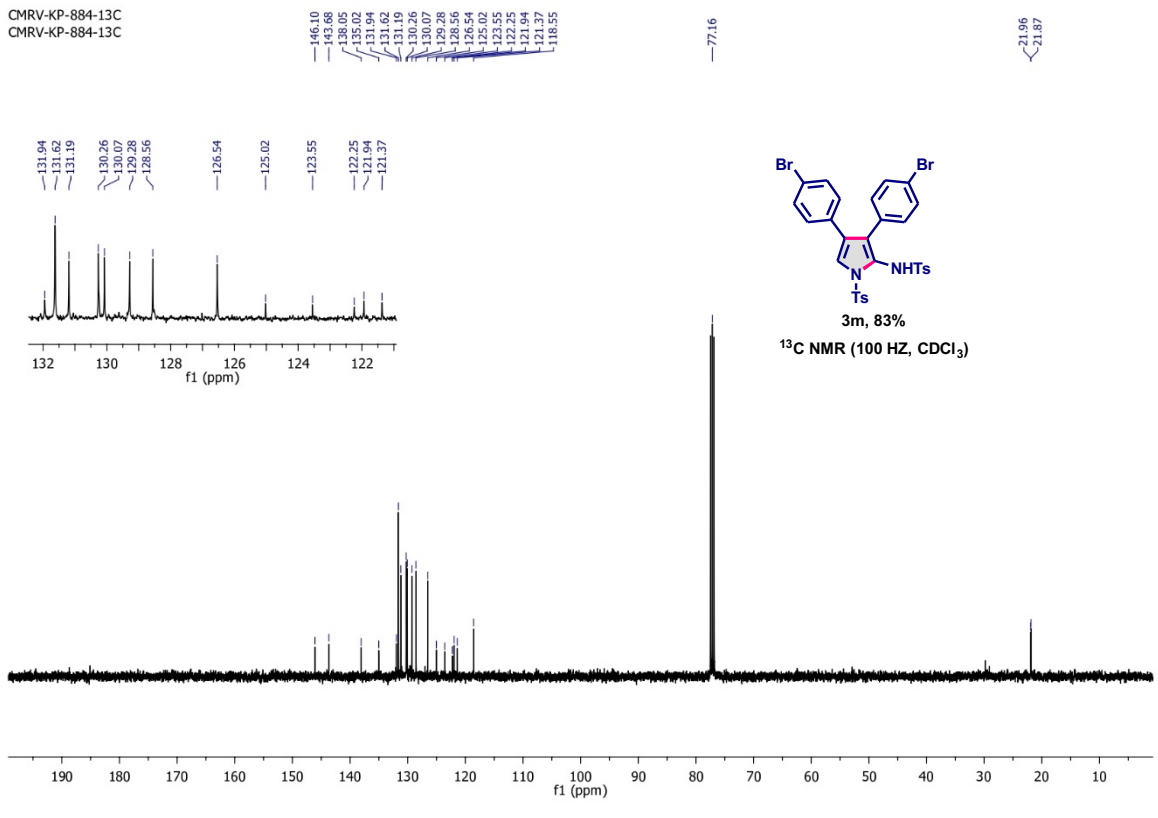




**3m, 83%**

**$^{1}$H NMR (400 HZ, CDCl$_3$)**

CMRV-KP-884-13C
CMRV-KP-884-13C

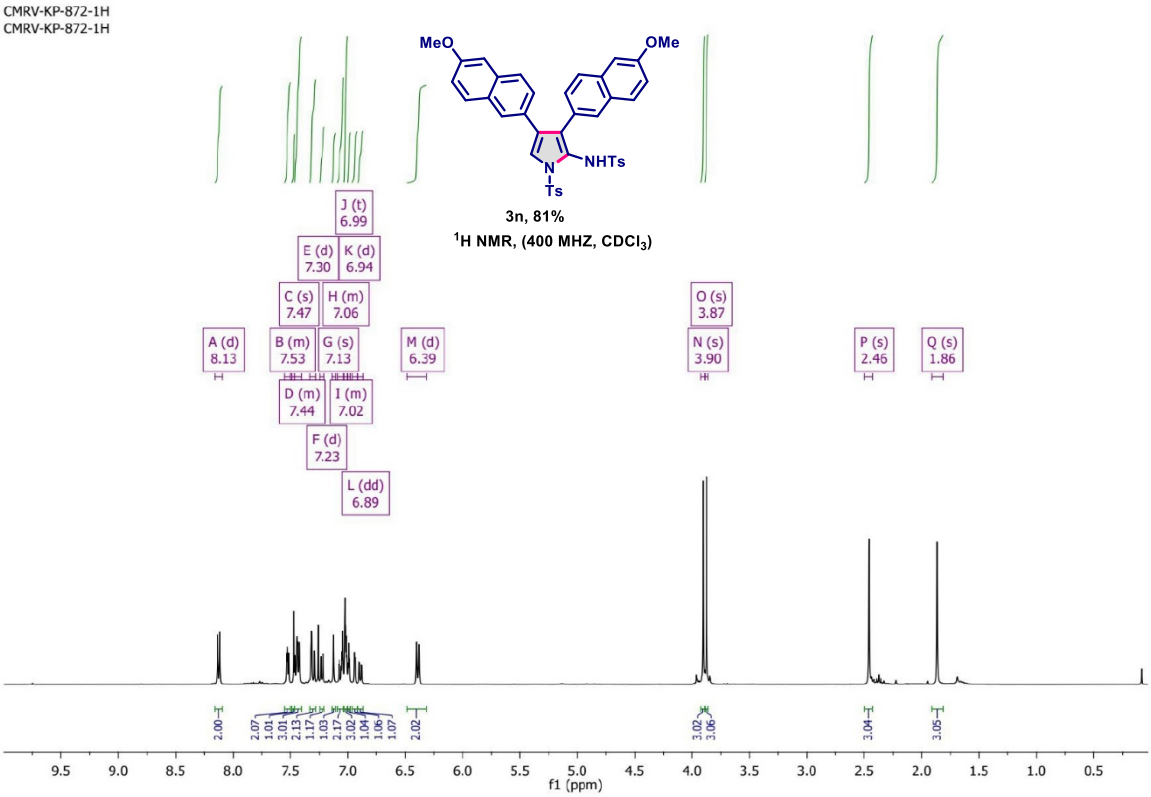


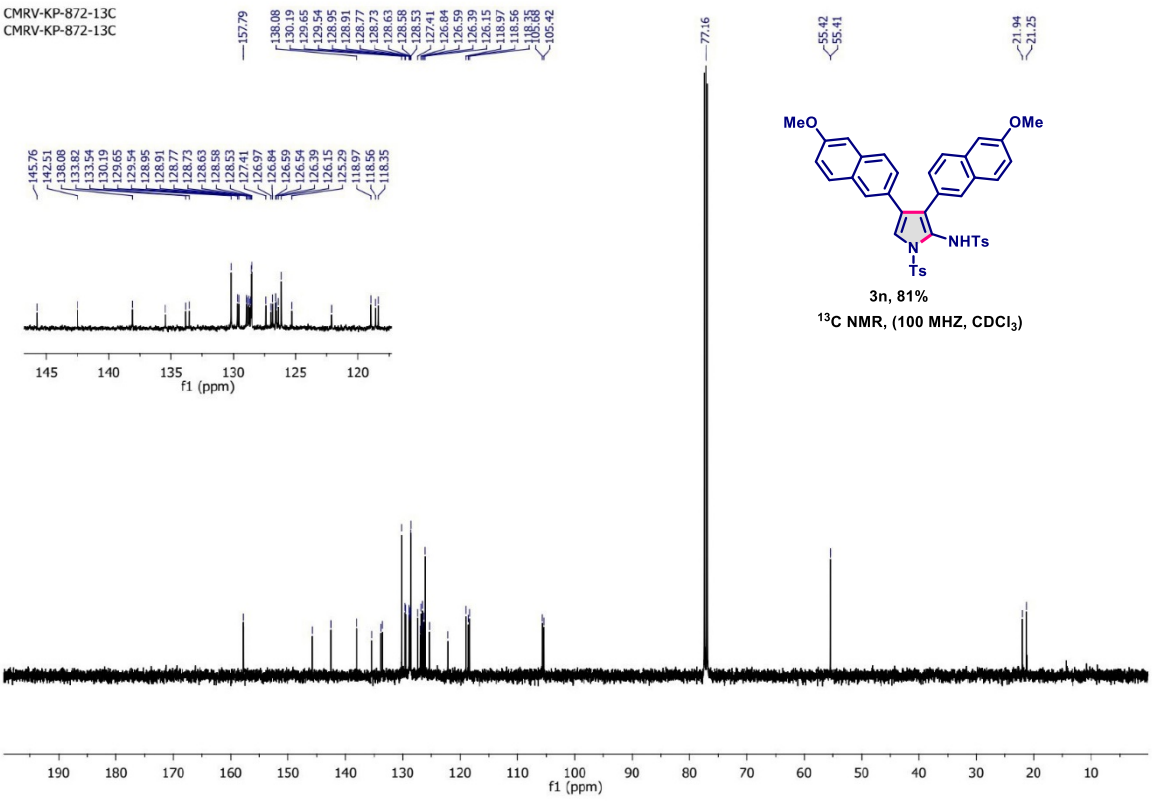


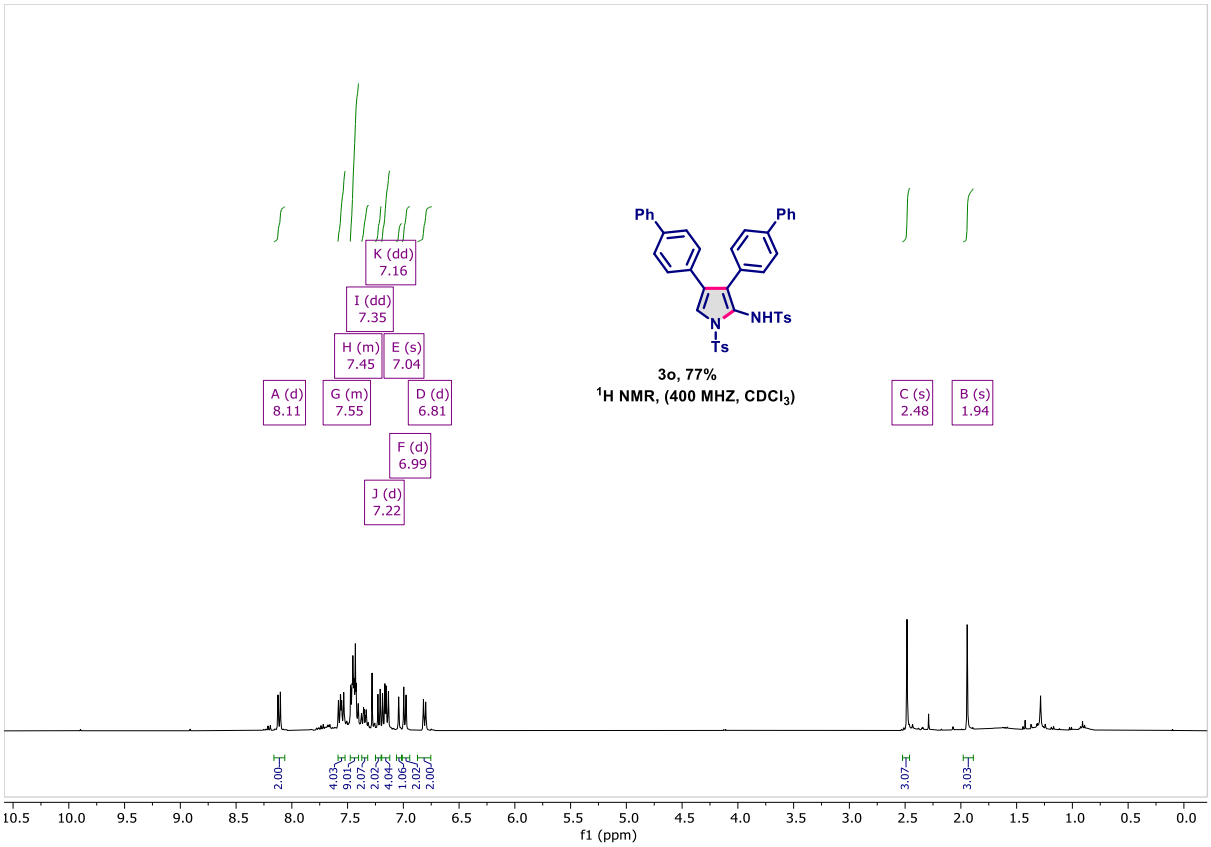


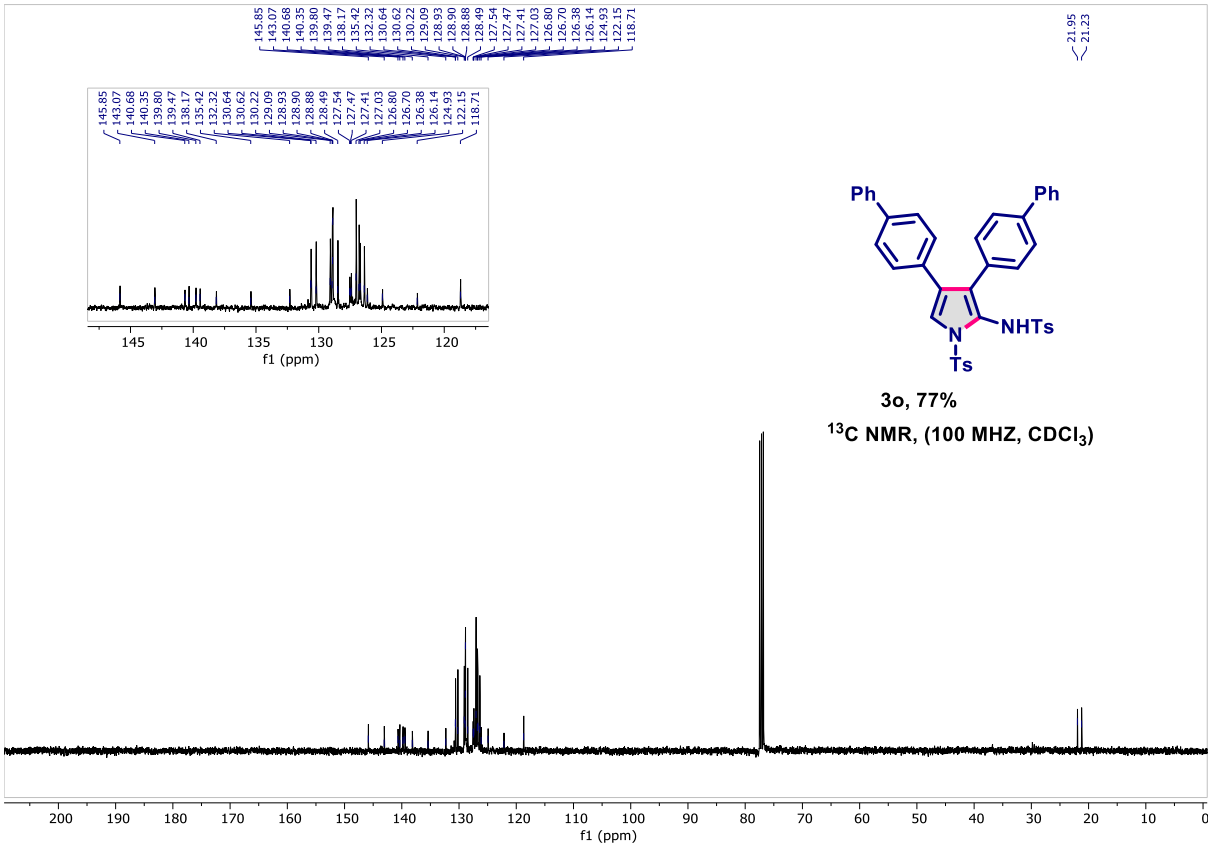
**3m, 83%**

**$^{13}$C NMR (100 HZ, CDCl$_3$)**

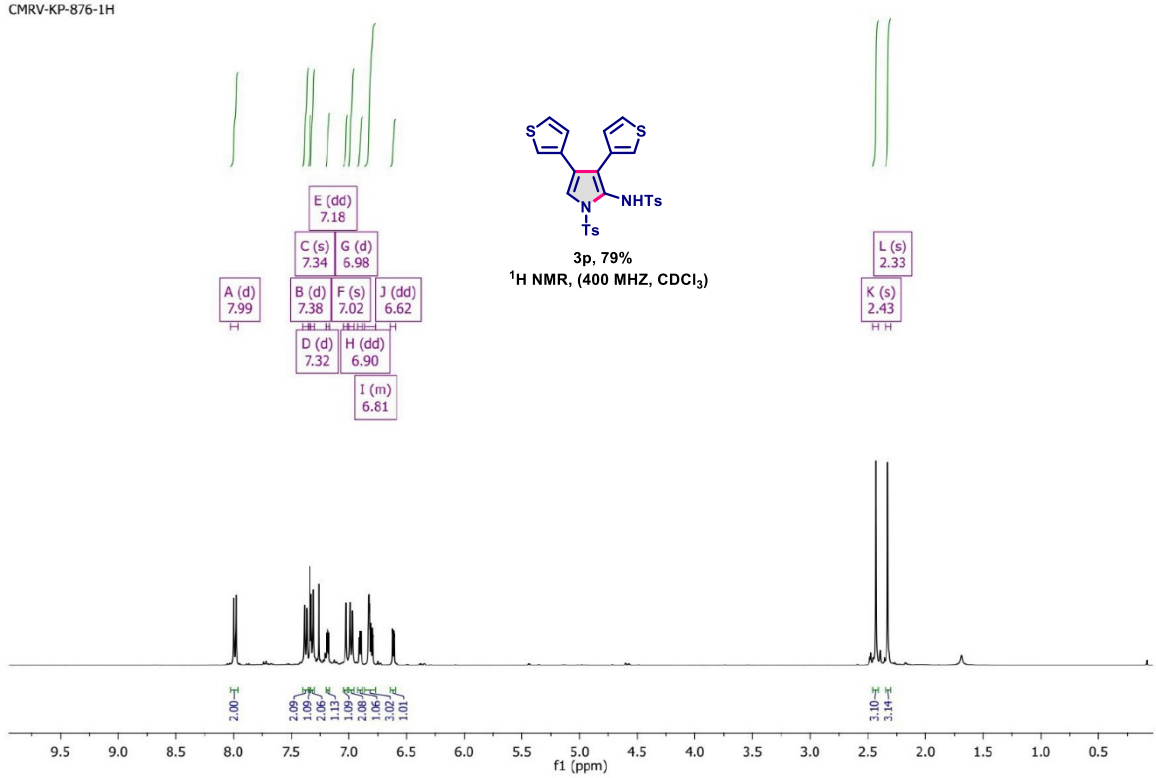

CMRV-KP-872-1H
CMRV-KP-872-1H
MeO
OMe
NHTs
N
Ts
3n, 81%
$^1$H NMR, (400 MHZ, CDCl$_3$)
J (t) 6.99
E (d) 7.30
K (d) 6.94
C (s) 7.47
H (m) 7.06
O (s) 3.87
A (d) 8.13
B (m) 7.53
G (s) 7.13
M (d) 6.39
N (s) 3.90
P (s) 2.46
Q (s) 1.86
D (m) 7.44
I (m) 7.02
F (d) 7.23
L (dd) 6.89
f1 (ppm)


CMRV-KP-872-13C
CMRV-KP-872-13C
MeO
OMe
NHTs
N
Ts
3n, 81%
$^{13}$C NMR, (100 MHZ, CDCl$_3$)
f1 (ppm)


K (dd) 7.16
I (dd) 7.35
H (m) 7.45
E (s) 7.04
A (d) 8.11
G (m) 7.55
D (d) 6.81
F (d) 6.99
J (d) 7.22
C (s) 2.48
B (s) 1.94
Ph
Ph
NHTs
N
Ts
3o, 77%
1H NMR, (400 MHZ, CDCl3)
f1 (ppm)

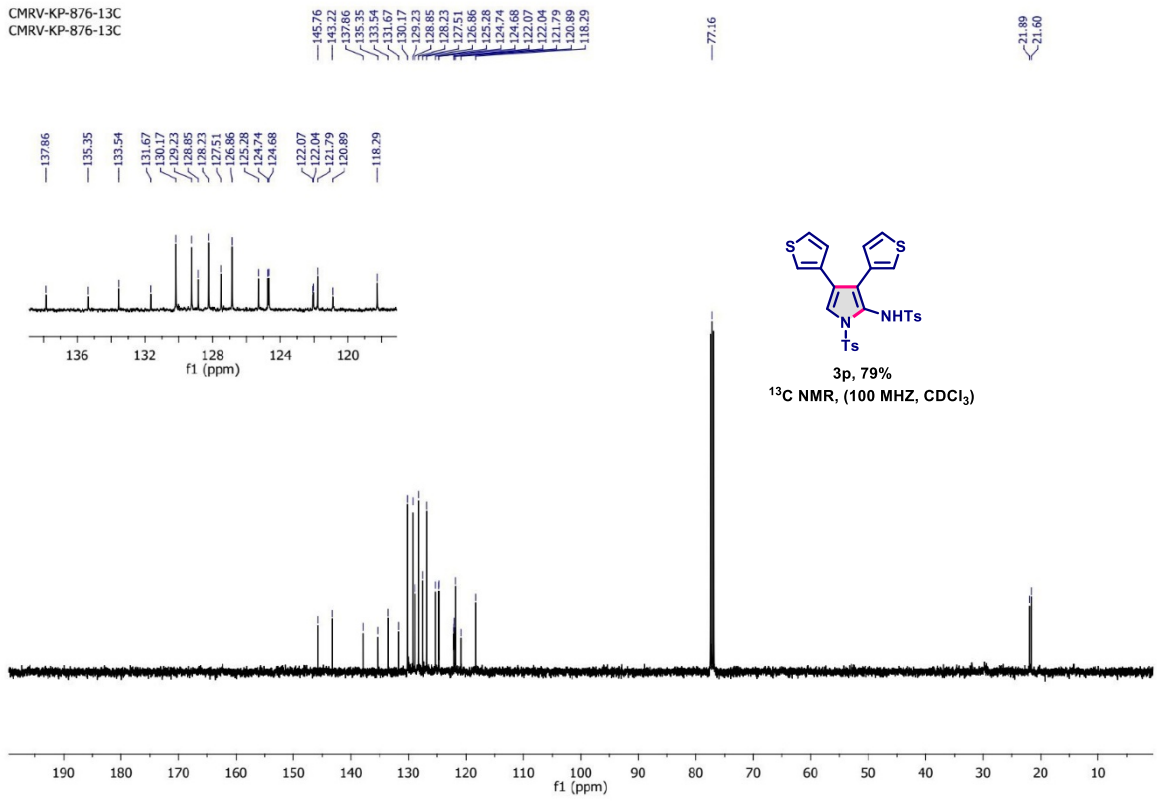

145.85
143.07
140.68
140.35
139.80
139.47
138.17
135.42
132.32
130.64
130.62
130.22
129.09
128.93
128.90
128.88
128.49
127.54
127.47
127.41
127.03
126.80
126.70
126.38
126.14
124.93
122.15
118.71
21.95
21.23
Ph
Ph
NHTs
N
Ts
3o, 77%
13C NMR, (100 MHZ, CDCl3)
f1 (ppm)

CMRV-KP-876-1H
CMRV-KP-876-1H



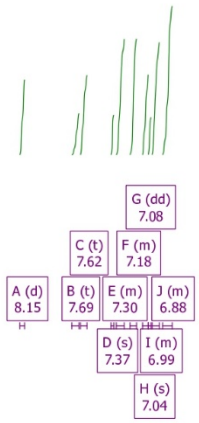

3p, 79%
$^{1}$H NMR, (400 MHZ, $CDCl_3$)

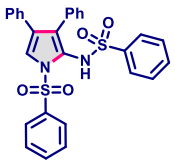
CMRV-KP-876-13C
CMRV-KP-876-13C



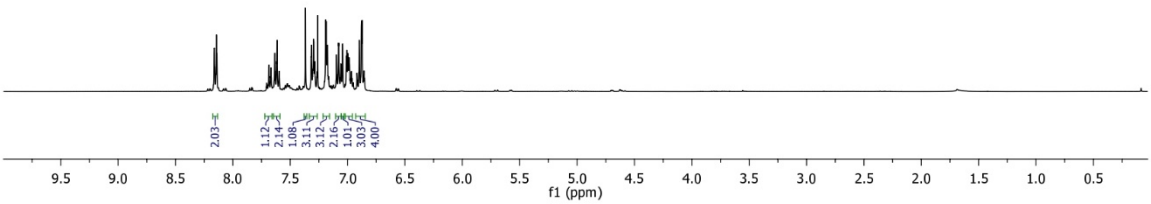

3p, 79%
$^{13}$C NMR, (100 MHZ, $CDCl_3$)

CMRV-KP-893-1H
CMRV-KP-893-1H



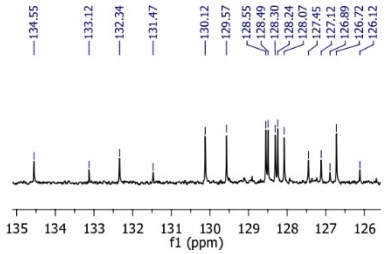



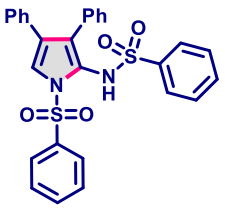
**4a, 80%**
**$^1$H NMR, (400 MHZ, $CDCl_3$)**



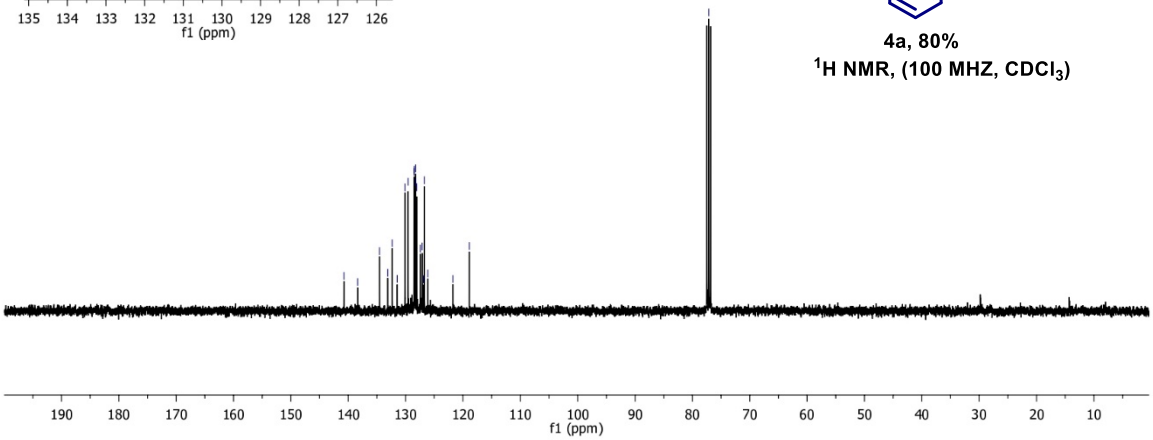

CMRV-KP-893-13C
CMRV-KP-893-13C

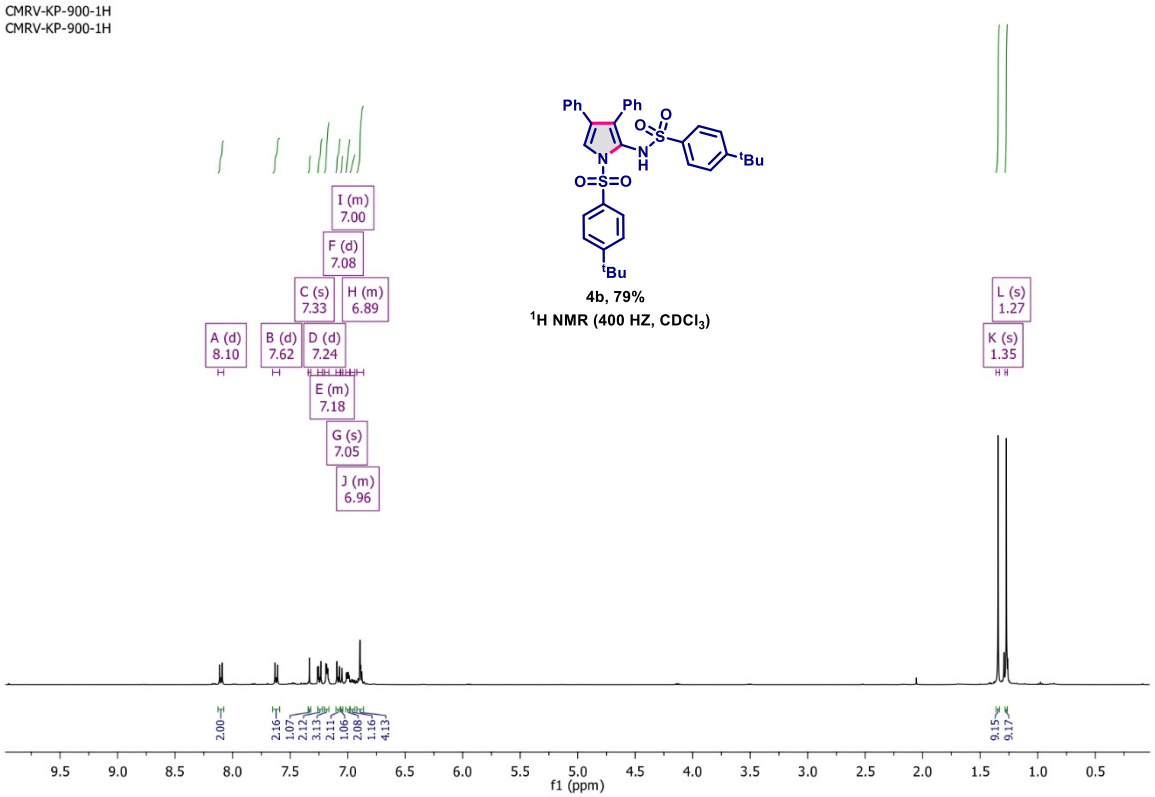




**4a, 80%**
**$^1$H NMR, (100 MHZ, $CDCl_3$)**

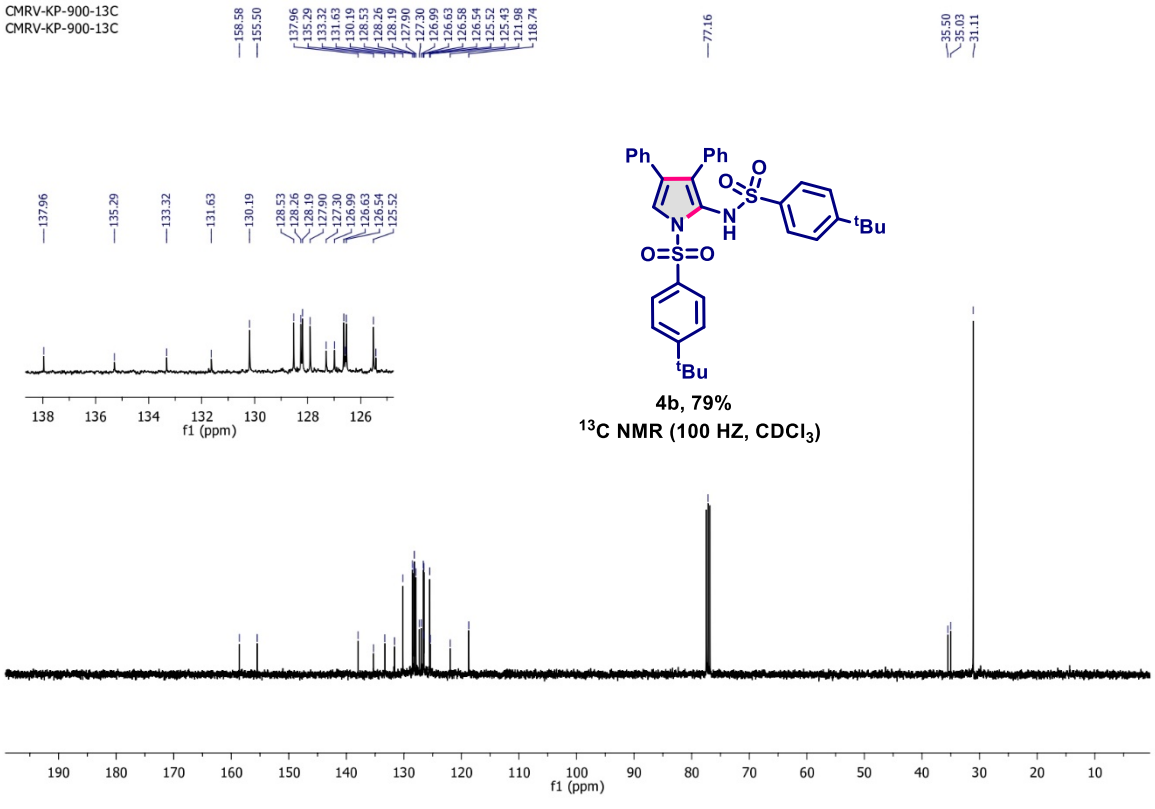







**4b, 79%**

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

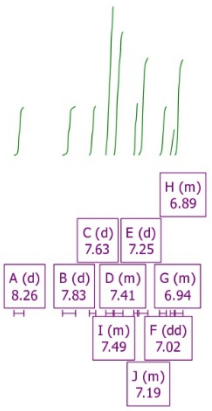


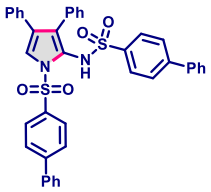



**4b, 79%**

**$^{13}$C NMR (100 HZ, $CDCl_3$)**

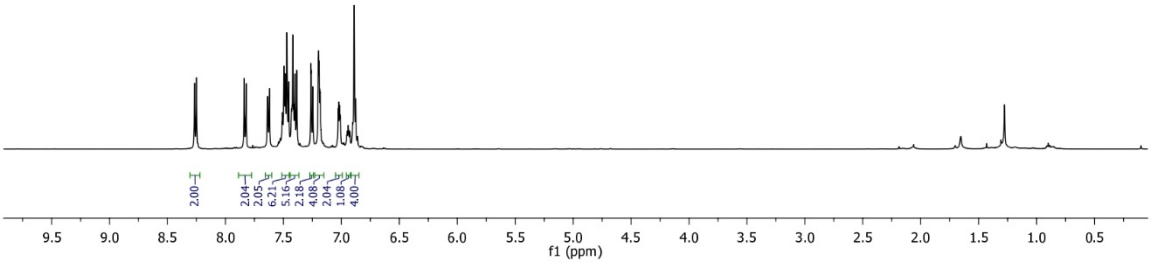
CMRV-KP-902-1H
CMRV-KP-902-1H



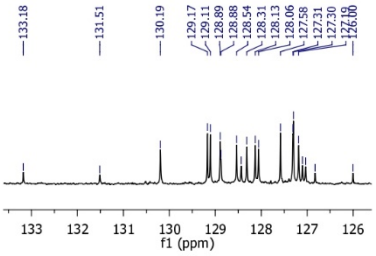



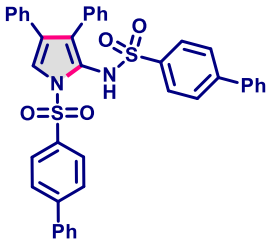

**4c, 82%**

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



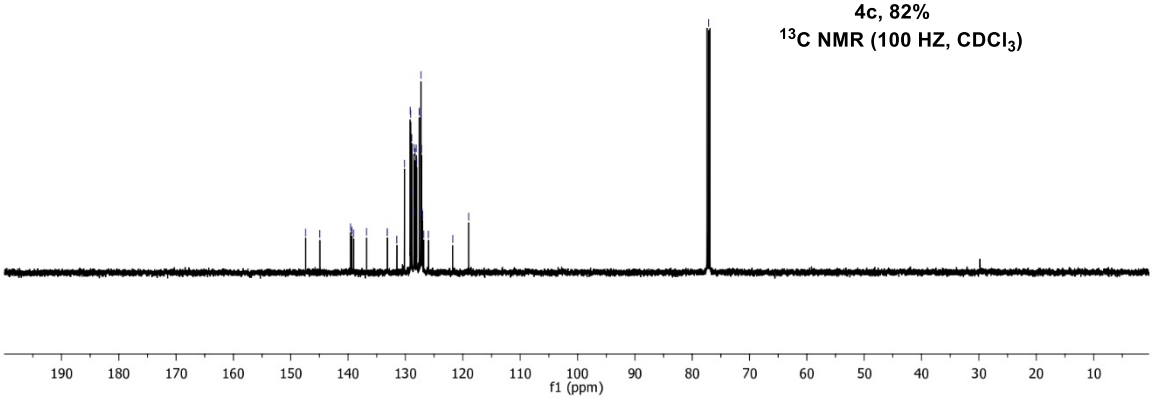

CMRV-KP-902-13C
CMRV-KP-902-13C

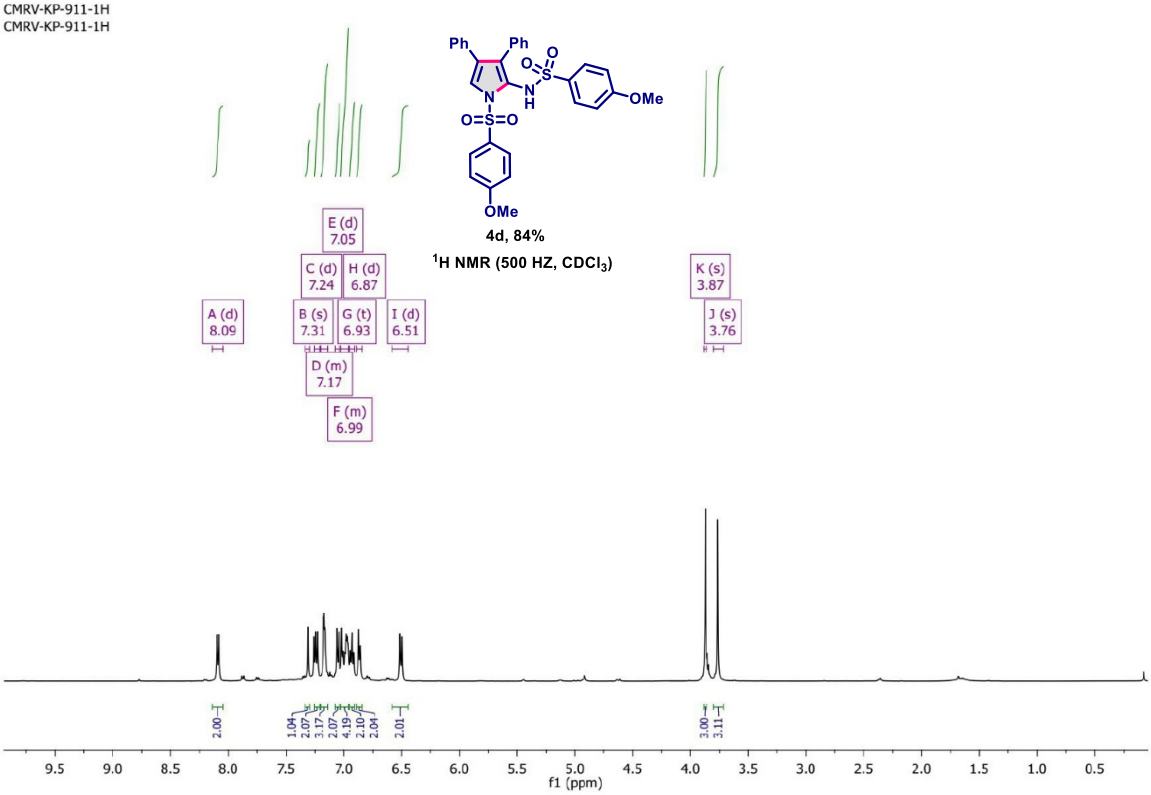



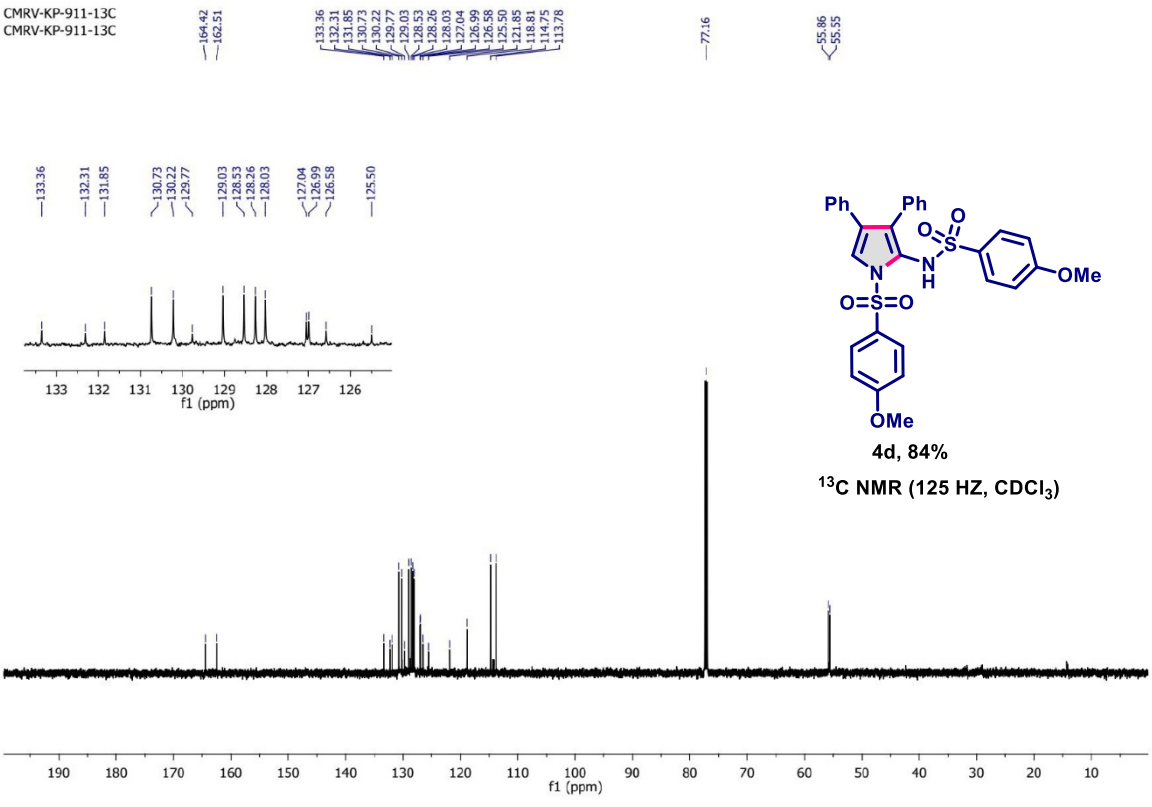



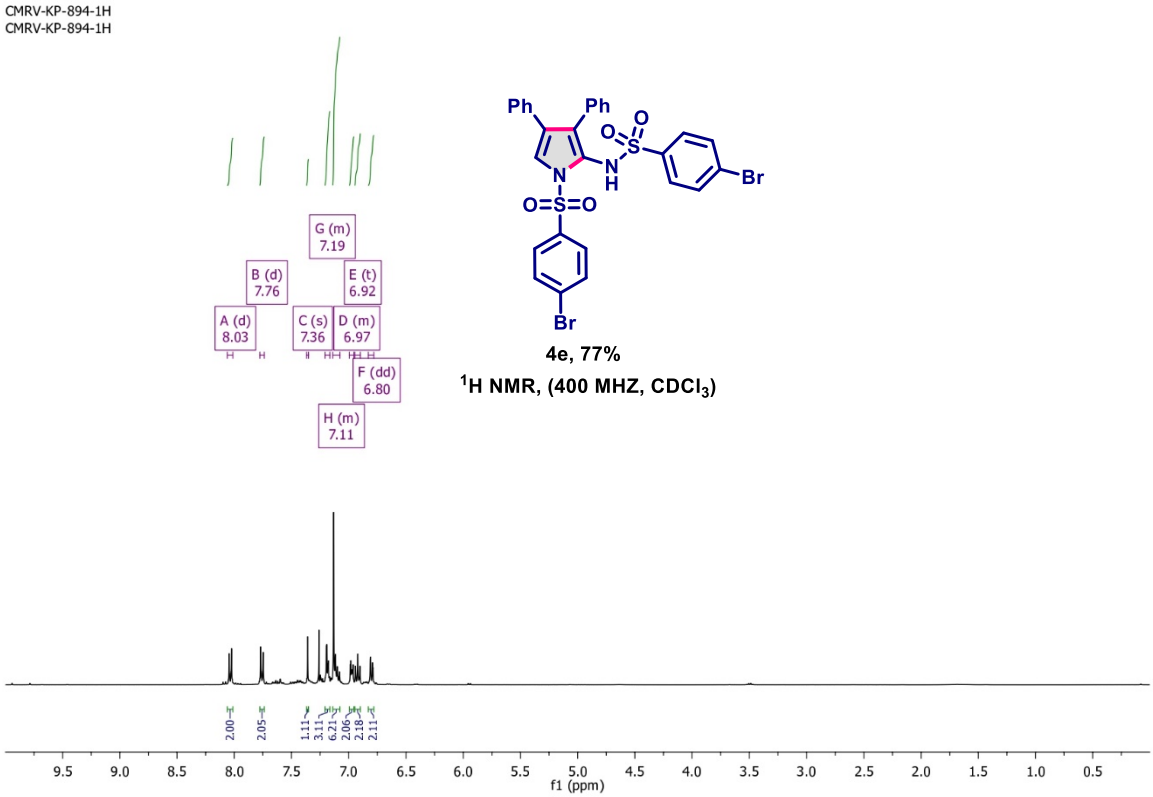

**4c, 82%**

**$^{13}$C NMR (100 HZ, $CDCl_3$)**



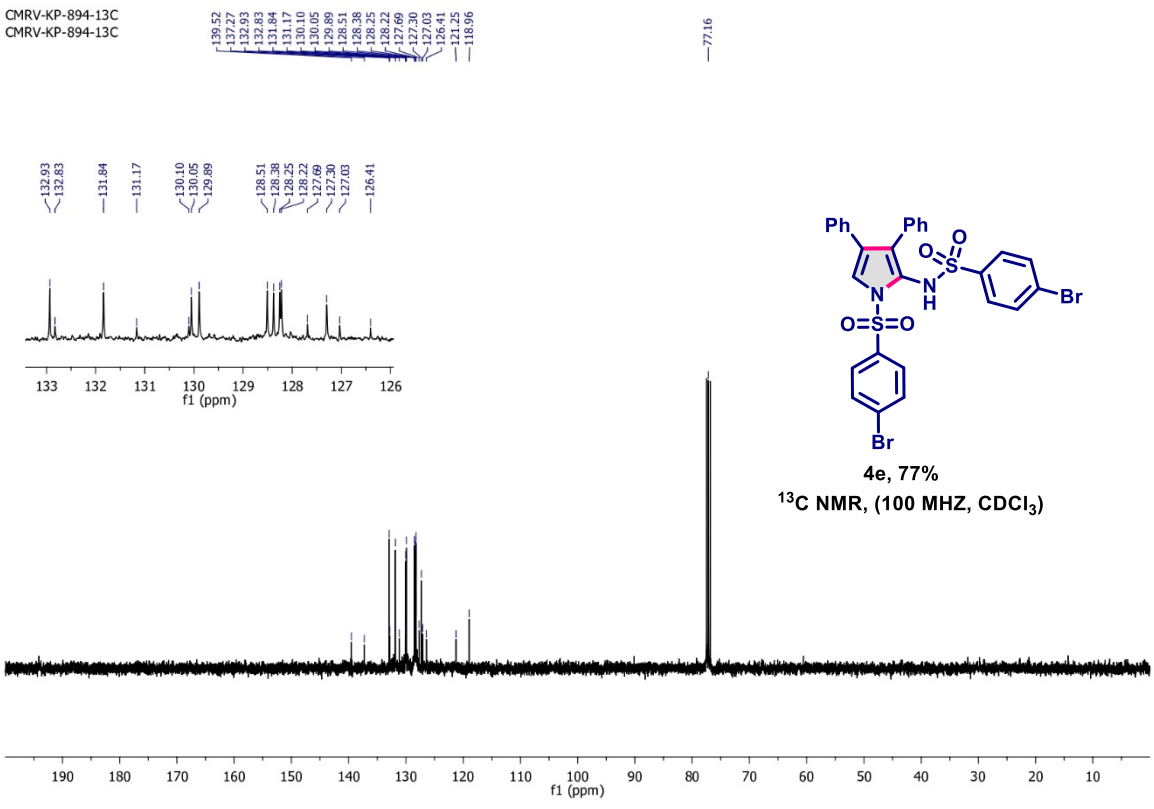

CMRV-KP-911-1H
CMRV-KP-911-1H
Ph
Ph
O
O
S
N
H
OMe
N
O=S=O
OMe
4d, 84%
$^1$H NMR (500 HZ, CDCl$_3$)
E (d) 7.05
C (d) 7.24
H (d) 6.87
K (s) 3.87
A (d) 8.09
B (s) 7.31
G (t) 6.93
I (d) 6.51
J (s) 3.76
D (m) 7.17
F (m) 6.99
2.00
1.04
2.07
3.17
2.07
4.19
2.10
2.04
2.01
3.00
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


CMRV-KP-911-13C
CMRV-KP-911-13C
164.42
162.51
133.36
132.31
131.85
130.73
130.22
129.77
129.03
128.53
128.26
128.03
127.04
126.99
126.58
125.50
121.85
118.81
114.75
113.78
77.16
55.86
55.55
133.36
132.31
131.85
130.73
130.22
129.77
129.03
128.53
128.26
128.03
127.04
126.99
126.58
125.50
133 132 131 130 129 128 127 126
f1 (ppm)
Ph
Ph
O
O
S
N
H
OMe
N
O=S=O
OMe
4d, 84%
$^{13}$C NMR (125 HZ, CDCl$_3$)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)




**4e, 77%**

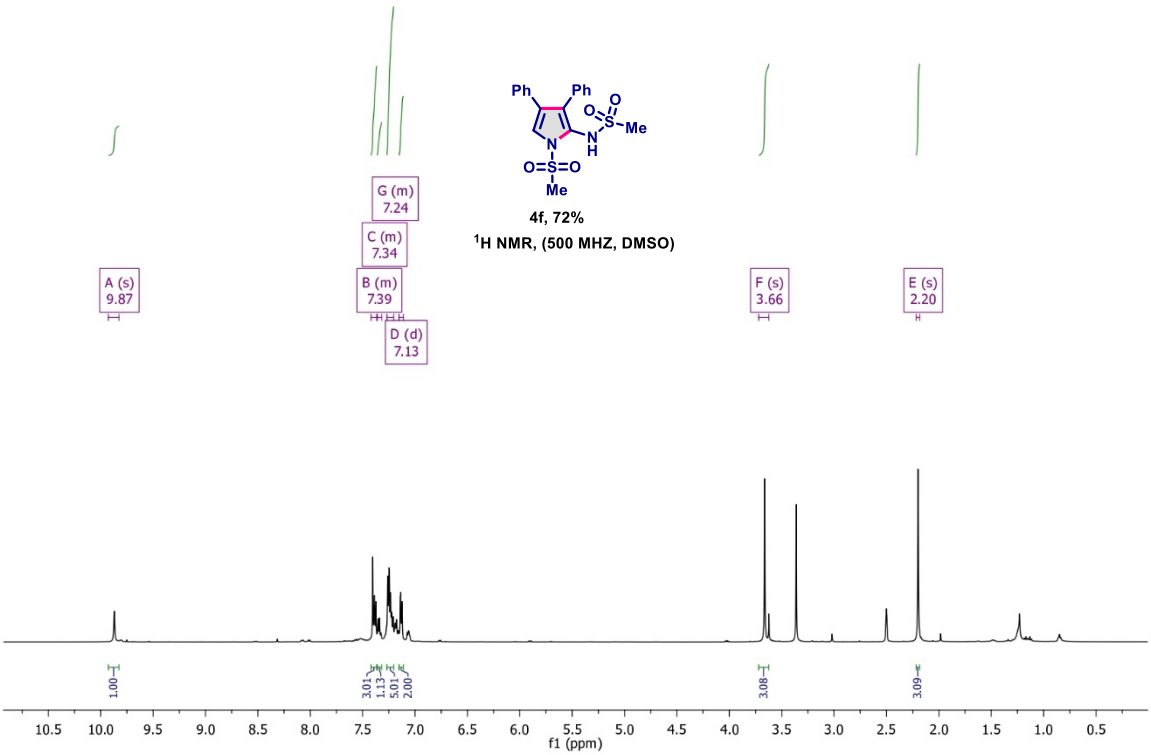
**$^{1}$H NMR, (400 MHZ, $CDCl_3$)**




**4e, 77%**

**$^{13}$C NMR, (100 MHZ, $CDCl_3$)**

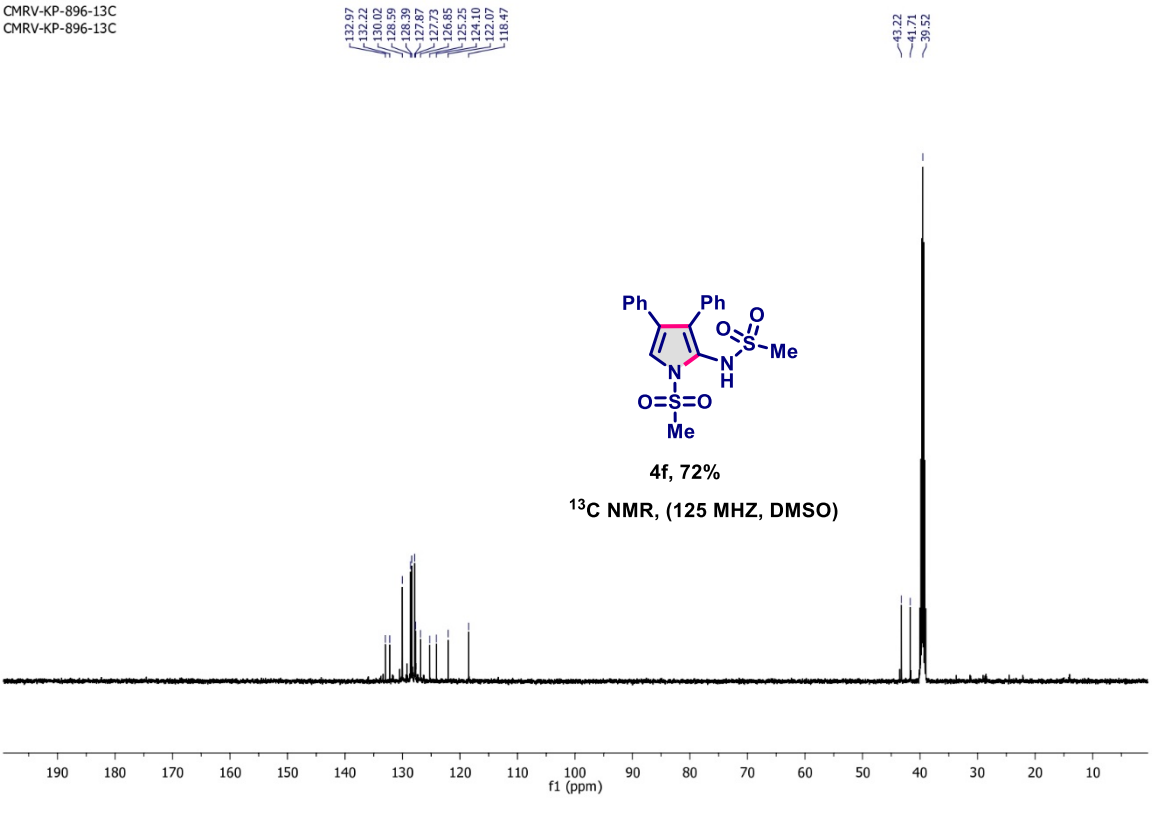
CMRV-KP-896-1H
CMRV-KP-896-1H




4f, 72%

$^{1}$H NMR, (500 MHZ, DMSO)

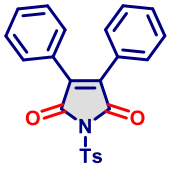
CMRV-KP-896-13C
CMRV-KP-896-13C




4f, 72%

$^{13}$C NMR, (125 MHZ, DMSO)

CMRV-KP-1277-1H
CMRV-KP-1277-1H

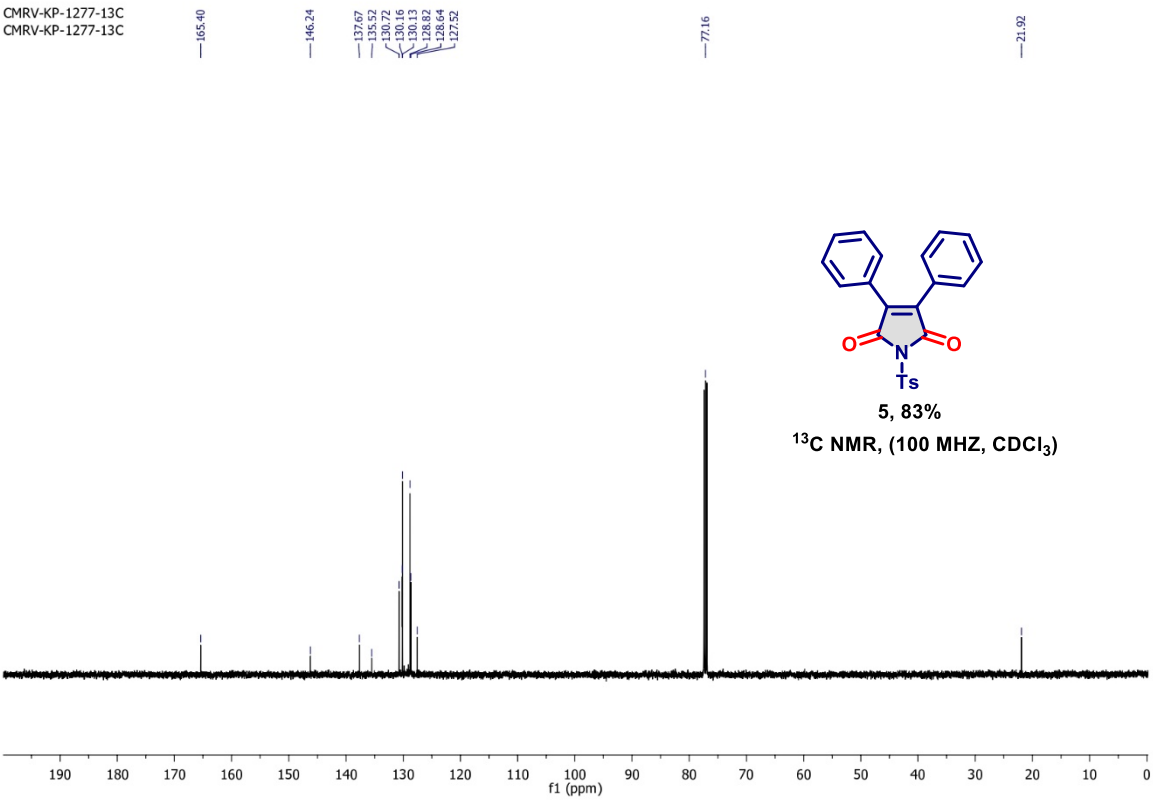



**5, 83%**

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




CMRV-KP-1277-13C
CMRV-KP-1277-13C



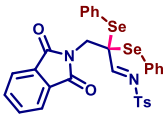




**5, 83%**

**$^{13}$C NMR, (100 MHZ, $CDCl_3$)**

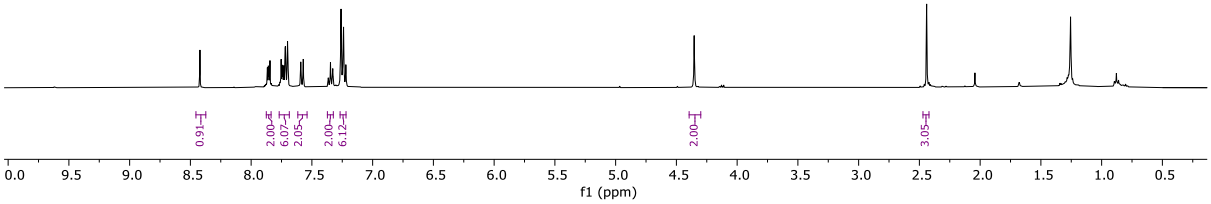
CMRV-KP-889-1H.1.fid
CMRV-KP-889-1H



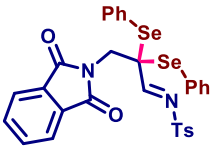

**7, 61%**

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



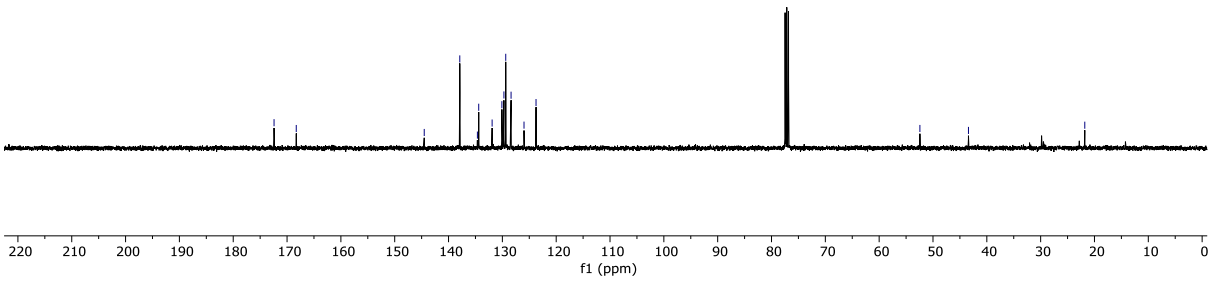




CMRV-KP-889-13C.1.fid
CMRV-KP-889-13C

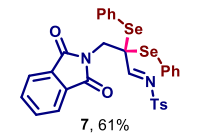

**7, 61%**

**$^{13}$C NMR, (100 MHZ, $CDCl_3$)**



CMRV-KP-889-77SE.1.fid
CMRV-KP-889-77SE

487.49




**7**, 61%

**$^{77}$Se NMR (95 MHz, $CDCl_3$)**