Supporting Information for

Coinage (Au, Ag, Cu) Metal-Catalyzed (3+2) Annulation of α-Aminoketones and Electron-Deficient Alkynes as a Route to 3-EWG-Substituted Pyrroles

Elena I. Chikunova,[a] Polina F. Kotikova,[a] Dmitry V. Dar'in,[a,b] Vadim Yu. Kukushkin,[a,c] and Alexey Yu. Dubovtsev*[a]

[a]Saint Petersburg State University, Universitetskaya Nab. 7/9, 199034 Saint Petersburg, Russian Federation

[b]Saint Petersburg Research Institute of Phthisiopulmonology, 191036 Saint Petersburg, Russian Federation

[c]Institute of Chemistry and Pharmaceutical Technologies, Altai State University, 656049 Barnaul, Russian Federation

E-mail: a.dubovtsev@spbu.ru (A.Yu.D.)

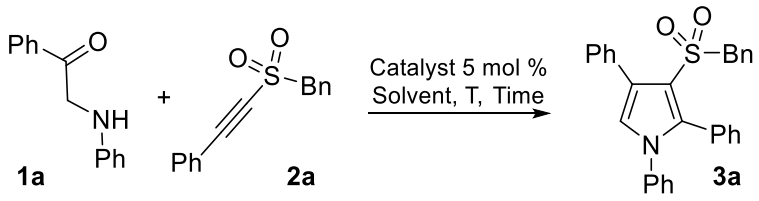
Table of Contents

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 $CDCl_3$. Chemical shifts (δ) are given in ppm relative to resonances of the solvents (^{1}H: δ = 7.26 for residual $CHCl_3$ peak; ^{13}C: δ = 77.2 for $CDCl_3$ peak). 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. Known α-aminoketones **1**,[21] alkynylsulfones **2**,[43–45] and alkynylphosphonate **2**[46] were prepared by the literature procedures. 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. Complete Optimization Studies

Table S1



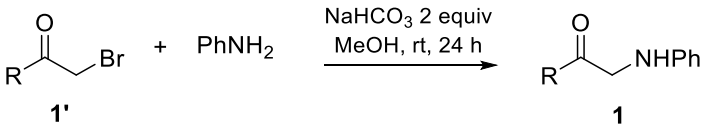
Entry[a]	Catalyst	Solvent	T, °C	Time, h	Yield of 3a, %[b]
1	none	DCE	80	20	–
2	$Zn(OTf)_2$	DCE	80	20	–
3	$FeCl_2$	DCE	80	20	–
4	$Sc(OTf)_3$	DCE	80	20	–
5	$FeCl_2$	DCE	80	20	–
6	TfOH	DCE	80	20	traces
7	**$Ph_3PAuNTf_2$**	**DCE**	**80**	**20**	**97**
8	$IPrAuNTf_2$	DCE	80	20	87
9	$PicAuCl_2$	DCE	80	20	25
10	**$AgNTf_2$**	**DCE**	**80**	**20**	**90**
11	$AgSbF_6$	DCE	80	20	61
12	AgOTf	DCE	80	20	57
13	$AgBF_4$	DCE	80	20	30
14	AgOAc	DCE	80	20	7
15	CuI	DCE	80	20	–
16	$Cu(OTf)_2$	DCE	80	20	73
17	$Cu(OAc)_2 \cdot H_2O$	DCE	80	20	73
18	$CuCl_2 \cdot 2H_2O$	DCE	80	20	66
19	$Cu(NTf_2)_2$	DCE	80	20	90
20	$CuPF_6(MeCN)_4$	DCE	80	20	90
21	$CuBF_4(MeCN)_4$	DCE	80	20	75
22	**CuOTf·1/2PhMe**	**DCE**	**80**	**20**	**95**
23	CuOTf·1/2PhMe	DCE	80	3	93
24	CuOTf·1/2PhMe	DCE	80	2	55
25	3 mol % $Ph_3PAuNTf_2$	DCE	80	3	48

26	CuOTf·1/2PhMe	DCE	60	3	33
27	CuOTf·1/2PhMe	PhMe	80	3	21
28	CuOTf·1/2PhMe	THF	80	3	21
29	CuOTf·1/2PhMe	MeOH	80	3	17
30	CuOTf·1/2PhMe	MeCN	80	3	–
31	CuOTf·1/2PhMe	DCM	RT	24	7
32	JohnPhosAuSbF$_6$(MeCN)	DCM	100	2	93[c]

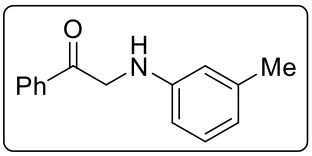
[a]All reactions were carried out on a 0.1 mmol scale (0.2 *M*). [b]Estimated by ^{1}H NMR spectroscopy using durene as an internal standard. [c]3 Equivalents of MgO were added.

3. Experimental Procedures and Characterization Data

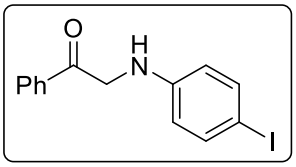
3.1. Synthesis of Starting α-Aminoketones



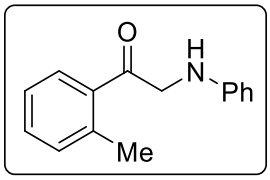
A 50 mL round-bottom flask was charged with aniline (466 mg, 5.0 mmol, 1 equiv), a bromoketone **1'** (5.0 mmol, 1 equiv), $NaHCO_3$ (840 mg, 10 mmol, 2 equiv), methanol (10 mL) and the suspension was stirred at room temperature for 24 h. During the process, a light yellow voluminous precipitate formed. After completion, the precipitate was separated on a Schott filter, and washed successively with cold methanol (5 mL) and water (20 mL). Then, the precipitate was dried at room temperature in air to afford the corresponding aminoketone **1**.



1-Phenyl-2-(3-tolylamino)ethan-1-one (1c): light yellow solid (710 mg, 63%); mp 79.0–81.0 °C (DCM); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.4 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.13 (t, J = 7.6 Hz, 1H), 6.67–6.53 (m, 3H), 4.63 (s, 2H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.1, 146.9, 139.4, 135.1, 134.0, 129.4, 129.0, 127.9, 119.4, 114.4, 110.8, 50.9, 21.8; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{15}H_{16}NO^+$: 226.1226; found: 226.1225.

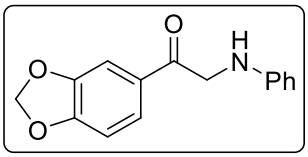


2-((4-Iodophenyl)amino)-1-phenylethan-1-one (1i): light yellow solid (1.21 mg, 72%); mp 132.5–134.0 °C (dec., DCM); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05–7.98 (m, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.7 Hz, 2H), 7.50–7.44 (m, 2H), 6.50 (d, J = 8.6 Hz, 2H), 4.98 (s, 1H), 4.57 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.7, 146.8, 138.1, 134.9, 134.2, 129.1, 127.9, 115.4, 78.6, 50.1; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{14}H_{13}INO^+$: 338.0036; found: 338.0030.

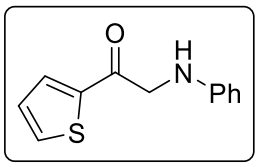


2-(Phenylamino)-1-(2-tolyl)ethan-1-one (1p): light yellow solid (541 mg, 48%); mp 79.5–81.0 °C (DCM); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, J = 7.6 Hz, 1H, Ar), 7.45 (t, J = 8.3 Hz, 1H, Ar), 7.32 (t, J = 7.9 Hz, 2H, Ar), 7.26–7.18 (m, 2H, Ar), 6.76 (t, J = 7.3 Hz, 1H, Ar), 6.70 (d, J = 7.5 Hz, 2H, Ar), 4.95 (br. s, 1H, NH), 4.51 (s, 2H, CH_2), 2.56 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.6, 147.3, 139.2, 135.4, 132.5, 132.3, 129.5, 128.3, 126.1,

118.0, 113.2, 52.4, 21.6; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{15}H_{16}NO^+$: 226.1226; found: 226.1224.



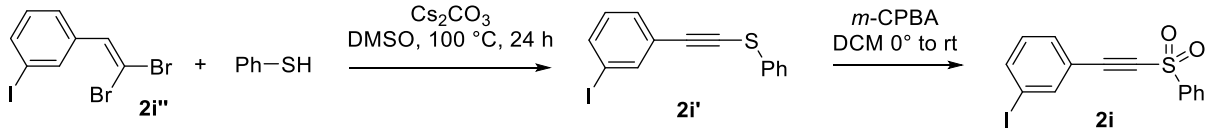
1-(Benzo[d][1,3]dioxol-5-yl)-2-(phenylamino)ethan-1-one (1q): light yellow solid (881 mg, 69%); mp 132.0–133.0 °C (DCM); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 8.2, 1.8 Hz, 1H), 7.49 (d, J = 1.7 Hz, 1H), 7.25–7.18 (m, 2H), 6.90 (d, J = 8.2 Hz, 1H), 6.75 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 7.7 Hz, 2H), 6.07 (s, 2H), 4.92 (s, 1H), 4.53 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.2, 152.5, 148.6, 147.3, 129.8, 129.5, 124.1, 117.9, 113.2, 108.3, 107.8, 102.2, 50.1; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{15}H_{14}NO_3^+$: 256.0968; found: 256.0970.



2-(Phenylamino)-1-(thiophen-2-yl)ethan-1-one (1r): light yellow solid (608 mg, 56%); mp 80.0–81.0 °C (DCM); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 3.8, 1.1 Hz, 1H, Ar), 7.71 (dd, J = 4.9, 1.2 Hz, 1H, Ar), 7.25–7.16 (m, 3H, Ar), 6.76 (t, J = 7.3 Hz, 1H, Ar), 6.70 (d, J = 7.7 Hz, 2H, Ar), 4.83 (br. s, 1H, NH), 4.55 (s, 2H, CH_2); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 188.6, 147.2, 141.5, 134.2, 132.0, 129.5, 128.4, 118.2, 113.2, 50.8; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{12}H_{12}NOS^+$: 218.0634; found: 218.0635.

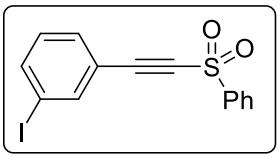
3.2. Synthesis of Starting Alkynylsulfones

Synthesis of 2i



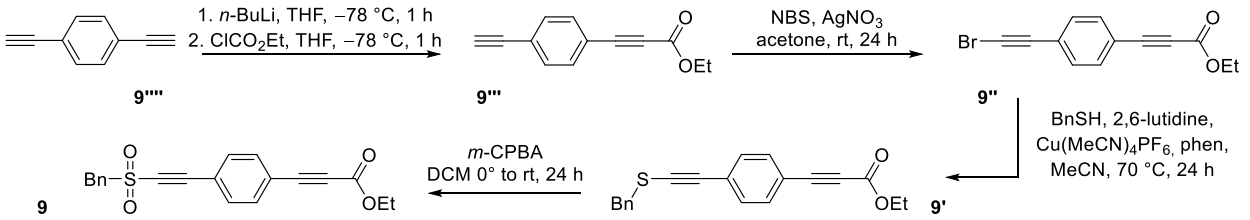
A 50 mL round-bottom flask was charged with 1-(2,2-dibromovinyl)-3-iodobenzene **2i''** (388 mg, 1.0 mmol), thiophenol (110 mg, 1.0 mmol, 1 equiv), Cs_2CO_3 (1.30 g, 4.0 mmol, 4 equiv), and DMSO (10 mL). The suspension was heated at 100 °C in an oil bath with stirring for 24 h. After completion, water (50 mL) was added, and the resulting emulsion was extracted by DCM (3×50 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated in vacuum, and the residue was separated by column chromatography (silica gel), eluting with hexane/EtOAc, to afford a crude alkynylsulfide **2i'**.

After that **2i'** was oxidized to the corresponding alkynylsulfone **2i'**. *m*-Chloroperoxybenzoic acid (77%, 672 mg, 3.0 mmol, 3.0 equiv) was added portionwise to a stirred solution of a crude alkynylsulfide **2i'** in dichloromethane (10 mL) cooled in an ice bath. Then, the resulting solution was stirred at room temperature for 24 h. Next, the reaction was subsequently washed with saturated $NaHCO_3$ (50 ml) and $Na_2S_2O_3$ (50 ml). The organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed in vacuum, and the residue was separated by column chromatography (silica gel), eluting with hexane/EtOAc, to afford alkynylsulfone **2i**.

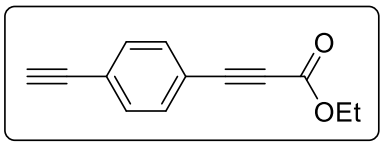


1-Iodo-3-((phenylsulfonyl)ethynyl)benzene (2i): colorless oil (291 mg, 79%); R_f 0.35 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.8 Hz, 2H), 7.86 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 7.4 Hz, 1H), 7.61 (t, J = 7.7 Hz, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.11 (t, J = 7.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.7, 141.1, 140.7, 134.5, 131.9, 130.3, 129.6, 127.7, 120.1, 93.7, 91.2, 86.4; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{14}H_9INaO_2S^+$: 390.9260; found: 390.9264.

Synthesis of 9

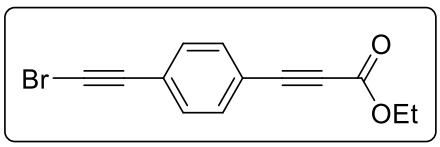


A flame-dried and degassed 3-necked 50 mL round bottom flask was charged with 1,4-diethynylbenzene **9''''** (631 mg, 5.0 mmol, 2 equiv) and anhydrous THF (10 mL). Under dry argon atmosphere, the stirred solution was cooled to –78 °C in an acetone/dry ice bath, and *n*-butyllithium (2.5 M in hexanes, 1.00 mL, 2.5 mmol, 1.0 equiv) was added dropwise during 1 h. The reaction mixture was kept for 1 h at –78 °C, and a solution of a fresh-distilled ethyl chloroformate (325 mg, 3.0 mmol, 1.2 equiv) in anhydrous THF (2 mL) was added dropwise. The reaction was allowed to warm to room temperature and then quenched by the addition of saturated aqueous NH_4Cl (30 ml). The resulting emulsion was extracted by DCM (3×30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration, the solution was concentrated in vacuum, and the residue was separated by column chromatography (silica gel), eluting with hexane/EtOAc, to afford **9'''**.



Ethyl 3-(4-ethynylphenyl)propiolate (9'''): colorless solid (119 mg, 24%); mp 75.0–77.0 °C (DCM); R_f 0.45 (hexane/EtOAc 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 3.22 (s, 1H), 1.35 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.0, 132.9, 132.3, 124.6, 120.1, 85.2, 82.8, 82.3, 80.4, 62.3, 14.2; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{13}H_{11}O_2^+$: 199.0754; found: 199.0747.

$AgNO_3$ (8.5 mg, 50 μmol, 10 mol %) was added to the solution of **9'''** (99.1 mg, 0.5 mmol, 1.0 equiv) and *N*-bromosuccinimide (178 mg, 1.0 mmol, 2.0 equiv) in acetone (10 mL). The resulting suspension was stirred at room temperature for 24 h. After completion, the solvent was removed in vacuum, and the residue was purified by silica gel chromatography, eluting with hexane/EtOAc, to afford bromoalkyne **9''**.

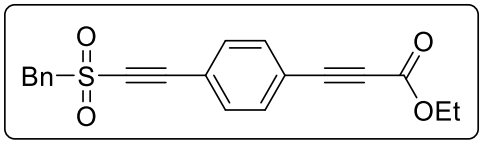


Ethyl 3-(4-(bromoethynyl)phenyl)propiolate (9''): yellow solid (130 mg, 94%); mp 65.0–67.0 °C (DCM); R_f 0.40 (hexane/EtOAc 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.5 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 4.30 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.0, 133.0, 132.2, 125.2, 119.9, 85.2, 82.4, 79.4, 62.4, 53.7, 14.2; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{13}H_{10}BrO_2^+$: 276.9859; found: 276.9857.

A 50 mL round-bottom flask was charged with bromoalkyne **9''** (83.1 mg, 0.3 mmol, 1.0 equiv), $Cu(MeCN)_4PF_6$ (22.4 mg, 60 μmol, 20 mol %), and 1,10-phenanthroline monohydrate

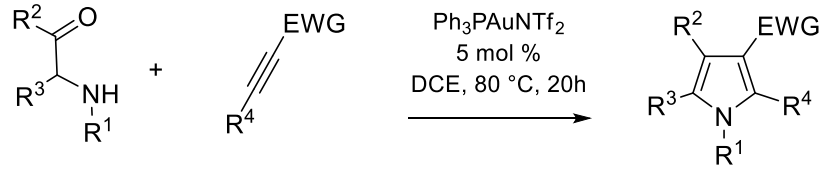
(10.2 mg, 60 μmol, 20 mol %). The flask was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. Dry degassed acetonitrile (10 mL), 2,6-lutidine (64.2 mg, 0.6 mmol, 2.0 equiv) and benzyl mercaptan (37.3 mg, 0.3 mmol, 1.0 equiv) were next added and the dark red suspension was stirred at 70 °C in an oil bath for 24 h. After completion, all volatile components were removed in vacuum, the dark green residue was suspended in DCM (50 mL) and filtered through a short pad of silica gel. The solvent was evaporated under reduced pressure to afford a crude alkynylsulfide **9'**, which was used in the next step without further purification.

m-Chloroperoxybenzoic acid (77%, 202 mg, 0.9 mmol, 3.0 equiv) was added portionwise to a stirred solution of a crude alkynylsulfide **9'** in dichloromethane (10 mL) cooled in an ice bath. Then, the resulting solution was stirred at room temperature for 24 h. Next, the reaction mixture was diluted with DCM (50 mL) and successively washed with saturated $NaHCO_3$ (50 ml) and $Na_2S_2O_3$ (50 ml). The organic layer was dried over anhydrous Na_2SO_4. After filtration, the solvent was removed in vacuum, and the residue was separated by column chromatography (silica gel), eluting with hexane/EtOAc, to afford alkynylsulfone **9**.



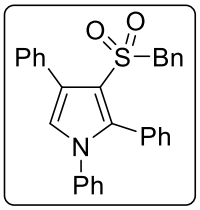
Ethyl 3-(4-((benzylsulfonyl)ethynyl)phenyl)propiolate (9): yellowish solid (76.1 mg, 73%); mp 92.0–93.0 °C (DCM); R_f 0.27 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.4 Hz, 2H), 7.52–7.36 (m, 7H), 4.51 (s, 2H), 4.31 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.6, 133.1, 132.8, 131.4, 129.7, 129.1, 127.2, 123.2, 119.6, 92.5, 84.9, 83.9, 83.6, 64.7, 62.5, 14.2; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{20}H_{17}O_4S^+$: 353.0842; found: 353.0839.

3.3. General Procedure for the Synthesis of 3-EWG-Substituted Pyrroles

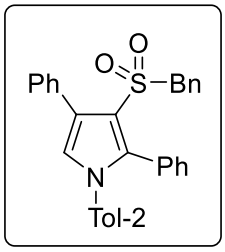


1 **2, 5, 7, 9, 10** **3, 4, 6, 8, 10, 11**

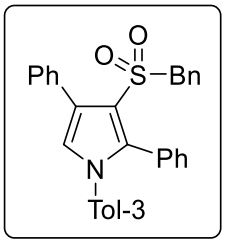
$Ph_3PAuNTf_2$ (7.4 mg, 10.0 μmol, 5 mol %) was added to the solution of α-aminoketone (0.24 mmol, 1.2 equiv) and electron-deficient alkyne (0.2 mmol, 1.0 equiv) in dry DCE (1.0 mL) in a flame-dried 10 mL flask. The resulting mixture was stirred at 80 °C in an oil bath for 20 h. After completion, the solvent was removed in vacuum, and the residue was purified by silica gel chromatography to afford the corresponding pyrrole.



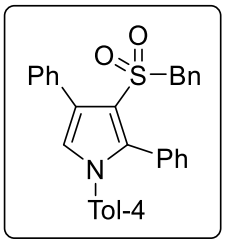
3-(Benzylsulfonyl)-1,2,4-triphenyl-1*H*-pyrrole (3a): colorless solid (83.6 mg, 93%); mp 168.0–169.0 °C (DCM); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69–7.64 (m, 2H), 7.47–7.39 (m, 3H), 7.32–7.19 (m, 7H), 7.12 (t, J = 7.6 Hz, 2H), 7.04–6.98 (m, 4H), 6.94 (s, 1H), 6.83–6.76 (m, 2H), 3.88 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.2, 138.7, 133.2, 131.7, 131.0, 130.7, 129.6, 129.4, 129.1, 128.6, 128.4, 128.4, 128.2, 127.9, 127.8, 127.3, 126.3, 126.3, 122.9, 117.7, 62.2; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{29}H_{23}NNaO_2S^+$: 472.1347; found: 472.1346. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 91% yield.



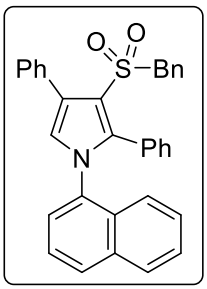
3-(Benzylsulfonyl)-2,4-diphenyl-1-(2-tolyl)-1*H*-pyrrole (3b): colorless solid (83.4 mg, 90%); mp 185.5–187.0 °C (DCM); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.0 Hz, 2H), 7.46 (t, J = 7.4 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.33 (t, J = 7.4 Hz, 1H), 7.28–7.24 (m, 2H), 7.20–6.96 (m, 9H), 6.78 (s, 1H), 6.71 (d, J = 7.1 Hz, 2H), 3.90 (s, 2H), 1.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.2, 137.5, 135.2, 133.3, 131.2, 131.0, 130.8, 130.7, 129.8, 129.5, 129.0, 128.6, 128.5, 128.4, 128.33, 128.28, 127.8, 127.0, 126.4, 125.9, 122.8, 116.4, 62.1, 17.7; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{30}H_{25}NNaO_2S^+$: 486.1498; found: 486.1509. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 82% yield.



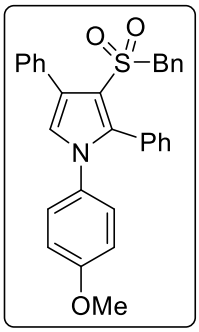
3-(Benzylsulfonyl)-2,4-diphenyl-1-(3-tolyl)-1*H*-pyrrole (3c): colorless solid (86.2 mg, 93%); mp 162.5–163.5 °C (DCM); R_f 0.55 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.0 Hz, 2H), 7.44 (t, J = 7.2 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.31 (t, J = 7.3 Hz, 1H), 7.26–7.19 (m, 3H), 7.13 (t, J = 6.6 Hz, 2H), 7.11–7.06 (m, 1H), 7.05–6.98 (m, 3H), 6.93 (s, 1H), 6.85 (br.s, 1H), 6.81 (d, J = 7.1 Hz, 2H), 6.76 (d, J = 7.8 Hz, 1H), 3.88 (s, 2H), 2.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.2, 139.1, 138.6, 133.3, 131.7, 131.0, 130.7, 129.7, 129.4, 128.8, 128.6, 128.6, 128.4 (×2), 128.2, 127.7, 127.2, 126.8, 126.1, 123.4, 122.9, 117.5, 62.2, 21.3; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{30}H_{26}NO_2S^+$: 464.1679; found: 464.1679. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 79% yield.



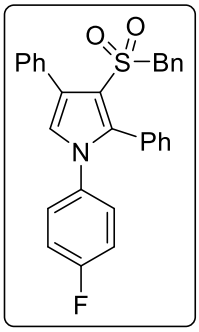
3-(Benzylsulfonyl)-2,4-diphenyl-1-(4-tolyl)-1*H*-pyrrole (3d): colorless solid (87.2 mg, 94%); mp 178.0–179.0 °C (DCM); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 6.9 Hz, 2H), 7.45 (t, J = 7.3 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.32 (t, J = 7.3 Hz, 1H), 7.26 (d, J = 7.7 Hz, 2H), 7.21 (d, J = 7.5 Hz, 1H), 7.13 (t, J = 7.6 Hz, 2H), 7.02 (t, J = 8.3 Hz, 4H), 6.94–6.86 (m, 3H), 6.81 (d, J = 7.1 Hz, 2H), 3.89 (s, 2H), 2.29 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.2, 137.9, 136.1, 133.3, 131.7, 131.0, 130.6, 129.72, 129.65, 129.4, 128.5, 128.3 (×2), 128.2, 127.7, 127.2, 126.0 (×2), 122.9, 117.4, 62.2, 21.1; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{30}H_{25}NNaO_2S^+$: 486.1498; found: 486.1504. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 82% yield.



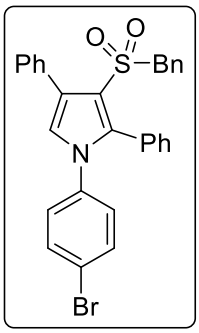
3-(Benzylsulfonyl)-1-(naphthalen-1-yl)-2,4-diphenyl-1*H*-pyrrole (3e): colorless solid (87.9 mg, 88%); mp 215.0–216.0 °C (DCM); R_f 0.55 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.1 Hz, 1H), 7.79–7.72 (m, 3H), 7.53 (ddd, J = 6.9, 4.6, 1.5 Hz, 2H), 7.47 (t, J = 7.4 Hz, 2H), 7.41 (d, J = 7.3 Hz, 1H), 7.39–7.31 (m, 4H), 7.29 (d, J = 8.0 Hz, 1H), 7.15 (d, J = 7.0 Hz, 1H), 7.11 (d, J = 6.8 Hz, 2H), 7.04 (t, J = 7.4 Hz, 1H), 6.94 (s, 1H), 6.94–6.89 (m, 2H), 6.68 (br.s, 2H), 3.95 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.3, 134.9, 133.9, 133.2, 131.1 (×2), 130.7, 130.7, 129.9, 129.5, 129.3, 128.5, 128.4 (×2), 128.3 (×2), 127.8, 127.5, 126.9, 126.8, 126.2, 125.8, 124.9, 124.1, 122.7, 116.6, 62.1; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{33}H_{25}NNaO_2S^+$: 522.1504; found: 522.1497. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 47% yield.



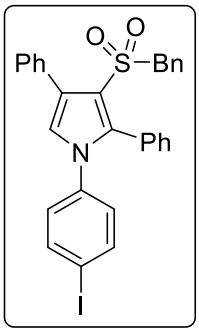
3-(Benzylsulfonyl)-1-(4-methoxyphenyl)-2,4-diphenyl-1*H*-pyrrole (3f): colorless solid (92.1 mg, 96%); mp 197.5–199.5 °C (DCM); R_f 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 2H), 7.39 (d, J = 7.0 Hz, 1H), 7.31 (d, J = 7.0 Hz, 1H), 7.26 (d, J = 7.6 Hz, 2H), 7.23–7.19 (m, 1H), 7.12 (t, J = 7.4 Hz, 2H), 7.01 (d, J = 7.2 Hz, 2H), 6.92 (d, J = 8.5 Hz, 2H), 6.89 (s, 1H), 6.79 (d, J = 7.1 Hz, 2H), 6.74 (d, J = 8.3 Hz, 2H), 3.88 (s, 2H), 3.75 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 139.4, 133.3, 131.7, 131.6, 131.0, 130.7, 129.8, 129.5, 128.5, 128.4 (×2), 128.2, 127.7, 127.5, 127.3, 125.9, 123.1, 117.2, 114.2, 62.2, 55.6; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{30}H_{25}NNaO_3S^+$: 502.1447; found: 502.1449. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 95% yield.



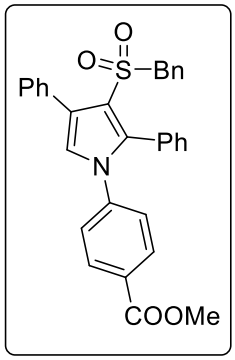
3-(Benzylsulfonyl)-1-(4-fluorophenyl)-2,4-diphenyl-1*H*-pyrrole (3g): colorless solid (72.0 mg, 77%); mp 183.0–184.5 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 6.8 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.35–7.26 (m, 2H), 7.23 (dd, J = 10.0, 7.4 Hz, 2H), 7.13 (t, J = 7.6 Hz, 2H), 7.03–6.96 (m, 4H), 6.94 (d, J = 8.1 Hz, 2H), 6.91 (s, 1H), 6.76 (d, J = 6.9 Hz, 2H), 3.88 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8 (d, J_F = 248.8 Hz), 139.4, 134.7 (d, J_F = 3.1 Hz), 133.0, 131.6, 131.0, 130.6, 129.4 (d, J_F = 6.1 Hz), 128.8, 128.4, 128.4, 128.3, 128.1, 128.0, 127.9, 127.4, 126.3, 122.8, 117.8, 116.1 (d, J_F = 22.9 Hz), 62.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –112.93; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{29}H_{22}FNNaO_2S^+$: 490.1247; found: 490.1256. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 82% yield.



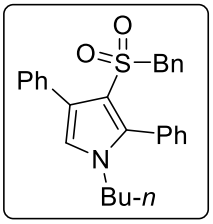
3-(Benzylsulfonyl)-1-(4-bromophenyl)-2,4-diphenyl-1*H*-pyrrole (3h): colorless solid (85.6 mg, 81%); mp 198.5–200.5 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, J = 6.9 Hz, 2H), 7.50–7.21 (m, 9H), 7.15 (t, J = 7.6 Hz, 2H), 7.00 (d, J = 7.5 Hz, 2H), 6.91 (s, 1H), 6.88 (d, J = 8.5 Hz, 2H), 6.78 (d, J = 7.6 Hz, 2H), 3.88 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.1, 137.7, 132.9, 132.3, 131.6, 131.0, 130.6, 129.3, 128.9, 128.4, 128.4, 128.3, 127.9, 127.7, 127.5, 126.6, 122.6, 121.8, 118.1, 62.1 (one signal merges with the others); **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{29}H_{22}BrNNaO_2S^+$: 550.0447; found: 552.0424. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 77% yield.



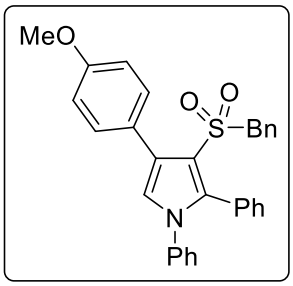
3-(Benzylsulfonyl)-1-(4-iodophenyl)-2,4-diphenyl-1*H*-pyrrole (3i): colorless solid (85.2 mg, 74%); mp 226.0–228.0 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, J = 6.8 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.47–7.37 (m, 3H), 7.31 (t, J = 7.3 Hz, 2H), 7.25–7.21 (m, 2H), 7.15 (t, J = 7.5 Hz, 2H), 6.99 (d, J = 7.3 Hz, 2H), 6.90 (s, 1H), 6.78 (d, J = 7.4 Hz, 2H), 6.74 (d, J = 8.2 Hz, 2H), 3.87 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.0, 138.4, 138.3, 132.9, 131.6, 131.0, 130.6, 129.3, 128.9, 128.4, 128.4, 128.3, 127.9 (×2), 127.5, 126.6, 122.5, 118.2, 93.1, 62.2 (one signal merges with the others); **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{29}H_{22}INNaO_2S^+$: 598.0308; found: 598.0318. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 94% yield.



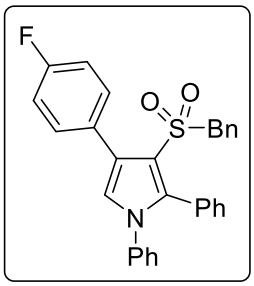
Methyl 4-(3-(benzylsulfonyl)-2,4-diphenyl-1*H*-pyrrol-1-yl)benzoate (3j): colorless solid (73.1 mg, 72%); mp 182.0–183.0 °C (DCM); R_f 0.40 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.5 Hz, 2H), 7.67 (d, J = 6.9 Hz, 2H), 7.45 (t, J = 7.2 Hz, 2H), 7.43–7.37 (m, 1H), 7.31 (t, J = 7.3 Hz, 1H), 7.27–7.22 (m, 3H), 7.13 (t, J = 7.6 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 7.2 Hz, 2H), 6.97 (s, 1H), 6.80 (d, J = 7.3 Hz, 2H), 3.88 (s, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 142.4, 139.0, 132.9, 131.6, 131.0, 130.6, 130.6, 129.4, 129.2, 129.2, 128.9, 128.4, 128.4, 128.2, 127.9, 127.5, 126.8, 125.9, 122.5, 118.5, 62.1, 52.4; **HRMS** (ESI): *m/z* [M + Na]$^+$ calcd. for $C_{31}H_{25}NNaO_4S^+$: 530.1402; found: 530.1393. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 82% yield.



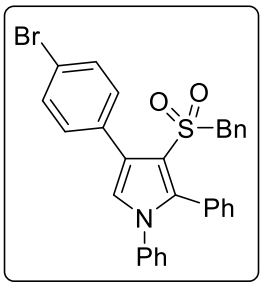
3-(Benzylsulfonyl)-1-butyl-2,4-diphenyl-1*H*-pyrrole (3k): colorless oil (64.4 mg, 75%); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.0 Hz, 2H), 7.42 (t, J = 7.3 Hz, 2H), 7.38–7.27 (m, 4H), 7.26–7.19 (m, 3H), 6.95 (d, J = 7.2 Hz, 2H), 6.75 (d, J = 7.0 Hz, 2H), 6.75 (s, 1H), 3.83 (s, 2H), 3.56 (t, J = 7.2 Hz, 2H), 1.54–1.46 (m, 2H), 1.14 (h, J = 7.4 Hz, 3H), 0.80 (t, J = 7.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.5, 133.6, 131.0, 131.0, 130.6, 130.2, 129.9, 128.9, 128.3, 128.2, 128.2, 127.6, 127.6, 125.4, 121.0, 115.7, 62.1, 47.0, 33.1, 19.7, 13.6; **HRMS** (ESI): *m/z* [M + H]$^+$ calcd. for $C_{27}H_{28}NO_2S^+$: 430.1835; found: 430.1828.



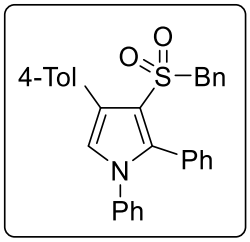
3-(Benzylsulfonyl)-4-(4-methoxyphenyl)-1,2-diphenyl-1*H*-pyrrole (3l): yellowish solid (73.9 mg, 77%); mp 157.7–159.7 °C (DCM); R_f 0.30 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.31 (t, J = 7.1 Hz, 2H), 7.26–7.17 (m, 5H), 7.10 (t, J = 7.3 Hz, 2H), 7.04–6.95 (m, 6H), 6.91 (s, 1H), 6.76 (d, J = 7.2 Hz, 2H), 3.89 (s, 2H), 3.87 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.4, 139.1, 138.7, 131.8, 131.7, 131.0, 129.7, 129.5, 129.1, 128.6, 128.4 (×2), 127.9, 127.3, 126.3, 125.9, 125.4, 122.6, 117.5, 113.7, 62.1, 55.5; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{30}H_{25}NNaO_3S^+$: 502.1453; found: 502.1449. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 89% yield.



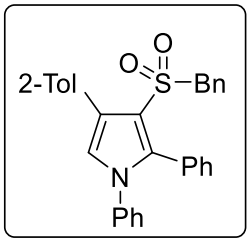
3-(Benzylsulfonyl)-4-(4-fluorophenyl)-1,2-diphenyl-1*H*-pyrrole (3m): colorless solid (81.4 mg, 87%); mp 183.0–184.5 °C (DCM); R_f 0.40 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 8.6, 5.6 Hz, 2H), 7.32 (t, J = 7.3 Hz, 1H), 7.27–7.21 (m, 6H), 7.17–7.06 (m, 4H), 7.04–6.95 (m, 4H), 6.90 (s, 1H), 6.84 (d, J = 7.2 Hz, 2H), 3.87 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.1, 138.6, 132.3, 132.2, 131.7, 131.0, 129.5, 129.3, 129.2, 128.8, 128.5, 128.4, 128.0, 127.4, 126.3, 125.5, 122.8, 117.6, 115.0 (d, J_F = 21.5 Hz), 62.4 (one signal merges with the others); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –114.86; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{29}H_{22}FNNaO_2S^+$: 490.1247; found: 490.1257. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 85% yield.



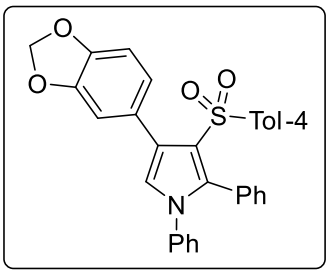
3-(Benzylsulfonyl)-4-(4-bromophenyl)-1,2-diphenyl-1*H*-pyrrole (3n): colorless solid (100.3 mg, 95%); mp 214.0–216.0 °C (DCM); R_f 0.55 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.9 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 7.33 (t, J = 7.2 Hz, 1H), 7.28–7.22 (m, 6H), 7.15 (t, J = 7.5 Hz, 2H), 7.05–6.95 (m, 4H), 6.91 (s, 1H), 6.85 (d, J = 7.4 Hz, 2H), 3.88 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.3, 138.5, 132.2, 132.1, 131.7, 131.2, 131.0, 129.4, 129.2, 129.2, 128.8, 128.5, 128.4, 128.1, 127.4, 126.3, 125.4, 122.8, 122.0, 117.5, 62.5; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{29}H_{22}BrNNaO_2S^+$: 550.0447; found: 550.0442. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 97% yield.



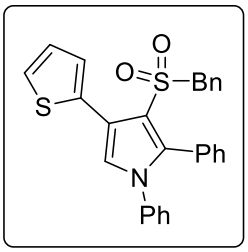
3-(Benzylsulfonyl)-1,2-diphenyl-4-(4-tolyl)-1*H*-pyrrole (3o): colorless solid (81.6 mg, 88%); mp 150.0–151.0 °C (DCM); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.0 Hz, 2H, Ar), 7.35–7.17 (m, 9H, Ar), 7.11 (t, J = 7.6 Hz, 2H, Ar), 7.05–6.95 (m, 4H, Ar), 6.93 (s, 1H, Ar), 6.77 (d, J = 7.1 Hz, 2H, Ar), 3.90 (s, 2H, CH_2), 2.43 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.1, 138.7, 137.5, 131.7, 131.0, 130.5, 130.2, 129.7, 129.5, 129.1, 129.0, 128.5, 128.3 (×2), 127.9, 127.2, 126.3, 126.2, 122.7, 117.5, 62.1, 21.4; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{30}H_{25}NNaO_2S^+$: 486.1498; found: 486.1483. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 83% yield.



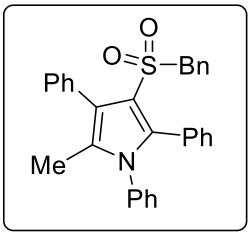
3-(Benzylsulfonyl)-1,2-diphenyl-4-(2-tolyl)-1*H*-pyrrole (3p): colorless solid (76.9 mg, 83%); mp 182.0–183.5 °C (DCM); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35–7.22 (m, 9H, Ar), 7.21–7.12 (m, 4H, Ar), 7.08–7.00 (m, 4H, Ar), 6.95 (d, J = 7.5 Hz, 2H, Ar), 6.82 (s, 1H, Ar), 3.89 (s, 2H, CH_2), 2.36 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.9, 138.8, 137.9, 133.1, 131.8, 131.1, 131.0, 129.8, 129.5, 129.3, 129.2, 128.7, 128.5, 128.4, 128.1, 127.8, 127.5, 126.2, 125.4, 125.0, 122.5, 118.6, 62.6, 21.0; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{30}H_{25}NNaO_2S^+$: 486.1498; found: 486.1497. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 78% yield.



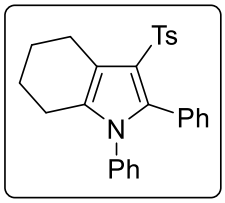
4-(Benzo[*d*][1,3]dioxol-5-yl)-3-(benzylsulfonyl)-1,2-diphenyl-1*H*-pyrrole (3q): colorless solid (82.9 mg, 84%); mp 154.0–155.0 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.25–7.19 (m, 9H), 7.07–7.02 (m, 2H), 7.00 (d, J = 8.1 Hz, 2H), 6.96 (d, J = 1.5 Hz, 1H), 6.91 (dd, J = 8.0, 1.6 Hz, 1H), 6.80 (d, J = 8.2 Hz, 1H), 6.79 (s, 1H), 6.00 (s, 2H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.1, 147.0, 142.7, 140.8, 138.7, 137.1, 132.0, 130.2, 129.1, 128.9, 128.7, 127.8, 127.6, 127.3, 127.2, 126.2, 125.8, 124.1, 122.6, 122.0, 111.5, 107.6, 101.1, 21.6; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{30}H_{24}NO_4S^+$: 494.1421; found: 494.1423. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 77% yield.



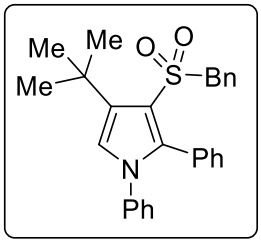
3-(Benzylsulfonyl)-1,2-diphenyl-4-(thiophen-2-yl)-1*H*-pyrrole (3r): colorless solid (82.9 mg, 91%); mp 195.5–197.0 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 3.0 Hz, 1H), 7.35 (d, J = 4.5 Hz, 1H), 7.32 (d, J = 7.2 Hz, 1H), 7.30–7.25 (m, 2H), 7.25–7.19 (m, 3H), 7.19–7.14 (m, 2H), 7.09 (s, 1H), 7.09–7.03 (m, 4H), 6.96 (dd, J = 6.1, 3.1 Hz, 2H), 6.61 (d, J = 7.4 Hz, 2H), 4.06 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.1, 138.3, 133.5, 131.5, 131.1, 129.5, 129.3, 129.1, 128.7, 128.6, 128.4, 128.4, 128.2, 128.1, 127.1, 126.4, 125.4, 123.5, 118.1, 117.0, 61.6; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{27}H_{21}NNaO_2S_2^+$: 478.0911; found: 478.0906. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 82% yield.



3-(Benzylsulfonyl)-5-methyl-1,2,4-triphenyl-1*H*-pyrrole (3s): colorless solid (91.7 mg, 99%); mp 169.0–170.0 °C (DCM); R_f 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.0 Hz, 2H), 7.46 (t, J = 7.4 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H), 7.29–7.25 (m, 5H), 7.12 (t, J = 7.4 Hz, 1H), 7.06–6.97 (m, 6H), 6.72 (d, J = 7.2 Hz, 2H), 3.83 (s, 2H), 1.95 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.6, 137.4, 133.7, 131.8, 131.6, 131.1, 130.1, 129.7, 129.1, 129.1, 128.6, 128.4, 128.4, 128.3, 128.2, 128.1, 127.5, 127.0, 122.0, 116.9, 62.2, 11.7; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{30}H_{25}NNaO_2S^+$: 486.1504; found: 486.1504. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 86% yield.

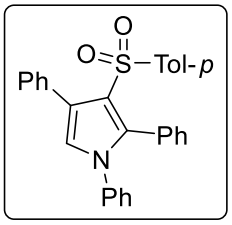


1,2-Diphenyl-3-tosyl-4,5,6,7-tetrahydro-1*H*-indole (3t): colorless solid (83.8 mg, 98%); mp 170.0–172.0 °C (DCM); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.2 Hz, 2H, Ar), 7.25–7.08 (m, 10H, Ar), 7.01–6.92 (m, 2H, Ar), 2.88 (t, J = 5.9 Hz, 2H, CH_2), 2.35 (s, 3H, Me), 2.28 (t, J = 5.9 Hz, 2H, CH_2), 1.85–1.69 (m, 4H, $2CH_2$); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.6, 141.6, 137.1, 136.1, 132.0, 130.4, 130.3, 129.2, 128.9, 128.23, 128.18, 128.0, 127.3, 127.0, 120.0, 117.9, 23.3, 23.0, 22.8, 22.7, 21.6; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{27}H_{25}NNaO_2S^+$: 450.1498; found: 450.1502.

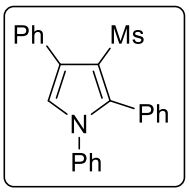


3-(Benzylsulfonyl)-4-(*tert*-butyl)-1,2-diphenyl-1*H*-pyrrole (3u): colorless solid (20.6 mg, 24%); mp 170.0–172.0 °C (DCM); R_f 0.50 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.36–7.15 (m, 9H), 7.09–7.03 (m, 6H), 6.76 (s, 1H), 4.08 (s, 2H), 1.46 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.7, 139.2, 135.1, 132.3, 131.3, 130.5,

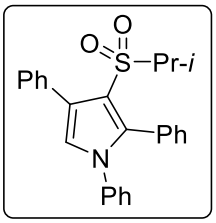
129.2, 129.0, 128.7, 128.5, 128.4, 127.7, 127.4, 126.3, 120.5, 119.0, 63.6, 32.5, 31.4; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{27}H_{27}NNaO_2S^+$: 452.1655; found: 452.1658. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 31% yield.



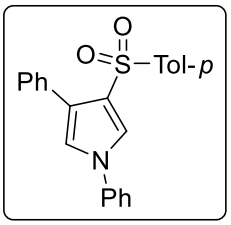
1,2,4-Triphenyl-3-tosyl-1*H*-pyrrole (4a): colorless solid (71.9 mg, 80%); mp 166.0–167.0 °C (DCM); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52–7.49 (m, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.40–7.33 (m, 3H), 7.32–7.28 (m, 1H), 7.27–7.21 (m, 7H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.09–7.05 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 1H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.6, 140.8, 138.8, 137.2, 133.6, 132.1, 130.8, 130.2, 129.1, 128.8, 128.7, 127.8, 127.7, 127.6, 127.4, 127.3, 126.2, 126.2, 122.7, 122.0, 21.5; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{29}H_{24}NO_2S^+$: 450.1522; found: 450.1535. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 84% yield.



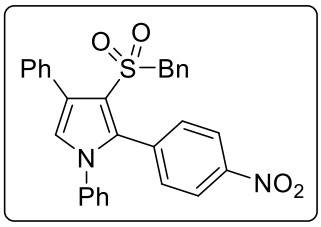
3-(Methylsulfonyl)-1,2,4-triphenyl-1*H*-pyrrole (4b): colorless solid (65.7 mg, 88%); mp 188.5–190.5 °C (DCM); R_f 0.25 (benzene/EtOAc 15:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 6.9 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 2H), 7.39–7.36 (m, 1H), 7.34 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.31 (d, *J* = 4.2 Hz, 1H), 7.30 (s, 1H), 7.27 (dd, *J* = 5.3, 2.0 Hz, 4H), 7.11 (dd, *J* = 7.5, 2.2 Hz, 2H), 6.95 (s, 1H), 2.69 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.7, 133.4, 131.9, 130.3, 130.0, 129.2, 128.9, 128.3, 128.0, 127.8, 127.7, 126.3, 125.5, 122.8, 121.2, 45.0 (one signal merges with the others); **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{23}H_{19}NNaO_2S^+$: 396.1029; found: 396.1025. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 86% yield.



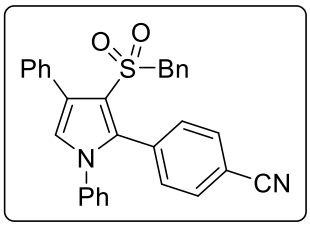
3-(Isopropylsulfonyl)-1,2,4-triphenyl-1*H*-pyrrole (4c): colorless solid (72.3 mg, 90%); mp 206.0–207.0 °C (hexane/EtOAc); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 6.7 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.1 Hz, 1H), 7.34–7.27 (m, 5H), 7.26–7.22 (m, 3H), 7.13–7.08 (m, 2H), 6.95 (s, 1H), 2.65 (hept, *J* = 7.0 Hz, 1H), 1.05 (d, *J* = 6.8 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.8, 138.3, 133.6, 131.9, 130.4, 130.2, 129.2, 128.8, 128.1, 127.9, 127.6, 127.6, 126.3, 126.1, 123.0, 117.5, 54.3, 15.0; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{25}H_{24}NO_2S^+$: 402.1522; found: 402.1526. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 83% yield.



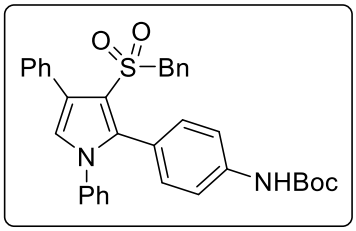
1,3-Diphenyl-4-tosyl-1*H*-pyrrole (4d): colorless solid (58.9 mg, 79%); mp 148.0–149.0 °C (DCM); R_f 0.70 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 2.6 Hz, 1H), 7.52–7.46 (m, 4H), 7.45–7.40 (m, 4H), 7.36 (t, J = 7.2 Hz, 1H), 7.34–7.29 (m, 3H), 7.08 (d, J = 8.1 Hz, 2H), 7.04 (d, J = 2.6 Hz, 1H), 2.32 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.3, 139.7, 139.2, 132.6, 130.1, 129.9, 129.3, 128.1, 127.6, 127.6, 127.4, 126.2, 125.6, 125.1, 121.1, 120.8, 21.6; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{23}H_{19}NNaO_2S^+$: 396.1029; found: 396.1029.



3-(Benzylsulfonyl)-2-(4-nitrophenyl)-1,4-diphenyl-1*H*-pyrrole (4e): colorless solid (54.4 mg, 55%); mp 228.0–230.0 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.7 Hz, 2H), 7.78 (d, J = 7.1 Hz, 2H), 7.51 (t, J = 7.3 Hz, 2H), 7.47–7.42 (m, 1H), 7.36 (t, J = 7.3 Hz, 1H), 7.30–7.26 (m, 5H), 7.03 (s, 1H), 6.99 (d, J = 7.3 Hz, 2H), 6.97–6.92 (m, 2H), 6.73 (d, J = 8.7 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.6, 137.9, 137.0, 136.4, 132.6, 132.5, 131.0, 130.7, 129.5, 129.4, 128.7, 128.6, 128.5 (×2), 128.3, 126.5, 126.4, 124.0, 122.2, 118.2, 62.1; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{29}H_{22}N_2O_4SNa^+$: 517.1192; found: 517.1193. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 87% yield.

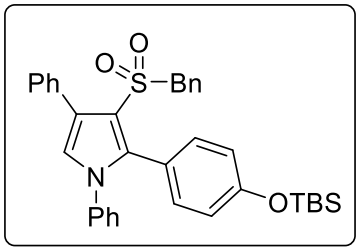


4-(3-(Benzylsulfonyl)-1,4-diphenyl-1*H*-pyrrol-2-yl)benzonitrile (4f): colorless solid (73.9 mg, 78%); mp 241.4–243.8 °C (DCM); R_f 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 6.8 Hz, 2H), 7.57 (t, J = 7.4 Hz, 2H), 7.51 (t, J = 7.3 Hz, 1H), 7.43–7.37 (m, 3H), 7.36–7.32 (m, 5H), 7.10–7.00 (m, 5H), 6.77 (d, J = 8.0 Hz, 2H), 3.96 (s, 2H) ;**^{13}C NMR**(101 MHz, $CDCl_3$) δ 138.0, 137.3, 134.5, 132.5, 132.3, 131.0, 130.8, 130.7, 129.4, 129.4, 128.6 (×2), 128.5, 128.4, 128.2, 126.4, 123.9, 118.6, 118.0, 112.3, 62.1; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{30}H_{22}N_2O_2SNa^+$: 497.1294; found: 497.1295. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 86% yield.

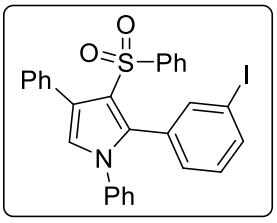


***tert*-Butyl (4-(3-(benzylsulfonyl)-1,4-diphenyl-1*H*-pyrrol-2-yl)phenyl)carbamate (4g):** colorless solid (103.9 mg, 92%); mp 147.0–149.0 °C (dec., DCM); R_f 0.26 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 6.9 Hz, 2H), 7.43 (t, J = 7.1 Hz, 2H), 7.38 (t, J = 7.1 Hz, 1H), 7.33–7.26 (m, 2H), 7.24 (d, J = 2.9

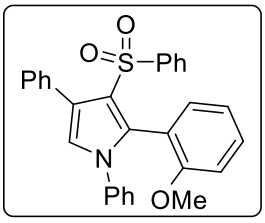
Hz, 4H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.04–6.96 (m, 4H), 6.91 (s, 1H), 6.69 (d, *J* = 8.1 Hz, 2H), 6.48 (s, 1H), 3.87 (s, 2H), 1.49 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 152.5, 138.9, 138.8, 138.7, 133.3, 132.4, 131.0, 130.7, 129.4, 129.2, 128.4, 128.4, 128.2, 128.0, 127.7, 126.3, 126.3, 123.8, 122.8, 117.4, 116.8, 80.8, 62.2, 28.4; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{34}H_{32}N_2NaO_4S^+$: 587.1975; found: 587.1977.



3-(Benzylsulfonyl)-2-(4-((tert-butyldimethylsilyl)oxy)phenyl)-1,4-diphenyl-1*H*-pyrrole (4h): colorless viscous oil (84.7 mg, 73%); R_f 0.50 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.61 (d, *J* = 6.9 Hz, 2H, Ar), 7.46–7.34 (m, 3H, Ar), 7.30–7.19 (m, 8H, Ar), 7.04–6.95 (m, 4H, Ar), 6.91 (s, 1H, Ar), 6.70 (d, *J* = 8.6 Hz, 2H, Ar), 6.59 (d, *J* = 8.6 Hz, 2H, Ar), 3.88 (s, 2H, CH_2), 0.94 (s, 9H, 3Me), 0.15 (s, 6H, 2Me); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 156.1, 138.9, 138.8, 133.3, 133.0, 131.0, 130.6, 129.4, 129.1, 128.3 (×2), 128.1, 127.8, 127.7, 126.4, 126.2, 122.5, 122.5, 119.1, 117.5, 62.1, 25.8, 18.4, –4.3; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{35}H_{37}NNaO_3SSi^+$: 602.2156; found: 602.2153.

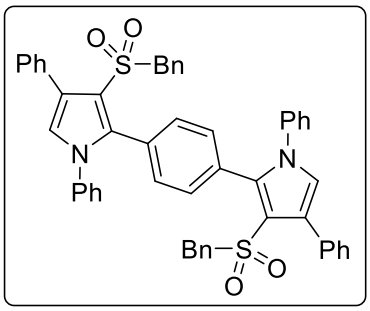


2-(3-Iodophenyl)-1,4-diphenyl-3-(phenylsulfonyl)-1*H*-pyrrole (4i): colorless solid (83.0 mg, 74%); mp 192.0–194.0 °C (hexane/EtOAc); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.63 (d, *J* = 7.9 Hz, 1H), 7.50–7.44 (m, 3H), 7.40–7.34 (m, 4H), 7.34–7.29 (m, 3H), 7.29–7.26 (m, 3H), 7.22 (t, *J* = 7.7 Hz, 2H), 7.10–7.04 (m, 2H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.84 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 143.2, 140.3, 138.3, 137.7, 135.3, 133.2, 132.3, 132.2, 131.4, 130.7, 129.3 (×2), 128.4, 128.2, 127.8, 127.6, 127.3, 126.4, 126.2, 123.0, 122.1, 93.1;**HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{20}INNaO_2S^+$: 584.0152; found: 584.0147. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 65% yield.

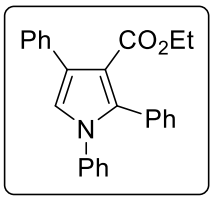


2-(2-Methoxyphenyl)-1,4-diphenyl-3-(phenylsulfonyl)-1*H*-pyrrole (4j): colorless solid (92.1 mg, 98%); mp 181.0–183.0 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.50 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.38 (td, *J* = 7.9, 1.6 Hz, 3H), 7.36–7.27 (m, 5H), 7.25–7.19 (m, 3H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.13–7.08 (m, 2H), 6.95 (t, *J* = 7.4 Hz, 1H), 6.86 (s, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 3.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) *δ* 157.8, 143.6, 139.1, 134.6, 134.0, 133.6, 131.7, 130.9, 130.7, 128.7, 128.0, 127.7 (×2), 127.2 (×2), 126.2, 125.6, 122.3, 121.3, 120.0, 119.3, 110.4, 55.0; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for

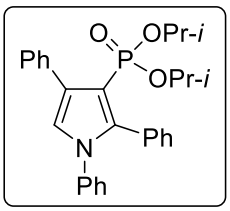
$C_{29}H_{23}NNaO_3S^+$: 488.1291; found: 488.1298. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 83% yield.



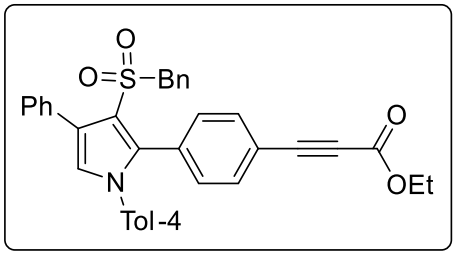
1,4-Bis(3-(benzylsulfonyl)-1,4-diphenyl-1*H*-pyrrol-2-yl)benzene (4k): colorless solid (112 mg, 68%); mp 298 °C (DCM); R_f 0.35 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (dt, J = 5.9, 1.5 Hz, 4H), 7.44 (t, J = 7.2 Hz, 4H), 7.41–7.36 (m, 2H), 7.27–7.23 (m, 8H), 7.12 (t, J = 7.6 Hz, 4H), 6.98–6.94 (m, 4H), 6.94–6.89 (m, 6H), 6.51 (s, 4H), 3.81 (s, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.4, 138.3, 133.1, 130.9, 130.7, 130.6, 129.8, 129.3, 129.2, 128.3 (×2), 128.2, 127.8, 127.8, 126.5, 126.1, 122.8, 117.9, 62.1; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{52}H_{40}N_2NaO_4S_2^+$: 843.2322; found: 843.2327. The pyrrole was also prepared using 5 mol % CuOTf·½PhMe as a catalyst in 84% yield.



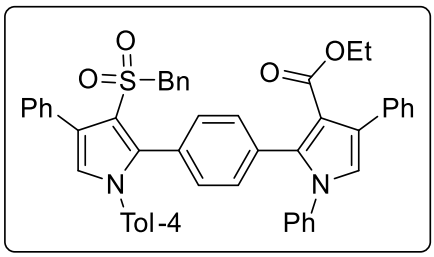
Ethyl 1,2,4-triphenyl-1*H*-pyrrole-3-carboxylate[21] **(6):** colorless solid (71.9 mg, 98%); mp 87.0–89.0 °C (DCM); R_f 0.45 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, J = 1.5 Hz, 1H), 7.52 (s, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.33–7.26 (m, 5H), 7.25 (s, 4H), 7.13–7.09 (m, 2H), 6.96 (s, 1H), 4.05 (q, J = 7.1 Hz, 2H), 0.94 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 139.4, 137.8, 135.1, 131.6, 131.2, 129.1, 129.0, 128.0, 127.9, 127.7, 127.4, 126.9, 126.6, 126.1, 122.1, 114.0, 59.9, 13.8; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{25}H_{21}NNaO_2^+$: 390.1465; found: 390.1468.



Diisopropyl (1,2,4-triphenyl-1*H*-pyrrol-3-yl)phosphonate (8): yellow oil (37.7 mg, 41%); mp 108.0–110.0 °C (DCM); R_f 0.40 (hexane/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.4 Hz, 2H), 7.33–7.27 (m, 3H), 7.26–7.18 (m, 6H), 7.10–7.03 (m, 2H), 6.96 (d, J = 4.8 Hz, 1H), 4.47 (dp, J = 7.6, 6.0 Hz, 2H), 1.09 (d, J = 6.1 Hz, 6H), 0.89 (d, J = 6.1 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.7 (d, J = 23.5 Hz), 139.5, 139.5, 135.7, 132.1, 131.8, 129.8, 129.5 (d, J_P = 11.1 Hz), 129.0, 128.0, 127.8, 127.5, 127.3, 126.7, 126.3, 122.9 (d, J = 14.2 Hz), 108.9 (d, J_P = 216.6 Hz), 70.2 (d, J_P = 6.3 Hz), 24.0 (d, J_P = 4.1 Hz), 23.5 (d, J_P = 5.2 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$) δ 13.74; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{28}H_{30}NO_3PNa^+$: 482.1856; found: 482.1861.



Ethyl 3-(4-(3-(benzylsulfonyl)-4-phenyl-1-(*p*-tolyl)-1*H*-pyrrol-2-yl)phenyl)propiolate (10) was prepared using 5 mol % CuOTf·½PhMe as a catalyst as a yellowish solid (90.7 mg, 81%,); mp 167.0–168.0 °C (DCM); R_f 0.25 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, J = 6.9 Hz, 2H), 7.47 (t, J = 7.2 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.33–7.23 (m, J = 7.3 Hz, 5H), 7.03 (d, J = 7.8 Hz, 2H), 6.98 (d, J = 7.0 Hz, 2H), 6.94 (s, 1H), 6.83 (d, J = 8.0 Hz, 2H), 6.65 (d, J = 7.9 Hz, 2H), 4.28 (q, J = 7.1 Hz, 2H), 3.88 (s, 2H), 2.29 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.1, 138.3, 138.1, 135.7, 132.9, 132.2, 131.8, 131.6, 131.0, 130.7, 129.8, 129.4, 128.5, 128.4, 128.4, 128.0, 126.1, 126.0, 123.6, 119.5, 117.5, 85.9, 81.4, 62.21, 62.18, 21.1, 14.2; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{35}H_{30}NO_4S^+$: 560.1890; found: 560.1882. The pyrrole was also prepared using 5 mol % $AgNTf_2$ as a catalyst in 83% yield.



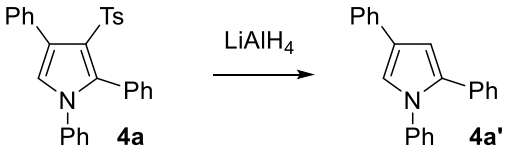
Ethyl 2-(4-(3-(benzylsulfonyl)-4-phenyl-1-(*p*-tolyl)-1*H*-pyrrol-2-yl)phenyl)-1,4-diphenyl-1*H*-pyrrole-3-carboxylate (11) was prepared on 0.1 mmol scale as a colorless solid (79.2 mg, 92%); mp 170.0–172.0 °C (DCM); R_f 0.50 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, J = 7.1 Hz, 2H), 7.51 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.3 Hz, 2H), 7.39–7.36 (m, 3H), 7.31–7.24 (m, 5H), 7.14 (t, J = 7.5 Hz, 2H), 7.05–6.99 (m, 5H), 6.98 (s, 1H), 6.95 (s, 1H), 6.94 (d, J = 7.4 Hz, 2H), 6.88–6.86 (m, 3H), 6.64 (d, J = 7.8 Hz, 2H), 4.00 (q, J = 7.1 Hz, 2H), 3.84 (s, 2H), 2.30 (s, 3H), 0.91 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.3, 139.2, 138.7, 137.9, 136.8, 136.0, 134.8, 133.2, 131.8, 131.0, 130.9, 130.7, 130.0, 129.7, 129.5, 129.2, 129.1, 129.0, 128.31, 128.29, 128.2, 128.1, 127.7, 127.22, 127.18, 126.7, 126.3, 126.1, 126.0, 123.1, 122.3, 117.6, 114.0, 62.1, 60.0, 21.2, 13.9; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{49}H_{41}N_2O_4S^+$: 753.2782; found: 753.2780.

Gram-Scale Synthesis of 4a

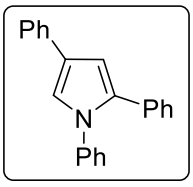
$Ph_3PAuNTf_2$ (111 mg, 0.15 mmol, 5 mol %) was added to the solution of 1-phenyl-2-(phenylamino)ethan-1-one (761 mg, 0.15 mmol, 1.2 equiv) and 1-methyl-4-((phenylethynyl)sulfonyl)benzene 769 mg (3.0 mmol, 1.0 equiv) in dry DCE (10 mL) in a flame-dried 50 mL flask. The resulting mixture was stirred at 80 °C in an oil bath for 20 h. After completion, the solvent was removed in vacuum, and the residue was purified by silica gel chromatography, eluting with hexane/EtOAc, to afford **4a** (1.13 g, 84%).

3.4. Post-Modifications of 3-Sulfonylpyrrole 4a

Desulfonation of 4a

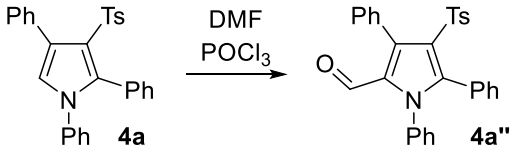


Lithium aluminium hydride (22.5 mg, 0.5 mmol, 5.0 equiv) was added portionwise to the solution of 3-sulfonylpyrrole **4a** (38.8 mg, 0.1 mmol, 1 equiv) in dry THF (3.0 mL) in a flame-dried 25 mL flask at room temperature. The resulting dark mixture was heated to 60 °C in an oil bath and stirred for 5 hours. After cooling to room temperature, the reaction mixture was quenched by the dropwise addition of water (1 mL). Then, the mixture was dilited with water (10 mL) and extracted with DCM (2×10 ml). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration, the solvent was removed in vacuo and the residue was purified by silica gel chromatography, eluting with hexane/EtOAc (8:1), to afford desulfonylated pyrrole **4a'**.



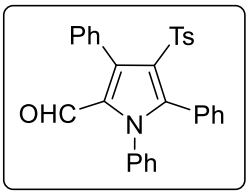
1,2,4-Triphenyl-1*H*-pyrrole (4a'): colorless solid (29.2 mg, 99%); mp 135.0–137.0 °C (DCM); R_f 0.50 (hexane/EtOAc 12:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 8.2, 1.1 Hz, 2H, Ar), 7.40–7.32 (m, 4H, Ar), 7.30 (d, J = 7.1 Hz, 1H, Ar), 7.24 (d, J = 2.0 Hz, 1H, Ar), 7.24–7.16 (m, 8H, Ar), 6.75 (d, J = 2.0 Hz, 1H, Ar); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.5, 135.3, 135.0, 132.9, 129.2, 128.8, 128.5, 128.3, 126.9, 126.7, 126.0, 125.8, 125.7, 125.3, 121.0, 108.9; **HRMS** (ESI): *m/z* $[M + H]^+$ calcd. for $C_{22}H_{18}N^+$: 296.1434; found: 296.1439.

Formylation of 4a



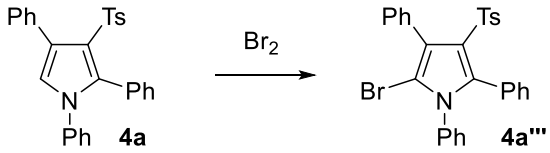
Phosphoryl chloride (23 mg, 0.15 mmol, 1.5 equiv) was added to a solution 3-sulfonylpyrrole **4a** (38.8 mg, 0.1 mmol, 1 equiv) in DMF (3.0 mL). The resulting mixture was stirred at 80°C for 24 h. Then, 10% aqueous solution of NaOH (10 mL) was added, and the reaction mixture was stirred at 80°C for 15 minutes. After cooling to room temperature, the reaction was extracted with DCM (2×20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After

filtration, the solvent was removed in vacuum, and the residue was separated by column chromatography (silica gel), eluting with hexane/EtOAc, to afford pyrrole carbaldehyde **4a''**.

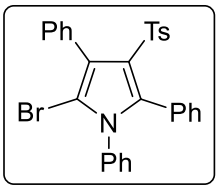


1,3,5-Triphenyl-4-tosyl-1*H*-pyrrole-2-carbaldehyde (4a''): colorless solid (37.2 mg, 78%); mp 202.0–203.0 °C (DCM); R_f 0.45 (hexane/EtOAc 2:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.26 (s, 1H, CHO), 7.48–7.39 (m, 5H, Ar), 7.32–7.27 (m, 1H, Ar), 7.26–7.21 (m, 5H, Ar), 7.19 (dd, J = 8.3, 1.6 Hz, 2H, Ar), 7.13 (d, J = 8.3 Hz, 2H, Ar), 7.10–7.06 (m, 2H, Ar), 7.01 (d, J = 8.0 Hz, 2H, Ar), 2.33 (s, 3H, Me); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 179.9, 143.4, 143.4, 139.8, 137.8, 136.8, 131.6, 131.5, 130.1, 129.6, 129.3, 129.1, 128.8, 128.7 (×2), 128.5, 128.2, 127.7, 127.6, 127.5, 124.0, 21.6; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{30}H_{23}NNaO_3S^+$: 500.1291; found: 500.1291.

Bromination of 4a



A solution of bromine (17.6 mg, 0.1 mmol, 1.1 equiv) in DCM (1 mL) was added dropwise to a solution 3-sulfonylpyrrole **4a** (38.8 mg, 0.1 mmol, 1 equiv) in DCM (1 mL). The light yellow solution was stirred at room temperature for 1 h. Subsequently, saturated aqueous $NaHCO_3$ (10 mL) and $Na_2S_2O_3$ (10 mL) were added and the mixture was extracted with DCM (3×10 mL). The combined organic extracts were dried over anhydrous Na_2SO_4. After filtration, the solvent was removed in vacuum to afford pure brominated pyrrole **4a'''**.



2-Bromo-1,3,5-triphenyl-4-tosyl-1*H*-pyrrole (4a'''): colorless solid (104.5 mg, 99%); mp 202.0–203.0 °C (DCM); R_f 0.30 (hexane/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.33 (m, 5H), 7.30–7.26 (m, 3H), 7.26–7.20 (m, 5H), 7.14 (d, J = 8.3 Hz, 2H), 7.13–7.08 (m, 2H), 6.99 (d, J = 8.2 Hz, 2H), 2.32 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 140.2, 138.7, 137.0, 132.6, 131.8, 131.5, 130.1, 129.1, 128.9, 128.9, 128.8, 128.8, 127.9, 127.7, 127.5, 127.4, 124.6, 122.7, 106.8, 21.6; **HRMS** (ESI): *m/z* $[M + Na]^+$ calcd. for $C_{29}H_{22}BrNNaO_2S^+$: 550.0447; found: 550.0446.

References

1 X. Li, M. Chen, X. Xie, N. Sun, S. Li and Y. Liu, Synthesis of Multiple-Substituted Pyrroles via Gold(I)-Catalyzed Hydroamination/Cyclization Cascade, *Org. Lett.*, 2015, **17**, 2984–2987.

2 E. I. Chikunova, V. Y. Kukushkin and A. Y. Dubovtsev, Atom-economic synthesis of β-ketosulfones based on gold-catalyzed highly regioselective hydration of alkynylsulfones, *Green Chem.*, 2022, **24**, 3314–3320.

3 E. I. Chikunova, D. V Dar'in, V. Y. Kukushkin and A. Y. Dubovtsev, Gold-Catalyzed Oxygen Transfer to Alkynylsulfones: A Diazo-Free Route to 4-Sulfonyl-1,3-Oxazoles, *Adv. Synth. Catal.*, 2022, **364**, 3697–3707.

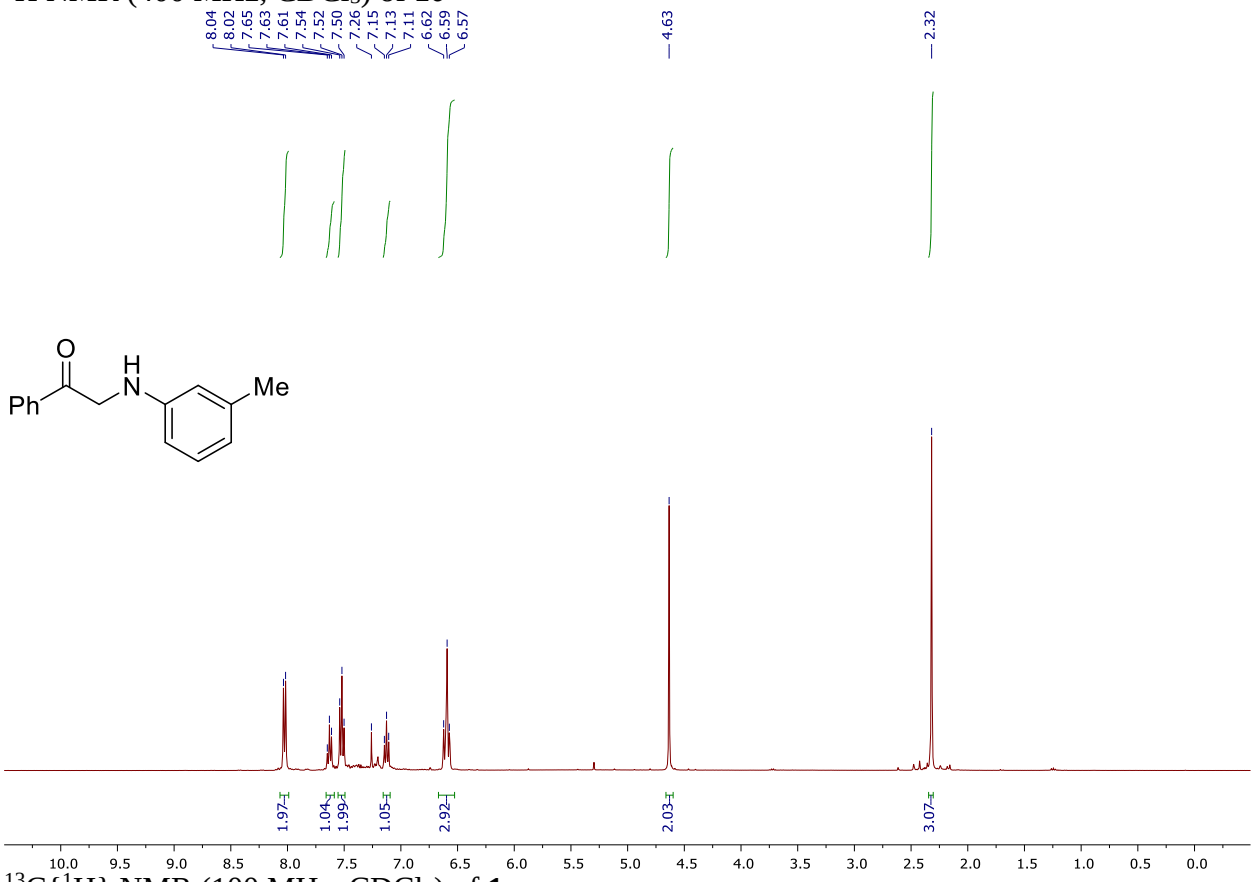
4 E. I. Chikunova, V. Y. Kukushkin and A. Y. Dubovtsev, Non-Friedländer Route to Diversely 3-Substituted Quinolines through Au(III)-Catalyzed Annulation Involving Electron-Deficient Alkynes, *Org. Lett.*, 2023, **25**, 8756–8760.

5 Y. Gao, G. Wang, L. Chen, P. Xu, Y. Zhao, Y. Zhou and L.-B. Han, Copper-Catalyzed Aerobic Oxidative Coupling of Terminal Alkynes with H-Phosphonates Leading to Alkynylphosphonates, *J. Am. Chem. Soc.*, 2009, **131**, 7956–7957.

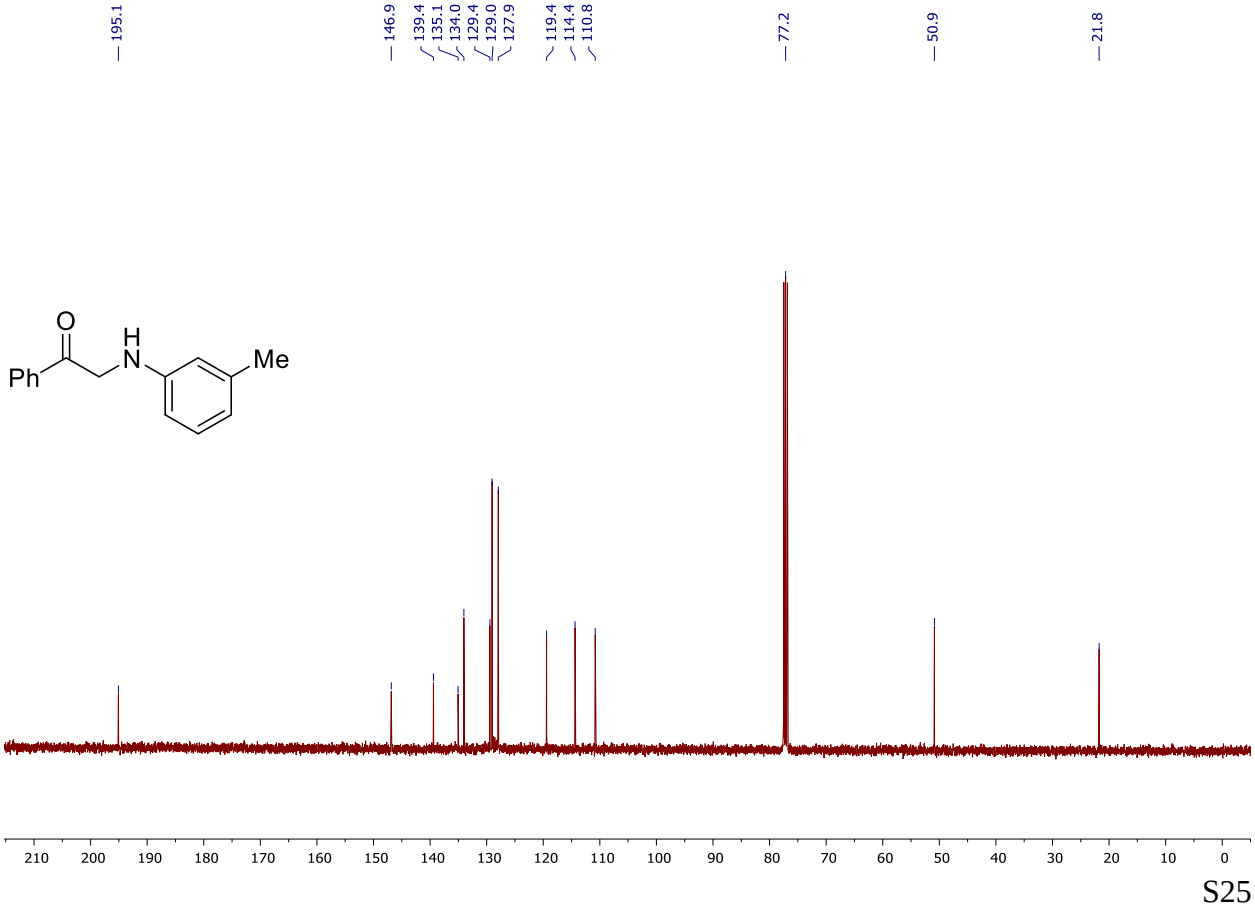
4. NMR Spectra

3.5.NMR Spectra of Starting α-Aminoketones

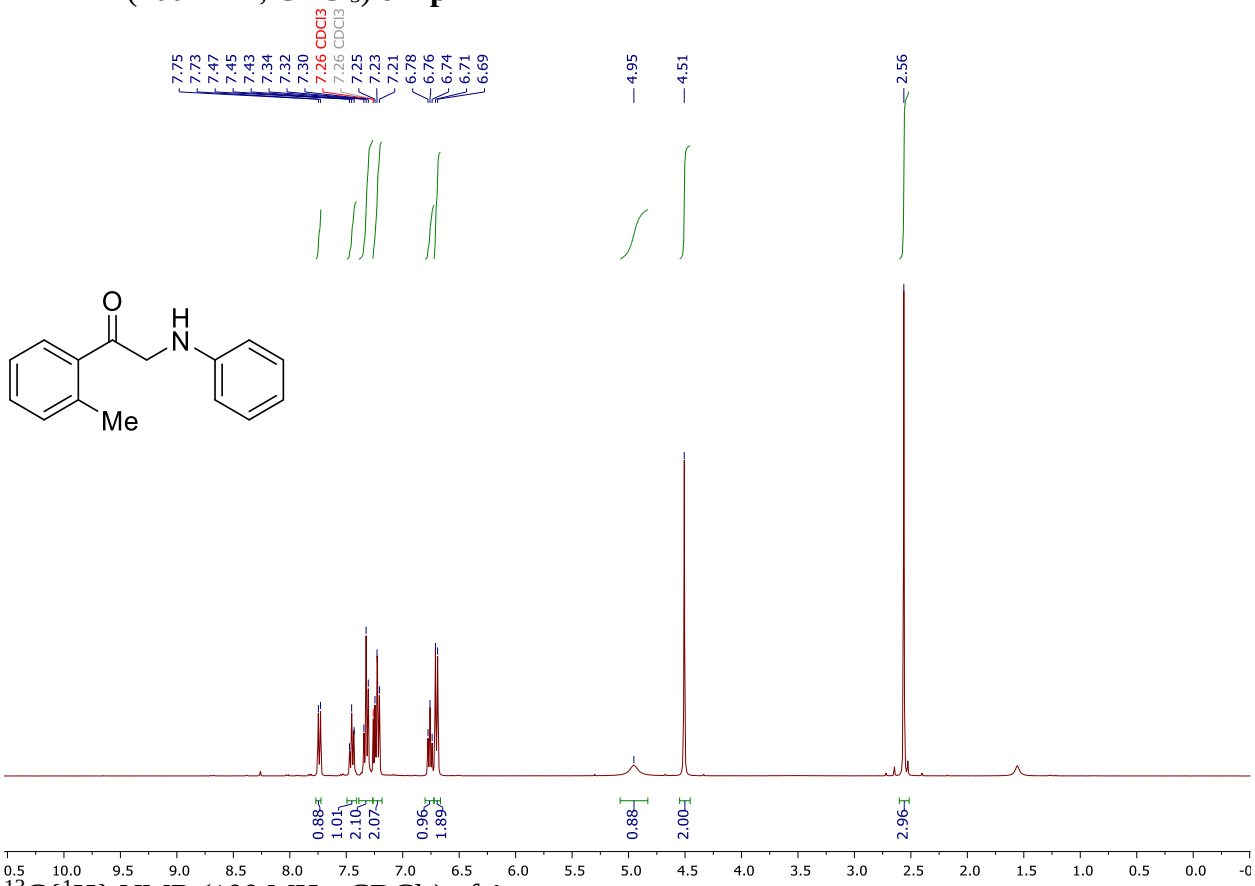
^{1}H NMR (400 MHz, $CDCl_3$) of **1c**



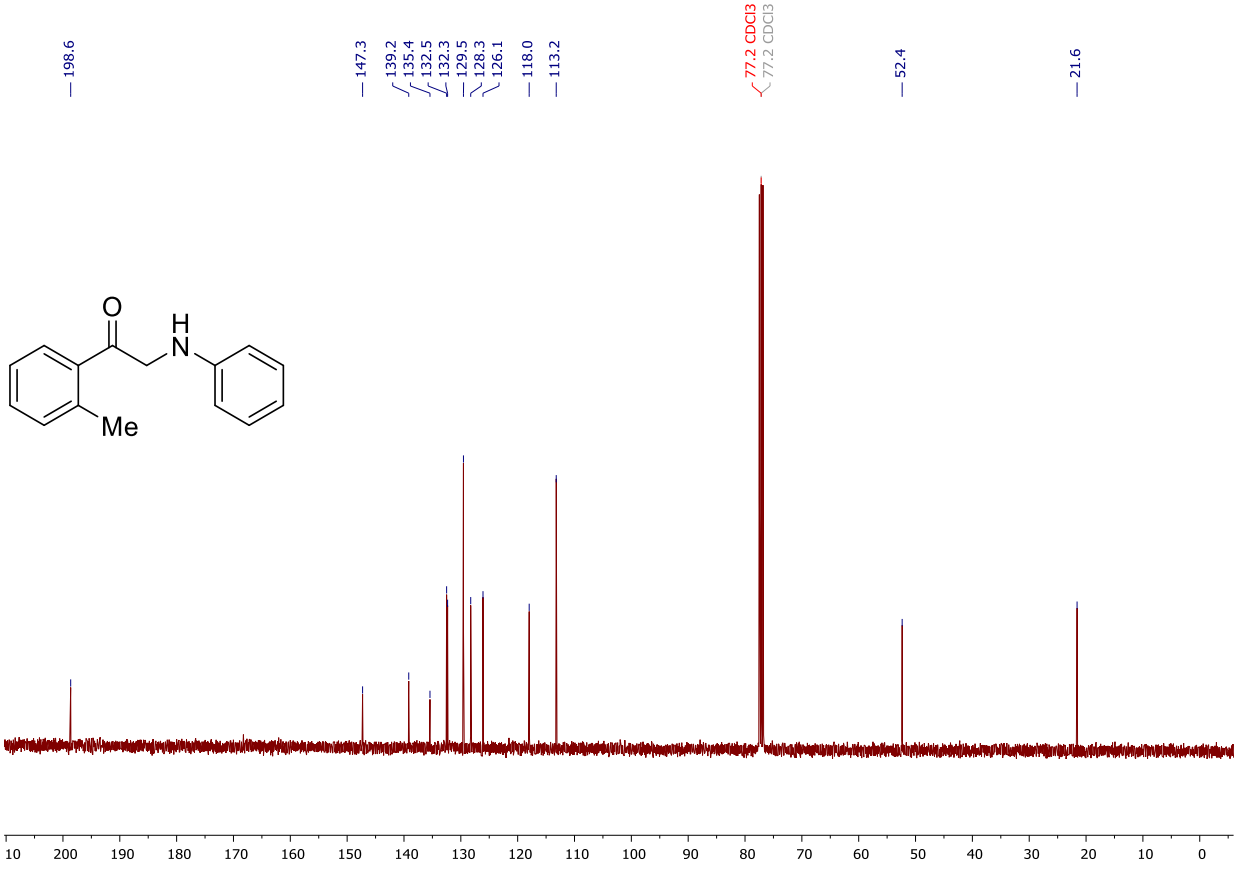
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **1c**



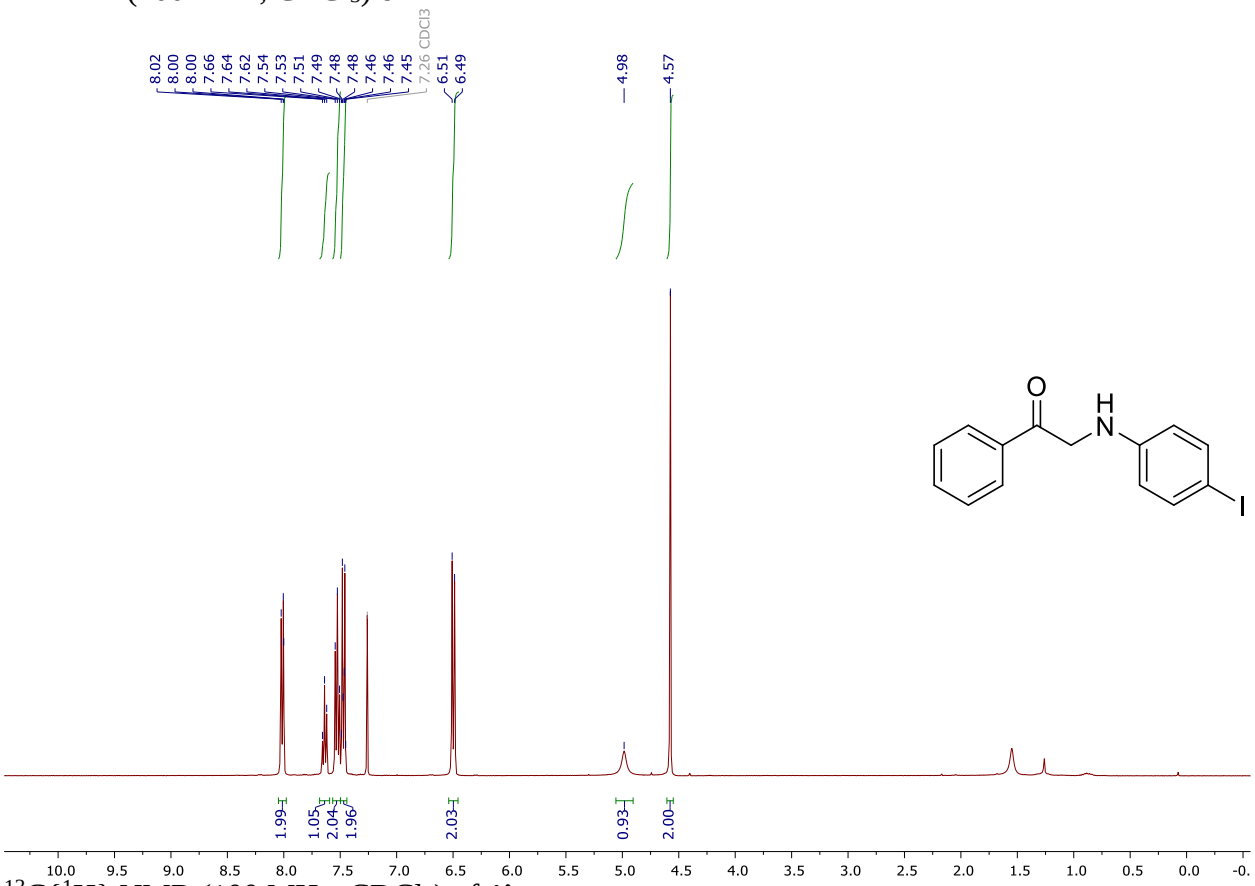
^{1}H NMR (400 MHz, $CDCl_3$) of **1p**



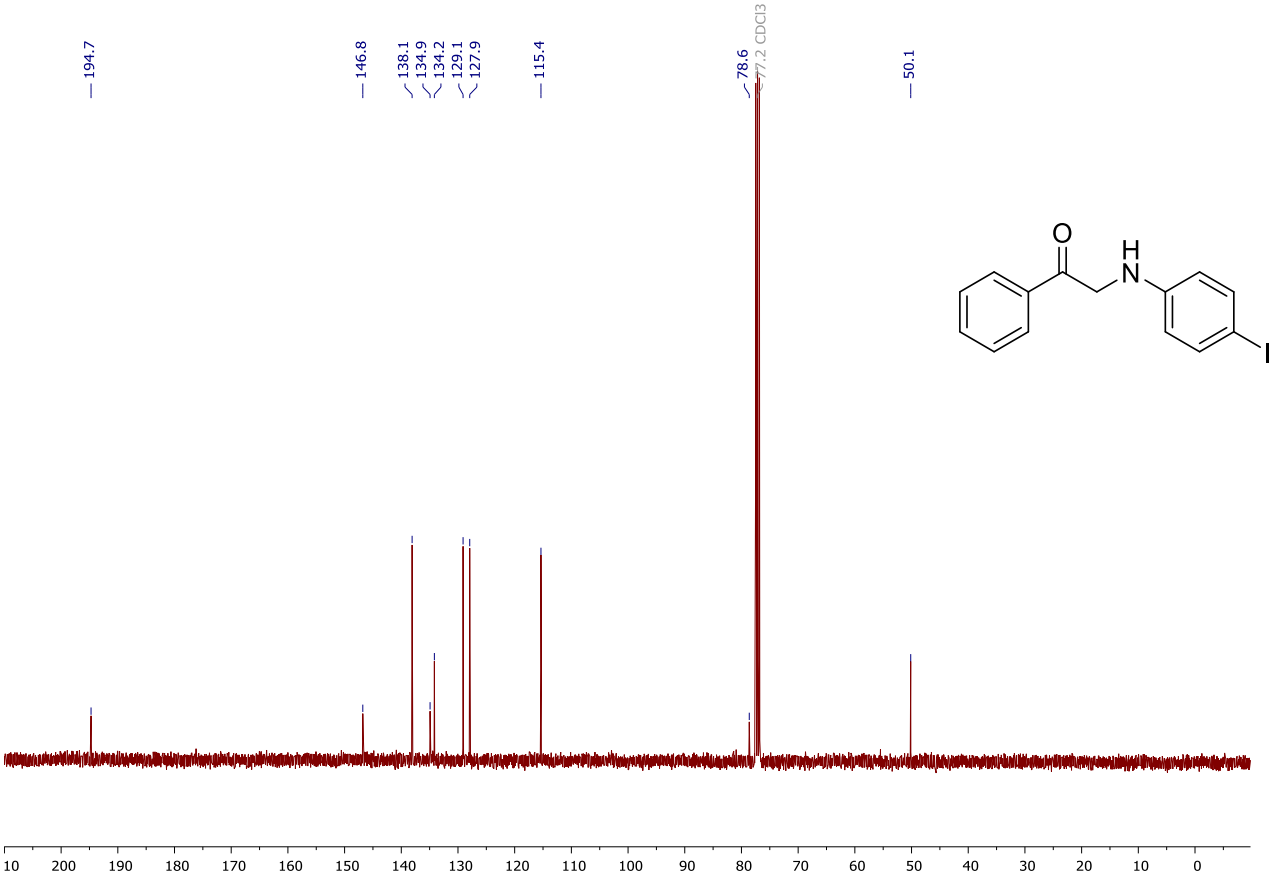
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **1p**



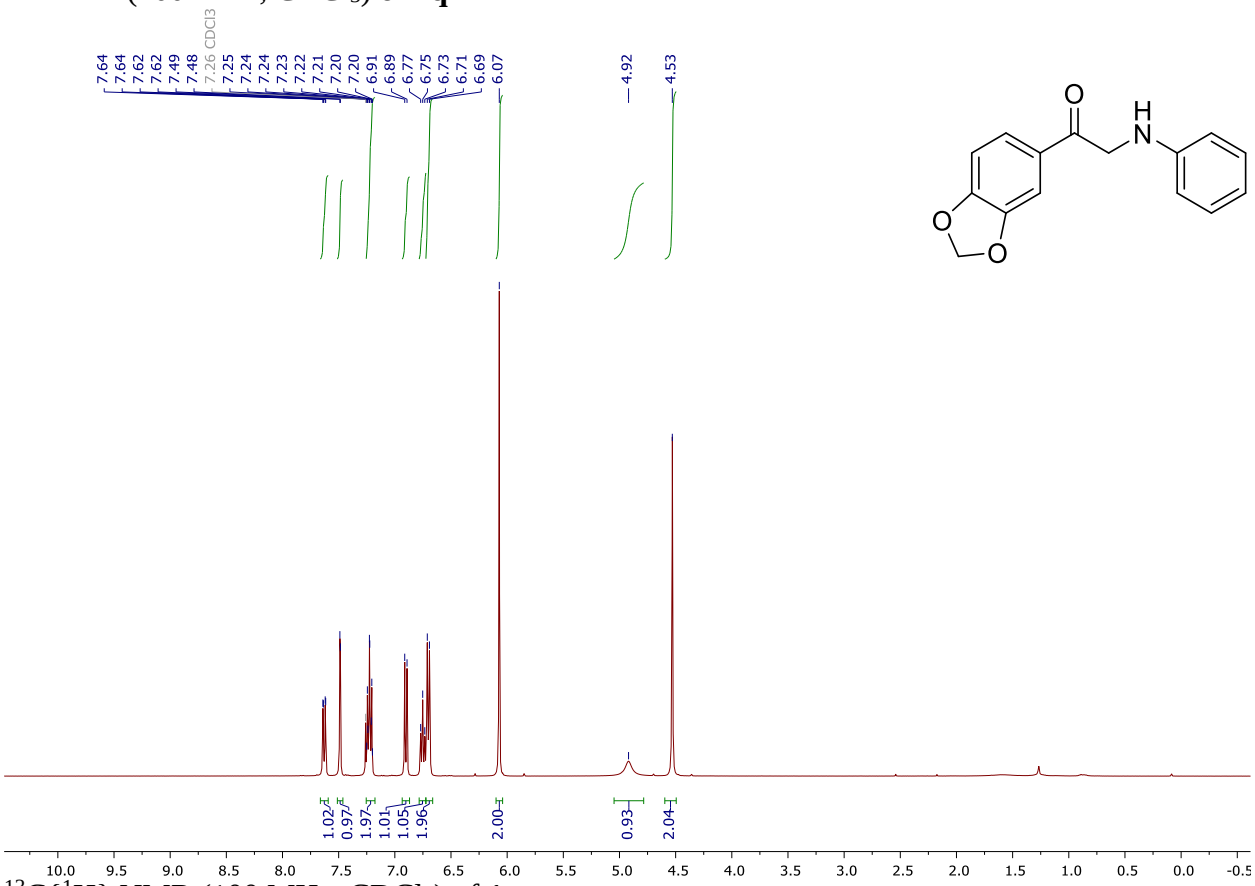
^{1}H NMR (400 MHz, $CDCl_3$) of **1i**



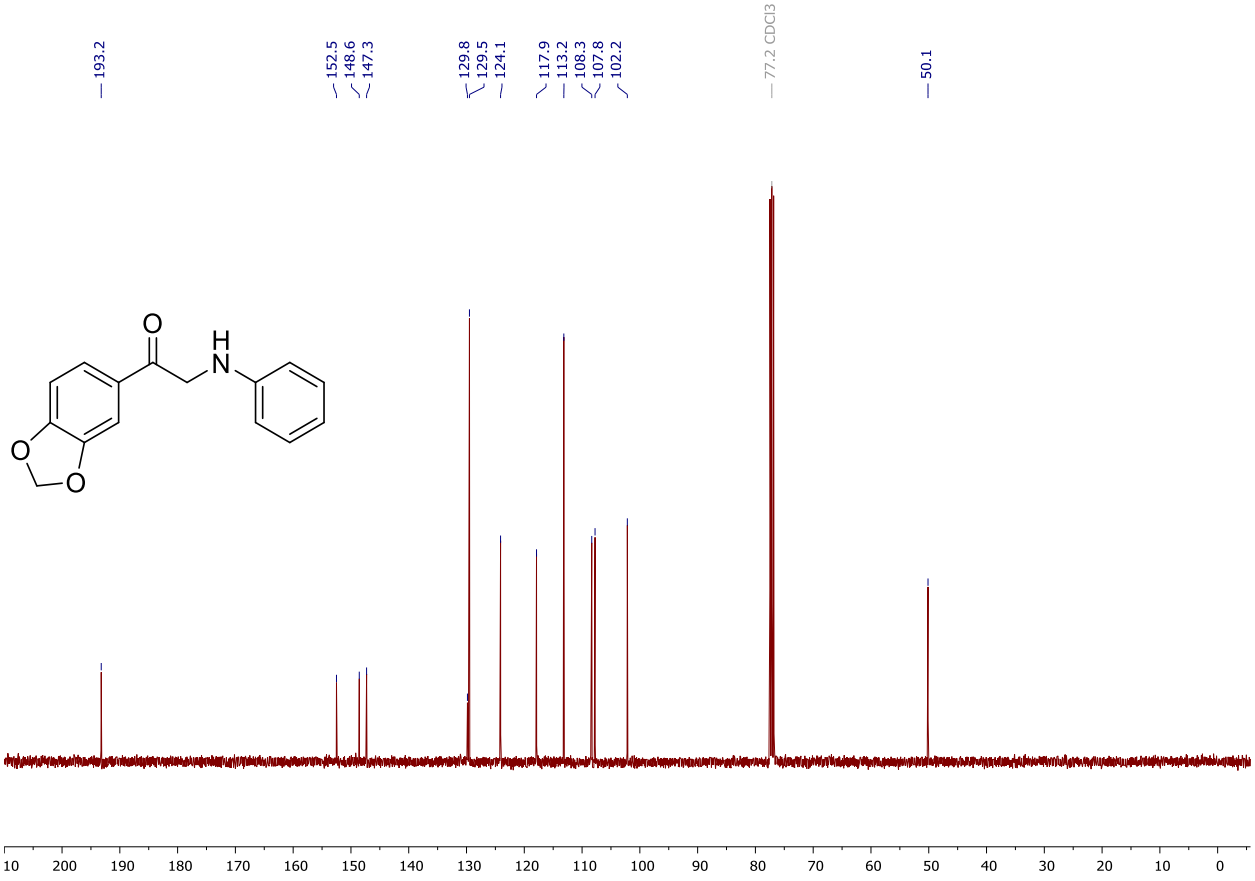
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **1i**



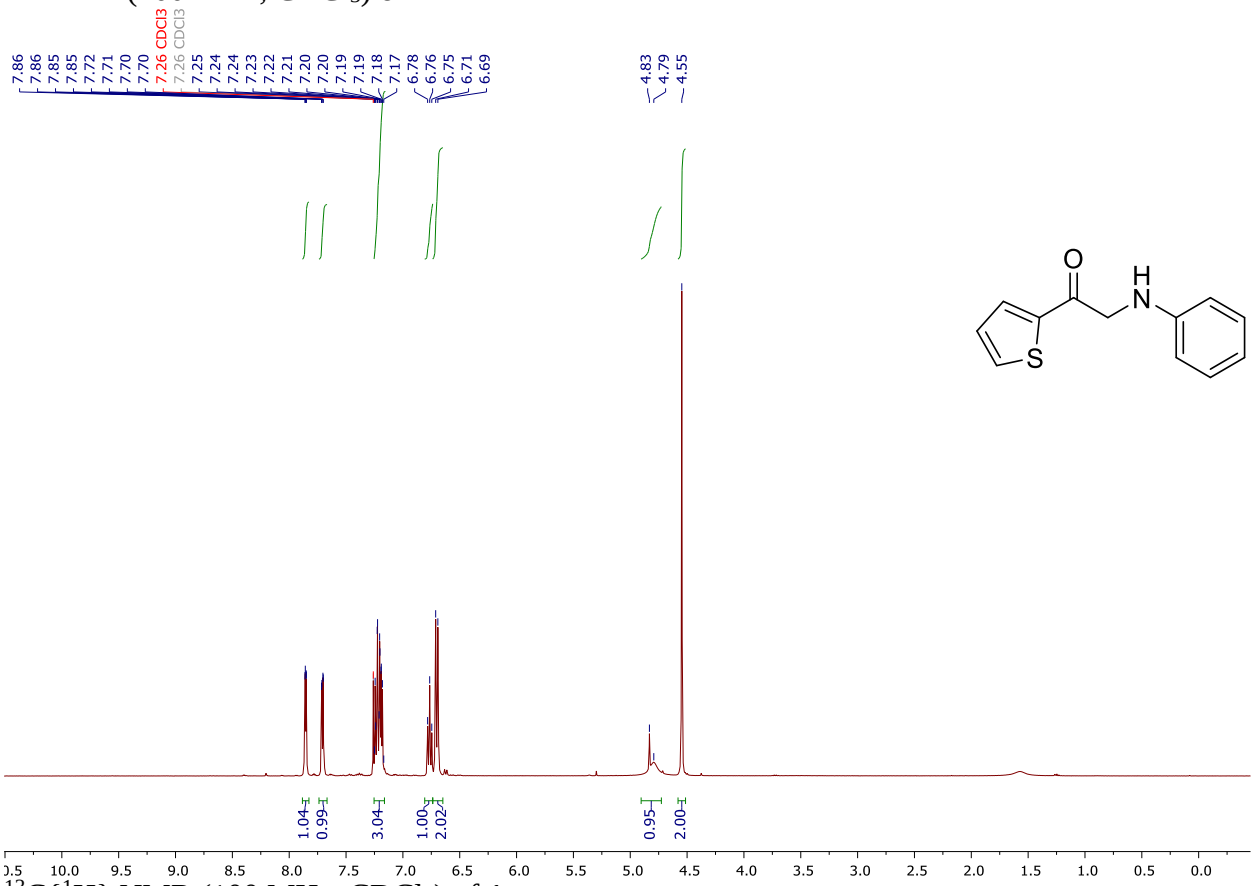
^{1}H NMR (400 MHz, $CDCl_3$) of **1q**



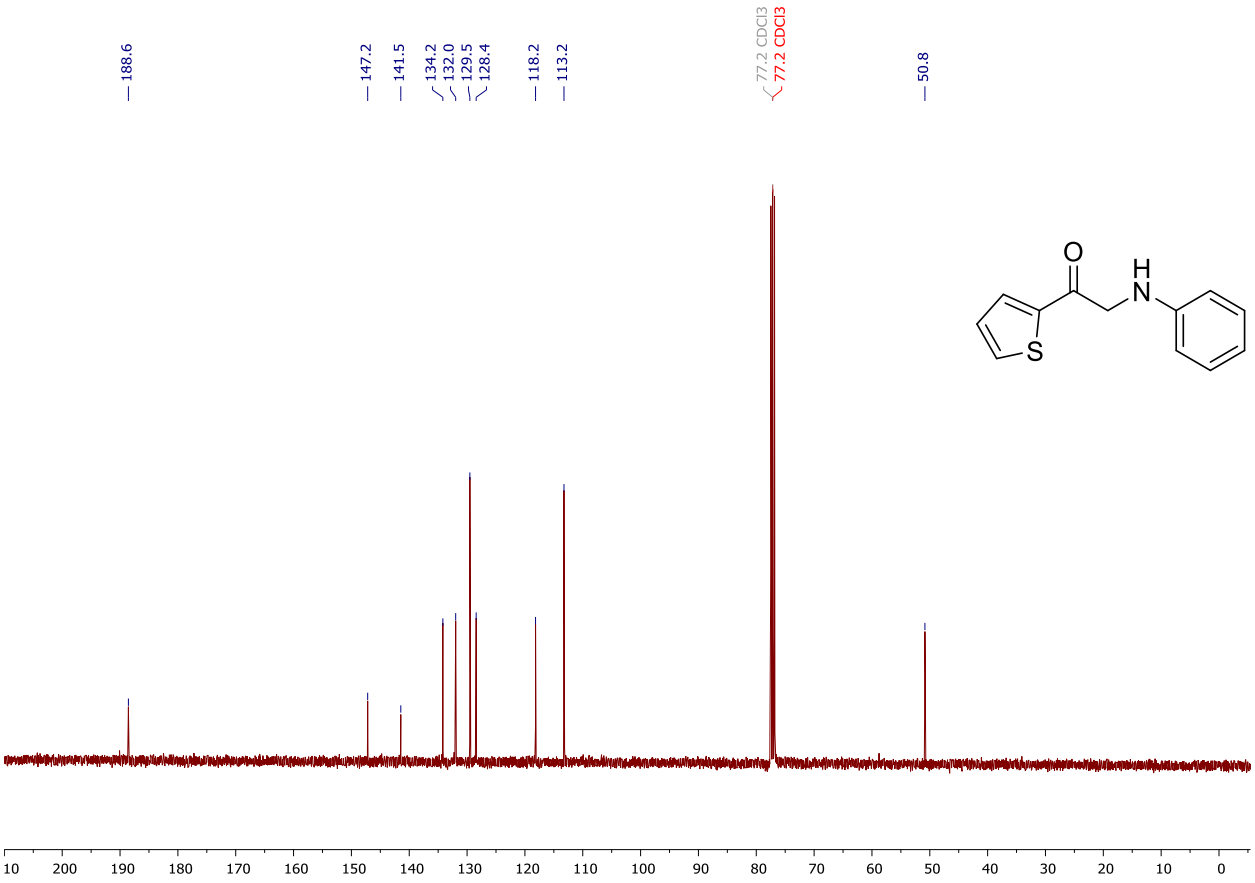
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **1q**



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

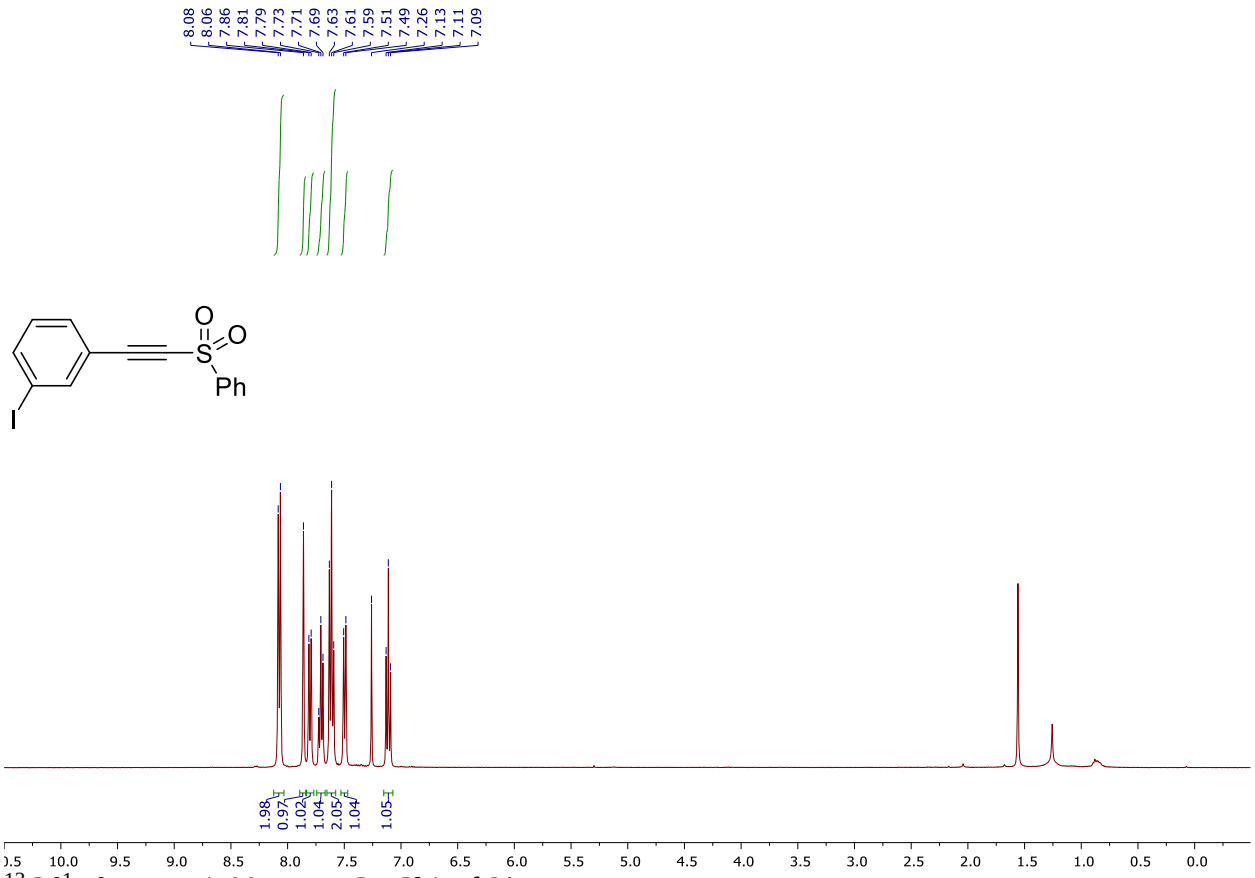


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **1r**

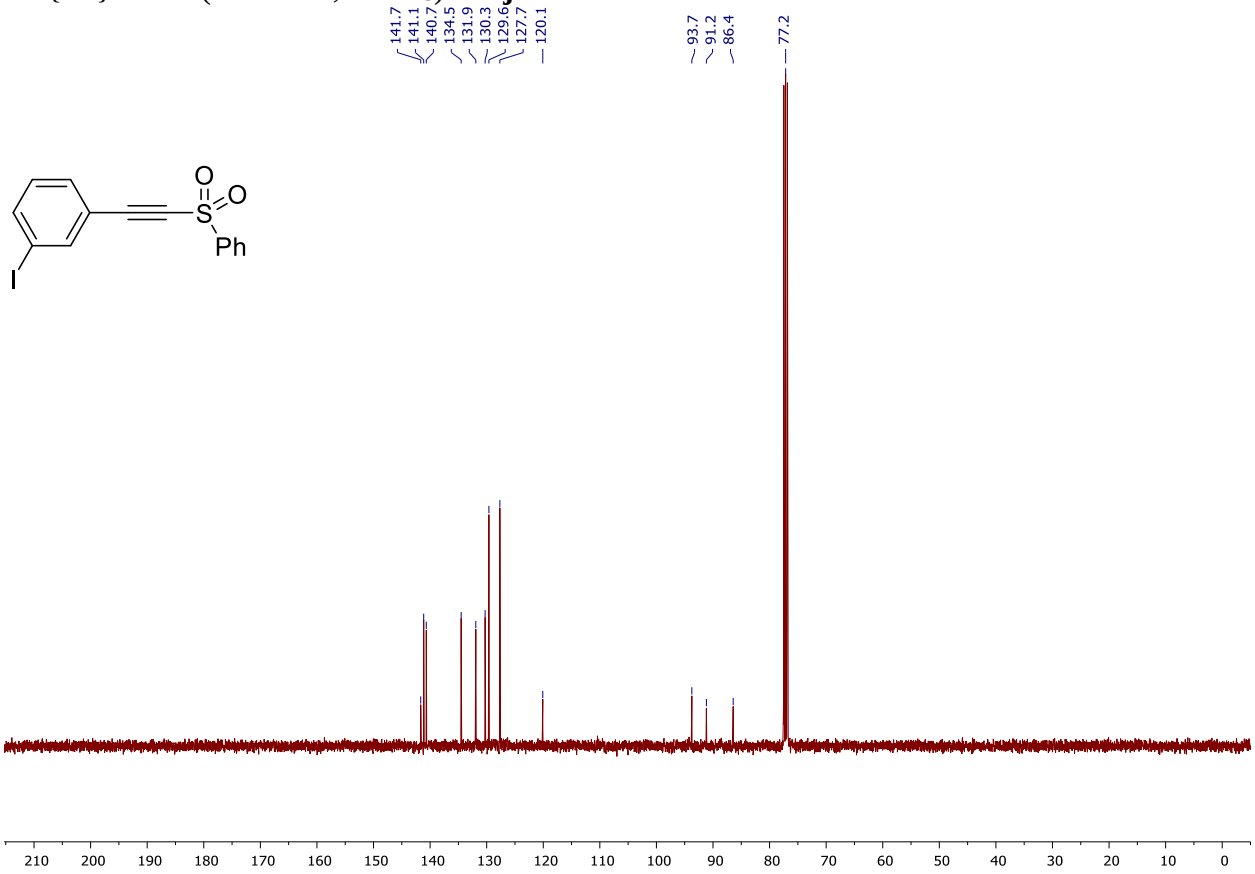


3.6.NMR Spectra of Starting Alkynylsulfones

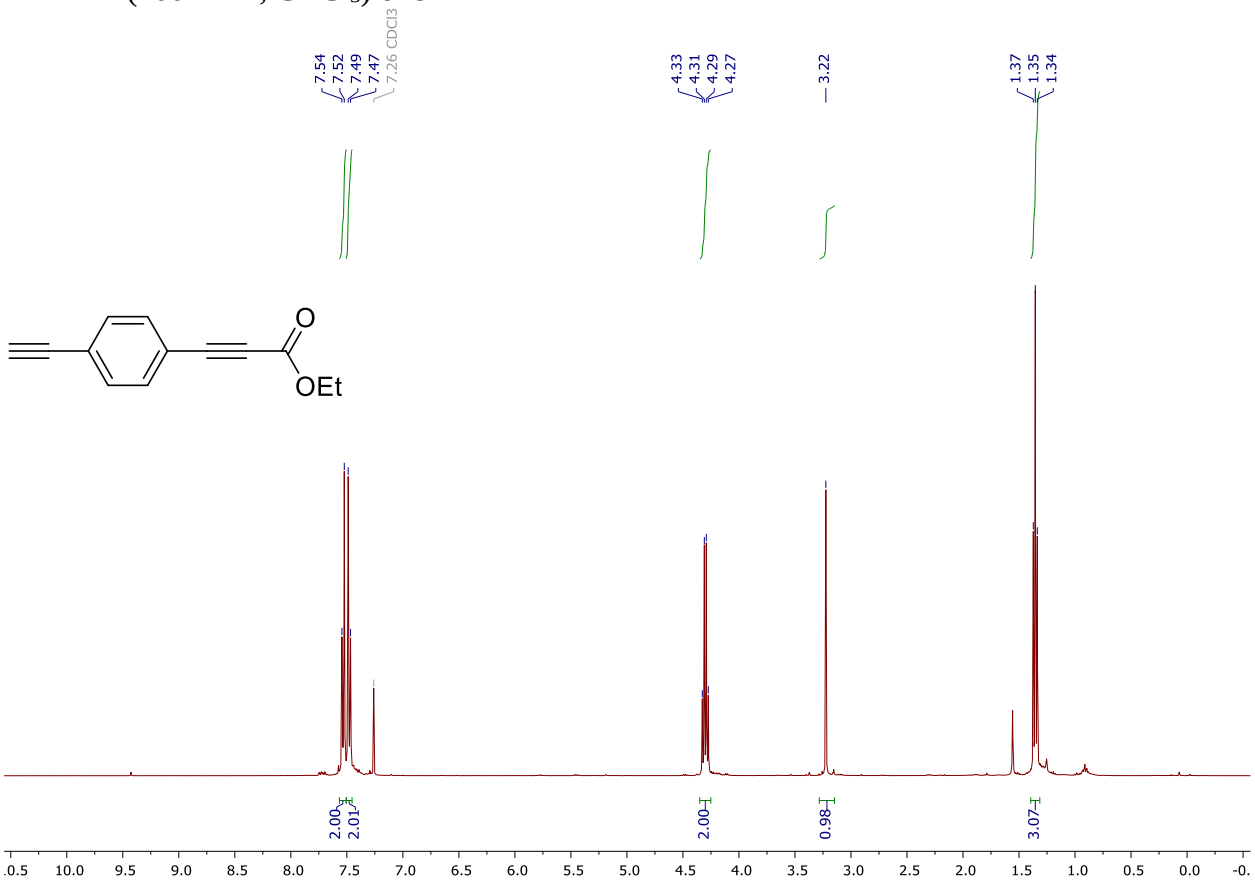
^{1}H NMR (400 MHz, $CDCl_3$) of **2j**



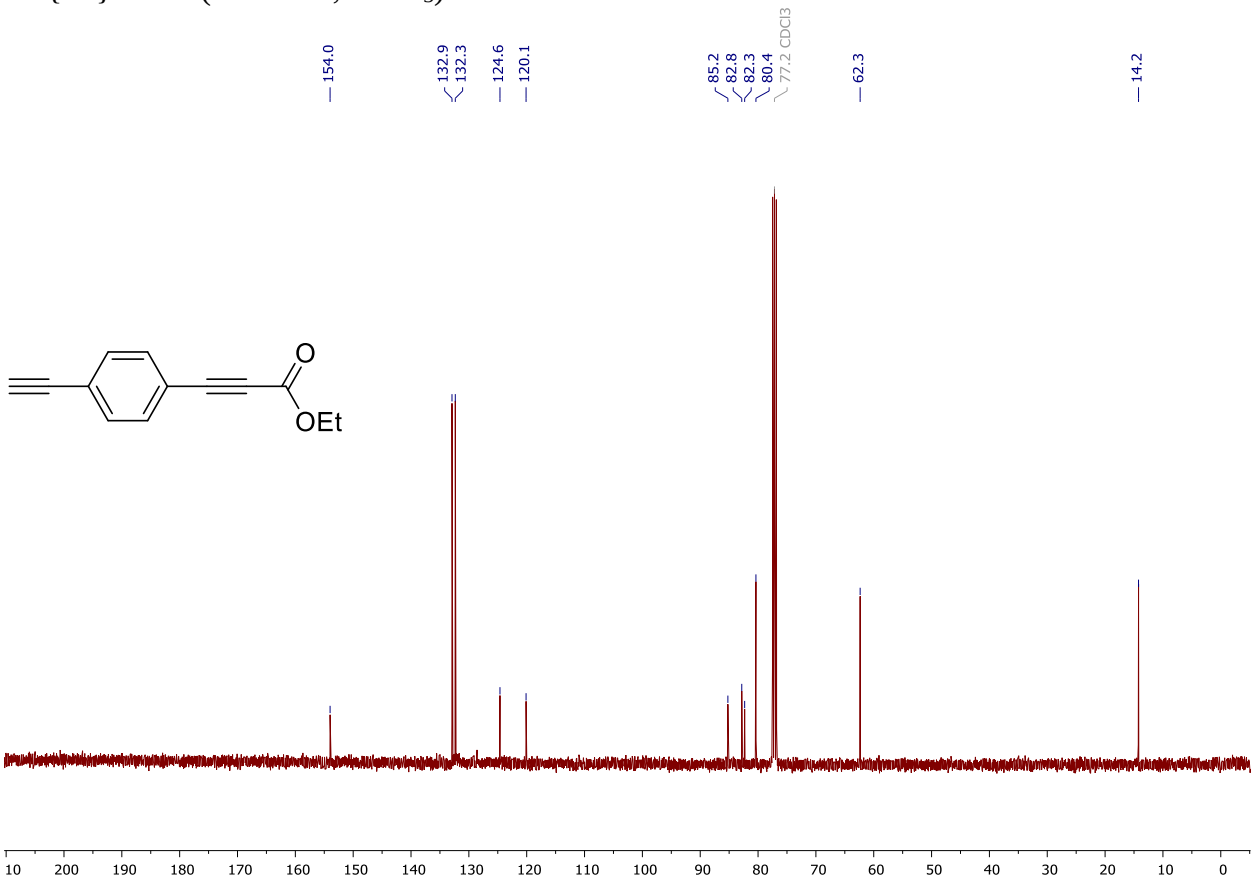
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **2j**



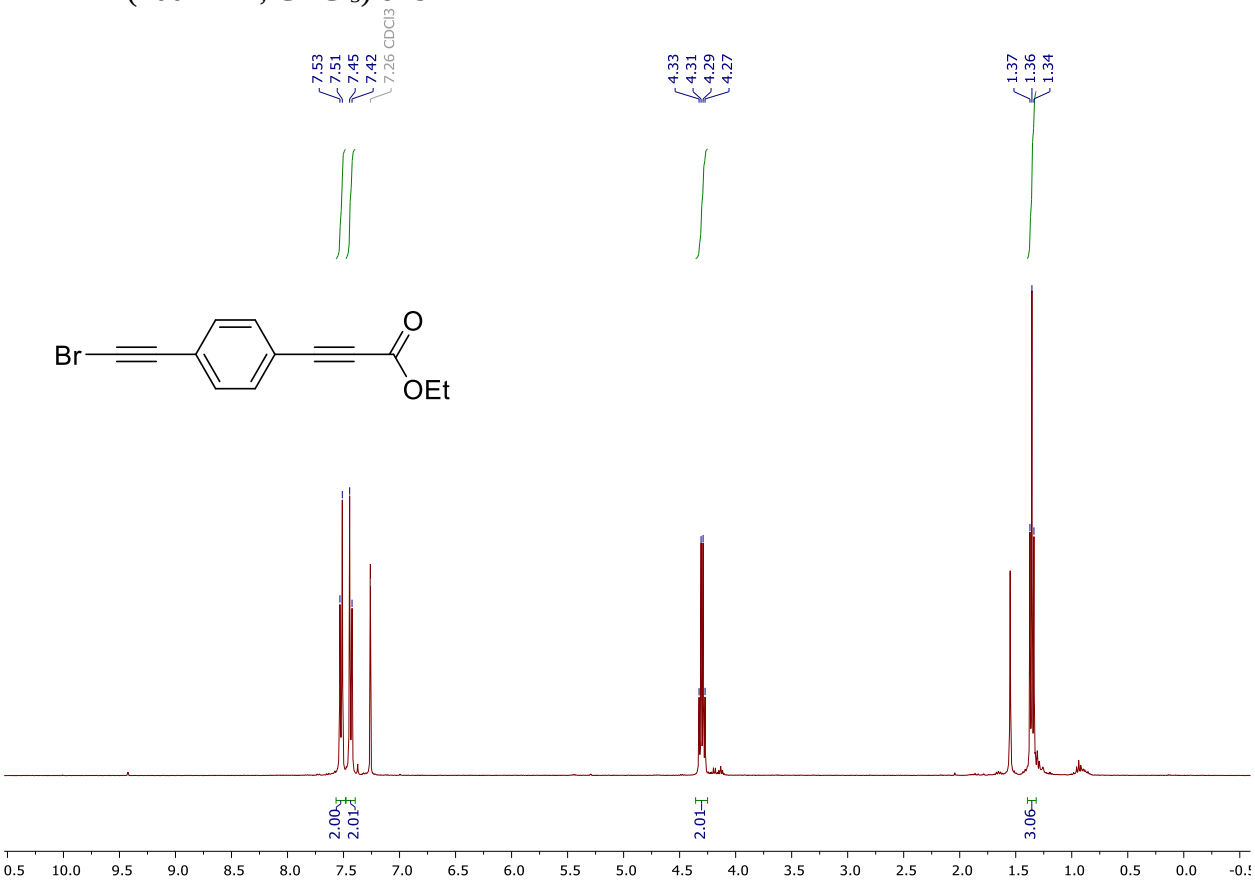
^{1}H NMR (400 MHz, $CDCl_3$) of **9'''**



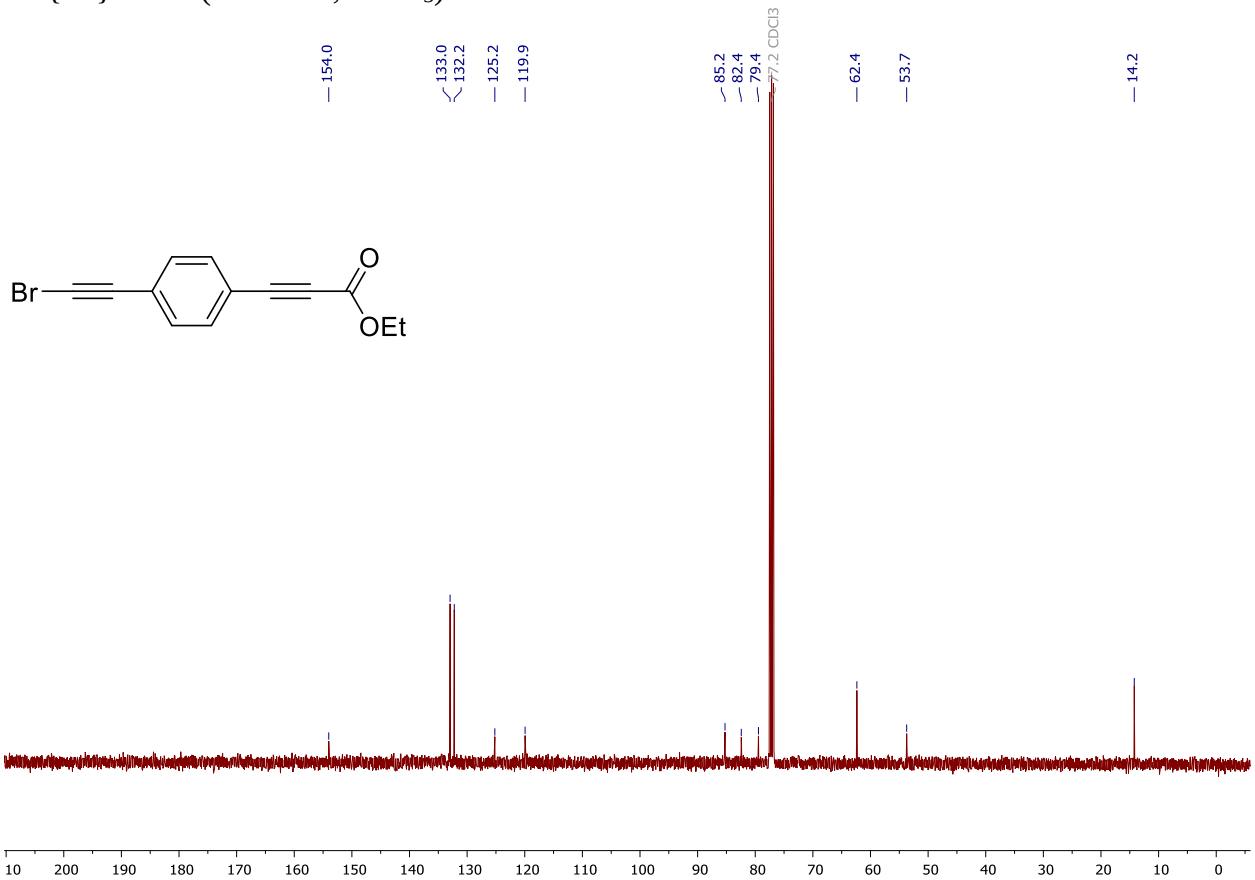
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **9'''**



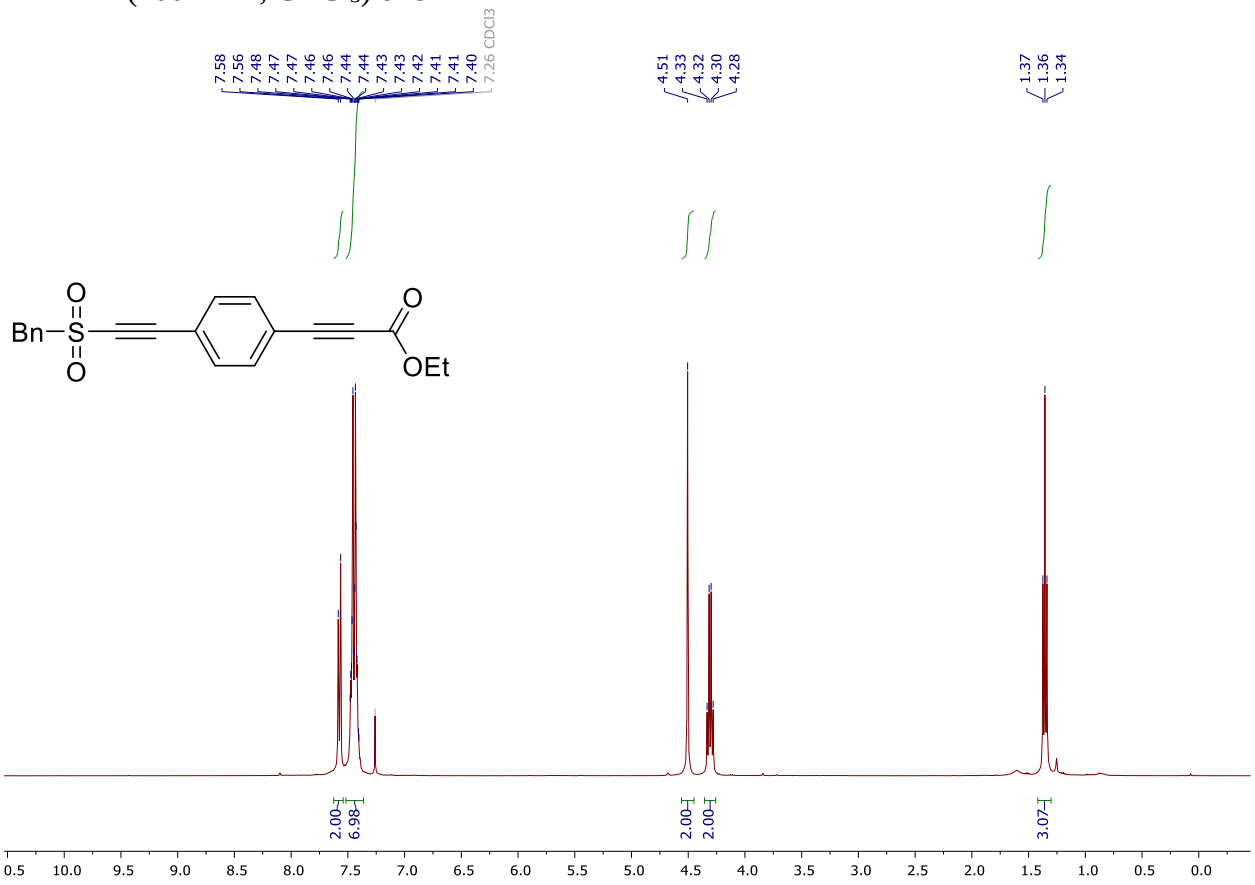
^{1}H NMR (400 MHz, $CDCl_3$) of **9''**



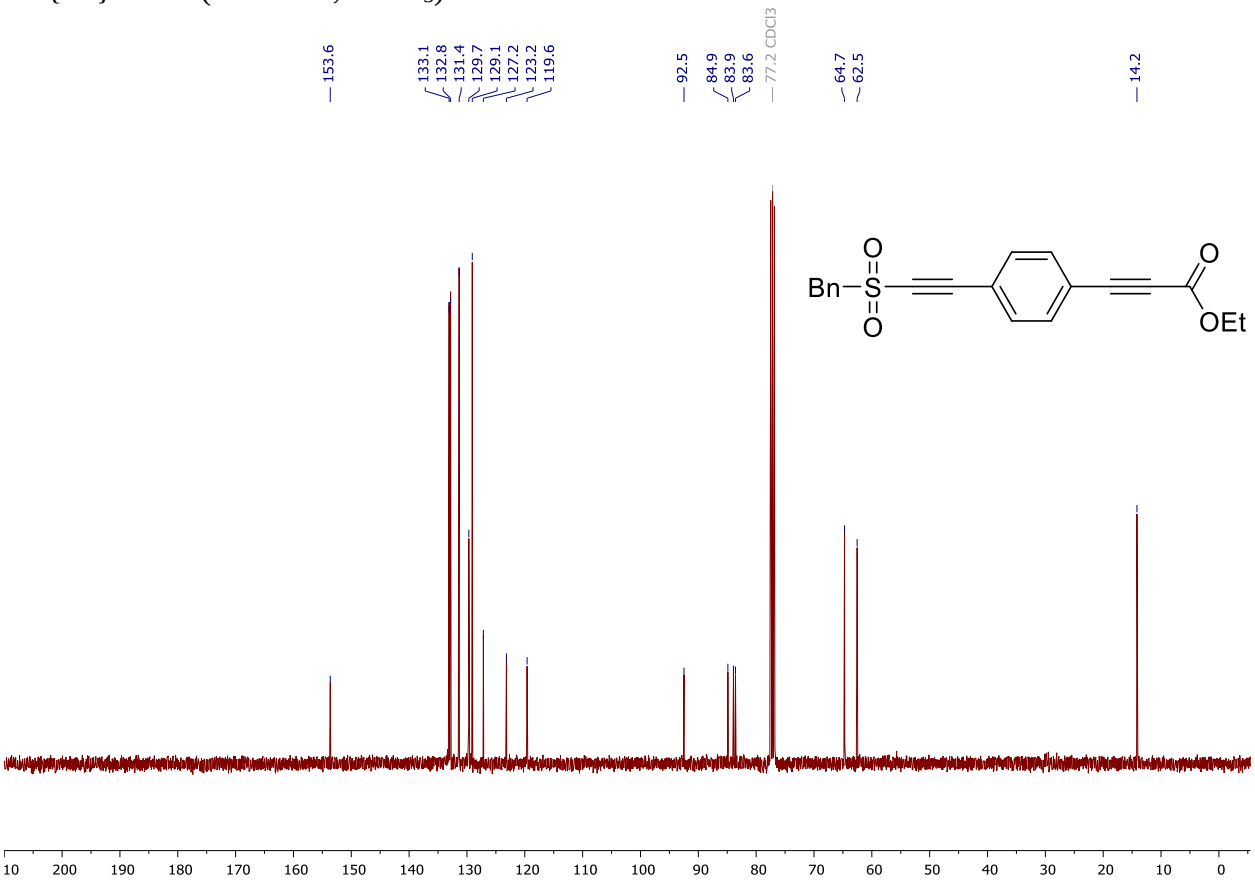
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **9''**



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

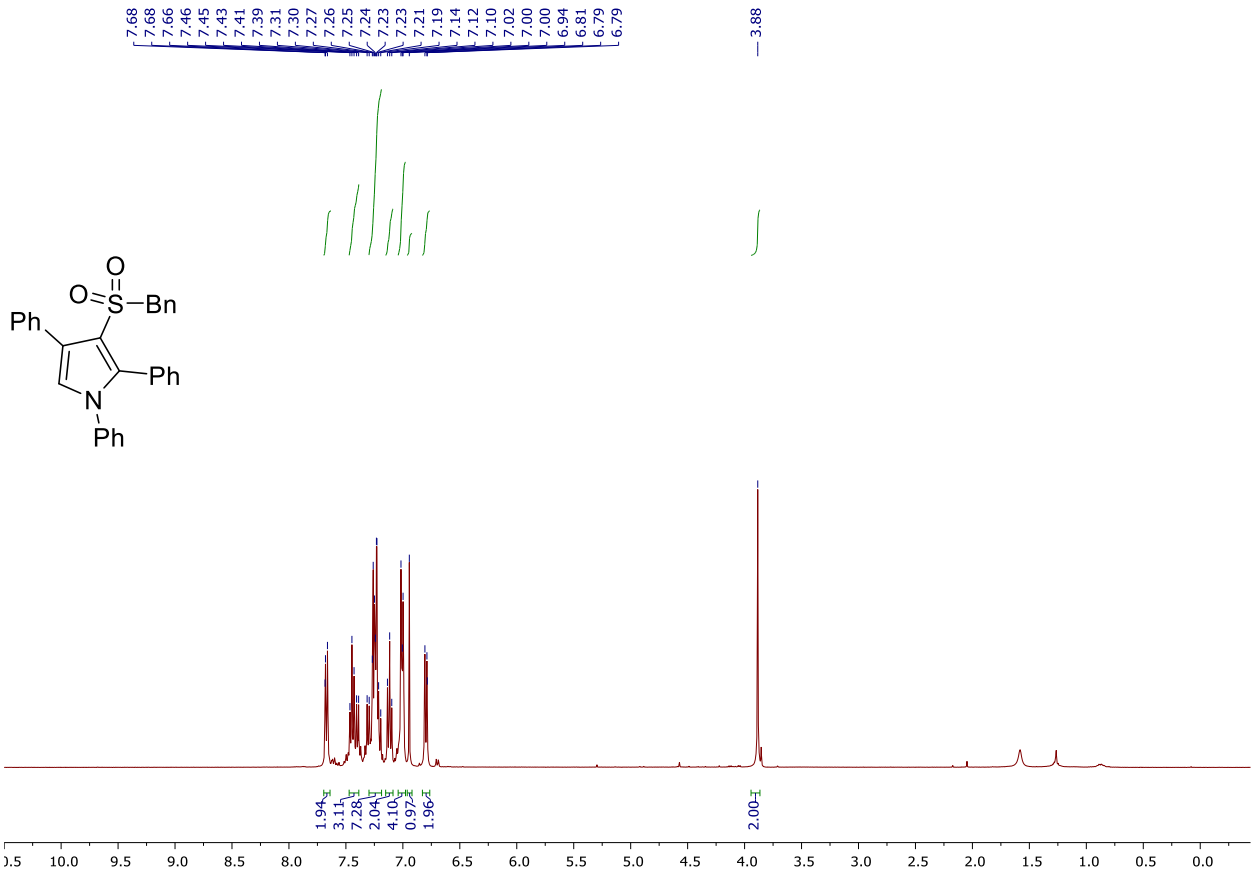


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **9**

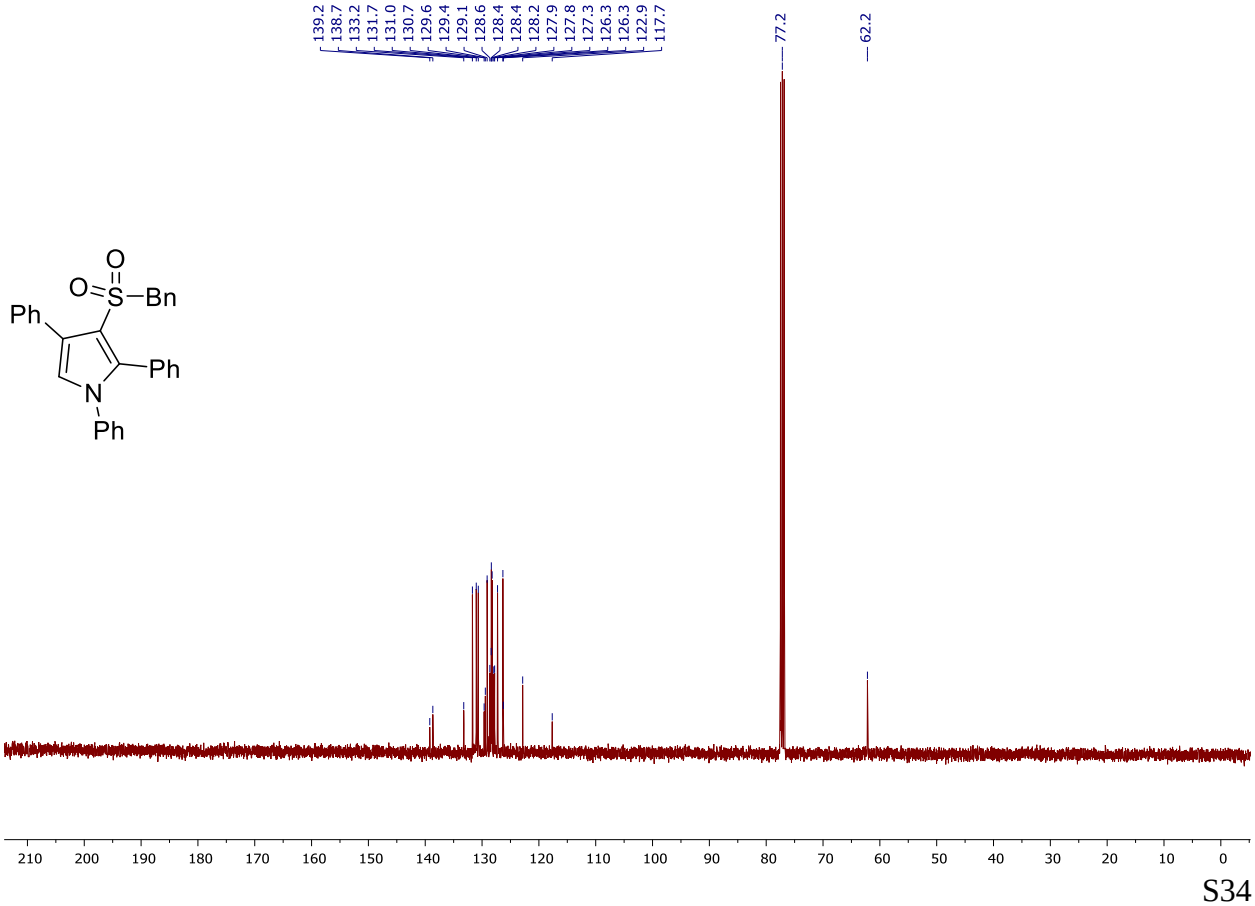


3.7.NMR Spectra of 3-EWG-Substituted Pyrroles

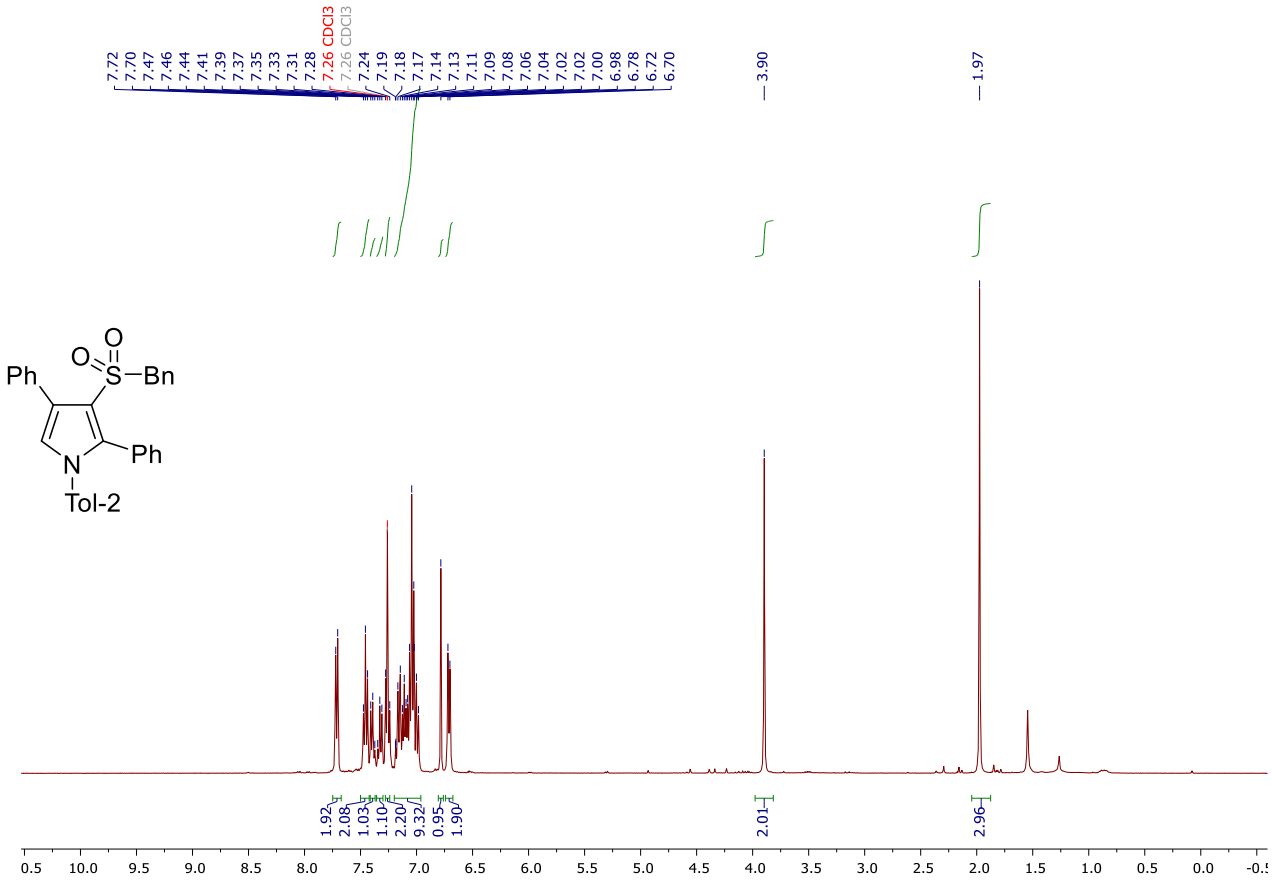
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



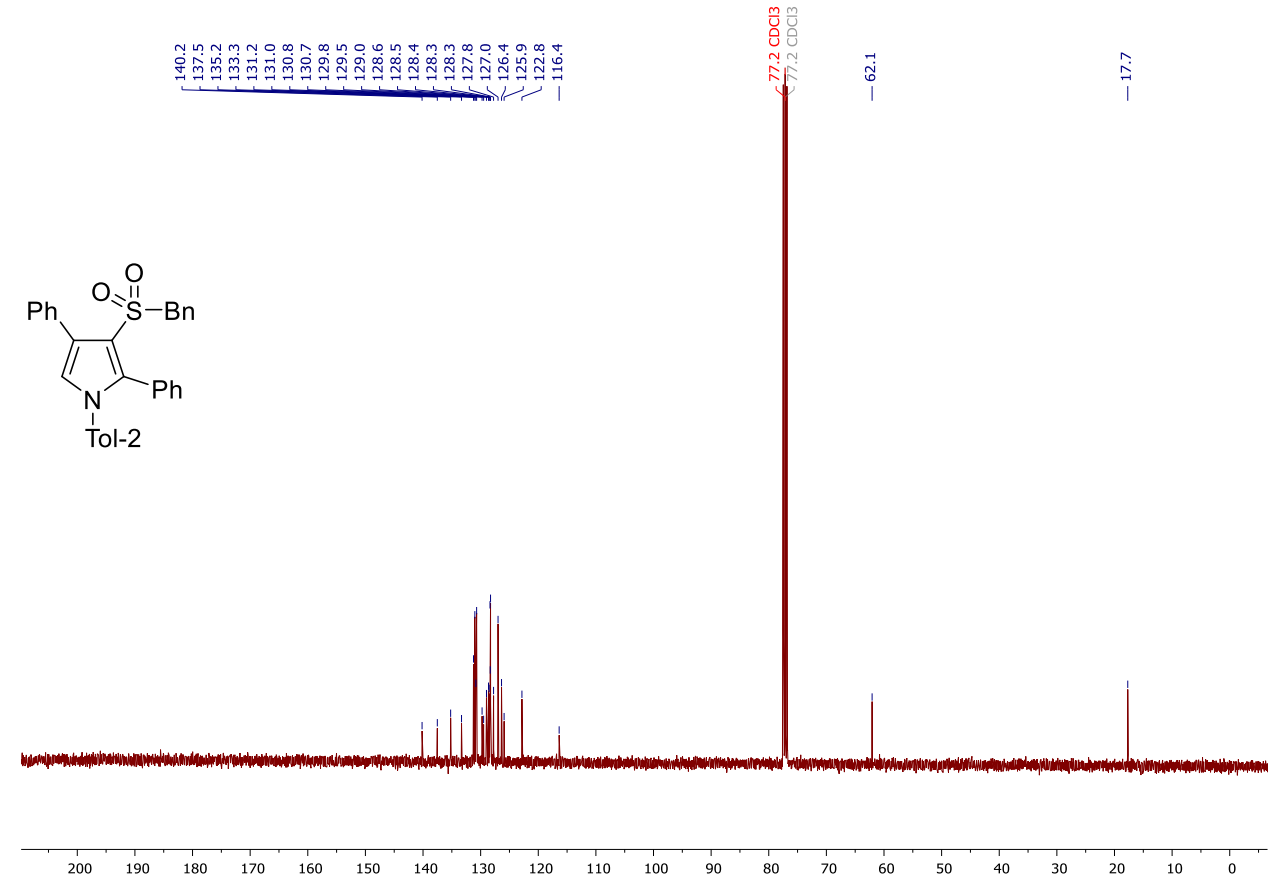
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3a**



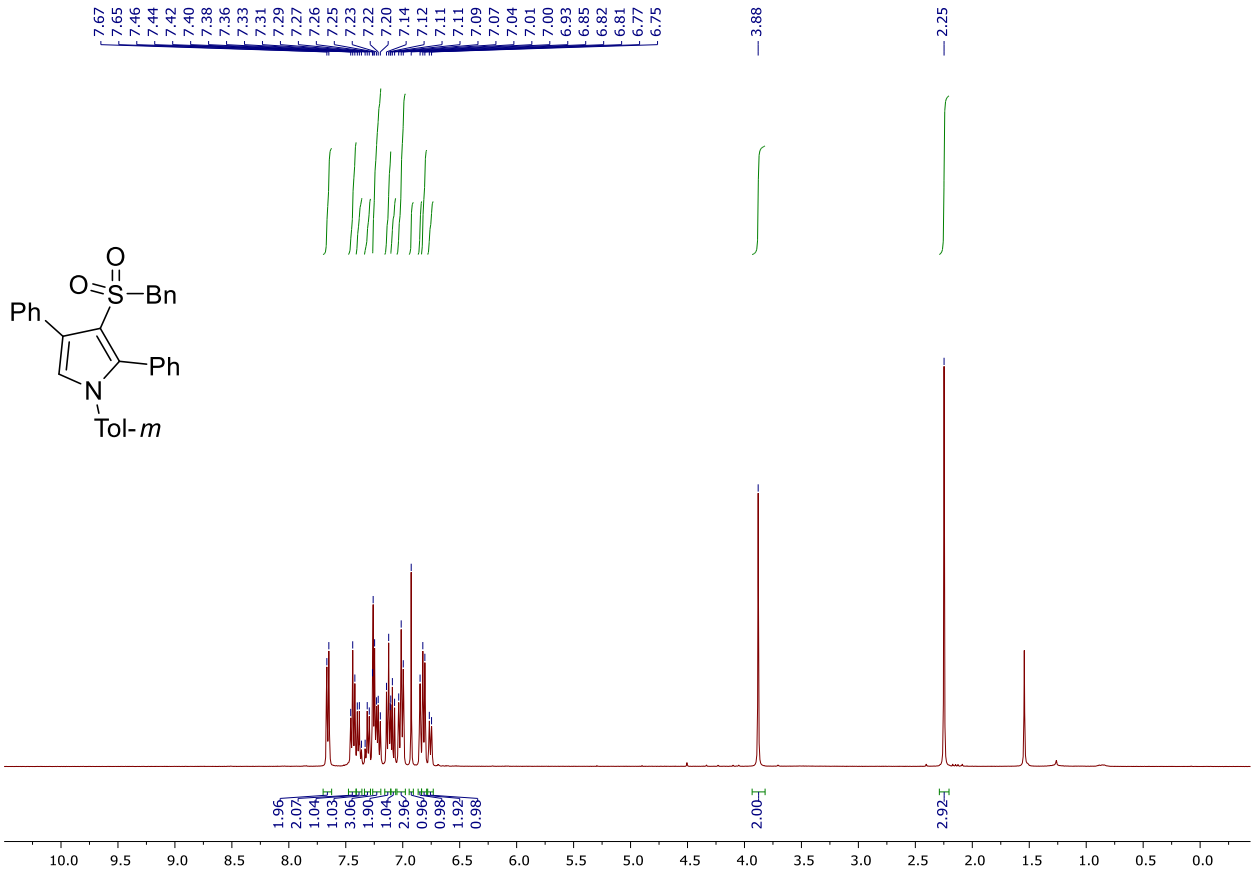
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



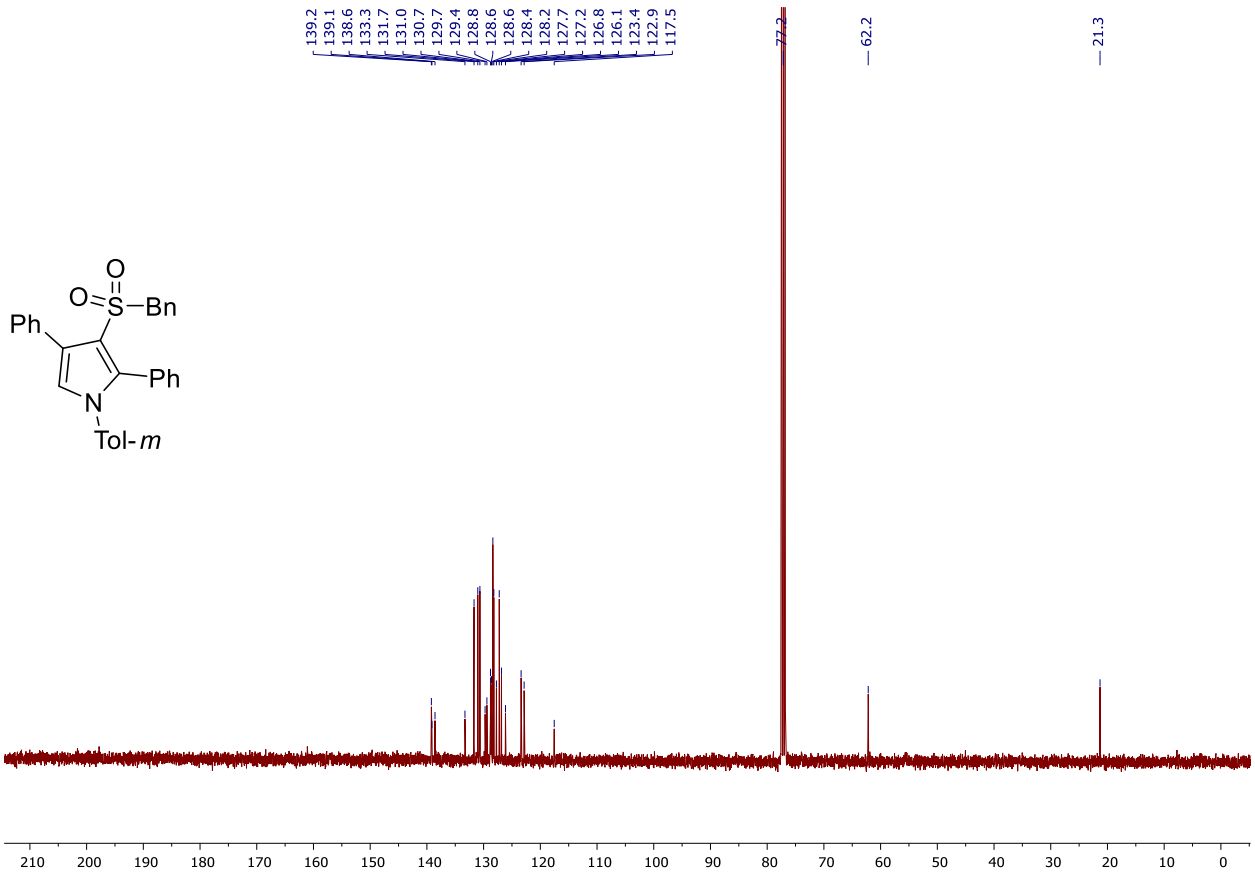
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3b**



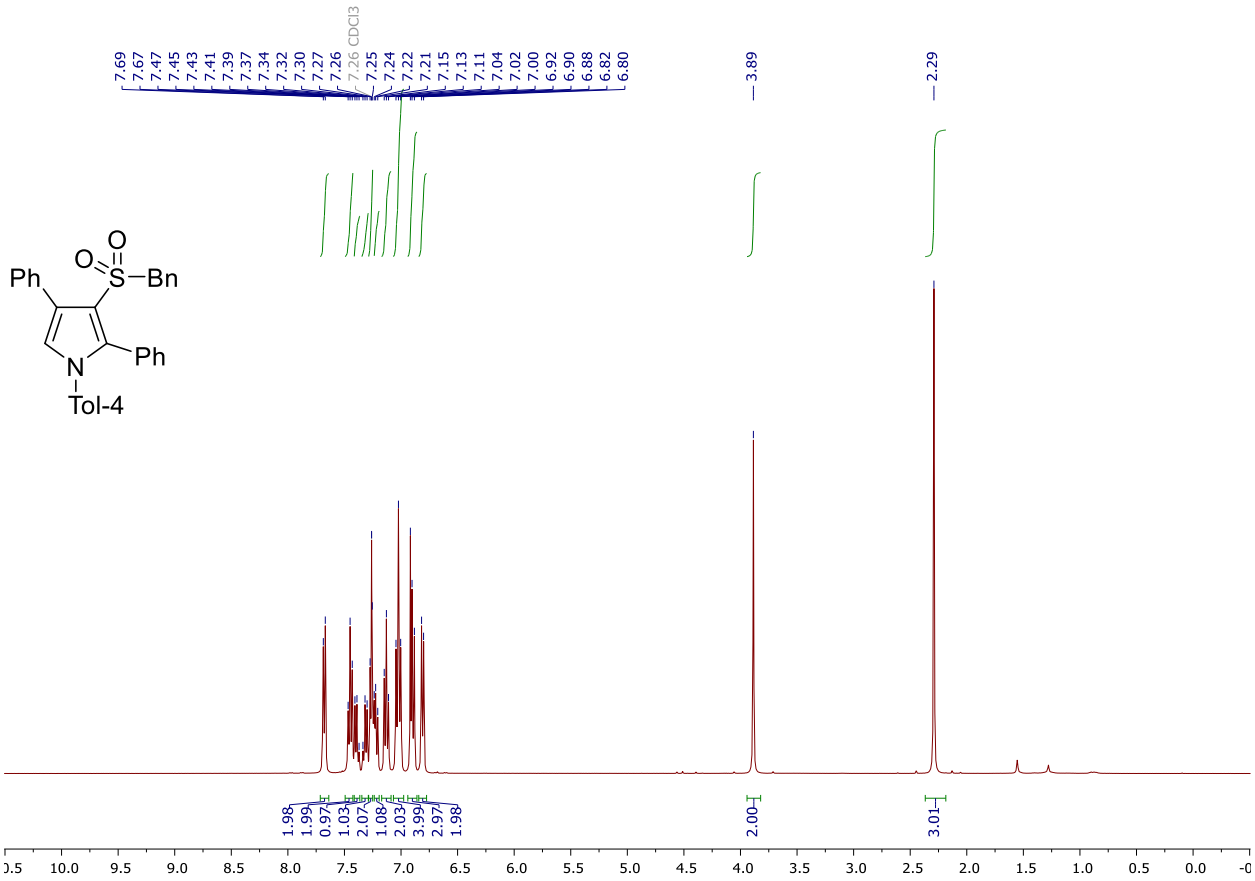
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



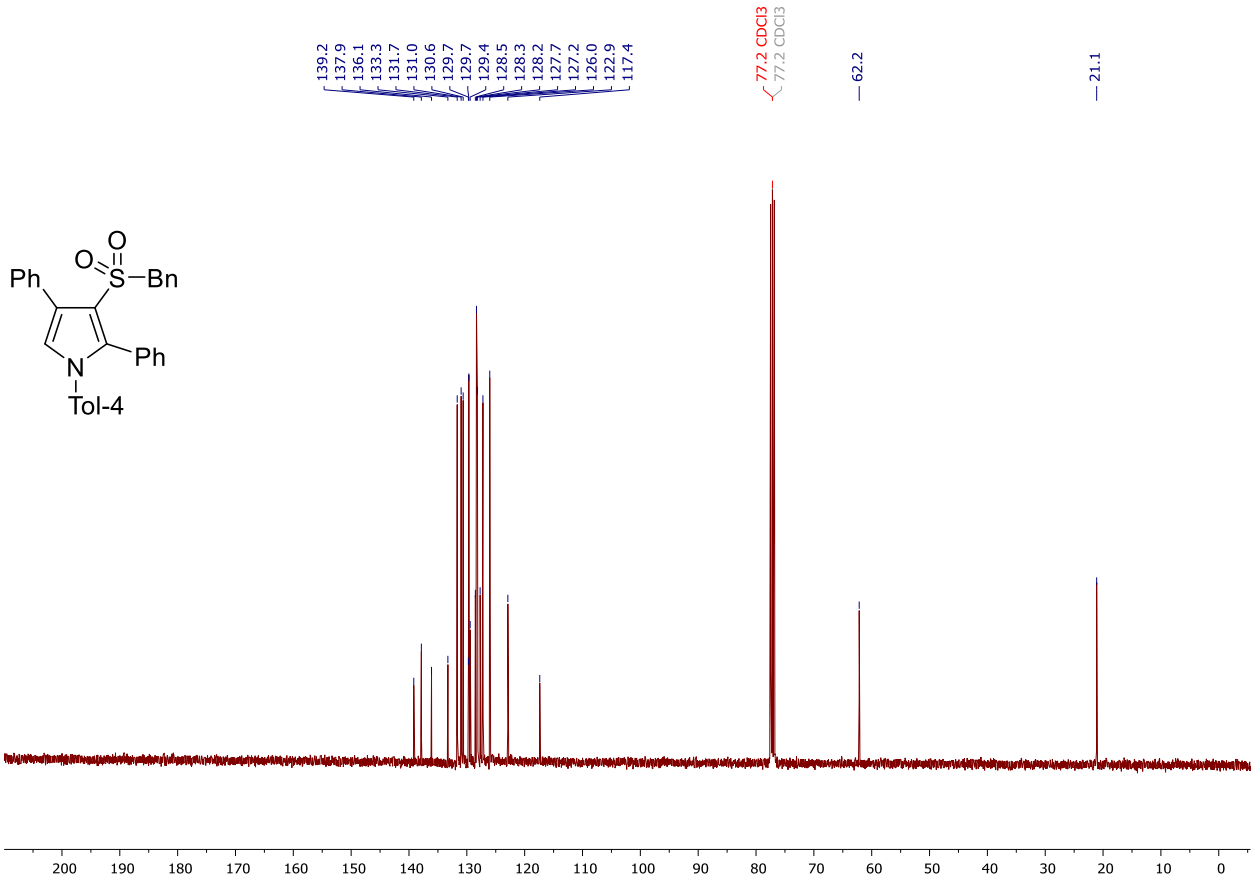
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3c**



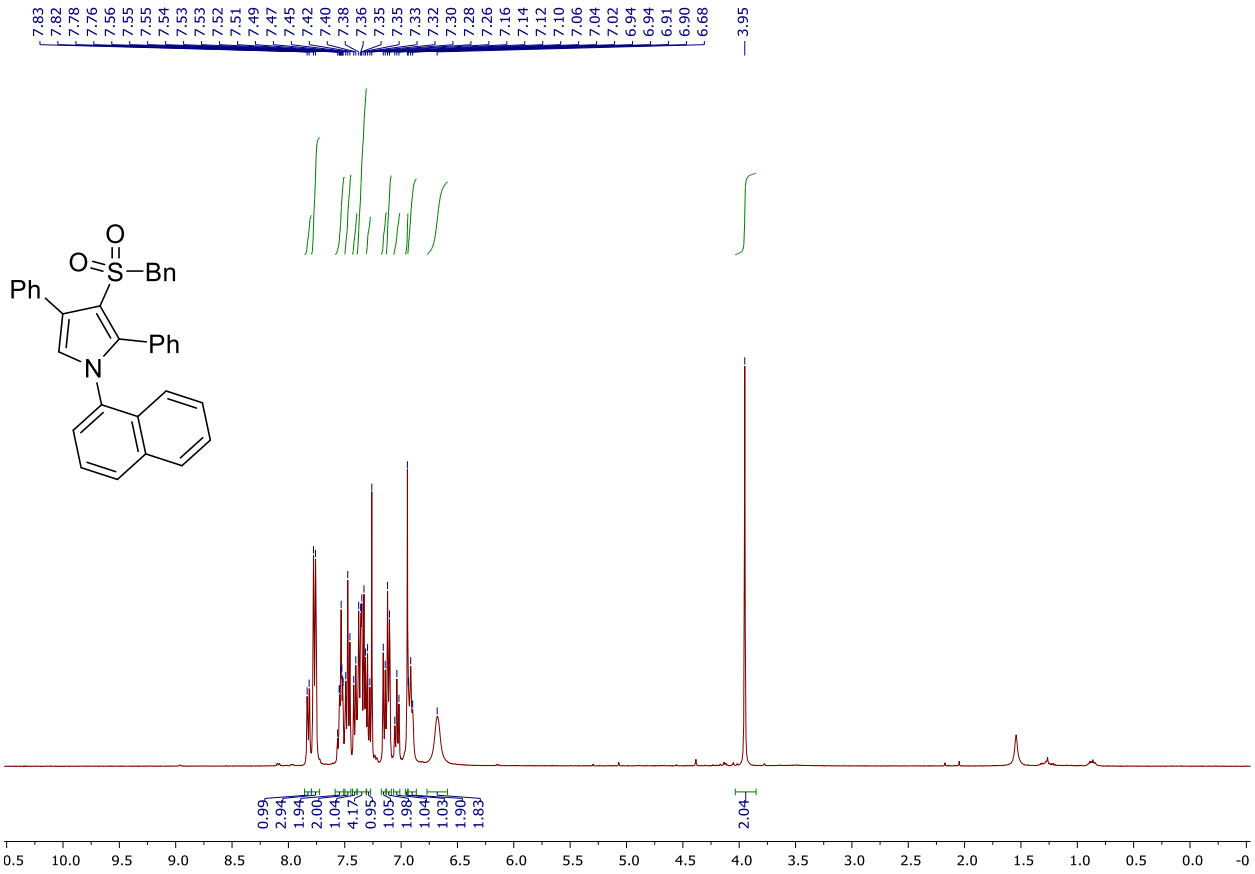
^{1}H NMR (400 MHz, $CDCl_3$) of **3d**



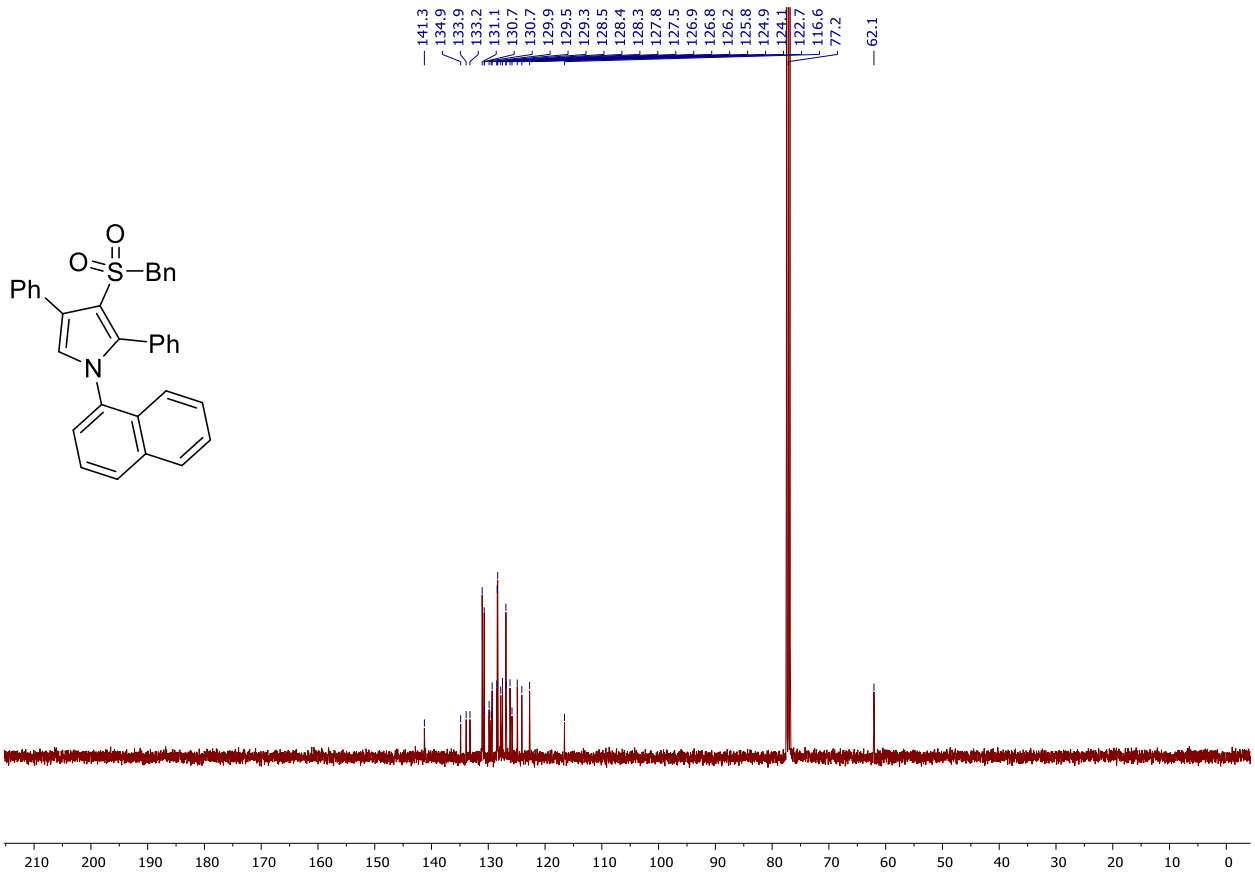
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3d**



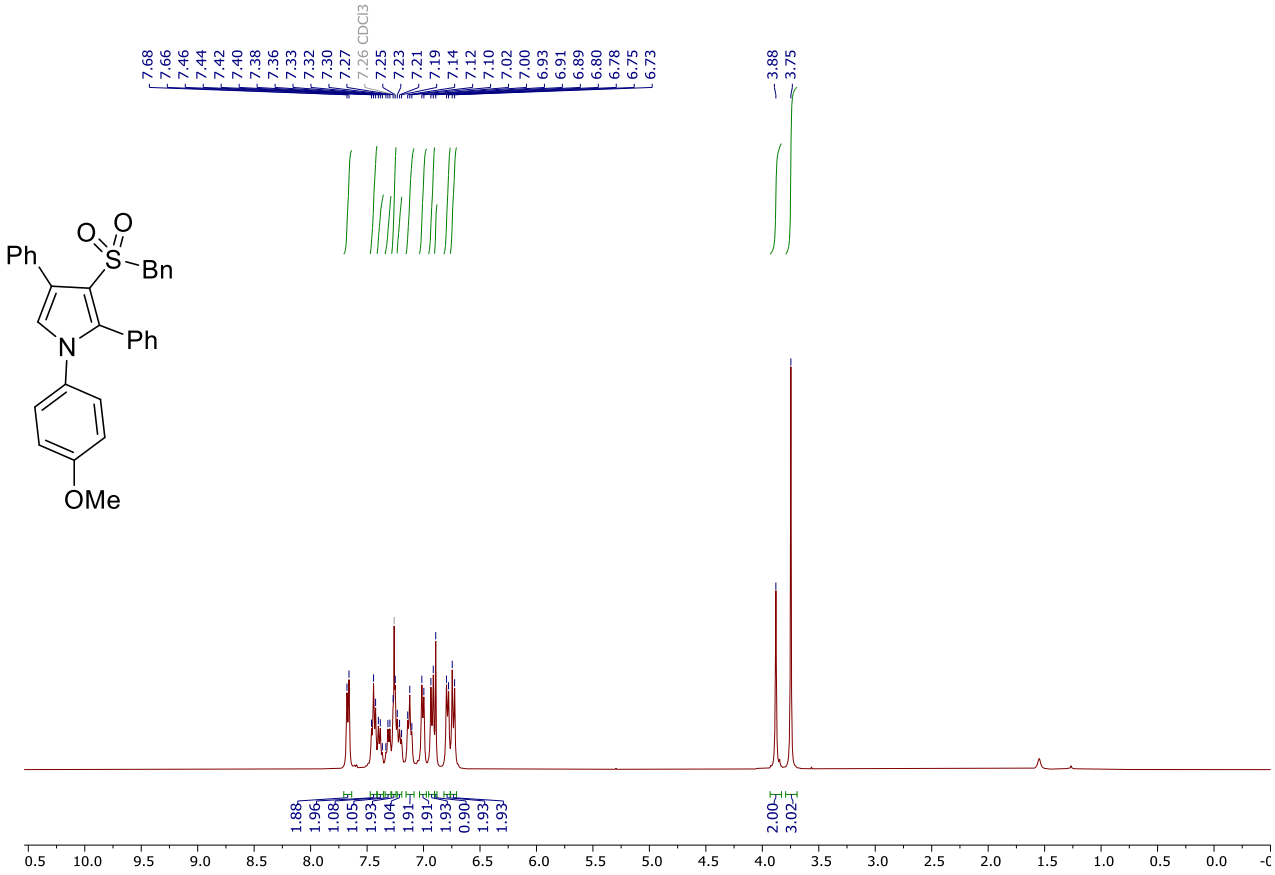
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



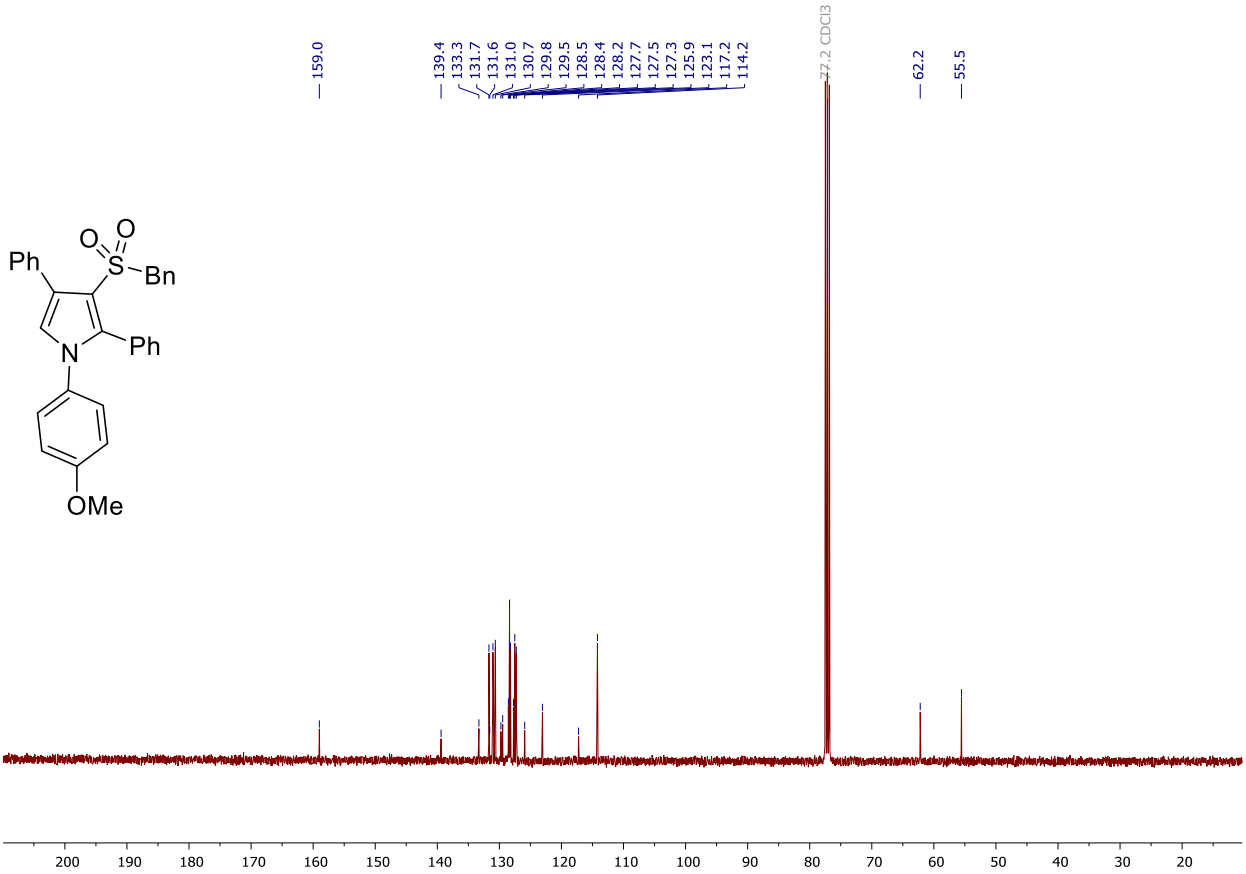
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3e**



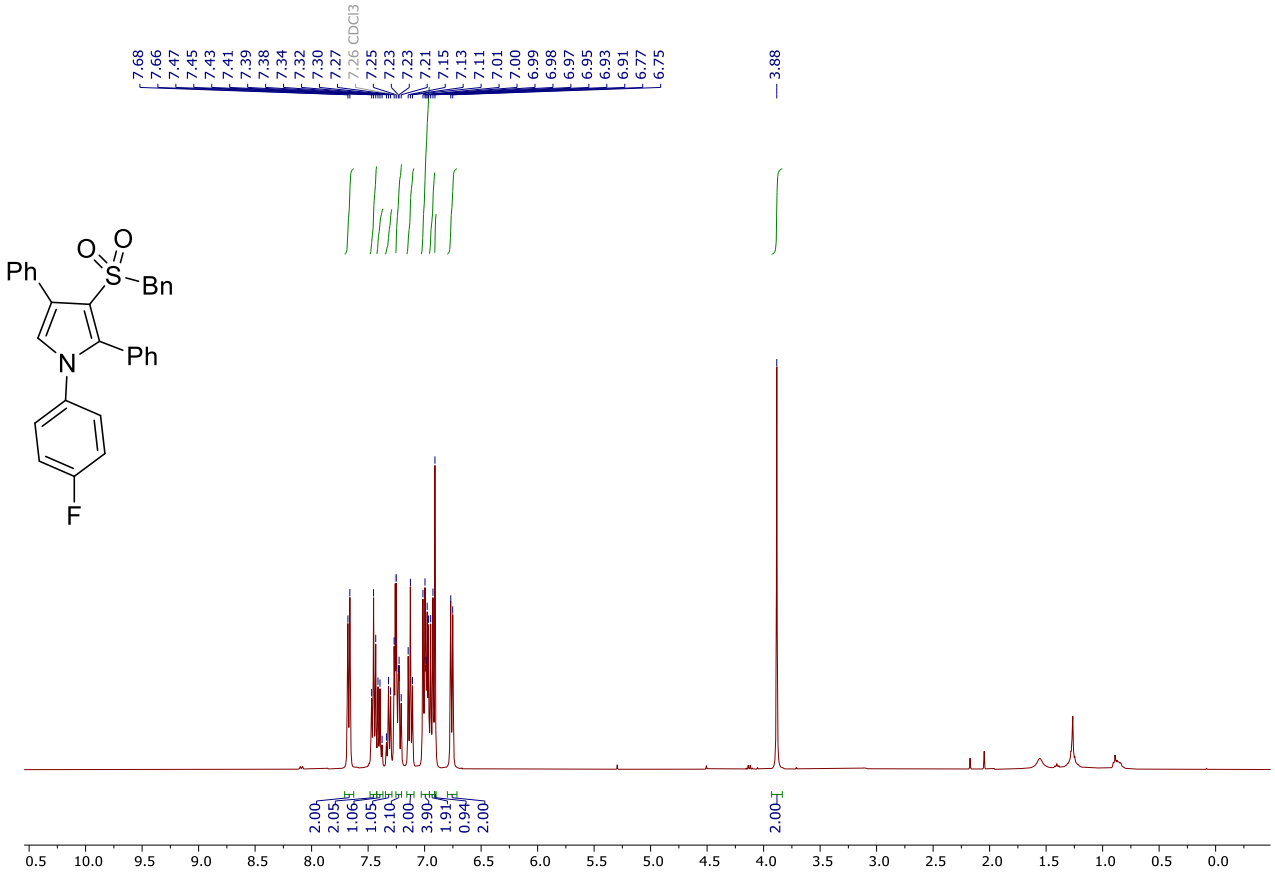
^{1}H NMR (400 MHz, $CDCl_3$) of **3f**



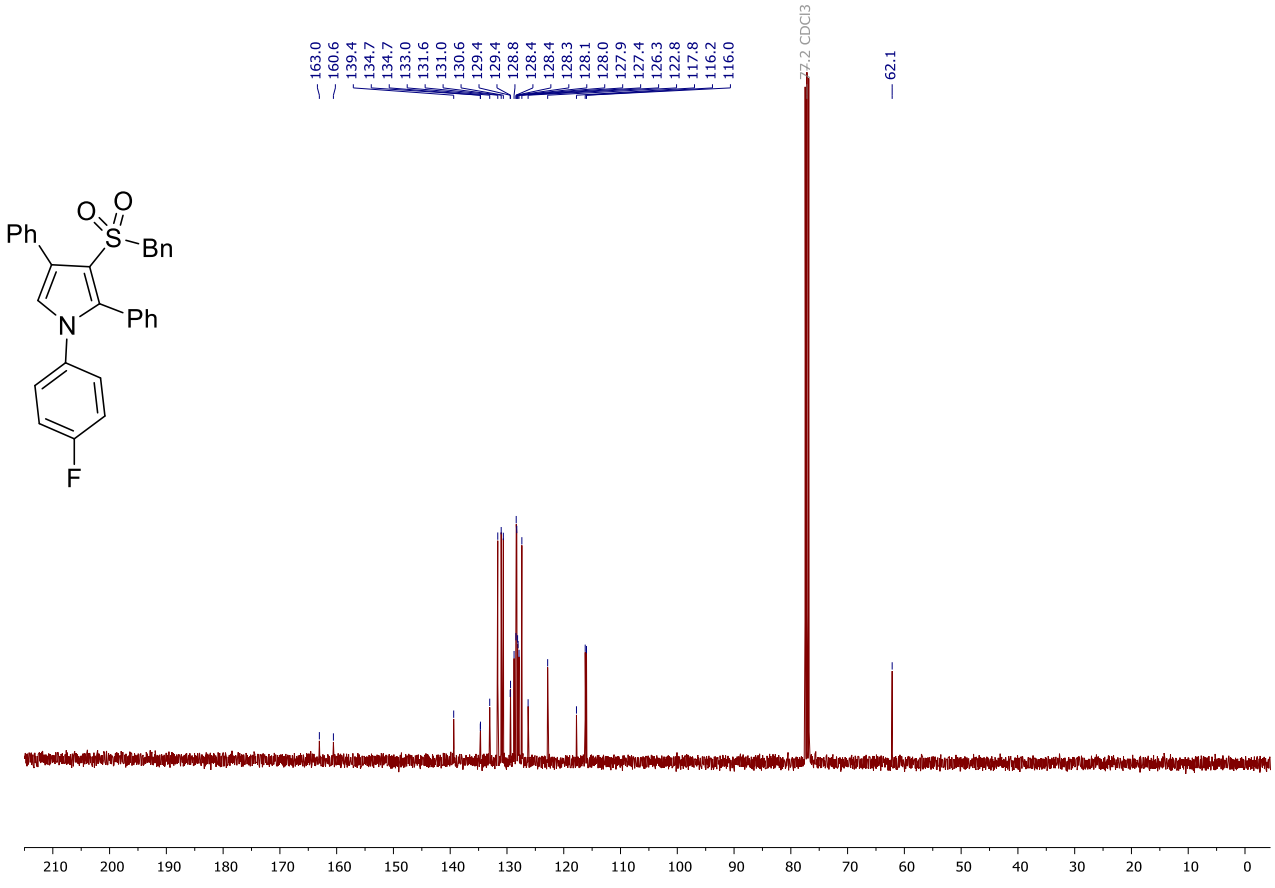
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3f**



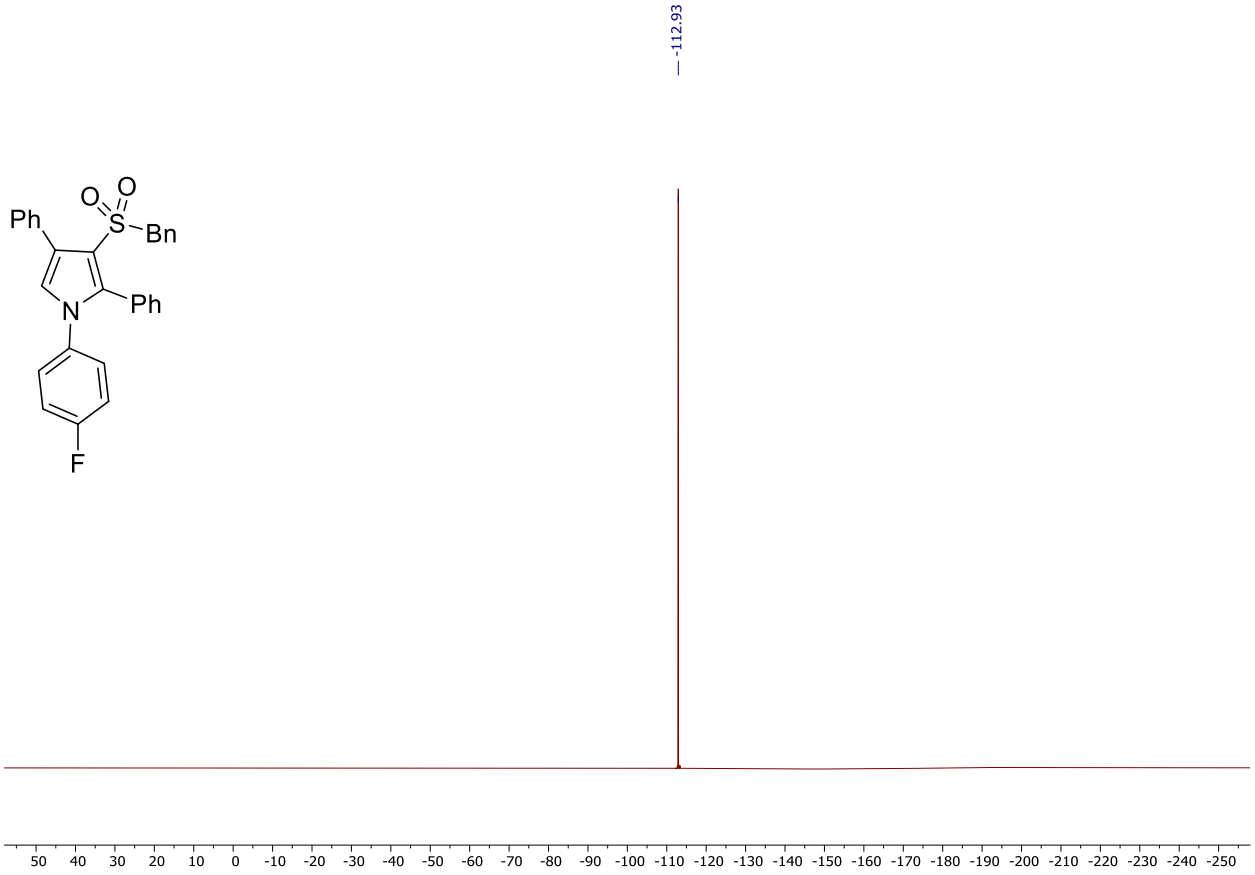
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



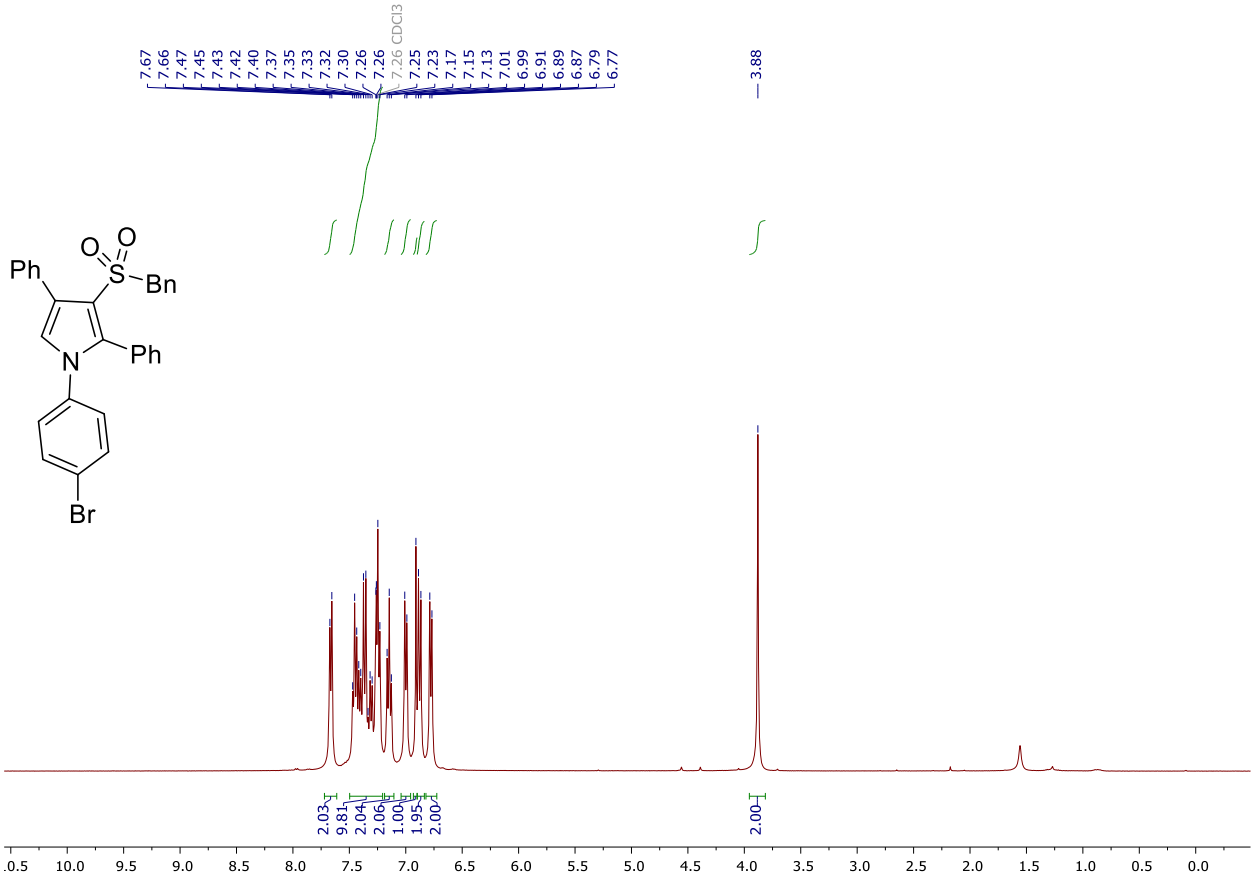
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3g**



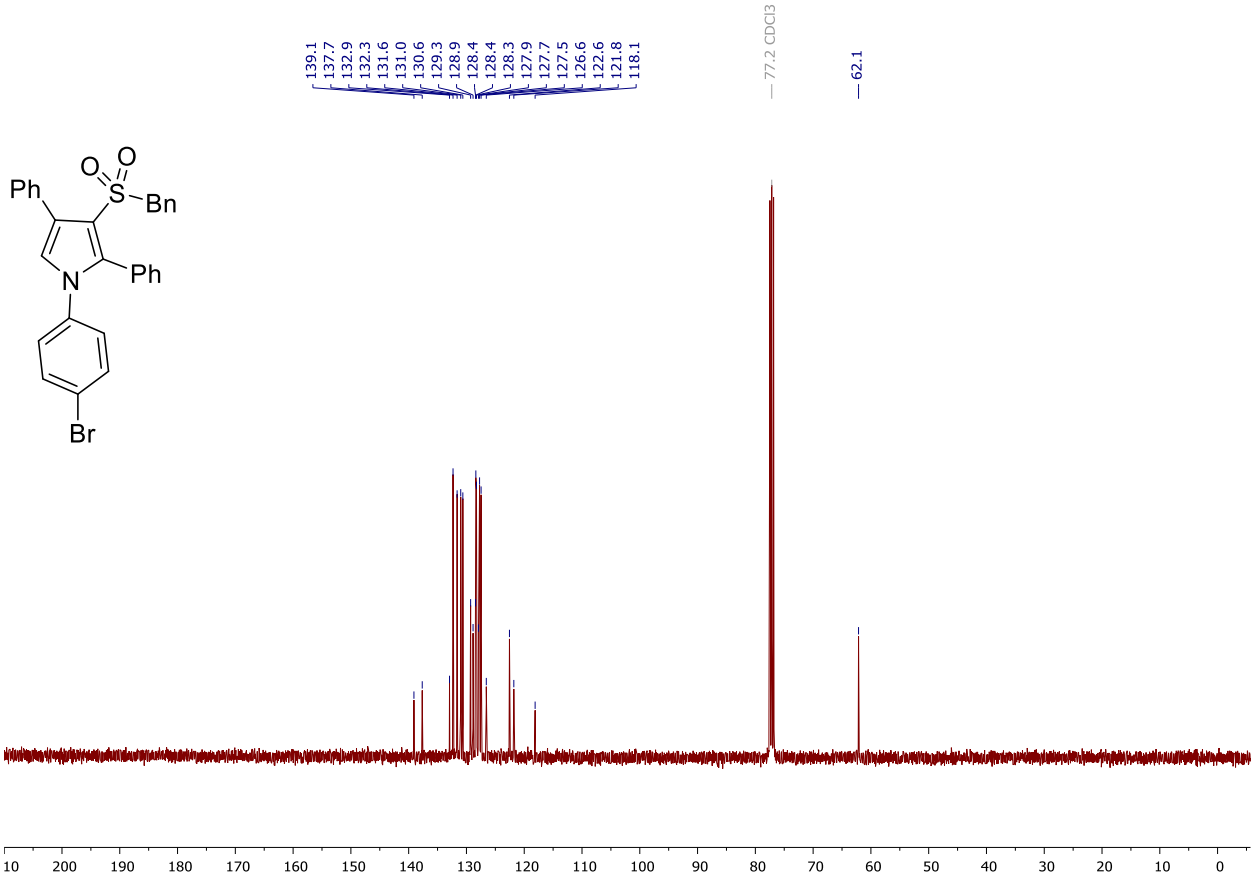
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **3g**



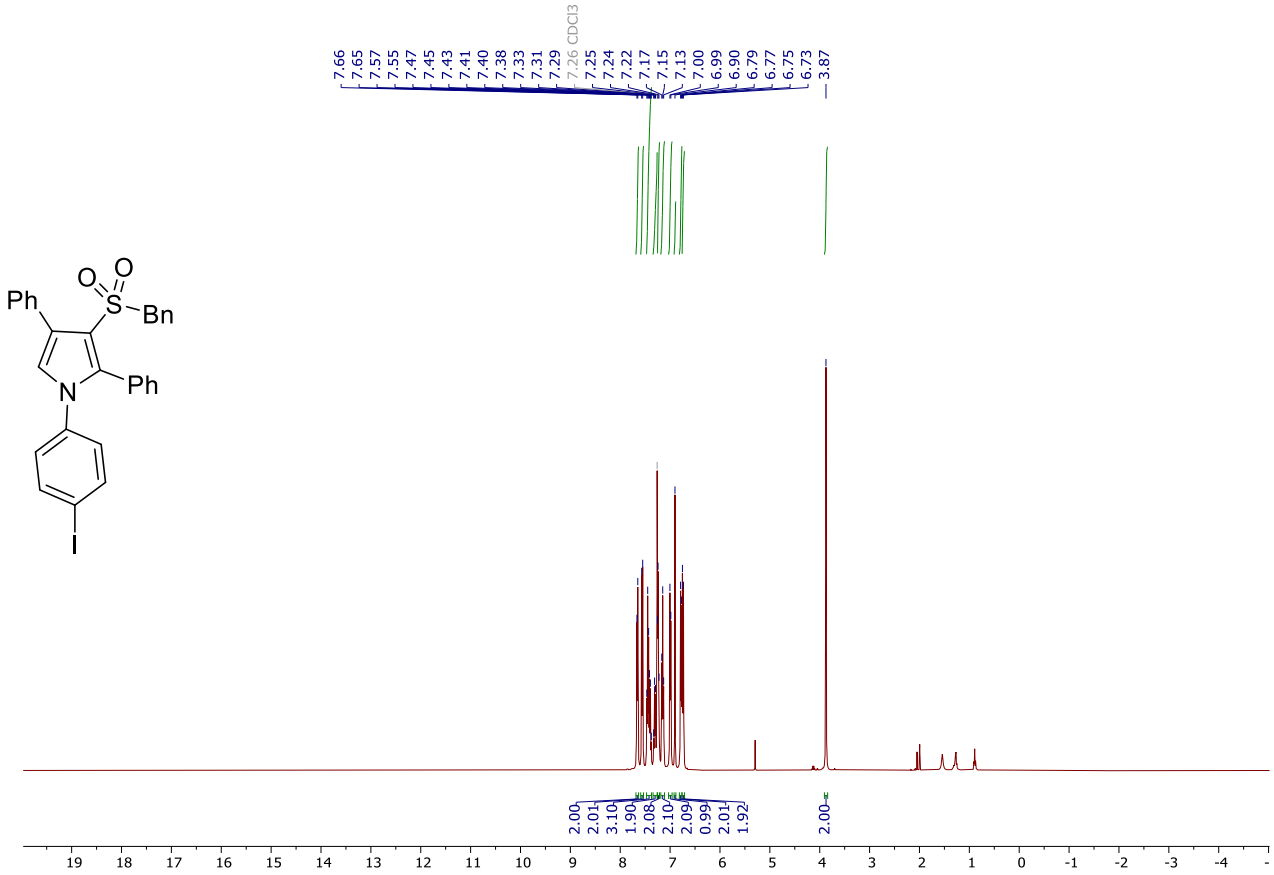
^{1}H NMR (400 MHz, $CDCl_3$) of **3h**



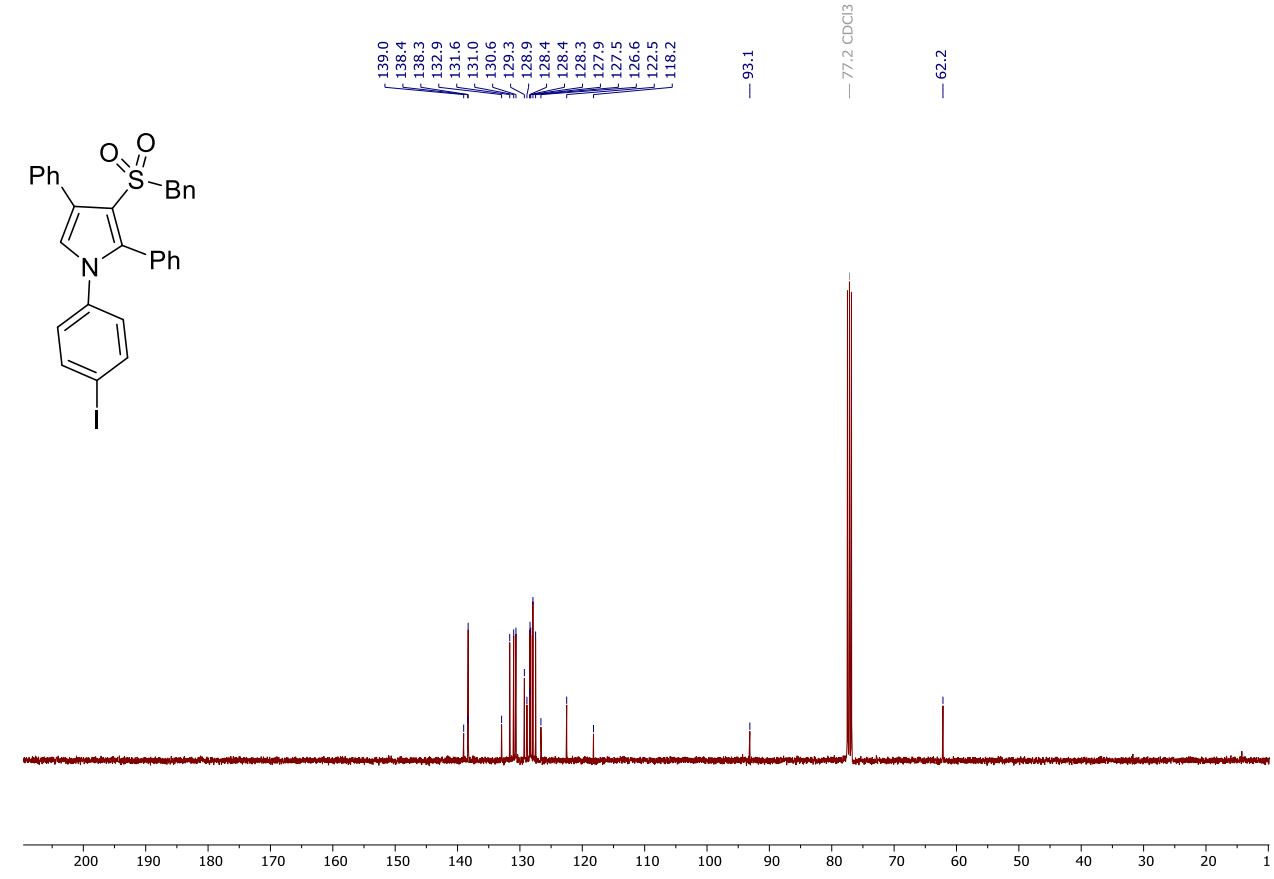
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3h**



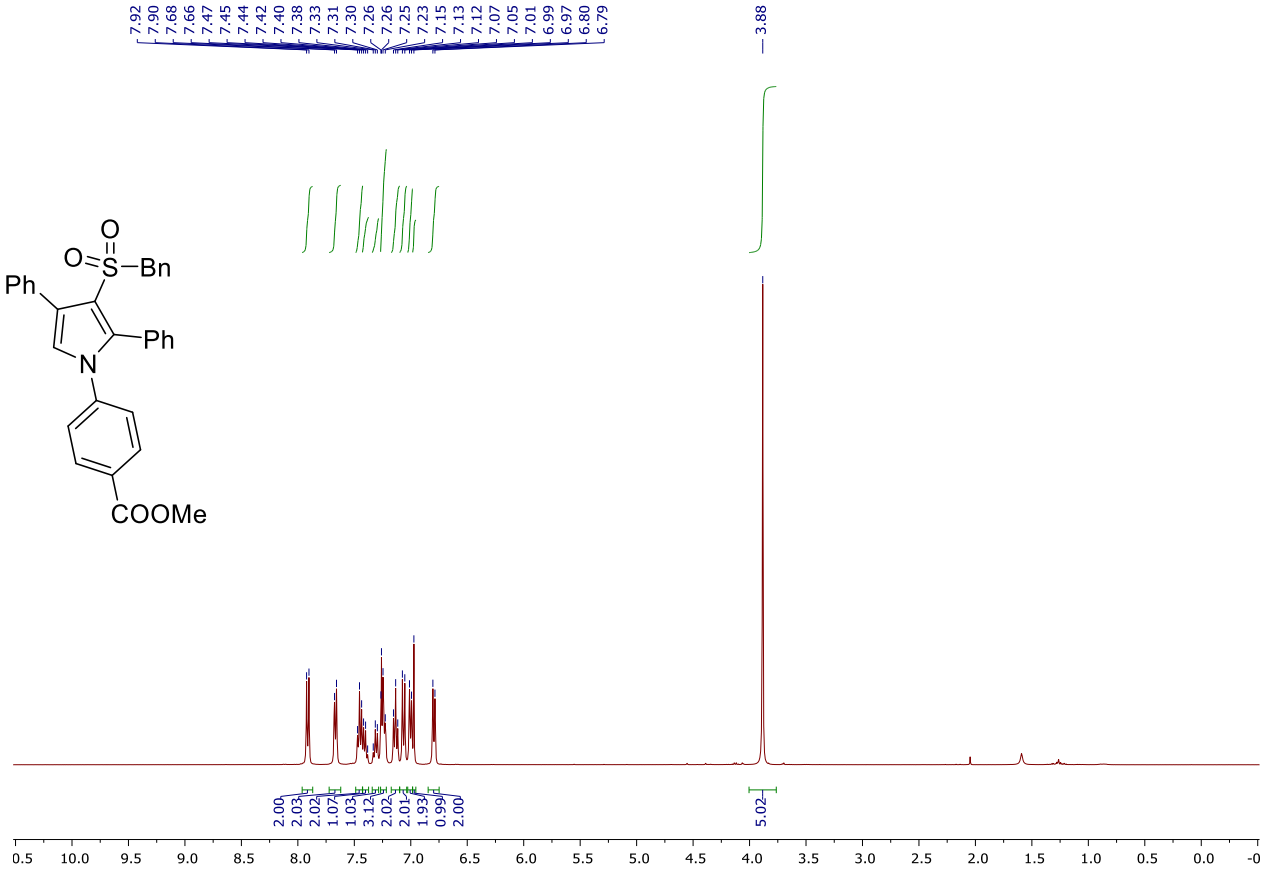
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



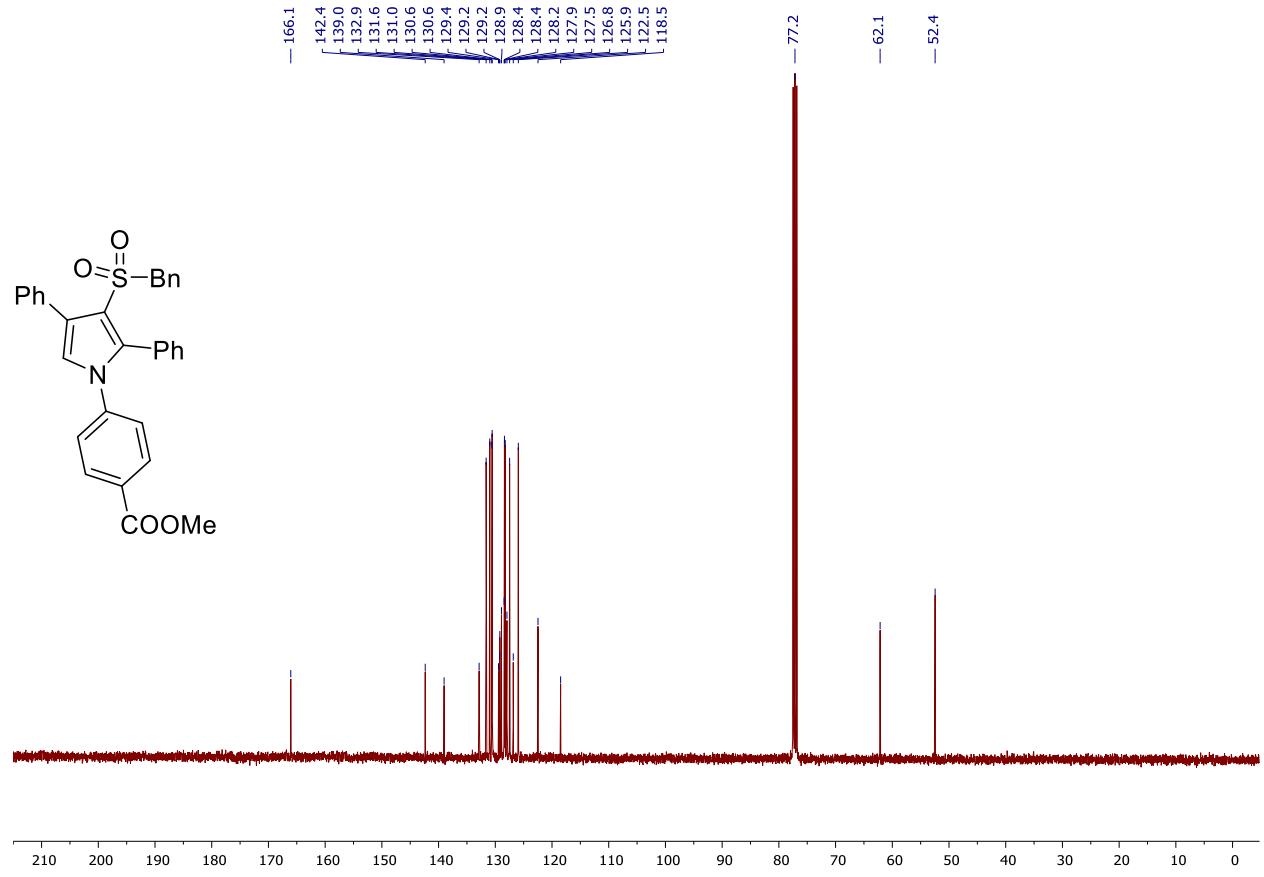
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3i**



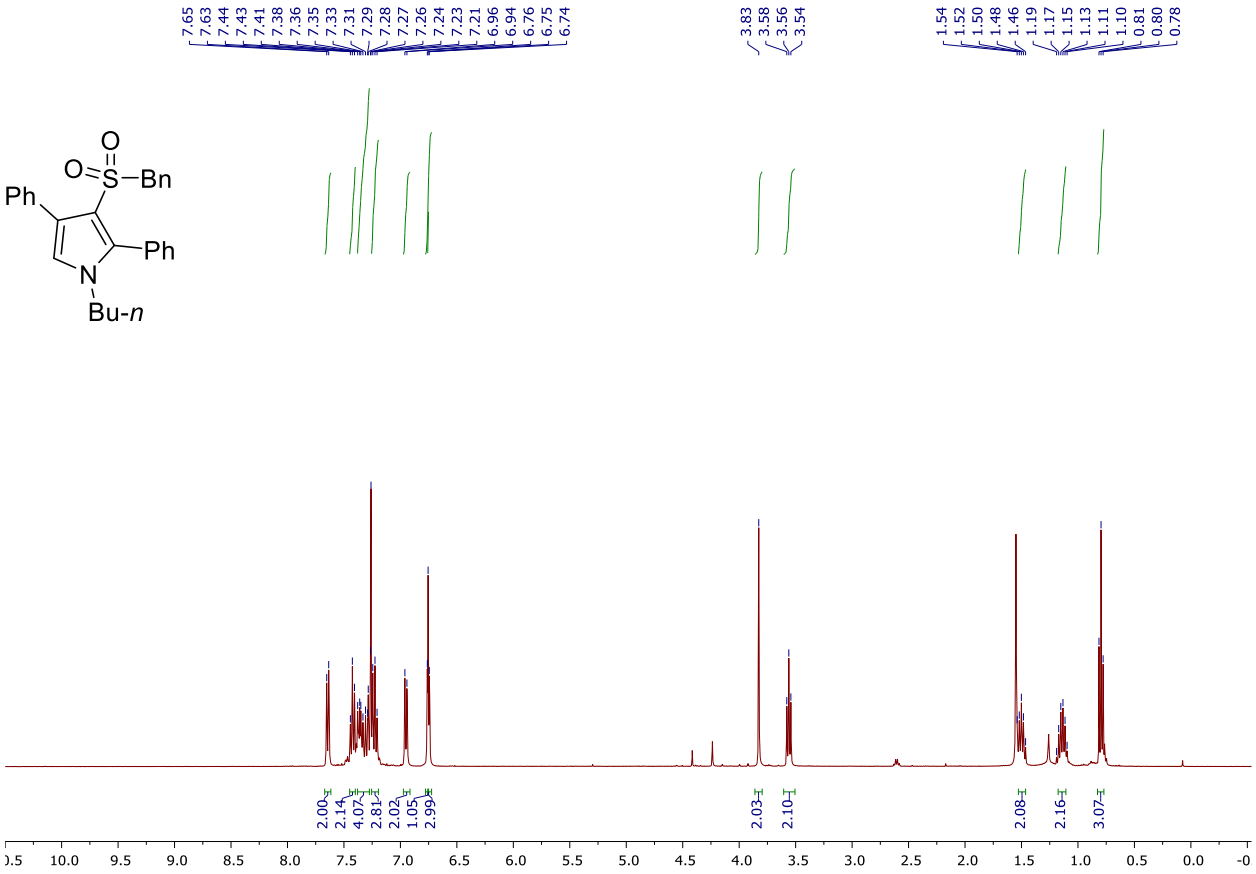
^{1}H NMR (400 MHz, $CDCl_3$) of **3j**



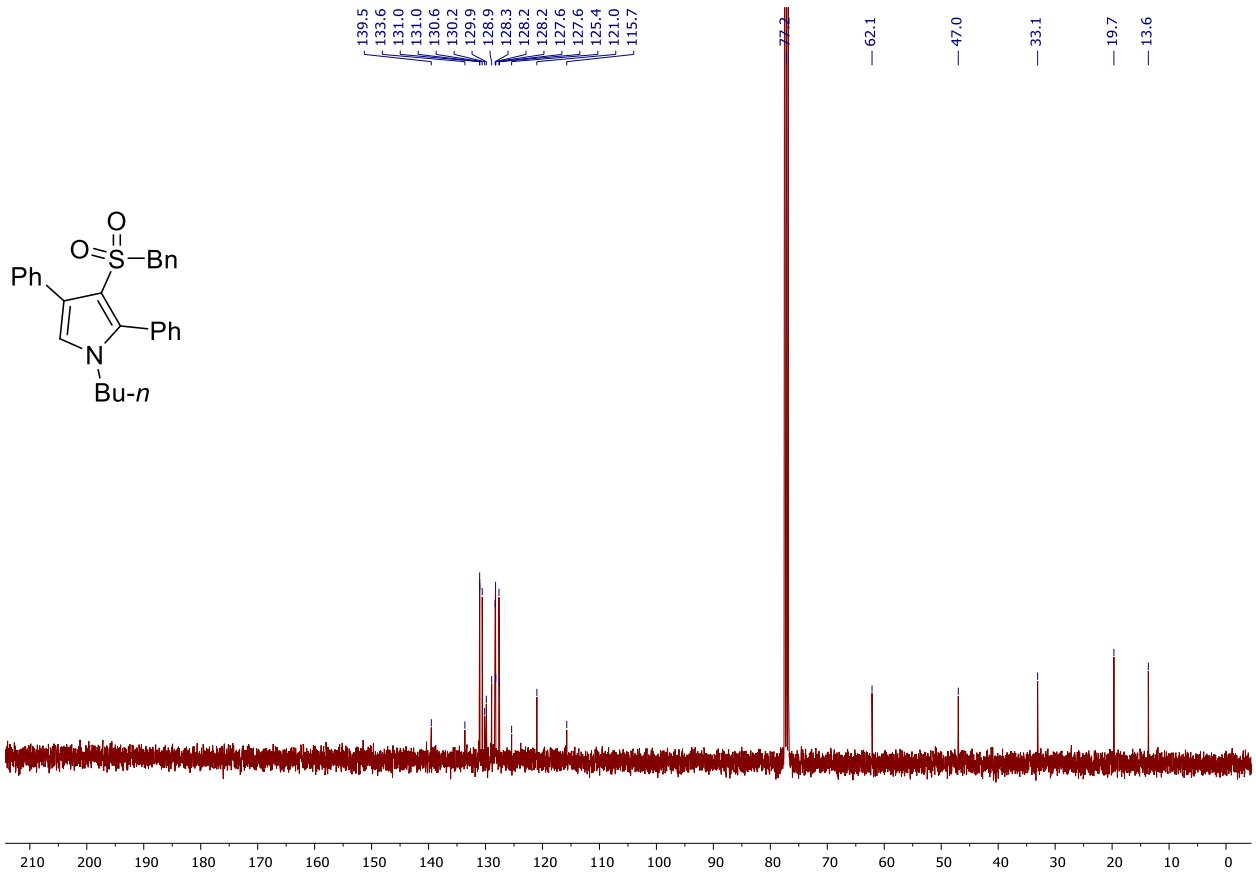
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3j**



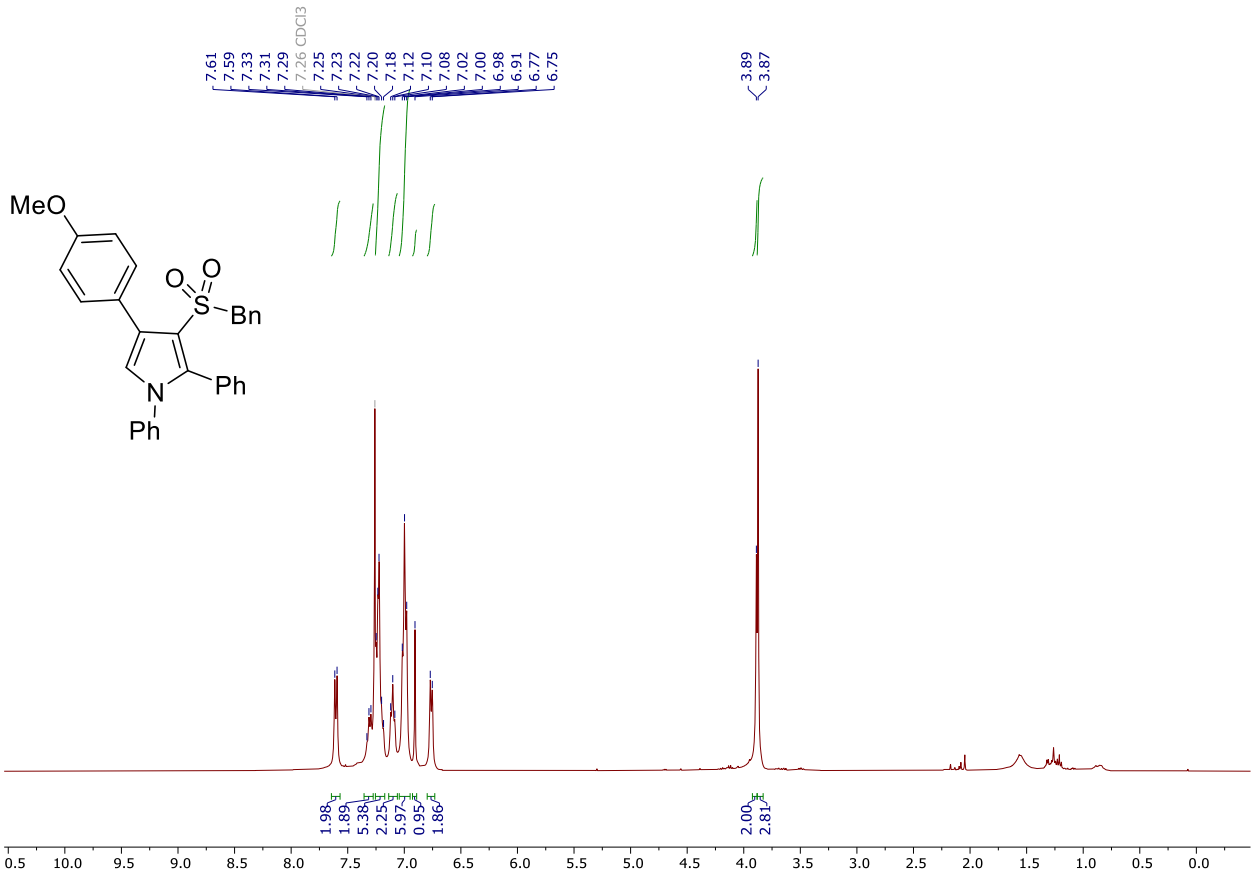
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



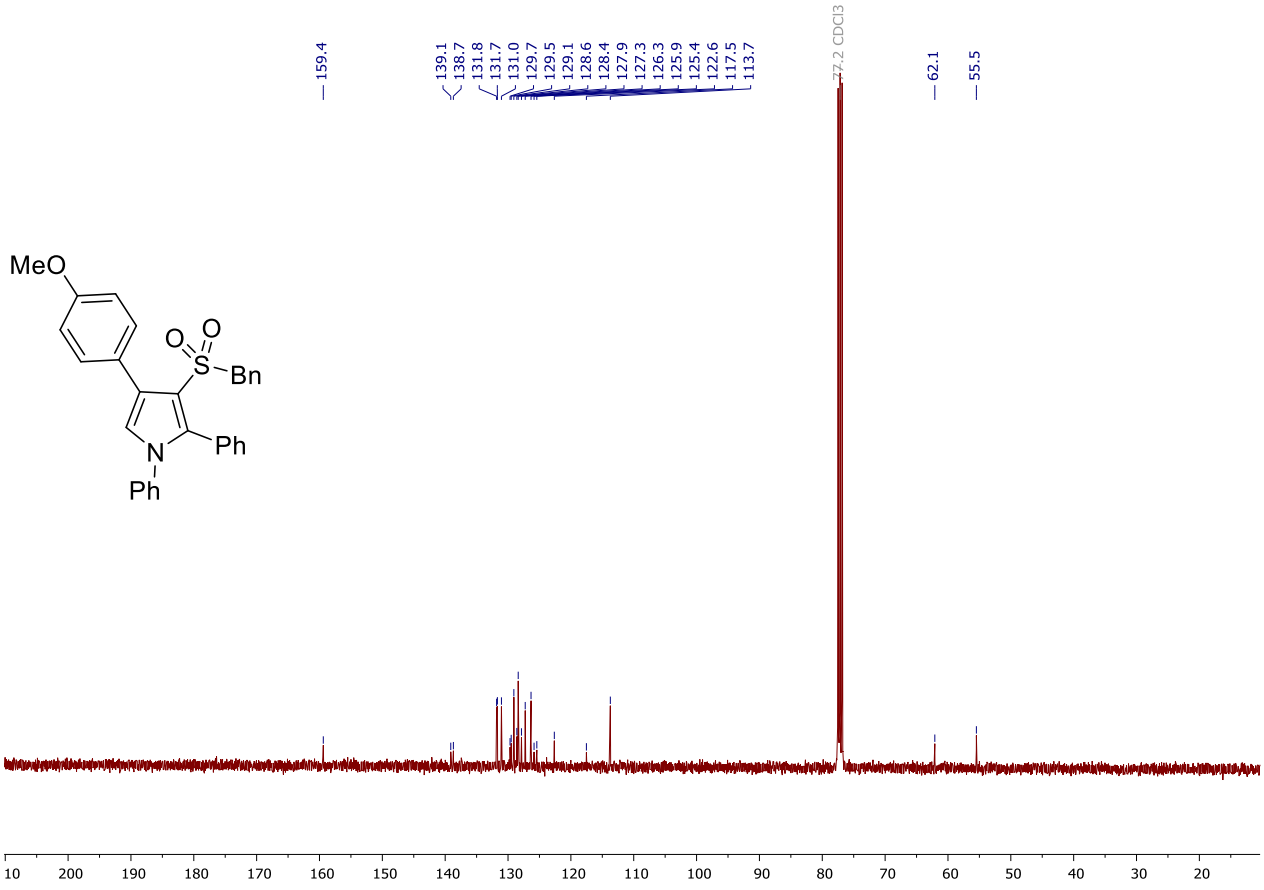
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3k**



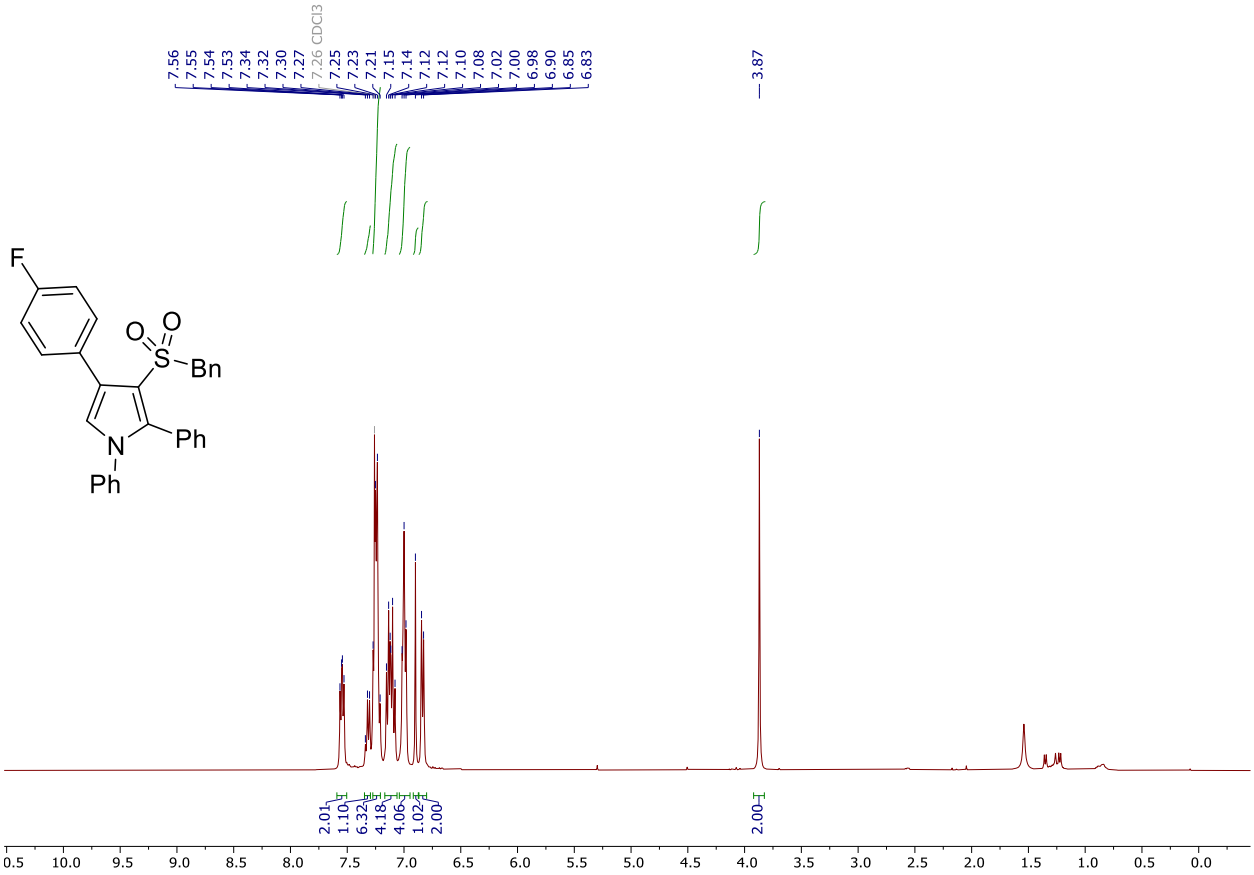
^{1}H NMR (400 MHz, $CDCl_3$) of **3l**



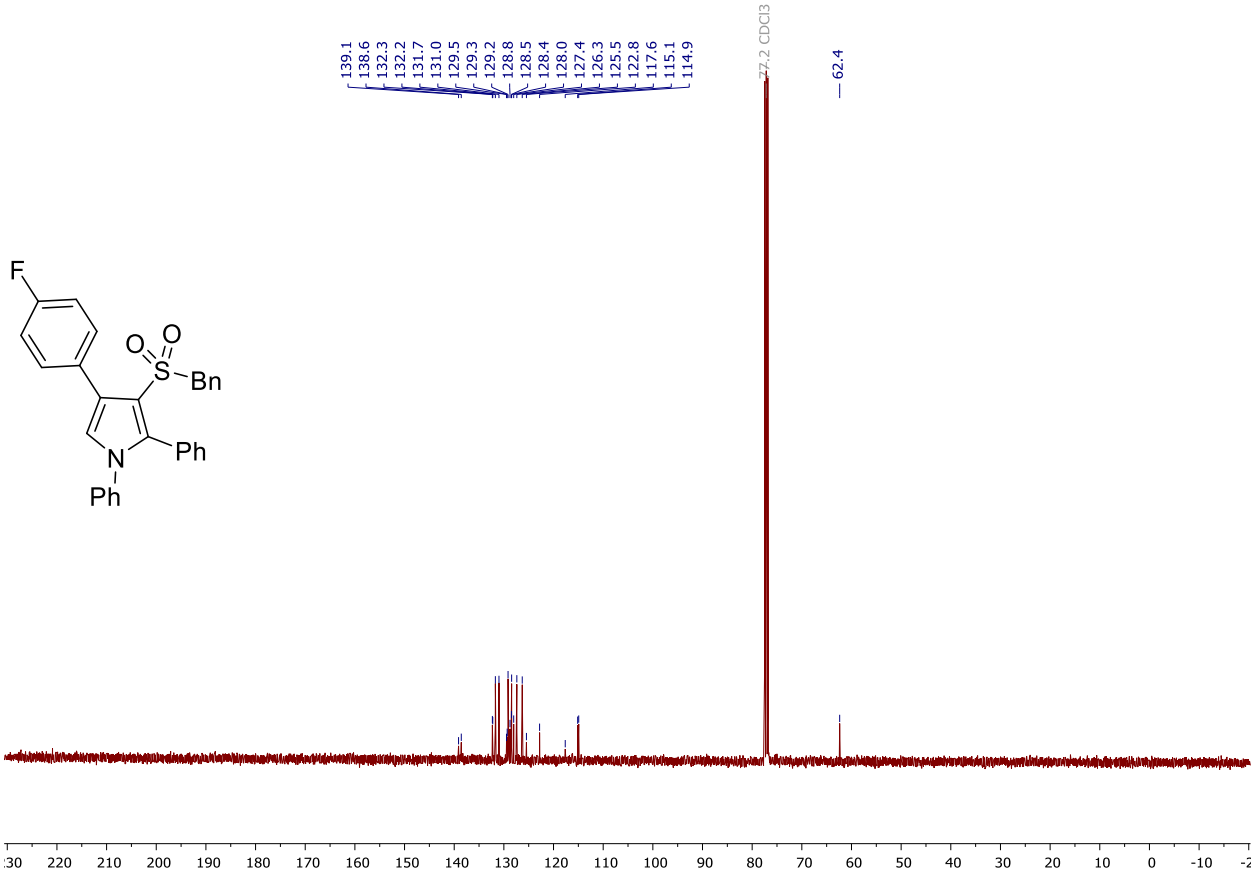
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3l**



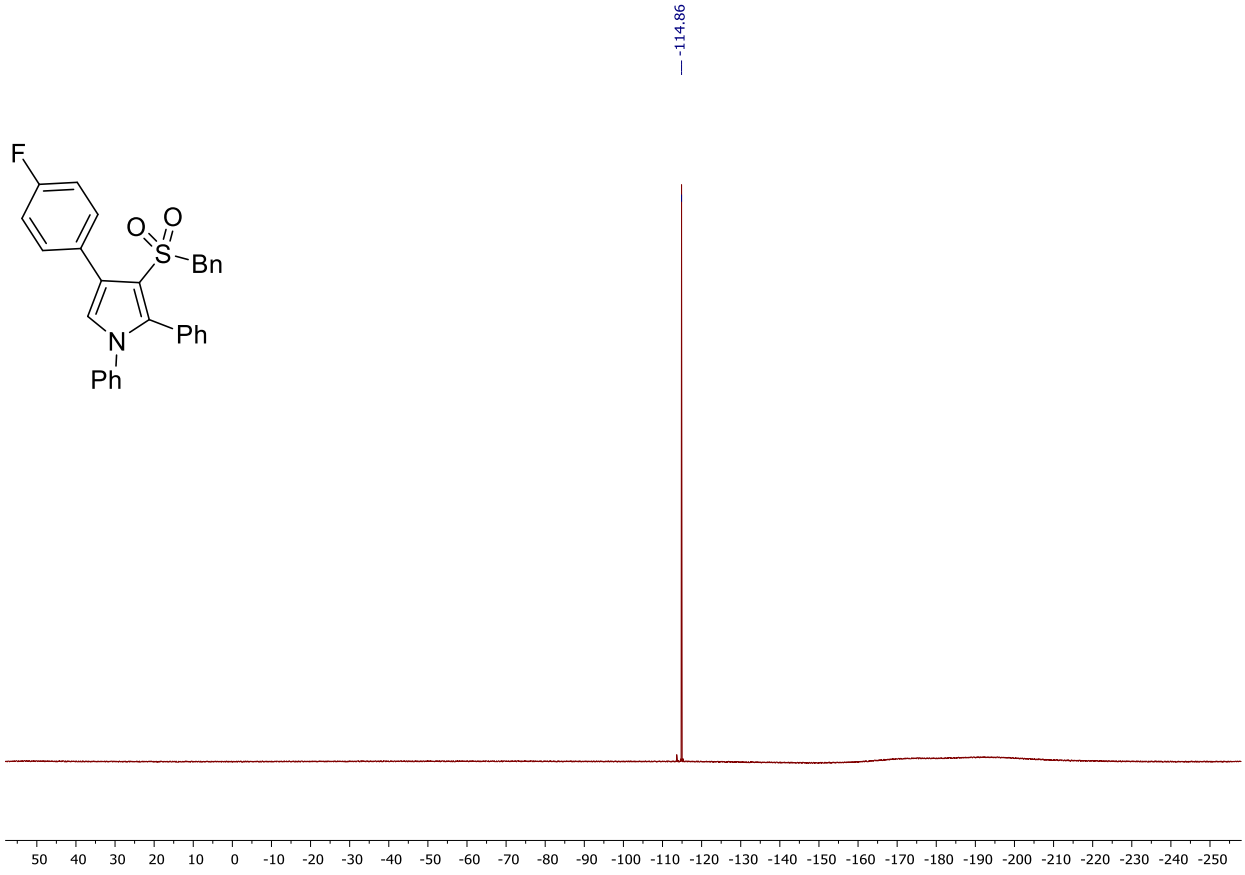
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



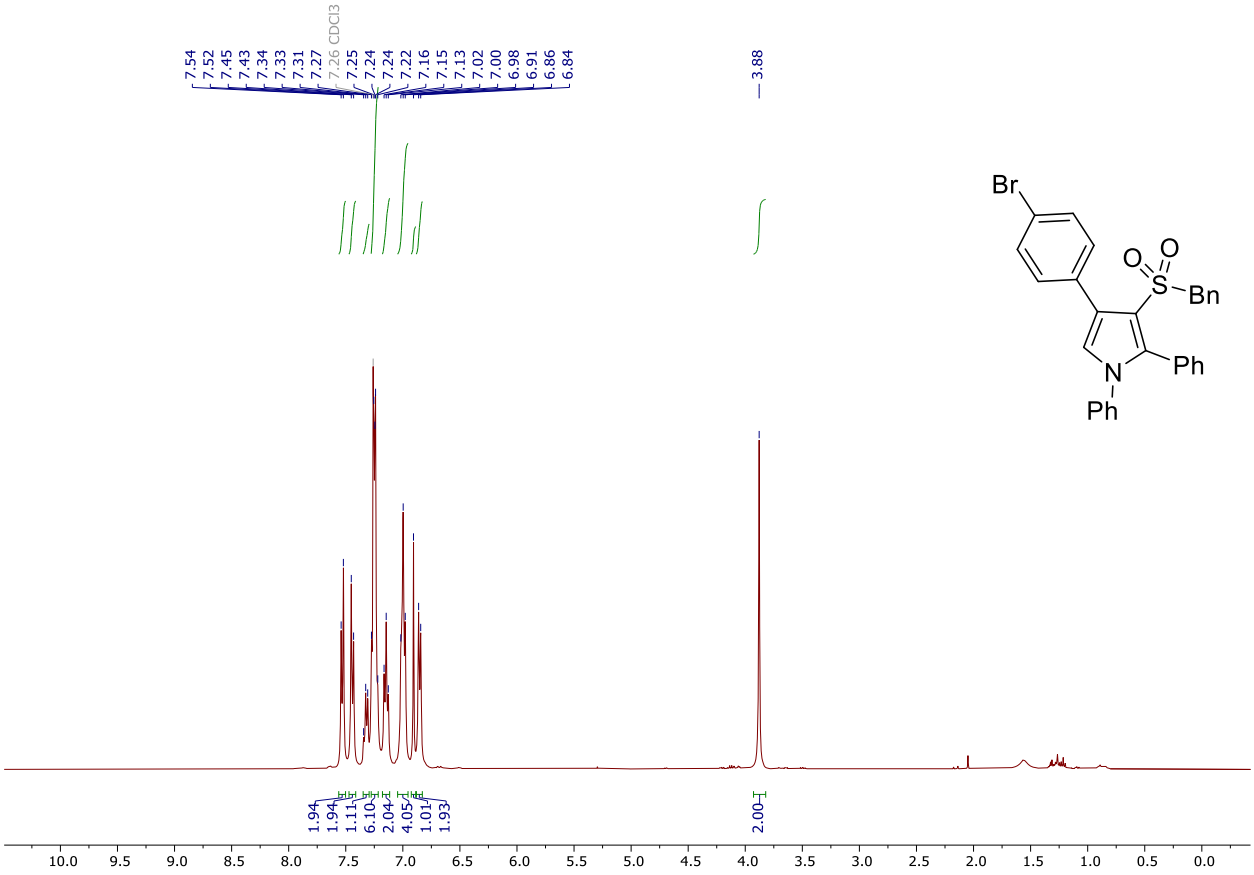
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3m**



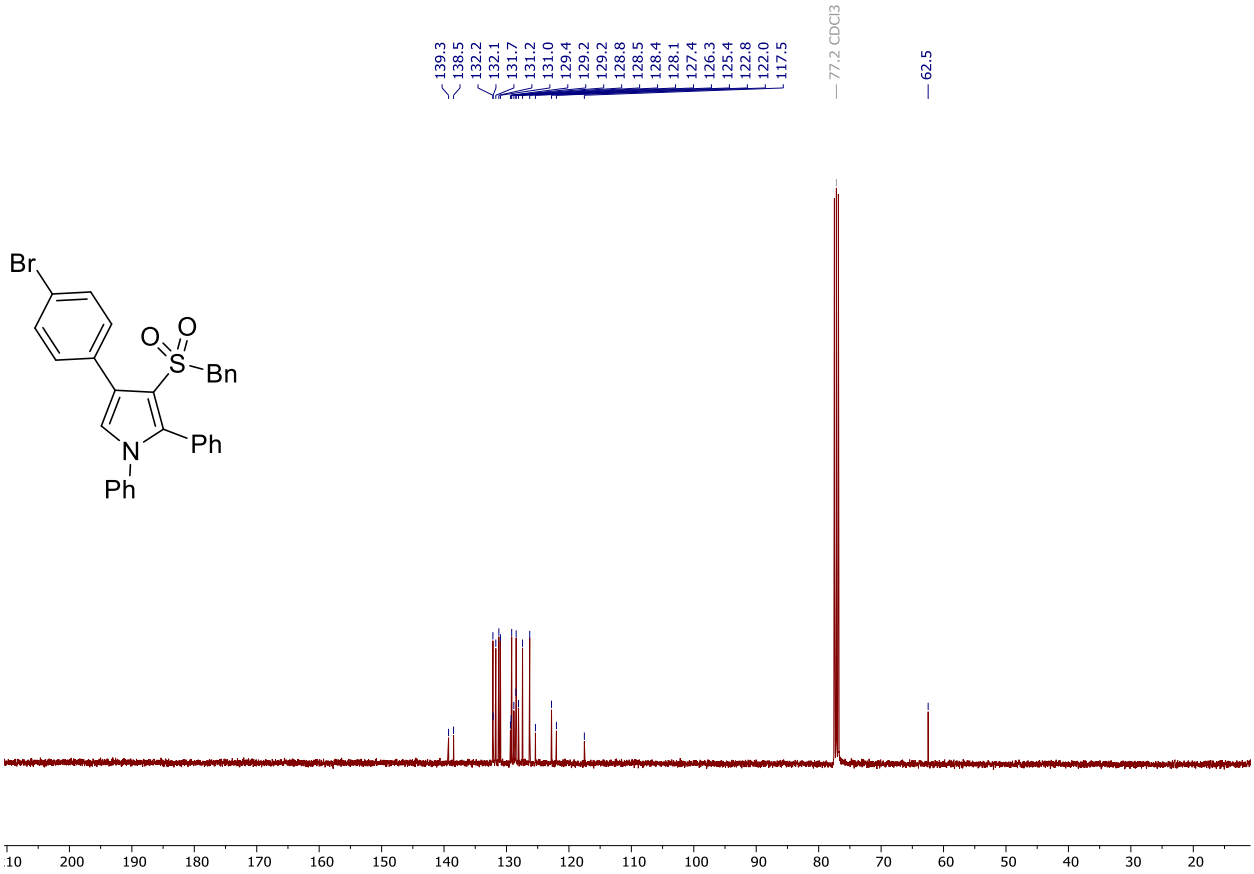
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **3m**



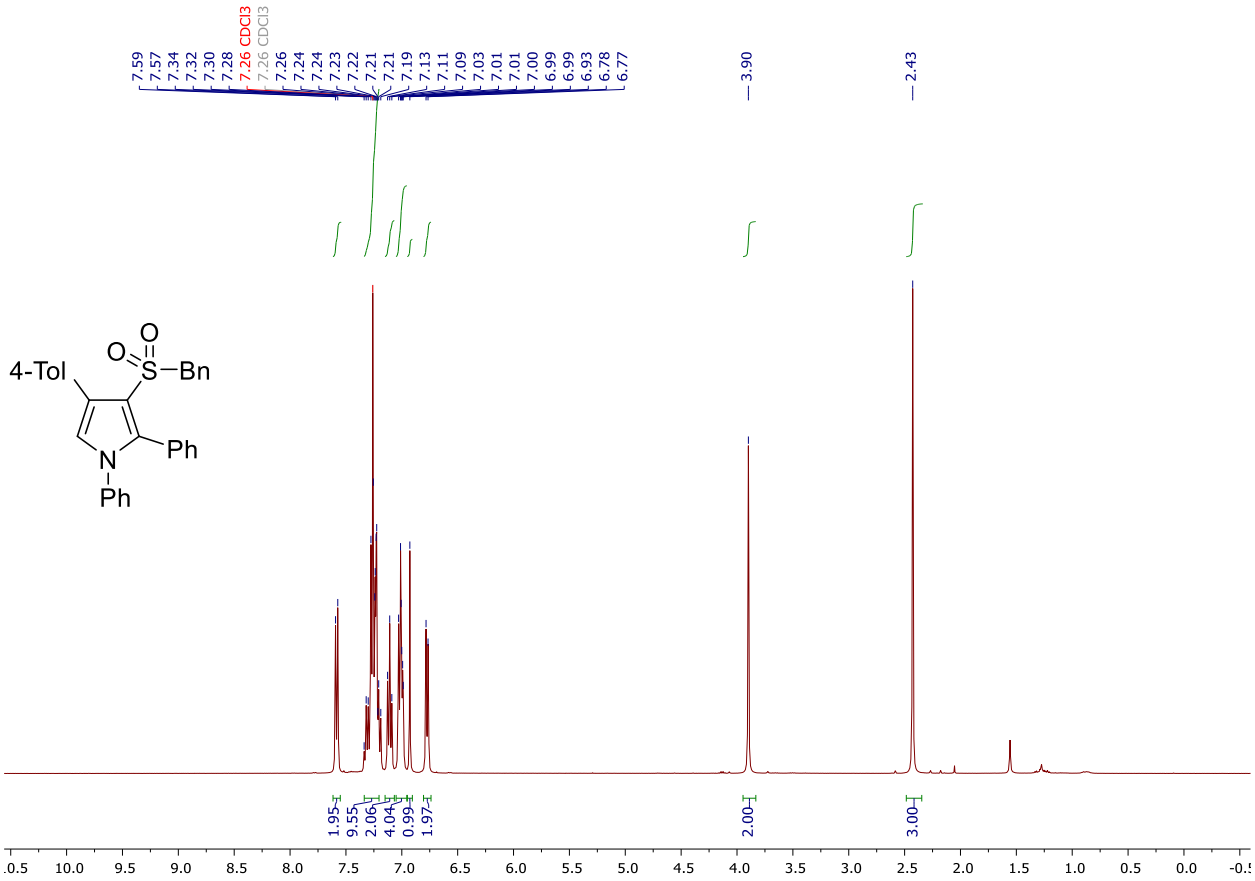
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



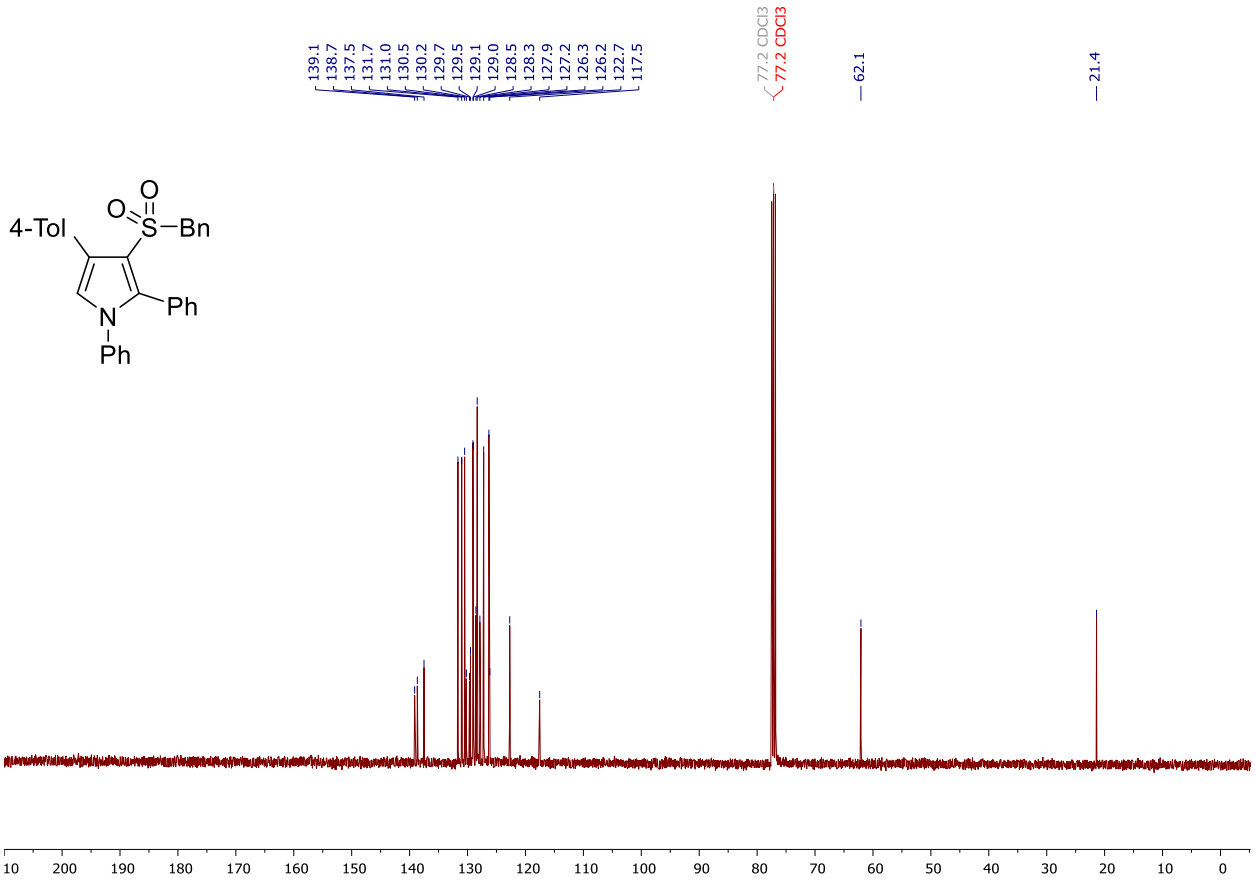
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3n**



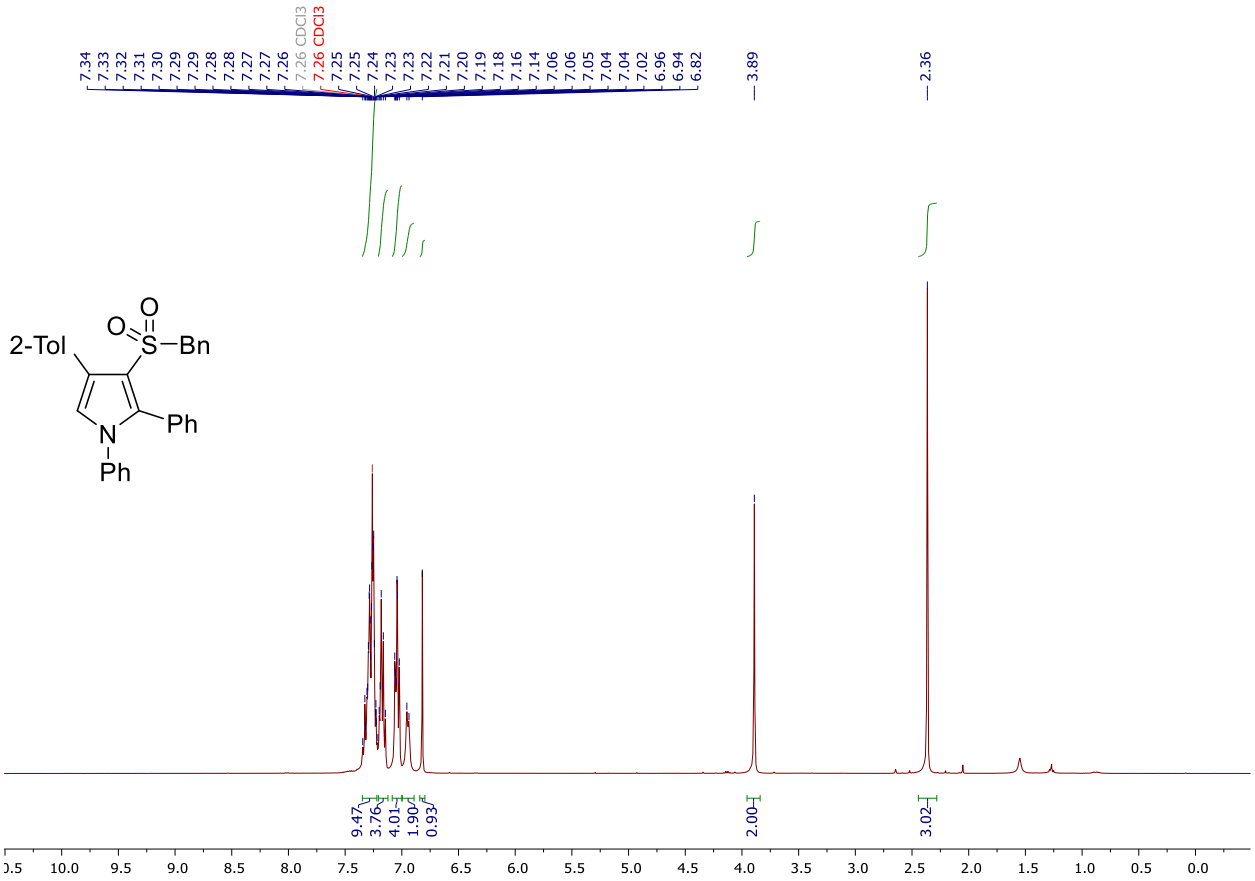
^{1}H NMR (400 MHz, $CDCl_3$) of **3o**



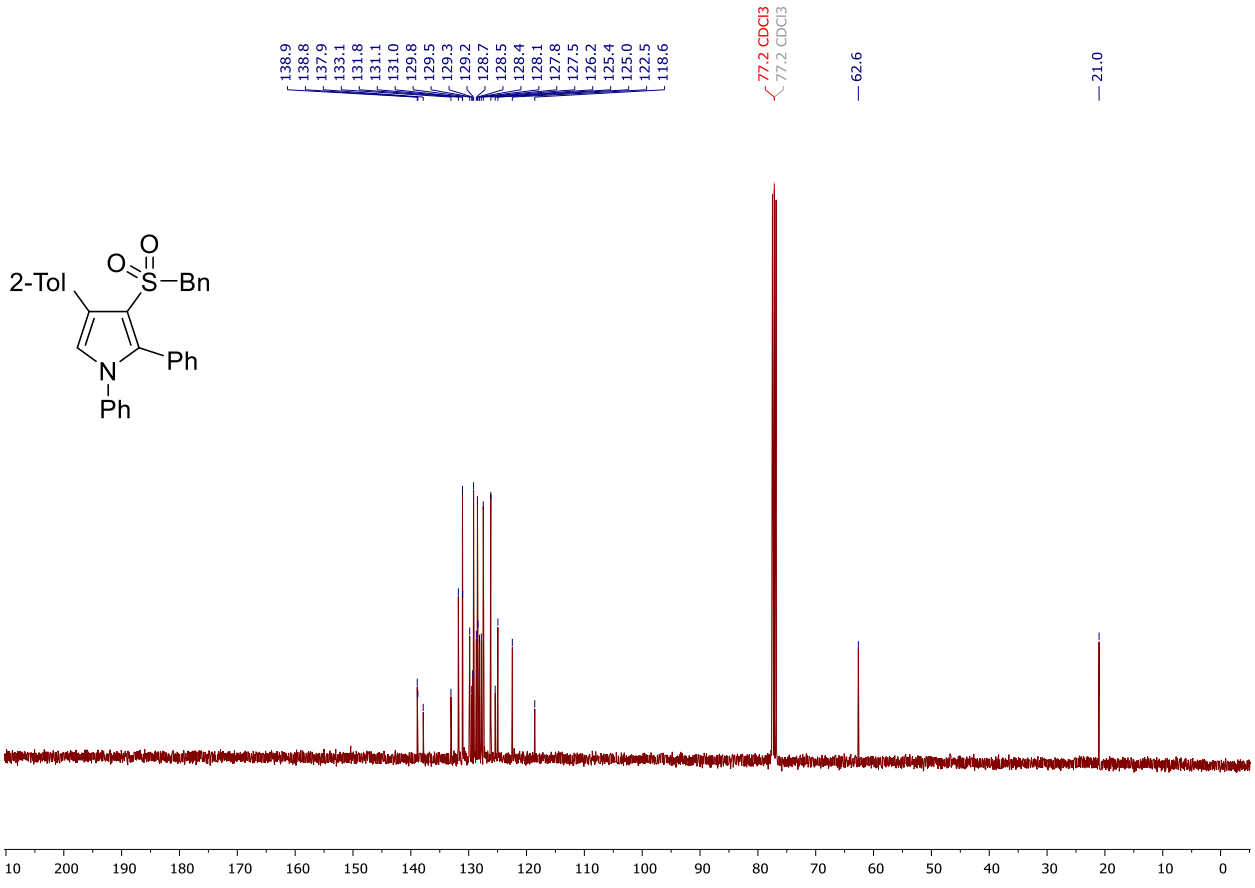
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3o**



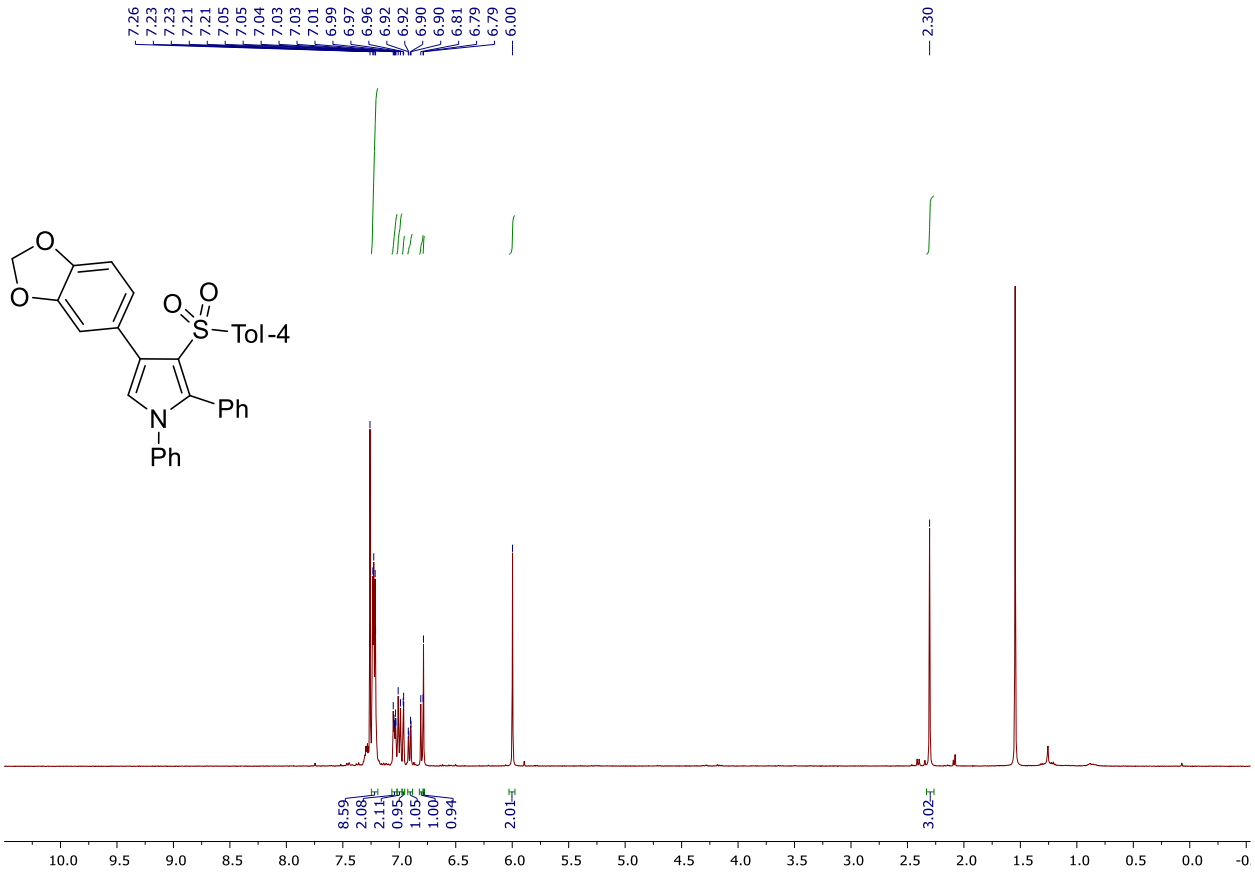
^{1}H NMR (400 MHz, $CDCl_3$) of **3p**



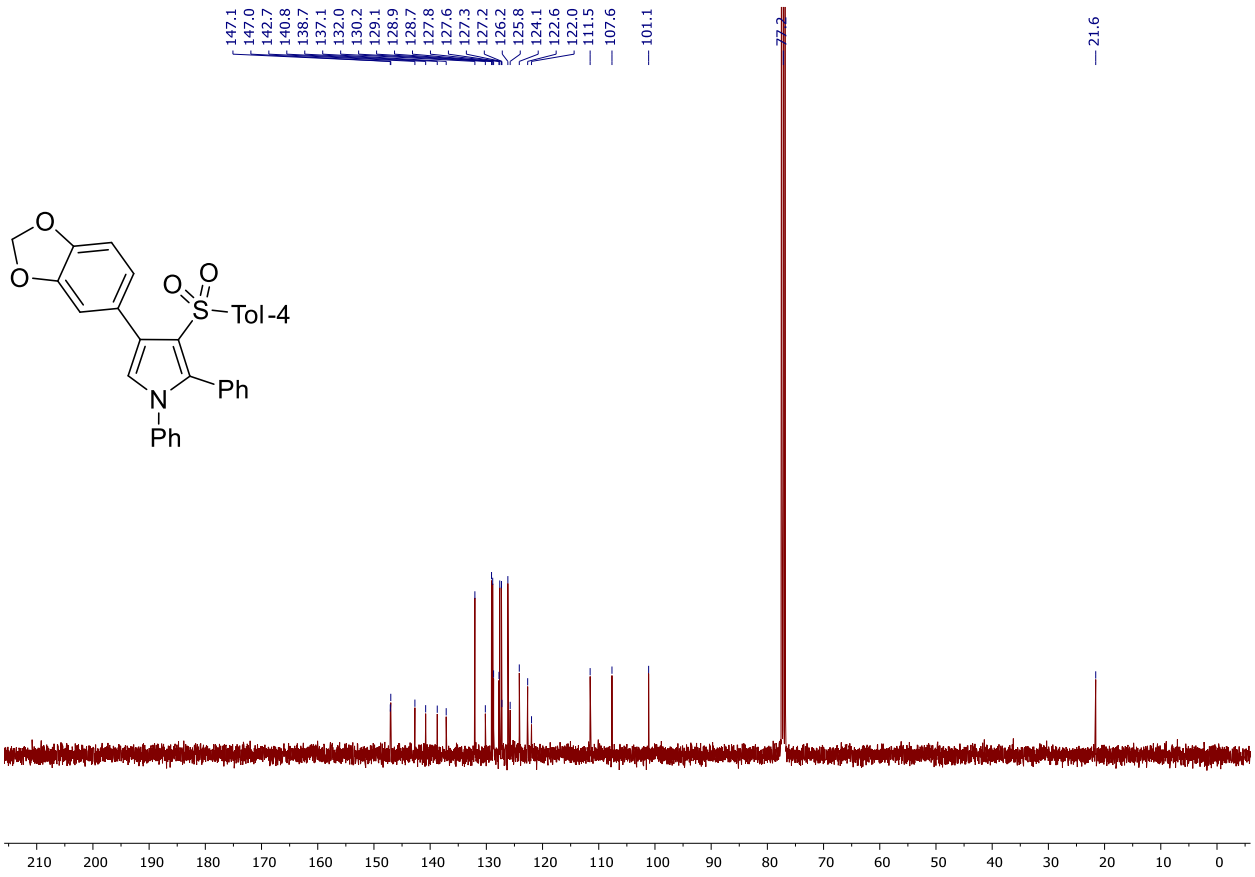
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3p**



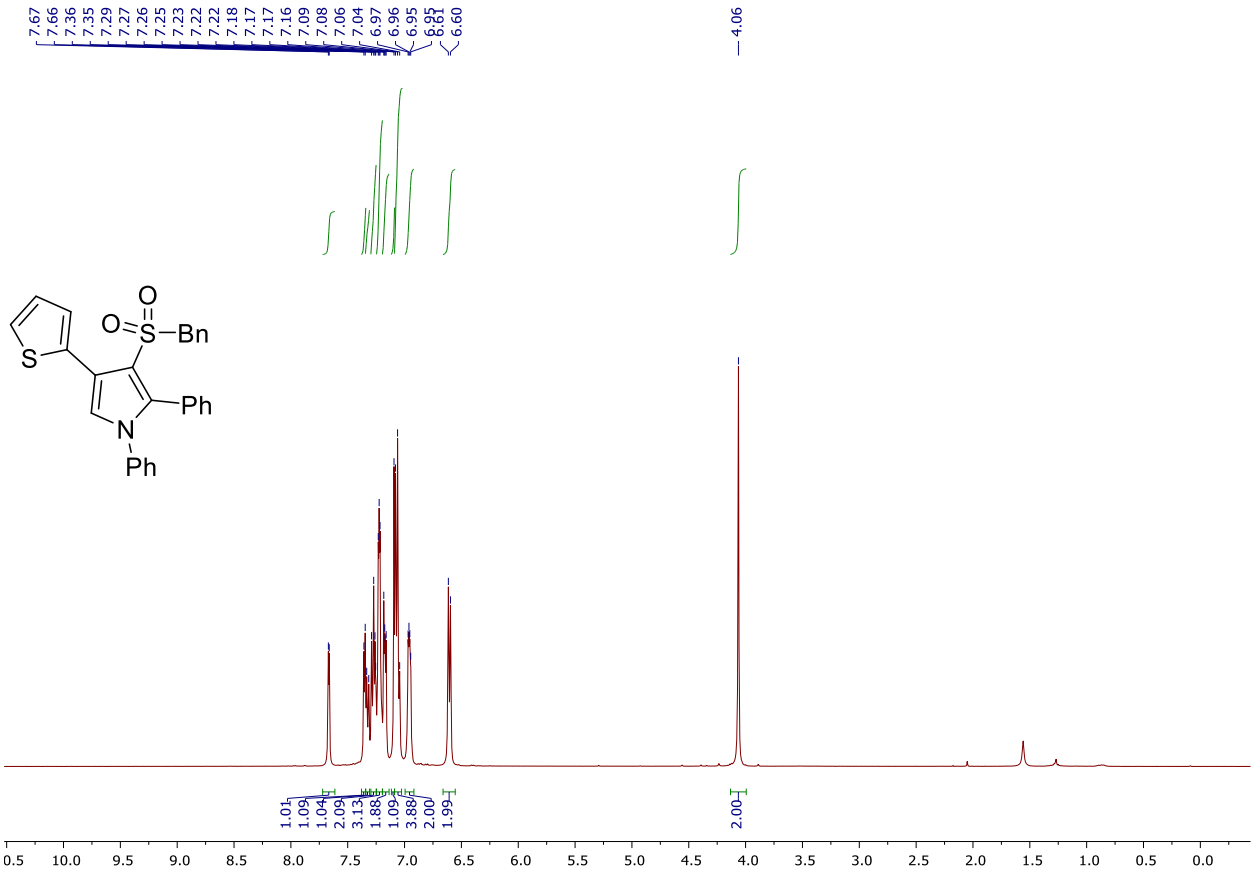
^{1}H NMR (400 MHz, $CDCl_3$) of **3q**



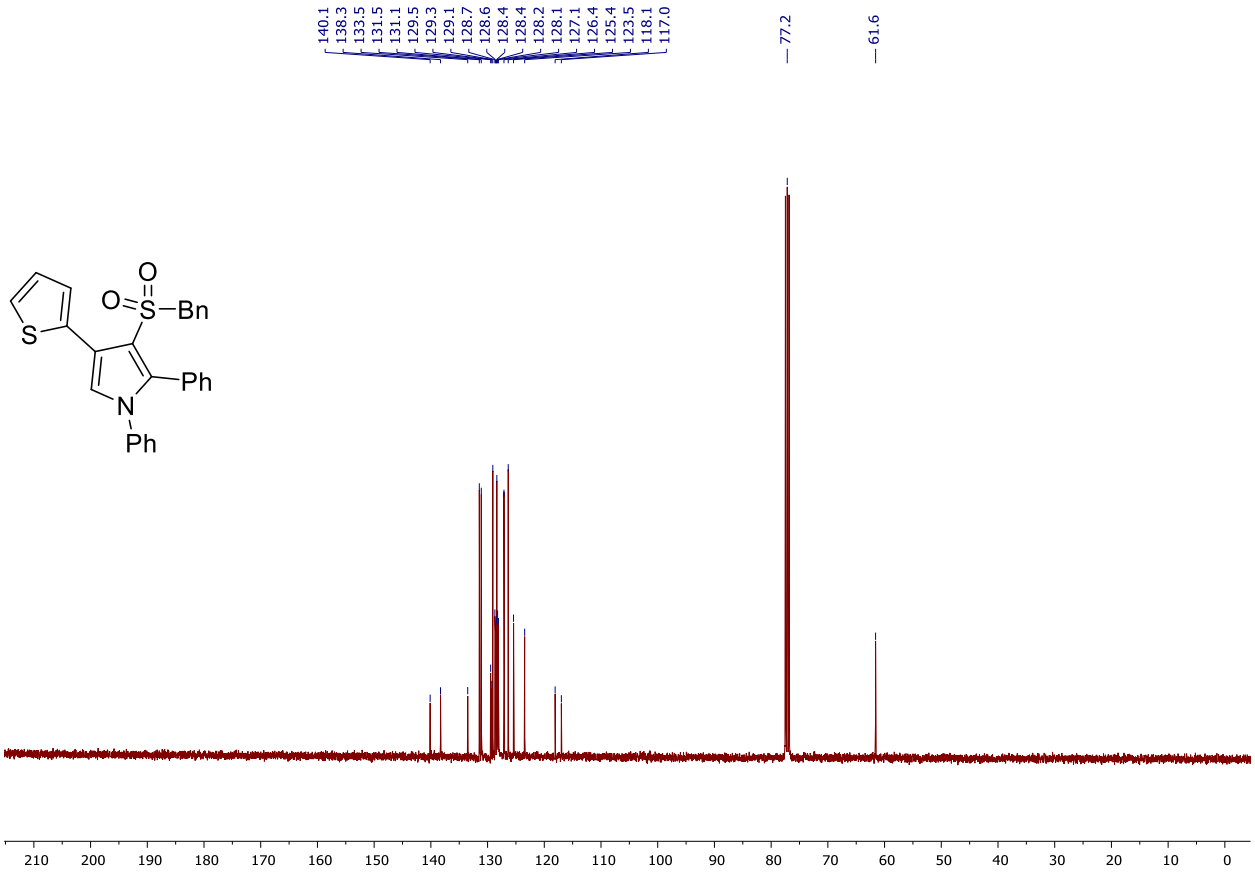
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3q**



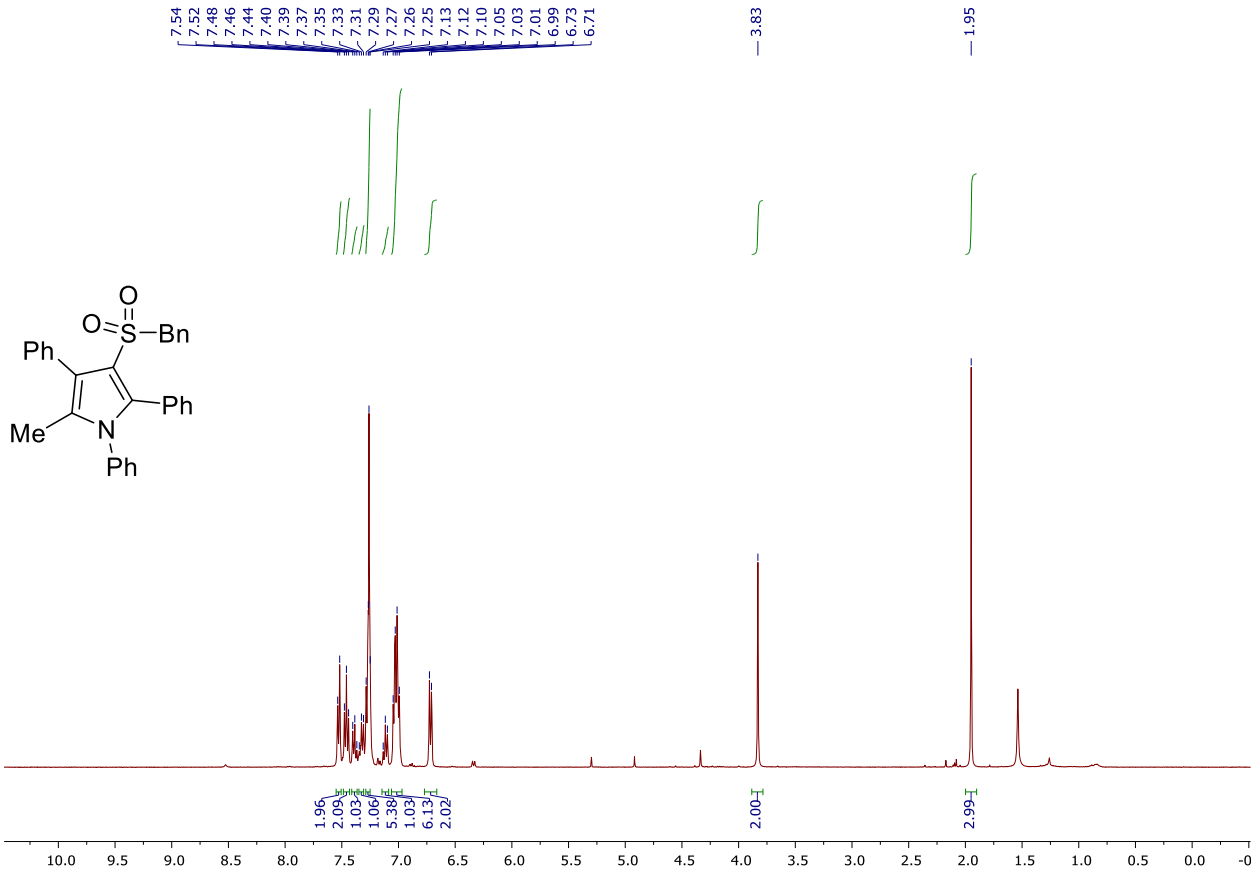
^{1}H NMR (400 MHz, $CDCl_3$) of **3r**



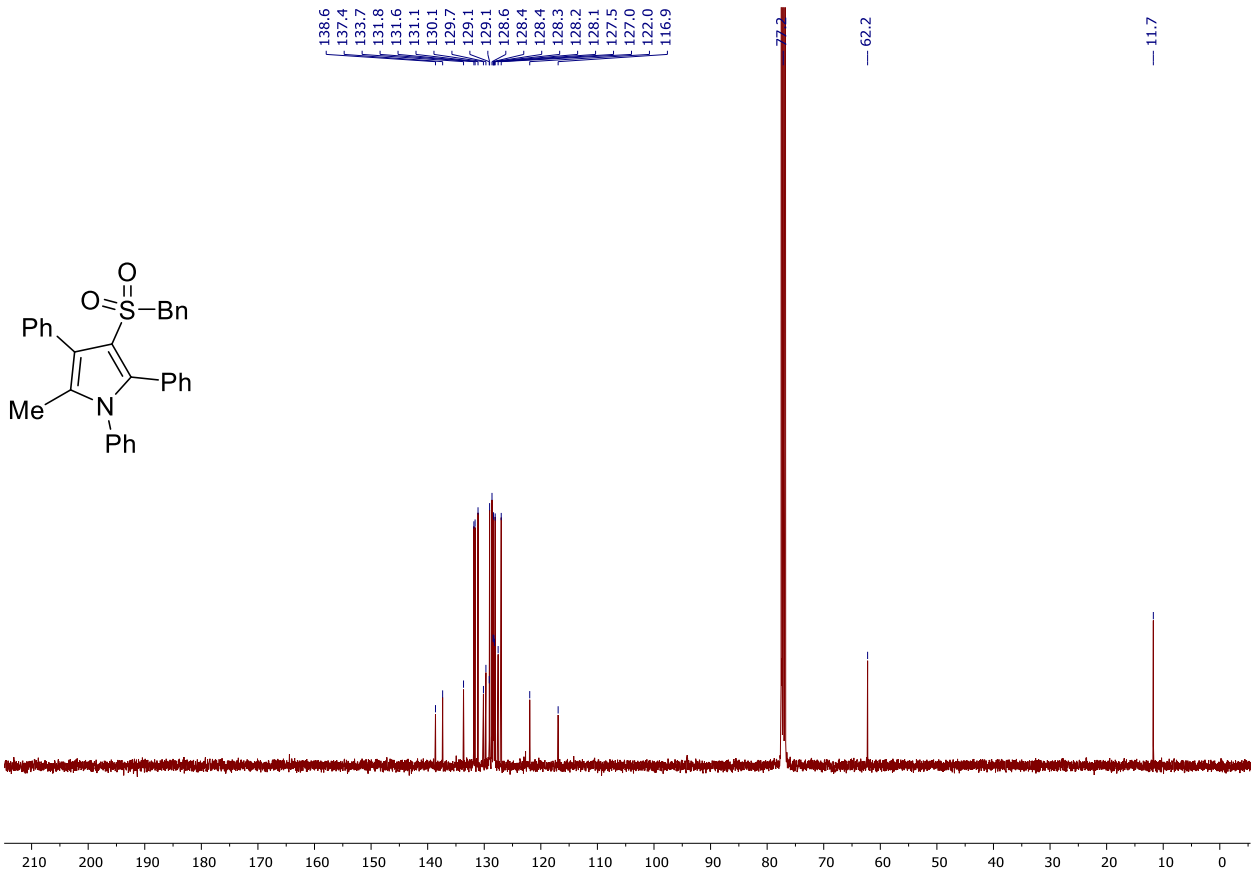
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3r**



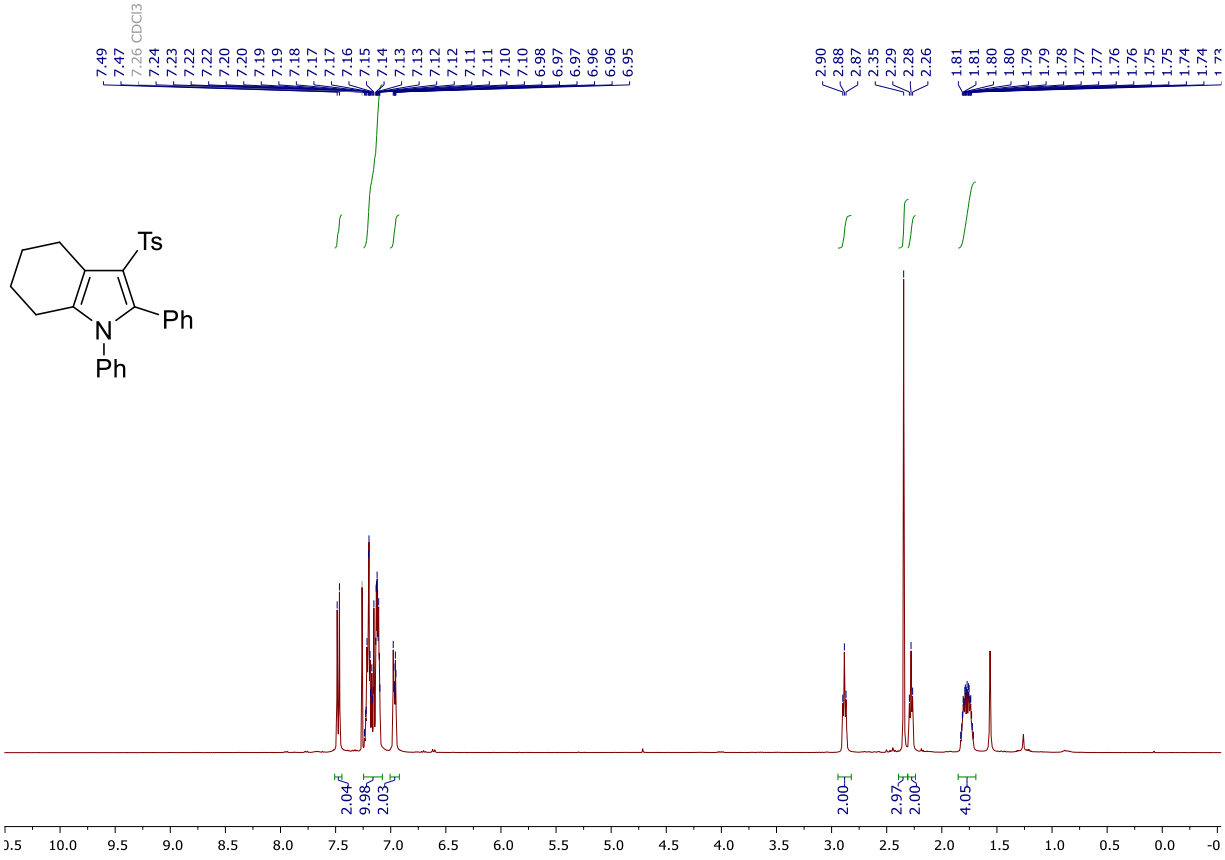
^{1}H NMR (400 MHz, $CDCl_3$) of **3s**



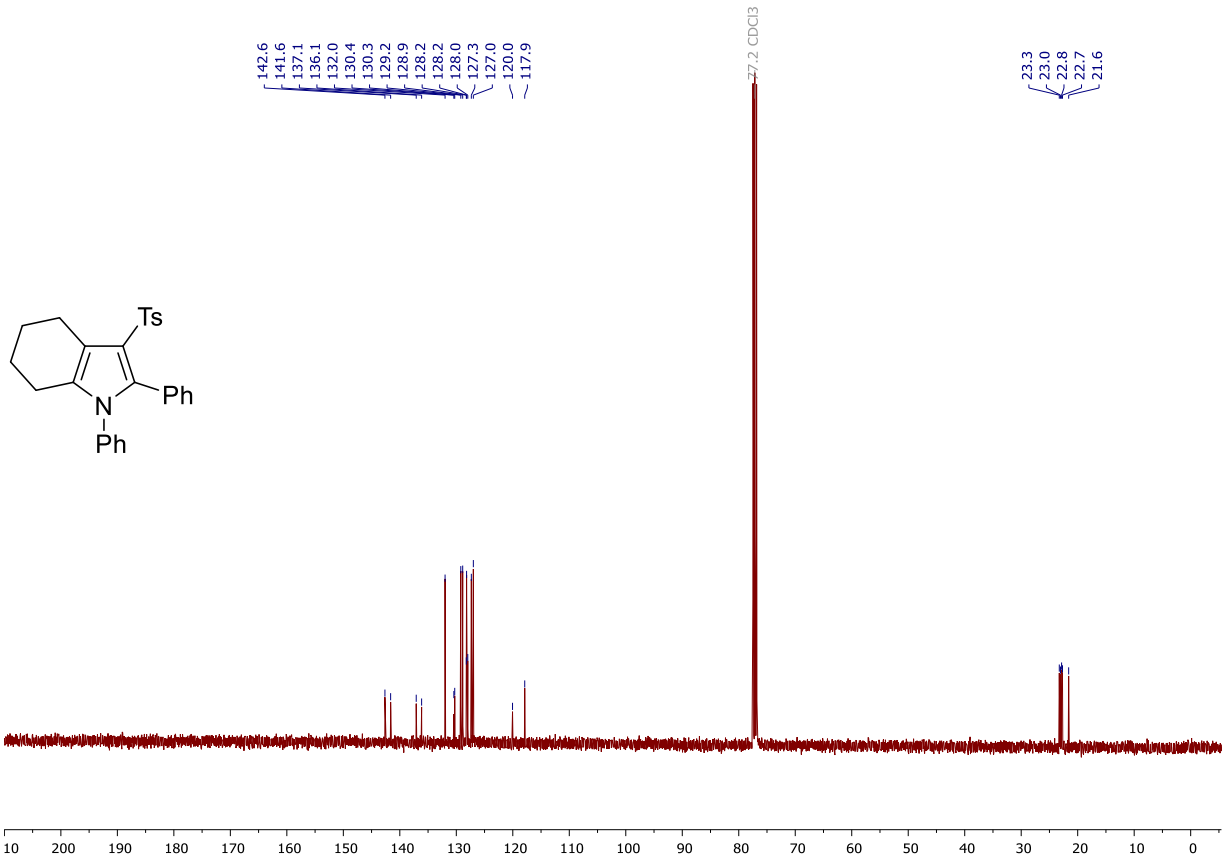
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3s**



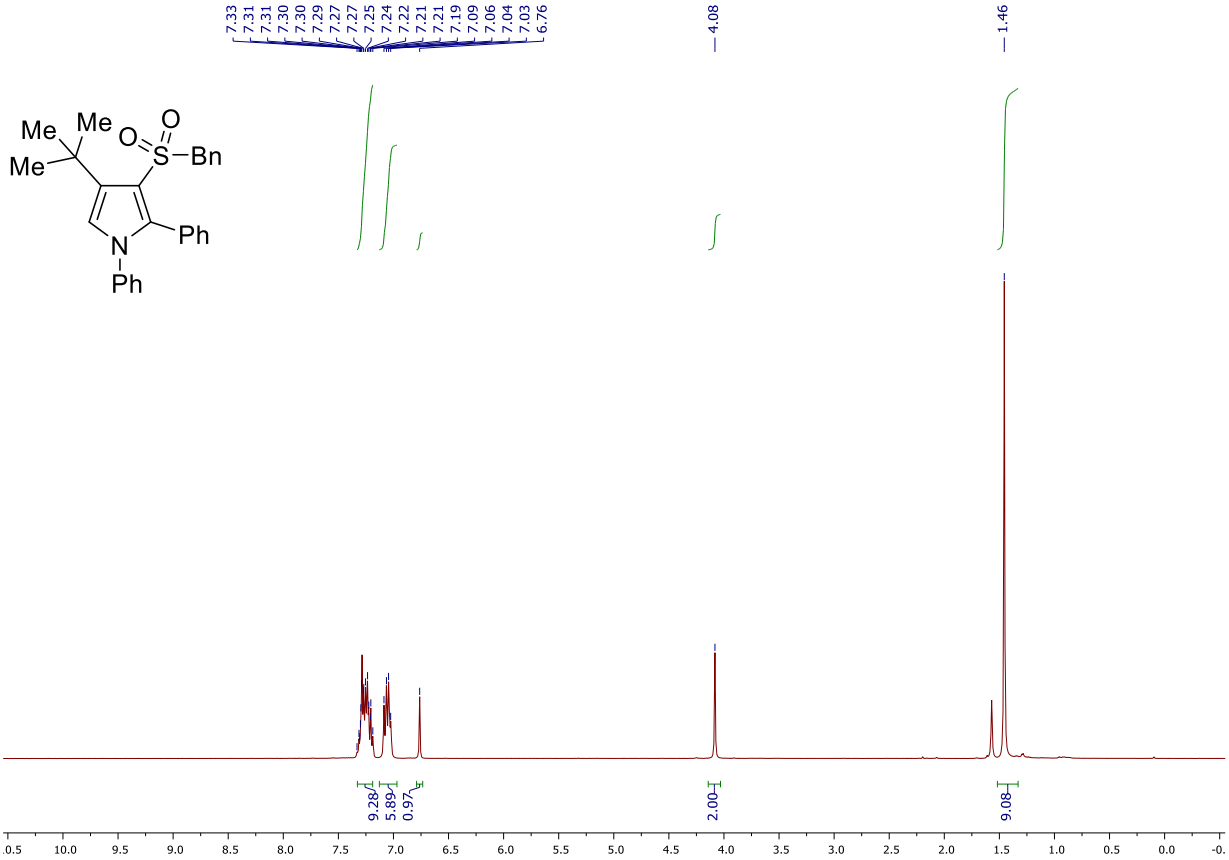
^{1}H NMR (400 MHz, $CDCl_3$) of **3t**



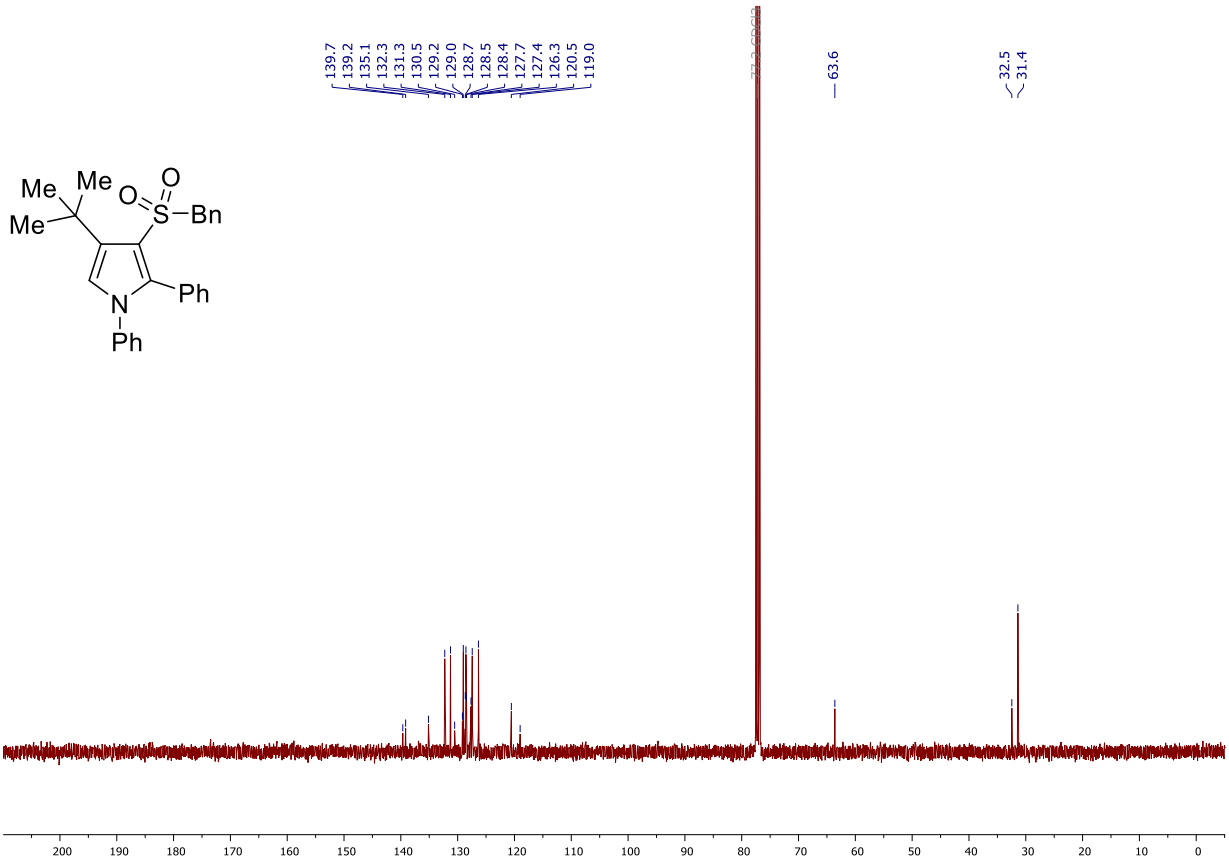
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3t**



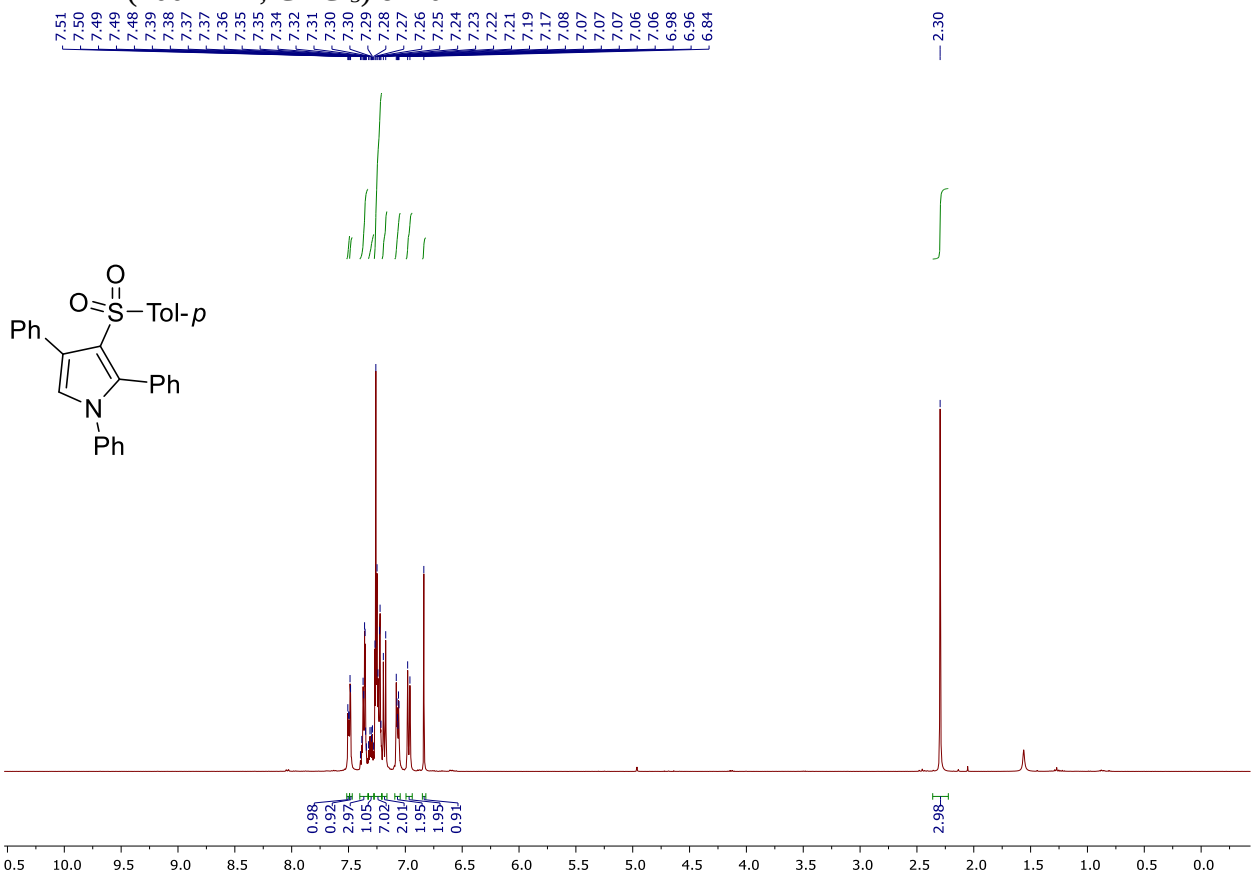
^{1}H NMR (400 MHz, $CDCl_3$) of **3u**



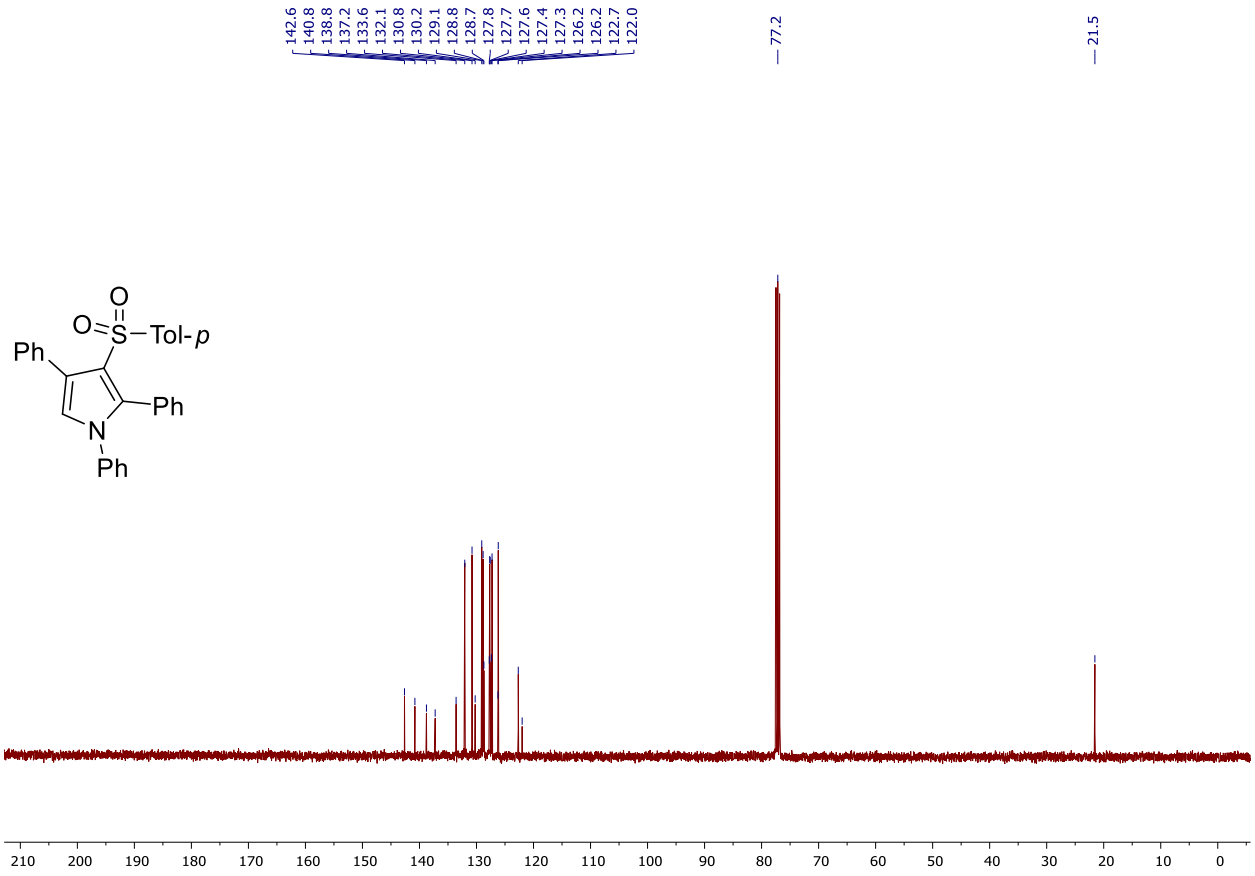
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **3u**



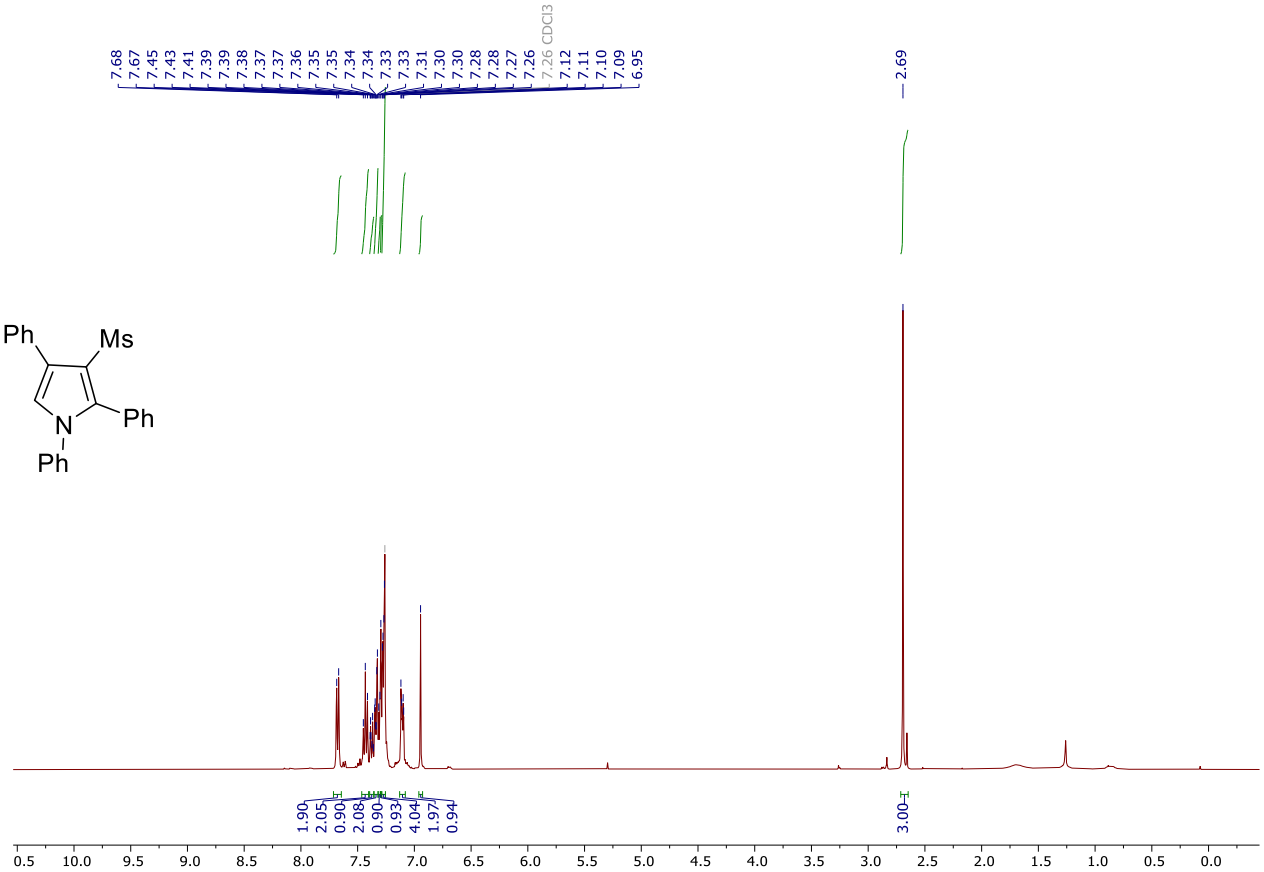
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



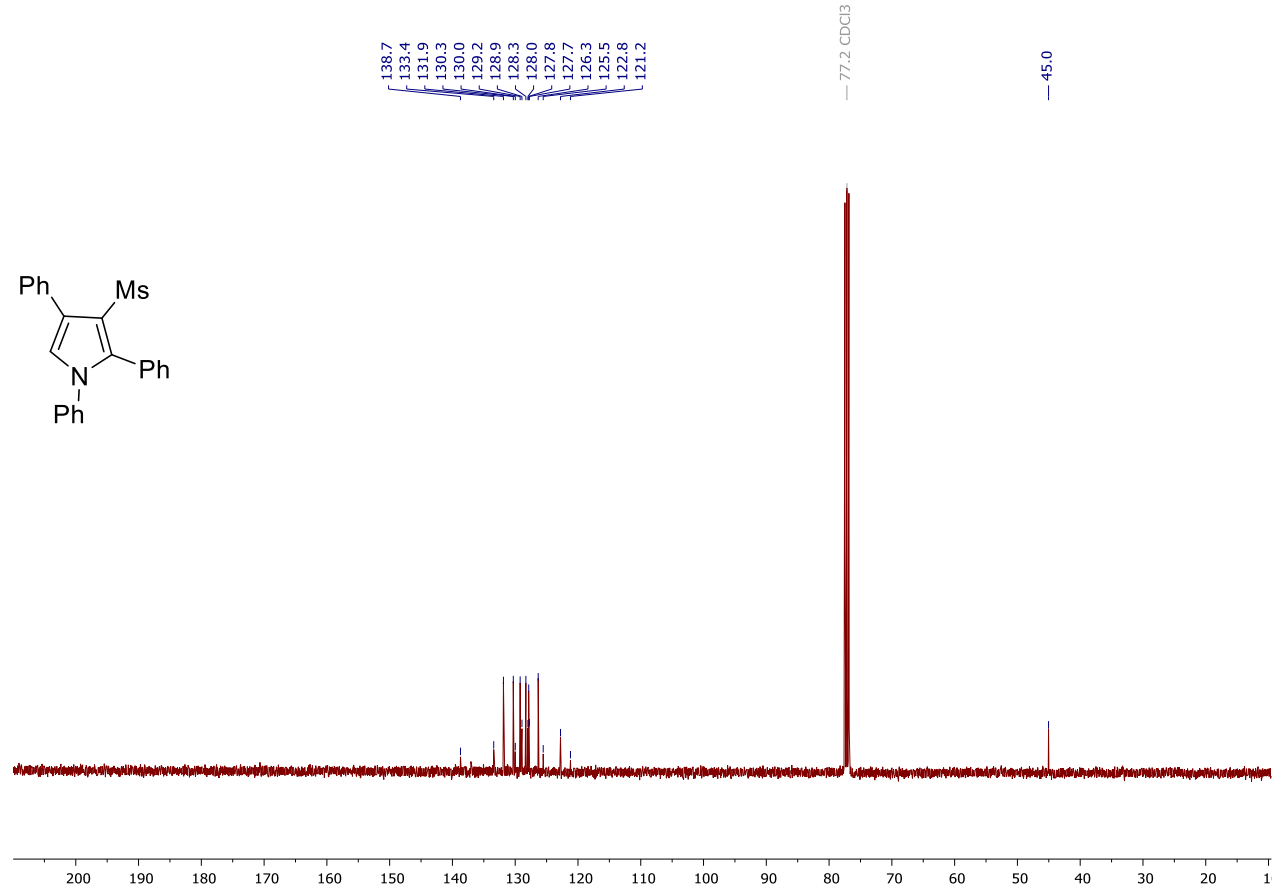
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4a**



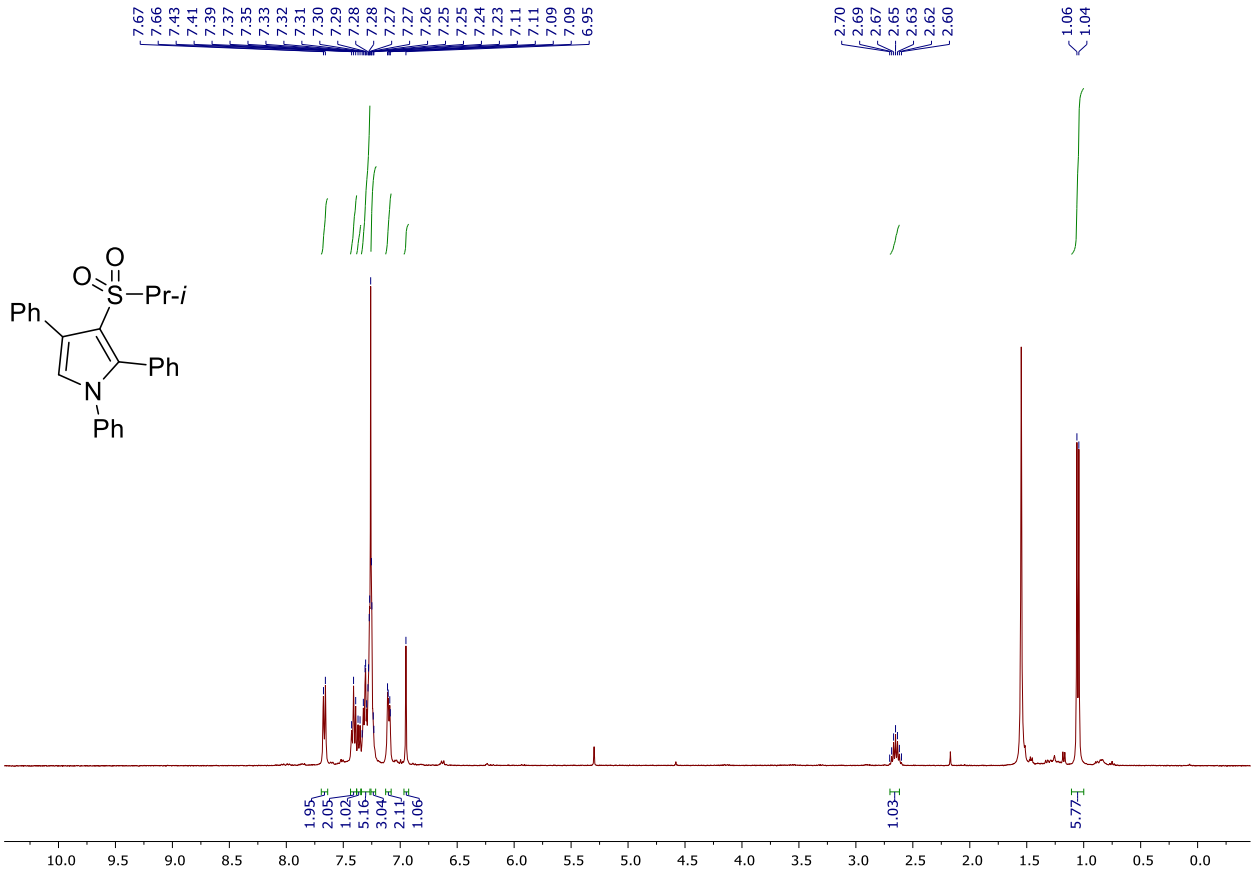
^{1}H NMR (400 MHz, $CDCl_3$) of **4b**



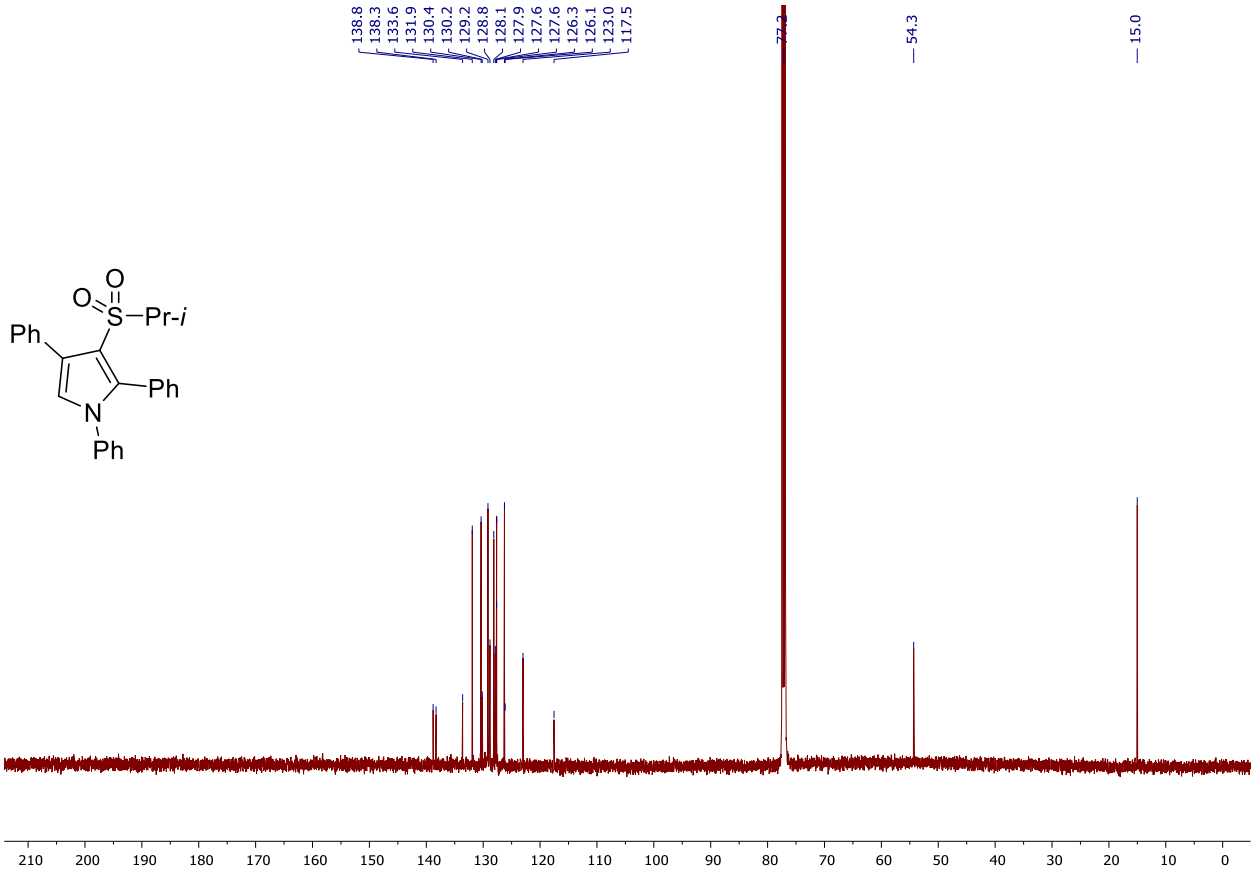
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4b**



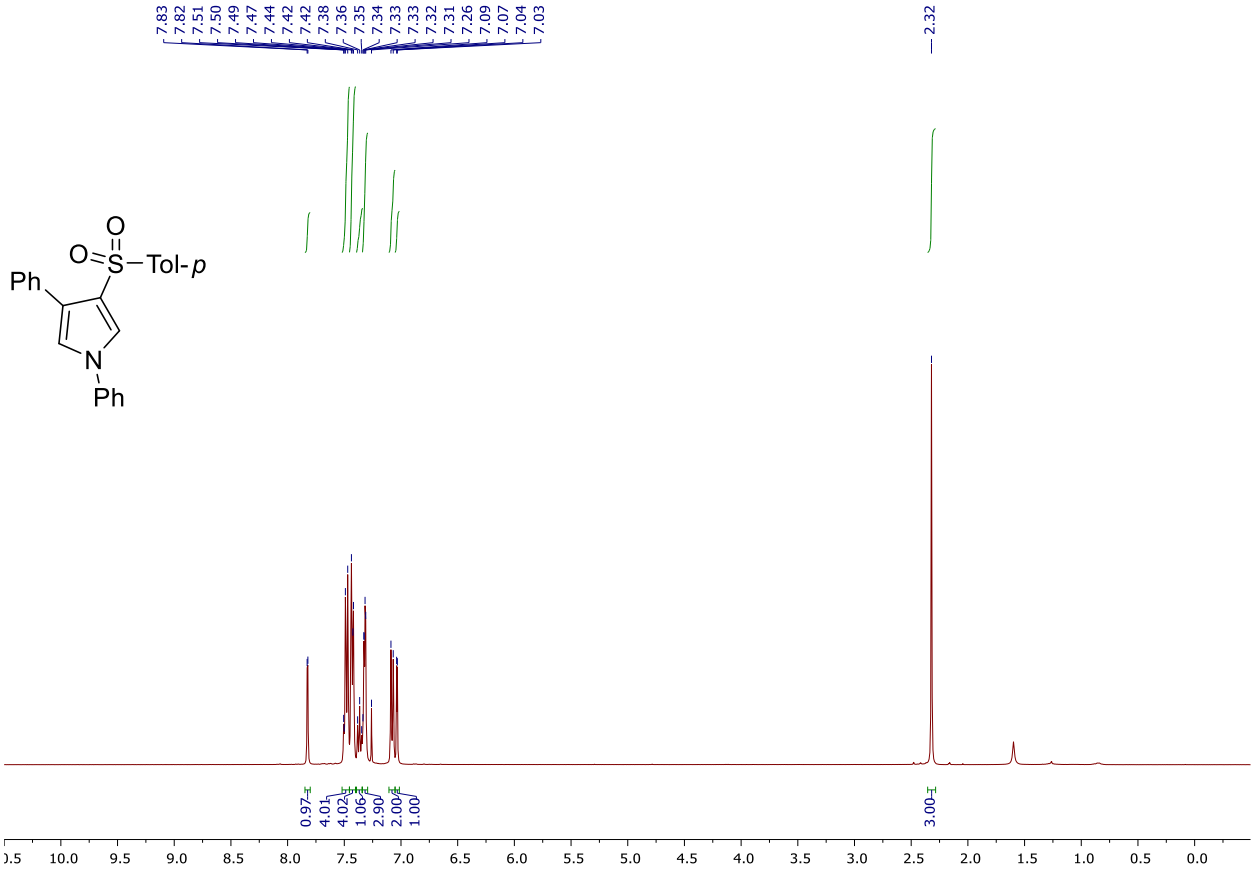
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**



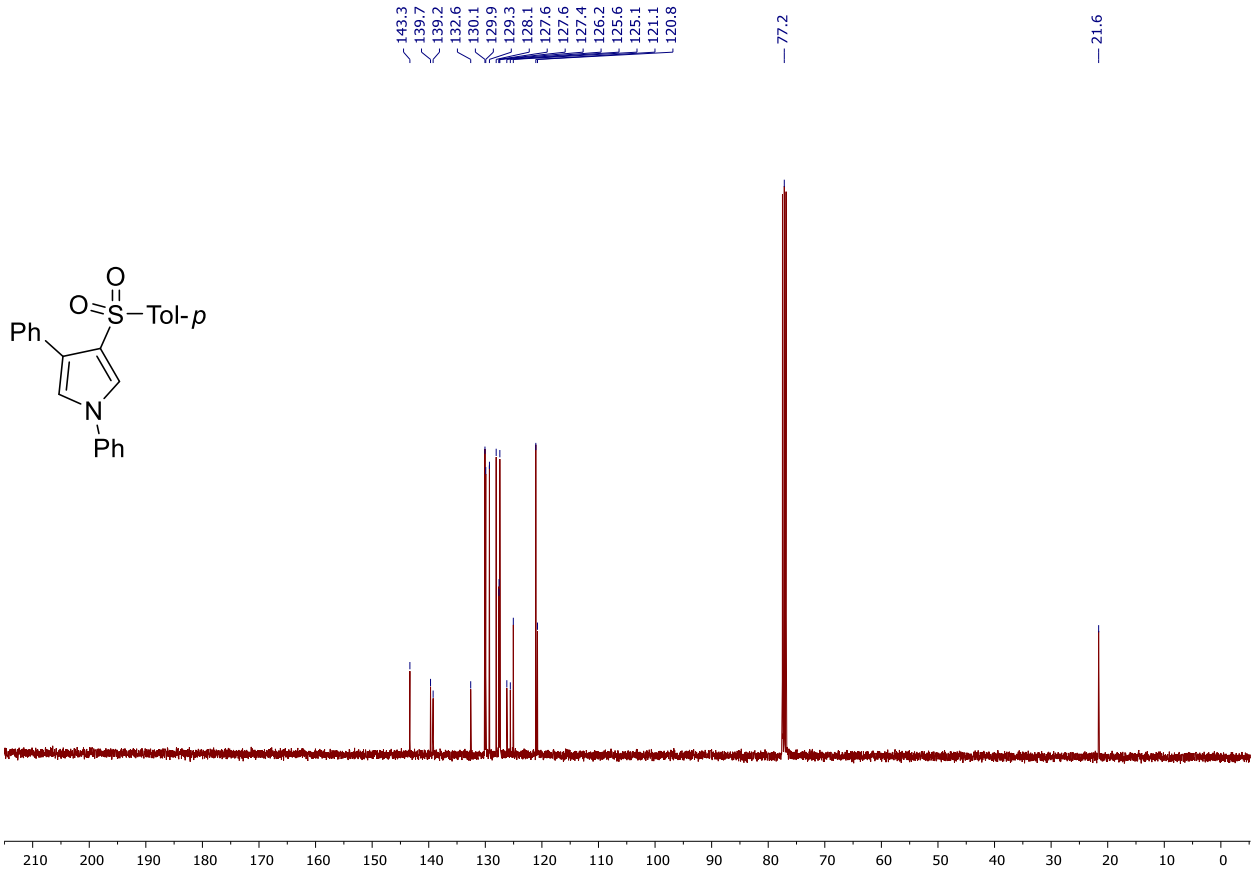
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4c**



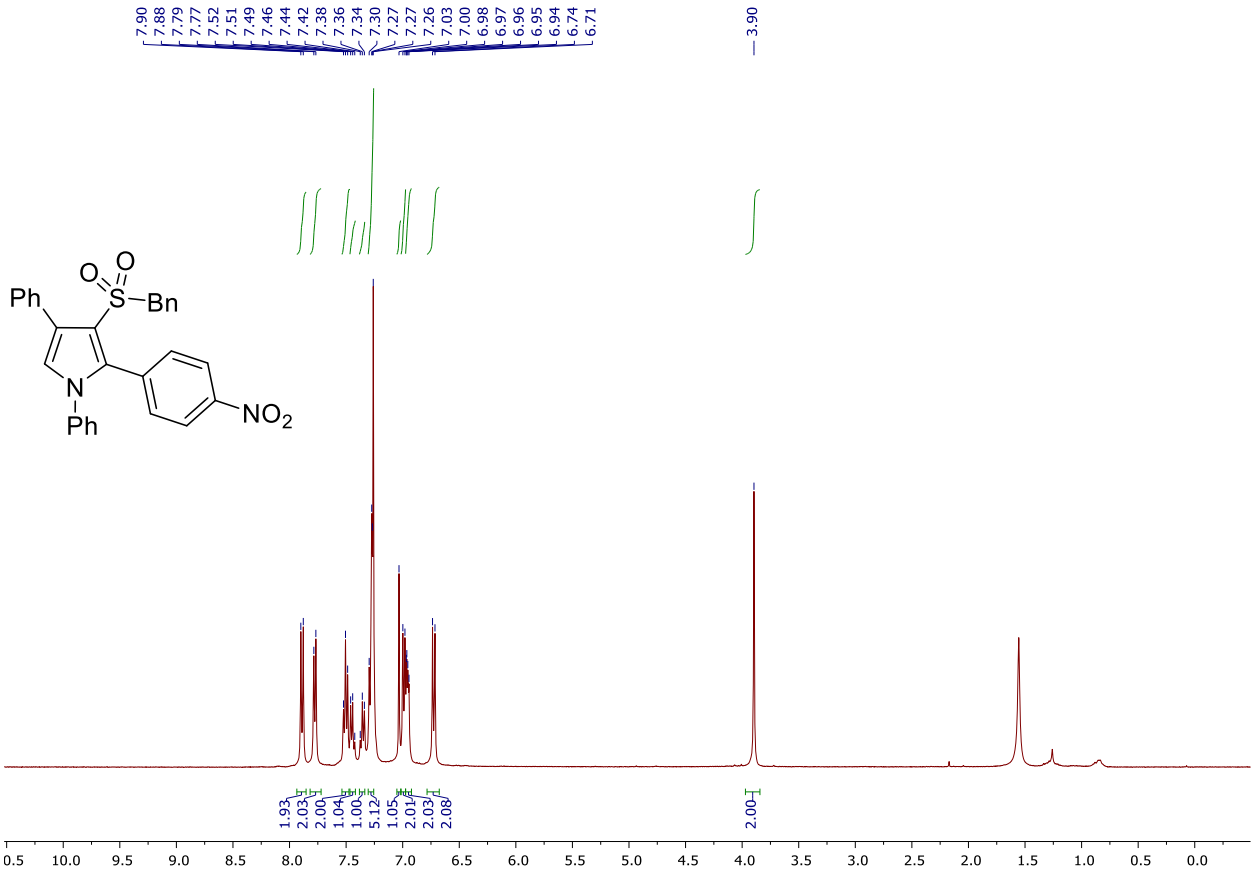
^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



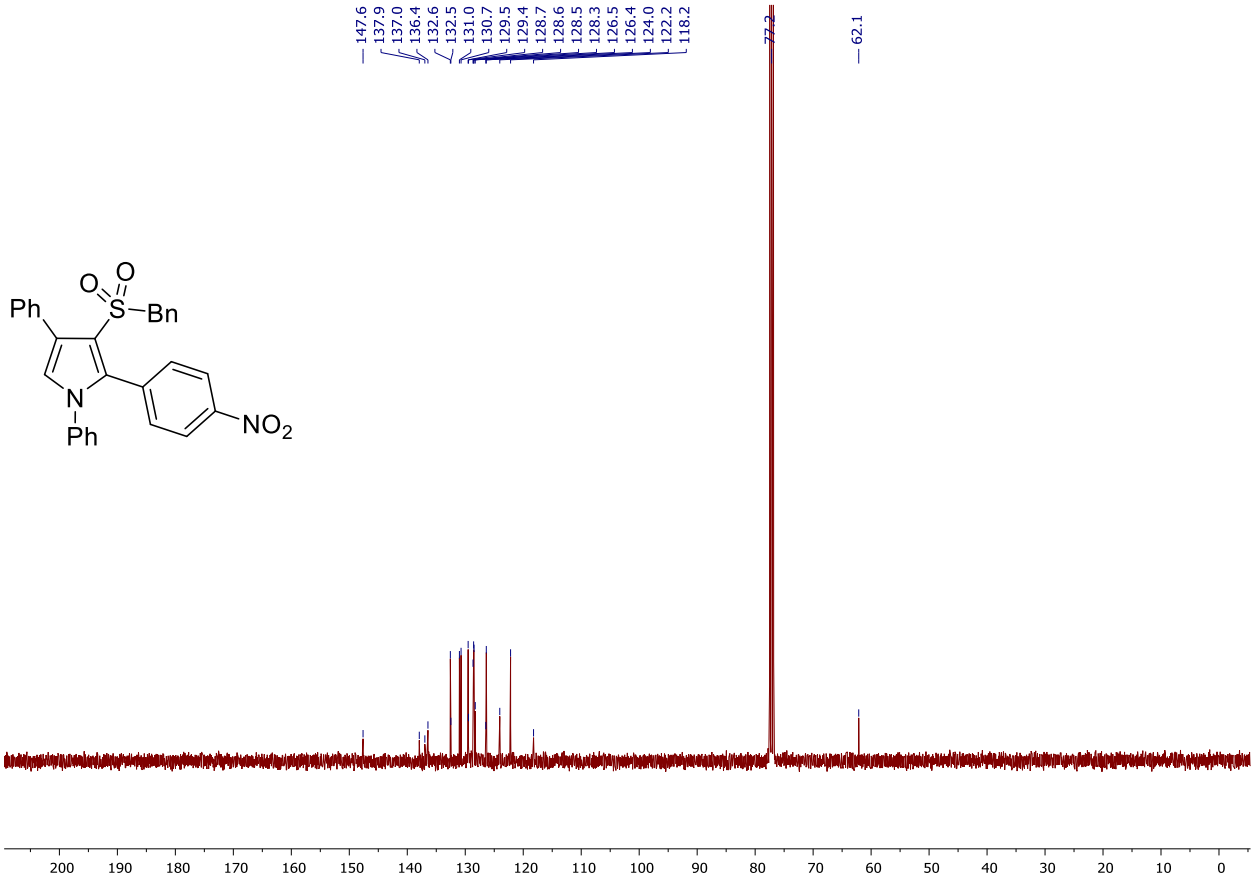
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4d**



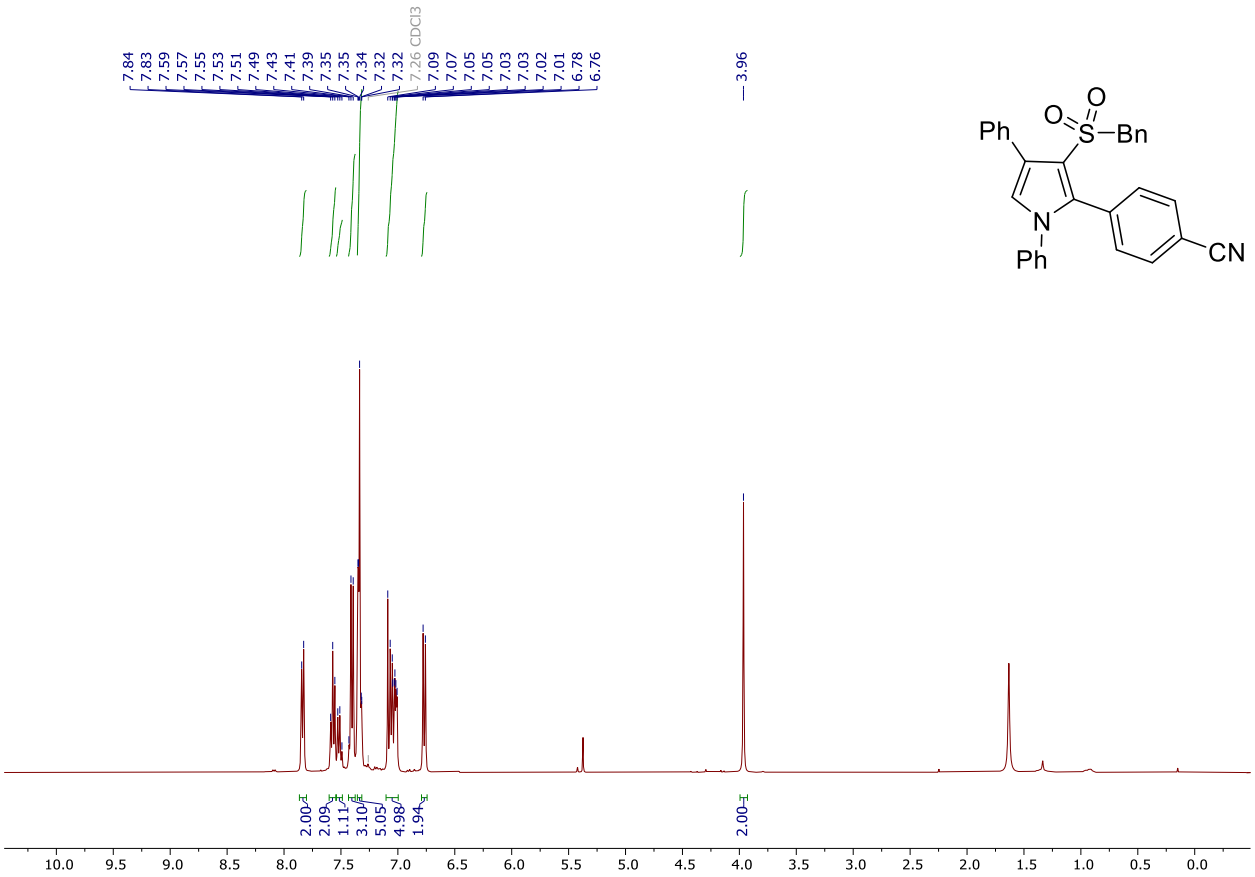
^{1}H NMR (400 MHz, $CDCl_3$) of **4e**



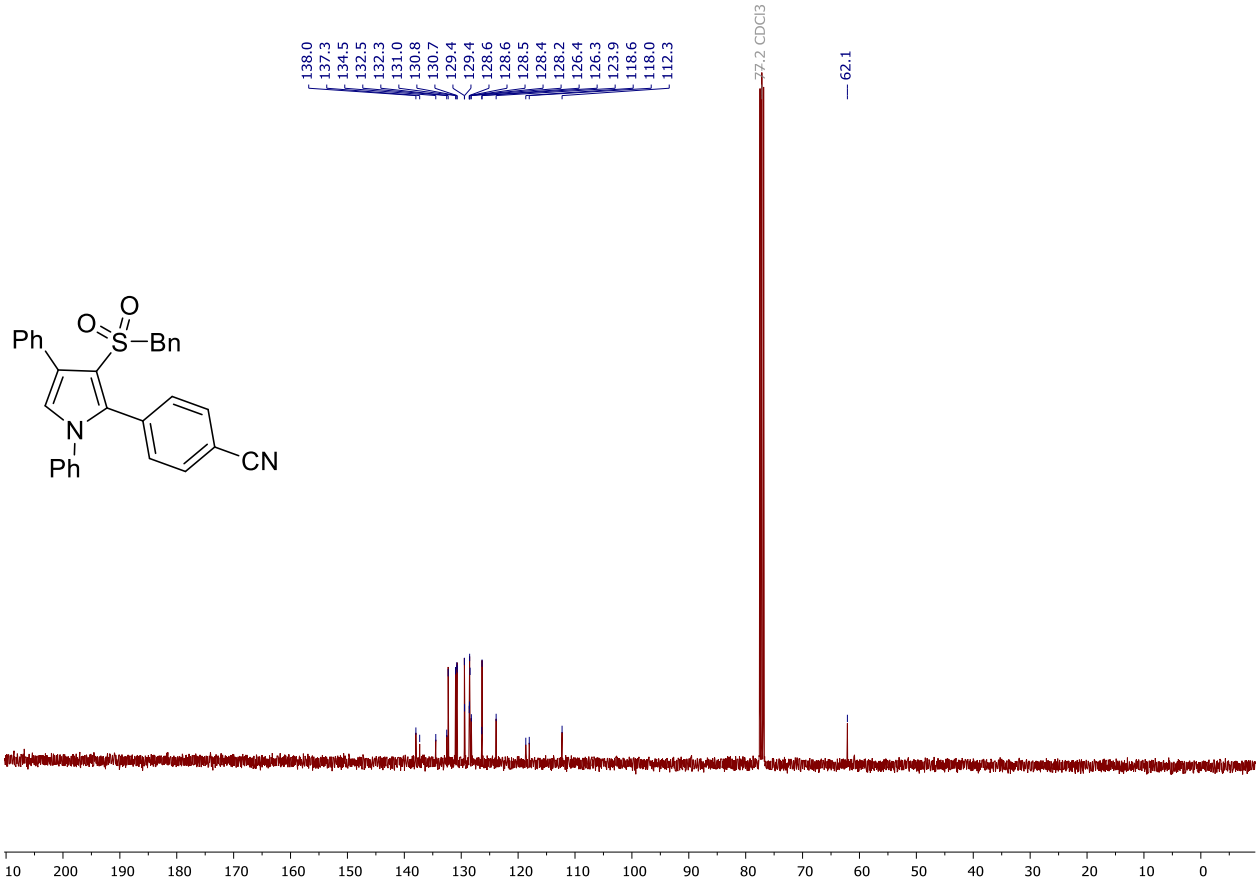
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4e**



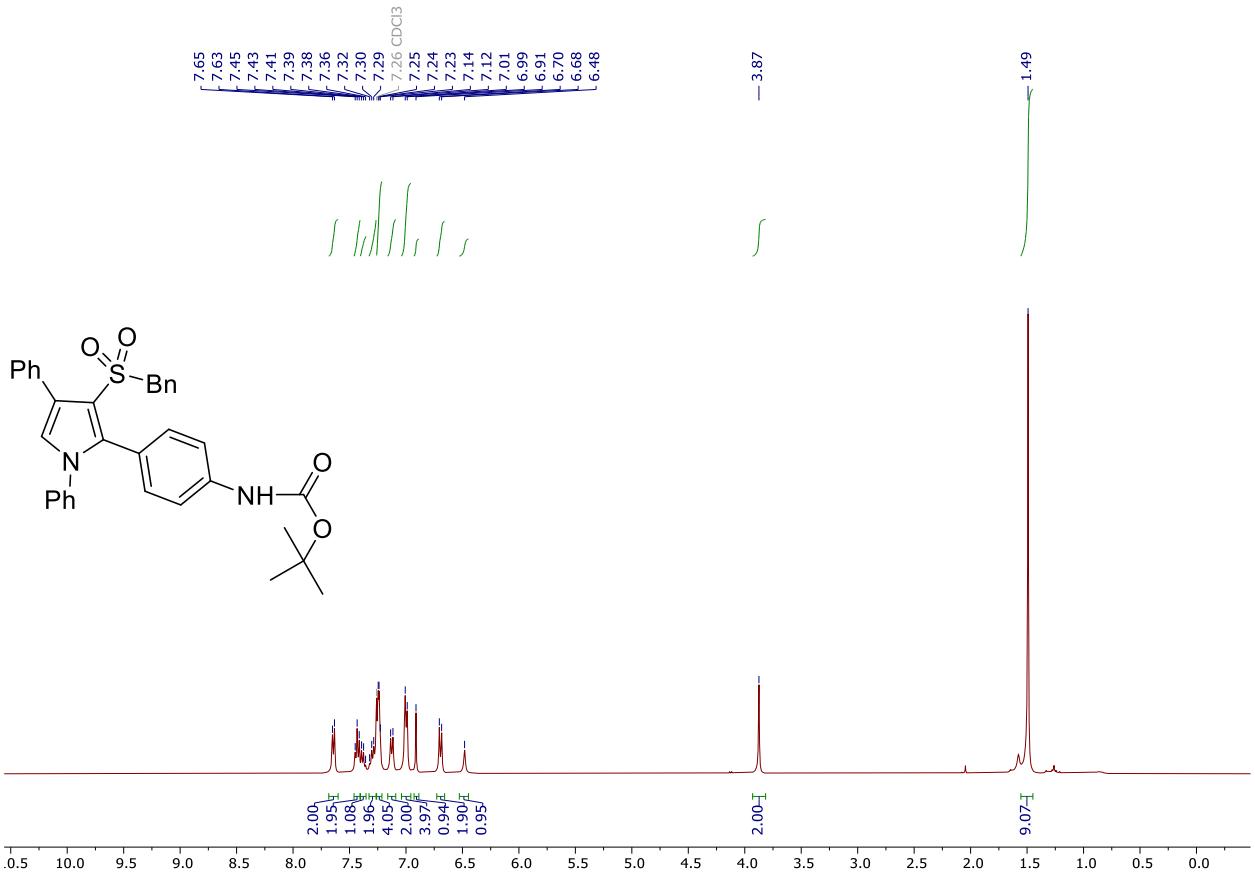
^{1}H NMR (400 MHz, $CDCl_3$) of **4f**



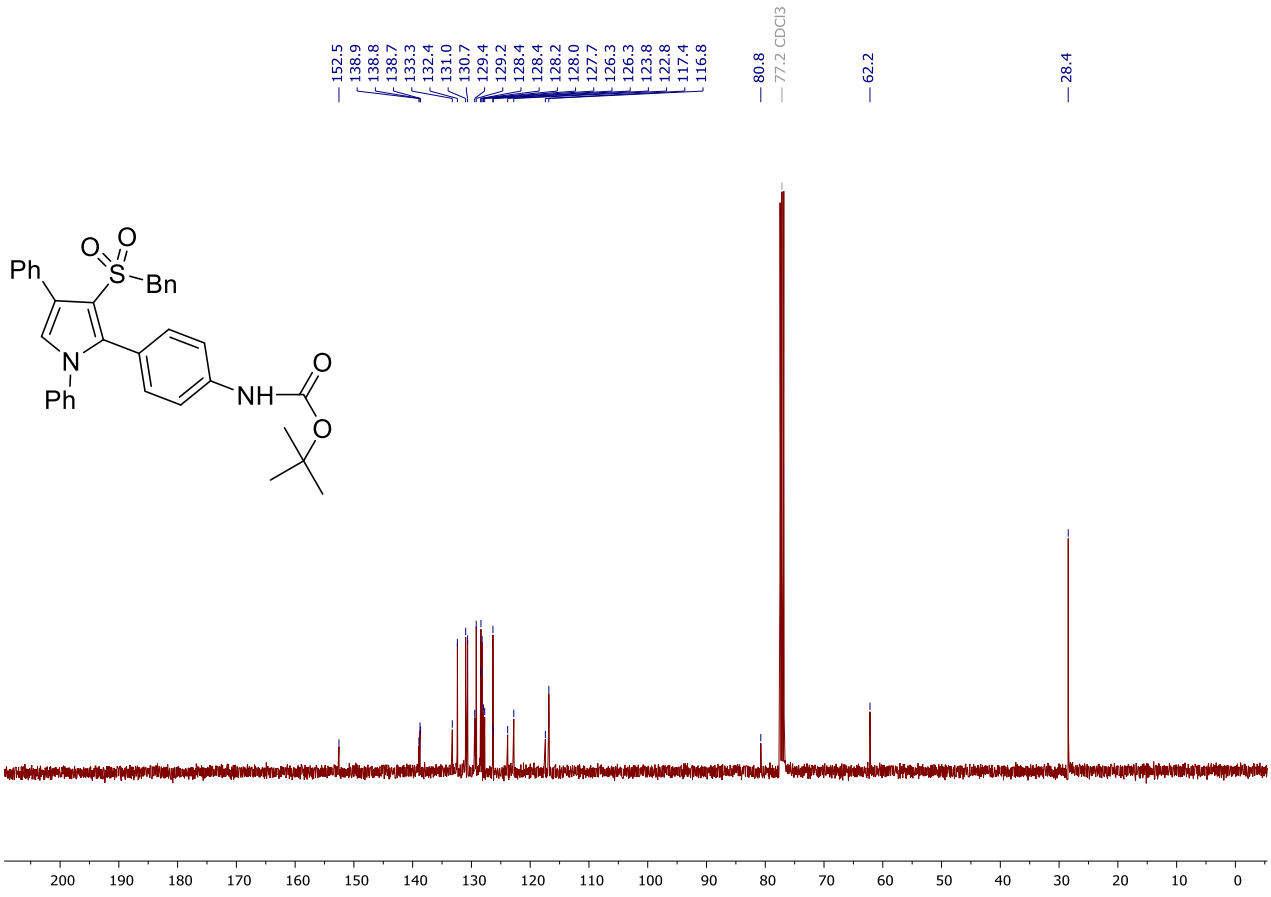
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4f**



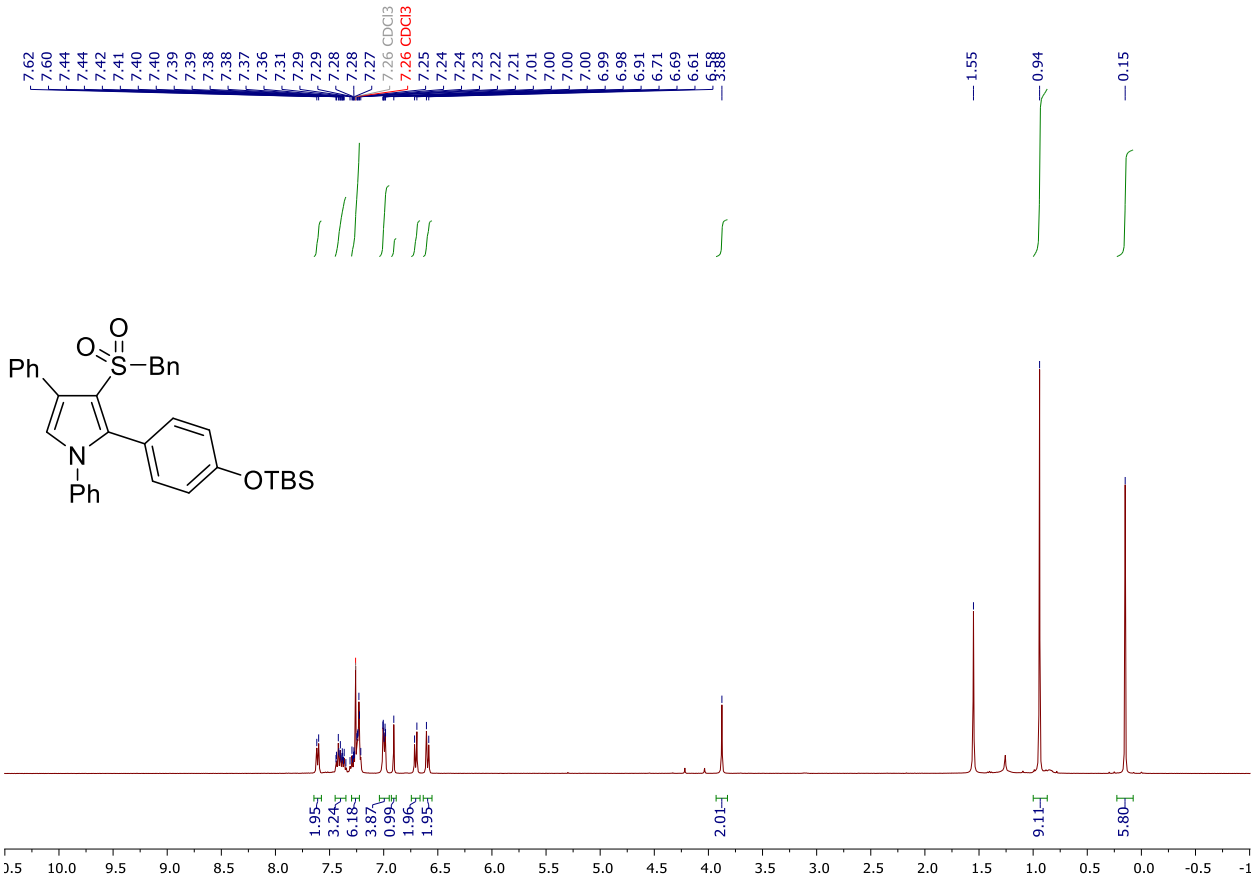
^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



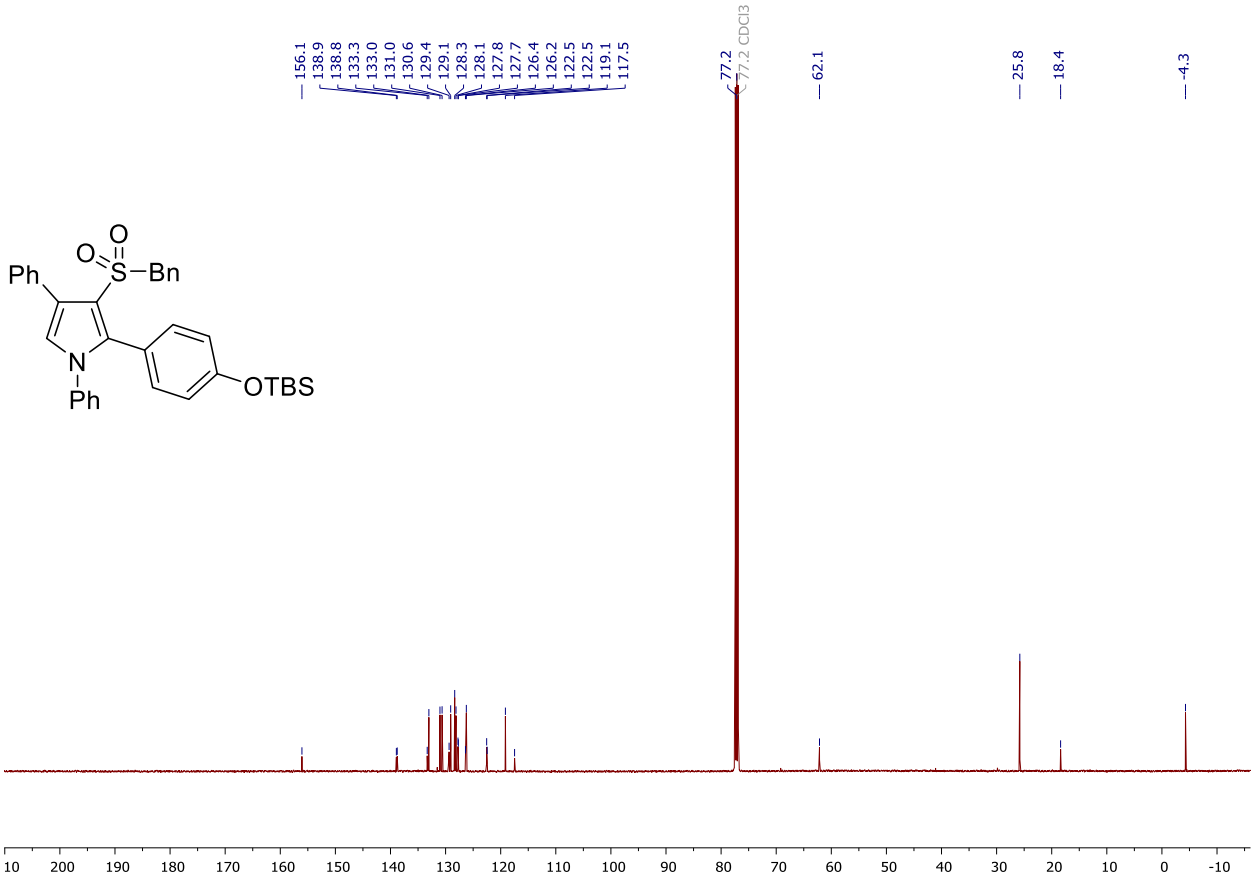
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4g**



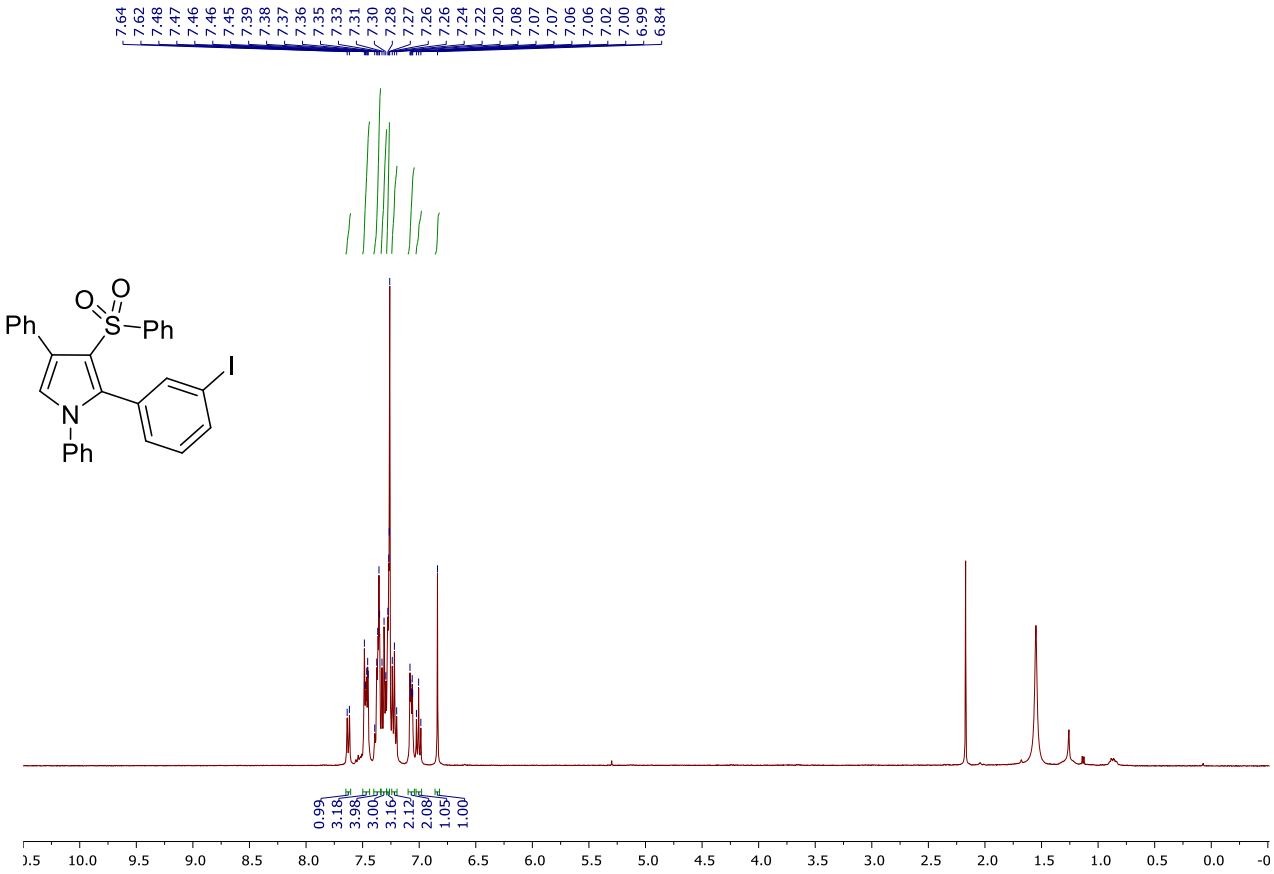
^{1}H NMR (400 MHz, $CDCl_3$) of **4h**



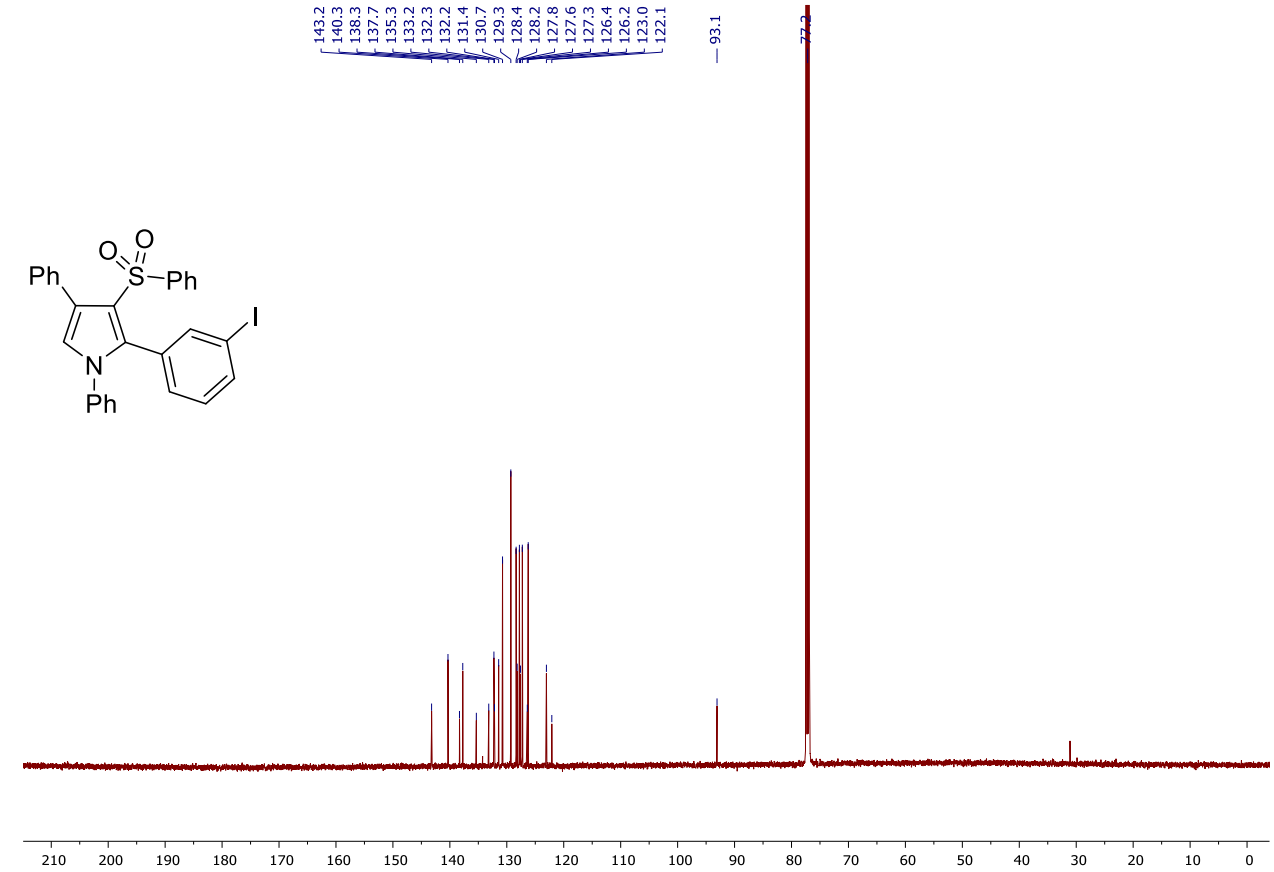
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4h**



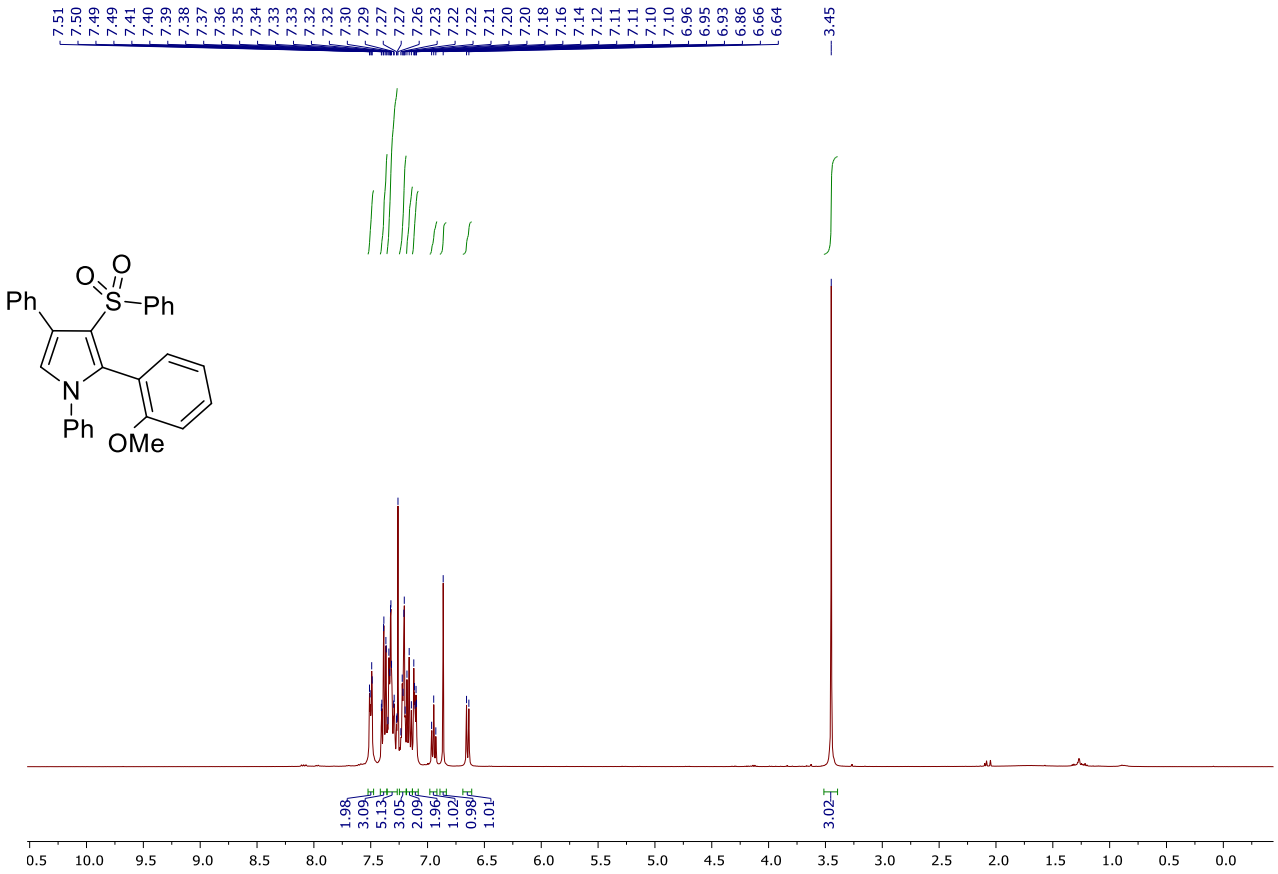
^{1}H NMR (400 MHz, $CDCl_3$) of **4i**



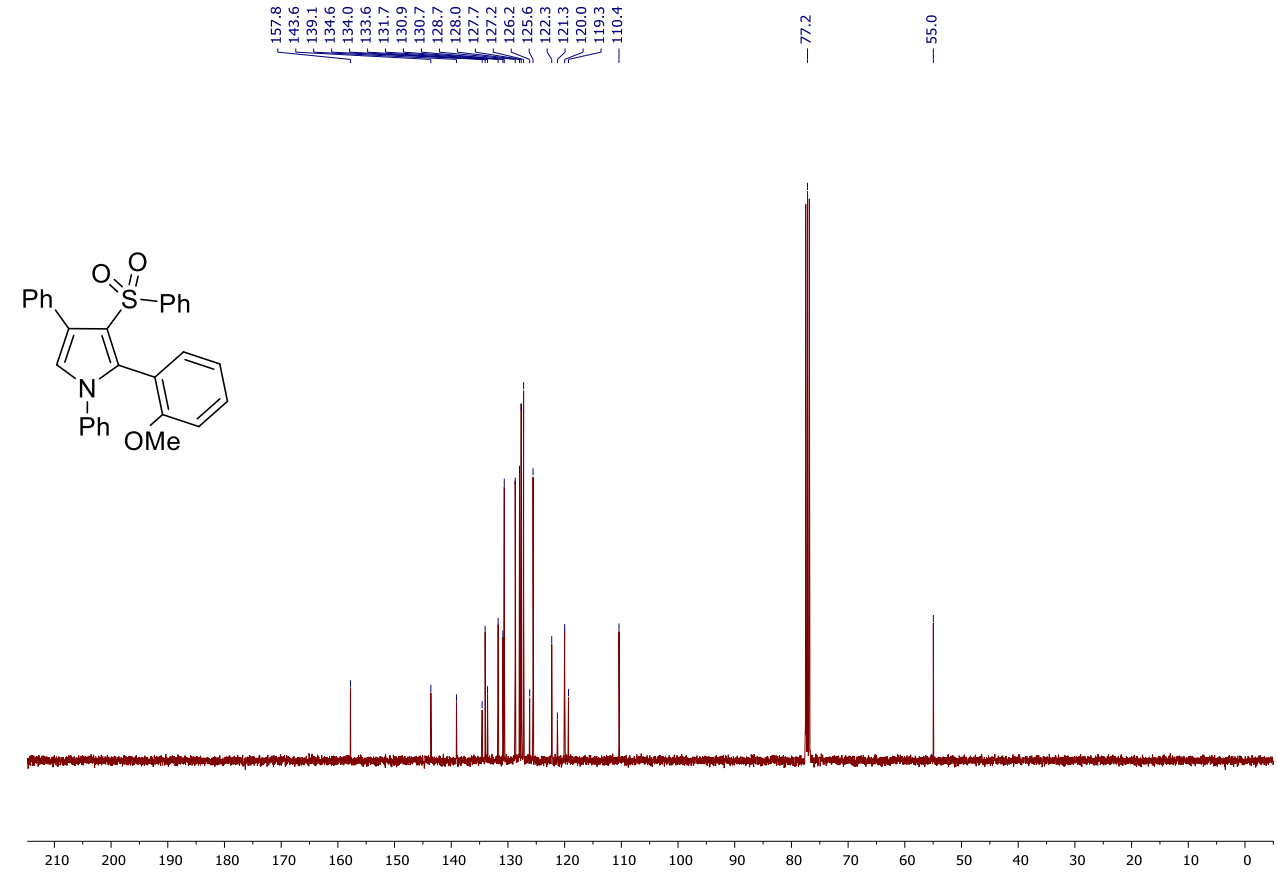
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4i**



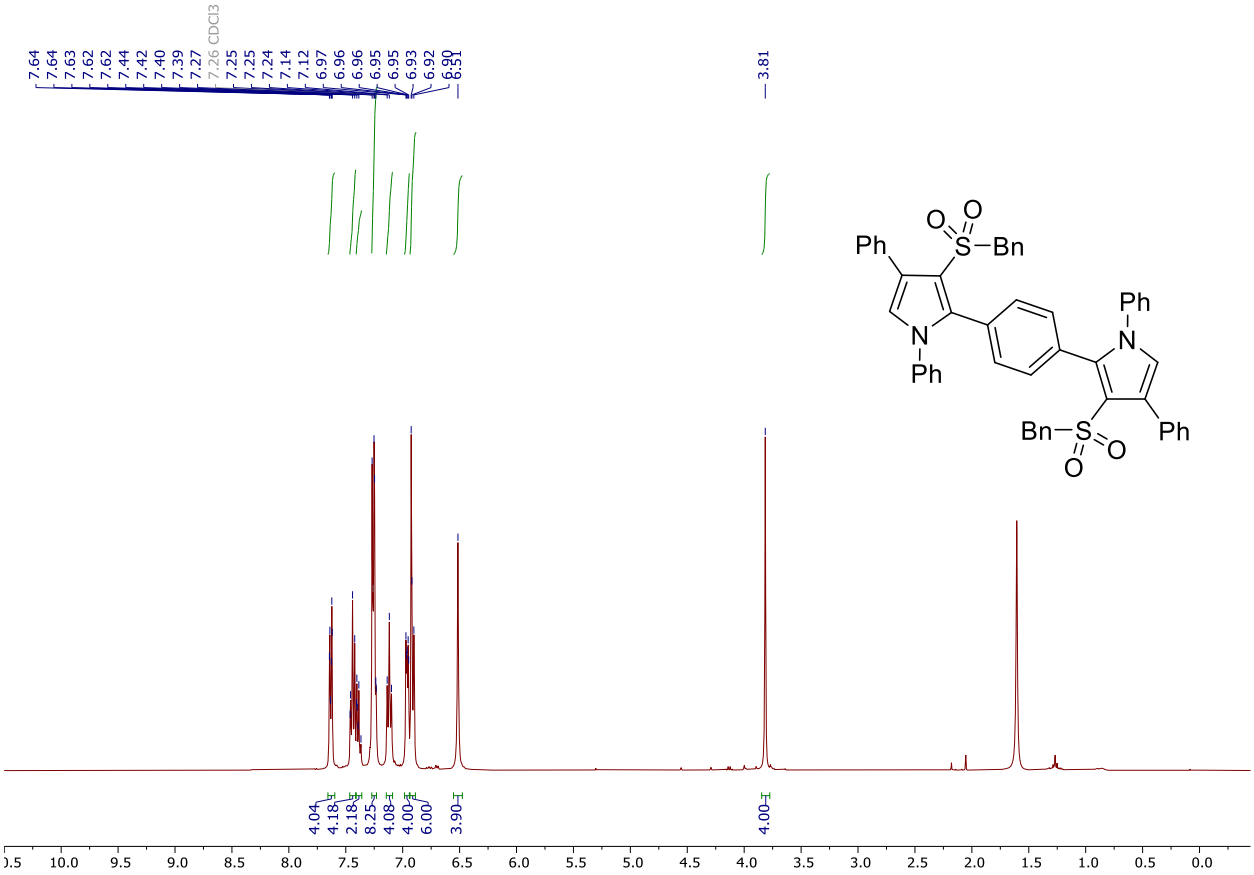
^{1}H NMR (400 MHz, $CDCl_3$) of **4j**



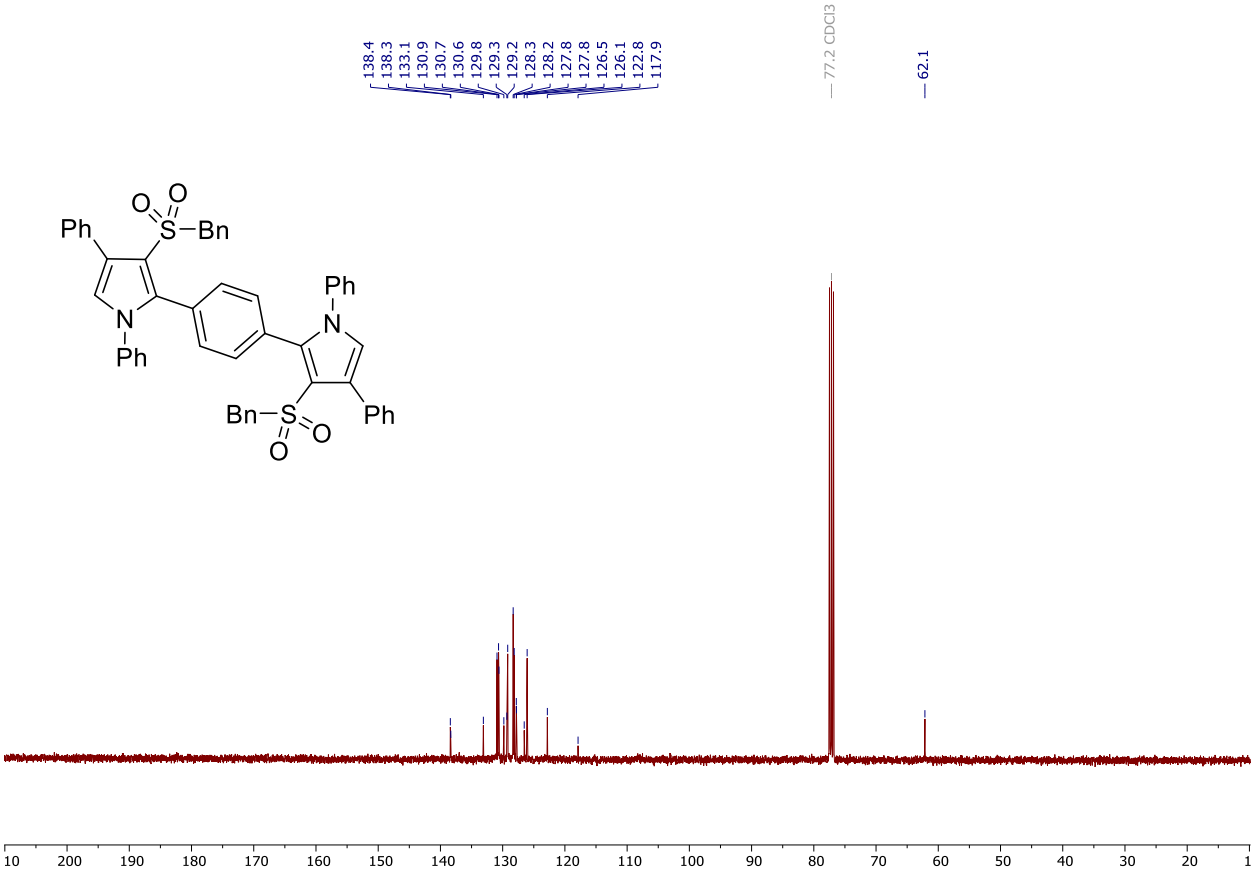
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4j**



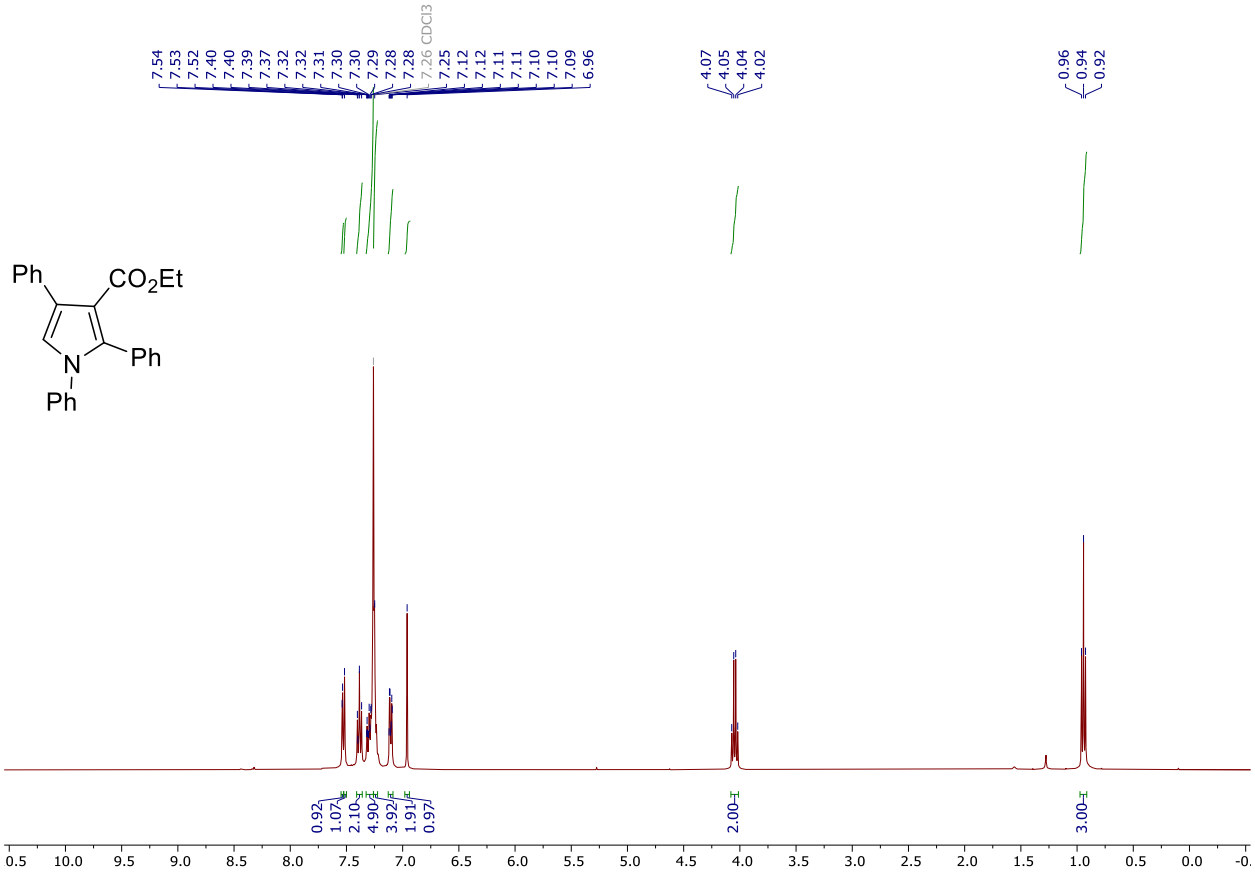
^{1}H NMR (400 MHz, $CDCl_3$) of **4k**



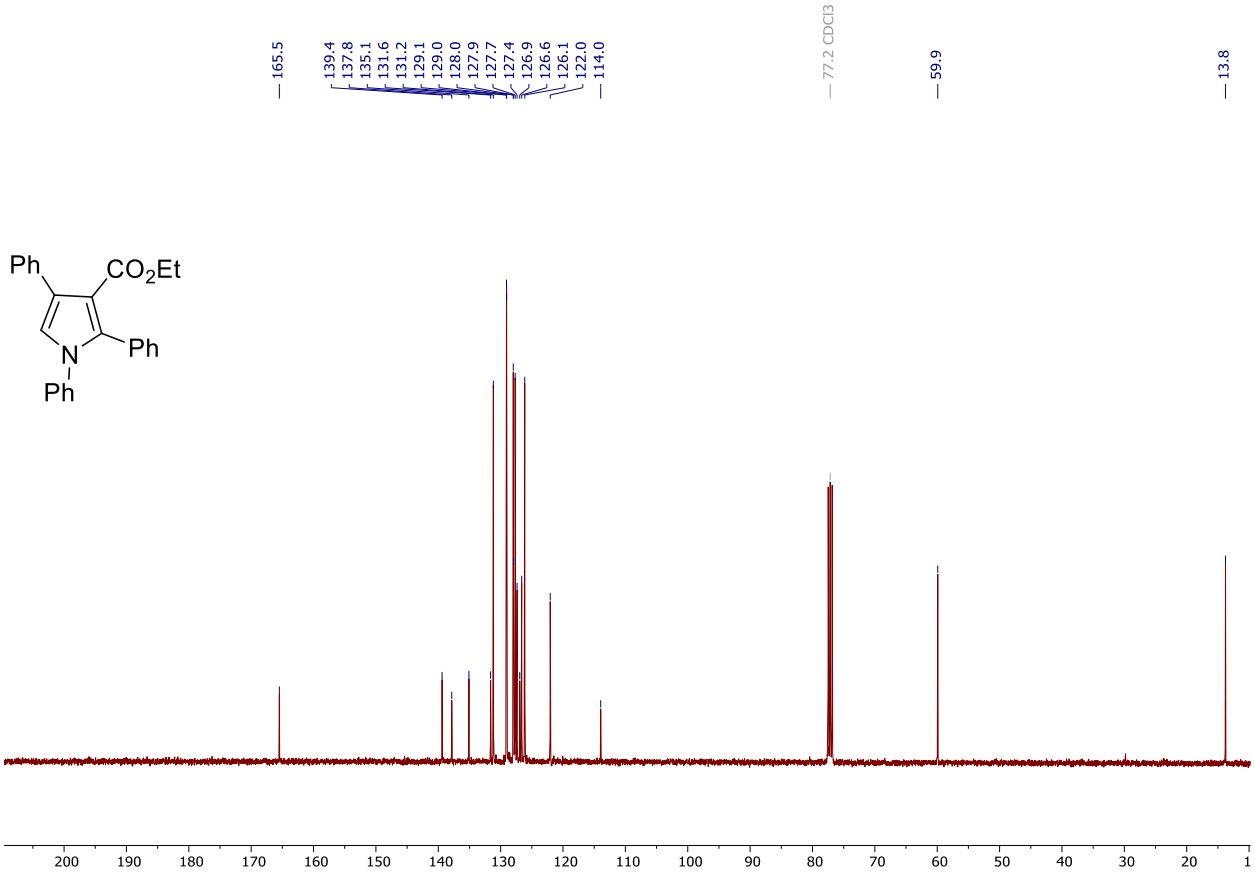
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4k**



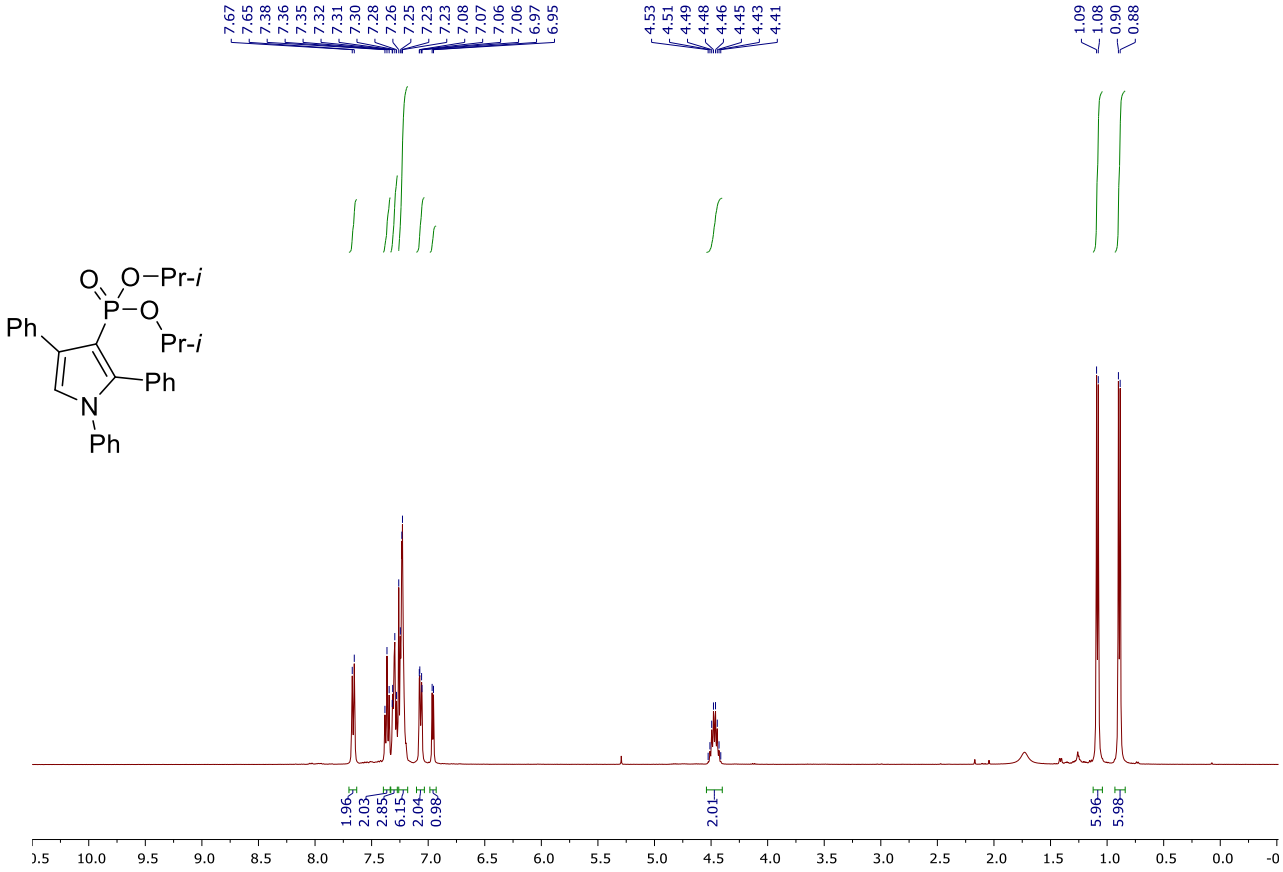
^{1}H NMR (400 MHz, $CDCl_3$) of **6**



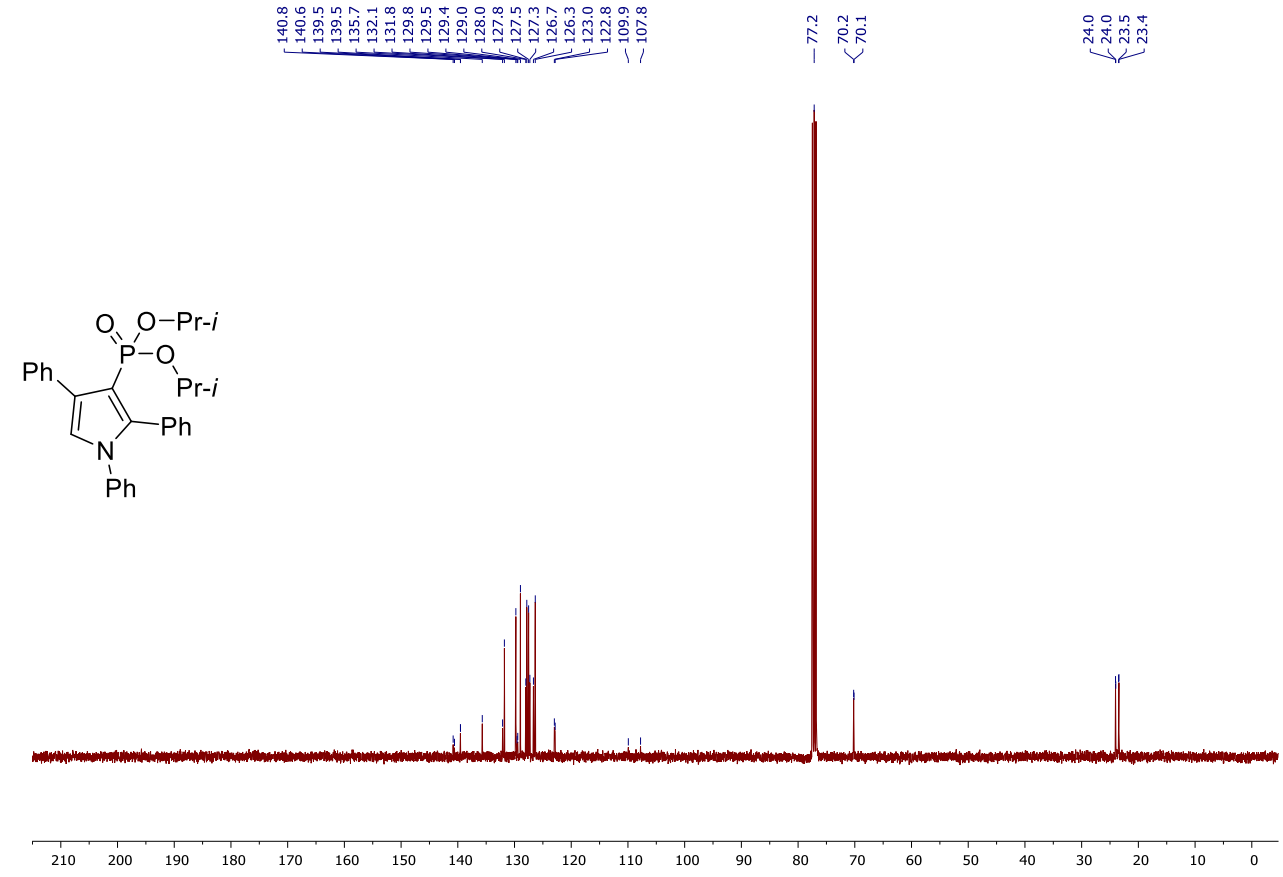
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **6**



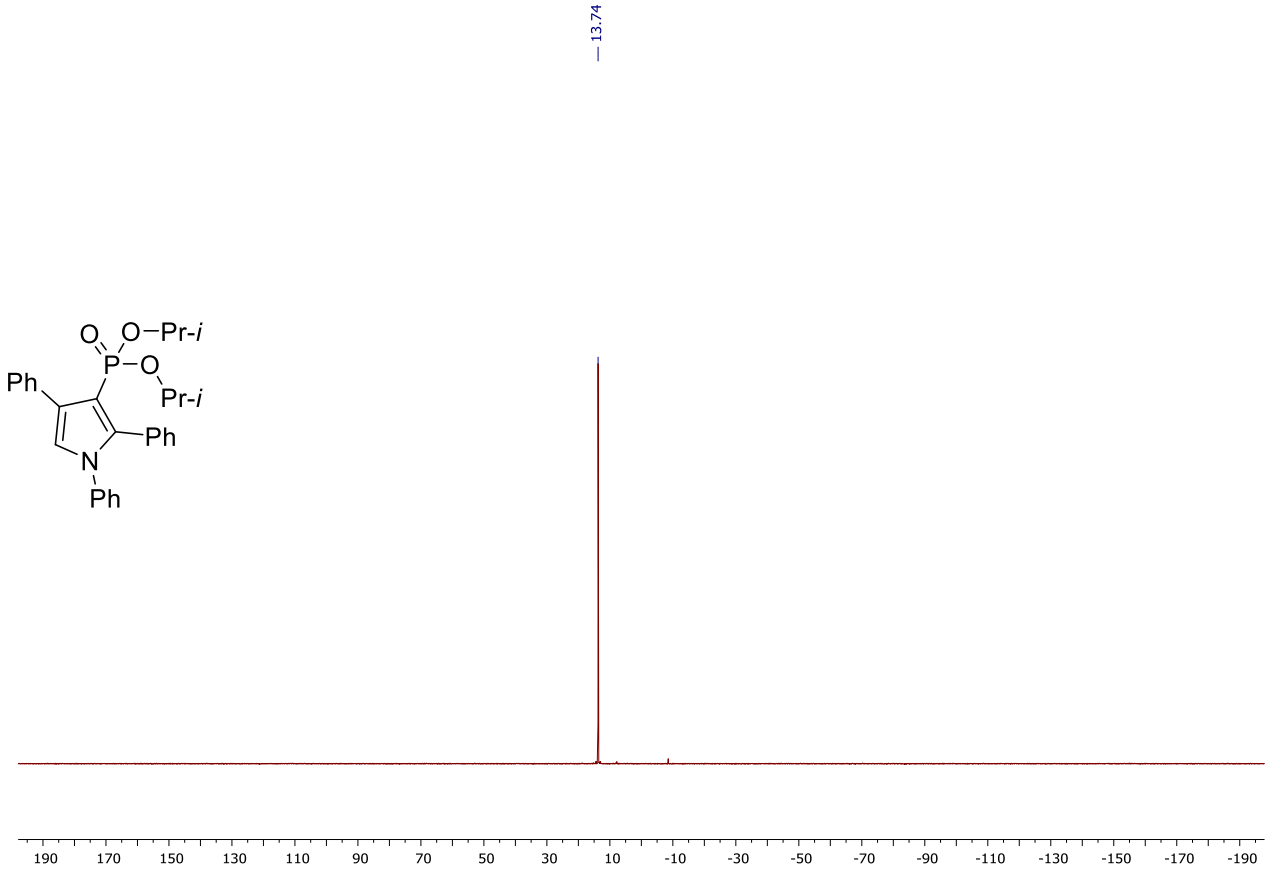
^{1}H NMR (400 MHz, $CDCl_3$) of **8**



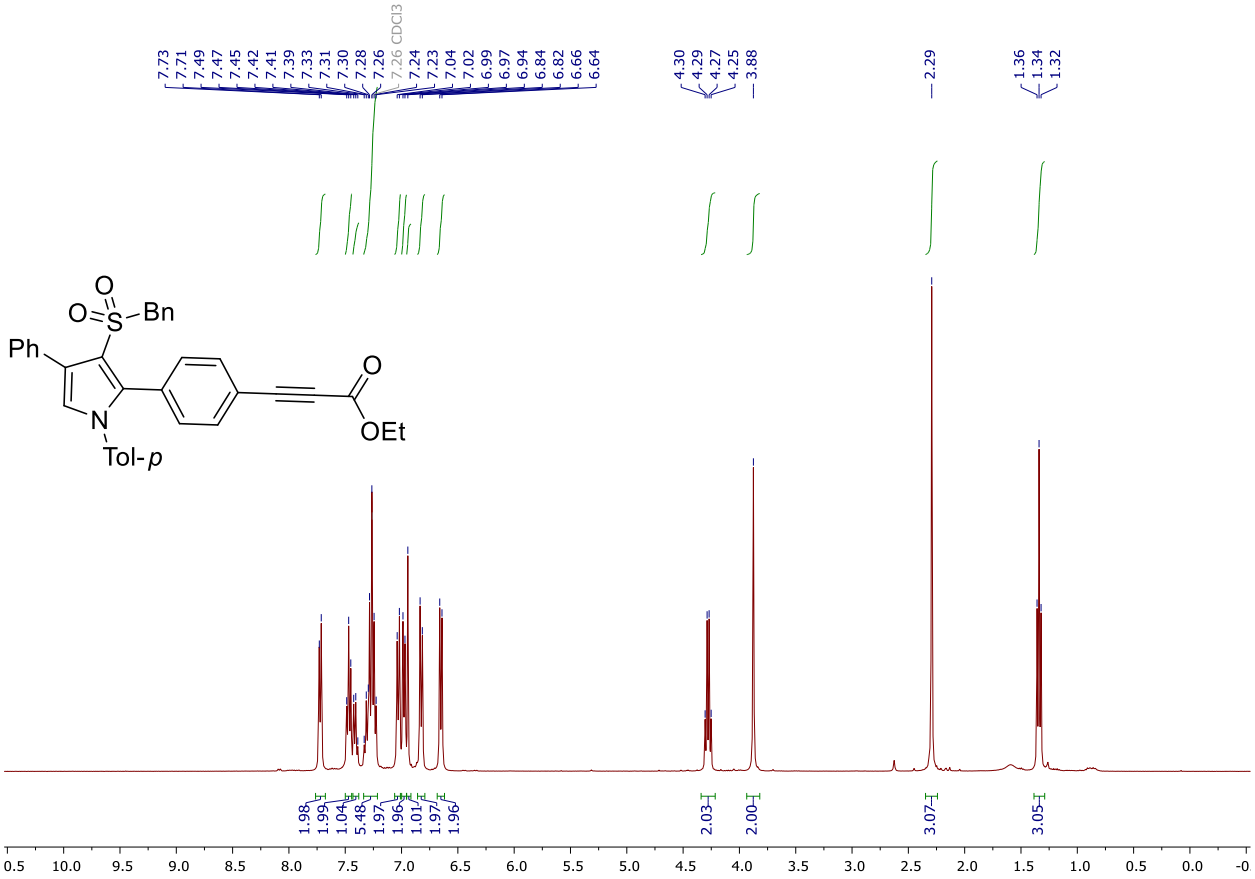
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **8**



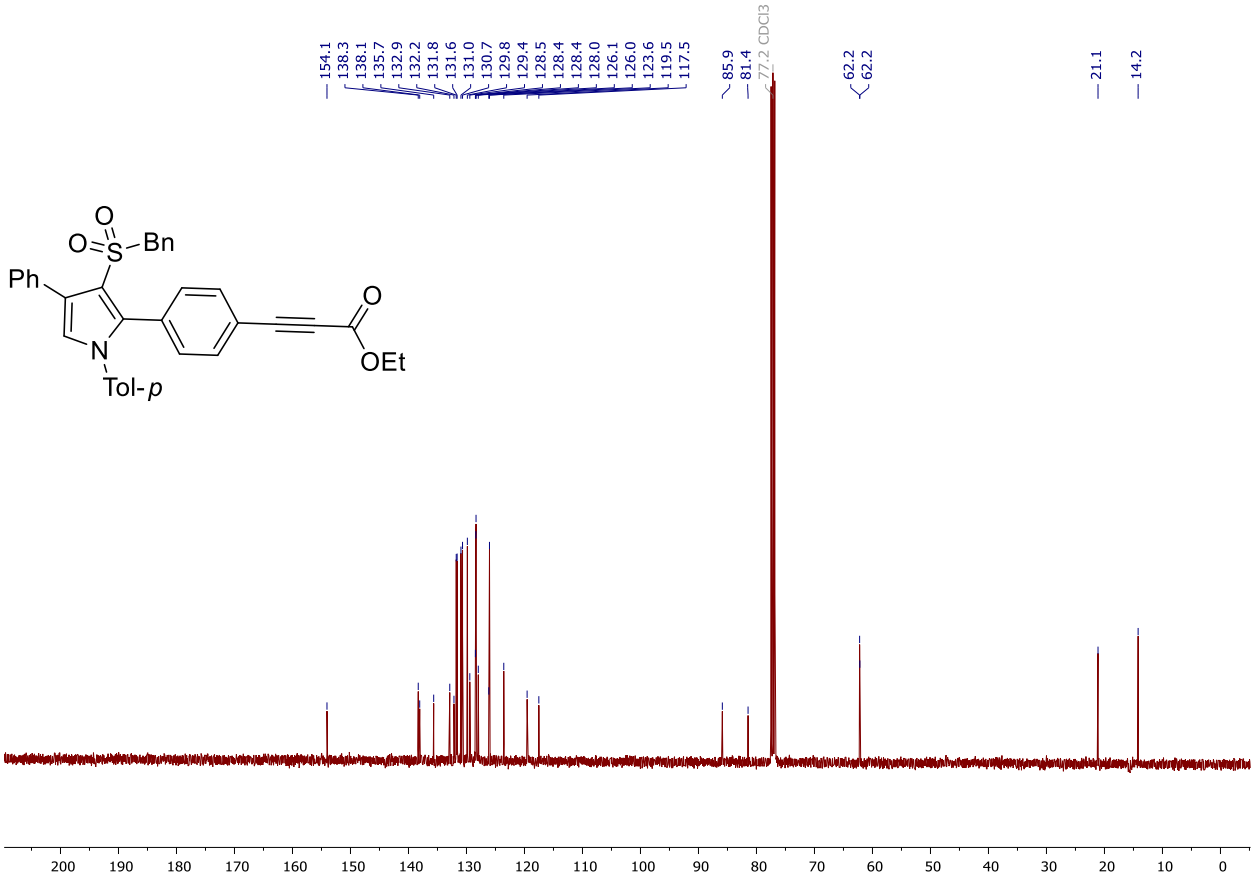
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) of **8**



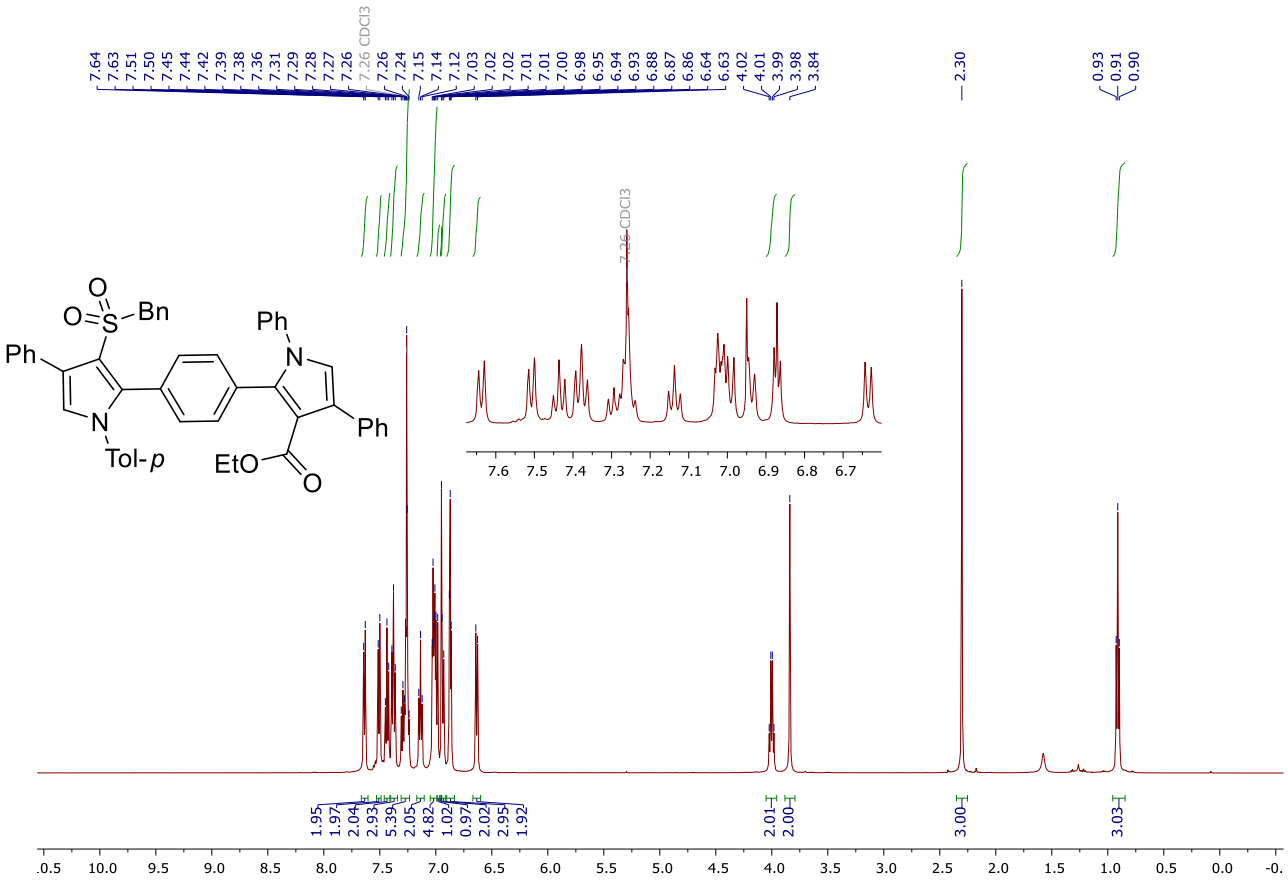
^{1}H NMR (400 MHz, $CDCl_3$) of **10**



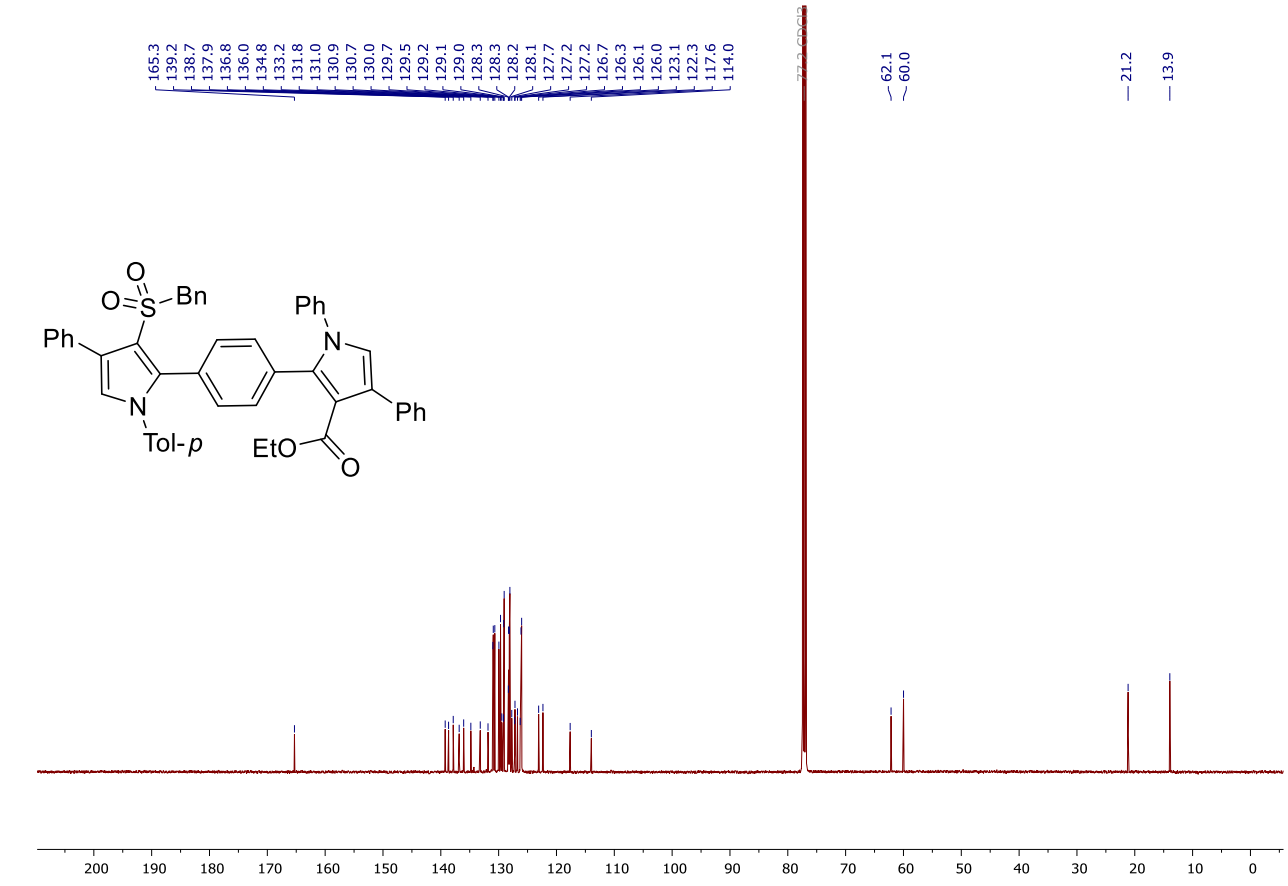
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **10**



^{1}H NMR (400 MHz, $CDCl_3$) of **11**

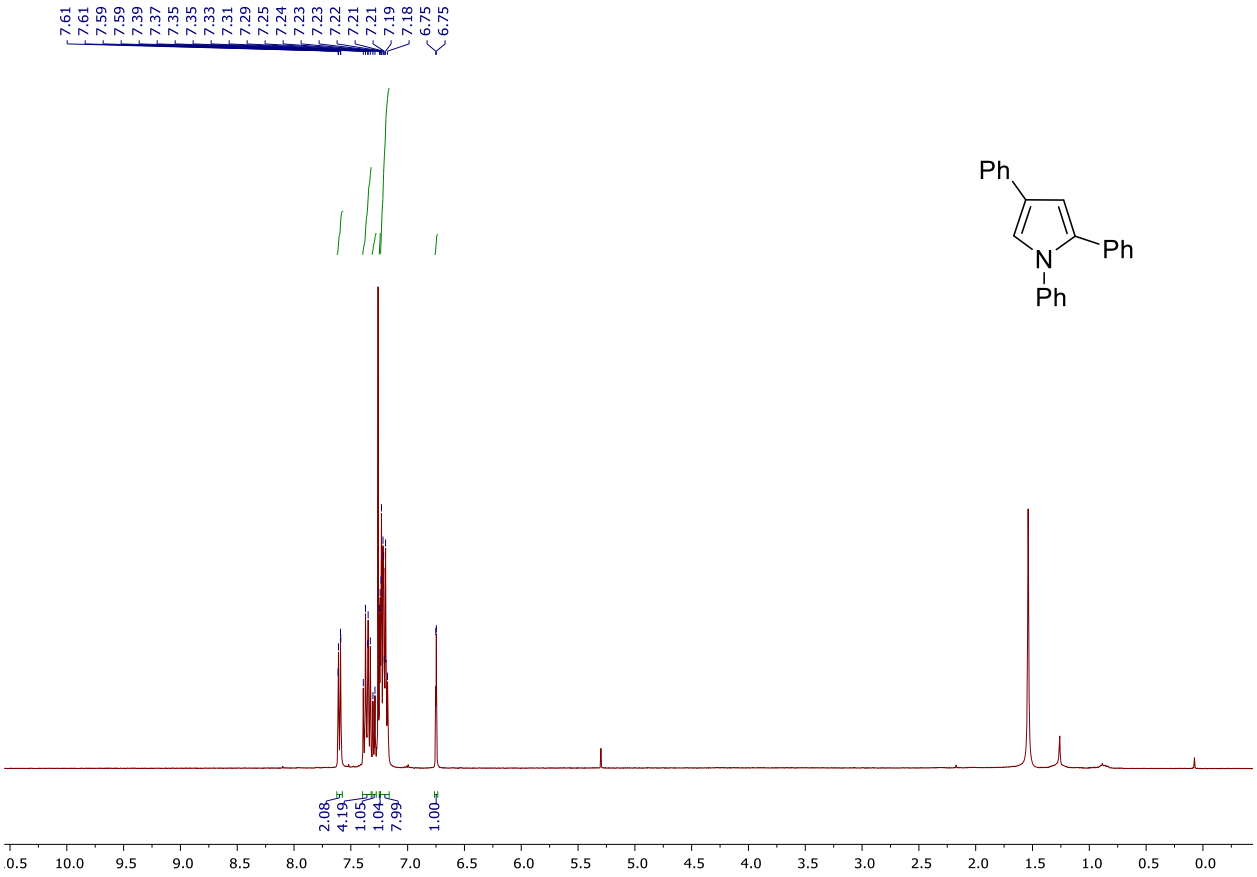


^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **12**

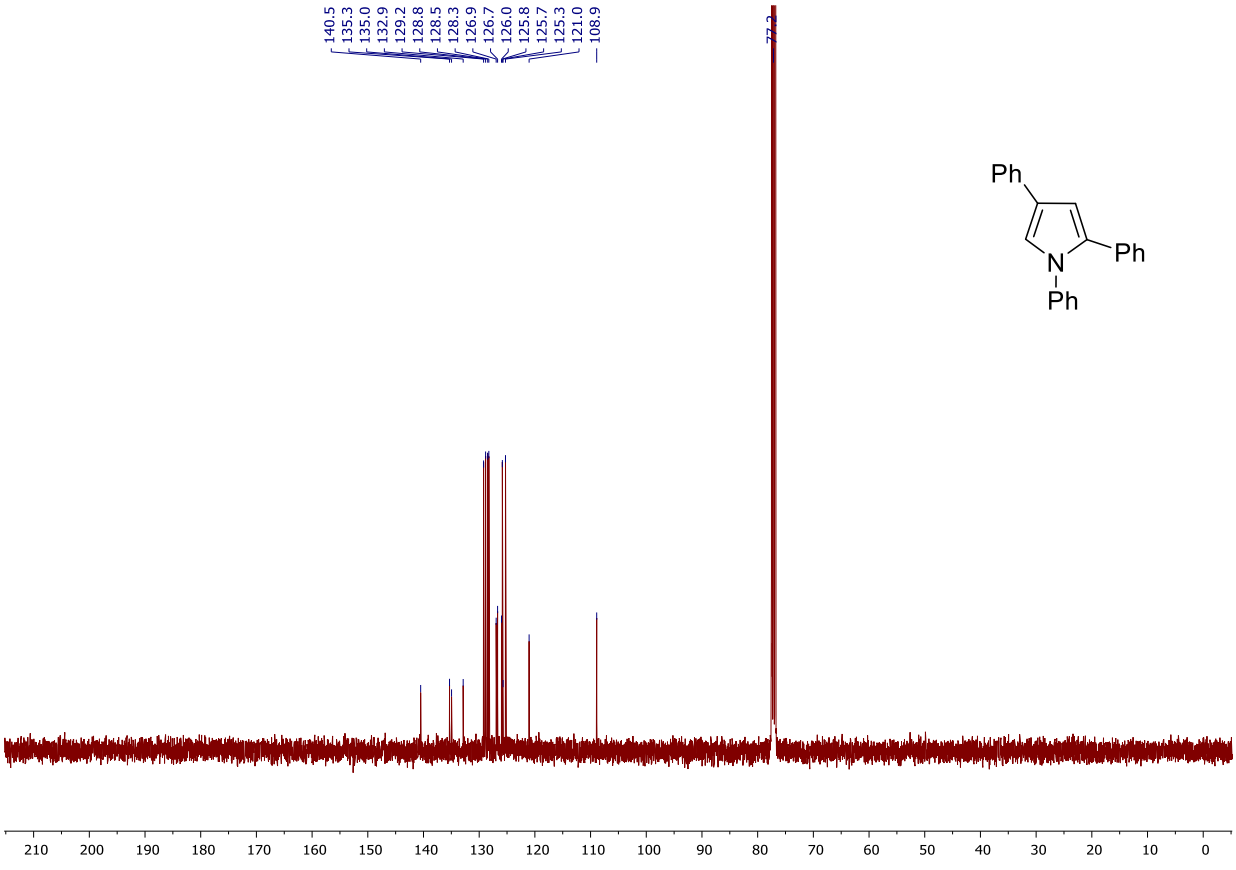


3.8.NMR Spectra of Other Products

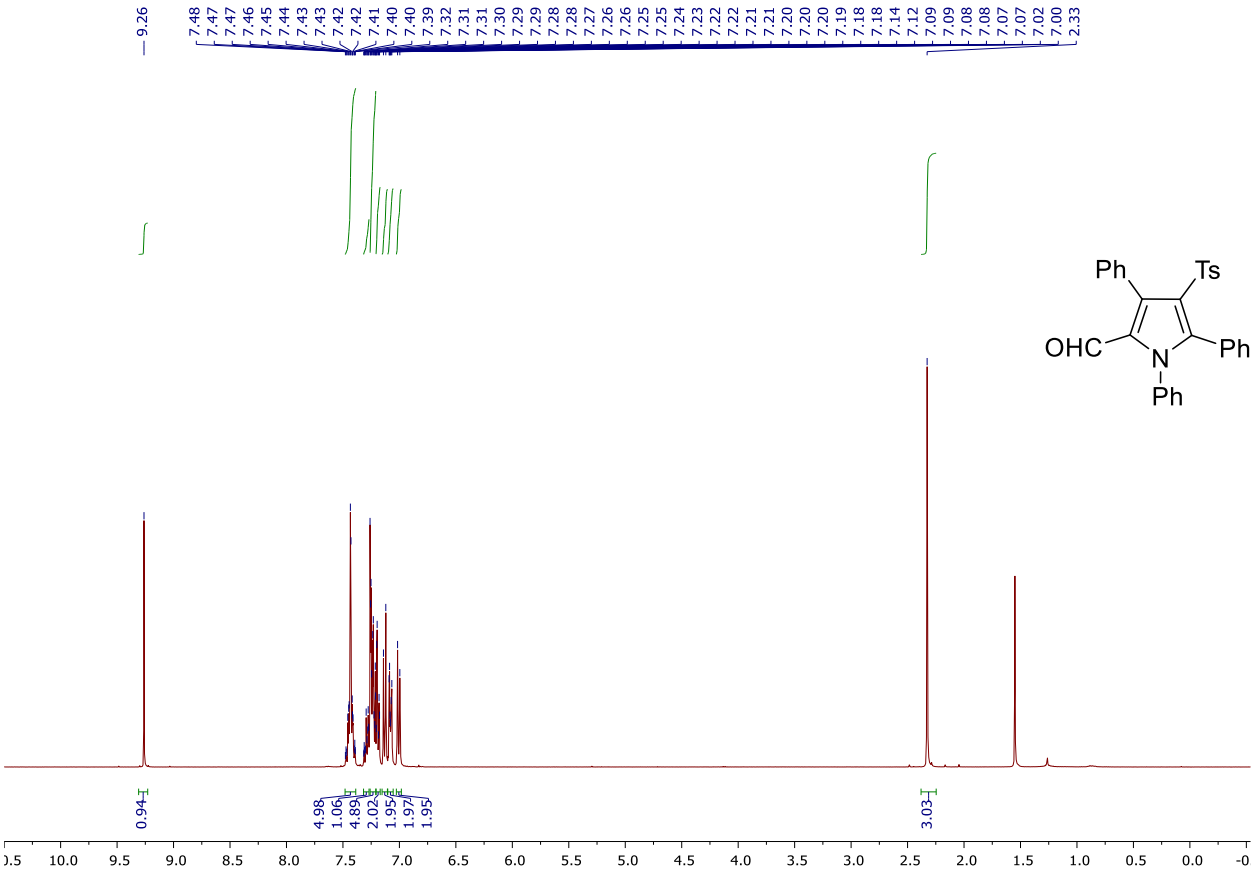
^{1}H NMR (400 MHz, $CDCl_3$) of **4a'**



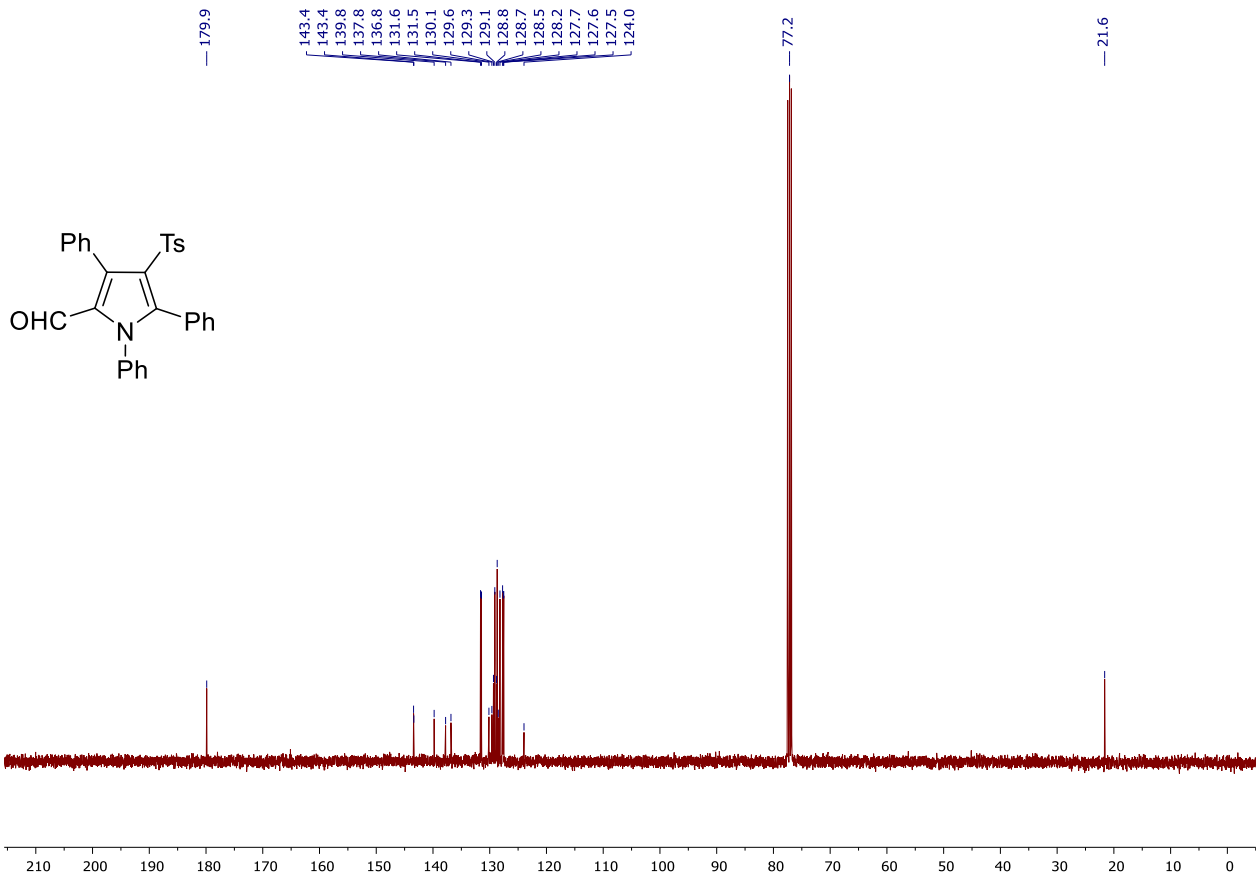
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4a'**



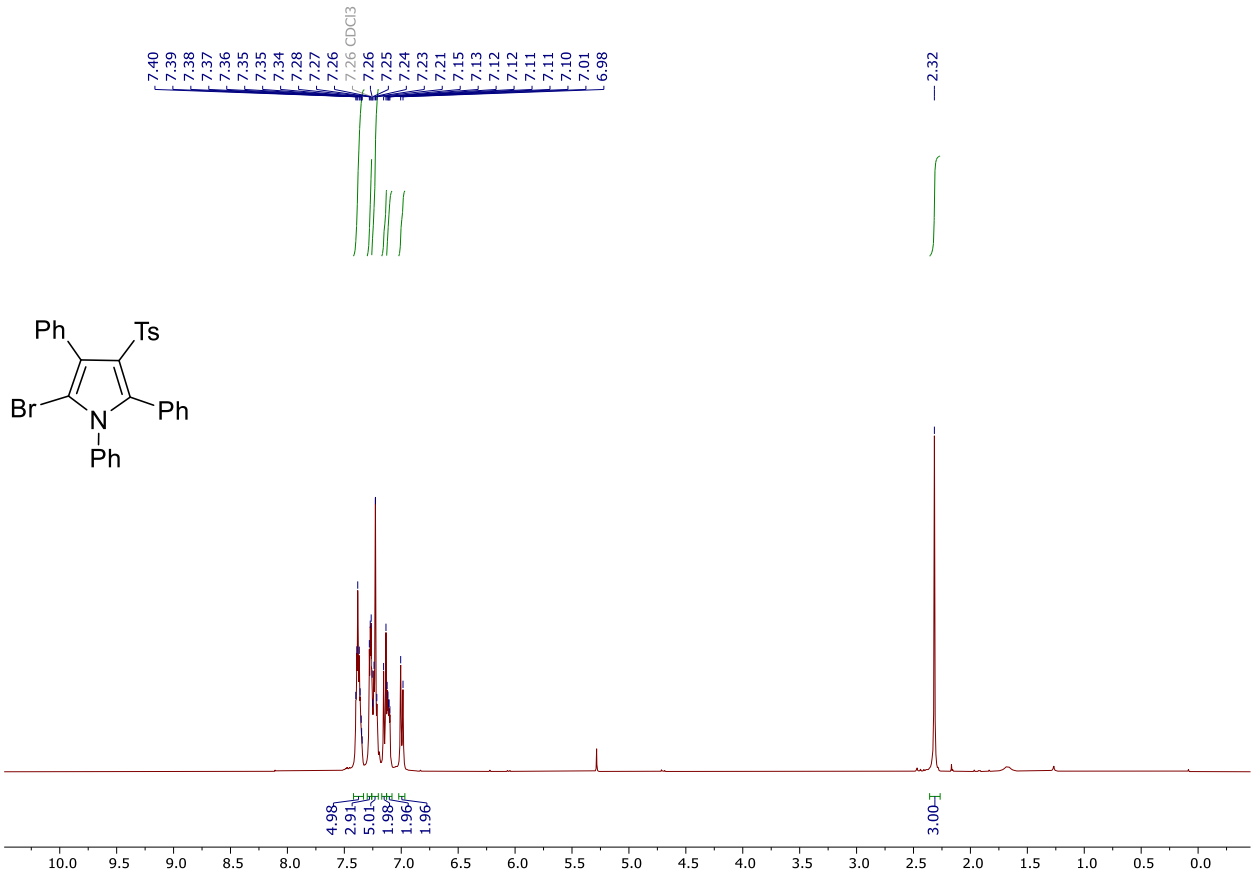
^{1}H NMR (400 MHz, $CDCl_3$) of **4a''**



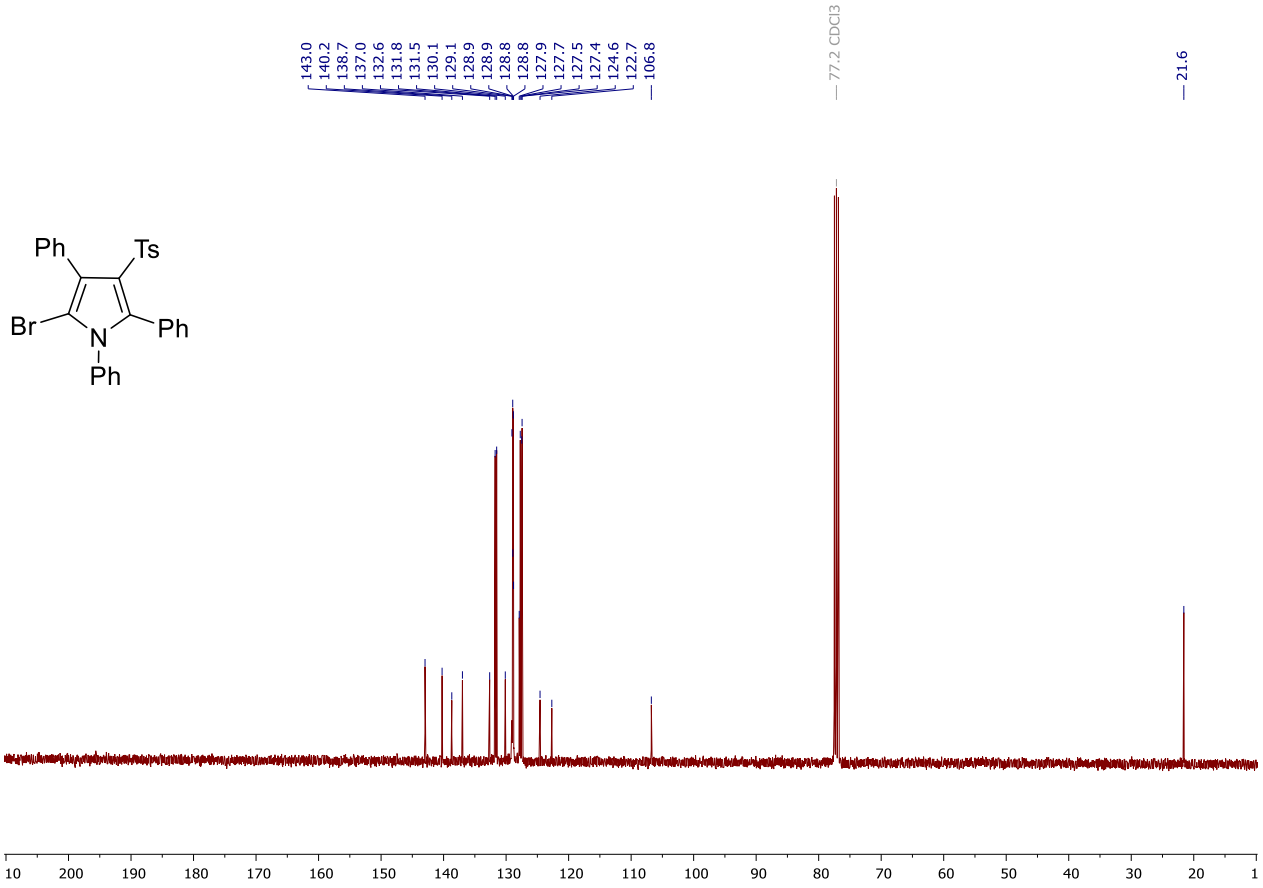
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4a''**



^{1}H NMR (400 MHz, $CDCl_3$) of **4a'''**



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of **4a'''**



4. Solid State Molecular Structures of 3o and 11

For single crystal X-ray diffraction experiments the single crystals of 3o and 11 were grown by slow evaporation of acetonitrile solutions. For single crystal X-ray diffraction experiment the crystals were fixed on a micro mount and placed on a SuperNova, Single source at offset/far, HyPix3000 diffractometer using Cu Kα monochromated radiation. The crystals were kept at 100(2) K during data collection. The structures have been solved by ShelXT [G. M. Sheldrick, *Acta Crystallogr. Sect. A* 2015, 71, 3- 8] structure solution programs using Intrinsic Phasing, respectively, and refined by means of the SHELXL program [G. M. Sheldrick, *Acta Crystallogr. Sect. C* 2015, 71, 3-8] incorporated in the OLEX2 program package [O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, 2009, 42, 339-341].

Crystal data and structure refinement for 3o

Bond precision:	C-C = 0.0020 A		Wavelength=1.54184
Cell:	a=9.7333(1)	b=15.2824(2)	c=16.1184(2)
	alpha=90	beta=91.158(1)	gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	2397.09(5)	2397.09(5)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	$C_{30}H_{25}NO_2S$	$C_{30}H_{25}NO_2S$
Sum formula	$C_{30}H_{25}NO_2S$	$C_{30}H_{25}NO_2S$
Mr	463.57	463.57
Dx,g cm-3	1.285	1.285
Z	4	4
Mu (mm-1)	1.412	1.412
F000	976.0	976.0
F000'	979.90	
h,k,lmax	11,18,19	11,18,19
Nref	4469	4465
Tmin,Tmax	0.844,0.893	0.861,1.000
Tmin'	0.809	

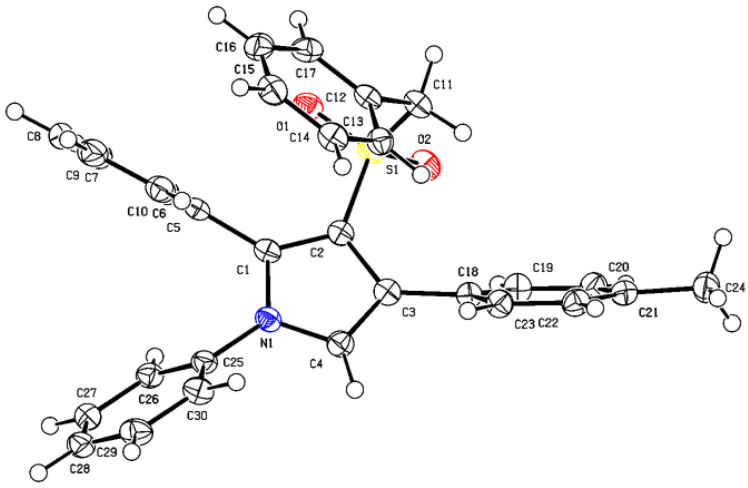
Correction method= # Reported T Limits: Tmin=0.861 Tmax=1.000
AbsCorr = MULTI-SCAN

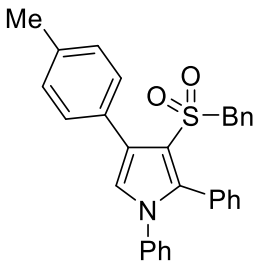
Data completeness= 0.999 Theta(max)= 69.142

R(reflections)= 0.0395(4001) wR2(reflections)= 0.1126(4465)

S = 1.090 Npar= 308

Molecular structure of 3o (50% probability amplitude displacement ellipsoids)





Crystal data and structure refinement for 11

Bond precision:	C-C = 0.0035 A	Wavelength=1.54184

Cell:	a=9.2439(2)	b=14.8214(4)	c=28.8605(7)
	alpha=90	beta=90	gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	3954.11(17)	3954.11(17)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	$C_{49}H_{40}N_2O_4S$	$C_{49}H_{40}N_2O_4S$
Sum formula	$C_{49}H_{40}N_2O_4S$	$C_{49}H_{40}N_2O_4S$
Mr	752.89	752.89
Dx,g cm-3	1.265	1.265
Z	4	4
Mu (mm-1)	1.109	1.109
F000	1584.0	1584.0
F000'	1589.70	
h,k,lmax	11,18,36	11,18,36
Nref	8650[4839]	7885
Tmin,Tmax	0.801,0.957	0.661,1.000
Tmin'	0.801	

Correction method= # Reported T Limits: Tmin=0.661 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.63/0.91 Theta(max)= 80.401

R(reflections)= 0.0355(7537) wR2(reflections)= 0.0959(7885)

S = 1.073 Npar= 507

Molecular structure of 11 (50% probability amplitude displacement ellipsoids)