

Supporting Information

Aryl Pyrazoles from Photocatalytic Cycloadditions of Arenediazonium

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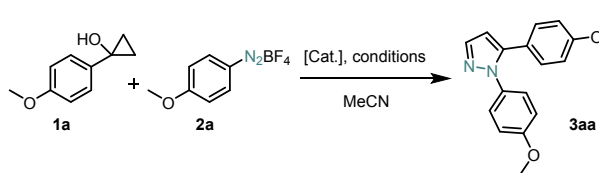
1 General information

All reagents and solvents were purchased from commercial suppliers (Acros, Alfa Aesar, Fisher, Fluka, Merck, Sigma Aldrich, Sojuz-Chimexport and TCI) and used as received. Diazonium salts were prepared by synthetic routes (*vide infra*), with the respective aniline precursors used without further purification as obtained from the vendors. The reactions were carried out in Rotilabo[®]-sample vials (6mL, Ø22mm, Roth) sealed with Rotilabo[®]-aluminum caps with septum (Ø20mm, Roth). Irradiation was performed with a blue high-power LED (Luxeon Rebel, Canada, P = 3.8 W, $\lambda_{\text{max}} = 450\text{nm}$). TLC was performed on the commercial SiO₂-coated aluminum plates (DC60 F254, Merck). Visualization was done by UV light (254 nm). Product yields were determined as isolated yields after flash column chromatography on silica gel (Acros Organics, mesh 35-70, 60 Å pore size).

Purity and structure confirmation of literature-known compounds was performed by ¹H NMR, ¹³C NMR, ¹⁹F NMR and MS. NMR spectral data were collected on a Bruker Avance 300 (300 MHz for ¹H; 75 MHz for ¹³C, 282 MHz for ¹⁹F) spectrometer, Bruker Avance 400 (400 MHz for ¹H; 100 MHz for ¹³C) spectrometer and a Bruker Avance 500 (500 MHz for ¹H; 125 MHz for ¹³C) spectrometer at 20°C. Chemical shifts are reported in δ/ppm , coupling constants J are given in Hertz. Solvent residual peaks were used as internal standard for all NMR measurements. The quantification of ¹H cores was obtained from integrations of appropriate resonance signals. Abbreviations used in NMR spectra: s –singlet, d –doublet, t –triplet, q –quartet, m –multiplet, bs –broad singlet, dd –doublet of doublet, ddd –doublet of doublet of doublet. Low-resolution mass spectrometry (LRMS) was carried out on an Agilent6890N GC-System with 5975 MS mass detector and H₂ as carrier gas. High resolution mass spectrometry (HRMS) was carried out by the Central Analytics at the department of chemistry, University of Hamburg. Abbreviations used in MS spectra: M –molar mass of target compound, EI –electron impact.

2 Optimization experiments

Table S1. Optimization of the photocatalytic pyrazole synthesis



Entry	Catalyst loading	Time/h	Additive	Yield % 3aa
1^a	2.5 mol%	18	-	42
2	5 mol%	18	-	85
3	5 mol%	0.33	-	87
4	2.5 mol%	0.33	-	79
5	2.5 mol%	0.15	-	81
6	0 mol%	0.33	-	3
7^b	2.5 mol%	0.33	-	0
8	5 mol%	0.33	air	65
9^c	5 mol%	0.33	-	55
10	5 mol%	0.33	DIPEA 20 mol%	56
11	5 mol%	0.33	CH ₃ COOH 20 mol%	49

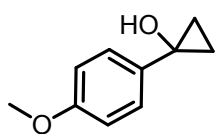
Reaction conditions: cyclopropanol **1a** (0.37 mmol, 1equiv.), diazonium salt **2a** (0.56 mmol, 1.5 equiv.), Ru(bpy)₃Cl₂·6H₂O (as indicated), RT, blue LED irradiation ($\lambda_{\text{max}}=455\text{ nm}$), flushed with nitrogen. ^aeosin Y was used instead of Ru(bpy)₃Cl₂·6H₂O, green LED irradiation instead of blue. T, 0 °C to RT, 4 ml of THF per mmol of substrate; ^bReaction was performed in the dark. ^cReaction run with 1 equiv. of **2a** instead of 1.5 equiv.

3 *General procedures for the synthesis of cyclopropanols (A, B)*

General procedure A: Simmons-Smith reaction

A dried 100 mL round bottomed Schlenk flask was equipped with a stir bar. The flask was evacuated, heated, flushed with nitrogen three times and sealed with a rubber septum. In a dry nitrogen atmosphere THF (20 mL, dry) and (*i*Pr)₂NH (1.5 mL, 11.0 mmol, 1.1 eq.) were added. At 0 °C *n*BuLi (7.0 mL, 1.6 mol L⁻¹ in hexane, 11.0 mmol, 1.1 eq.) was added to the stirring mixture dropwise via syringe. The mixture was warmed to room temperature and stirred for 1 h. To this mixture at 0 °C the parent ketone (10.0 mmol, 1.0 eq.) was added by syringe followed by TMSCl (1.4 mL, 11.0 mmol, 1.1 eq.). After the mixture was stirred for 2 h at room temperature, it was quenched by addition of NaHCO₃ solution (30 mL, sat.). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with a NaHCO₃ and brine solution (3 × 20 mL) and dried with Na₂SO₄ followed by filtration. The solvent was removed in vacuum. The crude enol ether was used without further purification. A dried 100 mL round bottomed Schlenk flask was equipped with a stir bar. The flask was evacuated, heated, flushed with nitrogen three times and sealed with a rubber septum. The crude enol ether was solved in DCM (20 mL, dry) and was transferred to the prepared Schlenk flask. To the stirring mixture CH₂I₂ (1.2 mL, 15.0 mmol, 1.5 eq.) was added followed by Et₂Zn (15 mL, 1 mol L⁻¹ in Et₂O, 15 mmol, 1.5 eq.) at 0 °C. The mixture was stirred overnight at room temperature. The reaction mixture was quenched with NH₄Cl solution (30 mL, sat.) and the precipitate was removed by filtration. The layers were separated and the aqueous layer was extracted with DCM (3 × 30 mL). The combined organic layers were washed with NaCl solution (3 × 30 mL, sat.) and dried with Na₂SO₄ followed by filtration. The solvent was removed in vacuum. A dried 100 mL round bottomed Schlenk flask was equipped with a stir bar. The flask was evacuated, heated, flushed with nitrogen three times and sealed with a rubber septum. The crude cyclopropanol ether was solved in MeOH (20 mL) and transferred to the prepared Schlenk flask. To the stirring mixture TMSCl (one drop) was added via syringe at 0 °C. The reaction was monitored by GC-MS. After completion the solvent was removed in vacuum and the residue was purified by column chromatography (silica gel, 1:9 EtOAc/pentane) to obtain pure product. The following cyclopropanol products were synthesized using the procedure described above:

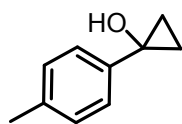
1-(4-methoxyphenyl)cyclopropan-1-ol (1a)



$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ 7.20-7.16 (m, 2H), 6.79-6.76 (m, 2H), 3.71 (s, 3H), 2.46 (bs, 1H), 1.20-1.18 (m, 2H), 0.91-0.85 (m, 2H).

Spectral data were consistent with literature¹

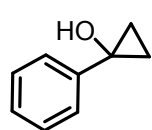
1-(*p*-tolyl)cyclopropan-1-ol (1b)



$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.29-7.20 (m, 4H), 2.86 (bs, 1H), 2.42 (s, 3H), 1.31-1.27 (m, 2H), 1.09-1.04 (m, 2H).

Spectral data were consistent with literature¹

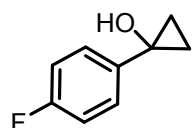
1-phenylcyclopropan-1-ol (1c)



$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ 7.39-7.19 (m, 5H), 2.68 (bs, 1H), 1.30-1.24 (m, 2H), 1.08-1.02 (m, 2H).

Spectral data were consistent with literature¹

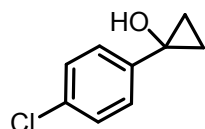
1-(4-fluorophenyl)cyclopropan-1-ol (1d)



$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.25-7.18 (m, 2H), 6.98-6.90 (m, 2H), 2.25 (s, 1H), 1.19-1.15 (m, 2H), 0.95-0.90 (m, 2H).

Spectral data were consistent with literature²

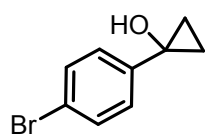
1-(4-chlorophenyl)cyclopropan-1-ol (1e)



$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.24-7.12 (m, 4H), 2.29 (s, 1H), 1.22-1.18 (m, 2H), 0.97-0.92 (m, 2H).

Spectral data were consistent with literature¹

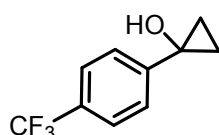
1-(4-bromophenyl)cyclopropan-1-ol (1f)



$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.39-7.34 (m, 2H), 7.12-7.07 (m, 2H), 2.25 (s, 1H), 1.23-1.18 (m, 2H), 0.97-0.93 (m, 2H).

Spectral data were consistent with literature²

1-(4-(trifluoromethyl)phenyl)cyclopropan-1-ol (1g)

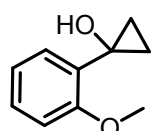


$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.59-7.55 (m, 2H), 7.39-7.36 (m, 2H), 2.44 (s, 1H), 1.38-1.34 (m, 2H), 1.13-1.08 (m, 2H).

$^{19}\text{F NMR}$ (376 MHz, CDCl_3): -62.37.

Spectral data were consistent with literature¹

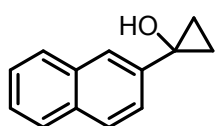
1-(2-methoxyphenyl)cyclopropan-1-ol (1h)



$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.30-7.19 (m, 2H), 6.94-6.88 (m, 2H), 3.94 (s, 3H), 3.59 (bs, 1H), 1.13-1.09 (m, 2H), 0.94-0.89 (m, 2H).

Spectral data were consistent with literature¹

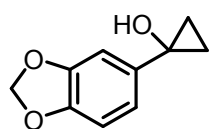
1-(naphthalen-2-yl)cyclopropan-1-ol (**1i**)



$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.87-7.77 (m, 4H), 7.52-7.42 (m, 2H), 7.32-7.26 (m, 1H), 2.51 (s, 1H), 1.34 (dd, $J = 4.2, 3.2$ Hz, 2H), 1.17 (dd, $J = 4.2, 3.2$ Hz, 2H).

Spectral data were consistent with literature¹

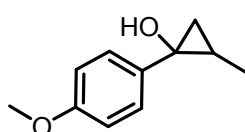
1-(benzo[d][1,3]dioxol-5-yl)cyclopropan-1-ol (**1j**)



$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 6.80-6.72 (m, 3H), 5.92 (s, 2H), 1.19-1.14 (m, 2H), 0.95-0.96 (m, 2H).

Spectral data were consistent with literature³

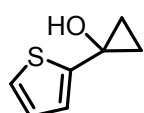
1-(4-methoxyphenyl)-2-methylcyclopropan-1-ol (**1l**)



$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.23-7.20 (m, 2H), 6.87-6.84 (m, 2H), 3.79 (s, 3H), 2.49 (bs, 1H), 1.32-1.39 (m, 3H), 1.18-1.10 (m, 2H), 0.76-0.72 (m, 1H).

Spectral data were consistent with literature⁴

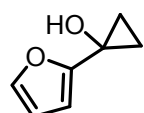
1-(thiophen-2-yl)cyclopropan-1-ol (**1o**)



$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.18 (dd, $J = 5.1, 1.3$ Hz, 1H), 6.94 (dd, $J = 5.1, 3.5$ Hz, 1H), 6.88 (dd, $J = 3.6, 1.3$ Hz, 1H), 2.61 (s, 1H), 1.32-1.28 (m, 2H), 1.09-1.05 (m, 2H).

Spectral data were consistent with literature¹

1-(furan-2-yl)cyclopropan-1-ol (**1p**)



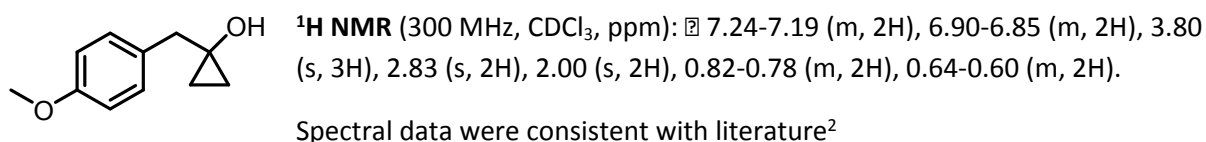
$^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ 7.29-7.26 (m, 1H), 6.30-6.28 (m, 1H), 6.20-6.18 (m, 1H), 3.23 (s, 1H), 1.12-1.09 (m, 2H), 1.06-1.03 (m, 2H).

Spectral data were consistent with literature²

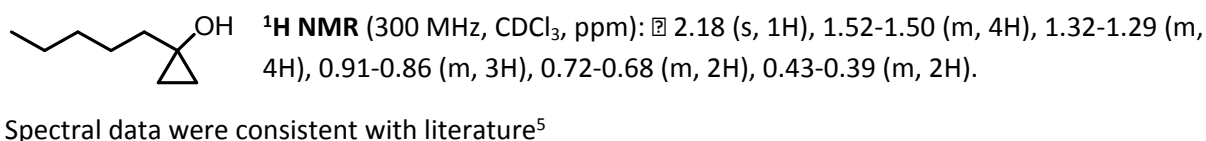
General Procedure B: Kulinkovich reaction

To an oven-dried round bottom flask (100 mL) equipped with a magnetic stir bar, the ester (10.0 mmol) was dissolved in dry diethyl ether (30 mL). $\text{Ti}(\text{i-PrO})_4$ (14.0 mmol, 1.4 equiv) was added to the solution and stirred for 2 min. Then ethylmagnesium bromide (28.0 mmol, 28 mL, 1.0 M in THF) was added dropwise to the solution over 2-3 h. The solution generally turned dark green. After stirring at room temperature for additional 30 min the reaction mixture was cooled with an ice bath and hydrolyzed by slow addition of cold 10% H_2SO_4 solution (50 mL) and then extracted with ether (3 x 40 mL). The combined organic layers were washed with saturated NaHCO_3 solution, brine and dried (Mg_2SO_4). After evaporation of solvent under reduced pressure the cyclopropanol products can be purified using distillation or column chromatography on silica gel. However, in most cases they are pure enough to be used directly in the next step. The following cyclopropanol products were synthesized using the procedure described above:

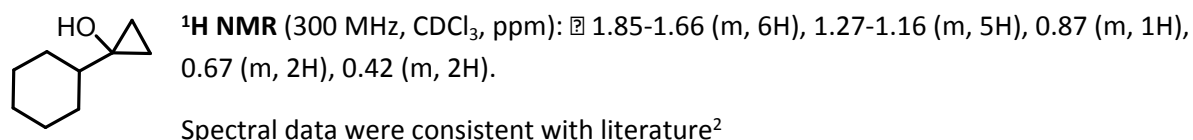
1-(4-methoxybenzyl)cyclopropan-1-ol (1k)



1-pentylcyclopropan-1-ol (1m)



1-cyclohexylcyclopropan-1-ol (1n)



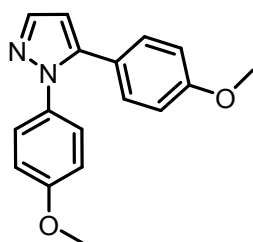
4 *General procedure for the synthesis of arenediazonium salts (C)*

The parent aniline (30 mmol) was dissolved in 32% aqueous tetrafluoroboric acid (12mL) at room temperature. Afterwards, an aqueous solution of sodium nitrite (30 mmol) in water (4 mL) was added dropwise at 0 °C over 5 min. The resulting mixture was stirred for 40 min and the precipitate was collected by filtration and re-dissolved in minimum amount of acetone. Then, diethyl ether was added until precipitation of diazonium tetrafluoroborate, which is filtered, washed several times with diethyl ether and dried in the air.

5 General procedure for the synthesis of *N*-aryl pyrazoles (D)

A vial was charged with Ru(bpy)₃Cl₂·6H₂O (18.5 μmol, 5 mol%), the corresponding cyclopropane-1-ol (0.37 mmol, 1 eq.) and the parent diazonium salt (0.56 mmol, 1.5 eq.). The vial was sealed and subsequently MeCN (5 mL) was added, and the reaction mixture was degassed, by purging with nitrogen over 10 min in dark. Light was switched on, and the reaction mixture was stirred at r.t. over 20 min. The reaction mixture was quenched with water (3 mL) and extracted with ethyl acetate (3 x 3 mL). The organic phase was separated and dried over Mg₂SO₄. Solids were filtered off and the volatiles were removed under reduced pressure to afford a viscous oil containing product. The crude product was further purified by column chromatography on silica gel using ethyl acetate/pentane (1:4) as eluent to afford the pure product.

1, 5-bis(4-methoxyphenyl)-1*H*-pyrazole (**3aa**)

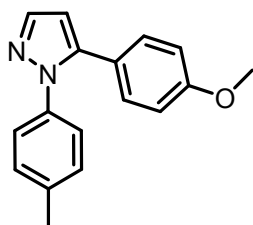


Following the general procedure D, **3aa** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a white solid (90.2 mg, 87% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.67 (d, *J* = 1.6 Hz, 1H), 7.11-7.25 (m, 4H), 6.79-6.89 (m, 4H), 6.43 (d, *J* = 1.9 Hz, 1H), 3.80 (s, 3H), 3.79 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 159.4, 158.7, 142.8, 139.8, 133.4, 130.0, 126.6, 123.0, 114.0, 113.9, 106.8, 55.5, 55.3.

GC-MS (EI) *m/z* (relative intensity): 280 (100) [M⁺], 281 (73), 265 (36).

Spectral data were consistent with literature.⁶

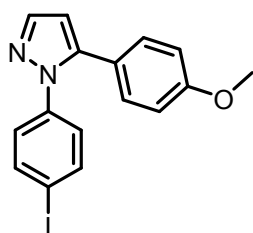
5-(4-methoxyphenyl)-1-(*p*-tolyl)-1*H*-pyrazole (**3ab**)



Following the general procedure D, **3ab** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a white solid (52.8 mg, 54% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.68 (d, *J* = 1.8 Hz, 1H), 7.20-7.11 (m, 6H), 6.85-6.80 (m, 2H), 6.43 (d, *J* = 1.9 Hz, 1H), 3.79 (s, 3H), 2.35 (s, 3H).

Spectral data were consistent with literature.⁷

1-(4-iodophenyl)-5-(4-methoxyphenyl)-1*H*-pyrazole (**3ac**)

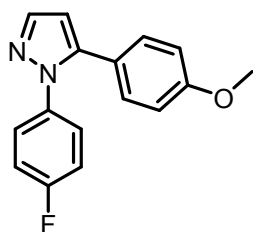


55.4.

Following the general procedure D, **3ac** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellowish solid (68.2 mg, 49% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.70 (d, *J* = 1.8 Hz, 1H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 1.8 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 159.8, 143.1, 140.7, 139.9, 138.1, 130.2, 126.8, 122.7, 114.2, 108.0, 92.4,

HRMS (EI): *m/z* = calcd. for C₁₆H₁₃IN₂O⁺: 376.0067, found: 376.0075.

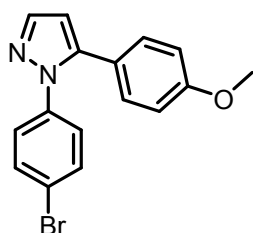
1-(4-fluorophenyl)-5-(4-methoxyphenyl)-1H-pyrazole (3ad)



Following the general procedure D, **3ad** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellowish solid (77.3 mg, 78% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.68 (d, *J* = 1.8 Hz, 1H), 7.26-7.30 (m, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 1.8 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 161.6, 159.7, 143.0, 140.3, 136.4, 130.1, 126.9, 122.7, 115.8, 114.0, 107.3, 55.4. ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -114.2 (s, 1F).

Spectral data were consistent with literature.⁶

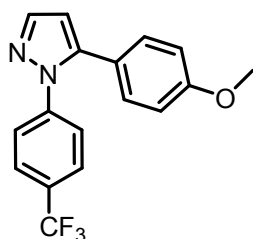
1-(4-bromophenyl)-5-(4-methoxyphenyl)-1H-pyrazole (3ae)



Following the general procedure D, **3ae** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellow solid (68.1 mg, 56% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.70 (d, *J* = 1.8 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.8 Hz, 2H), 7.14 (d, *J* = 8.9 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 1.8 Hz, 1H), 3.81 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 159.7, 143.0, 140.6, 139.2, 132.0, 130.1, 126.6, 122.7, 121.0, 114.1, 107.8, 55.4.

GC-MS (EI) *m/z* (relative intensity): 330 (28) [M⁺], 328 (46), 205 (21), 157 (23), 102 (75), 89 (62), 76 (95), 75 (100), 64 (83), 50 (78).

5-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)-1H-pyrazole (3af)

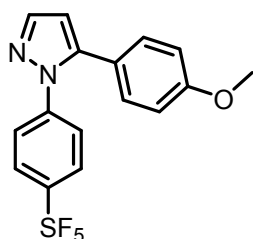


Following the general procedure D, **3af** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellowish solid (64.7 mg, 55% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.73 (d, *J* = 1.8 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.47 (d, *J* = 1.9 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 159.9, 143.2, 142.9, 141.1, 130.2, 129.0, 126.1, 124.8, 123.9, 122.5, 114.2, 108.4, 55.4. ¹⁹F NMR (376 MHz, CDCl₃, ppm) δ -62.9 (s, 3F).

GC-MS (EI) *m/z* (relative intensity): 318 (48) [M⁺], 145 (45), 102 (38), 69 (100), 63 (39).

Spectral data were consistent with literature.⁸

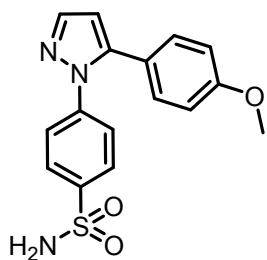
5-(4-Methoxyphenyl)-1-(4-(pentafluoro-sulfaneyl)phenyl)-1H-pyrazole (3ag)



Following the general procedure D, **3ag** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 95:5 to 9:1) as a yellow solid (94.5 mg, 68% yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.74 (d, *J* = 1.8 Hz, 1H), 7.71 (d, *J* = 9.0 Hz, 2H), 7.41 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.48 (d, *J* = 1.8 Hz, 1H), 3.84 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 160.1, 151.9, 143.4, 142.5, 141.4, 130.3, 126.9, 124.4, 122.5, 114.4, 108.8, 55.5. ¹⁹F NMR (282 MHz, CDCl₃, ppm): δ = 83.7 (quintet, *J* = 149.2 Hz, 1F), 62.8 (d, *J* = 149.2 Hz).

HRMS (EI): *m/z* = calcd. for C₁₆H₁₃F₅N₂OS⁺: 376.0663, found: 376.0661.

4-(5-(4-methoxyphenyl)-1H-pyrazol-1-yl)benzenesulfonamide (**3ah**)

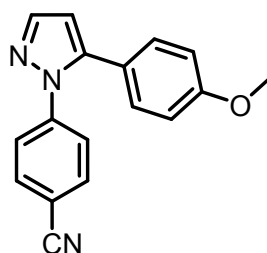


Following the general procedure D, **3ah** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 8:2 to 6:4) as a white solid (85.3 mg, 70% yield). ¹H-NMR (300 MHz, MeOD, ppm) δ: 7.97-7.86 (m, 2H), 7.77 (d, *J* = 1.8 Hz, 1H), 7.48-7.40 (m, 2H), 7.23-7.15 (m, 2H), 6.95-6.87 (m, 2H), 6.57 (d, *J* = 1.8 Hz, 1H), 3.81 (s, 3H). ¹³C NMR (75 MHz, MeOD, ppm): δ = 160.2, 143.8, 142.7, 142.6, 140.7, 129.9, 126.8, 125.3, 122.4, 113.9, 107.7, 54.4.

HRMS (ESI): *m/z* = calcd. for C₁₆H₁₂Cl₃N₂O [M-H]⁺: 330.0912, found: 330.0913.

M.p.: 185-190 °C

4-(5-(4-methoxyphenyl)-1H-pyrazol-1-yl)benzonitrile (**3ai**)

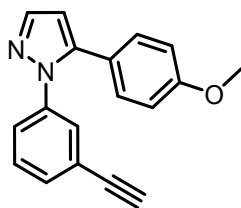


Following the general procedure D, **3ai** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellow-orange solid (78.3 mg, 77% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.74 (d, *J* = 1.74 Hz, 1H), 7.60 (m, 2H), 7.42 (m, 2H), 7.14 (m, 2H), 6.87 (m, 2H), 6.46 (d, *J* = 1.77 Hz, 1H), 3.82 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 160.0, 143.11, 143.3, 141.5, 132.9, 130.1, 124.9, 122.3, 118.3, 114.3, 110.4, 108.9, 55.4.

HRMS (ESI): *m/z* = calcd. for C₁₇H₁₄N₃O [M-H]⁺: 276.1131, found: 276.1123.

M.p.: 81-87 °C

1-(3-ethynylphenyl)-5-(4-methoxyphenyl)-1H-pyrazole (**3aj**)

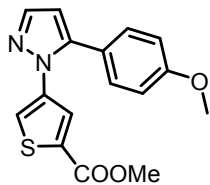


Following the general procedure D, **3aj** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellow oil (35.5 mg, 35% yield). ¹H-NMR (300 MHz, CDCl₃, ppm): δ = 7.62 (d, *J* = 1.8 Hz, 1H), 7.47 (t, *J* = 1.9 Hz, 1H), 7.34 (dt, *J* = 7.4, 1.6 Hz, 1H), 7.21-7.05 (m, 5 H), 6.80-6.75 (m, 2H), 6.37 (d, *J* = 1.8 Hz, 1H), 3.73 (s, 3H), 2.99 (s, 1H). ¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 159.8, 143.1, 140.7, 140.4, 131.1, 130.2, 128.9, 128.8, 125.8, 123.2,

122.8, 114.2, 107.7, 82.7, 78.2, 55.43.

HRMS (ESI): *m/z* = calcd. for C₁₈H₁₅N₂O [M-H]⁺: 275.1184, found: 275.1174.

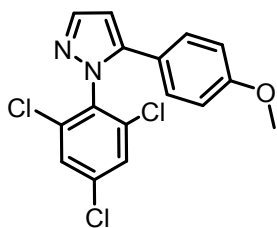
Methyl 3-(5-(4-methoxyphenyl)-1H-pyrazol-1-yl) thiophene-2-carboxylate (**3ak**)



Following the general procedure D, **3ak** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellowish solid (46.5 mg, 40% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.74 (d, *J* = 1.9 Hz, 1H), 7.53 (d, *J* = 5.2 Hz, 1H), 7.15 (d, *J* = 5.2 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.47 (d, *J* = 1.9 Hz, 1H), 3.78 (s, 3H), 3.61 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 160.5, 159.7, 145.3, 141.6, 140.7, 130.3, 129.4, 128.4, 126.9, 122.6, 113.9, 106.0, 55.4, 52.3.

HRMS (ESI): *m/z* = calcd. for C₁₆H₁₄N₂O₃S+•: 314.0720, found: 314.0716.

5-(4-methoxyphenyl)-1-(2,4,6-trichlorophenyl)-1H-pyrazole (3al)

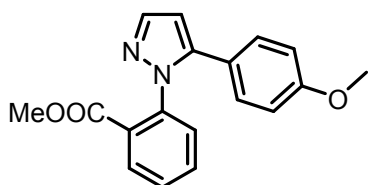


Following the general procedure D, **3al** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as an orange gum (65.4 mg, 50% yield). $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ = 7.81 (d, J = 1.83 Hz, 1H), 7.40 (s, 2H), 7.16 (m, 2H), 6.82 (m, 2H), 6.50 (d, J = 1.86 Hz, 1H), 3.78 (s, 3H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm): δ = 159.6, 145.47, 141.5, 135.9, 135.8, 129.1, 128.7, 121.9, 114.3, 105.9, 55.2.

HRMS (ESI): m/z = calcd. for $\text{C}_{16}\text{H}_{12}\text{Cl}_3\text{N}_2\text{O}$ $[\text{M}-\text{H}]^+$: 353.0015, found: 353.0025.

Methyl-2-(5-(4-methoxyphenyl)-1H-pyrazol-1-yl) benzoate (3am)



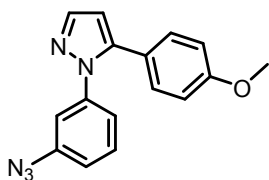
Following the general procedure D, **3am** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellow gum (76.5 mg, 67% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ = 7.85 (dd, J = 7.7, 1.6 Hz, 1H), 7.70 (d, J = 1.8 Hz, 1H), 7.50 (dt, J = 7.7, 1.7 Hz, 1H), 7.43 (dt, J = 7.6, 1.3 Hz, 1H), 7.30 (dd, J = 7.8, 1.2 Hz, 1H),

7.10 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 6.45 (d, J = 1.9 Hz, 1H), 3.76 (s, 3H), 3.63 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm): δ = 166.1, 159.5, 144.1, 140.2, 139.6, 132.2, 130.7, 132.6, 130.7, 129.8, 128.7, 128.4, 122.5, 113.9, 106.2, 55.4, 52.2.

HRMS (ESI): m/z = calcd. for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_3$ $[\text{M}-\text{H}]^+$: 309.1234, found: 309.1234.

1-(2-Azidophenyl)-5-(4-methoxyphenyl)-1H-pyrazole (3an)

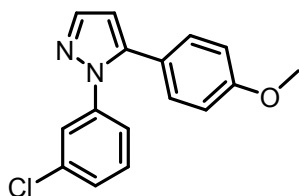


Following the general procedure D, **3an** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a white solid (62.3 mg, 58% yield). $^1\text{H NMR}$ (300 MHz, CDCl_3 , ppm): δ = 7.75 (d, J = 1.9 Hz, 1H), 7.42 (dt, J = 7.7, 1.6 Hz, 1H), 7.36-7.30 (m, 1H), 7.21-7.14 (m, 2H), 7.13 (d, J = 8.9 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 6.50 (d, J = 1.9 Hz, 1H), 3.84 (s, 3H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3 , ppm): δ = 159.6, 145.0, 140.8, 137.2, 131.7, 130.3, 129.9, 129.4, 125.3, 122.6, 119.8, 114.0, 106.0, 55.4.

HRMS (ESI): m/z = calcd. for $\text{C}_{16}\text{H}_{14}\text{N}_5\text{O}$ $[\text{M}-\text{H}]^+$: 292.1198, found: 292.1209.

1-(3-chlorophenyl)-5-(4-methoxyphenyl)-1H-pyrazole (3ao)

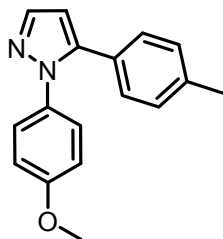


Following the general procedure D, **3ao** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellow solid (61.1 mg, 58% yield). $^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm): δ = 7.70 (d, J = 1.8 Hz, 1H), 7.43 (t, J = 1.8 Hz, 1H), 7.08-7.28 (m, 4H), 6.85 (d, J = 8.9 Hz, 2H), 6.44 (d, J = 1.8 Hz, 1H), 3.81 (s, 3H), 2.35 (s, 3H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm): δ = 159.8, 143.1, 141.1, 140.6, 134.6, 130.1, 129.8, 127.5, 125.3, 123.2, 122.5, 114.1, 107.9, 55.3.

GC-MS (EI) m/z (relative intensity): 284 (53) $[\text{M}^+]$, 111 (53), 102 (45), 89 (40), 76 (41), 75 (100), 62 (55), 51 (30).

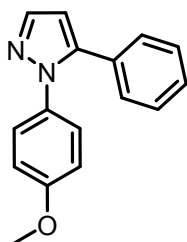
1-(4-methoxyphenyl)-5-(*p*-tolyl)-1*H*-pyrazole (**3ba**)



Following the general procedure D, **3ba** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a white solid (50.7 mg, 52% yield). ¹H-NMR (300 MHz, CDCl₃, ppm) δ: 7.68 (d, *J* = 1.8 Hz, 1H), 7.23–7.22 (m, 2H), 7.11–7.10 (m, 4H), 6.86–6.84 (m, 2H), 6.46 (d, *J* = 1.8 Hz, 1H), 3.81 (s, 3H), 2.34 (s, 3H).

Spectral data were consistent with literature.⁶

1-(4-methoxyphenyl)-5-phenyl-1*H*-pyrazole (**3ca**)

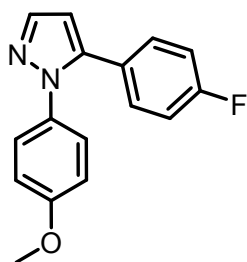


Following the general procedure D, **3ca** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a white solid (33.1 mg, 36% yield). ¹H-NMR (300 MHz, CDCl₃, ppm) δ: 7.61 (d, *J* = 1.8 Hz, 1H), 7.24–7.21 (m, 7H), 6.80–6.76 (m, 2H), 6.42 (d, *J* = 1.9 Hz, 1H), 3.73 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃, ppm) δ: 158.9, 143.0, 140.0, 133.6, 130.8, 128.8, 128.5, 128.2, 126.7, 114.2, 107.4, 55.6.

Spectral data were consistent with literature.⁶

5-(4-fluorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrazole (**3da**)

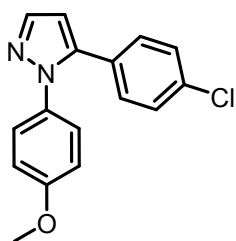


Following the general procedure D, **3da** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellowish solid (25.6 mg, 26% yield). ¹H-NMR (300 MHz, CDCl₃, ppm) δ: 7.68 (d, *J* = 1.9 Hz, 1H), 7.26–7.16 (m, 4H), 7.02–6.95 (m, 2H), 6.88–6.83 (m, 2H), 6.46 (d, *J* = 1.9 Hz, 1H), 3.81 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 164.1, 160.8, 158.9, 141.9, 139.9, 133.2, 130.5, 130.4, 126.8, 126.7, 126.6, 115.7, 115.4, 114.1, 107.2, 55.5. ¹⁹F-NMR (376.5 MHz, CDCl₃, ppm) δ: -113.12 (m, 1F)

HRMS (ESI): *m/z* = calcd. for C₁₆H₁₄FN₂O [M-H]⁺: 269.1090, found: 269.1110.

M.p.: 78–80 °C

5-(4-chlorophenyl)-1-(4-methoxyphenyl)-1*H*-pyrazole (**3ea**)



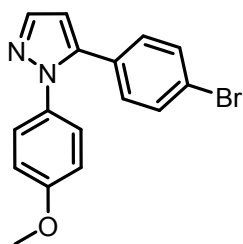
Following the general procedure D, **3ea** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellow solid (28.5 mg, 27% yield). ¹H-NMR (300 MHz, CDCl₃, ppm) δ: 7.61 (d, *J* = 1.9 Hz, 1H), 7.21–7.06 (m, 6H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.41 (d, *J* = 1.9 Hz, 1H), 3.74 (s, 3H).

¹³C-NMR (100.6 MHz, CDCl₃, ppm) δ: 159.1, 141.9, 140.1, 134.3, 133.2, 130.0, 129.2, 128.8, 126.8, 114.3, 107.5, 60.5, 55.6.

HRMS (ESI): *m/z* = calcd. for C₁₆H₁₄ClN₂O [M-H]⁺: 285.0789, found: 285.0775.

M.p.: 103–105 °C

5-(4-bromophenyl)-1-(4-methoxyphenyl)-1H-pyrazole (3fa)

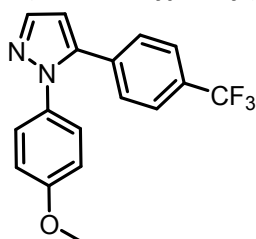


Following the general procedure D, **3fa** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellow solid (11.0 mg, 9% yield). ¹H-NMR (300 MHz, CDCl₃, ppm) δ: 7.68 (d, *J* = 1.9 Hz, 1H), 7.45–7.40 (m, 2H), 7.22–7.17 (m, 2H), 7.11–7.07 (m, 2H), 6.90–6.84 (m, 2H), 6.49 (d, *J* = 1.9 Hz, 1H), 3.82 (s, 3H). ¹³C-NMR (100.6 MHz, CDCl₃, ppm) δ: 159.1, 141.9, 140.2, 131.8, 130.3, 129.7, 126.8, 122.5, 114.4, 107.5, 55.6.

HRMS (ESI): *m/z* = calcd. for C₁₆H₁₄BrN₂O [M-H]⁺: 329.0290, found: 329.0291.

M.p.: 107-110 °C

1-(4-methoxyphenyl)-5-(4-(trifluoromethyl) phenyl)-1H-pyrazole (3ga)



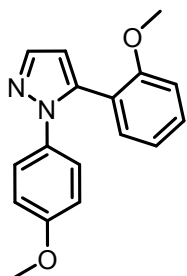
Following the general procedure D, **3ga** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellow solid (9.5 mg, 8% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.71 (d, *J* = 1.8 Hz, 1H), 7.57-7.54 (m, 2H), 7.39-7.32 (m, 2H), 7.23-7.18 (m, 2H), 6.91-6.85 (m, 2H), 6.55 (d, *J* = 1.8 Hz, 1H), 3.83 (s, 3H).

¹³C NMR (75 MHz, CDCl₃, ppm): δ = 160.0, 143.1, 143.3, 141.5, 132.9, 130.1, 124.9, 122.3, 118.3, 114.3, 110.4, 108.9, 55.4.

HRMS (ESI): *m/z* = calcd. for C₁₇H₁₄F₃N₂O [M-H]⁺: 319.1058, found: 319.1061.

Spectral data were consistent with literature.⁶

5-(2-methoxyphenyl)-1-(4-methoxyphenyl)-1H-pyrazole (3ha)

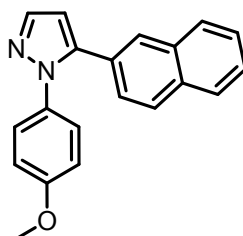


Following the general procedure D, **3ha** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a white solid (26.0 mg, 25% yield). ¹H-NMR (300 MHz, CDCl₃, ppm) δ: 7.63 (d, *J* = 1.8 Hz, 1H), 7.28–7.22 (m, 1H), 7.19–7.16 (m, 1H), 7.13–7.08 (m, 2H), 6.88 (td, *J* = 7.5, 1.1 Hz, 1H), 6.75–6.70 (m, 3H), 6.37 (d, *J* = 1.8 Hz, 1H), 3.70 (s, 3H), 3.38 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃, ppm) δ: 158.4, 156.7, 139.6, 134.5, 131.3, 130.2, 125.1, 120.6, 120.2, 113.6, 111.2, 108.3, 55.4, 55.0.

HRMS (ESI): *m/z* = calcd. for C₁₇H₁₇N₂O₂ [M-H]⁺: 281.1285, found: 281.1279.

M.p.: 65-68 °C

1-(4-methoxyphenyl)-5-(naphthalen-2-yl)-1H-pyrazole (3ia)

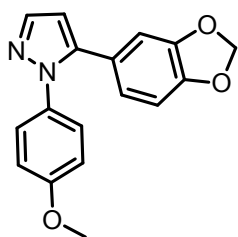


Following the general procedure D, **3ia** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 95:5 to 9:1) as a white solid (66.6 mg, 60% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.84-7.74 (m, 5H), 7.53-7.49 (m, 2H), 7.30-7.25 (m, 3H), 6.88-6.83 (m, 2H), 6.62 (d, *J* = 1.92 Hz, 1H), 3.81 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 158.8, 142.9, 140.1, 133.5, 133.1, 132.7, 128.2, 128.1, 128.0, 127.9, 127.7, 126.6, 126.5, 126.3, 114.1, 107.7, 55.5.

HRMS (ESI): *m/z* = calcd. for C₂₀H₁₇N₂O [M-H]⁺: 301.1341, found: 301.1333.

M.p.: 111-114 °C

5-(benzo[d]-1,3-dioxol-5-yl)-1-(4-methoxyphenyl)-1H-pyrazole (3ja)

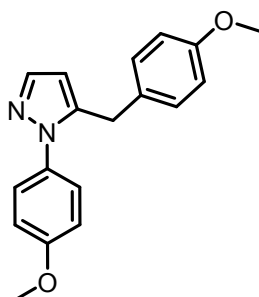


Following the general procedure D, **3ja** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a white solid (64.2 mg, 59% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.65 (d, *J* = 1.94 Hz, 1H), 7.24-7.21 (m, 2H), 6.88-6.85 (m, 2H), 6.76-6.68 (m, 3H), 6.41 (d, *J* = 1.92 Hz, 1H), 5.96 (s, 2H), 3.82 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 158.8, 142.9, 140.1, 133.5, 133.1, 132.7, 128.2, 128.1, 128.0, 127.9, 127.7, 126.6, 126.5, 126.3, 114.1, 107.7, 55.5.

HRMS (ESI): *m/z* = calcd. for C₁₇H₁₅N₂O₃ [M-H]⁺: 295.1083, found: 295.1074.

M.p.: 85-88 °C

5-(4-methoxybenzyl)-1-(4-methoxyphenyl)-1H-pyrazole (3ka)

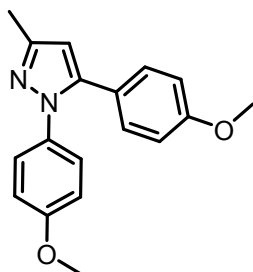


Following the general procedure D, **3ka** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as an orange gum (27.4 mg, 25% yield). ¹H-NMR (300 MHz, CDCl₃, ppm) δ: 7.49 (d, *J* = 1.8 Hz, 1H), 7.20-7.17 (m, 2H), 6.95-6.90 (m, 2H), 6.87-6.82 (m, 2H), 6.75-6.70 (m, 2H), 3.82 (s, 2H), 3.76 (s, 3H), 3.70 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃, ppm) δ: 159.2, 158.3, 142.5, 139.5, 132.9, 130.3, 129.5, 126.9, 114.1, 113.9, 106.5, 55.5, 55.3.

HRMS (ESI): *m/z* = calcd. for C₁₈H₁₉N₂O₂ [M-H]⁺: 295.1447, found: 295.1444.

1,5-bis(4-methoxyphenyl)-3-methyl-1H-pyrazole (3la)

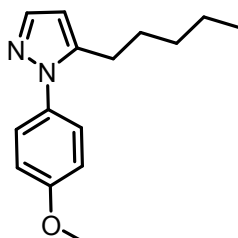


Following the general procedure D, **3la** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a white solid (98.1 mg, 90% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.20-7.11 (m, 4H), 6.84-6.79 (m, 4H), 6.22 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 2.36 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 159.3, 158.5, 148.9, 143.5, 133.6, 129.8, 126.6, 123.2, 114.0, 113.8, 106.6, 55.4, 55.2, 13.6.

HRMS (ESI): *m/z* = calcd. for C₁₈H₁₉N₂O₂ [M-H]⁺: 295.1441, found: 295.1449.

M.p.: 85-89°C

1-(4-methoxyphenyl)-5-pentyl-1H-pyrazole (3ma)

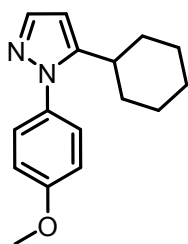


Following the general procedure D, **3ma** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellowish oil (22.7 mg, 25% yield). ¹H-NMR (300 MHz, CDCl₃, ppm) δ: 7.55(d, *J* = 1.8 Hz, 1H), 7.35-7.28 (m, 2H), 7.01-6.93 (m, 2H), 6.17 (d, *J* = 1.8 Hz, 1H), 3.85 (s, 3H), 2.61-2.55 (m, 2H), 1.59-1.54 (m, 2H), 1.30-1.22 (m, 4H), 0.87-0.83 (m, 3H).

¹³C NMR (75 MHz, CDCl₃, ppm): δ = 159.1, 143.9, 139.4, 133.5, 126.9, 114.2, 104.8, 55.5, 31.4, 29.7, 28.5, 26.1, 22.3, 13.9.

HRMS (ESI): *m/z* = calcd. for C₁₅H₂₀N₂O [M-H]⁺: 245.1654, found: 245.1662.

1-(4-methoxyphenyl)-5-cyclohexyl-1H-pyrazole (3na)



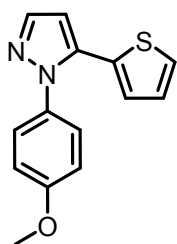
29.9, 26.4, 26.0.

Following the general procedure D, **3na** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a white solid (11.5 mg, 12% yield). ¹H-NMR (300 MHz, CDCl₃, ppm) δ: 7.55 (d, *J* = 1.9 Hz, 1H), 7.33–7.26 (m, 2H), 7.00–6.95 (m, 2H), 6.17 (d, *J* = 1.9 Hz, 1H), 3.86 (s, 3H), 2.59 (tt, *J* = 11.7, 3.4 Hz, 1H), 1.94–1.65 (m, 7H), 1.42–1.17 (m, 10H), 0.90–0.83 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃, ppm) δ: 159.4, 149.6, 139.6, 133.2, 127.3, 114.3, 103.0, 55.7, 35.3, 33.6,

HRMS (ESI): *m/z* = calcd. for C₁₆H₂₁N₂O [M-H]⁺: 257.1654, found: 257.1654.

M.p.: 53-55°C

1-(4-methoxyphenyl)-5-(thiophen-2-yl)-1H-pyrazole (3oa)



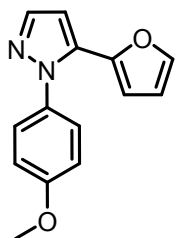
114.2, 106.9, 55.5.

Following the general procedure D, **3oa** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a dark yellow solid (20.9 mg, 22% yield). ¹H-NMR (300 MHz, CDCl₃, ppm) δ: 7.65 (d, *J* = 1.9 Hz, 1H), 7.33–7.28 (m, 2H), 7.25 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.95–6.93 (m, 2H), 6.92–6.90 (m, 1H), 6.83 (dd, *J* = 3.6 Hz, 1.2 Hz, 1H), 6.55 (d, *J* = 1.9 Hz, 1H), 3.95 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃, ppm) δ: 159.7, 139.9, 137.1, 132.9, 131.6, 127.7, 127.5, 127.3, 126.9, 126.3, 123.6,

HRMS (ESI): *m/z* = calcd. for C₁₄H₁₃N₂OS [M-H]⁺: 257.0749, found: 257.0753.

M.p.: 81-87 °C

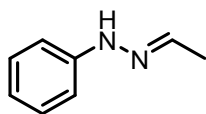
5-(furan-2-yl)-1-(4-methoxyphenyl)-1H-pyrazole (3pa)



Following the general procedure D, **3pa** was isolated by flash chromatography on silica (gradient: pentane/EtOAc, from 9:1 to 8:2) as a yellow gum (17.9 mg, 20% yield). ¹H NMR (300 MHz, CDCl₃, ppm): δ = 7.65 (d, *J* = 1.8 Hz, 1H), 7.38 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.34-7.30 (m, 2H), 6.97-6.93 (m, 2H), 6.65 (d, *J* = 1.8 Hz, 1H), 6.31 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.88 (dd, *J* = 3.5, 0.7 Hz, 1H), 3.86 (s, 3H). ¹³C NMR (75 MHz, CDCl₃, ppm): δ = 159.6, 144.7, 142.4, 139.9, 134.6, 133.3, 127.4, 114.2, 111.2, 108.4, 105.4, 55.6. **HRMS (ESI):** *m/z* = calcd. for C₁₄H₁₃N₂O₂ [M-H]⁺: 241.0972, found: 241.0974.

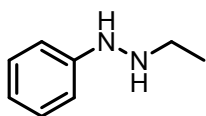
6 Synthesis of the diazene model compound (5)

Acetaldehyde phenylhydrazone (S1)



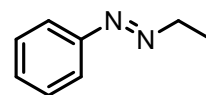
Acetaldehyde (7.6 mL, 6.0 g, 0.14 mol) was dissolved in aqueous ethanol, prepared by mixing ethanol (24 mL) and water (4 mL), and the reaction mixture was placed in ice-water cooling bath. Phenylhydrazine (10.9 mL, 12.0 g, 0.11 mol) was added in portions. Evolution of heat was observed after addition of each portion, and reaction mixture was let to cool before adding further phenylhydrazine to the reaction. After addition was finished, crystallization of product occurred, and after stirring the reaction mixture for further 1 h, crystals were filtered off and washed with small amount of aqueous ethanol. Product was obtained as oil, which solidified on standing at room temperature (8.6 g, 58%), that was according to NMR analysis a mixture of E- and Z- isomers. Solid was used without further separation in the next step.

2-ethyl-1-phenylhydrazine (S2)



Dry, argon flushed, flask was charged with lithium aluminum hydride (1.14 g, 30 mmol), to which dry THF (20 mL) was added, and the reaction mixture was stirred for 10 min under argon. Reaction mixture was then cooled to 5 °C by an ice-water cooling bath, and the solution of acetaldehyde phenylhydrazone (mixture of isomers, 4.03 g, 30 mmol) in dry THF (10 mL) was added dropwise to the well-stirred reaction mixture. After the addition was complete, the reaction was stirred for further 20 min at 5 °C, after which the cooling bath was removed. Reaction mixture was then heated up to reflux, stirred for 40 min, and then let to cool to room temperature. Flask with the reaction mixture was then placed in an ice-water cooling bath, and diethylether saturated with water (15 mL) was carefully added. The white aluminum salts were filtered off on frit and washed several times with diethylether. Combined organic fractions were concentrated on rotary evaporator, and the residue was subjected to vacuum distillation. Fraction containing the product distilled off between 74 °C – 77 °C at 3 mbar. Product was collected as colorless oil (1.4 g, 34%), that was unstable on air, and progressively darkened when stored at room temperature.¹**¹H NMR** (300 MHz, CDCl₃, ppm): δ 1.05 (t, $J = 7.3$ Hz, 3H), 2.83 (q, $J = 7.1$ Hz, 2H), 4.97 (bs, 2H), 6.78 (tt, $J = 7.4$ Hz, $J = 1.1$ Hz, 1H), 6.78-6.81 (m, 2H), 7.10-7.16 (m, 2 H). Spectral data were consistent with literature¹⁰

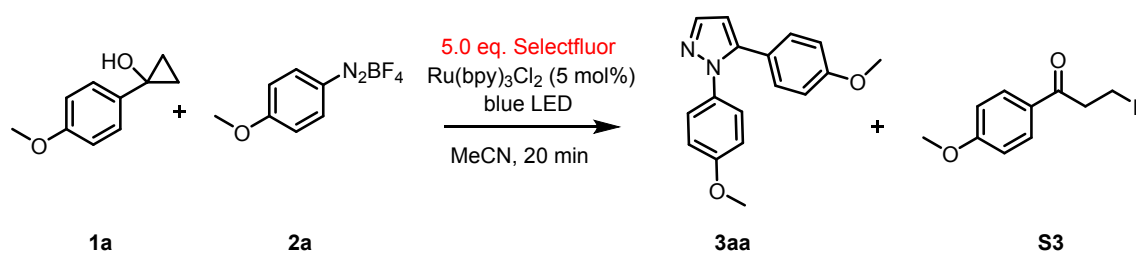
2-ethyl-1-phenyldiazene (5)



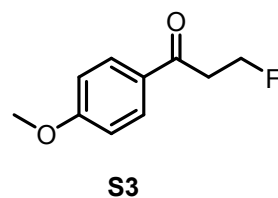
2-ethyl-1-phenylhydrazine (108 mg, 0.78 mmol) was dissolved in 1 M aqueous sulfuric acid (3 mL) at room temperature. Iron (III) sulfate hydrate (400 mg) was added in single portion, and the reaction mixture was stirred under argon for 30 min. Iron salts dissolved over this period. The reaction mixture was extracted with diethylether (10 mL), and the organic fraction was washed with saturated aqueous sodium bicarbonate (10 mL), water (10 mL) and brine (10 mL), before it was dried over sodium sulfate. Solids were filtered off and solvent was evaporated in vacuo to obtain product (97 mg, 93%) as quickly yellowing oil. Sample was used immediately to measure cyclic voltammetry. Compound quickly deteriorates at ambient conditions, with main decomposition product being the acetaldehyde phenylhydrazone, which could be seen on the ¹H NMR spectra measured within 1 h of the synthesis of the diazene compound.

¹H NMR (300 MHz, CDCl₃, ppm): δ 1.46 (t, $J = 7.4$ Hz, 3H), 4.11 (q, $J = 7.4$ Hz, 2H), 4.97 (bs, 2H), 7.41-7.50 (m, 3H), 7.65-7.70 (m, 2 H). Spectral data were consistent with literature¹¹

7 Radical scavenger experiments



A vial was charged with Ru(bpy)₃Cl₂·6H₂O (18.5 μmol, 5 mol%), 1-(4-methoxyphenyl)cyclopropane-1-ol (0.37 mmol, 1 eq.) the parent diazonium salt (0.56 mmol, 1.5 eq.), and the radical scavenger (Selectfluor, 1.85 mmol, 5.0 equiv.). The vial was sealed and subsequently MeCN (5 mL) was added, and the reaction mixture was degassed, by purging with nitrogen over 10 min in dark. Light was switched on, and the reaction mixture was stirred at r.t. over 20 min. The reaction mixture was quenched with water (3 mL) and extracted with ethyl acetate (3 x 3 mL). The organic phase was separated and dried over MgSO₄. Solids were filtered off and the volatiles were removed under reduced pressure to afford a viscous oil containing product. The crude product was purified by column chromatography on silica gel. The conversion of **1a** was 56%, the yield of **3aa** and **S3** were respectively of 35% (35.9 mg) and 22% (15 mg). ¹H NMR (300 MHz, CDCl₃, ppm): δ 7.98-7.91 (m, 2H), 6.97-6.92 (m, 2H), 4.95 (t, J = 6.1 Hz, 1H), 4.83 (t, J = 6.1 Hz, 1H), 3.87 (s, 3H), 3.36 (t, J = 6.1 Hz, 1H), 3.30 (t, J = 6.1 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃, ppm): δ -220.76 /-221.16 (m, 1F).⁹



-220.6983
-220.9368
-220.9789
-221.0595
-221.1020
-221.1415

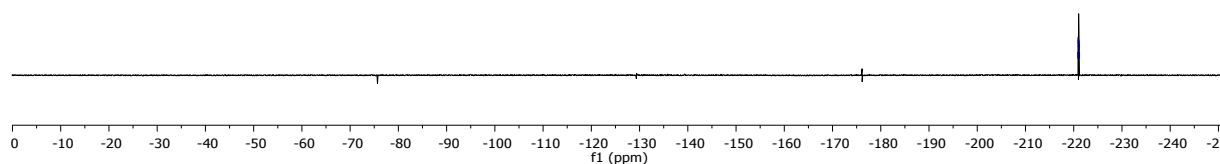
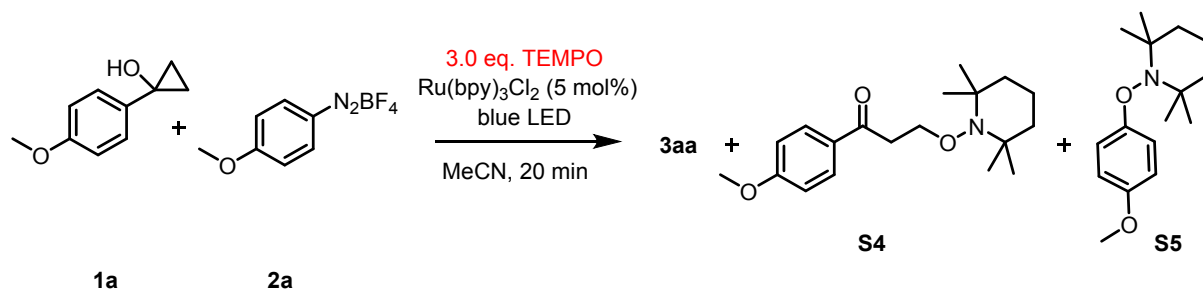
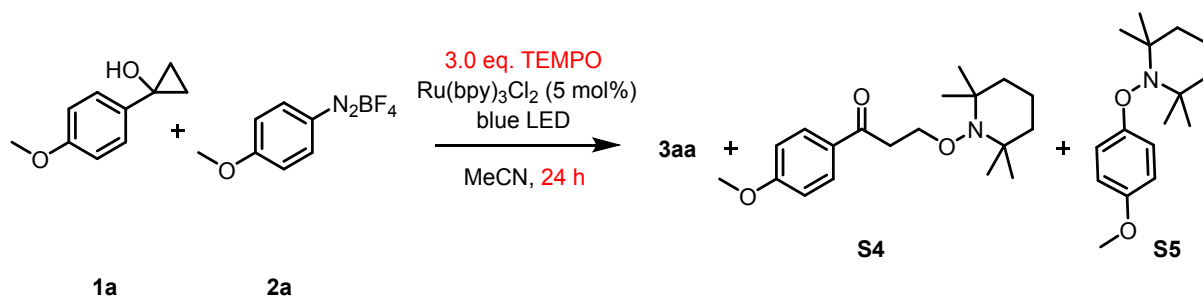


Figure S1. ¹⁹F NMR (376 MHz, CDCl₃, ppm): of 3-fluoro-1-(4-methoxyphenyl)propan-1-one isolated from the reaction with Selectfluor.



Following the same procedure as above except 2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) (174.3 mg, 1.11 mmol, 3.0 eq.) was added instead of Selectfluor, the reaction afforded **3aa** < 10%, the products **S4** and **S5** were not detected by GC/MS.



Following the same procedure as above except 2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) (174.3 mg, 1.11 mmol, 3.0 eq.) was added and the reaction time was extended to 24 h, the reaction afforded **3aa** < 10%, the product **S4** was not detected and **S5** was detected by GC/MS.

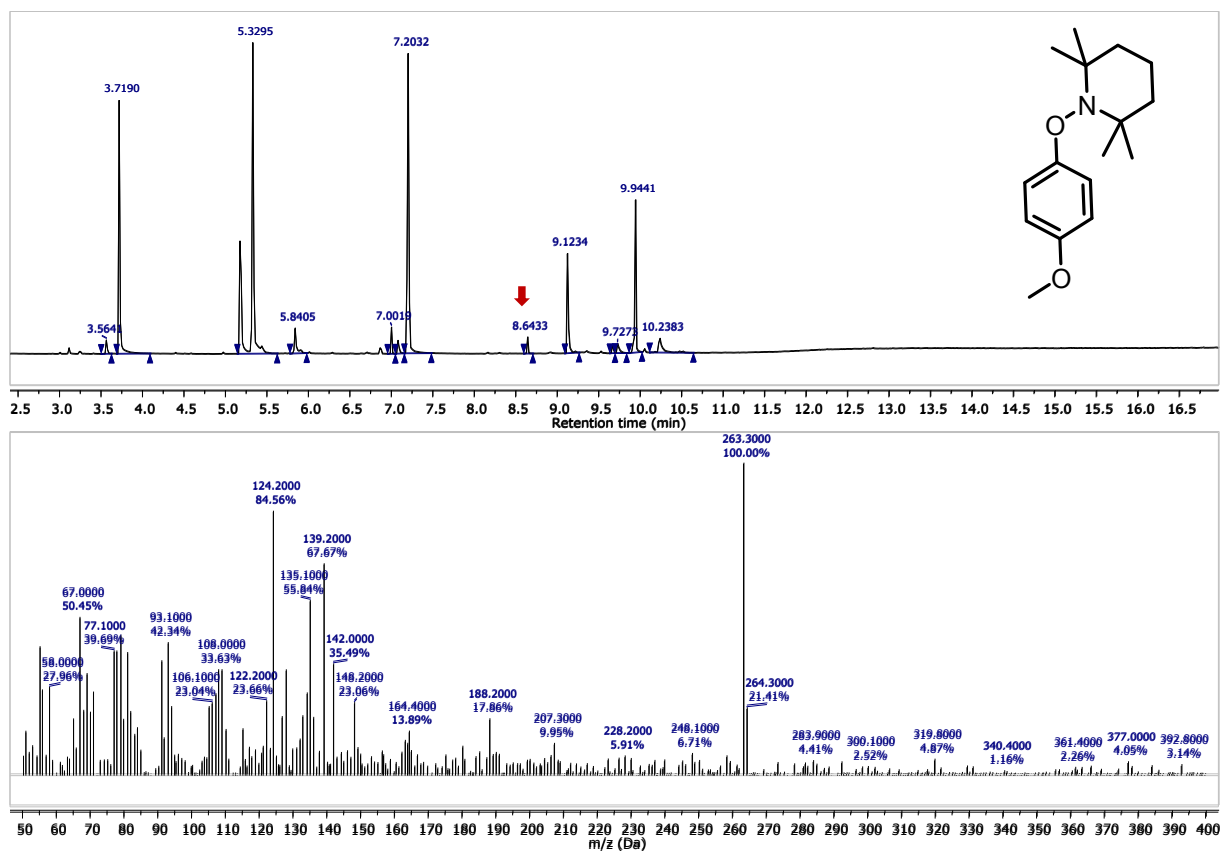


Figure S2. GC-MS of crude reaction mixture after 24 h in presence of 3.0 eq. TEMPO.

8 Redox properties

Experimental procedure for cyclic voltammetry

The experiments were carried out in a conventional three electrode cell using a Parstat 4000 (Ametek, Berwin, USA). A glassy carbon disc (diameter: 1.6 mm) served as the working electrode and a platinum wire as counter electrode. The glassy carbon disc was polished using polishing alumina (0.05 μm) prior to each experiment. As reference a Ag/AgNO₃ electrode (silver wire in 0.1 M NBu₄ClO₄/CH₃CN solution; c(AgNO₃) = 0.01 M; $E_0 = -87$ mV vs. the ferrocene redox couple) was used and this compartment was separated from the rest of the cell with a Vycor frit. As a solvent, anhydrous acetonitrile (Sigma-Aldrich) stored over molecular sieves was used. Tetrabutylammonium hexafluorophosphate was used as a conductive salt to obtain final electrolyte concentration of 100 mmol/L. Analyzed samples were dissolved in electrolyte solution in concentrations of 1-5 mmol/l. Electrochemical cell was dried in oven prior to each experiment, flushed with argon and charged with 4 ml of electrolyte/analyte solution. The electrolyte solution containing analyte was then degassed with a stream of argon for at least five minutes prior to recording. Measurements were performed at scan rate of 100 mV/s. Thermodynamic redox potentials were approximated as the half-wave experimental potential. Redox properties of the photocatalyst in acetonitrile were taken from literature.¹²

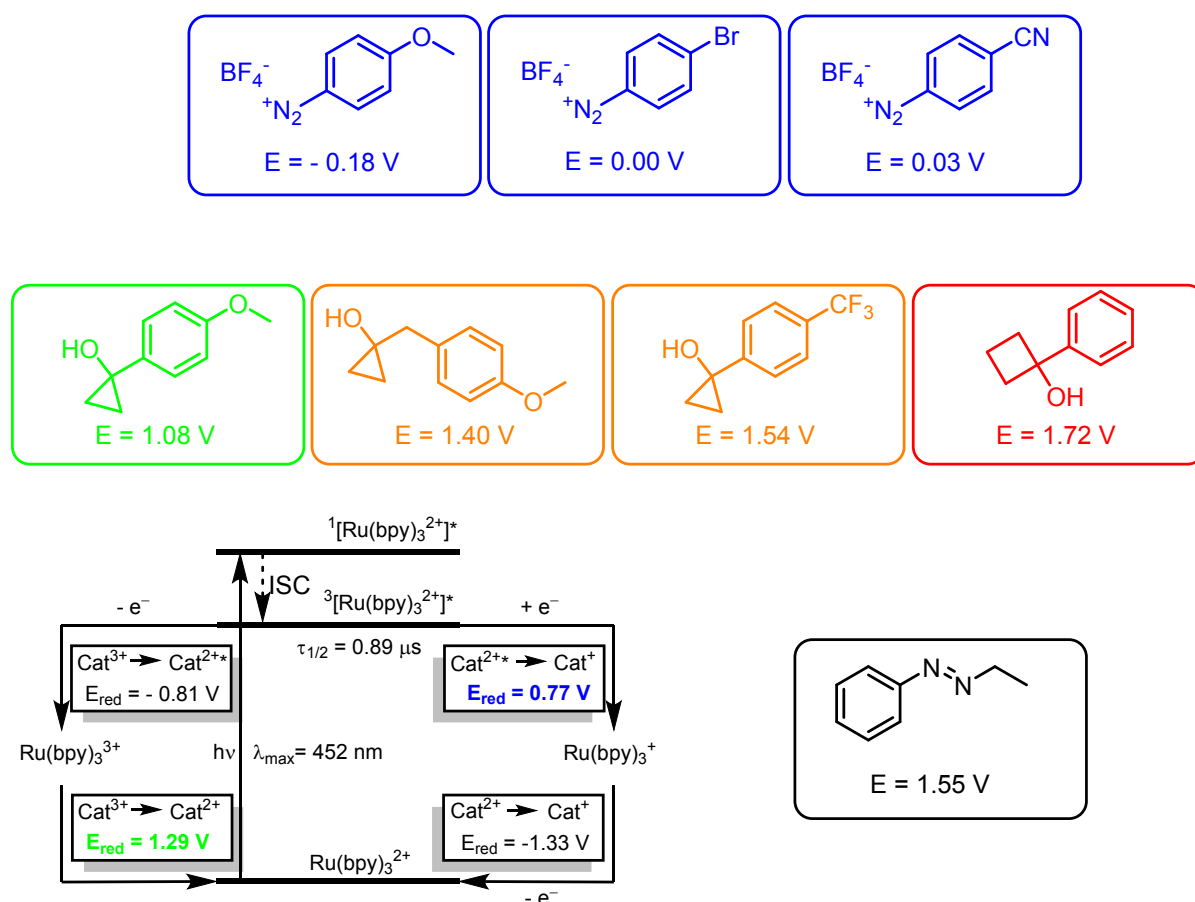
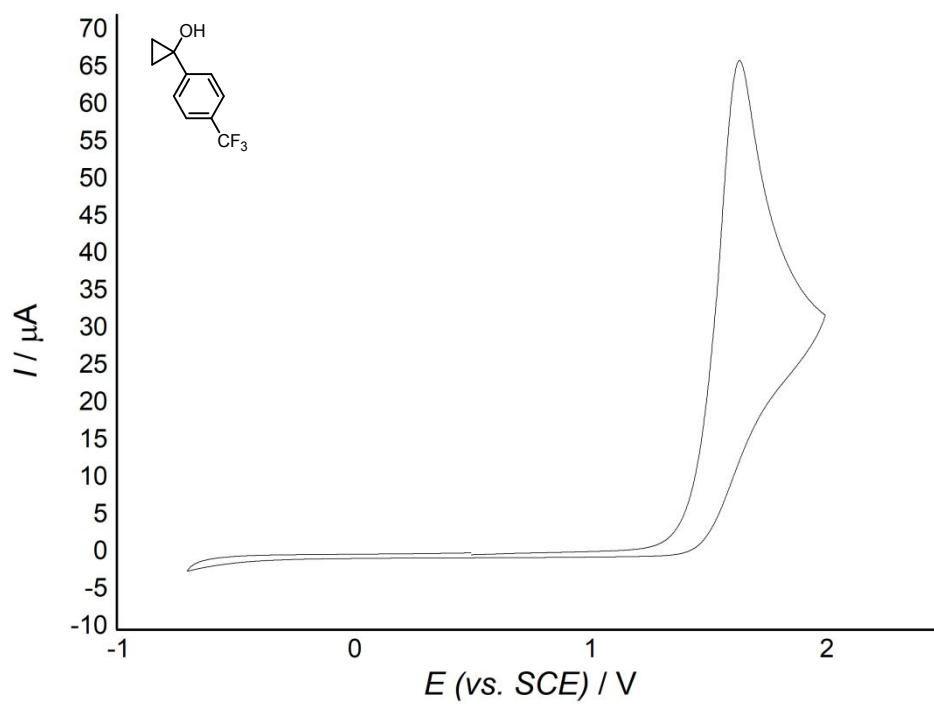
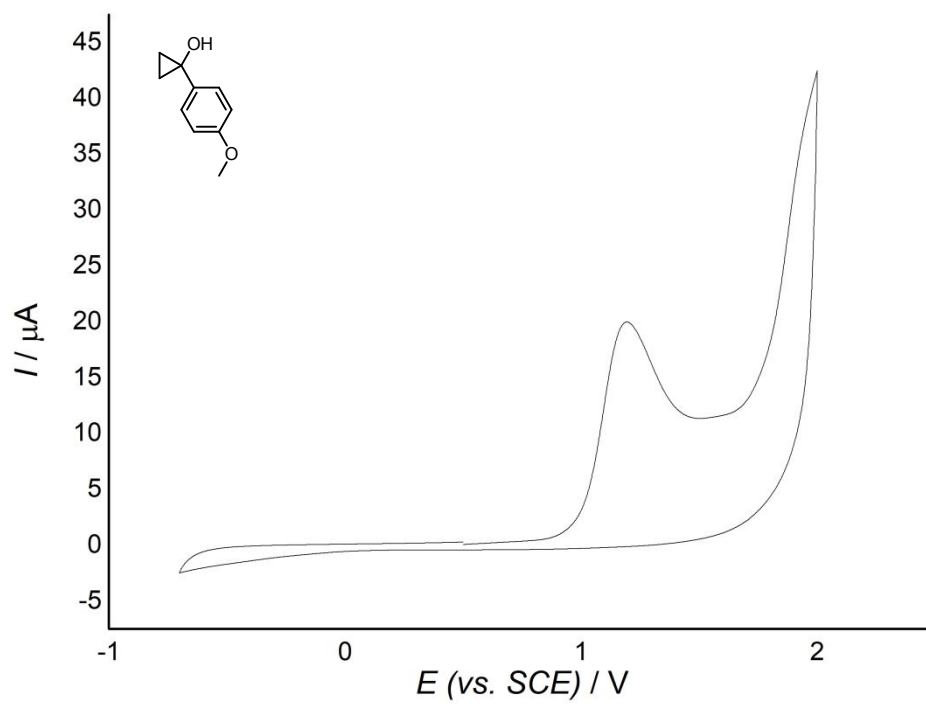
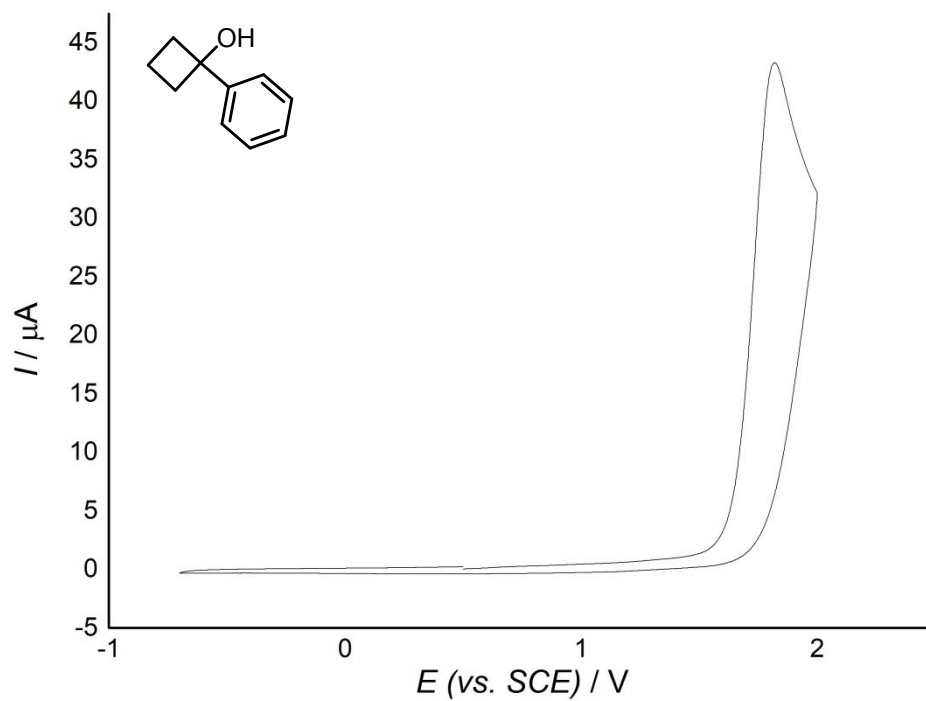
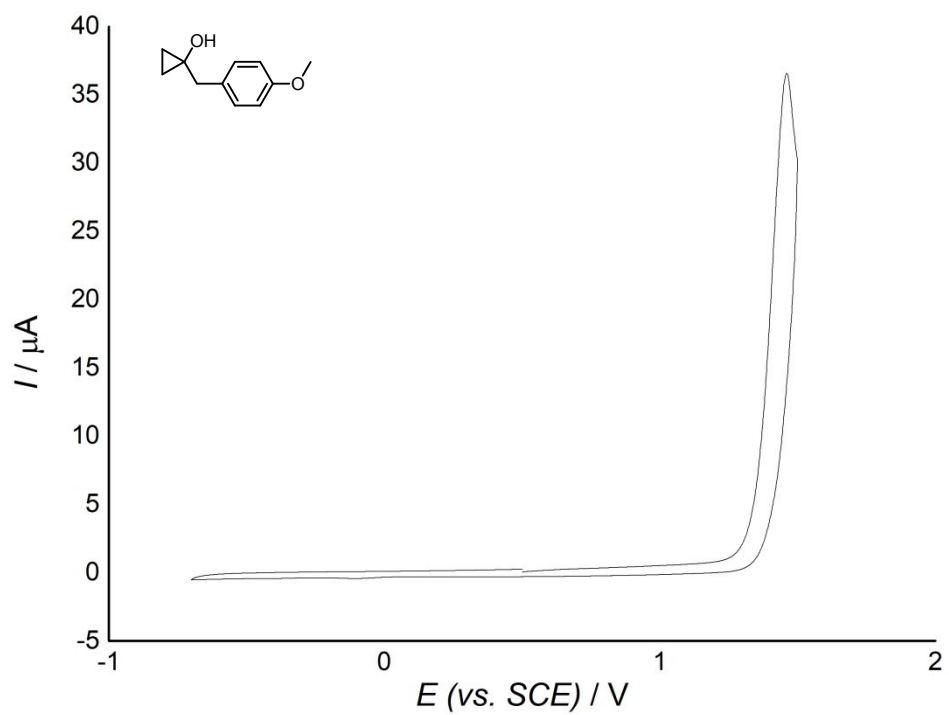
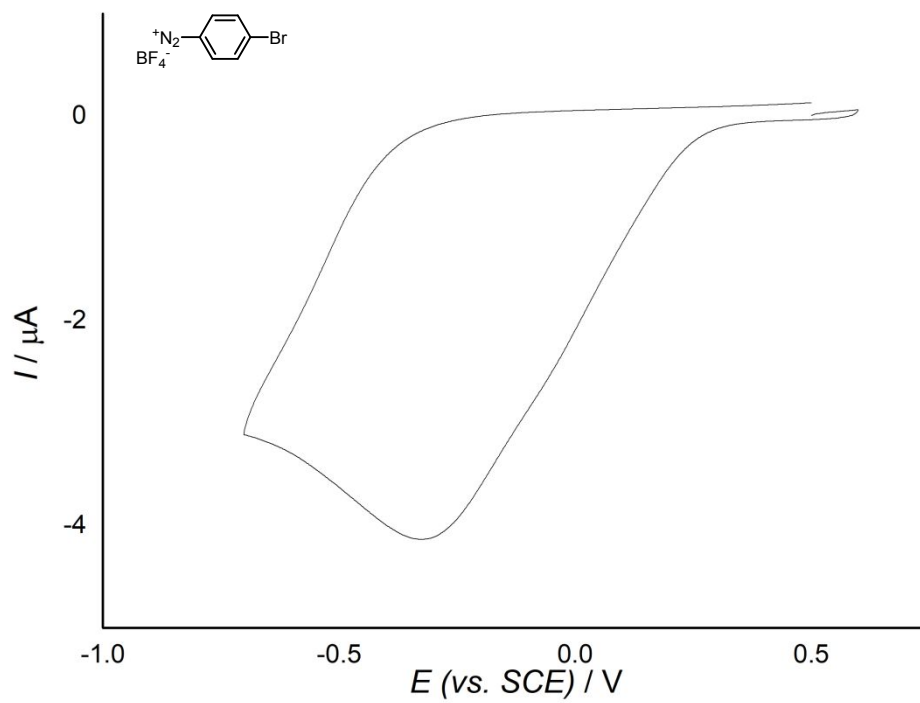
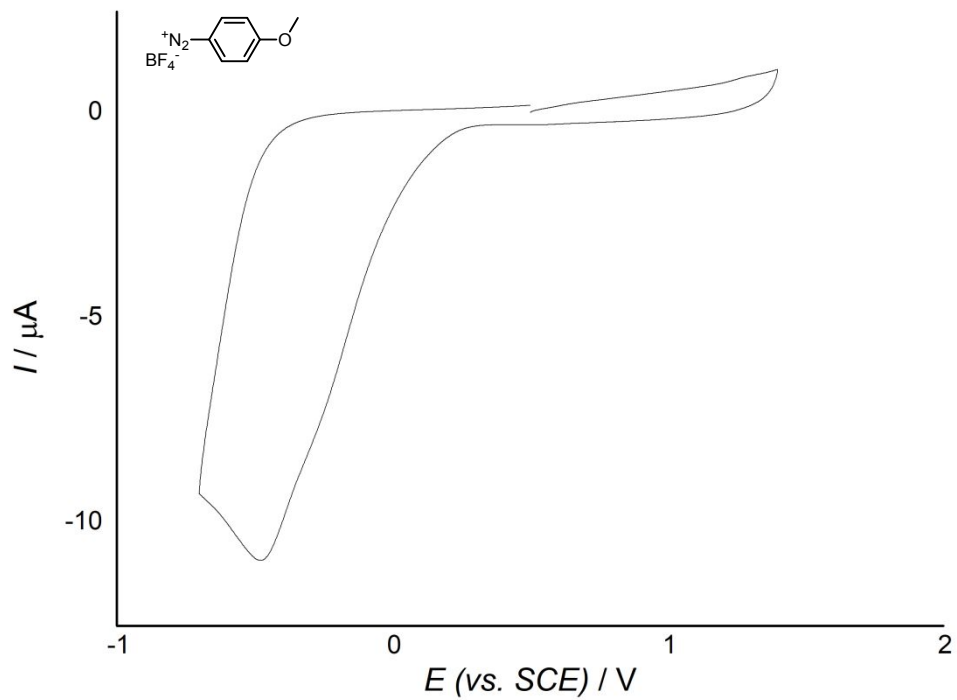


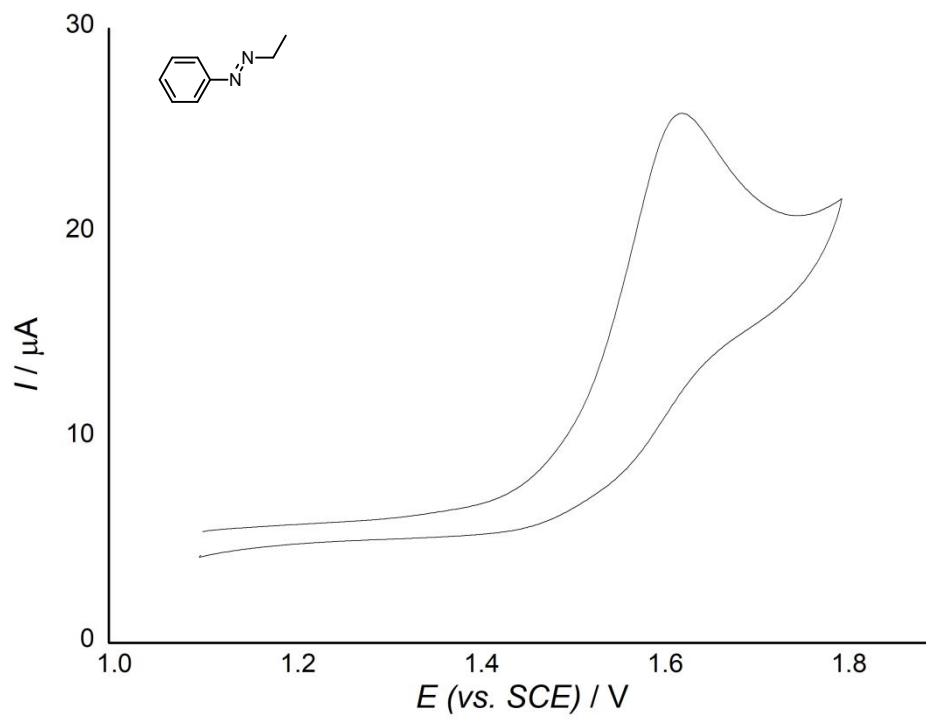
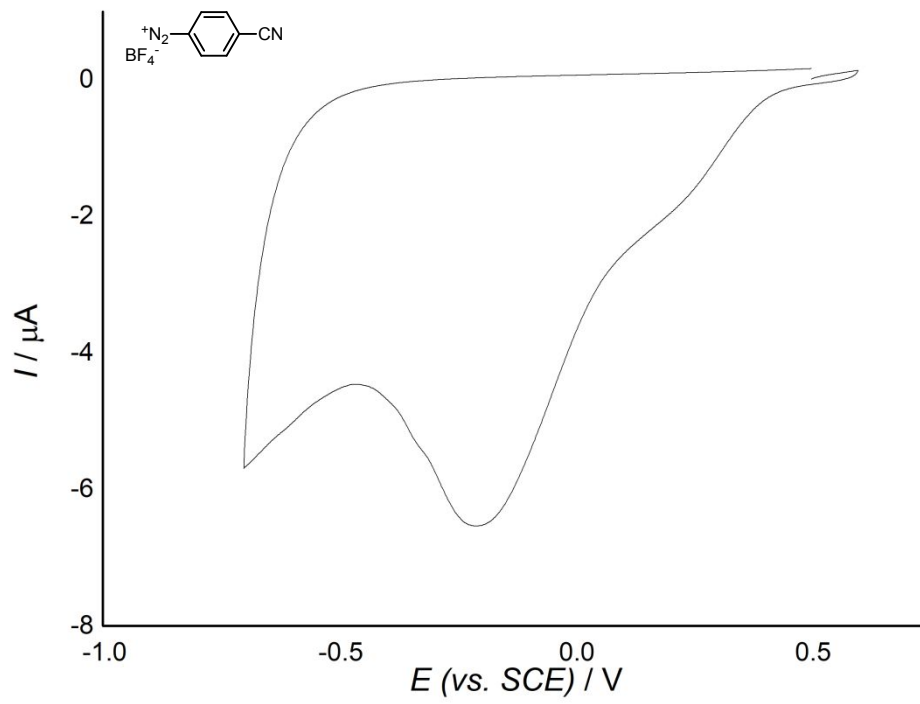
Figure S3. Reduction potentials of starting materials obtained from cyclic voltammetry, and their comparison with the redox properties of the ruthenium photocatalyst.¹²

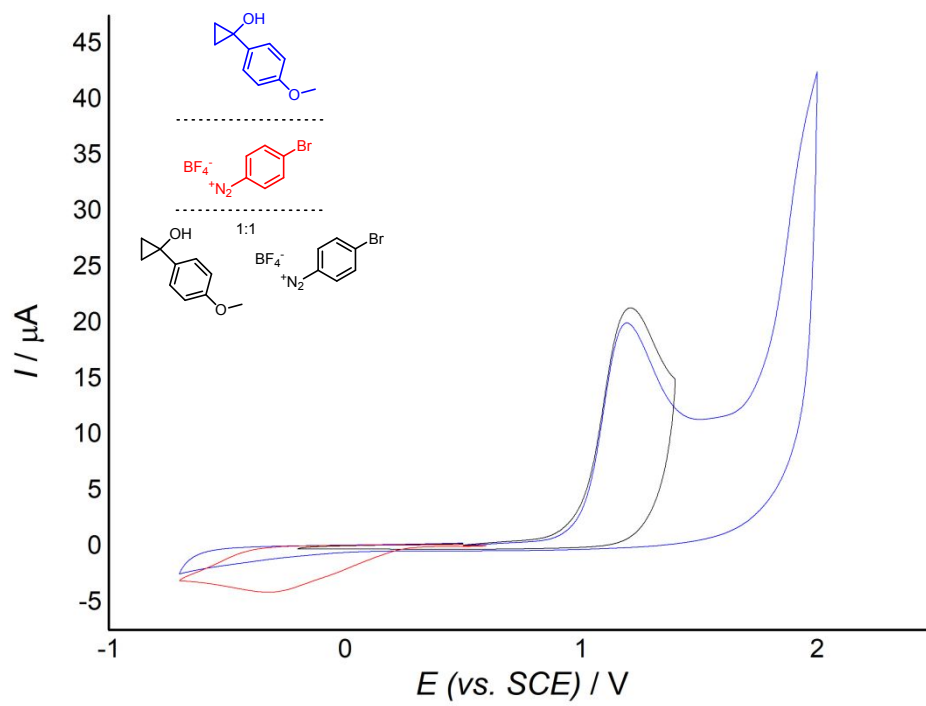
Results of the cyclic voltammetry measurements











9 Fluorescence quenching

UV/Vis absorption and fluorescence spectra were measured with a Specord 50 UV/Vis spectrophotometer (Analytic Jena) and a FluoroMax4 spectrofluorimeter (Horiba Scientific), respectively. Concentration of Ru(bpy)₃Cl₂ was chosen such, that the absorbance at the excitation wavelength, 450 nm, did not exceed 0.1 absorbance units. Both excitation as well as emission slits were 5 nm wide. Emission spectra were recorded in the region 480 nm – 860 nm. Emission values were corrected taking into account the wavelength dependence of detector, and the internal filter effect of the quencher, where applicable. Corrected emission spectra were integrated, and the integral values were used to estimate the quenching constant K_{SV} using the Stern-Volmer equation¹³:

$$\frac{I_0}{I} - 1 = K_{SV} \cdot c(Q)$$

where I_0 and I is the total intensity of the fluorescence in the absence of quencher, and in the presence of quencher in concentration $c(Q)$, respectively. It should be noted, that constant K_{SV} is derived from the life-time of the quenched excited species τ and from the rate constant of the bimolecular quenching k ¹³:

$$K_{SV} = \tau \cdot k$$

When both quencher and the quenched excited species are charged, reaction rate is no longer constant with respect to quencher, as it is dependent on the total ionic strength of the solution, behavior known as kinetic salt effect.¹⁴ To take this into account, we can use the Brønsted-Bjerrum equation¹⁵ derived from the Debye-Hückel extended theory:

$$\ln(k) = \ln(k_0) + \frac{e^3 \cdot \sqrt{N_A}}{4 \cdot \pi \cdot \sqrt{2 \cdot (\epsilon_r \cdot \epsilon_0 \cdot k_B \cdot T)^3}} \cdot \sqrt{1000} \cdot z_a \cdot z_b \cdot \frac{2 \cdot \sqrt{I}}{1 + B \cdot \sqrt{I}} = \ln(k_0) + A \cdot z_a \cdot z_b \cdot \frac{2 \cdot \sqrt{I}}{1 + B \cdot \sqrt{I}}$$

where e is the elementary charge; N_A is the Avogadro's number; ϵ_r is the relative permittivity of the solvent; ϵ_0 is the permittivity of vacuum; k_B is the Boltzmann's constant; T is the thermodynamic temperature; z_A and z_B are the charges of the quencher and the quenched molecule and I is the ionic strength (using mol/dm³ units). Factor $\sqrt{1000}$ comes from the unit conversion of ionic strength (from mol/m³ to the usual mol/dm³). k_0 and k are quenching rates at ionic strengths of zero and I , respectively. Constant B is dependent on the size of the interacting species, but can be approximated in most cases as unity without any significant error.¹⁵ For acetonitrile we can calculate, that $A = 3.351$ at 300 K. Using this equation, we can write the following for Stern-Volmer quenching:

$$\ln(K_{SV}) = \ln(\tau) + \ln(k) = \ln(\tau) + \ln(k_0) + A \cdot z_a \cdot z_b \cdot \frac{2 \cdot \sqrt{I}}{1 + B \cdot \sqrt{I}} = \ln(K_{SV0}) + A \cdot z_a \cdot z_b \cdot \frac{2 \cdot \sqrt{I}}{1 + B \cdot \sqrt{I}}$$

where K_{SV0} is the Stern-Volmer quenching constant at zero ionic strength. Furthermore:

$$\ln\left(\frac{I_0}{I} - 1\right) = \ln(K_{SV}) + \ln[c(Q)] = \ln[c(Q)] + \ln(K_{SV0}) + A \cdot z_a \cdot z_b \cdot \frac{2 \cdot \sqrt{I}}{1 + B \cdot \sqrt{I}}$$

$$Q = \ln\left(\frac{I_0}{I} - 1\right) - A \cdot z_a \cdot z_b \cdot \frac{2 \cdot \sqrt{I}}{1 + B \cdot \sqrt{I}} = \ln[c(Q)] + \ln(K_{SV0})$$

By plotting quantity Q (vide supra) against natural logarithm of quencher concentration, we can obtain K_{SV0} – the Stern-Volmer quenching constant at zero ionic strength even for charged pair quencher-luminescent dye, which occurs in our case – diazonium salts and $\text{Ru}(\text{bpy})_3^{2+}$.

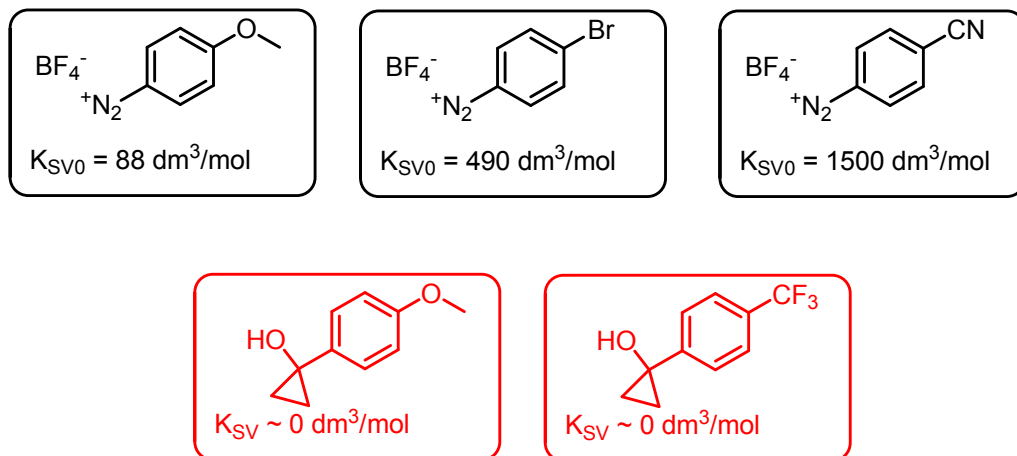


Figure S4. Stern-Volmer quenching constants of excited $\text{Ru}(\text{bpy})_3^{2+}$ with substrates.

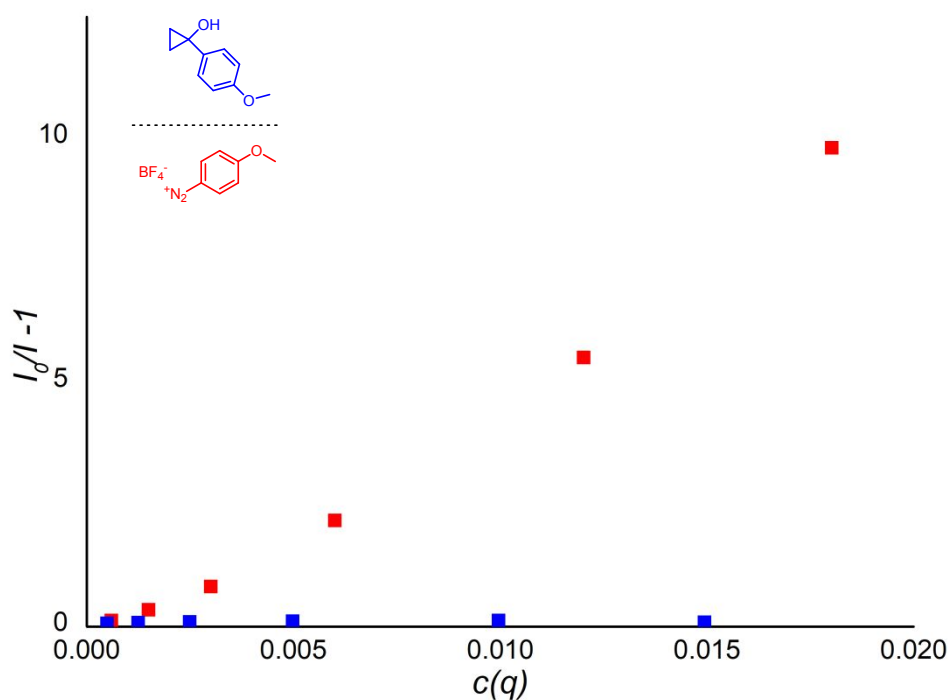


Figure S5. Quenching of luminescence of $\text{Ru}(\text{bpy})_3^{2+}$ with **1a** and **2a**.

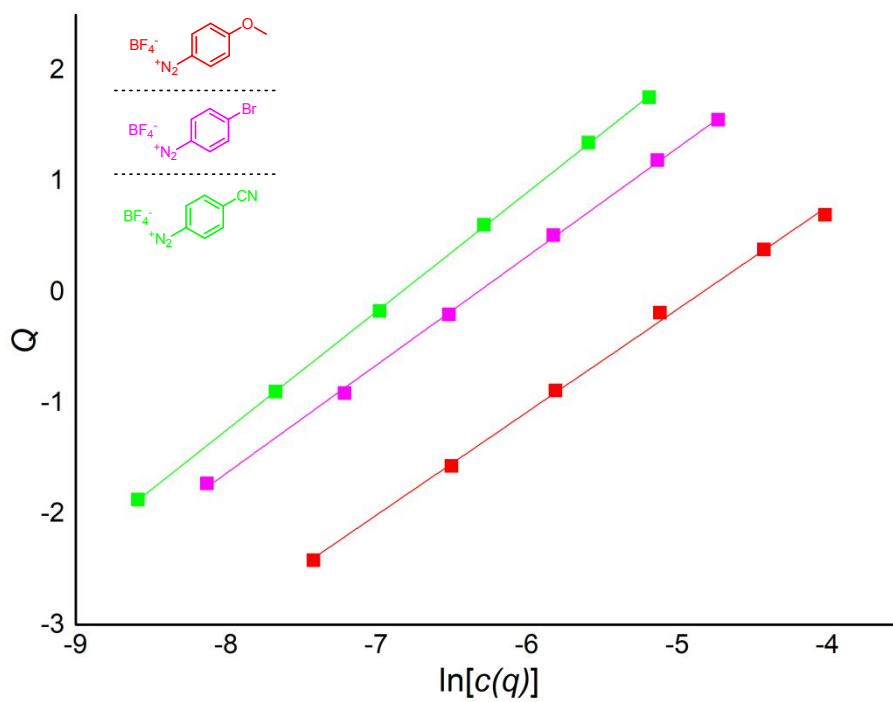
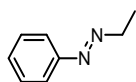


Figure S6. Modified Stern-Volmer plot of diazonium salt quenching of Ru(bpy)₃²⁺ luminescence.

10 DFT calculations

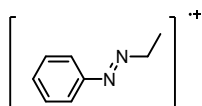
Conformation analysis was performed using Spartan program package.¹⁶ Quantum chemical calculations were performed using Gaussian G16 software package.¹⁷ Geometry optimization of minima involved were performed at B3LYP level of theory and 6-31+G(d) basis set. All the calculations were performed using conductor-like polarized continuum model to account for the effects of solvation. Frequency calculations were performed on the minima in order to ascertain the type of stationary point as well as to obtain zero-point vibrational energies. Thermodynamic properties were calculated at 298 Kelvin. A quasiharmonic correction was applied during the entropy calculation by setting all positive frequencies that are less than 100 cm⁻¹ to 100 cm⁻¹.¹⁸ Single point energy calculations were done using B3LYP level of theory and 6-311++G(2df,2p) basis set. Calculated values were used to obtain the absolute reduction potential. Absolute reduction potential was referenced by subtracting the absolute energy of hydrogen electrode (4.28 eV).¹⁹

Calculated geometries:



C	2.80034300	-0.98725200	0.20267500
C	1.44057600	-1.28423500	0.07550500
C	0.50884300	-0.25227200	-0.09641000
C	0.93863600	1.08491600	-0.14689700
C	2.29573200	1.37461500	-0.02134300
C	3.22950200	0.34205800	0.15434100
H	3.51993800	-1.79003500	0.33749800
H	1.08615800	-2.31081200	0.10875000
H	0.21014800	1.87666100	-0.28442700
H	2.63185400	2.40748300	-0.06099100
H	4.28607100	0.57721500	0.25103500
N	-0.85491700	-0.67374100	-0.21569700
N	-1.69950300	0.23861700	-0.32736800
C	-3.07716000	-0.25108600	-0.44489400
H	-3.09394500	-1.34873700	-0.44627800
H	-3.44816500	0.11116900	-1.41306100
C	-3.94053000	0.32637600	0.68091800

H	-3.90616100	1.42137500	0.68141600
H	-4.98176700	0.01433600	0.54548100
H	-3.59883100	-0.03150400	1.65864700



C	2.78265000	-1.04377700	0.18846100
C	1.41992800	-1.29482100	0.05747800
C	0.54991900	-0.20307300	-0.09832900
C	1.00710700	1.13088900	-0.12623700
C	2.36974900	1.35479900	0.00632000
C	3.25372500	0.27383600	0.16245000
H	3.47461100	-1.87050300	0.30996100
H	1.02168000	-2.30374100	0.07288900
H	0.30362500	1.94779500	-0.24792000
H	2.75065900	2.37098400	-0.01159600
H	4.31765900	0.46541600	0.26417200
N	-0.80546100	-0.50638400	-0.22859300
N	-1.76775600	0.17576900	-0.37312700
C	-3.19162500	-0.19617100	-0.49243100
H	-3.22497100	-1.27795000	-0.65284000
H	-3.54638300	0.32450200	-1.38559500
C	-3.95769000	0.24703600	0.75406400
H	-3.88865400	1.32833300	0.89942100
H	-5.00920300	-0.01756800	0.60620100
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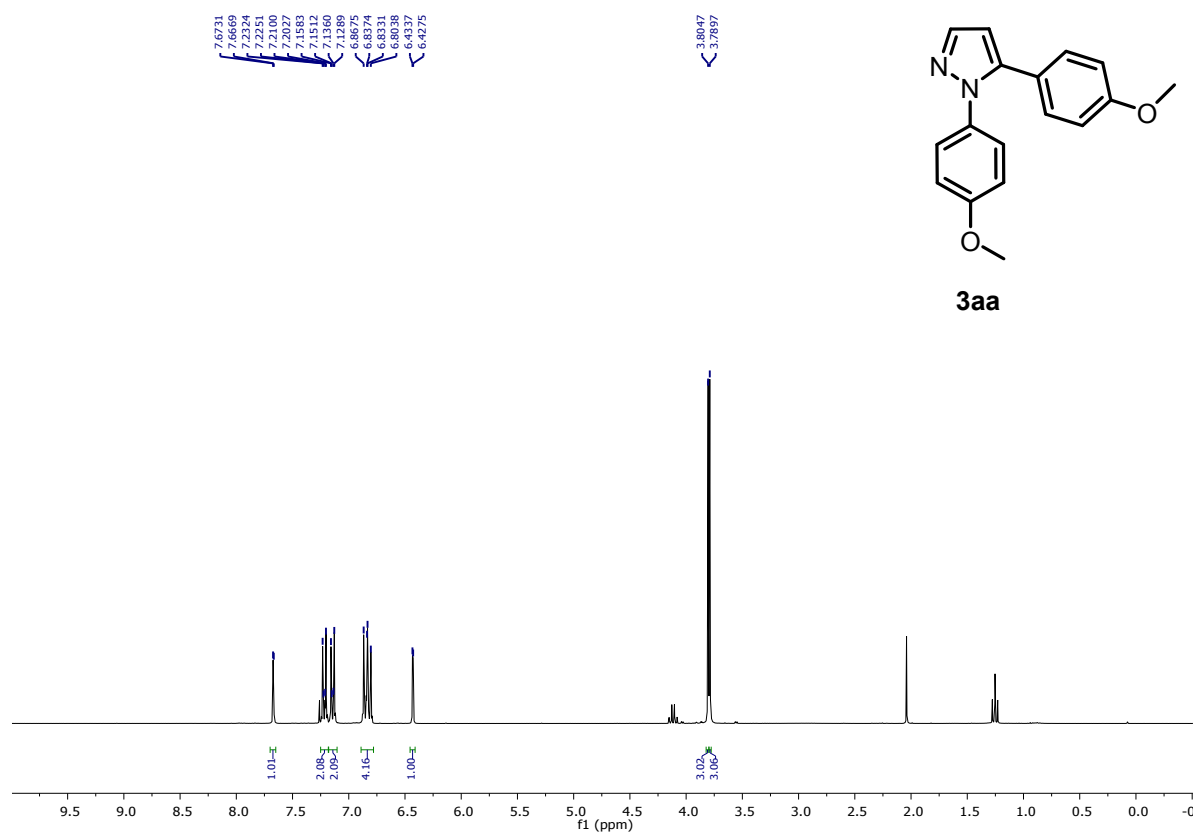
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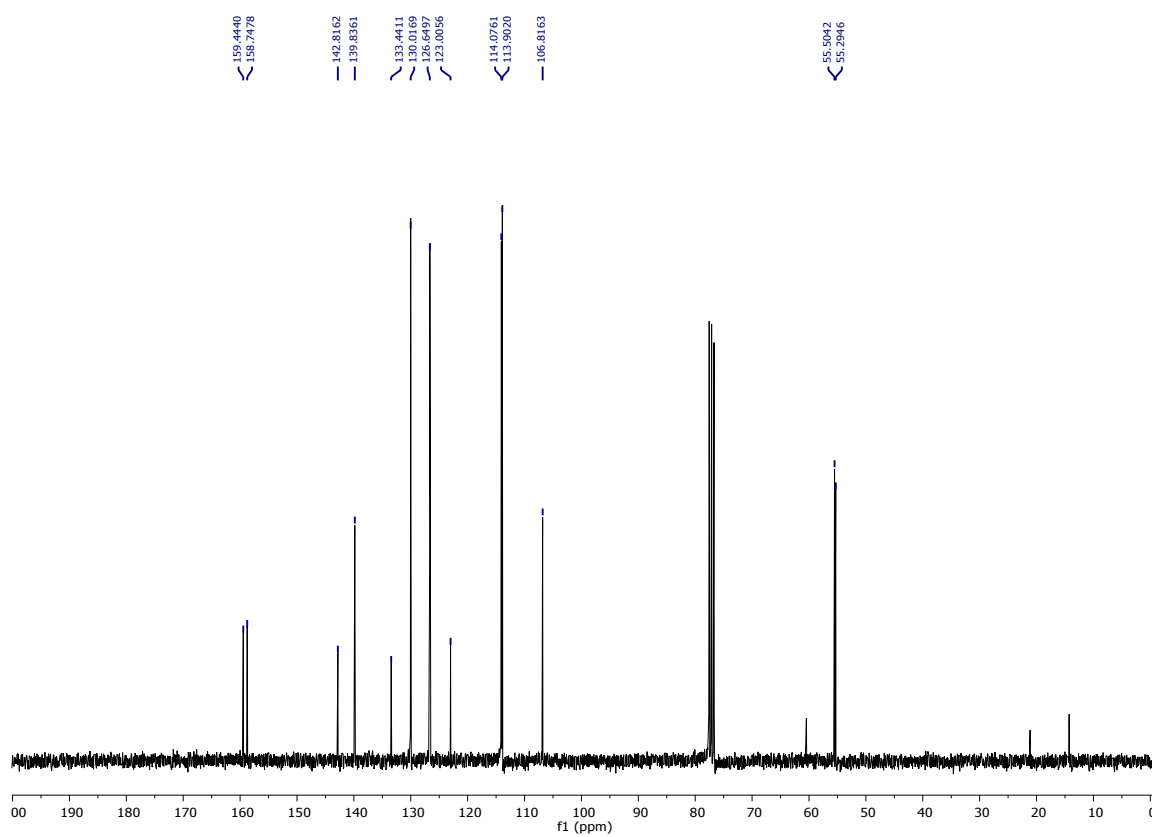
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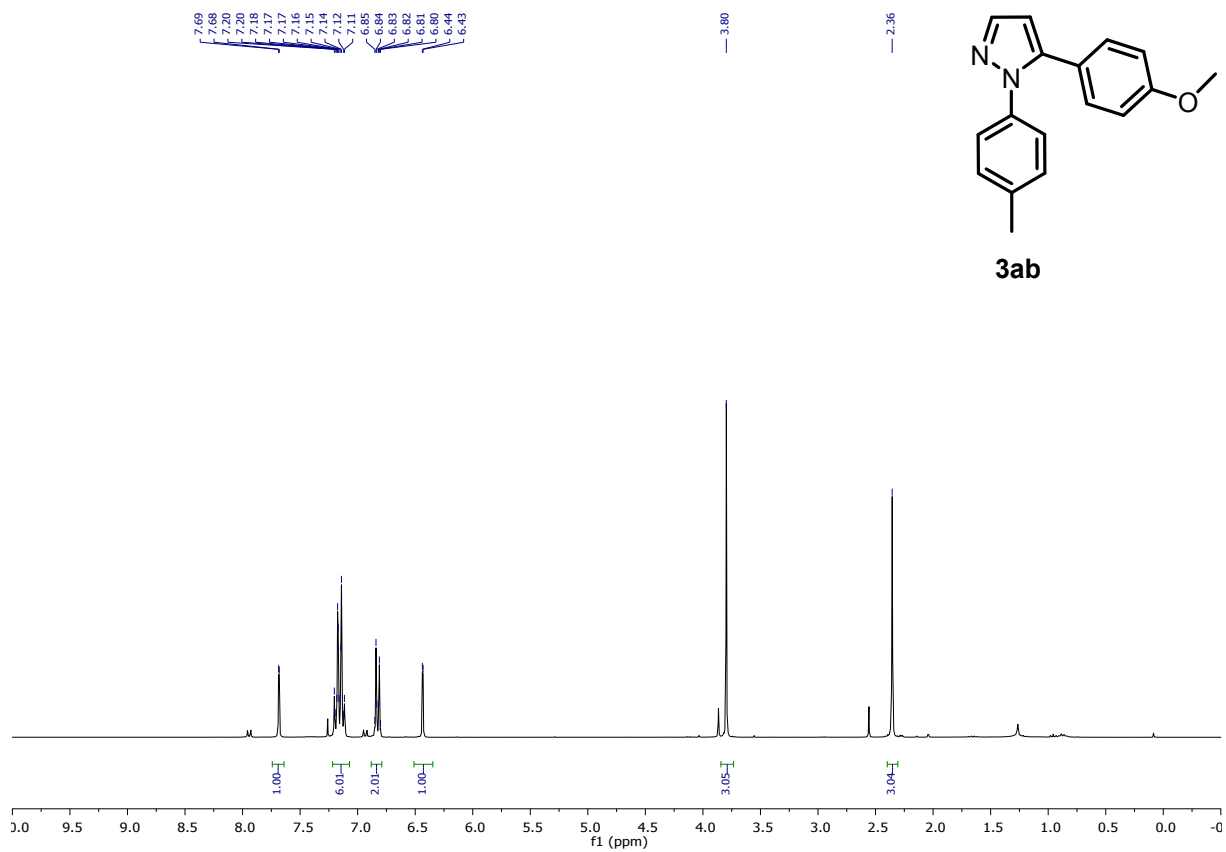
12 Characterization of products



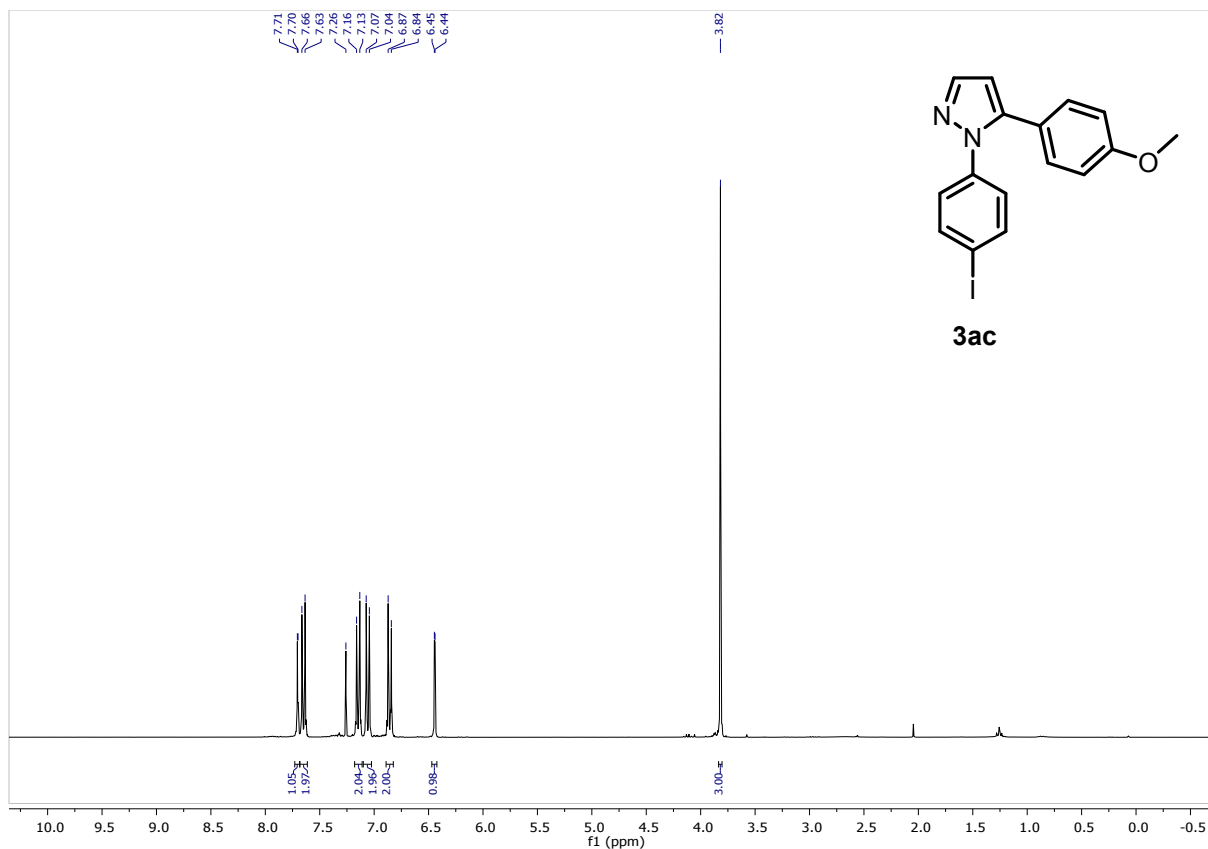
¹H NMR (400 MHz, CDCl₃) of 1, 5-bis(4-methoxyphenyl)-1H-pyrazole



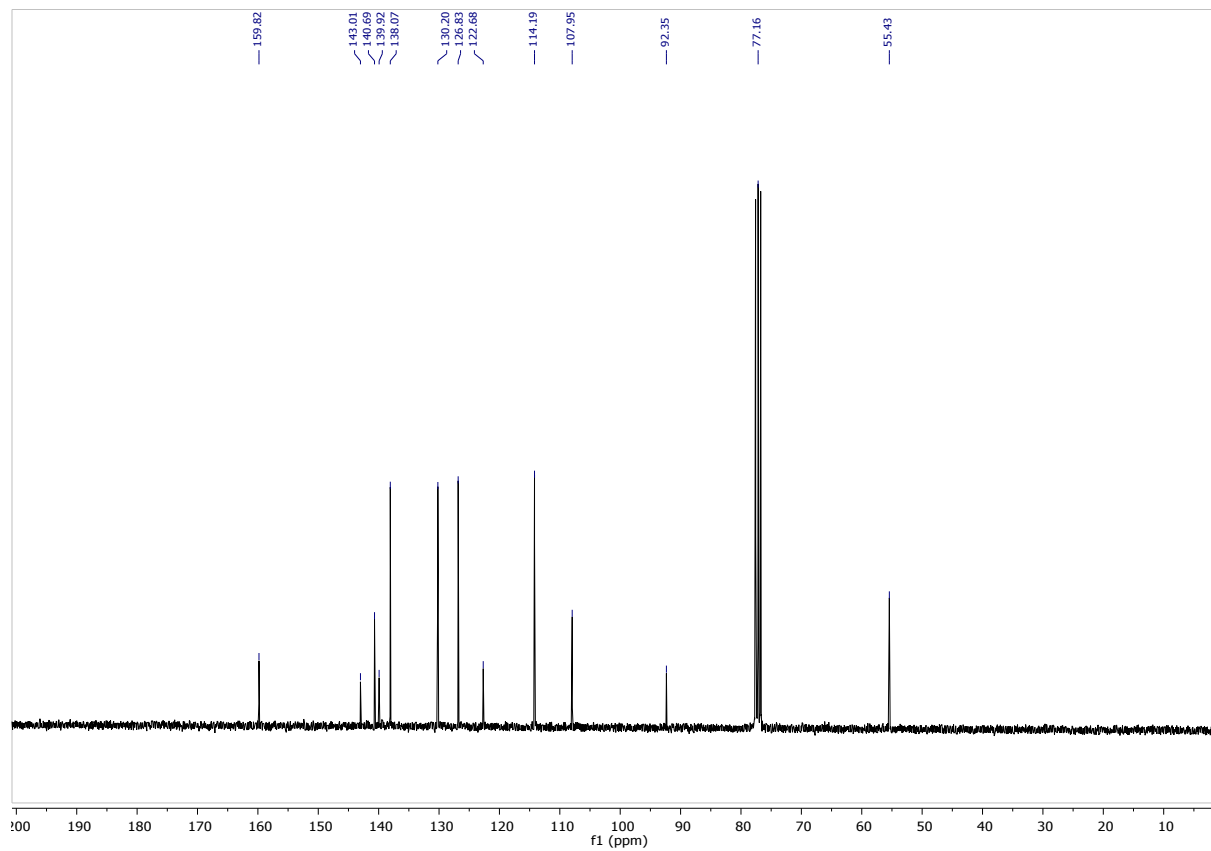
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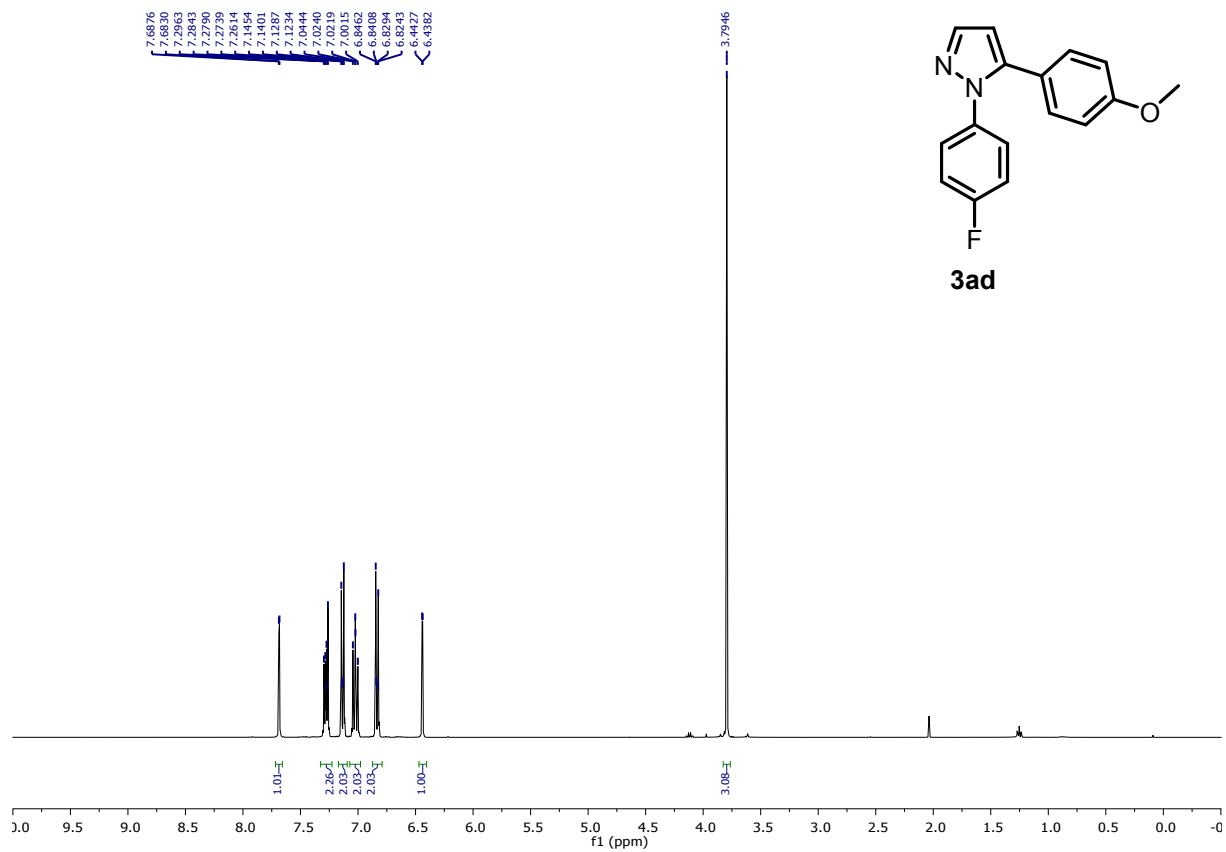
¹H NMR (400 MHz, CDCl₃) of 5-(4-methoxyphenyl)-1-(*p*-tolyl)-1*H*-pyrazole



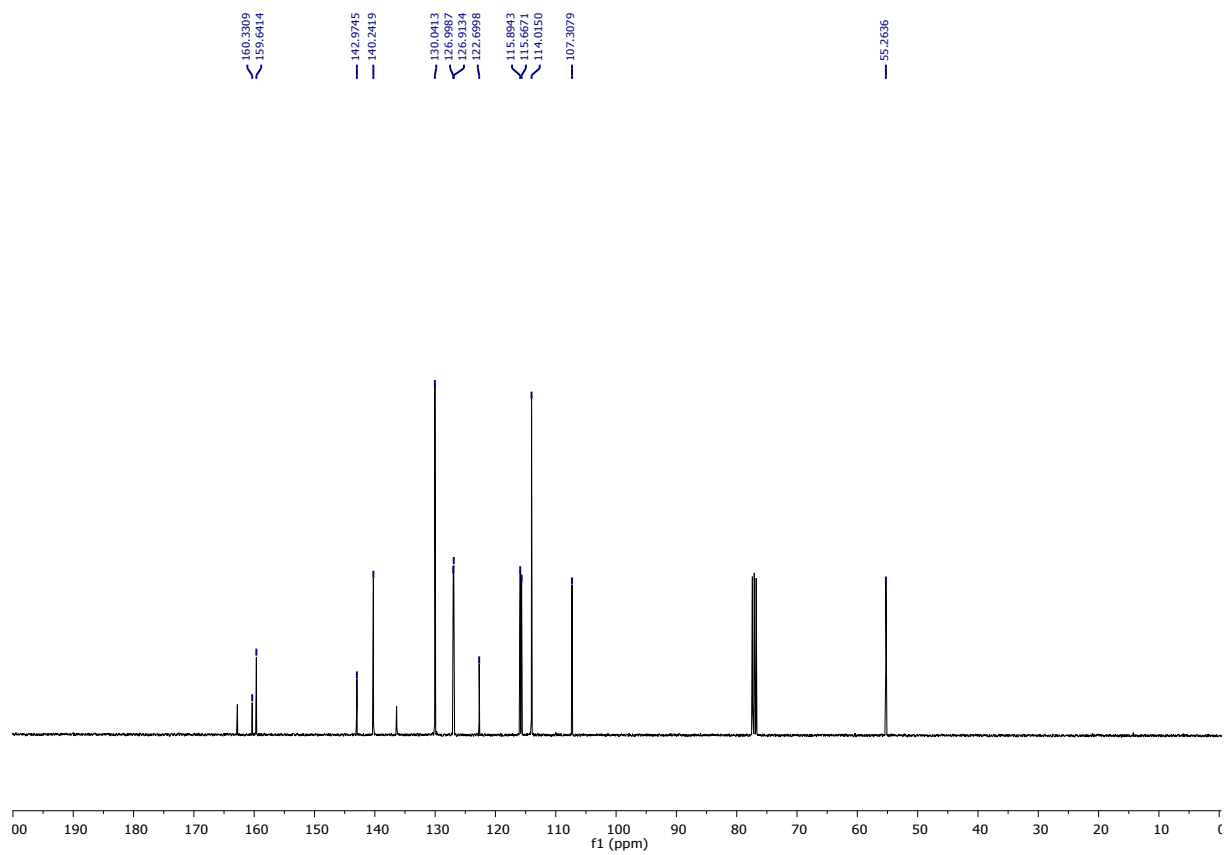
^1H NMR (300 MHz, CDCl_3) of 1-(4-Iodophenyl)-5-(4-methoxyphenyl)-1H-pyrazole



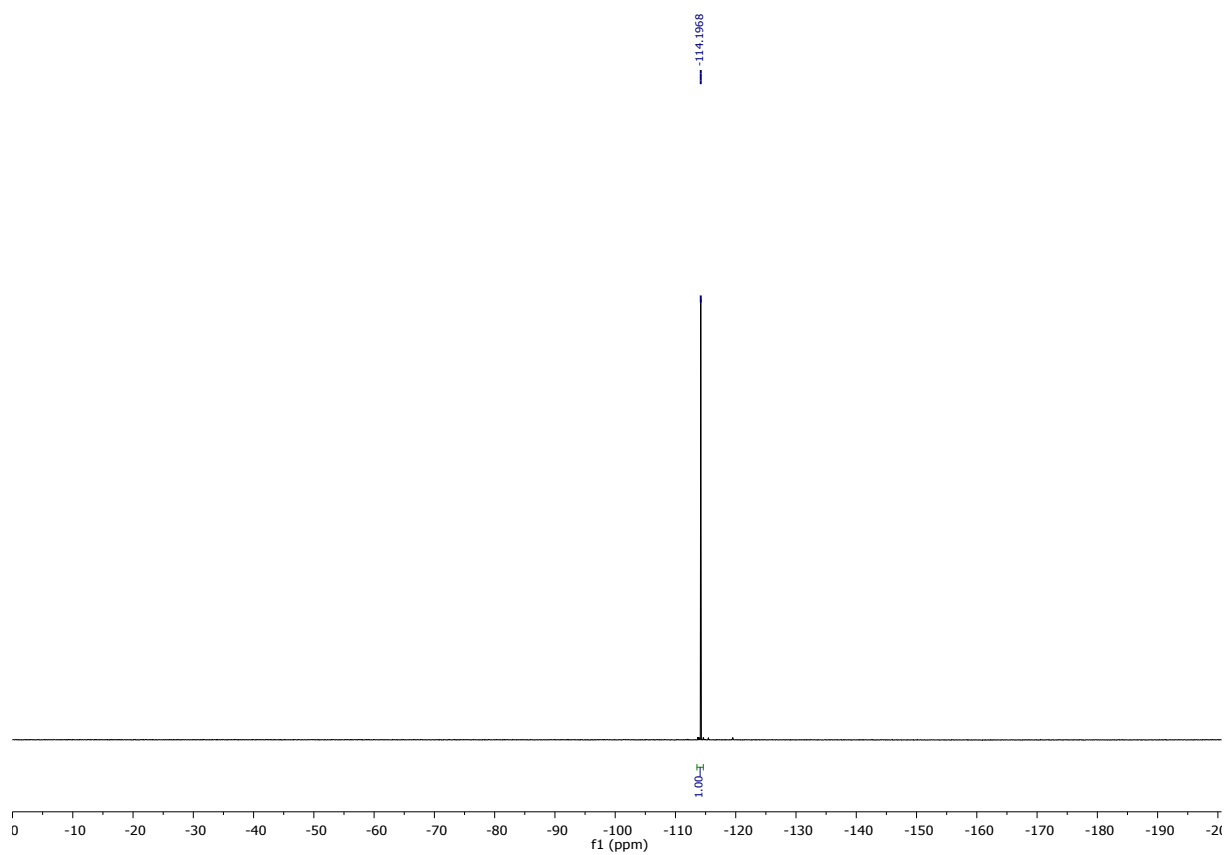
^{13}C NMR (75 MHz, CDCl_3) of 1-(4-Iodophenyl)-5-(4-methoxyphenyl)-1H-pyrazole



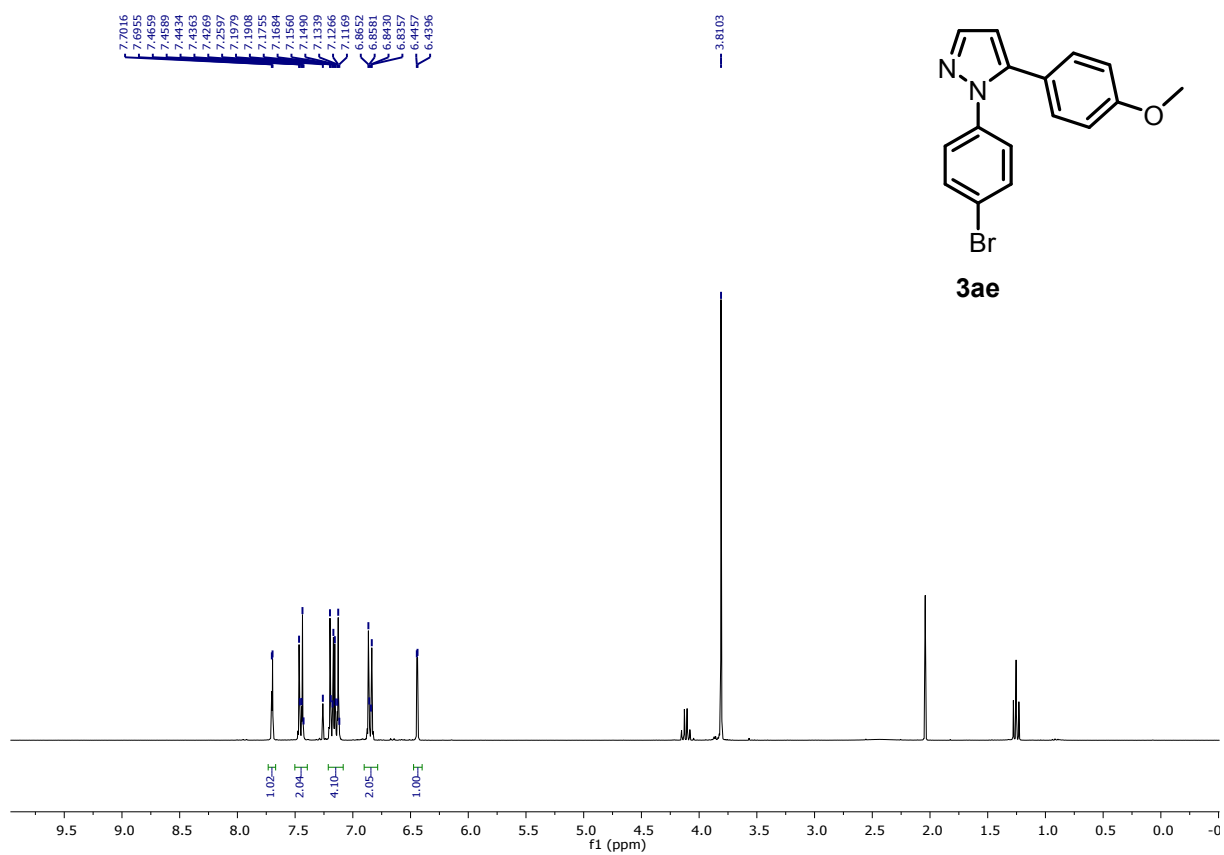
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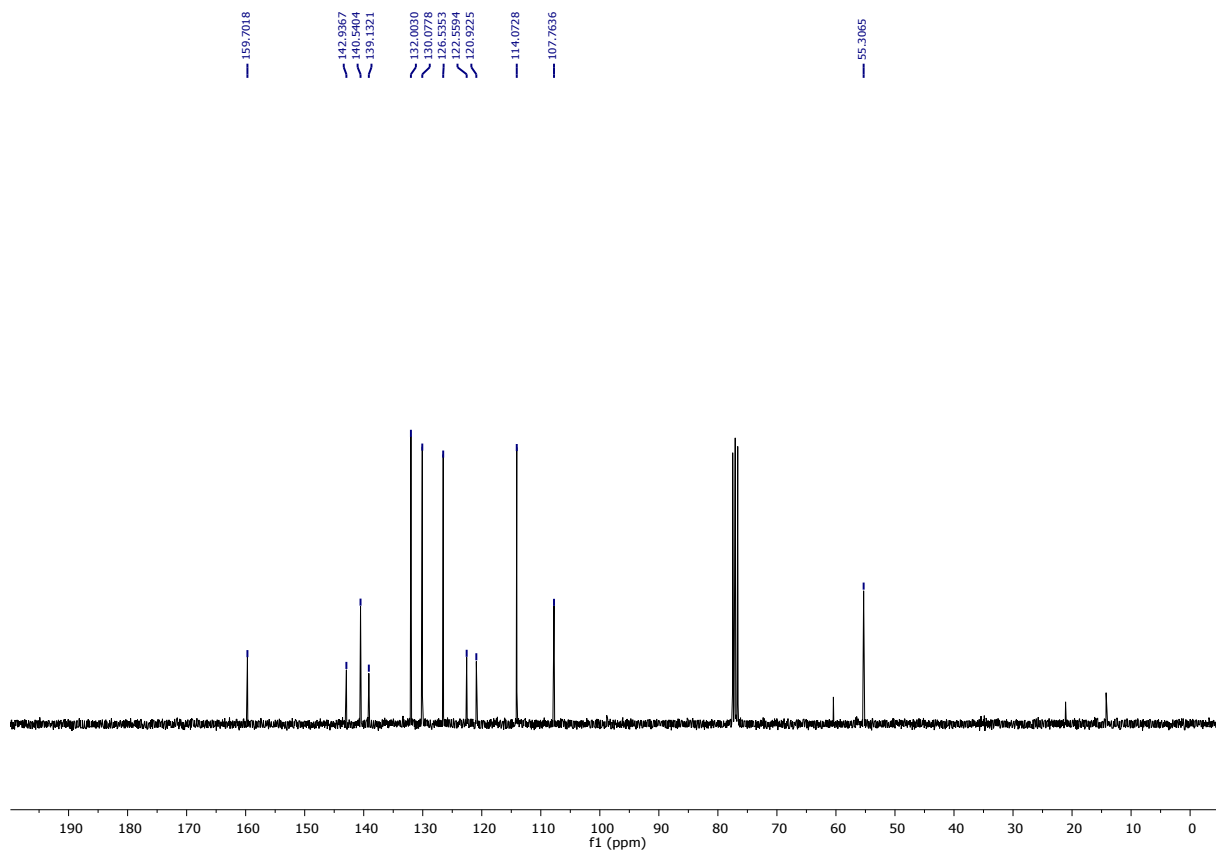
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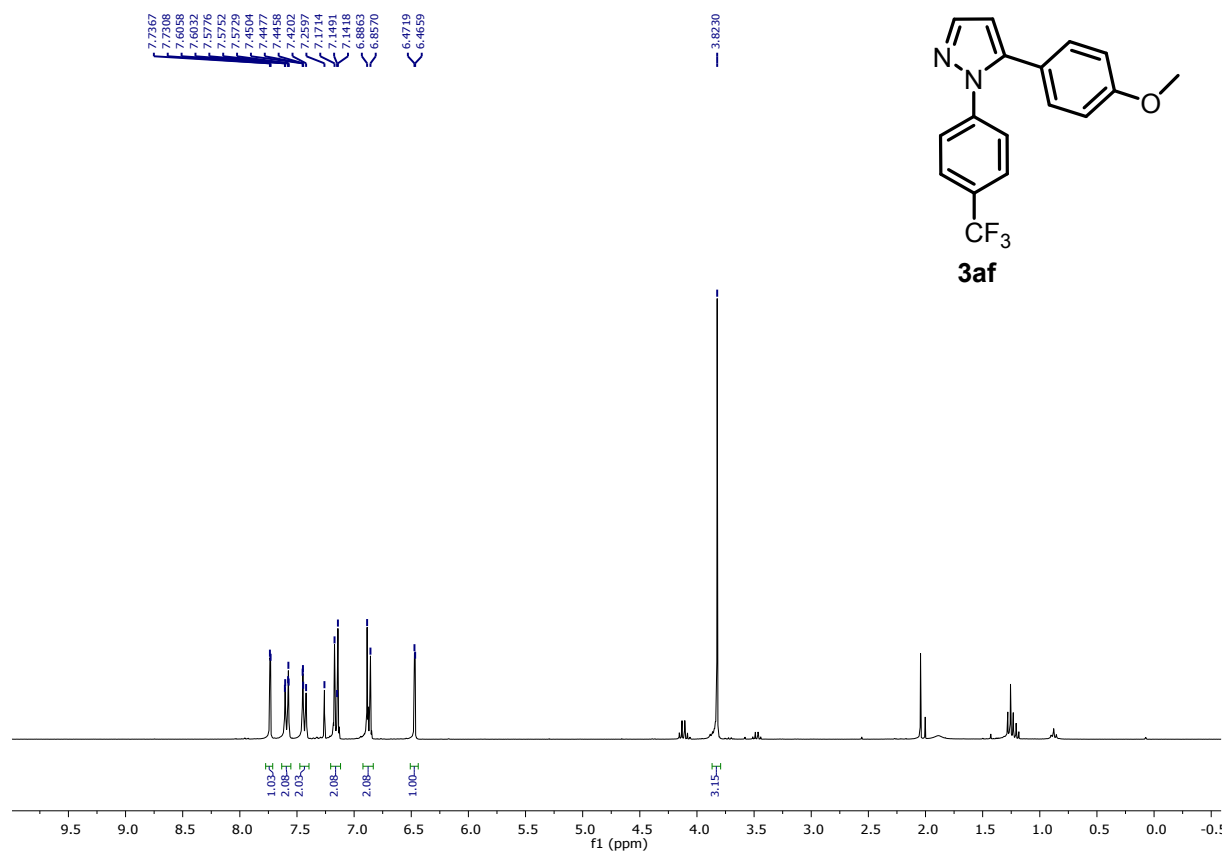
^{19}F NMR (376 MHz, CDCl_3) of 1-(4-fluorophenyl)-5-(4-methoxyphenyl)-1*H*-pyrazole



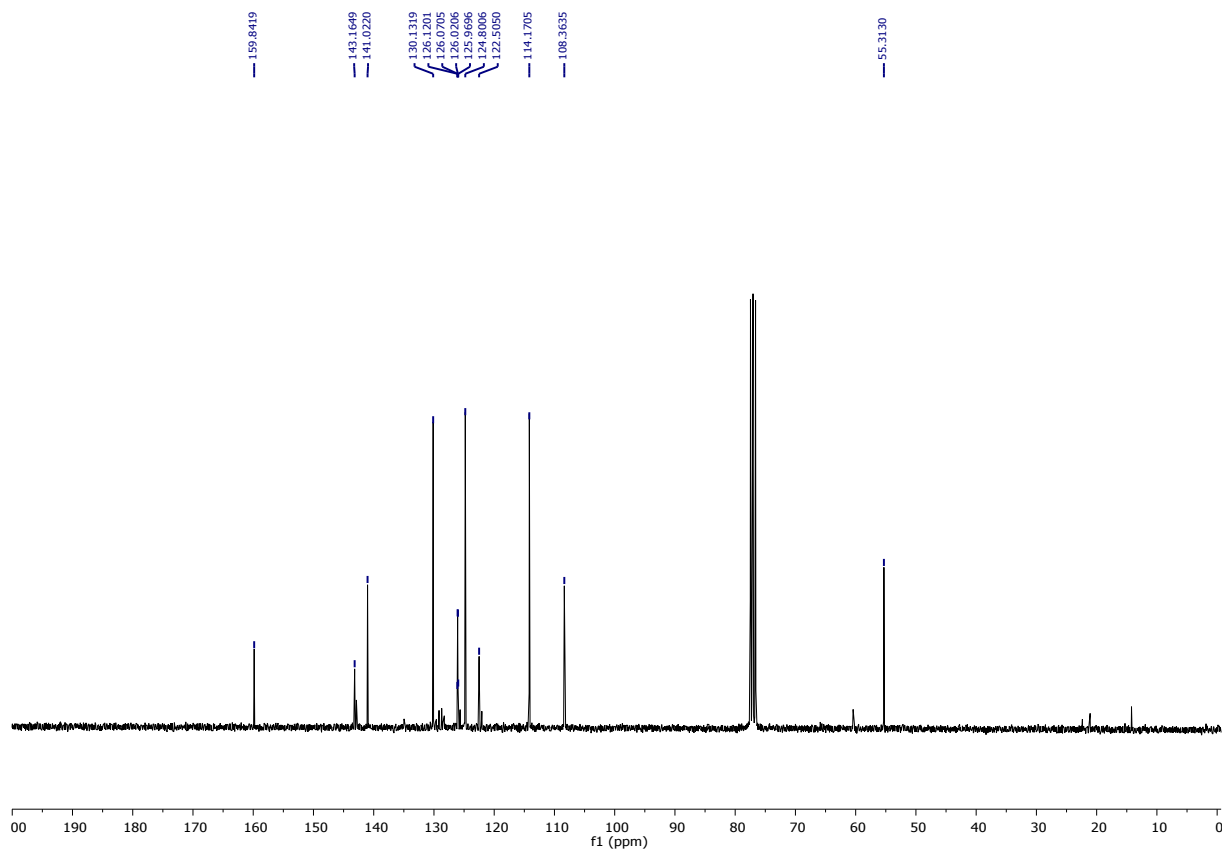
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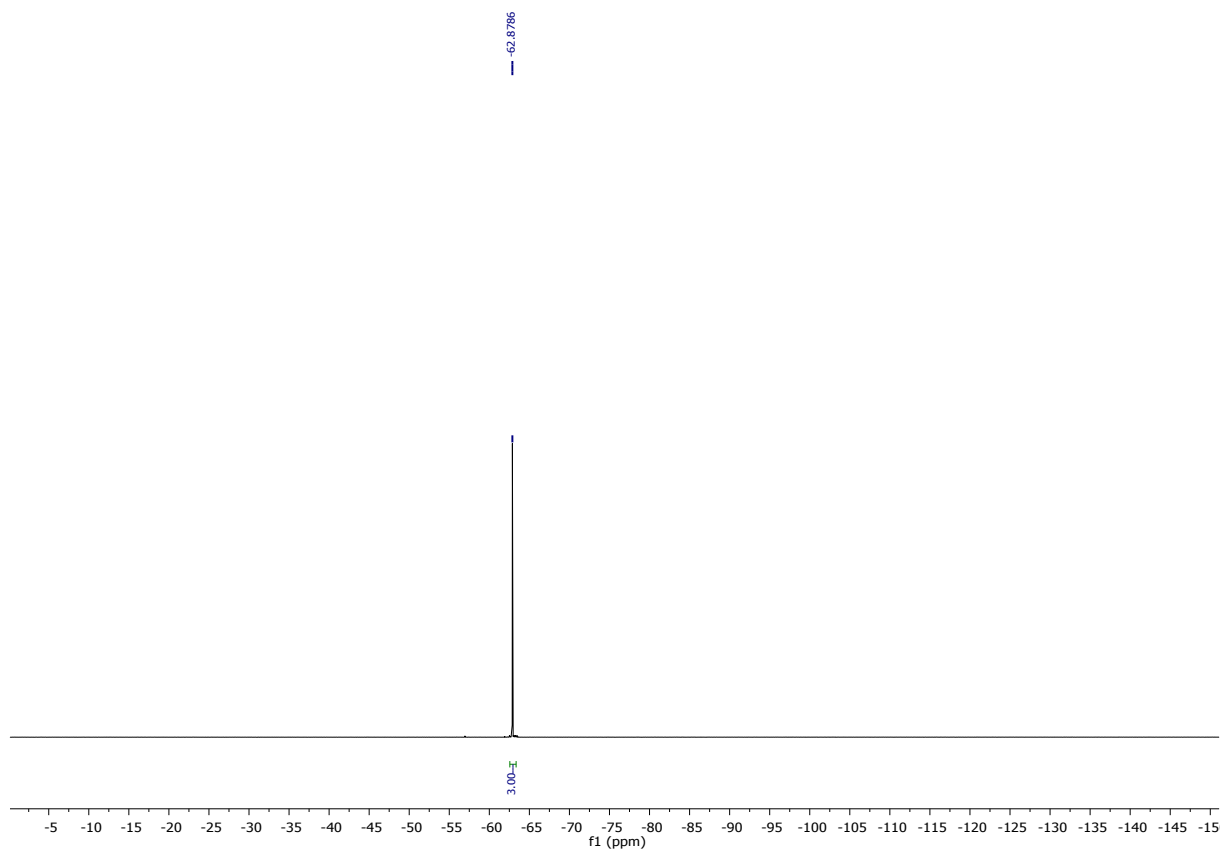
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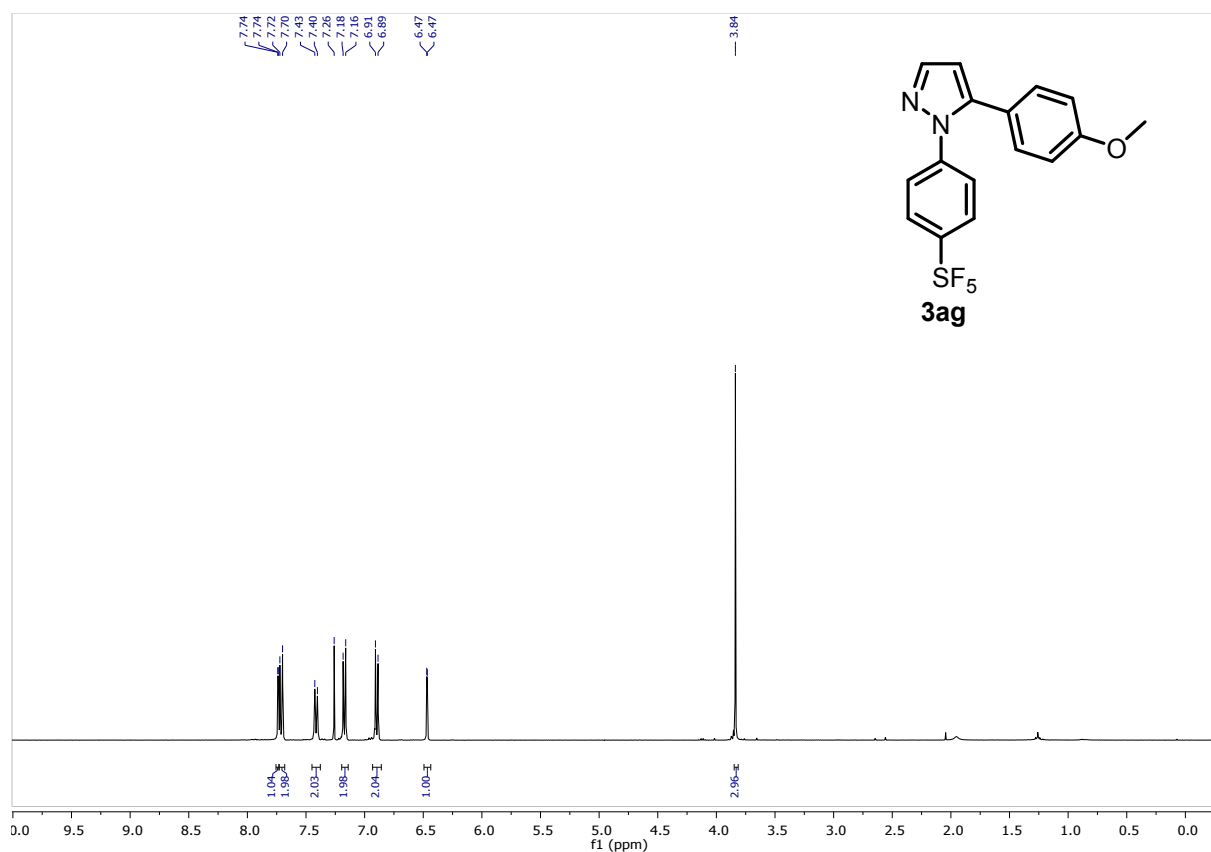
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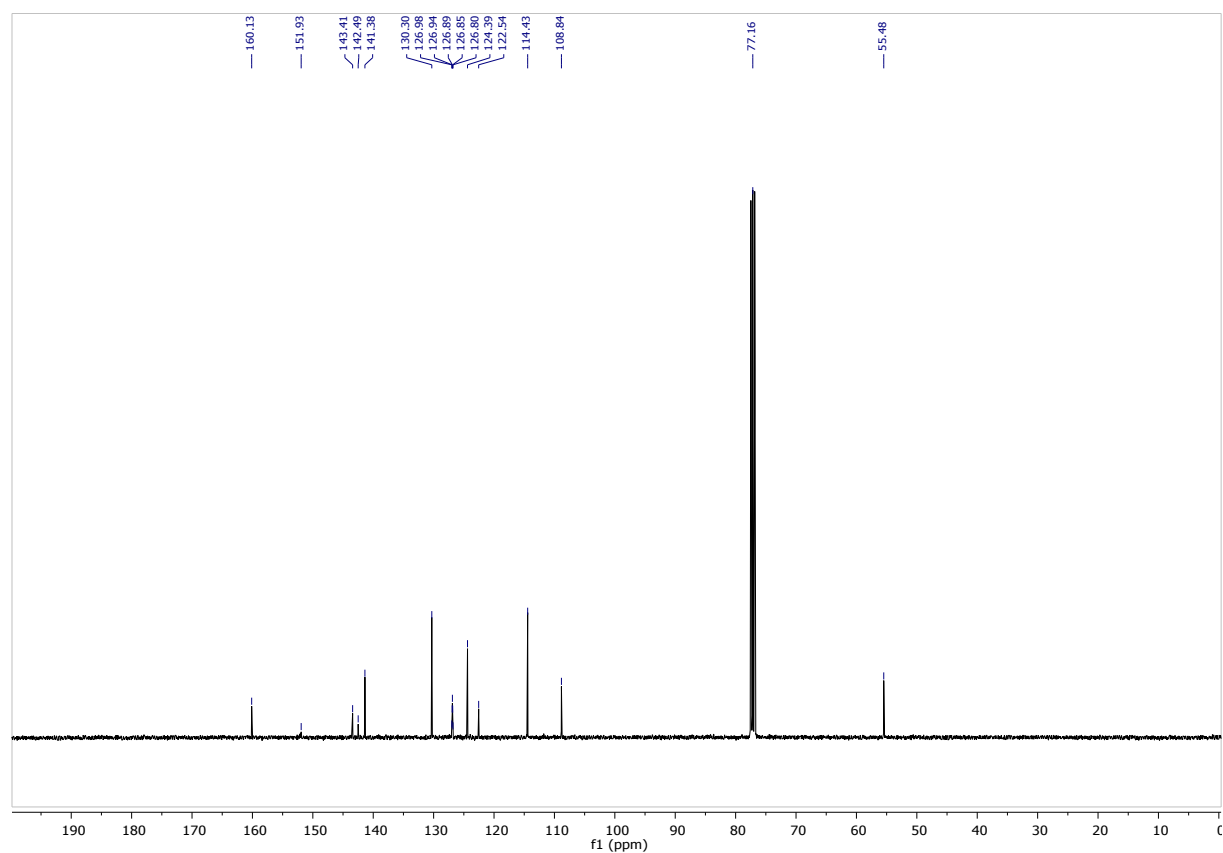
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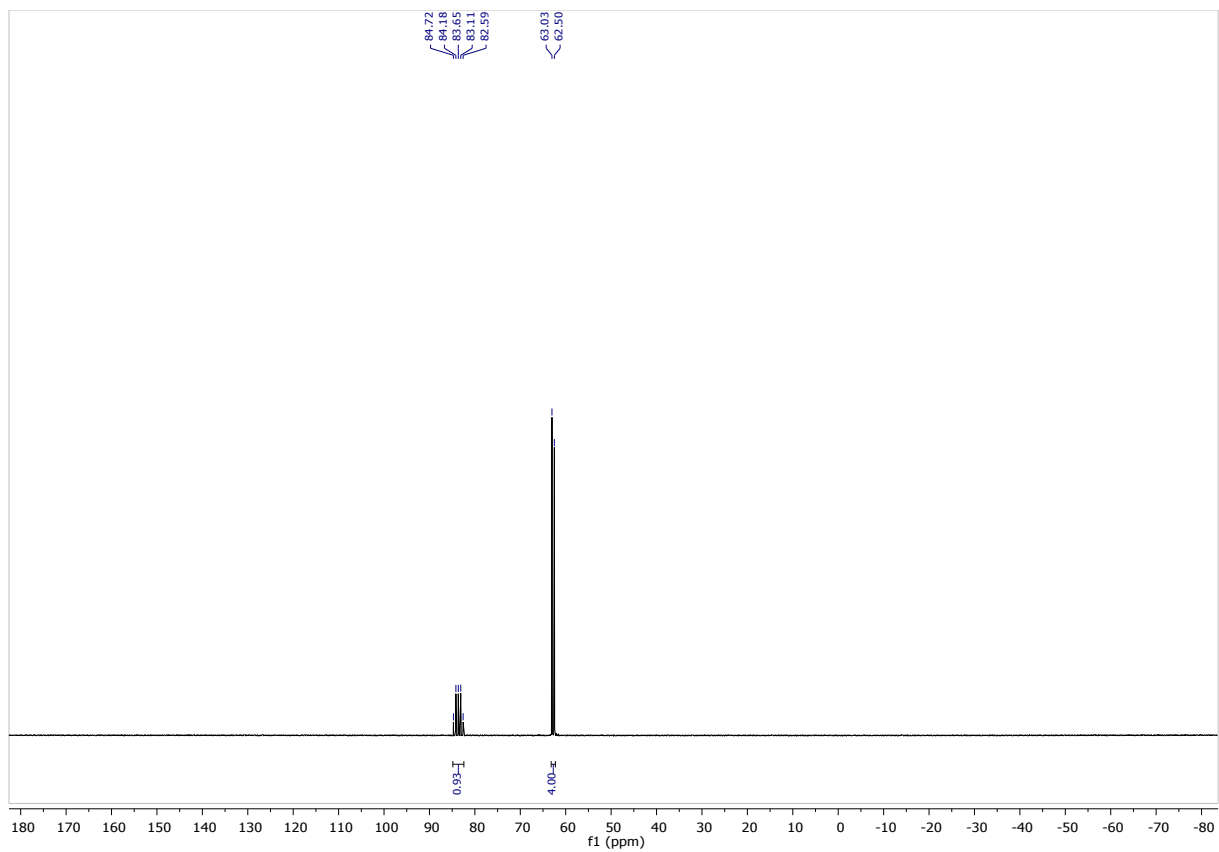
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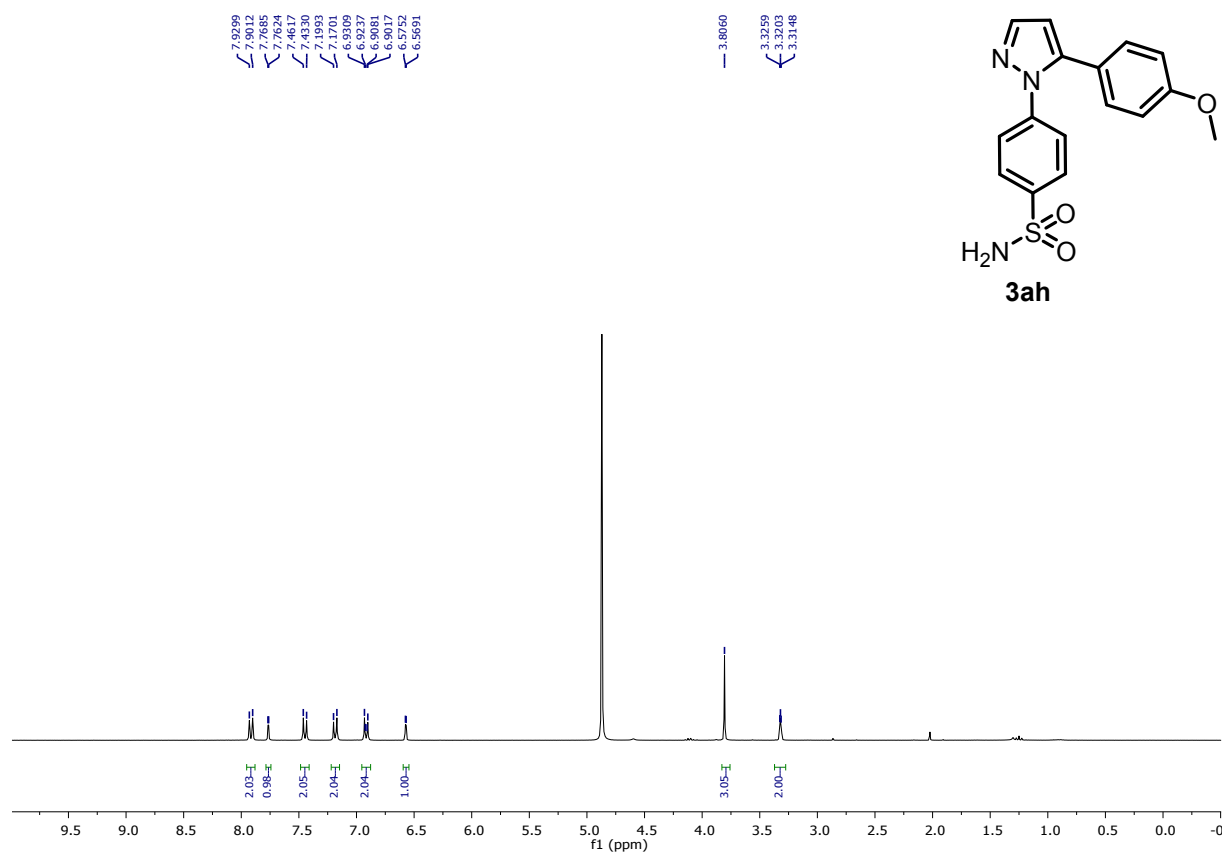


$^1\text{H NMR}$ (400 MHz, CDCl_3) of 5-(4-Methoxyphenyl)-1-(4-(pentafluoro-sulfanyl)phenyl)-1H-pyrazole

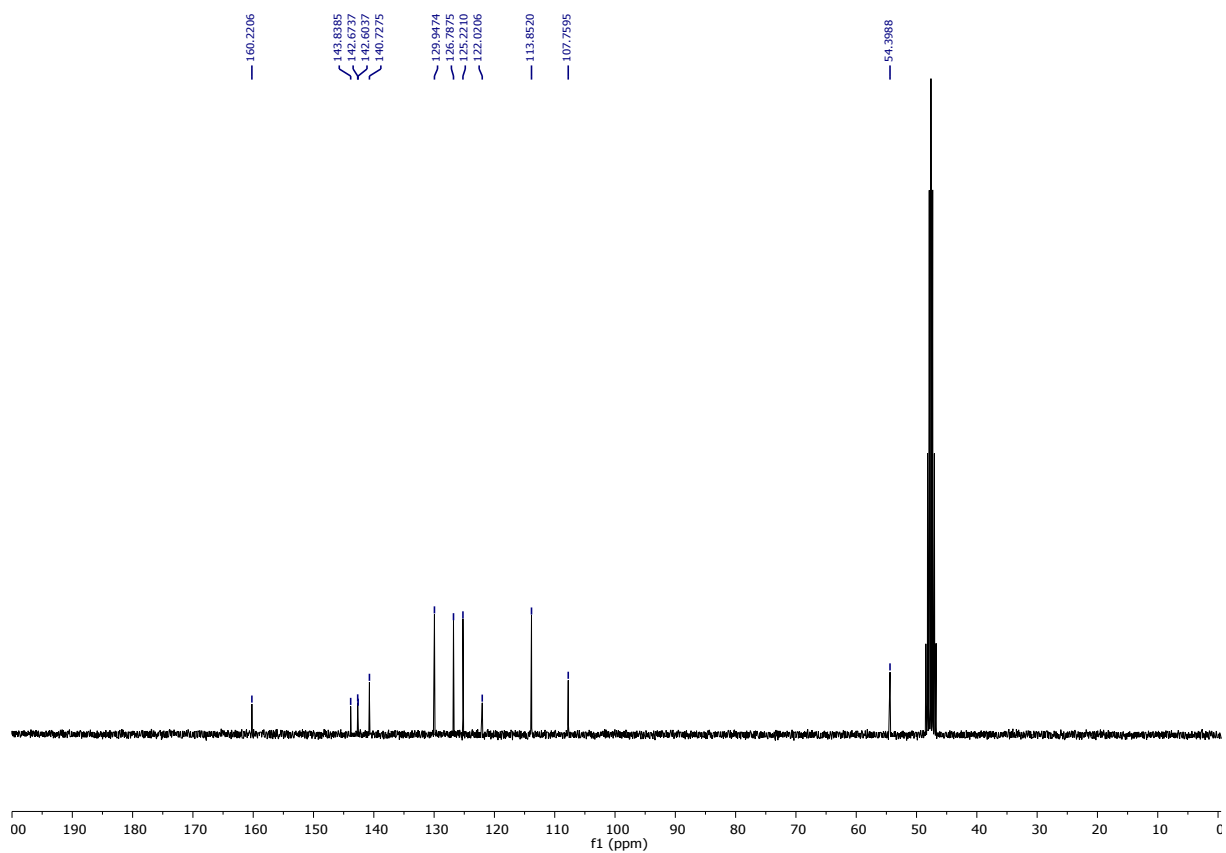


$^{13}\text{C NMR}$ (100 MHz, CDCl_3) of 5-(4-Methoxyphenyl)-1-(4-(pentafluoro-sulfanyl)phenyl)-1H-pyrazole

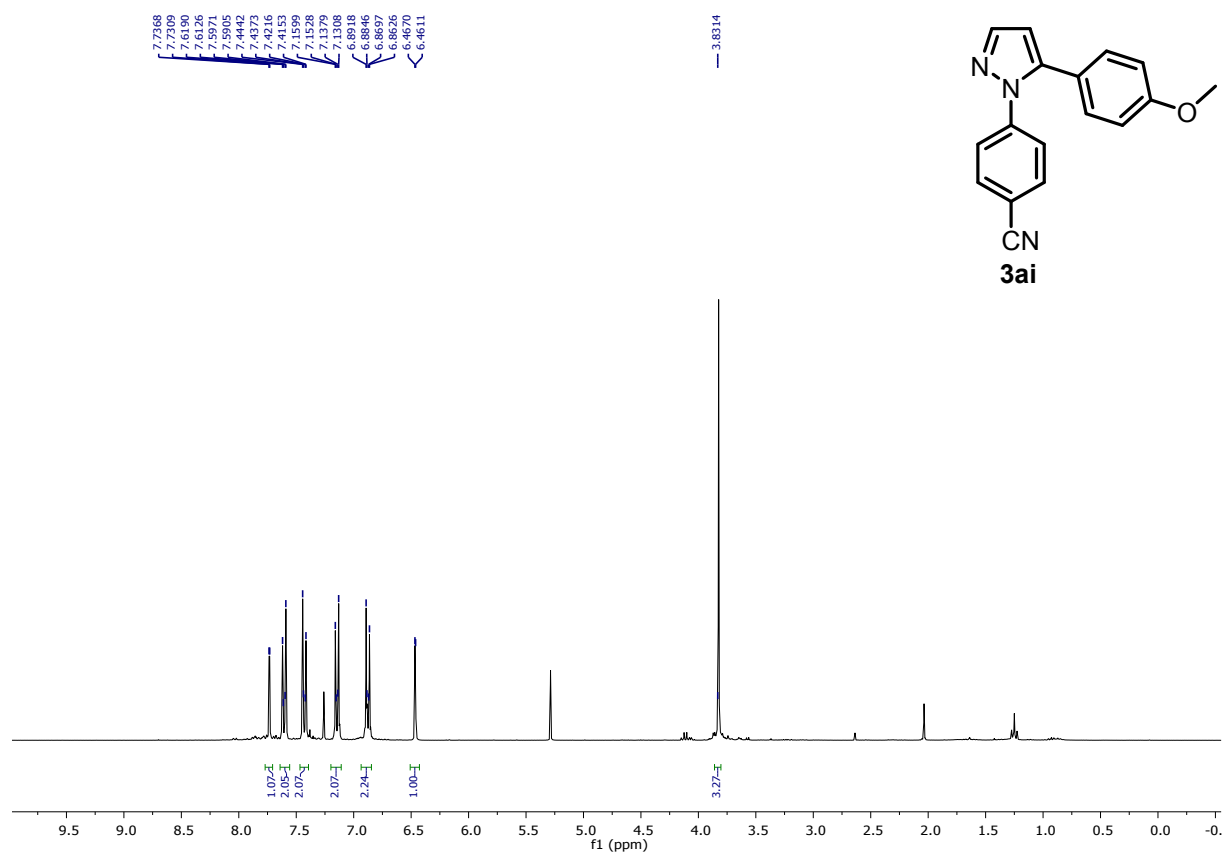




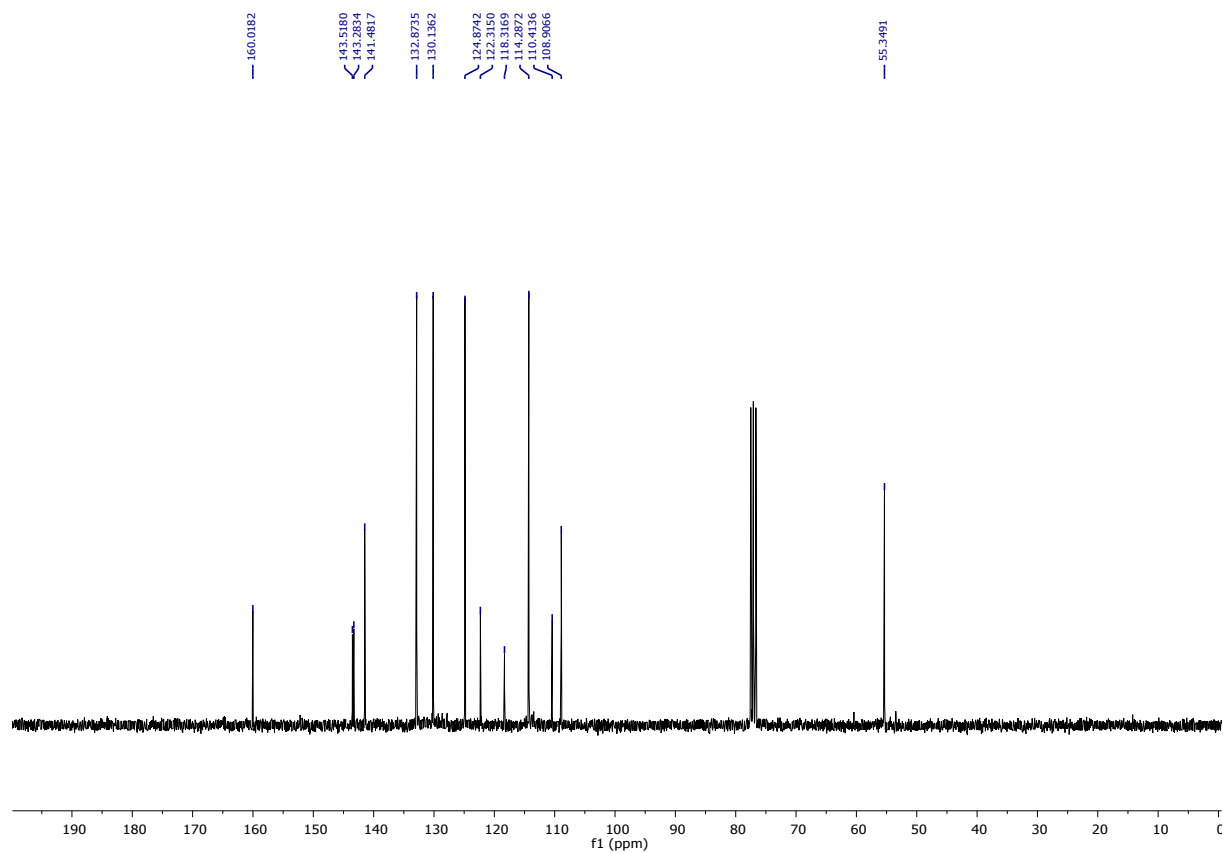
¹H NMR (300 MHz, MeOD) of 4-(5-(4-methoxyphenyl)-1H-pyrazol-1-yl)benzenesulfonamide



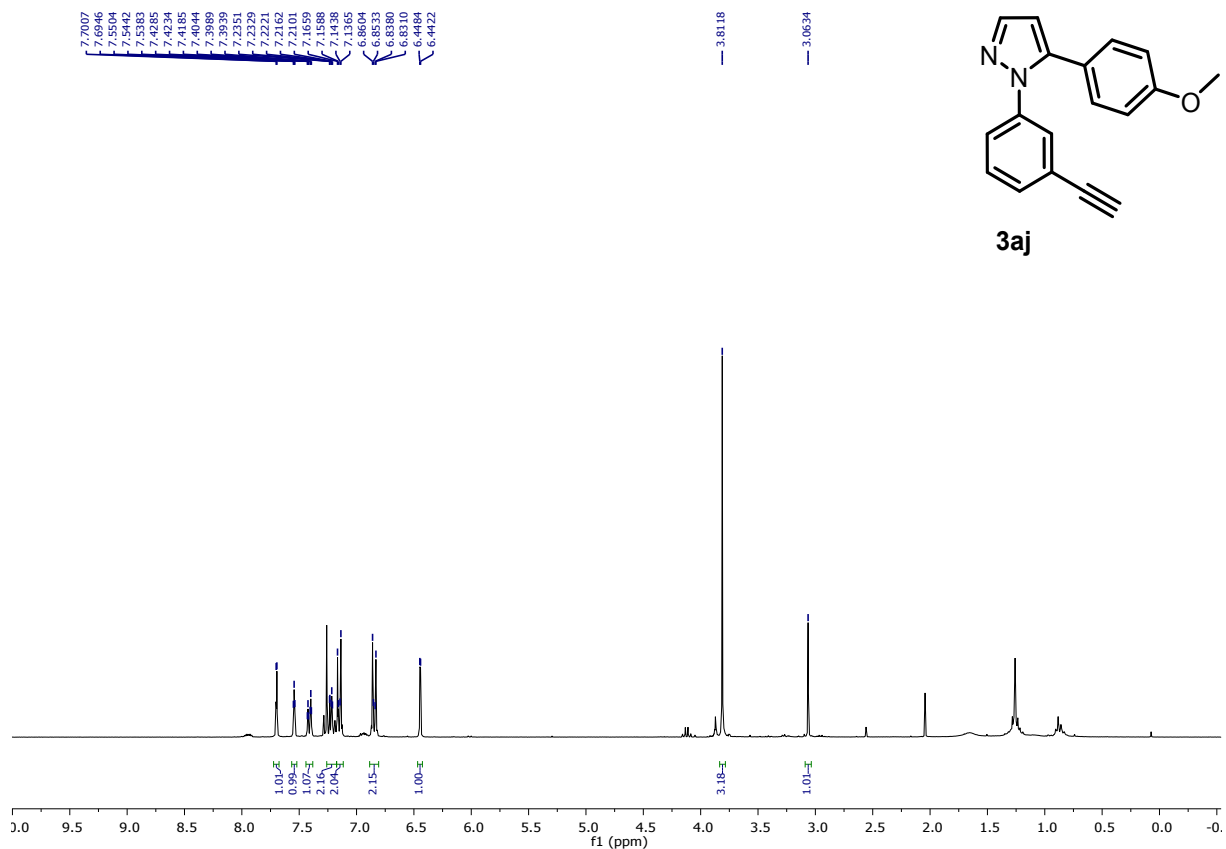
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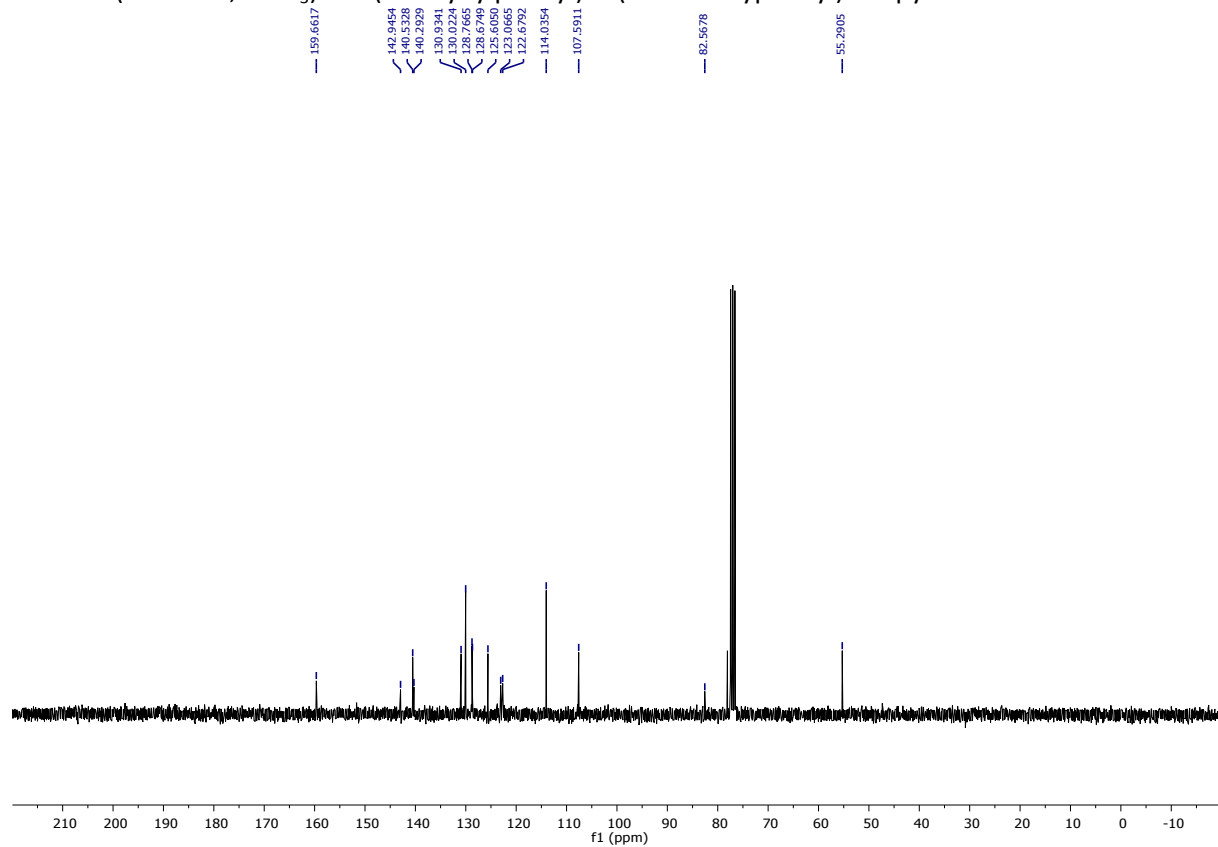
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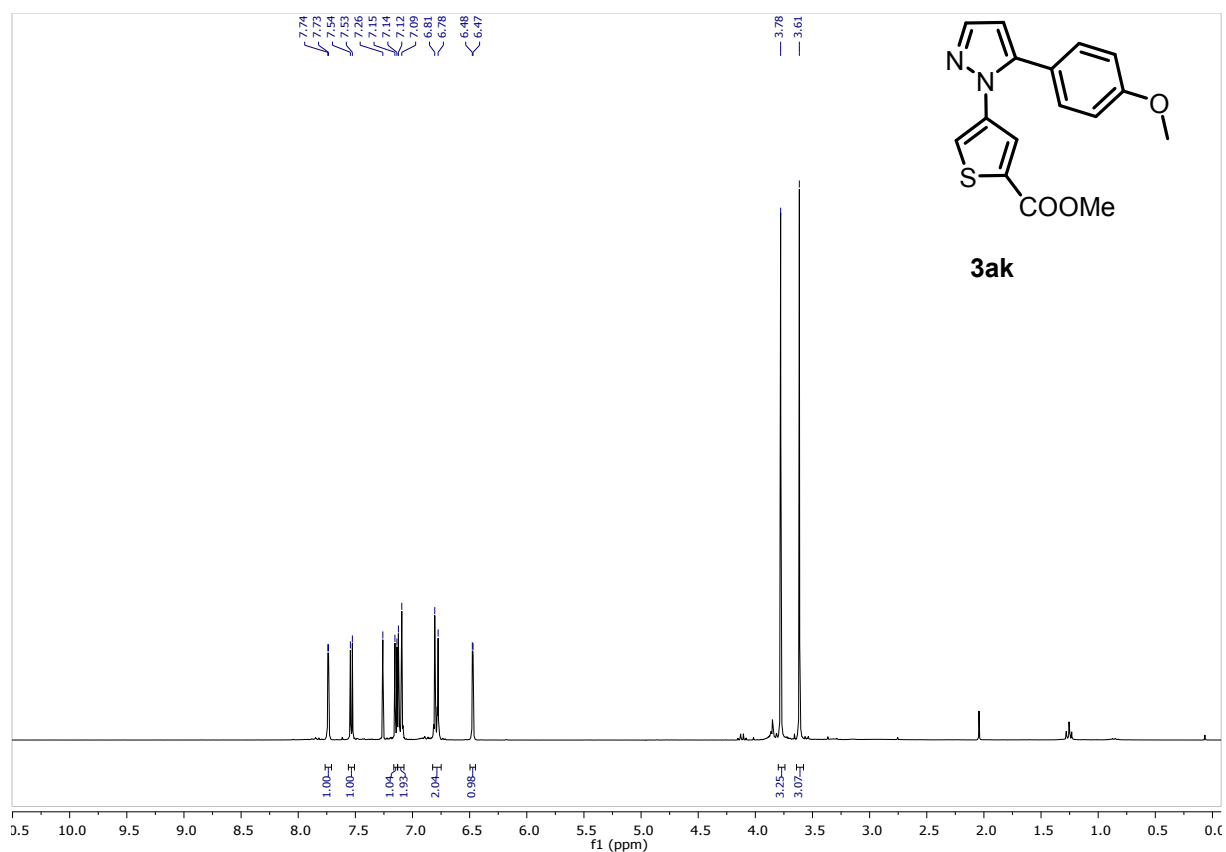
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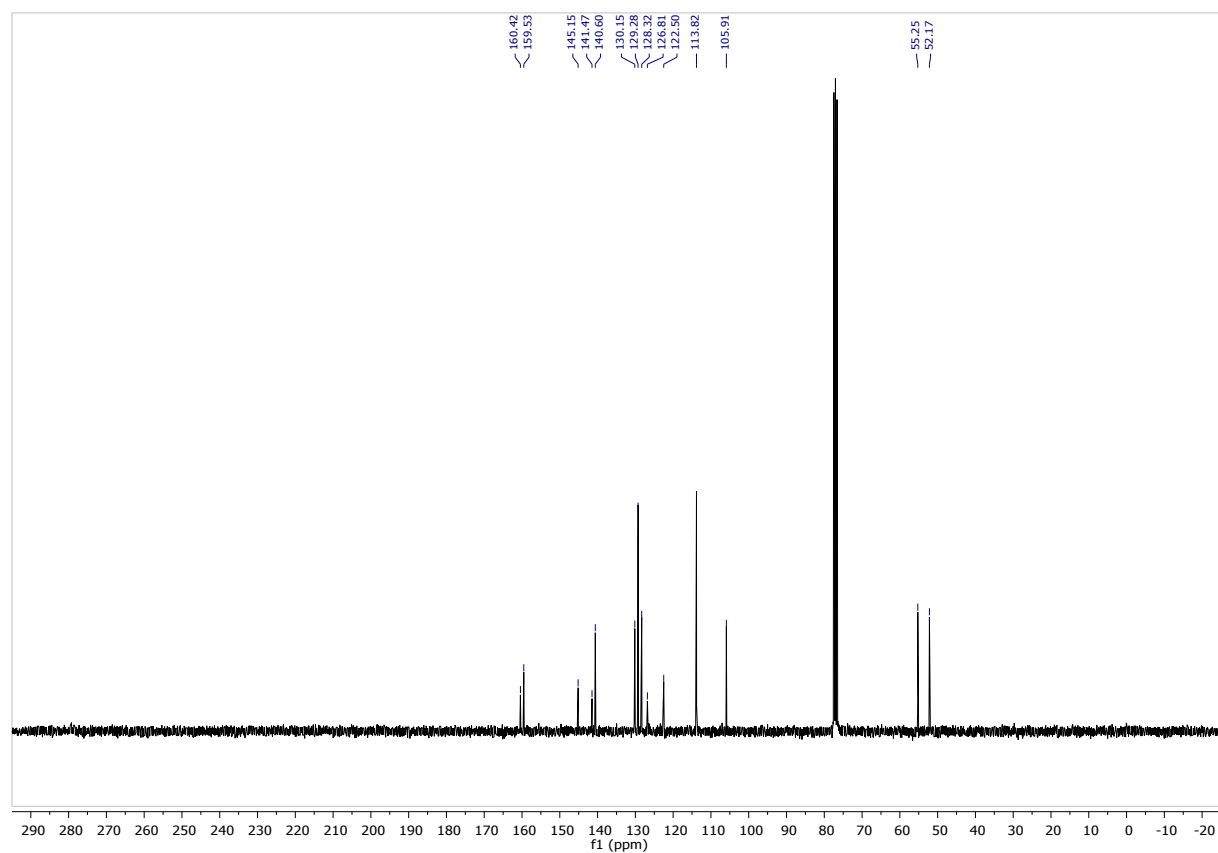
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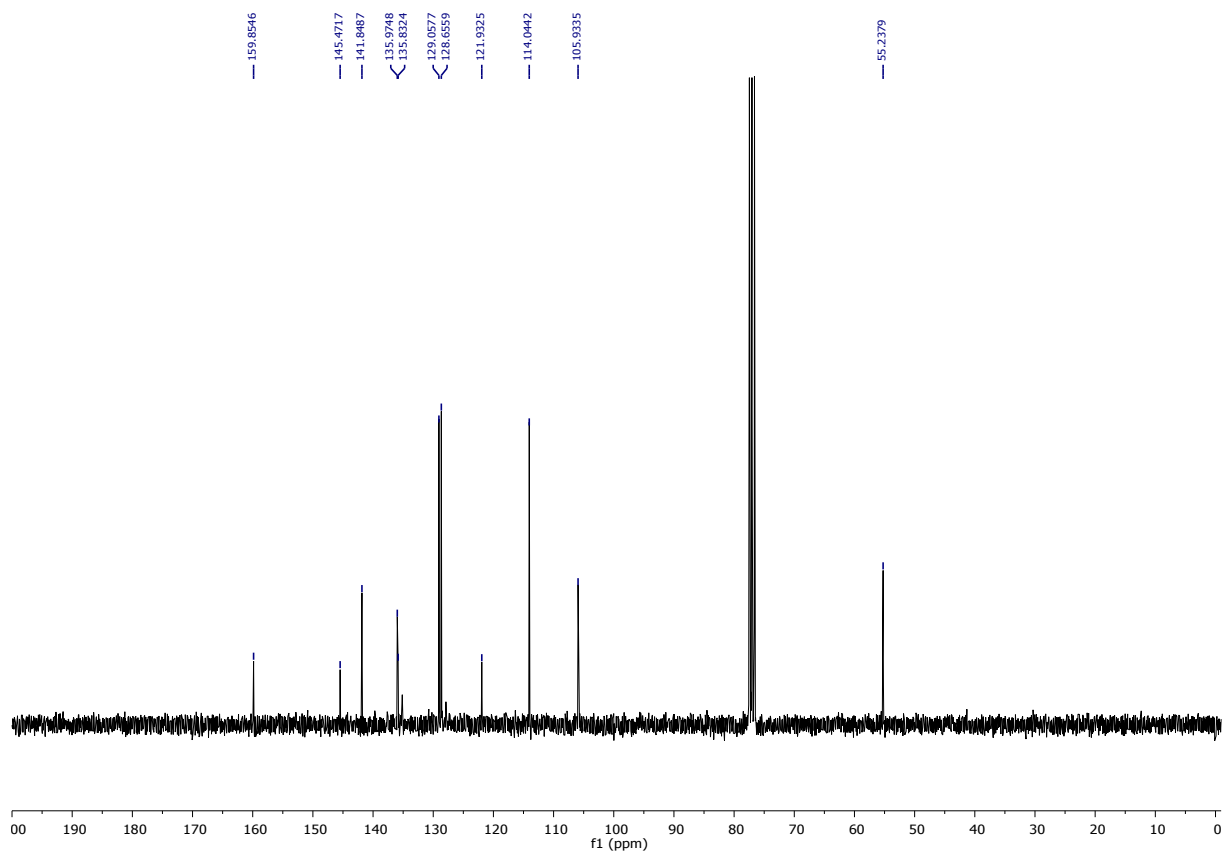
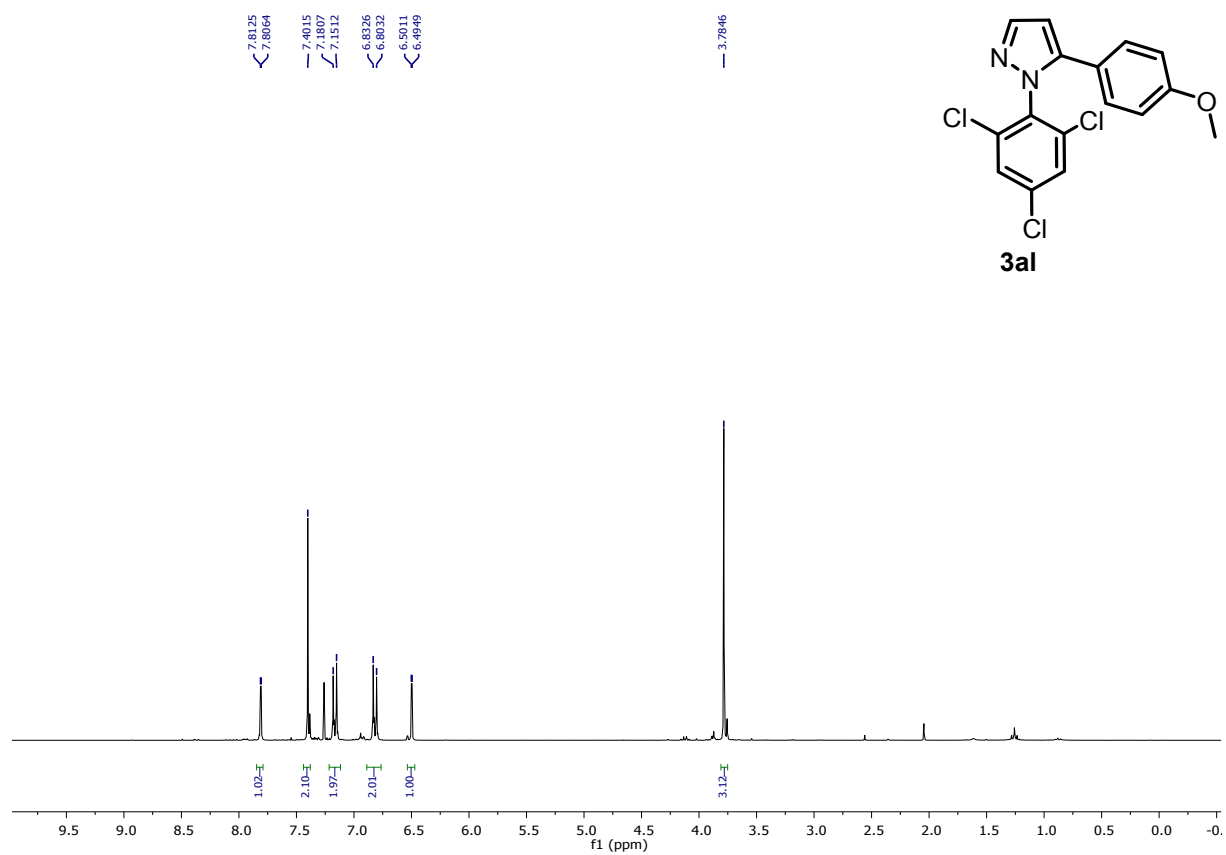
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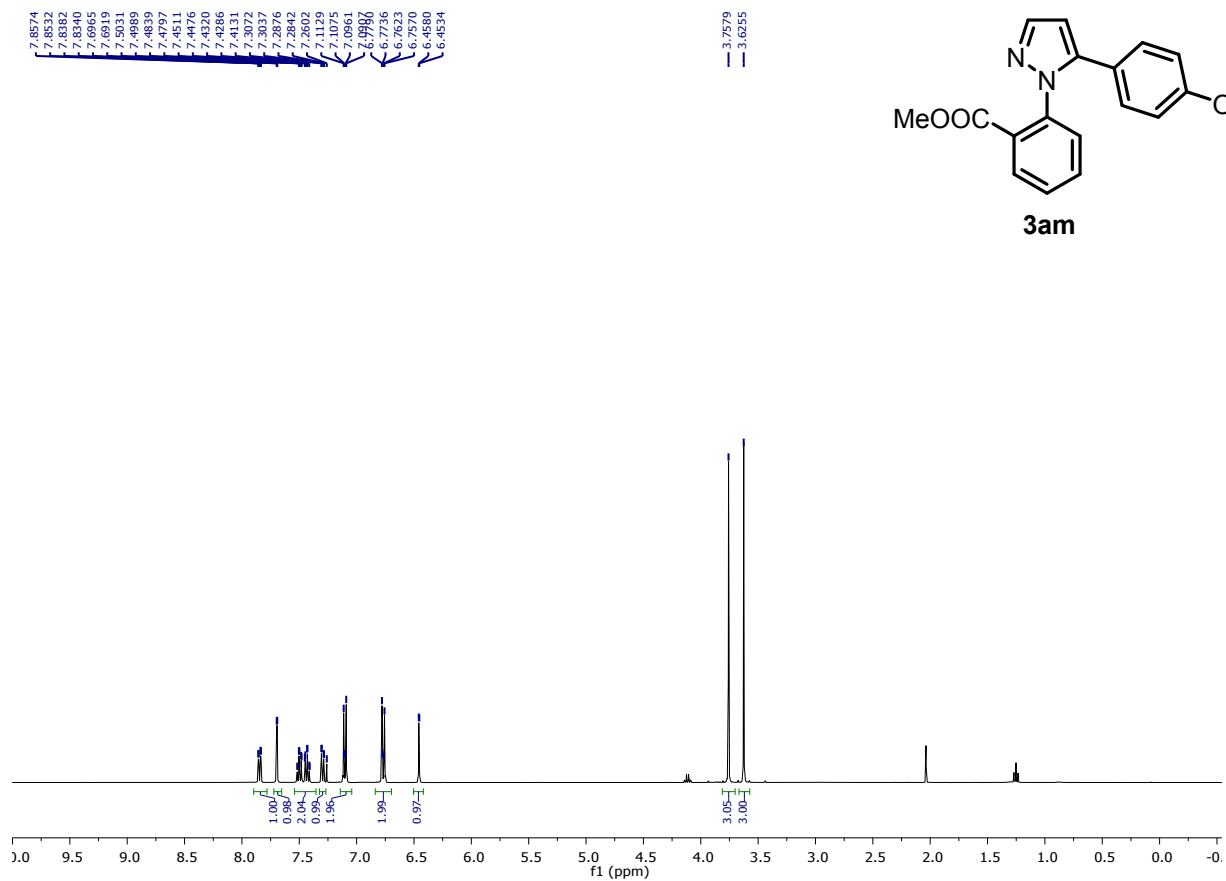


¹H NMR (300 MHz, CDCl₃) of Methyl 3-(5-(4-methoxyphenyl)-1H-pyrazol-1-yl) thiophene-2-carboxylate

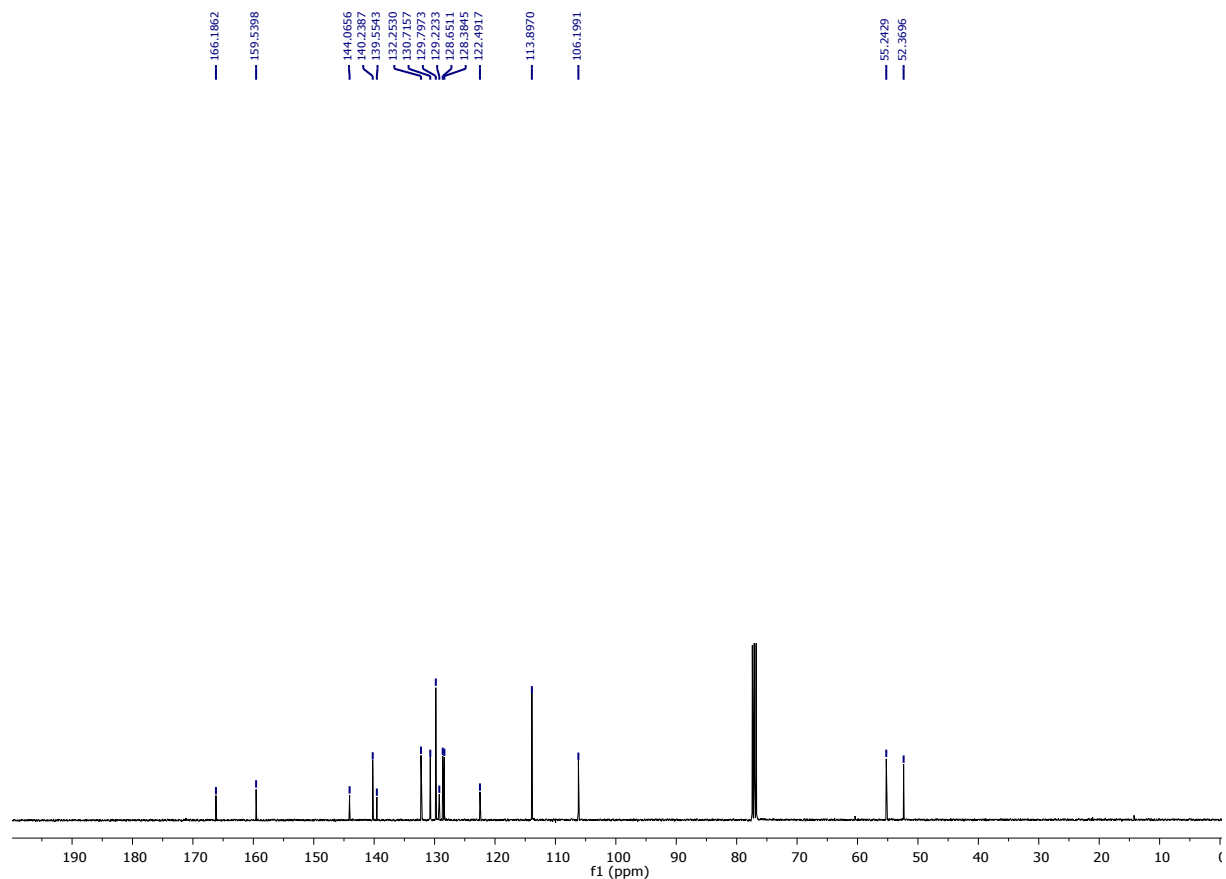


¹³C NMR (75 MHz, CDCl₃) of Methyl 3-(5-(4-methoxyphenyl)-1H-pyrazol-1-yl) thiophene-2-carboxylate

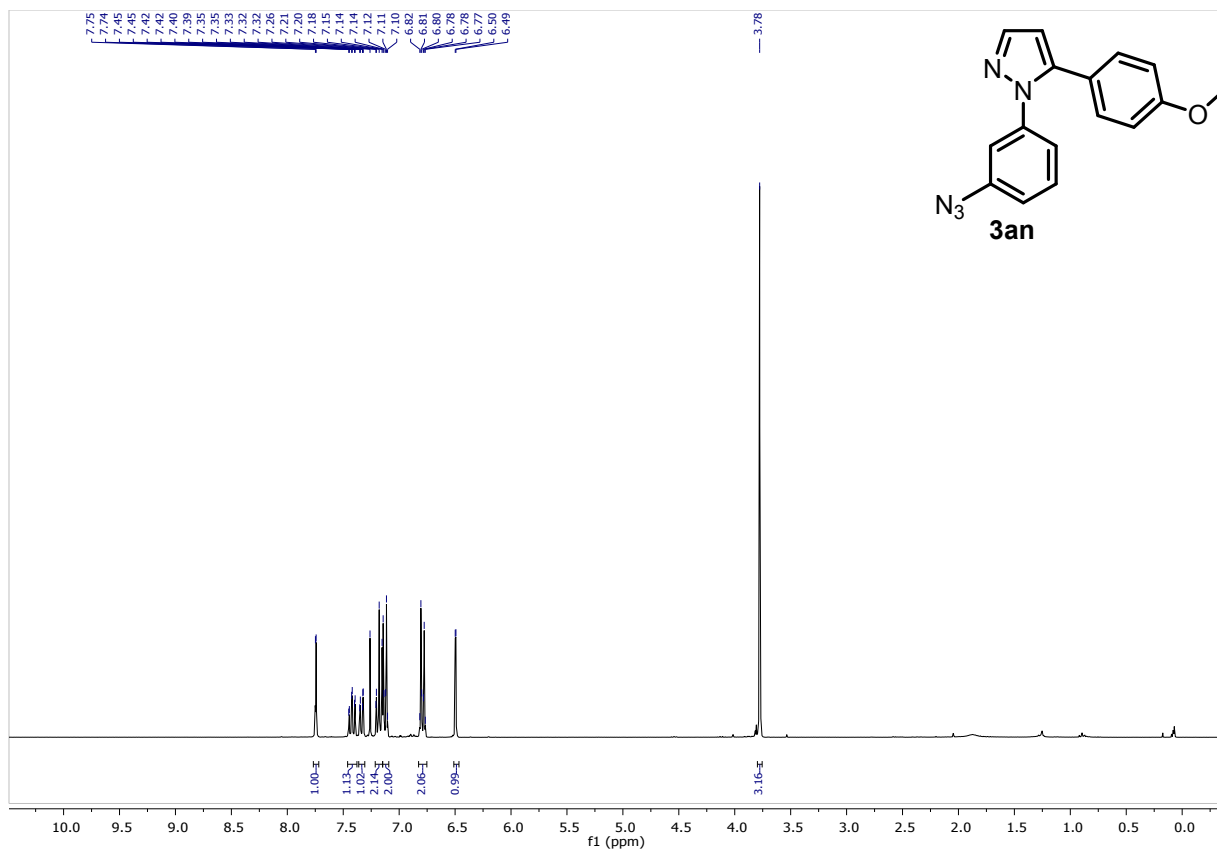




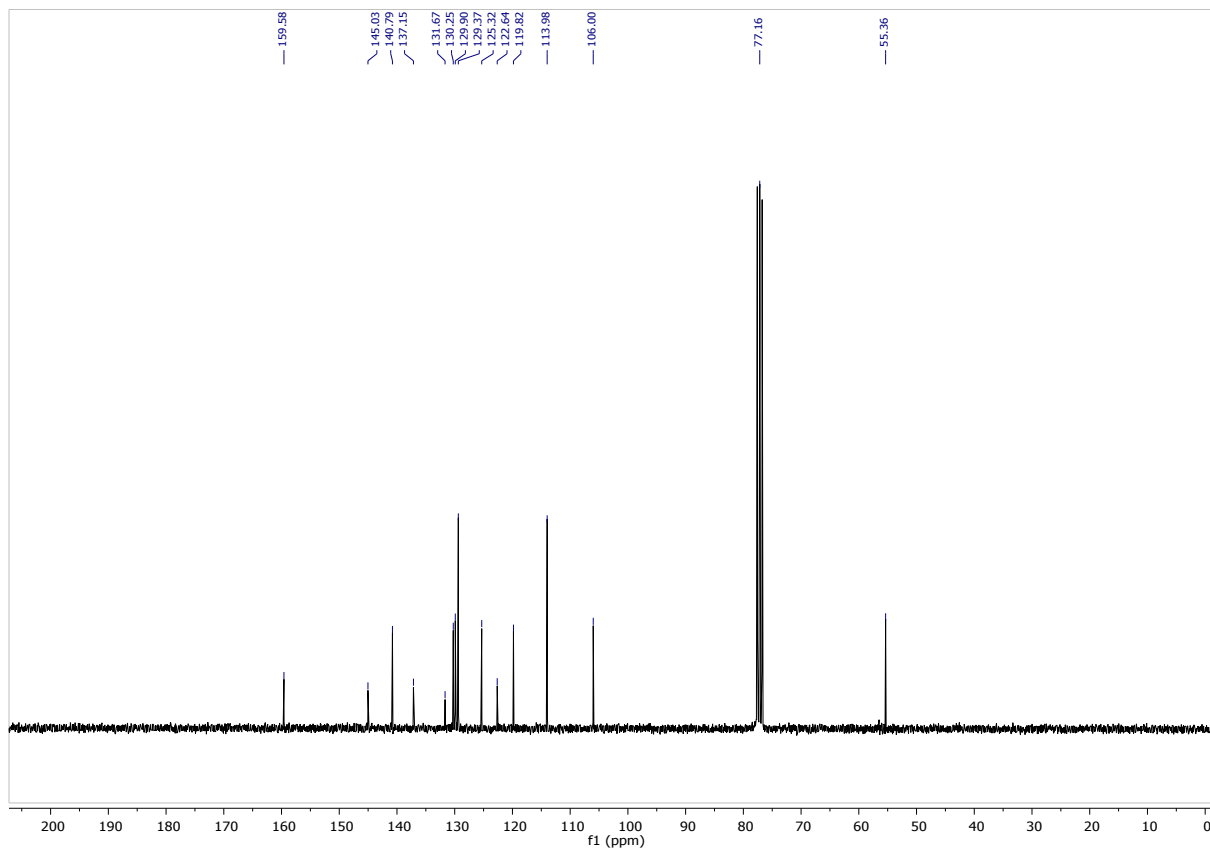
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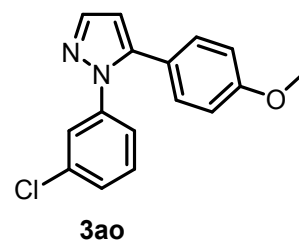
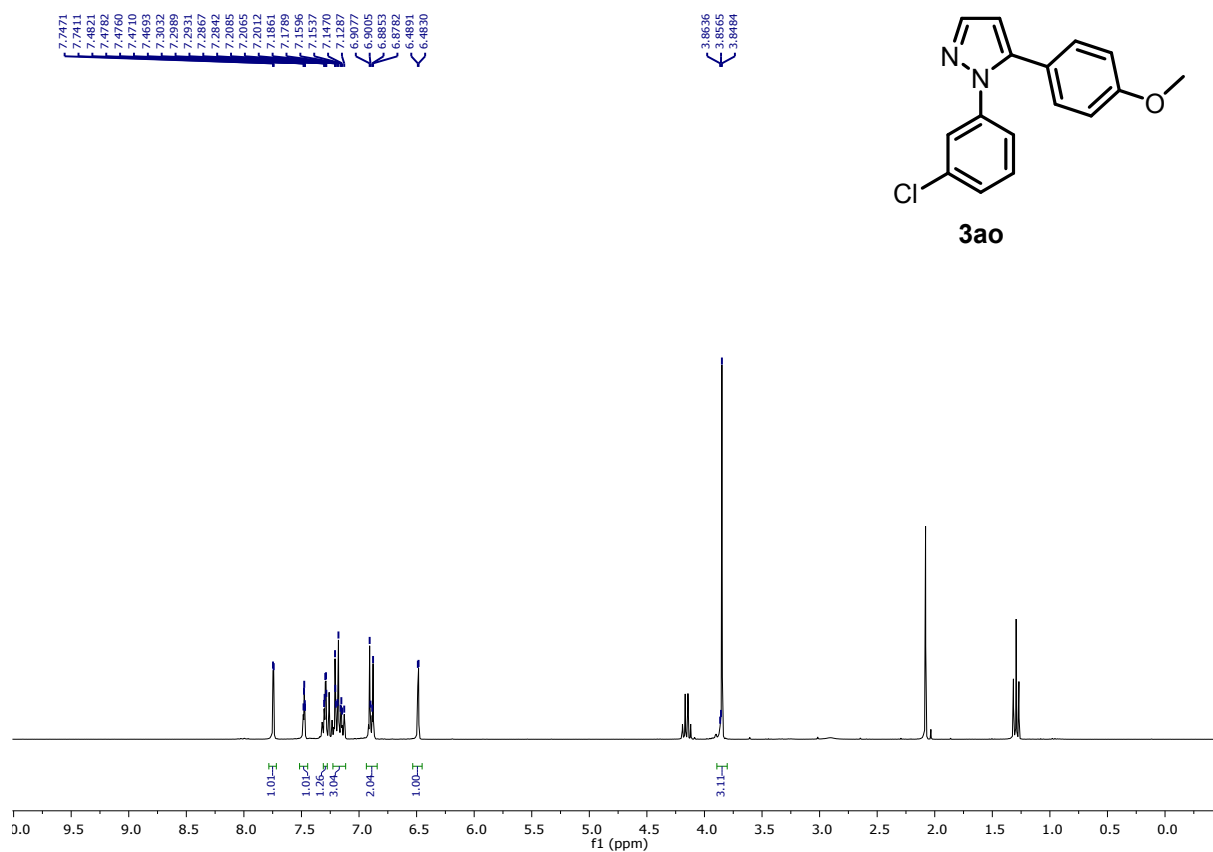
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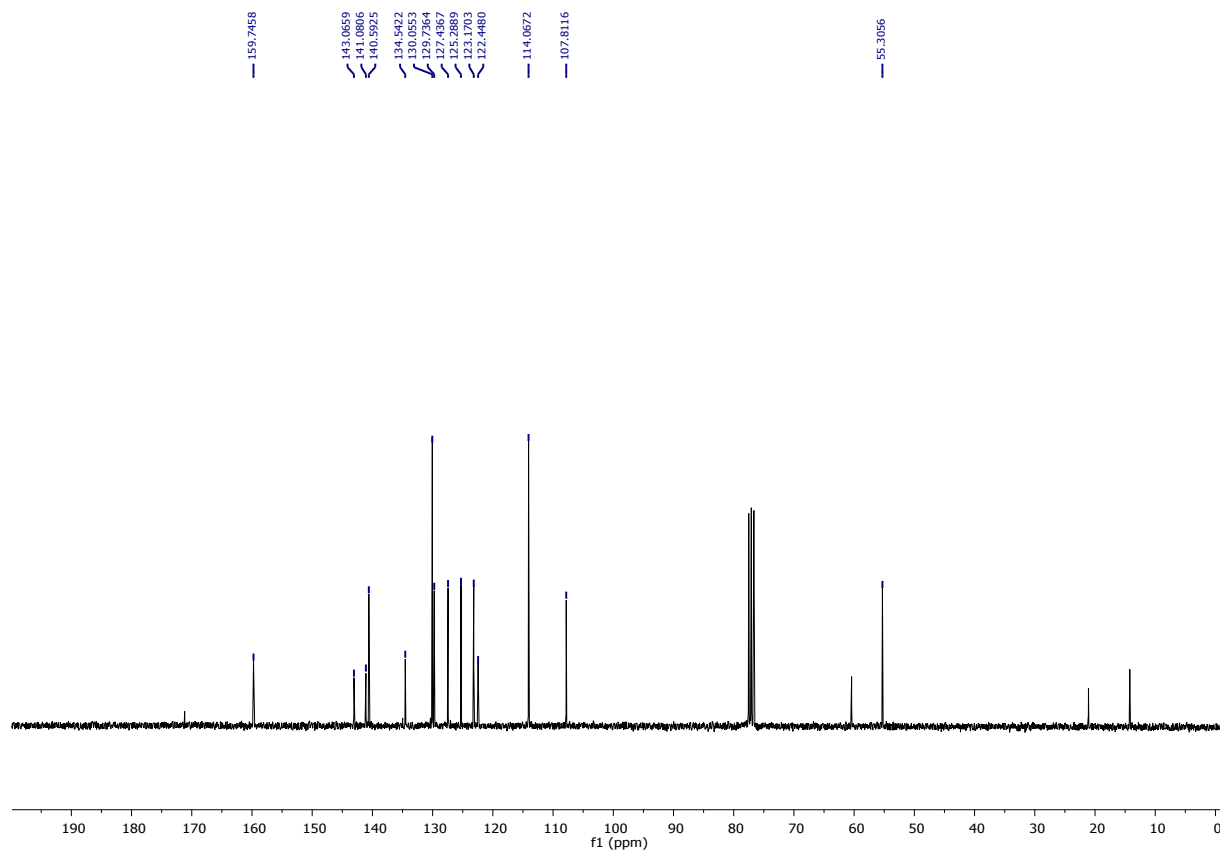
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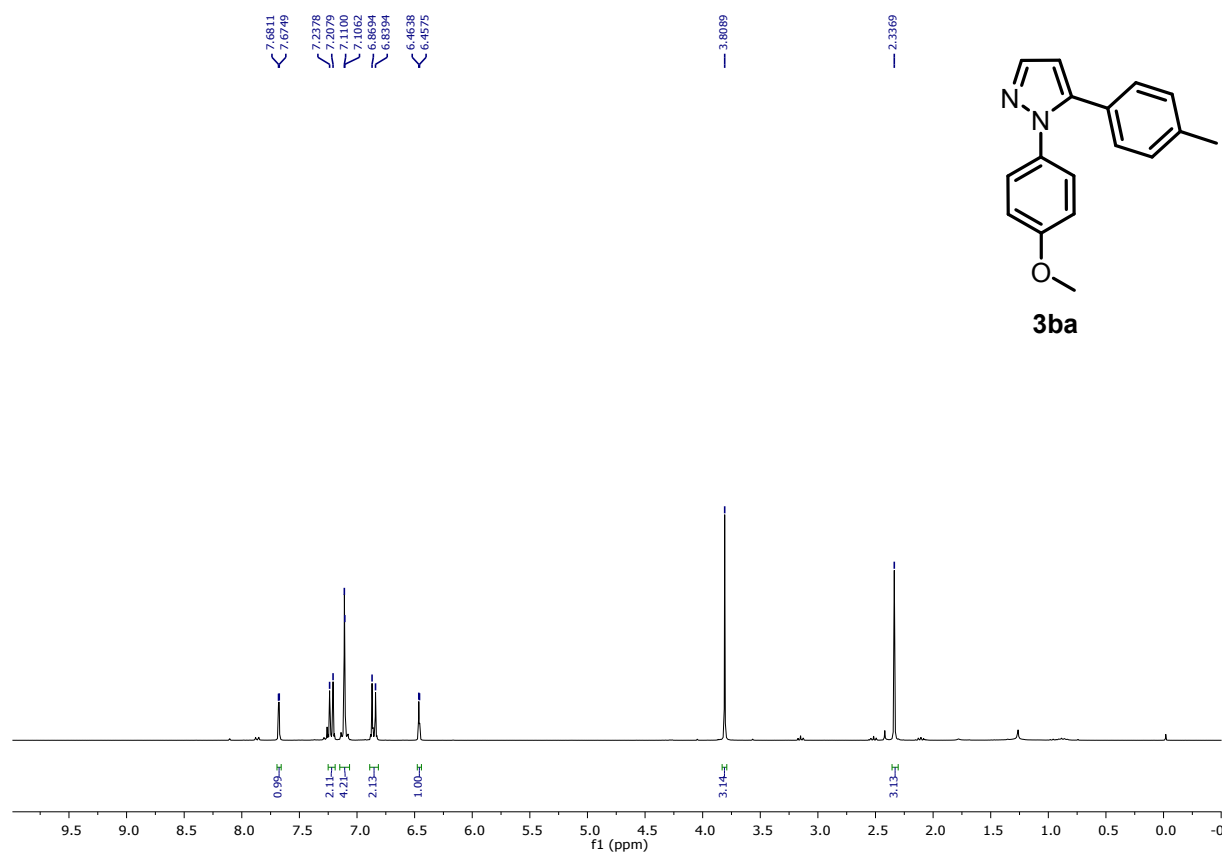
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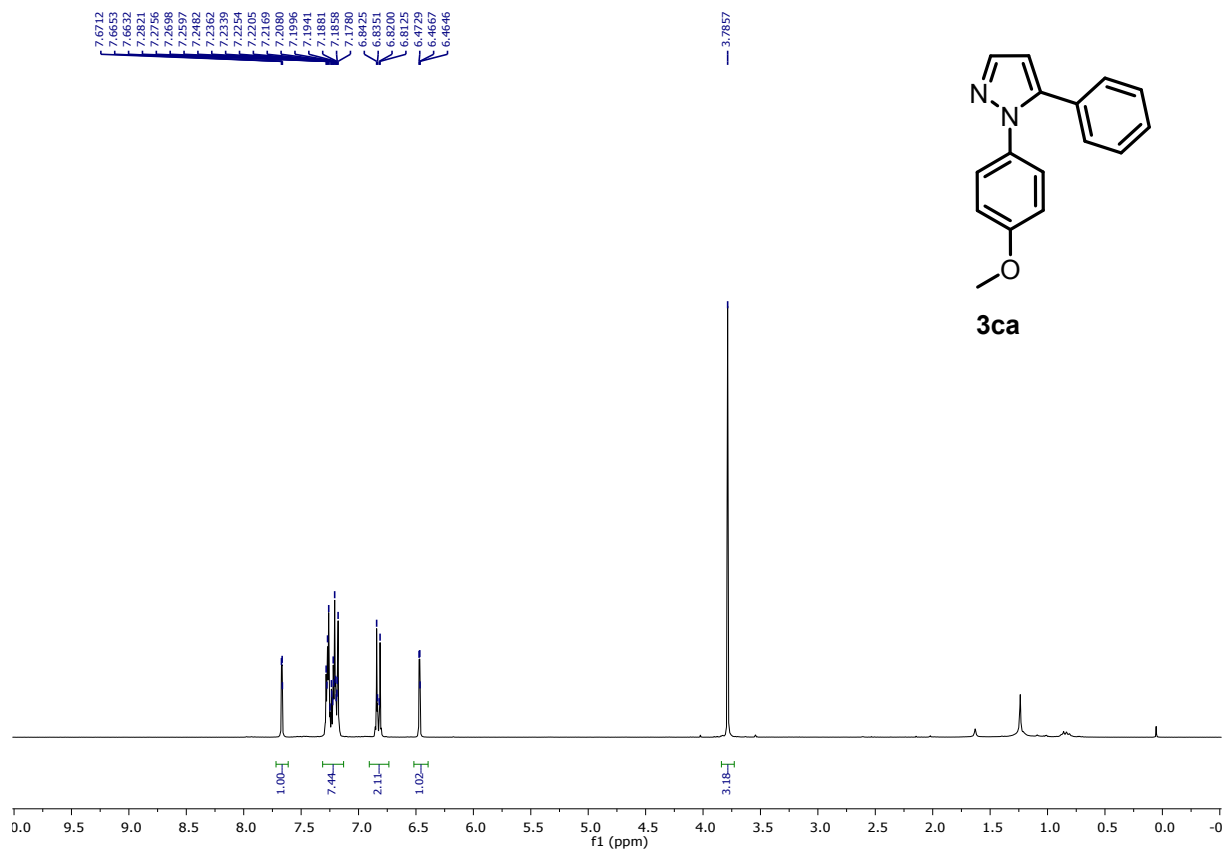


¹H NMR (400 MHz, CDCl₃) of 1-(3-chlorophenyl)-5-(4-methoxyphenyl)-1H-pyrazole

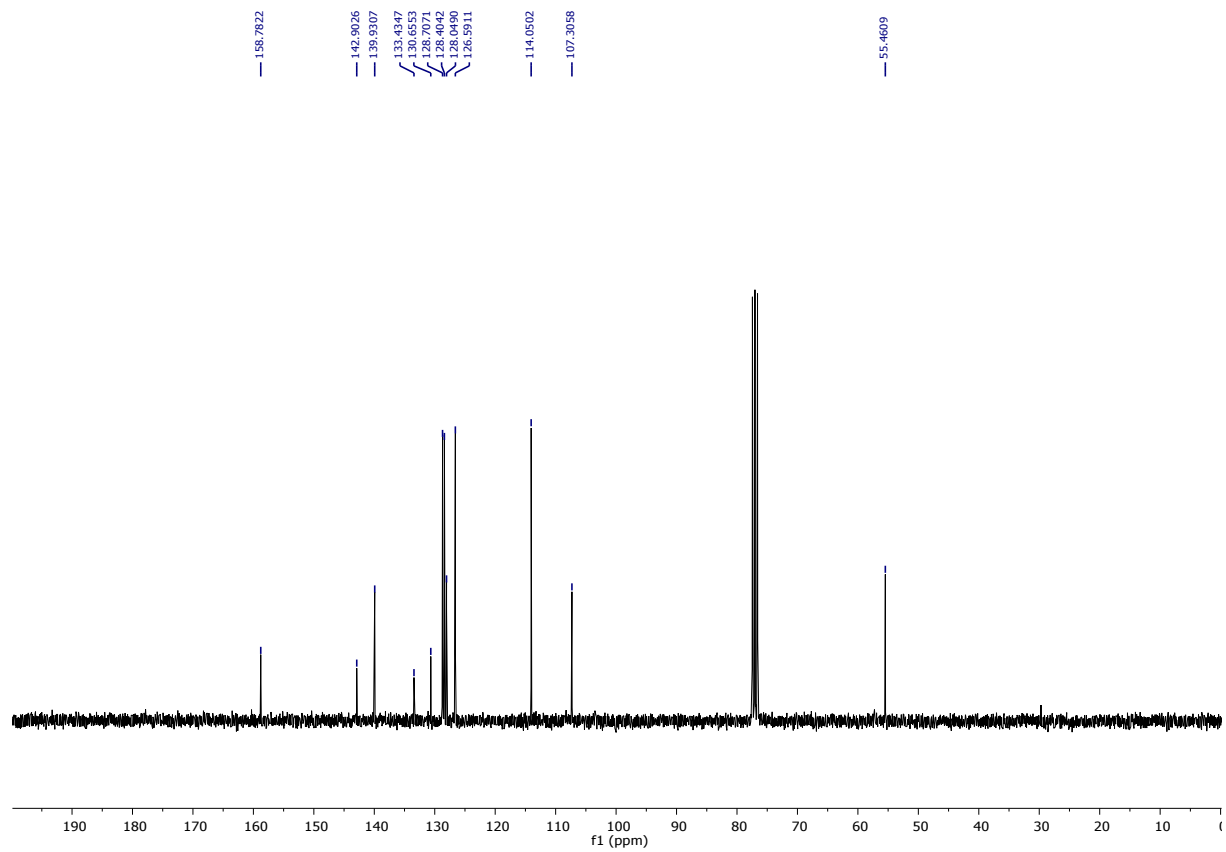


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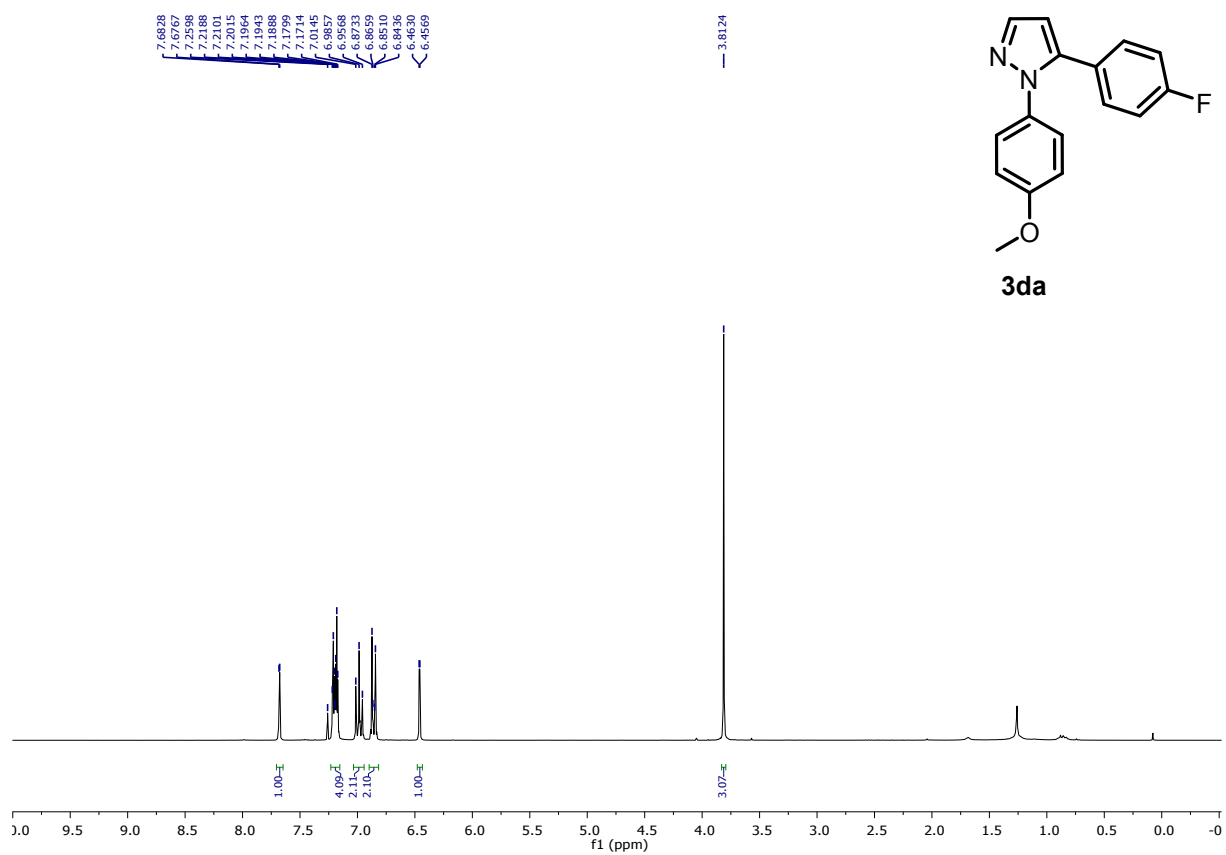




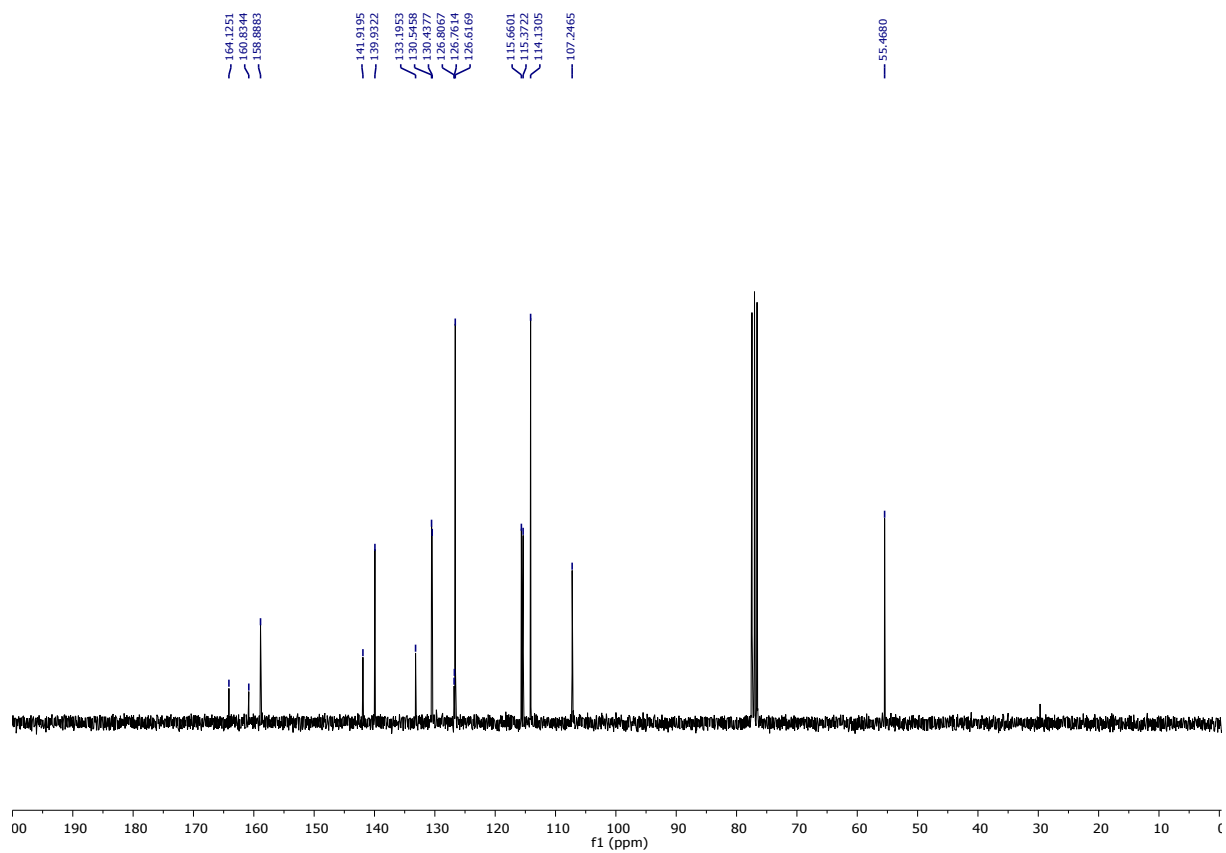
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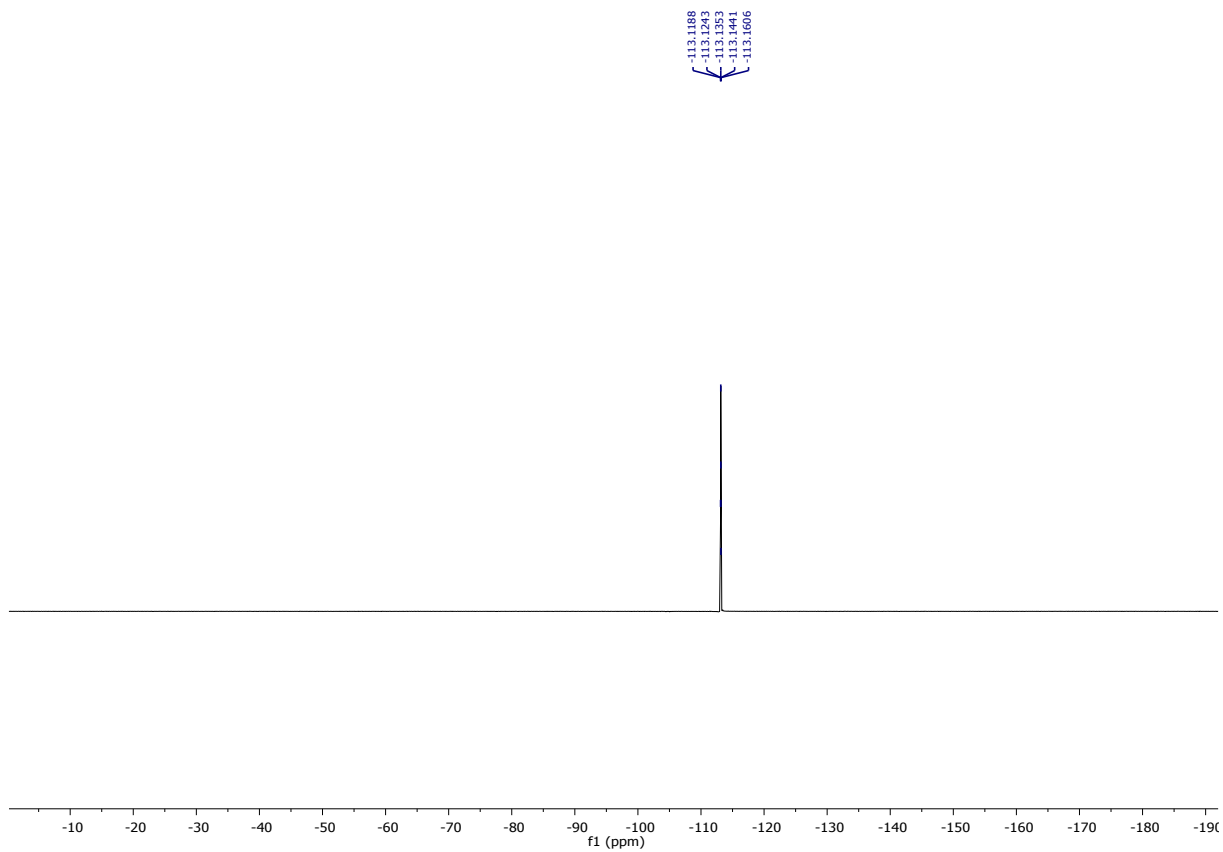
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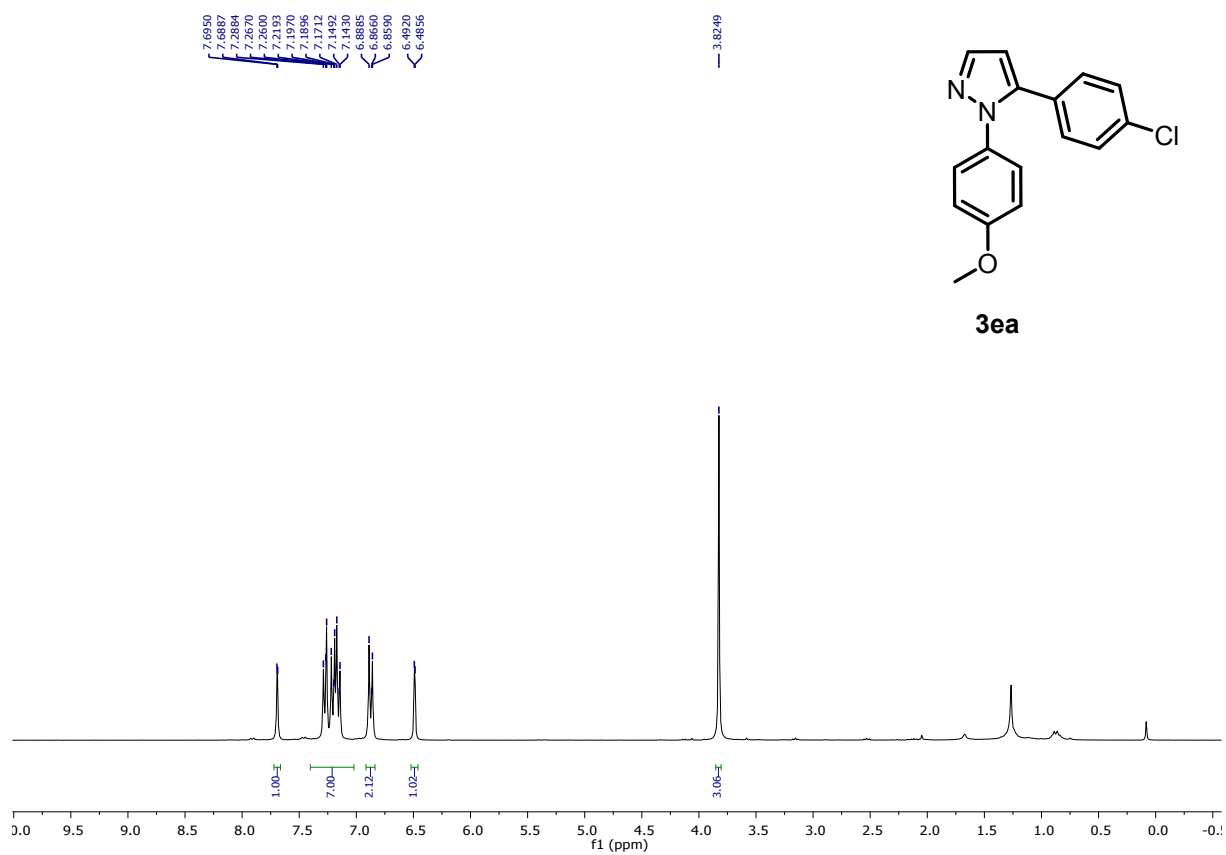


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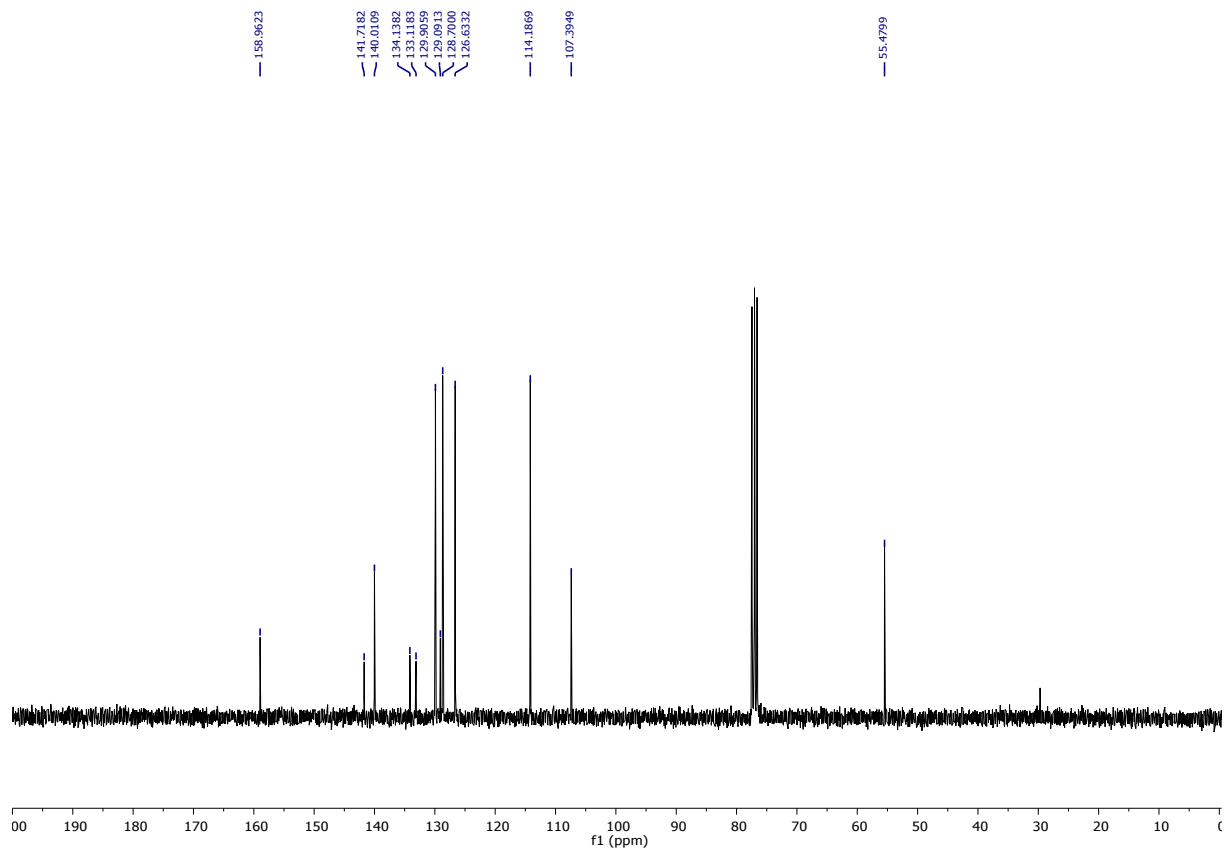


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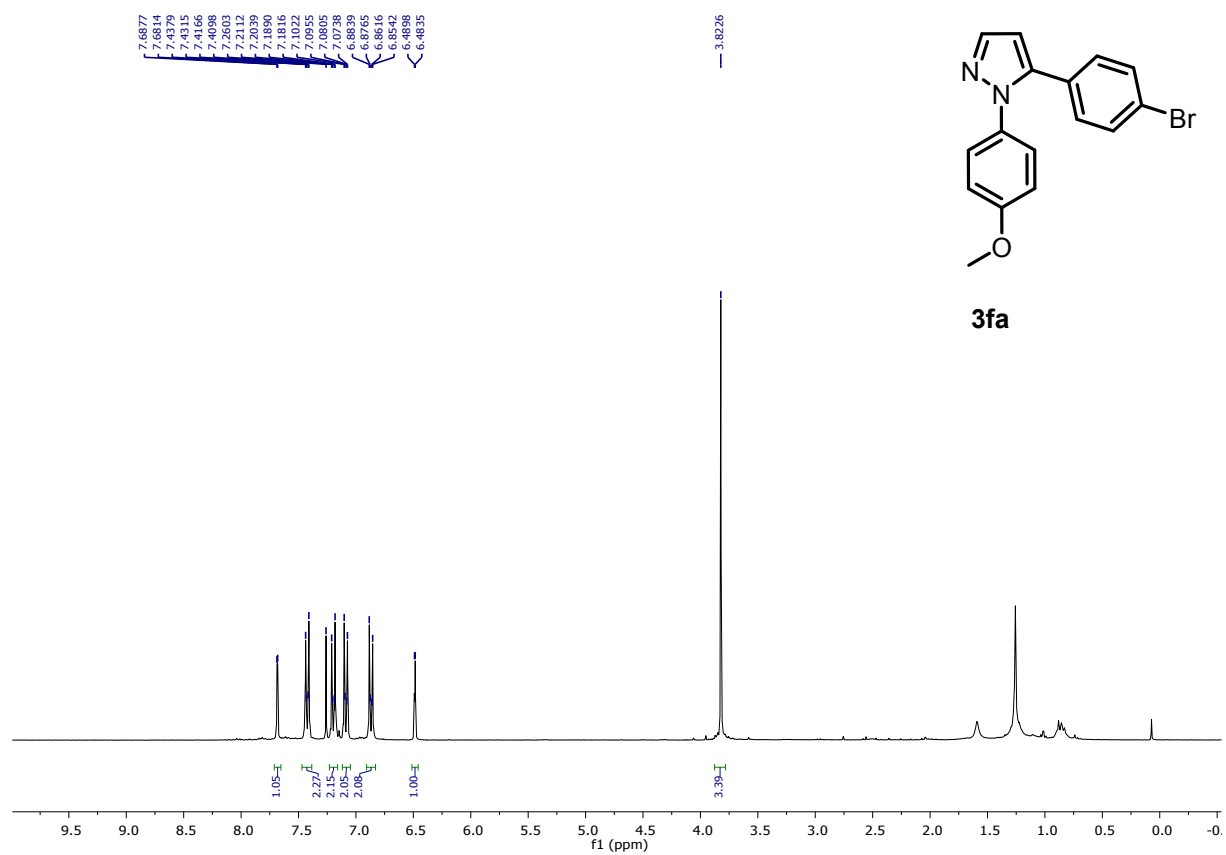




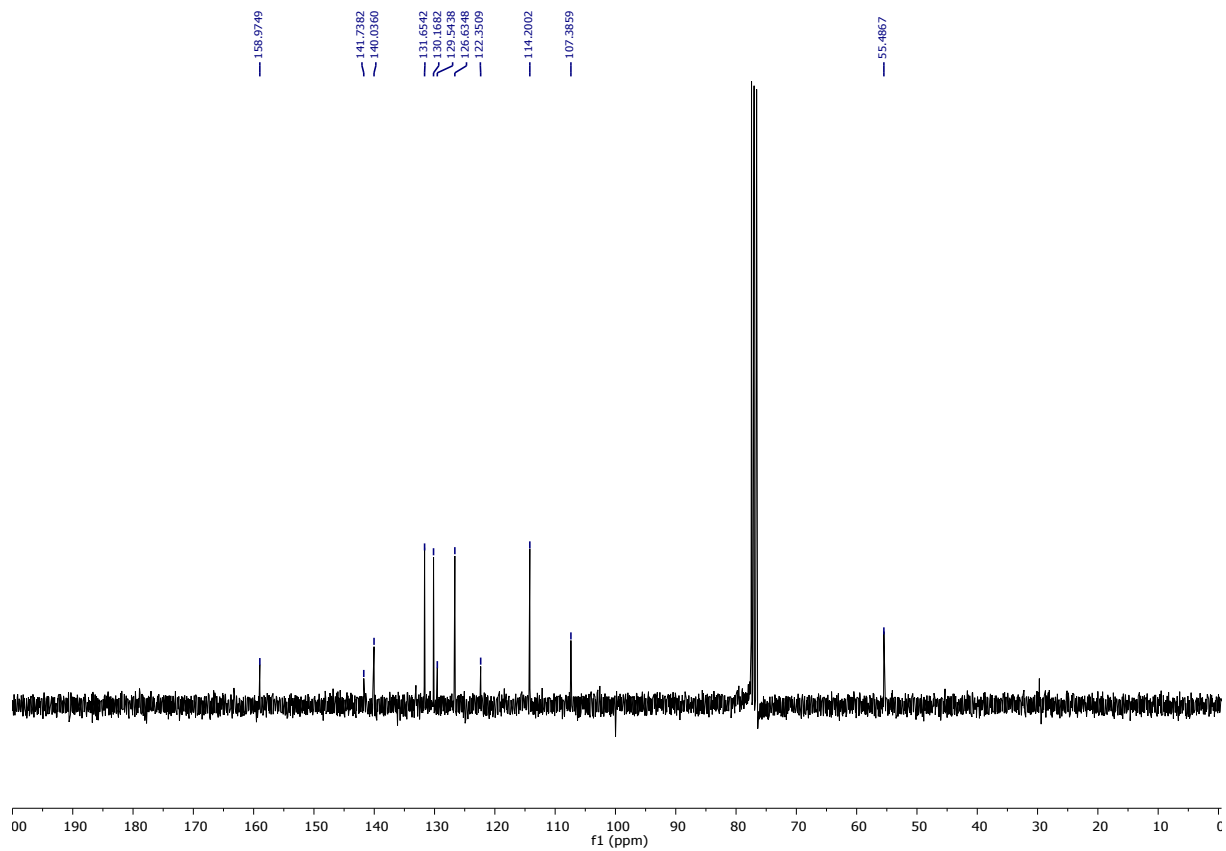
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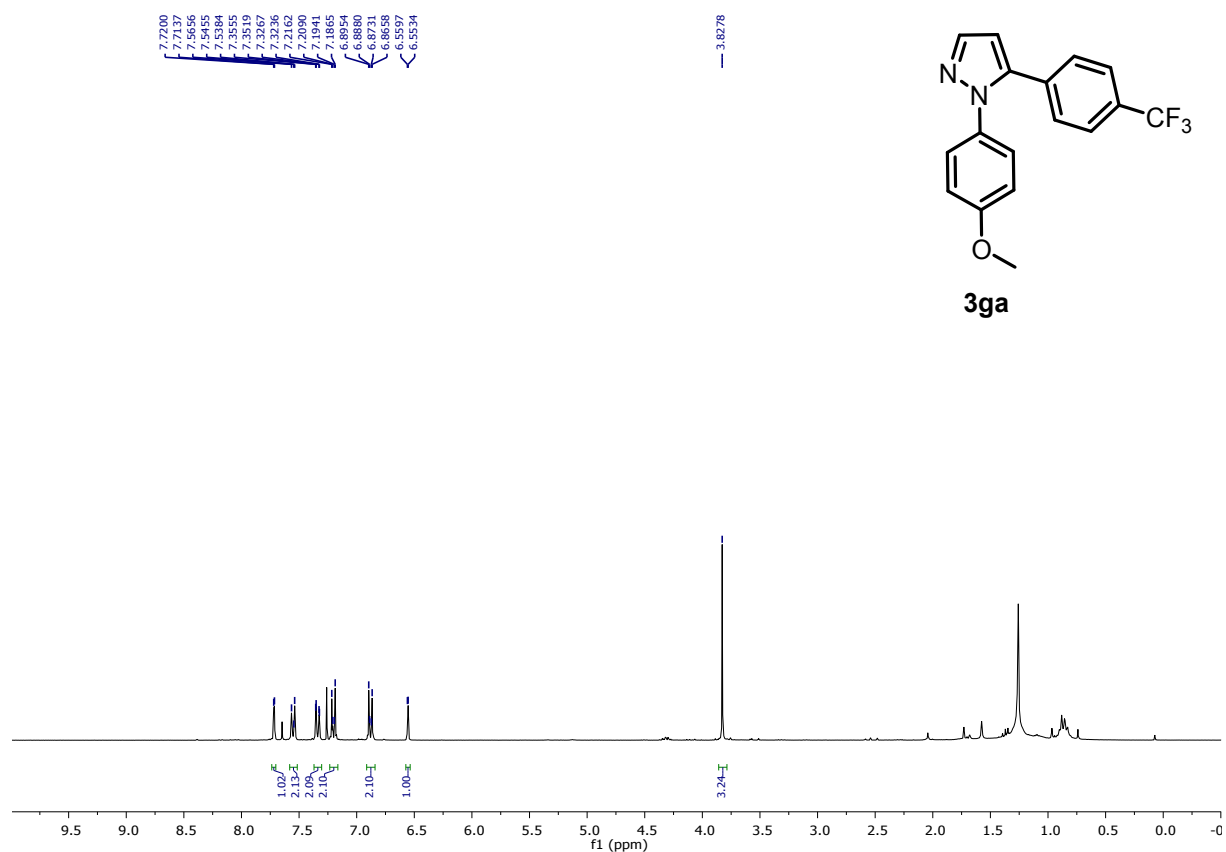
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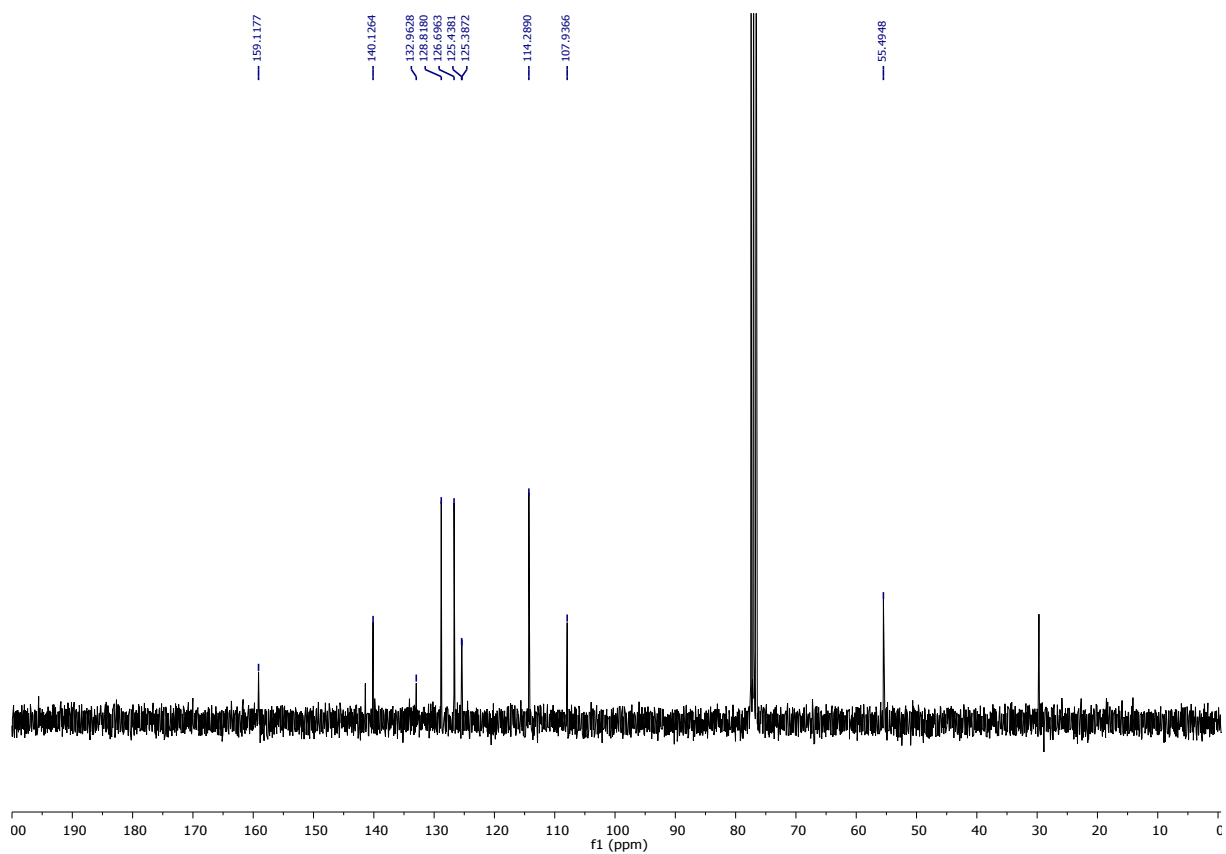
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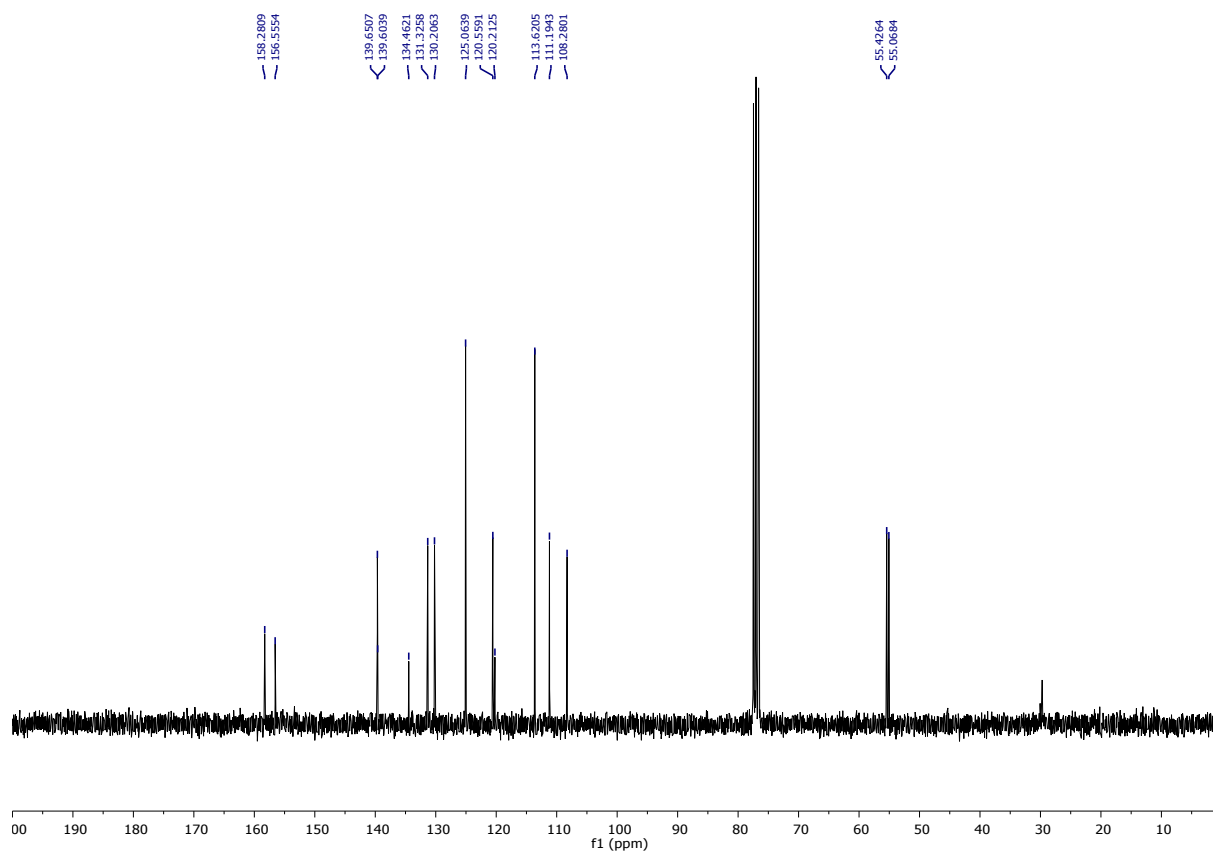
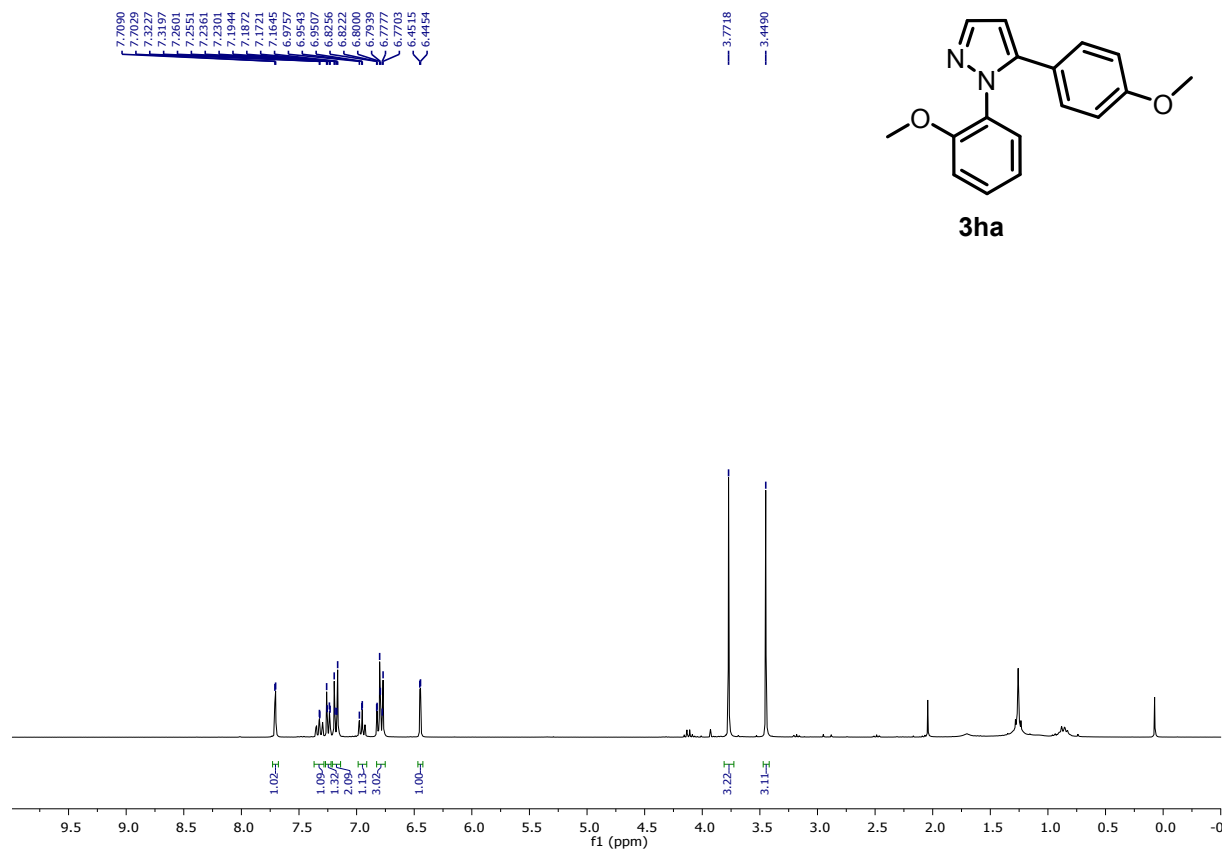
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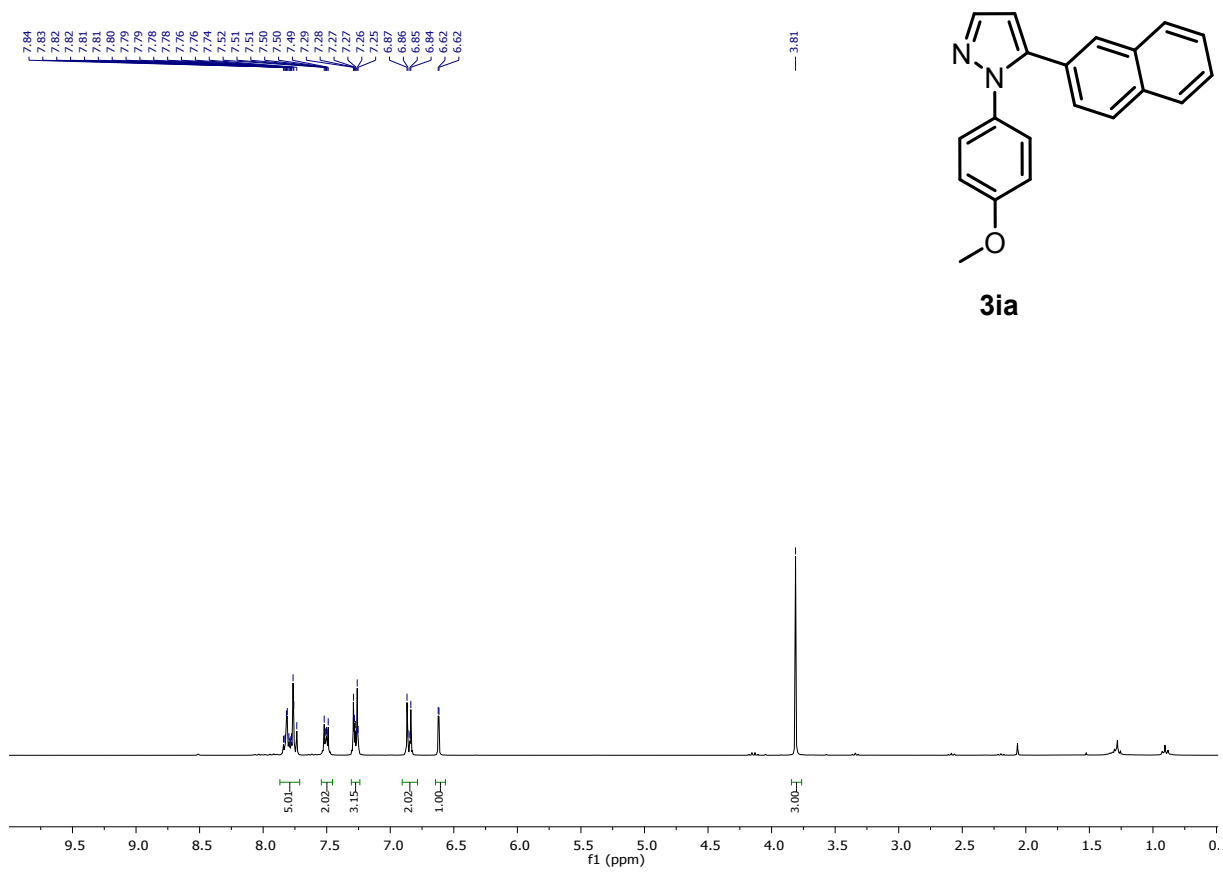


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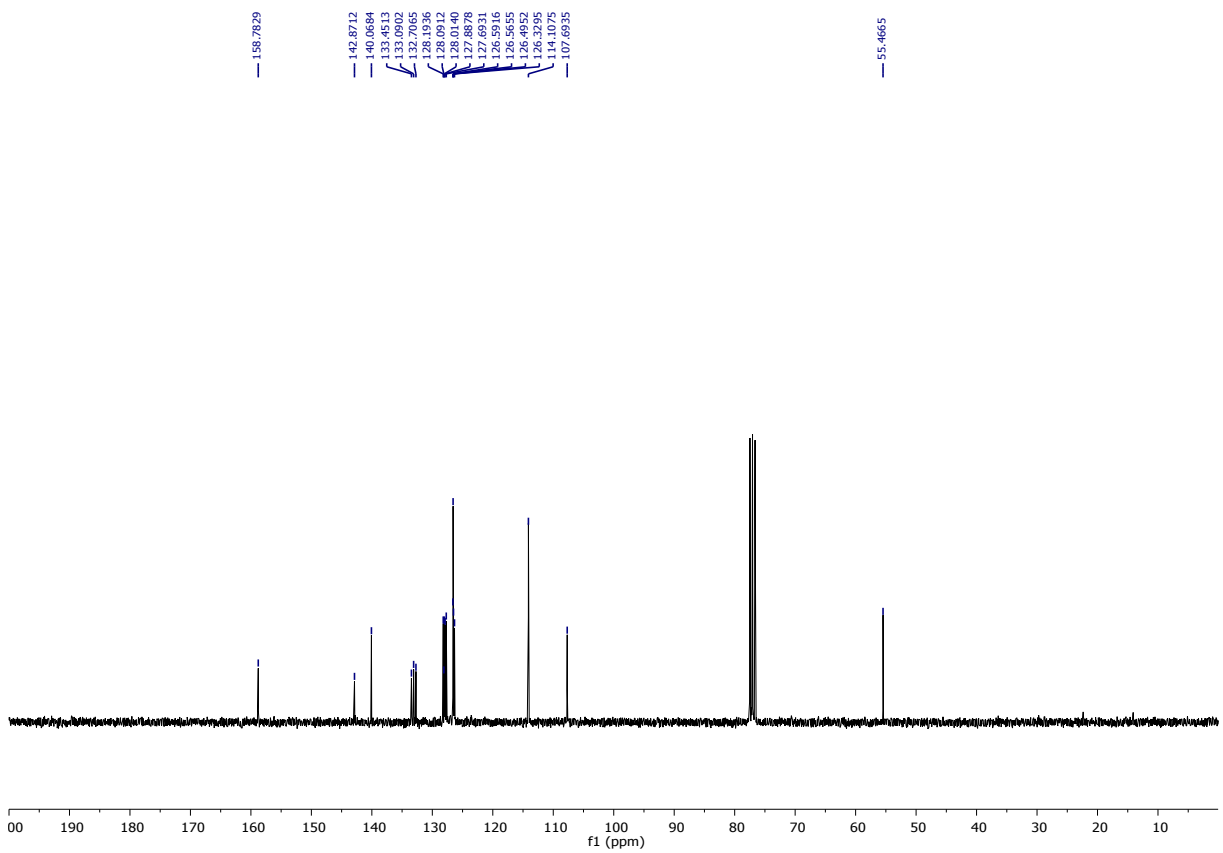


¹³C NMR (75 MHz, CDCl₃) of 1-(4-methoxyphenyl)-5-(4-(trifluoromethyl) phenyl)-1H-pyrazole

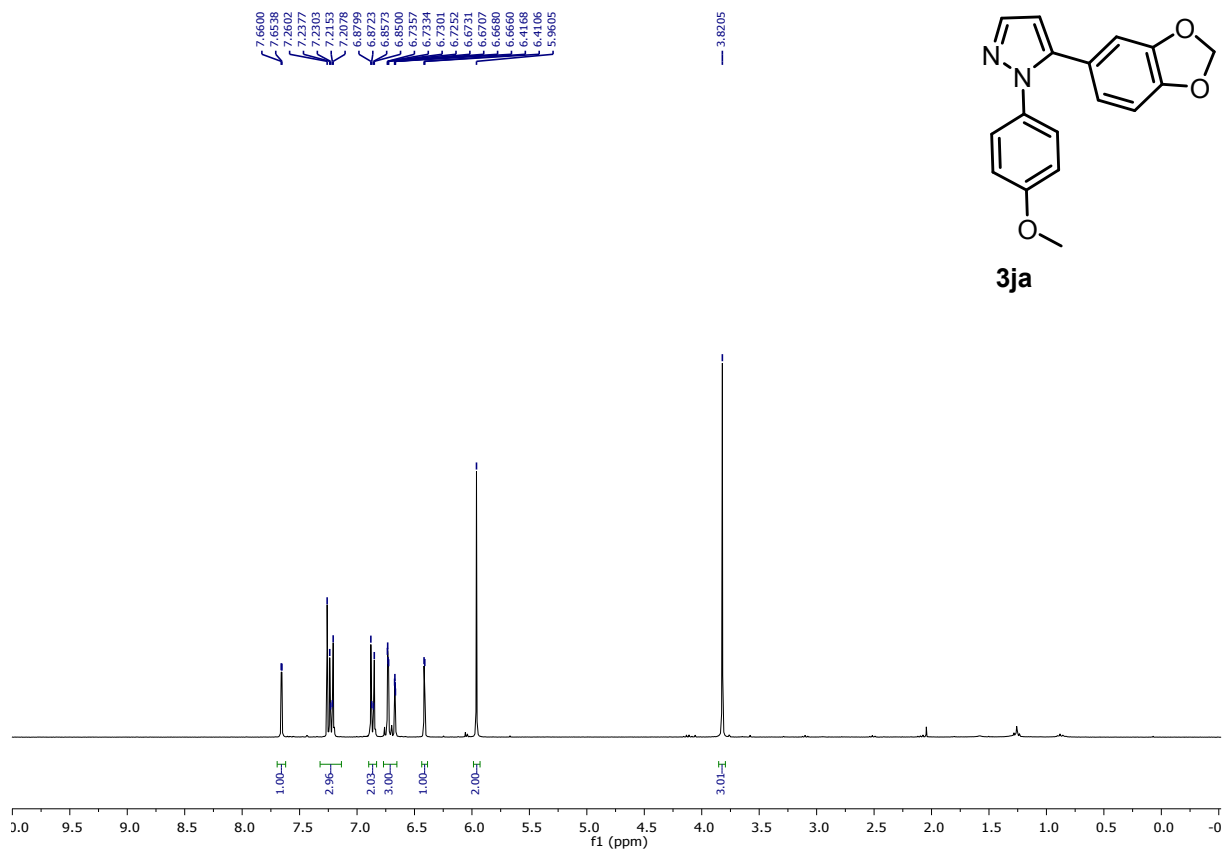




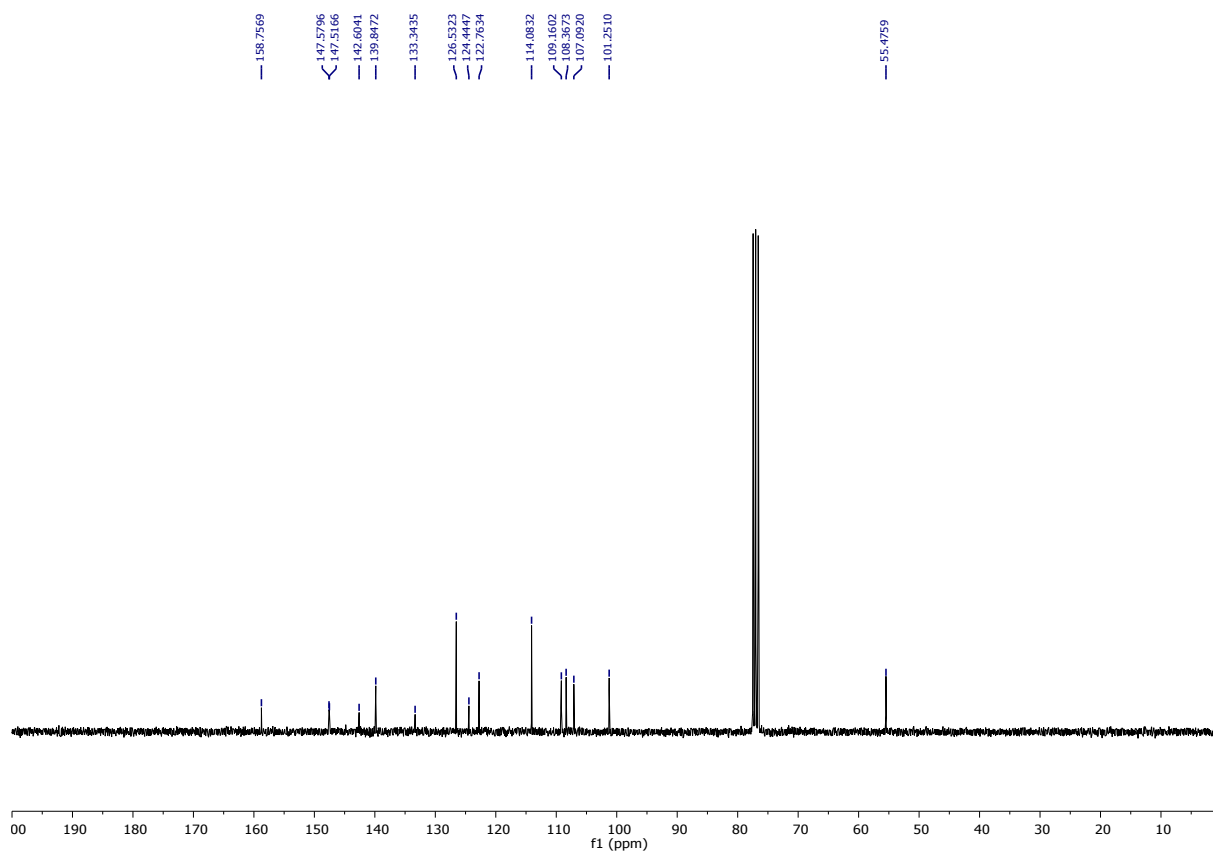
^1H NMR (300 MHz, CDCl_3) of 1-(4-methoxyphenyl)-5-(naphthalen-2-yl)-1H-pyrazole



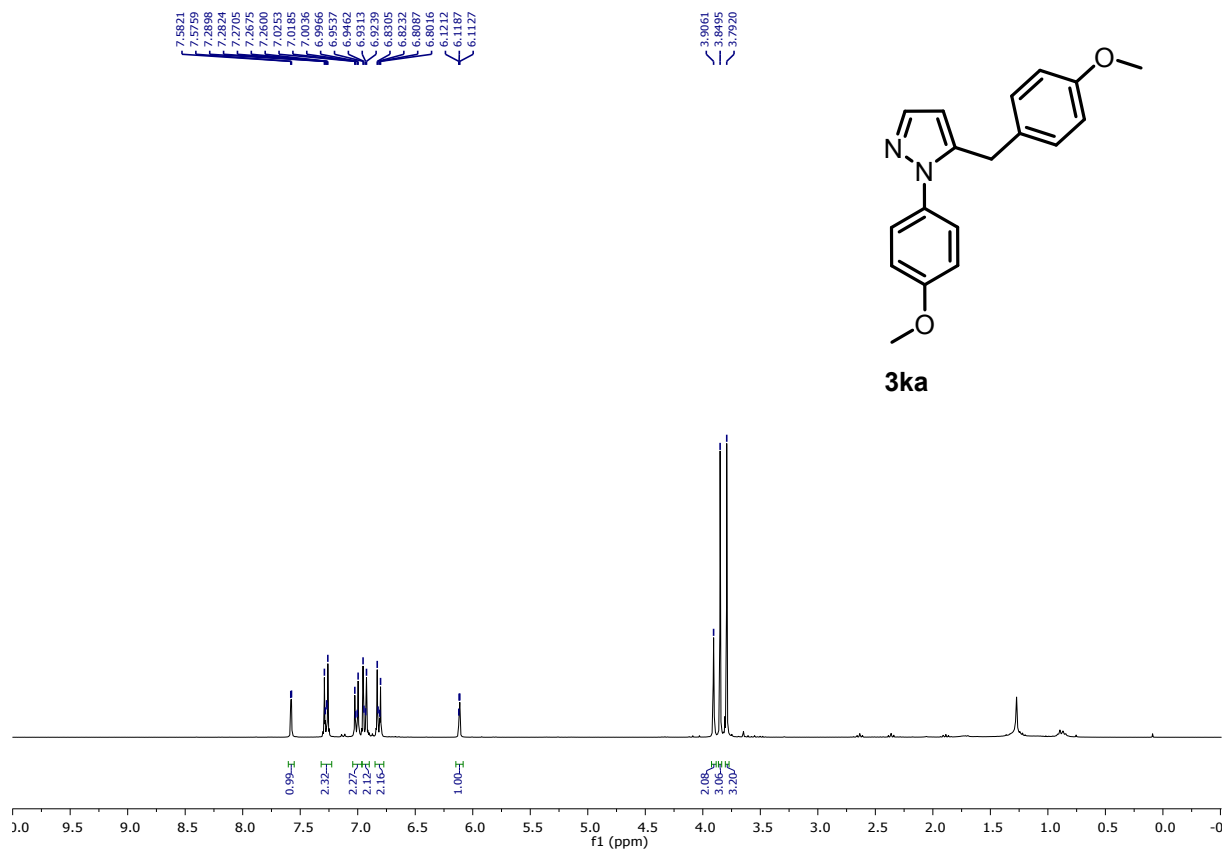
^{13}C NMR (75 MHz, CDCl_3) of 1-(4-methoxyphenyl)-5-(naphthalen-2-yl)-1H-pyrazole



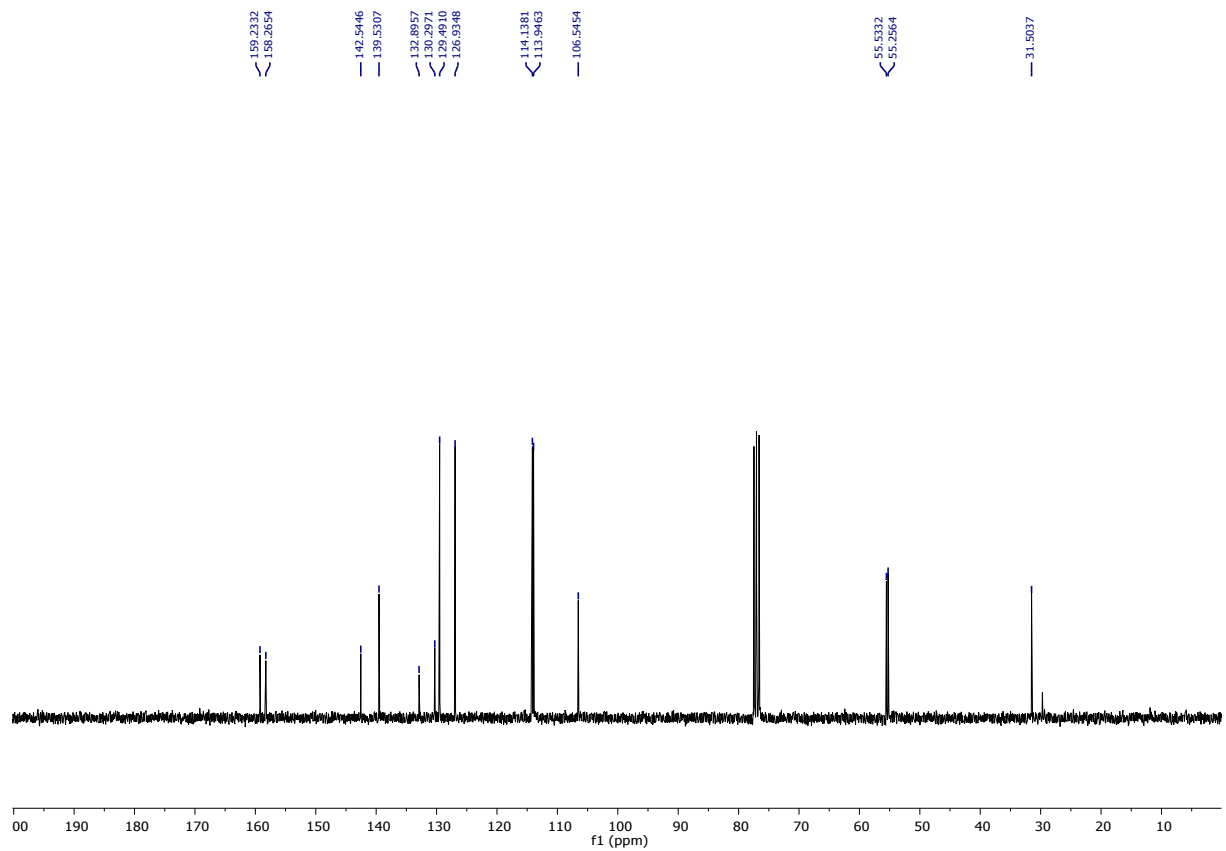
¹H NMR (300 MHz, CDCl₃) of 5-(benzo[d][1,3]dioxol-5-yl)-1-(4-methoxyphenyl)-1H-pyrazole



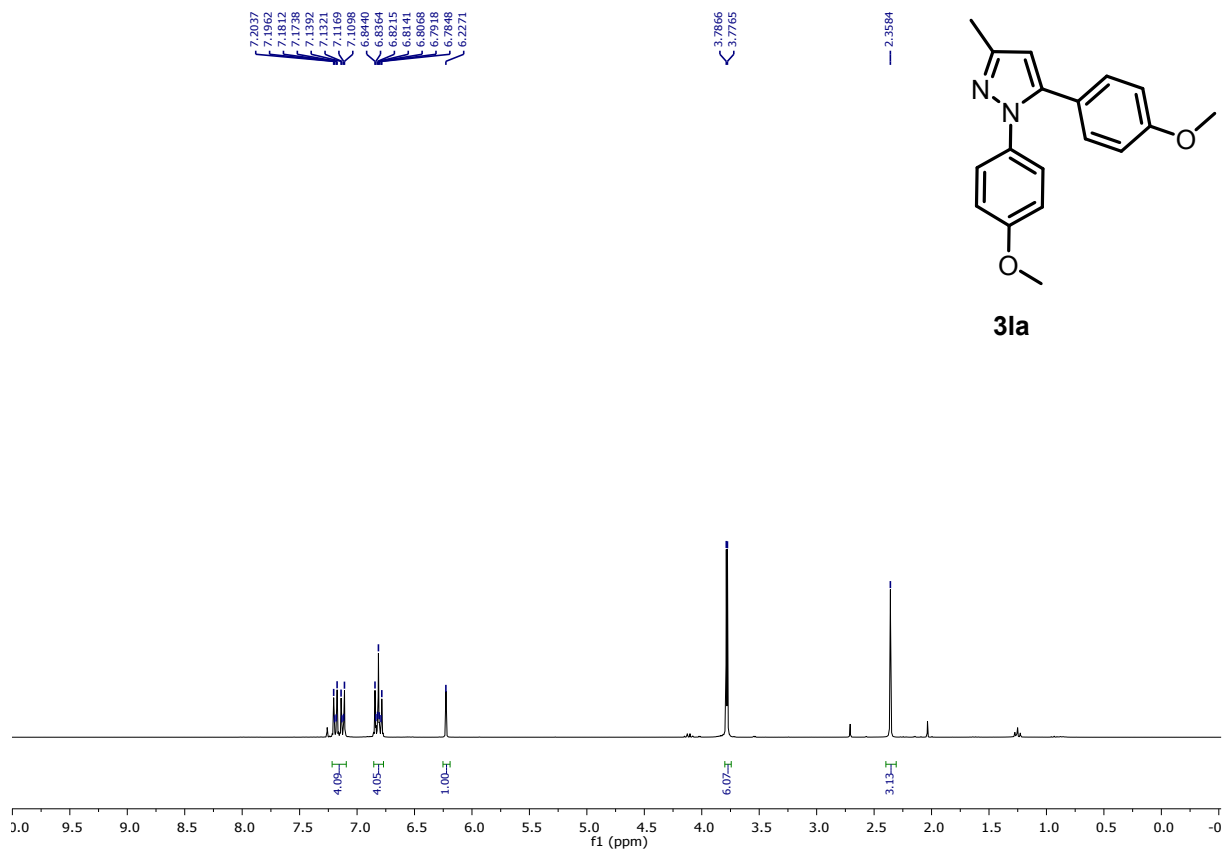
¹³C NMR (75 MHz, CDCl₃) of 5-(benzo[d][1,3]dioxol-5-yl)-1-(4-methoxyphenyl)-1H-pyrazole



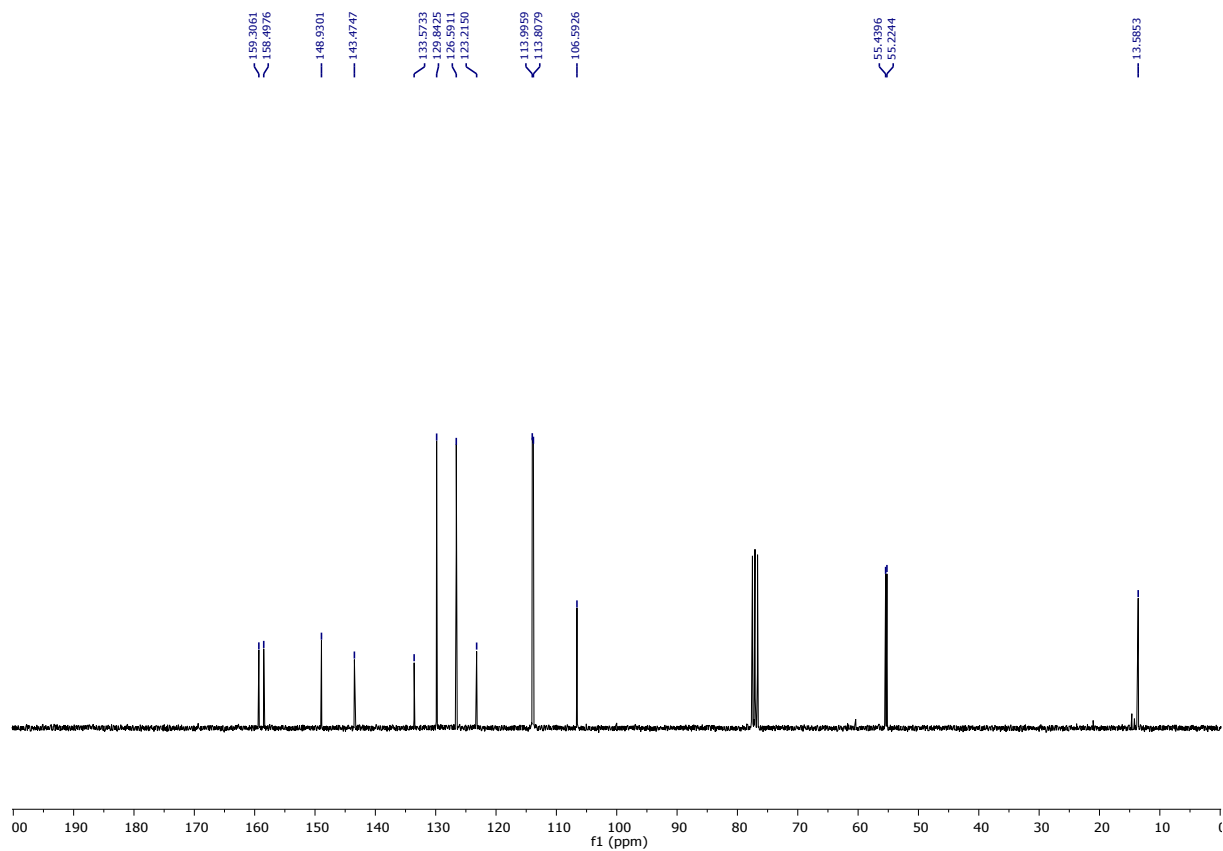
¹H NMR (300 MHz, CDCl₃) of 5-(4-methoxybenzyl)-1-(4-methoxyphenyl)-1H-pyrazole



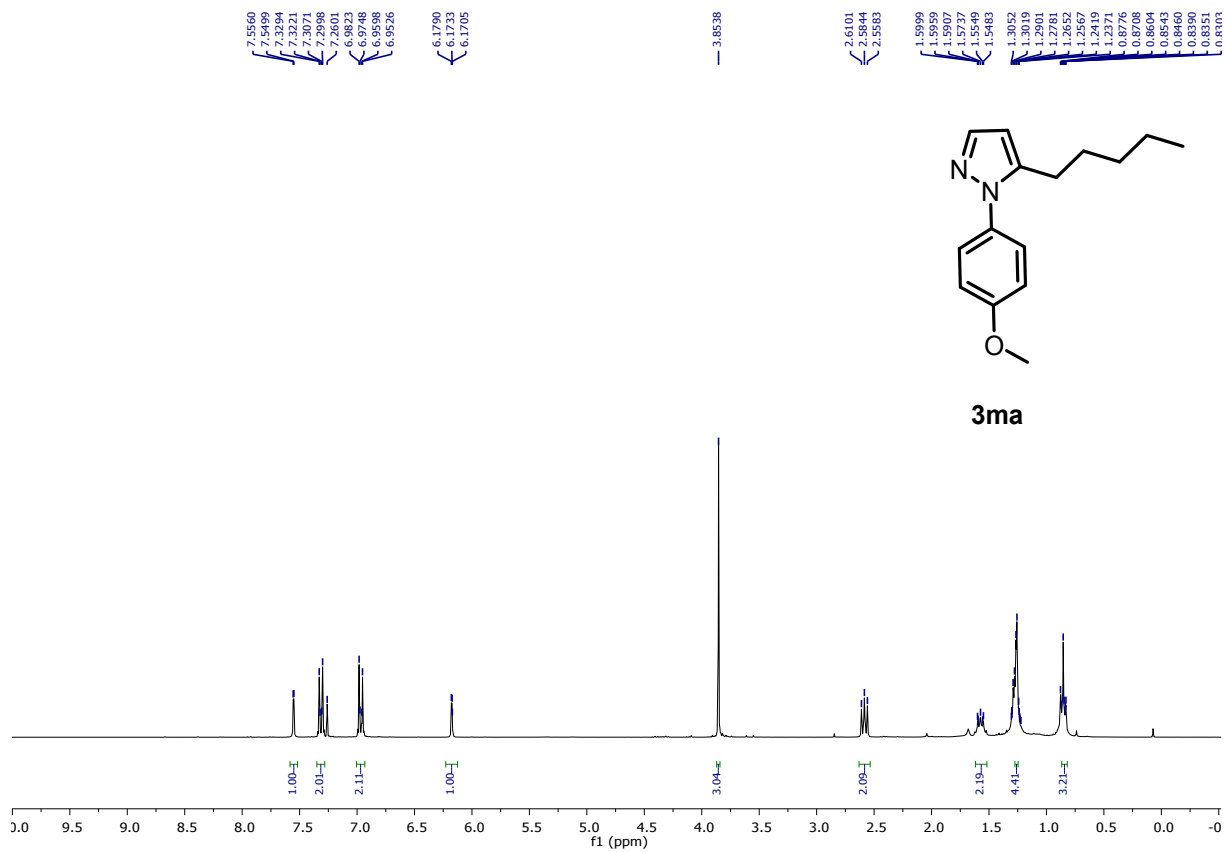
¹³C NMR (100 MHz, CDCl₃) of 5-(4-methoxybenzyl)-1-(4-methoxyphenyl)-1H-pyrazole



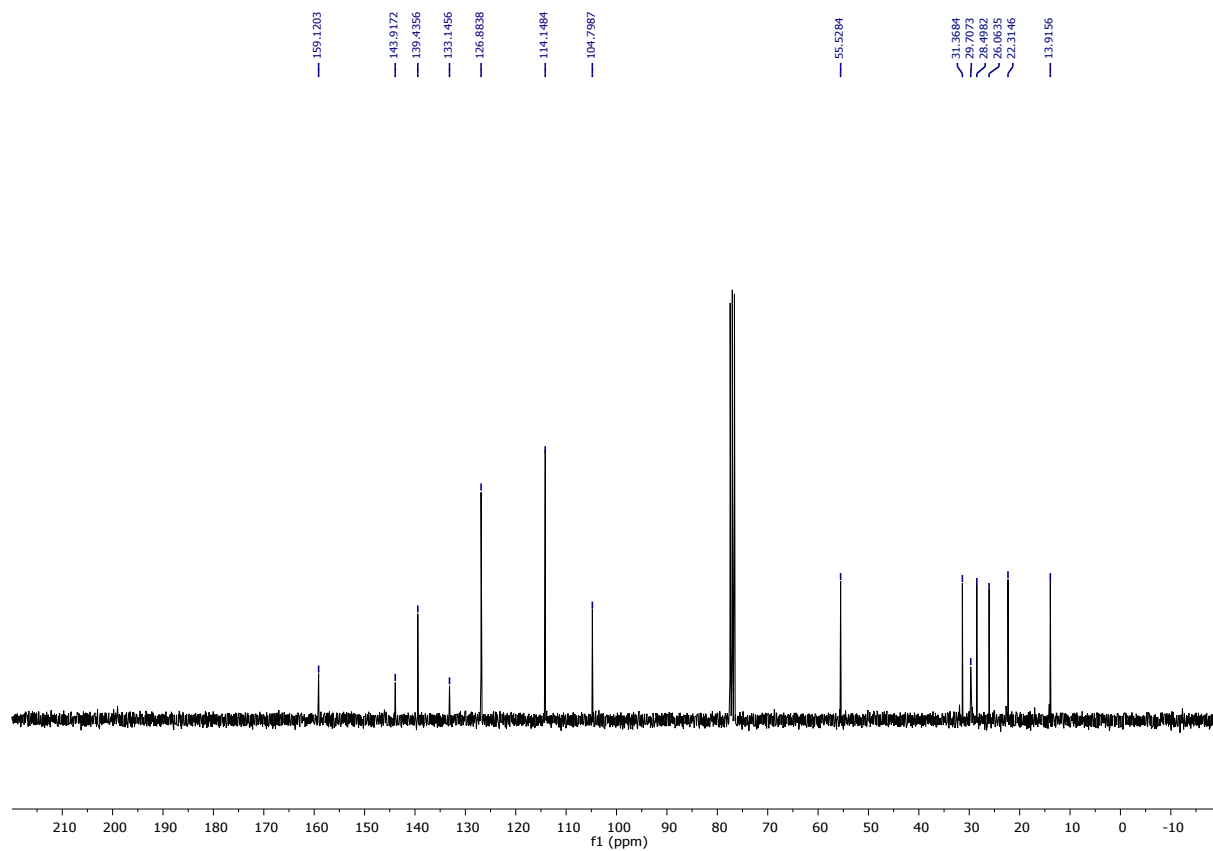
¹H NMR (300 MHz, CDCl₃) of 1,5-bis(4-methoxyphenyl)-3-methyl-1H-pyrazole



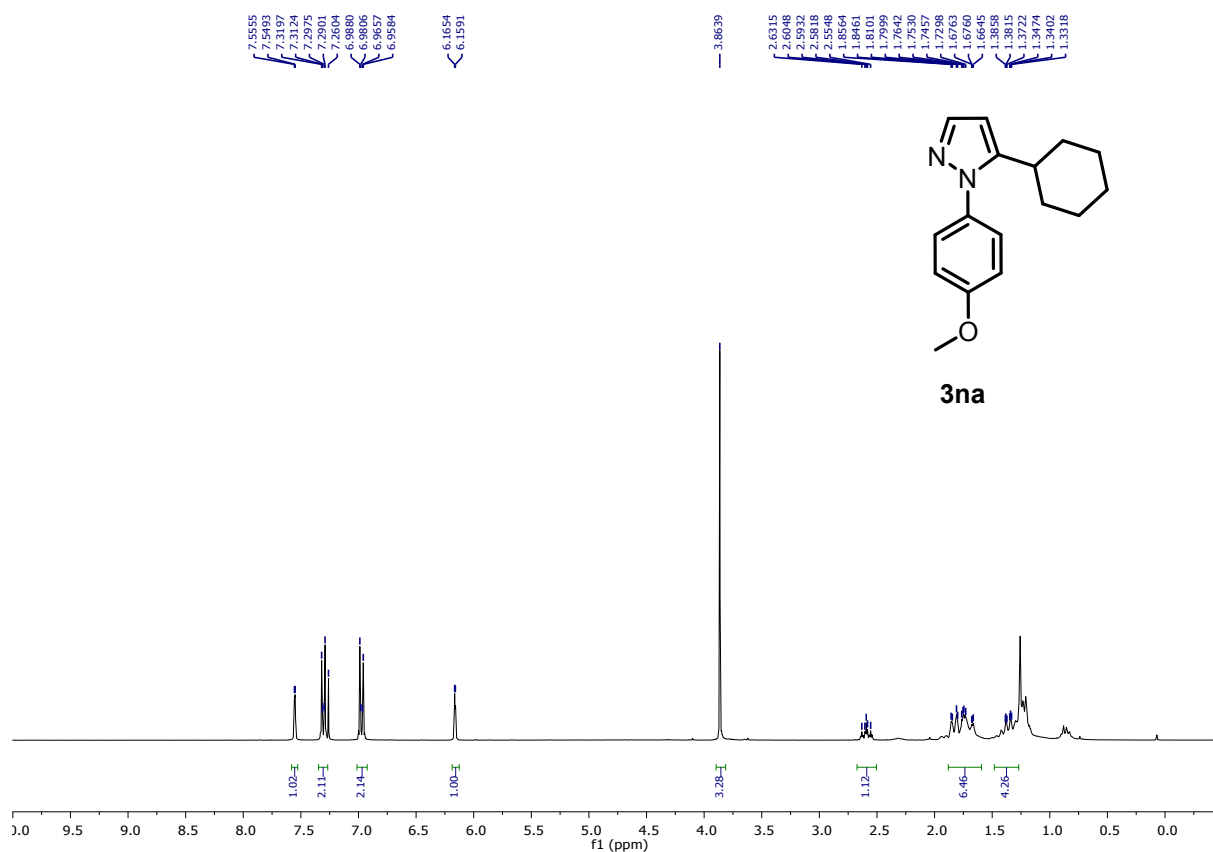
¹³C NMR (75 MHz, CDCl₃) of 1,5-bis(4-methoxyphenyl)-3-methyl-1H-pyrazole



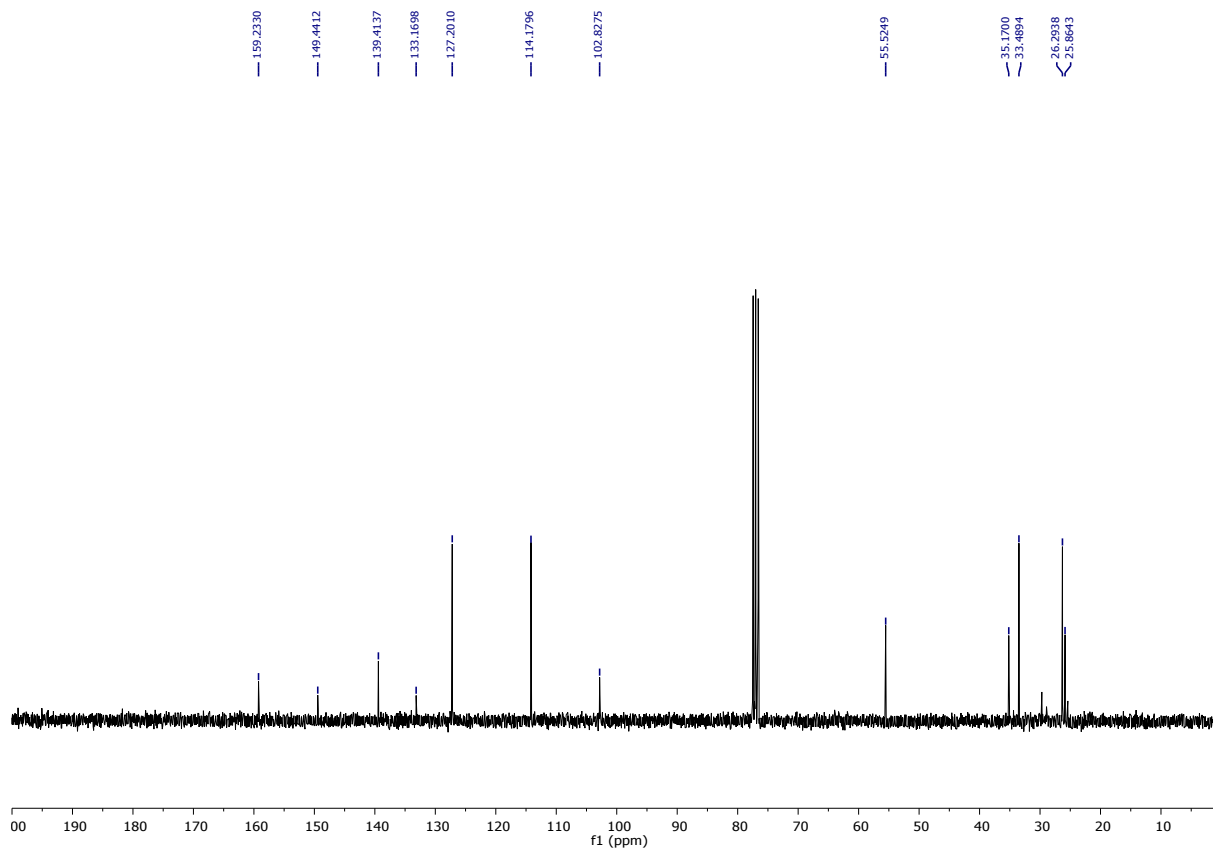
¹H NMR (300 MHz, CDCl₃) of 1-(4-methoxyphenyl)-5-pentyl-1H-pyrazole



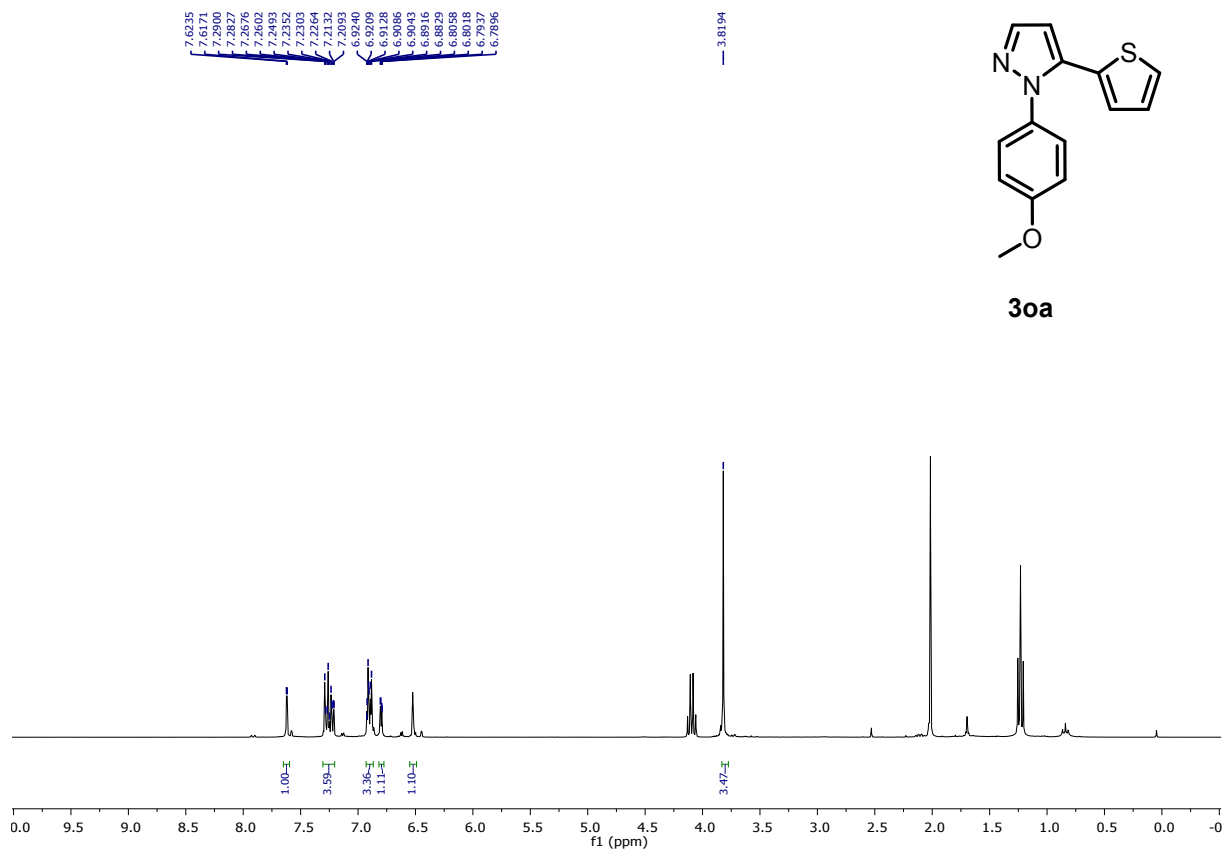
¹³C NMR (75 MHz, CDCl₃) of 1-(4-methoxyphenyl)-5-pentyl-1H-pyrazole



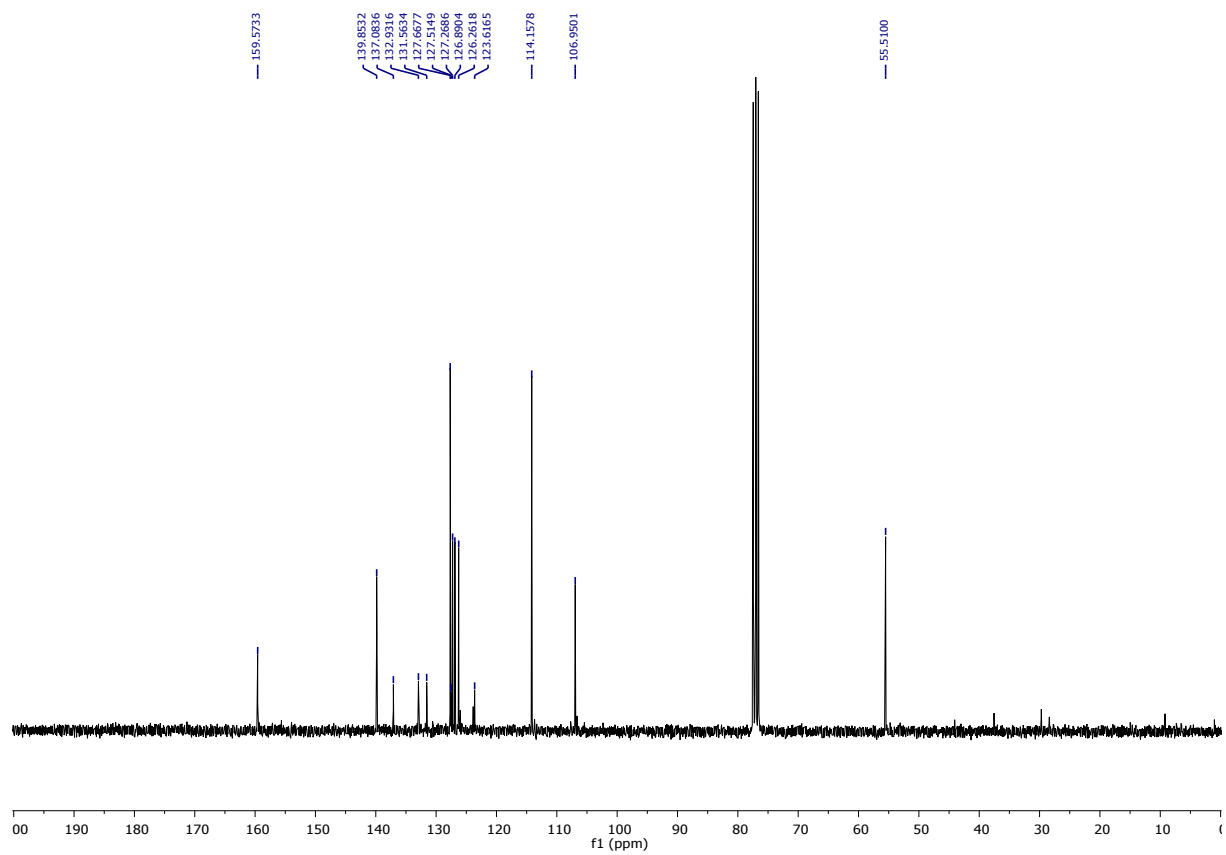
¹H NMR (300 MHz, CDCl₃) of 1-(4-methoxyphenyl)-5-cyclohexyl-1H-pyrazole



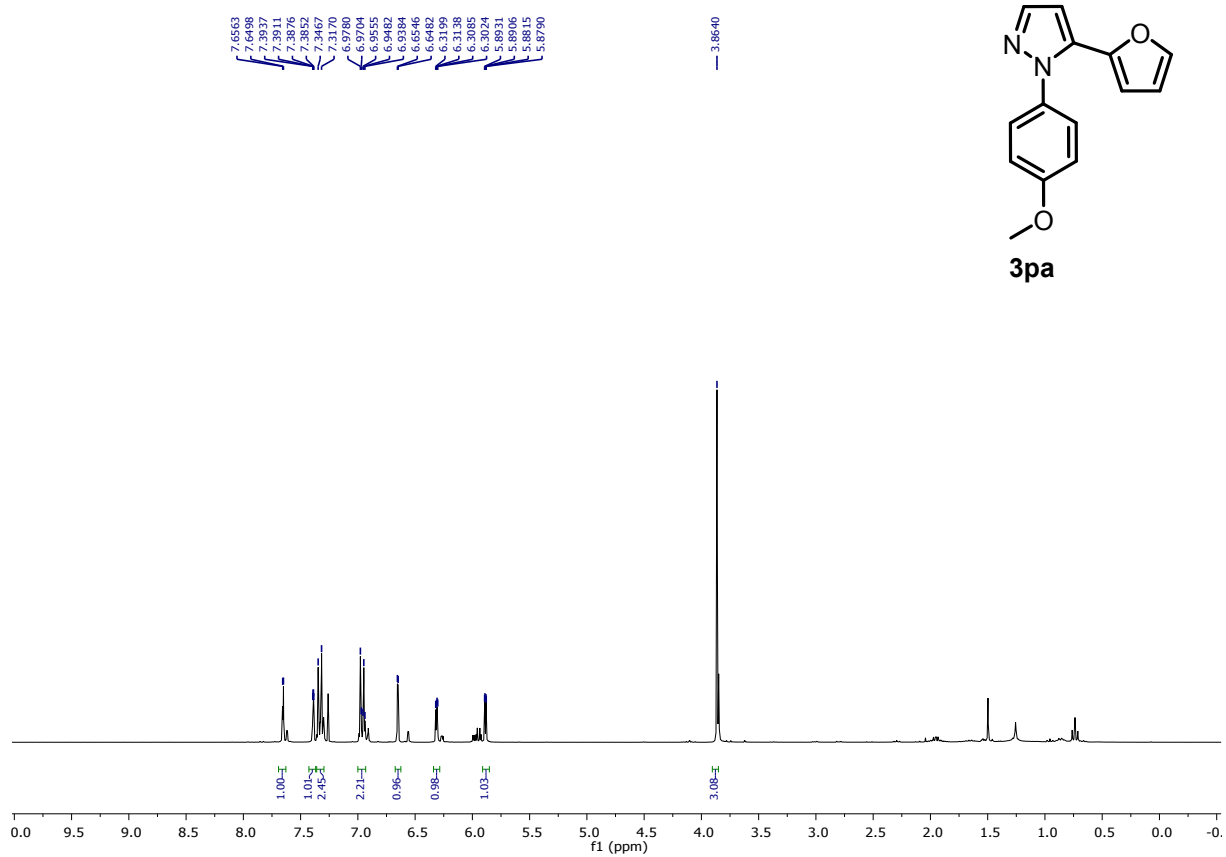
¹³C NMR (100 MHz, CDCl₃) of 1-(4-methoxyphenyl)-5-cyclohexyl-1H-pyrazole



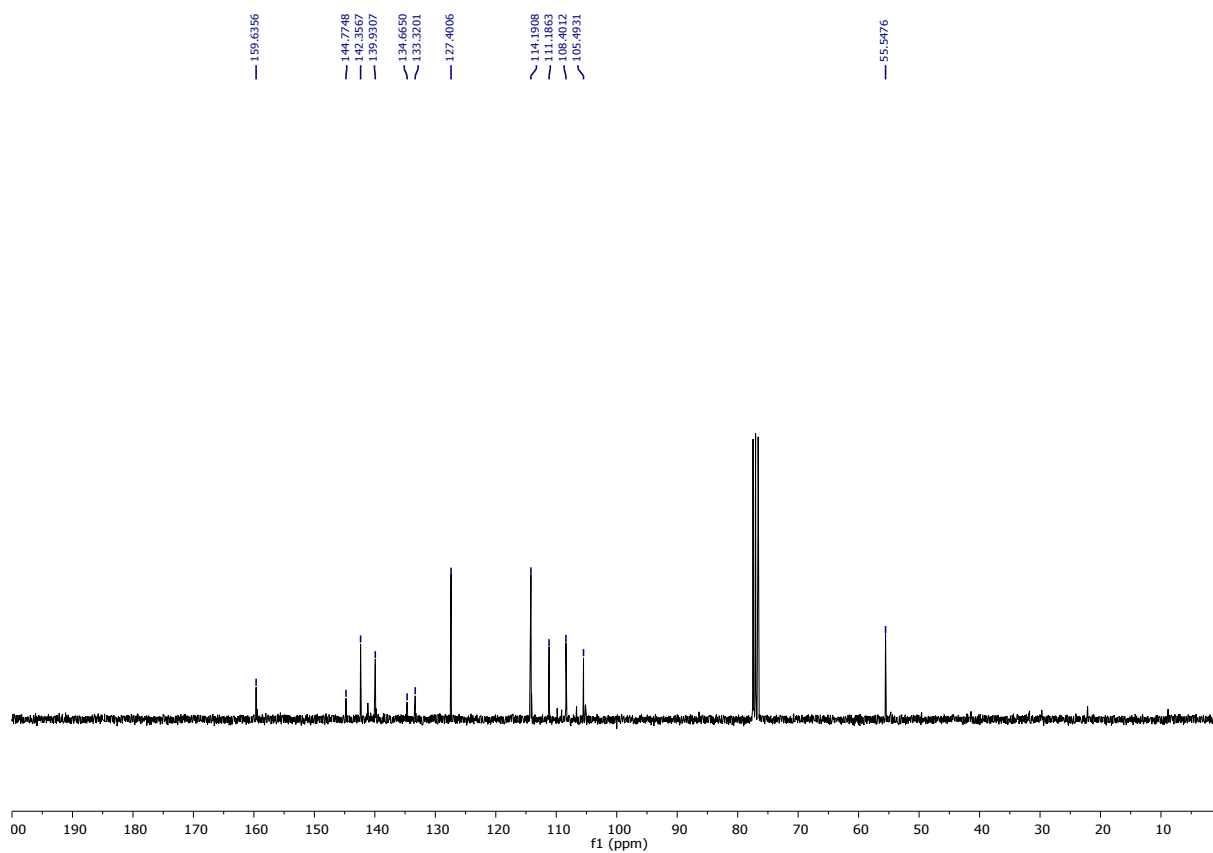
$^1\text{H NMR}$ (300 MHz, CDCl_3) of 1-(4-methoxyphenyl)-5-(thiophen-2-yl)-1H-pyrazole



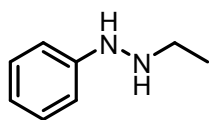
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) of 1-(4-methoxyphenyl)-5-(thiophen-2-yl)-1H-pyrazole



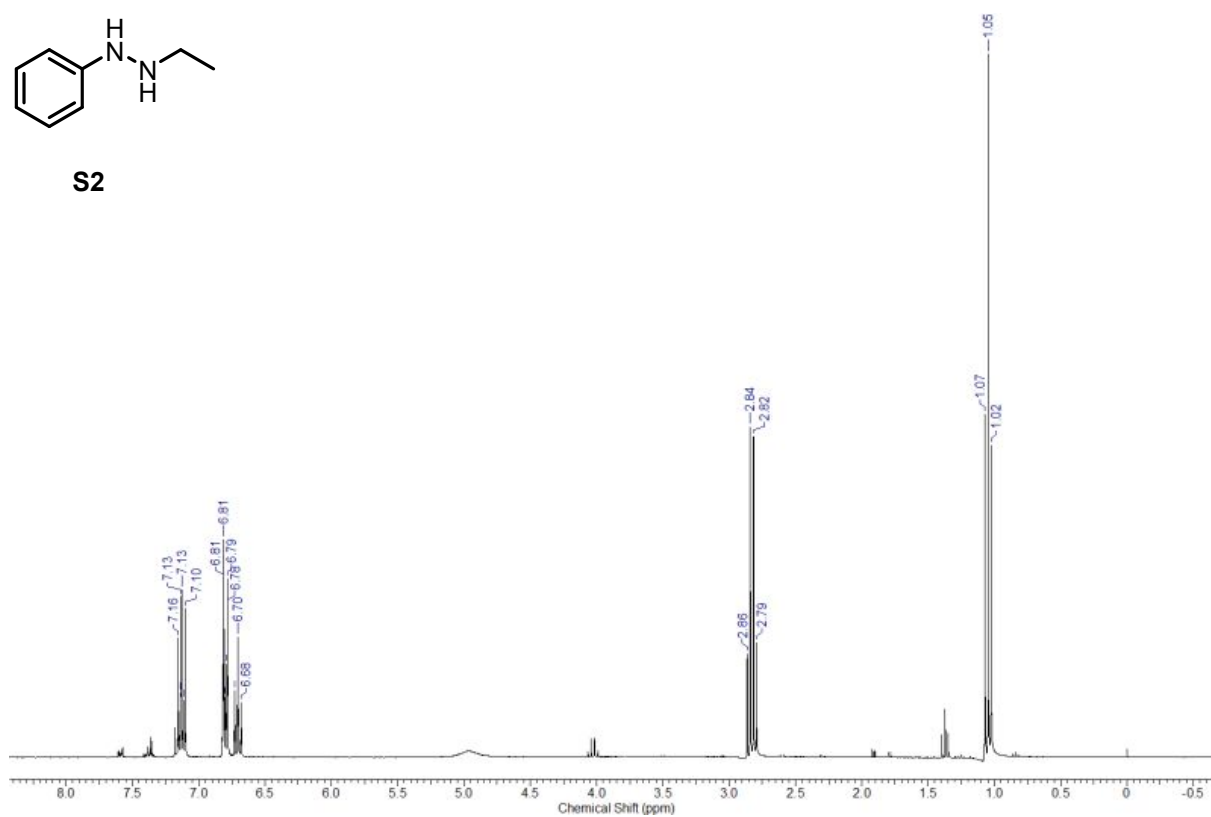
¹H NMR (300 MHz, CDCl₃) of 5-(furan-2-yl)-1-(4-methoxyphenyl)-1H-pyrazole



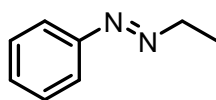
¹³C NMR (75 MHz, CDCl₃) of 5-(furan-2-yl)-1-(4-methoxyphenyl)-1H-pyrazole



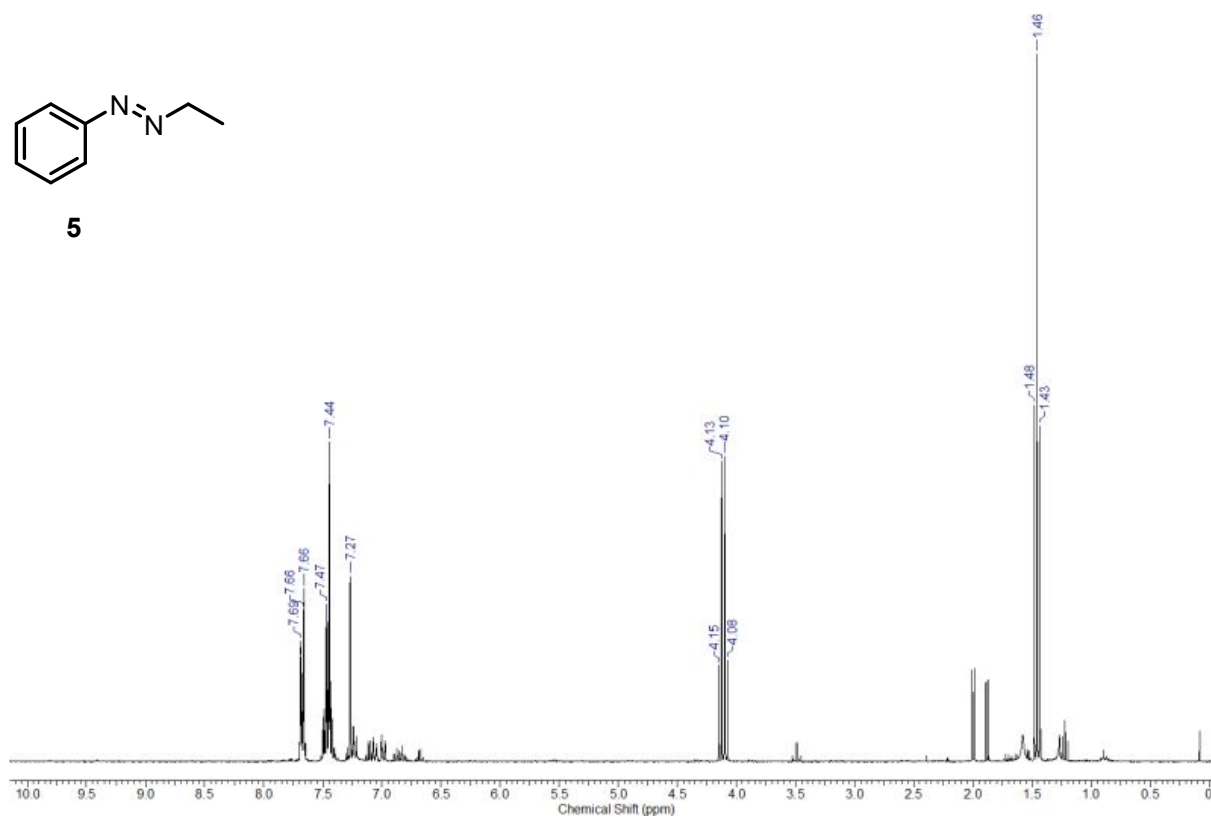
S2



¹H NMR of 2-ethyl-1-phenylhydrazine



5



¹H NMR of 2-ethyl-1-phenyldiazene