Supporting Information

Electrocatalytic dehydrogenative and defluorinative coupling between aldehyde-derived N,N-dialkylhydrazones and fluoromalonates: synthesis of 2-pyrazolines

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1. General informations

Unless otherwise stated, all reagents were obtained from commercial suppliers and used without further purification.

Analytical thin layer chromatography was performed on silica gel aluminum plates with F-254 indicator; spots were visualized by UV light (254 nm) and/or by staining with a $KMnO_4$ solution. Flash column chromatographies were performed on kieselgel 35-70 μm particle sized silica gel (200-400 mesh).

^{1}H, ^{13}C and ^{19}F NMR analyses were recorded on Bruker Avance 300, 400 or 500 spectrometers in $CDCl_3$, CD_3CN or CD_3OD. The chemical shifts (δ) are reported in parts per million (ppm) and were referenced to the residual isotopomer solvent signals ($CHCl_3$: δ = 7.26 ppm; CH_3CN: δ = 1.94 ppm; CH_3OH: δ = 3.31 ppm) for ^{1}H NMR spectra, to the solvent signal ($CDCl_3$: δ = 77.16 ppm; CD_3CN: δ = 1.32 ppm; CD_3OD: δ = 49.00 ppm) for ^{13}C NMR spectra. Coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

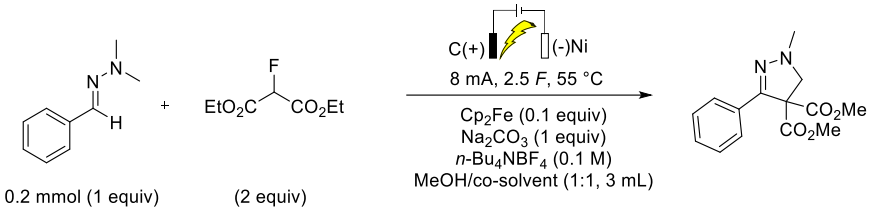
HRMS were determined on a Waters XevoQTof spectrometer using an electrospray ionization coupled with a time of flight analyzer (ESI-TOF) after dissolving the analyte in CH_3CN.

Infrared spectra were recorded on an IR spectrometer (Perkin Elmer BX FT-IR), and absorption frequencies were reported in reciprocal centimeters (cm^{-1}).

Electrochemical synthetic reactions were carried out with an IKA ElectraSyn 2.0 Pro apparatus using IKA electrodes.

2. Optimization of the reaction conditions (additional experiments)

Table S1: Evaluation of various solvent systems

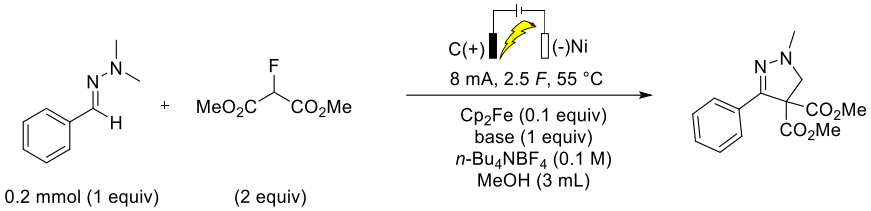


0.2 mmol (1 equiv) (2 equiv)

Entry	Co-solvent	Yield (%)[a]
1	THF	44
2[b]	THF	13
3	-	54
4	CH_3CN	45
5[c]	CH_3CN	5
6	DCE	50
7	Acetone	43
8	HFIP	0
9	DMF	44
10	DMSO	42

[a] NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [b] rt instead of 55 °C. [c] Reaction in CH_3CN (3 mL) without MeOH but in the presence of 2 equiv of MeONa.

Table S2: Evaluation of various Brønsted bases

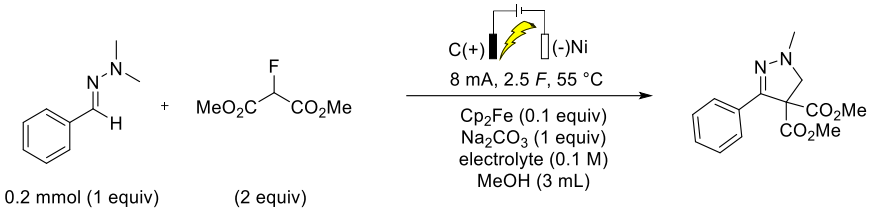


0.2 mmol (1 equiv) (2 equiv)

Entry	Co-solvent	Yield (%)[a]
1	Na_2CO_3	50
2	Na_2CO_3[b]	39
3	Na_2CO_3[c]	51
4	Cs_2CO_3	31
5	K_2CO_3	44
6	K_3PO_4	15
7	$NaHCO_3$	48
7	NaOAc	46
8	2,6-Lutidine	42
9	DABCO	9
10	*t*-BuONa	25

[a] NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

Table S3: Evaluation of various electrolytes

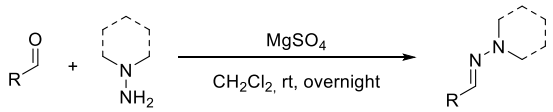


Entry	electrolyte	Yield (%)[a]
1	*n*-Bu_4NBF_4	50
2	Et_4NOTs	54
3	*n*-Bu_4NPF_6	26
4	*n*-Bu_4NClO_4	50
5	$LiClO_4$	54
6	$LiBF_4$	53
7	$NaBF_4$	62
8	KPF_6	58
9	$LiPF_6$	34
10	NH_4Br	64
11	NaBr	53
12	Et_4NBr	58
13	*n*-Bu_4NBr	8
14	KBr	11
15	NH_4I	10
16	NH_4NO_3	56
17	NH_4Cl	15

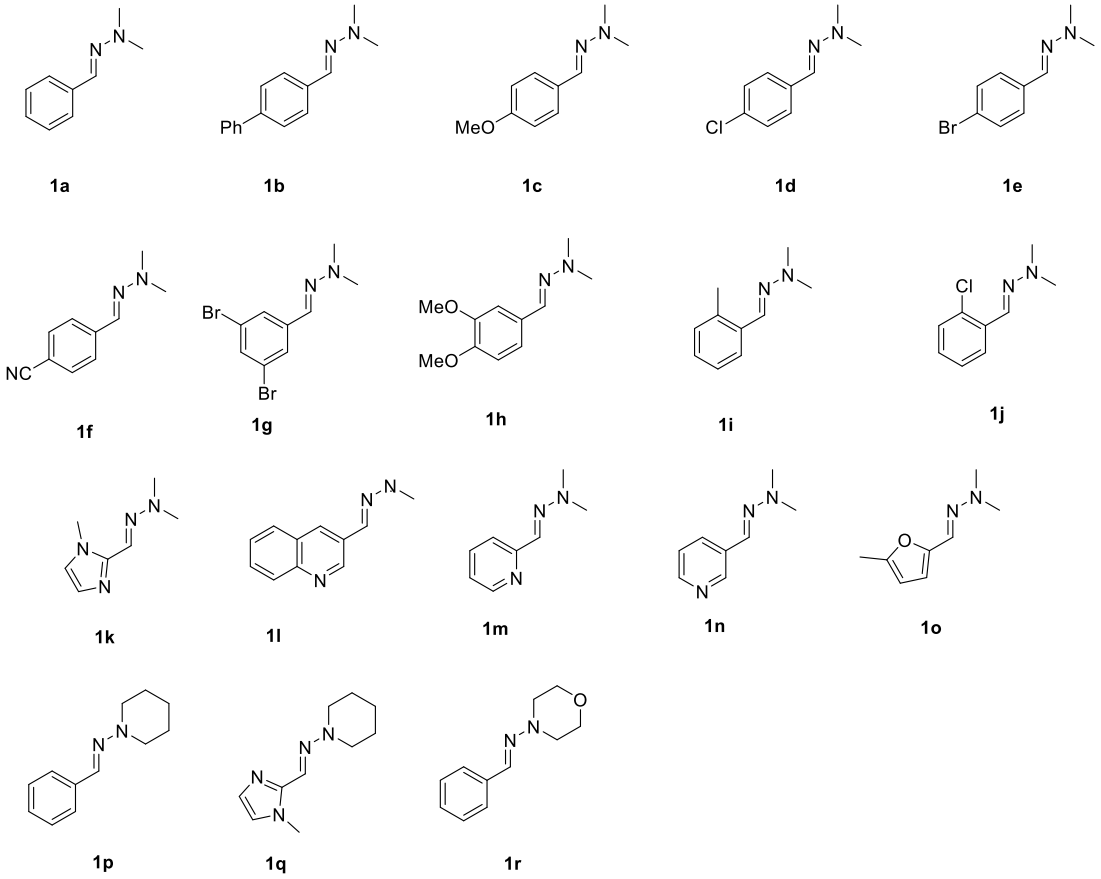
[a] NMR yield using 1,3,5-trimethoxybenzene as an internal standard.

3. Preparation of the aldehyde-derived *N,N*-dialkylhydrazones

General procedure A

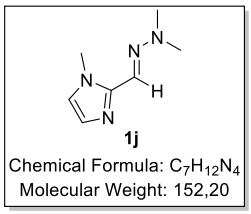


To a suspension of $MgSO_4$ (2 equiv) in freshly distilled dichloromethane (25 mL) were sequentially added the aldehyde (8 mmol, 1 equiv) and the hydrazine (1.33 equiv) under argon. The resulting mixture was stirred vigorously overnight at room temperature. After filtration and evaporation of the volatiles, the residue was either directly used in the electrochemical transformation (N,N-dimehthylhydrazone **1a-1n**) or purified by flash column chromatography (hydrazone **1o**).



Spectroscopic data of hydrazones **1a**-**1i** and **1k**-**1n** matched those reported in the literature.[1]

2-((2,2-dimethylhydrazineylidene)methyl)-1-methyl-1H-imidazole (**1j**)



Following the general procedure A using 1-methyl-1H-imidazole-2-carbaldehyde (8 mmol, 881 mg), piperidin-1-amine (810 µL) and $MgSO_4$ (1.93 g), hydrazine **1j** was obtained as black oil (1.166 g 7.66 mmol, 96%).
IR: ν 3370, 2863, 1467, 1042 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 0.6 Hz, 1H), 6.99 (d, *J* = 1.2 Hz, 1H), 6.79 (d, *J* = 1.2 Hz, 1H), 3.86 (s, 3H), 2.95 (s, 6H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$) δ 144.3, 127.6, 125.0, 122.7, 42.6, 35.4; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_7H_{13}N_4]^+$ ($[M+H]^+$): 153.1140, found: 153.1133.

4. Electrochemical access to 2-pyrazolines

4.1. Synthetic procedure

General procedure B

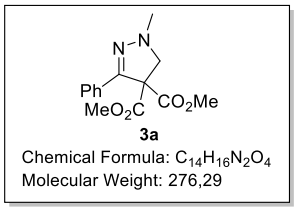
An Electrasyn undivided cell (10 mL) was charged with a magnetic stir bar, hydrazone **1** (0.4 mmol, 1.0 equiv.), Na_2CO_3 (42.4 mg, 0.4 mmol, 1 equiv), Cp_2Fe (7.4 mg, 0.04 mmol, 0.1 equiv), NH_4Br (79 mg, 0.8 mmol, 2 equiv). The vial was closed with the ElectraSyn cap holding the electrodes (anode: Graphite SK-50, cathode: Nickel plate) and flushed under argon for 2 min. Dimethyl-2-fluoromalonate **2** (120 mg, 0.8 mmol, 2.0 equiv) was added as a solution in MeOH (6 mL). Argon gas (balloon) was bubbled

through the solution during 5 minutes. The electrolysis was carried out at room temperature under constant current (8 mA) and was stopped after 3 h 20 min (electricity = 2.5 F.mol^{-1}). The reaction mixture was poured in water (10 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE/EtOAc) to yield the desired product.

1 mmol scale experiment: An Electrasyn undivided cell (20 mL) was charged with a magnetic stir bar, hydrazone **1k** (152.2 mg, 1 mmol, 1.0 equiv.), Na_2CO_3 (106 mg, 1 mmol, 1 equiv), Cp_2Fe (18.6 mg, 0.1 mmol, 0.1 equiv), NH_4Br (196 mg, 2 mmol, 2 equiv). The vial was closed with the ElectraSyn cap holding the electrodes (anode: Graphite SK-50, cathode: Nickel plate) and flushed under argon for 2 min. Dimethyl-2-fluoromalonate **2** (300 mg, 1 mmol, 2.0 equiv) was added as a solution in MeOH (12 mL). Argon gas (balloon) was bubbled through the solution during 5 minutes. The electrolysis was carried out at room temperature under constant current (8 mA) and was stopped after 8 h 22 min (electricity = 2.5 F.mol^{-1}). The reaction mixture was poured in water (20 mL) and extracted with EtOAc (3x20 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by flash column chromatography on silica gel (PE/EtOAc) to yield **3k** as a yellow oil (154 mg, 0.549 mmol, 55%).

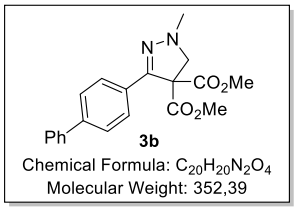
4.2. Characterization of 2-pyrazolines **3**

Dimethyl 1-methyl-3-phenyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3a**)



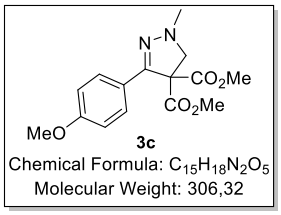
Following the general procedure B using hydrazone **1a** (59.3 mg), **3a** was obtained as a white gum (59.9 mg, 0.217 mmol, 54%).
IR: *v* 1080, 1201, 1270, 1435, 1734 cm-1; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.70 – 7.62 (m, 2H), 7.36 – 7.27 (m, 3H), 3.87 (s, 2H), 3.76 (s, 6H), 2.97 (s, 3H) ; **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 169.0, 146.6, 131.7, 128.7, 128.3, 126.8, 68.9, 66.5, 53.4, 42.5; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{14}H_{17}N_2O_4]^+$ ($[M+H]^+$): 277.1188, found: 277.1190.

Dimethyl 3-([1,1'-biphenyl]-4-yl)-1-methyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3b**)



Following the general procedure B using hydrazone **1b** (90 mg), **3b** was obtained as a white gum (71 mg, 0.202 mmol, 50%).
IR: *v* 2955, 1732, 1265, 766 cm^{-1}; **^{1}H {^{13}C} NMR** (400 MHz, $CDCl_3$): δ 7.77 – 7.73 (m, 2H), 7.63 – 7.54 (m, 4H), 7.47 – 7.41 (m, 2H), 7.37 – 7.32 (m, 1H), 3.91 (s, 2H), 3.80 (s, 6H), 3.00 (s, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ 169.1, 146.2, 141.3, 140.6, 130.6, 128.9, 127.6, 127.2, 127.1, 127.0, 68.8, 66.5, 53.6, 42.6; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{20}H_{21}N_2O_4]^+$ ($[M+H]^+$): 353.1501, found: 353.1506.

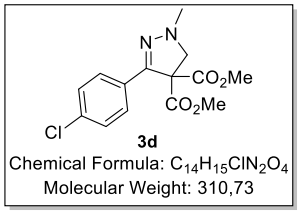
Dimethyl 3-(4-methoxyphenyl)-1-methyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3c**)



3c
Chemical Formula: $C_{15}H_{18}N_2O_5$
Molecular Weight: 306,32

Following the general procedure B using hydrazone **1c** (71 mg), **3c** was obtained as a yellow oil (71 mg, 0.232 mmol, 58%).
IR: *v* 2956, 1732, 1250, 835 cm^{-1}; **^{1}H {^{13}C} NMR** (400 MHz, $CDCl_3$): δ 7.65 – 7.56 (m, 2H), 6.86 – 6.82 (m, 2H), 3.83 (s, 2H), 3.80 (s, 3H), 3.76 (s, 6H), 2.93 (s, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ 169.1, 160.1, 146.7, 128.4, 124.3, 113.8, 69.0, 66.5, 55.4, 53.5, 42.8; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{15}H_{19}N_2O_5]^+$ ($[M+H]^+$): 307.1294, found: 307.1295.

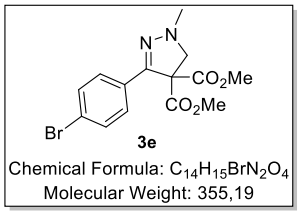
Dimethyl 3-(4-chlorophenyl)-1-methyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3d**)



3d
Chemical Formula: $C_{14}H_{15}ClN_2O_4$
Molecular Weight: 310,73

Following the general procedure B using hydrazone **1d** (73 mg) and dimethyl-2-fluoromalonate (90 mg, 0.6 mmol, 1.5 equiv instead of 2 equiv to ease the purification by flash column chromatography), **3c** was obtained as a yellow oil (61 mg, 0.1963 mmol, 49%).
IR: *v* 2956, 1732, 1266, 832 cm^{-1}; **^{1}H {^{13}C} NMR** (400 MHz, $CDCl_3$): δ 7.63 – 7.58 (m, 2H), 7.30 – 7.25 (m, 2H), 3.88 (s, 2H), 3.77 (s, 6H), 2.97 (s, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ 168.9, 145.3, 134.5, 130.2, 128.5, 128.1, 68.7, 66.4, 53.6, 42.4; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{14}H_{16}ClN_2O_4]^+$ ($[M+H]^+$): 311.0799, found: 311.0797.

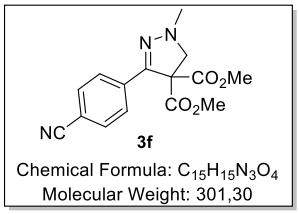
Dimethyl 3-(4-bromorophenyl)-1-methyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3e**)



3e
Chemical Formula: $C_{14}H_{15}BrN_2O_4$
Molecular Weight: 355,19

Following the general procedure B using hydrazone **1e** (91 mg) and dimethyl-2-fluoromalonate (90 mg, 0.6 mmol, 1.5 equiv instead of 2 equiv to ease the purification by flash column chromatography), **3e** was obtained as a yellow oil (77 mg, 0.218 mmol, 55%).
IR: *v* 2955, 1733, 1267, 829 cm^{-1}; **^{1}H {^{13}C} NMR** (400 MHz, $CDCl_3$): δ 7.56 – 7.52 (m, 2H), 7.46 – 7.42 (m, 2H), 3.88 (s, 2H), 3.77 (s, 6H), 2.97 (s, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ 168.9, 145.3, 131.5, 130.7, 128.3, 122.8, 68.7, 66.4, 53.6, 42.4; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{14}H_{16}BrN_2O_4]^+$ ($[M+H]^+$): 355.0293, found: 355.0291.

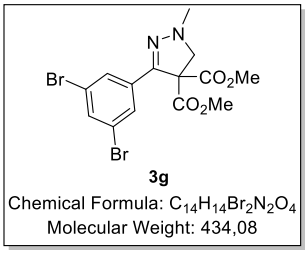
Dimethyl 3-(4-cyanophenyl)-1-methyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3f**)



3f
Chemical Formula: $C_{15}H_{15}N_3O_4$
Molecular Weight: 301,30

Following the general procedure B using hydrazone **1f** (69 mg), **3f** was obtained as a yellow oil (56 mg, 0.186 mmol, 47%).
IR: *v* 2959, 1722, 1267, 769 cm^{-1}; **^{1}H {^{13}C} NMR** (400 MHz, $CDCl_3$): δ 7.77 – 7.74 (m, 2H), 7.59 – 7.56 (m, 2H), 3.95 (s, 2H), 3.78 (s, 6H), 3.02 (s, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ 168.6, 143.6, 136.2, 132.0, 126.9, 119.0, 111.4, 68.2, 66.1, 53.7, 42.0; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{15}H_{16}N_3O_4]^+$ ($[M+H]^+$): 302.1141, found: 302.1141.

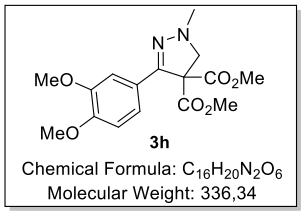
Dimethyl 3-(3,5-dibromophenyl)-1-methyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3g**)



3g
Chemical Formula: $C_{14}H_{14}Br_2N_2O_4$
Molecular Weight: 434,08

Following the general procedure B using hydrazone **1g** (122 mg), **3g** was obtained as a white gum (95 mg, 0.219 mmol, 55%).
IR: *v* 2954, 1734, 1268, 708 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.74 (d, *J* = 1.7 Hz, 2H), 7.56 (t, *J* = 1.7 Hz, 1H), 3.91 (s, 2H), 3.81 (s, 6H), 2.99 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 168.5, 143.0, 135.3, 133.6, 128.3, 122.8, 68.4, 66.3, 53.7, 42.1; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{14}H_{15}Br_2N_2O_4]^+$ ($[M+H]^+$): 432.9399, found: 432.9392.

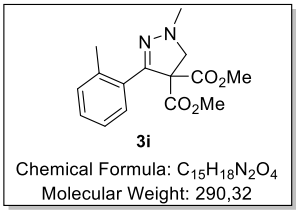
Dimethyl 3-(3,4-dimethoxyphenyl)-1-methyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3h**)



3h
Chemical Formula: $C_{16}H_{20}N_2O_6$
Molecular Weight: 336,34

Following the general procedure B using hydrazone **1h** (83 mg), **NF2-220** was obtained as a yellow oil (66 mg, 0.196 mmol, 49%).
IR: *v* 2956, 1733, 1251, 729 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.35 (d, *J* = 2.1 Hz, 1H), 7.12 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.84 (s, 2H), 3.76 (s, 6H), 2.93 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 169.1, 149.8, 148.8, 146.6, 124.6, 119.8, 110.6, 109.9, 69.0, 66.6, 55.9, 55.9, 53.4, 42.7; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{16}H_{21}N_2O_6]^+$ ($[M+H]^+$): 337.1400, found: 337.1398.

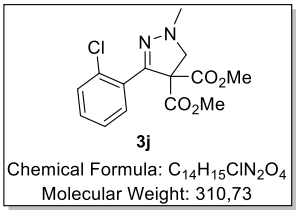
Dimethyl 1-methyl-3-(o-tolyl)-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3i**)



3i
Chemical Formula: $C_{15}H_{18}N_2O_4$
Molecular Weight: 290,32

Following the general procedure B using hydrazone **1i** (65 mg), **3i** was obtained as a yellow oil (66 mg, 0.227 mmol, 57%).
IR: *v* 2957, 1734, 1270, 1084 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.33 – 7.28 (m, 1H), 7.24 – 7.19 (m, 2H), 7.19 – 7.09 (m, 1H), 3.83 (s, 2H), 3.72 (s, 6H), 2.96 (s, 3H), 2.40 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 168.8, 146.5, 138.3, 131.1, 131.0, 128.7, 128.6, 125.3, 71.0, 65.5, 53.3, 42.9, 21.1; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{15}H_{19}N_2O_4]^+$ ($[M+H]^+$): 291.1345, found: 291.1342.

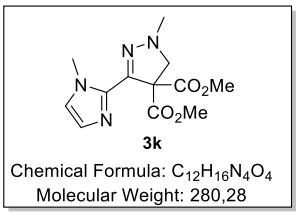
Dimethyl 3-(2-chlorophenyl)-1-methyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3j**)



3j
Chemical Formula: $C_{14}H_{15}ClN_2O_4$
Molecular Weight: 310,73

Following the general procedure B using hydrazone **1j** (73 mg), **3j** was obtained as a colorless oil (23 mg, 0.074 mmol, 19%).
IR: *v* 2956, 1733, 1172, 760 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.64 – 7.55 (m, 1H), 7.40 – 7.35 (m, 1H), 7.33 – 7.26 (m, 2H), 3.86 (s, 2H), 3.72 (s, 6H), 2.98 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 167.8, 144.6, 134.5, 132.2, 131.5, 130.2, 129.3, 126.6, 70.6, 64.0, 53.5, 42.7; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{14}H_{16}ClN_2O_4]^+$ ($[M+H]^+$): 311.0799, found: 311.0795.

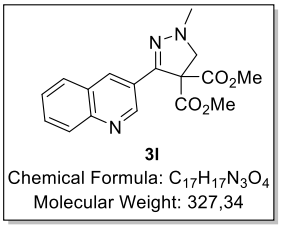
Dimethyl 1-methyl-3-(1-methyl-1H-imidazol-2-yl)-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3k**)



3k
Chemical Formula: $C_{12}H_{16}N_4O_4$
Molecular Weight: 280,28

Following the general procedure B using hydrazone **1k** (61 mg), **3k** was obtained as a yellow oil (86 mg, 0.307 mmol, 77%).
IR: *v* 2956, 1732, 1270, 727 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 6.99 (d, *J* = 1.1 Hz, 1H), 6.82 (d, *J* = 1.1 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 2H), 3.75 (s, 6H), 2.92 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 168.9, 141.2, 139.4, 128.7, 123.3, 69.0, 65.7, 53.4, 42.5, 35.5; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{12}H_{17}N_4O_4]^+$ ($[M+H]^+$): 281.1250, found: 281.1243.

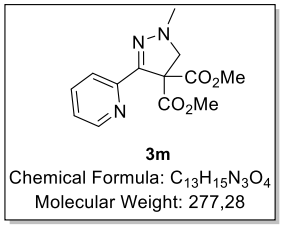
Dimethyl 1-methyl-3-(quinolin-3-yl)-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3l**)



3l
Chemical Formula: $C_{17}H_{17}N_3O_4$
Molecular Weight: 327,34

Following the general procedure B using hydrazone **1l** (80 mg), **3l** was obtained as a yellow oil (55 mg, 0.168 mmol, 42%).
IR: *v* 2955, 1733, 1268, 753 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 9.30 (d, *J* = 2.3 Hz, 1H), 8.28 (d, *J* = 1.3 Hz, 1H), 8.07 (d, *J* = 8.9 Hz, 1H), 7.81 – 7.75 (m, 1H), 7.68 (ddd, *J* = 8.5, 6.9, 1.5 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 3.96 (s, 2H), 3.79 (s, 6H), 3.05 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 168.7, 149.4, 147.5, 143.5, 132.8, 129.8, 129.3, 128.4, 127.6, 127.1, 125.2, 68.8, 66.0, 53.7, 42.3; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{17}H_{18}N_3O_4]^+$ ($[M+H]^+$): 328.1297, found: 328.1294.

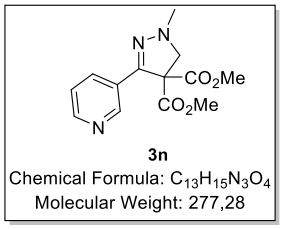
Dimethyl 1-methyl-3-(pyridin-2-yl)-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3m**)



3m
Chemical Formula: $C_{13}H_{15}N_3O_4$
Molecular Weight: 277,28

Following the general procedure B using hydrazone **1m** (60 mg), **3m** was obtained as a yellow oil (76 mg, 0.191 mmol, 48%).
IR: *v* 2954, 1732, 1268, 794 cm^{-1}; **^{1}H {^{13}C} NMR** (400 MHz, $CDCl_3$): δ 8.47 (ddd, *J* = 4.9, 1.8, 1.0 Hz, 1H), 7.90 (dt, *J* = 8.0, 1.1 Hz, 1H), 7.63 (ddd, *J* = 8.0, 7.5, 1.8 Hz, 1H), 7.14 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 3.90 (s, 2H), 3.76 (s, 6H), 3.01 (s, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ 169.4, 150.8, 148.7, 148.4, 136.0, 122.8, 120.7, 67.4, 66.4, 53.4, 42.3; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{13}H_{16}N_3O_4]^+$ ($[M+H]^+$): 278.1141, found: 278.1140.

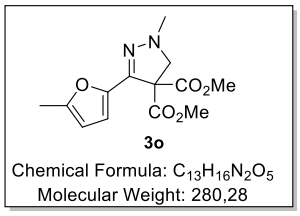
Dimethyl 1-methyl-3-(pyridin-3-yl)-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3n**)



3n
Chemical Formula: $C_{13}H_{15}N_3O_4$
Molecular Weight: 277,28

Following the general procedure B using hydrazone **1n** (60 mg), **3n** was obtained as a yellow oil (53 mg, 0.274 mmol, 69%).
IR: *v* 2958, 1723, 1268, 769 cm^{-1}; **^{1}H {^{13}C} NMR** (400 MHz, $CDCl_3$): δ 8.84 (dd, *J* = 2.3, 0.9 Hz, 1H), 8.47 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.95 (ddd, *J* = 8.1, 2.3, 1.6 Hz, 1H), 7.22 (ddd, *J* = 8.1, 4.8, 0.9 Hz, 1H), 3.88 (s, 2H), 3.75 (s, 6H), 2.96 (s, 3H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ 168.5, 149.1, 147.9, 143.2, 133.8, 127.9, 123.1, 68.5, 65.9, 53.6, 42.2; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{13}H_{16}N_3O_4]^+$ ($[M+H]^+$): 278.1141, found: 278.1144.

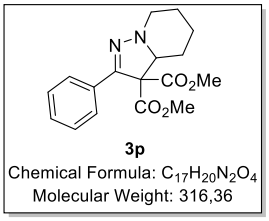
Dimethyl 1-methyl-3-(5-methylfuran-2-yl)-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3o**)



3o
Chemical Formula: $C_{13}H_{16}N_2O_5$
Molecular Weight: 280,28

Following the general procedure B using hydrazone **1o** (61 mg), **3o** was obtained as a yellow oil (51 mg, 0.182 mmol, 45%).
IR: *v* 2954, 1734, 1268, 709 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 6.43 (dd, *J* = 3.4, 0.6 Hz, 1H), 6.00 (dq, *J* = 3.2, 1.0 Hz, 1H), 3.82 (s, 2H), 3.77 (s, 6H), 2.95 (s, 3H), 2.32 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 168.5, 153.7, 145.1, 138.9, 111.6, 107.9, 68.5, 65.5, 53.5, 42.7, 13.9; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{13}H_{17}N_2O_5]^+$ ($[M+H]^+$): 281.1137, found: 281.1138.

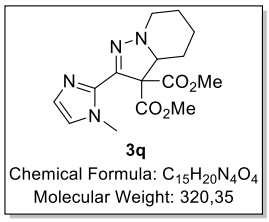
Dimethyl 2-phenyl-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyridine-3,3(3*a*H)-dicarboxylate (**3p**)



3p
Chemical Formula: $C_{17}H_{20}N_2O_4$
Molecular Weight: 316,36

Following the general procedure B using hydrazone **1p** (75.3 mg), **3p** was obtained as a white gum (64 mg, 0.203 mmol, 51%).
IR: *v* 2949, 1746, 1718, 1432, 1273, 1235, 1154, 1047, 769 cm^{-1}; **^{1}H {^{13}C} NMR** (400 MHz, $CDCl_3$): δ 7.60 – 7.56 (m, 2H), 7.33 – 7.26 (m, 3H), 3.92 – 3.87 (m, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 2.80 (td, *J* = 11.7, 3.5 Hz, 1H), 1.94 – 1.85 (m, 2H), 1.79 – 1.53 (m, 3H), 1.44 – 1.21 (m, 2H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ 168.4, 167.5, 146.3, 132.3, 128.5, 128.1, 126.9, 74.0, 70.2, 53.3, 52.8, 52.5, 25.8, 25.0, 24.0; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{17}H_{21}N_2O_4]^+$ ($[M+H]^+$): 317.1501, found: 317.1515.

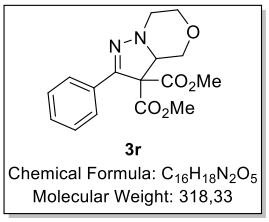
Dimethyl 2-(1-methyl-1H-imidazol-2-yl)-4,5,6,7-tetrahydropyrazolo[1,5-*a*]pyridine-3,3(3*a*H)-dicarboxylate (**3q**)



3q
Chemical Formula: $C_{15}H_{20}N_4O_4$
Molecular Weight: 320,35

Following the general procedure B using hydrazone **1q** (76.9 mg), **3q** was obtained as a yellow oil (56.3 mg, 0.176 mmol, 44%).
IR: *v* 2955, 1737, 1274, 1050 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.04 (d, *J* = 1.2 Hz, 1H), 6.86 (d, *J* = 1.1 Hz, 1H), 3.89 (s, 3H), 3.88 – 3.83 (m, 4H), 3.75 (s, 3H), 3.67 (dd, *J* = 11.8, 2.7 Hz, 1H), 2.81 (td, *J* = 11.7, 3.4 Hz, 1H), 2.00 – 1.85 (m, 2H), 1.81 – 1.56 (m, 3H), 1.43 – 1.26 (m, 1H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 168.7, 167.2, 128.0, 123.3, 74.0, 70.0, 53.7, 53.0, 52.8, 35.7, 29.8, 25.9, 25.1, 24.0; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{15}H_{21}N_4O_4]^+$ ($[M+H]^+$): 321.1563, found: 321.1566.

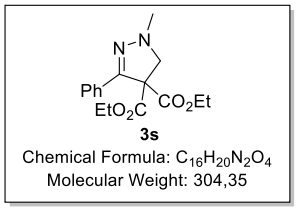
Dimethyl 2-phenyl-3*a*,4,6,7-tetrahydro-3H-pyrazolo[5,1-*c*][1,4]oxazine-3,3-dicarboxylate (**3r**)



3r
Chemical Formula: $C_{16}H_{18}N_2O_5$
Molecular Weight: 318,33

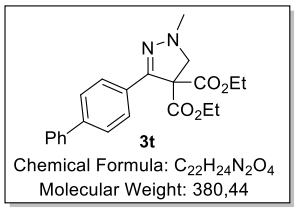
Following the general procedure B using hydrazone **1r** (76.1 mg), **3r** was obtained as a white gum (26.1 mg, 0.082 mmol, 20%).
IR: *v* 2955, 1732, 1435, 1266, 1232, 1101 cm^{-1}; **^{1}H {^{13}C} NMR** (400 MHz, $CDCl_3$): δ 7.67 – 7.58 (m, 2H), 7.37 – 7.27 (m, 3H), 4.13 (dd, *J* = 10.6, 3.5 Hz, 1H), 3.99 – 3.85 (m, 2H), 3.80 – 3.61 (m, 9H), 3.24 (td, *J* = 11.3, 10.7, 3.7 Hz, 1H); **^{13}C {^{1}H} NMR** (100 MHz, $CDCl_3$): δ 168.0, 167.0, 147.3, 131.8, 128.9, 128.3, 127.0, 70.6, 69.4, 66.5, 66.4, 53.6, 53.1, 51.6; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{16}H_{19}N_2O_5]^+$ ($[M+H]^+$): 319.1294, found: 319.1292.

Diethyl 1-methyl-3-phenyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3s**)



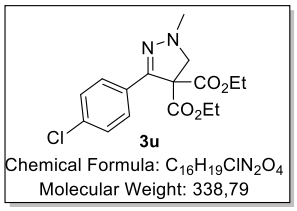
Following the general procedure B using hydrazone **1a** (59.3 mg) and diethylfluoromalonate (120 μL) in EtOH at 65 °C instead of MeOH at 55 °C, **3s** was obtained as a colorless oil (86.8 mg, 0.301 mmol, 71%).
IR: *v* 2987, 1733, 1266, 1078 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.73 – 7.67 (m, 2H), 7.34 – 7.27 (m, 3H), 4.24 (qd, *J* = 7.1, 3.8 Hz, 4H), 3.87 (s, 2H), 2.97 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 168.5, 147.1, 131.8, 128.7, 128.1, 127.2, 69.3, 66.3, 62.6, 42.6, 14.0; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{16}H_{21}N_2O_4]^+$ ($[M+H]^+$): 305.1501, found: 305.1502.

Diethyl 3-([1,1'-biphenyl]-4-yl)-1-methyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3t**)



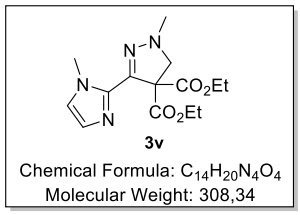
Following the general procedure B using hydrazone **1b** (89.7 mg) and diethylfluoromalonate (120 μL) in EtOH at 65 °C instead of MeOH at 55 °C, **3t** was obtained as a yellow gum-oil (97.6 mg, 0.257 mmol, 64%).
IR: *v* 2982, 1730, 1262, 766 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.84 – 7.76 (m, 2H), 7.65 – 7.53 (m, 4H), 7.49 – 7.40 (m, 2H), 7.34 (t, *J* = 7.3 Hz, 1H), 4.27 (qd, *J* = 7.1, 3.1 Hz, 4H), 3.91 (s, 2H), 3.00 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 6H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 168.5, 146.5, 141.1, 140.6, 130.8, 128.9, 127.5, 127.4, 127.0, 126.7, 69.1, 66.3, 62.6, 42.6, 14.0; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{22}H_{25}N_2O_4]^+$ ($[M+H]^+$): 381.1814, found: 381.1804.

Diethyl 3-([1,1'-biphenyl]-4-yl)-1-methyl-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3u**)



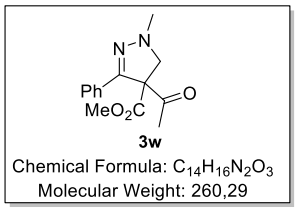
Following the general procedure B using hydrazone **1d** (72.8 mg) and diethylfluoromalonate (120 μL) in EtOH at 65 °C instead of MeOH at 55 °C, **3u** was obtained as a yellow oil (69.4 mg, 0.205 mmol, 51%).
IR: *v* 2982, 1732, 1262, 1012 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 4.37 – 4.12 (m, 4H), 3.89 (s, 2H), 2.98 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 168.3, 145.5, 134.4, 130.4, 128.3, 128.3, 69.0, 66.2, 62.7, 42.4, 14.0; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{16}H_{20}ClN_2O_4]^+$ ($[M+H]^+$): 339.1112, found: 339.1110.

Diethyl 1-methyl-3-(1-methyl-1H-imidazol-2-yl)-1,5-dihydro-4H-pyrazole-4,4-dicarboxylate (**3v**)



Following the general procedure B using hydrazone **1k** (60.9 mg) and diethylfluoromalonate (120 μL) in EtOH at 65 °C instead of MeOH at 55 °C, **3v** was obtained as a yellow oil (52.9 mg, 0.172 mmol, 43%).
IR: *v* 2983, 1728, 1265, 1079 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 6.99 (d, *J* = 1.1 Hz, 1H), 6.84 (d, *J* = 1.1 Hz, 1H), 4.31 – 4.18 (m, 4H), 3.86 (s, 3H), 3.78 (s, 2H), 2.95 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 6H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 168.4, 141.5, 139.6, 128.6, 123.0, 69.3, 65.3, 62.3, 42.5, 35.3, 13.8; **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{14}H_{21}N_4O_4]^+$ ($[M+H]^+$): 309.1563, found: 309.1551.

Methyl 4-acetyl-1-methyl-3-phenyl-4,5-dihydro-1H-pyrazole-4-carboxylate (**3w**)

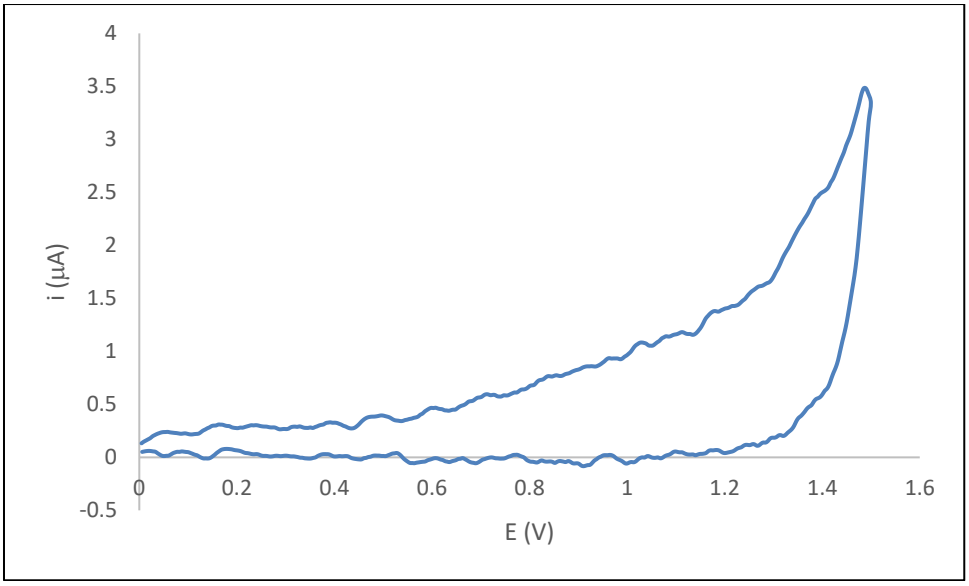


Following the general procedure **B** using hydrazone **1a** (59.3 mg) and methyl 2-fluoro-3-oxobutanoate (107.3 mg), **3w** was obtained as a yellow oil (35 mg, 0.135 mmol, 34%).

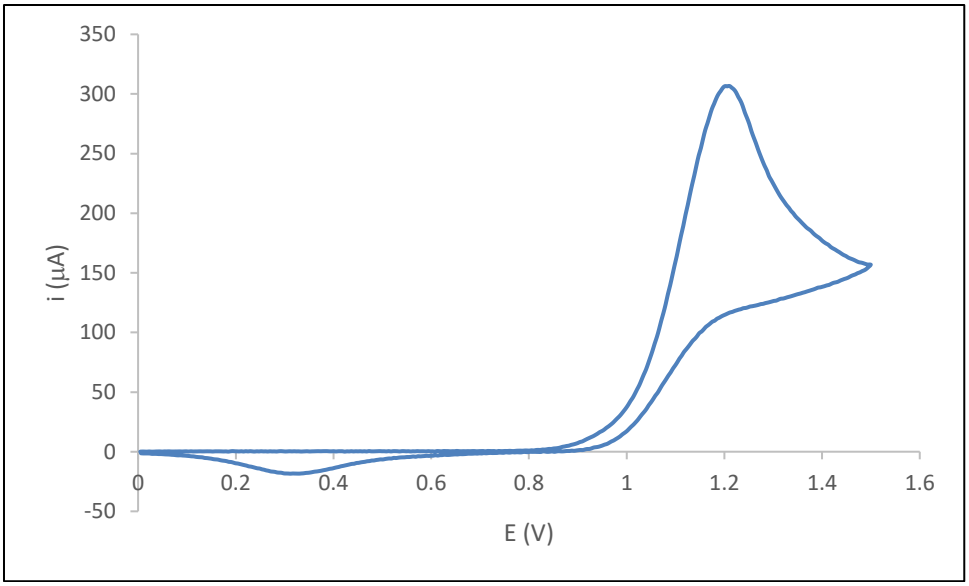
IR: *v* 2955, 1712, 1260, 693 cm^{-1}; **^{1}H {^{13}C} NMR** (300 MHz, $CDCl_3$): δ 7.64 – 7.59 (m, 2H), 7.35 – 7.28 (m, 3H), 3.89 (d, *J* = 10.2 Hz, 1H), 3.76 (s, 3H), 3.70 (d, *J* = 16.1 Hz, 1H), 2.98 (s, 3H), 2.25 (s, 3H); **^{13}C {^{1}H} NMR** (75 MHz, $CDCl_3$): δ 202.0, 169.5, 146.6, 131.8, 128.8, 128.5, 126.8, 75.4, 65.2, 53.2, 42.6, 28.0; **HRMS (ESI^{+})**: *m/z* calcd for $[C_{14}H_{17}N_2O_3]^+$ ($[M+H]^+$): 261.1239, found: 261.1233.

5. Cyclic voltammetry analysis

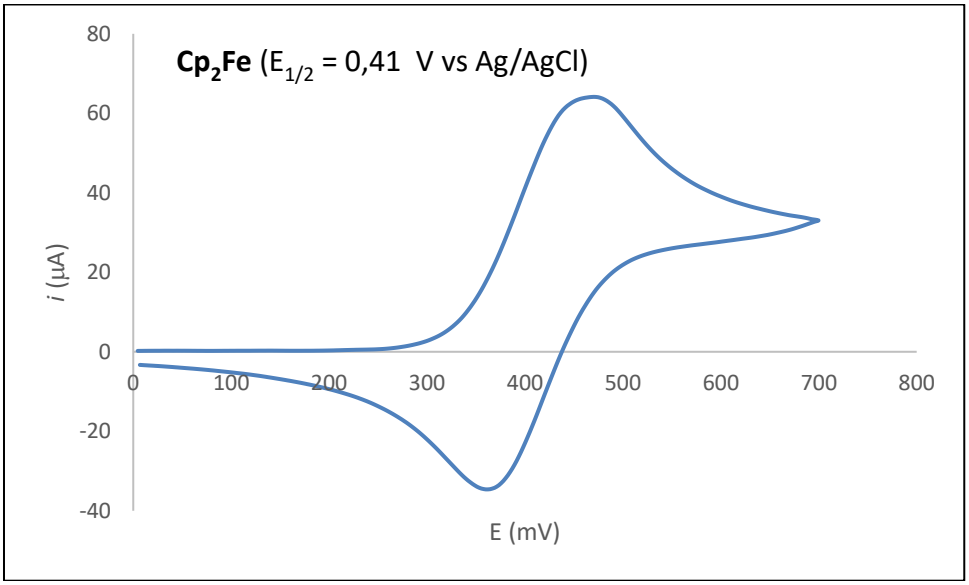
Cyclic voltammetry analyses were carried out in a three-electrode cell with a potentiostat.
Working electrode: Glassy Carbon (3 mm diameter); Counter electrode: Pt wire; Reference electrode: AgCl/Ag (aqueous NaCl 3 M).



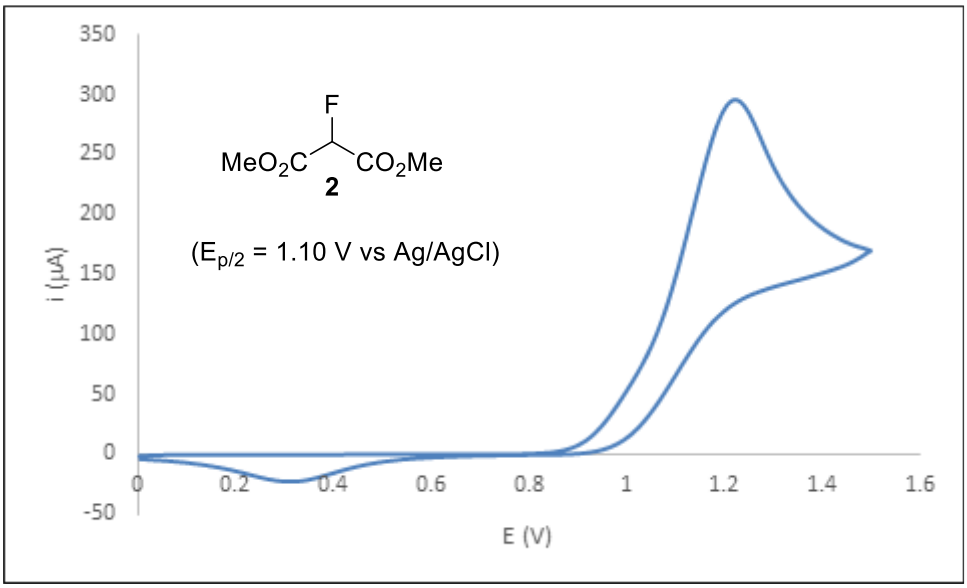
$LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 1.5 V; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$



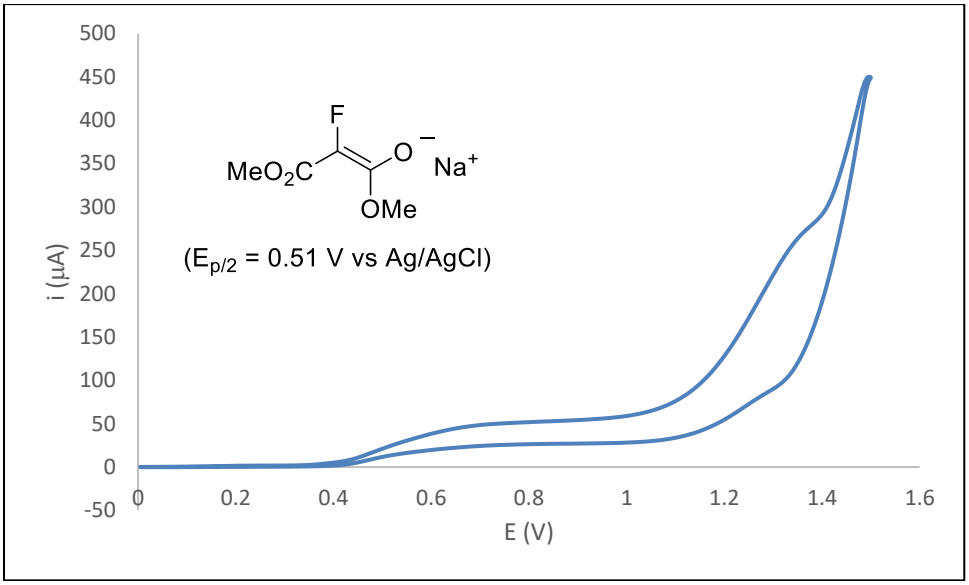
NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 1.5 V; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$



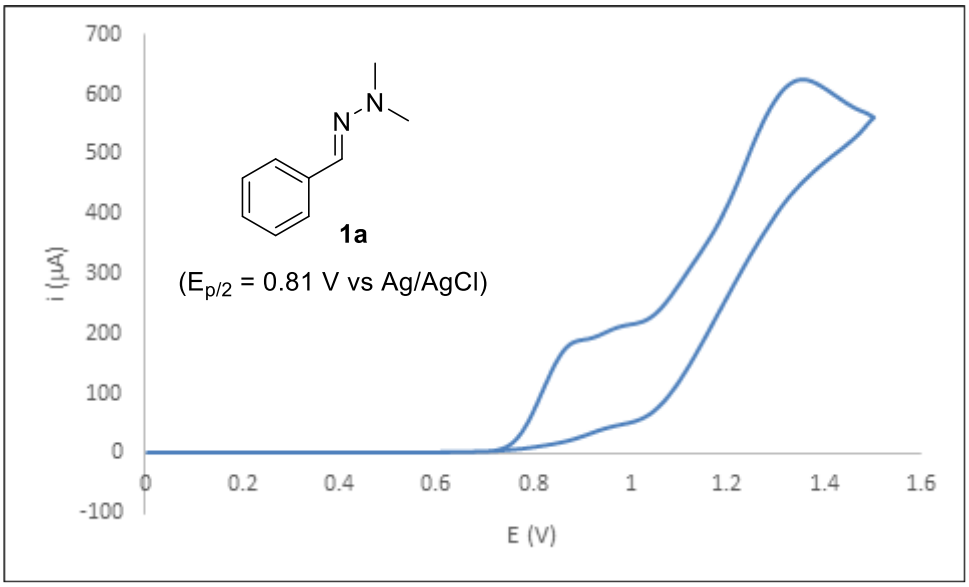
Ferrocene (2.5 mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 700 mV; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$.



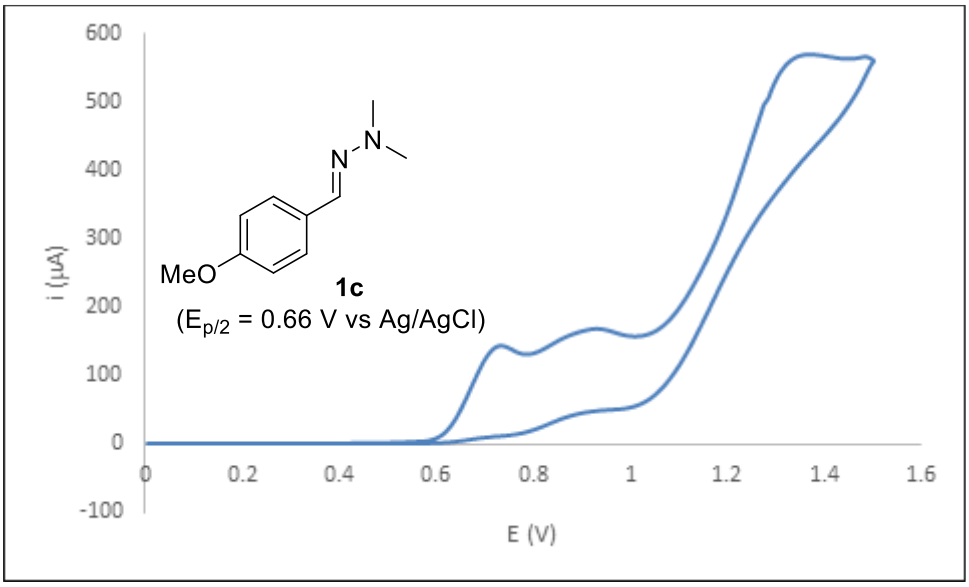
Dimethyl-2-fluoromalonate (8mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 1.5 V; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$



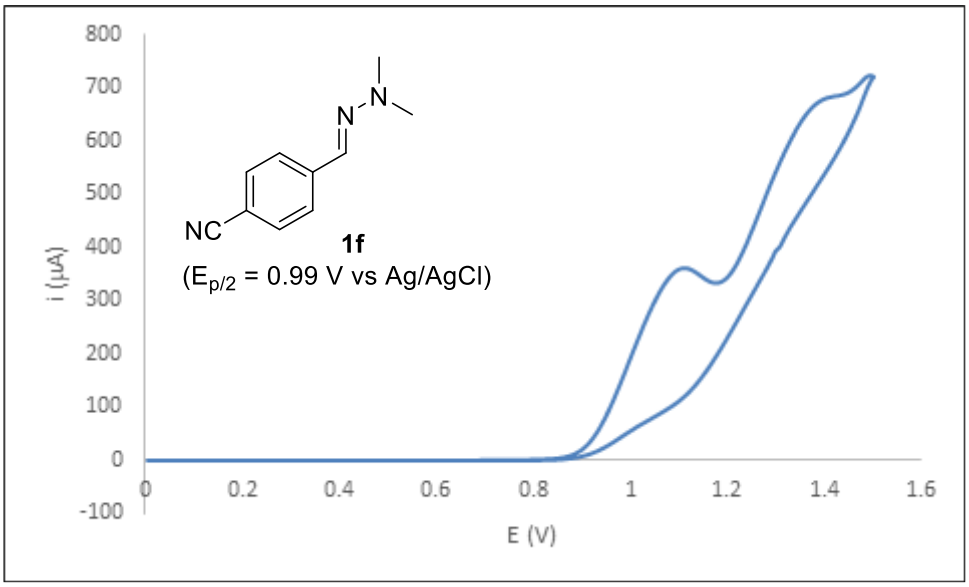
Dimethyl-2-fluoromalonate (8mM), MeONa (32mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 1.5 V; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$



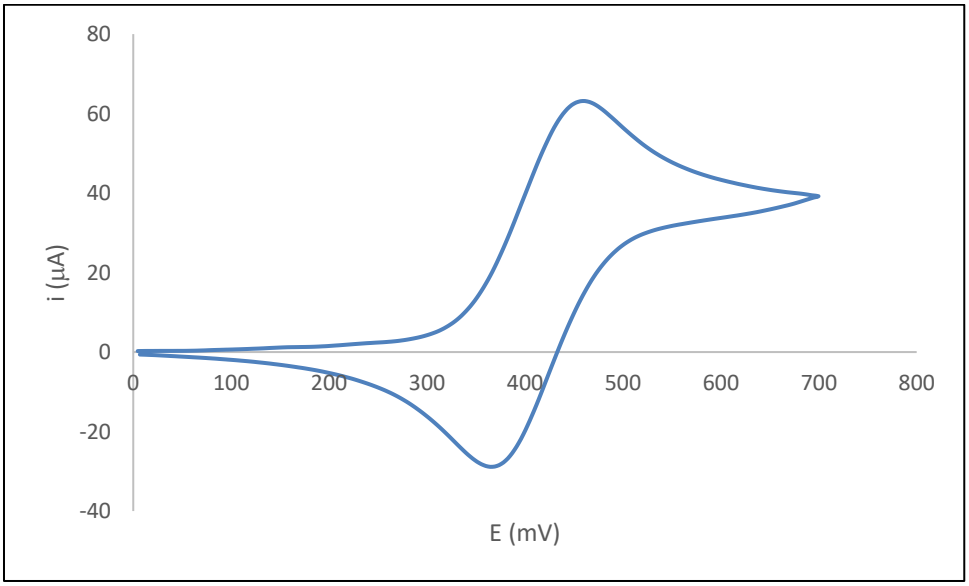
Hydrazone **1a** (8mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 1.5 V; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$



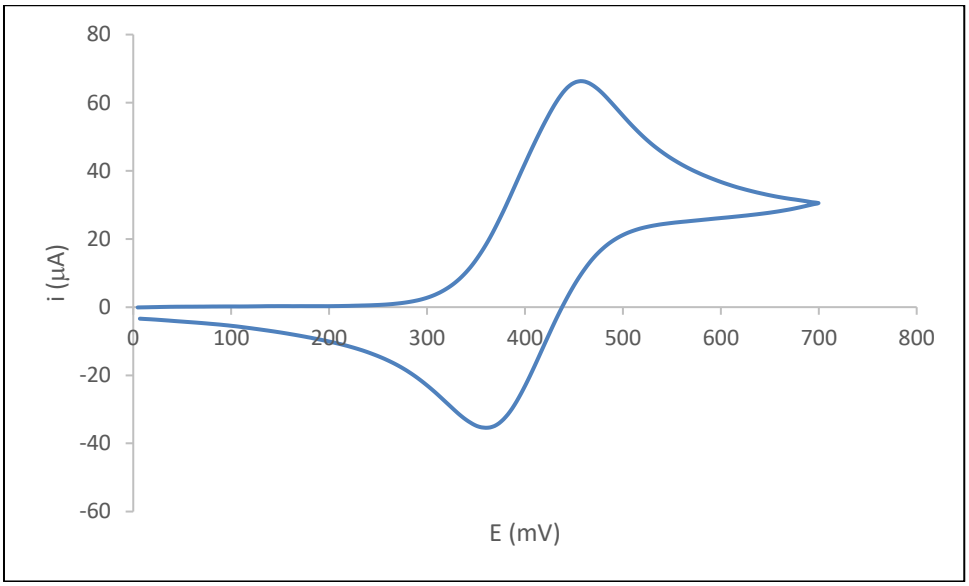
Hydrazone **1c** (8mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 1.5 V; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$



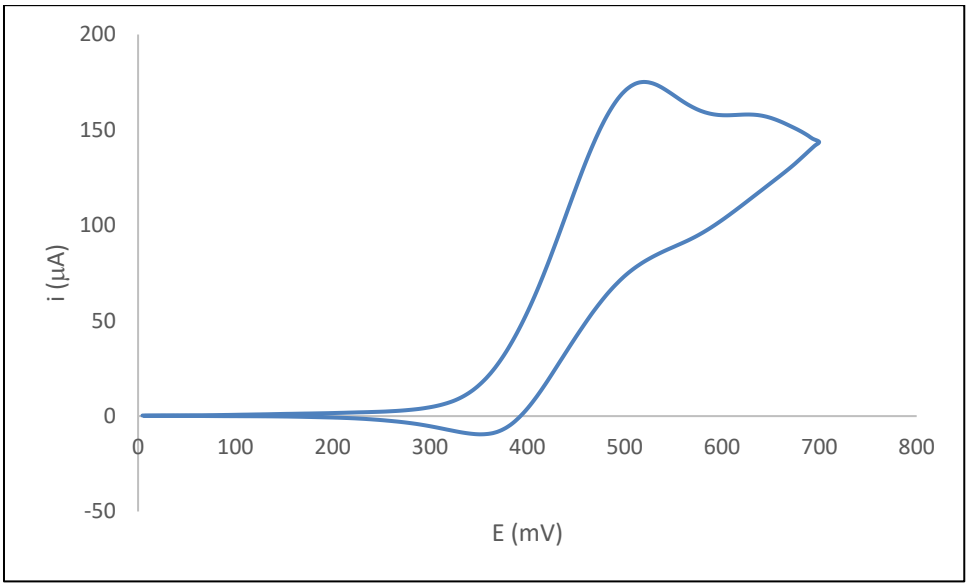
Hydrazone **1f** (8mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 1.5 V; E (end) = 0 V; Sweep rate: 100 $mV.s^{-}$



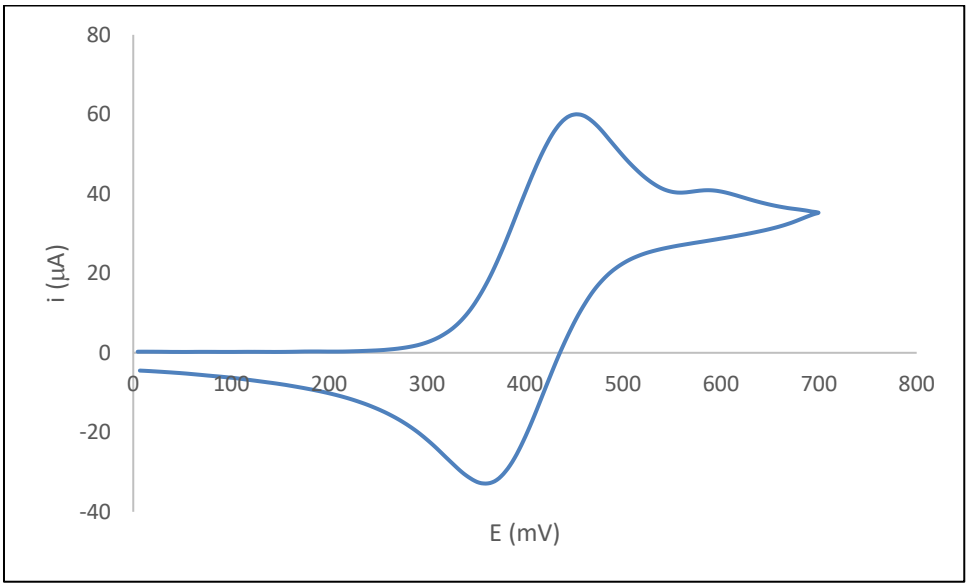
MeONa (32mM), ferrocene (2.5mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 1.5 V; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$



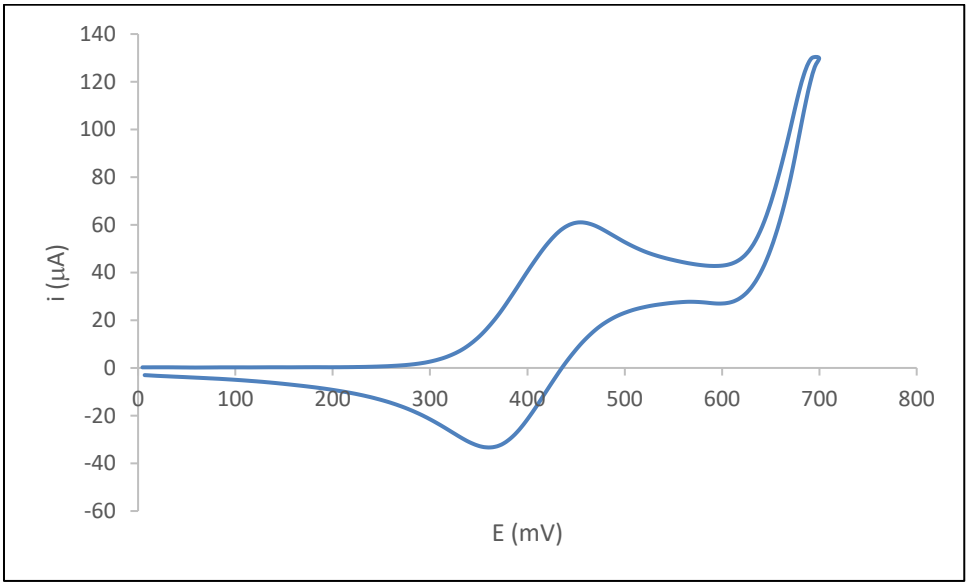
Dimethyl-2-fluoromalonate (8mM), ferrocene (2.5mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 700 mV; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$



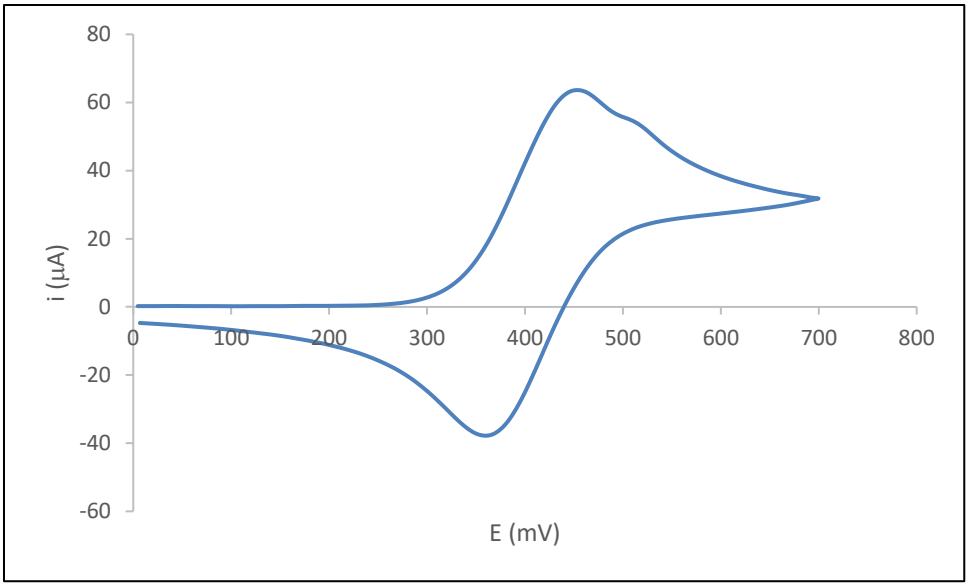
Dimethyl-2-fluoromalonate (8mM), MeONa (32mM), ferrocene (2.5mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 700 mV; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$



Hydrazone **1a** (8mM), ferrocene (2.5mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 700 mV; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$

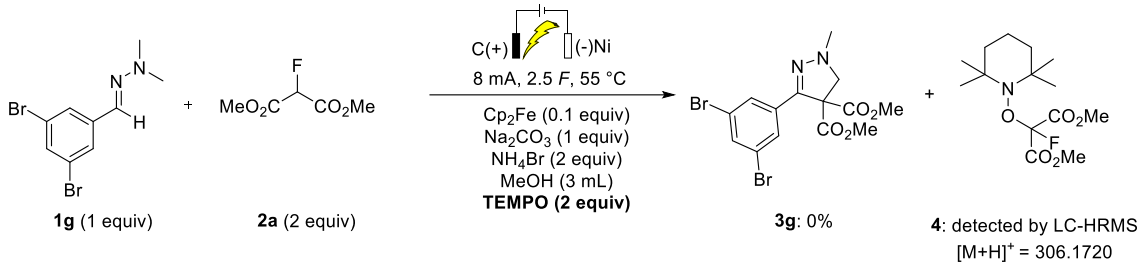


Hydrazone **1c** (8mM), ferrocene (2.5mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 700 mV; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$

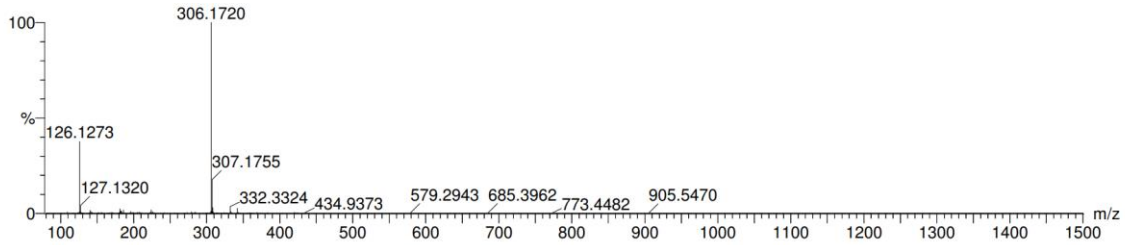


Hydrazone **1f** (8mM), ferrocene (2.5mM), NH_4Br (16mM), $LiClO_4$ (0.1M) in MeOH
E (initial) = 0 V; E (high) = 700 mV; E (end) = 0 V; Sweep rate: 100 $mV.s^{-1}$

6. Radical trapping experiment



An Electrasyn undivided cell (5 mL) was charged with a magnetic stir bar, hydrazone **1g** (61 mg, 0.2 mmol, 1.0 equiv.), Na_2CO_3 (21.2 mg, 0.2 mmol, 1 equiv), Cp_2Fe (3.7 mg, 0.02 mmol, 0.1 equiv), NH_4Br (39.2 mg, 0.4 mmol, 2 equiv). The vial was closed with the ElectraSyn cap holding the electrodes (anode: Graphite SK-50, cathode: Nickel plate) and flushed under argon for 2 min. Dimethyl-2-fluoromalonate **2** (60 mg, 0.4 mmol, 2.0 equiv) was added as a solution in MeOH (6 mL). Argon gas (balloon) was bubbled through the solution during 5 minutes. The electrolysis was carried out at room temperature under constant current (8 mA) and was stopped after 1 h 40 min (electricity = 2.5 $F.mol^{-1}$). 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) was added as NMR internal standard. The reaction mixture was poured in water (10 mL) and extracted with EtOAc (3x10 mL). The combined organic phases were washed with brine, dried over $MgSO_4$, filtered and concentrated under vacuum. ^1H NMR analysis of the crude reaction mixture indicated total recovery of hydrazone **1g** while **3g** could not be detected. Additionally, TEMPO adduct **4** was detected by LC-HRMS. **HRMS (ESI$^+$)**: *m/z* calcd for $[C_{14}H_{25}NO_5F]^+$ ($[M+H]^+$): 306.1717, found: 306.1720.

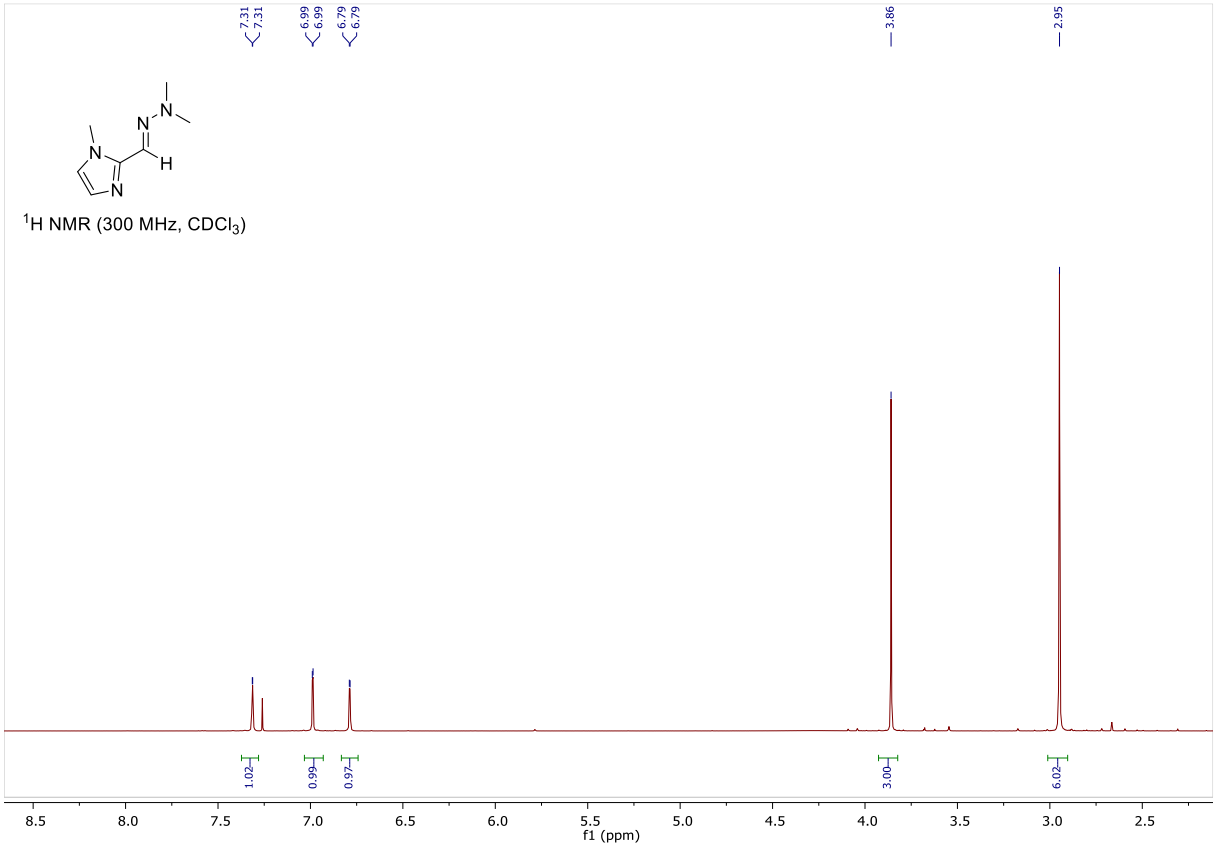


Minimum:				-1.5			
Maximum:		10.0	5.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
306.1720	306.1717	0.3	1.0	2.5	1808.7	0.0	C14 H25 N O5 F

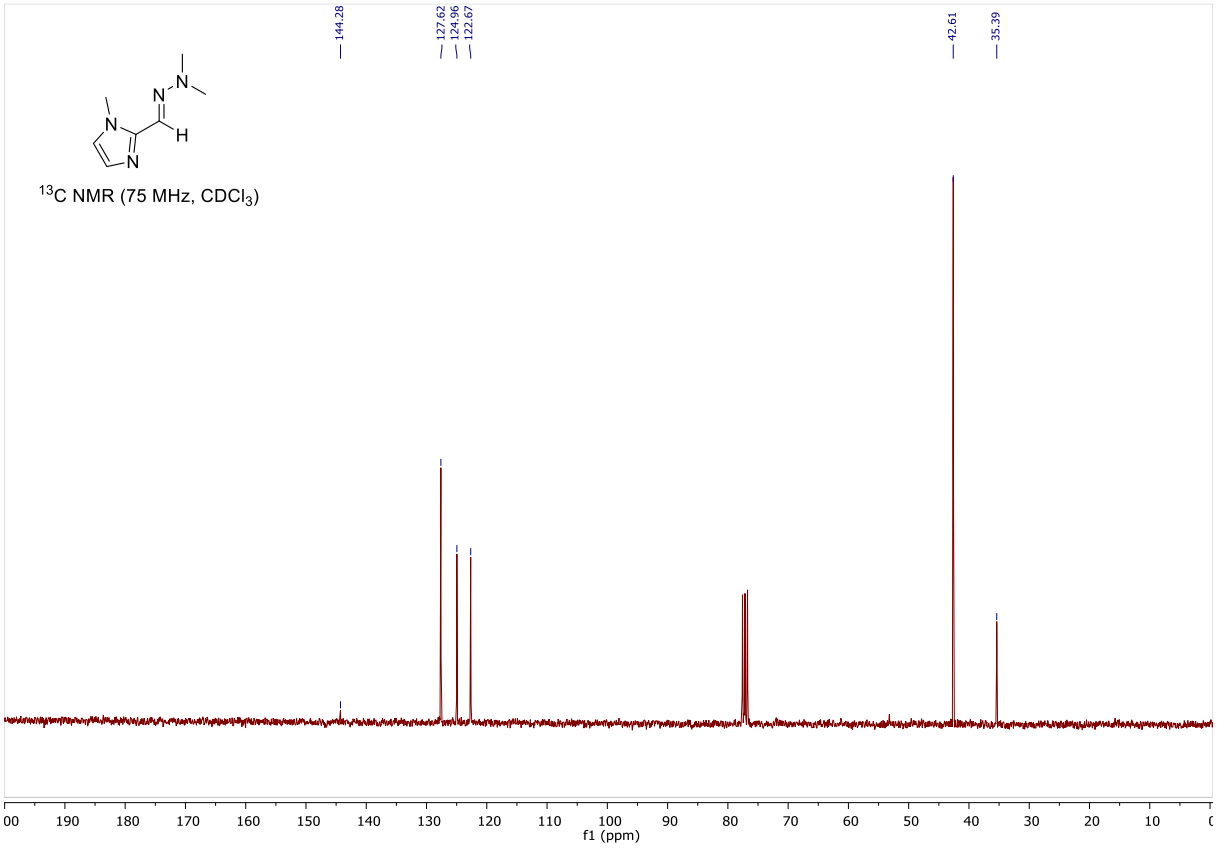
References

[1] (a) Dubrovskiy, A. V.; Larock, R. C. *Org. Lett.* **2011**, *13*, 4136. (b) Cioc, R. C.; Crockatt, M.; van der Waal, J. C.; Bruijnincx, P. C. A. *ChemSusChem.* **2022**, *15*, e202201139. (c) Ros, A.; Estepa, B.; López-Rodríguez, R.; Álvarez, E.; Fernández, R.; Lassaletta, J. M. *Angew. Chem. Int. Ed.* **2011**, *50*, 11724. (d) Tan, Z.; Zhang, S.; Zhang, Y.; Li, Y.; Ni, M.; Feng, B. *J. Org. Chem.* **2017**, *82*, 9384. (e) Ros, A.; López-Rodríguez, R.; Estepa, B.; Álvarez, E.; Fernández, R.; Lassaletta, J. M. *J. Am. Chem. Soc.* **2012**, *134*, 4573. (f) Li, X.; Golz, C.; Alcarazo, M. *Angew. Chem. Int. Ed.* **2021**, *60*, 694.

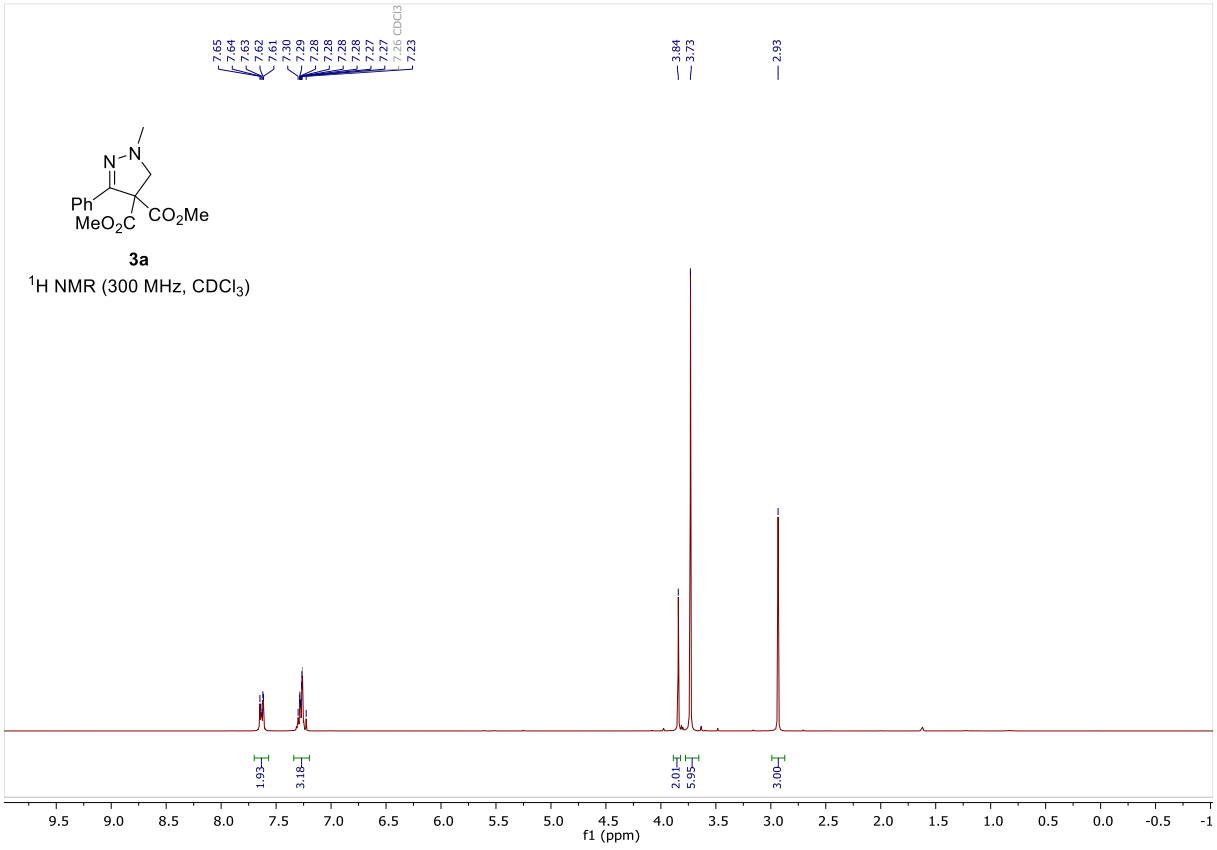
7. NMR spectra



^{1}H NMR (300 MHz, $CDCl_3$)

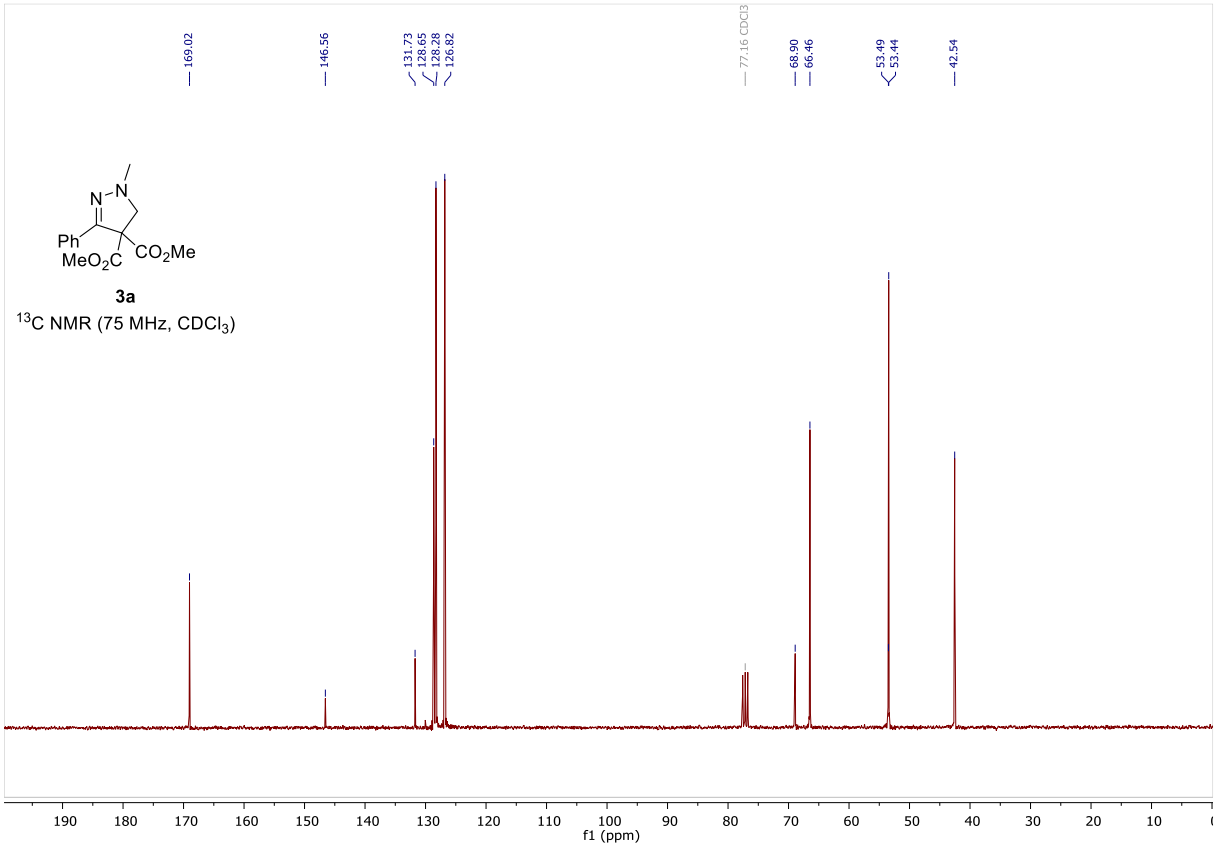


^{13}C NMR (75 MHz, $CDCl_3$)



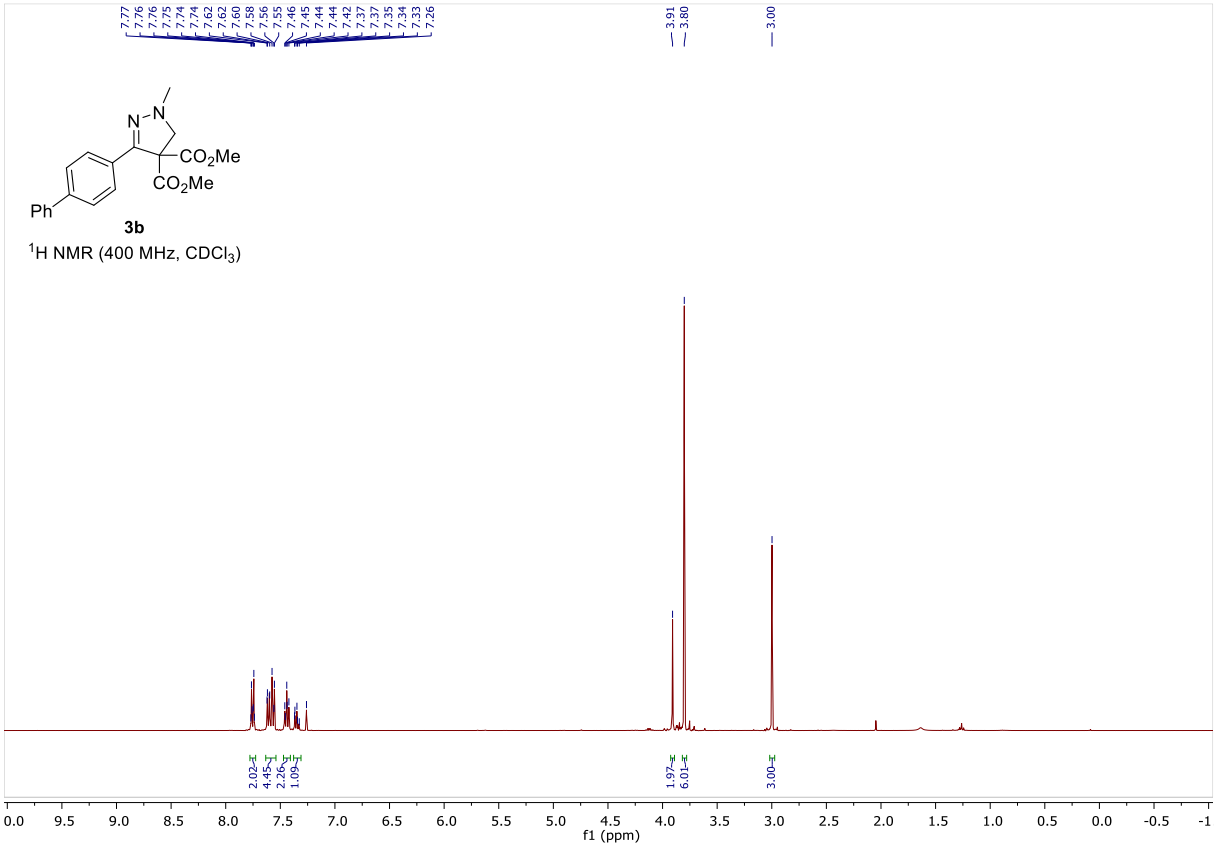
3a

^{1}H NMR (300 MHz, $CDCl_3$)



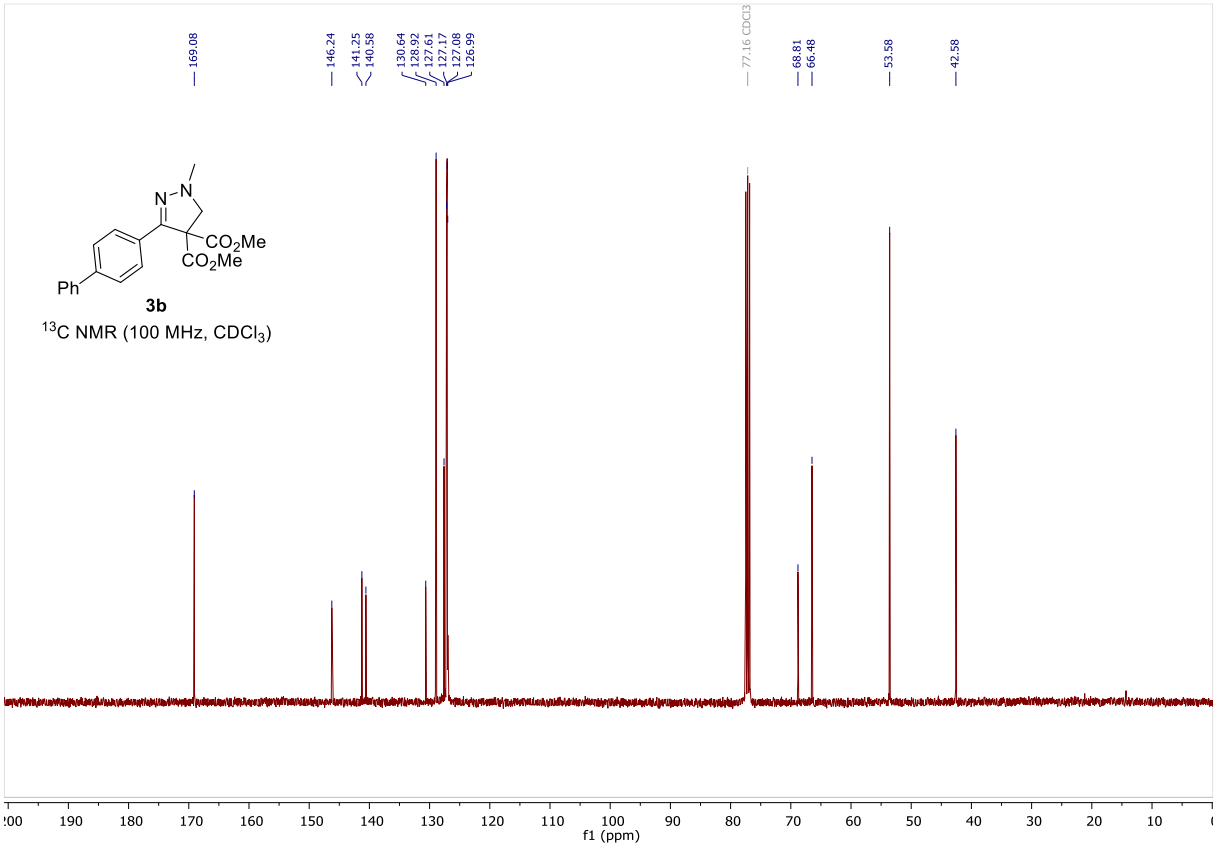
3a

^{13}C NMR (75 MHz, $CDCl_3$)



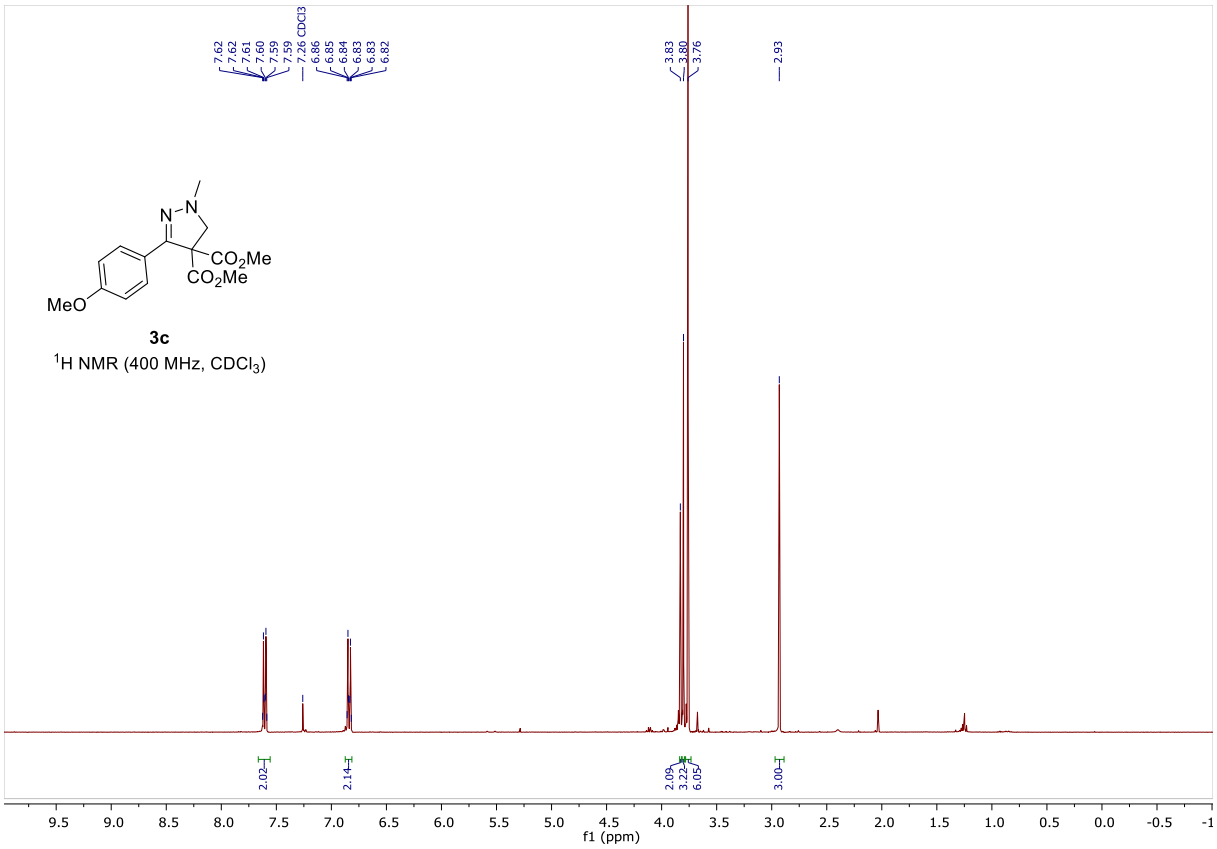
3b

^{1}H NMR (400 MHz, $CDCl_3$)



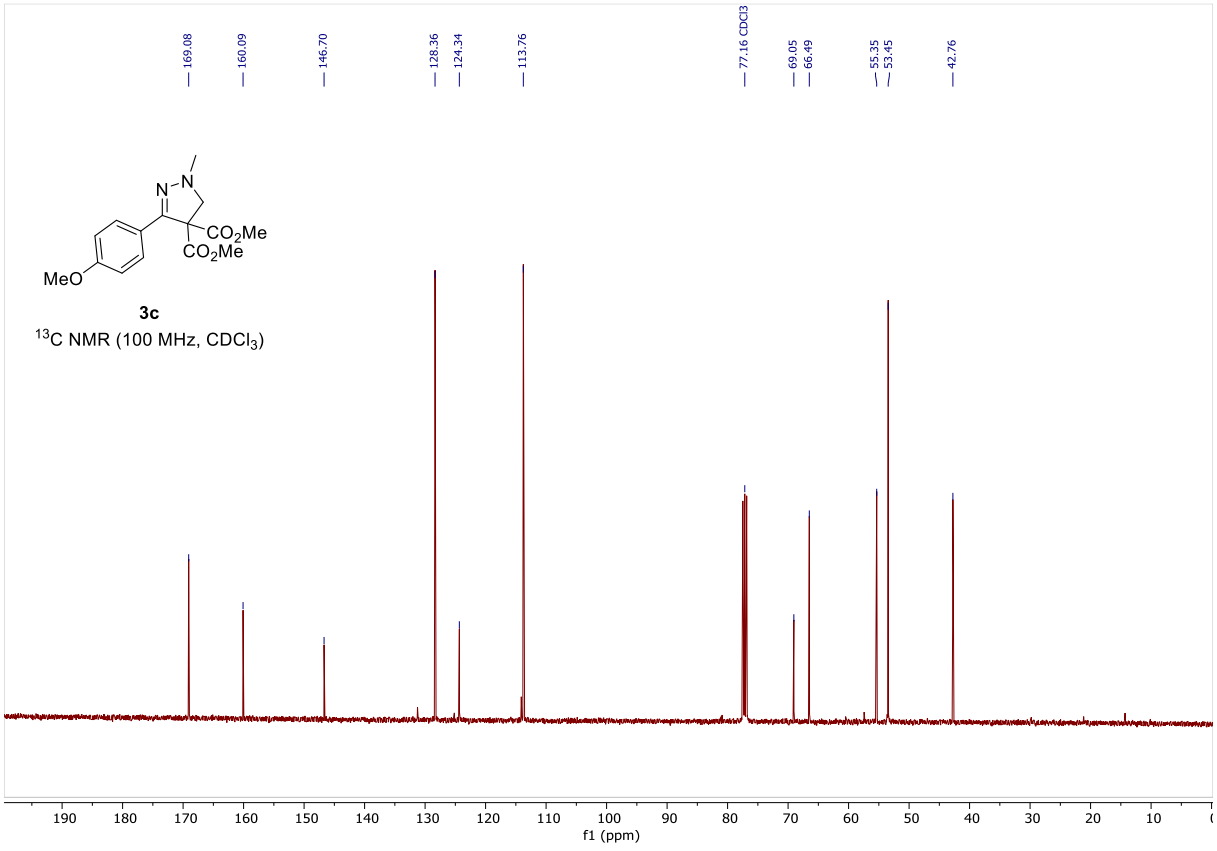
3b

^{13}C NMR (100 MHz, $CDCl_3$)



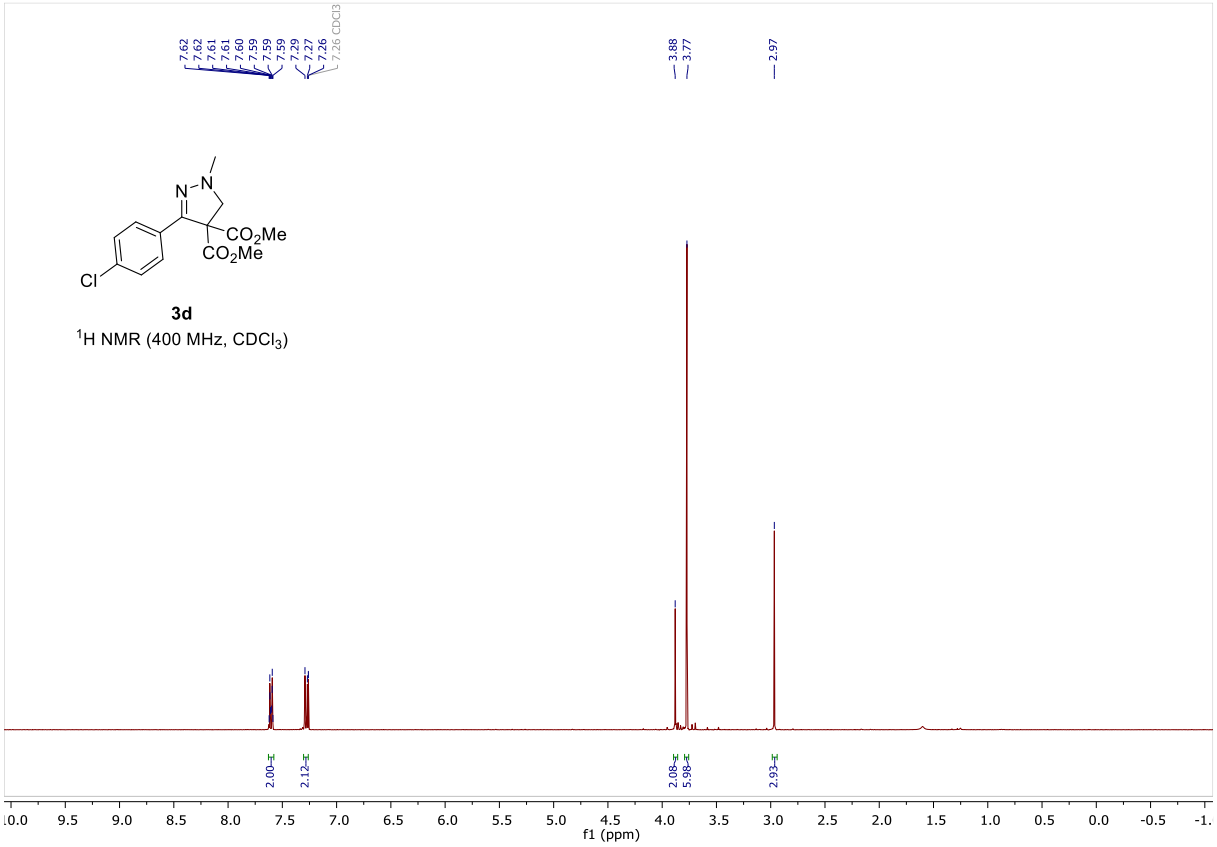
3c

^{1}H NMR (400 MHz, $CDCl_3$)



3c

^{13}C NMR (100 MHz, $CDCl_3$)



3d

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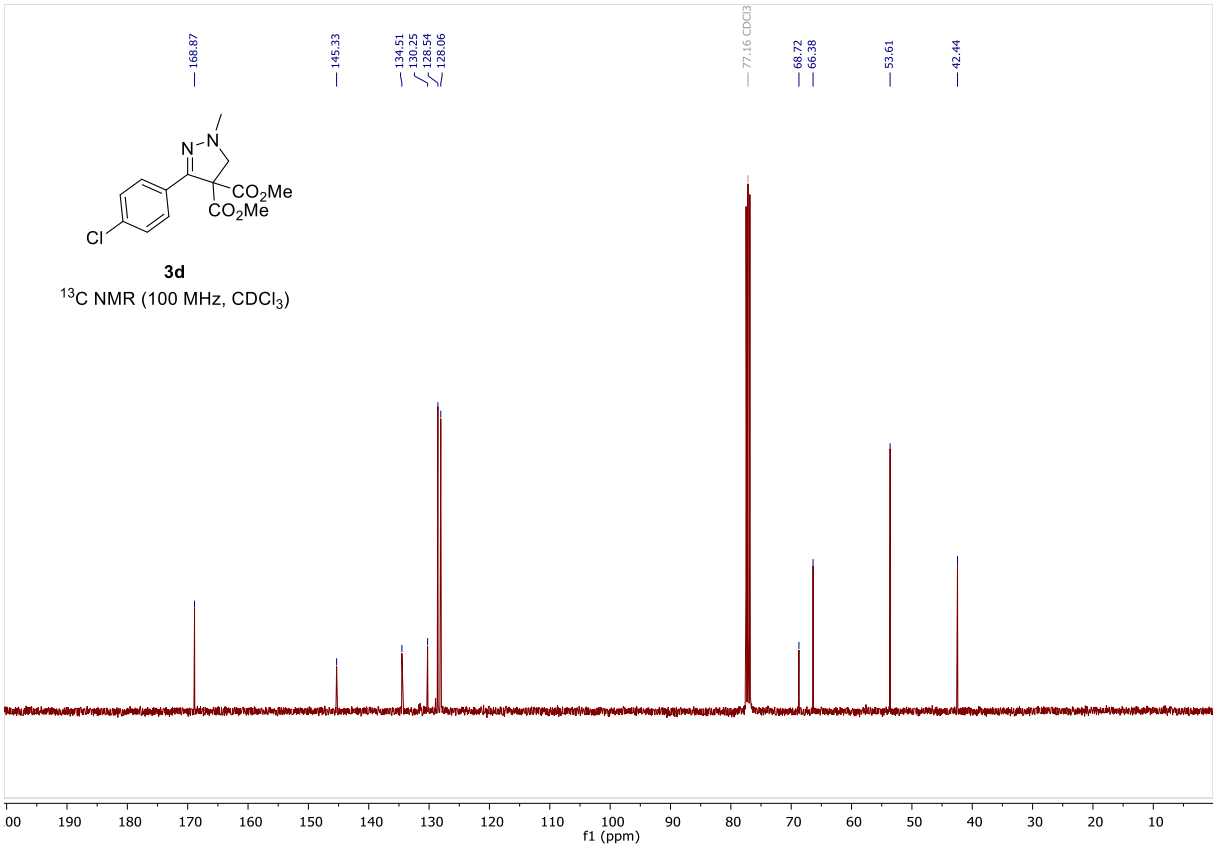

3d

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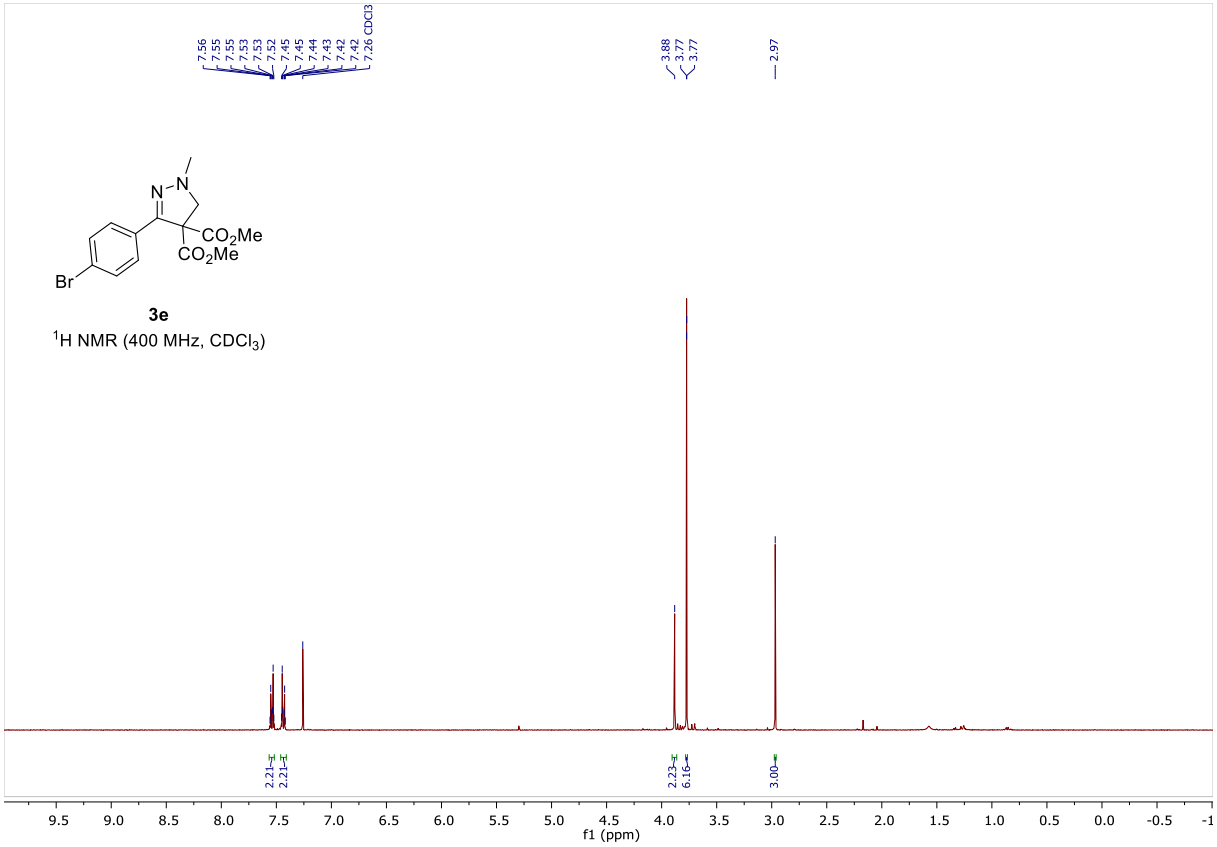

3e

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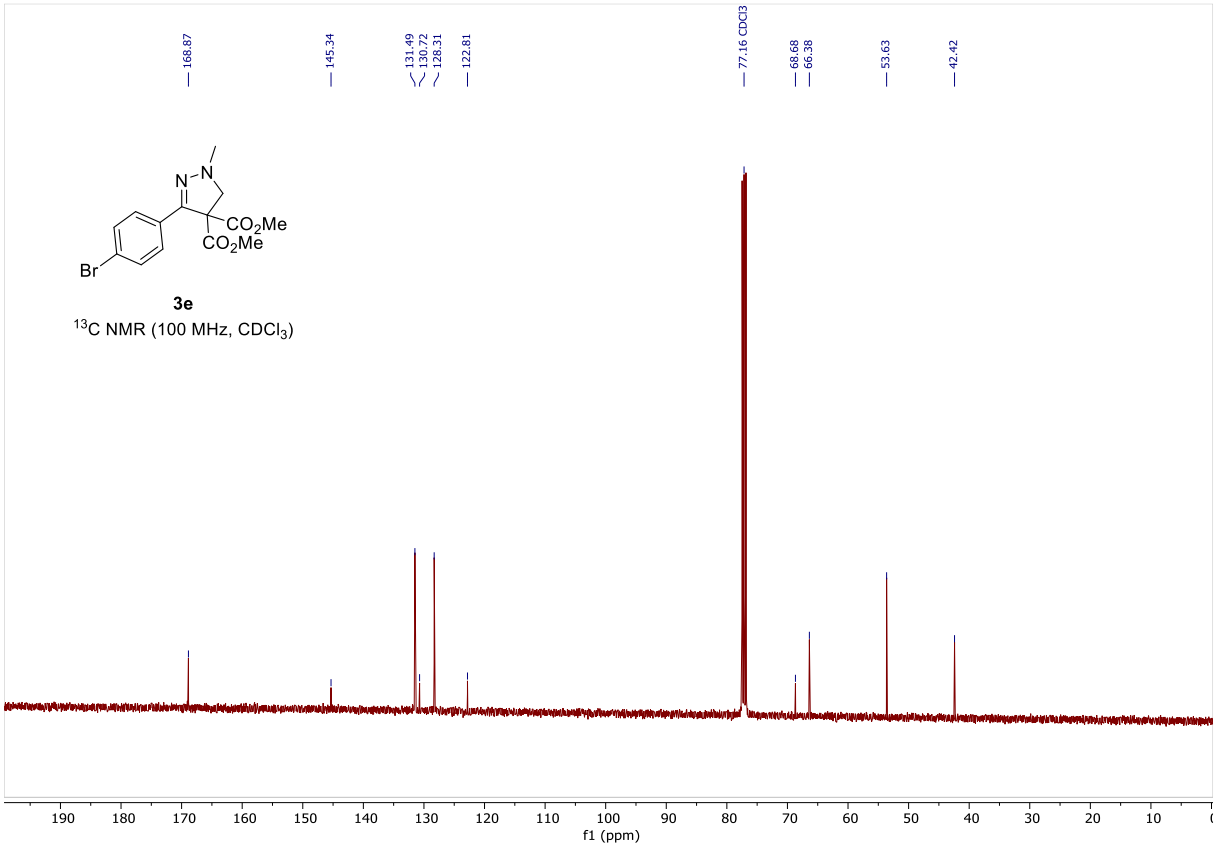

3e

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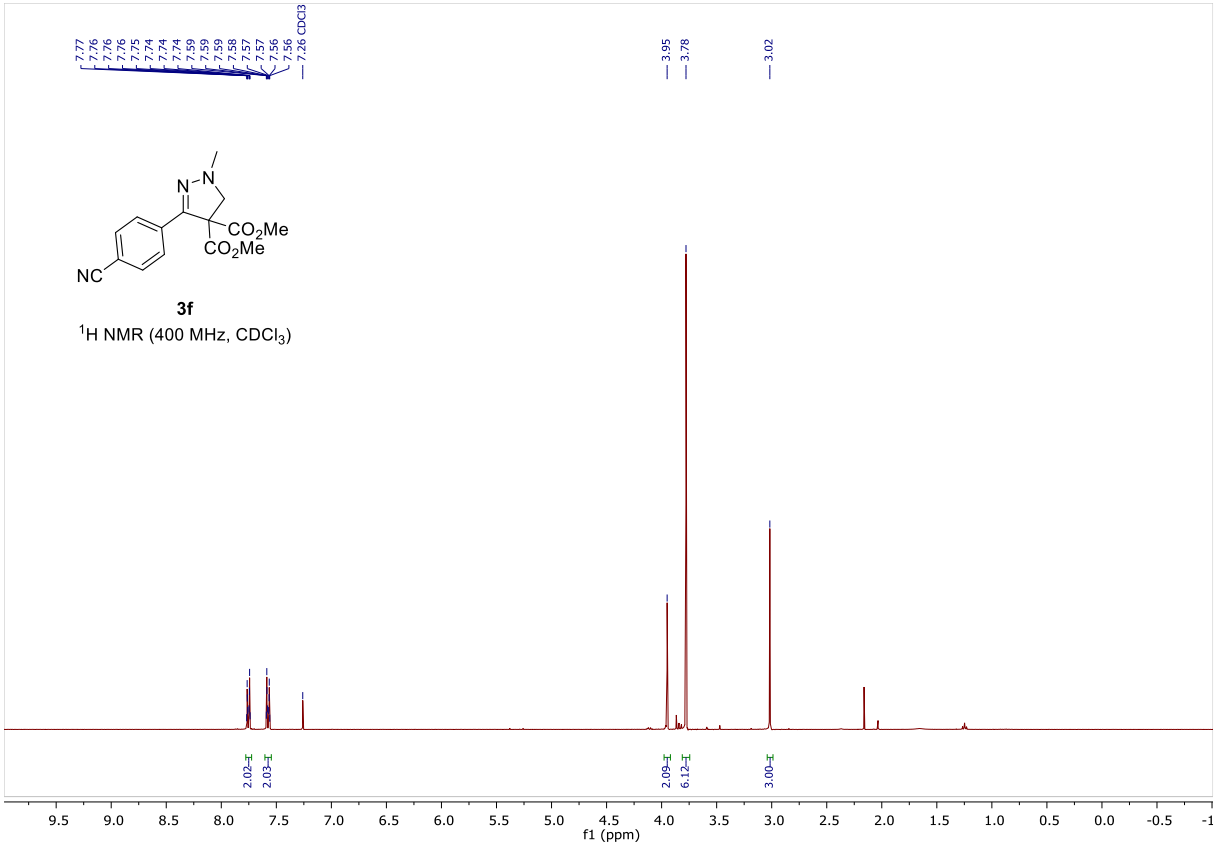

3f

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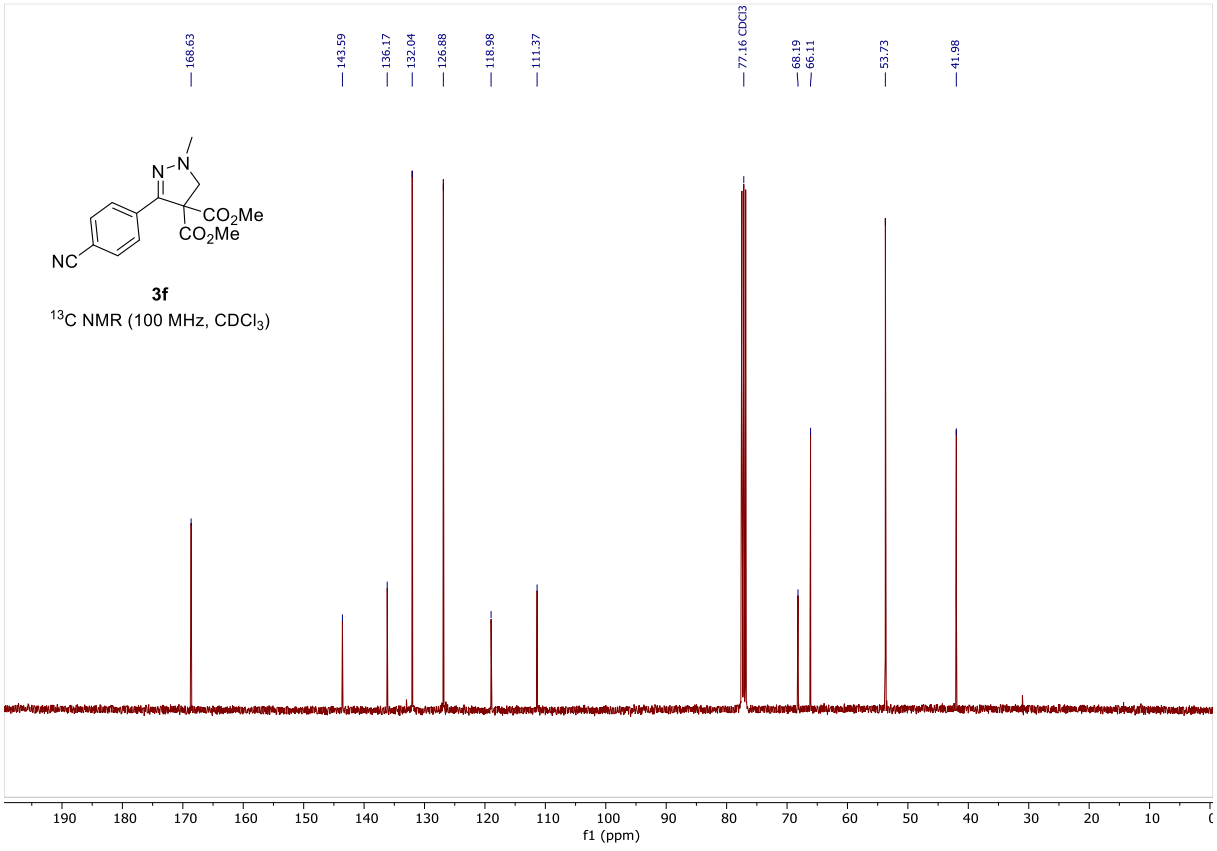

3f

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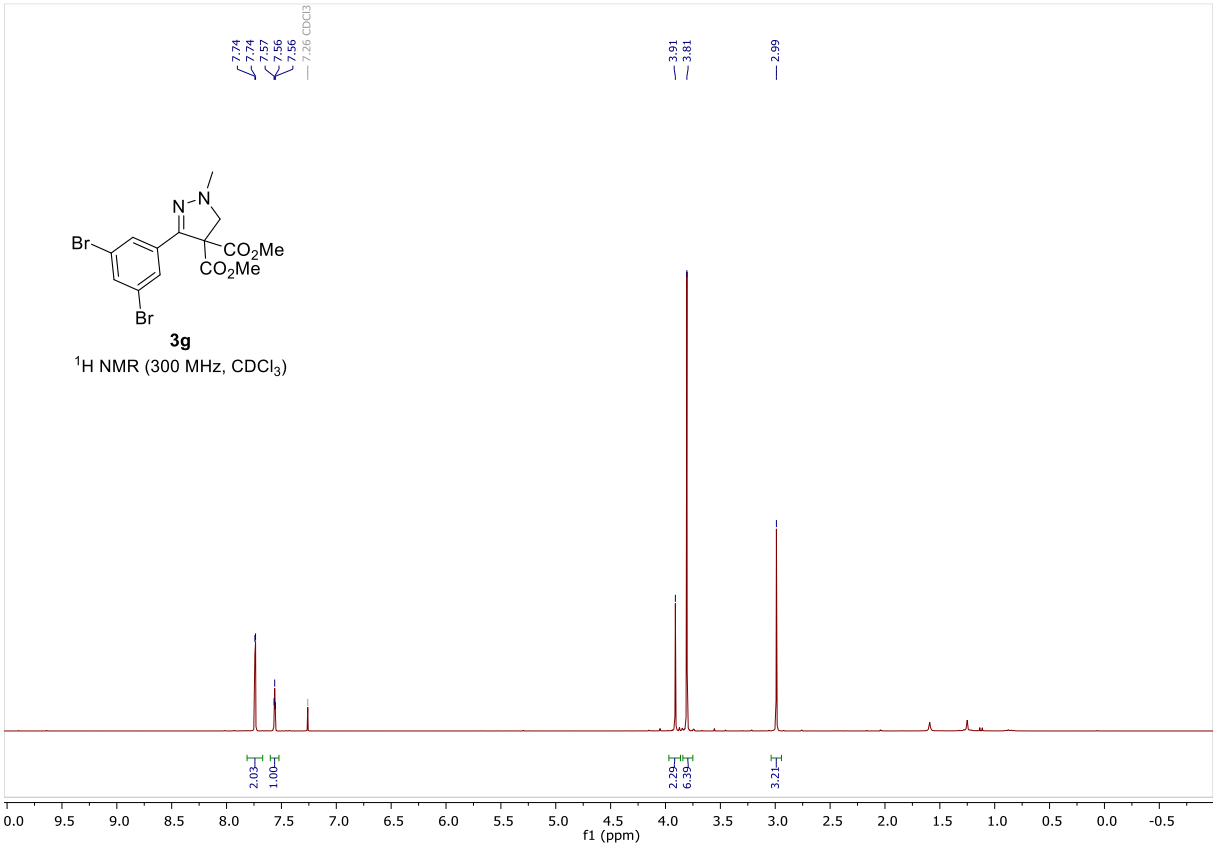

3g

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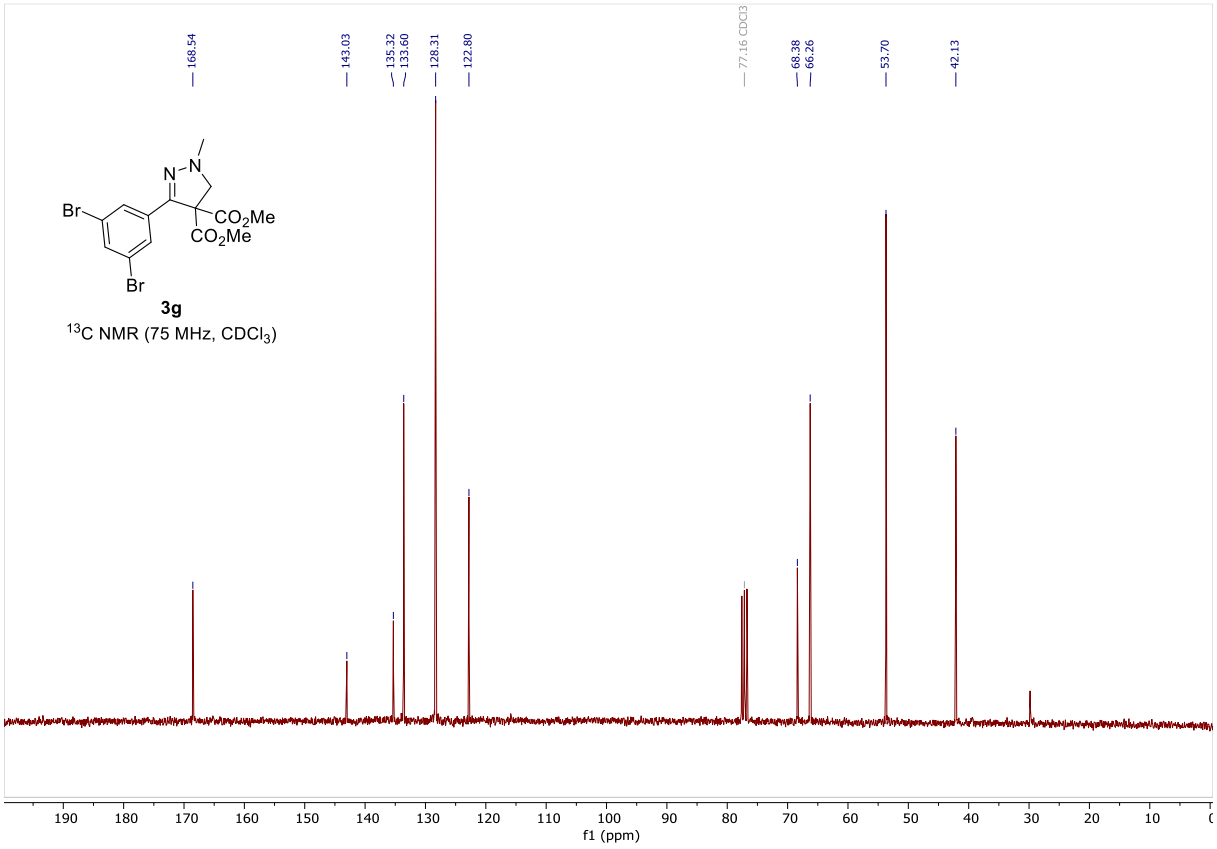

3g

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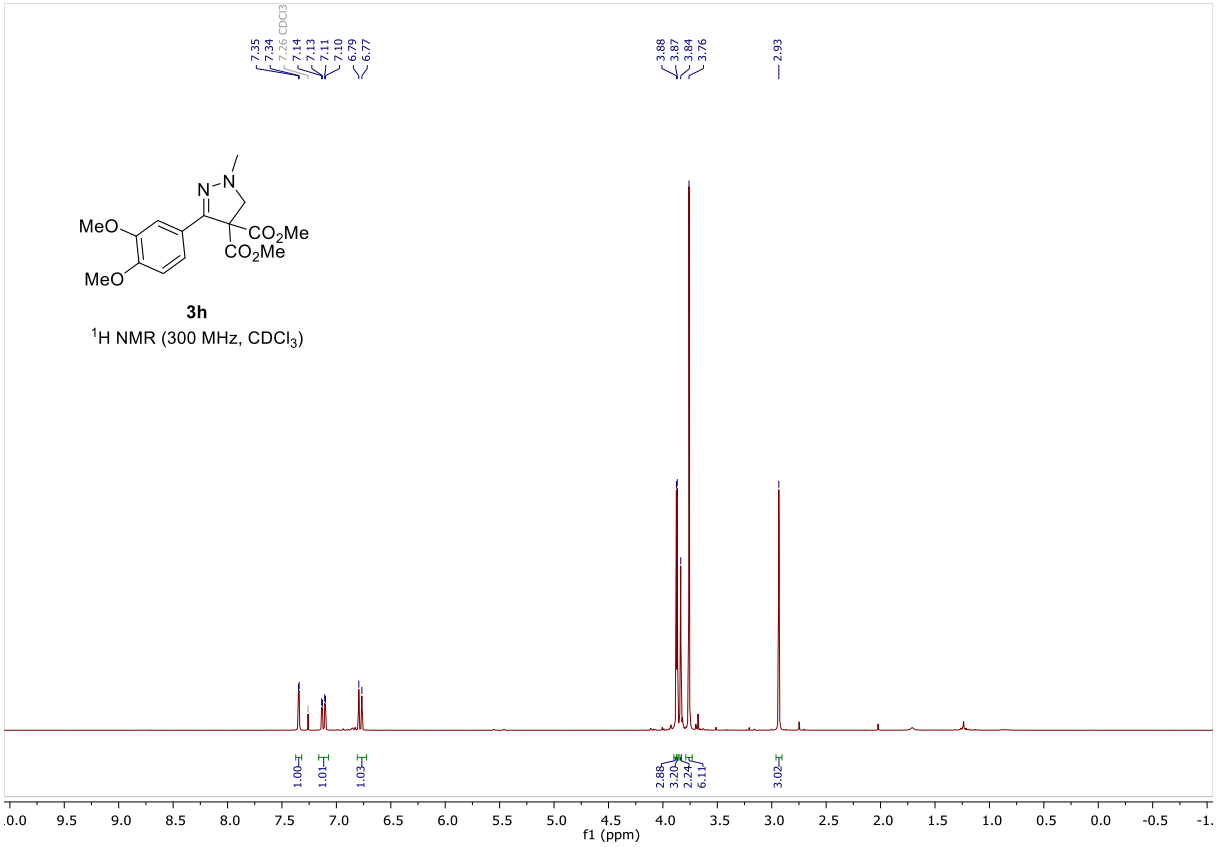

3h

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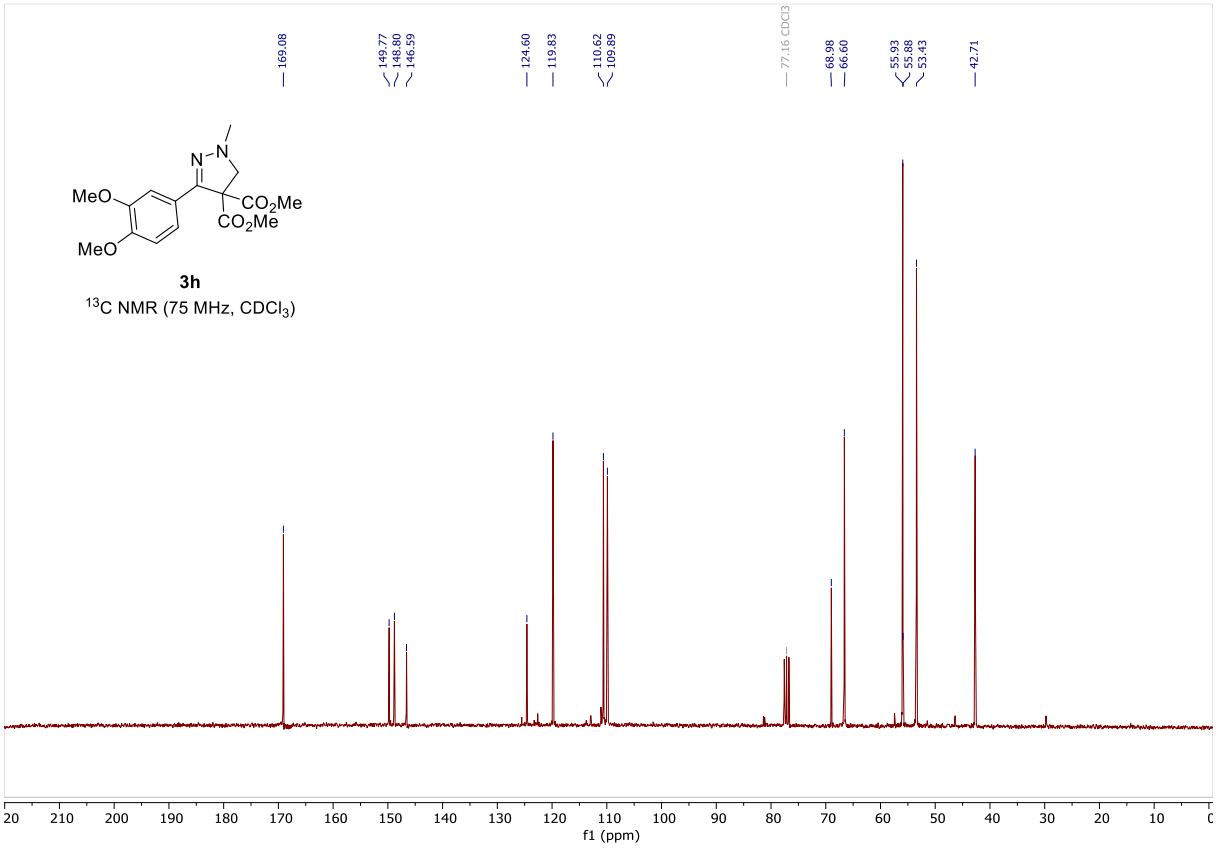

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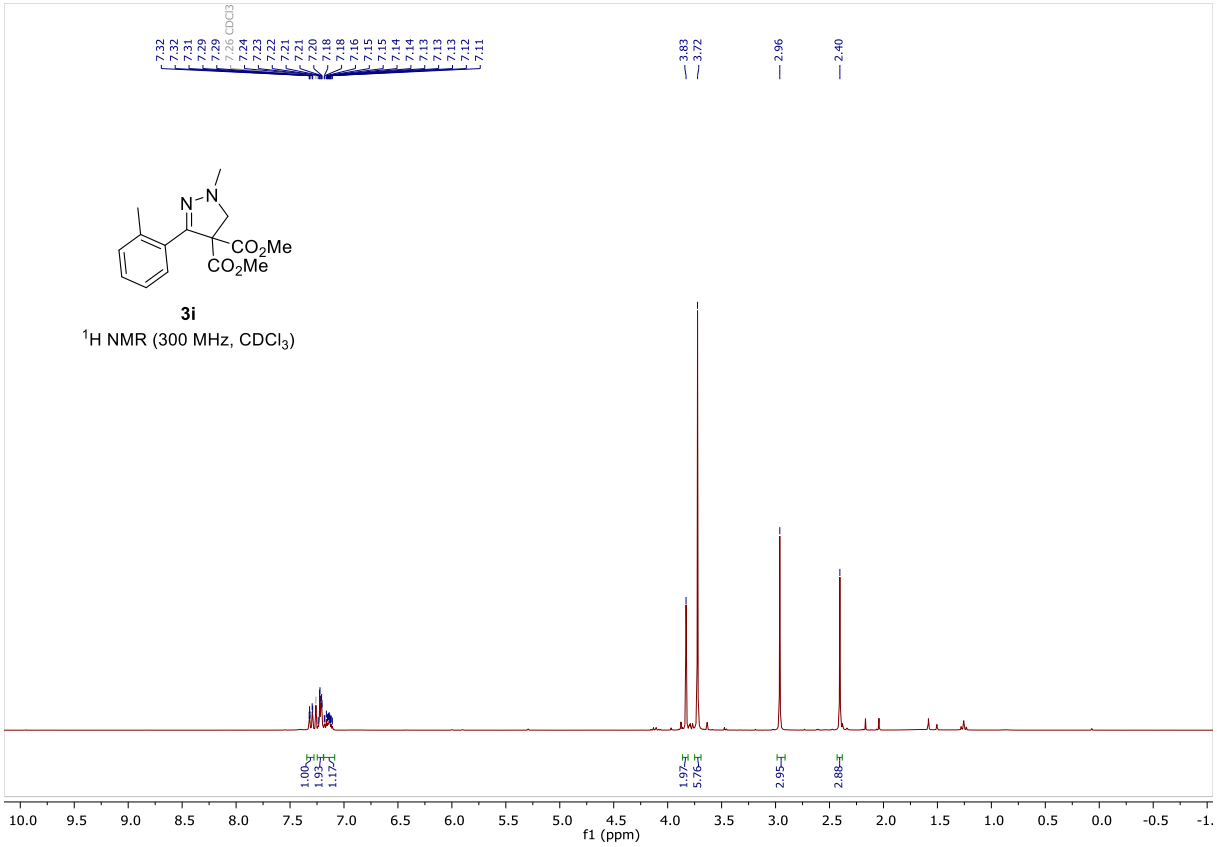

3i

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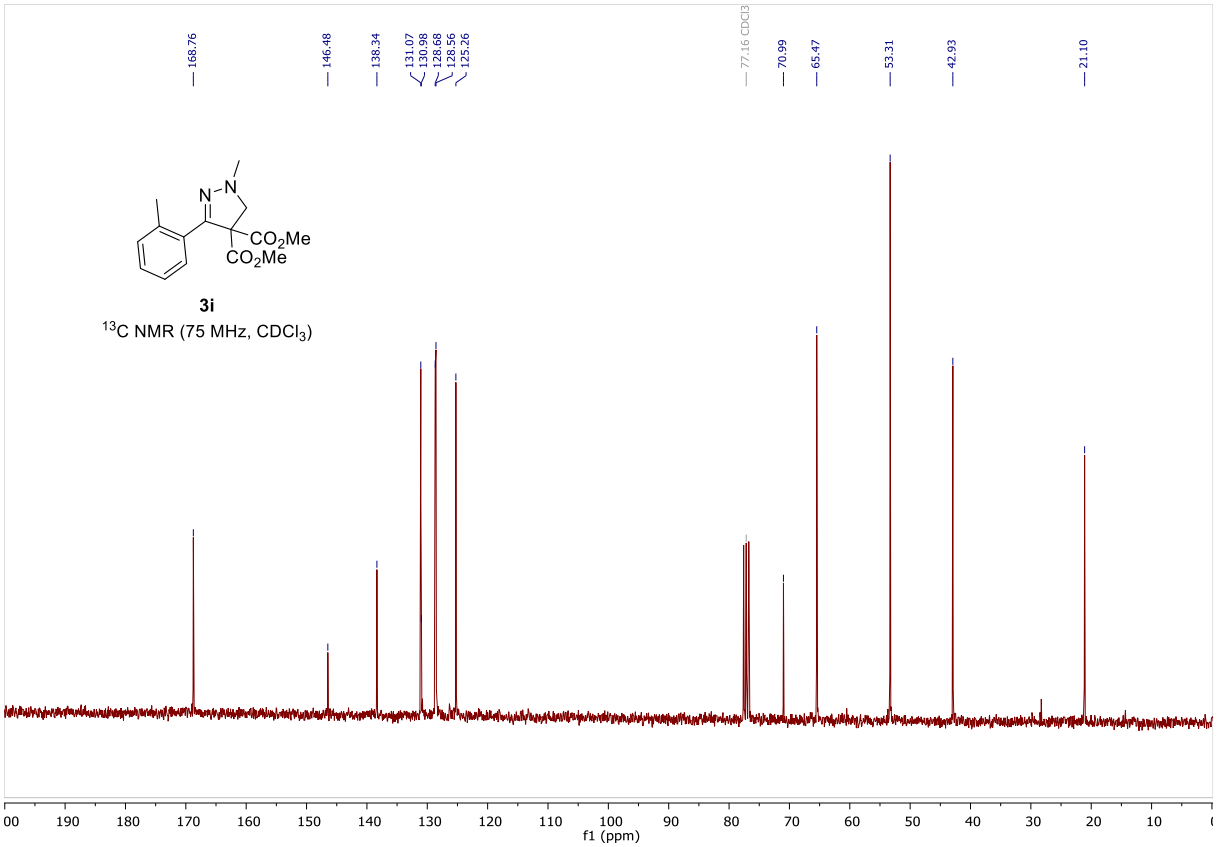

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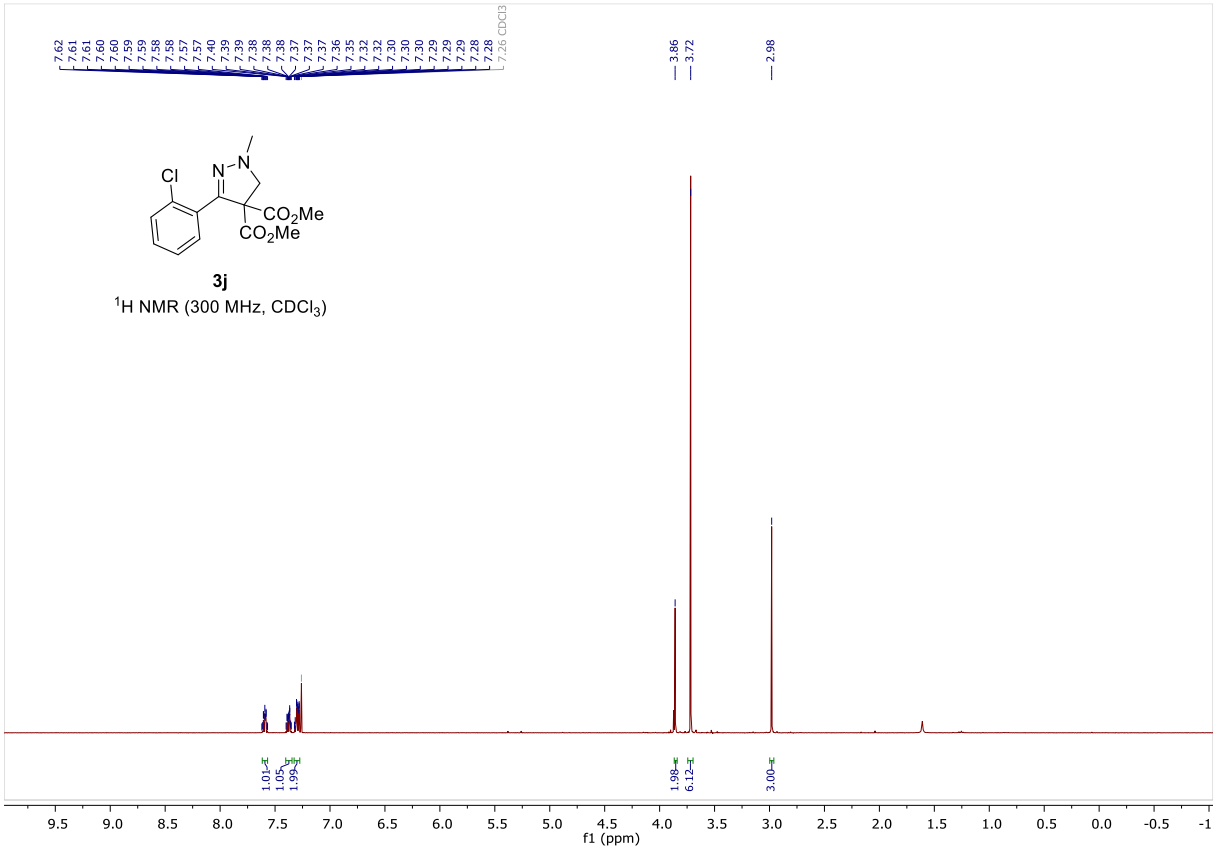

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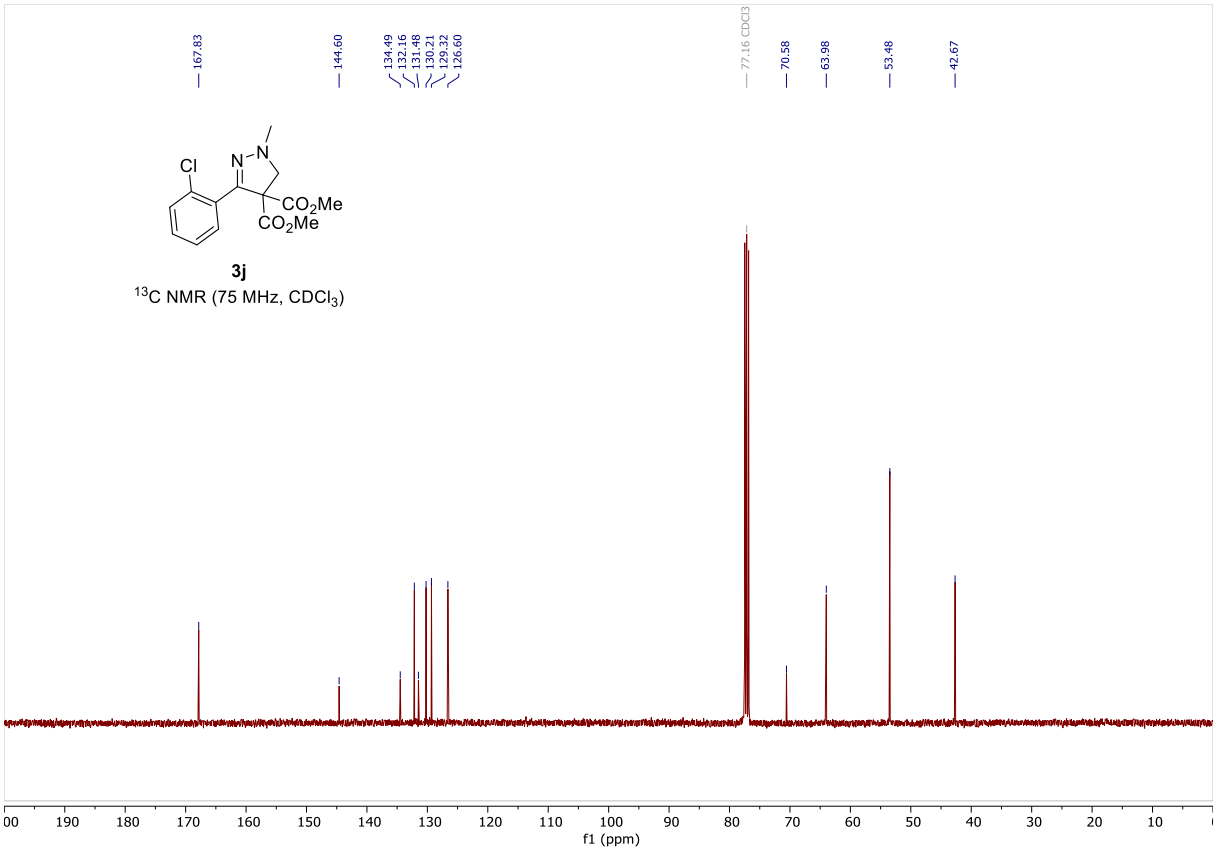

3j

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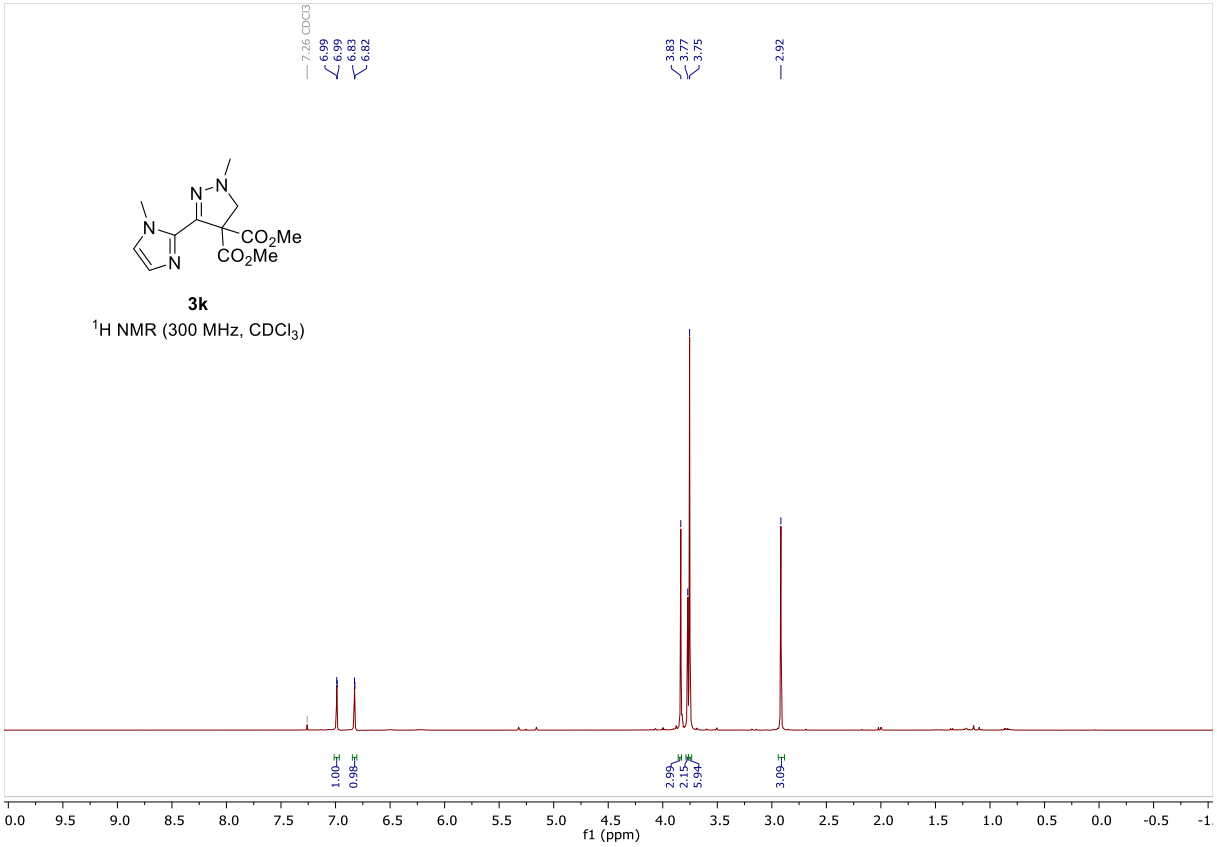

3k

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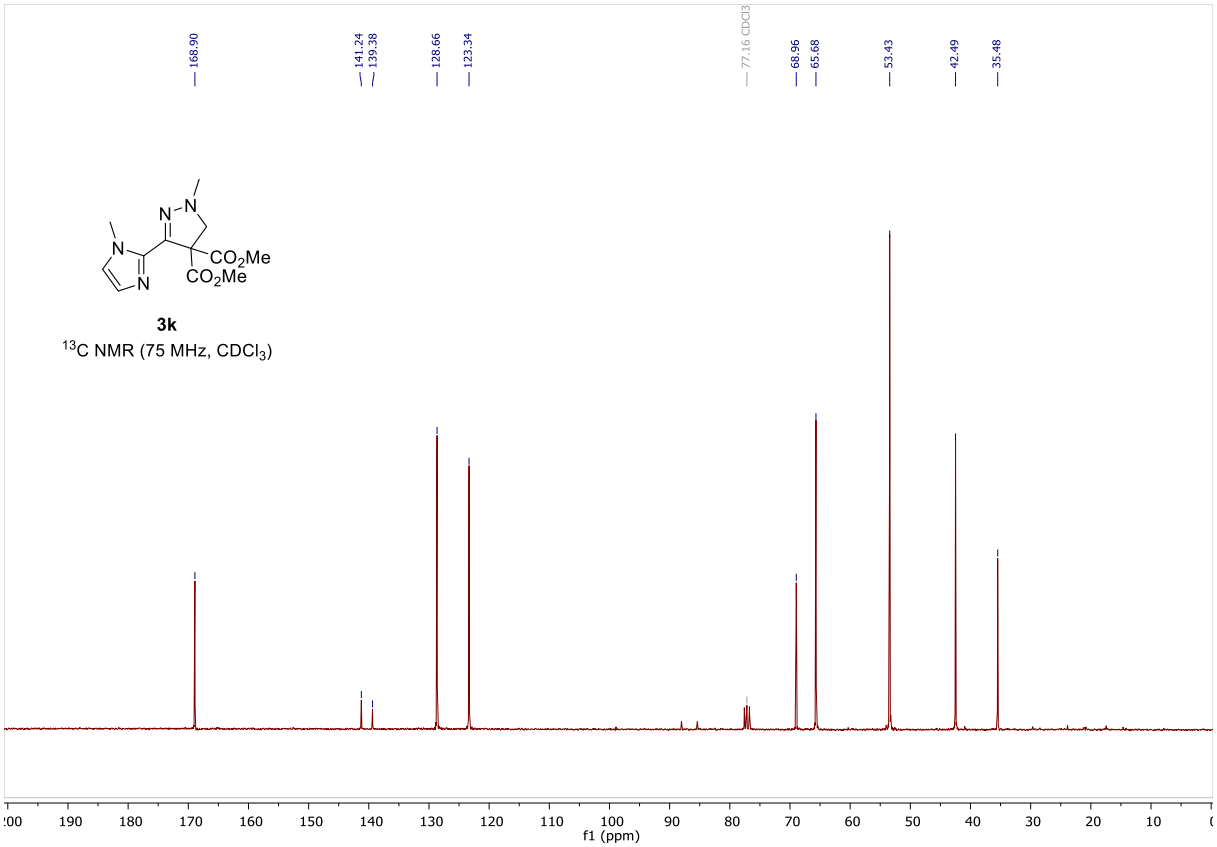

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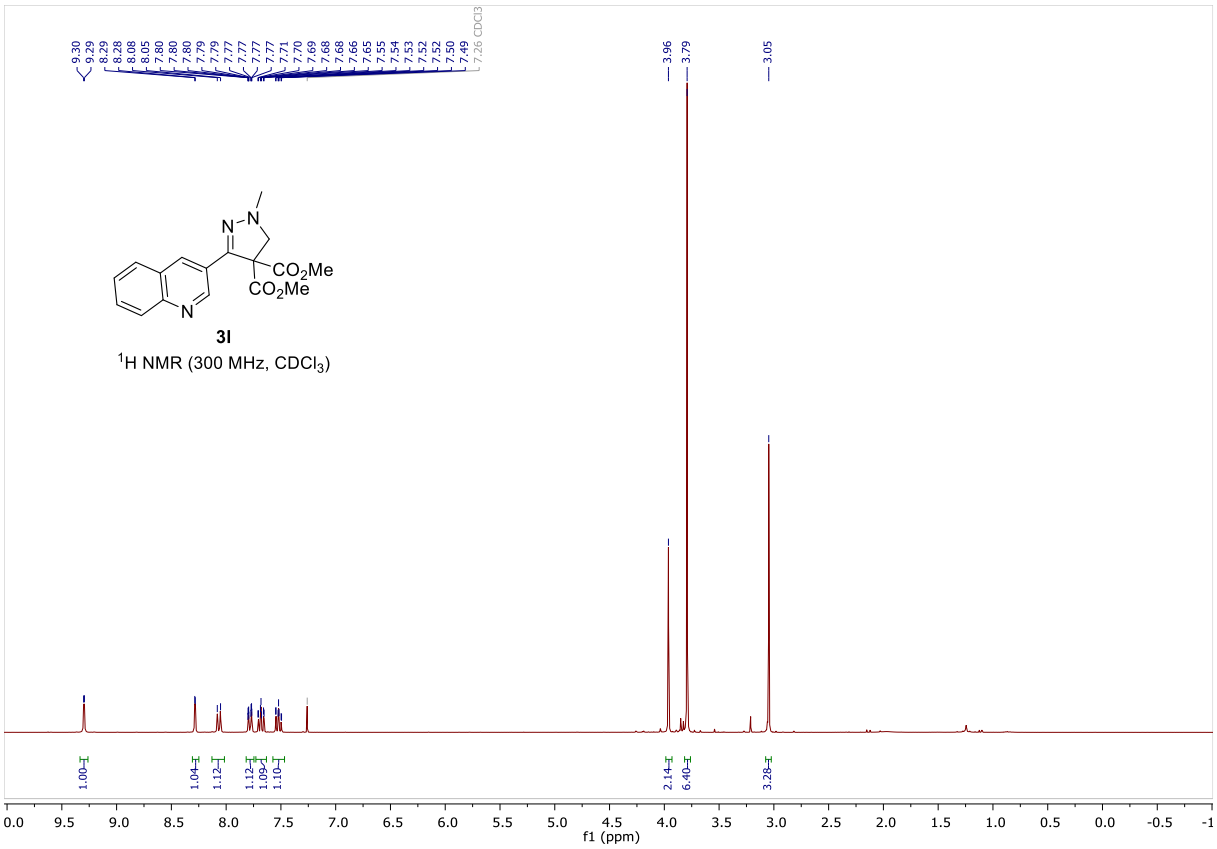
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7.79
7.79
7.77
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7.77
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7.54
7.53
7.52
7.52
7.50
7.49
7.26 CDCl3
3.96
3.79
3.05
N
N
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CO2Me
N
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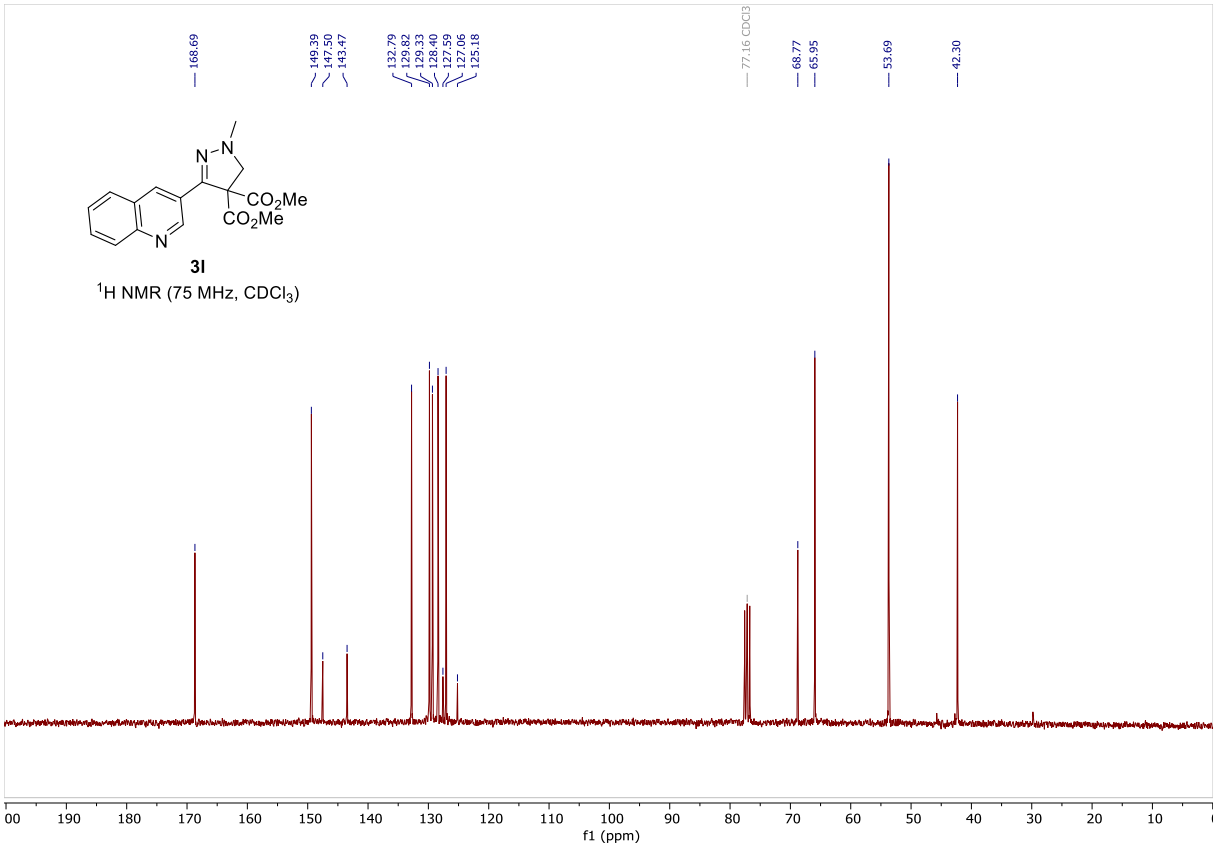
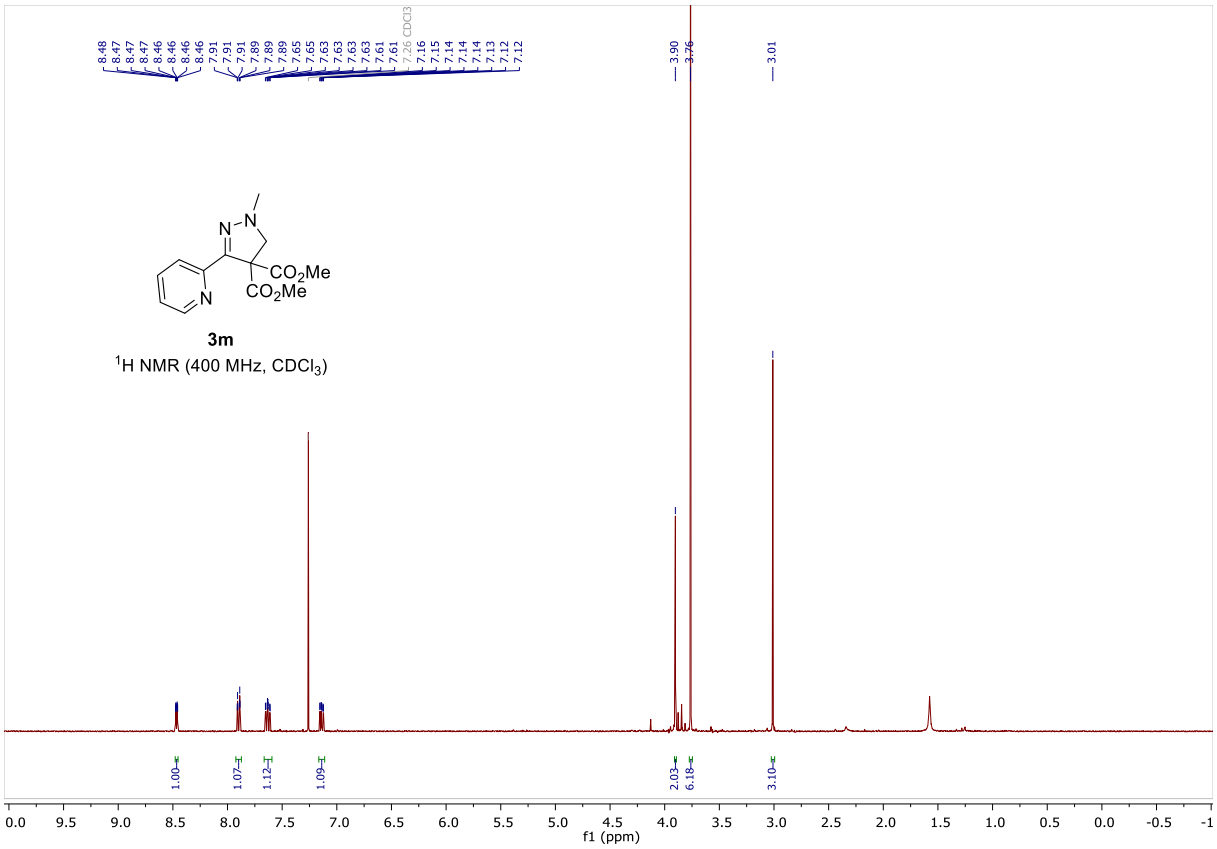
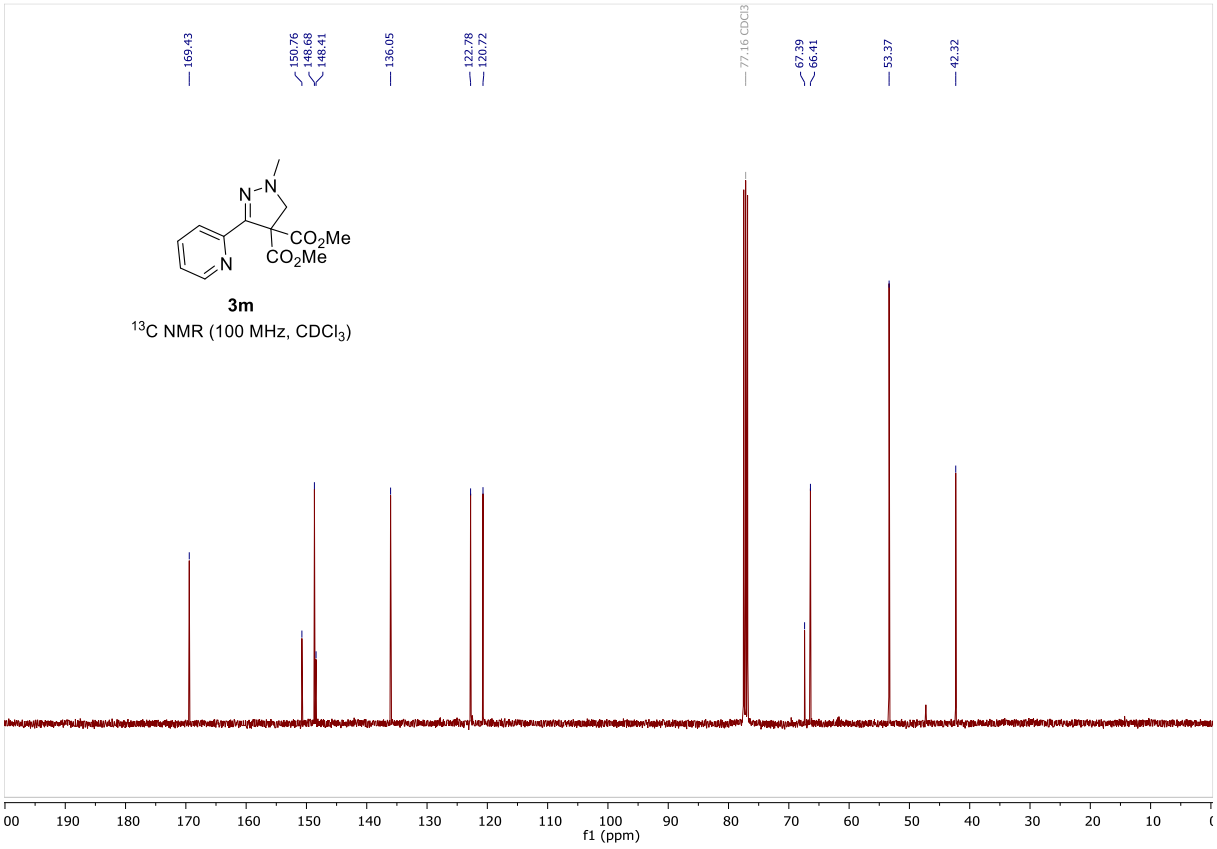
1H NMR (300 MHz, CDCl3)
1.00
1.04
1.12
1.12
1.09
1.10
2.14
6.40
3.28
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


168.69
149.39
147.50
143.47
132.79
129.82
129.33
128.40
127.59
127.06
125.18
77.16 CDCl3
68.77
65.95
53.69
42.30
N
N
CO2Me
CO2Me
N
3I
1H NMR (75 MHz, CDCl3)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



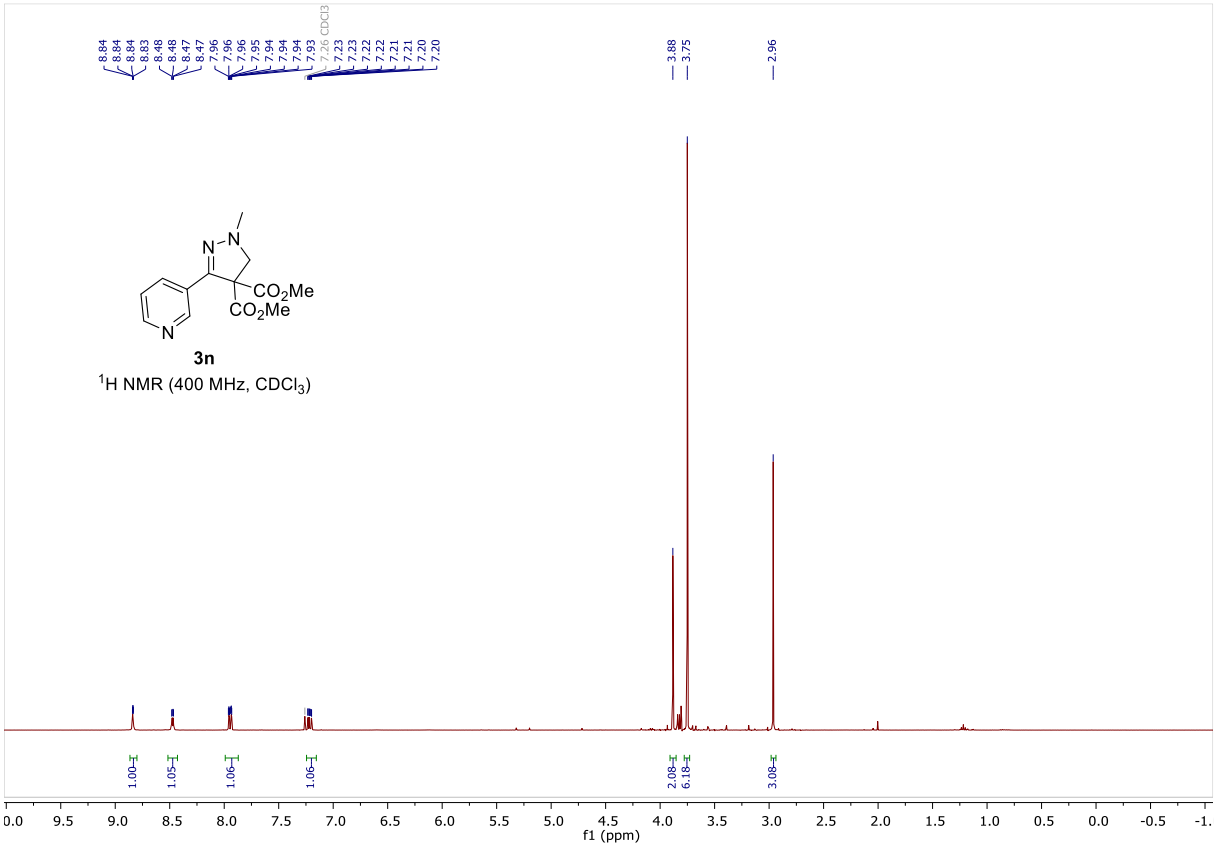
3m

^{1}H NMR (400 MHz, $CDCl_3$)



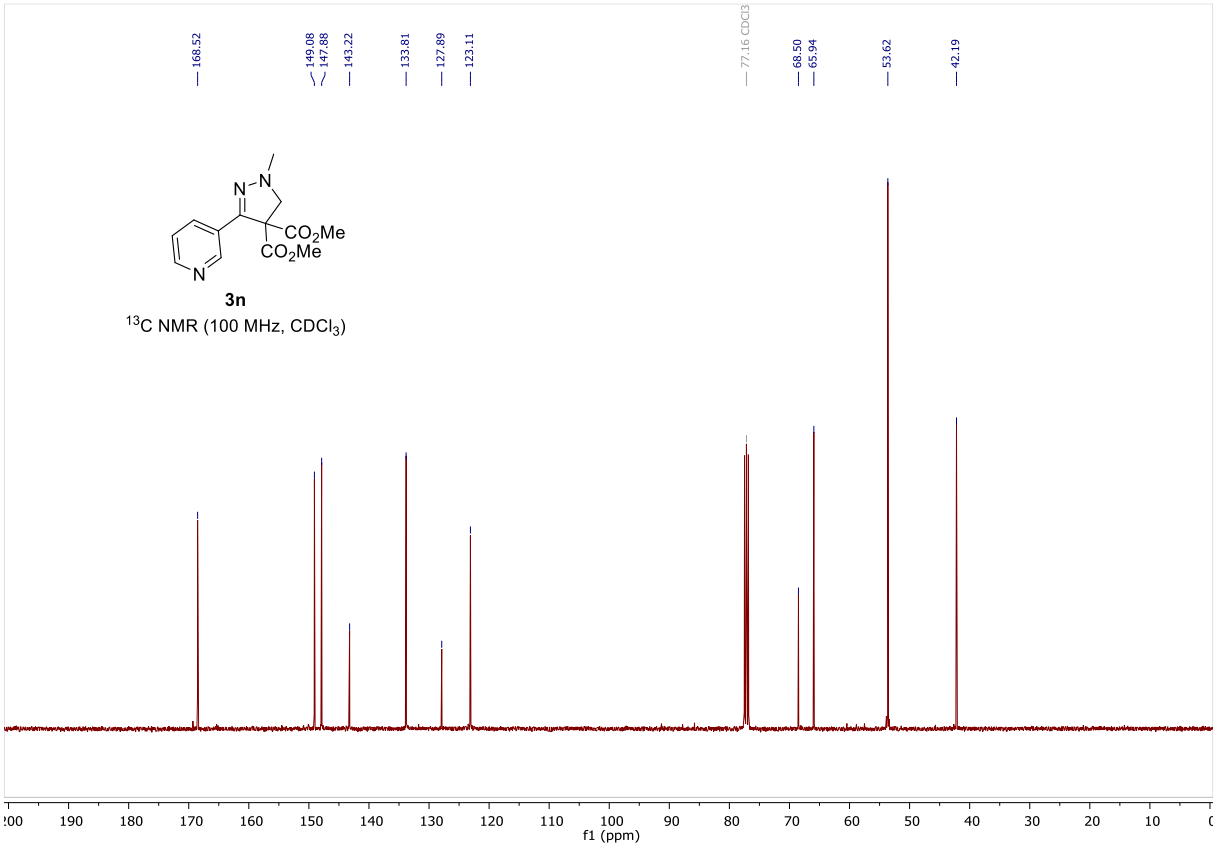
3m

^{13}C NMR (100 MHz, $CDCl_3$)



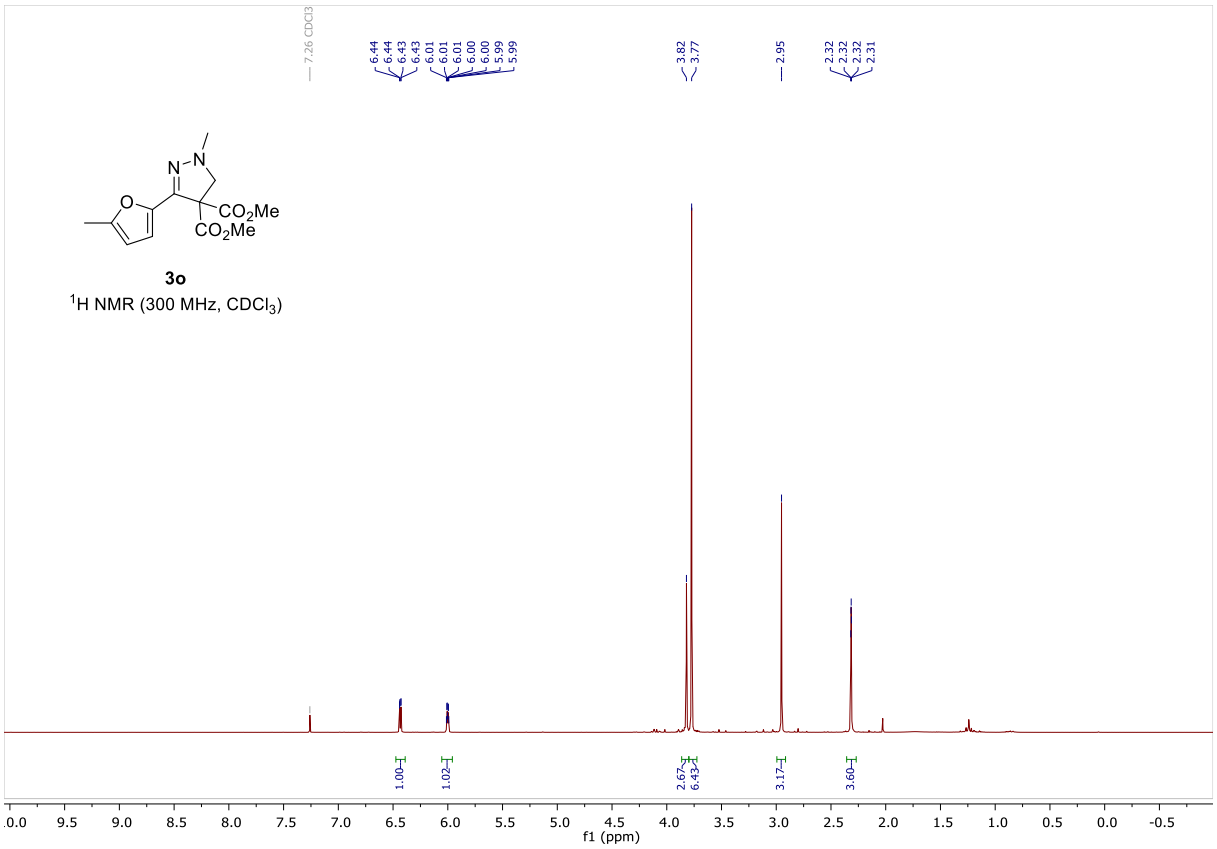
3n

^{1}H NMR (400 MHz, $CDCl_3$)



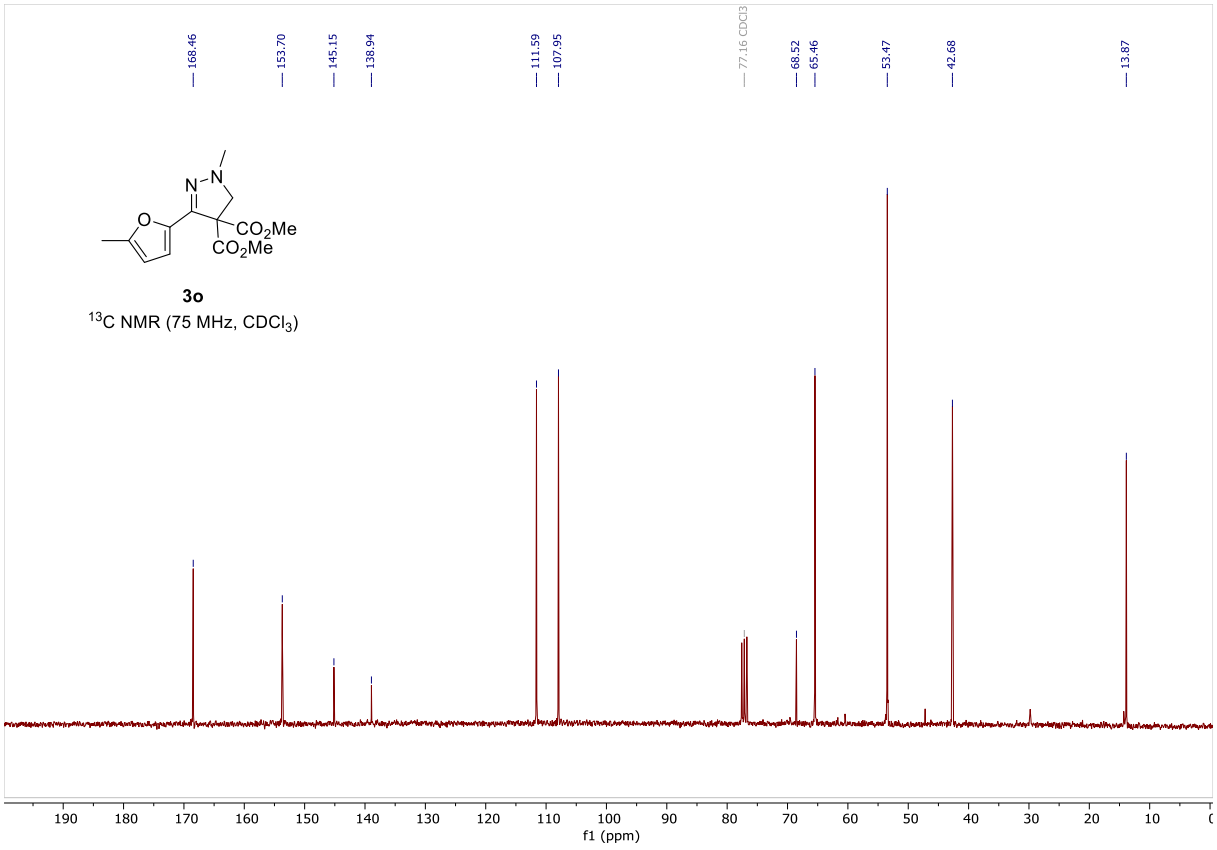
3n

^{13}C NMR (100 MHz, $CDCl_3$)



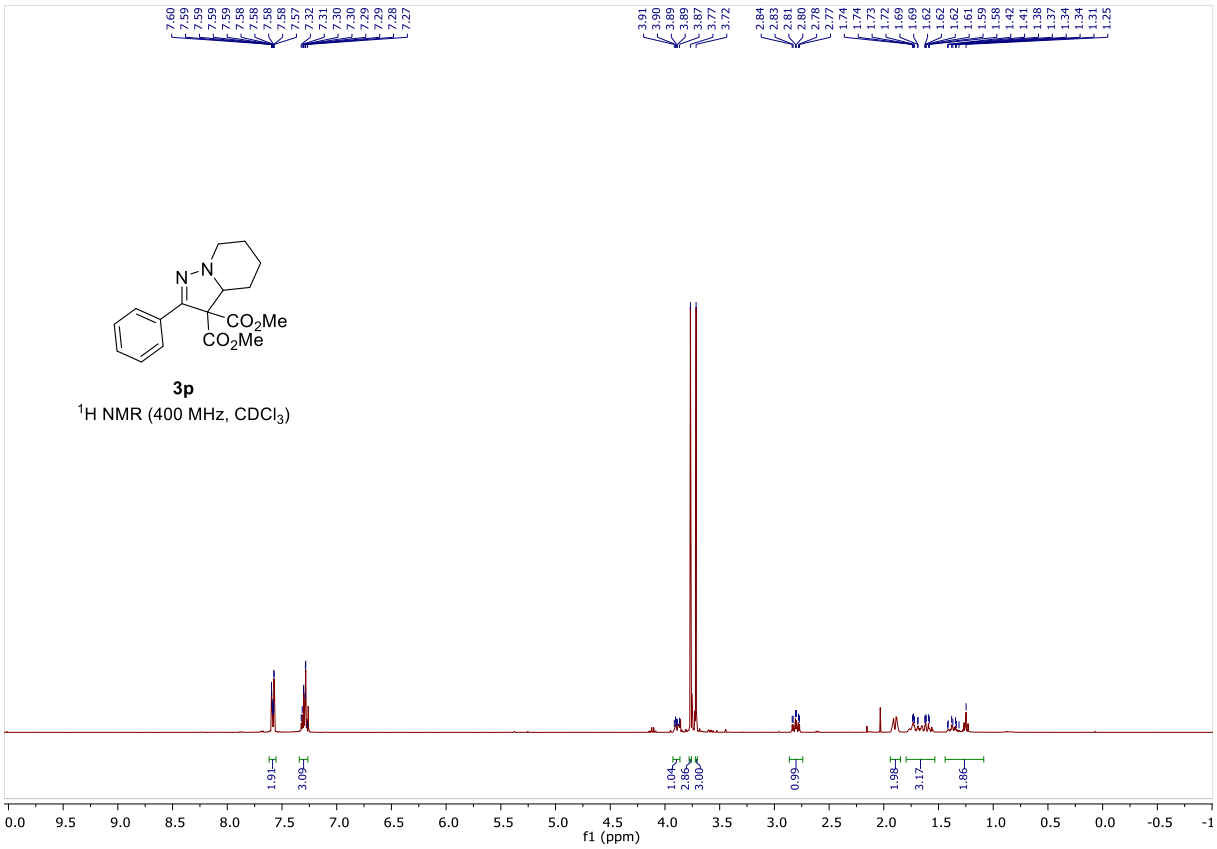
3o

^{1}H NMR (300 MHz, $CDCl_3$)



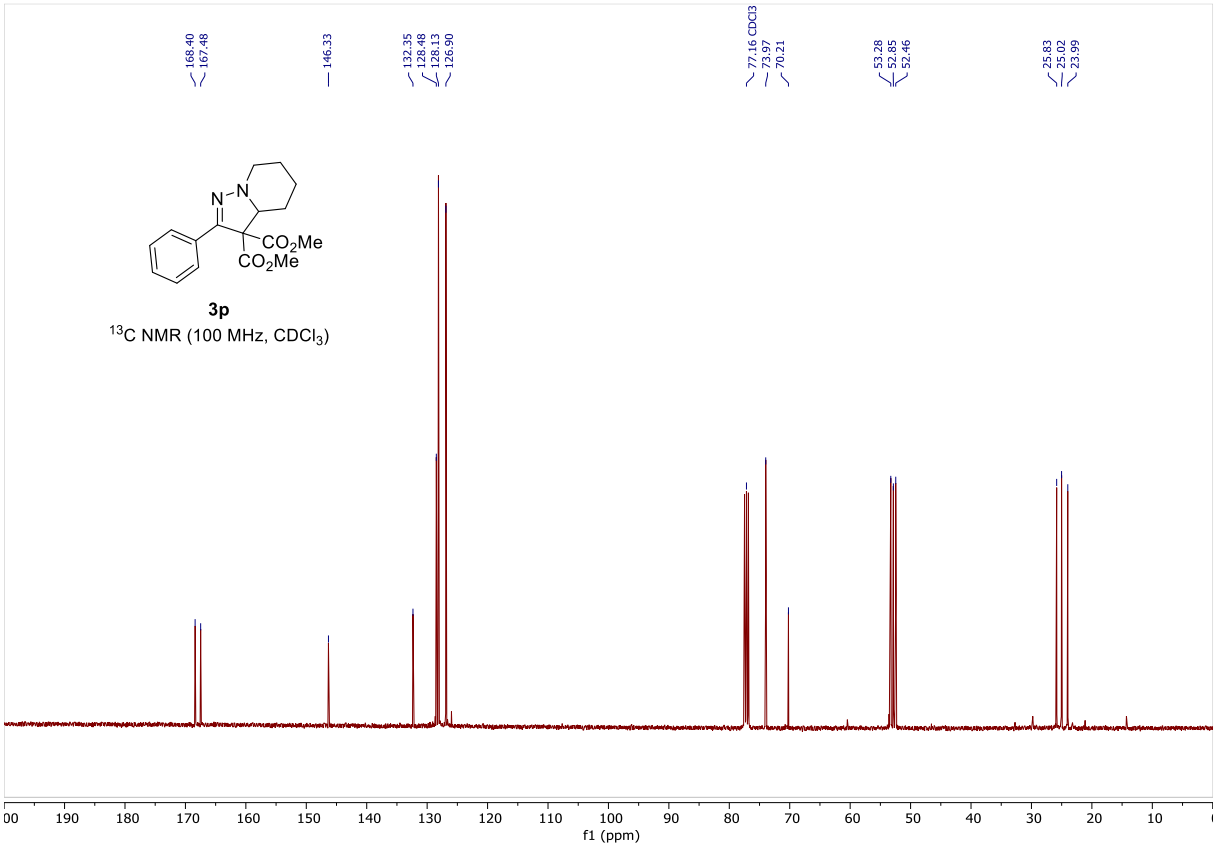
3o

^{13}C NMR (75 MHz, $CDCl_3$)



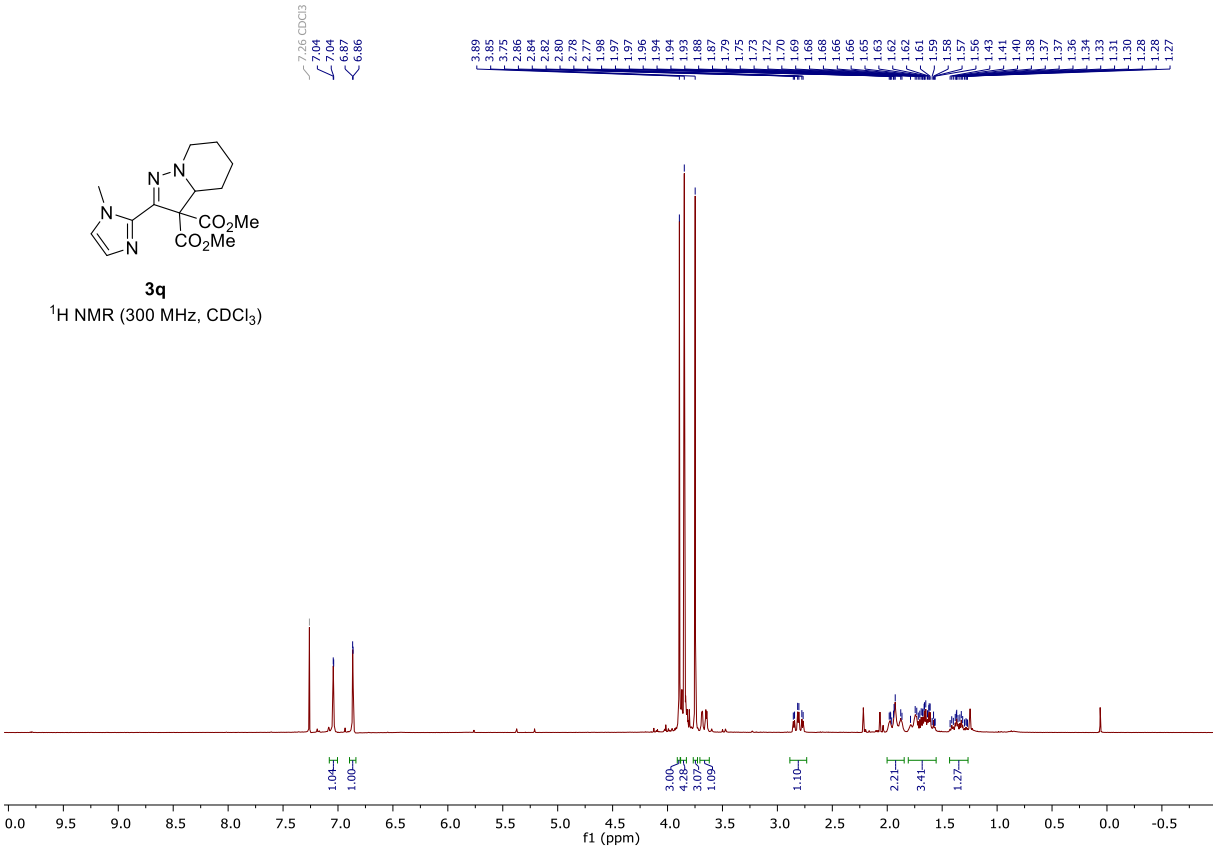
3p

^{1}H NMR (400 MHz, $CDCl_3$)



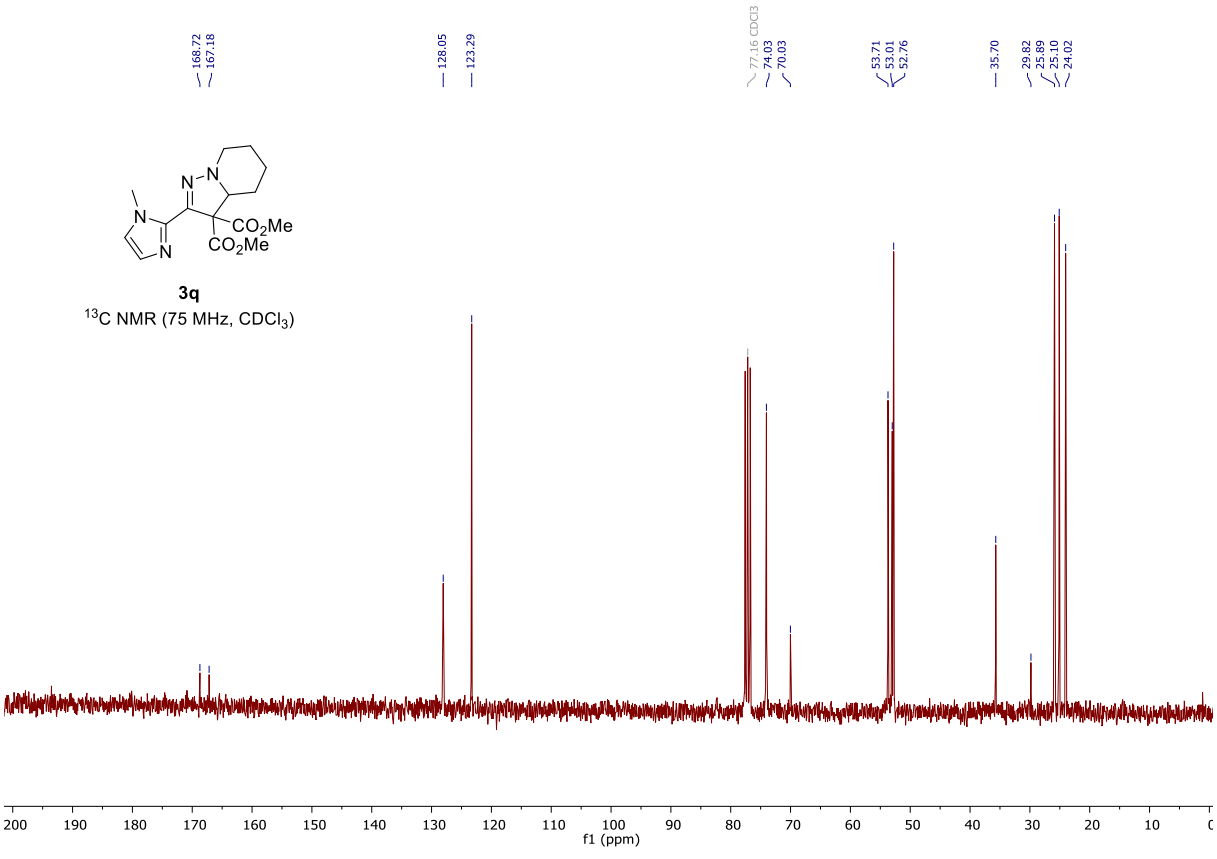
3p

^{13}C NMR (100 MHz, $CDCl_3$)



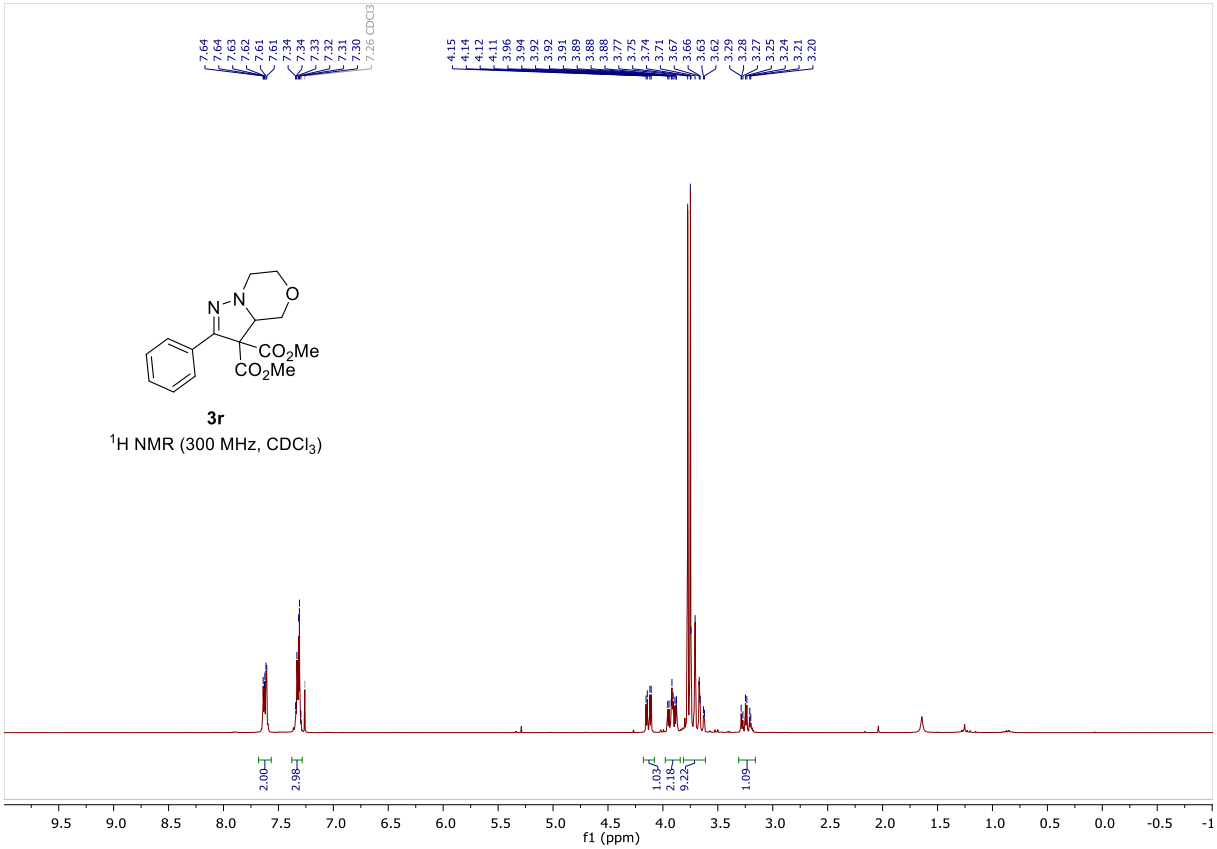
3q

^{1}H NMR (300 MHz, $CDCl_3$)



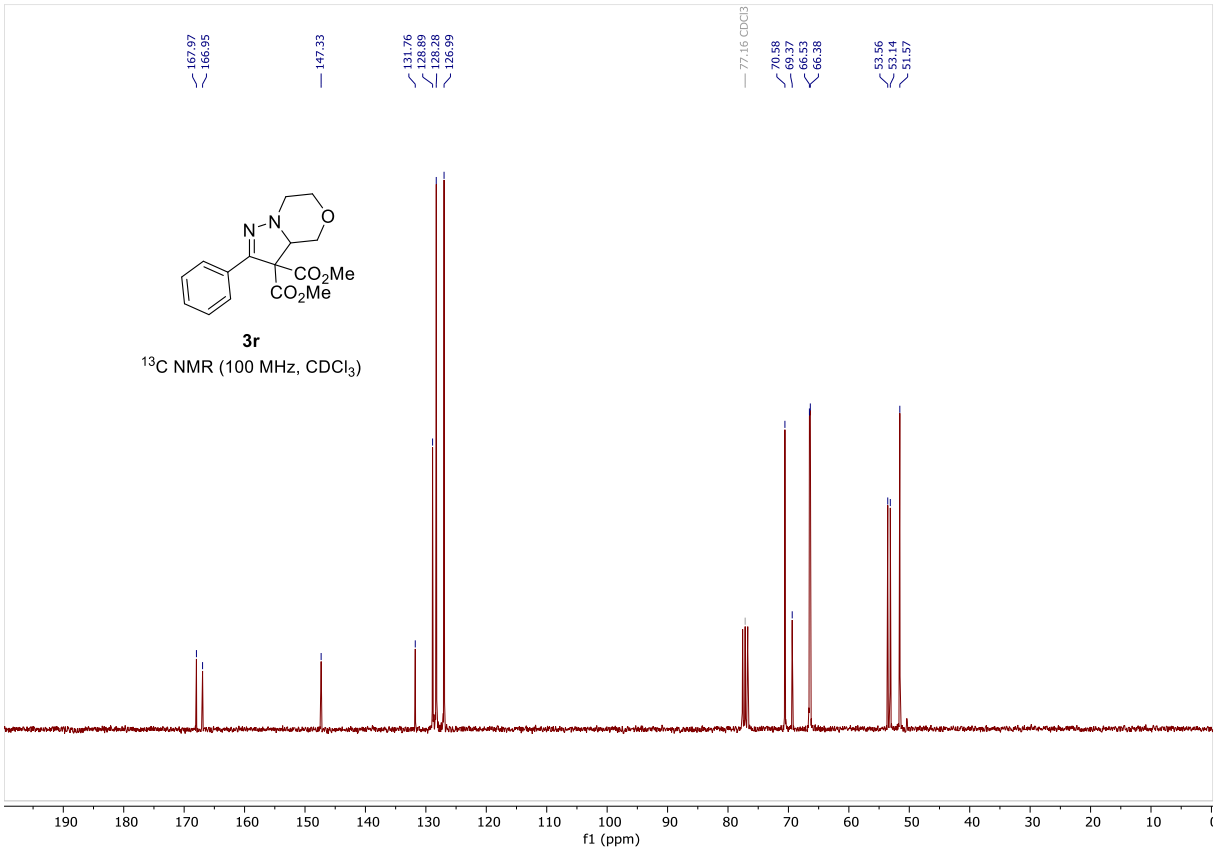
3q

^{13}C NMR (75 MHz, $CDCl_3$)



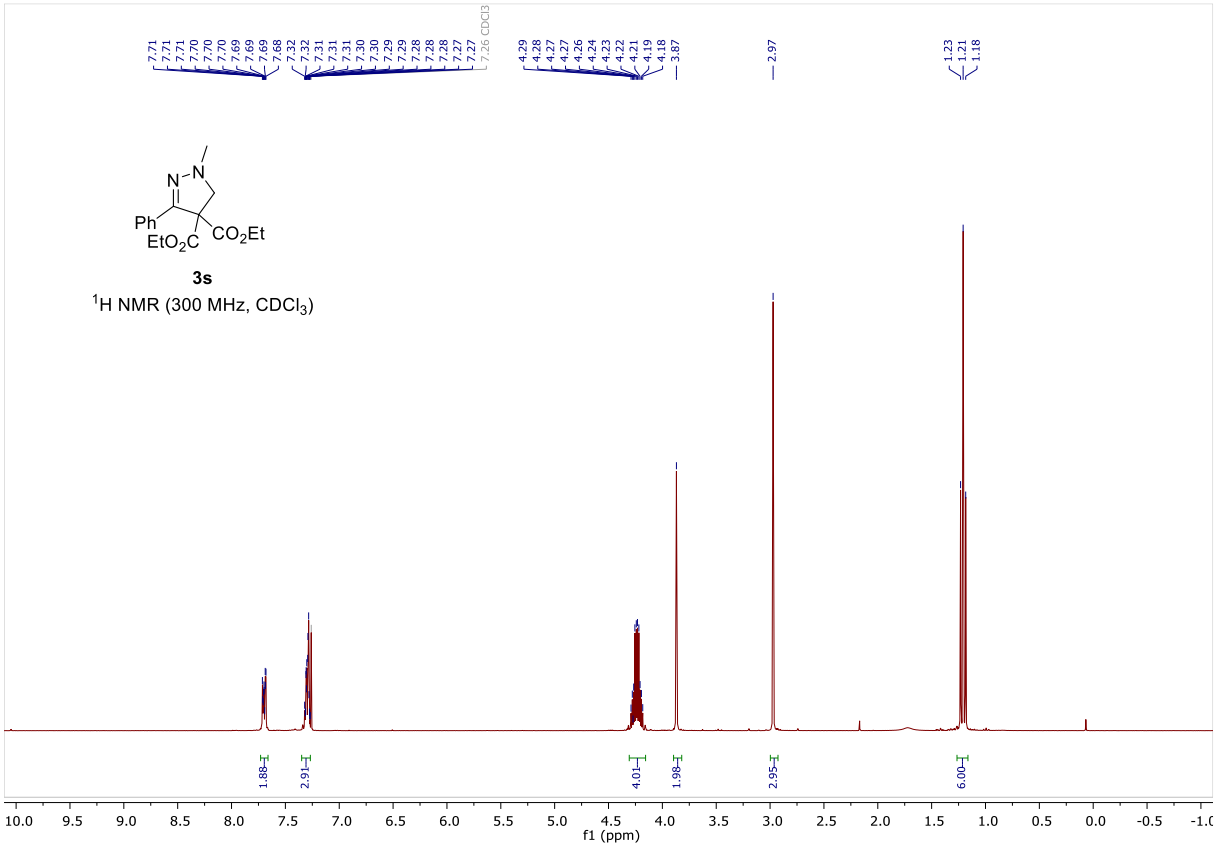
3r

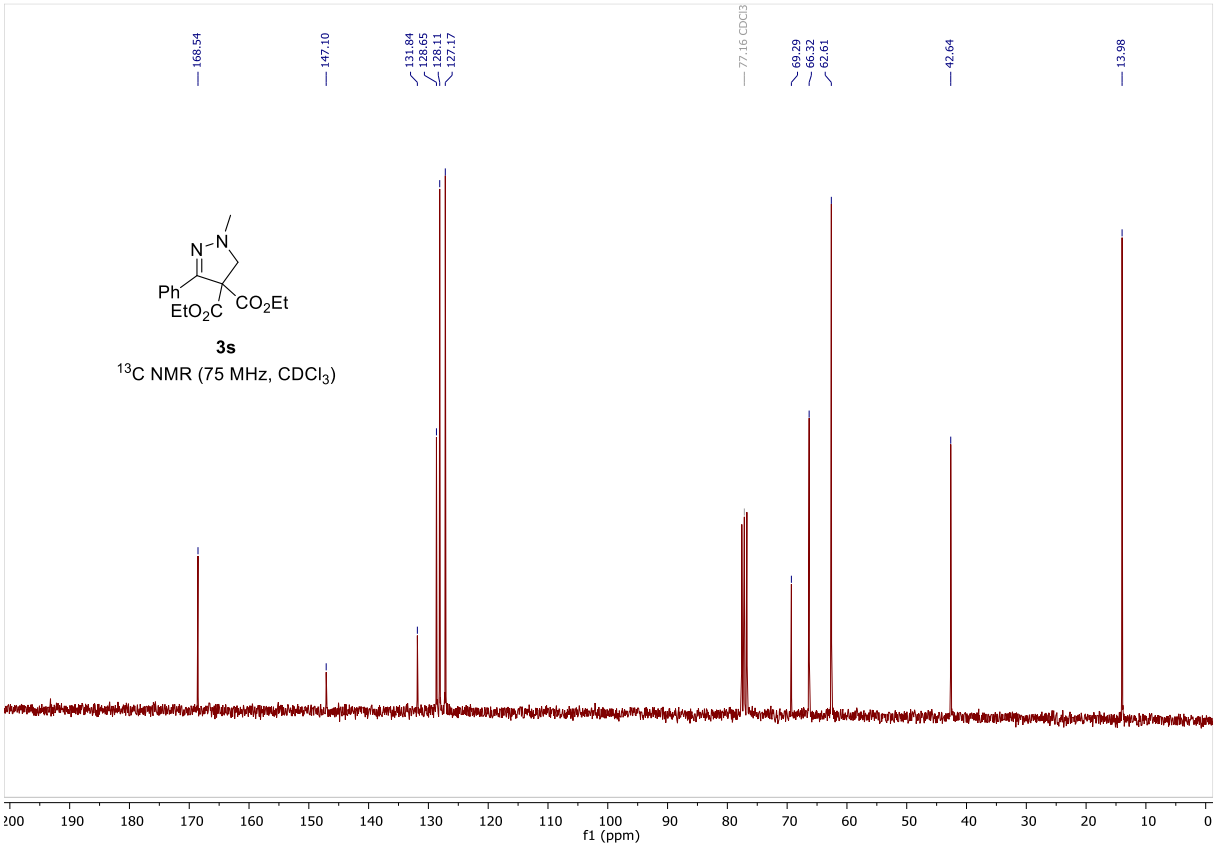
^{1}H NMR (300 MHz, $CDCl_3$)

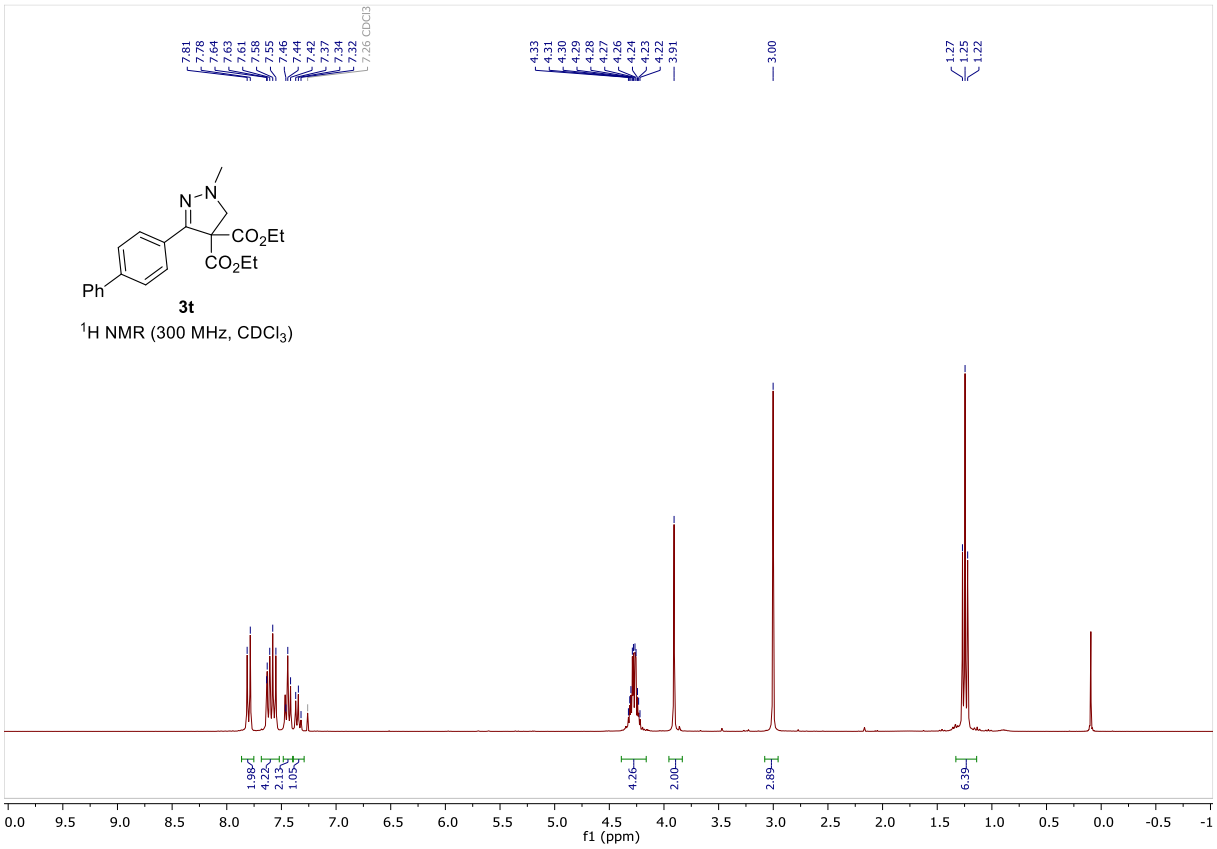


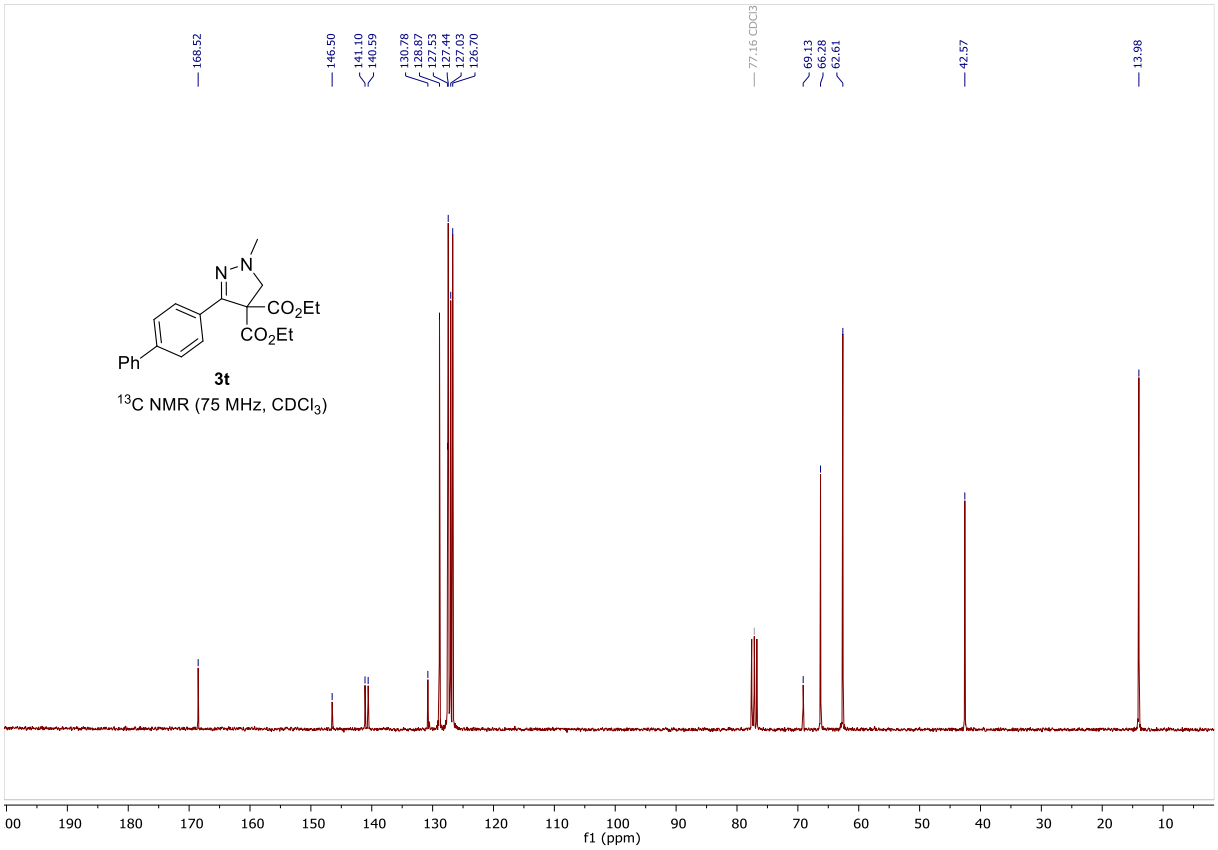
3r

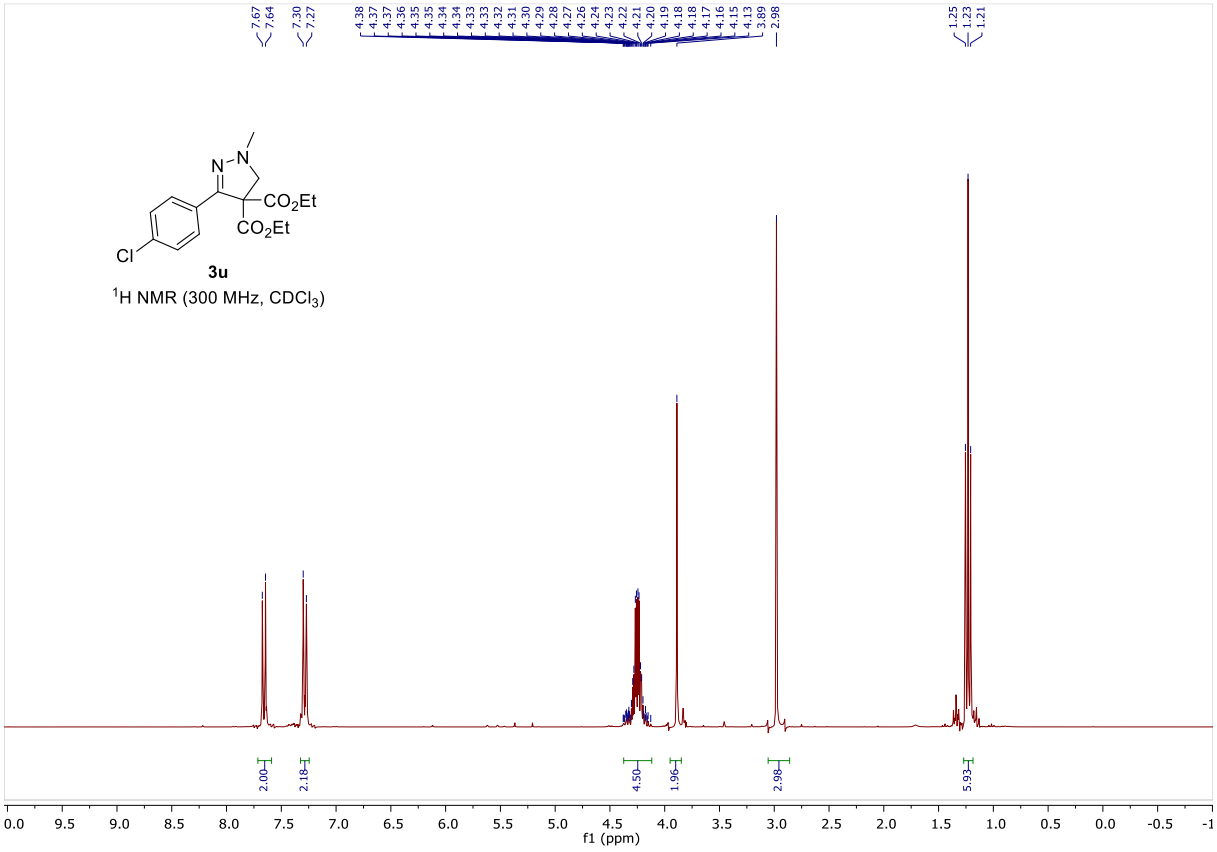
^{13}C NMR (100 MHz, $CDCl_3$)


7.71
7.71
7.71
7.70
7.70
7.70
7.69
7.69
7.69
7.68
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.28
7.27
7.27
7.26 CDCl3
4.29
4.28
4.27
4.27
4.26
4.24
4.23
4.22
4.21
4.19
4.18
3.87
2.97
1.23
1.21
1.18
Ph
EtO2C
CO2Et
3s
1H NMR (300 MHz, CDCl3)
1.88
2.91
4.01
1.98
2.95
6.00
f1 (ppm)


168.54
147.10
131.84
128.65
128.11
127.17
77.16 CDCl3
69.29
66.32
62.61
42.64
13.98
Ph
EtO2C
CO2Et
3s
13C NMR (75 MHz, CDCl3)
f1 (ppm)

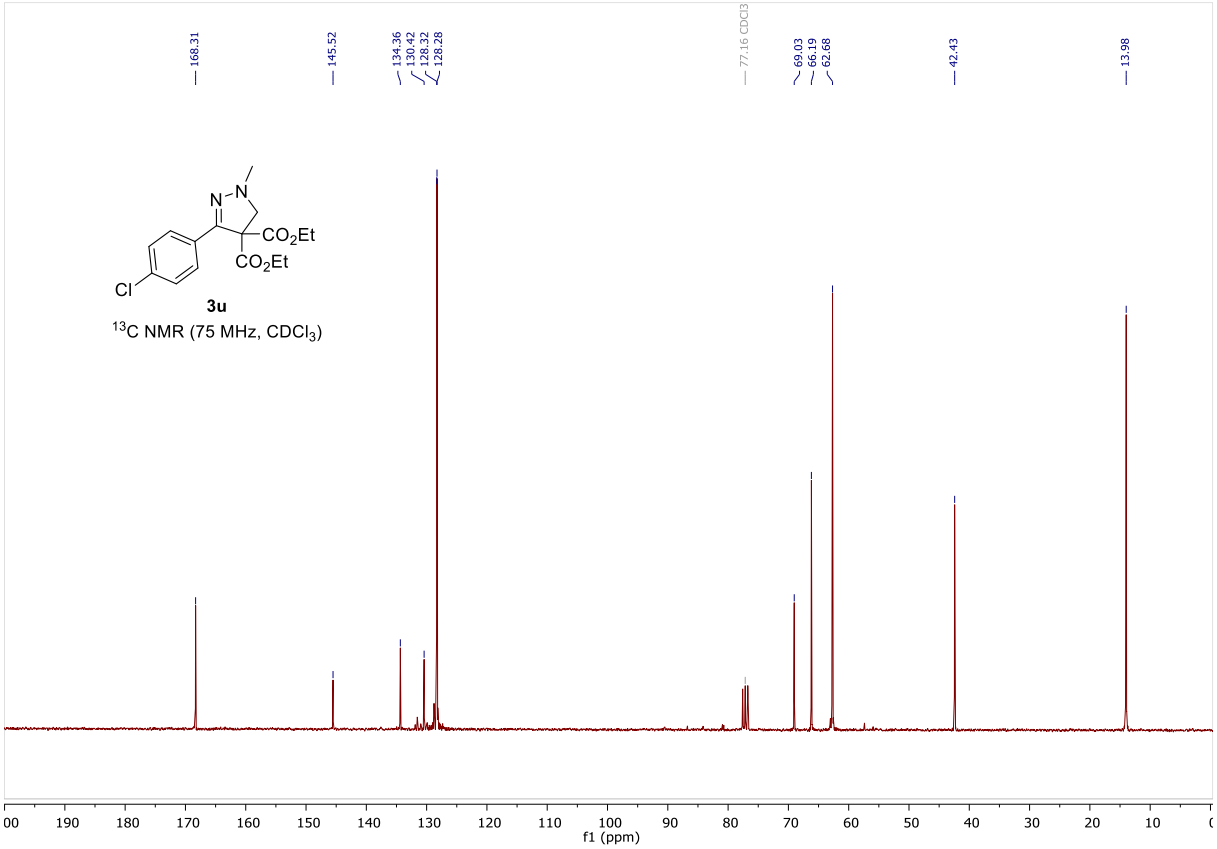

7.81
7.78
7.64
7.63
7.61
7.58
7.55
7.46
7.44
7.42
7.37
7.34
7.32
7.26 CDCl3
4.33
4.31
4.30
4.29
4.28
4.27
4.26
4.24
4.23
4.22
3.91
3.00
1.27
1.25
1.22
N
N
CO2Et
CO2Et
Ph
3t
1H NMR (300 MHz, CDCl3)
1.98
4.22
2.13
1.05
4.26
2.00
2.89
6.39
f1 (ppm)


168.52
146.50
141.10
140.59
130.78
128.87
127.53
127.44
127.03
126.70
77.16 CDCl3
69.13
66.28
62.61
42.57
13.98
N
N
CO2Et
CO2Et
Ph
3t
13C NMR (75 MHz, CDCl3)
f1 (ppm)



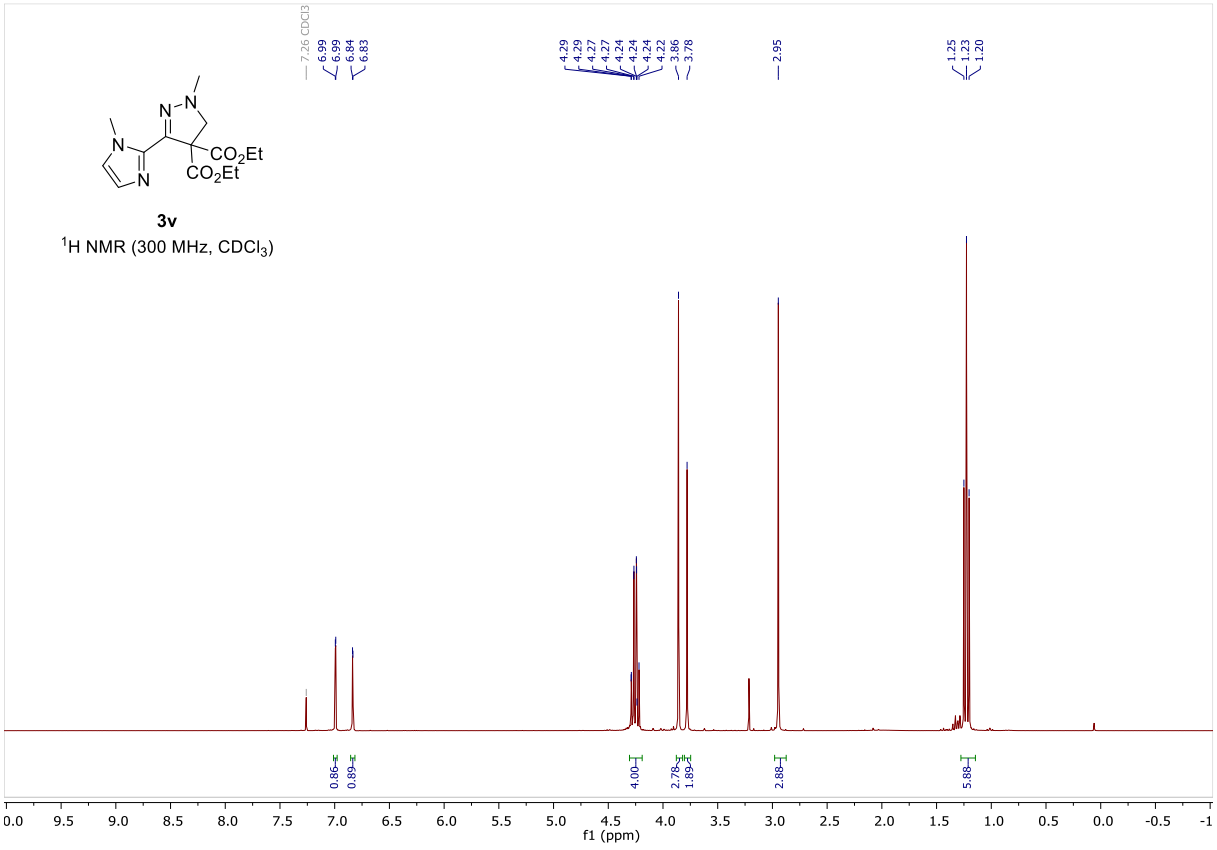
3u

^{1}H NMR (300 MHz, $CDCl_3$)



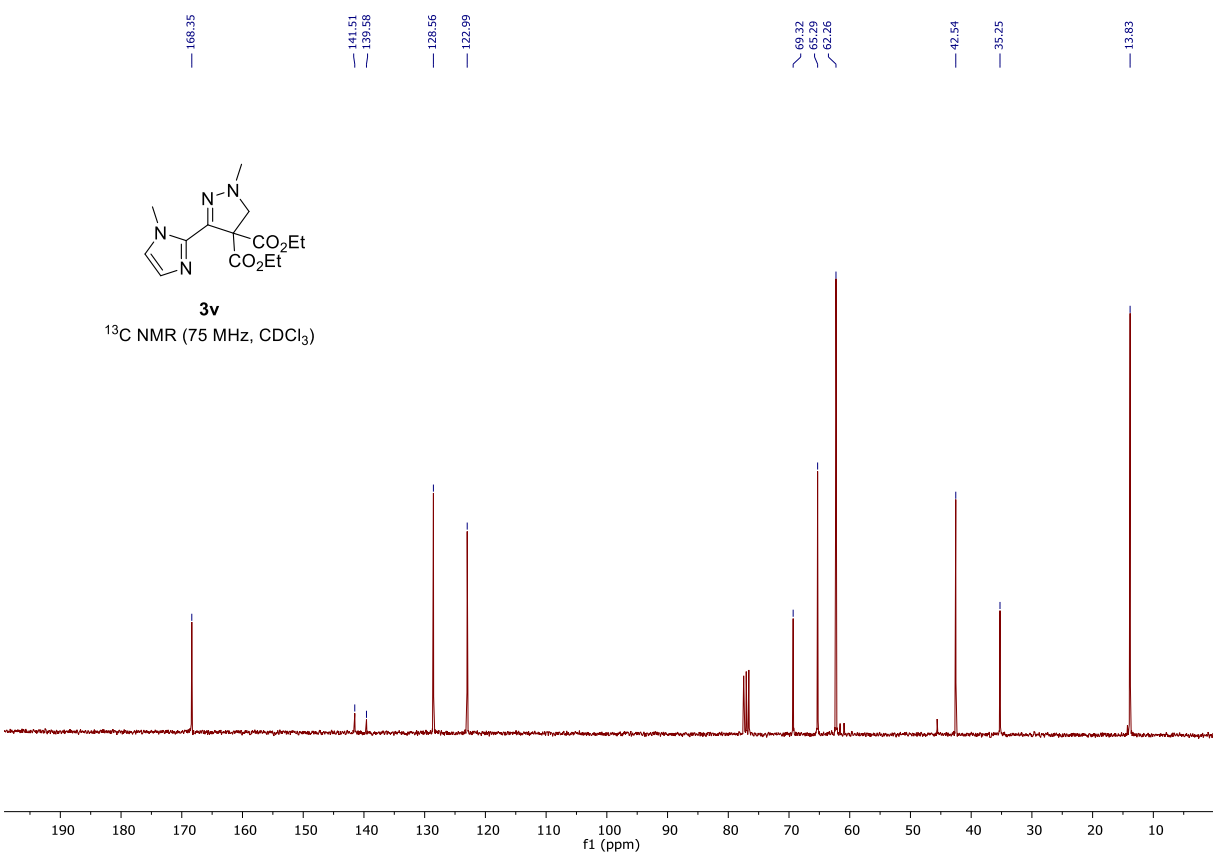
3u

^{13}C NMR (75 MHz, $CDCl_3$)



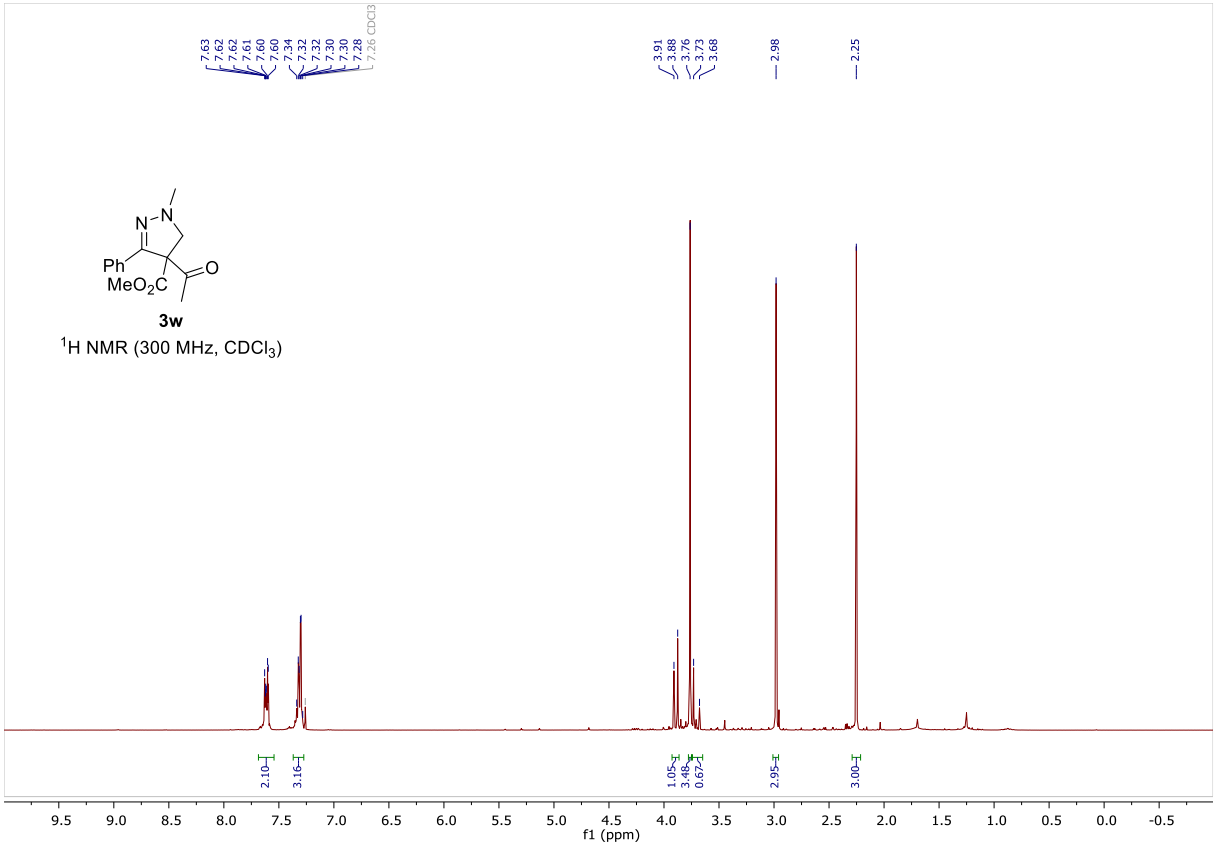
3v

^{1}H NMR (300 MHz, $CDCl_3$)



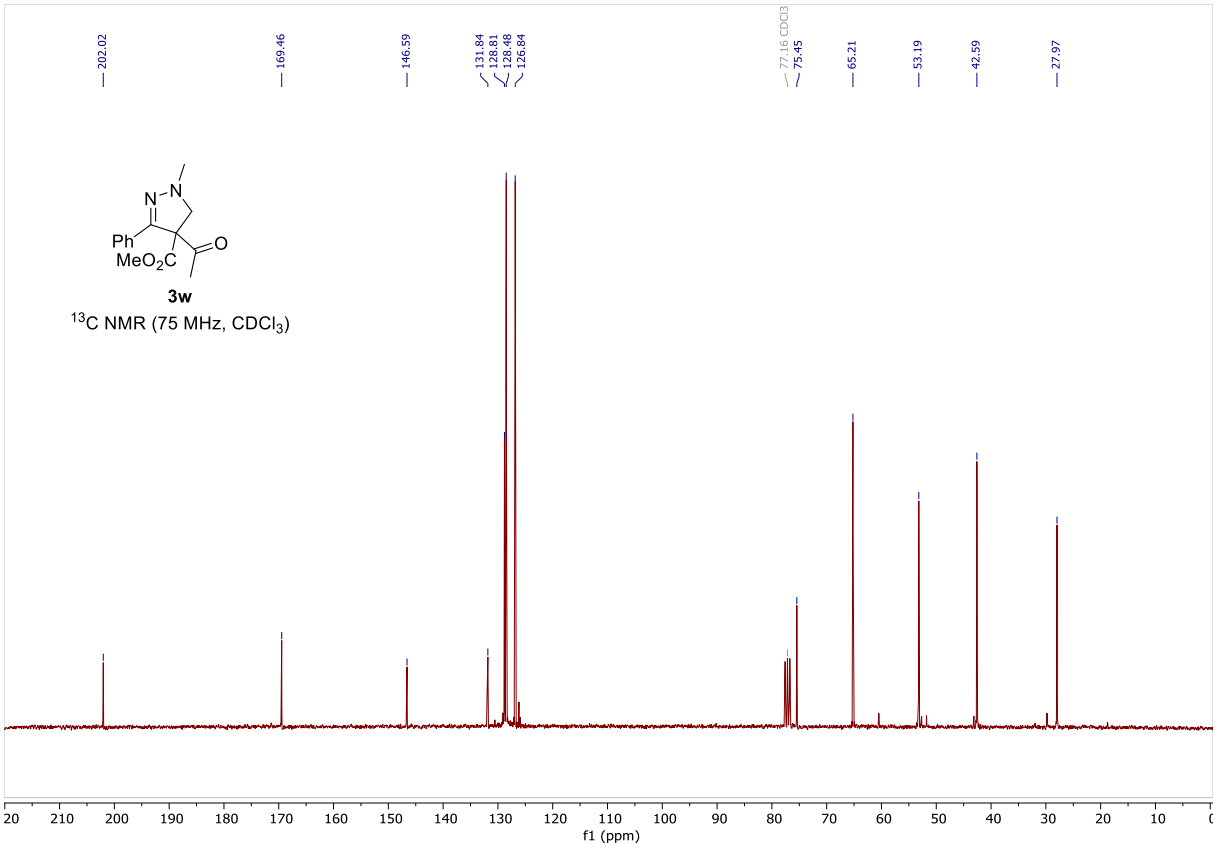
3v

^{13}C NMR (75 MHz, $CDCl_3$)



3w

^{1}H NMR (300 MHz, $CDCl_3$)



3w

^{13}C NMR (75 MHz, $CDCl_3$)