Electrophotocatalysis with a Trisaminocyclopropenium Radical Dication.

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1. General Information

Commercially available reagents were purchased from Sigma Aldrich, Matrix Chemical, AKSci, Alfa Aesar, Oakwood chemical or TCI, and used as received unless otherwise noted. Silica gel 60 (230-400 mesh) from SiliCycle was used for chromatography, and Merck silica gel plates with a fluorescence F_{254} indicator were used for thin-layer chromatography (TLC) analysis. ^{1}H and ^{13}C NMR spectra were recorded on Mercury-300 (300 MHz), Inova-400 (400 MHz), and Inova-500 (500 MHz) spectrometers. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) relative to residual chloroform (7.26 ppm) or dimethyl sulfoxide (2.50 ppm) as internal standards. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constant in Hertz (Hz) and number of hydrogen atoms based on integration intensities. ^{13}C NMR chemical shifts are reported in ppm relative to the central peak of $CDCl_3$ (77.16 ppm) CD_3OD (49.00 ppm) or $(CD_3)_2SO$ (39.52 ppm) as internal standards. ^{19}F NMR chemical shifts are reported in ppm relative to the central peak of $C_6H_5CF_3$ (-63.72 ppm) as an internal standard. Cyclic voltammetry was performed at 25 °C on a BASi Epsilon potentiostat using a glassy carbon working electrode, a platinum wire counter electrode, and Ag/AgCl reference electrodes which were obtained from CH Instruments. The mass spectral (MS) data were obtained on a Thermo Fisher Scientific Exactive series DART Mass Spectrometer. Anhydrous acetonitrile was purchased as Sure/Seal™ bottles from Sigma-Aldrich.

2. General Procedures

Electrode preparation

Materials used for set-up:

Platinum wire (13039-BU from Alfa Aesar, 25 cm). Woods clamp lamp light with aluminum reflector (Amazon, 150 Watt 8.5 inch). Compact fluorescent light bulb (Amazon, 5000K daylight, 23W). Holmes Lil' Blizzard 8-inch oscillating table fan (Amazon). June gold 2.0 mm 2B pencil lead refills (Amazon). GW Instek bench power supply (Newark Element14 Electronics, gps-3030d). Carbon felt (cut around 7 mm x 7 mm x 7 mm) from C200 Soft Carbon Battery Felt (fuelcellstore, Product Code: 1595010).

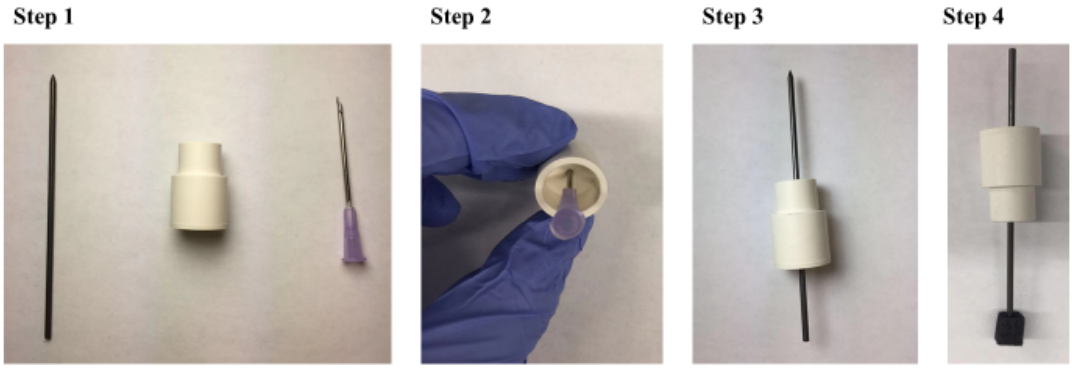


Fig. S1. Anode set up

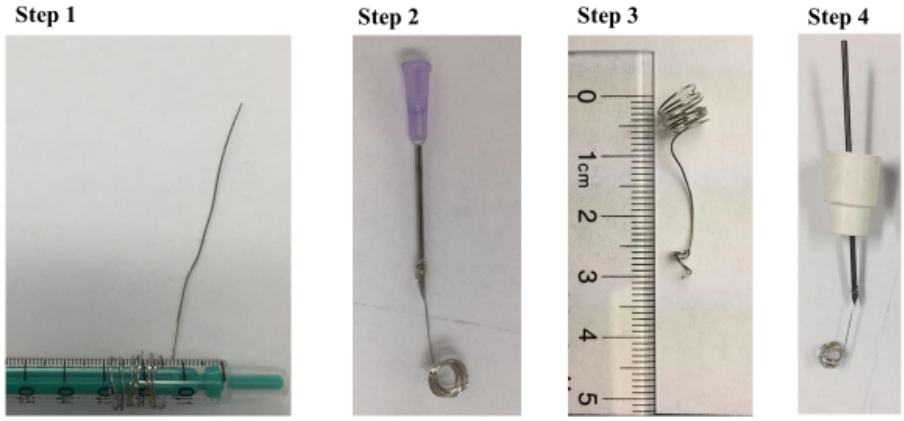


Fig. S2. Cathode set up

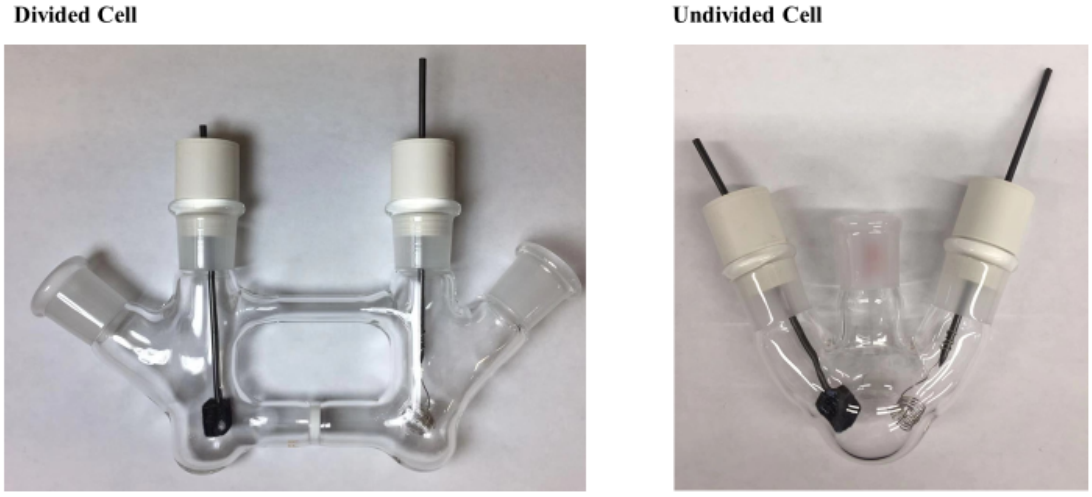


Fig. S3. Divided cell and undivided cell set up

Anode set-up: A septum was pierced with a needle, and a 2B pencil lead was inserted through the hole. A small square (~7 mm x 7 mm) of carbon felt was cut from the sheet, and this square was impaled onto the pencil lead.

Cathode set-up: A second septum was pierced with a needle, and a 2B pencil lead was inserted through the hole. Approximately 20 cm of the 25 cm platinum wire was coiled by wrapping it around a 1 mL syringe or other similarly sized object. At the other end of the wire, a smaller coil was made, and this coil was wrapped around the pencil lead.

Divided cell: The H-type divided cell with a fine glass filter was custom made by the Cornell chemistry glass shop.

Undivided cell: A simple 10 mL three-neck flask was used.

Procedure A for compounds 6, 10-24, 42-44

An oven-dried custom-made H-type divided cell was equipped with a stir bar on both sides, a carbon felt anode, and a platinum wire cathode. TAC **1** (15.2 mg, 0.032 mmol), nitrogen heterocycle (0.4 mmol), $LiClO_4$ (255.3 mg, 2.4 mmol) and arene (if it is solid) were added in the anodic chamber. The cathodic chamber was charged with $LiClO_4$ (255.3 mg, 2.4 mmol). The cell was sealed using a rubber septum and parafilm then flushed with nitrogen gas for 5 min. The anodic chamber was then sequentially charged with CH_3CN (2.0 mL) and arene (2.0 mL) via syringe. The cathodic chamber was then charged with CH_3CN (4 mL) and acetic acid (229 μL, 4.0 mmol, 10 equiv.) via syringe. Each chamber was then purged with nitrogen gas for an additional 5 min. The solution was stirred at room temperature under the irradiation from two 23W CFL bulbs, and electrolysis was initiated at a constant voltage of 1.5 V for the specified amount of time. The system was kept cool using a fan throughout the duration of the reaction. After completion of the reaction (as determined by TLC), the reaction mixture was subsequently poured into a saturated sodium bicarbonate solution (ca. 20 mL). The carbon felt anode was washed with EtOAc (3×5 mL) in an ultrasonic bath. The aqueous layer was separated and extracted with EtOAc (3×10 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration *in vacuo*, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

Procedure B for compounds 25-41

To an oven-dried 10-mL three-neck flask equipped with a stir bar, a carbon felt anode, and a platinum wire cathode was added TAC **1** (15.2 mg, 0.032 mmol), nitrogen heterocycle (0.4 mmol), and $LiClO_4$ (255.3 mg, 2.4 mmol). The cell was sealed using a rubber septum and parafilm then flushed with nitrogen gas for 5 min, followed by the sequential addition via syringe of CH_3CN (6 mL), arene (195 μL – 2.0 mL) and acetic acid (229 μL, 4.0 mmol). The reaction mixture was then purged with nitrogen gas for an additional 5 min. The solution was then stirred at room temperature under the irradiation from two 23W CFL bulbs and electrolysis was initiated at a constant voltage of 1.5 V for the specified amount of time. The system was kept cool using a fan throughout the duration of the reaction. After completion of the reaction (as determined by TLC), the reaction mixture was subsequently poured into a saturated sodium bicarbonate solution (ca. 20 mL). The carbon felt anode was washed with EtOAc (3×5 mL) in an ultrasonic bath. The aqueous layer was separated and extracted with EtOAc (3×10 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration *in vacuo*, the crude residue was subjected to flash column chromatography on silica gel to yield the desired product.

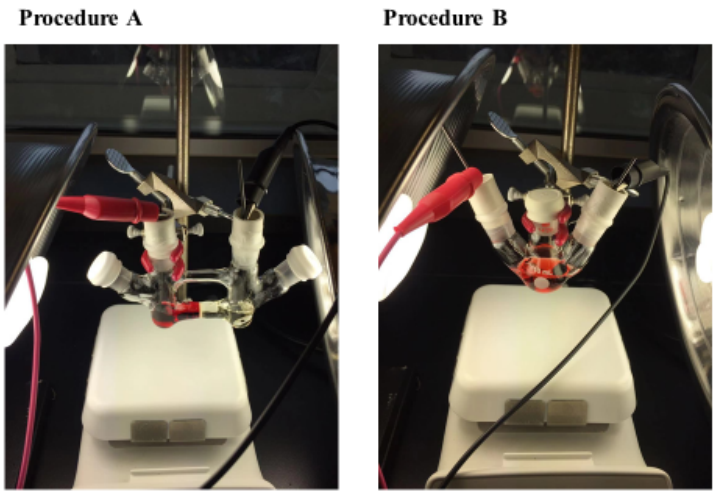


Fig. S4. Reaction set up

Notes for procedure:

1. Even though this reaction has not been found to be sensitive to water, anhydrous lithium perchlorate and anhydrous acetonitrile were used.

2. Because the carbon felt can absorb a significant amount of reaction solution, it should be rinsed in an ultrasonic bath for 5 min or more to obtain optimal product yields.

3. In the undivided cell, it is best to keep the anode and cathode relatively close (~0.5-1.0 cm) to one another; however, they should not touch.

4. For the cathode, the platinum wire should be immersed in the solution, but not the pencil lead to which it is attached.

5. The carbon felt should be replaced for each reaction.

6. After the reaction, care should be taken when removing the septum in case of pressure build up from hydrogen gas generation.

7. The system was kept cool using a fan.

8. High stirring speed is required.

Preparation of TAC 1 Catalysts

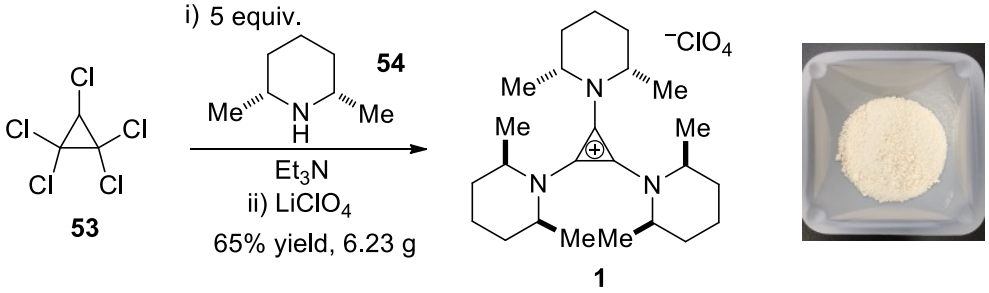


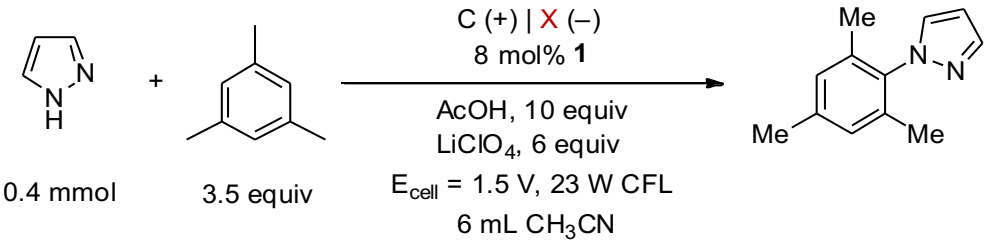
Fig. S5. TAC 1 synthesis

A round bottom flask was charged with 150 mL of DCM and pentachlorocyclopropane (2.86 mL, 20 mmol). The flask was cooled to 0 ºC, and the mixture of *cis*-2,6-dimethylpiperidine (13.5 mL, 100 mmol) and Et_3N (13.9 mL, 100 mmol) was added in slowly. The reaction was stirred for 3 h at 0 ºC and then for 24 h at rt. The reaction was transferred to a separatory funnel and washed sequentially with 1M HCl (100 mL), water (200 mL), and brine (200 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resulting solids were washed with EtOAc to give **TAC 1•Cl** as a white powder. The resulting solids were recrystallized from isopropanol to give **TAC 1•Cl** as white crystals. The resulting crystals were dissolved in DCM (20 mL) and $LiClO_4$ solution (20 mL, 5.0 M) was added. The solution was stirred for 8 h and the biphasic solution was transferred to a separatory funnel. The aqueous layer was separated and extracted with DCM (20 mL). Then the combined organic layers were washed twice with $LiClO_4$ solution (20 mL, 5.0 M). The organic layer was separated, dried over anhydrous Na_2SO_4 and concentrated *in vacuo* to produce **1** in 6.23 g (13.1 mmol, 65% yield for two steps) as a white solid.

^{1}H NMR (500 MHz, Chloroform-*d*) δ 3.91 – 3.81 (m, 6H), 1.93 – 1.87 (m, 6H), 1.79 – 1.76 (m, 3H), 1.68 – 1.64 (m, 6H), 1.61 – 1.54 (m, 3H), 1.37 (d, J = 7.1 Hz, 18H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 117.0, 53.5, 29.6, 21.8, 12.6.

3. Optimization of Reaction Conditions

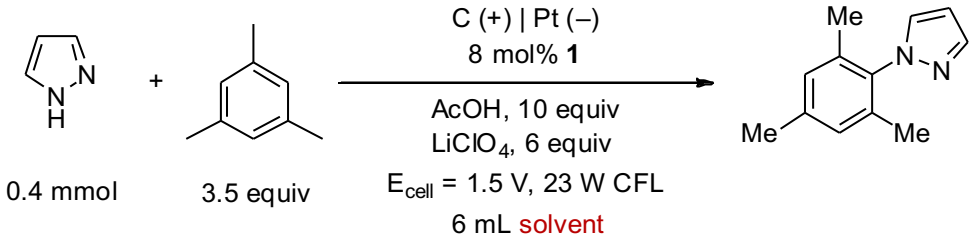
We chose mesitylene and pyrazole as our model reaction to probe reaction conditions. A typical reaction procedure is: to an oven-dried 10 mL three neck flask equipped with a stir bar, an anode and a cathode, was added **1** (15.2 mg, 0.032 mmol), pyrazole (0.4 mmol, 27.2 mg), and $LiClO_4$ (255.3 mg, 2.4 mmol). The cell was sealed using a rubber septum and parafilm and was then flushed with nitrogen gas for 5 min, followed by the sequential addition via syringe of solvent (6 mL), mesitylene (1.4 mmol, 195 µL, 3.5 equiv), and acid. The reaction mixture was then purged with nitrogen gas for an additional 5 min. The solution was then stirred at room temperature under the irradiation of light and electrolysis was initiated at a constant voltage of 1.5 V for the specified amount of time. The system was kept cool using a fan throughout the duration of the reaction. After completion of the reaction (as determined by TLC), the reaction mixture was subsequently poured into a saturated sodium bicarbonate solution (ca. 20 mL). The carbon felt anode was washed with EtOAc (3×5 mL) in an ultrasonic bath. The aqueous layer was separated and extracted with EtOAc (3×10 mL), and the combined organic layers were washed with brine and dried over anhydrous Na_2SO_4. Following concentration *in vacuo*, to the crude residue was added 0.7 mL $CDCl_3$ followed by dibromomethane (13.9 µL, 0.2 mmol) as internal standard, which was subsequently submitted for 1H NMR analysis.



electrode material	yield
Pt	**80% (80%)**
C	**50%**

Yields determined by ^{1}H NMR against CH_2Br_2
Isolated yield was in parentheses

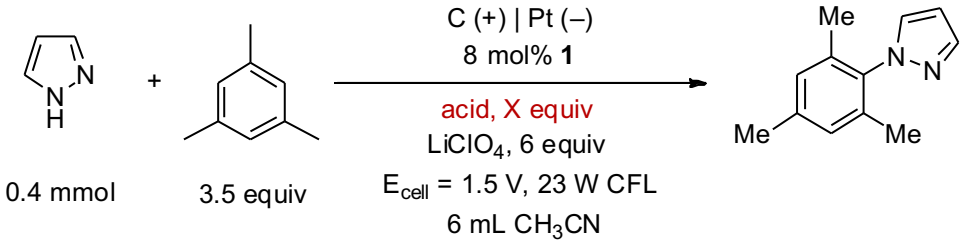
Fig. S6. Evaluation of electrode material



solvent	yield
CH_3CN	**80%**
DMF	**0%**
DCM	**trace**

Yields determined by ^{1}H NMR against CH_2Br_2

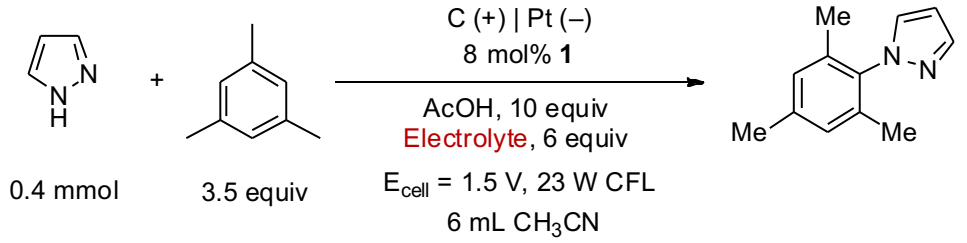
Fig. S7. Evaluation of solvent



acid	**yield**
CH_3COOH, 1 equiv	**8%**
CH_3COOH, 10 equiv	**80%**
CH_3COOH, 100 equiv	**56%**
CF_3COOH, 10 equiv	**<5%**

Yields determined by ^1H NMR against CH_2Br_2

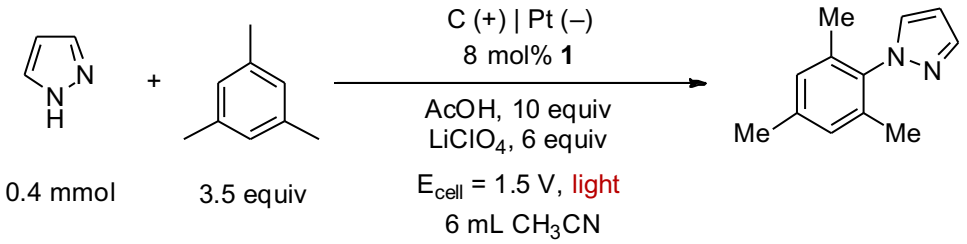
Fig. S8. Evaluation of acid



electrolyte	**yield**
$LiClO_4$	**80%**
LiTFSI	**<5%**
none	**0**

Yields determined by ^1H NMR against CH_2Br_2

Fig. S9. Evaluation of electrolyte

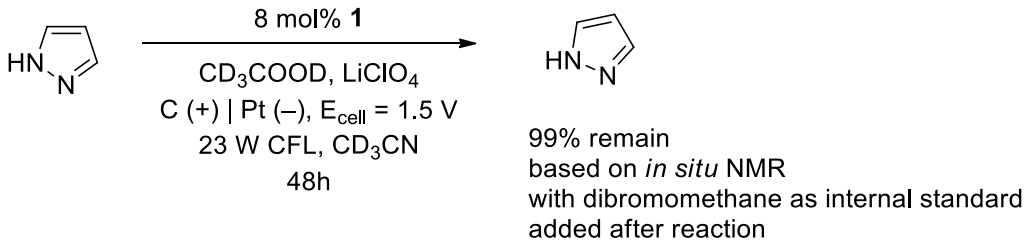


light	**yield**
CFL	**80%**
green LED	**26%**

Yields determined by ^{1}H NMR against CH_2Br_2

Fig. S10. Evaluation of light

5. Control Experiments



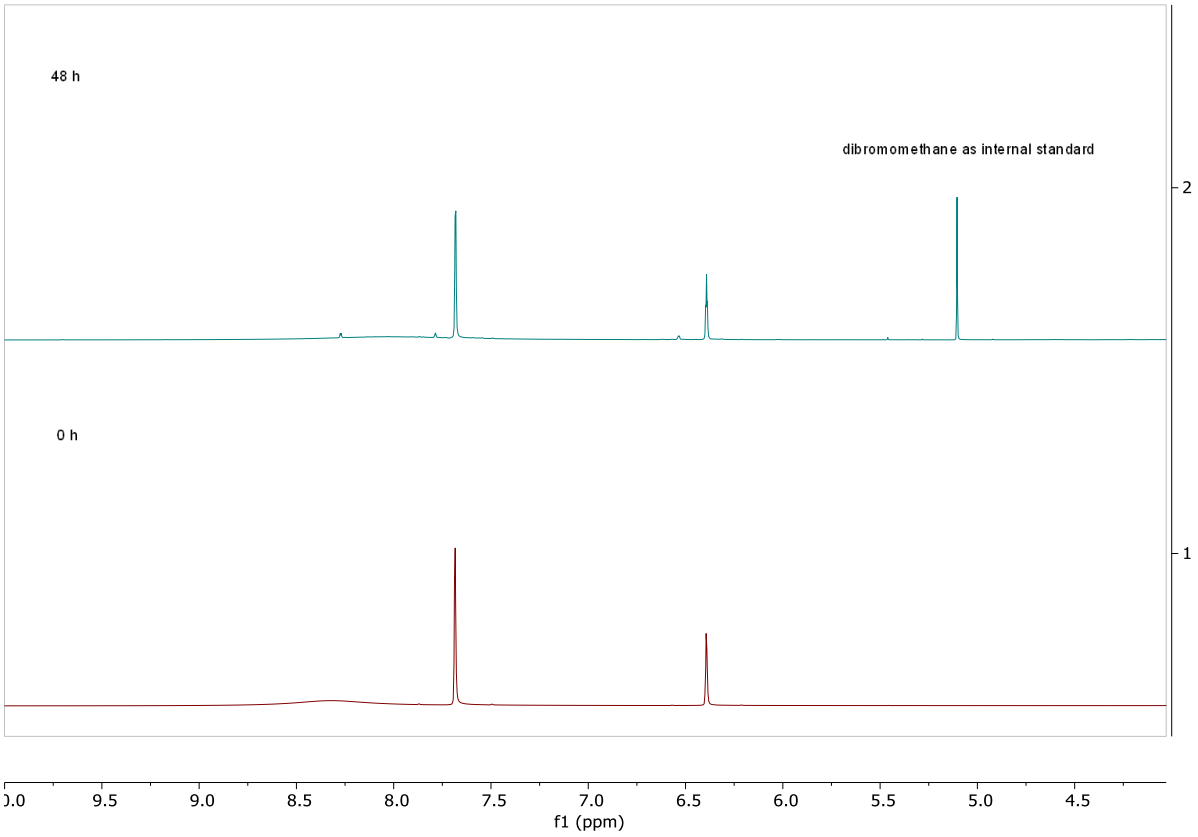


Fig. S11. Control experiment of pyrazole

6. Catalyst Stability Study

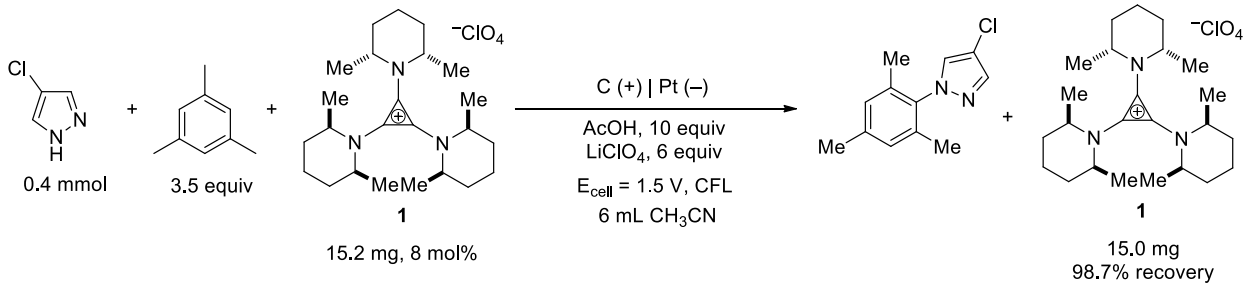
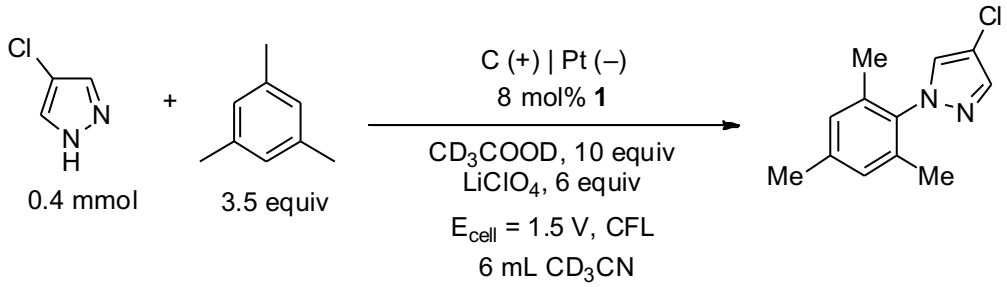


Fig. S12. Catalyst recovery experiment

In situ NMR analysis:



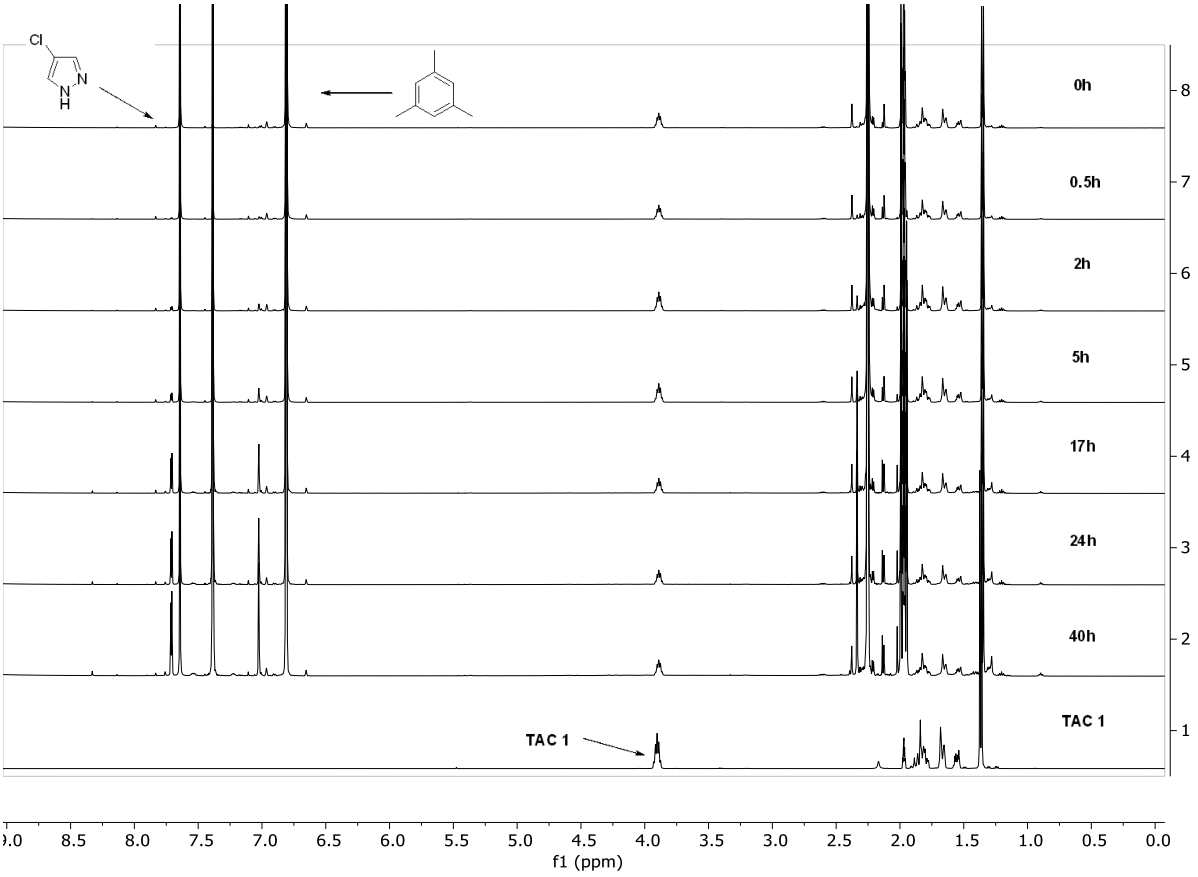


Fig S13. *in situ* ^{1}H NMR analysis of **TAC 1**

7. Cyclic Voltammetry Studies

General information: Cyclic voltammetry (CV) experiments were conducted in a 10 mL glass vial fitted with a glassy carbon working electrode, an Ag/AgCl reference electrode, and a platinum wire counter electrode. The solution of interest was purged with nitrogen for 3 minutes before data collection. Current was reported in μA. Scan rate: 100 mV/s, Bu_4NPF_6 as supporting electrolyte (0.1 M).

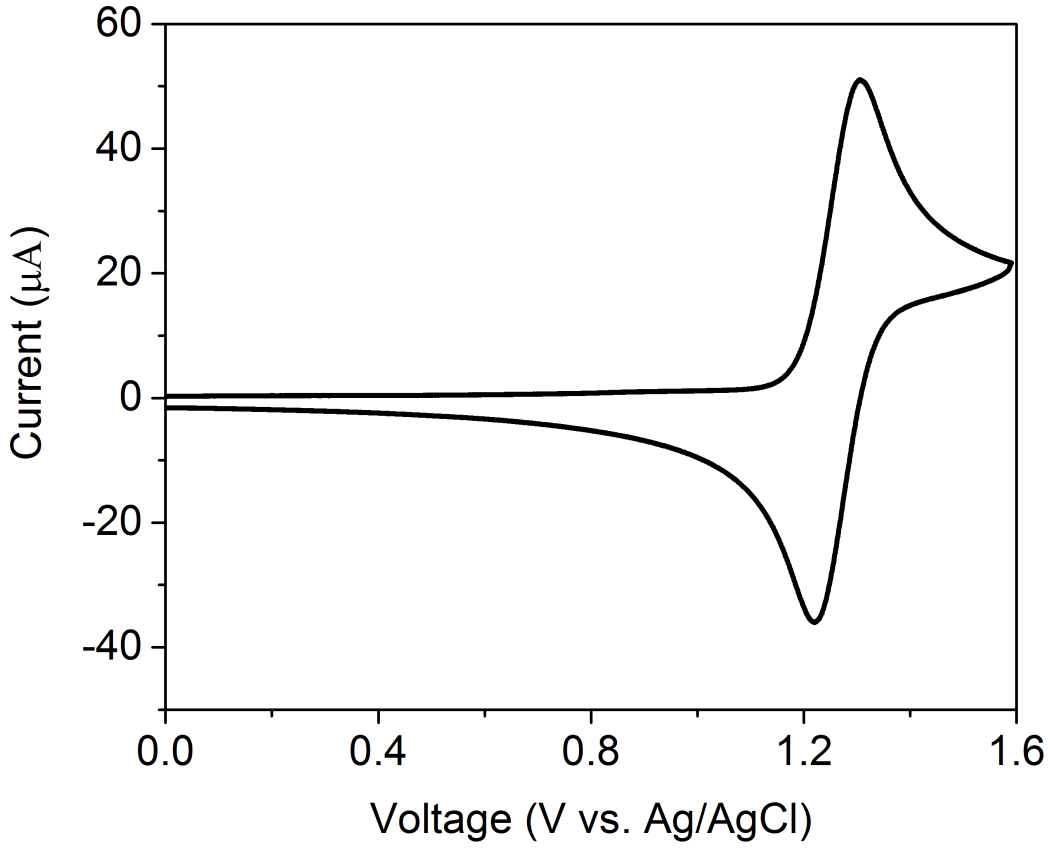
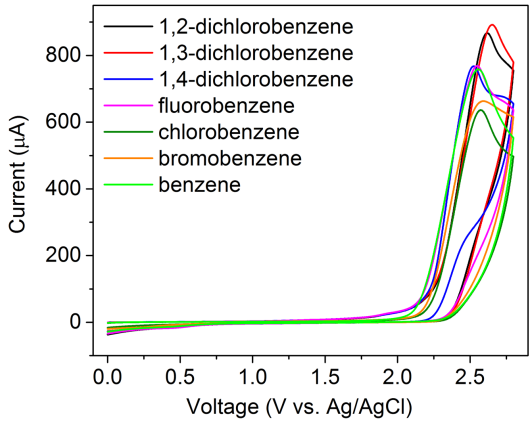
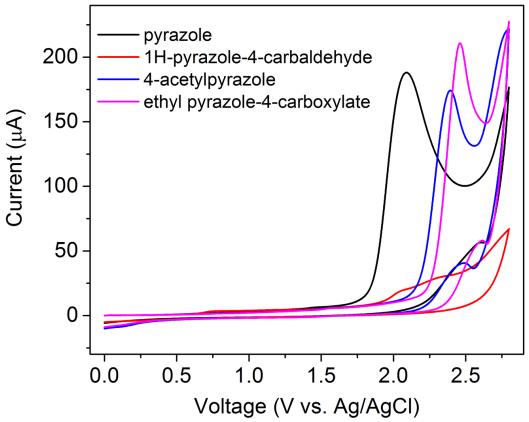


Figure S14. Cyclic voltammogram of **1** [5.0 mM] in [0.1 M] Bu_4NPF_6 in CH_3CN. Scan rate: 100 mV/s. $E_{1/2}$(**1**) = +1.26 V vs SCE





Comparation of azoles and arenes:

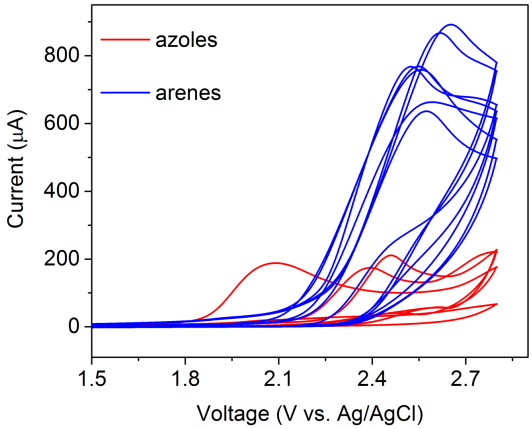


Figure S15. Cyclic voltammogram of azoles and arenes [10 mM] in [0.1 M] Bu_4NPF_6 in CH_3CN. Scan rate: 100 mV/s.

8. Absorption Spectra

UV-Vis Spectrum of **2·(ClO$_4$)$_2$** was tested in a 1 cm path length quartz and analyzed using a Perkin Elmer Lambda 35 UV/Vis Spectrophotometer. **2·(ClO$_4$)$_2$** was prepared by direct electrolysis the solution of **1** (50 mg), LiClO$_4$ (100 mg), CH$_3$COOH (0.1 mL) in CH$_3$CN (6.0 mL).

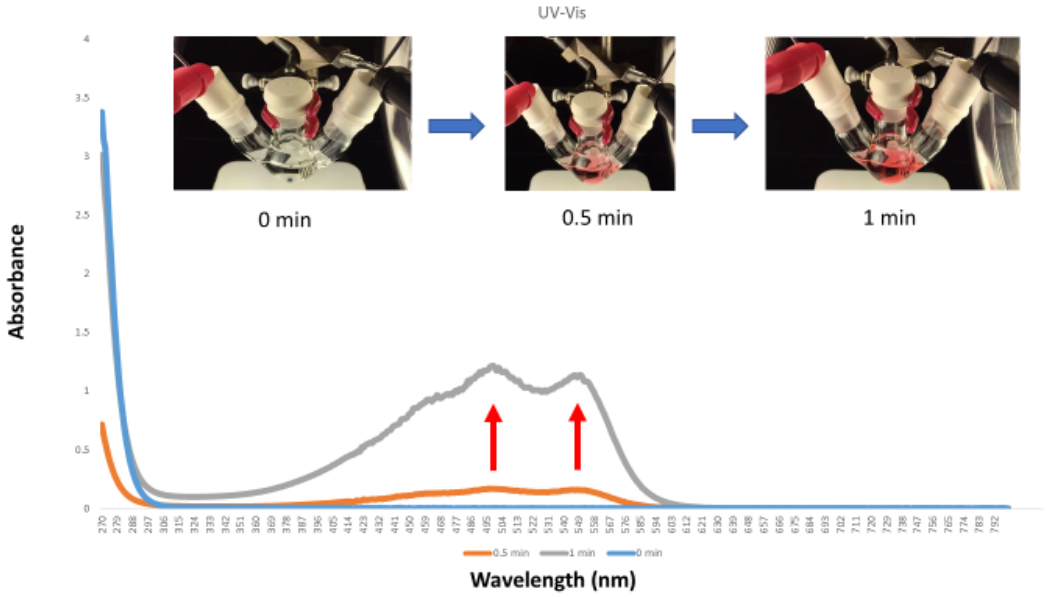


Fig. S16. UV-vis spectrum of **2·(ClO$_4$)$_2$**

9. Evaluation of the Excited State Potential (*S1*)

Using the data collected from the cyclic voltammetry studies (Fig. S16) and from the absorption spectra (Fig. S18) of the **2·(ClO$_4$)$_2$**, we could estimate the redox potential of the excited of **2·(ClO$_4$)$_2$** employing the following Equation 1:

$$E(\mathbf{2}^*/\mathbf{1}) = E(\mathbf{2}/\mathbf{1}) + E_{0\text{-}0}(\mathbf{2}^*/\mathbf{2}) \quad \text{Eq. 1}$$

$E(\mathbf{2}/\mathbf{1})$ is +1.26 V vs SCE (Fig. S16), while $E_{0\text{-}0}(\mathbf{2}^*/\mathbf{2})$ was determined using the position of the tail of the peak with the longest wavelength in the absorption spectrum. This wavelength was found to be 600 nm (Fig. S18), which translates to an $E_{0\text{-}0}(\mathbf{2}^*/\mathbf{2})$ of 2.07 eV. $E(\mathbf{2}^*/\mathbf{1})$ = +1.26 + 2.07 = +3.33 V (vs SCE)

10. Kinetic Isotope Effect Experiments (KIE) (*S2*)

The KIE value was determined from an intermolecular competition reaction. Reaction was run in 0.4 mmol scale in undivided cell.

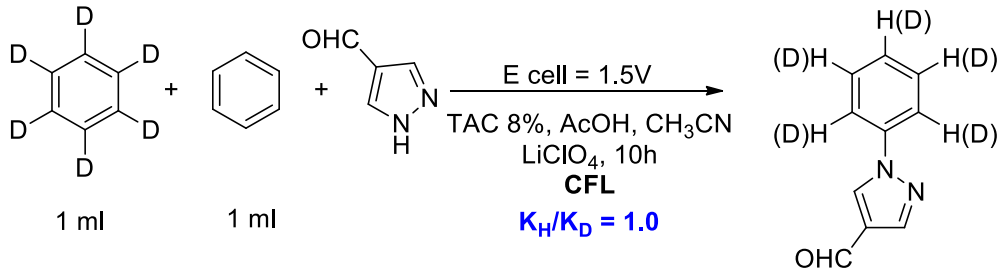


Fig S17. Kinetic isotope effect experiments

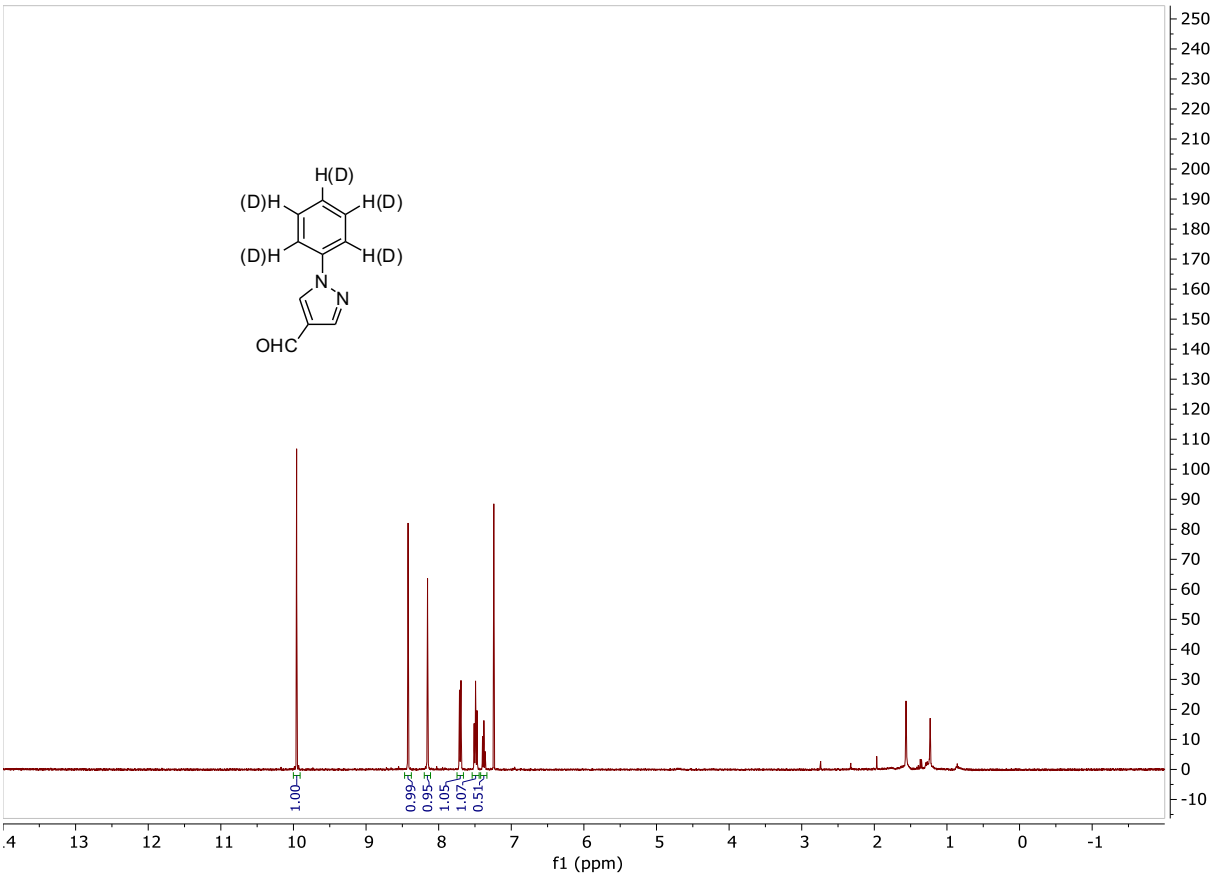


Fig. S18. NMR Spectral Data of Deuterated 4-Chloro-1-mesityl-1H-pyrazole

11. X-ray Crystallography Data

X-ray diffraction data was collected on a Bruker Apex II diffractometer. Crystal data, data collection and refinement parameters are summarized in Fig. S24. The structures were solved by using direct methods and standard difference map techniques and were refined by full-matrix least-squares procedures on F^2 with SHELXTL (Version 2014/7) (*S3-S5*).

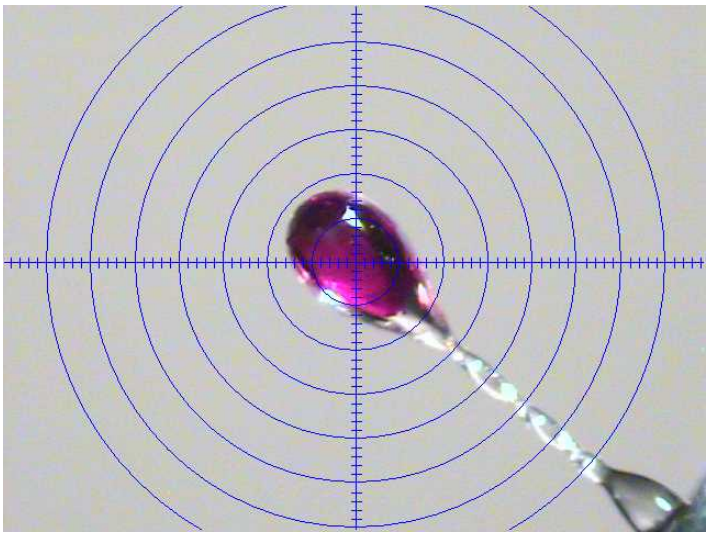


Fig. S19. Picture of Crystal

Synthesis of Crystal:

An electrochemical cell with a microporous polyethylene divider was equipped with a stir bar on each side and a carbon felt electrode on each side. The cell was charged with 20 mL of 0.5 M solution of $LiClO_4$ in acetonitrile. **TAC 1·ClO₄** (1.00 g, 2.12 mmol) was added to the anodic side in 1 mL of acetonitrile and AcOH (1.14 mL, 20 mmol) was added to the cathodic side. Electrolysis was then initiated at 2.0V while stirring, which was maintained until the current dropped to 1 mA (roughly 8 hr). The solution from the cathodic side was transferred to a flask and concentrated *in vacuo*. The resulting solid was stirred in DCM (20 mL) for 1 hr and subsequently filtered through a cotton plug. The solution was concentrated *in vacuo* to give **2·(ClO₄)₂** as a dark red powder (0.53 g, 0.93 mmol, 44% yield). **2·(ClO₄)₂** (100 mg, 0.18 mmol) was dissolved in 1 mL of acetonitrile and Et_2O was allowed to diffuse into the solution at–14 ºC for 1 week, resulting in dark red columns suitable for X-ray diffraction.

Left: before electrolysis, Right: electrolysis initiated

Fig. S20. Crystal synthesis

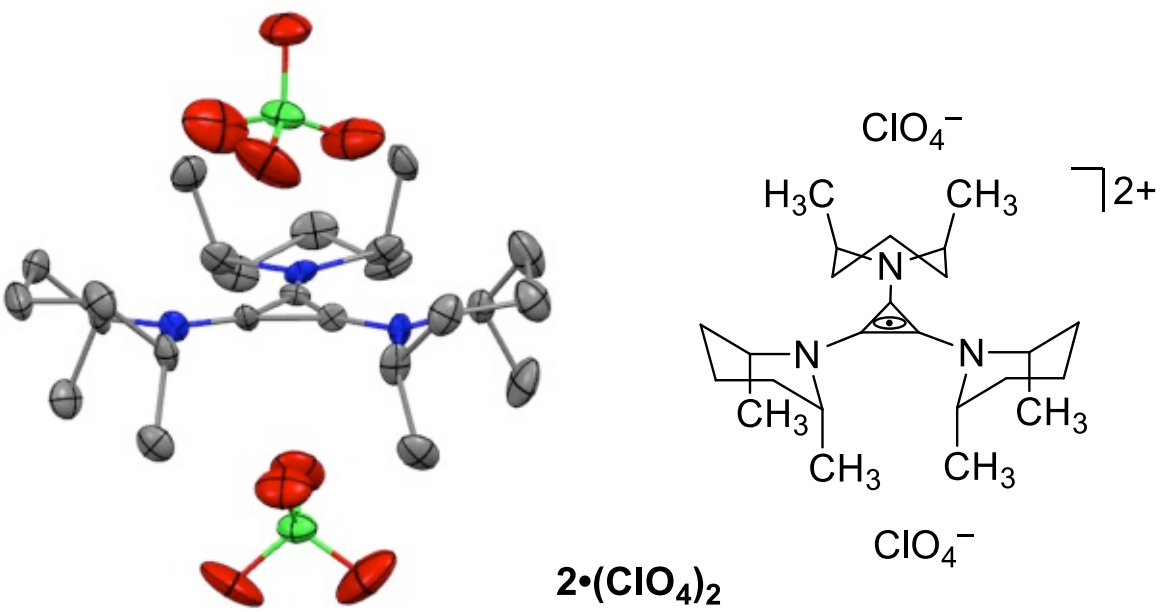


Fig. S21. X-ray Structure Determination of **2·(ClO$_4$)$_2$**

	2·(ClO$_4$)$_2$ (CSD#: 1892753)
lattice	Monoclinic
formula	$C_{24}H_{42}Cl_2N_3O_8$
formula weight	571.50
space group	*P2$_1$/c*
a/Å	19.5306(16)
b/Å	11.7733(9)
c/Å	57.147(5)
α/°	90
β/°	90.0835(13)
γ/°	90
V/Å^3	13140.3(18)
Z	16
temperature (K)	210(2)
radiation (λ, Å)	0.71073

ρ (calcd.) g cm^{-3}	1.156
μ (Mo Kα), mm^{-1}	0.241
θ max, deg.	26.371
no. of data collected	162493
no. of data	26900
no. of parameters	1359
R_1 [$I > 2\sigma(I)$]	0.1064
wR_2 [$I > 2\sigma(I)$]	0.2695
R_1 [all data]	0.1951
wR_2 [all data]	0.3234
GOF	1.024
R_{int}	0.1502

Fig S22. Crystal data and structure refinement for **2·(ClO$_4$)$_2$**

12. Computational Data

All calculations were performed with ORCA (*S6*), an open-source quantum chemistry package.

Cartesian coordinates of the atoms in TAC radical dication were extracted from the crystal structure, having added hydrogen atoms in the expected configurations. These atomic positions were then used to initialize a geometry optimization, using the B3LYP exchange-correlation functional, the cc-pVDZ basis set, and an implicit solvation model for acetonitrile. With the resulting geometry, the unrestricted Kohn-Sham equations were solved. The molecular orbitals in Fig. 4 were generated using an iso-surface value of 0.06, with the VMD program (*S7*).

Time-Dependent Density Functional Theory (TD-DFT) (*S8*) is a computational technique to calculate excited electronic states, which are assumed to be (linear combinations of) single-particle excitations from the ground-state. The physical result we wish to emphasize is that the first and second excited states of TAC radical dication are energetically separated by ~5 nm, and correspond predominately to excitations from the ground-state HOMO-1 and HOMO-2 to the SOMO.

We have verified that using a larger basis set (cc-pVTZ) does not change the energetics and orbital characters of the relevant lowest-energy excited states. As additional checks, we ran the original calculation but with the ωB97x exchange-correlation functional, and also the more systematic Equation of Motion Coupled Cluster method with Single and Double excitations (EOM-CCSD) with localized orbitals (*S9*). In both cases, while the excitation energies were shifted from the original B3LYP/cc-pVDZ calculation, the first and second excited states were again separated by ~5 nm. In the former calculation, the relevant excited states were characterized by identical orbital transitions.

Cartesian Coordinates for Geometry Optimized Structure of **2**

Atom	X	Y	Z
N	25.197507	9.8133958	-1.03502
N	21.637893	8.8464044	-1.09876

N	23.522327	8.8377518	2.097436
C	24.121849	9.3947121	-0.40714
C	22.747953	9.0404926	-0.42326
C	23.470129	9.0325176	0.799183
H	24.408603	10.548619	4.263632
H	26.097558	10.442766	3.712552
C	19.578484	9.7332976	0.013938
H	20.217892	10.473675	0.518326
H	19.105999	10.214077	-0.85369
H	18.783093	9.4321991	0.712945
C	21.248362	10.524999	-2.91879
H	21.838996	11.244308	-2.33107
H	21.455569	10.695959	-3.98652
H	20.182931	10.725795	-2.74196
C	25.576357	8.7395331	-3.26287
H	25.017699	7.8637704	-2.89798
H	25.353467	8.8727891	-4.3329
H	26.650309	8.5308897	-3.15991
C	27.327839	8.7338384	-0.28355
H	26.738759	7.8492537	0.003613
H	27.77605	8.5460491	-1.26875
H	28.143621	8.8584275	0.444885
C	22.511894	7.4306616	3.888353
H	21.605417	7.3443438	4.507461
H	22.626749	6.4786012	3.343715
C	23.754112	7.6770767	4.746708
H	23.902205	6.831629	5.436379
H	23.624935	8.5753807	5.373232
C	24.977387	7.8163669	3.839618
H	25.134743	6.8700327	3.295292
H	25.89161	8.0124483	4.420905
C	27.21274	11.260919	-0.76283
H	26.660987	12.15356	-0.42347
H	28.1935	11.276862	-0.26387
C	27.35326	11.304535	-2.28432
H	27.974261	10.468441	-2.64673
H	27.86881	12.231045	-2.58162
C	25.962527	11.265698	-2.91763
H	26.017986	11.282596	-4.01688
H	25.397803	12.160955	-2.60676
C	25.155819	10.017519	-2.52373
H	24.102036	10.221786	-2.74706
C	26.473478	10.008613	-0.26492
H	26.149333	10.202284	0.764267
C	19.568725	7.4509145	-1.18217
H	20.089818	6.4804476	-1.13438
H	18.599262	7.3250019	-0.67608
C	19.390654	7.8520978	-2.64677

H	18.799175	8.7785653	-2.73387
H	18.828407	7.0690225	-3.17881
C	20.767803	8.0202981	-3.28906
H	20.68988	8.3171373	-4.34615
H	21.299829	7.0543848	-3.26131
C	21.633916	9.0772139	-2.585
H	22.6728	8.9110516	-2.89387
C	20.373881	8.4788297	-0.37137
H	20.713558	7.9832778	0.544902
C	22.264396	8.5528386	2.867078
H	21.556004	8.1824713	2.119094
C	21.689212	9.8375185	3.481698
H	21.622205	10.644757	2.73646
H	20.672853	9.6130504	3.839579
H	22.278632	10.19661	4.336327
C	24.841323	8.9521819	2.810595
H	25.593902	8.7812509	2.031594
C	25.04794	10.356789	3.391901
H	24.850991	11.135901	2.639457

Frontier Orbital Energies from DFT Calculation:

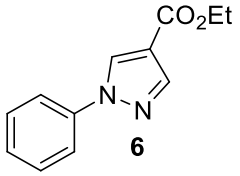
	Alpha			**Beta**		
	Orbital #	**Occupancy**	**Energy (eV)**	**Orbital #**	**Occupancy**	**Energy (eV)**
HOMO-5	97	1	-9.18	97	1	-9.17
HOMO-4	98	1	-9.08	98	1	-9.07
HOMO-3	99	1	-9.02	99	1	-9.00
HOMO-2	100	1	-8.91	100	1	-8.61
HOMO-1	101	1	-8.88	101	1	-8.58
SOMO	102	1	-7.09	102	0	-5.11
LUMO	103	0	-0.72	103	0	-0.33
LUMO+1	104	0	-0.70	104	0	-0.30
LUMO+2	105	0	0.34	105	0	0.38

Lowest Energy Excited States from TD-DFT Calculation:

	Energy (eV)	**Wavelength (nm)**	**Transition Orbitals**	**% Composition (c^2)**
State 1	2.70	460	102a -> 104a	0.03
			101b -> 102b	0.94
State 2	2.73	454	102a -> 103a	0.03
			100b -> 102b	0.94
State 3	2.90	427	99a -> 102a	0.98
State 4	3.03	410	95b -> 102b	0.01
			96b -> 102b	0.01

			98b -> 102b	0.97
State 5	3.148	394	97b -> 102b	0.98

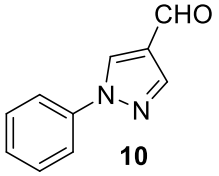
13. Characterization



6

***Ethyl 1-phenyl-1H-pyrazole-4-carboxylate* (6):** The title compound was prepared from benzene (2.0 mL) and ethyl 1H-pyrazole-4-carboxylate (0.4 mmol, 56.0 mg) according to general procedure A with an irradiation/electrolysis time of 60 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a white solid in 65% yield (56.2 mg).

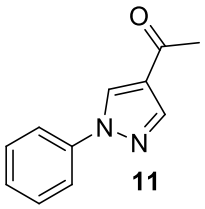
6: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.12 (s, 1H), 7.74 – 7.72 (m, 2H), 7.52 – 7.49 (m, 2H), 7.39 – 7.36 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 162.9, 142.2, 139.4, 130.0, 129.6, 127.6, 119.6, 117.0, 60.5, 14.4. MS (DART) exact mass: calculated for $(M+H)^+$: 217.0972; found: 217.0979.



10

***1-Phenyl-1H-pyrazole-4-carbaldehyde* (10):** The title compound was prepared from benzene (2.0 mL) and 1H-pyrazole-4-carbaldehyde (0.4 mmol, 38.4 mg) according to general procedure A with an irradiation/electrolysis time of 60 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a white solid in 61% yield (42.0 mg).

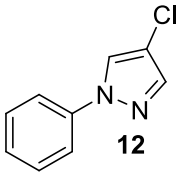
10: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 8.44 (s, 1H), 8.17 (s, 1H), 7.73 – 7.71 (m, 2H), 7.56 – 7.46 (m, 2H), 7.44 – 7.35 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 184.1, 141.7, 139.2, 130.0, 129.7, 128.1, 125.7, 119.8. MS (DART) exact mass: calculated for $(M+H)^+$: 173.0709; found: 173.0719



11

***1-(1-Phenyl-1H-pyrazol-4-yl)ethanone* (11):** The title compound was prepared from benzene (2.0 mL) and 1-(1H-pyrazol-4-yl)ethanone (0.4 mmol, 44.0 mg) according to general procedure A with an irradiation/electrolysis time of 60 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a white solid in 60% yield (44.7 mg).

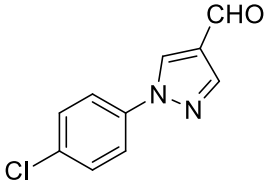
11: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 0.6 Hz, 1H), 8.10 (s, 1H), 7.76 – 7.65 (m, 2H), 7.53 – 7.45 (m, 2H), 7.41 – 7.33 (m, 1H), 2.50 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.08, 141.56, 139.32, 129.67, 129.08, 127.77, 125.64, 119.74, 28.07. MS (DART) exact mass: calculated for $(M+H)^+$: 187.0866; found: 187.0876.



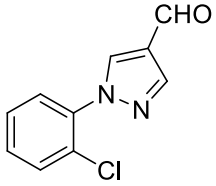
12

4-Chloro-1-phenyl-1H-pyrazole **(12):** The title compound was prepared from benzene (2.0 mL) and 4-chloro-1H-pyrazole (0.4 mmol, 41.0 mg) according to general procedure A with an irradiation/electrolysis time of 60 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a white solid in 45% yield (32.1 mg).

12: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.64-7.63 (m, 3H), 7.48-7.45 (m, 2H), 7.33-7.30 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.8, 139.5, 129.6, 127.0, 124.8, 119.0, 112.4. MS (DART) exact mass: calculated for $(M+H)^+$: 179.0371; found: 179.0377.



13a



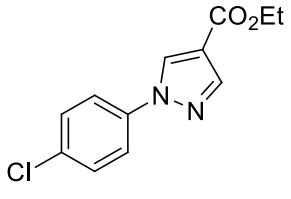
13b

1-(4-chlorophenyl)-1H-pyrazole-4-carbaldehyde **(13a) and** ***1-(2-chlorophenyl)-1H-pyrazole-4-carbaldehyde*** **(13b):** The title compounds were prepared from chlorobenzene (2.0 mL) and 1H-pyrazole-4-carbaldehyde (0.4 mmol, 38.4 mg) according to general procedure A with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 15% EtOAc/hexanes to yield a white solid in 56% yield (46.3 mg) as a mixture of para and ortho isomers. The crude isomer ratio of the mixture was 4:1:1 (*p*:*m*:*o*) as determined by ^{1}H NMR of reaction solution.

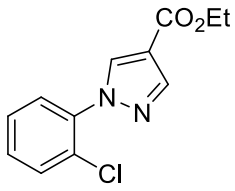
13a: ^{1}H NMR (500 MHz, Chloroform-d) δ 9.96 (s, 1H), 8.41 (s, 1H), 8.15 (s, 1H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (126 MHz, Chloroform-d) δ 183.9, 141.9, 137.7, 133.7, 129.9, 129.9, 125.9, 121.0.

13b: ^{1}H NMR (500 MHz, Chloroform-d) δ 9.97 (s, 1H), 8.41 (s, 1H), 8.16 (s, 1H), 7.68-7.67 (m, 2H), 7.49-7.47 (m, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 184.0, 141.3, 135.1, 130.9, 130.2, 129.9, 129.9, 128.4, 128.0, 127.7.

MS (DART) exact mass: calculated for $(M+H)^+$: 187.1235; found: 187.1228.



14a



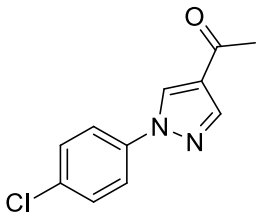
14b

Ethyl 1-(4-chlorophenyl)-1H-pyrazole-4-carboxylate **(14a) and ethyl 1-(2-chlorophenyl)-1H-pyrazole-4-carboxylate (14b):** The title compounds were prepared from chlorobenzene (2.0 mL) and ethyl 1H-pyrazole-4-carboxylate (0.4 mmol, 56.0 mg) according to general procedure A with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 20% EtOAc/hexanes to yield a white solid in 46% (46.1 mg). The ratio of the mixture was 10:1 (*p*:*o*) as determined by ^{1}H NMR of reaction solution.

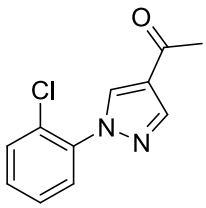
14a: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.14 (s, 1H), 8.16 (s, 1H), 8.04 – 7.87 (m, 2H), 7.67 – 7.52 (m, 2H), 4.28 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.5, 142.5, 138.2, 132.0, 130.0, 121.2, 117.0, 60.5, 17.3, 14.8.

14b: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.14 (s, 1H), 8.16 (s, 1H), 8.04 – 7.87 (m, 2H), 7.67 – 7.52 (m, 2H), 4.28 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.5, 142.5, 138.2, 132.0, 131.9, 130.0, 129.1, 121.2, 117.0, 60.5, 17.3, 14.8.

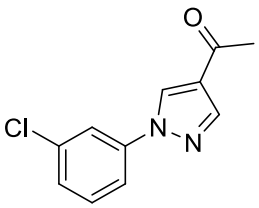
MS (DART) exact mass: calculated for $(M+H)^+$: 251.0582; found: 251.0593.



15a



15b



15c

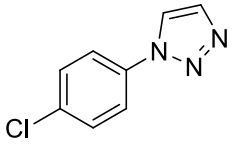
1-(1-(4-chlorophenyl)-1H-pyrazol-4-yl)ethanone **(15a), 1-(1-(2-chlorophenyl)-1H-pyrazol-4-yl)ethenone (15b) and 1-(1-(3-chlorophenyl)-1H-pyrazol-4-yl)ethanone (15c):** The title compounds were prepared from chlorobenzene (2.0 mL) and 1-(1H-pyrazol-4-yl)ethanone (0.4 mmol, 44.0 mg) according to general procedure A with an irradiation/electrolysis time of 80 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 20% EtOAc/hexanes to yield a white solid in 55% yield (48.6 mg). The ratio of the mixture was 8:3:1 (*p*:*o*:*m*) as determined by ^{1}H NMR of reaction solution.

15a: ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.24 (s, 1H), 8.20 (s, 1H), 7.97 – 7.94 (m, 2H), 7.62 – 7.60 (m, 2H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6, mixture of **a, b and c**) δ 192.2, 192.2, 141.8, 141.4, 138.3, 136.0, 132.0, 131.8, 131.3, 131.0, 130.1, 129.2, 128.9, 128.9, 128.8, 126.0, 125.1, 121.1, 28.5, 17.3.

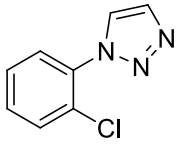
15b: ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.84 (s, 1H), 8.20 (s, 1H), 7.74 - 7.04 (m, 4H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6, mixture of **a, b and c**) δ 192.2, 192.2, 141.8, 141.4, 138.3, 136.0, 132.0, 131.8, 131.3, 131.0, 130.1, 129.2, 128.9, 128.9, 128.8, 126.0, 125.1, 121.1, 28.5, 17.3.

15c: ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.58 (s, 1H), 8.16 (s, 1H), 7.74 - 7.55 (m, 3H), 7.04 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6, mixture of **a, b and c**) δ 192.2, 192.2, 141.8, 141.4, 138.3, 136.0, 132.0, 131.8, 131.3, 131.0, 130.1, 129.2, 128.9, 128.9, 128.8, 126.0, 125.1, 121.1, 28.5, 17.3.

MS (DART) exact mass: calculated for $(M+H)^+$: 221.0476; found: 221.0487.



16a



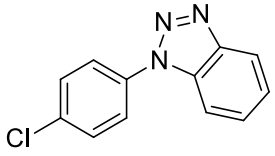
16b

1-(4-chlorophenyl)-1H-1,2,3-triazole **(16a) and 1-(2-chlorophenyl)-1H-1,2,3-triazole (16b):** The title compounds were prepared from chlorobenzene (2.0 mL) and 1H-1,2,3-triazole (0.4 mmol, 27.6 mg) according to general procedure A with an irradiation/electrolysis time of 80 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 30% EtOAc/hexanes to yield a white solid in 31% (22.3 mg). The ratio of the mixture was 3:1 (*p*:*o*) as determined by ^{1}H NMR of reaction solution.

16a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 1.1 Hz, 1H), 7.86 (d, *J* = 1.1 Hz, 1H), 7.72 – 7.70 (m, 2H), 7.52 – 7.51 (m, 2H). ^{13}C NMR (126 MHz, Methanol-d_4, mixture of **a and b**) δ 135.7, 134.3, 134.0, 133.0, 131.3, 130.5, 129.7, 127.9, 126.8, 122.8, 121.8.

16b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 5.0 Hz, 1H), 7.87 (s, 1H), 7.64 - 7.58 (m, 2H), 7.47 – 7.46 (m, 2H). ^{13}C NMR (126 MHz, Methanol-d_4, mixture of **a and b**) δ 135.7, 134.3, 134.0, 133.0, 131.3, 130.5, 129.7, 127.9, 126.8, 122.8, 121.8.

MS (DART) exact mass: calculated for $(M+H)^+$: 180.0323; found: 180.0330.

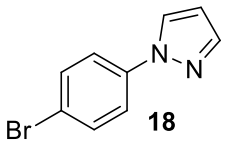


17

1-(4-chlorophenyl)-1H-benzo[d][1,2,3]triazole **(17)**: The title compound was prepared from chlorobenzene (2.0 mL) and 1H-benzo[d][1,2,3]triazole (0.4 mmol, 47.6 mg) according to general procedure A with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 30% EtOAc/hexanes to yield a white solid in 35% yield (32.2 mg). The ratio of the mixture was 10:1 (*p*:*o*) as determined by ^{1}H NMR of reaction solution.

17: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 8.3 Hz, 1H), 7.80 – 7.70 (m, 3H), 7.64 – 7.54 (m, 3H), 7.48 – 7.44 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 135.6, 134.5, 132.2, 130.1, 128.6, 124.6, 124.0, 120.5, 110.1.

MS (DART) exact mass: calculated for $(M+H)^+$: 230.0480; found: 230.0492.

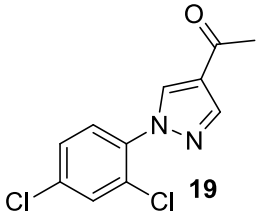


18

1-(4-bromophenyl)-1H-pyrazole **(18)**: The title compound was prepared from bromobenzene (2.0 mL) and 1H-pyrazole (0.4 mmol, 27.2 mg) according to general procedure A with an irradiation/electrolysis time of 96 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 15% EtOAc/hexanes to yield a white solid in 35% (31.2 mg). The ratio of the mixture was 3:1 (*p*:*o*) as determined by ^{1}H NMR of reaction solution.

18: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 2.5 Hz, 1H), 7.72 (d, *J* = 1.7 Hz, 1H), 7.60 – 7.52 (m, 4H), 6.46 (t, *J* = 2.1 Hz, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 141.4, 139.2, 132.5, 126.6, 120.6, 119.6, 108.1.

MS (DART) exact mass: calculated for $(M+H)^+$:222.9865; found:222.9878.

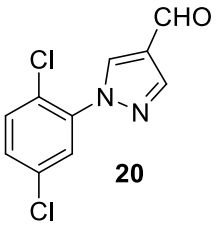


19

1-(1-(2,4-dichlorophenyl)-1H-pyrazol-4-yl)ethanone **(19)**: The title compound was prepared from 1,3-dichlorobenzene (2.0 mL) and 1-(1H-pyrazol-4-yl)ethanone (0.4 mmol, 44.0 mg) according to general procedure A with an irradiation/electrolysis time of 80 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 20% EtOAc/hexanes to yield a white solid in 40% yield (40.8 mg).

19: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 8.14 (s, 1H), 7.62 – 7.55 (m, 2H), 7.42 (dd, *J* = 8.6, 2.3 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.9, 141.6, 136.0, 135.3, 133.8, 130.6, 129.1, 128.5, 128.2, 125.3, 28.1.

MS (DART) exact mass: calculated for $(M+H)^+$: 255.0086; found: 255.0099.



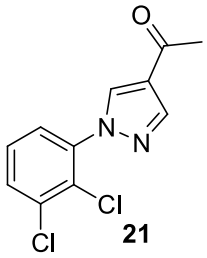
20

1-(2,5-dichlorophenyl)-1H-pyrazole-4-carbaldehyde **(20)**: The title compound was prepared from 1,4-dichlorobenzene (8 mmol, 1.176 g) and 1H-pyrazole-4-carbaldehyde (0.4 mmol, 38.4 mg) according to general procedure A with an irradiation/electrolysis time of 72 hours. The crude residue was purified by

column chromatography on silica gel with an eluent of hexanes to 20% EtOAc/hexanes to yield a light yellow solid in 42% yield (40.5 mg).

20: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 8.44 (s, 1H), 8.20 (s, 1H), 7.69 – 7.68 (m, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.40 – 7.38 (m, 1H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 183.9, 135.0, 133.8, 131.8, 130.1, 127.7, 126.2.

MS (DART) exact mass: calculated for $(M+H)^+$: 240.9930; found: 240.9941.

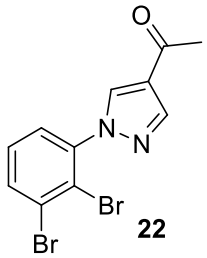


21

1-(1-(2,3-dichlorophenyl)-1H-pyrazol-4-yl)ethanone **(21)**: The title compound was prepared from 1,2-dichlorobenzene (2.0 mL) and 1-(1H-pyrazol-4-yl)ethanone (0.4 mmol, 44.0 mg) according to general procedure A with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 20% EtOAc/hexanes to yield a white solid in 30% yield (30.6 mg).

21: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 8.09 (s, 1H), 7.94 – 7.82 (m, 1H), 7.56 – 7.56 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.8, 142.8, 138.4, 133.9, 131.7, 131.3, 129.0, 126.2, 121.6, 118.5, 28.1.

MS (DART) exact mass: calculated for $(M+H)^+$:255.0086; found:255.0099.

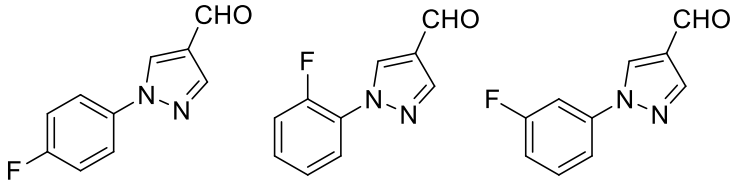


22

1-(4-bromophenyl)-1H-pyrazole **(22)**: The title compound was prepared from 1,2-dibromobenzene (2.0 mL) and 1-(1H-pyrazol-4-yl)ethanone (0.4 mmol, 44.0 mg) according to general procedure A with an irradiation/electrolysis time of 96 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 20% EtOAc/hexanes to yield a light yellow solid in 31% yield (42.7 mg).

22: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 8.12 (s, 1H), 8.07 (d, *J* = 2.6 Hz, 1H), 7.75 (d, *J* = 8.7 Hz, 1H), 7.56 (dd, *J* = 8.7, 2.6 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 191.8, 143.1, 142.0, 138.9, 134.4, 129.0, 126.2, 124.6, 123.7, 119.2, 28.1.

MS (DART) exact mass: calculated for $(M+H)^+$: 342.9076; found: 342.9094 and 344.9074.



23a **23b** **23c**

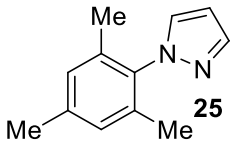
1-(4-fluorophenyl)-1H-pyrazole-4-carbaldehyde **(23a),** ***1-(2-fluorophenyl)-1H-pyrazole-4-carbaldehyde*** **(23b) and** ***1-(3-fluorophenyl)-1H-pyrazole-4-carbaldehyde*** **(23c)**: The title compounds were prepared from fluorobenzene (2.0 mL) and 1H-pyrazole-4-carbaldehyde (0.4 mmol, 38.4 mg) according to general procedure A with an irradiation/electrolysis time of 60 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a colorless oil in 36% yield (27.4 mg). The ratio of the mixture was 5:1:1 (*p*:*o*:*m*) as determined by ^{1}H NMR of reaction solution.

23a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 8.38 (s, 1H), 8.16 (s, 1H), 7.71 – 7.68 (m, 2H), 7.22 – 7.18 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a, b and c**) δ 184.0, 184.0, 162.0 (d, *J* = 249.5 Hz), 153.1 (d, *J* = 249.5 Hz), 141.8, 141.7, 141.1, 134.6, 134.5, 123.0, 129.7, 129.3, 129.2, 128.1, 125.8, 125.3, 125.2, 124.6, 121.8 (d, *J* = 8.8 Hz), 119.8, 117.1 (d, *J* = 21.4 Hz).116.7 (d, *J* = 23.9 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -113.3 (m).

23b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 8.53 (s, 1H), 8.19 (s, 1H), 7.95 – 7.91 (m, 1H), 7.73 – 7.68 (m, 1H), 7.53 – 7.28 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a, b and c**) δ 184.0, 184.0, 162.0 (d, *J* = 249.5 Hz), 153.1 (d, *J* = 249.5 Hz), 141.8, 141.7, 141.1, 134.6, 134.5, 123.0, 129.7, 129.3, 129.2, 128.1, 125.8, 125.3, 125.2, 124.6, 121.8 (d, *J* = 8.8 Hz), 119.8, 117.1 (d, *J* = 21.4 Hz).116.7 (d, *J* = 23.9 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -124.7 (m).

23c: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.97 (s, 1H), 8.44 (s, 1H), 8.17 (s, 1H), 7.73 – 7.68 (m, 1H), 7.53 – 7.28 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a, b and c**) δ 184.0, 184.0, 162.0 (d, *J* = 249.5 Hz), 153.1 (d, *J* = 249.5 Hz), 141.8, 141.7, 141.1, 134.6, 134.5, 123.0, 129.7, 129.3, 129.2, 128.1, 125.8, 125.3, 125.2, 124.6, 121.8 (d, *J* = 8.8 Hz), 119.8, 117.1 (d, *J* = 21.4 Hz).116.7 (d, *J* = 23.9 Hz). ^{19}F NMR (470 MHz, Chloroform-*d*) δ -124.7 (m).

MS (DART) exact mass: calculated for $(M+H)^{+}$: 191.0615; found: 191.0626.

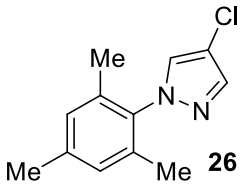


25

1-mesityl-1H-pyrazole **(25)**: The title compound was prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv.) and 1H-pyrazole (0.4 mmol, 27.2 mg) according to general procedure B with an irradiation/electrolysis time of 48 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a colorless oil in 80% yield (59.6 mg).

25: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.78 – 7.66 (m, 1H), 7.43 (d, *J* = 2.2 Hz, 1H), 6.94 (s, 2H), 6.43 (s, 1H), 2.33 (s, 3H), 1.97 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.0, 138.7, 137.0, 135.9, 130.8, 128.8, 105.7, 21.1, 17.2.

MS (DART) exact mass: calculated for $(M+H)^+$: 187.1235; found: 187.1239.

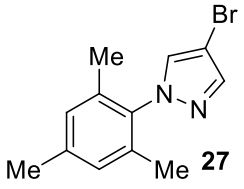


26

4-Chloro-1-mesityl-1H-pyrazole **(26)**: The title compound was prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv.) and 4-chloro-1H-pyrazole (0.4 mmol, 41.0 mg) according to general procedure B with an irradiation/electrolysis time of 48 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a colorless oil in 82% yield (72.4 mg).

26: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.42 (s, 1H), 6.94 (s, 2H), 2.33 (s, 3H), 1.98 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.3, 138.6, 136.5, 135.7, 128.9, 128.8, 110.4, 21.1, 17.2.

MS (DART) exact mass: calculated for $(M+H)^+$: 221.0840; found: 221.0852.

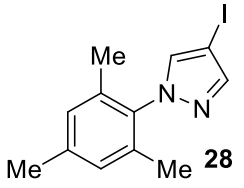


27

4-Bromo-1-mesityl-1H-pyrazole **(27)**: The title compound was prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv) and 4-bromo-1H-pyrazole (0.4 mmol, 58.8 mg) according to general procedure B with an irradiation/electrolysis time of 60 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a colorless oil in 69% yield (73.2 mg).

27: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (s, 1H), 7.45 (s, 1H), 6.94 (s, 2H), 2.33 (s, 3H), 1.98 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.7, 139.3, 136.5, 135.7, 131.0, 128.9, 93.5, 21.1, 17.2.

MS (DART) exact mass: calculated for $(M+H)^+$: 265.0335; found:265.0348.



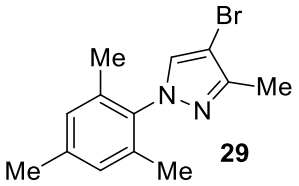
28

4-Iodo-1-mesityl-1H-pyrazole **(28)**: The title compound was prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv) and 4-iodo-1H-pyrazole (0.4 mmol, 77.6 mg) according to general procedure B with an

irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a colorless oil in 58% yield (72.4 mg).

28: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 (s, 1H), 7.50 (s, 1H), 6.96 (s, 2H), 2.35 (s, 3H), 1.99 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 145.2, 139.3, 136.3, 135.7, 135.2, 128.9, 56.6, 21.1, 17.2.

MS (DART) exact mass: calculated for $(M+H)^+$: 313.0196; found: 313.0211.

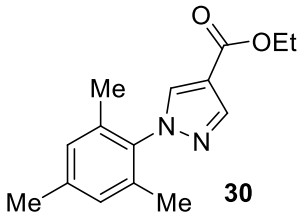


29

4-Bromo-1-mesityl-3-methyl-1H-pyrazole **(29)**: The title compound was prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv.) and 4-bromo-3-methyl-1H-pyrazole (0.4 mmol, 64.4 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 15% EtOAc/hexanes to yield a light yellow oil in 83% yield (92.7 mg).

29: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.39 (s, 1H), 6.94 (s, 2H), 2.34 (m, 6H), 2.01 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.0, 139.0, 136.6, 135.8, 131.3, 128.8, 94.2, 21.1, 17.3, 12.1.

MS (DART) exact mass: calculated for $(M+H)^+$: 279.0491; found: 279.0506.

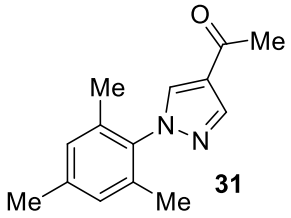


30

ethyl 1-mesityl-1H-pyrazole-4-carboxylate **(30)**: The title compound was prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv) and ethyl 1H-pyrazole-4-carboxylate (0.4 mmol, 56.0 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 15% EtOAc/hexanes to yield a light yellow oil in 71% yield (73.4 mg).

30: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.11 (s, 1H), 7.92 (s, 1H), 6.94 (s, 2H), 4.32 (q, J = 7.1 Hz, 2H), 2.32 (s, 3H), 1.97 (s, 6H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 163.2, 141.6, 139.4, 136.1, 135.4, 134.5, 128.9, 115.6, 60.3, 21.1, 17.2, 14.4.

MS (DART) exact mass: calculated for $(M+H)^+$: 259.1441; found: 259.1454.

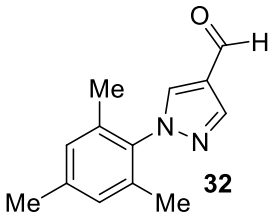


31

1-(1-mesityl-1H-pyrazol-4-yl)ethanone **(31)**: The title compound was prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv.) and 1-(1H-pyrazol-4-yl)ethanone (0.4 mmol, 44.0 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 15% EtOAc/hexanes to yield a light yellow oil in 75% yield (68.5 mg).

31: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.92 (s, 1H), 6.95 (s, 2H), 2.48 (s, 3H), 2.32 (s, 3H), 1.97 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.3, 141.0, 139.6, 136.0, 135.3, 133.7, 129.0, 124.5, 28.0, 21.1, 17.2.

MS (DART) exact mass: calculated for $(M+H)^+$: 229.1335; found: 229.1349.

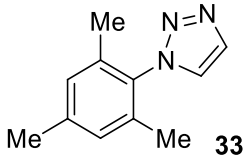


32

1-mesityl-1H-pyrazole-4-carbaldehyde **(32)**: The title compound was prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv.) and 1H-pyrazole-4-carbaldehyde (0.4 mmol, 38.4 mg) according to general procedure B with an irradiation/electrolysis time of 60 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a colorless oil in 67% yield (57.4 mg).

32: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.97 (d, J = 1.8 Hz, 1H), 8.19 (s, 1H), 7.99 (d, J = 2.2 Hz, 1H), 6.98 (s, 2H), 2.35 (s, 3H), 2.00 (d, J = 2.3 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 184.2, 141.2, 139.8, 135.9, 135.2, 134.7, 129.1, 124.7, 21.1, 17.2.

MS (DART) exact mass: calculated for $(M+H)^+$: 215.1179; found: 215.1191.



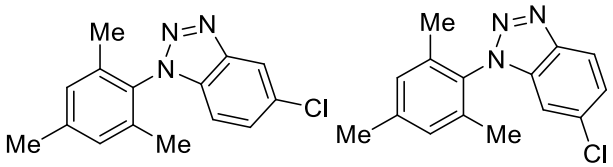
33

1-mesityl-1H-1,2,3-triazole **(33)**: The title compound was prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv.) and 1H-1,2,3-triazole (0.4 mmol, 27.6 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on

silica gel with an eluent of hexanes to 15% EtOAc/hexanes to yield a light yellow oil in 65% yield (48.7 mg).

33: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 1.0 Hz, 1H), 7.62 (d, *J* = 1.0 Hz, 1H), 6.99 (s, 2H), 2.35 (s, 3H), 1.94 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 140.1, 135.1, 133.5, 129.1, 125.5, 21.1, 17.2.

MS (DART) exact mass: calculated for $(M+H)^+$: 188.1182; found:118.1192.



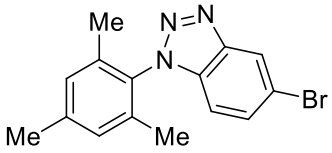
34a **34b**

5-chloro-1-mesityl-1H-benzo[d][1,2,3]triazole **(34a) and 6-chloro-1-mesityl-1H-benzo[d][1,2,3]triazole (34b):** The title compounds were prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv.) and 5-chloro-1H-benzo[d][1,2,3]triazole (0.4 mmol, 61.4 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 30% EtOAc/hexanes to yield a light yellow oil in 51% yield (55.4 mg). The ratio of the mixture was 1:1 (***a*:*b***) as determined by ^{1}H NMR of reaction solution.

34a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.13 (d, *J* = 1.9 Hz, 1H), 7.44 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.06 (s, 2H), 2.40 (s, 3H), 1.85 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 146.1, 144.1, 140.6, 140.6, 136.1, 136.1, 134.5, 132.6, 131.1, 130.0, 129.5, 129.43, 129.0, 125.3, 121.1, 119.5, 110.7, 109.5, 21.2, 17.4, 17.3.

34b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.5 Hz, 1H), 7.38 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.20 (d, *J* = 2.0 Hz, 1H), 7.06 (s, 2H), 2.40 (s, 3H), 1.87 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 146.1, 144.1, 140.6, 140.6, 136.1, 136.1, 134.5, 132.6, 131.1, 130.0, 129.5, 129.43, 129.0, 125.3, 121.1, 119.5, 110.7, 109.5, 21.2, 17.4, 17.3.

MS (DART) exact mass: calculated for $(M+H)^+$: 272.0949; found: 272.0961.

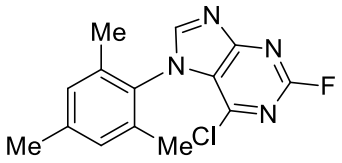


35

5-bromo-1-mesityl-1H-benzo[d][1,2,3]triazole **(35):** The title compound was prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv.) and 5-bromo-1H-benzo[d][1,2,3]triazole (0.4 mmol, 79.2 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 30% EtOAc/hexanes to yield a white solid in 75% yield (94.9 mg). The ratio of the mixture was 1:1 (***a*:*b***) as determined by ^{1}H NMR of reaction solution.

35: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.32 (d, *J* = 1.6 Hz, 1H), 7.57 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 1H), 7.06 (s, 2H), 2.40 (s, 3H), 1.86 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.7, 140.6, 136.1, 132.9, 131.4, 131.2, 129.4, 122.8, 117.3, 111.1, 21.2, 17.3.

MS (DART) exact mass: calculated for $(M+H)^+$:316.0444; found: 316.0462.

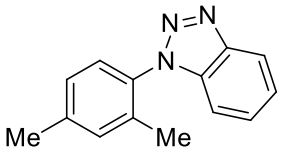


36

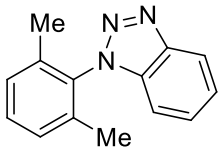
***6-chloro-2-fluoro-7-mesityl-7H-purine* (36)**: The title compound was prepared from mesitylene (1.4 mmol, 195 µL, 3.5 equiv.) and 6-chloro-2-fluoro-7H-purine (0.4 mmol, 69.0 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 30% EtOAc/hexanes to yield a light yellow solid in 50% yield (58.1 mg).

36: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.04 (s, 2H), 2.36 (s, 3H), 1.95 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.2 (d, *J* = 221.8 Hz), 153.8 (d, *J* = 16.4 Hz), 153.2 (d, *J* = 16.4 Hz), 146.4 (d, *J* = 3.8 Hz), 140.7, 135.5, 130.0 (d, *J* = 5.0 Hz), 129.7, 128.4, 21.2, 17.7. ^{19}F NMR (470 MHz, Chloroform-*d*) δ -48.55.

MS (DART) exact mass: calculated for $(M+H)^+$: 291.0807; found: 291.0822.



37a



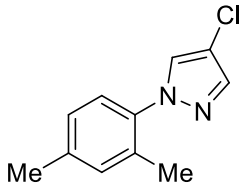
37b

1-(2,4-dimethylphenyl)-1H-benzo[d][1,2,3]triazole* (37a) and 1-(2,6-dimethylphenyl)-1H-benzo[d][1,2,3]triazole (37b):** The title compounds were prepared from m-xylene (2.0 mL) and 1H-benzo[d][1,2,3]triazole (0.4 mmol, 47.6 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 20% EtOAc/hexanes to yield a light yellow solid in 82% yield (73.2 mg). The ratio of the mixture was 6:1 (a*:*b***) as determined by ^{1}H NMR of reaction solution.

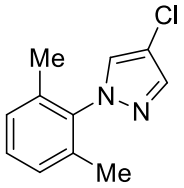
37a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.59 – 7.45 (m, 1H), 7.42 – 7.39 (m, 1H), 7.34 – 7.32 (m, 1H), 7.27 – 7.25 (m, 2H), 7.20 – 7.18 (m, 1H), 2.44 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 145.6, 140.2, 134.9, 134.0, 132.7, 132.3, 127.9, 127.6, 126.7, 124.1, 120.0, 110.2, 21.3, 17.7.

37b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.17 – 8.13 (m, 1H), 7.59 – 7.45 (m, 1H), 7.42 – 7.39 (m, 1H), 7.34 – 7.32 (m, 1H), 7.27 – 7.25 (m, 2H), 7.20 – 7.18 (m, 1H), 1.91 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 145.6, 140.2, 134.9, 134.0, 132.7, 132.3, 127.9, 127.6, 126.7, 124.1, 120.0, 110.2, 21.3, 17.7.

MS (DART) exact mass: calculated for $(M+H)^+$: 224.1182; found: 224.1193.



38a



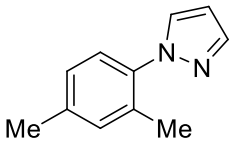
38b

4-chloro-1-(2,4-dimethylphenyl)-1H-pyrazole **(38a) and 4-chloro-1-(2,6-dimethylphenyl)-1H-pyrazole (38b):** The title compounds were prepared from m-xylene (2.0 mL) and 4-chloro-1H-pyrazole (0.4 mmol, 41.0 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a light yellow oil in 87% yield (71.9 mg). The ratio of the mixture was 10:1 (***a*:*b***) as determined by ^{1}H NMR of reaction solution.

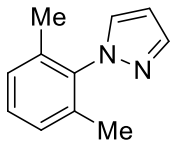
38a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.64 (s, 1H), 7.58 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 1.9 Hz, 1H), 7.10 (dd, *J* = 7.9, 2.0 Hz, 1H), 2.39 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 138.9, 138.6, 137.2, 133.4, 132.0, 128.5, 127.3, 125.9, 110.7, 21.1, 17.8.

38b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 9.0 Hz, 1H), 7.46 (d, *J* = 14.5 Hz, 1H), 7.20 – 7.09 (m, 2H), 6.97 – 6.97 (m, 1H), 2.01 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 138.9, 138.6, 137.2, 133.4, 132.0, 128.5, 127.3, 125.9, 110.7, 21.1, 17.8.

MS (DART) exact mass: calculated for $(M+H)^+$: 207.0684; found: 207.0695.



39a



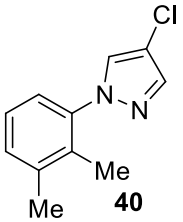
39b

1-(2,4-dimethylphenyl)-1H-pyrazole **(39a) and 1-(2,6-dimethylphenyl)-1H-pyrazole (39b):** The title compounds were prepared from m-xylene (2.0 mL) and 1H-pyrazole (0.4 mmol, 27.2 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a light yellow oil in 71% (48.9 mg). The ratio of the mixture was 11:1 (***a*:*b***) as determined by ^{1}H NMR of reaction solution.

39a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.59 – 7.58 (m, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.14 (s, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 6.44 – 6.44 (m, 1H), 2.39 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 140.1, 138.3, 137.7, 133.5, 131.8, 130.6, 127.1, 126.0, 106.0, 21.1, 17.9.

39b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.48 – 7.47 (m, 1H), 7.24 – 7.09 (m, 3H), 6.47 (s, 1H), 2.03 (s, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 140.1, 138.3, 137.7, 133.5, 131.8, 130.6, 127.1, 126.0, 106.0, 21.1, 17.9.

MS (DART) exact mass: calculated for $(M+H)^+$: 173.1073; found: 173.1083.

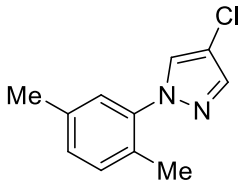


40

4-chloro-1-(2,3-dimethylphenyl)-1H-pyrazole **(40)**: The title compound was prepared from *o*-xylene (2.0 mL) and 4-chloro-1H-pyrazole (0.4 mmol, 41.0 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a colorless oil in 61% yield (50.4 mg).

40: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.64 (s, 1H), 7.45 (d, *J* = 2.4 Hz, 1H), 7.34 (dd, *J* = 8.1, 2.5 Hz, 1H), 7.22 (d, *J* = 8.1 Hz, 1H), 2.34 (2, 3H), 2.31 (2, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.1, 138.1, 137.8, 135.6, 130.5, 124.8, 120.4, 116.3, 111.9, 20.0, 19.3.

MS (DART) exact mass: calculated for $(M+H)^+$: 207.0684; found: 207.0694.

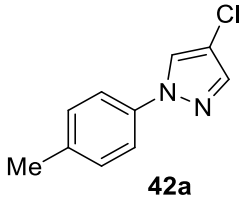


41

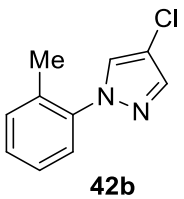
4-chloro-1-(2,5-dimethylphenyl)-1H-pyrazole **(41)**: The title compound was prepared from *p*-xylene (2.0 mL) and 4-chloro-1H-pyrazole (0.4 mmol, 41.0 mg) according to general procedure B with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a colorless oil in 56% yield (46.3 mg).

41: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.63 (s, 1H), 7.58 (s, 1H), 7.20 – 7.18 (m, 1H), 7.16 – 7.10 (m, 2H), 2.35 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 139.3, 138.7, 136.6, 131.2, 130.2, 129.6, 128.4, 126.5, 110.8, 20.7, 17.5.

MS (DART) exact mass: calculated for $(M+H)^+$: 207.0684; found: 207.0696.



42a



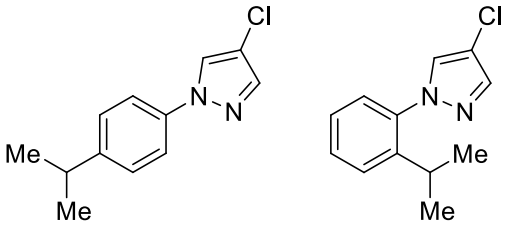
42b

4-chloro-1-(p-tolyl)-1H-pyrazole **(42a) and** ***4-chloro-1-(o-tolyl)-1H-pyrazole*** **(42b)**: The title compounds were prepared from toluene (2.0 mL) and 4-chloro-1H-pyrazole (0.4 mmol, 41.0 mg) according to general procedure A with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a colorless oil in 55% yield (42.4 mg). The ratio of the mixture was 7:1 (*p*:*o*) as determined by ^{1}H NMR of reaction solution.

42a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.64 (s, 1H), 7.57 – 7.49 (m, 2H), 7.28 – 7.26 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 139.3, 139.2, 137.6, 137.0, 130.1, 129.3, 127.81, 124.8, 119.8, 119.0, 112.1, 21.5, 21.0.

42b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.65 (s, 1H), 7.57 – 7.49 (m, 1H), 7.44 – 7.41 (m, 1H), 7.37 – 7.34 (m, 1H), 7.16 – 7.14 (m, 1H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 139.3, 139.2, 137.6, 137.0, 130.1, 129.3, 127.81, 124.8, 119.8, 119.0, 112.1, 21.5, 21.0.

MS (DART) exact mass: calculated for $(M+H)^{+}$:193.0527; found:193.0539.



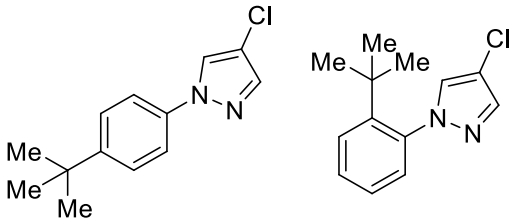
43a **43b**

4-chloro-1-(4-isopropylphenyl)-1H-pyrazole **(43a) and** ***4-chloro-1-(2-isopropylphenyl)-1H-pyrazole*** **(43b)**: The title compounds were prepared from cumene (2.0 mL) and 4-chloro-1H-pyrazole (0.4 mmol, 41.0 mg) according to general procedure A with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a colorless oil in 45% (39.7 mg). The ratio of the mixture was 6:1 (*p*:*o*) as determined by ^{1}H NMR of reaction solution.

43a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.65 (s, 1H), 7.57 – 7.55 (m, 2H), 7.34 – 7.32 (m, 2H), 3.02 – 2.93 (m, 1H), 1.30 (d, J = 7.2 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 148.0, 139.3, 139.2, 137.8, 129.4, 128.3, 127.5, 126.4, 124.8, 119.1, 116.5, 112.0, 34.2, 33.7, 24.0.

43b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.66 (s, 1H), 7.46 – 7.39 (m, 3H), 7.28 – 7.20 (m, 1H), 3.02 – 2.93 (m, 1H), 1.30 – 1.27 (m, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 148.0, 139.3, 139.2, 137.8, 129.4, 128.3, 127.5, 126.4, 124.8, 119.1, 116.5, 112.0, 34.2, 33.7, 24.0.

MS (DART) exact mass: calculated for $(M+H)^{+}$: 221.0840; found: 221.0852.



44a **44b**

1-(4-(tert-butyl)phenyl)-4-chloro-1H-pyrazole **(44a) and** ***1-(2-(tert-butyl)phenyl)-4-chloro-1H-pyrazole*** **(44b)**: The title compounds were prepared from tert-butylbenzene (2.0 mL) and 4-chloro-1H-pyrazole (0.4 mmol, 41.0 mg) according to general procedure A with an irradiation/electrolysis time of 72 hours. The crude residue was purified by column chromatography on silica gel with an eluent of hexanes to 10% EtOAc/hexanes to yield a colorless oil in 62% yield (58.2 mg). The ratio of the mixture was 4:1 (*p*:*o*) as determined by ^{1}H NMR of reaction solution.

44a: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.65 (s, 1H), 7.58 – 7.56 (m, 2H), 7.50 – 7.48 (m, 2H), 1.37 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 153.2, 150.2, 139.2, 137.8, 137.4, 130.4, 130.2, 129.2, 126.4, 125.1, 124.8, 124.2, 118.7, 116.5, 116.3, 112.1, 34.6, 31.4, 31.3, 31.3.

44b: ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (s, 1H), 7.70 (s, 1H), 7.76 – 7.76 (m, 1H), 7.42 – 7.40 (m, 2H), 7.29 – 7.28 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (126 MHz, Chloroform-*d*, mixture of **a and b**) δ 153.2, 150.2, 139.2, 137.8, 137.4, 130.4, 130.2, 129.2, 126.4, 125.1, 124.8, 124.2, 118.7, 116.5, 116.3, 112.1, 34.6, 31.4, 31.3, 31.3.

MS (DART) exact mass: calculated for $(M+H)^{+}$:235.0997; found: 235.1008.

14. References

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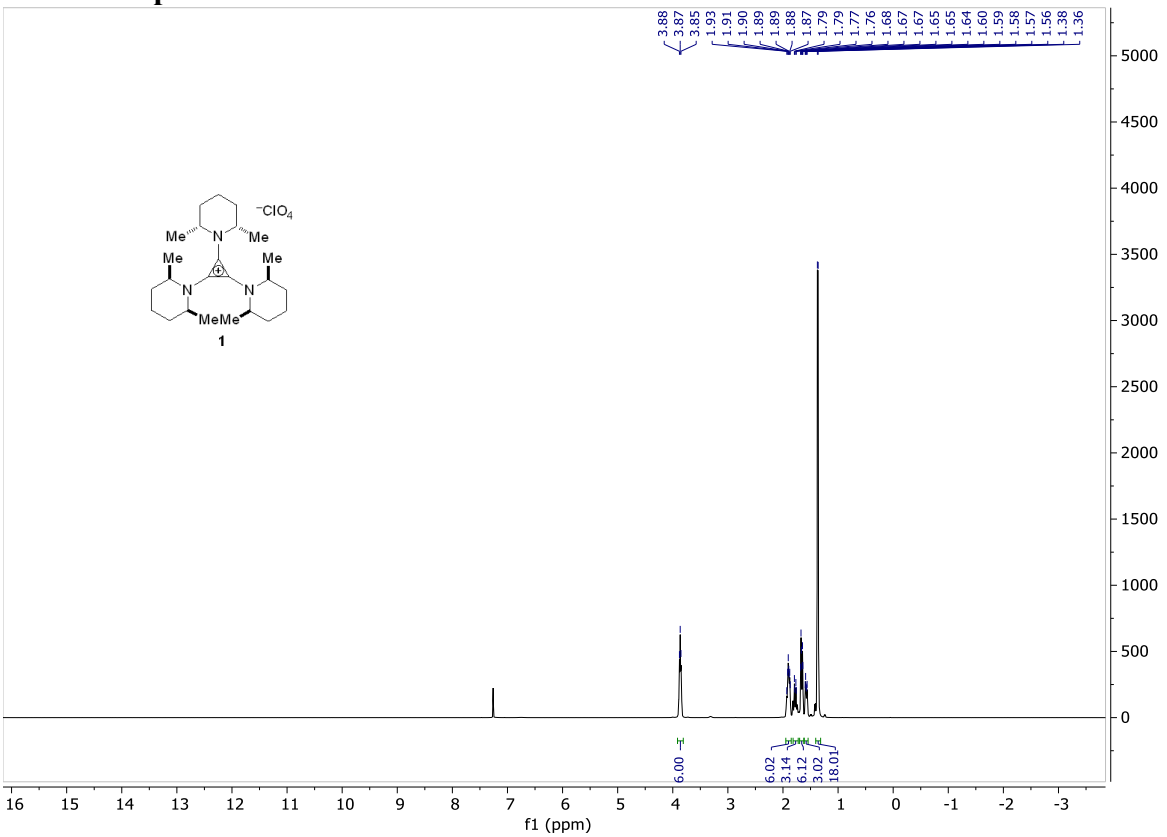
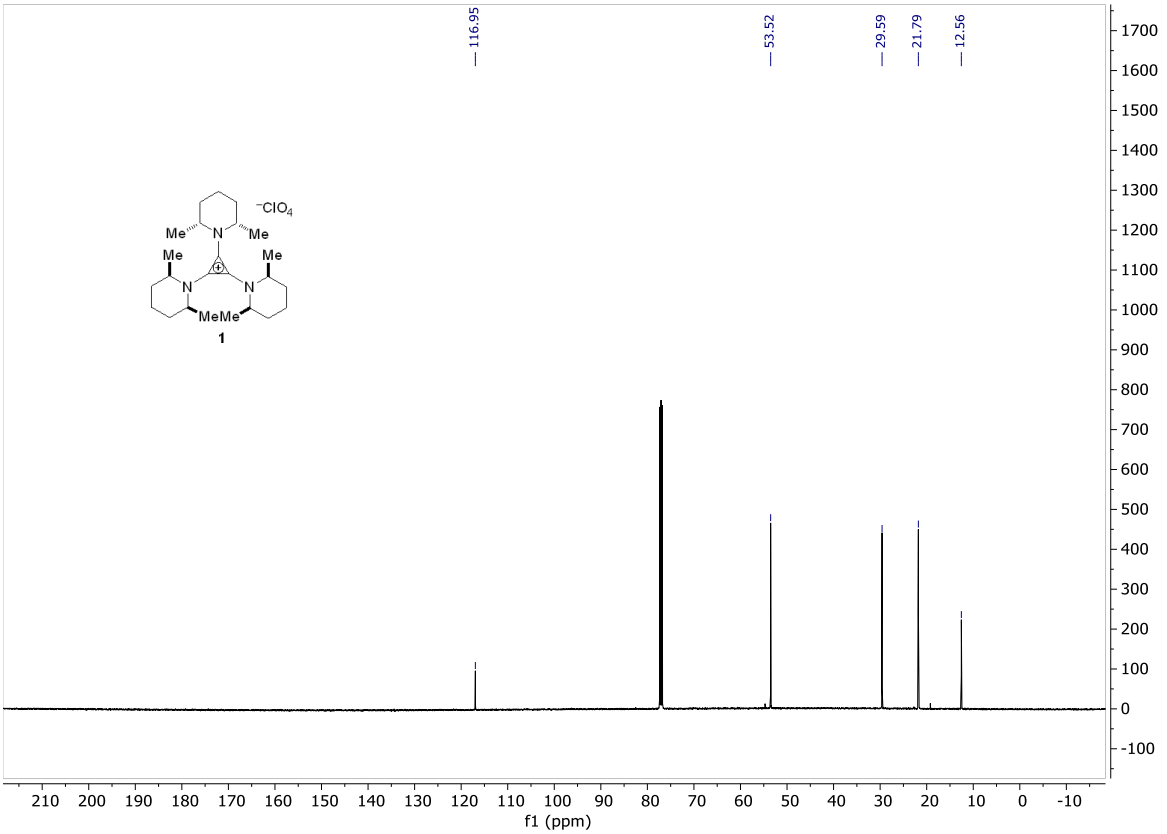
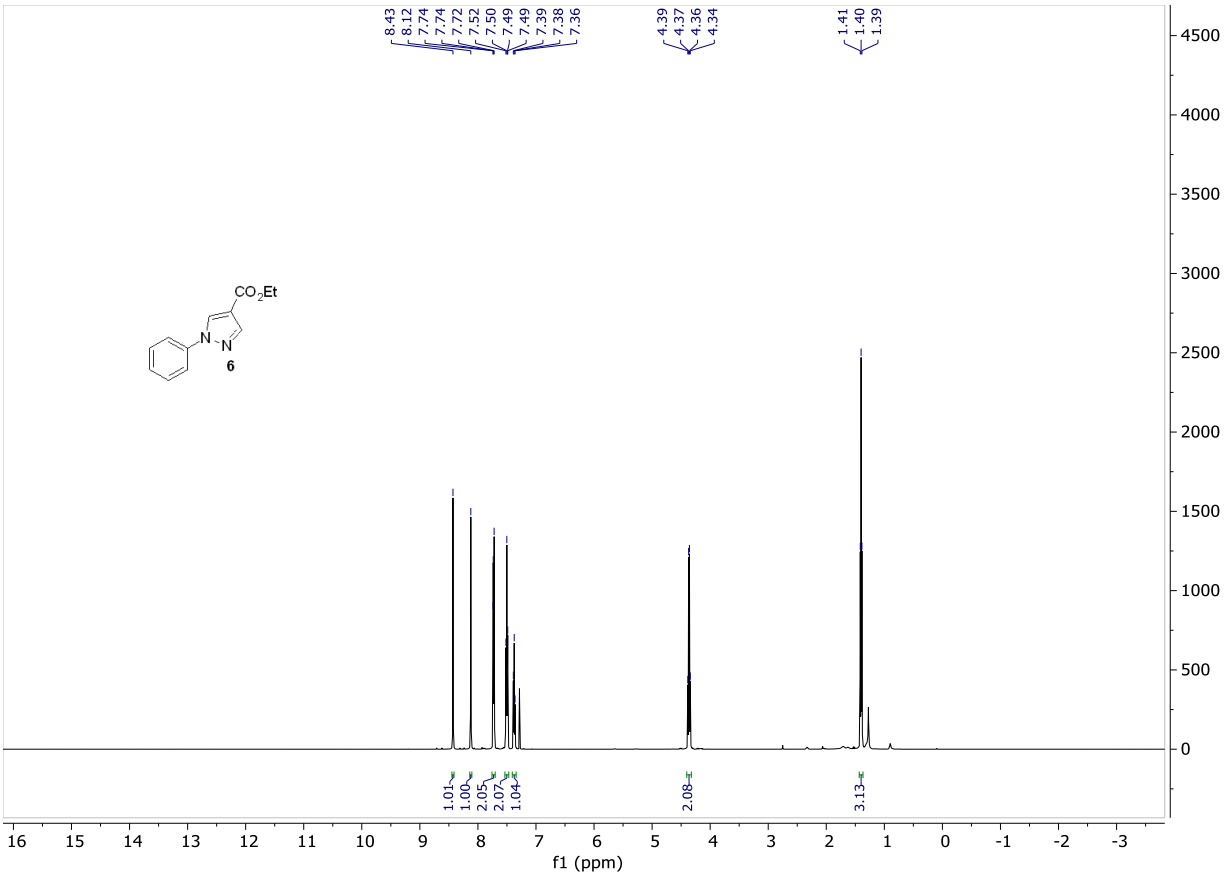
15. NMR Spectral Data



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4.37
4.36
4.34
1.41
1.40
1.39
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1.01
1.00
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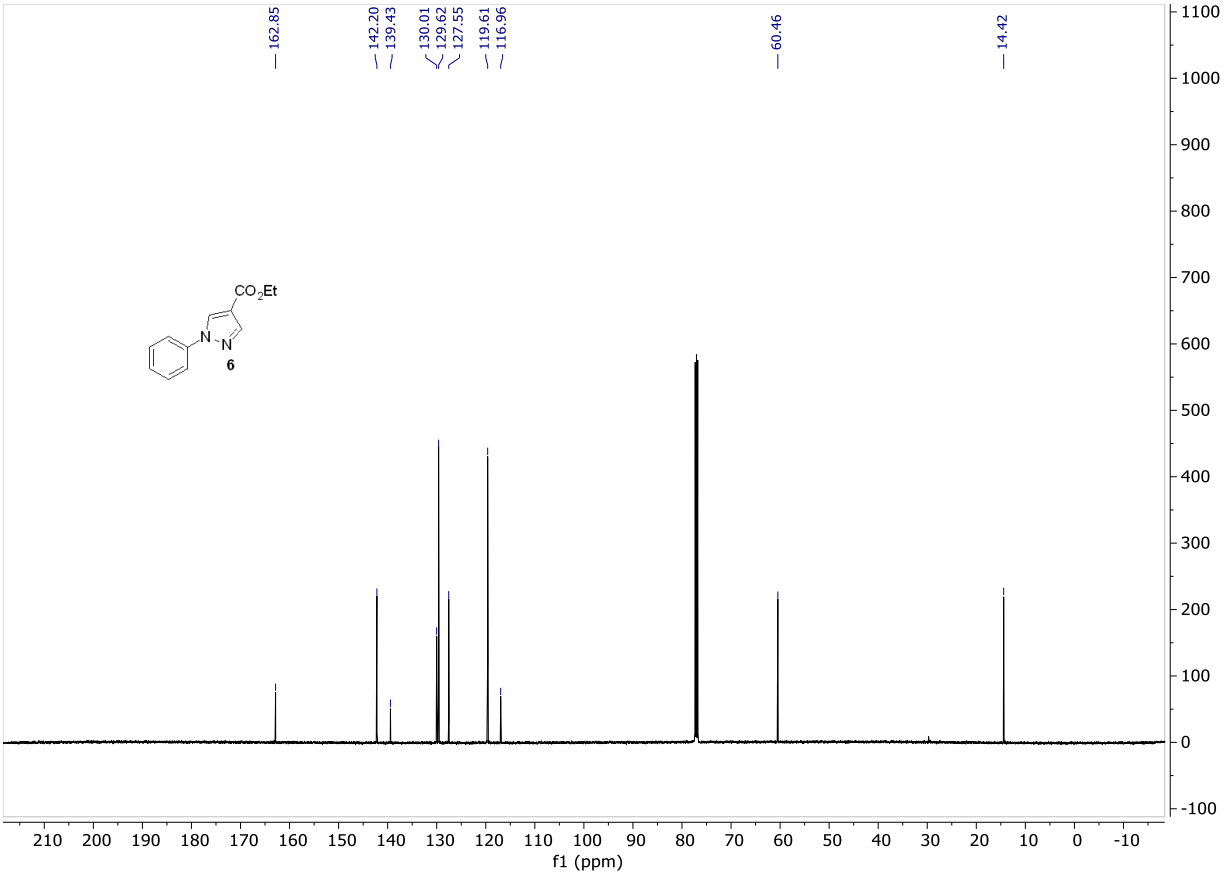
2.07
1.04
2.08
3.13
f1 (ppm)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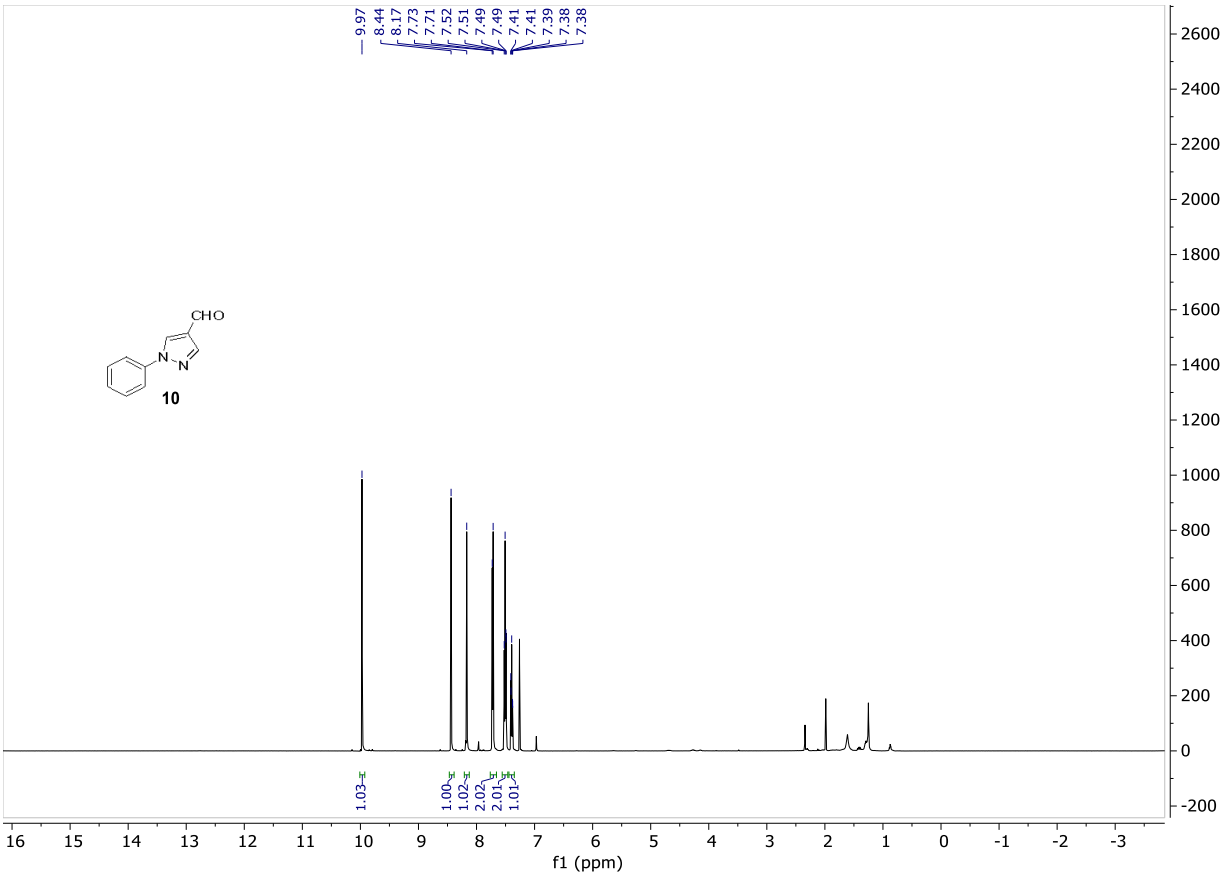
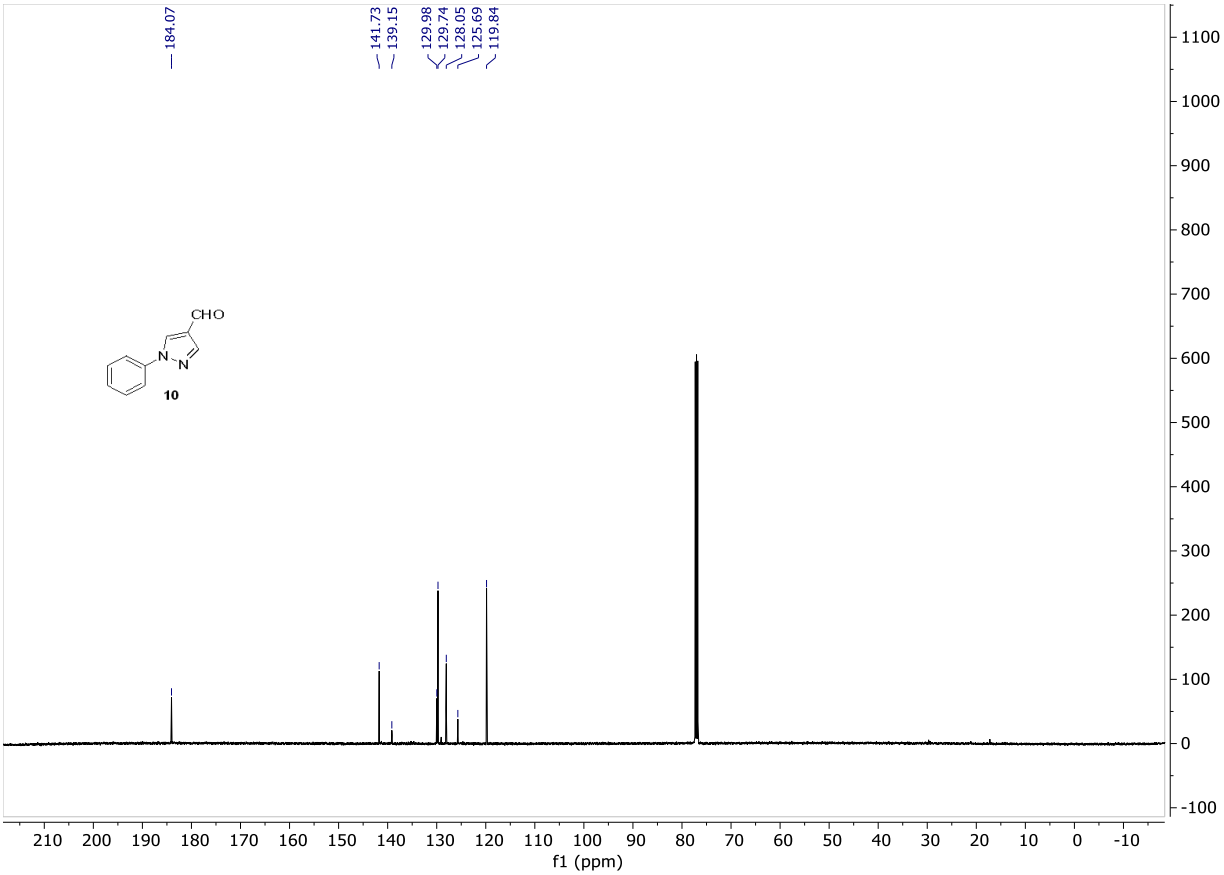
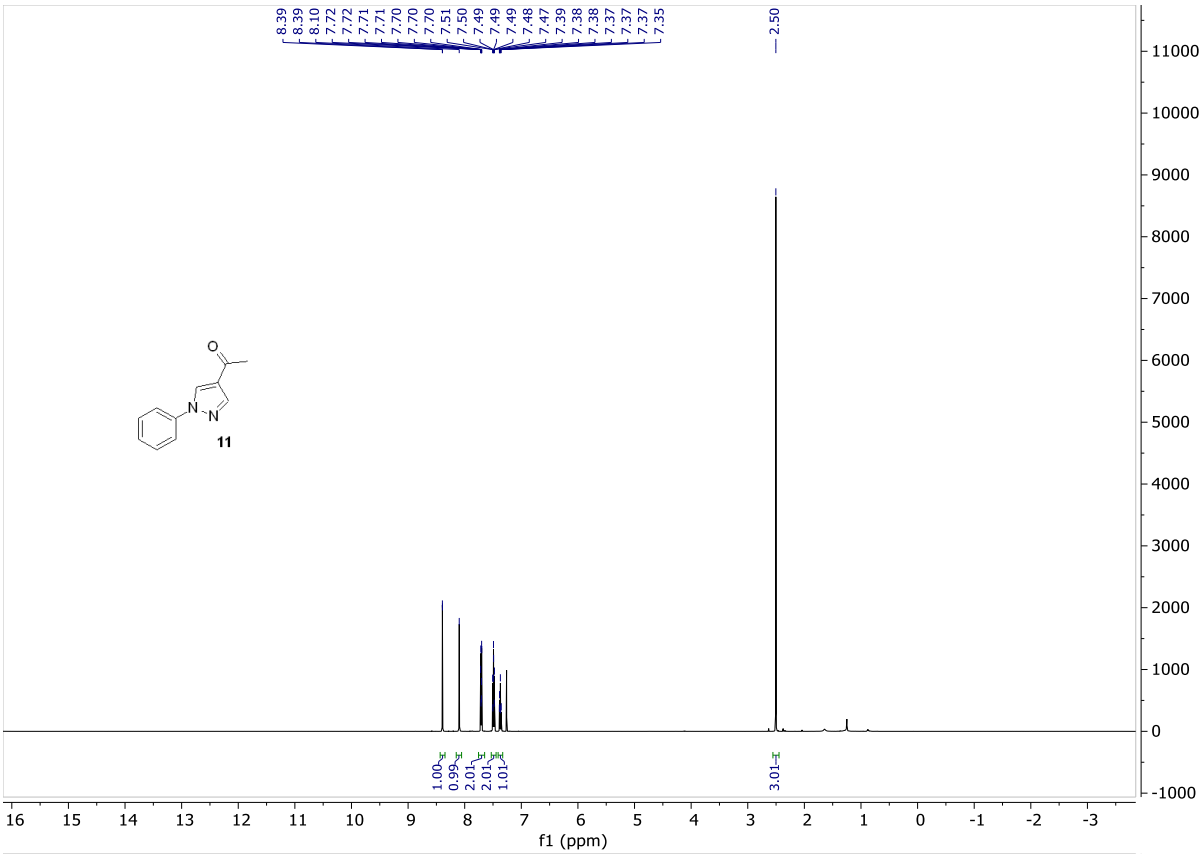
14.42
CO2Et
N
N
6
f1 (ppm)


9.97
8.44
8.17
7.73
7.71
7.52
7.51
7.49
7.49
7.41
7.41
7.39
7.38
7.38
CHO
10
1.03
1.00
1.02
2.02
2.01
1.01
f1 (ppm)


184.07
141.73
139.15
129.98
129.74
128.05
125.69
119.84
CHO
10
f1 (ppm)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8.39
8.10
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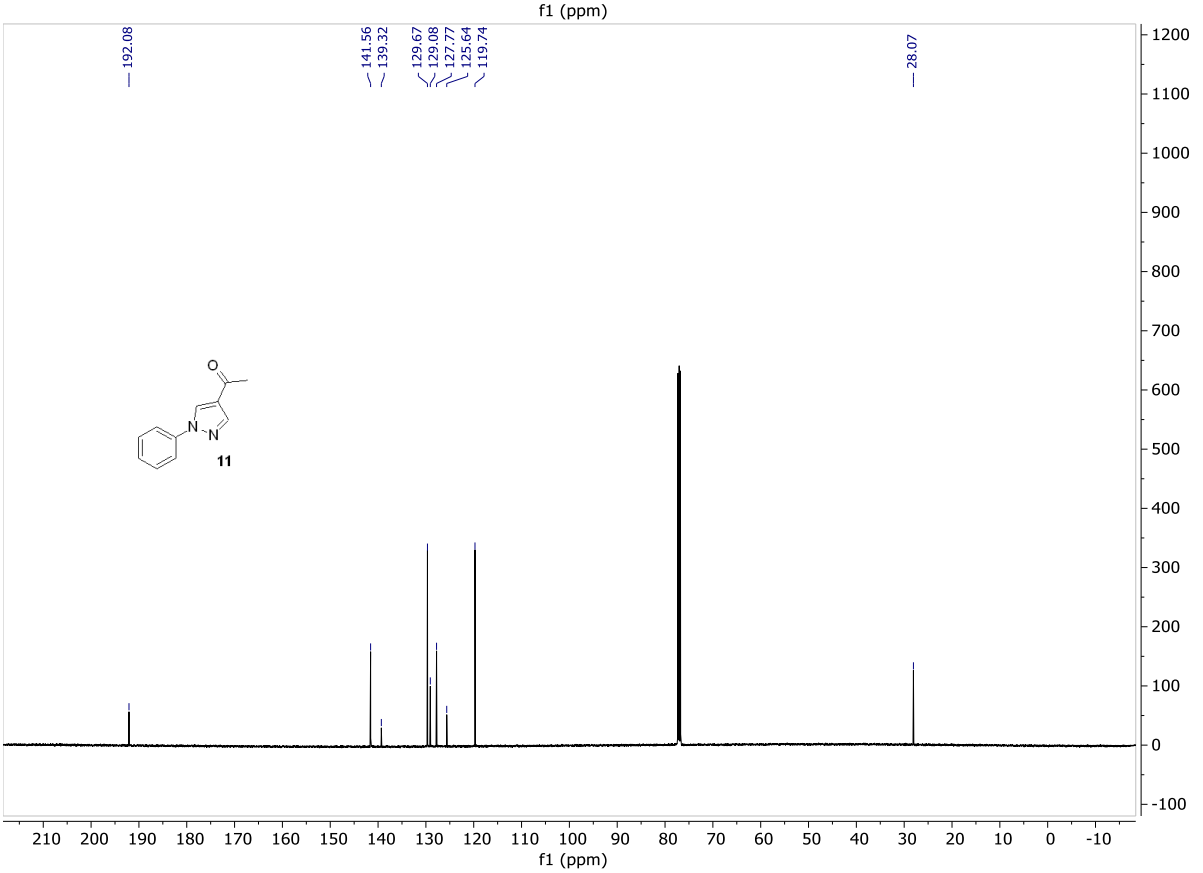
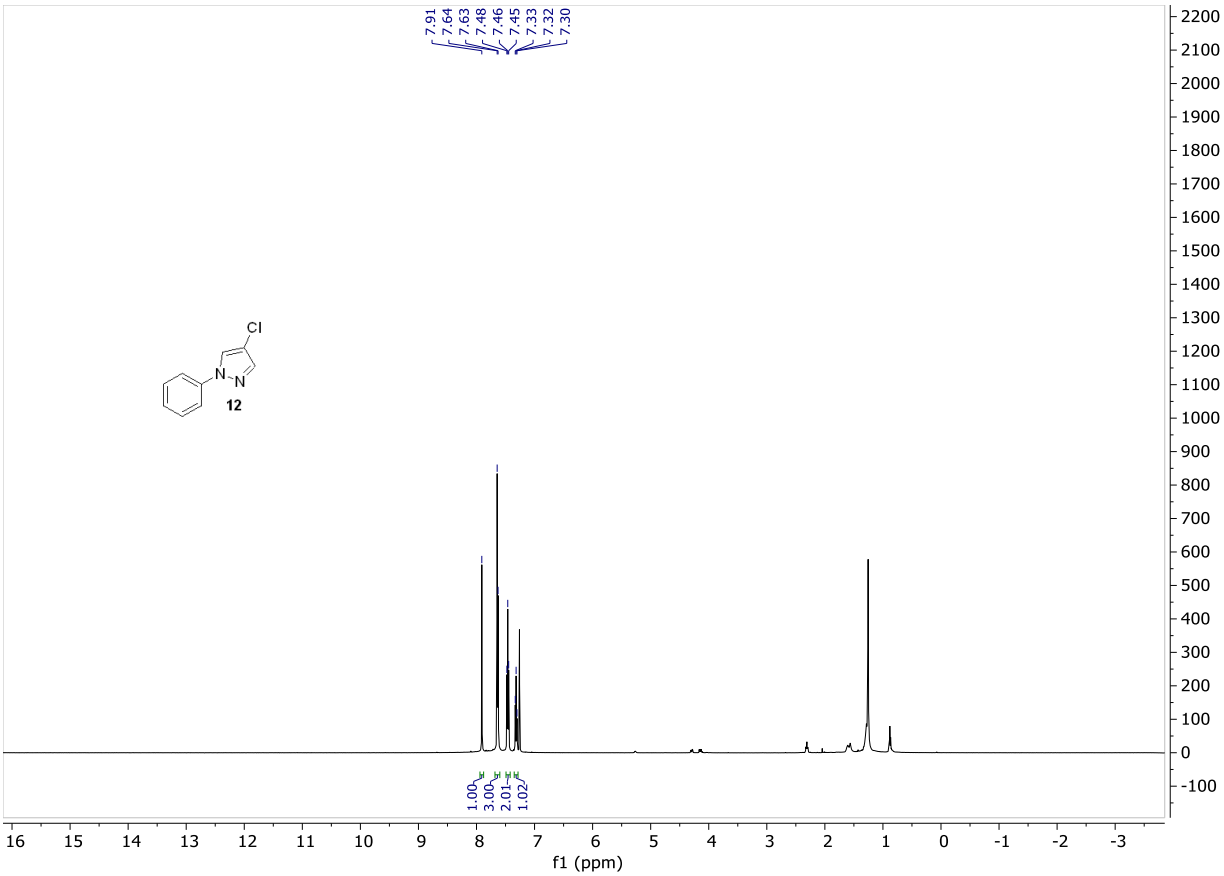
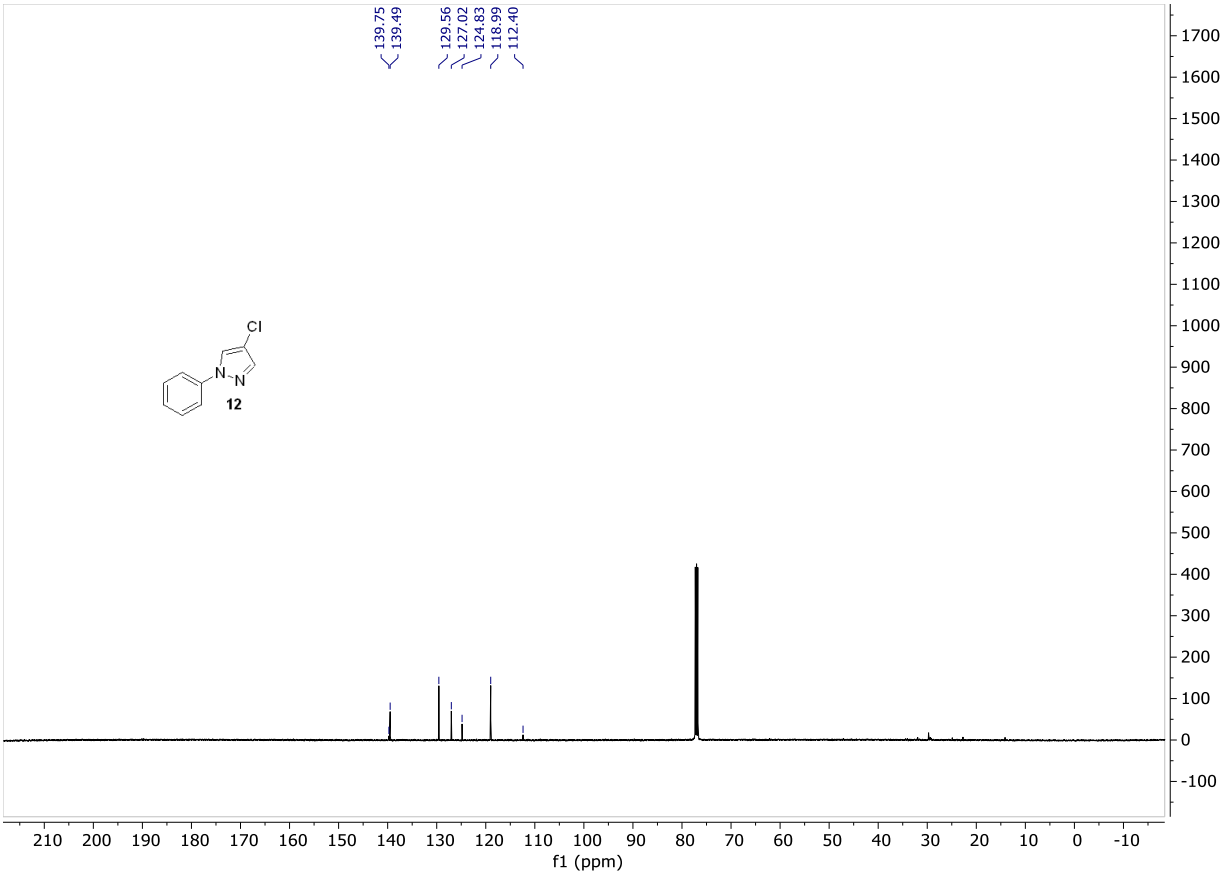
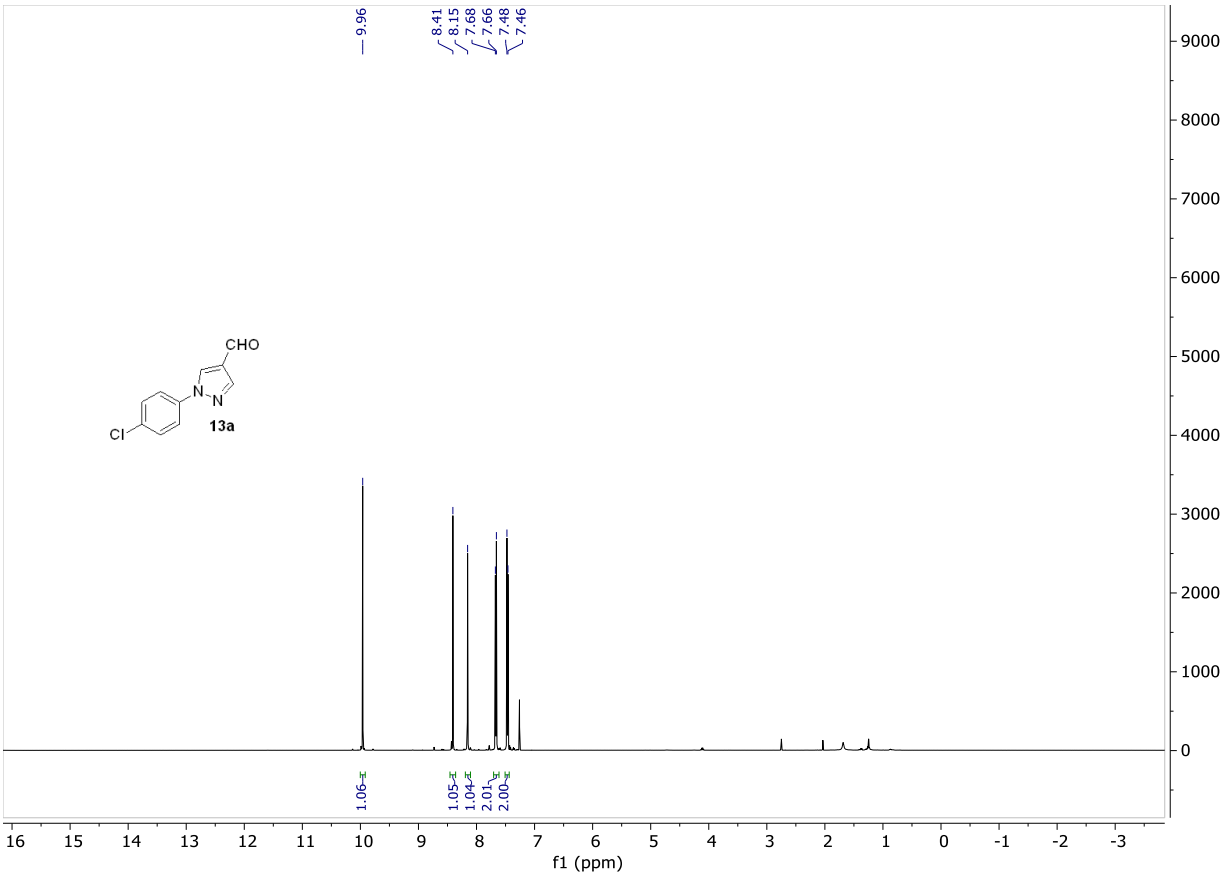
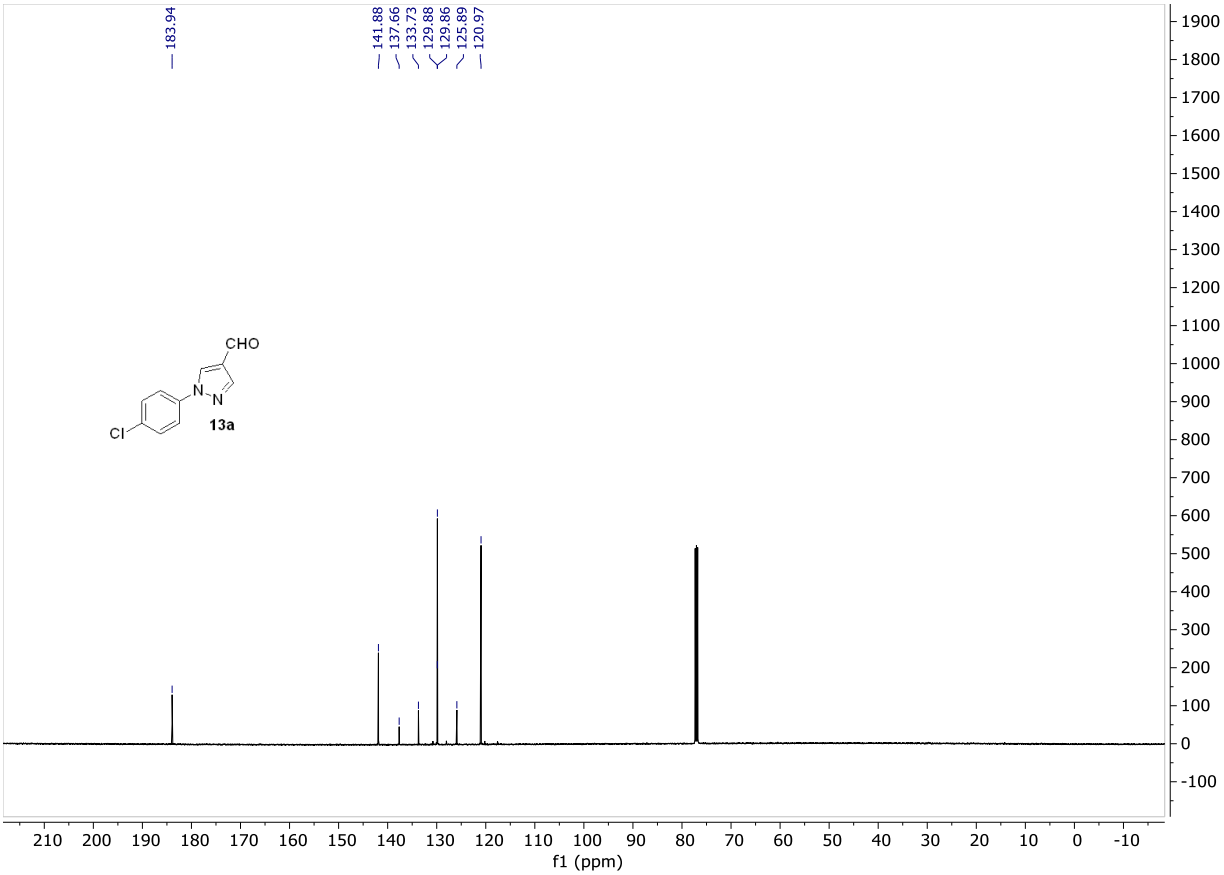
7.72
7.71
7.71
7.70
7.70
7.70
7.51
7.50
7.49
7.49
7.49
7.48
7.47
7.39
7.38
7.38
7.37
7.37
7.37
7.35
2.50
11
1.00
0.99
2.01
2.01
1.01
3.01
f1 (ppm)


192.08
141.56
139.32
129.67
129.08
127.77
125.64
119.74
28.07
11
f1 (ppm)


7.91
7.64
7.63
7.48
7.46
7.45
7.33
7.32
7.30
Cl
N
N
12
1.00
3.00
2.01
1.02
f1 (ppm)


139.75
139.49
129.56
127.02
124.83
118.99
112.40
Cl
N
N
12
f1 (ppm)


9.96
8.41
8.15
7.68
7.66
7.48
7.46
CHO
N
N
Cl
13a
1.06
1.05
1.04
2.01
2.00
f1 (ppm)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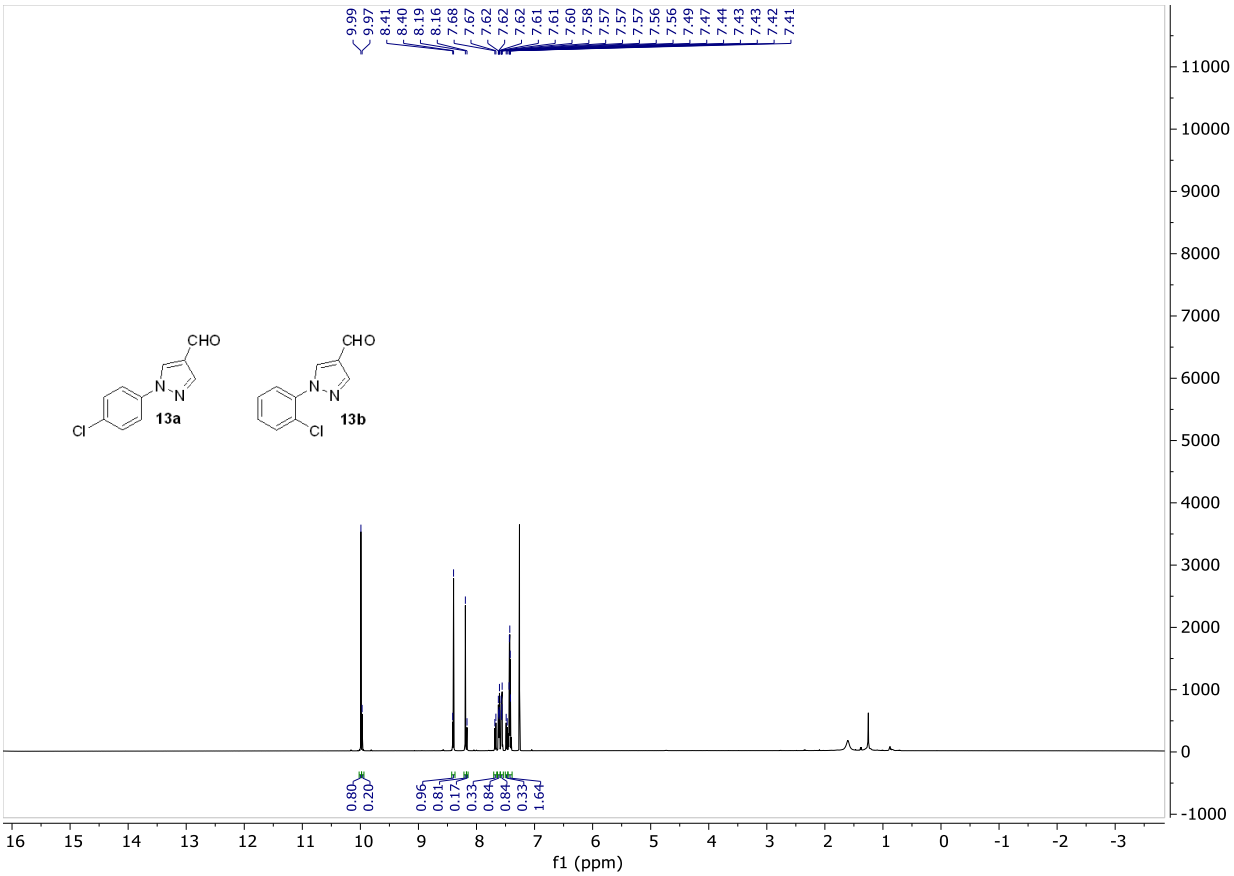
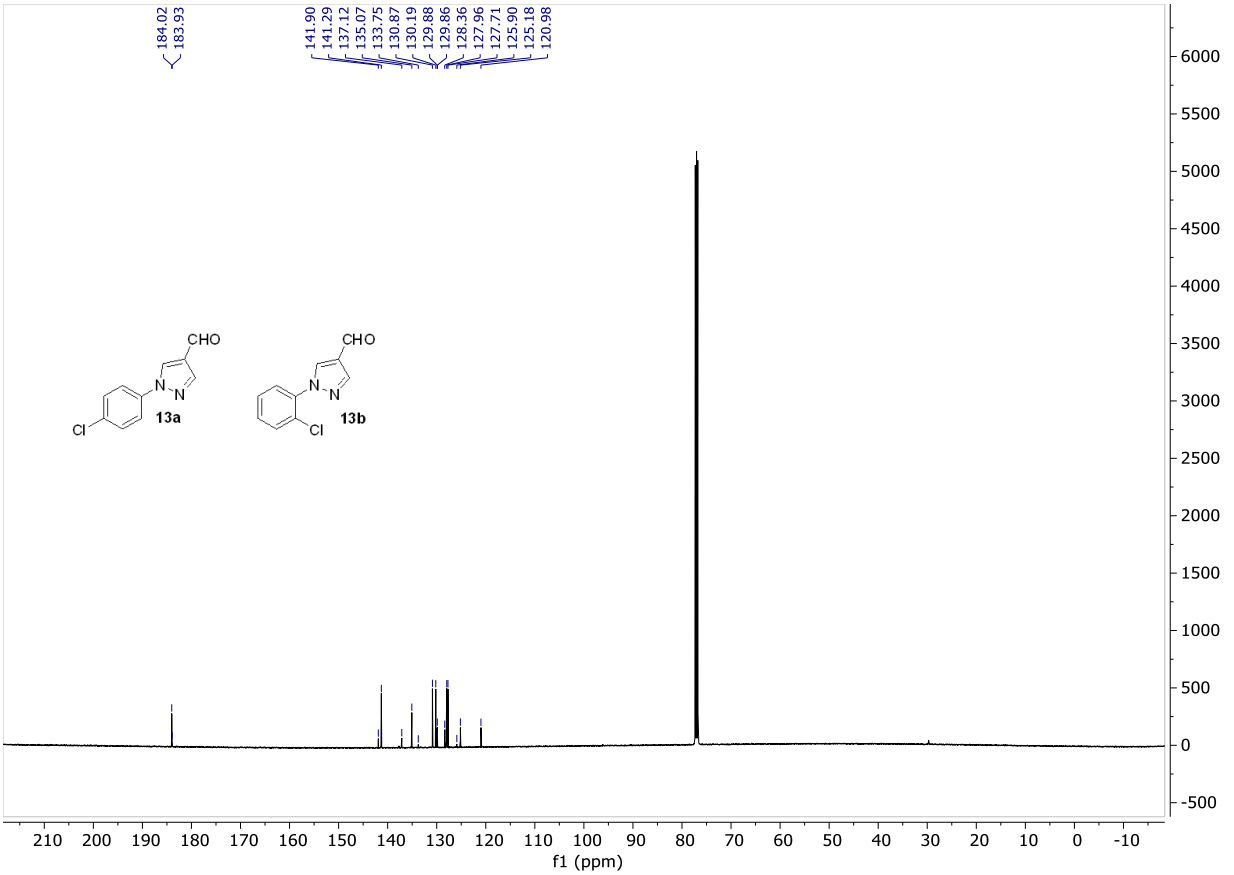
129.88
129.86
125.89
120.97
CHO
N
N
Cl
13a
f1 (ppm)


9.99
9.97
8.41
8.40
8.19
8.16
7.68
7.67
7.62
7.62
7.62
7.61
7.61
7.60
7.58
7.57
7.57
7.57
7.56
7.56
7.49
7.47
7.44
7.43
7.43
7.42
7.41
CHO
13a
CHO
13b
0.80
0.20
0.96
0.81
0.17
0.33
0.84
0.84
0.33
1.64
f1 (ppm)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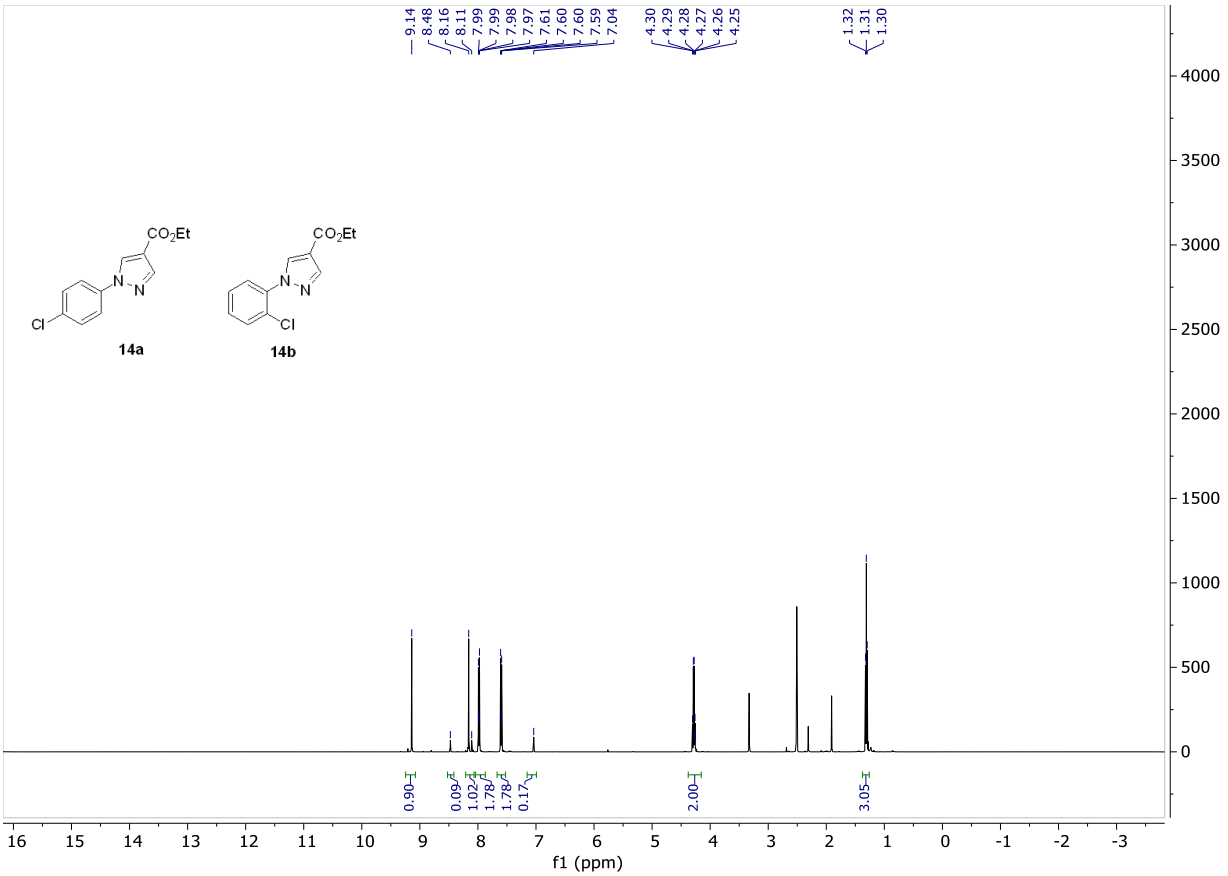
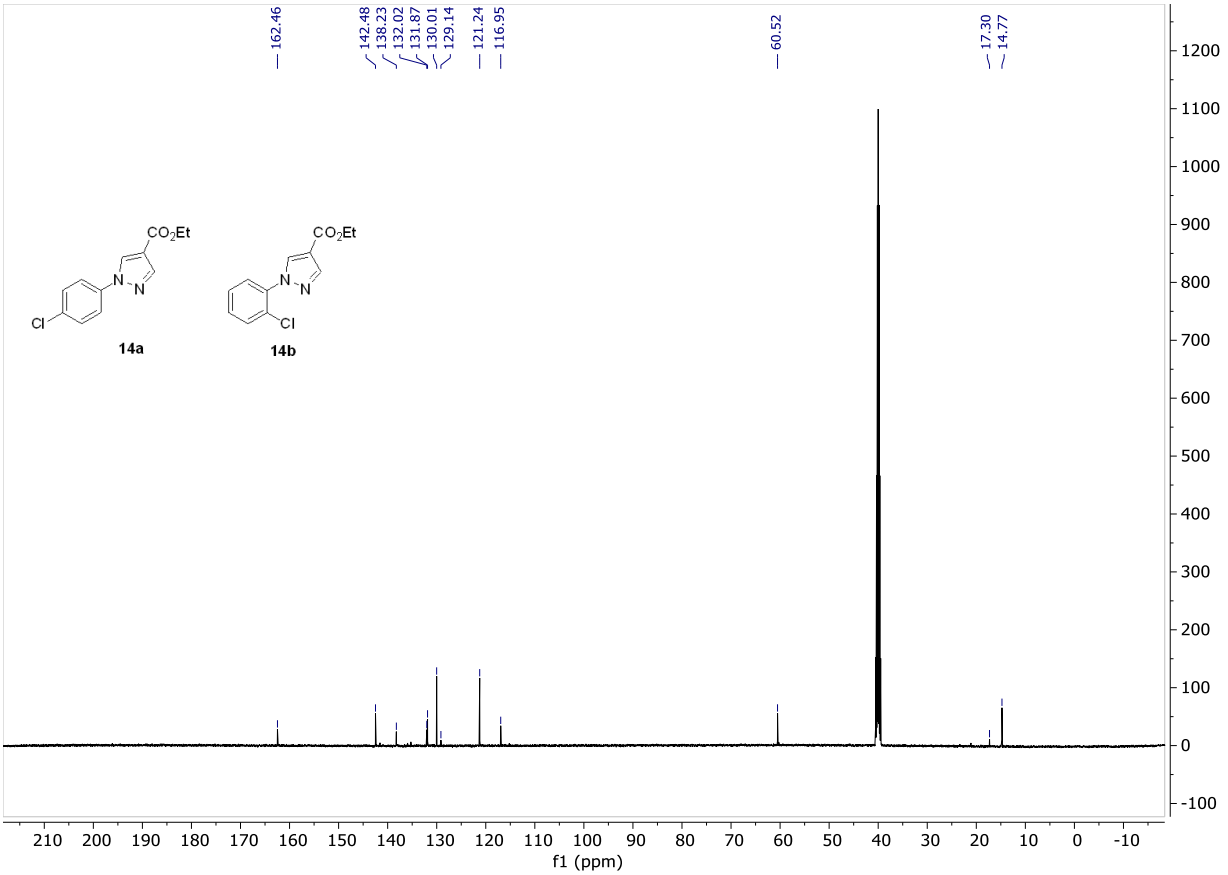
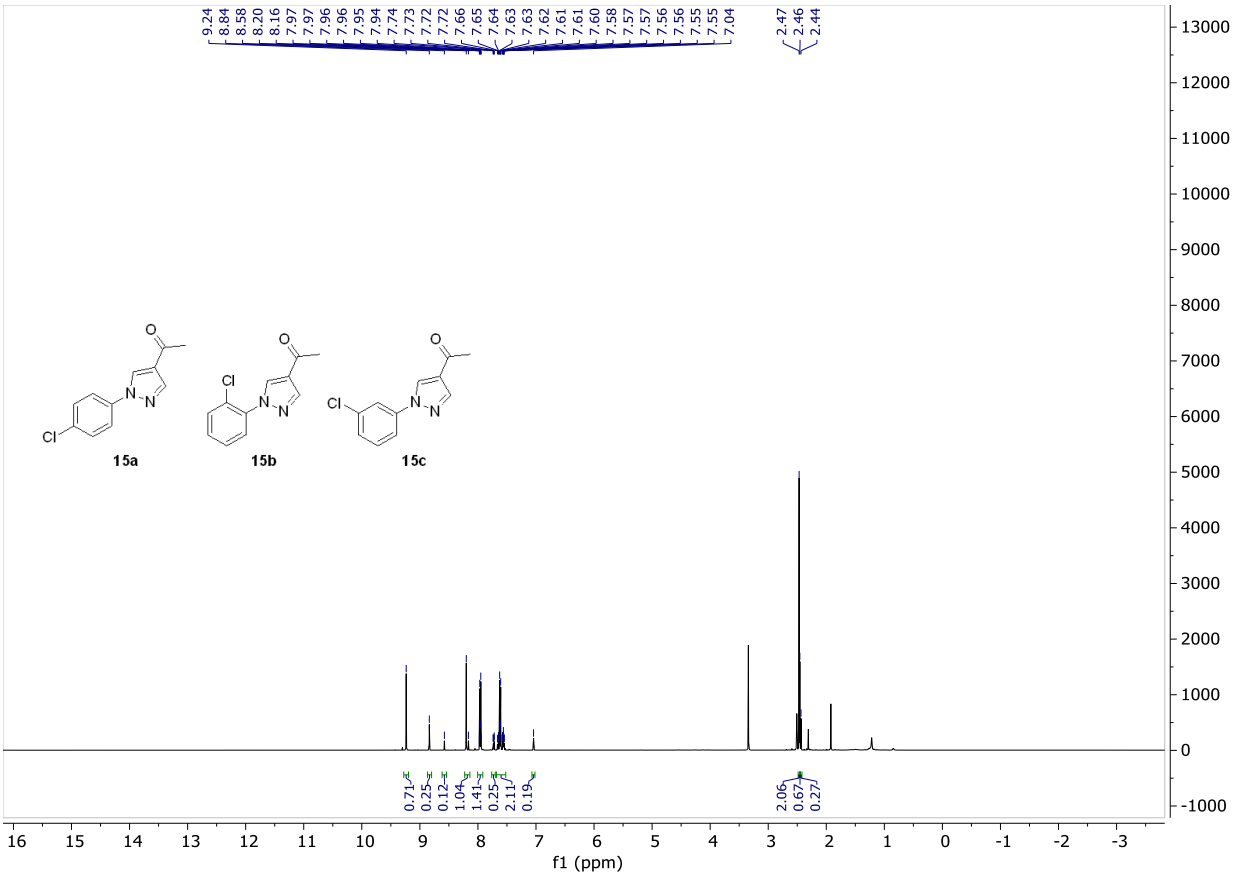
183.93
141.90
141.29
137.12
135.07
133.75
130.87
130.19
129.88
129.86
128.36
127.96
127.71
125.90
125.18
120.98
CHO
13a
CHO
13b
f1 (ppm)


9.14
8.48
8.16
8.11
7.99
7.99
7.98
7.97
7.61
7.60
7.60
7.59
7.04
4.30
4.29
4.28
4.27
4.26
4.25
1.32
1.31
1.30
CO2Et
N
N
Cl
14a
14b
0.90
0.09
1.02
1.78
1.78
0.17
2.00
3.05
f1 (ppm)


162.46
142.48
138.23
132.02
131.87
130.01
129.14
121.24
116.95
60.52
17.30
14.77
CO2Et
N
N
Cl
14a
14b
f1 (ppm)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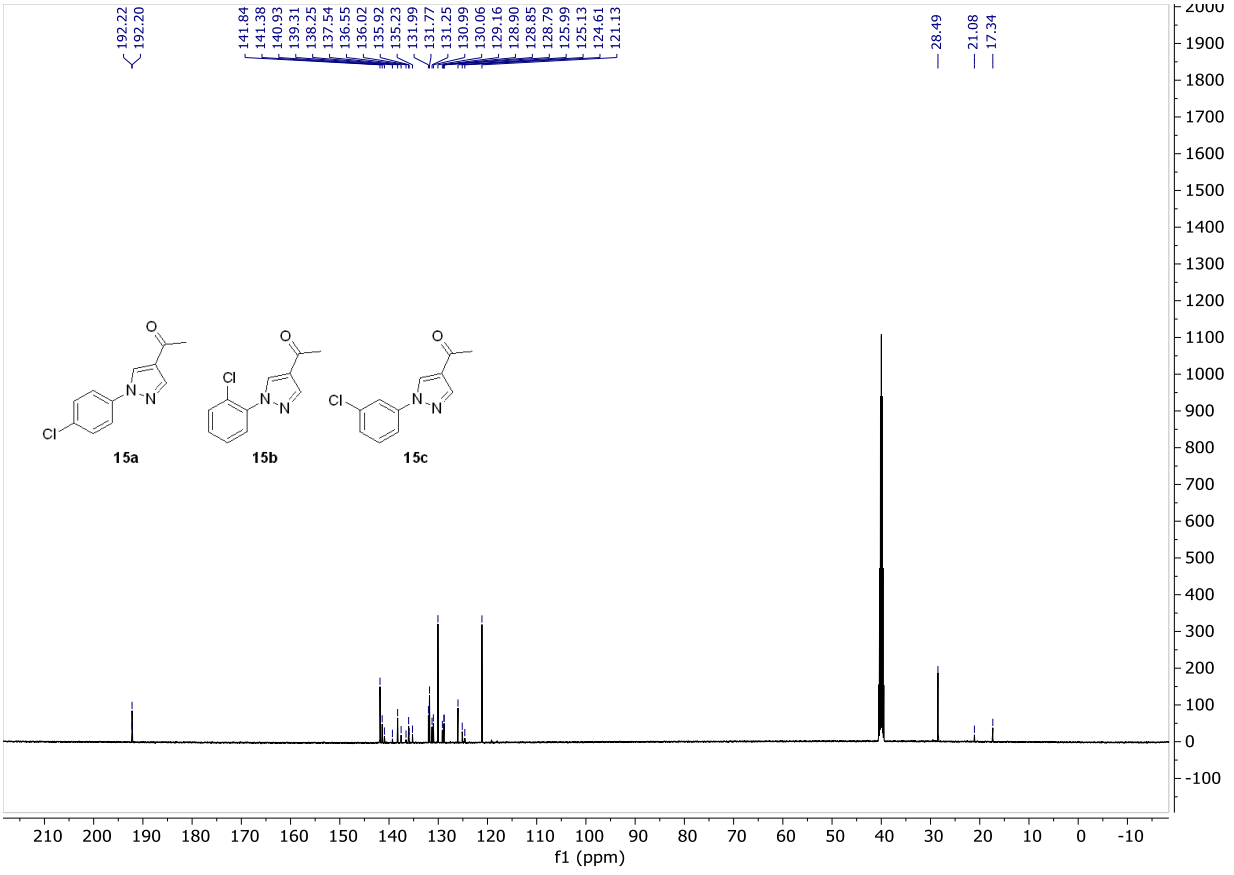
8.58
8.20
8.16
7.97
7.97
7.96
7.96
7.95
7.94
7.74
7.73
7.72
7.72
7.66
7.65
7.64
7.63
7.63
7.62
7.61
7.61
7.60
7.58
7.57
7.57
7.56
7.56
7.55
7.55
7.04
2.47
2.46
2.44
15a
15b
15c
0.71
0.25
0.12
1.04
1.41
0.25
2.11
0.19
2.06
0.67
0.27
f1 (ppm)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192.20
141.84
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140.93
139.31
138.25
137.54
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136.02
135.92
135.23
131.99
131.77
131.25
130.99
130.06
129.16
128.90
128.85
128.79
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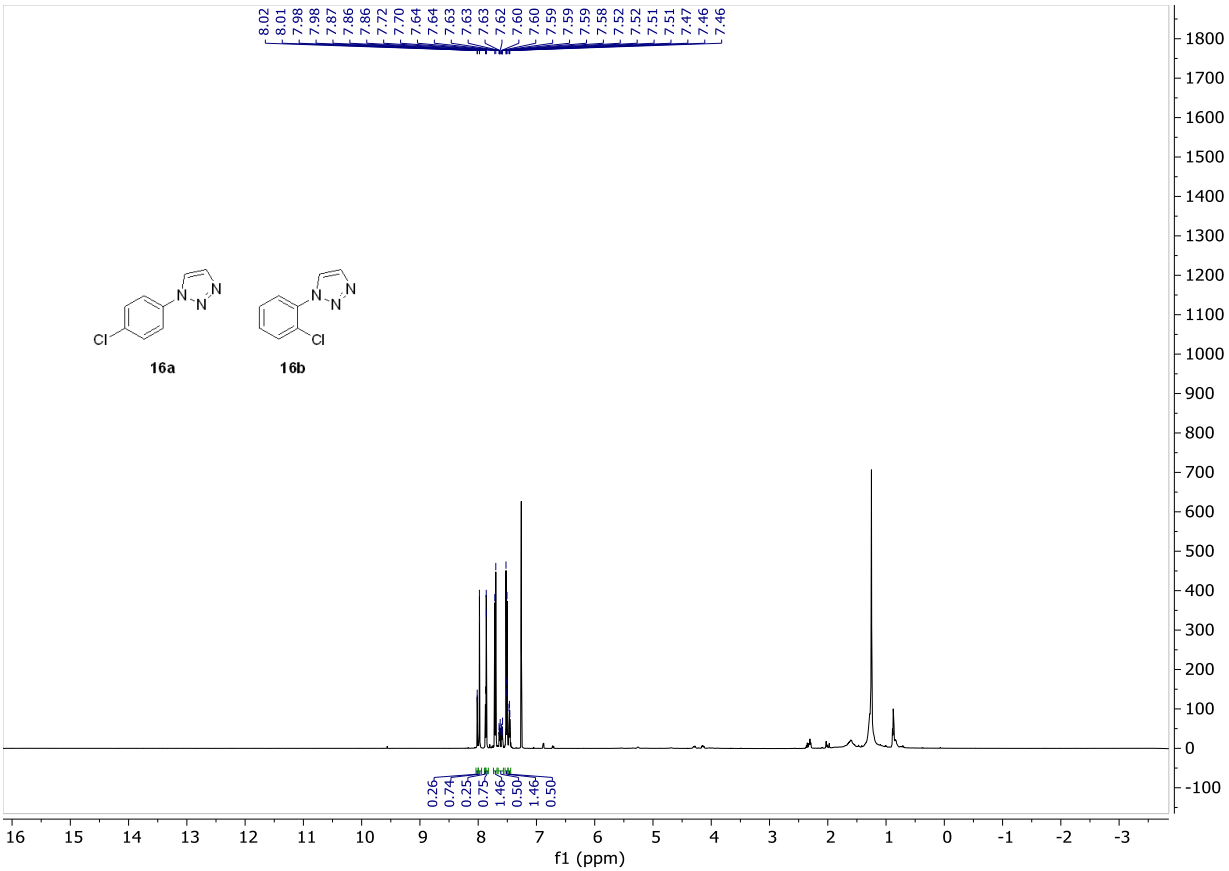
125.13
124.61
121.13
28.49
21.08
17.34
15a
15b
15c
f1 (ppm)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8.01
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7.98
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7.86
7.86
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7.63
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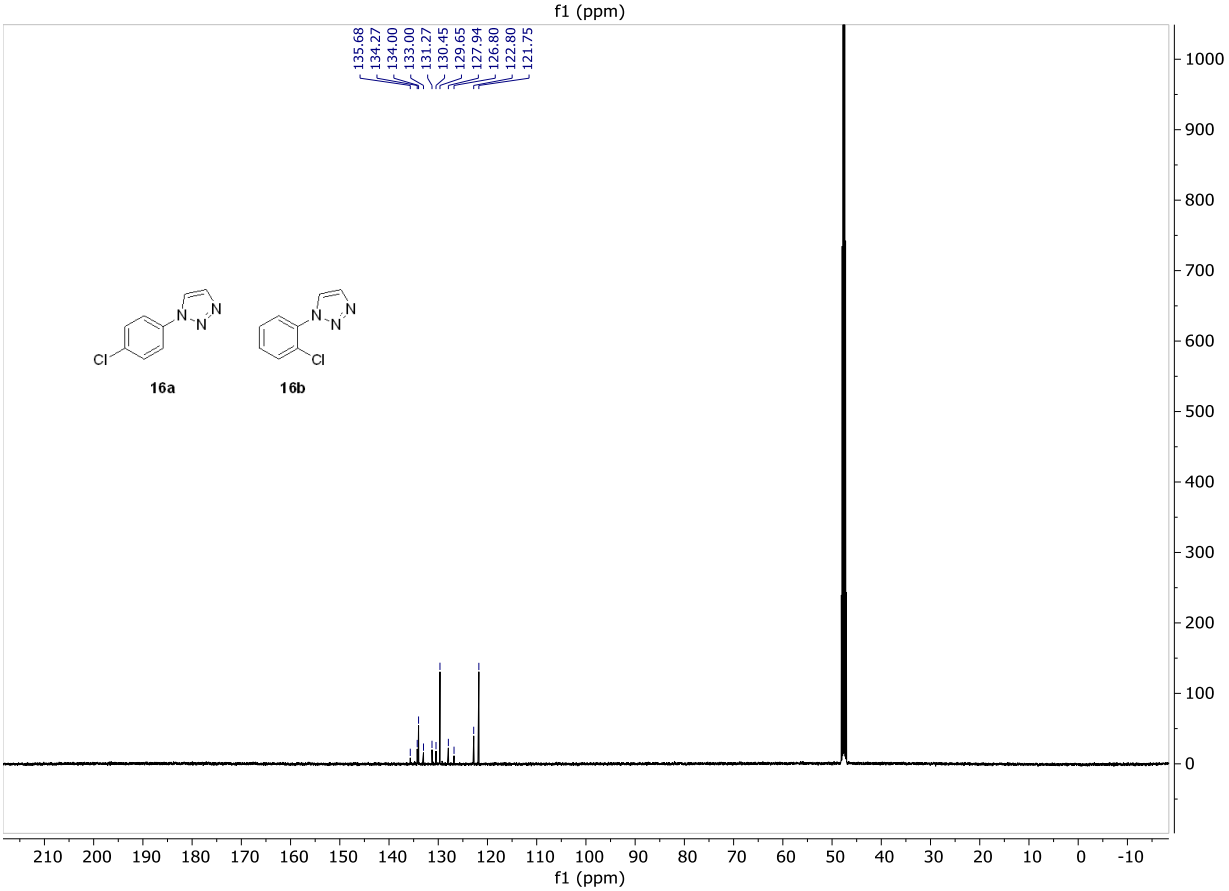
7.63
7.62
7.60
7.60
7.59
7.59
7.59
7.58
7.52
7.52
7.51
7.51
7.47
7.46
7.46
Cl
16a
Cl
16b
0.26
0.74
0.25
0.75
1.46
0.50
1.46
0.50
f1 (ppm)


135.68
134.27
134.00
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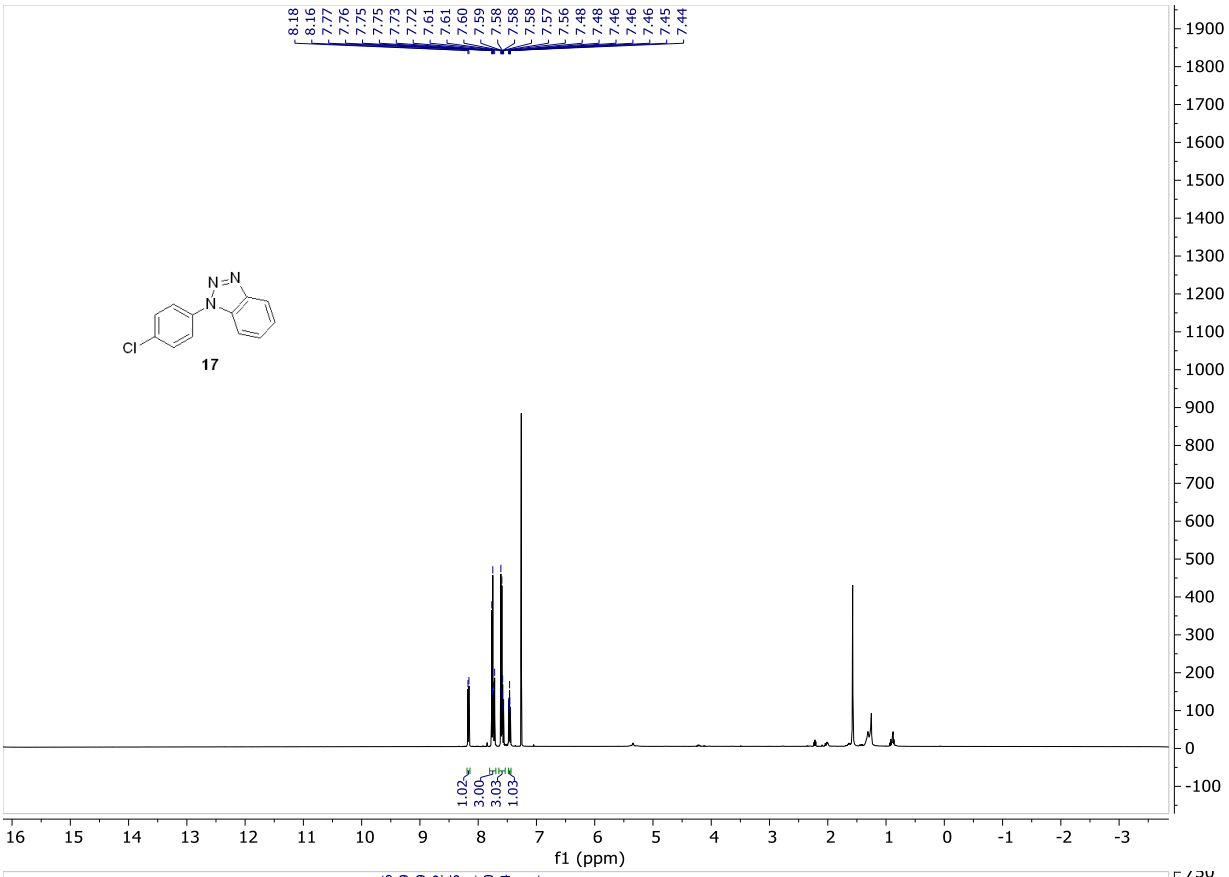
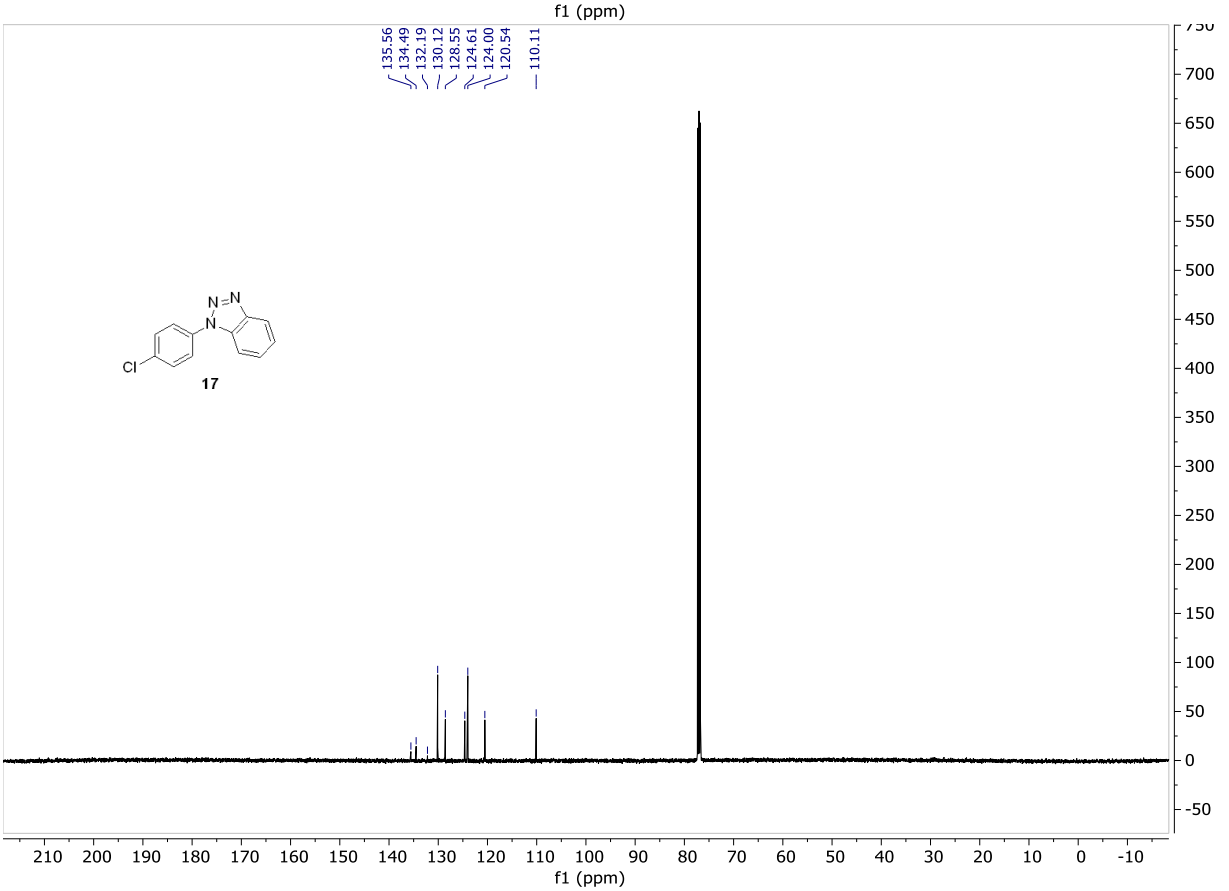
129.65
127.94
126.80
122.80
121.75
Cl
16a
Cl
16b
f1 (ppm)


8.18
8.16
7.77
7.76
7.75
7.75
7.73
7.72
7.61
7.61
7.60
7.59
7.58
7.58
7.58
7.57
7.56
7.48
7.48
7.46
7.46
7.46
7.45
7.44
Cl
17
1.02
3.00
3.03
1.03
f1 (ppm)


135.56
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130.12
128.55
124.61
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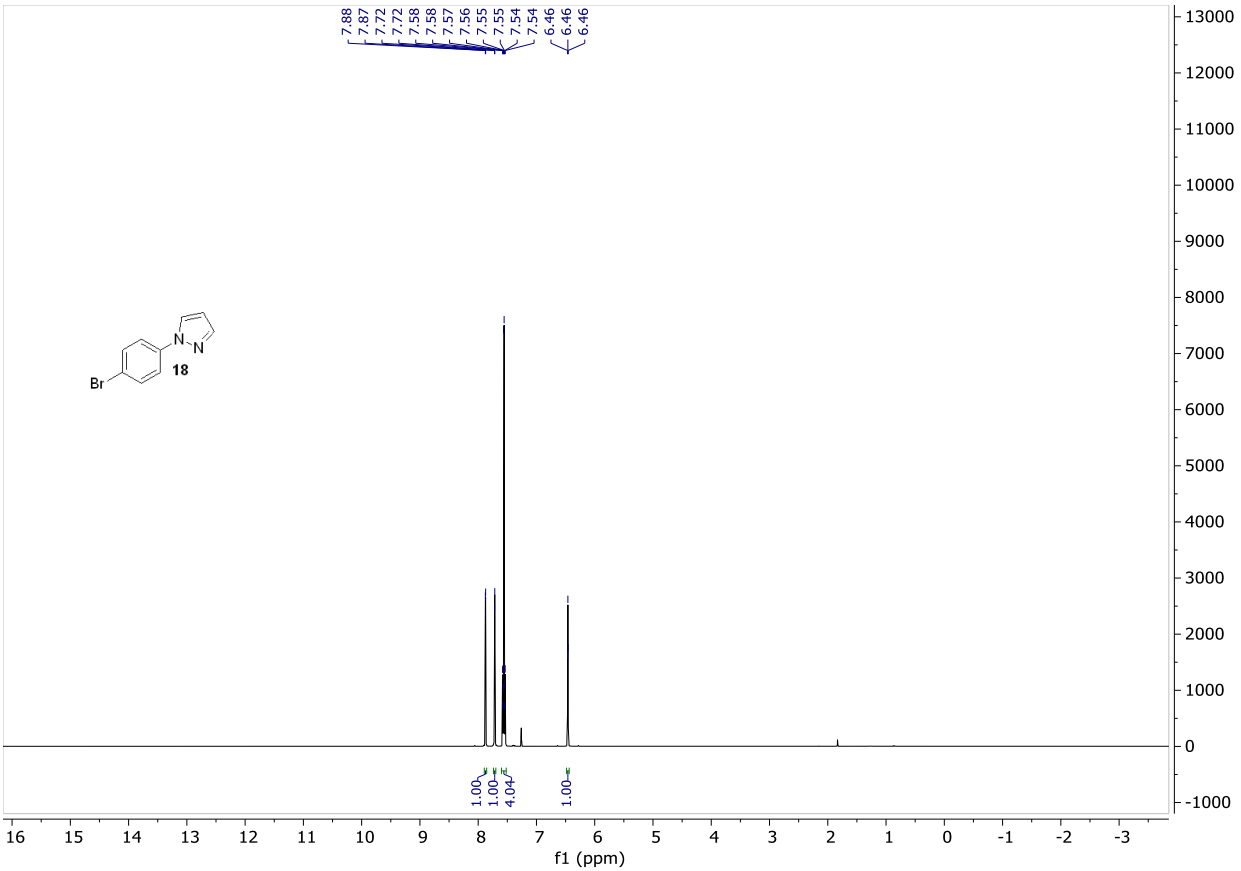
120.54
110.11
Cl
17
f1 (ppm)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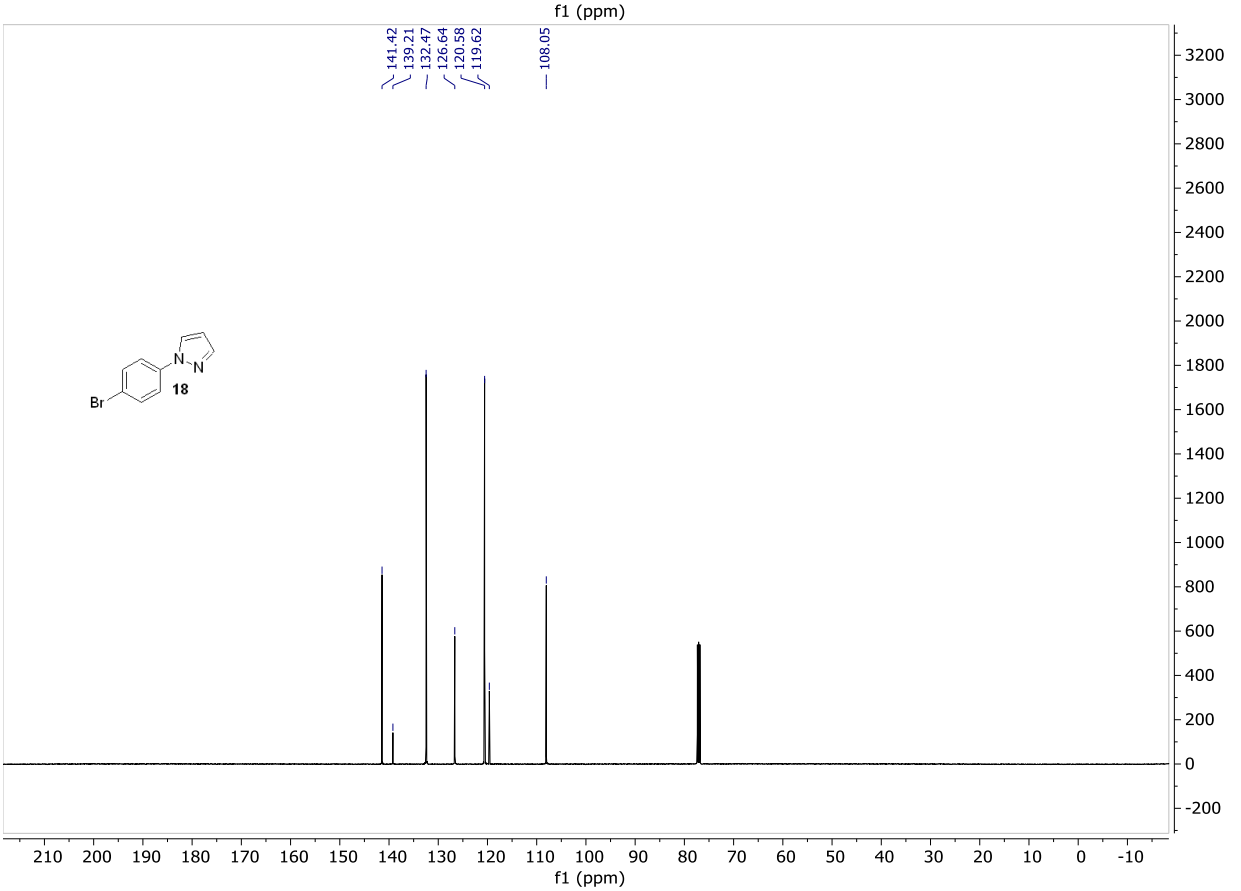
7.87
7.72
7.72
7.58
7.58
7.57
7.56
7.55
7.55
7.54
7.54
6.46
6.46
6.46
Br
N
N
18
1.00
1.00
4.04
1.00
f1 (ppm)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132.47
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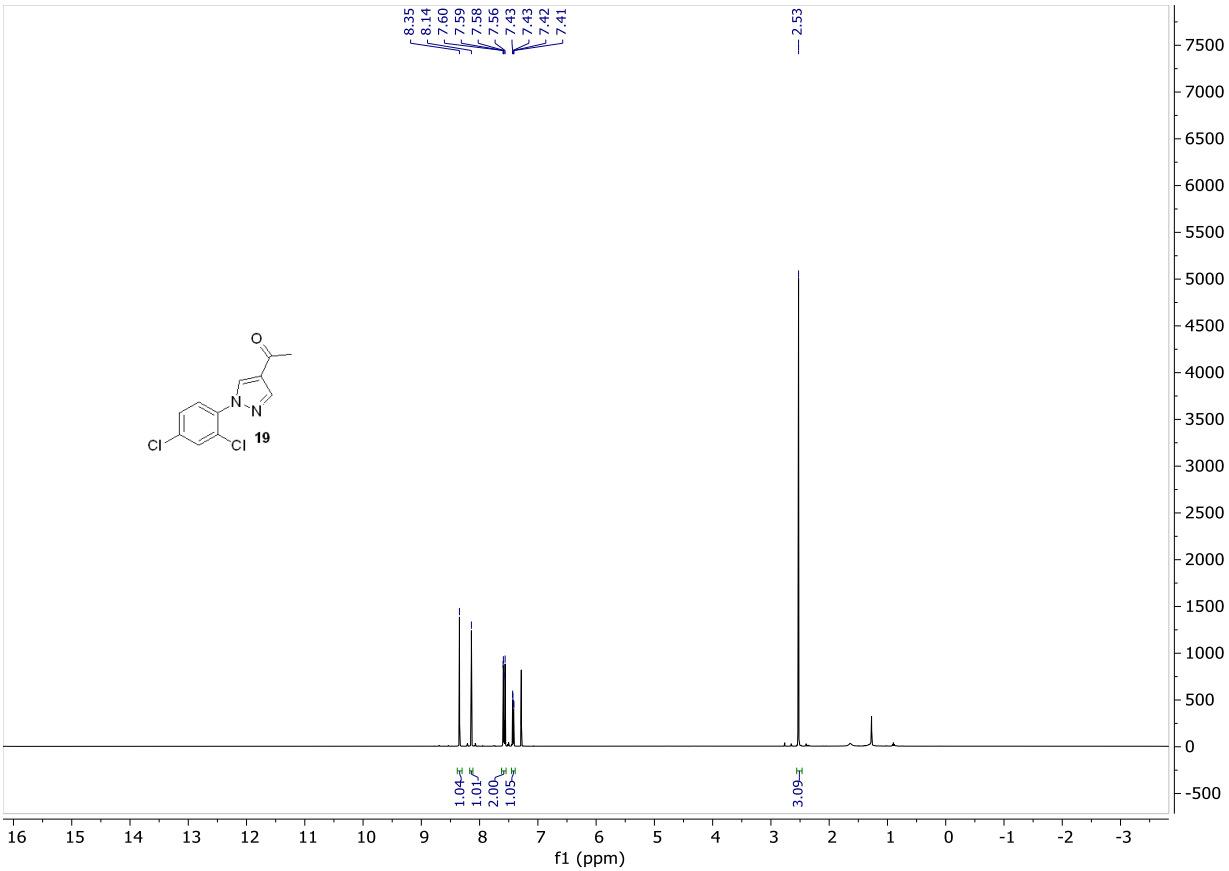
120.58
119.62
108.05
Br
N
N
18
f1 (ppm)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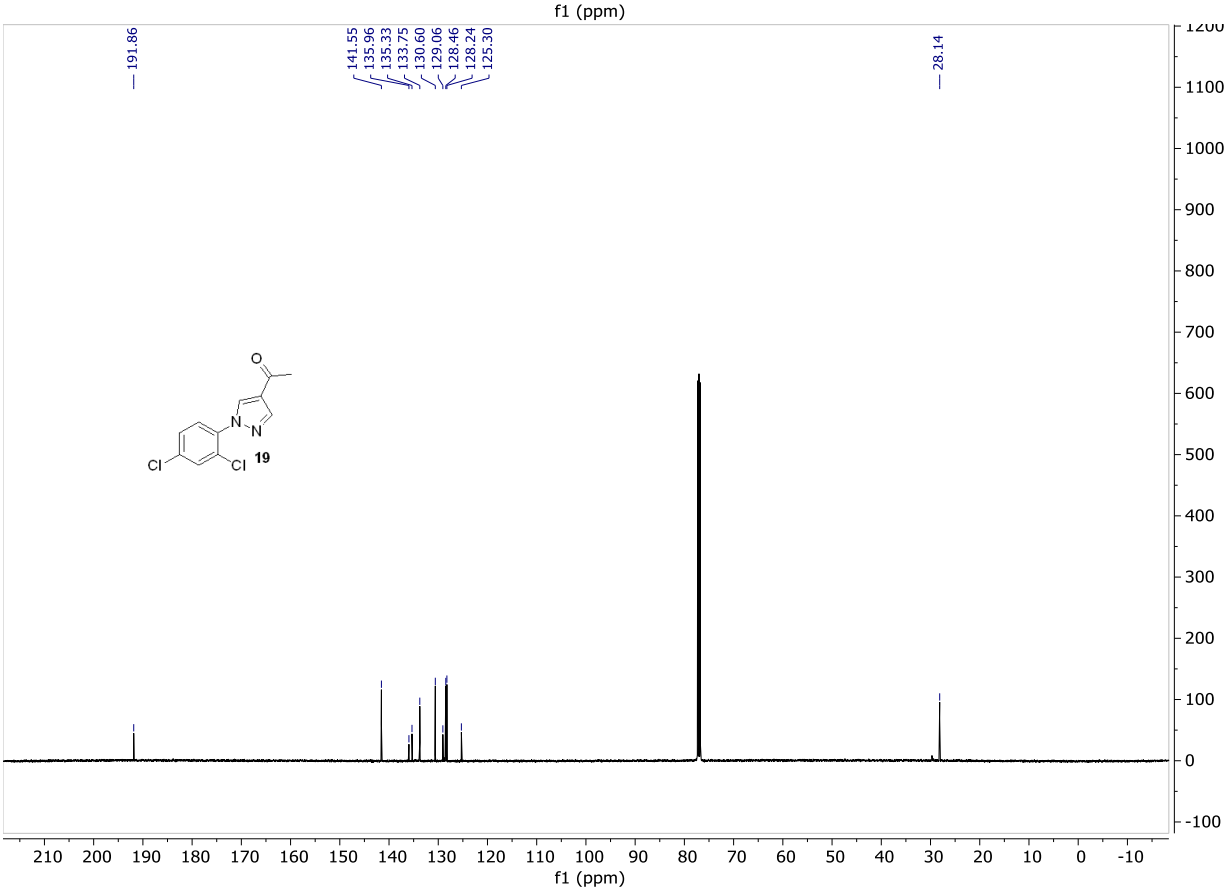
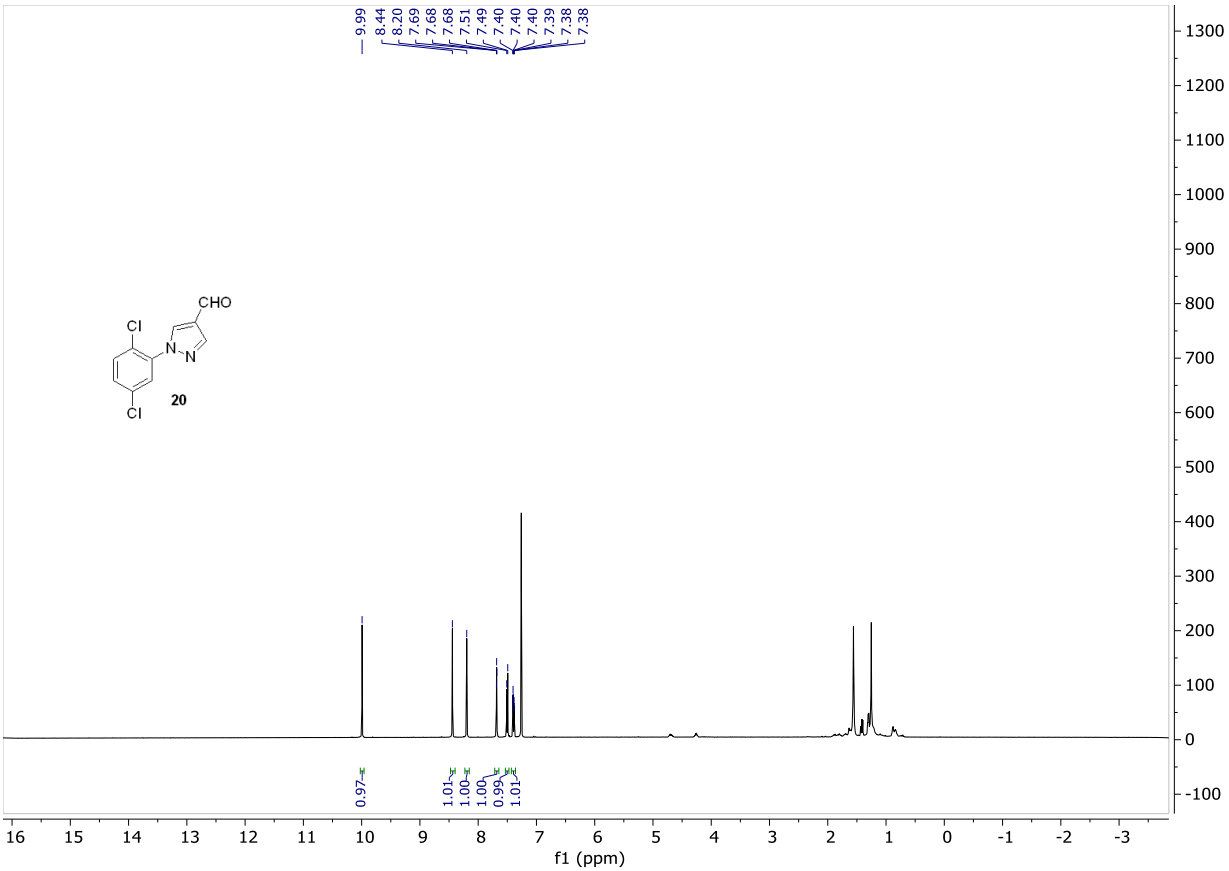
8.14
7.60
7.59
7.58
7.56
7.43
7.43
7.42
7.41
2.53
1.04
1.01
2.00
1.05
3.09
f1 (ppm)
19


191.86
141.55
135.96
135.33
133.75
130.60
129.06
128.46
128.24
125.30
28.14
f1 (ppm)
19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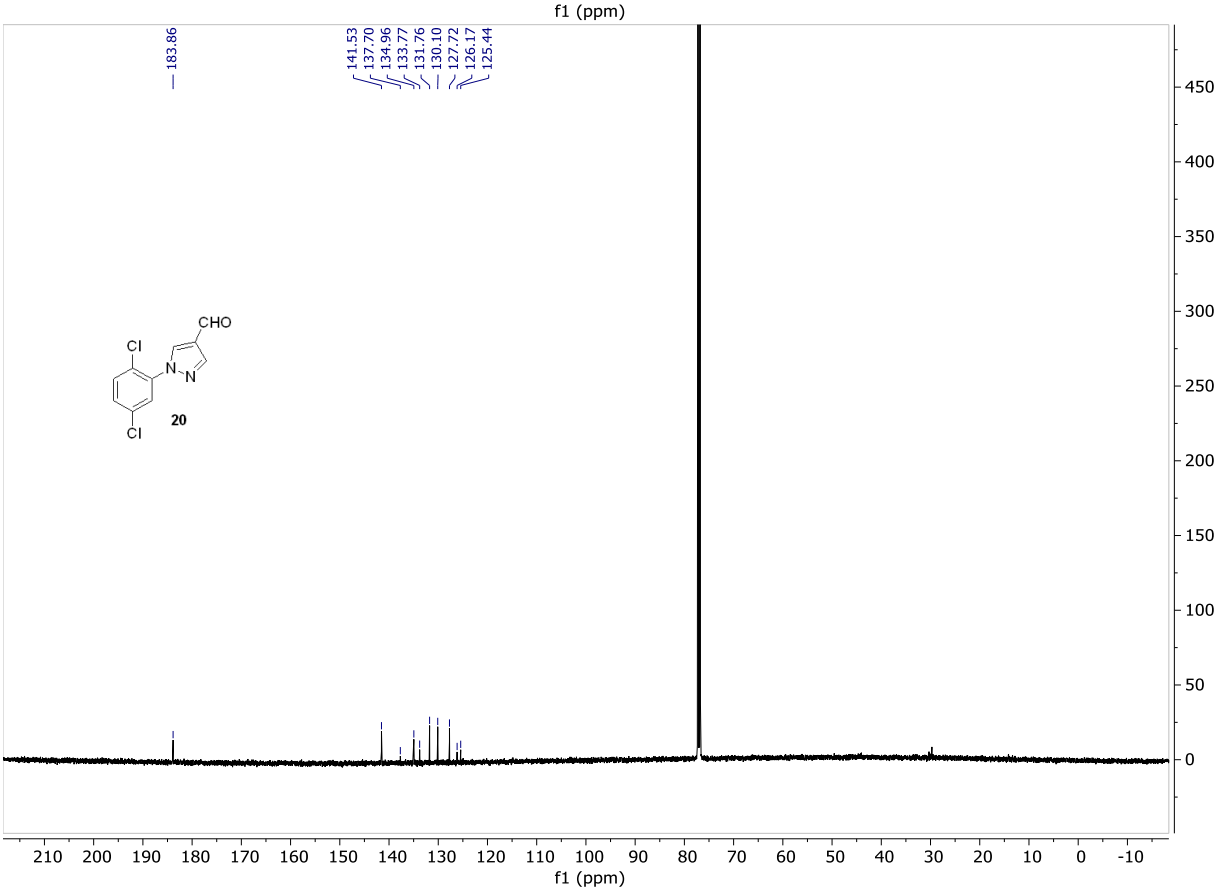
7.68
7.68
7.51
7.49
7.40
7.40
7.40
7.39
7.38
7.38
CHO
Cl
N
N
Cl
20
0.97
1.01
1.00
1.00
0.99
1.01
f1 (ppm)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141.53
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127.72
126.17
125.44
CHO
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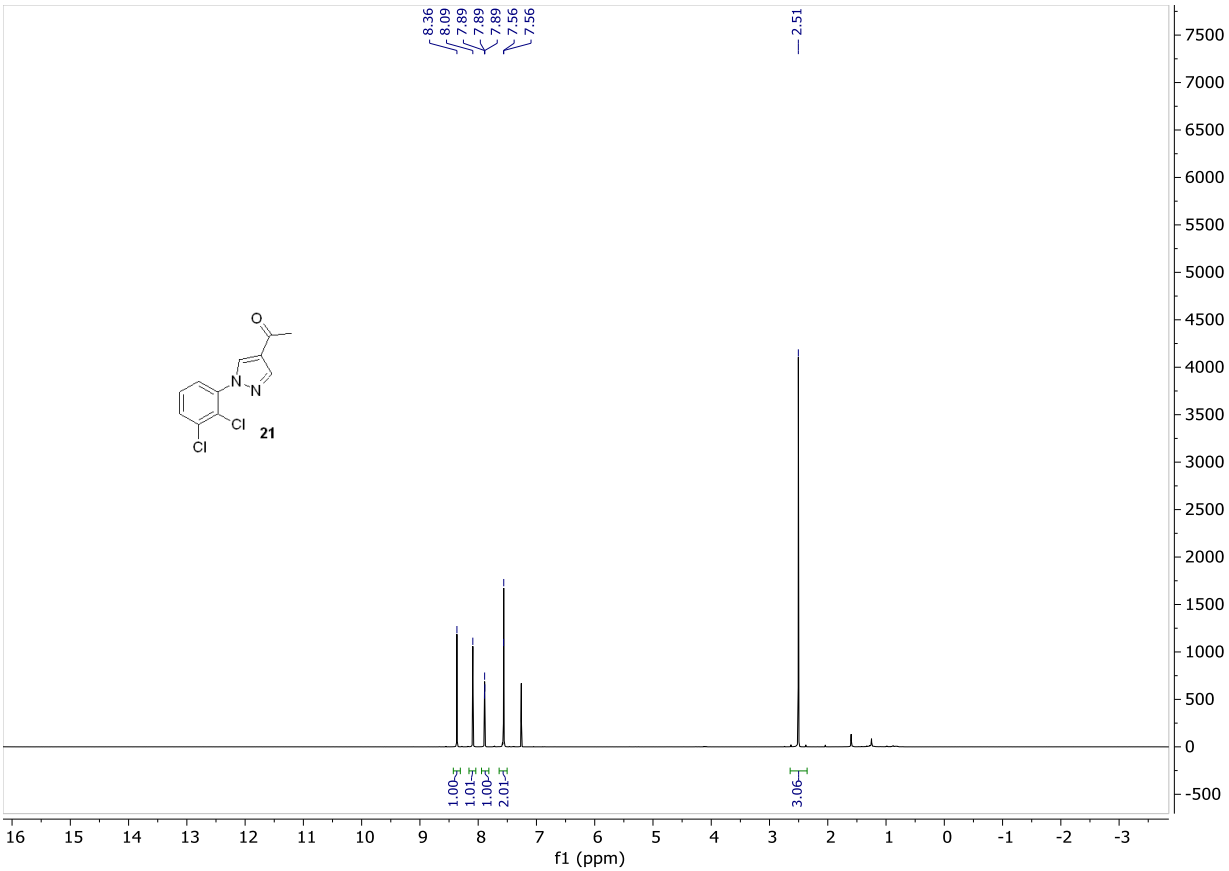
N
Cl
20
f1 (ppm)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8.09
7.89
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7.89
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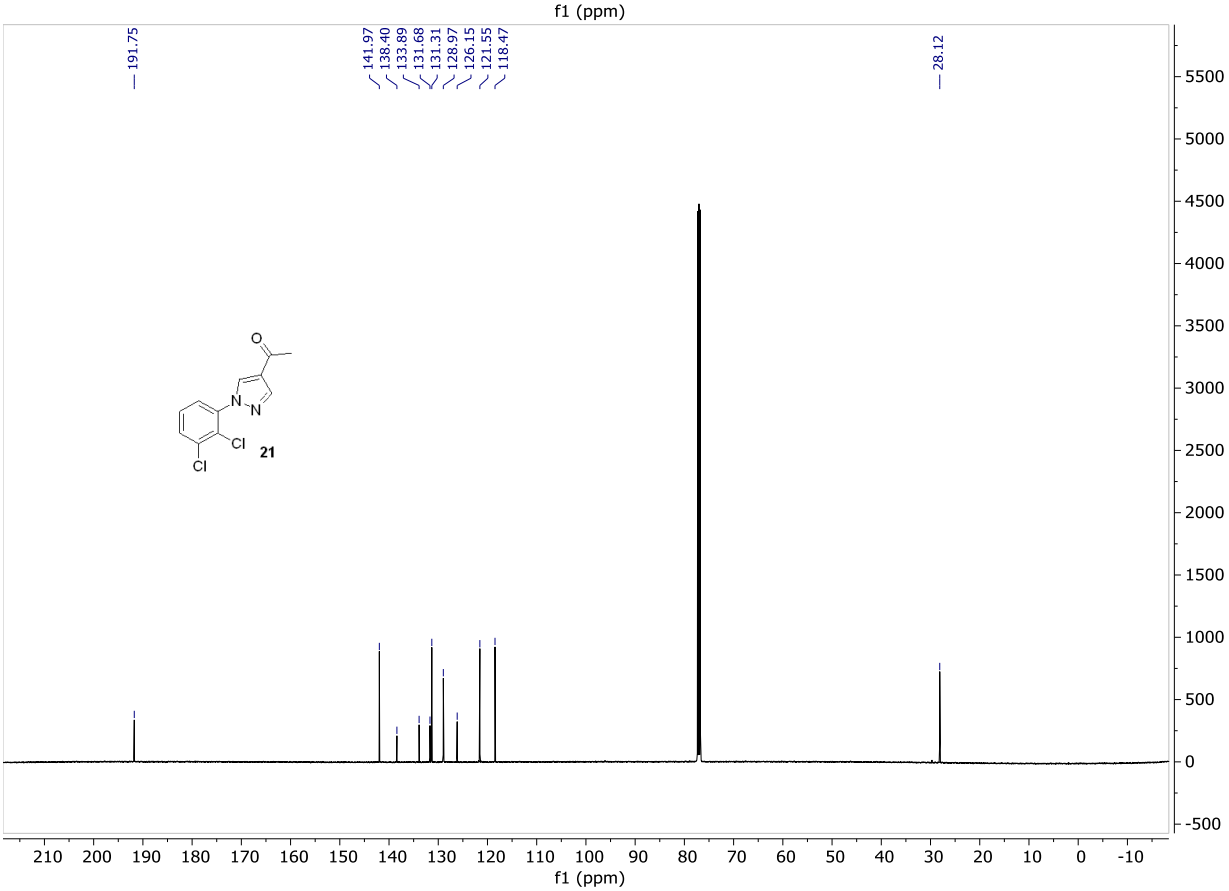
7.56
2.51
1.00
1.01
1.00
2.01
3.06
f1 (ppm)
21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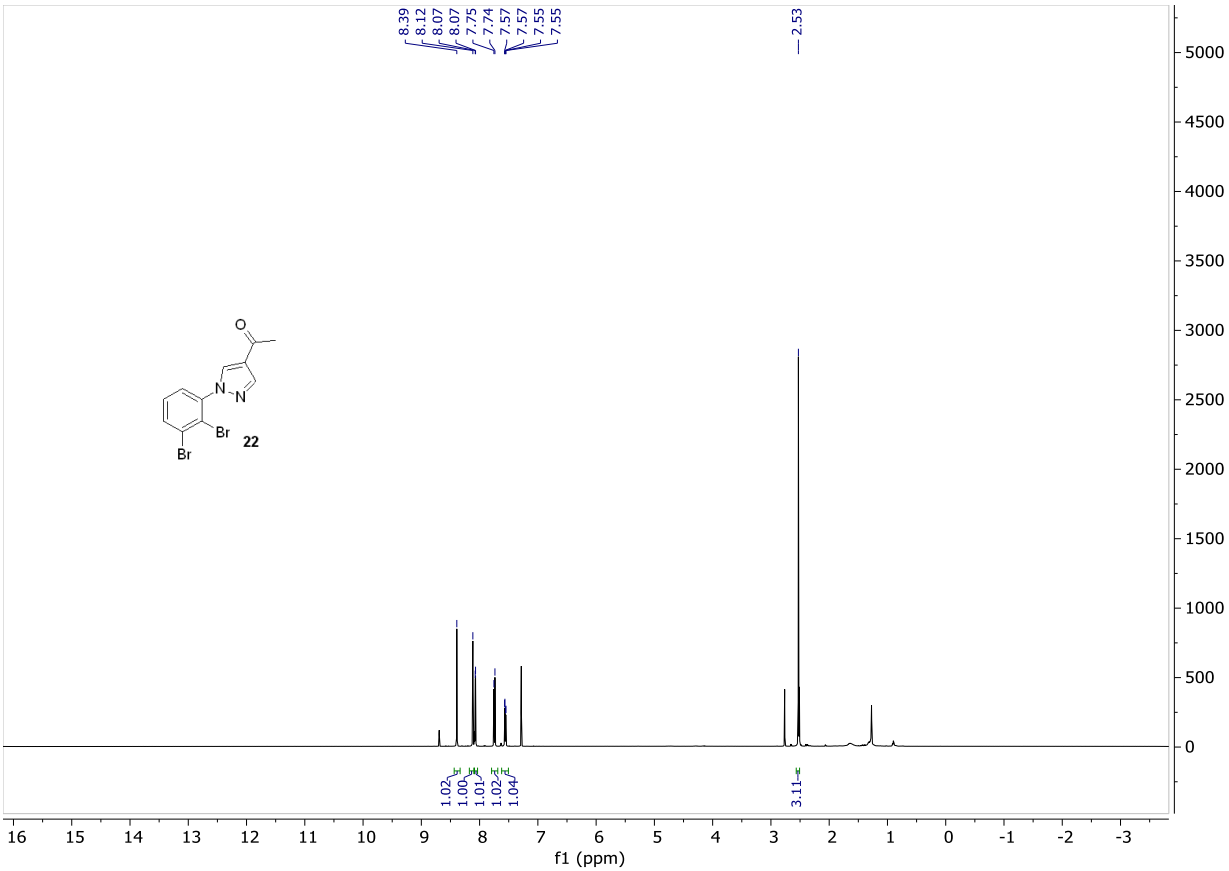
133.89
131.68
131.31
128.97
126.15
121.55
118.47
28.12
f1 (ppm)
21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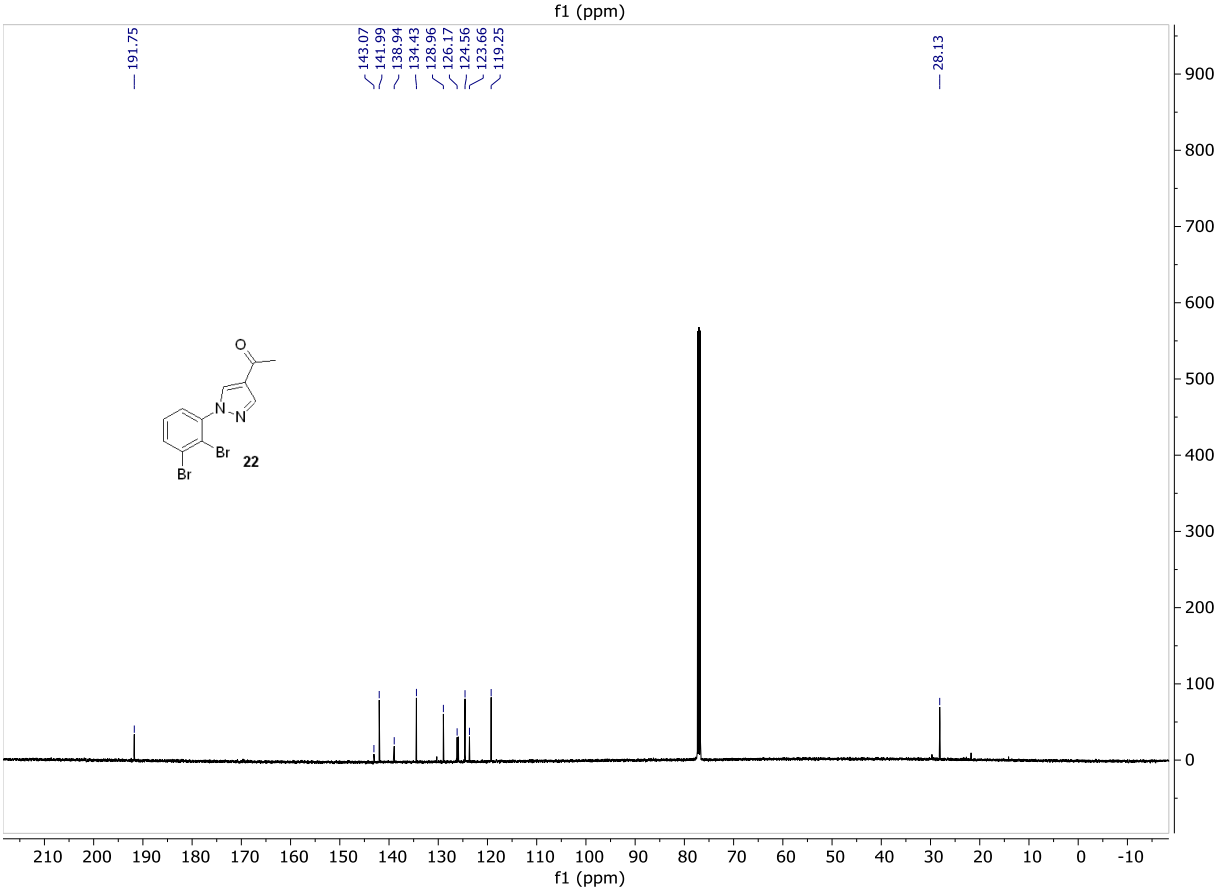
8.12
8.07
8.07
7.75
7.74
7.57
7.57
7.55
7.55
2.53
O
N
N
Br
Br
22
1.02
1.00
1.01
1.02
1.04
3.11
f1 (ppm)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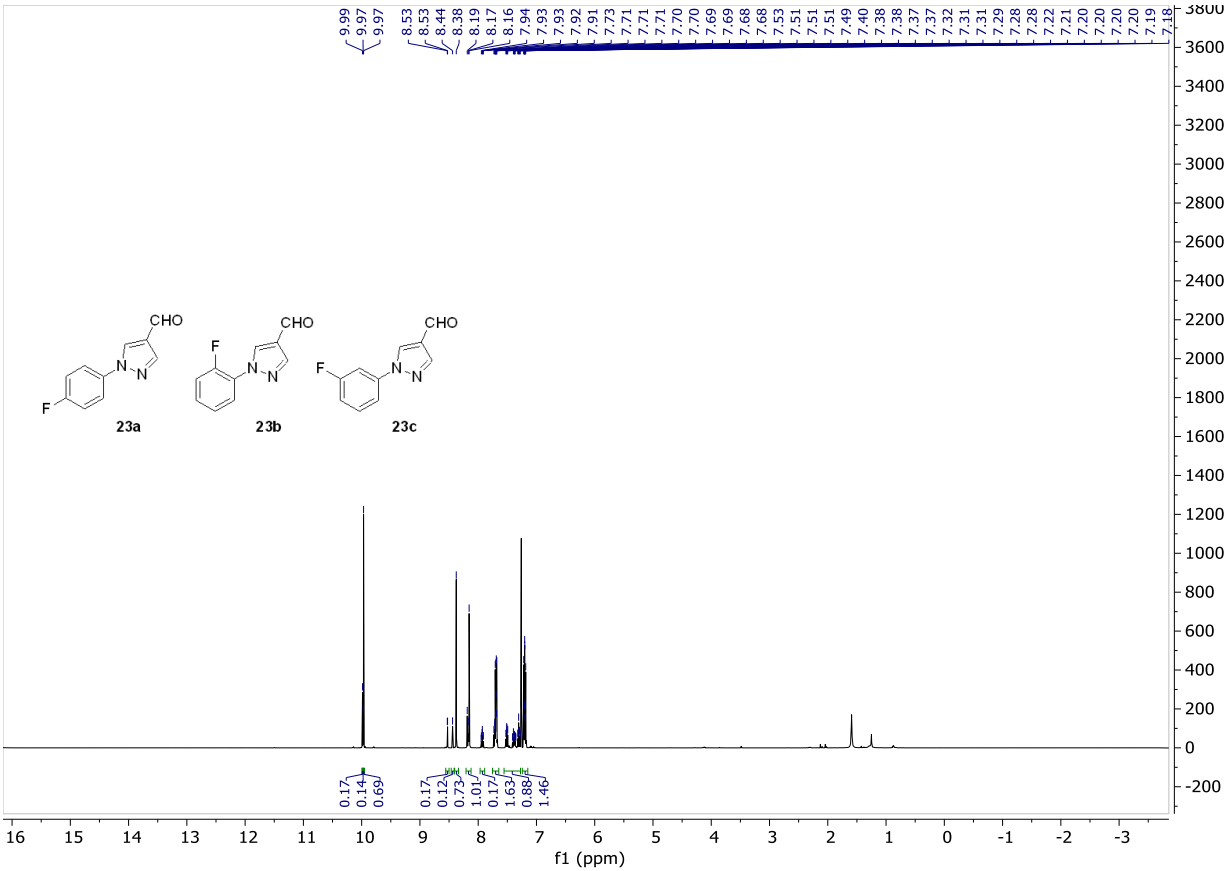
141.99
138.94
134.43
128.96
126.17
124.56
123.66
119.25
28.13
O
N
N
Br
Br
22
f1 (ppm)


9.99
9.97
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8.17
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7.92
7.91
7.73
7.71
7.71
7.71
7.70
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7.69
7.69
7.68
7.68
7.53
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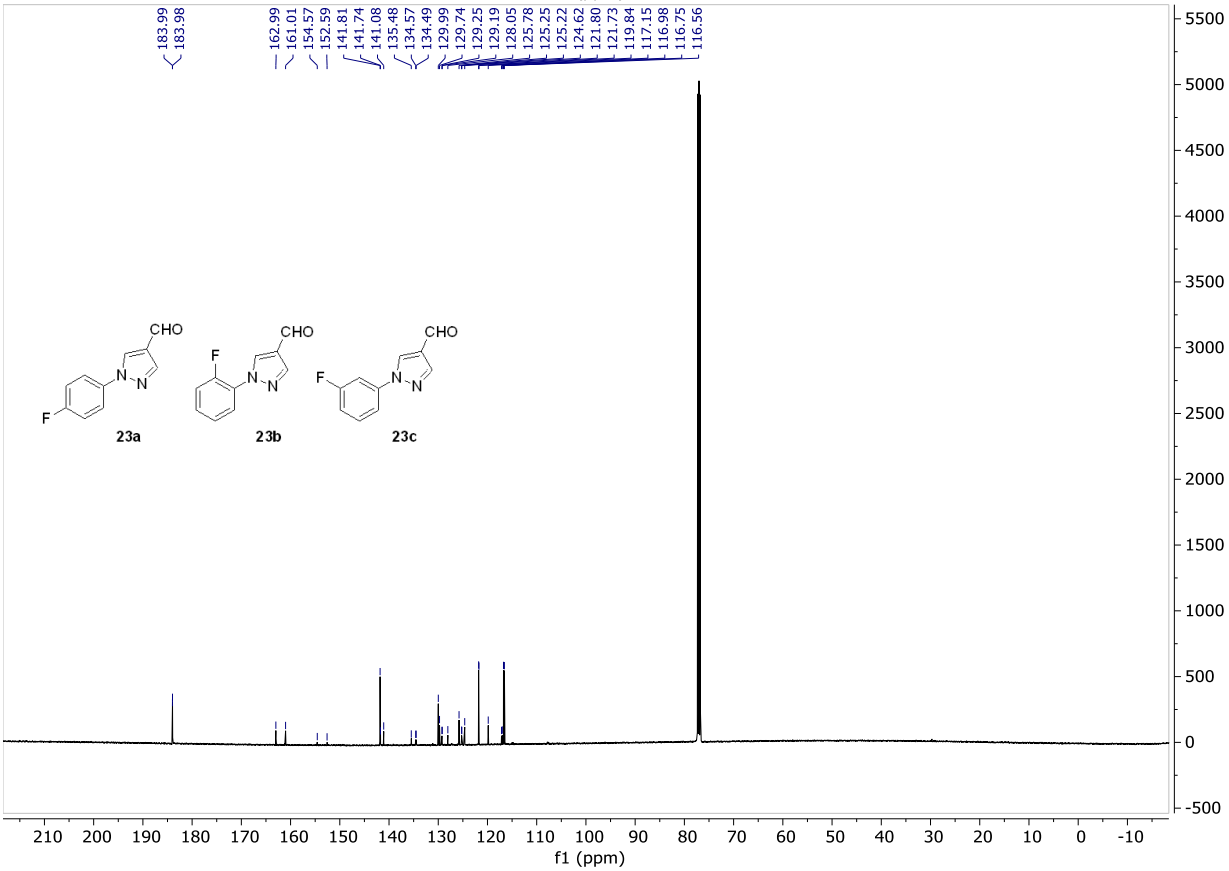
7.51
7.51
7.49
7.40
7.38
7.38
7.37
7.37
7.32
7.31
7.31
7.29
7.28
7.28
7.22
7.21
7.20
7.20
7.20
7.20
7.19
7.18
CHO
F
N
N
23a
CHO
F
N
N
23b
CHO
F
N
N
23c
0.17
0.14
0.69
0.17
0.12
0.73
1.01
0.17
1.63
0.88
1.46
f1 (ppm)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183.98
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161.01
154.57
152.59
141.81
141.74
141.08
135.48
134.57
134.49
129.99
129.74
129.25
129.19
128.05
125.78
125.25
125.22
124.62
121.80
121.73
119.84
117.15
116.98
116.75
116.56
CHO
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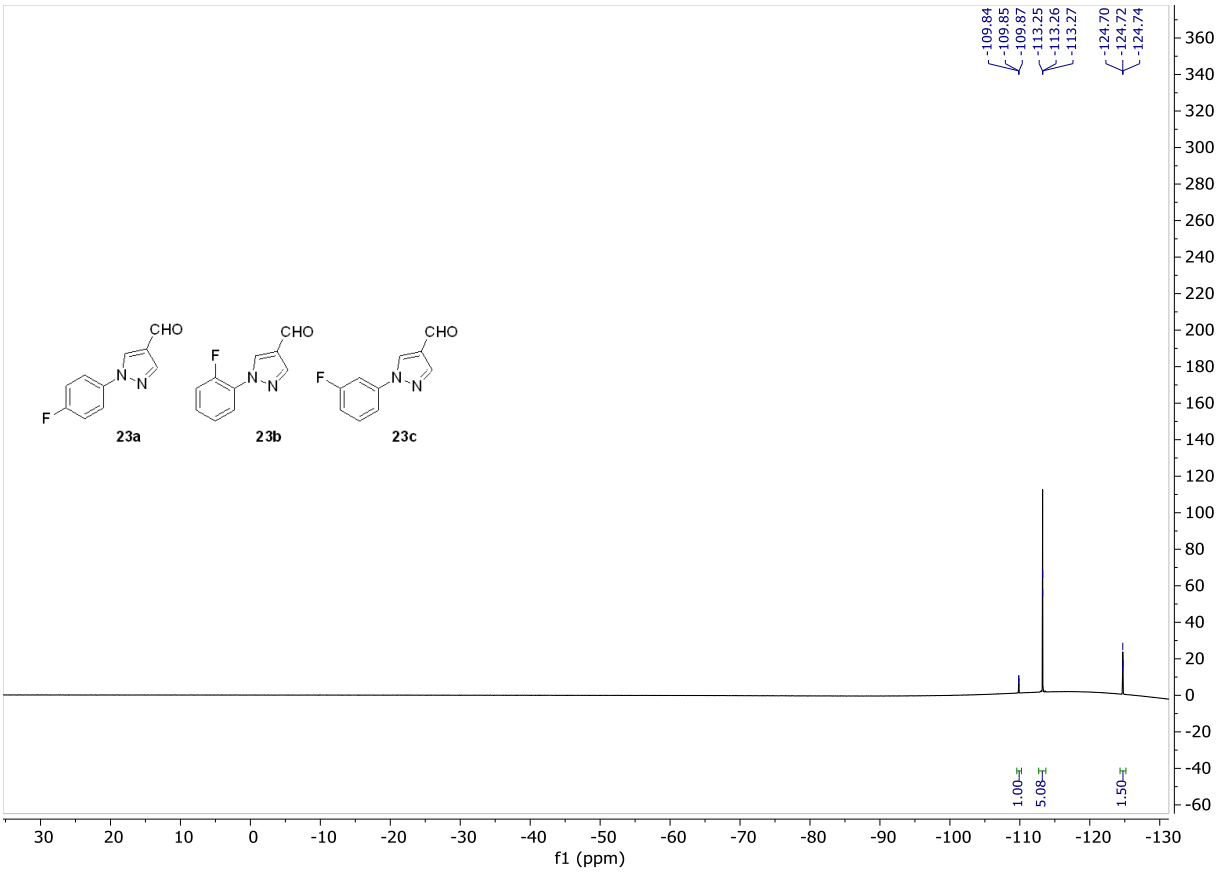
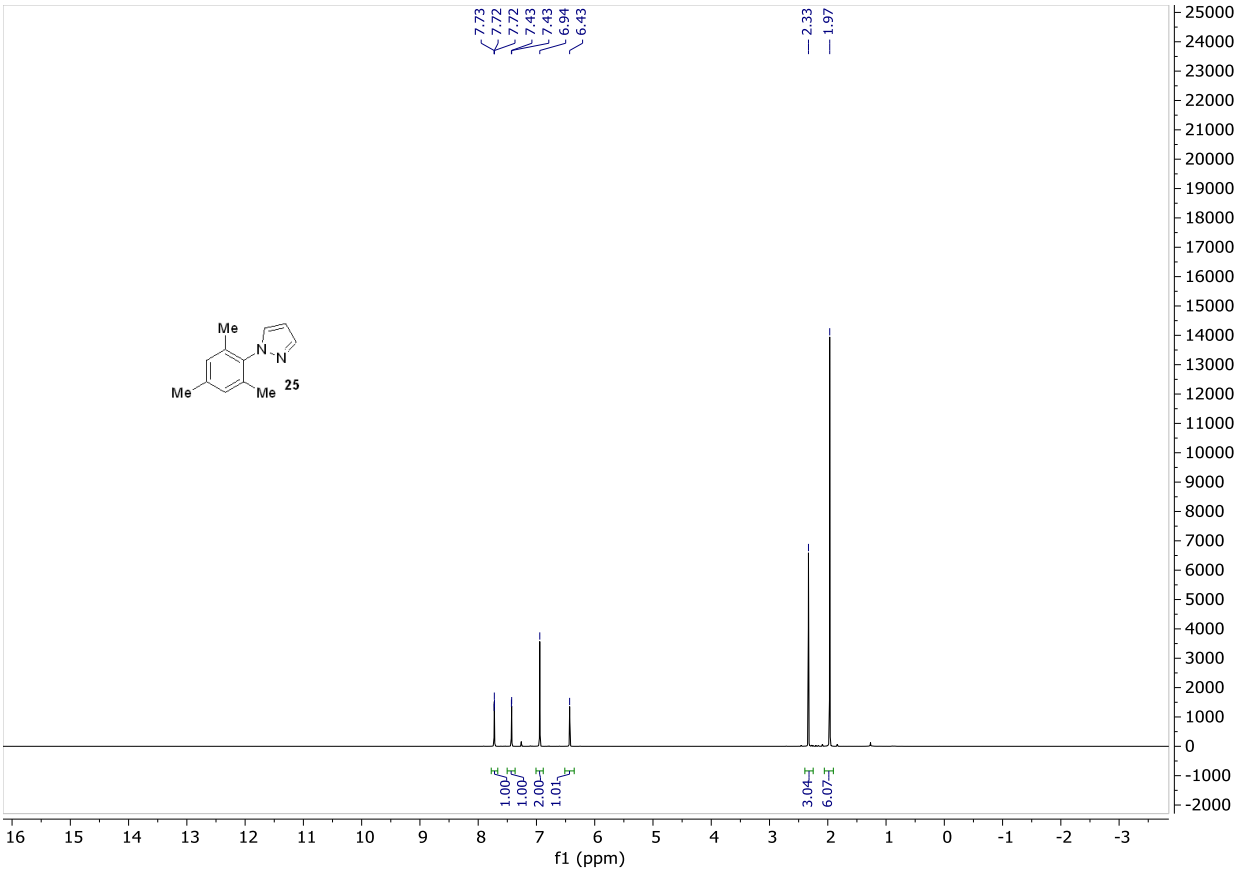
N
N
23a
CHO
F
N
N
23b
CHO
F
N
N
23c
f1 (ppm)


-109.84
-109.85
-109.87
-113.25
-113.26
-113.27
-124.70
-124.72
-124.74
CHO
F
23a
23b
23c
1.00
5.08
1.50
f1 (ppm)


7.73
7.72
7.72
7.43
7.43
6.94
6.43
2.33
1.97
Me
Me
Me
25
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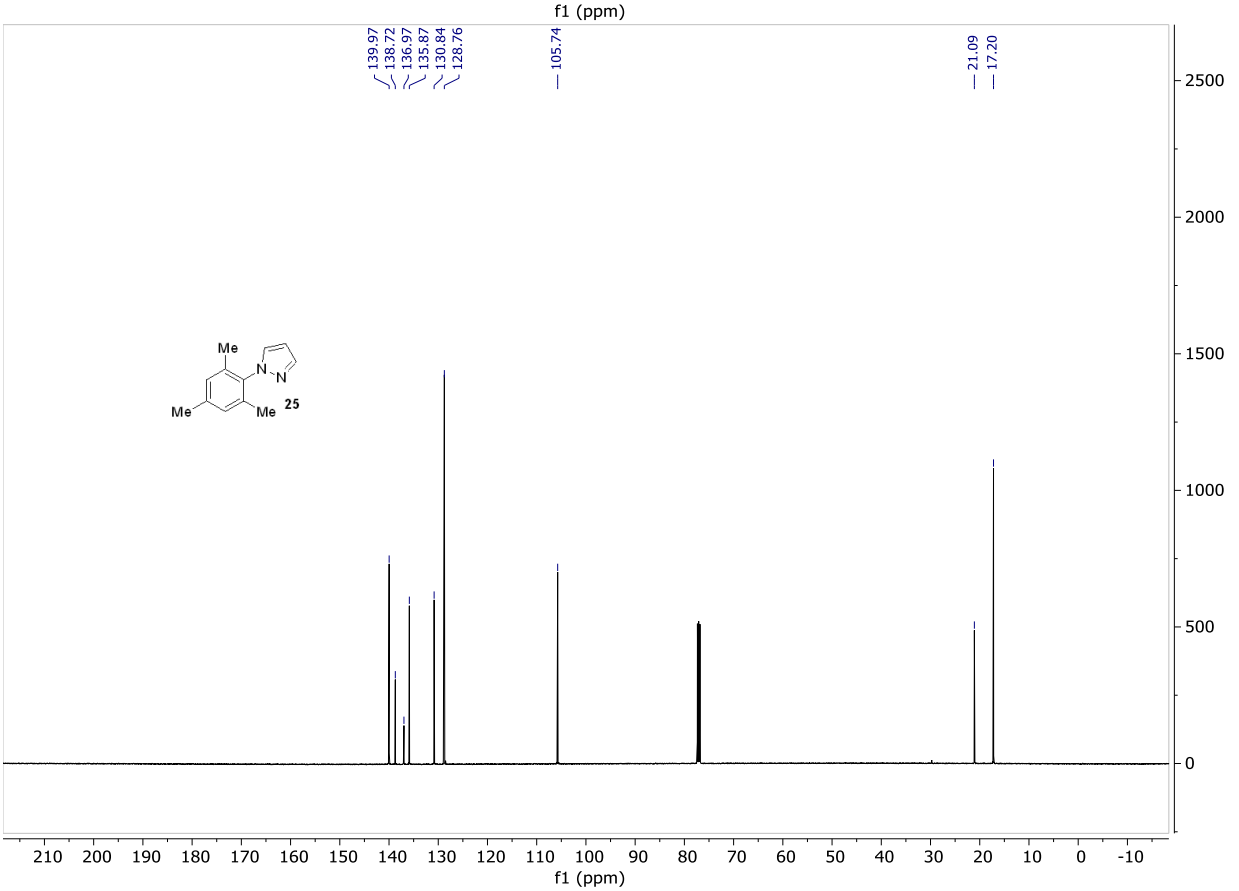
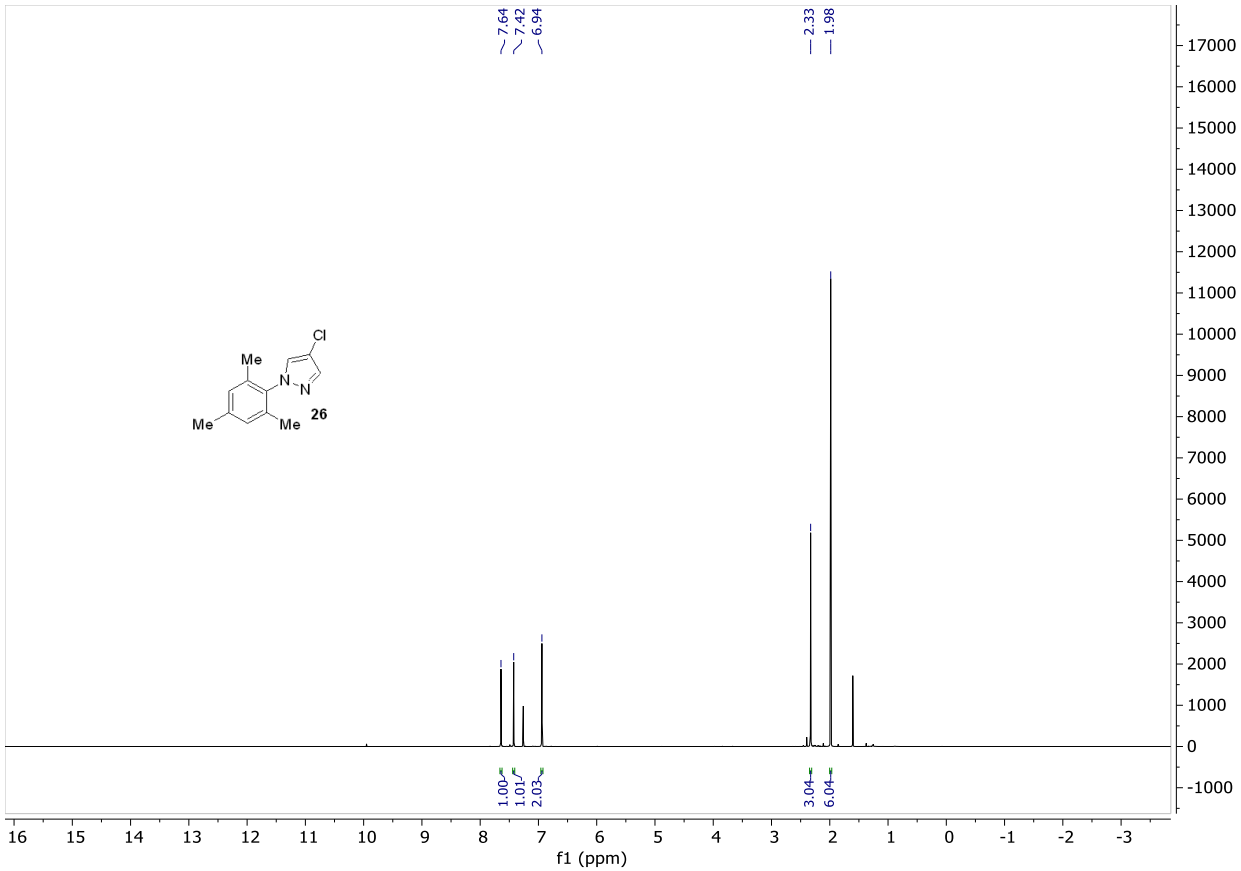
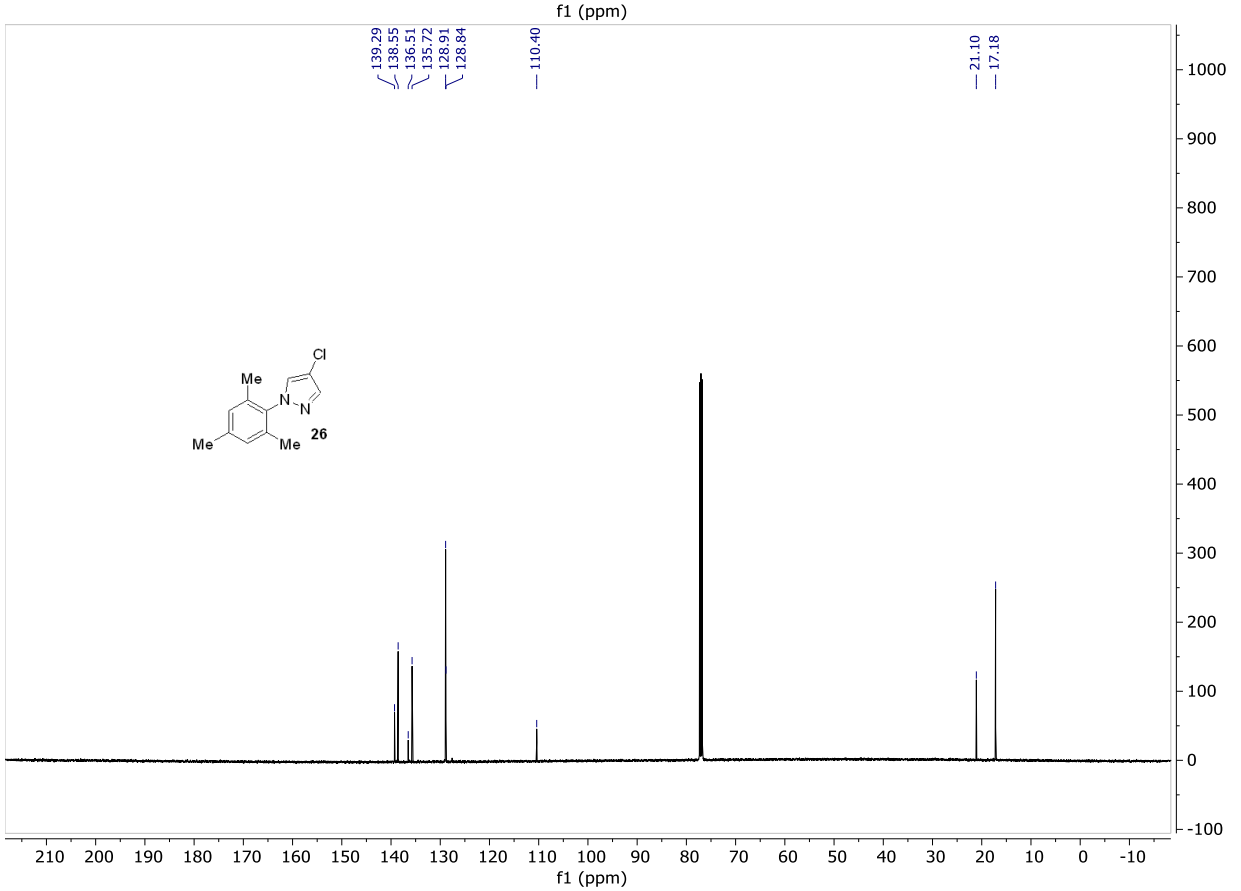
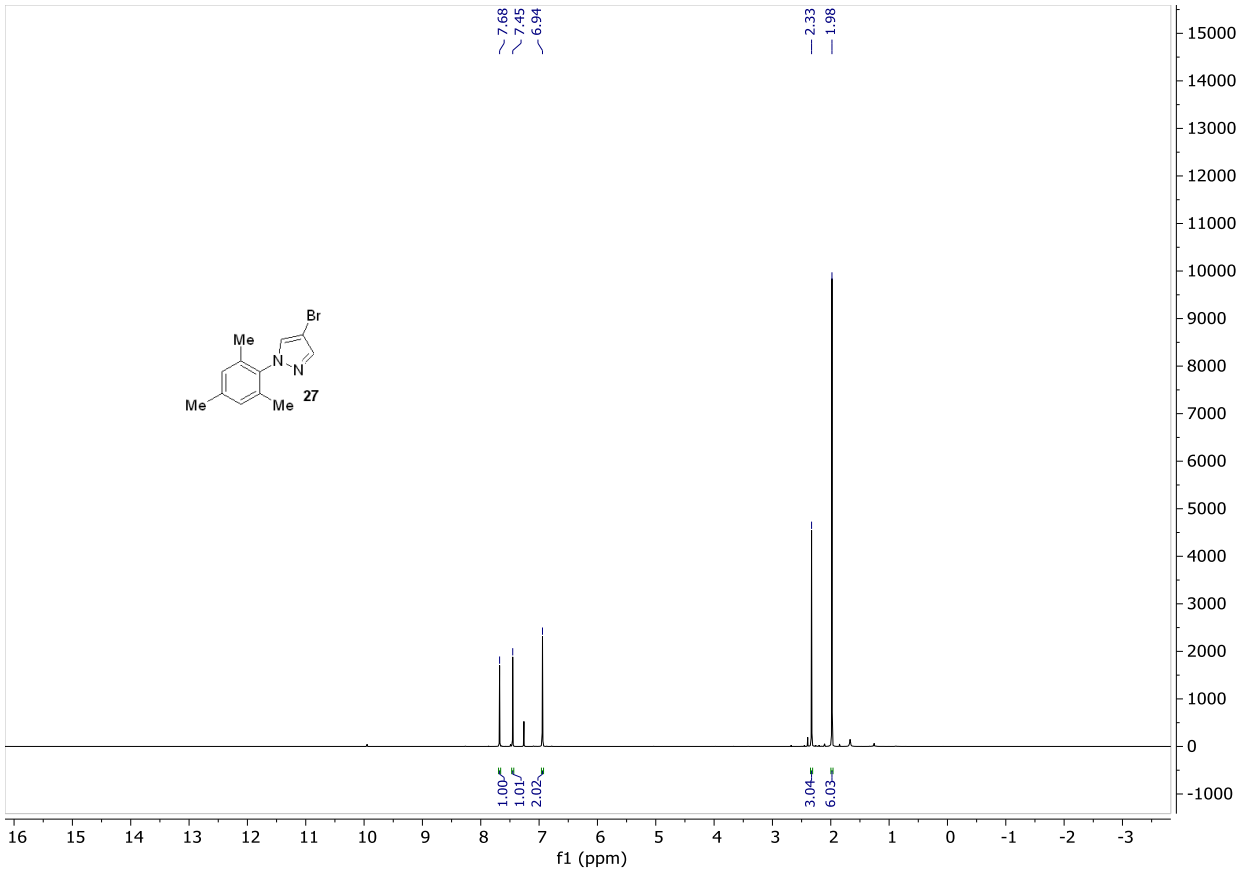
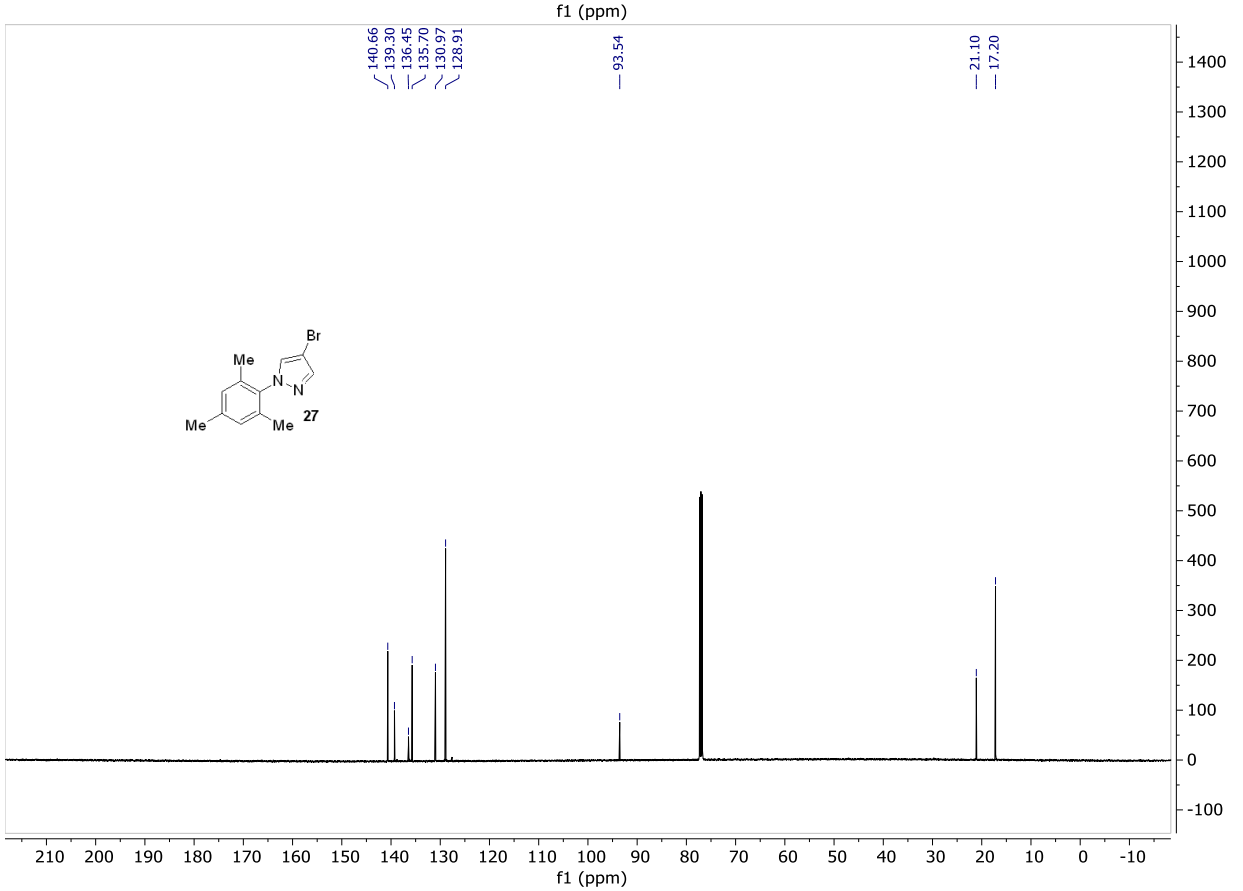
1.00
2.00
1.01
3.04
6.07
f1 (ppm)

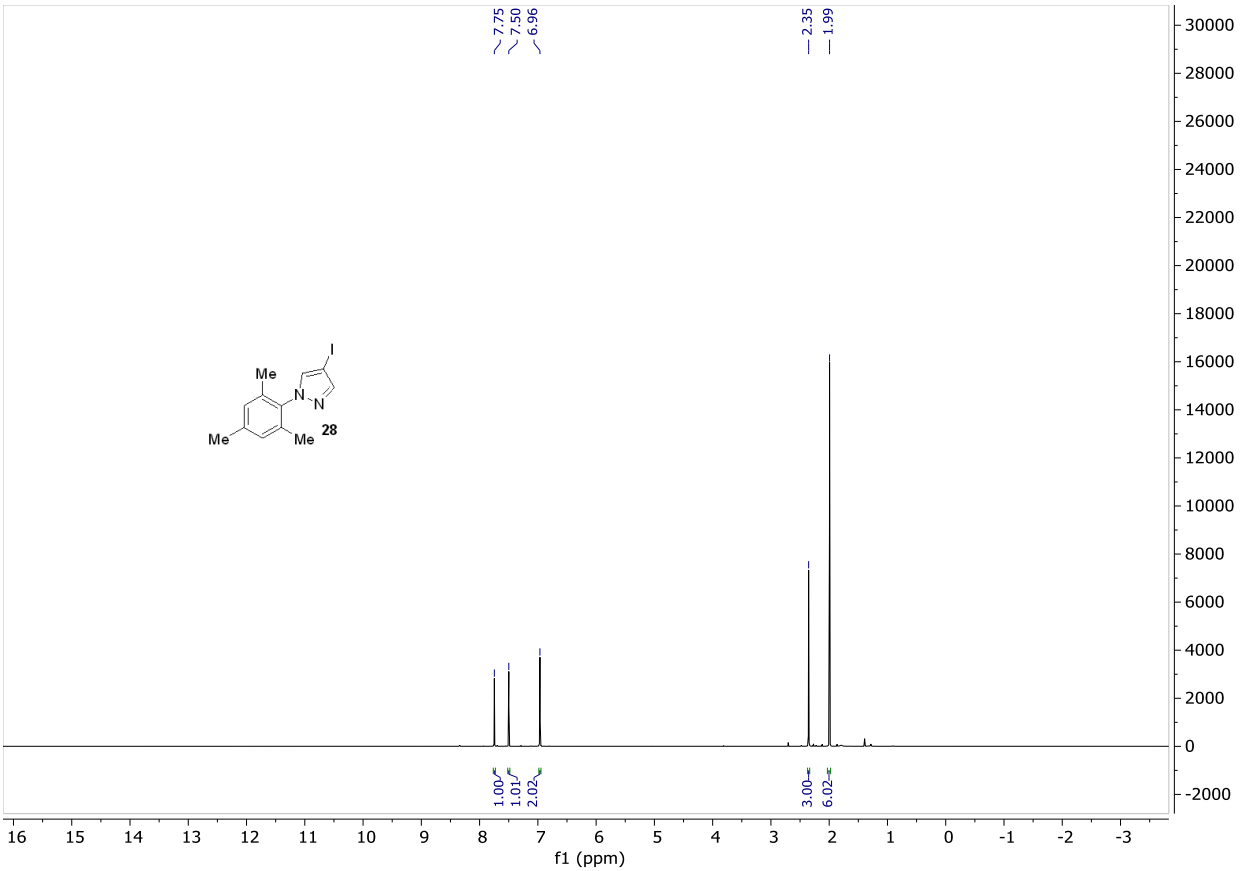

139.97
138.72
136.97
135.87
130.84
128.76
105.74
21.09
17.20
Me
Me
Me
25
f1 (ppm)

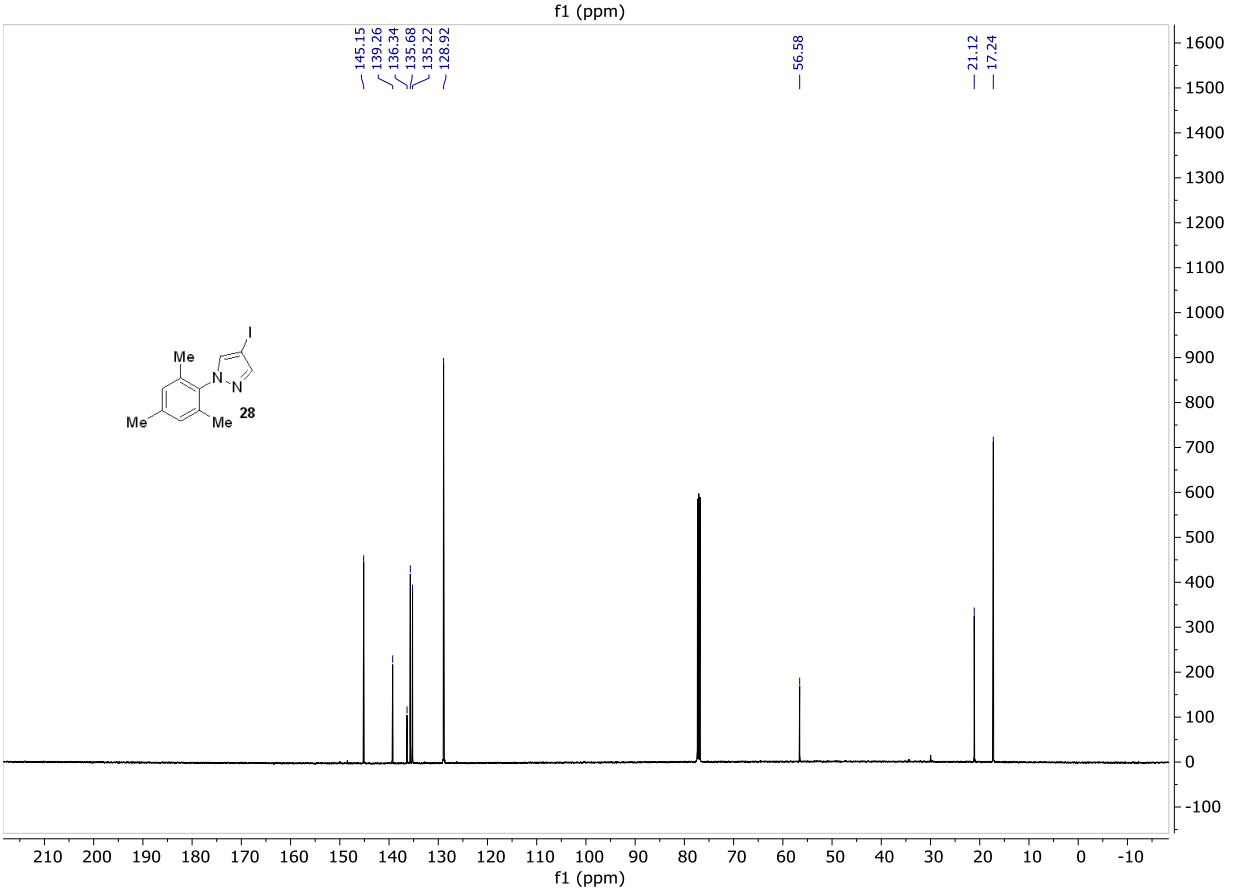

7.64
7.42
6.94
2.33
1.98
Cl
Me
N
N
Me
Me
26
1.00
1.01
2.03
3.04
6.04
f1 (ppm)

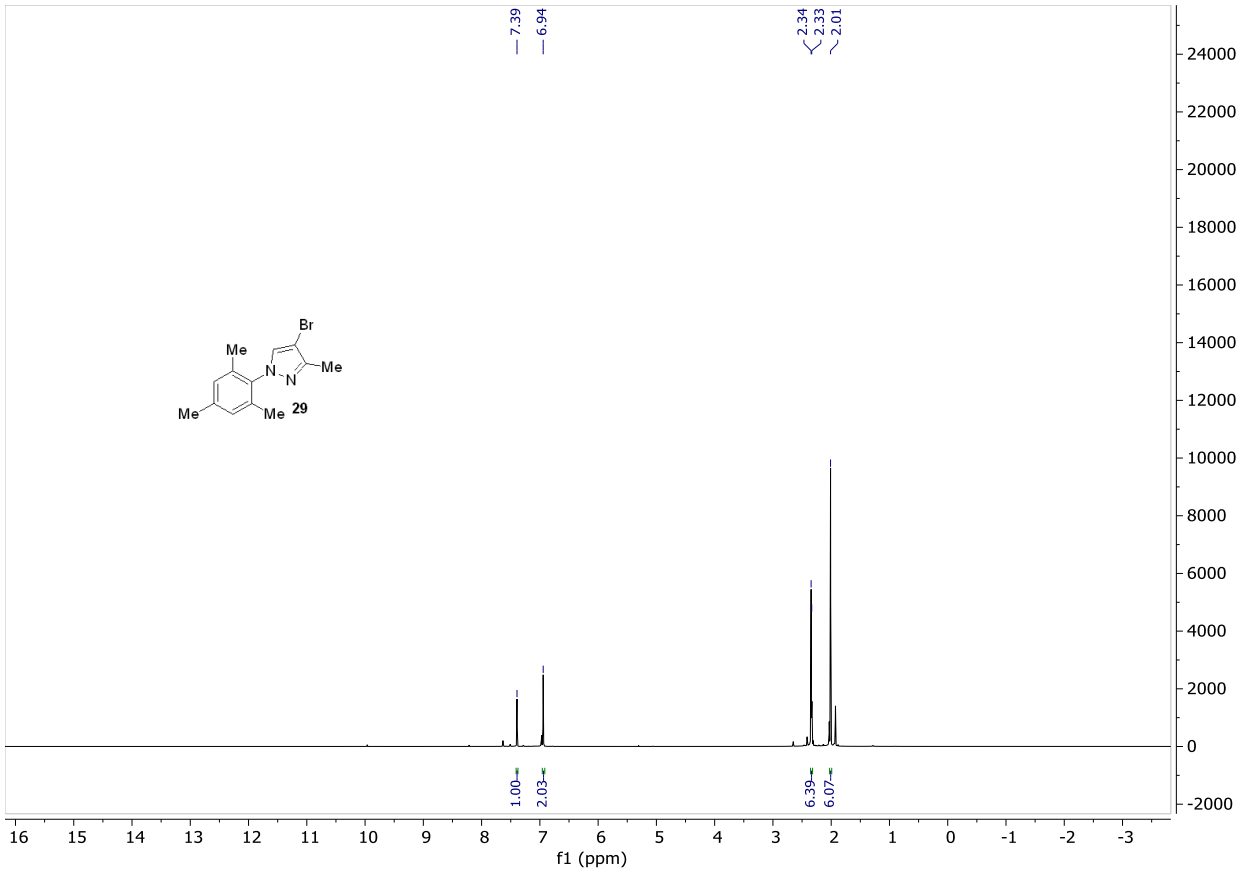

139.29
138.55
136.51
135.72
128.91
128.84
110.40
21.10
17.18
Cl
Me
N
N
Me
Me
26
f1 (ppm)

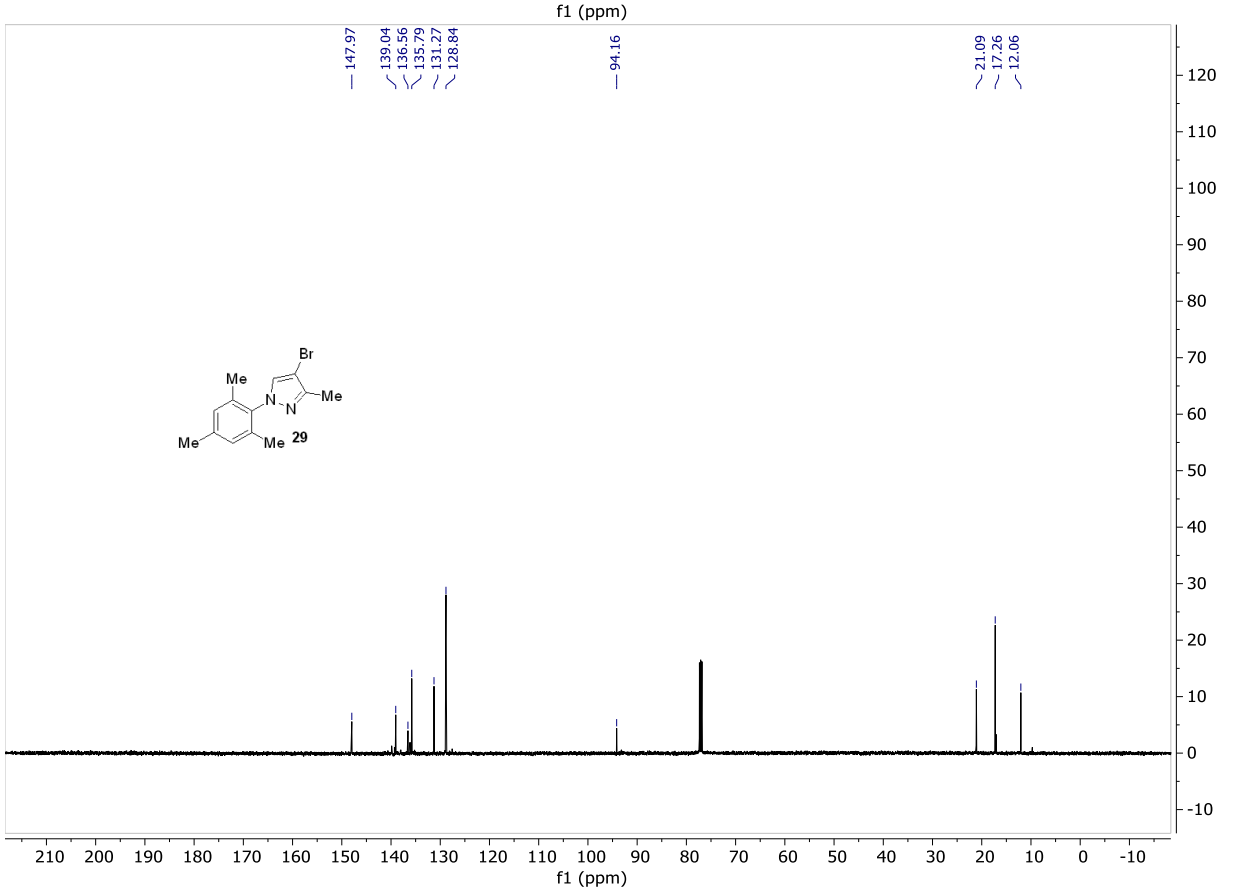

7.68
7.45
6.94
2.33
1.98
Br
Me
N
N
Me
Me
27
1.00
1.01
2.02
3.04
6.03
f1 (ppm)

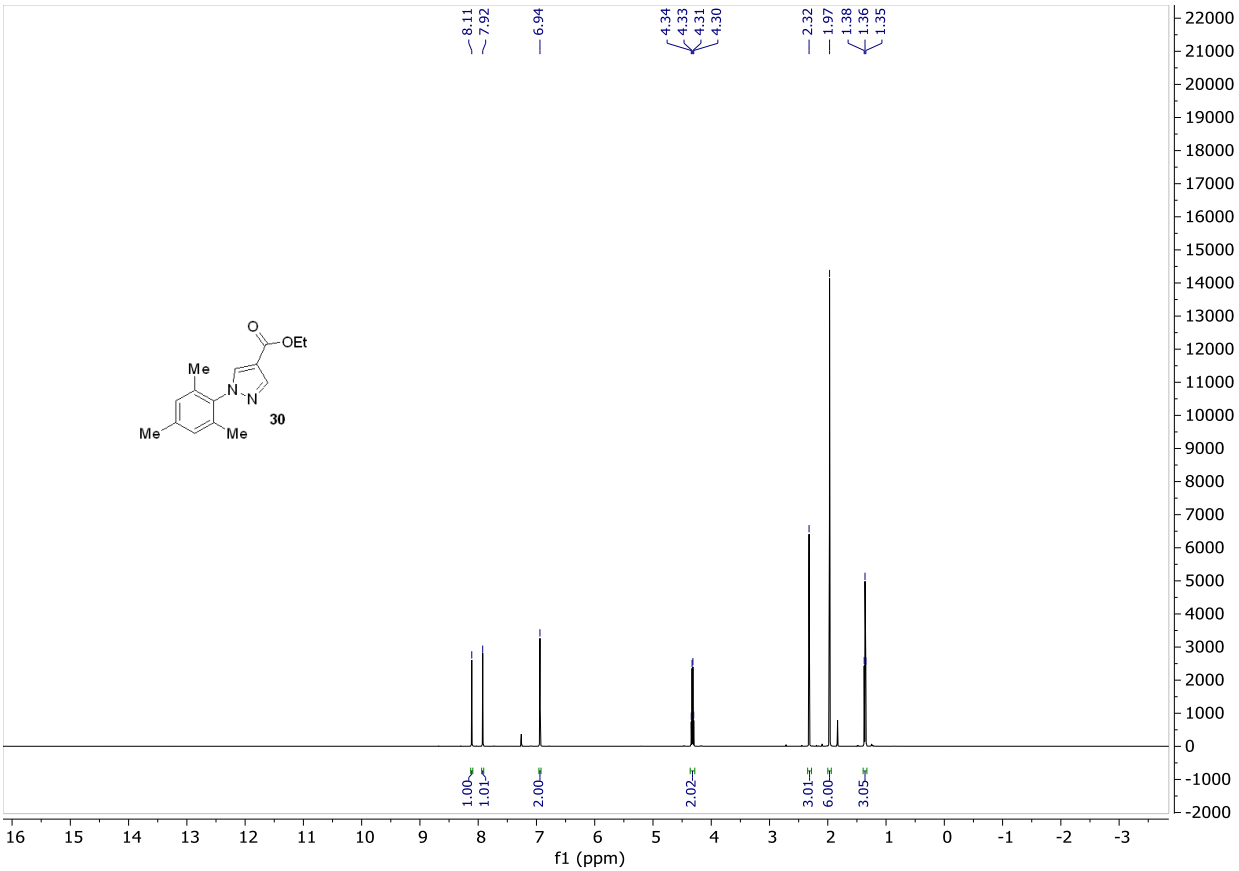

140.66
139.30
136.45
135.70
130.97
128.91
93.54
21.10
17.20
Br
Me
N
N
Me
Me
27
f1 (ppm)

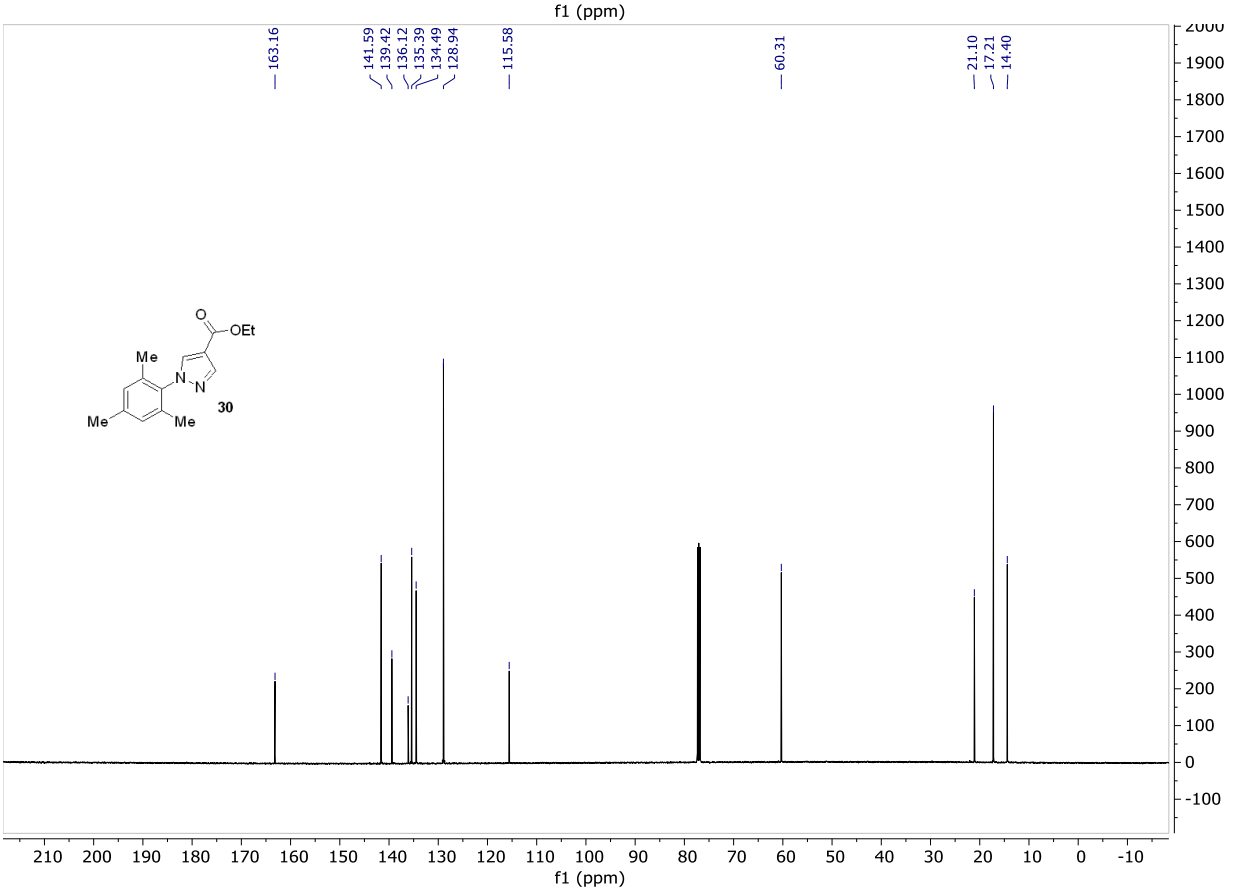

7.75
7.50
6.96
2.35
1.99
Me
Me
Me
I
N
N
28
1.00
1.01
2.02
3.00
6.02
f1 (ppm)

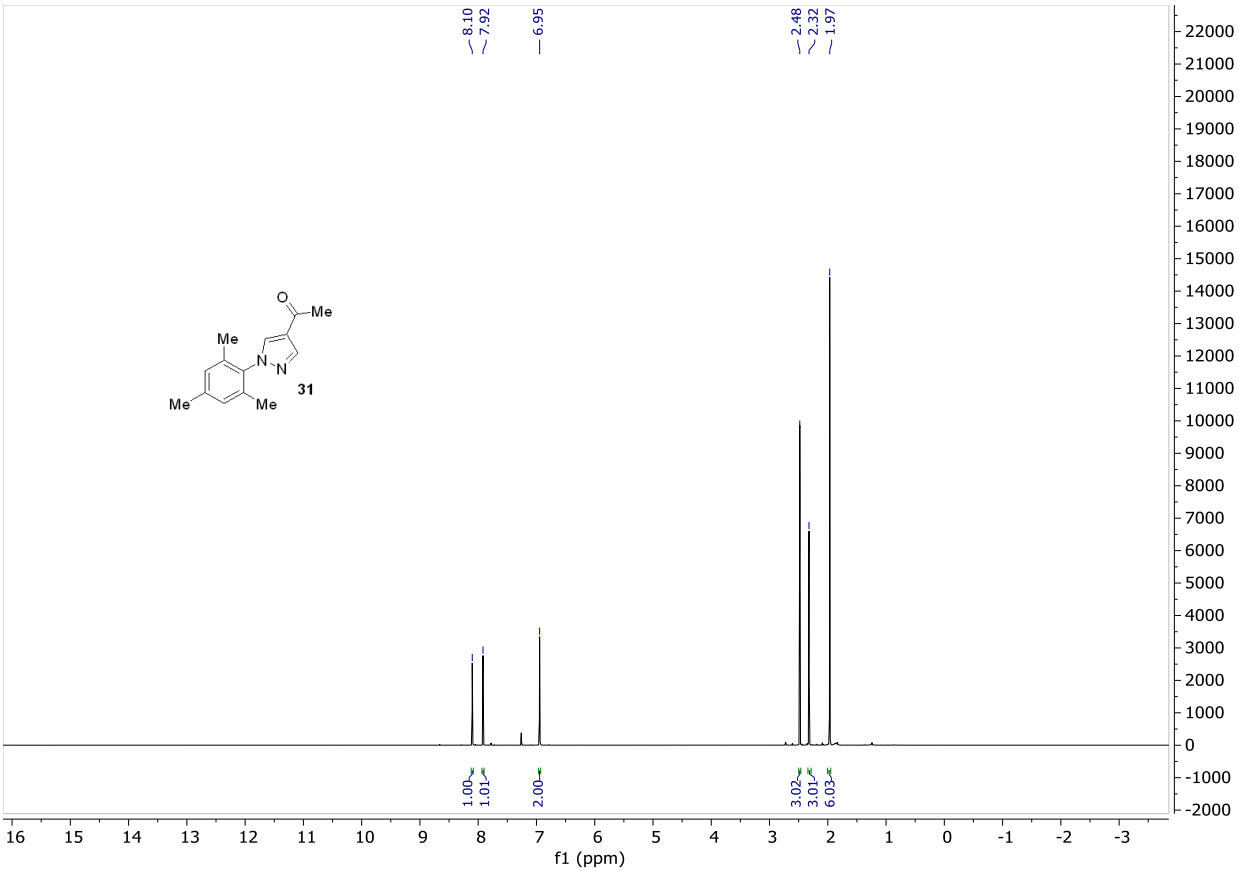

145.15
139.26
136.34
135.68
135.22
128.92
56.58
21.12
17.24
Me
Me
Me
I
N
N
28
f1 (ppm)

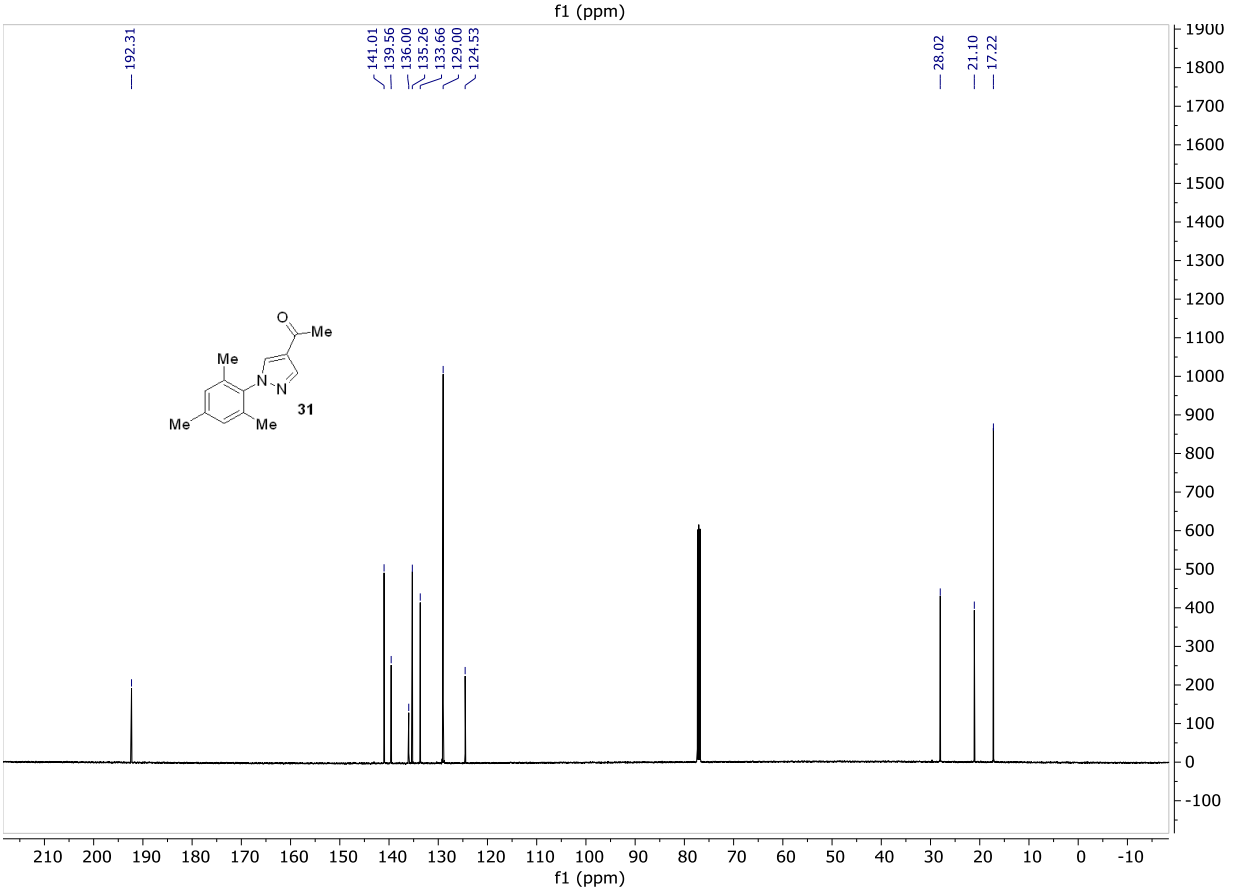

7.39
6.94
2.34
2.33
2.01
Br
Me
Me
N
N
Me
Me
Me
29
1.00
2.03
6.39
6.07
f1 (ppm)

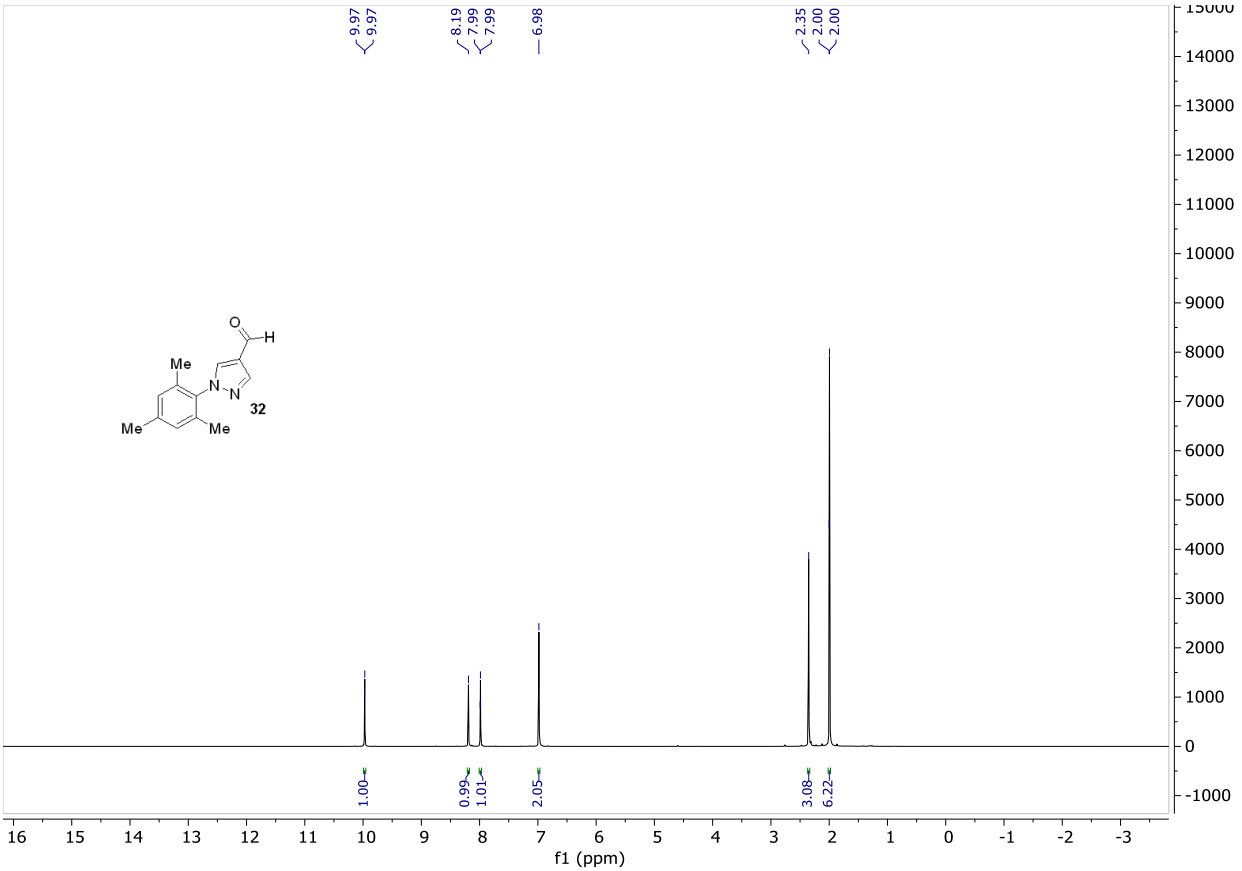

147.97
139.04
136.56
135.79
131.27
128.84
94.16
21.09
17.26
12.06
Br
Me
Me
N
N
Me
Me
Me
29
f1 (ppm)

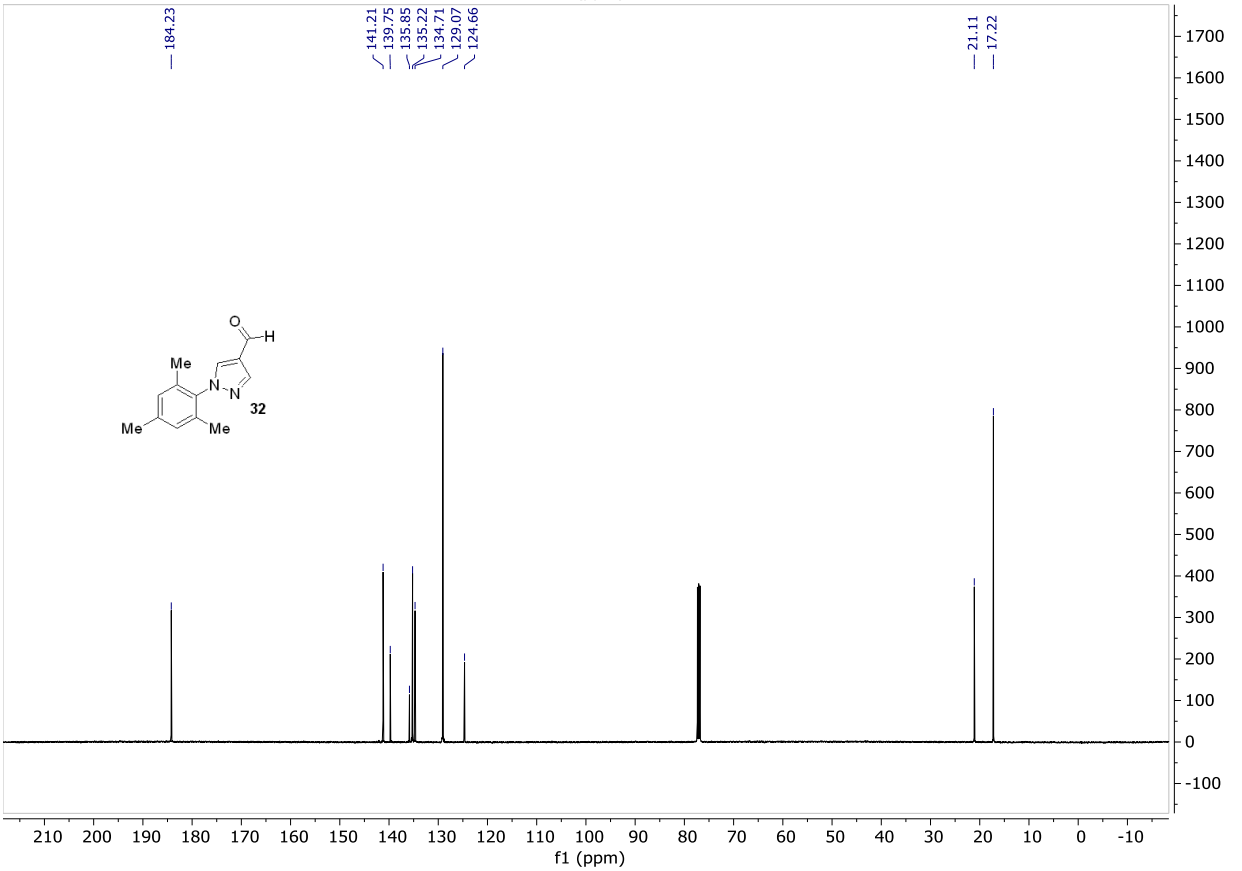

8.11
7.92
6.94
4.34
4.33
4.31
4.30
2.32
1.97
1.38
1.36
1.35
O
OEt
Me
N
N
Me
Me
30
1.00
1.01
2.00
2.02
3.01
6.00
3.05
f1 (ppm)

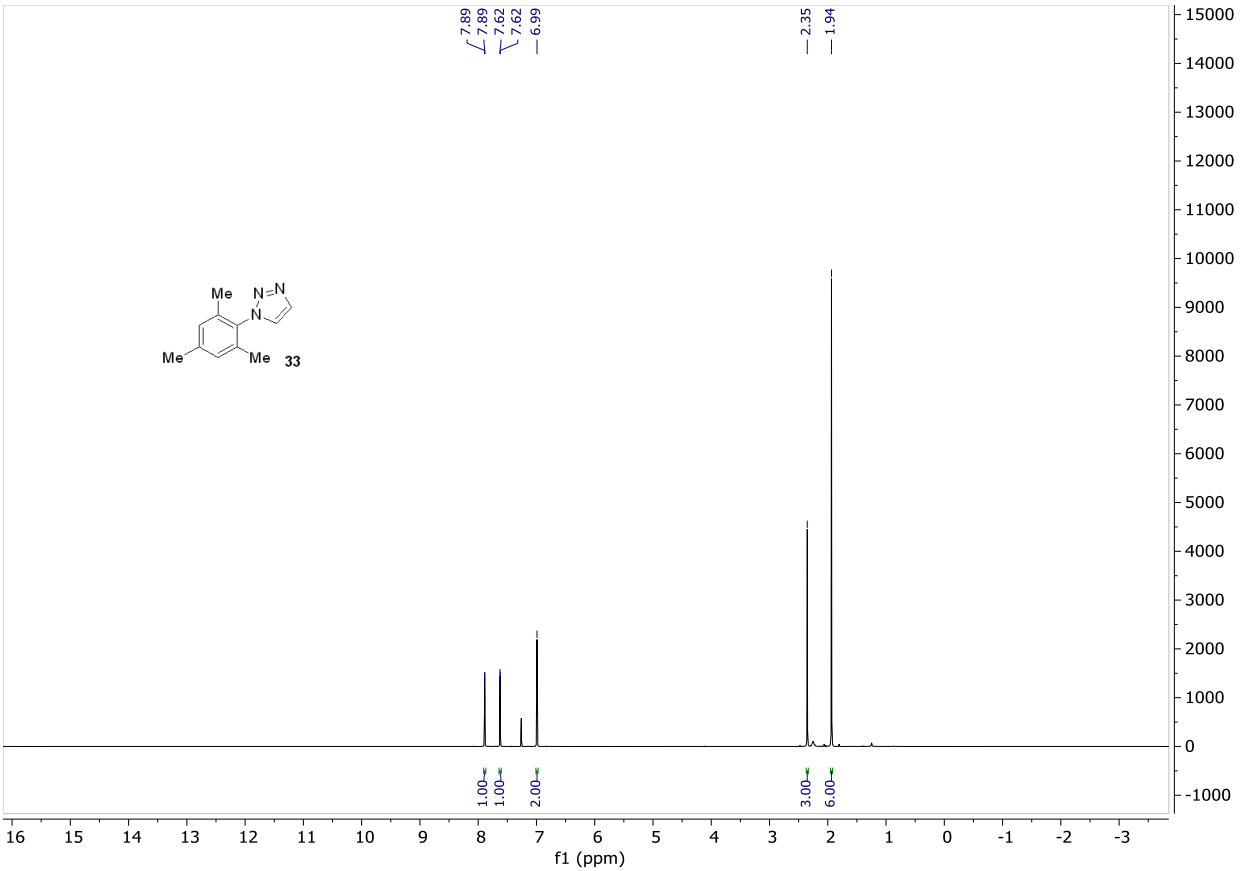

163.16
141.59
139.42
136.12
135.39
134.49
128.94
115.58
60.31
21.10
17.21
14.40
O
OEt
Me
N
N
Me
Me
30
f1 (ppm)

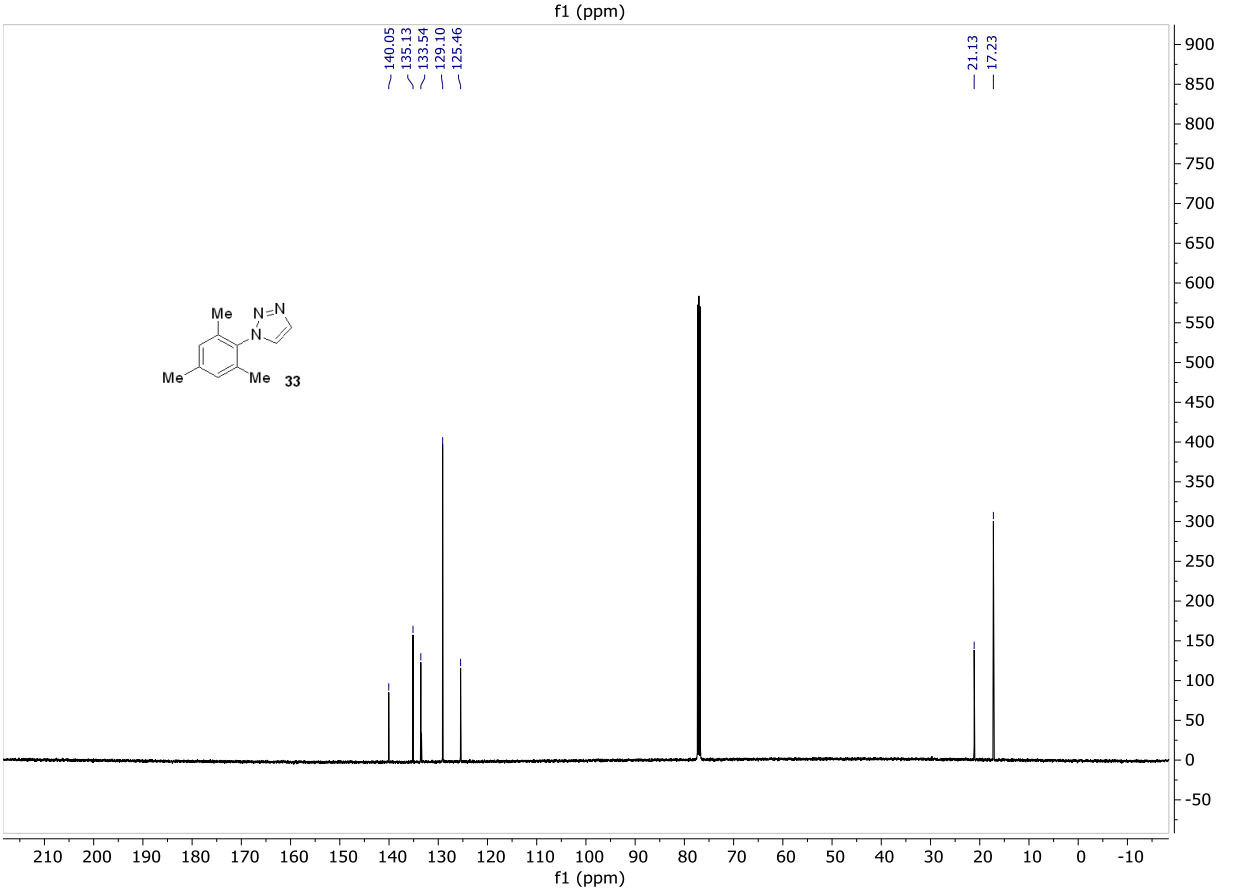

8.10
7.92
6.95
2.48
2.32
1.97
Me
Me
Me
Me
N
N
O
31
1.00
1.01
2.00
3.02
3.01
6.03
f1 (ppm)

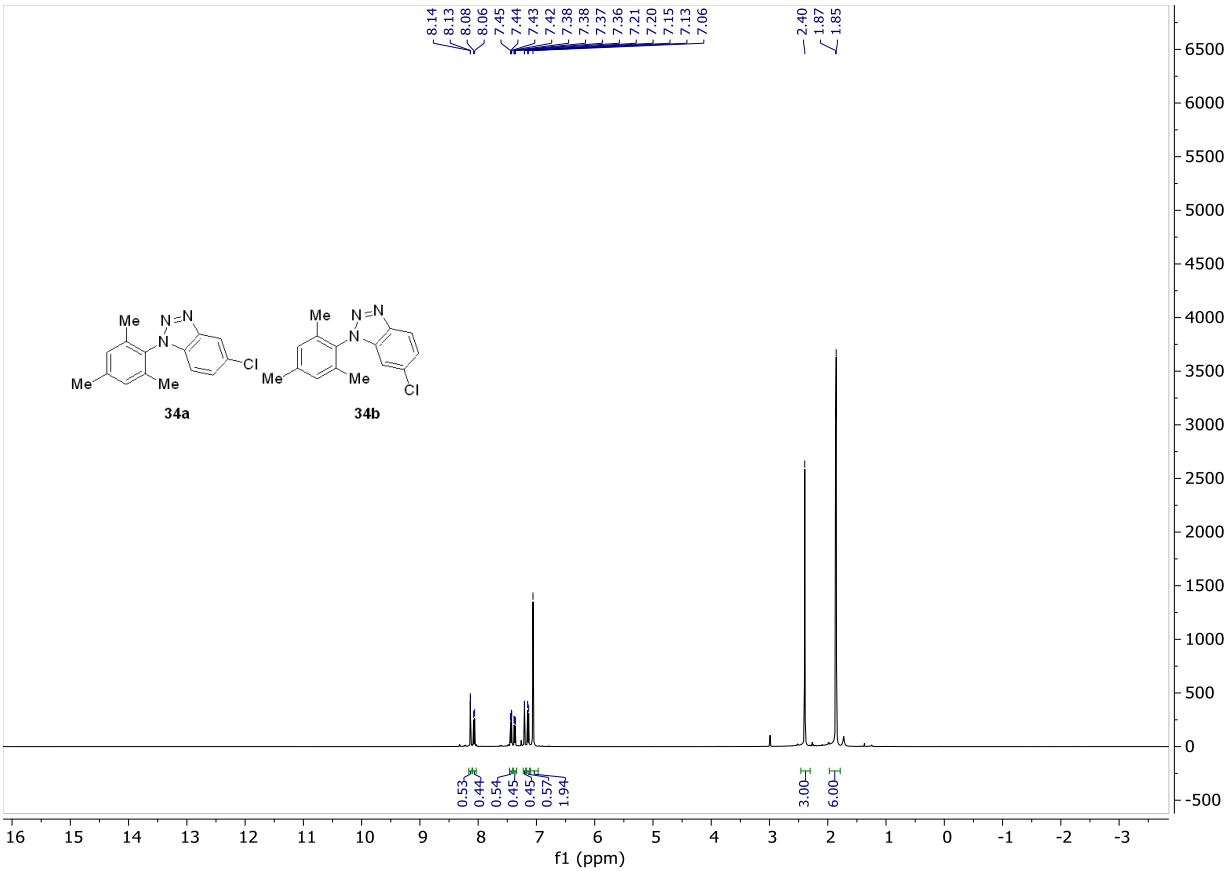

192.31
141.01
139.56
136.00
135.26
133.66
129.00
124.53
28.02
21.10
17.22
Me
Me
Me
Me
N
N
O
31
f1 (ppm)

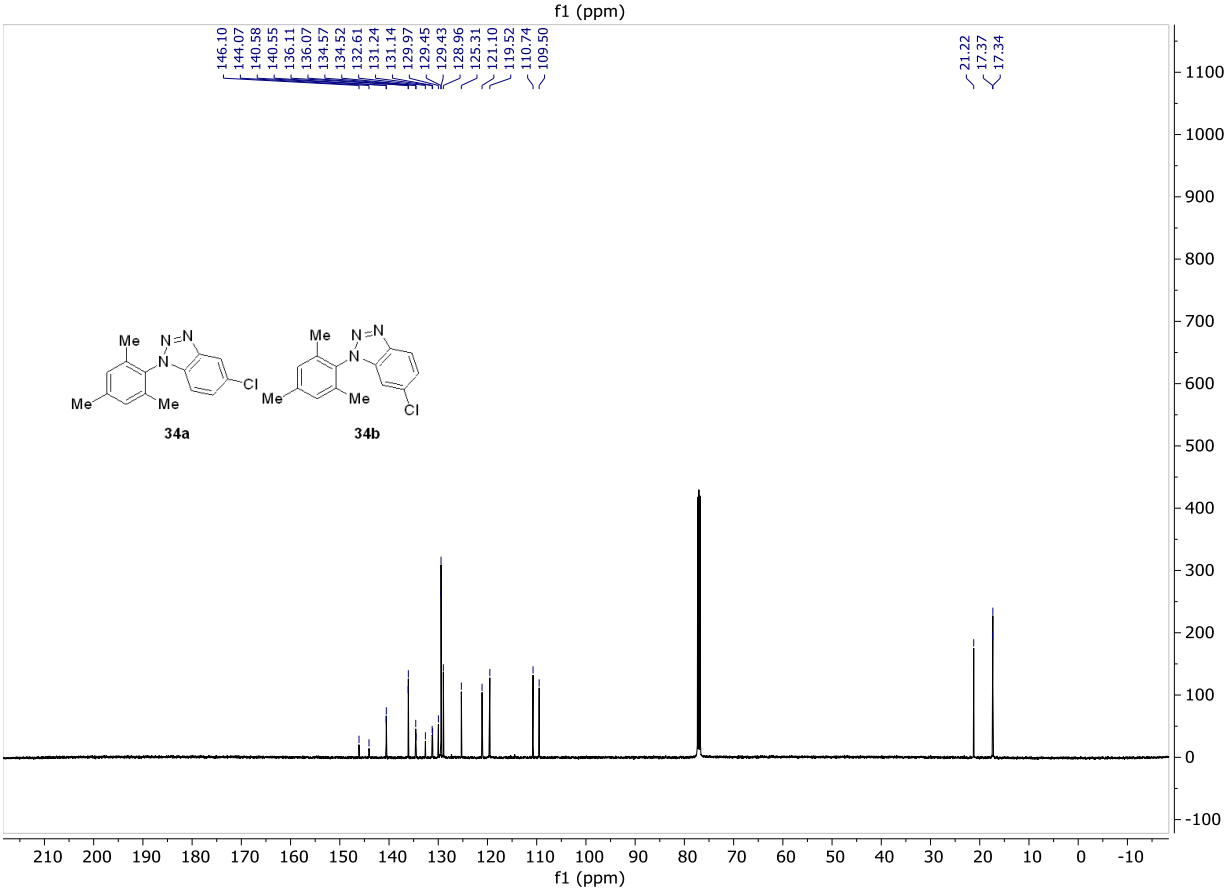

9.97
9.97
8.19
7.99
7.99
6.98
2.35
2.00
2.00
Me
Me
Me
32
1.00
0.99
1.01
2.05
3.08
6.22
f1 (ppm)


184.23
141.21
139.75
135.85
135.22
134.71
129.07
124.66
21.11
17.22
Me
Me
Me
32
f1 (ppm)


7.89
7.89
7.62
7.62
6.99
2.35
1.94
Me
Me
Me
33
1.00
1.00
2.00
3.00
6.00
f1 (ppm)


140.05
135.13
133.54
129.10
125.46
21.13
17.23
Me
Me
Me
33
f1 (ppm)


8.14
8.13
8.08
8.06
7.45
7.44
7.43
7.42
7.38
7.38
7.37
7.36
7.21
7.20
7.15
7.13
7.06
2.40
1.87
1.85
Me
N=N
N
Cl
Me
Me
34a
Me
N=N
N
Cl
Me
Me
34b
0.53
0.44
0.54
0.45
0.45
0.57
1.94
3.00
6.00
f1 (ppm)


146.10
144.07
140.58
140.55
136.11
136.07
134.57
134.52
132.61
131.24
131.14
129.97
129.45
129.43
128.96
125.31
121.10
119.52
110.74
109.50
21.22
17.37
17.34
Me
N=N
N
Cl
Me
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34a
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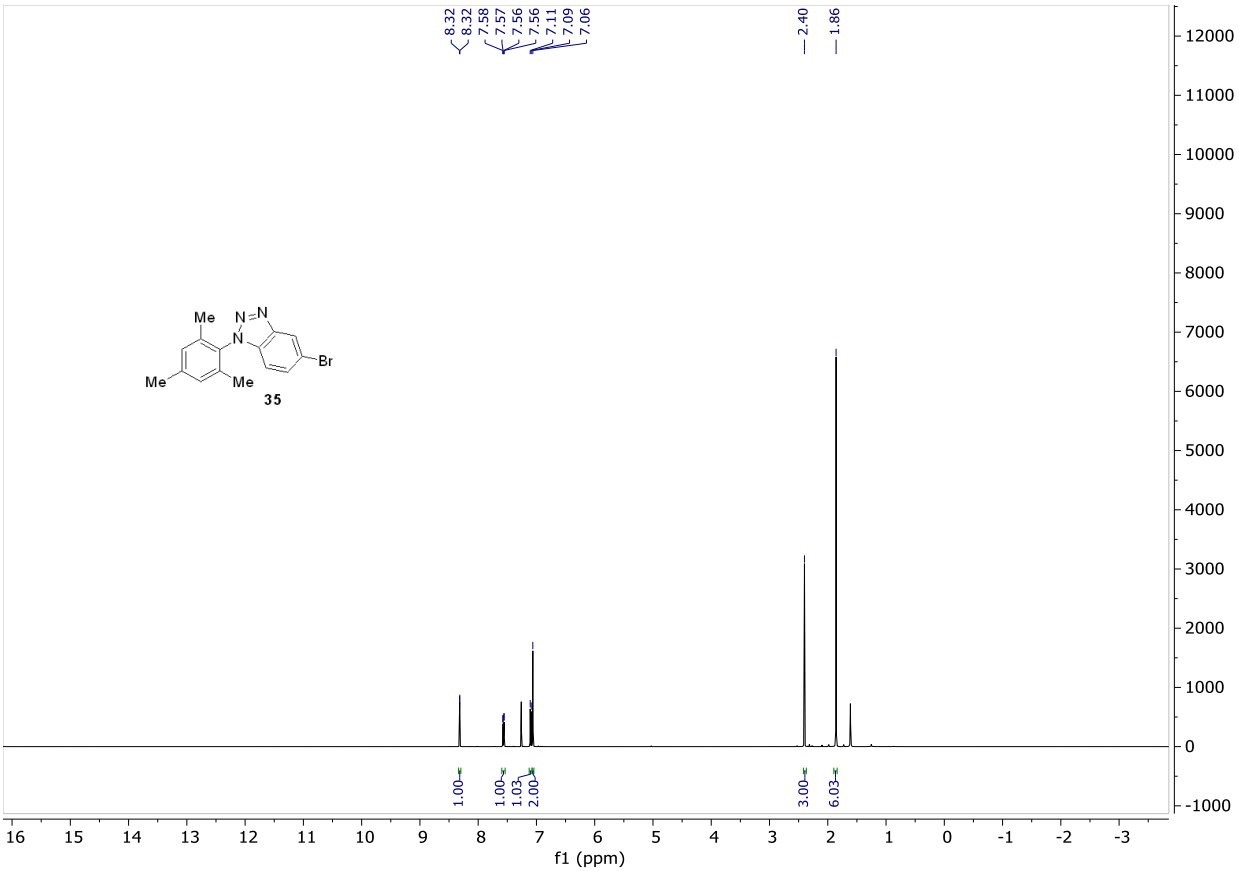
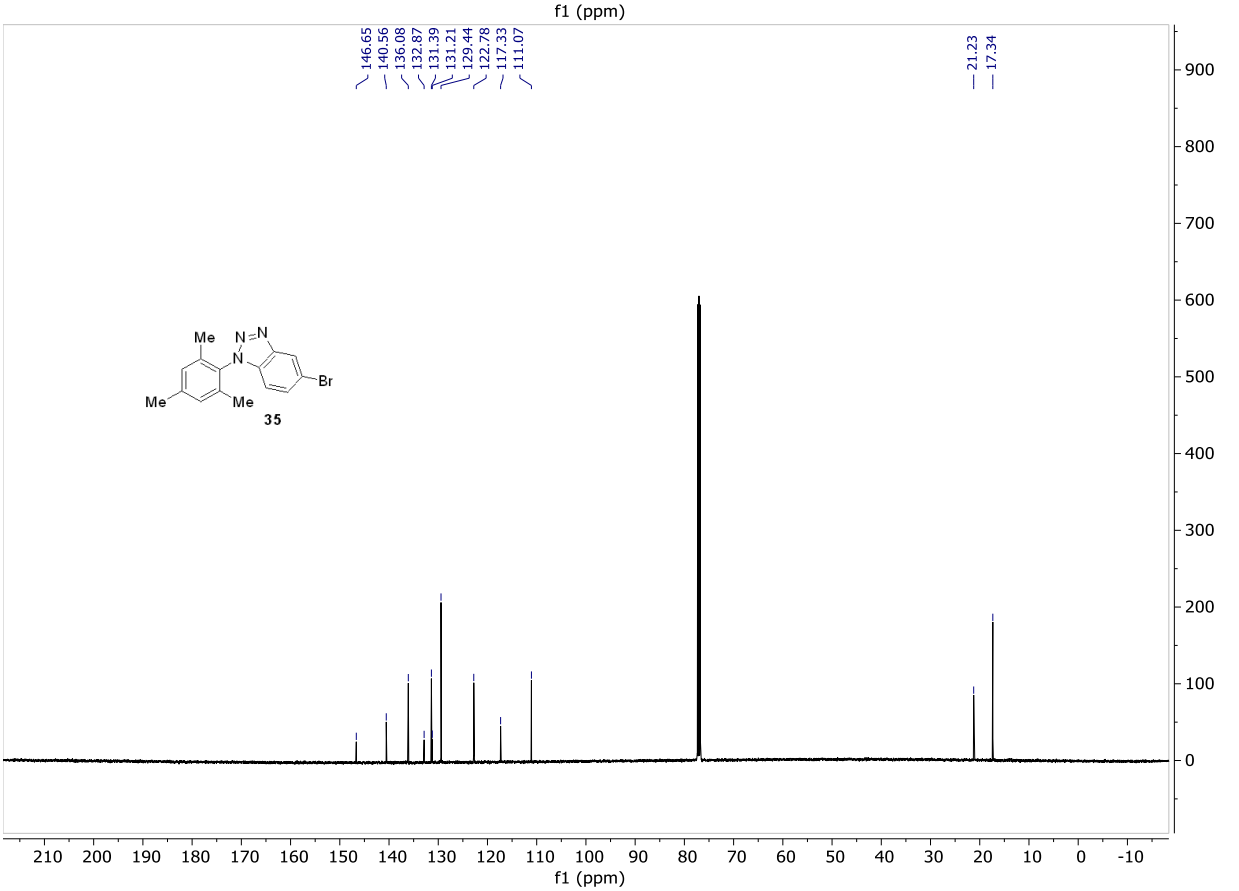
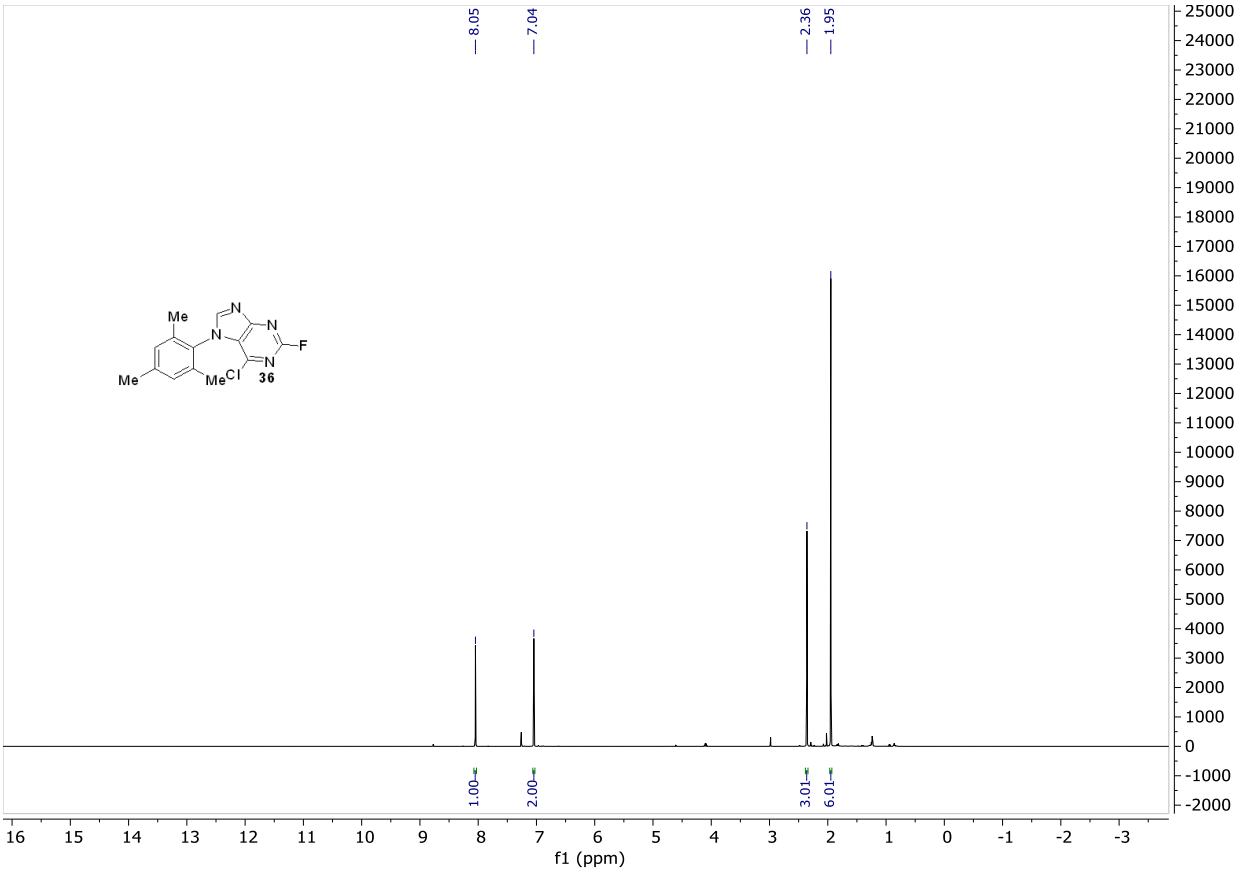
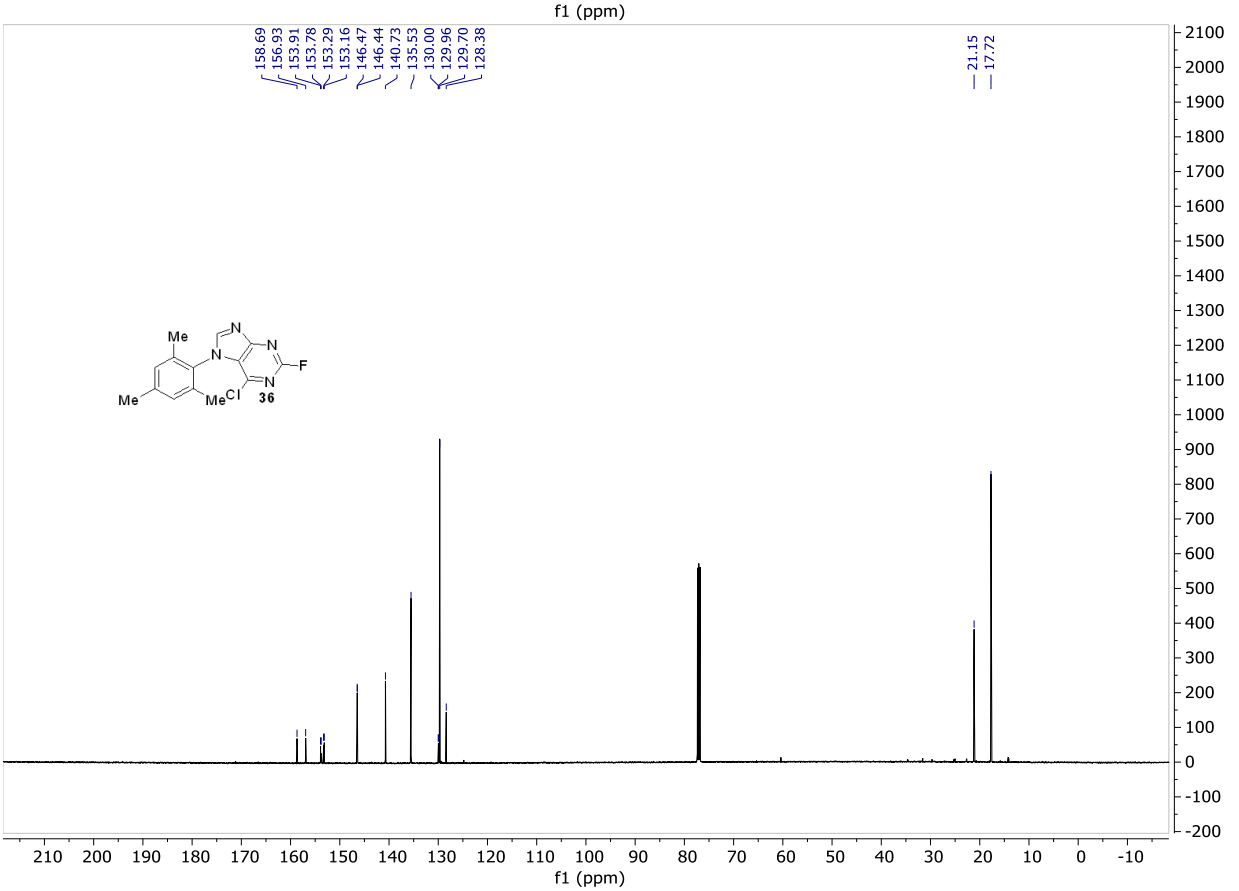
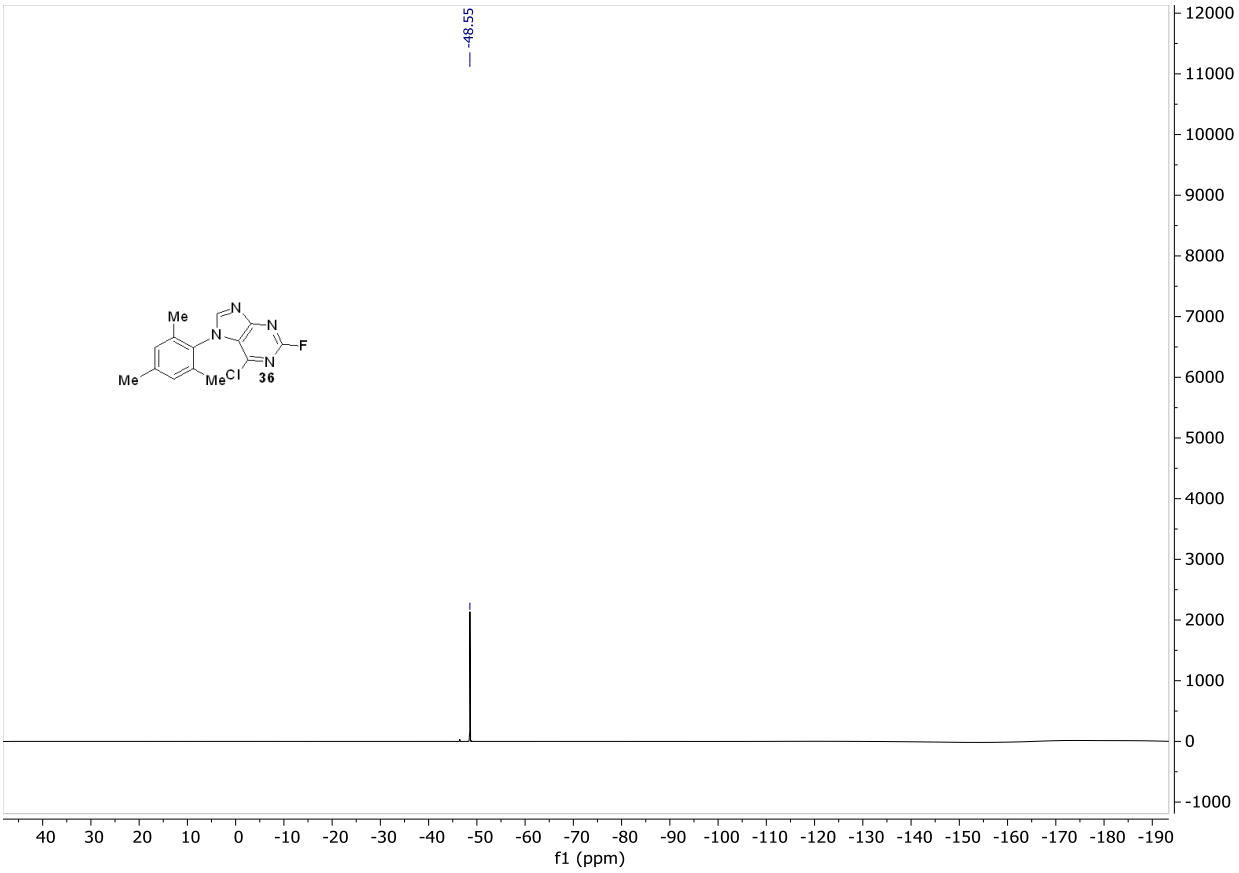
N=N
N
Cl
Me
Me
34b
f1 (ppm)

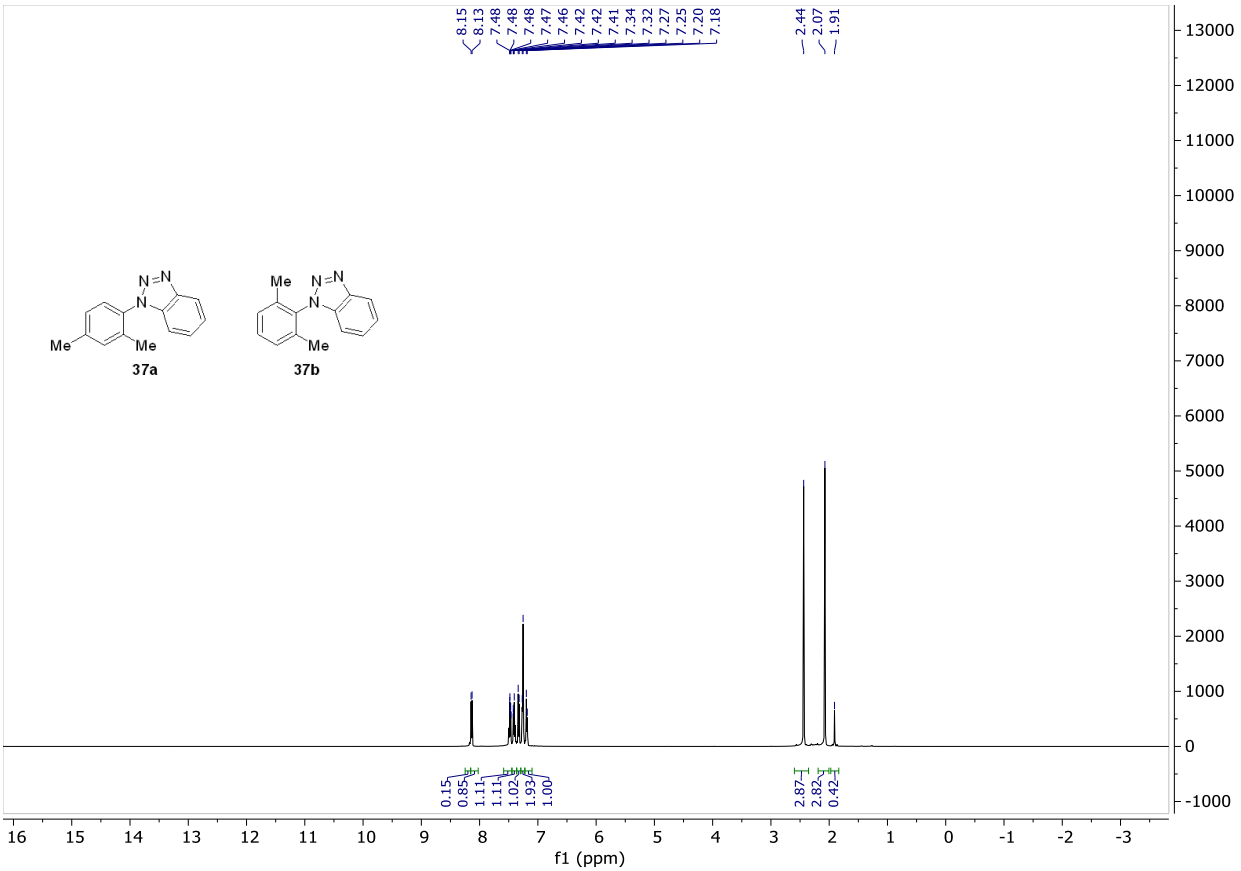

8.32
8.32
7.58
7.57
7.56
7.56
7.11
7.09
7.06
2.40
1.86
Me
N
N
Br
Me
Me
35
1.00
1.00
1.03
2.00
3.00
6.03
f1 (ppm)

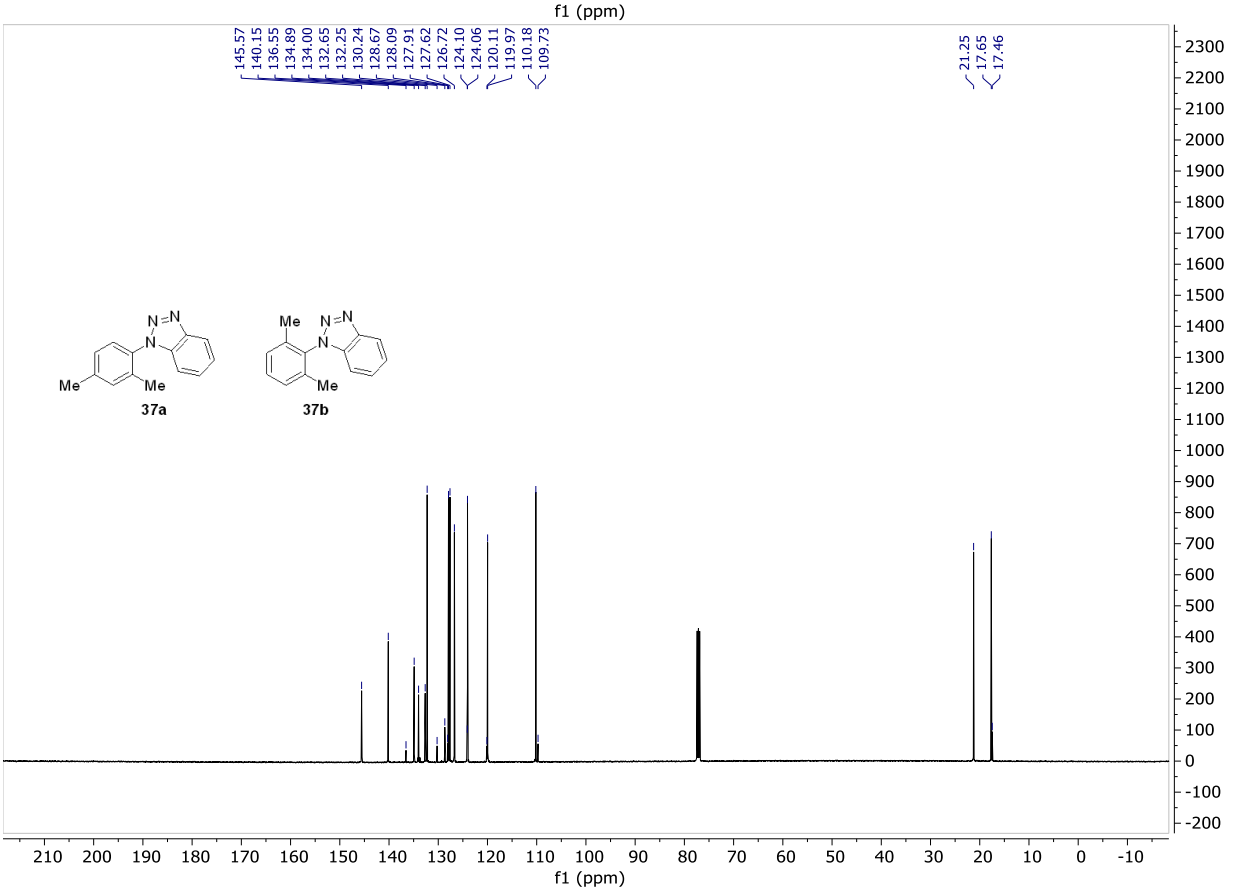

146.65
140.56
136.08
132.87
131.39
131.21
129.44
122.78
117.33
111.07
21.23
17.34
Me
N
N
Br
Me
Me
35
f1 (ppm)

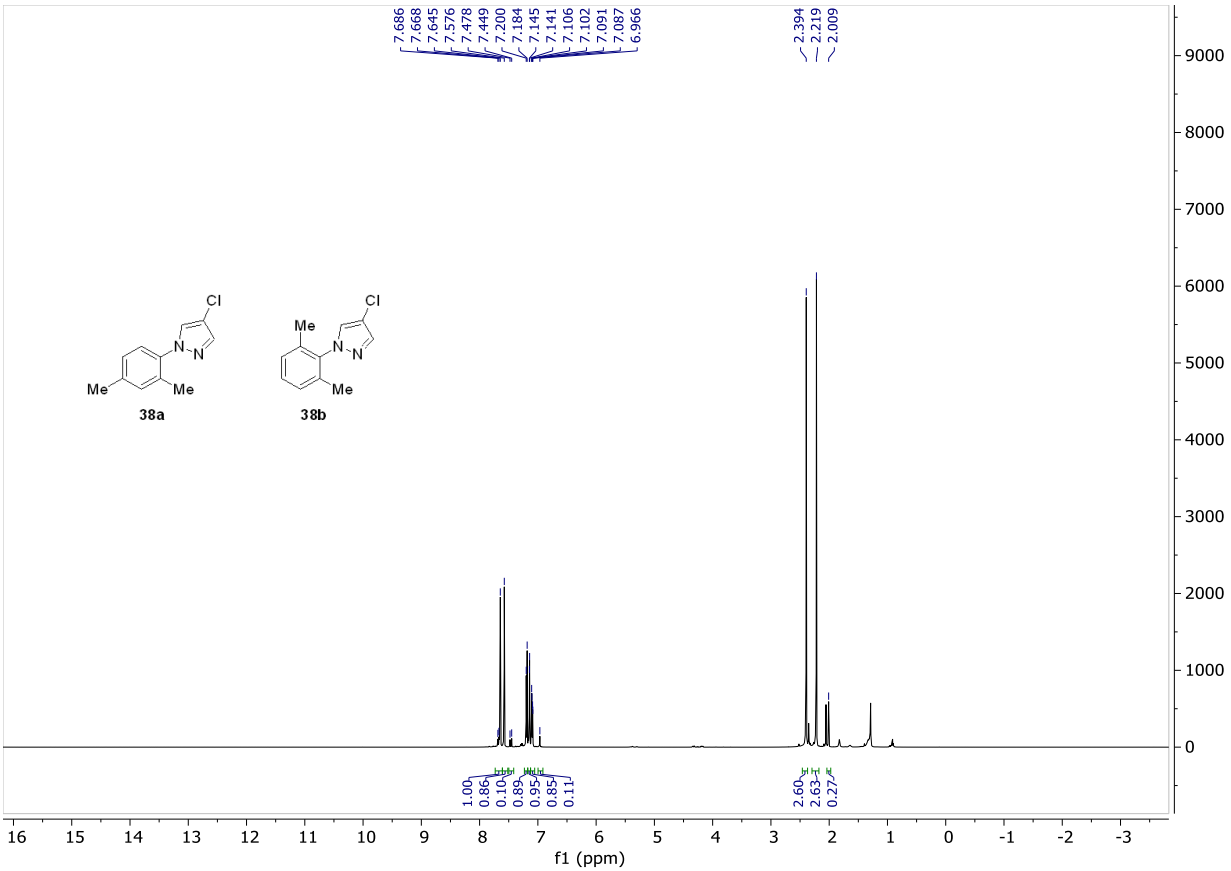

8.05
7.04
2.36
1.95
1.00
2.00
3.01
6.01
f1 (ppm)
Me
Me
Me
Cl
F
36

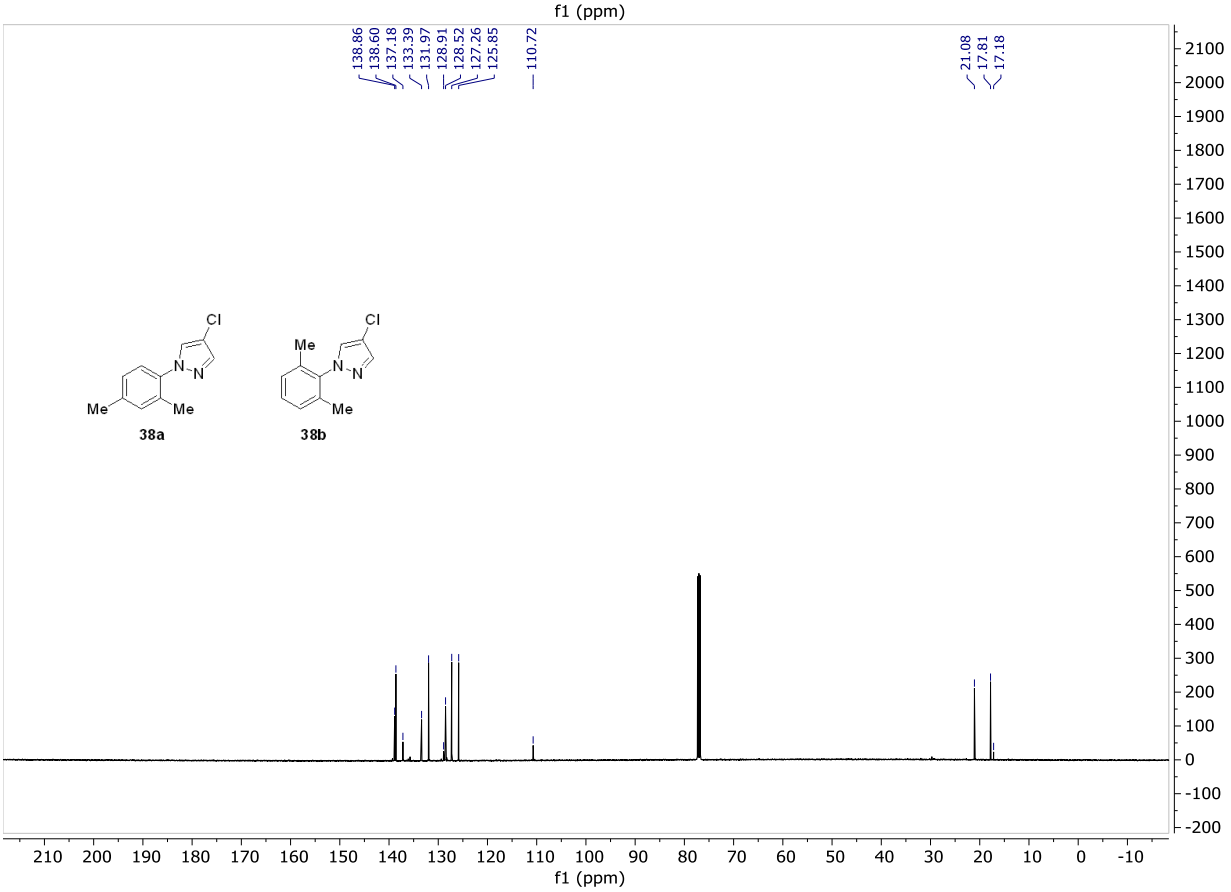

158.69
156.93
153.91
153.78
153.29
153.16
146.47
146.44
140.73
135.53
130.00
129.96
129.70
128.38
21.15
17.72
f1 (ppm)
Me
Me
Me
Cl
F
36

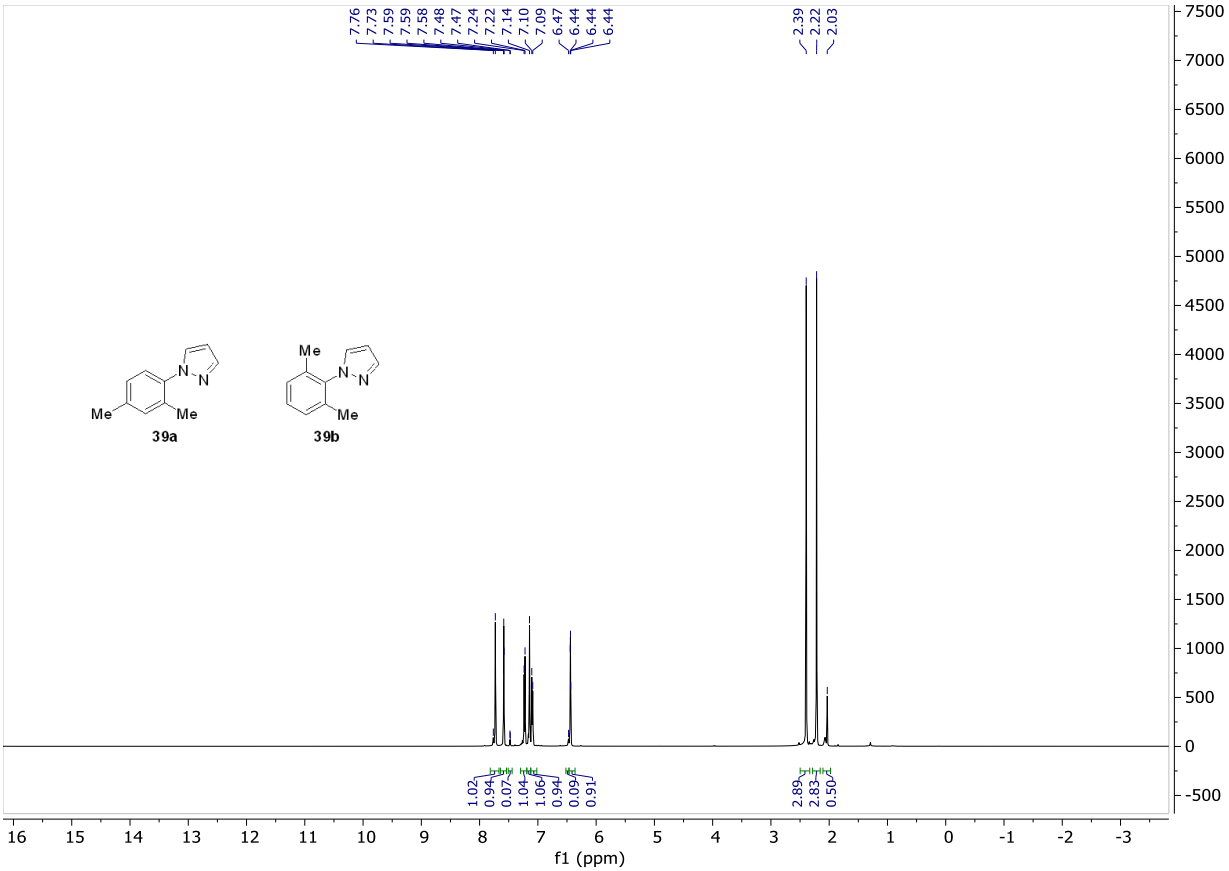

-48.55
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)
Me
N
N
N
F
Me
Me
Cl
36

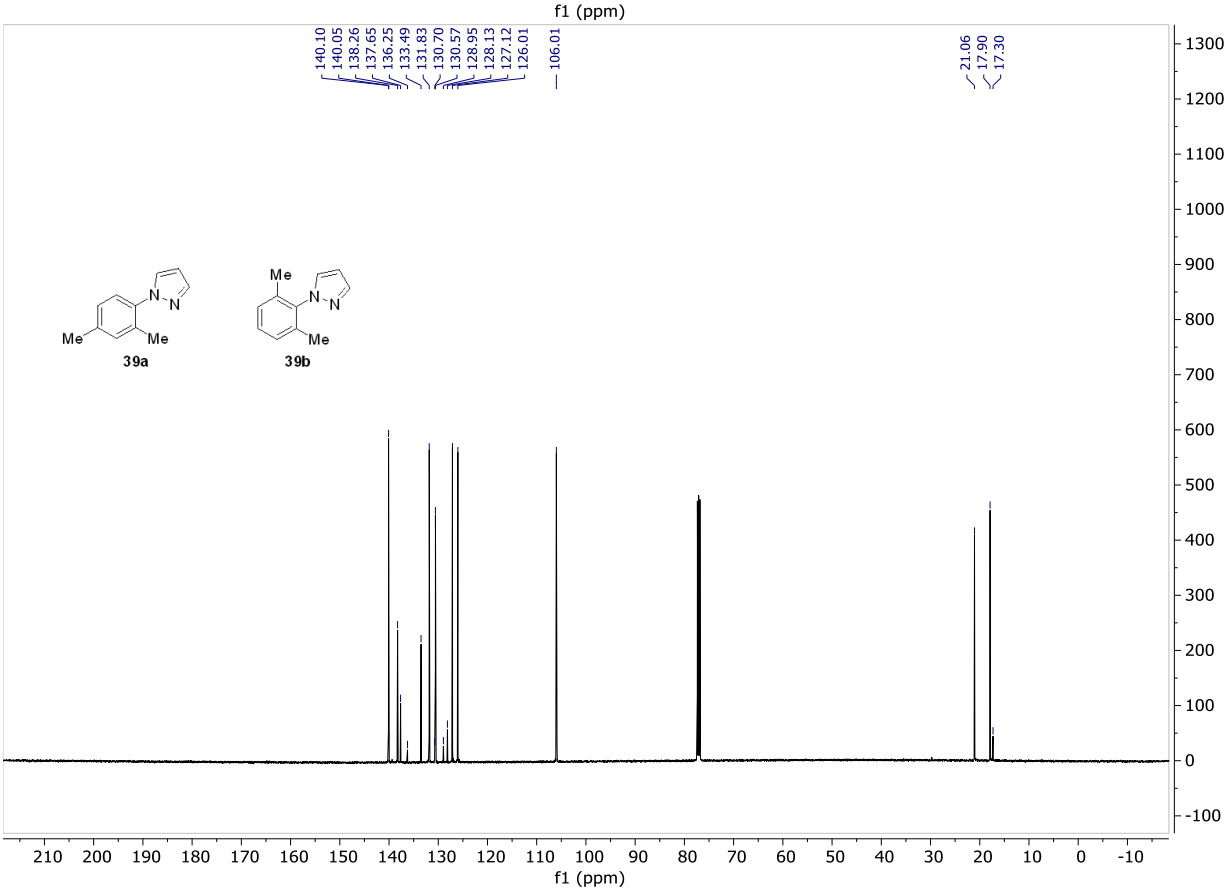

8.15
8.13
7.48
7.48
7.48
7.47
7.46
7.42
7.42
7.41
7.34
7.32
7.27
7.25
7.20
7.18
2.44
2.07
1.91
0.15
0.85
1.11
1.11
1.02
1.93
1.00
2.87
2.82
0.42
f1 (ppm)
37a
37b

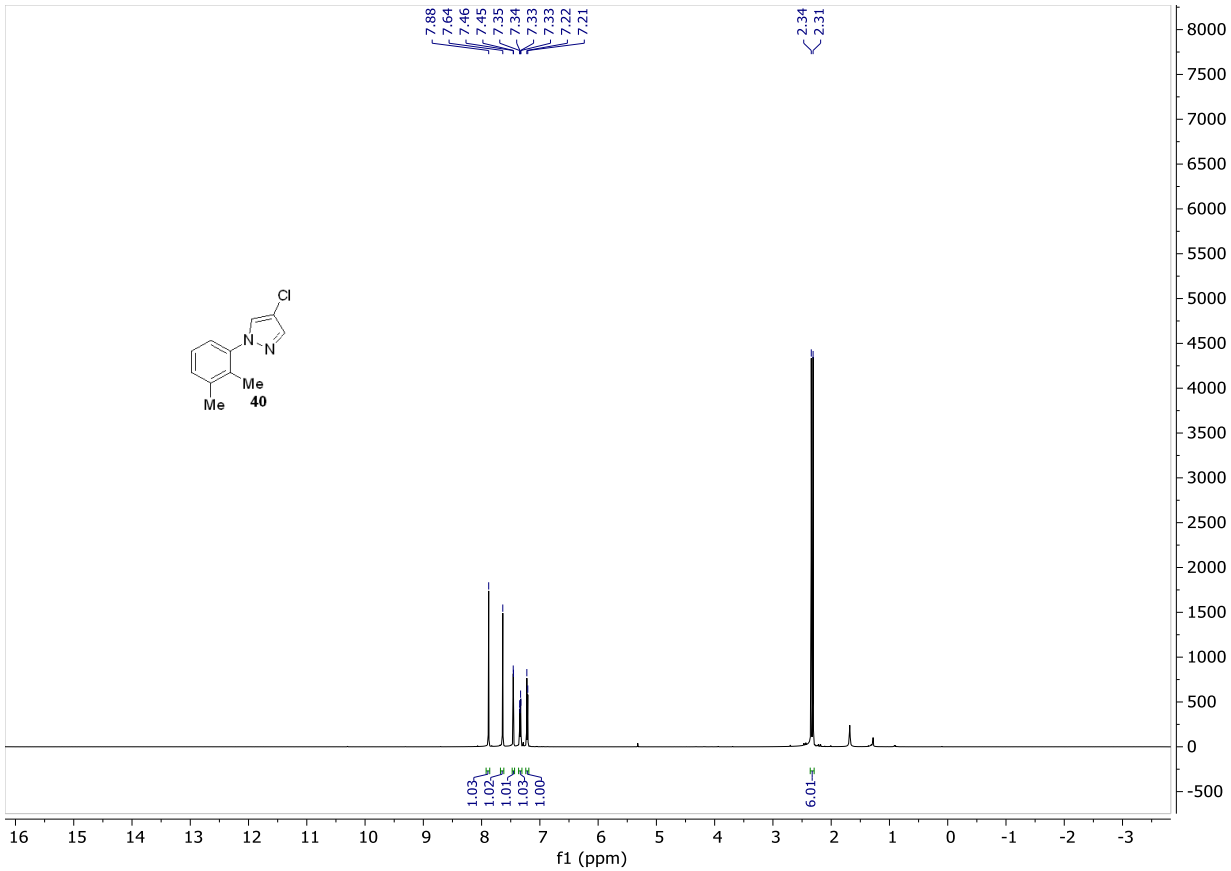

145.57
140.15
136.55
134.89
134.00
132.65
132.25
130.24
128.67
128.09
127.91
127.62
126.72
124.10
124.06
120.11
119.97
110.18
109.73
21.25
17.65
17.46
f1 (ppm)
37a
37b

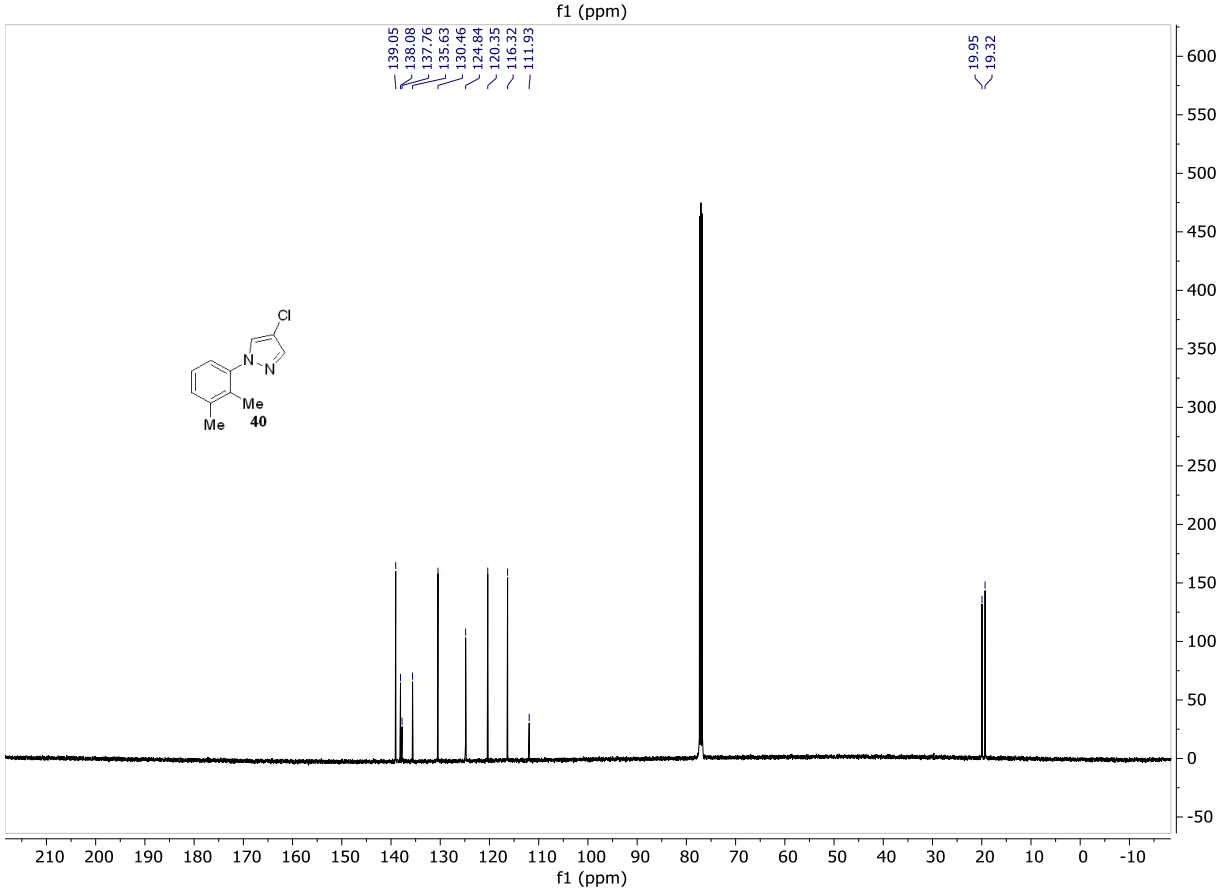

7.686
7.668
7.645
7.576
7.478
7.449
7.200
7.184
7.145
7.141
7.106
7.102
7.091
7.087
6.966
2.394
2.219
2.009
Cl
N
N
Me
Me
38a
Cl
Me
N
N
Me
38b
1.00
0.86
0.10
0.89
0.95
0.85
0.11
2.60
2.63
0.27
f1 (ppm)

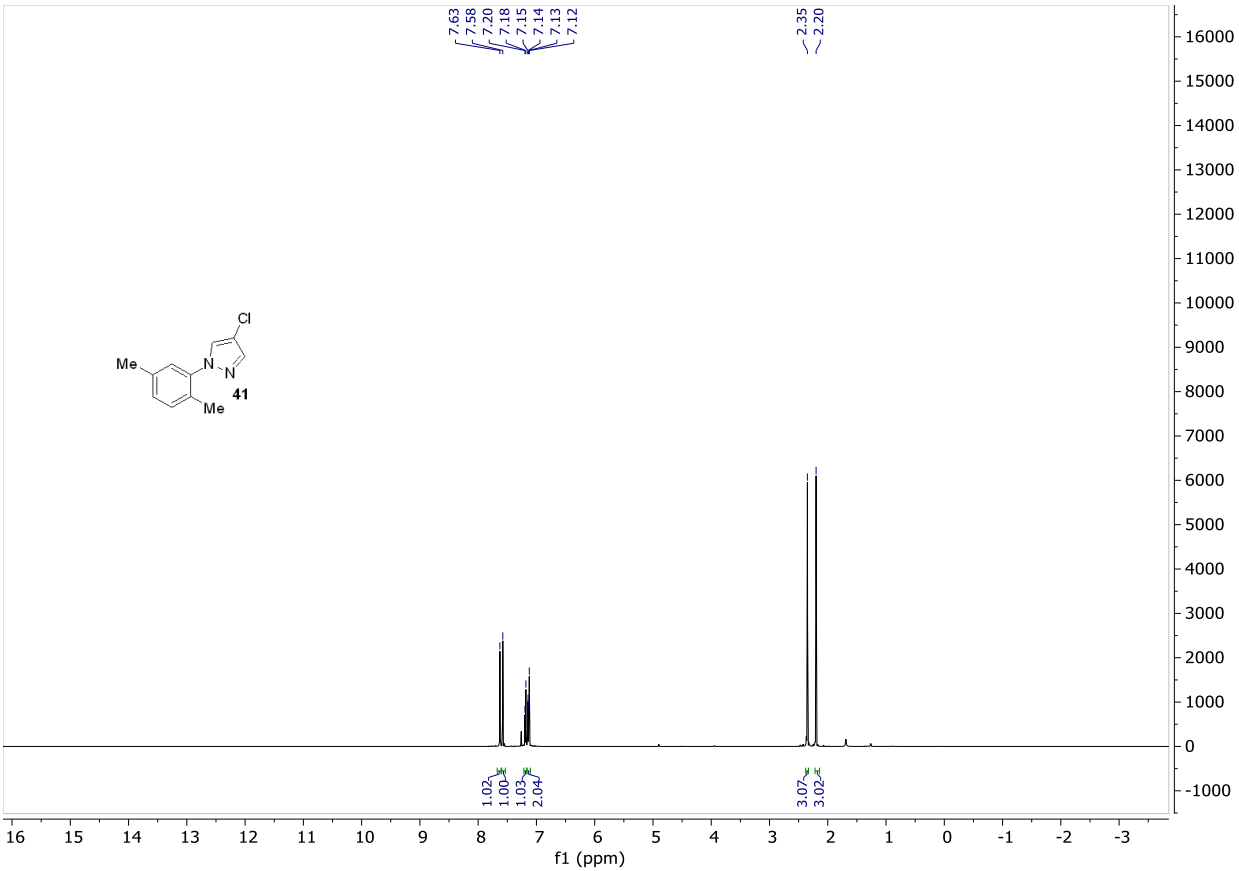

138.86
138.60
137.18
133.39
131.97
128.91
128.52
127.26
125.85
110.72
21.08
17.81
17.18
Cl
N
N
Me
Me
38a
Cl
Me
N
N
Me
38b
f1 (ppm)

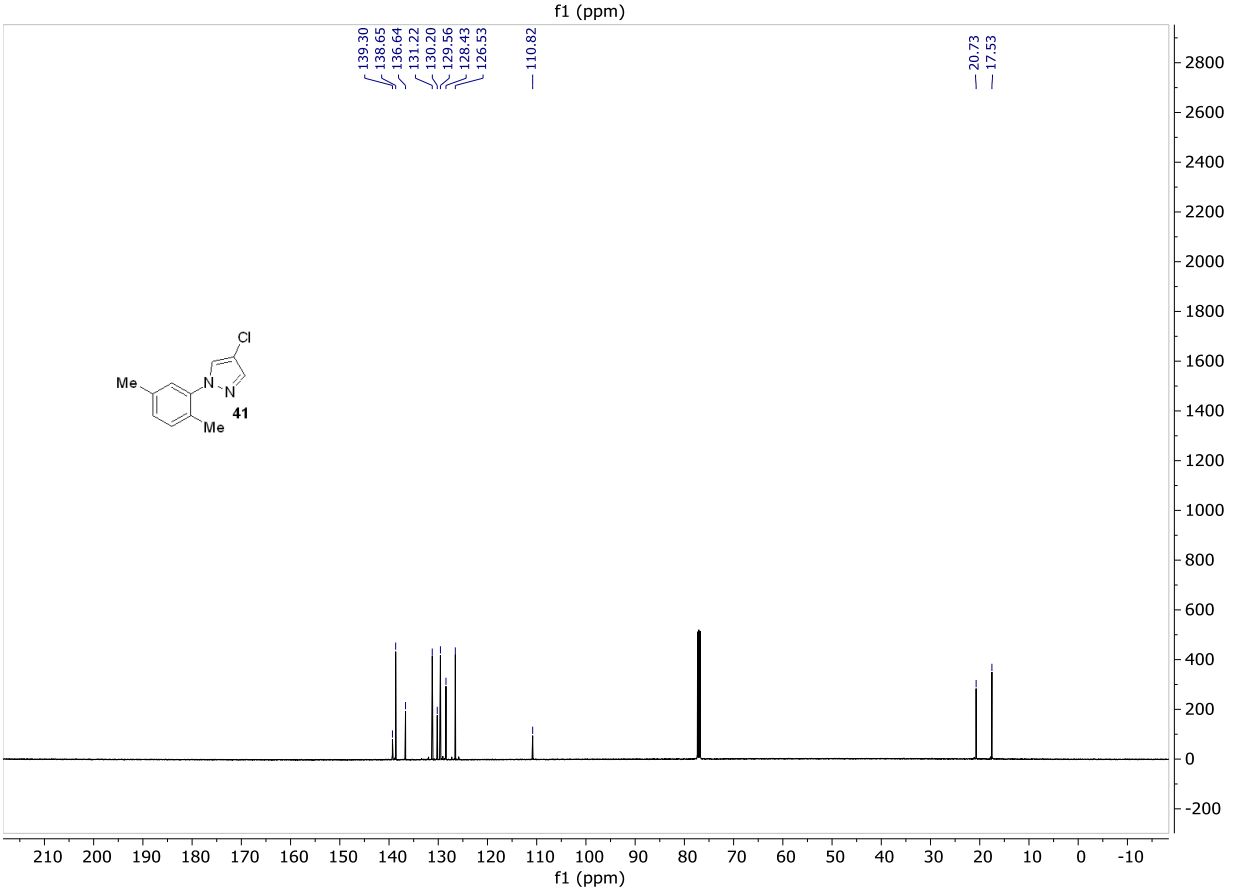

7.76
7.73
7.59
7.59
7.58
7.48
7.47
7.24
7.22
7.14
7.10
7.09
6.47
6.44
6.44
6.44
2.39
2.22
2.03
Me
Me
39a
Me
Me
39b
1.02
0.94
0.07
1.04
1.06
0.94
0.09
0.91
2.89
2.83
0.50
f1 (ppm)

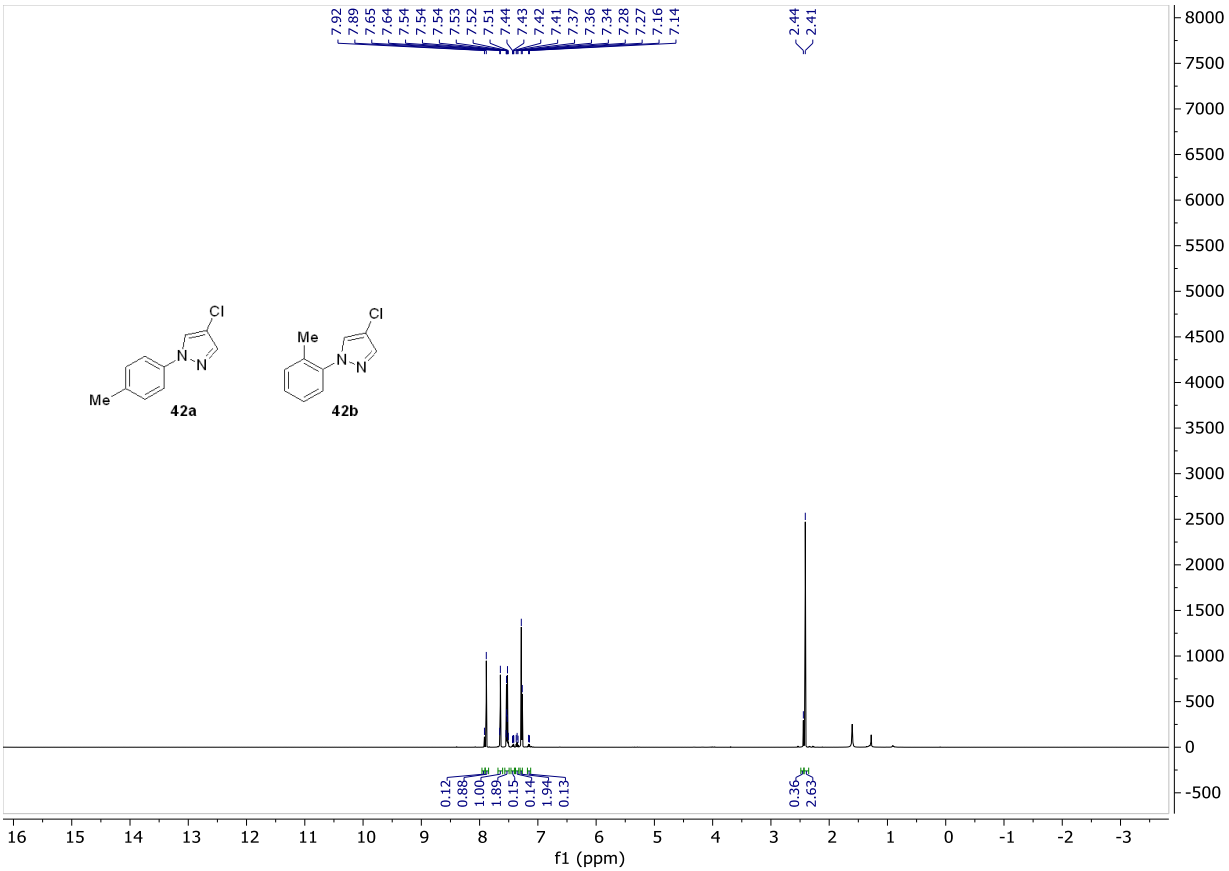

140.10
140.05
138.26
137.65
136.25
133.49
131.83
130.70
130.57
128.95
128.13
127.12
126.01
106.01
21.06
17.90
17.30
Me
Me
39a
Me
Me
39b
f1 (ppm)

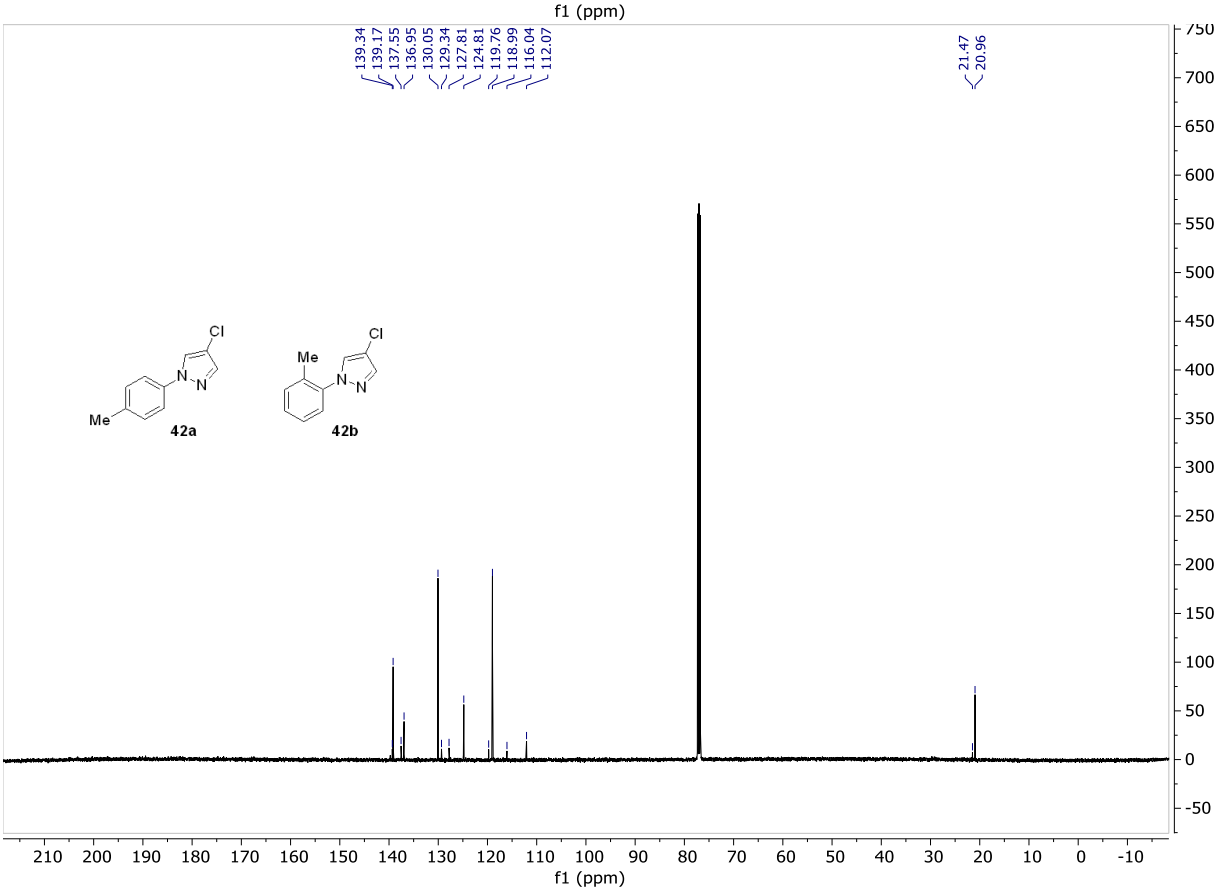

7.88
7.64
7.46
7.45
7.35
7.34
7.33
7.33
7.22
7.21
2.34
2.31
Cl
N
N
Me
Me
40
1.03
1.02
1.01
1.03
1.00
6.01
f1 (ppm)

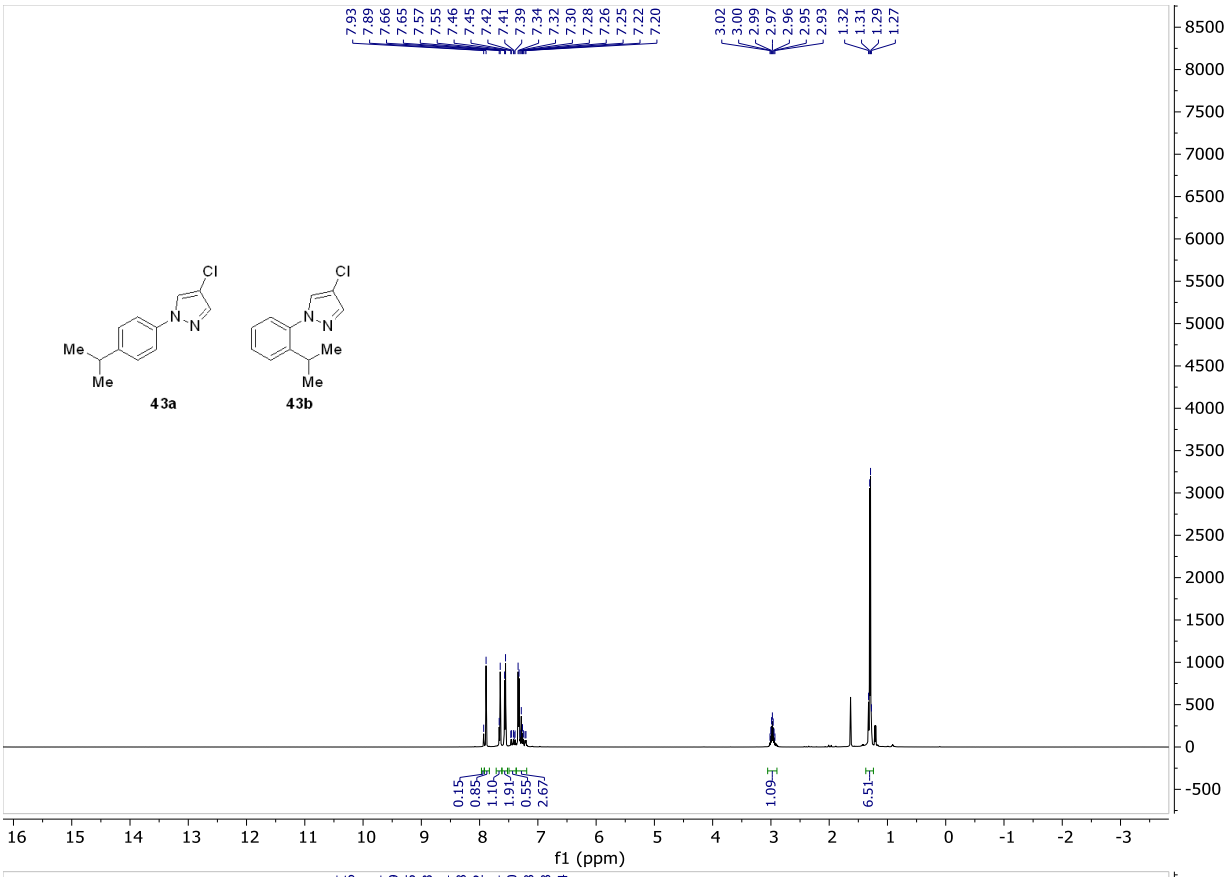

139.05
138.08
137.76
135.63
130.46
124.84
120.35
116.32
111.93
19.95
19.32
Cl
N
N
Me
Me
40
f1 (ppm)

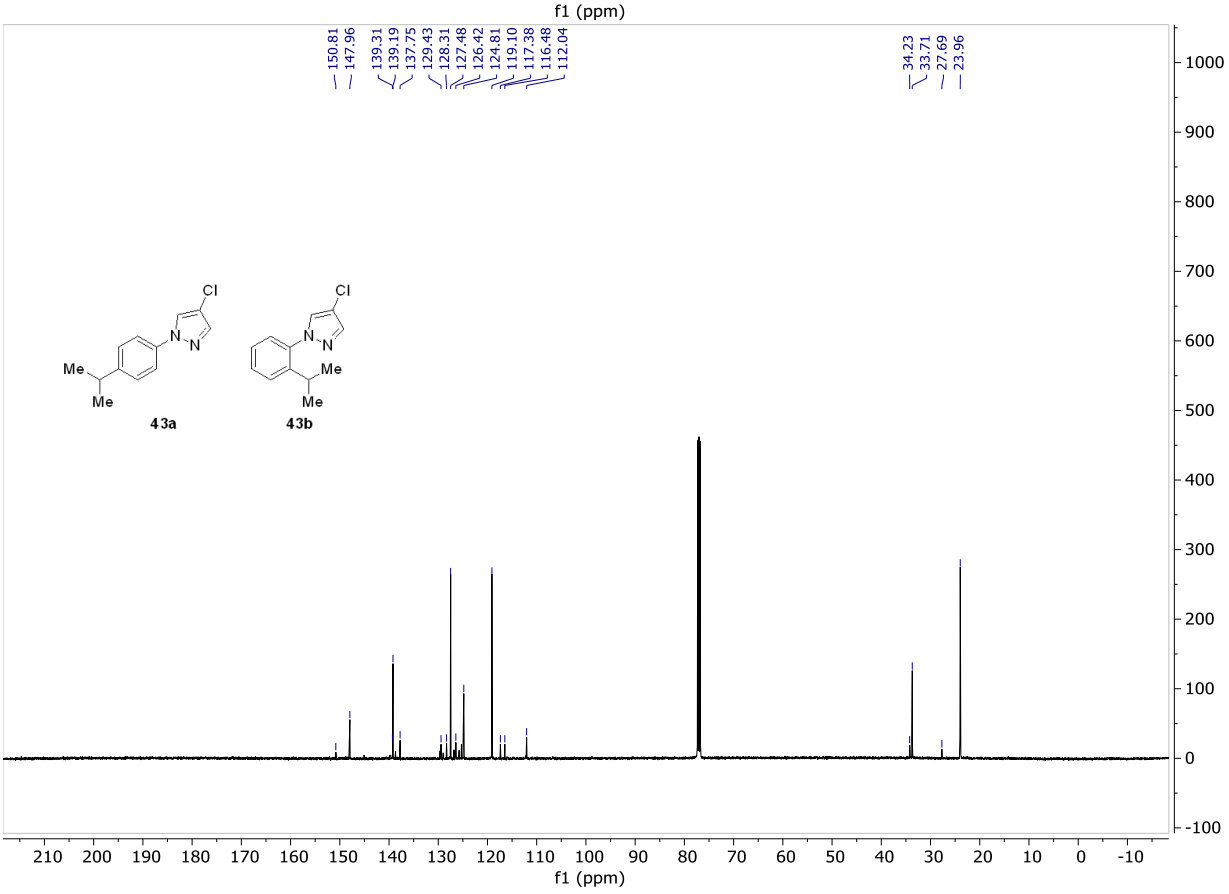

7.63
7.58
7.20
7.18
7.15
7.14
7.13
7.12
2.35
2.20
Cl
Me
N
N
Me
41
1.02
1.00
1.03
2.04
3.07
3.02
f1 (ppm)

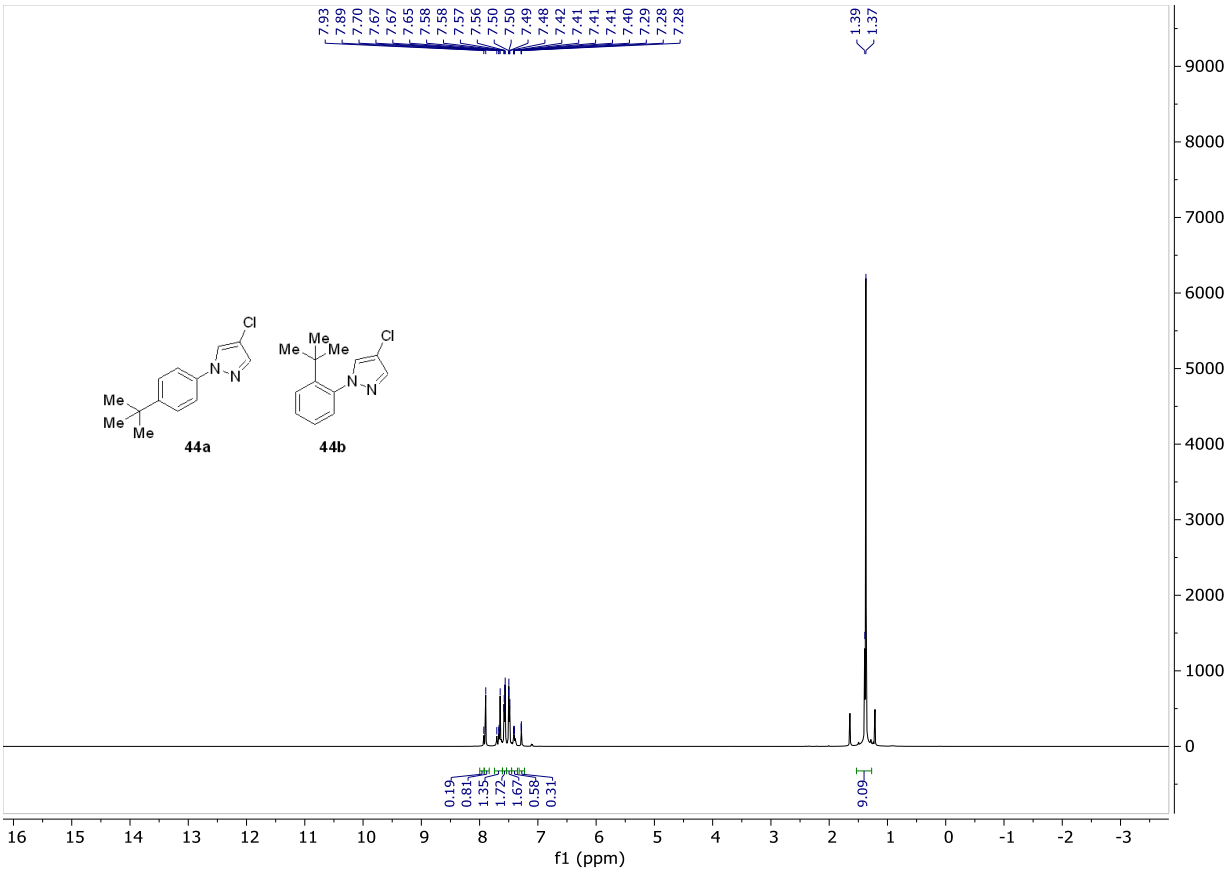

139.30
138.65
136.64
131.22
130.20
129.56
128.43
126.53
110.82
20.73
17.53
Cl
Me
N
N
Me
41
f1 (ppm)

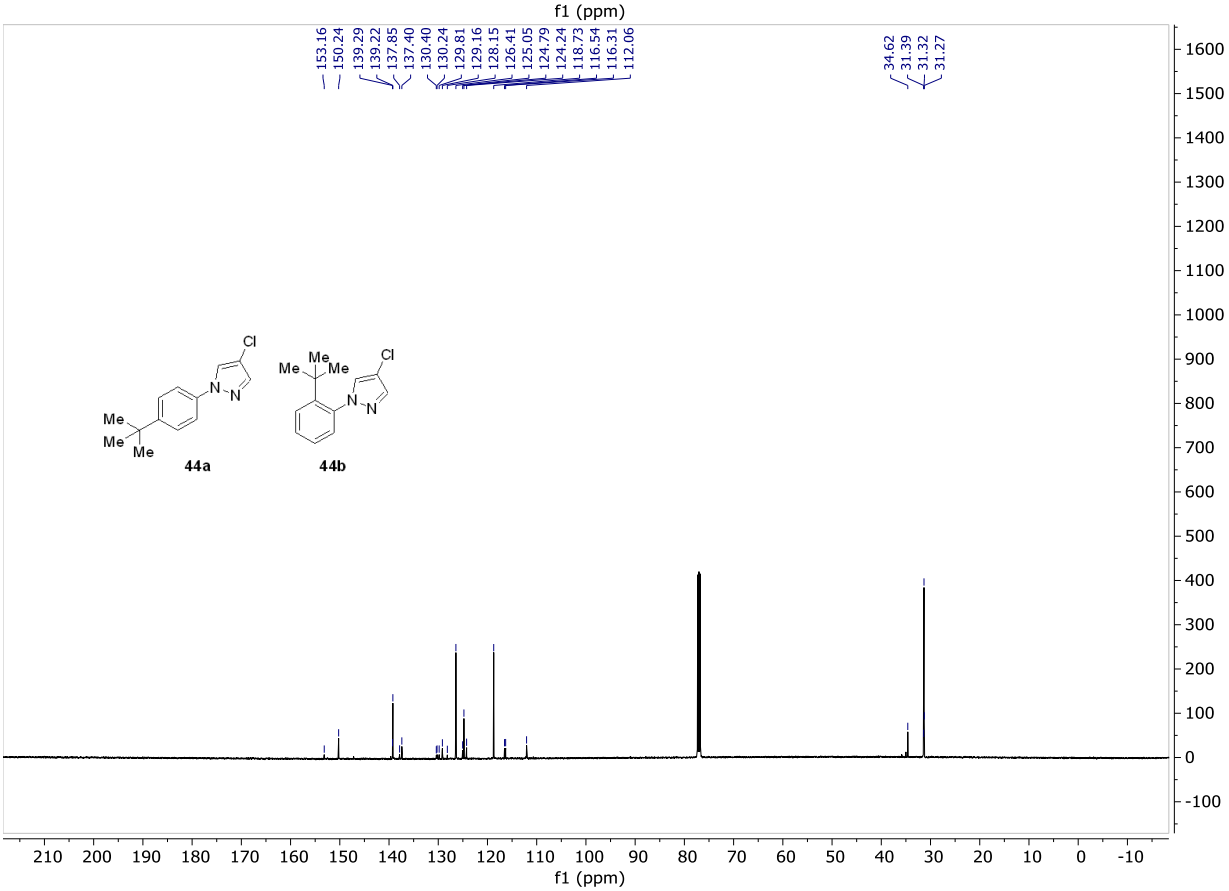

7.92
7.89
7.65
7.64
7.54
7.54
7.54
7.53
7.52
7.51
7.44
7.43
7.42
7.41
7.37
7.36
7.34
7.28
7.27
7.16
7.14
2.44
2.41
Cl
N
N
Me
42a
Me
Cl
N
N
42b
0.12
0.88
1.00
1.89
0.15
0.14
1.94
0.13
0.36
2.63
f1 (ppm)


139.34
139.17
137.55
136.95
130.05
129.34
127.81
124.81
119.76
118.99
116.04
112.07
21.47
20.96
Cl
N
N
Me
42a
Me
Cl
N
N
42b
f1 (ppm)


7.93
7.89
7.66
7.65
7.57
7.55
7.46
7.45
7.42
7.41
7.39
7.34
7.32
7.30
7.28
7.26
7.25
7.22
7.20
3.02
3.00
2.99
2.97
2.96
2.95
2.93
1.32
1.31
1.29
1.27
Cl
N
N
Me
Me
43a
Cl
N
N
Me
Me
43b
0.15
0.85
1.10
1.91
0.55
2.67
1.09
6.51
f1 (ppm)


150.81
147.96
139.31
139.19
137.75
129.43
128.31
127.48
126.42
124.81
119.10
117.38
116.48
112.04
34.23
33.71
27.69
23.96
Cl
N
N
Me
Me
43a
Cl
N
N
Me
Me
43b
f1 (ppm)


7.93
7.89
7.70
7.67
7.67
7.65
7.58
7.58
7.57
7.56
7.50
7.50
7.49
7.48
7.42
7.41
7.41
7.41
7.40
7.29
7.28
7.28
1.39
1.37
Cl
Me
Me
Me
44a
Me
Me
Me
Cl
44b
0.19
0.81
1.35
1.72
1.67
0.58
0.31
9.09
f1 (ppm)


153.16
150.24
139.29
139.22
137.85
137.40
130.40
130.24
129.81
129.16
128.15
126.41
125.05
124.79
124.24
118.73
116.54
116.31
112.06
34.62
31.39
31.32
31.27
Cl
Me
Me
Me
44a
Me
Me
Me
Cl
44b
f1 (ppm)