Supporting Information for

Modular Approach to Non-aromatic and Aromatic Pyrroles through Gold-catalyzed [3+2] Cycloaddition of 2*H*-Azirines and Ynamides

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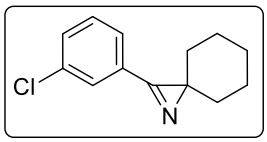
1. General Remarks

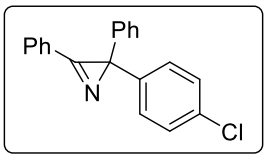
NMR spectra were recorded at ambient temperature with a Bruker Avance III 400 instrument at 400.13 MHz (^{1}H NMR) and 100.61 MHz (^{13}C NMR) in $CDCl_3$, CD_2Cl_2 and DMSO-d_6. Chemical shifts (δ) are given in ppm relative to resonances of the solvents (^{1}H: δ = 7.26 for residual $CHCl_3$ peak, δ = 5.32 for residual CH_2Cl_2 peak, δ = 2.50 for residual DMSO peak; ^{13}C: δ = 77.2 for $CDCl_3$ peak, δ = 54.0 for CD_2Cl_2 peak, δ = 39.5 for DMSO-d_6). Mass-spectra were recorded on Bruker MicroTOF (ESI) and Bruker maXis HRMS-ESI-QTOF instruments. Chromatographic separation was carried out on Macherey−Nagel silica gel 60 M (0.04−0.063 mm). Analytical TLC was performed on unmodified Merck ready-to-use plates (TLC silica gel 60 F254); detection was achieved with a UV lamp. Melting points were measured with Stuart smp30 apparatus. Gold complexes ($Ph_3PAuNTf_2$,[1] $IPrAuNTf_2$,[2] $PicAuCl_2$[3]), known 2*H*-azirines (**1a**,[4] **1c**,**h**,[5] **1d**,[6] **1f**,**g**,[7] **4**[8]) and known ynamides (**2a**,**ag**,[9] **2b**,**e**,**f**,**i**,[10] **2c,n,v**,[11] **2g**,**t**,[12] **2k**,[13] **2l**,[14] **2m**,[15] **2q**,**r**,[16] **2s**[17], **2u**[18]) were prepared by the literature procedures. Starting bromoethynes[12] and 1,1-dibromo-1-alkenes[19] were synthesized according to the published protocols. The solvents were purified using standard techniques and stored over activated 4 Å molecular sieves before use. Other chemicals were purchased from commercial suppliers and were used as received.

2. Experimental Procedures and Characterization Data

2.1. Synthesis of Starting 2*H*-Azirines 1

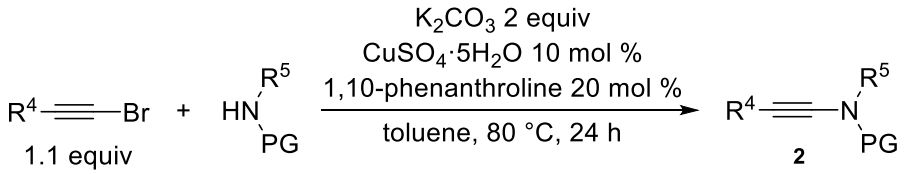


Azirine **1b** (0.20 g, 20%) was prepared from (3-chlorophenyl)(cyclohexyl)methanone (1.0 g, 4.5 mmol) and 1,1-dimethylhydrazine according to the literature procedure.[5] Eluent for chromatography EtOAc – hexane, 1:10. Pale yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (t, J = 1.9 Hz, 1H, Ar), 7.72 (dd, J = 7.4, 1.6 Hz, 1H, Ar), 7.53 (dt, J = 8.1, 1.7 Hz, 1H, Ar), 7.50–7.44 (m, 1H, Ar), 1.96–1.83 (m, 2H, CH), 1.67–1.52 (m, 8H, CH); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.9, 135.3, 132.6, 130.6, 128.9, 128.0, 127.0, 41.4, 35.5, 26.6, 26.1; HRMS (ESI): *m/z* $[M + H]^+$ calcd. for $C_{13}H_{15}ClN^+$: 220.0888; found 220.0887.

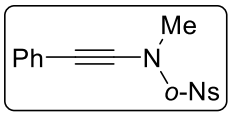


Azirine **1e** (0.78 g, 16%) was prepared from 2-(4-chlorophenyl)-1,2-diphenylethan-1-one (4.88 g, 16 mmol) and hydroxylamine hydrochloride according to the literature procedure.[20] Eluent for chromatography EtOAc – hexane, 1:20. Pale yellow solid, mp 78–80 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dt, J = 6.8, 1.5 Hz, 2H, Ar), 7.64–7.54 (m, 3H, Ar), 7.33–7.25 (m, 10H, Ar); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 141.2, 140.4, 133.5, 133.1, 129.9, 129.6, 129.6, 128.6, 128.6, 128.3, 127.5, 123.9, 44.3; HRMS (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{20}H_{14}ClNNa^+$: 326.0707; found 326.0707.

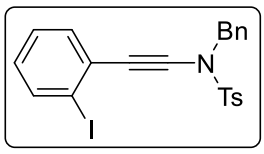
2.2. Synthesis of Starting Ynamides 2 from Bromoethynes



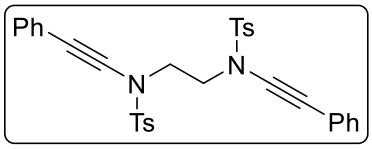
A 50 mL round-bottom flask was charged with amide (1.0 mmol), K_2CO_3 (277 mg, 2.0 mmol, 2.0 equiv), 1,10-phenanthroline monohydrate (39.6 mg, 0.2 mmol, 20 mol %) and $CuSO_4 \cdot 5H_2O$ (25.0 mg, 0.1 mmol, 10 mol %). The flask was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. Dry and degassed toluene (10 mL) and bromoethyne (1.1 mmol, 1.1 equiv) were next added and the brown suspension was heated at 80 °C for 24 h with stirring. After completion, all volatile components were removed in vacuo and the residue was purified by silica gel chromatography eluting with hexane/EtOAc to afford ynamides **2**.



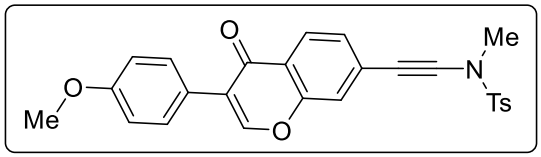
***N*-Methyl-2-nitro-*N*-(phenylethynyl)benzenesulfonamide (2d)**: orange solid (260 mg, 82%); mp 82.0–84.0 °C (DCM); R_f 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (dd, J = 7.7, 1.5 Hz, 1H, Ar), 7.82–7.70 (m, 3H, Ar), 7.38–7.33 (m, 2H, Ar), 7.32–7.27 (m, 3H, Ar), 3.40 (s, 3H, NMe); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.2, 134.9, 132.1, 131.9, 131.6, 130.2, 128.5, 128.4, 124.5, 122.3, 82.4, 70.4, 39.9; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{15}H_{13}N_2O_4S^+$: 317.0591; found: 317.0596.



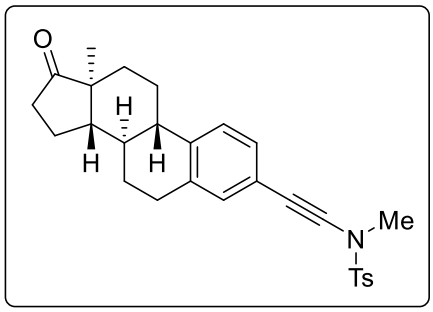
***N*-Benzyl-*N*-((2-iodophenyl)ethynyl)-4-methylbenzenesulfonamide (2j)**: yellowish solid (434 mg, 89%); mp 64.0–66.0 °C (DCM); R_f 0.55 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.3 Hz, 2H, Ar), 7.75 (d, J = 7.9 Hz, 2H, Ar), 7.44–7.39 (m, 2H, Ar), 7.35–7.29 (m, 5H, Ar), 7.24–7.19 (m, 2H, Ar), 6.93–6.88 (m, 1H, Ar), 4.67 (s, 2H, NCH_2), 2.43 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.8, 138.5, 134.8, 134.4, 132.0, 129.9, 129.6, 129.0, 128.7, 128.6, 128.4, 127.9, 127.7, 99.6, 86.5, 73.8, 55.9, 21.7; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{22}H_{19}INO_2S^+$: 488.0176; found: 488.0184.



***N*,*N*'-(Ethane-1,2-diyl)bis(4-methyl-*N*-(phenylethynyl)benzenesulfonamide) (2w)**: brown oil (239 mg, 42%); R_f 0.50 (hexane/EtOAc 2:1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 4H, Ar), 7.36–7.31 (m, 8H, Ar), 7.30–7.25 (m, 6H, Ar), 3.77 (s, 4H, $2NCH_2$), 2.42 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.2, 134.3, 131.6, 130.1, 128.4, 128.1, 128.0, 122.7, 81.9, 71.3, 49.8, 21.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{32}H_{29}N_2O_4S_2^+$: 569.1564; found: 569.1545.

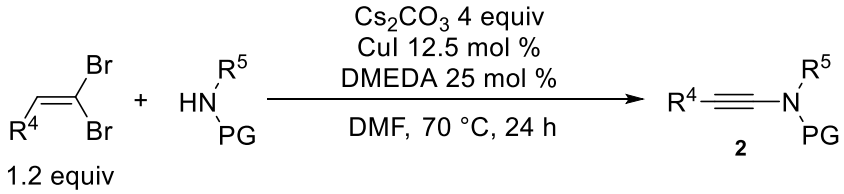


***N*-((3-(4-Methoxyphenyl)-4-oxo-4*H*-chromen-7-yl)ethynyl)-*N*,4-dimethylbenzenesulfonamide (2x)**: colorless solid (400 mg, 87%); mp 155.0–156.0 °C (hexane/EtOAc); R_f 0.25 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.46 (s, 1H, Ar), 8.07 (d, J = 8.3 Hz, 1H, Ar), 7.89 (d, J = 8.3 Hz, 2H, Ar), 7.61 (d, J = 1.2 Hz, 1H, Ar), 7.57–7.50 (m, 4H, Ar), 7.41 (dd, J = 8.3, 1.4 Hz, 1H, CH), 6.99 (d, J = 8.8 Hz, 2H, Ar), 3.78 (s, 3H, OMe), 3.19 (s, 3H, NMe), 2.43 (s, 3H, Me); **^{13}C NMR** (101 MHz, DMSO-d_6) δ 174.8, 159.2, 155.5, 154.1, 145.6, 132.3, 130.4, 130.1, 127.8, 127.7, 127.3, 126.0, 123.9, 123.8, 122.8, 119.5, 113.7, 88.4, 68.3, 55.2, 39.2, 21.2; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{26}H_{22}NO_5S^+$: 460.1213; found: 460.1219.

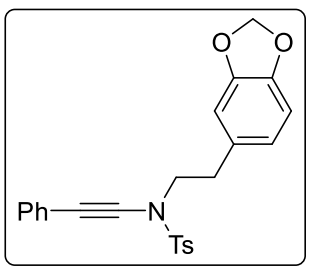


***N*,4-Dimethyl-*N*-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)ethynyl)benzenesulfonamide (2y)**: colorless solid (323 mg, 70%); mp 166.0–168.0 °C (hexane/EtOAc); R_f 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H, Ar), 7.36 (d, J = 8.1 Hz, 2H, Ar), 7.21 (d, J = 8.0 Hz, 1H, Ar), 7.13 (d, J = 8.8 Hz, 2H, Ar), 3.13 (s, 3H, NMe), 2.87 (dd, J = 8.8, 4.1 Hz, 2H, CH_2), 2.55–2.37 (m, 5H, CH), 2.34–2.24 (m, 1H, CH), 2.19–1.94 (m, 4H, CH), 1.73–1.34 (m, 7H, CH), 0.91 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.7, 144.8, 140.0, 136.7, 133.5, 132.1, 129.9, 128.9, 128.0, 125.4, 120.1, 83.4, 69.1, 50.6, 48.1, 44.6, 39.5, 38.1, 36.0, 31.7, 29.2, 26.5, 25.7, 21.8, 21.7, 14.0; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{28}H_{32}NOS^+$: 462.2097; found: 452.2078.

2.3. Synthesis of Starting Ynamides 2 from 1,1-Dibromo-1-alkenes

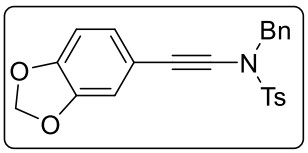


A 50 mL round-bottom flask was charged with amide (1.0 mmol), 1,1-dibromo-1-alkene (1.2 mmol, 1.2 equiv.), Cs_2CO_3 (1.30 g, 4.0 mmol, 4.0 equiv), and copper(I) iodide (24 mg, 0.125 mmol, 12.5 mol %). The flask was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. Dry and degassed DMF (5 mL) and *N*,*N*'- dimethylethylenediamine (22 mg, 0.25 mmol, 25 mol %) were next added and the blue or green suspension was heated at 70 °C for 24 h with stirring. After completion, all volatile components were removed in vacuo and the residue was purified by silica gel chromatography eluting with hexane/EtOAc to afford ynamides **2**.

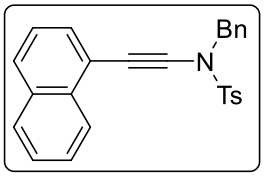


***N*-(2-(Benzo[*d*][1,3]dioxol-5-yl)ethyl)-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (2h)**: yellowish solid (377 mg, 90%); mp 84.0–86.0 °C (DCM); R_f 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 6.8 Hz, 2H, Ar), 7.44–7.38 (m, 2H, Ar), 7.35–7.30 (m, 5H, Ar), 6.74–6.61 (m, 3H, Ar), 5.90 (s, 2H, CH_2), 3.68–3.61 (m, 2H, NCH_2), 2.93 (t, J = 7.3 Hz, 2H, CH_2), 2.45 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 146.5, 144.7, 134.7, 131.5, 131.3, 129.8, 128.4,

128.0, 127.7, 122.9, 122.0, 109.4, 108.4, 101.0, 82.3, 71.5, 53.1, 34.3, 21.7; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{24}H_{22}NO_4S^+$: 420.1265; found: 420.1253.

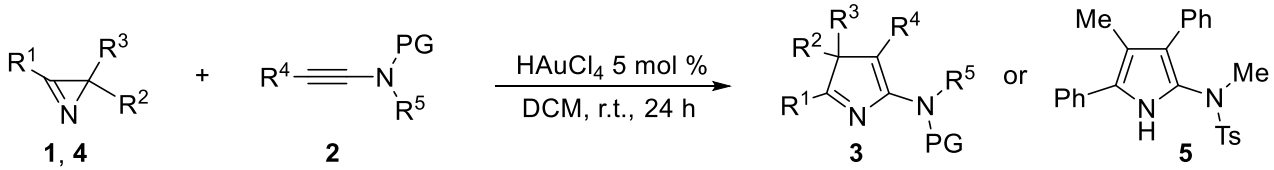


***N*-(Benzo[*d*][1,3]dioxol-5-ylethynyl)-*N*-benzyl-4-methylbenzenesulfonamide (2o)**[11]: yellowish solid (304 mg, 75%); mp 103.0–105.0 °C (DCM); R_f 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.3 Hz, 2H, Ar), 7.35–7.28 (m, 7H, Ar), 6.78 (dd, J = 8.1, 1.5 Hz, 1H, Ar), 6.71–6.67 (m, 2H, Ar), 5.93 (s, 2H, CH_2), 4.56 (s, 2H, NCH_2), 2.45 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.8, 147.4, 144.7, 134.9, 134.7, 129.9, 129.0, 128.7, 128.4, 127.9, 126.3, 116.0, 111.8, 108.5, 101.4, 81.1, 71.3, 55.9, 21.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{23}H_{20}NO_4S^+$: 406.1108; found: 406.1119.

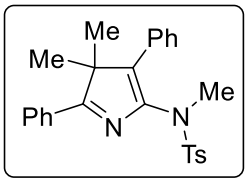


***N*-Benzyl-4-methyl-*N*-(naphthalen-1-ylethynyl)benzenesulfonamide (2p)**: yellowish solid (210 mg, 51%); mp 93.5–95.5 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 8.3 Hz, 2H, Ar), 7.85 (d, J = 8.2 Hz, 1H, Ar), 7.80 (d, J = 7.8 Hz, 1H, Ar), 7.75 (d, J = 8.2 Hz, 1H, Ar), 7.50–7.41 (m, 5H, Ar), 7.39–7.32 (m, 6H, Ar), 4.71 (s, 2H, NCH_2), 2.45 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.9, 134.8, 134.6, 133.2, 133.1, 130.0, 129.4, 129.2, 128.8, 128.6, 128.2, 128.1, 128.0, 126.6, 126.4, 126.3, 125.3, 120.7, 87.3, 70.2, 55.8, 21.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{26}H_{22}NO_2S^+$: 412.1366; found: 412.1372.

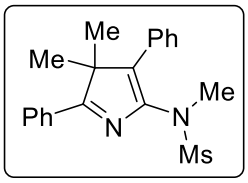
2.4. General Procedure for the Synthesis of 3*H*-Pyrroles 3 and 1*H*-Pyrrole 5



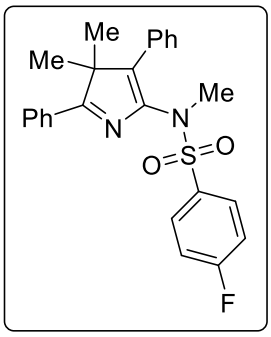
$HAuCl_4$ (3.4 mg, 10.0 μmol, 5 mol %) was added to the solution of 2*H*-azirine (**1** or **4**, 0.24 mmol, 1.2 equiv) and ynamide (**2**, 0.2 mmol) in DCM (0.5 mL). The resulting mixture was stirred at room temperature for 24 h. After completion, all volatile components were removed in vacuum and the residue was purified by silica gel column chromatography eluting with hexane/EtOAc to afford products **3** or **5**.



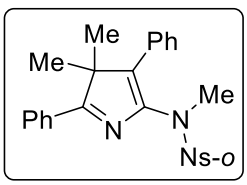
***N*-(3,3-Dimethyl-2,4-diphenyl-3*H*-pyrrol-5-yl)-*N*,4-dimethylbenzenesulfonamide (3a)**: colorless solid (79.2 mg, 92%); mp 110.0–112.0 °C (DCM); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 6.6, 3.2 Hz, 2H, Ar), 7.79 (d, J = 8.3 Hz, 2H, Ar), 7.48–7.33 (m, 8H, Ar), 7.29 (d, J = 8.1 Hz, 2H, Ar), 3.05 (s, 3H, NMe), 2.45 (s, 3H, Me), 1.51 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.6, 145.0, 143.4, 142.1, 136.3, 132.9, 132.7, 130.4, 129.33, 129.30, 128.7, 128.6, 128.5, 128.1, 128.0, 57.7, 37.0, 22.6, 21.7; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{26}H_{27}N_2O_2S^+$: 431.1788; found: 431.1777.



***N*-(3,3-Dimethyl-2,4-diphenyl-3*H*-pyrrol-5-yl)-*N*-methylmethanesulfonamide (3b)**: colorless solid (69.5 mg, 98%); mp 145.0–146.5 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 6.5, 2.9 Hz, 2H, Ar), 7.50–7.39 (m, 7H, Ar), 7.38–7.33 (m, 1H, Ar), 3.19 (s, 3H, Me), 3.11 (s, 3H, NMe), 1.52 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.2, 145.2, 140.9, 132.8, 132.4, 130.6, 129.3, 128.7, 128.6, 128.12, 128.07, 57.9, 39.1, 37.5, 22.7; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{20}H_{23}N_2O_2S^+$: 355.1475; found: 355.1479.

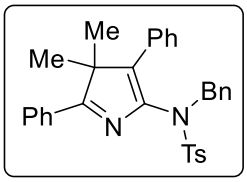


***N*-(3,3-Dimethyl-2,4-diphenyl-3*H*-pyrrol-5-yl)-4-fluoro-*N*-methylbenzenesulfonamide (3c)**: colorless solid (66.9 mg, 77%); mp 197.0–199.0 °C (DCM); R_f 0.35 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95–7.89 (m, 4H, Ar), 7.48–7.35 (m, 8H, Ar), 7.19–7.13 (m, 2H, Ar), 3.04 (s, 3H, NMe), 1.52 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.8, 165.3 (d, J_F = 254.0 Hz), 144.8, 142.5, 135.3 (d, J_F = 3.3 Hz), 132.8, 132.5, 131.44 (d, J_F = 9.3 Hz), 130.6, 129.3, 128.8, 128.6, 128.1, 128.0, 115.8 (d, J_F = 22.5 Hz), 57.8, 37.1, 22.6; ^{19}F NMR (376 MHz, CDCl3) δ –105.9; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{25}H_{24}FN_2O_2S^+$: 435.1538; found: 435.1537.

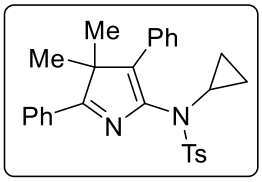


***N*-(3,3-Dimethyl-2,4-diphenyl-3*H*-pyrrol-5-yl)-*N*-methyl-2-nitrobenzenesulfonamide (3d)**: yellowish solid (81.2 mg, 88%); mp 144.0–146.0 °C (DCM); R_f 0.40 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (dd, J = 7.5, 1.7 Hz, 1H, Ar), 7.89 (dd, J = 7.7, 1.8 Hz, 2H, Ar), 7.70–7.63 (m, 2H, Ar), 7.62–7.58 (m, 1H, Ar), 7.47–7.30 (m, 8H, Ar), 3.21 (s, 3H, NMe), 1.51 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.0, 148.8, 144.0, 141.8, 133.7, 133.4, 132.8, 132.3, 132.0, 131.4, 130.6, 129.2, 128.7, 128.6, 128.2, 128.1,

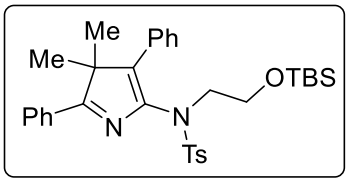
124.0, 58.2, 37.8, 22.5; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{25}H_{24}N_3O_4S^+$: 462.1483; found: 462.1481.



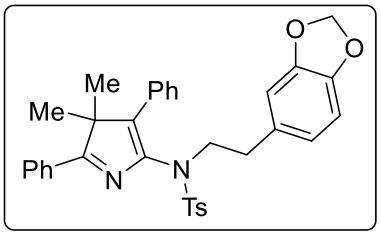
***N*-Benzyl-*N*-(3,3-dimethyl-2,4-diphenyl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3e)**: colorless solid (99.3 mg, 98%); mp 108.0–110.0 °C (DCM); R_f 0.40 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 6.6, 3.2 Hz, 2H, Ar), 7.80 (d, *J* = 8.3 Hz, 2H, Ar), 7.48–7.43 (m, 3H, Ar), 7.31 (d, *J* = 8.1 Hz, 2H, Ar), 7.29–7.20 (m, 4H, Ar), 7.18–7.13 (m, 2H, Ar), 7.02 (d, *J* = 7.1 Hz, 2H, Ar), 6.80 (dd, *J* = 8.1, 1.4 Hz, 2H, Ar), 4.52 (s, 2H, NCH_2), 2.48 (s, 3H, Me), 1.30 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.1, 146.3, 143.5, 141.9, 136.8, 135.6, 133.1, 132.1, 130.3, 129.9, 129.7, 129.4, 128.8, 128.6, 128.2, 128.0, 127.82, 127.81, 127.7, 57.9, 52.7, 22.0, 21.8; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{32}H_{31}N_2O_2S^+$: 507.2101; found: 507.2095.



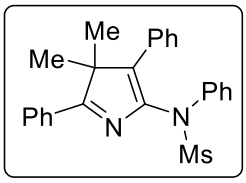
***N*-Cyclopropyl-*N*-(3,3-dimethyl-2,4-diphenyl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3f)**: colorless solid (74.0 mg, 81%); mp 148.0–149.5 °C (DCM); R_f 0.40 (hexane/EtOAc 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98–7.93 (m, 2H, Ar), 7.86 (d, *J* = 8.3 Hz, 2H, Ar), 7.47–7.43 (m, 3H, Ar), 7.42–7.40 (m, 4H, Ar), 7.39–7.34 (m, 1H, Ar), 7.30 (d, *J* = 8.1 Hz, 2H, Ar), 2.60 (tt, *J* = 6.7, 3.6 Hz, 1H, NCH), 2.46 (s, 3H, Me), 1.51 (s, 6H, 2Me), 0.68–0.55 (m, 4H, $2CH_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.4, 144.7, 143.5, 143.1, 136.7, 133.1, 132.7, 130.3, 129.6, 129.2, 129.1, 128.6, 128.3, 128.1, 127.9, 57.7, 30.9, 22.5, 21.8, 7.6; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{28}H_{29}N_2O_2S^+$: 457.1945; found: 457.1932.



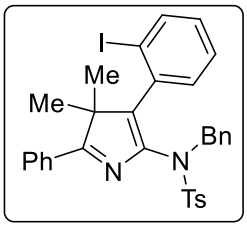
***N*-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-*N*-(3,3-dimethyl-2,4-diphenyl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3g)**: reddish oil (102.3 mg, 89%); R_f 0.60 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, *J* = 6.6, 3.0 Hz, 2H, Ar), 7.79 (d, *J* = 8.2 Hz, 2H, Ar), 7.50 (d, *J* = 7.0 Hz, 2H, Ar), 7.46–7.34 (m, 6H, Ar), 7.26 (d, *J* = 8.0 Hz, 2H, Ar), 3.59–3.54 (m, 2H, CH_2), 3.52–3.46 (m, 2H, CH_2), 2.44 (s, 3H, Me), 1.51 (s, 6H, 2Me), 0.79 (s, 9H, 3Me), –0.06 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.5, 144.2, 143.4, 143.2, 137.0, 132.9, 132.7, 130.4, 129.6, 129.3, 128.7, 128.7, 128.4, 128.1, 128.0, 61.2, 58.0, 50.9, 26.0, 22.6, 21.7, 18.4, –5.2; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{33}H_{43}N_2O_3SSi^+$: 575.2759; found: 575.2741.



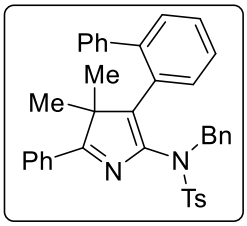
***N*-(2-(Benzo[*d*][1,3]dioxol-5-yl)ethyl)-*N*-(3,3-dimethyl-2,4-diphenyl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3h)**: colorless solid (101.6 mg, 90%); mp 109.5–111.5 °C (DCM); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 6.6, 3.0 Hz, 2H, Ar), 7.78 (d, J = 8.2 Hz, 2H, Ar), 7.49–7.36 (m, 8H, Ar), 7.26 (d, J = 8.1 Hz, 2H, Ar), 6.62 (d, J = 7.8 Hz, 1H, Ar), 6.49–6.44 (m, 2H, Ar), 5.86 (s, 2H, CH_2), 3.58–3.52 (m, 2H, NCH_2), 2.63–2.57 (m, 2H, CH_2), 2.44 (s, 3H, Me), 1.53 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.4, 147.6, 146.2, 144.5, 143.4, 142.8, 136.9, 133.0, 132.6, 132.3, 130.4, 129.6, 129.3, 128.72, 128.67, 128.4, 128.1, 128.0, 121.8, 109.4, 108.3, 100.9, 58.0, 50.5, 34.6, 22.6, 21.7; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{34}H_{33}N_2O_4S^+$: 565.2156; found: 565.2159.



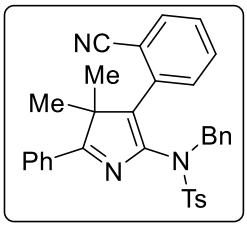
***N*-(3,3-Dimethyl-2,4-diphenyl-3*H*-pyrrol-5-yl)-*N*-phenylmethanesulfonamide (3i)**: colorless solid (75.0 mg, 90%); mp 176.0–178.0 °C (MeCN); R_f 0.65 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14–8.09 (m, 2H, Ar), 7.52–7.47 (m, 3H, Ar), 7.35–7.30 (m, 5H, Ar), 7.28–7.20 (m, 5H, Ar), 3.33 (s, 3H, Me), 1.49 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.9, 145.0, 142.9, 141.1, 132.9, 132.0, 130.7, 129.4, 129.2, 128.8, 128.4, 128.2, 128.0, 127.5, 127.4, 57.7, 39.7, 22.3; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{25}H_{25}N_2O_2S^+$: 417.1632; found: 417.1626.



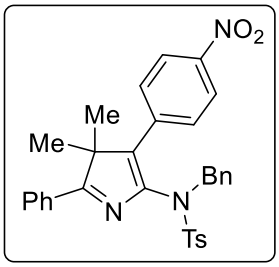
***N*-Benzyl-*N*-(4-(2-iodophenyl)-3,3-dimethyl-2-phenyl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3j)**: colorless oil (115.0 mg, 91%); R_f 0.40 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dd, J = 6.6, 3.1 Hz, 2H, Ar), 7.92 (d, J = 8.0 Hz, 1H, Ar), 7.71 (d, J = 8.2 Hz, 2H, Ar), 7.50–7.44 (m, 3H, Ar), 7.35–7.30 (m, 1H, Ar), 7.21 (d, J = 8.1 Hz, 2H, Ar), 7.17–7.03 (m, 6H, Ar), 6.96 (dd, J = 7.7, 1.5 Hz, 1H, Ar), 4.80 (d, J = 15.5 Hz, 1H, NCH), 4.61 (d, J = 15.5 Hz, 1H, NCH), 2.33 (s, 3H, Me), 1.53 (s, 3H, Me), 1.37 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.6, 144.4, 143.3, 141.8, 139.6, 137.6, 137.4, 136.7, 133.2, 132.5, 130.5, 129.5, 129.2, 128.9, 128.7 (×2), 128.2 (×2), 127.5, 127.4, 101.4, 59.8, 53.1, 24.0, 22.9, 21.7; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{32}H_{30}IN_2O_2S^+$: 633.1068; found: 633.1067.



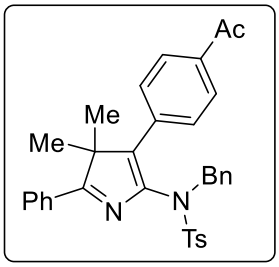
***N*-(4-([1,1'-Biphenyl]-2-yl)-3,3-dimethyl-2-phenyl-3*H*-pyrrol-5-yl)-*N*-benzyl-4-methylbenzenesulfonamide (3k)**: colorless solid (101.4 mg, 87%); mp 189.5–191.5 °C (MeCN); R_f 0.45 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 2H, Ar), 7.81 (dd, J = 7.3, 2.0 Hz, 2H, Ar), 7.46–7.36 (m, 5H, Ar), 7.35–7.32 (m, 2H, Ar), 7.30–7.22 (m, 3H, Ar), 7.19–7.11 (m, 6H, Ar), 7.09–7.05 (m, 2H, Ar), 6.83 (d, J = 7.7 Hz, 1H, Ar), 4.83 (d, J = 16.1 Hz, 1H, NCH), 4.72 (d, J = 16.1 Hz, 1H, NCH), 2.45 (s, 3H, Me), 1.12 (s, 3H, Me), 0.56 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.1, 145.2, 143.4, 142.7, 142.3, 141.3, 137.6, 136.7, 133.3, 132.7, 130.8, 130.7, 130.2, 129.8, 129.2, 129.1, 128.53, 128.52, 128.4, 128.3, 128.10, 128.07, 127.5, 127.01, 126.95, 59.9, 53.3, 24.8, 21.8, 21.2; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{38}H_{35}N_2O_2S^+$: 583.2414; found: 583.2409.



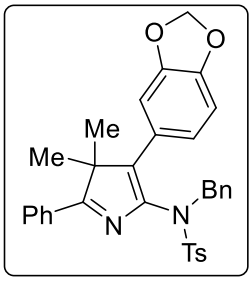
***N*-Benzyl-*N*-(4-(2-cyanophenyl)-3,3-dimethyl-2-phenyl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3l)**: yellowish solid (96.8 mg, 91%); mp 141.0–143.0 °C (DCM); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82–7.77 (m, 4H, Ar), 7.66–7.63 (m, 1H, Ar), 7.48–7.39 (m, 5H, Ar), 7.31–7.25 (m, 3H, Ar), 7.24–7.19 (m, 2H, Ar), 7.16 (d, J = 7.2 Hz, 2H, Ar), 6.45–6.42 (m, 1H, Ar), 4.83 (s, 2H, NCH_2), 2.46 (s, 3H, Me), 1.37 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.9, 144.8, 143.6, 142.0, 136.6, 136.2, 136.1, 133.1, 133.0, 132.1, 131.9, 130.7, 129.7, 129.5, 128.7, 128.6, 128.39, 128.36, 128.1, 127.9, 119.0, 115.3, 60.3, 53.0, 22.6, 21.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{33}H_{30}N_3O_2S^+$: 532.2054; found: 532.2049.



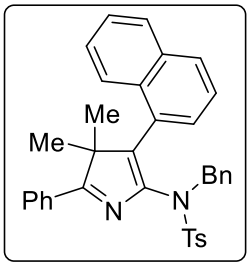
***N*-Benzyl-*N*-(3,3-dimethyl-4-(4-nitrophenyl)-2-phenyl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3m)**: yellowsih solid (108.1 mg, 98%); mp 196.0–198.0 °C (DCM); R_f 0.60 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.8 Hz, 2H, Ar), 7.92–7.87 (m, 2H, Ar), 7.80 (d, J = 8.2 Hz, 2H, Ar), 7.51–7.44 (m, 3H, Ar), 7.34 (d, J = 8.1 Hz, 2H, Ar), 7.30–7.24 (m, 1H, Ar), 7.22–7.16 (m, 2H, Ar), 7.08 (d, J = 7.2 Hz, 2H, Ar), 6.94 (d, J = 8.8 Hz, 2H, Ar), 4.55 (s, 2H, NCH_2), 2.49 (s, 3H, Me), 1.34 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.3, 147.3, 144.2, 143.9, 143.2, 139.4, 136.4, 135.4, 132.5, 130.9, 130.5, 130.1, 129.6, 128.8, 128.7, 128.4, 128.2, 128.1, 123.0, 58.3, 52.7, 22.2, 21.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{32}H_{30}N_3O_4S^+$: 552.1952; found: 552.1962.



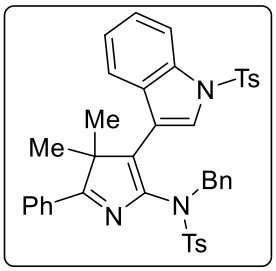
***N*-(4-(4-Acetylphenyl)-3,3-dimethyl-2-phenyl-3*H*-pyrrol-5-yl)-*N*-benzyl-4-methylbenzenesulfonamide (3n)**: colorless solid (98.8 mg, 90%); mp 161.5–163.5 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 7.5, 2.0 Hz, 2H, Ar), 7.84–7.79 (m, 4H, Ar), 7.49–7.43(m, 3H, Ar), 7.32 (d, J = 8.1 Hz, 2H, Ar), 7.26–7.22 (m, 1H, Ar), 7.19–7.14 (m, 2H, Ar), 7.05 (d, J = 7.2 Hz, 2H, Ar), 6.91 (d, J = 8.3 Hz, 2H, Ar), 4.54 (s, 2H, NCH_2), 2.62 (s, 3H, Me), 2.48 (s, 3H, Me), 1.31 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 198.1, 181.8, 145.2, 143.7, 142.6, 137.5, 136.6, 136.2, 135.4, 132.8, 130.6, 130.0, 129.8, 129.5, 128.72, 128.71, 128.3, 128.0 (×2), 127.8, 58.1, 52.7, 26.8, 22.1, 21.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{34}H_{33}N_2O_3S^+$: 549.2207; found: 549.2206.



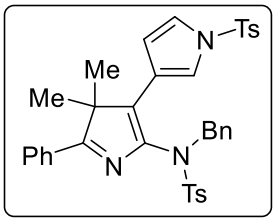
***N*-(4-(Benzo[*d*][1,3]dioxol-5-yl)-3,3-dimethyl-2-phenyl-3*H*-pyrrol-5-yl)-*N*-benzyl-4-methylbenzenesulfonamide (3o)**: colorless solid (107.9 mg, 98%); mp 118.0–120.0 °C (DCM); R_f 0.40 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89–7.86 (m, 2H, Ar), 7.82 (d, J = 8.1 Hz, 2H, Ar), 7.46–7.43 (m, 3H, Ar), 7.32 (d, J = 8.2 Hz, 2H, Ar), 7.25–7.14 (m, 3H, Ar), 7.06 (d, J = 7.3 Hz, 2H, Ar), 6.69 (d, J = 8.0 Hz, 1H, Ar), 6.28 (d, J = 8.0 Hz, 1H, Ar), 6.20 (s, 1H, Ar), 5.96 (s, 2H, CH_2), 4.53 (s, 2H, NCH_2), 2.48 (s, 3H, Me), 1.27 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.0, 147.2, 147.1, 146.1, 143.5, 142.0, 136.9, 135.7, 133.1, 130.3, 130.0, 129.4, 128.8, 128.7, 128.2, 128.0, 127.9, 125.6, 123.5, 110.2, 107.9, 101.1, 57.8, 52.7, 22.1, 21.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{33}H_{31}N_2O_4S^+$: 551.2000; found: 551.1998.



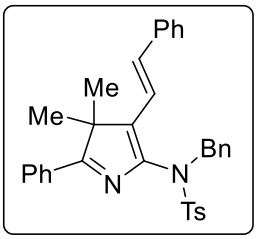
***N*-Benzyl-*N*-(3,3-dimethyl-4-(naphthalen-1-yl)-2-phenyl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3p)**: colorless solid (74.6 mg, 67%); mp 89.0–91.0 °C (DCM); R_f 0.70 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, J = 6.6, 3.0 Hz, 2H, Ar), 7.83 (d, J = 8.3 Hz, 2H, Ar), 7.74 (d, J = 8.2 Hz, 2H, Ar), 7.51–7.47 (m, 3H, Ar), 7.44–7.33 (m, 3H, Ar), 7.25–7.17 (m, 4H, Ar), 7.13–7.07 (m, 2H, Ar), 6.95 (d, J = 7.4 Hz, 2H, Ar), 6.72 (d, J = 7.0 Hz, 1H, Ar), 4.56–4.47 (m, 2H, NCH_2), 2.44 (s, 3H, Me), 1.36 (s, 3H, Me), 1.27 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.0, 144.2, 143.4, 142.1, 137.1, 136.0, 133.6, 133.3, 133.0, 130.4, 129.7, 129.5, 129.3, 128.8, 128.74, 128.70, 128.33, 128.29, 128.1, 127.9, 127.7, 127.1, 125.9, 125.7, 124.9, 59.6, 52.8, 23.2, 22.4, 21.7; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{36}H_{33}N_2O_2S^+$: 557.2258; found: 557.2259.



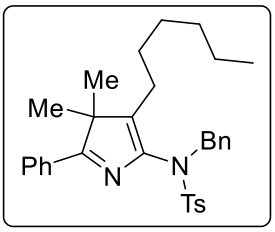
***N*-Benzyl-*N*-(3,3-dimethyl-2-phenyl-4-(1-tosyl-1*H*-indol-3-yl)-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3q)**: colorless solid (137.2 mg, 98%); mp 191.5–193.0 °C (DCM); R_f 0.35 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94–7.90 (m, 3H, Ar), 7.82 (d, J = 8.3 Hz, 2H, Ar), 7.77 (d, J = 8.2 Hz, 2H, Ar), 7.49–7.43 (m, 3H, Ar), 7.31–7.27 (m, 4H, Ar), 7.25–7.20 (m, 2H, Ar), 7.13–7.08 (m, 1H, Ar), 7.01–6.96 (m, 1H, Ar), 6.94–6.89 (m, 2H, Ar), 6.83 (d, J = 7.5 Hz, 2H, Ar), 6.72 (d, J = 7.9 Hz, 1H, Ar), 4.49 (s, 2H, NCH_2), 2.46 (s, 3H, Me), 2.34 (s, 3H, Me), 1.31 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.5, 145.0, 144.8, 143.6, 137.5, 136.8, 135.6, 135.3, 134.8, 133.1, 131.2, 130.6, 130.1, 129.4, 129.3, 128.7, 128.6, 128.2, 128.1, 127.9, 127.1, 126.8, 124.5, 123.5, 121.7, 113.8, 113.4, 58.5, 52.5, 22.5, 21.79, 21.77; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{41}H_{38}N_3O_4S_2^+$: 700.2299; found: 700.2289.



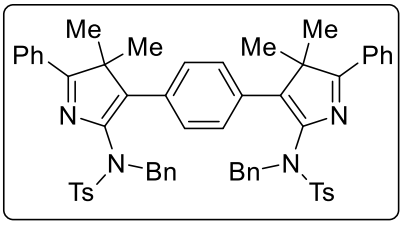
***N*-Benzyl-*N*-(4',4'-dimethyl-5'-phenyl-1-tosyl-1*H*,4'*H*-[3,3'-bipyrrol]-2'-yl)-4-methylbenzenesulfonamide (3r)**: brown solid (113.1 mg, 87%); mp 92.0–94.0 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.76 (m, 6H, Ar), 7.44–7.39 (m, 3H, Ar), 7.36–7.30 (m, 4H, Ar), 7.28–7.25(m, 1H, Ar), 7.08–6.99 (m, 4H, Ar), 6.98–6.92 (m, 2H, Ar), 6.69 (dd, J = 3.2, 1.5 Hz, 1H, Ar), 4.54 (s, 2H, NCH_2), 2.48 (s, 3H, Me), 2.42 (s, 3H, Me), 1.31 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.0, 145.2, 143.7, 141.1, 139.7, 136.3, 136.2, 135.0, 132.7, 130.2 (×2), 129.8, 129.4, 128.9, 128.7, 128.0, 127.8, 127.8, 127.1, 120.7, 119.4, 118.9, 114.2, 56.7, 53.2, 23.3, 21.82, 21.80; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{37}H_{36}N_3O_4S_2^+$: 650.2142; found: 650.2121.



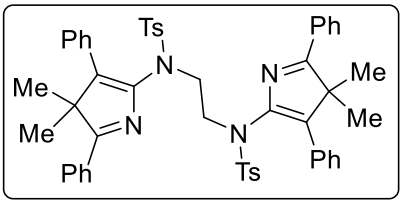
(*E*)-*N*-Benzyl-*N*-(3,3-dimethyl-2-phenyl-4-styryl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3s): yellow solid (78.8 mg, 74%); mp 131.5–133.5 °C (DCM); R_f 0.65 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.81 (m, 4H, Ar), 7.45–7.39 (m, 5H, Ar), 7.39–7.21 (m, 7H, Ar), 7.20–7.11 (m, 3H, Ar), 6.89 (d, J = 16.9 Hz, 1H, CH), 6.70 (d, J = 17.0 Hz, 1H, CH), 4.72 (s, 2H, NCH_2), 2.45 (s, 3H, Me), 1.44 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.6, 144.0, 143.9, 143.7, 137.9, 136.5, 135.8, 132.7, 130.3, 129.7, 129.54, 129.49, 128.7, 128.6, 128.5, 128.2, 127.91, 127.89, 127.8, 126.8, 119.2, 55.4, 53.2, 23.8, 21.7; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{34}H_{33}N_2O_2S^+$: 533.2258; found: 533.2268.



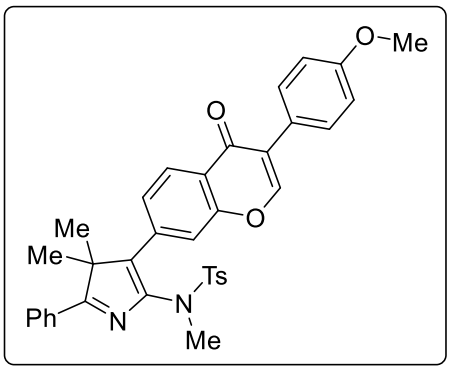
***N*-Benzyl-*N*-(4-hexyl-3,3-dimethyl-2-phenyl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3t)**: colorless oil (59.7 mg, 58%); R_f 0.50 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79–7.73 (m, 4H, Ar), 7.42–7.37 (m, 3H, Ar), 7.30 (d, J = 8.1 Hz, 2H, Ar), 7.27–7.23 (m, 2H, Ar), 7.21–7.19 (m, 3H, Ar), 4.60 (s, 2H, NCH_2), 2.46 (s, 3H, Me), 2.11–2.05 (m, 2H, CH_2), 1.29–1.24 (m, 2H, CH_2), 1.23 (s, 6H, 2Me), 1.19–1.13 (m, 4H, $2CH_2$), 1.10–1.03 (m, 2H, CH_2), 0.89 (t, J = 7.2 Hz, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.9, 148.3, 143.4, 141.0, 136.7, 136.1, 133.4, 130.1, 129.8, 129.4, 128.6, 128.5, 128.2, 127.9, 127.6, 57.1, 52.7, 31.8, 30.4, 27.9, 24.6, 22.8, 22.1, 21.7, 14.3; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{32}H_{39}N_2O_2S^+$: 515.2727; found: 515.2716.



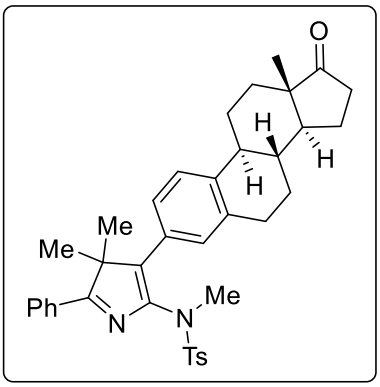
***N*,*N*'-(1,4-Phenylenebis(3,3-dimethyl-2-phenyl-3*H*-pyrrole-4,5-diyl))bis(*N*-benzyl-4-methylbenzenesulfonamide) (3v)**: yellowish solid (172.1 mg, 92%); mp 213.5–215.0 °C (DCM); R_f 0.55 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95–7.90 (m, 8H, Ar), 7.49–7.44 (m, 6H, Ar), 7.37 (d, J = 8.1 Hz, 4H, Ar), 7.28–7.18 (m, 6H, Ar), 7.04 (d, J = 6.7 Hz, 4H, Ar), 6.85 (s, 4H, Ar), 4.54 (s, 4H, $2NCH_2$), 2.51 (s, 6H, 2Me), 1.36 (s, 12H, 4Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.2, 146.0, 143.5, 142.1, 136.8, 135.3, 133.1, 131.3, 130.3, 129.8, 129.4, 129.0, 128.8, 128.6, 128.4, 128.02, 127.99, 57.9, 53.0, 22.3, 21.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{58}H_{55}N_4O_4S_2^+$: 935.3660; found: 935.3653.



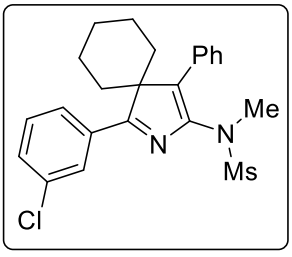
***N*,*N*'-(Ethane-1,2-diyl)bis(*N*-(3,3-dimethyl-2,4-diphenyl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide) (3w)**: gray solid (147.8 mg, 86%); mp 210.5–212.5 °C (DCM); R_f 0.55 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.84 (dd, J = 8.1, 1.4 Hz, 4H, Ar), 7.61 (d, J = 8.2 Hz, 4H, Ar), 7.48–7.35 (m, 12H, Ar), 7.30–7.26 (m, 4H, Ar), 7.22 (d, J = 8.0 Hz, 4H, Ar), 3.34 (s, 4H, $2NCH_2$), 2.42 (s, 3H, 2Me), 1.39 (s, 12H, 4Me); **^{13}C NMR** (101 MHz, CD_2Cl_2) δ 182.1, 145.3, 144.3, 143.2, 136.9, 133.2, 132.8, 130.9, 129.9, 129.8, 129.0, 128.9, 128.8, 128.5, 128.4, 58.4, 47.6, 22.6, 21.9; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{52}H_{51}N_4O_4S_2^+$: 859.3347; found: 859.3323.



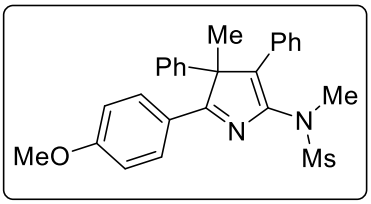
***N*-(4-(3-(4-Methoxyphenyl)-4-oxo-4*H*-chromen-7-yl)-3,3-dimethyl-2-phenyl-3*H*-pyrrol-5-yl)-*N*,4-dimethylbenzenesulfonamide (3x)**: yellow oil (117.3 mg, 95%); R_f 0.30 (DCM/MeOH 100:3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.3 Hz, 1H, Ar), 8.02 (s, 1H, Ar), 7.94–7.87 (m, 2H, Ar), 7.76 (d, J = 8.2 Hz, 2H, Ar), 7.67 (d, J = 1.3 Hz, 1H, Ar), 7.57–7.52 (m, 3H, Ar), 7.49–7.43 (m, 3H, Ar), 7.29 (d, J = 8.1 Hz, 2H, Ar), 7.00 (d, J = 8.7 Hz, 2H, Ar), 3.86 (s, 3H, OMe), 3.13 (s, 3H, NMe), 2.44 (s, 3H, Me), 1.59 (s, 6H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.8, 176.3, 159.8, 156.3, 152.7, 146.2, 143.7, 140.0, 138.6, 135.7, 132.4, 130.8, 130.3, 129.4, 128.8, 128.6, 128.2, 126.5, 126.0, 125.3, 124.3, 123.8, 118.5, 114.2, 58.0, 55.5, 36.9, 22.9, 21.7; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{36}H_{33}N_2O_5S^+$: 605.2105; found: 605.2103.



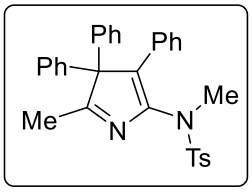
***N*-(3,3-Dimethyl-4-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)-2-phenyl-3*H*-pyrrol-5-yl)-*N*,4-dimethylbenzenesulfonamide (3y)**: yellow oil (116.5 mg, 96%); R_f 0.40 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (dd, J = 6.6, 3.2 Hz, 2H, Ar), 7.81 (d, J = 8.2 Hz, 2H, Ar), 7.47–7.38 (m, 3H, Ar), 7.34–7.23 (m, 4H, Ar), 7.20 (s, 1H, Ar), 3.04 (s, 3H, NMe), 2.96 (dd, J = 8.7, 3.9 Hz, 2H, CH_2), 2.57–2.29 (m, 6H, CH), 2.25–1.96 (m, 4H, CH), 1.74–1.43 (m, 12H, CH), 0.96 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 220.9, 181.4, 144.5, 143.3, 142.3, 139.5, 136.4, 136.2, 132.8, 130.3, 129.9, 129.6, 129.2, 128.7, 128.6, 128.0, 126.5, 125.3, 57.6, 50.7, 48.1, 44.6, 38.2, 37.0, 36.0, 31.8, 29.6, 26.7, 25.7, 22.68, 22.66, 21.7, 14.0; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{38}H_{43}N_2O_3S^+$: 607.2989; found: 607.2976.



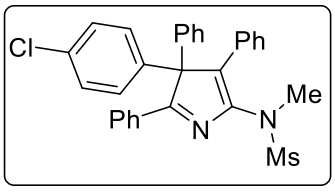
***N*-(1-(3-Chlorophenyl)-4-phenyl-2-azaspiro[4.5]deca-1,3-dien-3-yl)-*N*-methylmethanesulfonamide (3z)**: colorless solid (83.2 mg, 97%); mp 151.0–153.0 °C (DCM); R_f 0.25 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01–7.98 (m, 1H, Ar), 7.84 (d, J = 7.4 Hz, 1H, Ar), 7.45–7.30 (m, 7H, Ar), 3.05 (s, 3H, Me), 3.03 (s, 3H, NMe), 2.25–2.15 (m, 2H, CH_2), 1.85–1.77 (m, 2H, CH_2), 1.61–1.51 (m, 3H, CH_2), 1.44–1.25 (m, 3H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.2, 146.0, 145.4, 135.0, 134.9, 134.7, 130.1, 130.0, 129.8, 128.6, 128.3, 128.0, 126.5, 62.1, 38.8, 37.5, 30.5, 25.0, 22.1; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{23}H_{26}ClN_2O_2S^+$: 429.1399; found: 429.1385.



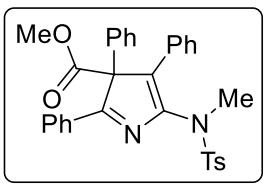
***N*-(2-(4-Methoxyphenyl)-3-methyl-3,4-diphenyl-3*H*-pyrrol-5-yl)-*N*-methylmethanesulfonamide (3aa)**: yellow solid (71.4 mg, 80%); mp 88.0–90.0 °C (DCM); R_f 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, J = 9.0 Hz, 2H, Ar), 7.37–7.27 (m, 3H, Ar), 7.24–7.17 (m, 5H, Ar), 7.14–7.09 (m, 2H, Ar), 6.79 (d, J = 9.0 Hz, 2H, Ar), 3.78 (s, 3H, OMe), 3.31 (s, 3H, Me), 3.21 (s, 3H, NMe), 1.71 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.9, 161.6, 146.2, 140.5, 137.9, 131.7, 130.0, 129.5, 128.4, 128.4, 128.0, 127.7, 126.4, 124.9, 114.0, 64.2, 55.4, 39.3, 37.4, 20.6; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{26}H_{27}N_2O_3S^+$: 447.1737; found: 447.1755.



***N*,4-Dimethyl-*N*-(2-methyl-3,3,4-triphenyl-3*H*-pyrrol-5-yl)benzenesulfonamide (3ab)**: in accordance with GP1 except that the reaction mixture was stirred at 40 °C for 72 h; brown solid (64.0 mg, 65%); mp 280.0–281.0 °C (dec., DCM); R_f 0.30 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz, 2H, Ar), 7.33–7.27 (m, 10H, Ar), 7.25–7.20 (m, 4H, Ar), 7.15–7.12 (m, 3H, Ar), 3.12 (s, 3H, NMe), 2.40 (s, 3H, Me), 2.05 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 185.4, 146.3, 143.6, 140.7, 137.3, 135.9, 132.1, 129.5, 129.04, 128.96, 128.7, 128.5, 128.0, 127.8, 127.7, 77.0, 36.3, 21.7, 17.1; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{31}H_{29}N_2O_2S^+$: 493.1945; found: 493.1930.

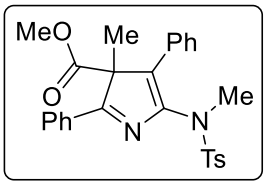


***N*-(3-(4-Chlorophenyl)-2,3,4-triphenyl-3*H*-pyrrol-5-yl)-*N*-methylmethanesulfonamide (3ac)**: in accordance with GP1 except that the reaction mixture in DCE with the added 4Å molecular sieves was stirred at 60 °C for 48 h; yellow solid (81.9 mg, 80%); mp 72.0–73.0 °C (DCM); R_f 0.25 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.3 Hz, 2H, Ar), 7.32 (t, J = 7.4 Hz, 1H, Ar), 7.27–7.12 (m, 14H, Ar), 7.00 (d, J = 6.7 Hz, 2H, Ar), 3.23 (s, 3H, Me), 3.19 (s, 3H, NMe); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.1, 146.8, 142.1, 135.9, 134.9, 133.7, 132.2, 131.5, 130.9, 130.4, 129.4, 129.1, 129.03, 129.00, 128.8, 128.4, 128.3, 128.2, 128.0, 75.2, 39.2, 37.2; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{30}H_{26}ClN_2O_2S^+$: 513.1399; found: 513.1396.

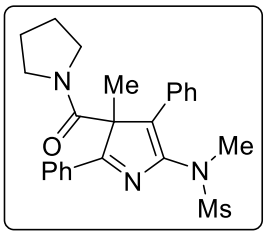


Methyl 5-((*N*,4-dimethylphenyl)sulfonamido)-2,3,4-triphenyl-3*H*-pyrrole-3-carboxylate (3ad): yellow solid (98.7 mg, 92%); mp 73.0–74.5 °C (DCM); R_f 0.55 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 2H, Ar), 7.69 (d, J = 7.3 Hz, 2H, Ar), 7.47 (d, J = 6.8 Hz, 2H, Ar), 7.38–7.27 (m, 8H, Ar), 7.25–7.19 (m, 5H, Ar), 3.66 (s, 3H, OMe), 3.14 (s, 3H, NMe), 2.47 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.8,

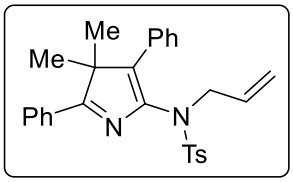
169.2, 148.9, 143.8, 137.9, 135.9, 134.0, 131.6, 131.0, 130.7, 129.4, 129.0, 128.9, 128.7, 128.53, 128.48, 128.40, 128.37, 128.1, 127.9, 74.5, 53.2, 36.8, 21.8; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{32}H_{29}N_2O_4S^+$: 537.1843; found537.1853.



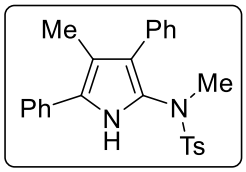
Methyl 5-((*N*,4-dimethylphenyl)sulfonamido)-3-methyl-2,4-diphenyl-3*H*-pyrrole-3-carboxylate (3ae): yellowish solid (85.4 mg, 90%); mp 146.5–148.0 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.2 Hz, 2H, Ar), 7.79 (d, J = 6.5 Hz, 2H, Ar), 7.61 (d, J = 7.4 Hz, 2H, Ar), 7.48–7.39 (m, 5H, Ar), 7.36–7.30 (m, 3H, Ar), 3.67 (s, 3H, OMe), 3.12 (s, 3H, NMe), 2.46 (s, 3H, Me), 1.67 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.3, 171.9, 148.1, 143.7, 135.8, 135.6, 131.8, 131.1, 131.0, 129.3, 129.0, 128.9, 128.9, 128.4, 127.9, 127.5, 65.4, 53.4, 36.7, 21.7, 20.1; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{27}H_{27}N_2O_4S^+$: 475.1687; found: 475.1687.



***N*-Methyl-*N*-(3-methyl-2,4-diphenyl-3-(pyrrolidine-1-carbonyl)-3*H*-pyrrol-5-yl)methanesulfonamide (3af)**: yellowish solid (61.3 mg, 70%); mp 170.0–172.0 °C (DCM); R_f 0.25 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (dd, J = 7.9, 1.5 Hz, 2H, Ar), 7.79 (d, J = 7.4 Hz, 2H, Ar), 7.50–7.37 (m, 5H, Ar), 7.31 (t, J = 7.4 Hz, 1H, Ar), 3.48 (t, J = 6.6 Hz, 2H, CH_2), 3.28 (s, 3H, Me), 3.24 (s, 3H, NMe), 3.14–3.04 (m, 1H, CH_2), 2.78–2.67 (m, 1H, CH_2), 1.72 (s, 3H, Me), 1.69–1.58 (m, 4H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 177.1, 167.1, 146.7, 135.4, 131.6, 131.5, 130.6, 129.2, 129.2, 128.7, 127.7, 127.5, 67.1, 48.1, 43.6, 38.9, 36.9, 26.3, 25.5, 23.6; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{24}H_{28}N_3O_3S^+$: 438.1846; found: 438.1865.

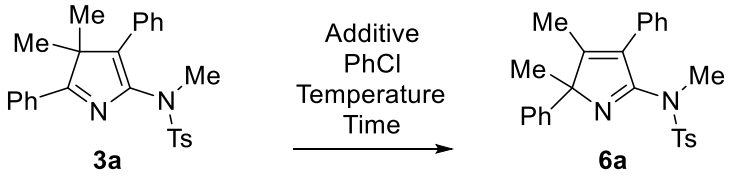


***N*-Allyl-*N*-(3,3-dimethyl-2,4-diphenyl-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (3ag)**: was prepared in PhCl at 60 °C for 3 h as a yellow oil (89.4 mg, 98%); R_f 0.40 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (dd, J = 6.6, 3.1 Hz, 2H, Ar), 7.81 (d, J = 8.2 Hz, 2H, Ar), 7.47–7.34 (m, 8H, Ar), 7.29 (d, J = 8.1 Hz, 2H, Ar), 5.67–5.55 (m, 1H, CH), 5.04–4.96 (m, 2H, 2CH), 3.99 (d, J = 6.7 Hz, 2H, NCH_2), 2.45 (s, 3H, Me), 1.48 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 181.3, 145.0, 143.4, 142.5, 137.0, 133.0, 132.9, 132.5, 130.4, 129.7, 129.3, 128.8, 128.6, 128.3, 128.1, 128.0, 119.0, 57.9, 52.0, 22.5, 21.7; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{28}H_{29}N_2O_2S^+$: 457.1945; found: 457.1948.



***N*,4-Dimethyl-*N*-(4-methyl-3,5-diphenyl-1*H*-pyrrol-2-yl)benzenesulfonamide (5)**: colorless solid (80.0 mg, 96%); mp 156.0–158.0 °C (DCM); R_f 0.40 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.46 (s, 1H, NH), 7.56 (d, J = 8.2 Hz, 2H, Ar), 7.50–7.40 (m, 4H, Ar), 7.31–7.24 (m, 3H, Ar), 7.19–7.15 (m, 1H, Ar), 7.14–7.08 (m, 2H, Ar), 6.63 (d, J = 6.9 Hz, 2H, Ar), 3.01 (s, 3H, NMe), 2.46 (s, 3H, Me), 2.06 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.0, 135.0, 134.4, 133.1, 129.9, 129.8, 128.9, 128.0, 127.8, 126.8, 126.6, 126.5, 126.3, 124.6, 121.2, 114.7, 38.8, 21.8, 11.3; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{25}H_{25}N_2O_2S^+$: 417.1632; found: 417.1644.

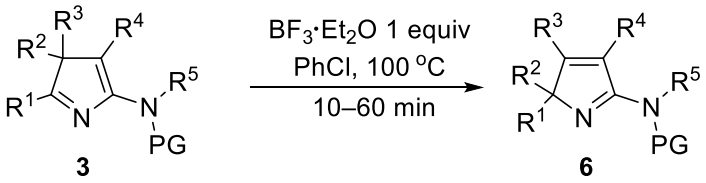
2.5 Complete Optimization of the Synthesis of 6a



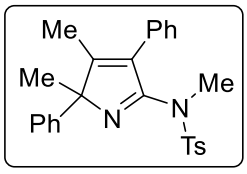
Entry[a]	Additive	mol %	Temperature, °C	Time, min	Yield,[b] %
1	MsOH	5	60	100	traces
2	TfOH	20	60	100	traces
3	**$BF_3 \cdot Et_2O$**	**100**	**100**	**10**	**86**
4	$BF_3 \cdot Et_2O$	50	100	60	48
5	$BF_3 \cdot Et_2O$	20	100	60	16
6	$BF_3 \cdot Et_2O$	10	100	60	5
7	MsOH	100	100	60	80

[a]All reactions were carried out on a 0.1 mmol scale (0.2 *M*); [b]Estimated by ^{1}H NMR spectroscopy using durene as an internal standard after the work-up with aqueous solution of $NaHCO_3$ and the subsequent extraction.

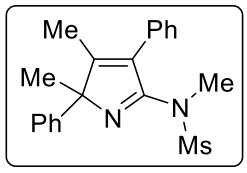
2.6 General Procedure for the Synthesis of 2*H*-Pyrroles 6



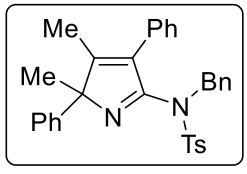
$BF_3{\cdot}Et_2O$ (14.2 mg, 0.1 mmol, 1 equiv) was added to the solution of 3*H*-pyrrole (**3**, 0.1 mmol) in PhCl (0.5 mL). The resulting mixture was heated (100 °C) with stirring in an oil bath for 10-60 min (the TLC control). After cooling to room temperature, the reaction mixture was quenched with saturated aqueous solution of $NaHCO_3$ (5 ml), and the mixture was extracted with DCM (3×5 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration, the solvent was removed in vacuum and the residue was purified by silica gel column chromatography, eluting with hexane/EtOAc to afford 2*H*-pyrroles **6**.



***N*-(2,3-Dimethyl-2,4-diphenyl-2*H*-pyrrol-5-yl)-*N*,4-dimethylbenzenesulfonamide (6a)**: off-white solid (37.0 mg, 86%); mp 114.5−116.0 °C (DCM); R_f 0.55 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H, Ar), 7.47–7.39 (m, 4H, Ar), 7.38–7.30 (m, 3H, Ar), 7.28–7.23 (m, 3H, Ar), 7.19 (d, J = 8.0 Hz, 2H, Ar), 2.96 (s, 3H, Me), 2.37 (s, 3H, Me), 1.86 (s, 3H, Me), 1.71 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.8, 166.4, 143.9, 139.0, 134.5, 133.2, 133.1, 129.4, 129.2, 128.9, 128.7, 128.5, 127.6, 127.4, 125.9, 79.9, 36.4, 21.7, 21.5, 12.5.; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{26}H_{27}N_2O_2S^+$: 431.1788; found: 431.1795.

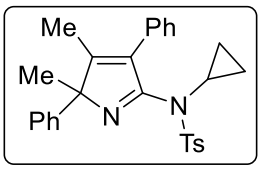


***N*-(2,3-Dimethyl-2,4-diphenyl-2*H*-pyrrol-5-yl)-*N*-methylmethanesulfonamide (6b)**: colorless oil (29.4 mg, 83%); R_f 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45–7.38 (m, 4H, Ar), 7.37–7.31 (m, 3H, Ar), 7.30–7.24 (m, 3H, Ar), 3.25 (s, 3H, Me), 2.91 (s, 3H, NMe), 1.82 (s, 3H, Me), 1.75 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.8, 166.1, 139.0, 132.4, 131.6, 129.0, 128.82, 128.78, 128.0, 127.5, 125.9, 80.2, 39.5, 36.0, 21.6, 12.3; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{20}H_{23}N_2O_2S^+$: 355.1475; found: 355.1486.

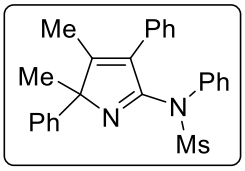


***N*-Benzyl-*N*-(2,3-dimethyl-2,4-diphenyl-2*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (6e)**: yellowish oil (42.5 mg, 84%); R_f 0.65 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J =

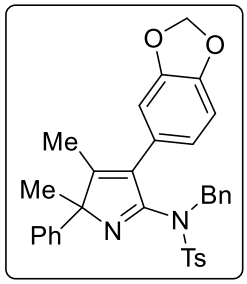
8.3 Hz, 2H, Ar), 7.45–7.34 (m, 3H, Ar), 7.28–7.11 (m, 12H, Ar), 6.99 (dd, *J* = 6.4, 2.9 Hz, 2H, Ar), 4.54 (s, 2H, CH_2), 2.39 (s, 3H, Me), 1.69 (s, 3H, Me), 1.62 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 165.6, 144.0, 135.6, 135.4, 134.9, 133.0, 129.9, 129.6 (×2), 128.73, 128.65, 128.4, 128.3, 128.0, 127.6, 127.5, 126.1, 80.1, 53.0, 21.7, 21.0, 12.4 (one peack is merged with others); **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{32}H_{31}N_2O_2S^+$: 507.2101; found: 507.2091.



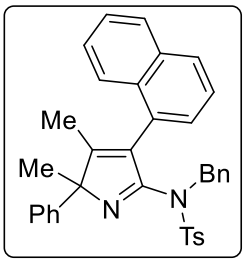
***N*-Cyclopropyl-*N*-(2,3-dimethyl-2,4-diphenyl-2*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (6f)**: yellowish oil (23.7 mg, 52%); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H, Ar), 7.46–7.40 (m, 2H, Ar), 7.38–7.31 (m, 5H, Ar), 7.31–7.26 (m, 3H, Ar), 7.21 (d, *J* = 8.1 Hz, 2H, Ar), 2.58 (br. s, 1H, NCH), 2.38 (s, 3H, Me), 1.83 (s, 3H, Me), 1.77 (s, 3H, Me), 0.75–0.57 (m, 4H, $2CH_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.8, 166.9, 144.1, 138.9, 135.7, 134.0, 132.9, 129.5, 129.4, 128.9, 128.8, 128.5, 127.7, 127.6, 126.0, 80.0, 30.6, 21.7, 21.6, 12.4, 7.6; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{28}H_{29}N_2O_2S^+$: 457.1945; found: 457.1950.



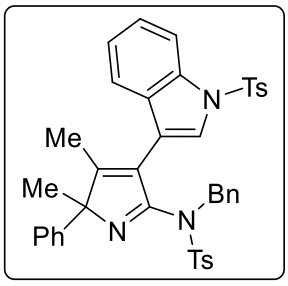
***N*-(2,3-Dimethyl-2,4-diphenyl-2*H*-pyrrol-5-yl)-*N*-phenylmethanesulfonamide (6i)**: yellow oil (32.1 mg, 77%); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39–7.36 (m, 4H, Ar), 7.32–7.28 (m, 1H, Ar), 7.18–7.13 (m, 3H, Ar), 7.13–7.05 (m, 5H, Ar), 6.99–6.96 (m, 2H, Ar), 3.40 (s, 3H, Me), 1.84 (s, 3H, Me), 1.72 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 165.1, 139.4, 137.3, 132.5, 131.8, 129.2, 128.9, 128.8, 128.7, 128.2, 128.1, 127.6, 127.5, 126.0, 80.7, 40.0, 21.8, 12.1; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{25}H_{25}N_2O_2S^+$: 417.1632; found: 417.1615.



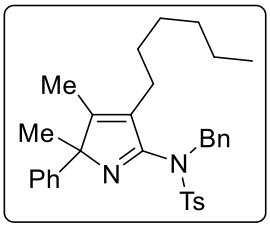
***N*-(4-(Benzo[*d*][1,3]dioxol-5-yl)-2,3-dimethyl-2-phenyl-2*H*-pyrrol-5-yl)-*N*-benzyl-4-methylbenzenesulfonamide (6o)**: colorless oil (42.4 mg, 77%); R_f 0.55 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H, Ar), 7.28–7.18 (m, 10H, Ar), 6.98 (dd, *J* = 6.4, 2.9 Hz, 2H, Ar), 6.84 (d, *J* = 8.5 Hz, 1H, Ar), 6.64–6.61 (m, 2H, Ar), 6.00 (s, 2H, CH_2), 4.56 (s, 2H, NCH_2), 2.39 (s, 3H, Me), 1.68 (s, 3H, Me), 1.61 (s, 3H, Me).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.0, 165.8, 147.6, 147.1, 144.1, 135.5, 135.4, 134.6, 129.9, 129.6, 128.69, 128.65, 128.4, 128.1, 128.0, 127.5, 127.4, 126.0, 123.2, 110.1, 108.3, 101.2, 79.9, 53.2, 21.7, 21.0, 12.5; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{33}H_{31}N_2O_4S^+$: 551.2000; found: 551.1998.



***N*-Benzyl-*N*-(2,3-dimethyl-4-(naphthalen-1-yl)-2-phenyl-2*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (6p)**: mixture of two rotamers; colorless oil (42.9 mg, 77%); R_f 0.65 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.8 Hz, 4H, Ar), 7.65 (d, J = 8.3 Hz, 2H, Ar), 7.61 (d, J = 8.3 Hz, 2H, Ar), 7.53–7.44 (m, 5H, Ar), 7.41–7.25 (m, 11H, Ar), 7.23–7.08 (m, 14H, Ar), 7.03 (d, J = 7.2 Hz, 4H, Ar), 4.59–4.43 (m, 4H, 2NCH_2), 2.38 (s, 6H, 2Me), 1.81 (s, 3H, Me), 1.70 (s, 3H, Me), 1.53 (s, 3H, Me), 1.51 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 170.3, 165.70, 165.67, 143.84, 143.80, 138.8, 138.7, 136.4, 136.2, 135.68, 135.65, 135.61, 133.82, 133.77, 132.8, 132.7, 132.1, 130.43, 130.36, 130.0, 129.9, 129.65, 129.61, 129.42, 129.38, 128.8, 128.75, 128.73, 128.68, 128.5 (×2), 128.32, 128.27(×2), 127.95, 127.86, 127.84, 127.5 (×2), 126.31, 126.27, 126.2, 126.08, 126.07, 125.91 (×2), 125.87, 125.33, 125.29, 80.4, 80.3, 52.6, 52.5, 21.71, 21.68 (×2), 12.8, 12.7; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{36}H_{33}N_2O_2S^+$: 557.2258; found: 557.2244.

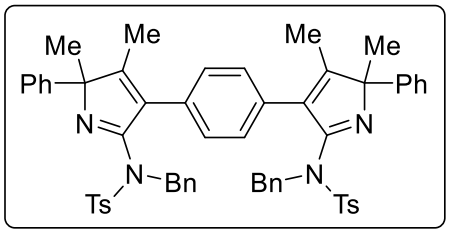


***N*-Benzyl-*N*-(2,3-dimethyl-2-phenyl-4-(1-tosyl-1*H*-indol-3-yl)-2*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (6q)**: beige solid (57.4 mg, 82%); mp 195.0−197.0 °C (*i*-PrOH); R_f 0.55 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.3 Hz, 1H, Ar), 7.96 (d, J = 8.4 Hz, 2H, Ar), 7.82 (s, 1H, Ar), 7.70 (d, J = 8.4 Hz, 2H, Ar), 7.31–7.21 (m, 6H, Ar), 7.22 (d, J = 8.0 Hz, 2H, Ar), 7.11 (t, J = 7.3 Hz, 2H, Ar), 7.01–6.97 (m, 2H, Ar), 6.95–6.87 (m, 4H, Ar), 6.81 (d, J = 7.9 Hz, 1H, Ar), 4.54–4.45 (m, 2H, CH_2), 2.40 (s, 3H, Me), 2.30 (s, 3H, Me), 1.68 (s, 3H, Me), 1.63 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.5, 166.3, 145.0, 144.2, 137.7, 135.3, 135.0, 134.9, 134.8, 130.6, 130.1, 129.6, 129.3, 128.7, 128.6, 128.3, 127.9, 127.6, 127.3, 127.2, 126.8, 125.9, 124.6, 123.3, 120.6, 114.0, 113.7, 80.6, 53.5, 21.7, 21.7, 21.0, 13.1; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{41}H_{38}N_3O_4S_2^+$: 700.2298; found: 700.2317.

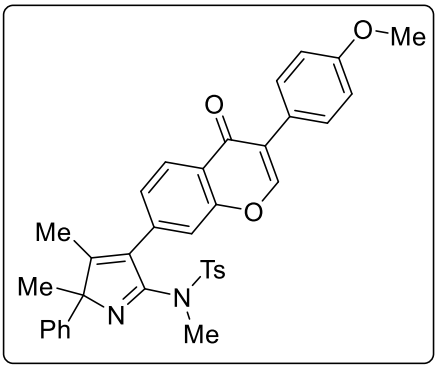


***N*-Benzyl-*N*-(4-hexyl-2,3-dimethyl-2-phenyl-2*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (6t)**: colorless solid (37.6 mg, 73%); mp 94.5–96.5 °C (DCM); R_f 0.70 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 2H, Ar), 7.32–7.28 (m, 2H, Ar), 7.25–7.23 (m, 3H, Ar), 7.22–7.18 (m, 5H, Ar), 6.86 (dd, J = 6.2, 2.7 Hz, 2H, Ar), 4.59 (d, J = 12.9 Hz, 1H, NCH), 4.51 (d, J = 12.9 Hz, 1H, NCH), 2.46 (br. s, 2H,CH_2), 2.38 (s, 3H, Me), 1.65 (s, 3H, Me), 1.49 (s, 3H, Me), 1.29–1.22 (m, 3H, CH_2), 1.19–1.10 (m, 5H, CH_2), 0.88 (t, J = 7.1 Hz, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ

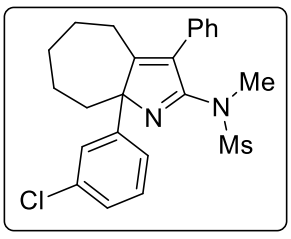
168.0, 165.9, 144.3, 138.4, 135.7, 135.5, 134.4, 130.0, 129.7, 128.7, 128.5, 128.4, 128.0, 127.3, 126.1, 79.8, 53.7, 31.8, 29.6, 28.7, 24.8, 22.8, 21.7, 20.8, 14.3, 12.1; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{32}H_{39}N_2O_2S^+$: 515.2727; found: 515.2723.



***N*,*N*'-(1,4-Phenylenebis(2,3-dimethyl-2-phenyl-2*H*-pyrrole-4,5-diyl))bis(*N*-benzyl-4-methylbenzenesulfonamide) (6v)**: colorless viscous oil (72.9 mg, 78%); R_f 0.40 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.1 Hz, 4H, Ar), 7.30–7.16 (m, 24H, Ar), 7.04–7.01 (m, 4H, Ar), 4.57 (s, 4H, $2CH_2$), 2.39 (s, 6H, 2Me), 1.77 (s, 6H, 2Me), 1.64 (s, 6H, 2Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.2, 165.6, 144.0, 138.4, 135.7, 135.3, 134.6, 132.1, 129.9, 129.6, 129.3, 128.8, 128.7, 128.5, 128.0, 127.5, 126.1, 80.2, 53.1, 21.7, 21.0, 12.6; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{58}H_{55}N_4O_4S_2^+$: 935.3659; found: 935.3659.

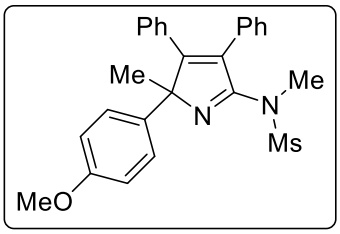


***N*-(4-(3-(4-Methoxyphenyl)-4-oxo-4*H*-chromen-7-yl)-2,3-dimethyl-2-phenyl-2*H*-pyrrol-5-yl)-*N*,4-dimethylbenzenesulfonamide (6x)**: yellowish oil (50.8 mg, 84%); R_f 0.15 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.2 Hz, 1H, Ar), 8.01 (s, 1H, Ar), 7.63 (d, J = 8.2 Hz, 2H, Ar), 7.57–7.51 (m, 3H, Ar), 7.46 (dd, J = 8.2, 1.2 Hz, 1H, Ar), 7.38–7.28 (m, 3H, Ar), 7.25–7.17 (m, 4H, Ar), 6.99 (d, J = 8.7 Hz, 2H, Ar), 3.85 (s, 3H, OMe), 3.08 (s, 3H, NMe), 2.37 (s, 3H, Me), 1.93 (s, 3H, Me), 1.75 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 176.3, 169.9, 166.0, 159.8, 156.3, 152.7, 144.4, 139.1, 138.1, 133.6, 132.4, 130.3, 129.6, 128.9, 128.6, 127.8, 126.5, 126.3, 125.9, 125.4, 124.3, 123.6, 118.4, 114.2, 80.3, 55.5, 37.0, 21.7, 21.5, 12.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{36}H_{33}N_2O_5S^+$: 605.2105; found: 605.2100.

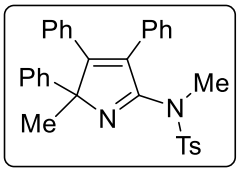


***N*-(8a-(3-Chlorophenyl)-3-phenyl-4,5,6,7,8,8a-hexahydrocyclohepta[*b*]pyrrol-2-yl)-*N*-methylmethanesulfonamide (6z)**: yellowish solid (30.0 mg, 70%); mp 95.5–97.0 °C (DCM); R_f 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.42 (m, 4H, Ar), 7.40–7.35 (m, 2H, Ar), 7.29–7.26 (m, 3H, Ar), 3.17 (s, 3H, Me), 2.89–2.82 (m, 1H, CH_2), 2.81 (s, 3H, NMe), 2.58 (ddd, J = 14.3, 7.8, 1.8 Hz, 1H, , CH_2), 2.50 (ddd, J = 15.6, 8.5, 3.6 Hz, 1H, CH_2), 2.11–2.02 (m, 1H, CH_2), 1.68–1.47 (m, 4H, CH_2), 1.44–1.36 (m, 2H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.2, 164.8, 142.2, 135.3, 134.6, 132.5, 130.1, 128.95, 128.94, 128.2, 127.8,

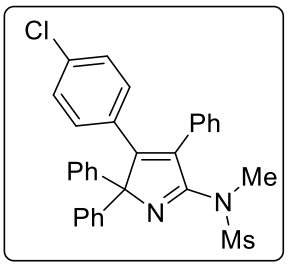
127.3, 125.2, 84.2, 39.7, 36.1, 35.9, 29.6, 28.4, 26.9, 24.5; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{23}H_{26}ClN_2O_2S^+$: 429.1399; found: 429.1415.



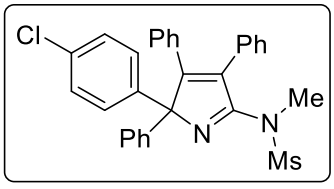
***N*-(2-(4-Methoxyphenyl)-2-methyl-3,4-diphenyl-2*H*-pyrrol-5-yl)-*N*-methylmethanesulfonamide (6aa)**: off-white solid (28.1 mg, 63%); mp 185.5–187.5 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.42 (m, 4H, Ar), 7.40–7.34 (m, 1H, Ar), 7.34–7.28 (m, 5H, Ar), 7.22 (d, J = 9.0 Hz, 2H, Ar), 6.87 (d, J = 8.9 Hz, 2H, Ar), 3.81 (s, 3H, OMe), 3.28 (s, 3H, Me), 2.81 (s, 3H, NMe), 1.99 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 165.2, 159.1, 141.1, 133.7, 132.8, 132.4, 129.5, 129.1, 128.9, 128.5, 128.31, 128.27, 127.6, 113.9, 87.5, 55.4, 40.0, 35.9, 14.3; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{26}H_{27}N_2O_3S^+$: 447.1737; found: 447.1736.



***N*,4-Dimethyl-*N*-(2-methyl-2,3,4-triphenyl-2*H*-pyrrol-5-yl)benzenesulfonamide (6ab)**: yellowish solid (36.9 mg, 75%); mp 151.0–153.0 °C (MeCN); R_f 0.55 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.3 Hz, 2H, Ar), 7.37–7.28 (m, 10H, Ar), 7.20–7.15 (m, 3H, Ar), 7.12–7.07 (m, 2H, Ar), 6.71 (d, *J* = 7.2 Hz, 2H, Ar), 3.01 (s, 3H, NMe), 2.37 (s, 3H, Me), 1.76 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.5, 166.4, 144.1, 137.8, 134.9, 134.4, 133.8, 132.9, 129.6, 129.5, 128.9, 128.82, 128.77, 128.5, 128.2, 128.2, 127.9, 127.8, 126.4, 80.6, 36.7, 21.7, 21.6; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{31}H_{29}N_2O_2S^+$: 493.1945; found: 493.1941.

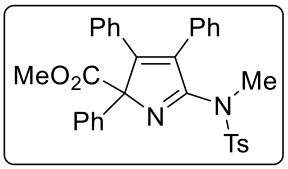


***N*-(3-(4-Chlorophenyl)-2,2,4-triphenyl-2*H*-pyrrol-5-yl)-*N*-methylmethanesulfonamide (6ac)**: colorless oil (30.8 mg, 60%); R_f 0.65 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.29 (m, 15H, Ar), 7.02 (d, *J* = 8.6 Hz, 2H, Ar), 6.70 (d, *J* = 8.6 Hz, 2H, Ar), 3.22 (s, 3H, Me), 2.92 (s, 3H, NMe).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 165.4, 138.8, 135.4, 134.4, 132.7, 131.8, 130.8, 129.5, 129.0, 128.6, 128.5 (×2), 128.4, 128.0, 88.3, 39.6, 36.1; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{30}H_{26}ClN_2O_2S^+$: 513.1399; found: 513.1396.

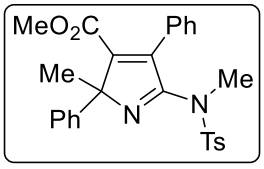


***N*-(2-(4-Chlorophenyl)-2,3,4-triphenyl-2*H*-pyrrol-5-yl)-*N*-methylmethanesulfonamide (6ac')**: colorless oil (15.9 mg, 31%); R_f 0.70 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33–7.28 (m, 11H, Ar), 7.25–7.21 (m, 3H, Ar), 7.15 (t, *J* = 7.4

Hz, 1H, Ar), 7.07–7.02 (m, 2H, Ar), 6.75 (d, *J* = 7.5 Hz, 2H, Ar), 3.23 (s, 3H, Me), 2.91 (s, 3H, NMe); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 165.6, 138.8, 137.7, 135.0, 134.0, 133.7, 131.9, 130.0, 129.5 (×2), 128.9, 128.6, 128.52, 128.50, 128.47, 128.4, 128.2, 128.1, 87.7, 39.6, 36.0; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{30}H_{26}ClN_2O_2S^+$: 513.1399; found: 513.1388.

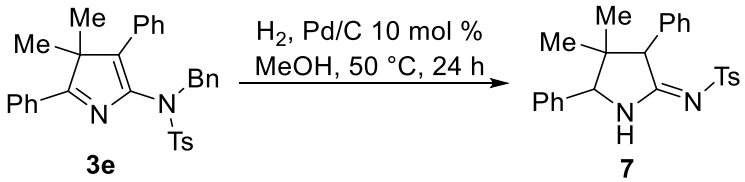


Methyl 5-((*N*,4-dimethylphenyl)sulfonamido)-2,3,4-triphenyl-2*H*-pyrrole-2-carboxylate (6ad): colorless oil (38.1 mg, 71%); R_f 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H, Ar), 7.33–7.24 (m, 10H, Ar), 7.22–7.17 (m, 3H, Ar), 7.16–7.10 (m, 2H, Ar), 6.90 (d, *J* = 7.3 Hz, 2H, Ar), 3.74 (s, 3H, OMe), 2.97 (s, 3H, NMe), 2.39 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 169.4, 163.0, 144.1, 137.5, 135.5, 134.1, 133.3, 132.3, 129.54, 129.51, 129.4, 129.3, 128.6, 128.4, 128.3, 128.2, 128.2, 128.0, 127.8, 88.8, 53.2, 36.6, 21.7; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{32}H_{29}N_2O_4S^+$: 537.1843; found: 537.1854.



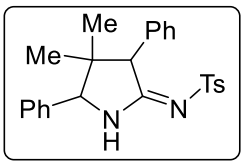
Methyl 5-((*N*,4-dimethylphenyl)sulfonamido)-2-methyl-2,4-diphenyl-2*H*-pyrrole-3-carboxylate (6ae): yellowish oil (35.1 mg, 74%); R_f 0.40 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H, Ar), 7.48–7.28 (m, 10H, Ar), 7.19 (d, *J* = 8.1 Hz, 2H, Ar), 3.80 (s, 3H, OMe), 2.96 (s, 3H, NMe), 2.38 (s, 3H, Me), 2.07 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.6, 169.3, 161.9, 144.1, 136.3, 135.9, 134.1, 132.6, 129.3, 129.19, 129.15, 128.9, 128.6, 128.3, 128.0, 126.7, 88.0, 53.1, 36.5, 21.7, 13.7; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{27}H_{27}N_2O_4S^+$: 475.1687; found: 475.1693.

2.6. Hydrogenation of 3e



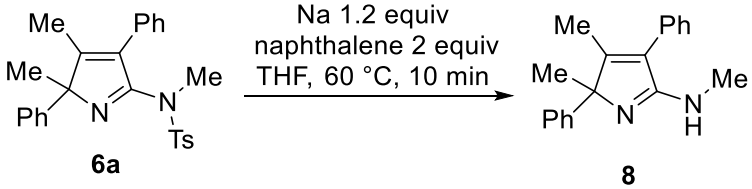
A 25 mL round-bottom flask containing **3e** (70.1 mg, 0.1 mmol) and 10% palladium on carbon (10.6 mg, 0.01 mmol, 10 mol %) was fitted with a rubber septum, evacuated under high vacuum and backfilled with hydrogen. Degassed MeOH (7 mL) was next added. The flask was equipped with a hydrogen balloon and the black suspension was heated at 50 °C for 24 h with stirring. After completion, the suspension was cooled to rt, all volatile components were removed in vacuum

and the residue was purified by silica gel column chromatography eluting with hexane/EtOAc to afford product **7**.

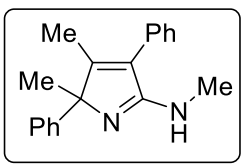


***(E)-N*-(4,4-Dimethyl-3,5-diphenylpyrrolidin-2-ylidene)-4-methylbenzenesulfonamide (7)**: colorless solid (19.3 mg, 46%); mp 191.0–193.0 °C (DCM); R_f 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34 (s, 1H, NH), 7.85 (d, J = 8.2 Hz, 2H, Ar), 7.43–7.35 (m, 3H, Ar), 7.32–7.24 (m, 7H, Ar), 7.12–7.07 (m, 2H, Ar), 4.72 (s, 1H, NCH), 3.93 (s, 1H, CH), 2.43 (s, 3H, Me), 1.18 (s, 3H, Me), 0.21 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.0, 143.0, 139.6, 135.4, 133.3, 130.6, 129.5, 128.8, 128.7, 128.1, 127.6, 127.0, 126.6, 70.6, 62.9, 46.1, 24.4, 21.7, 18.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{25}H_{27}N_2O_2S^+$: 419.1788; found: 419.1781.

2.7. Detosylation of 6a

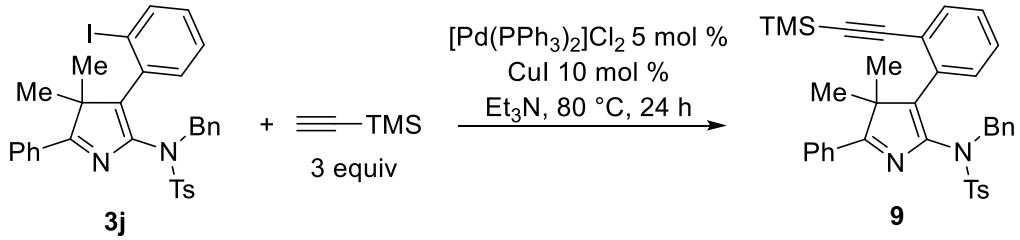


Sodium (2.8 mg, 0.12 mmol, 1.2 equiv) was added to the solution of naphthalene (25.6 mg, 0.20 mmol, 2.0 equiv) in dry THF (3.0 mL). The mixture was heated at 60 °C and stirred until deep green color was appeared. Then 2*H*-pyrrole **6a** (43.1 mg, 0.1 mmol) was added and the reaction mixture was stirred for 10 minutes (the TLC control). After cooling to room temperature, the reaction mixture was carefully quenched with water (5 ml) and the resulting emulsion was extracted with DCM (3×5 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration, the solvent was removed in vacuum and the residue was purified by alumina column chromatography, eluting first with hexane/EtOAc (4/1) and then with MeOH to afford product **8**.

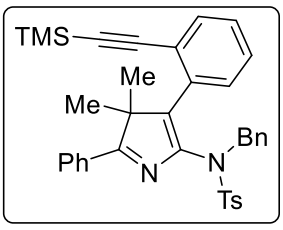


***N*,2,3-Trimethyl-2,4-diphenyl-2*H*-pyrrol-5-amine (8)**: brown oil (26.0 mg, 94%); R_f 1.0 (MeOH); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.37 (m, 4H, Ar), 7.35–7.30 (m, 2H, Ar), 7.29–7.26 (m, 3H, Ar), 7.25–7.21 (m, 3H, Ar), 3.06 (br. s, 3H, NMe), 1.89 (s, 3H, Me), 1.74 (s, 3H, Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 178.3, 164.2, 138.2, 129.5 (×2), 129.4, 129.3, 129.0, 128.3, 127.9, 125.8, 74.0, 31.2, 22.4, 11.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{19}H_{21}N_2^+$: 277.1700; found: 277.1702.

2.8.Sonogashira Coupling of 3j



A 25 mL round-bottom flask was charged with the solution of 3*H*-pyrrole **3j** (63.2 mg, 0.1 mmol) in triethylamine (3 ml). The flask was flushed with argon and then $Pd(PPh_3)_2Cl_2$ (3.5 mg, 0.005 mmol, 5 mol %), CuI (1.9 mg, 0.01 mmol, 10 mol %) were added to the solution. The flask was fitted with a rubber septum and ethynyltrimethylsilane (29.5 mg, 0.3 mmol, 3 equiv) was added using a syringe. The resulting black mixture was stirred at 80 °C for 20 h. After completion, all volatile components were removed in vacuo and the residue was purified by silica gel chromatography eluting with hexane/EtOAc to afford product **9**, which was obtained as a mixture with the starting pyrrole **3j** (53% of **9** according to ^{1}H NMR assay; both have the same R_f's).



***N*-Benzyl-*N*-(3,3-dimethyl-2-phenyl-4-(2-((trimethylsilyl)ethynyl)phenyl)-3*H*-pyrrol-5-yl)-4-methylbenzenesulfonamide (9)**: brown oil (41.0 mg, 53%-mixture with **3j**, 36%); R_f 0.40 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97–7.89 (m, 2H, Ar), 7.65 (d, J = 8.2 Hz, 2H, Ar), 7.54 (dd, J = 7.4, 1.4 Hz, 1H, Ar), 7.50–7.44 (m, 3H, Ar), 7.35–7.28 (m, 2H, Ar), 7.18–7.02 (m, 7H, Ar), 6.86–6.82 (m, 1H, Ar), 4.67 (s, 2H, NCH_2), 2.41 (s, 3H, Me), 1.43 (s, 6H, 2Me), –0.02 (s, 9H, 3Me); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.1, 144.8, 143.1, 142.5, 137.47, 136.6, 135.0, 133.3 (×2), 131.5, 130.4, 129.1, 128.8, 128.70 (×2), 128.25, 128.22, 128.0, 127.9, 127.2, 124.6, 105.3, 97.3, 60.0, 53.8, 22.8, 21.69, –0.2; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{37}H_{39}N_2O_2SSi^+$: 603.2497; found: 603.2511.

3. References

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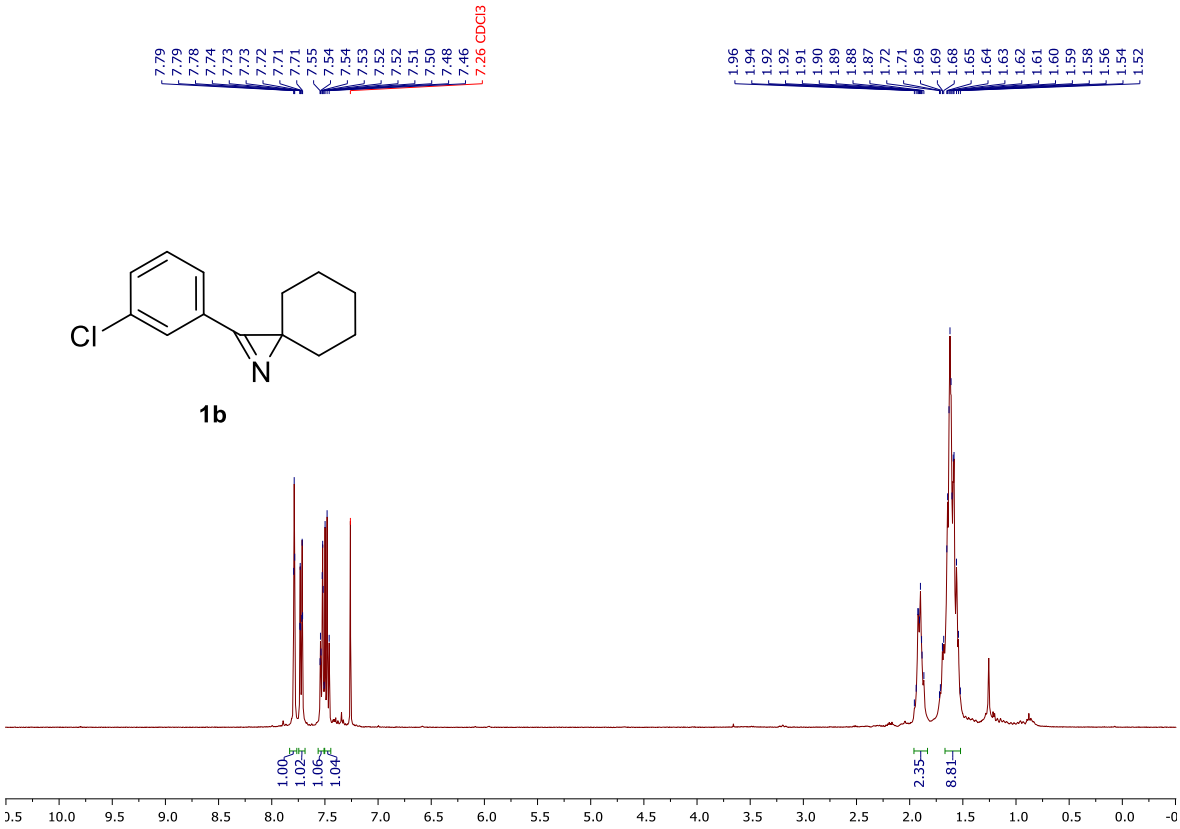
Substituted 2H-Azirines with α-Imino Rh(II) Carbenoids. *J. Org. Chem.* **2019**, *84* (7), 3743–3753. https://doi.org/10.1021/acs.joc.8b03205.

4. NMR Spectra

4.1. NMR Spectra of Starting 2*H*-Azirines 1

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



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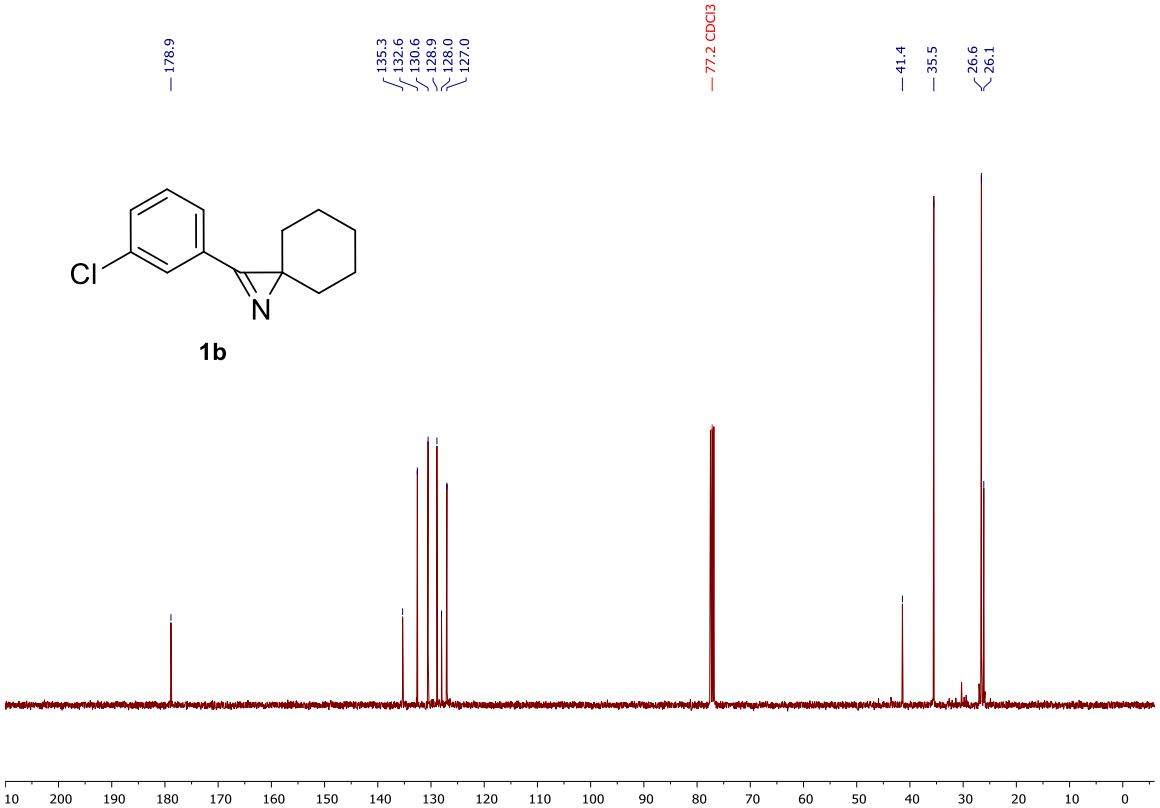
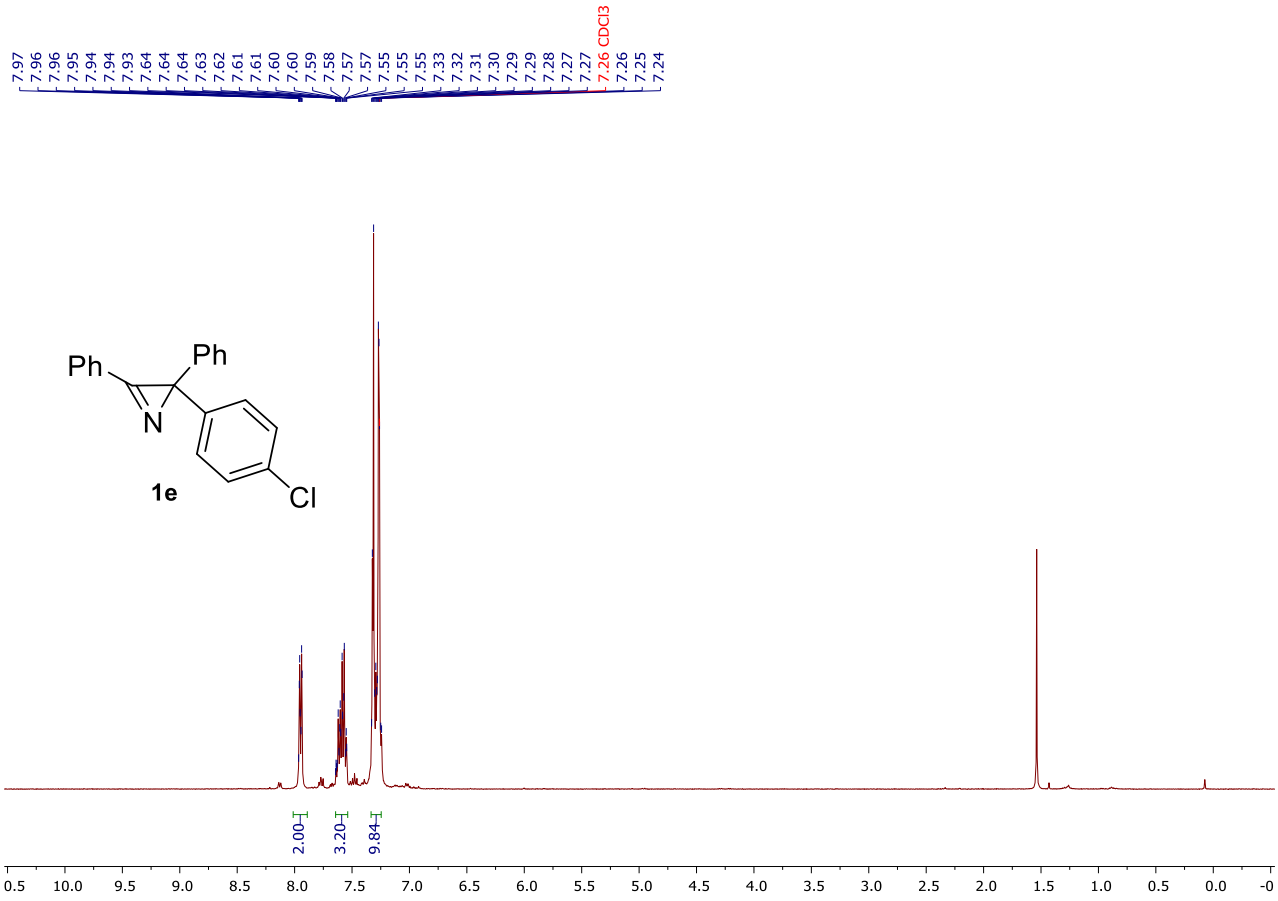


^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



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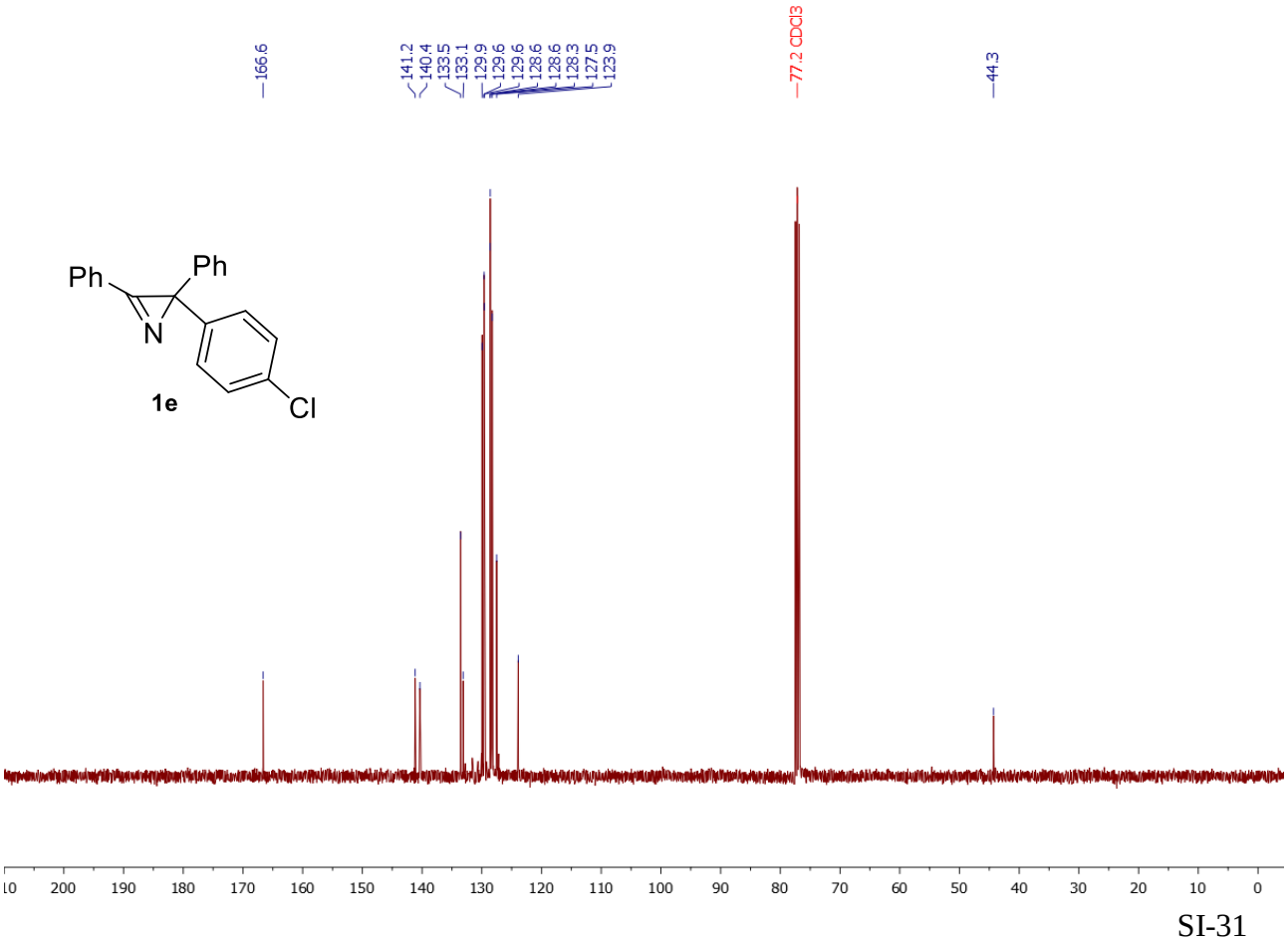

4.2.NMR Spectra of Starting Ynamides 2

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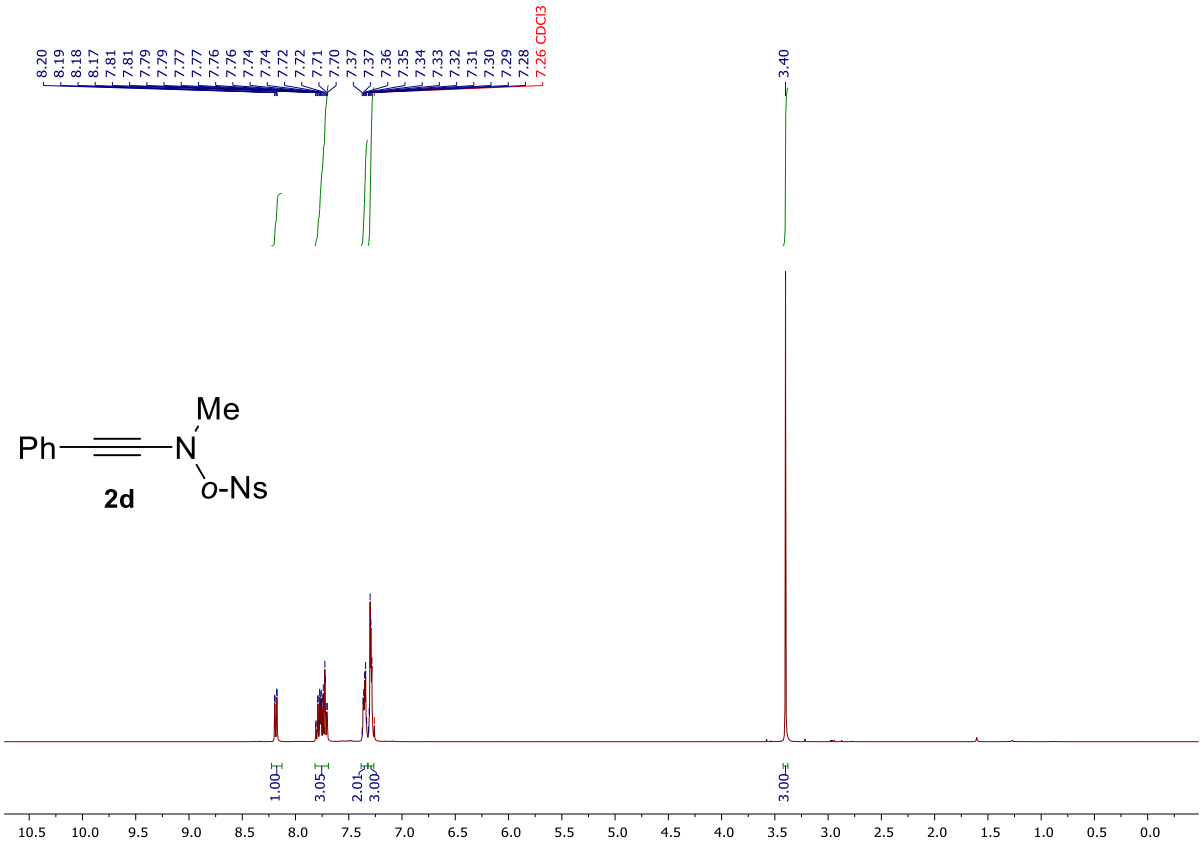

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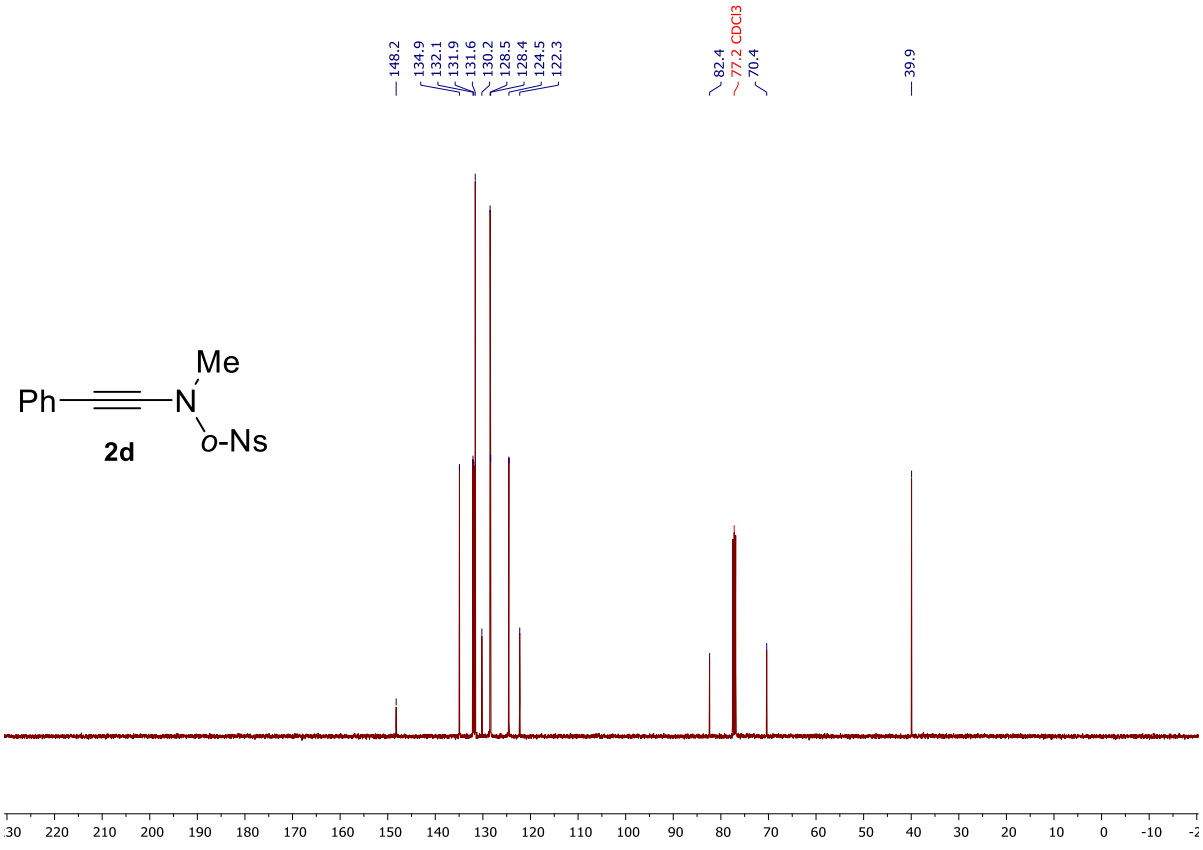

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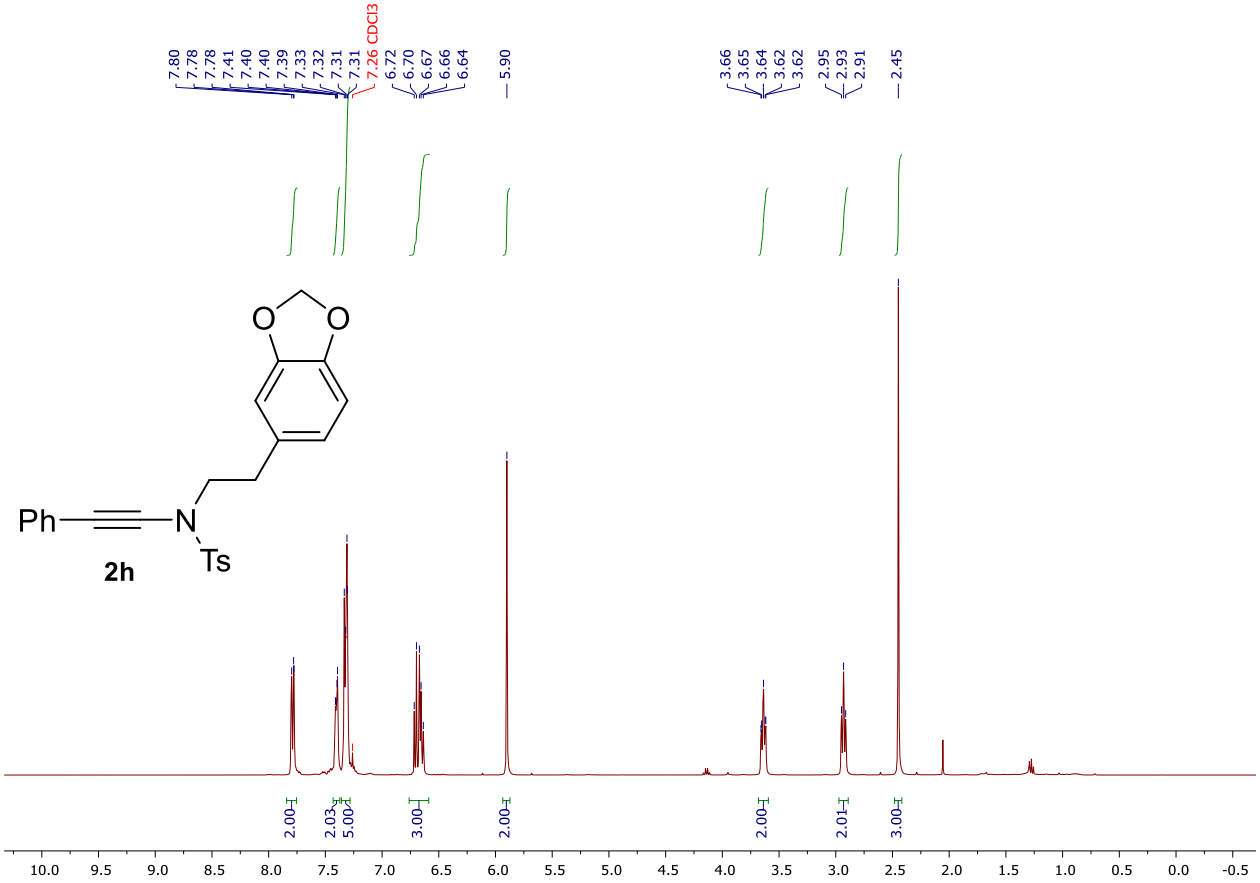
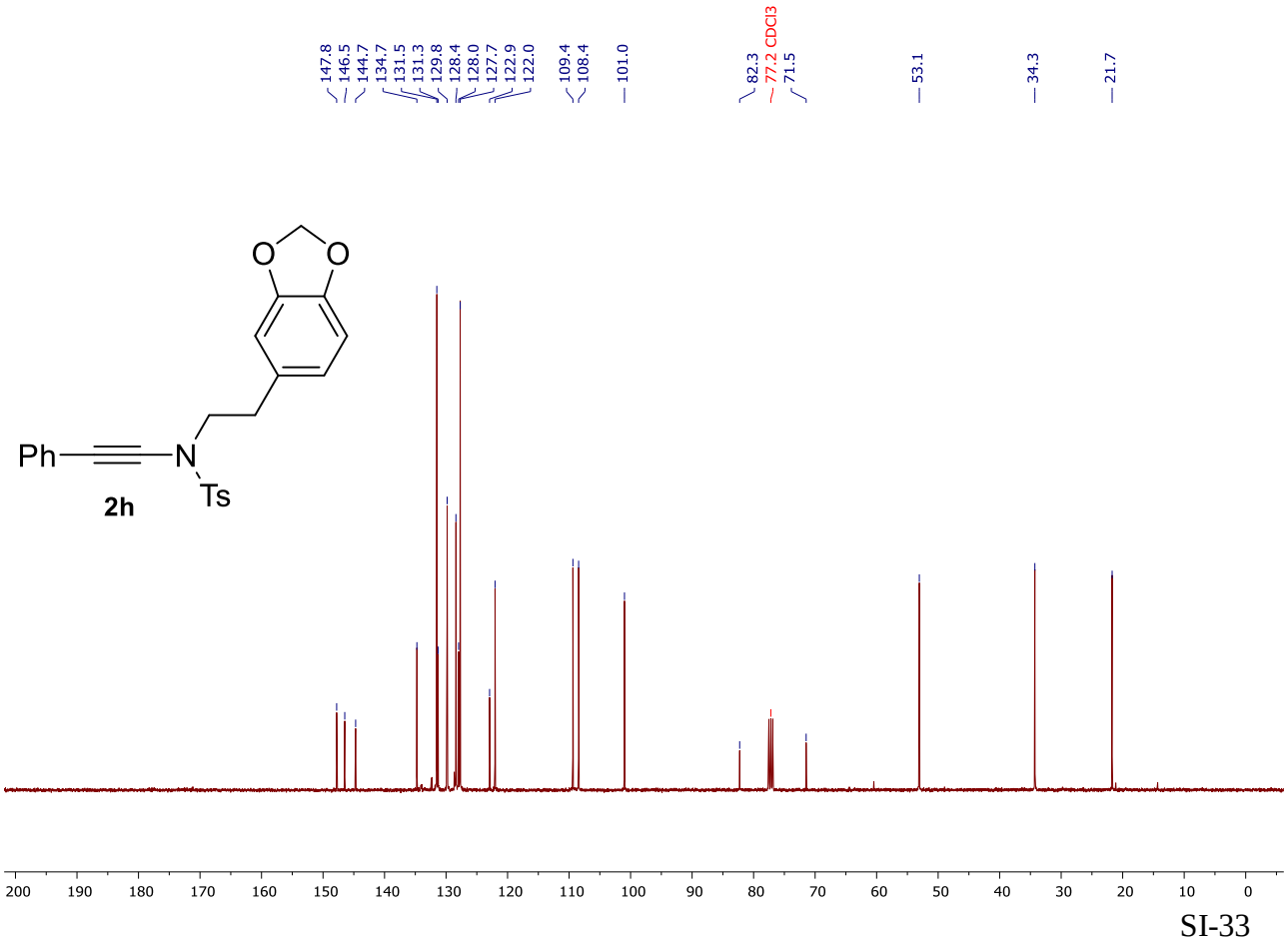
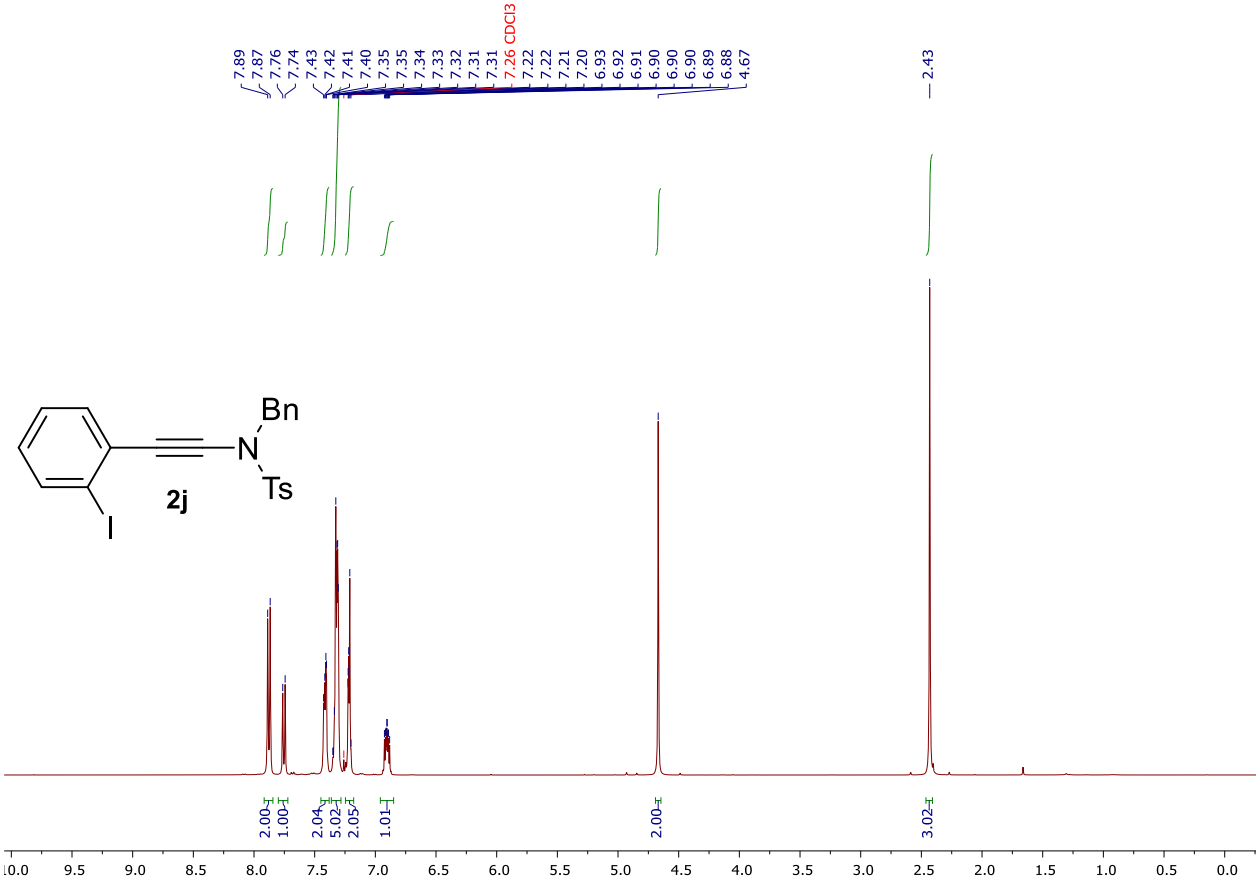


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2h**



^{1}H NMR (400 MHz, $CDCl_3$) of **2j**



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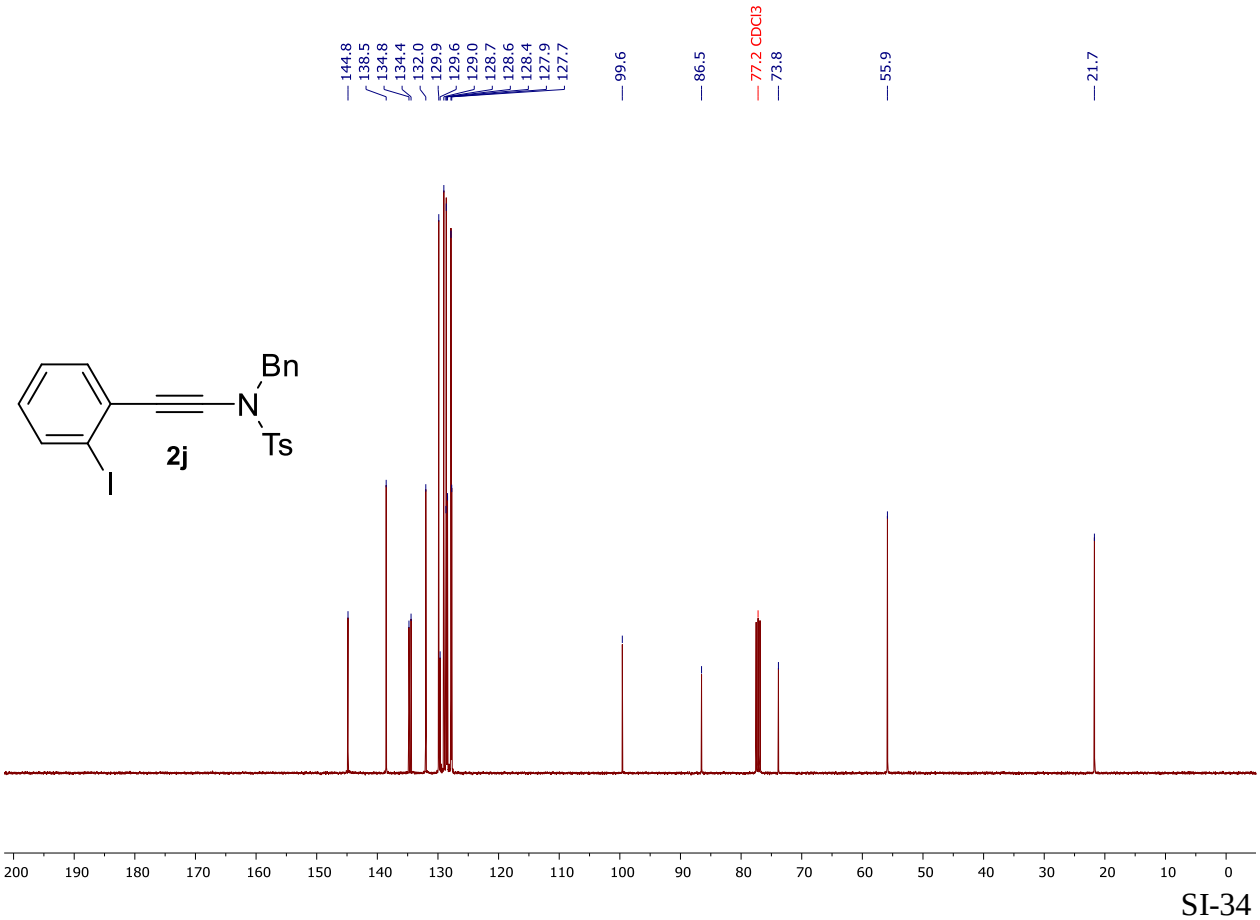

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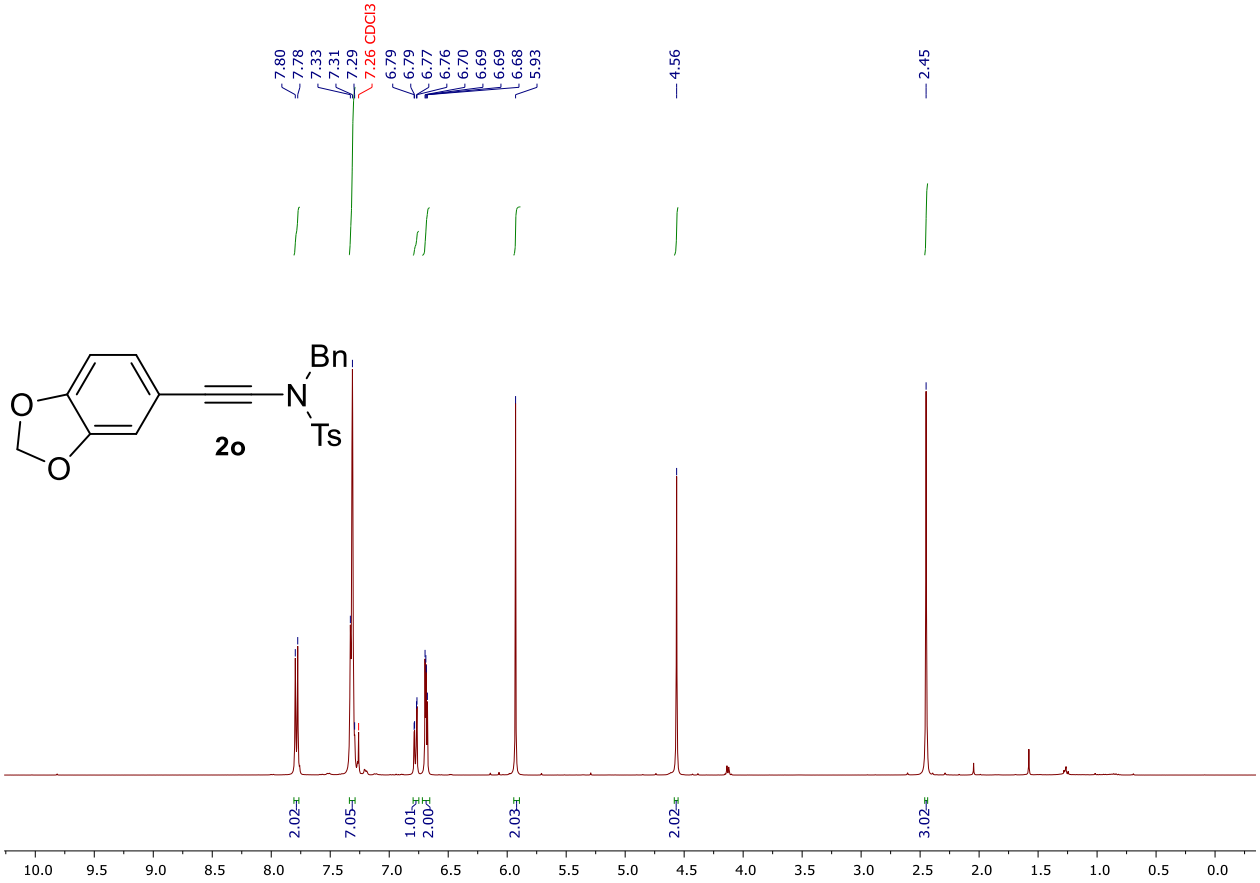

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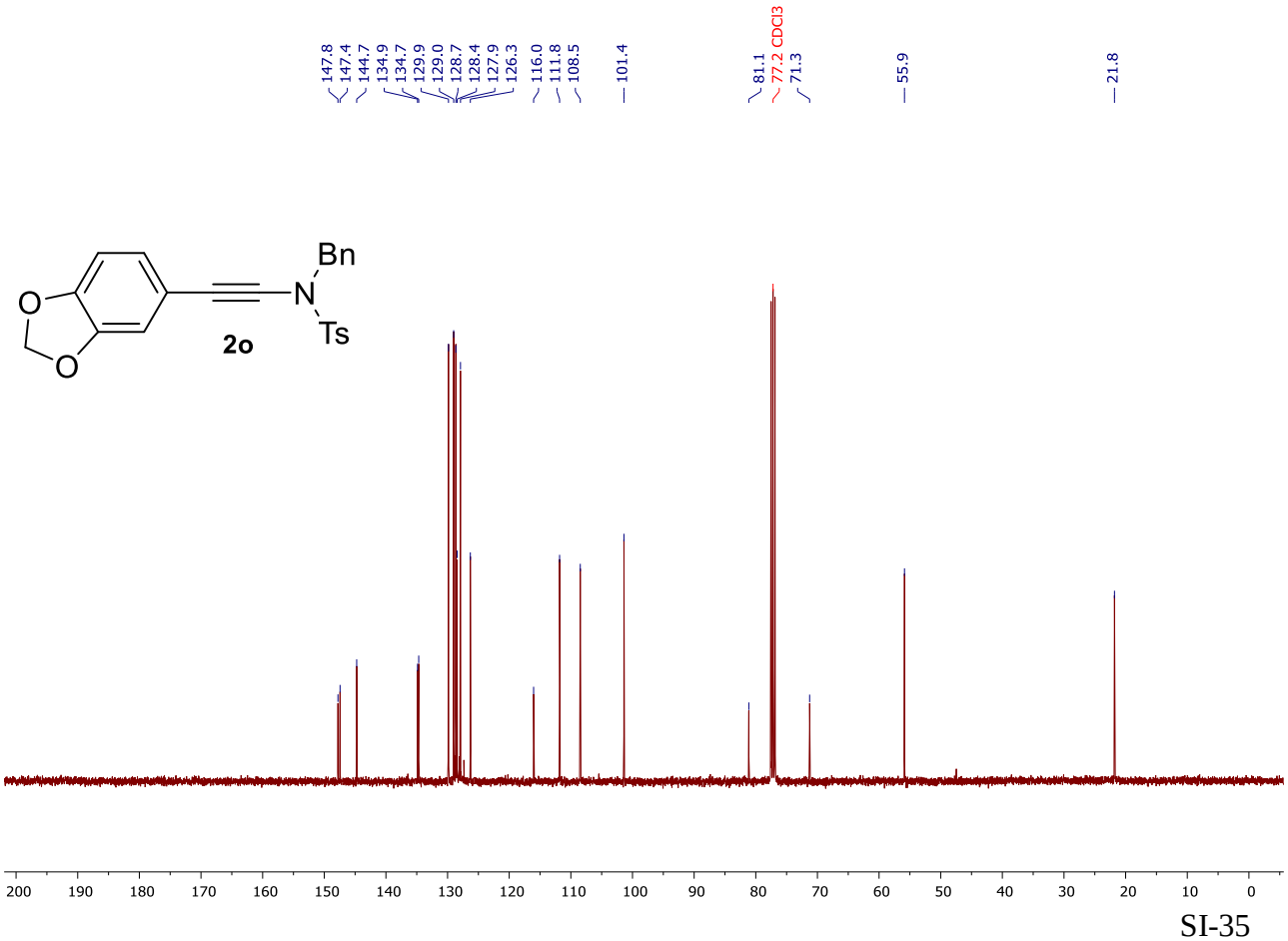
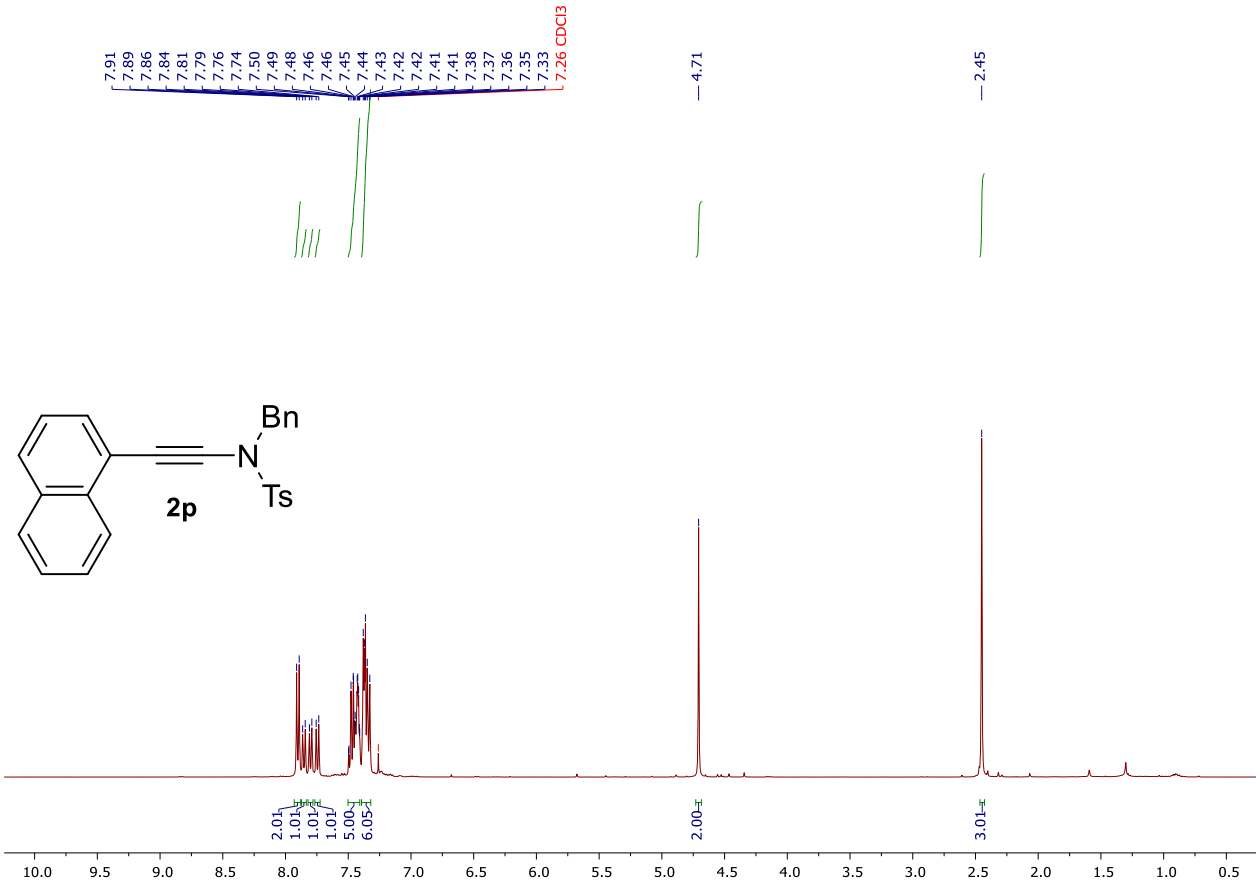


^{1}H NMR (400 MHz, $CDCl_3$) of **2p**



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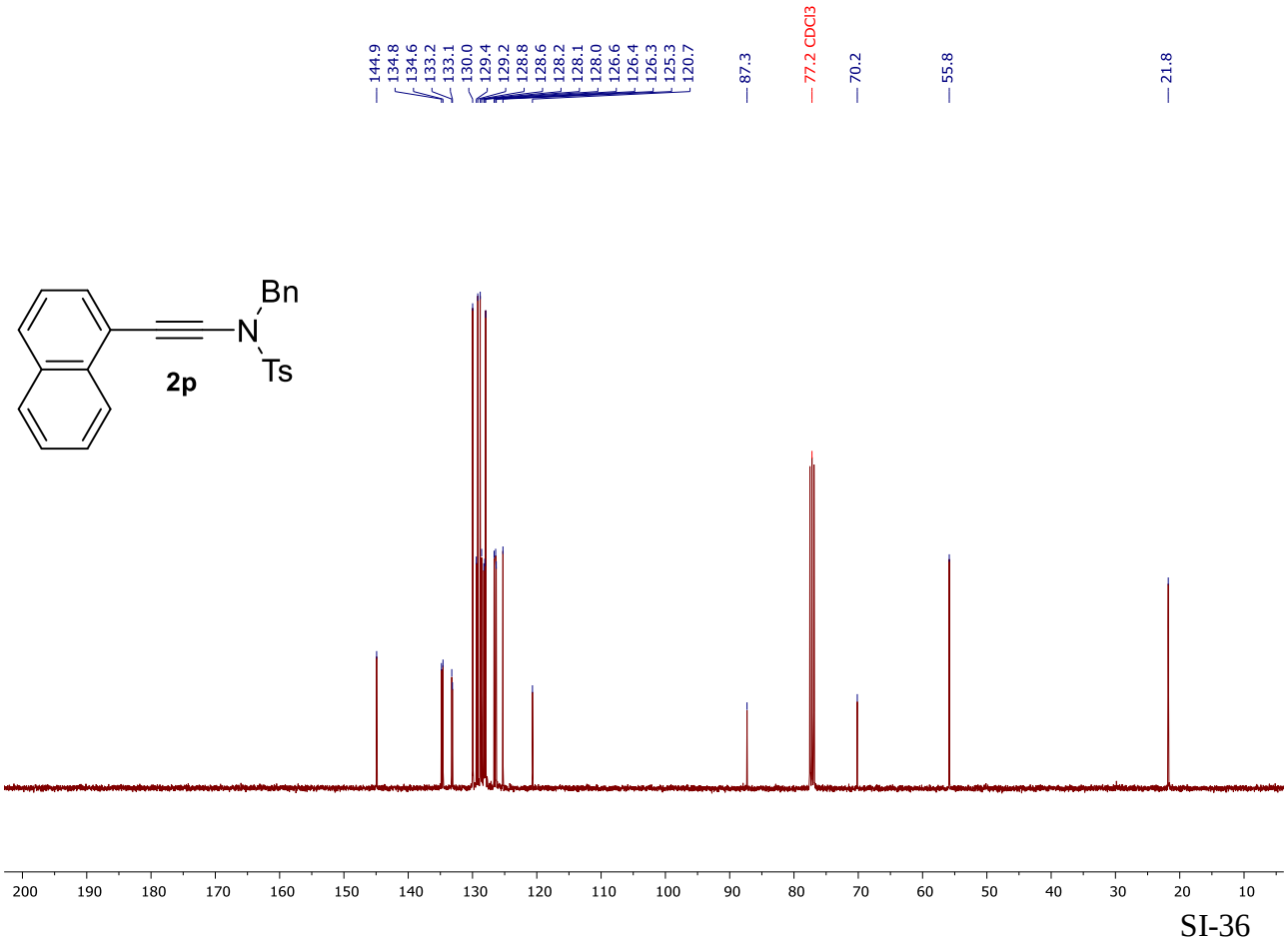

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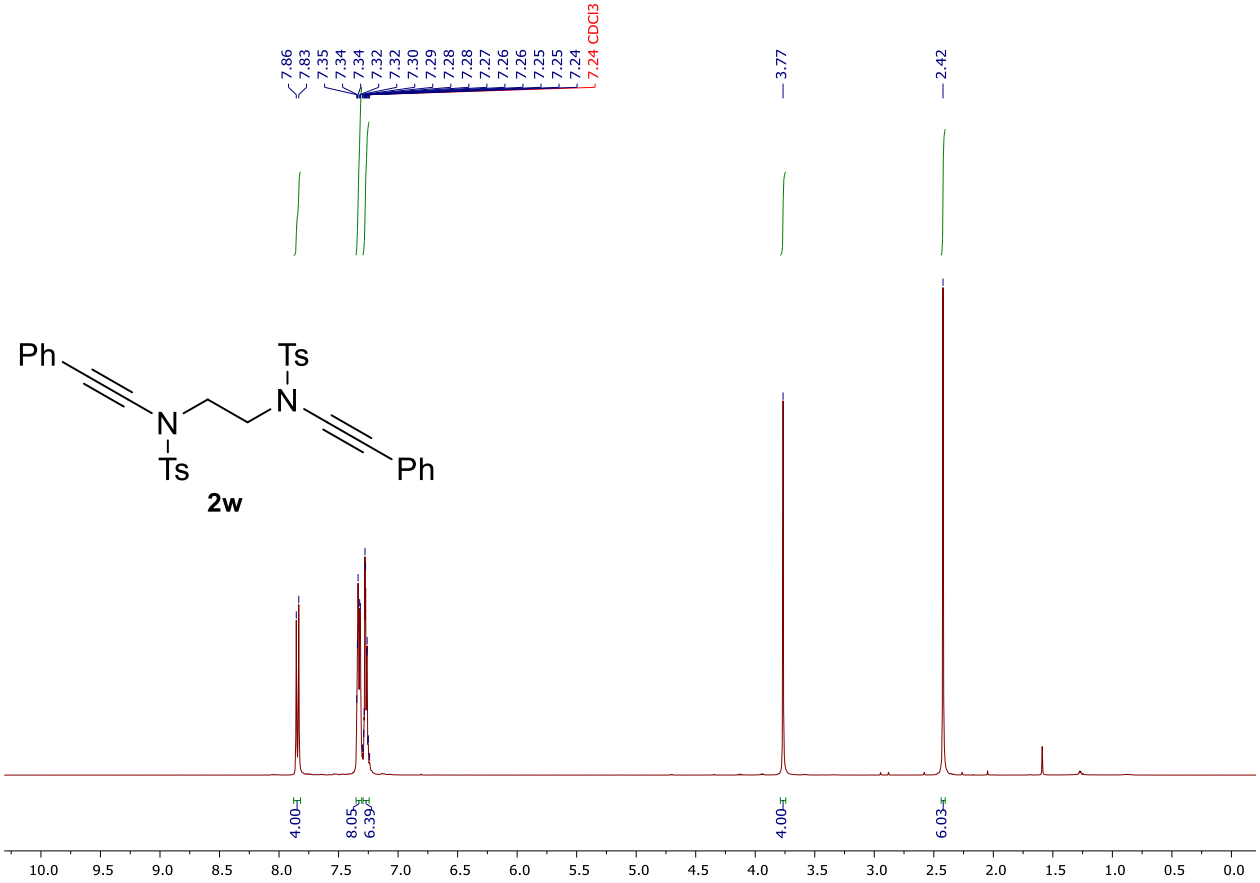

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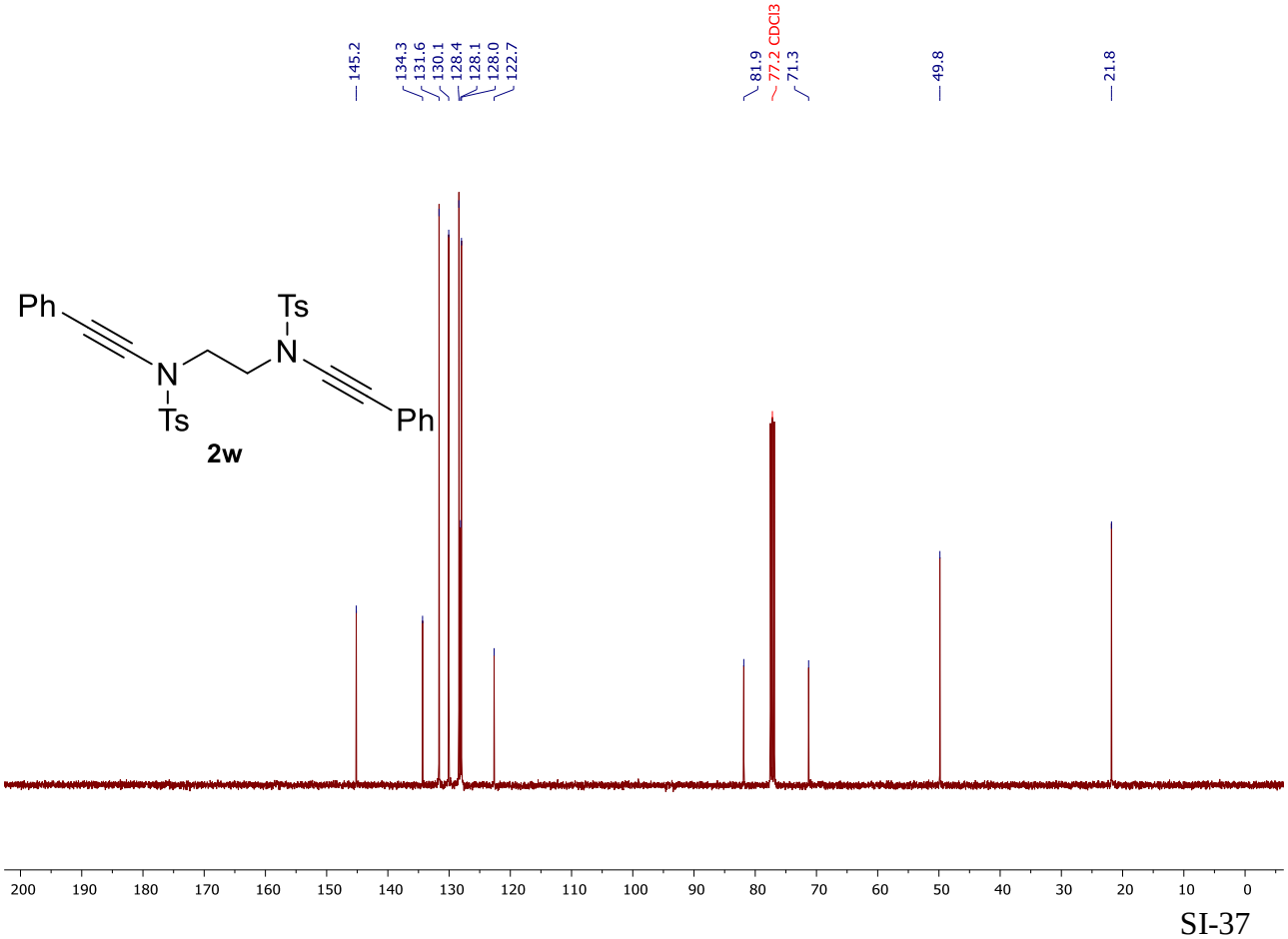
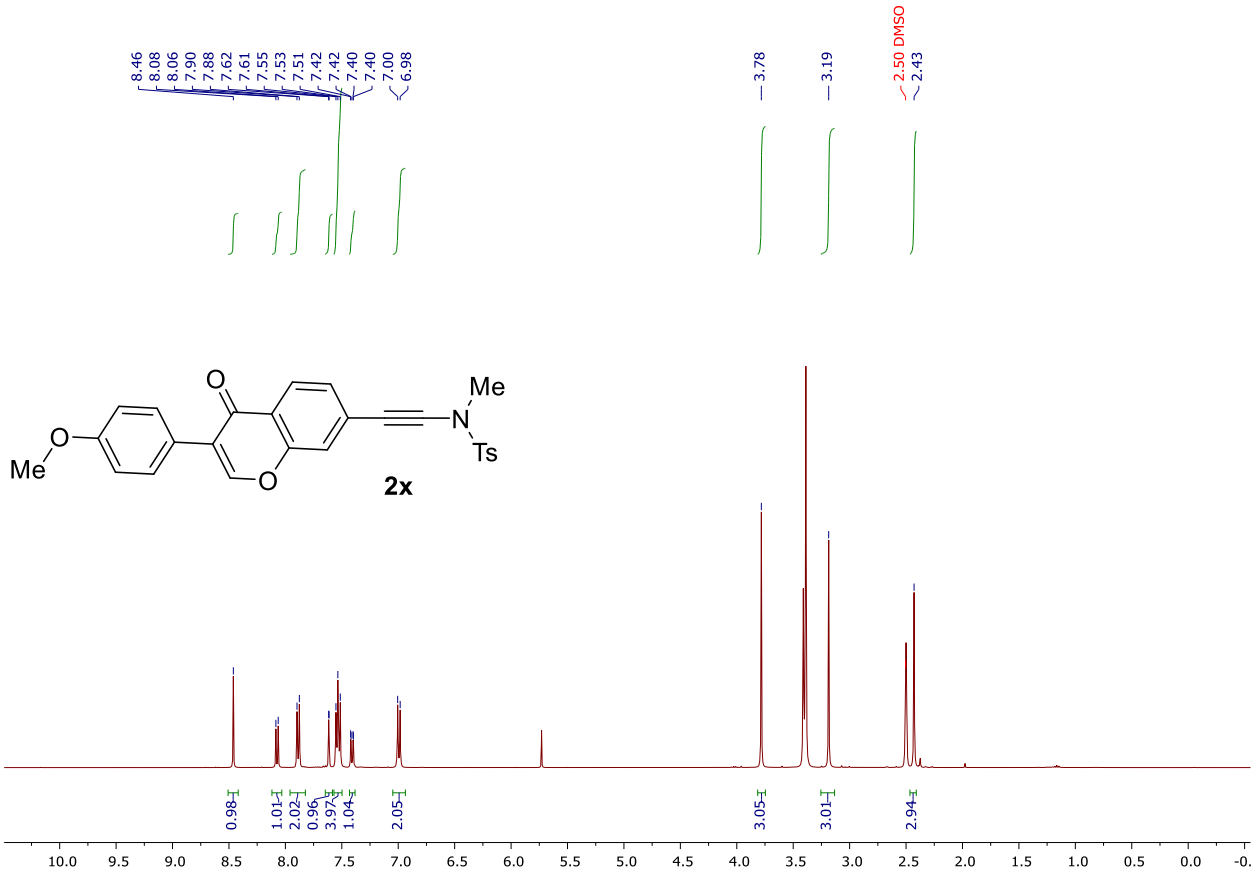
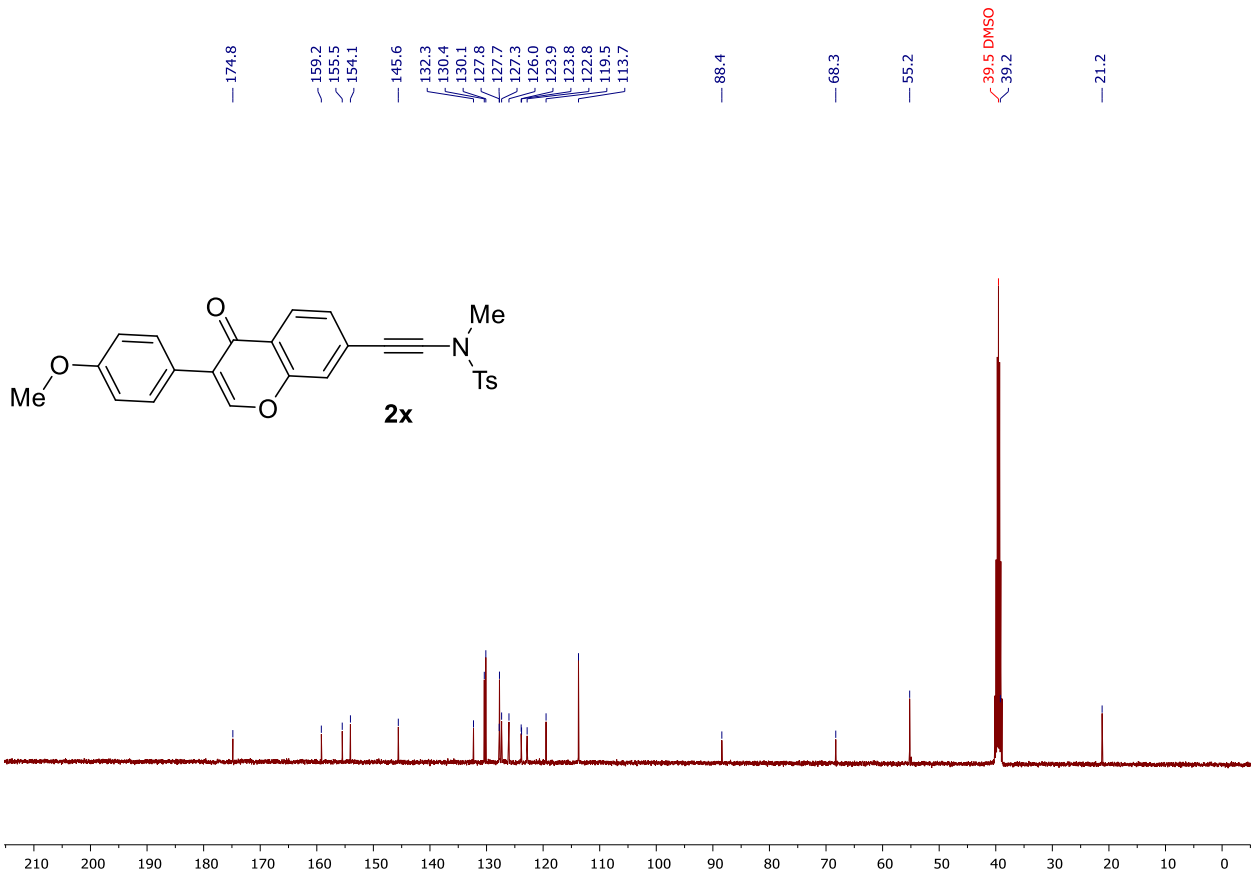


^{1}H NMR (400 MHz, DMSO-d_6) of **2x**



^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) of **2x**



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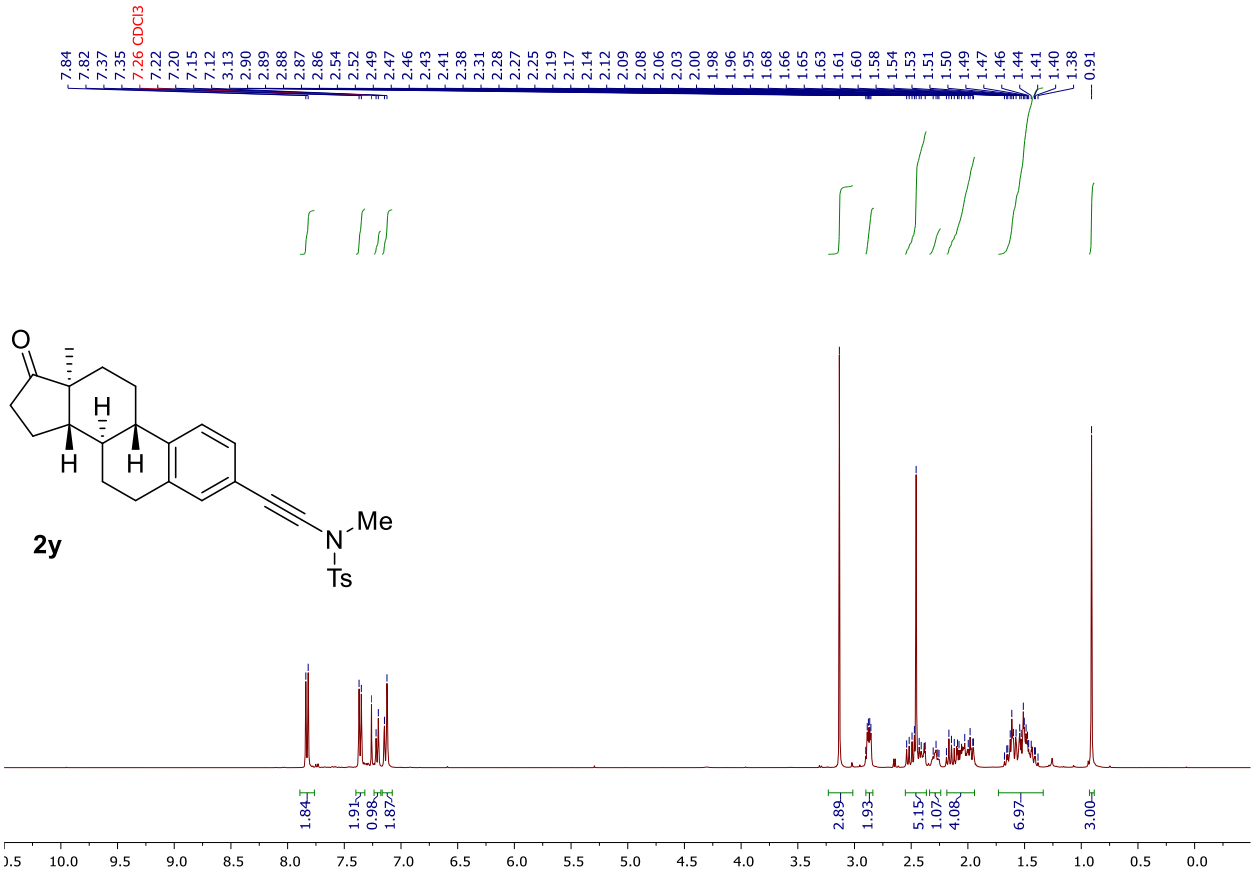

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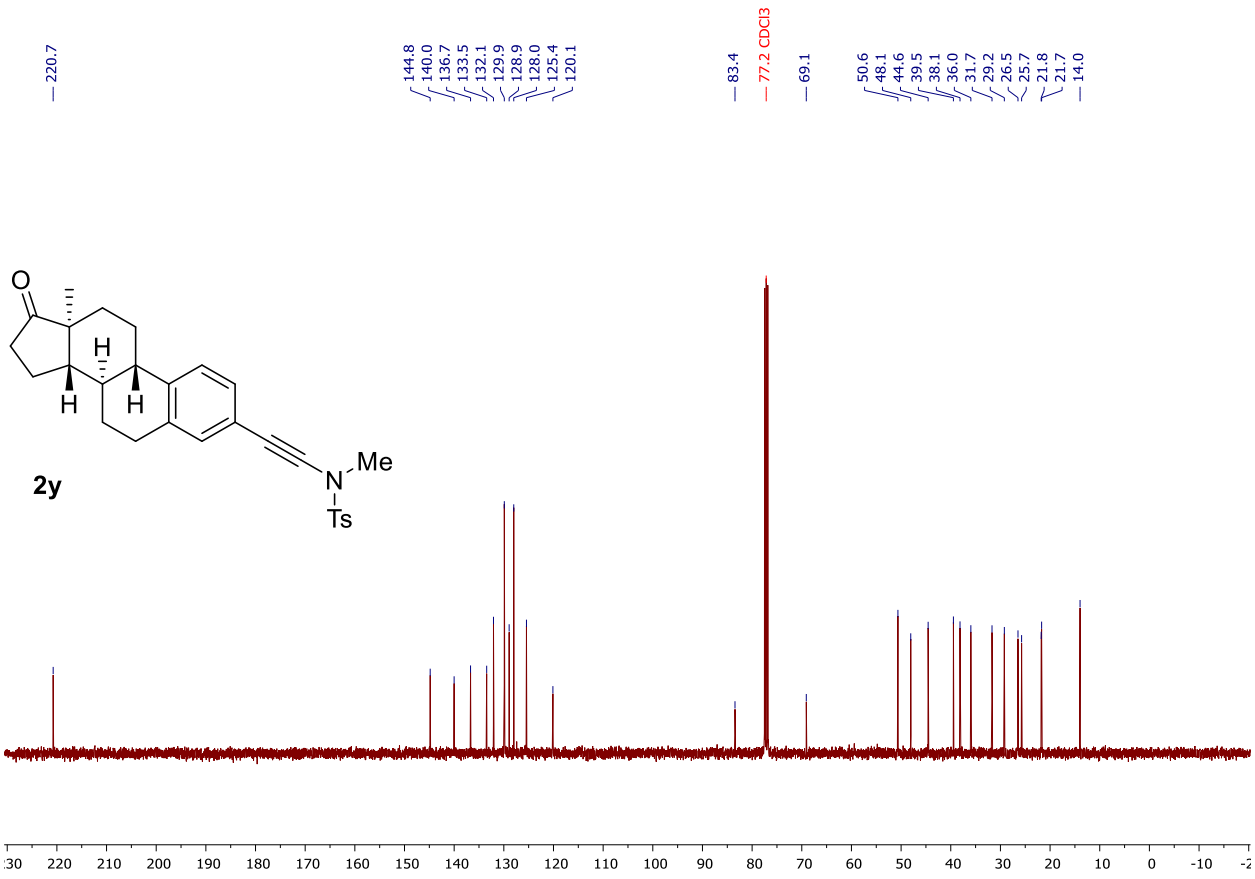
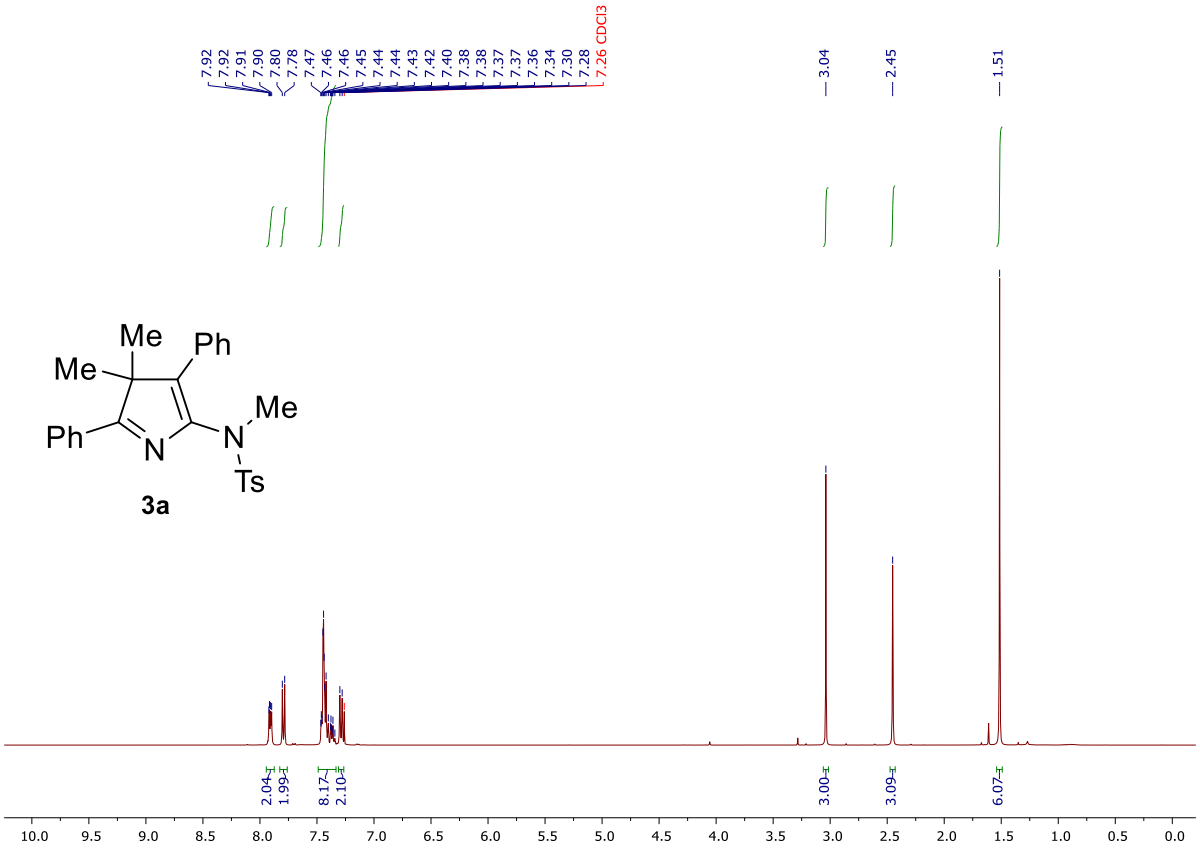
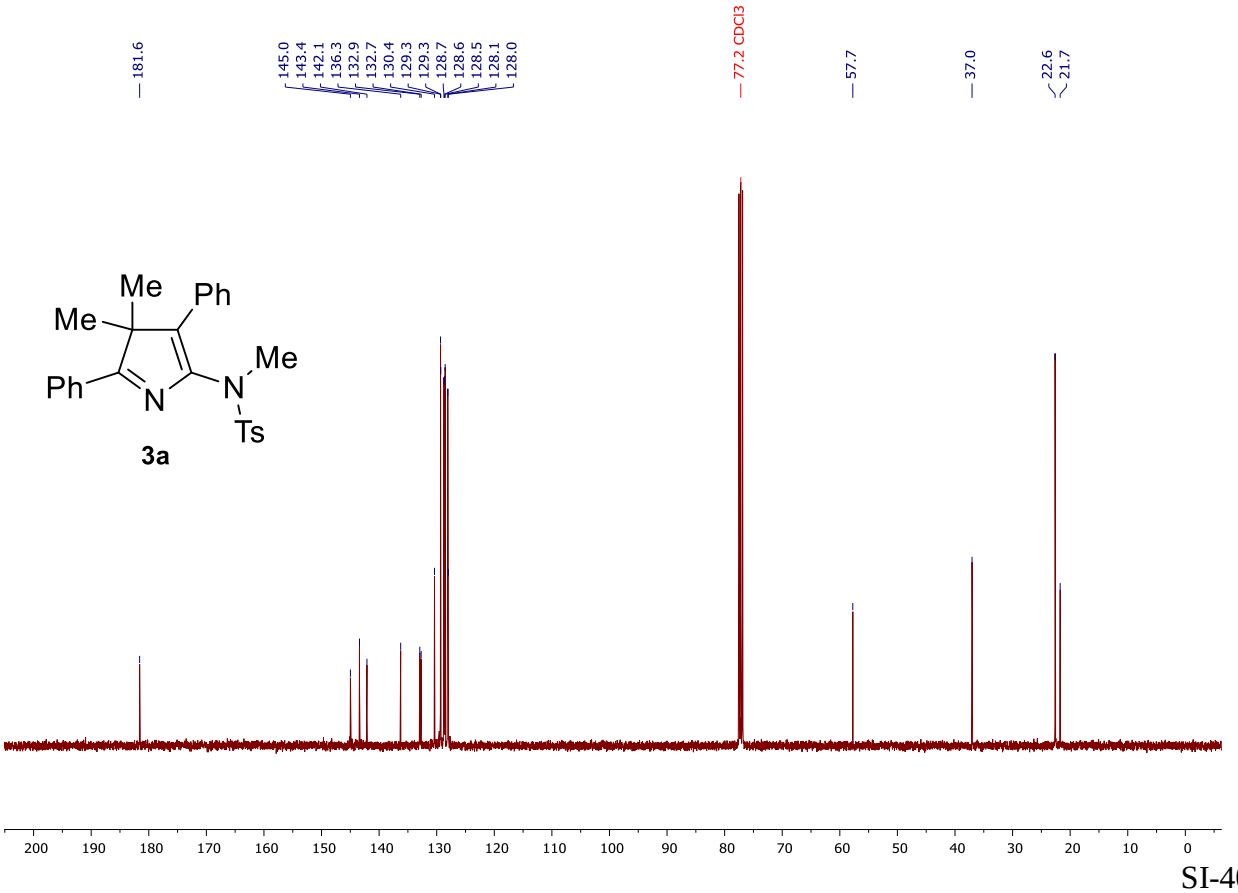


4.3.NMR Spectra of 3*H*-Pyrroles 3

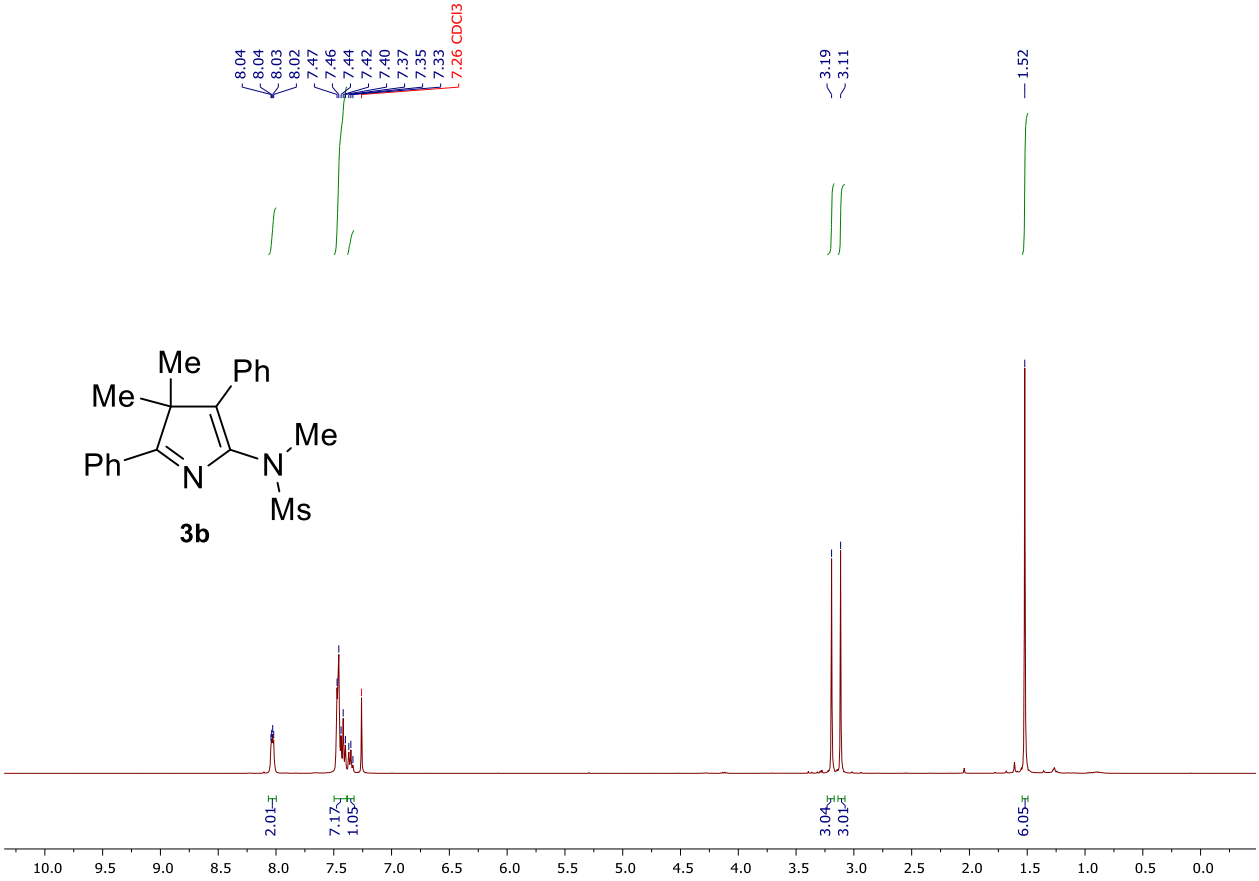
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



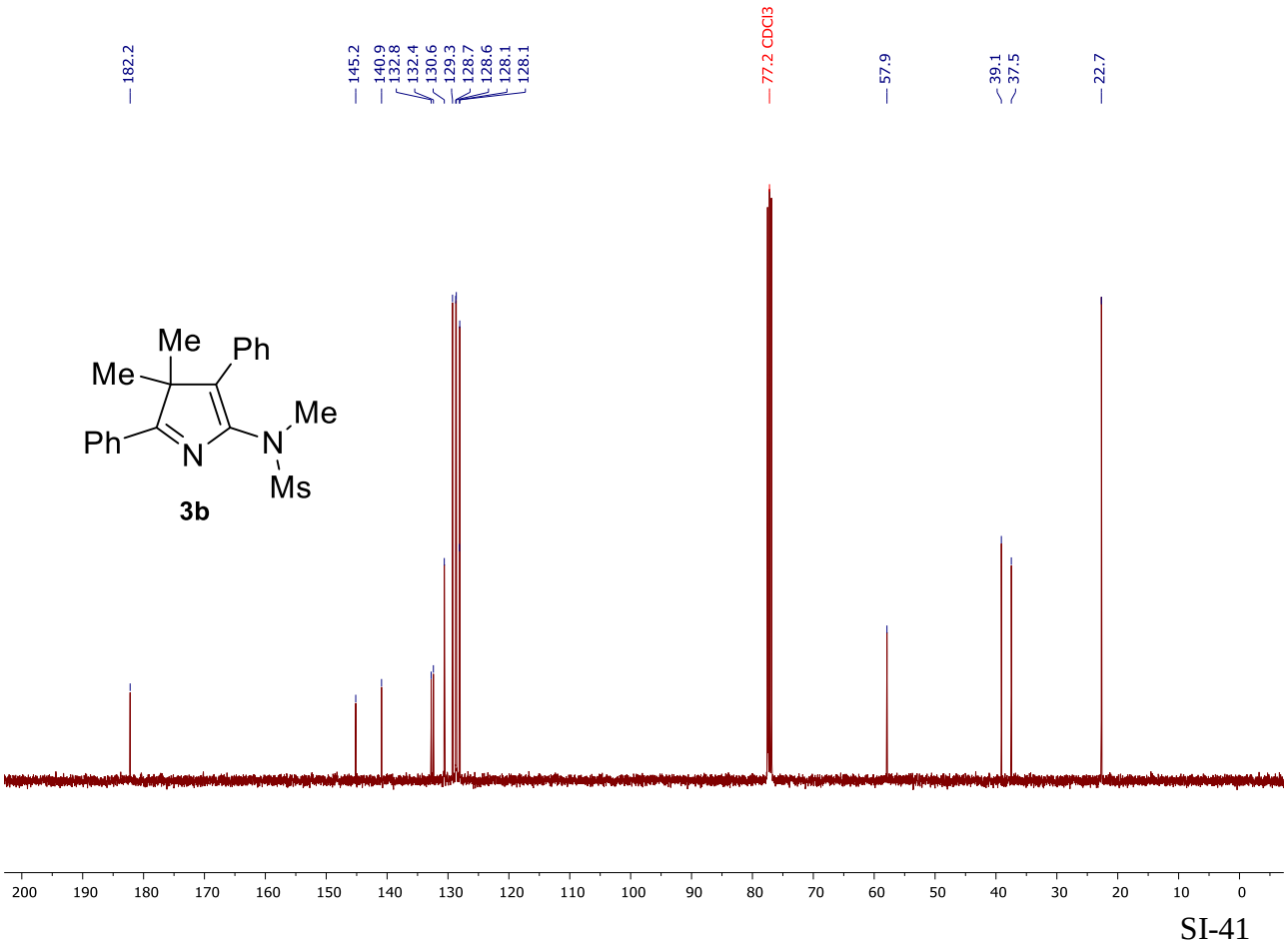
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3a**



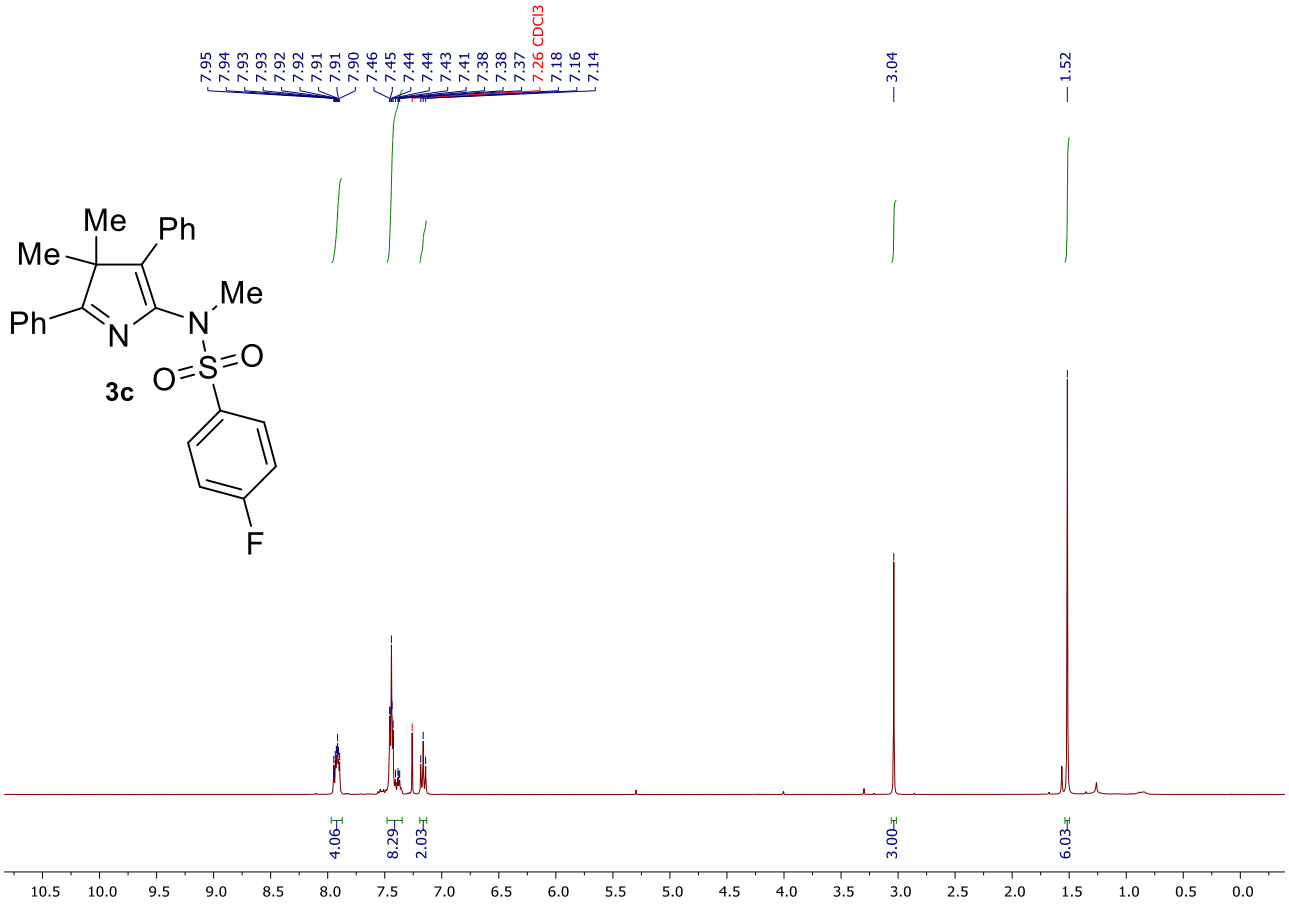
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



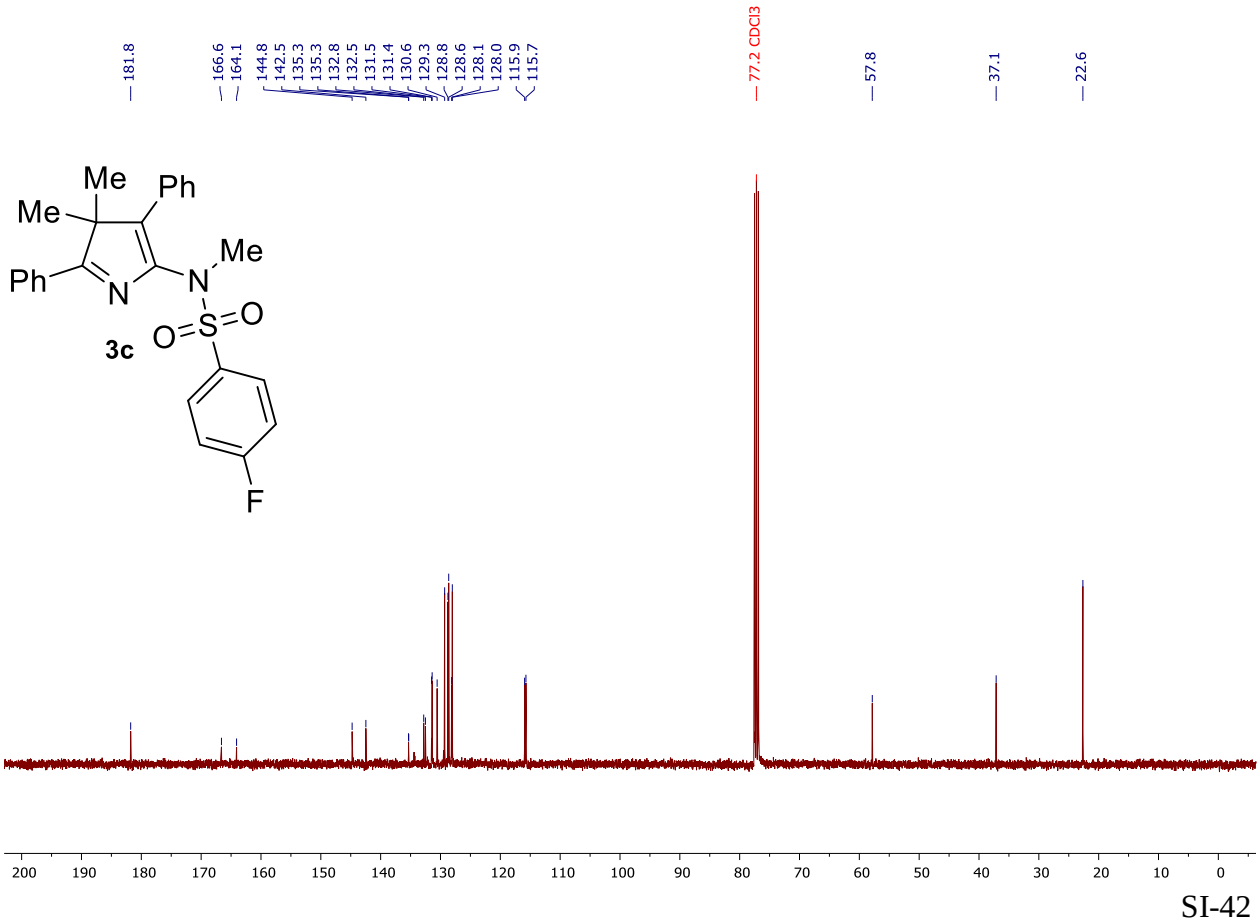
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3b**



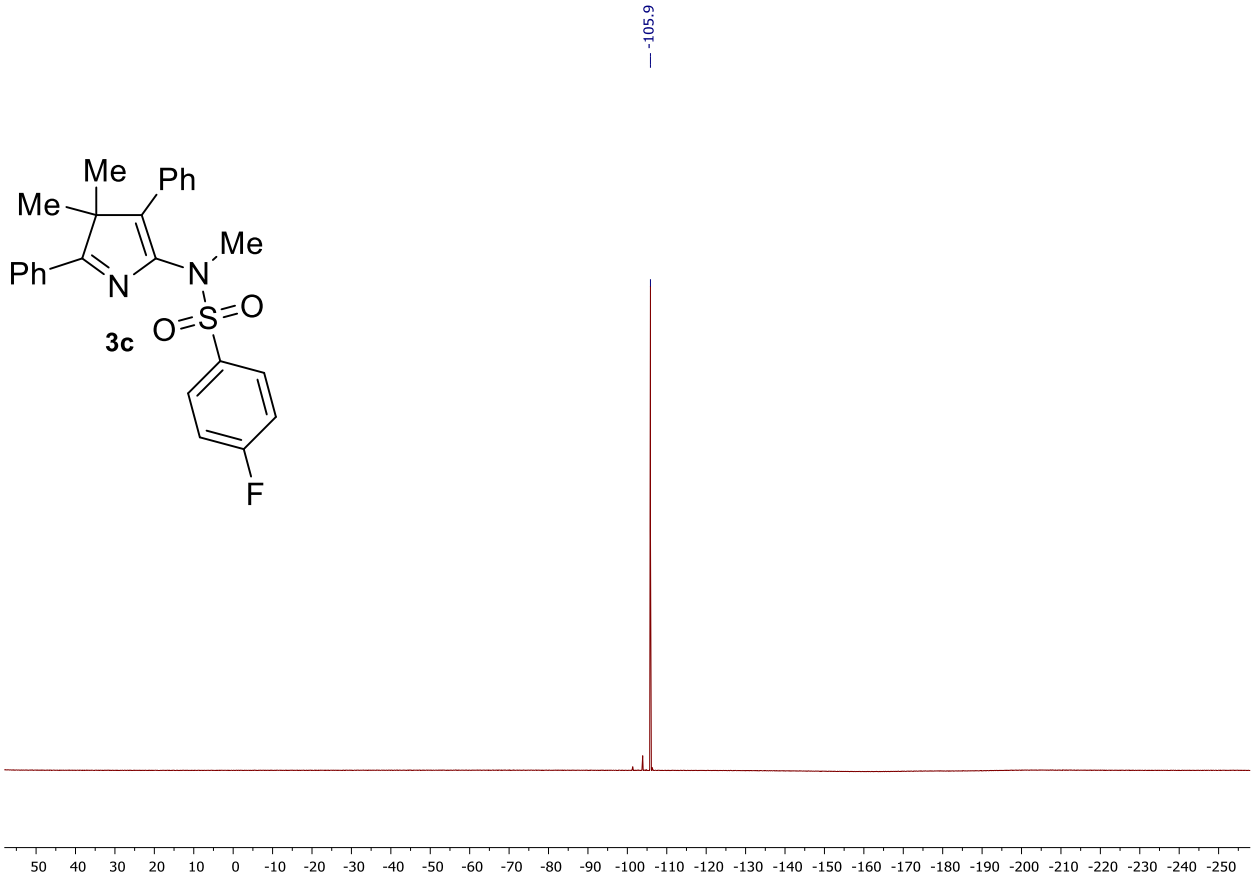
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



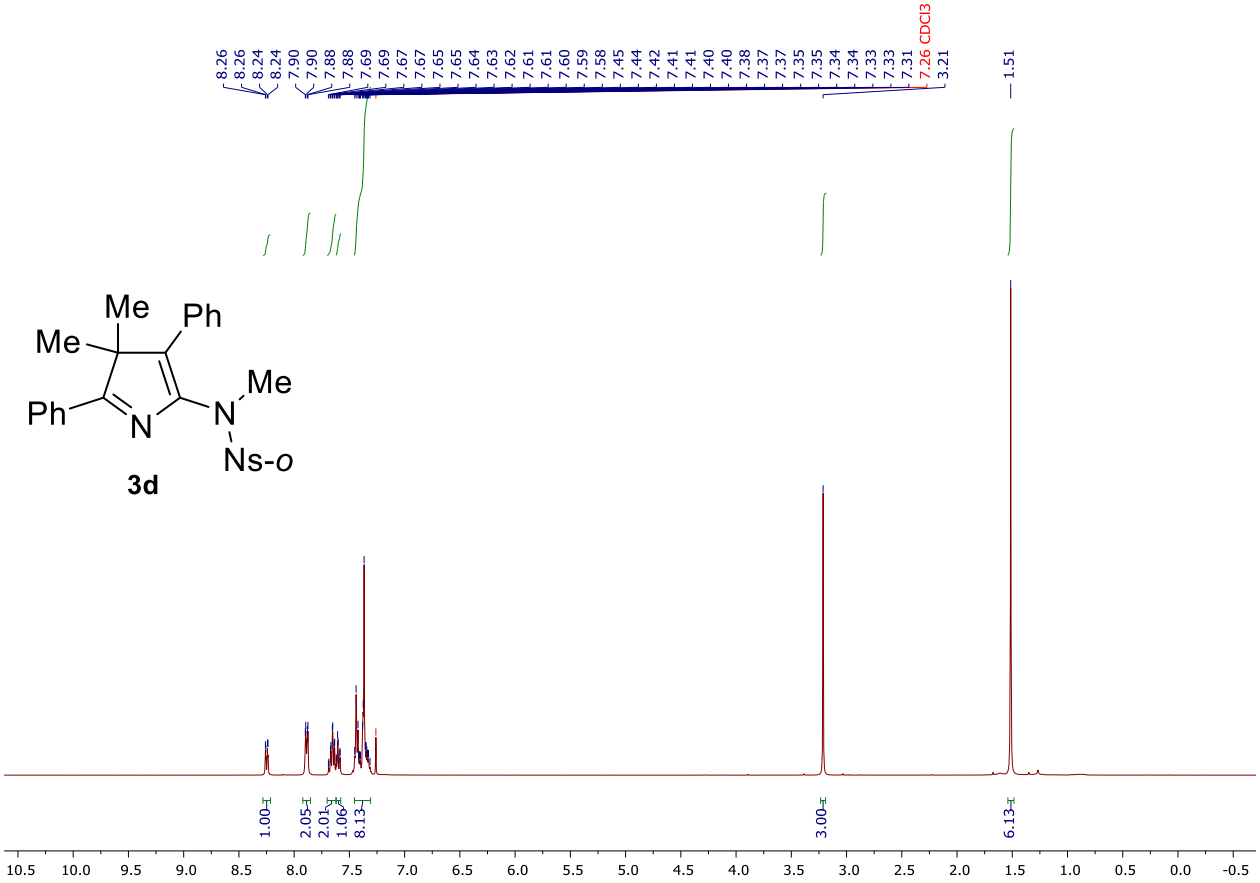
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3c**



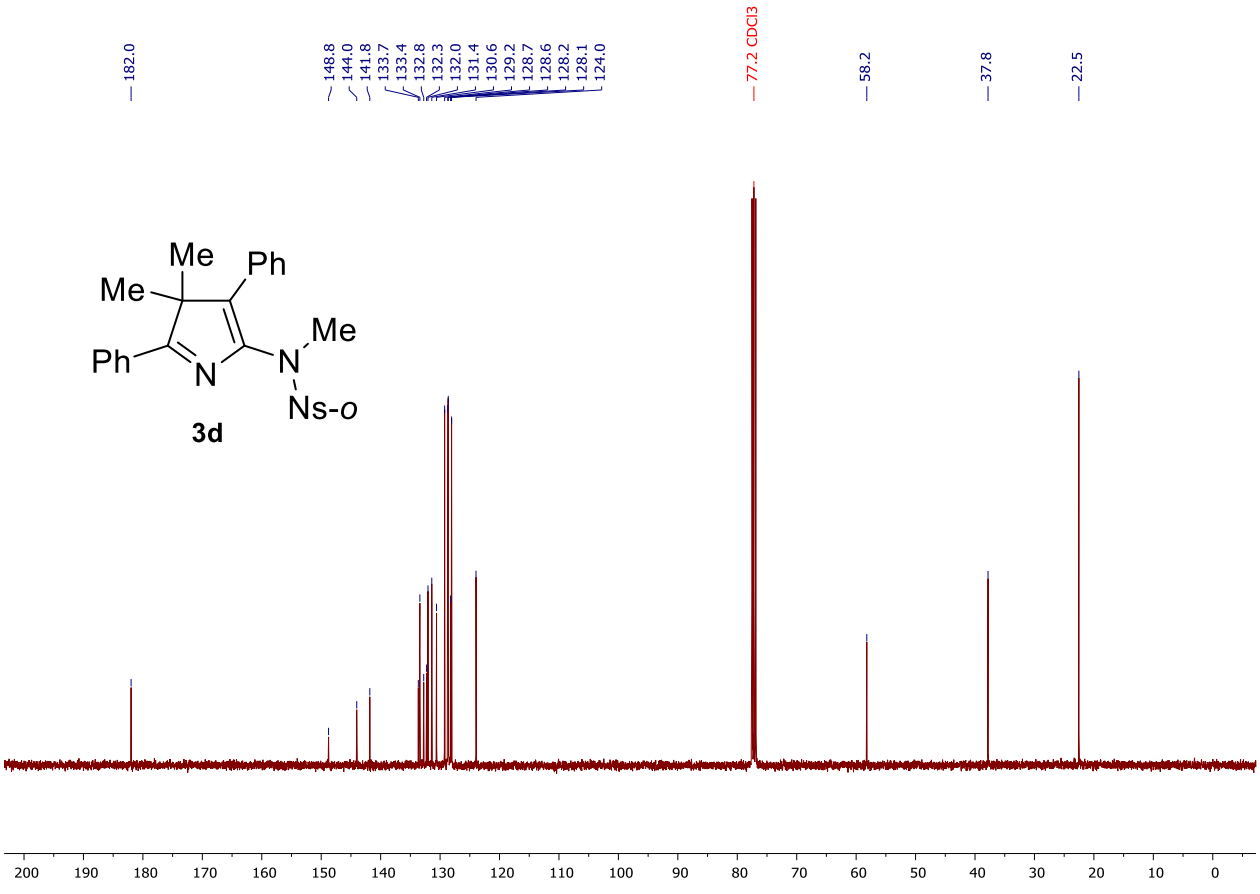
^{19}F NMR (376 MHz, $CDCl_3$) of **3c**



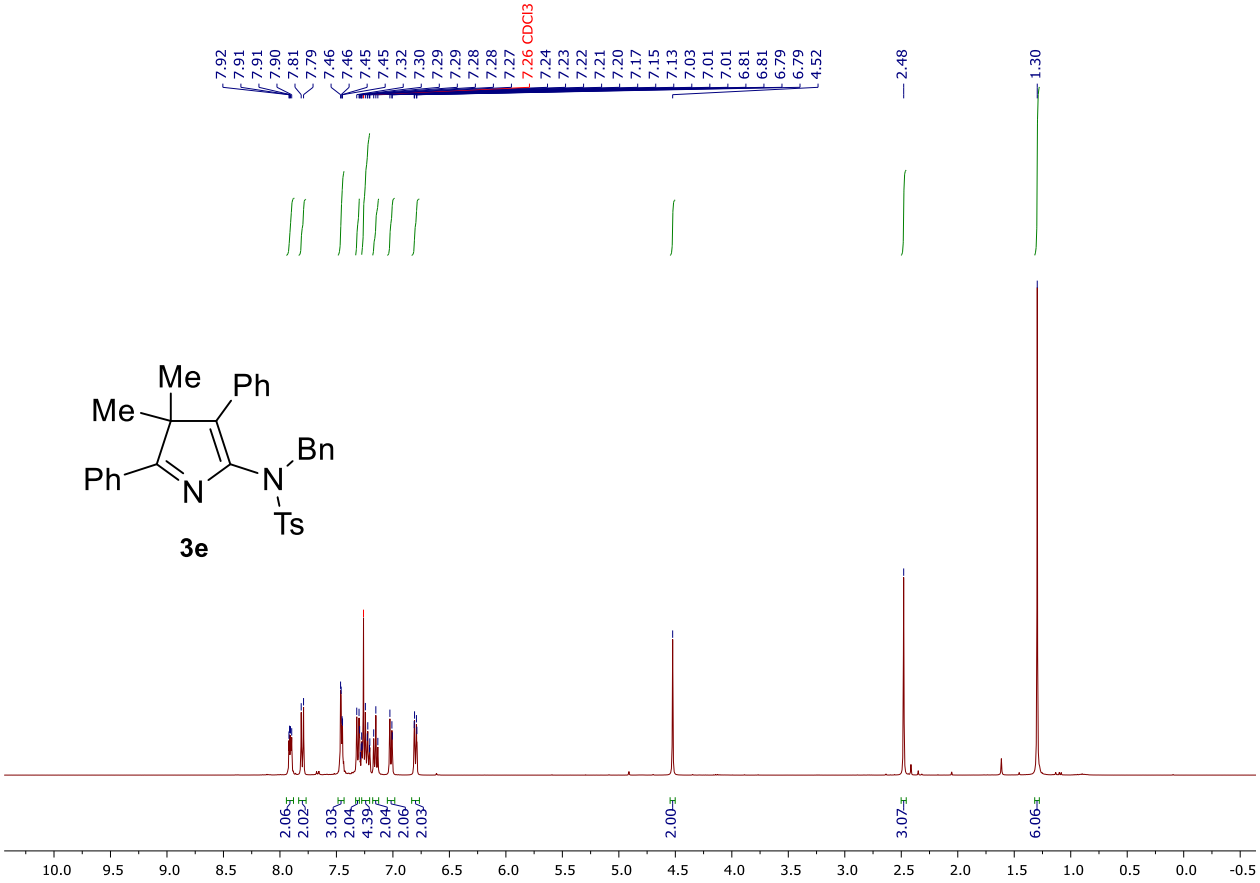
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3d**



^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



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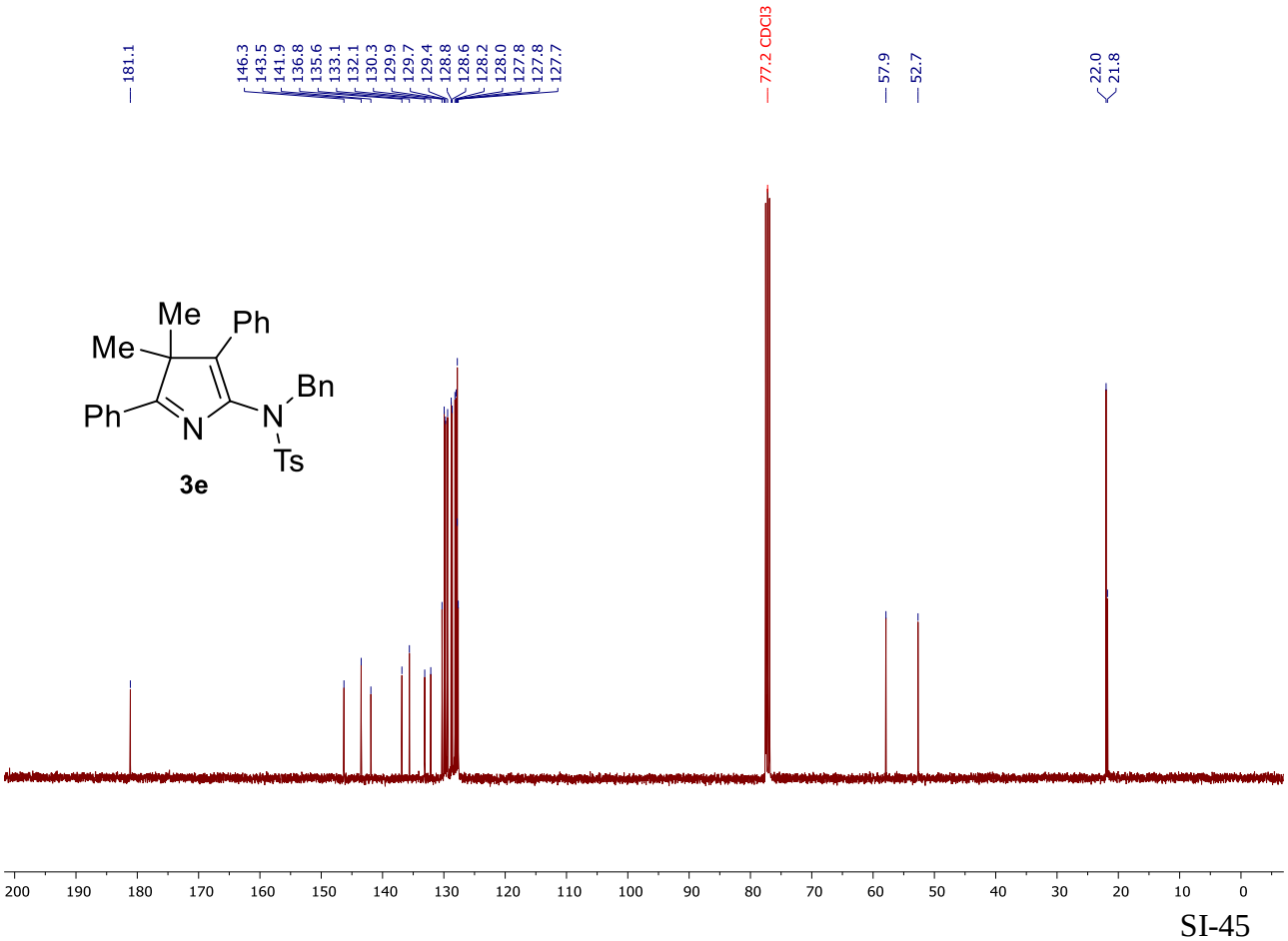
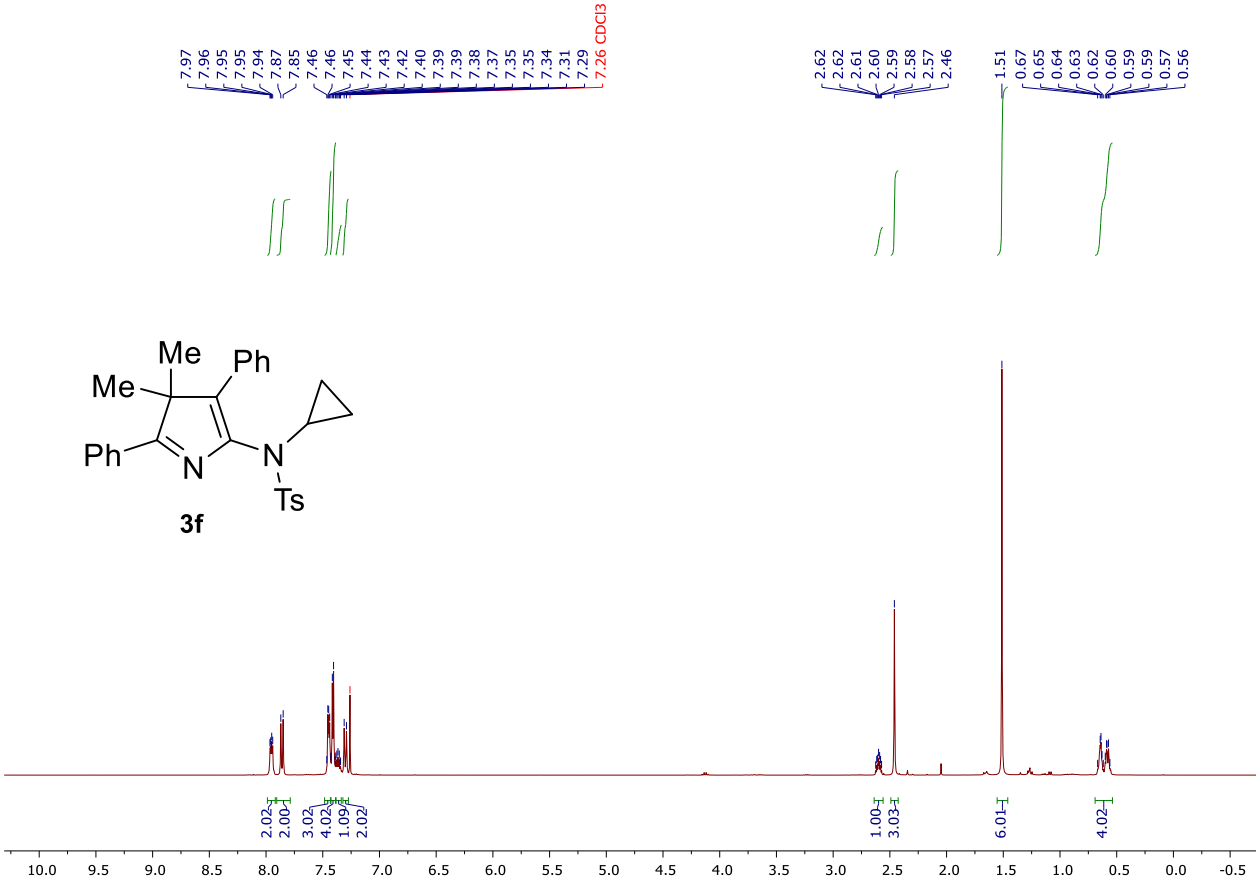
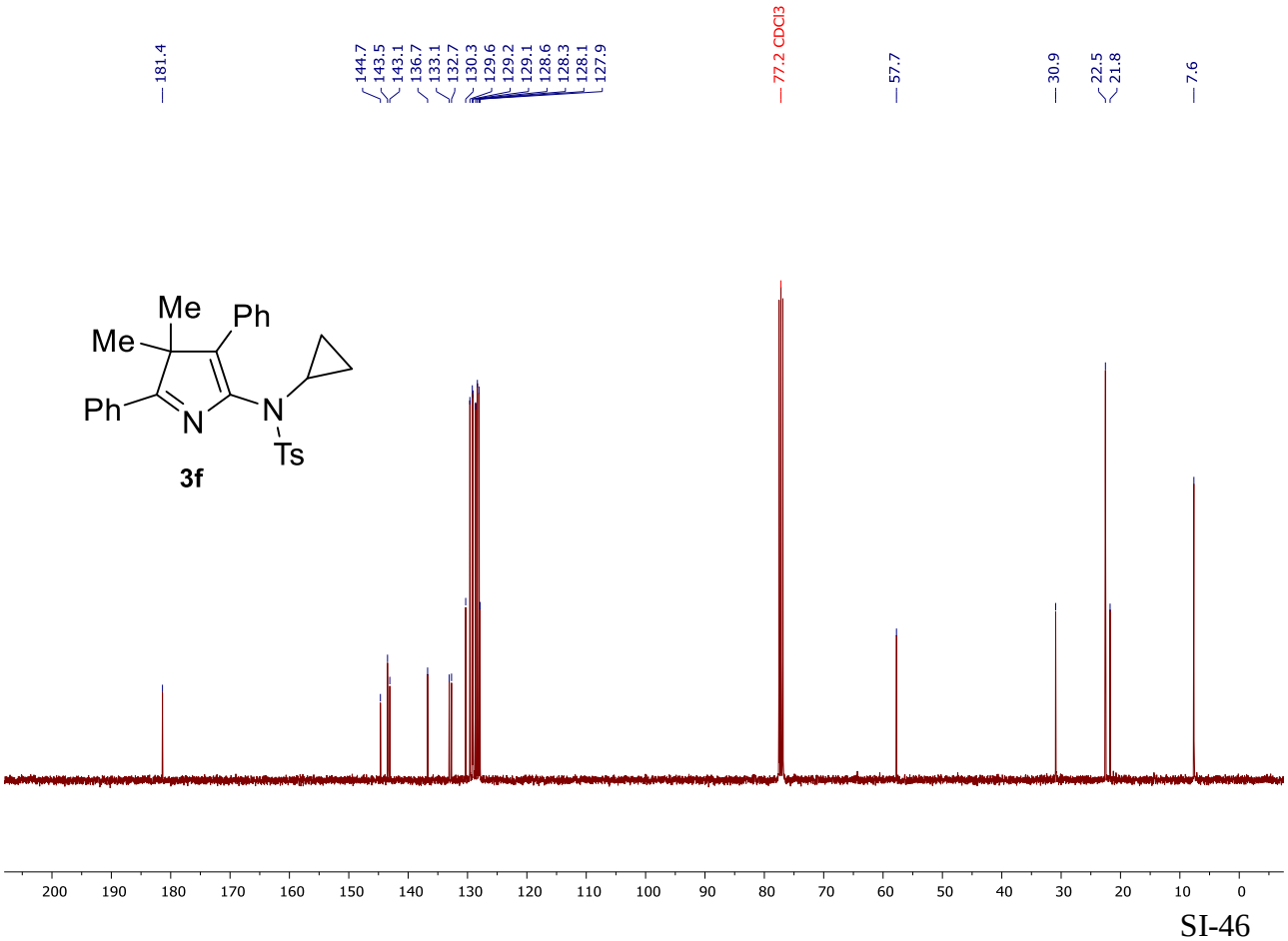


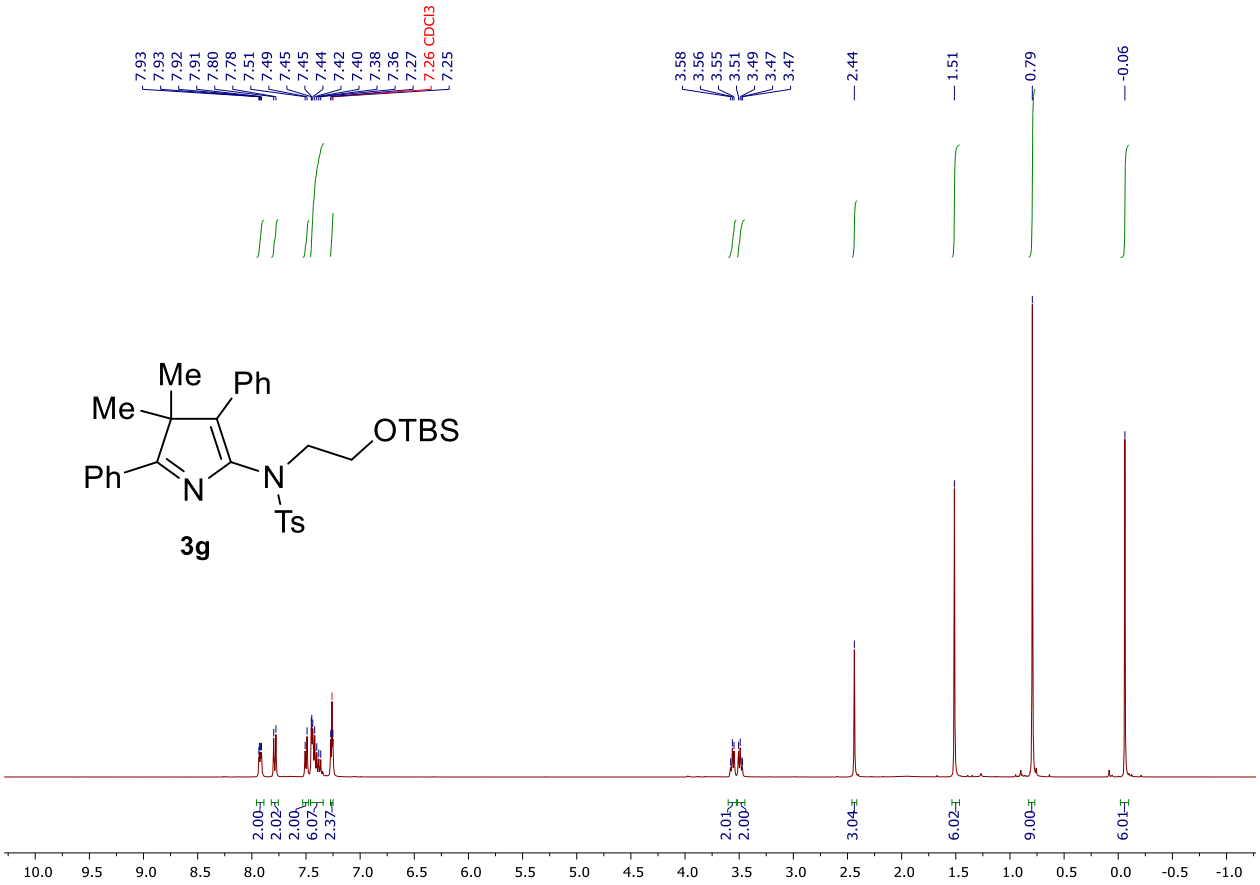
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



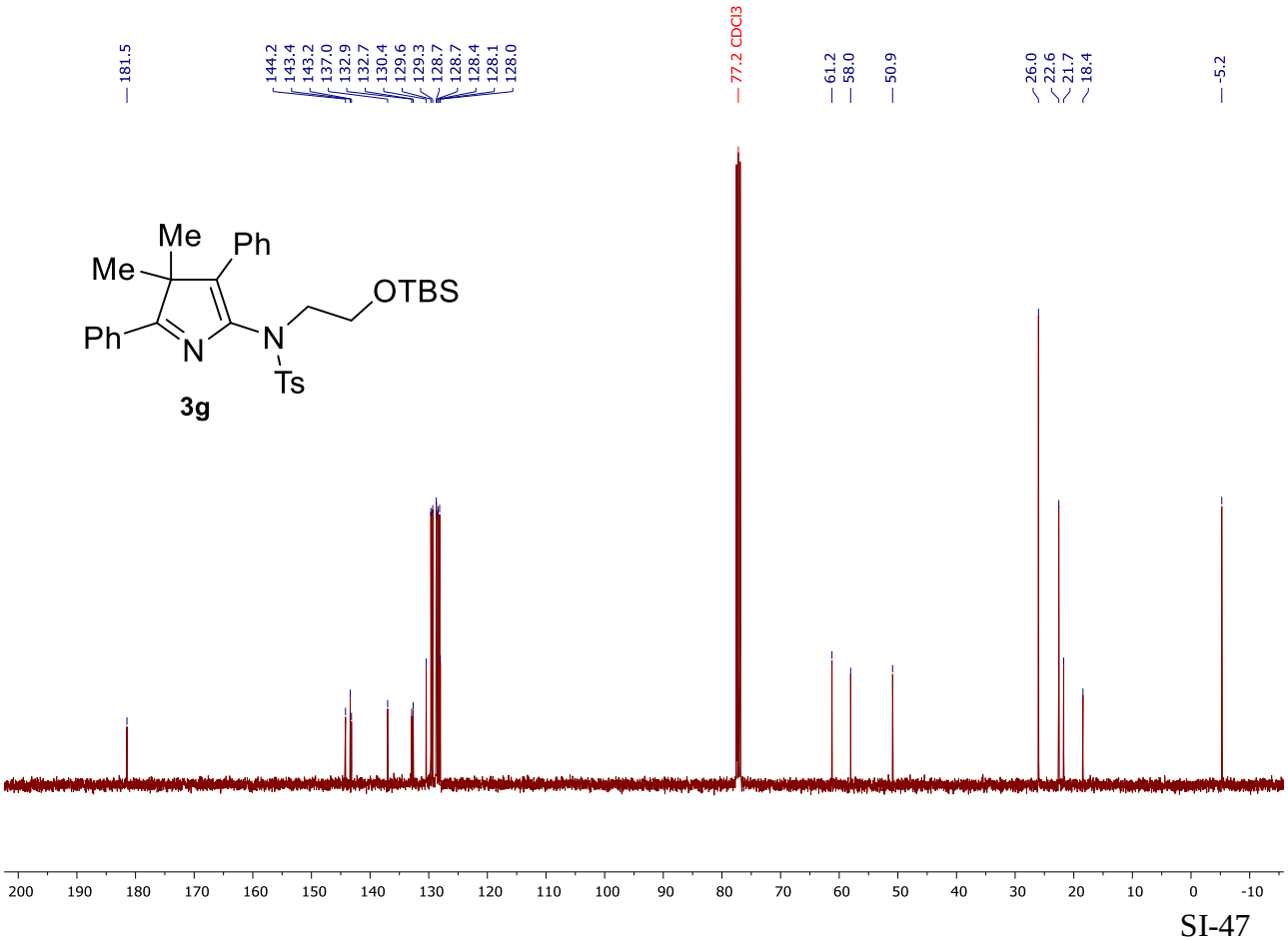
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3f**



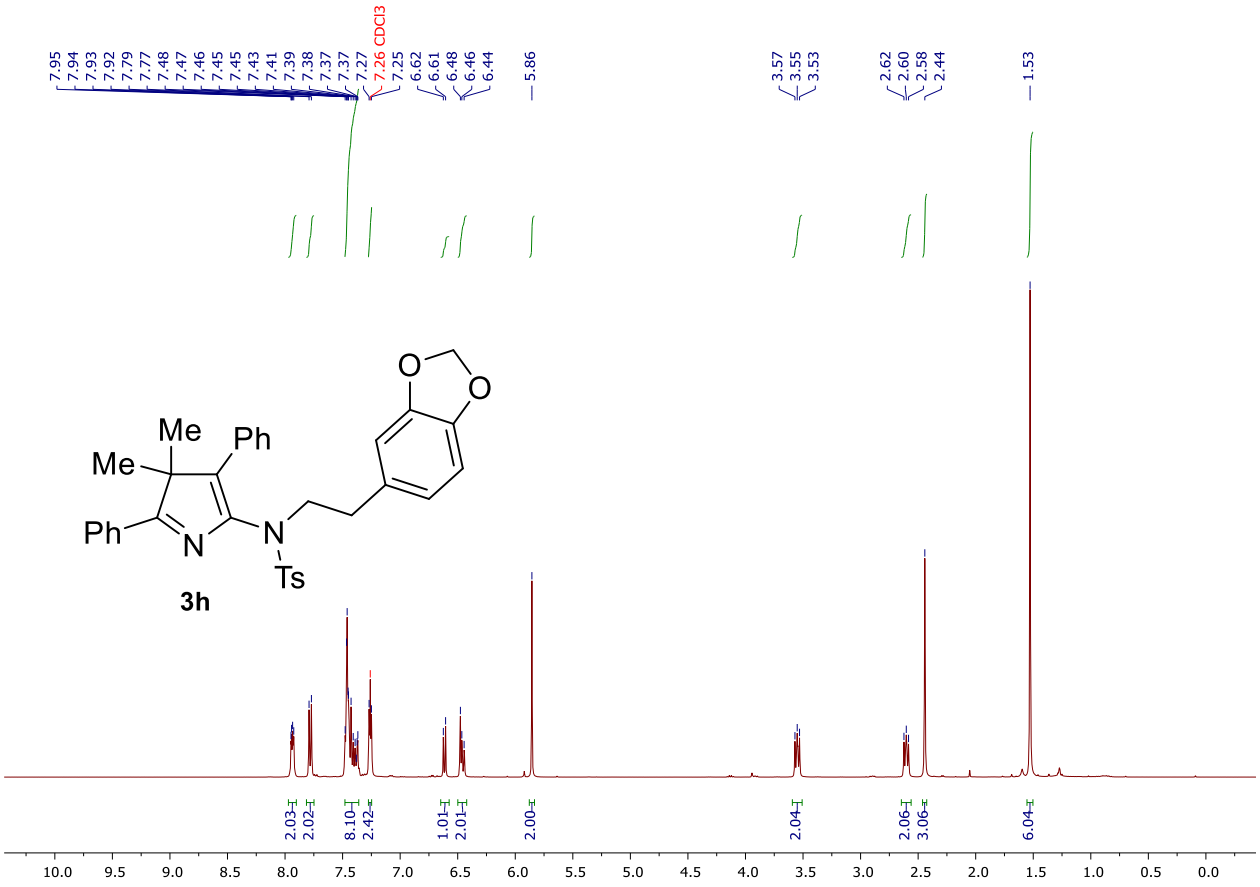
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



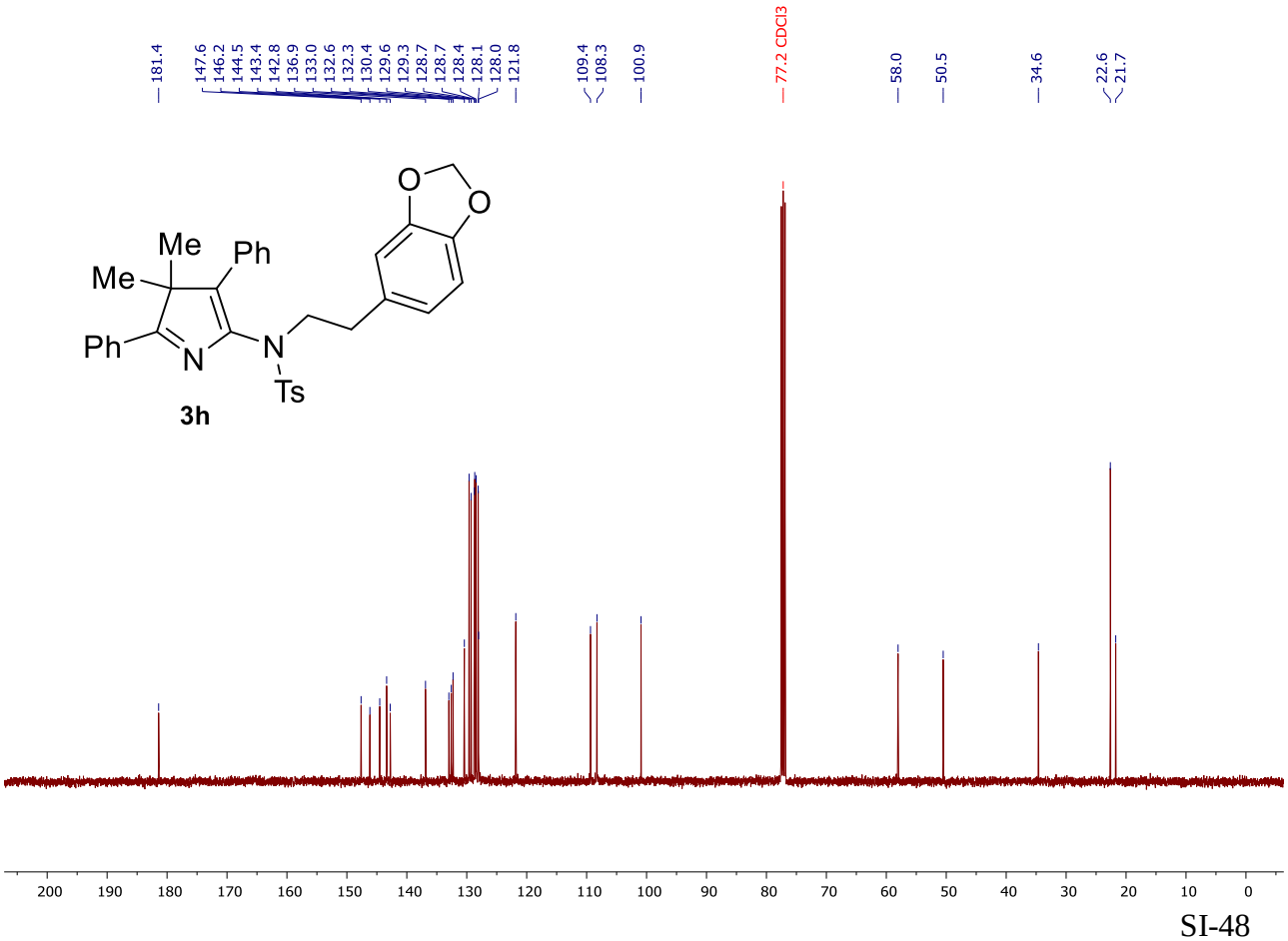
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3g**



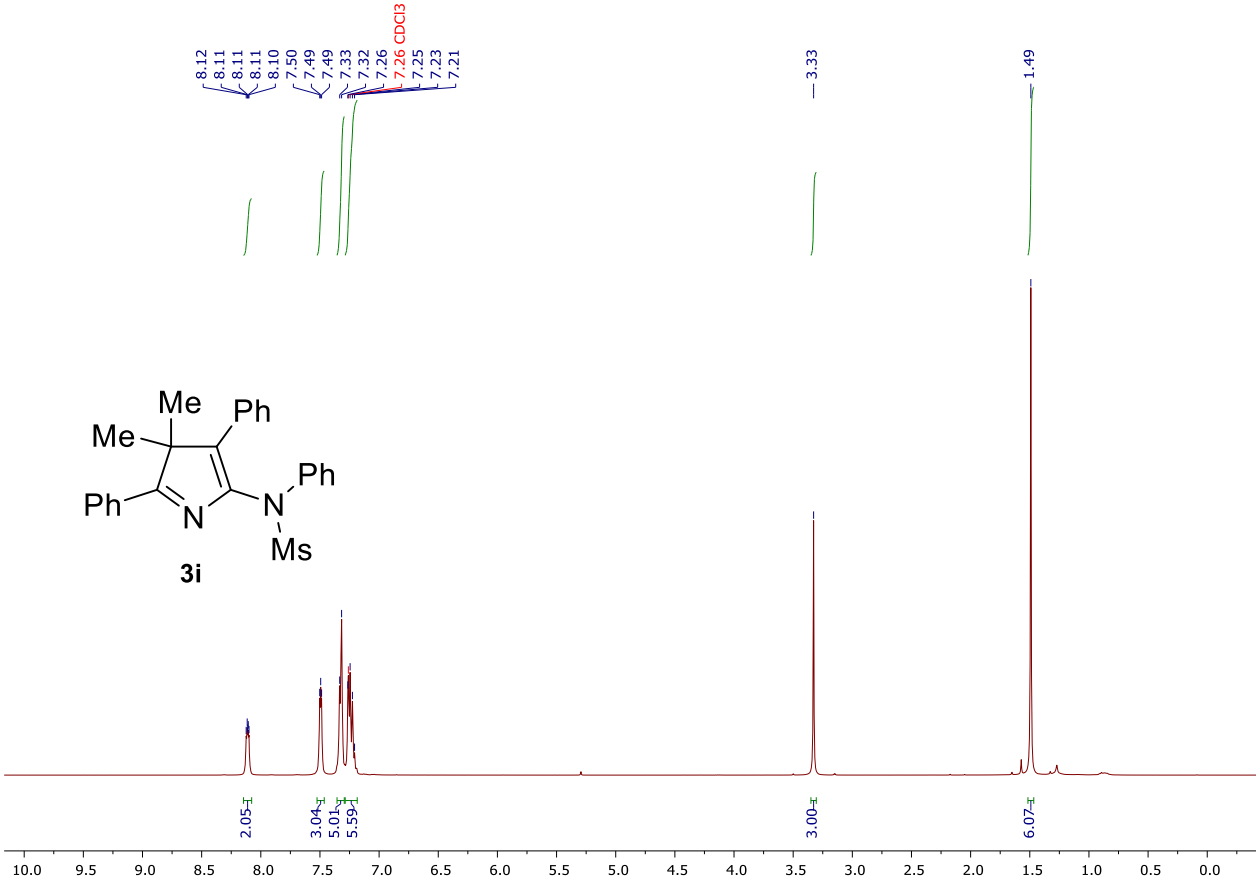
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



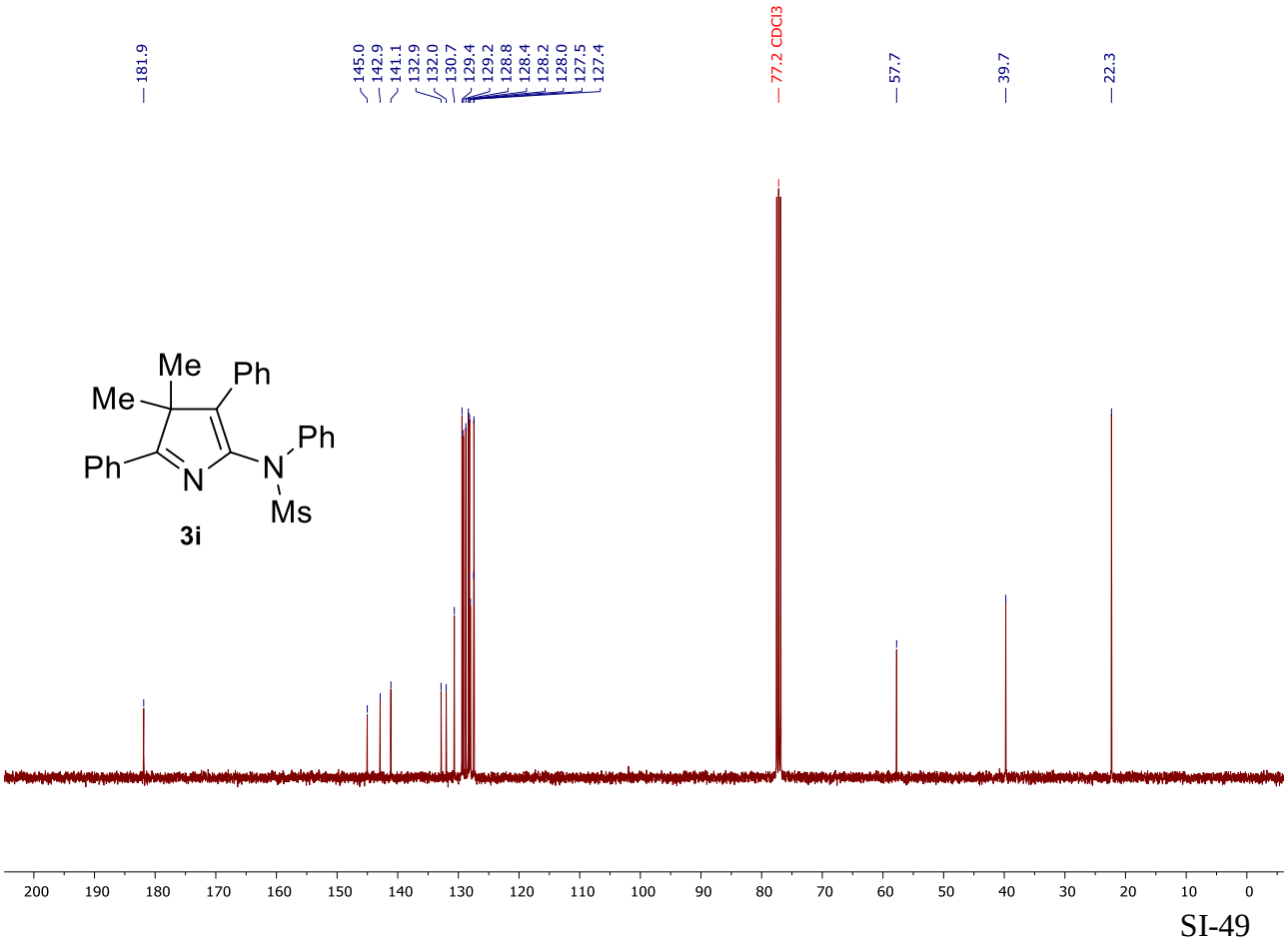
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3h**



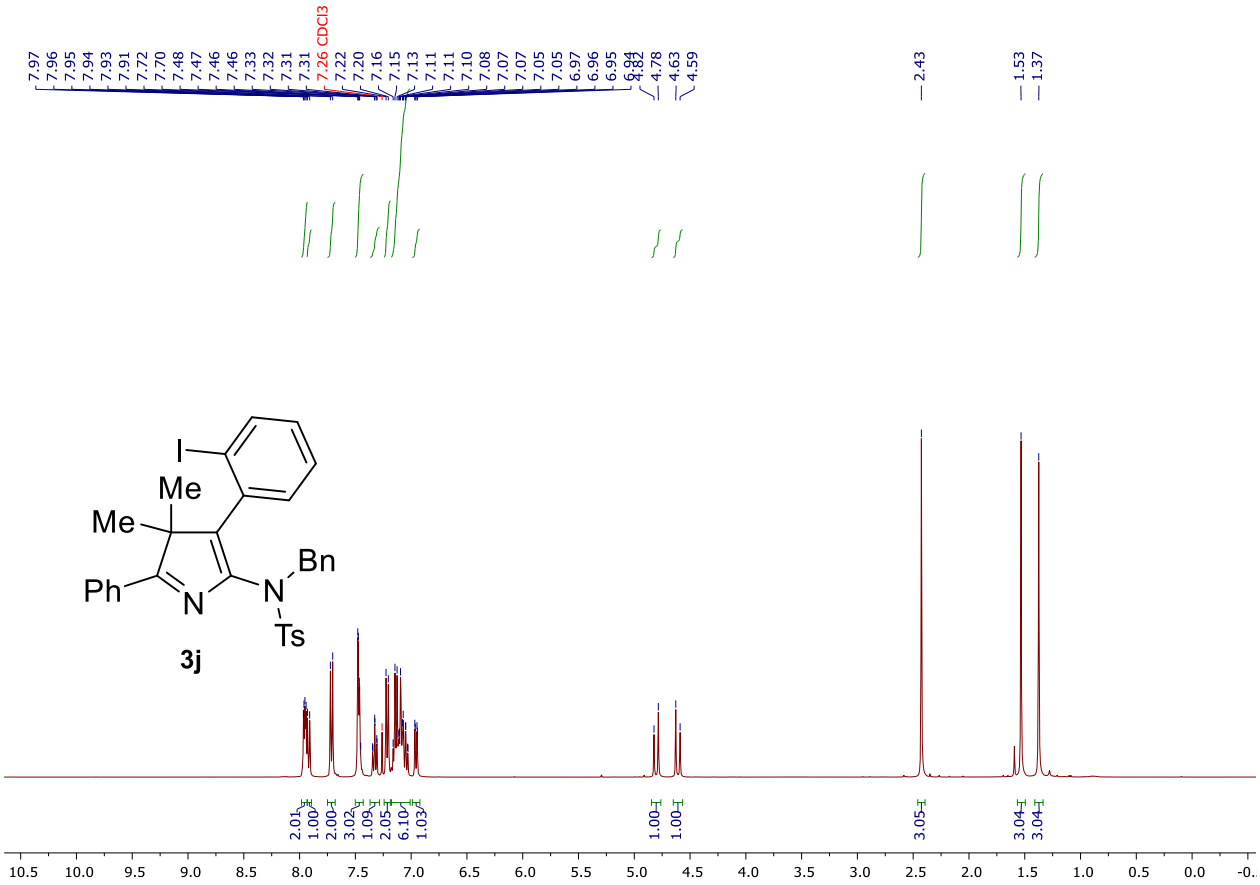
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



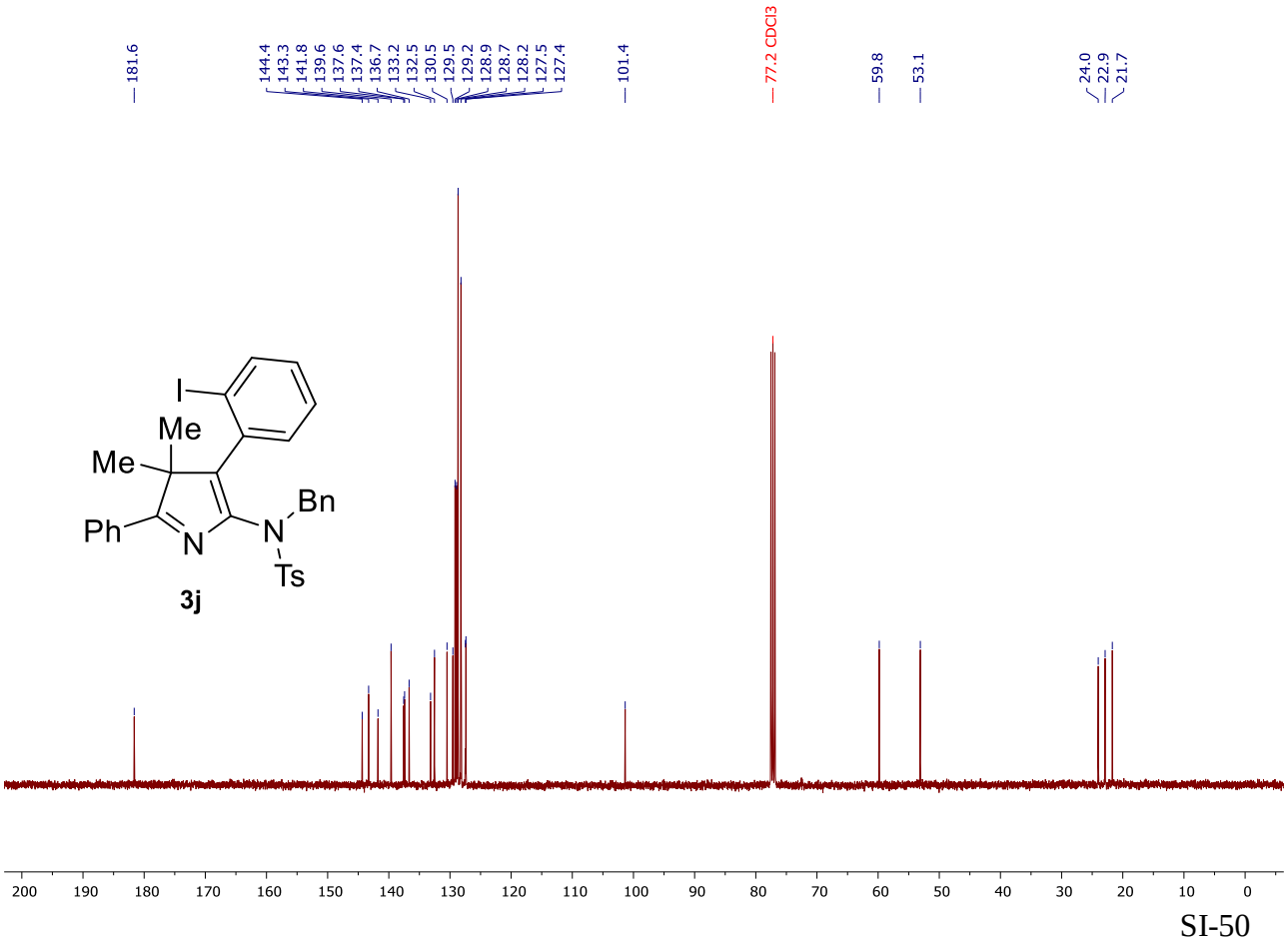
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3i**



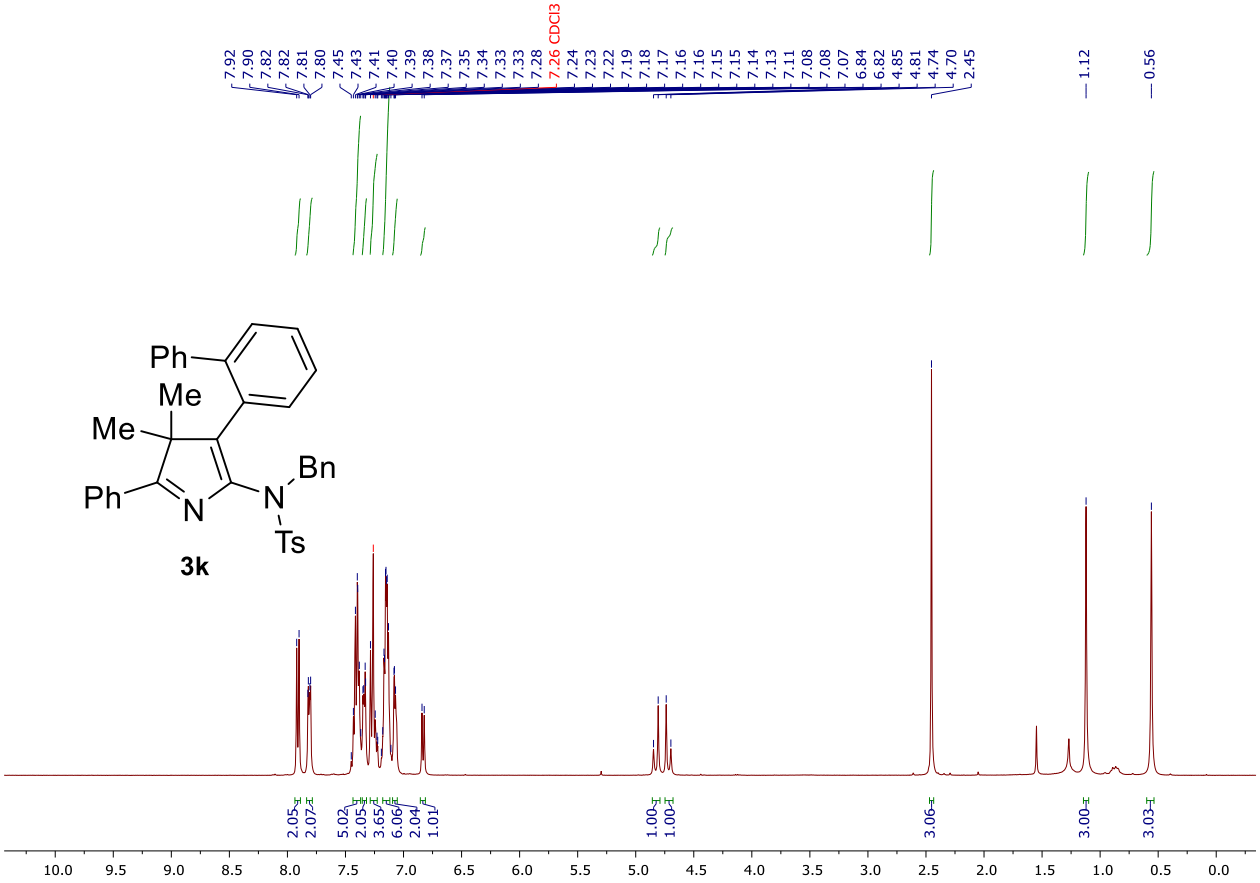
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



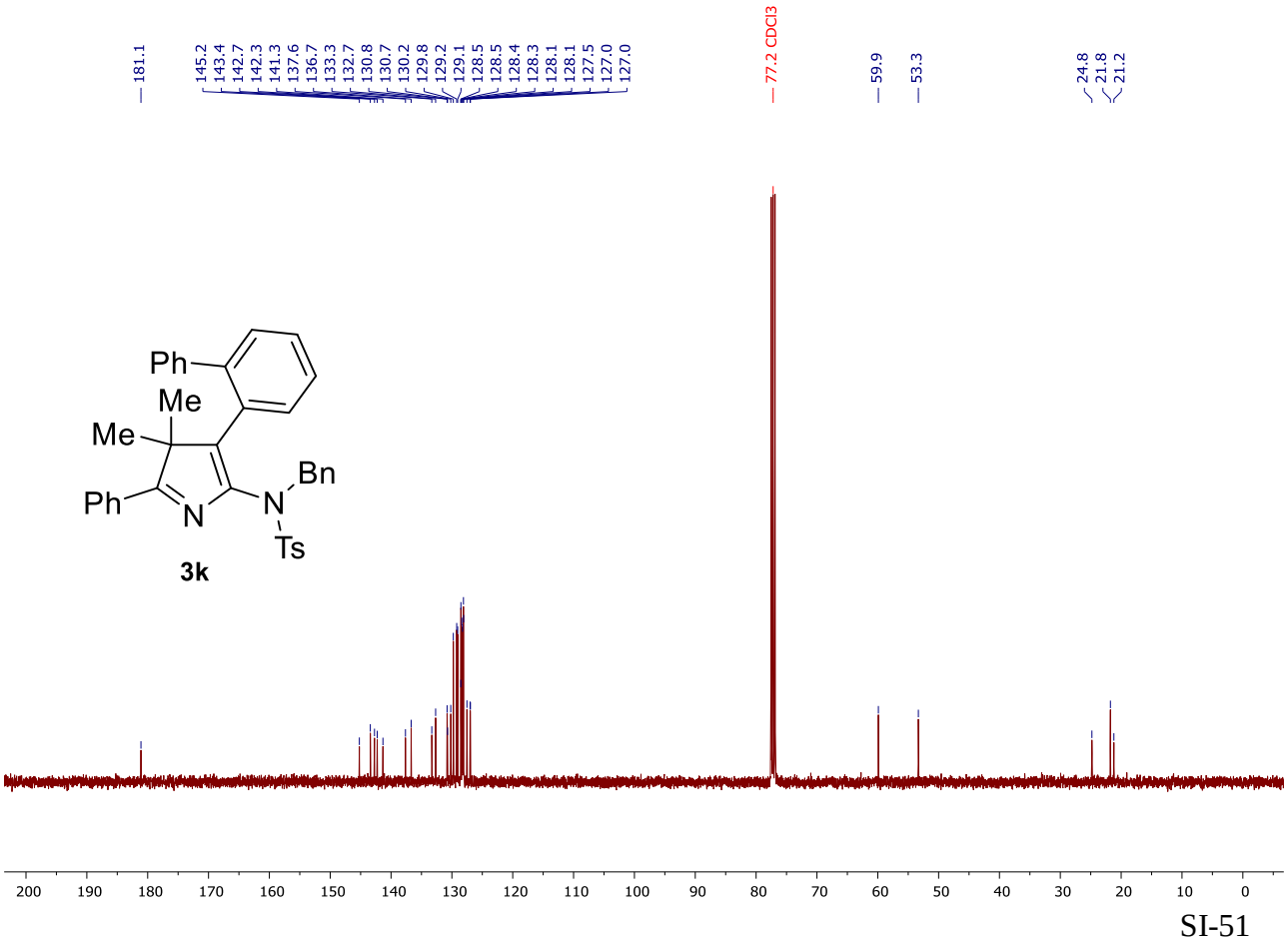
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3j**



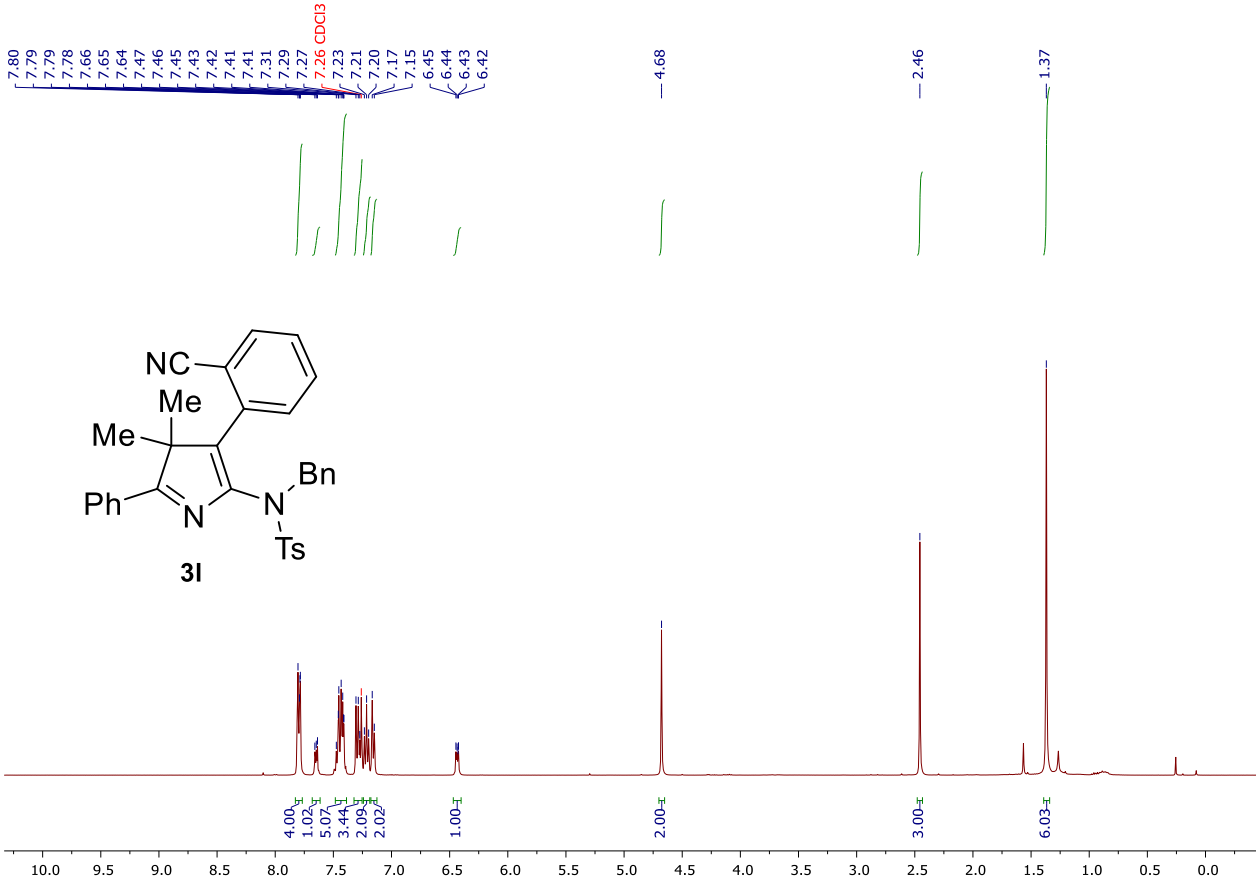
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



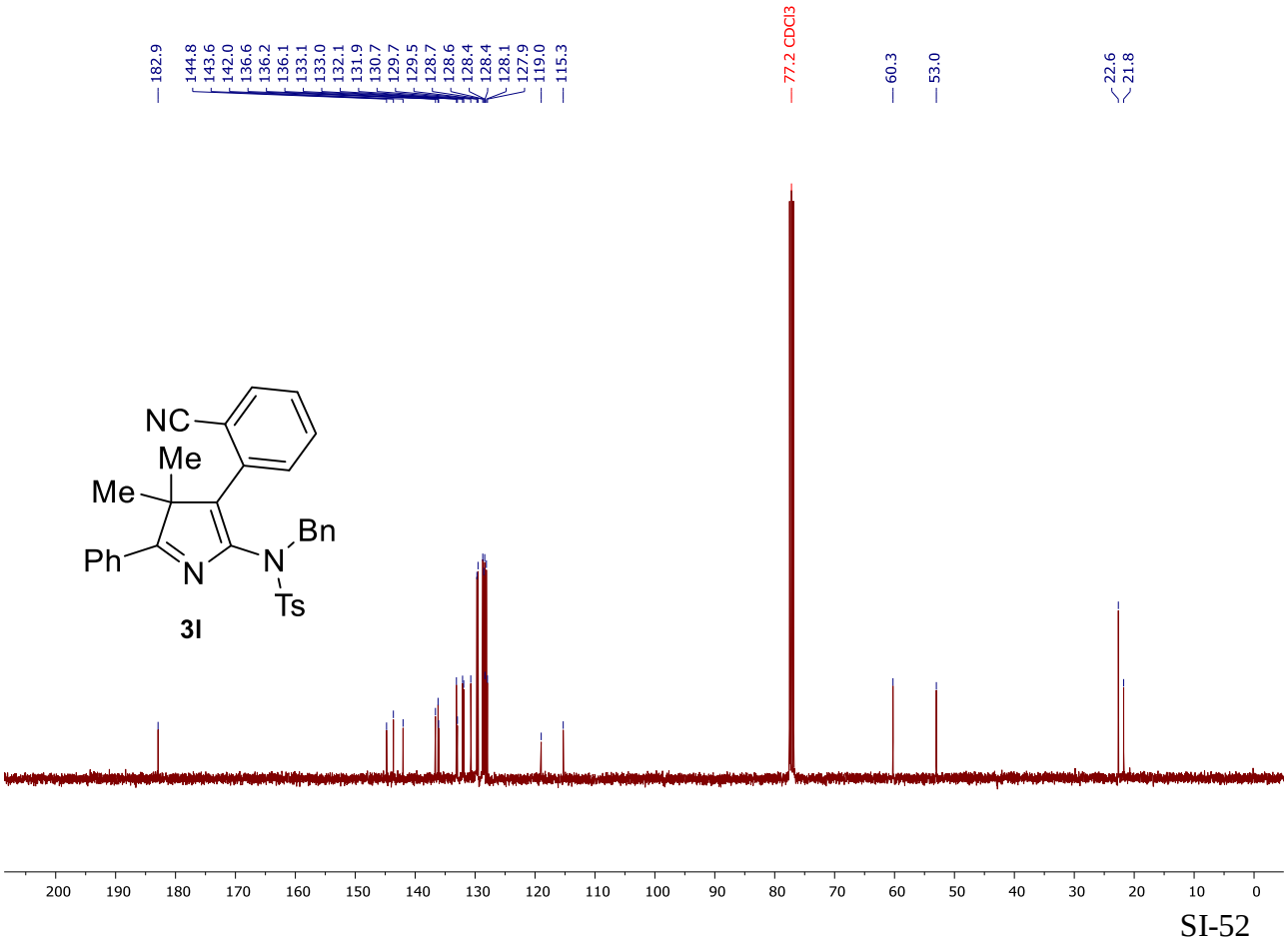
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3k**



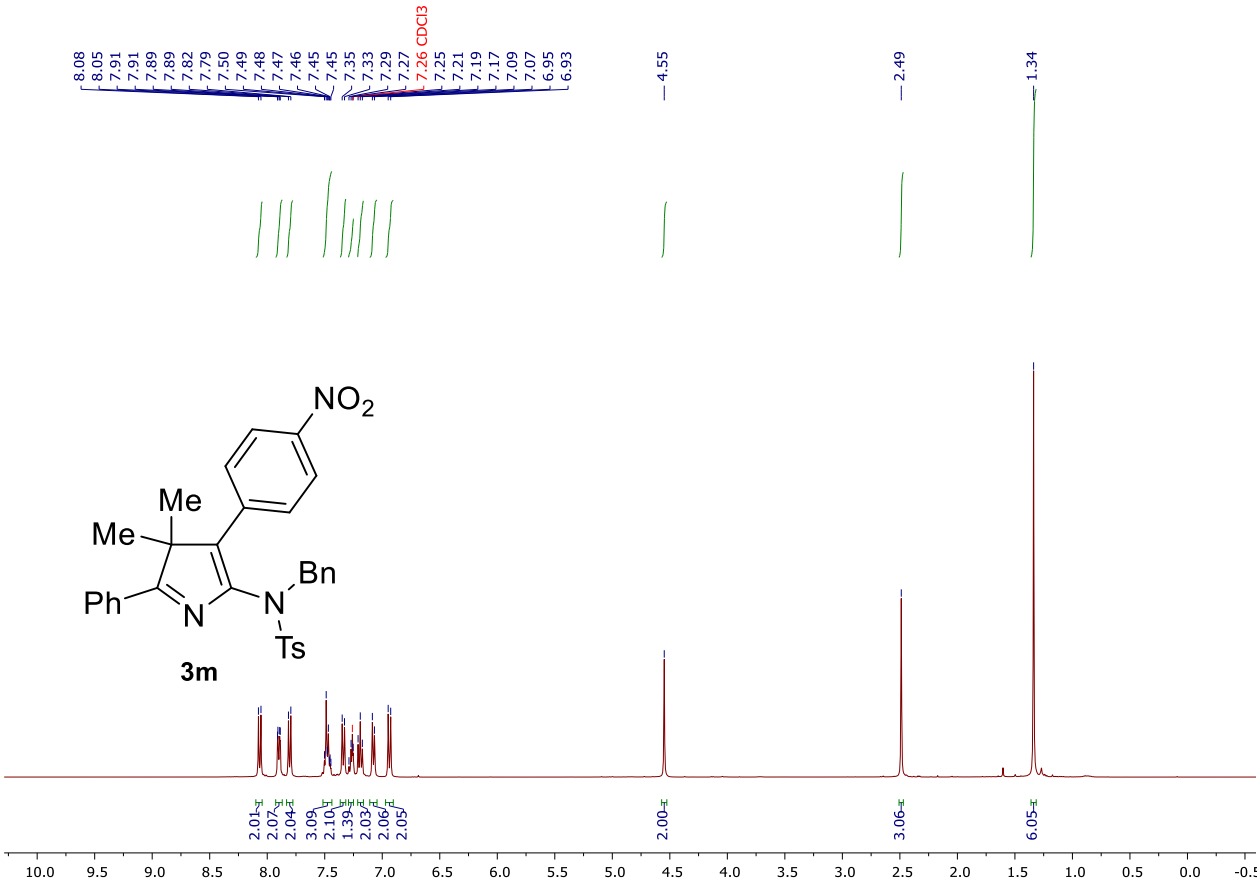
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



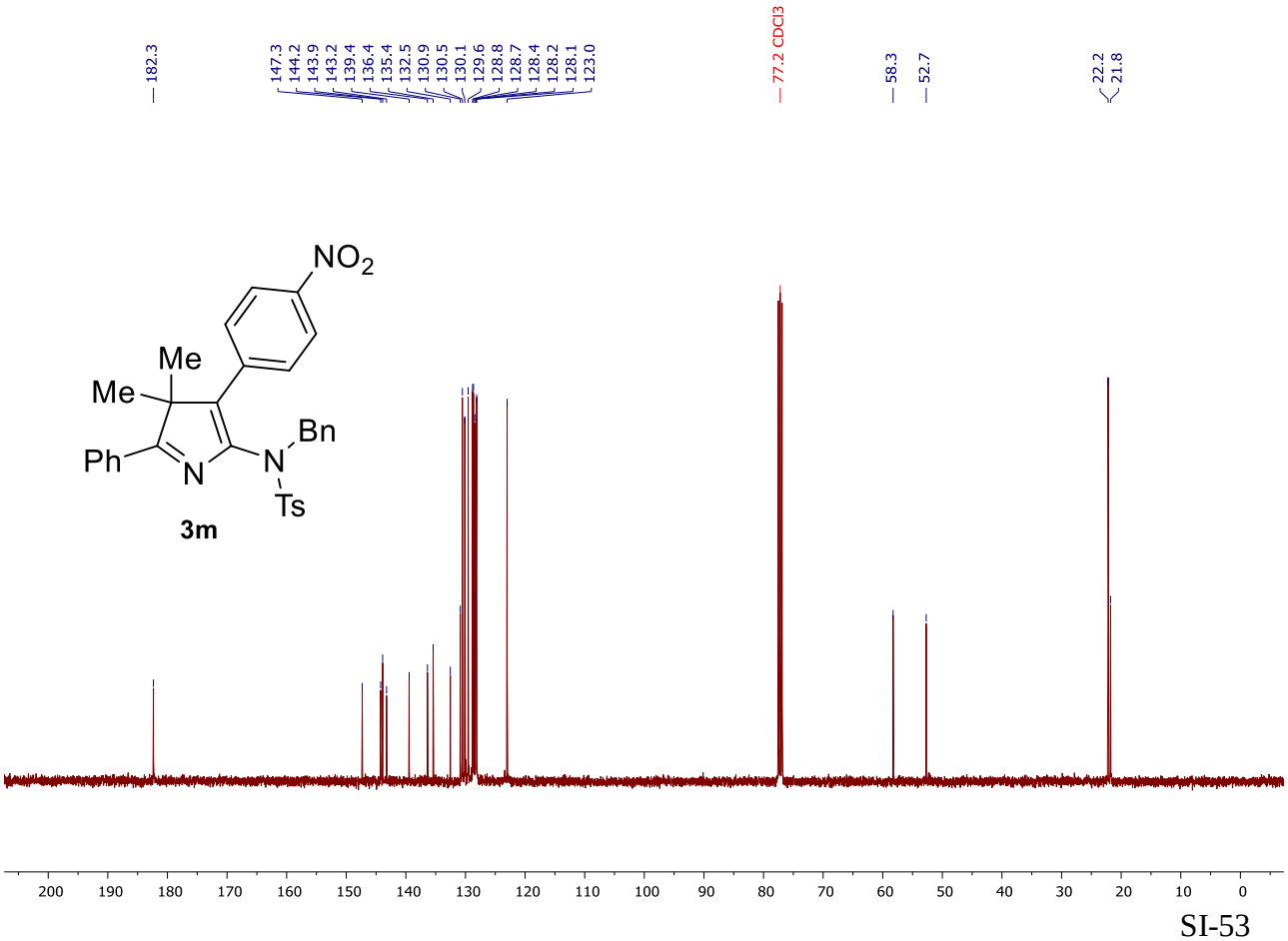
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3l**



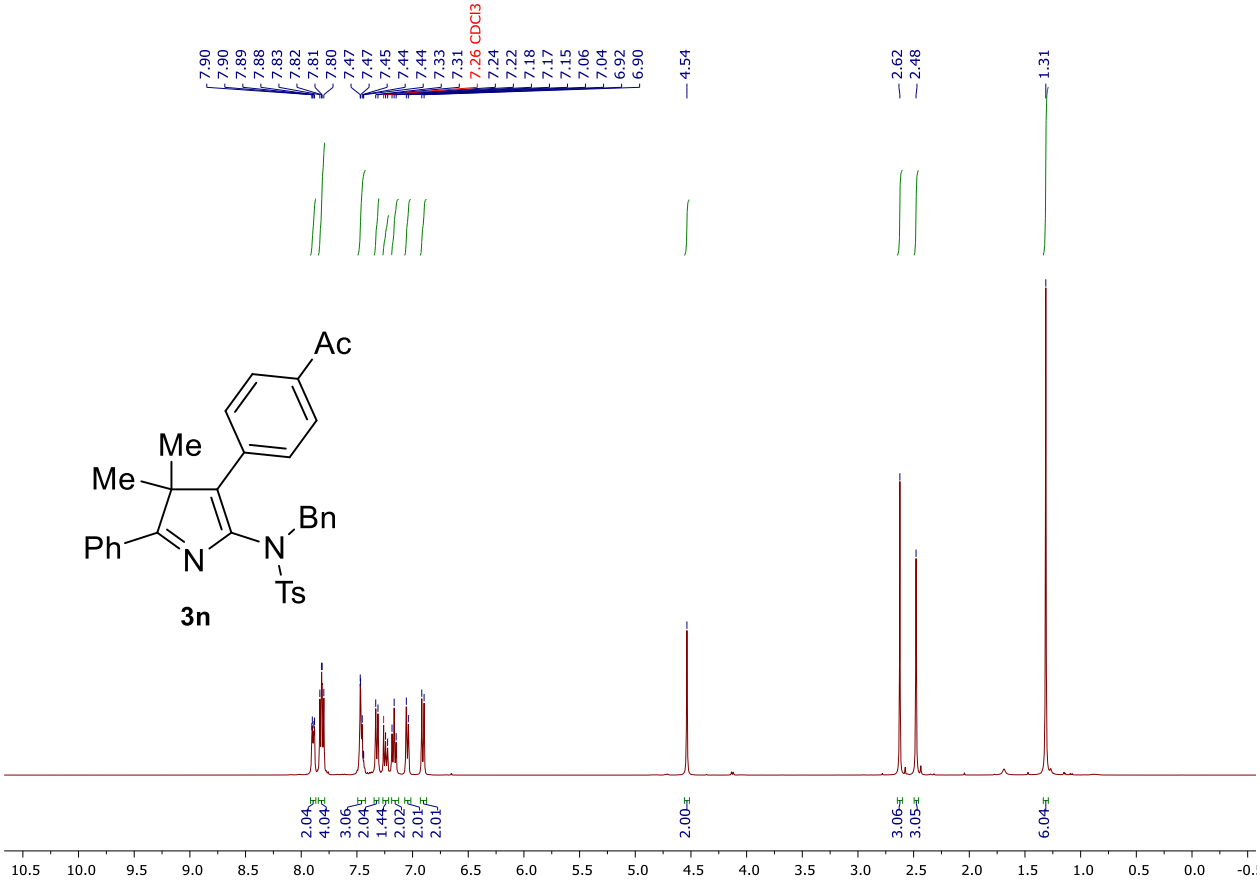
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



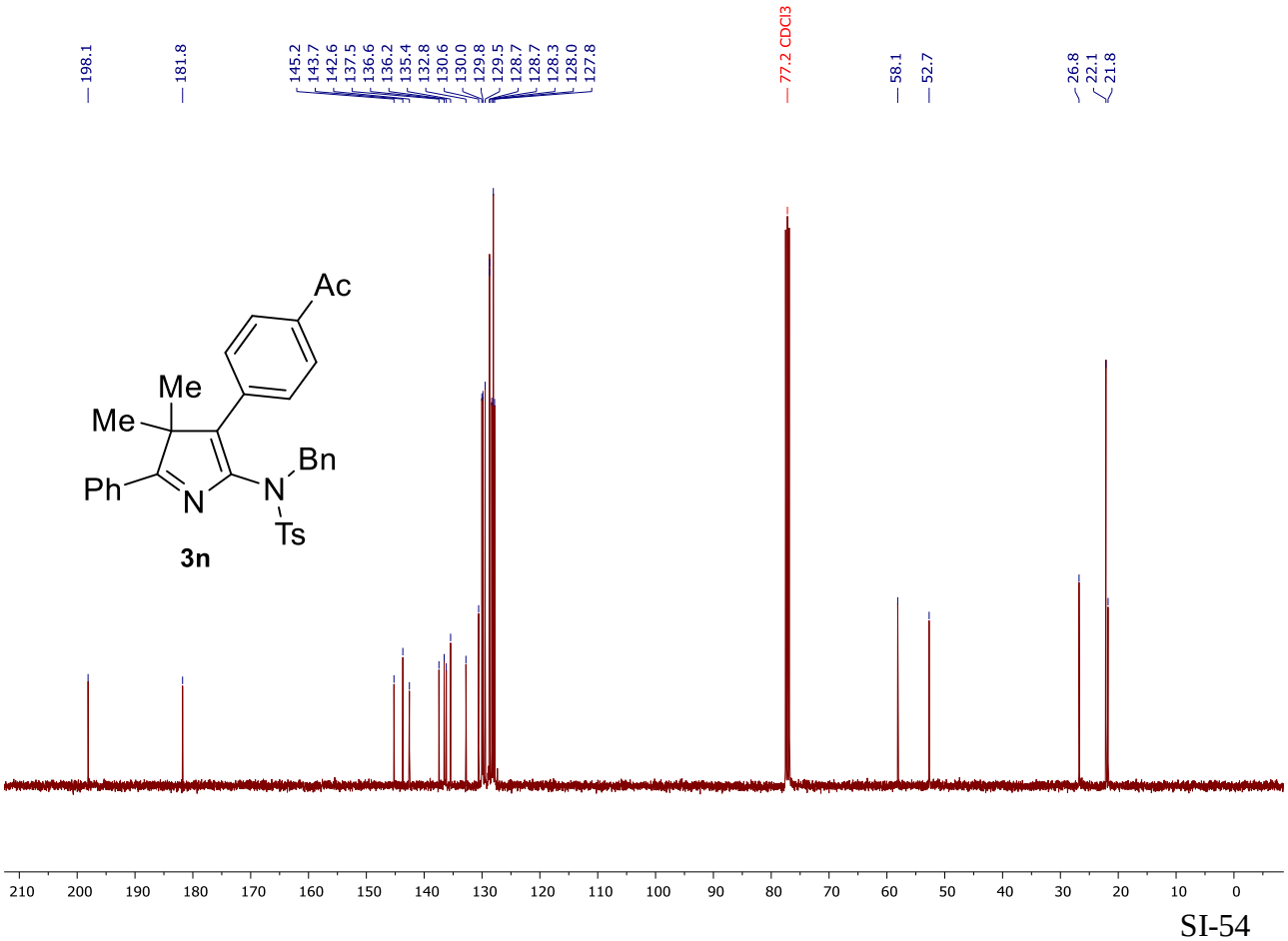
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3m**



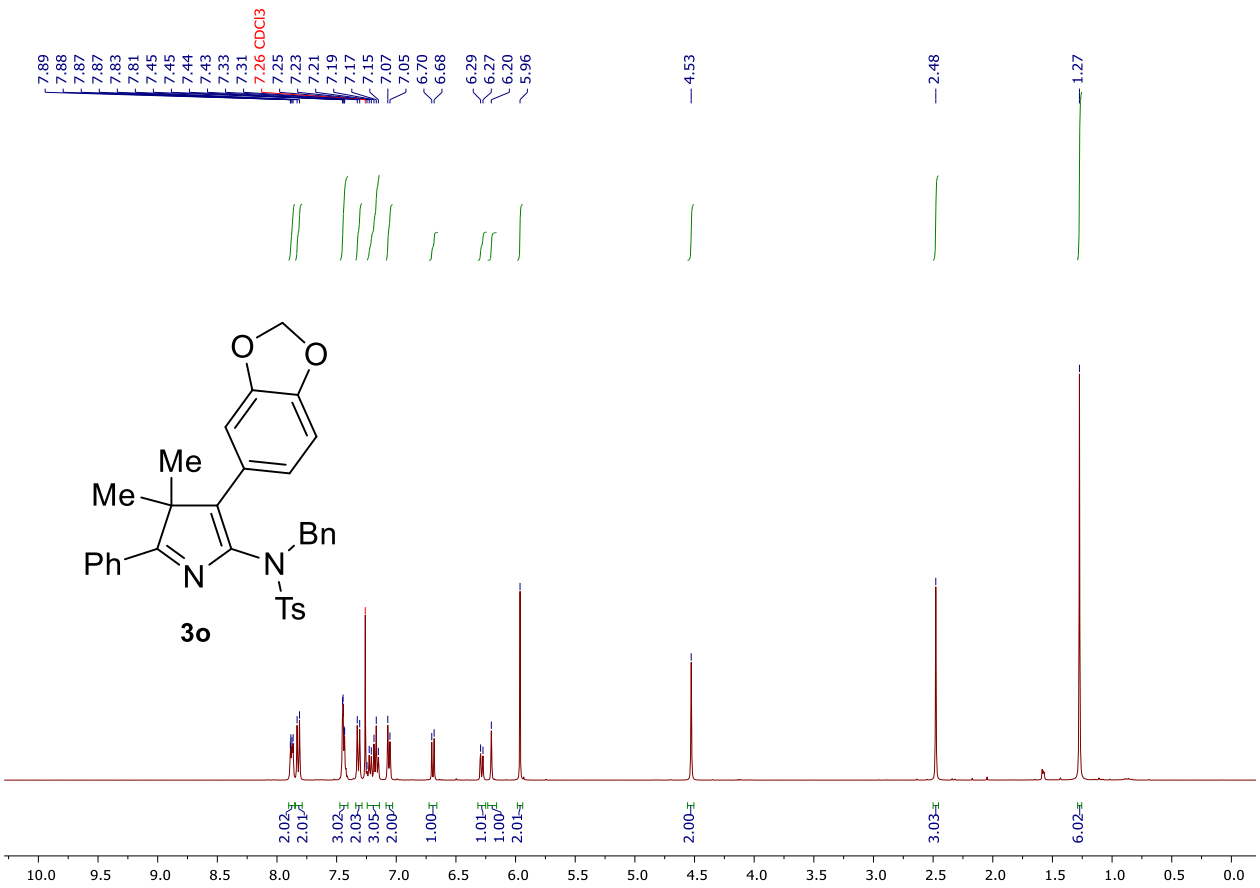
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



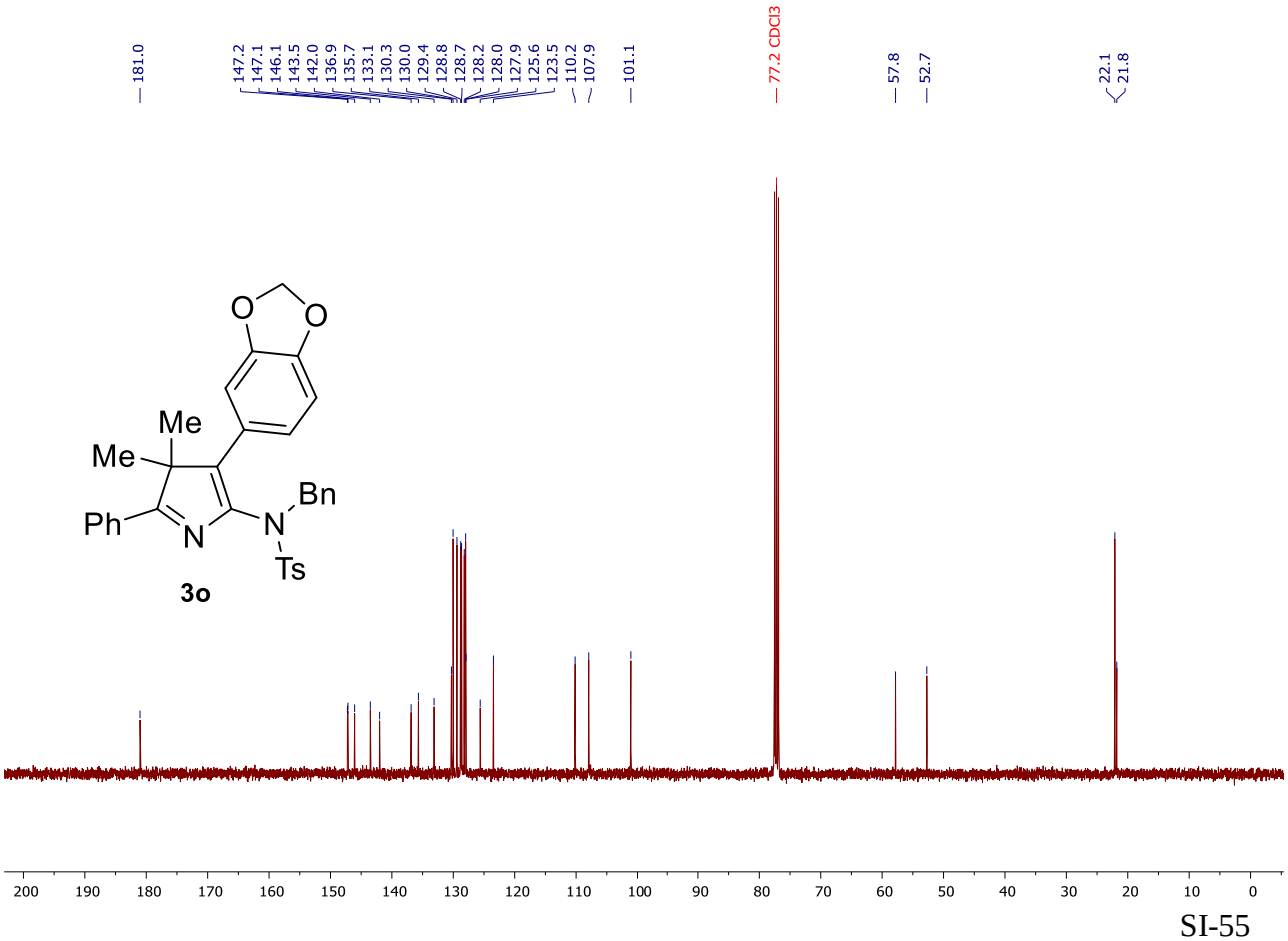
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3n**



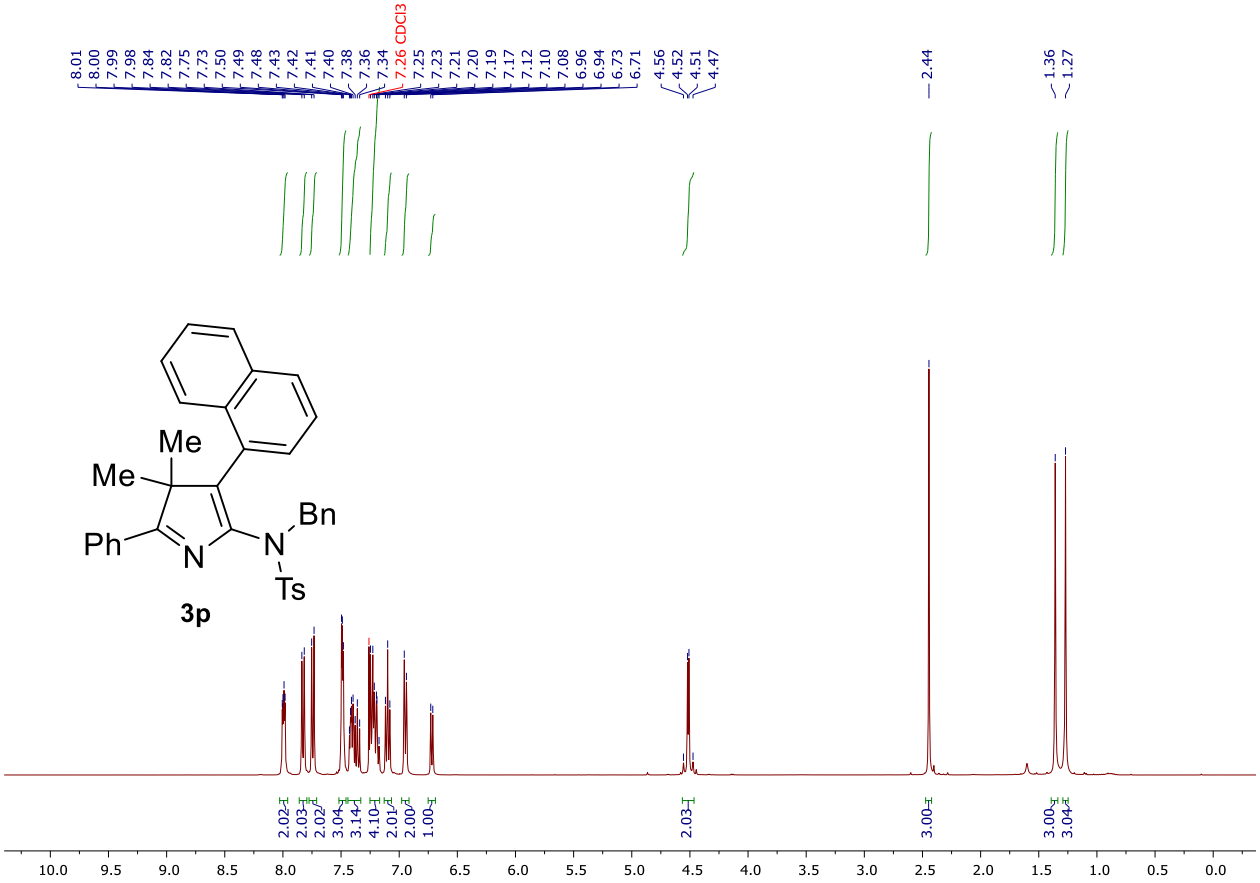
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



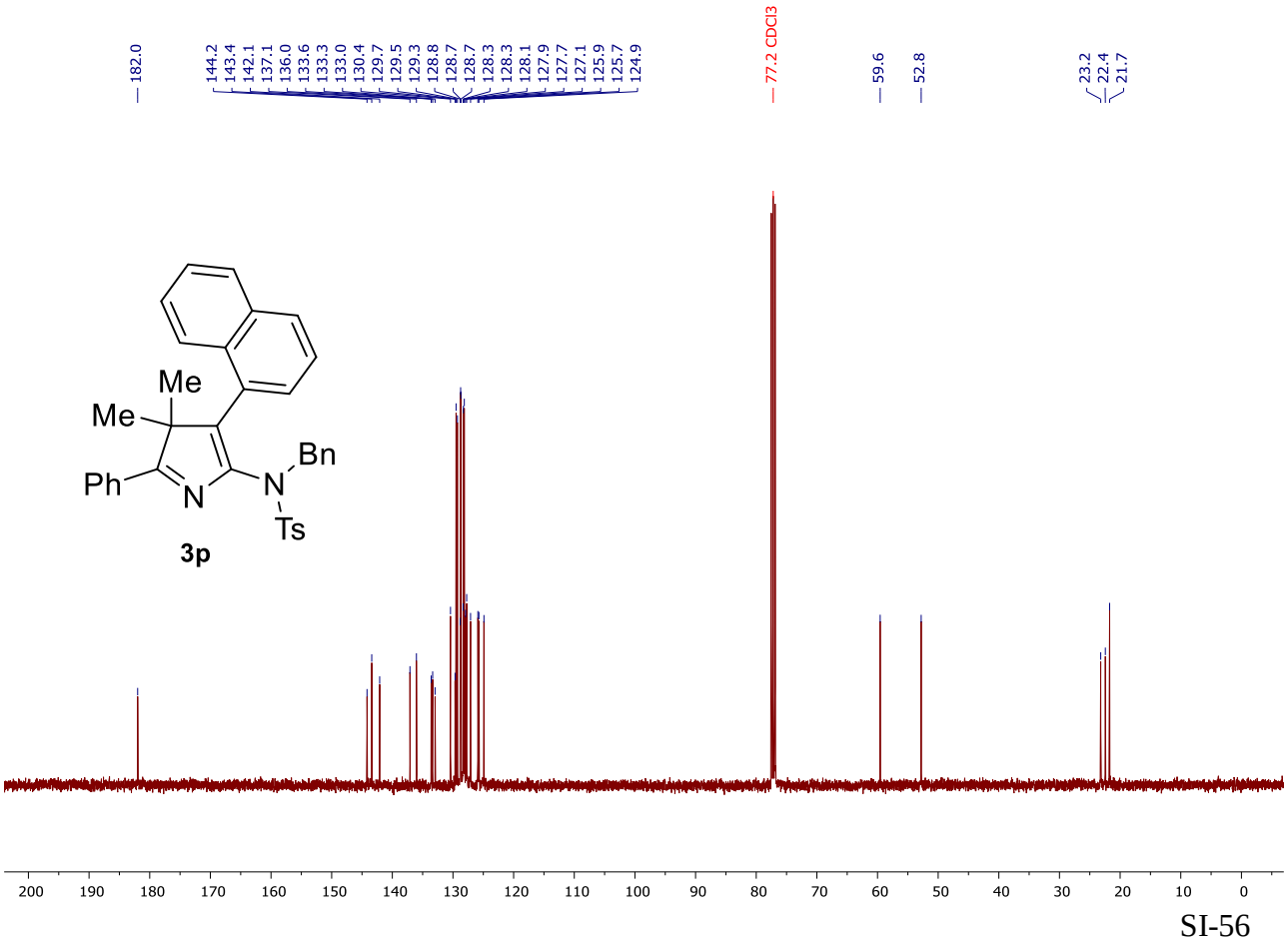
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3o**



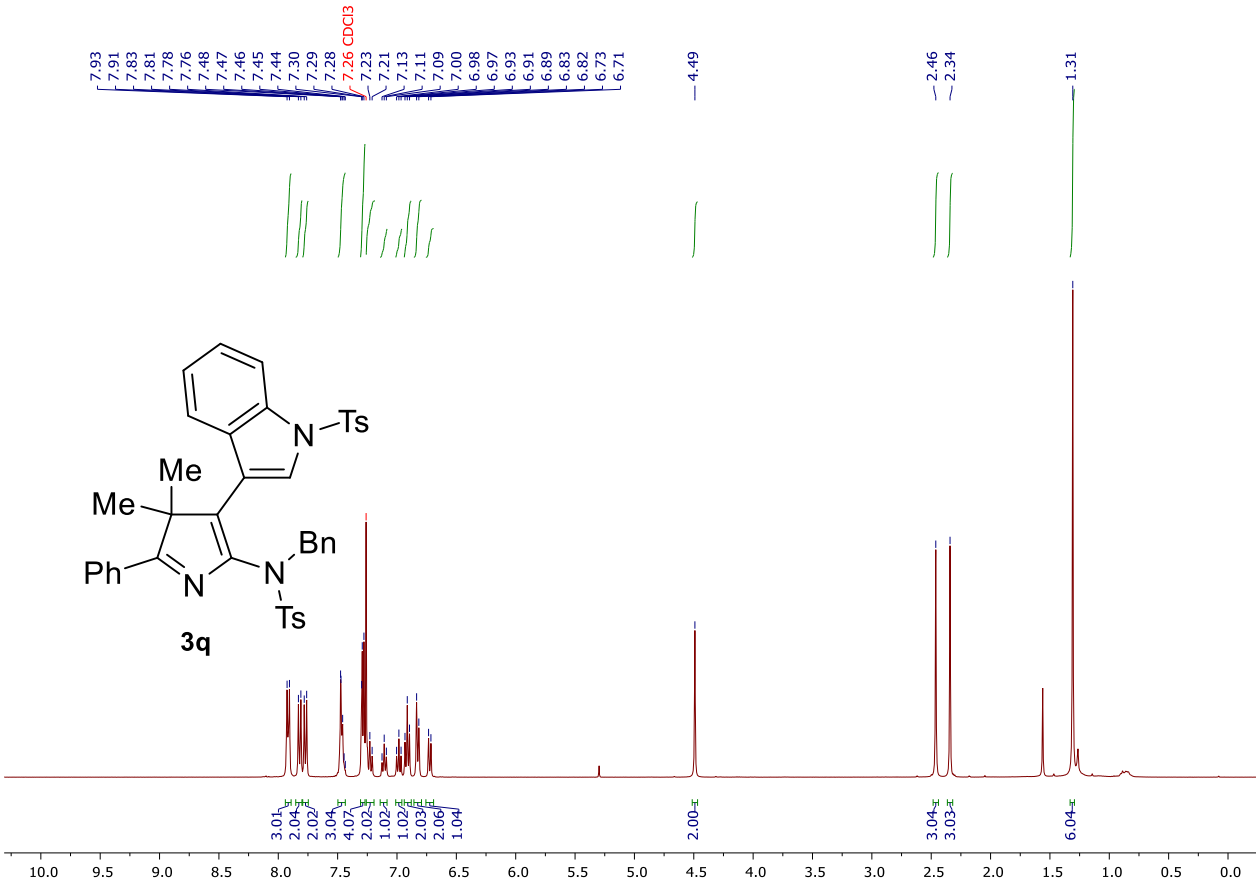
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



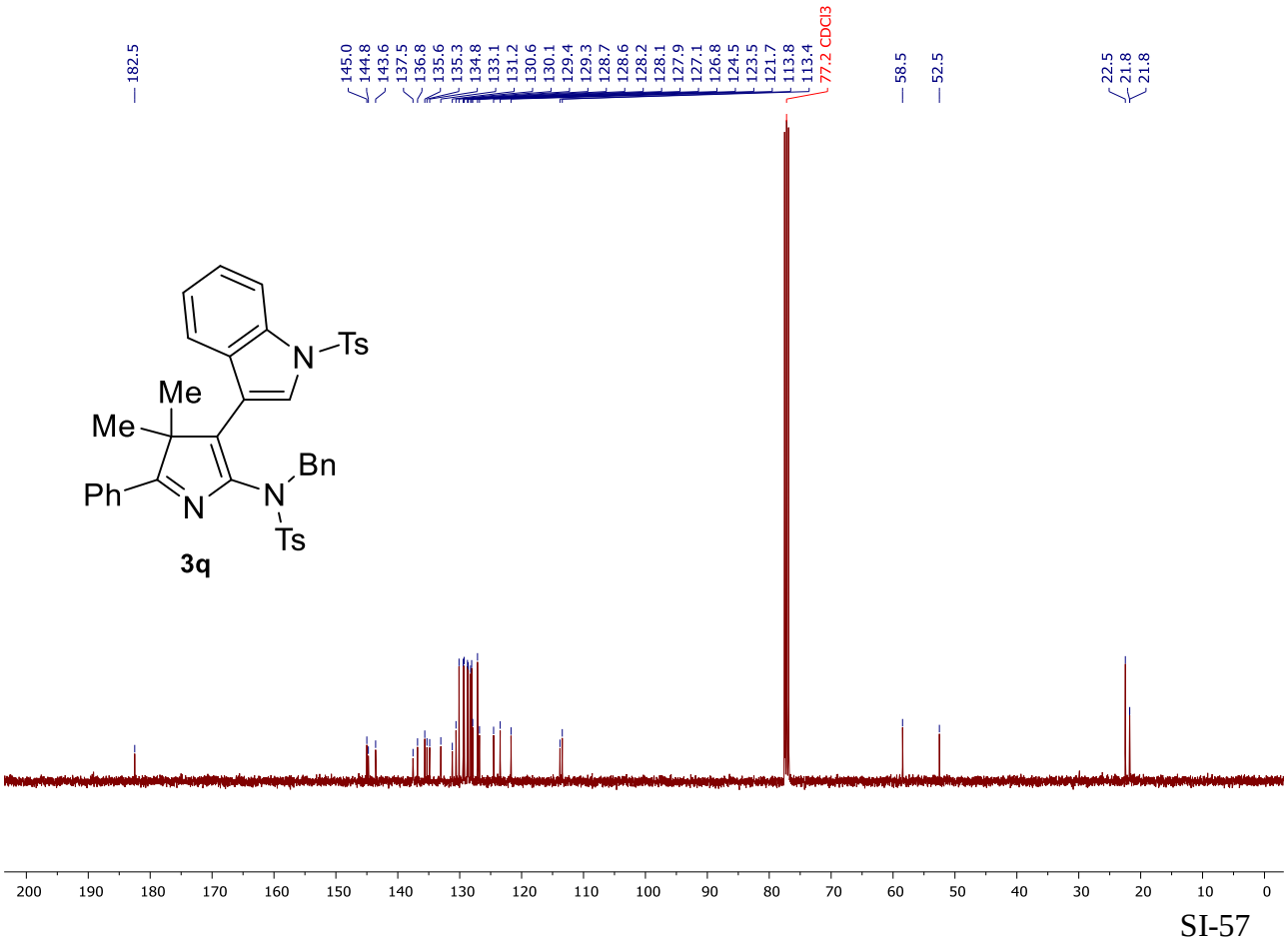
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3p**



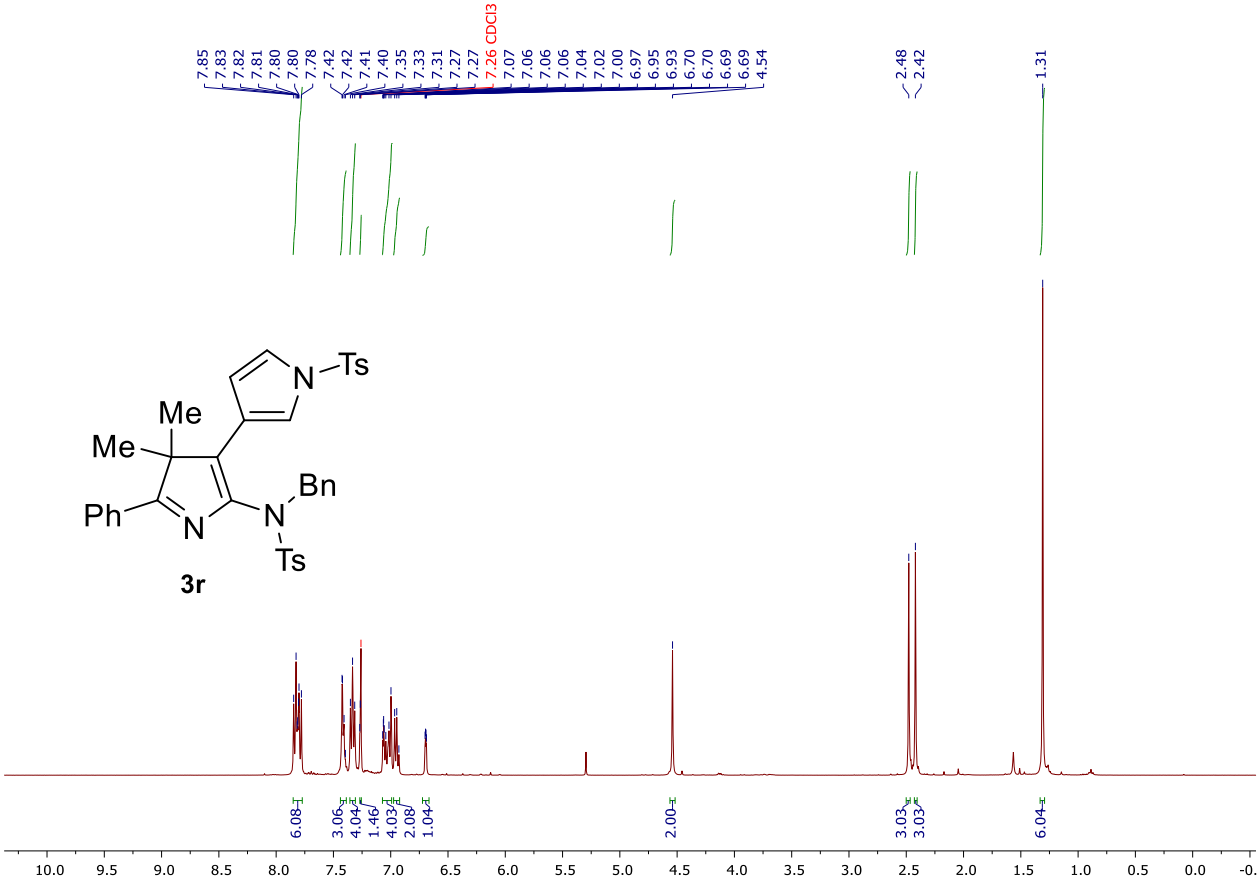
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



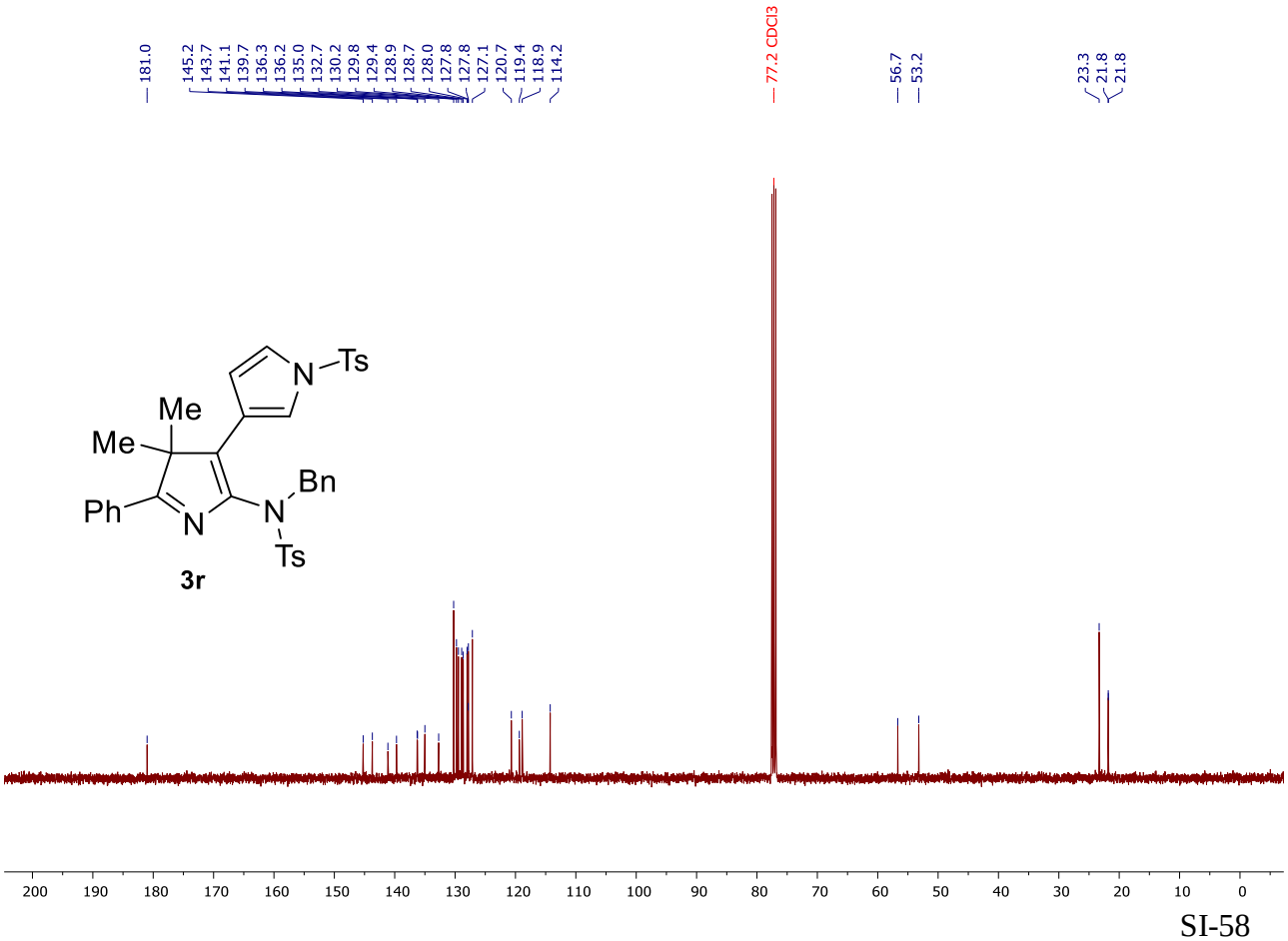
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3q**



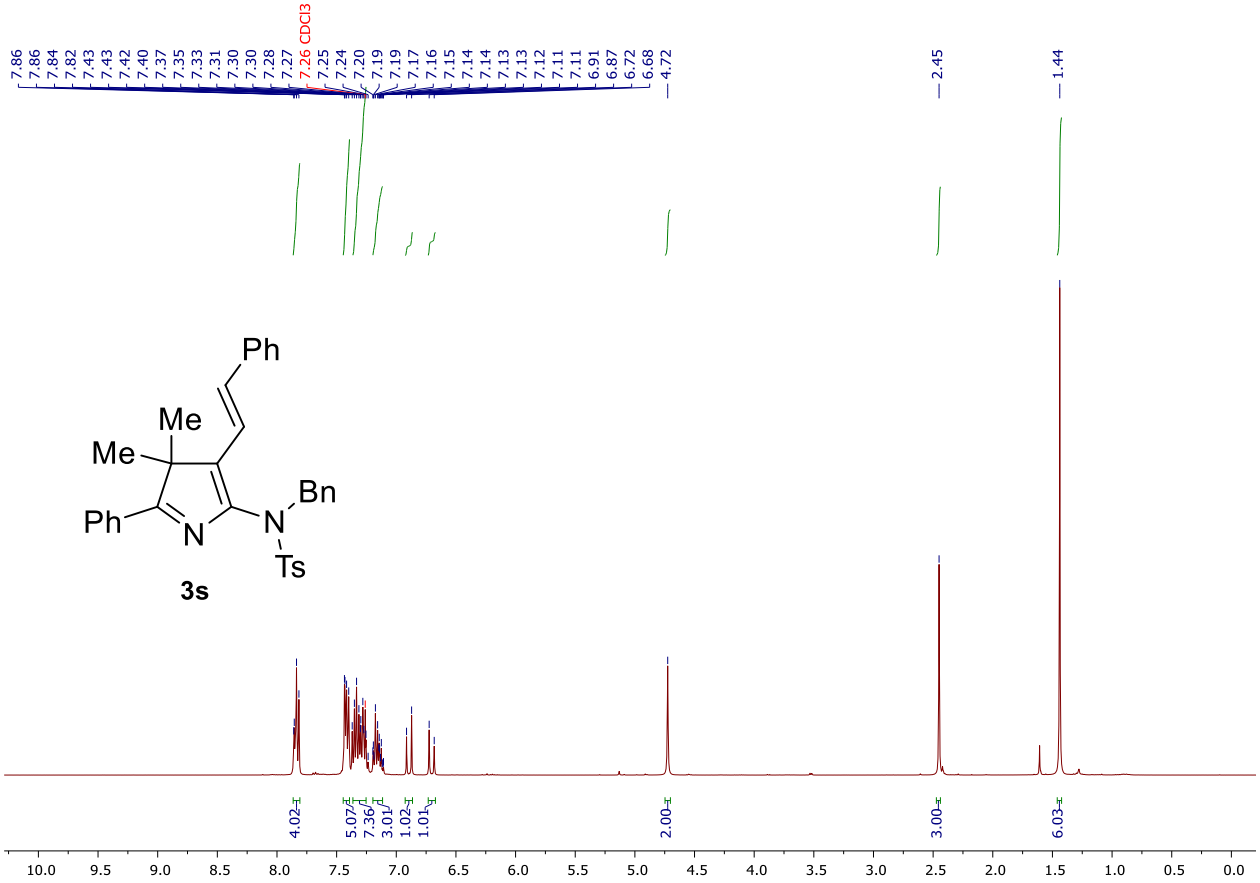
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



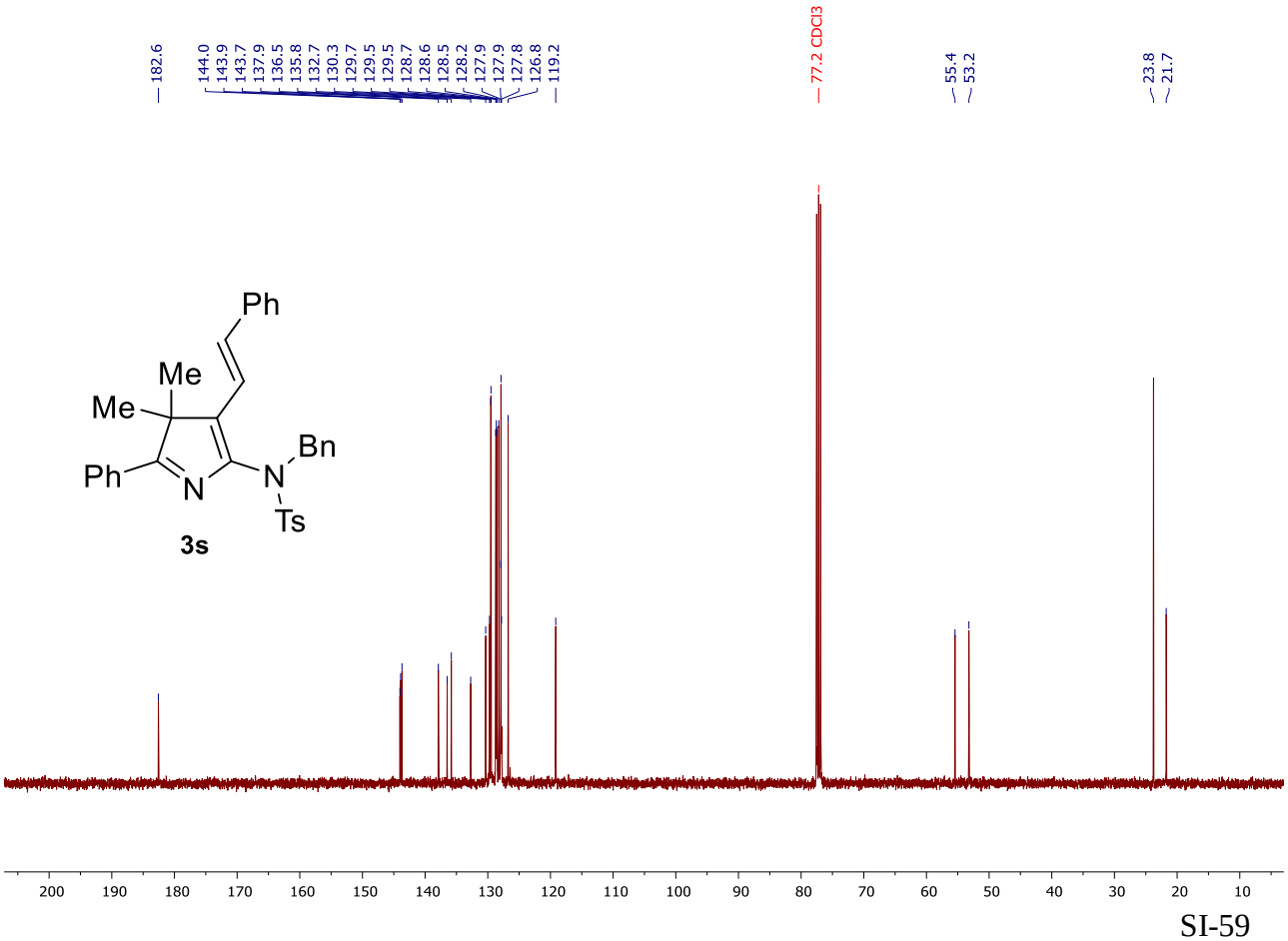
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3r**



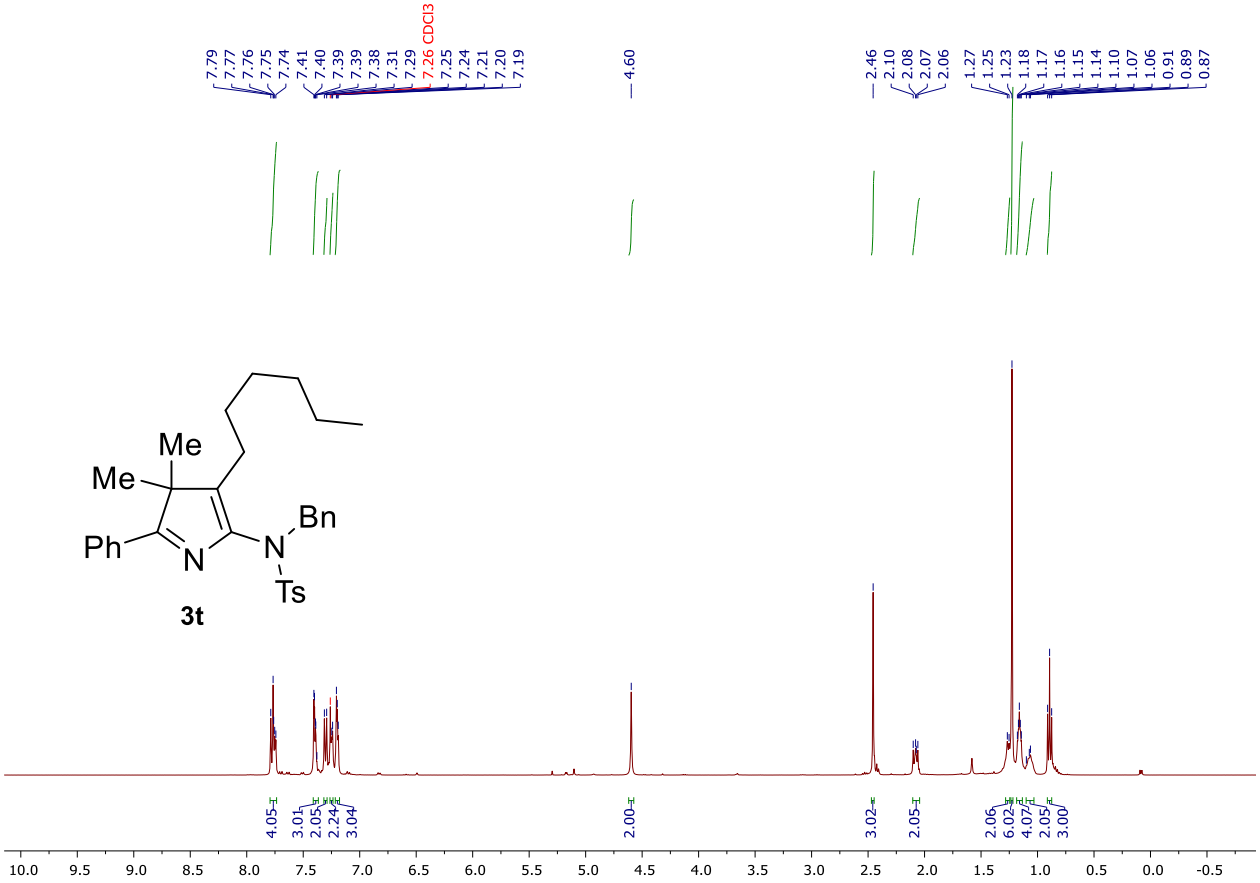
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



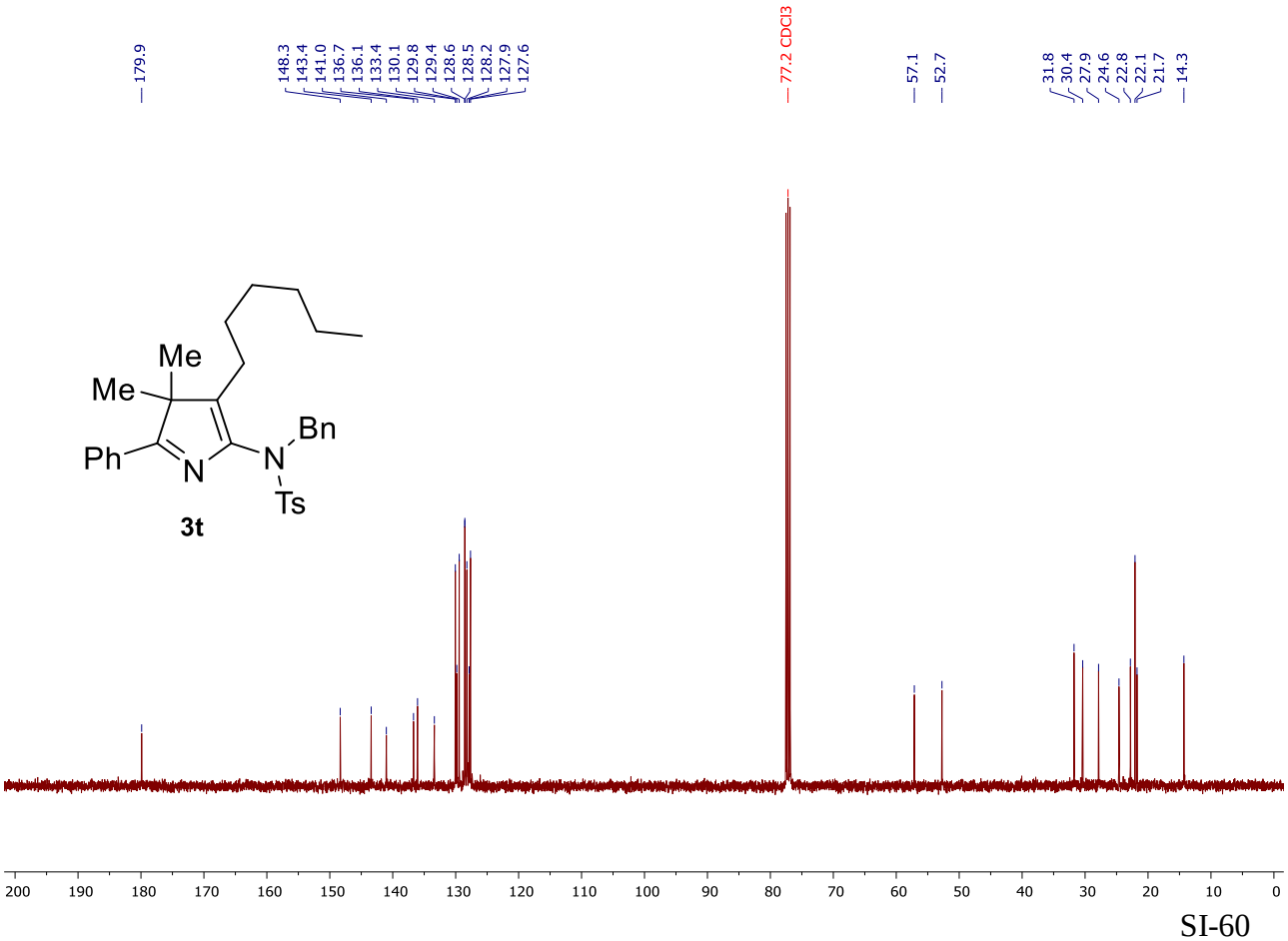
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3s**



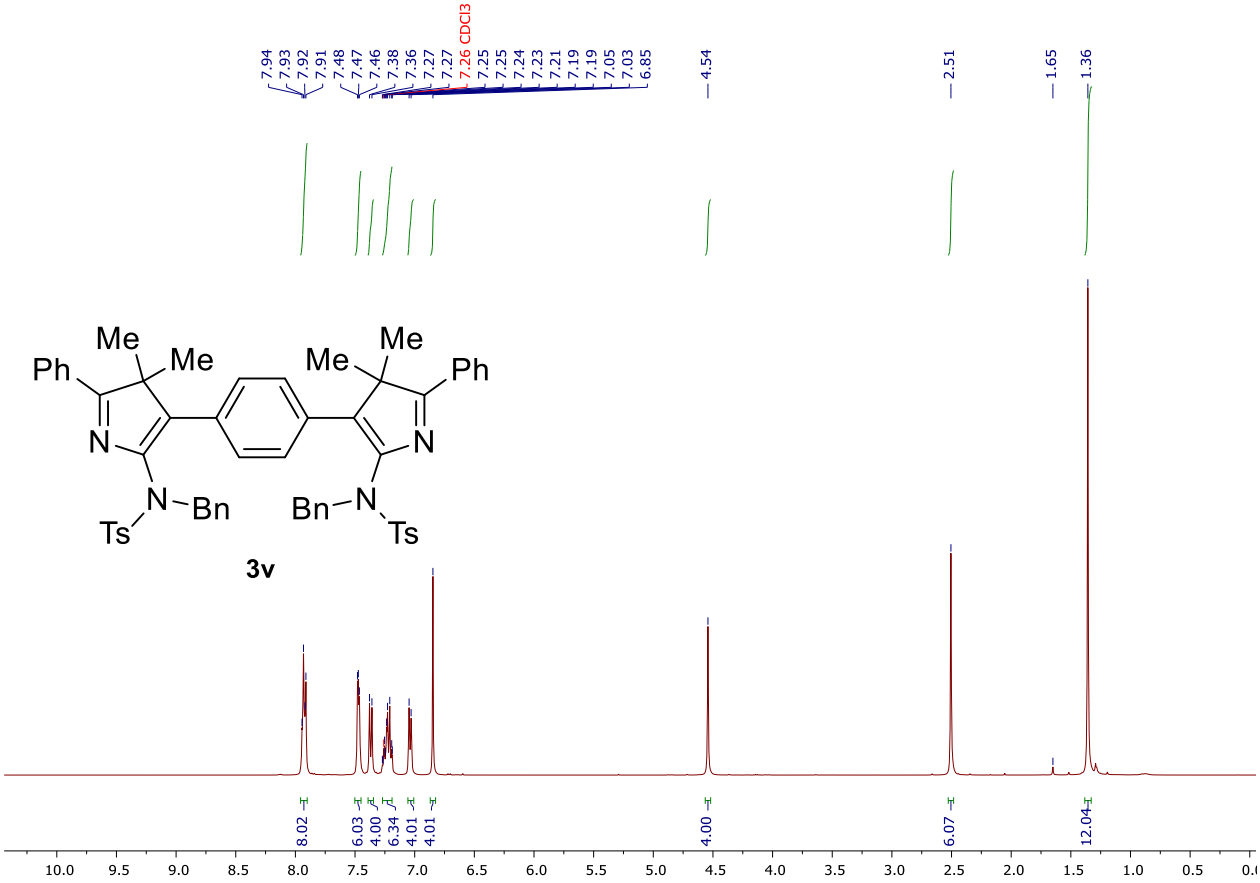
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



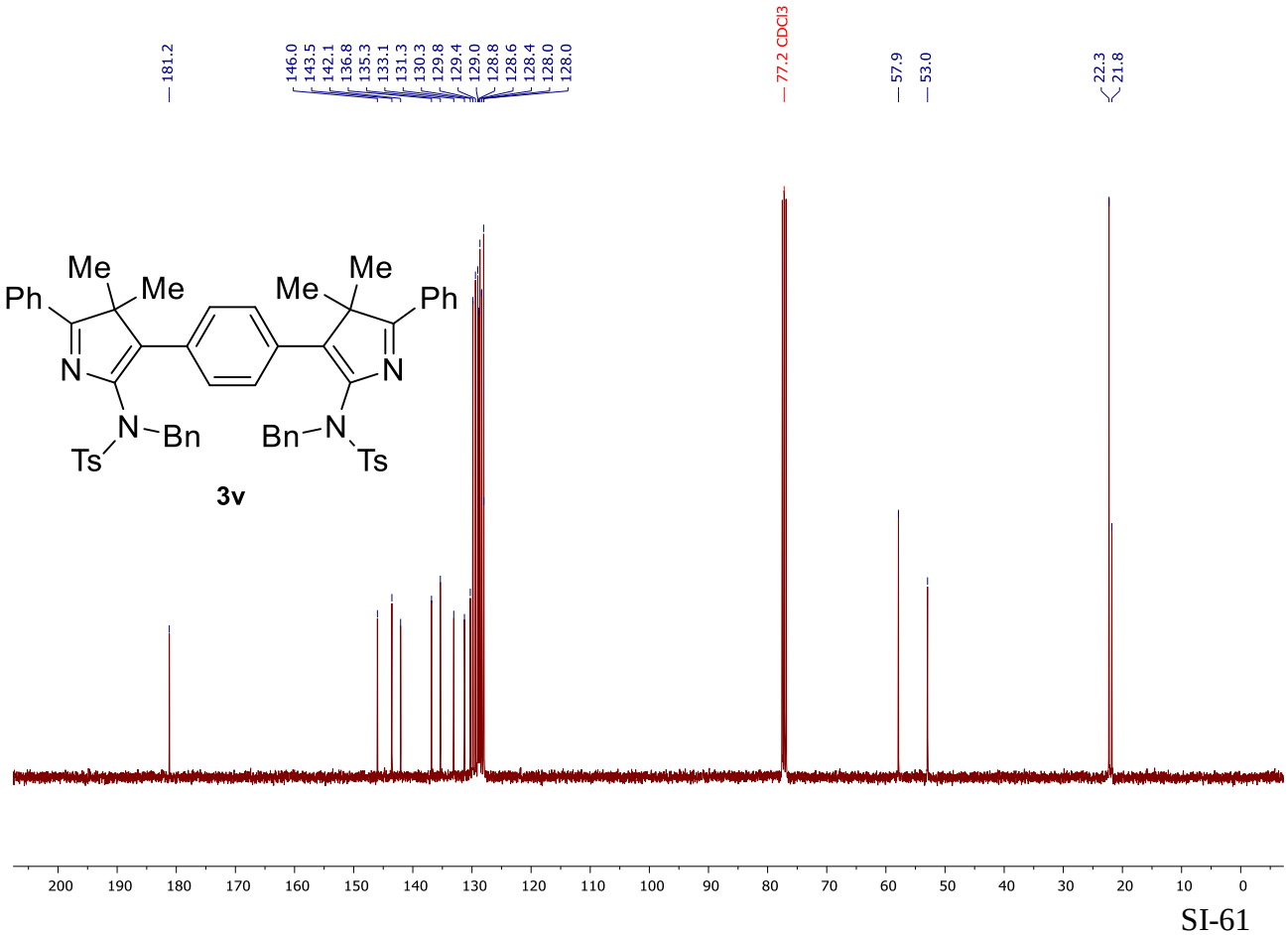
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3t**



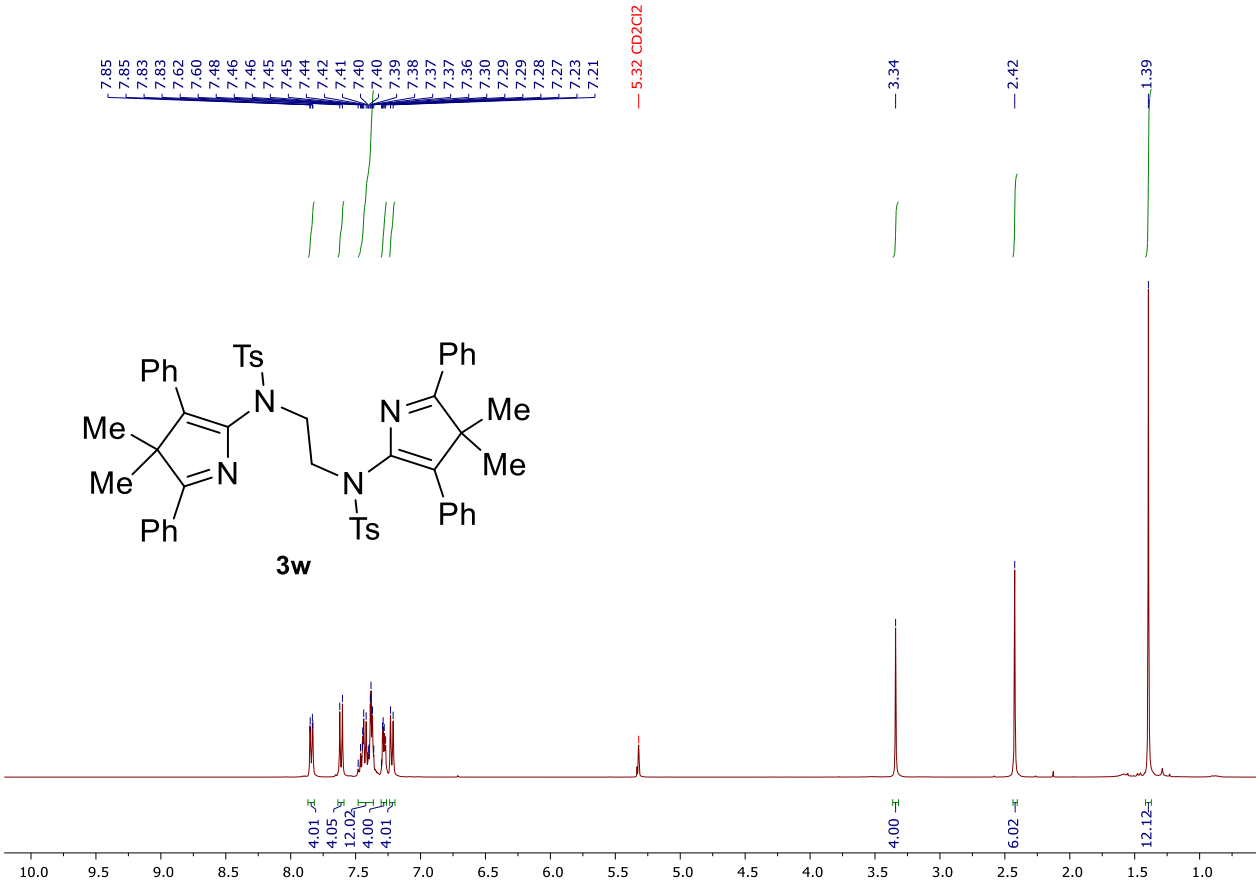
^{1}H NMR (400 MHz, $CDCl_3$) of **3v**



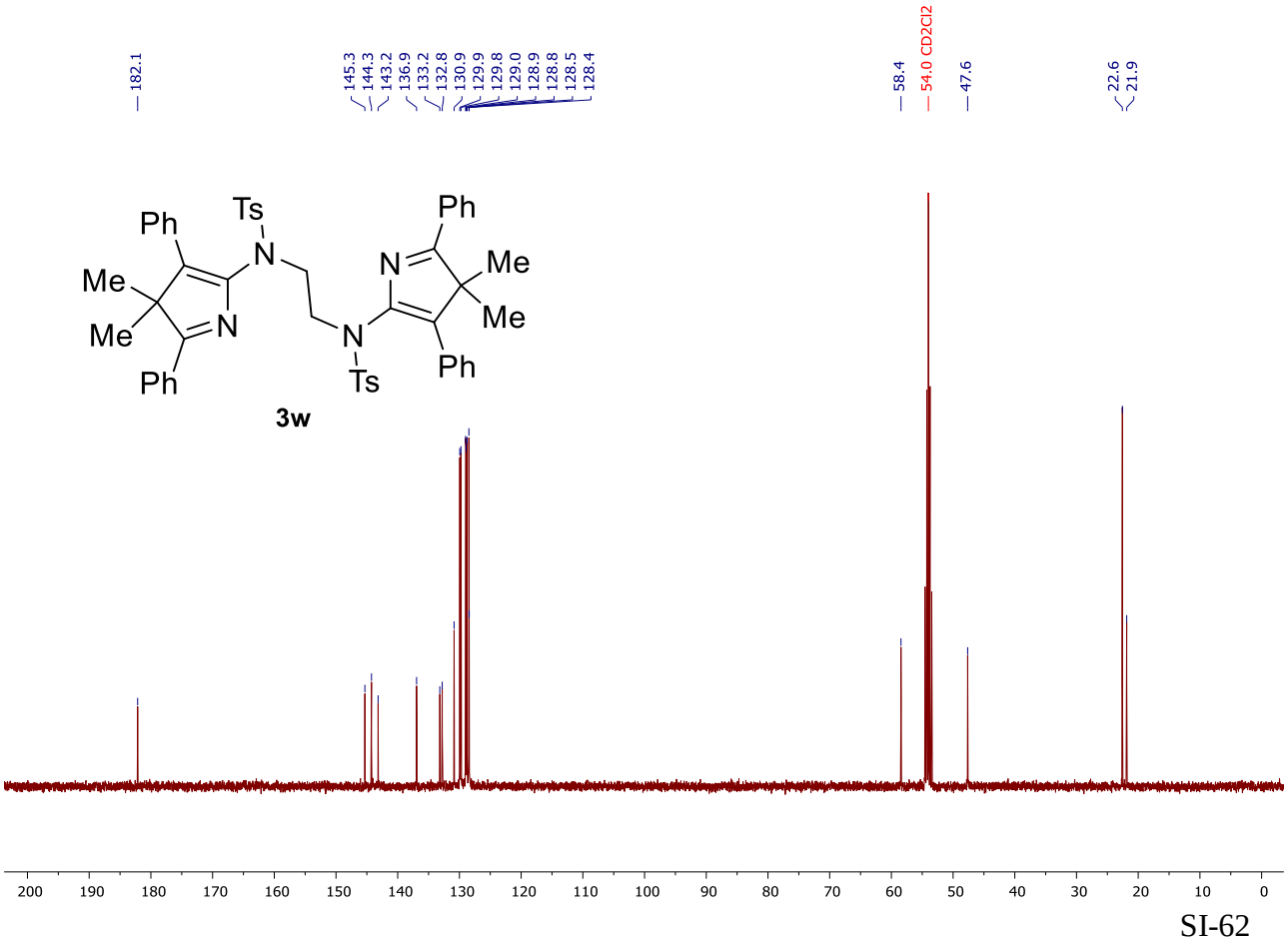
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3v**



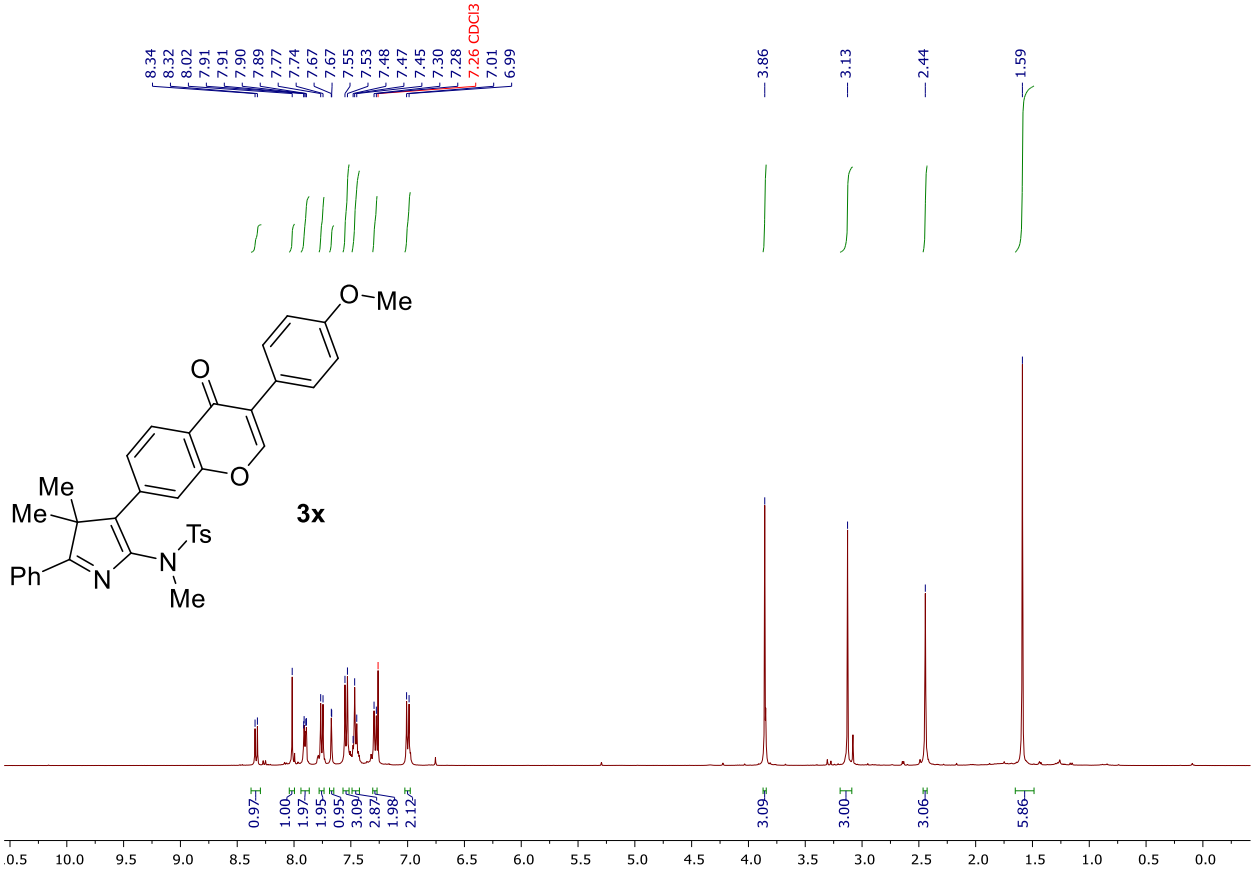
^{1}H NMR (400 MHz, $CDCl_3$) of **3w**



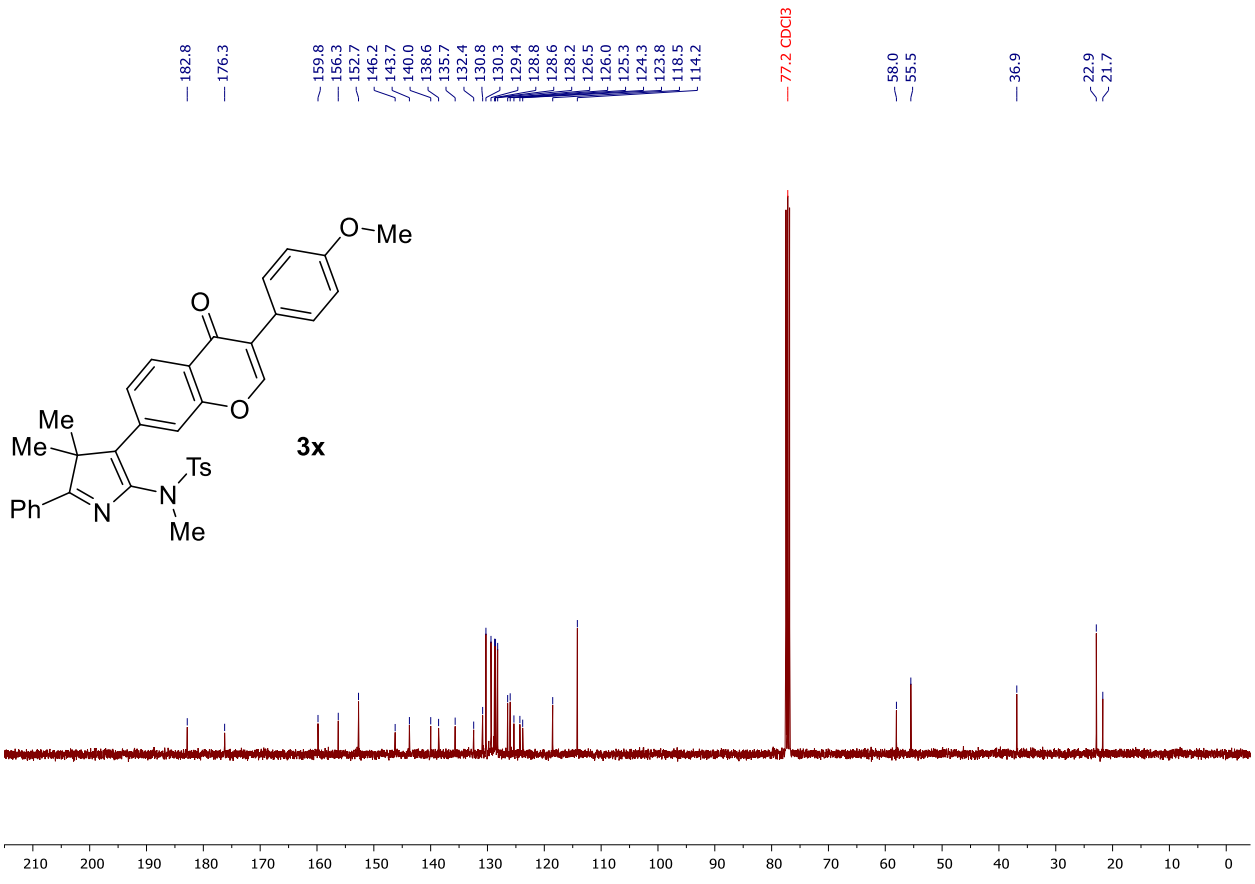
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3w**



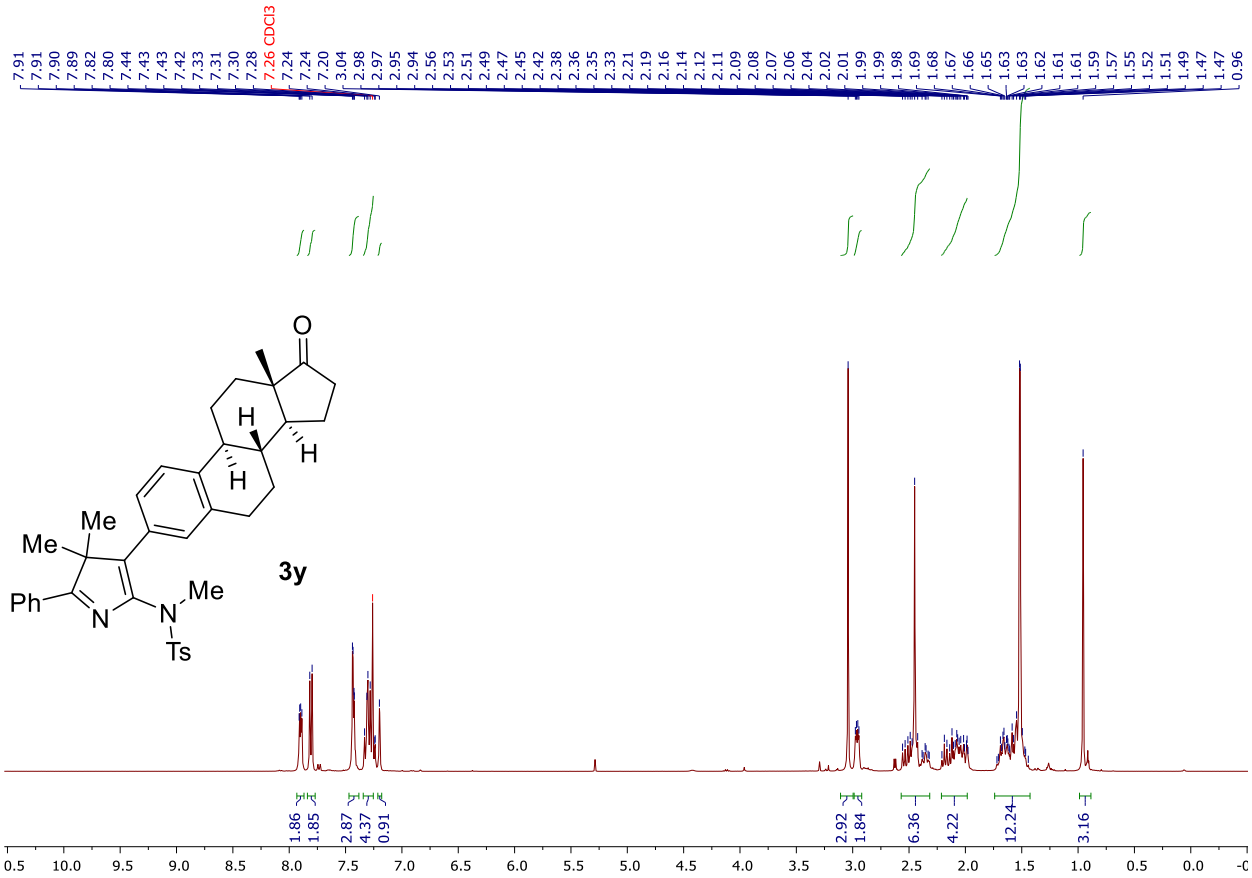
^{1}H NMR (400 MHz, $CDCl_3$) of **3x**



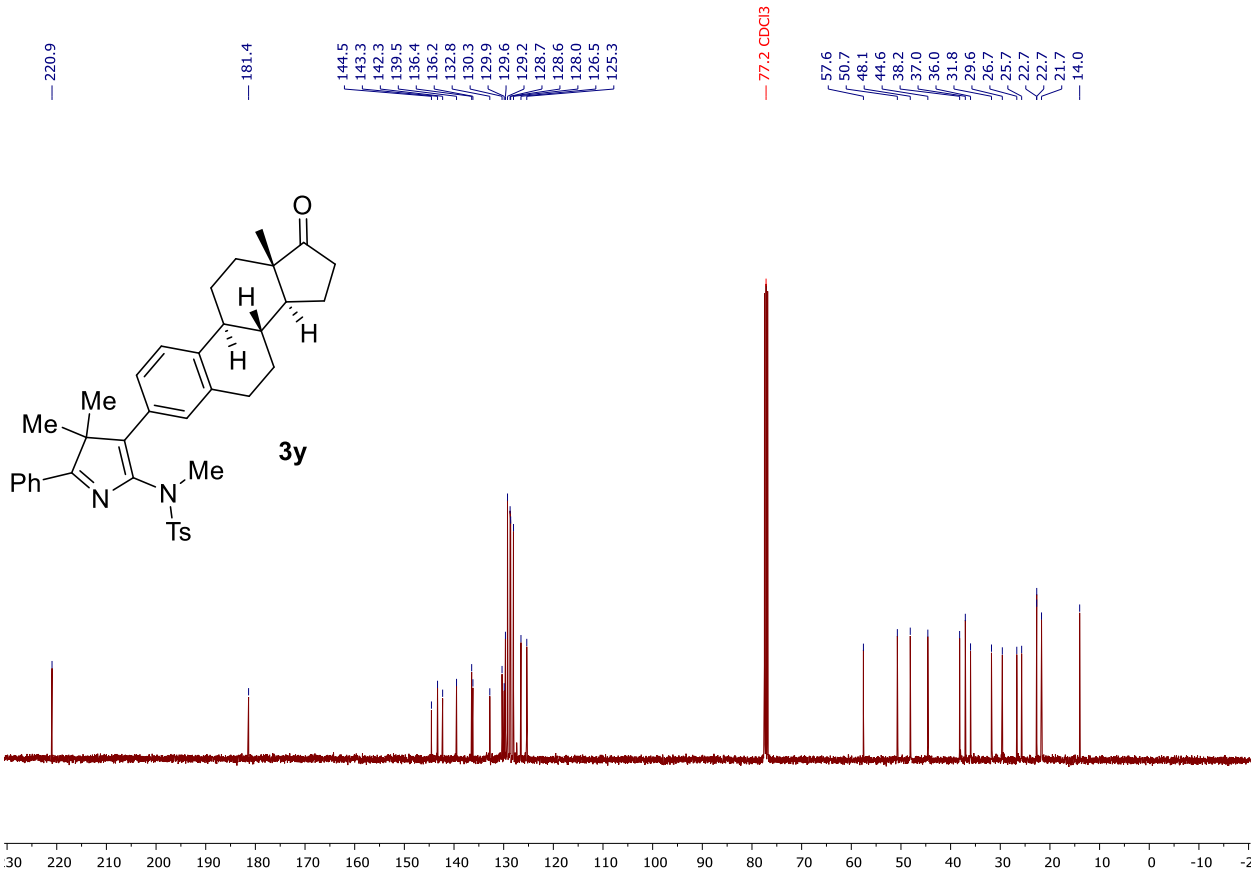
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3x**



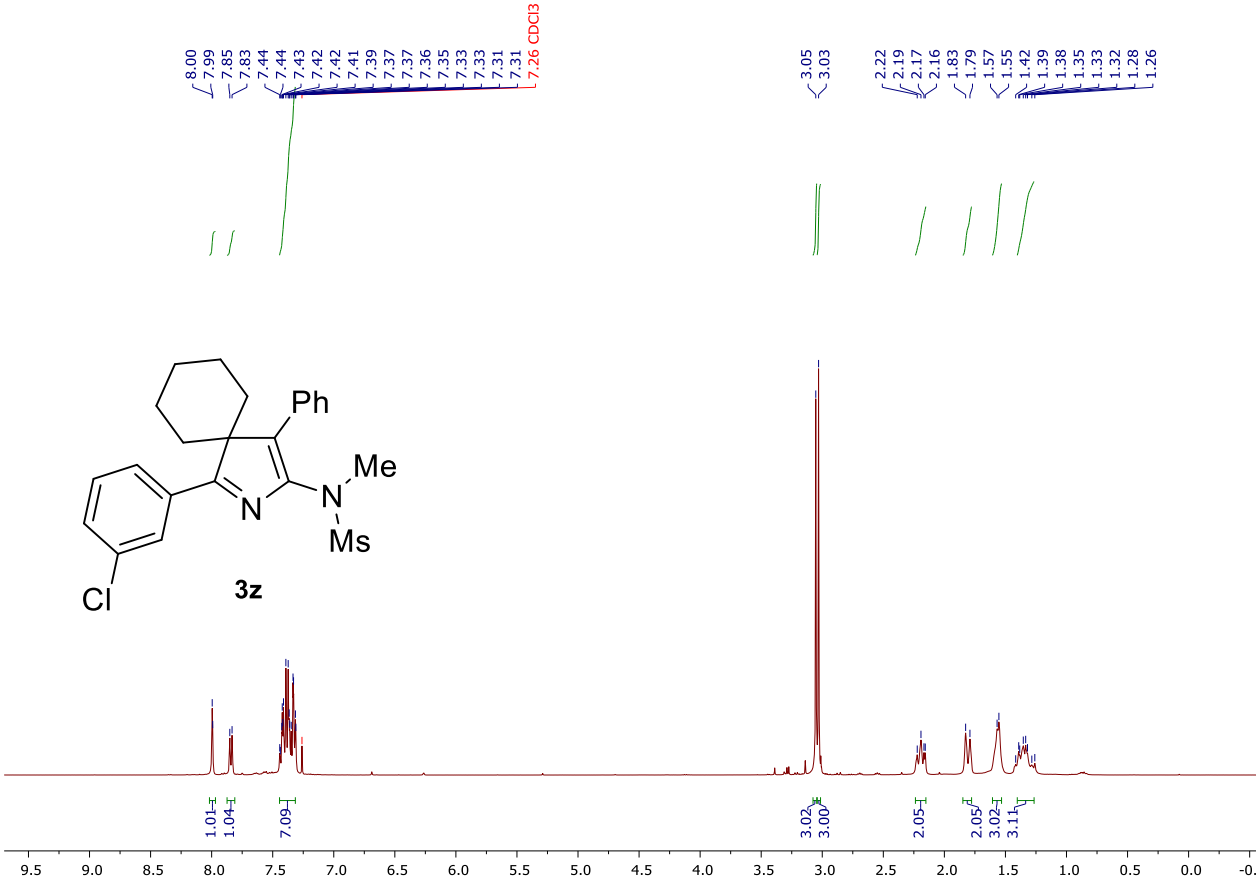
^{1}H NMR (400 MHz, $CDCl_3$) of **3y**



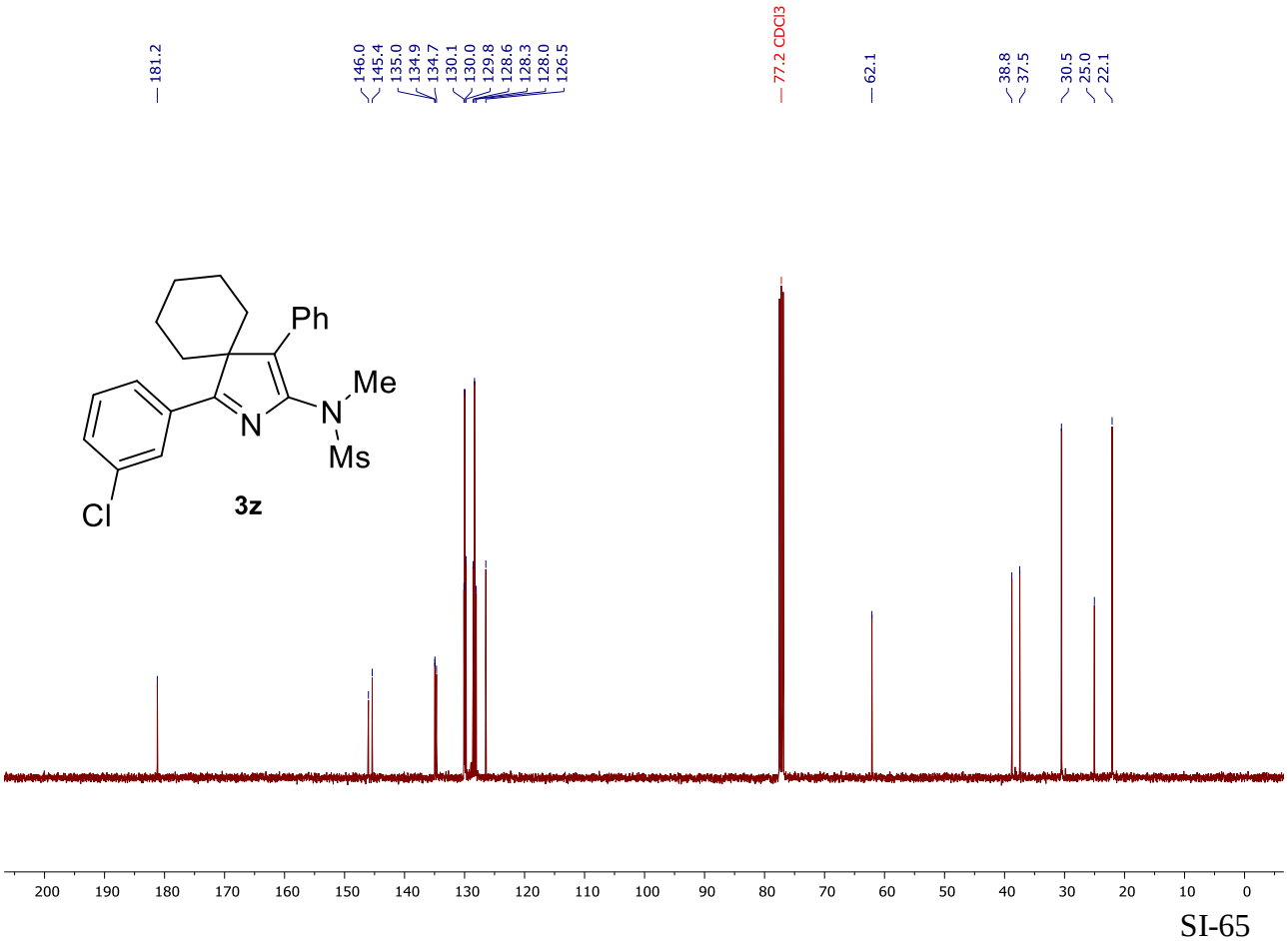
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3y**



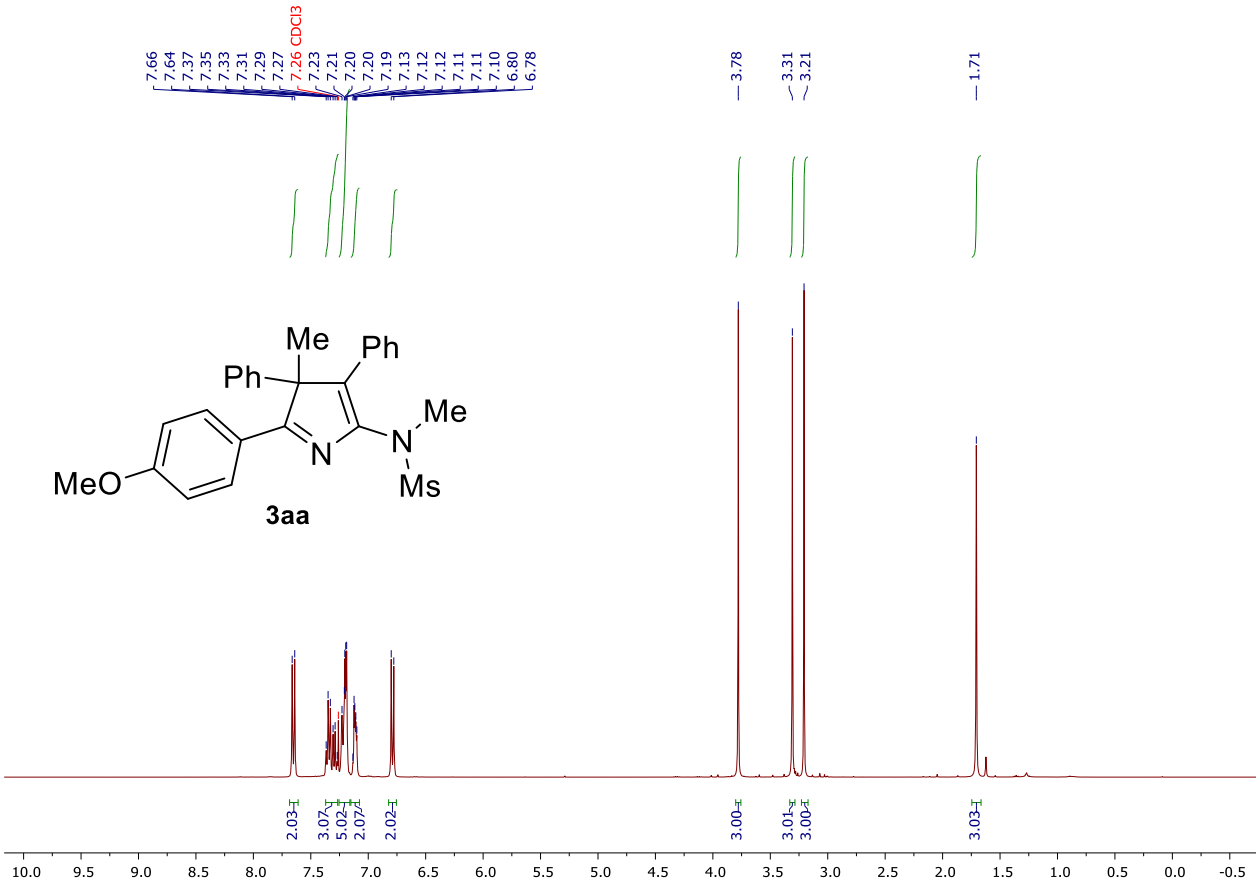
^{1}H NMR (400 MHz, $CDCl_3$) of **3z**



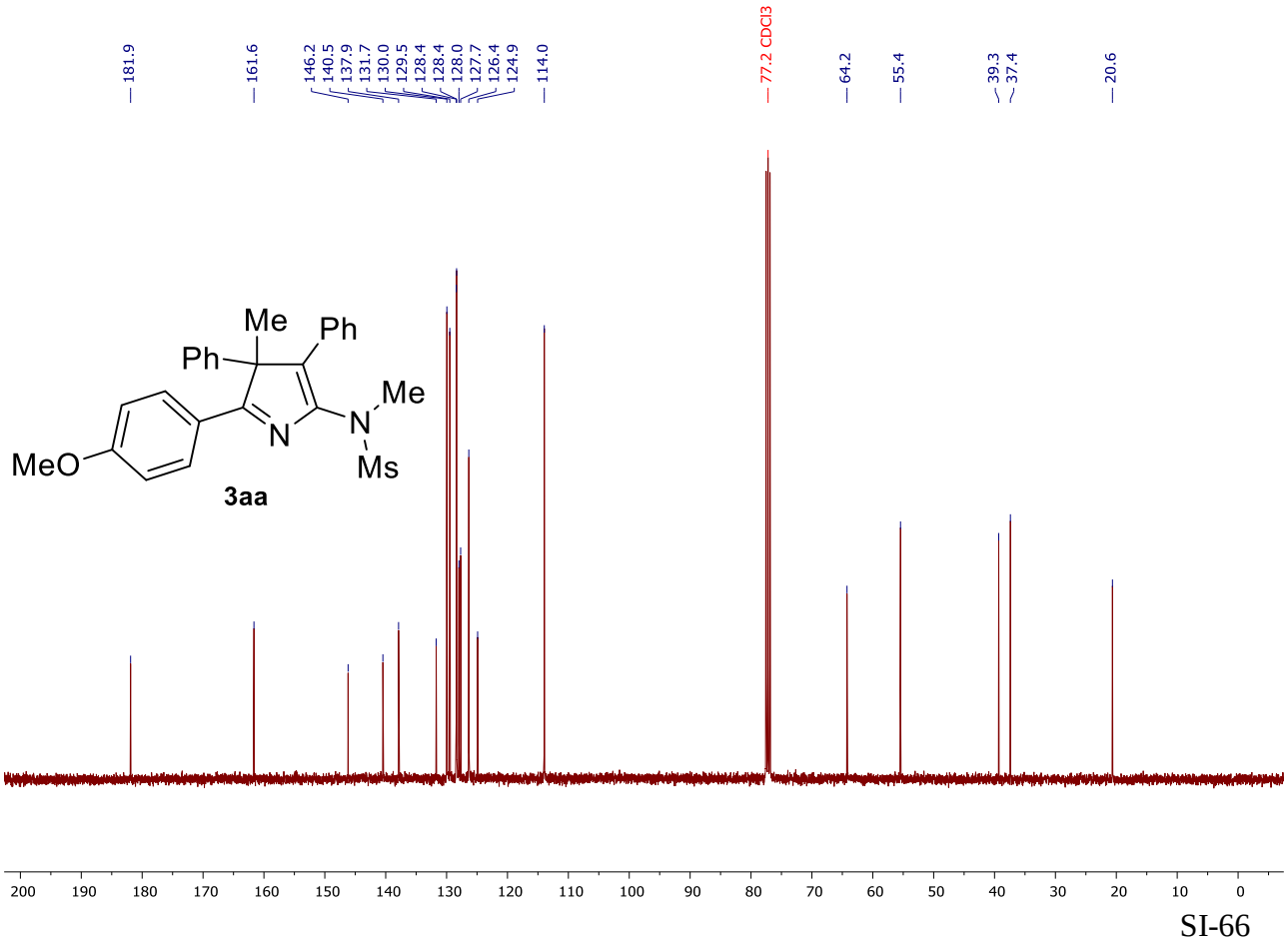
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3z**



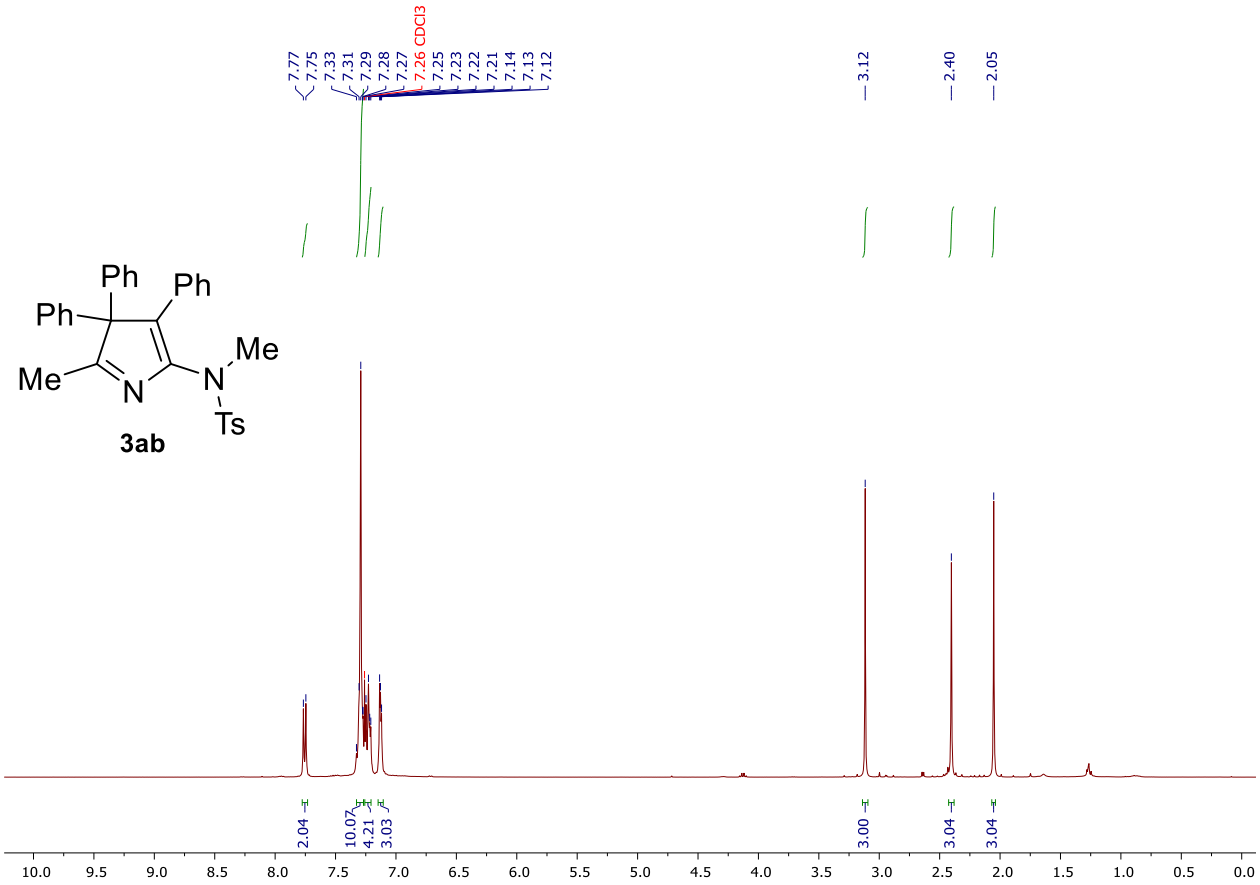
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



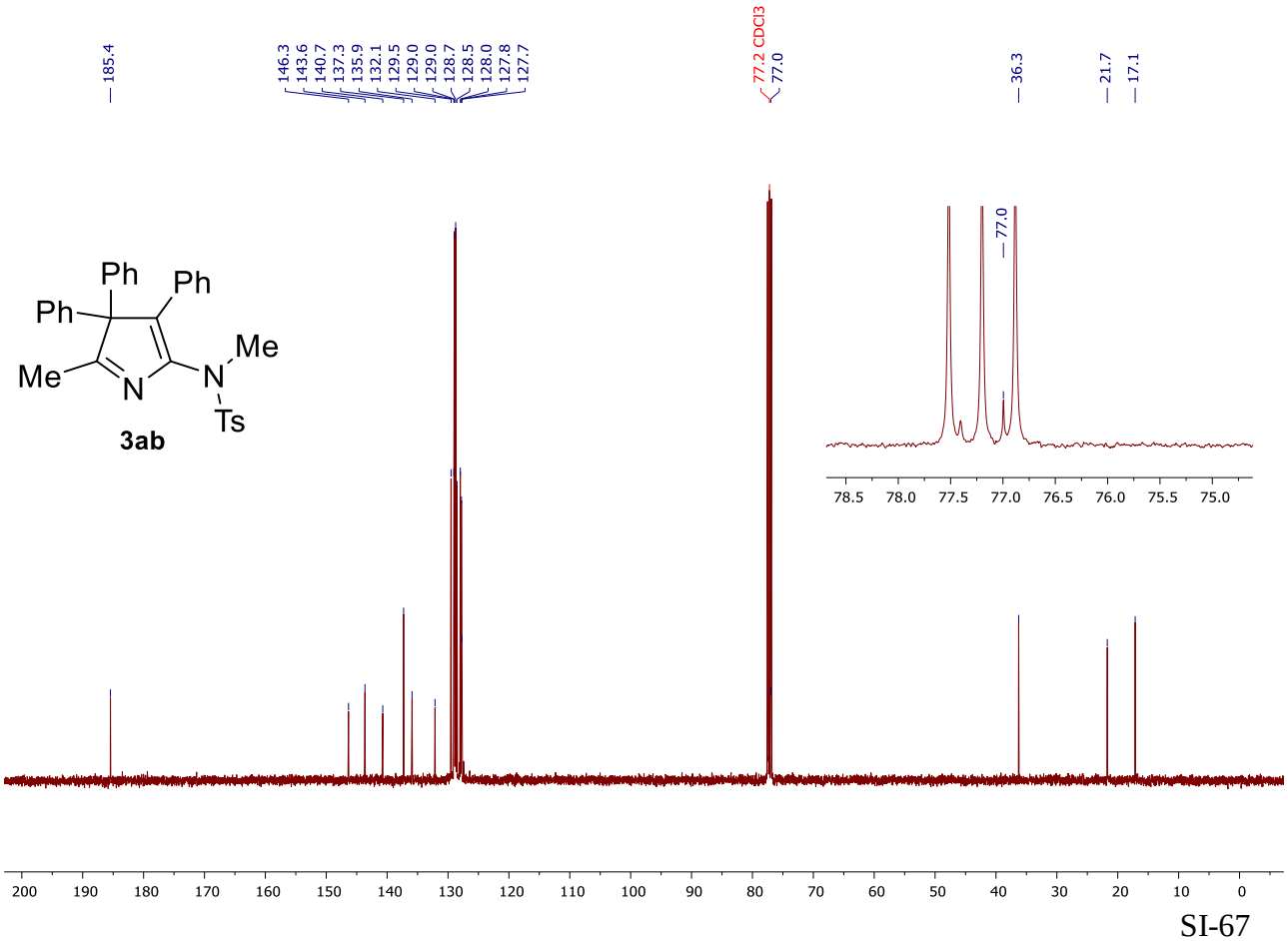
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3aa**



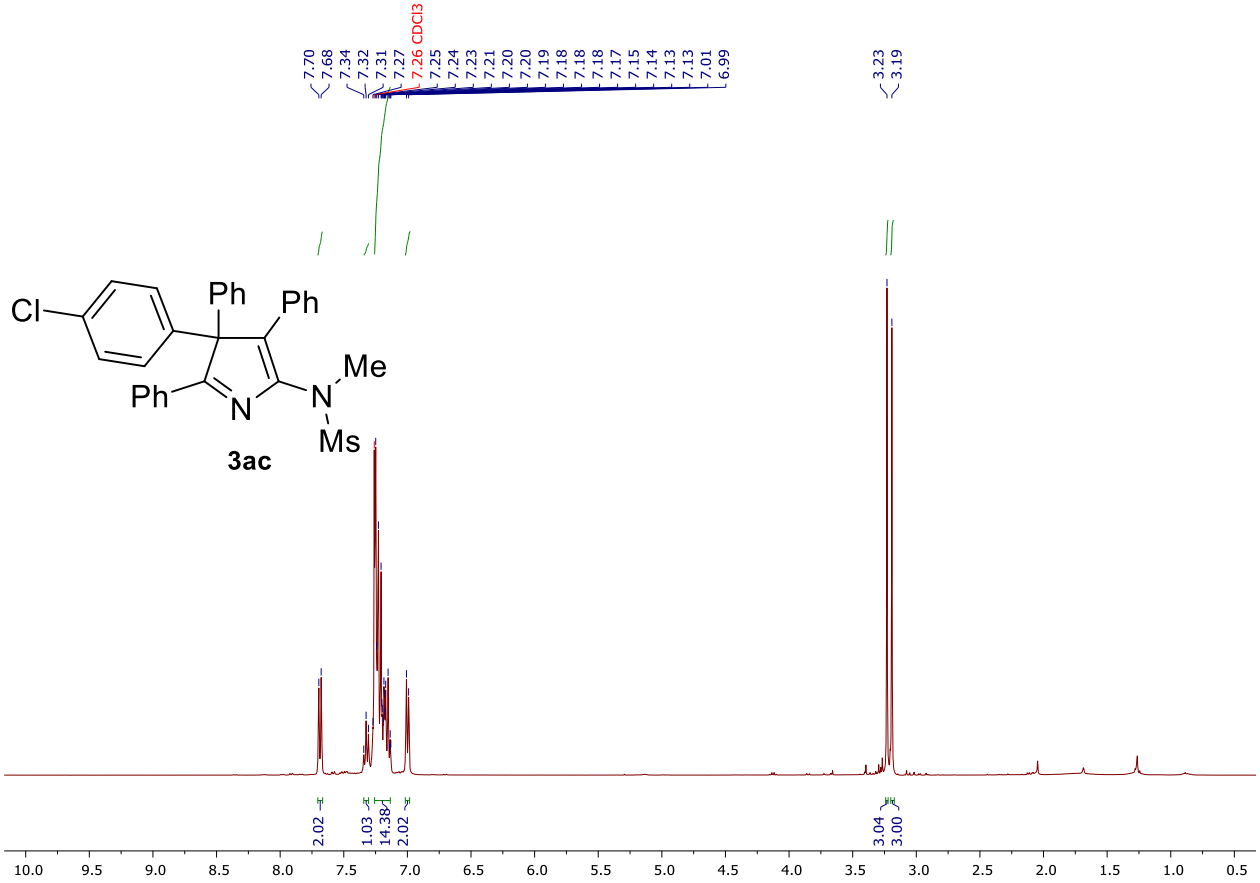
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



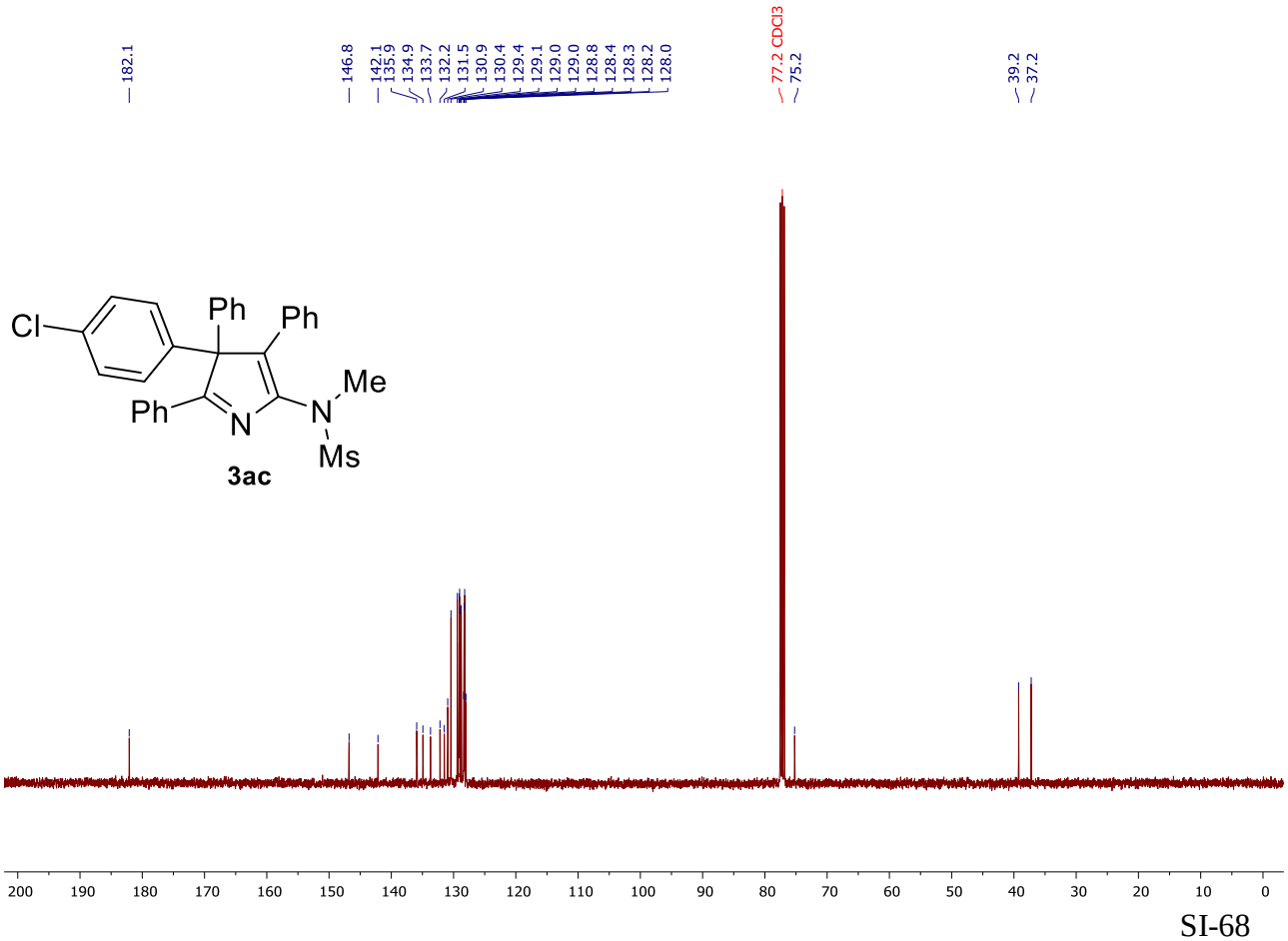
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3ab**



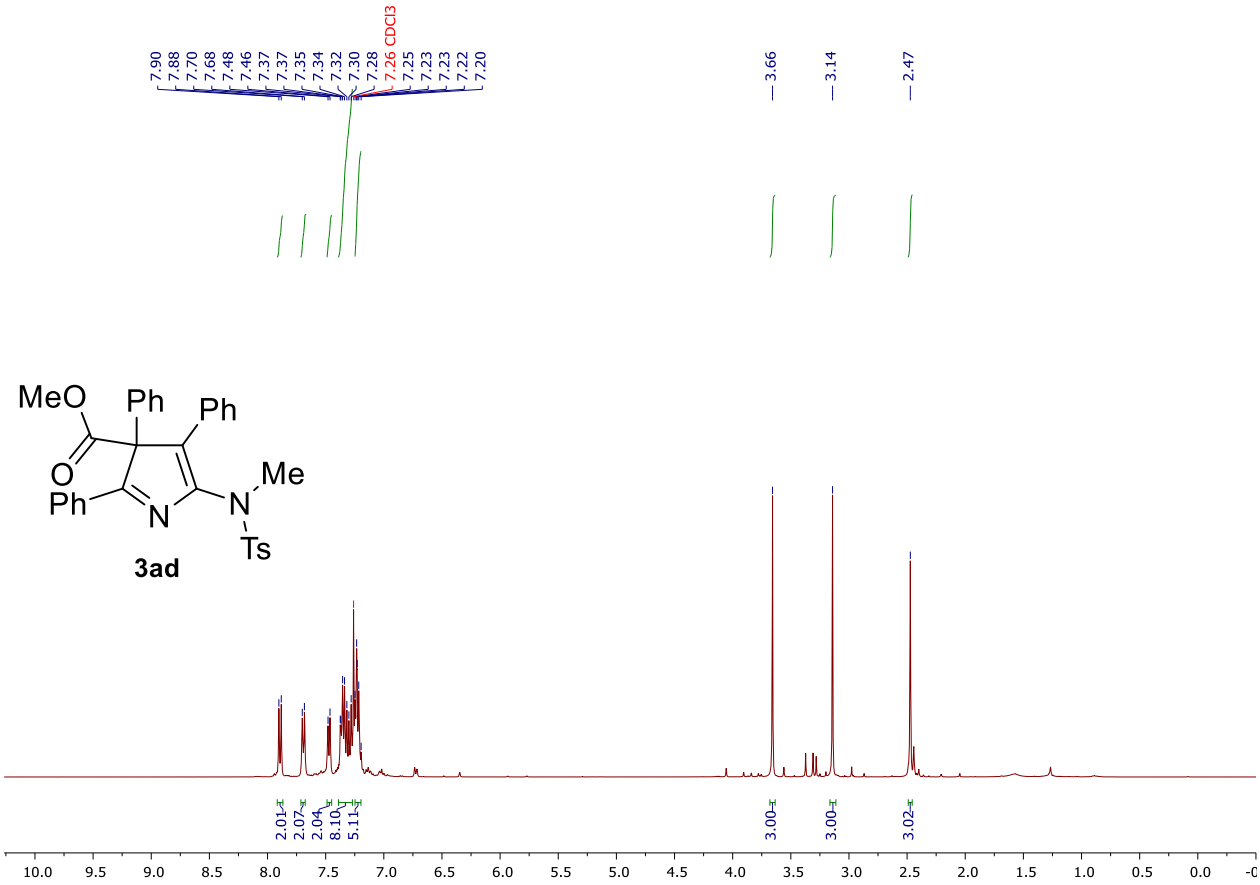
^{1}H NMR (400 MHz, $CDCl_3$) of **3ac**



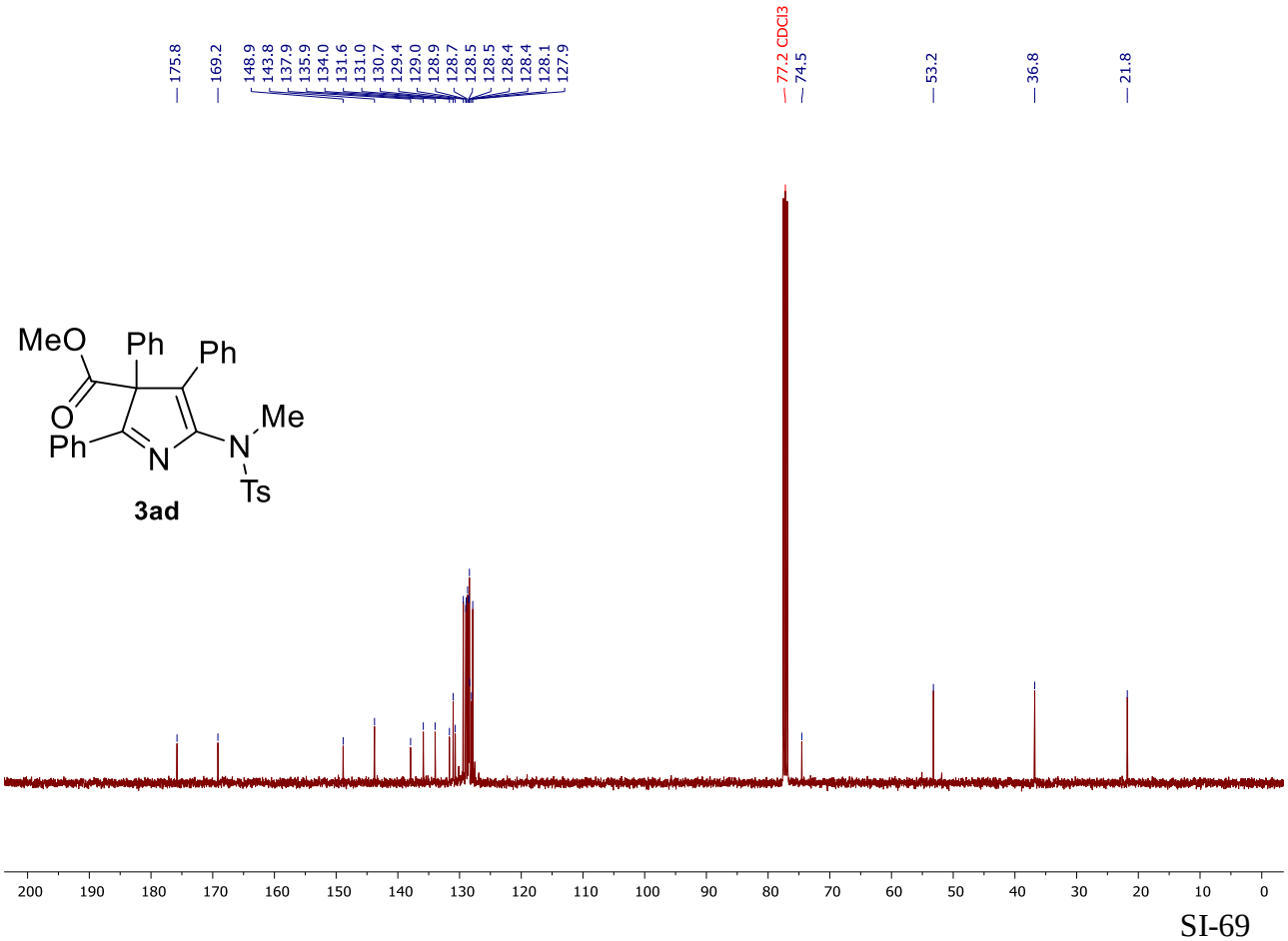
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3ac**



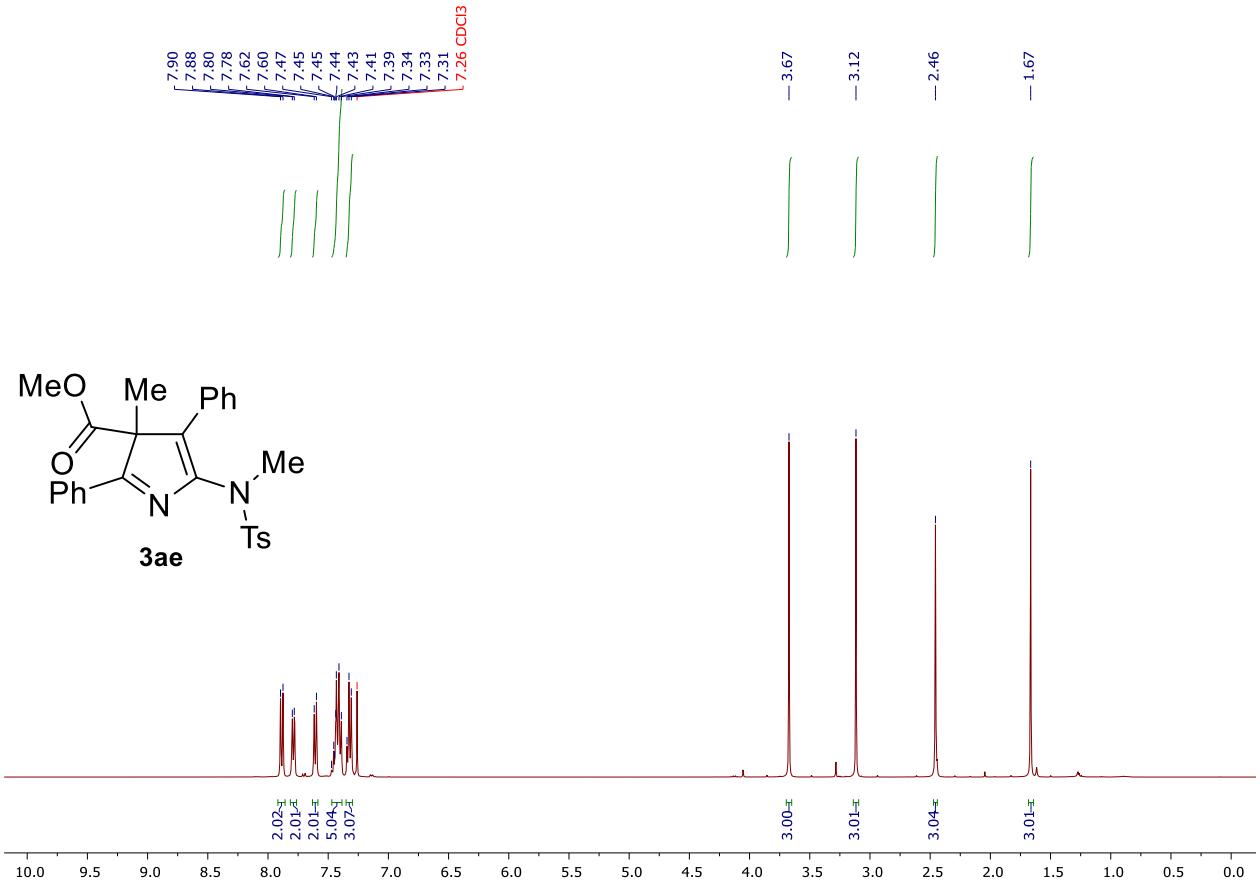
^{1}H NMR (400 MHz, $CDCl_3$) of **3ad**



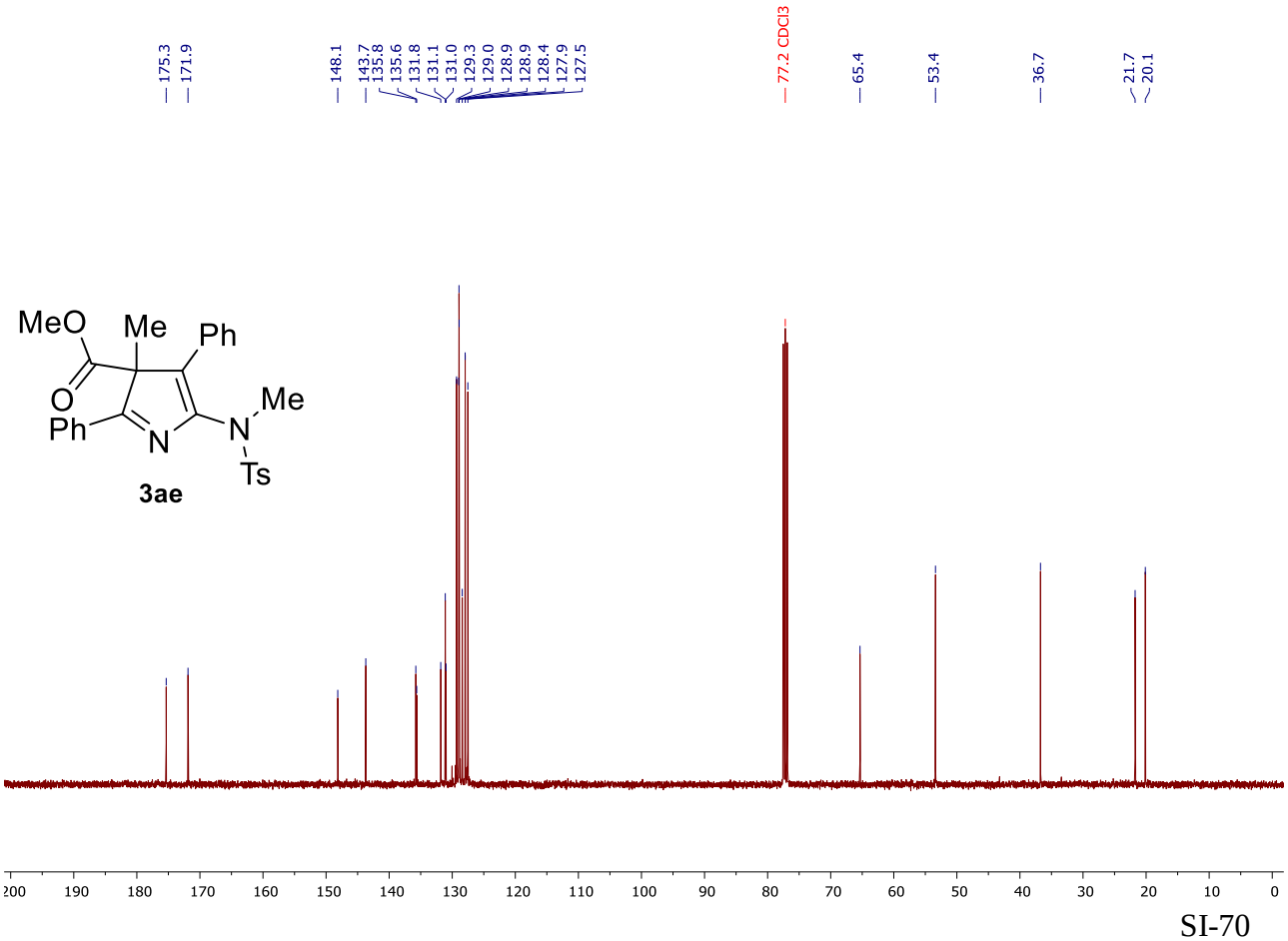
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3ad**



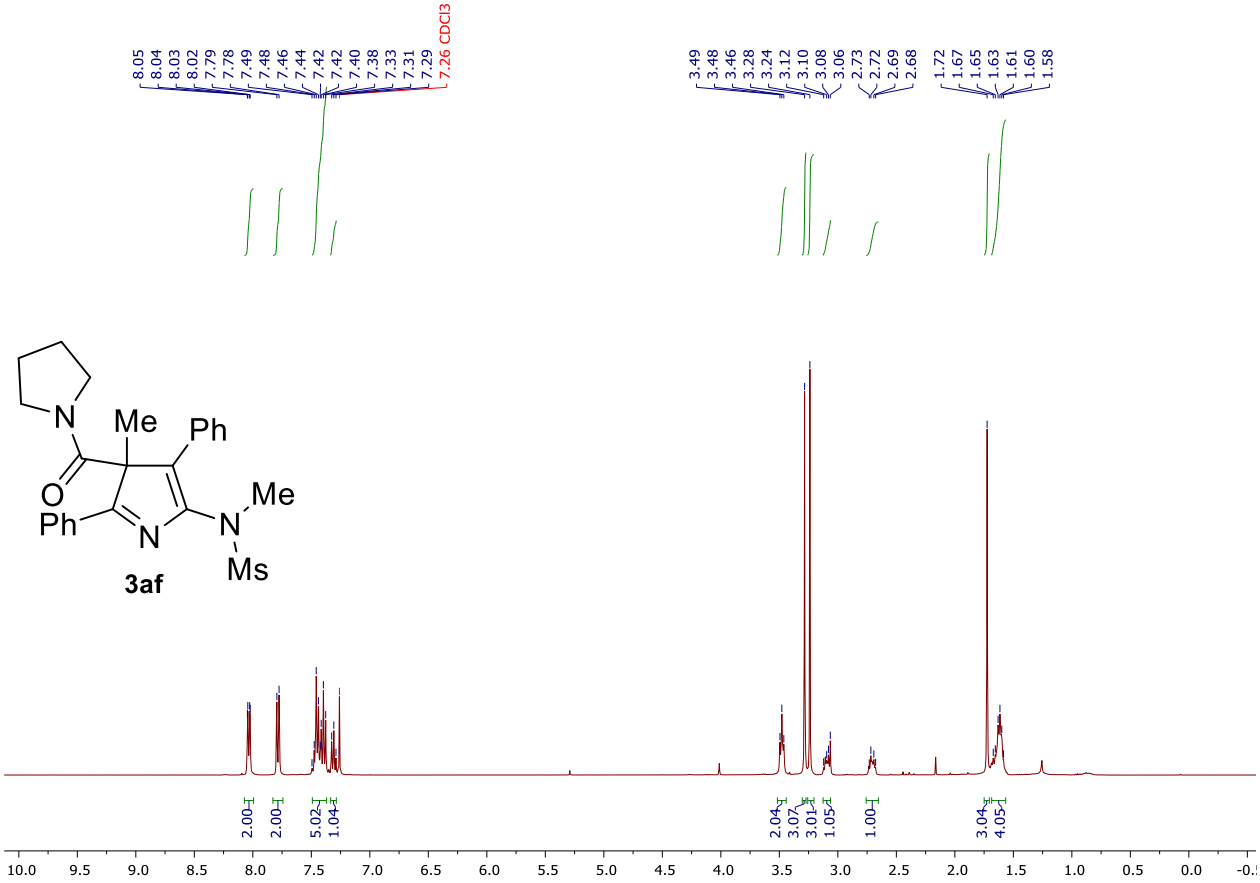
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**



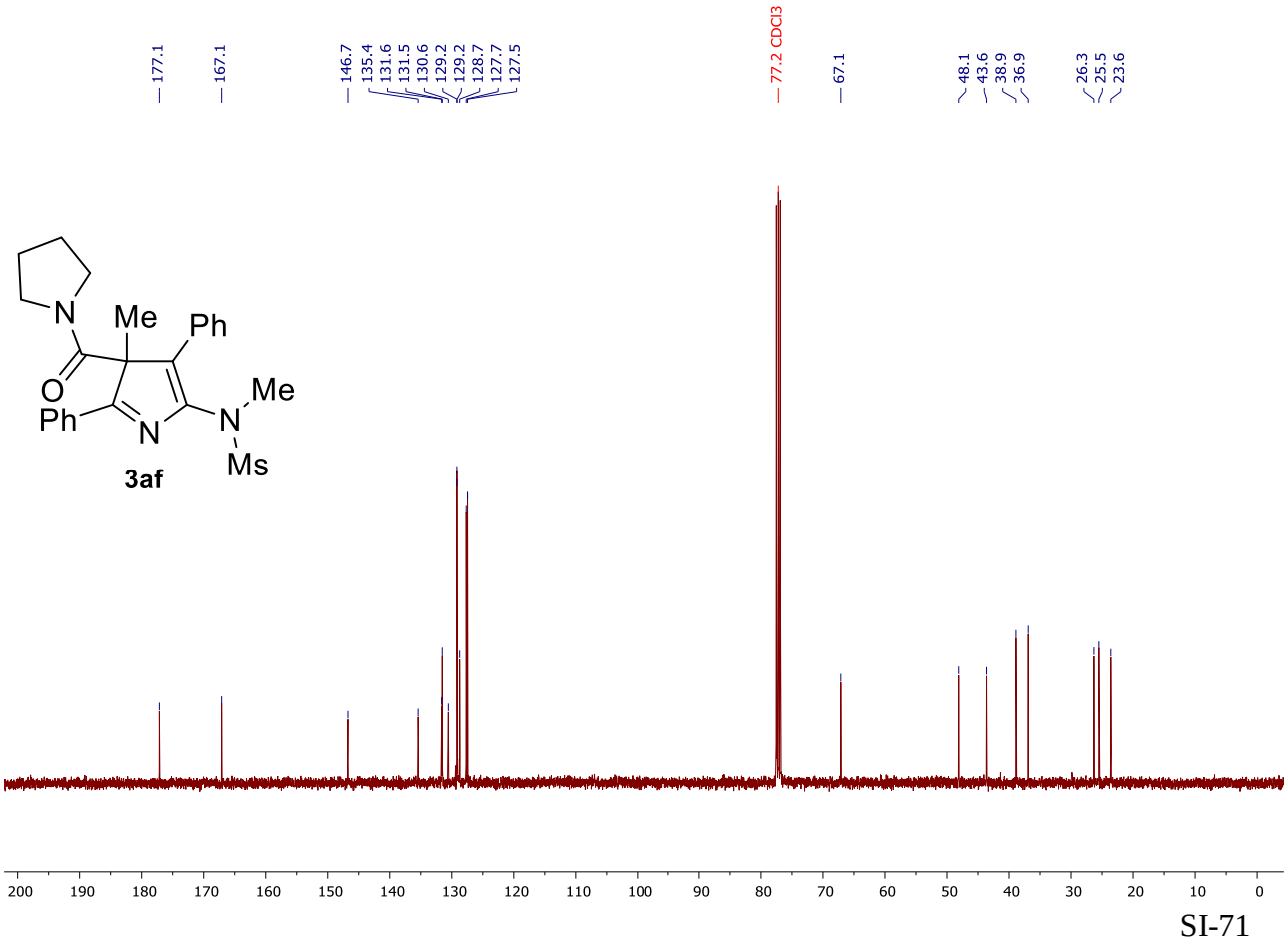
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3ae**



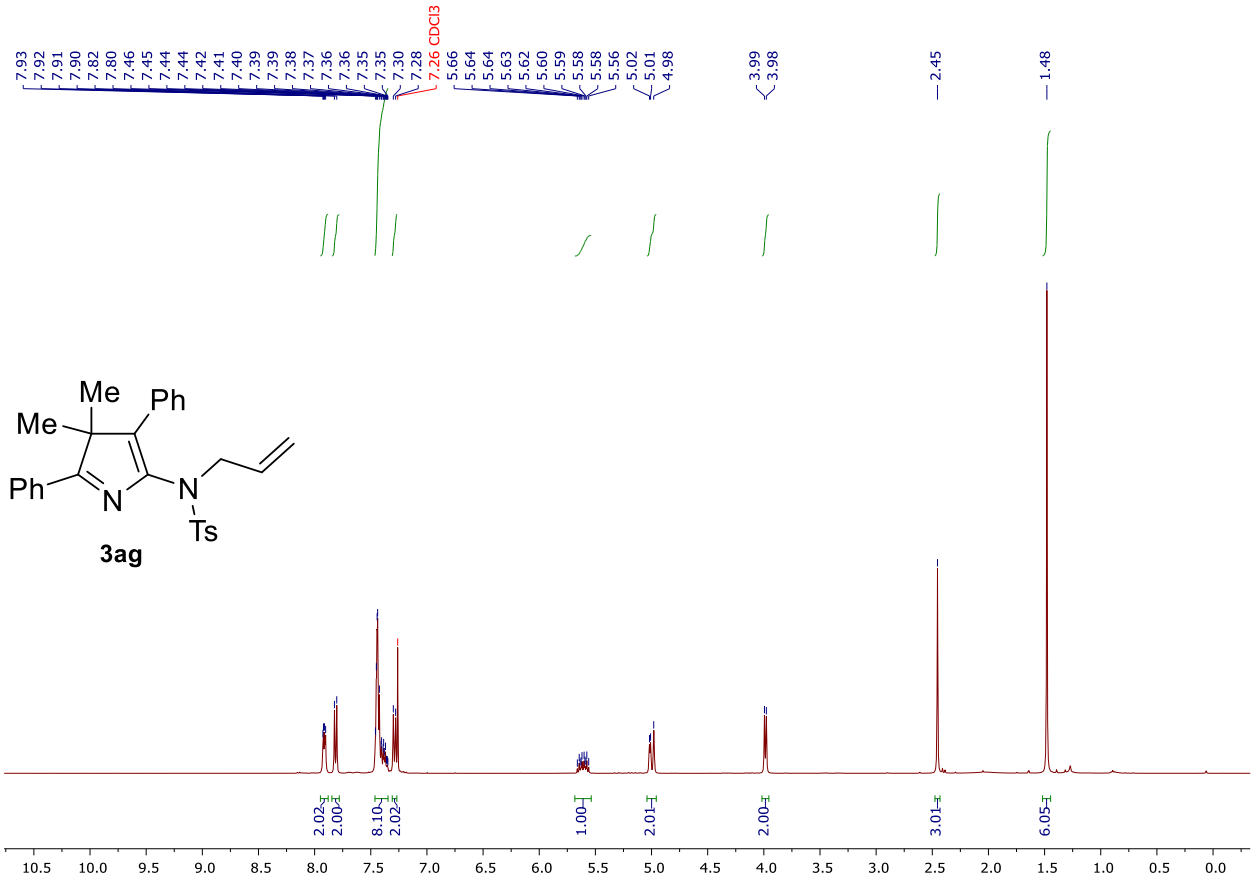
^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



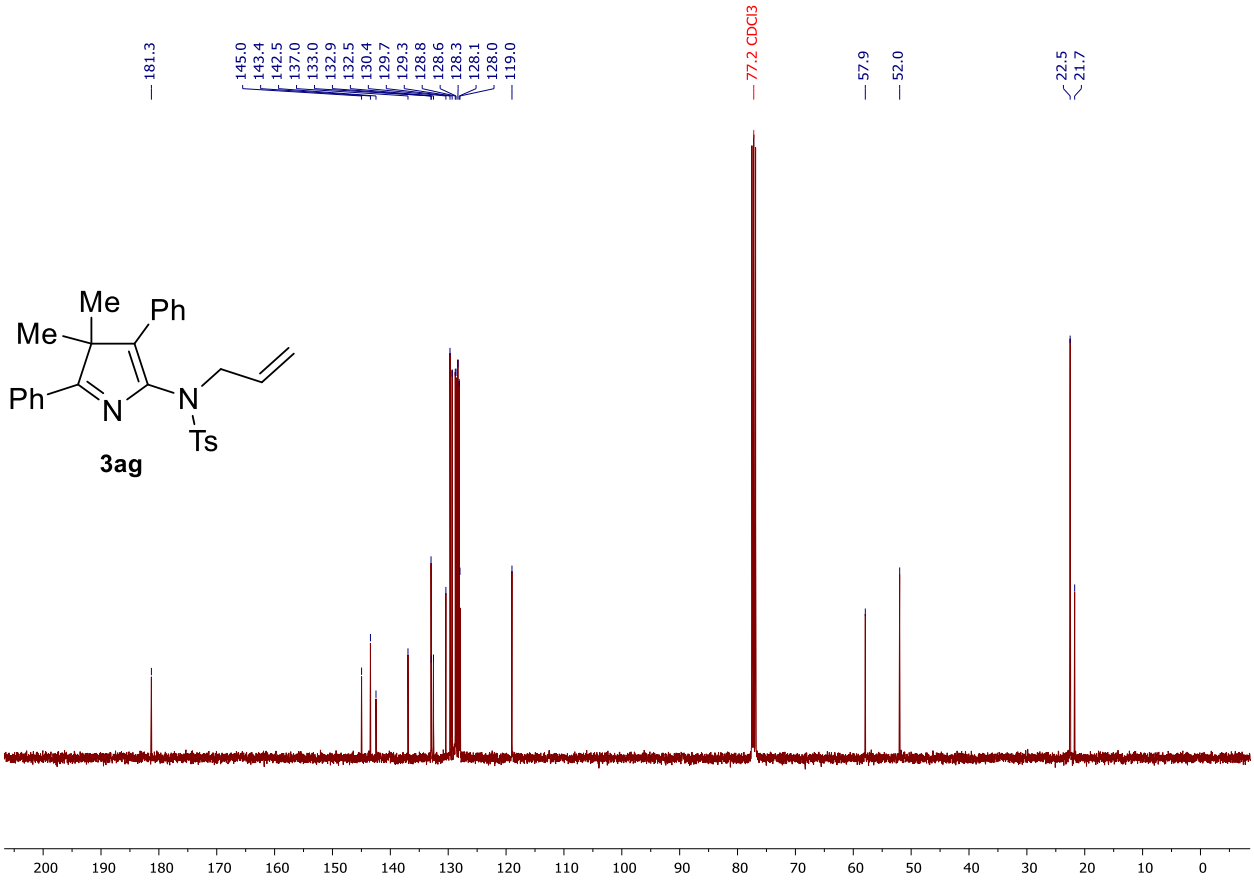
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3af**



^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**

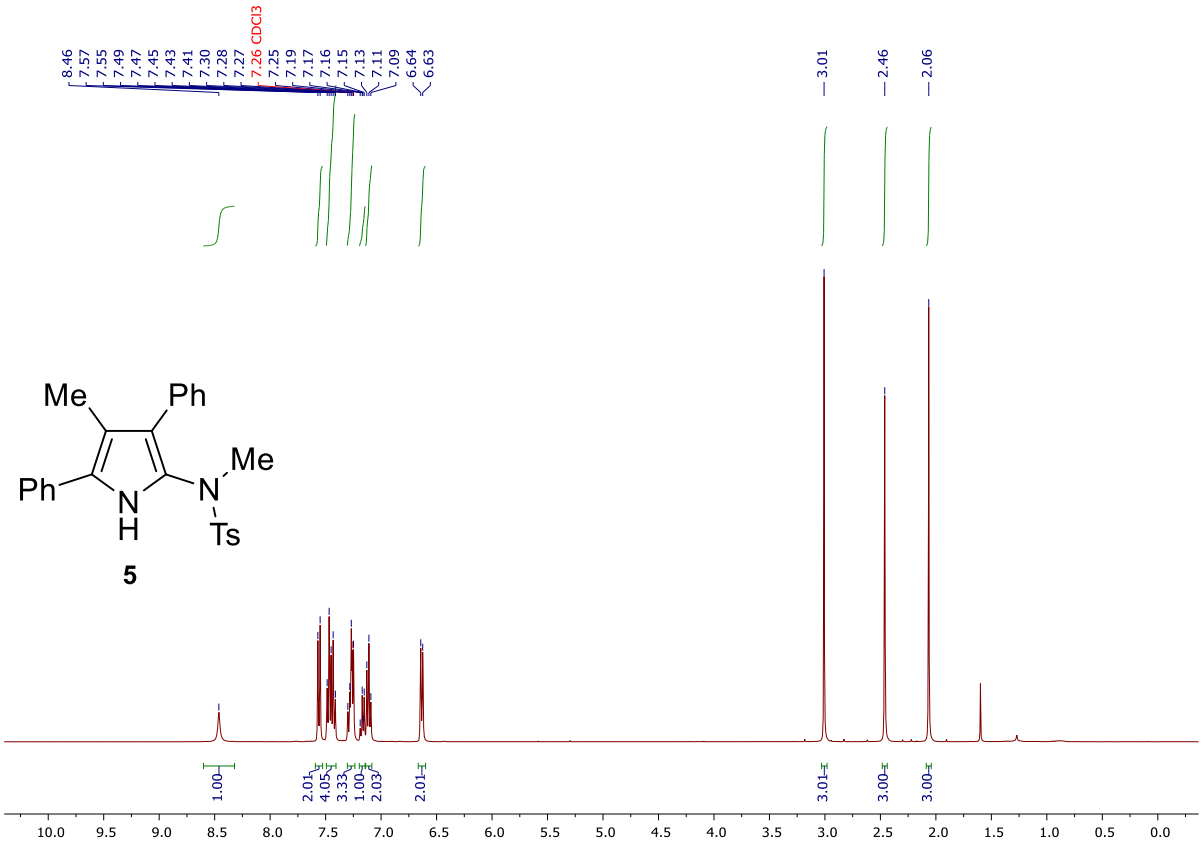


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3ag**

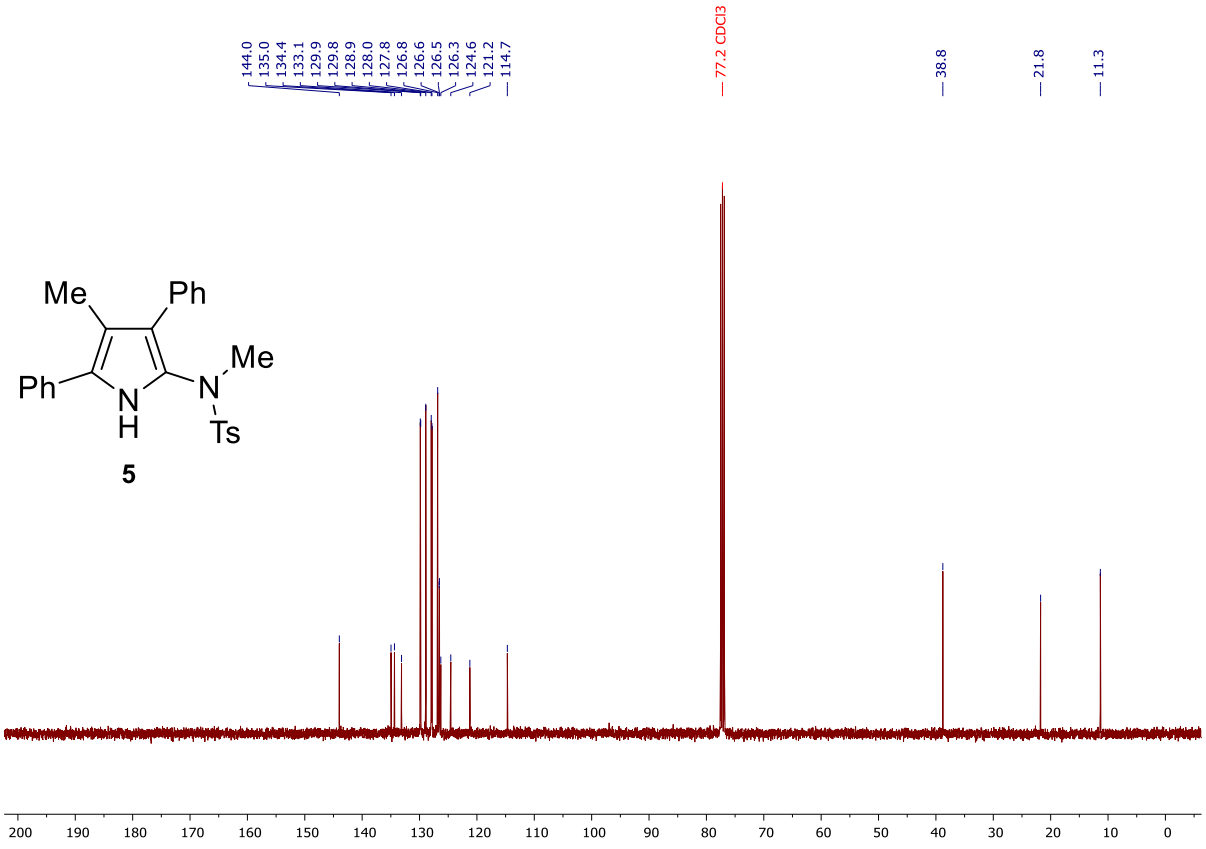


4.4.NMR Spectra of 1*H*-Pyrrole 5

^{1}H NMR (400 MHz, $CDCl_3$) of **5**

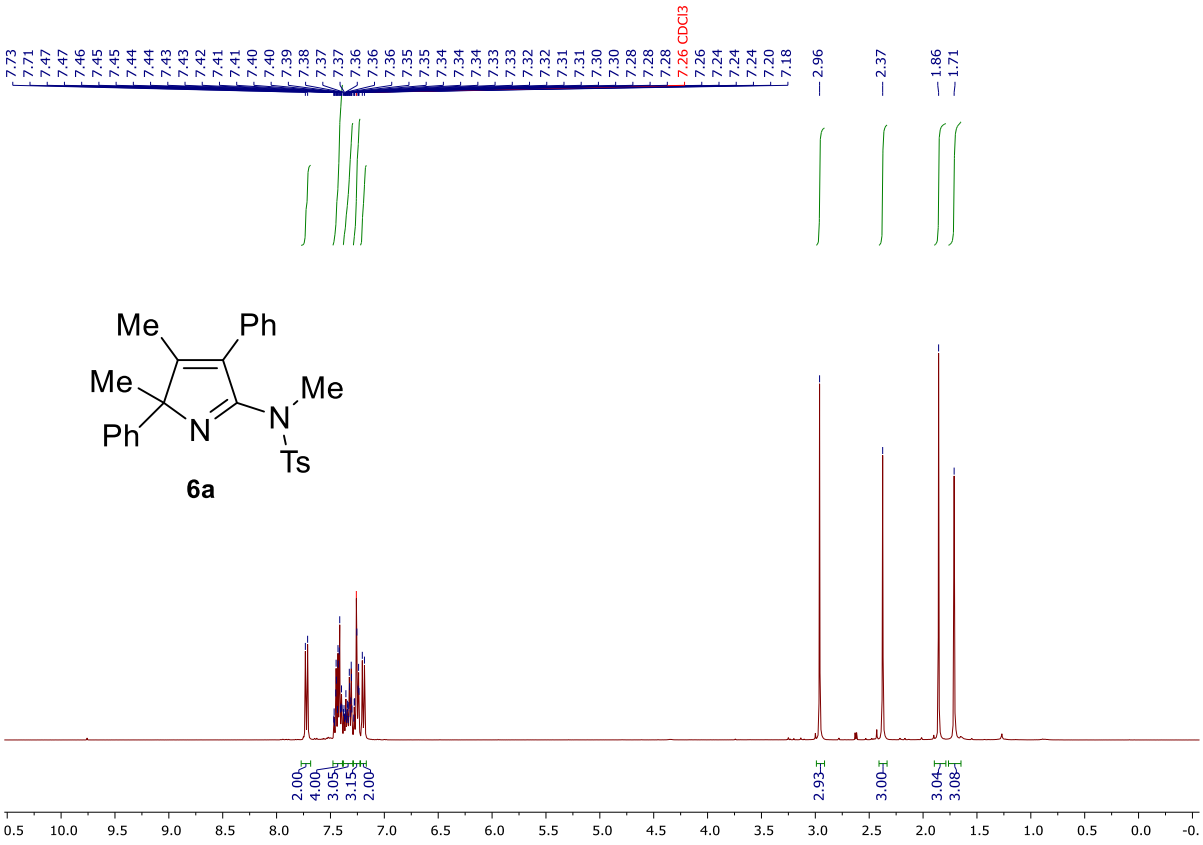


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **5**

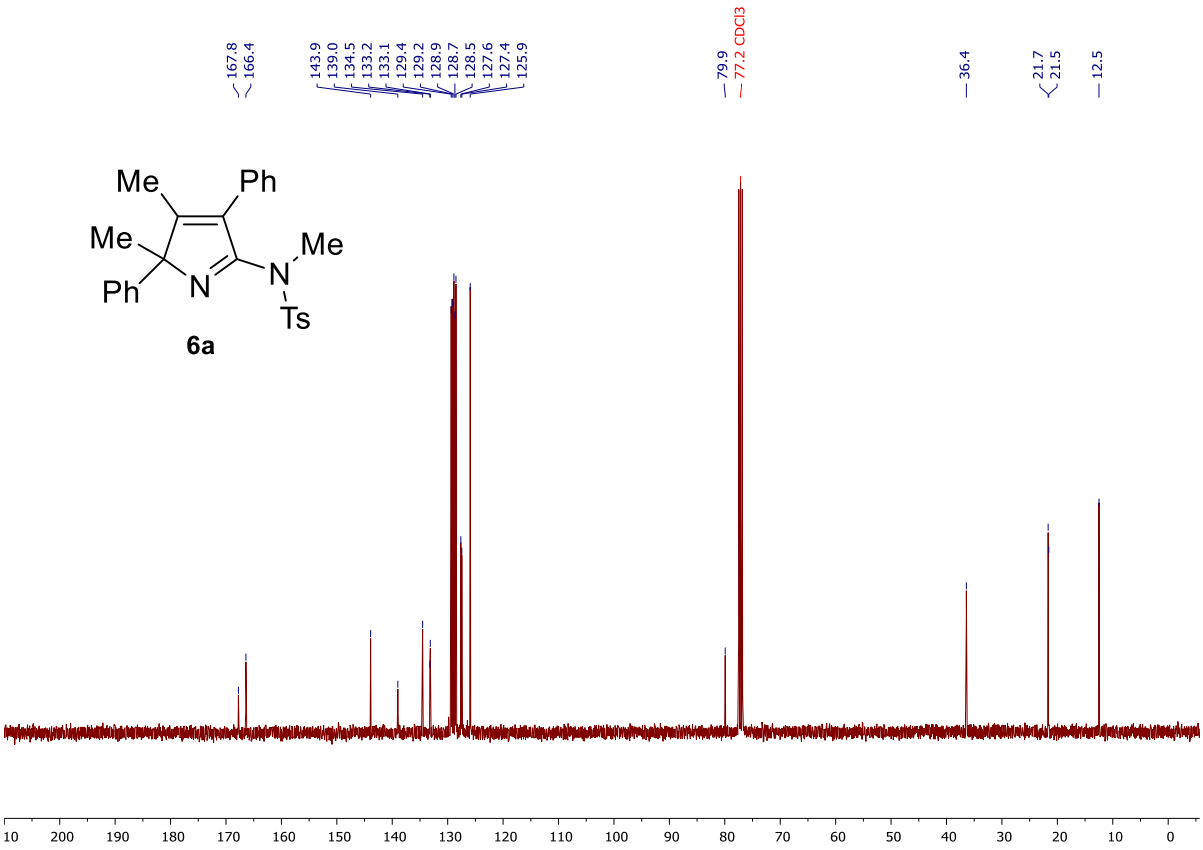


4.5. NMR Spectra of 2*H*-Pyrroles 6

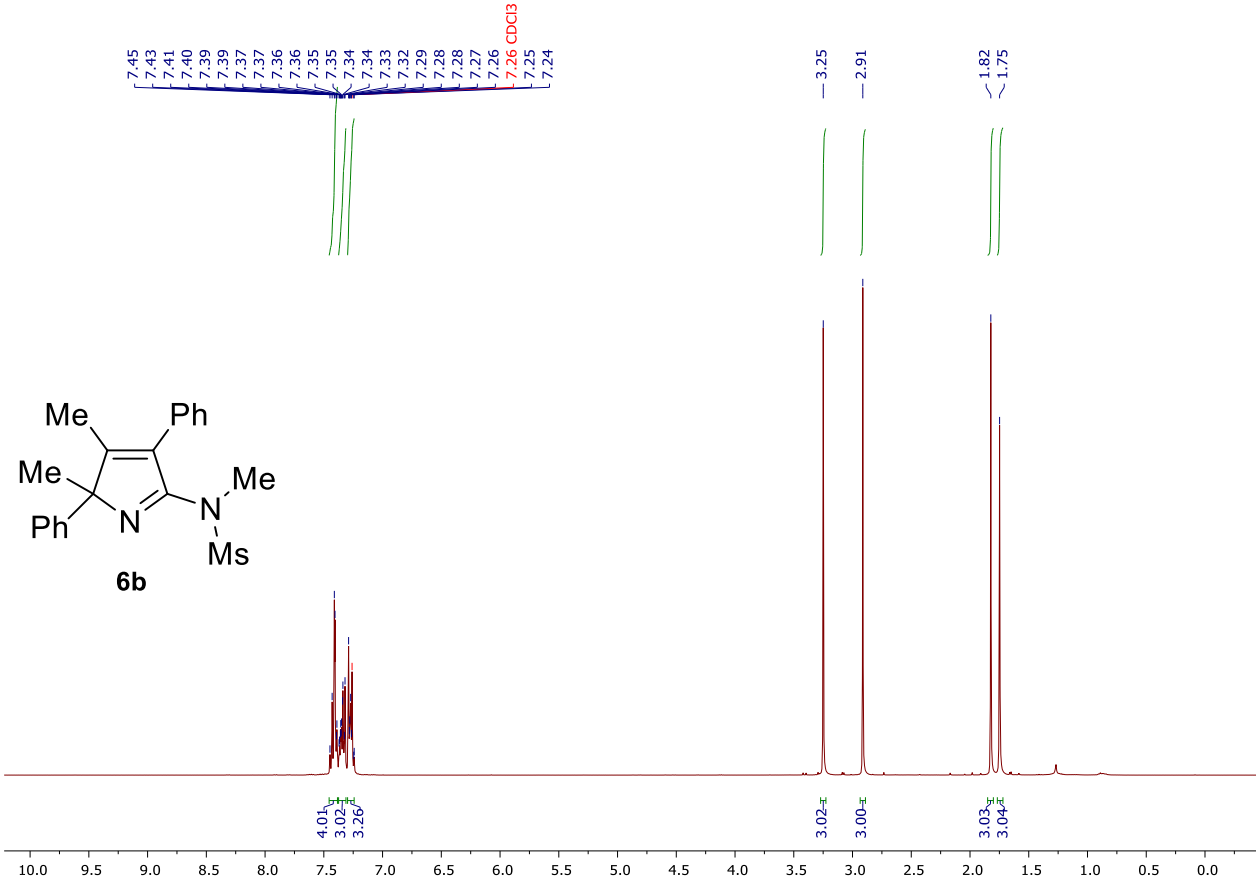
^{1}H NMR (400 MHz, $CDCl_3$) of **6a**



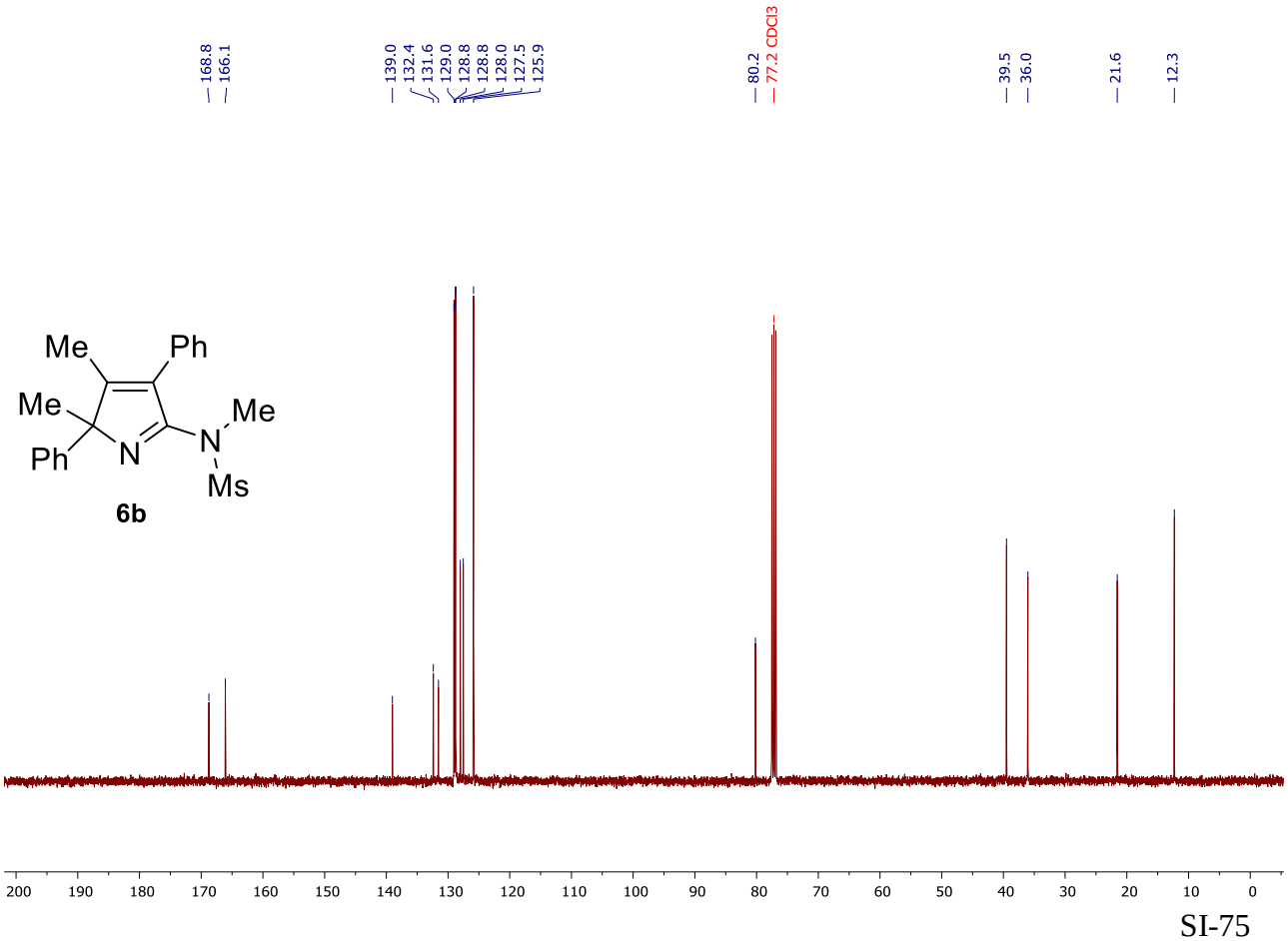
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6a**



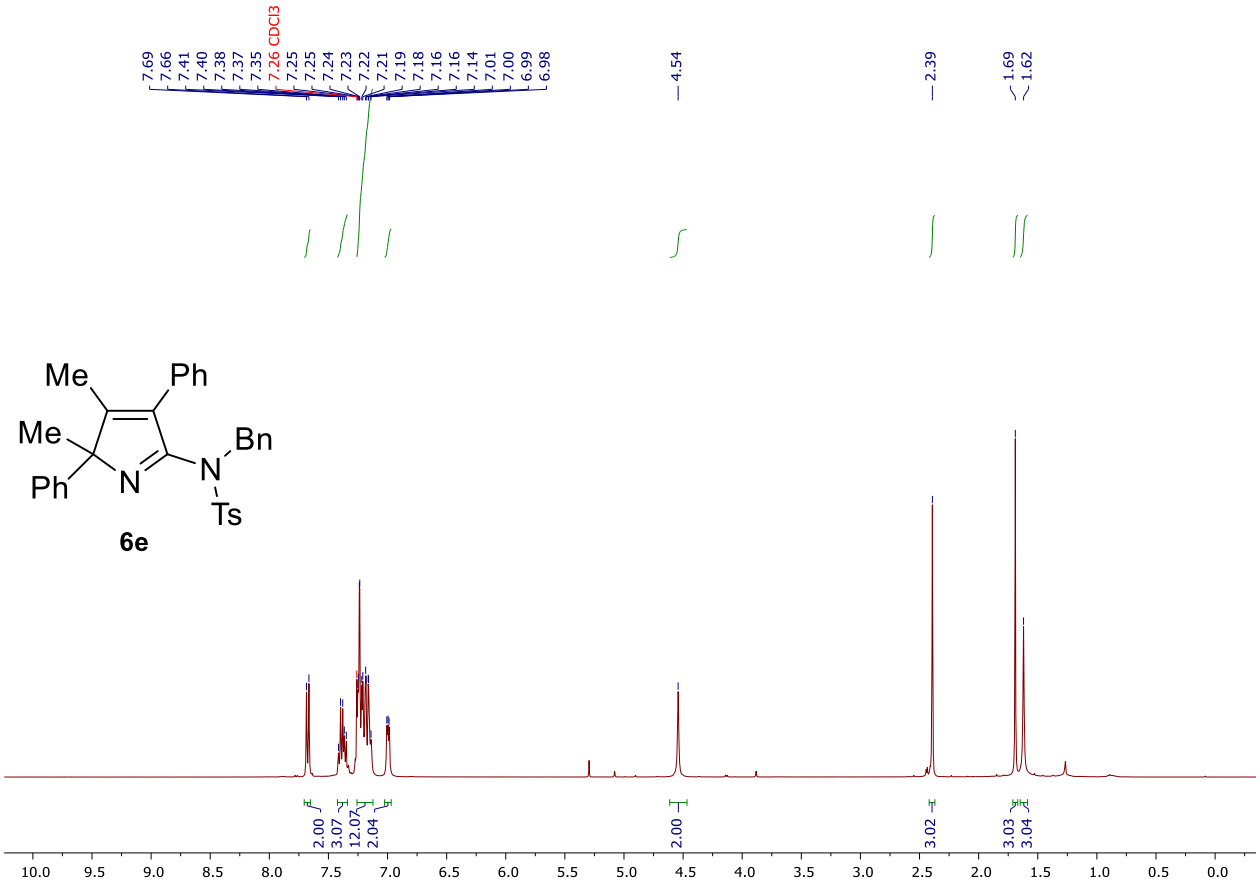
^{1}H NMR (400 MHz, $CDCl_3$) of **6b**



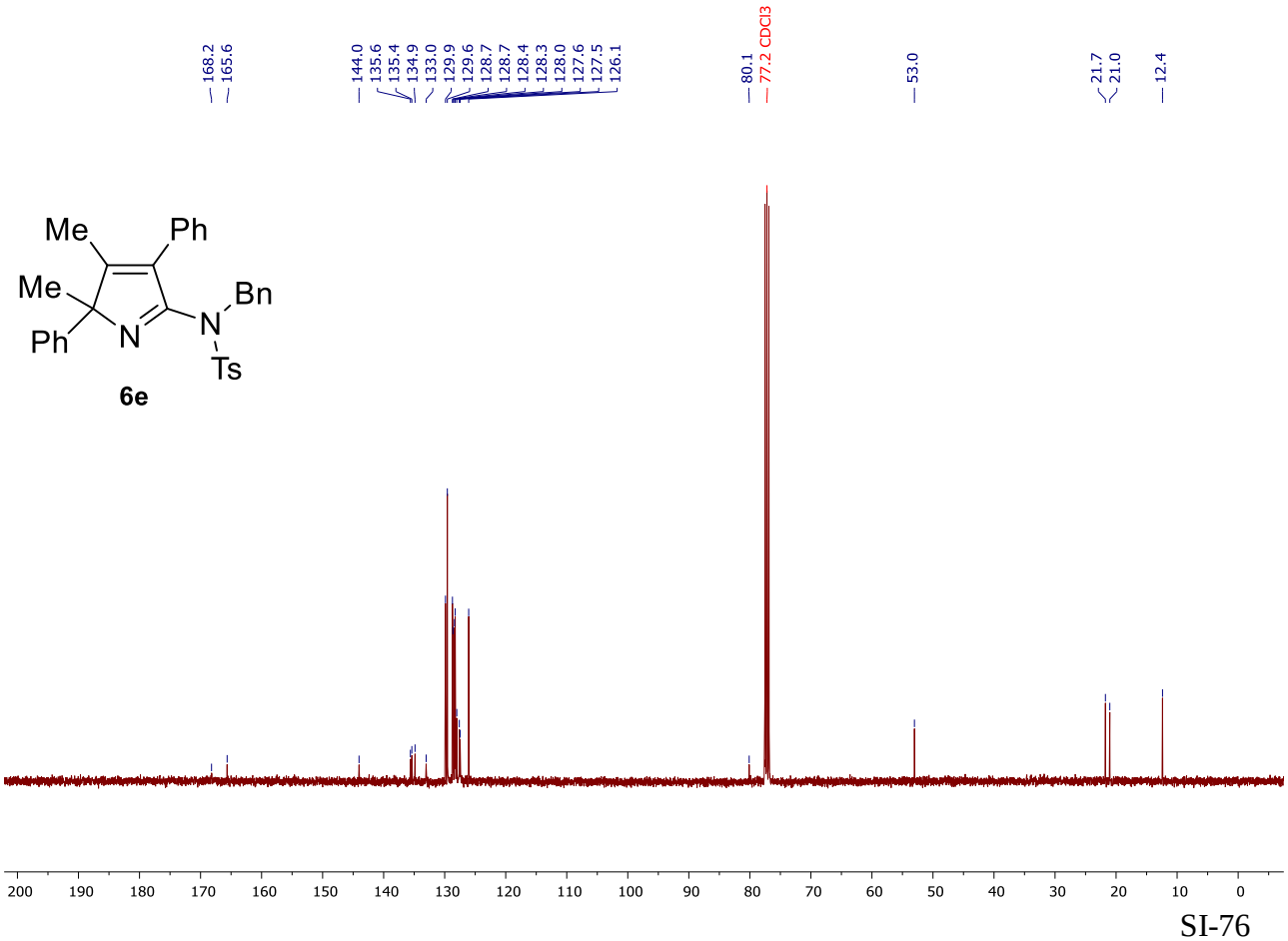
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6b**



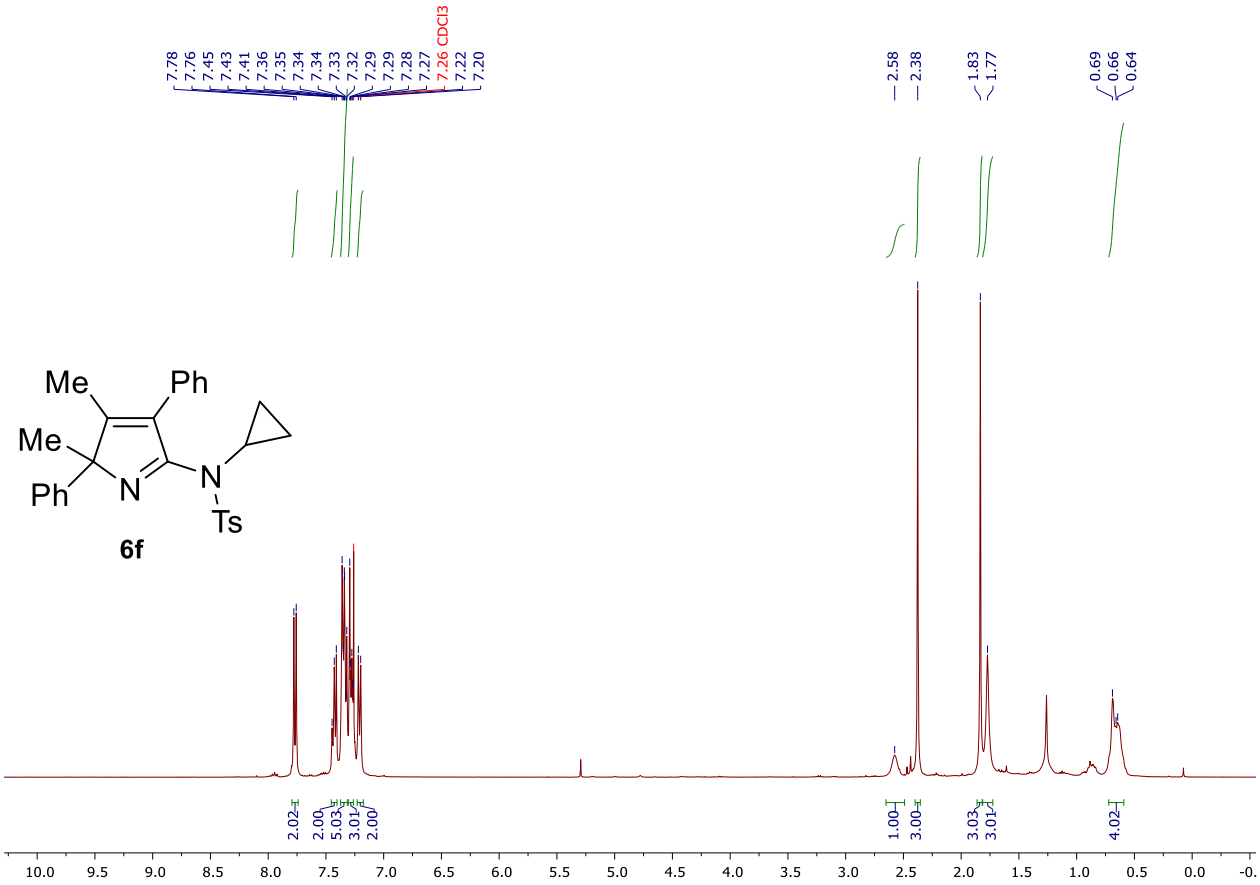
^{1}H NMR (400 MHz, $CDCl_3$) of **6e**



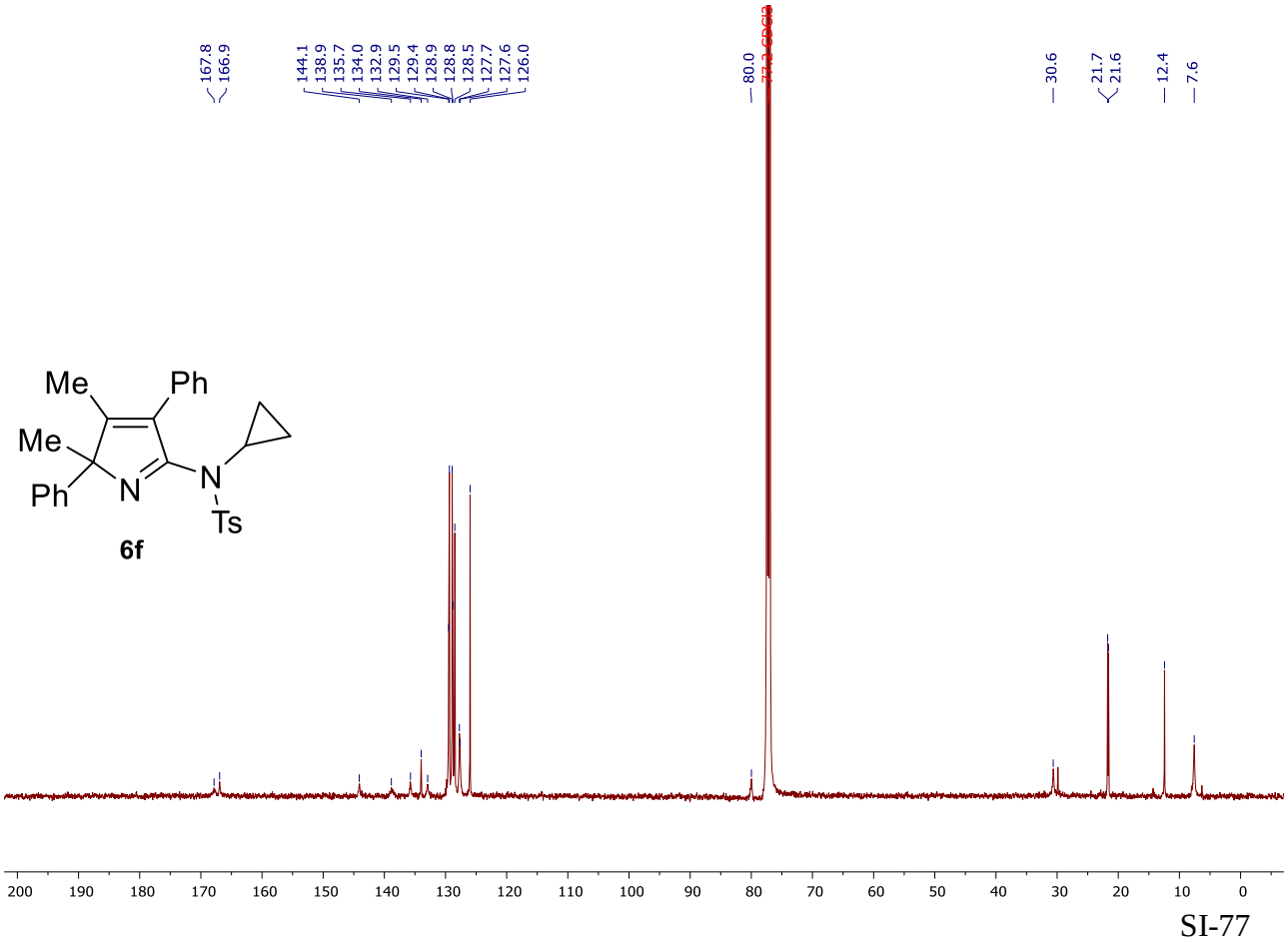
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6e**



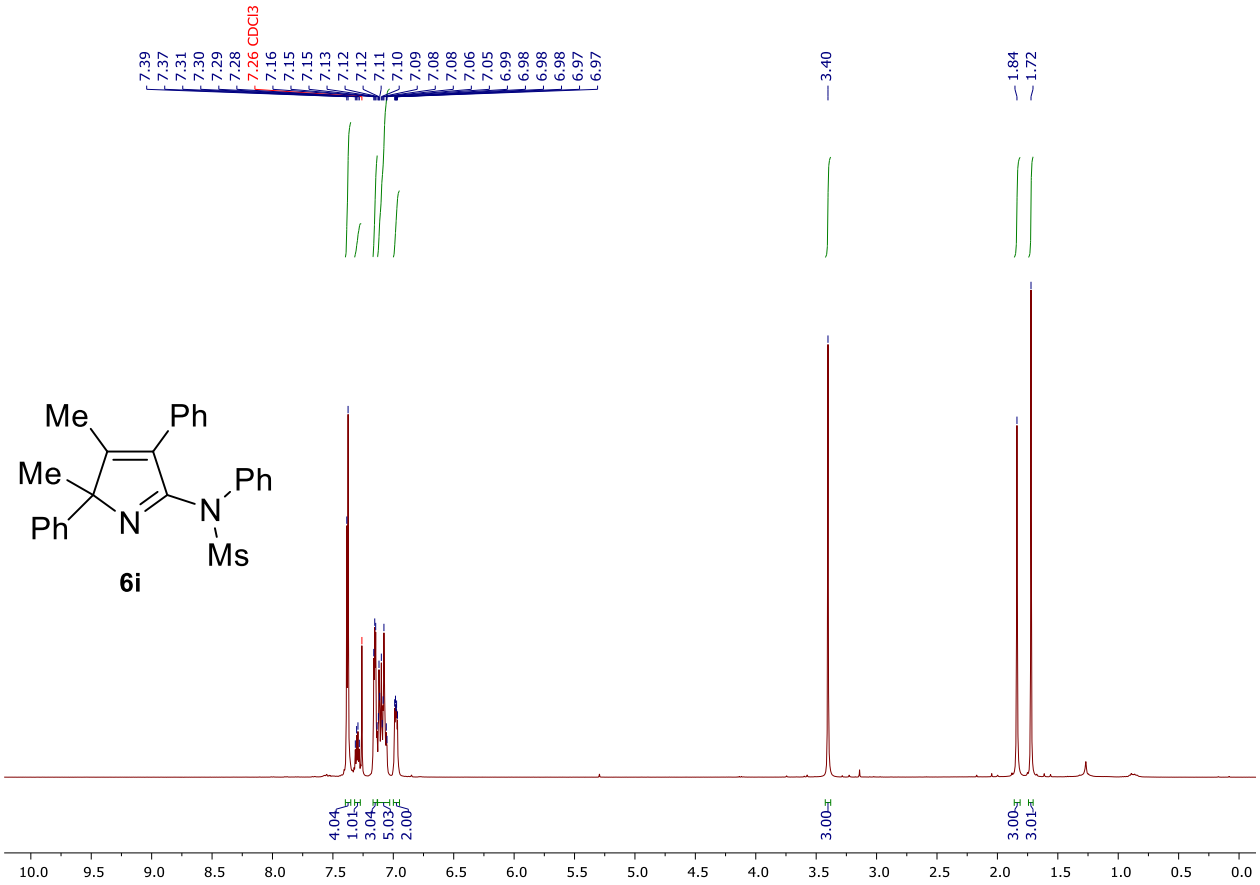
^{1}H NMR (400 MHz, $CDCl_3$) of **6f**



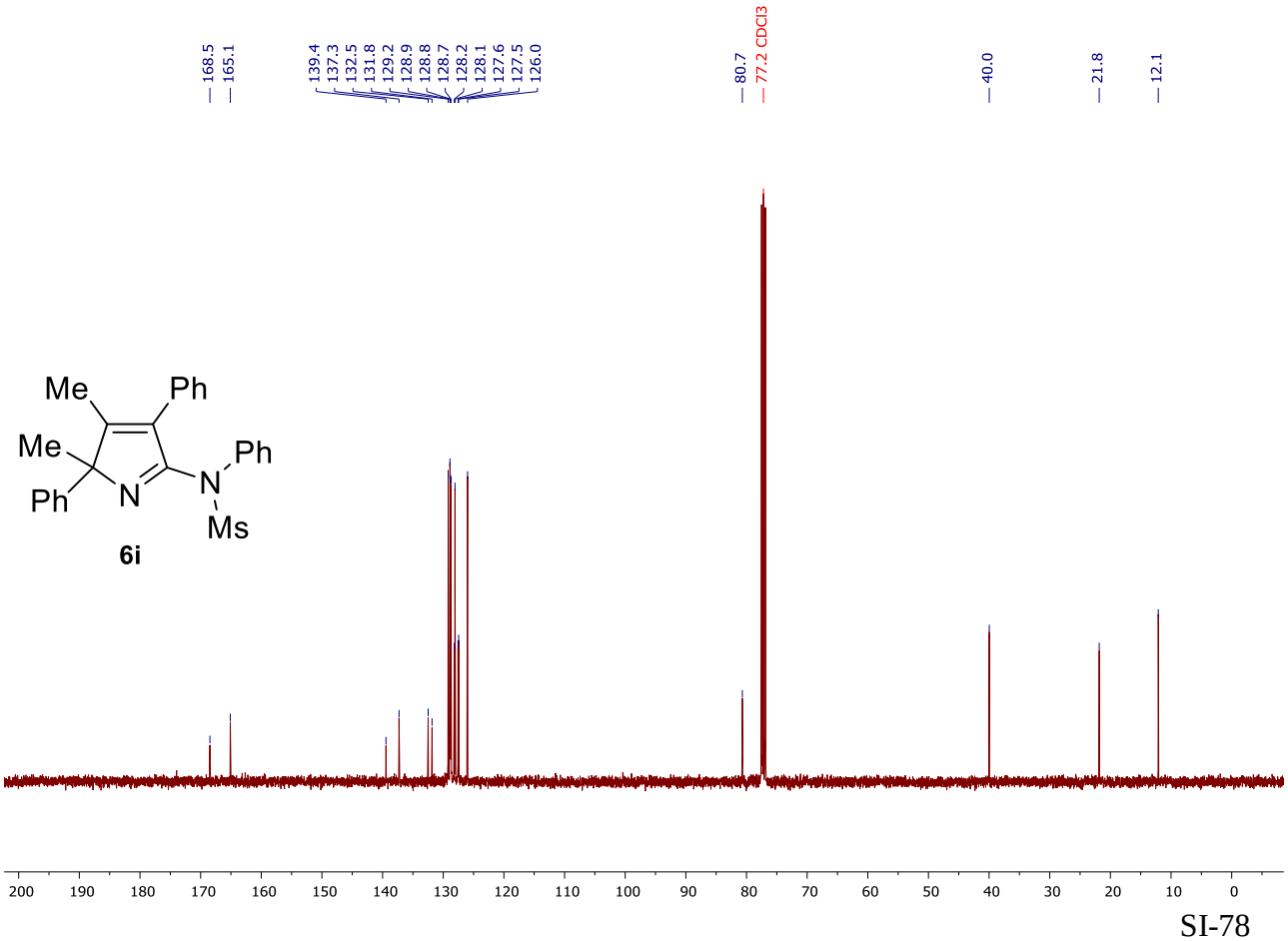
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6f**



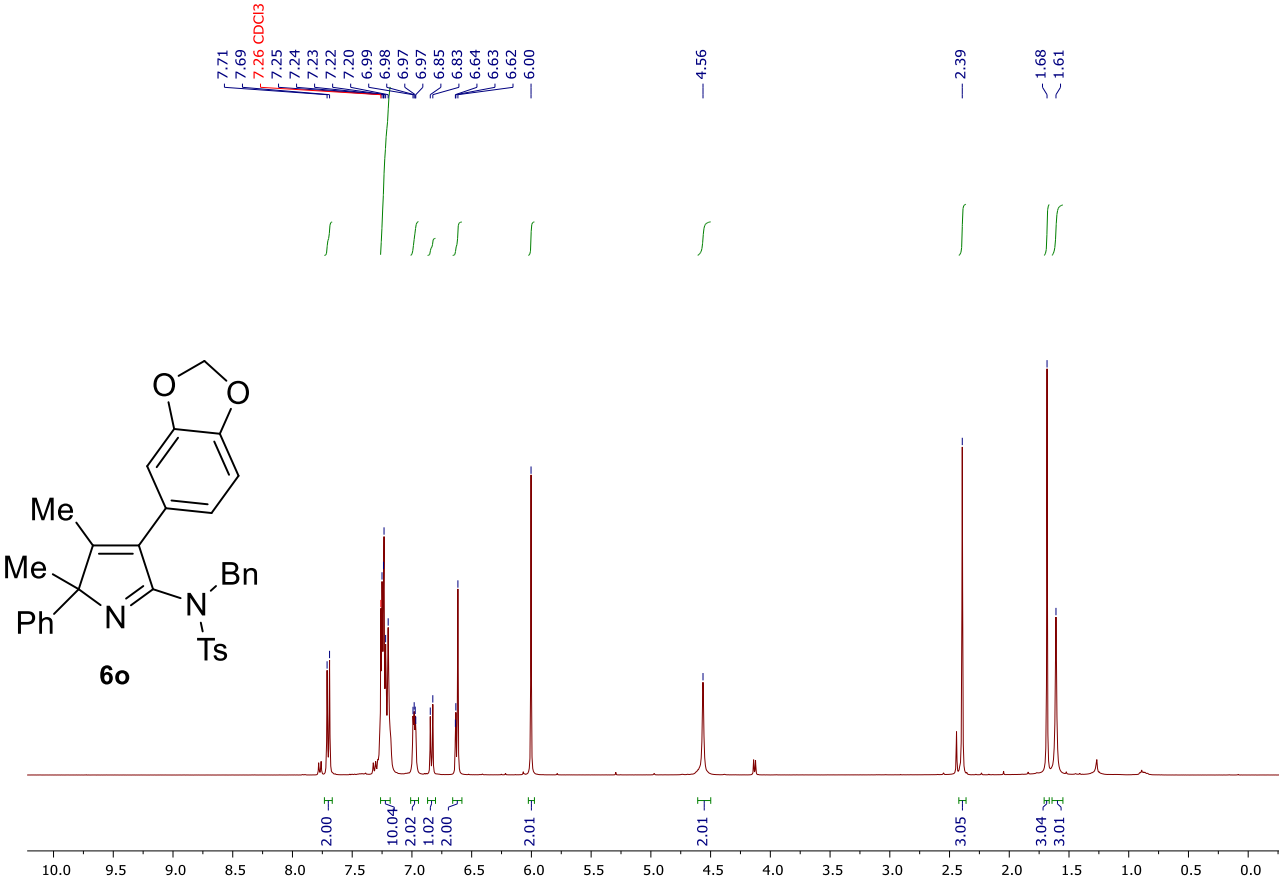
^{1}H NMR (400 MHz, $CDCl_3$) of **6i**



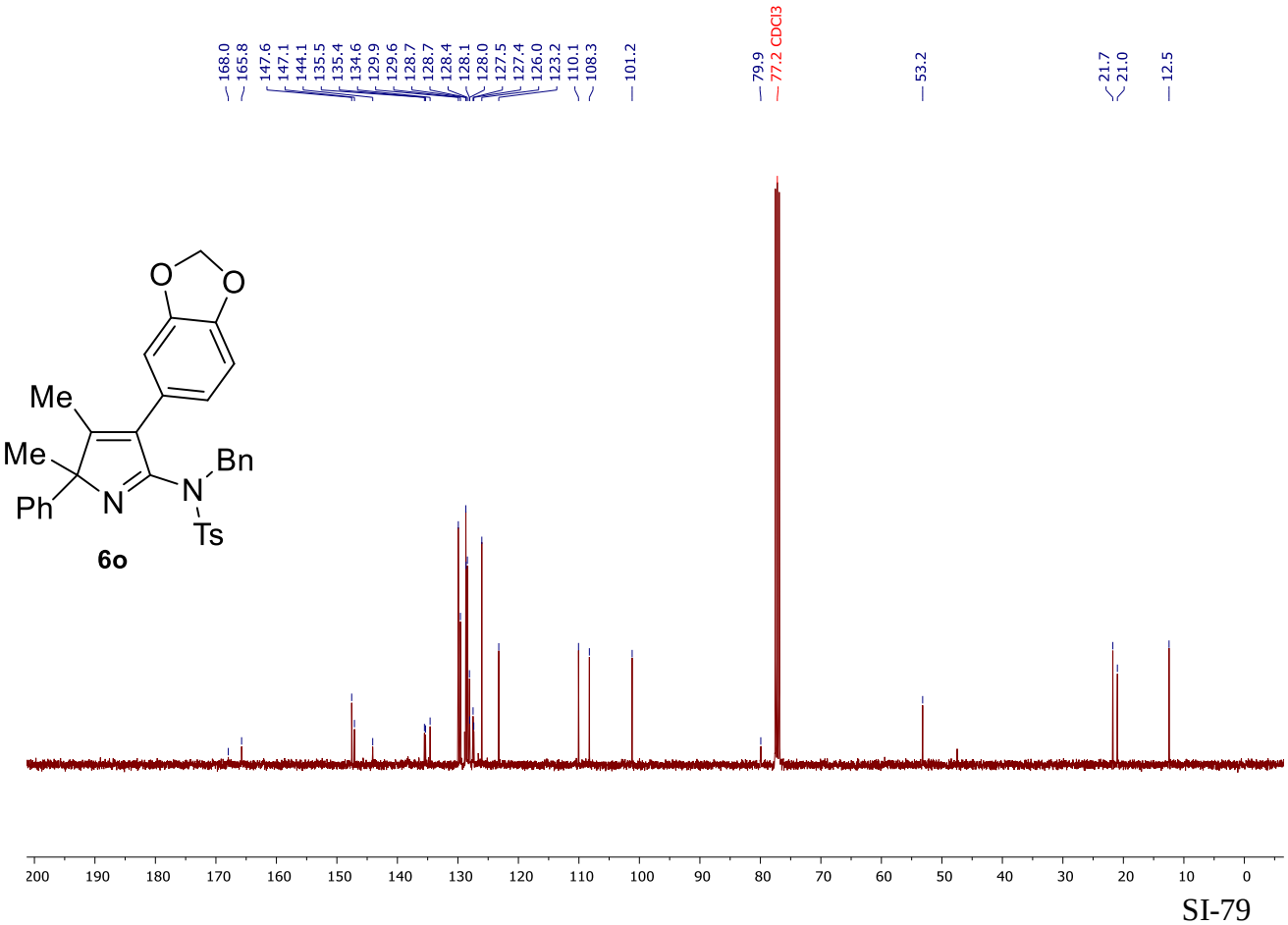
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6i**



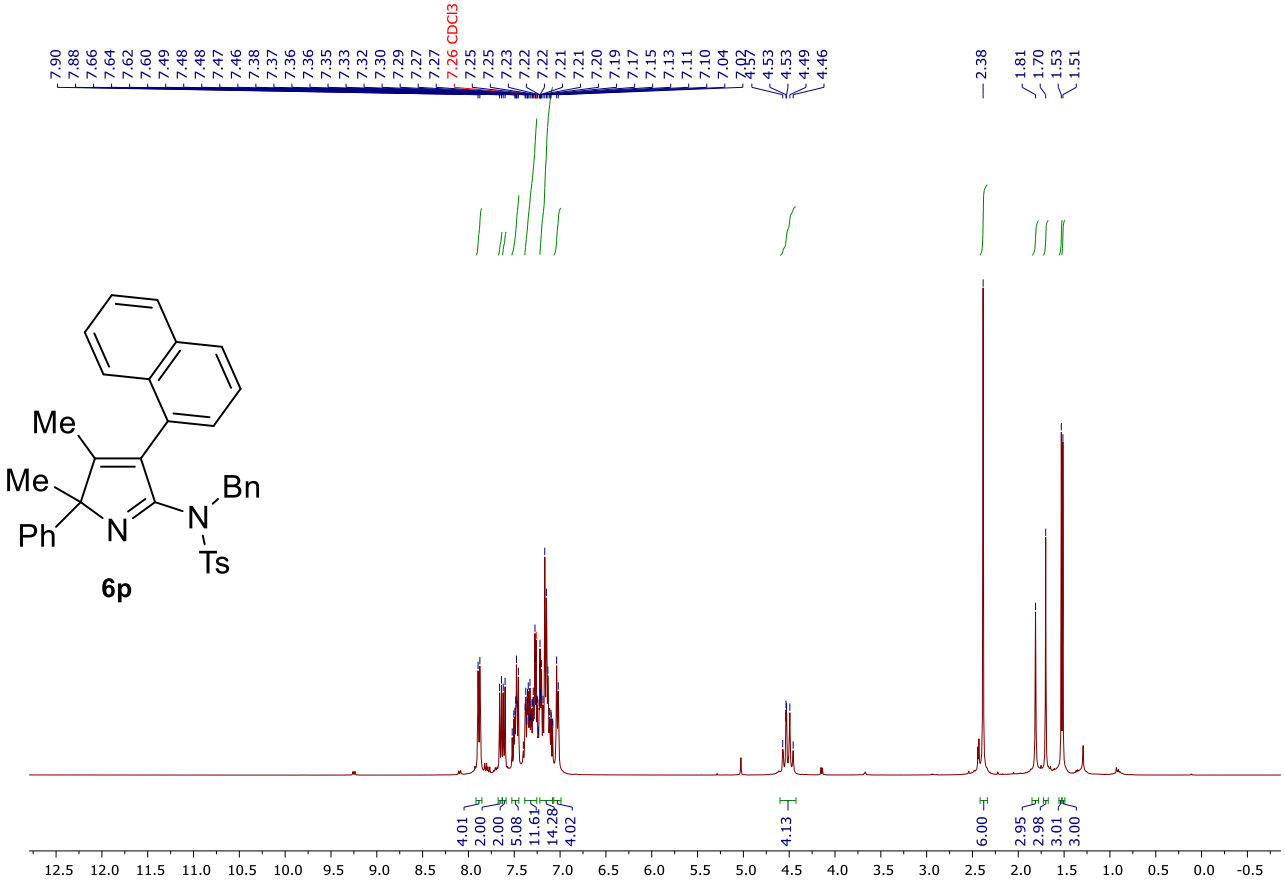
^{1}H NMR (400 MHz, $CDCl_3$) of **6o**



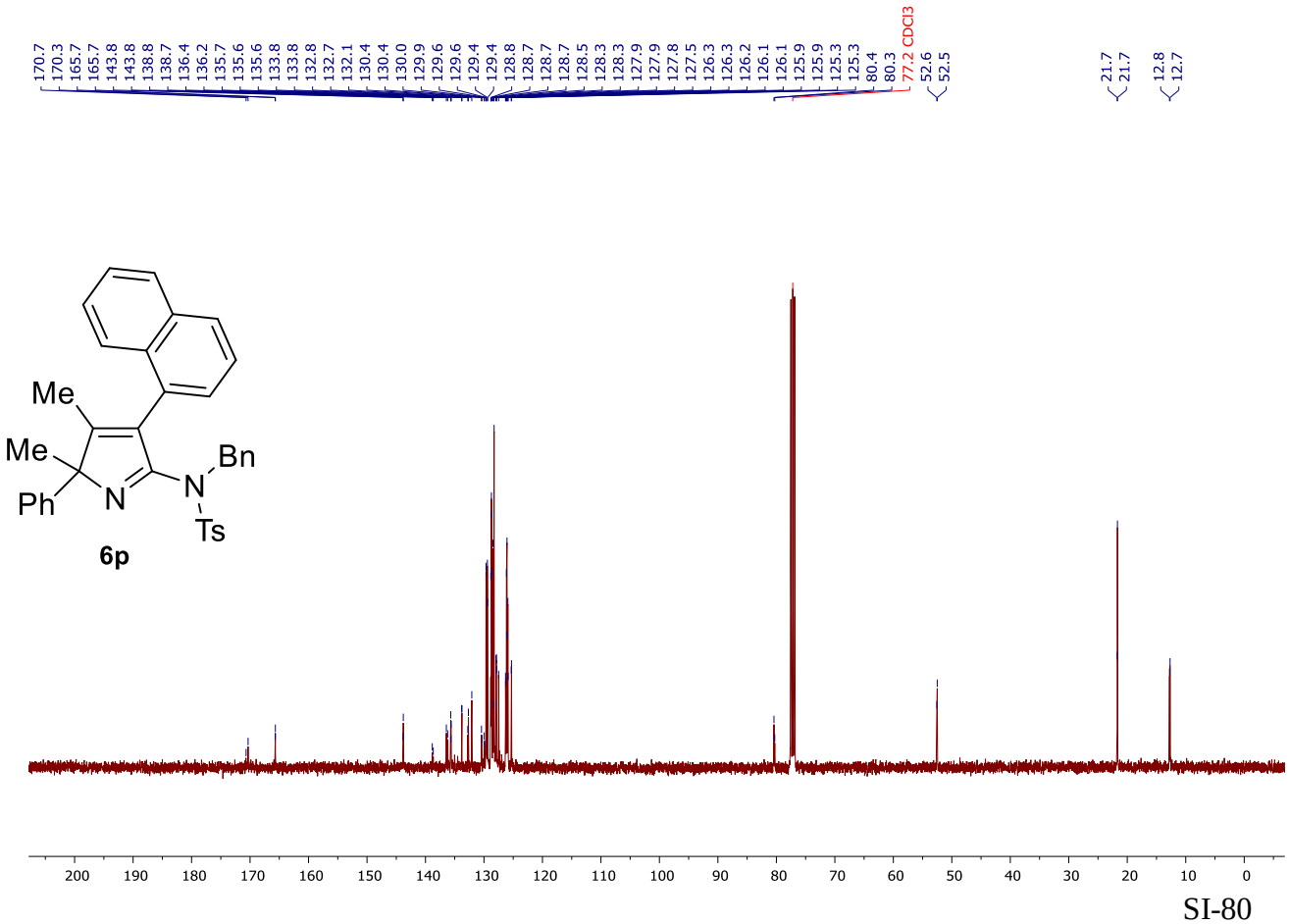
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6o**



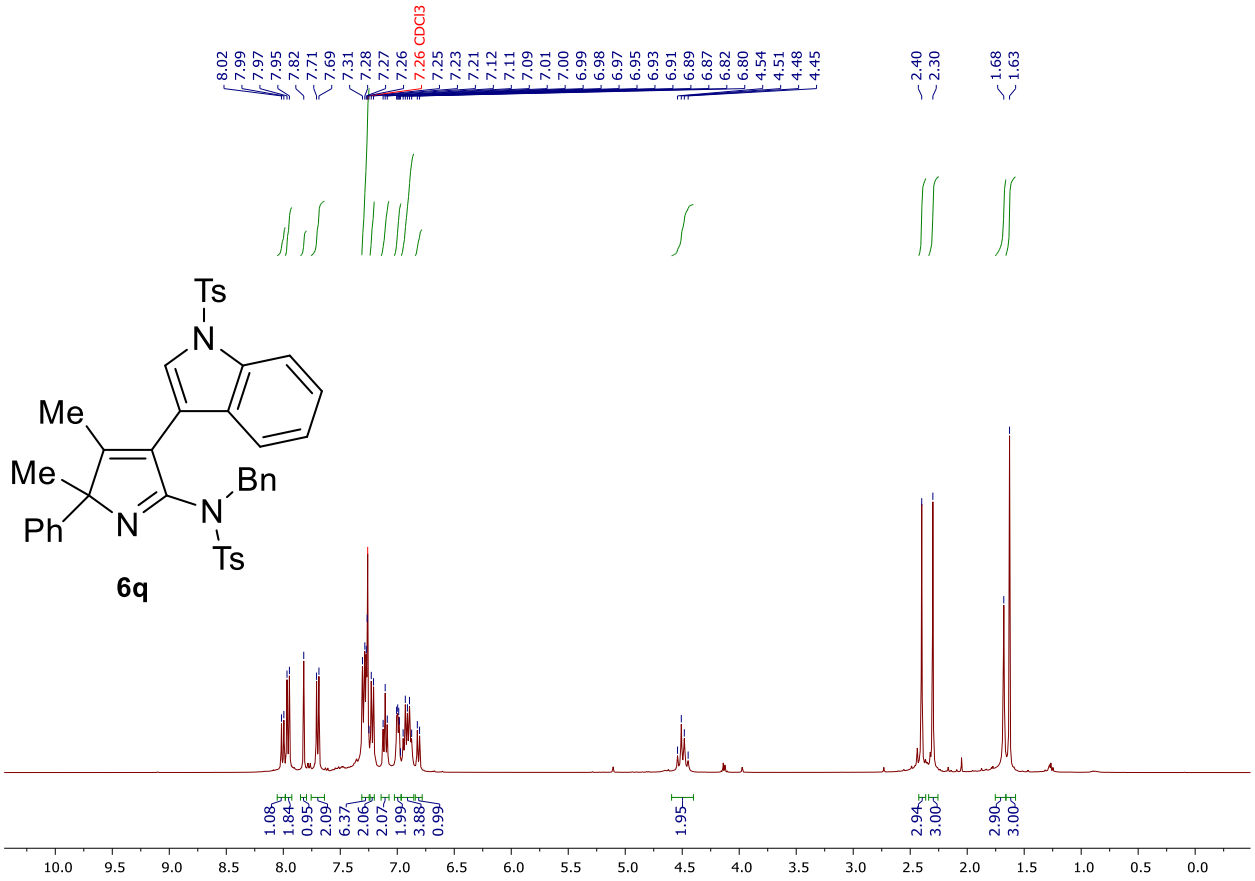
^{1}H NMR (400 MHz, $CDCl_3$) of **6p**



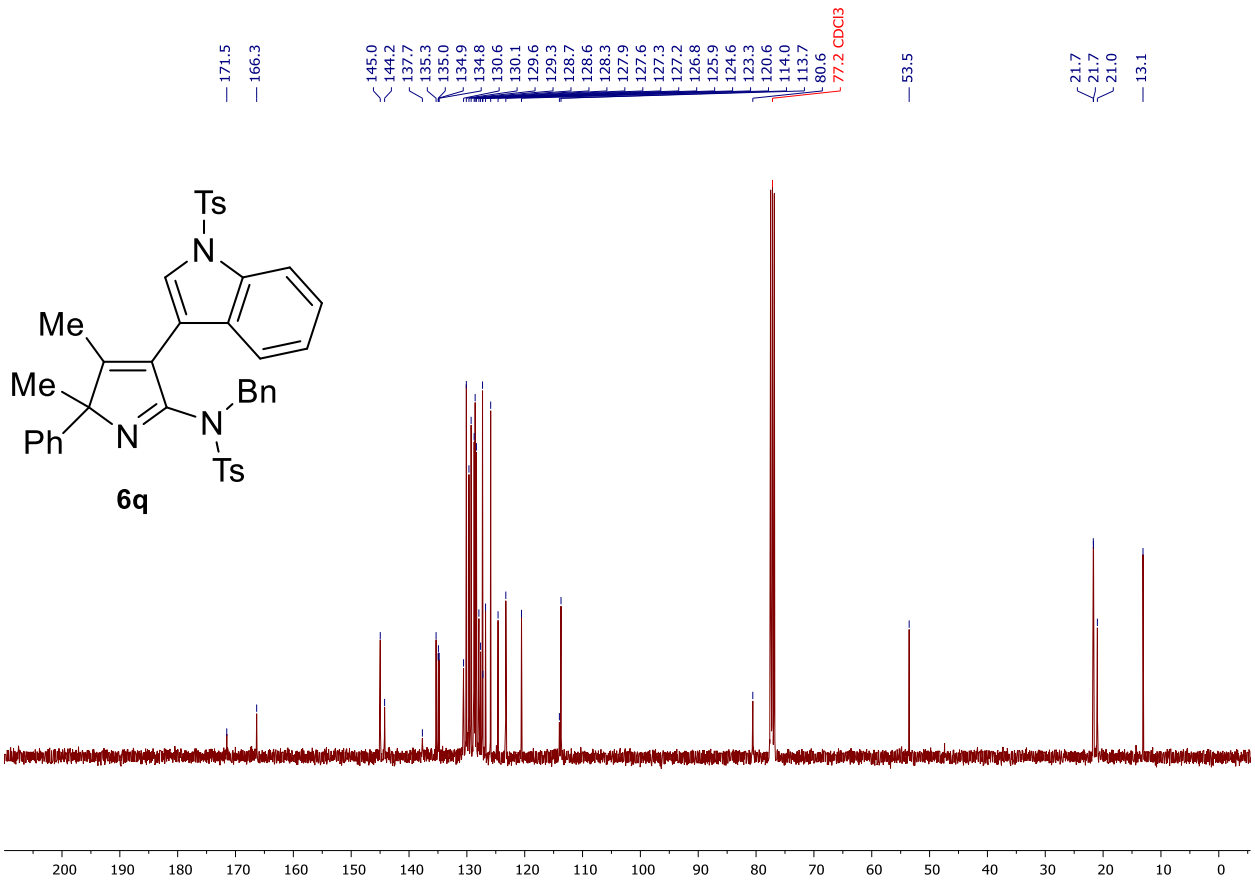
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6p**



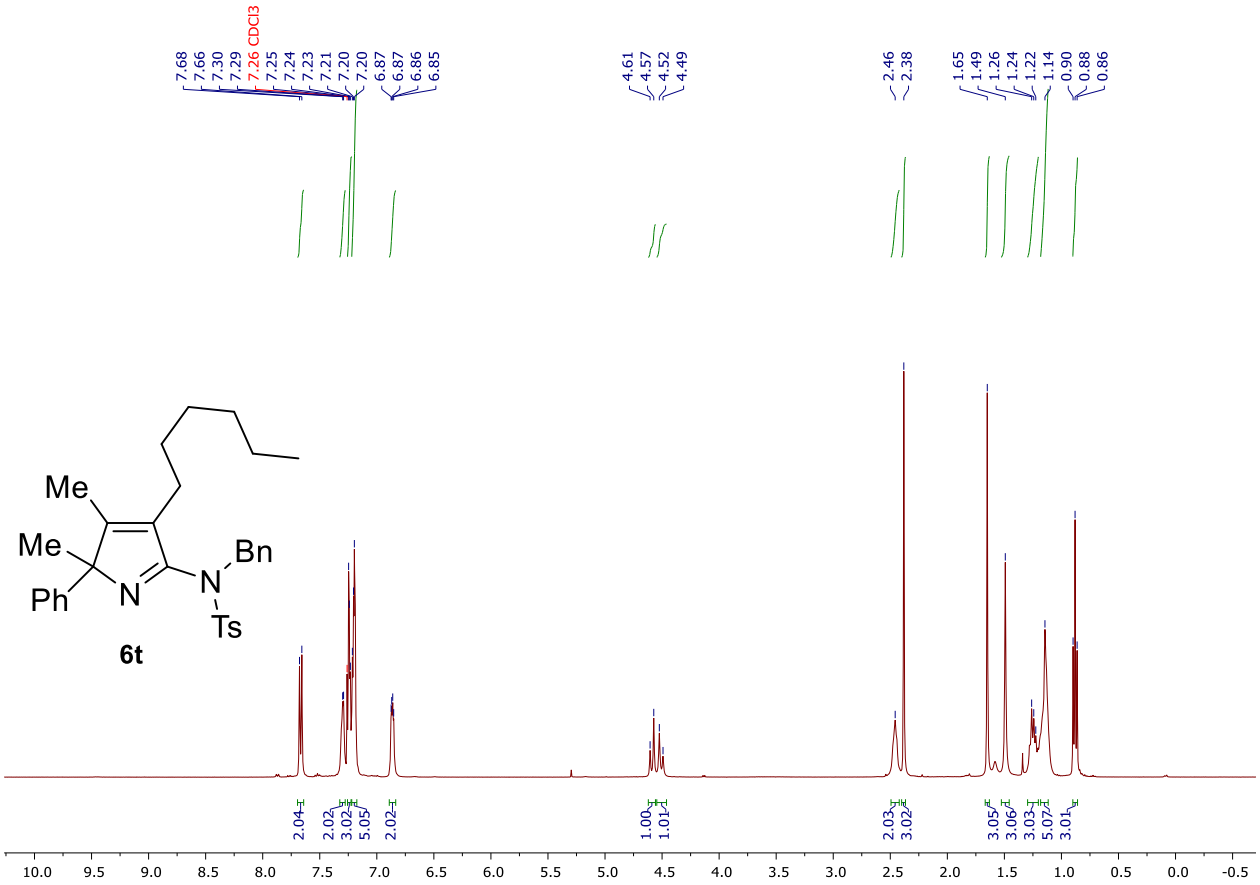
^{1}H NMR (400 MHz, $CDCl_3$) of **6q**



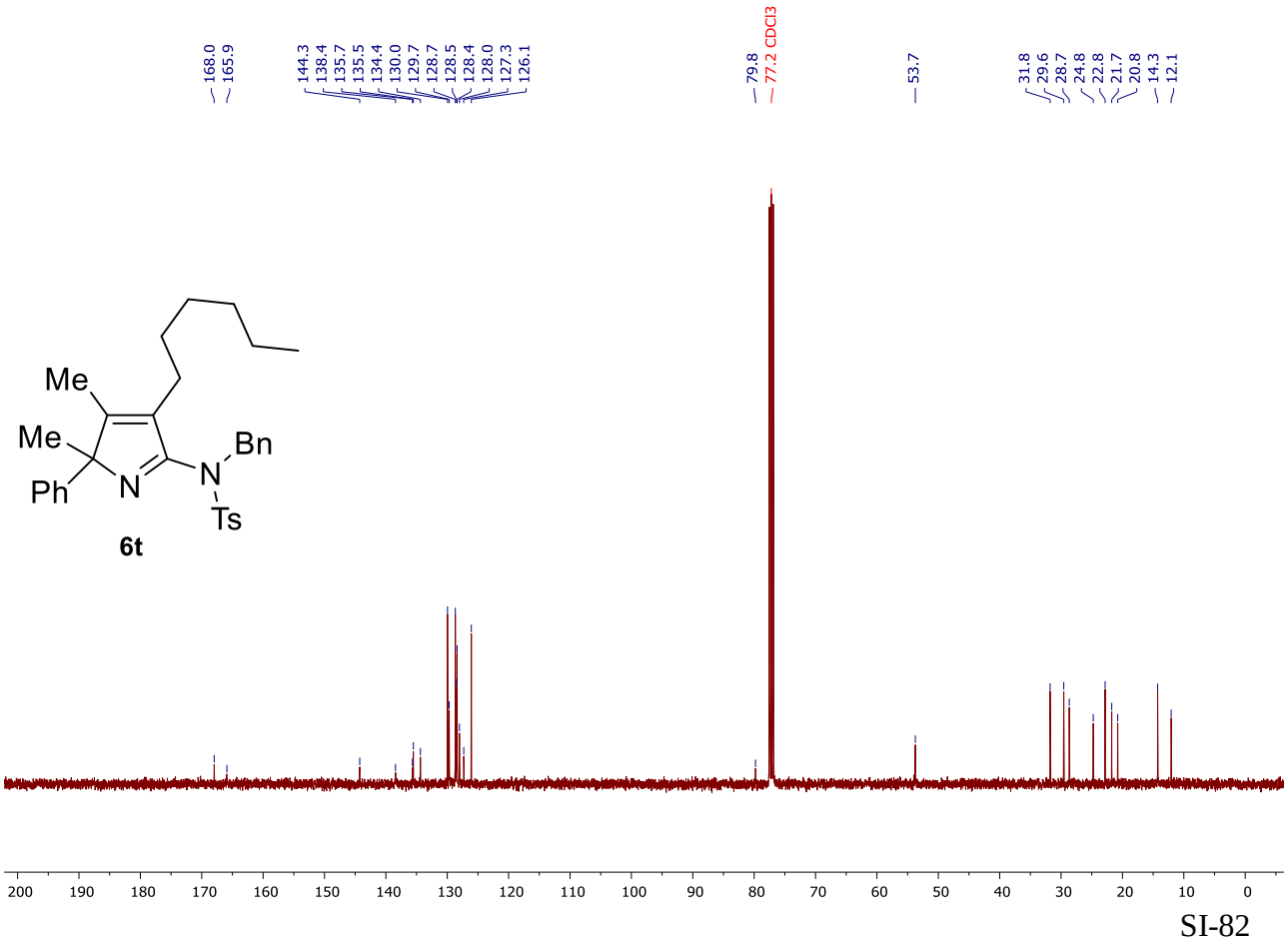
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6q**



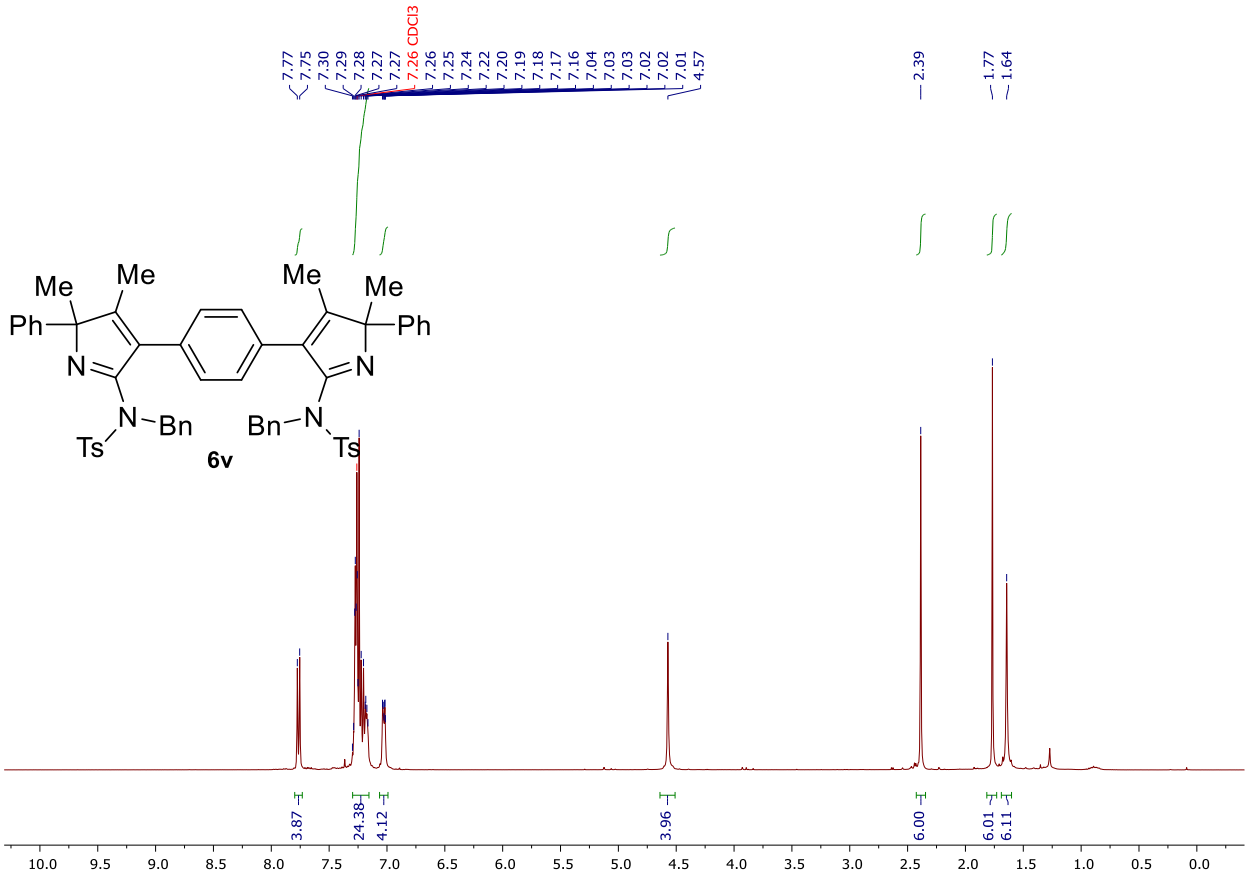
^{1}H NMR (400 MHz, $CDCl_3$) of **6t**



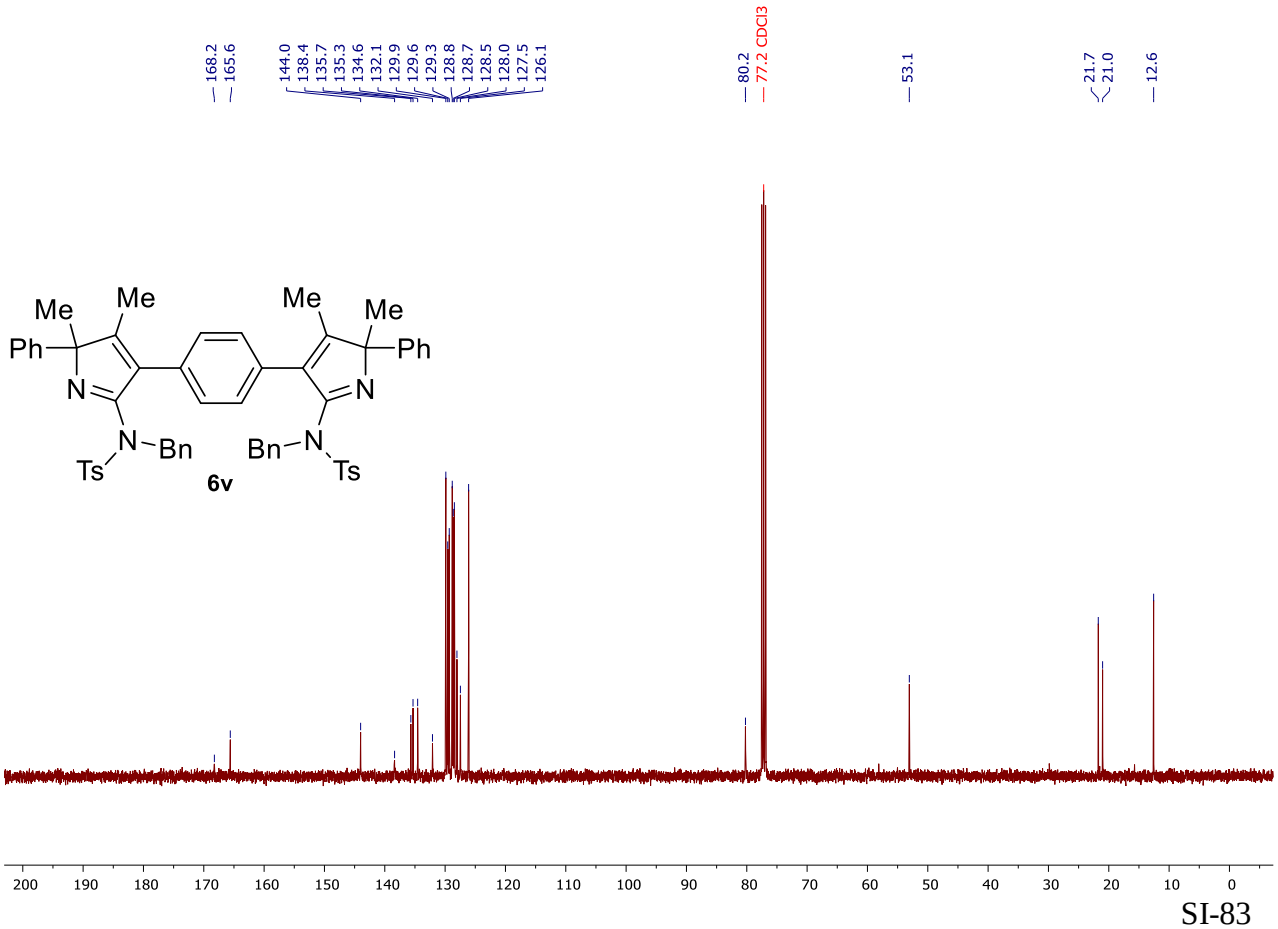
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6t**



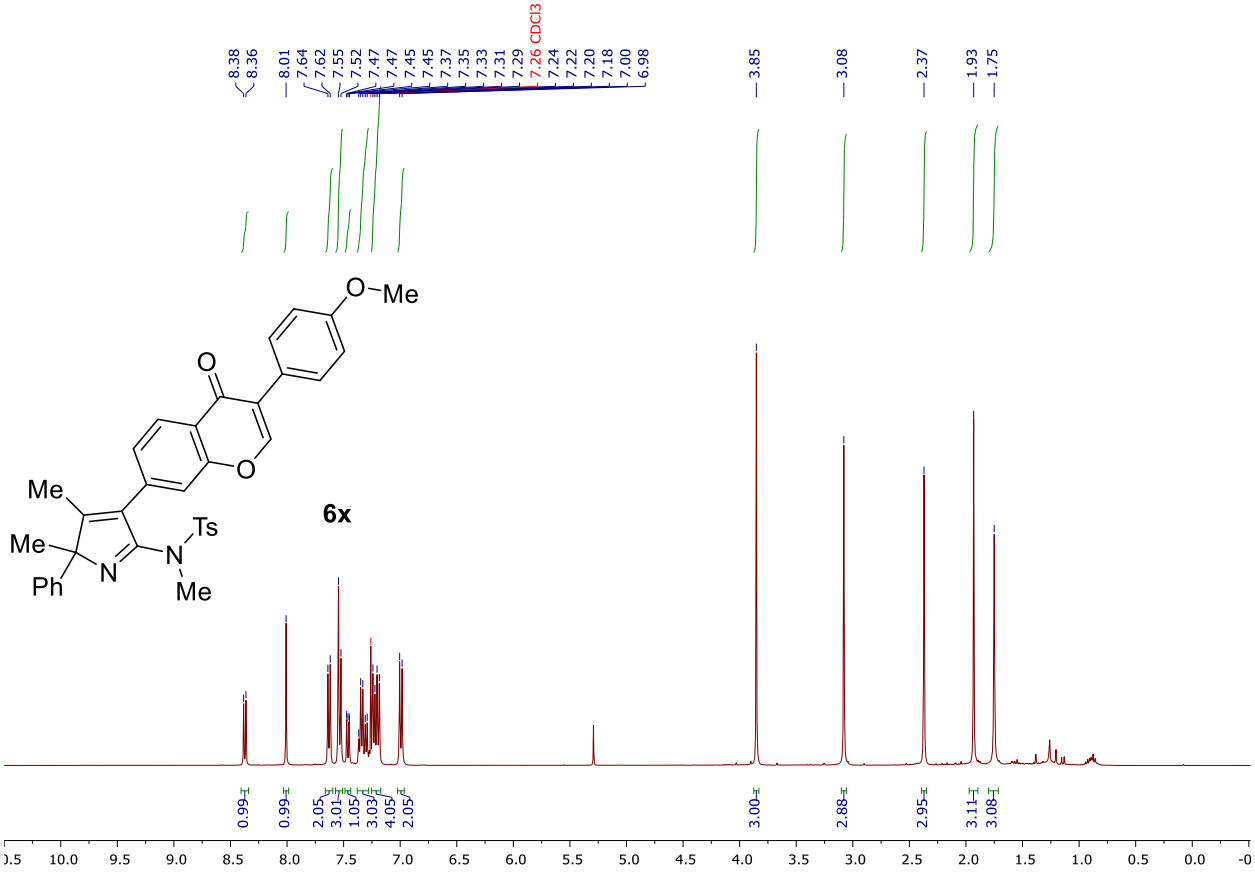
^{1}H NMR (400 MHz, $CDCl_3$) of **6v**



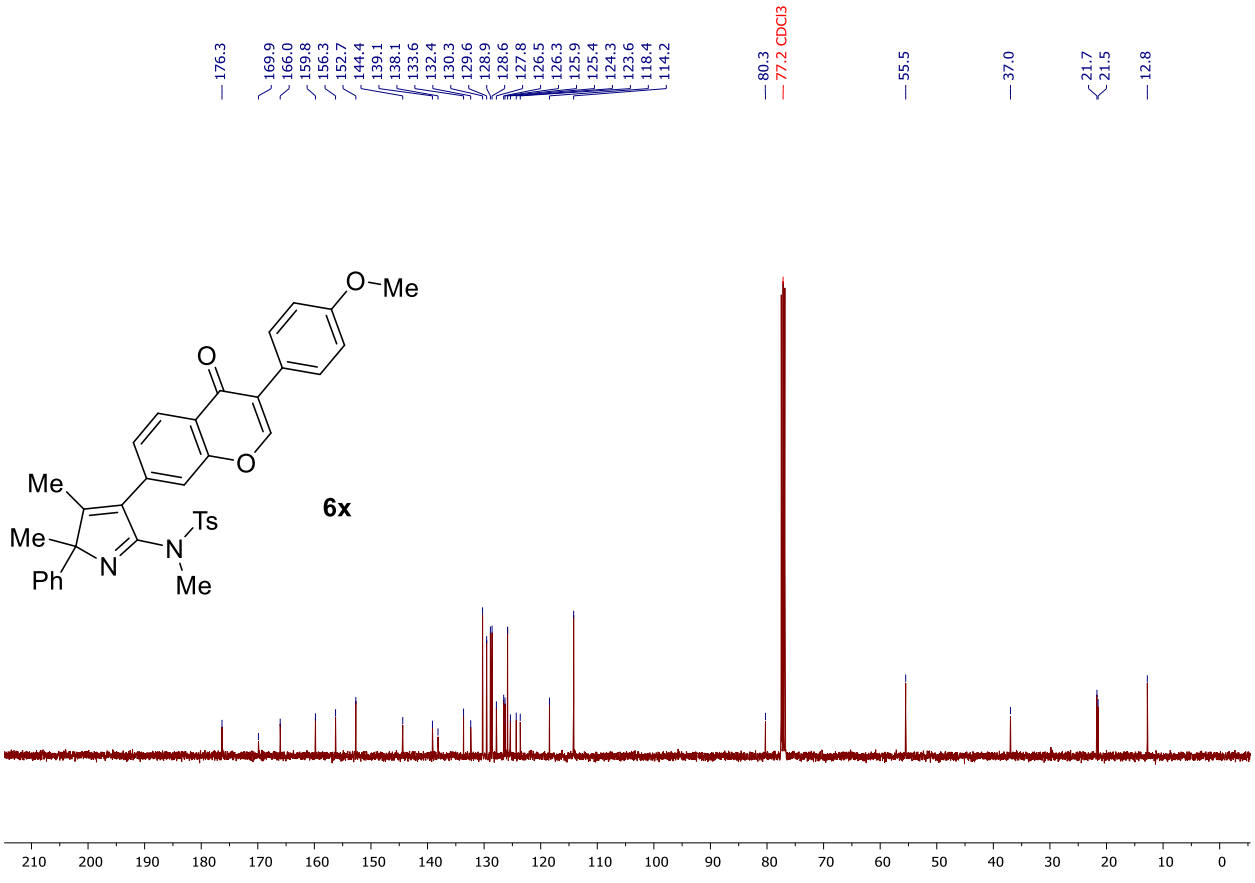
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6v**



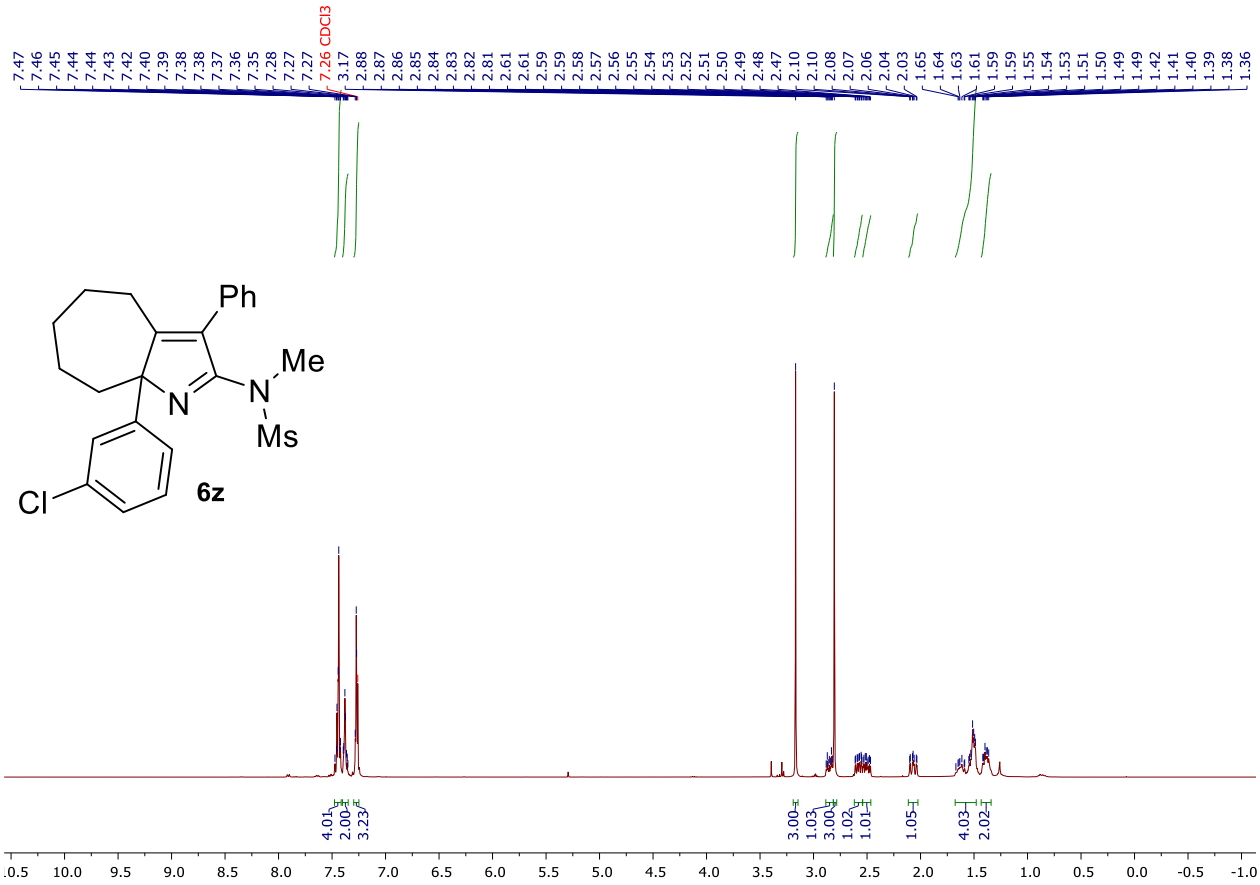
^{1}H NMR (400 MHz, $CDCl_3$) of **6x**



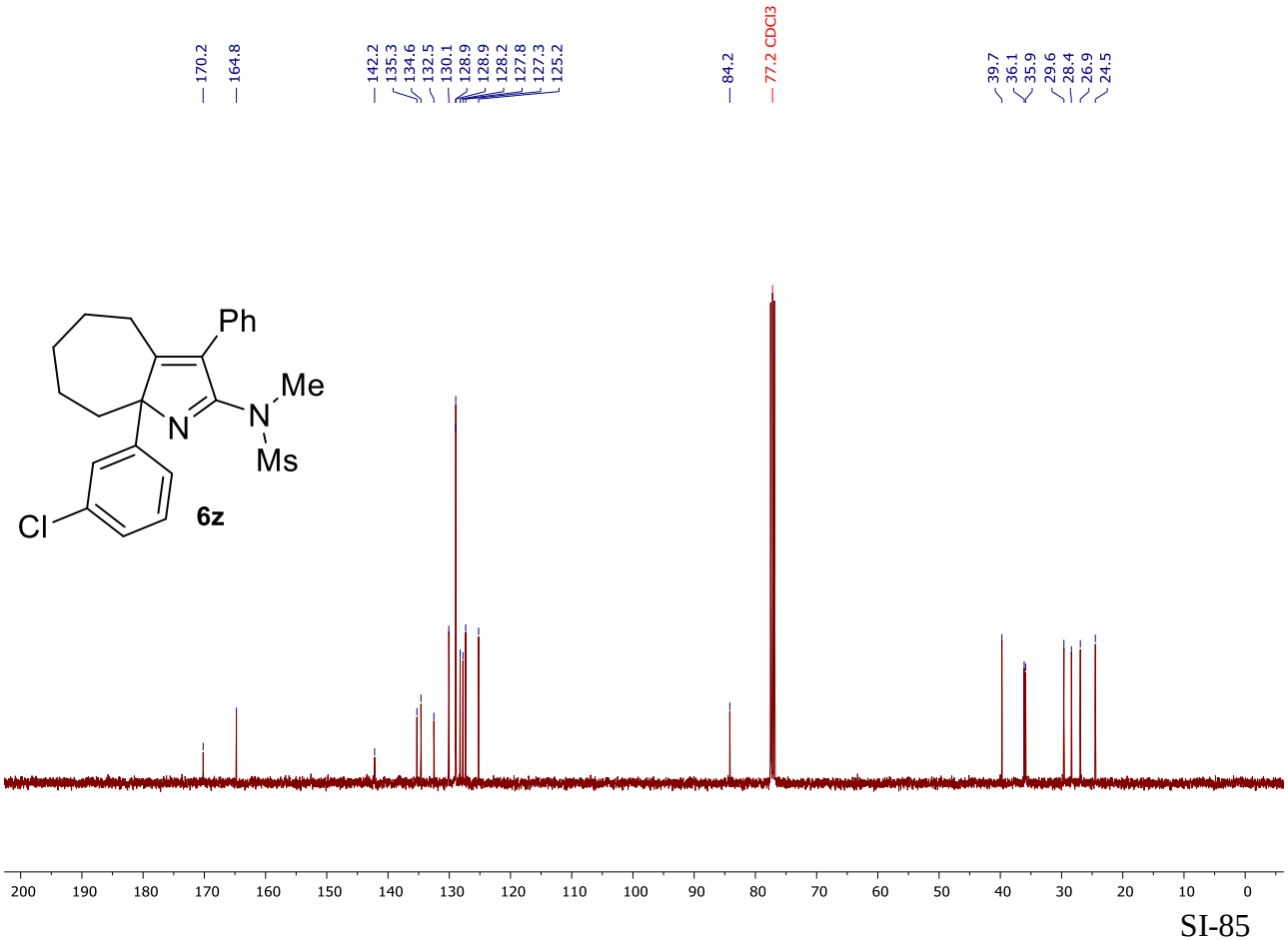
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6x**



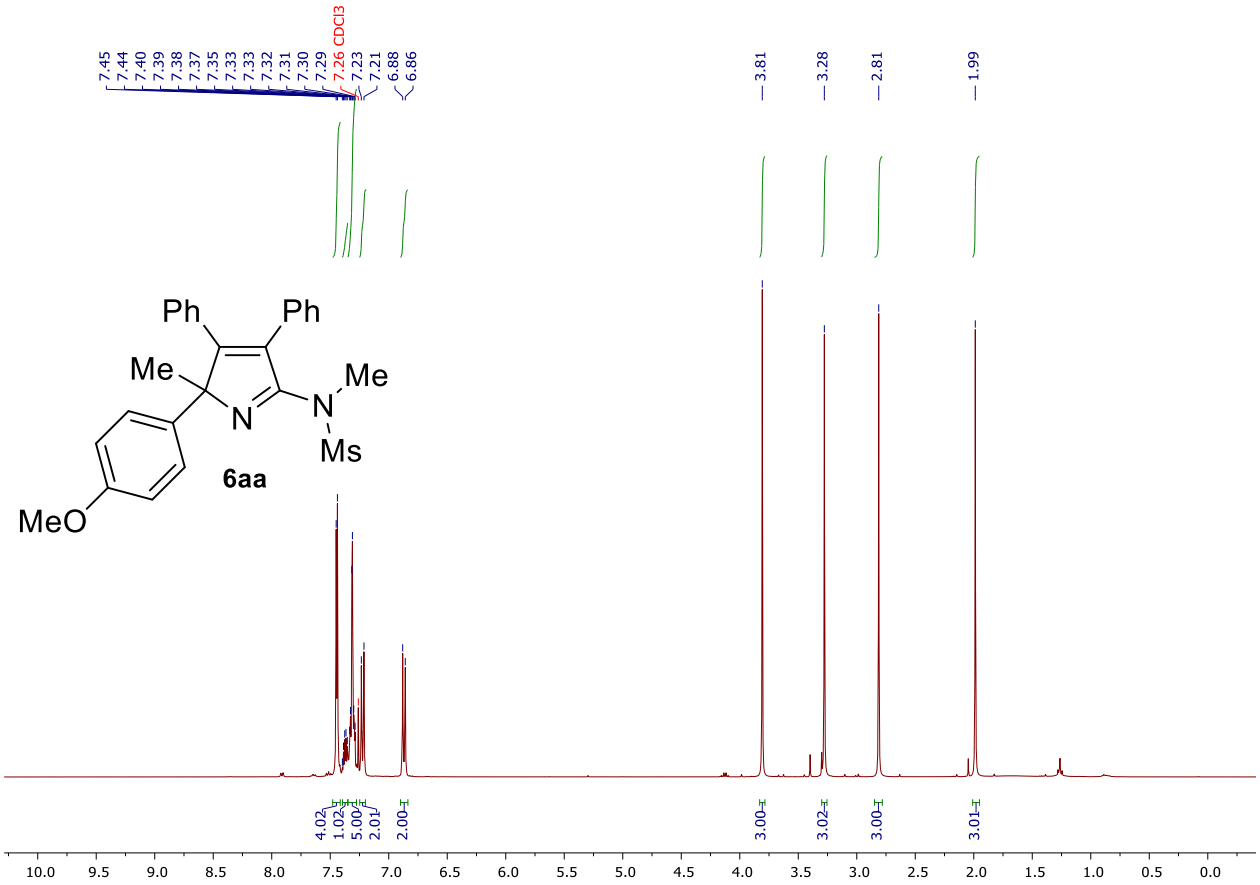
^{1}H NMR (400 MHz, $CDCl_3$) of **6z**



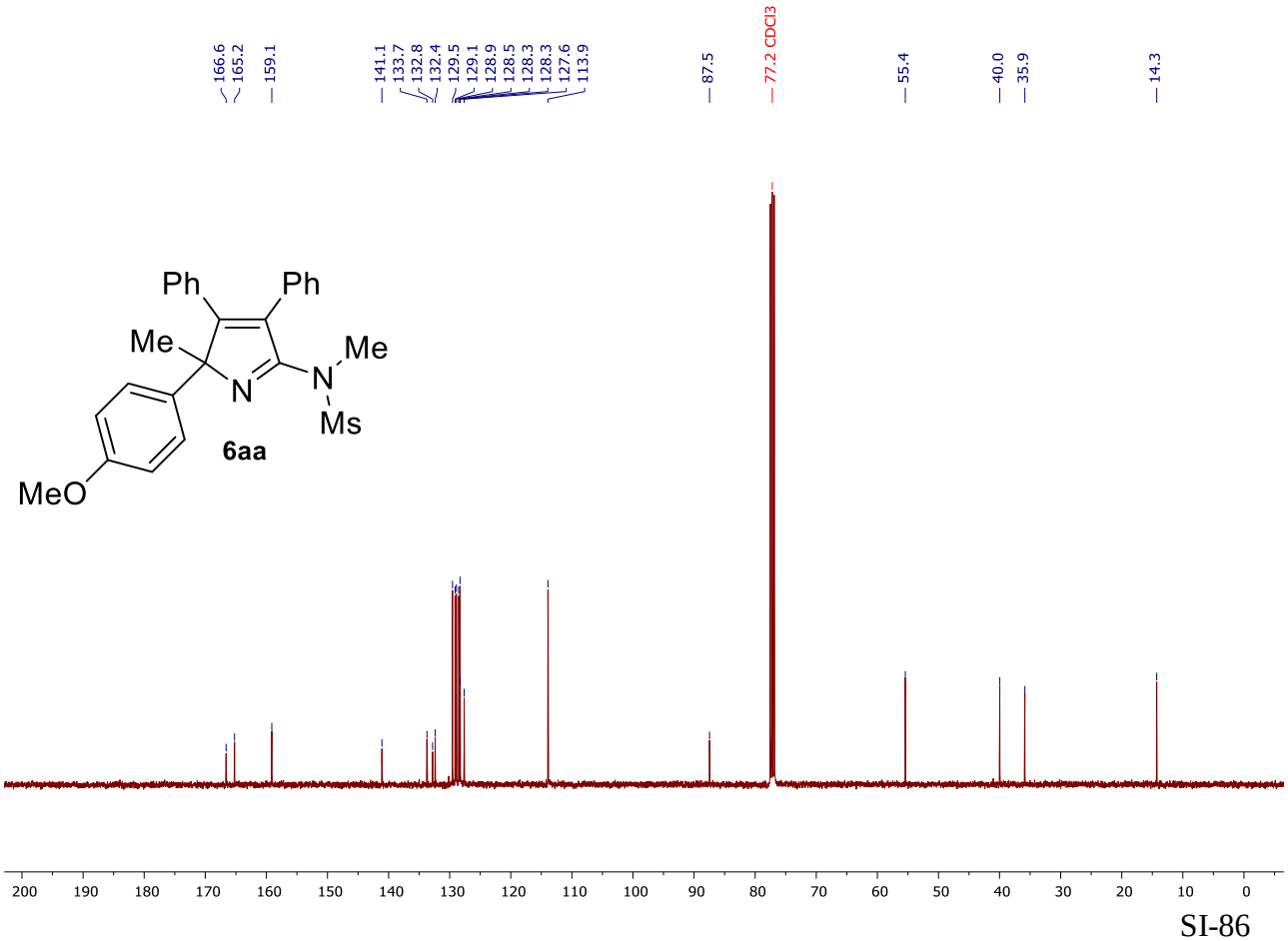
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6z**



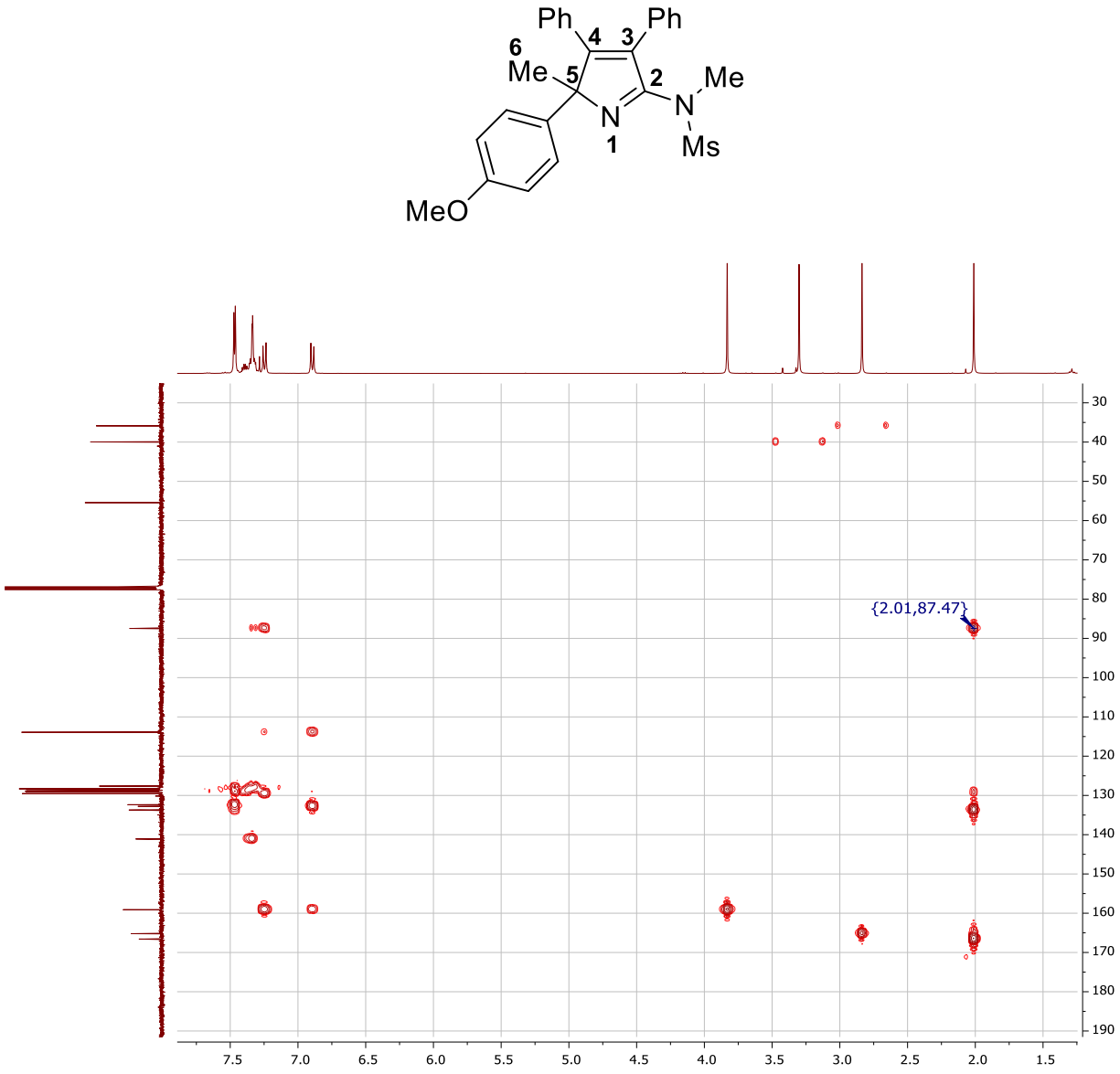
^{1}H NMR (400 MHz, $CDCl_3$) of **6aa**



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6aa**

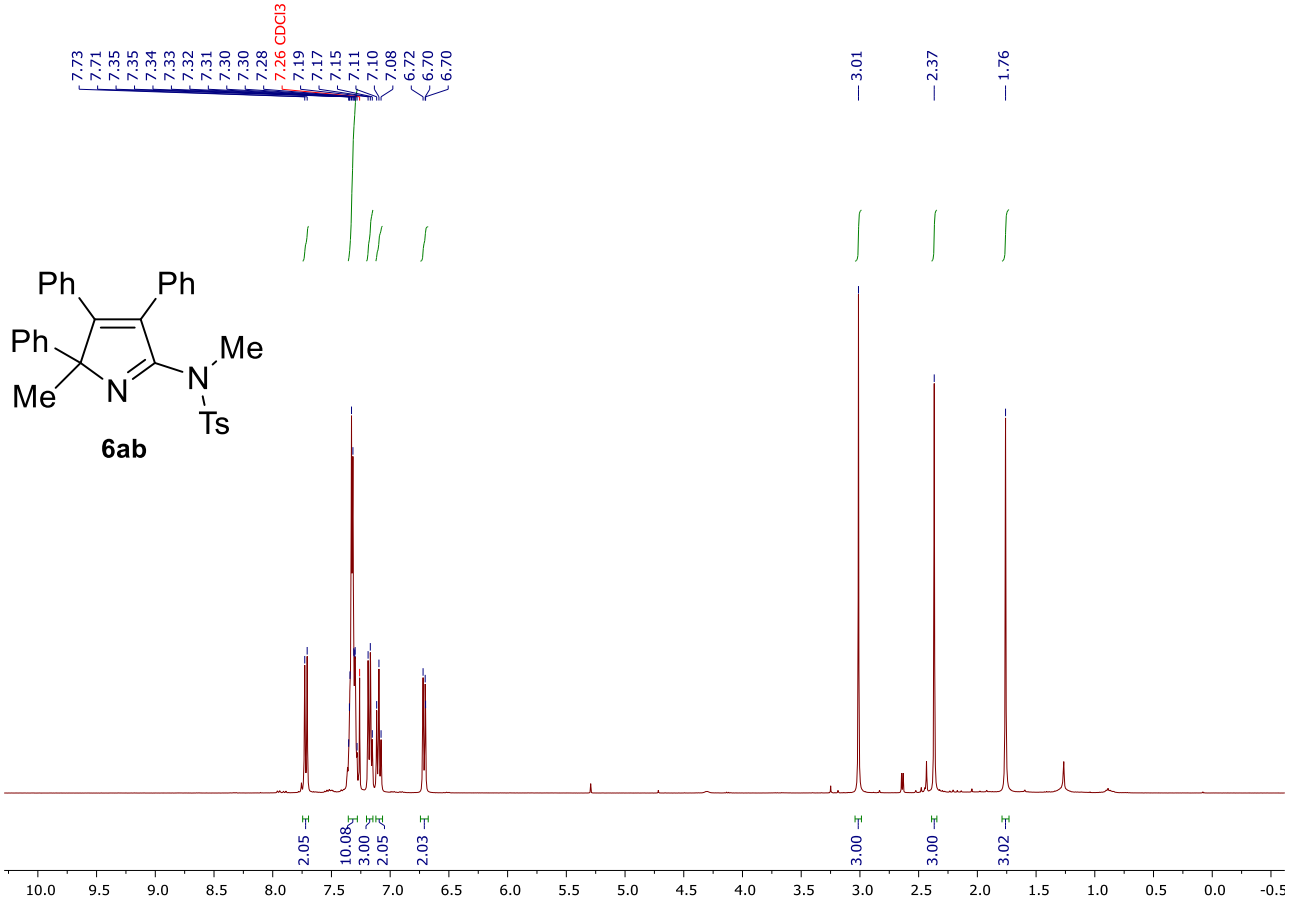


^{1}H-^{13}C HMBC for 2*H*-Pyrrole **6aa**

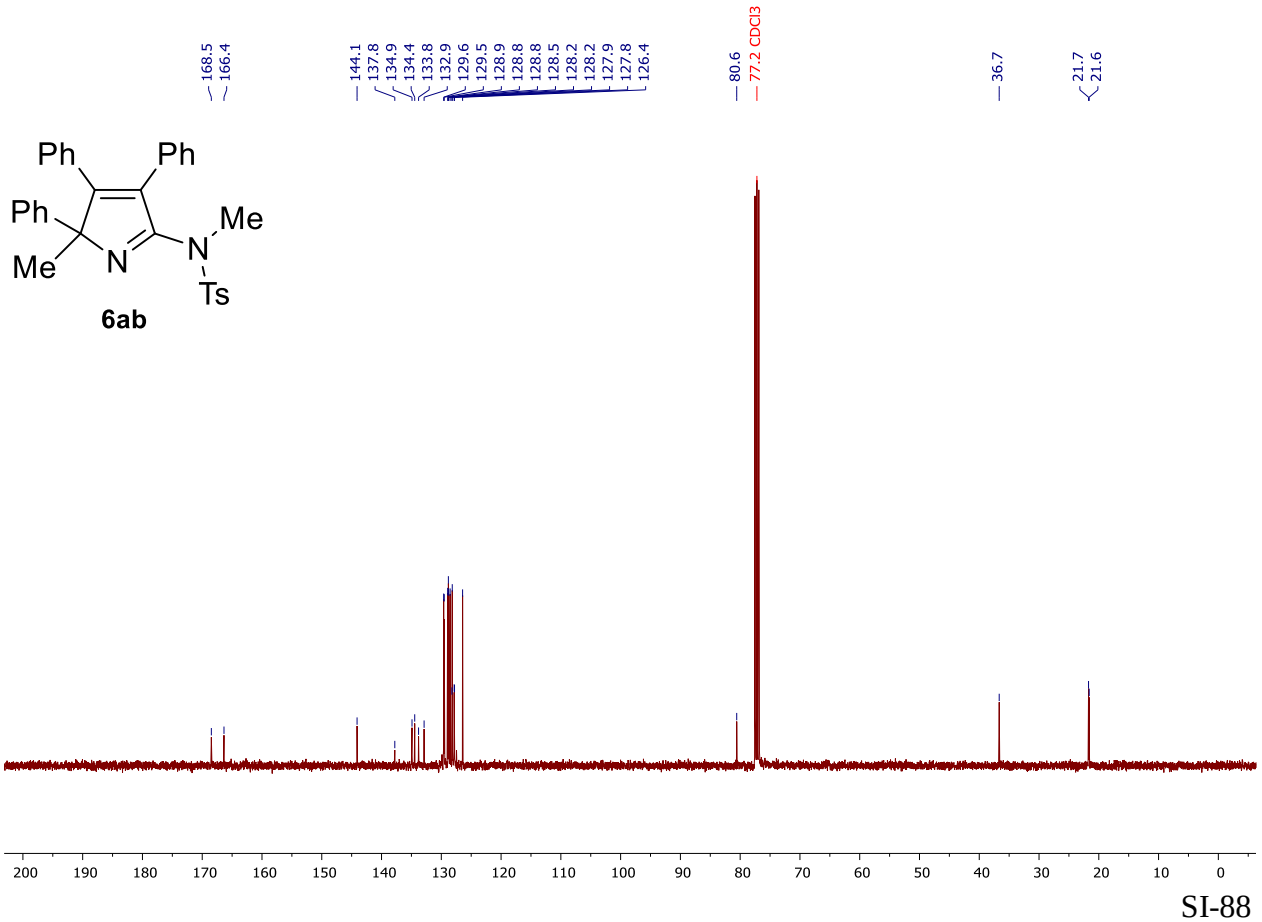


The cross peak between $C^{6}H_3$ and C^{5} (2.01, 87.47) corresponds to the proposed structure resulting from the [1,5]-shift of the methyl group to C^{5}.

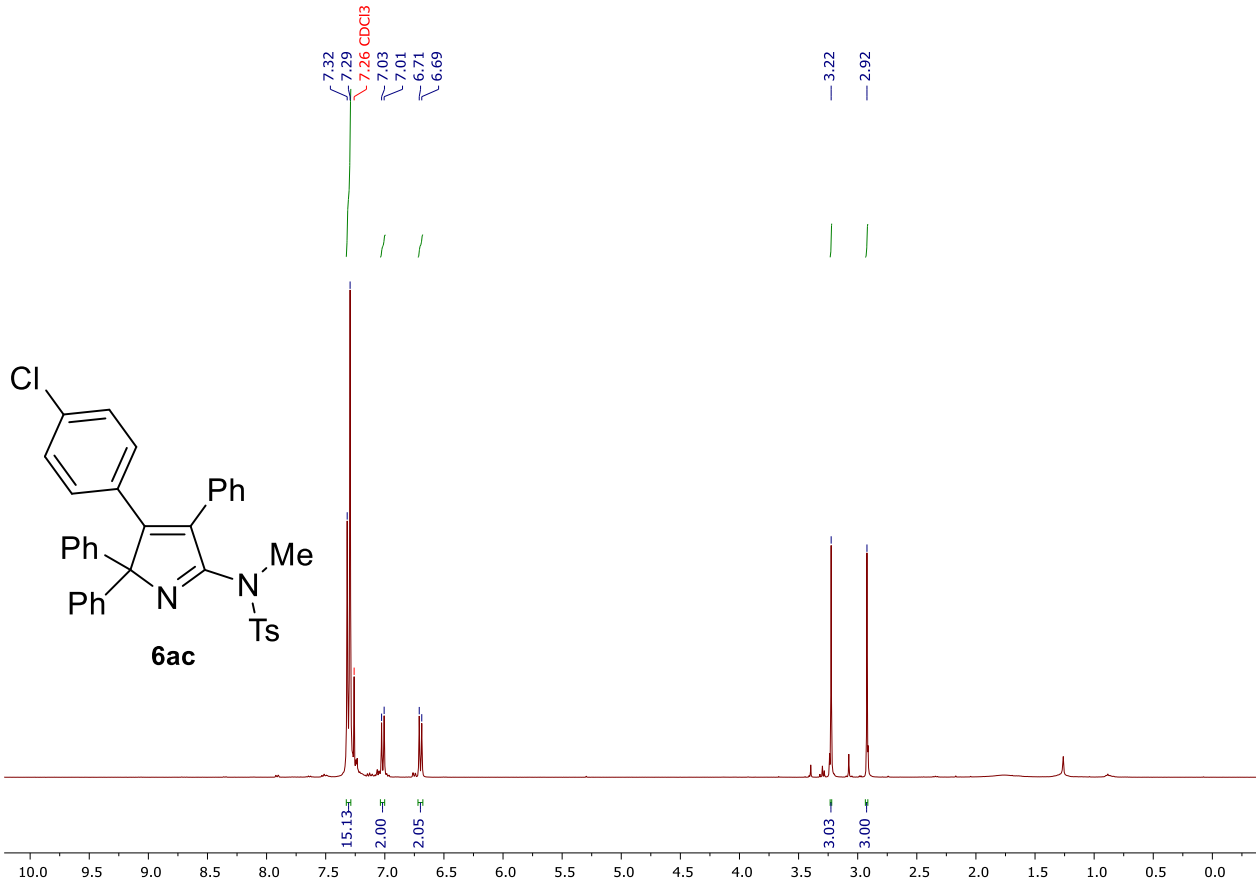
^{1}H NMR (400 MHz, $CDCl_3$) of **6ab**



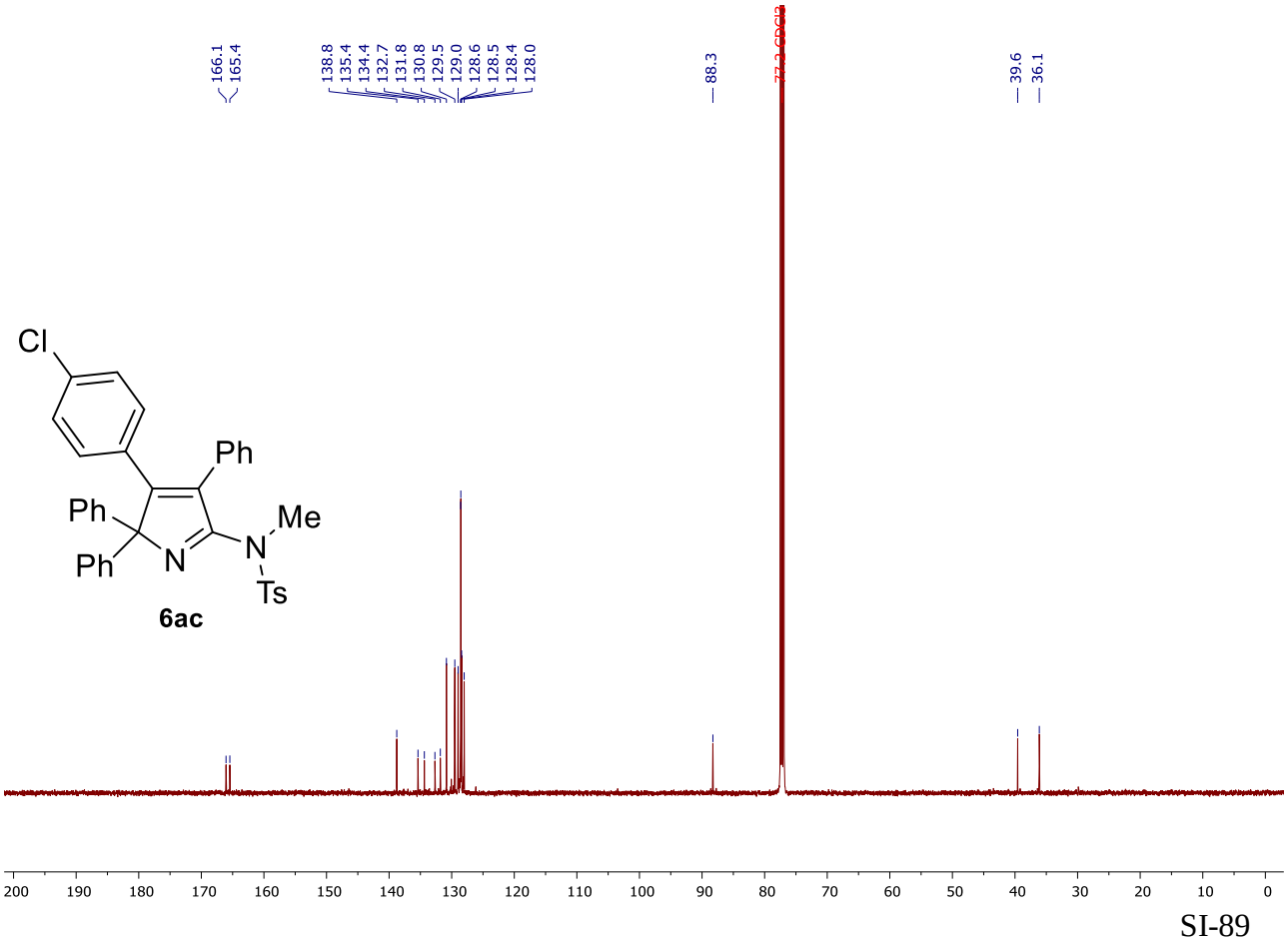
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6ab**



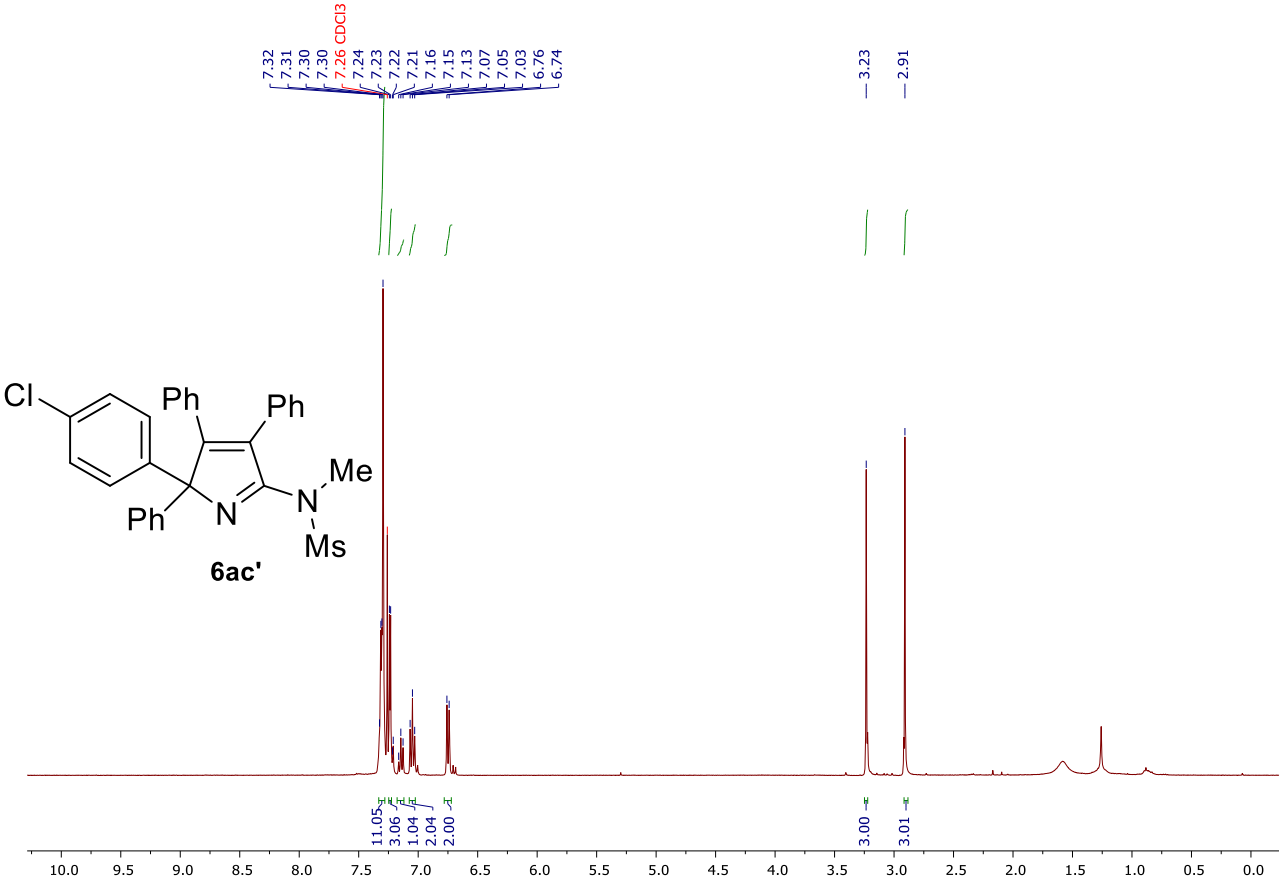
^{1}H NMR (400 MHz, $CDCl_3$) of **6ac**



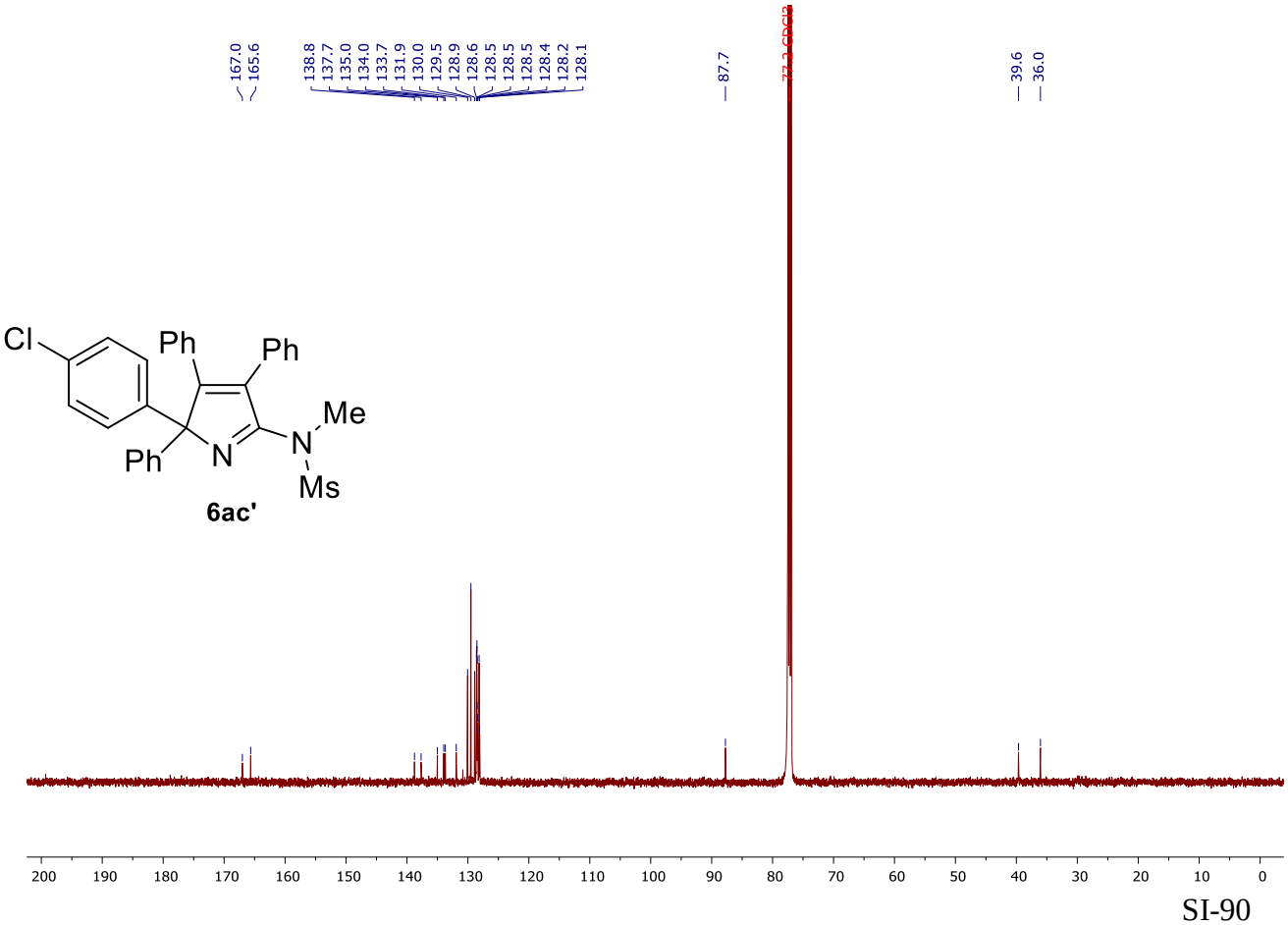
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6ac**



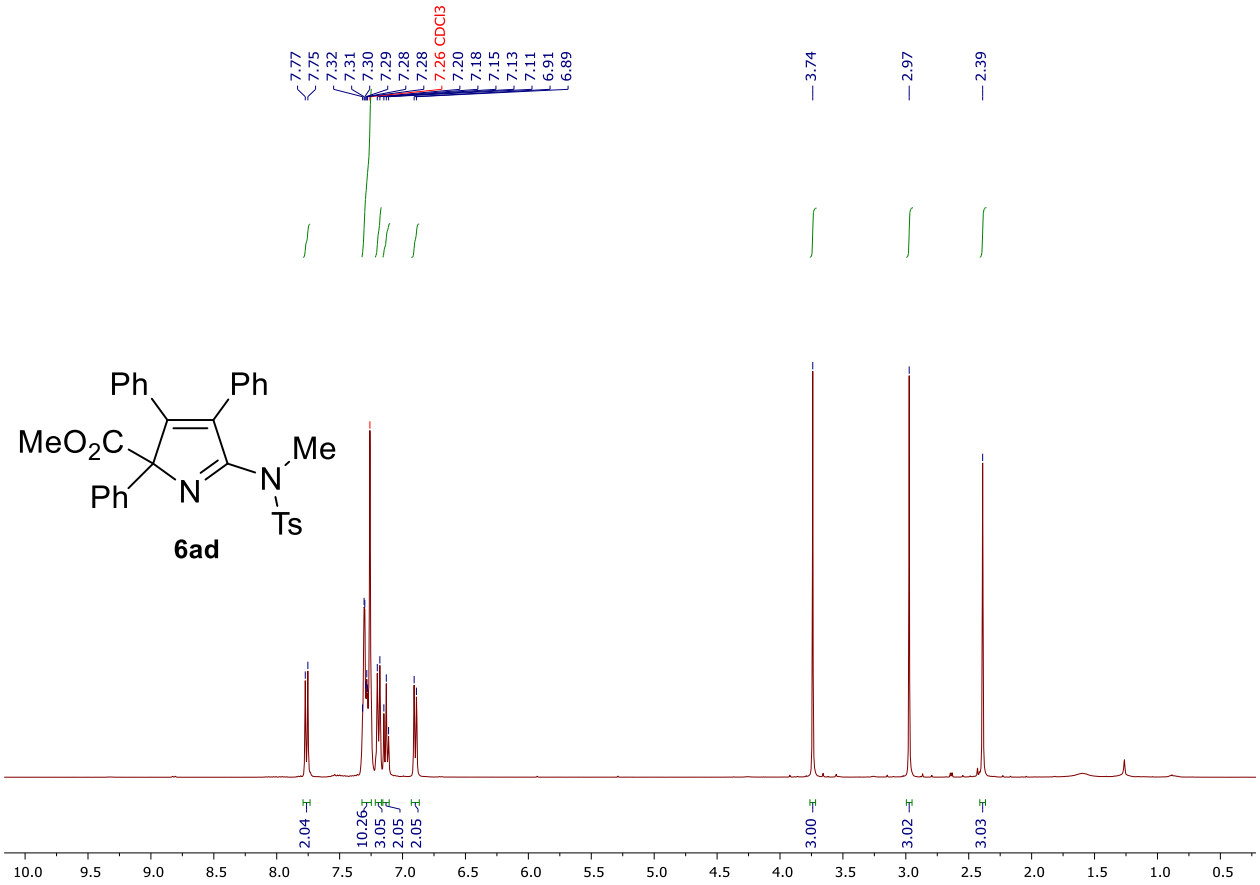
^{1}H NMR (400 MHz, $CDCl_3$) of **6ac'**



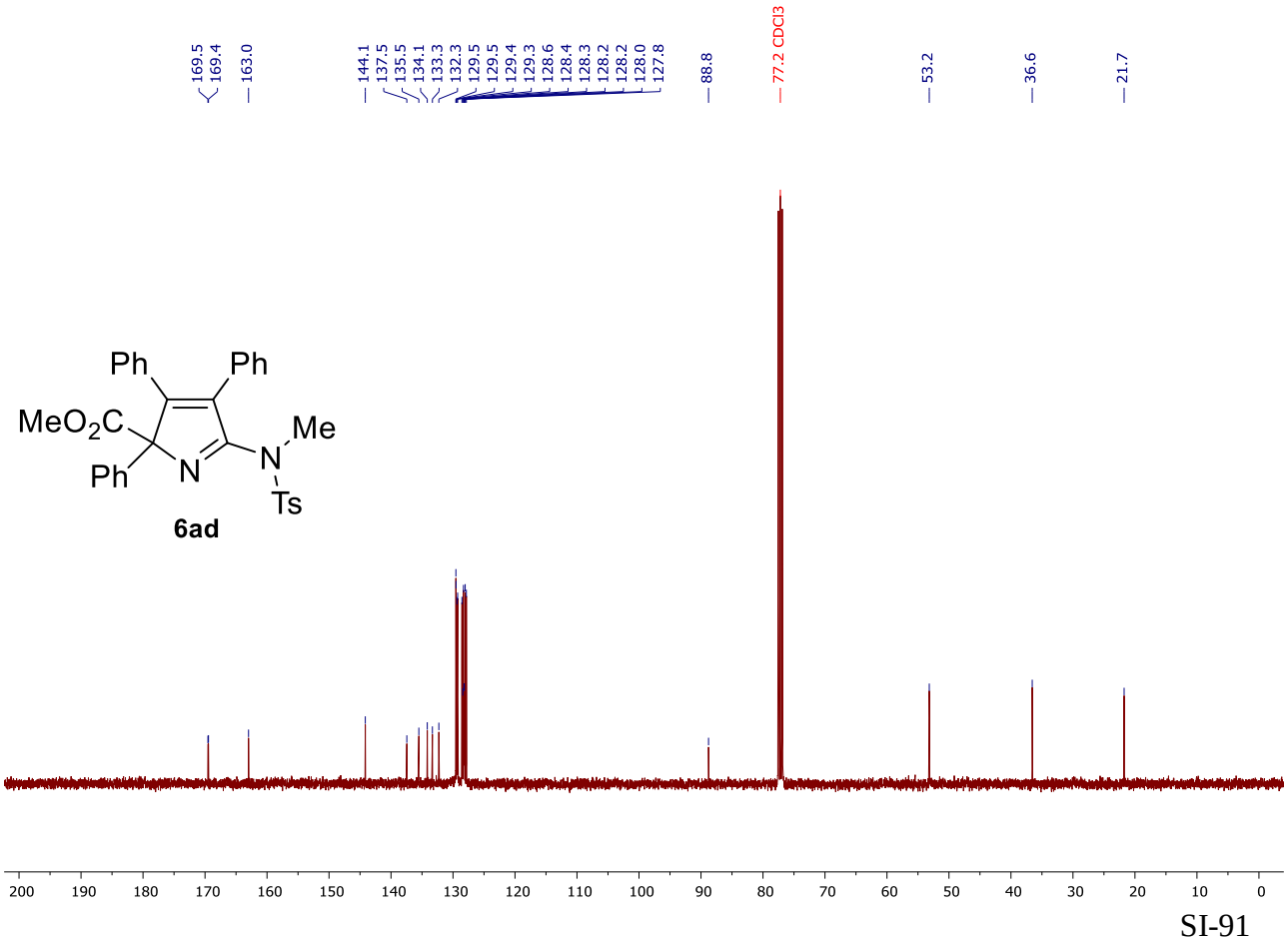
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6ac'**



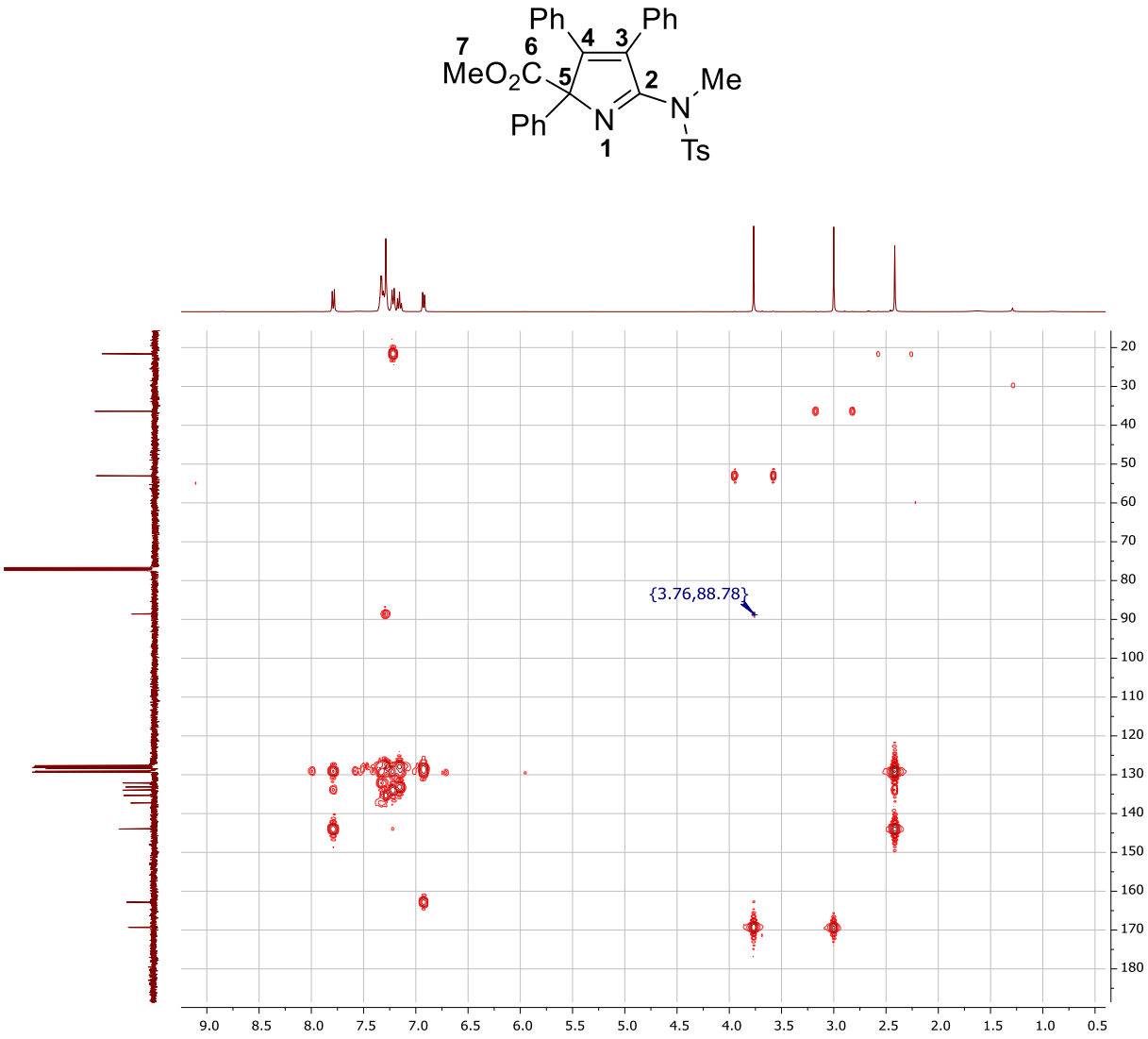
^{1}H NMR (400 MHz, $CDCl_3$) of **6ad**



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6ad**

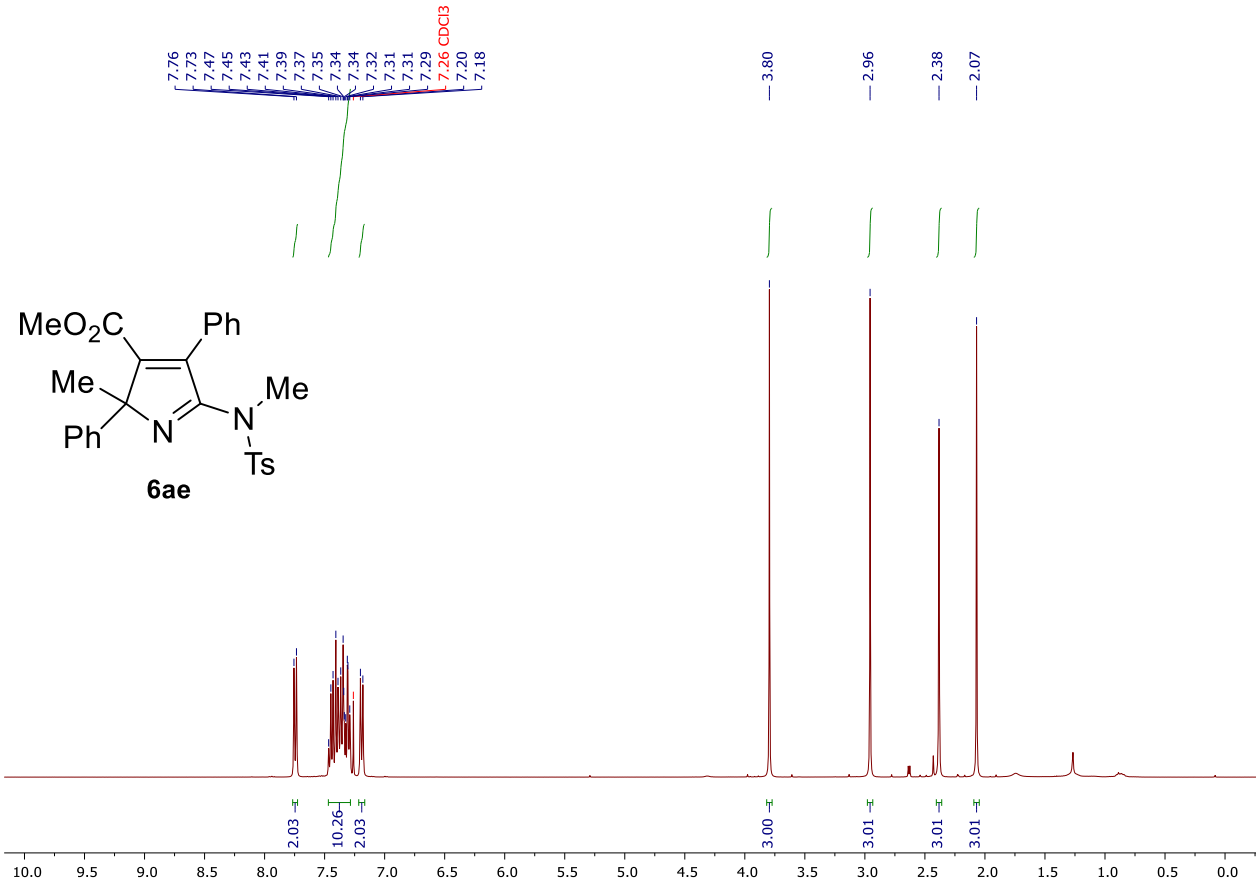


^{1}H-^{13}C HMBC for 2*H*-Pyrrole **6ad**

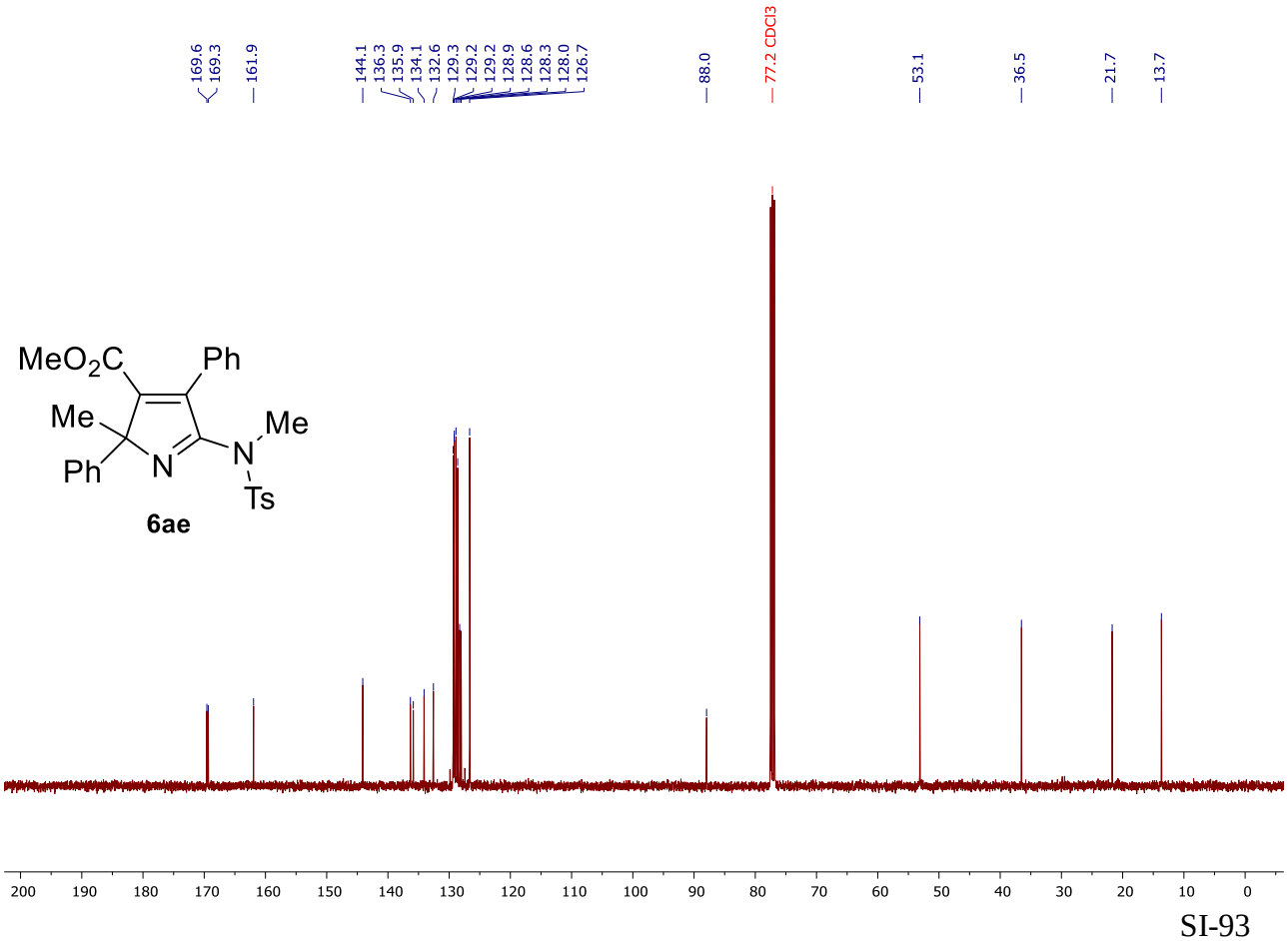


The weak cross peak between $C^{7}H_3$ and C^{5} (3.76, 88.78) corresponds to the proposed structure resulting from the [1,5]-shift of the methoxycarbonyl group to C^{5}.

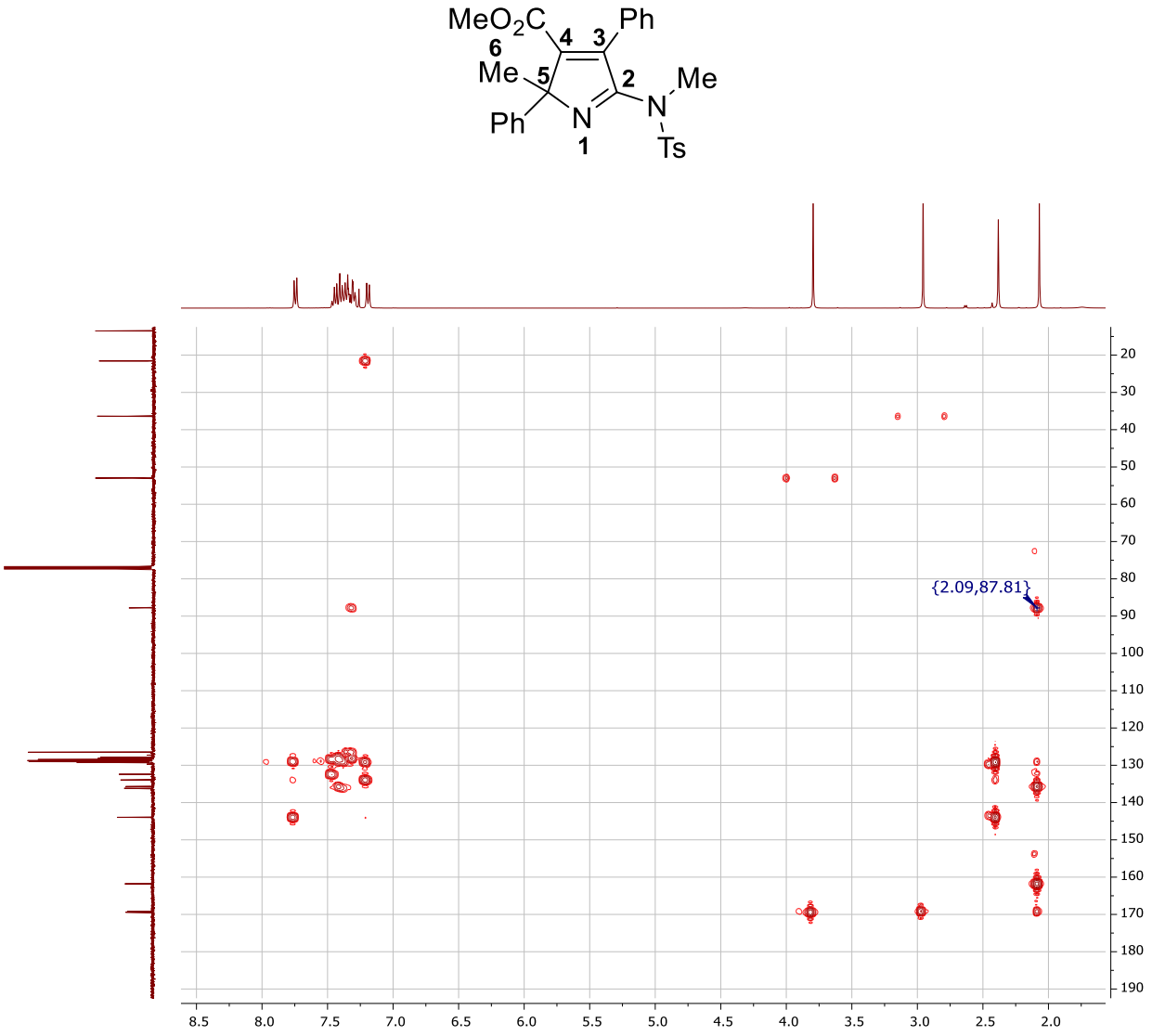
^{1}H NMR (400 MHz, $CDCl_3$) of **6ae**



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6ae**



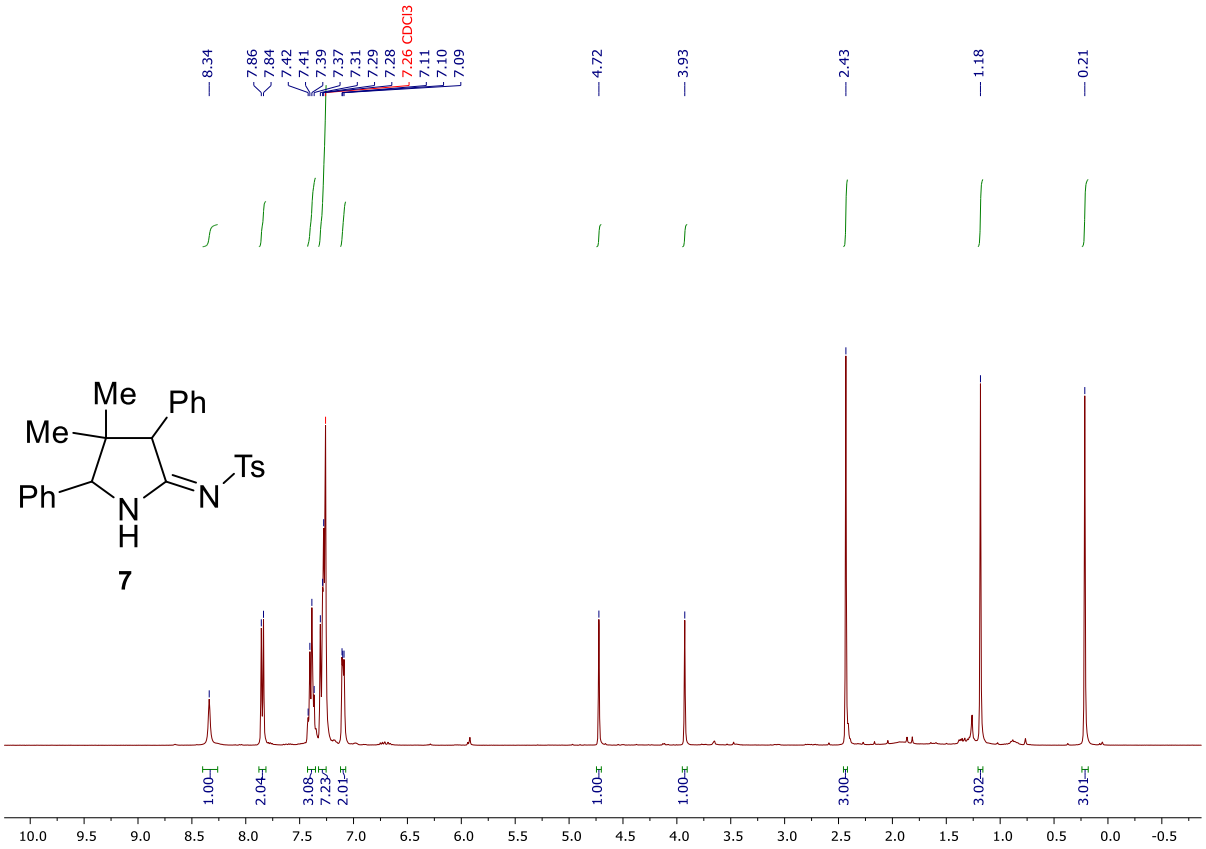
^{1}H-^{13}C HMBC for 2*H*-Pyrrole **6ae**



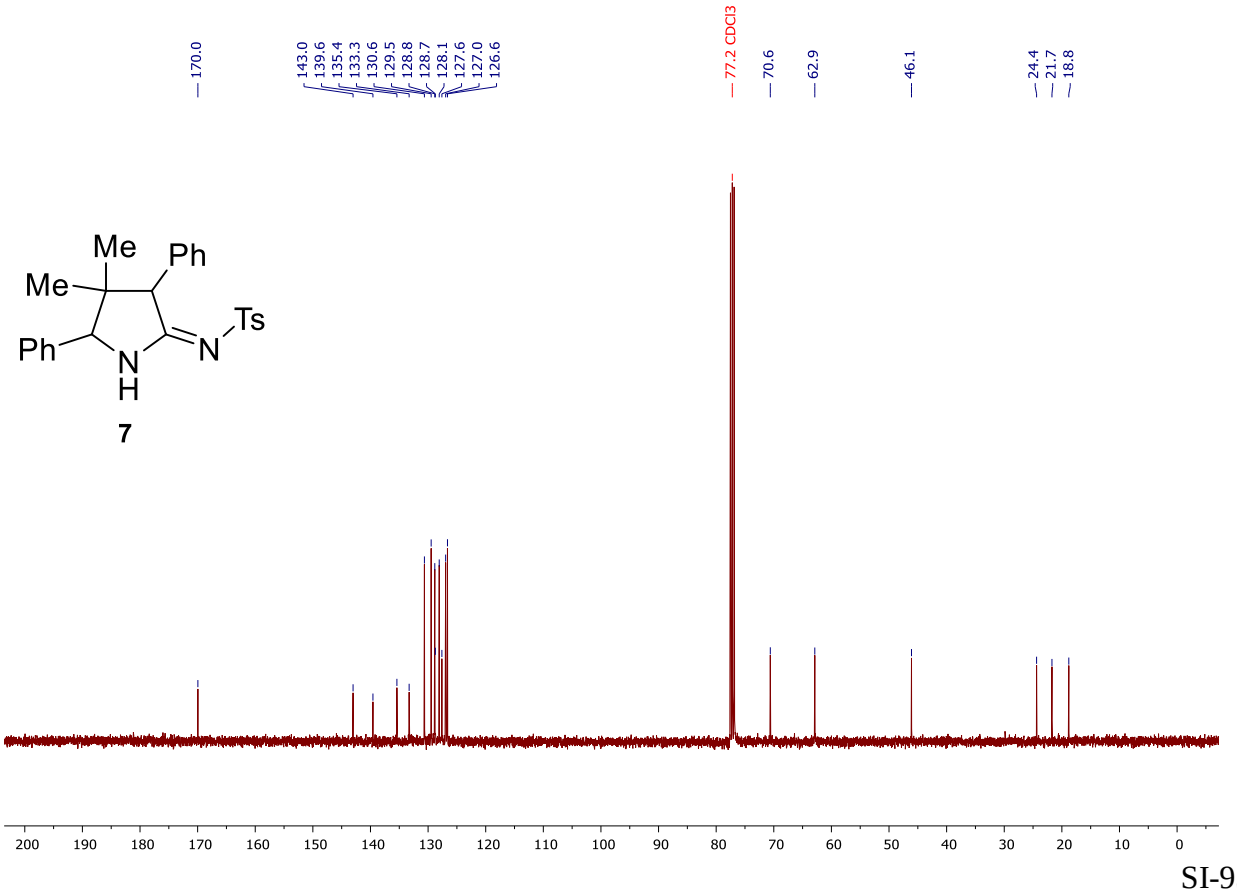
The cross peak between $C^{6}H_3$ and C^{5} (2.09, 87.81) corresponds to the proposed structure resulting from the [1,5]-shift of the methyl group to C^{5}.

4.6.NMR Spectra of Other Products

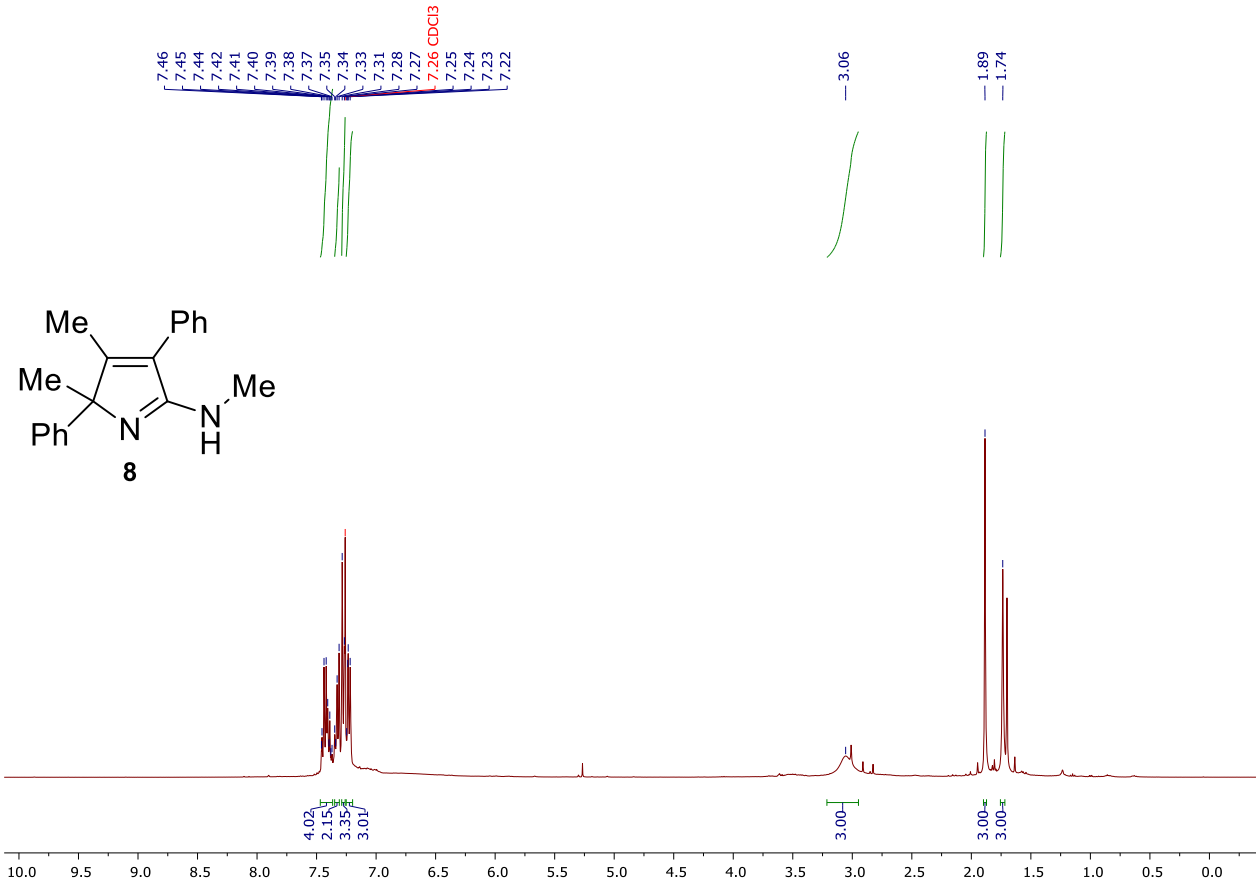
^{1}H NMR (400 MHz, $CDCl_3$) of **7**



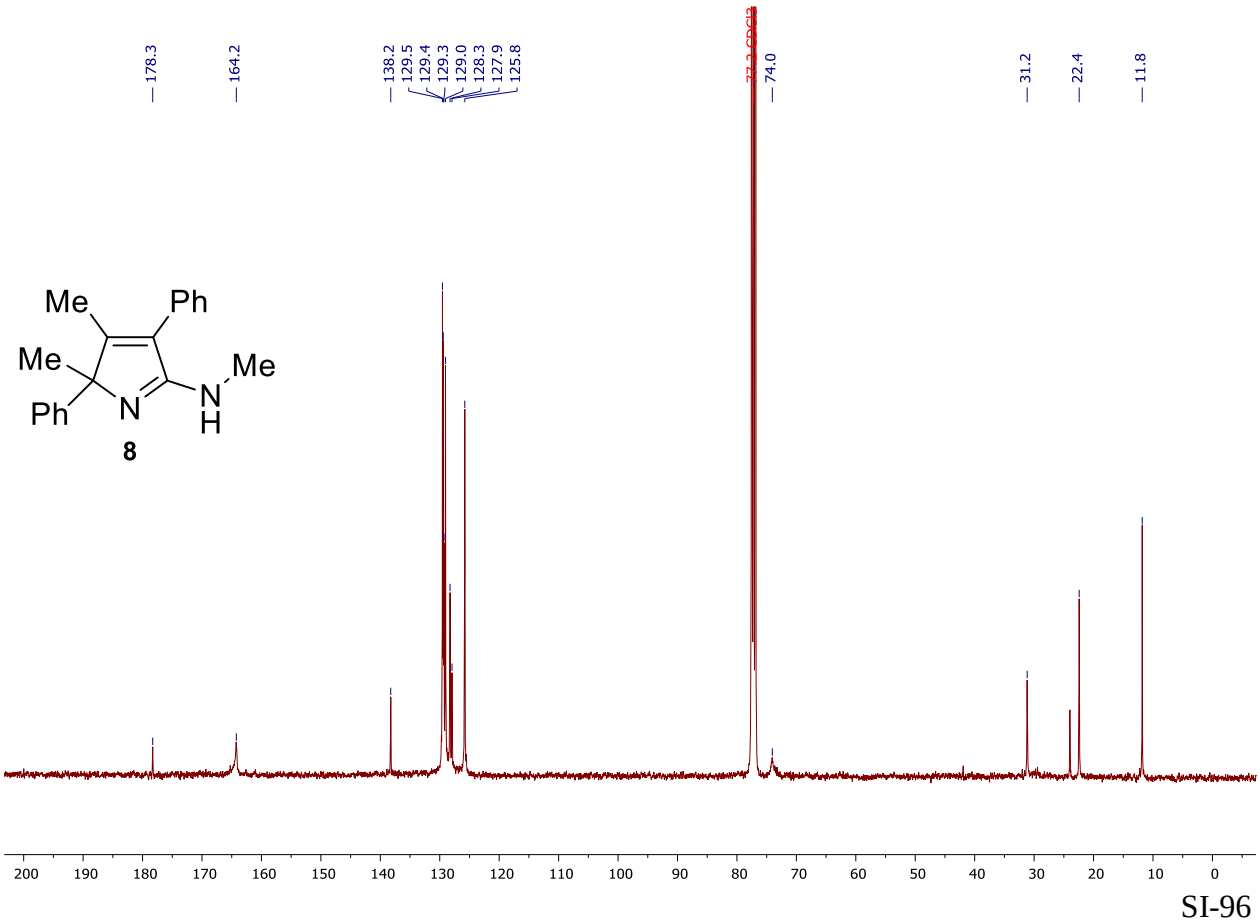
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **7**



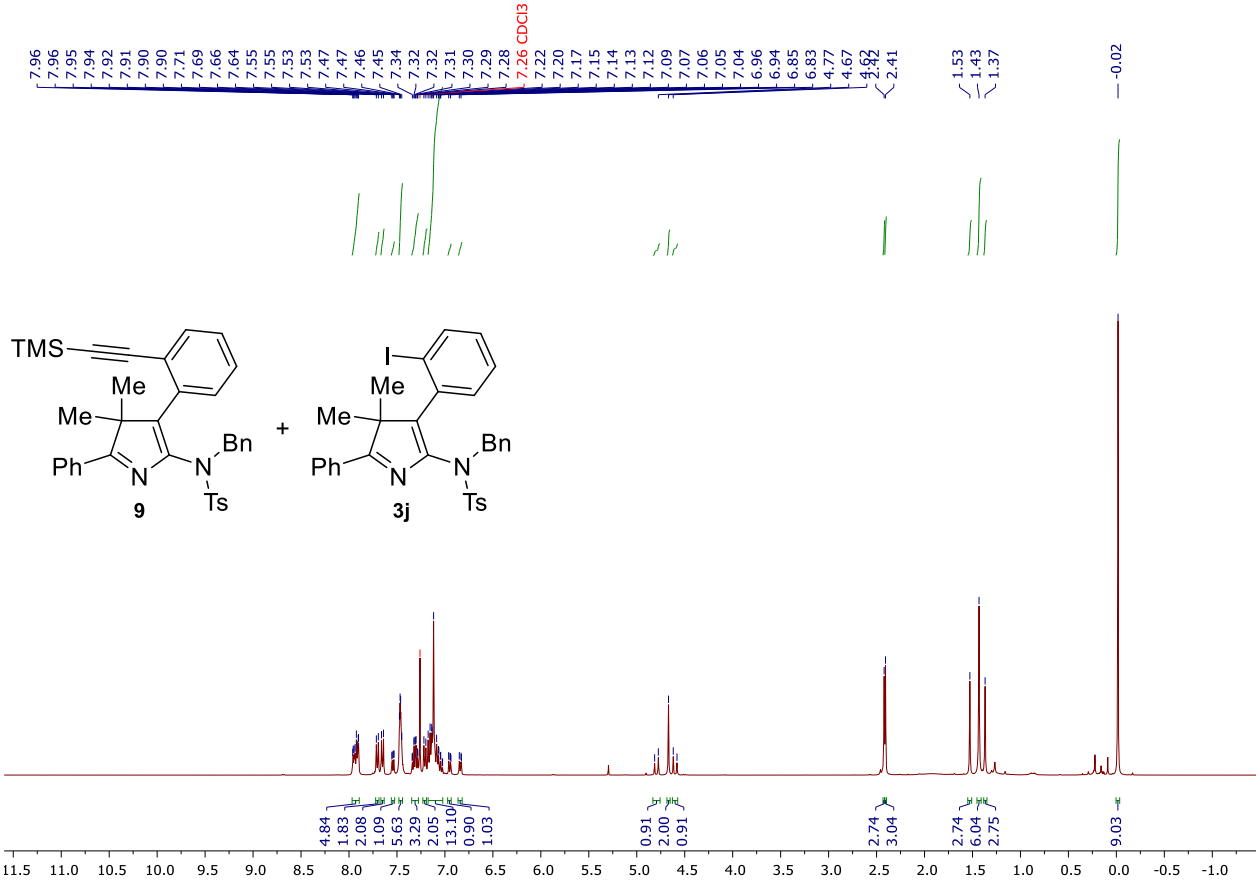
^{1}H NMR (400 MHz, $CDCl_3$) of **8**



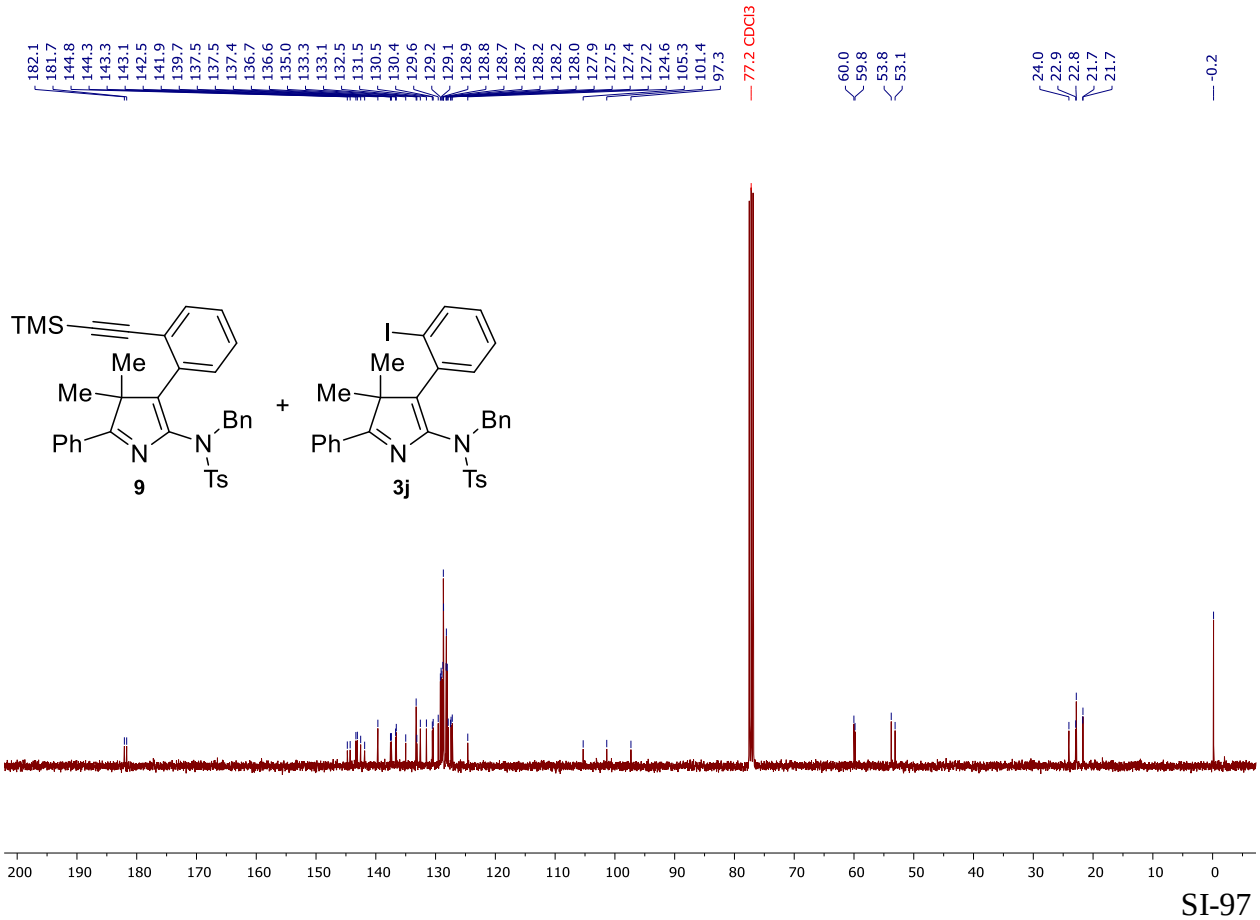
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **8**



^{1}H NMR (400 MHz, $CDCl_3$) of **9**



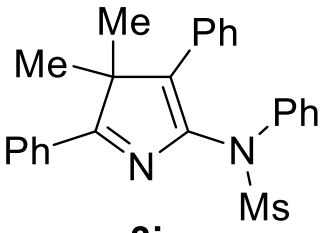
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **9**



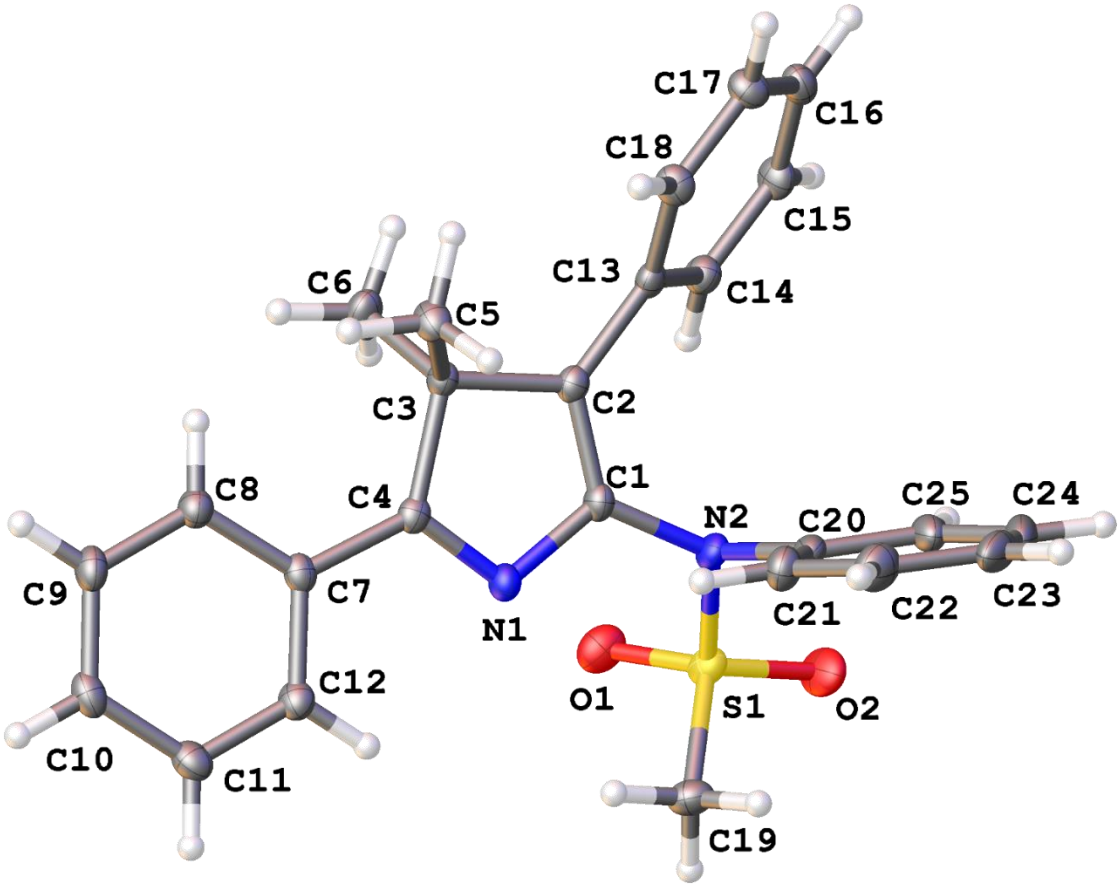
5. Solid State Molecular Structures of 3i, 3k and 6ab

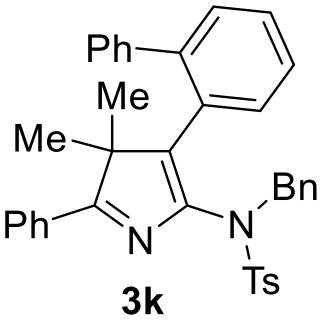
For single crystal X-ray diffraction experiments the single crystals of **3i**, **3k** and **6ab** were grown by slow evaporation of acetonitrile solution. Suitable crystals were fixed on a micro mount and placed on a **XtaLAB Synergy, Single source at home/near, HyPix** diffractometer (for **3i**) or **SuperNova, Single source at offset/far, HyPix3000** diffractometer (for **3k** and **6ab**) using CuKα monochromated radiation. All of crystals were measured at a temperature of 100(1) K. Using Olex2 [O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, **2009**, *42*, 339-341], the structures were solved with the SHELXT [G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2015, *71*, 3-8] structure solution program using Intrinsic Phasing and refined with the SHELXL [G. M. Sheldrick, *Acta Crystallogr. Sect. C* 2015, *71*, 3-8] refinement package using Least Squares minimisation.

Crystal data	**3i**	**3k**	**6ab**
Identification code	PhMs	PhPh	2H
CCDC Code	2175839	2175843	2175759
Empirical formula	$C_{25}H_{24}N_2O_2S$	$C_{38}H_{34}N_2O_2S$	$C_{31}H_{28}N_2O_2S$
Formula weight	416.52	582.73	492.61
Temperature/K	100(1)	100(1)	100(1)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	P-1	$P2_1/c$
a, Å	22.1190(2)	11.9683(2)	9.41500(10)
b, Å	9.22190(10)	12.3878(2)	29.9165(4)
c, Å	22.2350(2)	12.7373(2)	9.16980(10)
α, °	90	64.494(2)	90
β, °	109.0630(10)	64.434(2)	91.0470(10)
γ, °	90	70.9590(10)	90
Volume, $Å^3$	4286.75(8)	1514.48(5)	2582.37(5)
Z	8	2	4
ρ_{calc}, g/cm^3	1.291	1.278	1.267
μ, mm^{-1}	1.528	1.236	1.352
F(000)	1760.0	616.0	1040.0
Crystal size, mm^3	0.03 × 0.02 × 0.02	0.12 × 0.1 × 0.06	0.1 × 0.04 × 0.02
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection, °	4.892 to 160.136	8.028 to 138.352	5.908 to 134.986
Index ranges	$-28 \le h \le 28$, $-11 \le k \le 11$, $-22 \le l \le 28$	$-14 \le h \le 14$, $-15 \le k \le 14$, $-15 \le l \le 15$	$-11 \le h \le 11$, $-25 \le k \le 35$, $-10 \le l \le 10$
Reflections collected	34149	19956	12987
Independent reflections	9056 [R_{int} = 0.0381, R_{sigma} = 0.0362]	5597 [R_{int} = 0.0322, R_{sigma} = 0.0271]	4597 [R_{int} = 0.0273, R_{sigma} = 0.0288]
Data/restraints/parameters	9056/0/547	5597/0/391	4597/0/328
Goodness-of-fit on F^2	1.039	1.069	1.049
Final R indexes [I≥2σ (I)]	R_1 = 0.0356, wR_2 = 0.0891	R_1 = 0.0356, wR_2 = 0.0935	R_1 = 0.0361, wR_2 = 0.0913
Final R indexes [all data]	R_1 = 0.0408, wR_2 = 0.0921	R_1 = 0.0394, wR_2 = 0.0966	R_1 = 0.0401, wR_2 = 0.0936
Largest diff. peak/hole / $e \cdot Å^{-3}$	0.23/–0.40	0.22/–0.43	0.22/–0.39

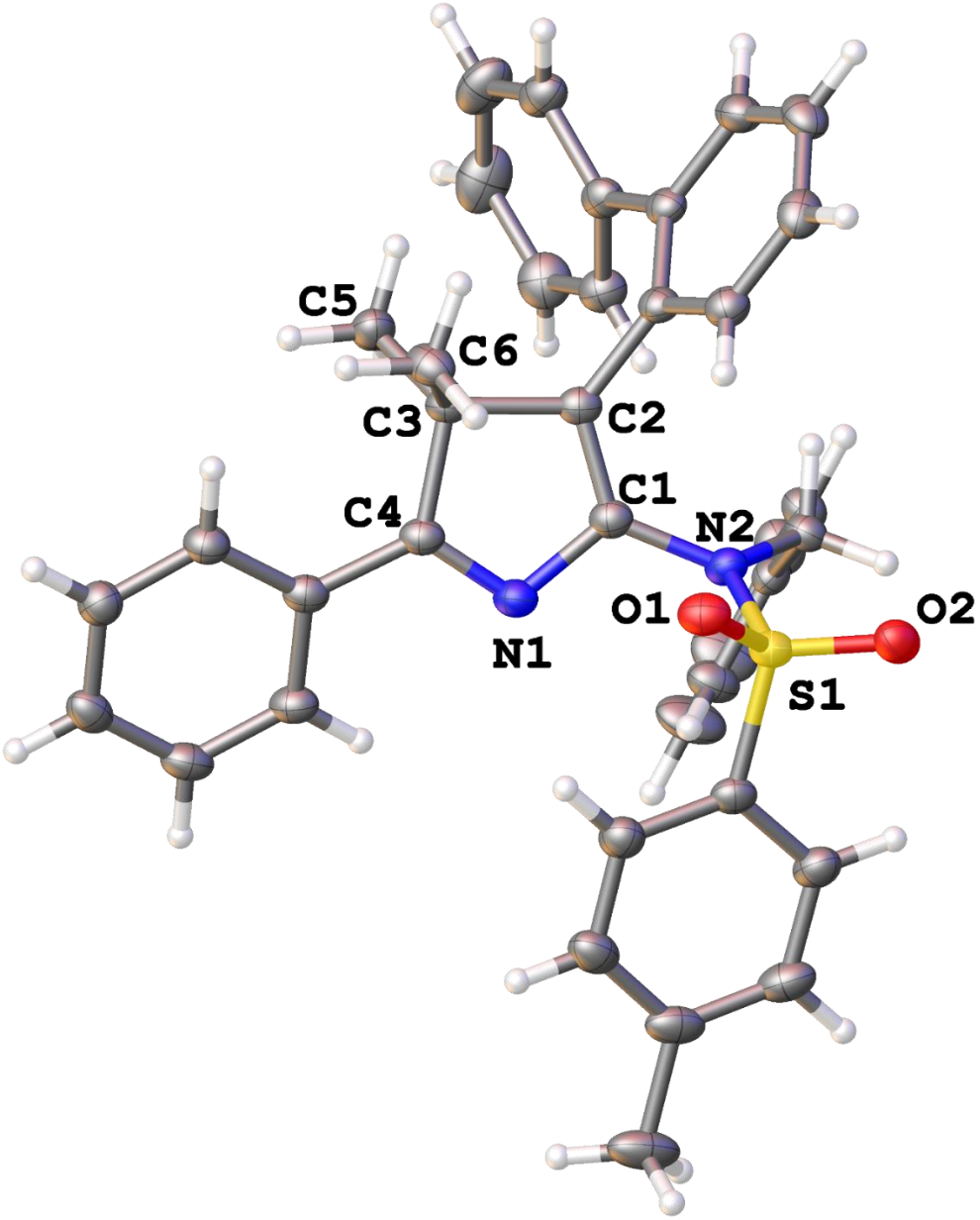

Me
Ph
Me
Ph
Ph
N
N
Ms

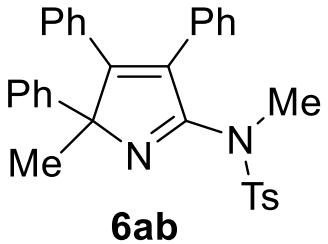
3i


C17
C16
C18
C15
C13
C14
C6
C5
C3
C2
C8
C4
C1
N2
C20
C25
C24
C9
C7
N1
C21
C22
C23
C12
O1
S1
O2
C10
C11
C19

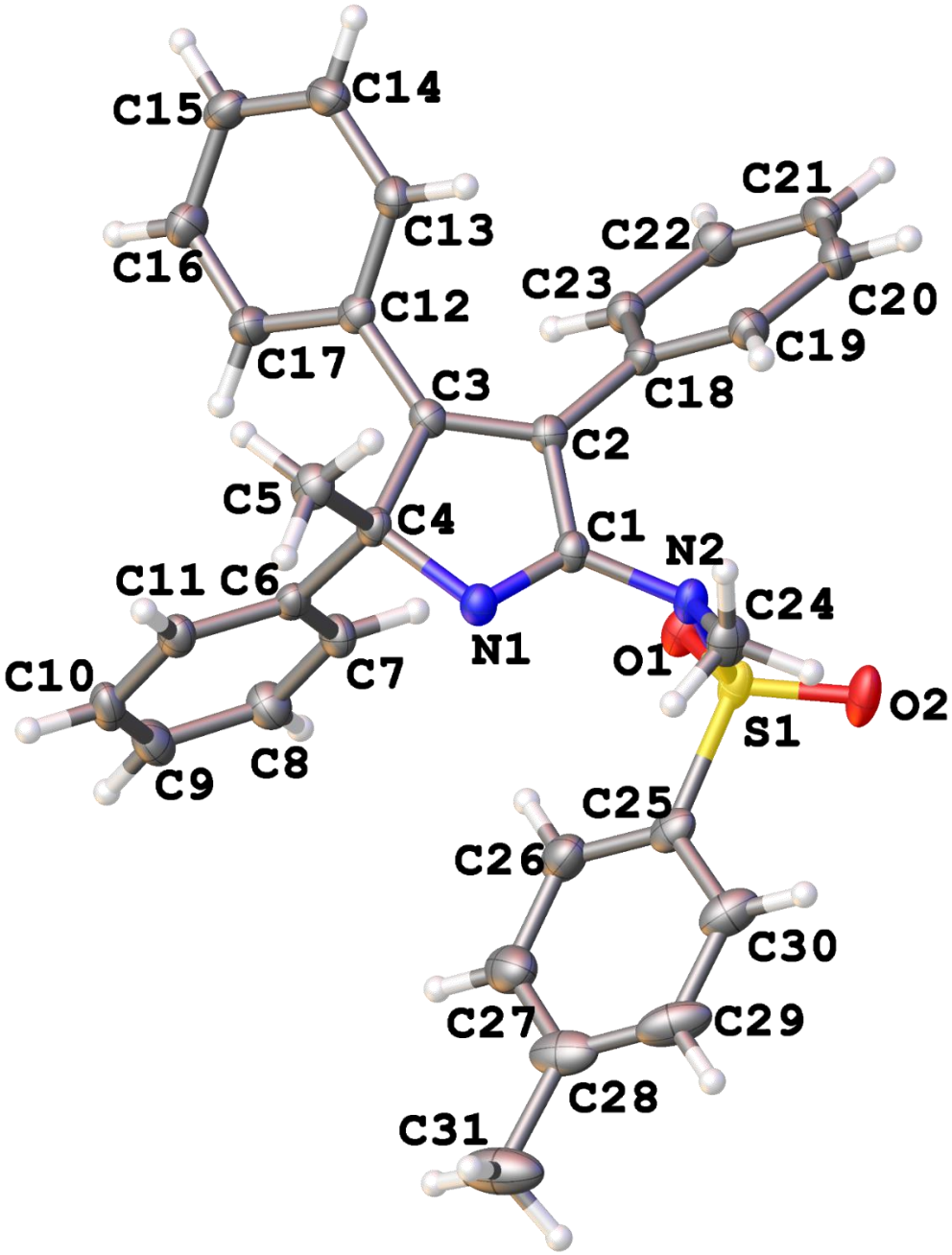


3k




Ph
Ph
Ph
Me
Me
N
N
Ts

6ab


C15
C14
C21
C13
C22
C16
C23
C20
C12
C19
C17
C3
C18
C2
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C1
N2
C11
C6
C24
N1
O1
C10
C7
O2
S1
C9
C8
C25
C26
C30
C27
C29
C28
C31