Supporting Information

Copper-catalyzed tandem cyclization/arylation of α,β-alkynic hydrazones with diaryliodonium salts: synthesis of *N*-arylpyrazoles

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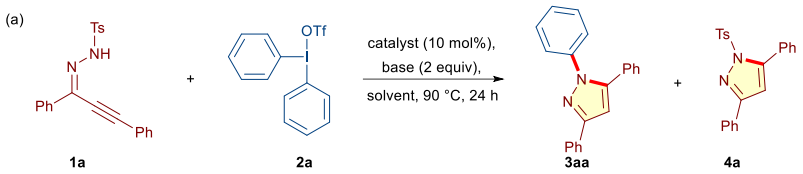
1. Complete Optimization Table:



Sl No	Cu catalyst (10 mol%)	Base/additives (2 equiv)	Solvent	Temp.	Yield of 3a (%)[b]	Yield of 4a (%)[b]
1	CuCl	dtbpy	DCE	90	62	28
2	CuCl	dtbpy	1,4-Dioxane	90	56	23
3	CuCl	dtbpy	Toluene	90	61	10
4	CuCl	dtbpy	DMF	90	82	0
5	CuCl	dtbpy	DMSO	90	64	21
6	CuBr	dtbpy	DMF	90	61	0
7	$Cu(OAc)_2$	dtbpy	DMF	90	79	0
8	Cu(OTf)2	dtbpy	DMF	90	71	0
9	CuI	dtbpy	DMF	90	68	0
10	CuTC	dtbpy	DMF	90	59	0
11	CuCl	DBU	DMF	90	52	Trace
12	CuCl	DABCO	DMF	90	76	Trace
13	CuCl	Et_3N	DMF	90	74	Trace
14	CuCl	K_2CO_3	DMF	90	46	38
15	CuCl	---	DMF	90	63	Trace
16	---	dtbpy	DMF	90	0	74
17[c]	CuCl	dtbpy	DMF	90	68	0
18[d]	CuCl	dtbpy	DMF	90	79	0
19	CuCl	dtbpy	DMF	rt	Trace	64
20	CuCl	dtbpy	DMF	110	81	0
21	CuCl	dtbpy	DMF	60	28	56
22[e]	CuCl	dtbpy	DMF	90	83	0
22[f]	CuCl	dtbpy	DMF	90	84	0
26[g]	CuCl	dtbpy	DMF	90	71	0

23[h]	CuCl	dtbpy	DMF	90	46	29
24[i]	CuCl	dtbpy	DMF	90	83	0
25[j]	CuCl	dtbpy	DMF	90	74	0

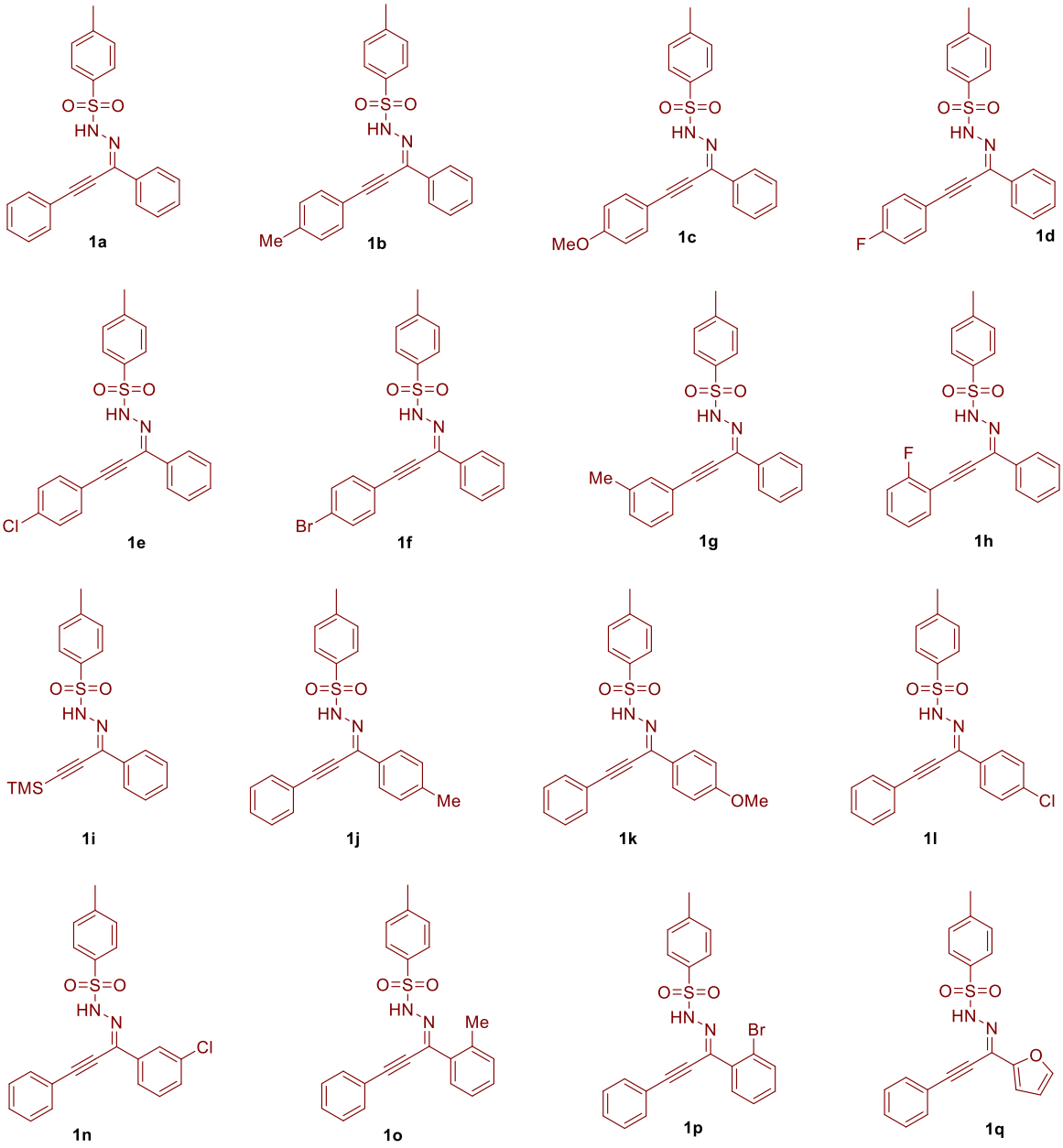
[a]Reaction Condition **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (10 mol%), base (2 equiv) and solvent (2 ml) under N_2 atmosphere at 90 °C for 24 h. [b]Isolated yield, [c]Using 5 mol% of CuCl, [d]Using 20 mol% of CuCl, [e]Using 1.5 equiv of **2a**, [f]Using 2 equiv of **2a**, [g]Using 1.5 equiv dtbpy, [h]Reaction was stirred for 12 h, [i]Reaction was stirred for 36 h, [j]under air.

2. Experimental Section

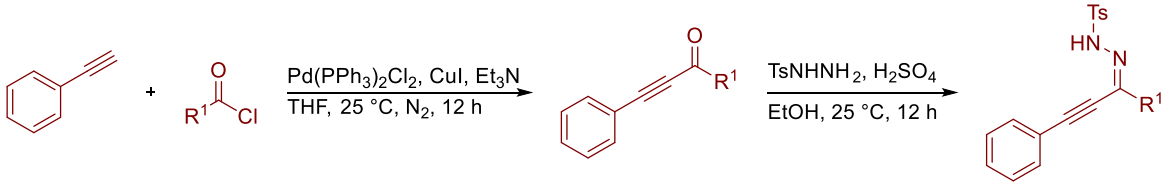
2.1. General Information: All the reactions were performed using pre-dried glassware and screw-cap vials. All the solvents were obtained from Merck (Emparta grade) and used without further drying or distillation. Terminal Alkyne, carboxylic acid derivatives, *p*-Toluenesulfonyl hydrazide, Copper catalyst and 2,6-Di-*tert*-butylpyridine (dtbpy) were obtained from commercial sources and used without further purification. All the acyl chloride were synthesized following the procedures given below.[1] The reported yields are of isolated compounds that are estimated to be >95% pure as determined by ^{1}H NMR and ^{13}C NMR. Thin layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F_{254} aluminum sheets with detection under UV light at 254 nm. Chromatographic separations were carried out on Avra silica gel (100-200 mesh or 230−400 mesh). Nuclear magnetic resonance (NMR) spectroscopy was performed using Bruker 500 MHz spectrometers. If not otherwise specified, chemical shifts (δ) are provided in ppm. HRMS spectra were recorded using Agilent 6546 LC/Q-TOF spectrometer. Single crystal X-ray diffractions were recorded using Rigaku Oxford diffractometer at 100 K.

2.2. Preparation of Starting Materials

The substrates of various α,β-alkynic hydrazones **(1a, 1b, 1c, 1d, 1e, 1f, 1k** and **1o),**[2] **(1g** and **1q)**[3] and **(1h, 1i, 1j, 1l** and **1n)**[4] were prepared following the previous literature procedures and obtained characterization data were in alignment with the literature reported data.

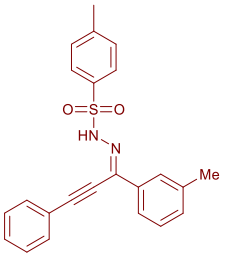


2.2.1 General procedure (GP1) for the synthesis of α,β-alkynic hydrazones



In a pre-dried Schlenk flask acyl chloride (1.2 equiv), $Pd(PPh_3)_2Cl_2$ (0.02 equiv), Et_3N (1.2 equiv) and anhydrous THF were added and the resulting solution was stirred for 10 minutes at 25 °C under N_2. Following the addition of CuI (0.04 equiv), the reaction mixture was stirred for an additional 10 minutes. Subsequently, the terminal alkyne (1.0 equiv) was added in a single portion and the solution was stirred under ambient conditions for 12 h. Ethyl acetate was added once the reaction was finished, and the solution was then with 0.1 N HCl in a separatory funnel. The organic phase was dried over Na_2SO_4 and evaporated using rotary evaporator to separate the layers. The crude product was then purified using flash chromatography on silica gel with hexane/ethyl acetate as the eluent to produce the α, β-alkynic ketones. Then, to a solution of α, β-alkynic ketones (1.0 equiv) and *p*-toluenesulfonyl hydrazide (1.1 equiv) in EtOH was added concentrated sulfuric acid (1.1 equiv) in a dropwise fashion at 25 ^oC and the solution was stirred for 12 h. After completion, the reaction mixture was concentrated, and the crude product was purified by column chromatography on silica gel with hexane/ethyl acetate as the eluent to produce corresponding α,β-alkynic hyrazone.

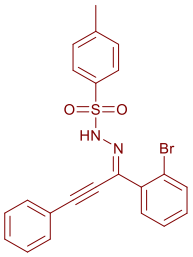
***(Z)*-4-Methyl-N'-(3-phenyl-1-(m-tolyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide (1m)**



The compound was prepared according to GP1 by adding concentrated sulfuric acid (30 µL, 0.55 mmol) dropwise over 1 min to a slurry of 3-phenyl-1-(m-tolyl)prop-2-yn-1-one (0.110 g, 0.5 mmol) and p-toluenesulfonyl hydrazide (0.103 g, 0.55 mmol) in EtOH (5 mL) at 25 ˚C. After 12 h, the crude product was purified by flash column chromatography on silica gel using 5% ethyl acetate in hexane to give **1m** as a white solid (0.153 g, 79%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.95 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.52 – 7.43 (m, 3H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 9.2 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 2.44 (s, 3H), 2.42 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.4, 138.3, 136.1, 135.7, 134.0, 132.4, 131.1, 130.6, 129.8, 128.9, 128.4, 128.1, 127.2, 124.1, 120.4, 104.6, 77.5, 21.7, 21.6. **HRMS-ESI** (m/z): calcd for $C_{23}H_{20}N_2O_2S$ $[M + H]^+$ 389.1318; found 389.1324.

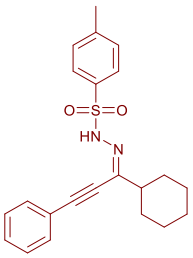
***(E)*-N'-(1-(2-Bromophenyl)-3-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (1p)**



The compound was prepared according to GP1 by adding concentrated sulfuric acid (30 µL, 0.55 mmol) dropwise over 1 min to a slurry of 1-(2-bromophenyl)-3-phenylprop-2-yn-1-one (0.143 g, 0.5 mmol) and p-toluenesulfonyl hydrazide (103 mg, 0.55 mmol) in EtOH (5 mL) at 25 ˚C. After 12 h, the crude product was purified by flash column chromatography on silica gel using 5% ethyl acetate in hexane to give **1p** as a white solid (0.161 g, 71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.70 – 7.52 (m, 3H), 7.48 – 7.37 (m, 4H), 7.35 – 7.31 (m, 3H), 7.25 – 7.20 (m, 1H), 2.44 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.6, 135.6, 135.50, 135.47, 133.9, 132.3, 131.3, 130.9, 130.6, 129.9, 128.8, 128.2, 127.6, 122.1, 120.5, 105.7, 78.2, 21.8. **HRMS-ESI** (m/z): calcd for $C_{22}H_{17}BrN_2O_2S$ $[M + H]^+$ 453.0267; found 453.0271.

***(Z)*-N'-(1-cyclohexyl-3-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (1r)**

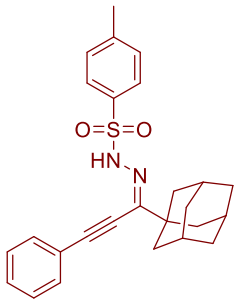


The compound was prepared according to GP1 by adding concentrated sulfuric acid (30 µL, 0.55 mmol) dropwise over 1 min to a slurry of 1-cyclohexyl-3-phenylprop-2-yn-1-one (0.106 g, 0.5 mmol) and p-toluenesulfonyl hydrazide (103 mg, 0.55 mmol) in EtOH (5 mL) at 25 ˚C.

After 12 h, the crude product was purified by flash column chromatography on silica gel using 5% ethyl acetate in hexane to give **1r** as a white solid (0.144 g, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.48 (m, 2H), 7.46 – 7.41 (m, 1H), 7.40 – 7.36 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 1.42 – 1.34 (m, 1H), 1.86 – 1.79 (m, 2H), 1.79 – 1.73 (m, 2H), 1.70 – 1.64 (m, 1H), 1.45 – 1.34 (m, 2H), 1.33 – 1.23 (m, 2H), 1.23 – 1.13 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 144.2, 143.8, 135.7, 132.3, 130.3, 129.7, 128.8, 128.0, 120.5, 103.6, 78.0, 44.5, 30.5, 25.9, 25.8, 21.8. **HRMS-ESI** (m/z): calcd for $C_{22}H_{24}N_2O_2S$ $[M + H]^+$ 381.1631; found 381.1636.

***(Z)*-N'-(1-((3r,5r,7r)-adamantan-1-yl)-3-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (1s)**

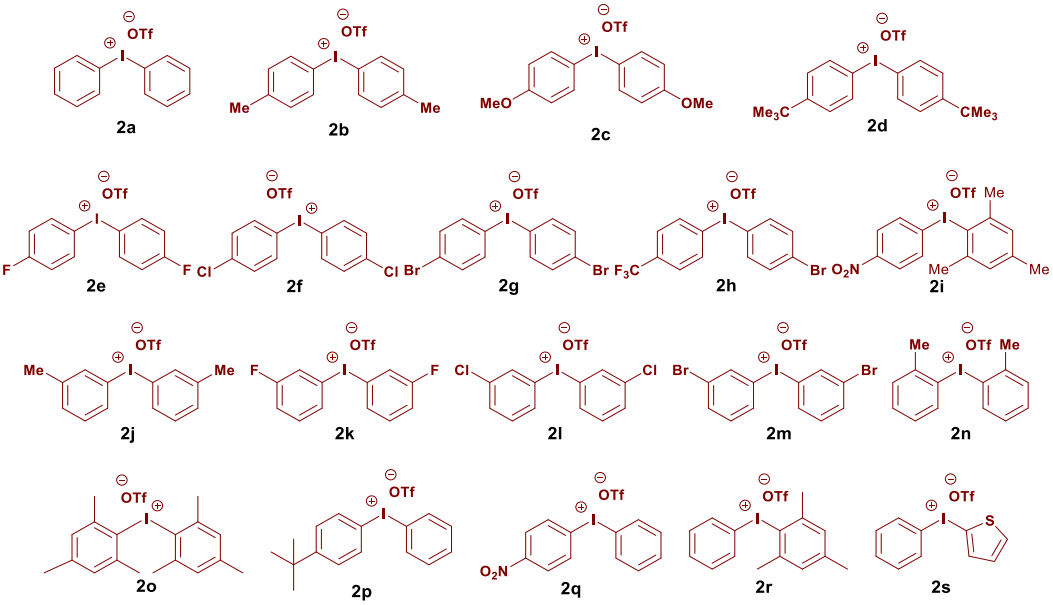


The compound was prepared according to GP1 by adding concentrated sulfuric acid (30 µL, 0.55 mmol) dropwise over 1 min to a slurry of 1-((3r, 5r, 7r)-adamantan-1-yl)-3-phenylprop-2-yn-1-one (0.132 g, 0.5 mmol) and p-toluenesulfonyl hydrazide (103 mg, 0.55 mmol) in EtOH (5 mL) at 25 ˚C. After 12 h, the crude product was purified by flash column chromatography on silica gel using 5% ethyl acetate in hexane to give **1s** as a white solid (0.148 g, 68%).

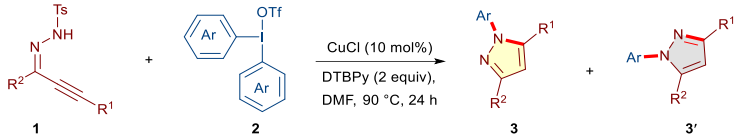
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.51 (m, 2H), 7.48 – 7.38 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 2.46 (s, 3H), 2.05 (br s, 3H), 1.82 (d, *J* = 2.1 Hz, 6H), 1.78 – 1.66 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 147.1, 144.0, 135.5, 132.1, 130.1, 129.5, 128.7, 127.9, 120.6, 103.9, 77.2, 40.1, 39.7, 36.6, 28.2, 21.6. **HRMS-ESI** (m/z): calcd for $C_{26}H_{28}N_2O_2S$ $[M + H]^+$ 433.1944; found 433.1950.

2.2.2. Preparation of Diaryliodonium salts:

The diaryliodonium salts (**2a–2p)** were prepared following the literature procedures and obtained characterization data were in alignment with the literature-reported data.[5]

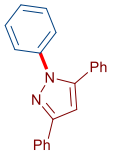


2.3. General procedure (GP2) for the synthesis of *N*-aryl Pyrazoles 3



A pre-dried Schlenk-tube was charged with copper(I) chloride (10 mol%), diaryliodonium salts (1.2 equiv), and hydrazone (1 equiv). The tube was evacuated and backfilled with nitrogen 3 times. Then a solution of 2,6-di-*tert*-butylpyridine (2 equiv) in DMF (2 ml) was added and the resulting reaction mixture was allowed to stir at 90 °C for 24 h. After completion, the reaction mixture was cooled to room temperature and quenched by the addition of sat. $NaHCO_3$ (5 ml). The resulting mixture was extracted with DCM (5 mL × 3), combined organic layers was dried over anhydrous Na_2SO_4, and concentrated under vacuum. The crude residue was purified by column chromatography (3-5% Ethyl acetate in hexane) to yield the corresponding pyrazole derivatives **3**.

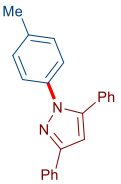
3,5-Diphenyl-1-(*p*-tolyl)-1*H*-pyrazole (3aa)[6]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), diphenyliodonium trifluoromethanesulfonate (0.103 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (3% ethyl acetate in hexane) gave **3aa** as a yellow solid (0.049 g, 82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.27 (m, 11H), 6.84 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.1, 144.5, 140.3, 133.2, 130.7, 129.4, 128.9, 128.8, 128.6, 128.4, 128.1, 127.6, 126.0, 125.4, 105.3.

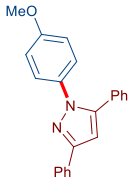
3,5-Diphenyl-1-(*p*-tolyl)-1*H*-pyrazole (3ab)[7]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), di-*p*-tolyliodonium trifluoromethanesulfonate (0.109 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (3% ethyl acetate in hexane) gave **3ab** as a white solid (0.045 g, 72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.39 – 7.34 (m, 4H), 7.33 – 7.26 (m, 4H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.85 (s, 1H), 2.39 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.6, 144.3, 137.5, 137.3, 132.9, 130.5, 129.4, 128.6, 128.5, 128.3, 128.1, 127.9, 125.7, 125.1, 104.8, 21.0.

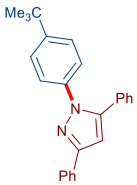
1-(4-Methoxyphenyl)-3,5-diphenyl-1*H*-pyrazole (3ac)[8]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), bis(4-methoxyphenyl)iodonium trifluoromethanesulfonate (0.117 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave **3ac** as a white solid (0.036 g, 56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.47 – 7.41 (m, 2H), 7.38 – 7.26 (m, 8H), 6.87 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 2.1 Hz, 1H), 3.80 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.0, 151.7, 144.4, 133.6, 133.3, 130.7, 128.8, 128.7, 128.6, 128.3, 128.0, 126.8, 125.9, 114.2, 104.7, 55.6.

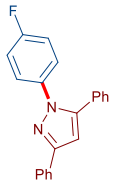
1-(4-(*tert*-Butyl)phenyl)-3,5-diphenyl-1*H*-pyrazole (3ad)[9]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), bis(4-(tert-butyl)phenyl)iodonium trifluoromethanesulfonate (0.130 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (3% ethyl acetate in hexane) gave **3ad** as a white solid (0.035 g, 50%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.1 Hz, 2H), 7.42 (t, J = 7.6 Hz, 2H), 7.36 – 7.27 (m, 2H), 7.34 – 7.28 (m, 8H), 6.83 (s, 1H), 1.33 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.7, 150.6, 144.3, 137.7, 133.2, 130.8, 128.8, 128.6, 128.5, 128.2, 127.9, 125.9, 125.8, 124.8, 105.0, 34.7, 31.4.

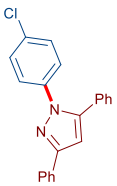
1-(4-Fluorophenyl)-3,5-diphenyl-1*H*-pyrazole (3ae)[10]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), bis(4-fluorophenyl)iodonium trifluoromethanesulfonate (0.111 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (4% ethyl acetate in hexane) gave **3ae** as a yellow solid (0.048 g, 77%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.32 (m, 6H), 7.30 – 7.26 (m, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.83 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.5 (d, *J* = 247.5Hz), 151.9, 144.4, 136.2 (d, *J* = 3.0 Hz), 132.8, 130.2, 128.62, 128.56, 128.46, 128.3, 128.0, 126.9 (d, *J* = 8.6 Hz), 125.7, 115.7 (d, *J* = 23 Hz), 105.1. **^{19}F{1H} NMR** (471 MHz, $CDCl_3$) δ -114.01.

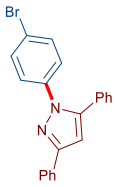
1-(4-Chlorophenyl)-3,5-diphenyl-1*H*-pyrazole (3af)[11]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), bis(4-chlorophenyl)iodonium trifluoromethanesulfonate (0.120 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (4% ethyl acetate in hexane) gave **3af** as a yellow solid (0.048 g, 73%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.30 (m, 10H), 6.86 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.3, 144.5, 138.7, 133.0, 132.9, 130.3, 129.1, 128.8, 128.74, 128.69, 128.6, 128.2, 126.3, 125.9, 105.6.

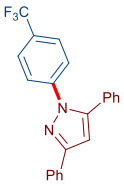
1-(4-Bromophenyl)-3,5-diphenyl-1*H*-pyrazole (3ag)[11]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), bis(4-bromophenyl)iodonium trifluoromethanesulfonate (0.141 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (4% ethyl acetate in hexane) gave **3ag** as a white solid (0.053 g, 71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.91 (m, 2H), 7.52 – 7.45 (m, 4H), 7.42 – 7.36 (m, 4H), 7.34 – 7.27 (m, 4H), 6.85 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.4, 144.6, 139.2, 132.9, 132.1, 130.4, 128.9, 128.82, 128.79, 128.7, 128.3, 126.7, 126.0, 121.1, 105.8.

3,5-Diphenyl-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazole (3ah)[12]

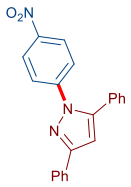


The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), bis(4-(trifluoromethyl)phenyl)iodonium trifluoromethanesulfonate (0.136 g, 0.24

mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave **3ah** as a white solid (0.044 g, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.3 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.40 – 7.33 (m, 4H), 7.32 – 7.26 (m, 2H), 6.83 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.8, 144.7, 142.9, 132.7, 130.3, 129.1 (q, *J* = 33 Hz), 128.91, 128.87 (2C), 128.85, 128.5, 126.2 (q, *J* = 4 Hz), 126.0, 124.9, 124.0 (q, *J* = 271 Hz), 106.4. **^{19}F{1H} NMR** (471 MHz, $CDCl_3$) δ -62.36.

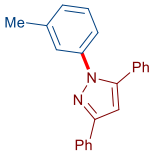
1-(4-Nitrophenyl)-3,5-diphenyl-1*H*-pyrazole (3ai)[11]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), mesityl (4-nitrophenyl) iodonium trifluoromethanesulfonate (0.124 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (4% ethyl acetate in hexane) gave **3ai** as a yellow solid (0.046 g, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 – 8.17 (m, 2H), 8.01 – 7.93 (m, 2H), 7.61 – 7.53 (m, 2H), 7.53 – 7.47 (m, 2H), 7.46 – 7.39 (m, 4H), 7.37 – 7.31 (m, 2H), 6.89 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 153.3, 145.8, 145.0, 144.9, 132.4, 130.1, 129.2, 129.0, 128.89, 128.85, 128.7, 126.0, 124.5, 124.5, 107.3.

3,5-Diphenyl-1-(m-tolyl)-1*H*-pyrazole (3aj)[10]

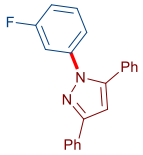


The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), di-m-tolyliodonium trifluoromethanesulfonate (0.109 g, 0.24 mmol) and 2,6-di-tert-

butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (4% ethyl acetate in hexane) gave **3aj** as a yellow oil (0.030 g, 48%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.2 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.25 – 7.16 (m, 7H), 7.08 (d, *J* = 7.7 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.73 (s, 1H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.9, 144.5, 140.1, 139.2, 133.2, 130.7, 128.81, 128.76, 128.7, 128.5, 128.38, 128.35, 128.1, 126.1, 125.9, 122.6, 105.2, 21.5.

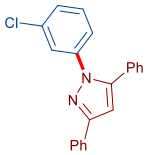
1-(3-Fluorophenyl)-3,5-diphenyl-1*H*-pyrazole (3ak)



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), bis(3-fluorophenyl)iodonium trifluoromethanesulfonate (0.112 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (4% ethyl acetate in hexane) gave **3ak** as a white solid (0.043 g, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.3 Hz, 2H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.38 – 7.32 (m, 4H), 7.31 – 7.23 (m, 3H), 7.21 – 7.15 (m, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.03 – 6.92 (m, 1H), 6.81 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 162.7 (d, *J* = 247.1 Hz), 152.4, 144.7, 141.6 (d, *J* = 10.2 Hz), 132.9, 130.4, 130.1 (d, *J* = 9.1 Hz), 128.89, 128.82, 128.76, 128.74, 128.3, 126.0, 120.8 (d, *J* = 3.2 Hz), 114.4 (d, *J* = 21.1 Hz), 112.7 (d, *J* = 24.7 Hz), 105.9. **^{19}F{1H} NMR** (471 MHz, $CDCl_3$) δ -111.28. **HRMS-ESI** (m/z): calcd for $C_{21}H_{15}FN_2$ $[M + H]^+$ 315.1292; found 315.1303.

1-(3-Chlorophenyl)-3,5-diphenyl-1*H*-pyrazole (3al)[13]

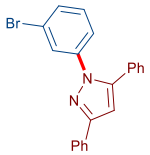


The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2

mmol), bis(3-chlorophenyl)iodonium trifluoromethanesulfonate (0.120 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (4% ethyl acetate in hexane) gave **3al** as a yellow oil (0.050 g, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.52 (t, *J* = 1.9 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.39 – 7.34 (m, 4H), 7.31 – 7.28 (m, 2H), 7.27 – 7.24 (m, 1H), 7.23 (t, *J* = 7.9 Hz, 1H), 7.20 – 7.10 (m, 1H), 6.83 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.5, 144.7, 141.2, 134.7, 132.8, 130.3, 129.8, 128.9, 128.84, 128.78, 128.4, 127.6, 126.0, 125.4, 123.3, 105.8.

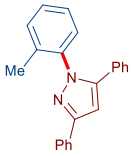
1-(3-Bromophenyl)-3,5-diphenyl-1*H*-pyrazole (3am)[13]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), bis(3-bromophenyl)iodonium trifluoromethanesulfonate (0.141 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (4% ethyl acetate in hexane) gave **3am** as a yellow oil (0.055 g, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.3 Hz, 2H), 7.71 (d, *J* = 1.7 Hz, 1H), 7.50 – 7.41 (m, 3H), 7.40 – 7.34 (m, 4H), 7.30 – 7.25 (m, 2H), 7.20 – 7.14 (m, 2H), 6.83 (s, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 152.4, 144.6, 141.2, 132.8, 130.4, 130.2, 130.0, 128.81, 128.76, 128.70 (2C), 128.3, 128.2, 125.9, 123.7, 122.5, 105.8.

3,5-Diphenyl-1-(o-tolyl)-1*H*-pyrazole (3an)[11]

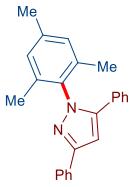


The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), di-o-tolyliodonium trifluoromethanesulfonate (0.110 g, 0.24 mmol) and 2,6-di-tert-

butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (3% ethyl acetate in hexane) gave **3an** as a yellow oil (0.036 g, 58%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.32 – 7.24 (m, 7H), 6.92 (s, 1H), 2.08 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.6, 145.4, 139.4, 135.6, 133.0, 131.0, 130.1, 128.9, 128.5, 128.3, 128.1, 128.0, 127.8, 127.7, 126.5, 125.7, 103.1, 17.6.

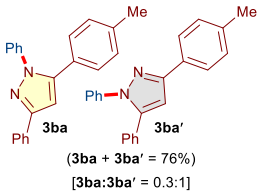
1-Mesityl-3,5-diphenyl-1*H*-pyrazole (3ao)[11]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.075 g, 0.2 mmol), dimesityliodonium trifluoromethanesulfonate (0.123 g, 0.24 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (4% ethyl acetate in hexane) gave **3ao** as a white solid (0.019 g, 31%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 7.94 (m, 2H), 7.54 – 7.44 (m, 2H), 7.42 – 7.36 (m, 1H), 7.34 – 7.25 (m, 5H), 6.98 (d, *J* = 3.3 Hz, 3H), 2.37 (s, 3H), 2.04 (s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 151.8, 145.3, 138.9, 136.4, 136.1, 133.5, 130.3, 129.2, 128.7, 128.6, 128.2, 127.9, 127.2, 125.8, 102.6, 21.2, 17.8.

1,3-Diphenyl-5-(p-tolyl)-1*H*-pyrazole (3ba)[7] **and 1,5-Diphenyl-3-(p-tolyl)-1*H*-pyrazole (3ba′)**[14]

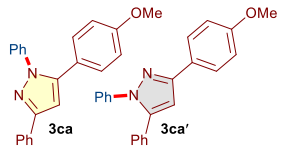


The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), *(Z)*-4-methyl-N'-(1-phenyl-3-(p-tolyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide (0.077 g, 0.2 mmol) and 2,6-

di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.3 ratio) **3ba** and **3ba′** as a white solid (0.047 g, 76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.88 (d, *J* = 8.0 Hz, 2H, minor), 7.84 – 7.77 (m, 2H, major), 7.45 – 7.07 (m, 24H), 6.78 (s, 2H), 2.38 (s, 3H, major), 2.34 (s, 3H, minor). **^{13}C NMR** (126 MHz, $CDCl_3$) major regioisomer δ 152.0, 144.2, 140.1, 137.7, 130.6, 130.2, 129.3, 128.8, 128.6, 128.4, 128.2, 127.3, 125.7, 125.3, 105.0, 21.3. minor regioisomer δ 151.9, 144.4, 140.2, 138.2, 130.6, 130.2, 129.1, 128.7, 128.6, 128.2, 127.9, 127.3, 125.8, 125.3, 104.9, 21.2.

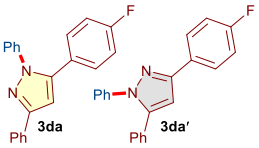
5-(4-Methoxyphenyl)-1,3-diphenyl-1*H*-pyrazole (3ca)[14] **and 4-(3-(4-Methoxyphenyl)-5-phenyl-1*H*-pyrazol-1-yl)benzene-1-ylium (3ca′)**[15]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), *(Z)*-N'-(3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.080 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.75 ratio) **3ca** and **3ca′** as a white solid (0.051 g, 78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (m, 2H, minor), 7.87 – 7.83 (m, 2H, major), 7.45 – 7.25 (m, 18H), 7.22 – 7.20 (m, 1H, minor), 7.20 – 7.17 (m, 1H, major), 6.98 – 6.96 (m, 1H, major), 6.96 – 6.94 (m, 1H, minor), 6.87 – 6.84 (m, 1H, major), 6.84 – 6.82 (m, 1H, minor), 6.76 (s, 1H, minor), 6.75 (s, 1H, major), 3.84 (s, 3H, major), 3.80 (s, 3H, minor). **^{13}C NMR** (126 MHz, $CDCl_3$) major regioisomer δ 159.7, 151.9, 144.4, 140.3, 130.8, 128.9, 128.8, 128.5, 128.0, 127.4, 127.2, 125.9, 125.4, 114.1, 104.9, 55.4. minor regioisomer δ 159.7, 151.9, 144.3, 140.4, 133.2, 130.1, 128.9, 128.7, 128.3, 127.4, 125.9, 125.4, 123.1, 114.0, 104.8, 55.4.

5-(4-Fluorophenyl)-1,3-diphenyl-1*H*-pyrazole (3da)[10] **and 3-(4-Fluorophenyl)-1,5-diphenyl-1*H*-pyrazole (3da′)**[10]



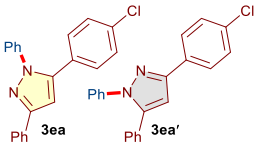
(**3da** + **3da′** = 72%)

[**3da**:**3da′** = 0.95:1]

The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-N'-(3-(4-fluorophenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.078 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.95 ratio) **3da** and **3da′** as a white solid (0.045 g, 72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.87 (m, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.39 – 7.30 (m, 16H), 7.29 – 7.23 (m, 4H), 7.15 – 7.09 (m, 1H, minor), 7.06 – 6.99 (m, 1H, major), 6.80 (s, 1H, major), 6.77 (s, 1H, minor). **^{13}C NMR** (126 MHz, $CDCl_3$) major regioisomer δ 162.7 (d, *J* = 248.9 Hz), 151.2, 144.6, 140.1, 130.72, 130.67, 129.1 (d, *J* = 7.9 Hz), 128.6, 128.5, 127.7, 127.6, 126.8 (d, *J* = 3.2 Hz), 125.4, 115.7 (d, *J* = 21.6 Hz), 105.1. minor regioisomer δ 162.9 (d, *J* = 246.5 Hz), 152.1, 143.5, 140.2, 133.1, 130.6, 129.4 (d, *J* = 2.5 Hz), 128.8 (d, *J* = 7.8 Hz), 128.2, 127.7, 127.6, 125.9, 125.4, 115.7 (d, *J* = 21.8 Hz), 105.3. **^{19}F{1H} NMR** (373 MHz, $CDCl_3$) δ -112.59, -114.05.

5-(4-Chlorophenyl)-1,3-diphenyl-1*H*-pyrazole (3ea)[10] **and 3-(4-Chlorophenyl)-1,5-diphenyl-1*H*-pyrazole (3ea′)**[10]



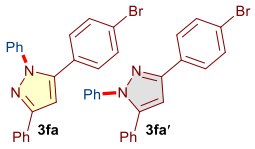
(**3ea** + **3ea′** = 78%)

[**3ba**:**3ba′** = 1:1]

The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-N'-(3-(4-chlorophenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.082 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:1 ratio) **3ea** and **3ea′** as a yellow solid (0.052 g, 78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 8.1, 0.9 Hz, 2H, **3ea**), 7.89 (dd, *J* = 8.9, 2.0 Hz, 2H, **3ea′**), 7.49 – 7.28 (m, 22H), 7.26 – 7.22 (m, 2H), 6.85 (s, 1H, **3ea**), 6.82 (s, 1H, **3ea′**). **^{13}C NMR** (126 MHz, $CDCl_3$) compound **3ea** δ 152.2, 144.7, 140.2, 133.8, 133.0, 129.2, 129.0, 128.9, 128.7, 128.5, 128.2, 127.7, 125.9, 125.5, 105.4. compound **3ea′** δ 151.0, 143.3, 140.0, 134.5, 131.7, 130.5, 130.1, 129.1, 128.9, 128.8, 127.8, 127.2, 125.4, 121.7, 105.2.

5-(4-Bromophenyl)-1,3-diphenyl-1*H*-pyrazole (3fa)[10] **and 3-(4-Bromophenyl)-1,5-diphenyl-1*H*-pyrazole (3fa′)**[10]

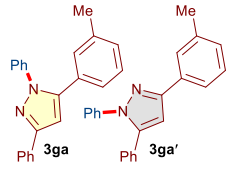


(**3fa** + **3fa′** = 75%)
[**3fa**:**3fa′** = 0.6:1]

The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-N'-(3-(4-bromophenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.090 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.6 ratio) **3fa** and **3fa′** as a yellow solid (0.056 g, 75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.5 Hz, 2H, minor), 7.83 (d, *J* = 8.4 Hz, 2H, major), 7.58 (d, *J* = 8.4 Hz, 2H, major), 7.51 – 7.44 (m, 4H), 7.44 – 7.33 (m, 14H), 7.32 – 7.27 (m, 2H, major), 7.18 (d, *J* = 8.4 Hz, 2H, minor), 6.85 (s, 1H, minor), 6.83 (s, 1H, major). **^{13}C NMR** (126 MHz, CDCl3) major regioisomer δ 150.9, 144.7, 140.0, 132.1, 131.8, 130.4, 129.0, 128.8, 128.54, 128.45, 127.6, 127.4, 125.3, 122.0, 105.1. minor regioisomer (125 MHz, CDCl3): δ 152.2, 143.2, 139.9, 132.9, 131.8, 130.3, 129.5, 129.15, 128.8, 128.2, 127.8, 125.9, 125.4, 122.7, 105.4.

1,5-Diphenyl-3-(m-tolyl)-1*H*-pyrazole (3ga) and 1,3-diphenyl-5-(m-tolyl)-1*H*-pyrazole (3ga′)[10]

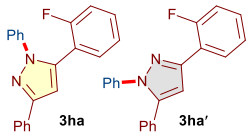


(**3ga** + **3ga′** = 73%)
[**3ga**:**3ga′** = 0.95:1]

The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-4-methyl-N'-(1-phenyl-3-(m-tolyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide (0.077 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.95 ratio) **3ga** and **3ga′** as a yellow oil (0.045 g, 73%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.1 Hz, 2H), 7.80 (s, 1H), 7.72 (d, *J* = 7.7 Hz, 1H, minor), 7.45 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.27 (m, 17H), 7.23 – 7.13 (m, 4H), 7.04 (d, *J* = 7.5 Hz, 1H, major), 6.83 (d, *J* = 3.2 Hz, 2H), 2.43 (s, 3H, Minor), 2.33 (s, 3H, Major). **^{13}C NMR** (126 MHz, $CDCl_3$) major regioisomer δ 152.1, 144.4, 140.2, 138.3, 133.0, 130.6, 128.9, 128.84, 128.77, 128.6, 128.5, 128.3, 127.4, 126.5, 125.4, 123.0, 105.3, 21.5. minor regioisomer δ 151.9, 144.6, 140.2, 138.2, 133.1, 130.5, 129.4, 129.1, 129.0, 128.7, 128.3, 128.0, 127.5, 125.9, 125.8, 125.3, 105.2, 21.4. **HRMS-ESI** (m/z): calcd for $C_{22}H_{18}N_2$ $[M]^+$ 310.1470; found 310.3104.

3-(2-Fluorophenyl)-1,5-diphenyl-1*H*-pyrazole (3ha) and 3-(2-fluorophenyl)-1,5-diphenyl-1*H*-pyrazole (3ha′)

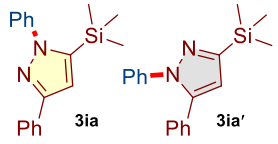


(**3ha** + **3ha′** = 75%)
[**3ha**:**3ha′** = 1:1]

The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-N'-(3-(2-fluorophenyl)-1-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.078 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:1 ratio) **3ha** and **3ha′** as a yellow oil (0.047 g, 75%).

^{1}H NMR (500 MHz, $CDCl_3$) inseparable regioisomer δ 8.22 – 8.16 (m, 1H), 8.02 – 7.93 (m, 2H), 7.50 – 7.44 (m, 2H), 7.44 – 7.30 (m, 17H), 7.30 – 7.06 (m, 6H), 7.02 (d, *J* = 3.9 Hz, 1H), 6.92 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) inseparable regioisomers δ 160.4 (d, *J* = 249.6 Hz), 159.5 (d, *J* = 250.1 Hz), 152.1, 146.7, 144.1, 140.2 (d, *J* = 24.7 Hz), 138.1, 133.0, 131.4 (d, *J* = 2.3 Hz), 130.7 (d, *J* = 8.2 Hz), 130.5, 129.3 (d, *J* = 8.4 Hz), 129.0, 128.9, 128.8, 128.7, 128.6 (d, *J* = 3.6 Hz), 128.5, 128.3, 128.0, 127.6, 127.4, 125.9, 125.4, 124.4, 124.3 (d, *J* = 3.4 Hz), 124.2 (d, *J* = 3.6 Hz), 121.0 (d, *J* = 11.9 Hz), 118.9 (d, *J* = 14.8 Hz), 116.2 (d, *J* = 21.6 Hz), 116.1, 116.0, 108.6 (d, *J* = 10.1 Hz), 106.8. **^{19}F{1H} NMR** (471 MHz, $CDCl_3$) δ -112.57, -115.83. **HRMS-ESI** (m/z): calcd for $C_{21}H_{15}FN_2$ $[M+H]^+$ 315.1292; found 315.1305.

1,3-Diphenyl-5-(trimethylsilyl)-1*H*-pyrazole (3ia) and 1,5-Diphenyl-3-(trimethylsilyl)-1*H*-pyrazole (3ia′)

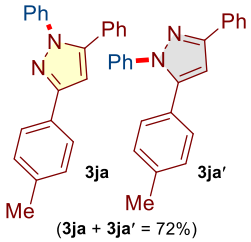


(**3ia** + **3ia′** = 64%)
[**3ia**:**3ia′** = 0.8:1]

The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-4-methyl-N'-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide (0.074 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (0.78:1 ratio) **3ia** and **3ia′** as a yellow oil (0.037 g, 64%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (br s, 4H), 7.16 (br s, 4H), 7.13 – 7.10 (m, 8H), 7.07 – 7.04 (m, 4H), 6.45 (s, 1H, major), 6.45 (s, 1H, minor), 0.21 (s, 9H, major), 0.21 (s, 9H, minor). **^{13}C NMR** (126 MHz, $CDCl_3$) major isomer δ 154.1, 140.4, 131.1, 128.9, 128.8, 128.5, 128.4, 128.1, 127.5, 125.6, 114.5, -0.8. minor isomer 154.1, 143.2, 129.1, 128.9, 128.8, 128.5, 128.0, 127.5, 127.4, 125.4, 114.1, -0.9. **HRMS-ESI** (m/z): calcd for $C_{18}H_{20}N_2Si$ $[M+H]^+$ 293.1169; found 293.1173.

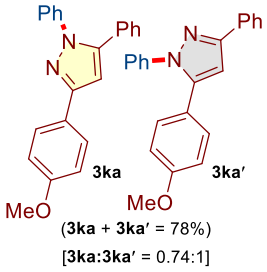
1,5-Diphenyl-3-(p-tolyl)-1*H*-pyrazole (3ja)[10] **and 1,3-Diphenyl-5-(p-tolyl)-1*H*-pyrazole (3ja′)**[10]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-4-methyl-N'-(3-phenyl-1-(p-tolyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide (0.077 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.95 ratio) **3ja** and **3ja′** as a white solid (0.044 g, 72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.44 – 7.30 (m, 16H), 7.28 (d, *J* = 7.1 Hz, 2H), 7.21 (d, *J* = 8.1 Hz, 2H, major), 7.16 (d, *J* = 8.1 Hz, 2H, minor), 6.83 (s, 2H), 2.43 (s, 3H, minor), 2.39 (s, 3H, major). **^{13}C NMR** (126 MHz, $CDCl_3$) major regioisomer δ 152.0, 144.5, 140.3, 138.4, 130.8, 129.3, 129.0, 128.7, 128.6, 128.1, 127.8, 127.5, 126.0, 125.5, 105.1, 21.4. minor regioisomer δ 152.1, 144.6, 140.3, 137.9, 133.2, 130.3, 129.5, 129.0, 128.9, 128.8, 128.4, 126.0, 125.9, 125.5, 105.2, 21.5.

5-(4-Methoxyphenyl)-1,3-diphenyl-1*H*-pyrazole (3ka)[10] **and 3-(4-Methoxyphenyl)-1,5-diphenyl-1*H*-pyrazole (3ka′)**[10]

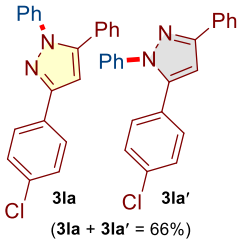


The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-N'-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.081 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column

chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.74 ratio) **3ka** and **3ka′** as a white solid (0.051 g, 78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H, minor), 7.92 – 7.85 (m, 2H, major), 7.51 – 7.27 (m, 18H), 7.26 – 7.19 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H, major), 6.88 (d, *J* = 8.8 Hz, 2H, minor), 6.84 – 6.72 (m, 2H), 3.88 (s, 3H, major), 3.84 (s, 3H, minor). ^{13}C NMR (126 MHz, $CDCl_3$) major regioisomer δ 159.7, 151.9, 144.4, 140.3, 130.8, 129.0 (2C), 128.8, 128.4, 127.4, 127.2, 125.4, 123.1, 114.2, 104.9, 55.4. minor regioisomer δ 159.7, 152.0, 144.4, 140.4, 133.3, 130.2, 129.0 (2C), 128.9, 128.6, 128.1, 125.9, 123.1, 114.1, 104.8, 55.4.

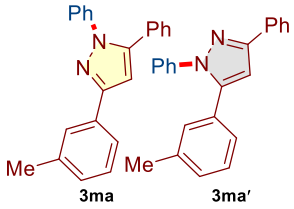
3-(4-chlorophenyl)-1,5-diphenyl-1*H*-pyrazole (3la)[10] **and 5-(4-Chlorophenyl)-1,3-diphenyl-1*H*-pyrazole (3la′)**[10]



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-N'-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.081 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:1 ratio) **3la** and **3la′** as a yellow oil (0.043 g, 66%).

^{1}H NMR (500 MHz, $CDCl_3$) inseparable regioisomer δ 7.94 – 7.90 (m, 2H), 7.89 – 7.83 (m, 2H), 7.46 – 7.42 (m, 2H), 7.41 – 7.38 (m, 2H), 7.38 – 7.34 (m, 9H), 7.33 – 7.30 (m, 6H), 7.28 – 7.24 (m, 3H), 7.23 – 7.18 (m, 2H), 6.81 (s, 1H), 6.79 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) inseparable regioisomer δ 152.2, 150.9, 144.7, 143.3, 140.1, 140.0, 134.5, 133.8, 133.0, 131.7, 130.5, 130.1, 129.2, 129.0, 128.92, 128.88 (2C), 128.83, 128.77, 128.6, 128.5, 128.2, 127.8, 127.7, 127.1, 125.9, 125.4, 125.4, 105.4, 105.2.

1,5-diphenyl-3-(m-tolyl)-1*H*-pyrazole (3ma)[10] **and 1,3-Diphenyl-5-(m-tolyl)-1*H*-pyrazole (3ma′)**



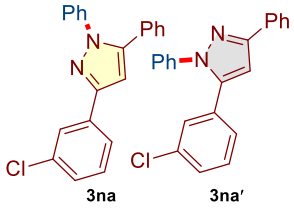
(**3ma** + **3ma′** = 68%)

[**3ma:3ma′** = 0.97:1]

The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-4-methyl-N'-(3-phenyl-1-(m-tolyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide (0.077 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.97 ratio) **3ma** and **3ma′** as a yellow soild (0.042 g, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.81 (s, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.29 (m, 17H), 7.23 – 7.13 (m, 4H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.86 – 7.81 (m, 2H), 2.44 (s, 3H, minor), 2.33 (s, 3H, major). **^{13}C NMR** (126 MHz, $CDCl_3$) major regioisomer δ 152.2, 144.4, 140.3, 138.3, 133.2, 130.6, 129.5, 128.9, 128.9, 128.8, 128.6, 128.4, 128.1, 127.5, 125.4, 123.1, 105.4, 21.5. minor regioisomer δ 152.0, 144.6, 140.3, 138.3, 133.0, 130.7, 129.1, 129.0, 128.7, 128.6, 128.4, 128.0, 127.5, 126.5, 126.0, 125.4, 105.2, 21.6. **HRMS-ESI** (m/z): calcd for $C_{22}H_{18}N_2$ $[M+H]^+$ 311.1543; found 311.1553

3-(3-Chlorophenyl)-1,5-diphenyl-1*H*-pyrazole (3na)[13] **and 5-(3-Chlorophenyl)-1,3-diphenyl-1*H*-pyrazole (3na′)**[17]



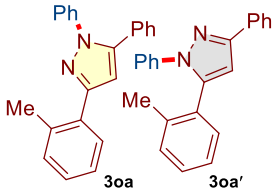
(**3na** + **3na′** = 69%)

[**3na:3na′** = 0.90:1]

The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-N'-(1-(3-chlorophenyl)-3-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.081 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.90 ratio) **3na** and **3na'** as a yellow oil (0.045 g, 69%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.92 (s, 1H), 7.80 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.40 – 7.27 (m, 20H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.12 – 7.07 (m, 1H), 6.85 (s, 1H, major), 6.82 (s, 1H, minor). **^{13}C NMR** (101 MHz, $CDCl_3$) major regioisomer δ 150.7, 144.7, 140.0, 135.0, 134.7, 132.3, 129.2, 128.8, 128.6, 128.5, 128.0, 127.7, 127.0, 125.9, 125.4, 124.0, 105.6. minor regioisomer 152.2, 142.9, 139.9, 134.5, 132.9, 130.4, 130.0, 129.8, 129.1, 128.8, 128.7, 128.5, 128.2, 127.9, 125.9, 125.4, 105.3.

1,3-Diphenyl-5-(o-tolyl)-1*H*-pyrazole (3oa)[10] **and 1,5-Diphenyl-3-(o-tolyl)-1*H*-pyrazole (3oa′)**[13]

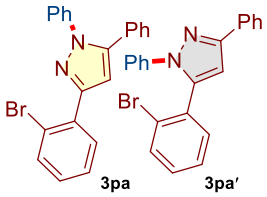


(**3oa** + **3oa′** = 61%)
[**3oa:3oa′** = 0.45:1]

The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (E)-4-methyl-N'-(3-phenyl-1-(o-tolyl)prop-2-yn-1-ylidene)benzenesulfonohydrazide (0.077 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.45 ratio) **3oa** and **3oa'** as a yellow oil (0.038 g, 61%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.5 Hz, 2H), 7.81 – 7.73 (m, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.46 – 7.20 (m, 23H), 6.78 (s, 1H, major), 6.74 (s, 1H, minor), 2.66 (s, 3H, minor), 2.08 (s, 3H, major). **^{13}C NMR** (101 MHz, $CDCl_3$) major regioisomer δ 152.5, 143.4, 140.2, 136.2, 133.1, 132.9, 130.9, 129.4, 128.9, 128.8, 128.7, 128.6, 127.9, 127.3, 125.8, 123.7, 106.2, 20.0. minor regioisomer δ 152.5, 143.4, 140.2, 136.2, 133.1, 132.9, 130.9, 130.7, 129.4, 128.9, 128.6, 128.3, 127.9, 127.3, 125.9, 125.2, 108.3, 21.5.

3-(2-bromophenyl)-1,5-diphenyl-1*H*-pyrazole (3pa)[13] **and 5-(2-Bromophenyl)-1,3-diphenyl-1*H*-pyrazole (3pa′)**

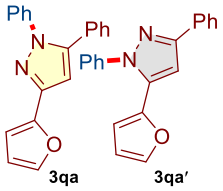


(**3pa** + **3pa′** = 71%)
[**3pa:3pa′** = 0.35:1]

The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (E)-N'-(1-(2-bromophenyl)-3-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.090 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.35 ratio) **3pa** and **3pa'** as a yellow oil (0.053 g, 71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.0 Hz, 2H, major), 7.92 (d, *J* = 7.7, 1H, minor), 7.73 (d, *J* = 8.0 Hz, 1H, minor), 7.65 (d, *J* = 8.1 Hz, 1H, major), 7.48 (t, *J* = 7.7 Hz, 2H), 7.45 – 7.22 (m, 21H), 7.10 (s, 1H, minor), 6.88 (s, 1H, major). **^{13}C NMR** (126 MHz, CDCl3) major regioisomer δ 151.6, 142.6, 140.1, 133.2, 132.3, 130.5, 128.8, 128.7, 128.4, 128.1, 127.5, 127.4, 127.2, 125.9, 125.3, 124.1, 106.8. minor regioisomer δ 151.1, 143.3, 140.0, 134.2, 133.6, 133.0, 132.5, 131.3, 130.5, 129.3, 129.0, 128.9, 128.5, 128.4, 127.6, 122.1, 109.0. **HRMS-ESI** (m/z): calcd for $C_{21}H_{15}BrN_2$ $[M+H]^+$ 377.0471; found 377.0485.

1,5-Diphenyl-3-(thiophen-2-yl)-1*H*-pyrazole (3qa)[13] **and 1,3-Diphenyl-5-(thiophen-2-yl)-1*H*-pyrazole (3qa′)**



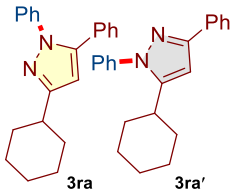
(**3qa** + **3qa′** = 68%)
[**3qa**:**3qa′** = 0.49:1]

The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (E)-4-methyl-N'-(3-phenyl-1-(thiophen-2-yl)prop-2-yn-1-ylidene)benzenesulfonohydrazide (0.076 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.49 ratio) **3qa** and **3qa'** as a yellow oil (0.041 g, 68%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.51 – 7.39 (m, 11H), 7.38 – 7.22 (m, 10H), 7.10 (dd, *J* = 5.0, 3.6 Hz, 1H, minor), 6.97 (dd, *J* = 5.1, 3.6 Hz, 1H, major), 6.89 (s, 1H, major), 6.86 (dd, *J* = 3.5, 0.8 Hz, 1H), 6.74 (s, 1H, minor). **^{13}C NMR** (126 MHz, $CDCl_3$) major regioisomer δ 151.9, 139.9, 139.8, 138.3, 132.8, 131.3, 129.1, 128.7, 128.4, 128.1, 127.4, 126.6, 126.3, 125.9, 105.0. minor regioisomer δ 147.3, 144.4, 136.3, 130.3, 129.0, 128.8,

128.53, 128.46, 127.6, 127.5, 127.3, 125.4, 124.9, 124.2, 105.2. **HRMS-ESI** (m/z): calcd for $C_{19}H_{14}N_2O$ $[M+H]^+$ 287.1179; found 287.1178.

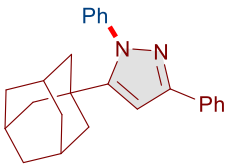
5-Cyclohexyl-1,3-diphenyl-1*H*-pyrazole (3ra) and 3-Cyclohexyl-1,5-diphenyl-1*H*-pyrazole (3ra′)



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), (Z)-N'-(1-cyclohexyl-3-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.076 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (7% ethyl acetate in hexane) gave inseparable mixture of two regioisomers (1:0.3 ratio) **3ra** and **3ra'** as a yellow solid (0.055 g, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 2H), 7.56 – 7.49 (m, 5H), 7.47 – 7.38 (m, 7H), 7.36 – 7.24 (m, 6H), 6.57 (s, 1H, major), 6.36 (s, 1H, minor), 2.84 – 2.76 (m, 1H, minor), 2.74 – 2.66 (m, 1H, major), 2.18 – 2.01 (m, 2H, minor), 1.99 – 1.63 (m, 9H), 1.58 – 1.39 (m, 4H), 1.38 – 1.11 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) inseparable mixture of regioisomers δ 159.1, 151.5, 150.9, 143.2, 140.3, 140.1, 133.5, 131.0, 129.2, 128.8, 128.7, 128.6, 128.4, 128.1, 128.0, 127.7, 127.0, 126.0, 125.7, 125.2, 105.1, 100.8, 37.7, 35.4, 33.6, 33.4, 26.5, 26.3, 26.2, 25.9. **HRMS-ESI** (m/z): calcd for $C_{21}H_{22}N_2$ $[M+H]^+$ 303.1861; found 303.1982.

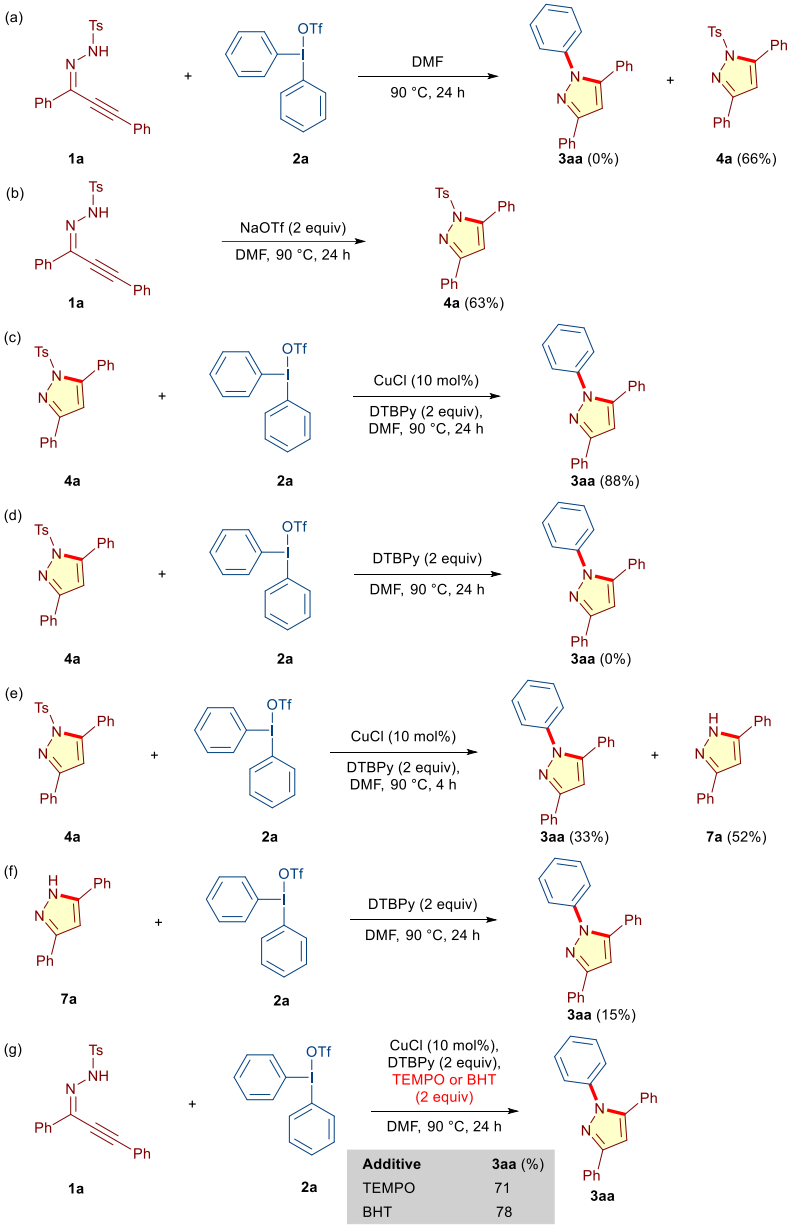
3-((3r, 5r, 7r)-Adamantan-1-yl)-1,5-diphenyl-1*H*-pyrazole (3sa)



The compound was prepared according to GP2 using copper(I) chloride (0.001 g, 0.02 mmol), diphenyliodonium trifluoromethanesulfonate (0.108 g, 0.25 mmol), N'-((*Z*)-1-((3r,5r,7r)-adamantan-1-yl)-3-phenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.086 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (43 µL, 0.4 mmol). After 24 h, purification by column chromatography (6% ethyl acetate in hexane) gave **3sa** as a yellow solid (0.034 g, 48%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 – 7.24 (d, *J* = 4.1 Hz, 4H), 7.23 – 7.20 (m, 4H), 7.18 (br s, 2H), 6.31 (s, 1H), 2.04 (br s, 3H), 2.01 (br s, 6H), 1.75 (br s, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.8, 142.9, 140.4, 131.2, 128.8, 128.7, 128.3, 127.9, 126.9, 125.3, 104.1, 42.6, 36.9, 34.2, 28.7. **HRMS-ESI** (m/z): calcd for $C_{25}H_{26}N_2$ $[M+H]^+$ 355.2169; found 355.2170.

2.5. Control Experiments: -



a) The reaction was performed according to GP2 using *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.037 g, 0.1 mmol), diphenyliodonium trifluoromethanesulfonate (0.086 g, 0.2 mmol). After 24 h, purification by column chromatography (10% ethyl acetate in hexane) gave **4a** as a white solid (0.024 g, 66%).

b) The reaction was performed according to GP2 using *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (0.037 g, 0.1 mmol), sodium trifluoromethanesulfonate (0.069 g, 0.2 mmol). After 24 h, purification by column chromatography (10% ethyl acetate in hexane) gave **4a** as a white solid (0.021 g, 63%).

c) The reaction was performed according to GP2 using copper(I) chloride (0.5 mg, 0.01 mmol), 3,5-diphenyl-1-tosyl-1*H*-pyrazole (0.037 g, 0.1 mmol), diphenyliodonium trifluoromethanesulfonate (0.086 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (22 µL, 0.2 mmol). After 24 h, purification by column chromatography (3% ethyl acetate in hexane) gave **3aa** as a yellow solid (0.026 g, 88%).

d) The reaction was performed according to GP2 using 3,5-diphenyl-1-tosyl-1*H*-pyrazole (0.037 g, 0.1 mmol), diphenyliodonium trifluoromethanesulfonate (0.086 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (22 µL, 0.2 mmol).

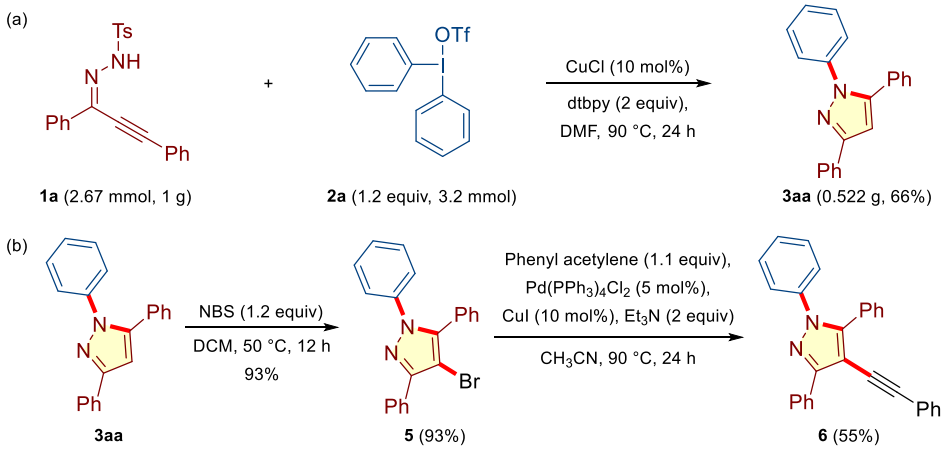
e) The reaction was performed according to GP2 using copper(I) chloride (0.5 mg, 0.01 mmol), 3,5-diphenyl-1-tosyl-1*H*-pyrazole (0.037 g, 0.1 mmol), diphenyliodonium trifluoromethanesulfonate (0.086 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (22 µL, 0.2 mmol). After 4 h, purification by column chromatography (3% ethyl acetate in hexane) gave **3aa** as a yellow solid (0.010 g, 33%) and **7a** as a white solid (0.011 g, 52%).

f) The reaction was performed according to GP2 using 3,5-diphenyl-1*H*-pyrazole (0.022 g, 0.1 mmol), diphenyliodonium trifluoromethanesulfonate (0.086 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (22 µL, 0.2 mmol). After 24 h, purification by column chromatography (3% ethyl acetate in hexane) gave **3aa** as a yellow solid (0.004 g, 15%).

g) The reaction was performed according to GP2 using copper(I) chloride (0.5 mg, 0.01 mmol), 3,5-diphenyl-1-tosyl-1*H*-pyrazole (0.037 g, 0.1 mmol), diphenyliodonium trifluoromethanesulfonate (0.086 g, 0.2 mmol), TEMPO (0.030 g, 0.2 mmol) and 2,6-di-tert-butylpyridine (22 µL, 0.2 mmol). After 24 h, purification by column chromatography (3% ethyl acetate in hexane) gave **3aa** as a yellow solid (0.021 g, 71%).

The reaction was performed according to GP2 using copper(I) chloride (0.5 mg, 0.01 mmol), 3,5-diphenyl-1-tosyl-1*H*-pyrazole (0.037 g, 0.1 mmol), diphenyliodonium trifluoromethanesulfonate (0.086 g, 0.2 mmol), BHT (0.044 g, 0.2 mmol) and 2,6-di-*tert*-butylpyridine (22 µL, 0.2 mmol). After 24 h, purification by column chromatography (3% ethyl acetate in hexane) gave **3aa** as a yellow solid (0.023 g, 78%).

2.6. Scale up experiment and Post-Synthetic Modifications: -



a) The reaction was performed according to GP2 using copper(I) chloride (0.027 g, 0.27 mmol), *(Z)*-N'-(1,3-diphenylprop-2-yn-1-ylidene)-4-methylbenzenesulfonohydrazide (1 g, 2.67 mmol), diphenyliodonium trifluoromethanesulfonate (1.4 g, 3.2 mmol) and 2,6-di-tert-butylpyridine (1.1 g, 5.4 mmol). After 24 h, purification by column chromatography (3% ethyl acetate in hexane) gave **3aa** as a yellow solid (0.522 g, 66%).

b) In a pre-dried flask compound **3aa** (0.074 g, 0.25 mmol, 1.0 equiv.) and NBS (0.054 mg, 0.3 mmol, 1.2 equiv.) were dissolved in dichloromethane (5 mL) and stirred at 50 ˚C. After 12 h, the reaction mixture was evaporated under vacuum and the crude mixture was purified by column chromatography (1% ethyl acetate in hexane) to afford the desired product **5** as a white solid (0.087 g, 93%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.53 – 7.48 (m, 2H), 7.47 – 7.40 (m, 4H), 7.39 – 7.36 (m, 2H), 7.34 – 7.28 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 149.8, 142.1, 139.9, 132.1, 130.3, 129.1 (2C), 128.9, 128.6, 128.5, 128.4, 128.1, 127.6, 124.8, 95.0.

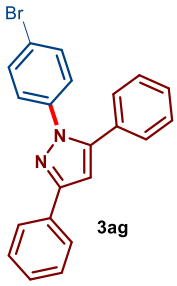
In a pre-dried Schlenk flask **5** (0.094 g, 0.25 mmol, 1 equiv), $Pd(PPh_3)_2Cl_2$ (0.009 g, 0.012 mmol, 0.05 equiv), Et_3N (71 µl, 0.5 mmol, 2 equiv) and anhydrous CH_3CN (2.5 ml) were added and stirred for 10 minutes at 25 °C under N_2. Subsequently, CuI (0.005 g, 0.025 mmol, 0.1 equiv) was added and the reaction mixture was stirred for an additional 10 minutes. Then phenyl acetylene (31 µl, 0.27 mmol, 1.1 equiv) was added in a single portion and the resulting mixture was stirred at 90 °C for 12 hours. After completion, the reaction was quenched by sat. $NaHCO_3$ (5 ml) solution and the aqueous layer was extracted with ethyl acetate (5 mL × 3). The organic phase was dried over Na_2SO_4 and concentrated using rotary evaporator. The crude

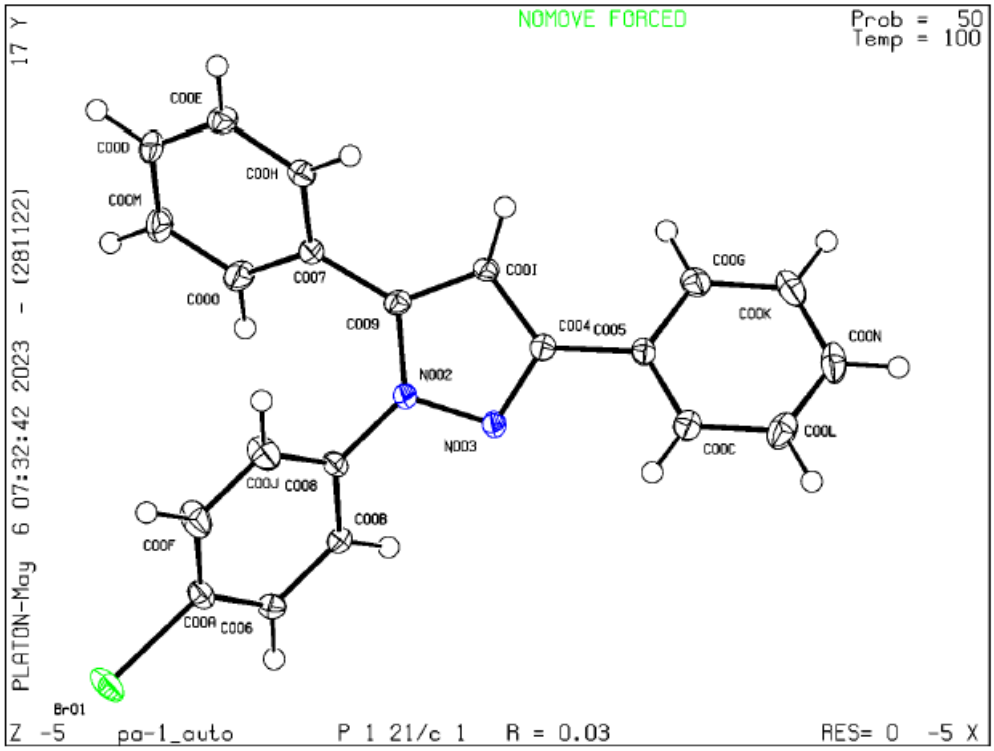
product was then purified using flash chromatography on silica gel (2% ethyl acetate in hexane) to afford the desired product **6**.as a yellow oil (0.055 g, 55%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 – 8.25 (m, 2H), 7.58 – 7.44 (m, 5H), 7.43 – 7.35 (m, 10H), 7.34 – 7.28 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 152.2, 145.8, 139.7, 132.6, 131.1, 129.7, 129.1, 129.0, 128.8, 128.4 (2C), 128.3 (2C), 127.9, 127.7, 127.2, 125.3, 123.8, 102.3, 93.4, 82.7.

3. Crystallographic data of 1-(4-Bromophenyl)-3,5-diphenyl-1*H*-pyrazole (3ag): -

The crystal **3ag** was prepared by slow evaporation of solvent from a concentrated solution of **3ag** in ethanol.





Crystal Structure data table of 3ag

Empirical formula	$C_{21}H_{15}BrN_2$
CCDC No	2261058
Formula weight	375.26
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	10.9325(5)
b/Å	16.9864(7)
c/Å	9.6085(5)
α/°	90
β/°	108.177(5)
γ/°	90
Volume/Å^3	1695.29(14)
Z	4
ρ_{calc}g/cm^3	1.470
μ/mm^{-1}	2.428
F(000)	760.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.21 to 60.568
Index ranges	$-14 \leq h \leq 15$, $-21 \leq k \leq 22$, $-11 \leq l \leq 12$
Reflections collected	16688
Independent reflections	4120 [R_{int} = 0.0386, R_{sigma} = 0.0346]
Data/restraints/parameters	4120/0/217
Goodness-of-fit on F^2	0.828
Final R indexes [I>=2σ (I)]	R_1 = 0.0321, wR_2 = 0.0986
Final R indexes [all data]	R_1 = 0.0437, wR_2 = 0.1067
Largest diff. peak/hole / e Å^{-3}	0.43/-0.30

4. References

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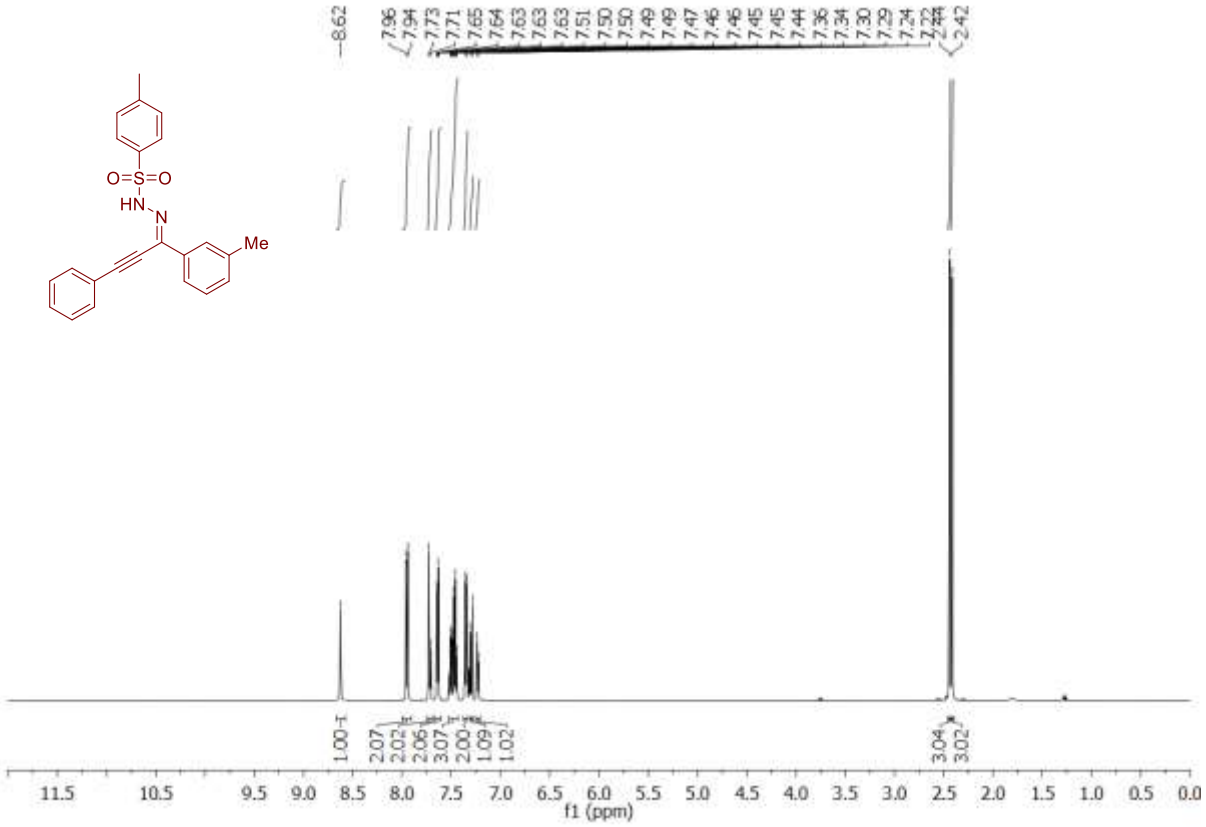
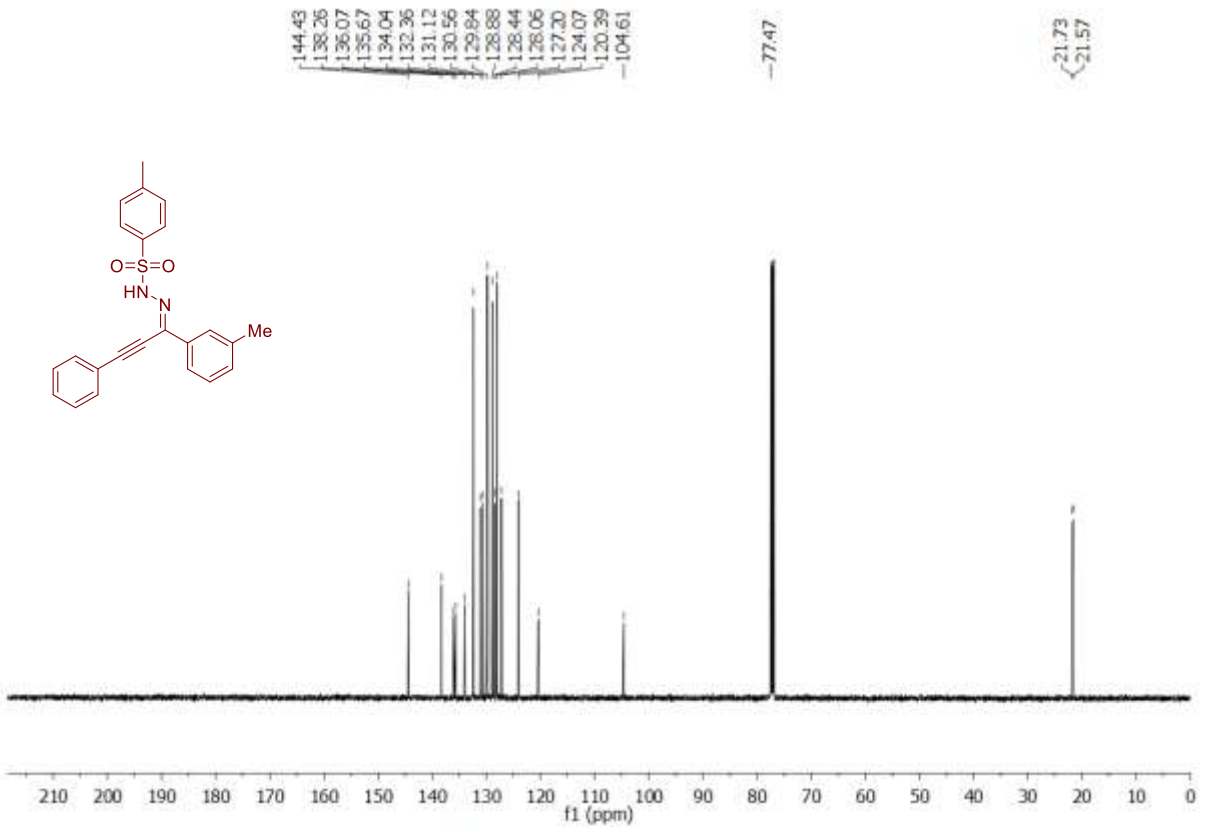
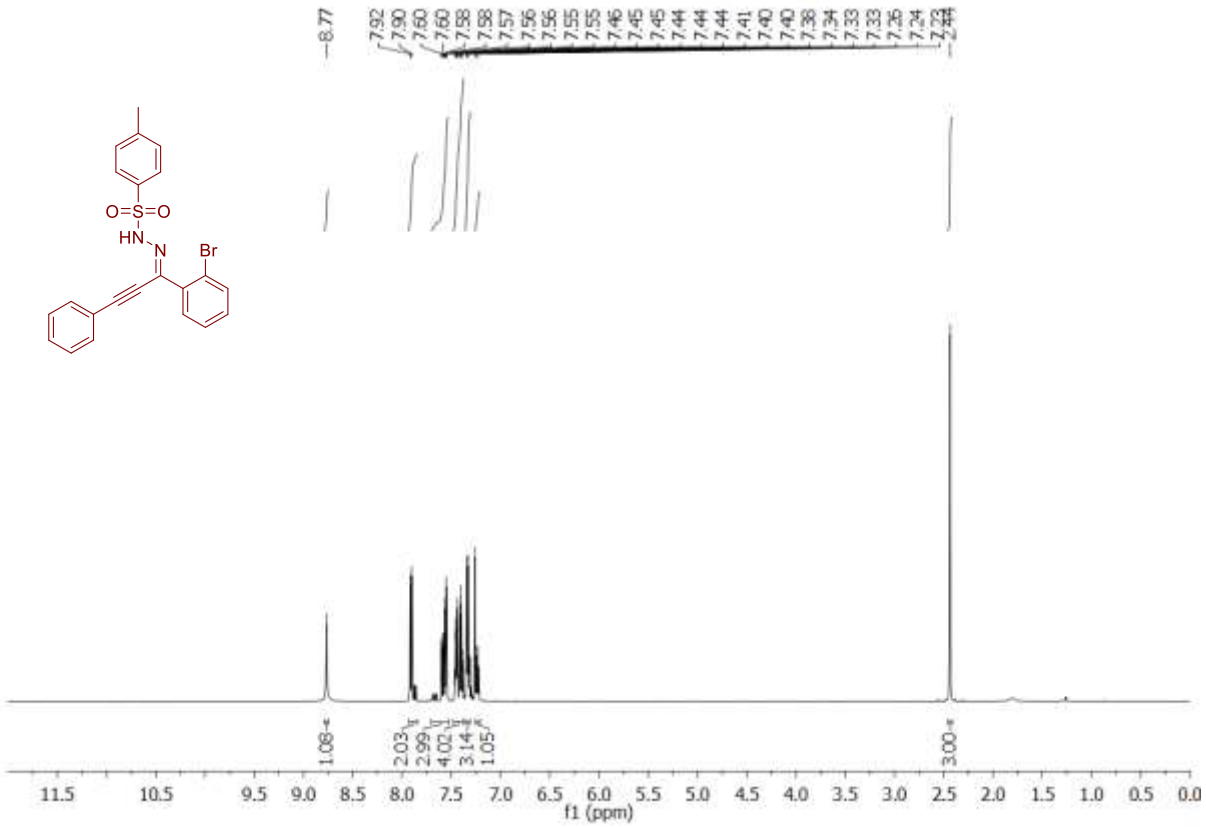
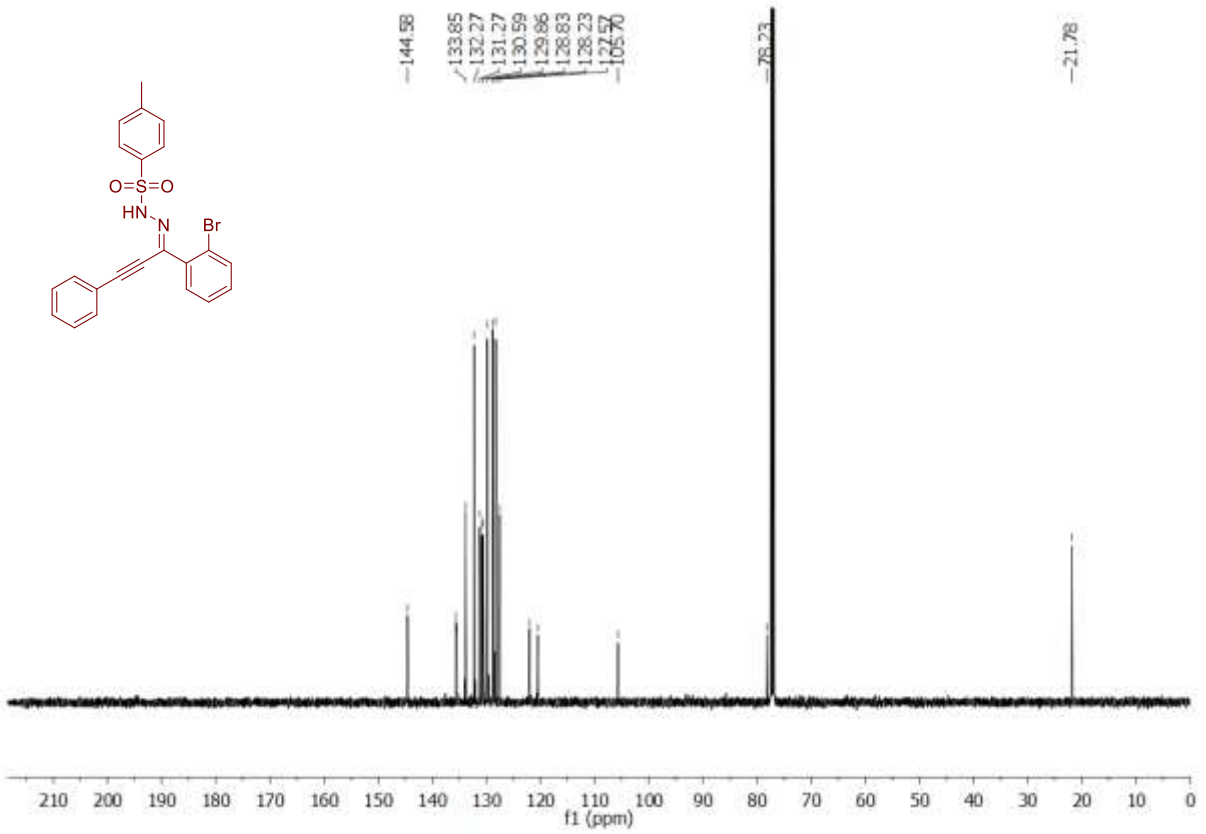
5. NMR Spectra of Compounds ^{1}H and ^{13}C NMR of 1m



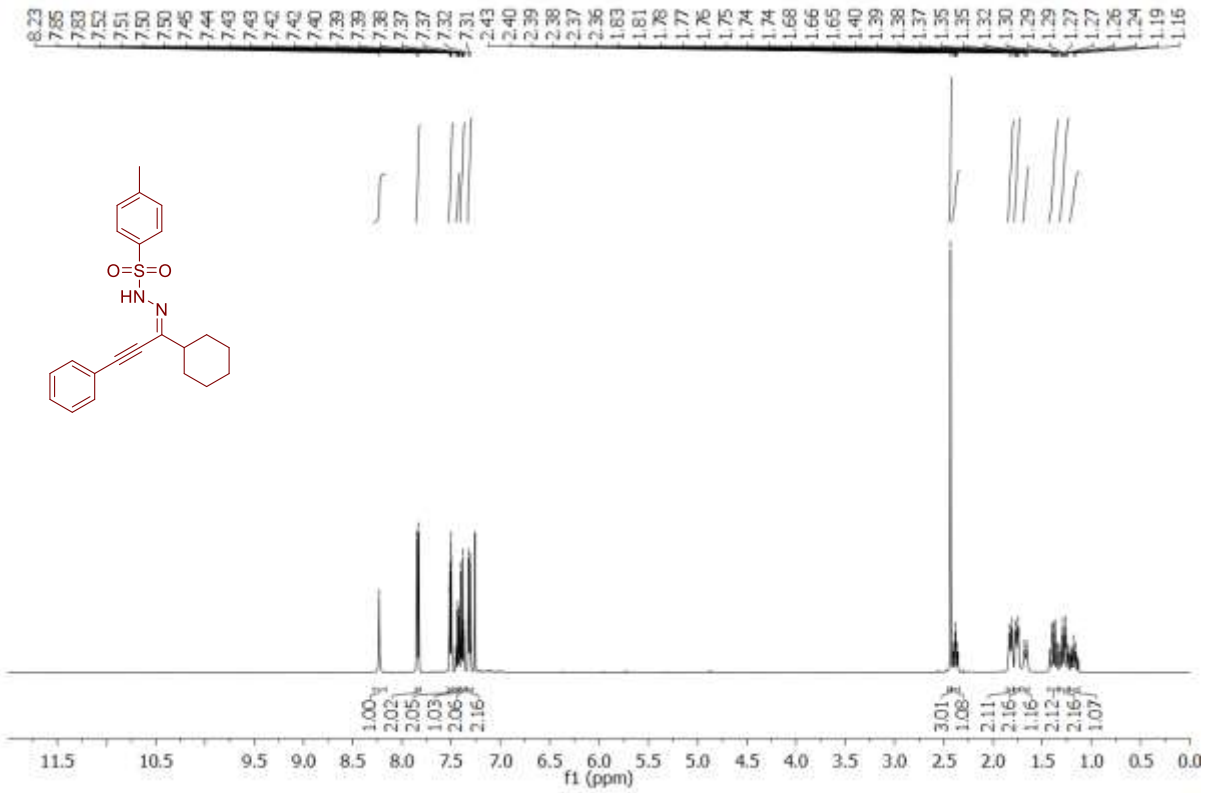


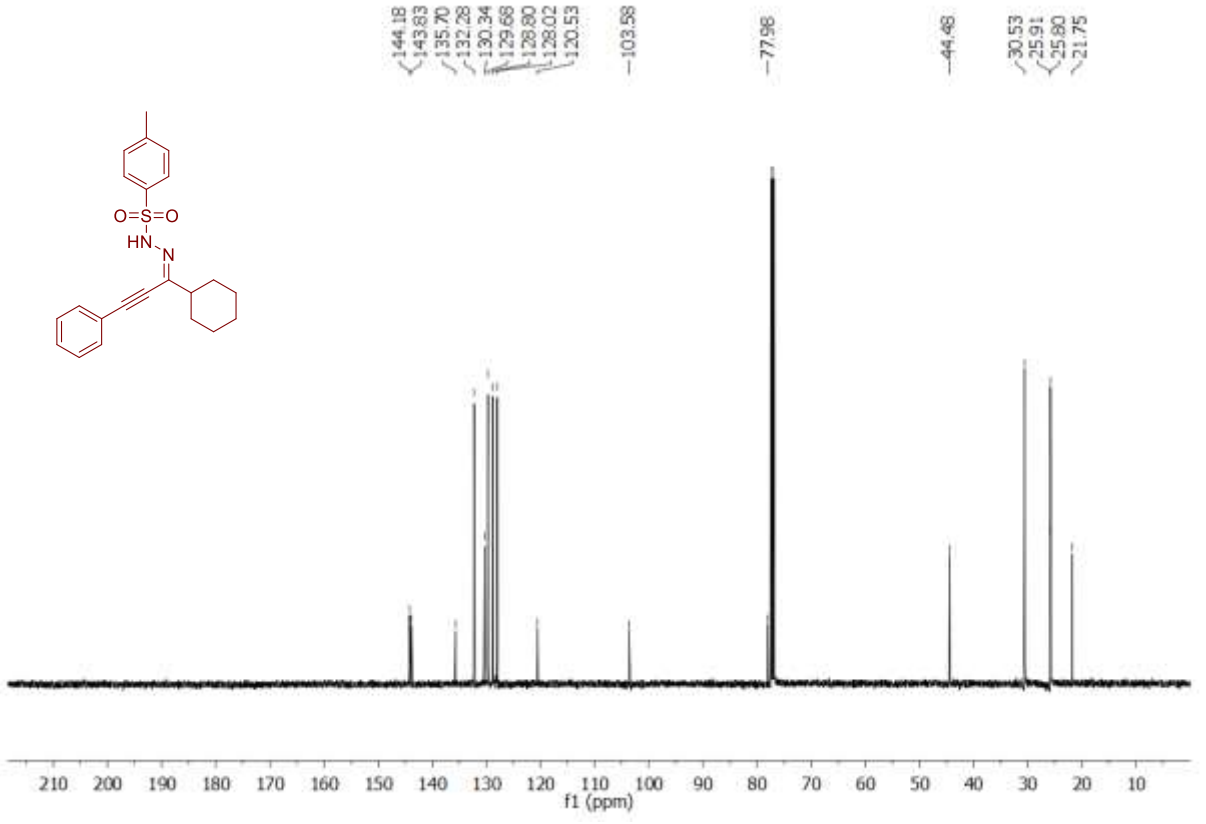
^{1}H and ^{13}C NMR of 1p



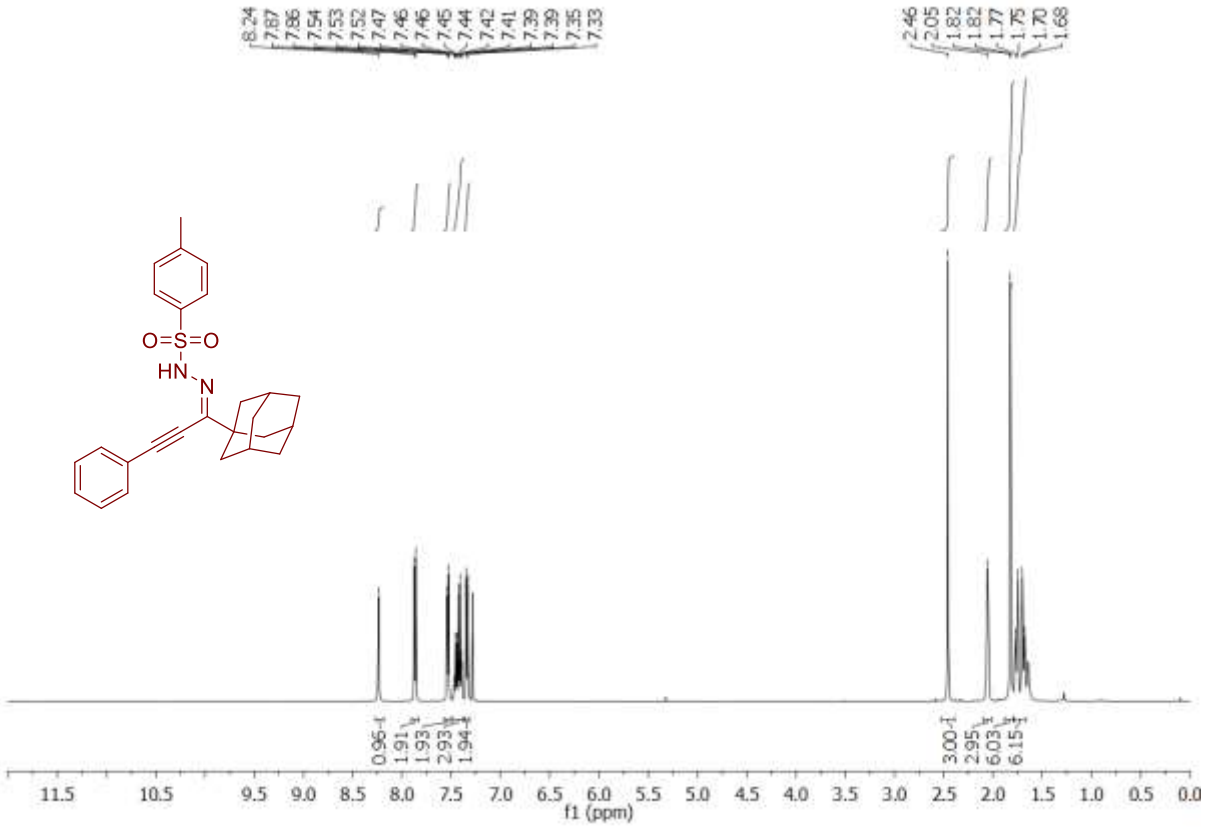


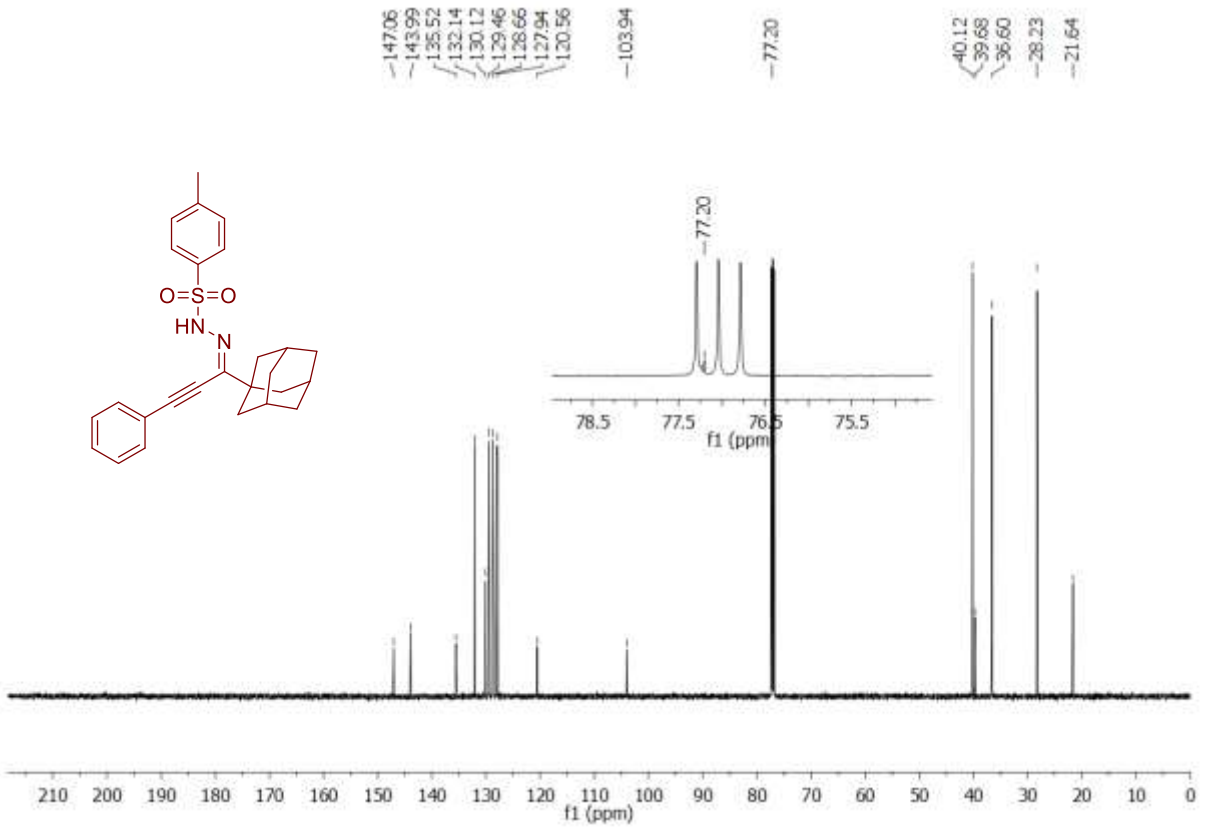
^{1}H and ^{13}C NMR of 1r



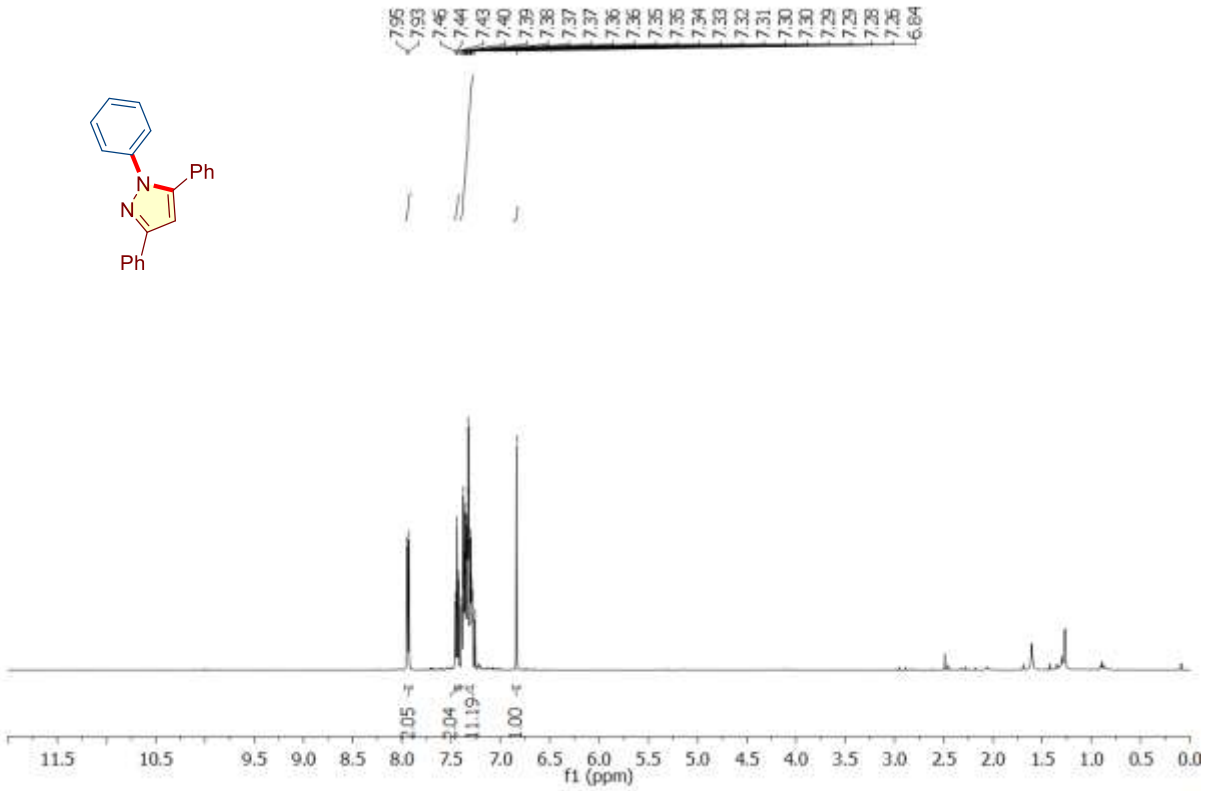


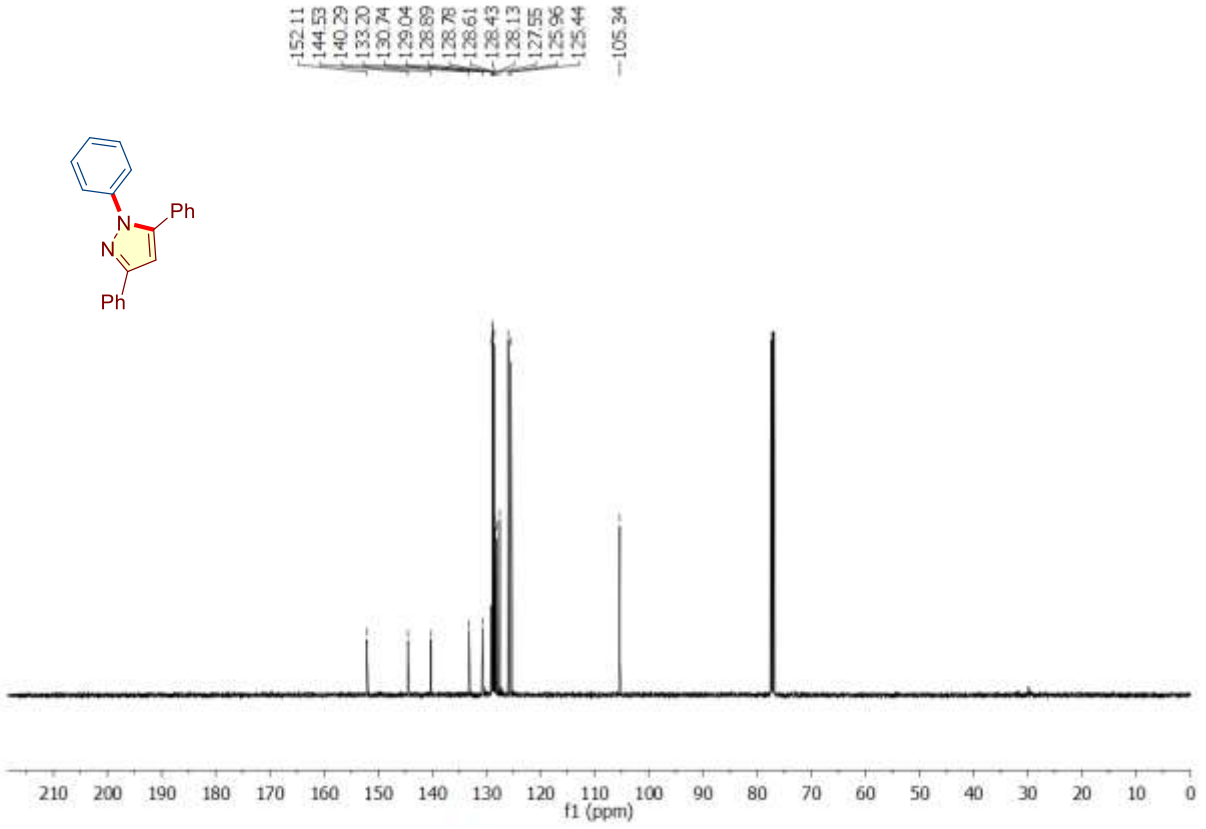
^{1}H and ^{13}C NMR of 1s



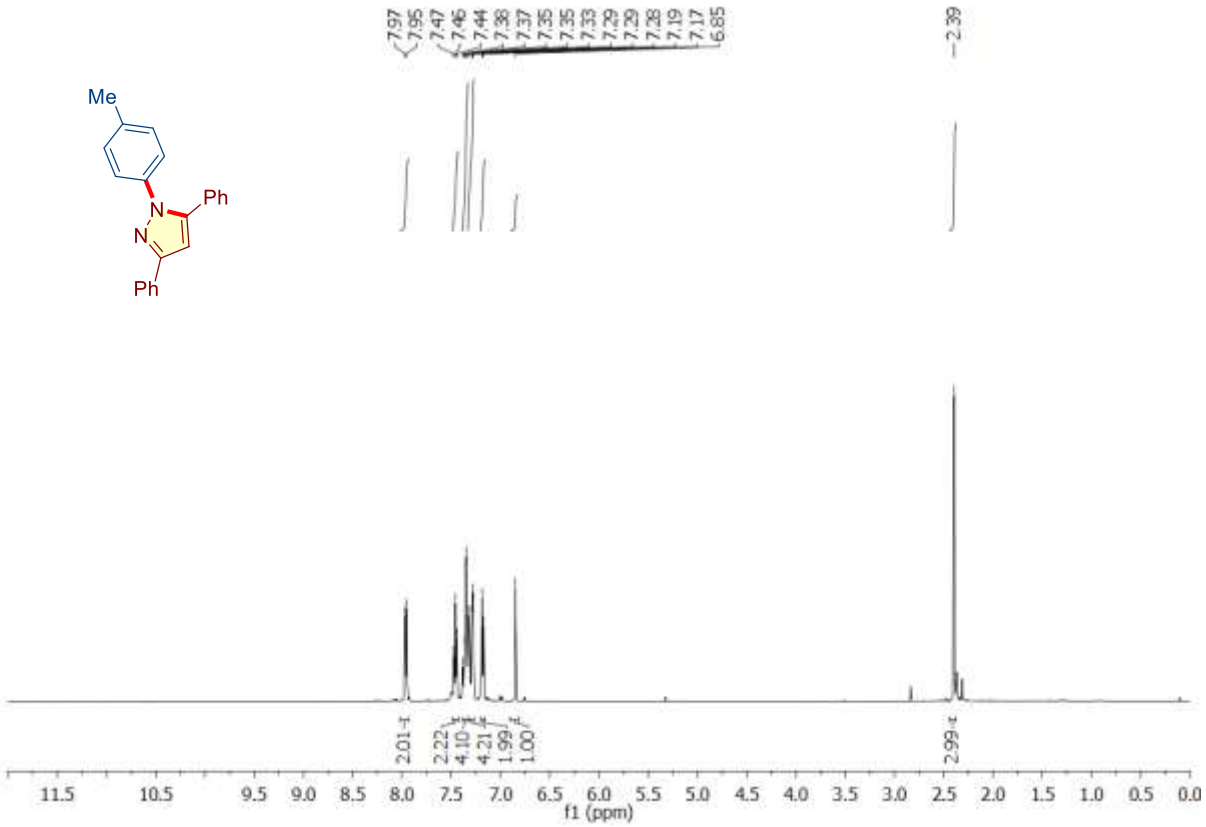


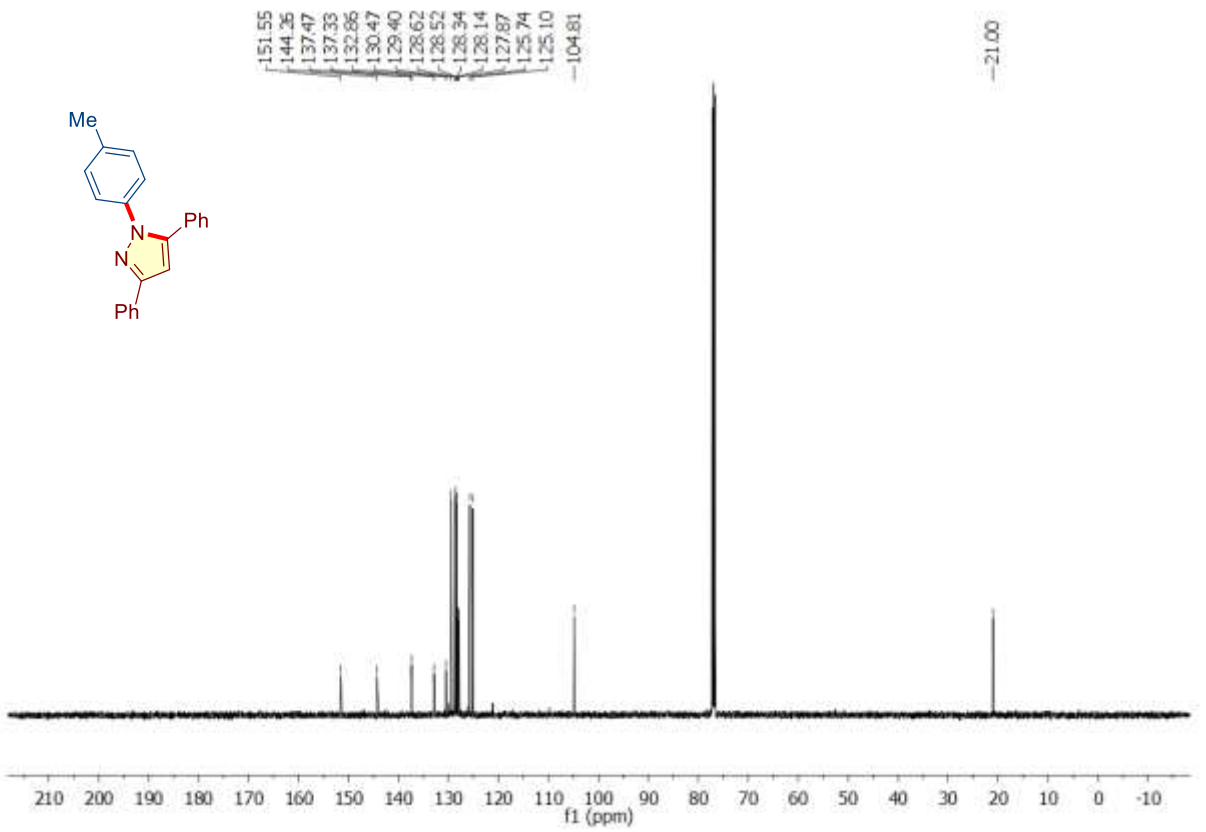
^{1}H and ^{13}C NMR of 3aa



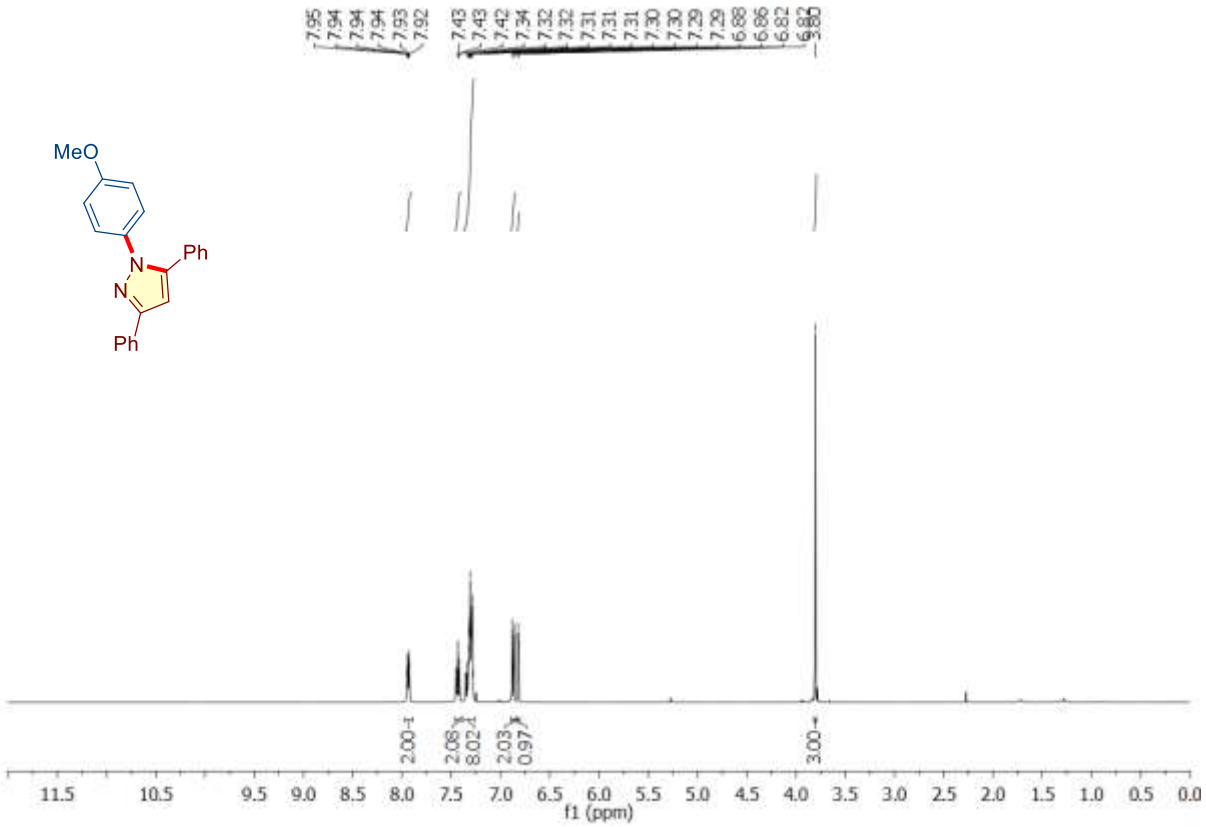


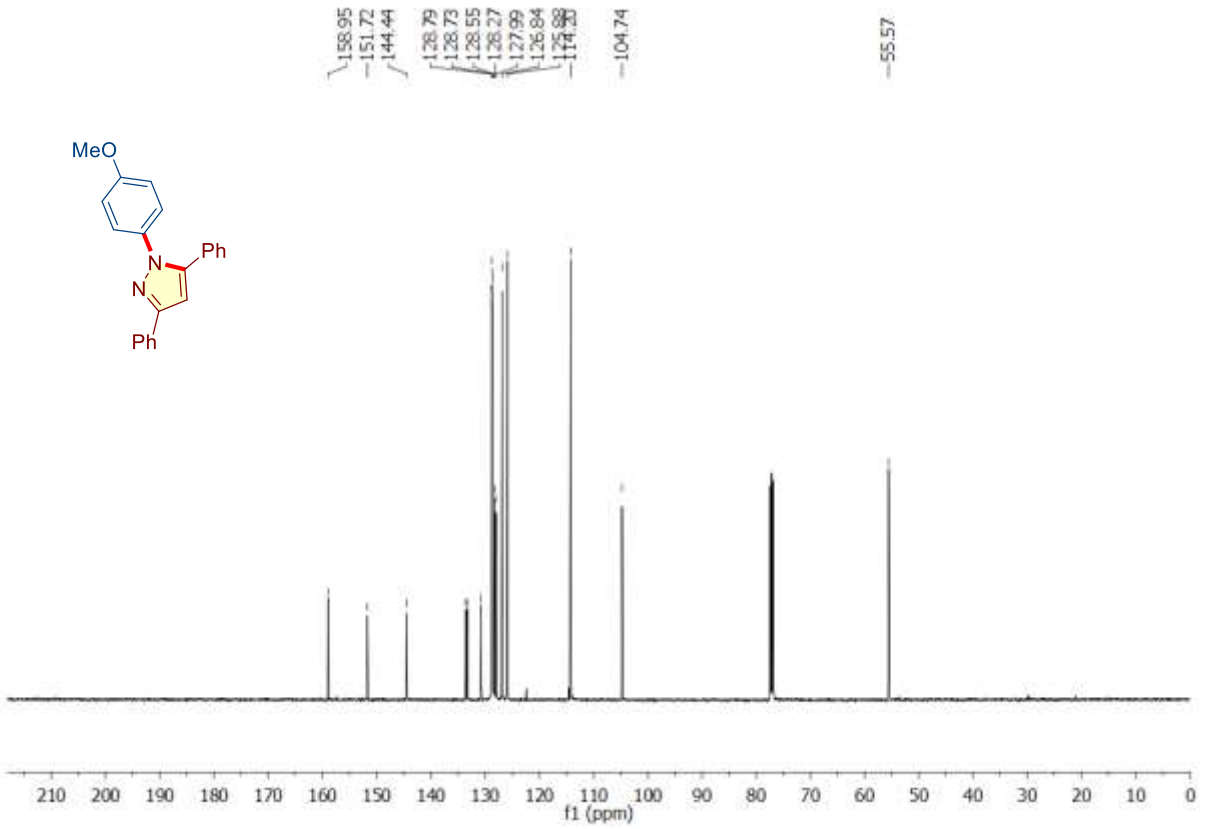
^{1}H and ^{13}C NMR of 3ab



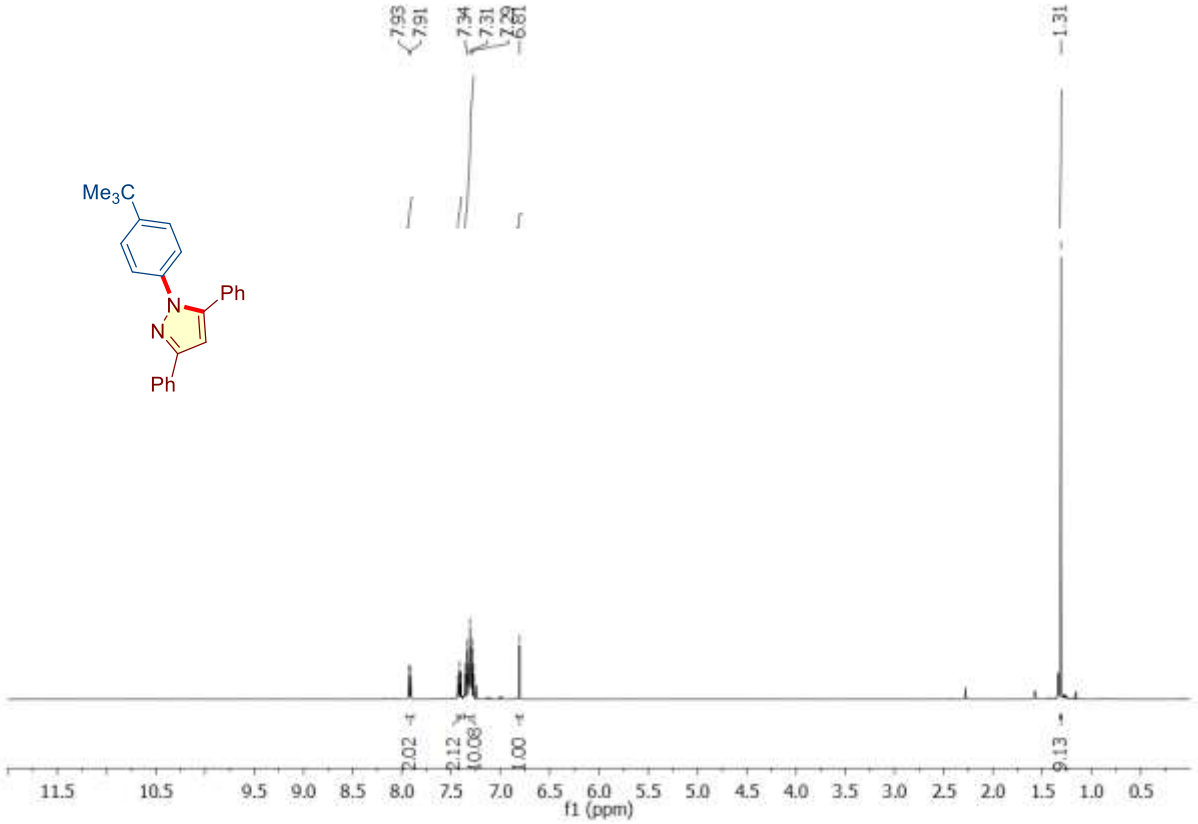


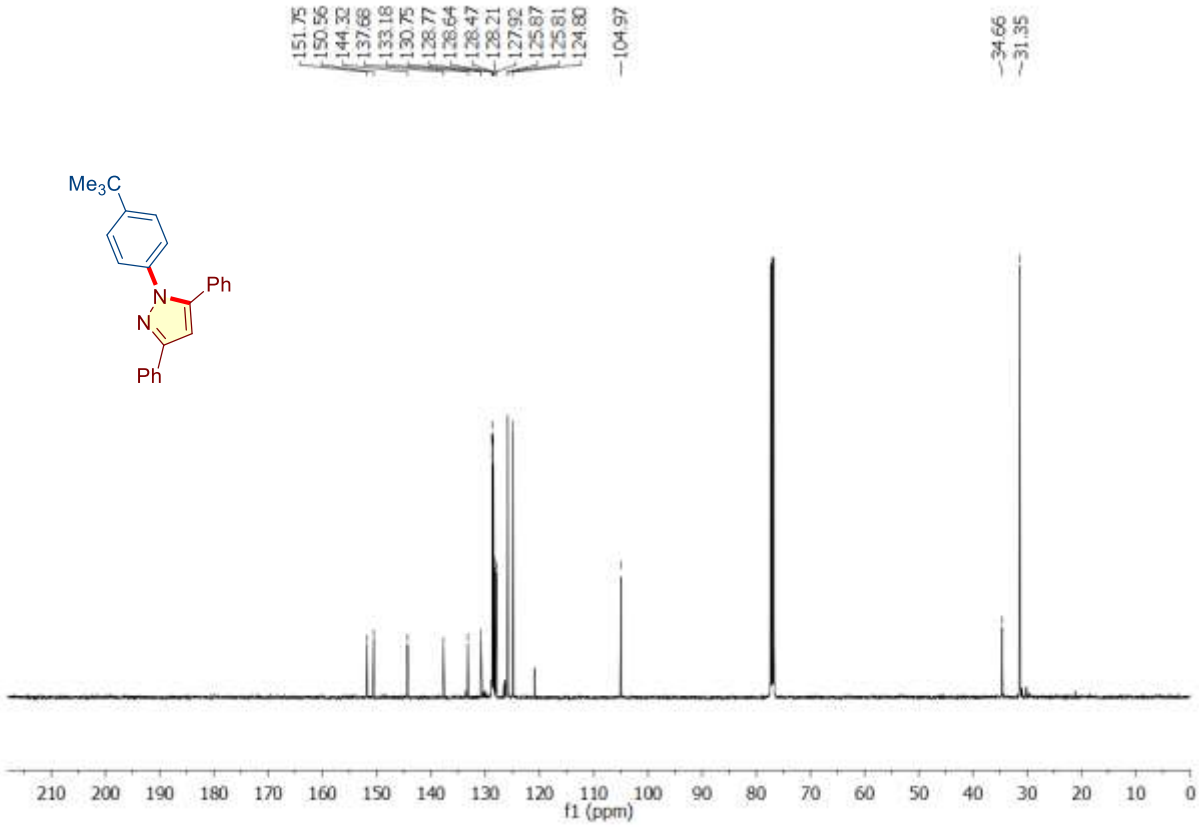
^{1}H and ^{13}C NMR of 3ac



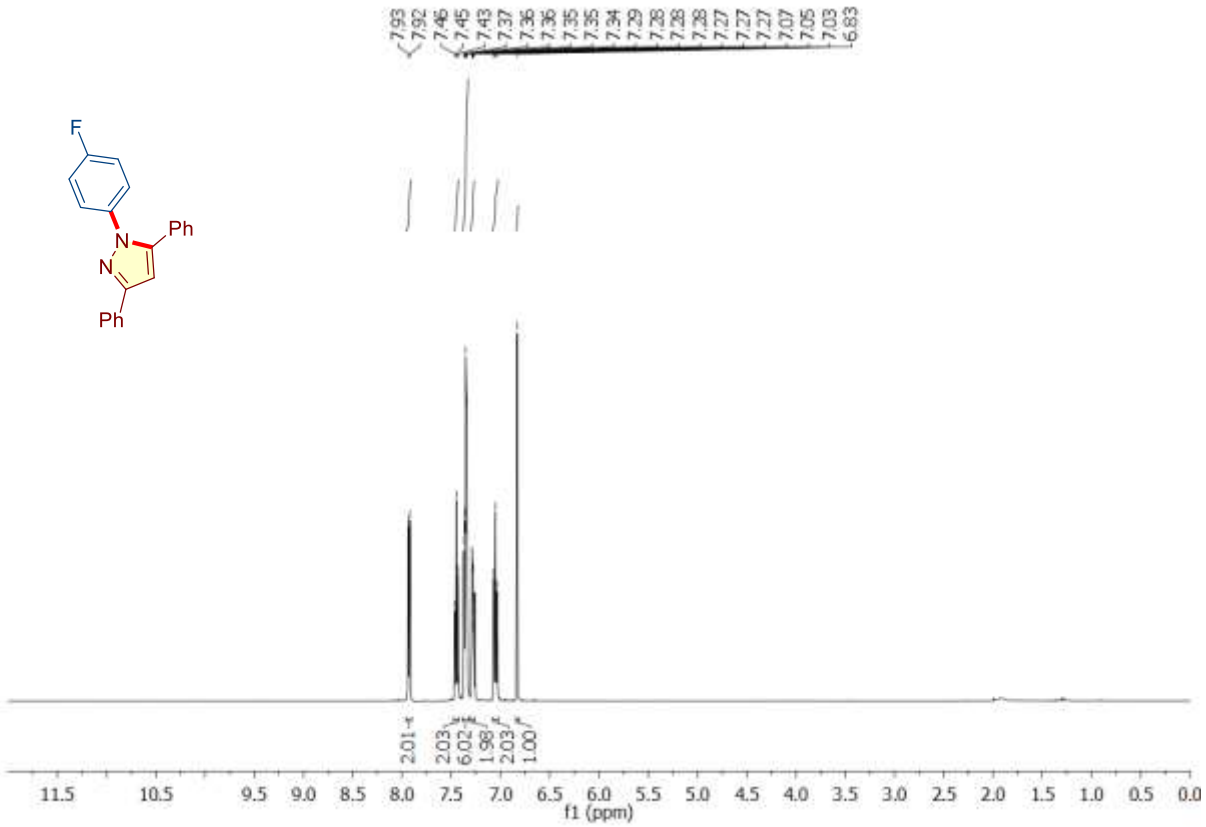


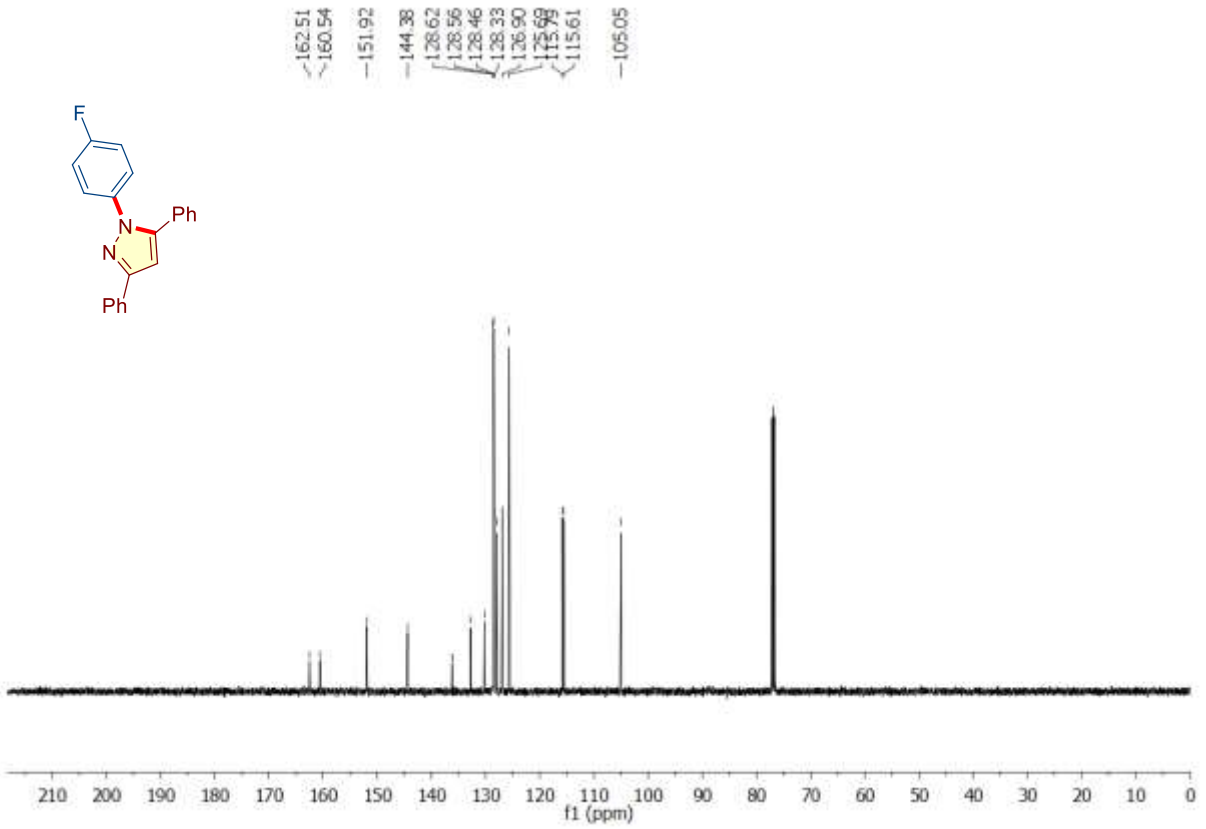
^{1}H and ^{13}C NMR of 3ad



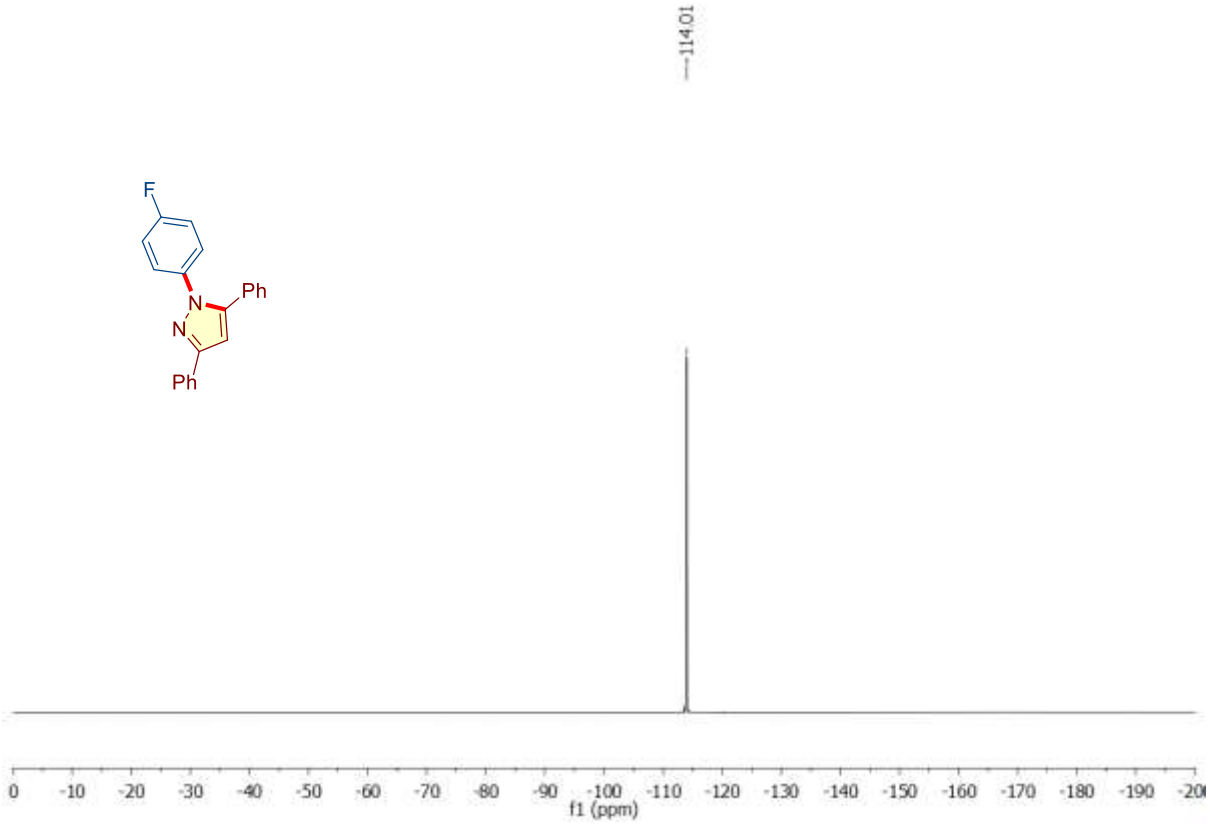


^{1}H and ^{13}C NMR of 3ae

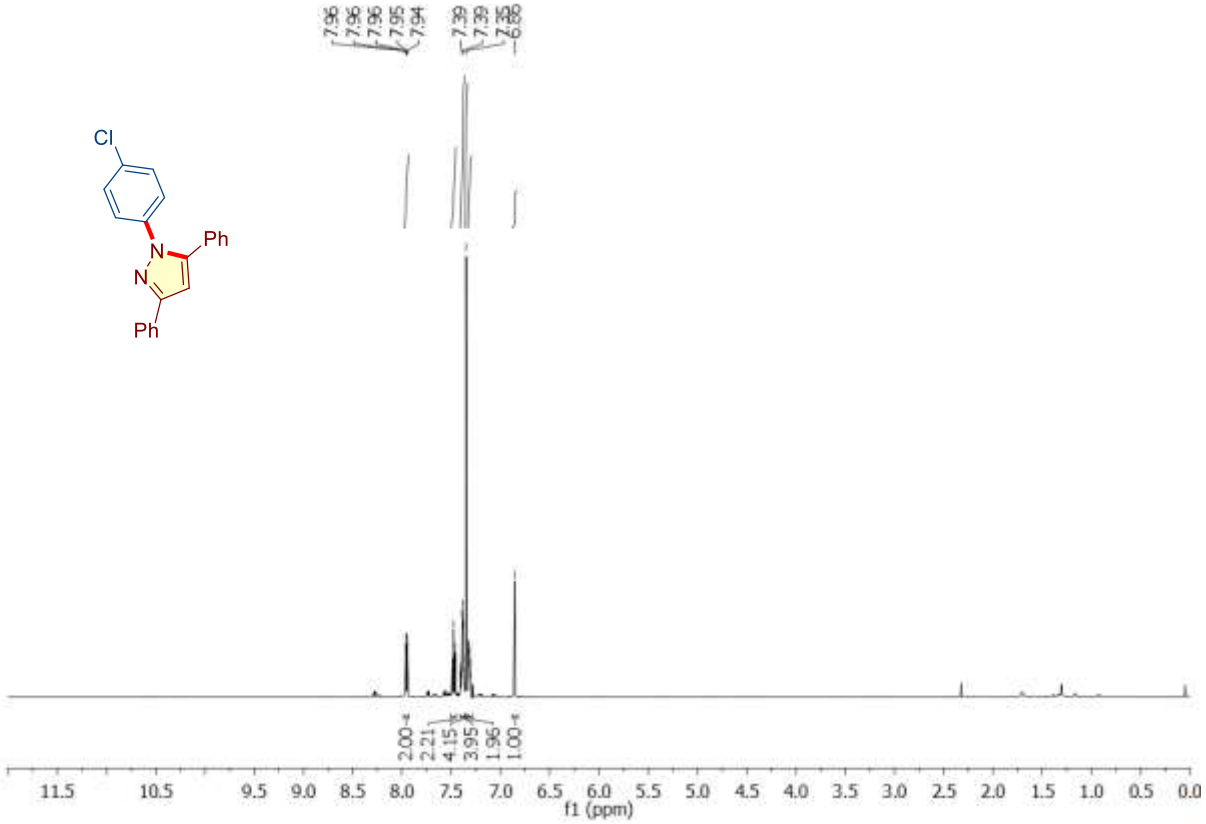


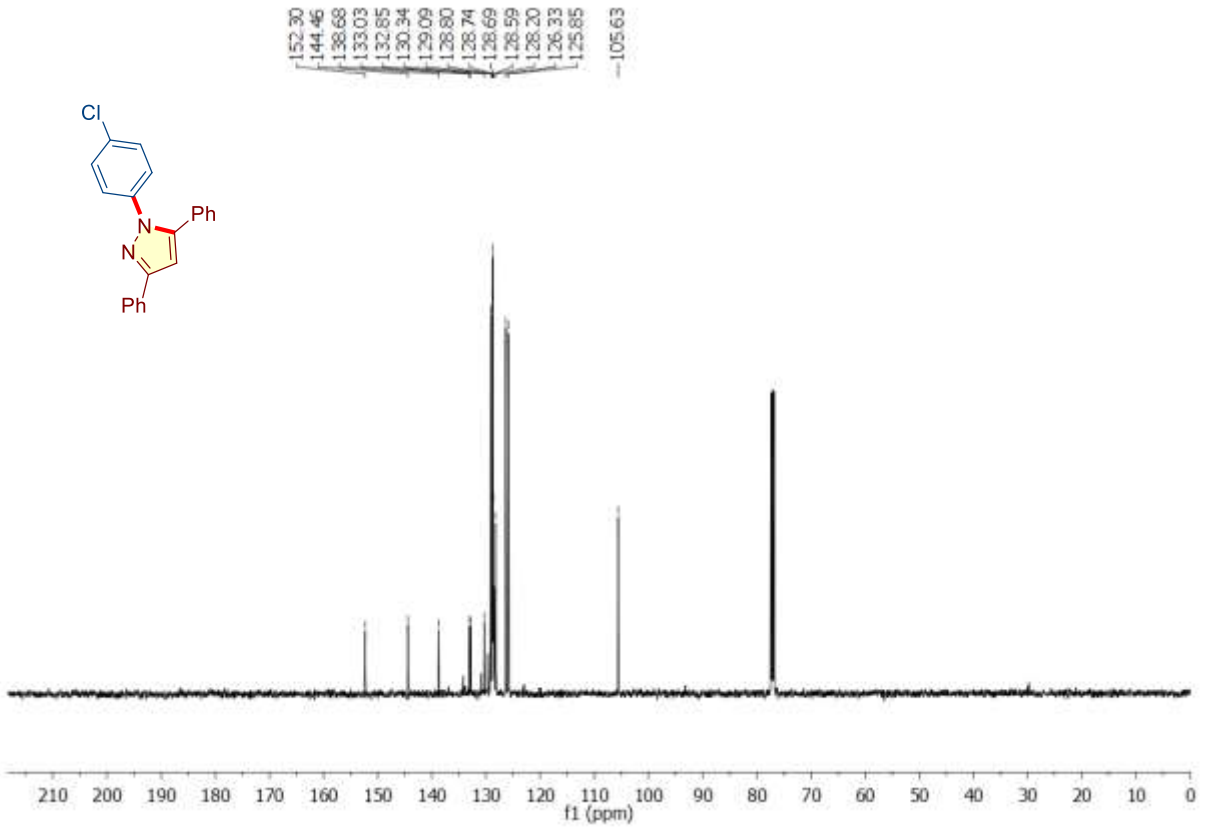


$^{19}F\{1H\}$ NMR of 3ae

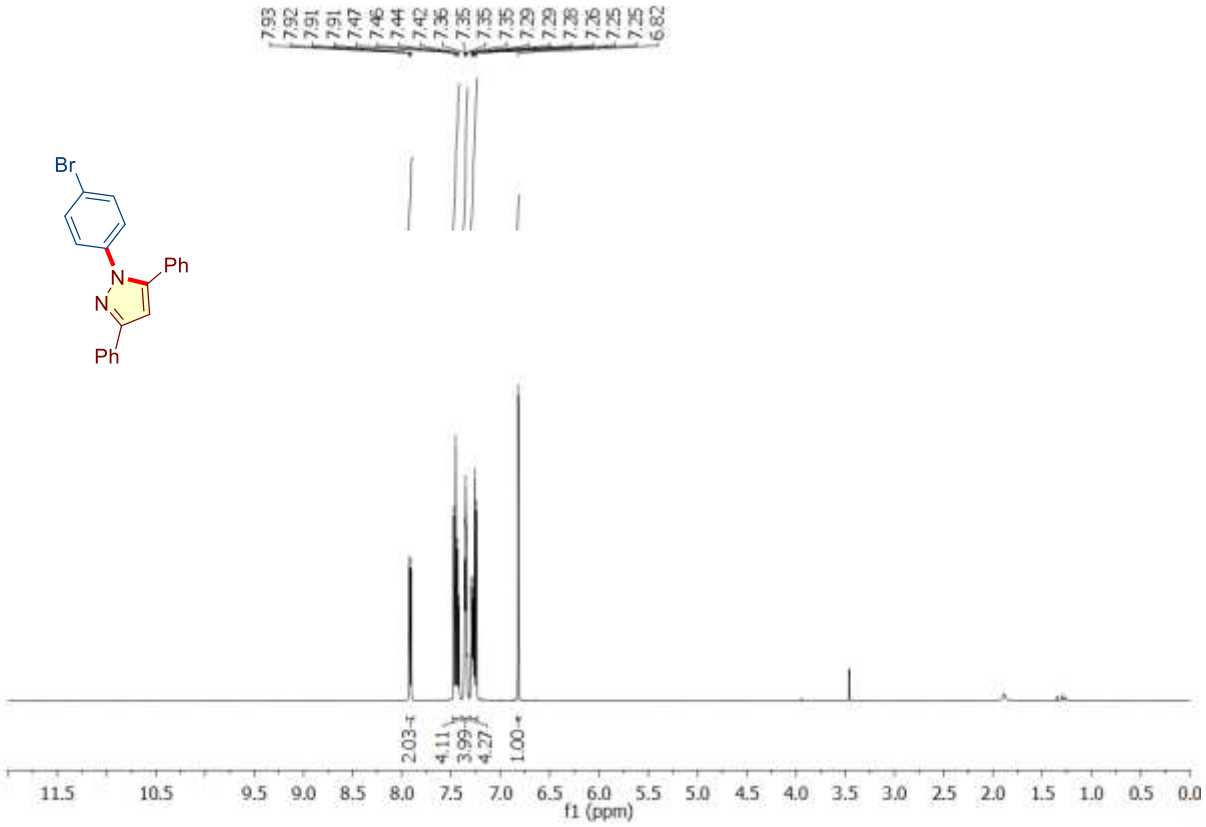


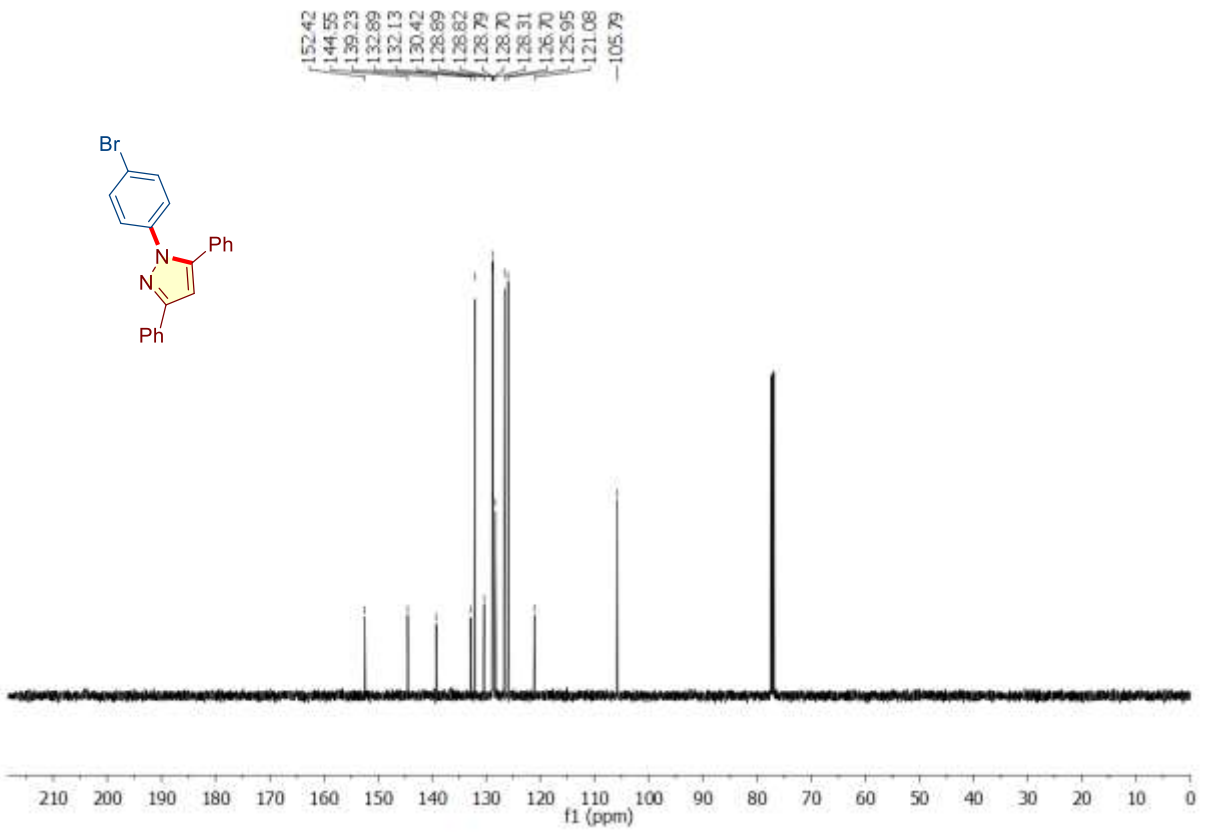
^{1}H and ^{13}C NMR of 3af



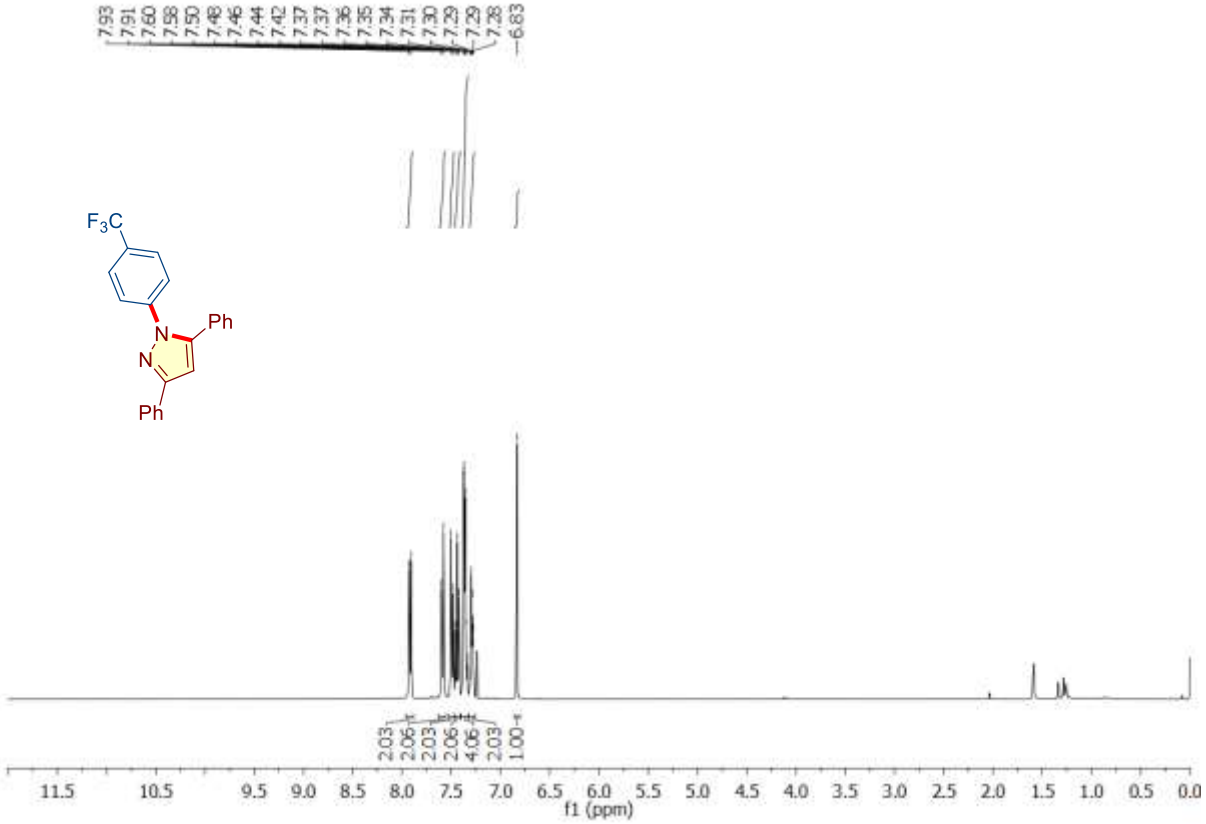


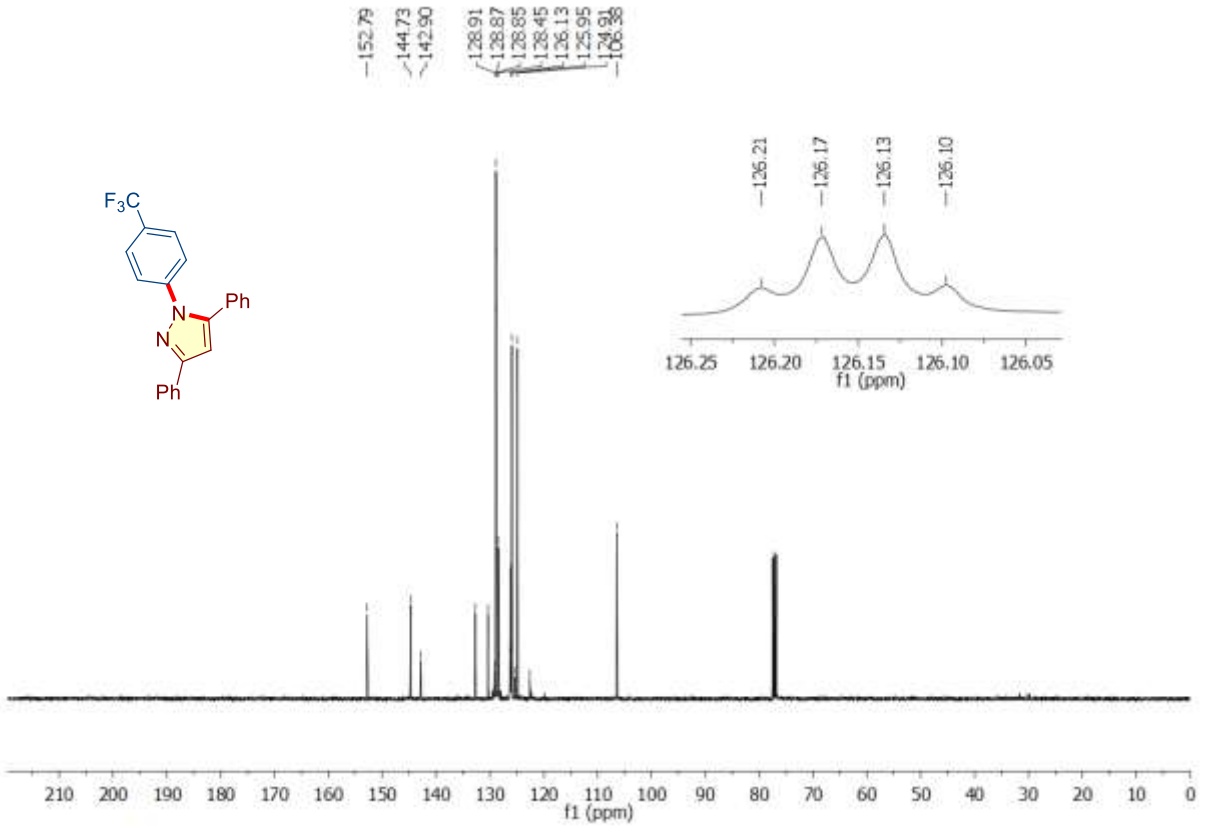
^{1}H and ^{13}C NMR of 3ag



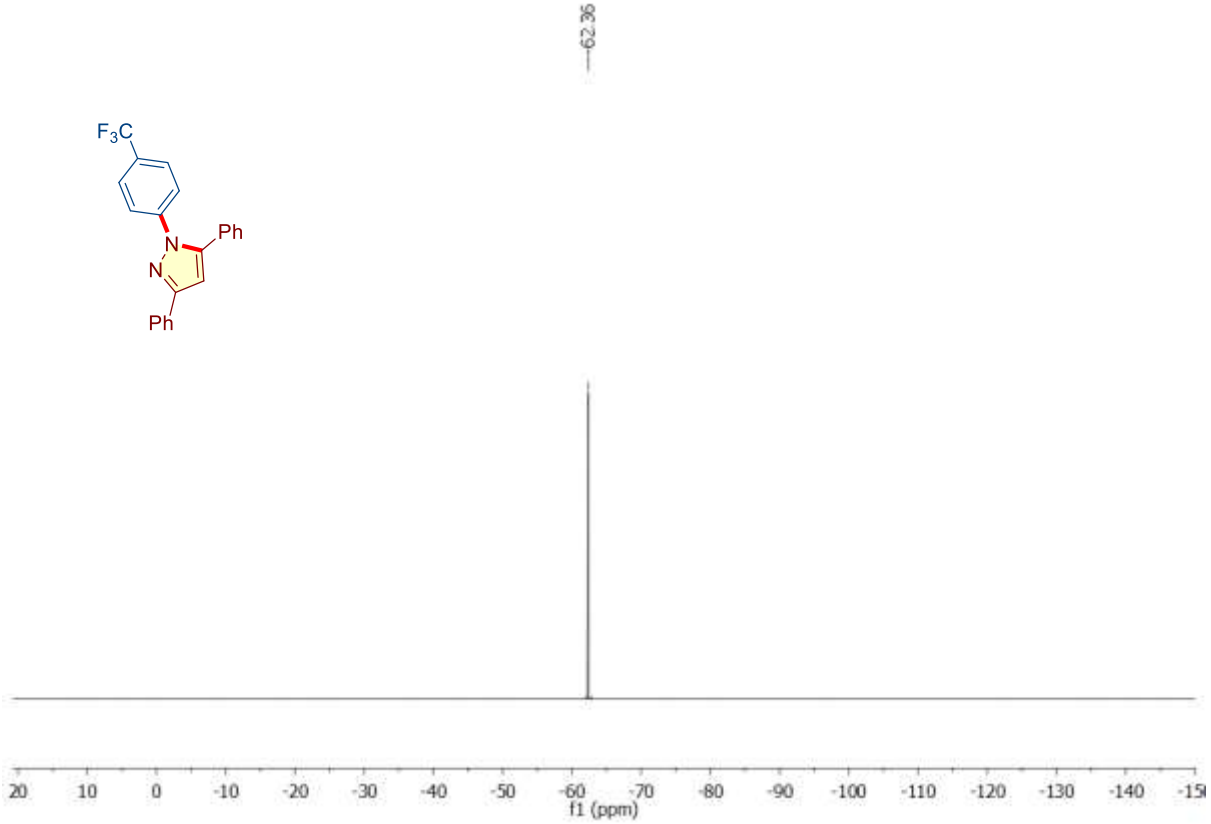


^{1}H and ^{13}C NMR of 3ah

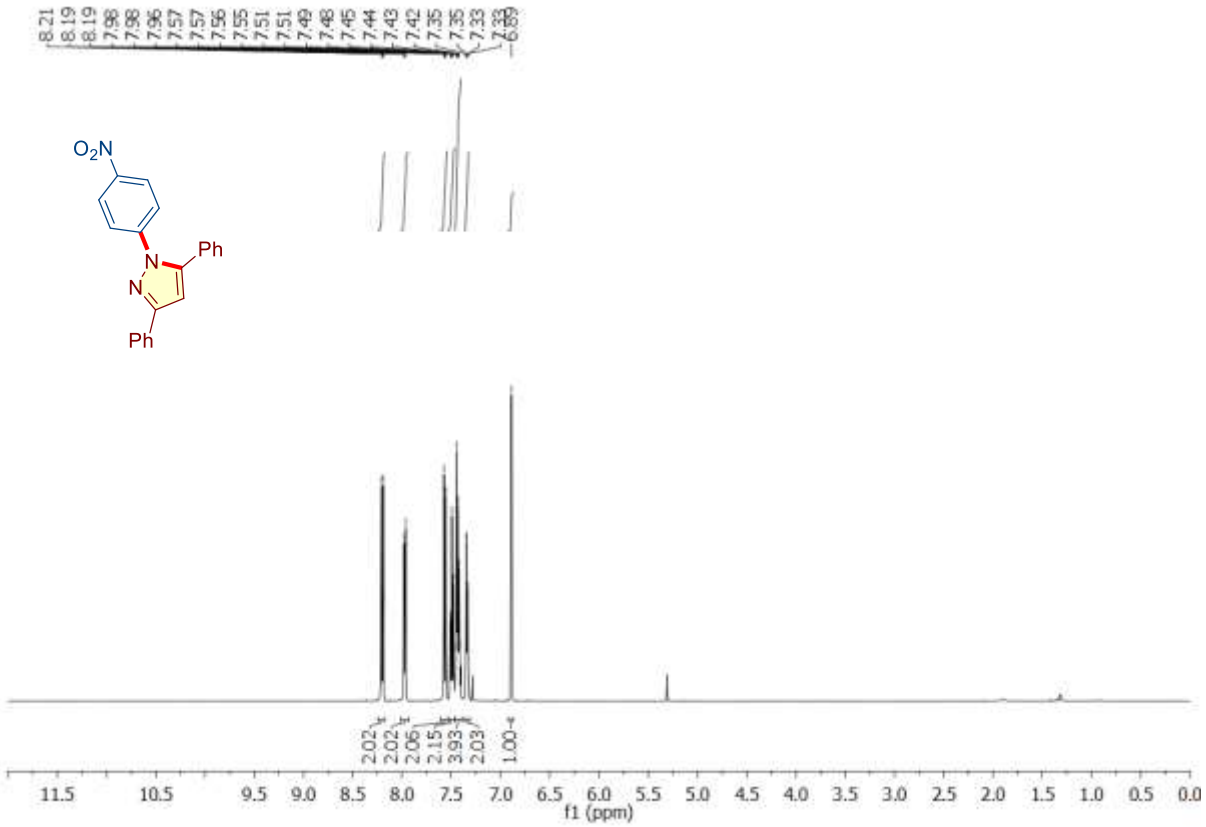


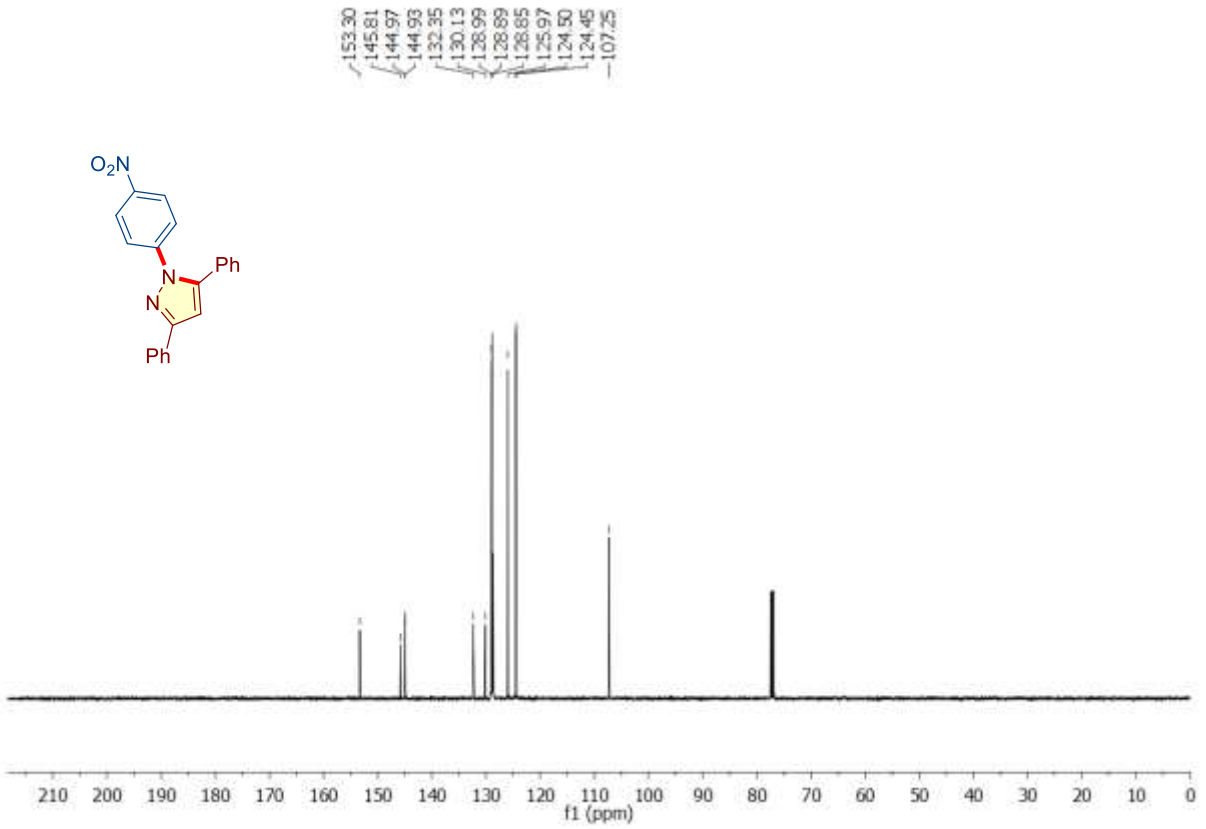


$^{19}F\{1H\}$ NMR of 3ah

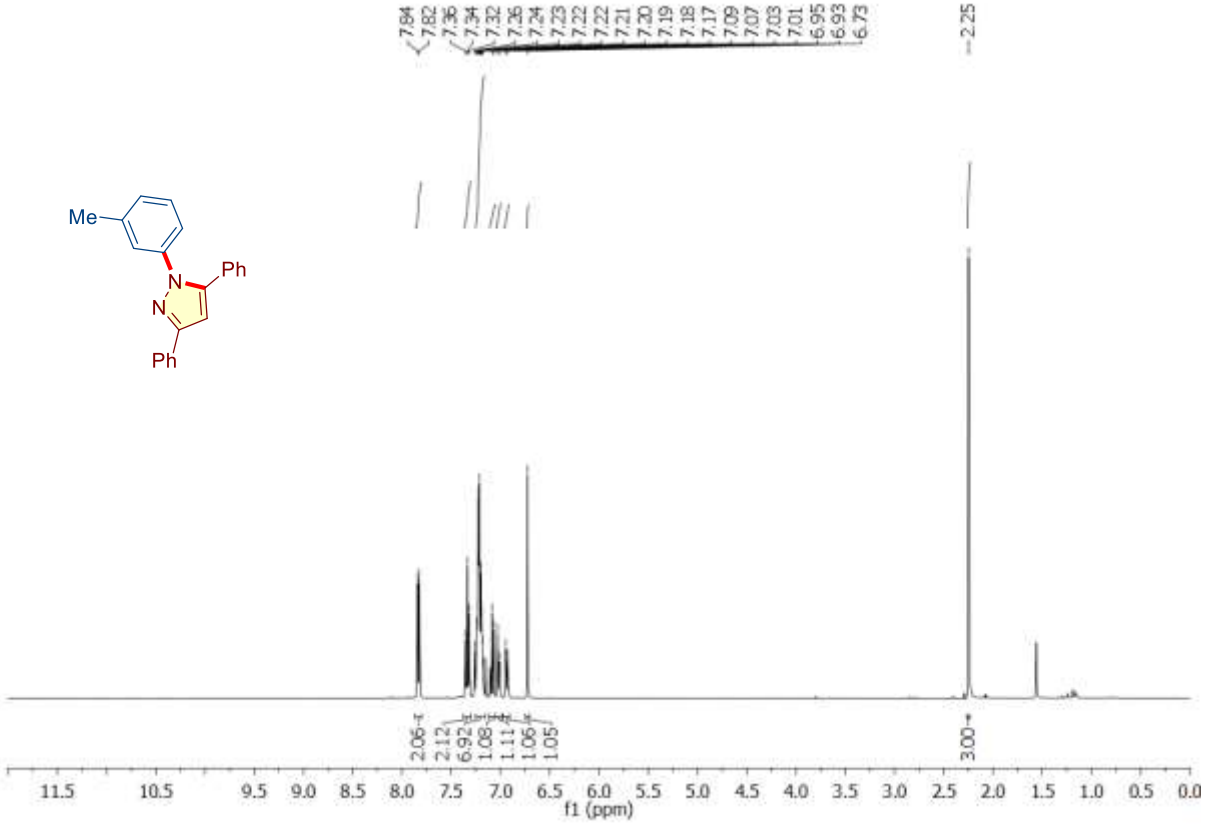


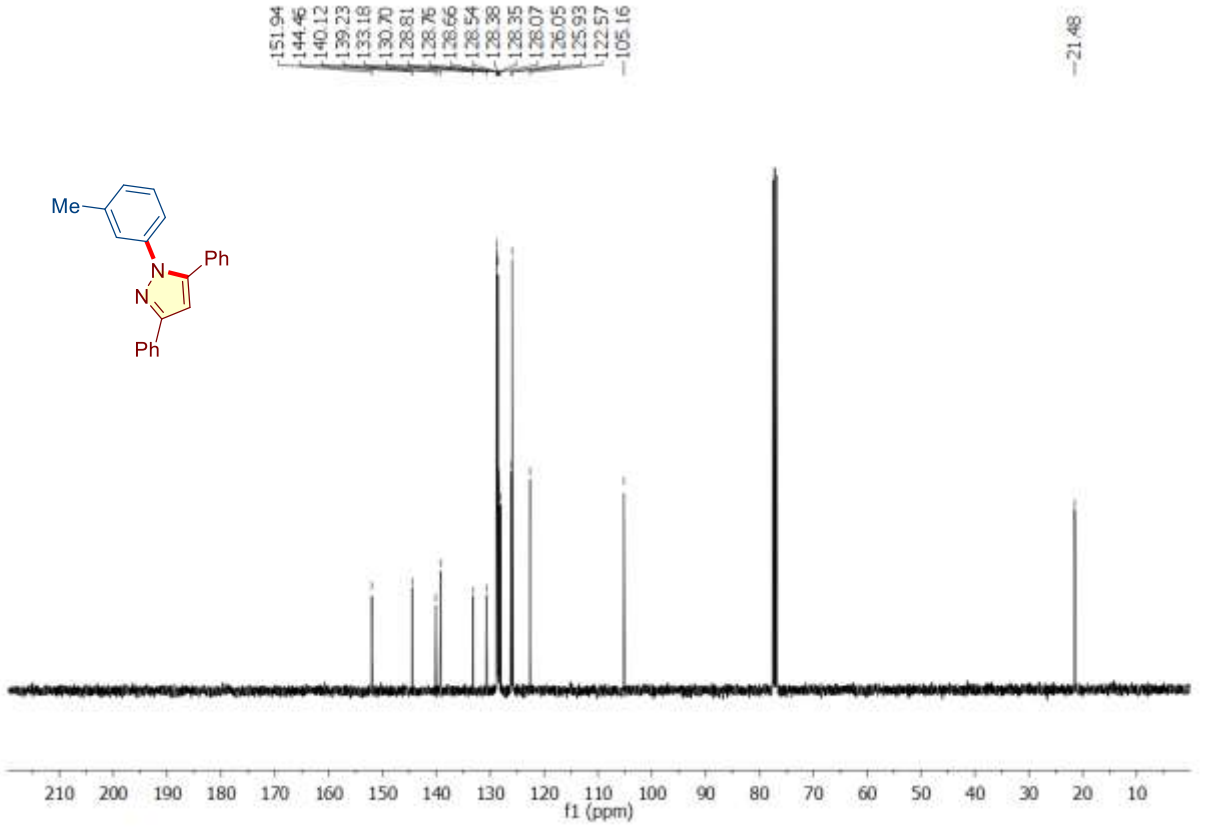
^{1}H and ^{13}C NMR of 3ai



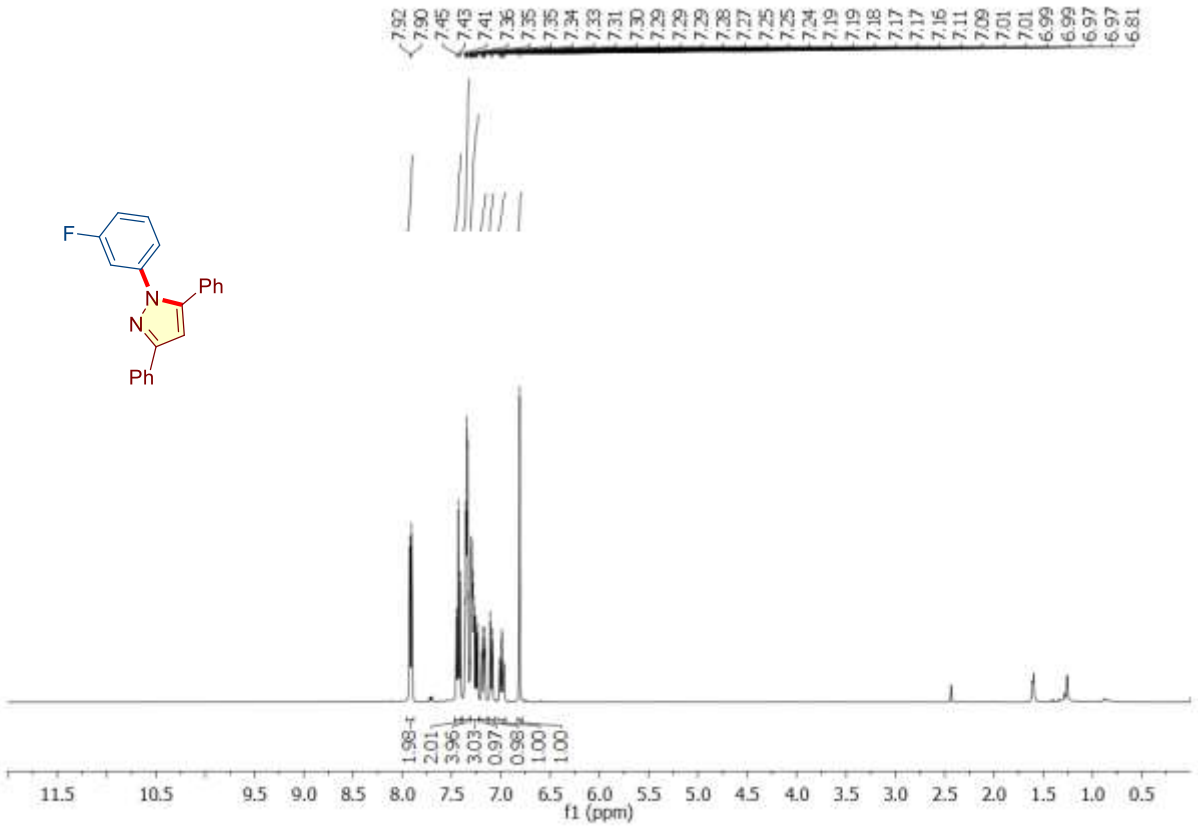


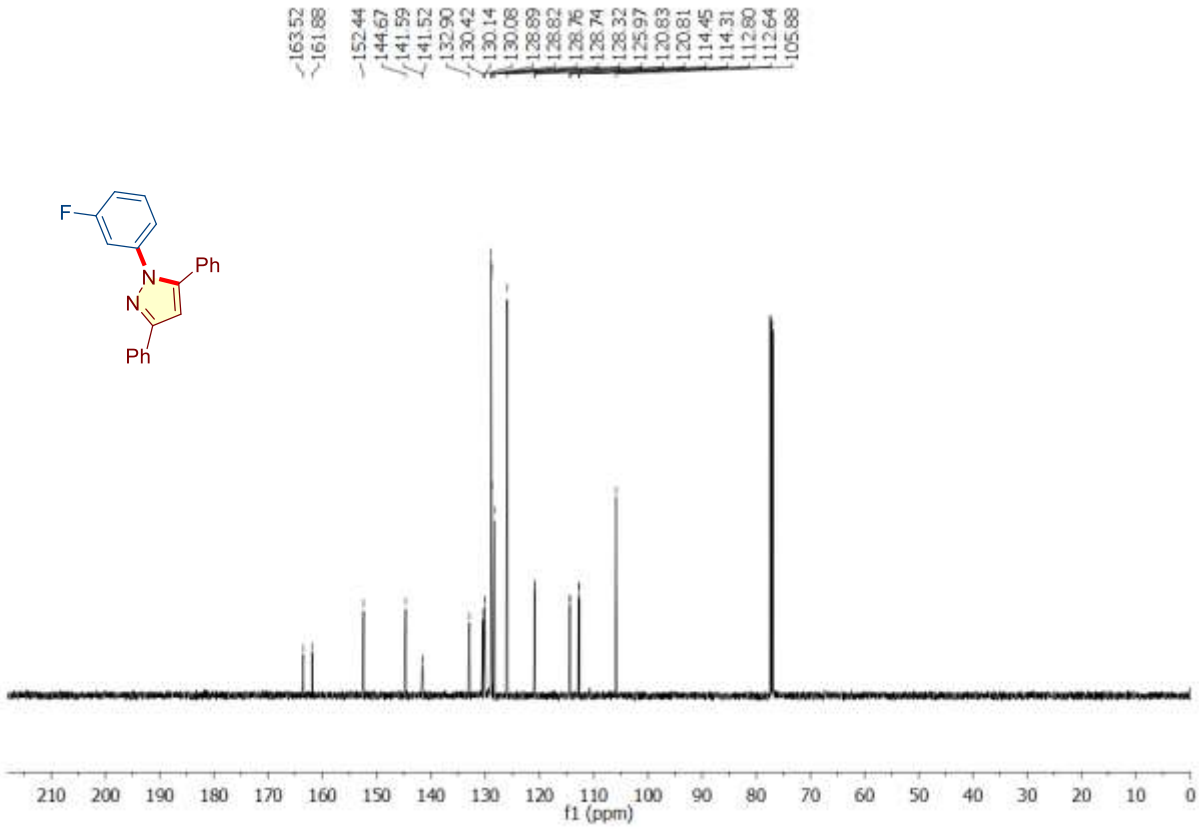
^{1}H and ^{13}C NMR of 3aj



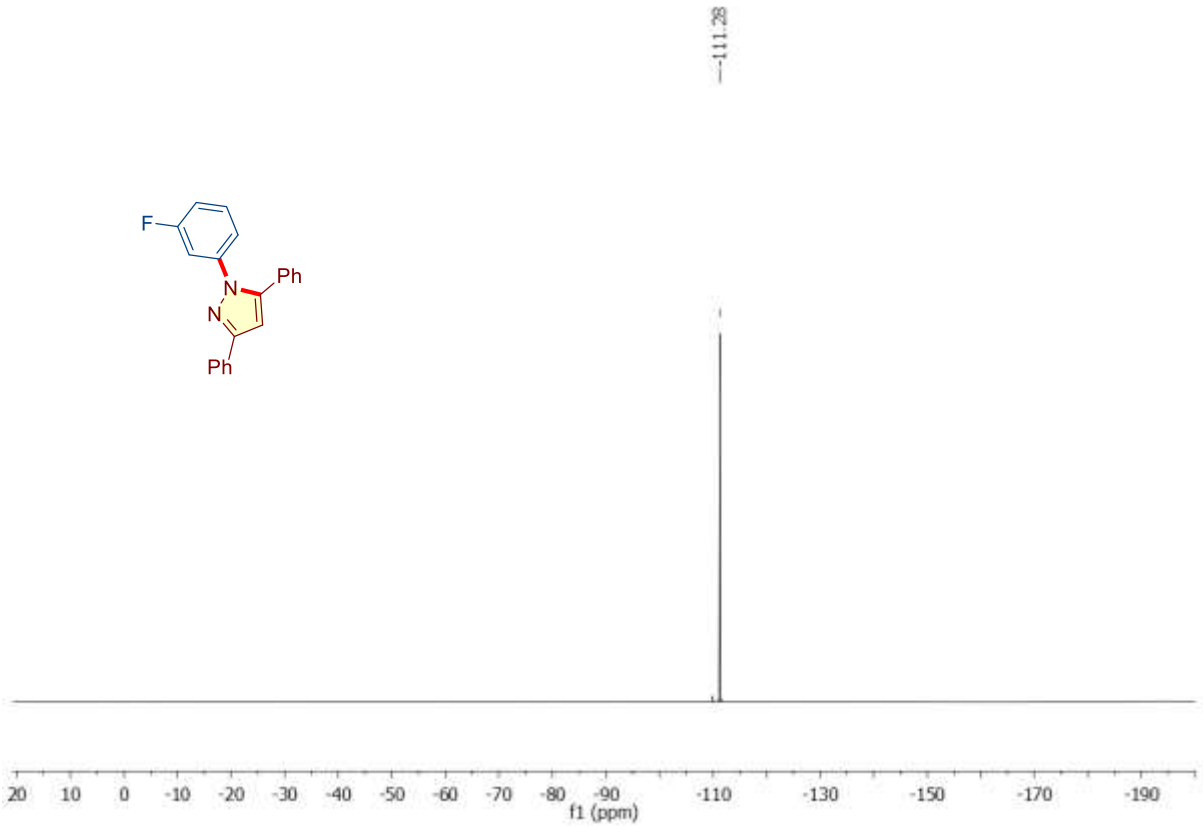


^{1}H and ^{13}C NMR of 3ak

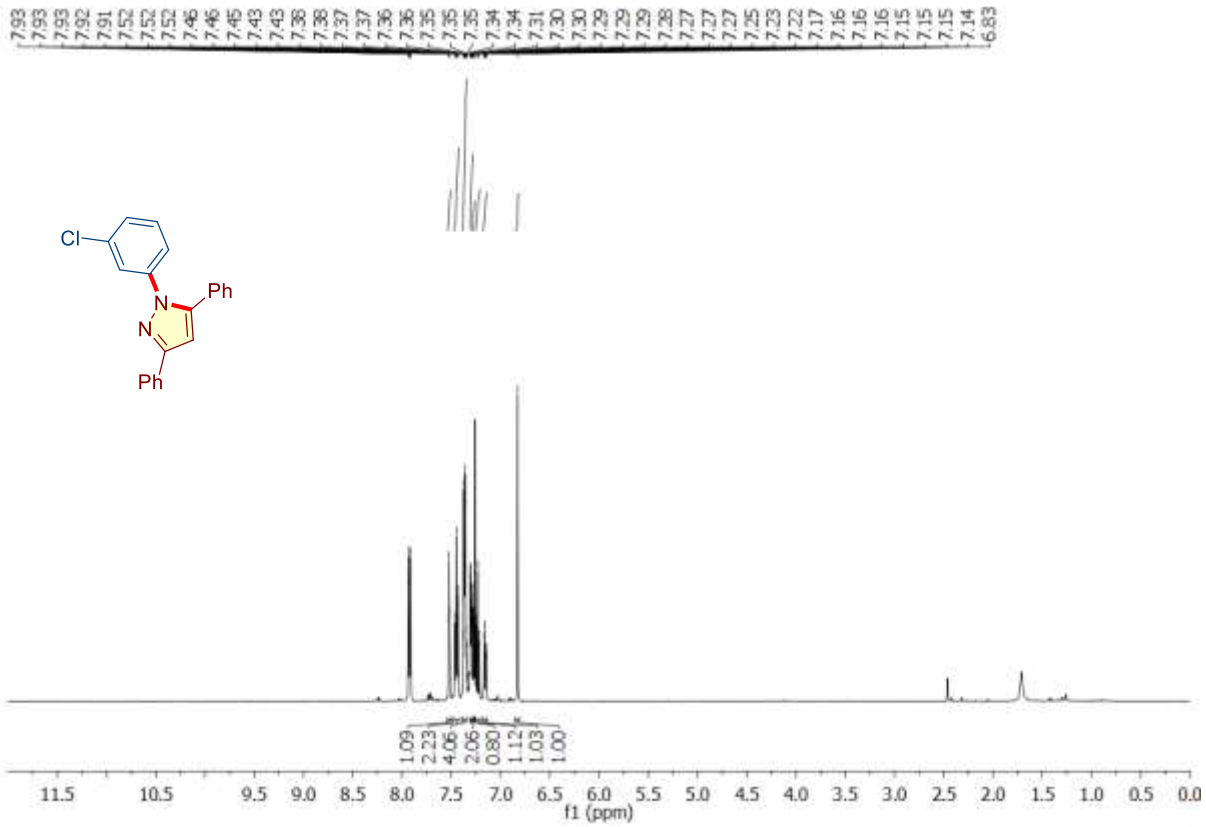


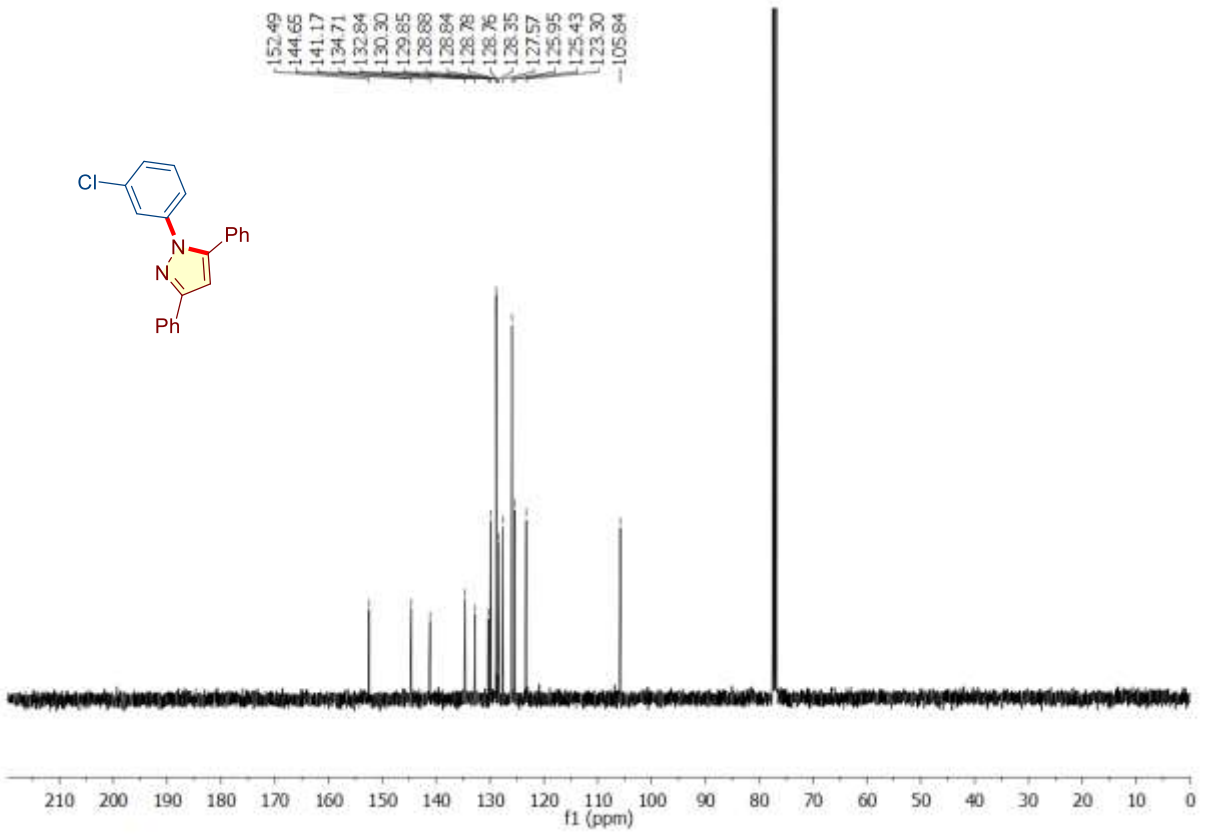


$^{19}F\{1H\}$ NMR of 3ak

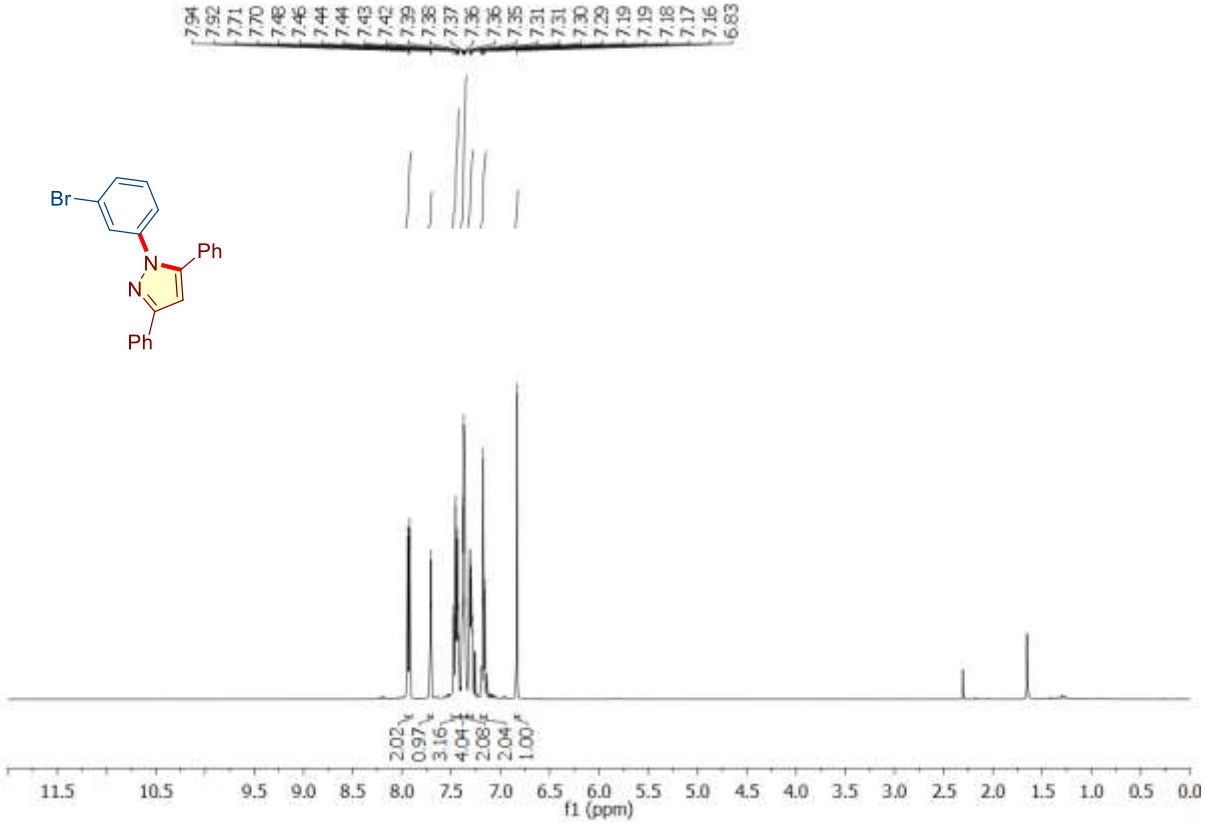


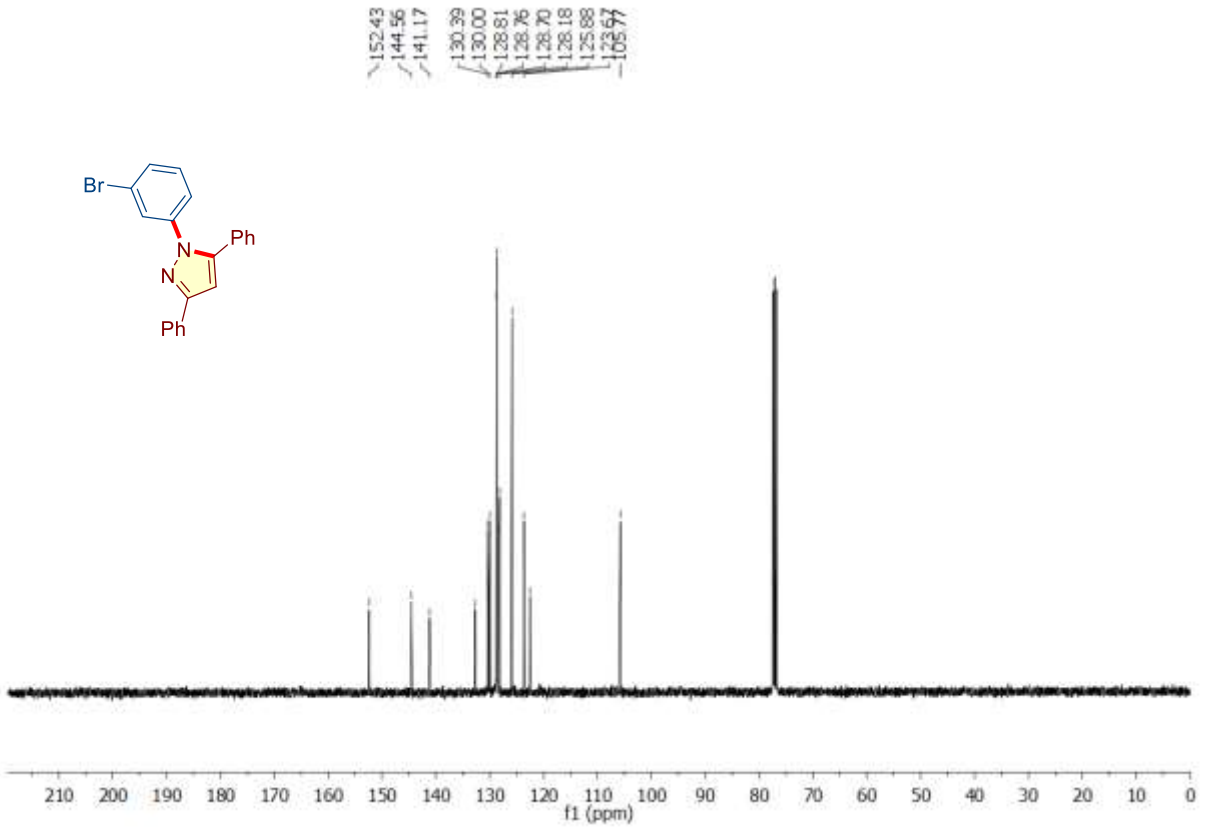
^{1}H and ^{13}C NMR of 3al



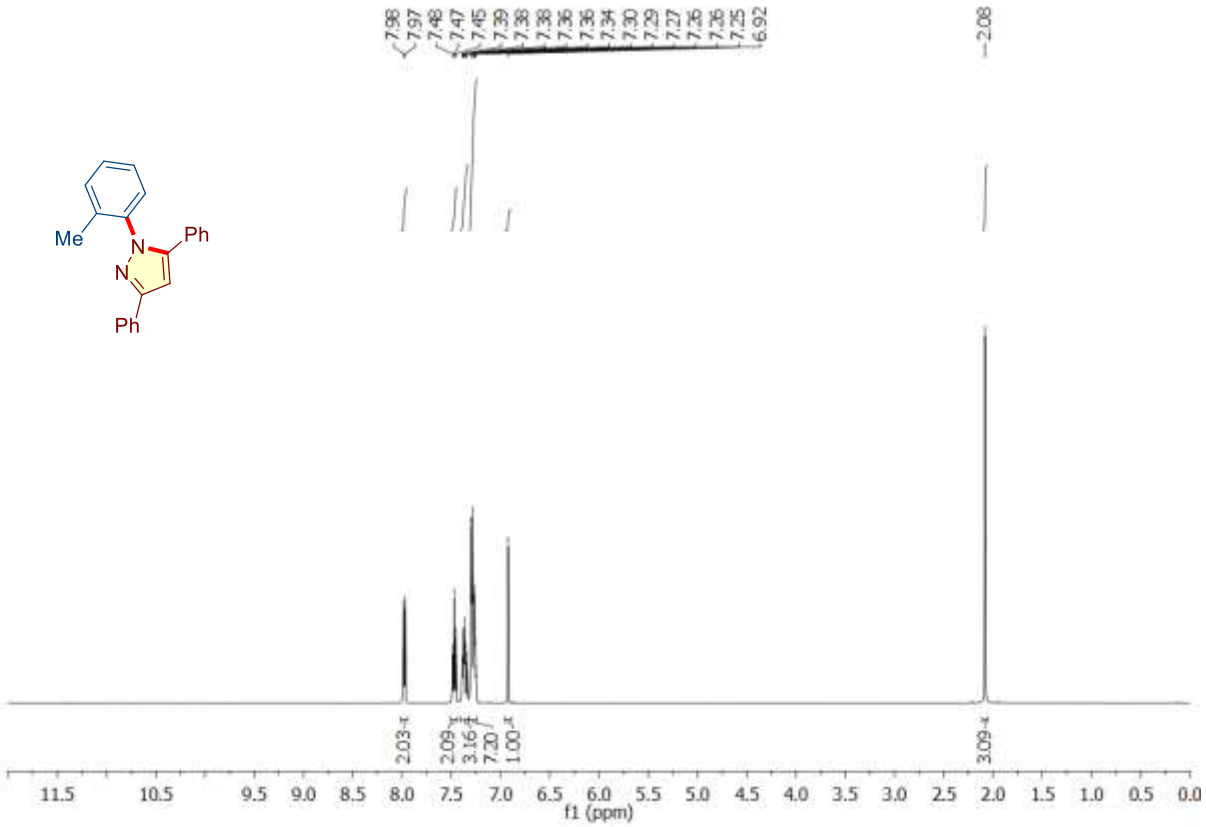


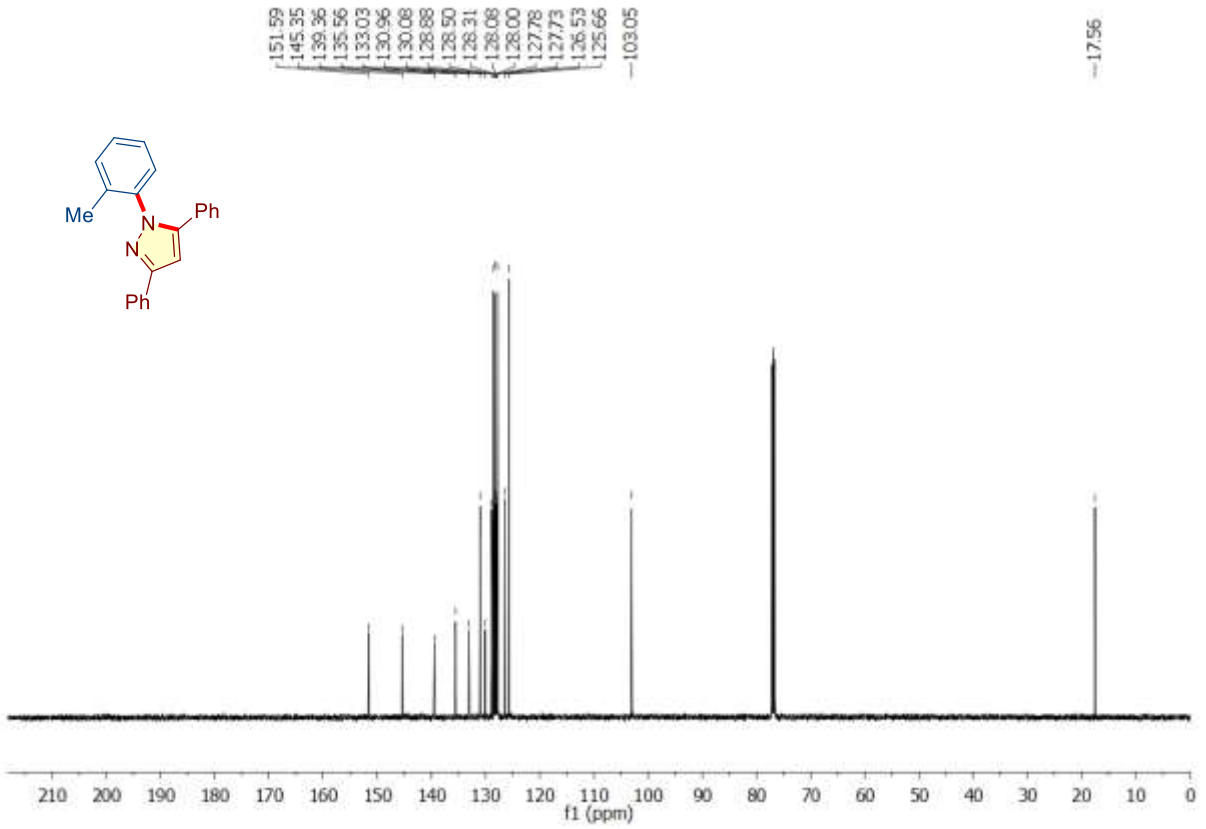
^{1}H and ^{13}C NMR of 3am



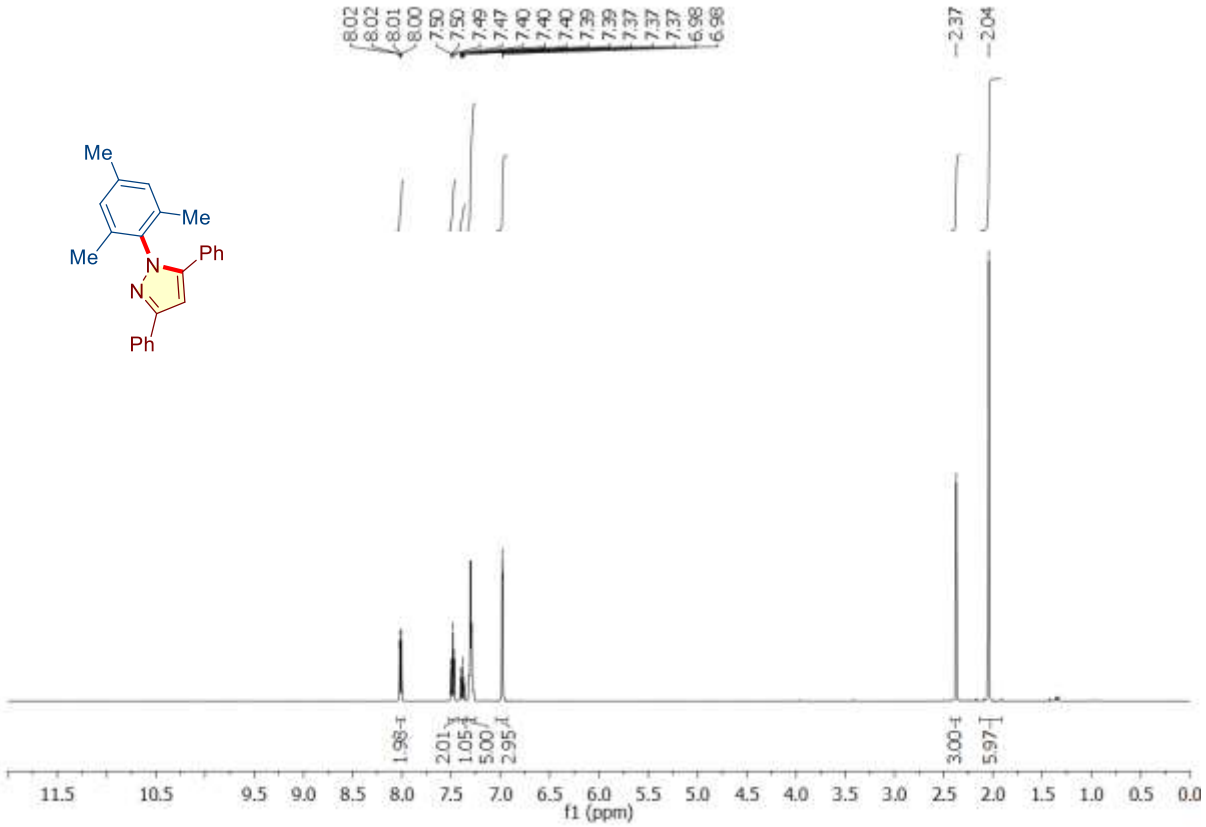


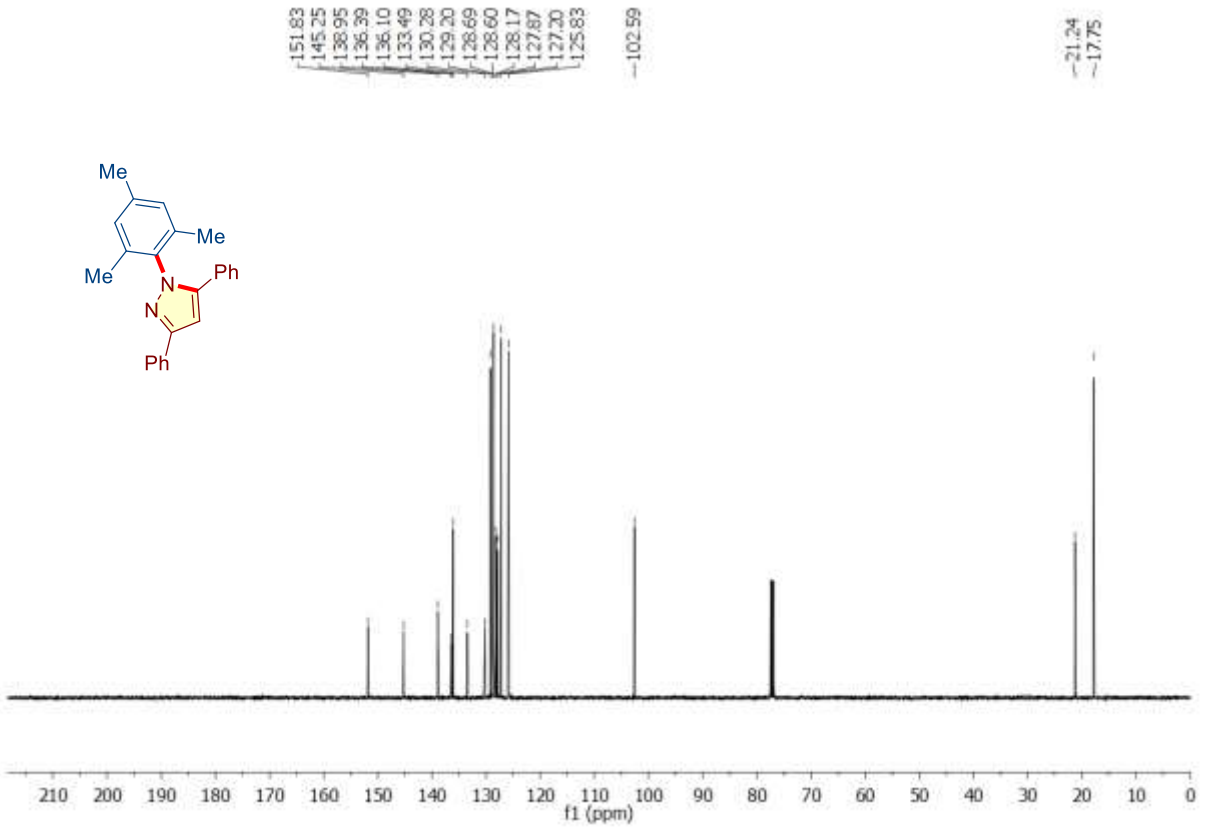
^{1}H and ^{13}C NMR of 3an



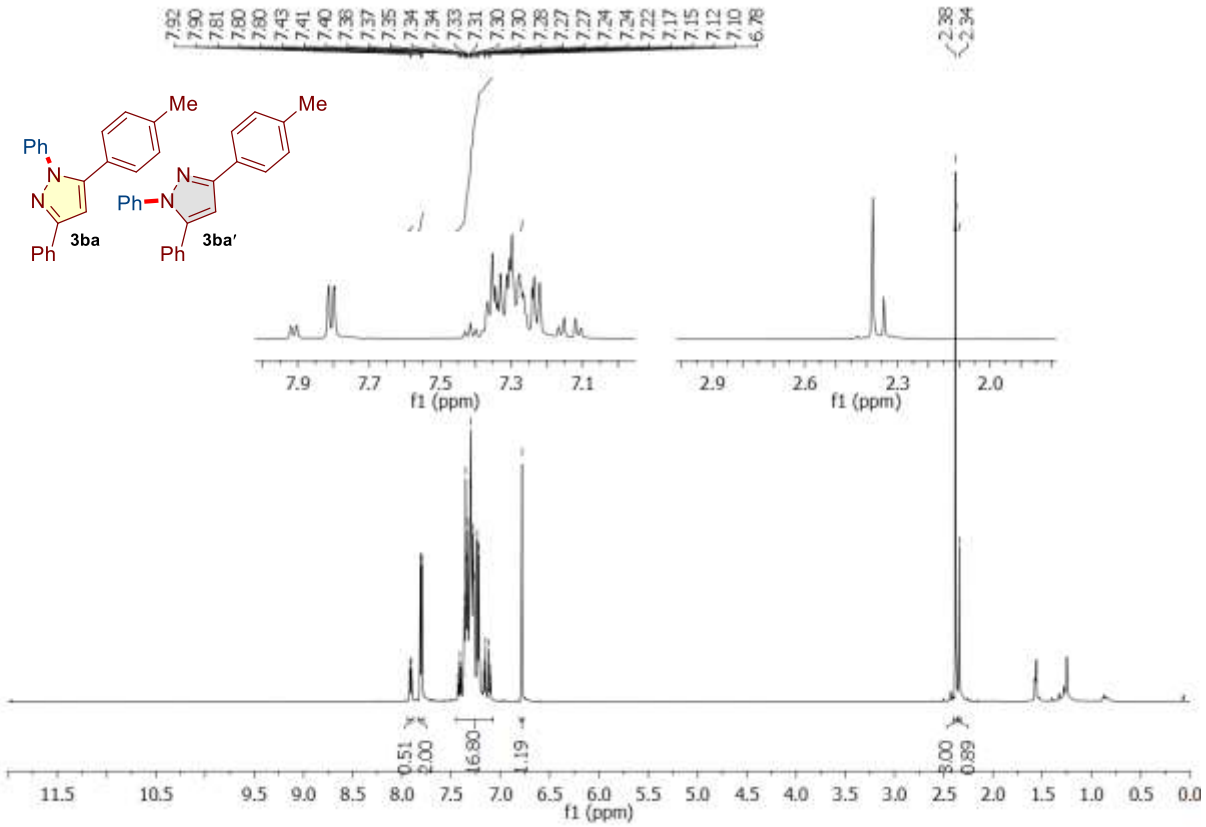


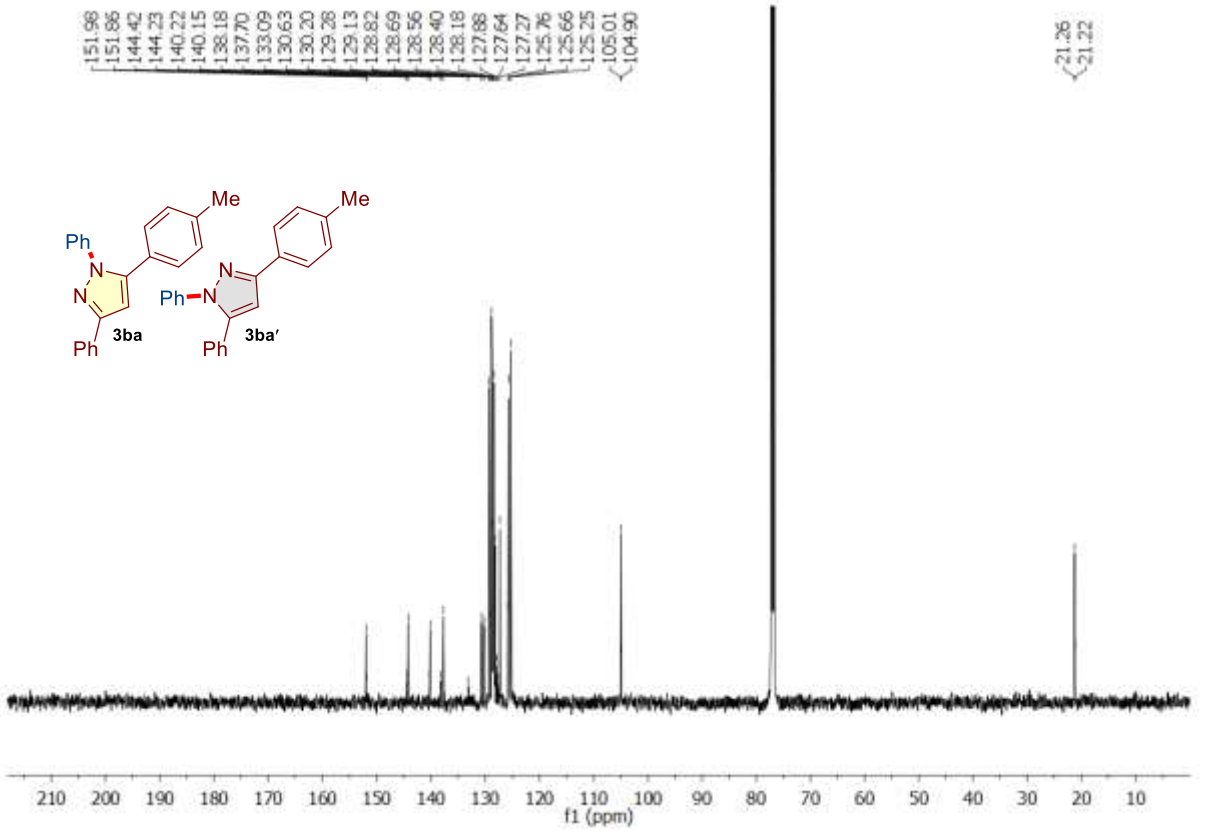
^{1}H and ^{13}C NMR of 3ao



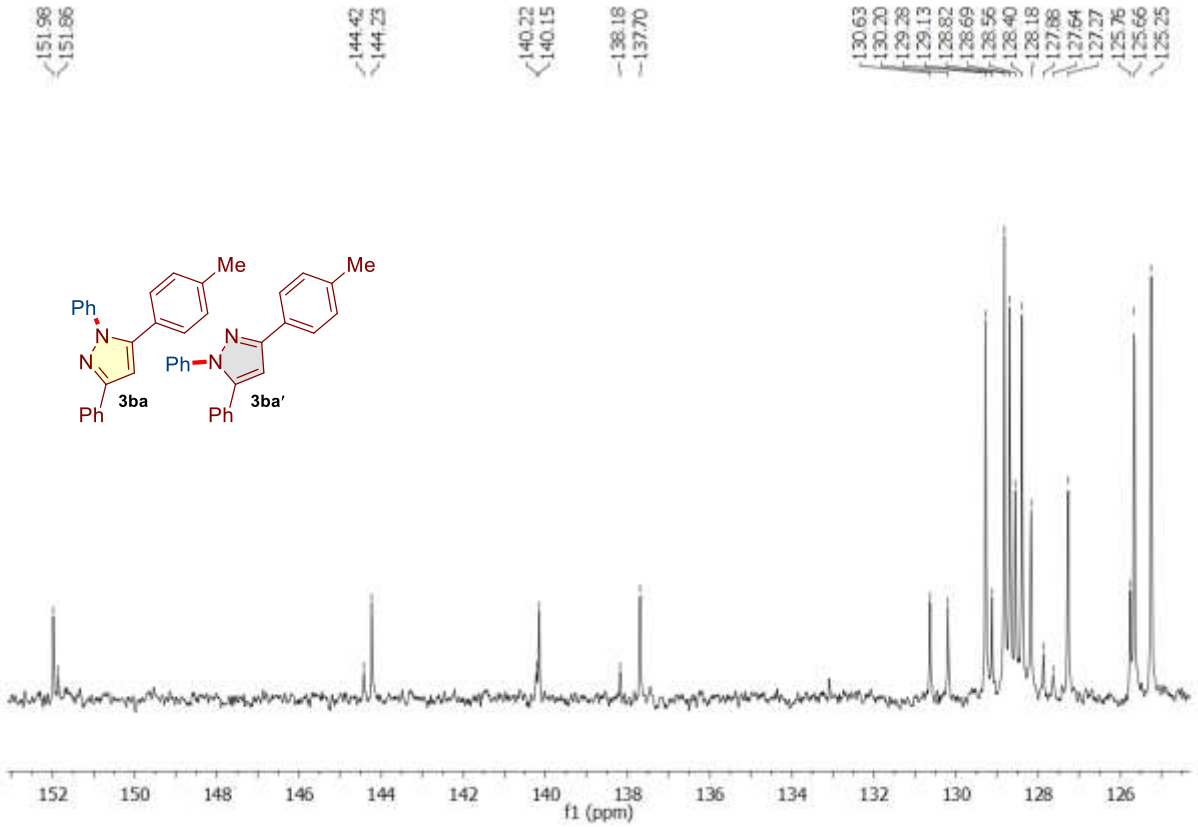


^{1}H and ^{13}C NMR of 3ba and 3ba'

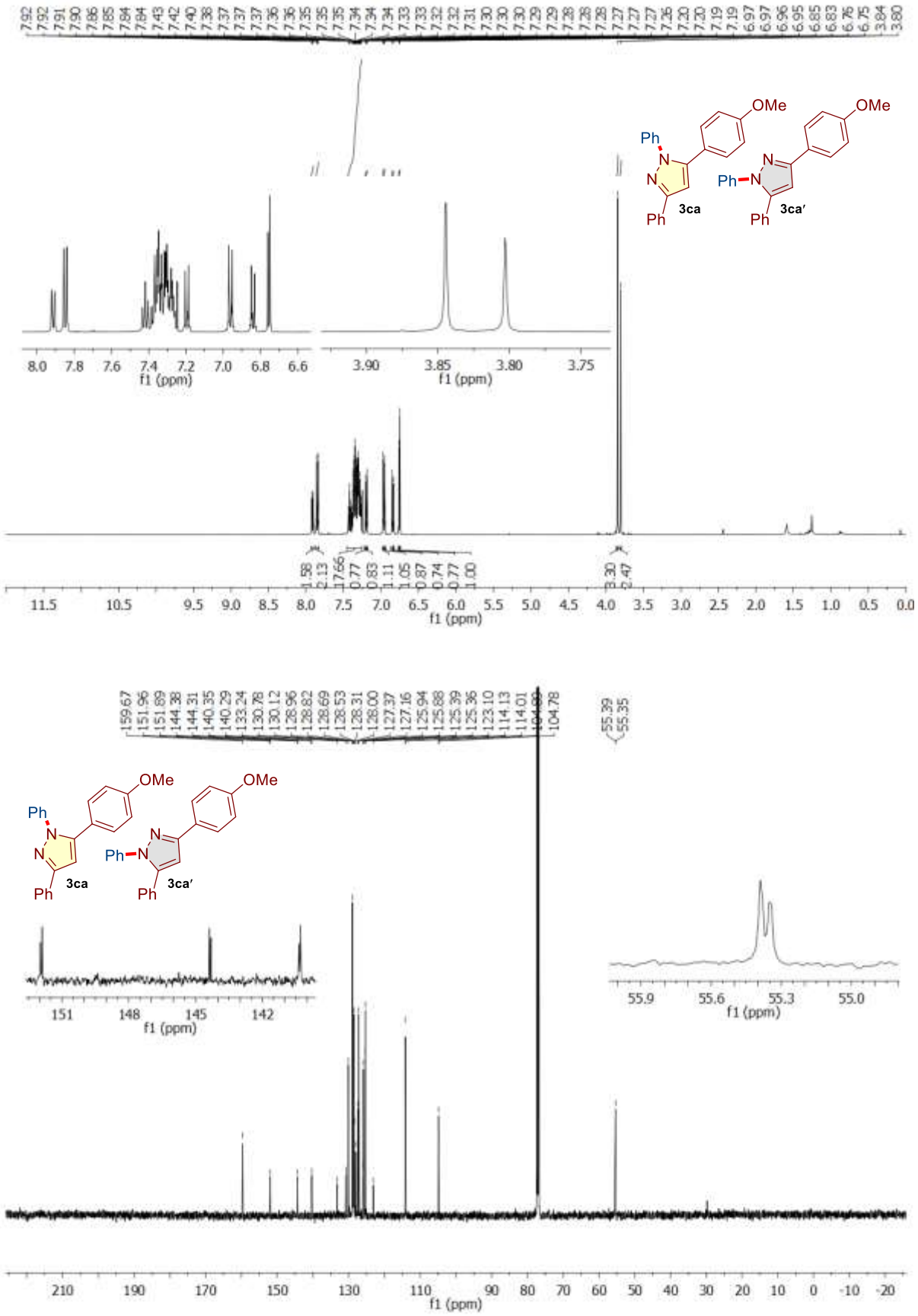




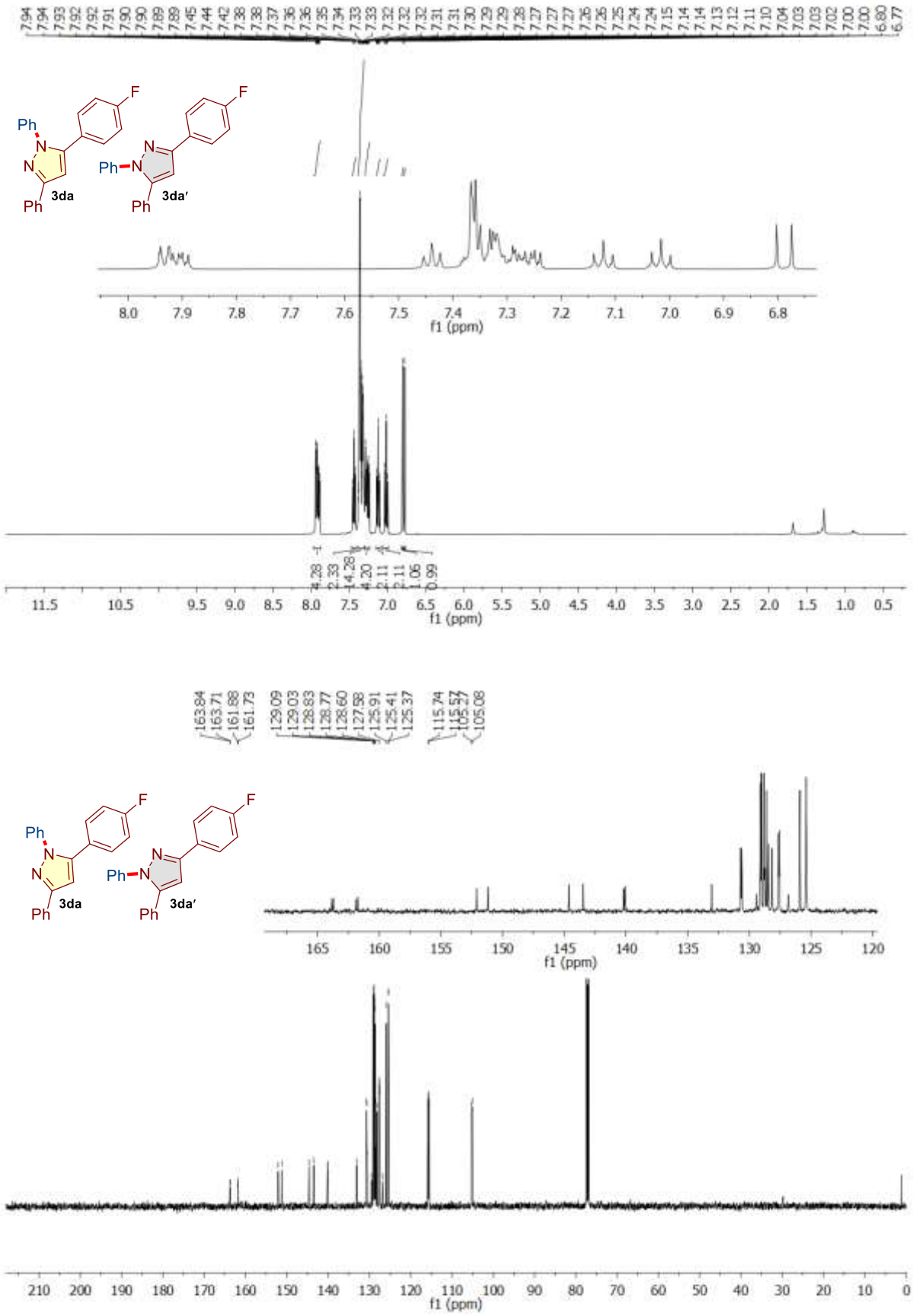
^{13}C NMR of 3ba and 3ba' (expansion)



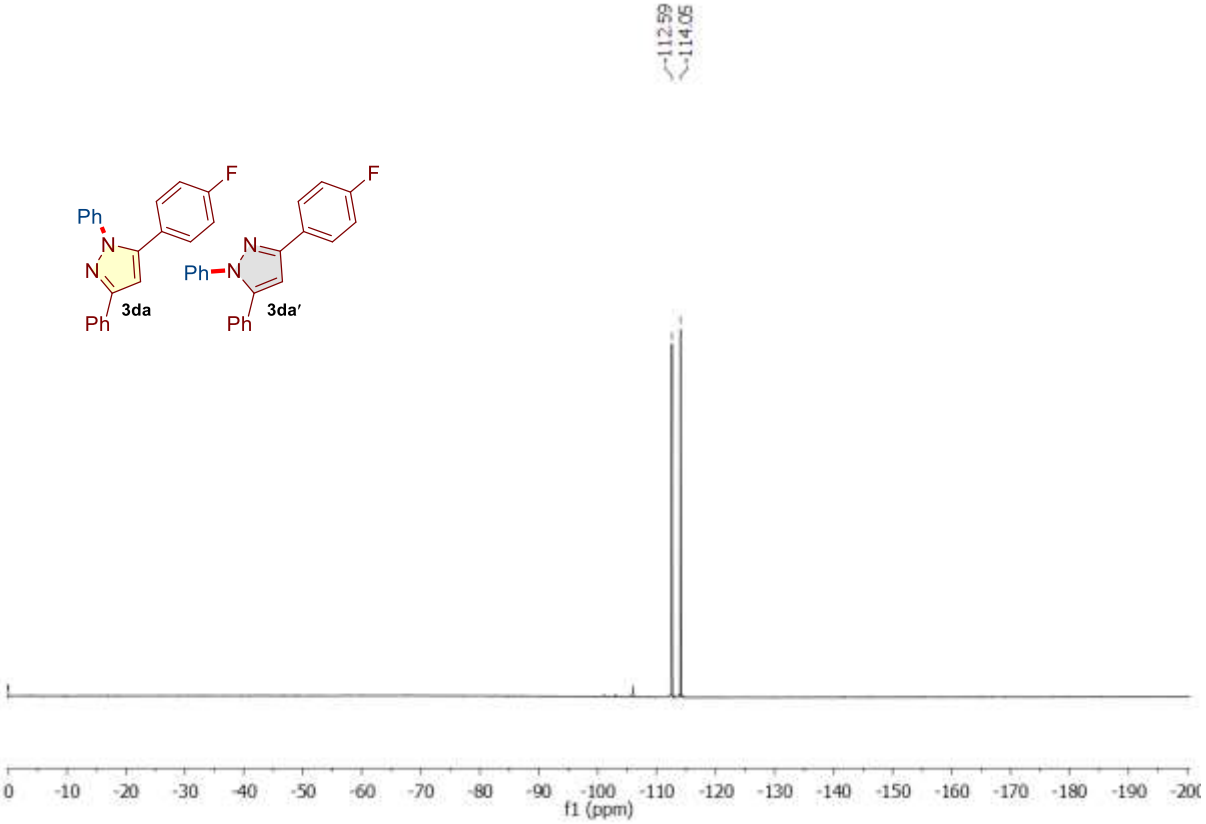
^{1}H and ^{13}C NMR of 3cb and 3cb'



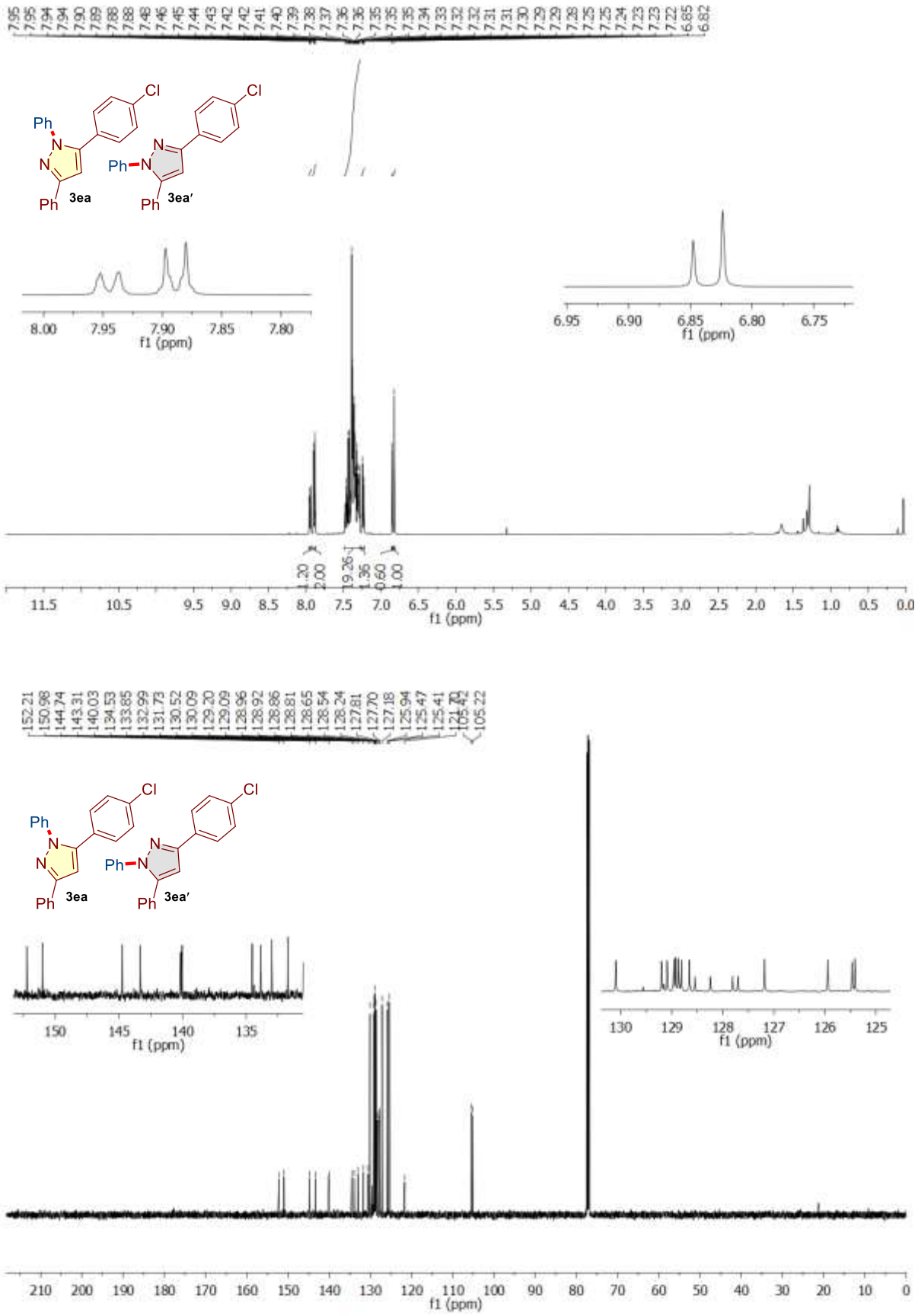
^{1}H and ^{13}C NMR of 3da and 3da'



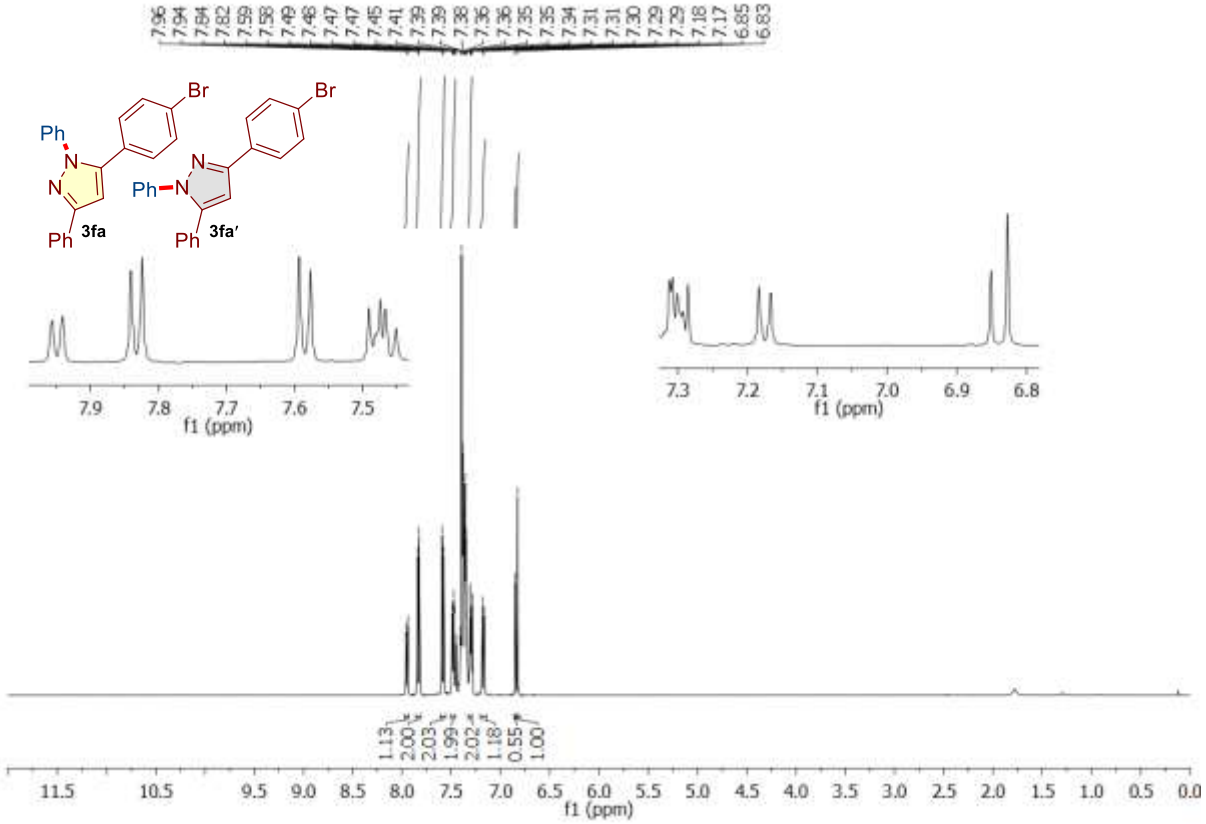
^{19}F{1H} NMR of 3da and 3da'

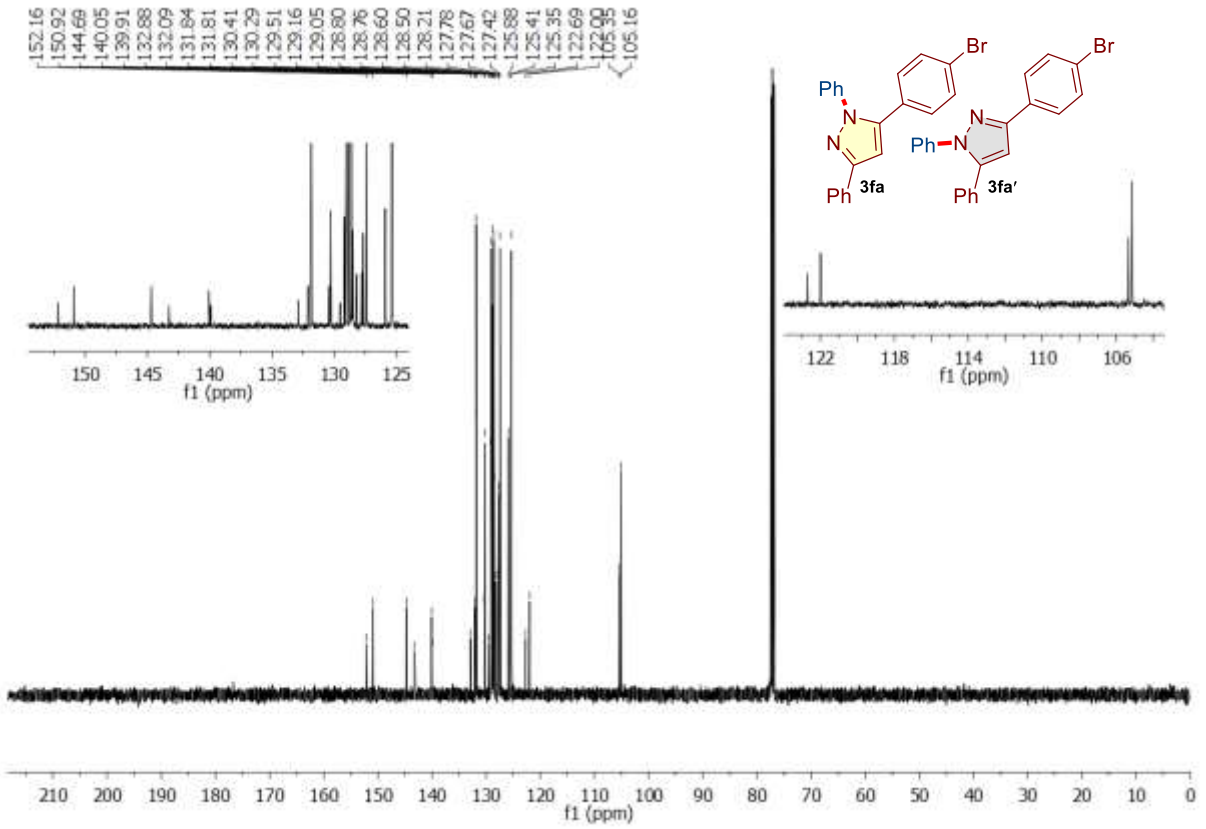


^{1}H and ^{13}C NMR of 3ea and 3ea'

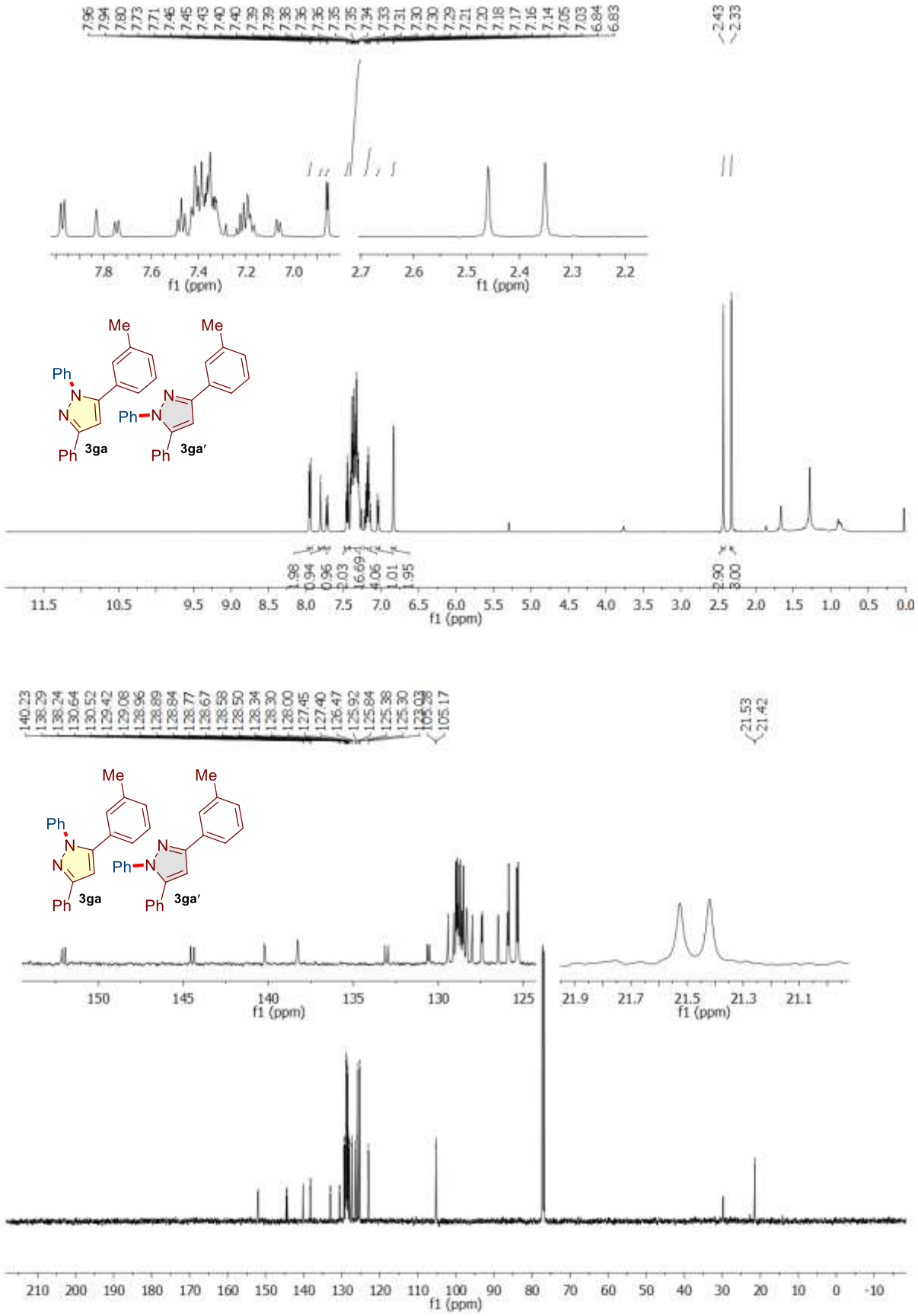


^{1}H and ^{13}C NMR of 3fa and 3fa'

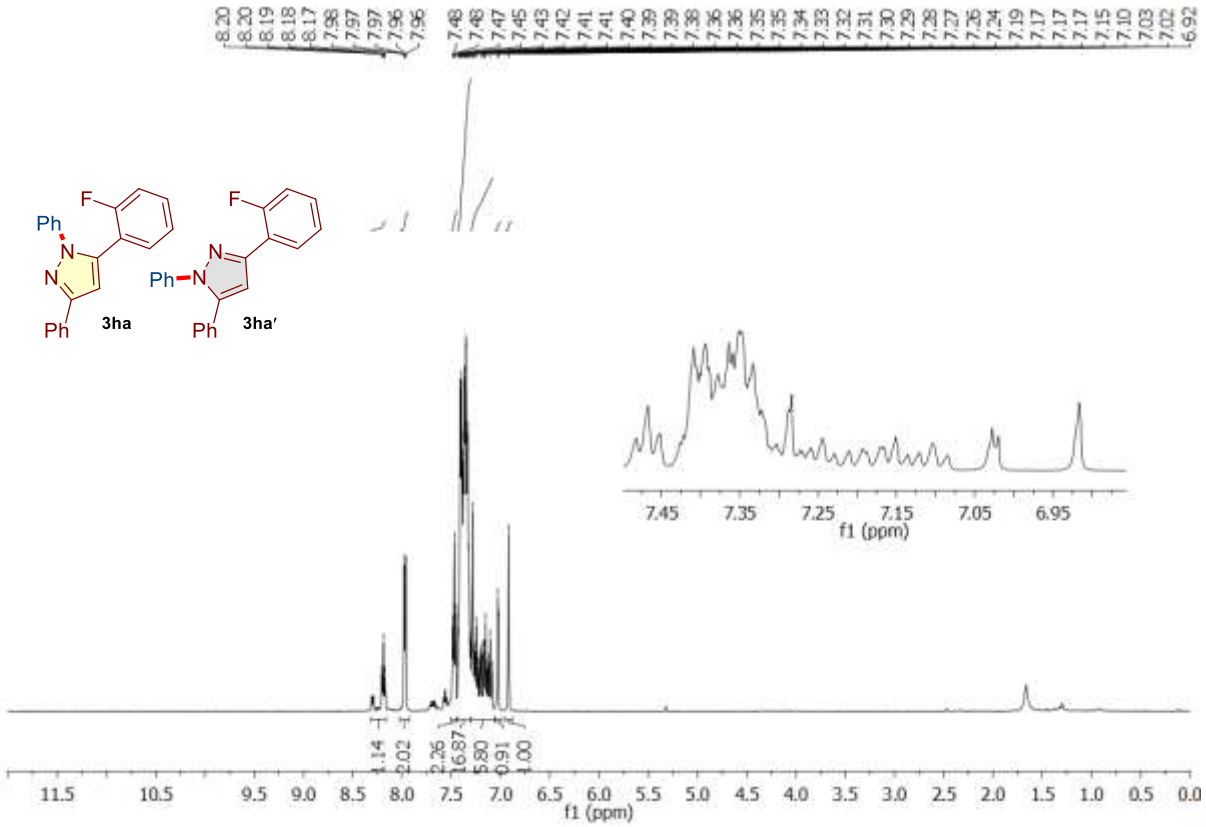


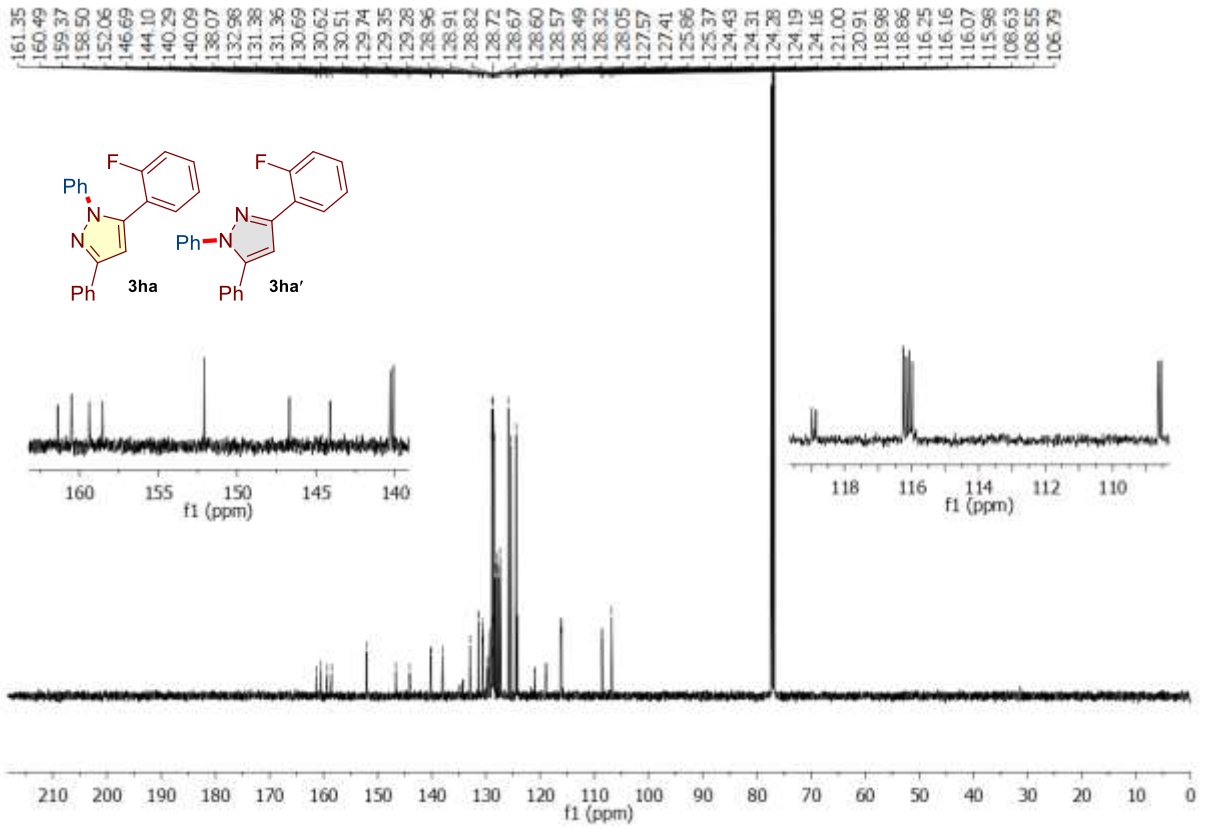


^{1}H and ^{13}C NMR of 3ga and 3ga'

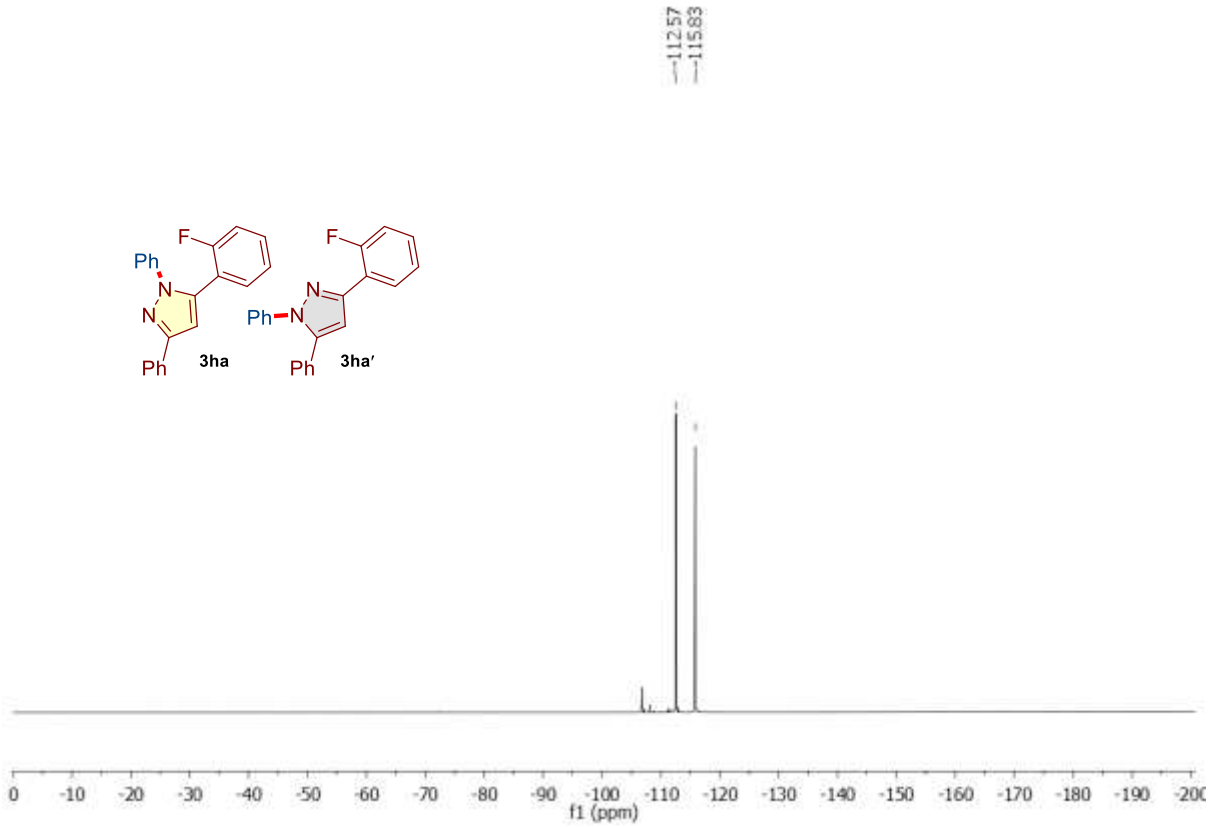


^{1}H and ^{13}C NMR of 3ha and 3ha'

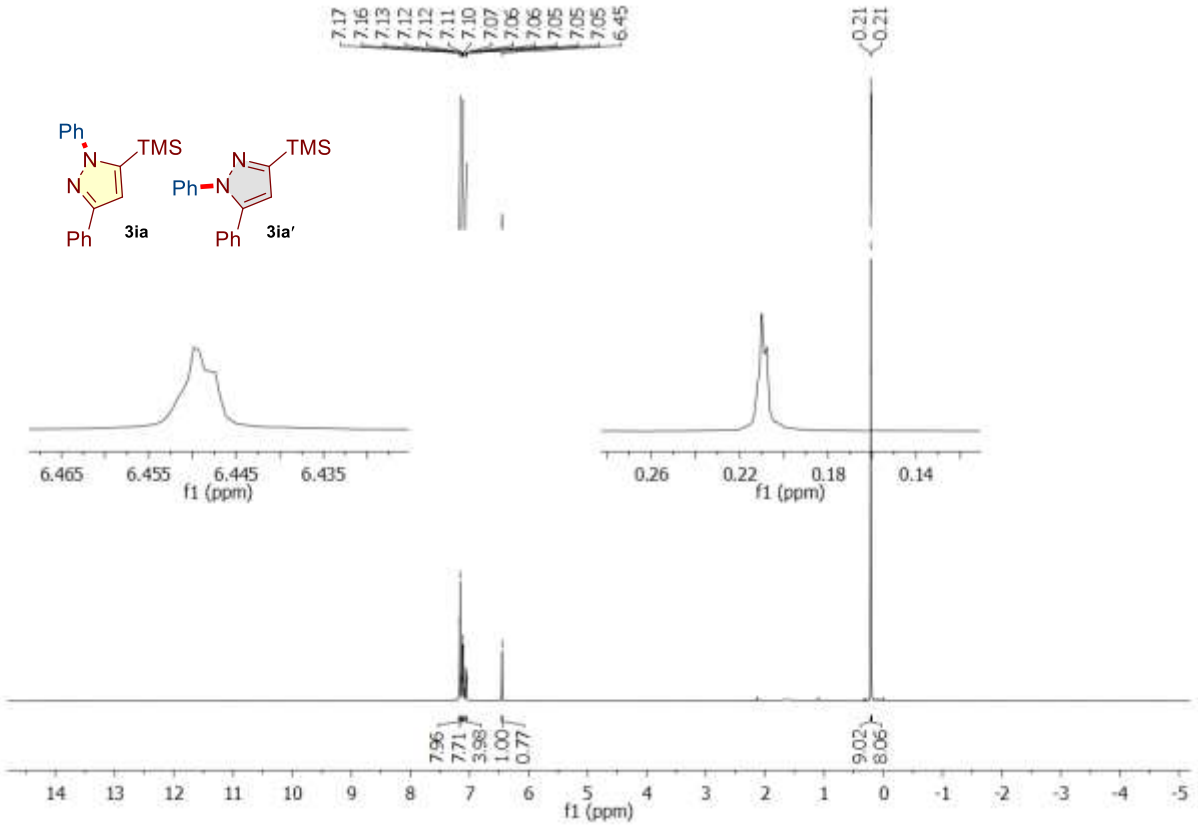


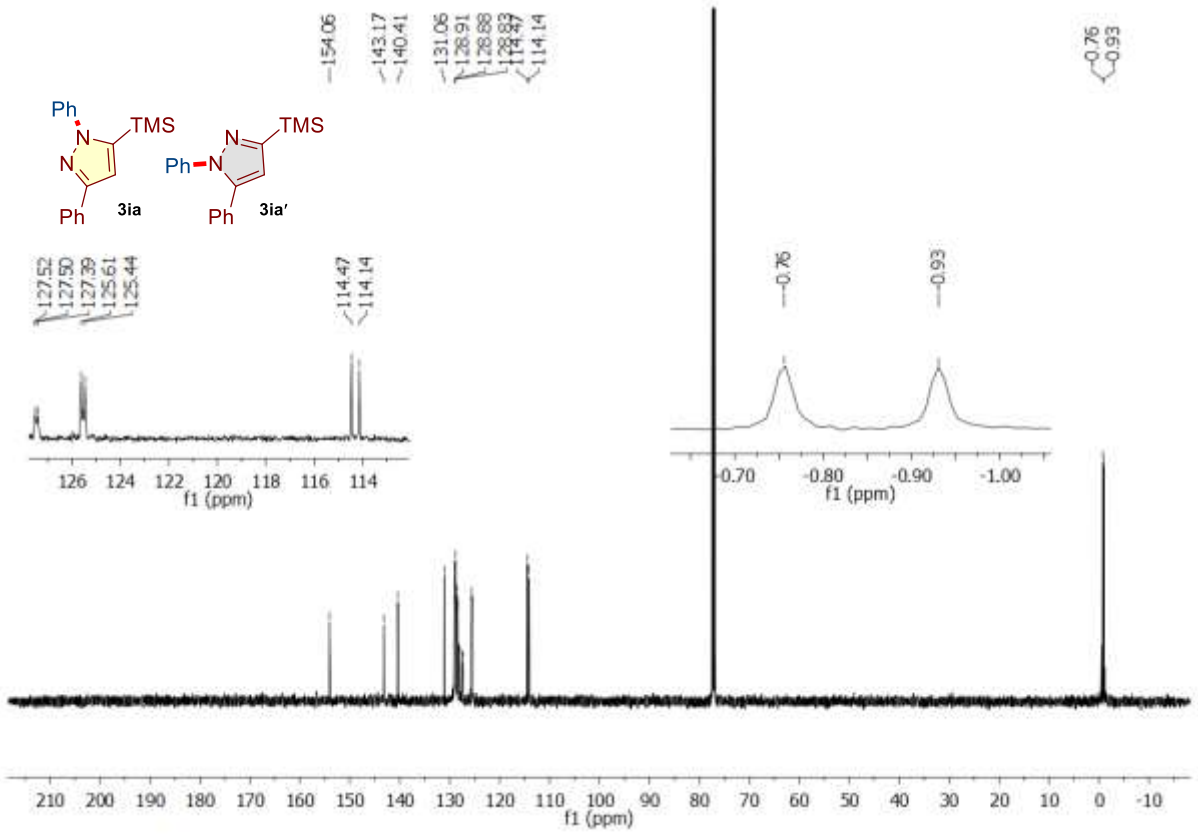


^{19}F{1H} NMR of 3ha and 3ha'

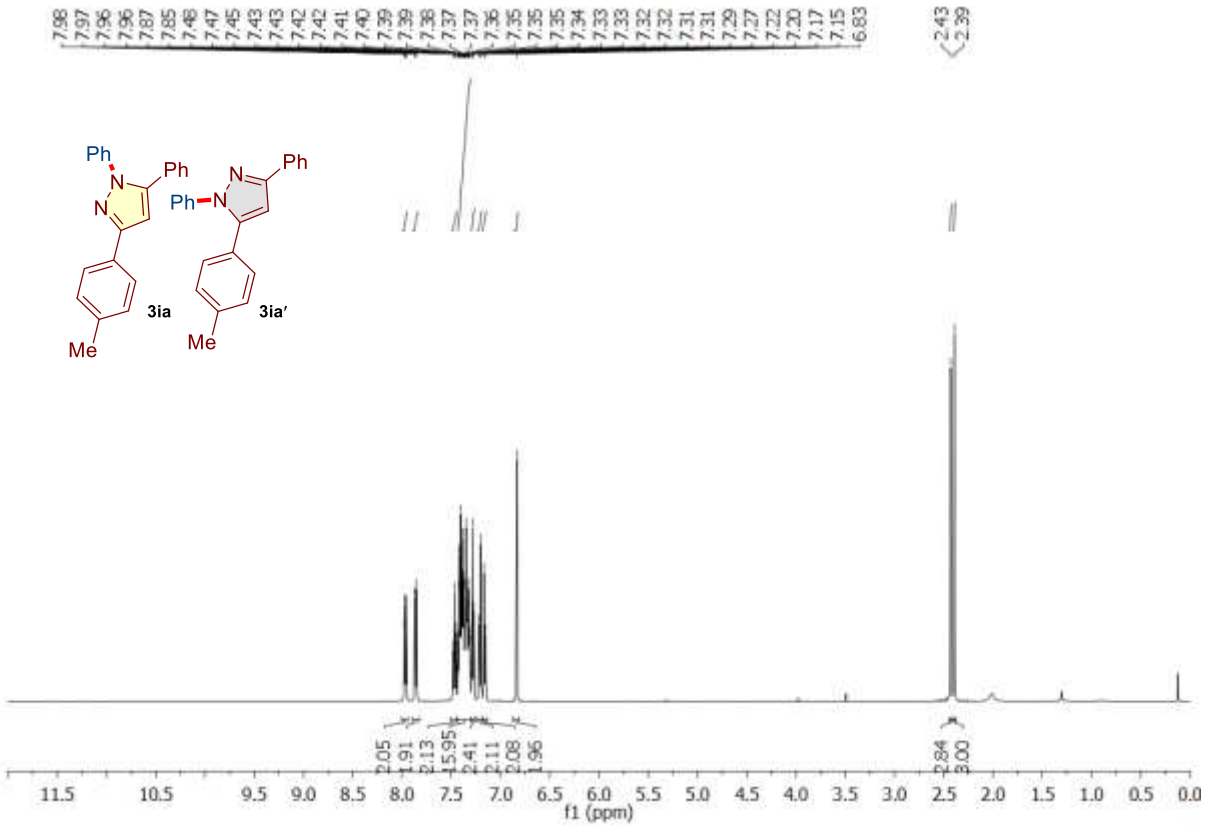


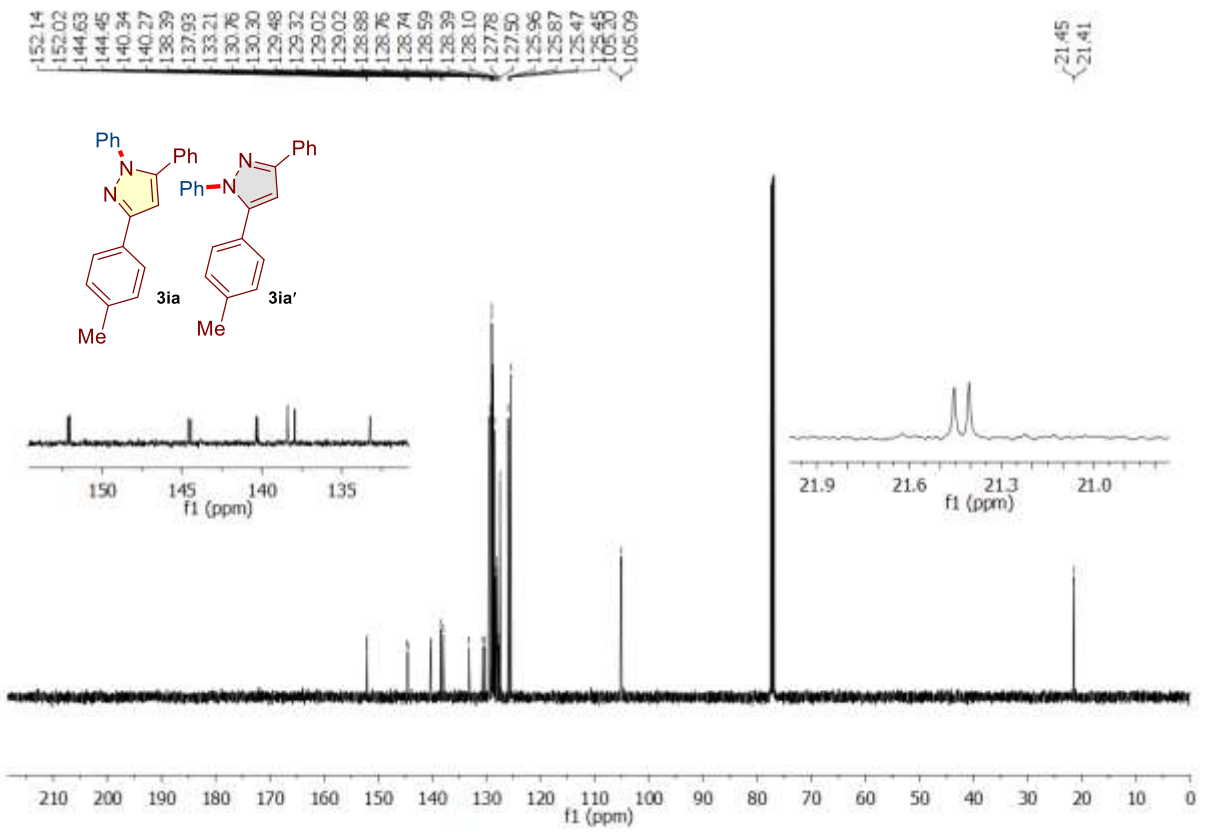
^{1}H and ^{13}C NMR of 3ia and 3ia'



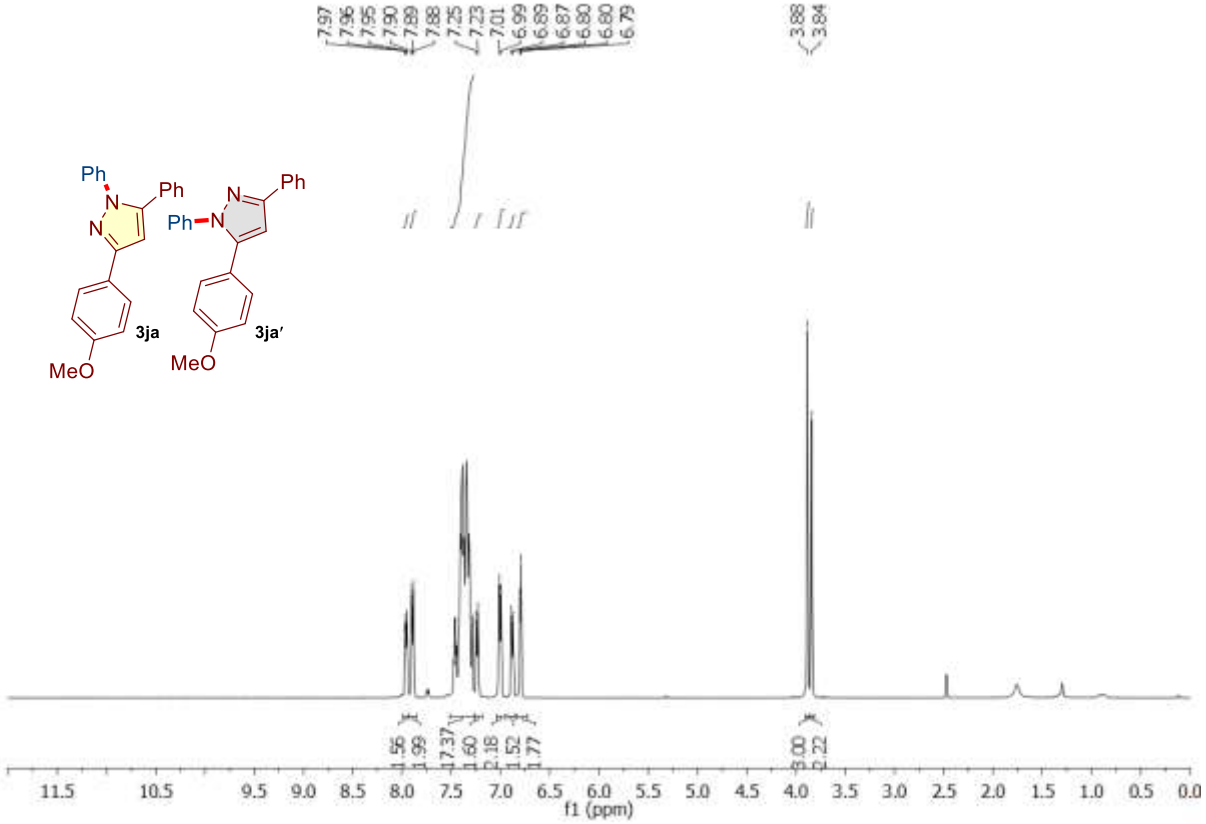


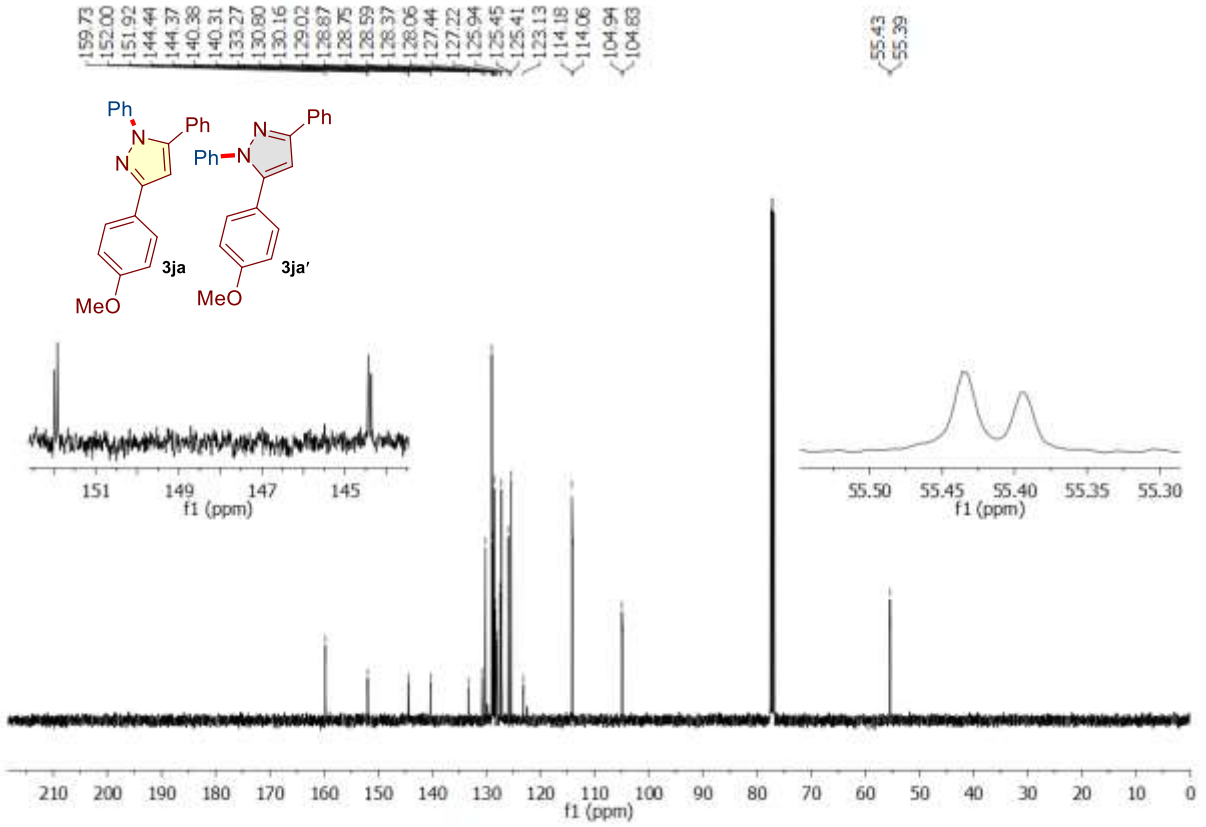
^{1}H and ^{13}C NMR of 3ja and 3ja'



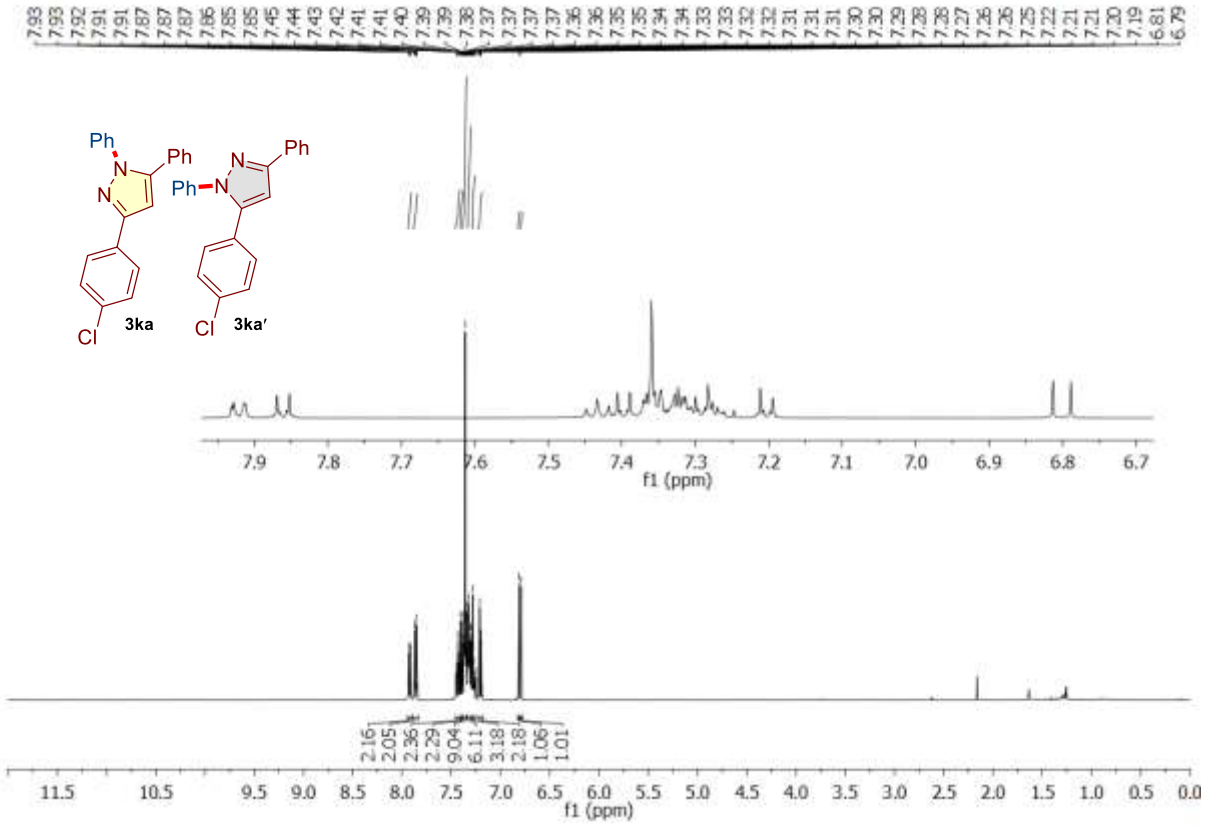


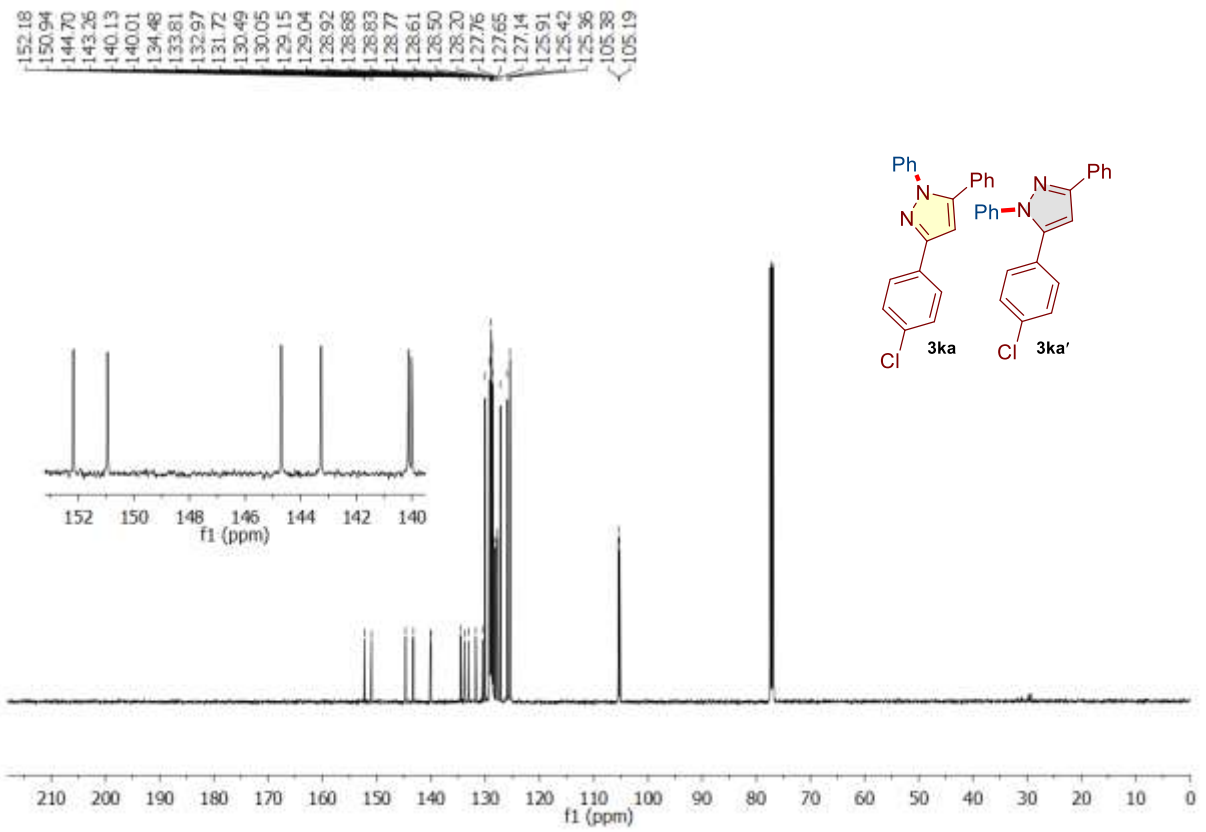
^{1}H and ^{13}C NMR of 3kaand 3ka’



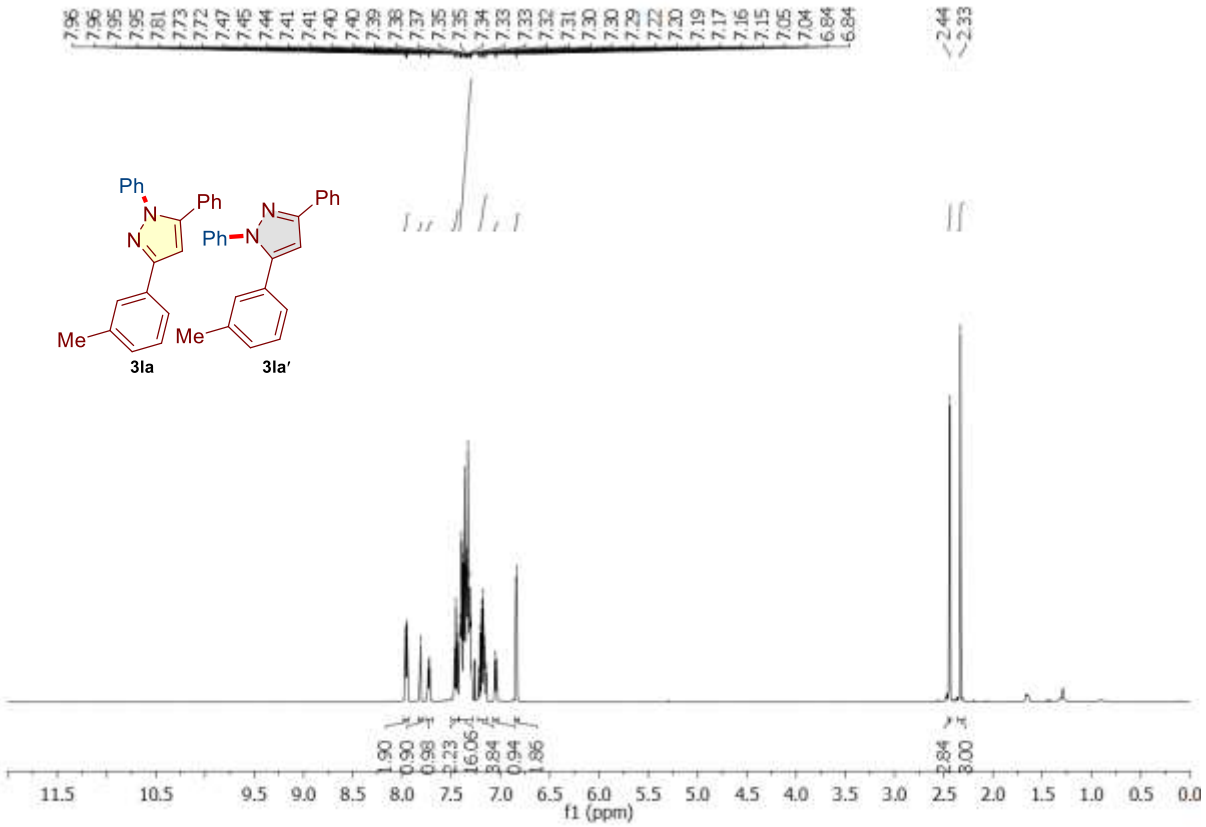


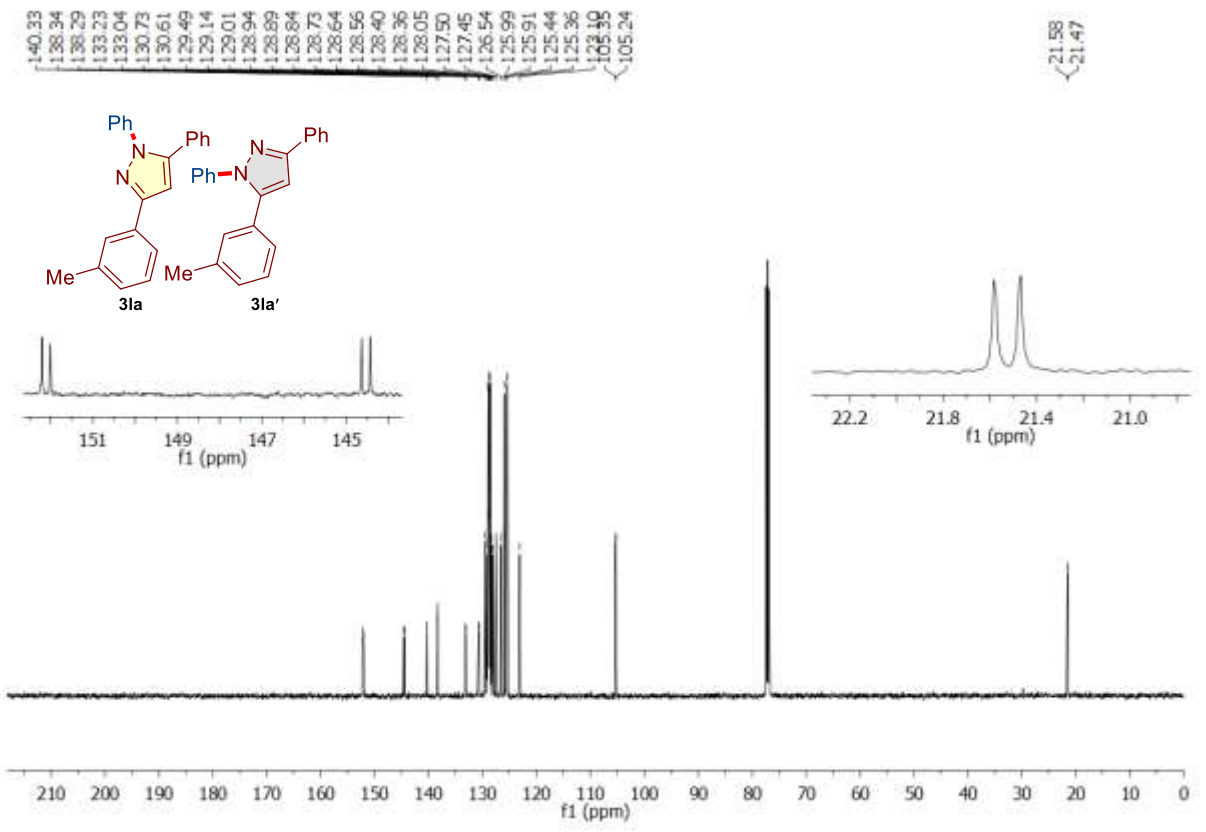
^{1}H and ^{13}C NMR of 3la and 3la'



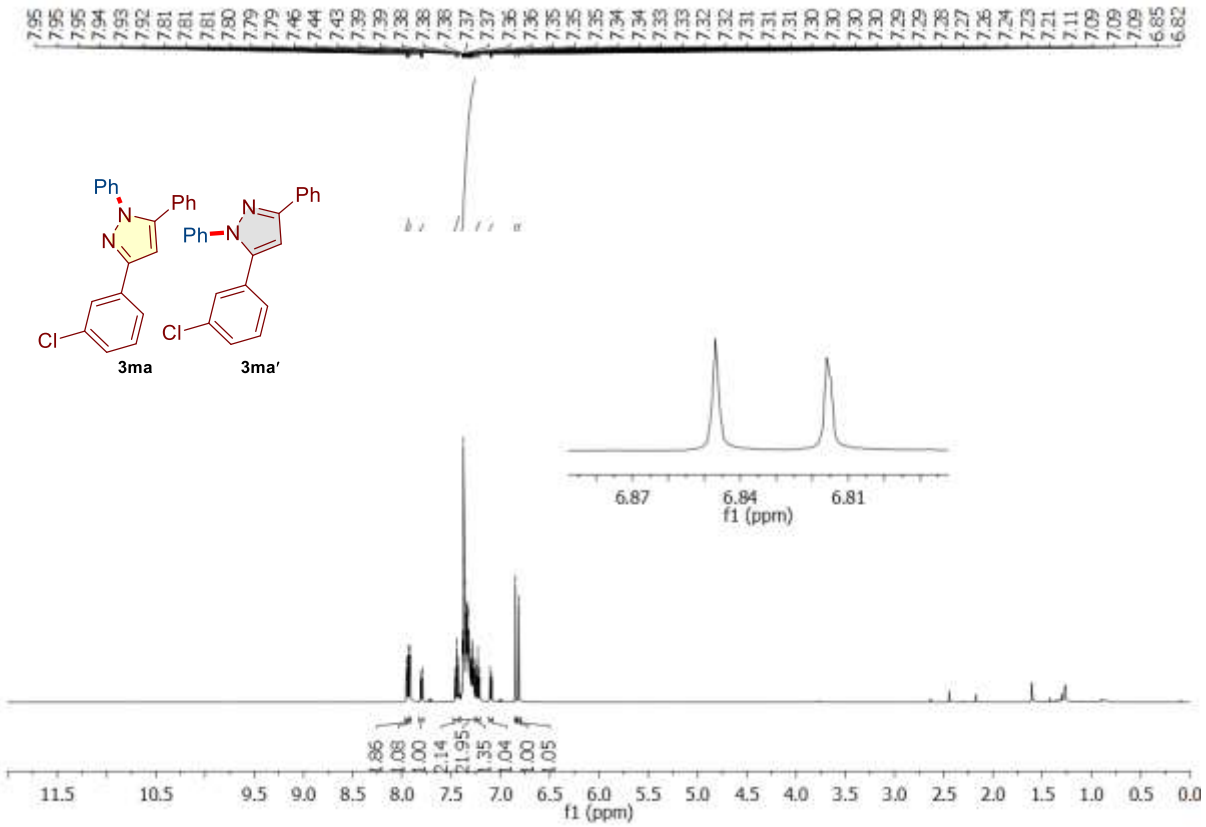


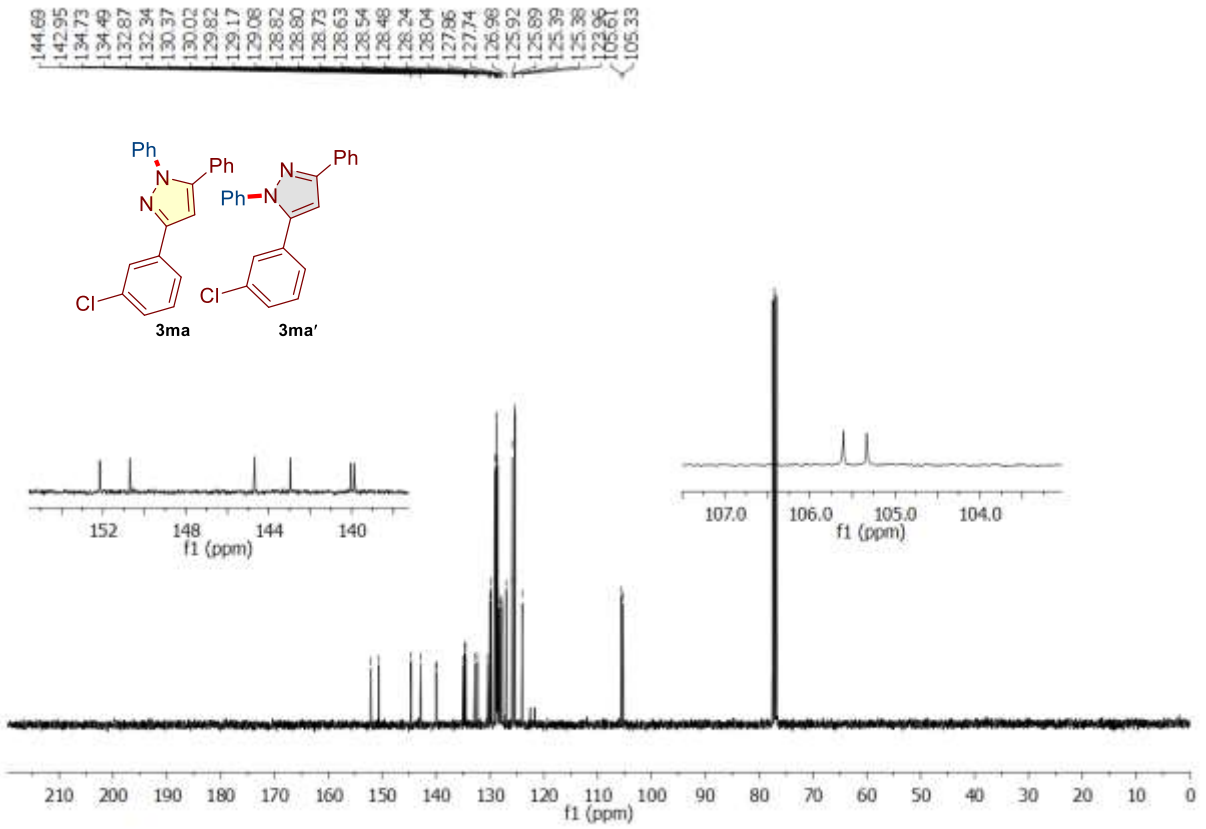
^{1}H and ^{13}C NMR of 3ma and 3ma'



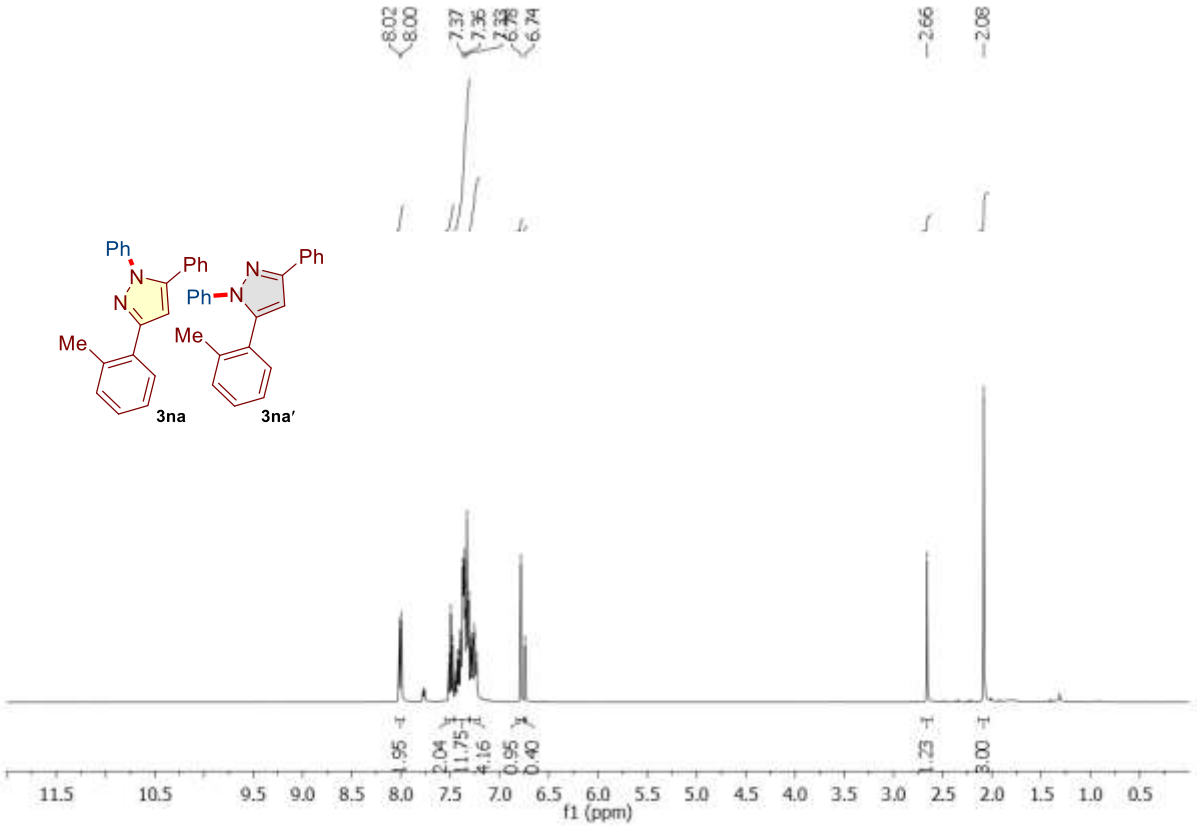


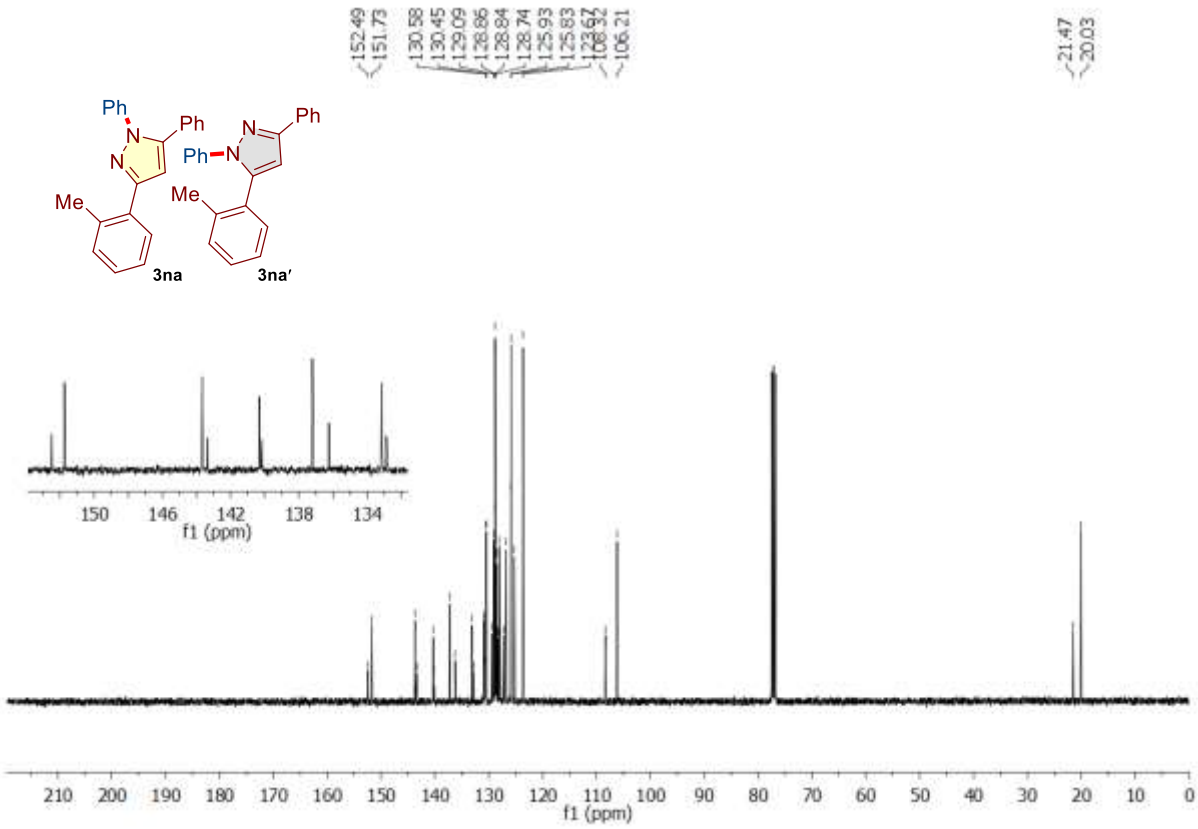
^{1}H and ^{13}C NMR of 3na and 3na'



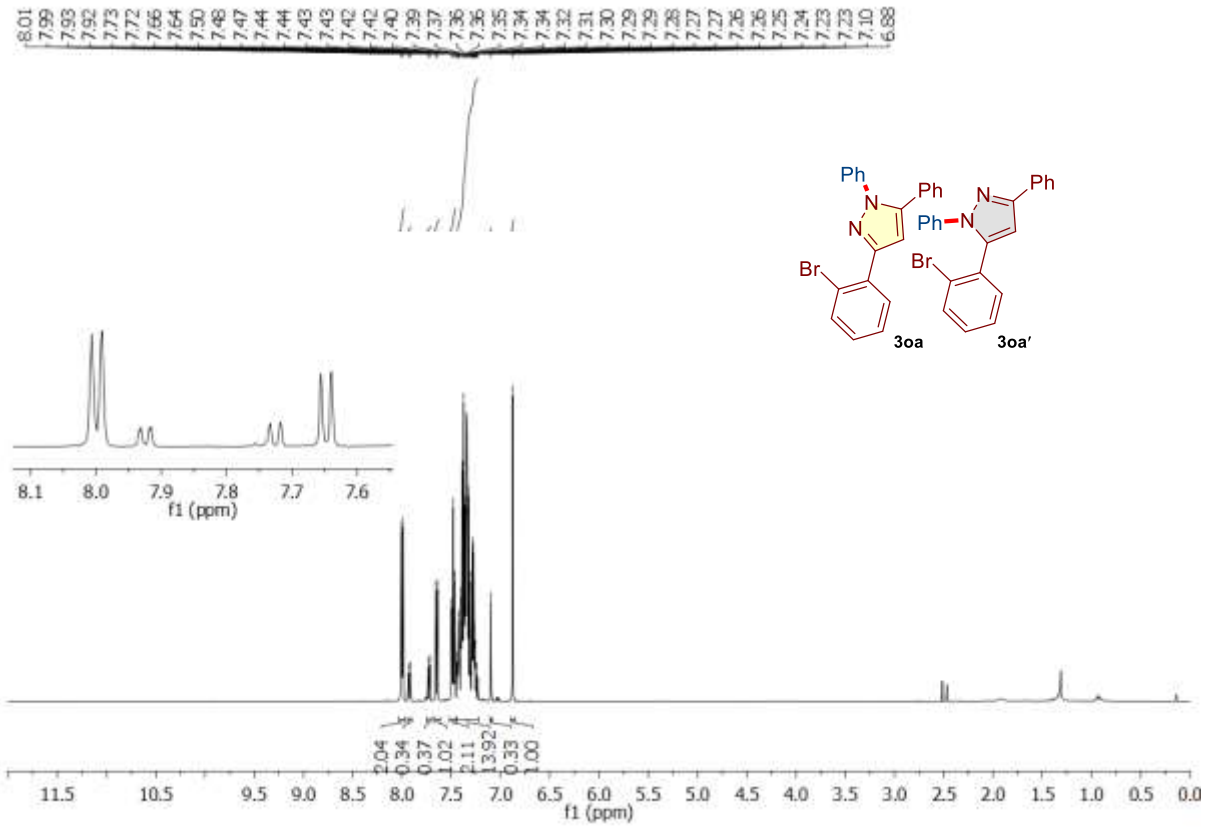


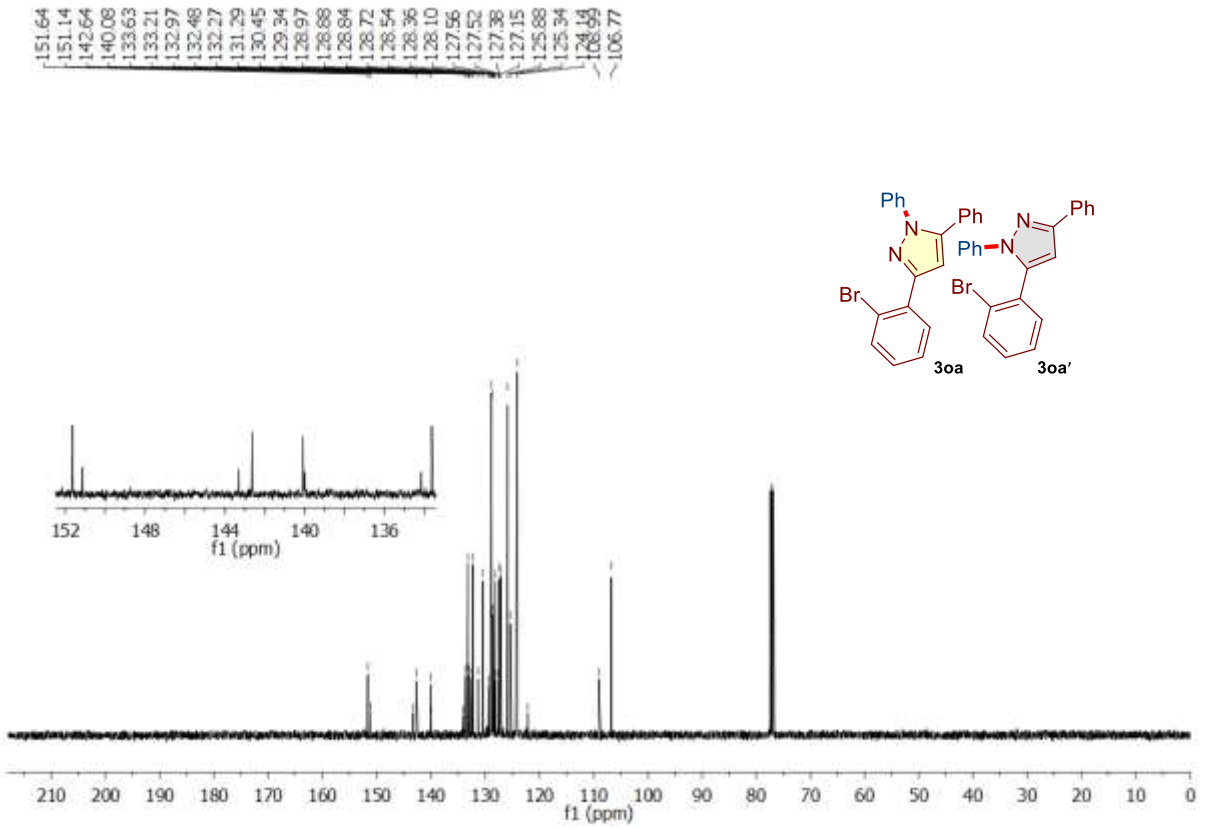
^{1}H and ^{13}C NMR of 3oa and 3oa'



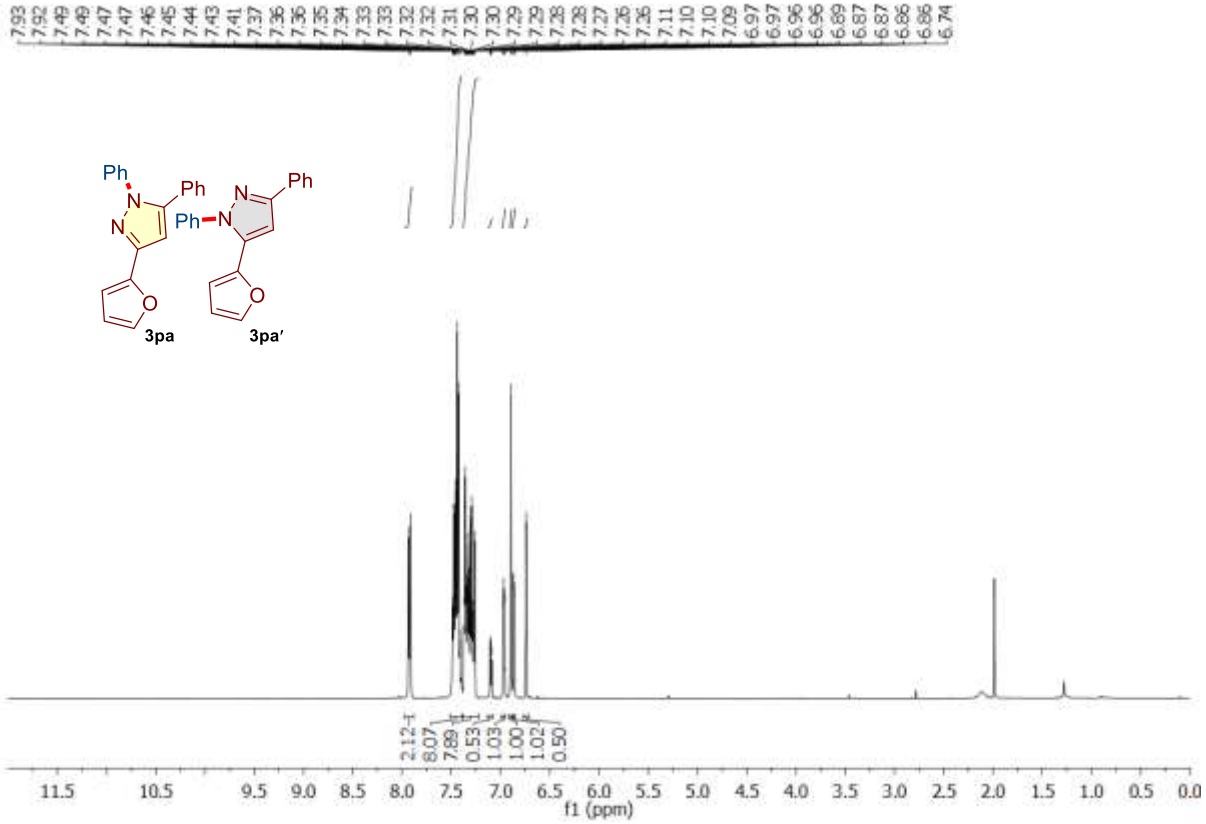


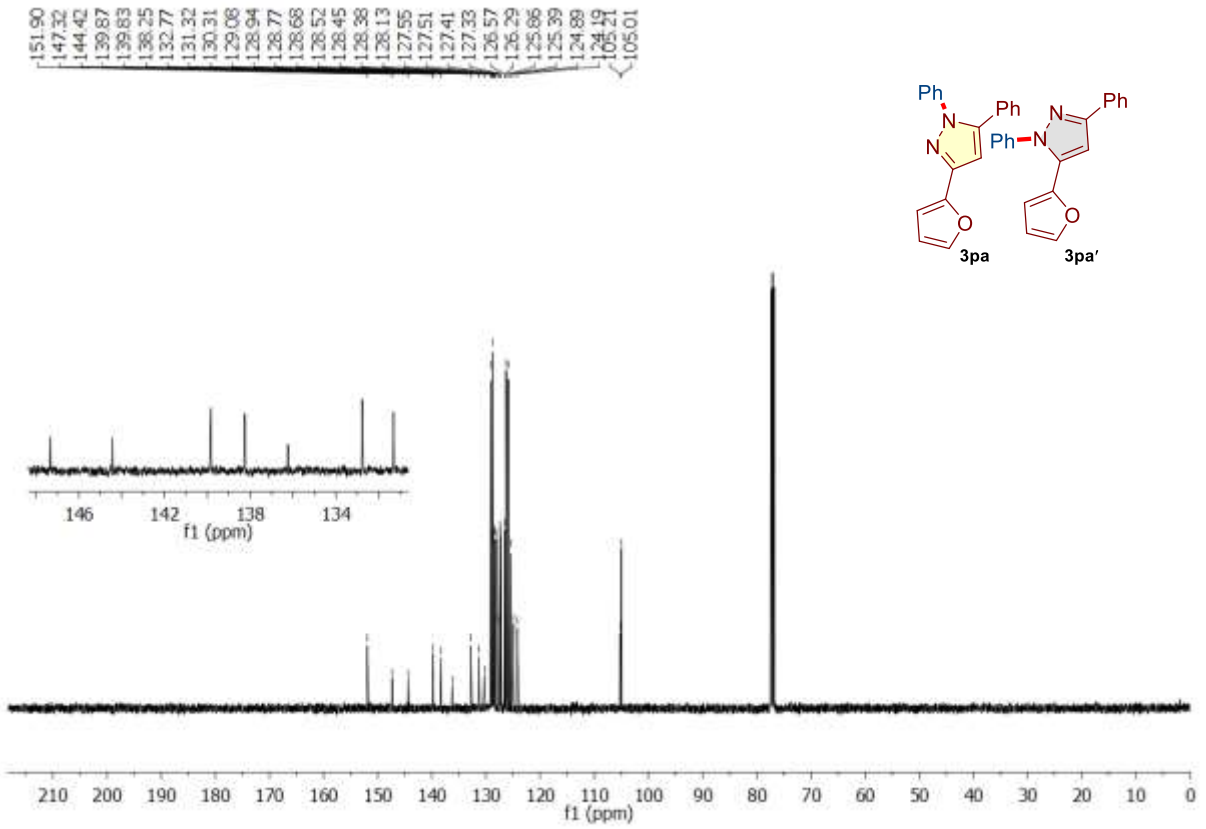
^{1}H and ^{13}C NMR of 3pa and 3pa'



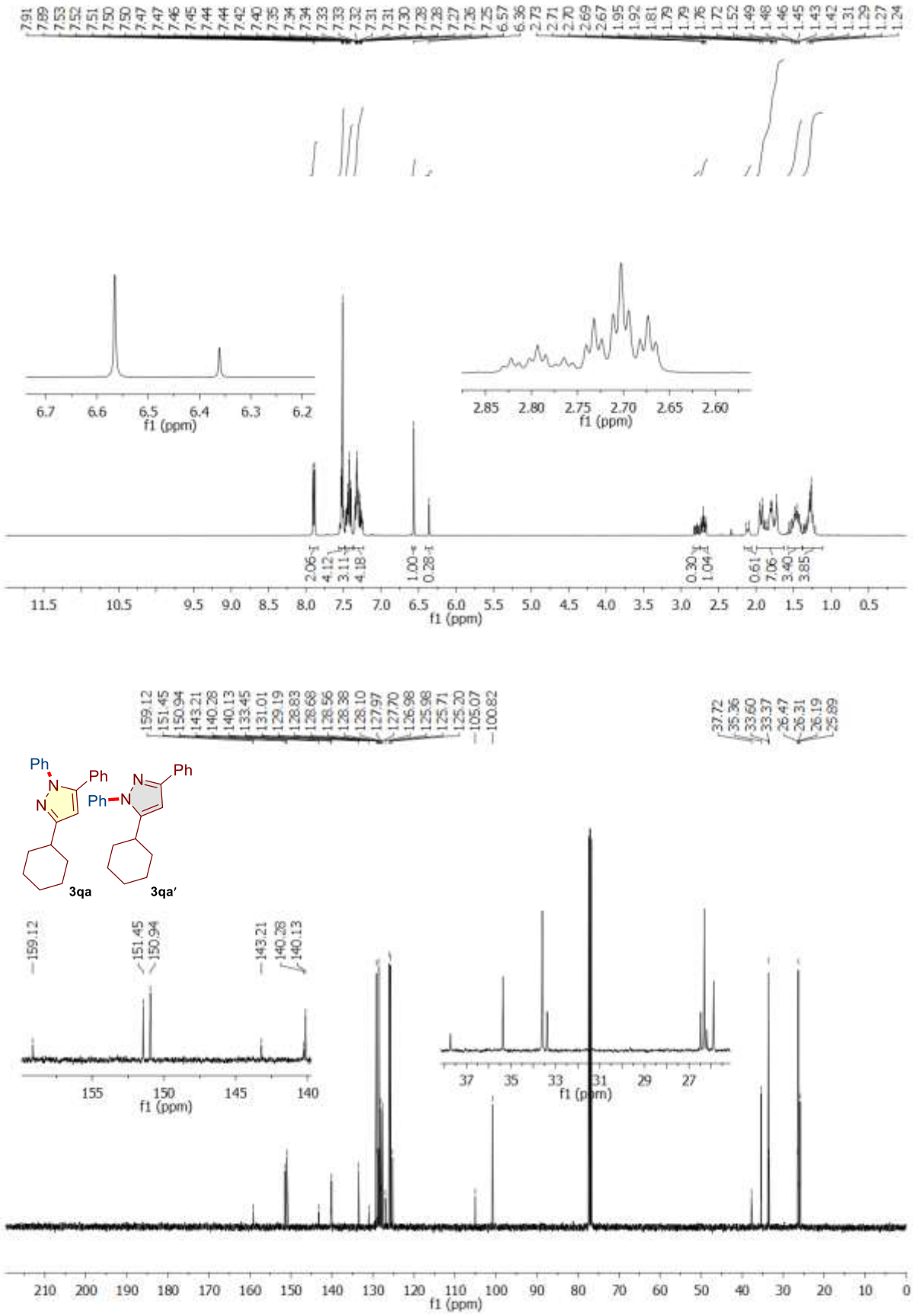


^{1}H and ^{13}C NMR of 3qa and 3qa'

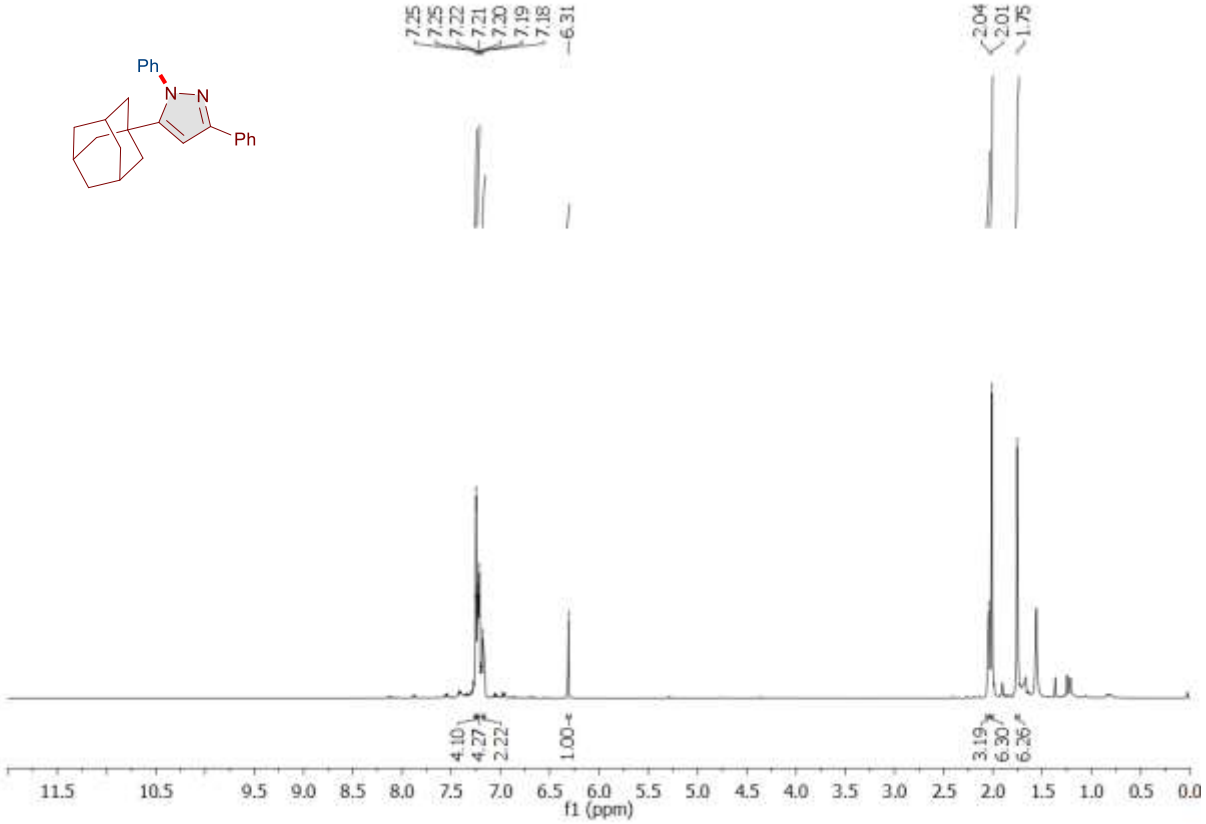


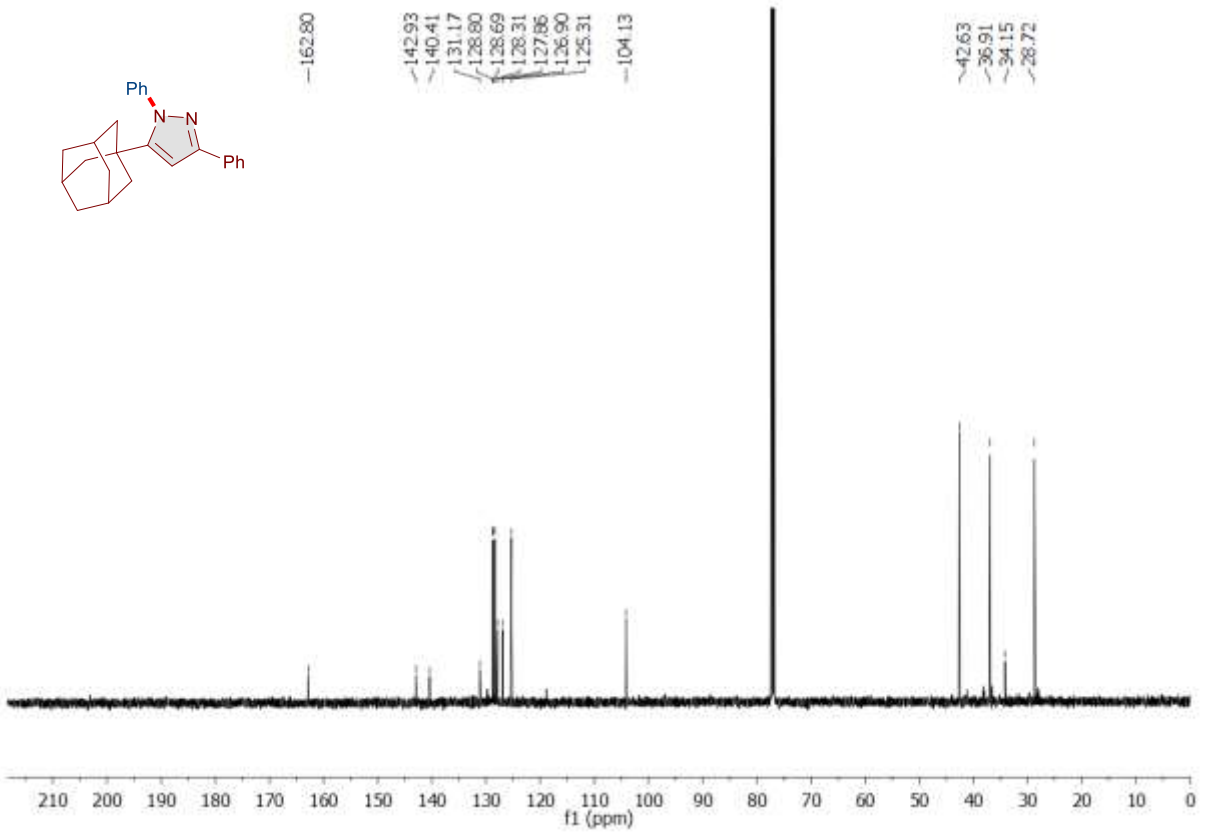


^{1}H and ^{13}C NMR of 3ra and 3ra'

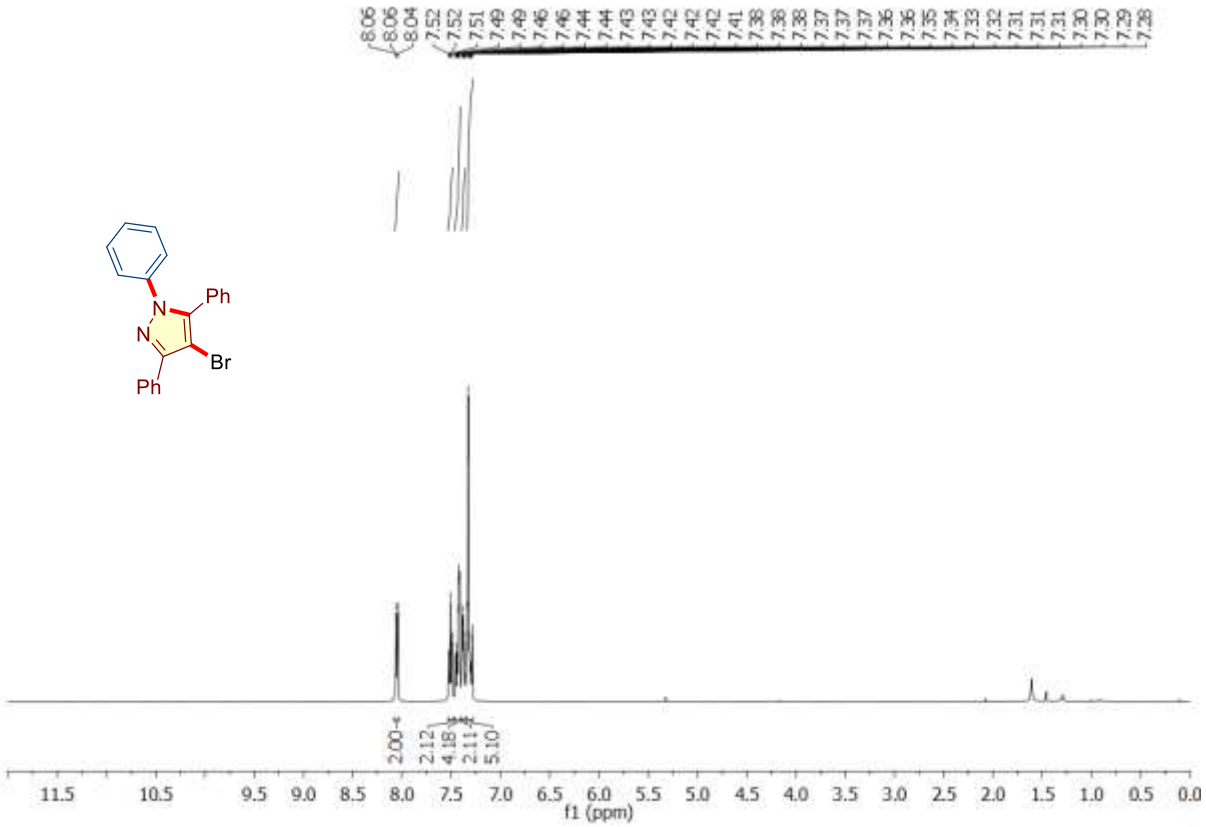


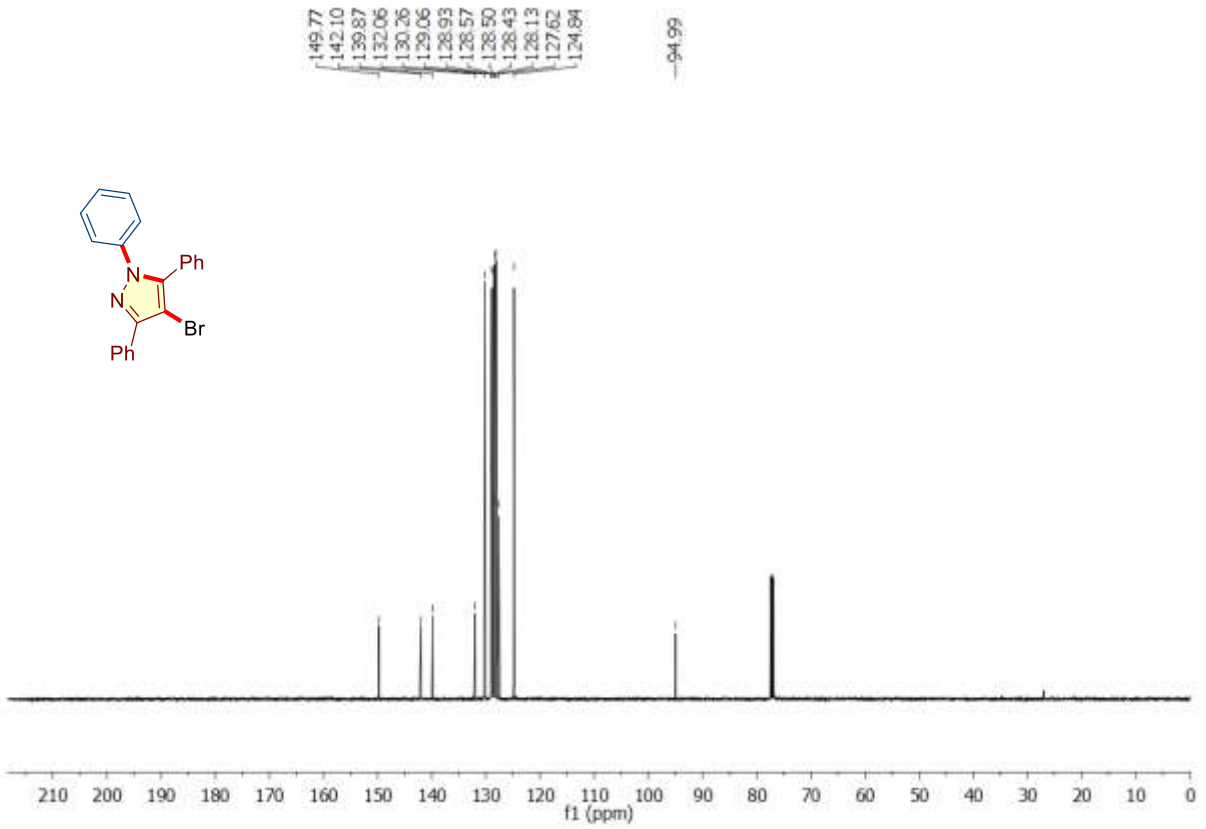
^{1}H and ^{13}C NMR of 3sa





^{1}H and ^{13}C NMR of 5





^{1}H and ^{13}C NMR of 6