# Nucleophilic *ortho*-allylation of pyrroles and pyrazoles: an accelerated Pummerer/thio-Claisen rearrangement sequence

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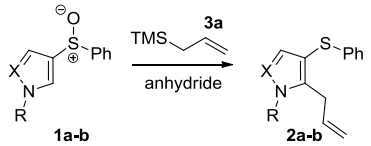
**Contents**

## Optimization Table:

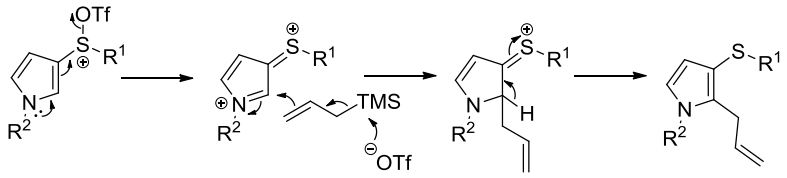



| entry | X | R | solvent | anhydride | conditions | yield (%) |
|---|---|---|---|---|---|---|
| 1 | N | Me | MeCN | TFAA | -40 °C to rt; 2 h | <5 |
| 2 | N | Me | $CH_2Cl_2$ | TFAA | -78 °C; 2 h | 10 |
| 3 | N | Me | $CH_2Cl_2$ | TFAA | -78 °C to rt; 2 h | 14 |
| 4 | N | Me | $CH_2Cl_2$ | TFAA | -78 °C to rt; 18 h | 24 |
| 5 | N | Me | DCE | TFAA | -78 °C to 40°C 2 h | 18 |
| 6 | N | Me | DCE | TFAA | -78 °C to 60°C 2 h | 13 |
| 7 | N | Me | $CH_2Cl_2$ | $Tf_2O$ | -78 °C to rt; 2 h | 47 |
| 8 | N | Me | $CH_2Cl_2$ | $Tf_2O$ | -78 °C to rt; 18 h | 53 |
| 9 | N | Me | $CH_2Cl_2$ | $Tf_2O$ | -78 °C to 40°C; 2 h | 40 |
| 10 | N | Me | DCE | $Tf_2O$ | -78 °C to 60°C; 2 h | 18 |
| 11 | N | Me | $CH_2Cl_2$ | - | -78 °C to rt; 2 h | - |
| 12 | C | Ts | $CH_2Cl_2$ | $Tf_2O$ | -78 °C to rt; 18 h | 14[a] |
| 13 | C | Ts | $CH_2Cl_2$ | TFAA | -78 °C to rt; 18 h | 41[a] |
| 14 | C | Ts | MeCN | $Tf_2O$ | -40 °C to rt; 18 h | 20[a] |
| 15 | C | Ts | MeCN | TFAA | -40 °C to rt; 18 h | 98[a] |
| 16 | C | Ts | MeCN | TFAA | -40 °C to rt; 2 h | 95[a] |
| 17 | C | Ts | MeCN | TFAA | -40 °C to 0 °C; 2 h | 96[a] |
| 18 | C | Ts | MeCN | TFAA | -40 °C; 2 h | 92[a] |
| 19 | C | Ts | MeCN | TFAA | -40 °C to 60 °C; 2 h | 98[a] |

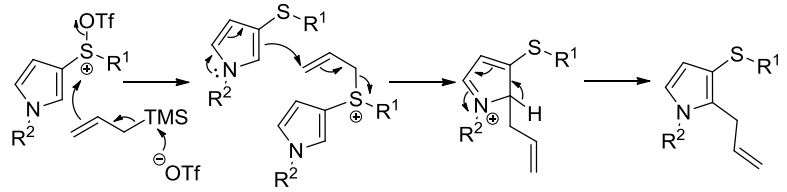
[a]Yields determined by $^1$H NMR.

## Alternative Reaction pathways:

*vinylogous Pummerer*

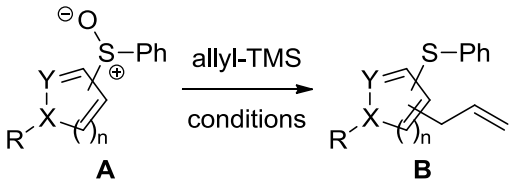



*Friedel-Crafts type*

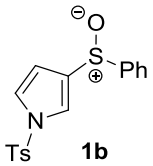
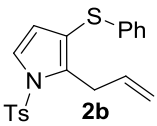
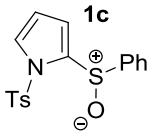
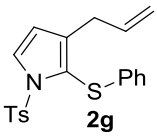
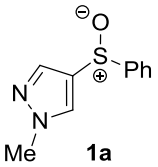
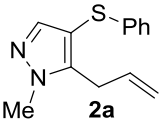
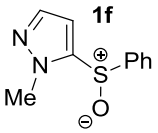
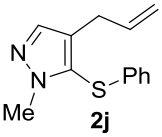
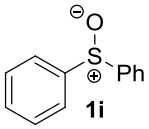
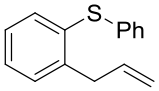


**Reaction Halftime:**

Oven-dried NMR-tubes were flushed with $N_2$, before adding a solution of sulfoxide **A** (0.056 mmol), allyltrimethylsilane (0.141 mmol) in the corresponding solvent (0.75 mL) with 1,2-dichloroethane as internal standard. Triflic anhydride (20.0 µL, 0.141 mmol) was added and the reaction was monitored by $^1$H NMR spectroscopy until 50% conversion to allylation product **B** was reached.




**A** **B**

| entry | A | B | $R_2O$ | solvent | $t_{1/2}$ (t) | RV[a] |
|---|---|---|---|---|---|---|
| 1 |  **1b** |  **2b** | TFAA | MeCN | <2 min | 1500 |
| 2 |  **1c** |  **2g** | TFAA | MeCN | <2 min | 1500 |
| 3 |  **1a** |  **2a** | $Tf_2O$ | $CH_2Cl_2$ | 16 h | 3.2 |
| 4 |  **1f** |  **2j** | $Tf_2O$ | $CH_2Cl_2$ | 3 min | 1020 |
| 5 |  **1i** | **2o**  | $Tf_2O$ | $CH_2Cl_2$ | 51 h | 1 |

[a] Relative reaction values

Relative $t_{1/2}$ as determined by individual experiments show relative reaction values of the overall transformation from sulfoxides **A** to *ortho*-allylation products **B**. Interestingly, sulfoxide activation competition study (Scheme 2B) shows a ratio of 4.5 : 1 favouring sulfoxide **1a** with respect to **1f,** despite a much slower overall conversion. The decreased rate acceleration of the overall transformation from **1a** compared to that of **1f** is in

agreement with the decreased activation of the C-5 position of pyrazole, compared to the more activated C-4 position, leading to a slower rearrangement.

**General experimental:**

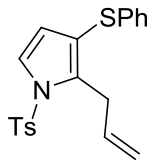
All experiments were performed under an atmosphere of nitrogen, using anhydrous solvents, unless stated otherwise. THF was distilled from sodium/benzophenone and $CH_2Cl_2$ was distilled from $CaH_2$. All other solvents and reagents were purchased from commercial sources and used as supplied.

$^1$H NMR spectra were recorded at 300, 400 or 500 MHz. $^{13}$C NMR spectra were recorded at 75, 100 or 125 MHz. All chemical shift values are reported in ppm, with coupling constants in Hz. Mass spectra were obtained using positive or negative electrospray (ES), electron ionization (EI) or chemical ionization (CI) methodology. Infra-red spectra were recorded as evaporated films or neat using FT/IR spectrometers. Melting points were measured on solids as obtained after chromatography.

Column chromatography was carried out using 35 – 70 μ, 60Å silica gel. Routine TLC analysis was carried out on silica gel 60 F254 coated aluminium sheets of 0.2 mm thickness. Plates were viewed using a 254 nm ultraviolet lamp and developed by dipping in aqueous potassium permanganate solution.

**General Procedure A: *ortho*-allylation reaction:**

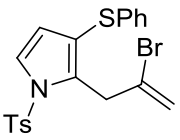
**2-Allyl-3-(phenylsulfanyl)-1-tosyl-1H-pyrrole 2b**




An oven dried tube was flushed with $N_2$, before adding a solution containing 3-(phenylsulfinyl)-1-tosyl-1H-pyrrole (19.4 mg, 0.056 mmol) and allyltrimethylsilane (22.4 μL, 0.141 mmol) in MeCN (0.75 mL). Trifluoroacetic anhydride (20.0 μL, 0.141 mmol) was added at -40 °C and the reaction mixture was allowed to warm to room temperature over night before quenching with aqueous saturated $NaHCO_3$ (1 mL) and extraction with EtOAc (3 × 2 mL). The combined organic layer was dried ($Na_2SO_4$) and concentrated *in vacuo*. The crude product was purified by preparative thin layer chromatography on silica gel eluting with 15% EtOAC in *n*-hexane to yield the product (18.4 mg, 89% yield) as a yellow oil; $\nu_{max}$ (neat)/cm$^{-1}$ 2921, 2880, 2359, 1638, 1596, 1582, 1477, 1439, 1368, 1292, 1188, 1174, 1145, 1120, 1087, 1024, 991, 916, 877, 811, 738, 672; $\delta_H$ (500 MHz, $CD_3CN$) 2.42 (3H, s, C*H*$_3$), 3.61 (2H, dt, *J* 6.0, 1.6, C*H*$_2$CH=CH$_2$), 4.75 - 4.80 (1H, m, CH$_2$CH=C*H*$_2$), 4.81 - 4.86 (1H, m, CH$_2$CH=C*H*$_2$), 5.72 (1H, ddt, *J* 17.0, 10.1, 6.0, CH$_2$C*H*=CH$_2$),

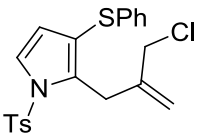
6.35 (1H, d, *J* 3.5, HetAr-*H*), 6.96 - 7.02 (2H, m, Ar-*H*), 7.10 - 7.15 (1H, m, Ar-*H*), 7.17 - 7.23 (2H, m, Ar-*H*), 7.41 (2H, d, *J* 8.2, Ar-*H*), 7.44 (1H, d, *J* 3.5, HetAr-*H*), 7.75 (2H, d, *J* 8.2, Ar-*H*); $\delta_C$ (125 MHz, $CD_3CN$) 22.0 (*C*$H_3$), 30.4 (*C*$H_2$CH=$CH_2$), 116.8 (*C*), 117.0 ($CH_2$CH=*C*$H_2$), 118.2 (HetAr-*C*H), 124.5 (HetAr-*C*H), 127.0 (Ar-*C*H), 128.0 (Ar-*C*H), 128.3 (Ar-*C*H), 130.3 (Ar-*C*H), 131.6 (Ar-*C*H), 136.2 ($CH_2$*C*H=$CH_2$), 136.8 (*C*), 137.8 (*C*), 138.7 (*C*), 147.5 (*C*); *m/z* (ES+) (M + H), 370; (Found: M + H, 370.0937. $C_{20}H_{20}NO_2S_2$ requires M, 370.0930).

**2-(2-Bromoallyl)-3-(phenylsulfanyl)-1-tosyl-1H-pyrrole 2c**




As described in general procedure A, 3-(phenylsulfinyl)-1-tosyl-1H-pyrrole (19.4 mg, 0.056 mmol), (2-bromoallyl)trimethylsilane (27.1 mg, 0.141 mmol), trifluoroacetic anhydride (20.0 µL, 0.141 mmol) and MeCN (0.75 mL), after purification by preparative thin layer chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, gave the product (22.1 mg, 88% yield) as a yellow oil; $\nu_{max}$ (neat)/$cm^{-1}$ 3045, 2905, 1730, 1598, 1442, 1358, 1262, 1166, 1086, 815, 751, 667; $\delta_H$ (400 MHz, $CD_3CN$) 2.42 (3H, s, C*H*$_3$), 4.04 (2H, t, *J* 1.5, C*H*$_2$C(Br)=$CH_2$), 5.08 - 5.11 (1H, m, $CH_2$C(Br)=C*H*$_2$), 5.25 - 5.28 (1H, m, $CH_2$C(Br)=C*H*$_2$), 6.39 (1H, d, *J* 3.5 HetAr-*H*), 7.03 - 7.09 (2H, m, Ar-*H*), 7.13 - 7.18 (1H, m, Ar-*H*), 7.19 - 7.25 (2H, m, Ar-*H*), 7.41 (2H, d, *J* 8.3, Ar-*H*), 7.50 (1H, d, *J* 3.3, HetAr-*H*), 7.75 (2H, d, *J* 8.6, Ar-*H*); $\delta_C$ (100 MHz, $CD_3CN$) 22.0 (*C*$H_3$), 37.8 (*C*$H_2$C(Br)=$CH_2$), 118.0 (HetAr-*C*H), 119.1 ($CH_2$C(Br)=*C*$H_2$), 119.4 (*C*), 125.3 (HetAr-*C*H), 127.4 (Ar-*C*H), 128.4 (Ar-*C*H), 128.6 (Ar-*C*H), 130.4 (Ar-*C*H), 130.5 (*C*), 131.6 (Ar-*C*H), 134.5 (*C*), 136.5 (*C*), 137.9 (*C*), 147.7 (*C*); *m/z* (EI), (Found: M, 446.9968. $C_{20}H_{18}NO_2BrS_2$ requires M, 446.9957).

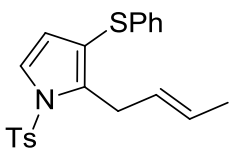
**2-(2-(Chloromethyl)allyl)-3-(phenylsulfanyl)-1-tosyl-1H-pyrrole 2d**




As described in general procedure A, 3-(phenylsulfinyl)-1-tosyl-1H-pyrrole (19.4 mg, 0.056 mmol), ((2-(chloromethyl)allyl)trimethylsilane (23.8 mg, 0.141 mmol), trifluoroacetic anhydride (20.0 µL, 0.141 mmol) and MeCN (0.75 mL), after purification by preparative thin layer chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, gave the product (20.2 mg, 86% yield) as a yellow oil; $\nu_{max}$ (neat)/$cm^{-1}$ 3072, 2965, 1635, 1597, 1442, 1361, 1263, 1164, 1086, 813, 754, 667; $\delta_H$ (500 MHz, $CD_3CN$) 2.42 (3H, s, C*H*$_3$), 3.70 (2H, s, C*H*$_2$C($CH_2$Cl)=$CH_2$), 4.10 (2H, s, $CH_2$C(C*H*$_2$Cl)=$CH_2$), 4.21 - 4.25 (1H, m, $CH_2$C($CH_2$Cl)=C*H*$_2$), 4.91 - 4.96 (1H, m, $CH_2$C($CH_2$Cl)=C*H*$_2$), 6.40 (1H, d, *J* 3.8, HetAr-*H*), 7.01 - 7.06 (2H, m, Ar-*H*), 7.12 - 7.16 (1H, m, Ar-*H*), 7.18 - 7.24 (2H, m, Ar-*H*),

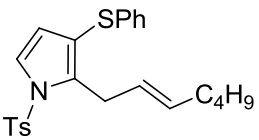
7.40 (2H, d, *J* 8.1, Ar-*H*), 7.49 (1H, d, *J* 3.8, HetAr-*H*), 7.74 (2H, d, *J* 8.1, Ar-*H*); $\delta_C$ (125 MHz, $CD_3CN$) 22.0 (*C*$H_3$), 30.2 (*C*$H_2$C($CH_2$Cl)=$CH_2$), 49.6 ($CH_2$C(*C*$H_2$Cl)=$CH_2$), 116.3 ($CH_2$C($CH_2$Cl)=*C*$H_2$), 118.0 (HetAr-*C*H), 118.4 (Ar-*C*H), 124.9 (Ar-*C*H), 127.2 (Ar-*C*H), 128.3 (Ar-*C*H), 128.5 (Ar-*C*H), 130.4 (HetAr-*C*H), 131.6 (*C*), 136.1 (*C*), 136.6 (*C*), 138.4 (*C*), 144.1 (*C*), 147.6 (*C*); *m/z* (EI), (Found: M, 417.0612. $C_{21}H_{20}NO_2ClS_2$ requires M, 417.0618).

**(*E*)-2-(But-2-en-1-yl)-3-(phenylsulfanyl)-1-tosyl-1H-pyrrole 2e**




As described in general procedure A, 3-(phenylsulfinyl)-1-tosyl-1H-pyrrole (19.4 mg, 0.056 mmol), but-2-enyltrimethylsilane (*E*/*Z* = 5/1) (18.1 mg, 0.141 mmol), trifluoroacetic anhydride (20.0 µL, 0.141 mmol) and MeCN (0.75 mL), after purification by preparative thin layer chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, gave an inseparable mixture of (*E*)-2-(but-2-en-1-yl)-3-(phenylsulfanyl)-1-tosyl-1H-pyrrole and (*Z*)-2-(but-2-en-1-yl)-3-(phenylsulfanyl)-1-tosyl-1H-pyrrole product (19.9 mg, 93% yield, *E*/*Z* = 11/1) as a yellow oil; $\nu_{max}$ $cm^{-1}$ 2921, 1719, ,1597, 1444, 1369, 1169, 1088, 1022, 813, 751; $\delta_H$ (500 MHz, $CD_3CN$) 1.35 - 1.39 (3H, m, (*E*)-CHC*H*$_3$), 1.58 - 1.61 (3H, m, (*Z*)-CHC*H*$_3$), 2.41 (3H, s, (*E*)-C*H*$_3$), 2.42 (3H, s, (*Z*)-C*H*$_3$), 3.52 - 3.56 (2H, m, (*E*)-C*H*$_2$CH), 3.59 - 3.63 (2H, m, (*Z*)-C*H*$_2$CH), 5.08 - 5.17 (1H, dqt, *J* 15.1, 6.3, 1.6, (*E*)-$CH_2$CHC*H*$CH_3$; 1H, m, (*Z*)-$CH_2$C*H*$CHCH_3$), 5.23 (1H, dtq, *J* 15.4, 6.0, 1.6, $CH_2$C*H*$CHCH_3$), 5.32 (1H, dqt, *J* 10.6, 6.7, 1.9, (*Z*)-$CH_2$CHC*H*$CH_3$), 6.34 (1H, d, *J* 3.5 (*Z*)-HetAr-*H*), 6.35 (1H, d, *J* 3.5, (*E*)-HetAr-*H*), 6.99 - 7.02 (2H, m, (*E*)-Ar-*H*; 2H, m, (*Z*)-Ar-*H*), 7.10 - 7.14 (1H, m, (*E*)-Ar-*H*; 1H, m, (*Z*)-Ar-*H*), 7.18 - 7.23 (2H, m, (*E*)-Ar-*H*; 2H, m, (*Z*)-Ar-*H*), 7.37 - 7.45 (3H, m, (*E*)-Ar-*H* & (*E*)-HetAr-*H*; 3H, m, (*Z*)-Ar-*H* & (*Z*)-HetAr-*H*), 7.70 - 7.75 (2H, m, (*E*)-Ar-*H*; 2H, m, (*Z*)-Ar-*H*); For major isomer: $\delta_C$ (125 MHz, $CD_3CN$) 18.2 (CH*C*$H_3$), 22.0 (*C*$H_3$), 29.3 (*C*$H_2$CHCH$CH_3$), 116.3 (*C*), 118.1 (HetAr-*C*H), 124.3 (HetAr-*C*H), 127.0 (Ar-*C*H), 128.1 (Ar-*C*H), 128.2 ($CH_2$CH*C*H$CH_3$), 128.4 (Ar-*C*H), 128.5 ($CH_2$*C*HCH$CH_3$), 130.3 (Ar-*C*H), 131.6 (Ar-*C*H), 136.9 (*C*), 138.8 (*C*), 138.9 (*C*), 147.5 (*C*); *m/z* (EI) M, 383; (Found: M, 383.1013. $C_{21}H_{21}NO_2S_2$ requires M, 383.1008).

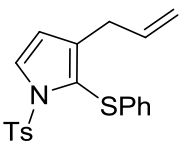
**(*E*)-2-(Hept-2-en-1-yl)-3-(phenylsulfanyl)-1-tosyl-1H-pyrrole 2f**




As described in general procedure A, 3-(phenylsulfinyl)-1-tosyl-1H-pyrrole (19.4 mg, 0.056 mmol), (*Z*)-hept-2-enyltrimethylsilane (*E*/*Z* = 1/9) (23.9 mg, 0.141 mmol), trifluoroacetic anhydride (20.0 µL, 0.141 mmol) and MeCN (0.75 mL), after purification by preparative thin layer chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, gave an inseparable mixture of (*E*)-2-(hept-2-

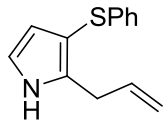
en-1-yl)-3-(phenylsulfanyl)-1-tosyl-1H-pyrrole and (*Z*)-2-(hept-2-en-1-yl)-3-(phenylsulfanyl)-1-tosyl-1H-pyrrole product (20.0 mg, 84% yield, *E*/*Z* = 17/1) as a colourless oil; $\nu_{max}$ $cm^{-1}$ 2919, 2890, 1562, 1472, 1270, 1161, 1105, 764, 668, 751; $\delta_H$ (500 MHz, $CD_3CN$) 0.81 (3H, t, *J* 7.3, (*E*)-$CH_2CH_3$), 0.85 (3H, t, *J* 6.9, (*Z*)-$CH_2CH_3$), 1.04 - 1.12 (2H, m, (*E*)-$CH_2CH_2$), 1.12 - 1.20 (2H, m, (*E*)-$CH_2CH_2$; 2H, m, (*Z*)-$CH_2CH_2$), 1.22 - 1.26 (2H, m, (*Z*)-$CH_2CH_2$), 1.72 (2H, m, (*E*)-CHCHC$H_2$), 2.03 - 2.08 (2H, m, (*Z*)-CHCHC$H_2$), 2.41 (3H, s, (*E*)-$CH_3$), 2.42 (3H, s, (*Z*)-$CH_3$), 3.55 (2H, d, *J* 6.0, (*E*)-Ph-$CH_2$CH), 3.59 (2H, d, *J* 6.3, (*Z*)-Ph-$CH_2$CH), 5.11 - 5.28 (2H, m, 2 × (*E*)-C*H*; 2H, m, 2 × (*Z*)-C*H*), 6.33 (1H, d, *J* 3.5, (*Z*)-HetAr-*H*), 6.35 (1H, d, *J* 3.5, (*E*)-HetAr-*H*), 6.92 - 6.97 (2H, m, (*Z*)-Ar-*H*), 6.97 - 7.02 (2H, m, (*E*)-Ar-*H*), 7.09 - 7.14 (1H, m, (*E*)-Ar-*H*; 1H, m, (*Z*)-Ar-*H*), 7.17 - 7.23 (2H, m, (*E*)-Ar-*H*; 2H, m, (*Z*)-Ar-*H*), 7.38 - 7.45 (3H, m, (*E*)-Ar-*H* & (*E*)-HetAr-*H*; 3H, m, (*Z*)-Ar-*H* & (*Z*)-HetAr-*H*), 7.73 (2H, d, *J* 8.2, (*E*)-Ar-*H*; 2H, (*Z*)-Ar-*H*); For major isomer: $\delta_C$ (125 MHz, $CD_3CN$) 14.2 ($CH_2CH_3$), 21.7 ($CH_3$), 22.9 ($CH_2CH_2$), 29.0 (Ph-$CH_2$CH), 31.9 ($CH_2CH_2$), 32.6 ($CHCH_2$), 115.8 (*C*), 117.8 (HetAr-*C*H), 123.9 (HetAr-*C*H), 126.6 (Ar-*C*H), 126.7 (*C*HCH), 127.6 (Ar-*C*H), 128.0 (Ar-*C*H), 130.0 (Ar-*C*H), 131.3 (Ar-*C*H), 133.4 (CH*C*H), 136.6 (*C*), 138.6 (*C*), 138.7 (*C*), 147.1 (*C*); *m/z* (EI), (Found: M, 425.1479. $C_{24}H_{27}NO_2S_2$ requires M, 425.1478).

**3-Allyl-2-(phenylsulfanyl)-1-tosyl-1H-pyrrole 2g**



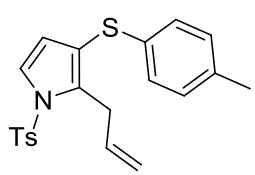

As described in general procedure A, 2-(phenylsulfinyl)-1-tosyl-1H-pyrrole (19.4 mg, 0.056 mmol), allyltrimethylsilane (22.4 µL, 0.141 mmol), trifluoroacetic anhydride (20.0 µL, 0.141 mmol) and MeCN (0.75 mL), after purification by preparative thin layer chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, gave the product (17.4 mg, 84% yield) as a colourless oil; $\nu_{max}$ (neat)/$cm^{-1}$ 2922, 1729, 1596, 1581, 1478, 1439, 1367, 1292, 1249, 1173, 1084, 1023, 995, 916, 811, 737, 672; $\delta_H$ (500 MHz, $CD_3CN$) 2.28 (3H, s, $CH_3$), 3.17 (2H, dt, *J* 6.5, 1.3, $CH_2CH{=}CH_2$), 4.92 - 4.99 (2H, m, $CH_2CH{=}CH_2$), 5.79 (1H, ddt, *J* 16.8, 10.3, 6.6, $CH_2CH{=}CH_2$), 6.42 (1H, d, *J* 3.8, HetAr-*H*), 6.65 - 6.69 (2H, m, Ar-*H*), 7.02 - 7.11 (3H, m, Ar-*H*), 7.15 (2H, d, *J* 8.2, Ar-*H*), 7.67 - 7.73 (3H, m, 2 × Ar-*H* & HetAr-*H*); $\delta_C$ (125 MHz, $CD_3CN$) 21.6 ($CH_3$), 31.7 ($CH_2CH{=}CH_2$), 113.7 (HetAr-*C*H), 116.3 (*C*), 116.6 ($CH_2CH{=}CH_2$), 126.0 (Ar-*C*H), 126.3 (Ar-*C*H), 127.5 (HetAr-*C*H), 128.8 (Ar-*C*H), 129.8 (Ar-*C*H), 130.8 (Ar-*C*H), 135.9 (*C*), 137.0 ($CH_2CH{=}CH_2$), 138.4 (*C*), 139.2 (*C*), 146.7 (*C*); *m/z* (ES+) (M + H), 370; (Found: M + H, 370.0936. $C_{20}H_{20}NO_2S_2$ requires M, 370.0930).

**2-Allyl-3-(phenylsulfanyl)-1H-pyrrole 2h**




An oven-dried tube was flushed with $N_2$, before addition of a solution containing 3-(phenylsulfinyl)-1H-pyrrole (14.0 mg, 0.073 mmol) and allyltrimethylsilane (30.0 µL, 0.183 mmol) in $CH_2Cl_2$ (1.2 mL). Trifluoroacetic anhydride (26.0 µL, 0.183 mmol) was added at -40 °C and the reaction mixture was allowed to warm to 0 °C for 2 h before quenching with aqueous saturated $NaHCO_3$ (1 mL) and extraction with EtOAc (3 × 2 mL). The combined organic layer was dried ($Na_2SO_4$) and concentrated *in vacuo*. The crude product was purified by preparative thin layer chromatography on silica gel eluting with 10% EtOAC in *n*-hexane to yield the product (5.9 mg, 49% yield) as a yellow oil; $\nu_{max}$ (neat)/$cm^{-1}$ 3414, 3070, 3002, 2961, 2924, 2853, 1673, 1638, 1581, 1553, 1476, 1438, 1259, 1082, 1068, 1023, 918, 892, 796, 738, 719, 690; $\delta_H$ (300 MHz, $CDCl_3$) 3.46 (2H, d, *J* 6.8, C*H*$_2$CH=CH$_2$), 5.05 - 5.21 (2H, m, CH$_2$CH=C*H*$_2$), 5.87 (1H, ddt, *J* 16.9, 10.1, 6.7, CH$_2$C*H*=CH$_2$), 6.30 (1H, m, HetAr-*H*), 6.80 (1H, m, HetAr-*H*), 6.99 - 7.11 (3H, m, Ar-*H*), 7.14 - 7.24 (2H, m, Ar-*H*), 8.24 (1H, br. s., N-H); $\delta_C$ (75 MHz, $CDCl_3$) 30.3 (*C*H$_2$CH=CH$_2$), 105.2 (*C*), 115.03 (HetAr-*C*H), 117.2 (CH$_2$CH=*C*H$_2$), 117.3 (HetAr-*C*H), 124.4 (Ar-*C*H), 125.4 (Ar-*C*H), 128.6 (Ar-*C*H), 134.8 (*C*), 135.0 (CH$_2$*C*H=CH$_2$), 140.5 (*C*); *m/z* (EI) M, 215; (Found: M, 215.0768. $C_{13}H_{13}NS$ requires M, 215.0763).

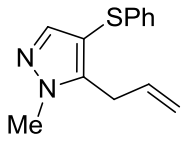
**2-Allyl-3-(p-tolylsulfanyl)-1-tosyl-1H-pyrrole 2n**




As described in general procedure A, 2-(*p*-tolylsulfinyl)-1-tosyl-1H-pyrrole (18.0 mg, 0.050 mmol), allyltrimethylsilane (20.0 µL, 0.125 mmol), trifluoroacetic anhydride (18.0 µL, 0.125 mmol) and MeCN (0.75 mL), after purification by preparative thin layer chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, gave the product (17.2 mg, 90% yield) as a yellow oil; $\nu_{max}$ (neat)/$cm^{-1}$ 2922, 2854, 1596, 1490, 1379, 1268, 1176, 1122, 1088, 1023, 917, 806, 751, 674, 596; $\delta_H$ (500 MHz, $CD_3CN$) 2.25 (3H, s, C*H*$_3$), 2.42 (3H, s, C*H*$_3$), 3.61 (2H , dt, *J* 5.8, 1.6, C*H*$_2$CH=CH$_2$), 4.75 - 4.87 (2H, m, CH$_2$CH=C*H*$_2$), 5.73 (1H, ddt, *J* 17.1, 10.2, 5.8, CH$_2$C*H*=CH$_2$), 6.32 (1H, d, *J* 3.5 HetAr-*H*), 6.93 (2H, d, *J* 8.2 Ar-*H*), 7.03 (2H, d, *J* 7.9 Ar-*H*), 7.38 - 7.43 (3H, m, 2 × Ar-*H* & HetAr-*H*), 7.73 (2H, d, *J* 8.2, Ar-*H*); $\delta_C$ (125 MHz, $CD_3CN$) 20.9 (*C*H$_3$), 21.7 (*C*H$_3$), 30.2 (*C*H$_2$CH=CH$_2$), 116.6 (CH$_2$CH=*C*H$_2$), 117.4 (*C*), 117.7 (HetAr-*C*H), 124.0 (HetAr-*C*H), 128.0 (Ar-*C*H), 128.4 (Ar-*C*H), 130.7 (Ar-*C*H), 131.4 (Ar-*C*H), 134.5 (*C*), 136.0 (CH$_2$*C*H=CH$_2$), 136.6 (*C*), 137.0 (*C*), 137.0 (*C*), 147.2 (*C*); *m/z* (EI) M, 383; (Found: M, 383.1014. $C_{21}H_{21}NO_2S_2$ requires M, 383.1008).

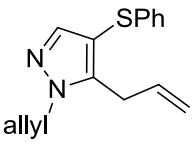
**General Procedure B: *ortho*-allylation reaction:**

**5-Allyl-1-methyl-4-(phenylsulfanyl)-1H-pyrazole 2a**



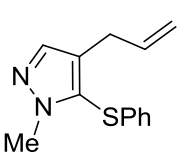

An oven-dried tube was flushed with $N_2$, before adding a solution containing 1-methyl-4-(phenylsulfinyl)-1H-pyrazole (10.3 mg, 0.050 mmol) and allyltrimethylsilane (20.0 µL, 0.125 mmol) in $CH_2Cl_2$ (0.75 mL). Triflic anhydride (21.0 µL, 0.125 mmol) was added at -78 °C and the reaction mixture was allowed to warm to room temperature over night before quenching with aqueous saturated $NaHCO_3$ (1 mL) and extraction with EtOAc (3 × 2 mL). The combined organic layer was dried ($Na_2SO_4$) and concentrated *in vacuo*. The crude product was purified by preparative thin layer chromatography on silica gel eluting with 20% EtOAC in *n*-hexane to yield the product (5.5 mg, 53% yield) as a yellow oil; $\nu_{max}$ (neat)/$cm^{-1}$ 2923, 2853, 1725, 1639, 1582, 1478, 1437, 1168, 1083, 985, 917, 736, 690; $\delta_H$ (300 MHz, $CDCl_3$) 3.48 (2H, d, *J* 6.0, C*H*$_2$CH=CH$_2$), 3.86 (3H, s, C*H*$_3$), 4.89 - 5.11 (2H, m, CH$_2$CH=C*H*$_2$), 5.70 (1H, ddt, *J* 17.0, 12.1, 6.0, CH$_2$C*H*=CH$_2$), 7.03 - 7.13 (3H, m, Ar-*H*), 7.15 - 7.24 (2H, m, Ar-*H*), 7.60 (1H, s, HetAr-*H*); $\delta_C$ (75 MHz, $CDCl_3$) 28.2 (*C*H$_2$CH=CH$_2$), 37.4 (*C*H$_3$), 110.4 (*C*), 117.2 (CH$_2$CH=*C*H$_2$), 125.1 (Ar-*C*H), 125.9 (Ar-*C*H), 128.7 (Ar-*C*H), 129.9 (*C*), 132.7 (CH$_2$*C*H=CH$_2$), 139.0 (*C*), 144.0 (HetAr-*C*H); *m/z* (EI) M, 230; (Found: M, 230.0871. $C_{13}H_{14}N_2S$ requires M, 230.0872).

**1,5-Diallyl-4-(phenylsulfanyl)-1H-pyrazole 2i**



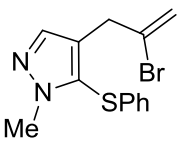

As described in general procedure B, 1-allyl-4-(phenylsulfinyl)-1H-pyrazole (30.0 mg, 0.129 mmol), allyltrimethylsilane (24.0 µL, 0.129 mmol), triflic anhydride (54.0 µL, 0.323 mmol) in $CH_2Cl_2$ (1.50 mL) and 2 h MW heating at 100 °C, after purification by preparative thin layer chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, gave the product (14.3 mg, 45% yield) as a brown oil; $\nu_{max}$ (neat)/$cm^{-1}$ 2923, 2851, 1638, 1582, 1513, 1477, 1438, 1299, 1115, 1083, 1024, 985, 916, 857, 738, 689, 660, 631; $\delta_H$ (500 MHz, $CDCl_3$) 3.49 (2H, d, *J* 6.3, C*H*$_2$CH=CH$_2$), 4.77 (2H, dt, *J* 5.5, 1.3, N-C*H*$_2$CH=CH$_2$), 4.94 - 5.00 (1H, m, CH$_2$CH=C*H*$_2$), 5.04 - 5.11 (1H, m, CH$_2$CH=C*H*$_2$), 5.27 (1H, dd, *J* 10.1, 1.3, CH$_2$CH=C*H*$_2$), 5.70 (1H, ddt, *J* 17.0, 10.1, 6.0, CH$_2$CH=C*H*$_2$), 5.99 (1H, ddt, *J* 16.7, 10.1, 5.4, CH$_2$CH=C*H*$_2$), 7.04 - 7.12 (3H, m, Ar-*H*), 7.18 - 7.23 (2H, m, Ar-C*H*), 7.66 (1H, s, HetAr-*H*); $\delta_C$ (125 MHz, $CDCl_3$) 28.0 (*C*H$_2$CH=CH$_2$), 52.7 (N-*C*H$_2$CH=CH$_2$), 106.1 (*C*), 117.2 (CH$_2$CH=*C*H$_2$), 117.8 (CH$_2$CH=*C*H$_2$), 125.1 (Ar-*C*H), 125.9 (Ar-*C*H), 128.8 (Ar-*C*H), 132.5 (CH$_2$*C*H=CH$_2$), 132.9 (CH$_2$*C*H=CH$_2$), 138.9 (*C*), 144.3 (HetAr-*C*H), 144.4 (*C*); *m/z* (ES+) (M + H), 257; (Found: M + H, 257.1108. $C_{15}H_{16}N_2S$ requires M, 257.1107).

**4-Allyl-1-methyl-5-(phenylsulfanyl)-1H-pyrazole 2j**



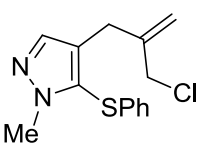
As described in general procedure B, 1-methyl-5-(phenylsulfinyl)-1H-pyrazole (0.150 g, 0.727 mmol), allyltrimethylsilane (0.31 mL, 1.82 mmol), triflic anhydride (0.29 mL, 1.82 mmol) in $CH_2Cl_2$ (10.0 mL), after purification by preparative thin layer chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, gave the product (0.137 g, 82% yield) as a yellow oil; $\nu_{max}$ (neat)/$cm^{-1}$ 2939, 1680, 1635, 1581, 1519, 1477, 1437, 1387, 12116, 1080, 994, 918, 855, 742, 691, 648; $\delta_H$ (300 MHz, $CDCl_3$) 3.28 (2H, d, *J* 6.4, C*H*$_2$CH=CH$_2$), 3.85 (3H, s, C*H*$_3$), 4.97 - 5.09 (2H, m, CH$_2$CH=C*H*$_2$), 5.89 (1H, ddt, *J* 17.1, 10.0, 6.4, CH$_2$C*H*=CH$_2$), 6.92 - 7.00 (2H, m, Ar-*H*), 7.12 - 7.26 (3H, m, Ar-*H*), 7.50 (1H, s, HetAr-*H*); $\delta_C$ (75 MHz, $CDCl_3$) 29.0 (*C*H$_2$CH=CH$_2$), 36.9 (*C*H$_3$), 115.5 (CH$_2$CH=*C*H$_2$), 125.8 (*C*), 126.0 (Ar-*C*H), 126.3 (Ar-*C*H), 127.8 (*C*), 129.2 (Ar-*C*H), 135.6 (*C*), 136.5 (CH$_2$*C*H=CH$_2$), 138.7 (HetAr-*C*H); *m/z* (EI) M, 230; (Found: M, 230.0878. $C_{13}H_{14}N_2S$ requires M, 230.0872).

**4-(2-Bromoallyl)-1-methyl-5-(phenylsulfanyl)-1H-pyrazole 2k**



As described in general procedure B, 1-methyl-5-(phenylsulfinyl)-1H-pyrazole (15.5 mg, 0.075 mmol), (2-bromoallyl)trimethylsilane (36.0 mg, 0.188 mmol), triflic anhydride (32.0 µL, 0.188 mmol) in $CH_2Cl_2$ (0.75 mL) and 2 h MW heating at 60 °C, after purification by preparative thin layer chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, gave the product (14.6 mg, 63% yield) as a yellow oil; $\nu_{max}$ (neat)/$cm^{-1}$ 2920, 2851, 1629, 1581, 1476, 1388, 1266, 1102, 891, 772, 688; $\delta_H$ (500 MHz, $CDCl_3$) 3.67 (2H, s, C*H*$_2$C(Br)=CH$_2$), 3.85 (3H, s, C*H*$_3$), 5.40 - 5.42 (1H, m, CH$_2$C(Br)=C*H*$_2$), 5.56 (1H, m, CH$_2$C(Br)=C*H*$_2$), 6.96 - 7.00 (2H, m, Ar-*H*), 7.14 - 7.19 (1H, m, Ar-*H*), 7.23 - 7.27 (2H, m, Ar-*H*), 7.60 (1H, s, HetAr-*H*); $\delta_C$ (125 MHz, $CDCl_3$) 37.0 (*C*H$_2$C(Br)=CH$_2$), 37.1 (*C*H$_3$), 117.6 (CH$_2$C(Br)=*C*H$_2$), 123.4 (*C*), 126.2 (Ar-*C*H), 126.5 (Ar-*C*H), 129.3 (Ar-*C*H), 131.8 (*C*), 135.0 (*C*), 139.1 (HetAr-*C*H), 139.2 (*C*); *m/z* (EI) M, 308 $^{79}$Br, 310 308 $^{81}$Br; (Found: M, 307.9973. $C_{13}H_{13}N_2BrS$ requires M, 307.9977).

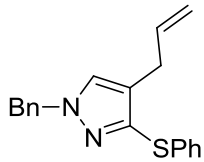
**4-(2-(Chloromethyl)allyl)-1-methyl-5-(phenylsulfanyl)-1H-pyrazole 2l**



As described in general procedure B, 1-methyl-5-(phenylsulfinyl)-1H-pyrazole (15.5 mg, 0.075 mmol), ((2-(chloromethyl)allyl)trimethylsilane (31.8 mg, 0.188 mmol), triflic anhydride (32.0 µL, 0.188 mmol) in $CH_2Cl_2$ (0.75 mL) and 2 h MW heating at 60 °C, after purification by preparative thin layer

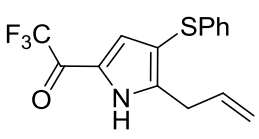
chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, gave the product (10.9 mg, 52% yield) as a yellow oil; $\nu_{max}$ (neat)/$cm^{-1}$ 2918, 2361, 1582, 1437, 1264, 913, 751, 669; $\delta_H$ (400 MHz, $CDCl_3$) 3.42 (2H, s, C*H*$_2$C(CH$_2$Cl)=CH$_2$), 3.86 (3H, s, C*H*$_3$), 3.97 - 4.01 (2H, m, CH$_2$C(C*H*$_2$Cl)=CH$_2$), 4.93 - 4.96 (1H, m, CH$_2$C(CH$_2$Cl)=C*H*$_2$), 5.11 - 5.15 (1H, m, CH$_2$C(CH$_2$Cl)=C*H*$_2$), 6.93 - 6.99 (2H, m, Ar-*H*), 7.14 - 7.19 (1H, m, Ar-*H*), 7.22 - 7.27 (2H, m, Ar-*H*), 7.53 (1H, s, HetAr-*H*); $\delta_C$ (125 MHz, $CDCl_3$) 28.6 (*C*H$_2$C(CH$_2$Cl)=CH$_2$), 37.1 (*C*H$_3$), 47.6 (CH$_2$C(*C*H$_2$Cl)=C), 115.9 (CH$_2$C(CH$_2$Cl)=*C*H$_2$), 124.2 (*C*), 126.1 (Ar-*C*H), 126.5 (Ar-*C*H), 129.0 (*C*), 129.3 (Ar-*C*H), 135.3 (*C*), 139.1 (HetAr-*C*H), 143.6 (*C*); *m/z* (EI) M, 278 $^{35}$Cl, 310 280 $^{37}$Cl; (Found: M, 278.0636. $C_{14}H_{15}N_2ClS$ requires M, 278.0639).

**4-Allyl-1-benzyl-3-(phenylsulfanyl)-1H-pyrazole 2m**




As described in general procedure B, 1-benzyl-3-(phenylsulfinyl)-1H-pyrazole (10.0 mg, 0.035 mmol), allyltrimethylsilane (14.0 µL, 0.089 mmol), triflic anhydride (15.0 µL, 0.089 mmol) in $CH_2Cl_2$ (0.50 mL) and 2 h MW heating at 100 °C, after purification by preparative thin layer chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, gave the product (8.3 mg, 77% yield) as a brown oil; $\nu_{max}$ (neat)/$cm^{-1}$ 3062, 2923, 2851, 1716, ,1638, 1581, 1495, 1478, 1455, 1439, 1392, 1260, 1096, 1080, 1021, 913, 849, 798, 722, 688; $\delta_H$ (300 MHz, $CDCl_3$) 3.26 (2H, d, *J* 6.6, C*H*$_2$CH=CH$_2$), 4.95 - 5.09 (2H, m, CH$_2$CH=C*H*$_2$), 5.38 (2H, s, Ph-C*H*$_2$), 5.87 (1H, ddt, *J* 17.0, 9.8, 6.4, CH$_2$C*H*=CH$_2$), 6.86 - 6.94 (2H, m, Ar-*H*), 7.10 - 7.24 (8H, m, Ar-*H*), 7.57 (1H, s, HetAr-*H*); $\delta_C$ (75 MHz, $CDCl_3$) 29.0 (*C*H$_2$CH=CH$_2$), 53.4 (Ph-*C*H$_2$), 115.6 (CH$_2$CH=*C*H$_2$), 121.9 (*C*), 125.9 (Ar-*C*H), 126.3 (Ar-*C*H), 127.6 (Ar-*C*H), 127.7 (Ar-*C*H), 128.5 (Ar-*C*H), 129.1 (Ar-*C*H), 135.0 (*C*), 135.5 (*C*), 136.3 (CH$_2$*C*H=CH$_2$), 136.7 (*C*), 139.5 (HetAr-*C*H); *m/z* (ES+) (M + H), 307; (Found: M + H, 307.1255. $C_{19}H_{19}N_2S$ requires M, 307.1264).

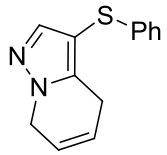
**1-(5-Allyl-4-(phenylsulfanyl)-1H-pyrrol-2-yl)-2,2,2-trifluoroethanone 7a**




An oven dried tube was flushed with $N_2$, before adding a solution containing 3-(phenylsulfinyl)-1H-pyrrole (14.0 mg, 0.073 mmol) and allyltrimethylsilane (30.0 µL, 0.183 mmol) in $CH_2Cl_2$ (1.2 mL). Trifluoroacetic anhydride (26.0 µL, 0.183 mmol) was added at -40 °C and the reaction mixture was allowed to warm to room temperature for 3 h before quenching with aqueous saturated $NaHCO_3$ (1 mL) and extraction with EtOAc (3 × 2 mL). The combined organic layer was dried ($Na_2SO_4$) and concentrated *in vacuo*. The crude product was purified by

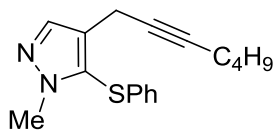
preparative thin layer chromatography on silica gel eluting with 10% EtOAC in *n*-hexane to yield the product (11.0 mg, 48% yield) as a brown solid; $\nu_{max}$ (neat)/$cm^{-1}$ 3272, 2924, 2852, 1642, 1583, 1547, 1503, 1476, 1439, 1331, 1243, 1196, 1146, 1071, 1025, 990, 926, 887, 858, 766, 746, 691, 635; $\delta_H$ (300 MHz, $CDCl_3$) 3.50 (2H, d, *J* 6.8, C*H*$_2$CH=CH$_2$), 5.16 - 5.31 (2H, m, CH$_2$CH=C*H*$_2$), 5.76 - 5.91 (1H, m, CH$_2$C*H*=CH$_2$), 7.06 - 7.18 (3H, m, Ar-*H*), 7.22 - 7.29 (2H, m, Ar-*H*), 7.30 - 7.36 (1H, m, HetAr-*H*), 9.47 (1H, br. S, N-H); $\delta_C$ (100 MHz, $CDCl_3$) 30.6 (*C*H$_2$CH=CH$_2$), 110.4 (q, *J* 288, *C*F$_3$), 112.6 (*C*), 119.9 (CH$_2$CH=*C*H$_2$), 124.8 (*C*), 125.7 (Ar-*C*H), 126.5 (Ar-*C*H), 128.1 (HetAr-*C*H), 129.1 (Ar-*C*H), 131.8 (CH$_2$*C*H=CH$_2$), 137.6 (*C*), 146.2 (*C*), 182.4 (q, *J* 38, *C*=O); *m/z* (ES-) (M - H, 310; (Found: M - H, 310.0522. $C_{15}H_{11}F_3NOS$ requires M - H, 310.0518).

**3-(Phenylsulfanyl)-4,7-dihydropyrazolo[1,5-a]pyridine 7b**




To a solution of 1,5-diallyl-4-(phenylsulfanyl)-1H-pyrazole (5.5 mg, 0.021 mmol) in $CH_2Cl_2$ (3.0 mL) Hoveyda-Grubbs II catalyst (2.70 mg, 0.0043 mmol) was added and the reaction was stirred over night at room temperature. The crude reaction mixture was then concentrated *in vacuo* and purified by preparative thin layer chromatography on silica gel eluting with 15% EtOAC in petroleum ether (40 – 60 °C) to give the product (4.1 mg, 84% yield) as a colourless oil; $\nu_{max}$ (neat)/$cm^{-1}$ 2922, 2852, 1667, 1582, 1499, 1477, 1438, 1426, 1415, 1347, 1165, 1082, 1022, 982, 882, 860, 737, 689, 674; $\delta_H$ (500 MHz, $CDCl_3$) 3.35 - 3.40 (2H, m, C*H*$_2$), 4.78 - 4.85 (2H, m, C*H*$_2$), 5.95 - 6.01 (2H, m, 2 × C*H*), 7.05 - 7.13 (3H, m, Ar-H), 7.19 - 7.25 (2H, m, Ar-H), 7.72 (1H, s, HetAr-H); $\delta_C$ (125 MHz, $CDCl_3$) 23.2 (*C*H$_2$), 47.8 (*C*H$_2$), 113.0 (*C*), 120.5 (*C*H), 121.2 (*C*H), 125.2 (Ar-*C*H), 125.9 (Ar-*C*H), 128.9 (Ar-*C*H), 129.8 (*C*), 138.3 (*C*), 144.1 (HetAr-*C*H); *m/z* (ES+) (M + H), 229; (Found: M + H, 229.0793. $C_{13}H_{13}N_2S$ requires M, 229.0794).

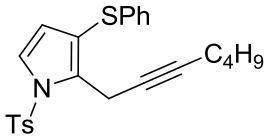
**4-(Hept-2-yn-1-yl)-1-methyl-5-(phenylsulfanyl)-1H-pyrazole 8a**




An oven dried tube was flushed with $N_2$, before adding a solution containing 1-methyl-5-(phenylsulfinyl)-1H-pyrazole (15.5 mg, 0.075 mmol) and hept-2-ynyltrimethylsilane (31.5 mg, 0.188 mmol) in $CH_2Cl_2$ (0.75 mL). Triflic anhydride (31.0 µL, 0.188 mmol) followed by 2,6-di-*tert*-butylpyridine (43.6 µL, 0.188 mmol) were added at -40 °C and the reaction mixture was allowed to warm to room temperature over night before quenching with aqueous saturated $NaHCO_3$ (1 mL) and extraction with EtOAc (3 × 2 mL). The combined organic layer was dried

($Na_2SO_4$) and concentrated *in vacuo*. The crude product was purified by preparative thin layer chromatography on silica gel eluting with 15% EtOAc in *n*-hexane, to yield the product (15.1 mg, 71% yield) as a colourless oil; $\nu_{max}$ (neat)/$cm^{-1}$ 2919, 2841, 1673, 1556, 1479, 1442, 1362, 1269, 753, 668; $\delta_H$ (500 MHz, $CDCl_3$) 0.90 (3H, t, *J* 6.9 $CH_2CH_3$), 1.34 - 1.49 (4H, m, 2 × $CH_2$), 2.13 (2H, tt, *J* 6.9, 2.4, $CCH_2$), 3.40 (2H, t, *J* 2.4, Ph-$CH_2$C), 3.84 (3H, s, $CH_3$), 6.96 - 7.01 (2H, m, Ar-*H*), 7.14 - 7.19 (1H, m, Ar-*H*), 7.22 - 7.26 (2H, m, Ar-*H*), 7.66 (1H, s, HetAr-*H*); $\delta_C$ (125 MHz, $CDCl_3$) 13.6 ($CH_2CH_3$), 15.0 (Ph-$CH_2$C), 18.4 ($CCH_2$), 21.9 ($CH_2CH_2$), 31.0 ($CH_2CH_2$), 37.0 ($CH_3$), 77.2 (C≡C), 81.2 (C≡C), 124.3 (*C*), 126.1 (Ar-*C*H), 126.4 (Ar-*C*H), 127.4 (*C*), 129.3 (Ar-*C*H), 135.1 (*C*), 138.6 (HetAr-*C*H); *m/z* (EI) M, 284; (Found: M, 284.1338. $C_{17}H_{20}N_2S$ requires M, 284.1342).

**2-(Hept-2-yn-1-yl)-3-(phenylsulfanyl)-1-tosyl-1H-pyrrole 8b**



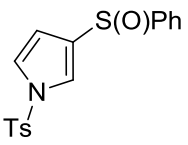

An oven dried tube was flushed with $N_2$, before adding a solution containing 3-(phenylsulfinyl)-1-tosyl-1H-pyrrole (19.4 mg, 0.056 mmol) and hept-2-ynyltrimethylsilane (23.7 mg, 0.141 mmol) in MeCN (0.75 mL). Trifluoroacetic anhydride (20.0 µL, 0.141 mmol) followed by 2,6-di-*tert*-butylpyridine (32.7 µL, 0.141 mmol) were added at -40 °C and the reaction mixture was allowed to warm to room temperature over night before quenching with aqueous saturated $NaHCO_3$ (1 mL) and extraction with EtOAc (3 × 2 mL). The combined organic layer was dried ($Na_2SO_4$) and concentrated *in vacuo*. The crude product was purified by preparative thin layer chromatography on silica gel eluting with 15% EtOAC in *n*-hexane to yield **8b** (21.6 mg, 91% yield) as a yellow oil; $\nu_{max}$ (neat)/$cm^{-1}$ 2929, 1723, 1598, 1446, 1340, 1163, 1087, 1023, 814, 751, 668; $\delta_H$ (500 MHz, $CD_3CN$) 0.82 (3H, t, *J* 6.9, $CH_2CH_3$), 1.15 - 1.26 (4H, m, 2 × $CH_2$), 1.87 (2H, tt, *J* 6.9, 2.4, $CCH_2$), 2.42 (3H, s, $CH_3$), 3.84 (2H, t, *J* 2.4, Ph-$CH_2$C), 6.34 (1H, d, *J* 3.5, HetAr-*H*), 7.05 - 7.09 (2H, m, Ar-*H*), 7.12 - 7.16 (1H, m, Ar-*H*), 7.20 - 7.24 (2H, m, Ar-*H*), 7.40 - 7.44 (3H, m, 2 × Ar-*H* & HetAr-*H*), 7.83 (2H, d, *J* 8.5, Ar-*H*); $\delta_C$ (125 MHz, $CD_3CN$) 13.9 ($CH_2CH_3$), 16.2 (Ph-$CH_2$C), 18.9 ($CCH_2$), 21.8 ($CH_3$), 22.7 ($CH_2CH_2$), 31.6 ($CH_2CH_2$), 76.5 (C≡C), 82.4 (C≡C), 116.4 (*C*), 117.7 (HetAr-*C*H), 124.2 (HetAr-*C*H), 126.9 (Ar-*C*H), 128.1 (Ar-*C*H), 128.3 (Ar-*C*H), 130.1 (Ar-*C*H), 131.2 (Ar-*C*H), 135.5 (*C*), 136.5 (*C*), 138.0 (*C*), 147.2 (*C*); *m/z* (EI), (Found: M, 423.1318. $C_{24}H_{25}NO_2S_2$ requires M, 423.1321).

**Substrate synthesis:**

The following compounds are known in the literature: 2-(phenylsulfanyl)-1-tosyl-1H-pyrrole,[1] 3-(phenylsulfanyl)-1-tosyl-1H-pyrrole,[1] 2-(phenylsulfinyl)-1-tosyl-1H-pyrrole,[2] 3-(phenylsulfinyl)-1H-pyrrole,[3] 2-(p-tolylsulfanyl)-1-tosyl-1H-pyrrole,[2] 1-methyl-5-(phenylsulfanyl)-1H-pyrazole.[4]

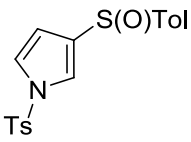
**General Procedure C: Sulfide oxidation:**

**3-(Phenylsulfinyl)-1-tosyl-1H-pyrrole 1b**




To a solution of 3-(phenylsulfanyl)-1-tosyl-1H-pyrrole (1.1 g, 3.34 mmol) in $CH_2Cl_2$ (33.0 mL) *m*-CPBA (0.75 g, 3.34 mmol) was added slowly at 0 °C. The reaction mixture was then allowed to warm to room temperature over night before quenching with aqueous saturated $NaHCO_3$ (20 mL). The aqueous layer was then extracted with $CH_2Cl_2$ (3 × 10 mL) and the combined organic layer washed with brine (20 mL), dried ($Na_2SO_4$) and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with 5% $Et_2O$ in chloroform to yield the product (0.77 g, 67% yield) as a yellow oil; $\nu_{max}$ (neat)/$cm^{-1}$ 3129, 2981, 1594, 1463, 1443, 1373, 1286, 1207, 1189, 1170, 1083, 1041, 997, 953, 811, 749, 669, 630; $\delta_H$ (500 MHz, $CDCl_3$) 2.44 (3H, s, C*H*$_3$), 6.25 (1H, dd, *J* 3.5, 1.6, HetAr-*H*), 7.15 (1H, dd, *J* 3.5, 2.4, HetAr-*H*), 7.34 (2H, d, *J* 8.2, Ar-*H*), 7.45 - 7.53 (3H, m, Ar-*H*), 7.56 (1H, t, *J* 1.7, HetAr-*H*), 7.59 – 7.64 (2H, m Ar-*H*), 7.77 (2H, d, *J* 8.2 Ar-C*H*); $\delta_C$ (125 MHz, $CDCl_3$) 21.7 (*C*H$_3$), 110.5 (HetAr-*C*H), 122.0 (HetAr-*C*H), 122.6 (HetAr-*C*H), 124.5 (Ar-*C*H), 127.3 (Ar-*C*H), 129.2 (Ar-*C*H), 130.3 (Ar-*C*H), 130.9 (Ar-*C*H), 132.3 (*C*), 134.9 (*C*), 144.0 (*C*), 146.1 (*C*); *m/z* (ES+) (M + H), 346; (Found: M + H, 346.0563. $C_{17}H_{16}NO_3S_2$ requires M, 346.0567).

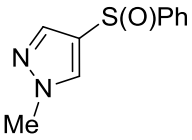
**3-(p-Tolylsulfinyl)-1-tosyl-1H-pyrrole 1h**




As described in general procedure C, 3-(p-tolylsulfanyl)-1-tosyl-1H-pyrrole (75.0 mg, 0.218 mmol), *m*-CPBA (49.0 g, 0.218 mmol) and $CH_2Cl_2$ (2.2 mL), after purification by column chromatography on silica gel eluting with 5% $Et_2O$ in chloroform, gave the product (70.0 mg, 89% yield) as a brown oil: $\nu_{max}$ (neat)/$cm^{-1}$ 2922, 2361, 1713, 1594, 1463, 1377, 1224, 1172, 1084, 1049, 807, 751, 702, 669, 588; $\delta_H$ (500 MHz, $CD_3CN$) 2.36 (3H, s, C*H*$_3$), 2.40 (3H, s, C*H*$_3$), 6.27 (1H, d, *J* 2.2, HetAr-*H*), 7.23 (1H, dd, *J* 3.2, 2.2, HetAr-*H*), 7.32 (2H, d, *J* 7.9, Ar-*H*), 7.40 (2H, d, *J* 8.3, Ar-*H*), 7.48 (2H, d, *J* 7.9, Ar-*H*), 7.64 - 7.70 (1H, m, HetAr-*H*), 7.83 (2H, d, *J* 8.3, Ar-*H*); $\delta_C$ (125 MHz, $CD_3CN$) 21.4 (*C*H$_3$),

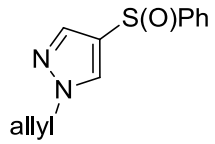
21.8 (*C*$H_3$), 111.2 (HetAr-*C*H), 122.9 (HetAr-*C*H), 124.0 (HetAr-*C*H), 125.2 (Ar-*C*H), 128.2 (Ar-*C*H), 131.0 (Ar-*C*H), 131.5 (Ar-*C*H), 134.5 (*C*), 135.04 (*C*), 135.7 (*C*), 142.7 (*C*), 147.8 (*C*); *m/z* (ES+) (M + H), 360.

**1-Methyl-4-(phenylsulfinyl)-1H-pyrazole 1a**



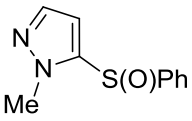

As described in general procedure C, 1-methyl-4-(phenylsulfanyl)-1H-pyrazole (0.30 g, 1.58 mmol), *m*-CPBA (0.39 g, 1.73 mmol) and $CH_2Cl_2$ (3.15 mL), after purification by column chromatography on silica gel eluting with 5% MeOH in $CH_2Cl_2$, gave the product (0.19 mg, 59% yield) as a colourless oil; $\nu_{max}$ (neat)/$cm^{-1}$ 3101, 2938, 1674, 1514, 1476, 1442, 1377, 1305, 1189, 1117, 1037, 975, 859, 751, 693, 653, 621; $\delta_H$ (300 MHz, $CDCl_3$) 3.89 (3H, s, C*H*$_3$), 7.43 - 7.55 (4H, m, 3 × Ar-*H* & HetAr-*H*), 7.59 (1H, s, HetAr-*H*), 7.62 - 7.71 (2H, m, Ar-*H*); $\delta_C$ (75 MHz, $CDCl_3$) 39.4 (*C*$H_3$), 124.4 (Ar-*C*H), 126.3 (*C*), 129.1 (Ar-*C*H), 130.8 (Ar-*C*H), 131.3 (HetAr-*C*H), 138.4 (HetAr-*C*H), 144.3 (*C*); *m/z* (ES+) (M + H), 207; (Found: M + H, 207.0590. $C_{10}H_{11}N_2OS$ requires M, 207.0587).

**1-Allyl-4-(phenylsulfinyl)-1H-pyrazole 1e**



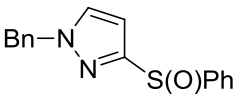

To a solution of 4-(phenylsulfanyl)pyrazole (0.20 g, 1.14 mmol) in DMF (1.7 mL) was added KOH (76.0 mg, 1.36 mmol) at room temperature. After complete dissolution allyl bromide (0.15 g, 1.25 mmol) was added and the reaction mixture was stirred overnight before the quenching with water (5.5 mL) and stirring for a further 30 min. The reaction mixture was extracted with $CH_2Cl_2$ (4 × 5mL) and the combined organic layers were washed with water (20 mL), dried ($Na_2SO_4$) and concentrated *in vacuo* to give 1-allyl-4-(phenylsulfanyl)-1H-pyrazole (0.17 g, 71%). The crude product was then oxidized as described in procedure A, using *m*-CPBA (89.0 mg, 0.40 mmol) and $CH_2Cl_2$ (7.9 mL). Column chromatography on silica gel eluting with 50% EtOAc in petreoleum ether (40 – 60 °C), gave the product (75.0 mg, 61% yield) as a white solid: $\nu_{max}$ (neat)/$cm^{-1}$ 3091, 2360, 1645, 1509, 1476, 1443, 1378, 1175, 1112, 1083, 1038, 986, 918, 859, 749, 689, 655, 628; $\delta_H$ (500 MHz, $CDCl_3$) 4.66 (2H, d, *J* 6.3, C*H*$_2$CH=CH$_2$), 5.16 - 5.28 (2H, m, CH$_2$CH=C*H*$_2$), 5.91 (1H, ddt, *J* 16.9, 10.4, 6.2, CH$_2$C*H*=CH$_2$), 7.41 - 7.48 (4H, m, 3 × Ar-C*H* & HetAr-C*H*), 7.58 - 7.63 (2 × Ar-C*H* & HetAr-C*H*); $\delta_C$ (125 MHz, $CDCl_3$) 55.3 (*C*H$_2$CH=CH$_2$), 120.1 (CH$_2$CH=*C*H$_2$), 124.4 (Ar-*C*H), 126.4 (*C*), 129.2 (Ar-*C*H), 130.4 (*C*H), 130.8 (*C*H), 131.4 (CH$_2$*C*H=CH$_2$), 138.4 (HetAr-*C*H), 144.3 (*C*); *m/z* (ES+) (M + H), 233; (Found: M + H, 233.0749. $C_{12}H_{13}N_2OS$ requires M, 233.0744).

**1-Methyl-5-(phenylsulfinyl)-1H-pyrazole 1f**



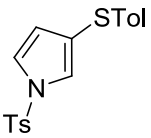
As described in general procedure C, 1-methyl-5-(phenylsulfanyl)-1H-pyrazole (0.70 g, 3.68 mmol), *m*-CPBA (0.82 g, 3.68 mmol) and $CH_2Cl_2$ (7.4 mL), after purification by column chromatography on silica gel eluting with 5% MeOH in $CH_2Cl_2$, gave the product (0.56 g, 74% yield) as a colourless oil; $\nu_{max}$ (neat)/$cm^{-1}$ 3056, 2944, 2361, 1581, 1475, 1441, 1384, 1275, 1189, 1082, 1041, 922, 786, 750, 694, 649, 546; $\delta_H$ (300 MHz, $CDCl_3$) 3.92 (3H, s, C*H*$_3$), 6.44 (1H, d, *J* 1.9 HetAr-*H*), 7.44 - 7.66 (6H, m, 5 × Ar-*H* & HetAr-*H*); $\delta_C$ (75 MHz, $CDCl_3$) 37.9 (*C*H$_3$), 109.8 (HetAr-*C*H), 124.8 (Ar-*C*H), 129.4 (Ar-*C*H), 131.3 (Ar-*C*H), 138.4 (HetAr-*C*H), 141.6 (*C*), 141.8 (*C*); *m/z* (ES+) (M + H), 207; (Found: M + H, 207.0583. $C_{10}H_{11}N_2OS$ requires M, 207.0587).

**1-Benzyl-3-(phenylsulfinyl)-1H-pyrazole 1g**



As described in general procedure C, 1-benzyl-3-(phenylsulfanyl)-1H-pyrazole (0.25 g, 0.94 mmol), *m*-CPBA (0.11 g, 0.47 mmol) and $CH_2Cl_2$ (9.4 mL), after purification by column chromatography on silica gel eluting with 40% EtOAc in petroleum ether (40 – 60 °C), gave the product (0.11 g, 85% yield) as a white solid: $\nu_{max}$ (neat)/$cm^{-1}$ 3059, 1605, 1581, 1496, 1476, 1455, 1442, 1397, 1297, 1272, 1157, 1085, 1045, 1020, 997, 921, 784, 748, 715, 688, 658; $\delta_H$ (300 MHz, $CDCl_3$) 5.30 - 5.44 (2H, m, C*H*$_2$), 6.22 (1H, d, *J* 1.9, HetAr-*H*), 6.89 - 6.98 (2H, m, Ar-*H*), 7.04 - 7.12 (4H, m, Ar-*H*), 7.22 - 7.39 (5H, m, 4 × Ar-*H* & HetAr-*H*); $\delta_C$ (75 MHz, $CDCl_3$) 54.4 (*C*H$_2$), 109.3 (HetAr-*C*H), 124.7 (Ar-*C*H), 127.6 (Ar-*C*H), 128.0 (Ar-*C*H), 128.6 (Ar-*C*H), 129.3 (Ar-*C*H), 131.3 (Ar-*C*H), 135.8 (*C*), 139.2 (HetAr-*C*H), 142.1 (*C*), 143.0 (*C*); *m/z* (ES+) (M + H), 283; (Found: M + H, 283.0892. $C_{16}H_{15}N_2OS$ requires M, 283.0900).

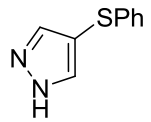
**3-(p-Tolylthio)-1-tosyl-1H-pyrrole 5b**



A solution containing 2-(p-tolylsulfanyl)-1-tosyl-1H-pyrrole (1.30 g, 3.77 mmol), TFA (8.0 mL, 105 mmol) in DCE (8.0 mL) was refluxed over night before concentrating *in vacuo.* The crude product was purified by column chromatography on silica gel eluting with 15% EtOAc in *n*-hexane to yield the product (0.81 g, 62% yield) as a brown oil: $\nu_{max}$ (neat)/$cm^{-1}$ 3165, 2361, 1731, 1594, 1491, 1460, 1372, 1271, 1171, 1088, 1053, 806, 755, 703, 670, 589; $\delta_H$ (500 MHz, $CD_3CN$) 2.25 (3H, s, C*H*$_3$), 2.39 (3H, s, C*H*$_3$), 6.28 (1H, dd, *J* 3.2, 1.6, HetAr-*H*), 7.02 - 7.08 (4H, m, Ar-*H*), 7.26 (1H, dd, *J* 3.2, 2.2, HetAr-*H*), 7.36 - 7.43 (3H, m, 2 × Ar-*H* & HetAr-*H*), 7.81 (2H, d, *J* 8.8, Ar-*H*); $\delta_C$ (125 MHz,

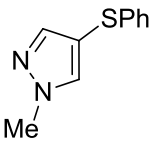
$CD_3CN$) 21.3 (*C*$H_3$), 22.0 (*C*$H_3$), 119.2 (HetAr-*C*H), 119.5 (*C*), 123.7 (HetAr-*C*H), 125.5 (HetAr-*C*H), 128.3 (Ar-*C*H), 129.6 (Ar-*C*H), 131.1 (Ar-*C*H), 131.7 (Ar-*C*H), 134.5 (*C*), 136.5 (*C*), 137.8 (*C*), 147.6 (*C*); *m/z* (EI) M, 343; (Found: M, 343.0697. $C_{18}H_{17}NO_2S_2$ requires M, 343.0695).

**4-(Phenylsulfanyl)-1H-pyrazole**



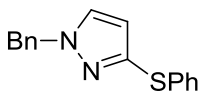

To a solution of 4-bromopyrazole (1.91 g, 13.0 mmol) in THF (40.0 mL) was added *n*-BuLi (19.5 mL, 26.0 mmol) at -78 °C. The reaction mixture was then stirred at 0 °C for 90 min before the addition of S-phenyl benzenethiosulfonate (6.51 g, 26.0 mmol) at -78 °C. The reaction mixture was then allowed to warm to room temperature over night, quenched with aqueous $NH_4Cl$ (50 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried ($Na_2SO_4$) and concentrated *in vacuo*. Column chromatography on silica gel eluting with 5% MeOH in $CH_2Cl_2$ gave the product (1.85 g, 81% yield) as a colourless oil; $\nu_{max}$ (neat)/$cm^{-1}$ 3151, 3057, 2925, 1582, 1476, 1440, 1371, 1327, 1137, 1084, 1027, 970, 942, 867, 815, 689, 658, 623; $\delta_H$ (300 MHz, $CDCl_3$) 6.95 - 7.07 (3H, m, Ar-*H*), 7.09 - 7.19 (2H, m, Ar-*H*), 7.68 (2H, s, HetAr-*H*); $\delta_C$ (75 MHz, $CDCl_3$) 107.9 (*C*), 125.5 (Ar-*C*H), 126.5 (Ar-*C*H), 128.9 (Ar-*C*H), 138.6 (*C*), 139.2 (HetAr-*C*H); *m/z* (EI) M, 176; (Found: M, 176.0399. $C_9H_8N_2S$ requires M, 176.0403).

**1-Methyl-4-(phenylsulfanyl)-1H-pyrazole**




To a solution of 1-methyl-4-(phenylsulfanyl)-1H-pyrazole (0.50 g, 2.84 mmol) in acetone (19.0 mL) was added KOH (0.98 g, 7.10 mmol) followed by iodomethane (0.71 mL, 11.4 mmol). After stirring over night at room temperature the reaction mixture was filtered and concentrated *in vacuo.* Column chromatography on silica gel eluting with 15% EtOAc in *n*-hexane gave the product (0.43 g, 79% yield) as a yellow oil; $\nu_{max}$ (neat)/$cm^{-1}$ 3058, 2936, 2361, ,1581, 1516, 1477, 1438, 1367, 1325, 1181, 1118, ,1083, 1024, 977, 858, 815, 741, 692, 657, 624; $\delta_H$ (300 MHz, $CDCl_3$) 3.87 (3H, s, C*H*$_3$), 6.96 - 7.07 (3H, m, Ar-*H*), 7.09 - 7.20 (2H, m, Ar-*H*), 7.45 (1H, s, HetAr-*H*), 7.51 (1H, s, HetAr-*H*); $\delta_C$ (75 MHz, $CDCl_3$) 39.3 (*C*$H_3$), 107.4 (*C*), 125.3 (Ar-*C*H), 126.2 (Ar-*C*H), 128.8 (Ar-*C*H), 135.2 (HetAr-*C*H), 138.9 (*C*), 144.7 (HetAr-*C*H); *m/z* (EI) M, 190; (Found: M, 190.0556. $C_{10}H_{10}N_2S$ requires M, 190.0559).

**1-Benzyl-3-(phenylsulfanyl)-1H-pyrazole**

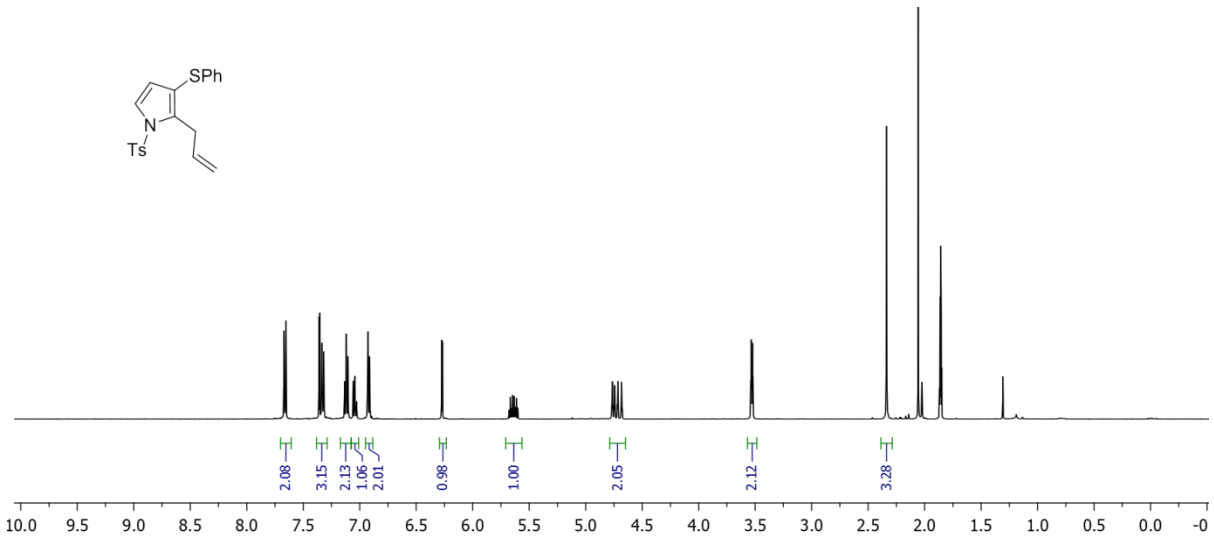



A solution of 5-(phenylsulfanyl)pyrazole (0.44 g, 2.50 mmol) benzyl chloride (0.32 g, 2.50 mmol) and NaOH (0.17 g, 4.25 mmol) in DMSO (1.72 mL) was stirred at room temperature. After complete consumption of starting material, monitored by TLC, the reaction mixture was diluted with water (15 mL) and extracted with cyclohexane (4 × 15 mL). The combined organic layer was washed with saturated aqueous $Na_2CO_3$ (30 mL), dried ($Na_2SO_4$) and concentrated *in vacuo.* The crude product was purified by column chromatography on silica gel eluting with 5% EtOAc in petroleum ether (40 – 60 °C) to yield the product (0.15 g, 22% yield) as a colourless oil: $\nu_{max}$ (neat)/$cm^{-1}$ 3061, 3031, 2933, 1604, 1581, 1495, 1477, 1455, 1439, 1415, 1391, 1317, 1300, 1274, 1157, 1080, 1023, 999, 921, 784, 737, 688, 661; $\delta_H$ (300 MHz, $CDCl_3$) 5.39 (2H, s, C*H*$_2$), 6.58 (1H, d, *J* 1.9, HetAr-*H*), 6.97 - 7.07 (2H, m, Ar-*H*), 7.10 - 7.26 (8H, m, Ar-*H*), 7.65 (1H, d, *J* 1.9, HetAr-*H*); $\delta_C$ (75 MHz, $CDCl_3$) 53.2 (*C*H$_2$), 114.4 (HetAr-*C*H), 126.4 (Ar-*C*H), 127.3 (Ar-*C*H), 127.6 (2 × Ar-*C*H), 128.5 (Ar-*C*H), 129.2 (Ar-*C*H), 130.5 (*C*), 135.4 (*C*), 136.6 (*C*), 139.7 (HetAr-*C*H); *m/z* (ES+) (M + H), 267; (Found: M + H, 267.0953. $C_{16}H_{15}N_2S$ requires M, 267.0951).

## $^{1}$H and $^{13}$C NMR spectra:

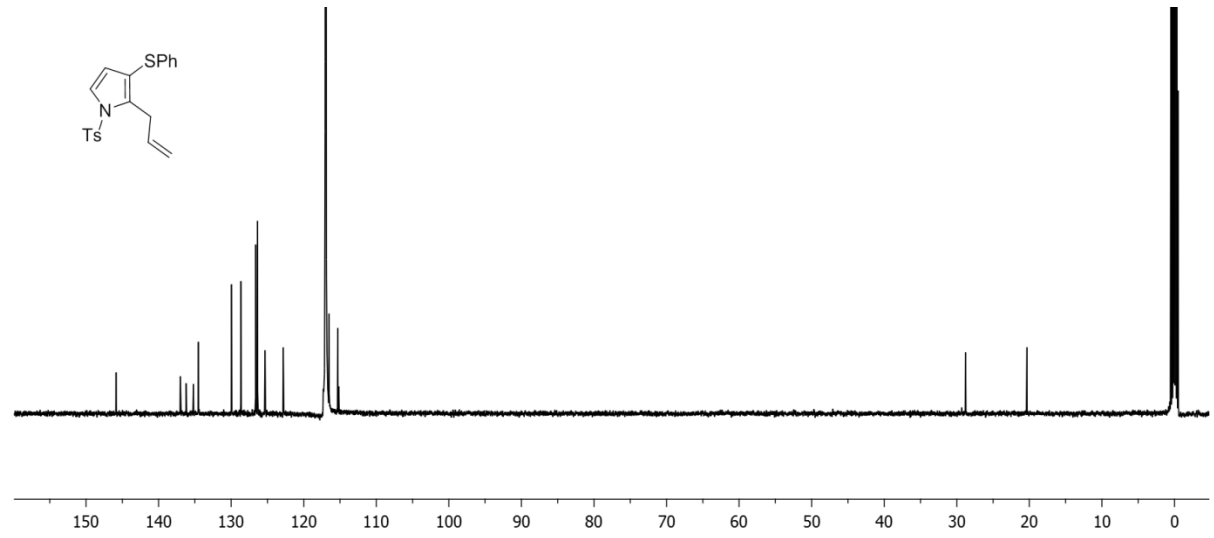
$^{1}$H NMR (500 MHz, $CD_3CN$)

Compound **2b**



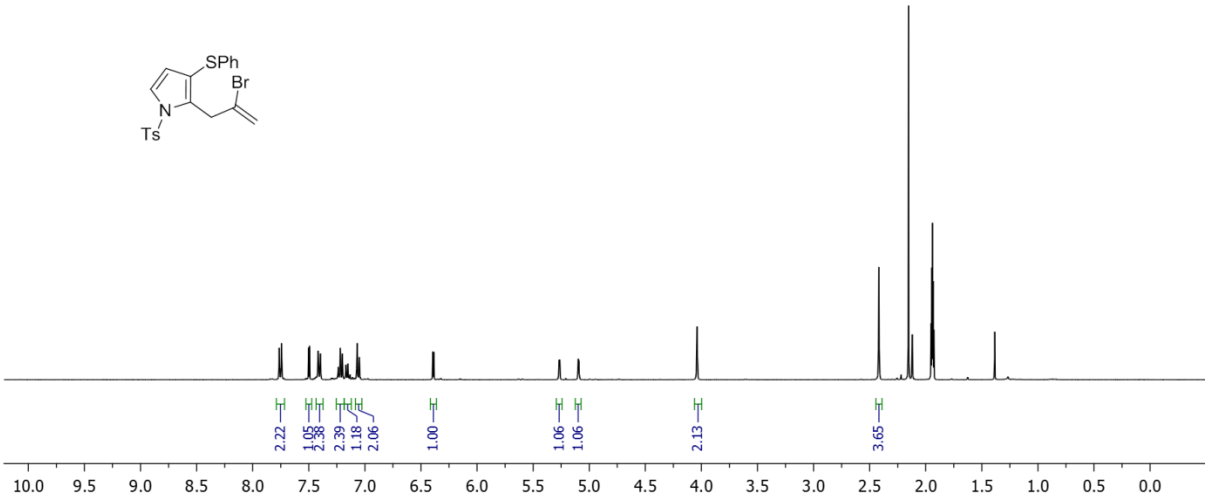

$^{13}$C NMR (125 MHz, $CD_3CN$)

Compound **2b**



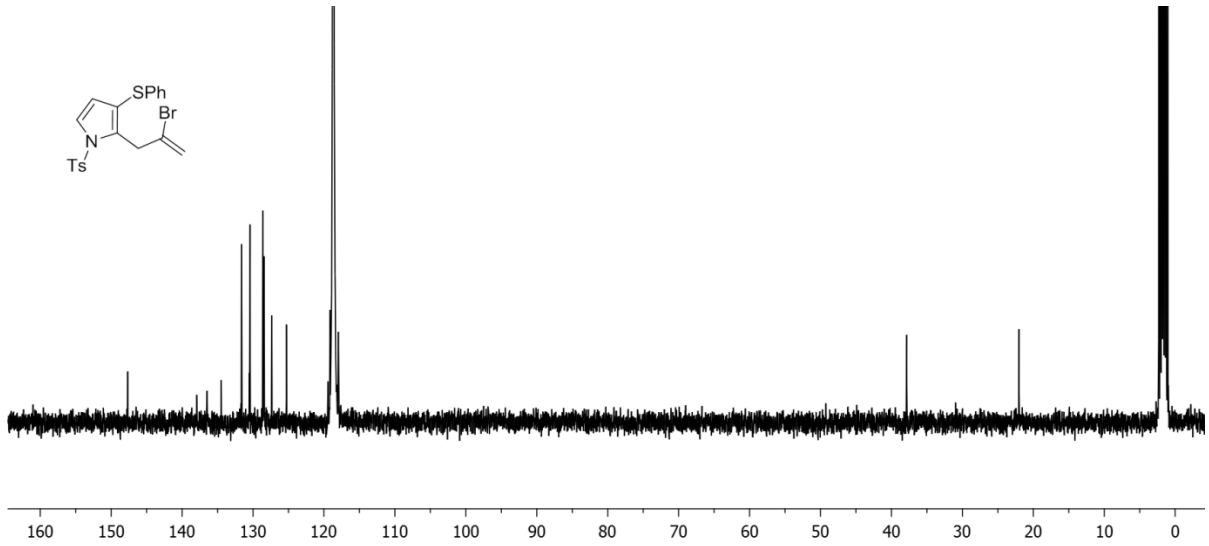
$^{1}$H NMR (400 MHz, $CD_3CN$)

Compound **2c**



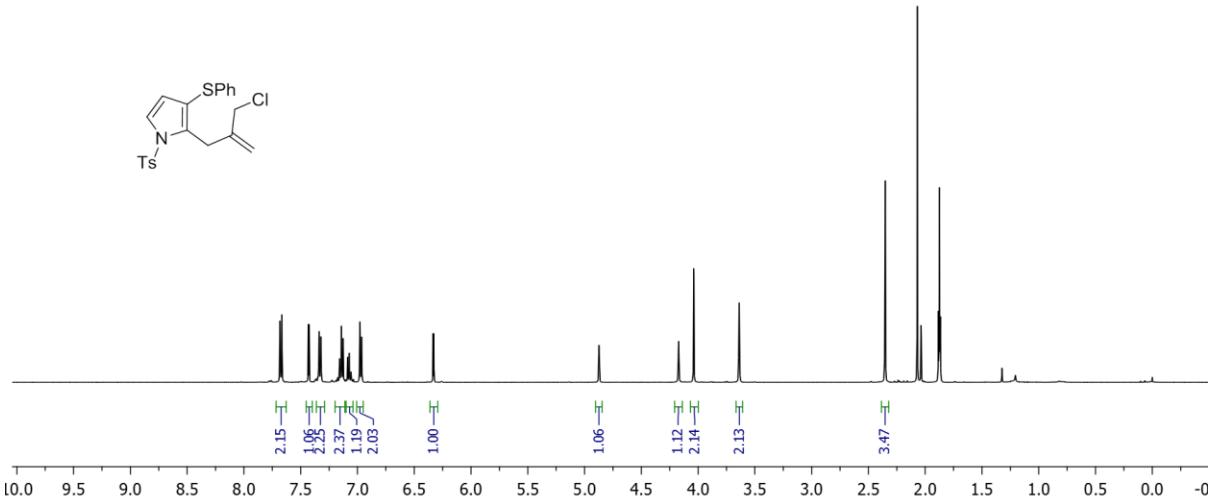

$^{13}$C NMR (100 MHz, $CD_3CN$)

Compound **2c**



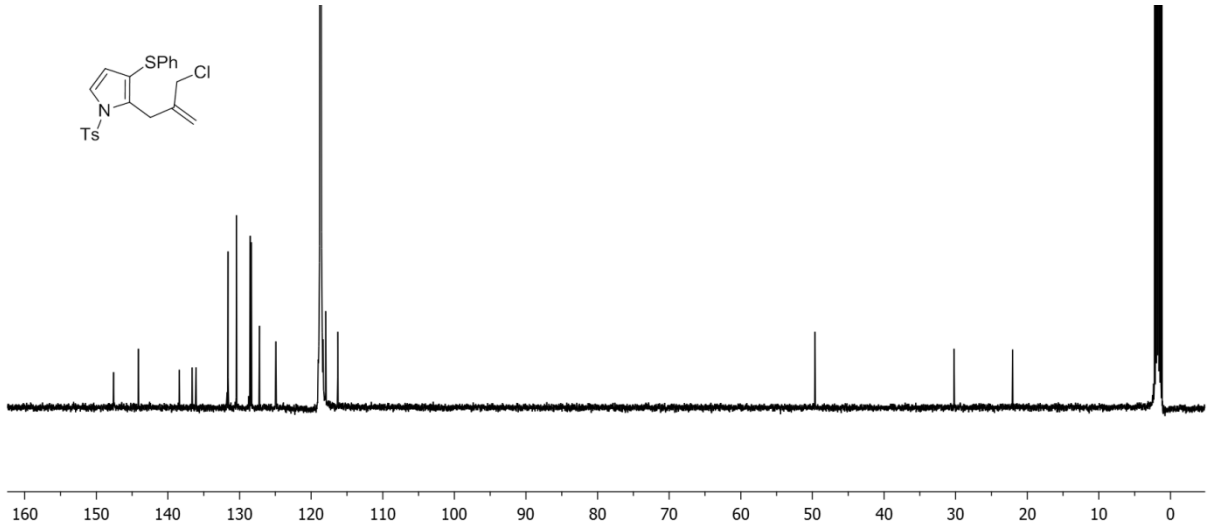
$^{1}$H NMR (500 MHz, $CD_3CN$)

Compound **2d**



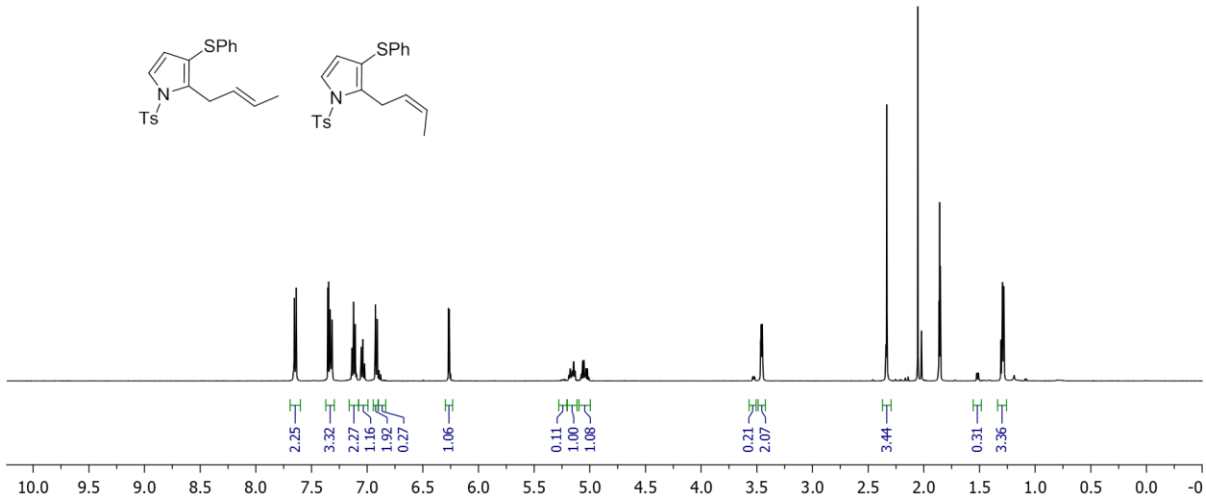

$^{13}$C NMR (125 MHz, $CD_3CN$)

Compound **2d**



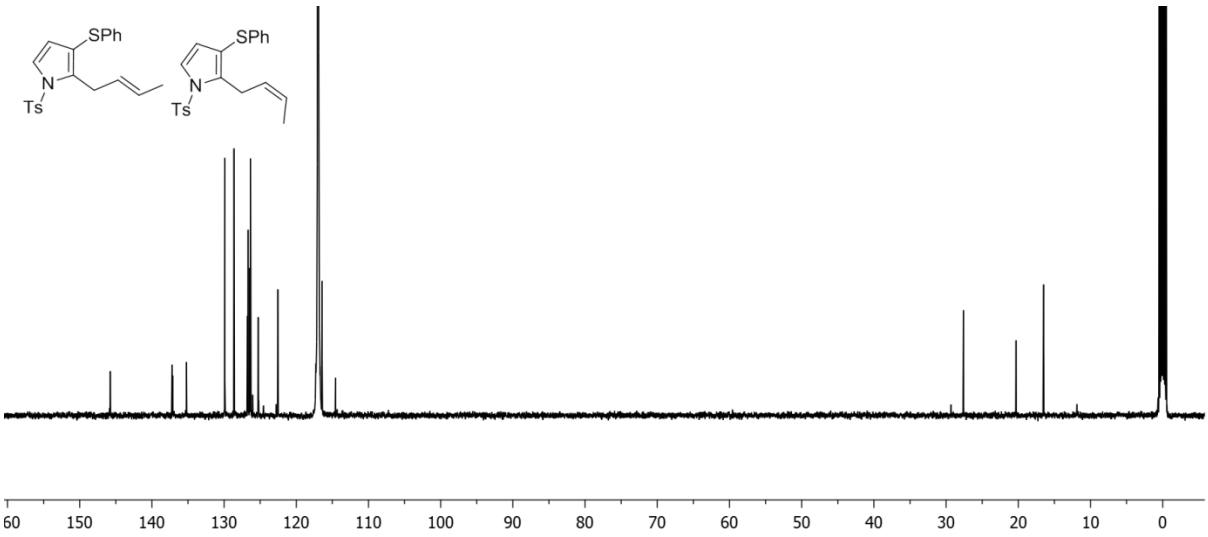
$^{1}$H NMR (500 MHz, $CD_3CN$)

Compound **2e**, inseparable mixture of stereoisomers (E/Z = 11/1)



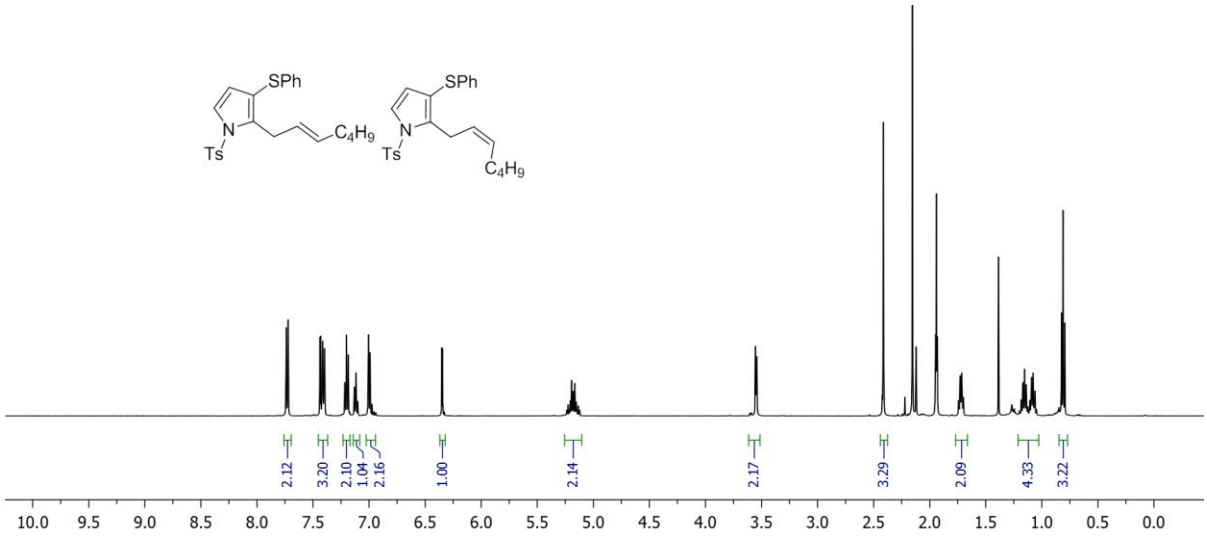

$^{13}$C NMR (125 MHz, $CD_3CN$)

Compound **2e**, inseparable mixture of stereoisomers (E/Z = 11/1)



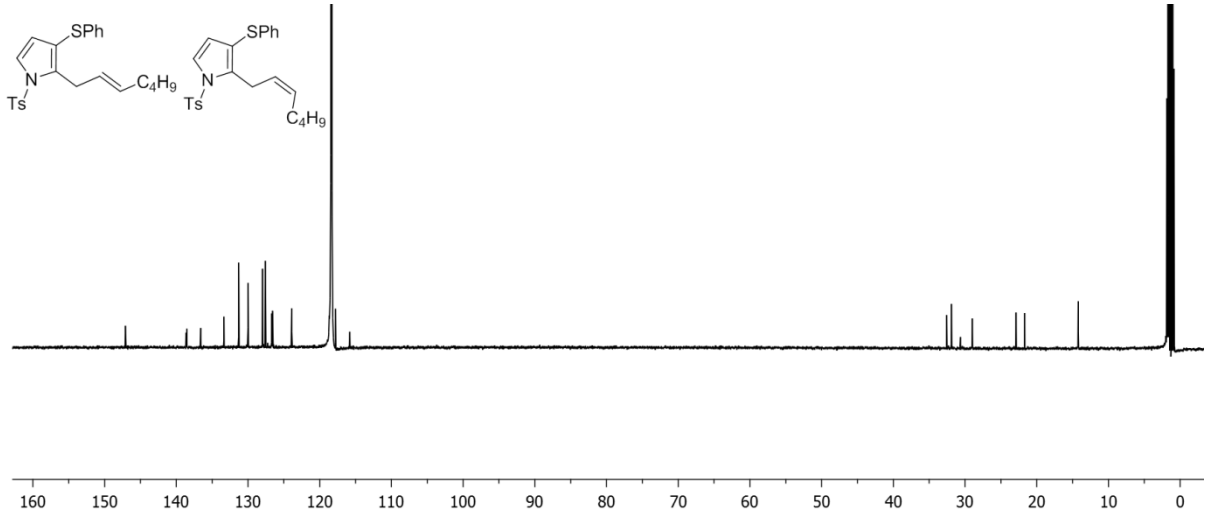
$^{1}$H NMR (500 MHz, $CD_3CN$)

Compound **2f**, inseparable mixture of stereoisomers (E/Z = 17/1)



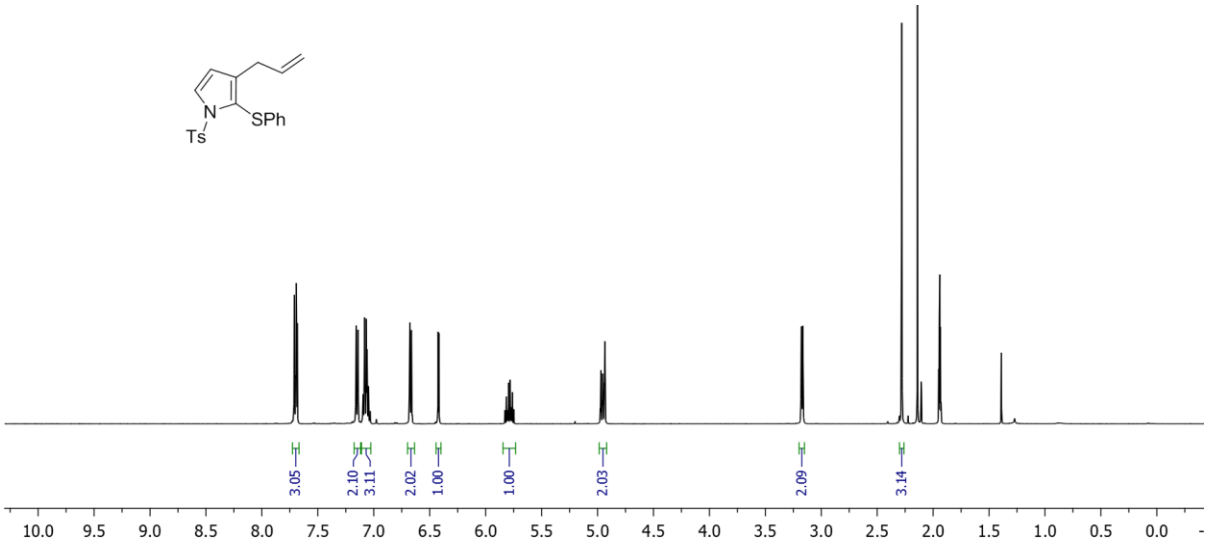

$^{13}$C NMR (125 MHz, $CD_3CN$)

Compound **2f**, inseparable mixture of stereoisomers (E/Z = 17/1)



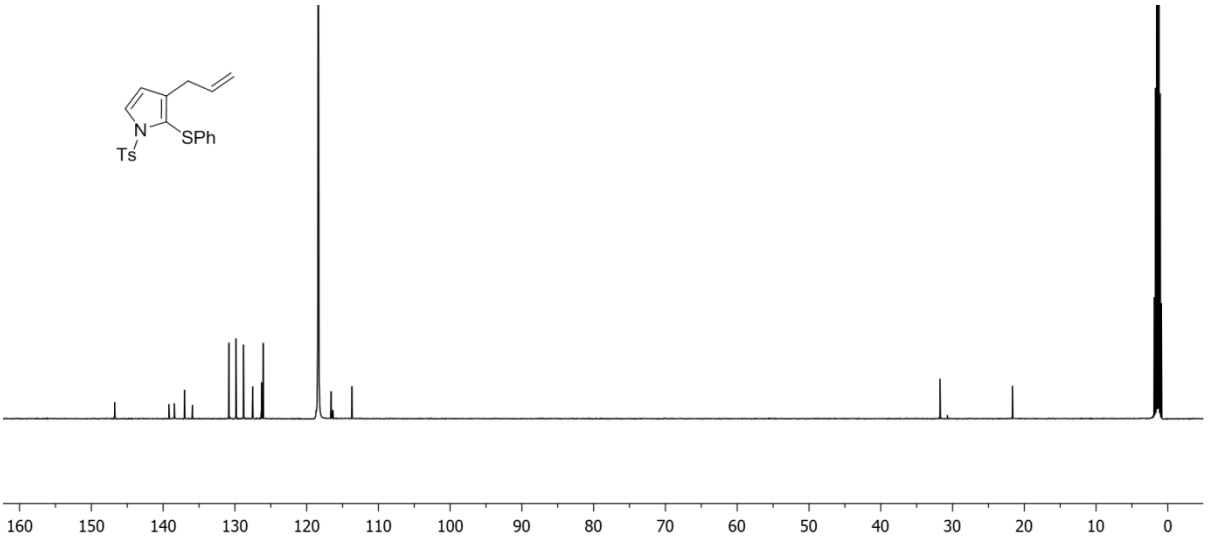
$^{1}$H NMR (500 MHz, $CD_3CN$)

Compound **2g**



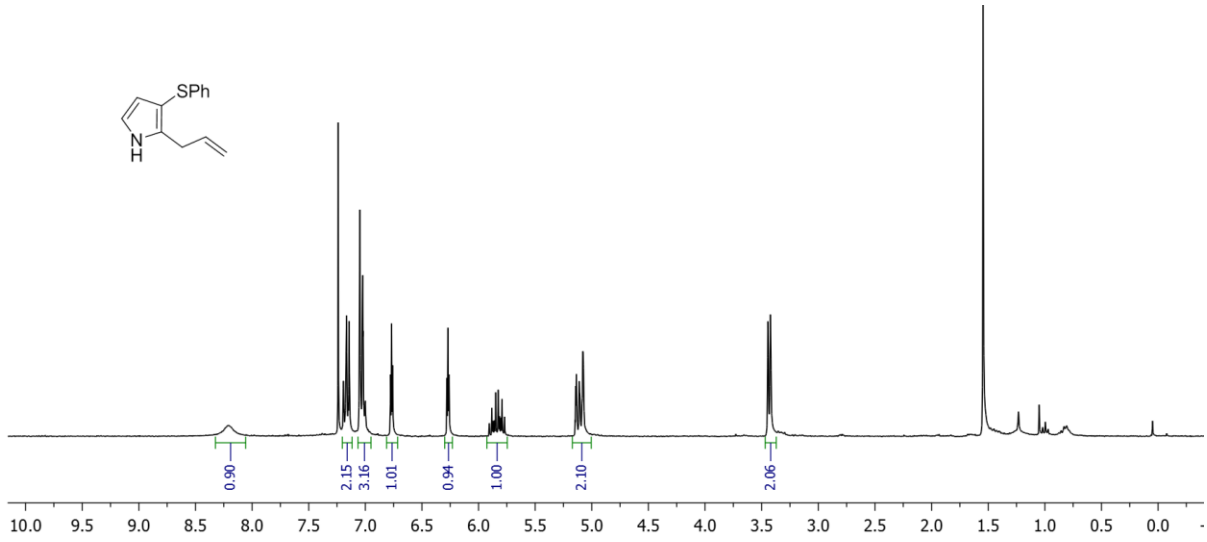

$^{13}$C NMR (125 MHz, $CD_3CN$)

Compound **2g**



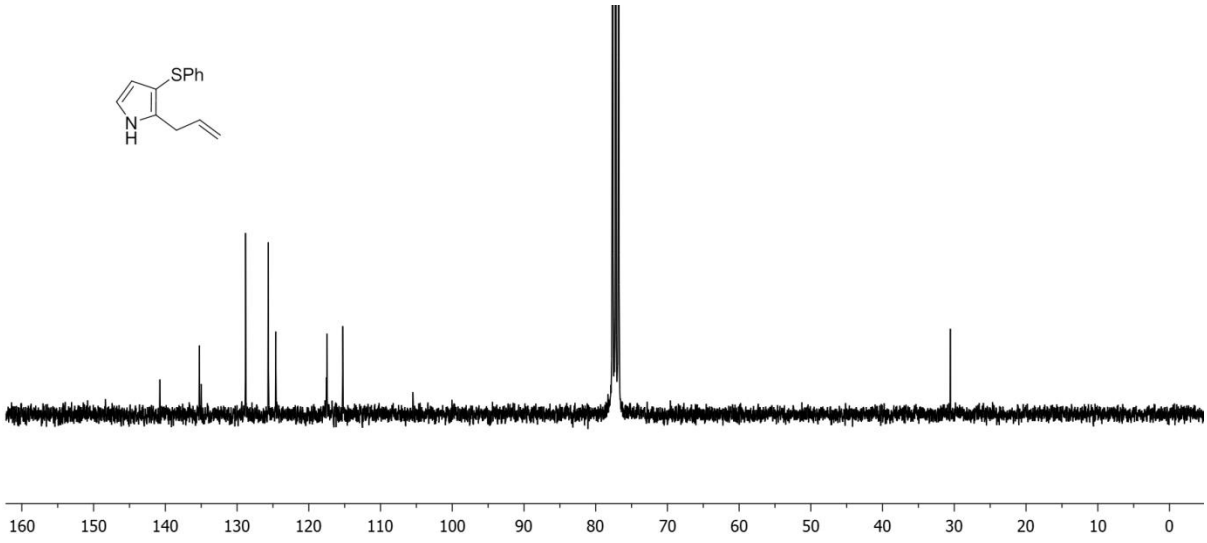
$^{1}$H NMR (300 MHz, $CDCl_3$)

Compound **2h**



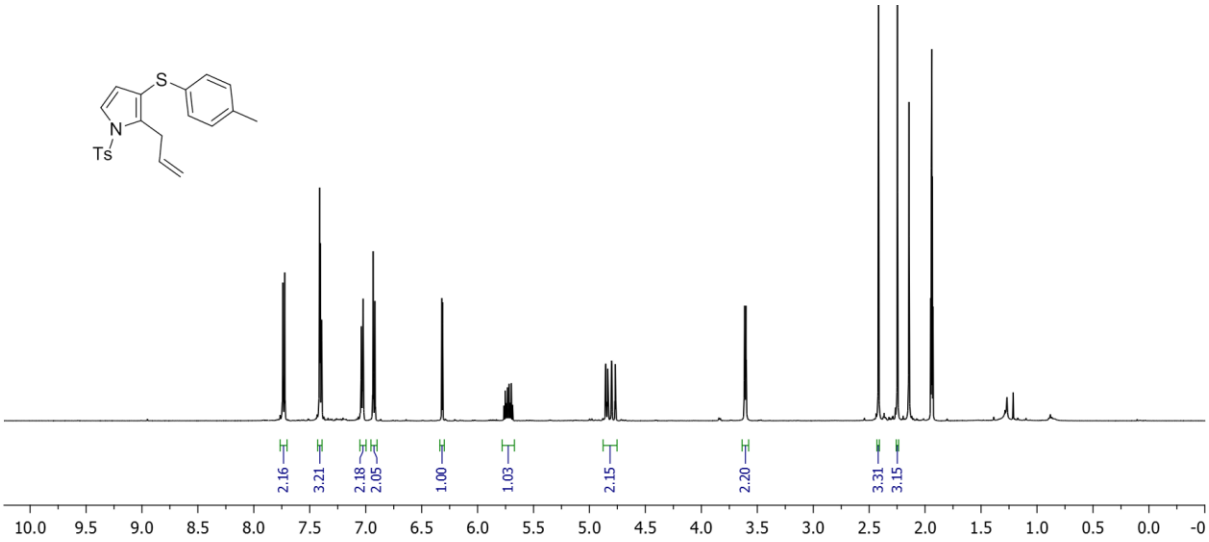

$^{13}$C NMR (75 MHz, $CDCl_3$)

Compound **2h**



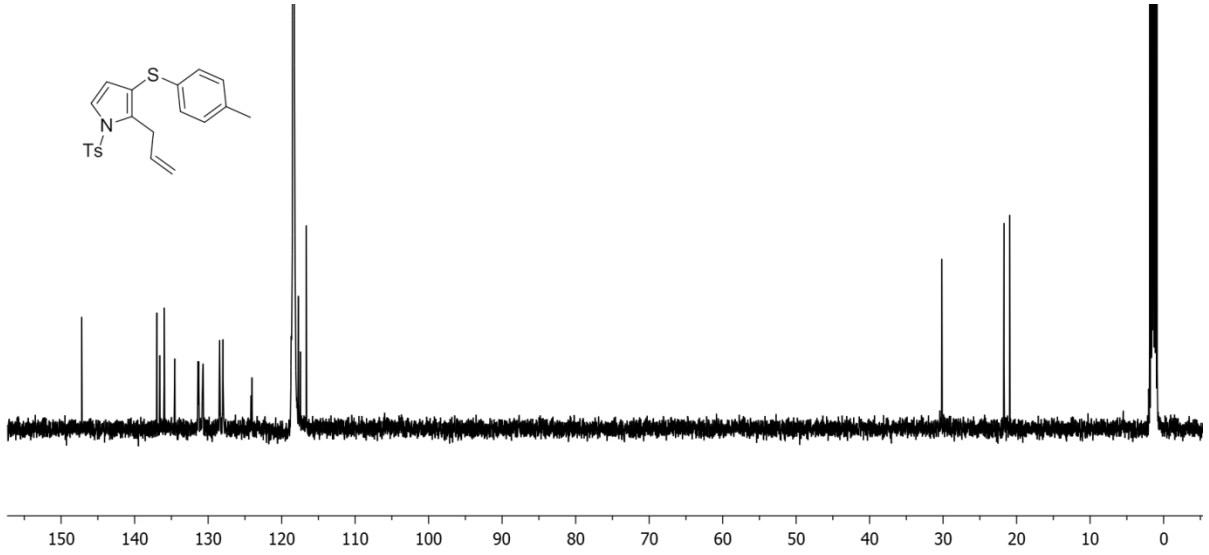
$^{1}$H NMR (500 MHz, $CD_3CN$)

Compound **2n**



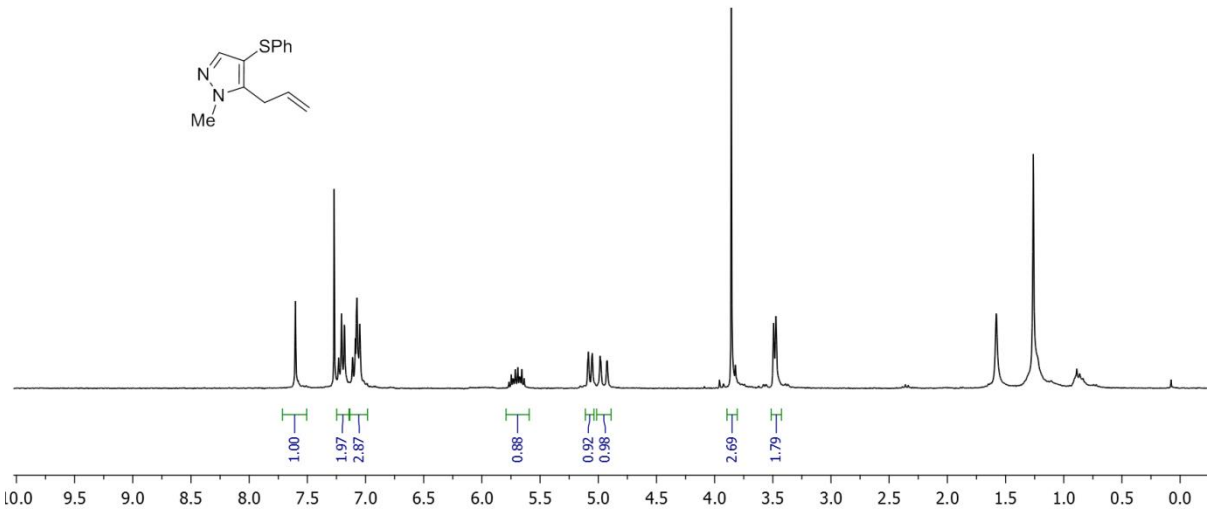

$^{13}$C NMR (125 MHz, $CD_3CN$)

Compound **2n**



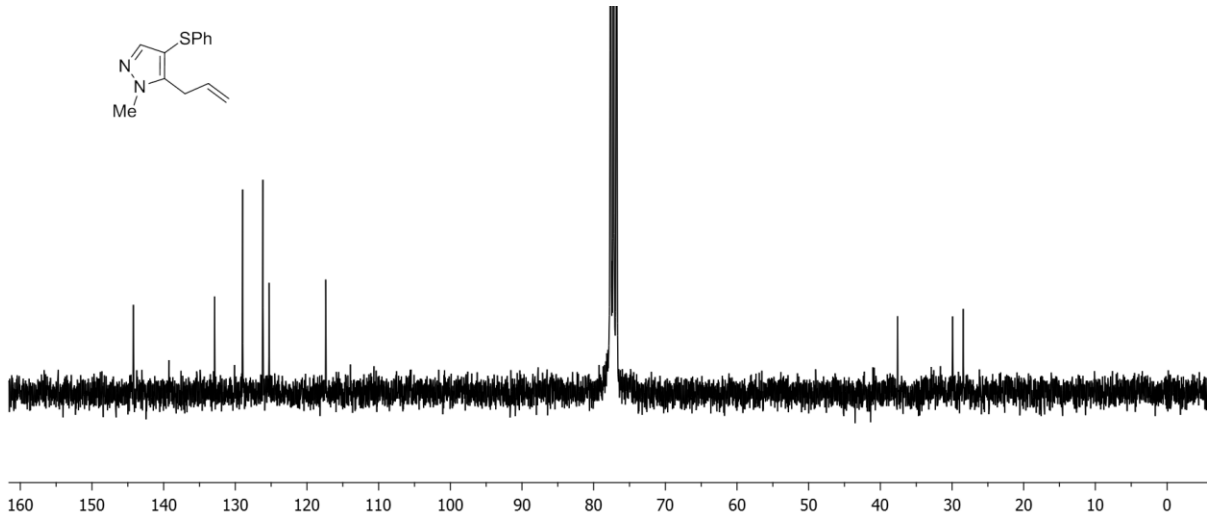
$^{1}$H NMR (300 MHz, $CDCl_3$)

Compound **2a**



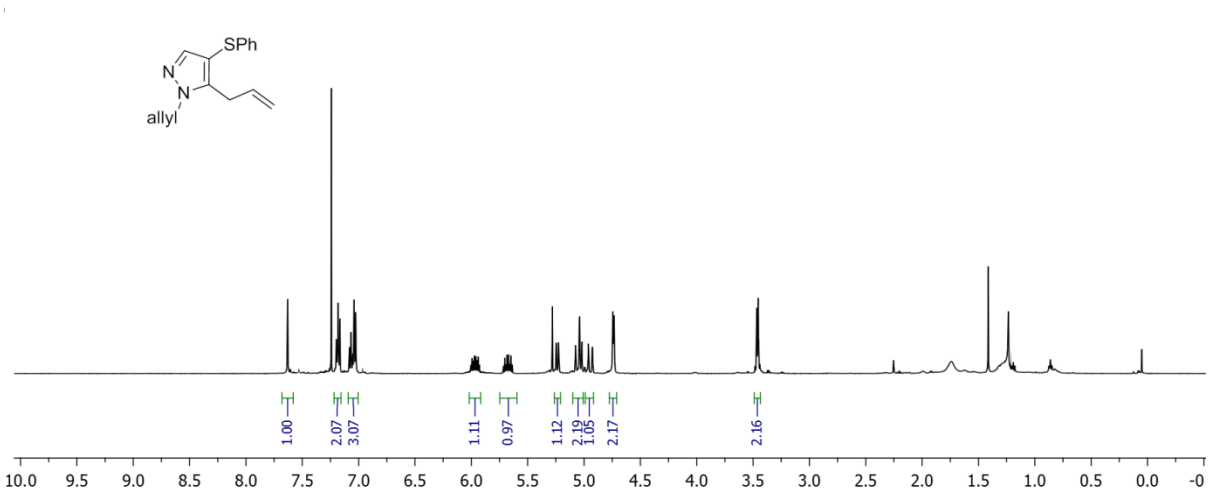

$^{13}$C NMR (75 MHz, $CDCl_3$)

Compound **2a**



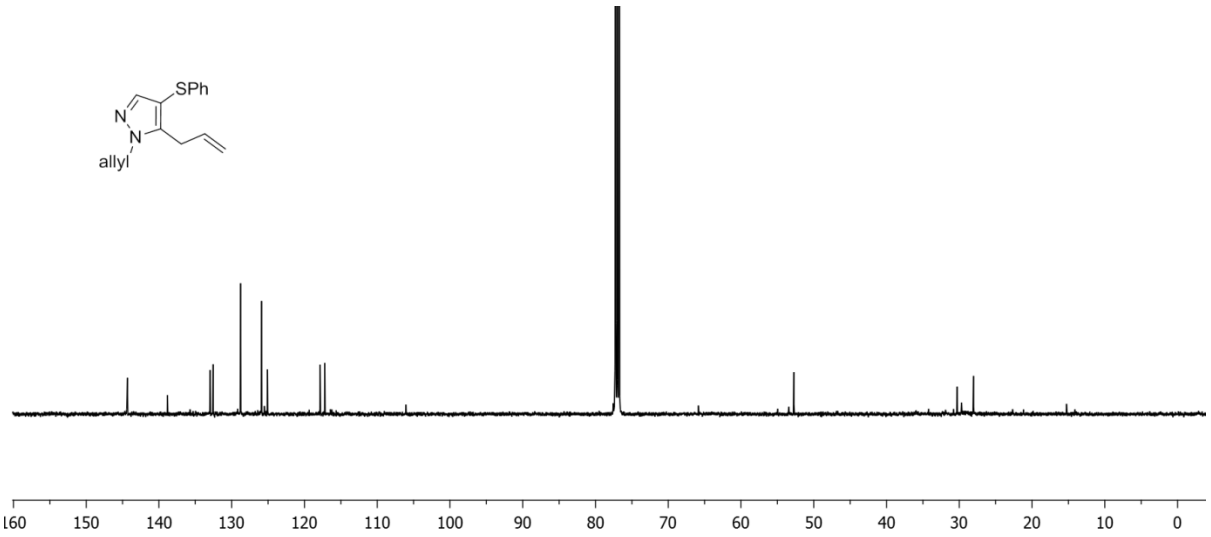
$^{1}$H NMR (500 MHz, $CDCl_3$)

Compound **2i**



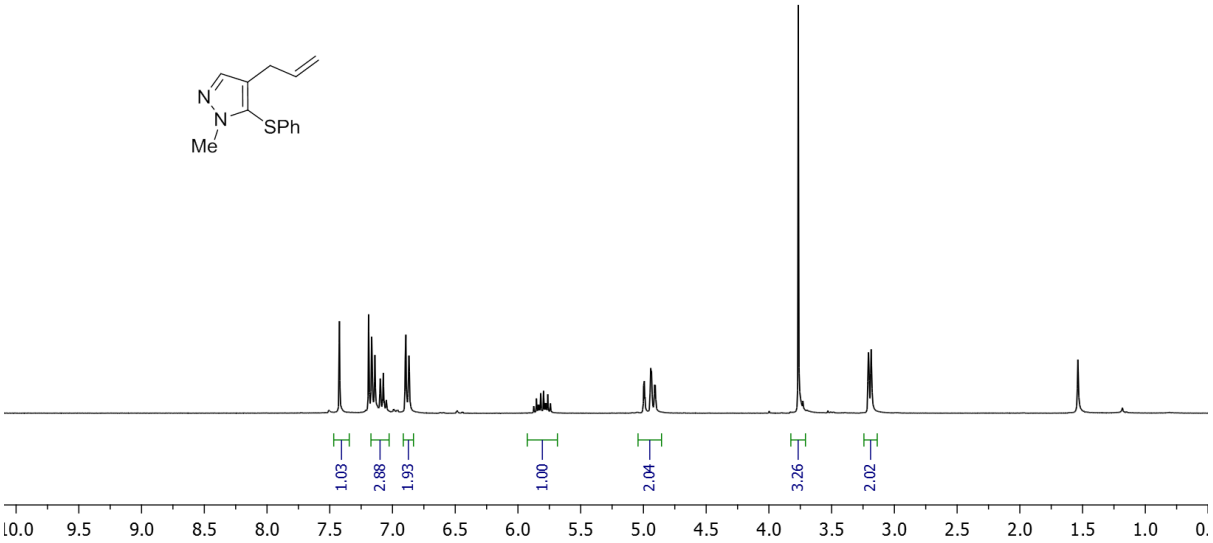

$^{13}$C NMR (125 MHz, $CDCl_3$)

Compound **2i**



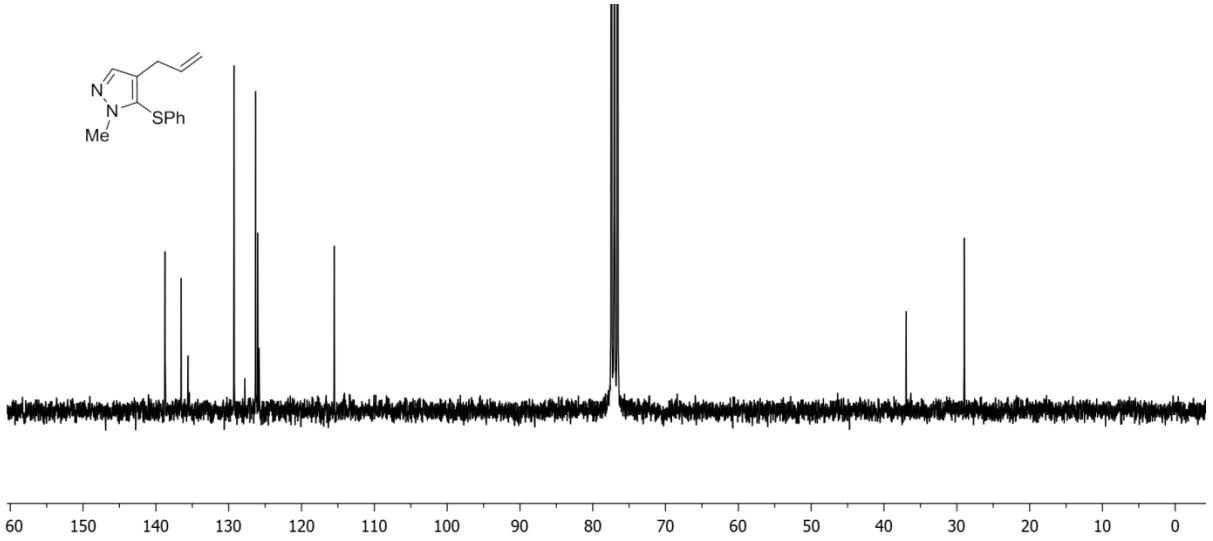
$^{1}$H NMR (300 MHz, $CDCl_3$)

Compound **2j**



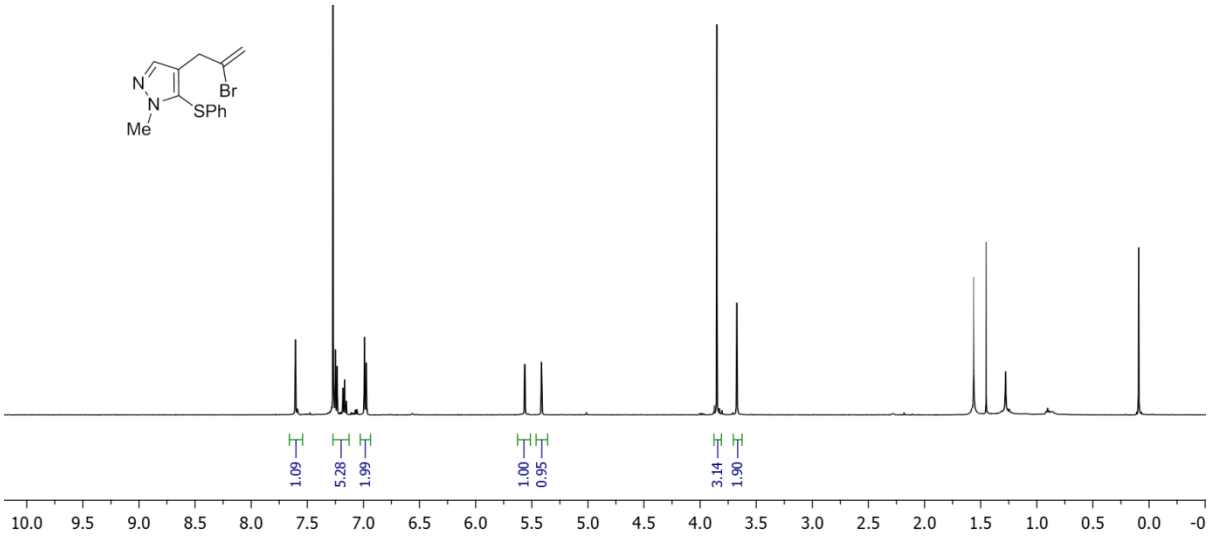

$^{13}$C NMR (75 MHz, $CDCl_3$)

Compound **2j**



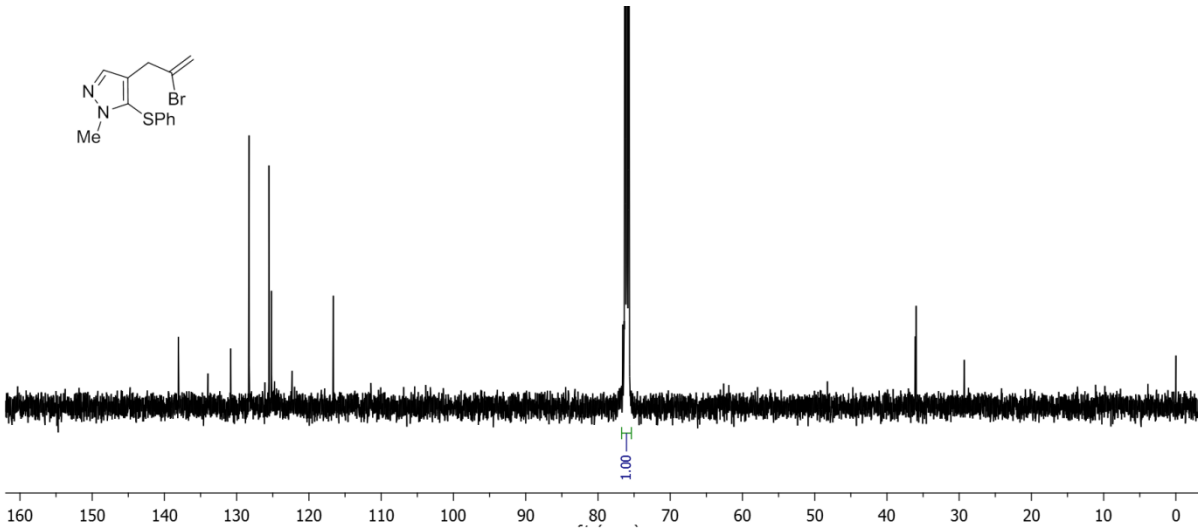
$^{1}$H NMR (500 MHz, $CDCl_3$)

Compound **2k**



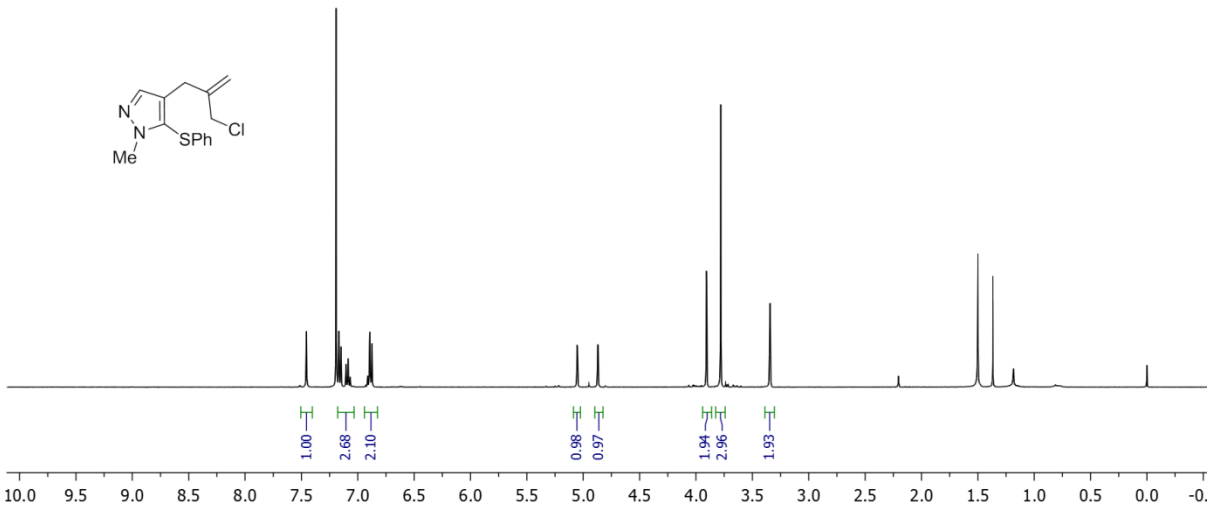

$^{13}$C NMR (125 MHz, $CDCl_3$)

Compound **2k**



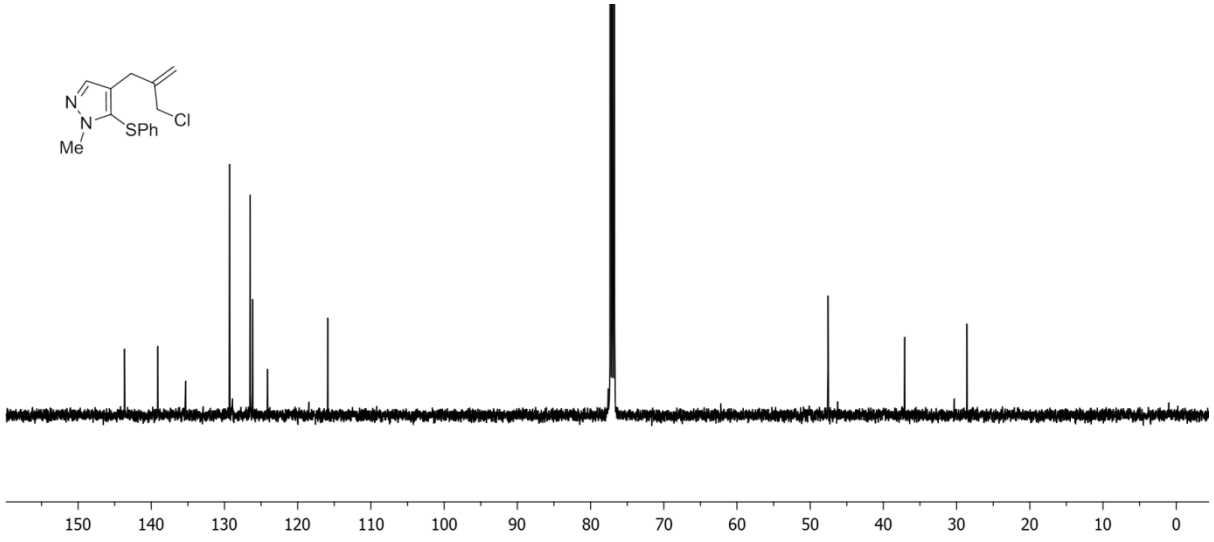
$^{1}$H NMR (400 MHz, $CDCl_3$)

Compound **2l**



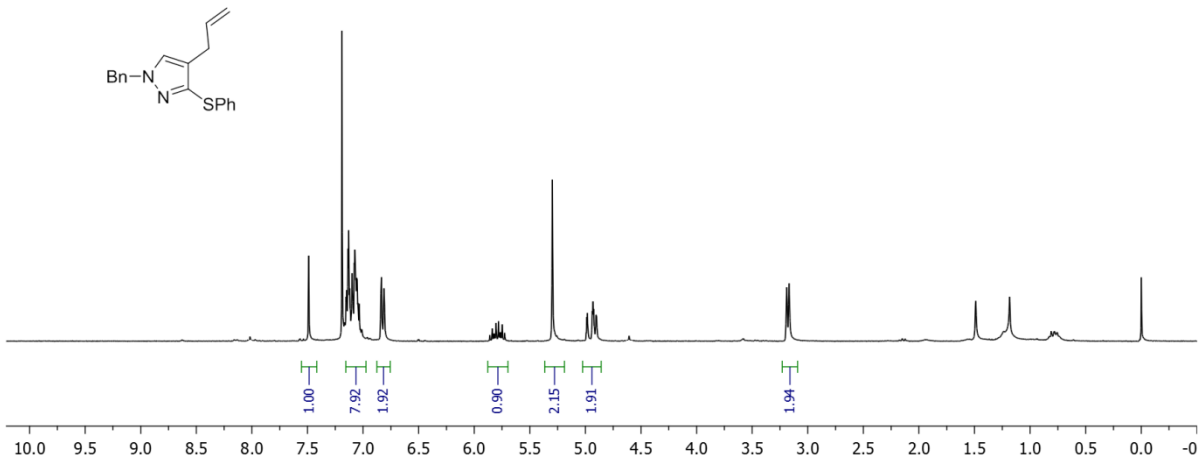

$^{13}$C NMR (125 MHz, $CDCl_3$)

Compound **2l**



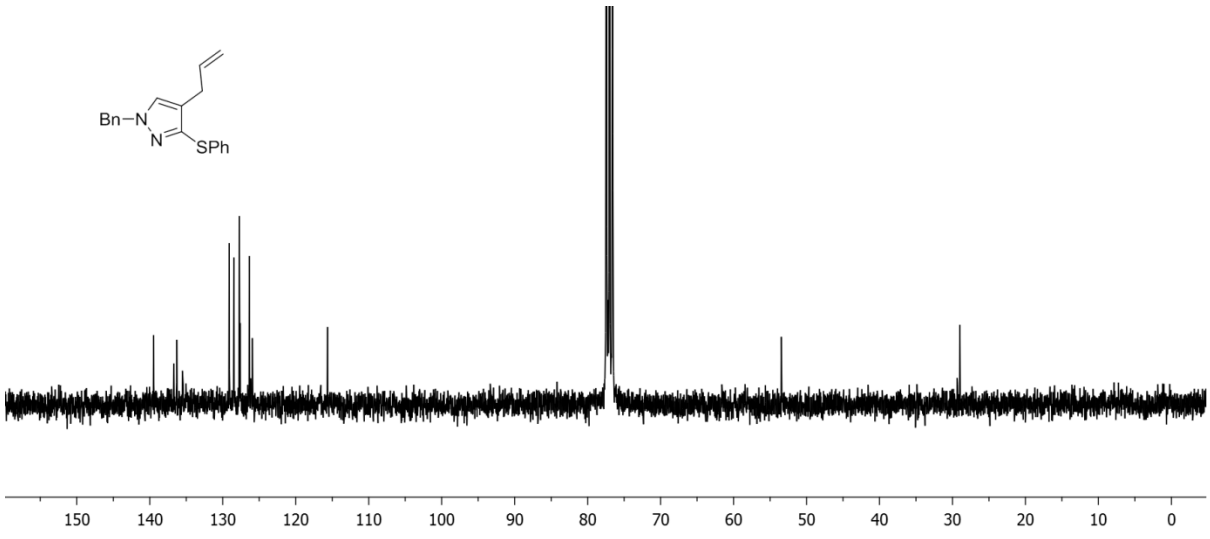
$^{1}$H NMR (300 MHz, $CDCl_3$)

Compound **2m**



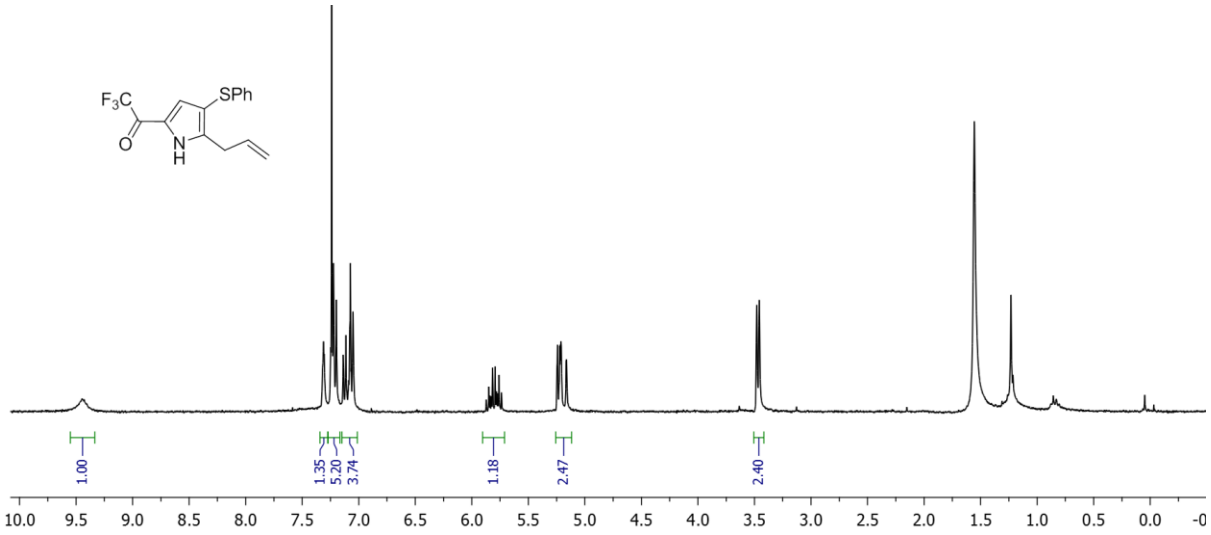

$^{13}$C NMR (75 MHz, $CDCl_3$)

Compound **2m**



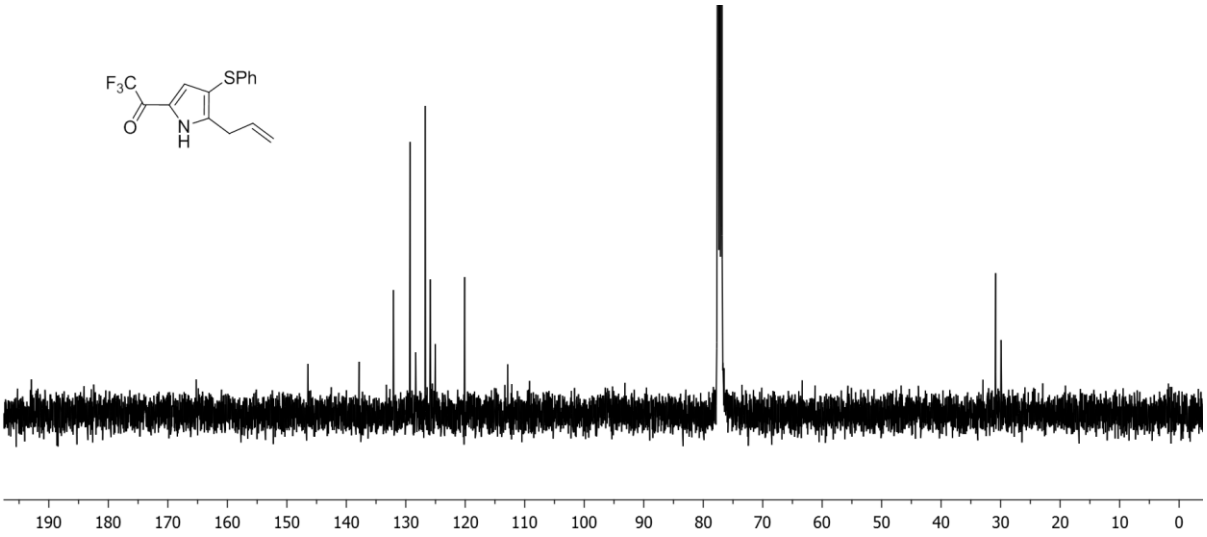
$^{1}$H NMR (300 MHz, $CDCl_3$)

Compound **7a**



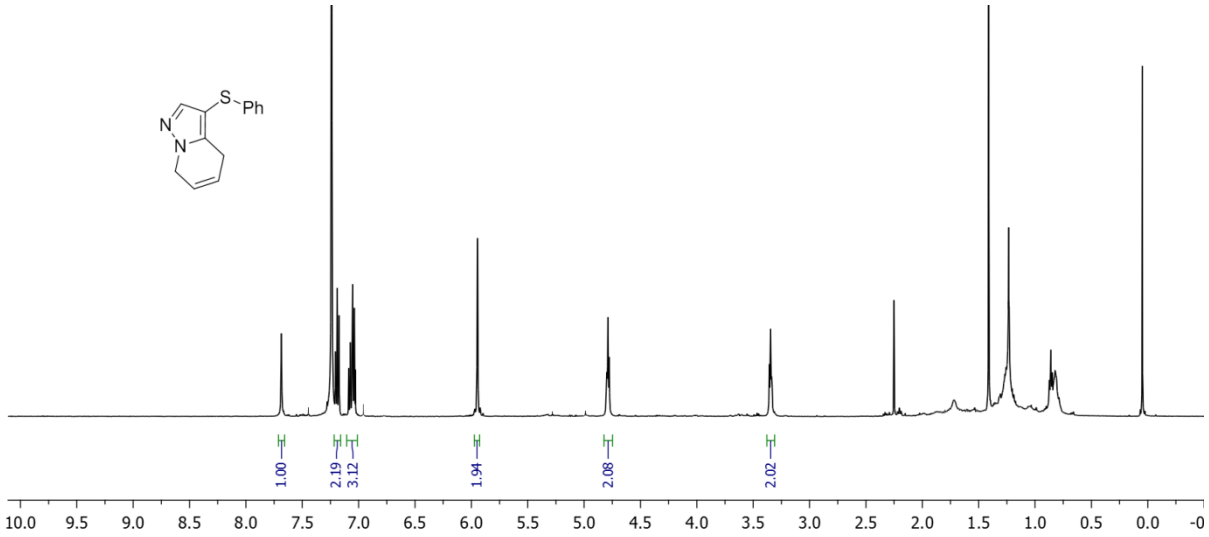

$^{13}$C NMR (100 MHz, $CDCl_3$)

Compound **7a**



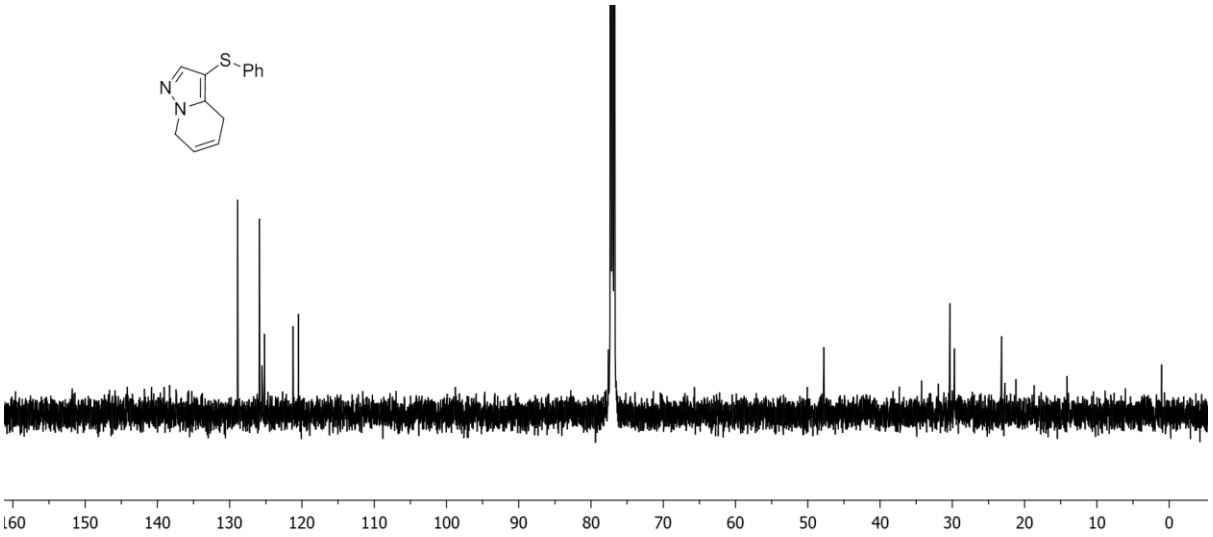
$^{1}$H NMR (500 MHz, $CDCl_3$)

Compound **7b**



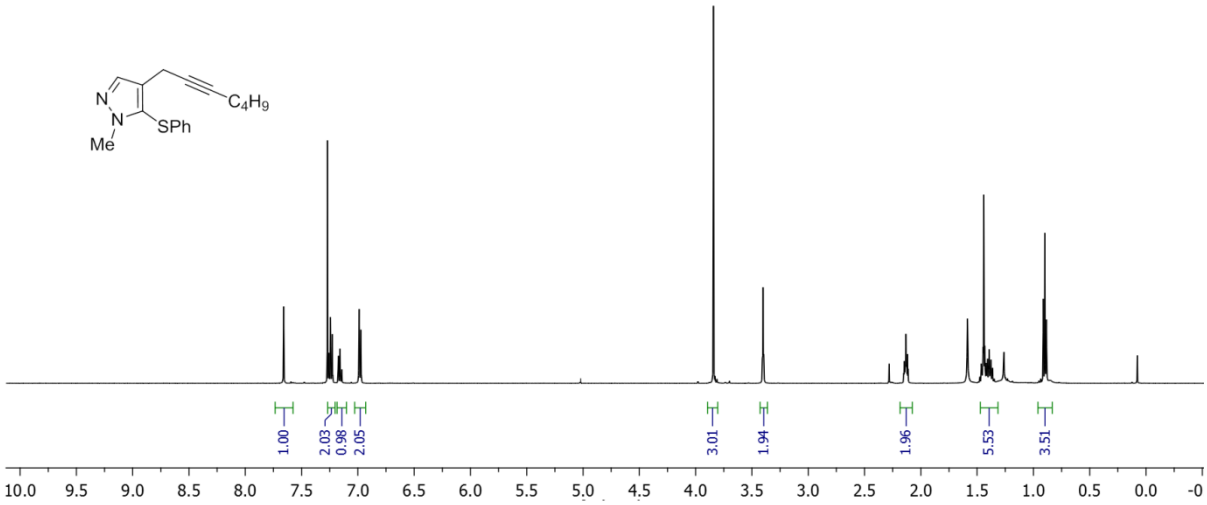

$^{13}$C NMR (125 MHz, $CDCl_3$)

Compound **7b**



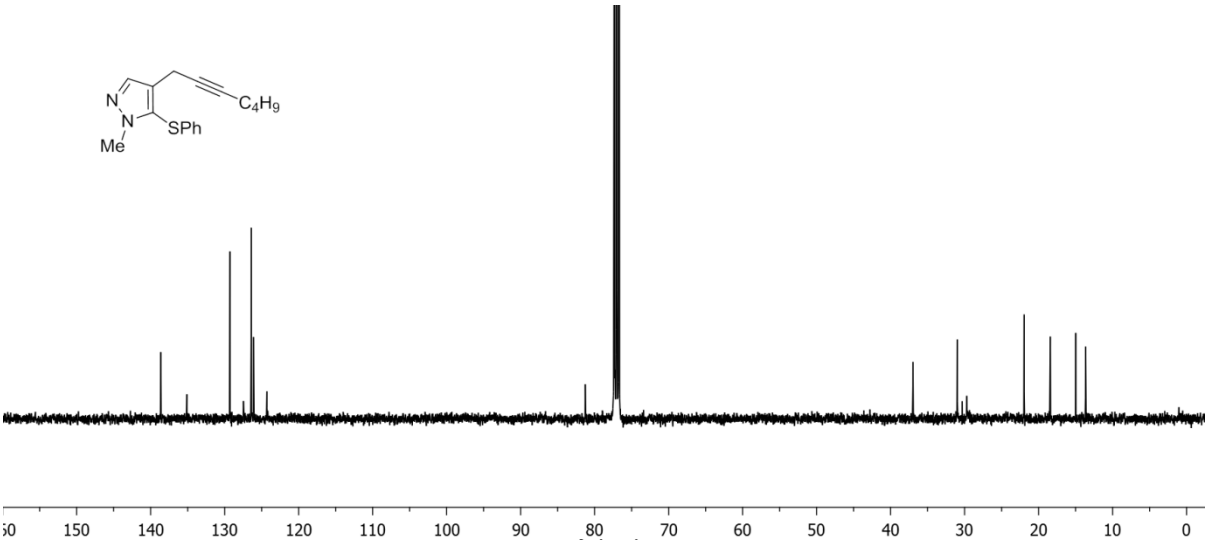
$^{1}$H NMR (500 MHz, $CDCl_3$)

Compound **8a**



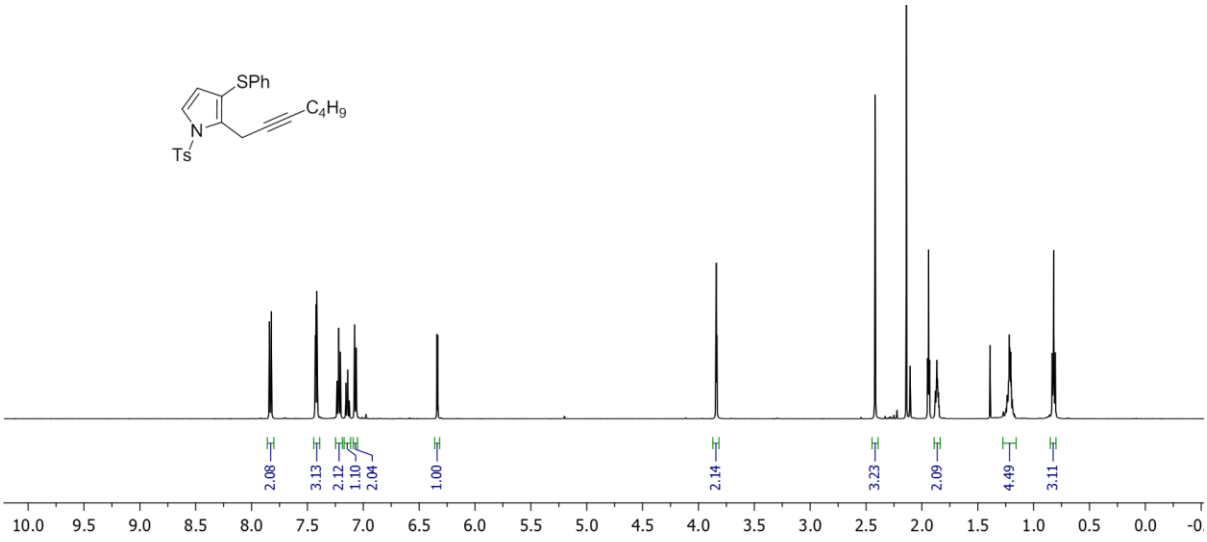

$^{13}$C NMR (125 MHz, $CDCl_3$)

Compound **8a**



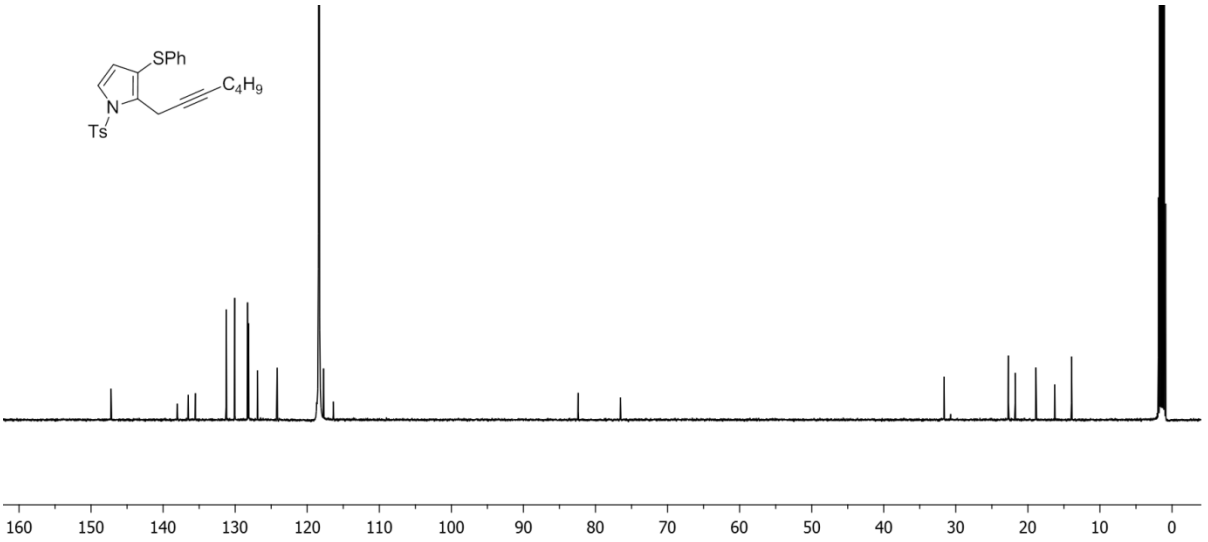
$^{1}$H NMR (500 MHz, $CD_3CN$)

Compound **8b**



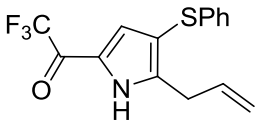

$^{13}$C NMR (125 MHz, $CD_3CN$)

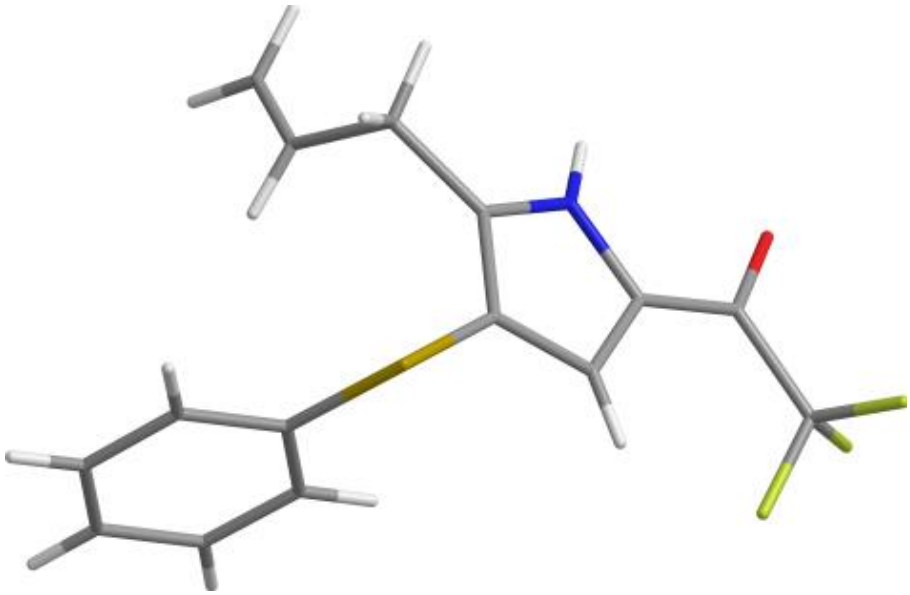
Compound **8b**



**X-ray crystal structure of 7a:**

CCDC 941977



**References:**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2. Thompson, A.; Garabatos-Perera, J. R.; Gillis, H. M. *Can. J. Chem.* **2008**, *86*, 676.
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