Supplementary Information

Azolation of Benzylic C–H Bonds via Photoredox-Catalyzed Carbocation Generation

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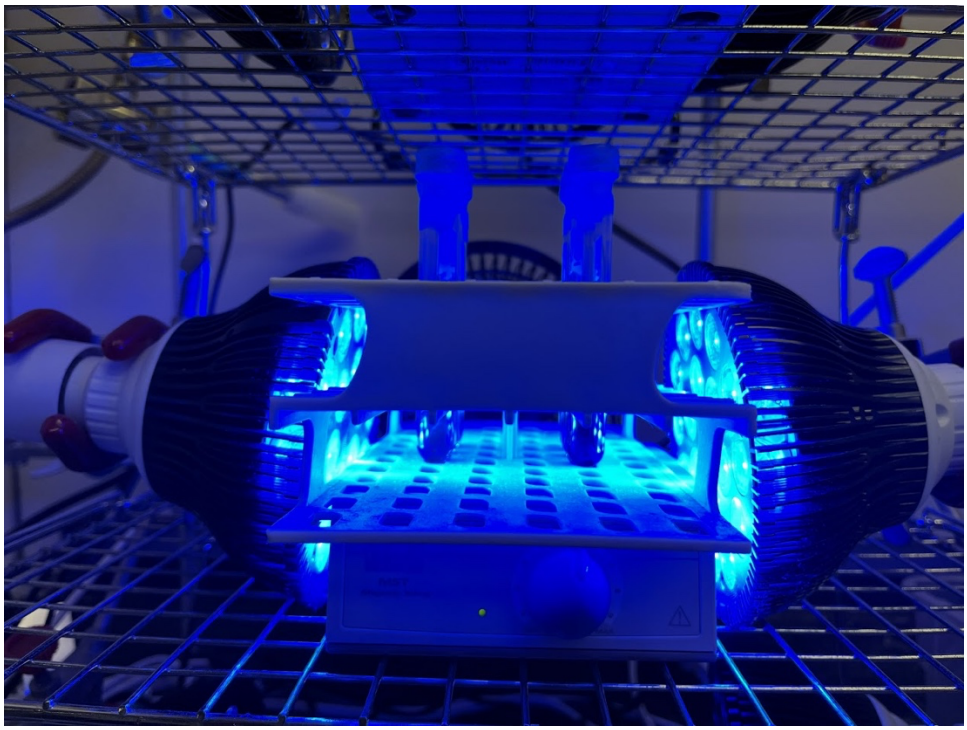
1. General Information

Materials: Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] Anhydrous benzene was purchased from Millipore Sigma and arrived in a SureSeal bottle. Anhydrous ethyl acetate was purchased from Acros and arrived in an AcroSeal bottle. Other solvents were purified by passage through columns of activated alumina, or according to the method of Grubbs.[2] Luperox® *tert*-Butyl peroxybenzoate (TBPB) and other peresters were purchased from Millipore Sigma. Tris[2-(2,4-difluorophenyl)pyridine]iridium(III), or $Ir(dFppy)_3$, was purchased from Millipore Sigma and Strem. All other photocatalysts used in this paper were purchased from Strem. No additional precautions were taken to keep reagents moisture free.

Methods: Organic solutions were concentrated under reduced pressure on an IKA rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow column chromatography on silica gel (40-60 Å, purchased from Oakwood) according to the method of Still.[3] Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed by fluorescence quenching or by p-anisaldehyde or $KMnO_4$ stain. Preparatory thin-layer chromatography was performed with glass-backed silica plates from SiliCycle (1,000 µm, 20 x 20 cm, F254). HIGROW blue LED light bulbs (36W, 450-460nm) were used as our light source for all photoredox-catalyzed reactions. Westpointe Electrical Co high velocity fans (4") were used to keep the reactions at room temperature.

Instrumentation: 1 H NMR spectra were recorded on a Bruker BioSpin 500MHz Avance III Digital NMR spectrometer unless otherwise noted and are internally referenced to the residual protio solvent signal of $CDCl_3$ (7.26 ppm) with the following shorthand for multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, br = broad, coupling constant = J (Hz). ^{13}C NMR spectra were acquired using a Bruker BioSpin Avance III Digital NMR spectrometer (126MHz) and calibrated using the solvent signal ($CDCl_3$ 77.16 ppm). High Resolution Mass spectra were obtained on a Thermo Scientific Q Exactive Orbitrap mass spectrometer. Low resolution mass spectra were acquired on an Agilent 7890A/5075C gas chromatography-mass spectrometer. Cyclic voltammograms were obtained utilizing a EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273 with a glassy carbon working electrode, silver wire counter electrode, and reference saturated calomel electrode (SCE). UV-Visible spectroscopy was obtained using Evolution 300 UV-Visible spectrophotometer from Thermo Electron Corporation.

Light Sources: Blue LED light bulbs (36W, 450-460nm) purchased from Amazon were used as the light source for all photoredox catalysis reactions. Brand is HIGROW and the items were specified for aquarium use. Dimensions: 4.7x4.7x4.5 inches, ASIN B075RYNP18.



2. General Procedure for the Survey of *N*-Alkoxypyridinium Reagents

An 8 mL vial was equipped with a stir bar, $Ir(dFppy)_3$ (1.5 mg, 0.002 mmol, 0.01 equiv.), the respective N-alkoxypyridinium tetrafluoroborate reagent (0.3 mmol, 1.5 equiv.), 4-bromopyrazole (88 mg, 0.6 mmol, 3 equiv.) and anhydrous 1,2-dichloroethane: 1,1,1,3,3,3-hexafluoro-2-propanol (DCE:HFIP, 7:3, 1 mL, 0.2 M). Indane (24.5 µL, 0.20 mmol, 1 equiv.) was next added to the solution. The reaction was capped and sparged with nitrogen (solution for 4 minutes, headspace for 6 minutes), and then sealed with parafilm. The

reaction was placed in front of one 36W blue LED lamp (4 inches between light source and vial) with a personal fan adjacent to the setup for temperature control (room temperature). The reaction was let run for 24-72 hours and then quenched by exposure to air. The crude reaction mixture was concentrated in vacuo, then subjected to flash chromatography on silica gel to afford the desired product.

3. Additional Regioselectivity Experiments

3.1 Extra Unsymmetrical Substrates

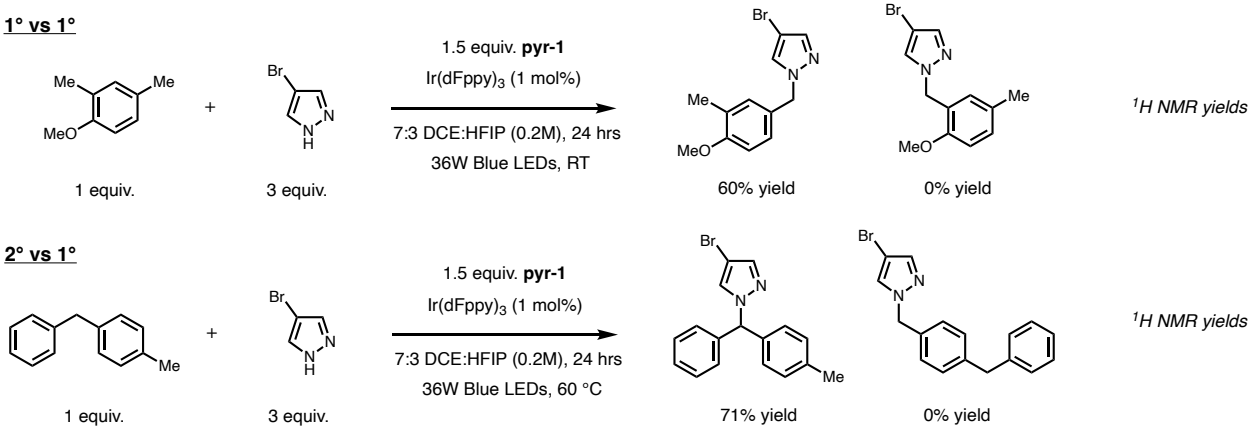


Figure S1. Additional Unsymmetrical Substrates for Regioselectivity Considerations

We observe a preference for secondary benzylic C–H functionalization over primary benzylic, and that sterics may play a role in the selectivity between an ortho and para benzylic C–H functionalization, with azolation of the para methyl group being preferred.

3.2 Competition Experiments

Rxn	photocatalyst	Yield of A	Yield of B	time
1	$Ir(dFppy)_3$ (1 mol%)	31%	3%	24 hrs
2	Eosin Y (5 mol%)	80%	18%	48 hrs

Figure S2. Competition Experiment from Figure 4

Indeed, similar to the outcome of the unsymmetrical substrates, we observed a preference for secondary benzylic over tertiary benzylic sites. Under our standard conditions, we observed a 10.3:1 ratio for 2°:3°. Our current hypothesis is the HAT abstraction at a tertiary benzylic C–H site is slower than that at a secondary benzylic C–H, possibly due to a more hindered environment at the 3° C–H, thus leading to good selectivity. Although selectivity was good, we conducted a photocatalyst screen in an attempt to

increase the efficiency of the product formation. Interestingly, we discovered that higher yields could be obtained with Eosin Y photocatalyst, albeit with lower selectivity of 6:1.

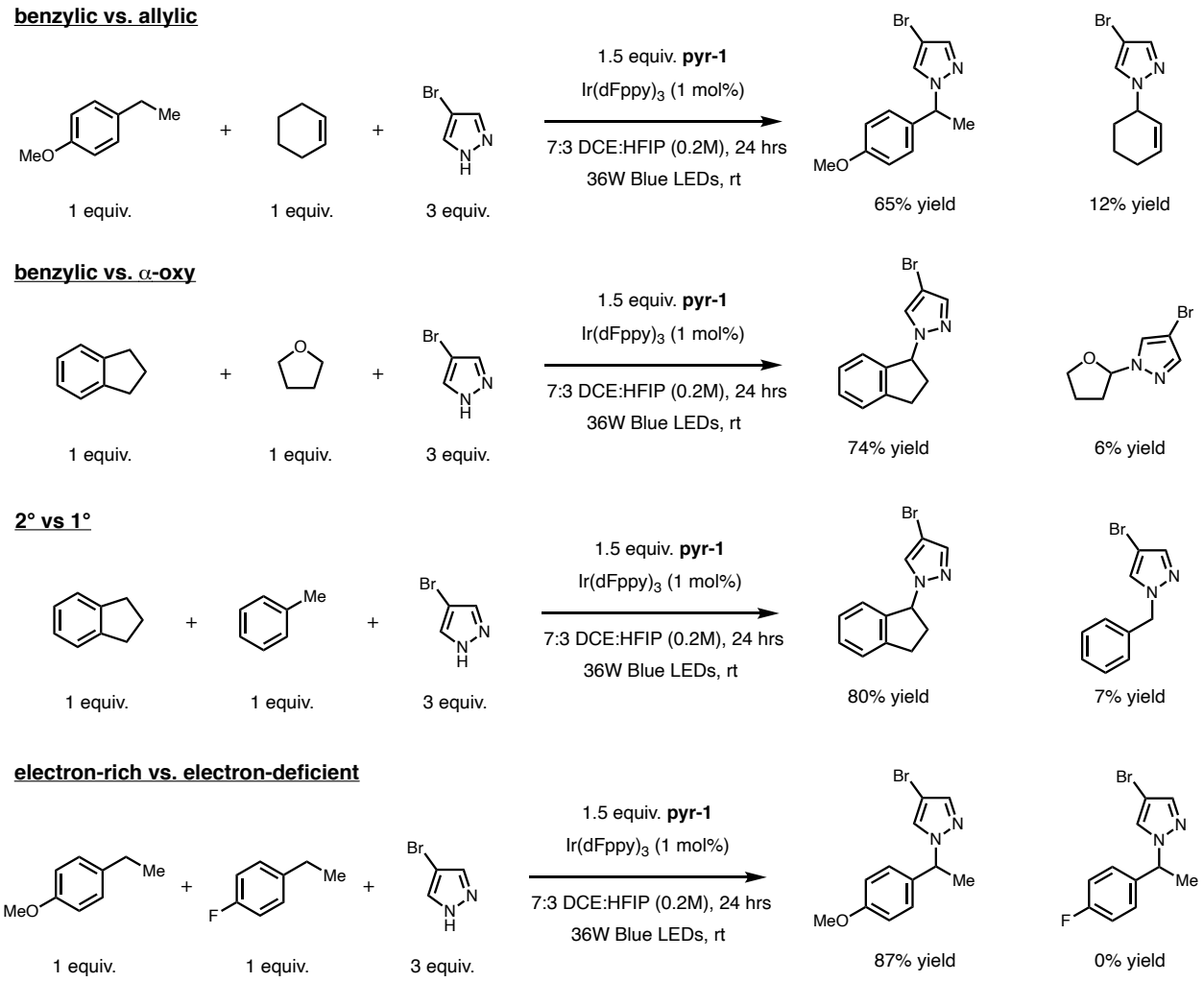


Figure S3. Additional Competition Experiments

The photocatalytic protocol shows a preference for secondary benzylic C–H sites over allylic, α-oxy, and primary benzylic. Additionally, a competition experiment between electron-rich and electron deficient arenes found that selective functionalization of the electron-rich substrate could be achieved. Lastly, we observed that tertiary benzylic C–H sites are preferentially functionalized over primary.

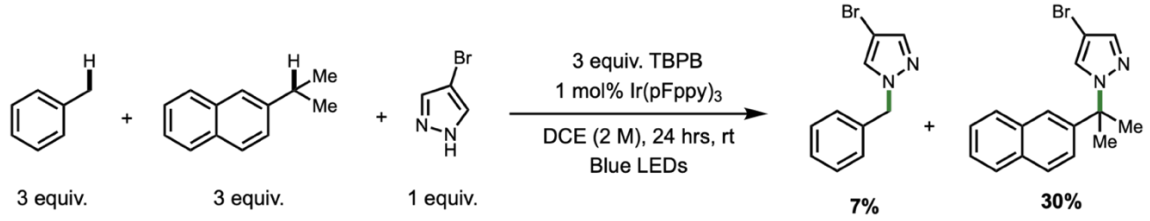


Figure S4: Tertiary vs. Primary Competition Experiment

4. General Procedures for C-H Azolation of Secondary Benzylic C–H Substrates

4.1 General Procedure A

An 8 mL vial was equipped with a stir bar, $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-*N*-methoxy pyridinium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), heterocycle (1.5 mmol, 3 equiv.) and anhydrous 1,2-dichloroethane: 1,1,1,3,3,3-hexafluoro-2-propanol (DCE:HFIP, 7:3, 2.5 mL, 0.2 M). Indane (61.3 μL, 0.500 mmol, 1 equiv.) was next added to the solution. The reaction was capped and sparged with nitrogen (solution for 4 minutes, headspace for 6 minutes), and then sealed with parafilm. The reaction was placed in front of one 36W blue LED lamp (4 inches between light source and vial) with a personal fan adjacent to the setup for temperature control (room temperature). The reaction was let run for 24-72 hours and then quenched by exposure to air. The crude reaction mixture was concentrated in vacuo, then subjected to flash chromatography on silica gel to afford the desired product.

4.2 General Procedure B

An 8 mL vial was equipped with a stir bar, $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-*N*-methoxy pyridinium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), heterocycle (1.5 mmol, 3 equiv.) and anhydrous 1,2-dichloroethane: 1,1,1,3,3,3-hexafluoro-2-propanol (DCE:HFIP, 7:3, 2.5 mL, 0.2 M). Indane (61.3 μL, 0.500 mmol, 1 equiv.) was added to the solution. The reaction was capped and sparged with nitrogen (solution for 4 minutes, headspace for 6 minutes), and then sealed with parafilm. The reaction was placed in an oil bath with one 36W blue LED lamp next to it (4 inches between light source and vial). The reaction was to let it run at 60 ºC for 24-48 hours, cooled to room temperature and then quenched by exposure to air. The crude reaction mixture was concentrated in vacuo, then subjected to flash chromatography on silica gel to afford the desired product.

4.3 General Procedure C

An 8 mL vial was equipped with a stir bar, $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-N-methoxy pyridinium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), heterocycle (1.5 mmol, 3 equiv.) and anhydrous 1,2-dichloroethane: 1,1,1,3,3,3-hexafluoro-2-propanol (DCE:HFIP, 7:3, 2.5 mL, 0.2 M). 1-Ethyl-4-methoxybenzene (71.1 μL, 0.500 mmol, 1 equiv.) was added to the solution. The reaction was capped and sparged with nitrogen (solution for 4 minutes, headspace for 6 minutes), and then sealed with parafilm. The reaction was placed in front of one 36W blue LED lamp (4 inches between light source and vial) with a personal fan adjacent to the setup for temperature control (room temperature). The reaction was let run for 24-72 hours and then quenched by exposure to air. The crude reaction mixture was concentrated in vacuo, then subjected to flash chromatography on silica gel to afford the desired product.

4.4 General Procedure D

An 8 mL vial was equipped with a stir bar, $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-N-methoxy pyridinium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), heterocycle (1.5 mmol, 3 equiv.) and anhydrous 1,2-dichloroethane: 1,1,1,3,3,3-hexafluoro-2-propanol (DCE:HFIP, 7:3, 2.5 mL, 0.2 M). 1-Ethyl-4-methoxybenzene (71.1 μL, 0.500 mmol, 1 equiv.) was added to the solution. The reaction was capped and sparged with nitrogen (solution for 4 minutes, headspace for 6 minutes), and then sealed with parafilm. The reaction was placed in an oil bath with one 36W blue LED lamp next to it (4 inches between light source and vial). The reaction was to let it run at 60 ºC for 24-48 hours, cooled to room

temperature and then quenched by exposure to air. The crude reaction mixture was concentrated in vacuo, then subjected to flash chromatography on silica gel to afford the desired product.

4.5 General Procedure E

An 8 mL vial was equipped with a stir bar, $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-N-methoxy pyridinium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and anhydrous 1,2-dichloroethane: 1,1,1,3,3,3-hexafluoro-2-propanol (DCE:HFIP, 7:3, 2.5 mL, 0.2 M). Next, the respective hydrocarbon (0.500 mmol, 1 equiv.) was added to the solution. The reaction was capped and sparged with nitrogen (solution for 4 minutes, headspace for 6 minutes), and then sealed with parafilm. The reaction was placed in front of one 36W blue LED lamp (4 inches between light source and vial) with a personal fan adjacent to the setup for temperature control (room temperature). The reaction was let run for 24-72 hours and then quenched by exposure to air. The crude reaction mixture was concentrated in vacuo, then subjected to flash chromatography on silica gel to afford the desired product.

4.6 General Procedure F

An 8 mL vial was equipped with a stir bar, $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-N-methoxy pyridinium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and anhydrous 1,2-dichloroethane: 1,1,1,3,3,3-hexafluoro-2-propanol (DCE:HFIP, 7:3, 2.5 mL, 0.2 M). Next, the respective hydrocarbon (0.500 mmol, 1 equiv.) was added to the solution. The reaction was capped and sparged with nitrogen (solution for 4 minutes, headspace for 6 minutes), and then sealed with parafilm. The reaction was placed in an oil bath with one 36W blue LED lamp next to it (4 inches between light source and vial). The reaction was to let it run at 60 ºC for 24-48 hours, cooled to room temperature and then quenched by exposure to air. The crude reaction mixture was concentrated in vacuo, then subjected to flash chromatography on silica gel to afford the desired product.

5. General Procedures for C-H Azolation of Tertiary Benzylic C–H Substrates

5.1 General Procedure G

An 8 mL vial was equipped with a stir bar, $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), molecular sieve 3Å (75 mg), heterocycle (0.500 mmol, 1 equiv.) and anhydrous 1,2-dichloroethane (0.25 mL, 2 M). 2-Isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.) was added to the solution. The reaction was capped and sparged with nitrogen (solution for 4 minutes, headspace for 6 minutes), and then sealed with parafilm. The reaction was placed in front of one 36W blue LED lamp (4 inches between light source and vial) with a personal fan adjacent to the setup for temperature control (room temperature). The reaction was let run for 24-96 hours and then quenched by exposure to air. The crude reaction mixture was concentrated in vacuo, then subjected to flash chromatography on silica gel to afford the desired product.

5.2 General Procedure H

An 8 mL vial was equipped with a stir bar, $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), molecular sieve 3Å (75 mg), heterocycle (0.500 mmol, 1 equiv.) and anhydrous

1,2-dichloroethane (0.25 mL, 2 M). 2-Isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.) was added to the solution. The reaction was capped and sparged with nitrogen (solution for 4 minutes, headspace for 6 minutes), and then sealed with parafilm. The reaction was placed in front of one 36W blue LED lamp (4 inches between light source and vial). The reaction was to let it run at 60 ºC for 24-48 hours, cooled to room temperature and then quenched by exposure to air The crude reaction mixture was concentrated in vacuo, then subjected to flash chromatography on silica gel to afford the desired product.

5.3 General Procedure I

An 8 mL vial was equipped with a stir bar, $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), molecular sieve 3Å (75 mg), 4-bromo-pyrazole (73 mg, 0.50 mmol, 1 equiv.) and anhydrous 1,2-dichloroethane (0.25 mL, 2 M). Next, the respective hydrocarbon (1.5 mmol, 3 equiv.) was added to the solution. The reaction was capped and sparged with nitrogen (solution for 4 minutes, headspace for 6 minutes), and then sealed with parafilm. The reaction was placed in front of one 36W blue LED lamp (4 inches between light source and vial) with a personal fan adjacent to the setup for temperature control (room temperature). The reaction was let run for 24-48 hours and then quenched by exposure to air. The crude reaction mixture was concentrated in vacuo, then subjected to flash chromatography on silica gel to afford the desired product.

5.4 General Procedure J

An 8 mL vial was equipped with a stir bar, $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), molecular sieve 3Å (75 mg), 4-bromo-pyrazole (73 mg, 0.50 mmol, 1 equiv.) and anhydrous 1,2-dichloroethane (0.25 mL, 2 M). Next, the respective hydrocarbon (1.5 mmol, 3 equiv.) was added to the solution. The reaction was capped and sparged with nitrogen (solution for 4 minutes, headspace for 6 minutes), and then sealed with parafilm. The reaction was placed in front of one 36W blue LED lamp (4 inches between light source and vial). The reaction was to let it run at 60 ºC for 24-48 hours, cooled to room temperature and then quenched by exposure to air The crude reaction mixture was concentrated in vacuo, then subjected to flash chromatography on silica gel to afford the desired product.

6. General Procedure for the Synthesis of *N*-alkoxypyridinium tetrafluoroborate reagents

6.1 General Procedure K

Trialkyloxonium tetrafluoroborate (1.05 equiv) was added to a solution of the corresponding pyridine *N*-oxide (1 equiv) in dichloromethane (0.5M) at room temperature. The mixture was stirred at room temperature overnight, before methanol was added. The solvents were removed in vacuo, and the corresponding *N*-alkoxypyridinium tetrafluoroborate was recrystallized in MeOH.[4]

6.2 General Procedure L

Trialkyloxonium tetrafluoroborate (1.2 equiv) was added to a solution of the corresponding pyridine *N*-oxide (1 equiv) in dichloromethane (0.5M) at room temperature. The mixture was stirred at room temperature for 48h before methanol was added. The solvents were removed in vacuo, and the corresponding *N*-alkoxypyridinium tetrafluoroborate was recrystallized in methanol (1 mL) and diethyl ether (20 mL) solution at -20 ºC. A white solid product was obtained.

7. Stern-Volmer experiment

Fluorescence quenching experiments were performed on a Cary Eclipse Fluorometer (Varian). In a typical experiment, a 0.5 μM solution of $Ir(dFppy)_3$ in anhydrous 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3) was added to the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing by bubbling a stream of nitrogen for 10 minutes, the emission of the sample was collected. All solutions were excited at $\lambda = 380$ nm (absorption maximum of the photocatalyst) and the emission intensity at 480 nm was observed (emission maximum). Plots were constructed according to the Stern–Volmer equation $I_0/I = 1 + kq\tau_0[Q]$.

Excited State Quenching Experiments

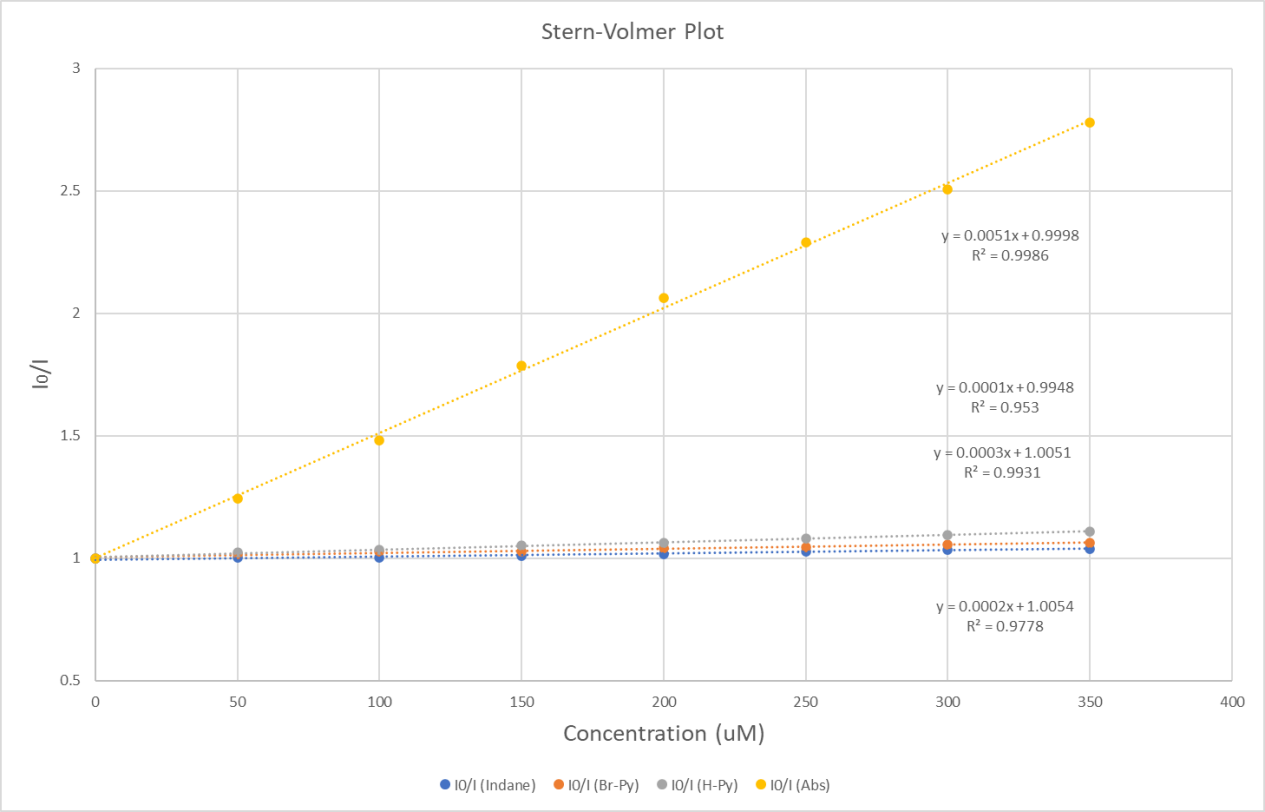
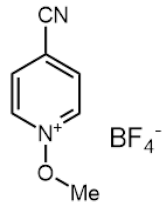


Figure S5: Stern-Volmer quenching plot

8. Cyclic voltammetry experiment

Electrochemical potentials were obtained following the literature procedure.[7] Cyclic voltammograms were collected with a EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273. Samples were prepared with 0.01 M of substrate in 10 mL of 0.1 M electrolyte, *tetra*-*n*-butylammonium hexafluorophosphate in anhydrous acetonitrile. The solution was degassed while stirring for 10 minutes. CV was measured by employing glossy carbon as working electrode, platinum wire as counter electrode, 1 M KCl silver-silver chloride reference electrode, and a scan rate of 100 mV/s. Reductions were measured by scanning potentials in the negative direction with a starting point of 0.1 V and a vertex potential of -2.0 V.



4-Cyano-*N*-methoxy pyridinium tetrafluoroborate ($E_{p/2}$ = -0.44 V)

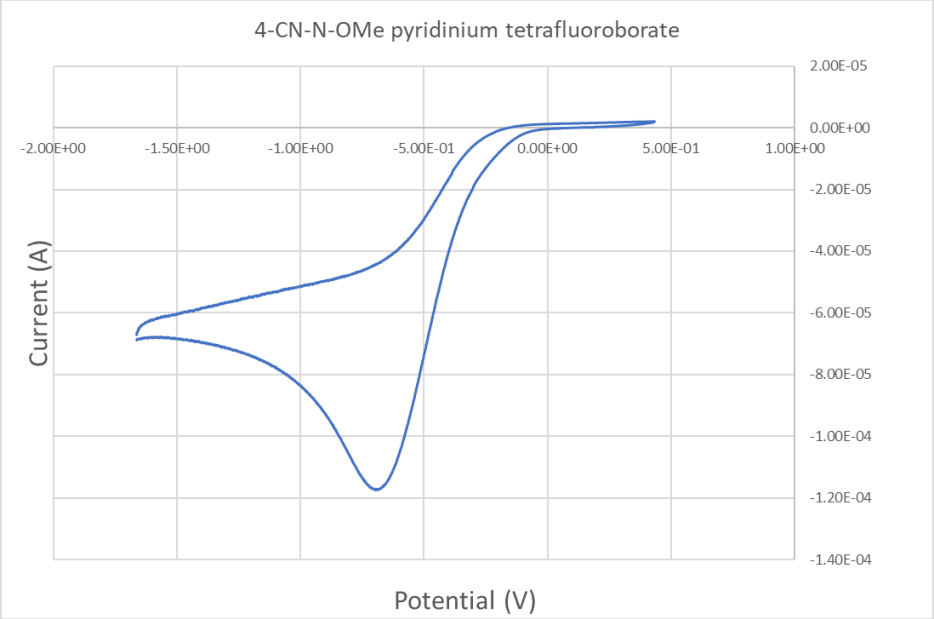
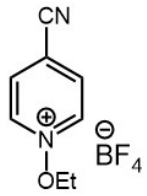


Figure S6: Cyclic Voltammogram for 4-CN-*N*-OMe abstractor



4-Cyano-*N*-ethoxy pyridinium tetrafluoroborate ($E_{p/2}$ = -0.63 V)

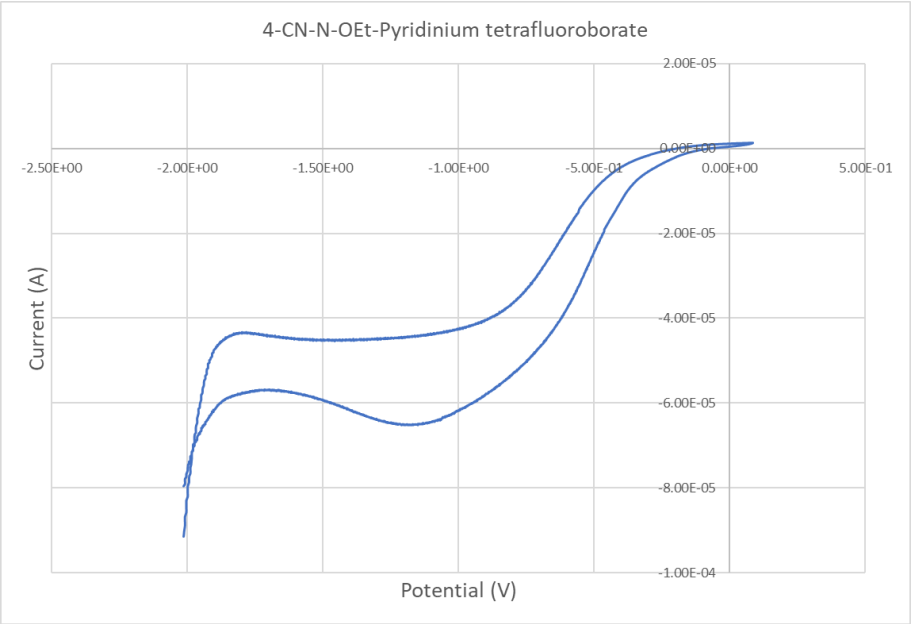
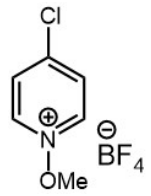


Figure S7: Cyclic Voltammogram for 4-CN-*N*-OEt abstractor



4-Chloro-*N*-methoxy pyridinium tetrafluoroborate ($E_{p/2}$ = -0.68 V)

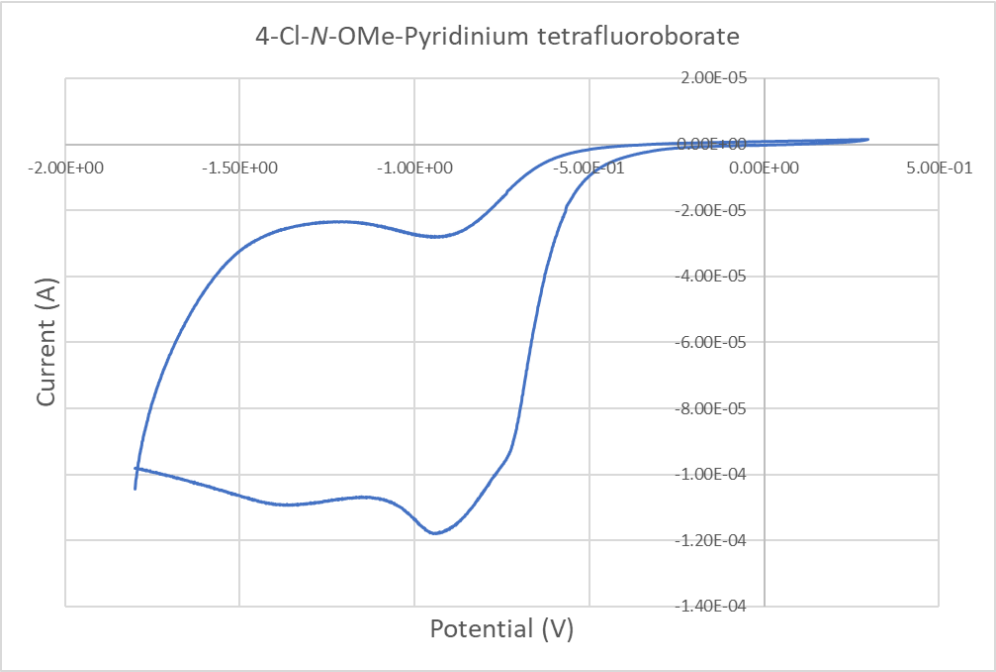
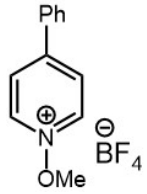


Figure S8: Cyclic Voltammogram for 4-Cl-*N*-OMe abstractor



4-Phenyl-*N*-methoxy pyridinium tetrafluoroborate ($E_{p/2}$ = -0.55 V)

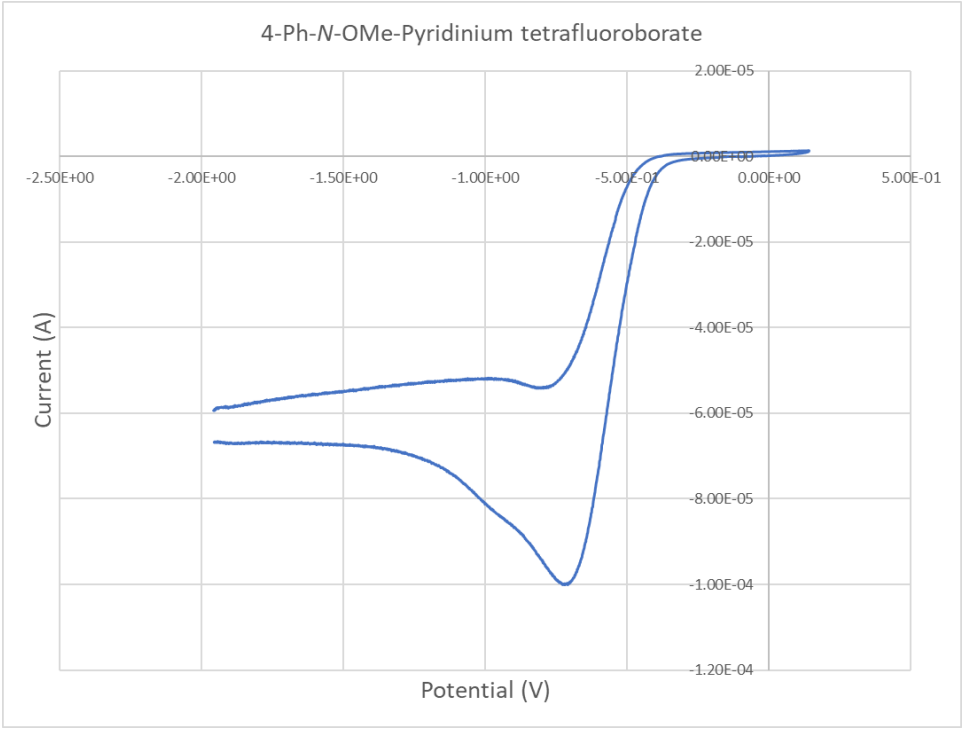
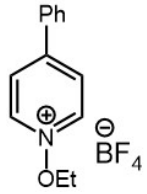


Figure S9: Cyclic Voltammogram for 4-Ph-*N*-OMe abstractor



4-Phenyl-*N*-ethoxy pyridinium tetrafluoroborate ($E_{p/2}$ = -0.57 V)

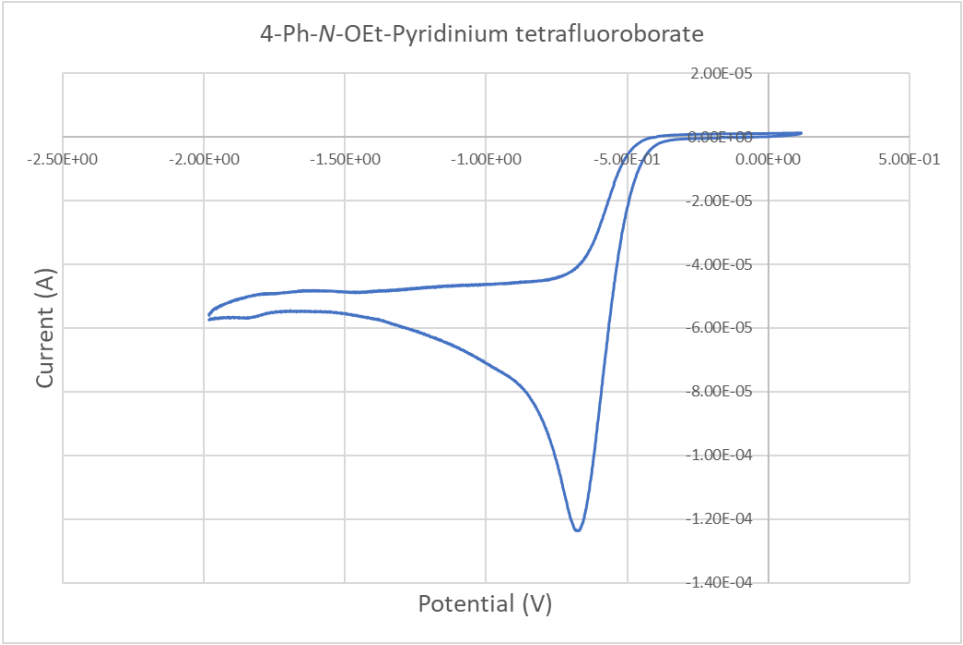
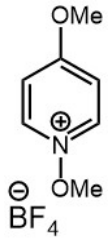


Figure S10: Cyclic Voltammogram for 4-Ph-*N*-OEt abstractor



4-methoxy-*N*-methoxy pyridinium tetrafluoroborate ($E_{p/2}$ = -1.0 V)

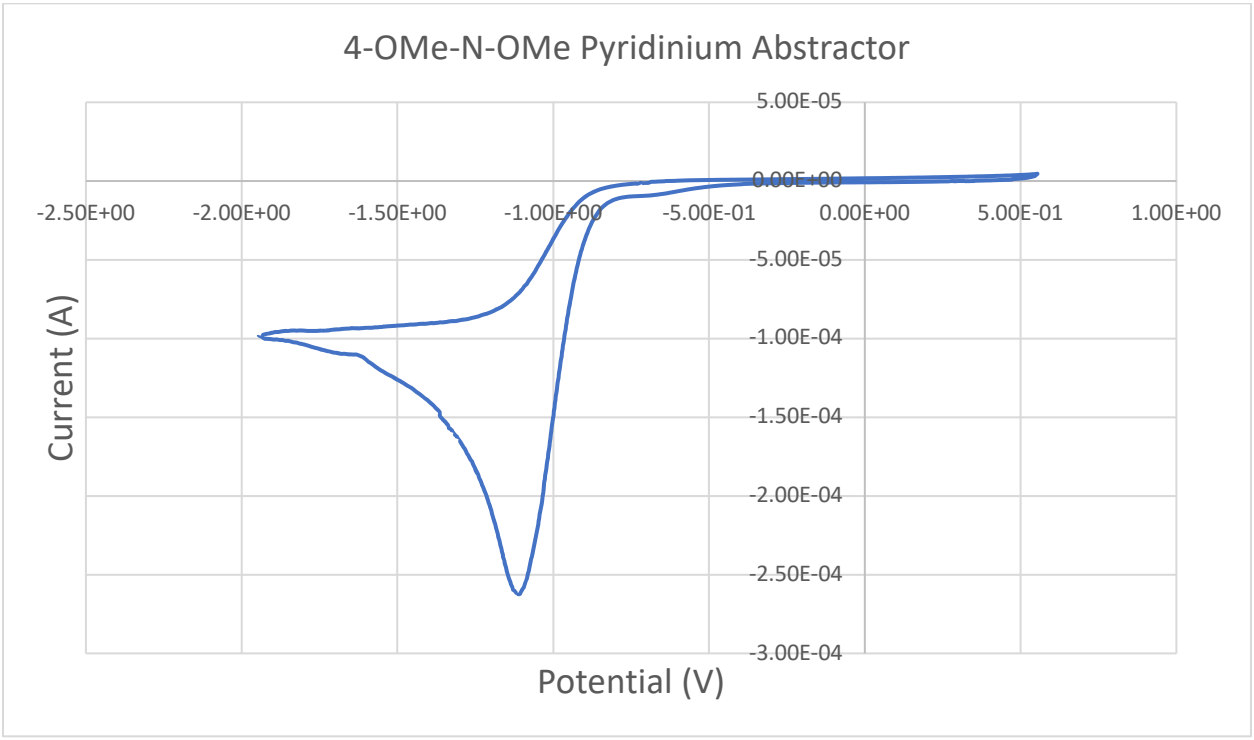
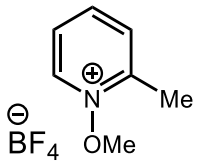


Figure S11. Cyclic Voltammogram for 4-OMe-*N*-OMe abstractor



2-methyl-*N*-methoxypyridinium tetrafluoroborate ($E_{p/2}$ = -0.79 V)

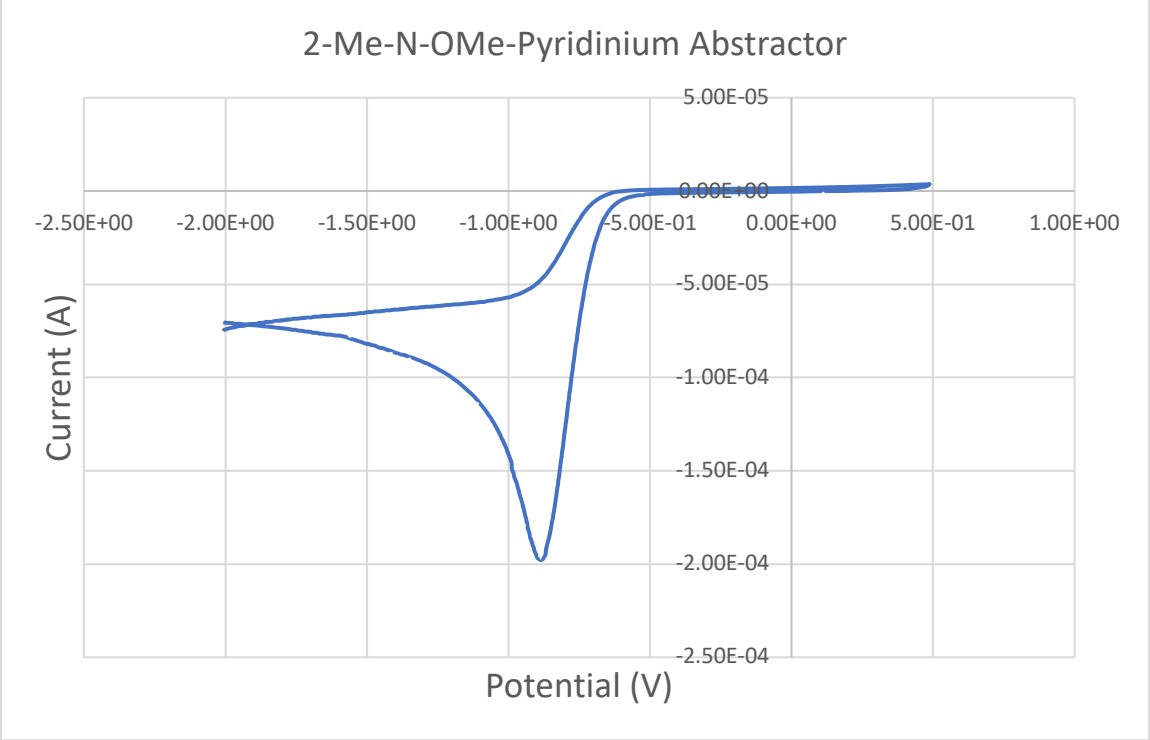
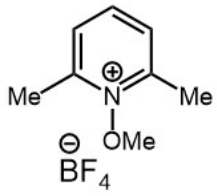


Figure S12. Cyclic Voltammogram of 2-Me-*N*-OMe abstractor



2,6-dimethyl-*N*-methoxypyridinium tetrafluoroborate ($E_{p/2}$ = -0.86 V)

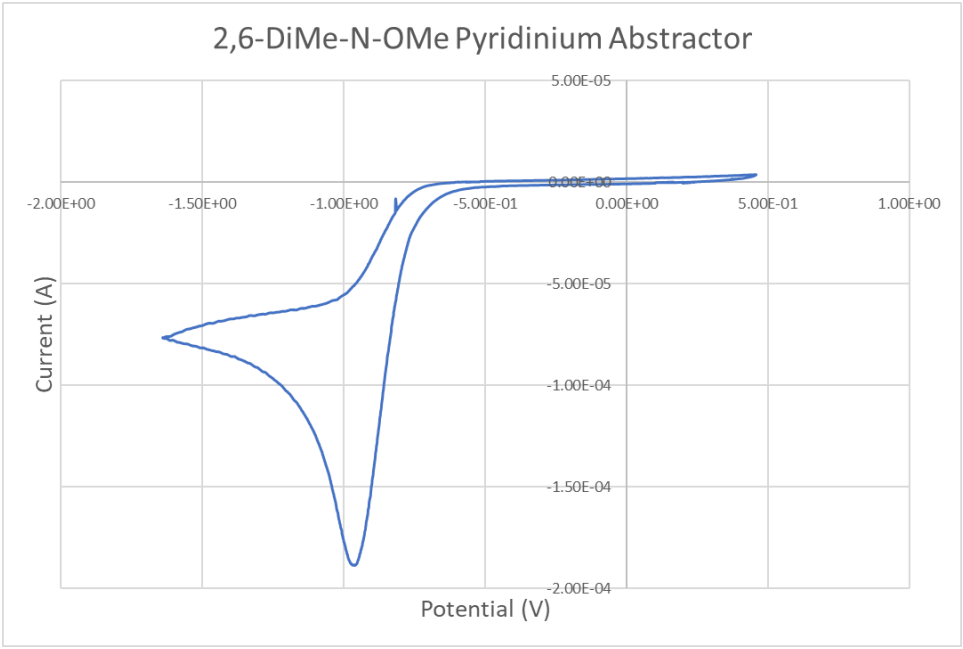
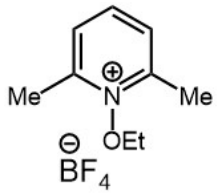


Figure S13. Cyclic Voltammogram of 2,6-dimethyl-*N*-methoxypyridinium abstractor



2,6-dimethyl-*N*-ethoxypyridinium tetrafluoroborate ($E_{p/2}$ = -0.88 V)

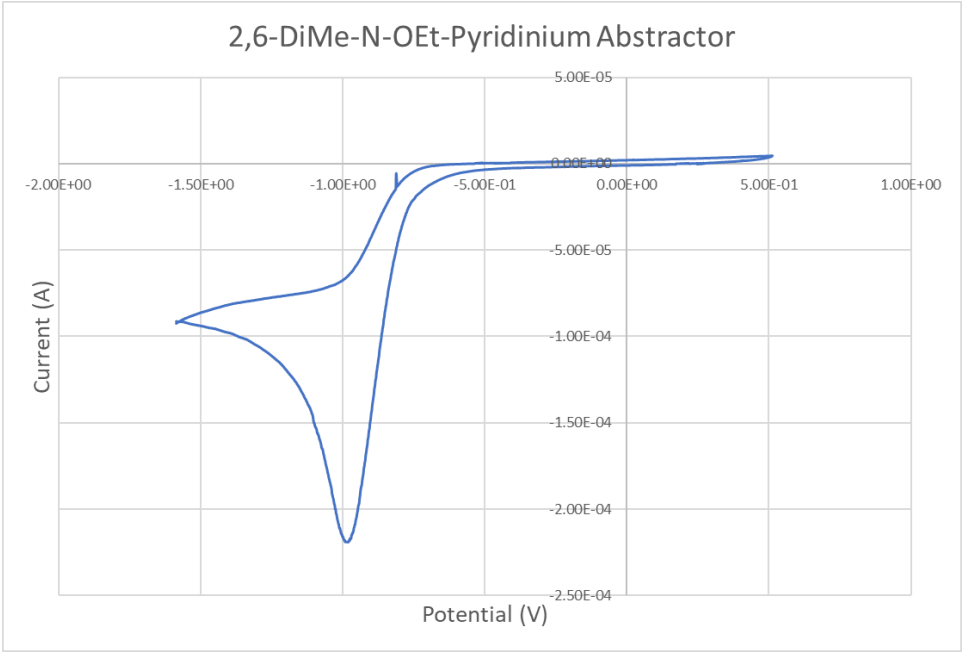
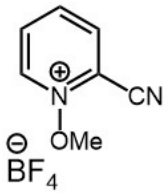


Figure S14. Cyclic Voltammogram of 2,6-dimethyl-*N*-ethoxypyridinium abstractor



2-cyano-*N*-methoxypyridinium tetrafluoroborate ($E_{p/2}$ = -0.59 V)

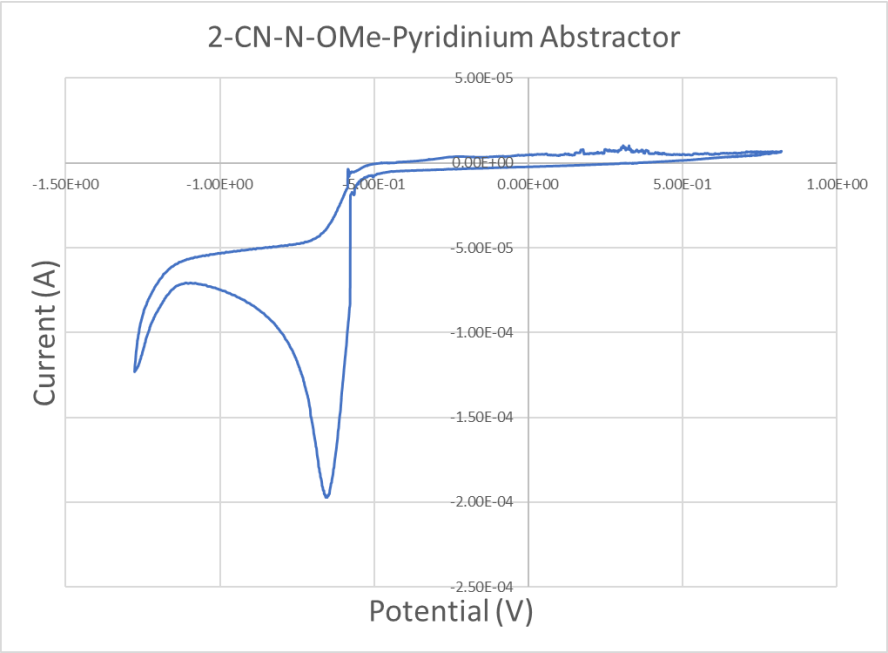


Figure S15. Cyclic Voltammogram of 2-cyano-*N*-methoxypyridinium abstractor

9. UV-Visible Absorption Experiments and Discussion

9.1 Absorption spectra of indane with pyr-1/2/3/4/5

UV-Visible absorption spectra were measured in a 1 cm quartz cuvette utilizing Evolution 300 UV-Visible spectrophotometer from Thermo Electron Corporation. Absorption spectra of each individual reaction components, different abstractors and mixtures were recorded. For 4-CN-*N*-OMe pyridinium tetrafluoroborate and 4-CN-*N*-OEt pyridinium tetrafluoroborate with indane in anhydrous 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (DCE: HFIP, 7:3, 0.2 M) a bathochromic shift was observed. This indicates the formation of an electron donor-acceptor complex (Figure S13 & S14).

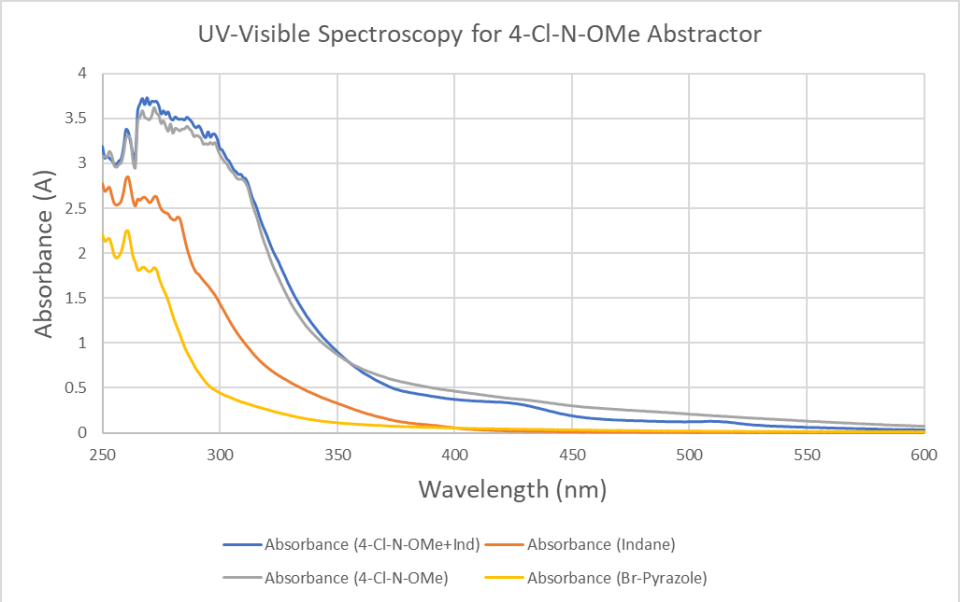


Figure S16: UV-Visible absorption spectra for 4-Cl-*N*-OMe abstractor

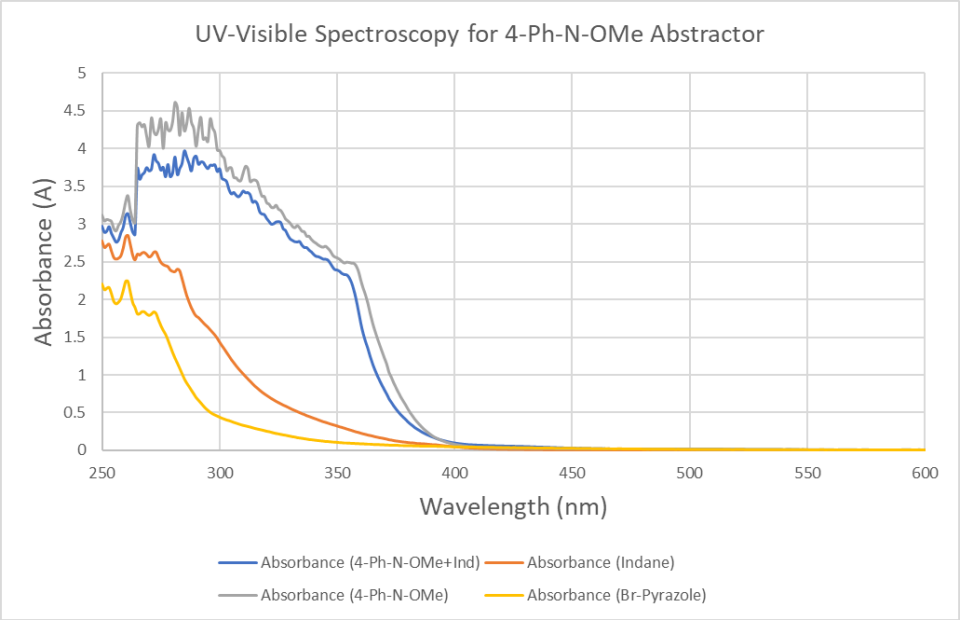


Figure S17: UV-Visible absorption spectra for 4-Ph-*N*-OMe abstractor

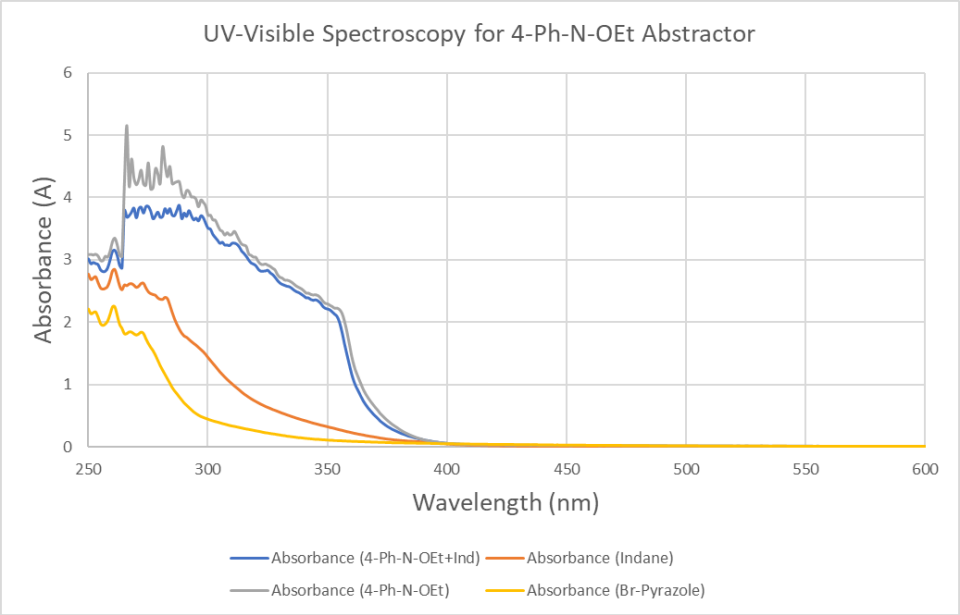


Figure S18: UV-Visible absorption spectra for 4-Ph-*N*-OEt abstractor

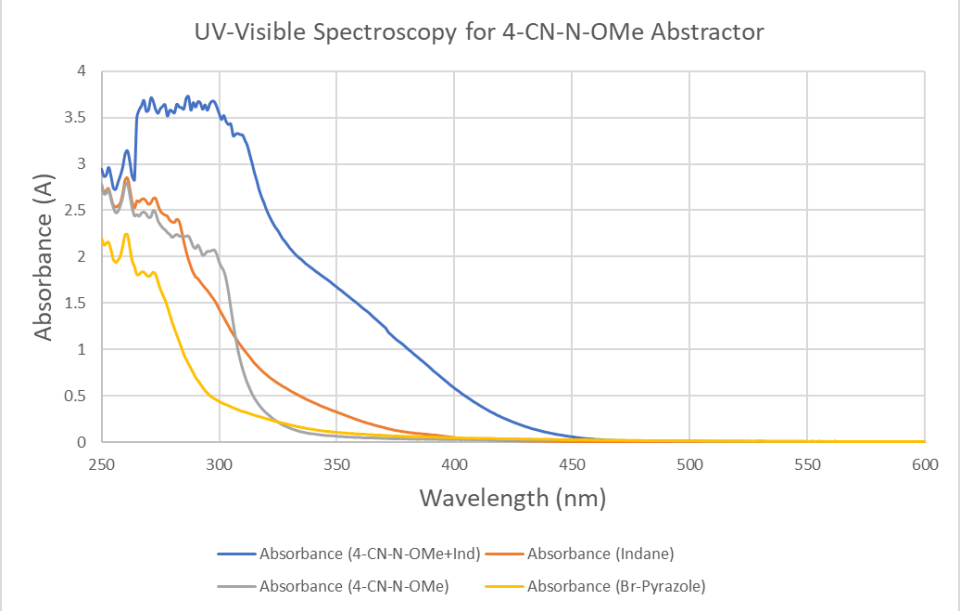


Figure S19: UV-Visible absorption spectra for 4-CN-*N*-OMe abstractor

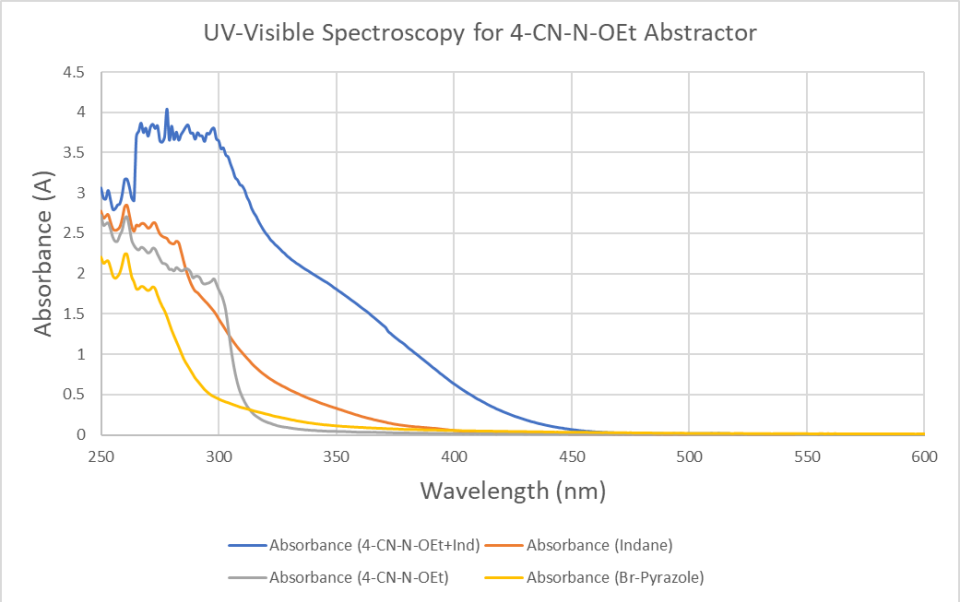
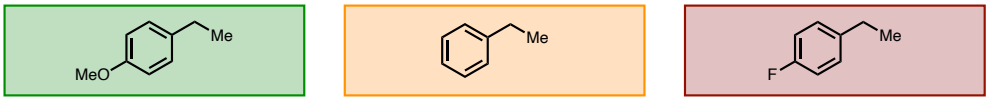


Figure S20: UV-Visible absorption spectra for 4-CN-*N*-OEt abstractor

9.2 Alternative N-alkoxypyridinium reagents and their UV-vis spectra with 4-ethylanisole, ethylbenzene, and 1-ethyl-4-fluorobenzene

To probe a correlation between reduction potential of the N-alkoxypyridinium reagents and substrate, *N*-alkoxypyridinium reagents pyr-1 to pyr-9 were synthesized. Specifically, we looked at more electron-donating groups in an attempt to identify the reduction potential (or electron acceptor ability) requirement for the EDA complex. Reagents pyr-6, pyr-7, pyr-8, pyr-9 were synthesized for this effort. We cross examined them with electron-rich, electron-neutral, and electron-deficient C–H arene substrates.

EDA complex correlation to reduction potential and electronics of arene



pyridinium reagent	$E_{p/2}$ vs. SCE	UV-vis: red-shift into visible light?	% yld	UV-vis: red-shift into visible light?	% yld	UV-vis: red-shift into visible light?	% yld
pyr-1	-0.44V	yes, 400-450 nm	90%	no	26%	no	20%
pyr-2	-0.63V	yes, 400-450 nm	89%	no	14%	no	14%
pyr-3	-0.68V	yes, 400-450 nm	6%	yes, 400-450 nm	3%	yes, 400-450 nm	3%
pyr-4	-0.55V	no	27%	no	3%	no	2%
pyr-5	-0.57V	no	25%	no	4%	no	4%
pyr-6	-1.00V	no	3%	no	<1%	no	<1%
pyr-7	-0.79V	no	8%	no	4%	no	1%
pyr-8	-0.88V	no	9%	no	3%	no	<1%
pyr-9	-0.86V	no	5%	no	<1%	no	<1%

Note: yields were obtained with 1 equiv. of the indicated C–H precursors, azole (3 equiv.), pyridinium reagent (1.5 equiv.), $Ir(dFppy)_3$ (1 mol%), 7:3 DCE:HFIP, blue LEDs, 24 hrs., r.t.

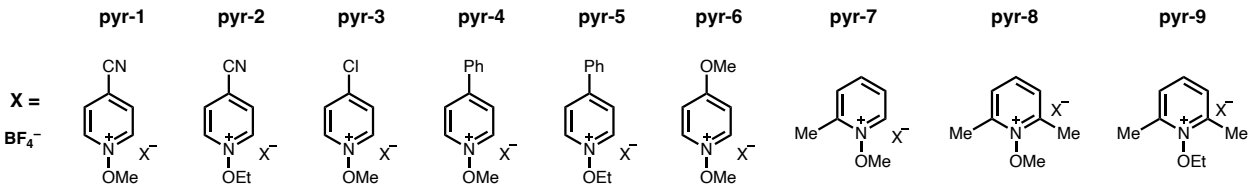


Figure S21: Table Indicating Presence of Bathochromic Shifts in UV-vis Between Three Electronically Varying C–H Substrates and All Pyridinium Reagents

New peaks in the visible light region that are independent from the absorption of the individual reagents were only observed for electron-rich C–H substrate 4-ethylanisole, and when using pyr-1, pyr-2, and pyr-3. We are continuing to investigate the role of Cl on the pyridinium reagent in the EDA mechanism, however, use of pyr-3 did not give yields above 6% in the C–H azolation of each substrate. We did not find a consistent trend between the $E_{p/2}$ of the pyridinium reagent and detection of an EDA complex in the visible light region for electron-deficient functionality on the pyridinium. However, we did observe that, generally, installation of electron-rich functionality on the pyridinium reagents raised the reduction potential of the reagents and did not result in a new absorption peak.

The EDA complex appears to be largely dependent on solvent and **the electronic nature of the C–H substrate**. We observed that *N*-alkoxypyridinium reagents that possessed reduction potentials higher than approximately -0.7V vs SCE did not result in detection of an EDA complex in the visible light region.

More specifically, we wanted to probe the impact of moving the cyano group to the 2 position on the pyridinium. Interestingly, this caused a decrease in the reduction potential (less oxidizing) and resulted in little to no yield of product across an array of C–H precursors. Again, we are still evaluating the importance of having electron-withdrawing groups at the 4 position of the pyridinium reagent.

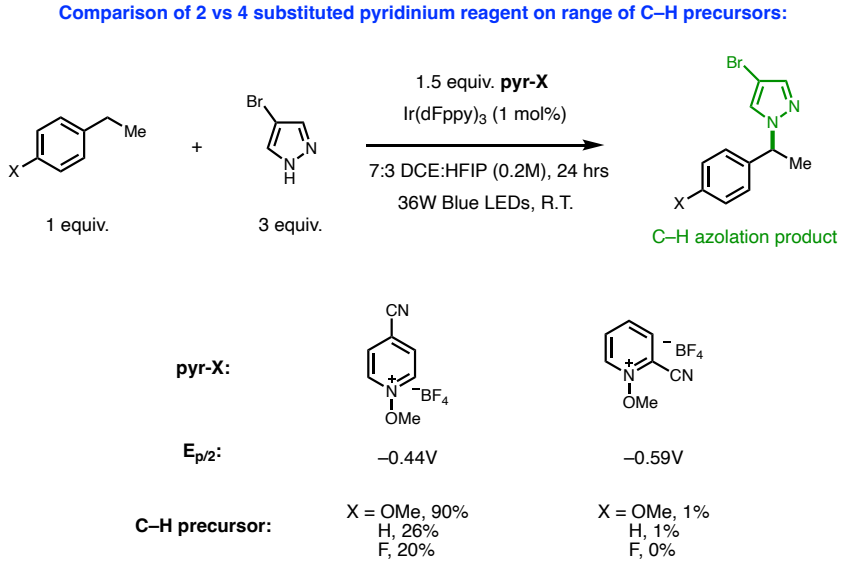
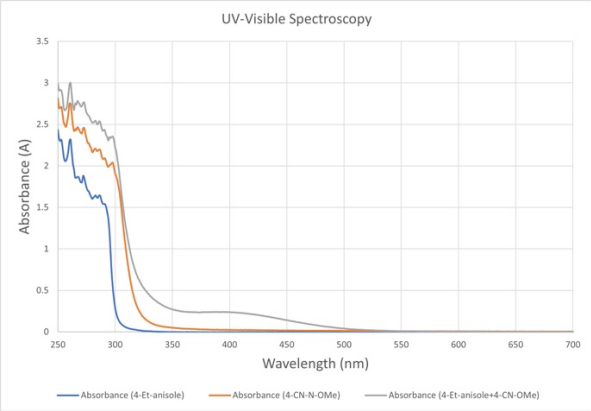


Figure S22: Comparing 2- vs 4-cyano pyridinium reagents in the reaction

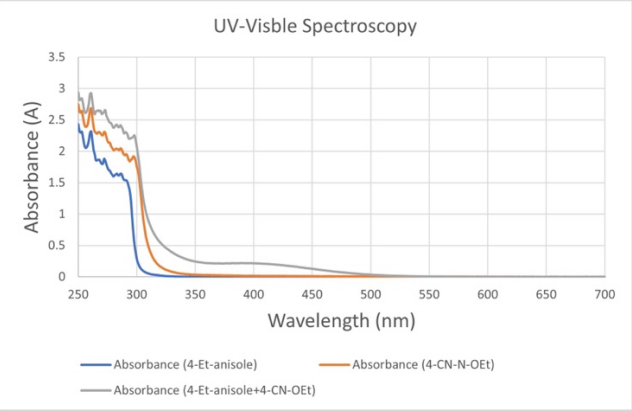
All UV-vis spectra are reported here. The following data was collected at [0.1M] of the indicated C–H arene and pyridinium reagent in 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (DCE: HFIP, 7:3):

UV-vis Data for 4-ethylanisole

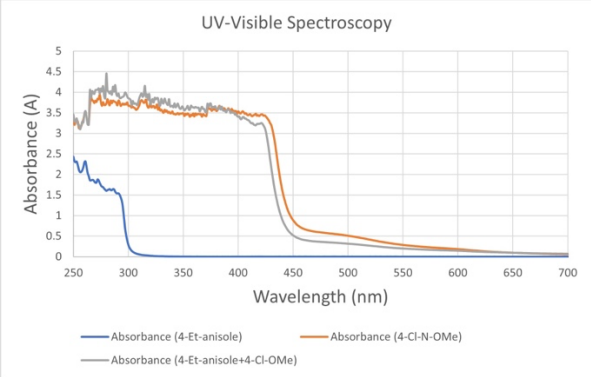
4-ethylanisole + pyr-1:



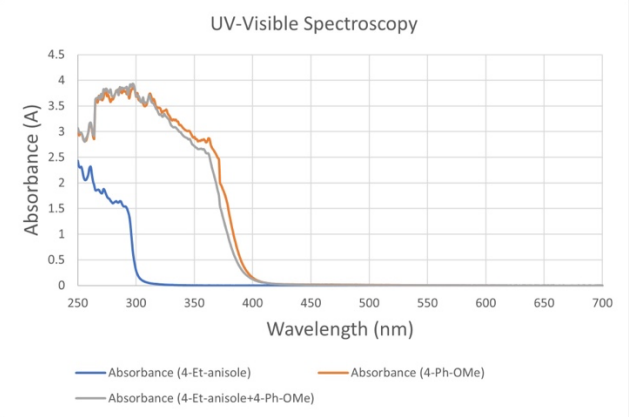
4-ethylanisole + pyr-2:



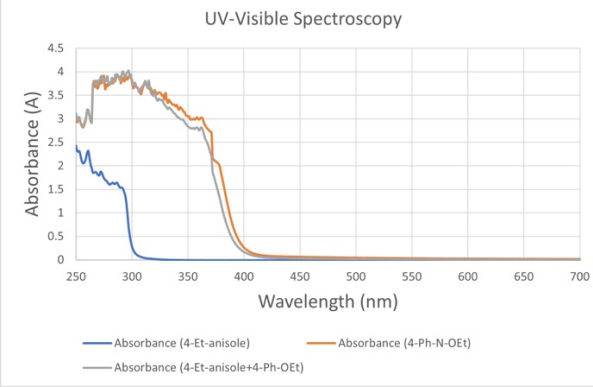
4-ethylanisole + pyr-3:



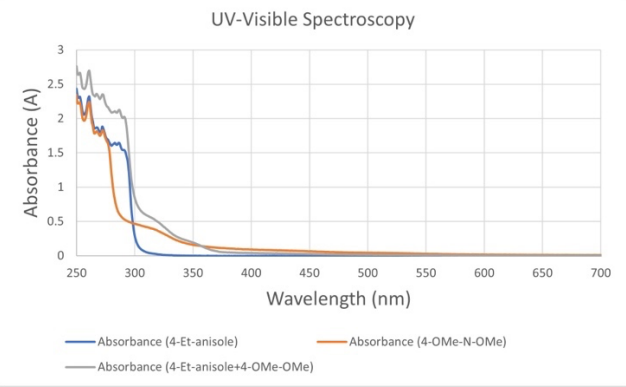
4-ethylanisole + pyr-4:



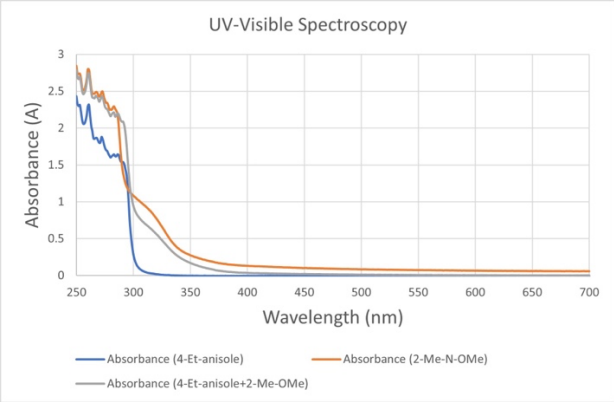
4-ethylanisole + pyr-5:



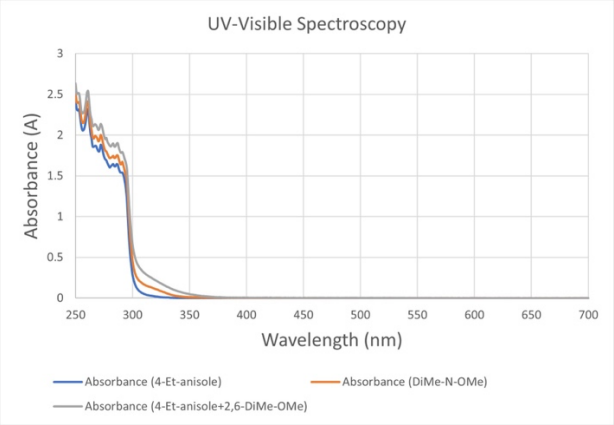
4-ethylanisole + pyr-6:



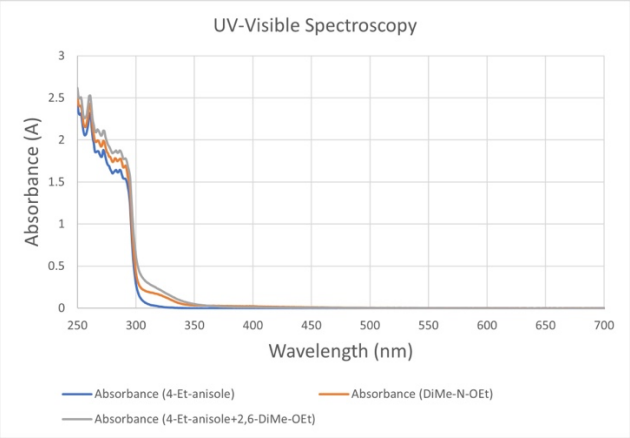
4-ethylanisole + pyr-7:



4-ethylanisole + pyr-8:

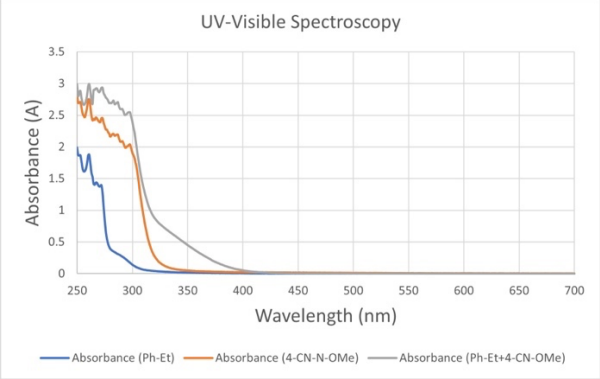


4-ethylanisole + pyr-9:

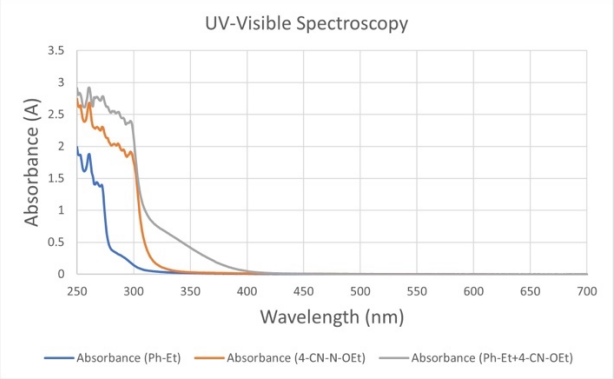


UV-vis Data for ethyl benzene

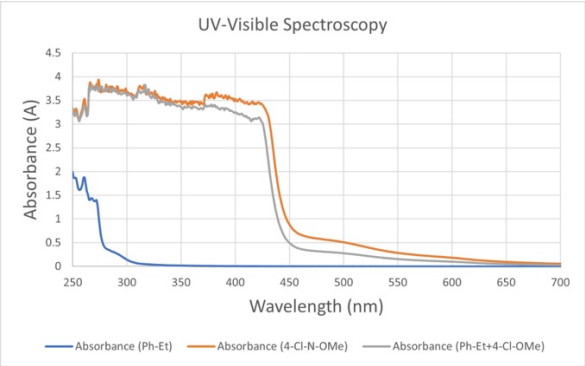
Ethyl benzene + pyr-1:



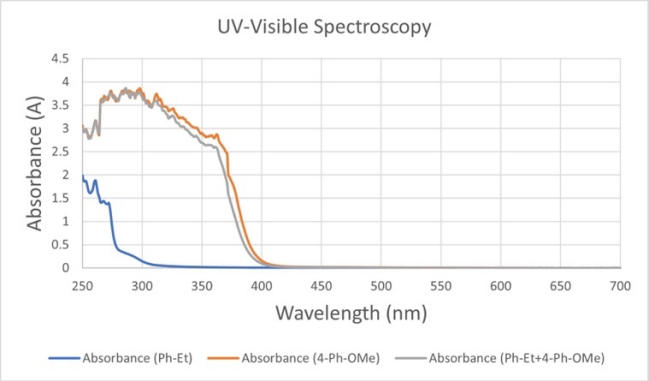
ethyl benzene + pyr-2:



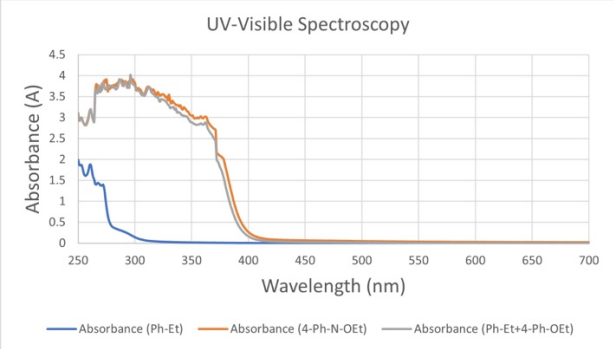
Ethyl benzene + pyr-3:



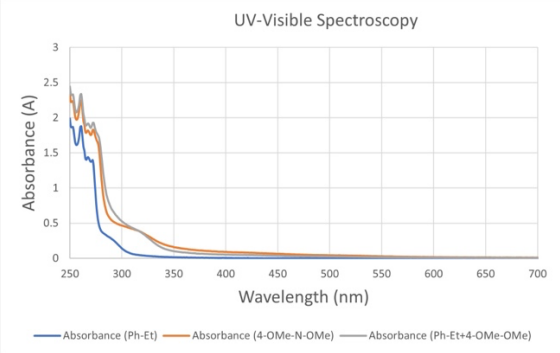
Ethyl benzene + pyr-4:



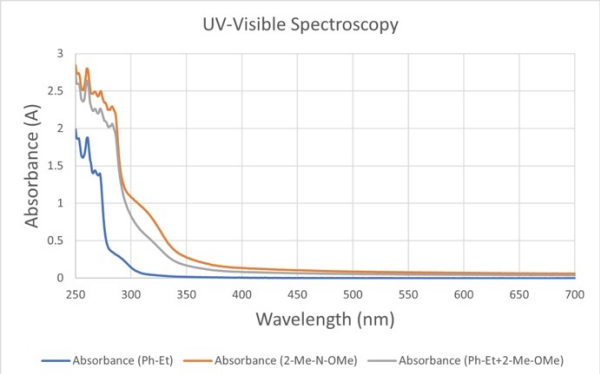
Ethyl benzene + pyr-5:



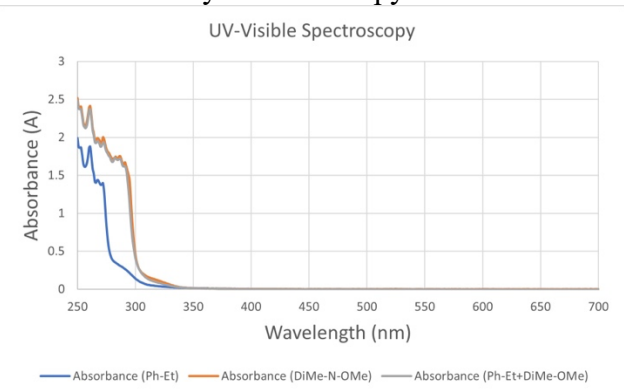
Ethyl benzene + pyr-6:



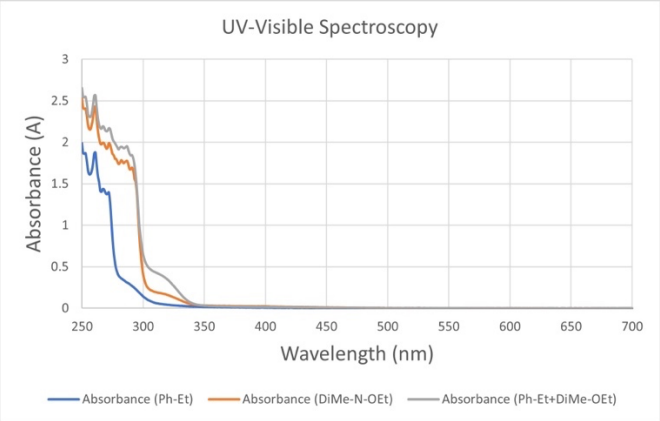
Ethyl benzene + pyr-7:



Ethyl benzene + pyr-8:

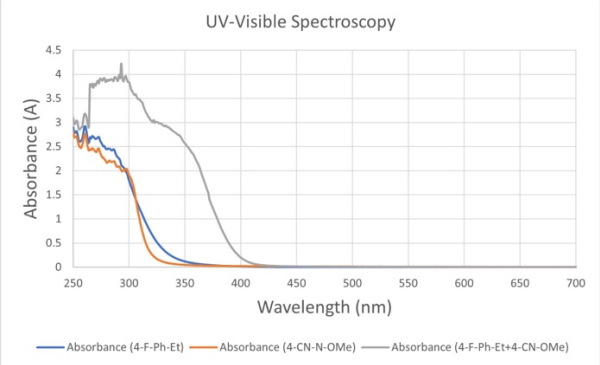


Ethyl benzene + pyr-9:

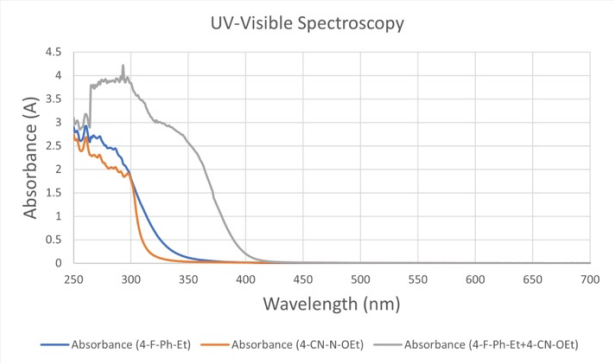


UV-vis Data for 1-ethyl-4-fluorobenzene

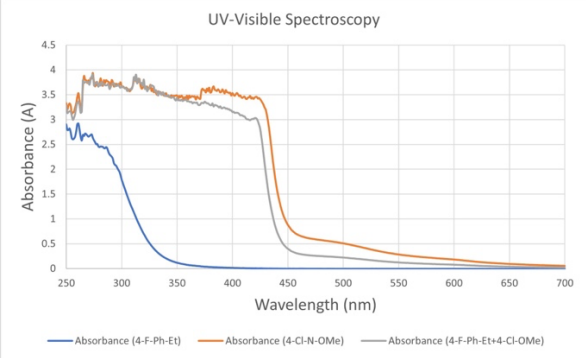
1-ethyl-4-fluorobenzene + pyr-1:



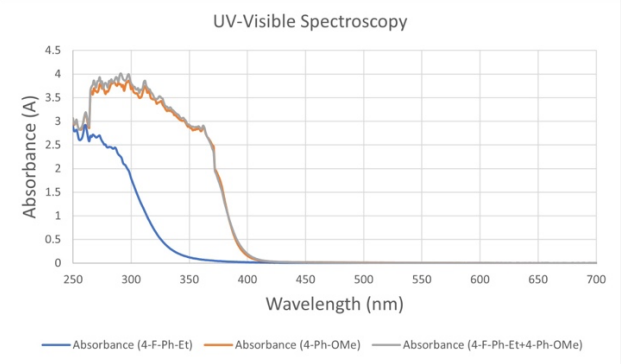
1-ethyl-4-fluorobenzene + pyr-2:



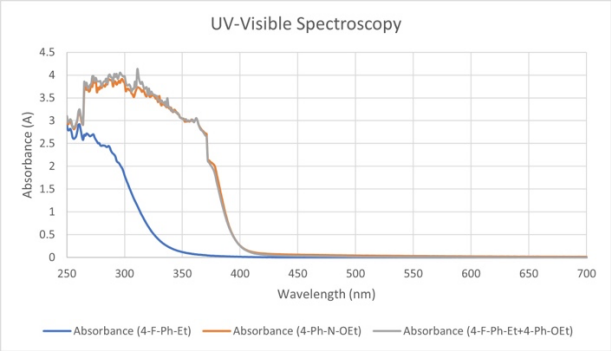
1-ethyl-4-fluorobenzene + pyr-3:



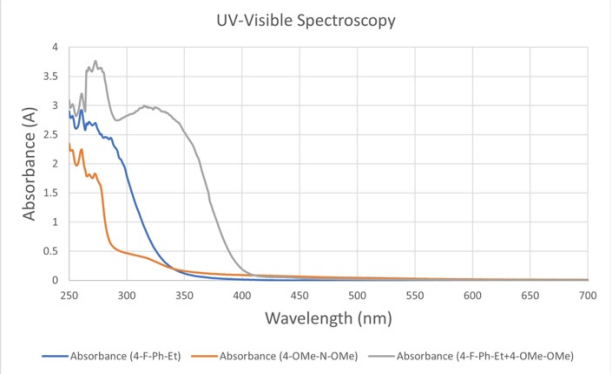
1-ethyl-4-fluorobenzene + pyr-4:



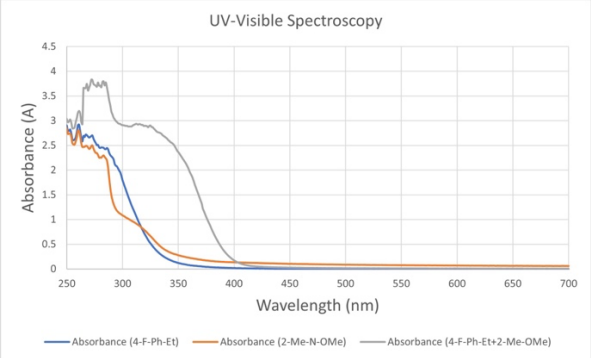
1-ethyl-4-fluorobenzene + pyr-5:



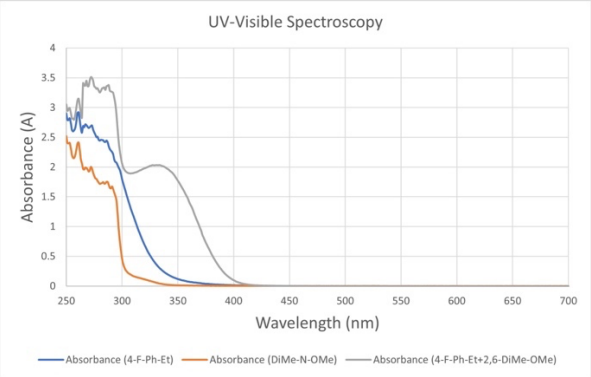
1-ethyl-4-fluorobenzene + pyr-6:



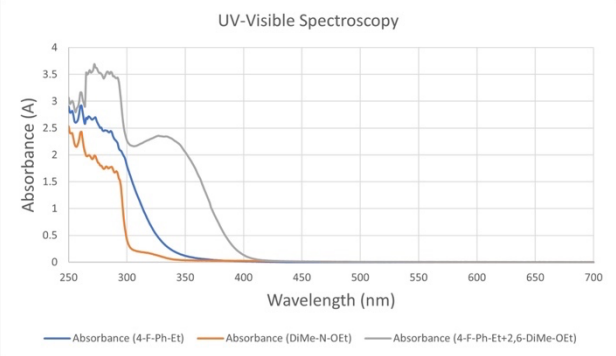
1-ethyl-4-fluorobenzene + pyr-7:



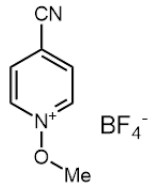
1-ethyl-4-fluorobenzene + pyr-8:



1-ethyl-4-fluorobenzene + pyr-9:



10. Characterization of *N*-alkoxypyridinium reagents



4-cyano-1-methoxypyridin-1-ium tetrafluoroborate **(pyr-1)**[4]

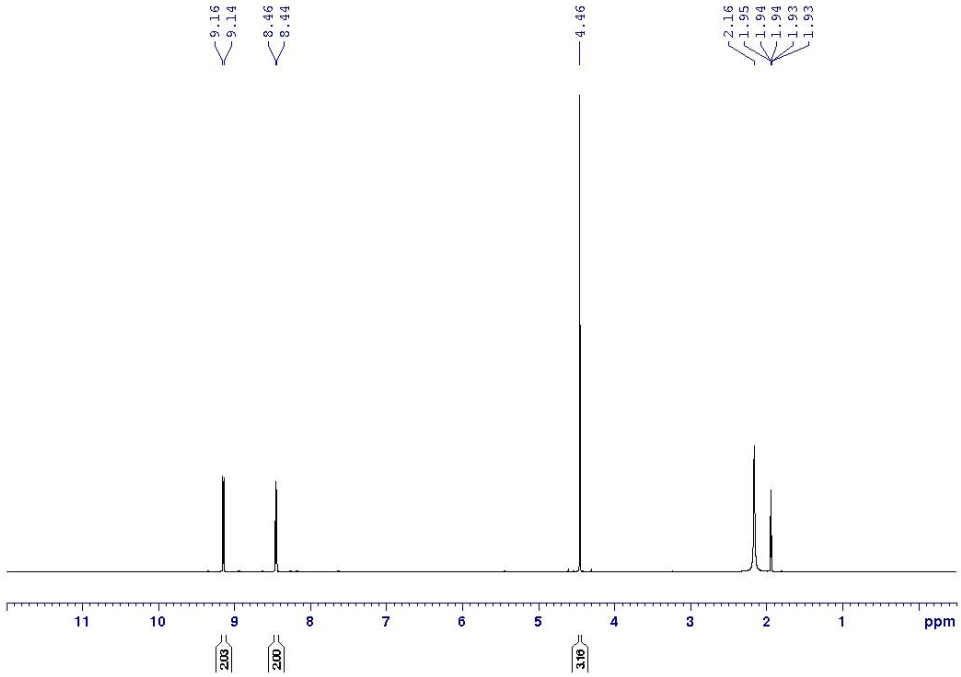
Following the general procedure K, trimethyloxonium tetrafluoroborate (12.9 g, 87.5 mmol, 1.05 equiv.) and 4-cyanopyridine *N*-oxide (10 g, 83.3 mmol, 1 equiv.) were stirred in 180 mL of dichloromethane for 24 h. Recrystallization from methanol afforded 16.39 g.

Isolated Yield: 89%

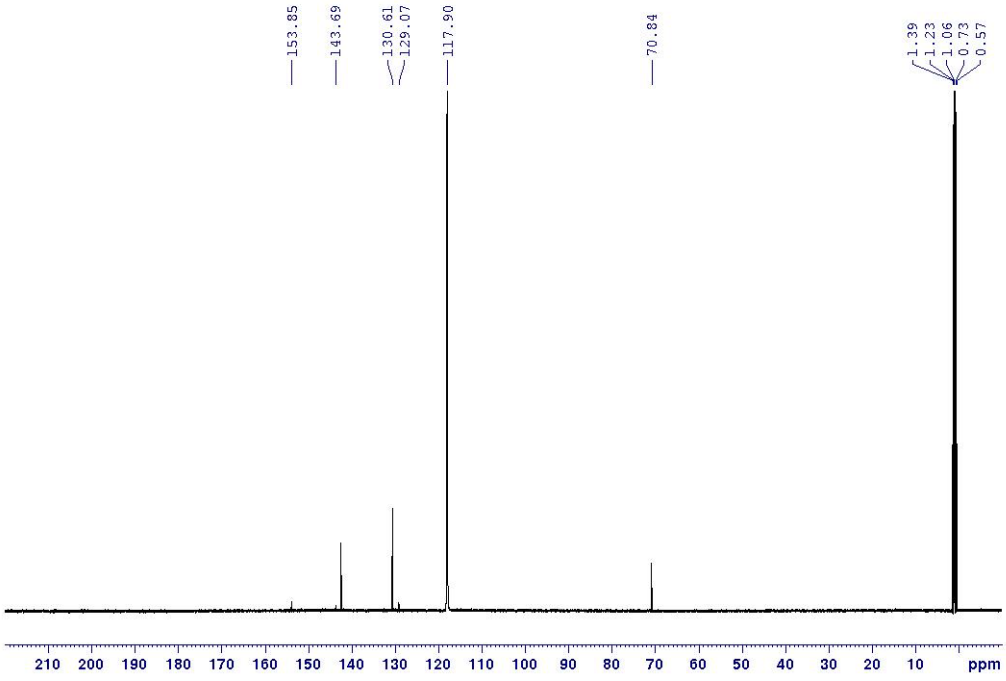
^{1}H NMR (500MHz, Acetonitrile-d_3): δ 9.14 (d, *J*=7.2 Hz, 2H), 8.44 (d, *J*=7.2 Hz, 2H), 4.45 (s, 3H).

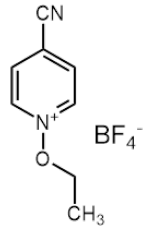
^{13}C NMR (126MHz, Acetonitrile-d_3): δ 153.8, 143.6, 130.6, 129.0, 117.9, 70.8.

^{1}H NMR:



^{13}C NMR:





4-cyano-1-ethoxypyridin-1-ium tetrafluoroborate **(pyr-2)**[4]

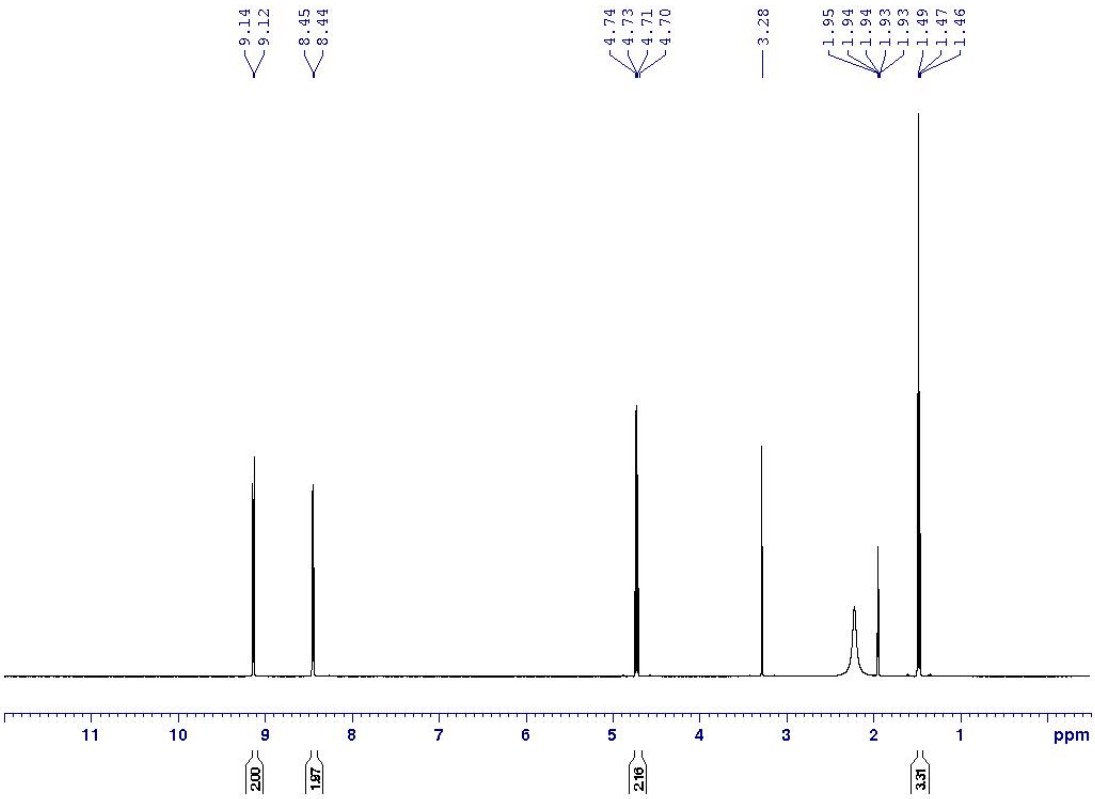
Following the general procedure K, triethyloxonium tetrafluoroborate (751.1 µL , 5.250 mmol, 1.05 equiv.) and 4-cyanopyridine *N*-oxide (600.5 mg, 5.000 mmol, 1 equiv.) were stirred in 10 mL of dichloromethane for 24 h. Recrystallization from methanol afforded 601.5 mg.

Isolated Yield: 51%

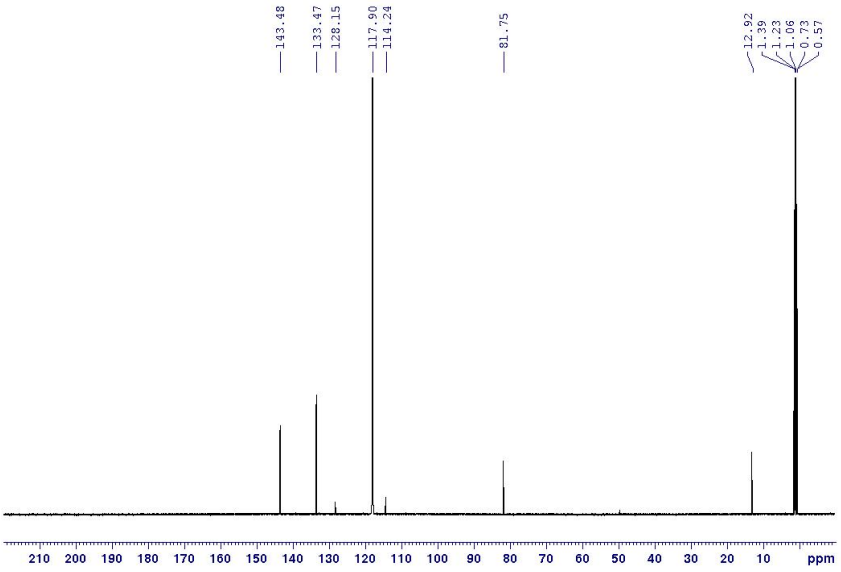
^{1}H NMR (500MHz, Acetonitrile-d_3): δ 9.13 (d, *J*=7.3 Hz, 2H), 8.44 (d, *J*=7.3 Hz, 2H), 4.71(q, *J*=6.9 Hz, 2H), 1.47 (t, *J*=6.9 Hz, 3H).

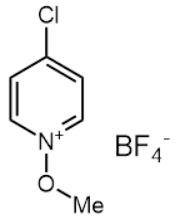
^{13}C NMR (126MHz, Acetonitrile-d_3): δ 143.4, 133.4, 128.1, 117.9, 114.2, 81.7, 12.9.

^{1}H NMR:



^{13}C NMR:





4-chloro-1-methoxypyridin-1-ium tetrafluoroborate **(pyr-3)**[4]

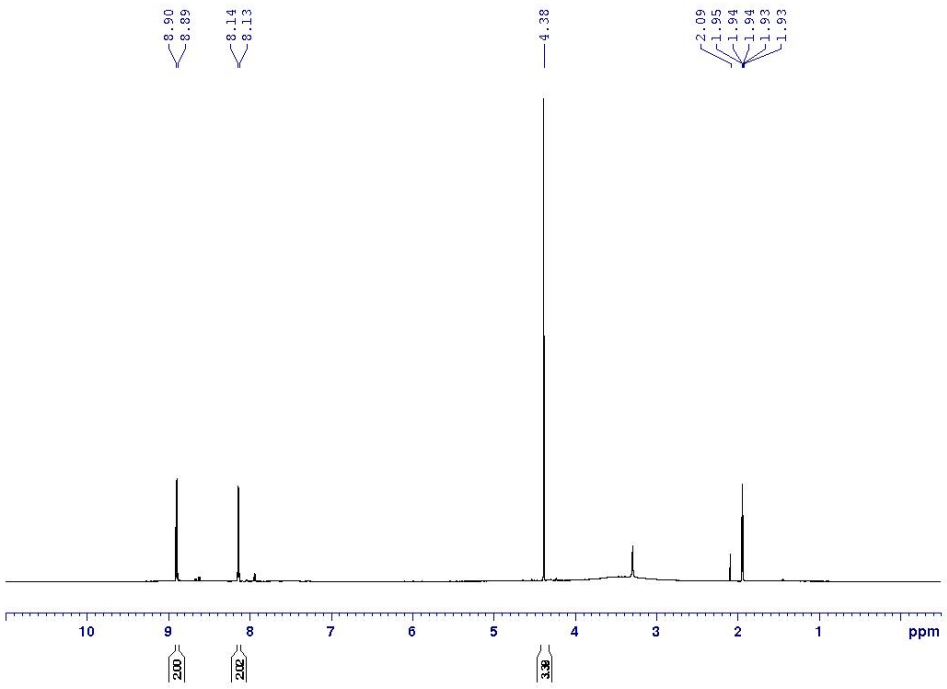
Following the general procedure K, trimethyloxonium tetrafluoroborate (776.5 mg, 5.250 mmol, 1.05 equiv.) and 4-chloropyridine *N*-oxide (647.7 mg, 5.000 mmol, 1 equiv.) were stirred in 10 mL of dichloromethane for 24 h. Recrystallization from methanol afforded 659.5 mg.

Isolated Yield: 57%

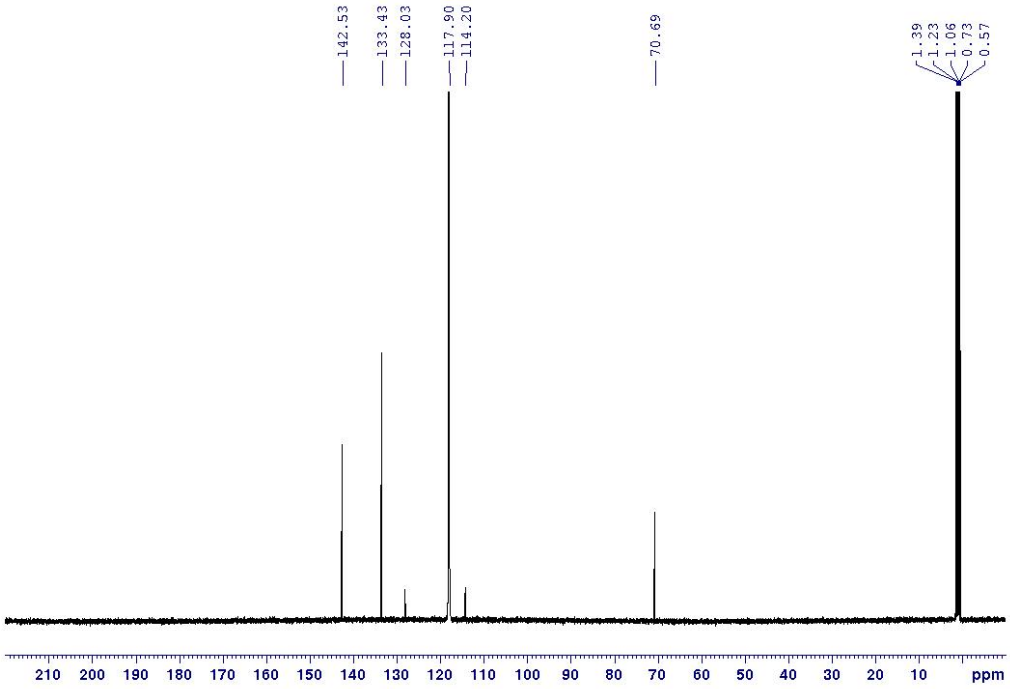
^{1}H NMR (500MHz, Acetonitrile-d_3): δ 8.89 (d, *J*=7.3 Hz, 2H), 8.13 (d, *J*=7.3 Hz, 2H), 4.38 (s, 3H).

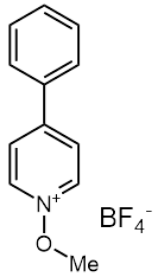
^{13}C NMR (126MHz, Acetonitrile-d_3): δ 142.5, 133.4, 128.0, 117.9, 114.2, 70.6.

^{1}H NMR:



^{13}C NMR:





1-methoxy-4-phenylpyridin-1-ium tetrafluoroborate **(pyr-4)**[4]

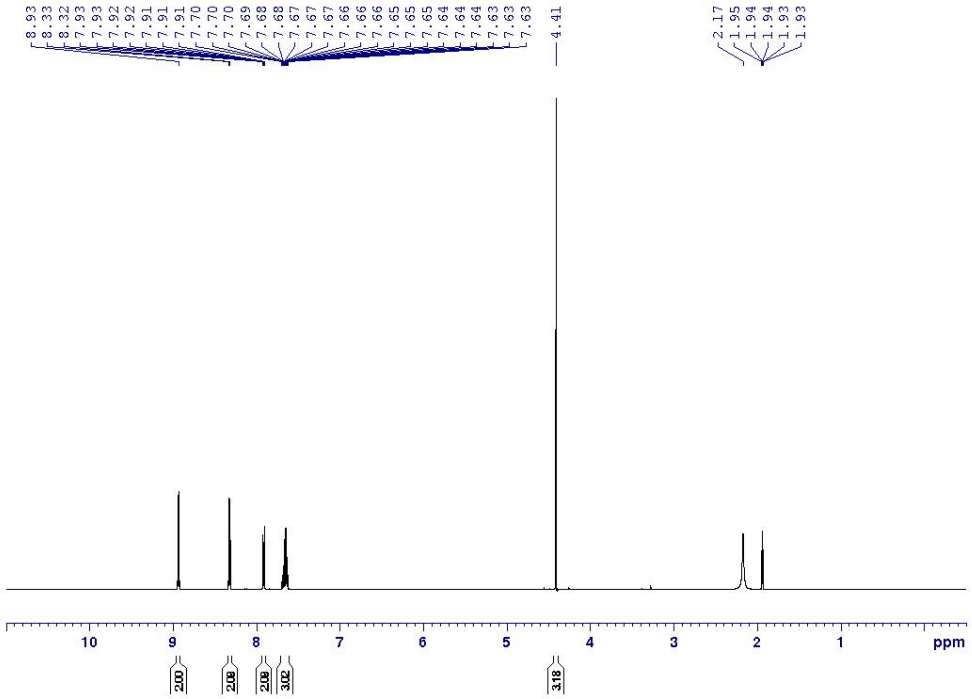
Following the general procedure K, trimethyloxonium tetrafluoroborate (776.5 mg, 5.250 mmol, 1.05 equiv) and 4-phenylpyridine *N*-oxide (856 mg, 5.00 mmol, 1 equiv.) were stirred in 10 mL of dichloromethane for 24 h. Recrystallization from methanol afforded 573.3 mg.

Isolated Yield:42%

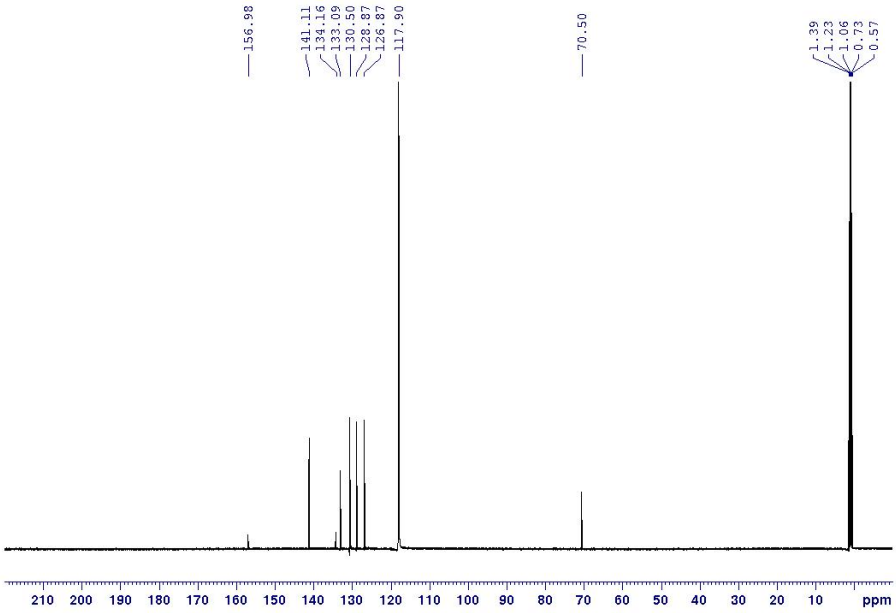
^{1}H NMR (500MHz, Acetonitrile-*d*$_3$): δ 8.93 (d, *J*=7.3 Hz, 2H), 8.32 (d, *J*=7.3 Hz, 2H), 7.93-7.90 (m, 2H), 7.70-7.61 (m, 3H), 4.41 (s, 3H).

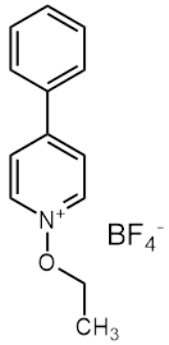
^{13}C NMR (126MHz, Acetonitrile-*d*$_3$): δ 156.9, 141.1, 134.1, 133.0, 130.5, 128.8, 126.8, 117.8, 70.4.

^{1}H NMR:



^{13}C NMR:





1-ethoxy-4-phenylpyridin-1-ium tetrafluoroborate **(pyr-5)**

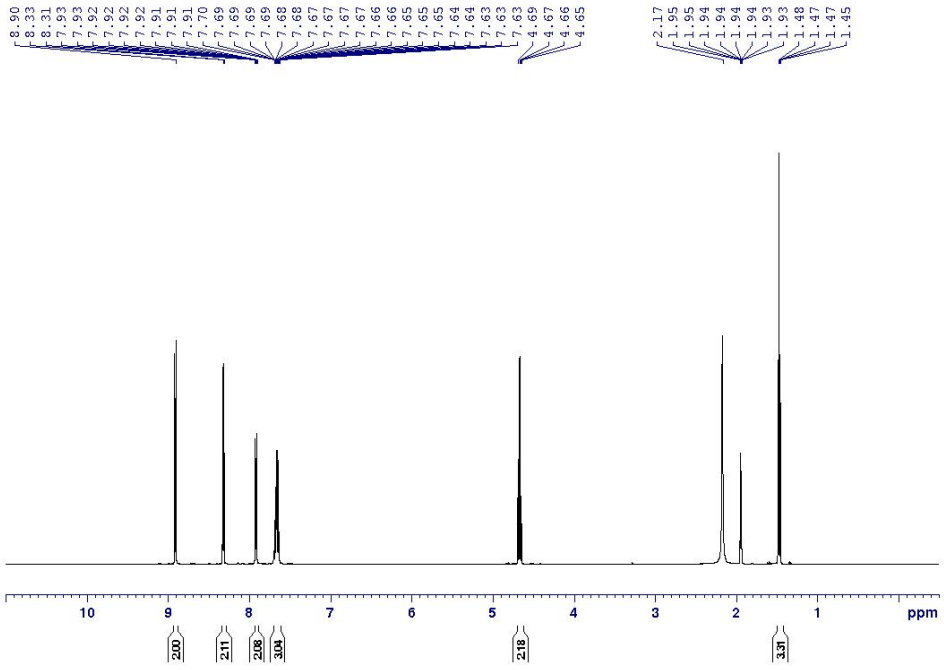
Following the general procedure K, triethyloxonium tetrafluoroborate (751.1 µL , 5.250 mmol, 1.05 equiv.) and 4-phenylpyridine *N*-oxide (856 mg, 5.00 mmol, 1 equiv.) were stirred in 10 mL of dichloromethane for 24 h. Recrystallization from methanol afforded 574 mg.

Isolated Yield: 40%

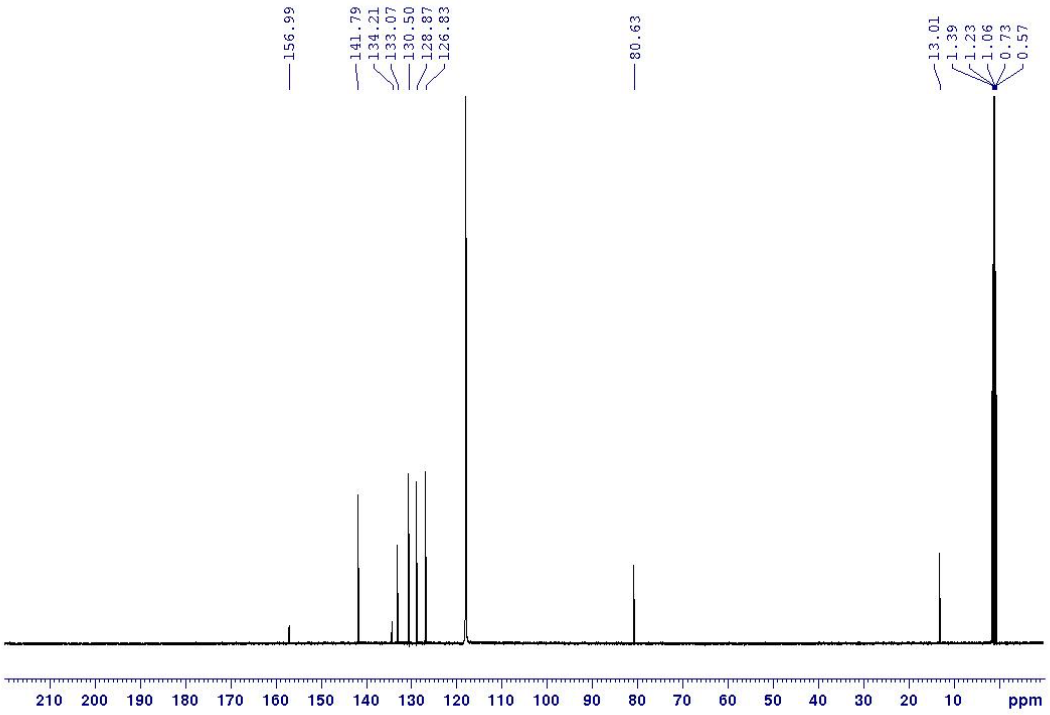
^{1}H NMR (500MHz, Chloroform-*d*): δ 8.91 (d, *J*=7.3 Hz, 2H), 8.32 (d, *J*=7.3 Hz, 2H), 7.93-7.90 (m, 2H), 7.69-7.62 (m, 3H), 4.66 (q, *J*=6.9 Hz, 3H), 1.46 (t, *J*=6.9 Hz, 3H).

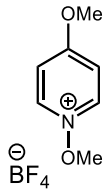
^{13}C NMR (126MHz, Acetonitrile-d_3): δ 156.9, 141.7, 134.2, 133.0, 130.5, 128.8, 126.8, 80.6, 13.0.

^{1}H NMR:



^{13}C NMR:



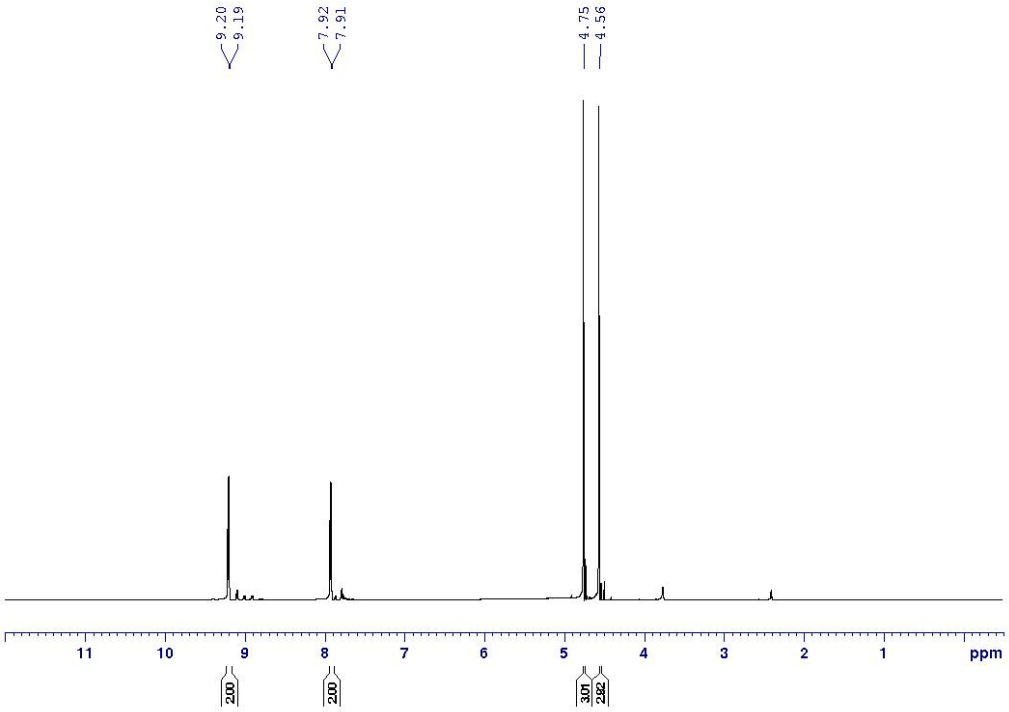


1,4-dimethoxypyridin-1-ium tetrafluoroborate (**pyr-6**)

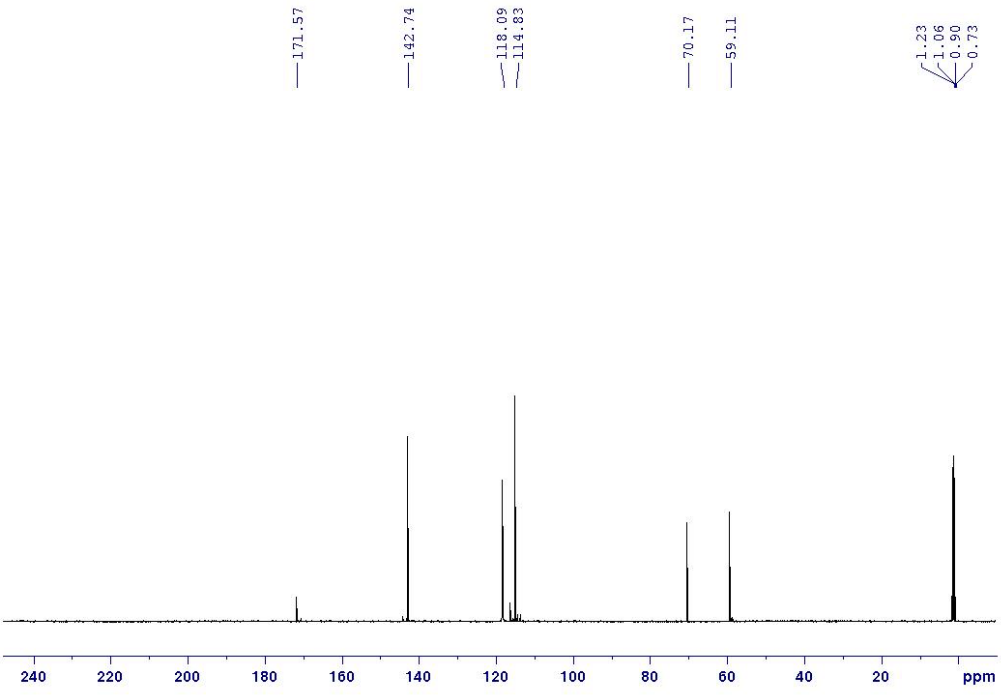
Following the general procedure L, trimethyloxonium tetrafluoroborate (888 mg, 6.00 mmol, 1.2 equiv.) and 4-methoxypyridine *N*-oxide (625.6 mg, 5.000 mmol, 1 equiv.) were stirred in 10 mL of dichloromethane for 48 h. Recrystallization from a methanol and diethyl ether solution at -20 ºC afforded 419.7 mg.

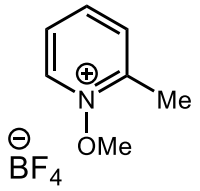
Isolated Yield: 37%
^{1}H NMR (500MHz, Acetonitrile-d_3): δ 9.19 (d, *J*=7.7Hz, 2H), 7.91 (d, *J*=7.9 Hz, 2H), 4.75 (s, 3H), 4.56 (s, 3H).
^{13}C NMR (126MHz, Acetonitrile-d_3): δ 171.5, 142.7, 118.0, 114.8. 70.1, 59.1.

^{1}H NMR:



^{13}C NMR



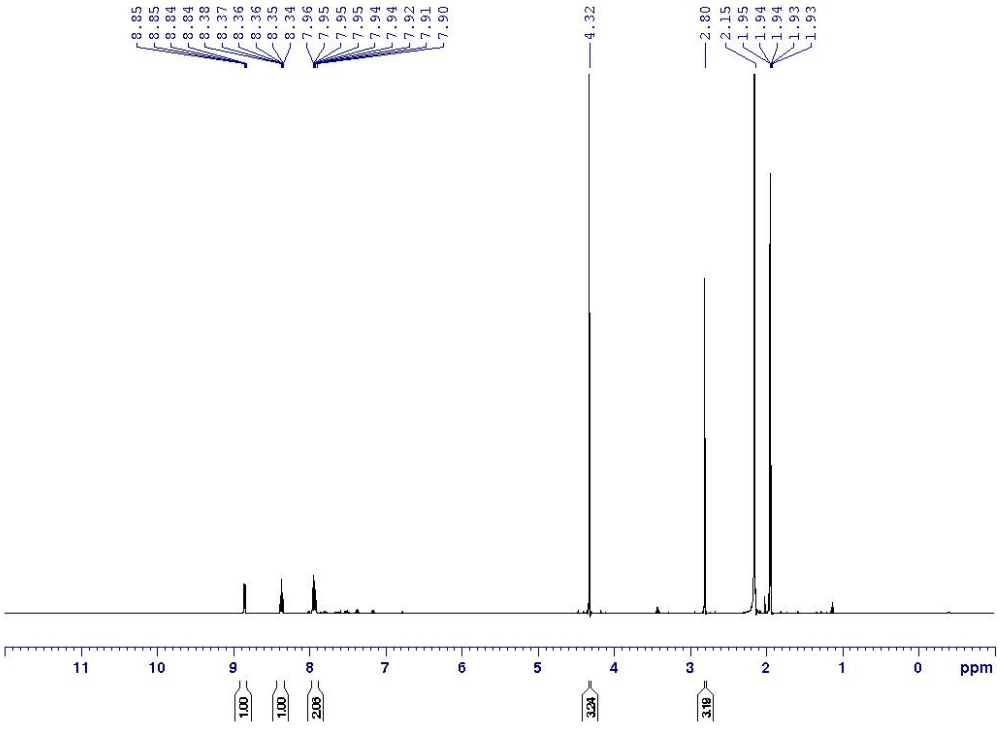


1-methoxy-2-methylpyridin-1-ium tetrafluoroborate (**pyr-7**)

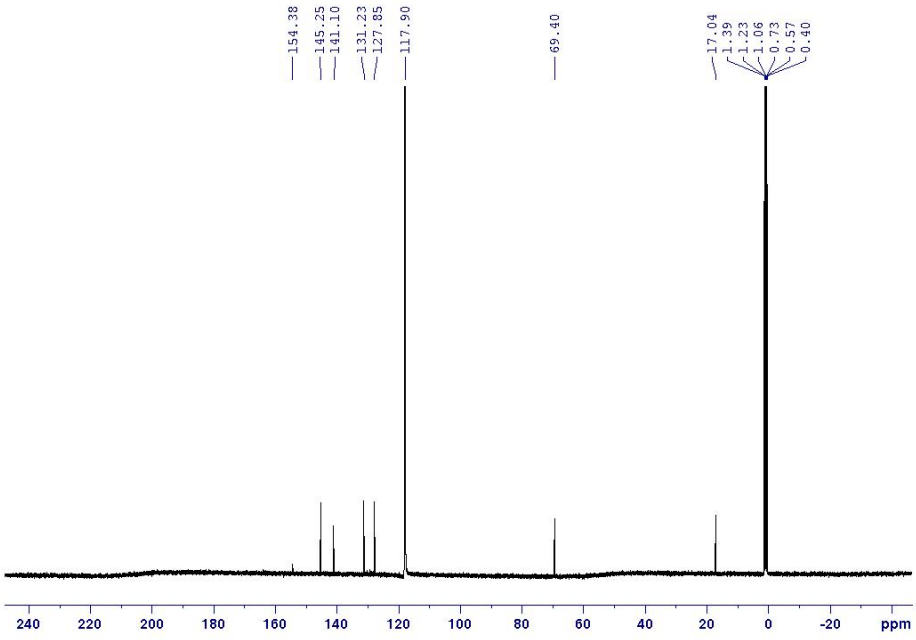
Following the general procedure L, trimethyloxonium tetrafluoroborate (888 mg, 6.00 mmol, 1.2 equiv.) and 2-methylpyridine *N*-oxide (545.7 mg, 5.000 mmol, 1 equiv.) were stirred in 10 mL of dichloromethane for 48 h. Recrystallization from methanol and diethyl ether solution at -20 ºC afforded 400 mg.

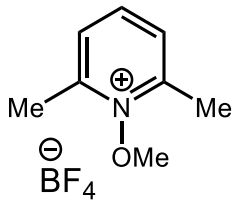
Isolated Yield: 38%
^{1}H NMR (500MHz, Acetonitrile-d_3): δ 8.84 (dd, *J*=1.2, 6.6 Hz, 1H), 8.36 (td, *J*=2, 7.8 Hz, 1H), 7.90-7.95 (m, 2H), 4.21 (s, 3H), 2.8 (s, 3H).
^{13}C NMR (126MHz, Acetonitrile-d_3): δ 154.3, 145.2, 141.0, 131.2, 127.8, 117.9, 69.4, 17.0.

^{1}H NMR:



^{13}C NMR:



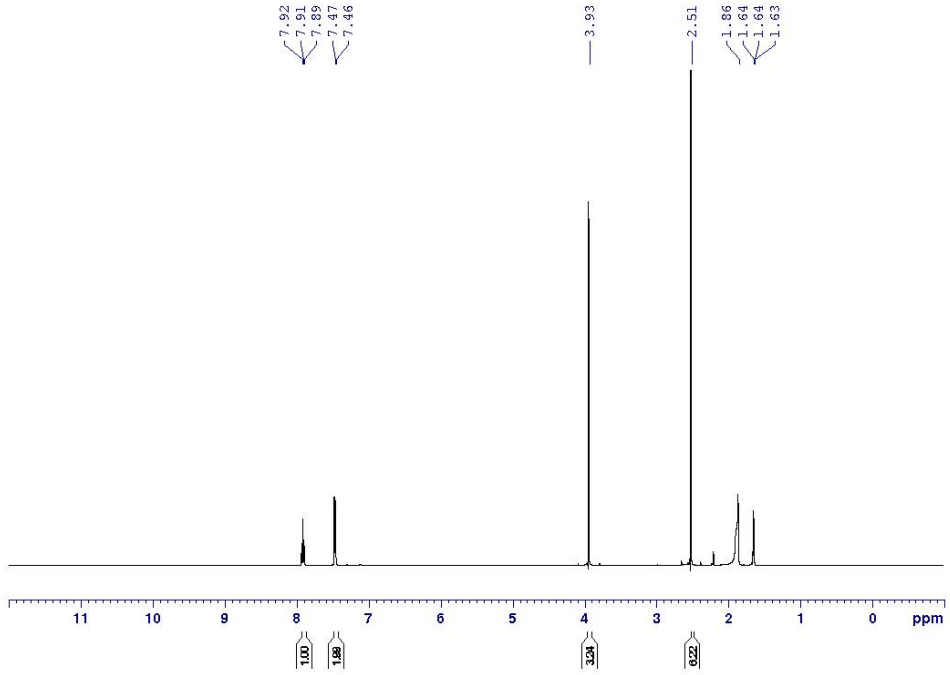


1-methoxy-2,6-dimethylpyridin-1-ium tetrafluoroborate (**pyr-8**)

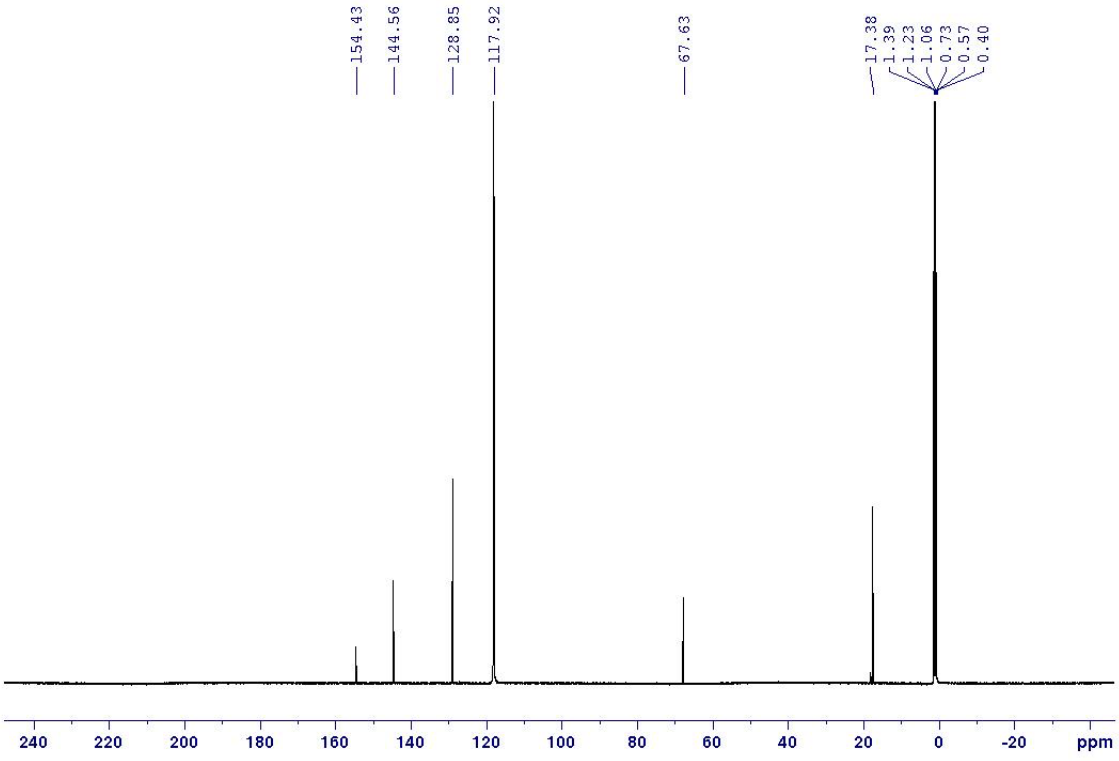
Following the general procedure L, trimethyloxonium tetrafluoroborate (888 mg, 6.00 mmol, 1.2 equiv.) and 2,6-dimethylpyridine *N*-oxide (559 mg, 5.00 mmol, 1 equiv.) were stirred in 10 mL of dichloromethane for 48 h. Recrystallization from methanol and diethyl ether solution at -20 ^{o}C afforded 587.3 mg.

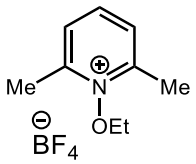
Isolated Yield: 52%
^{1}H NMR (500MHz, Acetonitrile-d_3): δ 7.91 (t, *J*=7.8, 6.6 Hz, 1H), 7.46 (d, *J*=7.9 Hz, 2H), 3.93 (s, 3H), 2.51 (s, 6H).
^{13}C NMR (126MHz, Acetonitrile-d_3): δ 154.4, 144.5, 128.8, 117.9, 67.6, 17.3.

^{1}H NMR:



^{13}C NMR:



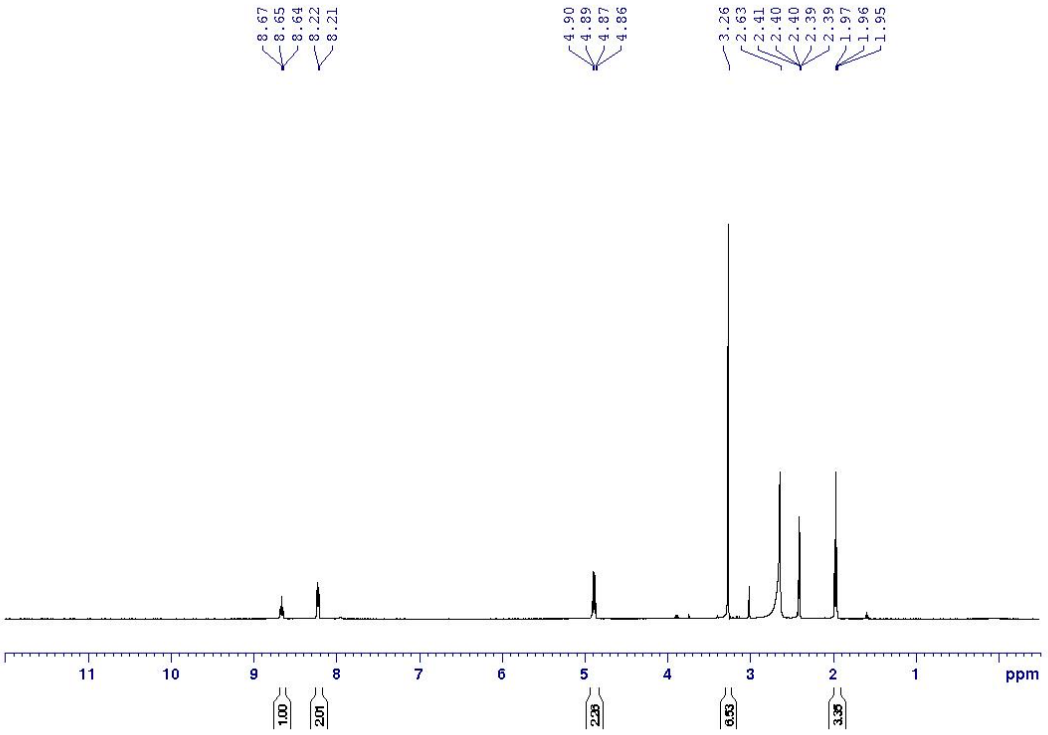


1-Ethoxy-2,6-dimethylpyridin-1-ium tetrafluoroborate (**pyr-9**)

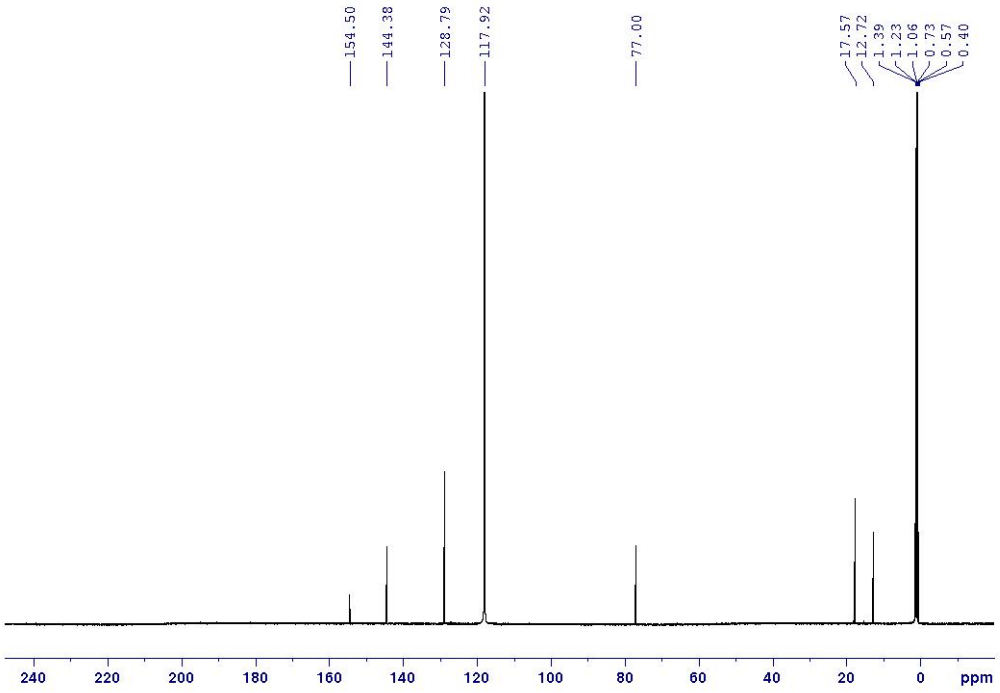
Following the general procedure L, triethyloxonium tetrafluoroborate (1140 mg, 6.000 mmol, 1.2 equiv.) and 2,6-dimethylpyridine *N*-oxide (558.8 mg, 5.000 mmol, 1 equiv.) were stirred in 10 mL of dichloromethane for 48 h. Recrystallization from methanol and diethyl ether solution at -20 ºC afforded 585.3 mg.

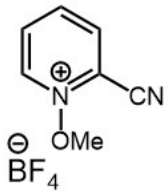
Isolated Yield: 49%
^{1}H NMR (500MHz, Acetonitrile-d_3): δ 8.65 (t, *J*=7.9, 6.6 Hz, 1H), 8.21 (d, *J*=7.9 Hz, 2H), 4.87 (q, *J*=7.0 Hz, 2H), 3.25 (s, 6H), 1.95 (t, *J*=7.0 Hz, 3H).
^{13}C NMR (126MHz, Acetonitrile-d_3): δ 154.5, 144.3, 128.7, 117.9, 77.0, 17.5, 12.7.

^{1}H NMR:



^{13}C NMR:





2-cyano-1-methoxypyridin-1-ium tetrafluoroborate (pyr-10)

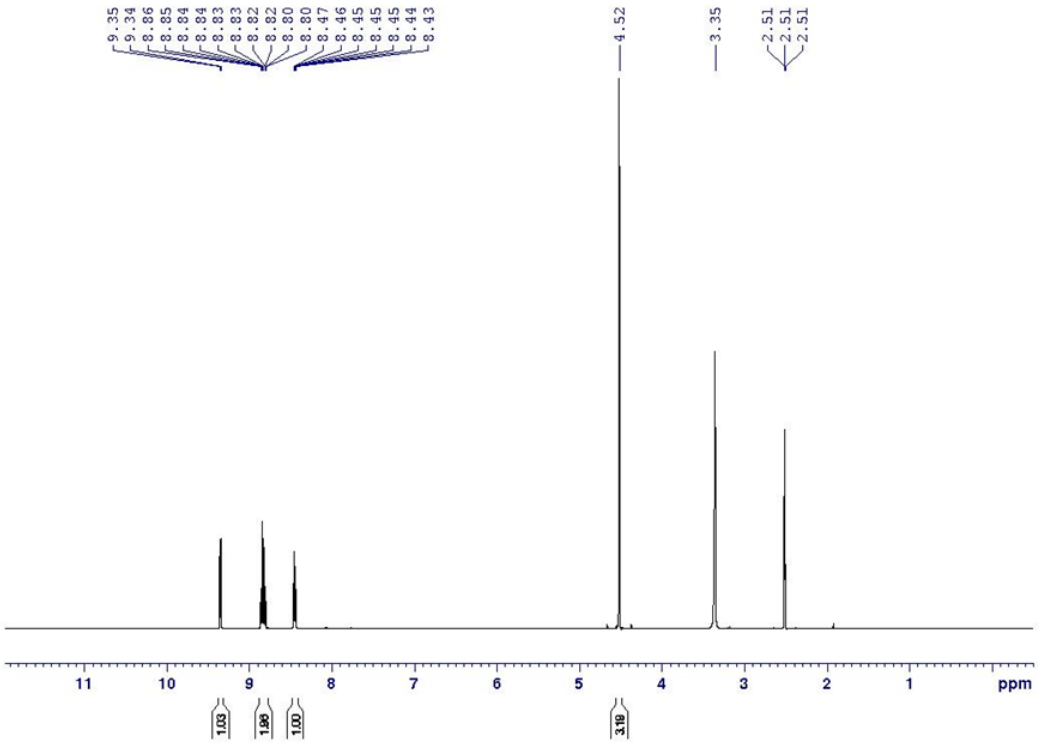
Following the general procedure K, trimethyloxonium tetrafluoroborate (776.5 mg, 5.250 mmol, 1.05 equiv.) and 2-cyanopyridine *N*-oxide (520.1 mg, 5.000 mmol, 1 equiv.) were stirred in 10 mL of dichloromethane for 24 h. Recrystallization from methanol afforded 665.7 mg.

Isolated Yield: 60%

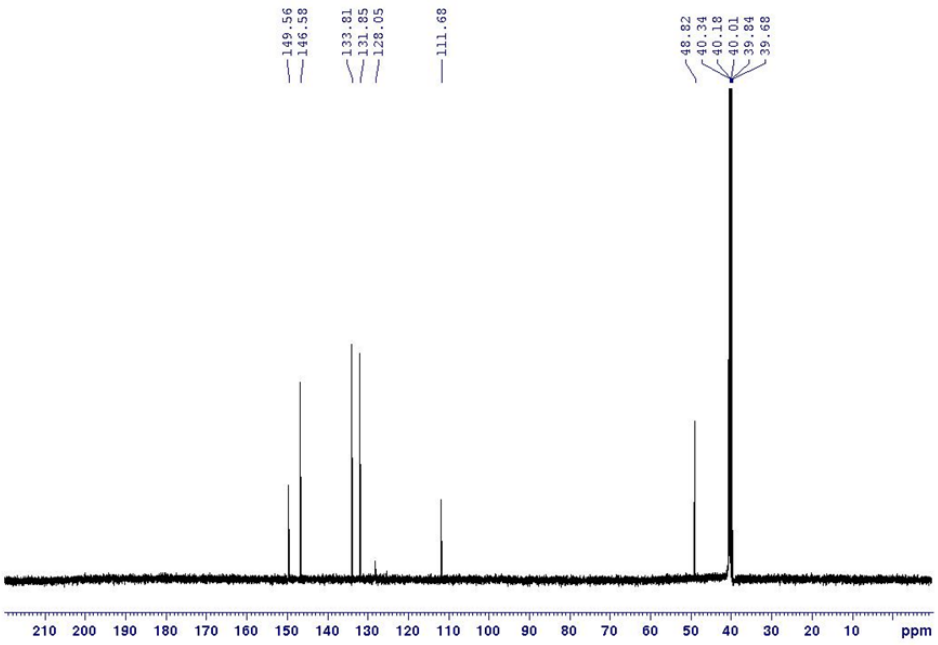
^{1}H NMR (500MHz, DMSO-*d*$_6$): δ 9.34 (d, *J*=6.0 Hz, 1H), 8.85-8.80 (m, 3H), 8.46-8.43 (m, 1H), 4.51 (s, 3H).

^{13}C NMR (126MHz, DMSO-*d*$_6$): δ 149.5, 146.5, 133.8, 131.8, 128.0, 111.6, 48.8

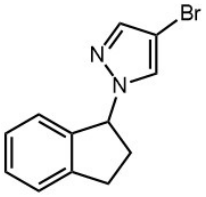
^{1}H NMR



^{13}C NMR



11. Characterization of C–H Azolation Products



4-bromo-1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazole (**1**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 105 mg pure product.

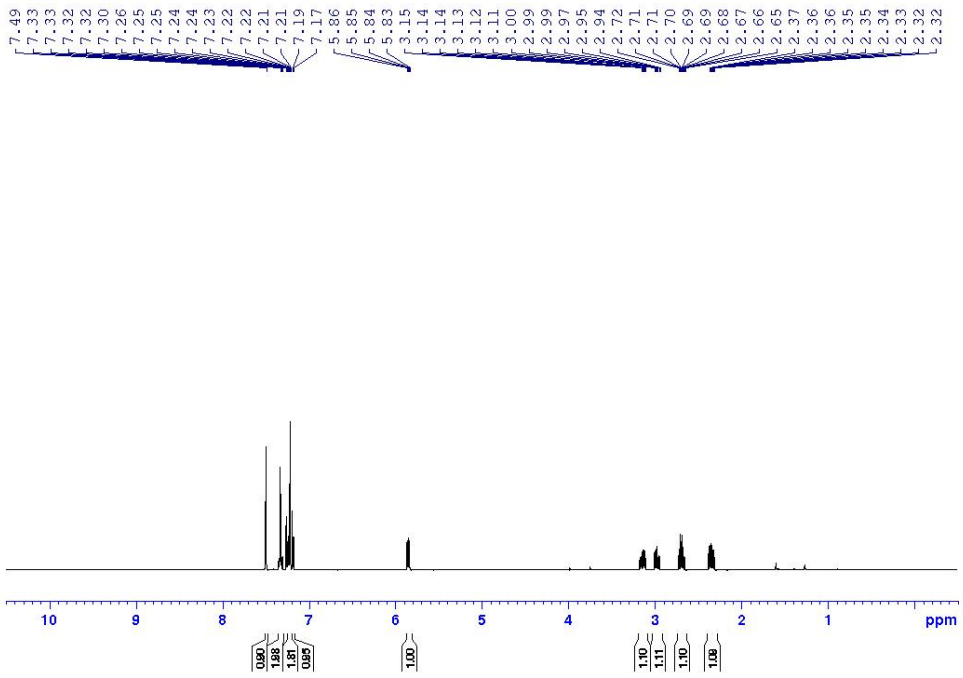
Isolated Yield: 80%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.49 (s, 1H), 7.34-7.30 (m, 2H), 7.25-7.21 (m, 2H), 7.18 (d, J = 7.5 Hz, 1H), 5.84 (dd, J = 7.9, 5.6 Hz, 1H), 3.17-3.11 (m, 1H), 3.00-2.94 (m, 1H), 2.72-2.65 (m, 1H), 2.37-2.31 (m, 1H).

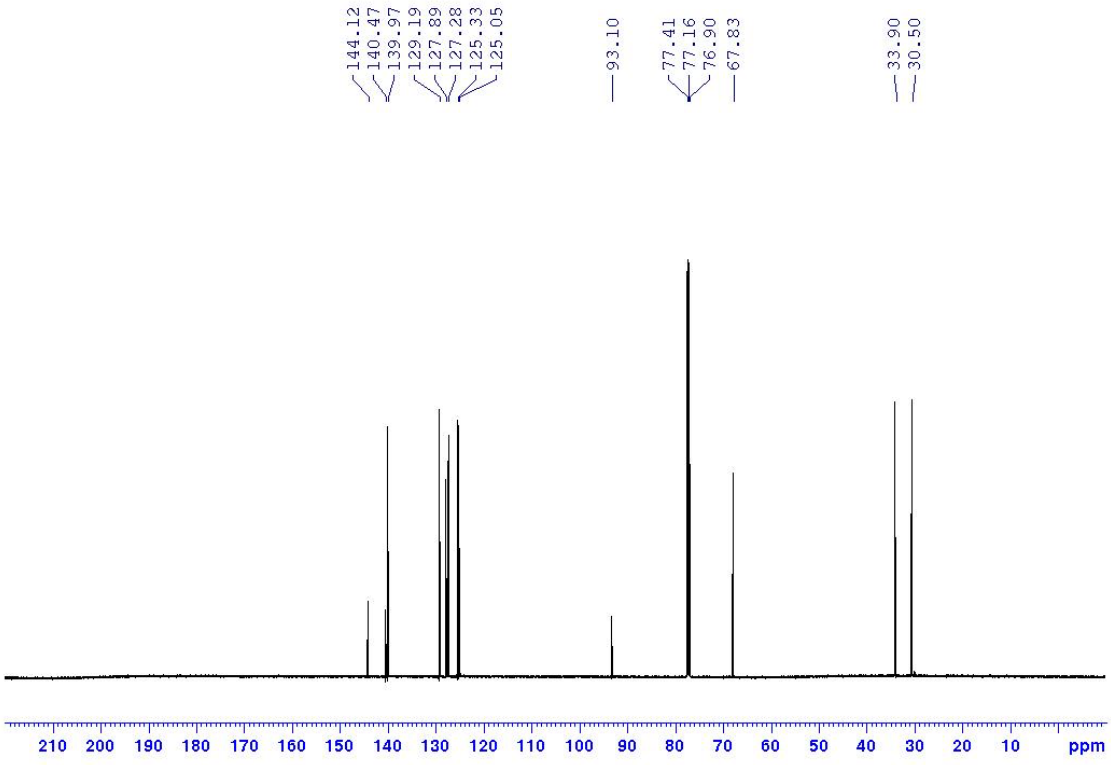
^{13}C NMR (126MHz, Chloroform-*d*): δ 144.1, 140.5, 139.9, 129.2, 127.9, 127.3, 125.3, 125.1, 93.1, 67.8, 33.9, 30.5.

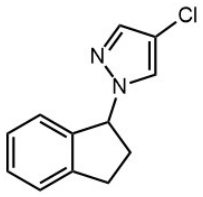
HRMS (ESI): calculated $[M+H]^+$ as 263.0178, found 263.0175

^{1}H NMR:



^{13}C NMR:





4-chloro-1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazole (**2**)[8]

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-chloro-1*H*-pyrazole (153.8 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 77 mg pure product.

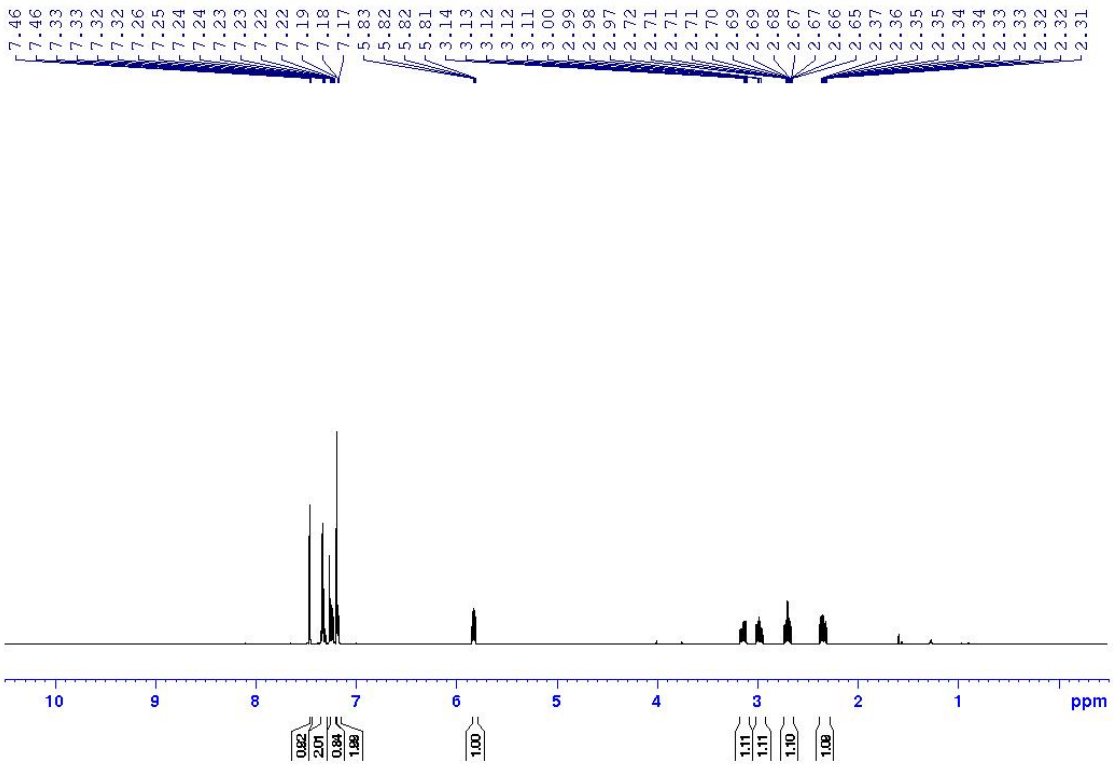
Isolated Yield: 70%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.45 (d, J = 0.5 Hz, 1H), 7.34-7.30 (m, 2H), 7.25-7.22 (m, 1H), 7.18-7.17 (m, 2H), 5.82 (dd, J = 8.1, 5.7 Hz, 1H), 3.17-3.11 (m, 1H), 3.00-2.94 (m, 1H), 2.72-2.65 (m, 1H), 2.37-2.31 (m, 1H).

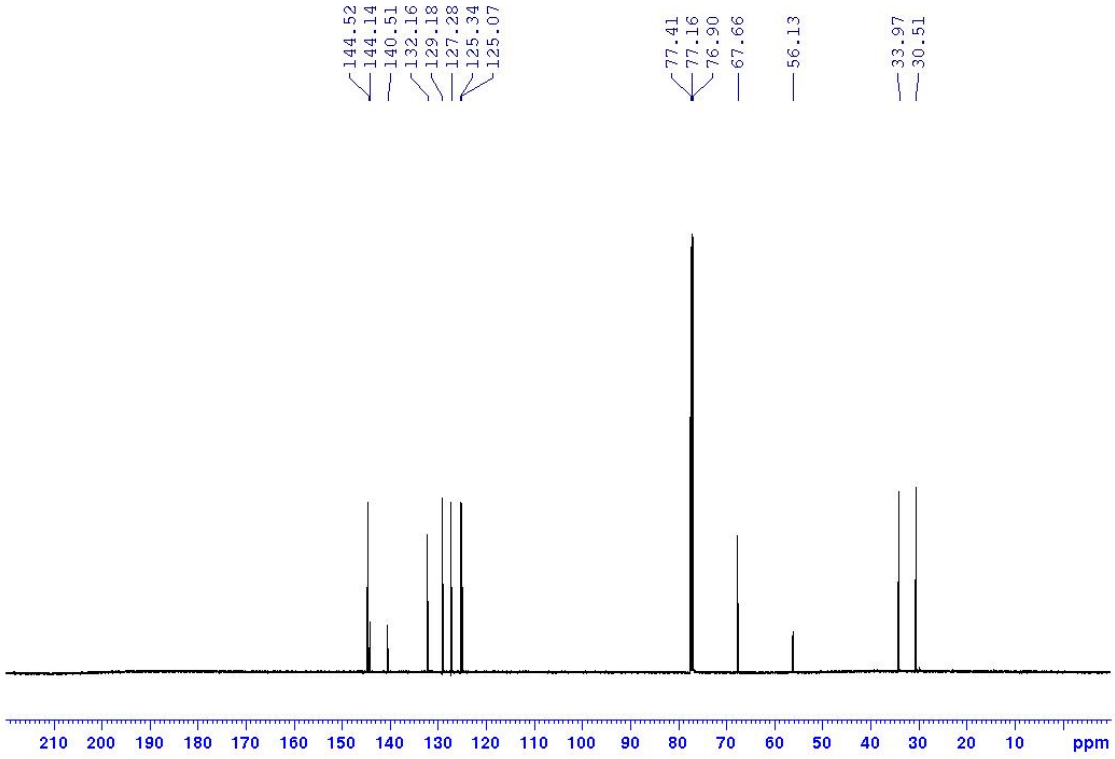
^{13}C NMR (126MHz, Chloroform-*d*): δ 144.1, 140.5, 137.8, 129.2, 127.3, 125.7, 125.3, 125.0, 109.9, 67.9, 33.9, 30.5.

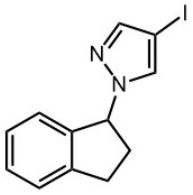
HRMS (ESI): calculated $[M+H]^+$ as 219.0684, found 219.0681

^{1}H NMR:



^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-4-iodo-1H-pyrazole (**3**)[8]

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-iodo-1*H*-pyrazole (291 mg, 1.50 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 124 mg pure product.

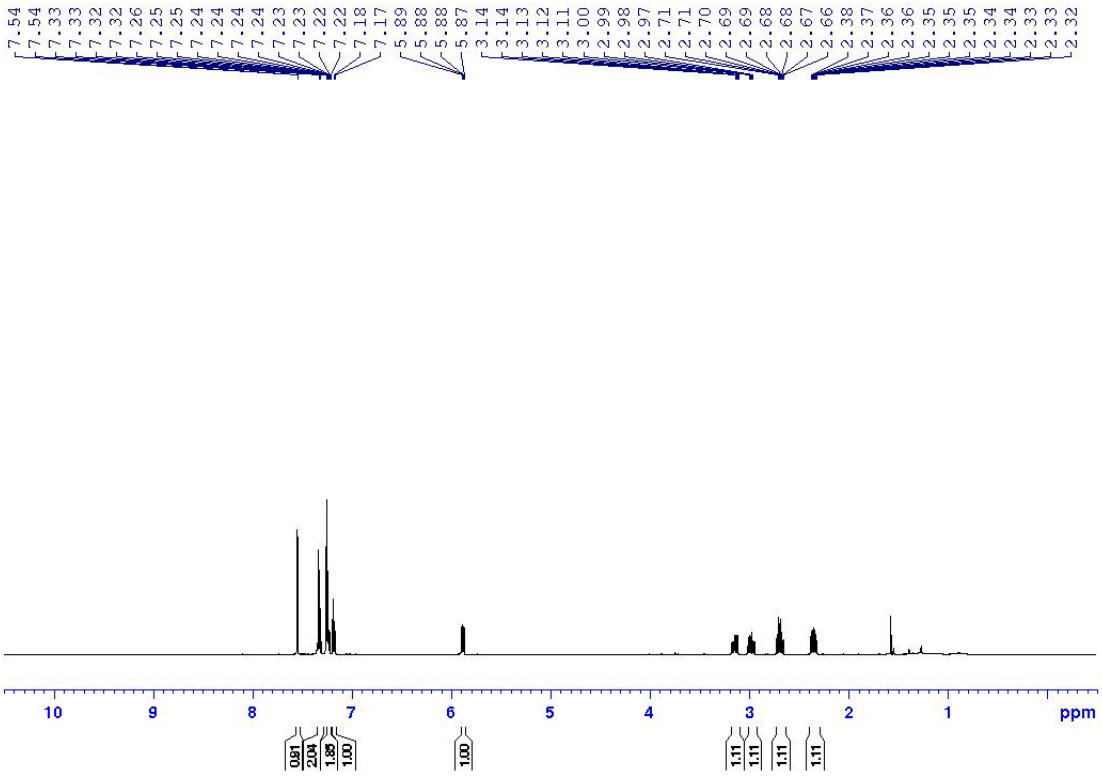
Isolated Yield: 80%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.54 (d, J = 0.4 Hz, 1H), 7.35-7.30 (m, 2H), 7.25-7.22 (m, 2H), 7.17 (d, J = 7.6 Hz, 1H), 5.87 (dd, J = 8.1, 5.6 Hz, 1H), 3.17-3.11 (m, 1H), 3.00-2.94 (m, 1H), 2.72-2.65 (m, 1H), 2.38-2.31 (m, 1H).

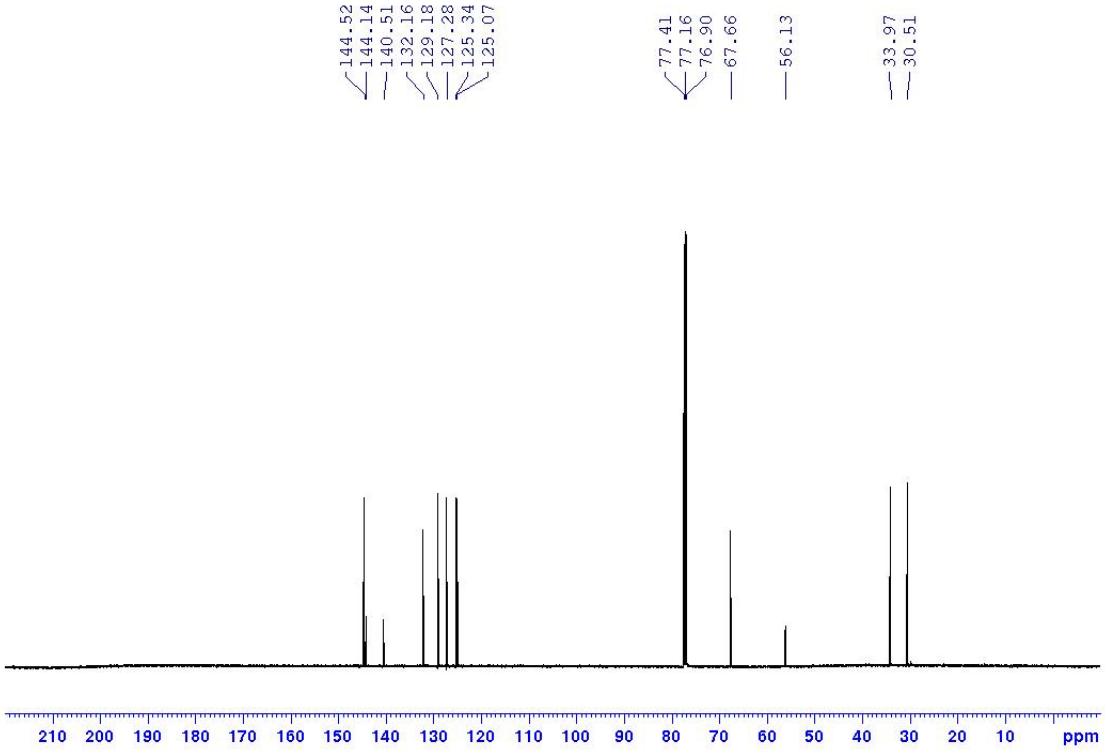
^{13}C NMR (126MHz, Chloroform-*d*): δ 144.5, 144.1, 140.5, 132.2, 129.2, 127.3, 125.3, 125.1, 67.7, 56.1, 33.9, 30.5.

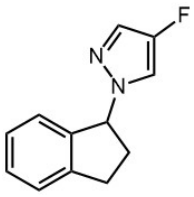
HRMS (ESI): calculated $[M+H]^+$ as 311.0040, found 311.0035

^{1}H NMR:



^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-4-fluoro-1H-pyrazole (**4**)[8]

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-fluoro-1*H*-pyrazole (129.1 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 68 mg pure product.

Isolated Yield: 67%

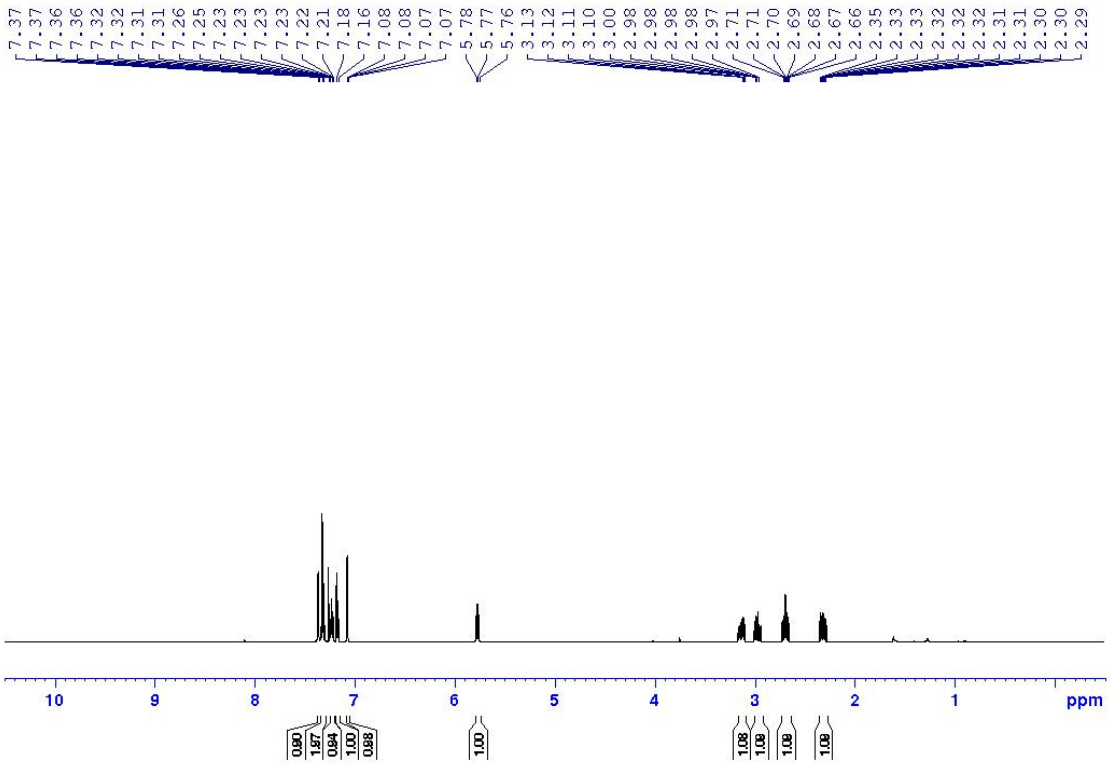
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.36 (dd, J = 4.5, 0.7 Hz, 1H), 7.34-7.29 (m, 2H), 7.25-7.21 (m, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.07 (dd, J = 4.7, 0.8 Hz, 1H), 5.77 (t, J = 6.9 Hz, 1H), 3.16-3.10 (m, 1H), 2.99-2.93 (m, 1H), 2.72-2.65 (m, 1H), 2.35-2.28 (m, 1H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 149.9 (d, J = 246.5), 143.9, 140.7, 129.1, 127.2, 126.2 (d, J = 13.5 Hz), 125.3, 124.9, 113.7 (d, J = 27.8 Hz), 68.1, 33.8, 30.5.

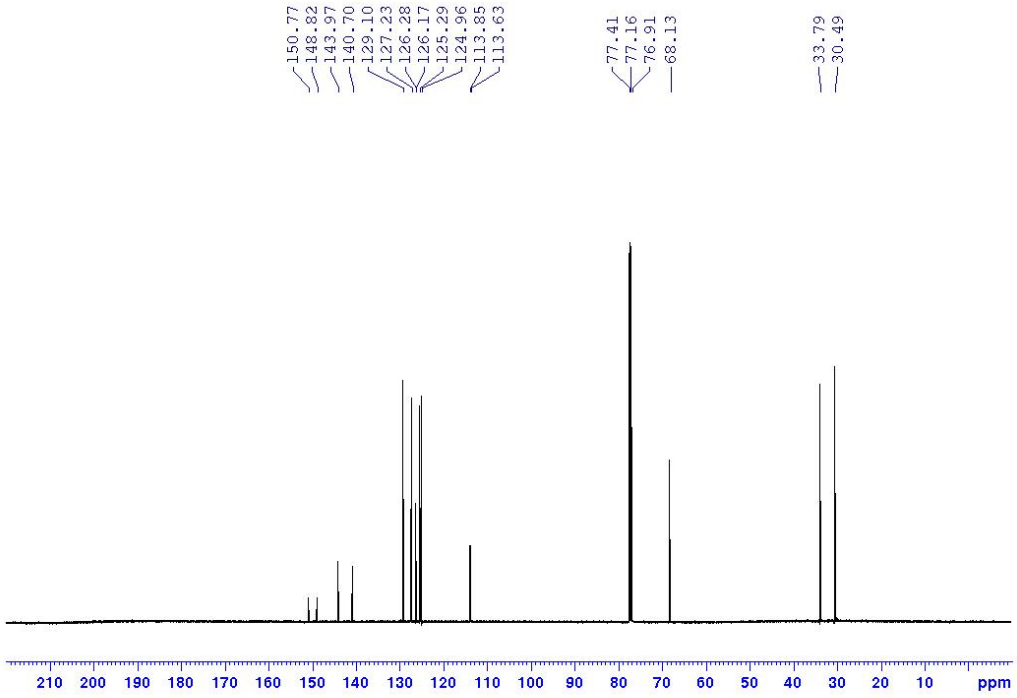
^{19}F NMR (377MHz, Chloroform-*d*): δ -176.5

HRMS (ESI): calculated $[M+H]^+$ as 203.0979, found 203.0977

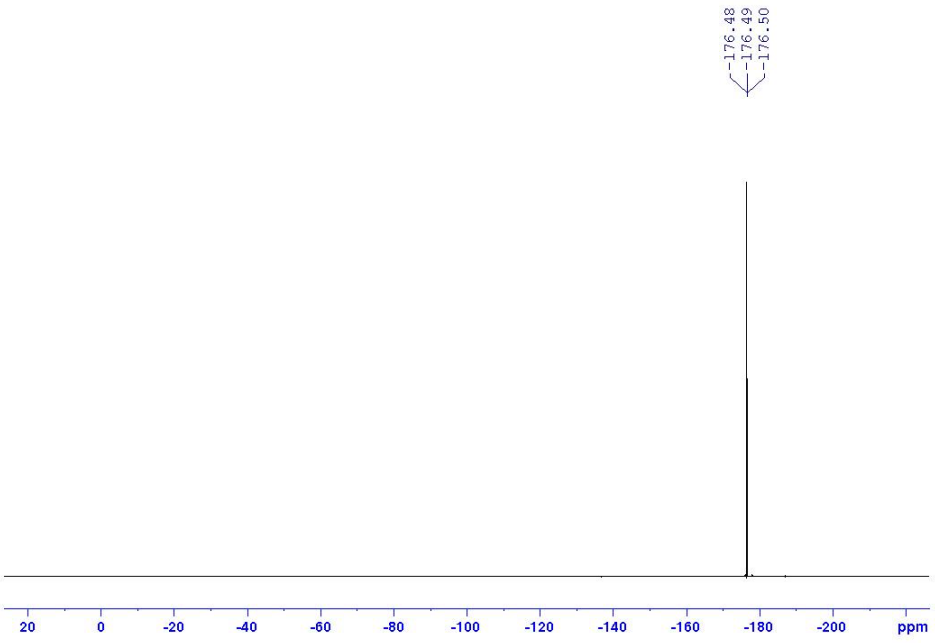
^{1}H NMR:

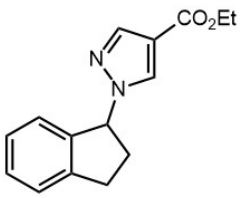


^{13}C NMR:



^{19}F NMR:





ethyl 1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazole-4-carboxylate (**5**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), ethyl 1*H*-pyrazole-4-carboxylate (210.2 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 96 mg pure product.

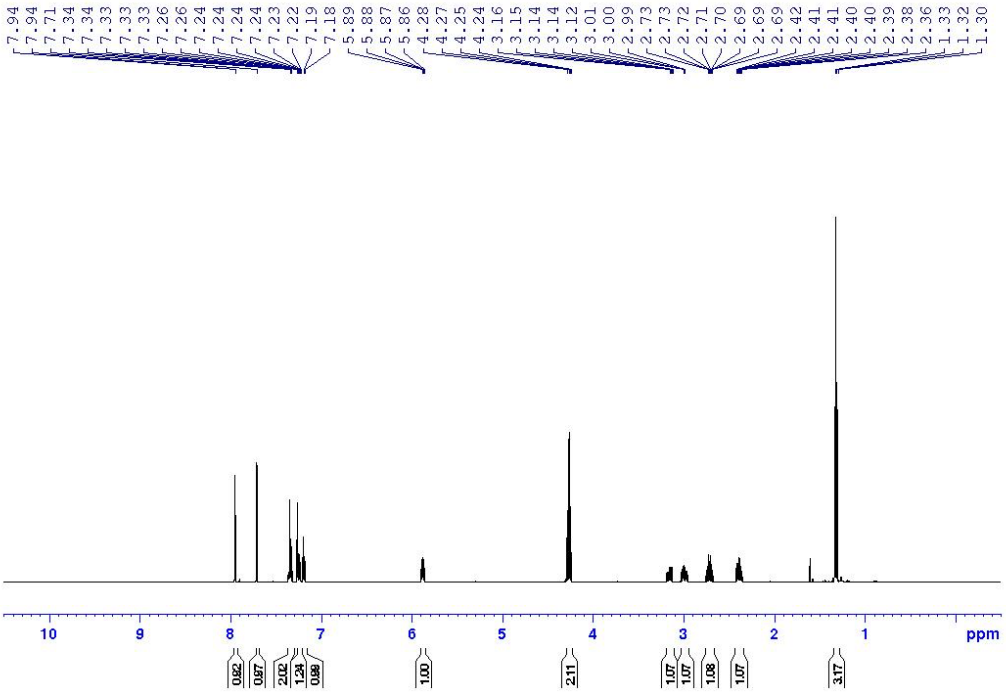
Isolated Yield: 75%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.94 (d, J = 0.5 Hz, 1H), 7.71 (s, 1H), 7.36-7.31 (m, 2H), 7.25-7.22 (m, 1H), 7.18 (d, J = 7.6 Hz, 1H), 5.87 (dd, J = 8.4, 5.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.19-3.12 (m, 1H), 3.02-2.96 (m, 1H), 2.75-2.68 (m, 1H), 2.42-2.35 (m, 1H), 1.32 (t, J = 7.2 Hz, 3H).

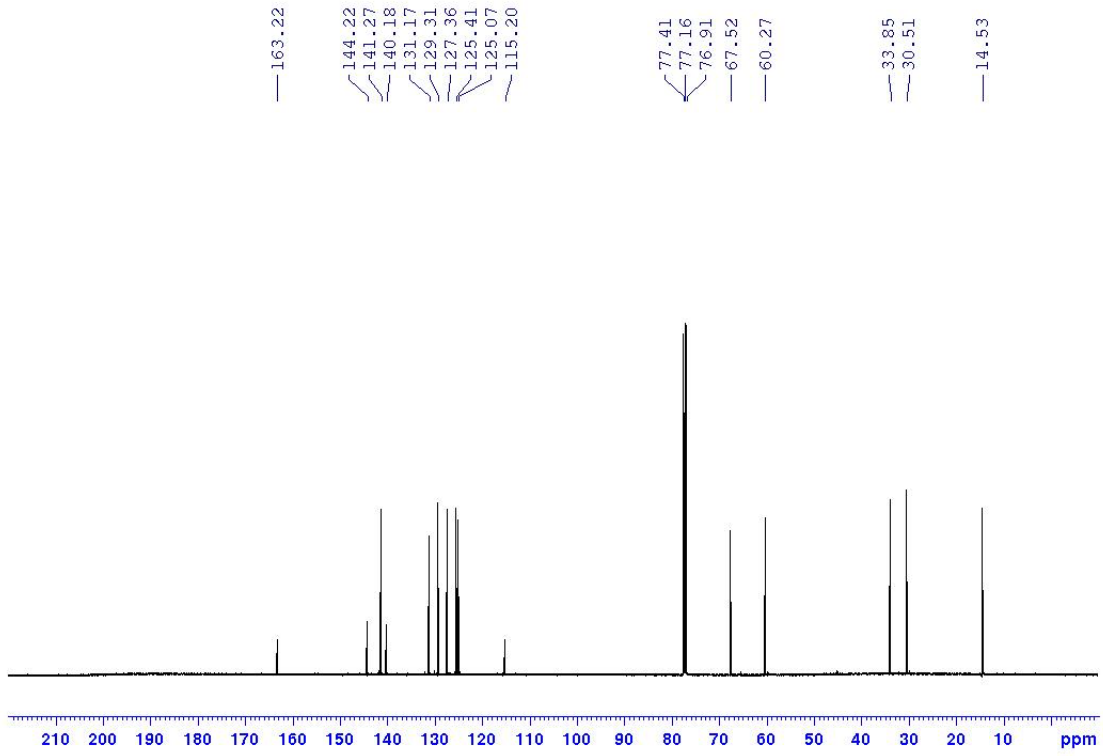
^{13}C NMR (126MHz, Chloroform-*d*): δ 163.2, 144.2, 141.3, 140.2, 131.2, 129.3, 127.4, 125.4, 125.1, 115.2, 67.5, 60.3, 33.8, 30.5, 14.5.

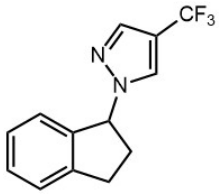
HRMS (ESI): calculated $[M+H]^+$ as 257.1285, found 257.1280

^{1}H NMR:



^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-4-(trifluoromethyl)-1H-pyrazole (**6**)[8]

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-(trifluoromethyl)-1*H*-pyrazole (204.1 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 104 mg pure product.

Isolated Yield: 83%

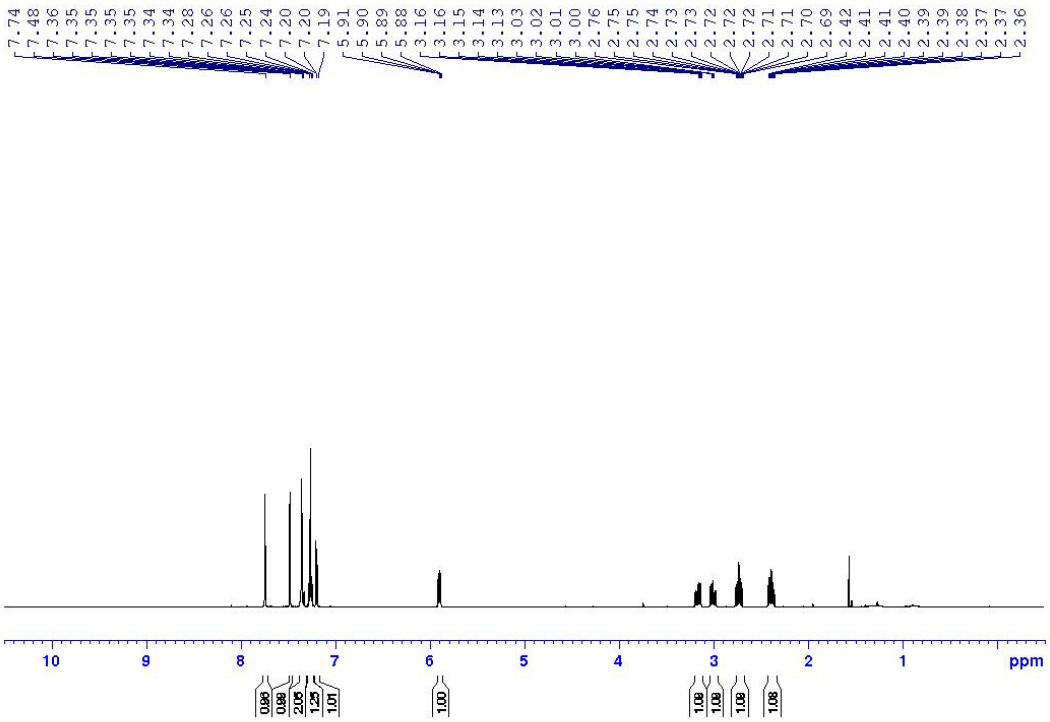
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.74 (s, 1H), 7.48 (s, 1H), 7.37-7.33 (m, 2H), 7.28-7.24 (m, 1H), 7.19 (d, J = 7.8 Hz, 1H), 5.89 (dd, J = 7.8, 2.5 Hz, 1H), 3.19-3.13 (m, 1H), 3.03-2.97 (m, 1H), 3.02-2.96 (m, 1H), 2.76-2.69 (m, 1H), 2.42-2.35 (m, 1H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 144.3, 140.0, 137.2 (q, J = 2.4 Hz), 129.4, 127.4, 127.1 (q, J = 3.4 Hz), 125.5, 125.1, 122.8 (q, J = 264.2 Hz), 113.6 (q, J = 38.0 Hz), 67.6, 60.3, 33.9, 30.5.

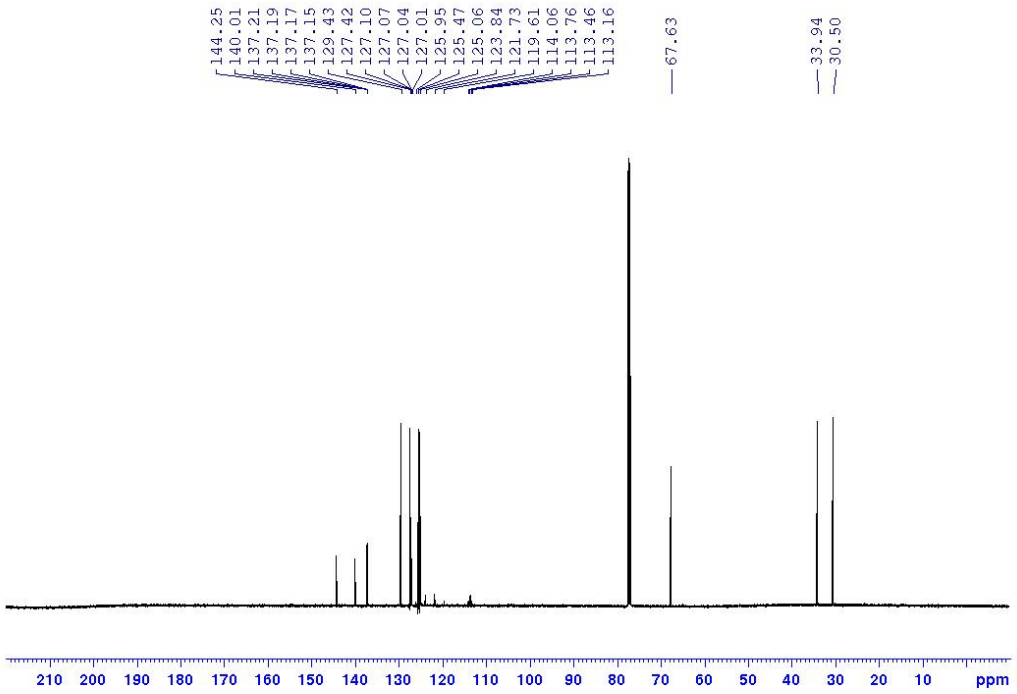
^{19}F NMR (377MHz, Chloroform-*d*): δ -56.3

HRMS (ESI): calculated $[M+H]^+$ as 253.0947, found 253.0944

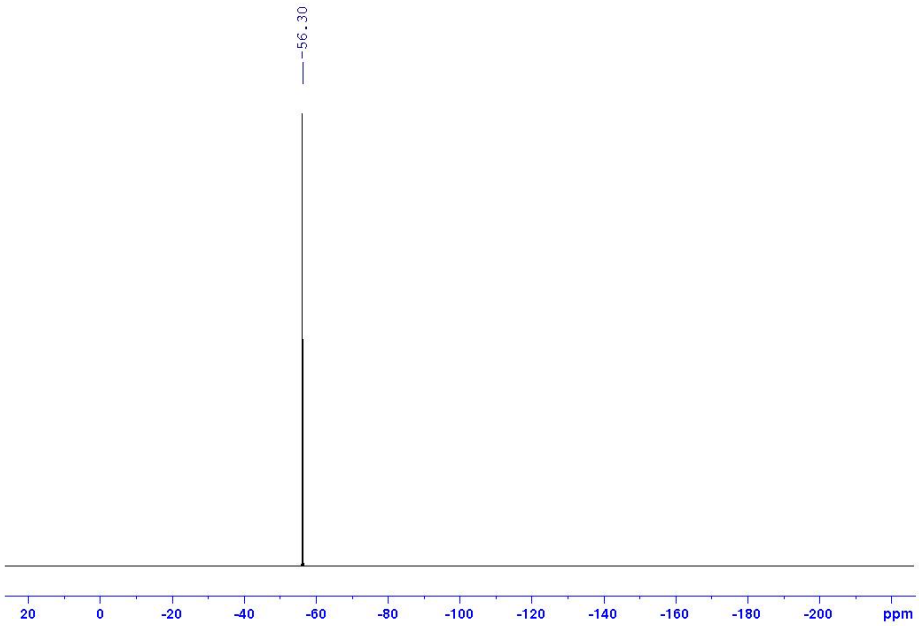
^{1}H NMR:

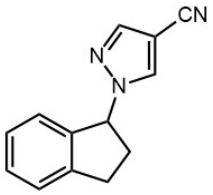


^{13}C NMR:



^{19}F NMR:





1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazole-4-carbonitrile (**7**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-cyano-1*H*-pyrazole (129.1 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 87 mg pure product.

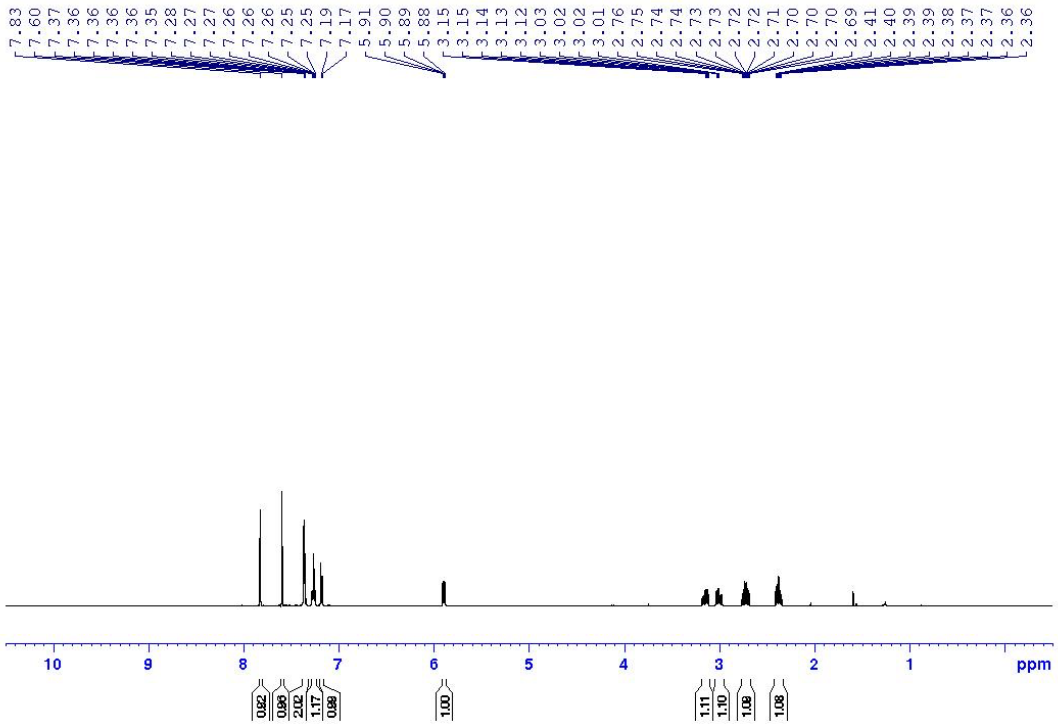
Isolated Yield: 84%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.83 (s, 1H), 7.59 (s, 1H), 7.37-7.34 (m, 2H), 7.28-7.25 (m, 1H), 7.18 (d, J = 7.6 Hz, 1H), 5.89 (dd, J = 5.0, 2.9 Hz, 1H), 3.18-1.12 (m, H), 3.03-2.97 (m, 1H), 2.76-2.69 (m, 1H), 2.41-2.34 (m, 1H).

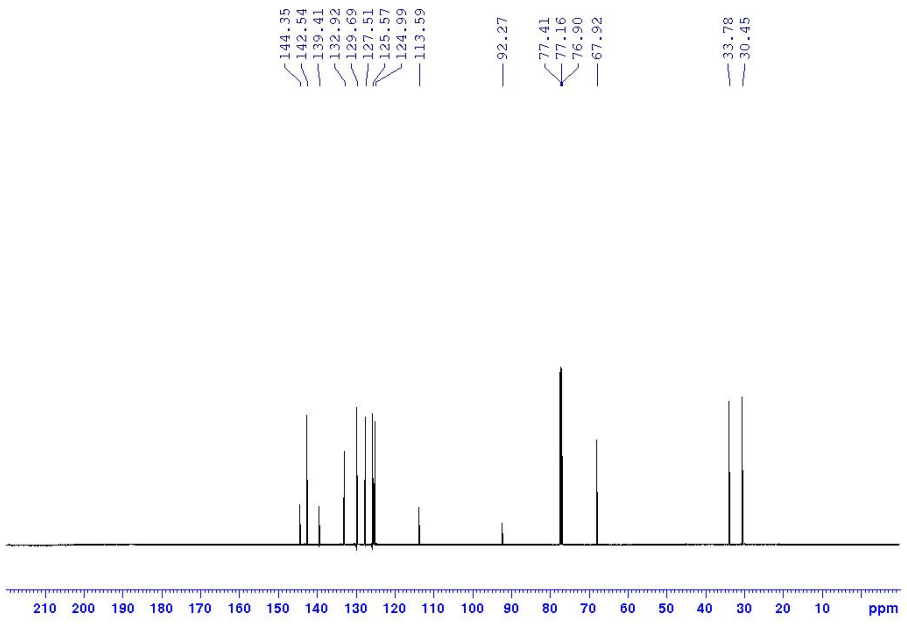
^{13}C NMR (126MHz, Chloroform-*d*): δ 144.3, 142.5, 139.4, 132.9, 129.7, 127.5, 125.6, 124.9, 113.6, 92.3, 67.9, 33.8, 30.4.

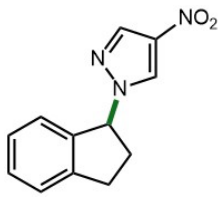
HRMS (ESI): calculated $[M+H]^+$ as 210.1026, found 210.1023

^{1}H NMR:



^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-4-nitro-1H-pyrazole (**8**)[8]

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-nitro-1*H*-pyrazole (169.6 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 72 hr. Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 98 mg pure product.

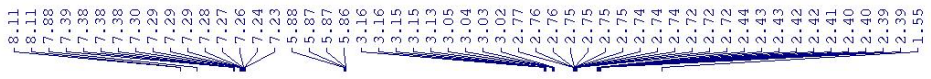
Isolated Yield: 86%

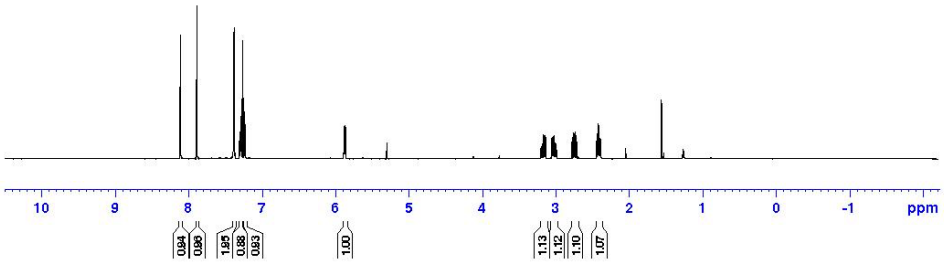
^{1}H NMR (500MHz, Chloroform-*d*): δ 8.10 (d, J = 0.5 Hz, 1H), 7.88 (s, 1H), 7.38-7.37 (m, 2H), 7.30-7.27 (m, 1H), 7.24 (d, J = 7.4 Hz, 1H), 5.87 (dd, J = 4.6, 3.3 Hz, 1H), 3.19-3.13 (m, 1H), 3.05-2.99 (m, 1H), 2.78-2.71 (m, 1H), 2.44-2.38 (m, 1H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 144.5, 138.9, 136.1, 129.9, 127.7, 127.2, 125.7, 125.1, 68.5, 33.7, 30.4.

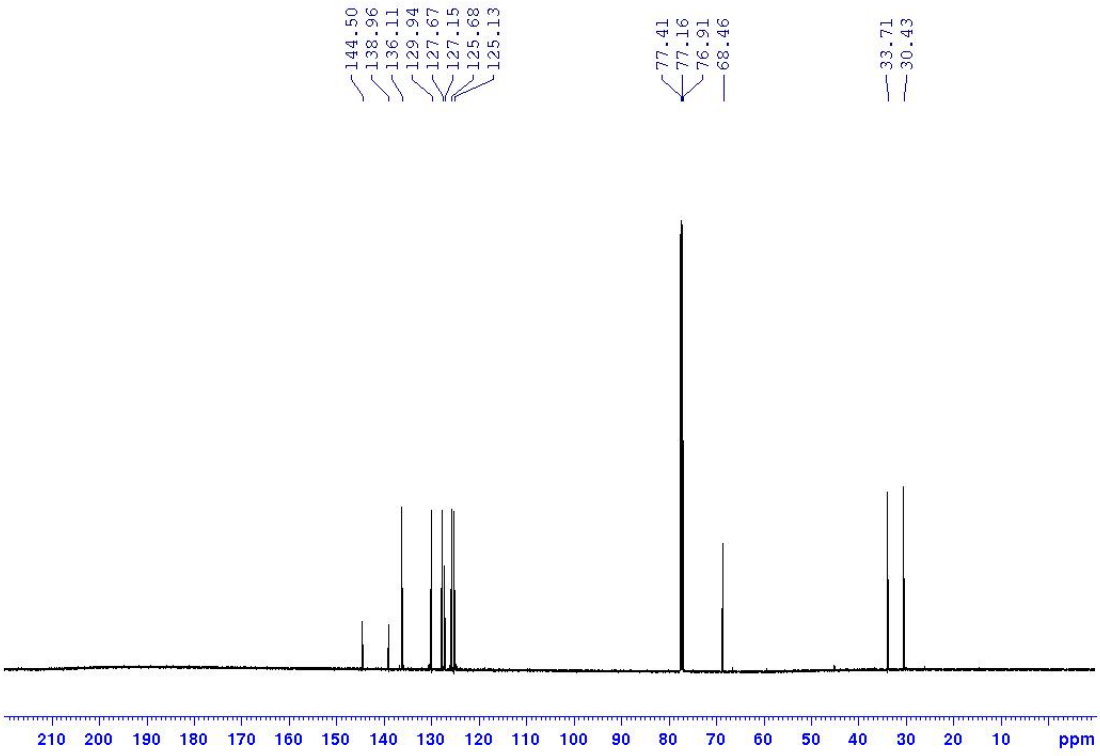
HRMS (ESI): calculated $[M+H]^+$ as 230.0924, found 230.0922

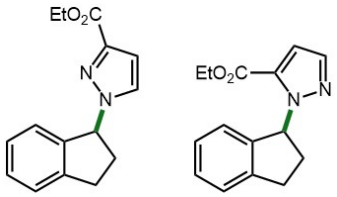
^{1}H NMR:





^{13}C NMR:





ethyl 1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazole-3-carboxylate (**9**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), ethyl 1*H*-pyrazole-3-carboxylate (210.2 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (5-12% ethyl acetate in hexanes, silica gel) afforded 110 mg pure product.

Isolated Yield: 87% (1:1)

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.48 (d, J = 1.9 Hz, 1H), 7.31-7.29 (m, 1H), 7.25-7.23 (m, 1H), 7.17-7.14 (m, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.91 (dd, J = 6.2, 1.9 Hz, 1H), 6.87 (d, J = 2.0 Hz, 1H), 4.39

(q, J = 7.2 Hz, 2H), 3.32-2.26 (m, 1H), 3.03-2.96 (m, 1H), 2.71-2.64 (m, 1H), 2.57-2.50 (m, 1H), 1.41 (t, J = 7.1 Hz, 3H).

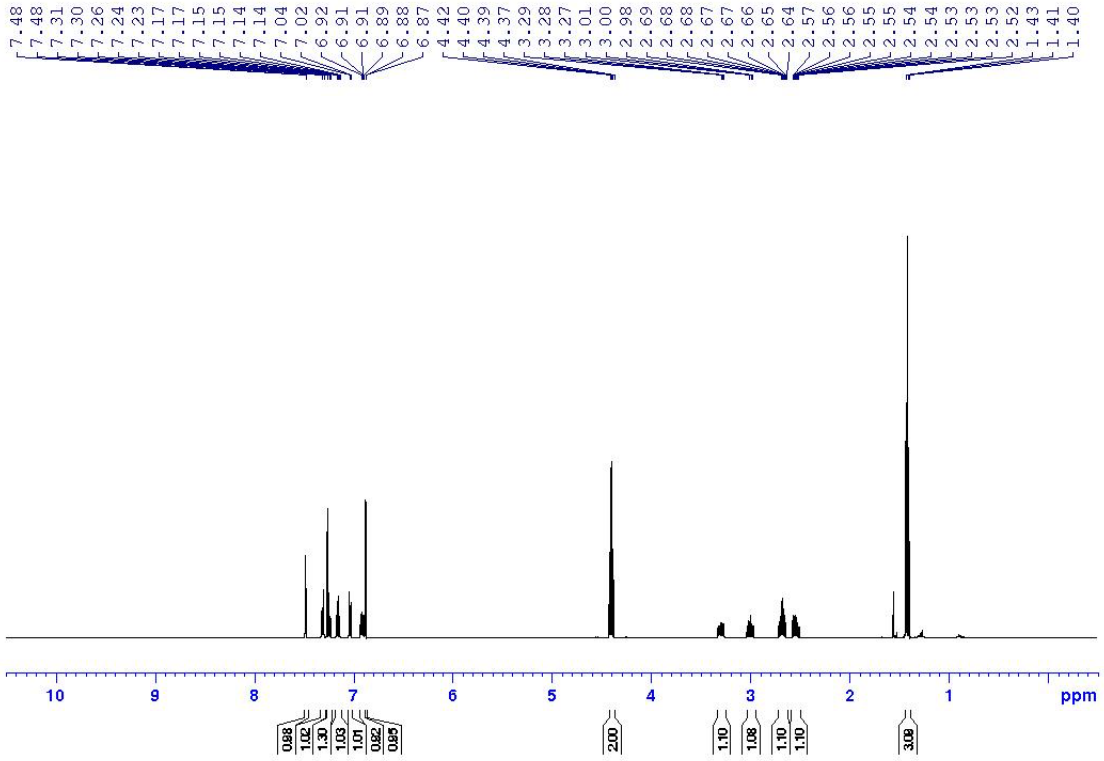
^{13}C NMR (126MHz, Chloroform-*d*): δ 160.3, 143.9, 142.1, 138.7, 132.7, 128.4, 126.8, 125.1, 124.5, 111.4, 64.8, 61.2, 33.1, 31.1, 14.4.

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.35-7.31 (m, 2H), 7.25-7.21 (m, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.13 (d, J = 2.5 Hz, 1H), 6.78 (d, J = 2.4 Hz, 1H), 6.04 (dd, J = 5.8, 2 Hz, 1H), 4.42 (q, J = 7.1 Hz, 2H), 3.16-3.09 (m, 1H), 3.02-2.96 (m, 1H), 2.79-2.72 (m, 1H), 2.36-2.29 (m, 1H), 1.41 (t, J = 7.2 Hz, 3H).

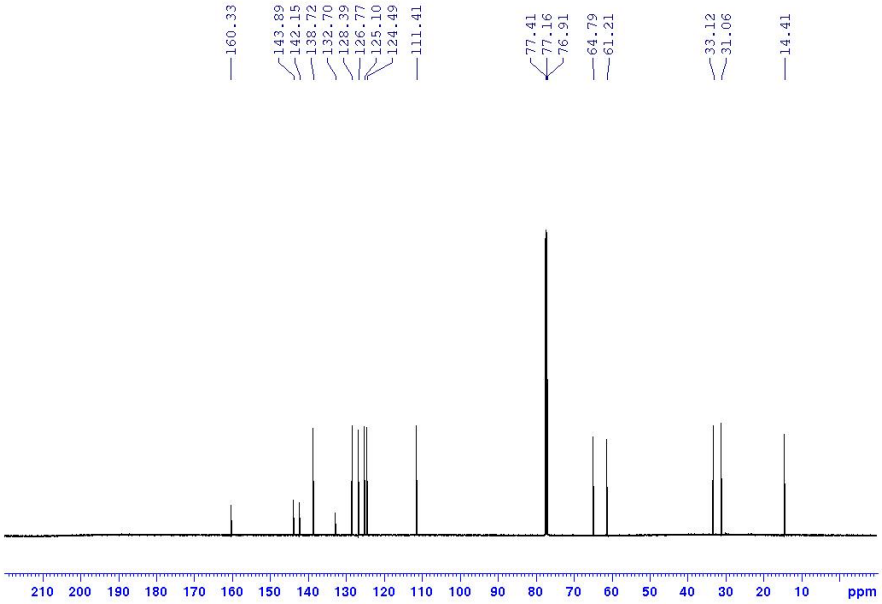
^{13}C NMR (126MHz, Chloroform-*d*): δ 162.7, 144.2, 143.5, 140.4, 129.2, 128.5, 127.4, 125.3, 125.2, 109.3, 68.1, 61.1, 34.4, 30.5, 14.6.

HRMS (ESI): calculated $[M+H]^+$ as 257.1285, found 257.1279.

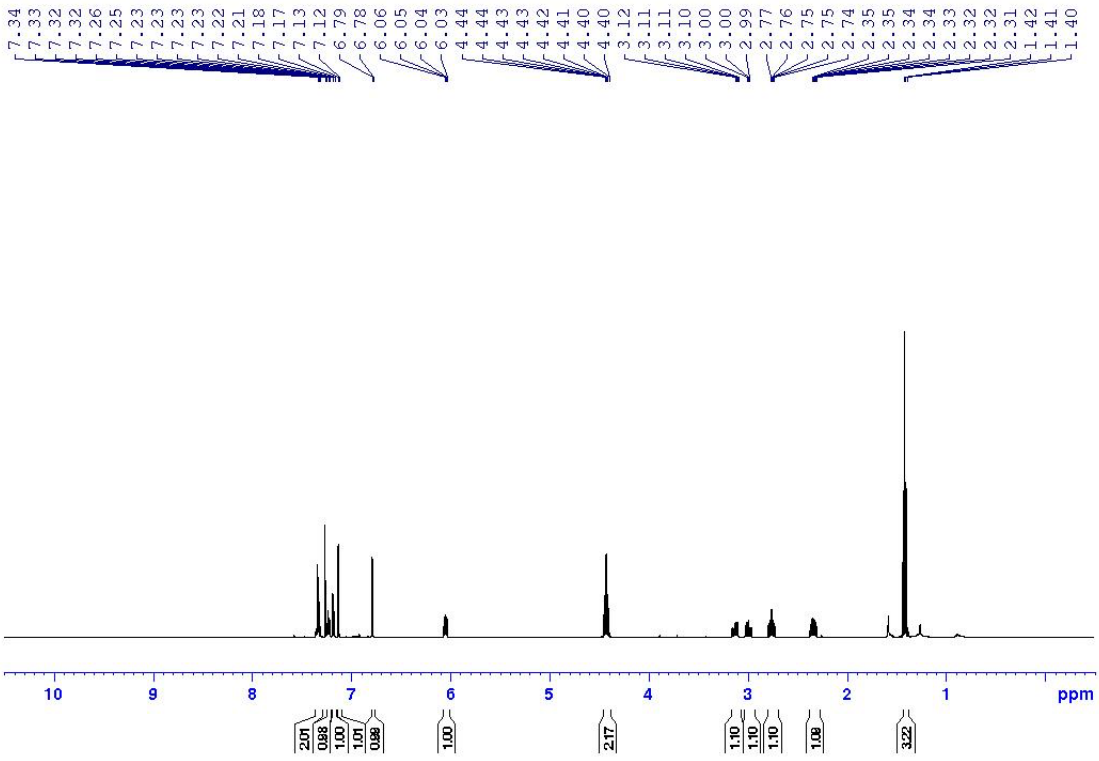
^{1}H NMR:



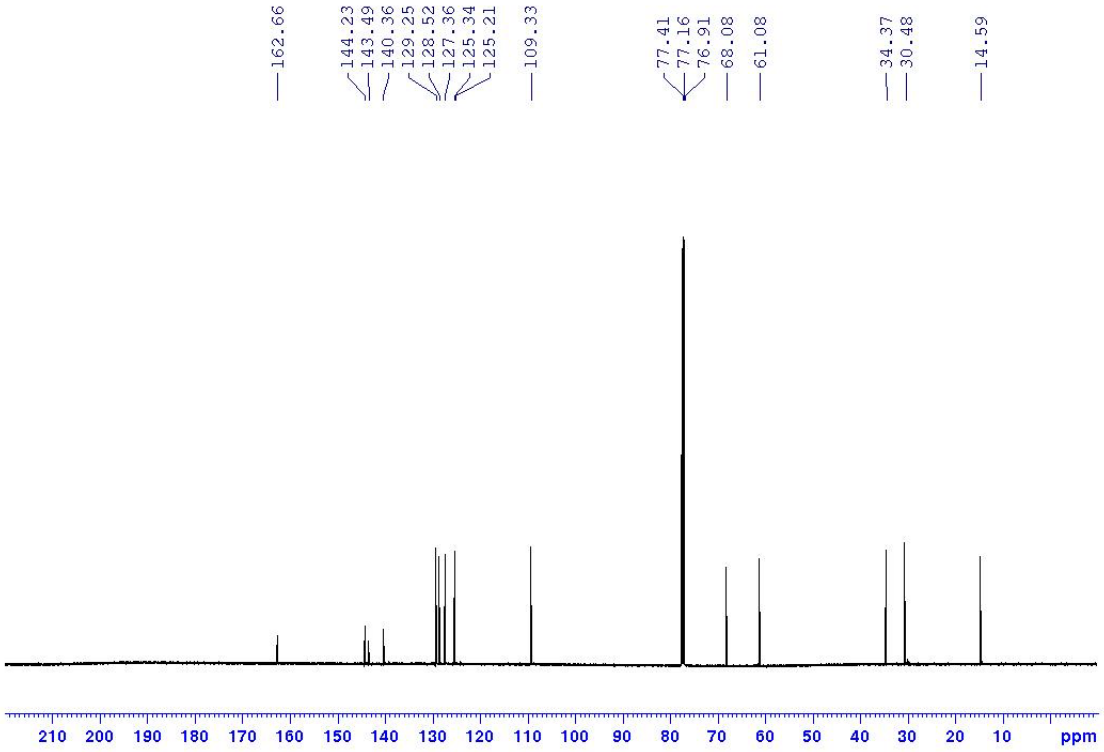
^{13}C NMR:

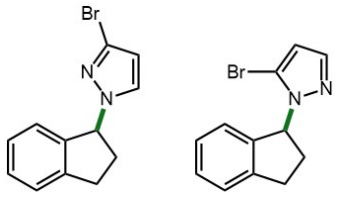


^{1}H NMR:



^{13}C NMR:





3-bromo-1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazole (**10**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 3-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 102 mg pure product.

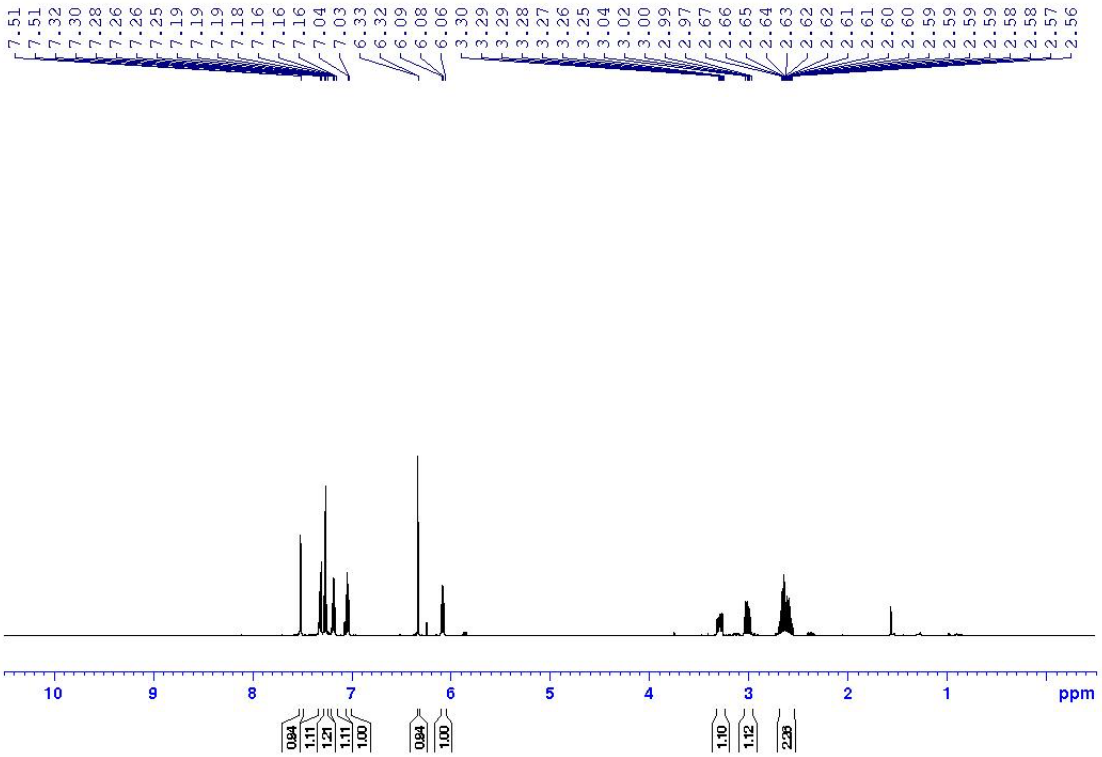
Isolated Yield: 88% (13:1)

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.51 (d, J = 1.8 Hz, 1H), 7.33-7.30 (m, 1H), 7.28-7.25 (m, 1H), 7.19-7.16 (m, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.32 (d, J = 1.9 Hz, 1H), 6.07 (t, J = 7.5 Hz, 1H), 3.31-3.25 (m, 1H), 3.04-2.97 (m, 1H), 2.68-2.55 (m, 2H).

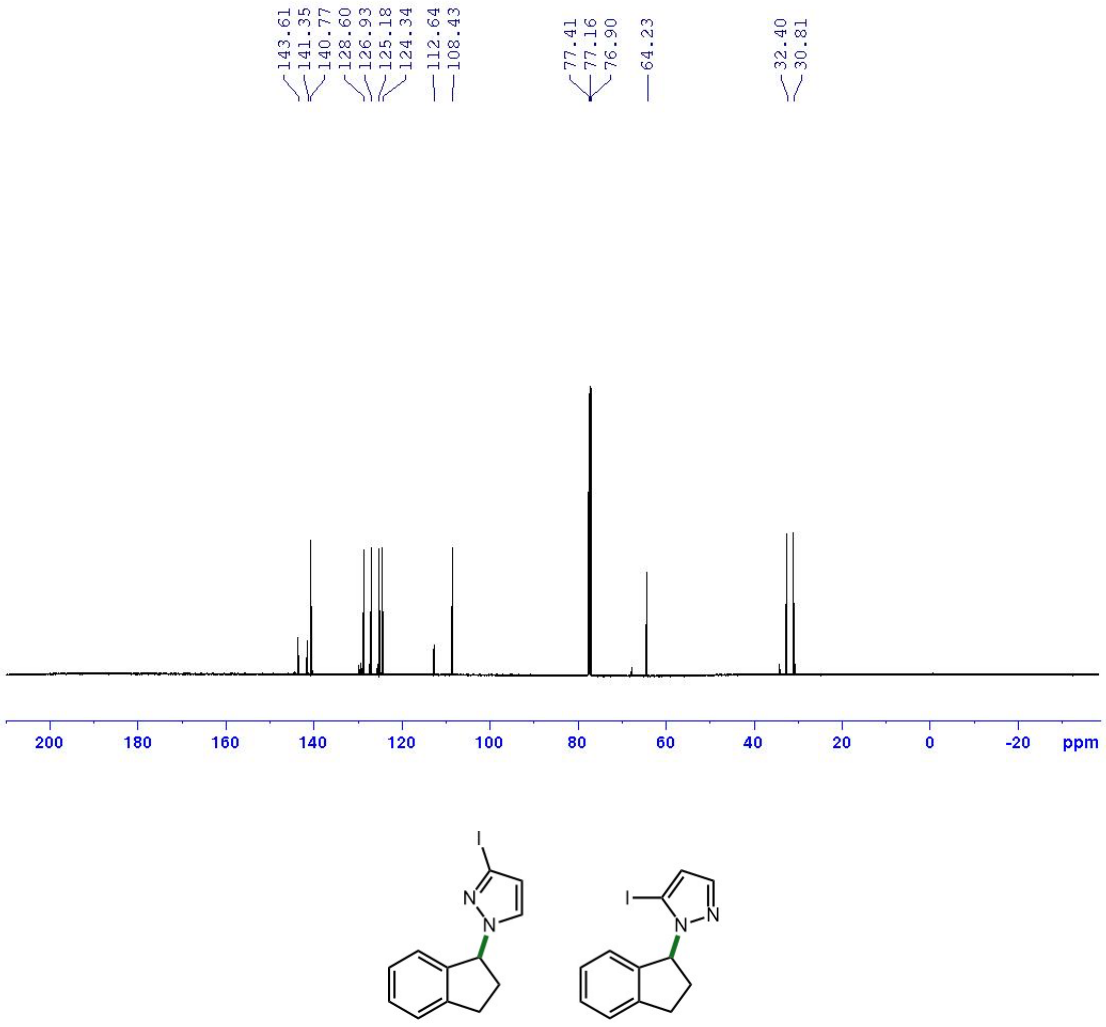
^{13}C NMR (126MHz, Chloroform-*d*): δ 143.6, 141.4, 140.8, 128.6, 126.9, 125.2, 124.3, 112.6, 108.4, 64.2, 32.4, 30.8.

HRMS (ESI): calculated $[M+H]^+$ as 263.0178, found 263.0178.

^{1}H NMR:



^{13}C NMR:



3-iodo-1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazole (**11**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 3-iodo-1*H*-pyrazole (291.0 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (8% ethyl acetate in hexanes, silica gel) afforded 124 mg pure product.

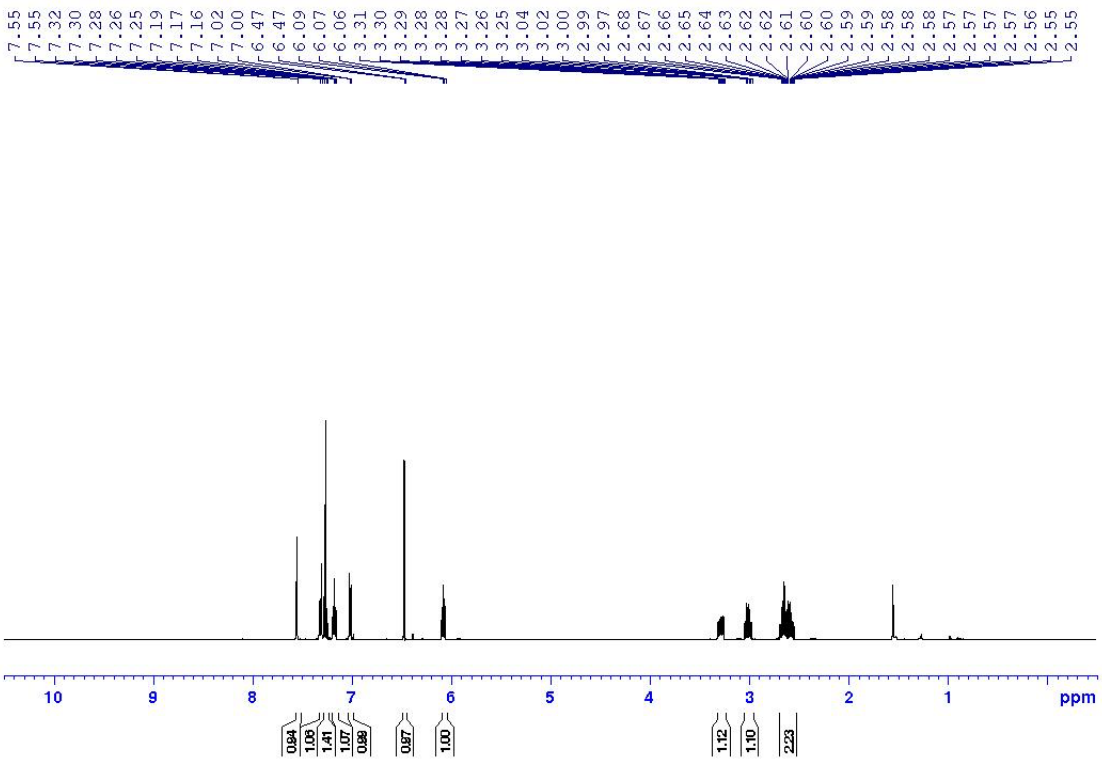
Isolated Yield: 80% (5:1)

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.55 (d, J = 1.5 Hz, 1H), 7.33-7.30 (m, 1H), 7.28-7.25 (m, 1H), 7.19-7.16 (m, 1H), 7.01 (d, J = 7.6 Hz, 1H), 6.46 (d, J = 1.9 Hz, 1H), 6.07 (t, J = 7.5 Hz, 1H), 3.31-3.25 (m, 1H), 3.04-2.97 (m, 1H), 2.68-2.54 (m, 2H).

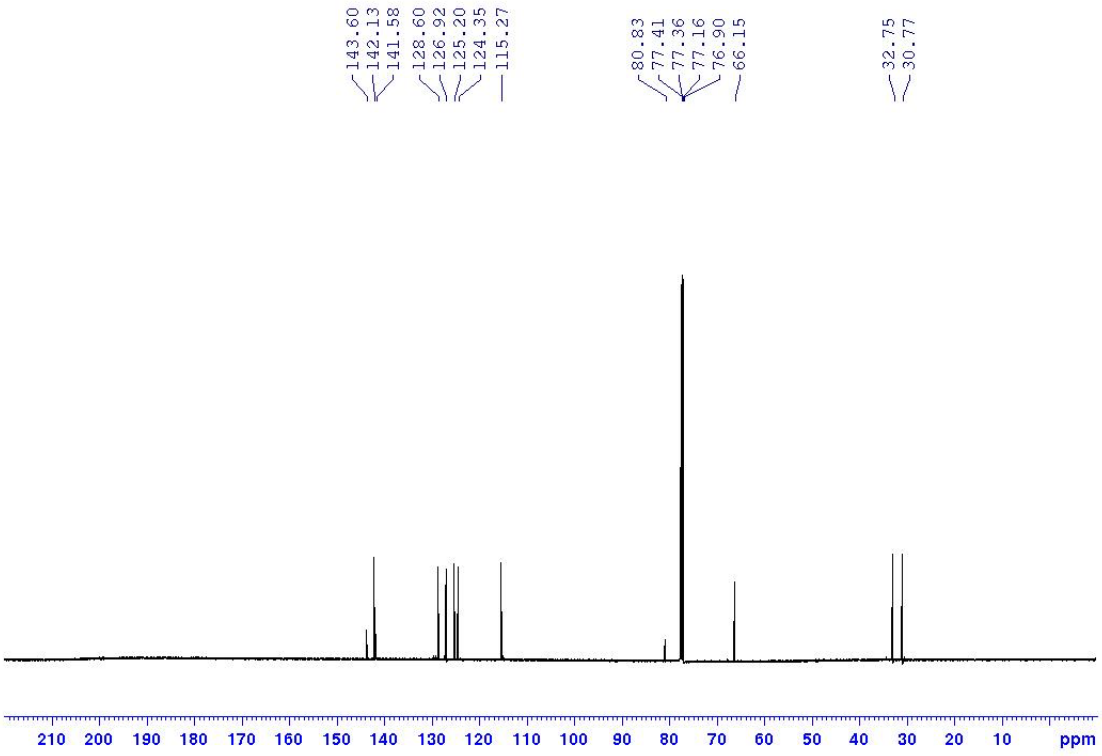
^{13}C NMR (126MHz, Chloroform-*d*): δ 143.6, 142.1, 141.6, 128.6, 126.9, 125.2, 124.3, 115.3, 80.8, 66.2, 32.7, 30.8.

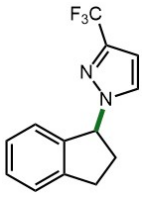
HRMS (ESI): calculated $[M+H]^+$ as 311.0040, found 311.0031.

^{1}H NMR:



^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-3-(trifluoromethyl)-1H-pyrazole (**12**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), Ir(dFppy)$_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 3-trifluoromethyl-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 85 mg pure product.

Isolated Yield: 67%

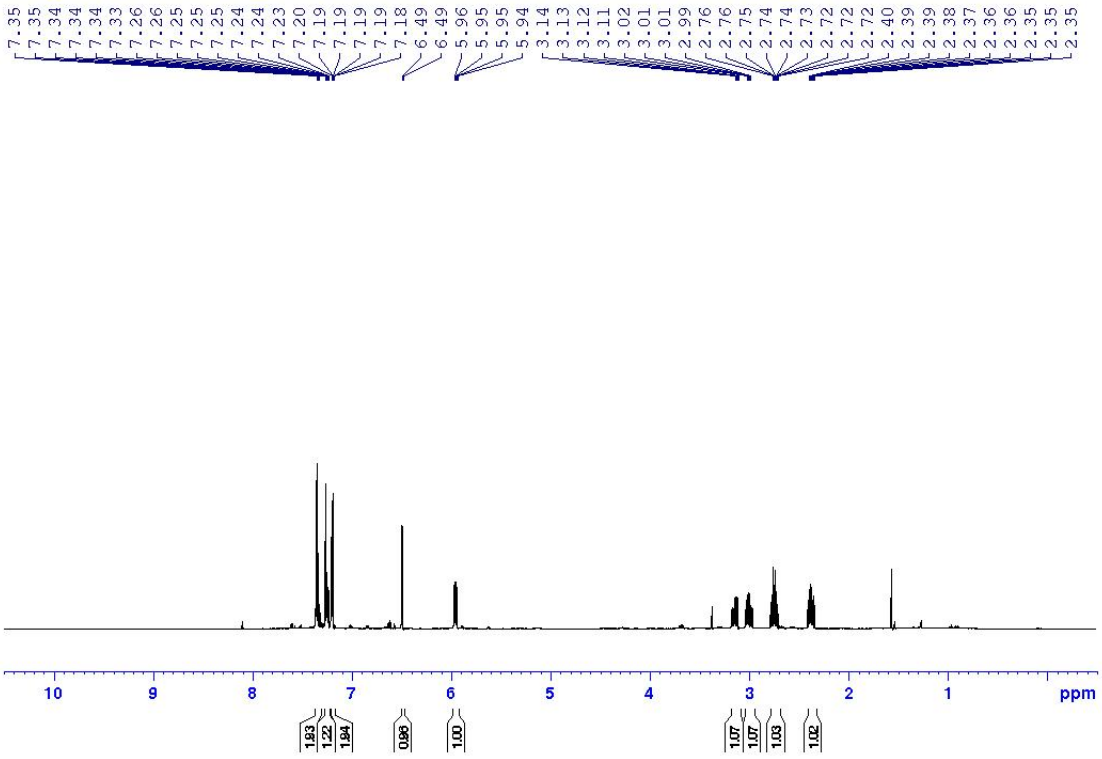
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.35-7.31 (m, 2H), 7.26-7.23 (m, 1H), 7.20-7.18 (m, 2H), 6.49 (d, J = 2.4 Hz, 1H), 5.95 (dd, J = 5.6, 2.2 Hz, 1H), 3.17-3.10 (m, 1H), 3.02-2.96 (m, 1H), 2.78-2.70 (m, 1H), 2.40-2.33 (m, 1H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 144.2, 140.1, 129.3, 128.7, 127.3, 125.4, 125.1, 104.5, 67.8, 34.1, 30.4.

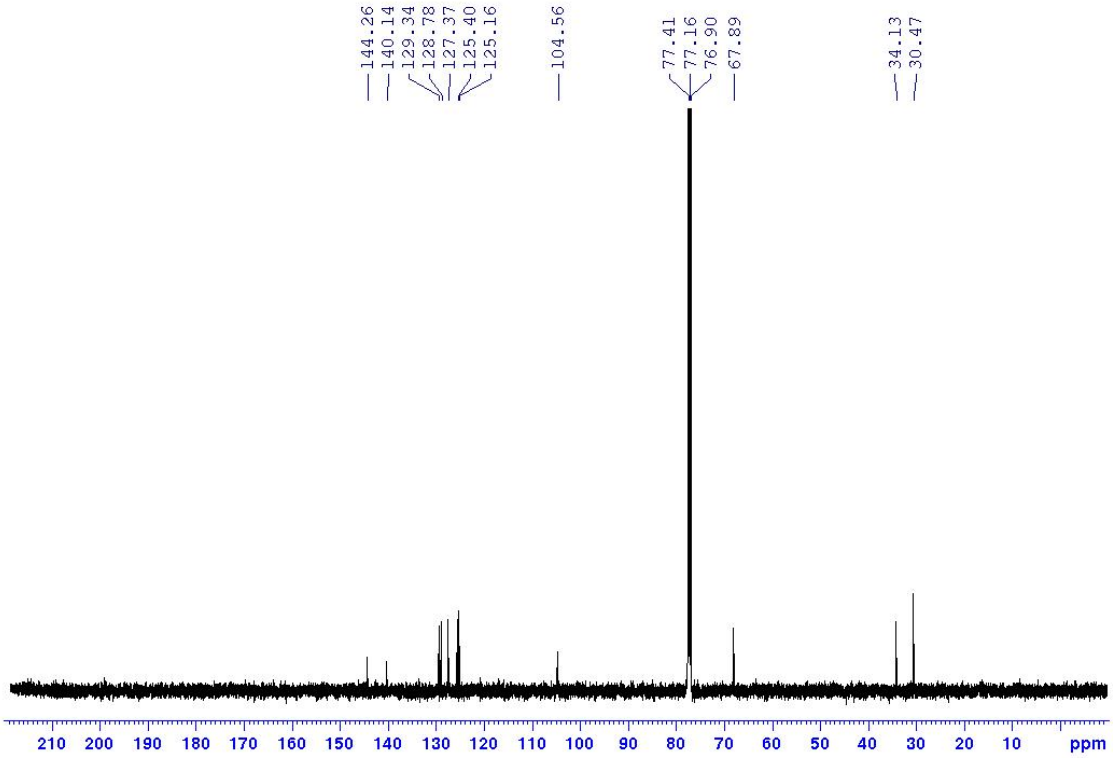
HRMS (ESI): calculated $[M+H]^+$ as 253.0947, found 253.0939.

^{19}F NMR (377MHz, Chloroform-*d*): δ -56.2

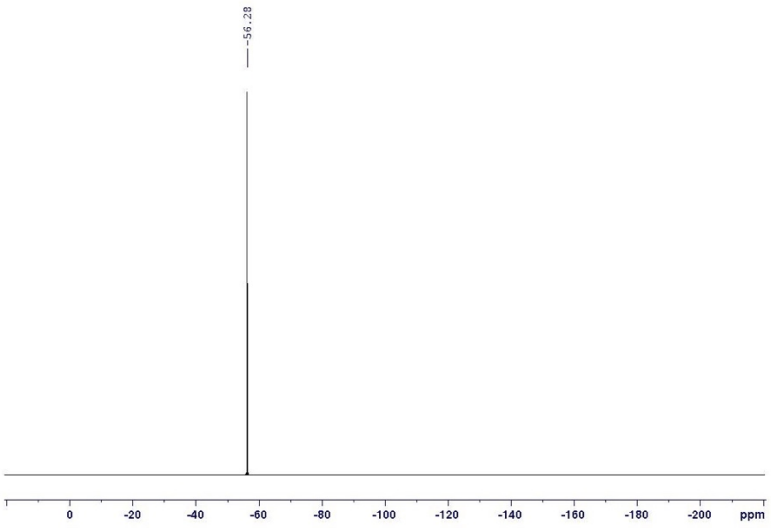
^{1}H NMR:

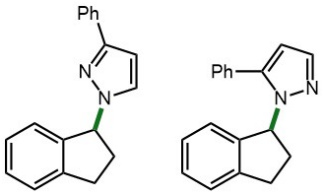


^{13}C NMR:



19F NMR:





1-(2,3-dihydro-1H-inden-1-yl)-3-phenyl-1H-pyrazole (**13**)

Synthesized according to the general procedure B for heterocycle addition with indane (61.3 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 3-phenyl-1*H*-pyrazole (216.3 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (12% ethyl acetate in hexanes, silica gel) afforded 46 mg pure product.

Isolated Yield: 35% (2:1)

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.84-7.82 (m, 2H), 7.41-7.38 (m, 1H), 7.35-7.22 (m, 5H), 7.25-7.22 (m, 1H), 7.18 (d, J = 7.6 Hz, 1H), 5.87 (dd, J = 8.4, 5.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.19-3.12 (m, 1H), 3.02-2.96 (m, 1H), 2.75-2.68 (m, 1H), 2.42-2.35 (m, 1H), 1.32 (t, J = 7.2 Hz, 3H).

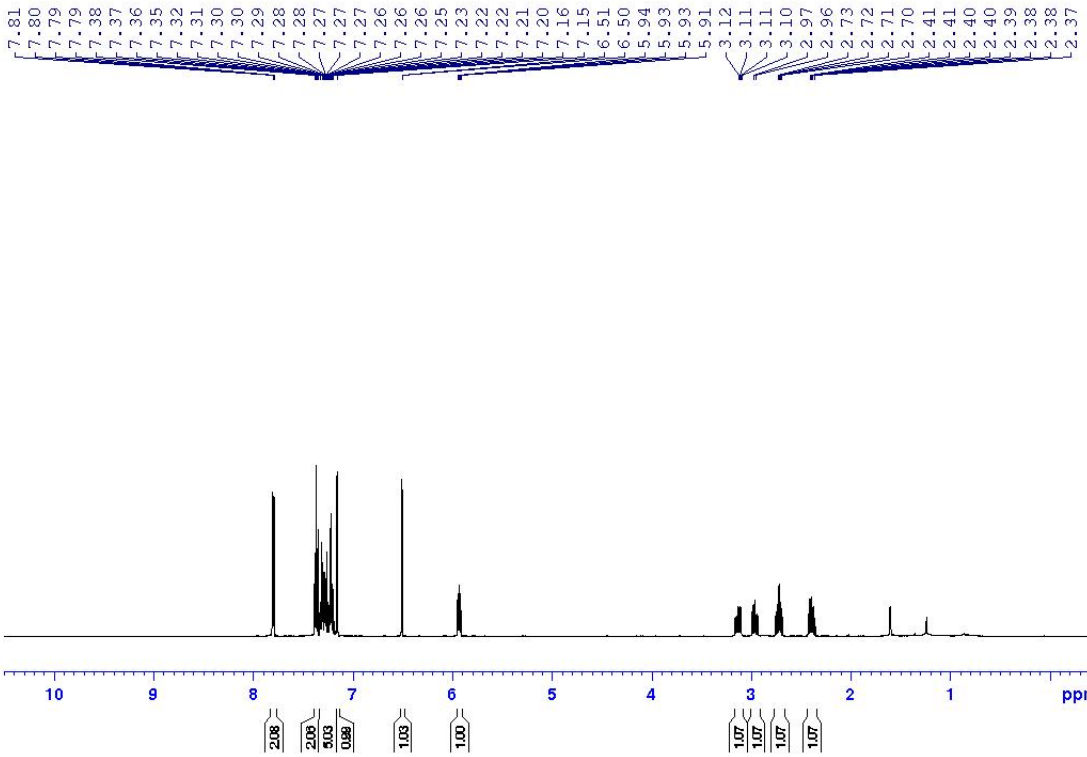
^{13}C NMR (126MHz, Chloroform-*d*): δ 151.4, 144.2, 141.2, 133.8, 128.9, 128.7, 128.6, 127.6, 127.1, 125.8, 125.2, 103.0, 67.2, 34.2, 30.6.

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.56 (d, J = 1.7 Hz, 1H), 7.50-7.43 (m, 5H), 7.27 (d, J =7.5 Hz, 1H), 7.22 (t, J = 7.3 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 6.33 (d, J = 1.8 Hz, 1H), 5.91 (t, J = 7.9 Hz, 1H), 3.23-3.18 (m, 1H), 2.95-2.88 (m, 1H), 2.73-2.65 (m, 1H), 2.59-2.53 (m, 1H).

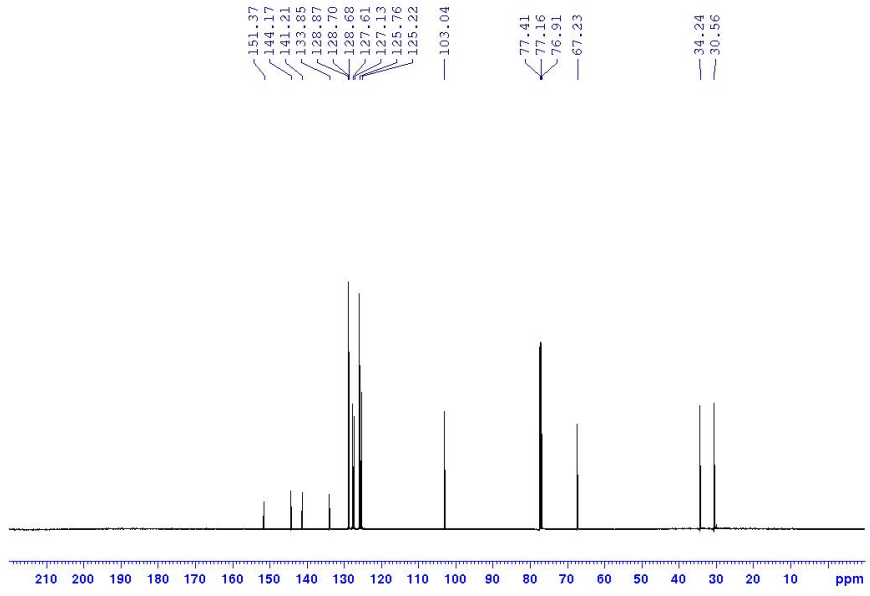
^{13}C NMR (126MHz, Chloroform-*d*): δ 144.5, 143.3, 142.6, 139.6, 131.2, 129.3, 128.9, 128.7, 128.3, 126.9, 125.2, 123.8, 106.1, 63.4, 33.3, 30.7.

HRMS (ESI): calculated $[M+H]^+$ as 261.1386, found 261.1385.

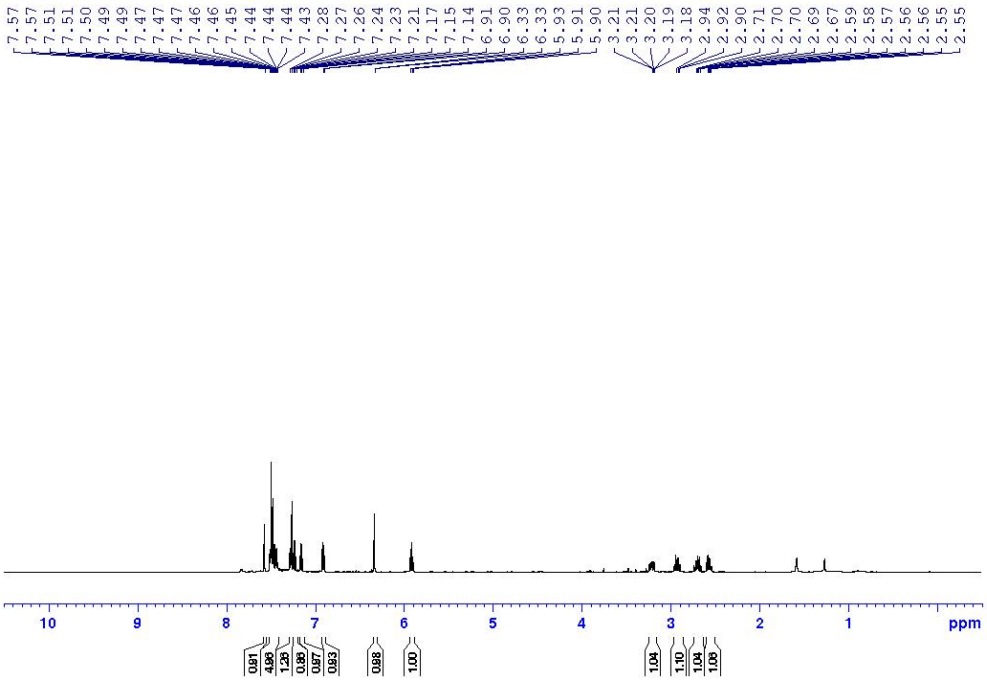
^{1}H NMR:



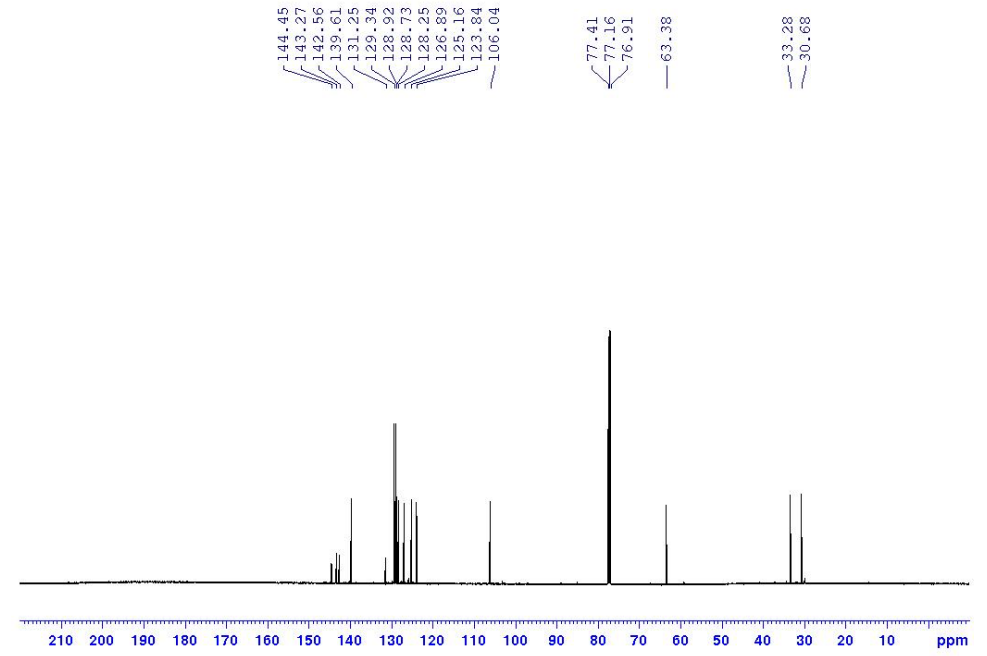
^{13}C NMR:

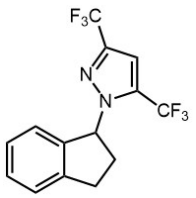


^{1}H NMR:



^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-3,5-bis(trifluoromethyl)-1H-pyrazole (**14**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.75 mmol, 1.500 equiv.), 3,5-bis(trifluoromethyl)-1*H*-pyrazole (306.12 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (3% ethyl acetate in hexanes, silica gel) afforded 120 mg pure product.

Isolated Yield: 75%

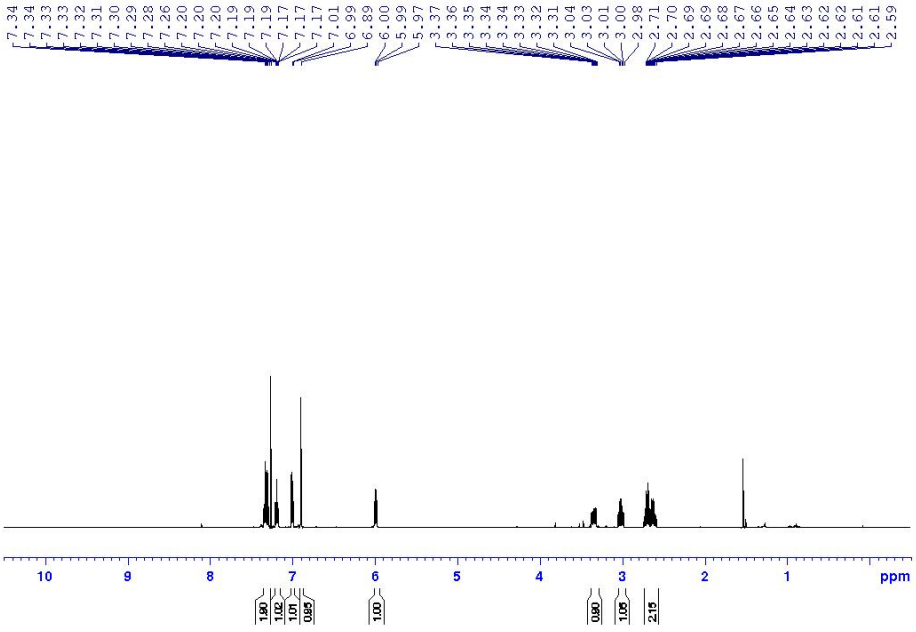
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.34-7.28 (m, 2H), 7.20-7.17 (m, 1H), 7.00 (d, J = 7.7 Hz, 1H), 6.89 (s, 1H), 5.99 (t, J = 7.2 Hz, 1H), 3.37-3.31 (m, 1H), 3.01 (qt, J = 7.6 Hz, 1H), 2.73-2.58 (m, 2H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 143.9, 144.3 (q, J = 39.2 Hz), 140.1, 133.7 (q, J = 39.6 Hz), 130.2, 129.9, 129.1, 127.1, 125.3, 124.8, 124.2, 123.7, 122.9, 121.6, 120.7, 119.4, 118.6, 117.3, 116.4, 105.7, 66.4, 33.2, 30.9.

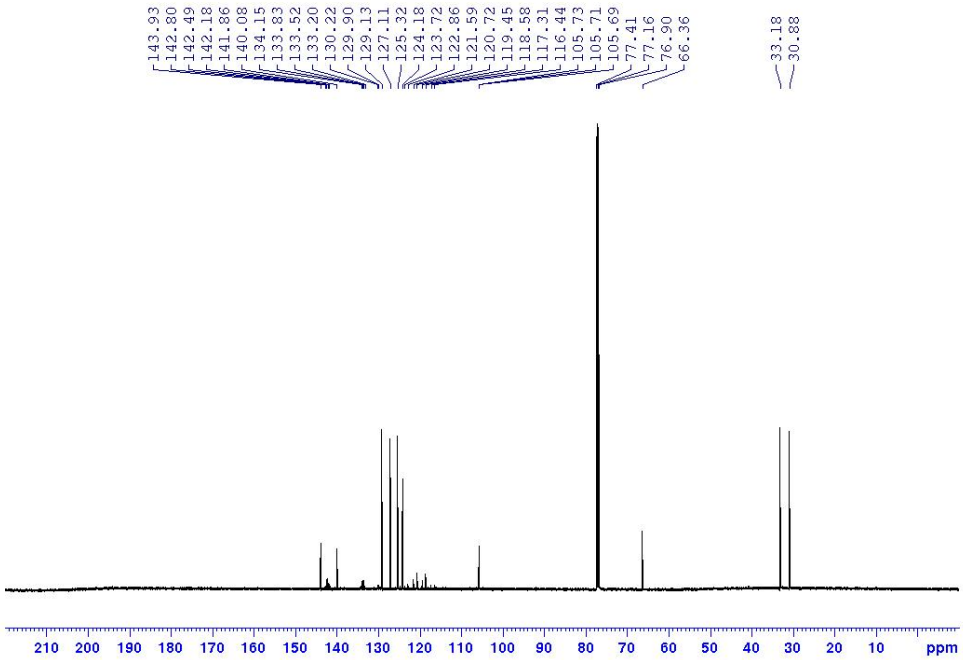
^{19}F NMR (377MHz, Chloroform-*d*): δ -58.9, -62.3.

HRMS (ESI): calculated $[M+NH_4]^+$ as 338.1086, found 338.1081

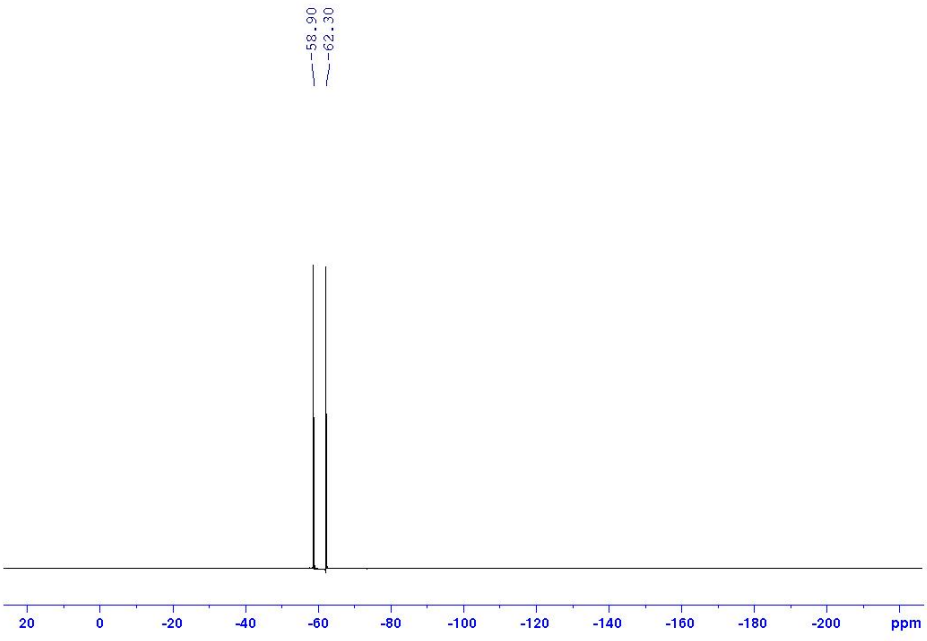
^{1}H NMR:

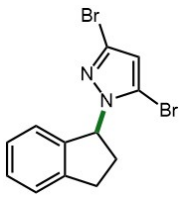


^{13}C NMR:



^{19}F NMR:





3,5-dibromo-1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazole (**15**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 3,5-dibromo-1*H*-pyrazole (338.8 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (3% ethyl acetate in hexanes, silica gel) afforded 129 mg pure product.

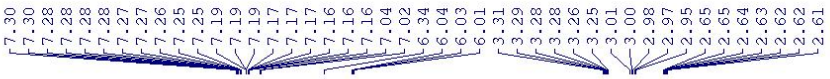
Isolated Yield: 76%

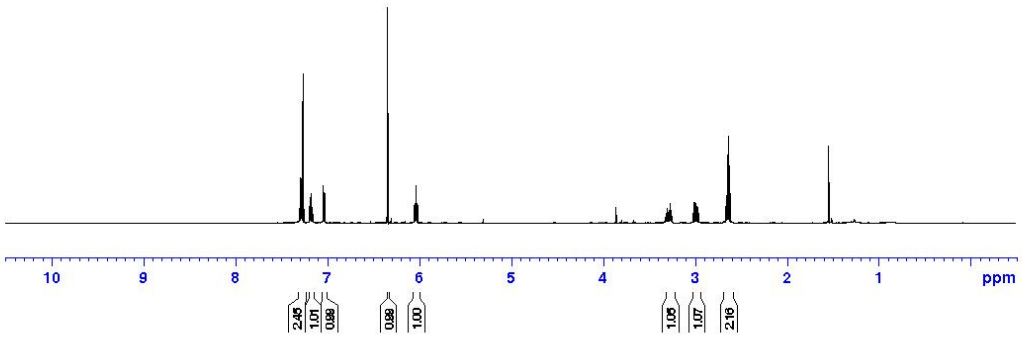
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.29-7.24 (m, 2H), 7.18-7.15 (m, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.33 (s, 1H), 6.02 (t, J = 7.6 Hz, 1H), 3.30-3.24 (m, 1H), 3.01-2.95 (m, 1H), 2.65-2.60 (m, 1H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 143.6, 140.9, 128.7, 126.94, 126.9, 125.2, 124.2, 114.0, 110.9, 65.1, 32.1, 30.7.

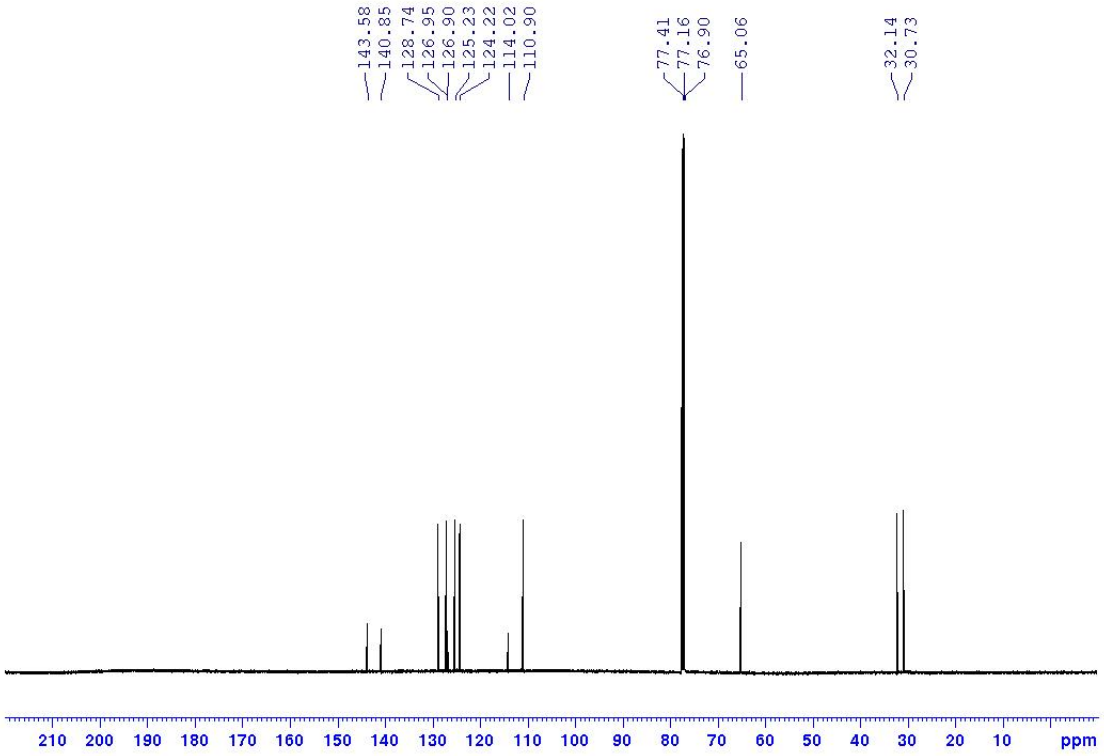
HRMS (ESI): calculated $[M+H]^+$ as 340.9283, found 340.9281.

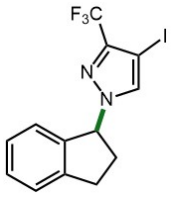
^{1}H NMR:





^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-4-iodo-3-(trifluoromethyl)-1H-pyrazole (**16**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-iodo-3-(trifluoromethyl)-1*H*-pyrazole (393.0 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 148 mg pure product.

Isolated Yield: 78%

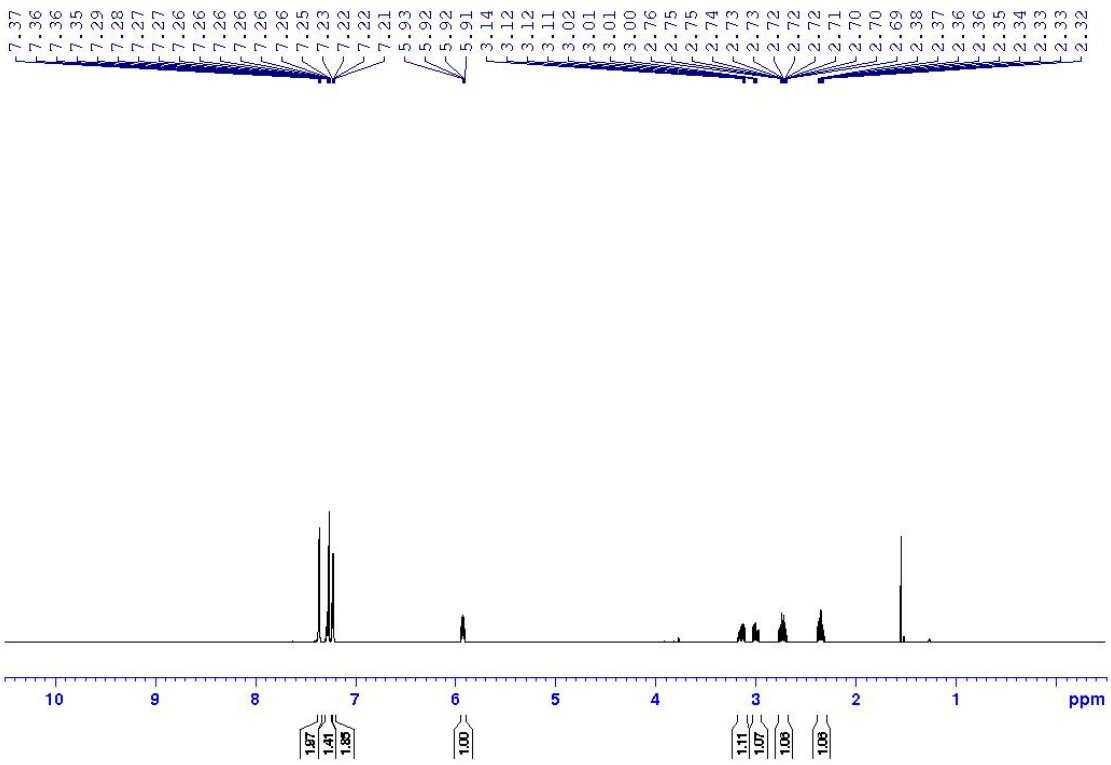
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.36-7.35 (m, 1H), 7.29-7.24 (m, 1H), 7.22-7.21 (m, 2H), 5.92 (dd, J = 5, 2.9 Hz, 1H), 3.16-3.10 (m, 1H), 3.02-2.96 (m, 1H), 2.76-2.68 (m, 1H), 2.37-2.31 (m, 1H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 144.4, 143.6 (q, J = 36.6 Hz), 139.4, 134.9, 129.7, 127.5, 125.5, 125.3, 121.0 (q, J = 268.3 Hz), 68.5, 54.1, 34.1, 30.4.

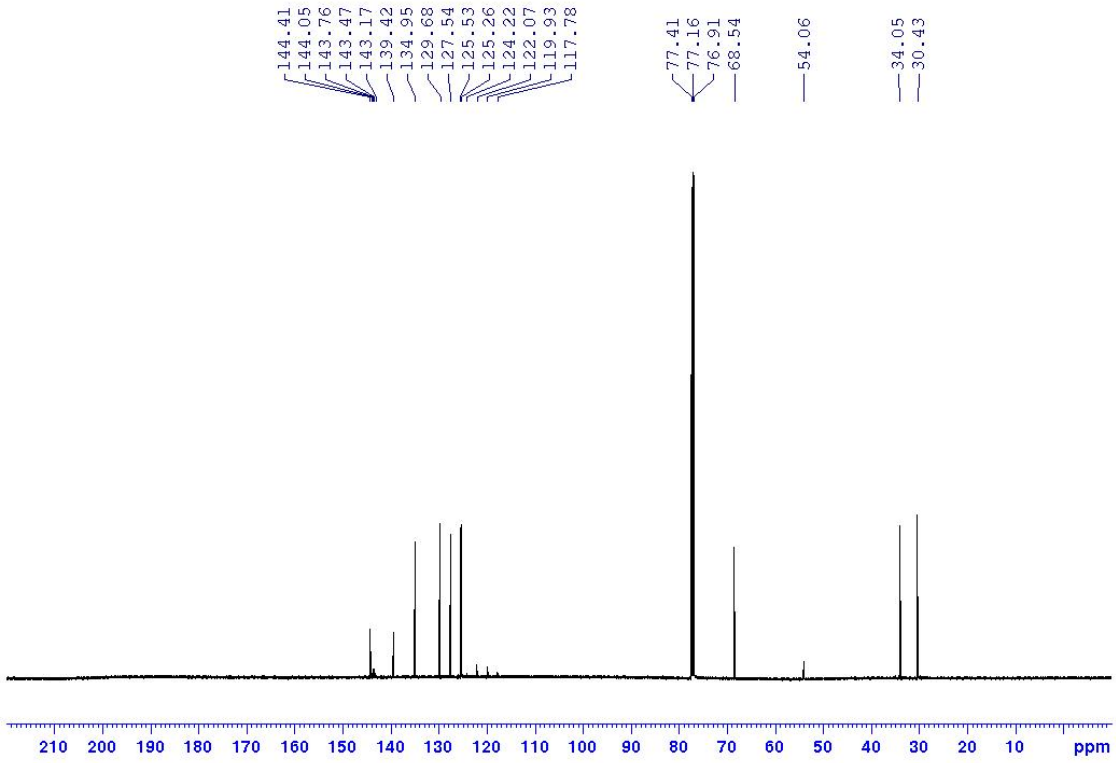
HRMS (ESI): calculated $[M+H]^+$ as 378.9914, found 378.9911.

^{19}F NMR (377MHz, Chloroform-*d*): δ -61.6

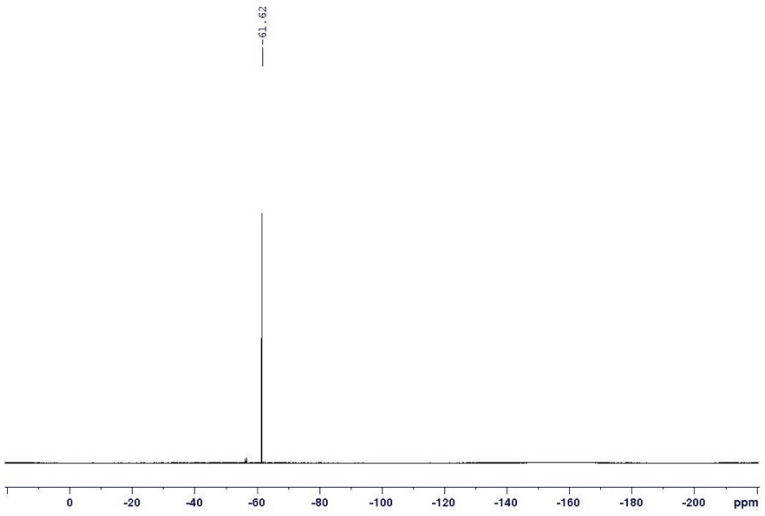
^{1}H NMR:

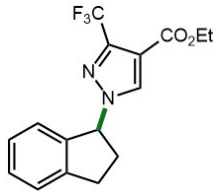


^{13}C NMR:



^{19}F NMR:





ethyl-1-(2,3-dihydro-1H-inden-1-yl)-3-(trifluoromethyl)-1H-pyrazole-4-carboxylate (**17**)

Synthesized according to the general procedure B for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), ethyl 3-(trifluoromethyl)-1*H*-pyrazole-4-carboxylate (312.2 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (8% ethyl acetate in hexanes, silica gel) afforded 109 mg pure product.

Isolated Yield: 67%

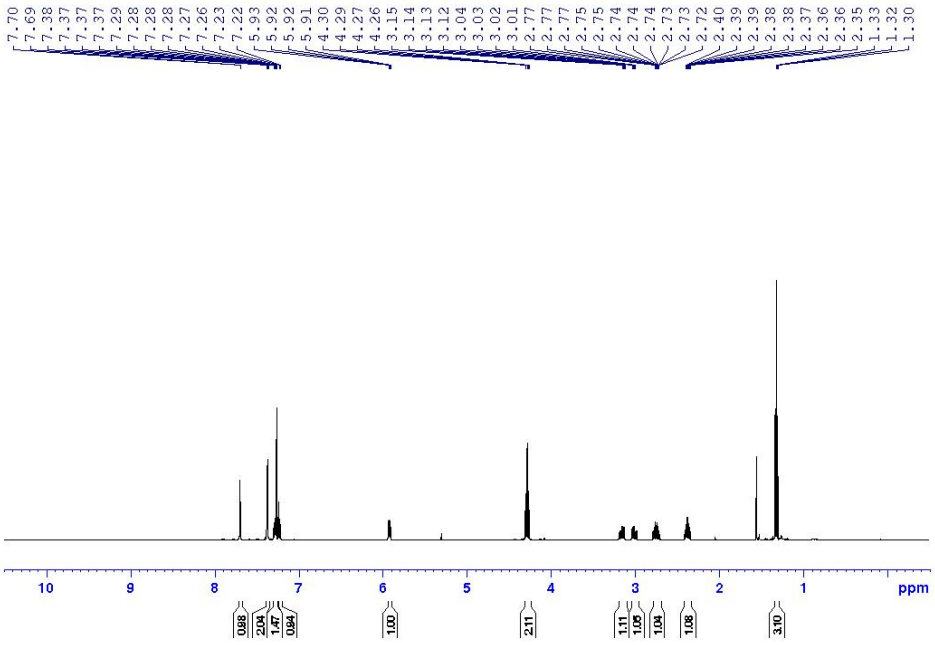
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.69 (d, J = 0.8 Hz, 1H), 7.37-7.36 (m, 2H), 7.29-7.25 (m, 1H), 7.22 (d, J = 7.5 Hz, 1H), 5.91 (dd, J = 4.9, 3 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.18-3.12 (m, 1H), 3.04-2.98 (m, 1H), 2.78-2.71 (m, 1H), 2.40-2.34 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 161.1, 144.5, 141.6 (q, J = 152.0 Hz), 139.1, 133.8, 129.8, 127.6, 120.5 (q, J = 267.9 Hz), 113.4, 68.3, 61.0, 33.9, 30.4, 14.2.

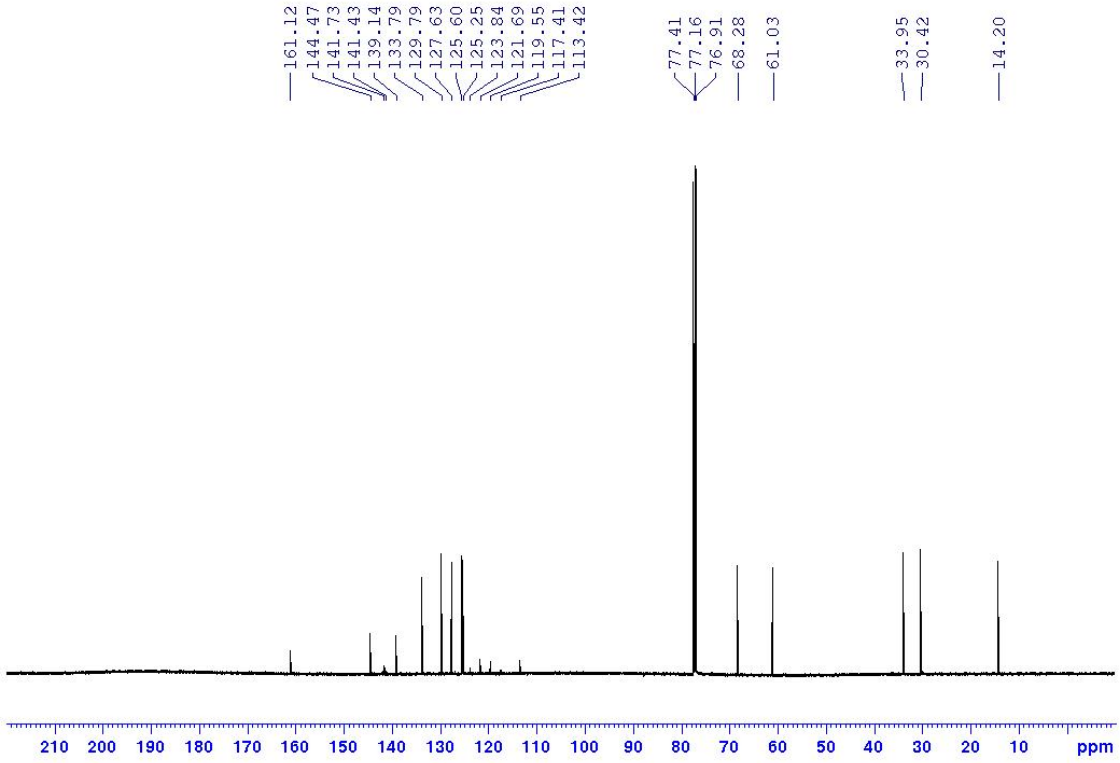
^{19}F NMR (377MHz, Chloroform-*d*): δ -61.9

HRMS (ESI): calculated $[M+H]^+$ as 325.1158, found 325.1154

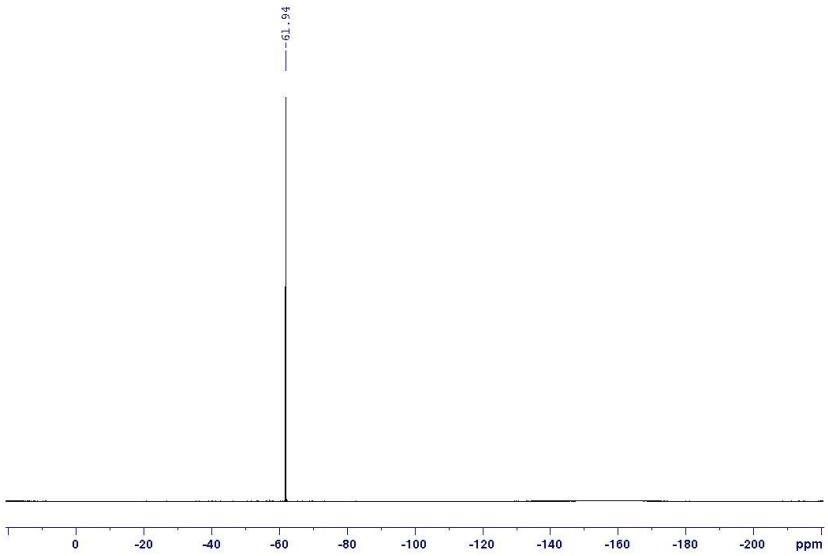
^{1}H NMR:

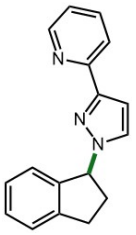


^{13}C NMR:



^{19}F NMR:





2-(1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazol-3-yl)pyridine (**18**)

Synthesized according to the general procedure B for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 2-(1*H*-pyrazol-3-yl) pyridine (217.8 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 36 hr. Purification with flash chromatography (30% ethyl acetate in hexanes, silica gel) afforded 25 mg pure product.

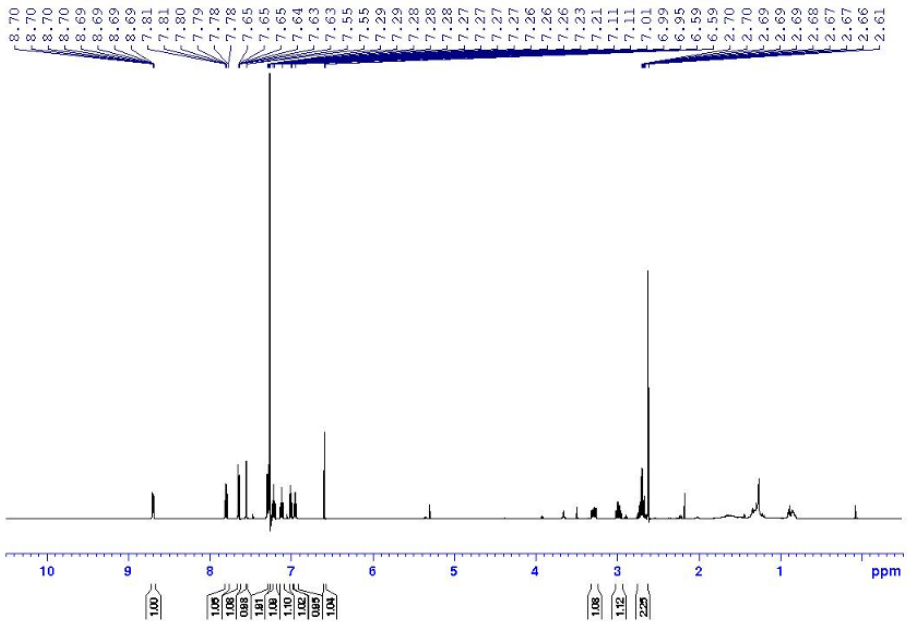
Isolated Yield: 20%

^{1}H NMR (500MHz, Chloroform-*d*): δ 8.70-8.68 (m, 1H), 7.79 (td, J = 7.9, 1.8 Hz, 1H), 7.64 (dt, J = 7.9, 1.1 Hz, 1H), 7.54 (d, J = 1.8 Hz, 1H), 7.29-7.25 (m, 2H), 7.22-7.19 (m, 1H), 7.12-7.09 (m, 1H), 7.00 (d, J = 7.7 Hz, 1H), 6.94 (t, J = 7.6 Hz, 1H), 6.59 (d, J = 1.9 Hz, 1H), 3.31-3.25 (m, 1H), 3.01-2.94 (m, 1H), 2.74-2.64 (m, 2H).

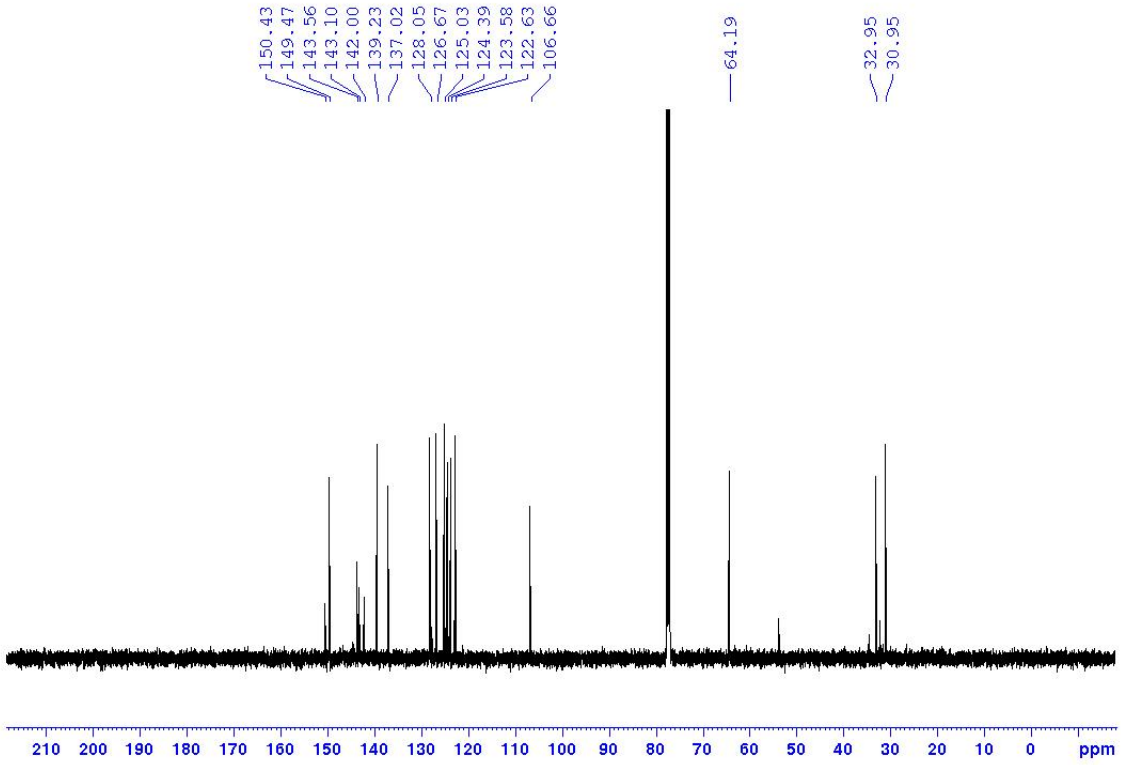
^{13}C NMR (126MHz, Chloroform-*d*): δ 150.4, 149.4, 143.5, 143.0, 142.0, 139.2, 137.0, 128.0, 126.6, 125.0, 124.3, 123.5, 122.6, 106.6, 64.1, 32.9, 30.9

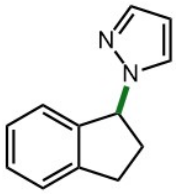
HRMS (ESI): calculated $[M+H]^+$ as 262.1339, found 262.1338.

^{1}H NMR:



^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazole (**19**)

Synthesized according to the general procedure B for heterocycle addition with indane (61.3 μL, 0.500 mmol, 1 equiv.), Ir(dFppy)$_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 1*H*-pyrazole (102.1 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 53 mg pure product.

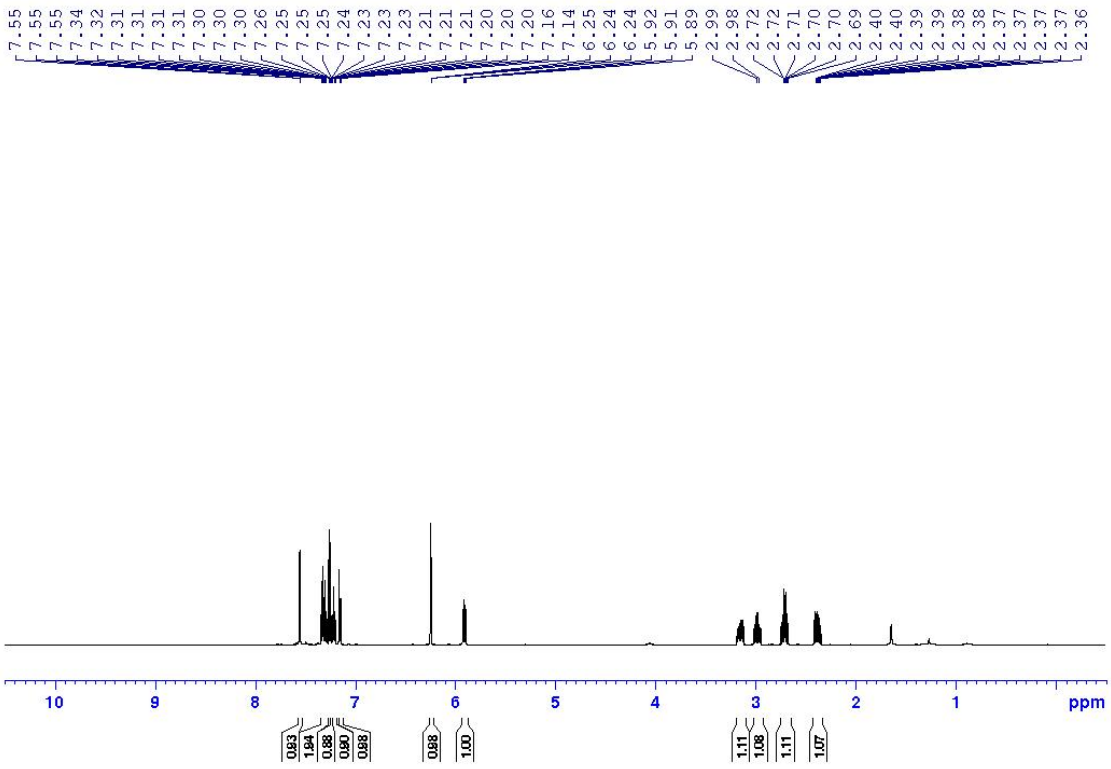
Isolated Yield: 55%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.55-7.54 (m, 1H), 7.33-7.28 (s, 1H), 7.24 (dd, J = 1.9, 0.5 Hz, 1H), 7.22-7.19 (m, 1H), 7.15 (d, J = 7.6 Hz, 1H), 6.24 (t, J = 2.1 Hz, 1H), 5.90 (t, J = 7.3 Hz, 1H), 3.17-3.11 (m, 1H), 3.00-2.94 (m, 1H), 2.73-2.66 (m, 1H), 2.41-2.34 (m, 1H).

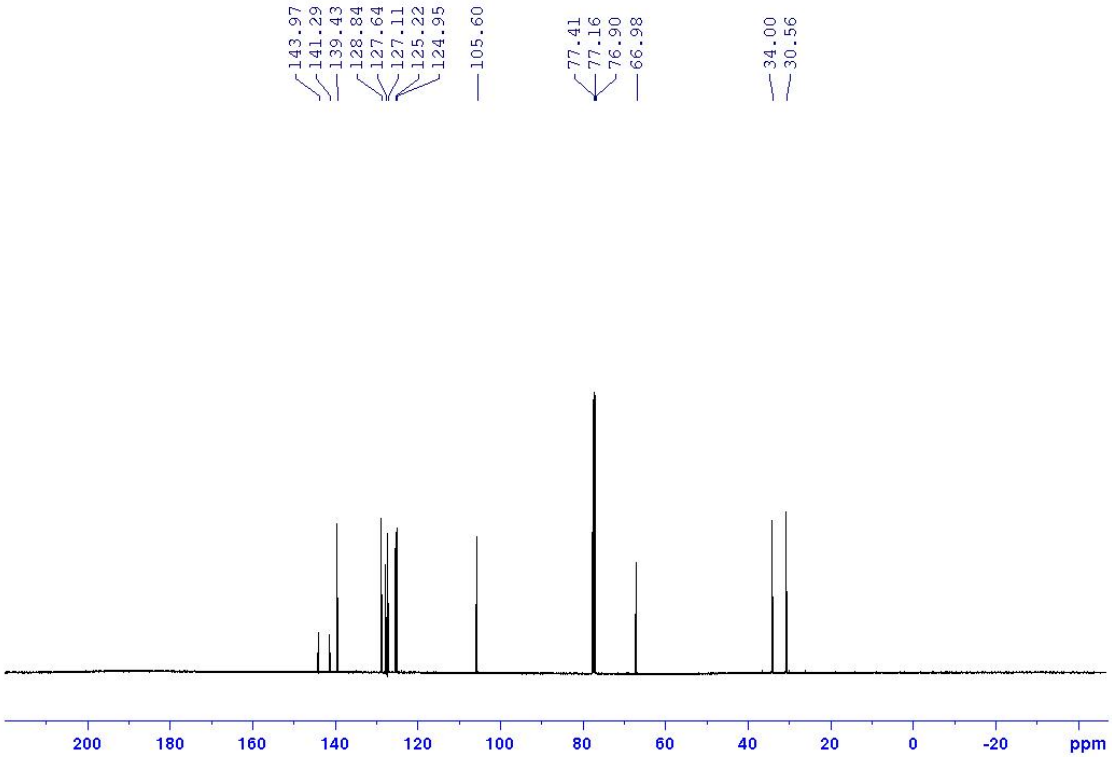
^{13}C NMR (126MHz, Chloroform-*d*): δ 143.9, 141.3, 139.4, 128.8, 127.6, 127.1, 125.2, 124.9, 105.6, 66.9, 34.0, 30.6.

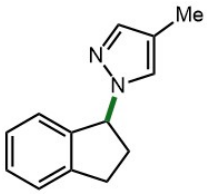
HRMS (ESI): calculated $[M+H]^+$ as 185.1073, found 185.1072.

^{1}H NMR:



^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-4-methyl-1H-pyrazole (**20**)

Synthesized according to the general procedure B for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-methyl-1*H*-pyrazole (124.0 µL, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 43 mg pure product.

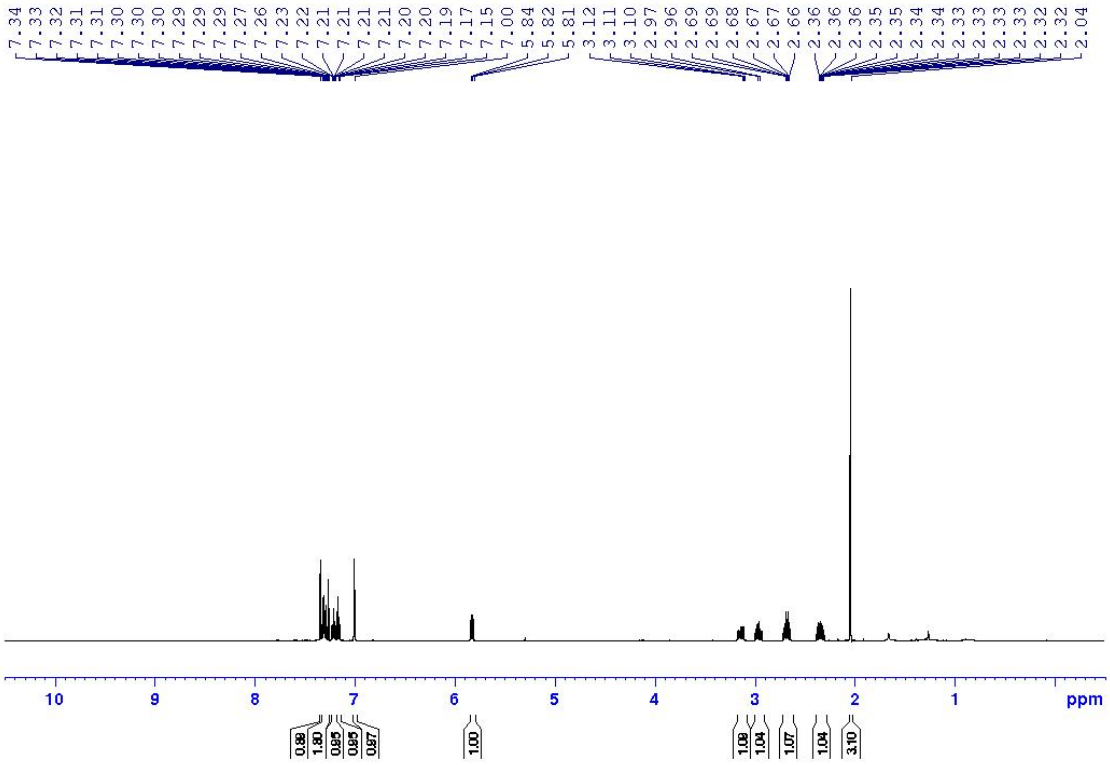
Isolated Yield: 43%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.34 (s, 1H), 7.32-7.27 (m, 2H), 7.22-7.19 (m, 1H), 7.16 (d, J = 7.5 Hz, 1H), 7.00 (t, J = 0.6 Hz, 1H), 5.82 (t, J = 7.2 Hz, 1H), 3.16-3.10 (m, 1H), 2.98-2.92 (m, 1H), 2.70-2.63 (m, 1H), 2.37-2.30 (m, 1H), 2.03 (s, 3H).

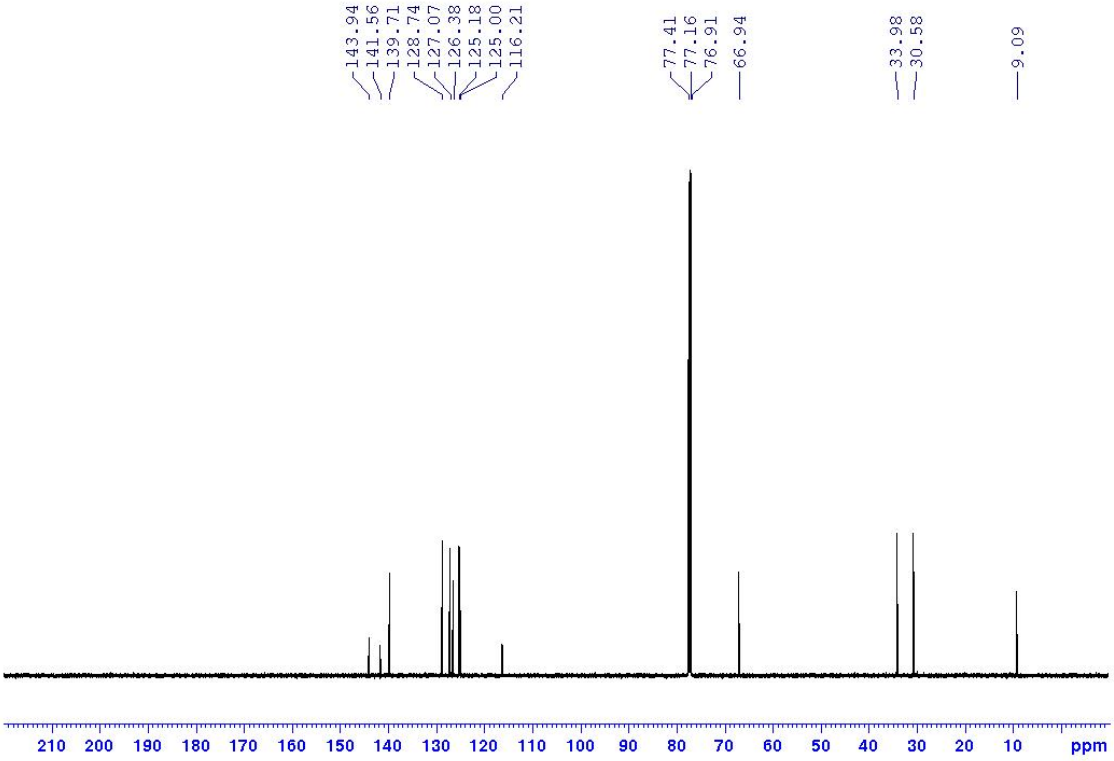
^{13}C NMR (126MHz, Chloroform-*d*): δ 143.9, 141.5, 139.7, 128.7, 127.1, 126.4 125.2, 125.0, 116.2, 66.9, 33.9, 30.6, 9.1.

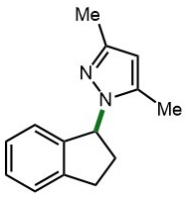
HRMS (ESI): calculated $[M+H]^+$ as 199.1230, found 199.1231.

^{1}H NMR:



^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-3,5-dimethyl-1H-pyrazole (**21**)

Synthesized according to the general procedure B for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 3,5-dimethyl-1*H*-pyrazole (144.2 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 72 hr. Purification with flash chromatography (8% ethyl acetate in hexanes, silica gel) afforded 68 mg pure product.

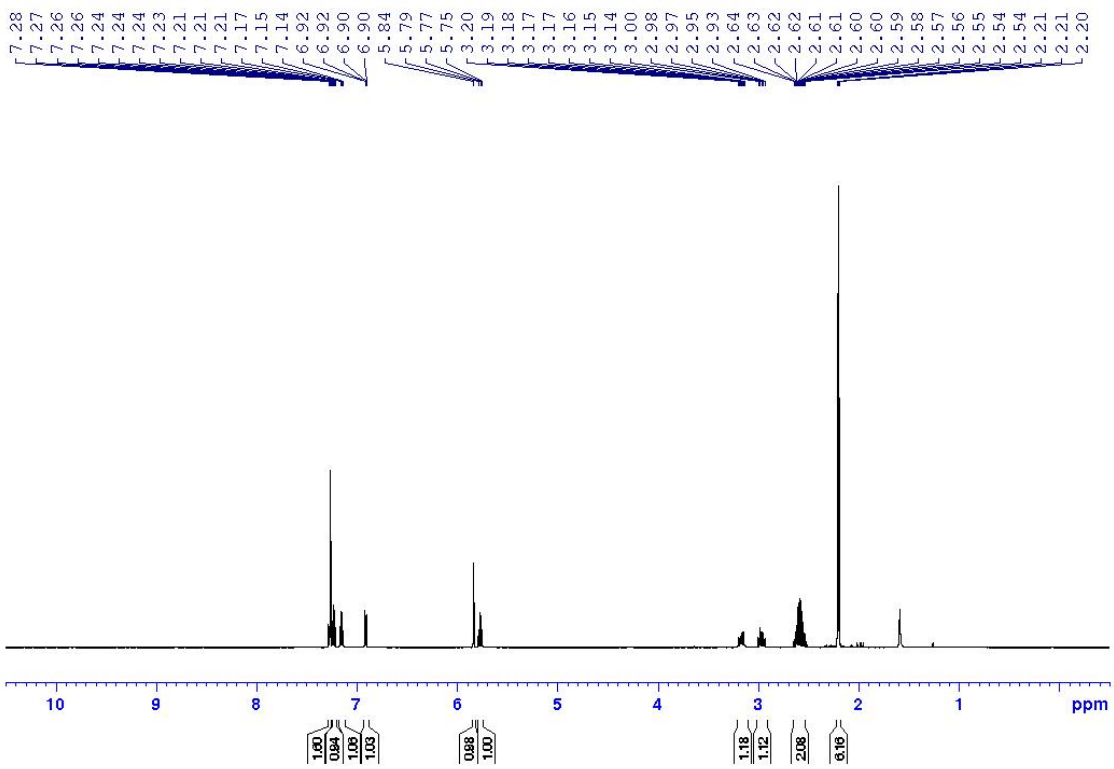
Isolated Yield: 64%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.28-7.26 (m, 1H), 7.24-7.21 (m, 1H), 7.15 (t, J = 7.4 Hz, 1H), 6.91 (dd, J = 7.5, 0.5 Hz, 1H), 5.83 (s, 1H), 5.76 (t, J = 8.4 Hz, 1H), 3.19-3.14 (m, 1H), 2.99-2.93 (m, 1H), 2.64-2.51 (m, 2H),2.20 (s, 3H), 2.19 (s, 3H).

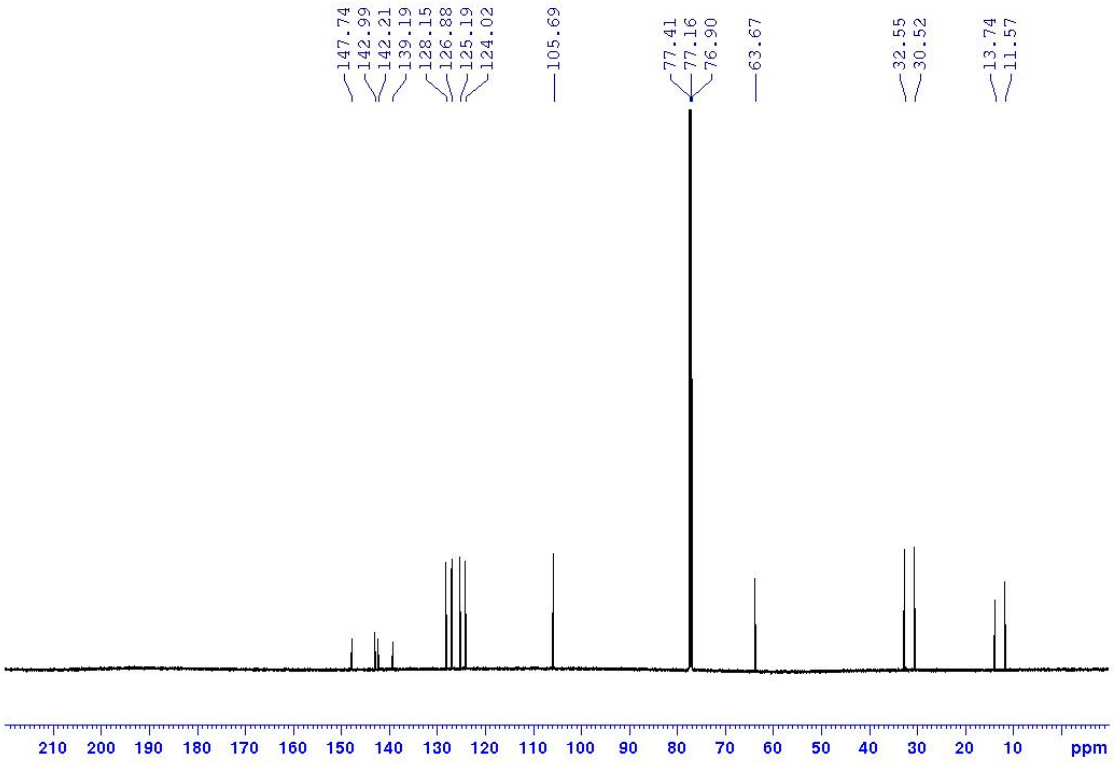
^{13}C NMR (126MHz, Chloroform-*d*): δ 147.7, 142.9, 142.2, 139.2, 128.2, 126.9, 125.2, 124.0, 105.7, 63.7, 32.5, 30.5, 13.7, 11.6.

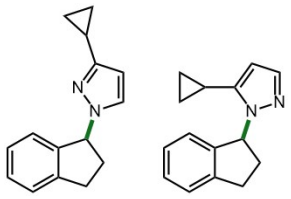
HRMS (ESI): calculated $[M+H]^+$ as 213.1386, found 213.1385.

^{1}H NMR:



^{13}C NMR:





3-cyclopropyl-1-(2,3-dihydro-1H-inden-1-yl)-1H-pyrazole (**22**)

Synthesized according to the general procedure B for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 3-cyclopropyl-1*H*-pyrazole (162.2 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 35 mg pure product (Regio isomeric mixture).

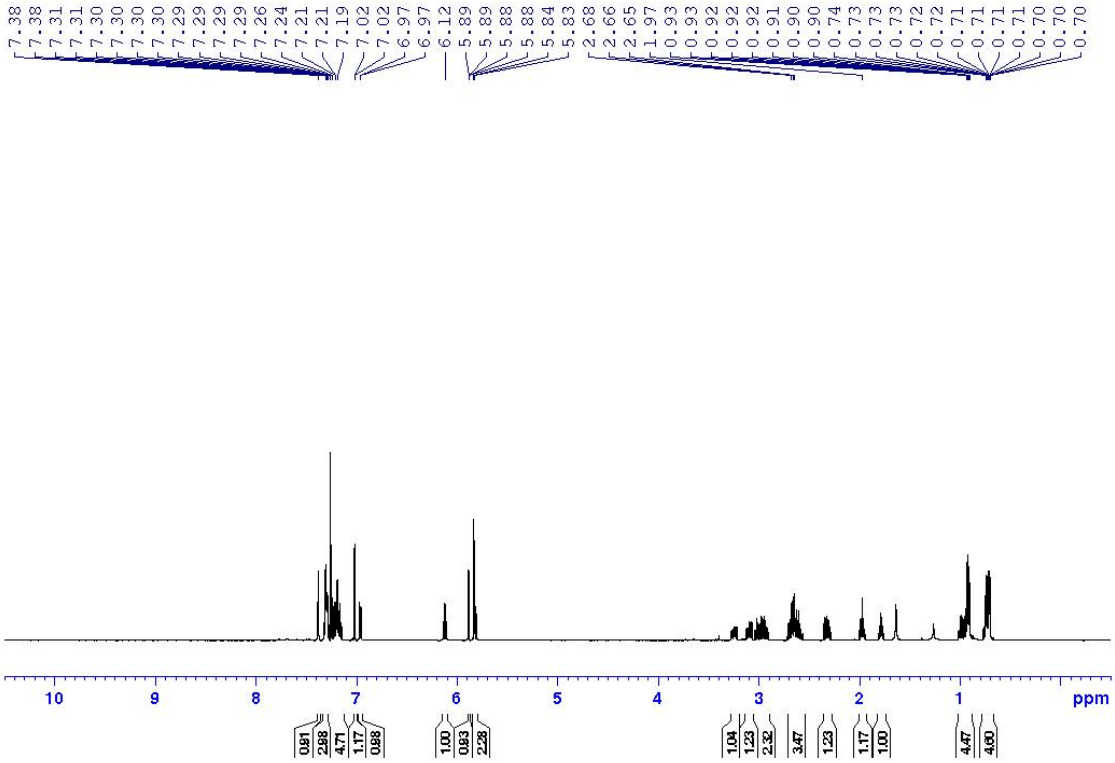
Isolated Yield: 31% (1.2:1)

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.38 (d, J = 1.8 Hz, 1H), 7.32-7.28 (m, 3H), 7.27-7.15 (m, 4H), 7.02 (d, J = 2.3 Hz, 1H), 6.95 (dd, J = 7.5, 0.4 Hz, 1H), 6.11 (t, J = 7.9 Hz, 1H), 5.88 (dd, J = 1.8, 0.7 Hz, 1H), 5.83-5.80 (m, 2H), 3.26-3.21 (m, 1H), 3.12-3.06 (m, 1H), 3.03-2.90 (m, 2H), 2.71-2.56 (m, 3H), 2.35-2.28 (m, 1H), 1.99-1.94 (m, 1H), 1.80-1.75 (m, 1H), 1.01-0.89 (m, 4H), 0.77-0.69 (m, 4H).

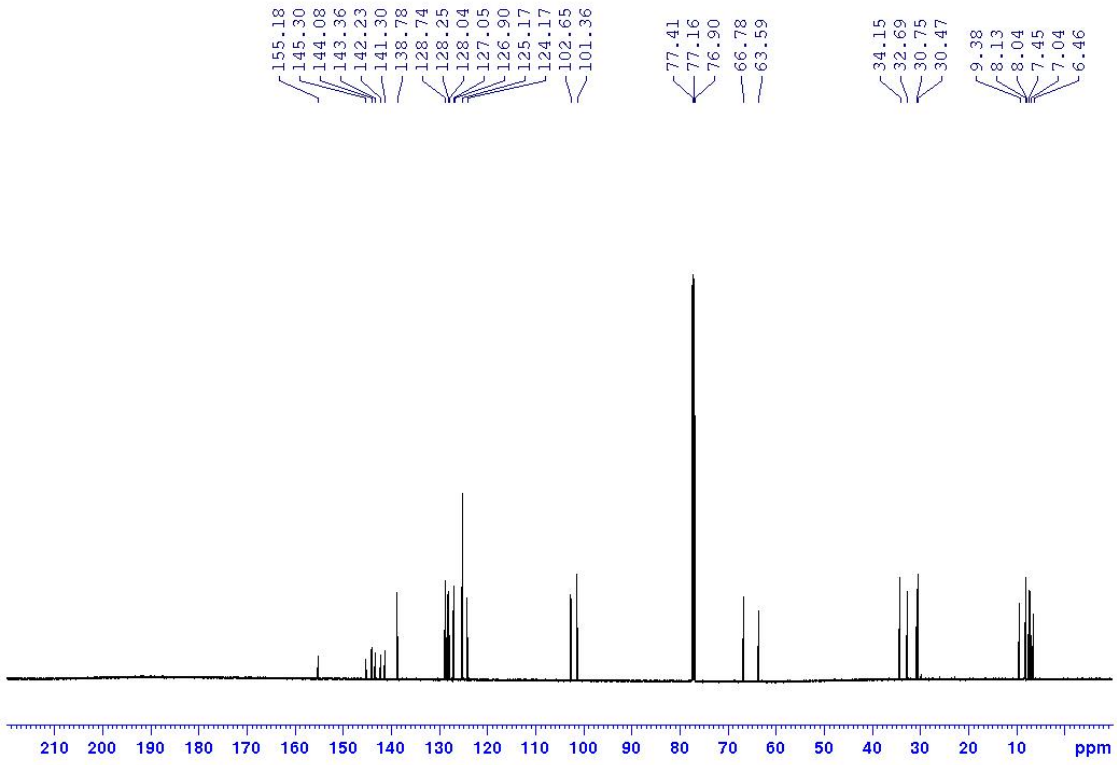
^{13}C NMR (126MHz, Chloroform-*d*): δ 155.2, 145.3, 144.1, 143.4, 142.2, 141.3, 138.8, 128.7, 128.2, 128.0, 127.1, 126.9, 125.2, 124.2, 102.7, 101.4, 66.8, 63.6, 34.2, 32.7, 30.7, 30.5, 9.4, 8.1, 8.0, 7.5, 7.0, 6.5.

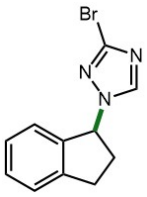
HRMS (ESI): calculated $[M+H]^+$ as 225.1386, found 225.1383.

^{1}H NMR:



^{13}C NMR:





3-bromo-1-(2,3-dihydro-1H-inden-1-yl)-1H-1,2,4-triazole (**23**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 3-bromo-1*H*-1,2,4-triazole (221.9 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (10-12% ethyl acetate in hexanes, silica gel) afforded 95 mg pure product.

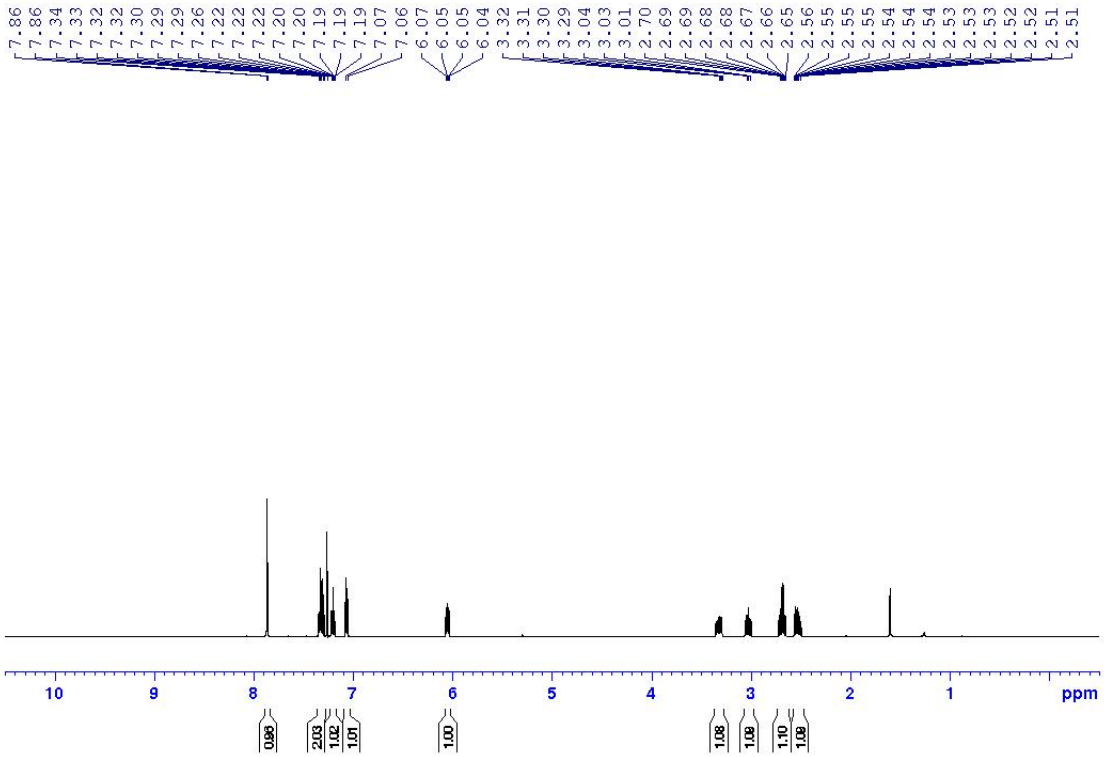
Isolated Yield: 72%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.86 (d, J = 0.4 Hz, 1H), 7.34-7.28 (m, 2H), 7.21-7.18 (m, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.05 (dd, J = 8.0, 6.2 Hz, 1H), 3.35-3.29 (m, 1H), 3.05-2.99 (m, 1H), 2.72-2.65 (m, 1H), 2.56-2.49 (m, 1H).

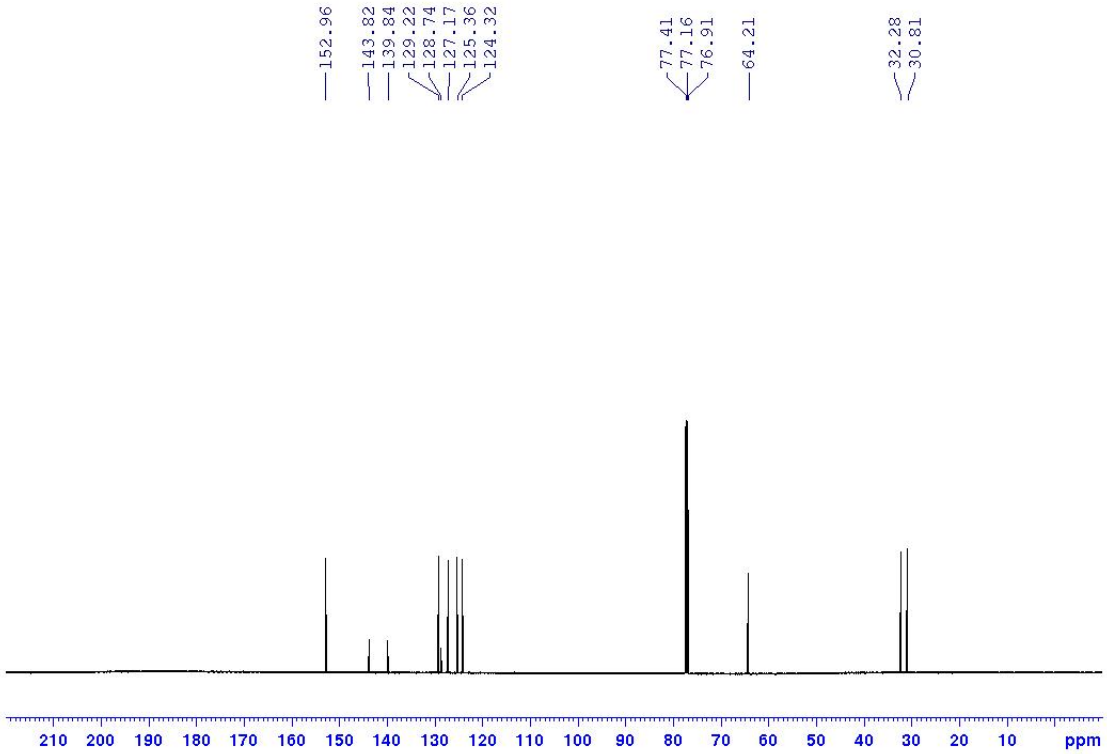
^{13}C NMR (126MHz, Chloroform-*d*): δ 152.9, 143.8, 139.8, 129.2, 128.7, 127.2, 125.3, 124.3, 64.2, 32.3, 30.8.

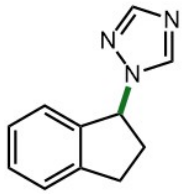
HRMS (ESI): calculated $[M+H]^+$ as 264.0136, found 264.0110

^{1}H NMR:



^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-1H-1,2,4-triazole (**24**)

Synthesized according to the general procedure B for heterocycle addition with indane (61.3 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 1*H*-1,2,4-triazole (103.6 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (15% ethyl acetate in hexanes, silica gel) afforded 44 mg pure product.

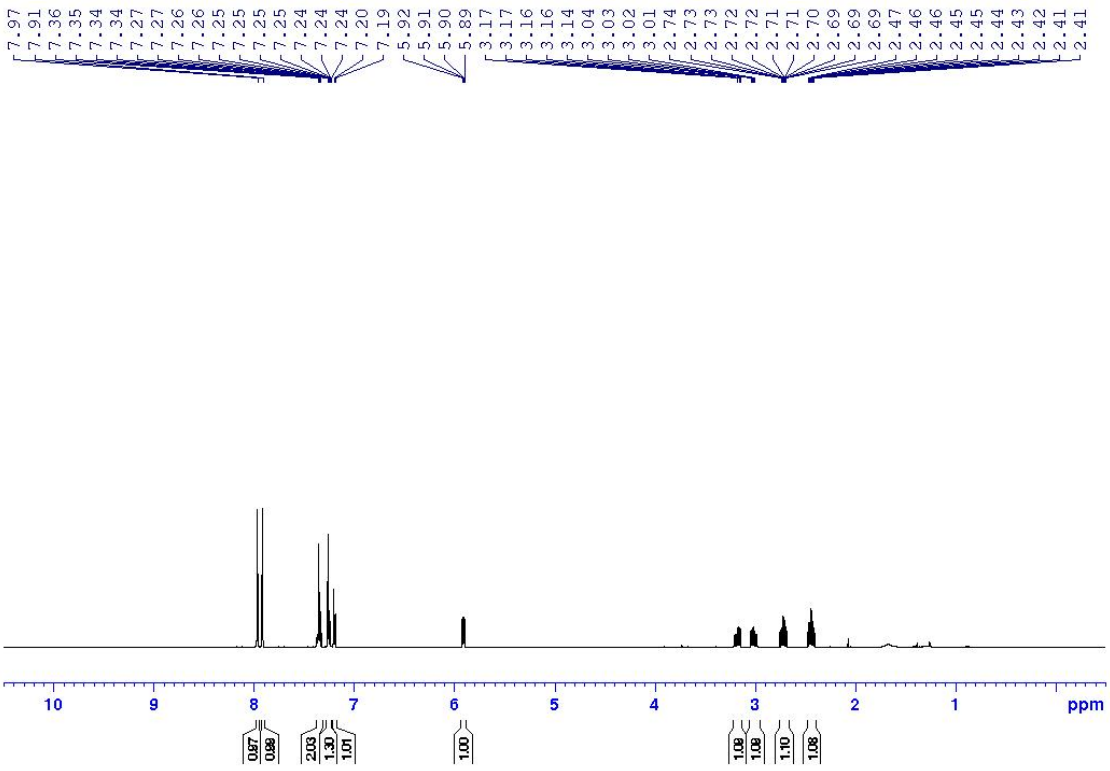
Isolated Yield: 47%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.96 (s, 1H), 7.91 (s, 1H), 7.37-7.32 (m, 2H), 7.26-7.23 (m, 1H), 7.19 (d, J = 7.6 Hz, 1H), 5.90 (dd, J = 7.9, 5.1 Hz, 1H), 3.20-3.14 (m, 1H), 3.03-2.97 (m, 1H), 2.74-2.67 (m, 1H), 2.46-2.40 (m, 1H).

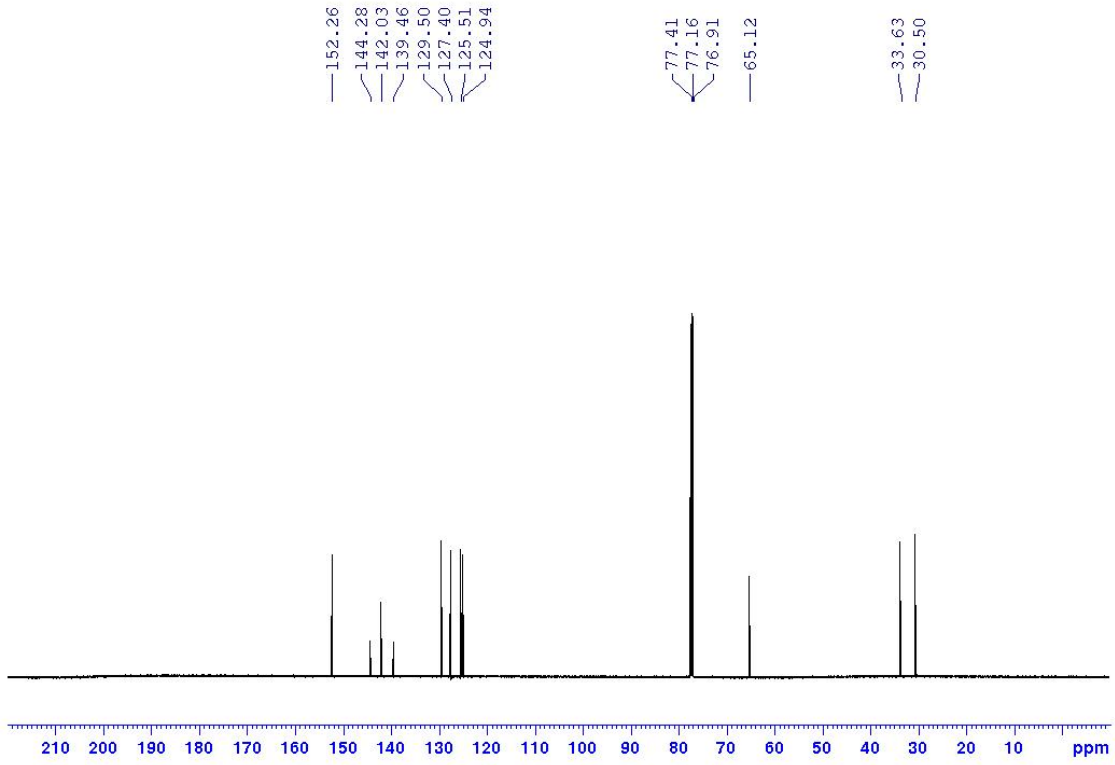
^{13}C NMR (126MHz, Chloroform-*d*): δ 152.2, 144.3, 142.0, 139.4, 129.5, 127.4, 125.5, 124.9, 65.1, 33.6, 30.5.

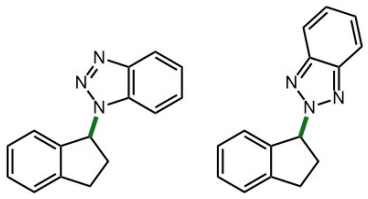
HRMS (ESI): calculated $[M+H]^+$ as 186.1026, found 186.1027.

^{1}H NMR:



^{13}C NMR:





1-(2,3-dihydro-1H-inden-1-yl)-1H-benzo[d][1,2,3]triazole (**25**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 1*H*-benzo[*d*][1,2,3]triazole (178.7 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (10-15% ethyl acetate in hexanes, silica gel) afforded 83 mg pure product.

Isolated Yield: 70% (1:2)

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.87-7.83 (m, 2H), 7.37-7.34 (m, 3H), 7.32-7.29 (m, 1H), 7.20-7.15 (m, 2H), 6.48 (dd, J = 7.3, 6.8 Hz, 1H), 3.48-3.42 (m, 1H), 3.14-3.08 (m, 1H), 2.91-2.81 (m, 2H).

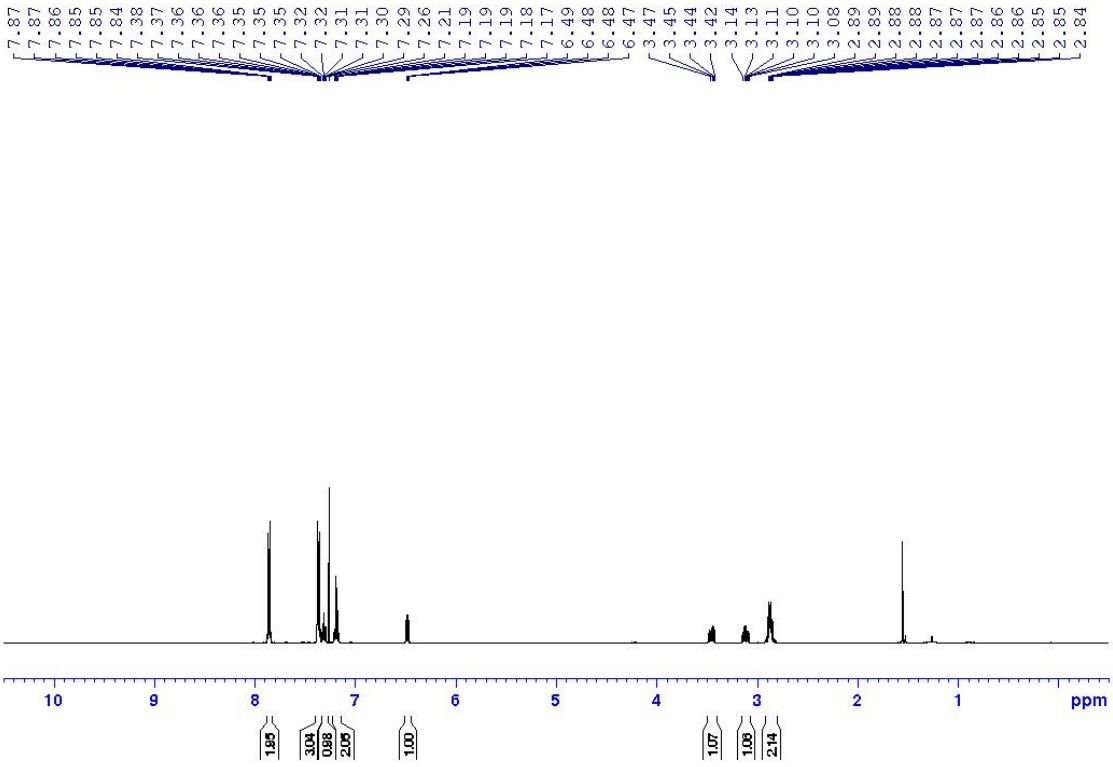
^{13}C NMR (126MHz, Chloroform-*d*): δ 144.5, 144.1, 140.6, 129.2, 127.1, 126.3, 125.3, 124.9, 118.3, 71.4, 32.9, 31.1.

^{1}H NMR (500MHz, Chloroform-*d*): δ 8.07-8.05 (m, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.36-7.26 (m, 3H), 7.18-7.15 (m, 1H), 7.00 (d, J = 7.7 Hz, 1H), 6.92-6.90 (m, 1H), 6.65 (t, J = 7.7 Hz, 1H), 3.35-3.29 (m, 1H), 3.18-3.12 (m, 1H), 2.91-2.84 (m, 1H), 2.58-2.50 (M, 1H).

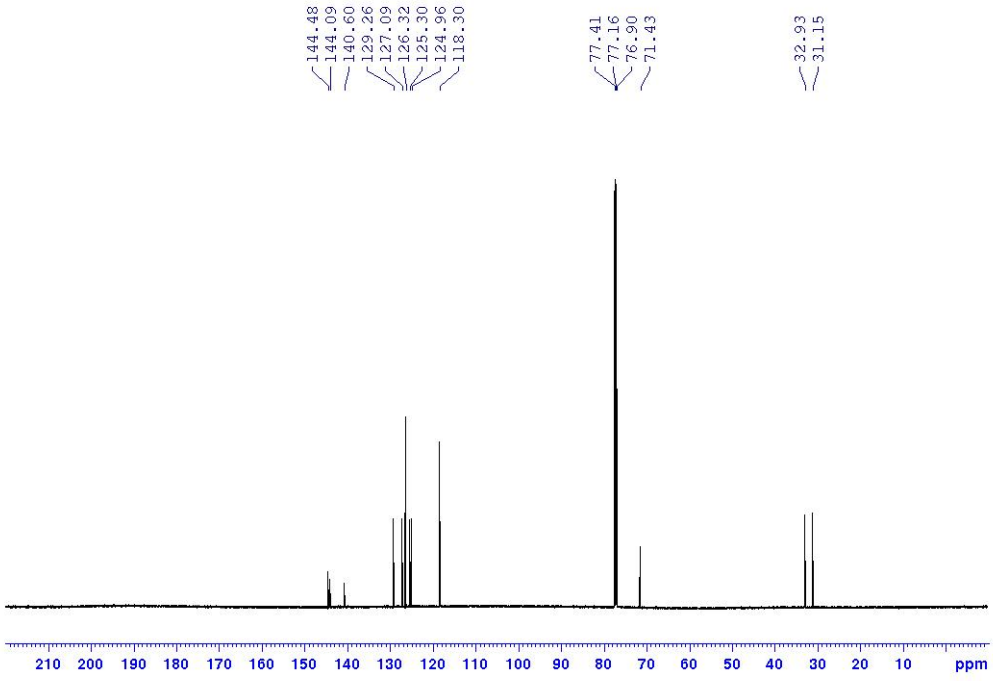
^{13}C NMR (126MHz, Chloroform-*d*): δ 146.9, 143.7, 139.4, 131.8, 129.3, 127.3, 125.4, 124.9, 123.9, 120.3, 110.5, 65.0, 32.7, 30.9.

HRMS (ESI): calculated $[M+H]^+$ as 236.1182, found 236.1182.

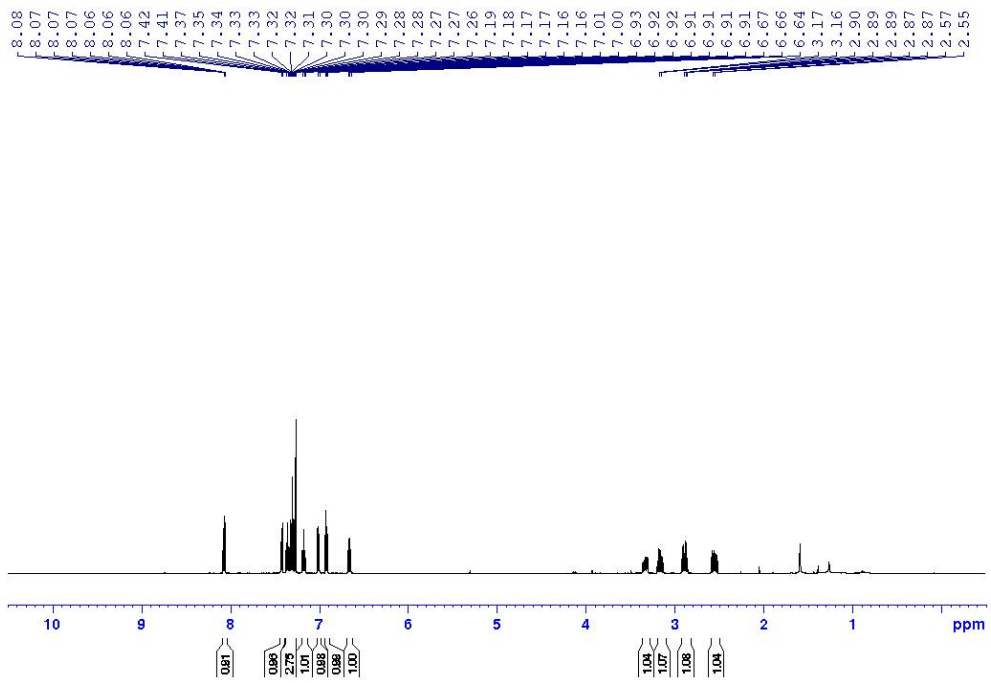
^{1}H NMR:



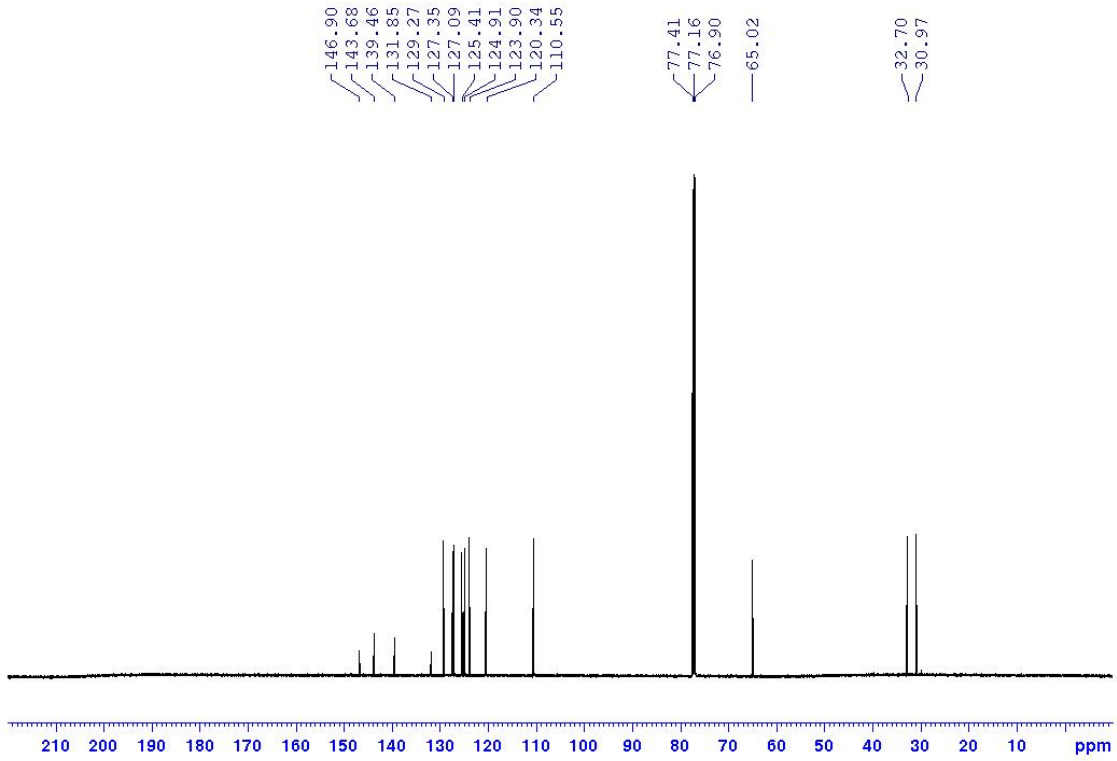
^{13}C NMR:

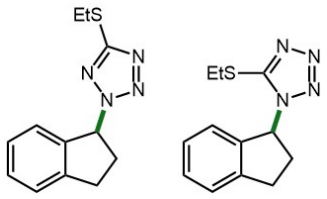


^{1}H NMR:



^{13}C NMR:





2-(2,3-dihydro-1H-inden-1-yl)-5-(ethylthio)-2H-tetrazole (**26**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), Ir(dFppy)$_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 5-(ethylthio)-2H-tetrazole (195.3 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 72 hr. Purification with flash chromatography (7-12% ethyl acetate in hexanes, silica gel) afforded 105 mg pure product.

Isolated Yield: 85% (1.2:1)

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.34-7.30 (m, 2H), 7.23-7.18 (m, 2H), 6.34 (dd, J = 7.5 5.6 Hz, 1H), 3.40-3.33 (m, 1H), 3.17 (q, J = 7.4 Hz, 2H), 3.09-3.03 (m, 1H), 2.80-2.70 (m, 2H), 1.39 (t, J = 7.4 Hz, 3H).

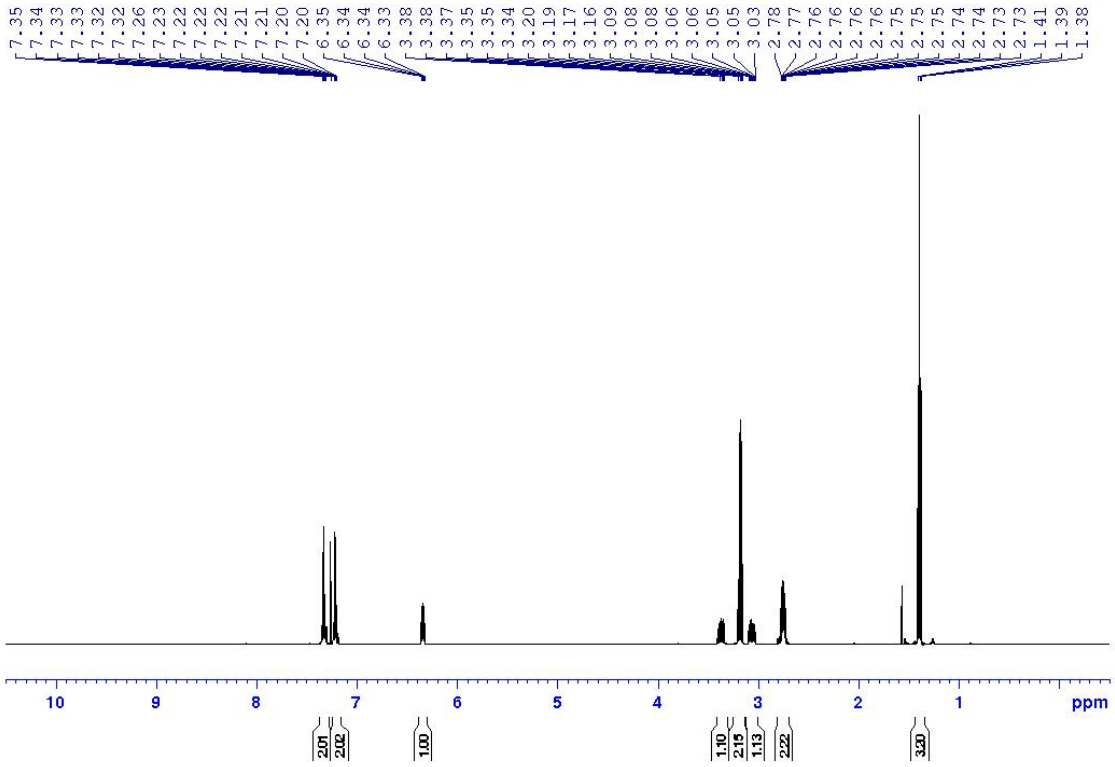
^{13}C NMR (126MHz, Chloroform-*d*): δ 164.3, 144.2, 139.1, 129.6, 127.2, 125.3, 124.9, 68.7, 32.0, 30.9, 26.6, 15.0.

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.35-7.31 (m, 2H), 7.21-7.18 (m, 1H), 7.08 (d, J = 7.7 Hz, 1H), 6.03 (dd, J = 8.4, 5.8 Hz, 1H), 3.41-3.30 (m, 2H), 3.08-3.02 (m, 1H), 2.76-2.69 (m, 1H), 2.58-2.52 (m, 1H), 1.46 (t, J = 7.4 Hz, 3H).

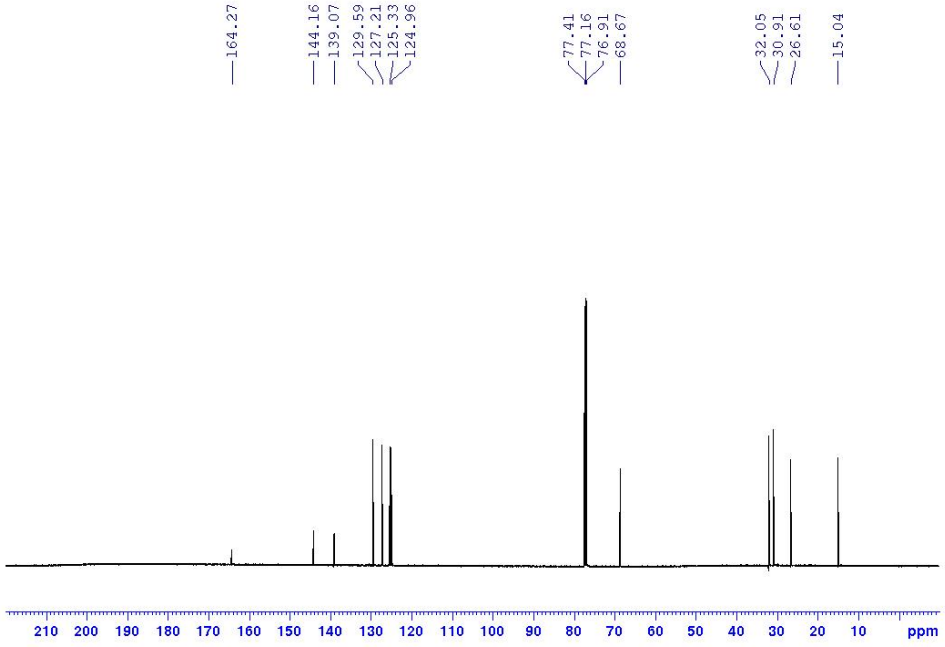
^{13}C NMR (126MHz, Chloroform-*d*): δ 153.4, 144.1, 138.6, 129.6, 127.3, 125.4, 124.7, 63.3, 32.1, 30.9, 27.9, 14.9.

HRMS (ESI): calculated $[M+H]^+$ as 247.1012, found 247.1009.

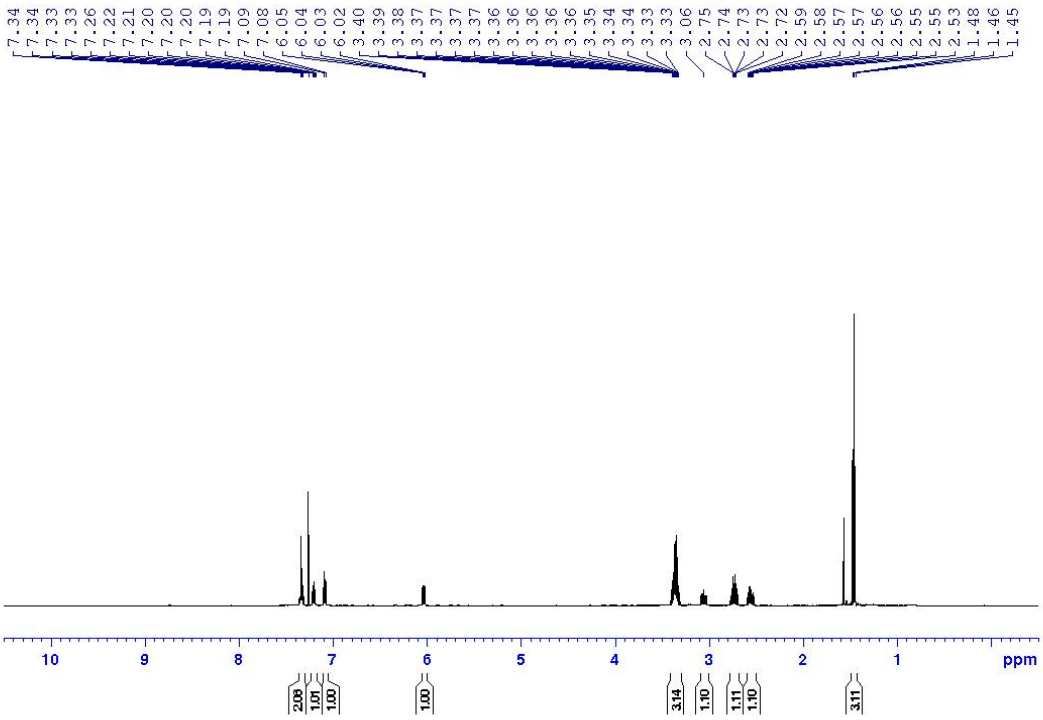
^{1}H NMR:



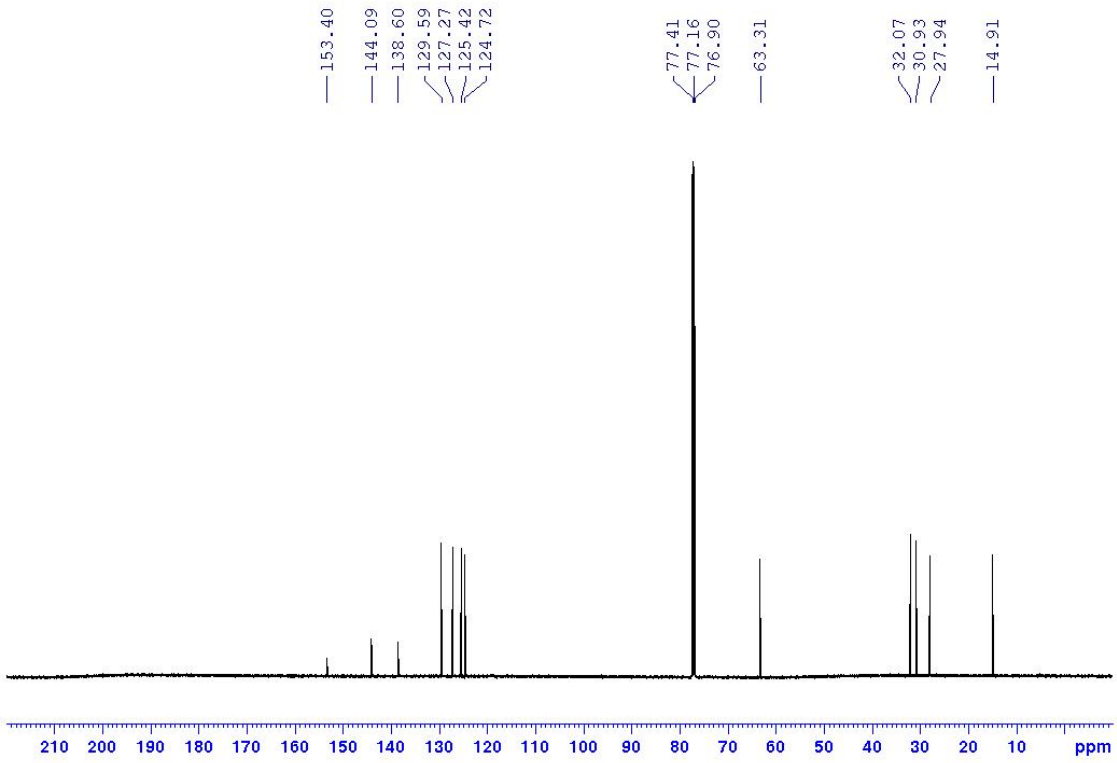
^{13}C NMR:

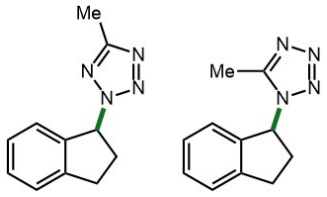


^{1}H NMR:



^{13}C NMR:





2-(2,3-dihydro-1H-inden-1-yl)-5-methyl-2H-tetrazole (**27**)[7]

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 5-methyl-2*H*-tetrazole (126.1 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 72 hr. Purification with flash chromatography (10-50% ethyl acetate in hexanes, silica gel) afforded 77 mg pure product.

Isolated Yield: 78% (1.5:1)

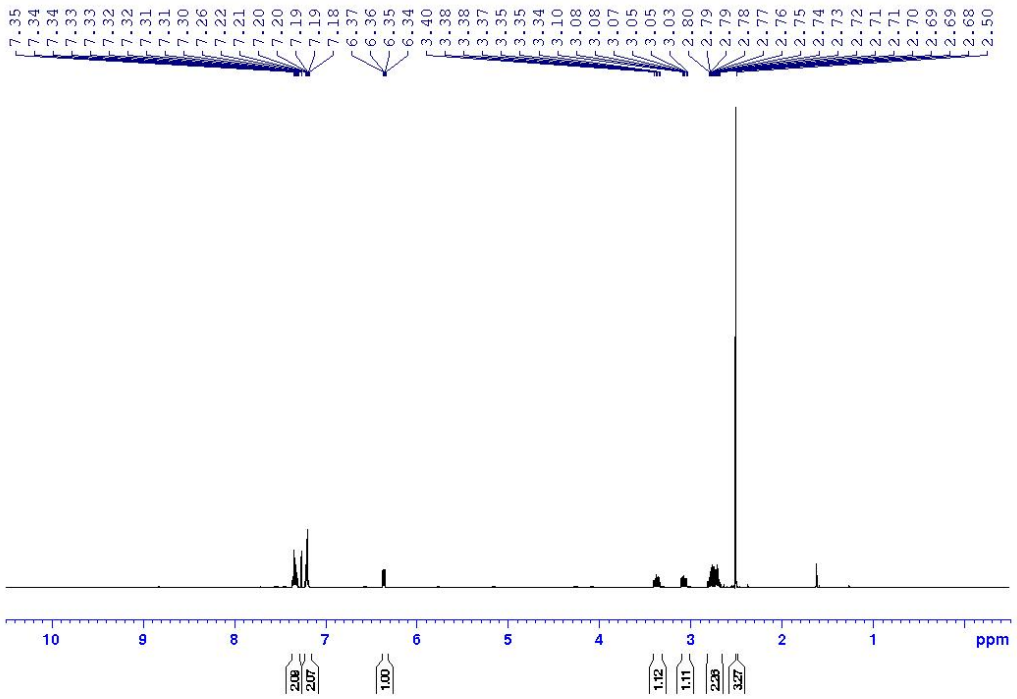
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.36-7.30 (m, 2H), 7.22-7.18 (m, 2H), 6.35 (dd, J = 7.9, 5.2 Hz, 1H), 3.39-3.33 (m, 1H), 3.09-3.03 (m, 1H), 2.80-2.66 (m, 2H), 2.49 (s, 3H).

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.36-7.31 (m, 2H), 7.21 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 6.12 (dd, J = 8.2, 6.5 Hz, 1H), 3.11-3.04 (m, 1H), 2.82-2.75 (m, 1H), 2.48-2.39 (m, 1H), 2.42 (s, 3H).

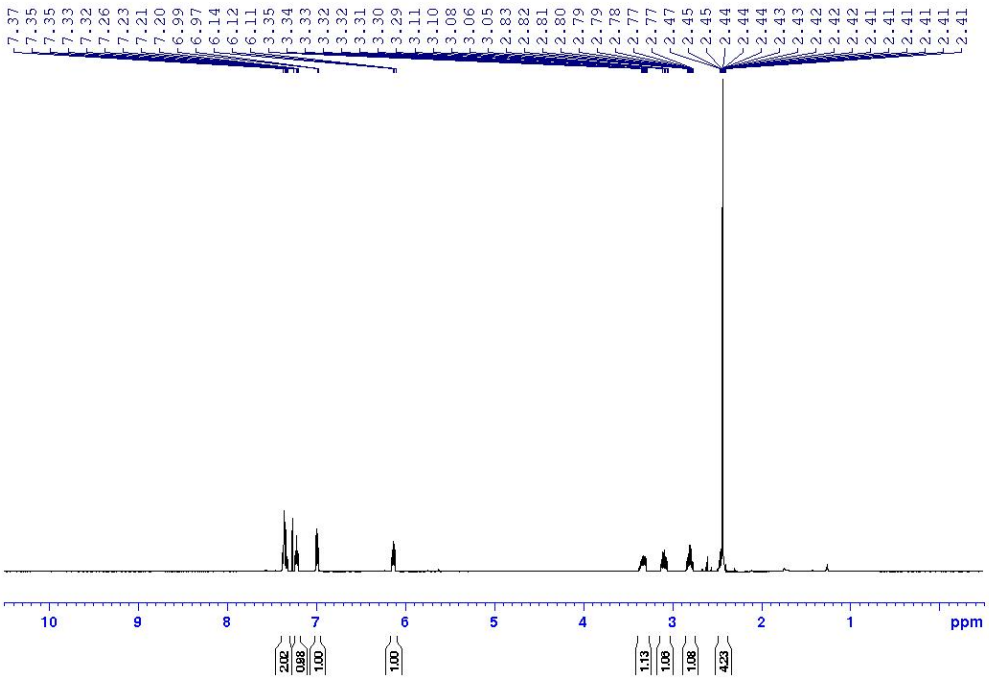
^{13}C NMR (126MHz, Chloroform-*d*): δ 151.0, 143.7, 138.6, 129.6, 127.5, 125.5, 124.2, 63.2, 32.7, 30.7, 9.6.

HRMS (ESI): calculated $[M+H]^+$ as 201.1135, found 201.1134.

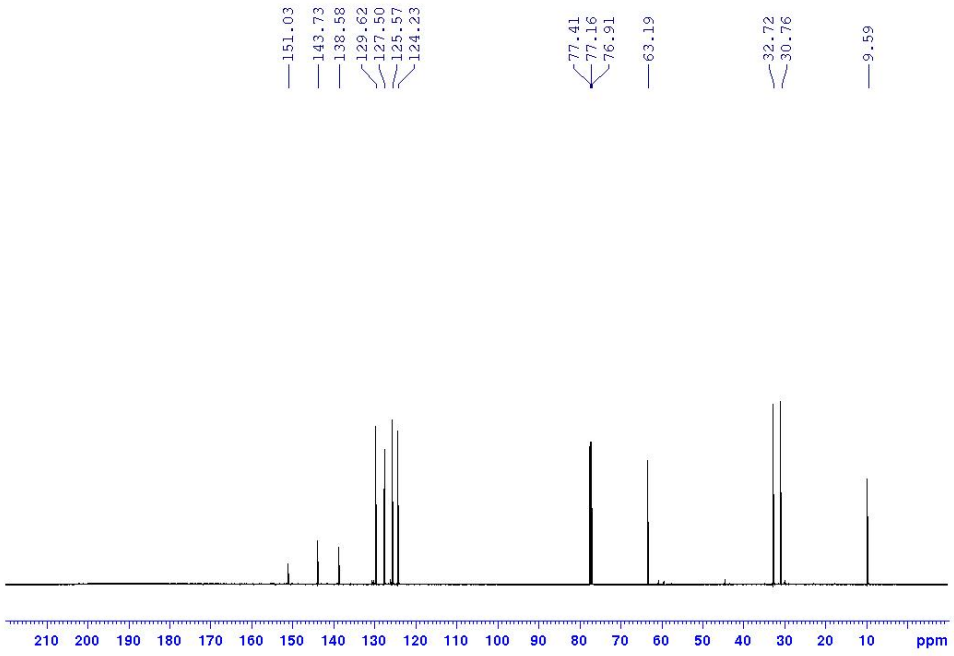
^{1}H NMR:

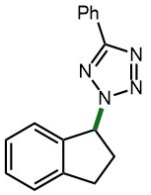


^{1}H NMR:



^{13}C NMR:





2-(2,3-dihydro-1H-inden-1-yl)-5-phenyl-2H-tetrazole (**28**)

Synthesized according to the general procedure A for heterocycle addition with indane (61.3 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 5-phenyl-2*H*-tetrazole (219.2 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (7% ethyl acetate in hexanes, silica gel) afforded 115 mg pure product.

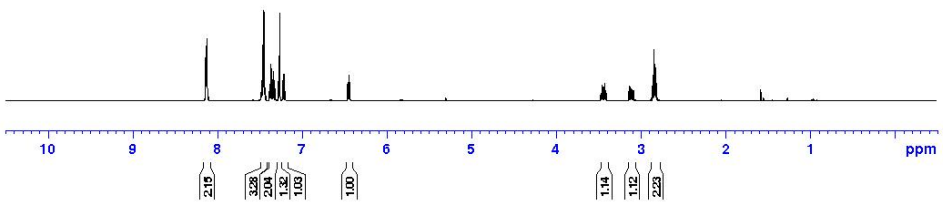
Isolated Yield: 88%

^{1}H NMR (500MHz, Chloroform-*d*): δ 8.13-8.11 (m, 2H), 7.47-7.43 (m, 3H), 7.37 (d, J = 7.6 Hz, 1H), 7.34-7.31 (m, 1H), 7.27-7.25 (m, 1H), 7.22-7.19 9m, 1H), 6.44 (t, J = 6.8 Hz, 1H), 3.43 (dt, J = 16, 7.1 Hz, 1H), 3.13-3.07 9m, 1H), 2.85-2.80 (m, 2H).

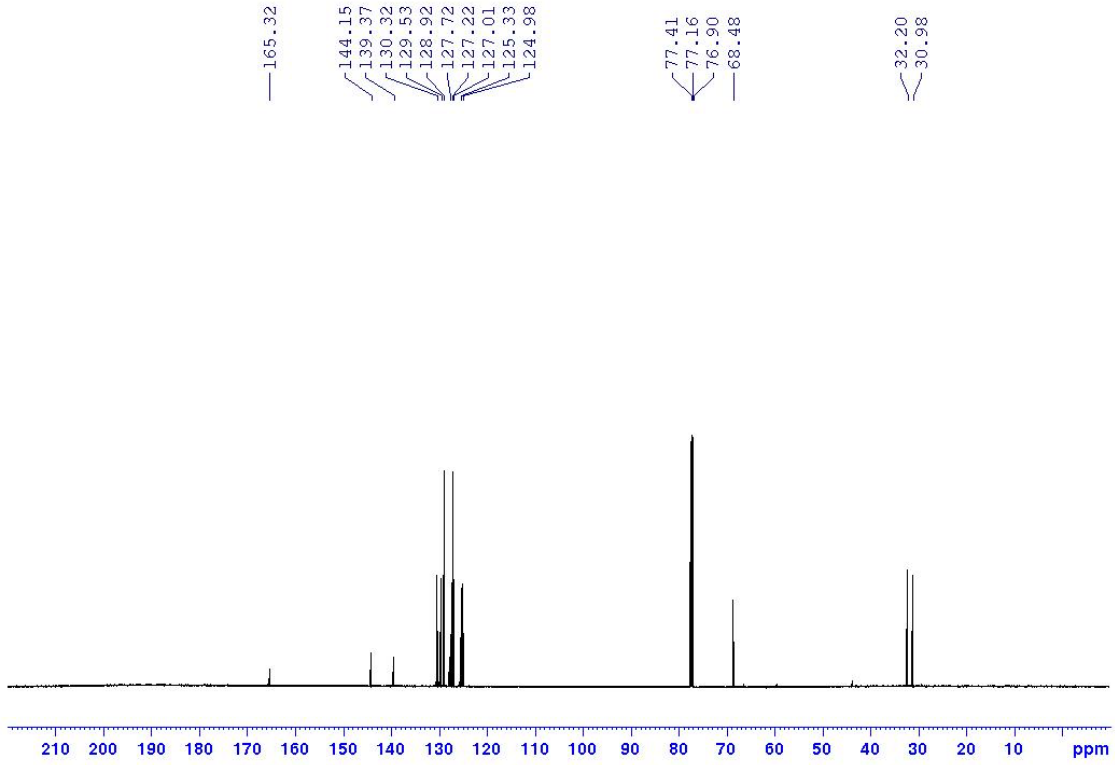
^{13}C NMR (126MHz, Chloroform-*d*): δ 165.3, 144.1, 139.4, 130.3, 129.5, 128.9, 127.7, 127.2, 127.0, 125.3, 124.9, 68.5, 32.2, 30.9.

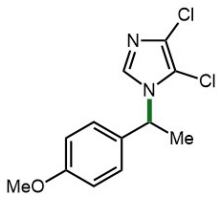
HRMS (ESI): calculated $[M+H]^+$ as 263.1291, found 263.1290.

^{1}H NMR:



^{13}C NMR:





4,5-dichloro-1-(1-(4-methoxyphenyl)ethyl)-1H-imidazole (**29**)

Synthesized according to the general procedure C for heterocycle addition with 1-ethyl-4-methoxybenzene (71.1 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4,5-dichloro-1*H*-imidazole (205.4 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (20% ethyl acetate in hexanes, silica gel) afforded 110 mg pure product.

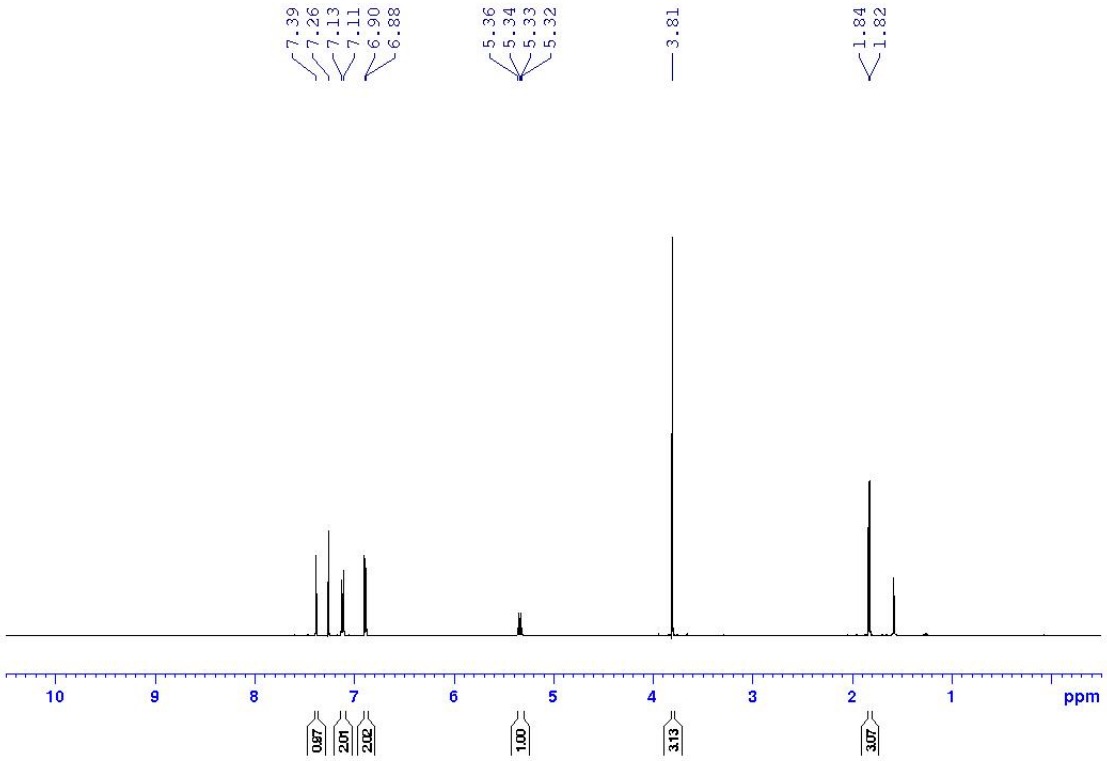
Isolated Yield: 80%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.38 (s, 1H), 7.13-7.10 (m ,2H), 6.90-6.87 (m, 2H), 5.33 (q, J = 7.1 Hz, 1H), 3.80 (s, 3H), 1.82 (d, J = 7.1 Hz).

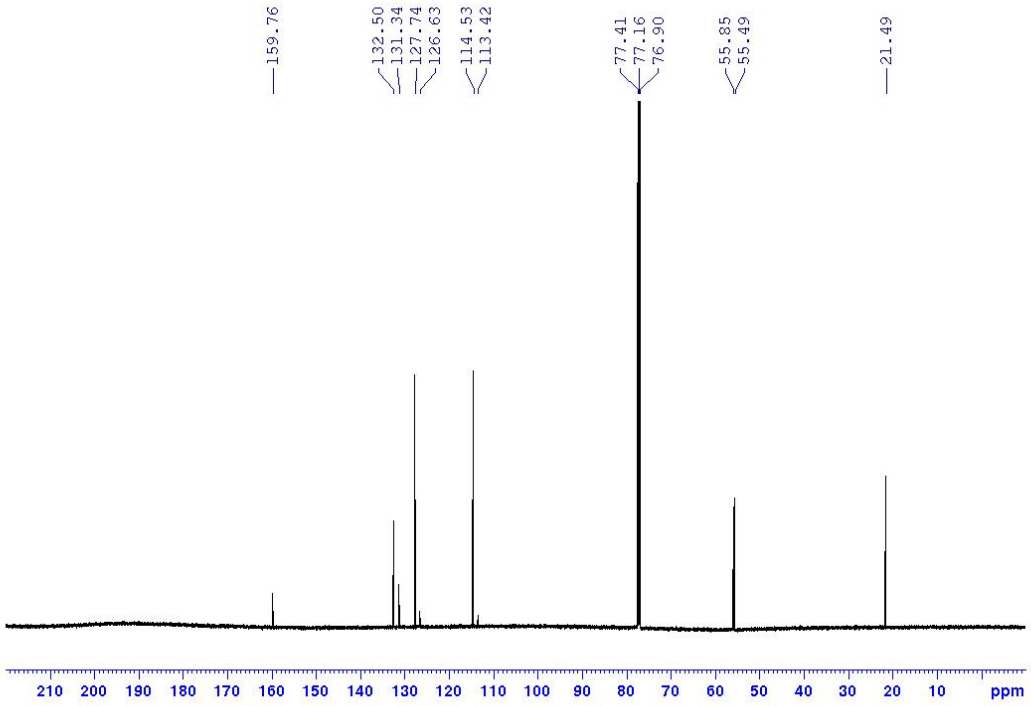
^{13}C NMR (126MHz, Chloroform-*d*): δ 159.7, 132.5, 131.3, 127.7, 126.6, 114.5, 113.4, 55.8, 55.5, 21.5.

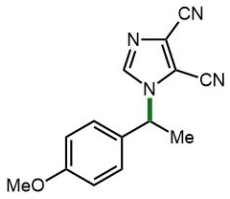
HRMS (ESI): calculated $[M+H]^+$ as 271.0399, found 271.0399.

^{1}H NMR:



^{13}C NMR:





1-(1-(4-methoxyphenyl)ethyl)-1H-imidazole-4,5-dicarbonitrile (**30**)

Synthesized according to the general procedure C for heterocycle addition with 1-ethyl-4-methoxybenzene (71.1 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 1*H*-imidazole-4,5-dicarbonitrile (177.2 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 72 hr. Purification with flash chromatography (30% ethyl acetate in hexanes, silica gel) afforded 85 mg pure product.

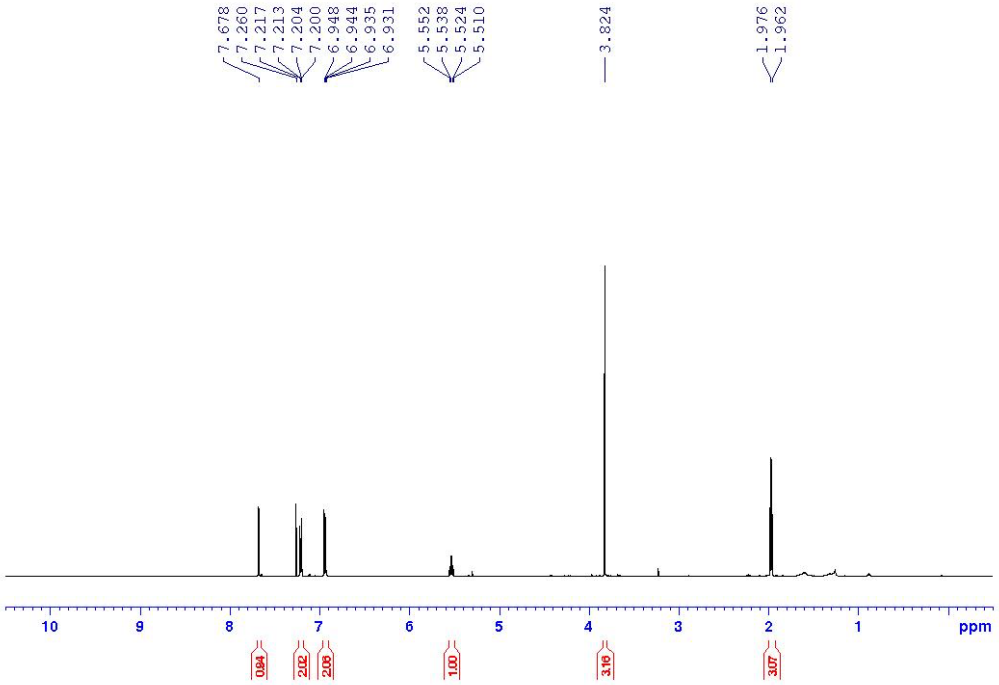
Isolated Yield: 67%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.67 (s, 1H), 7.21-7.20 (m, 2H), 6.94-6.93 (m, 2H), 5.53 (q, J = 7.1 Hz, 1H), 3.82 (s, 3H), 1.96 (d, J = 7.1 Hz, 3H).

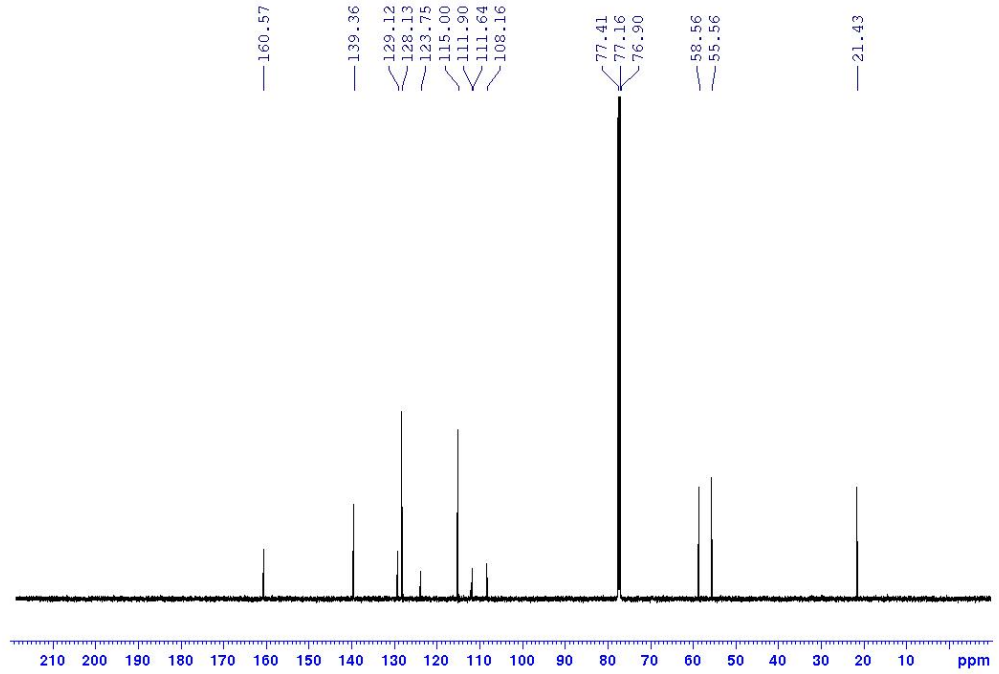
^{13}C NMR (126MHz, Chloroform-*d*): δ 160.5, 139.3, 129.1, 128.1, 123.7, 115.0, 111.9, 111.6, 108.1, 58.5, 55.5, 21.4.

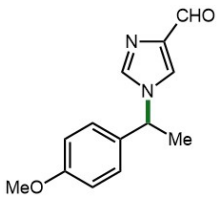
HRMS (ESI): calculated $[M+NH_4]^+$ as 270.1354, found 270.1545

^{1}H NMR:



^{13}C NMR:





1-(1-(4-methoxyphenyl)ethyl)-1H-imidazole-4-carbaldehyde (**31**)

Synthesized according to the general procedure C for heterocycle addition with 1-ethyl-4-methoxybenzene (71.1 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 1*H*-imidazole-4-carbaldehyde (144.1 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (40% ethyl acetate in hexanes, silica gel) afforded 37 mg pure product.

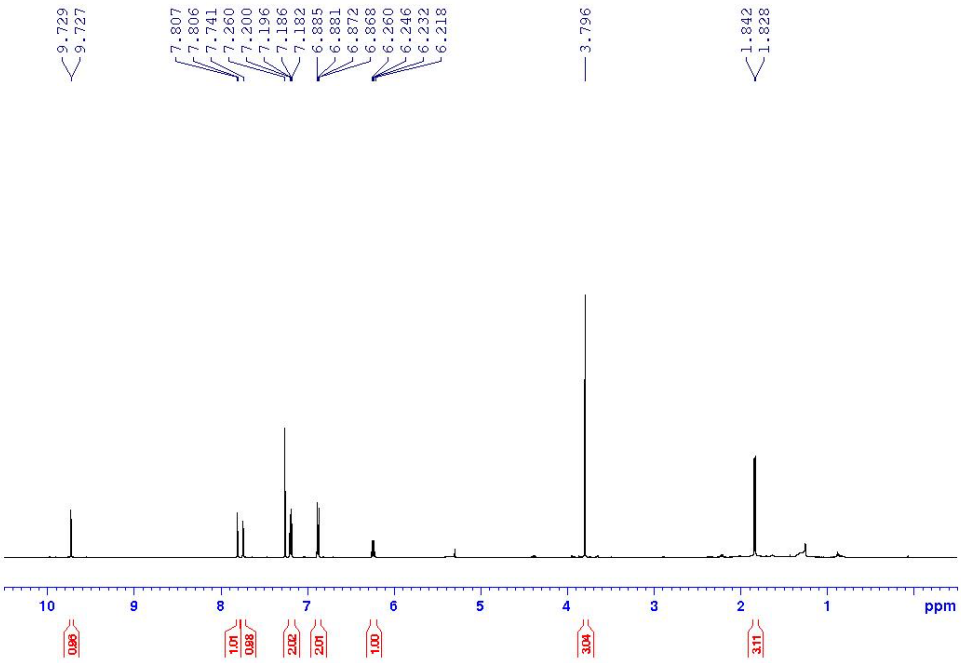
Isolated Yield: 32%

^{1}H NMR (500MHz, Chloroform-*d*): δ 9.72 (d, J = 1Hz, 1H), 7.80 (d, J = 0.7 Hz, 1H), 7.74 (s, 1H), 7.19-7.18 (m, 2H), 6.88-6.86 (m, 2H), 6.23 (q, J = 7.1 Hz, 1H), 3.79 (s, 3H), 1.83 (d, J = 7.1 Hz, 3H).

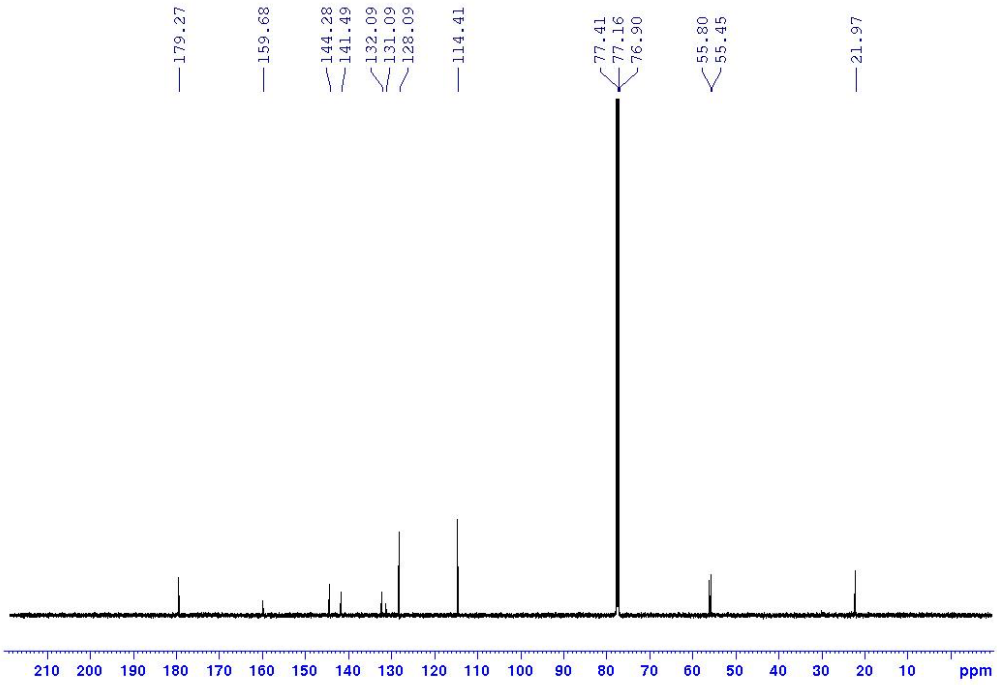
^{13}C NMR (126MHz, Chloroform-*d*): δ 179.2, 159.6, 144.2, 141.4, 132.0, 131.0, 128.0, 114.4, 55.8, 55.4, 21.9.

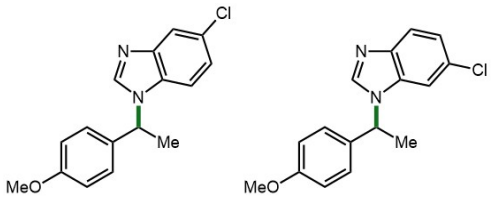
HRMS (ESI): calculated $[M+H]^+$ as 231.1128, found 231.1128.

^{1}H NMR:



^{13}C NMR:





5-chloro-1-(1-(4-methoxyphenyl)ethyl)-1H-benzo[d]imidazole (**32**)

Synthesized according to the general procedure C for heterocycle addition with 1-ethyl-4-methoxybenzene (71.1 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 5-chloro-1*H*-benzo[*d*]imidazole (228.9 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 72 hr. Purification with flash chromatography (55% ethyl acetate in hexanes, silica gel) afforded 65 mg pure product.

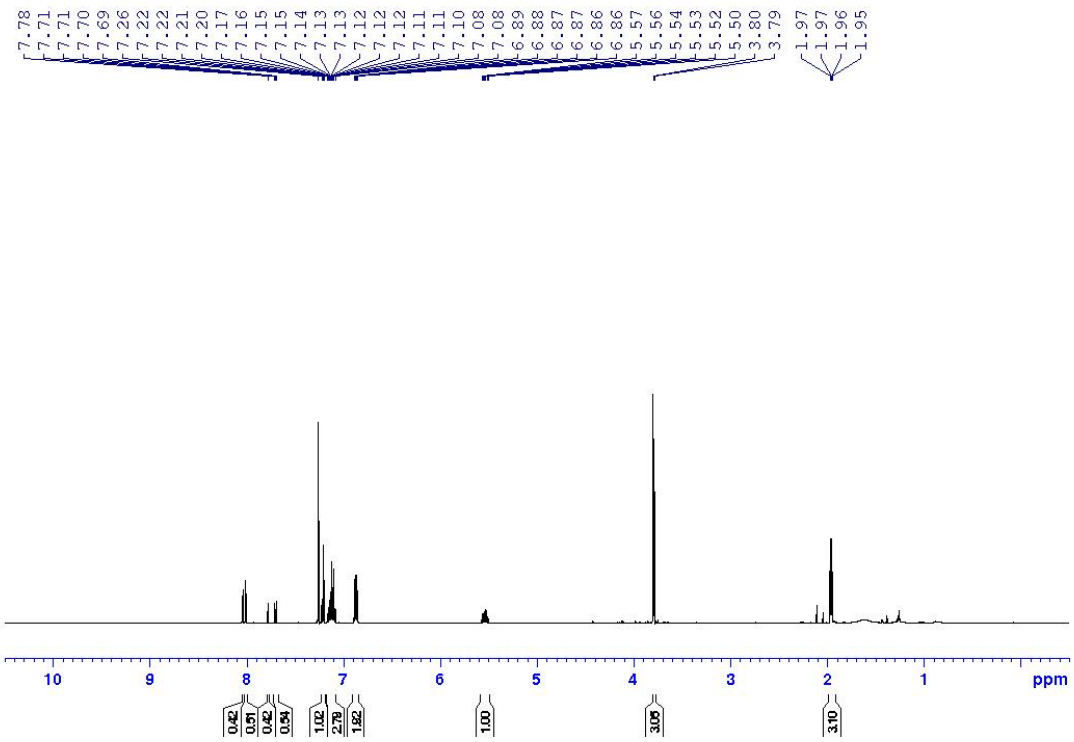
Isolated Yield: 45% (1:1)

^{1}H NMR (500MHz, Chloroform-*d*): δ 8.03 (s, 0.5 H), 8.00 (s, 0.5 H), 7.77 (dd, J = 1.9, 0.4 Hz, 0.5 H), 7.70 (dd, J = 7.8, 1.5 Hz, 0.5 H), 7.22-7.20 (m, 1H), 7.16-7.08 (m, 3H), 6.88-6.85 (m, 2H), 5.57-5.50 (m, 1H), 3.79 (s, 1.5 H), 3.78 (s, 1.5 H), 1.96 (d, J = 2.1 Hz, 1.5 H), 1.95 (d, J = 2.1 Hz, 1.5 H)

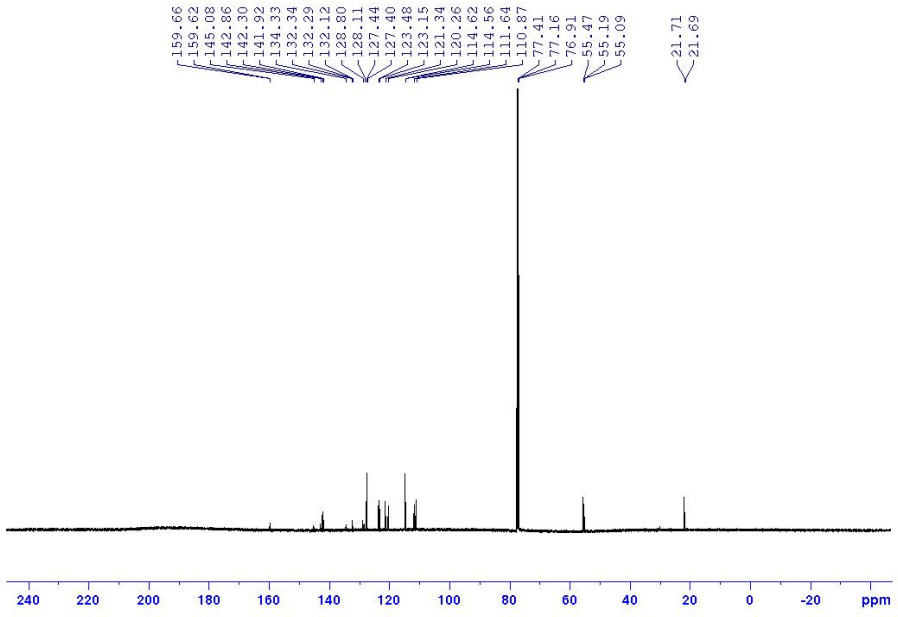
^{13}C NMR (126MHz, Chloroform-*d*): δ 159.65, 145.0, 142.8, 142.3, 141.9, 132.3, 131.1, 128.8, 128.1, 127.43, 127.40, 123.4, 123.1, 121.3, 120.2. 114.6, 111.6, 110.8, 55.1, 21.7.

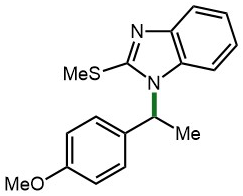
HRMS (ESI): calculated $[M+H]^+$ as 287.0951, found 287.0923.

^{1}H NMR:



^{13}C NMR:





1-(1-(4-methoxyphenyl)ethyl)-2-(methylthio)-1H-benzo[d]imidazole (**33**)

Synthesized according to the general procedure D for heterocycle addition with 1-ethyl-4-methoxybenzene (71.1 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 2-(methylthio)-1*H*-benzo[*d*]imidazole (246.4 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Purification with flash chromatography (7% ethyl acetate in dichloromethane, silica gel) afforded 57 mg pure product.

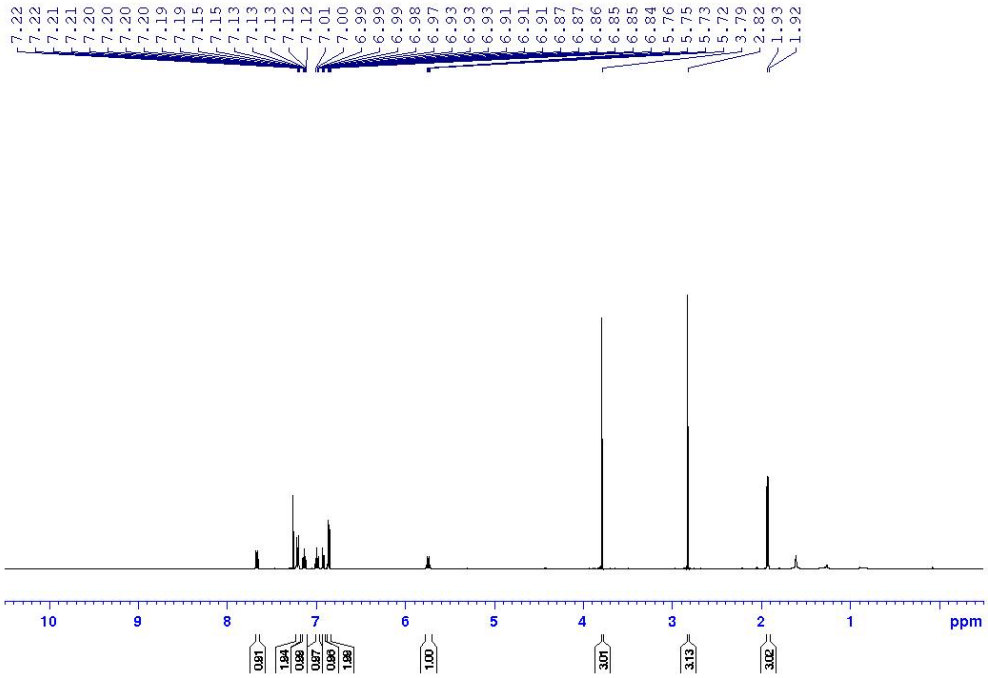
Isolated Yield: 38%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.66 (dt, J = 8, 0.9 Hz, 1H), 7.22-7.19 (m, 2H), 7.14-7.11 (m, 1H), 7.00-6.97 (m, 1H), 6.91 (dt, J = 8, 0.9 Hz, 1H), 6.87-6.84 (m, 2H), 5.73 (q, J = 7.1 Hz, 1H), 3.78 (s, 3H), 2.82 (s, 3H), 1.92 (d, J = 7.1 Hz, 3H).

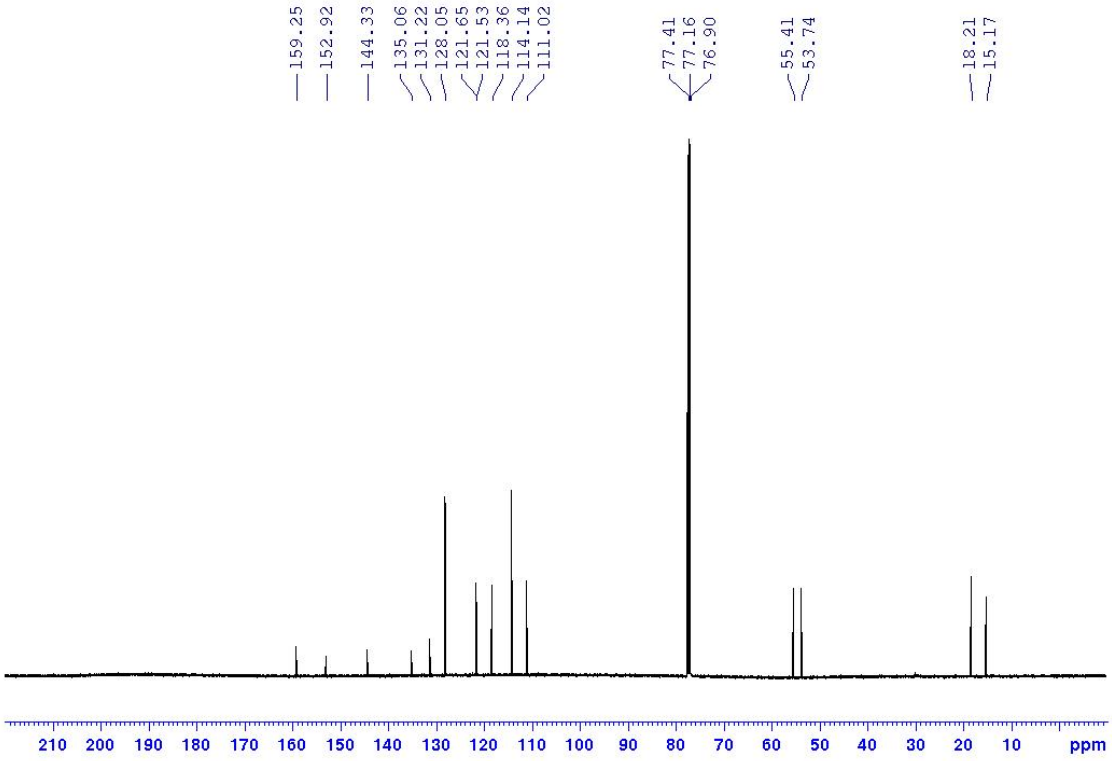
^{13}C NMR (126MHz, Chloroform-*d*): δ 159.2, 152.9, 144.3, 135.0, 131.2, 128.0, 121.6, 121.5, 118.4, 114.1, 111.0, 55.4, 53.7, 18.2, 15.2.

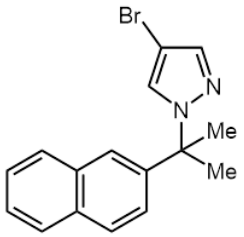
HRMS (ESI): calculated $[M+H]^+$ as 299.1213, found 299.1214.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(2-(naphthalen-2-yl)propan-2-yl)-1*H*-pyrazole (**34**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-bromo-1H-pyrazole (73.5 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (5% diethyl ether in hexanes, silica gel) afforded 100.5 mg pure product.

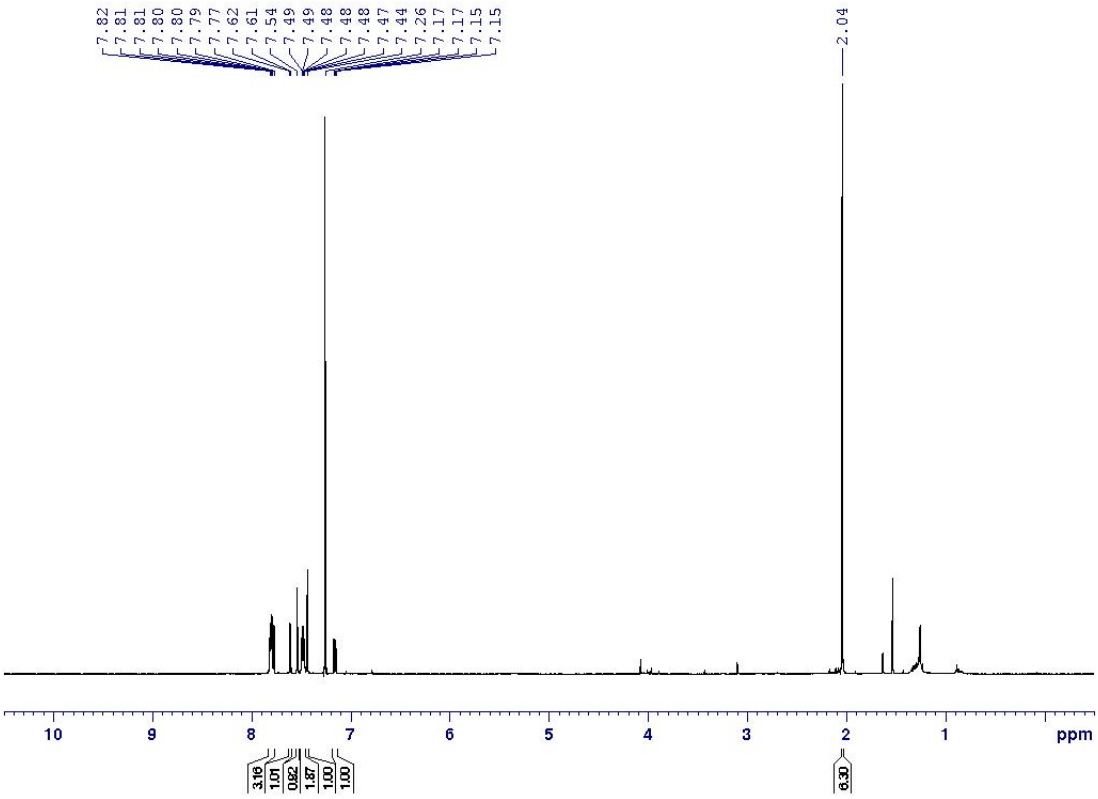
Isolated Yield: 64%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.82-7.77 (m, 3H), 7.61 (d, J=1.9 Hz, 1H), 7.54 (s, 1H), 7.49-7.47 (m, 2H), 7.44 (s, 1H), 7.16 (dd, J = 8.6, 2.0 Hz, 1H), 2.04 (s, 6H).

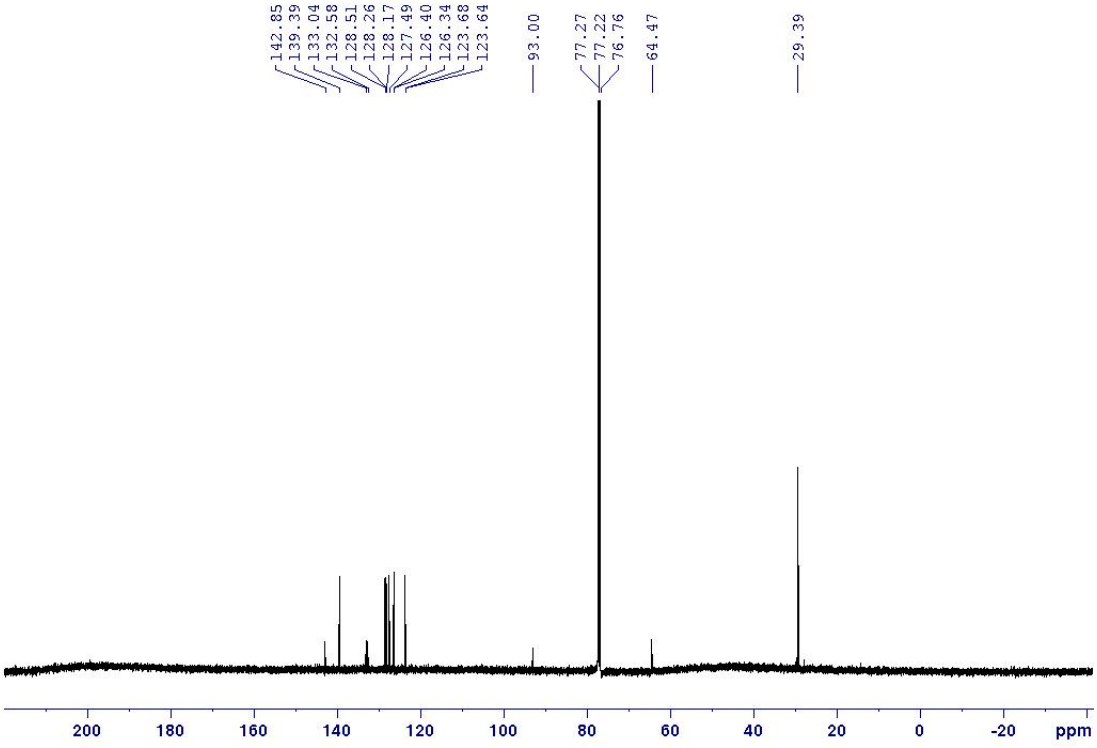
^{13}C NMR (126MHz, Chloroform-*d*): δ 142.8, 139.3, 133.0, 132.6, 128.5, 128.2, 128.1, 127.5, 126.4, 126.3, 123.7, 123.6, 93.0, 64.4, 29.3.

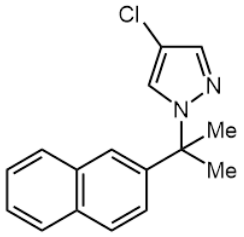
HRMS (ESI): calculated $[M+H]^+$ as 315.0492, found 315.0493

^{1}H NMR:



^{13}C NMR:





4-chloro-1-(2-(naphthalen-2-yl)propan-2-yl)-1*H*-pyrazole (**35**)

Synthesized according to the general procedure H, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-chloro-1*H*-pyrazole (51.26 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (5% diethyl ether in hexanes, silica gel) afforded 87.9 mg pure product.

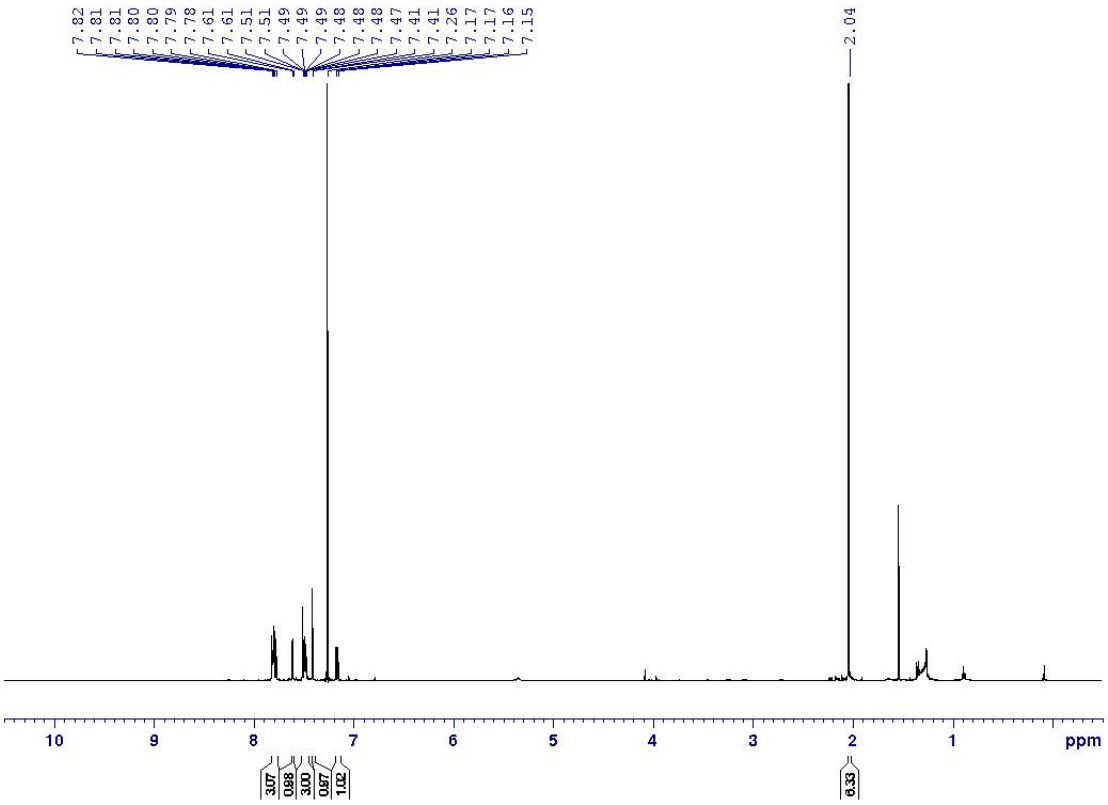
Isolated Yield: 62%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.82-7.78 (m, 3H), 7.61 (d, J=2.1 Hz, 1H), 7.50-7.47 (m, 3H), 7.41(d, J=0.65 Hz, 1H), 7.16 (dd, J = 8.6, 2.0 Hz, 1H), 2.04 (s, 6H).

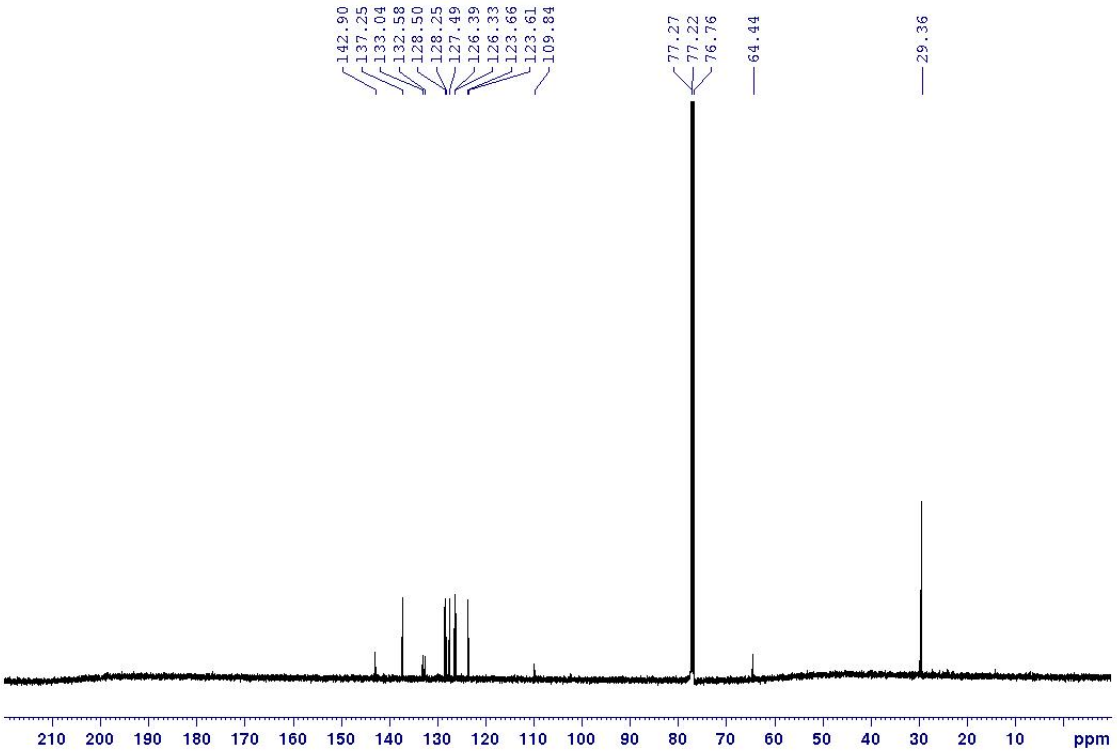
^{13}C NMR (126MHz, Chloroform-*d*): δ 142.9, 137.2, 133.04, 132.5, 128.5, 128.2, 127.4, 126.3, 126.3, 123.6, 123.6, 109.8, 64.4, 29.3.

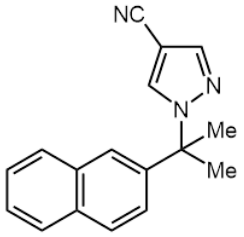
HRMS (ESI): calculated $[M+H]^+$ as 271.0997, found 271.0998

^{1}H NMR:



^{13}C NMR:





1-(2-(naphthalen-2-yl)propan-2-yl)-1*H*-pyrazole-4-carbonitrile (**36**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-cyano-1*H*-pyrazole (46.5 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (15% ethyl acetate in hexanes, silica gel) afforded 71.8 mg pure product.

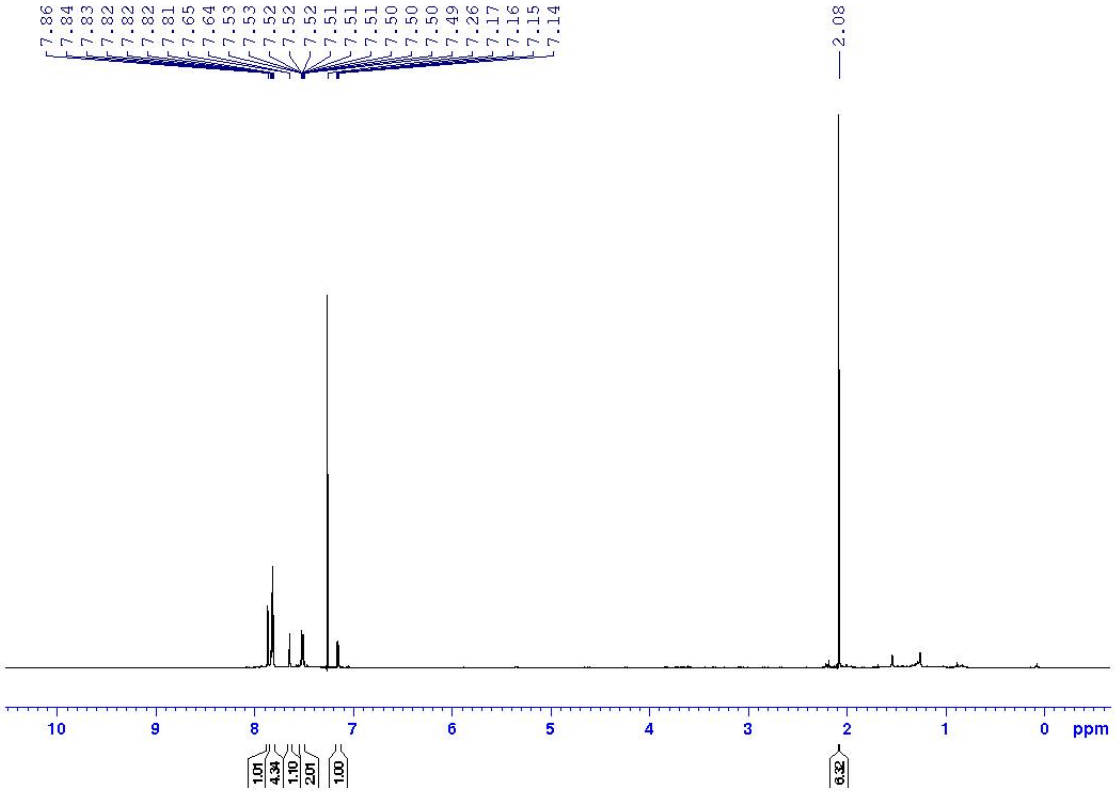
Isolated Yield: 55%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.86 (s, 1H), 7.83-7.81(m, 4H), 7.64 (d, *J*=1.8 Hz, 1H), 7.53-7.49 (m, 2H), 7.15 (dd, *J* = 3.7, 1.6 Hz, 1H), 2.08 (s, 6H).

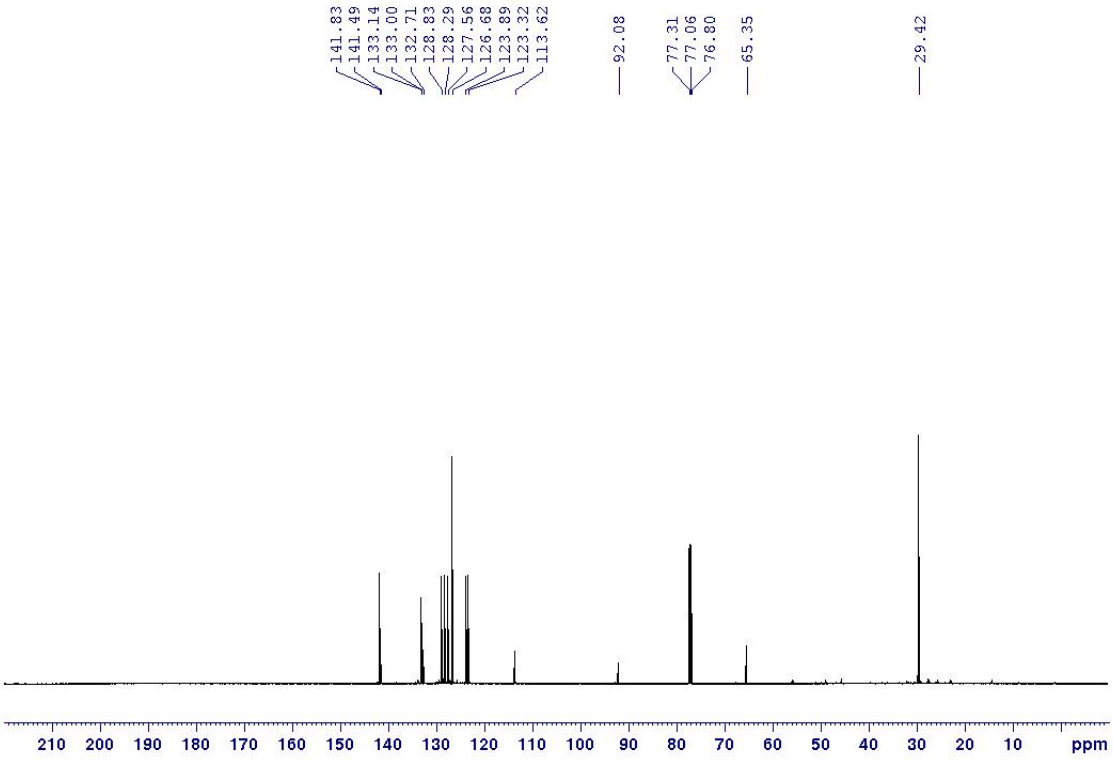
^{13}C NMR (126MHz, Chloroform-*d*): δ 141.8, 141.5, 133.1, 133.0, 132.7, 128.8, 128.3, 127.6, 126.7, 123.9, 123.3, 113.6, 92.1, 65.3, 29.4.

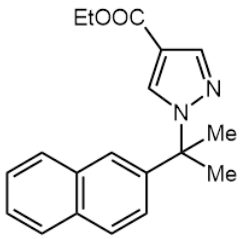
HRMS (ESI): calculated $[M+H]^+$ as 262.1339, found 262.1339

^{1}H NMR:



^{13}C NMR:





ethyl 1-(2-(naphthalen-2-yl)propan-2-yl)-1*H*-pyrazole-4-carboxylate (**37**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), ethyl 1*H*-pyrazole-4-carboxylate (70.07 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (25% diethy lether in hexanes, silica gel) afforded 80.1 mg pure product.

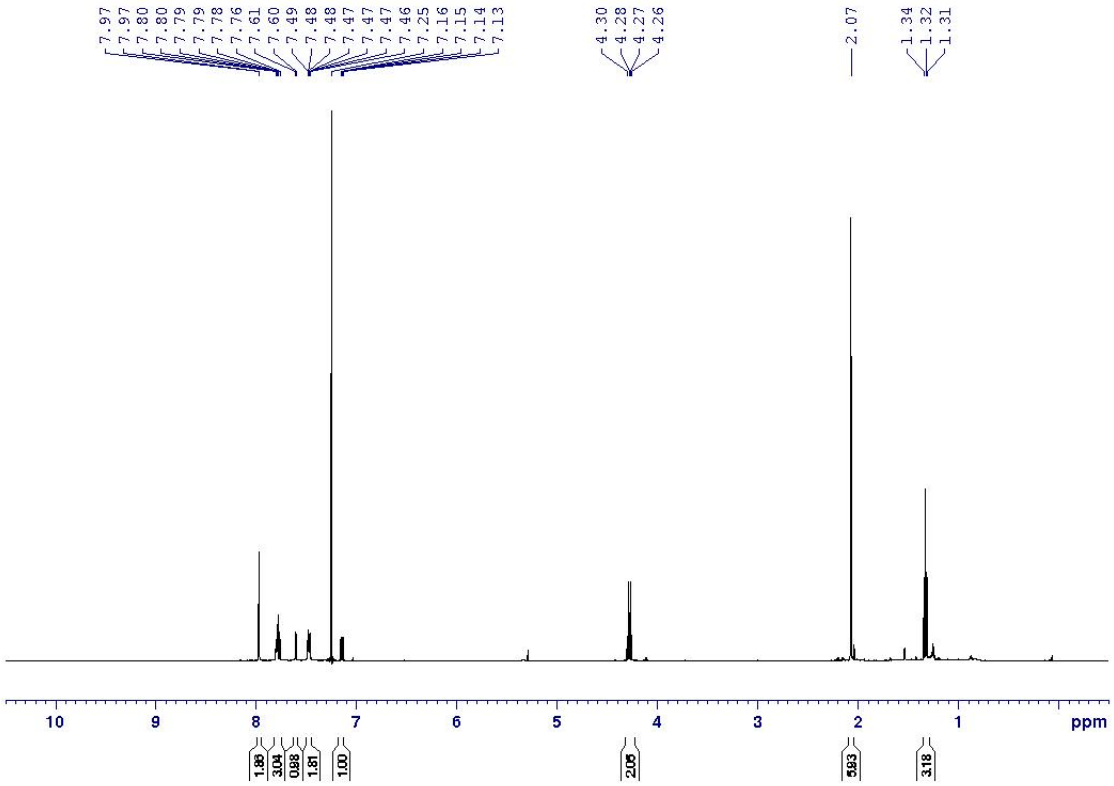
Isolated Yield: 52%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.97 (brs, 2H), 7.80-7.76 (m, 3H), 7.60 (d, *J* = 1.8 Hz, 1H), 7.48-7.46 (m, 2H), 7.14 (dd, *J* = 8.7, 2.0 Hz, 1H), 4.27 (q, 2H, *J*=7.1 Hz, 2H), 2.06 (s, 6H), 1.32 (t, *J*=7.1 Hz, 3H).

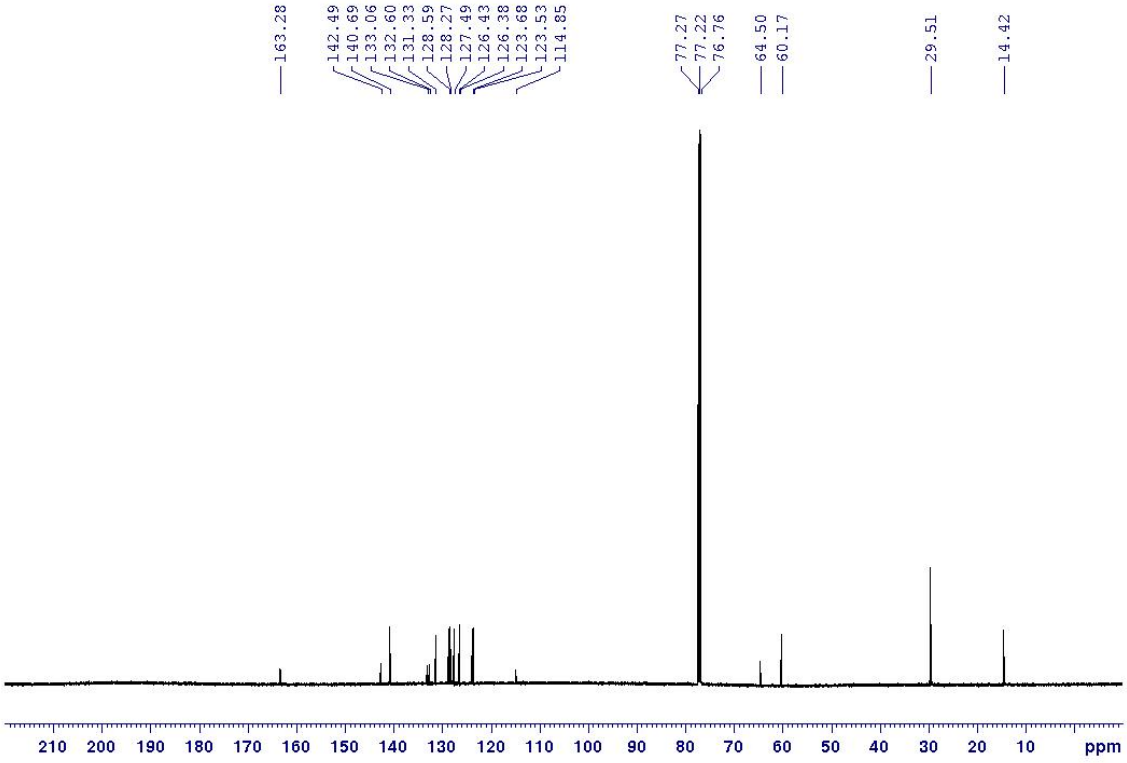
^{13}C NMR (126MHz, Chloroform-*d*): δ 163.2, 142.4, 140.6, 133.0, 132.6, 131.3, 128.5, 128.2, 127.4, 126.4, 126.3, 123.6, 123.5, 114.8, 64.5, 60.2, 29.5, 14.4.

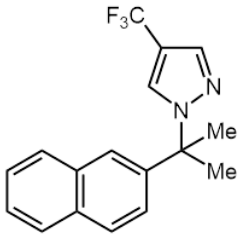
HRMS (ESI): calculated $[M+H]^+$ as 309.1598, found 309.1599

^{1}H NMR:



^{13}C NMR:





1-(2-(naphthalen-2-yl)propan-2-yl)-4-(trifluoromethyl)-1*H*-pyrazole (**38**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), Ir(pFppy)3 (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-(trifluoromethyl)-1*H*-pyrazole (68.04 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (5% diethyl ether in hexanes, silica gel) afforded 100.4 mg pure product.

Isolated Yield: 66%

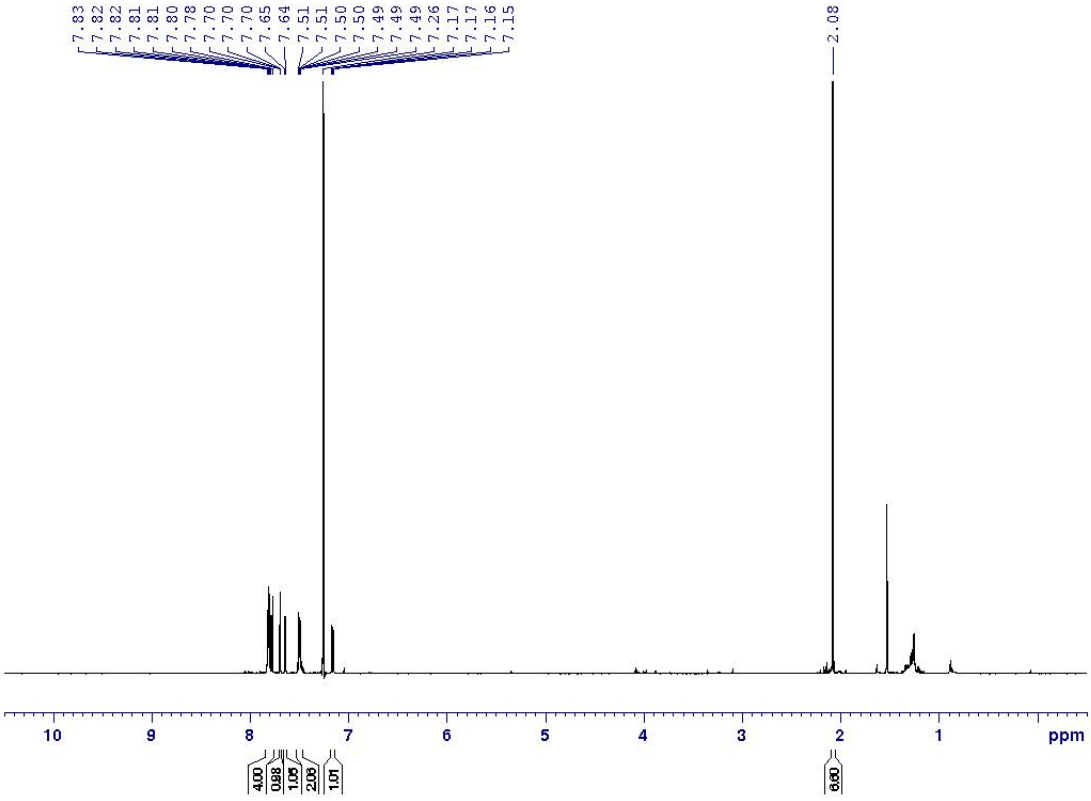
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.83-7.77 (m, 4H), 7.69 (t, *J*=0.75 Hz, 1H), 7.64 (d, *J*=2.0 Hz, 1H), 7.50-7.49 (m, 2H), 7.15 (dd, *J* = 8.7, 2.0 Hz, 1H), 2.08 (s, 6H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 142.2, 136.5, 136.5, 133.0, 132.6, 128.7, 128.7, 127.5, 127.2, 127.2, 126.5, 123.8, 123.5, 64.7, 29.5.

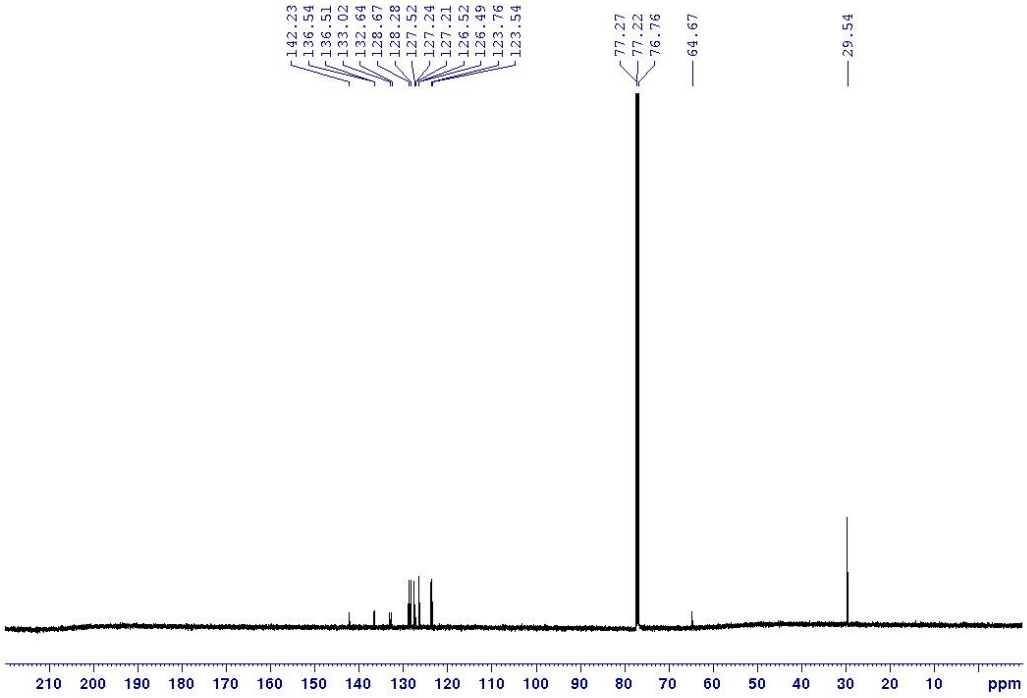
^{19}F NMR (377MHz, Chloroform-*d*): δ -56.1

HRMS (ESI): calculated $[M+H]^+$ as 305.1260, found 305.1263

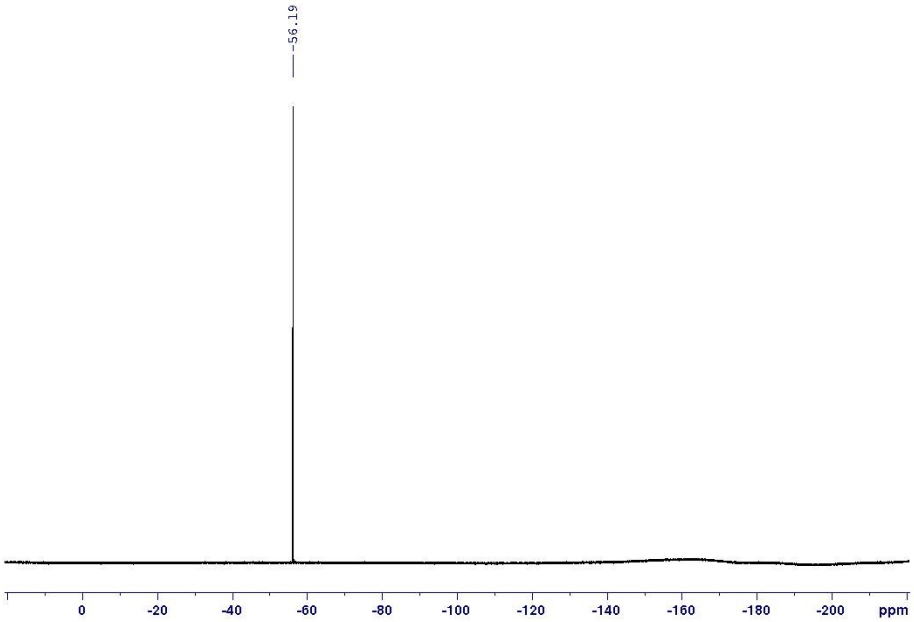
^{1}H NMR:

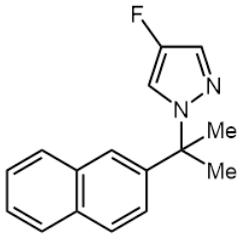


^{13}C NMR:



^{19}F NMR:





4-fluoro-1-(2-(naphthalen-2-yl)propan-2-yl)-1*H*-pyrazole (**39**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-(fluoro)-1*H*-pyrazole (43.03 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (5% diethyl ether in hexanes, silica gel) afforded 76.3 mg pure product.

Isolated Yield: 60%

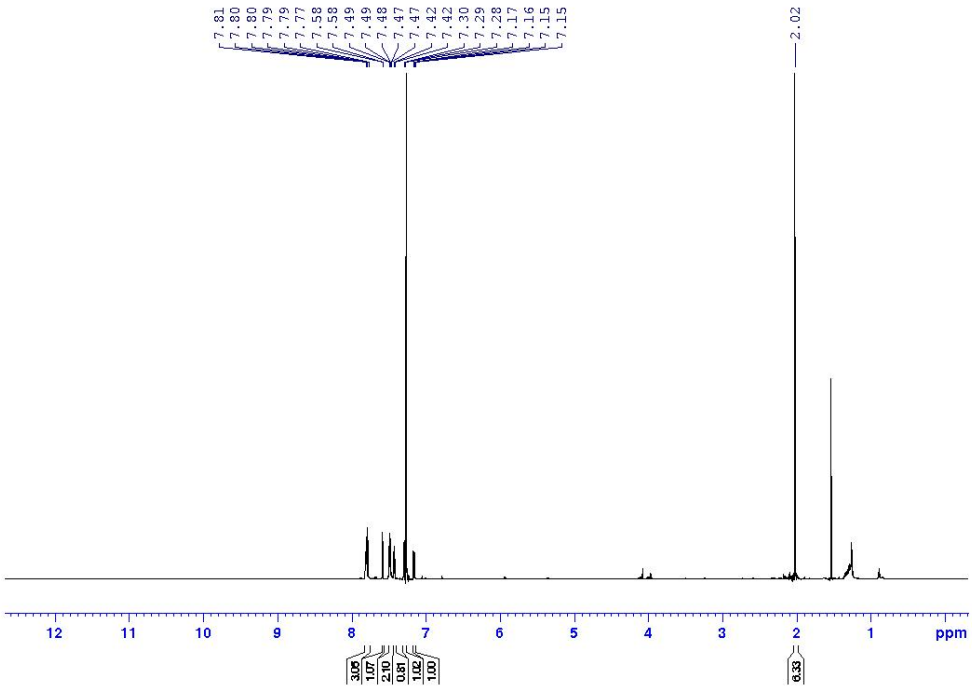
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.80-7.76 (m, 3H), 7.57 (d, *J*=1.8 Hz, 1H), 7.48-7.46 (m, 2H), 7.41(d, *J*=4.4 Hz, 1H), 7.29-7.28 (m, 1H), 7.15 (dd, *J* = 8.7, 2.0 Hz, 1H), 2.02 (s, 6H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 143.2, 133.0, 132.5, 129.4, 129.1, 129.0, 128.4, 128.2, 128.2, 128.2, , 127.4, 126.3, 125.7, 125.6, 123.6, 123.5, 114.3, 114.1, 64.3, 29.2.

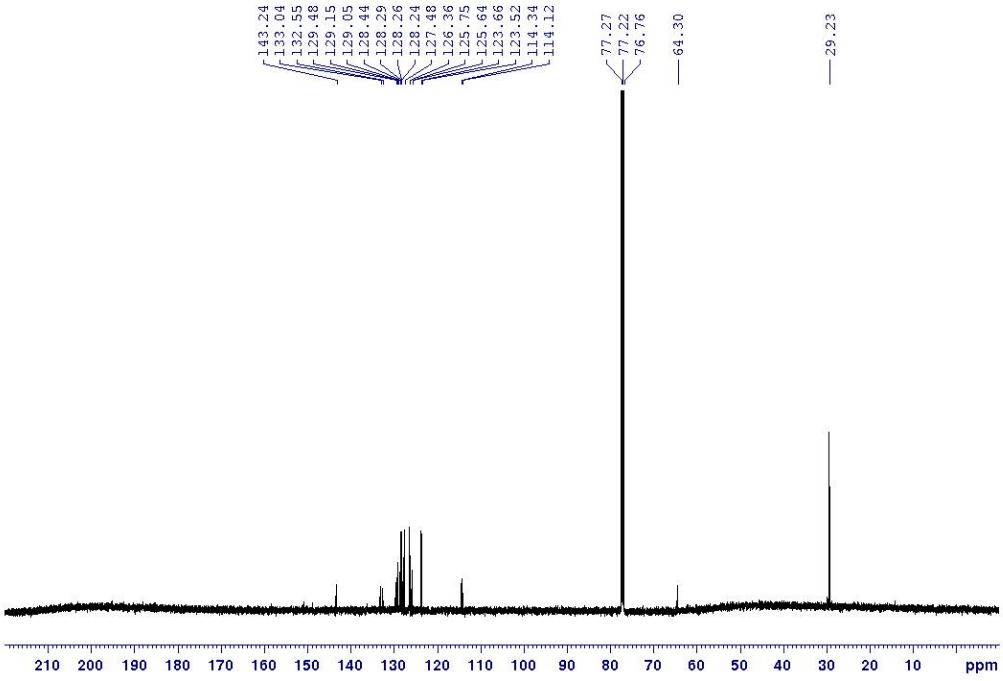
HRMS (ESI): calculated $[M+H]^+$ as 255.1292, found 255.1292

^{19}F NMR (377MHz, Chloroform-*d*): δ -176.8 (1F, t, J =3.8 Hz)

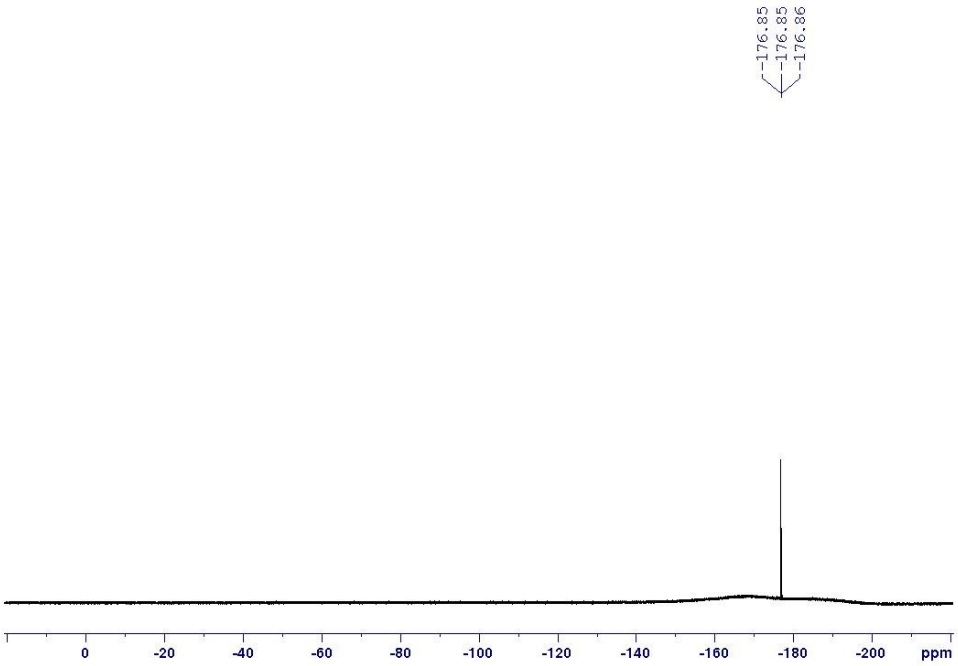
^{1}H NMR:

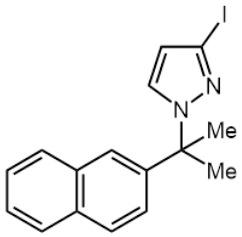


^{13}C NMR:



^{19}F NMR:





3-Iodo-1-(2-(naphthalen-2-yl)propan-2-yl)-1*H*-pyrazole (**40**)

Synthesized according to the general procedure G, 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 3-iodo-1*H*-pyrazole (96.99 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (3.5% diethyl ether in hexanes, silica gel) afforded 114.1 mg pure product.

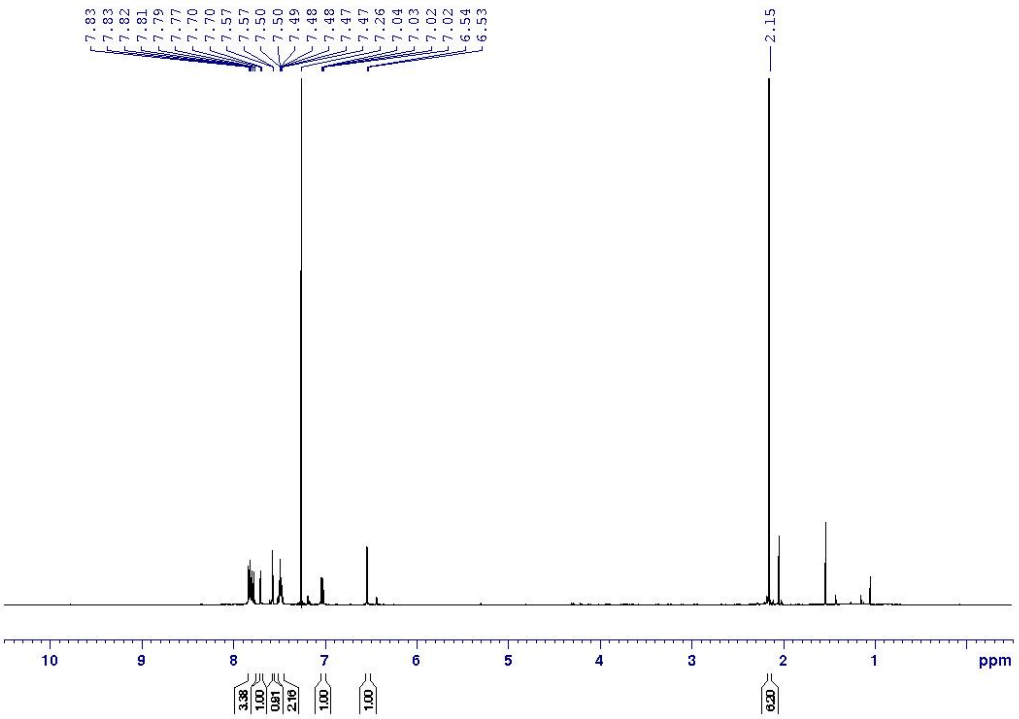
Isolated Yield: 63%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.83-7.77 (m, 3H), 7.69 (d, *J*=1.9 Hz, 1H), 7.56 (d. *J*=1.8, 1H), 7.49-7.47 (m, 2H), 7.02 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.53 (d, *J*=1.8, 1H), 2.15 (s, 6H).

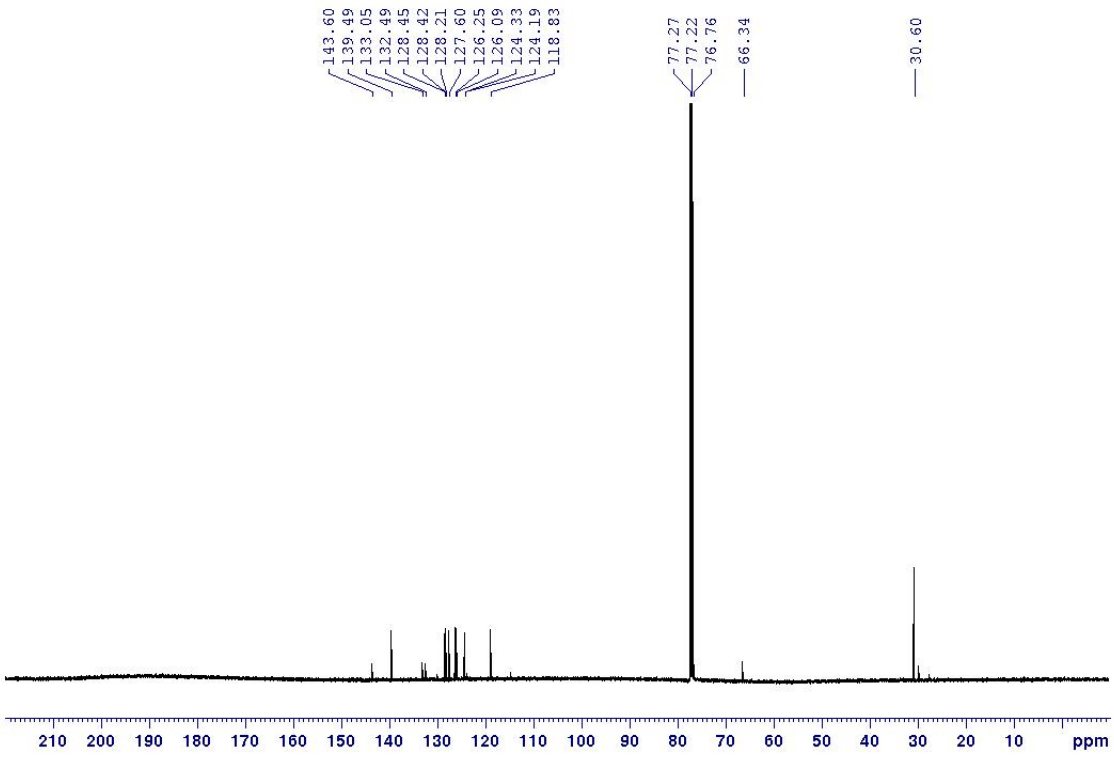
^{13}C NMR (126MHz, Chloroform-*d*): δ 143.6, 139.4, 133.0, 132.4, 128.5, 128.4, 128.4, 128.2, 127.5, 126.2, 126.0, 124.3, 124.1, 118.8, 66.3, 30.5.

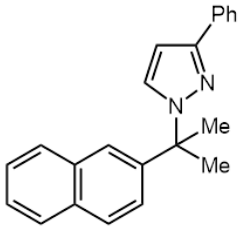
HRMS (ESI): calculated $[M+H]^+$ as 363.0353, found 363.0350

^{1}H NMR:



^{13}C NMR:





1-(2-(naphthalen-2-yl)propan-2-yl)-3-phenyl-1*H*-pyrazole (**41**)

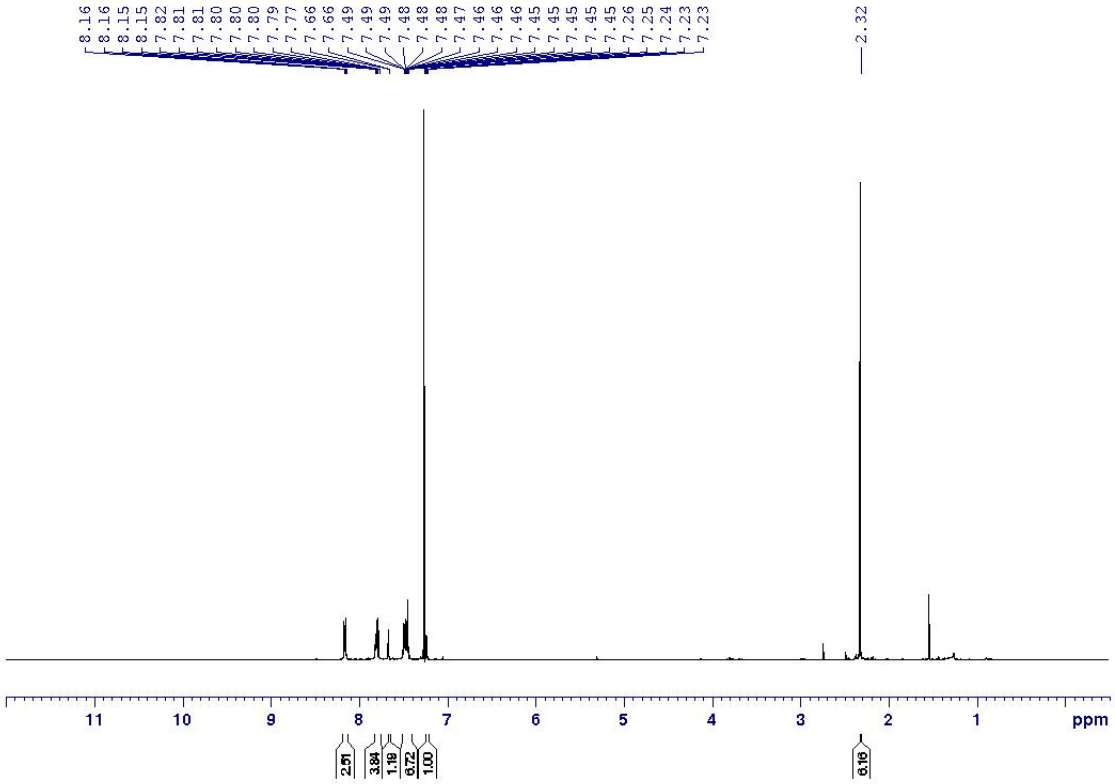
Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 3-phenyl-1*H*-pyrazole (720.8 mg, 0.5000 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (15% diethyl ether in hexanes, silica gel) afforded 35.9 mg pure product.

Isolated Yield: 23%

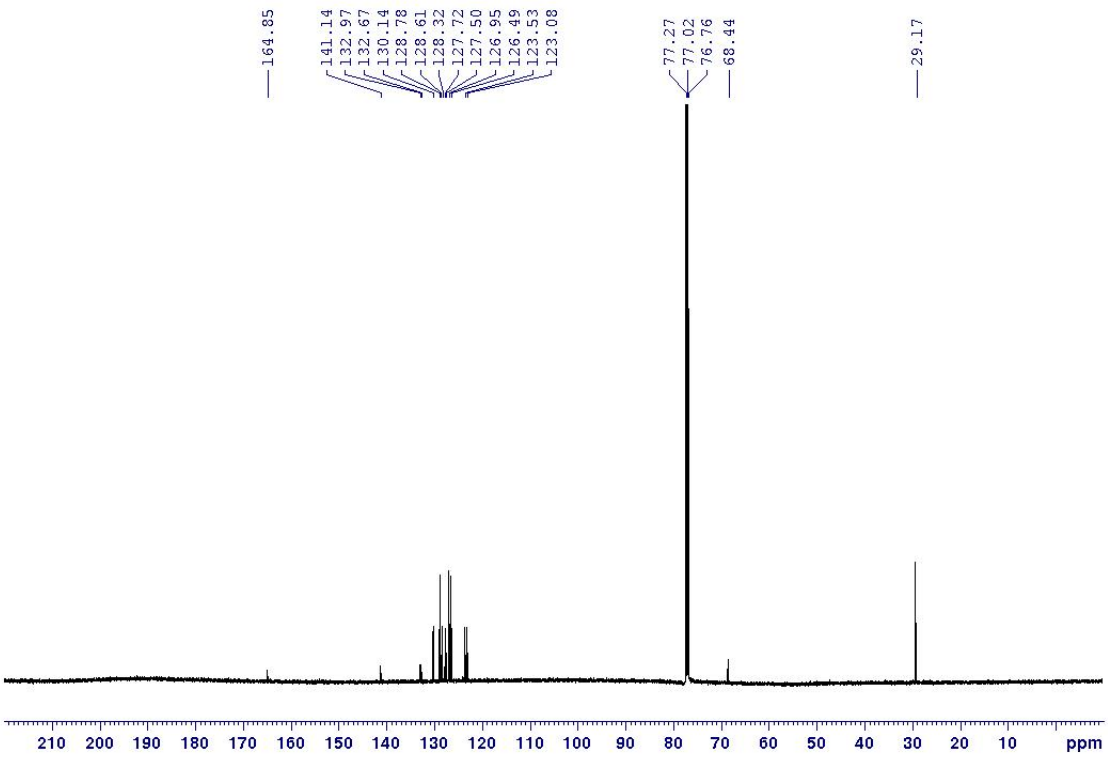
^{1}H NMR (500MHz, Chloroform-*d*): δ 8.16-8.14 (m, 2H), 7.81-7.77 (m, 4H), 7.66 (d, *J*=1.95 Hz, 1H), 7.49-7.44 (m, 6H), 7.23 (dd, *J* = 8.7, 2.1 Hz, 1H), 2.31 (s, 6H).

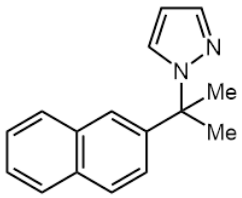
^{13}C NMR (126MHz, Chloroform-*d*): δ 164.8, 141.1, 132.9, 132.6, 130.1, 128.7, 128.6, 128.3, 127.7, 127.5, 126.9, 126.5, 123.5, 123.1, 68.4, 29.1.

^{1}H NMR:



^{13}C NMR:





1-(2-(naphthalen-2-yl)propan-2-yl)-1*H*-pyrazole (**42**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 1*H*-pyrazole (34.04 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 66.34 mg pure product.

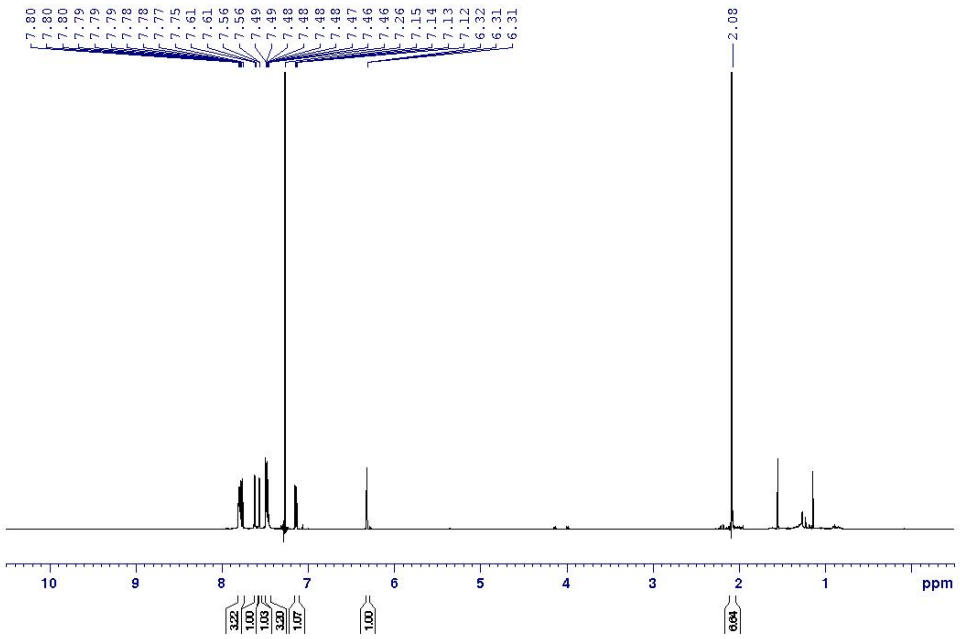
Isolated Yield: 50%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.80-7.75 (m, 3H), 7.61 (d, *J*=1.35 Hz, 1H), 7.56 (d, *J*=1.9 Hz, 1H), 7.48-7.46 (m, 3H), 7.13 (dd, *J* = 8.6, 2.1 Hz, 1H), 6.31 (t, *J*=1.9, 1H), 2.08 (s, 6H).

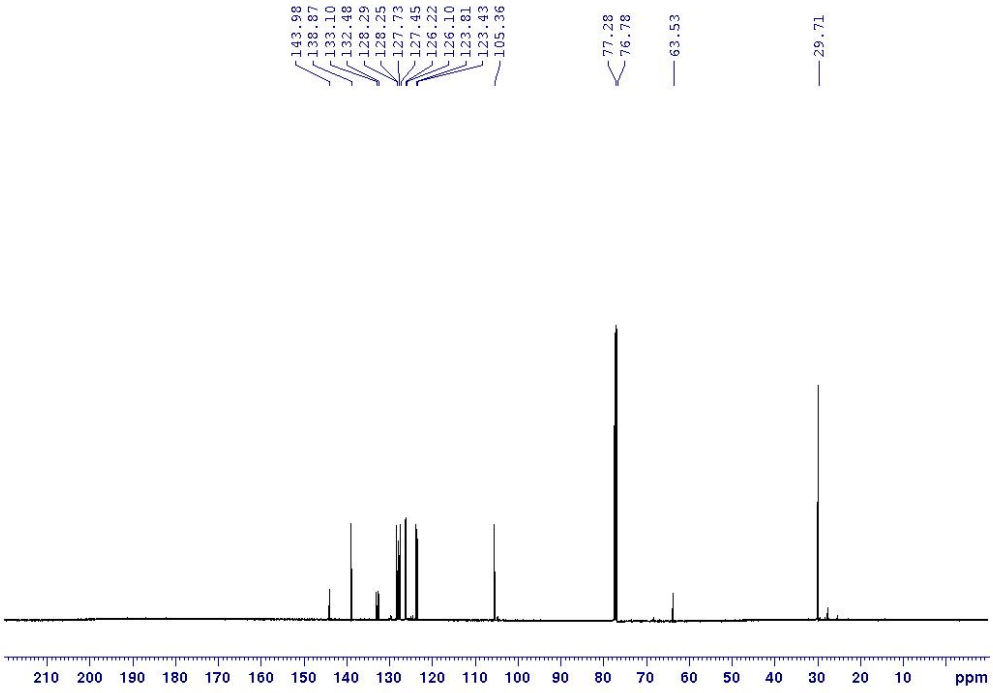
^{13}C NMR (126MHz, Chloroform-*d*): δ 143.9, 138.8, 133.1, 132.5, 128.3, 128.2, 127.7, 127.4, 126.2, 126.1, 123.8, 123.4, 105.3, 63.5, 29.7.

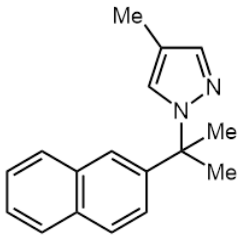
HRMS (ESI): calculated $[M+H]^+$ as 235.1386, found 235.1385.

^{1}H NMR:



^{13}C NMR:





4-methyl-1-(2-(naphthalen-2-yl)propan-2-yl)-1*H*-pyrazole (**43**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-methyl-1*H*-pyrazole (41.5 µL, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (12% diethyl ether in hexanes, silica gel) afforded 42.5 mg pure product.

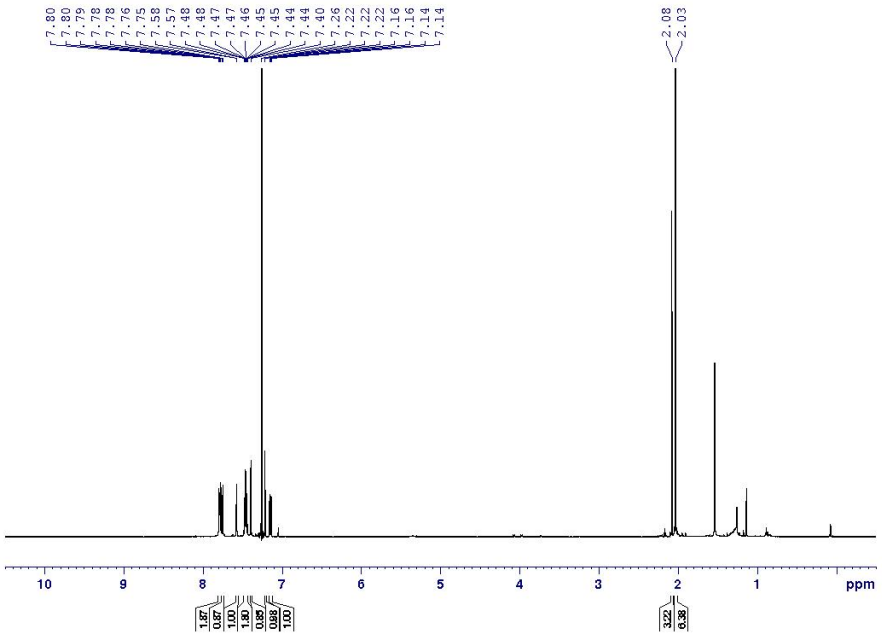
Isolated Yield: 34%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.80-7.78 (m, 2H), 7.75 (d, *J*=8.7 Hz, 1H), 7.57 (d, *J*=1.8 Hz, 1H), 7.48-7.43 (m, 2H), 7.39 (s, 1H), 7.21 (t, *J*=0.75 Hz, 1H), 7.14 (dd, *J* = 8.6, 2.0 Hz, 1H), 2.07 (s, 3H), 2.03 (s, 6H).

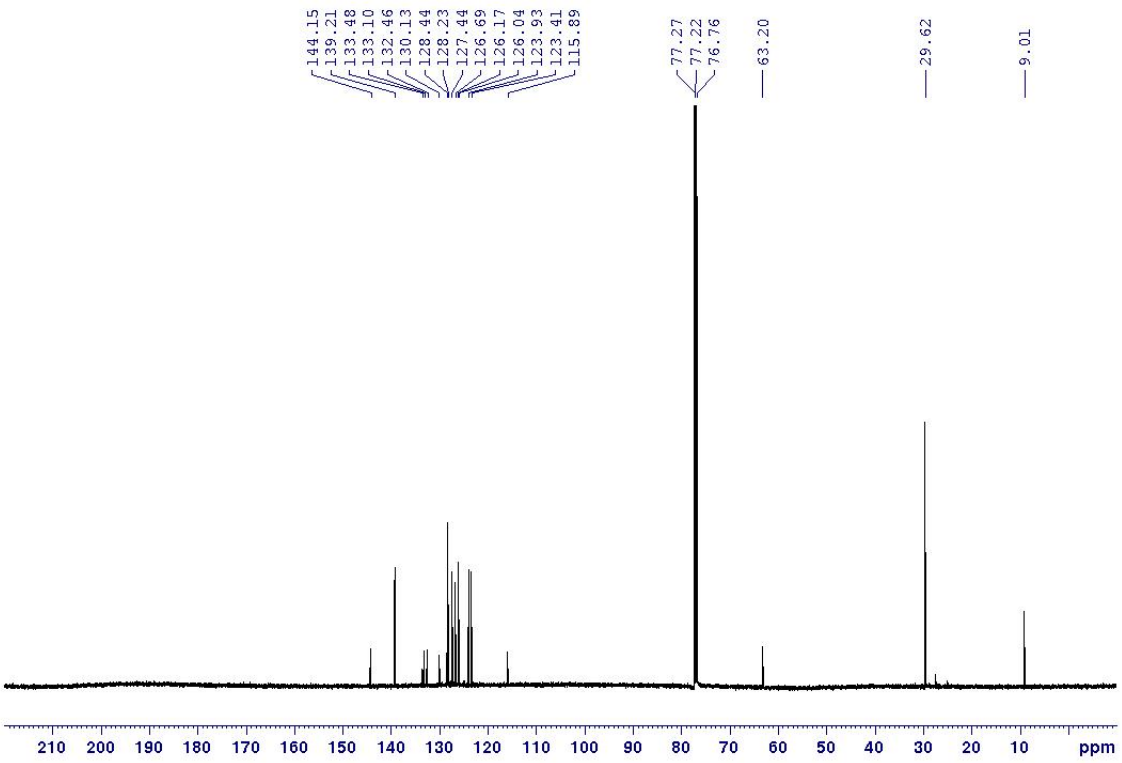
^{13}C NMR (126MHz, Chloroform-*d*): δ 144.1, 139.2, 133.0, 132.3, 128.2, 127.4, 126.6, 126.1, 126.0, 123.9, 123.4, 115.8, 63.2, 29.6, 9.0.

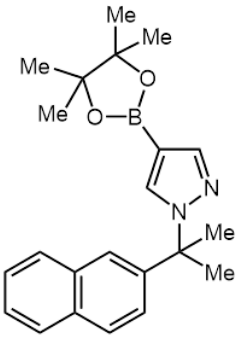
HRMS (ESI): calculated $[M+H]^+$ as 251.1543, found 251.1543

^{1}H NMR:



^{13}C NMR:





1-(2-(naphthalen-2-yl)propan-2-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrazole (**44**)

Synthesized according to the general G procedure, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-pyrazoleboronic acid pinacol ester (97.02 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (15% ethyl acetate in hexanes, silica gel) afforded 59.8 mg pure product.

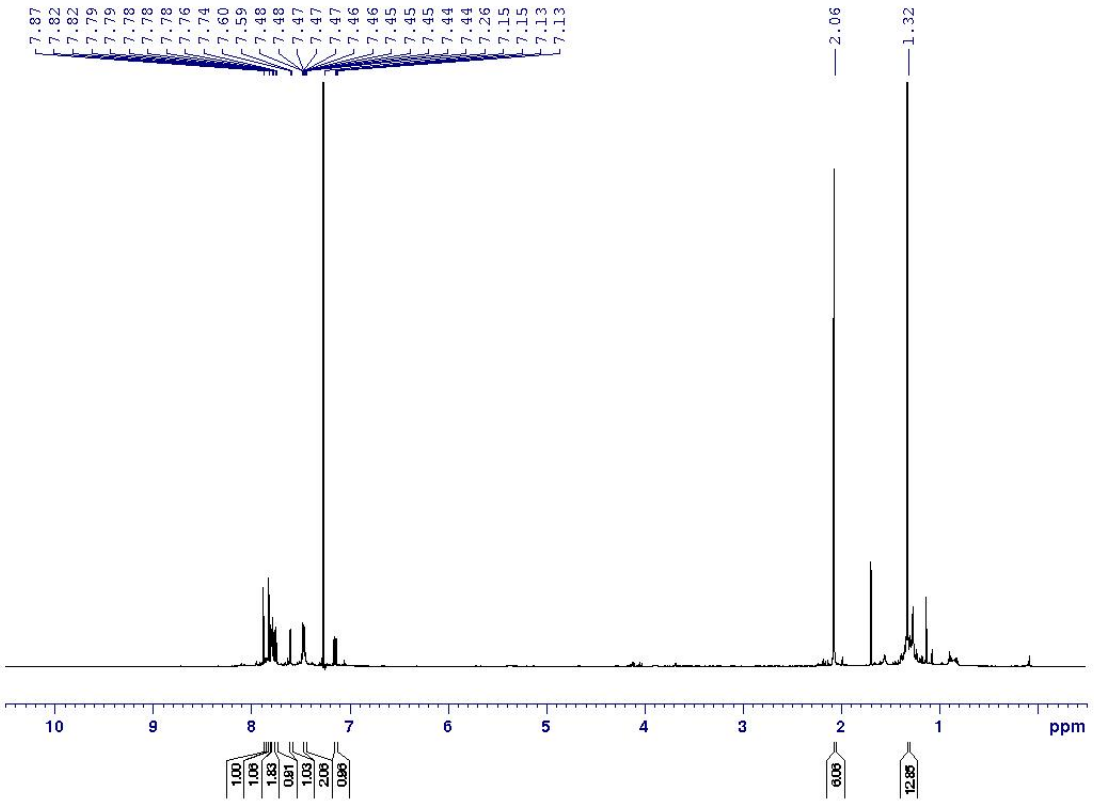
Isolated Yield: 33%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.87 (brs, 1H), 7.81 (d, *J*=0.55 Hz, 1H), 7.79-7.77 (m, 2H), 7.75 (d, *J*=8.6 Hz, 1H), 7.59 (d, *J*=2 Hz, 1H), 7.48-7.43 (m, 2H), 7.13 (dd, *J* = 8.6, 2.0 Hz, 1H), 2.06 (s, 3H), 1.32 (s, 12H).

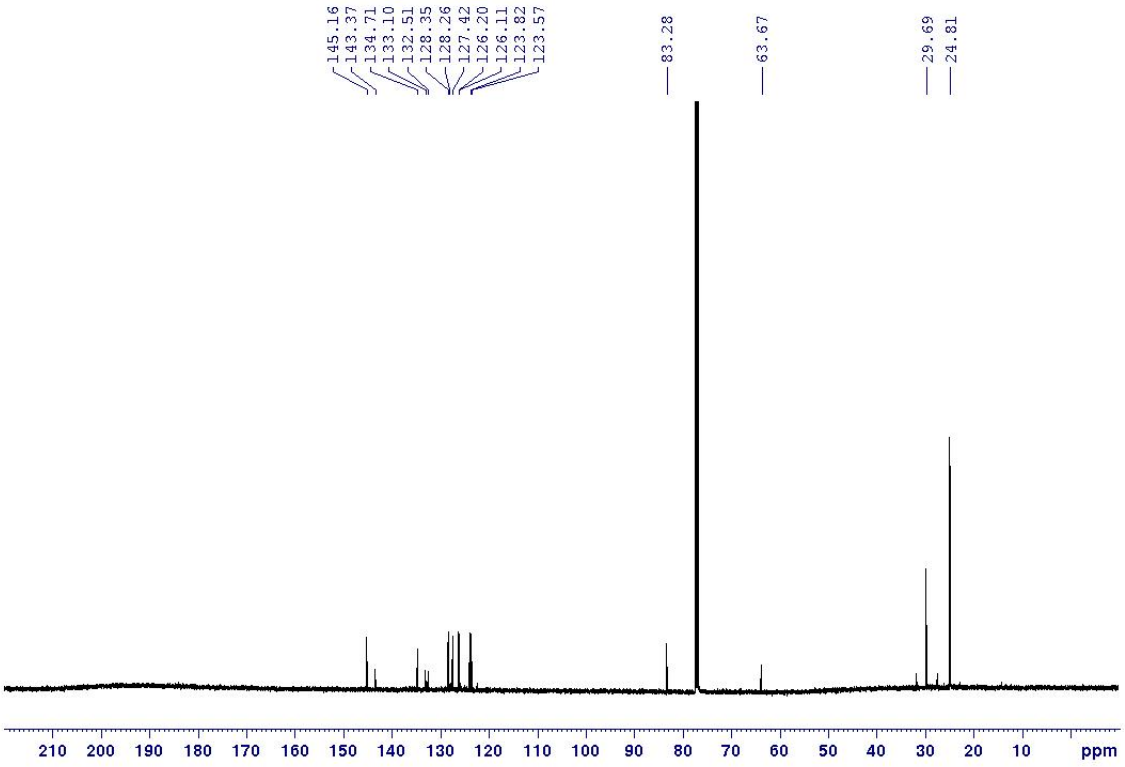
^{13}C NMR (126MHz, Chloroform-*d*): δ 145.1, 143.3, 134.7, 133.1, 132.5, 128.3, 128.2, 127.4, 126.2, 126.1, 123.8, 123.5, 83.2, 63.6, 29.7, 24.8.

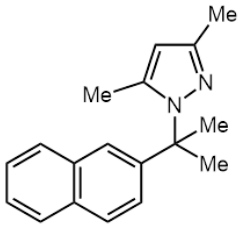
HRMS (ESI): calculated $[M+H]^+$ as 363.2239, found 363.2235

^{1}H NMR:



^{13}C NMR:





3,5-dimethyl-1-(2-(naphthalen-2-yl) propan-2-yl)-1*H*-pyrazole (**45**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), Ir(pFppy)$_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 3,5-dimethyl-1*H*-pyrazole (48.06 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (12% diethyl ether in hexanes, silica gel) afforded 23.8 mg pure product.

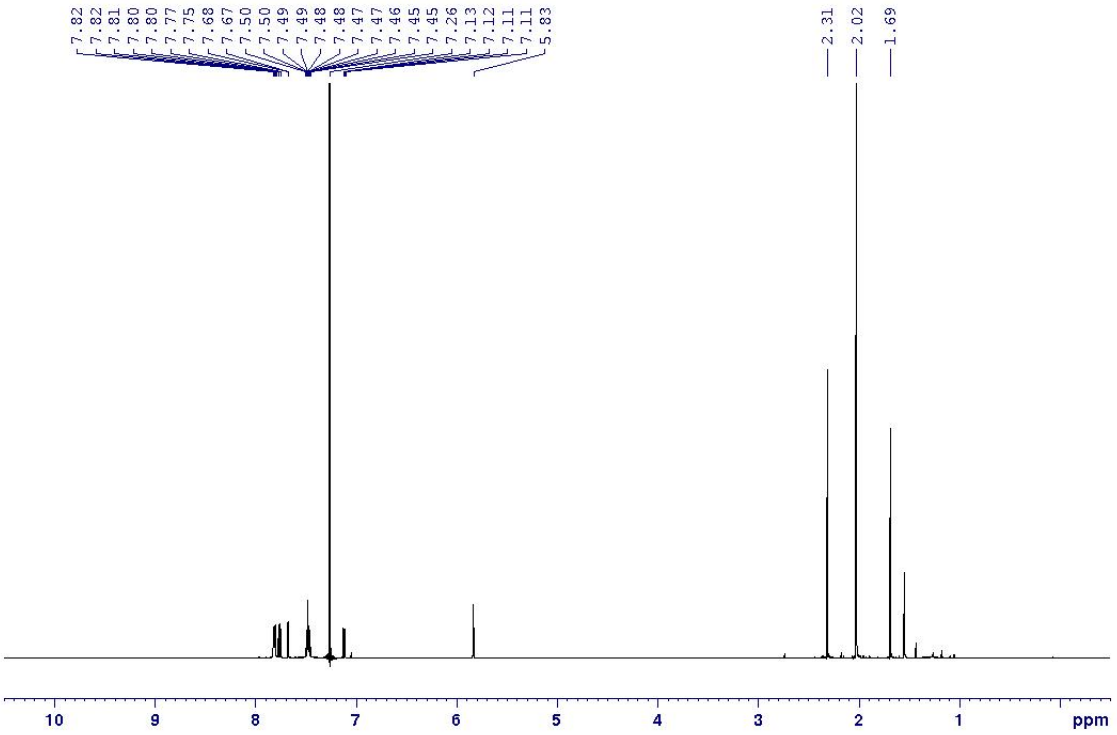
Isolated Yield: 18%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.82-7.79 (m, 2H), 7.76 (d, *J*=8.6 Hz, 1H), 7.67 (d, *J*=1.8 Hz, 1H), 7.50-7.44 (m, 2H), 7.11 (dd, *J* = 8.6, 2.0 Hz, 1H), 5.83 (s, 1H), 2.31(s, 3H), 2.02 (s, 6H), 1.68 (s, 3H).

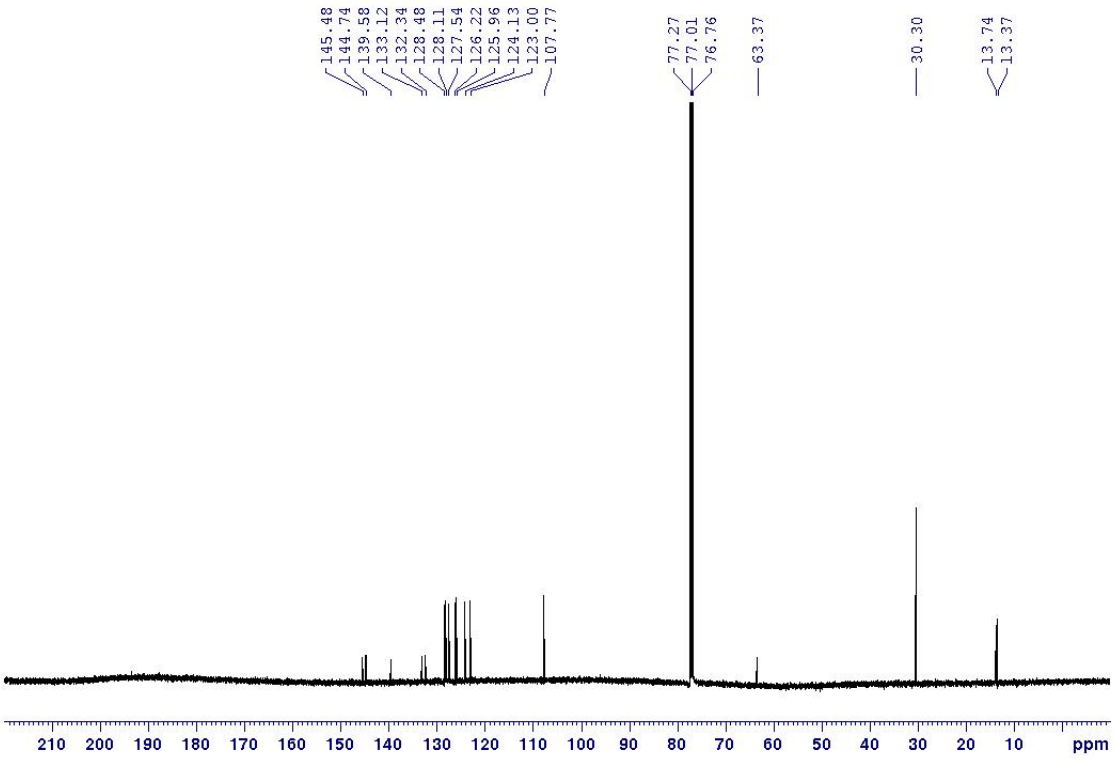
^{13}C NMR (126MHz, Chloroform-*d*): δ 145.4, 144.7, 139.5, 133.1, 132.3, 128.5, 128.1, 127.5, 126.2, 125.9, 124.1, 123.0, 107.7, 63.4, 30.3, 13.7, 13.3.

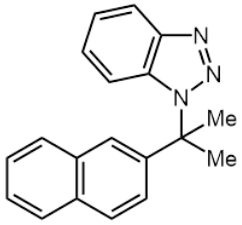
HRMS (ESI): calculated $[M+H]^+$ as 265.1704, found 265.1669

^{1}H NMR:



^{13}C NMR:





1-(2-(naphthalen-2-yl)propan-2-yl)-1*H*-benzo[d][1,2,3]triazole (**46**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), Ir(pFppy)$_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 1*H*-benzotriazole (59.5 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 37.3 mg pure product.

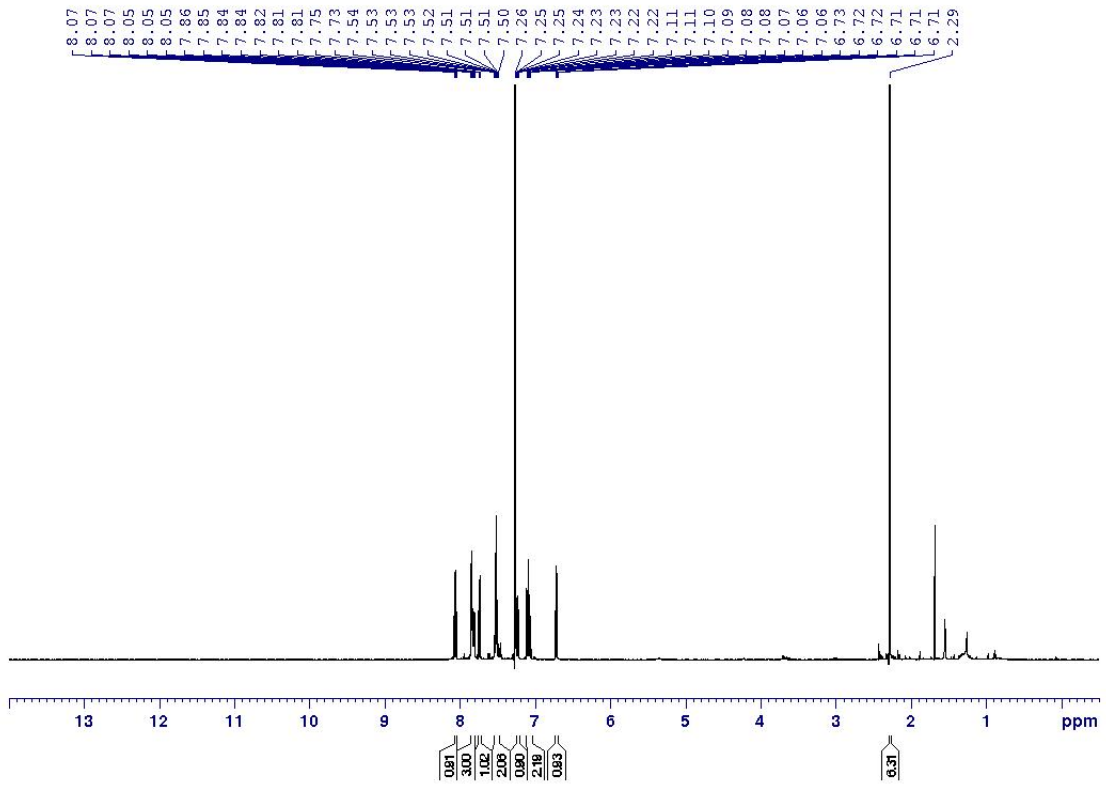
Isolated Yield: 26%

^{1}H NMR (500MHz, Chloroform-*d*): δ 8.05 (td, *J* = 8.4, 0.8 Hz, 1H), 7.85-7.80 (m, 3H), 7.74 (d, *J*=8.7, 1H), 7.54-7.49 (m, 2H), 7.25-7.21 (m, 1H), 7.11-7.06 (m, 2H), 6.71 (td, *J* = 8.4, 0.8 Hz, 1H), 2.29 (s, 6H).

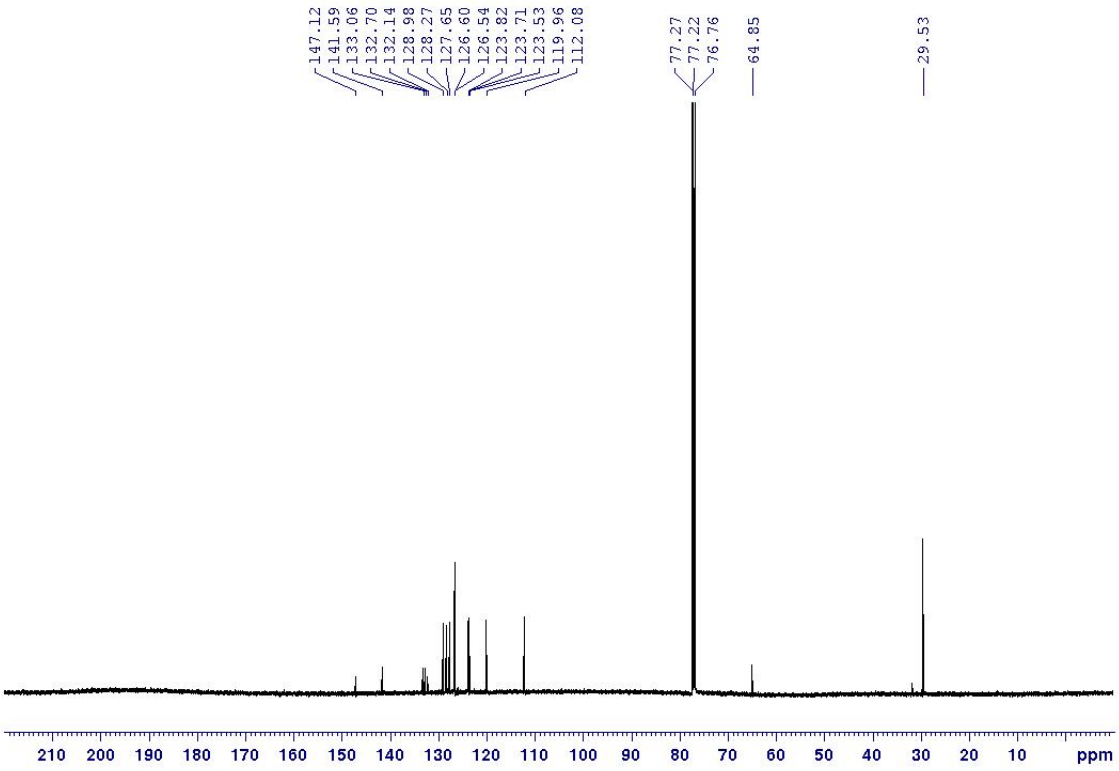
^{13}C NMR (126MHz, Chloroform-*d*): δ 147.1, 141.5, 133.0, 132.6, 132.1, 128.9, 128.2, 127.6, 126.6, 126.5, 123.8, 123.7, 123.5, 119.9, 112.0, 64.8, 29.5.

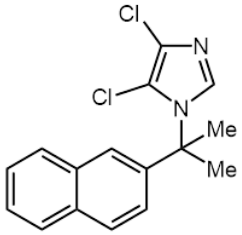
HRMS (ESI): calculated $[M+H]^+$ as 288.1495, found 288.1495

^{1}H NMR:



^{13}C NMR:





4,5-dichloro-1-(2-(naphthalen-2-yl)propan-2-yl)-1*H*-imidazole (**47**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), Ir(pFppy)$_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4,5-dichloro-1*H*-imidazole (68.5 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (50% ethyl acetate in hexanes, silica gel) afforded 76.3 mg pure product.

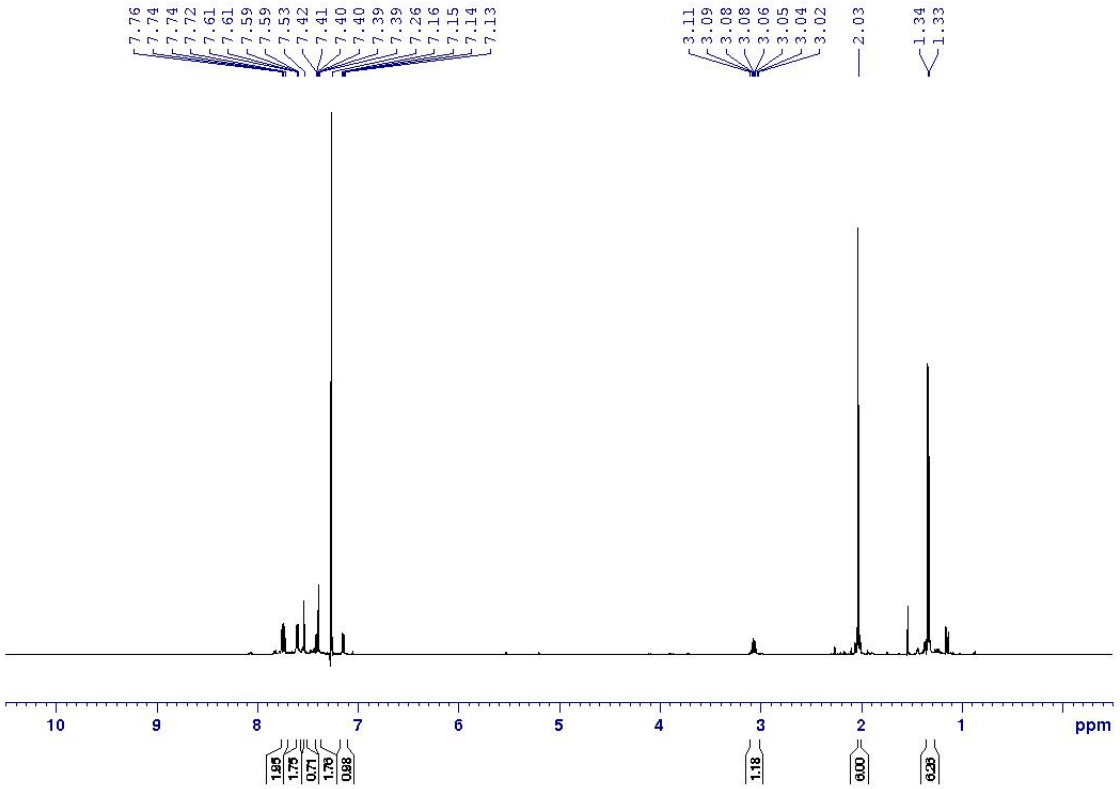
Isolated Yield: 50%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.84-7.80 (m, 3H), 7.74 (s, 1H), 7.74 (s, 1H), 7.65 (d, *J* = 1.8 Hz, 1H), 7.53-7.48 (m, 2H), 7.10 (dd, *J* = 8.6, 2.05 Hz, 1H), 2.07 (s, 6H).

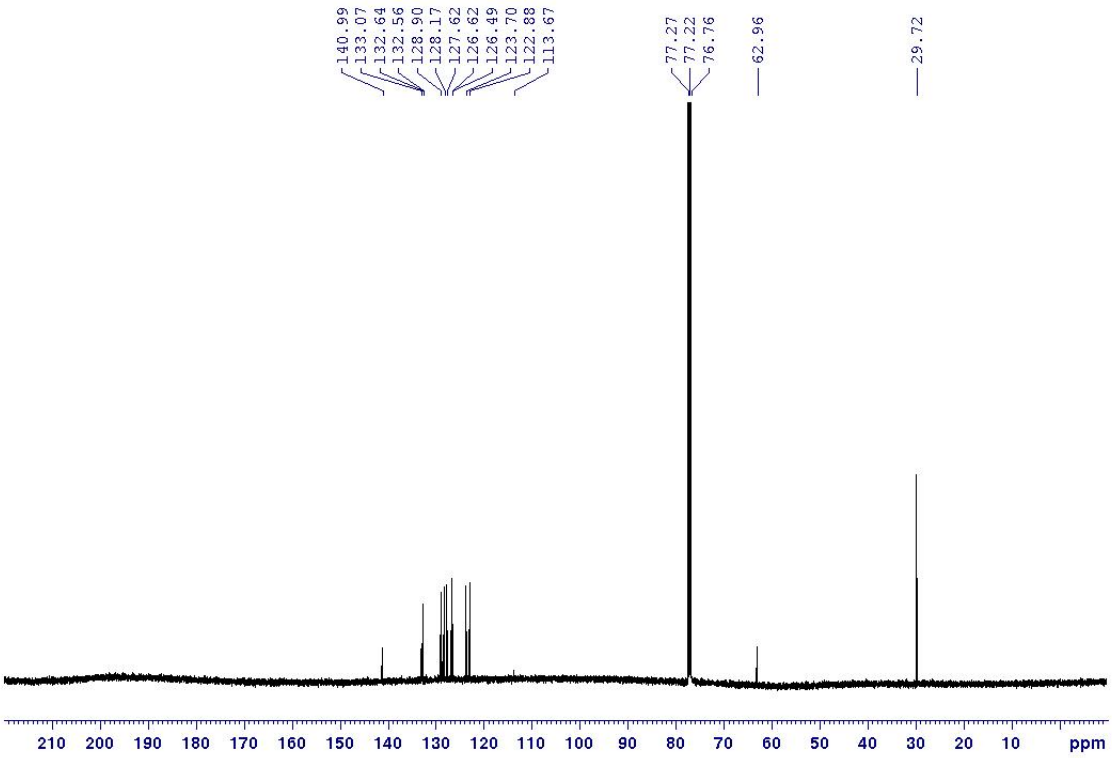
^{13}C NMR (126MHz, Chloroform-*d*): δ 140.9, 133.0, 132.6, 132.5, 128.9, 128.1, 127.6, 126.6, 126.4, 123.7, 122.8, 62.9, 29.7.

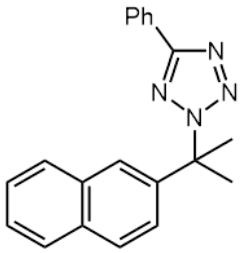
HRMS (ESI): calculated $[M+H]^+$ as 305.0607, found 305.0421

^{1}H NMR:



^{13}C NMR:





2-(2-(naphthalen-2-yl)propan-2-yl)-5-phenyl-2*H*-tetrazole (**48**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 5-phenyl-2*H*-tetrazole (73.07 mg, 0.5000 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (5% ethylacetate in hexanes, silica gel) afforded 114.7 mg pure product.

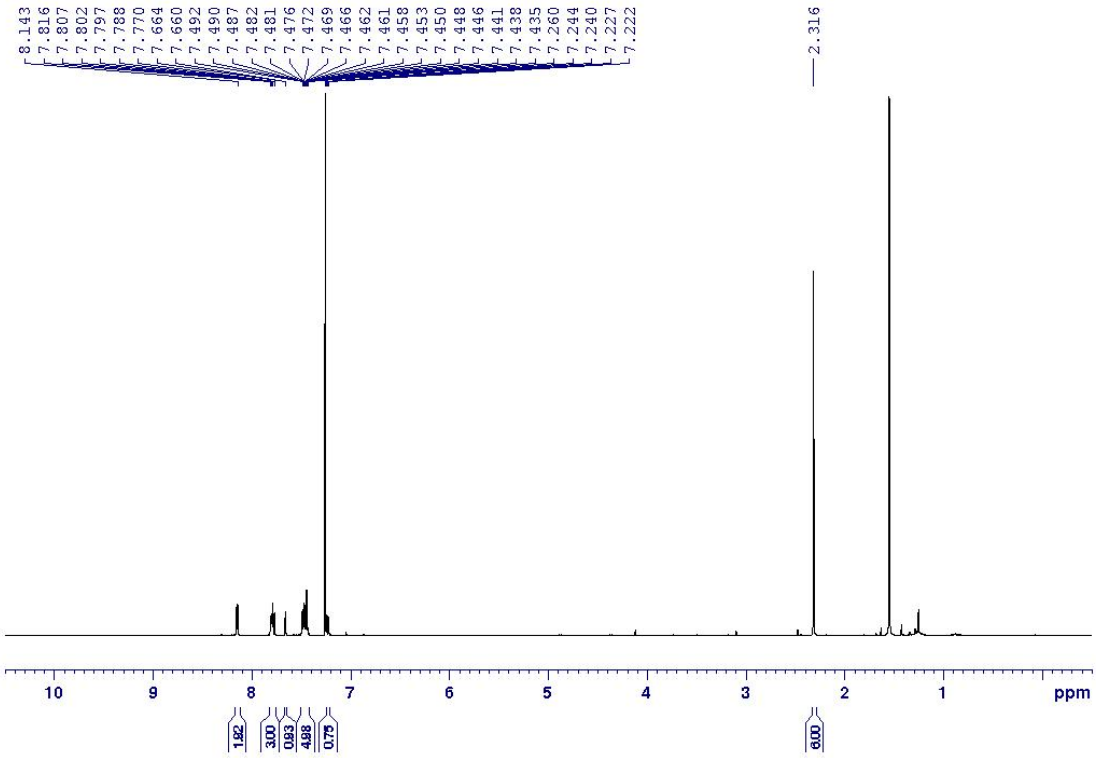
Isolated Yield: 73%

^{1}H NMR (500MHz, Chloroform-*d*): δ 8.16-8.14 (m, 2H), 7.81-7.77 (m, 3h), 7.66 (d, J=1.9 Hz, 1H), 7.49-7.43 (m, 5H), 7.22 (dd, J = 8.7, 2.0 Hz, 1H), 2.31 (s, 6H).

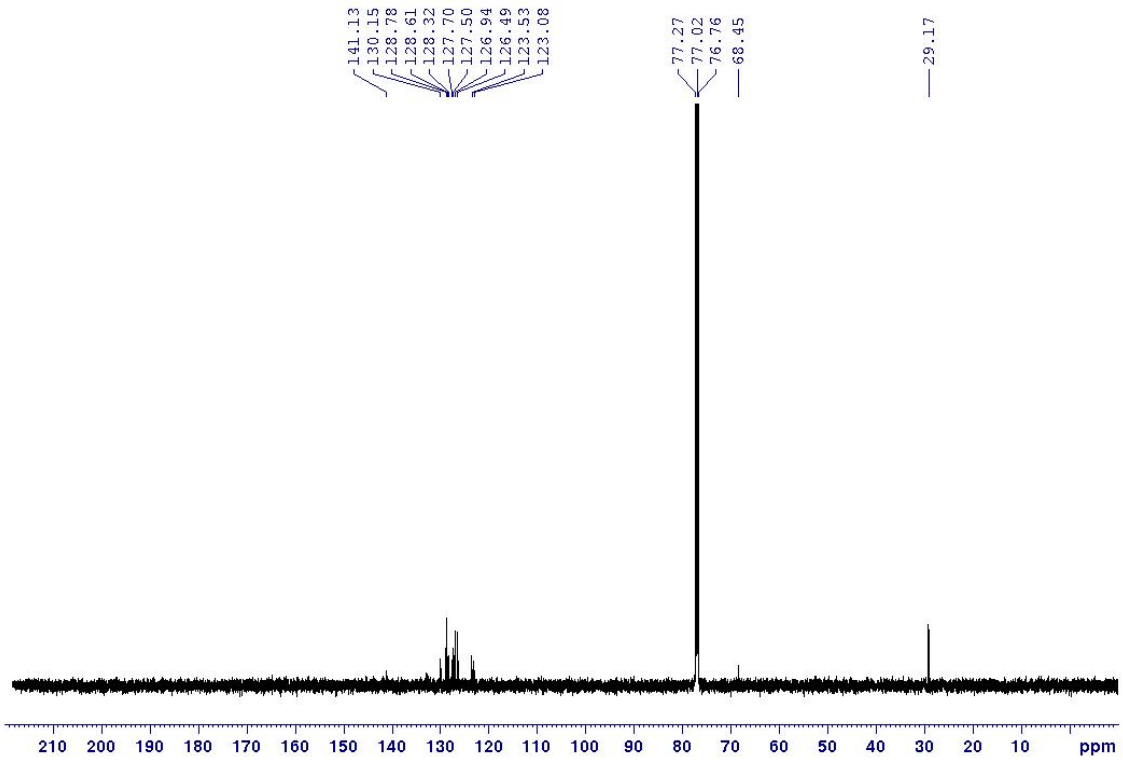
^{13}C NMR (126MHz, Chloroform-*d*): δ 141.1, 130.1, 128.7, 128.6, 128.3, 127.6, 127.5, 126.9, 126.4, 123.5, 123.0, 68.4, 29.1.

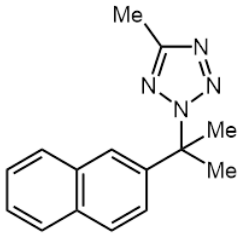
HRMS (ESI): calculated $[M+H]^+$ as 315.1609, found 315.1581

^{1}H NMR:



^{13}C NMR:





5-methyl-2-(2-(naphthalen-2-yl)propan-2-yl)-2*H*-tetrazole (**49**)

Synthesized according to the general procedure G, with 2-isopropylnaphthalene (261.8 µL, 1.500 mmol, 3 equiv.), Ir(pFppy)$_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 5-methyl-2*H*-tetrazole (42.04 mg, 0.5000 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (12% diethyl ether in hexanes, silica gel) afforded 50.5 mg pure product.

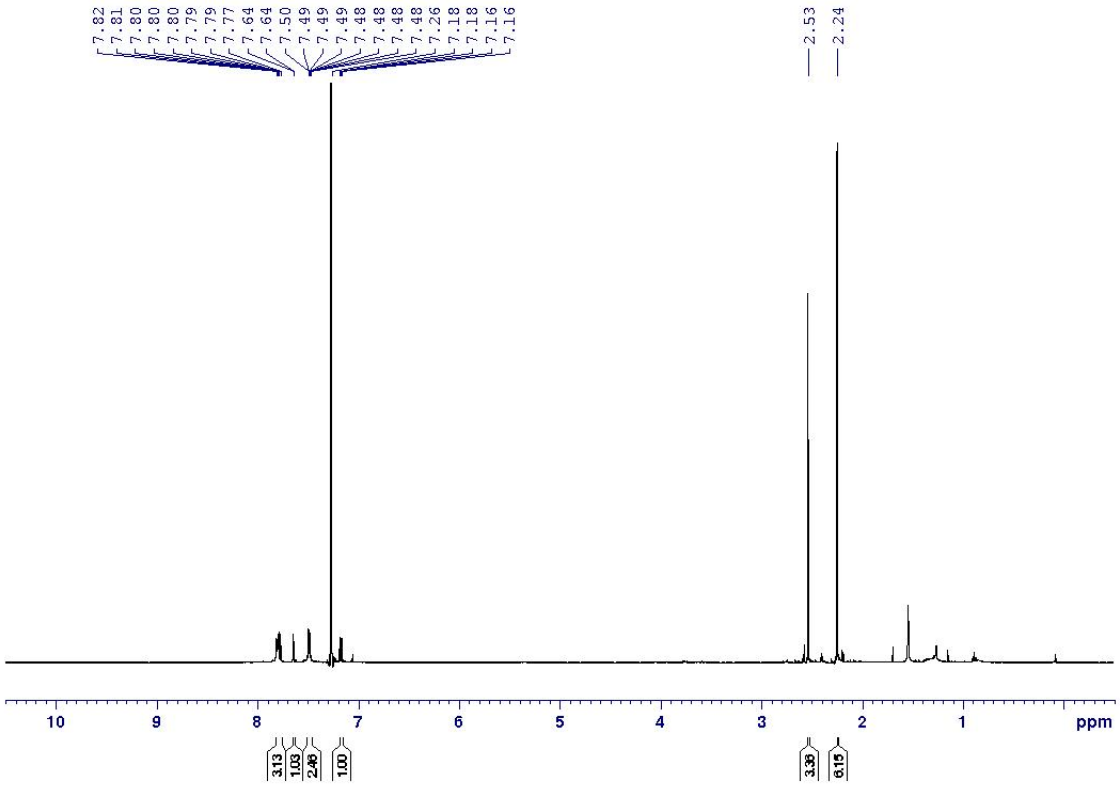
Isolated Yield: 40%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.81-7.76 (m, 3H), 7.64 (d, *J*=2.0 Hz, 1H), 7.49-7.47 (m, 2H), 7.16 (dd, *J*= 8.7, 2.0 Hz, 1H), 2.53 (s, 3H), 2.24 (s, 6H).

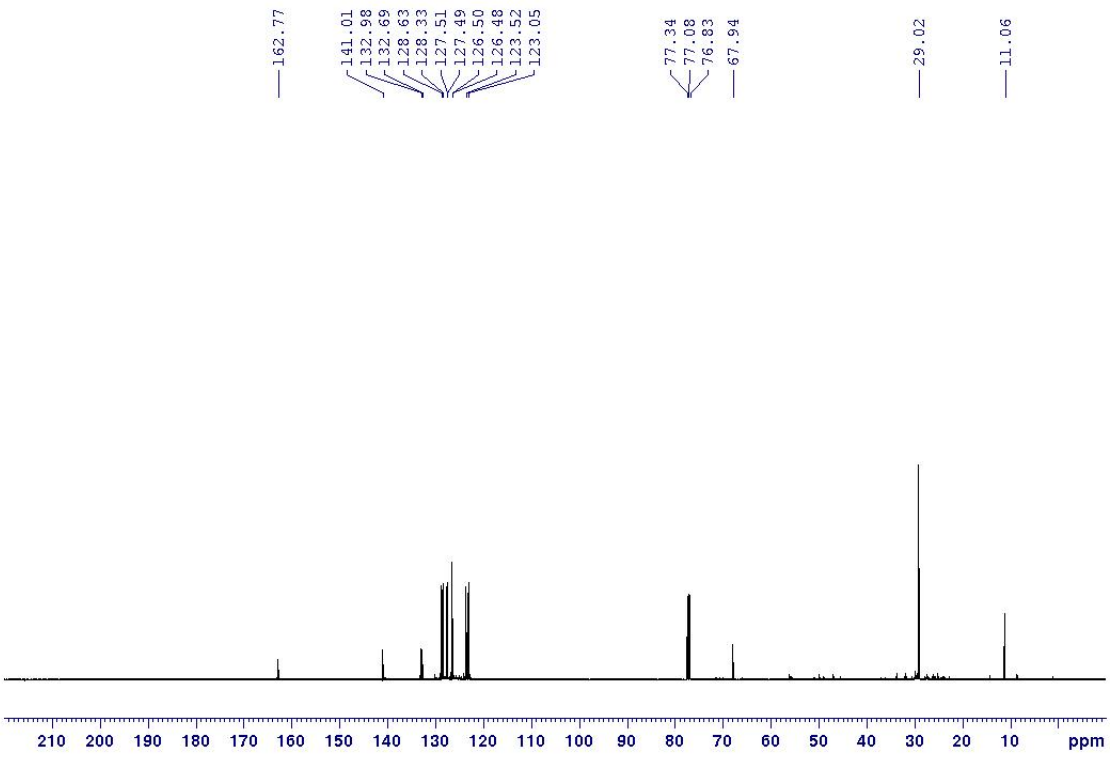
^{13}C NMR (126MHz, Chloroform-*d*): δ 162.7, 141.0, 132.9, 132.6, 128.6, 128.3, 127.5, 127.4, 126.5, 126.5, 126.4, 123.5, 123.0, 67.9, 29.0, 11.0.

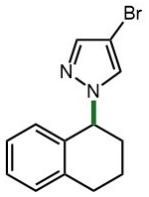
HRMS (ESI): calculated $[M+H]^+$ as 253.1453, found 253.1426

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(1,2,3,4-tetrahydronaphthalen-1-yl)-1H-pyrazole (**50**)

Synthesized according to the general procedure E for heterocycle addition with tetralin (64.1 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.46 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 91 mg pure product.

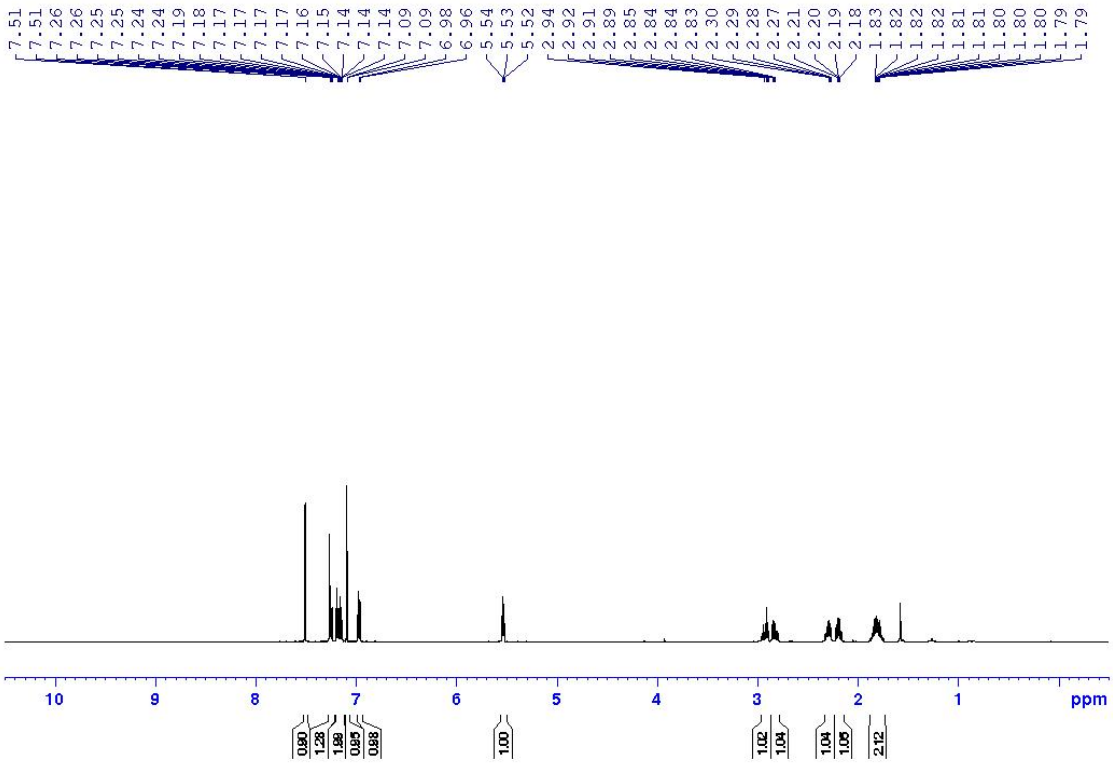
Isolated Yield: 66%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.50 (d, J = 0.6 Hz, 1H), 7.26-7.23 (m ,1H), 7.19-7.13 (m, 2H), 7.09 (d, J = 0.5 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 5.53 (t, J = 5.6 Hz, 1H), 2.92 (dt, J = 17 Hz, 1H), 2.85-2.79 (m, 1H), 2.32-2.26 (m, 1H), 2.21-2.15 (m, 1H), 1.87-1.73 (m, 2H).

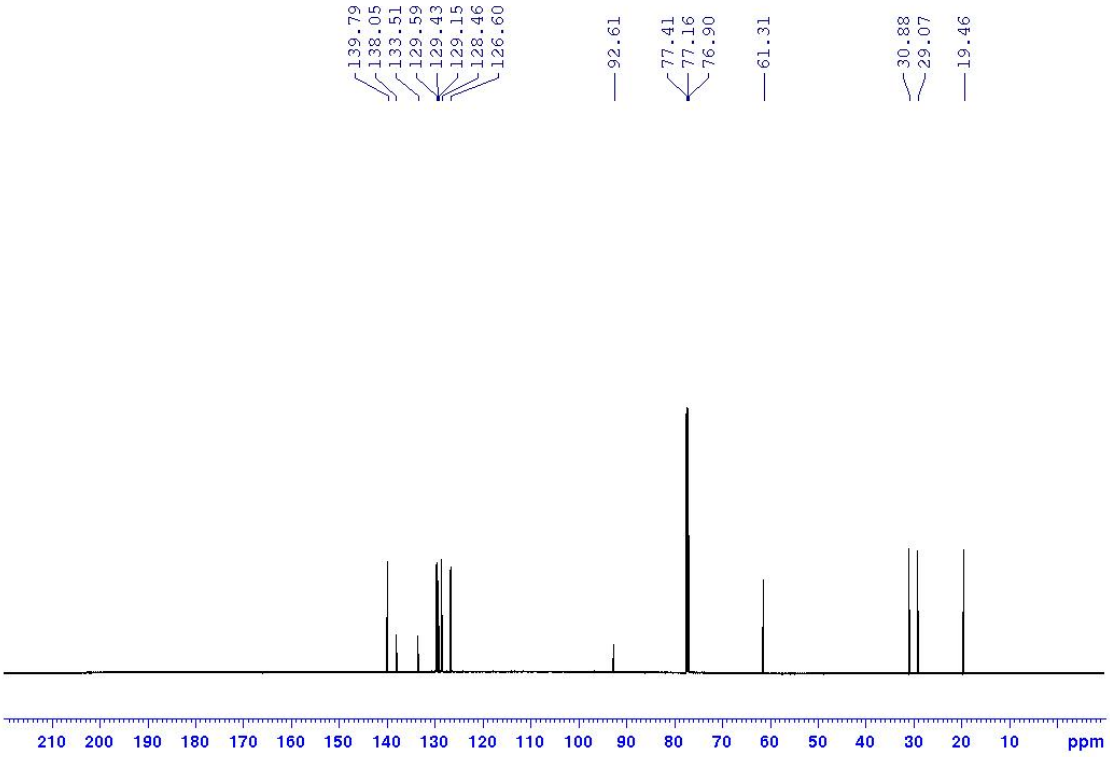
^{13}C NMR (126MHz, Chloroform-*d*): δ 139.7, 138.0, 133.5, 129.6, 129.4, 129.1, 128.4, 126.6, 92.6, 61.3, 30.9, 29.1, 19.4.

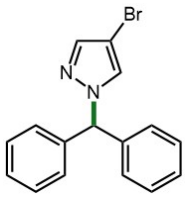
HRMS (ESI): calculated $[M+Na]^{+}$ as 299.0154, found 299.0157.

^{1}H NMR:



^{13}C NMR:





1-benzhydryl-4-bromo-1H-pyrazole (**51**)

Synthesized according to the general procedure F for heterocycle addition with diphenylmethane (83.6 µL, 0.500 mmol, 1 equiv.), Ir(dFppy)$_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (4% ethyl acetate in hexanes, silica gel) afforded 125 mg pure product.

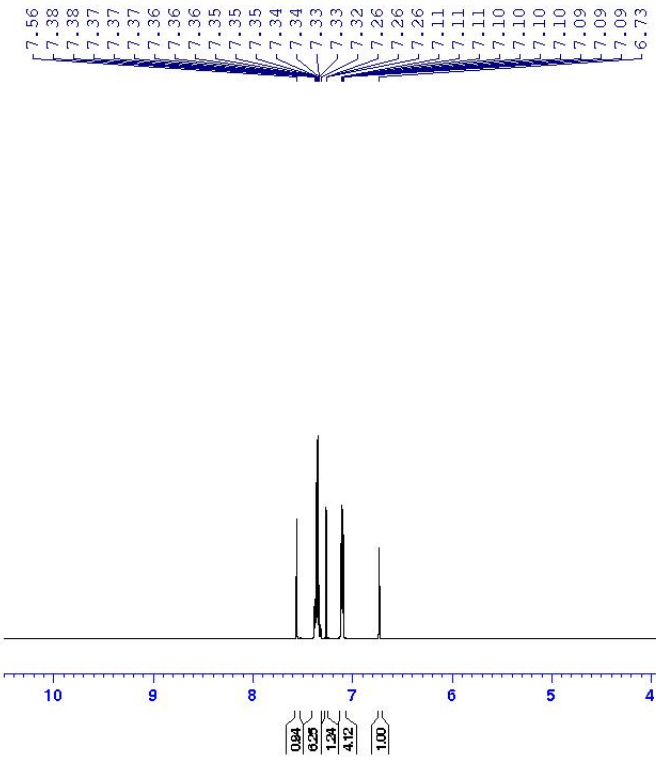
Isolated Yield: 56%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.55 (d, J = 0.6 Hz, 1H), 7.38-7.31 (m, 6H), 7.26 (d, J = 0.5 Hz, 1H), 7.11-7.08 (m, 4H), 6.73 (s, 1h).

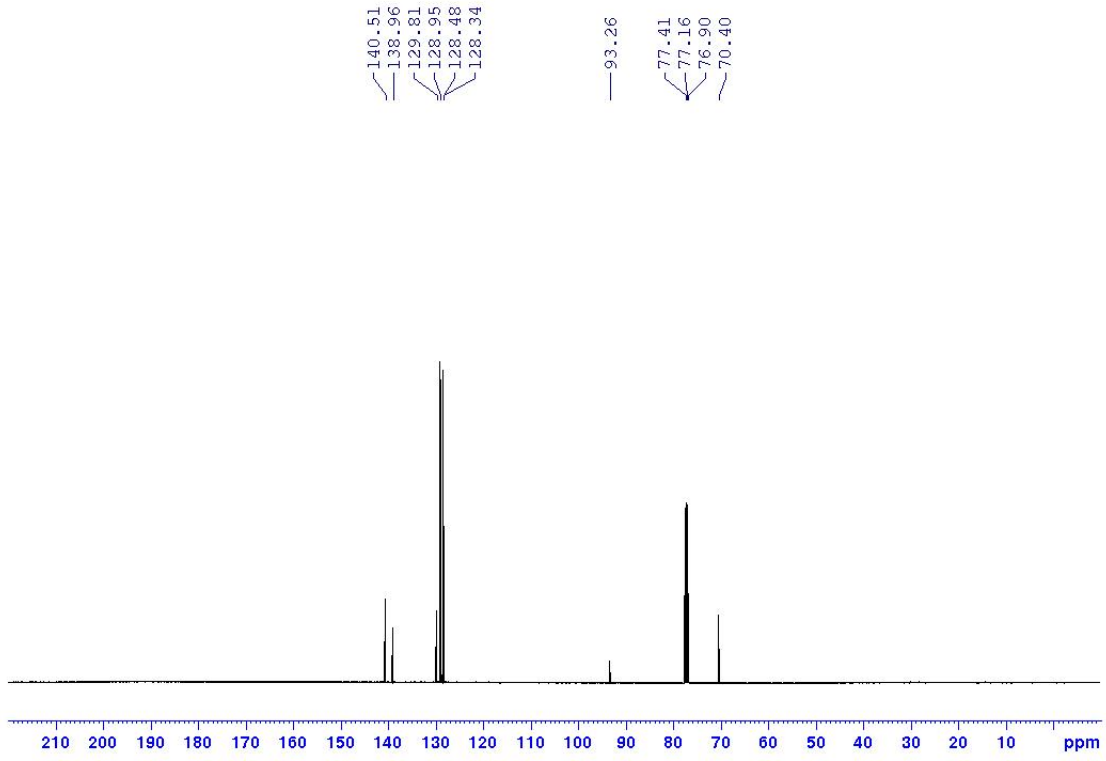
^{13}C NMR (126MHz, Chloroform-*d*): δ 140.5, 138.9, 129.8, 128.9, 128.5, 128.3, 93.2, 70.4.

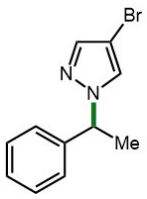
HRMS (ESI): calculated $[M+H]^+$ as 313.0335, found 313.0339.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(1-phenylethyl)-1H-pyrazole (**52**)

Synthesized according to the general procedure F for heterocycle addition with ethyl benzene (61.3 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (3% ethyl acetate in hexanes, silica gel) afforded 65 mg pure product.

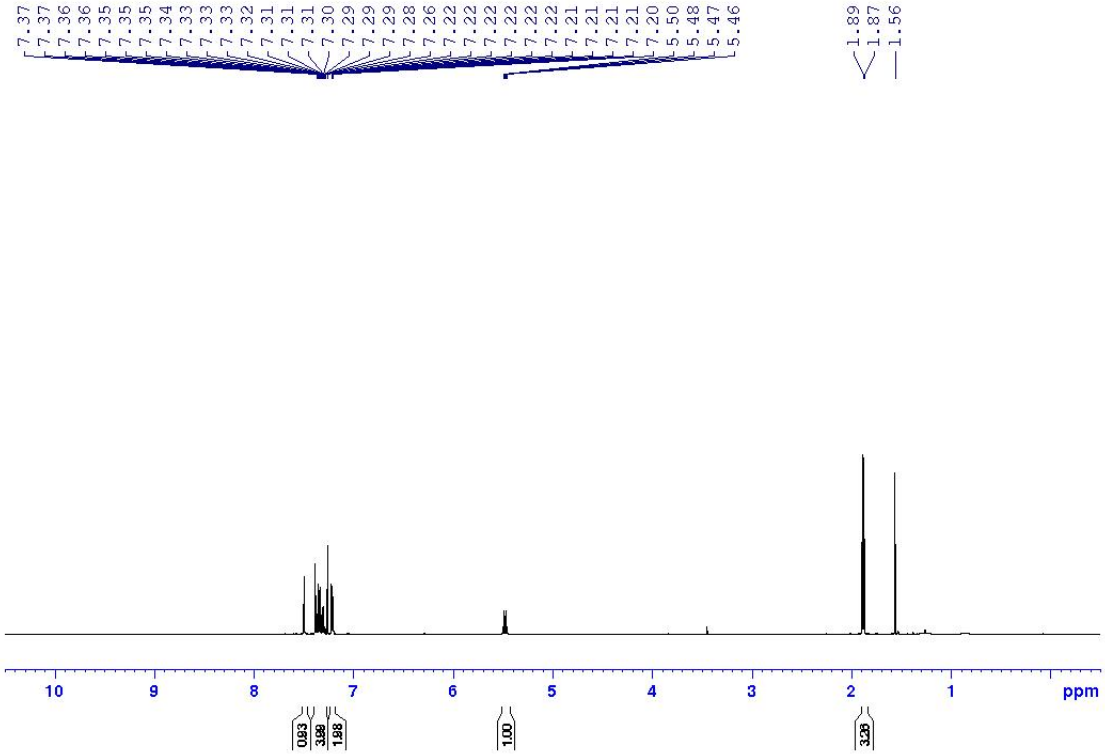
Isolated Yield: 52%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.49 (d, J = 0.4 Hz, 1H), 7.38 (d, J = 0.4 Hz, 1H), 7.36-7.32 (m, 2H), 7.30 (tt, J = 7.2, 1.5 Hz, 1H), 7.22-7.20 (m, 2H), 5.47 (q, J = 7.1 Hz, 1H), 1.87 (d, J = 7.1 Hz, 3H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 141.1, 139.7, 128.9, 128.3, 128.2, 126.5, 93.2, 62.0, 21.3.

HRMS (ESI): calculated $[M+H]^+$ as 251.0179, found 251.0178.

^{1}H NMR:


7.37
7.37
7.36
7.36
7.35
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.31
7.31
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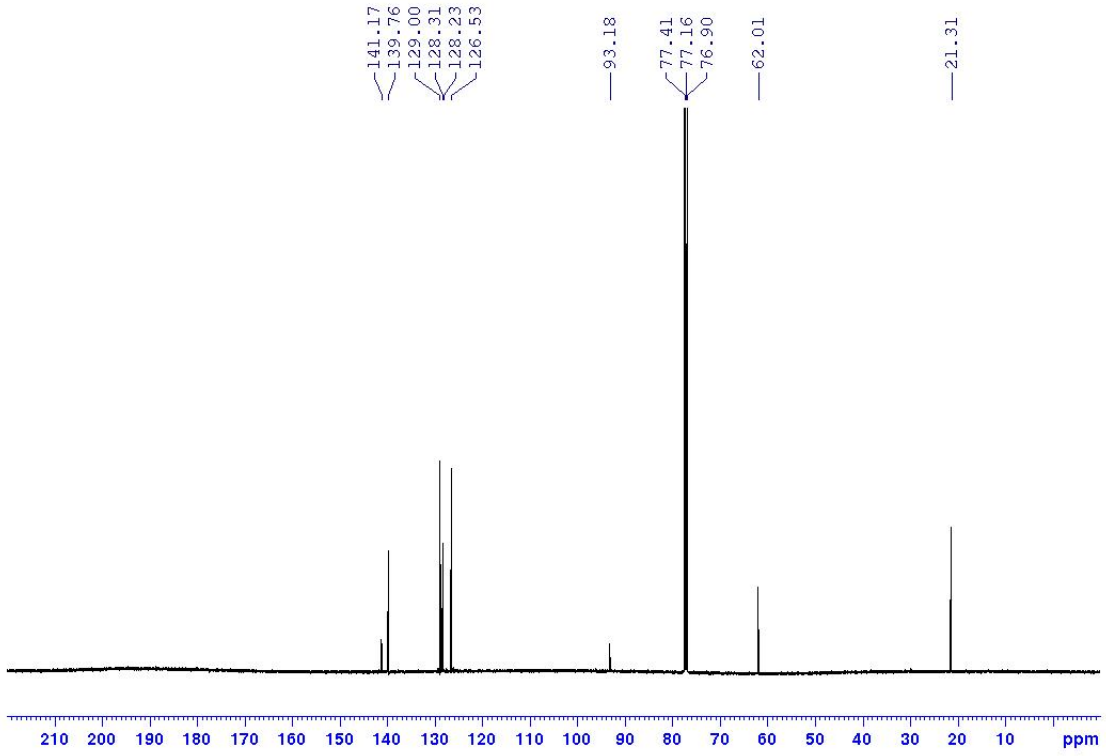
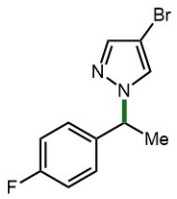
7.28
7.26
7.22
7.22
7.22
7.22
7.22
7.21
7.21
7.21
7.21
7.20
5.50
5.48
5.47
5.46
1.89
1.87
1.56
10
9
8
7
6
5
4
3
2
1
ppm
0.93
3.98
1.98
1.00
3.00

^{13}C NMR:





4-bromo-1-(1-(4-fluorophenyl)ethyl)-1H-pyrazole (**53**)

Synthesized according to the general procedure F for heterocycle addition with 4-fluoro-ethyl benzene (62.1 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 60 mg pure product.

Isolated Yield: 45%

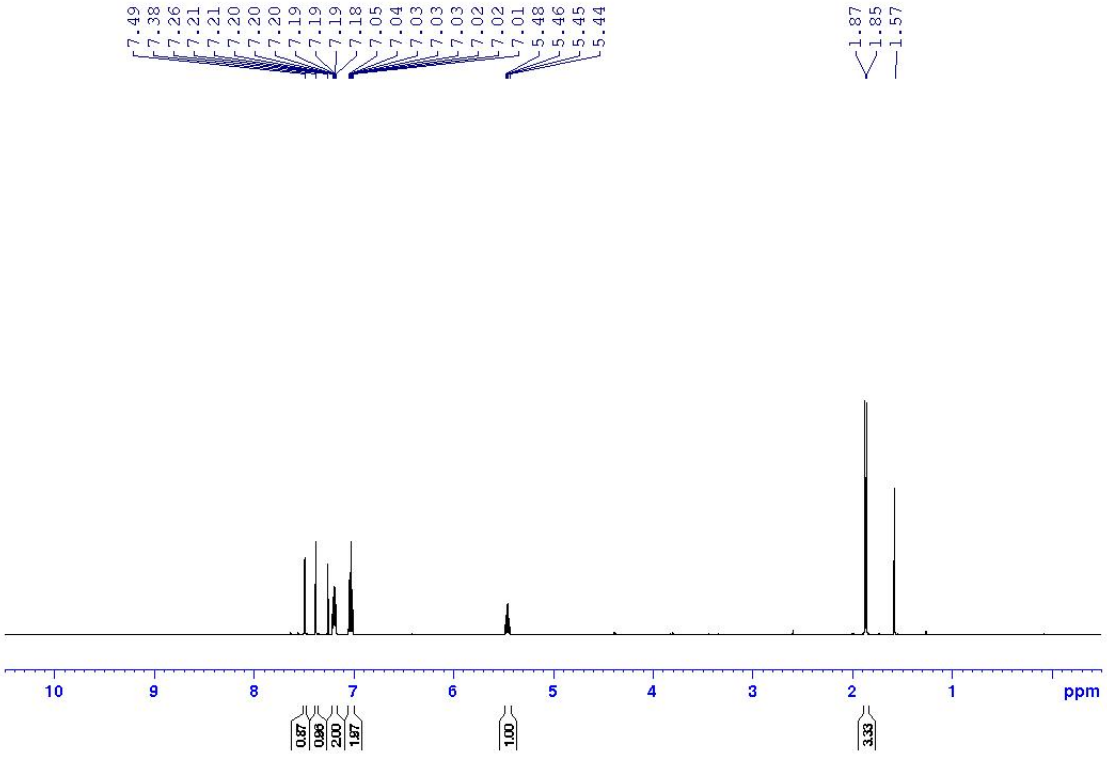
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.48 (s, 1H), 7.38 (s, 1H), 7.20-7.18 (m, 2H), 7.04-7.01 (m, 2H), 5.45 (q, J = 7.1 Hz, 1H), 1.86 (d, J = 7.1 Hz, 3H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 163.5, 161.6, 139.9, 137.0, 136.9, 128.3, 128.2, 128.1, 115.9, 115.8, 93.3, 61.3, 21.4.

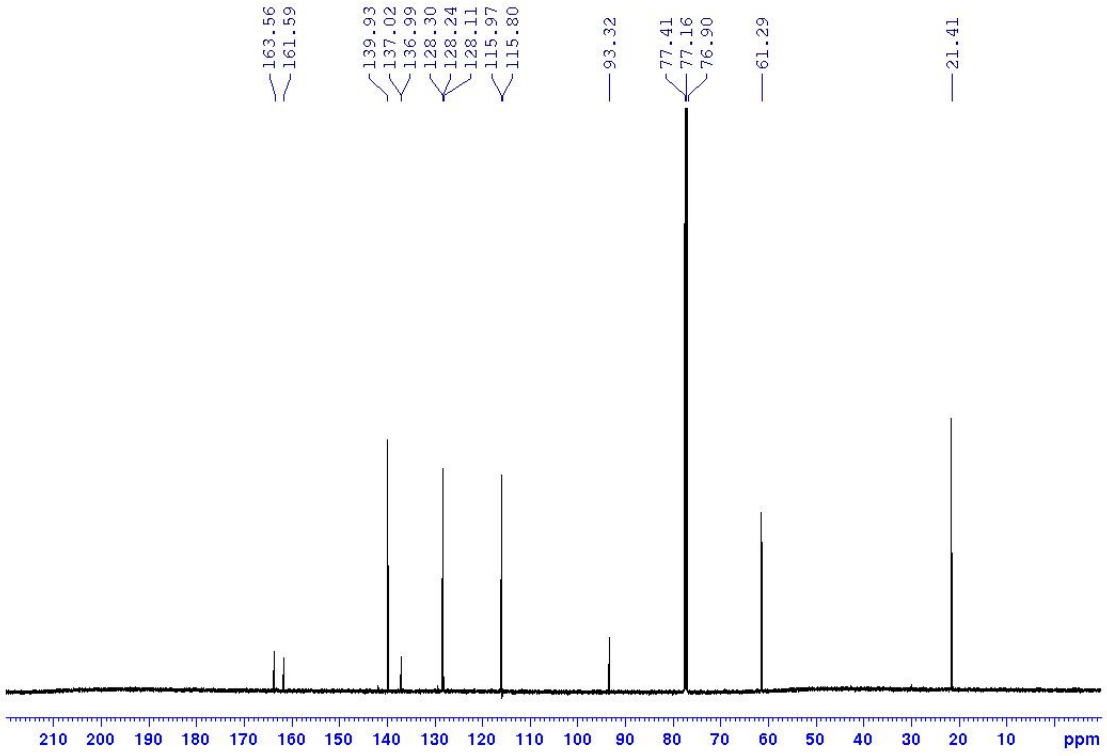
^{19}F NMR (377MHz, Chloroform-*d*): δ -113.9

HRMS (ESI): calculated $[M+H]^+$ as 269.0084, found 269.0084.

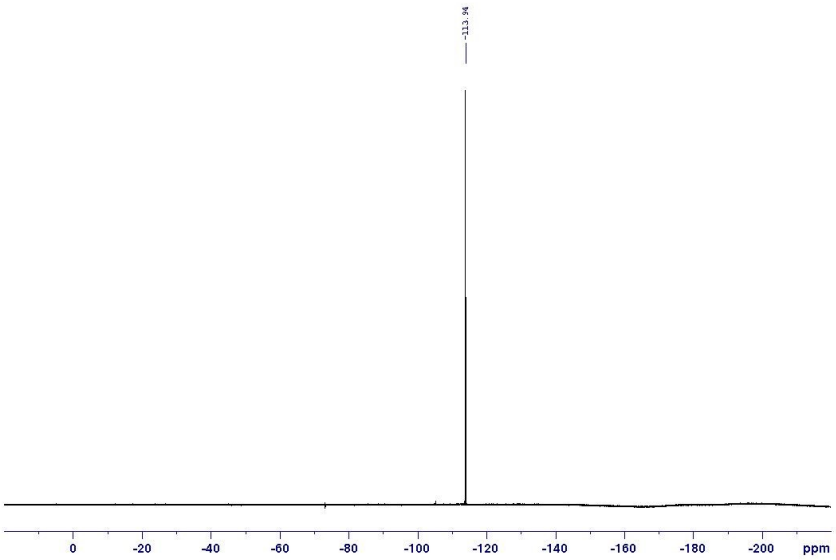
^{1}H NMR:

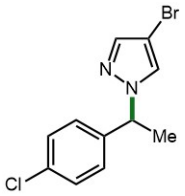


^{13}C NMR:



^{19}F NMR:





4-bromo-1-(1-(4-chlorophenyl)ethyl)-1H-pyrazole (**54**)

Synthesized according to the general procedure F for heterocycle addition with 4-chloro-ethyl benzene (67.3 μL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 58 mg pure product.

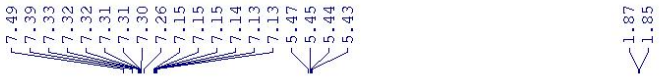
Isolated Yield: 41%

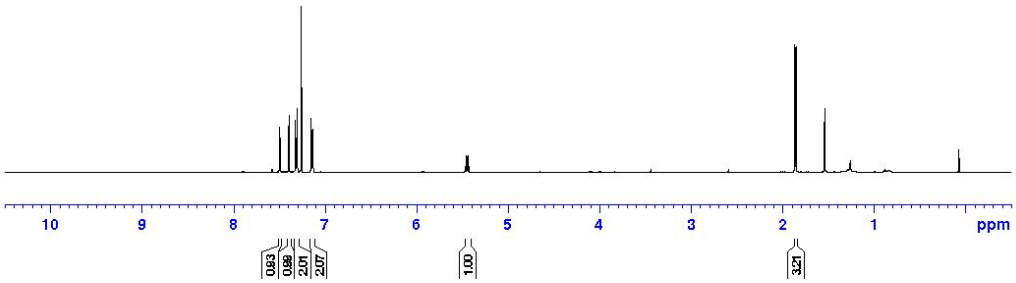
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.49 (s, 1H), 7.39 (s, 1H), 7.32-7.30 (m, 2H), 7.15-7.12 (m, 2H), 5.44 (q, J = 7.1 Hz, 1H), 1.85 (d, J = 7.1 Hz, 3H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 140.0, 139.8, 134.2, 129.2, 128.2, 127.9, 93.4, 61.3, 21.2.

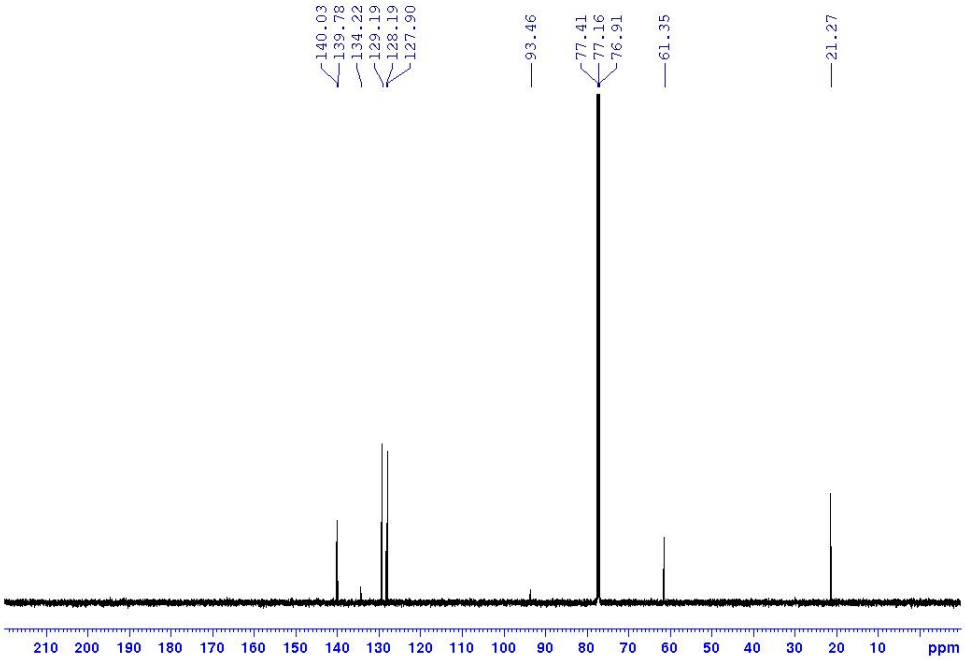
HRMS (ESI): calculated $[M+H]^+$ as 284.9789, found 284.9790.

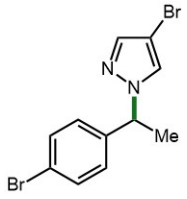
^{1}H NMR:





^{13}C NMR:





4-bromo-1-(1-(4-bromophenyl)ethyl)-1H-pyrazole (**55**)

Synthesized according to the general procedure F for heterocycle addition with 4-bromo-ethyl benzene (68.9 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 81 mg pure product.

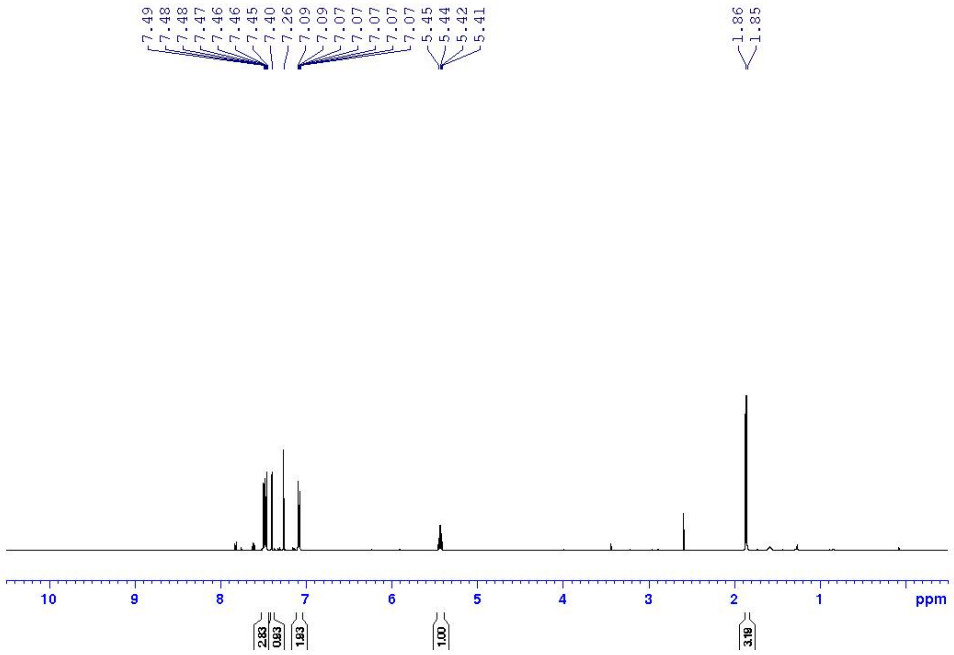
Isolated Yield: 49%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.49 (s, 1H), 7.48-7.45 (m, 2H), 7.39 (s, 1H), 7.09-7.06 (m, 2H), 5.42 (q, J = 7.1 Hz, 1H), 1.85 (d, J = 7.1 Hz, 3H).

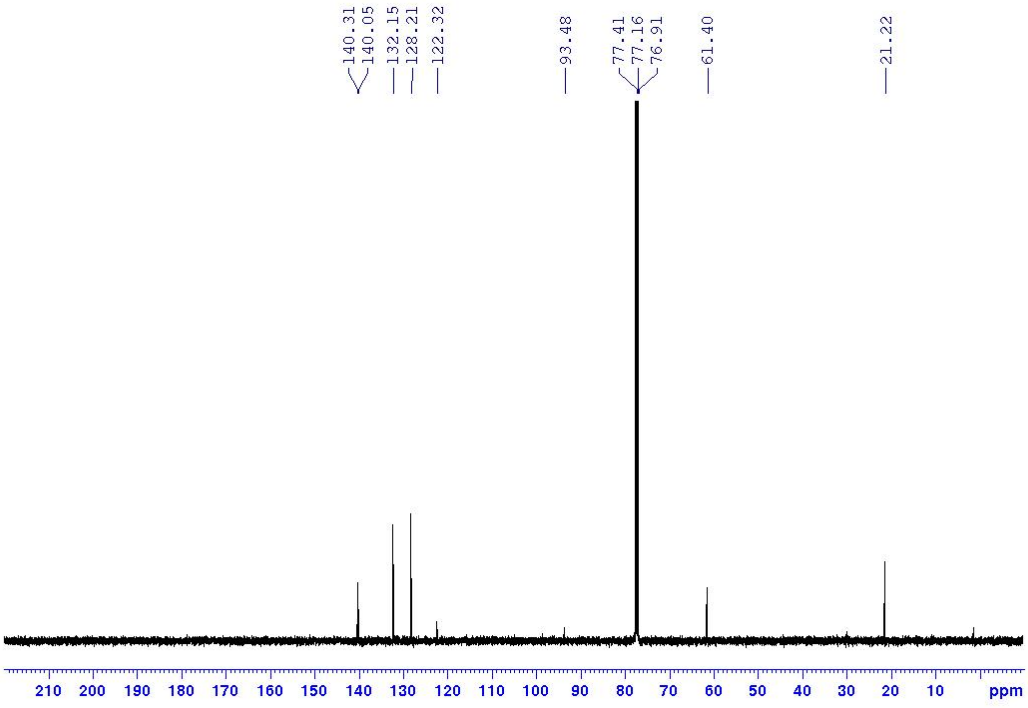
^{13}C NMR (126MHz, Chloroform-*d*): δ 140.3, 140.0, 132.1, 128.2, 122.3, 93.5, 61.4, 21.2.

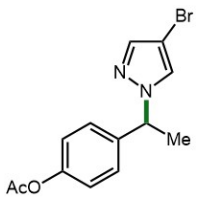
HRMS (ESI): calculated $[M+H]^+$ as 328.9284, found 328.9283.

^{1}H NMR:



^{13}C NMR:





4-(1-(4-bromo-1H-pyrazol-1-yl)ethyl)phenyl acetate (**56**)

Synthesized according to the general procedure F for heterocycle addition with 4-ethylphenyl acetate (80 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 50 mg pure product.

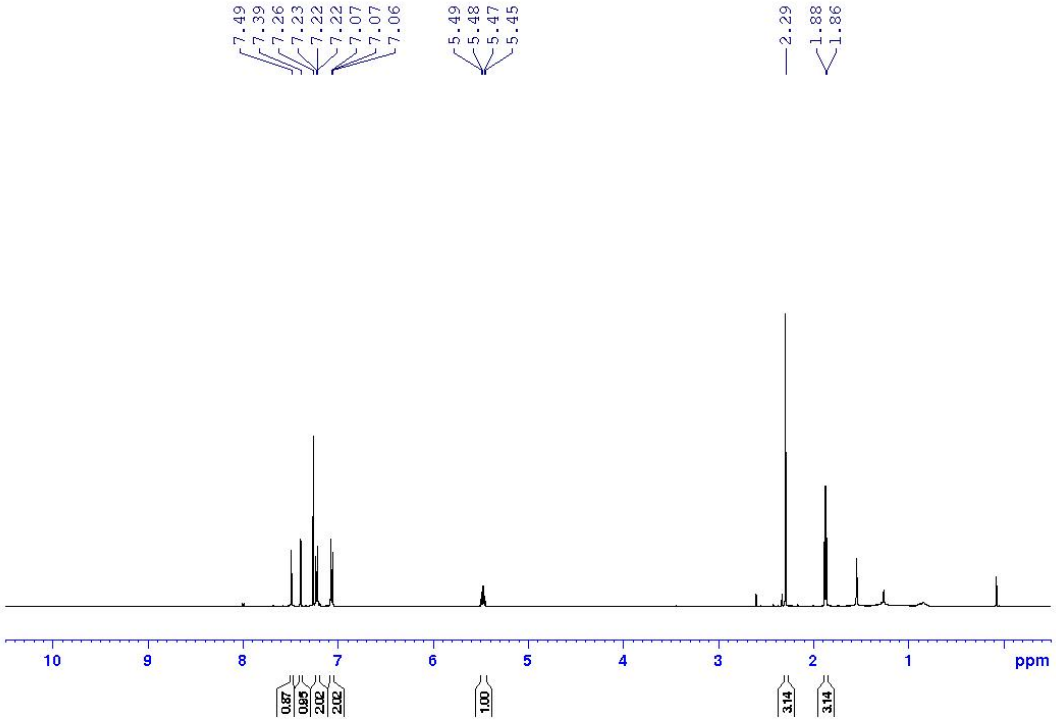
Isolated Yield: 32%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.49 (s, 1H), 7.39 (s, 1H), 7.23-7.21 (m, 2H), 7.07-7.05 (m, 2H), 5.47 (q, J = 7Hz, 1H), 2.29 (s, 3H), 1.86 (d, J = 7.1 Hz, 3H).

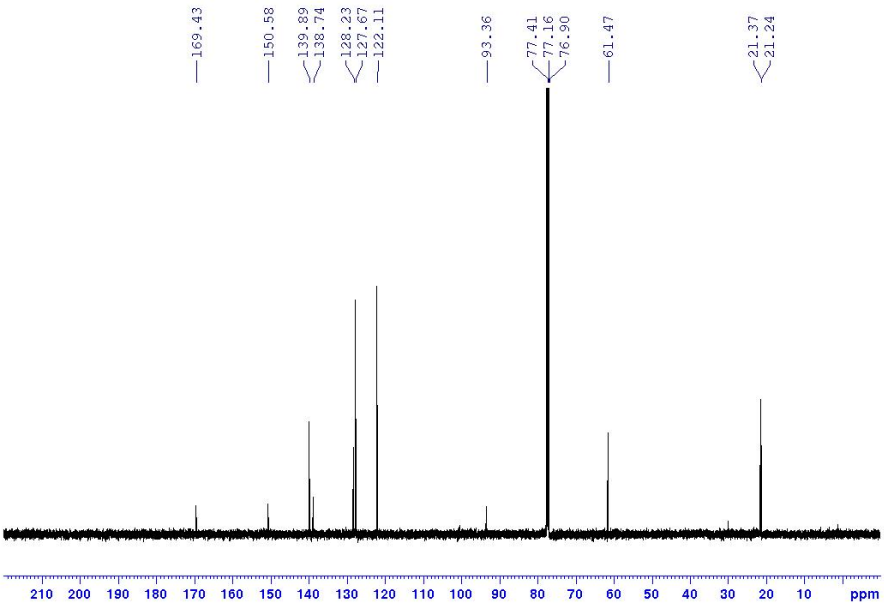
^{13}C NMR (126MHz, Chloroform-*d*): δ 169.4, 150.5, 139.9, 138.7, 128.2, 127.6, 122.1, 93.3, 61.4, 21.4, 21.2.

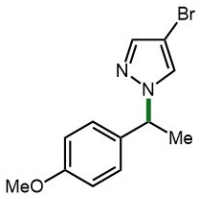
HRMS (ESI): calculated $[M+H]^+$ as 309.0233, found 309.0233.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(1-(4-methoxyphenyl)ethyl)-1H-pyrazole (**57**)

Synthesized according to the general procedure E for heterocycle addition with 4-ethylanisole (71.1 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 127 mg pure product.

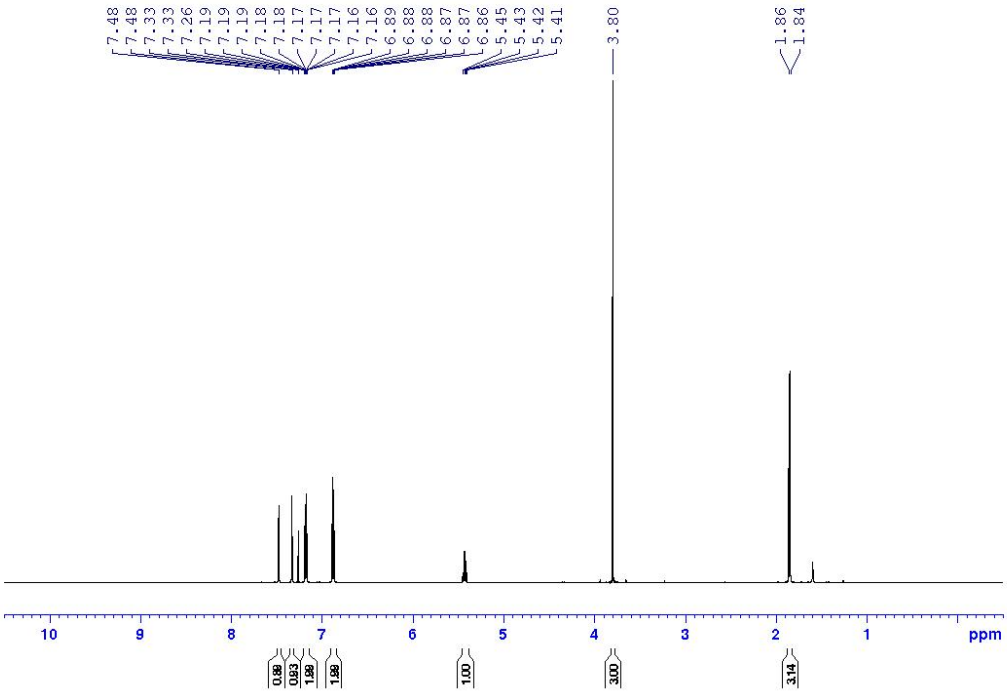
Isolated Yield: 90%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.47 (d, J = 0.5 Hz, 1H), 7.33 (d, J = 0.4 Hz, 1H), 7.19-7.16 (m, 2H), 6.89-6.86 (m, 2H), 5.42 (q, J = 7.1 Hz, 1H), 3.79 (s, 3H), 1.84 (d, J = 7.1 Hz, 3H).

^{13}C NMR (126MHz, Chloroform-*d*): δ 159.6, 139.6, 133.0, 128.0, 127.9, 114.3, 93.0, 61.5, 55.4, 21.3.

HRMS (ESI): calculated $[M+H]^+$ as 281.0289, found 281.0258.

^{1}H NMR: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7.18
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5.42
5.41
3.80
1.86
1.84
10
9
8
7
6
5
4
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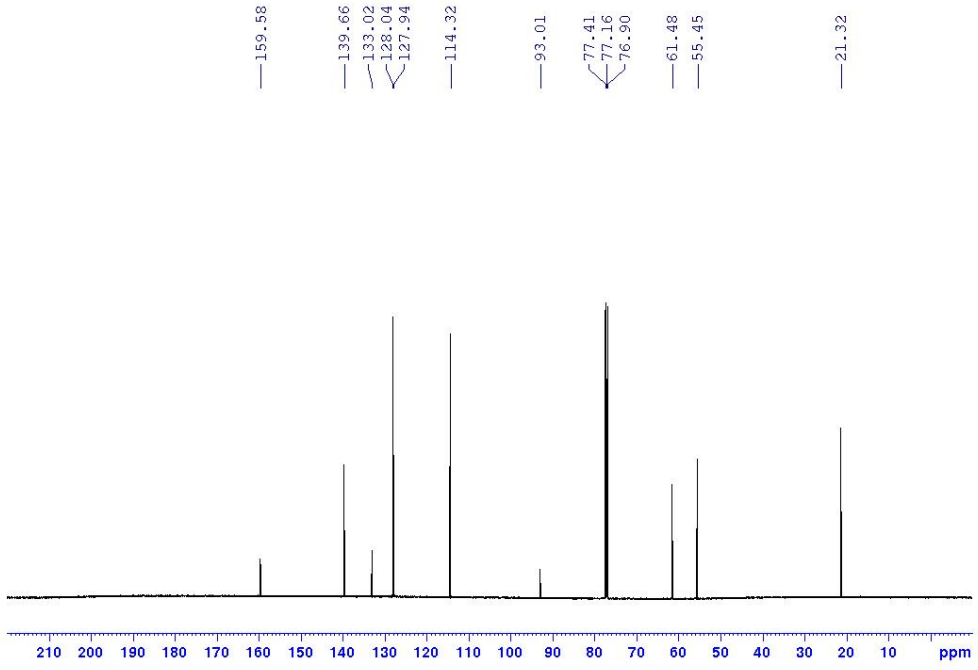
1.00
3.00
3.14

^{13}C NMR:


159.58
139.66
133.02
128.04
127.94
114.32
93.01
77.41
77.16
76.90
61.48
55.45
21.32
210
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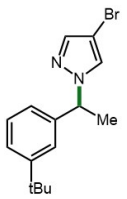
90
80
70
60
50
40
30
20
10
ppm



4-bromo-1-(1-(3-(tert-butyl)phenyl)ethyl)-1H-pyrazole (**58**)

Synthesized according to the general procedure F for heterocycle addition with 1-(tert-butyl)-3-ethylbenzene (94.4 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 86 mg pure product.

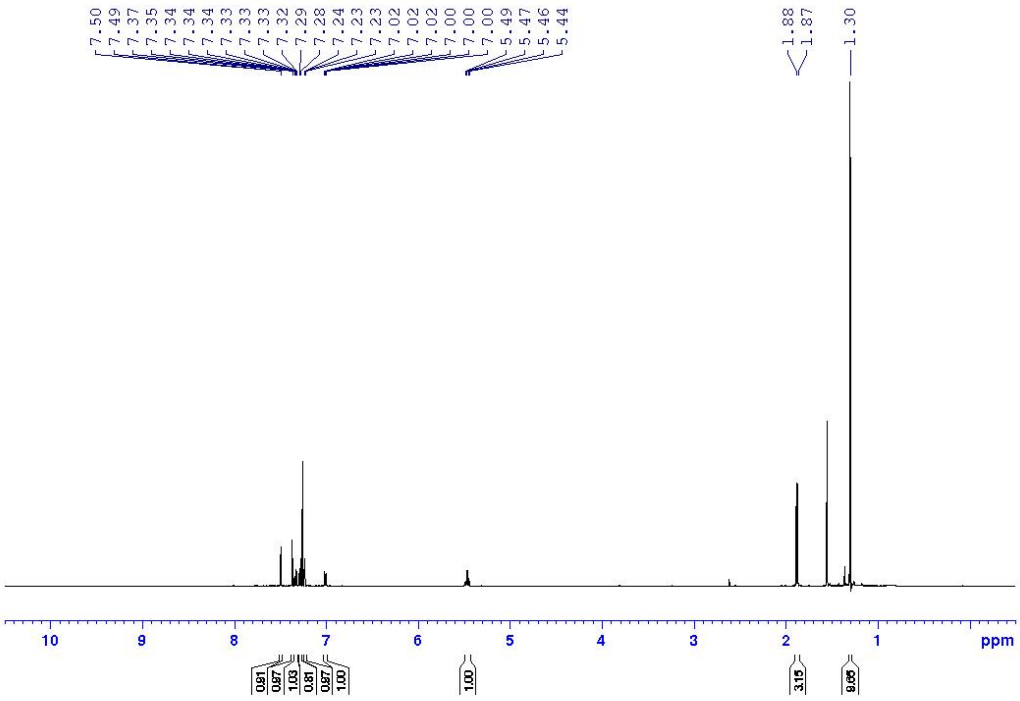
Isolated Yield: 56%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.49 (d, J = 0.5 Hz, 1H), 7.36 (s, 1H), 7.34-7.32 (m, 1H), 7.28 (d, J = 7.6 Hz, 1H), 7.23 (t, J = 1.9 Hz, 1H), 7.02-7.00 (m, 1H), 5.46 (q, J = 7.1 Hz, 1H), 1.87 (d, J = 7.1 Hz, 3H), 1.29 (s, 9H).

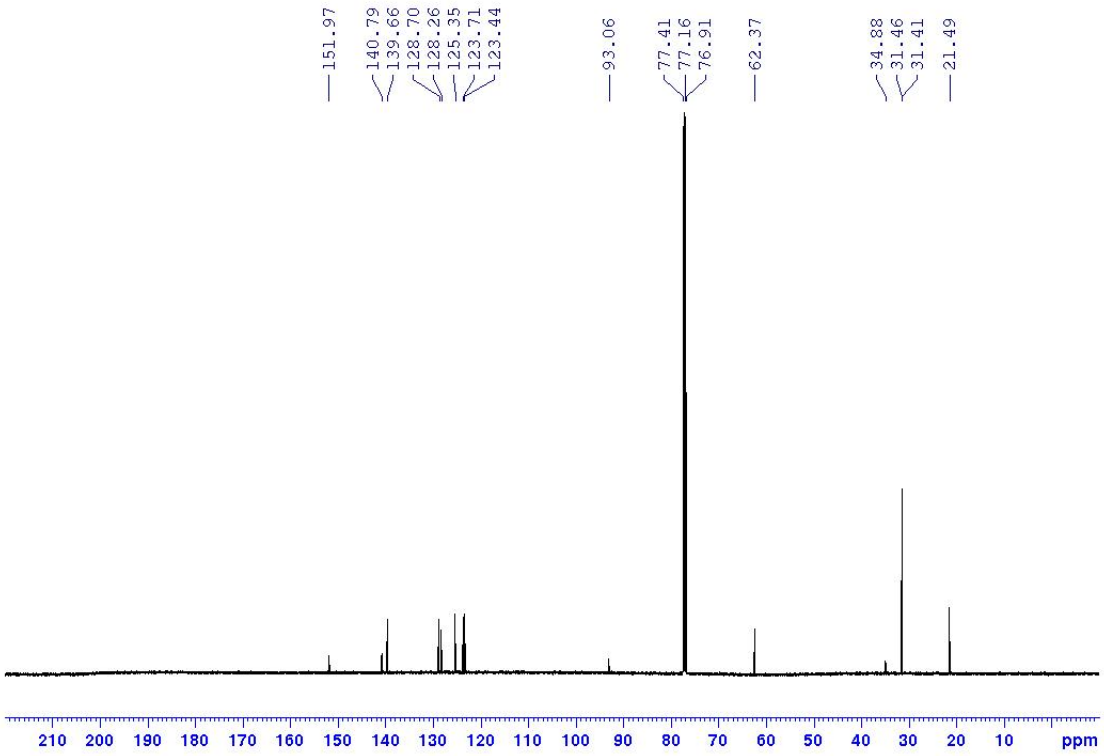
^{13}C NMR (126MHz, Chloroform-*d*): δ 151.9, 140.8, 139.6, 128.7, 128.2, 125.3, 123.7, 123.4, 93.1, 62.4, 34.9, 31.5, 31.4, 21.5.

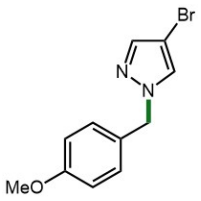
HRMS (ESI): calculated $[M+H]^+$ as 307.0805, found 307.0805.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(4-methoxybenzyl)-1H-pyrazole (**59**)

Synthesized according to the general procedure E for heterocycle addition with 4-methylanisole (63 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (12% ethyl acetate in hexanes, silica gel) afforded 97 mg pure product.

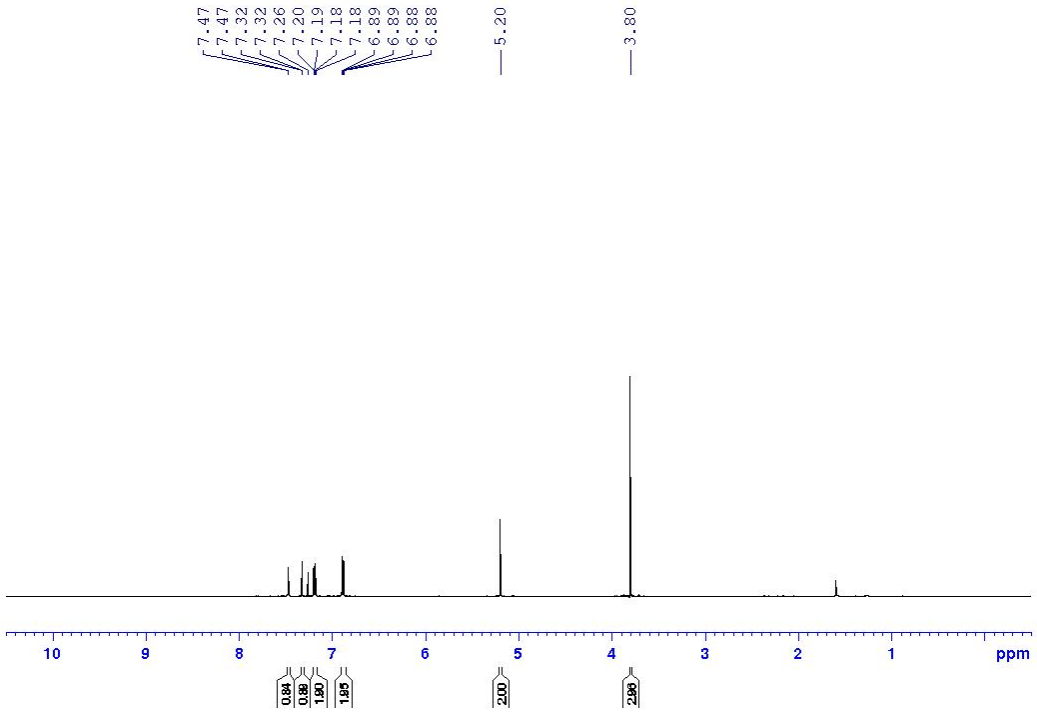
Isolated Yield: 72%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.47 (d, J = 0.5 Hz, 1H), 7.32 (d, J = 0.5 Hz, 1H), 7.19-7.18 (m, 2H), 6.90-6.87 (m, 2H), 5.19 (s, 2H), 3.80 (s, 3H).

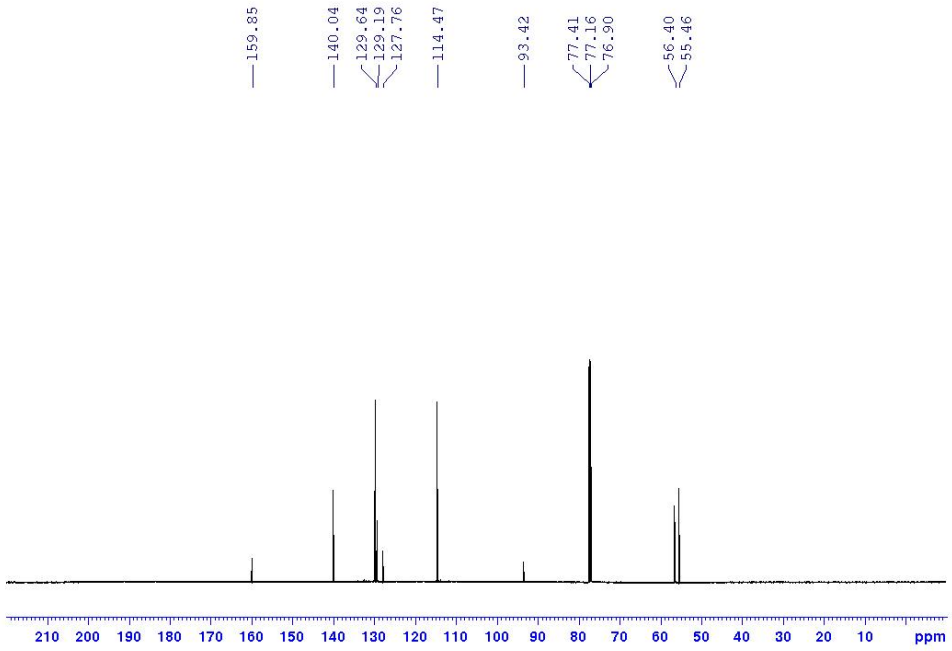
^{13}C NMR (126MHz, Chloroform-*d*): δ 159.8, 140.0, 129.6, 129.2, 127.7, 114.5, 93.4, 56.4, 55.4.

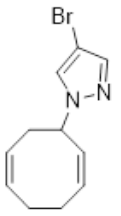
HRMS (ESI): calculated $[M+H]^+$ as 267.0128, found 267.0127.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-((2Z,6Z)-cycloocta-2,6-dien-1-yl)-1*H*-pyrazole (**60**)

Synthesized according to the general procedure for E with (1Z,5Z)-cycloocta-1,5-diene (61.5 µL, 0.500 mmol, 1 equiv.), $Ru(bpy)_3(PF_6)_2$ (4.2 mg, 0.0050 mmol, 0.01 equiv.) as the replacement photocatalyst, 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (111 mg, 0.500 mmol, 1 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane (2.5 mL, 0.2 M). Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 22.8 mg pure product.

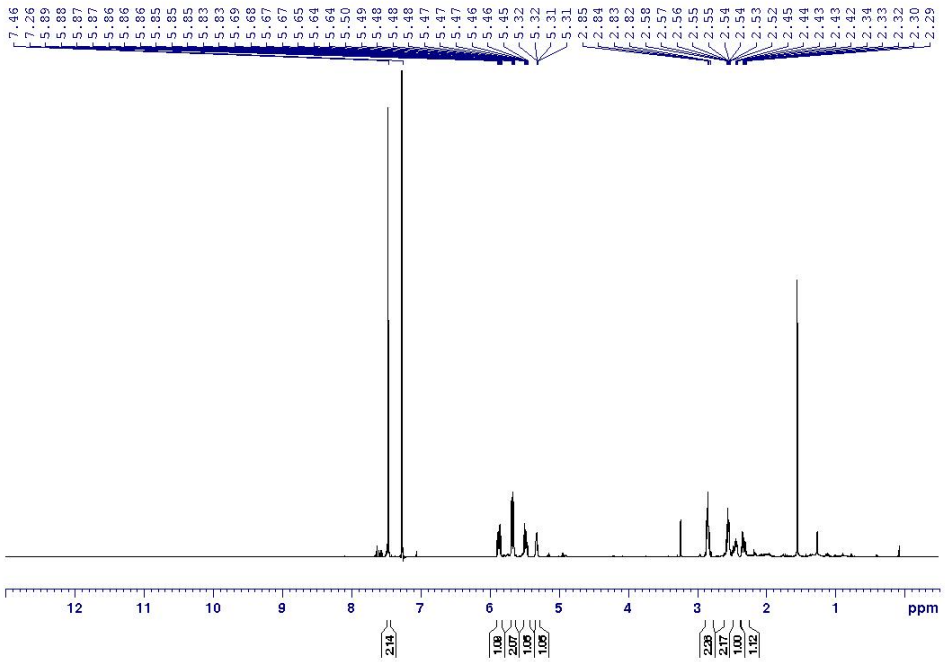
Isolated Yield: 18%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.46 (s, 2H), 5.88-5.83 (m, 1H), 5.68-5.64 (m, 2H), 5.52-5.44 (m, 1H), 5.33-5.29 (m, 1H), 2.85-2.81 (m, 2H), 2.57-2.52 (m, 2H), 2.48-2.40 (m, 1H), 2.35-2.27 (m, 1H).

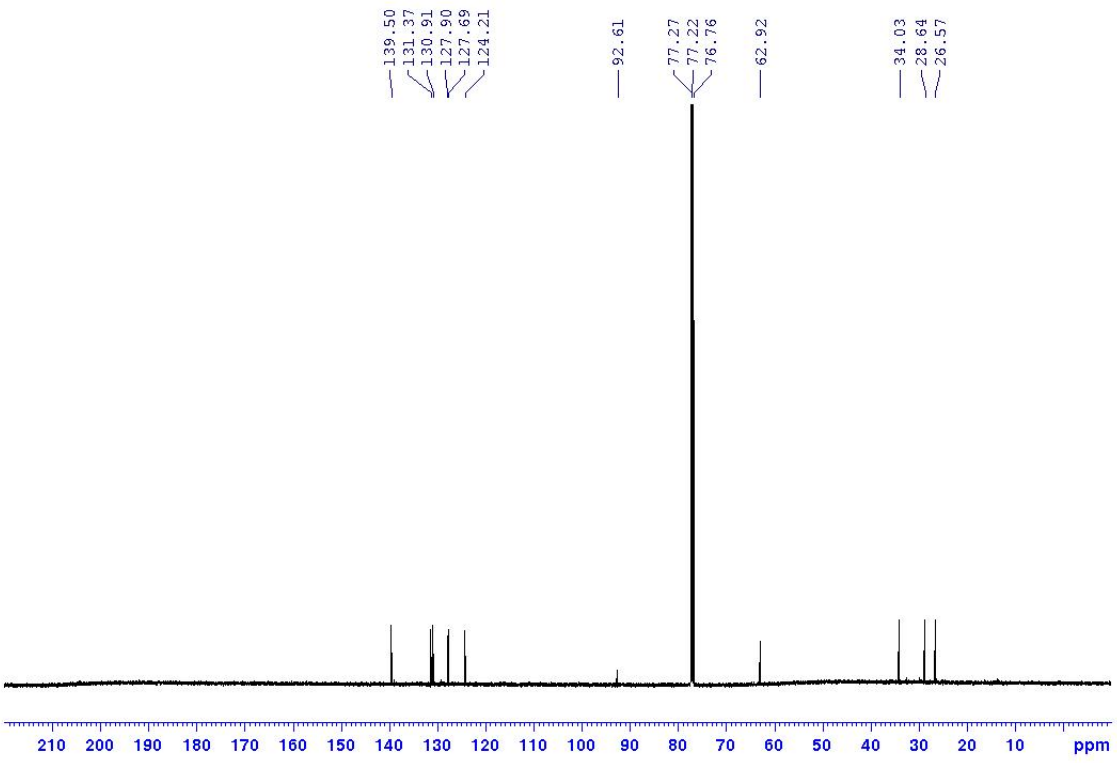
^{13}C NMR (126MHz, Chloroform-*d*): δ 139.5, 131.3, 130.91, 127.9, 127.7, 124.2, 92.6, 62.9, 34.0, 28.6, 25.5.

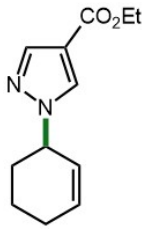
HRMS (ESI): calculated $[M+H]^+$ as 253.0335, found 253.0336

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(cyclohex-2-en-1-yl)-1H-pyrazole (**61**)

Synthesized according to the general procedure E for heterocycle addition with cyclohexene (253.2 µL, 2.500 mmol, 5 equiv.), Ir(dFppy)$_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), tert-butyl peroxybenzoate (143.0 µL, 0.7500 mmol, 1.5 equiv.), ethyl 1*H*-pyrazole-4-carboxylate (70.1 mg, 0.500 mmol, 1 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (7% ethyl acetate in hexanes, silica gel) afforded 5 mg pure product.

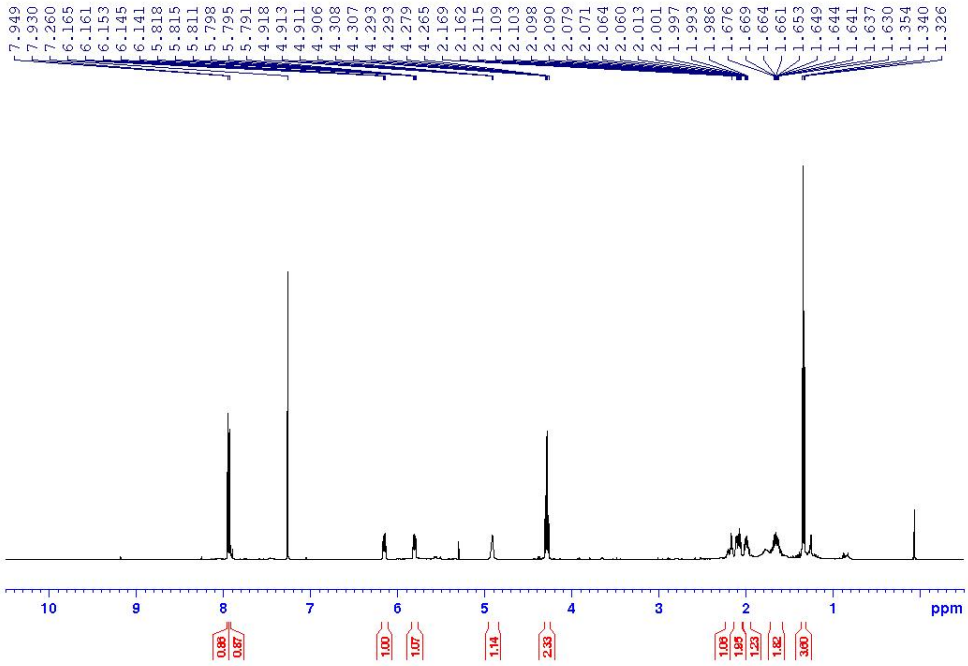
Isolated Yield: 45%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.94 (s, 1H), 7.93 (s, 1H), 6.15 (dtb, J =10, 3.8, 1.9 Hz, 1H), 5.82-5.78 (m, 1H), 4.92-4.88 (m, 1H), 4.28 (qd, J = 7.2, 0.5 Hz, 2H), 2.21-2.05 (m, 3H), 2.02-1.95 (m, 1H), 1.71-1.59 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H).

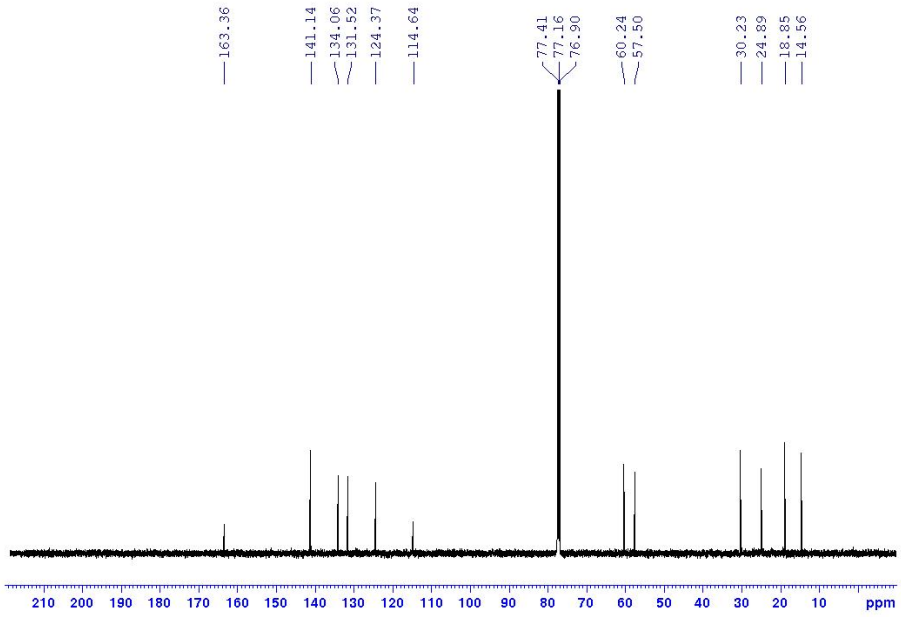
^{13}C NMR (126MHz, Chloroform-*d*): δ 163.3, 141.1, 134.0, 131.5, 124.3, 114.6, 60.2, 57.4, 30.2, 24.8, 18.8, 14.5.

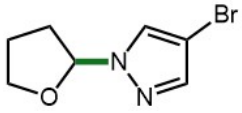
HRMS (ESI): calculated $[M+NH_4]^+$ as 222.1606, found 222.1297.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(tetrahydrofuran-2-yl)-1H-pyrazole (**62**)

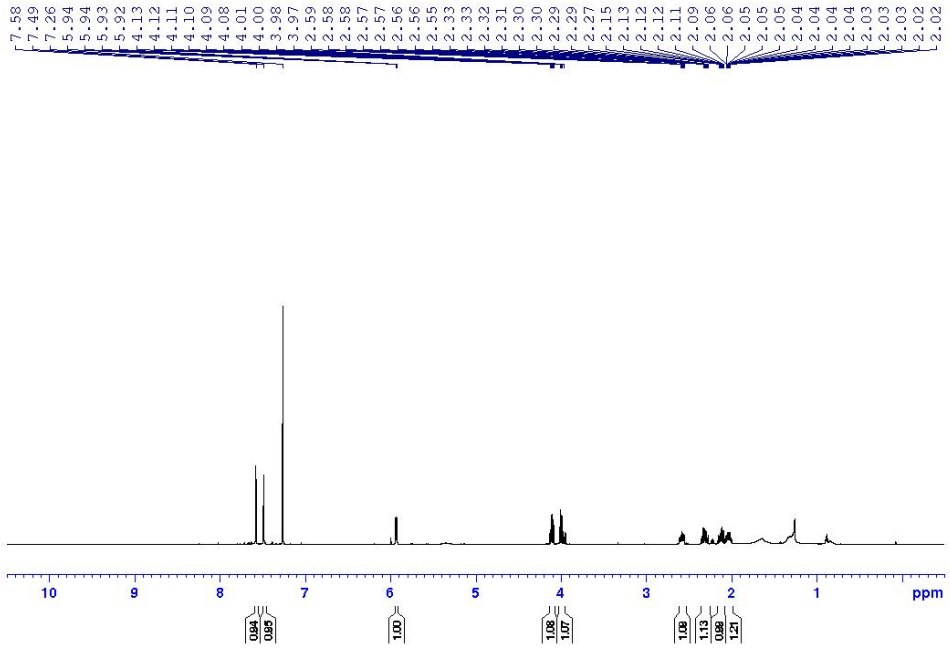
Synthesized according to the general procedure E for heterocycle addition with tetrahydrofuran (205 µL, 2.50 mmol, 5 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (73 mg, 0.500 mmol, 1 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (5% ethyl acetate in hexanes, silica gel) afforded 68 mg pure product.

Isolated Yield: 63%

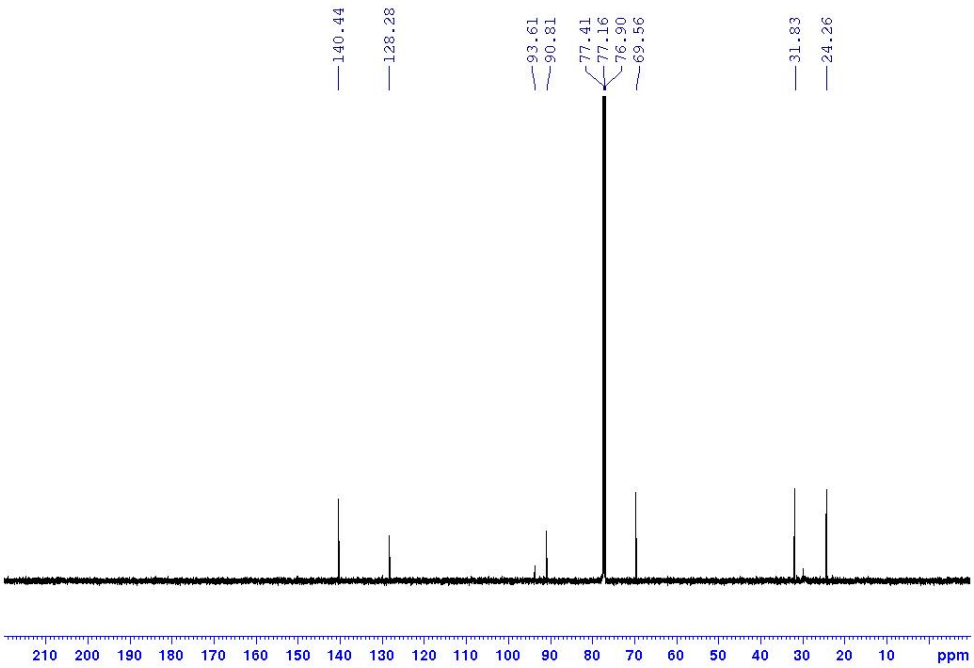
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.57 (s, 1H), 7.48 (s, 1H), 5.93 (dd, J = 6.7, 2.4 Hz, 1H), 4.12-4.08 (m, 1H), 4.01-3.96 (m, 1H), 2.60-2.55 (m, 1H), 2.34-2.27 (m, 1H), 2.16-2.09 (m, 1H), 2.07-1.99 (m, 1H).

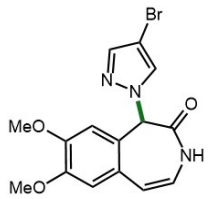
^{13}C NMR (126MHz, Chloroform-*d*): δ 140.4, 128.3, 93.6, 90.8, 69.5, 31.8, 24.2.

^{1}H NMR:



^{13}C NMR:





1-(4-bromo-1H-pyrazol-1-yl)-7,8-dimethoxy-1,3-dihydro-2H-benzo[d]azepin-2-one (**63**)

Synthesized according to the general procedure E for heterocycle addition with 7,8-dimethoxy-1,3-dihydro-2*H*-benzo[d]azepin-2-one (109.62 mg, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (10% ethyl acetate in dichloromethane, silica gel) afforded 87 mg pure product.

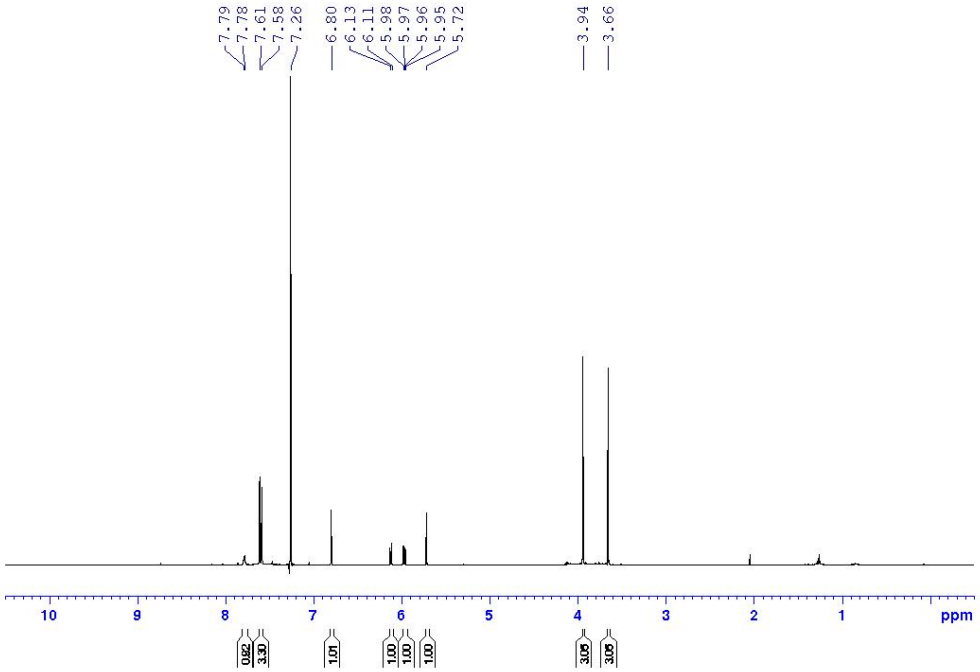
Isolated Yield: 48%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.77 (d, J = 5.1 Hz, 1H), 7.61 (s, 1H), 7.60-7.57 (m, 1H), 7.58 (s, 1), 6.79 (s, 1H), 6.12 (d, J = 9.1 Hz, 1H), 5.96 (dd, J = 8.9, 5.4 Hz, 1H), 5.71 (s, 1H), 3.94 (s, 3H), 3.65 (s, 3H).

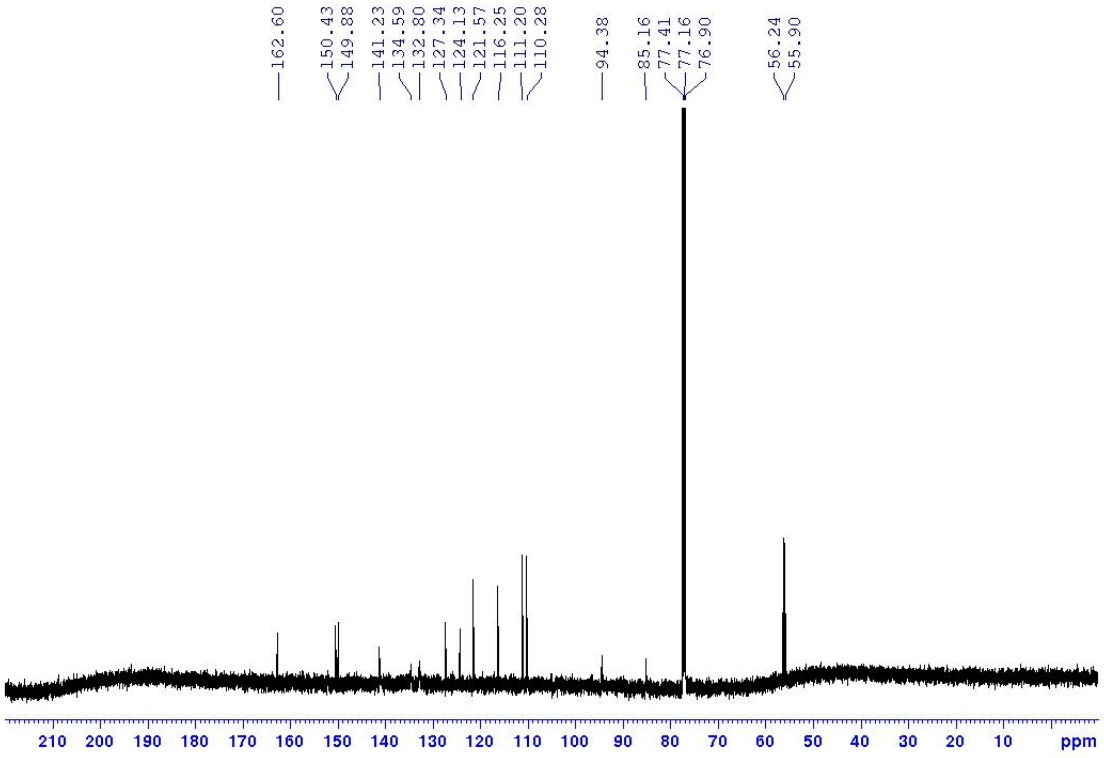
^{13}C NMR (126MHz, Chloroform-*d*): δ 162.6, 150.4, 149.9, 141.2, 134.6, 132.8, 127.3, 124.1, 121.6, 116.2, 111.2, 110.3, 94.4, 85.2, 56.2, 55.9.

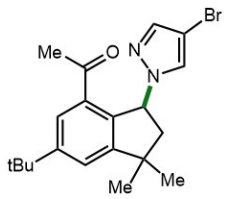
HRMS (ESI): calculated $[M+NH_4]^+$ as 364.0296, found 364.0089.

^{1}H NMR:



^{13}C NMR:





1-(3-(4-bromo-1H-pyrazol-1-yl)-6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)ethan-1-one (**64**)

Synthesized according to the general procedure E for heterocycle addition with celestolide (122.19 mg, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 48 hr. Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 135 mg pure product.

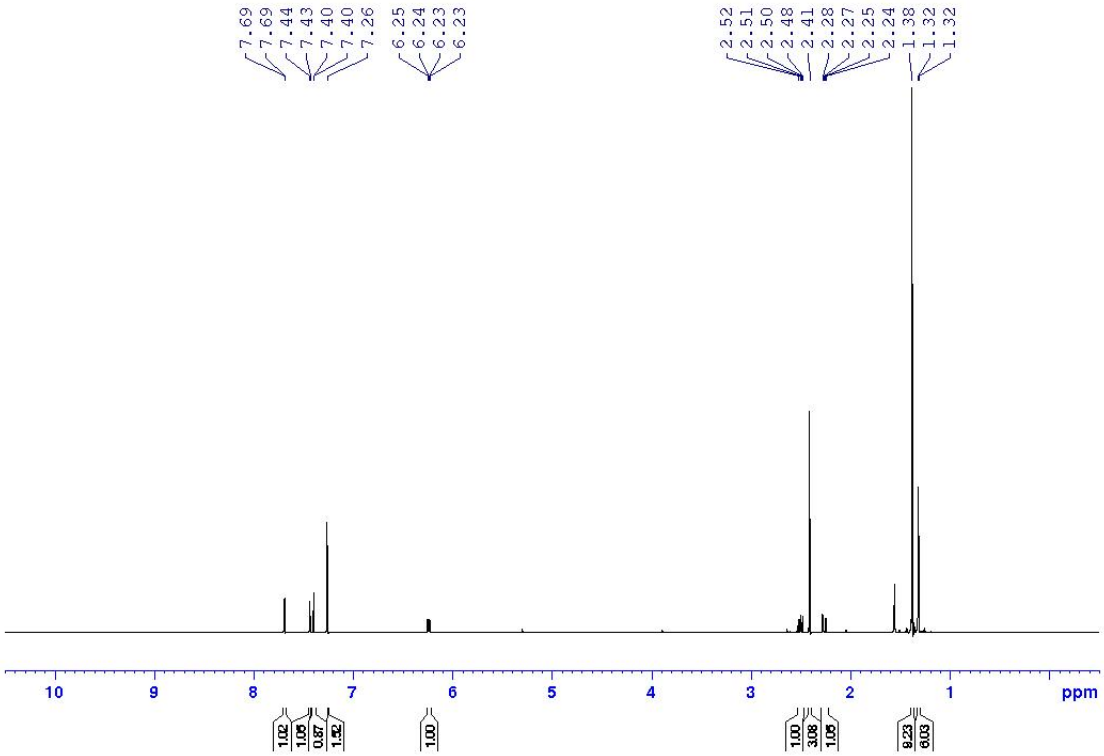
Isolated Yield: 70%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.69 (d, J = 1.8 Hz, 1H), 7.44 (d, J = 1.8 Hz, 1H), 7.39 (d, J = 0.5 Hz, 1H), 7.25 (s, 1H), 6.24 (dd, J = 8.4, 4.4 Hz, 1H), 2.5 (dd, J = 13.7, 8.4 Hz, 2.41 (s, 3H), 2.26 (dd, J = 13.5, 4.4 Hz, 1H), 1.38 (s, 9H), 1.32 (s, 3H), 1.31 (s, 3H).

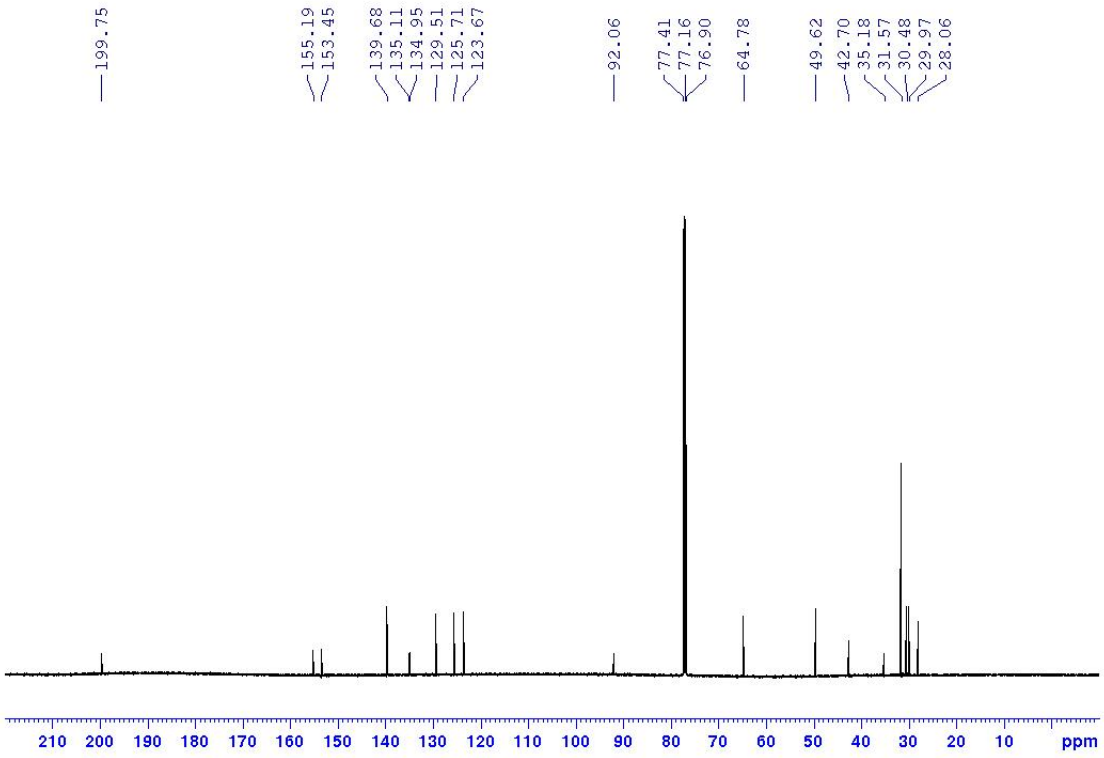
^{13}C NMR (126MHz, Chloroform-*d*): δ 199.8, 155.2, 153.5, 139.7, 135.1, 134.9, 129.5, 125.7, 123.7, 92.1, 64.8, 49.6, 42.7, 35.2, 31.6, 30.5, 29.9, 28.1.

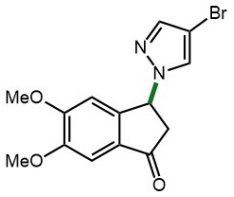
HRMS (ESI): calculated $[M+H]^+$ as 389.1223, found 389.1224.

^{1}H NMR:



^{13}C NMR:





3-(4-bromo-1H-pyrazol-1-yl)-5,6-dimethoxy-2,3-dihydro-1H-inden-1-one (**65**)

Synthesized according to the general procedure E for heterocycle addition with 5,6-dimethoxy-2,3-dihydro-1H-inden-1-one (96.1 mg, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (30% ethyl acetate in hexane, silica gel) afforded 76 mg pure product.

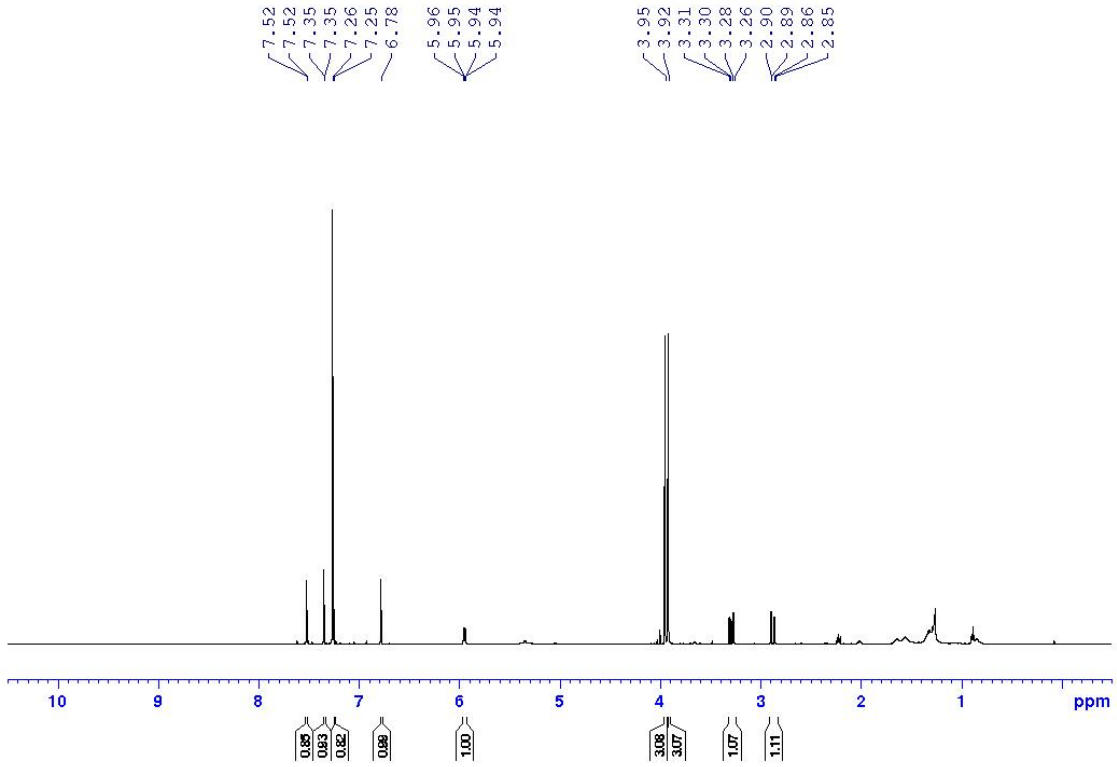
Isolated Yield: 45%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.51 (d, J = 0.5 Hz, 1H), 7.34 (d, J = 0.6 Hz, 1H), 7.24 (s, 1H), 6.78 (S, 1H), 5.95 (dd, J = 7.6, 3 HZ, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.28 (dd, J = 18.7, 7.6 HZ, 1H), 2.87 (dd, J = 18.8, 3.1 Hz, 1H).

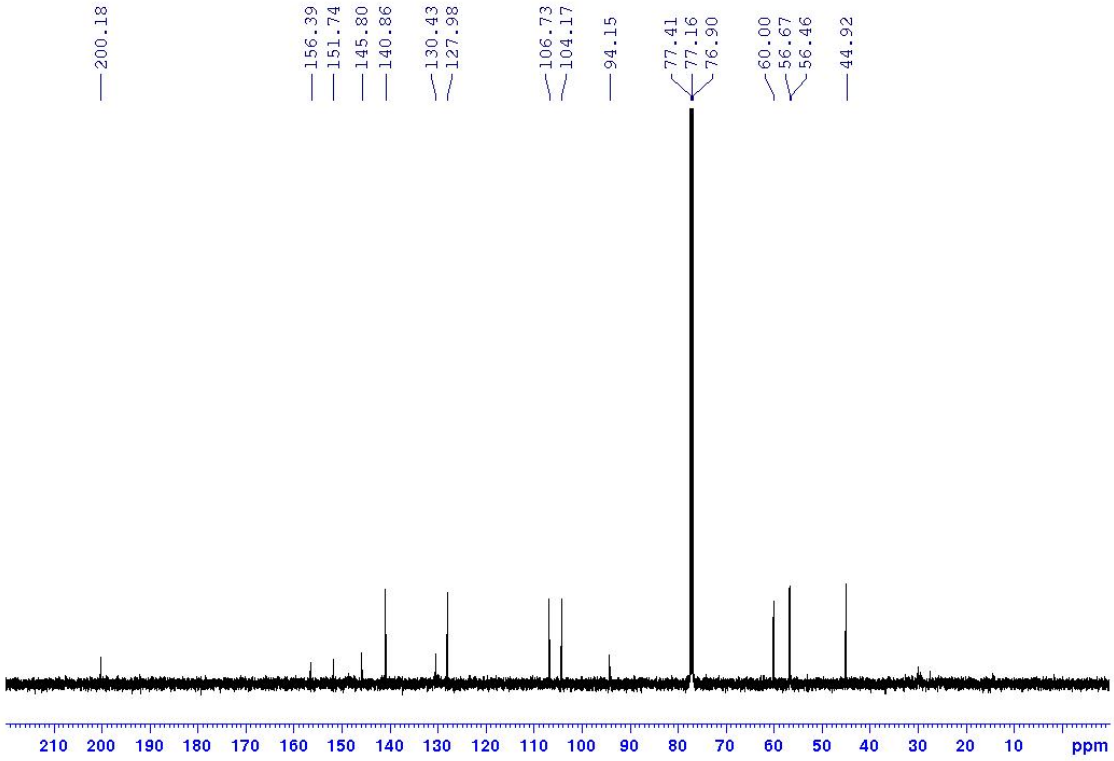
^{13}C NMR (126MHz, Chloroform-*d*): δ 200.2, 156.4, 151.7, 145.8, 140.9, 130.4, 127.9, 106.7, 104.2, 94.1, 60.0, 56.7, 56.5, 44.9.

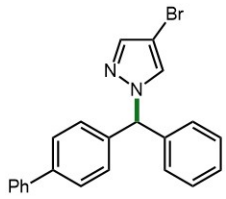
HRMS (ESI): calculated $[M+H]^+$ as 337.0187, found 337.0160.

^{1}H NMR:



^{13}C NMR:





1-([1,1'-biphenyl]-4-yl(phenyl)methyl)-4-bromo-1H-pyrazole (**66**)

Synthesized according to the general procedure E for heterocycle addition with 4-benzyl-1,1'-biphenyl (122.17 mg, 0.500 mmol, 1 equiv.), Ir(dFppy)$_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (4% ethyl acetate in hexanes, silica gel) afforded 125 mg pure product.

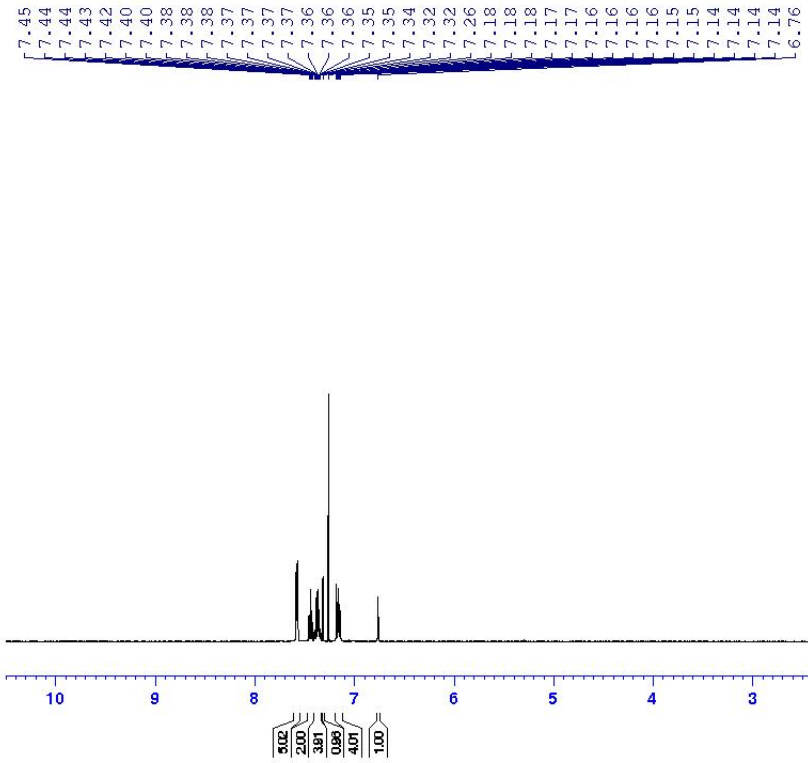
Isolated Yield: 74%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.58-7.56 (m, 5H), 7.45-7.42 (m, 2H), 7.40-7.33 (m, 4H), 7.31 (d, J = 0.6 Hz, 1H), 7.18-7.13 (m, 4H), 6.76 (s, 1H).

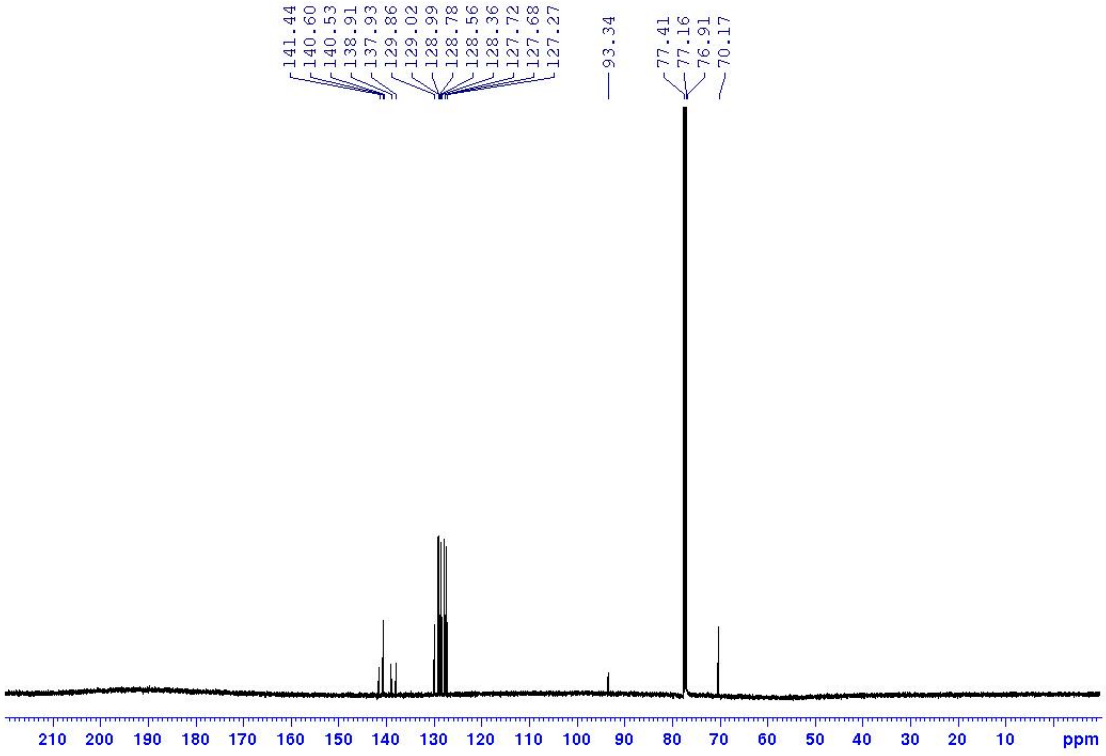
^{13}C NMR (126MHz, Chloroform-*d*): δ 141.4, 140.6, 140.5, 138.9, 137.9, 129.8, 129.0, 128.9, 128.8, 128.5, 128.3, 127.7, 127.6, 127.3, 93.3, 70.1.

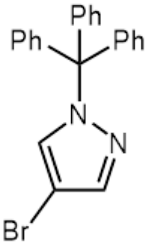
HRMS (ESI): calculated $[M+Na]^+$ as 411.0467, found 411.0468.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-trityl-1*H*-pyrazole (**67**)

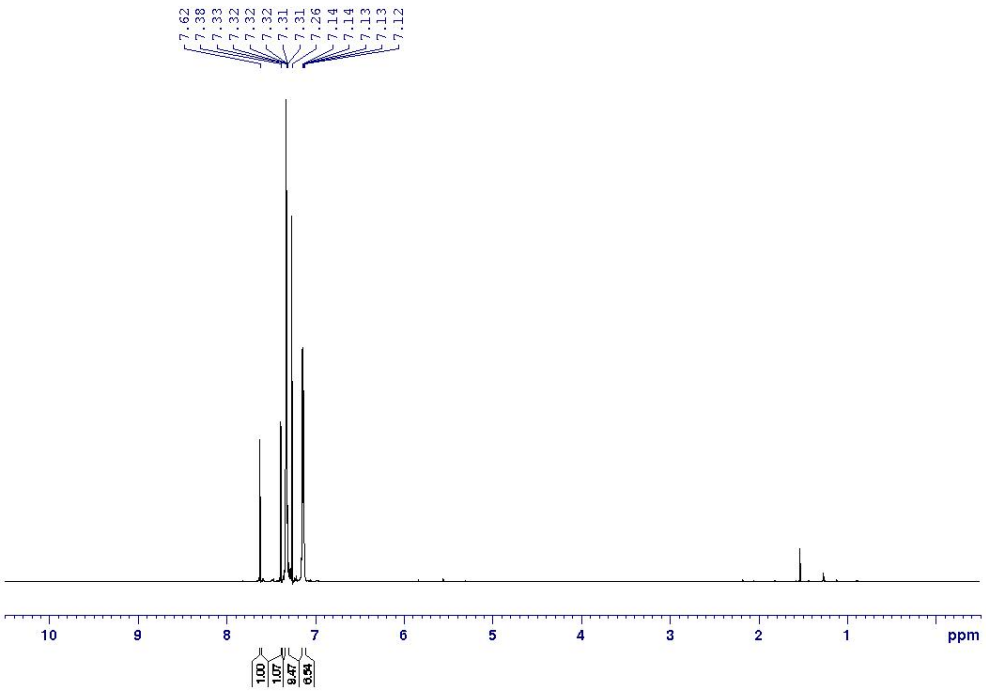
Synthesized according to the general procedure I for heterocycle addition with triphenylmethane (366.5 mg, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-bromo-1H-pyrazole (73.05 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 126.5 mg pure product.

Isolated Yield: 65%

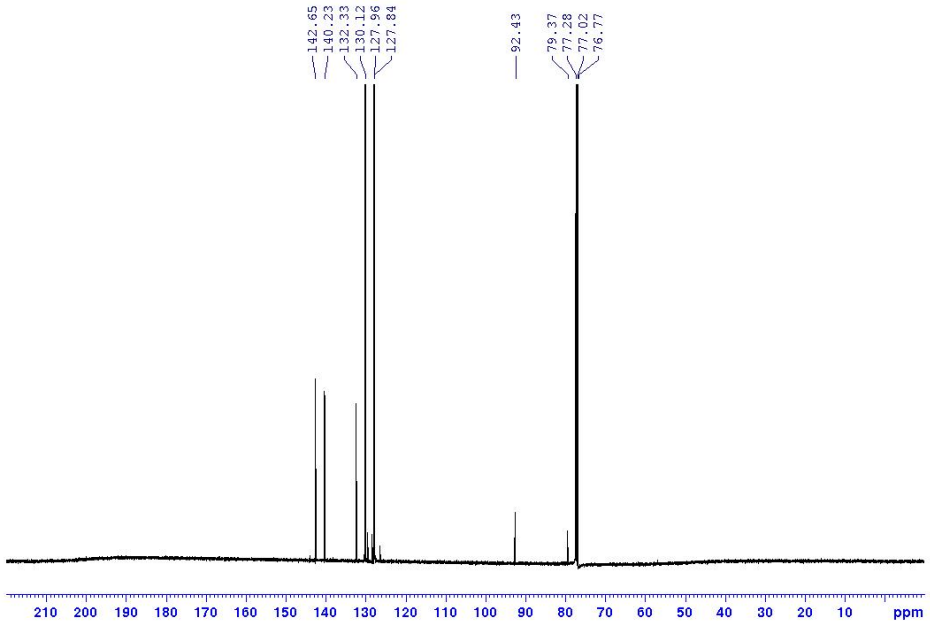
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.61 (s, 1H), 7.38 (s, 1H), 7.32-7.30 (m, 9H), 7.14-7.12 (m, 6H).

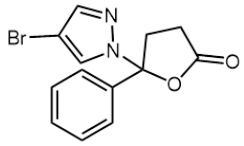
^{13}C NMR (126MHz, Chloroform-*d*): δ 142.6, 140.2, 132.3, 130.1, 127.9, 127.8, 92.4, 79.3.

^{1}H NMR:



^{13}C NMR:





(S)-5-(4-bromo-1*H*-pyrazol-1-yl)-5-phenyldihydrofuran-2(3H)-one (**68**)

Synthesized according to the general procedure I for heterocycle addition with 5-phenyldihydrofuran-2(3H)-one (243.3 mg, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-bromo-1H-pyrazole (73.05 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (25% diethyl ether in hexanes, silica gel) afforded 119.8 mg pure product.

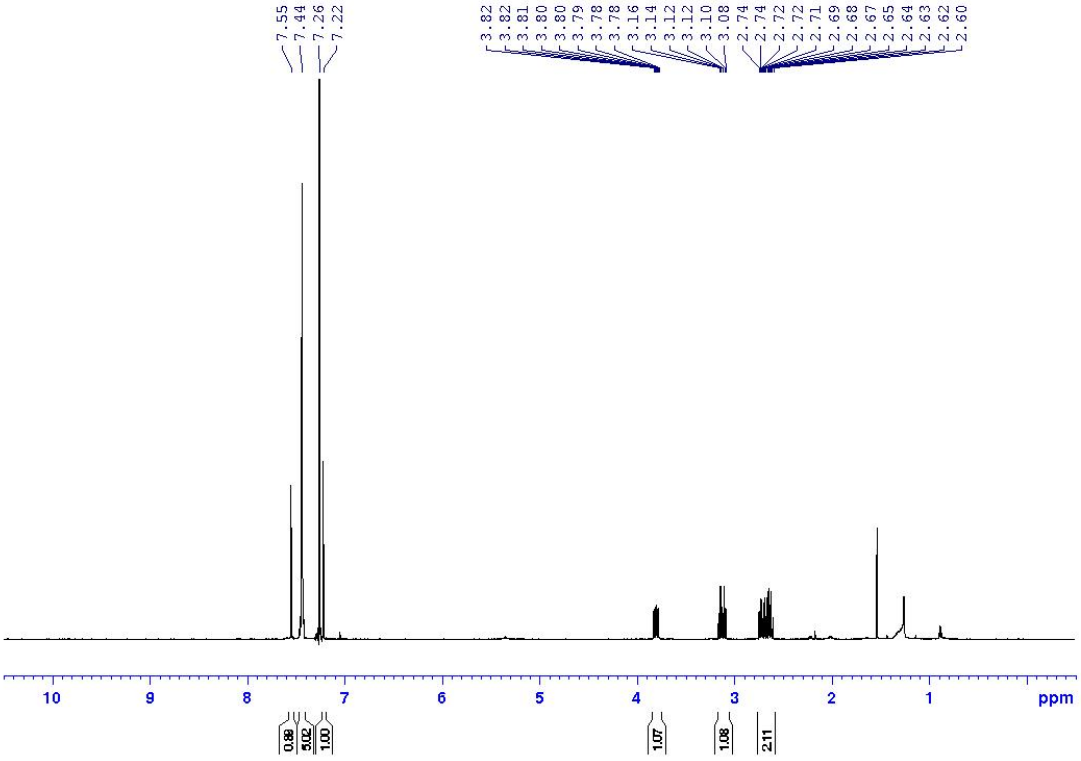
Isolated Yield: 78%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.55 (s, 1H), 7.44 (brs, 5H), 7.22 (s, 1H), 3.82-3.78 (m, 1H), 3.16-3.08(m, 1H), 2.74-2.60 (m, 2H).

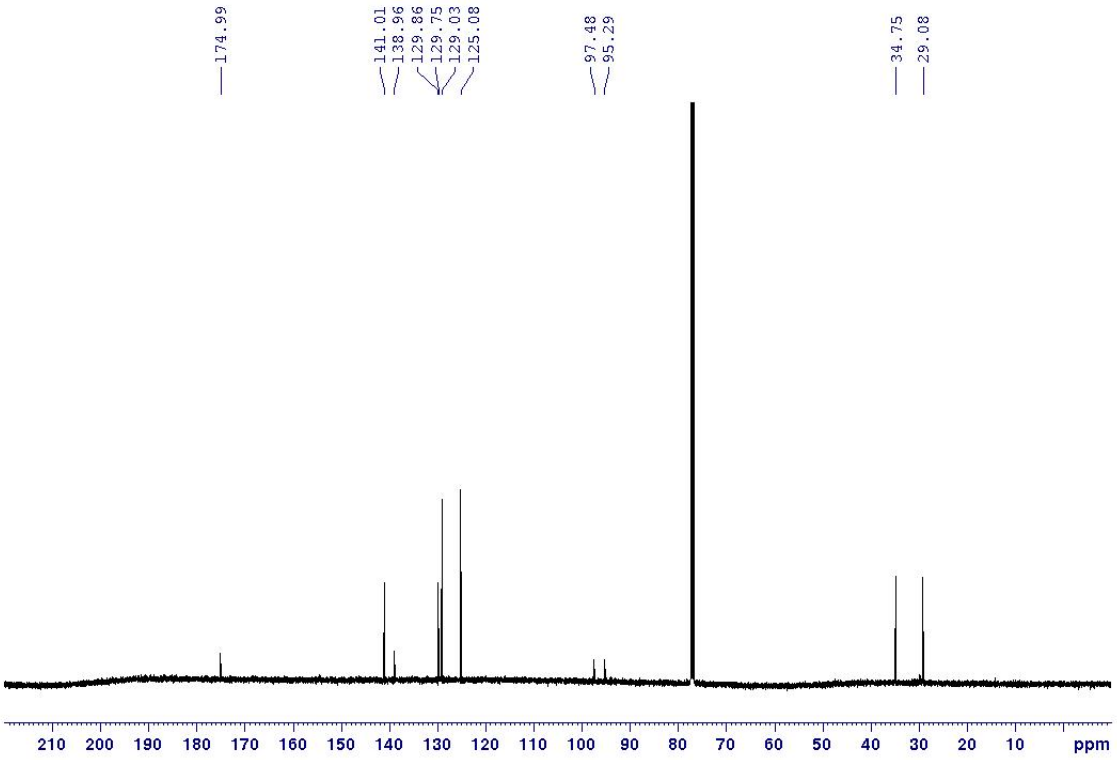
^{13}C NMR (126MHz, Chloroform-*d*): δ 174.9, 141.0, 138.9, 129.8, 129.7, 129.0, 125.1, 97.5, 95.3, 34.7, 29.0.

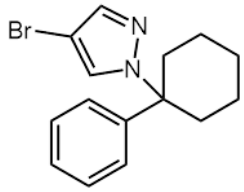
HRMS (ESI): calculated $[M+Na]^+$ as 328.9896, found 328.9897

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(1-phenylcyclohexyl)-1*H*-pyrazole (**69**)

Synthesized according to the general procedure J for heterocycle addition with cyclohexylbenzene (254.4 µL, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-bromo-1*H*-pyrazole (73.05 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (15% diethyl ether in hexanes, silica gel) afforded 30.5 mg pure product.

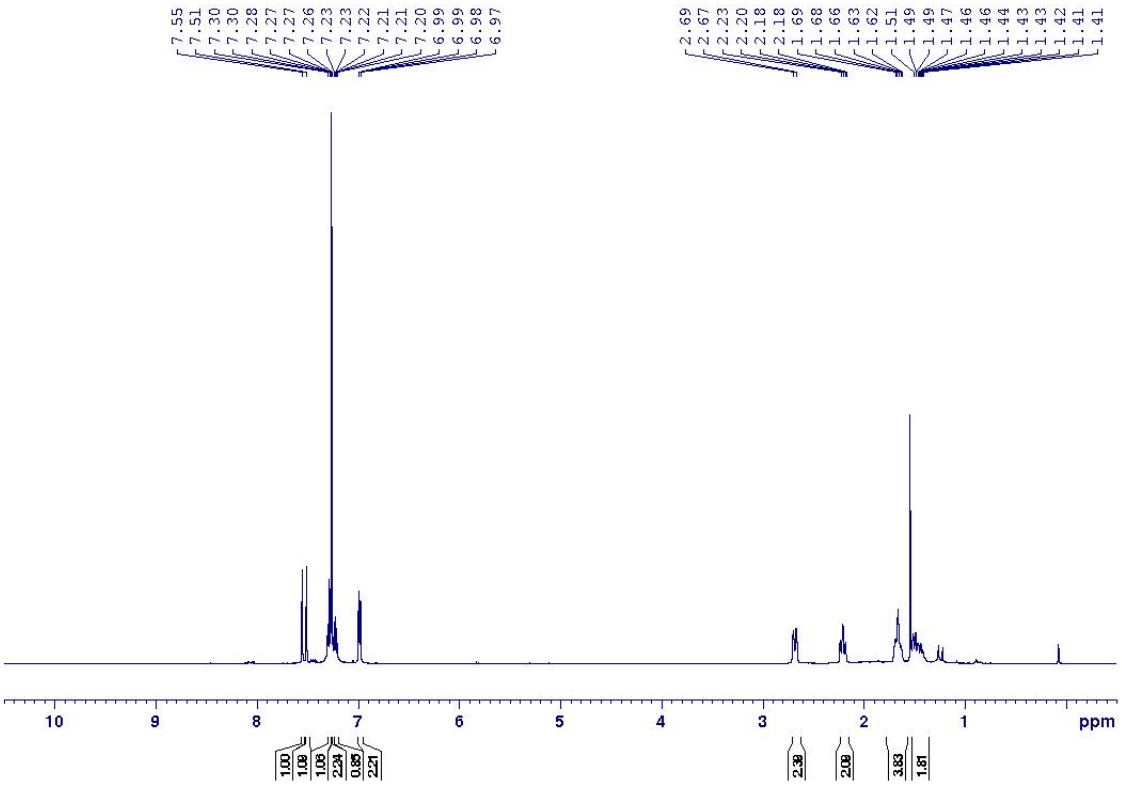
Isolated Yield: 20%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.55 (s, 1H), 7.51 (s, 1H), 7.30-7.27 (m, 1H), 7.26 (brs, 2H), 7.23-7.20 (m, 1H), 6.99-6.97 (m, 2H), 2.68 (brs, 2H), 2.22-2.17 (m, 2H), 1.68-1.62 (m, 4H), 1.51-1.41 (m, 2H).

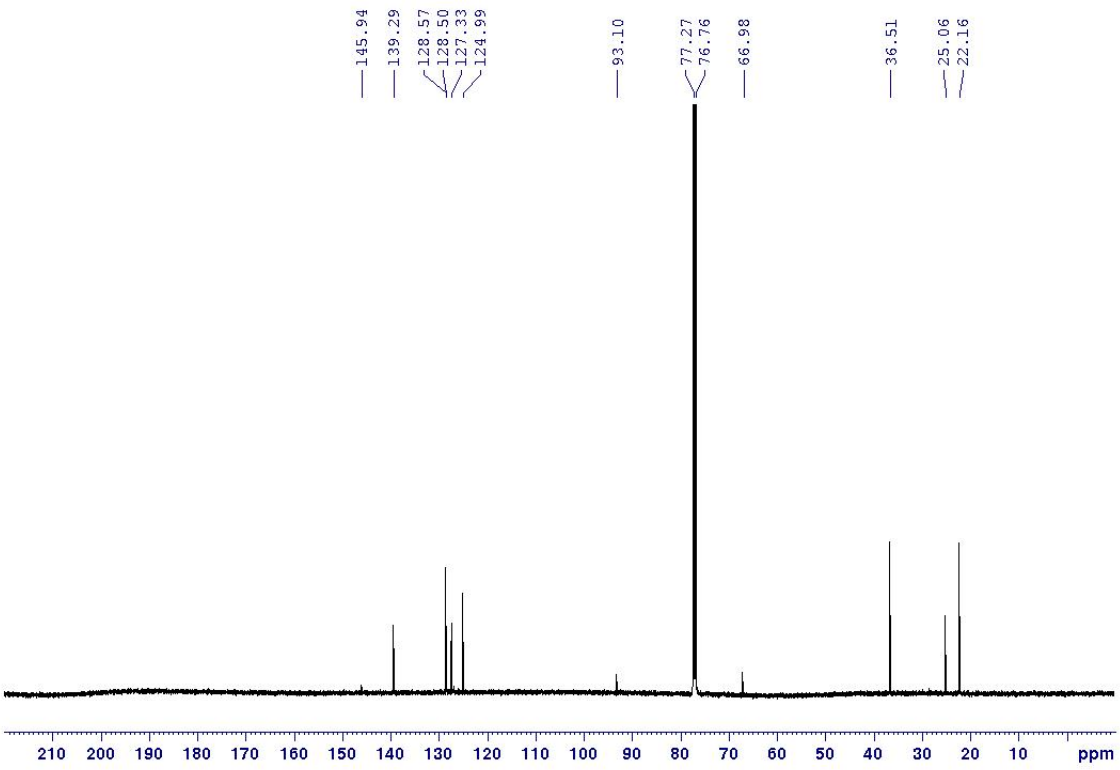
^{13}C NMR (126MHz, Chloroform-*d*): δ 145.9, 139.2, 128.5, 128.5, 127.3, 124.9, 93.1, 66.9, 36.5, 25.0, 22.1.

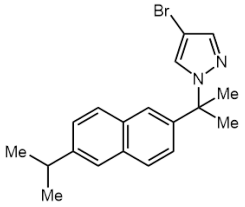
HRMS (ESI): calculated $[M+H]^+$ as 305.0648, found 305.0475

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(2-(6-isopropylnaphthalen-2-yl)propan-2-yl)-1*H*-pyrazole (**70**)

Synthesized according to the general procedure I for heterocycle addition with 2,6-diisopropylnaphthalene (318.5 mg, 1.500 mmol, 3 equiv.), Ir(pFppy)$_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-bromo-1*H*-pyrazole (73.05 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (10% diethyl ether in hexanes, silica gel) afforded 89.3 mg pure product.

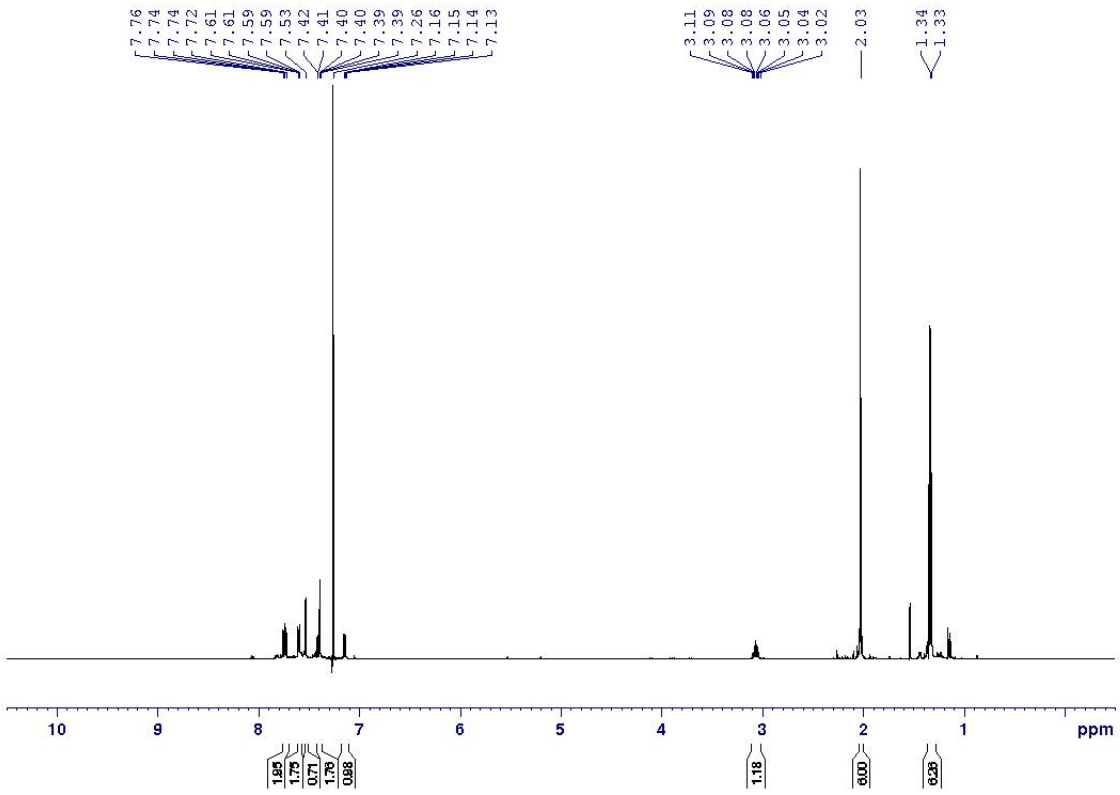
Isolated Yield: 50%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.75-7.71 (m, 2H), 7.61-7.59 (m, 2H), 7.53 (brs, 1H), 7.41-7.38 (m, 2H), 7.14 (dd, *J* = 8.7, 2.05 Hz, 1H), 3.06 (Sep, *J* = 6.9 Hz, 1H), 2.02 (s, 6H), 1.32 (d, *J*=6.9.1 Hz, 6H).

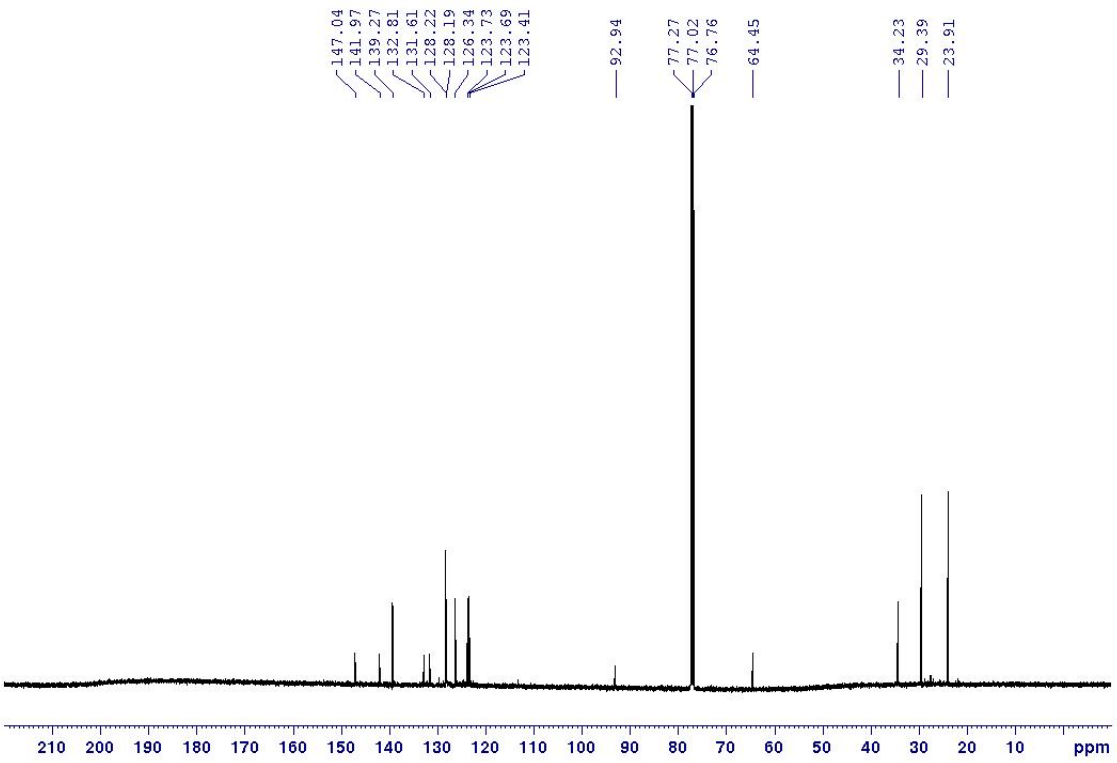
^{13}C NMR (126MHz, Chloroform-*d*): δ 147.0, 141.9, 139.3, 132.8, 131.6, 128.2, 128.2, 126.3, 123.7, 123.6, 123.4, 92.9, 64.4, 34.2, 29.3, 23.9.

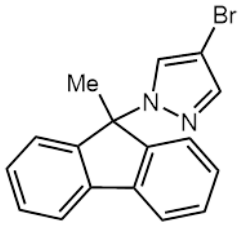
HRMS (ESI): calculated $[M+H]^+$ as 357.0961, found 356.0883

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(9-methyl-9*H*-fluoren-9-yl)-1*H*-pyrazole (**71**)

Synthesized according to the general procedure I for heterocycle addition with 9-methyl-9*H*-fluorene (270.36 mg, 1.500 mmol, 3 equiv.), $Ir(pFppy)_3$ (3.54 mg, 0.00500 mmol, 0.01 equiv.), TBPB (285.3 µL, 1.500 mmol, 3 equiv.), 4-bromo-1H-pyrazole (73.05 mg, 0.500 mmol, 1 equiv.), molecular sieve 3Å (75 mg) and 1,2-dichloroethane (0.25 mL, 2 M). Purification with flash chromatography (12% ethyl acetate in hexanes, silica gel) afforded 56.9 mg pure product.

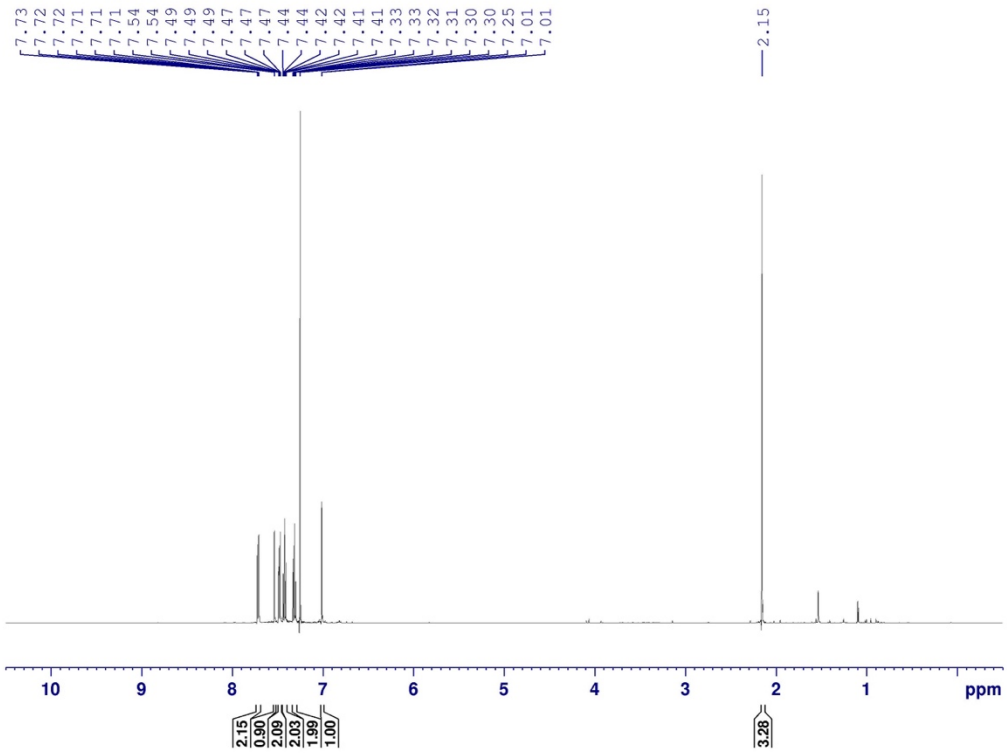
Isolated Yield: 35%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.72 (td, *J* = 7.5, 0.8 Hz, 2H), 7.53 (d, *J*=0.5 Hz, 1H), 7.47 (td, *J* = 7.4, 1.1 Hz, 2H), 7.42 (dt, *J* = 7.5, 0.8 Hz, 2H), 7.31 (dt, *J* = 7.5, 1.0 Hz, 2H), 7.01 (d, *J*=0.6 Hz, 1H), 2.15 (s, 3H).

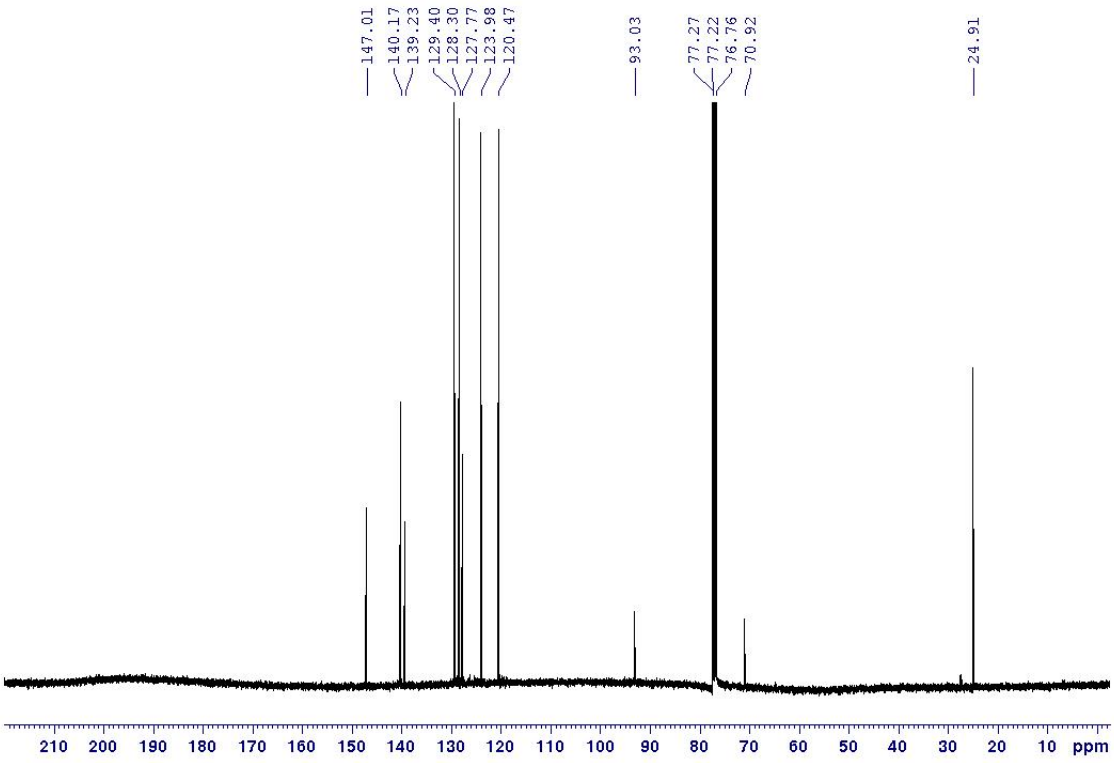
^{13}C NMR (126MHz, Chloroform-*d*): δ 147.0, 140.1, 139.2, 129.4, 128.3, 127.7, 123.9, 120.4, 93.0, 70.9, 24.9.

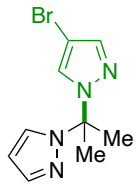
HRMS (ESI): calculated $[M+H]^+$ as 325.0340, found 325.0309

^{1}H NMR:



^{13}CNMR:





1-(2-(1H-pyrazol-1-yl)propan-2-yl)-4-bromo-1H-pyrazole (**72**)

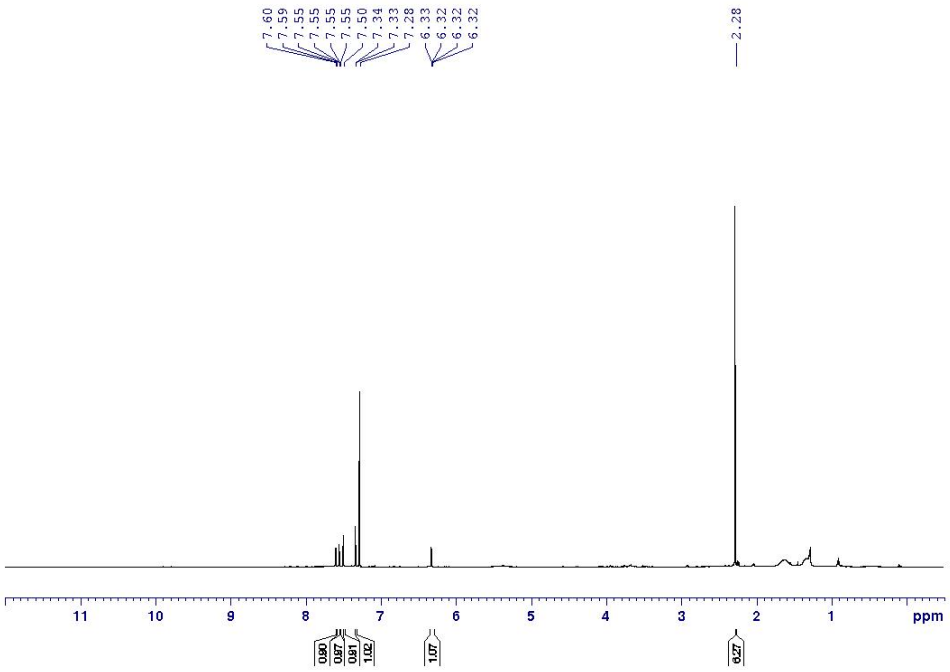
Synthesized according to the general procedure I, 1-isopropyl-1H-pyrazole (68.8 µL, 0.600 mmol, 3 equiv.), $Ir(pFppy)_3$ (1.42 mg, 0.00200 mmol, 0.01 equiv.), TBPB (114 µL, 0.600 mmol, 3 equiv.), 4-bromo-1*H*-pyrazole (29.4 mg, 0.200 mmol, 1 equiv.), molecular sieve 3A (20 mg) and 1,2-dichloroethane (0.2 mL, 1 M). Purification with flash chromatography (30% ethyl acetate in hexanes, silica gel) afforded pure product.

^{1}H NMR Yield: 29% product

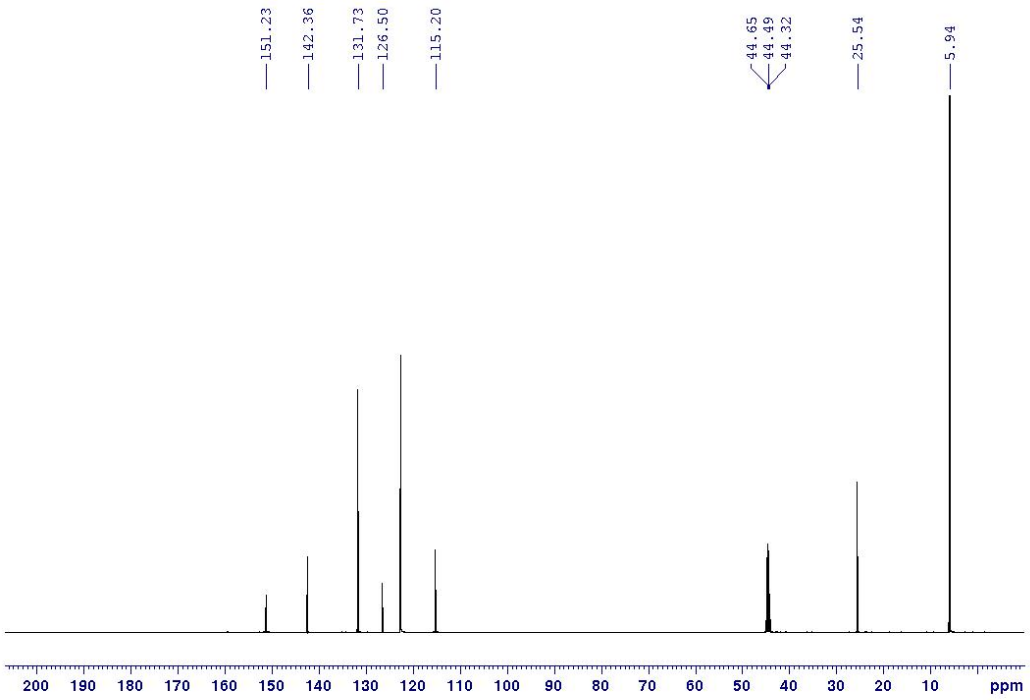
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.59 (d, *J*=1.5 Hz, 1H), 7.54 (dd, *J*=0.5, 2.5 Hz, 1H), 7.49 (s, 1H), 7.33 (d, *J*=0.5 Hz, 1H), 6.31-6.32(m, 1H), 2.27 (s, 6H).

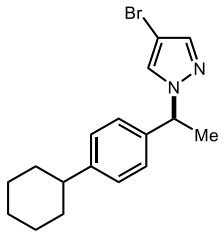
^{13}C NMR (126MHz, Chloroform-*d*): δ 151.2, 142.3, 131.7, 126.5, 115.1, 25.53, 5.9.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(1-(4-cyclohexylphenyl)ethyl)-1*H*-pyrazole (**73**)

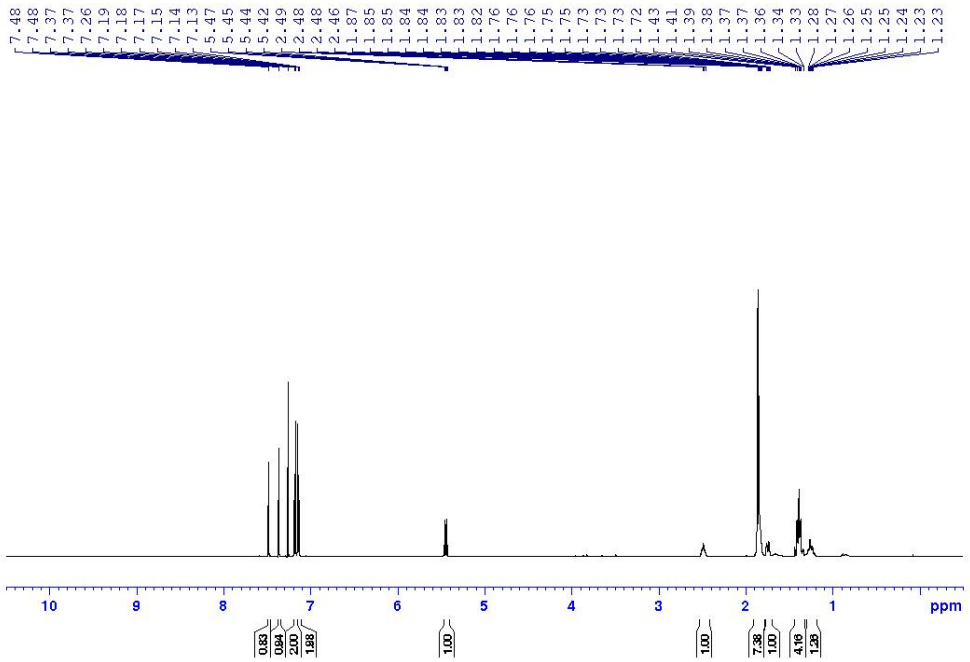
Synthesized according to the general procedure F, with 1-cyclohexyl-4-ethylbenzene (37.7 mg, 0.2 mmol, 1 equiv.), Eosin Y (6.48 mg, 0.01 mmol, 0.05 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (66.58 mg, 0.3 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (88 mg, 0.6 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 1 mL, 0.2 M). Reaction was run for 24 hr. Purification with preparative thin layer chromatography (5% ethyl acetate in hexanes, silica gel) afforded pure product.

^{1}H NMR Yield: 33% secondary product, 2% yield of the tertiary product

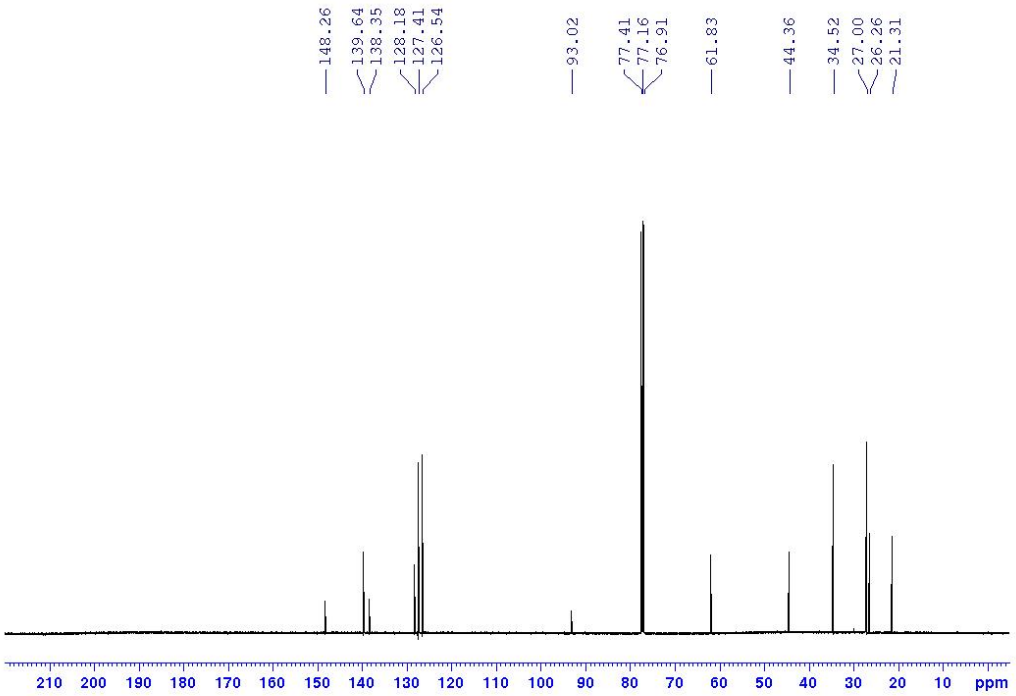
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.48 (d, J = 0.5 Hz, 1H), 7.36 (d, J = 0.5 Hz, 1H), 7.18-7.17 (m, 2H), 7.14-7.13 (m, 2H), 5.44 (q, J = 7.1 Hz, 1H), 2.51-2.45 (m, 1H), 1.86-1.81 (m, 7H), 1.76-1.72 (m, 1H), 1.43-1.33 (m, 4H), 1.28-1.20 (m, 1H).

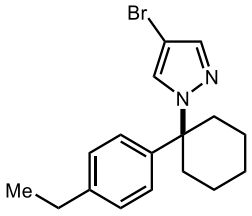
^{13}C NMR (126MHz, Chloroform-*d*): δ 148.2, 139.6, 138.3, 128.1, 127.4, 126.5, 93.0, 61.8, 44.3, 34.5, 26.99, 26.25, 21.3.

^{1}H NMR:



^{13}C NMR:



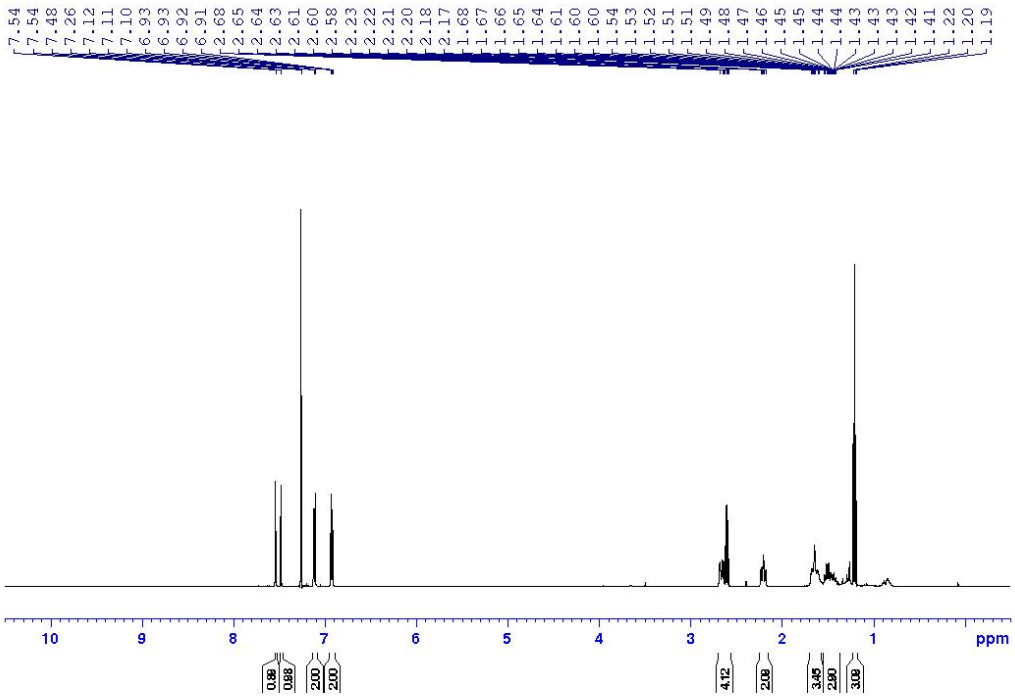


4-bromo-1-(1-(4-ethylphenyl)cyclohexyl)-1*H*-pyrazole

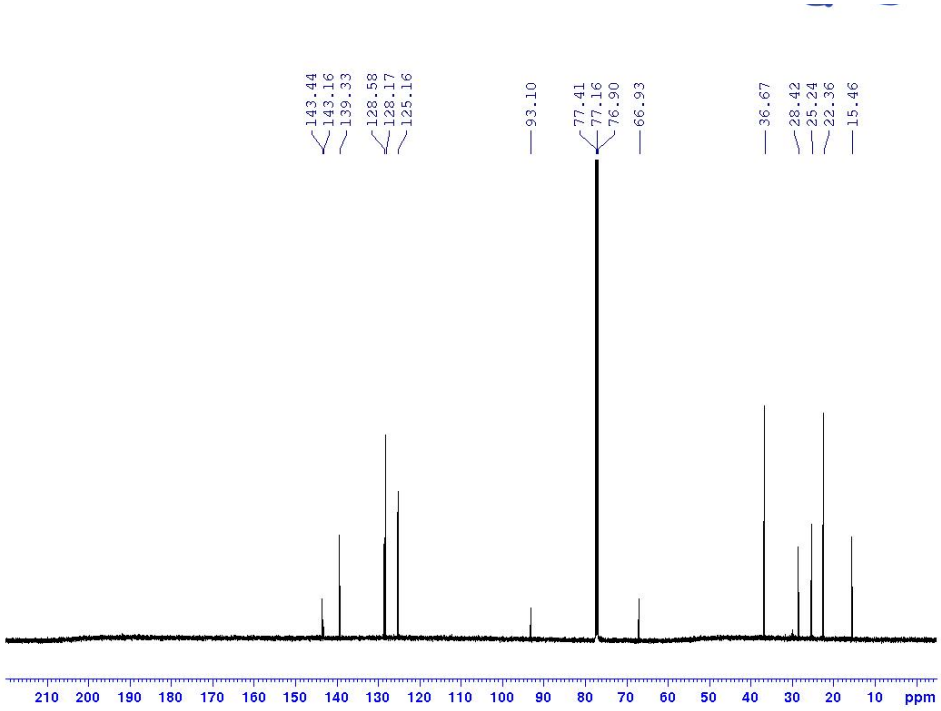
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.53 (d, J = 0.5 Hz, 1H), 7.47 (s, 1H), 7.12-7.10 (m, 2H), 6.93-6.91 (m, 2H), 2.67-2.64 (br, 2H), 2.60 (q, J = 7.6 Hz, 2H), 2.22-2.17 (m, 2H), 1.67-1.38 (m, 6H), 1.20 (t, J = 7.6 Hz, 3H).

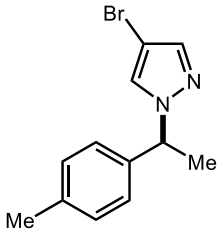
^{13}C NMR (126MHz, Chloroform-*d*): δ 143.4, 143.1, 139.3, 128.5, 128.1, 125.1, 93.0, 66.9, 36.6, 28.4, 25.2, 22.3, 15.4.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(1-(*p*-tolyl)ethyl)-1*H*-pyrazole (**74**)

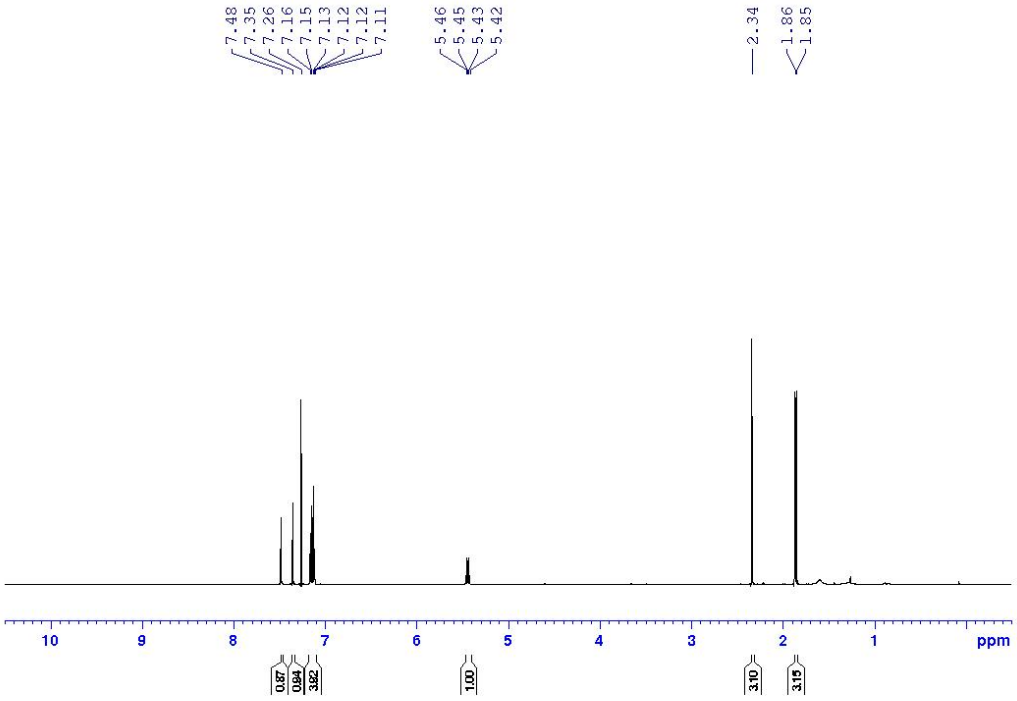
Synthesized according to the general procedure F for heterocycle addition with 4-ethyltoluene (27.9 µL, 0.2 mmol, 1 equiv.), $Ir(dFppy)_3$ (1.53 mg, 0.002 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (66.58 mg, 0.3 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (88 mg, 0.6 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 1 mL, 0.2 M). Reaction was run for 24 hr. Purification with preparative thin layer chromatography (5% ethyl acetate in hexanes, silica gel) afforded pure product.

^{1}H NMR Yield: 60% of the secondary product, 3% of the primary product

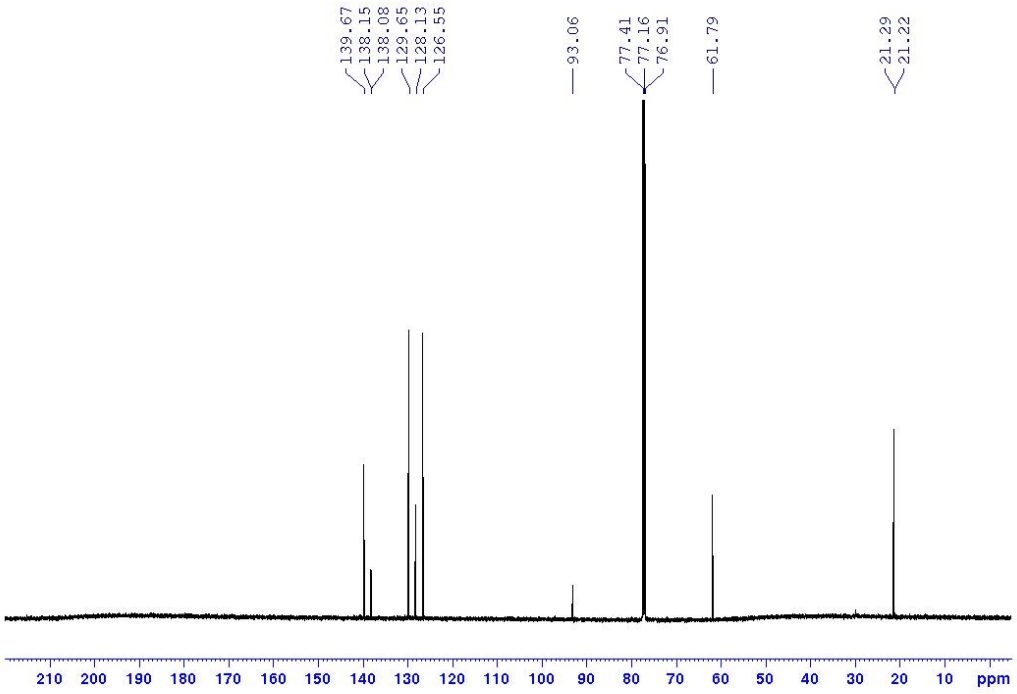
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.47 (s, 1H), 7.35 (s, 1H), 7.16-7.14 (m, 2H), 7.12-7.11 (m, 2H), 5.43 (q, J = 7.1 Hz, 1H), 2.33 (s, 3H), 1.85 (d, J = 7.1 Hz, 3H).

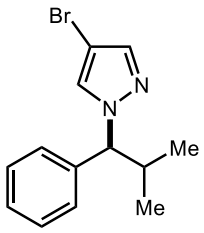
^{13}C NMR (126MHz, Chloroform-*d*): δ 139.6, 138.1, 138.0, 129.6, 128.1, 127.9, 126.5, 93.0, 61.7, 21.28, 21.22.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(2-methyl-1-phenylpropyl)-1*H*-pyrazole (**75**)

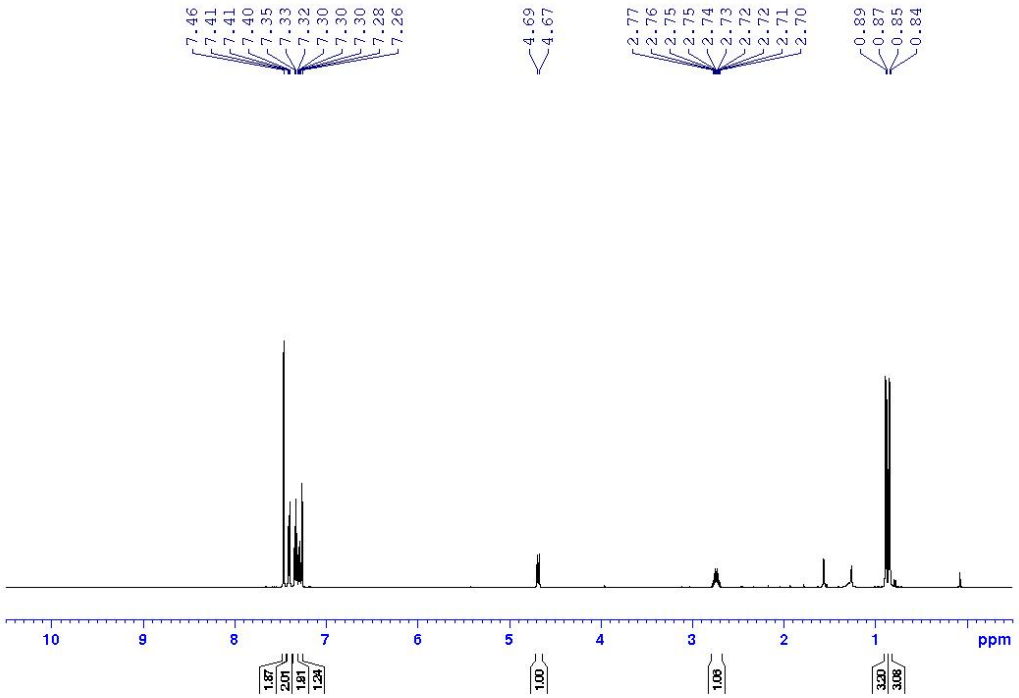
Synthesized according to the general procedure F, with isobutyl benzene (78.7 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (166.5 mg, 0.7500 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (4% ethyl acetate in hexanes, silica gel) afforded 35 mg pure product.

Isolated Yield: 25%

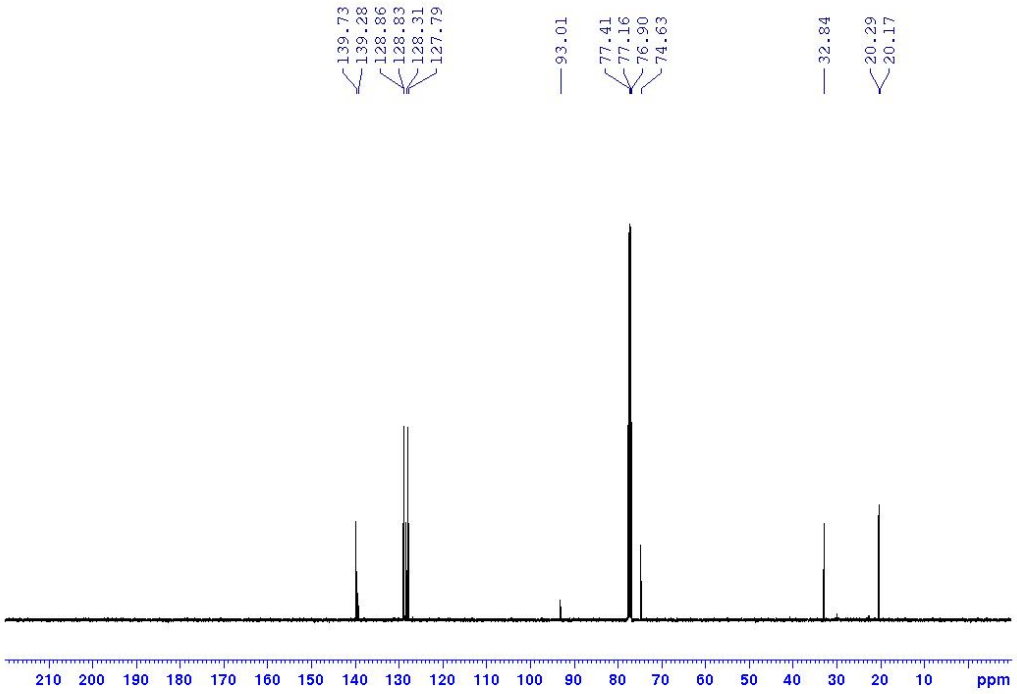
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.46 (s, 2H), 7.41-7.39 (m, 2H), 7.34-7.31 (m, 2H), 7.30-7.27 (m, 1H), 4.68 (d, J = 10.6 Hz, 1H), 2.77-2.69 (m, 1H), 0.88 (d, J = 6.5 Hz, 3H), 0.84 (d, J = 6.7 Hz, 3H).

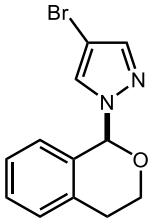
^{13}C NMR (126MHz, Chloroform-*d*): δ 139.7, 139.2, 128.86, 128.82, 128.3, 127.7, 93.0, 74.6, 32.8, 20.2, 20.1.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(isochroman-1-yl)-1*H*-pyrazole (**76**)

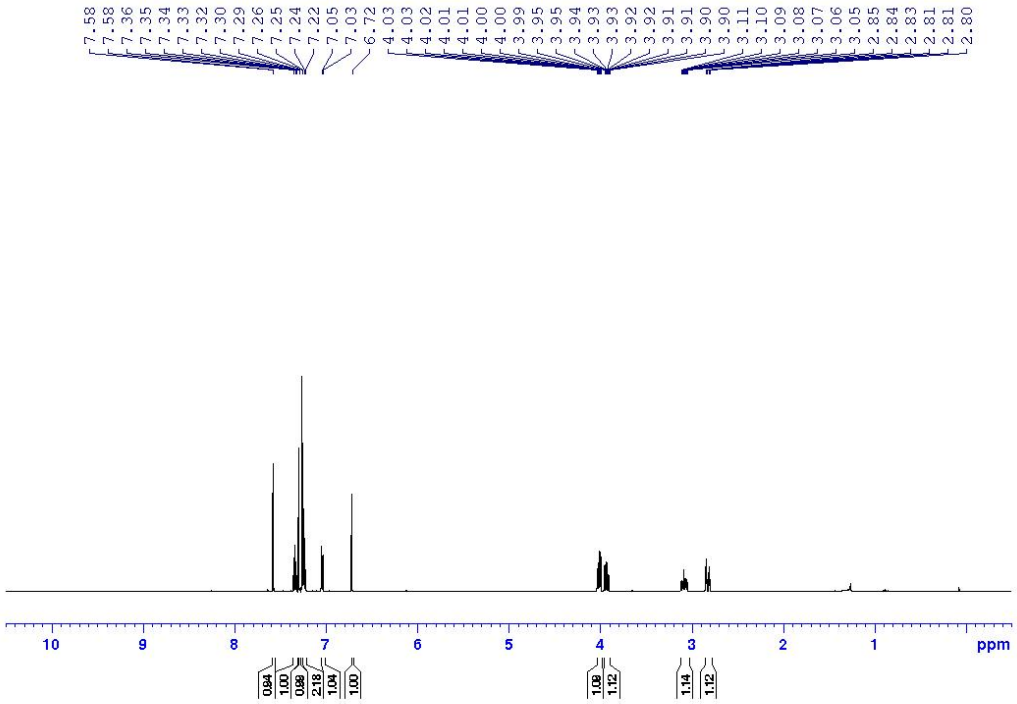
Synthesized according to the general procedure A for heterocycle addition with isochroman (25.2 µL, 0.2 mmol, 1 equiv.), Ir(dFppy)$_3$ (1.53 mg, 0.002 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (66.58 mg, 0.3 mmol, 1.5 equiv.), 4-bromo-1*H*-pyrazole (88 mg, 0.6 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 1 mL, 0.2 M). Reaction was run for 24 hr. Purification with preparative thin layer chromatography (5% ethyl acetate in hexanes, silica gel) afforded pure product.

^{1}H NMR Yield: 57%

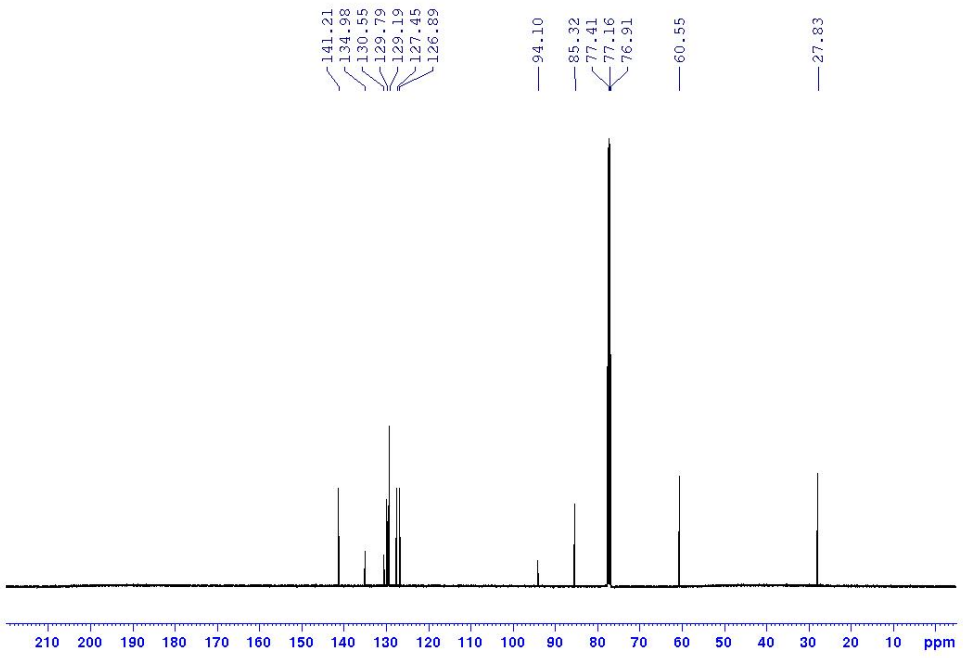
^{1}H NMR (500MHz, Chloroform-*d*): δ 7.57 (d, J = 0.6 Hz, 1H), 7.35-7.32 (m, 1H), 7.29 (d, J = 0.6 Hz, 1H), 7.23 (t, J = 7.5 Hz, 2H), 7.03 (d, J = 7.9 Hz, 1H), 6.71 (s, 1H), 4.03-3.99 (m, 1H), 3.95-3.90 (m, 1H), 3.11-3.04 (m, 1H), 2.82 (dt, J = 16.7, 3.4 Hz, 1H).

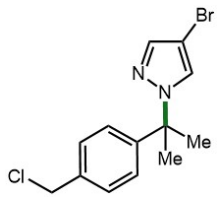
^{13}C NMR (126MHz, Chloroform-*d*): δ 141.2, 134.9, 130.5, 129.7, 129.1, 127.4, 126.8, 94.1, 85.3, 60.5, 27.8.

^{1}H NMR:



^{13}C NMR:





4-bromo-1-(2-(4-(chloromethyl)phenyl)propan-2-yl)-1H-pyrazole (**77**)

Synthesized according to the general procedure E for heterocycle addition with 1-(chloromethyl)-4-isopropylbenzene (55.4 µL, 0.500 mmol, 1 equiv.), $Ir(dFppy)_3$ (3.83 mg, 0.00500 mmol, 0.01 equiv.), 4-cyano-1-methoxypyridin-1-ium tetrafluoroborate (333 mg, 1.50 mmol, 3 equiv.), 4-bromo-1*H*-pyrazole (220.5 mg, 1.500 mmol, 3 equiv.) and 1,2-dichloroethane:1,1,1,3,3,3-hexafluoro-2-propanol (7:3, 2.5 mL, 0.2 M). Reaction was run for 24 hr. Purification with flash chromatography (10% ethyl acetate in hexanes, silica gel) afforded 63 mg pure product.

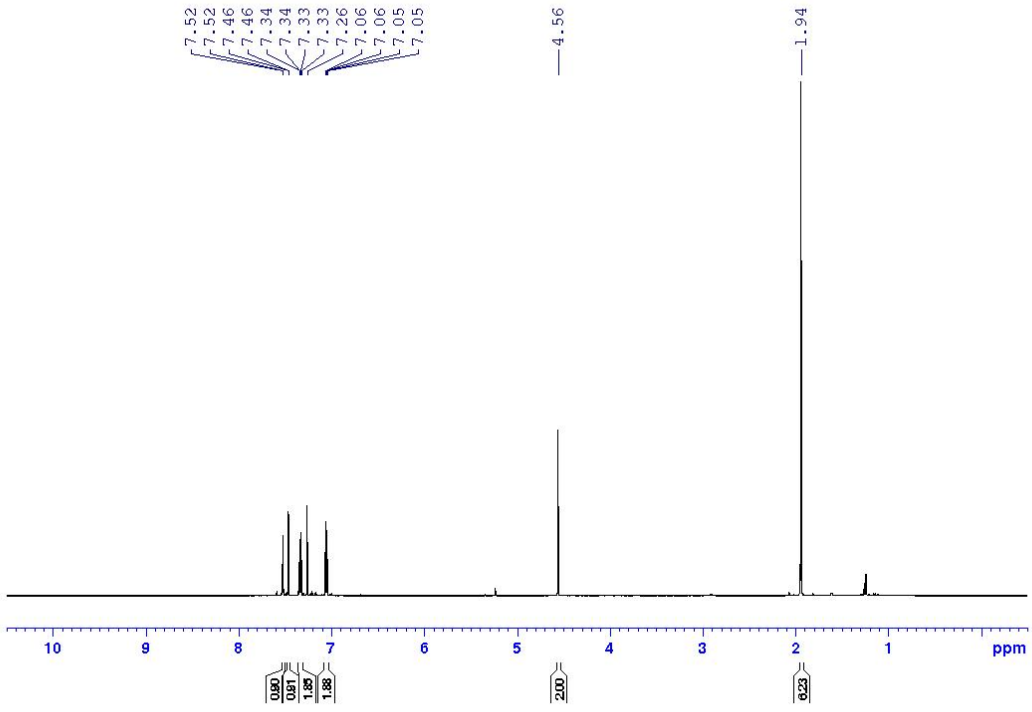
Isolated Yield: 40%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.52 (d, *J* = 0.5 Hz, 1H), 7.46 (d, J = 0.7 Hz, 1H), 7.34-7.32 (m, 2H), 7.06-7.04 (m, 2H), 4.55 (s, 2H), 1.94 (s, 6H).

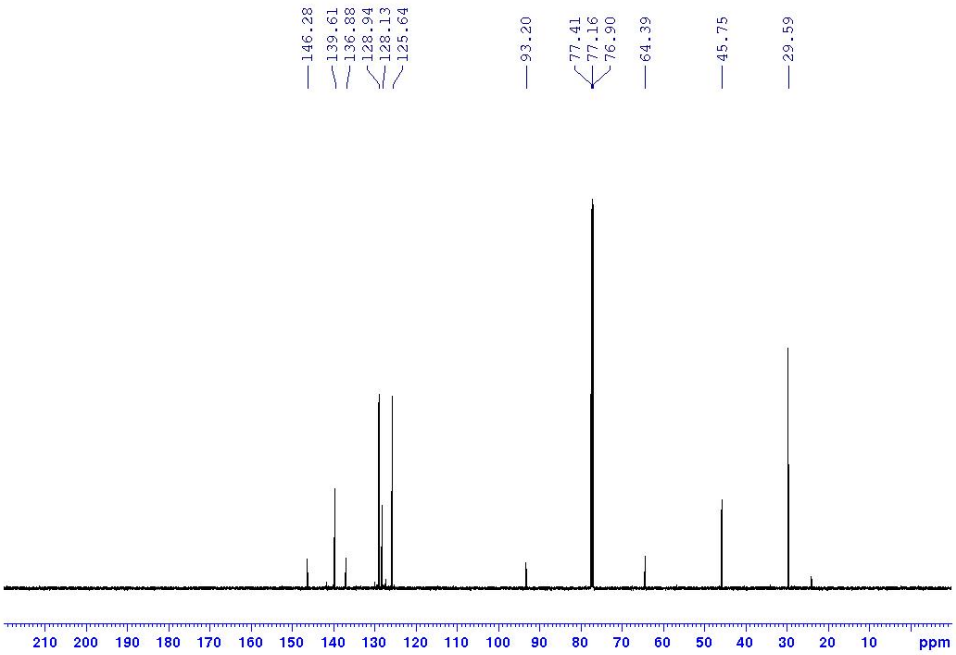
^{13}C NMR (126MHz, Chloroform-*d*): δ 146.3, 139.6, 136.9, 128.9, 128.1, 125.6, 93.2, 64.4, 45.8, 29.6.

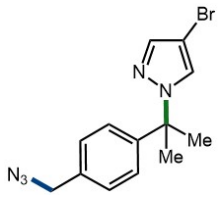
HRMS (ESI): calculated $[M+H]^+$ as 313.0102, found 313.0102.

^{1}H NMR:



^{13}C NMR:





1-(2-(4-(azidomethyl)phenyl)propan-2-yl)-4-bromo-1H-pyrazole (**78**)

In an 8 ml vial 4-bromo-1-(2-(4-(chloromethyl)phenyl)propan-2-yl)-1*H*-pyrazole (62.8 mg, 0.200 mmol, 1 equiv.) was dissolved in anhydrous DMSO (1 ml), then NaN_3 (19.5 mg, 0.300 mmol, 1.5 equiv.) was added to the solution and stirred for 12 hr. at room temperature. The mixture was diluted with water and extracted with CH_2Cl_2, and the organic layer was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using ethyl acetate/hexane to afford product as a colorless oil (58.3 mg, 91%).

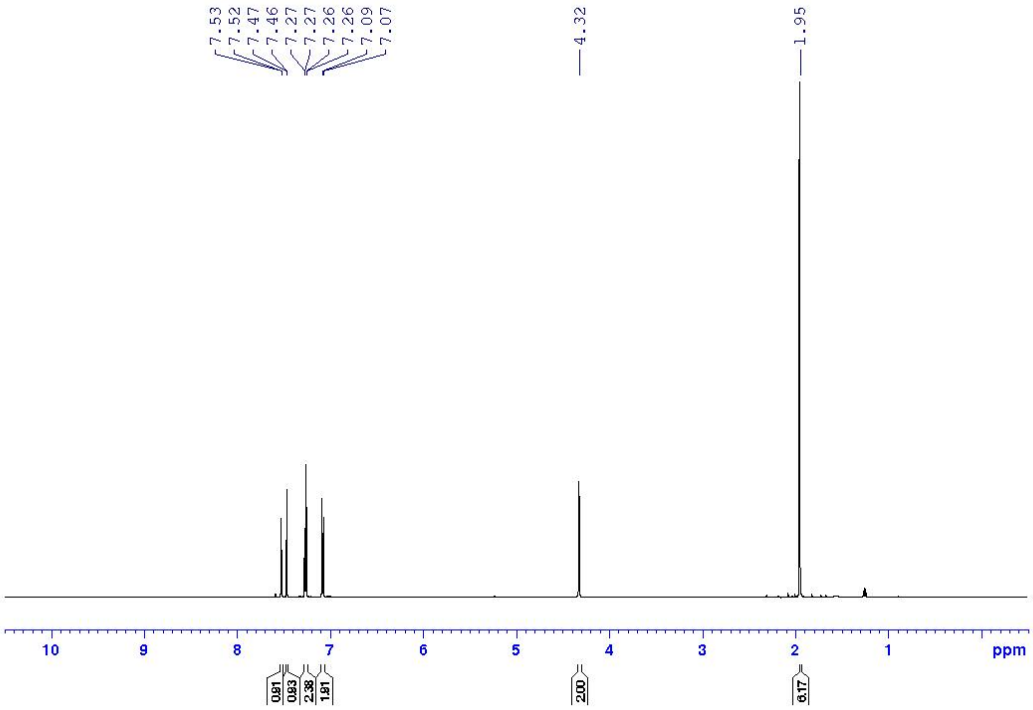
Isolated Yield: 91%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.52 (d, J = 0.5 Hz, 1H), 7.46 (d, J = 0.7 Hz, 1H), 7.27-7.25 (m, 2H), 7.09-7.06 (m, 2H), 4.32 (s, 2H), 1.94 (s, 6H).

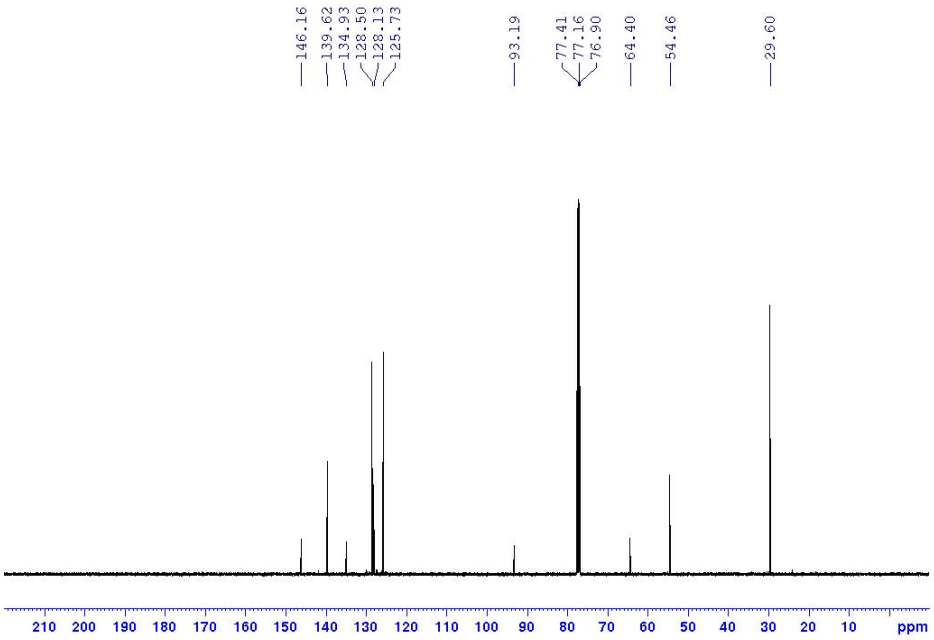
^{13}C NMR (126MHz, Chloroform-*d*): δ 146.2, 139.6, 134.9, 128.5, 128.1, 125.7, 93.2, 64.4, 54.5, 29.6.

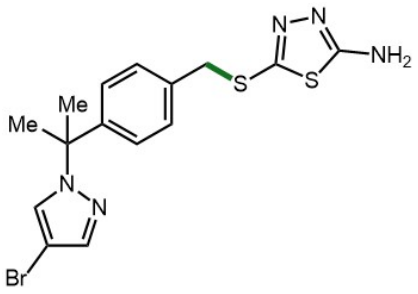
HRMS (ESI): calculated $[M+H]^+$ as 320.0506, found 320.0506.

^{1}H NMR:



^{13}C NMR:





5-((4-(2-(4-bromo-1*H*-pyrazol-1-yl)propan-2-yl)benzyl)thio)-1,3,4-thiadiazol-2-amine (**79**)[9]

In a three-necked round bottom flask 5-amino-1,3,4-thiadiazole-2-thiol (62.6 mg, 0.470 mmol) was taken in ethanol (0.25 mL). The aqueous KOH solution (340mg of KOH dissolved in 0.05 mL water) was added slowly. The reaction mass was stirred at the same temperature for 10 min. Subsequently, 4-bromo-1-(2-(4-(chloromethyl)phenyl)propan-2-yl)-1*H*-pyrazole (156.8 mg, 0.5000 mmol) was added dropwise. The reaction mass was stirred for 2–3h at 25–30°C. After completion of the reaction as per thin-layer chromatography (TLC), water (0.05 mL) was added to the reaction mass and stirred for 30 min and then reaction mass was filtered, afforded 170.3 mg pure product.

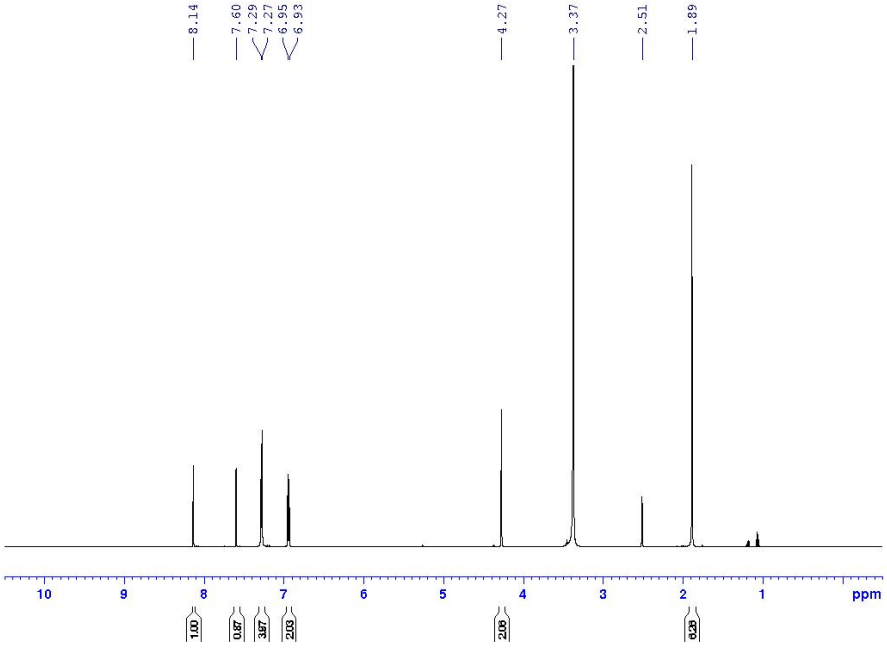
Isolated Yield: 83%

^{1}H NMR (500MHz, DMSO-*d*): δ 8.13 (s, 1H), 7.59 (s, 1H), 7.27 (d, *J*=8.2 Hz, 2H Ar and 2H Amin), 6.94 (d, *J*=8.3 Hz, 2H), 4.27 (s, 2H), 1.8 (s, 6H).

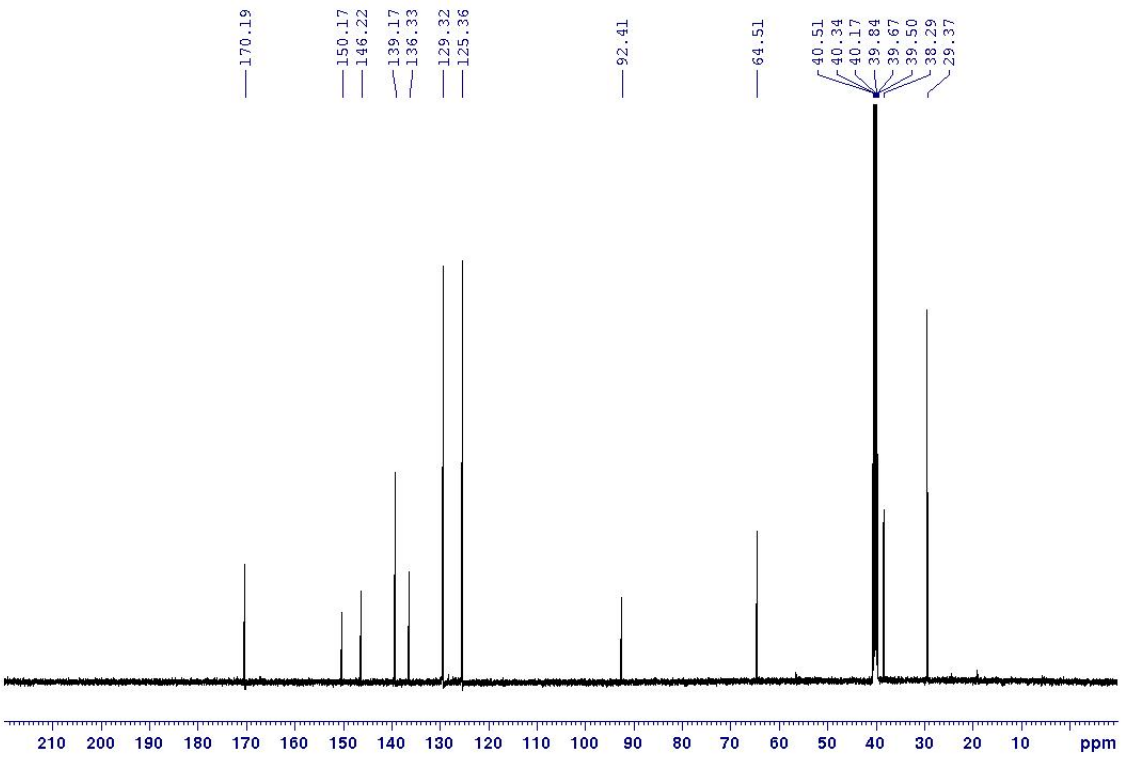
^{13}C NMR (126MHz, Chloroform-*d*): δ 170.2, 150.1, 146.2, 139.1, 136.3, 129.3, 125.3, 92.4, 64.5, 38.2, 29.3.

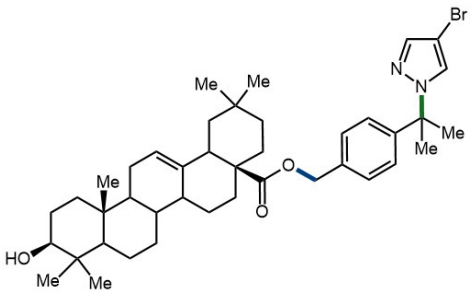
HRMS (ESI): calculated $[M-H]^{+}$ as 407.9957, found 407.9951

^{1}H NMR:



^{13}C NMR:





4-(2-(4-bromo-1H-pyrazol-1-yl)propan-2-yl)benzyl 10-hydroxy-2,2,9,9,12a-pentamethyl-1,3,4,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-octadecahydropicene-4a(2H)-carboxylate (**80**)

In an 8 ml vial oleanolic acid (91.34 mg, 0.2000 mmol, 1 equiv.) was added to a solution of 4-bromo-1-(2-(4-(chloromethyl)phenyl)propan-2-yl)-1*H*-pyrazole (112.9 mg, 0.3600 mmol, 1.8 equiv.) in DMF with K_2CO_3 (69.1 mg, 0.500 mmol, 2.5 equiv.). The reaction was stirred for 12 h at 55 ºC. The mixture was diluted with water and extracted with CH_2Cl_2, and the organic layer was dried with anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by column chromatography using DCM/acetone (10: 1) to afford product as a white solid (132 mg, 94%).[10]

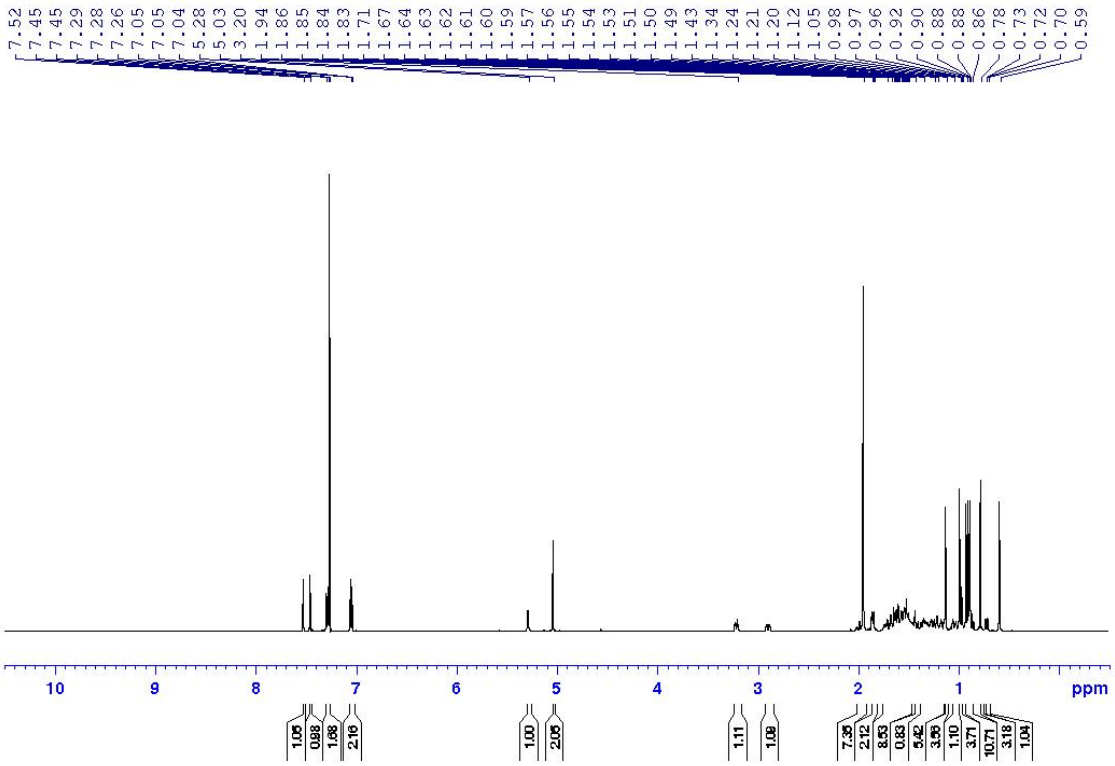
Isolated Yield: 94%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.52 (s, 1H), 7.45 (d, 0.4 Hz, 1H), 7.29-7.27 (m, 2H), 7.05-7.03 (m, 2H), 5.28 (t, J = 3.5 Hz, 1H), 5.03 (s, 2H), 3.21 (dd, J = 11.3, 4.2 Hz, 1H), 2.89 (dd, J = 13.9, 4.3 Hz, 1H), 2.00-1.95 (m, 1H), 1.94 (s, 6H), 1.85 (dd, J = 8.9, 3.6 Hz, 2H), 1.73-1.47 (m, 10H), 1.42-1.39 (m, 1H), 1.36-1.15 (m, 5H), 1.12 (s, 3H), 1.04-1.02 (m, 1H), 0.98 (s, 3H), 0.91 (s, 3H), 0.89 (s, 3H), 0.87 (s, 3H), 0.77 (s, 3H), 0.72-0.70 (m, 1H).

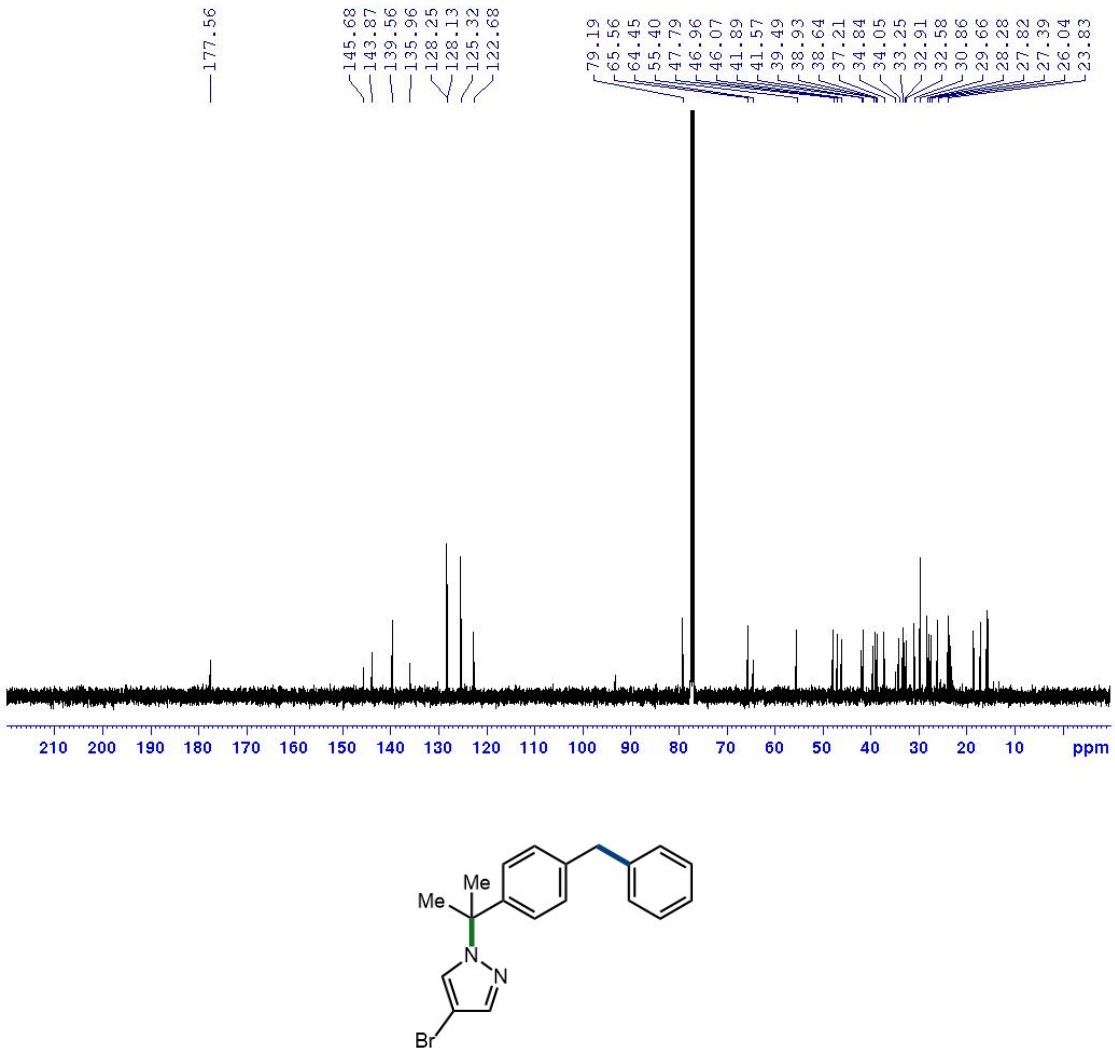
^{13}C NMR (126MHz, Chloroform-*d*): δ 177.6, 145.7, 143.9, 139.6, 135.9, 128.3, 128.1, 125.3, 122.7, 79.2, 65.6, 64.4, 55.4, 47.8, 46.9, 46.1, 41.9, 41.6, 39.5, 38.9, 38.6, 37.2, 34.8, 34.1, 33.2, 32.9, 32.6, 30.9, 29.7, 28.3, 27.8, 27.4, 26.0, 23.8, 23.6, 23.3, 18.5, 17.1, 15.7, 15.5.

HRMS (ESI): calculated $[M-H]^{+}$ as 737.3887.0731, found 737.3953

^{1}H NMR:



^{13}C NMR:



1-(2-(4-benzylphenyl)propan-2-yl)-4-bromo-1H-pyrazole (**81**)

A solution of potassium phenyltrifluoroborate (196.8 mg, 0.4000 mmol, 1 equiv.), Cs_2CO_3 (392 mg, 1.20 mmol, 3 equiv.), $PdCl_2(dppf)\cdot CH_2Cl_2$ (6.52 mg, 0.008000 mmol, 0.02 equiv.), and 4-bromo-1-(2-(4-(chloromethyl)phenyl)propan-2-yl)-1*H*-pyrazole (125.6mg, 0.4000 mmol, 1 equiv.) in THF/H_2O (10:1) (2 mL) was heated under a N_2 atmosphere in a sealed tube. The reaction mixture was stirred at 77 °C for 23 h, then cooled to rt and diluted with water (5 mL) followed by extraction with CH_2Cl_2 (10 mL x 3). The solvent was removed in vacuo and the crude product was purified by silica gel column chromatography as a colorless oil (78 mg).[11]

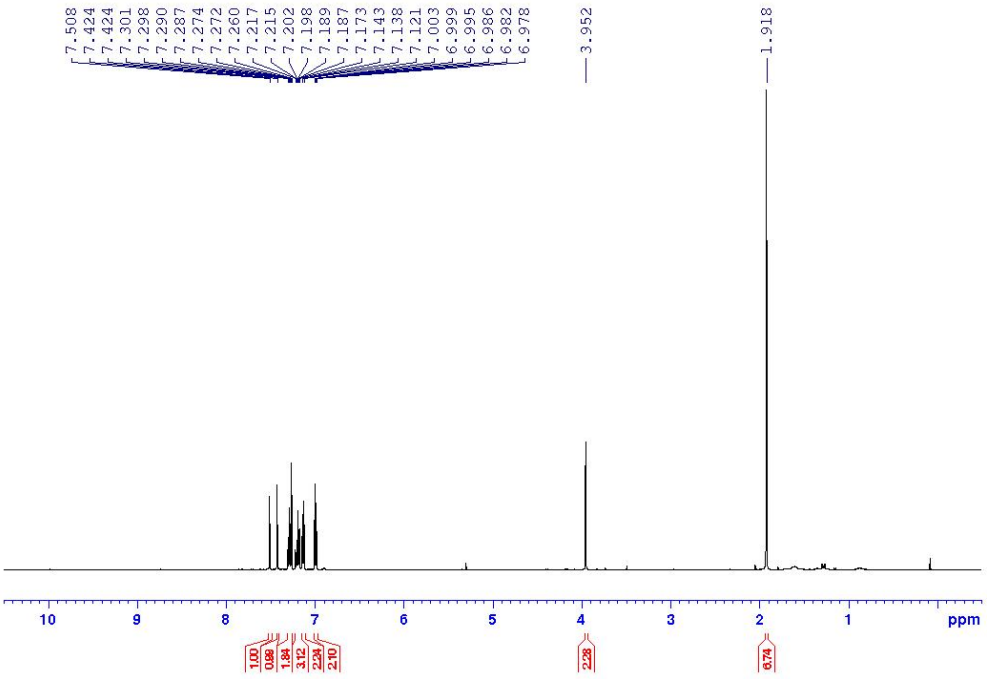
Isolated Yield: 55%

^{1}H NMR (500MHz, Chloroform-*d*): δ 7.50 (s, 1H), 7.41 (s, 1H), 7.30-7.25 (m, 2H), 7.21-7.17 (m, 3H), 7.13-7.12 (m, 2H), 7.00-6.98 (m, 2H), 3.95 (s, 2H), 1.91 (s, 6H).

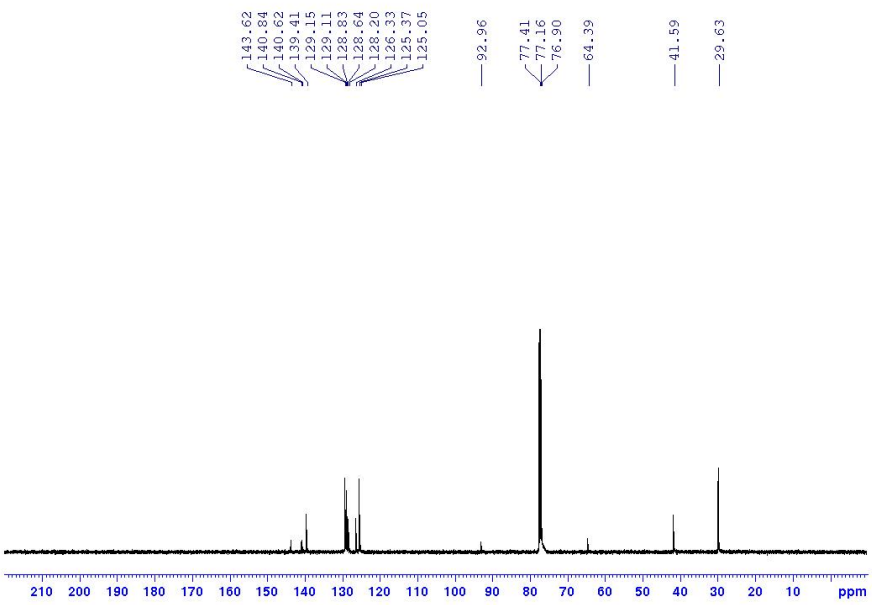
^{13}C NMR (126MHz, Chloroform-*d*): δ 143.6, 140.8, 140.6, 139.4, 129.14, 129.11, 128.8, 128.6, 128.1, 126.3, 125.3, 125.0, 92.9, 64.3, 41.5, 29.6.

HRMS (ESI): calculated $[M-H]^{+}$ as 355.0731, found 355.0780

^{1}H NMR:



^{13}C NMR:



12. Proposed Mechanism Involving EDA Complex

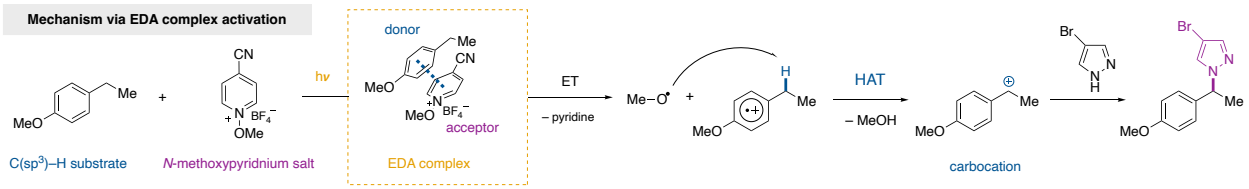


Figure S23: Proposed mechanism involving EDA complex

Presumably, the EDA complex facilitates an oxidation of the arene, which triggers fragmentation of **pyr-1** to release a methoxy radical. Subsequent HAT at the benzylic position of the resultant arene radical cation via the methoxy radical can generate the benzylic carbocation, which can undergo trapping via the pyrazole nucleophile. Further UV-vis studies suggest electron-neutral substrates, such as ethylbenzene, do not form an EDA complex, and instead follow the initially proposed photocatalyst-mediated mechanism. Additionally, we only observed evidence for an EDA complex in DCE:HFIP as the solvent. When only DCE is used, the EDA complex does not form. Further investigations are being conducted.

13. References

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