Supporting Information

LMCT enabled photo-decarboxylative C–N cross coupling of *α*, *β*-unsaturated acids with pyrazoles

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Contents

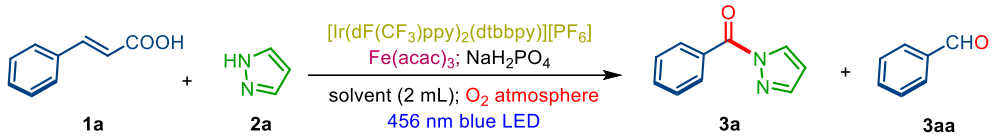
1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received commercially. Commercially available metal salt precursors were used without additional purification. Most of the chemicals used in the catalytic reactions were purified according to standard procedure.[S1] Reactants **1** and **2** were purchased from Sigma Aldrich, TCI India, Thermo Scientific and BLD Pharmatech India. and used as received. Reactions were irradiated with 40 W Kessil PR160L-456 nm LED (λ_{max}= 456 nm, average intensity of LED at 2x4 cm area is 137 mW/cm^2). Kessil PR160L-456 nm LED contains linear reflector and has upto 25% higher average intensity than Kessil PR160-456 nm LED. Distance between LED and reaction vessel surface was kept between 5-6 cm. 2 LEDs were used for irradiating 4 reaction vials and a cooling fan was used for maintaining the reaction temperature between 30-32 ºC Thin layer chromatography (TLC) was performed using silica gel percolated glass plates, which were visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (Silicycle Silica flash F60 (230-400 mesh)). ^{1}H NMR (300, 400 or 500 MHz), ^{13}C NMR (75, 101 or 126 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relatives to the residual signals of this solvent [δ 7.26 for ^{1}H (chloroform-d), δ 77.1 for ^{13}C (chloroform-d)]. Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet; dq, doublet of quartet; qd, quartet of doublet, *etc.* GC-MS measurements were conducted on an Thermo Fischer TRACE 1300 GC system equipped with a ISQ QD single quadrupole mass spectrometer. GC analysis was carried out using a TG-5MS column (30 m, 0.25 mm, 0.25μ). High resolution mass spectra were measured on Q-Tof micro-MS system by electron spray ionization (ESI) technique. Elemental analyses were performed on a Vario-EL cube elemental analyzer. Fourier transform infrared (FT-IR) FTIR analysis was carried out on a Perkin-Elmer Spectrometer. Optical absorption measurements were carried out by Shimadazu UV-vis-IR-3600 Plus spectrophotometer.

2. Experimental Section

2.1. Optimization of reaction condition

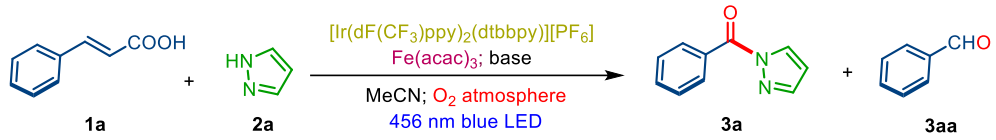
Table S1: Screening of solvent[a]



Entry	Solvent	Yield[b] (%) 3a:3aa
1	DMSO	NR
2	DMF	NR
3	DMA	NR
4	**CH_3CN**	**61:11**
5	THF	trace
6	1,4-Dioxane	trace
7	DCE	11:21
8	DCB	18:9
9	MeOH	NR
10	Toluene	NR
11	Water	NR
12	CCl_4	NR

[a]Reaction conditions: cinnamic acid **1a** (0.1 mmol), pyrazole **2a** (0.1 mmol), [Ir(dF(CF_3)ppy)$_2$(dtbbpy)][PF_6] (2 mol%), Fe(acac)$_3$ (20 mol%), NaH_2PO_4 (0.1 mmol), and solvent (2.0 mL) stirred at room temperature (RT) and oxygen atmosphere under 40W blue LED (456 nm) for 12 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction

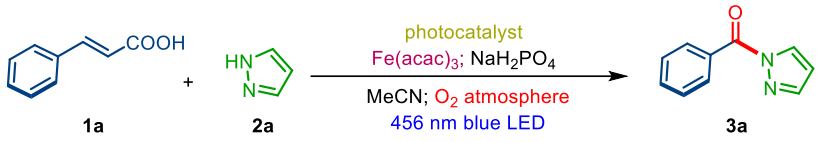
Table S2: Screening of base[a]

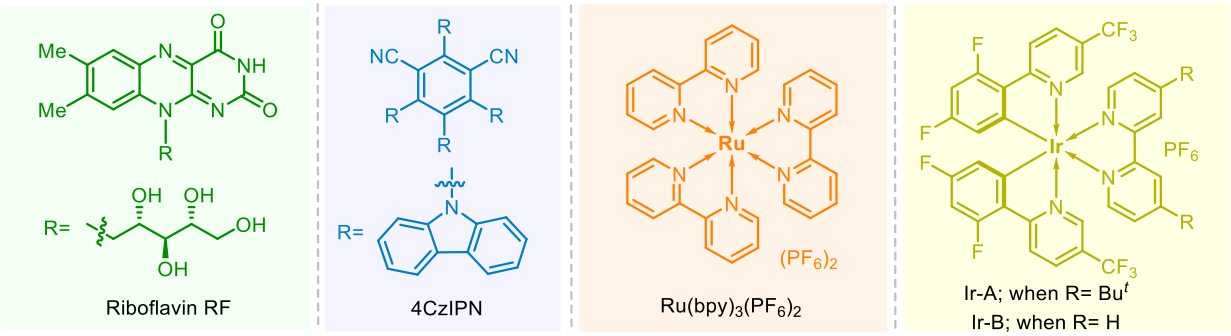


Entry	Base	Yield[b] (%) 3a:3aa
1	$NaHCO_3$	31:14
2	**NaH_2PO_4**	**61:11**
3	NaOAc	NR
4	K_2HPO_4	trace
5	Na_2HPO_4	23:8
6	KH_2PO_4	41:21
7	NaOH	NR
8	K_3PO_4	trace
9	Na_2CO_3	NR
10	K_2CO_3	NR
11	Cs_2CO_3	NR
12	pyridine/piperidine	NR

[a]Reaction conditions: cinnamic acid **1a** (0.1 mmol), pyrazole **2a** (0.1 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), base (0.1 mmol), and MeCN (2.0 mL) stirred at room temperature (RT) and oxygen atmosphere under 40W blue LED (456 nm) for 12 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction

Table S3: Screening of photoredox catalyst[a]

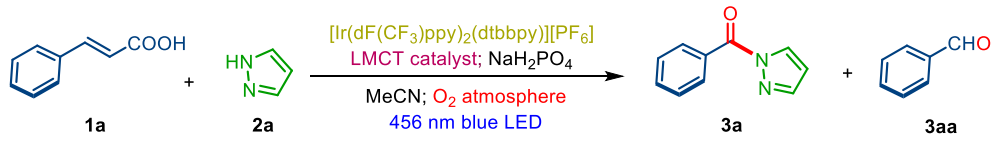




Entry	Photocatalyst	Yield[b] (%) 3a
1	Riboflavin	trace
2	4CzIPN	trace
3	Rose Bengal	NO
4	Eosin-Y	NO
5	Rhodamin-6G	trace
6	$Ru(bpy)_3[PF_6]_2$	trace
7	**Ir-A**	**61**
8	Ir-B	31

[a]Reaction conditions: cinnamic acid **1a** (0.1 mmol), pyrazole **2a** (0.1 mmol), photocatalyst (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol), and MeCN (2.0 mL) stirred at room temperature (RT) and oxygen atmosphere under 40W blue LED (456 nm) for 12 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NO = Not observed.

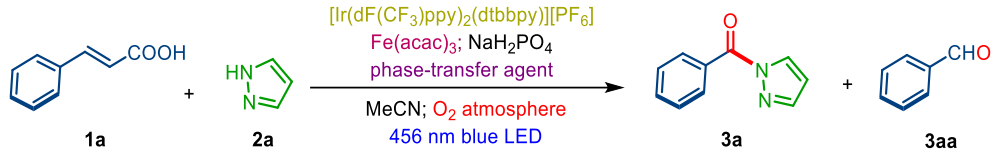
Table S4: Screening of LMCT catalyst[a]



Entry	LMCT-catalyst	Yield[b] (%) 3a:3aa
1	$FeCl_2$	NO:14
2	$FeCl_3$	NO:11
3	$Fe(OTf)_2$	trace
4	$Fe(acac)_2$	51:19
5	**$Fe(acac)_3$**	**61:11**
6	$Fe(BF_4)_2$	trace
7	$Fe_2(SO_4)_3$	trace
8	$CuCl_2$	NR
9	$NiCl_2$	NR
10	$PdCl_2$	NR
11	$Cu(OTf)_2$	NR
12	$Cu(OAc)_2$	NR
13	CuI	NR

[a]Reaction conditions: cinnamic acid **1a** (0.1 mmol), pyrazole **2a** (0.1 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), LMCT catalyst (20 mol%), NaH_2PO_4 (0.1 mmol), and MeCN (2.0 mL) stirred at room temperature (RT) and oxygen atmosphere under 40W blue LED (456 nm) for 12 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

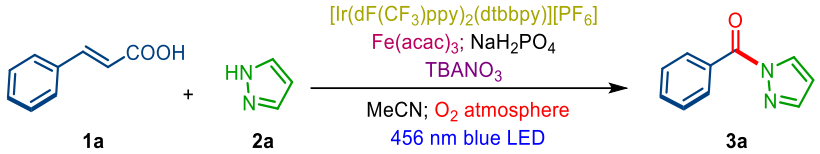
Table S5: Screening of additive[a]



Entry	Phase transfer agent	Yield[b] (%) 3a:3aa
1	TBACl	45:21
2	TBABr	21:08
3	TBAI	27:14
4	$TBAClO_4$	NR
5	**$TBANO_3$**	**68:2**
6	$TBAHSO_4$	NR
7	$MClO_4$ (M= Li/Na/K)	NR
8	$LiBF_4$	60:4
9	$Ca(ClO_4)_2$	NR
10	$NaBPh_4$	NR

[a]Reaction conditions: cinnamic acid **1a** (0.1 mmol), pyrazole **2a** (0.1 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol), phase-transfer agent as additive (0.1 mmol) and MeCN (2.0 mL) stirred at room temperature (RT) and oxygen atmosphere under 40W blue LED (456 nm) for 12 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

Table S6: Control experiment[a]



1a 2a 3a

Entry	Condition	Yield 3a (%)[b]
1	Without Ir-photocatalyst	NR
2	Without $Fe(acac)_3$	NR
3	Without $TBANO_3$	61
3	Without NaH_2PO_4	11
4	Without blue LED	NR
5	Inert atmosphere (O_2 free)	NR

[a]Reaction conditions: cinnamic acid **1a** (0.1 mmol), pyrazole **2a** (0.1 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol), phase-transfer agent as additive (0.1 mmol) and MeCN (2.0 mL) stirred at room temperature (RT) and oxygen atmosphere under 40W blue LED (456 nm) for 12 h. [b]Yield determined by GC using 1,4-dibromobutane as an internal standard. NR = No reaction.

Table S7: Light wavelength variation

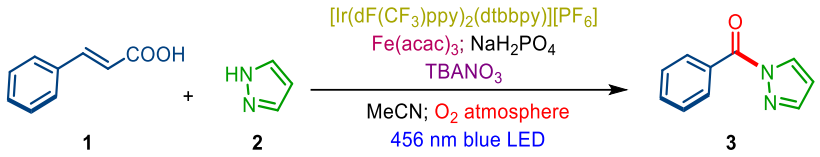
Entry	Condition	Yield (%)[b]
1	390 nm violet LED	NR
2	440 nm blue LED	21
3	**456 nm blue LED**	**68**
4	CFL 9W bulb	NR

Table S8: Reaction set-up

Entry	Condition	Yield (%)[b]
1	Open air	32
2	**Closed system purged with O_2**	**68**
3	Oxygen balloon	70
4	Inert	NR

2.2 Synthesis and characterization of *N*-benzoylpyrazole

2.2.1 General procedure for synthesis of *N*-benzoylpyrazole

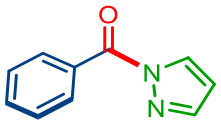


Scheme S1. Synthesis of *N*-benzoylpyrazole (**3a-3ze**).

Process: To a 15 mL clean, oven-dried reaction tube, cinnamic acid **1** (0.1 mmol), pyrazole **2** (0.1 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol), tetrabutylammonium nitrate $TBANO_3$ (0.1 mmol, 1 equiv.), double distilled acetonitrile (2.0 mL) were added in an open-air condition. The solution was then degassed and back-filled with oxygen gas thrice. Then, the solution was irradiated with 40 W Kessil PR160L-456 nm LED in a closed condition at room temperature for 12h. A cooling fan was used to maintain the reaction temperature between 30-32 ºC. After 12h, the reaction mixture was directly evaporated under reduced pressure and crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate (99:1) as an eluting system.

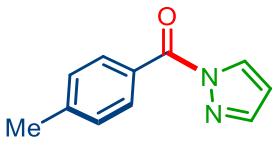
2.2.2 NMR characterization for *N-benzoylpyrazole* derivatives

phenyl(1H-pyrazol-1-yl)methanone (3a) [S2]



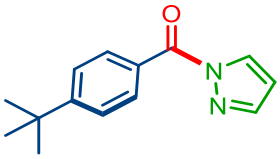
Following general procedure 2.2.1 using **1a** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 11.0 mg, Yield: 64%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.47 – 8.42 (m, 1H), 8.15 – 8.09 (m, 2H), 7.81 (s, 1H), 7.66 – 7.57 (m, 1H), 7.56 – 7.48 (m, 2H), 6.53 (dd, J = 2.8, 1.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.5, 144.6, 133.1, 131.60, 131.57, 130.5, 128.2, 109.5.

(1H-pyrazol-1-yl)(p-tolyl)methanone (3b) [S2]



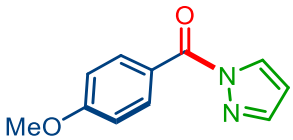
Following general procedure 2.2.1 using **1b** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), White solid, 12.4 mg, Yield: 67%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.8 Hz, 1H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.79 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.52 (d, *J* = 1.4 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.4, 144.4, 144.0, 131.7, 130.5, 128.9, 128.7, 109.3, 21.8.

(4-(tert-butyl)phenyl)(1H-pyrazol-1-yl)methanone (3c) [S2]



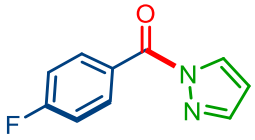
Following general procedure 2.2.1 using **1a** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 15.3 mg, Yield: 67%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 2.7 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 2H), 7.81 (s, 1H), 7.53 (d, *J* = 8.5 Hz, 2H), 6.52 – 6.51 (m, 1H), 1.36 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.4, 156.9, 144.4, 131.6, 130.5, 128.6, 125.3, 109.3, 35.2, 31.2.

(4-methoxyphenyl)(1H-pyrazol-1-yl)methanone (3d)



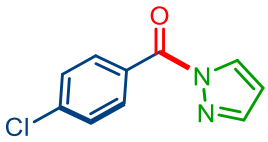
Following general procedure 2.2.1 using **1d** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 14.3 mg, Yield: 71%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.7 Hz, 1H), 8.22 (d, *J* = 8.9 Hz, 2H), 7.79 (s, 1H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.50 (s, 1H), 3.89 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.5, 163.7, 144.2, 134.3, 130.6, 123.6, 113.6, 109.1, 55.6. **HRMS (EI):** m/z Calcd for $C_{11}H_{10}N_2O_2$ $[M+H]^+$: 203.0815; Found: 203.0817.

(4-fluorophenyl)(1H-pyrazol-1-yl)methanone (3e) [S2]



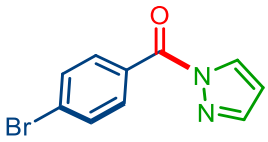
Following general procedure 2.2.1 using **1e** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 11.2 mg, Yield: 59%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.45 (d, J = 2.7 Hz, 1H), 8.23 (dd, J = 8.3, 5.8 Hz, 2H), 7.81 (s, 1H), 7.19 (t, J = 8.6 Hz, 2H), 6.54 – 6.53 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.8 (d, J = 255.5 Hz), 165.2, 144.7, 134.6 (d, J = 9.3 Hz), 130.6, 127.6 (d, J = 3.1 Hz), 115.5 (d, J = 21.9 Hz), 109.6.

(4-chlorophenyl)(1H-pyrazol-1-yl)methanone (3f) [S2]



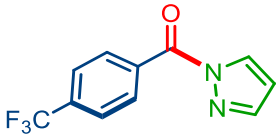
Following general procedure 2.2.1 using **1f** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 12.8 mg, Yield: 62%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.44 (d, J = 2.8 Hz, 1H), 8.12 (d, J = 8.5 Hz, 2H), 7.80 (s, 1H), 7.48 (d, J = 8.5 Hz, 2H), 6.54 – 6.53 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.3, 144.7, 139.7, 133.1, 130.5, 129.8, 128.5, 109.7.

(4-bromophenyl)(1H-pyrazol-1-yl)methanone (3g) [S2]



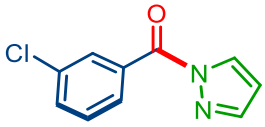
Following general procedure 2.2.1 using **1g** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 15.8 mg, Yield: 63%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.43 (d, J = 2.4 Hz, 1H), 8.04 (d, J = 8.6 Hz, 2H), 7.80 (s, 1H), 7.65 (d, J = 8.6 Hz, 2H), 6.53 (d, J = 1.3 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.5, 144.8, 133.2, 131.5, 130.5, 130.3, 128.4, 109.8.

(1H-pyrazol-1-yl)(4-(trifluoromethyl)phenyl)methanone (3h) [S2]



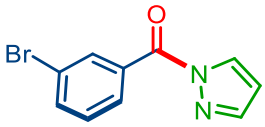
Following general procedure 2.2.1 using **1h** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 12.2 mg, Yield: 51%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.47 (d, J = 2.8 Hz, 1H), 8.23 (d, J = 8.2 Hz, 2H), 7.82 (s, 1H), 7.78 (d, J = 8.2 Hz, 2H), 6.57 (dd, J = 2.6, 1.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.4, 145.1, 134.9, 134.3 (q, J = 32.8 Hz), 131.8, 130.4, 125.1 (q, J = 3.6 Hz), 123.6 (q, J = 272.8 Hz), 110.1.

(3-chlorophenyl)(1H-pyrazol-1-yl)methanone (3j) [S2]



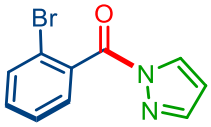
Following general procedure 2.2.1 using **1j** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 11.2 mg, Yield: 54%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (d, J = 2.6 Hz, 1H), 8.14 (s, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.82 (s, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.45 (t, J = 7.9 Hz, 1H), 6.55 (d, J = 1.3 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.1, 144.9, 134.3, 133.1, 131.6, 130.5, 129.8, 129.5, 109.9.

(3-bromophenyl)(1H-pyrazol-1-yl)methanone (3k) [S2]



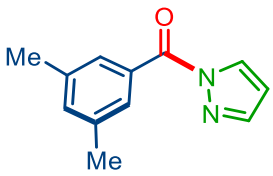
Following general procedure 2.2.1 using **1k** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 14.3 mg, Yield: 57%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.43 (d, J = 2.8 Hz, 1H), 8.28 (s, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.82 (s, 1H), 7.76 – 7.68 (m, 1H), 7.39 (t, J = 7.9 Hz, 1H), 6.54 (d, J = 1.2 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.0, 144.9, 136.0, 134.5, 133.4, 130.5, 130.2, 129.7, 122.2, 109.9.

(2-bromophenyl)(1H-pyrazol-1-yl)methanone (3m) [S2]



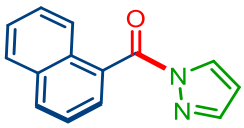
Following general procedure 2.2.1 using **1m** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 10.3 mg, Yield: 41%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 2.8 Hz, 1H), 7.76 (d, *J* = 0.7 Hz, 1H), 7.66 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.54 – 7.32 (m, 3H), 6.54 (dd, *J* = 2.9, 1.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.3, 145.3, 135.3, 133.0, 132.0, 129.6, 129.4, 127.1, 120.2, 110.5.

(3,5-dimethylphenyl)(1H-pyrazol-1-yl)methanone (3n)



Following general procedure 2.2.1 using **1n** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 12.6 mg, Yield: 63%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 2.9, 0.6 Hz, 1H), 7.80 (d, *J* = 0.7 Hz, 1H), 7.67 (s, 2H), 7.27 – 7.19 (m, 1H), 6.51 (dd, *J* = 2.8, 1.5 Hz, 1H), 2.39 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.0, 144.4, 137.9, 134.8, 131.5, 130.5, 129.0, 109.4, 21.3. **HRMS (EI):** m/z Calcd for $C_{12}H_{12}N_2O$ $[M+H]^+$: 201.1022; Found: 201.1029.

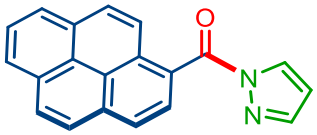
naphthalen-1-yl(1H-pyrazol-1-yl)methanone (3o) [S2]



Following general procedure 2.2.1 using **1o** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 11.1 mg, Yield: 50%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.7 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 1H), 7.96 (ddd, *J* = 21.7, 6.3, 3.2 Hz,

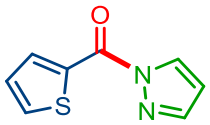
2H), 7.82 (d, J = 7.1 Hz, 1H), 7.76 (s, 1H), 7.61 – 7.50 (m, 3H), 6.57 – 6.56 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.4, 144.9, 133.5, 132.2, 130.9, 130.1, 129.8, 128.9, 128.6, 127.6, 126.6, 125.0, 124.3, 110.0.

(1H-pyrazol-1-yl)(pyren-1-yl)methanone (3p)



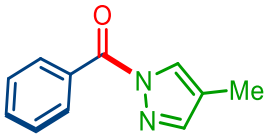
Following general procedure 2.2.1 using **1p** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 16.6 mg, Yield: 56%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.57 (d, J = 2.7 Hz, 1H), 8.37 – 7.98 (m, 9H), 7.79 (s, 1H), 6.59 – 6.58 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.8, 144.9, 133.7, 131.1, 130.5, 130.3, 129.6, 129.3, 127.7, 127.1, 126.5, 126.4, 126.2, 126.1, 124.6, 124.2, 124.1, 123.7, 109.9. **HRMS (EI):** m/z Calcd for $C_{20}H_{12}N_2O$ $[M+H]^+$: 297.1022; Found: 297.1020.

(1H-pyrazol-1-yl)(thiophen-2-yl)methanone (3q) [S2]



Following general procedure 2.2.1 using **1q** (0.1 mmol; 1.0 equiv.), pyrazole **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 7.4 mg, Yield: 42%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 – 8.33 (m, 2H), 7.87 – 7.70 (m, 2H), 7.19 (dd, J = 4.8, 4.1 Hz, 1H), 6.51 (dd, J = 2.7, 1.4 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 158.9, 144.1, 138.6, 137.4, 132.5, 129.9, 127.5, 109.7.

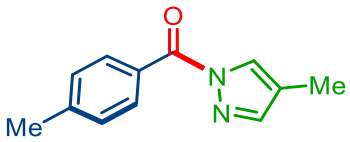
(4-methyl-1H-pyrazol-1-yl)(phenyl)methanone (3u)



Following general procedure 2.2.1 using **1a** (0.1 mmol; 1.0 equiv.), fomepizole **2b** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and

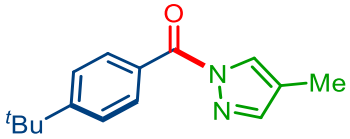
$TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 10.6 mg, Yield: 57%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.07 (d, *J* = 8.1 Hz, 2H), 7.67 – 7.41 (m, 4H), 2.16 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.3, 146.2, 132.8, 131.8, 131.3, 128.14, 128.06, 120.3, 8.9. **HRMS (EI):** m/z Calcd for $C_{11}H_{10}N_2O$ $[M+H]^+$: 187.0866; Found: 187.0861.

(4-methyl-1H-pyrazol-1-yl)(p-tolyl)methanone (3v)



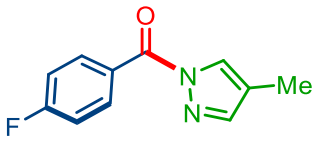
Following general procedure 2.2.1 using **1b** (0.1 mmol; 1.0 equiv.), fomepizole **2b** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 11.8 mg, Yield: 59%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.61 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H), 2.15 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.2, 146.0, 143.6, 131.5, 128.9, 128.8, 128.2, 120.1, 21.7, 8.9. **HRMS (EI):** m/z Calcd for $C_{12}H_{12}N_2O$ $[M+H]^+$: 201.1022; Found: 201.1023.

(4-(tert-butyl)phenyl)(4-methyl-1H-pyrazol-1-yl)methanone (3w)



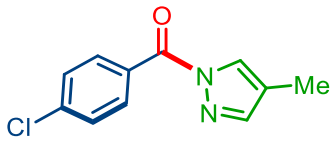
Following general procedure 2.2.1 using **1c** (0.1 mmol; 1.0 equiv.), fomepizole **2b** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 14.8 mg, Yield: 61%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.62 (s, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 2.16 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.3, 156.6, 146.1, 131.4, 128.9, 128.2, 125.2, 120.2, 35.2, 31.2, 9.0. **HRMS (EI):** m/z Calcd for $C_{15}H_{18}N_2O$ $[M+H]^+$: 243.1492; Found: 243.1495.

(4-fluorophenyl)(4-methyl-1H-pyrazol-1-yl)methanone (3x)



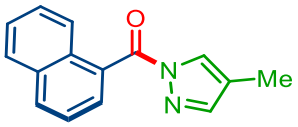
Following general procedure 2.2.1 using **1e** (0.1 mmol; 1.0 equiv.), fomepizole **2b** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 10.4 mg, Yield: 51%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 – 8.10 (m, 3H), 7.62 (s, 1H), 7.17 (t, J = 8.7 Hz, 2H), 2.16 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.6 (d, J = 254.8 Hz), 165.0, 146.3, 134.4 (d, J = 9.2 Hz), 128.3, 127.9, 120.5, 115.4 (d, J = 21.9 Hz), 9.0. **HRMS (EI):** m/z Calcd for $C_{11}H_9FN_2O$ $[M+H]^+$: 205.0772; Found: 205.0777.

(4-chlorophenyl)(4-methyl-1H-pyrazol-1-yl)methanone (3y)



Following general procedure 2.2.1 using **1f** (0.1 mmol; 1.0 equiv.), fomepizole **2b** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 11.5 mg, Yield: 52%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.17 (d, J = 0.9 Hz, 1H), 8.12 – 8.02 (m, 2H), 7.62 (s, 1H), 7.53 – 7.42 (m, 2H), 2.16 (d, J = 0.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.2, 146.4, 139.4, 133.0, 130.1, 128.5, 128.2, 120.7, 9.0. **HRMS (EI):** m/z Calcd for $C_{11}H_9ClN_2O$ $[M+H]^+$: 221.0476; Found: 221.0479.

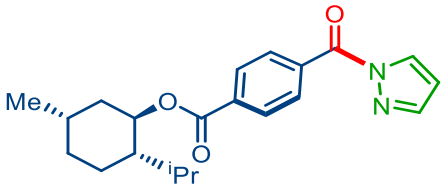
(4-methyl-1H-pyrazol-1-yl)(naphthalen-1-yl)methanone (3z)



Following general procedure 2.2.1 using **1o** (0.1 mmol; 1.0 equiv.), fomepizole **2b** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 9.9 mg, Yield: 42%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.21 (d, J = 0.8 Hz, 1H), 8.03 (d, J = 8.3 Hz, 1H), 7.97 – 7.85 (m, 2H), 7.77 (dd, J = 7.1, 1.2 Hz, 1H), 7.59 – 7.51 (m, 4H), 2.17 (d, J = 0.8 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$)

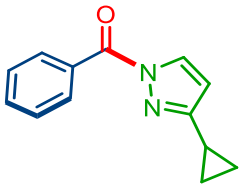
δ 167.3, 146.7, 133.5, 131.9, 130.9, 130.2, 128.6, 128.5, 127.8, 127.5, 126.5, 125.1, 124.3, 121.0, 9.0. **HRMS (EI):** m/z Calcd for $C_{15}H_{12}N_2O$ $[M+H]^+$: 237.1022; Found: 237.1025.

(1R,2S,5S)-2-isopropyl-5-methylcyclohexyl 4-(1H-pyrazole-1-carbonyl)benzoate (3za)



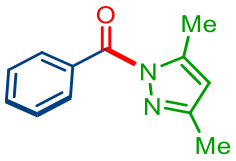
Following general procedure 2.2.1 using **1r** (0.1 mmol; 1.0 equiv.)[S3], **2a** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Gummy liquid, 14.6 mg, Yield: 41%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.8 Hz, 1H), 8.21 – 8.08 (m, 4H), 7.81 (s, 1H), 6.56 (d, *J* = 1.3 Hz, 1H), 4.96 (td, *J* = 10.9, 4.4 Hz, 1H), 2.20 – 2.07 (m, 1H), 2.00 – 1.88 (m, 1H), 1.74 (d, *J* = 11.8 Hz, 2H), 1.60 – 1.54 (m, 2H), 1.27 – 1.23 (m, 1H), 1.18 – 1.06 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 6H), 0.80 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 165.3, 144.9, 135.3, 134.6, 131.3, 130.4, 129.2, 109.9, 75.6, 47.4, 41.0, 34.4, 31.6, 26.7, 23.7, 22.1, 20.8, 16.6. **HRMS (EI):** m/z Calcd for $C_{21}H_{26}N_2O_3$ $[M+H]^+$: 355.2016; Found: 355.2010.

(3-cyclopropyl-1H-pyrazol-1-yl)(phenyl)methanone (3zb)



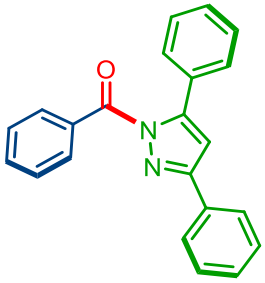
Following general procedure 2.2.1 using **1a** (0.1 mmol; 1.0 equiv.), 3-cyclopropyl-1H-pyrazole **2c** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 10.0 mg, Yield: 47%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 2.9 Hz, 1H), 8.13 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.64 – 7.52 (m, 1H), 7.48 (dd, *J* = 10.6, 4.7 Hz, 2H), 6.16 (d, *J* = 2.9 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.02 – 0.97 (m, 2H), 0.84 – 0.80 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.9, 160.9, 132.8, 131.8, 131.6, 131.2, 128.0, 106.6, 9.6, 8.4. **HRMS (EI):** m/z Calcd for $C_{13}H_{12}N_2O$ $[M+H]^+$: 213.1022; Found: 213.1028.

(3,5-dimethyl-1H-pyrazol-1-yl)(phenyl)methanone (3zc)



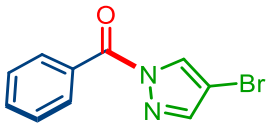
Following general procedure 2.2.1 using **1a** (0.1 mmol; 1.0 equiv.), 3,5-dimethyl-1H-pyrazole **2d** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 8.2 mg, Yield: 41%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 – 7.98 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 6.06 (s, 1H), 2.64 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 168.4, 152.2, 145.1, 133.4, 132.4, 131.4, 127.9, 111.1, 14.3, 13.9. **HRMS (EI):** m/z Calcd for $C_{12}H_{12}N_2O$ $[M+H]^+$: 201.1022; Found: 201.1025.

(3,5-diphenyl-1H-pyrazol-1-yl)(phenyl)methanone (3zd)



Following general procedure 2.2.1 using **1a** (0.1 mmol; 1.0 equiv.), 3,5-diphenyl-1H-pyrazole **2e** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 15.0 mg, Yield: 46%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, J = 7.6 Hz, 2H), 7.89 (d, J = 7.2 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.54 – 7.51 (m, 4H), 7.47 – 7.37 (m, 6H), 6.89 (s, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 167.5, 153.6, 148.7, 133.2, 132.5, 132.0, 131.8, 130.8, 129.1, 128.8, 128.5, 128.3, 128.0, 126.4, 109.0. **HRMS (EI):** m/z Calcd for $C_{22}H_{16}N_2O$ $[M+H]^+$: 325.1335; Found: 325.1331.

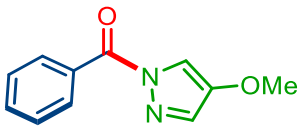
(4-bromo-1H-pyrazol-1-yl)(phenyl)methanone (3ze)



Following general procedure 2.2.1 using **1a** (0.1 mmol; 1.0 equiv.), 4-bromo-1H-pyrazole **2e** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was

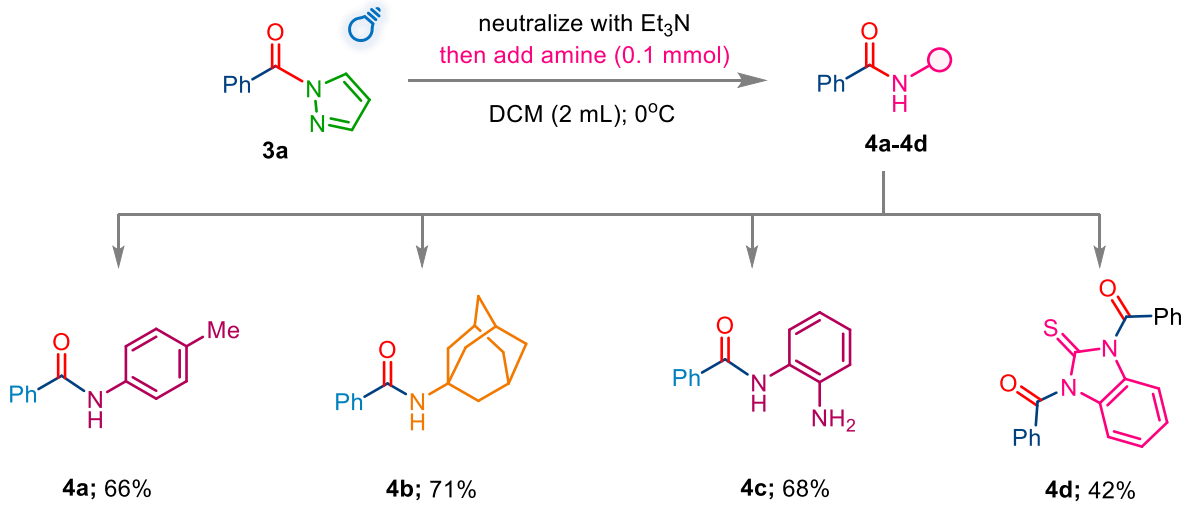
purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 9.8 mg, Yield: 39%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.45 (s, 1H), 8.09 – 8.07 (m, 2H), 7.74 (s, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.4, 145.0, 133.5, 131.6, 130.6, 130.4, 128.3, 99.4. **HRMS (EI):** m/z Calcd for $C_{10}H_7BrN_2O$ $[M+H]^+$: 250.9815; Found: 250.9811.

(4-methoxy-1H-pyrazol-1-yl)(phenyl)methanone (3zf)



Following general procedure 2.2.1 using **1a** (0.1 mmol; 1.0 equiv.), 4-methoxy-1H-pyrazole **2f** (0.1 mmol; 1.0 equiv.), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol) and $TBANO_3$ (0.1 mmol, 1 equiv.) in acetonitrile solvent (2.0 mL) under O_2 atmosphere. The product was purified by column chromatography (Hexane/Ethyl acetate, 99:1), Colourless solid, 4.7 mg, Yield: 23%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.4, 1.2 Hz, 2H), 7.96 (d, J = 0.7 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.53 – 7.44 (m, 2H), 3.84 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.4, 149.5, 136.3, 132.7, 131.5, 131.3, 128.1, 110.9, 58.9. **HRMS (EI):** m/z Calcd for $C_{11}H_{10}N_2O_2$ $[M+H]^+$: 203.0815; Found: 203.0816.

2.2.3 Further modifications of *N*-benzoylpyrazole



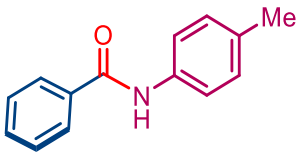
Scheme S2. Late-stage modifications of *N*-benzoylpyrazole (**4a-4d**).

Process: To a 15 mL clean, oven-dried reaction tube, corresponding amine (0.1 mmol), triethylamine (0.1 mmol) was added in DCM at 0°C sequentially. Then after 30 mins, *N*-benzoylpyrazole **2** (0.1 mmol)

was added and kept overnight. After completion (determined by TLC), the reaction mixture was directly evaporated under reduced pressure and crude mixture was purified by silica gel column chromatography (230-400 mesh size) using petroleum-ether/ethyl acetate (7:3) as an eluting system.

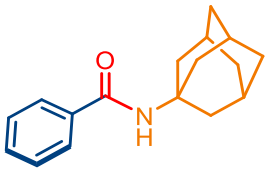
2.2.4 NMR characterization for *N-benzamide* derivatives

N-(p-tolyl)benzamide (4a)



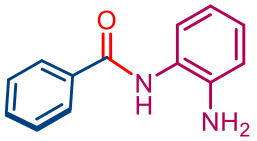
Following general procedure 2.2.3 using **3a** (0.1 mmol; 1.0 equiv.), *p*-toluidine (0.1 mmol; 1.0 equiv.). The product was purified by column chromatography (Hexane/Ethyl acetate, 9:1), White solid, 13.8 mg, Yield: 66%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (br, 1H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.53 – 7.49 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.9, 135.4, 135.1, 134.2, 131.7, 129.5, 128.7, 127.1, 120.5, 20.9. **HRMS (EI):** m/z Calcd for $C_{14}H_{13}NO$ $[M+H]^+$: 212.1070; Found: 212.1077.

N-((1R,3r)-adamantan-1-yl)benzamide (4b)



Following general procedure 2.2.3 using **3a** (0.1 mmol; 1.0 equiv.), adamantane amine (0.1 mmol; 1.0 equiv.). The product was purified by column chromatography (Hexane/Ethyl acetate, 9:1), White solid, 18.1 mg, Yield: 71%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.48 – 7.43 (m, 1H), 7.40 (t, *J* = 7.3 Hz, 2H), 5.82 (br, 1H), 2.12 (s, 9H), 1.81 – 1.56 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 136.1, 131.1, 128.5, 126.8, 52.4, 41.8, 36.5, 29.6. **HRMS (EI):** m/z Calcd for $C_{17}H_{21}NO$ $[M+H]^+$: 256.1696; Found: 256.1699.

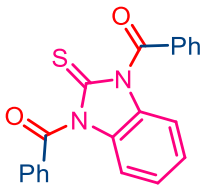
N-(2-aminophenyl)benzamide (4c)



Following general procedure 2.2.3 using **3a** (0.1 mmol; 1.0 equiv.), *o*-phenylenediammine (0.1 mmol; 1.0 equiv.). The product was purified by column chromatography (Hexane/Ethyl acetate, 7:3), White solid, 14.5 mg, Yield: 68%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (br, 1H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.54

(t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 7.7 Hz, 1H), 7.07 (td, J = 7.9, 1.2 Hz, 1H), 6.81 (t, J = 6.8 Hz, 2H), 3.57 (br, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 166.1, 140.6, 134.1, 131.9, 128.7, 127.4, 127.3, 125.4, 124.6, 119.8, 118.4. **HRMS (EI):** m/z Calcd for $C_{13}H_{12}N_2O$ $[M+H]^+$: 213.1022; Found: 213.1028.

N-(2-aminophenyl)benzamide (4d)

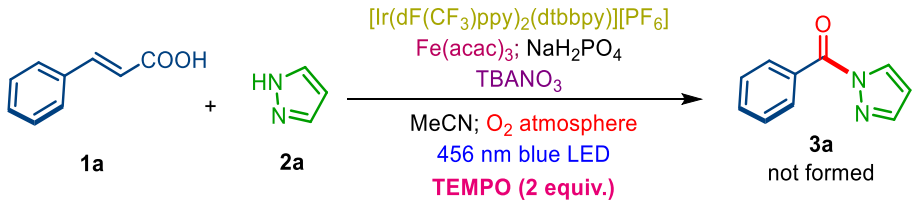


Following general procedure 2.2.3 using **3a** (0.1 mmol; 1.0 equiv.), 2-mercaptobenzimidazole (0.05 mmol; 0.5 equiv.). The product was purified by column chromatography (Hexane/Ethyl acetate, 8:2), Yellow solid, 15.1 mg, Yield: 42%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.7 Hz, 4H), 7.65 (t, J = 7.4 Hz, 2H), 7.50 (t, J = 7.8 Hz, 4H), 7.36 (dd, J = 6.0, 3.3 Hz, 2H), 7.28 (dd, J = 6.1, 3.2 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.3, 168.9, 134.7, 132.4, 131.6, 130.8, 129.0, 125.1, 112.0. **HRMS (EI):** m/z Calcd for $C_{21}H_{14}N_2O_2S$ $[M+H]^+$: 359.0849; Found: 359.0844.

3. Mechanistic Studies

3.1 Radical trapping experiment

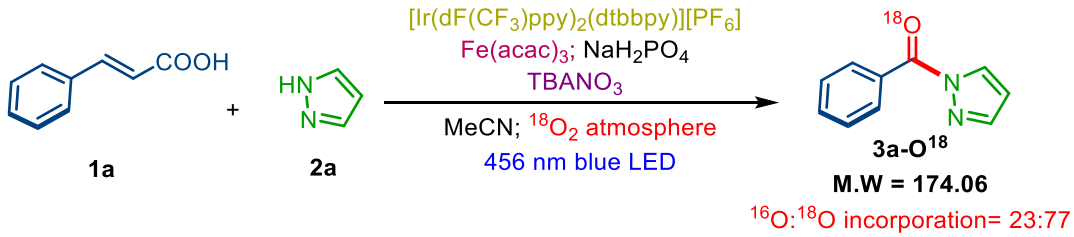
To a 30 mL clean Schlenk reaction tube, cinnamic acid **1** (0.1 mmol), pyrazole **2** (0.1 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol), tetrabutylammonium nitrate $TBANO_3$ (0.1 mmol, 1 equiv.), TEMPO (2 equiv.) double distilled acetonitrile (2.0 mL) were added in an open-air condition. The solution was then photo irradiated with 40 W Kessil PR160L-456 nm LED at room temperature for 6 hours. A cooling fan was used to maintain the reaction temperature between 30-32 ºC. After usual work-up procedure, the analysis of the crude material revealed no desired product formation. This result indicates that the reaction most likely proceeds via a radical pathway.



Scheme S3. Radical trapping experiment by TEMPO.

3.2 Isotope Labelling Experiments using $^{18}O_2$

To a 30 mL clean Schlenk reaction tube, cinnamic acid **1** (0.1 mmol), pyrazole **2** (0.1 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol), tetrabutylammonium nitrate $TBANO_3$ (0.1 mmol, 1 equiv.), double distilled acetonitrile (2.0 mL) were added in an open-air condition. Then, the solution was evacuated and backfilled with $^{18}O_2$ gas thrice and photo irradiated with 40 W Kessil PR160L-456 nm LED at room temperature for 12 hours. A cooling fan was used to maintain the reaction temperature between 30-32 ºC. After 12h of irradiation, ^{18}O labelling desired product **3a-O^{18}** was identified through GC-MS analysis. This observation suggests the involvement of oxygen gas (O_2 gas) in our methodology as a core unit for carbonyl **(>C=O)** group in our desired product **3a-O^{18}**.



Scheme S4. ^{18}O labelling experiments in presence of $^{18}O_2$.

GCMS Chromatogram

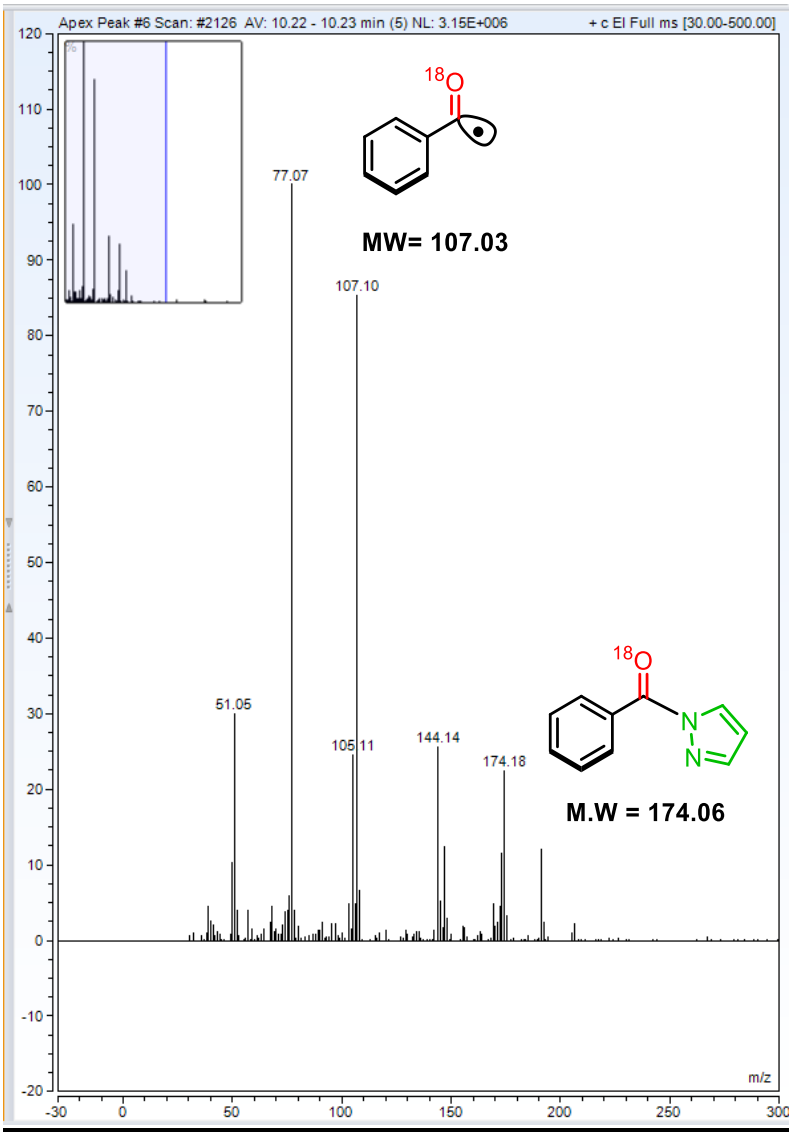


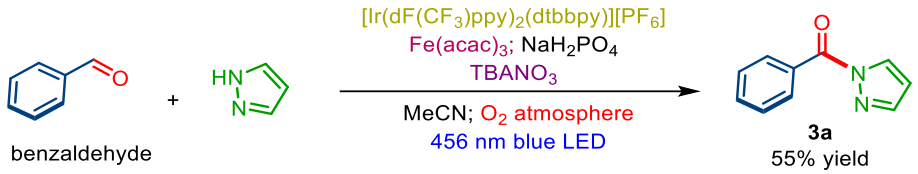
Fig. S1. GC-MS Spectra of **3a-O^{18}**

Isotope ratio calculation: The ratio of labelled product is calculated from benzoyl fragmentation of the desired product **3a-O^{18}**. The peak intensity for **^{16}O is nearly 25**, whereas, the peak intensity is **85 for ^{18}O** and the calculation is as mentioned below-

$$^{16}O = \frac{25}{25+85} = 22.7\% \qquad ^{18}O = \frac{85}{25+85} = 77.3\%$$

3.3 Intermediate Detection

In standard condition, benzaldehyde has been taken to check if it can form the desired product **3a**. We have observed 55% GC yield of desired product. It suggests benzaldehyde is an intermediate of current photo transformation.



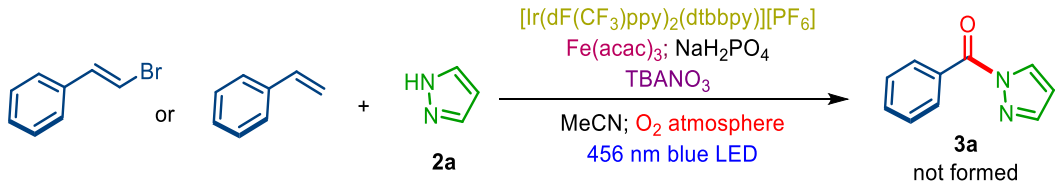
Scheme S5. Intermediate detection.

To elucidate the roles of each parameter, three reactions were performed removing photocatalyst or transition metal catalyst or oxygen gas. The result suggests only in absence of $Fe(acac)_3$, the poroduct has been formed from benzaldehyde. It clearly indicates $Fe(acac)_3$ has no role to convert benzaldehyde into **3a**. Thus, iron catalyst is only helping to generate benzaldehyde from cinnamic acid under standard conditions.

Removing parameter	Product **3a**	Conclusion
Ir-photocatalyst	not formed	**Ir** helps to convert benzaldehyde into **3a**
$Fe(acac)_3$	Formed (57%)	**Fe** has no role to convert benzaldehyde into **3a**
Oxygen gas	not formed	**O_2** helps to convert benzaldehyde into **3a**

3.4 Experimental procedure for other olefinic compounds

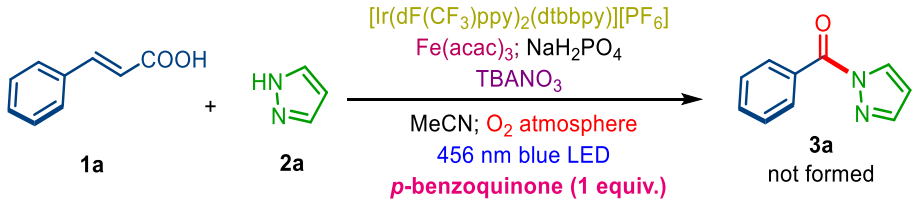
Initially, two 15 mL scintillating oven-dried reaction tubes were taken. To these solutions, pyrazole **2a** (0.1 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)][PF_6]$ (2 mol%), $Fe(acac)_3$ (20 mol%), NaH_2PO_4 (0.1 mmol), tetrabutylammonium nitrate $TBANO_3$ (0.1 mmol, 1 equiv.), double distilled acetonitrile (2.0 mL) were added in an open air condition. Then, 0.1 mmol of *β*-bromostyrene and styrene were added respectively and photoirradiated with 456 nm blue LED at room temperature for 12 hours. A cooling fan was used to maintain the reaction temperature between 30-32 ºC. After usual work-up procedure, the analysis of the crude material revealed no desired product formation in any of the cases. This result indicates that the reaction proceeds via decarboxylation which acts a crucial step in this current transformation.



Scheme S6. Reaction in presence of electronically different alkenes.

3.5 Reaction in presence of superoxide radical anion quencher [S4]

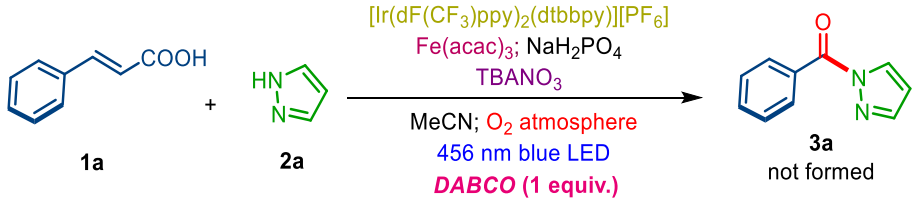
To check the involvement of superoxide radical anion in the reaction, the standard reaction of cinnamic acid (**1a**) and pyrazole (**2a)** was performed in presence of *p*-benzoquinone (0.1 mmol, 1.0 equiv.), a known superoxide radical anion quencher. Complete inhibition of the desired product formation was observed, suggesting the involvement of superoxide radical anion in this aerobic radical process for both methods.



Scheme S7. Radical quenching experiment by superoxide radical anion quencher.

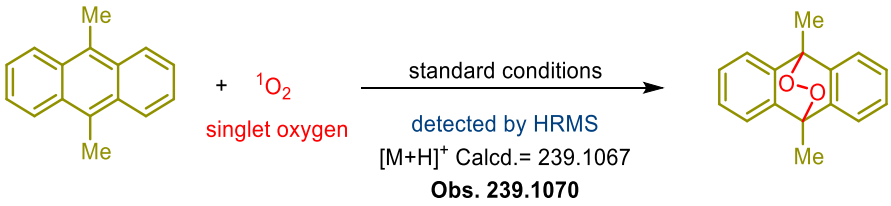
3.6 Reaction in presence of singlet oxygen $^1O_2$ quencher[S4]

To check the involvement of singlet oxygen in the reaction, the standard reaction between cinnamic acid (**1a**) and pyrazole (**2a)** was performed in presence of *DABCO* (0.1 mmol, 1.0 equiv.), a known singlet oxygen quencher. Complete inhibition of the desired product formation was observed, suggesting the involvement of singlet oxygen in this aerobic radical process.



Scheme S8. Singlet oxygen quenching experiment by DABCO.

<u>Trapping of singlet $^1O_2$</u>: To validate the formation of singlet oxygen, we conducted our standard reaction in presence of 9,10-dimethylanthracene, a known singlet oxygen quencher. After 4 hours, we have detected the formation of an adduct of 9,10-dimethylanthracene with aerial oxygen *via* HRMS analysis.



Scheme S9. Singlet oxygen quenching experiment by DABCO.

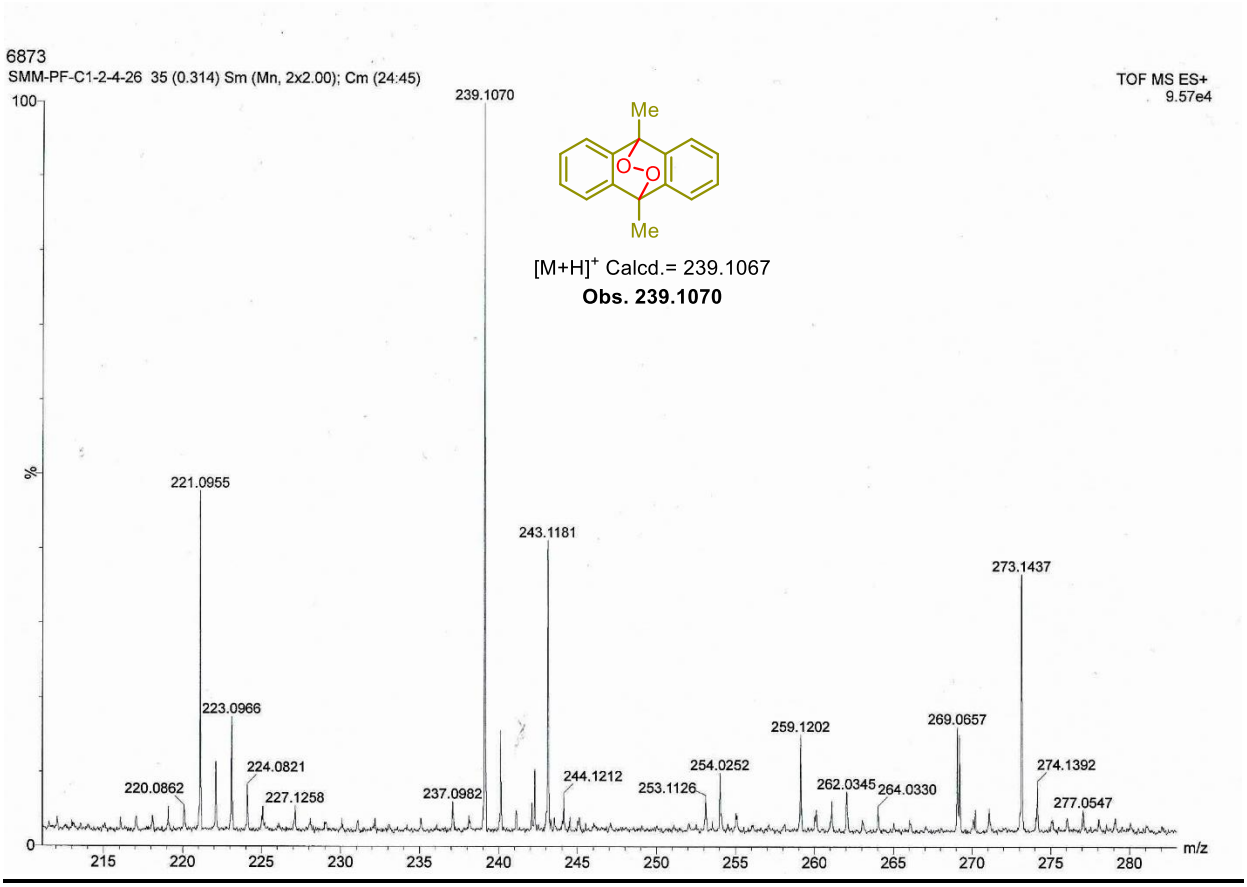


Fig. S2. HRMS spectra of adduct from 9,10-dimethylanthracene and oxygen.

3.7 Reaction in presence of peroxide radical quencher [S4]

Finally, the formation of peroxide anion is confirmed over the detection of hydrogen peroxide (H_2O_2). Initially, a reaction of cinnamic acid (**1a**) and pyrazole (**2a**) under standard conditions (0.1 mmol scale) were performed for 4 hours and the reaction mixture was quenched with distilled water and the aqueous layer was extracted with DCM. Thereafter, a colorless aqueous KI (0.5 M)/CH_3CO_2H solution was added to the aqueous extract and the color of aqueous solution immediately changed to yellow for both cases, which further transformed to dark brown. This color variation of colorless KI/CH_3CO_2H solution to dark brown indicates the presence of H_2O_2 in the reaction mixture.

3.8 Photophysical Studies for Fe(III)-based LMCT phenomena[S5]

A $Fe(acac)_3$ solution (0.1 mM in MeCN, 2 mL) was added to the UV-visible cell for measurement (brown). Next, $TBANO_3$ (1 mM) was added to the same UV-visible cell and spectra was recorded, which shows slight decrease in the absorbance peaks of $Fe(acac)_3$ (blue). Then, cinnamic acid (**1a)** and base NaH_2PO_4 was added sequentially to the solution, which shows slight decrease in the absorbance peak at 440 nm peak arises due to LMCT of iron catalyst. Then, the solution was irradiated under 456 nm blue

LED to facilitate LMCT event from cinnamic acid to iron center. At a shorter time of only 5 min (in pink), the peak sharply decreases clearly depicts strong LMCT between the species, and after 15 min of irradiation (in royal blue), the absorbance of $Fe(acac)_3$ diminished completely and the solution became colourless. (**Fig. S3**)

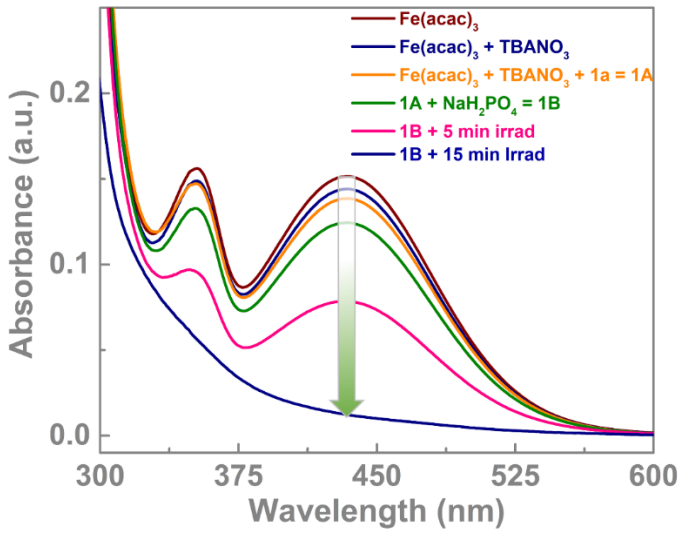


Fig. S3. UV-vis spectra for LMCT event.

3.9 Light on-off experiment

The initial control experiments during the reaction optimization studies have indicated that photoirradiation is essential for the process. To evaluate the role of light for the reaction, a light on/off experiment was conducted following the General procedure. The reactions were cycled through alternative irradiation and dark periods for 2 h and 1 h respectively, as summarized in **Table S9**. The yield of the reaction was determined by GCMS using 1,4-dibromobutane as an internal standard. The result suggests the reaction is highly dependent upon blue LED irradiation and no product has formed when the light was off. The yield of the product is average of two independent experiments under similar conditions.

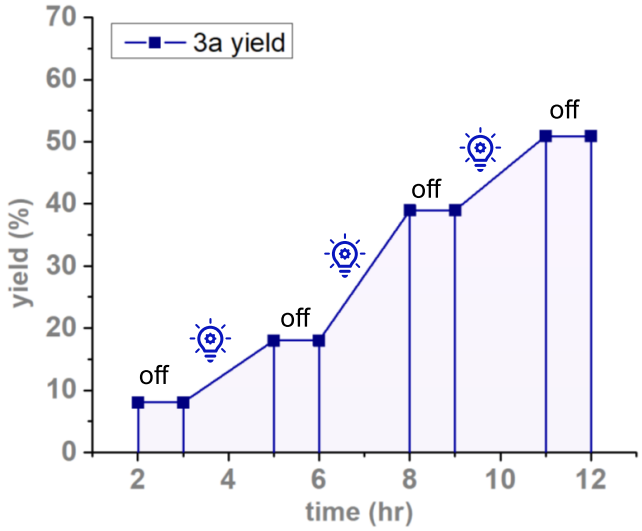


Fig. S4 Light on-off experiment.

Table S9: Light on-off experiment[a]

Time (h)	Yield (3a)[b] %	Condition of light
2	8	on
3	8	off
5	18	on
6	18	off
8	39	on
9	39	off
11	51	on
12	51	off

4. X-ray crystal structure determination of 3f

X-ray diffraction quality singles crystal of entry_**3f** were found by slow evaporating the chloroform solution of **3f**, and it was crystallized in the orthorhombic crystal system with **P 21 21 21** space group.

Crystallographic data (CCDC 2526706)

Compound reference	**Entry_3f**
Chemical formula	$C_{10}H_7ClN_2O$
Formula Mass	206.0247
Crystal system	orthorhombic
a/Å	3.8172(2)
b/Å	11.1945(5)
c/Å	21.6361(9)
α/°	90
β/°	90
γ/°	90
Unit cell volume/Å^3	924.55(7)
Temperature/K	166(2)
Space group	P 21 21 21
No. of formula units per unit cell, Z	4
Radiation type	MoKα
No. of reflections measured	30584
No. of independent reflections	1735
R_{int}	0.1177
Final R_1 values ($I > 2\sigma(I)$)	0.0317
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0742
Final R_1 values (all data)	0.0349
Final $wR(F^2)$ values (all data)	0.0750
CCDC number	2526706

Crystal structure image of 3f:

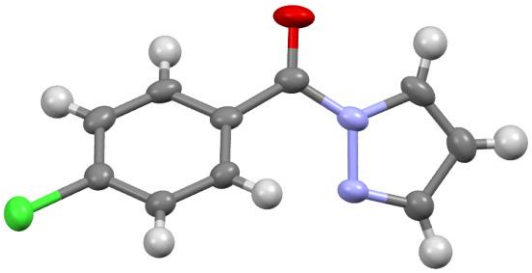


Fig. S5. X-ray crystal structure of **entry_3f**

5. References

S1. W. L. F. Armarego and D. D. Perrin, *Purification of Laboratory Chemicals* (Pergamon Press, Oxford, 1988) ed 3.

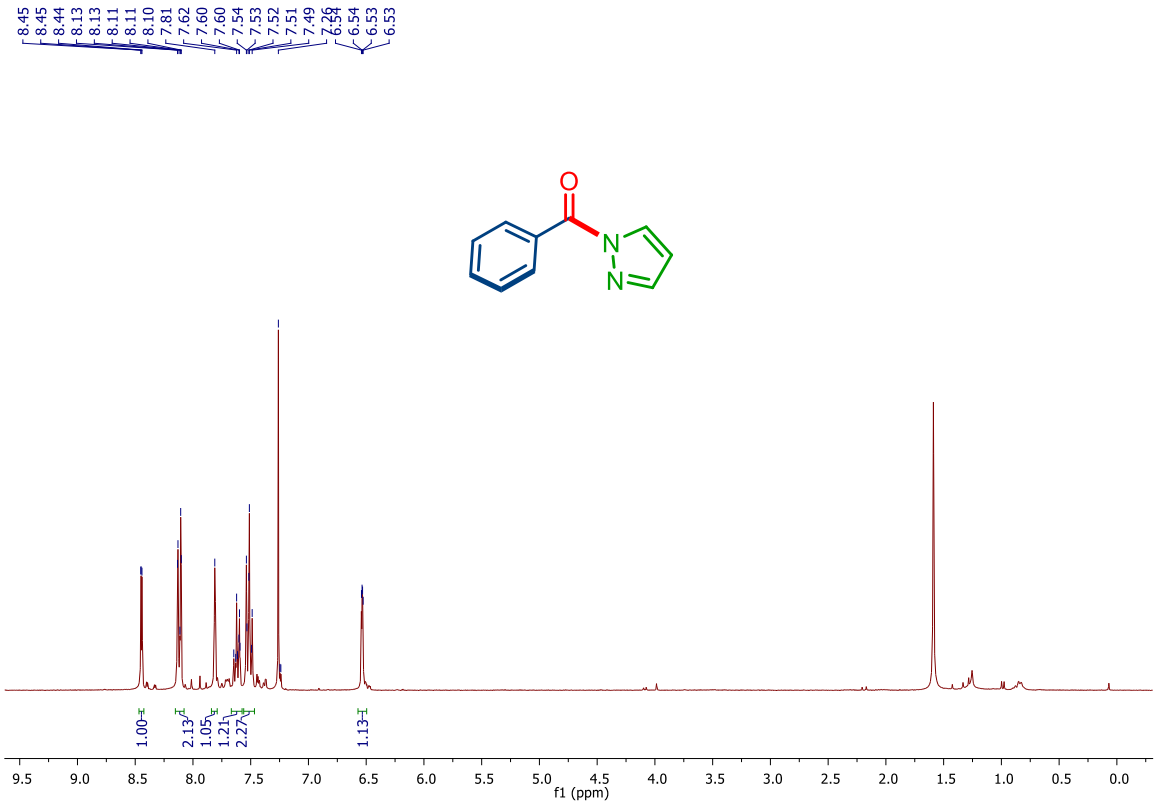
S2. (*a*) N. Gong, Z. Zhao, D. James Young, X. Cao, Z. Ren and H. Li, *Chem.─Eur. J.,* 2025, **31**, e202404225. (*b*) D. I. Ioannou, E. Bombonato, J. Sanramat, J. N. H. Reek and T. Noël, *Chem.─Eur. J.,* 2025, **31**, e02237.

S3. Z.-M. Lai, Y. Xie, L.-L. Huang, J. Guo and G. Lu, *Chem. Sci.*, 2025, **16**, 4352–4359.

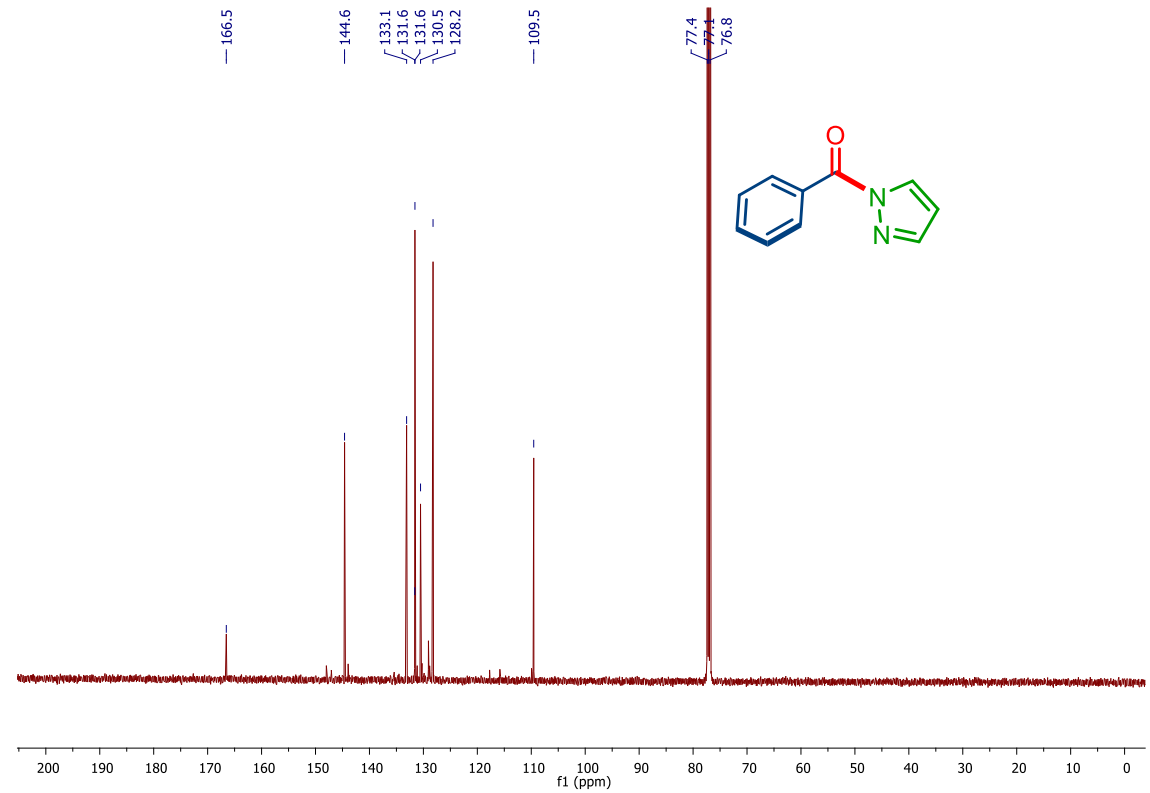
S4. S. Mondal, S. Banerjee, S. Bera, S. Mondal, S. P. Midya, R. Jana, R. K. Behera, A. Datta, N. Pradhan and P. Ghosh, *ACS Catal.,* 2024, **14**, 6633– 6643.

S5. S. Mondal, S. P. Midya, S. Ghosh, S. Maiti, S. Mondal, T. Jana and P. Ghosh, *Chem. Commun.,* 2025, **61**, 13457– 13460.

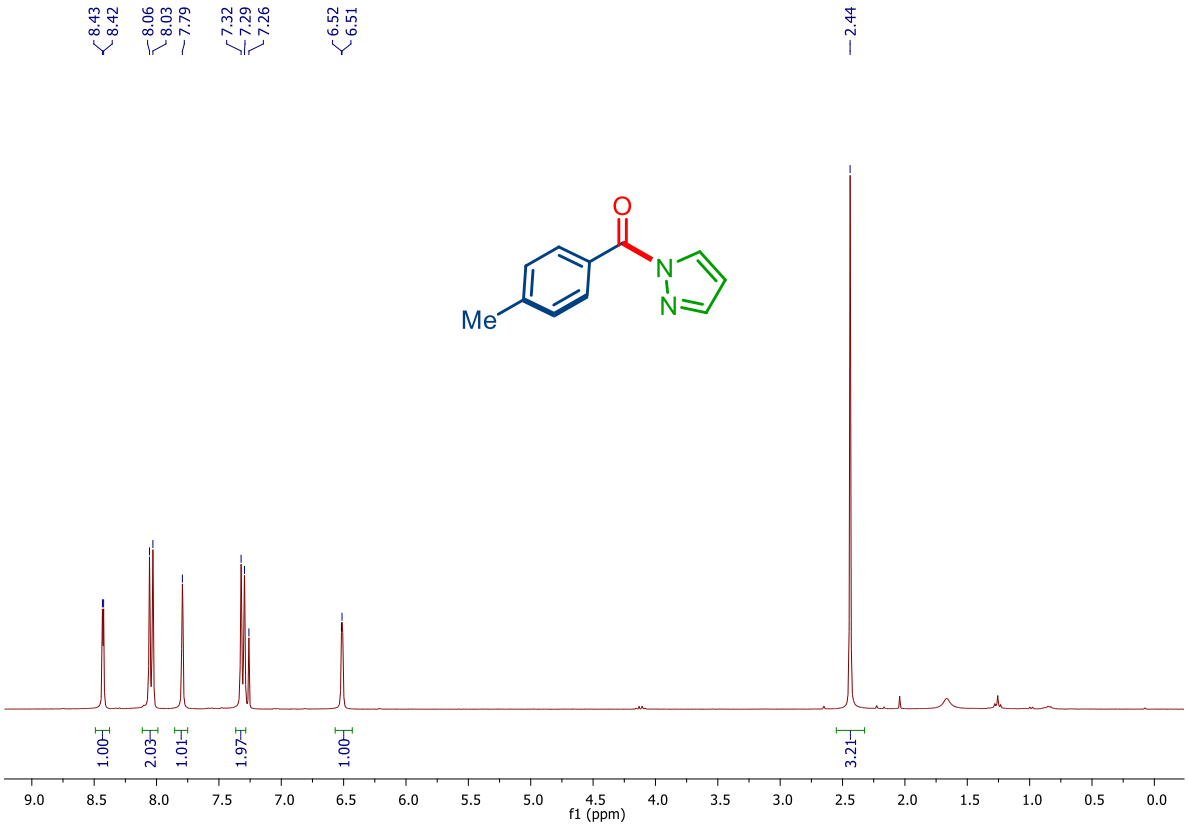
6. Copy of Spectra



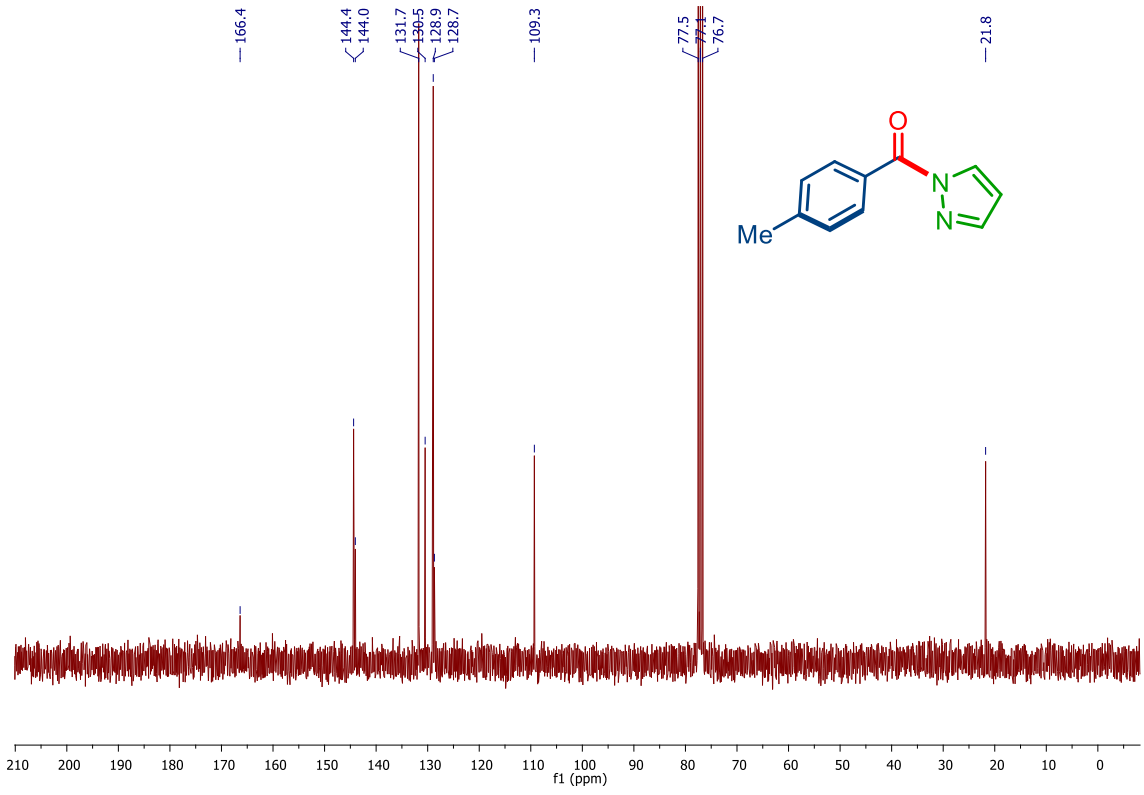
^{1}H NMR (300 MHz) spectrum of **3a** ($CDCl_3$, rt)



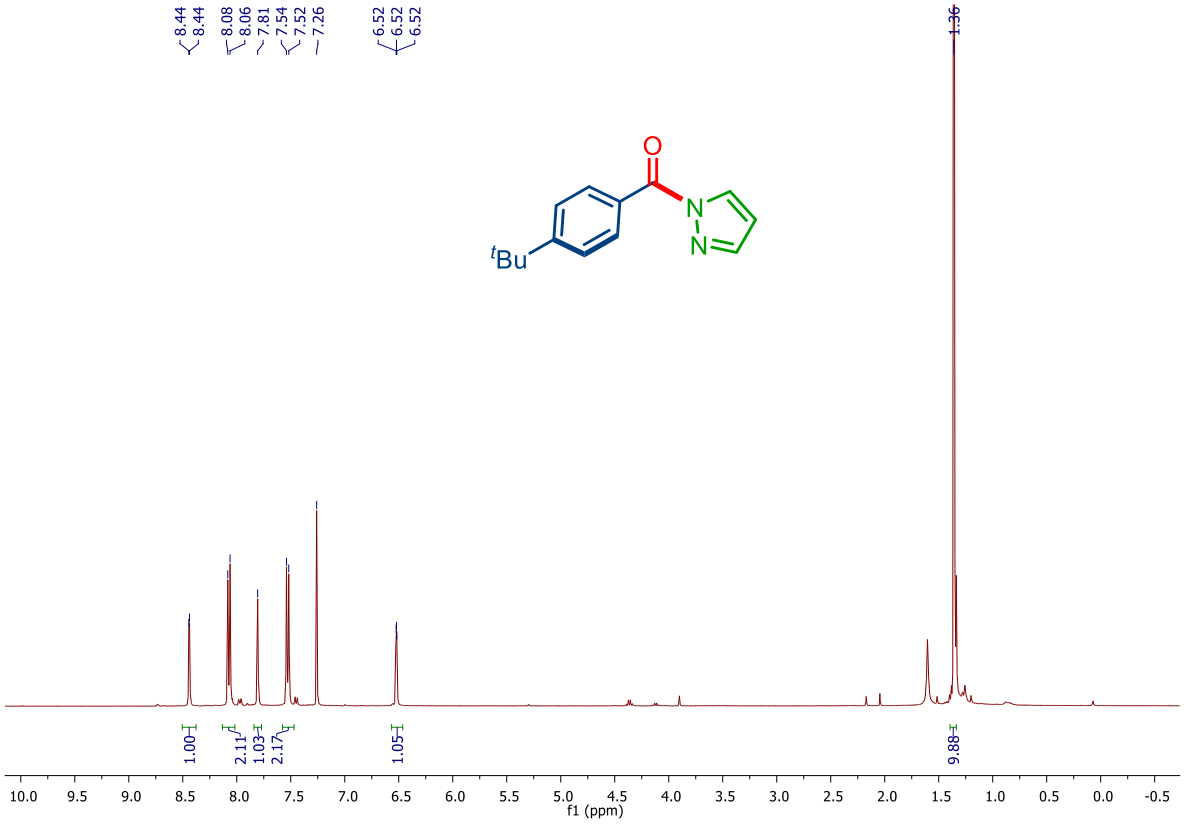
^{13}C{^{1}H} NMR (126 MHz) spectrum of **3a** ($CDCl_3$, rt)



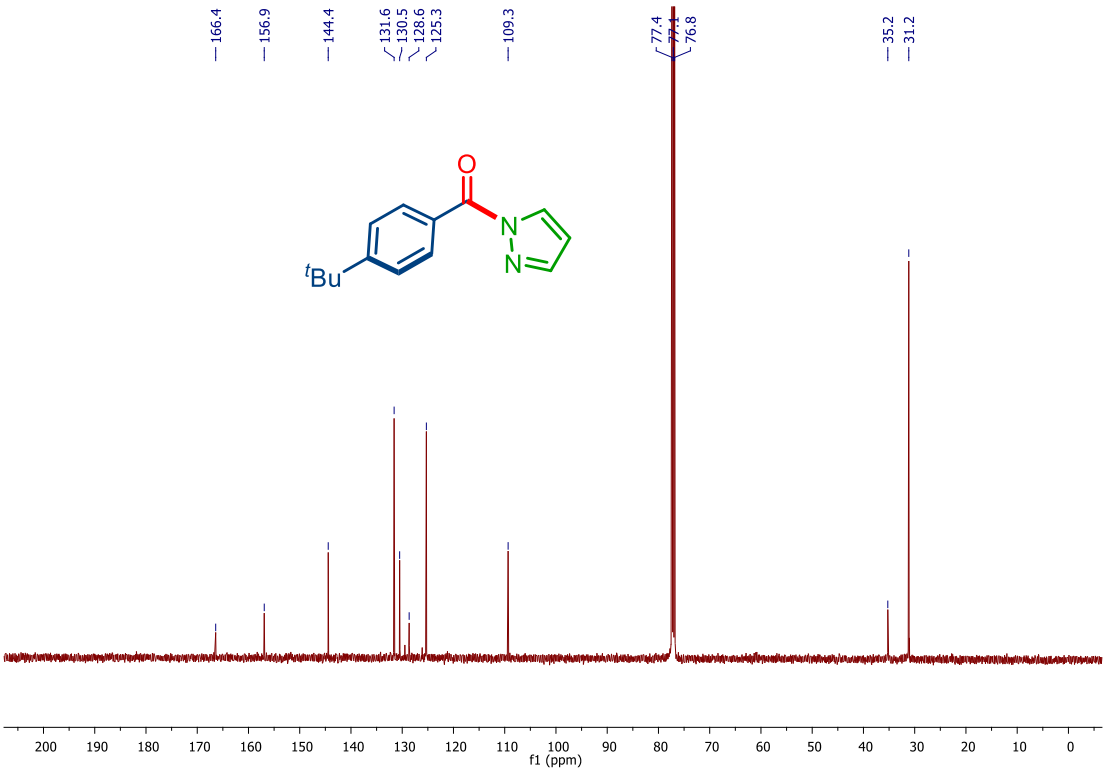
^{1}H NMR (300 MHz) spectrum of **3b** ($CDCl_3$, rt)



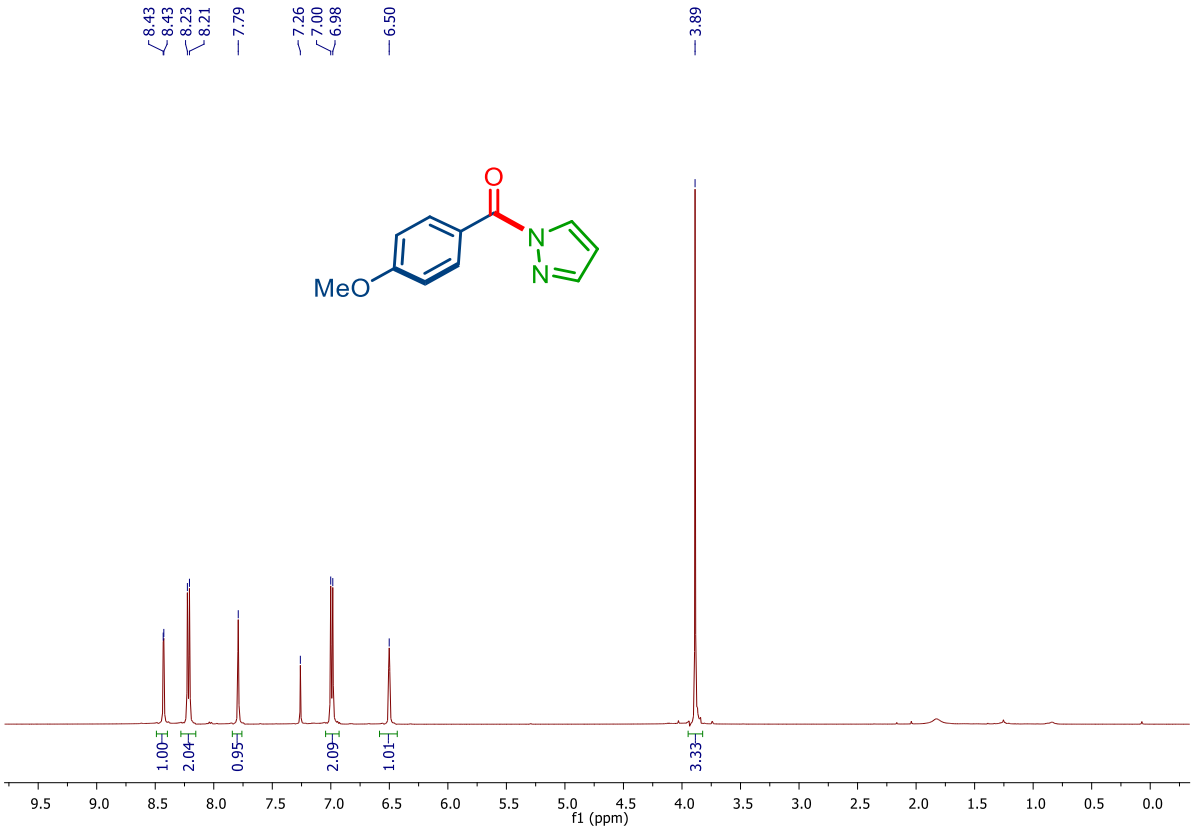
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3b** ($CDCl_3$, rt)



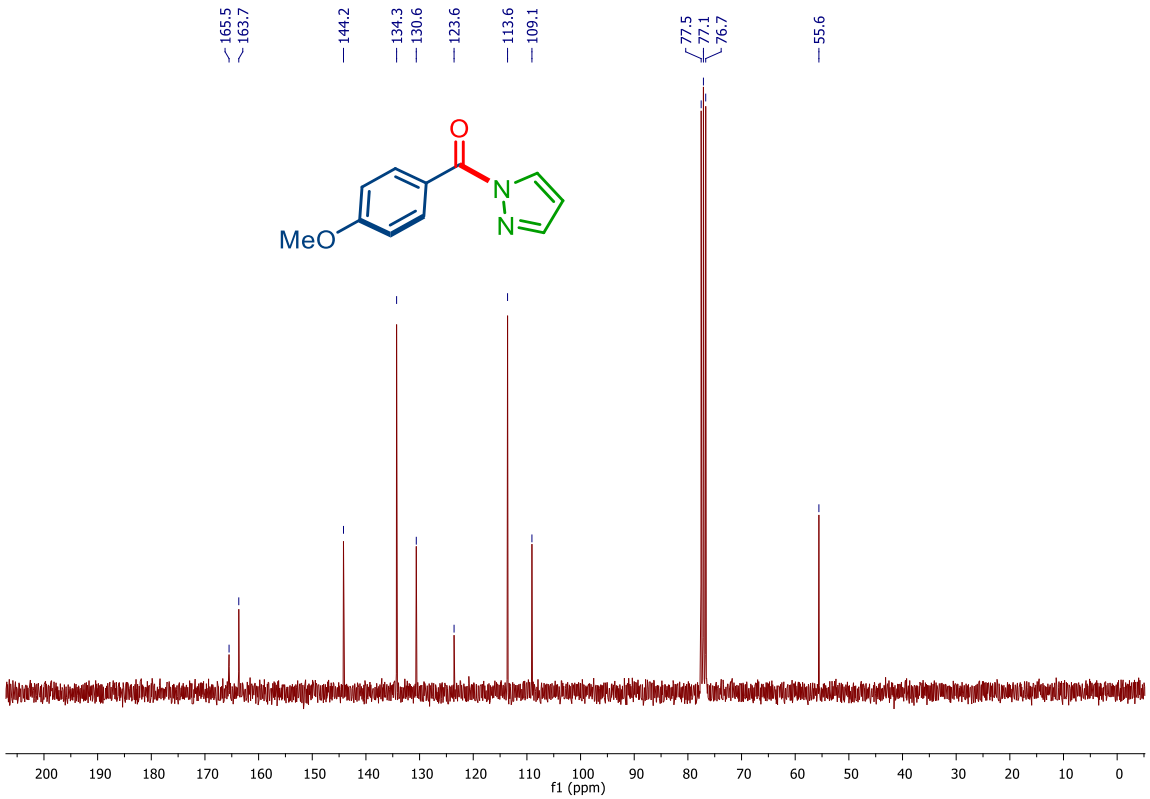
^{1}H NMR (400 MHz) spectrum of **3c** ($CDCl_3$, rt)



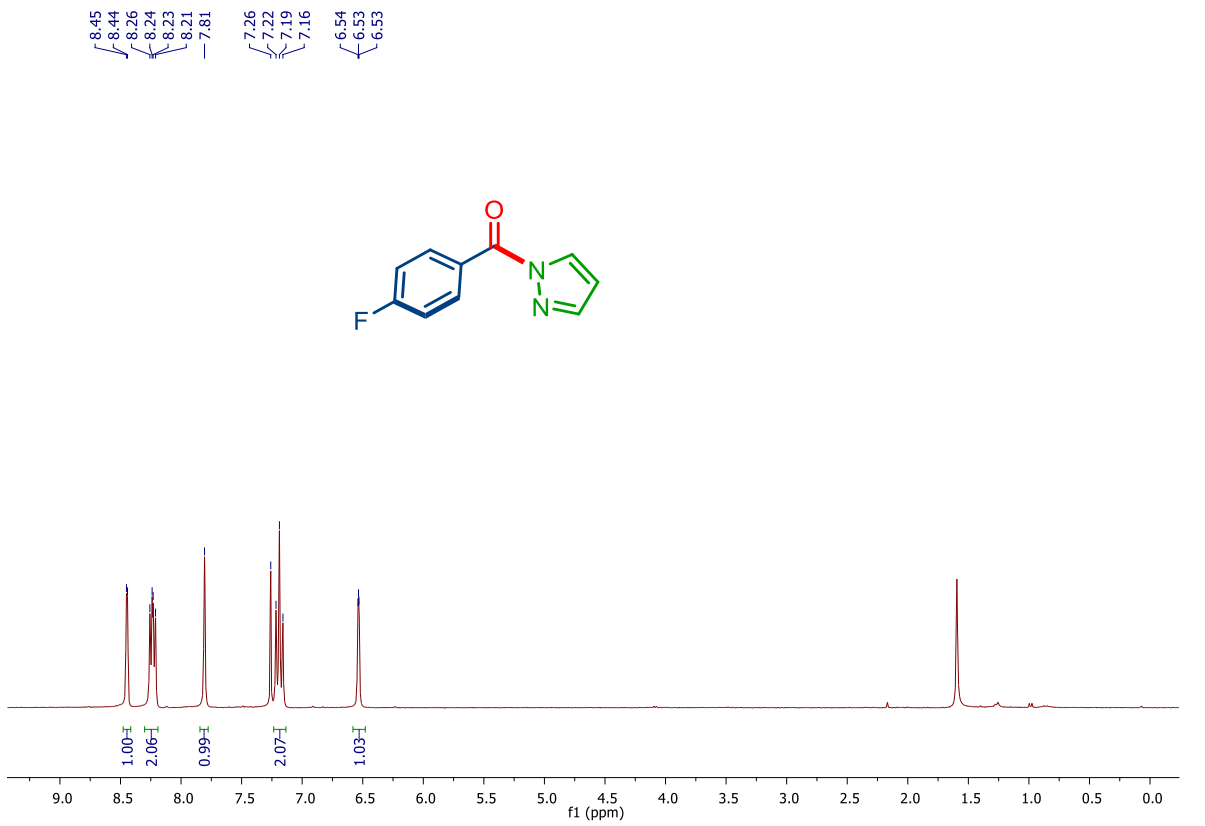
^{13}C{^{1}H} NMR (126 MHz) spectrum of **3c** ($CDCl_3$, rt)



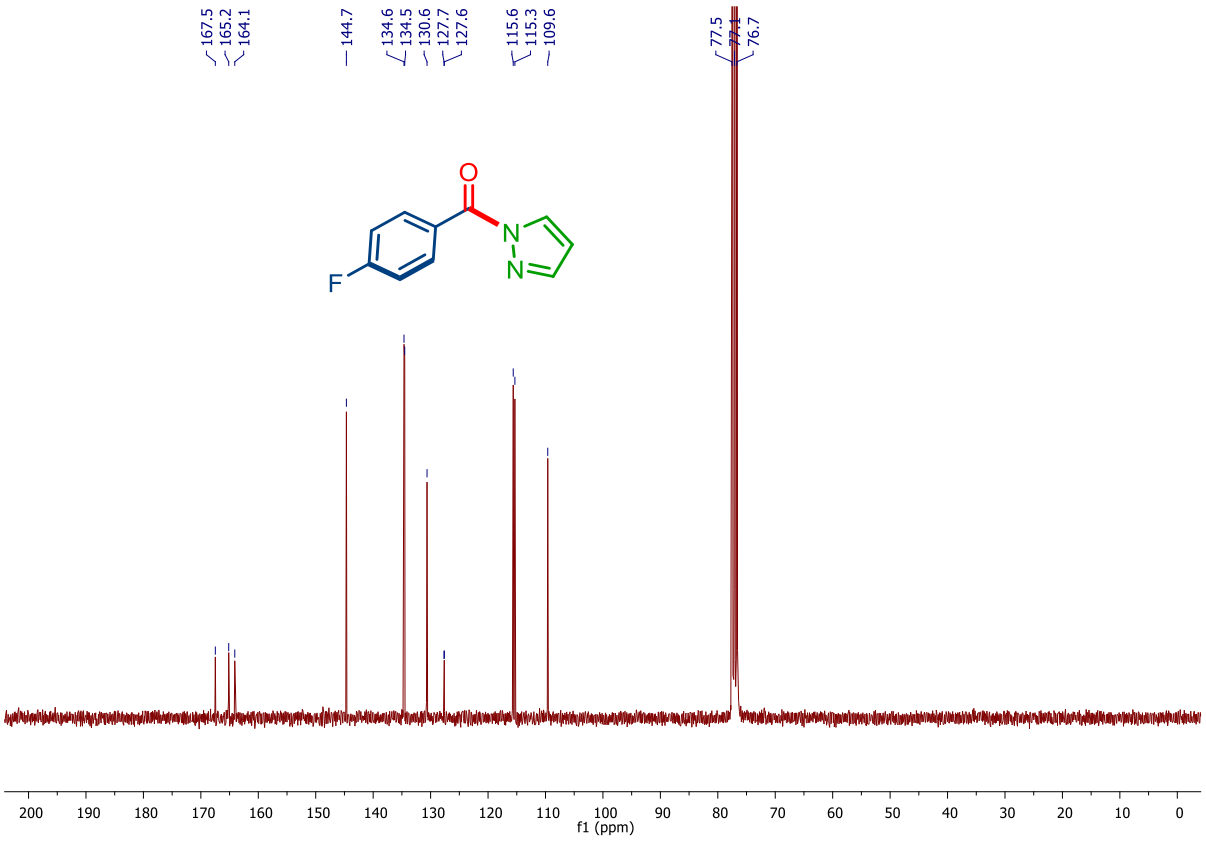
^{1}H NMR (500 MHz) spectrum of **3d** ($CDCl_3$, rt)



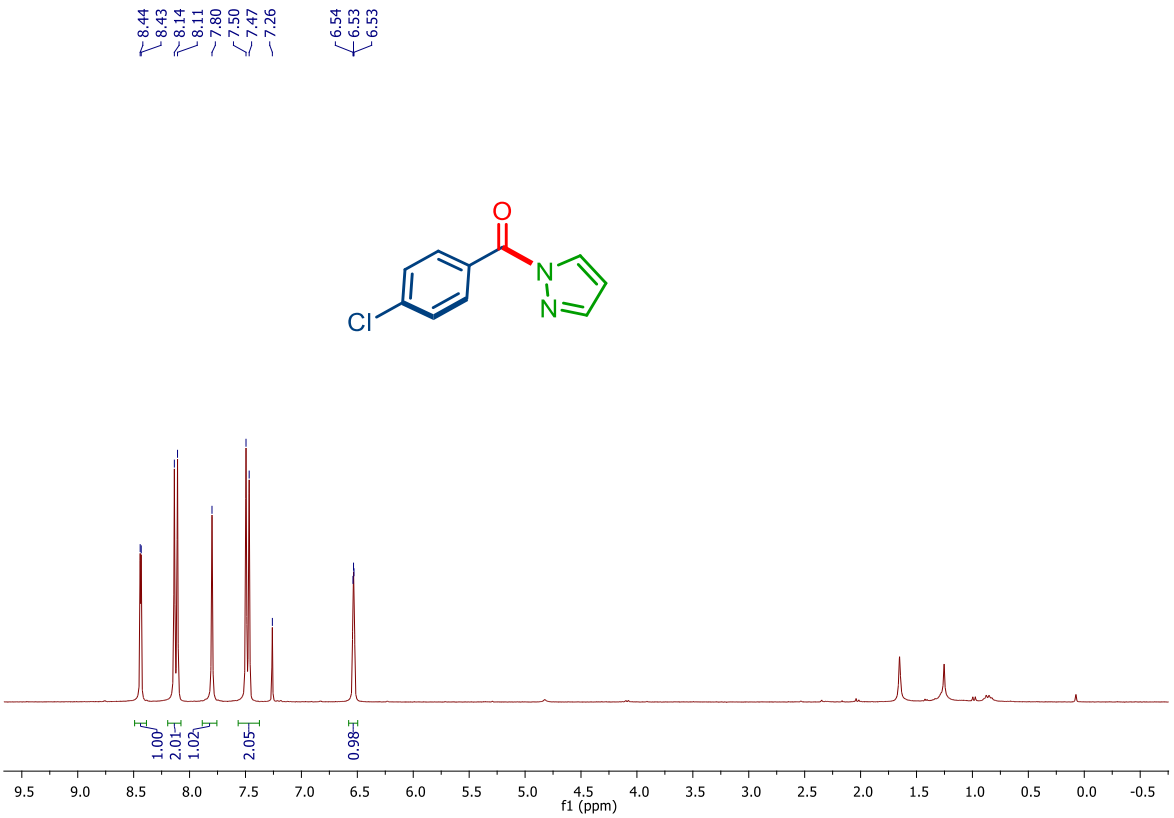
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3d** ($CDCl_3$, rt)



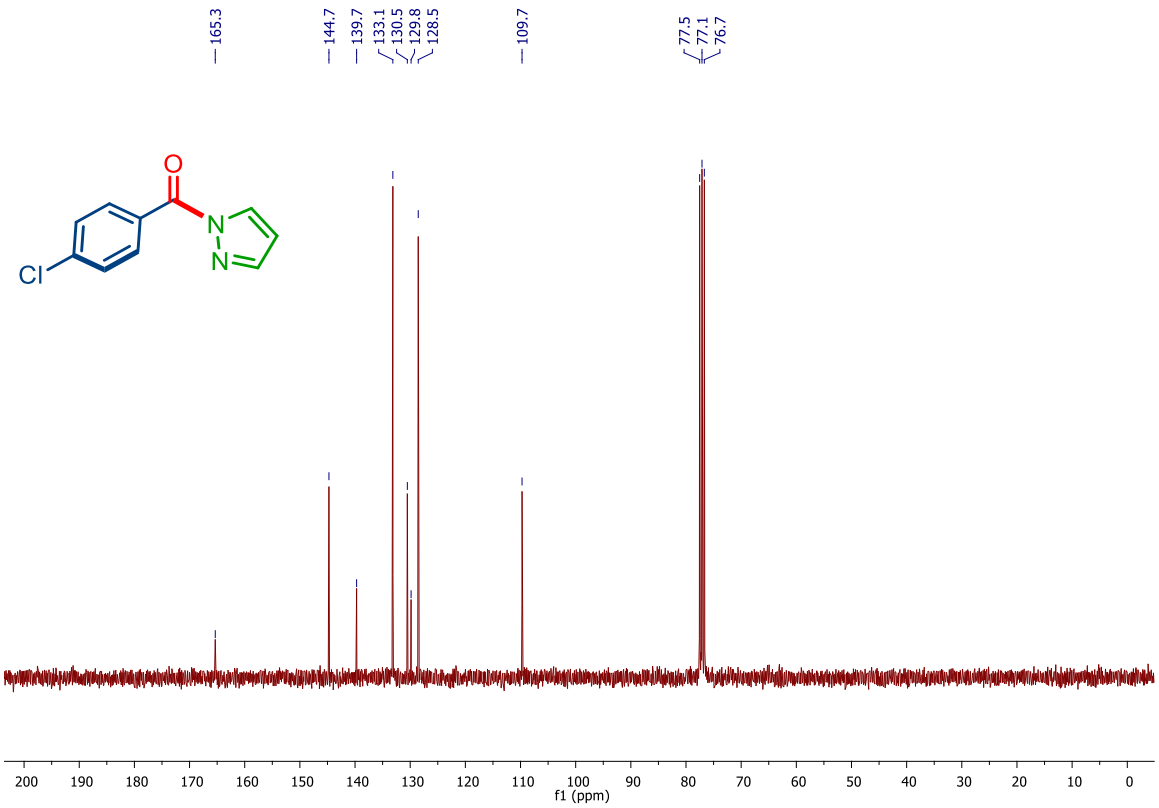
^{1}H NMR (300 MHz) spectrum of **3e** ($CDCl_3$, rt)



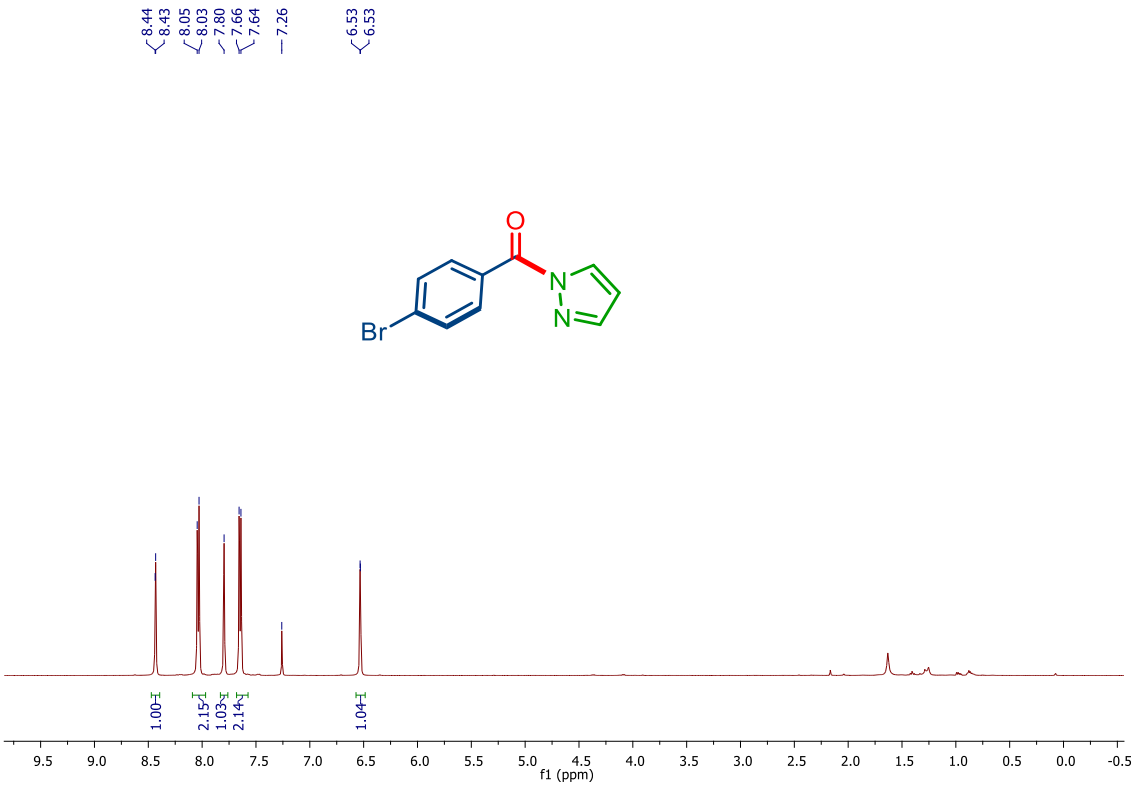
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3e** ($CDCl_3$, rt)



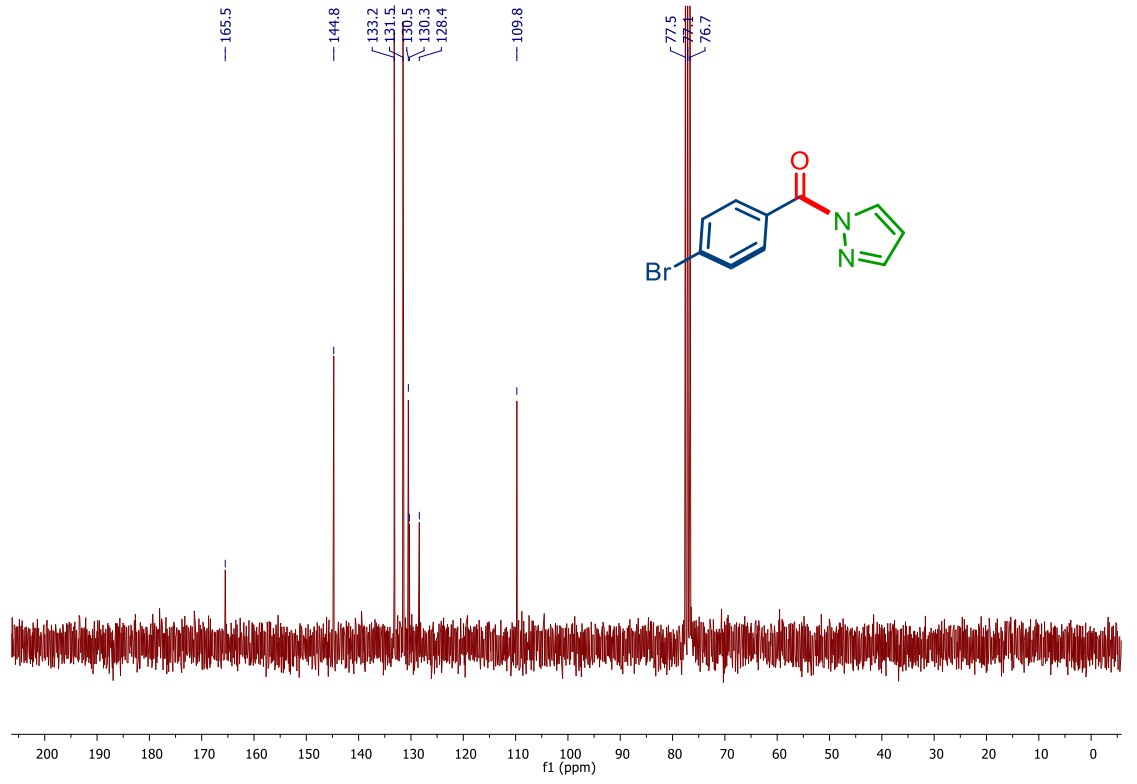
^{1}H NMR (300 MHz) spectrum of **3f** ($CDCl_3$, rt)



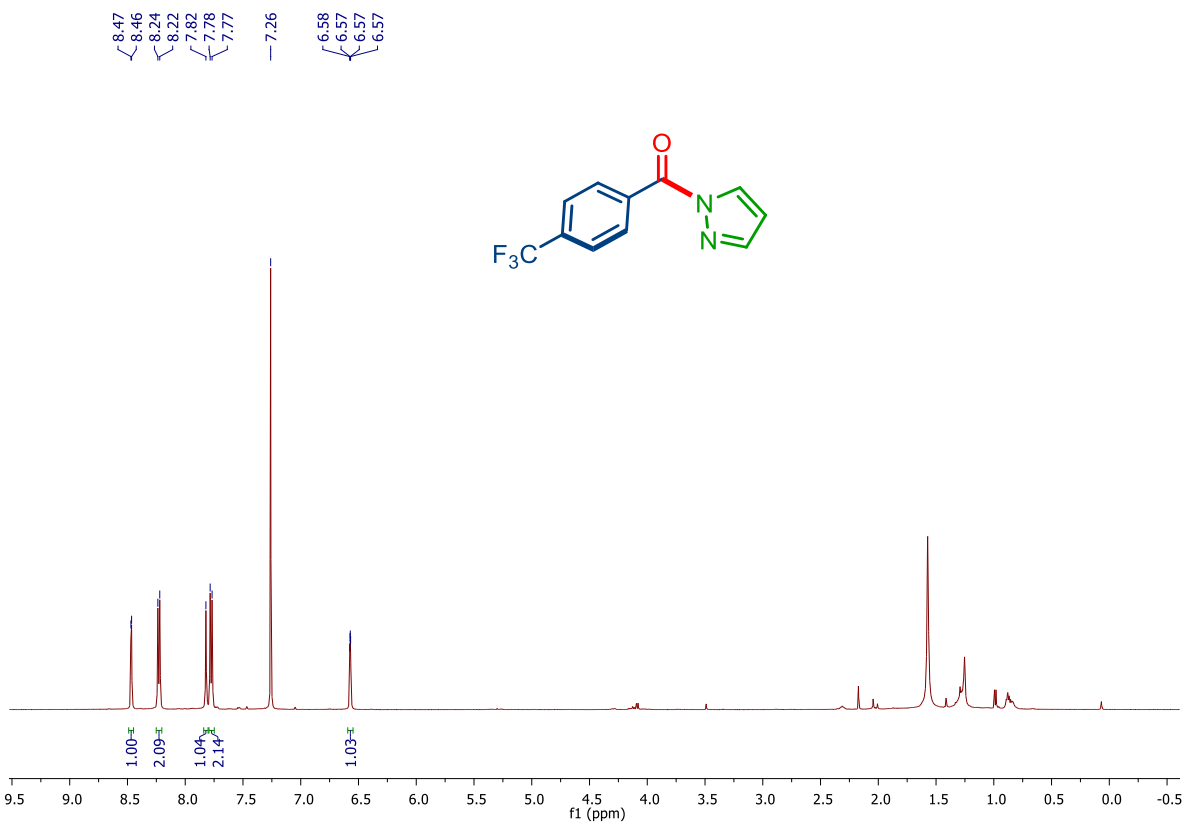
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3f** ($CDCl_3$, rt)



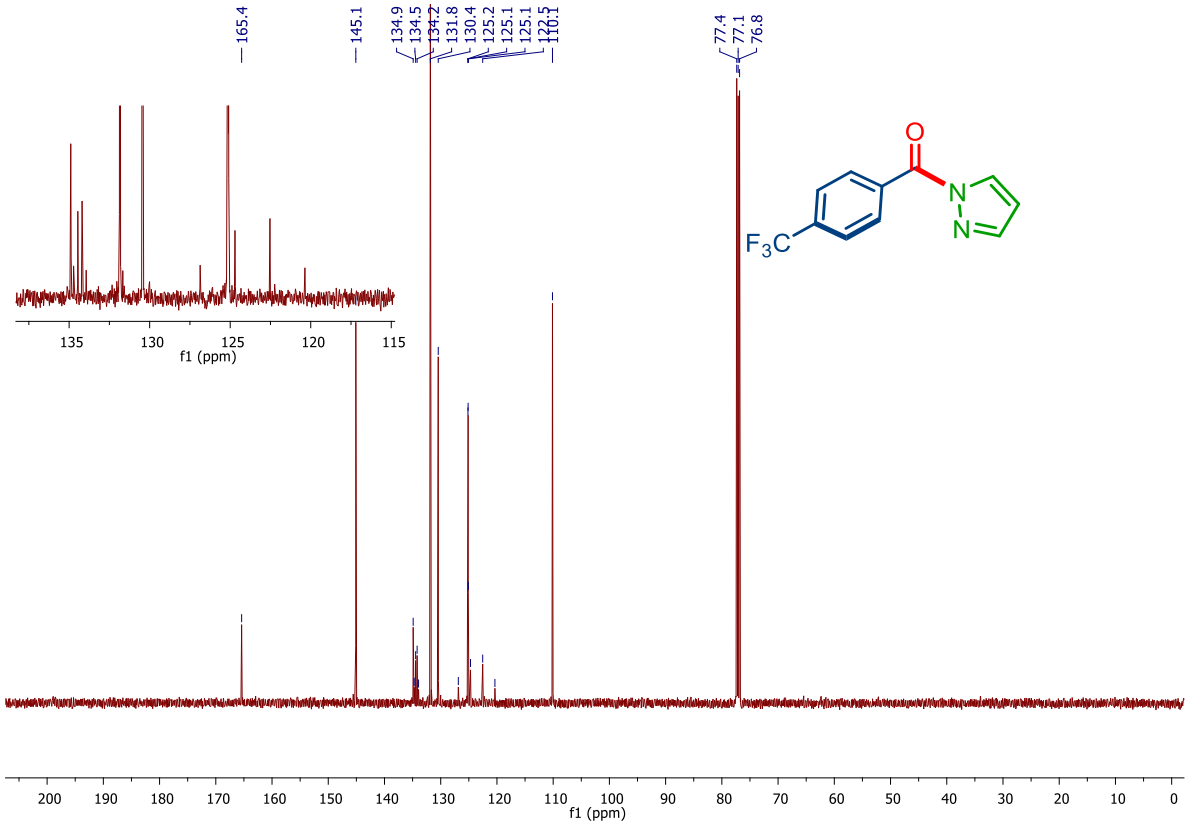
^{1}H NMR (500 MHz) spectrum of **3g** ($CDCl_3$, rt)



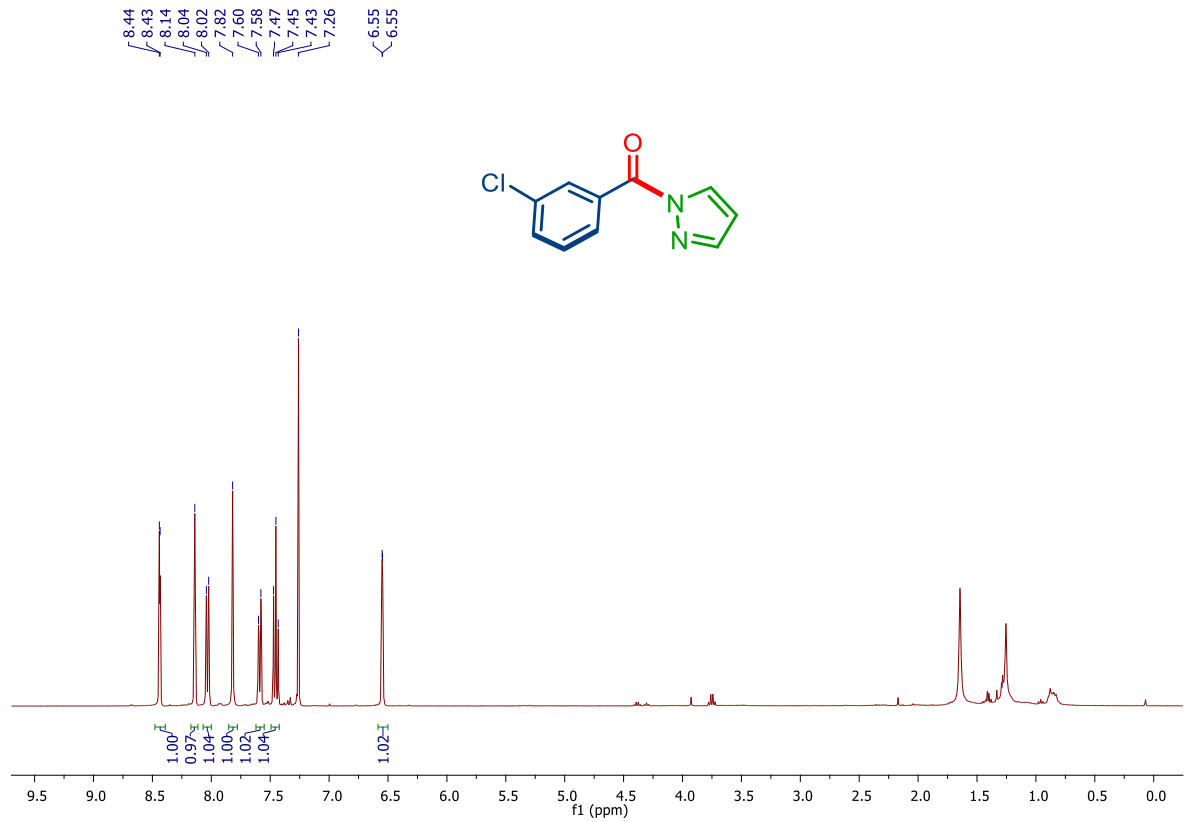
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3g** ($CDCl_3$, rt)



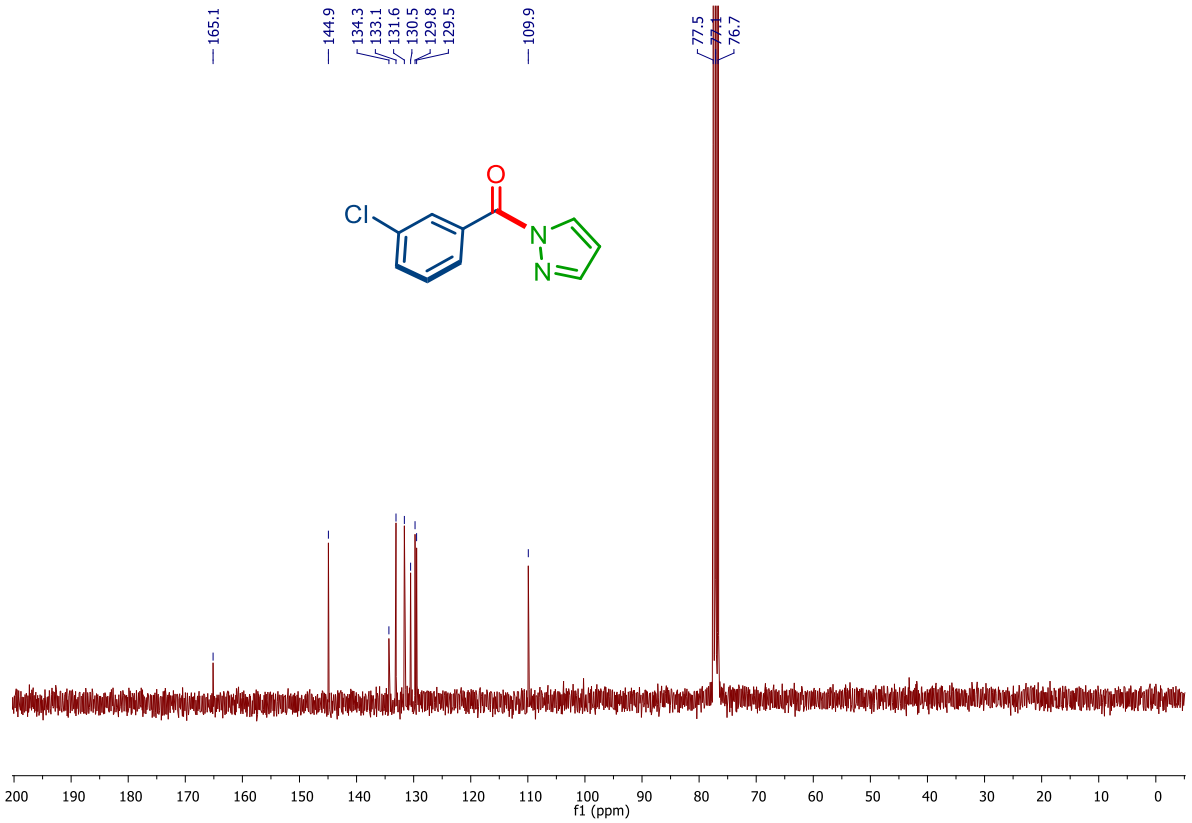
^{1}H NMR (500 MHz) spectrum of **3h** ($CDCl_3$, rt)



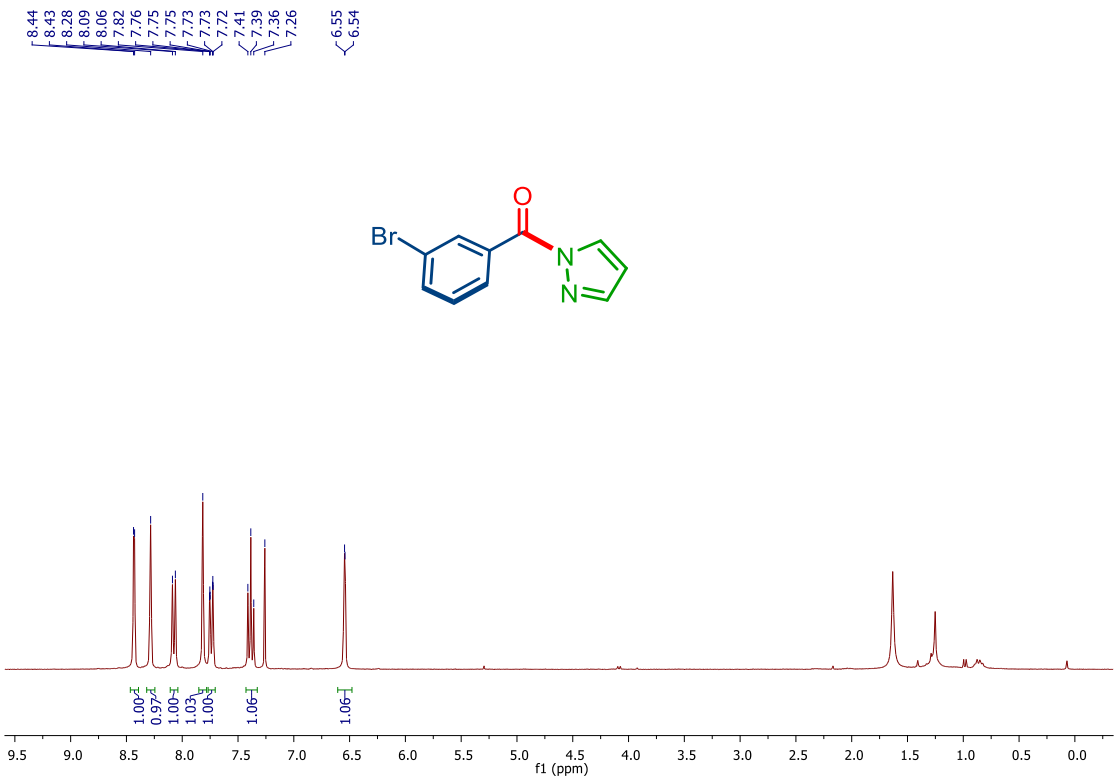
^{13}C{^{1}H} NMR (126 MHz) spectrum of **3h** ($CDCl_3$, rt)



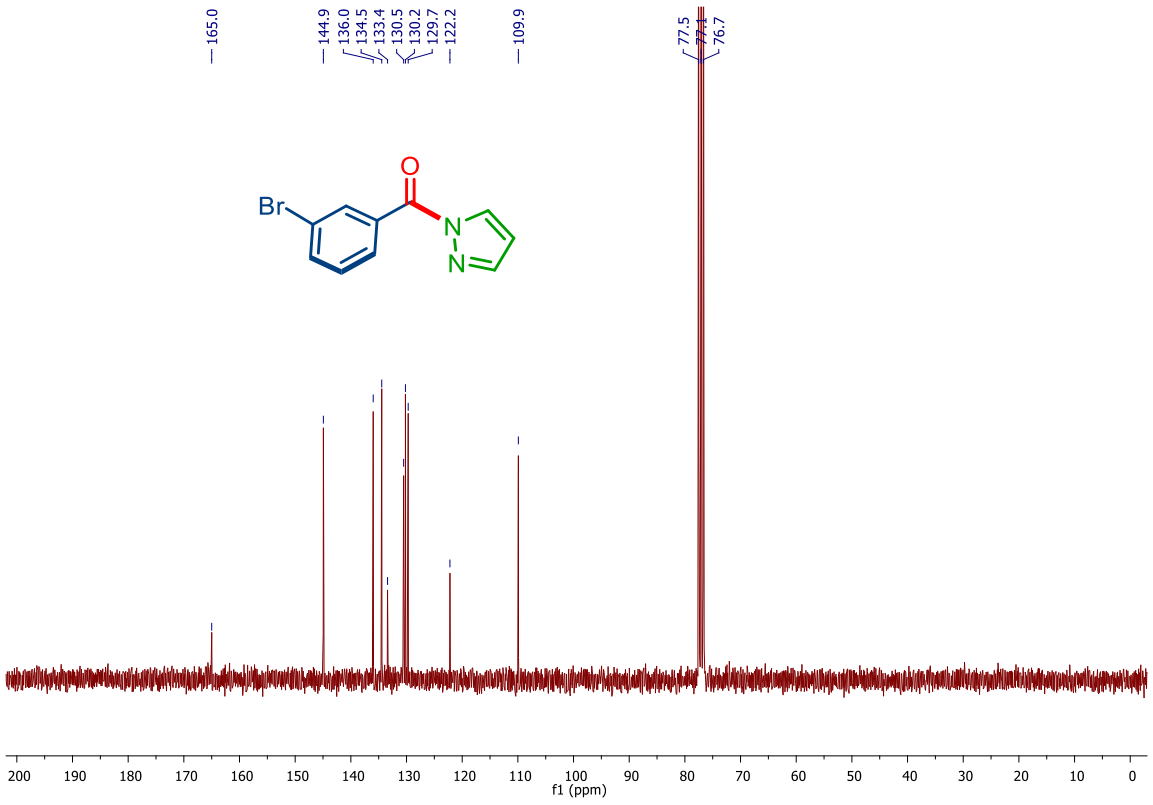
^{1}H NMR (400 MHz) spectrum of **3j** ($CDCl_3$, rt)



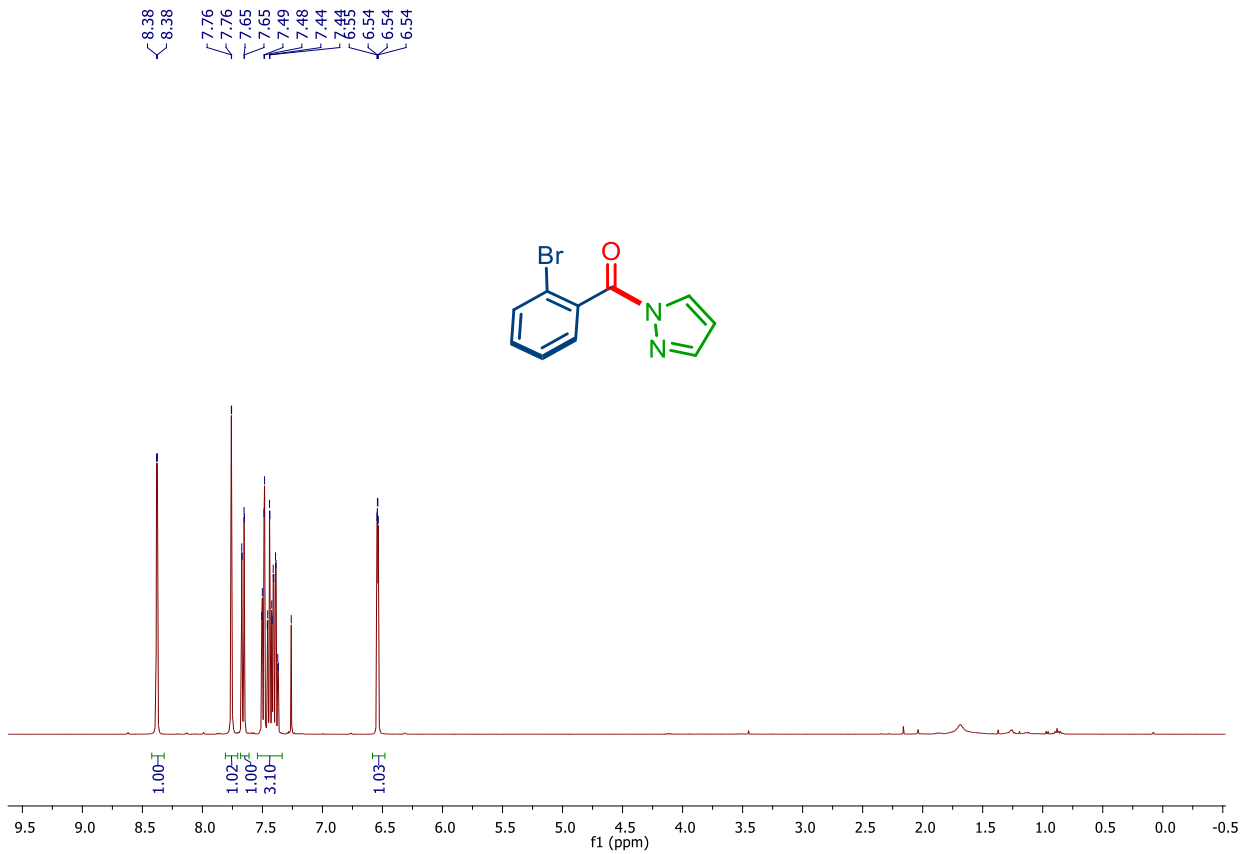
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3a** ($CDCl_3$, rt)



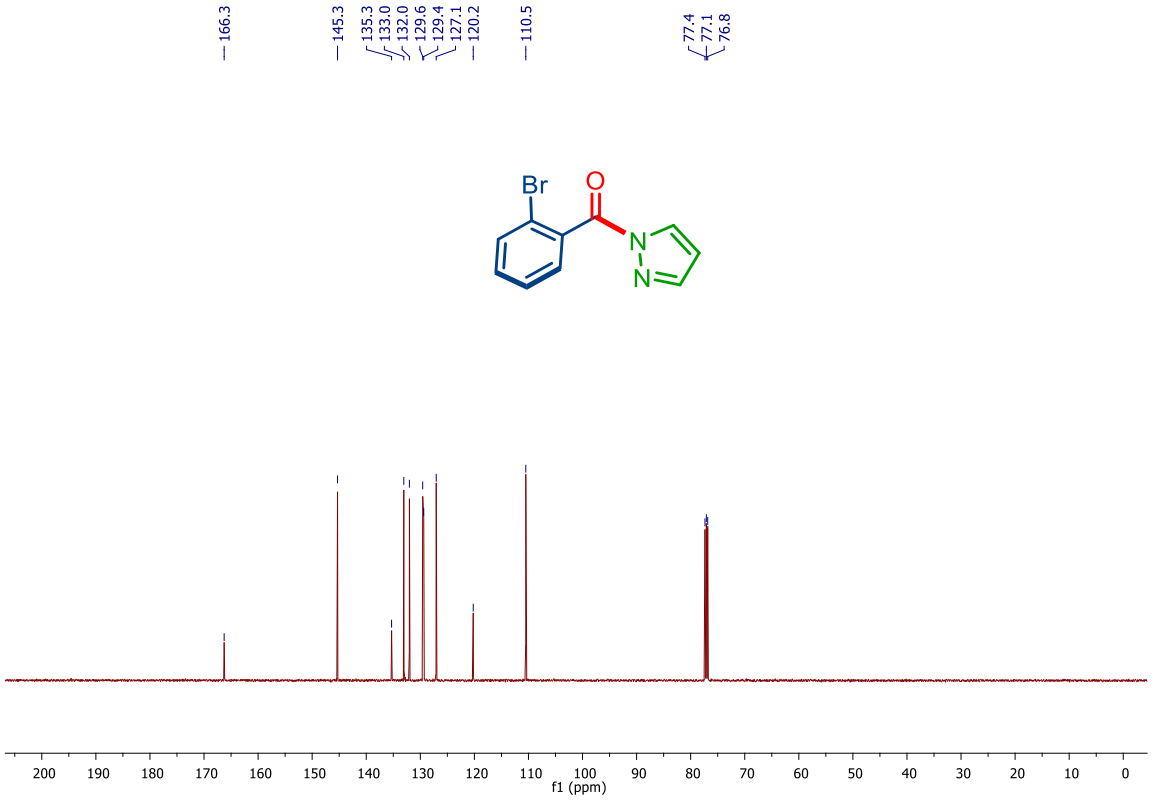
^{1}H NMR (300 MHz) spectrum of **3k** ($CDCl_3$, rt)



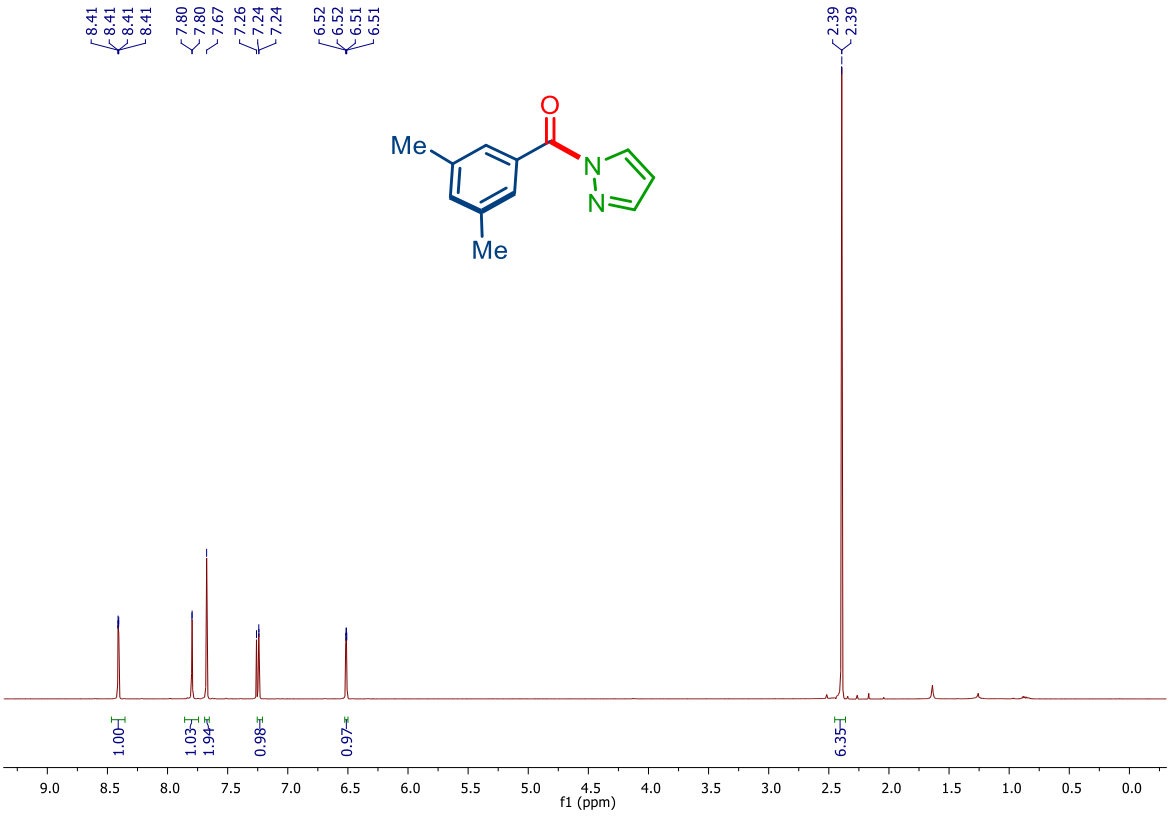
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3k** ($CDCl_3$, rt)



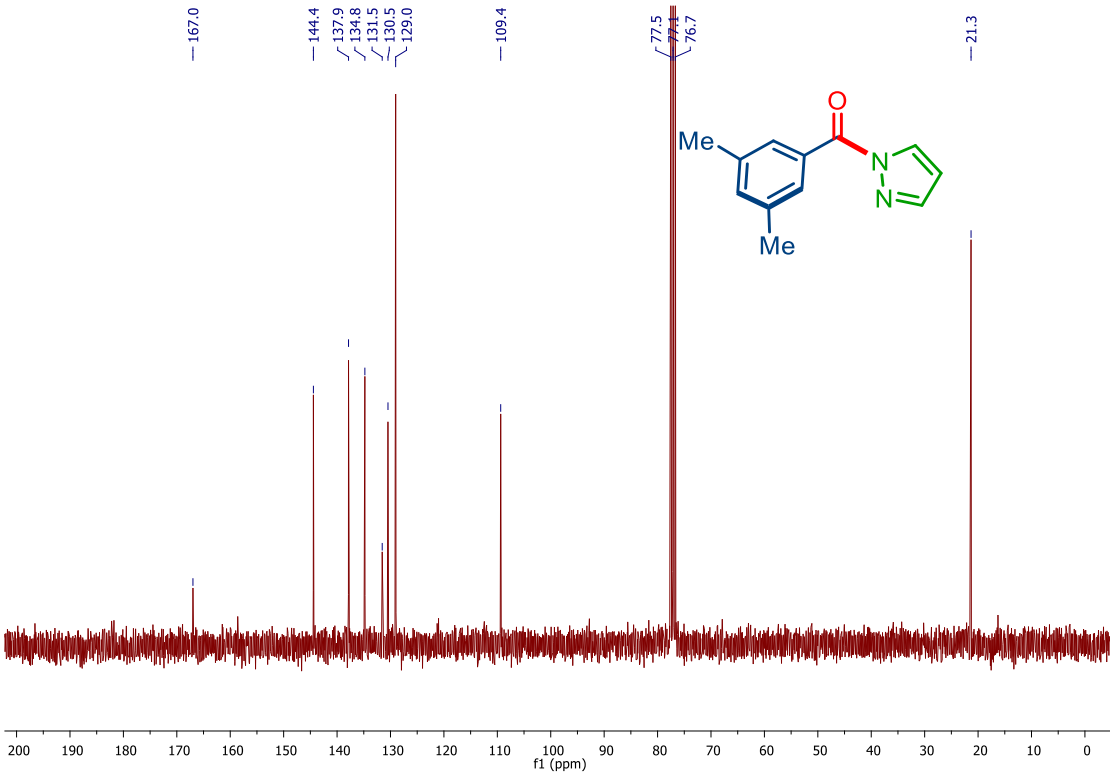
^{1}H NMR (400 MHz) spectrum of **3m** ($CDCl_3$, rt)



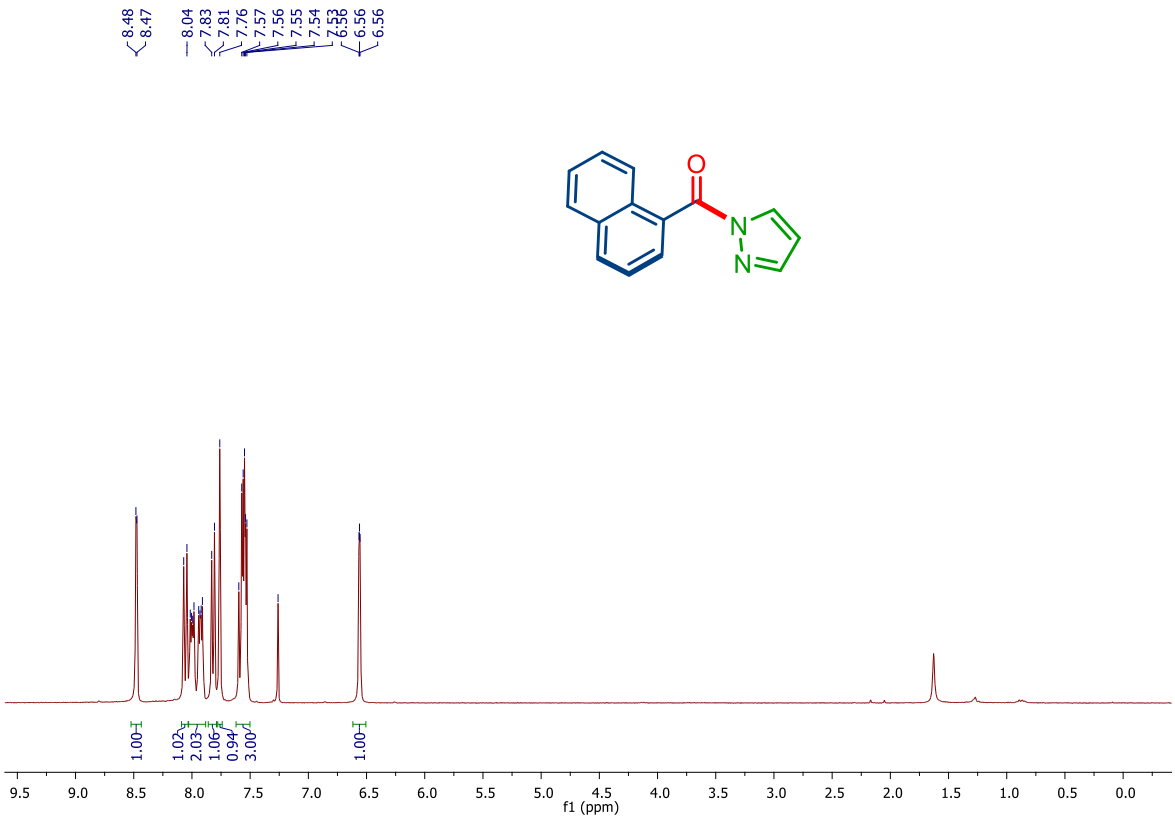
^{13}C{^{1}H} NMR (126 MHz) spectrum of **3m** ($CDCl_3$, rt)



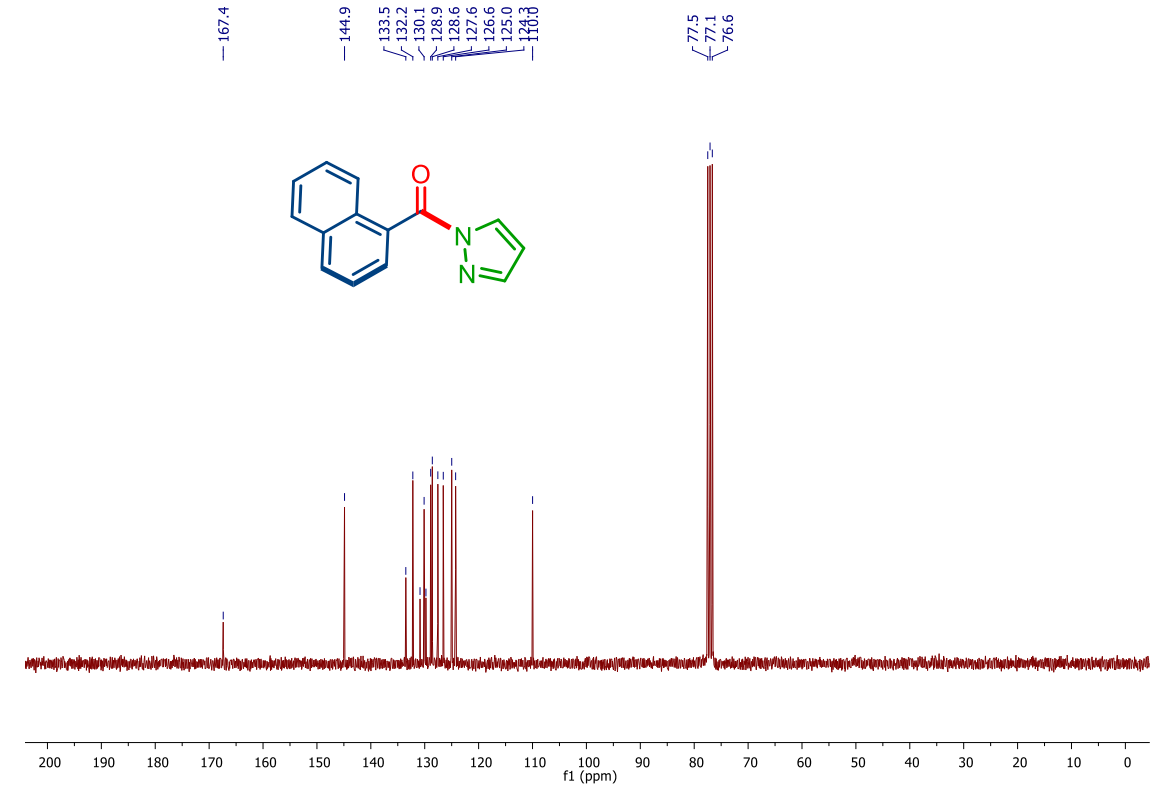
^{1}H NMR (500 MHz) spectrum of **3n** ($CDCl_3$, rt)



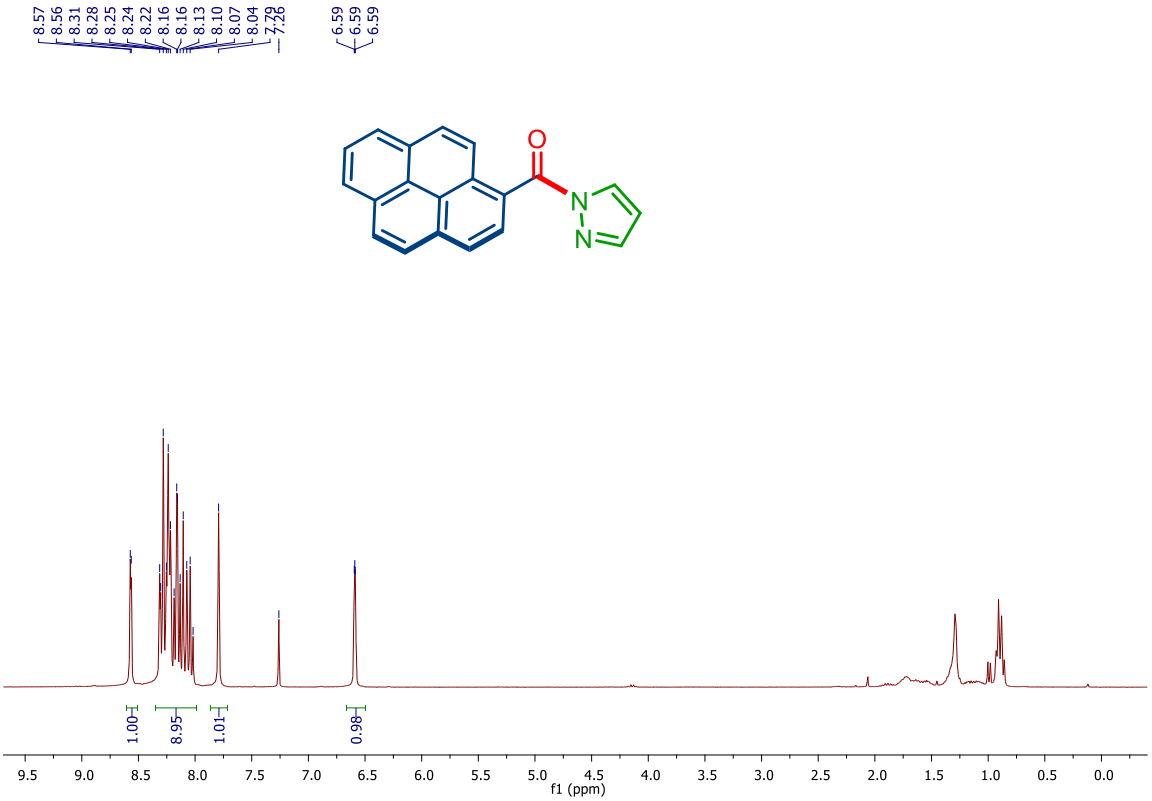
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3n** ($CDCl_3$, rt)



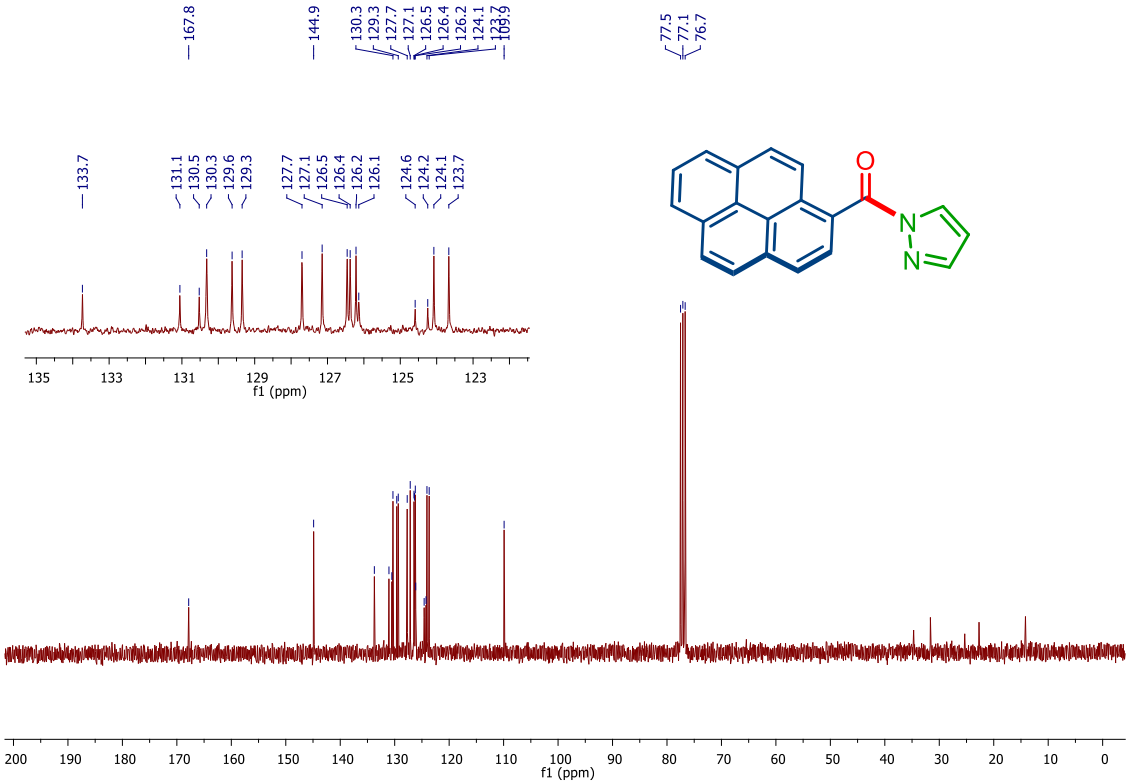
^{1}H NMR (300 MHz) spectrum of **3o** ($CDCl_3$, rt)



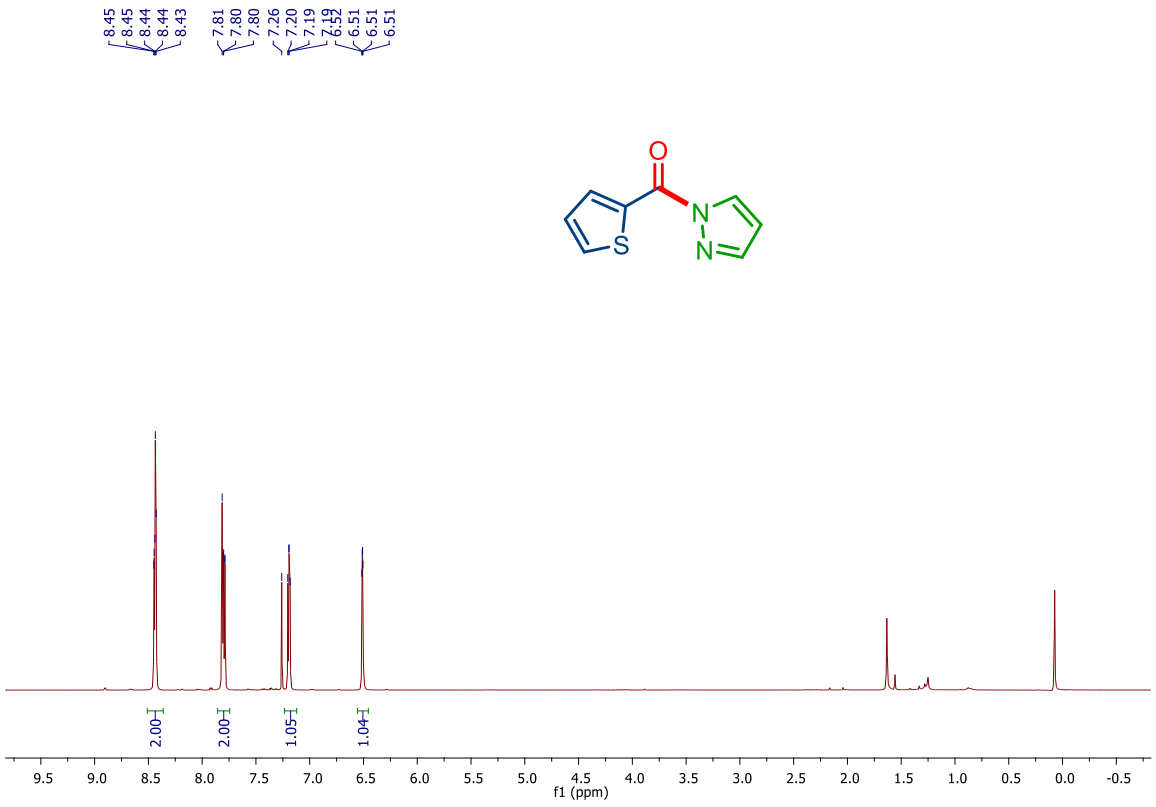
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3o** ($CDCl_3$, rt)



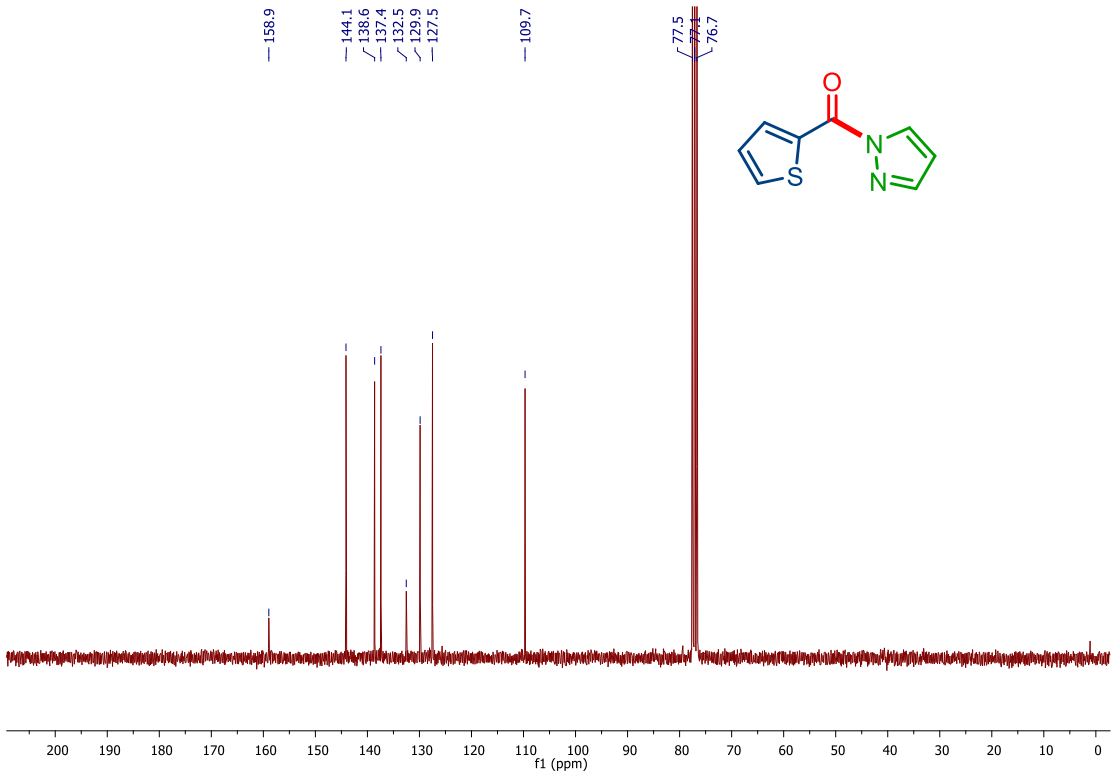
^{1}H NMR (300 MHz) spectrum of **3p** ($CDCl_3$, rt)



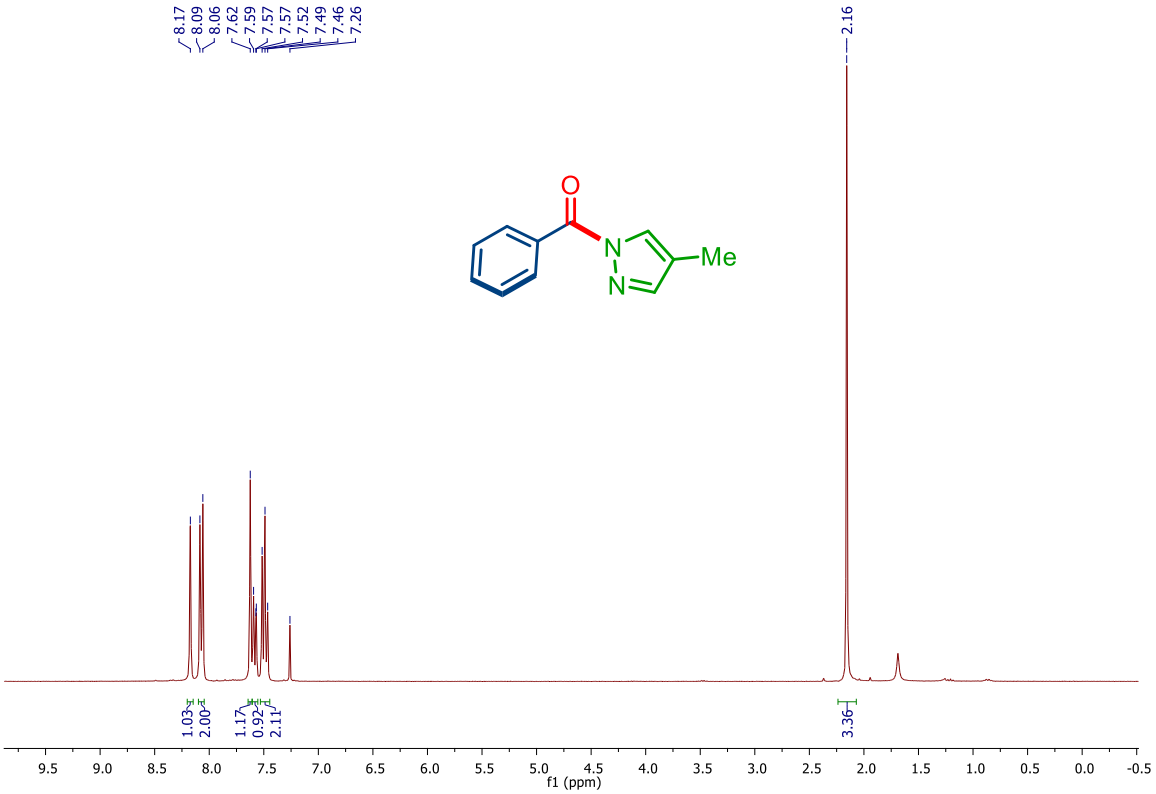
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3p** ($CDCl_3$, rt)



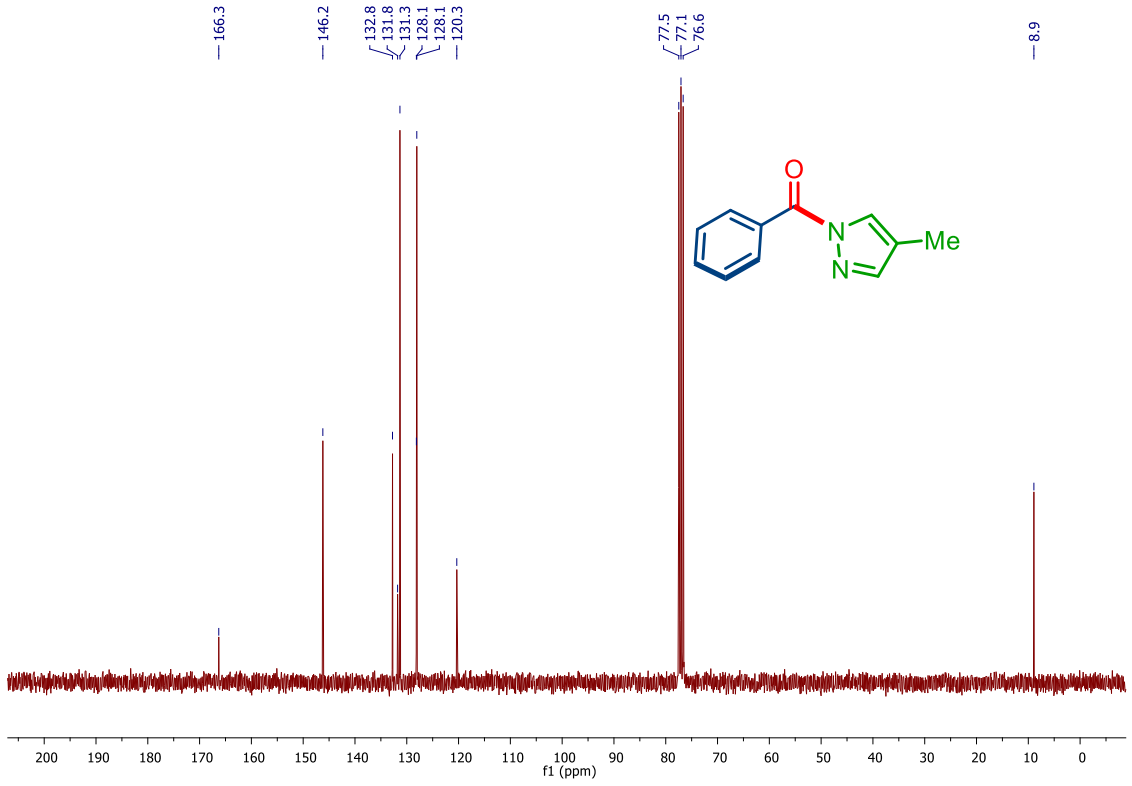
^{1}H NMR (400 MHz) spectrum of **3q** ($CDCl_3$, rt)



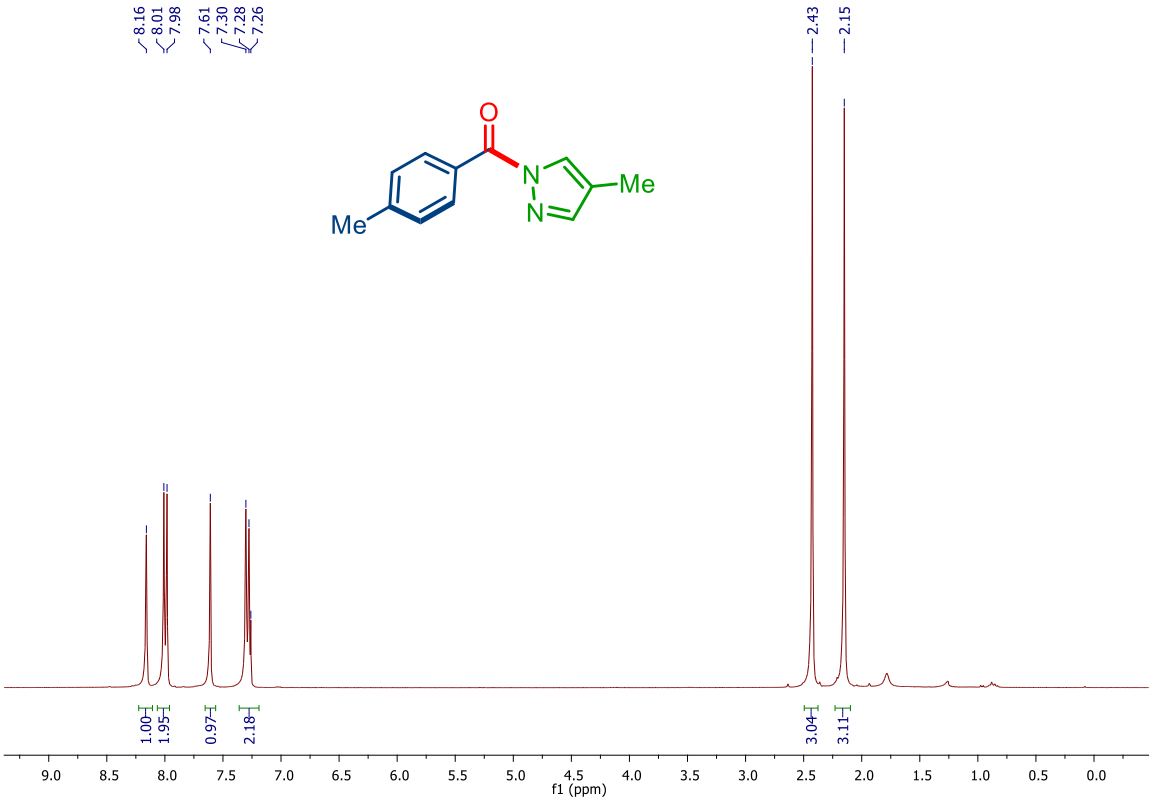
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3q** ($CDCl_3$, rt)



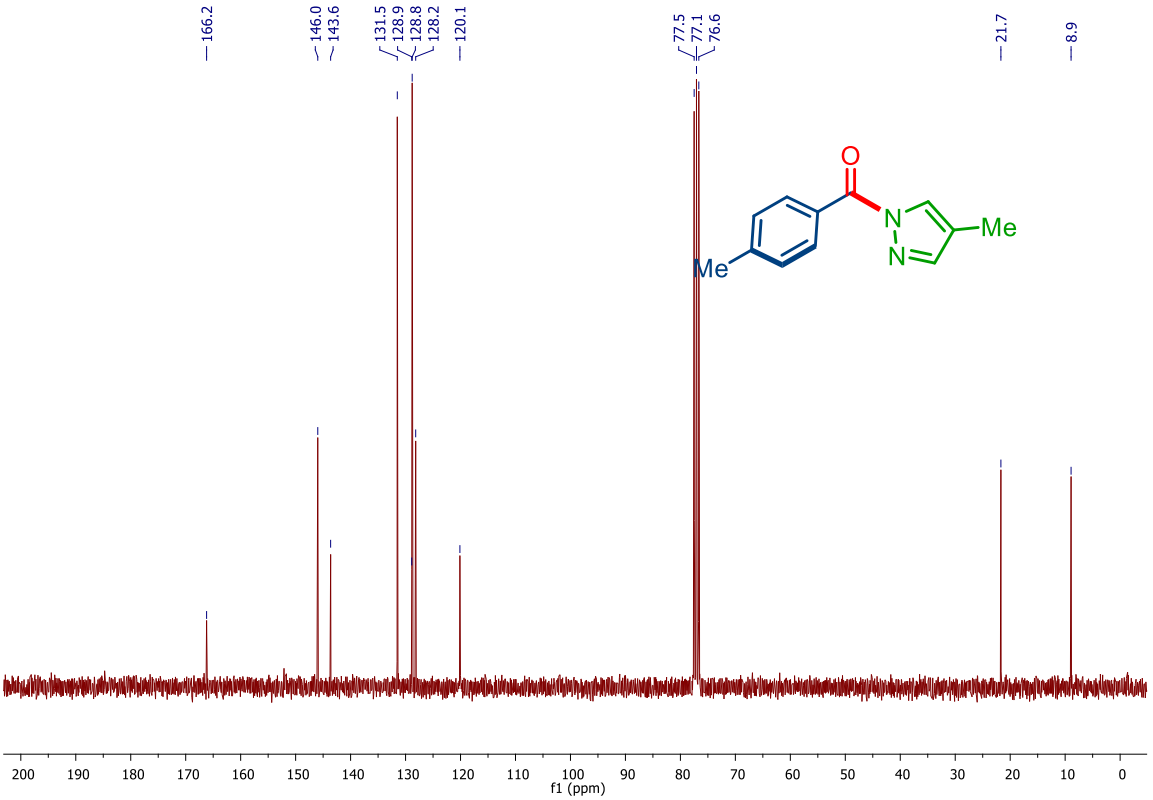
^{1}H NMR (300 MHz) spectrum of **3u** ($CDCl_3$, rt)



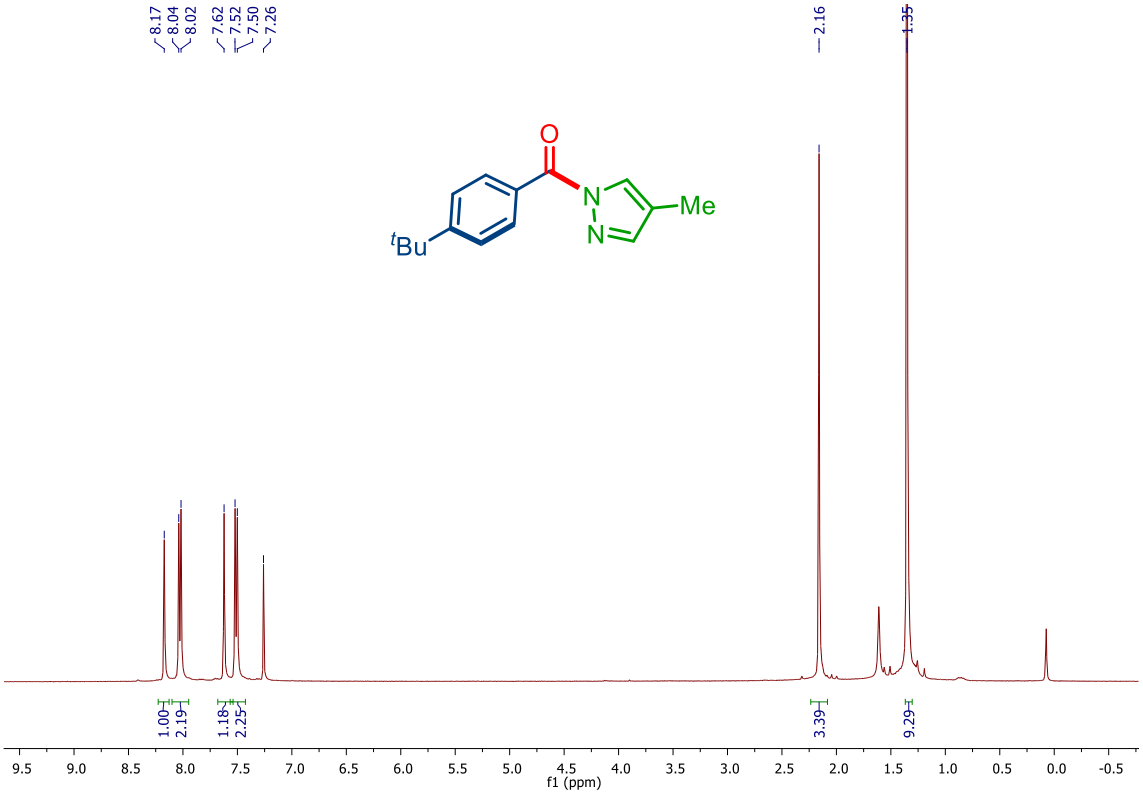
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3u** ($CDCl_3$, rt)



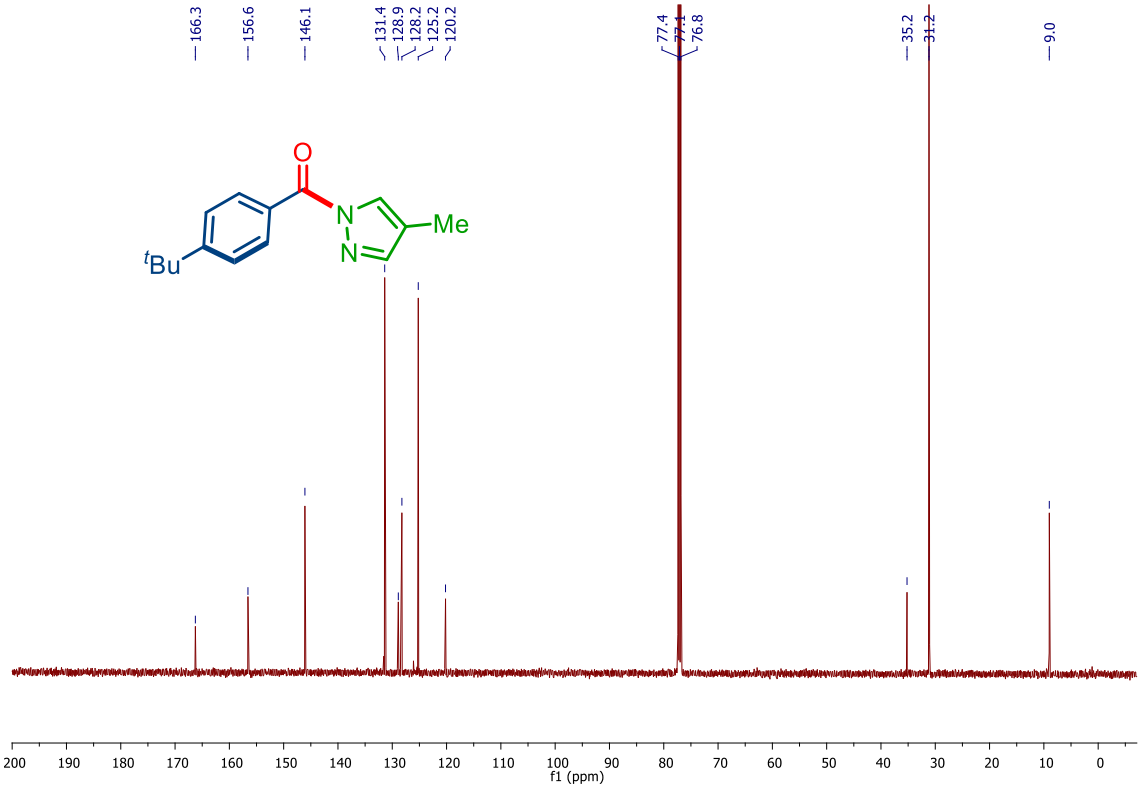
^{1}H NMR (300 MHz) spectrum of **3v** ($CDCl_3$, rt)



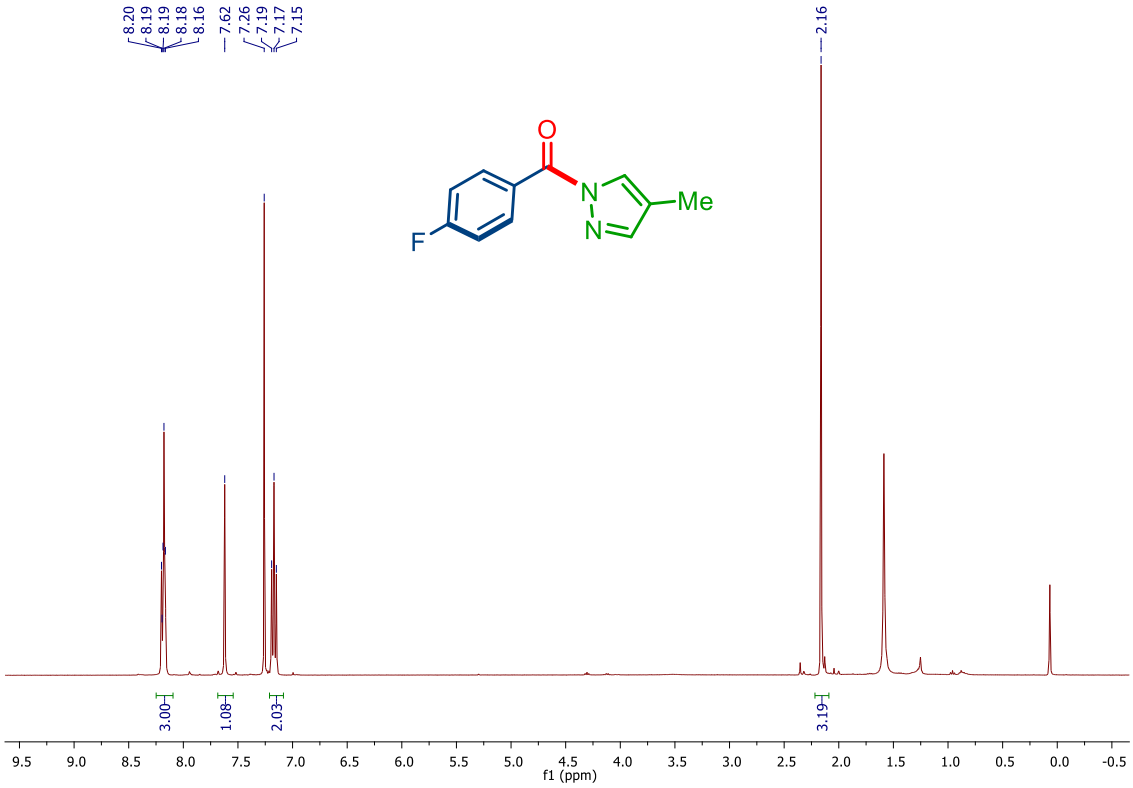
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3v** ($CDCl_3$, rt)



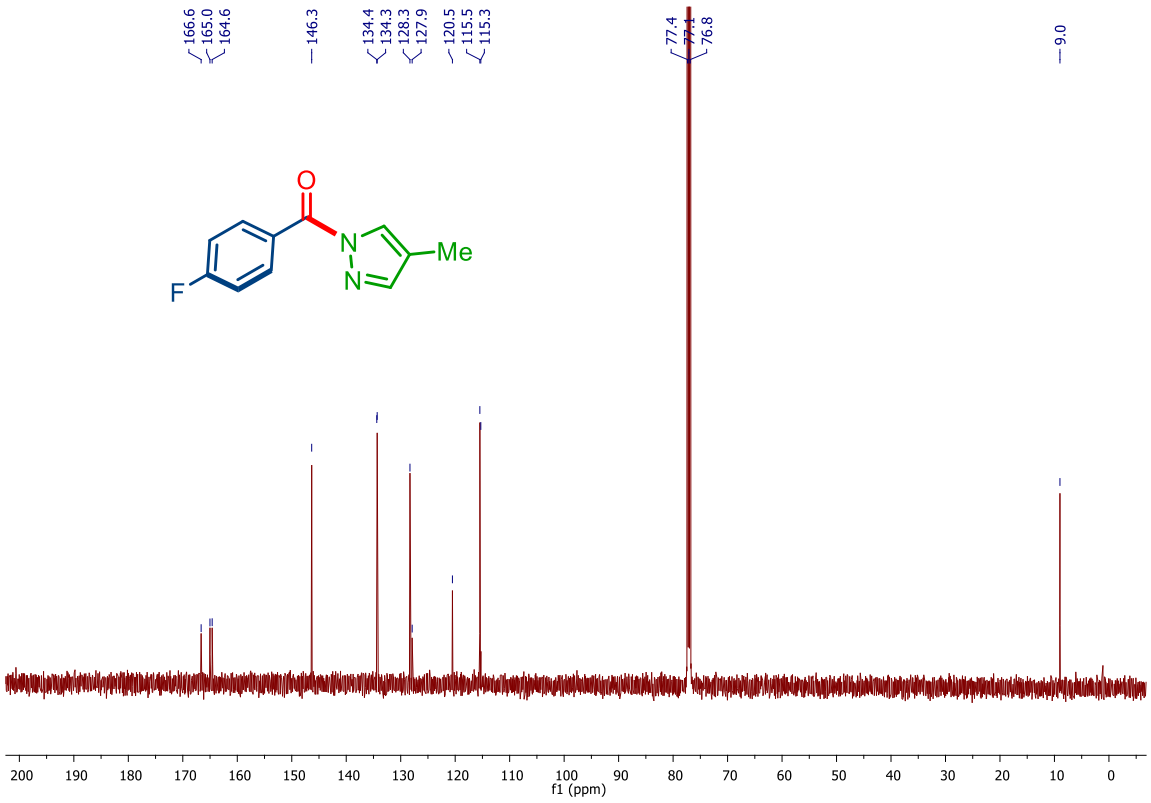
^{1}H NMR (400 MHz) spectrum of **3w** ($CDCl_3$, rt)



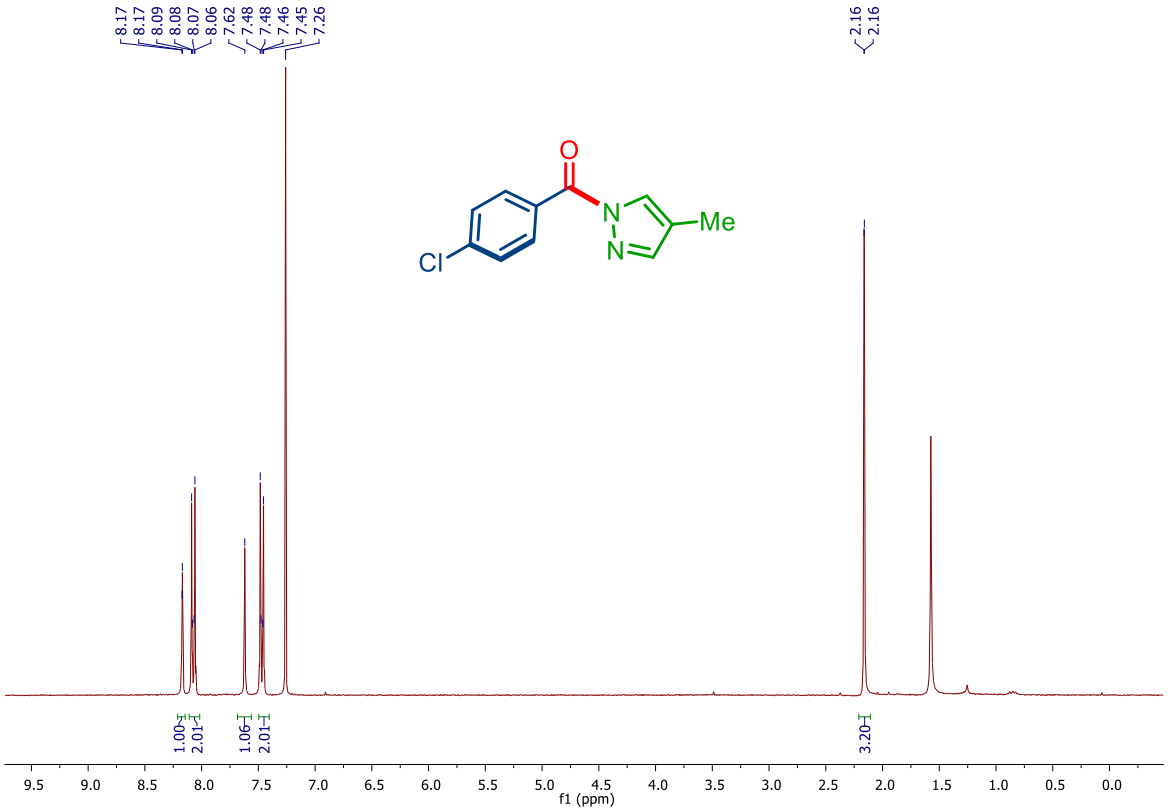
^{13}C{^{1}H} NMR (126 MHz) spectrum of **3w** ($CDCl_3$, rt)



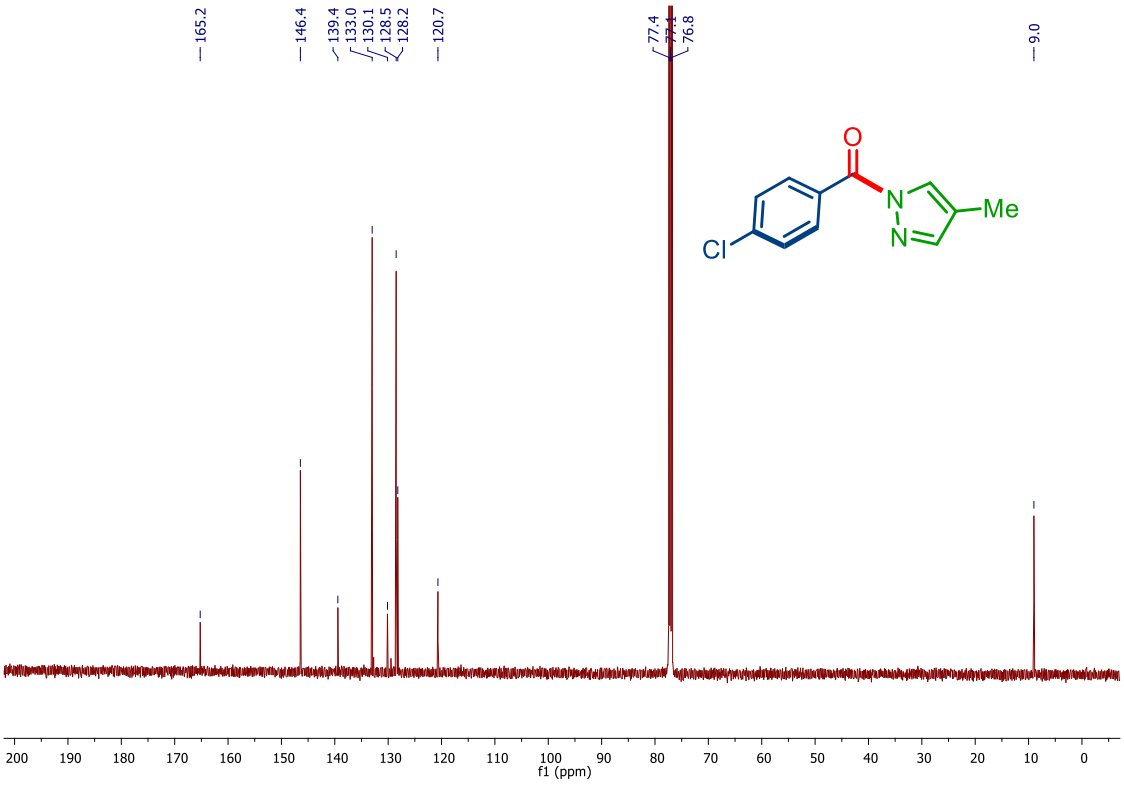
^{1}H NMR (400 MHz) spectrum of **3x** ($CDCl_3$, rt)



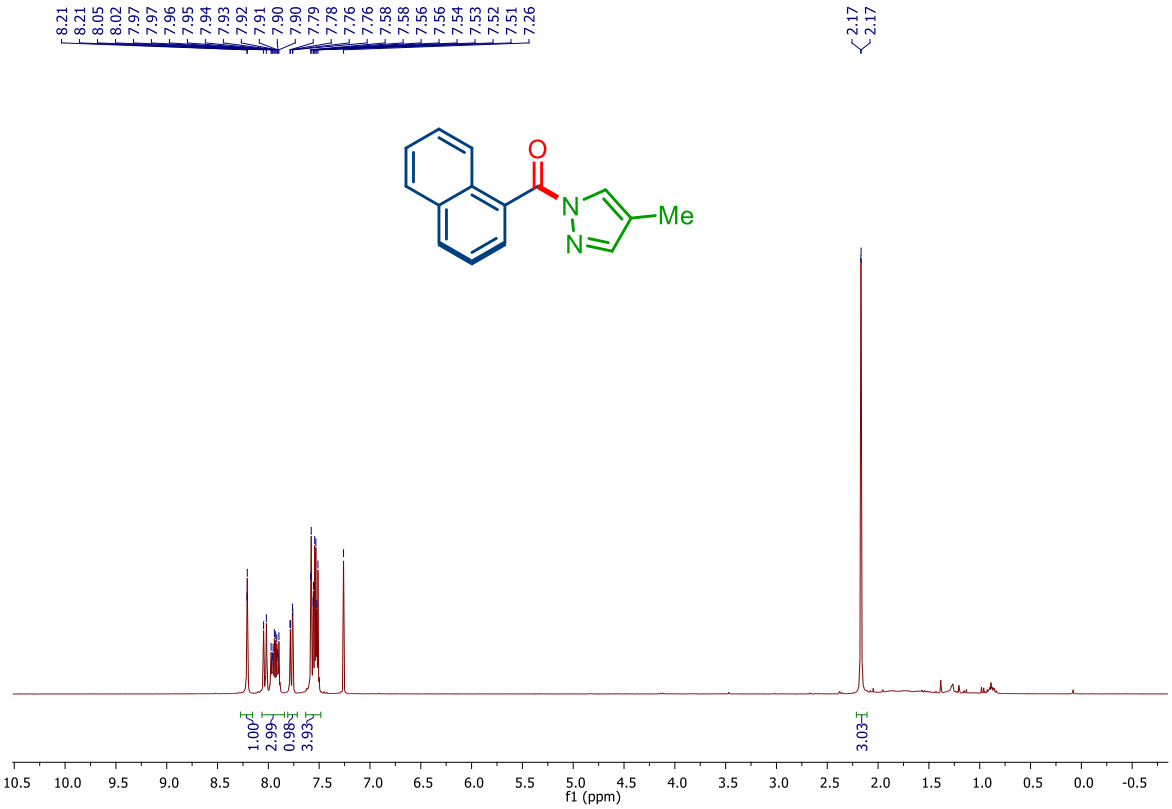
^{13}C{^{1}H} NMR (126 MHz) spectrum of **3x** ($CDCl_3$, rt)



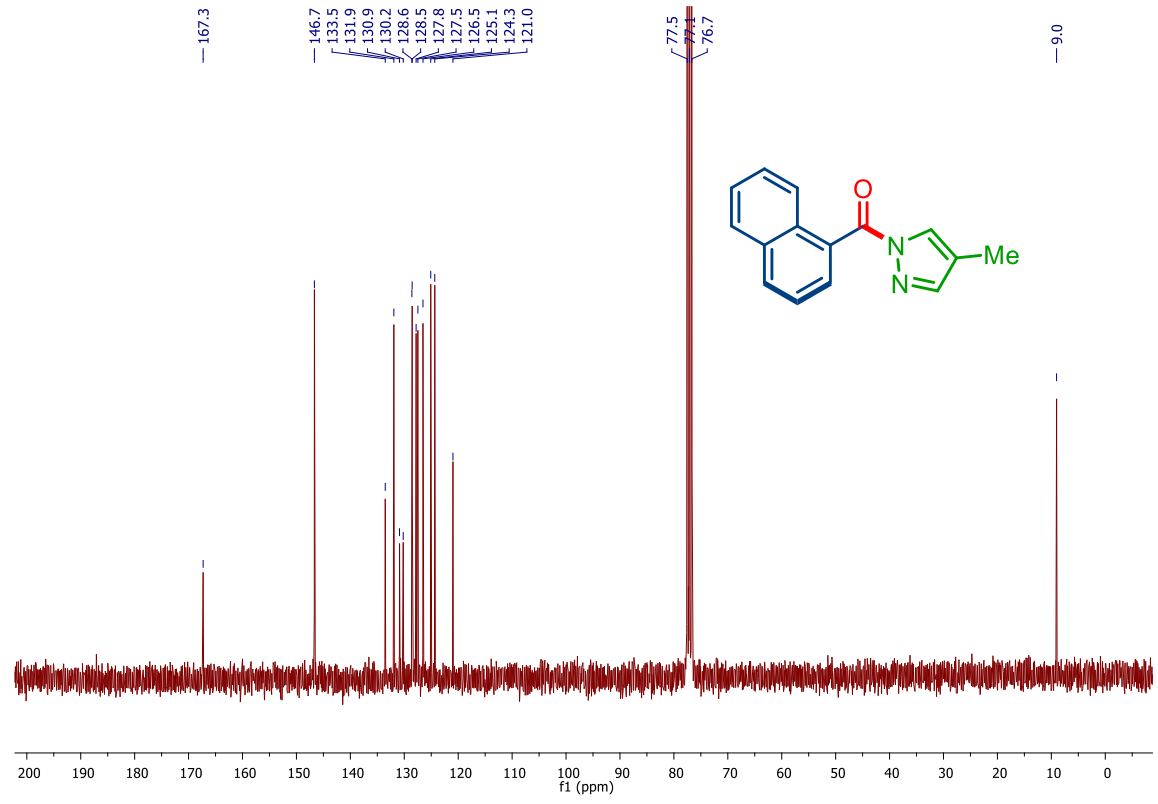
^{1}H NMR (300 MHz) spectrum of **3y** ($CDCl_3$, rt)



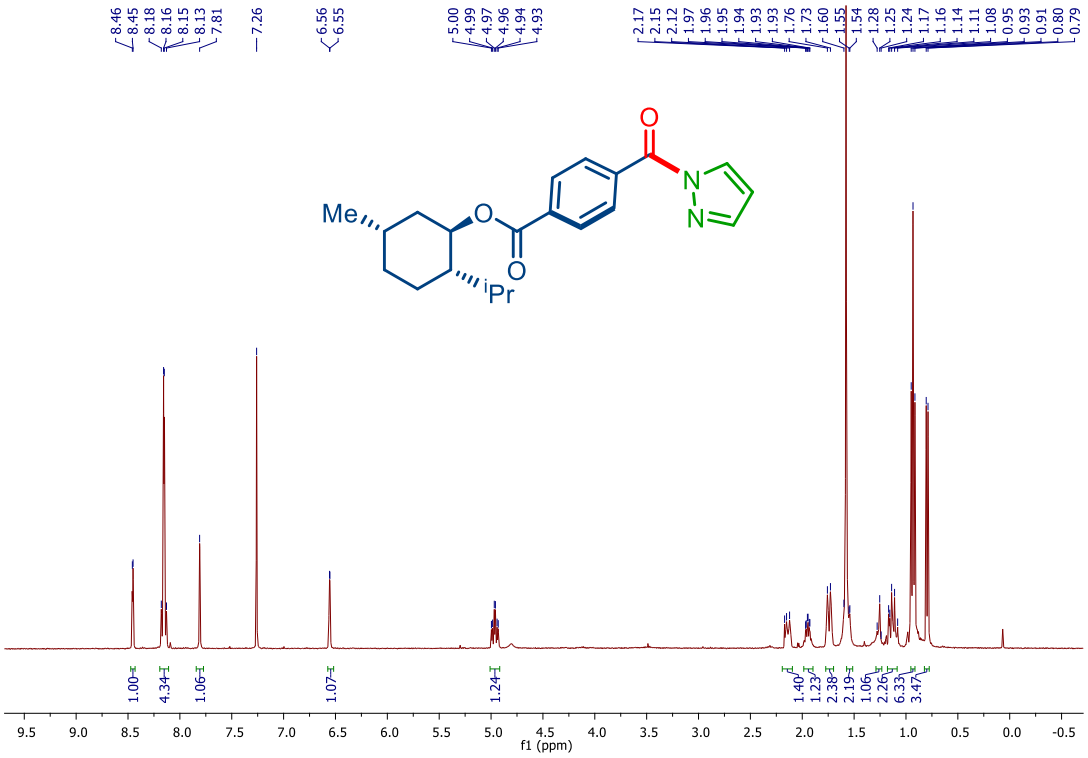
^{13}C{^{1}H} NMR (126 MHz) spectrum of **3y** ($CDCl_3$, rt)



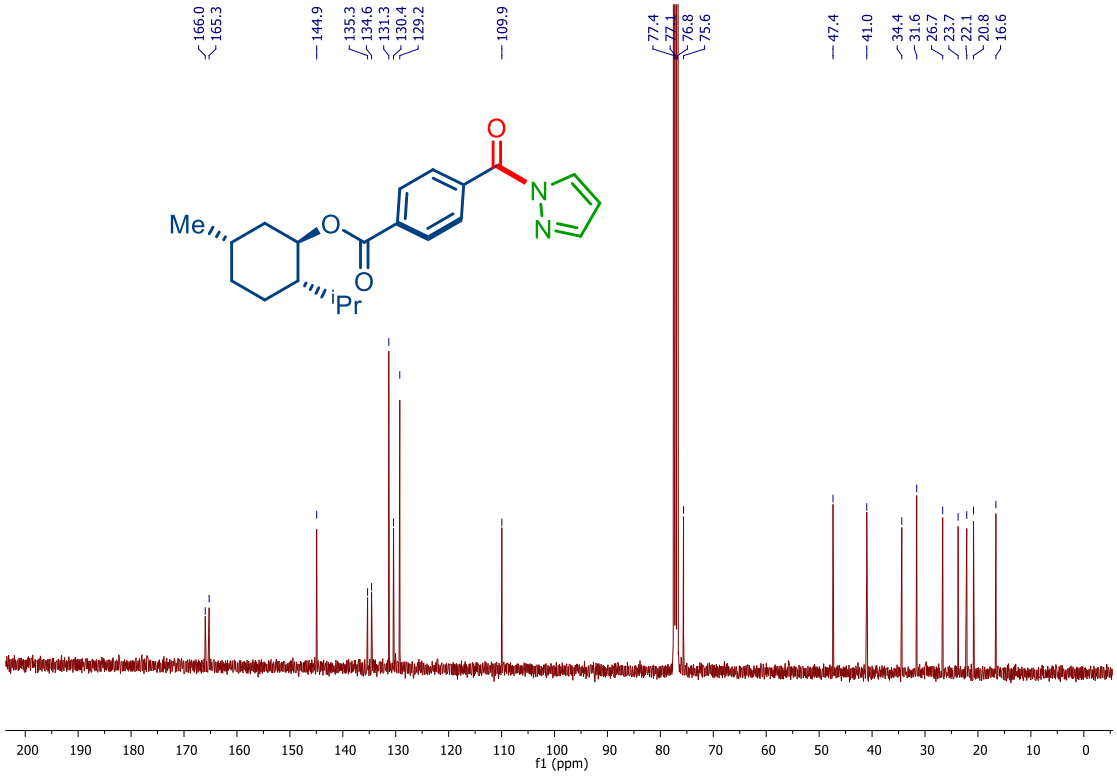
^{1}H NMR (300 MHz) spectrum of **3z** ($CDCl_3$, rt)



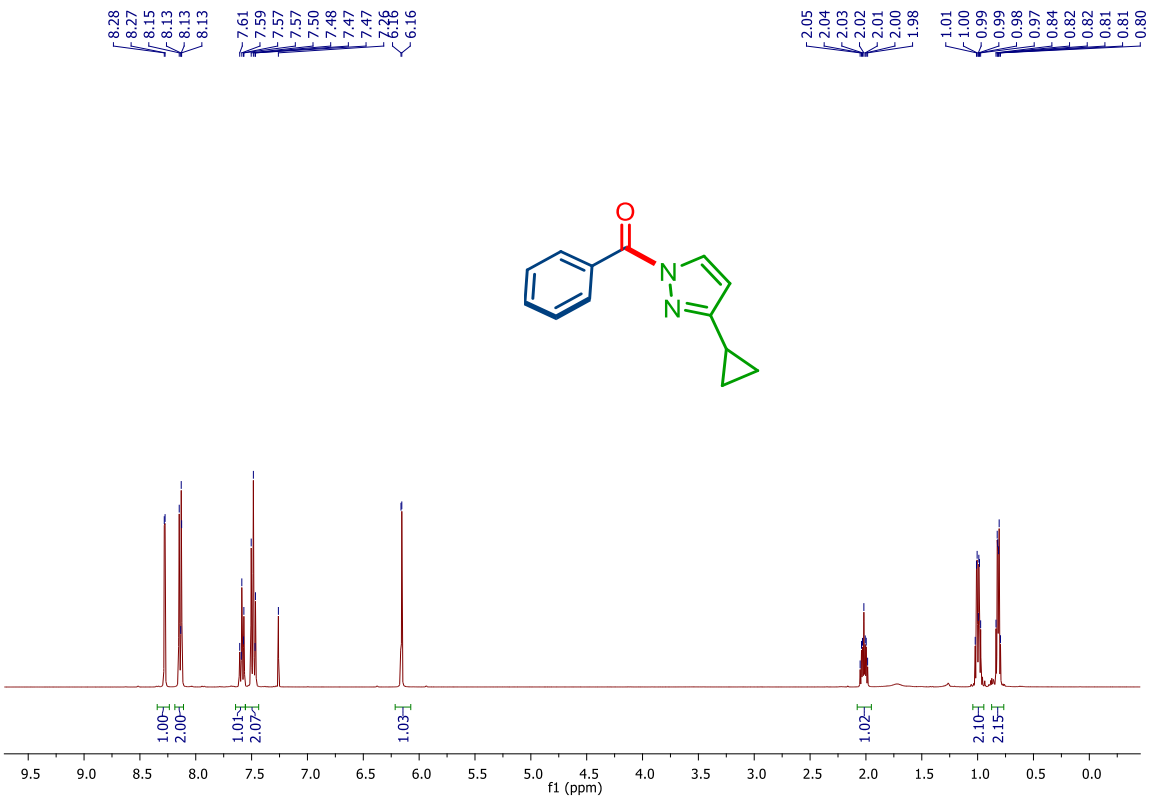
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3z** ($CDCl_3$, rt)



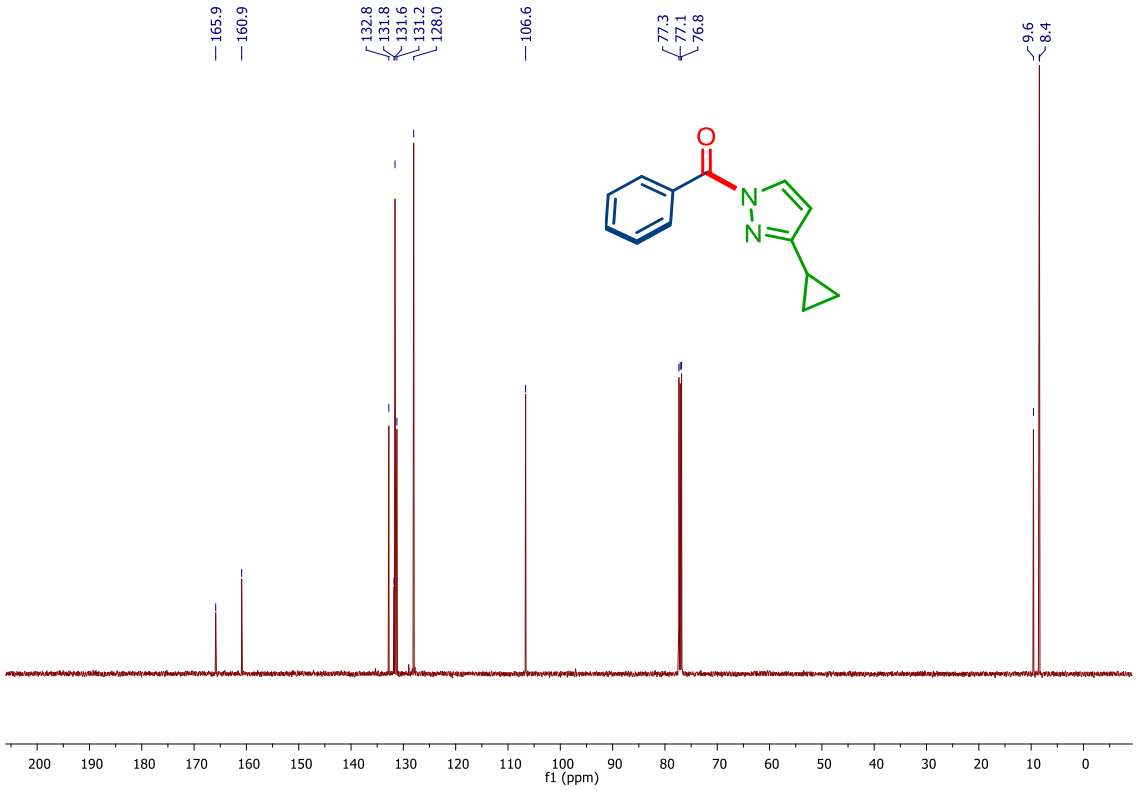
^{1}H NMR (400 MHz) spectrum of **3za** ($CDCl_3$, rt)



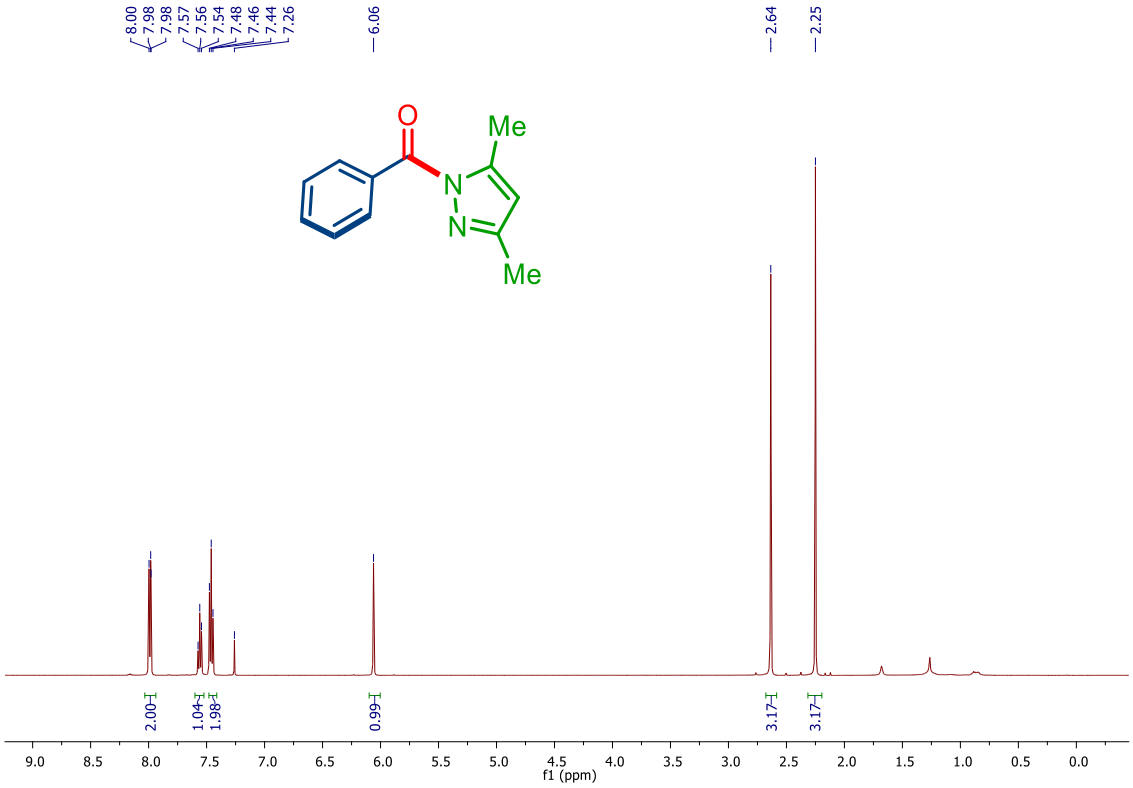
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3za** ($CDCl_3$, rt)



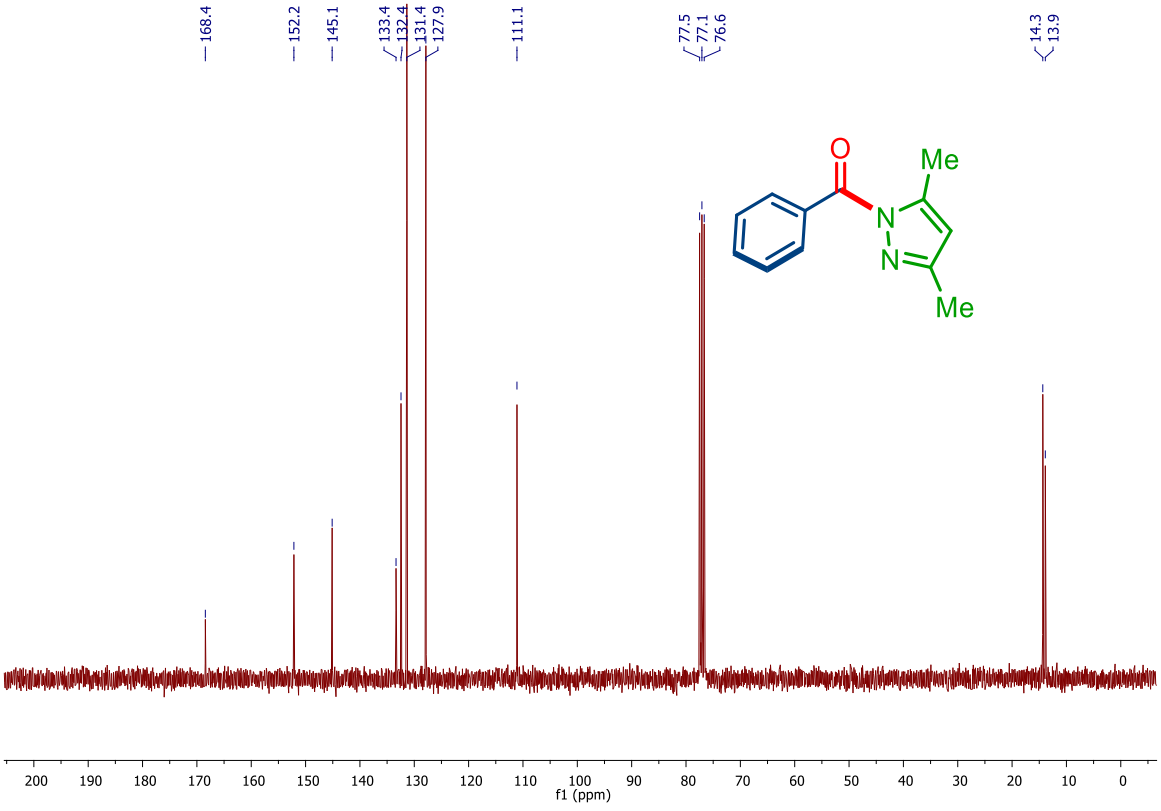
^{1}H NMR (400 MHz) spectrum of **3zb** ($CDCl_3$, rt)



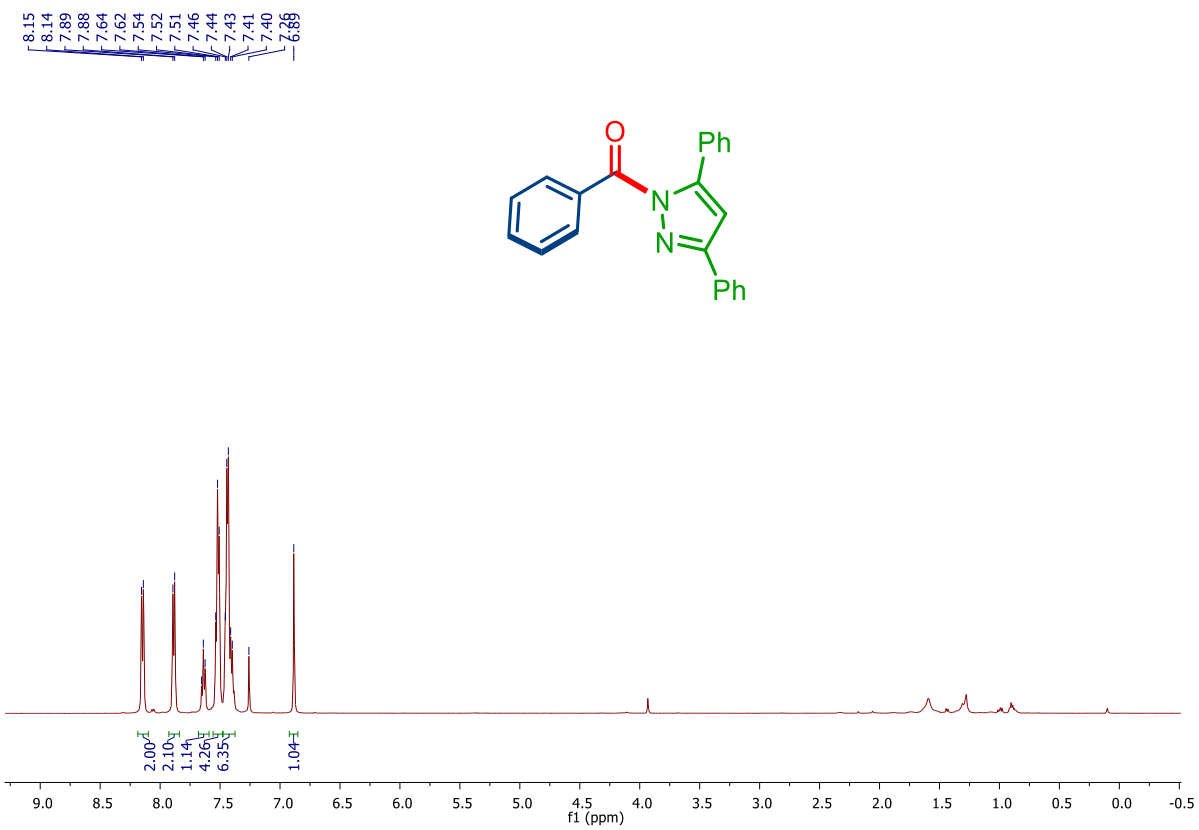
^{13}C{^{1}H} NMR (126 MHz) spectrum of **3zb** ($CDCl_3$, rt)



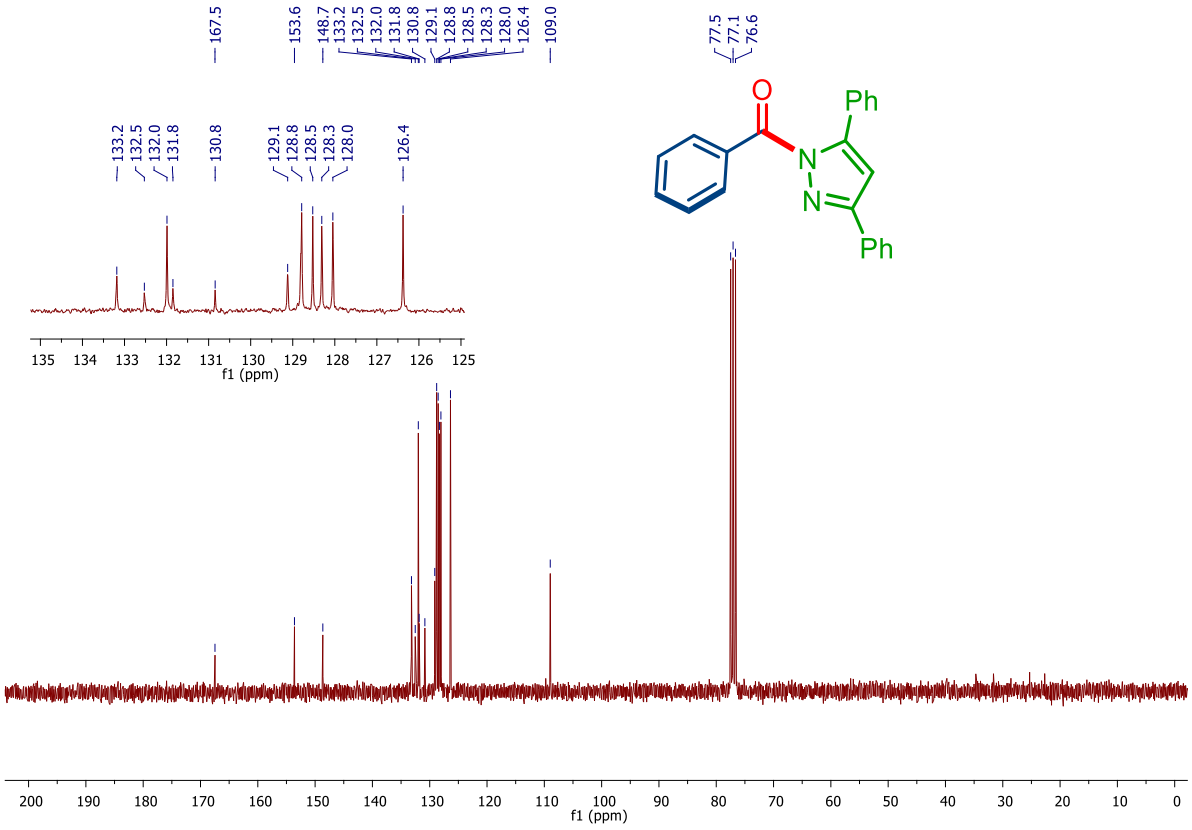
^{1}H NMR (500 MHz) spectrum of **3zc** ($CDCl_3$, rt)



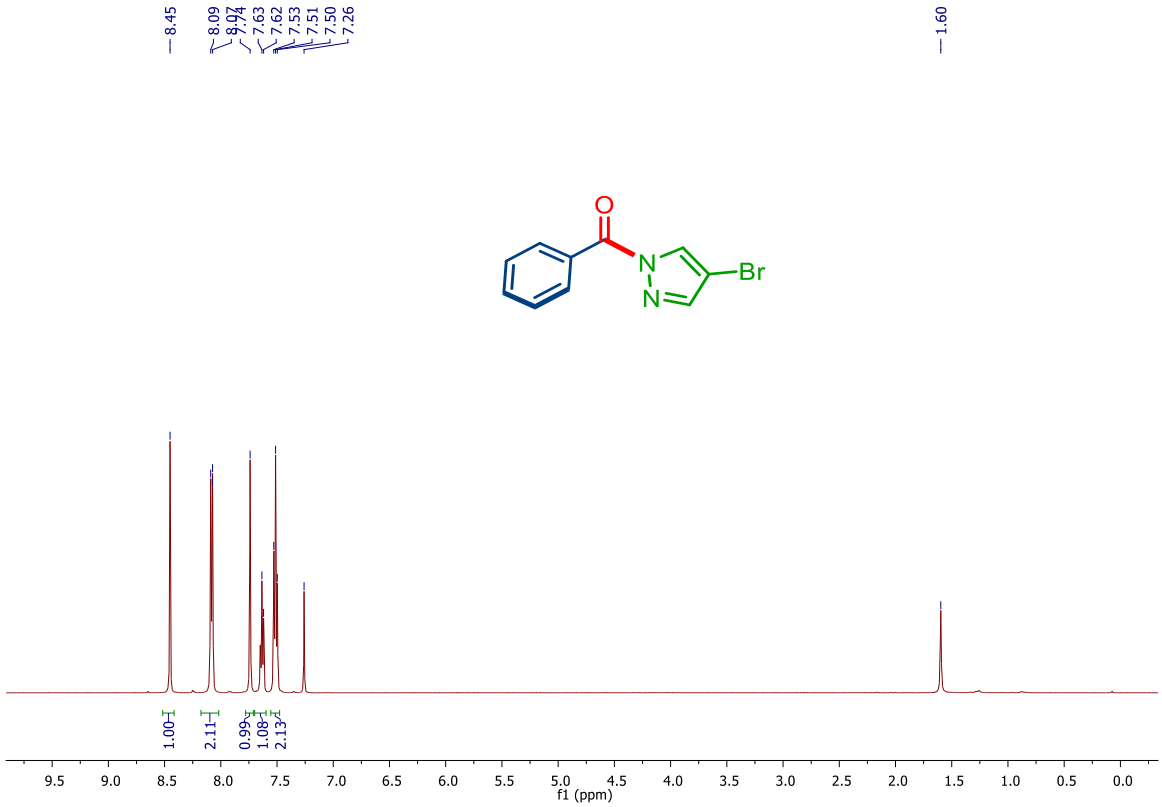
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3zc** ($CDCl_3$, rt)



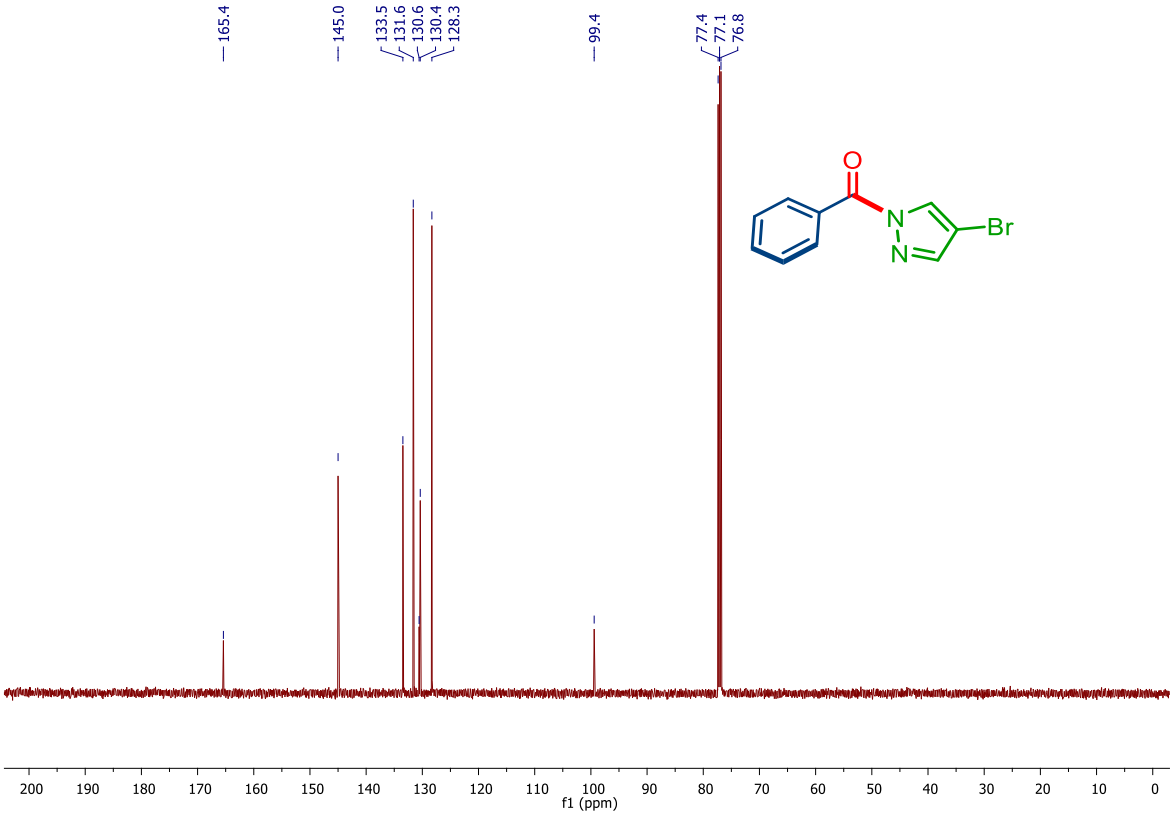
^{1}H NMR (500 MHz) spectrum of **3zd** ($CDCl_3$, rt)



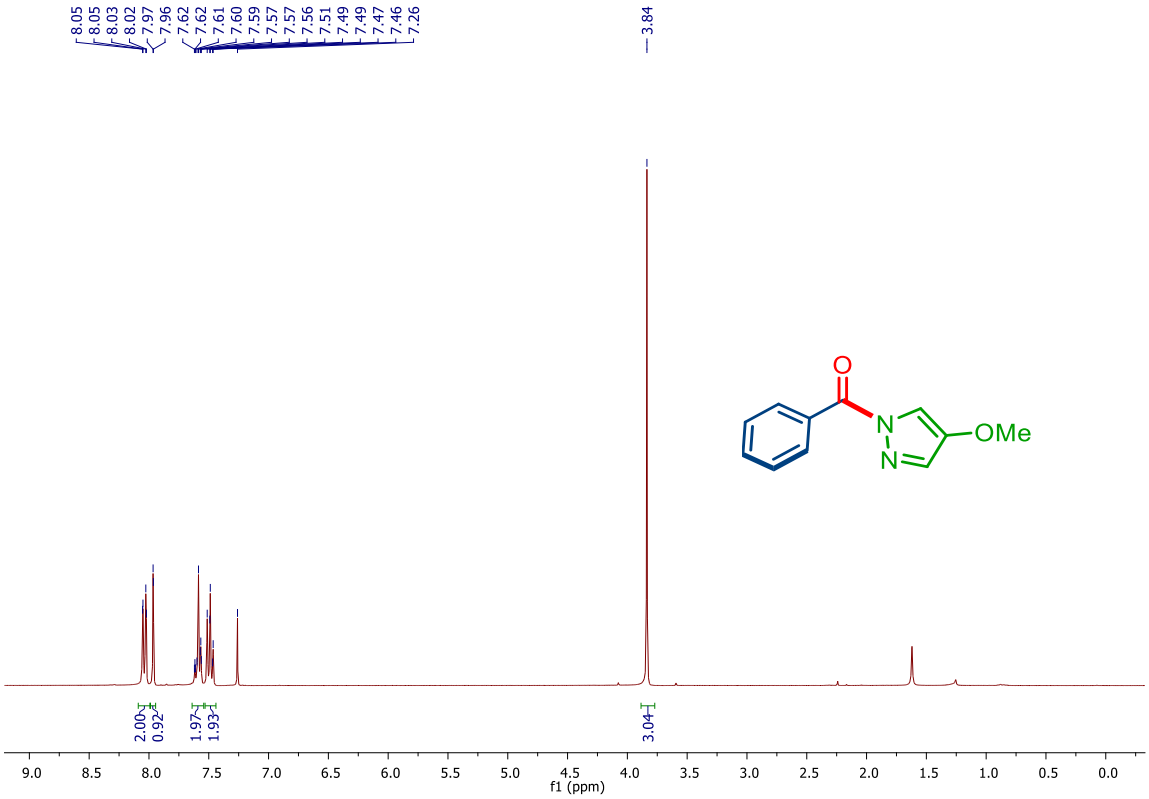
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3zd** ($CDCl_3$, rt)



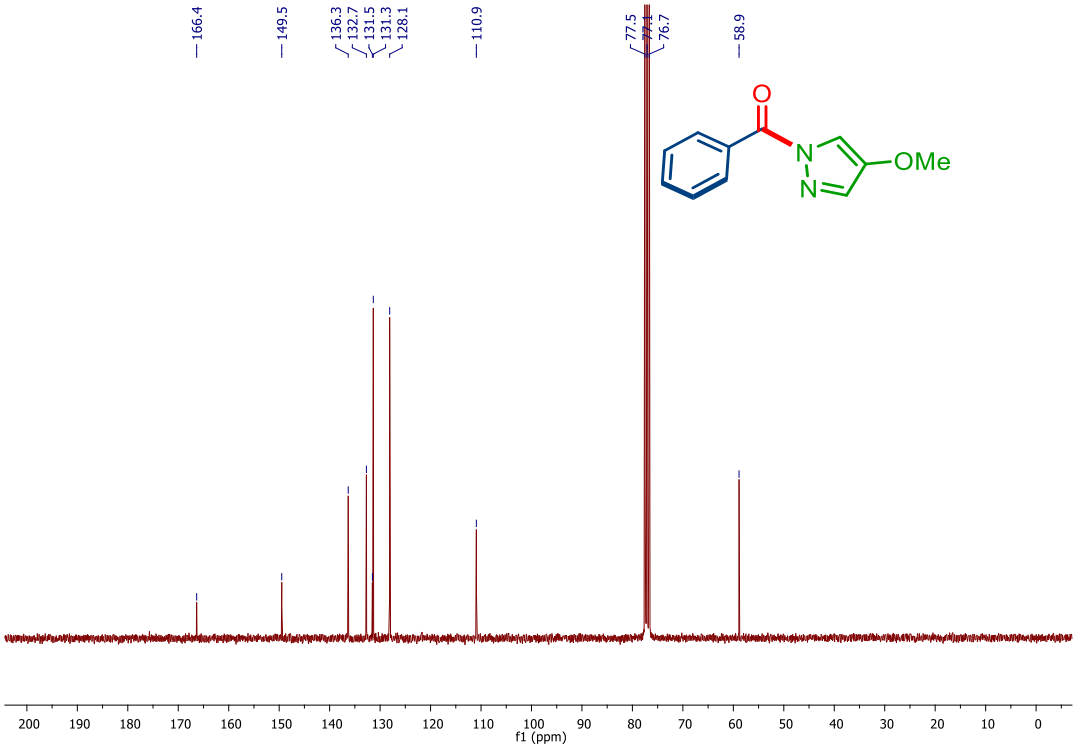
^{1}H NMR (500 MHz) spectrum of **3ze** ($CDCl_3$, rt)



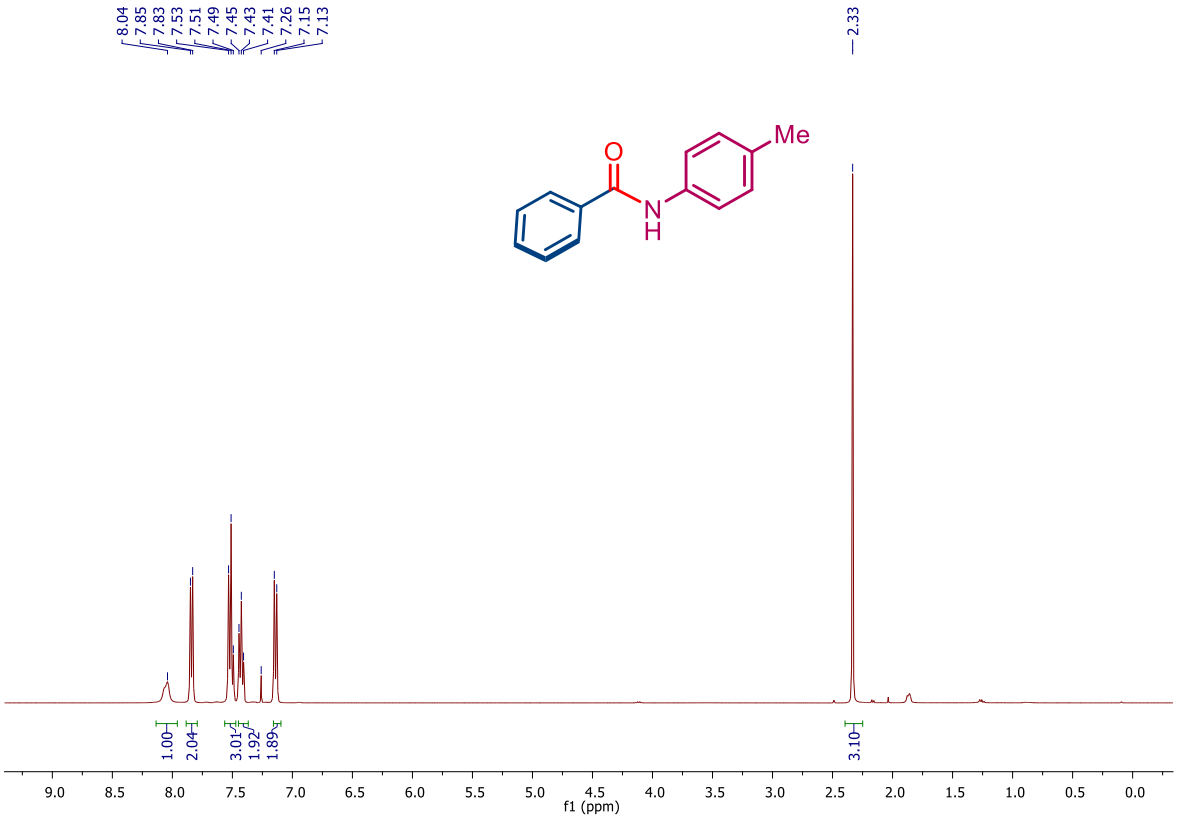
^{13}C{^{1}H} NMR (126 MHz) spectrum of **3ze** ($CDCl_3$, rt)



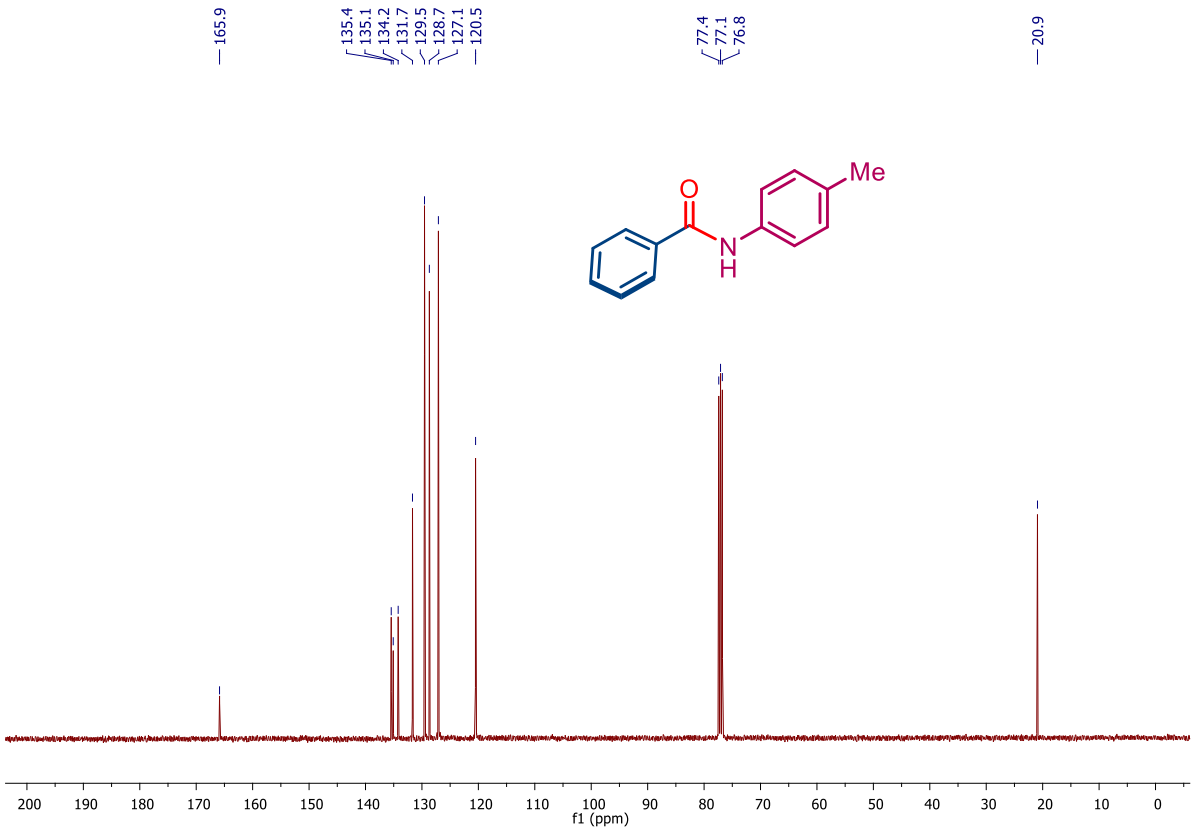
^{1}H NMR (300 MHz) spectrum of **3zf** ($CDCl_3$, rt)



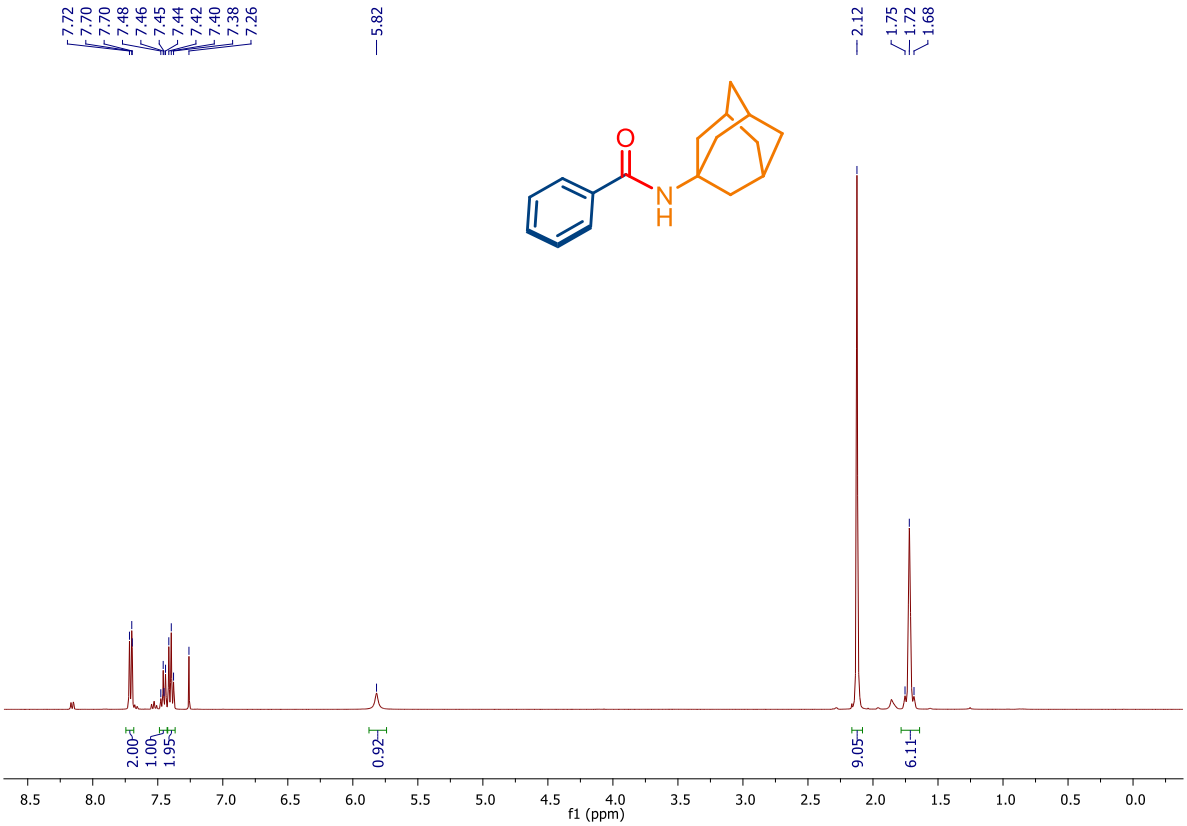
^{13}C{^{1}H} NMR (75 MHz) spectrum of **3zf** ($CDCl_3$, rt)



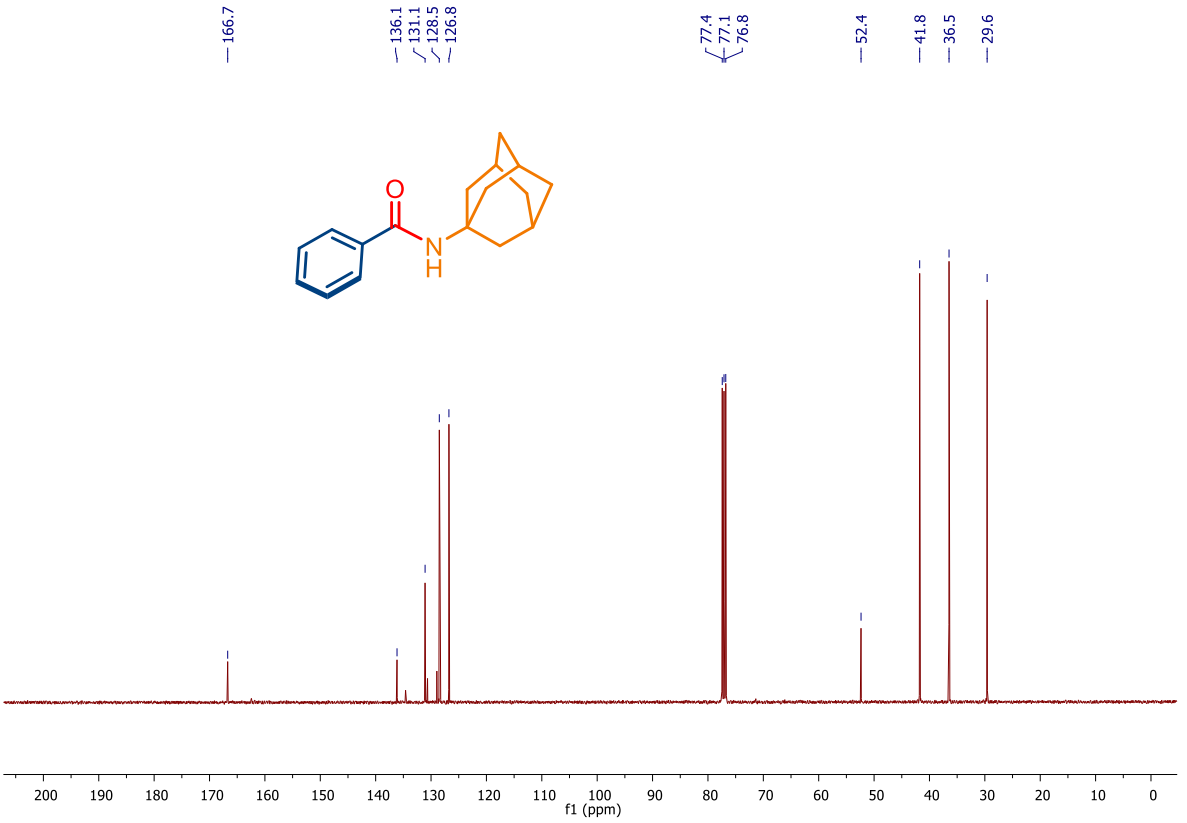
^{1}H NMR (400 MHz) spectrum of **4a** ($CDCl_3$, rt)



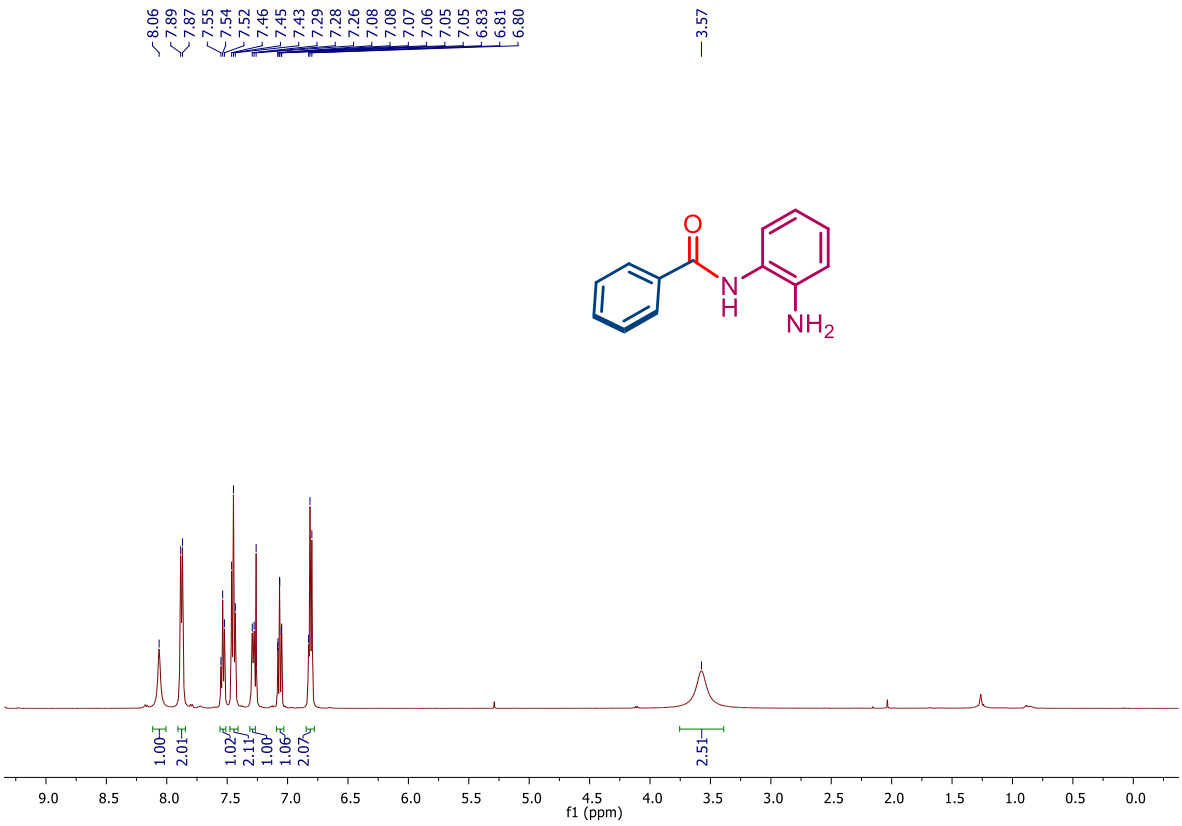
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4a** ($CDCl_3$, rt)



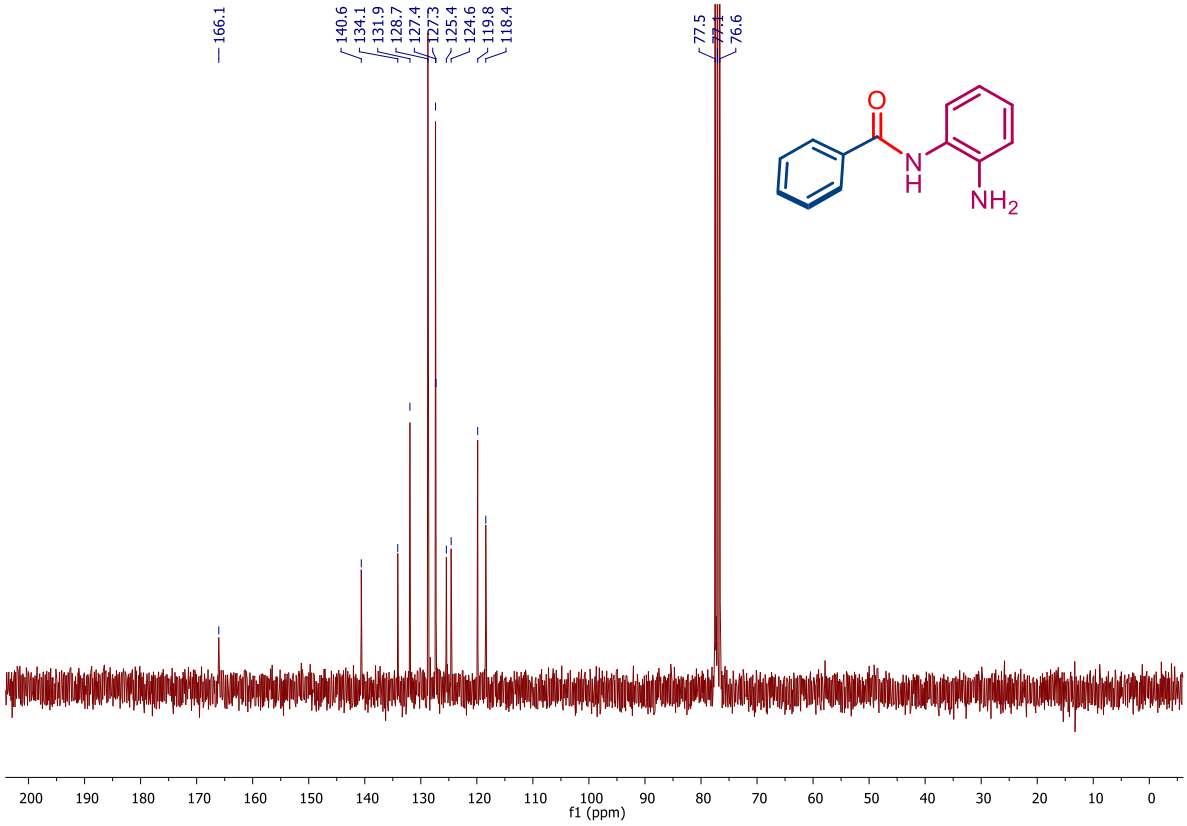
^{1}H NMR (400 MHz) spectrum of **4b** ($CDCl_3$, rt)



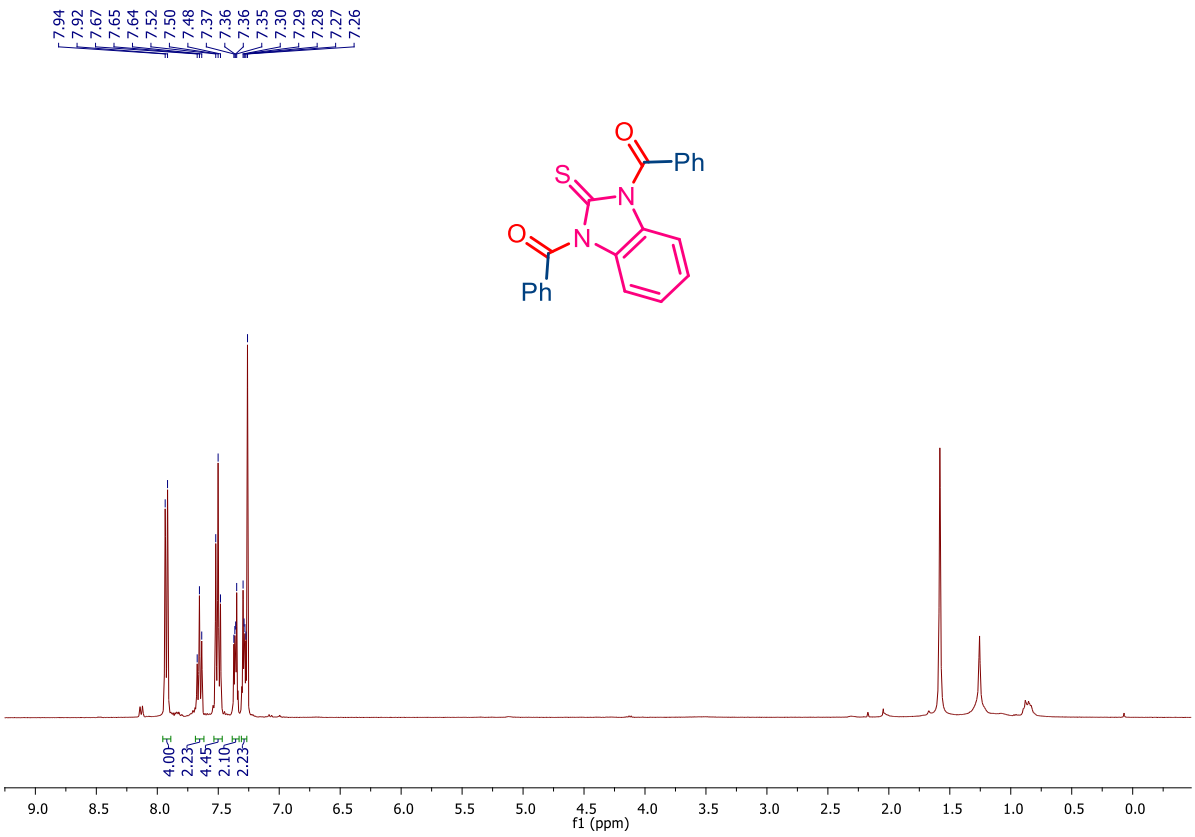
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4b** ($CDCl_3$, rt)



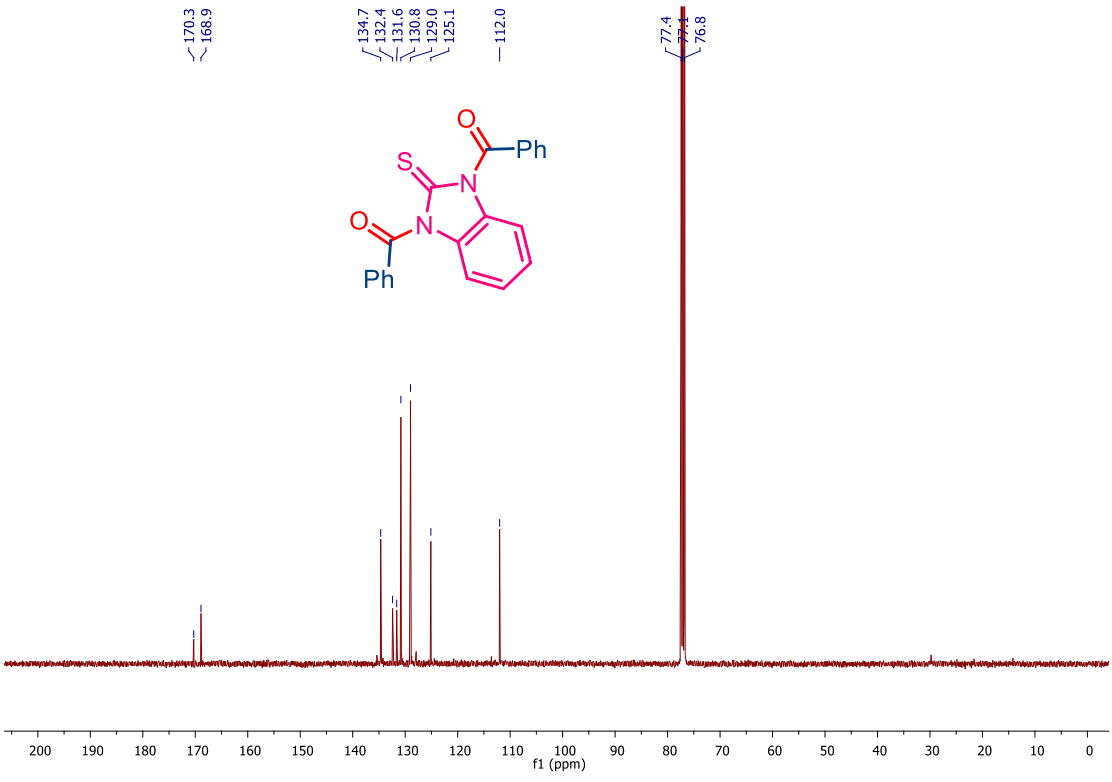
^{1}H NMR (500 MHz) spectrum of **4c** ($CDCl_3$, rt)



^{13}C{^{1}H} NMR (75 MHz) spectrum of **4c** ($CDCl_3$, rt)



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



^{13}C{^{1}H} NMR (101 MHz) spectrum of **4d** ($CDCl_3$, rt)