Supporting Information

Automated Multistep Synthesis of 2-Pyrazolines in Continuous Flow

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General experimental details

General methods: Reagents were obtained from commercial sources and used without purification. Solvents used in this work were HPLC grade and used without purification. Triethylamine was dried with calcium hydride, distilled, and stored under argon with molecular sieves (4 A). The removal of solvent under reduced pressure was carried out on a standard rotary evaporator. All the olefins are commercially available and were used as without further purification. Activated MnO_2 was purchased from Sigma-Aldrich (prod. number 217646). Hydrazones were synthesized following methods previously reported.[1] 2-furoyl hydrazone readily dimerized. To avoid dimers formation the hydrazone was prepared and its solvent evaporated with the rotatory evaporator's bath at room temperature. Excess solvent and hydrazine were removed on a high vacuum pump for 6 hours. The crude was stored overnight in a freezer and diluted with THF:MeOH 90:10 to 0.5 mol L−1 before being used. Unless otherwise stated, all the flow reactions were performed using a Vapourtec R-series platform. In-line IR spectroscopy was performed using the Mettler Toledo FlowIR® device.

Chromatography: Analytical thin-layer chromatography (TLC) was carried out on pre-coated glass plates (silica gel 60 F_{254}) from Merck. Compound spots were visualised under ultraviolet (UV) light (254 nm) and using ninhydrin or $KMnO_4$ stain solutions. Purification of the products were performed on SiliCycle SiliaSep™ 40–63mm 60 Å flash cartridges using an automated Biotage™ flash chromatography coupled with UV detector at 254 nm.

NMR spectroscopy: ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DPX-250 spectrometer or Bruker Avance III 500 MHz spectrometer with the residual solvent peak as the internal reference ($CDCl_3$ = 7.26 ppm, d_6-DMSO = 2.50 ppm, CD_3OD = 3.31 ppm). ^{1}H resonances are reported to the nearest 0.01 ppm. ^{13}C-NMR spectra were recorded on a Bruker DPX-250 spectrometer or Bruker Avance III 500 MHz spectrometer with the central resonance of the solvent peak as the internal reference ($CDCl_3$ = 77.16 ppm, d_6- DMSO = 39.52 ppm, CD_3OD = 49.00 ppm). All ^{13}C resonances are reported to the nearest 0.1 ppm. The multiplicity of ^{1}H signals are indicated as: s = singlet, d = doublet, dd = doublet of doublet, ddd = doublet of doublet of doublet, t = triplet, q = quadruplet, quint = quintet, sext = sextet, m = multiplet, br = broad, or combinations of thereof. Coupling constants (J) are quoted in Hz and reported to the nearest 0.1 Hz. Where appropriate, averages of the signals from peaks displaying multiplicity were used to calculate the value of the coupling constant. It was noted that some of the compounds were not completely stable when in $CDCl_3$ solution. That was observed when storing at 4°C overnight even after prior base washing of the $CDCl_3$.

High-resolution mass spectrometry (HRMS) High-resolution mass spectra were recorded on a Synapt mass spectrometer. The injection was performed by direct infusion using 15-30 V sampling cone, 3.5 kV capillarity, 4.0 V extraction cone, 120 °C source temperature, 175 °C desolvation temperature, with 1.0 min acquisition time with scans of 1.0 second and interscan time of 0.02 s.

Unless otherwise stated, reported mass correspond to the parent molecular ion associated with a proton $[M+H]^+$ or a sodium cation $[M+Na]^+$ (^{23}Na isotope). All *m/z* values are reported to four decimal places.

General procedure for the activation of the MnO^2 column

A glass column (Omnifit® column, 6.6 mm i.d. × 100 mm length) was packed with 3 g of activated MnO_2 (Sigma-Aldrich 217646) between pads of celite (~10 mm each). A solution of THF/Et_3N/MeOH 70:20:10 (v/v/v), 32 mL was passed through the column at a flow rate of 0.5 mL/min followed by a mixture of THF/MeOH 9:1 (3 mL).

Pumping a solution of hydrazine in THF

An initial problem was identified when the hydrazine solution was pumped continuously through the double reciprocating piston pumps (Vapourtec R-series). After a short period of operation, the performance of the pump was compromised owing to hydrazine reacting with the polymeric secondary seals of the pump, which produces particulates that sequentially caused the check valves to malfunction. Figure S1 shows secondary seals that have been exposed overnight to a hydrazine solution in THF (2 mol/L). Removal of these secondary seals from the hydrazine pump and inclusion of 10% methanol in the stock solution however prevented such blockages. This modification did not affect the operation of the pumps. Furthermore, in order to keep the primary seal clean, the back of the pump was flushed with solvent periodically using the flushing ports.

Figure S1: Left: Pump secondary seal exposed overnight to a solution of hydrazine in THF (1 mol/L). Right: Pump secondary seal exposed overnight to THF.

General procedure for the synthesis of 2-pyrazolines

A 1 mL sample loop was loaded with a solution containing a 0.5 M solution of the hydrazone in THF/MeOH 90:10 (v/v). The reaction mixture was pumped with THF/MeOH 90:10 (v/v) at a flow rate of 0.5 mL/min, through an activated column containing MnO_2 (see above) at room temperature. Formation of the diazo was observed as the appearance of an intense reddish solution. The diazo was collected in a vial under inert atmosphere and at 0 °C. To this diazo mixture was added a solution containing the olefin (1.2 eq., 0.6 mmol) and the reaction was stirred for 2 hours at room temperature. Up to 5 injections were done using the same column.

The crude reaction mixture was concentrated under reduced pressure, and it was purified by column chromatography (hexanes/EtOAc 5-100%).

Reservoir implementation

The reservoir utilised in this work was custom built in double jacketed glass, with connections compatible with the Vapourtec R-series module, where the temperature could be controlled to -5 °C and kept under nitrogen atmosphere (Figure S2).

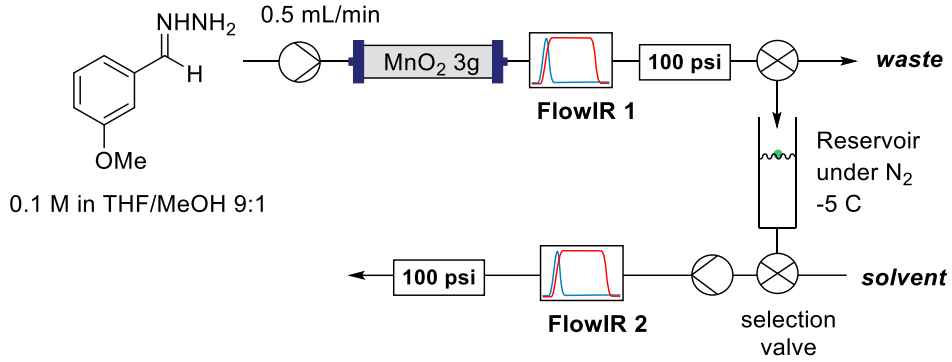


Figure S2: Left) MnO_2 column and custom-built reservoir. Right) Equipment setup for the evaluation of the reservoir storing the diazo compound solution.

To evaluate the stability of the solution containing the diazo compound a system was setup with 2 FlowIR units (Figure S2). In this setup a solution of a hydrazone was pumped through a column containing MnO2 to generate the respective diazo compounds, which was directed to the reservoir at -5°C and under nitrogen atmosphere. Once a reasonable volume of the solution was collected, it was pumped from the reservoir through a second FlowIR unit, while switching between solvent and solution. This aimed to evaluate if the solution could be split between different coupling partners. Both FlowIR units were following the IR signal at 2070 cm^{-1}, which corresponds to the diazo functional group (Figure S3).

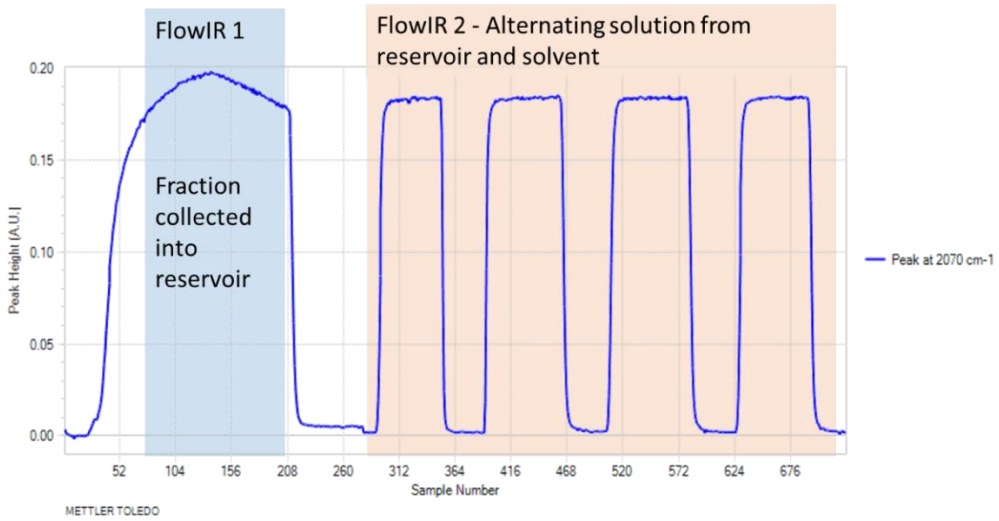


Figure S3: IR signal at 2070 cm^{-1} during production of diazo solution and pumping it from the reservoir.

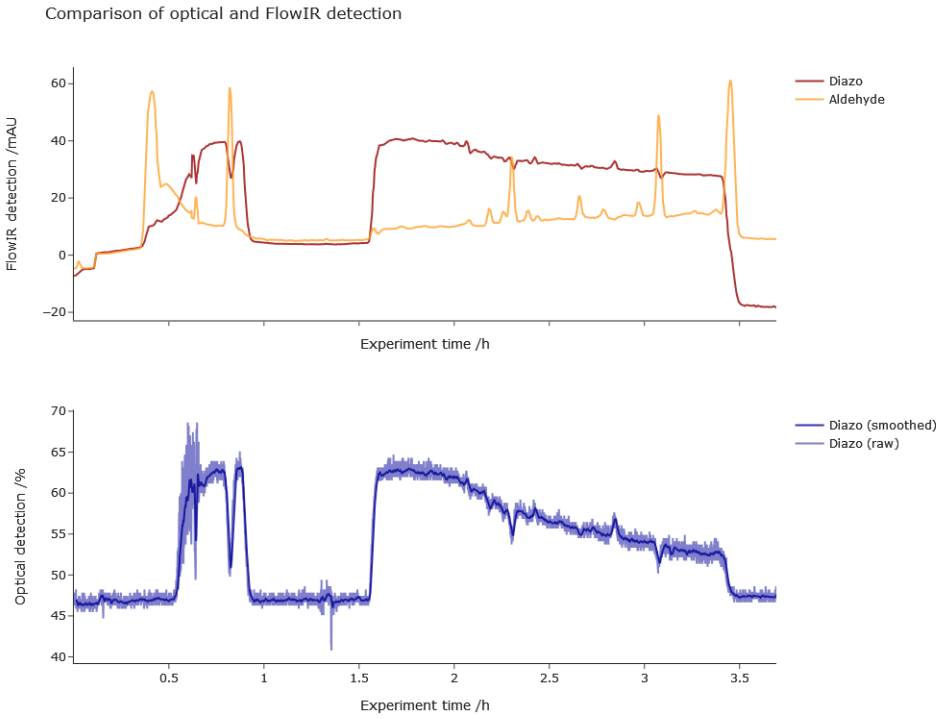
Webcam colorimeter

A colorimeter was therefore constructed by wrapping a clear PFA tubing around a white cylinder. A 3D printed part led to a small improvement, having walls to allow two layers of tubing in the coil which intensified the colour. A USB webcam was focused on the coiled tubing, and image processing functionality within the Octopus software was used to generate a measurement of the amount of diazo present. Two separate tubing-colorimeters were monitored using a single camera image. The tubing coils were clamped in position so that their positions within the image did not change during the process. To generate a numerical value, the following computation was carried out: First the area of interest for a particular coil was selected from the image using a crop function. Then the Euclidian colour distance of each pixel from yellow was calculated to give a grayscale image. After passing through an invert function, this produces a grayscale image which is brighter when more diazo species is present.

A numerical value was then generated by taking the mean intensity of each pixel in this processed image. This calculated data had a reasonably high degree of noise from the camera; after some optimisation it was found that taking the average value of a 45 second rolling window, the signal was

smoothed to a satisfactory level. Finally, the rate at which the 'diazo intensity' variable was updated was limited to once every 5 seconds. This was useful to reduce the frequency at which the flow rate was changed for any pumps that were controlled based on this signal.

When compared to an IR measurement taken at the same point in the system, we were pleased to find that although the colorimeter had a much lower sensitivity than the IR spectrometer, it produced the same signal profile, so we were confident that this could be used to trigger actions within the control protocol.



Iterative development of the two-step automated reaction system

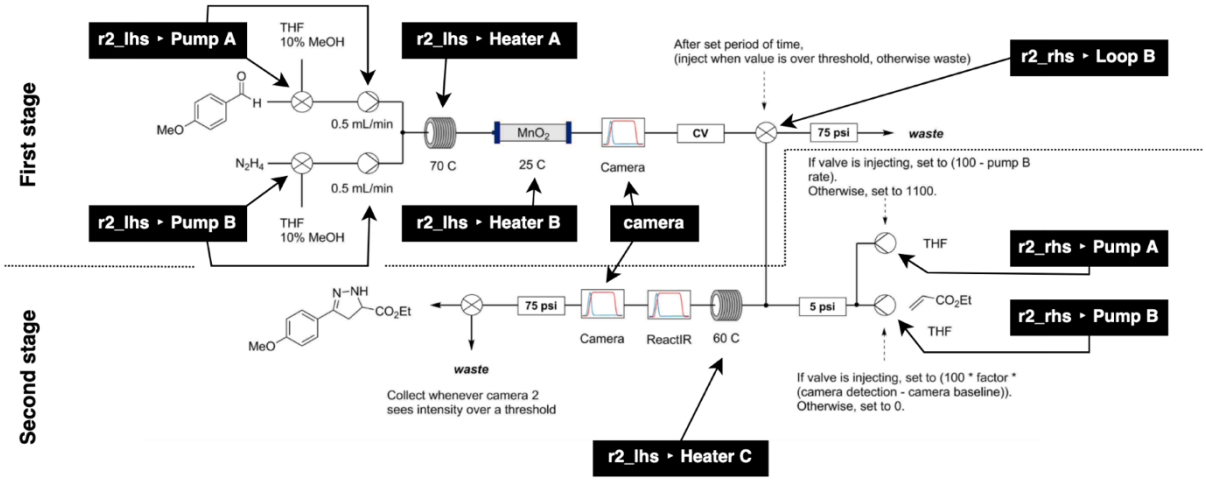
In this section, three iterations of process development for the automated two-step reaction are described, to illustrate the application of the Blocktopus GUI for implementing the control system.

Control of a two-stage experiment

Instruments

- First Vapourtec R2+/R4 system (**r2_lhs**) providing:
  - Pump for aldehyde, with low-pressure reagent/solvent selector valve (**r2_lhs ▸ Pump A**)
  - Pump for hydrazine, with low-pressure reagent/solvent selector valve (**r2_lhs ▸ Pump B**)
  - Reactor coil for aldehyde/hydrazine incubation (**r2_lhs ▸ Heater A**)
  - Reactor column with MnO_2 (**r2_lhs ▸ Heater B**)
  - Reactor coil for diazo/olefin incubation (**r2_lhs ▸ Heater C**)

    - High-pressure valve for hydrazine direction to waste/second stage (**r2_lhs ‣ Loop B**)
    - Low-pressure collection/waste valve (**r2_lhs ‣ Output**)
- Second Vapourtec R2+/R4 system (**r2_rhs**) providing:
    - Pump for solvent (**r2_rhs ‣ Pump A**)
    - Pump for olefin (**r2_rhs ‣ Pump B**)
- Microsoft LifeCam Cinema webcam (**camera**) observing both colorimetry coils.
- Mettler-Toledo FlowIR detector (**ir**), initially not used in the control protocol.



Protocol

Setup

1. Configure the instruments (the FlowIR is not used in the control protocol for this experiment).
2. Split the image from the single camera into two separate variables:
    a. Separately crop the image into two regions of interest;
    b. Extract the “yellowness” of each;
    c. Calculate their mean intensities (the image is 8-bit, so this is a value from 0-255);
    d. Take the mean value over a 45 second rolling window, so smooth out noise;
    e. Store the result in numeric variables (colour intensity lhs, colour intensity rhs). A new image is read from the camera every 1 second, and the variables are updated with each new image.

First stage

3. Set the reactor flow rates and heater temperatures.
4. Wait at least 5 minutes, and then until the heater at 70C (Heater A) is at the desired temperature.
5. Inject the reagents for 64 min;
6. Then flush the first half of the system with solvent for 20 min;
7. Then turn off heater A and heater B.

Second stage

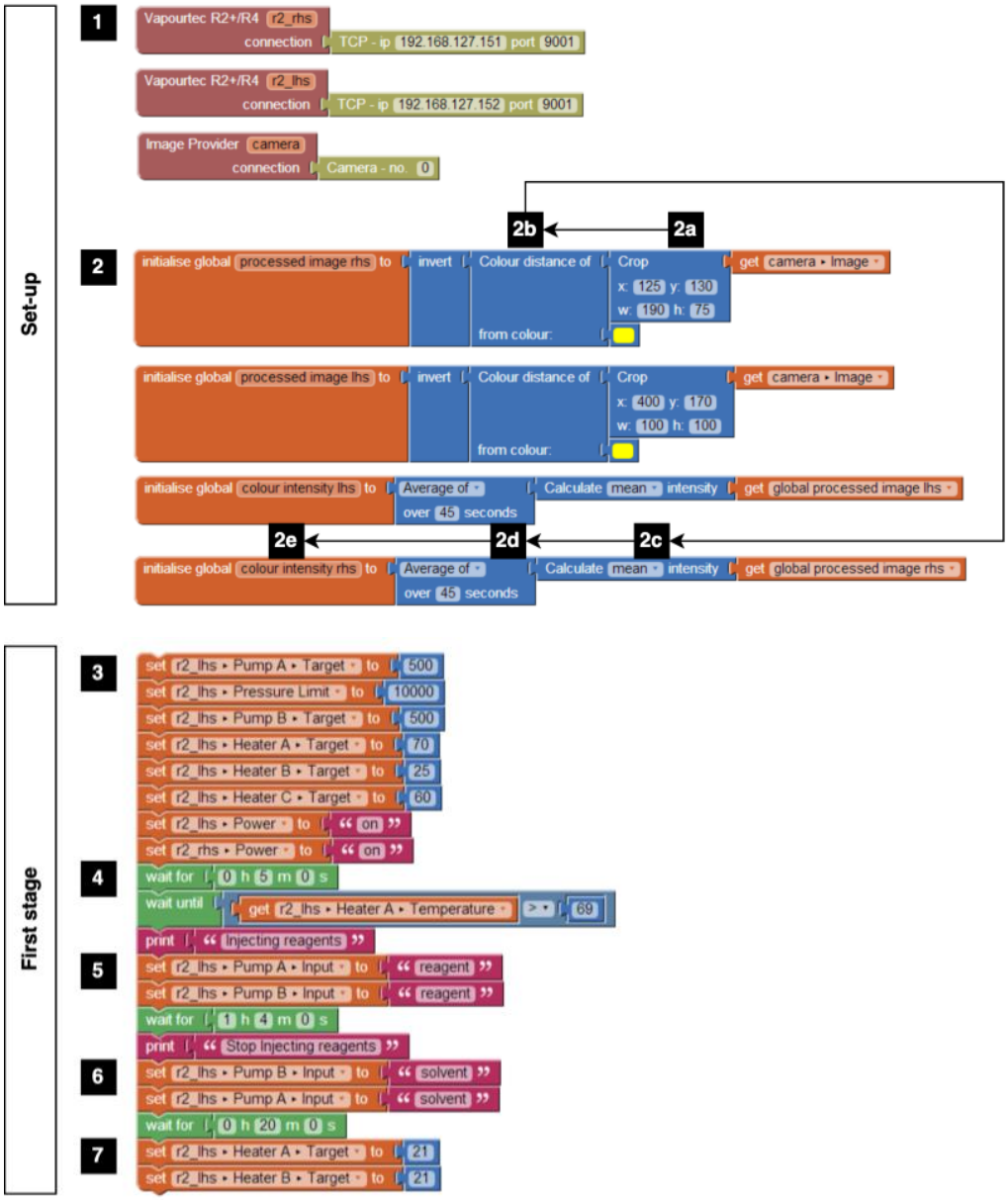
8. Allows 15 min for the reagents to pass through the heater and the MnO2 column.
9. Wait for the detection of the first colorimeter to reach a set threshold (95 units; empirically determined),
10. Direct the intermediate through to the second half of the system whenever the first colorimeter reading is above a threshold of 90 units (empirically determined)
11. Until this reading drops below another threshold (88 units; empirically determined) consistently for 10 min,

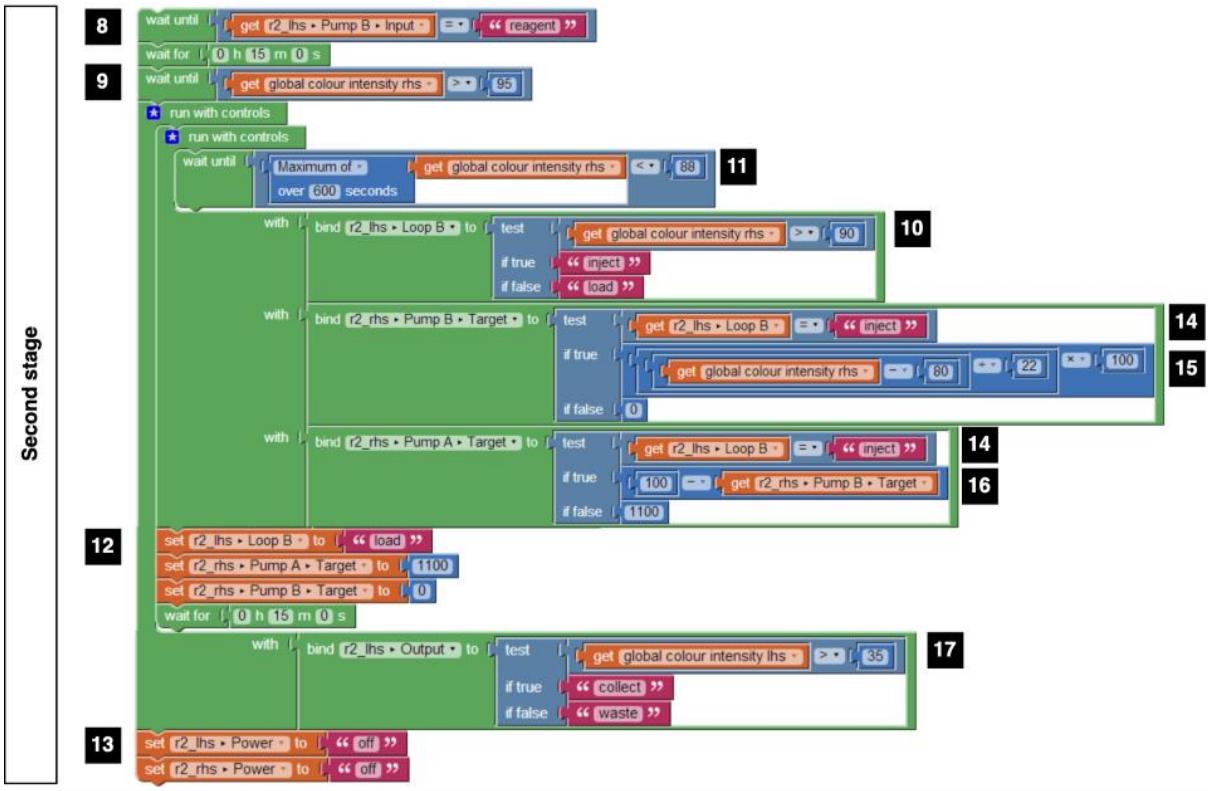
12. at which point the second half of the system is flushed with solvent (r2_rhs > Pump A) for 15 min,
13. and then the reactors are turned off.

During the second stage

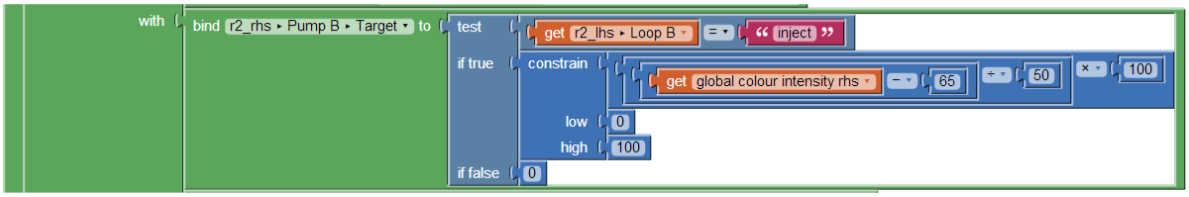
14. The second set of reagents are injected whenever the intermediate is being collected.
15. The flow rate of the pump injecting the second reagent is varied to match the amount of intermediate present (by an empirically determined factor)
16. The flow rate of make-up solvent is adjusted as well, to keep the total flow rate constant.
17. The output is directed to collection as long as the second colorimeter is detecting over a threshold value of 35 units (empirically determined).

Blocktopus control script



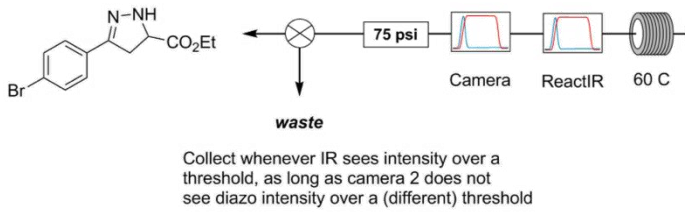


After testing, this protocol was adjusted to constrain **r2_rhs ▸ Pump B ▸ Target** to have values only between 0 and 100 uL/min.



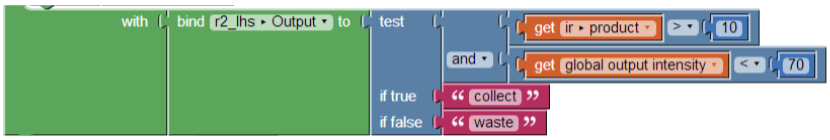
Inclusion of FlowIR data

With this observation of the FlowIR data under the conditions in hand, the protocol was adjusted to include the IR data.

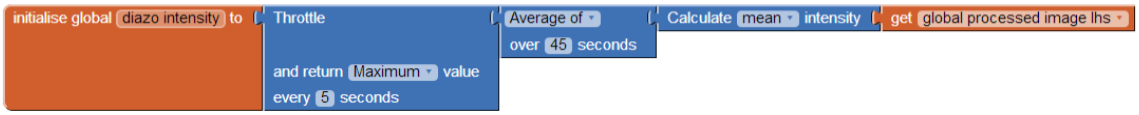


Add a connection to the FlowIR (**ir**) in the setup section (**1**). This required a separate script to be running on the PC alongside the Mettler Toledo software, providing access to data from a CSV file exported by the MT software at this IP address and port.

The product valve logic (**17**) was updated with the aim of increasing the purity of the product collected. The pyrazoline was collected whenever a certain threshold was met in the IR detection (indicating the presence of the pyrazoline C=O) but where the colorimetry detection was under another threshold (indicating a lack of unreacted diazo intermediate)



The colorimetry processing logic (**2**) was also modified. Since the intensity value was being used to set the flow rate of the pumps **r2_rhs ▸ Pump A** and **r2_rhs ▸ Pump B**, the fact the value of the variable was changing every second meant that there were frequent pump speed changes, which reduced the performance of the pump. By limiting the frequency at which the variable was updated, this was avoided.

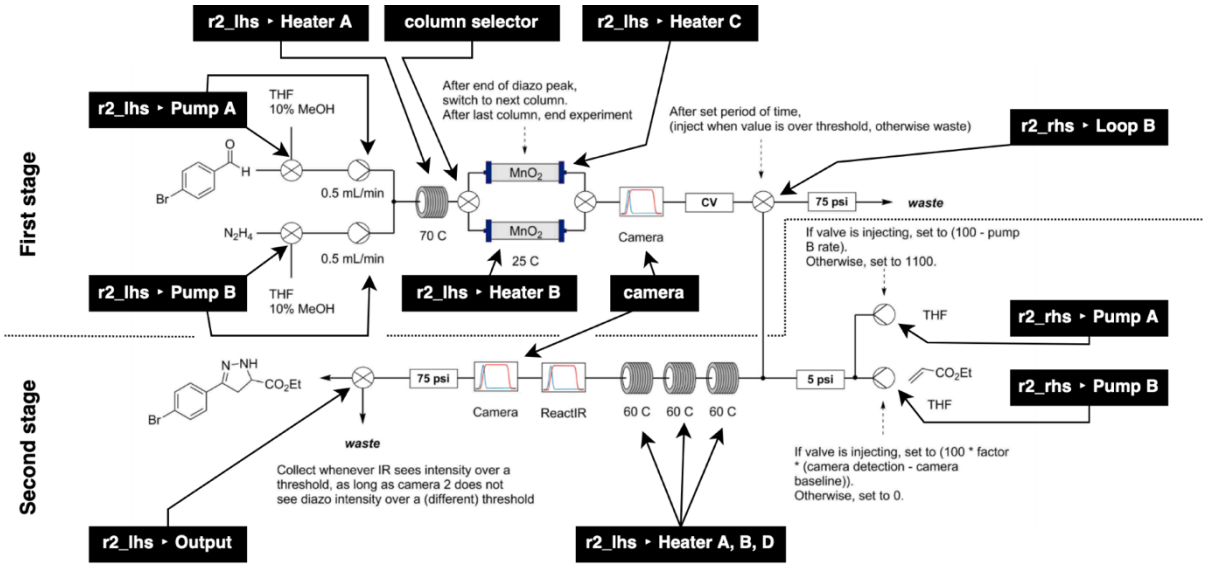


Disappointingly the use of IR data did not lead to improved reliability of the reagent collection, so control was reverted to the colorimetry data in the next iteration.

Addition of a column switcher

In a further modification with the intention of prolonging the duration of the experiment, a Vici Valco column switching valve (**column selector**) was added, such that multiple columns of the MnO_2 reagent could be used in sequence.

Residence in the second stage was extended by the addition of two extra reactor coils, and these were moved to the second R2+/R4 so that heater slots on the first R2+/R4 instrument were available for extra column reactors.



When the colorimeter detected a fall in the concentration of diazo intermediate, it triggered a column switch so that fresh MnO_2 could be used. The remainder of the control protocol could remain the same,

since the controlled diazo selection valve (**r2_lhs ‣ Loop B**) ensured that the intermediate was only directed towards the second stage of the reactor whenever its concentration was sufficient for the detection to be over the threshold.

Protocol

Setup

1. Configure the instruments (the FlowIR is not used in the control protocol for this experiment).
2. Split the image from the single camera into two separate variables:
    a. Separately crop the image into two regions of interest;
    b. Extract the "yellowness" of each;
    c. Calculate their mean intensities (the image is 8-bit, so this is a value from 0-255);
    d. Take the mean value over a 45 second rolling window, so smooth out noise;
    e. Set the maximum refresh frequency to once per 5 seconds.
    f. Store the result in numeric variables (**colour intensity lhs**, **colour intensity rhs**). A new image is read from the camera every 1 second, and the variables are updated with each new image.

First stage

3. Set the reactor flow rates and heater temperatures.
4. Wait at least 10 minutes, and then until the heater at 70C (Heater A) is at the desired temperature.
5. Inject the reagents. Reagent injection is now stopped by the column-switching logic.

Second set-up

6. Create a variable (**diazo trigger intensity**) to contain the threshold intensity (empirically determined), which is used to determine if the diazo intermediate is collected. The variable is never modified, but this allows the same value to be used in many formulae without having to enter it each time.
7. Create a variable to hold the current column number.
8. Only start the second stage once diazo begins to be injected.
9. Set the required temperatures and flow rates for **r2_rhs**.

Column switching

10. Allows 15 min for the reagents to pass through the heaters and the MnO2 column.
11. Wait for the detection of the first colorimeter to reach a set threshold (20 units below the defined threshold frequency);
12. For each of the two columns:
    a. Select the column using the valve.
    b. Wait until the detection level rises above the threshold.
    c. Wait at least 40 minutes, and then until the detection level falls below the threshold level, consistently for 10 minutes.

Second stage (runs until the last column is exhausted)

13. Direct the intermediate through to the second half of the system whenever the first colorimeter reading is above the threshold.
14. The second set of reagents are injected whenever the intermediate is being collected.
15. The flow rate of the pump injecting the second reagent is varied to match the amount of intermediate present (by an empirically determined factor)

16. The flow rate of make-up solvent is adjusted as well, to keep the total flow rate constant.

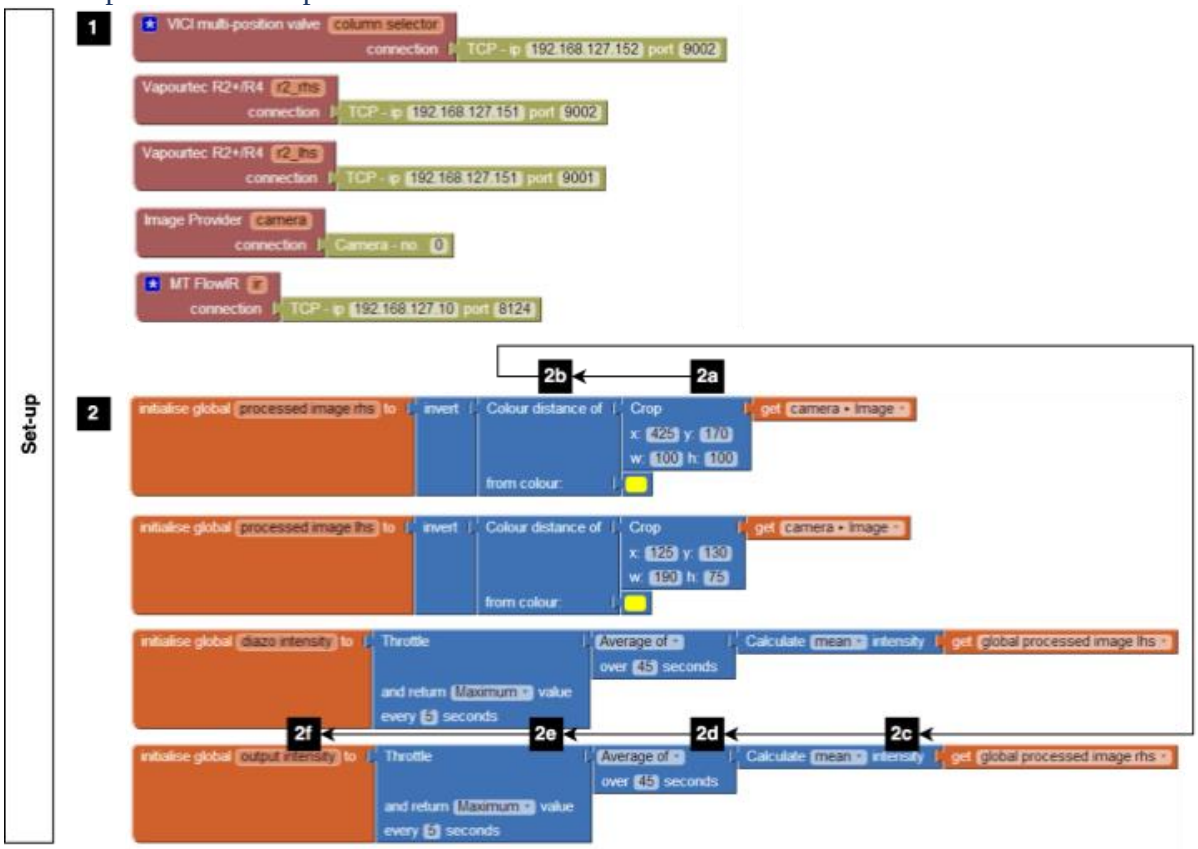
Flushing

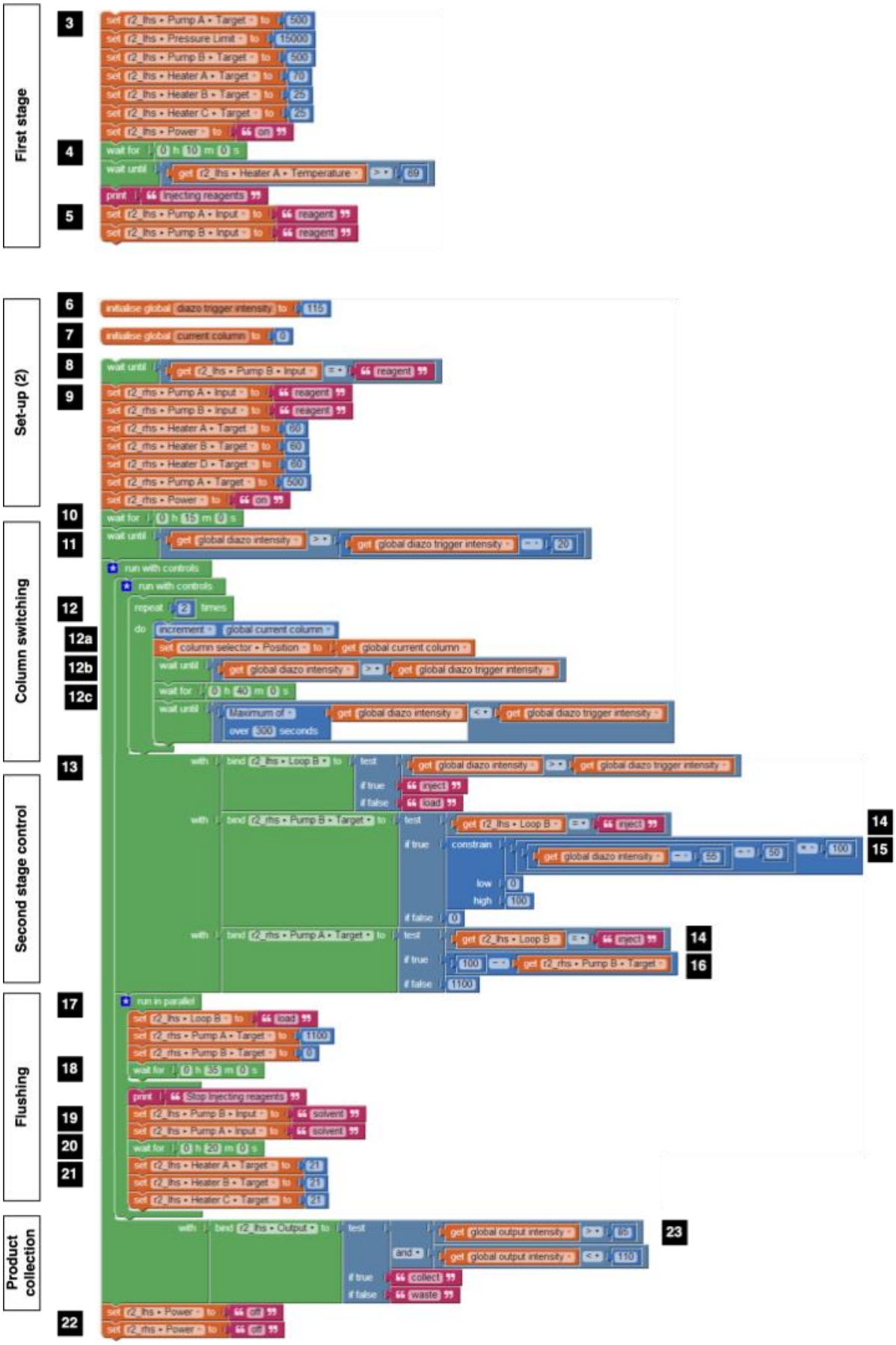
17. Once the last column is exhausted, stop collecting the intermediate and switch the second-stage pumps to inject solvent only.
18. Flush the second-stage part of the system for 35 min.
19. At the same time, stop injecting the aldehyde and hydrazine reagents.
20. Flush the first-stage part of the system for 20 min,
21. Turn off the heaters in the first-stage part of the system.
22. Once the flushing stages are complete, turn off the reactors.

Product collection

23. The output is directed to collection as long as the second colorimeter is detecting between 85 and 110 units (empirically determined). This had proved to be more effective than using the reading from the inline IR spectrometer.

Blocktopus control script




First stage
Set-up (2)
Column switching
Second stage control
Flushing
Product collection
3
4
5
6
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8
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10
11
12
12a
12b
12c
13
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15
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17
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19
20
21
22
23
set r2_lhs • Pump A • Target to 500
set r2_lhs • Pressure Limit to 15000
set r2_lhs • Pump B • Target to 500
set r2_lhs • Heater A • Target to 70
set r2_lhs • Heater B • Target to 25
set r2_lhs • Heater C • Target to 25
set r2_lhs • Power to on
wait for 0 h 10 m 0 s
wait until get r2_lhs • Heater A • Temperature > 69
print Injecting reagents
set r2_lhs • Pump A • Input to reagent
set r2_lhs • Pump B • Input to reagent
initialise global diazo trigger intensity to 115
initialise global current column to 0
wait until get r2_lhs • Pump B • Input = reagent
set r2_rhs • Pump A • Input to reagent
set r2_rhs • Pump B • Input to reagent
set r2_rhs • Heater A • Target to 60
set r2_rhs • Heater B • Target to 60
set r2_rhs • Heater D • Target to 60
set r2_rhs • Pump A • Target to 500
set r2_rhs • Power to on
wait for 0 h 15 m 0 s
wait until get global diazo intensity > get global diazo trigger intensity - 20
run with controls
run with controls
repeat 2 times
do
increment global current column
set column selector • Position to get global current column
wait until get global diazo intensity > get global diazo trigger intensity
wait for 0 h 40 m 0 s
wait until Maximum of get global diazo intensity < get global diazo trigger intensity over 600 seconds
with bind r2_lhs • Loop B to test get global diazo intensity > get global diazo trigger intensity
if true inject
if false load
with bind r2_rhs • Pump B • Target to test get r2_lhs • Loop B = inject
if true constrain get global diazo intensity - 65 - 50 * 100
low 0
high 100
if false 0
with bind r2_rhs • Pump A • Target to test get r2_lhs • Loop B = inject
if true 100 - get r2_rhs • Pump B • Target
if false 1100
run in parallel
set r2_lhs • Loop B to load
set r2_rhs • Pump A • Target to 1100
set r2_rhs • Pump B • Target to 0
wait for 0 h 35 m 0 s
print Stop injecting reagents
set r2_lhs • Pump B • Input to solvent
set r2_lhs • Pump A • Input to solvent
wait for 0 h 20 m 0 s
set r2_lhs • Heater A • Target to 21
set r2_lhs • Heater B • Target to 21
set r2_lhs • Heater C • Target to 21
with bind r2_lhs • Output to test get global output intensity > 85
and get global output intensity < 110
if true collect
if false waste
set r2_lhs • Power to off
set r2_rhs • Power to off

Characterization of the isolated compounds

Ethyl 5-(4-bromophenyl)-4,5-dihydro-1H-pyrazole-3-carboxylate (1)

Isolated as a pale-yellow oil in 81% yield.

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.47 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 4.97 (t, *J* = 10.9 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 3.37 (dd, *J* = 17.2, 11.1 Hz, 1H), 2.86 (dd, *J* = 17.3, 10.1 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 162.5 (C_0), 141.6 (C_0), 140.5 (C_0), 132.1 (CH), 128.0 (CH), 122.0 (C_0), 65.0 (CH), 61.3 (CH_2), 40.0 (CH_2), 14.3 (CH_3)

HRMS expected: 319.0058 $[M+Na]^+$ found: 319.0027 $[M+Na]^+$

5-(4-bromophenyl)-4,5-dihydro-1H-pyrazole-3-carbonitrile (6)

Isolated as a pale-yellow oil in 73% yield.

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.71 (br s, 1H), 5.02 (t, *J* = 11.1 Hz, 1H), 3.35 (dd, *J* = 16.9, 12.0 Hz, 1H), 2.84 (dd, *J* = 16.8, 10.0 Hz, 1H)

^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 139.1 (C_0), 132.3 (CH), 128.0 (CH), 122.5 (C_0), 122.3 (C_0), 114.5 (C_0), 64.5 (CH), 41.8 (CH_2)

HRMS expected: 249.9980 $[M+H]^+$ found: 249.9991 $[M+H]^+$

Ethyl 5-(4-bromophenyl)-4-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-3-carboxylate (11)

Isolated as a pale-yellow oil in 89% yield.

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.51 (d, *J* = 8.5 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.14 (d, *J* = 5.2 Hz, 1H), 4.32-4.24 (m, 2H), 3.88 (qd, *J* = 8.5, 5.4 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 161.5 (C_0), 138.3 (C_0), 132.6 (CH), 132.3 (C_0), 127.4 (CH), 124.7 (C_0, q, *J* = 280.3 Hz), 123.0 (C_0), 65.9 (CH), 61.6 (CH_2), 56.6 (CH, q, *J* = 29.5 Hz), 14.1 (CH_3)

^{19}F NMR (235 MHz, $CDCl_3$, ppm) δ −69.45 (d, *J* = 8.6 Hz, major isomer, 90%) −76.73, (d, *J* = 7.1 Hz, minor isomer, 10%)

HRMS expected: 365.0113 $[M+H]^+$ found: 365.0096 $[M+H]^+$

5-(4-bromophenyl)-3-(phenylsulfonyl)-4,5-dihydro-1H-pyrazole (16)

Isolated as a pale-orange solid in 58% yield.

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.99-7.97 (m, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.03 (t, *J* = 10.9 Hz, 1H), 3.42 (dd, *J* = 16.9, 11.6 Hz, 1H), 2.91 (dd, *J* = 16.8, 10.3 Hz, 1H)

^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 149.8 (C_0), 139.1 (C_0), 138.5 (C_0), 134.0 (CH), 132.1 (CH), 129.3 (CH), 128.3 (CH), 127.9 (CH), 122.4 (C_0), 66.0 (CH), 39.1 (CH)

HRMS expected: 364.9959 $[M+H]^+$ found: 364.9952 $[M+H]^+$

Ethyl 5-(3-nitrophenyl)-4,5-dihydro-1H-pyrazole-3-carboxylate (2)

Isolated as a white solid in 30% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 8.21-8.15 (m, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 6.63 (br s, 1H), 5.16 (t, *J* = 11.1 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.49 (dd, *J* = 17.4, 11.9 Hz, 1H), 2.91 (dd, *J* = 17.3, 10.4 Hz, 1H), 1.37 (t, *J* = 7.2 Hz, 3H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 162.3 (C_0), 148.6 (C_0), 143.5 (C_0), 141.9 (C_0), 132.5 (CH), 130.1 (CH), 123.1 (CH), 121.5 (CH), 64.7 (CH), 61.4 (CH_2), 40.3 (CH_2), 14.3 (CH_3)

HRMS expected: 264.0984 $[M+H]^+$ found: 264.0985 $[M+H]^+$

5-(3-nitrophenyl)-4,5-dihydro-1H-pyrazole-3-carbonitrile (7)

Isolated as a pale-yellow oil in 77% yield

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 8.25-8.12 (m, 2H), 7.72-7.50 (m, 2H), 6.70 (br s, 1H), 5.18 (td, *J* = 11.2, 2.3 Hz, 1H), 3.44 (dd, *J* = 16.9, 12.0 Hz, 1H), 2.88 (dd, *J* = 16.8, 10.7 Hz, 1H)

^{13}C NMR (63 MHz, DMSO-d_6, ppm) δ 148.4 (C_0), 143.9 (C_0), 133.8 (CH), 130.8 (CH), 123.2 (CH), 121.8 (CH), 119.8 (C_0), 116.2 (C_0), 63.6 (CH), 40.8 (CH_2)

HRMS expected: 217.0926 $[M+H]^+$ found: 217.0716 $[M+H]^+$

Ethyl 5-(3-nitrophenyl)-4-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-3-carboxylate (12)

Isolated as a white solid in 45% yield.

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 8.25-8.19 (m, 1H), 8.12 (s, 1H), 7.63-7.60 (m, 2H), 7.31 (br s, 1H), 5.33 (d, *J* = 5.8 Hz, 1H), 4.40-4.21 (m, 2H), 3.94 (qd, *J* = 8.3, 5.9 Hz, 1H), 134 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$, ppm) δ 161.2 (C_0), 148.7 (C_0), 141.3 (C_0), 132.5 (C_0), 131.9 (CH), 124.4 (C_0, q, *J* = 280 Hz), 123.6 (CH), 121.0 (CH), 65.2 (CH_2, q, *J* = 2.4 Hz), 61.6 (CH), 56.9 (CH_2, q, *J* = 30 Hz), 14.0 (CH_3)

^{19}F NMR (235 MHz, $CDCl_3$, ppm) δ −69.22 (d, *J* = 4.7 Hz)

HRMS expected: 354.0677 $[M+Na]^+$ found: 354.0648 $[M+Na]^+$

5-(3-nitrophenyl)-3-(phenylsulfonyl)-4,5-dihydro-1H-pyrazole (17)

Isolated as a colourless oil in 79% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 8.17-8.12 (m, 2H), 7.99-7.96 (m, 2H), 7.72-7.50 (m, 5H), 5.20 (t, *J* = 11.0 Hz, 1H), 3.52 (dd, *J* = 16.7, 11.2 Hz, 1H), 2.91 (dd, *J* = 16.8, 10.6 Hz, 1H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 149.5 (C_0), 148.3 (C_0), 142.2 (C_0), 138.2 (C_0), 134.1 (CH), 132.5 (CH), 130.0 (CH), 129.4 (CH), 128.1 (CH), 123.2 (CH), 121.3 (CH), 65.6 (CH), 39.3 (CH_2)

HRMS expected: 354.0525 $[M+Na]^+$ found: 354.0520 $[M+Na]^+$

Ethyl 5-(pyridin-3-yl)-4,5-dihydro-1H-pyrazole-3-carboxylate (3)

Isolated as a pale-yellow solid in 70% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 8.48-8.45 (m, 2H), 7.63 (dt, *J* = 7.9, 1.8 Hz, 1H), 7.23 (dd, *J* = 7.9, 4.9 Hz, 1H), 7.01 (br s, 1H), 4.99 (t, *J* = 11.0 Hz, 1H), 4.24 (q, *J* = 7.2 Hz, 2H), 3.36 (dd, *J* = 17.3, 11.9 Hz, 1H), 2.82 (dd, *J* = 17.2, 10.2 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 162.2 (C_0), 149.1 (CH), 147.8 (CH), 141.1 (C_0), 136.8 (C_0), 133.8 (CH), 123.6 (CH), 62.8 (CH), 61.0 (CH_2), 39.6 (CH_2), 14.0 (CH_3)

HRMS expected: 220.1086 $[M+H]^+$ found: 220.1074 $[M+H]^+$

5-(pyridin-3-yl)-4,5-dihydro-1H-pyrazole-3-carbonitrile (8)

Isolated as a pale-yellow solid in 41% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 8.60 (dd, *J* = 5.0, 1.4 Hz, 1H), 8.54 (d, *J* = 1.8 Hz, 1H), 7.68 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.35 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.88 (br s, 1H), 5.10 (dd, *J* = 11.2, 1.8 Hz, 1H), 3.41 (dd, *J* = 16.8, 12.0 Hz, 1H), 2.89 (dd, *J* = 16.9, 10.3 Hz, 1H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 150.1 (CH), 148.1 (CH), 135.6 (C_0), 133.9 (CH), 124.1 (CH), 122.5 (C_0), 114.2 (C_0), 62.8 (CH), 41.8 (CH_2)

HRMS expected: 173.0827 $[M+H]^+$ found: 173.0810 $[M+H]^+$

Ethyl 5-(pyridin-3-yl)-4-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-3-carboxylate (13)

Isolated as a pale-yellow oil in 56% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 8.53-8.51 (m, 1H), 8.43 (s, 1H), 7.54 (d, *J* = 8.0, 1H), 7.33-7.27 (m, 1H), 5.19 (d, *J* = 5.6 Hz, 1H), 4.34-4.20 (m, 2H), 3.95-3.82 (m, 1H), 1.31 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 161.3 (C_0), 150.1 (CH), 147.3 (CH), 135.0 (C_0), 133.6 (CH), 131.8 (C_0), 124.5 (C_0, q, *J* = 280.0 Hz), 124.1 (CH), 64.0 (q, *J* = 2.4 Hz), 61.4 (CH_2), 56.4 (CH, q, *J* = 29.7 Hz), 14.0 (CH_3)

^{19}F NMR (235 MHz, $CDCl_3$, ppm) δ −69.45 (d, *J* = 8.4 Hz)

HRMS expected: 288.0960 $[M+H]^+$ found: 288.0973 $[M+H]^+$

Ethyl 5-(4-fluorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-3-carboxylate (4)

Isolated as a pale-yellow oil in 74% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 7.39-7.33 (m, 2H), 7.06-6.99 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.12 (d, *J* = 17.1 Hz, 1H), 3.02 (d, *J* = 17.1 Hz, 1H), 1.60 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 162.7 (C_0), 161.9 (C_0, d, *J* = 246.1 Hz), 141.2 (C_0, d, *J* = 3.2 Hz), 140.7 (C_0), 127.0 (CH, d, *J* = 8.1 Hz), 115.4 (CH, d, *J* = 21.4 Hz), 69.4 (C_0), 61.1 (CH_2), 46.5 (CH_2), 27.4 (CH_3), 14.3 (CH_3)

^{19}F NMR (235 MHz, $CDCl_3$, ppm) δ −115.53 (tt, *J* = 8.8, 5.2 Hz)

HRMS expected: 273.1015 $[M+Na]^+$ found: 273.0987 $[M+Na]^+$

5-(4-fluorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-3-carbonitrile (9)

Isolated as a pale-yellow oil in 82% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 7.39-7.31 (m, 2H), 7.11-7.02 (m, 2H), 3.03 (s, 2H), 1.64 (s, 3H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 162.0 (C_0, d, *J* = 246.9 Hz), 139.9 (C_0, d, *J* = 3.2 Hz), 126.8 (CH, d, *J* = 7.8 Hz), 121.3 (C_0), 115.7 (CH, d, *J* = 21.4 Hz), 114.8 (C_0), 69.5 (C_0), 48.4 (CH_2), 27.0 (CH_3)

^{19}F NMR (235 MHz, $CDCl_3$, ppm) δ −114.64 (tt, *J* = 8.6, 5.1 Hz)

HRMS expected: 204.0937 $[M+H]^+$ found: 204.0904 $[M+H]^+$

5-(4-fluorophenyl)-5-methyl-3-(phenylsulfonyl)-4,5-dihydro-1H-pyrazole (19)

Isolated as a pale-yellow oil in 38% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 8.07-7.94 (m, 2H), 7.70-7.54 (m, 3H), 7.32-7.26 (m, 2H), 7.04-6.97 (m, 2H), 3.16 (d, *J* = 16.5 Hz, 1H), 3.02 (d, *J* = 16.5 Hz, 1H), 1.58 (s, 3H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 162.0 (C_0, d, *J* = 246.8 Hz), 148.6 (C_0), 140.1 (C_0, d, *J* = 3.3 Hz), 138.8 (C_0), 134.0 (CH), 129.4 (CH), 128.2 (CH), 127.0 (CH, d, *J* = 8.1 Hz), 115.5 (CH, d, *J* = 21.4 Hz), 71.1 (C_0), 45.5 (CH_2), 27.0 (CH_3)

^{19}F NMR (235 MHz, $CDCl_3$, ppm) δ −114.88 (tt, *J* = 8.7, 5.2 Hz)

HRMS expected: 319.0916 $[M+H]^+$ found: 319.0905 $[M+H]^+$

Ethyl 5-methyl-5-phenyl-4,5-dihydro-1H-pyrazole-3-carboxylate (14)

Isolated as a pale-yellow oil in 86% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 7.42-7.25 (m, 5H), 4.29 (q, *J* = 7.2 Hz, 2H), 3.09 (d, *J* = 2.3 Hz, 2H), 1.60 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 162.8 (C_0), 145.4 (C_0), 140.8 (C_0), 128.7 (CH), 127.3 (CH), 125.1 (CH), 69.9 (C_0), 61.1 (CH_2), 46.3 (CH_2), 27.5 (CH_3), 14.3 (CH_3)

HRMS expected: 255.1109 $[M+Na]^+$ found: 255.1095 $[M+Na]^+$

5-methyl-5-phenyl-4,5-dihydro-1H-pyrazole-3-carbonitrile (18)

Isolated as a pale-yellow oil in 68% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 7.42-7.32 (m, 5H), 3.05 (s, 2H), 1.65 (s, 3H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 144.0 (C_0), 128.9 (CH), 127.8 (CH), 125.0 (CH), 121.5 (C_0), 114.8 (C_0), 69.9 (C_0), 48.4 (CH_2), 27.0 (CH_3)

HRMS expected: 186.1031 $[M+H]^+$ found: 186.1026 $[M+H]^+$

Ethyl 5-(furan-2-yl)-4,5-dihydro-1H-pyrazole-3-carboxylate (5)

Isolated as a pale-yellow oil in 61% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 7.39-7.37 (m, 1H), 6.33 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.24 (d, *J* = 3.6 Hz, 1H), 5.04 (dd, *J* = 11.0, 8.4 Hz, 1H), 4.33 (q, *J* = 7.2 Hz, 2H), 3.26 (dd, *J* = 17.0, 11.1 Hz, 1H), 3.15 (dd, *J* = 17.2, 8.4 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 162.4 (C_0), 153.3 (C_0), 142.7 (CH), 142.6 (C_0), 110.4 (CH), 106.5 (CH), 61.3 (CH_2), 58.3 (CH), 36.1 (CH_2), 14.3 (CH_3)

HRMS expected: 209.0926 $[M+H]^+$ found: 209.0918 $[M+H]^+$

5-(furan-2-yl)-4,5-dihydro-1H-pyrazole-3-carbonitrile (16)

Isolated as a pale-yellow oil in 65% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 7.40 (d, *J* = 1.1 Hz, 1H), 6.36 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.28 (d, *J* = 3.3 Hz, 1H), 5.07 (dd, *J* = 11.5, 8.2 Hz, 1H), 3.23 (dd, *J* = 16.8, 11.5 Hz, 1H), 3.09 (dd, J 16.7, 8.2 Hz, 1H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 151.9 (C_0), 143.0 (CH), 123.1 (C_0), 114.3 (C_0), 110.5 (CH), 107.3 (CH), 57.9 (CH), 38.0 (CH_2)

HRMS expected: 162.0656 $[M+H]^+$ found: 162.0667 $[M+H]^+$

Ethyl 5-(furan-2-yl)-4-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-3-carboxylate (15)

Isolated as a pale-yellow oil in 51% yield.

^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 7.41-7.40 (m, 1H), 6.65 (br s, 1H), 6.38-6.35 (m, 1H), 6.33-6.31 (m, 1H), 5.22 (d, *J* = 4.5 Hz, 1H), 4.41-4.29 (m, 3H), 1.39 (t, *J* = 7.1 Hz, 3H)

^{13}C NMR of the major isomer (63 MHz, $CDCl_3$, ppm) δ 161.3 (C_0), 150.8 (C_0), 146.0 (C_0), 143.6 (CH), 124.6 (C_0, q, *J* = 280.5 Hz), 110.7 (CH), 107.7 (CH), 61.6 (CH_2), 60.1 (CH, q, *J* = 2.7 Hz), 53.3 (CH, q, *J* = 30.0 Hz), 14.1 (CH_3)

^{19}F NMR (235 MHz, $CDCl_3$, ppm) δ −69.41 (d, *J* = 8.7 Hz, 77%), −76.27 (d, *J* = 7.0 Hz, 23%)

HRMS expected: 299.0620 $[M+Na]^+$ found: 299.0634 $[M+Na]^+$

5-(furan-2-yl)-3-(phenylsulfonyl)-4,5-dihydro-1H-pyrazole (20)

Isolated as a pale-yellow oil in 75% yield.

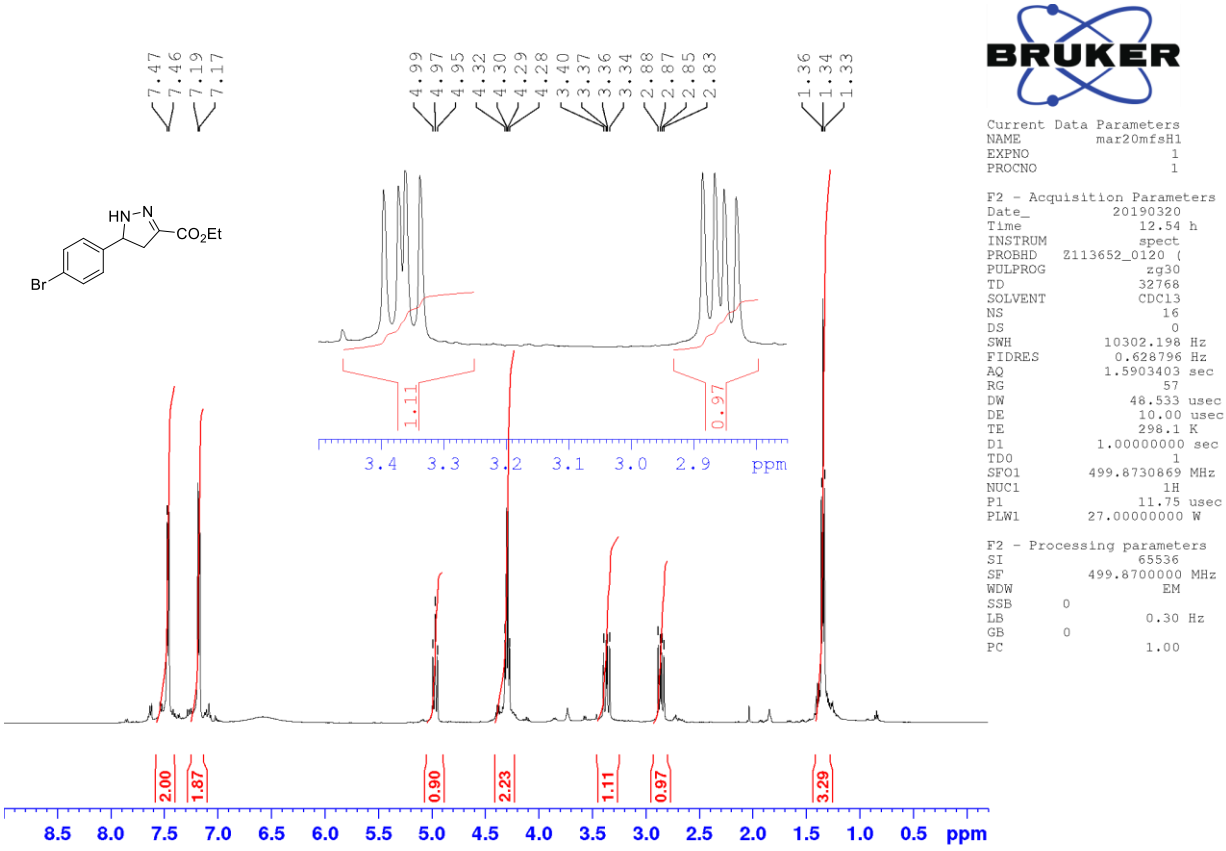
^{1}H NMR (250 MHz, $CDCl_3$, ppm) δ 8.03-7.97 (m, 2H), 7.72-7.55 (m, 3H), 7.34-7.32 (m, 1H), 6.30 (dd, *J* = 3.1, 2.0 Hz, 1H), 6.18 (d, *J* = 3.3 Hz, 1H), 5.07 (dd, *J* = 11.0, 8.3 Hz, 1H), 3.30 (dd, *J* = 16.7, 11.0 Hz, 1H), 3.16 (dd, *J* = 16.7, 8.3 Hz, 1H)

^{13}C NMR (63 MHz, $CDCl_3$, ppm) δ 152.1 (C_0), 150.6 (C_0), 143.0 (CH), 138.7 (C_0), 134.1 (CH), 129.4 (CH), 128.4 (CH), 110.5 (CH), 107.3 (CH), 59.5 (CH), 35.6 (CH_2)

HRMS expected: 277.0647 $[M+H]^+$ found: 277.0663 $[M+H]^+$

NMR Spectra for isolated compounds

Ethyl 5-(4-bromophenyl)-4,5-dihydro-1H-pyrazole-3-carboxylate

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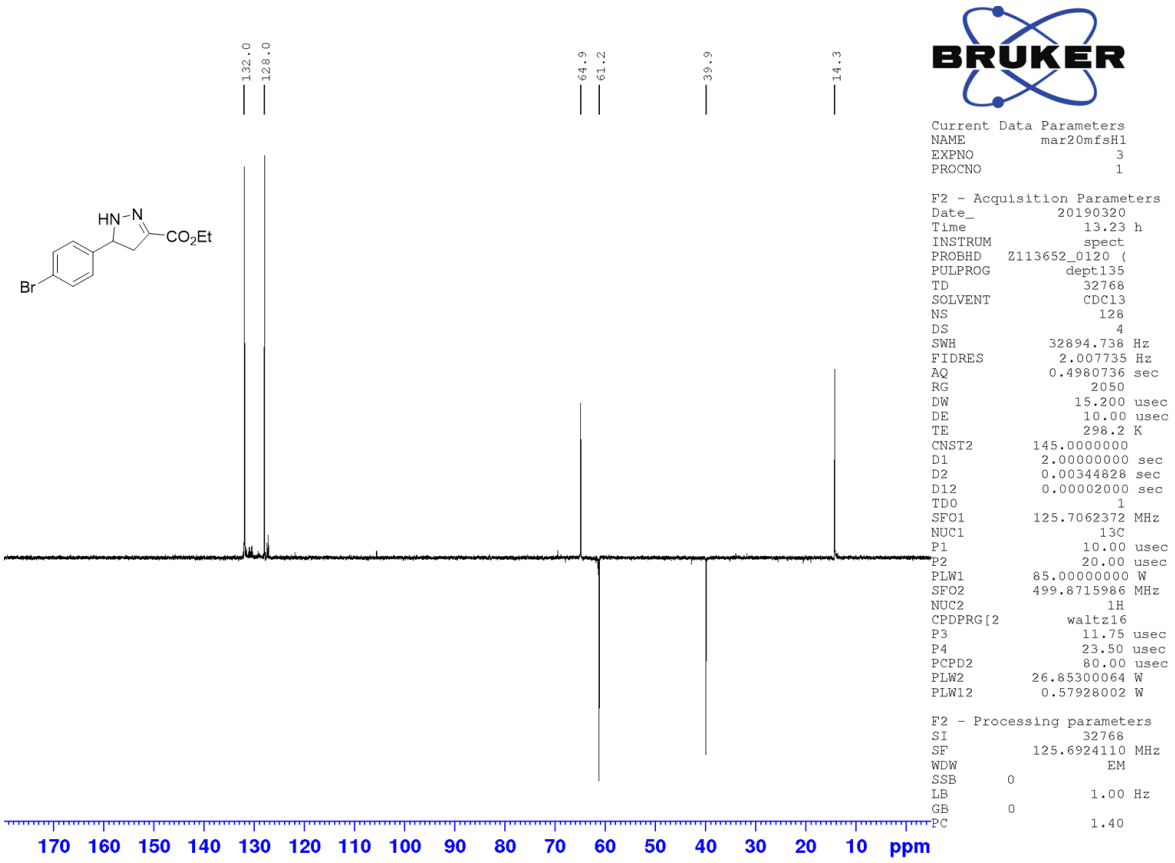
^{1}H NMR spectrum in $CDCl_3$, 500 MHz, of compound **1**

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CPDPRG[2         waltz16
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PLW2         26.85300064 W
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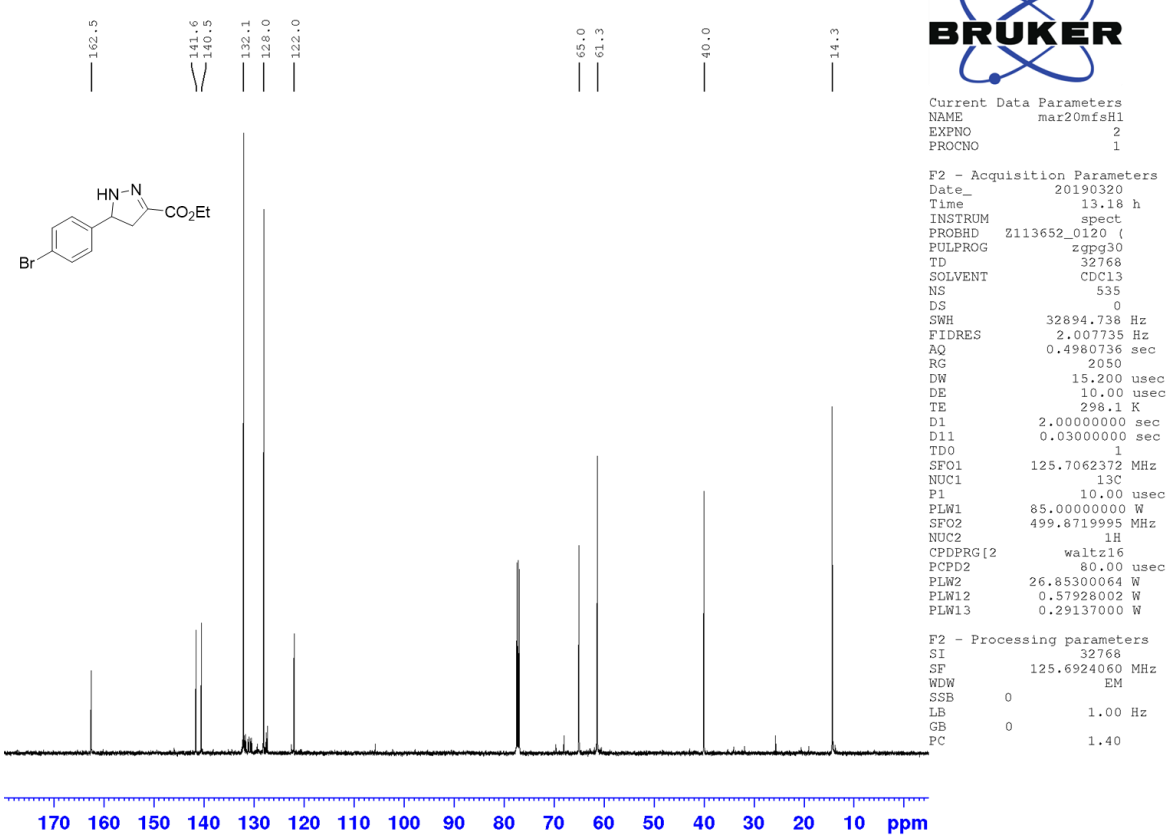
DEPT135 spectra in $CDCl_3$, 125 MHz, of compound **1**

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NUC2                1H
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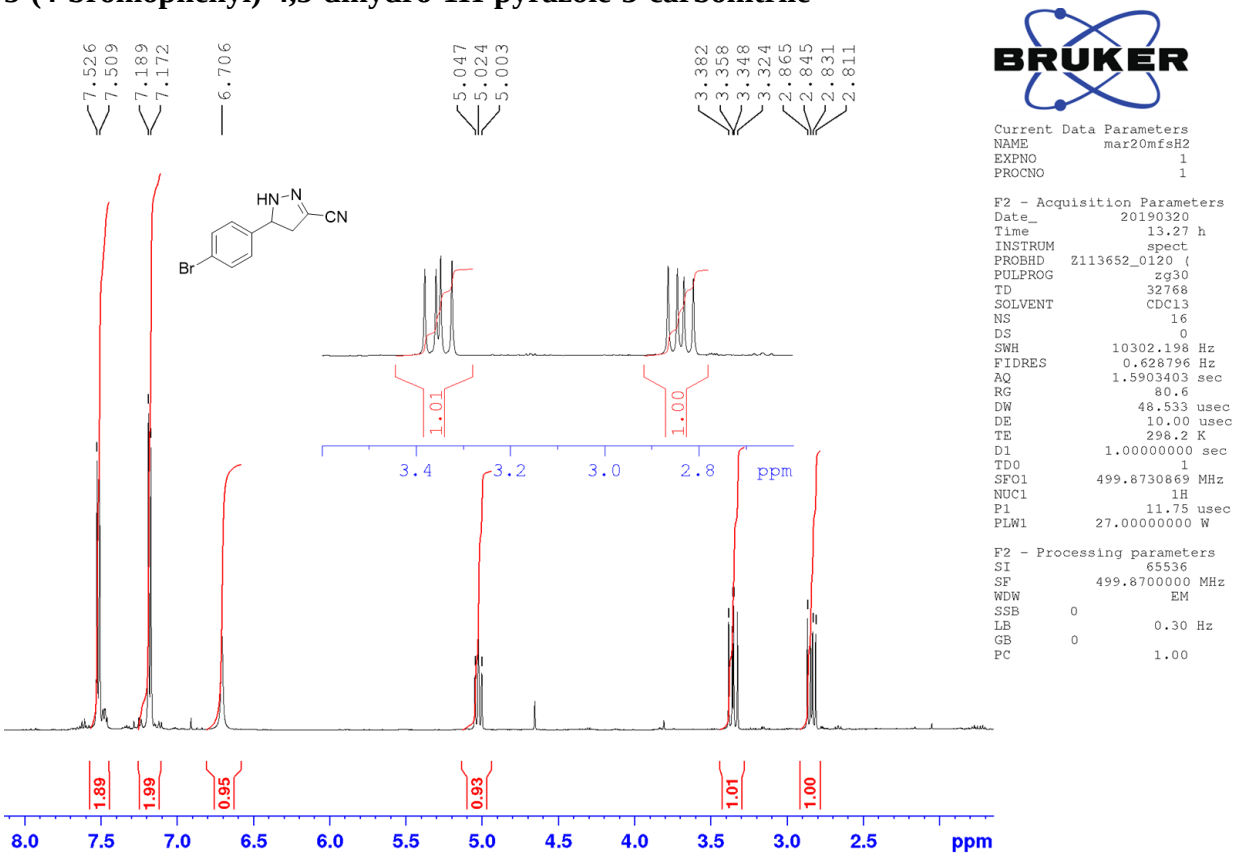
^{13}C NMR spectra in $CDCl_3$, 125 MHz, of compound **1**

5-(4-bromophenyl)-4,5-dihydro-1H-pyrazole-3-carbonitrile

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TD                32768
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FIDRES         0.628796 Hz
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RG                 80.6
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TE                298.2 K
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NUC1                  1H
P1                 11.75 usec
PLW1         27.00000000 W

F2 - Processing parameters
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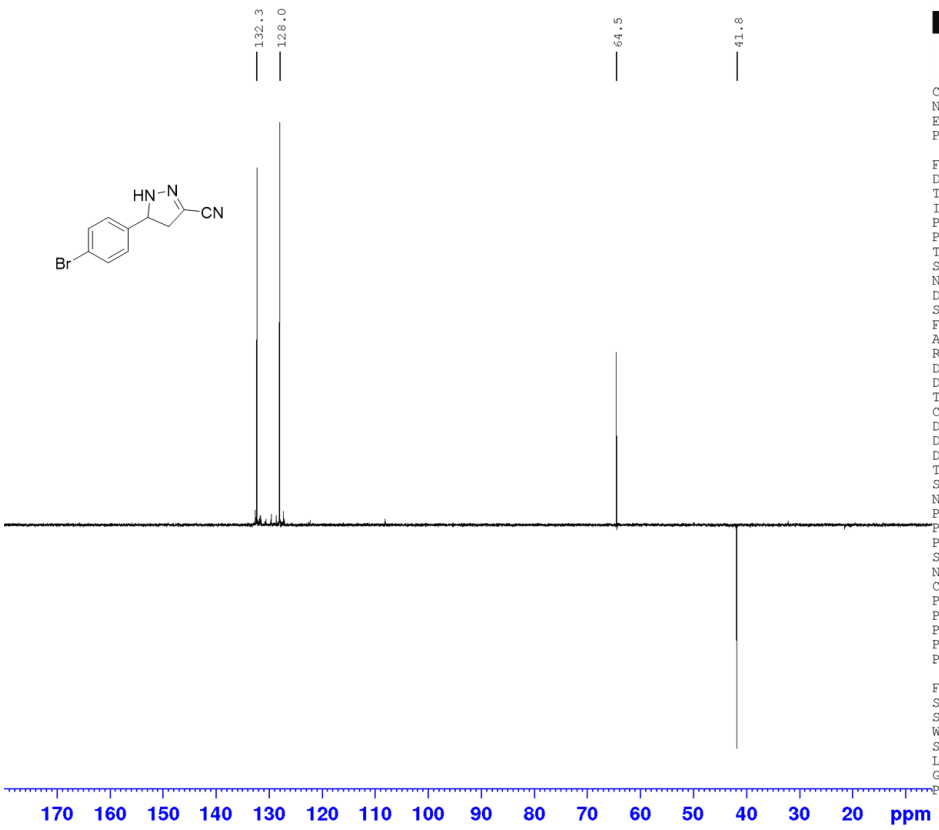
GB        0
PC                 1.00
```

^{1}H NMR spectrum in $CDCl_3$, 500 MHz, of compound **6**

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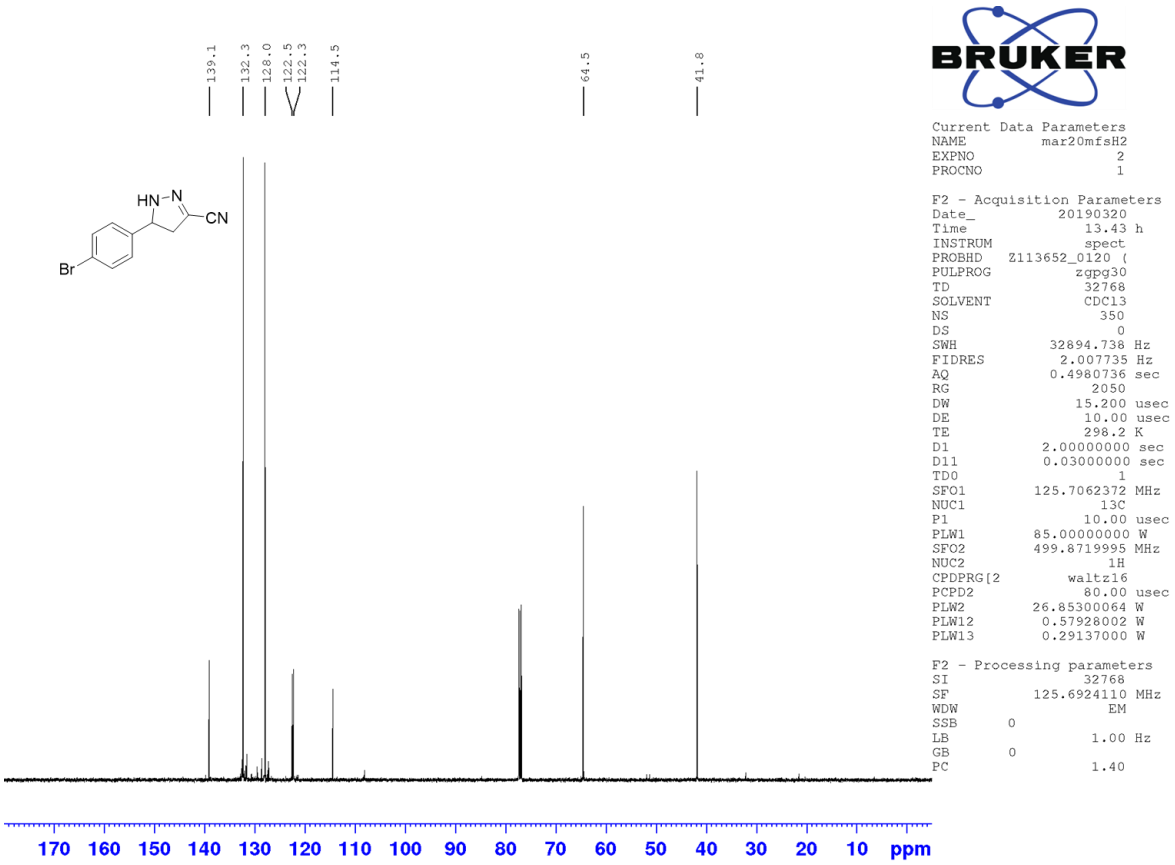
Current Data Parameters
NAME          mar20mfsH2
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190320
Time              13.48 h
INSTRUM            spect
PROBHD   Z113652_0120 (
PULPROG          dept135
TD                32768
SOLVENT           CDCl3
NS                  128
DS                    4
SWH           32894.738 Hz
FIDRES         2.007735 Hz
AQ            0.4980736 sec
RG                 2050
DW               15.200 usec
DE                10.00 usec
TE                298.1 K
CNST2        145.0000000
D1            2.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                    1
SFO1          125.7062372 MHz
NUC1                  13C
P1                10.00 usec
P2                20.00 usec
PLW1         85.00000000 W
SFO2          499.8715986 MHz
NUC2                  1H
CPDPRG[2          waltz16
P3                11.75 usec
P4                23.50 usec
PCPD2             80.00 usec
PLW2         26.85300064 W
PLW12         0.57928002 W

F2 - Processing parameters
SI                 32768
SF            125.6924110 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 125 MHz, of compound **6**



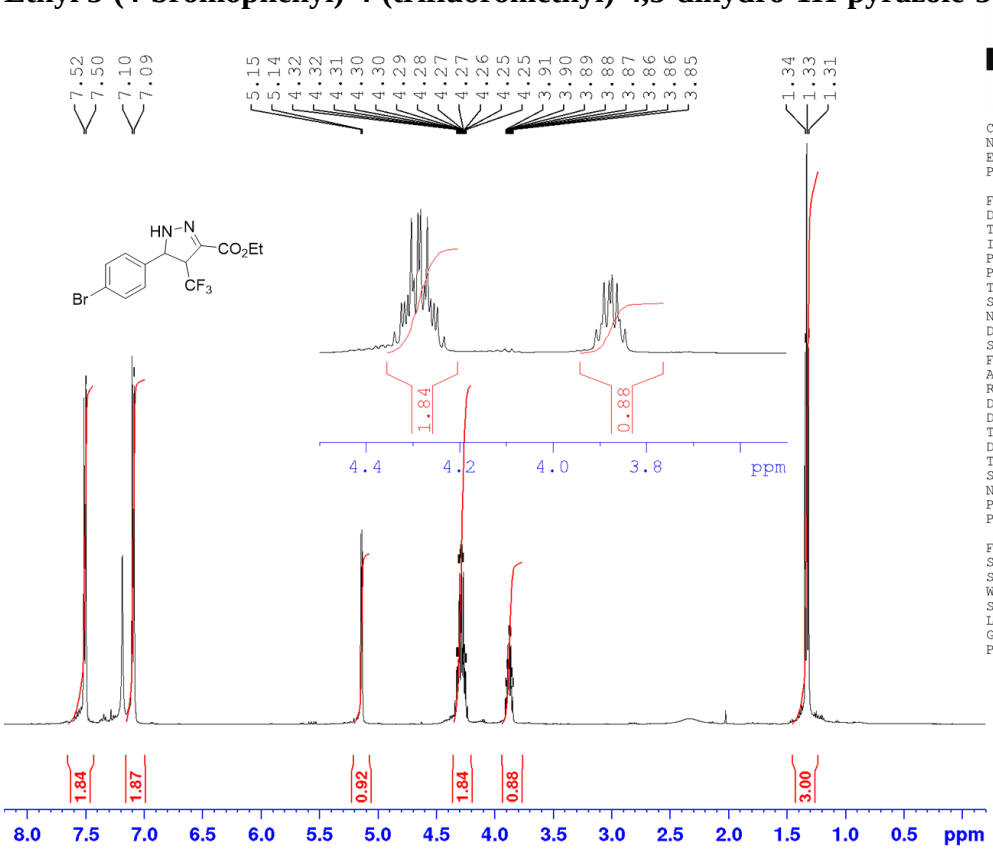

```
Current Data Parameters
NAME          mar20mfsH2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190320
Time              13.43 h
INSTRUM             spect
PROBHD   Z113652_0120 (
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  350
DS                    0
SWH           32894.738 Hz
FIDRES         2.007735 Hz
AQ            0.4980736 sec
RG                 2050
DW               15.200 usec
DE               10.00 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7062372 MHz
NUC1                13C
P1               10.00 usec
PLW1        85.00000000 W
SFO2        499.8719995 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2            80.00 usec
PLW2        26.85300064 W
PLW12        0.57928002 W
PLW13        0.29137000 W

F2 - Processing parameters
SI                32768
SF          125.6924110 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

^{13}C NMR spectrum in $CDCl_3$, 125 MHz, of compound **6**

Ethyl 5-(4-bromophenyl)-4-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-3-carboxylate

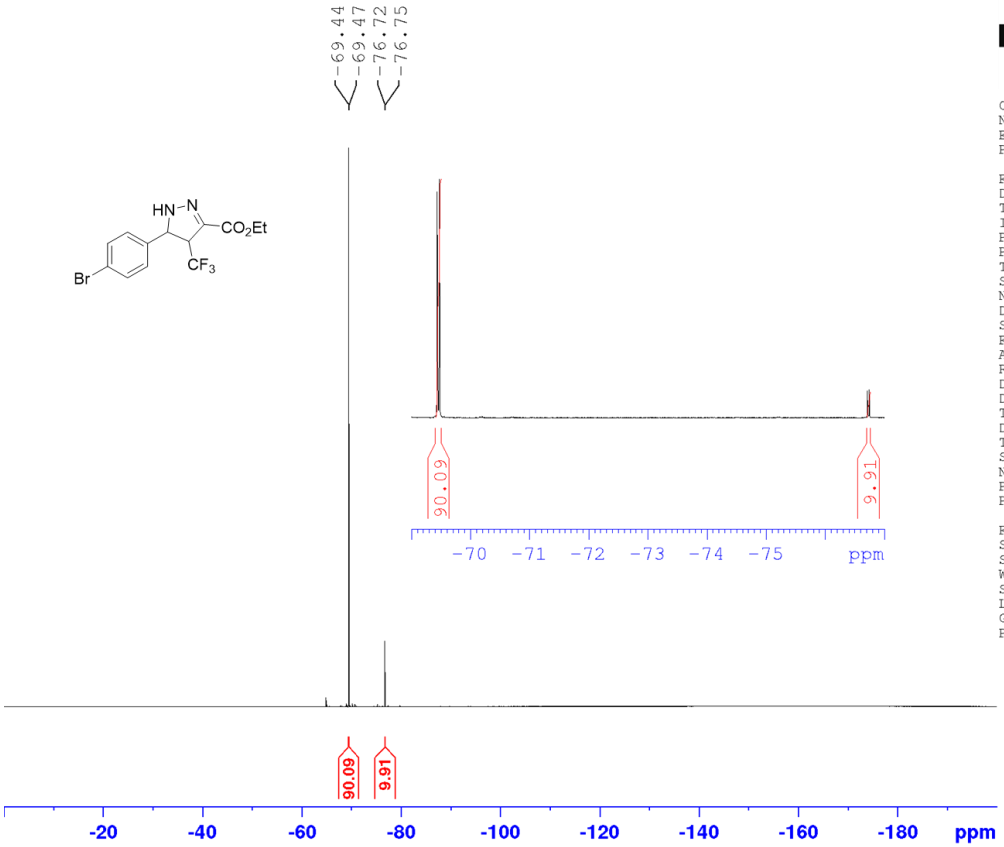



```
Current Data Parameters
NAME          mar20mfsH4
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190320
Time              16.03 h
INSTRUM             spect
PROBHD   Z113652_0120 (
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                    16
DS                     0
SWH           10302.198 Hz
FIDRES         0.628796 Hz
AQ            1.5903403 sec
RG                  50.8
DW                48.533 usec
DE                10.00 usec
TE                298.1 K
D1           1.00000000 sec
TD0                    1
SFO1        499.8730869 MHz
NUC1                  1H
P1                11.75 usec
PLW1         27.00000000 W

F2 - Processing parameters
SI                 65536
SF          499.8700000 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{1}H NMR spectrum in $CDCl_3$, 500 MHz, of compound **11**

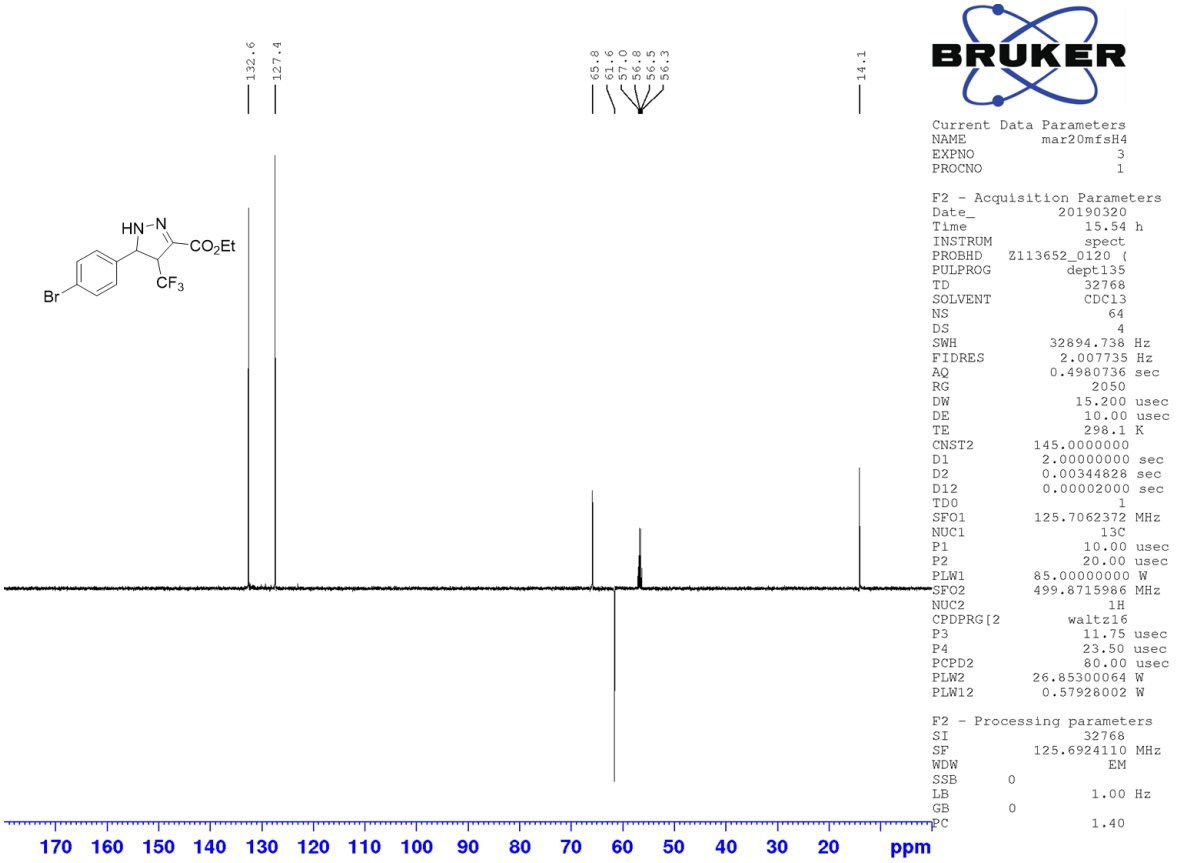



```
Current Data Parameters
NAME          ago06hmmH1
EXPNO                  2
PROCNO                 1

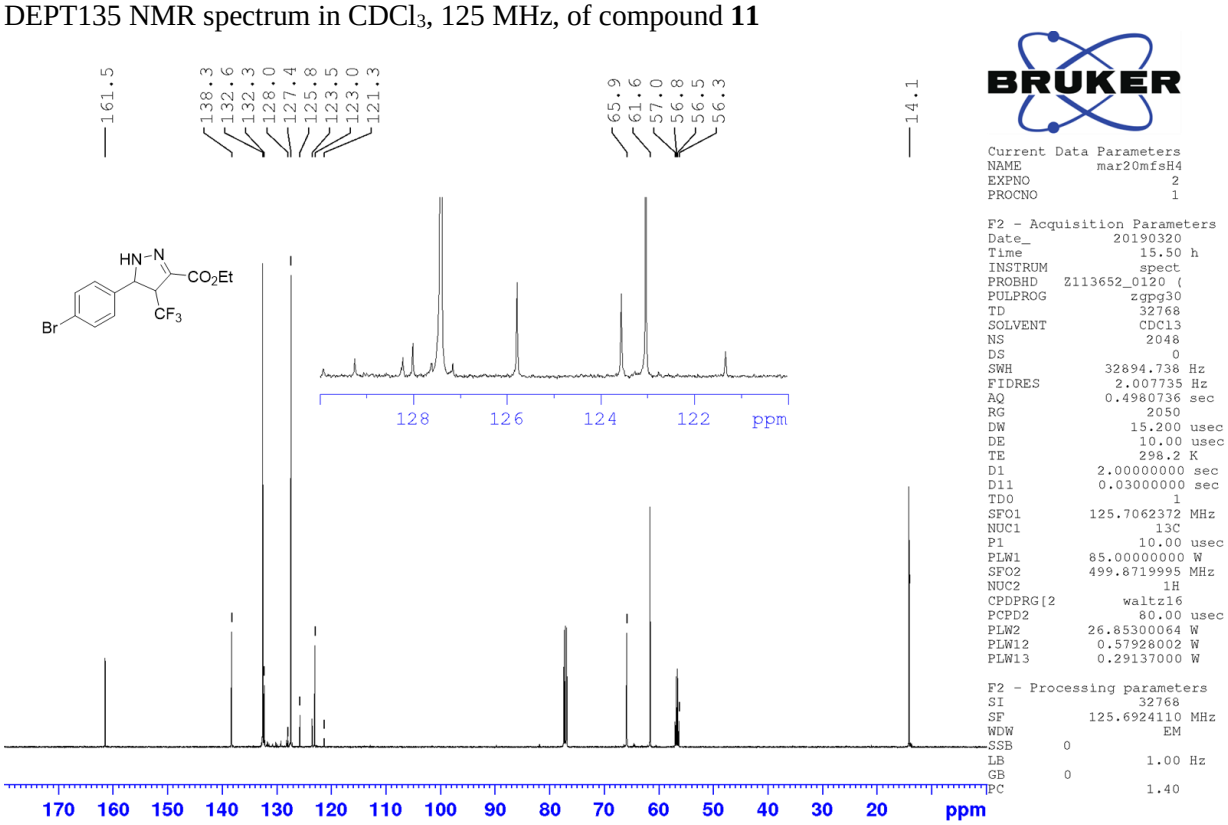
F2 - Acquisition Parameters
Date_           20190806
Time              18.16 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG           zgflqn
TD                131072
SOLVENT             CDCl3
NS                    16
DS                     4
SWH           56818.184 Hz
FIDRES         0.866977 Hz
AQ            1.1534336 sec
RG                 200.6
DW                8.800 usec
DE                6.50 usec
TE                298.1 K
D1           1.00000000 sec
TD0                    1
SFO1        235.3338140 MHz
NUC1                 19F
P1                15.00 usec
PLW1          6.80000019 W

F2 - Processing parameters
SI                 65536
SF          235.3573497 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{19}F NMR spectrum in $CDCl_3$, 235 MHz, of compound **11**

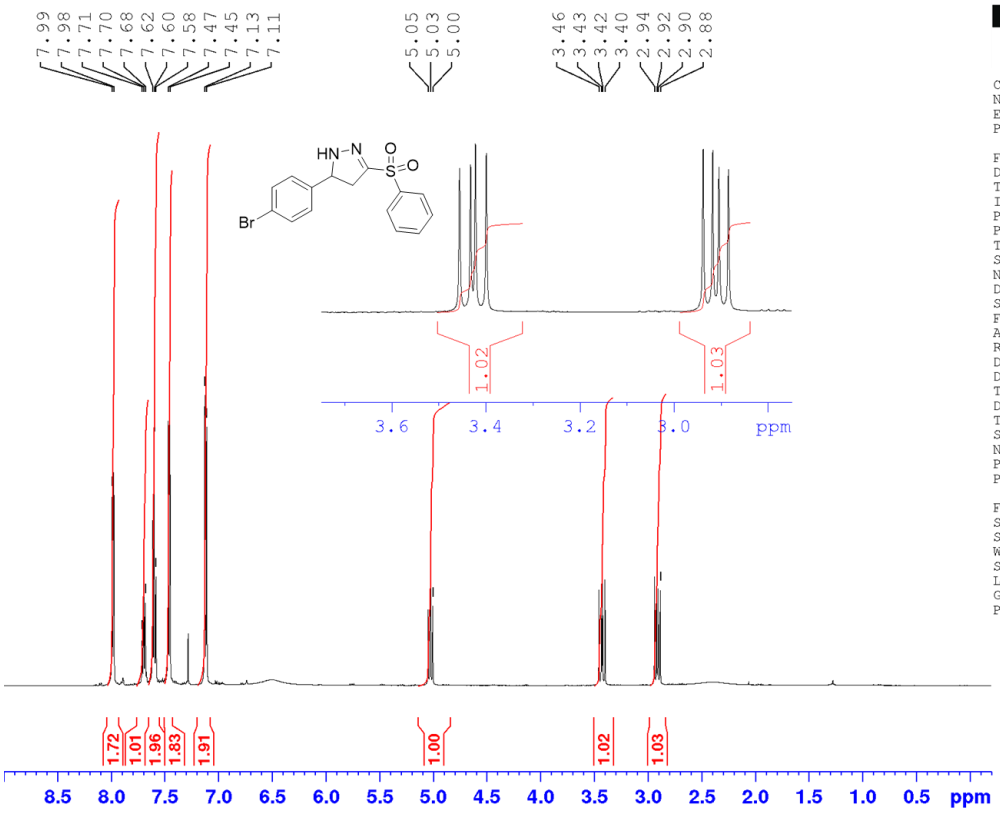


DEPT135 NMR spectrum in $CDCl_3$, 125 MHz, of compound **11**



^{13}C NMR spectrum in $CDCl_3$, 125 MHz, of compound **11**

5-(4-bromophenyl)-3-(phenylsulfonyl)-4,5-dihydro-1H-pyrazole

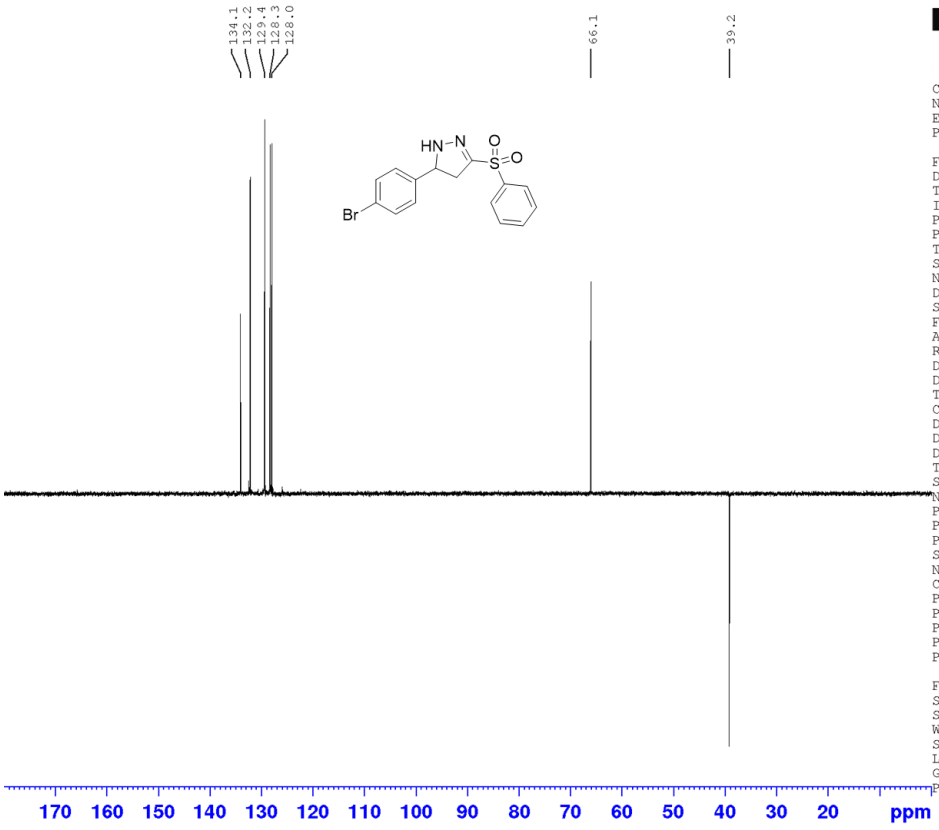



```
Current Data Parameters
NAME          mar20mfsH5
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190320
Time              16.07 h
INSTRUM            spect
PROBHD   Z113652_0120 (
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   16
DS                    0
SWH           10302.198 Hz
FIDRES         0.628796 Hz
AQ            1.5903403 sec
RG                  128
DW               48.533 usec
DE               10.00 usec
TE               298.2 K
D1            1.00000000 sec
TD0                   1
SFO1         499.8730869 MHz
NUC1                 1H
P1                11.75 usec
PLW1         27.00000000 W

F2 - Processing parameters
SI                65536
SF          499.8700000 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{1}H NMR spectrum in $CDCl_3$, 500 MHz, of compound **16**

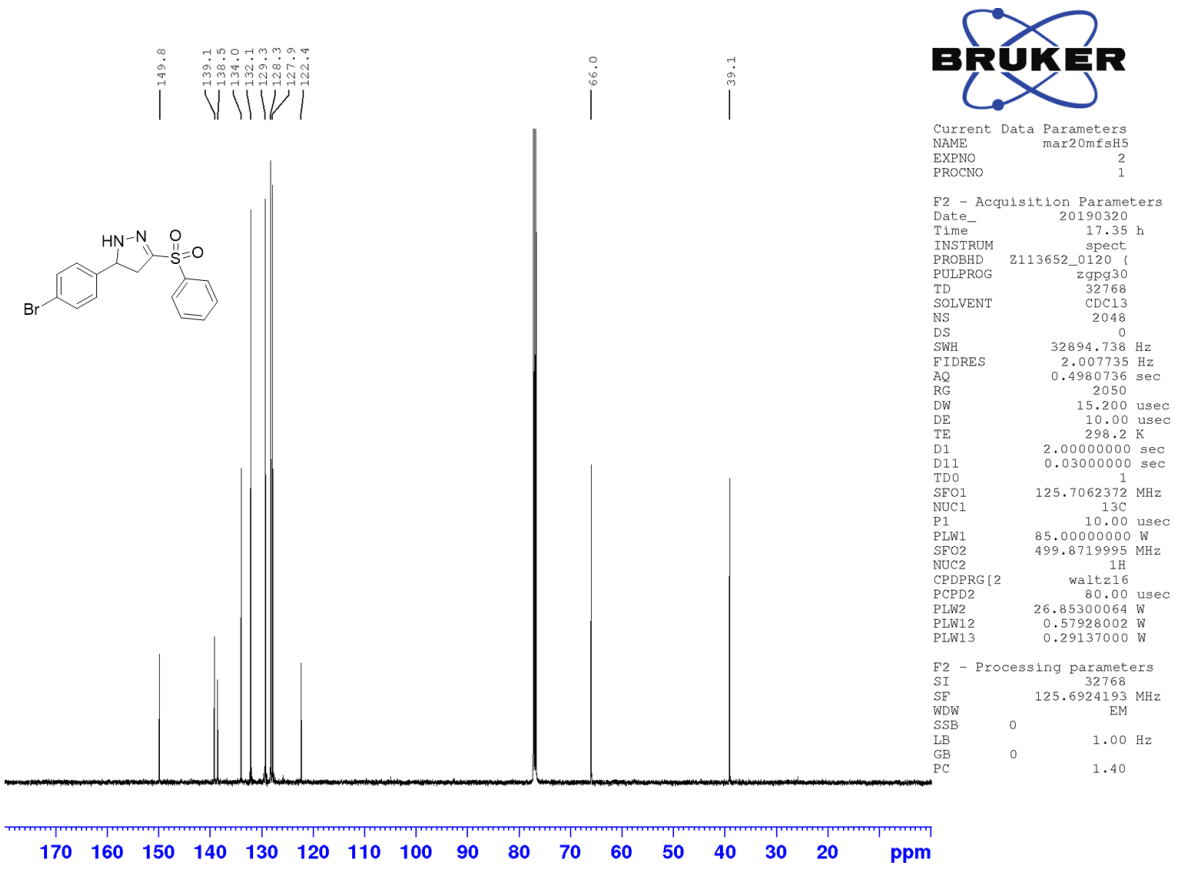



```
Current Data Parameters
NAME          mar20mfsH5
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190320
Time              17.57 h
INSTRUM            spect
PROBHD   Z113652_0120 (
PULPROG          dept135
TD                32768
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           32894.738 Hz
FIDRES         2.007735 Hz
AQ            0.4980736 sec
RG                 2050
DW               15.200 usec
DE               10.00 usec
TE               298.2 K
CNST2        145.0000000
D1            2.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                   1
SFO1         125.7062372 MHz
NUC1                 13C
P1                10.00 usec
P2                20.00 usec
PLW1         85.00000000 W
SFO2         499.8715986 MHz
NUC2                 1H
CPDPRG[2          waltz16
P3                11.75 usec
P4                23.50 usec
PCPD2             80.00 usec
PLW2         26.85300064 W
PLW12         0.57928002 W

F2 - Processing parameters
SI                32768
SF          125.6924110 MHz
WDW                  EM
SSB       0
LB             1.00 Hz
GB        0
PC                1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 125 MHz, of compound **16**



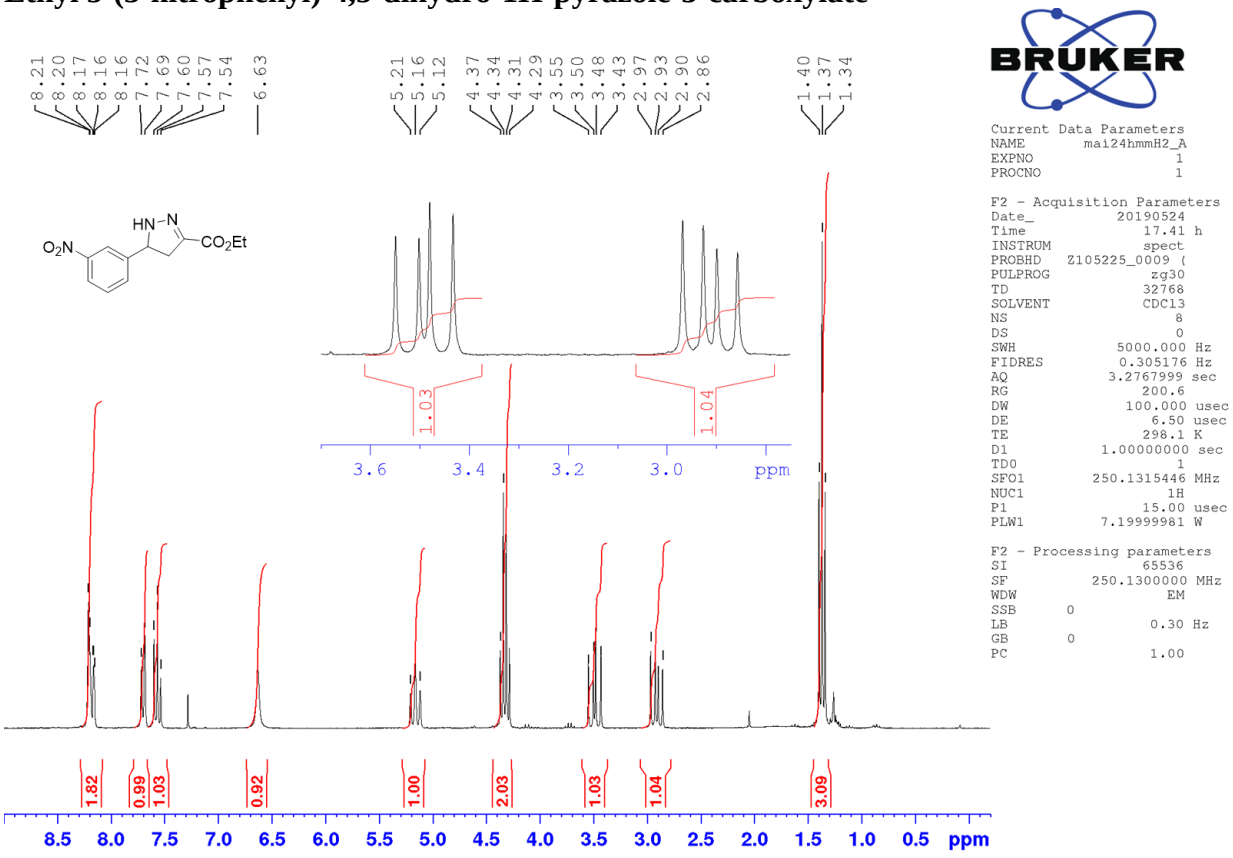
Current Data Parameters
NAME mar20mfsH5
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190320
Time 17.35 h
INSTRUM spect
PROBHD Z113652_0120 (
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 2048
DS 0
SWH 32894.738 Hz
FIDRES 2.007735 Hz
AQ 0.4980736 sec
RG 2050
DW 15.200 usec
DE 10.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 125.7062372 MHz
NUC1 13C
P1 10.00 usec
PLW1 85.00000000 W
SFO2 499.8719995 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 26.85300064 W
PLW12 0.57928002 W
PLW13 0.29137000 W

F2 - Processing parameters
SI 32768
SF 125.6924193 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR spectrum in $CDCl_3$, 125 MHz, of compound **16**

Ethyl 5-(3-nitrophenyl)-4,5-dihydro-1H-pyrazole-3-carboxylate

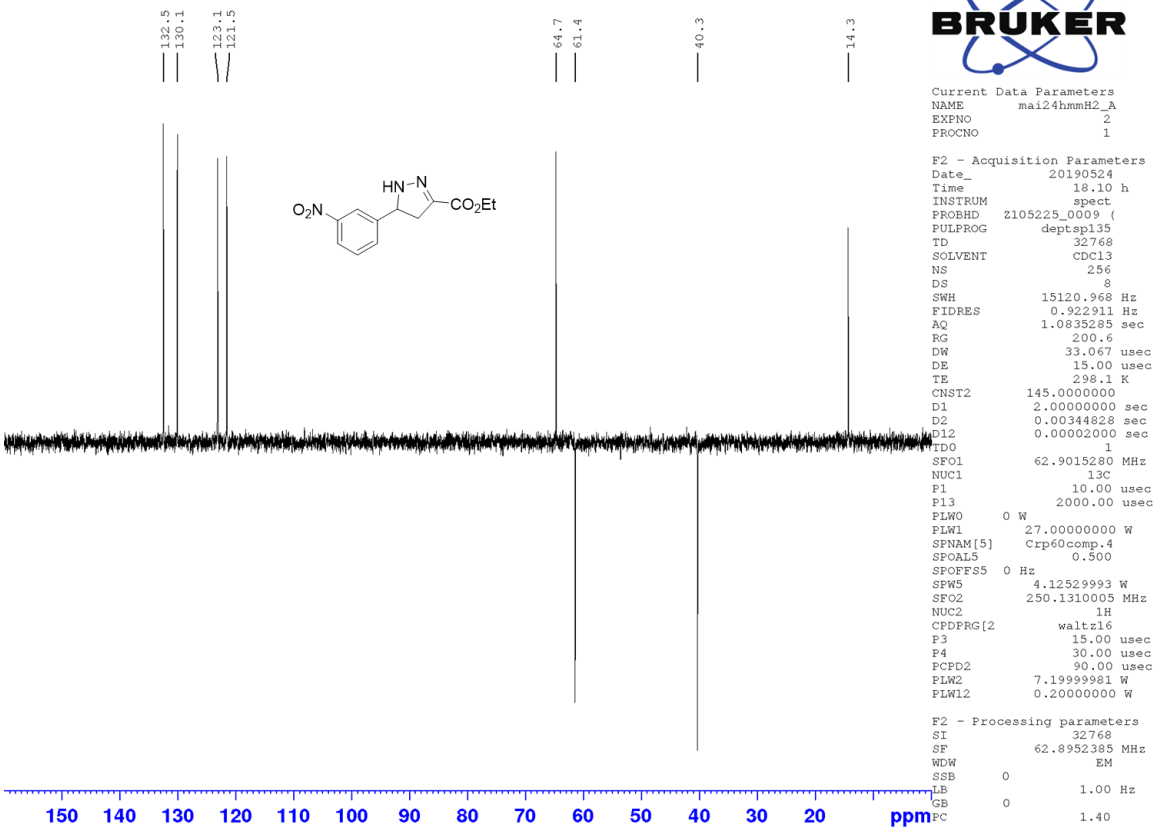



```
Current Data Parameters
NAME        mai24hmmH2_A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190524
Time               17.41 h
INSTRUM            spect
PROBHD    Z105225_0009 (
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             5000.000 Hz
FIDRES             0.305176 Hz
AQ              3.2767999 sec
RG                 200.6
DW                 100.000 usec
DE                   6.50 usec
TE                 298.1 K
D1              1.00000000 sec
TD0                    1
SFO1            250.1315446 MHz
NUC1                  1H
P1                  15.00 usec
PLW1            7.19999981 W

F2 - Processing parameters
SI                 65536
SF            250.1300000 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **2**

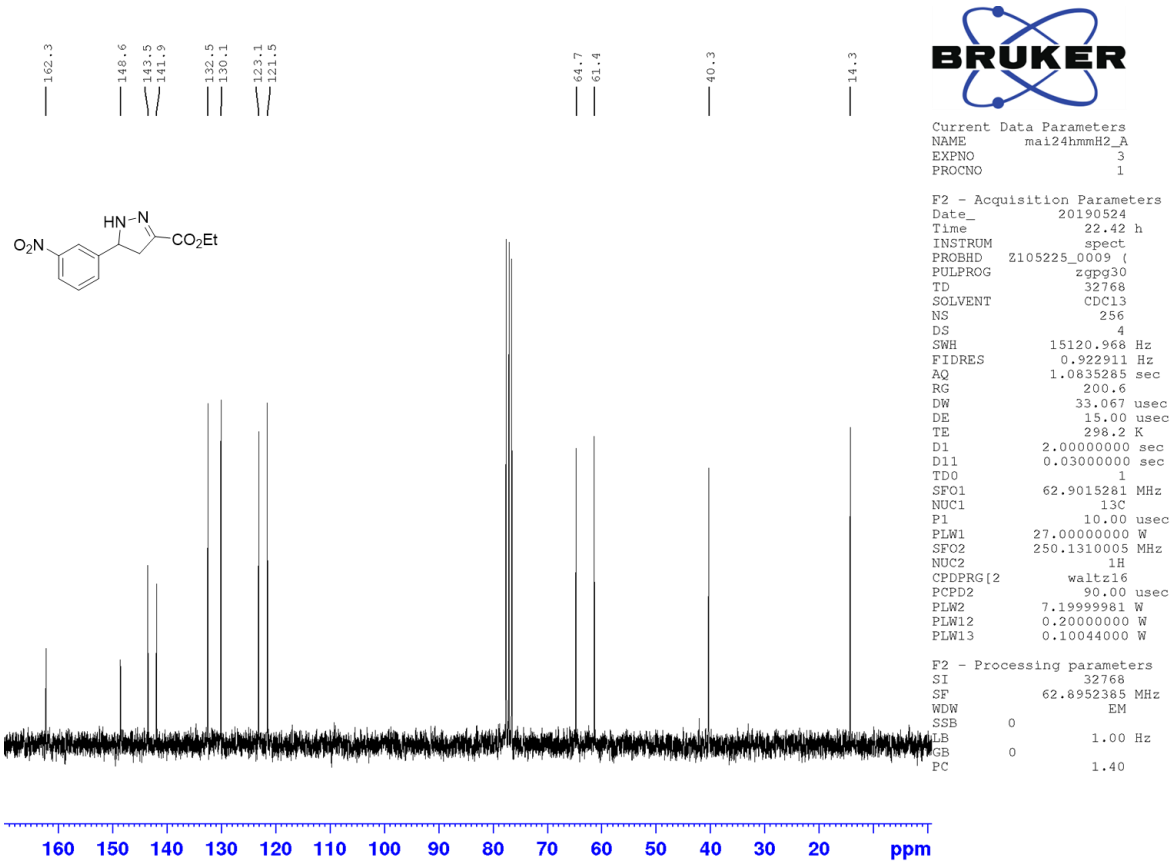



```
Current Data Parameters
NAME        mai24hmmH2_A
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190524
Time               18.10 h
INSTRUM            spect
PROBHD    Z105225_0009 (
PULPROG         deptsp135
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     8
SWH            15120.968 Hz
FIDRES             0.922911 Hz
AQ              1.0835285 sec
RG                 200.6
DW                 33.067 usec
DE                 15.00 usec
TE                 298.1 K
CNST2          145.0000000
D1              2.00000000 sec
D2              0.00344828 sec
D12             0.00002000 sec
TD0                    1
SFO1            62.9015280 MHz
NUC1                  13C
P1                  10.00 usec
P13               2000.00 usec
PLW0       0 W
PLW1        27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5            4.12529993 W
SFO2            250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
P3                  15.00 usec
P4                  30.00 usec
PCPD2               90.00 usec
PLW2            7.19999981 W
PLW12           0.20000000 W

F2 - Processing parameters
SI                 32768
SF              62.8952385 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **2**



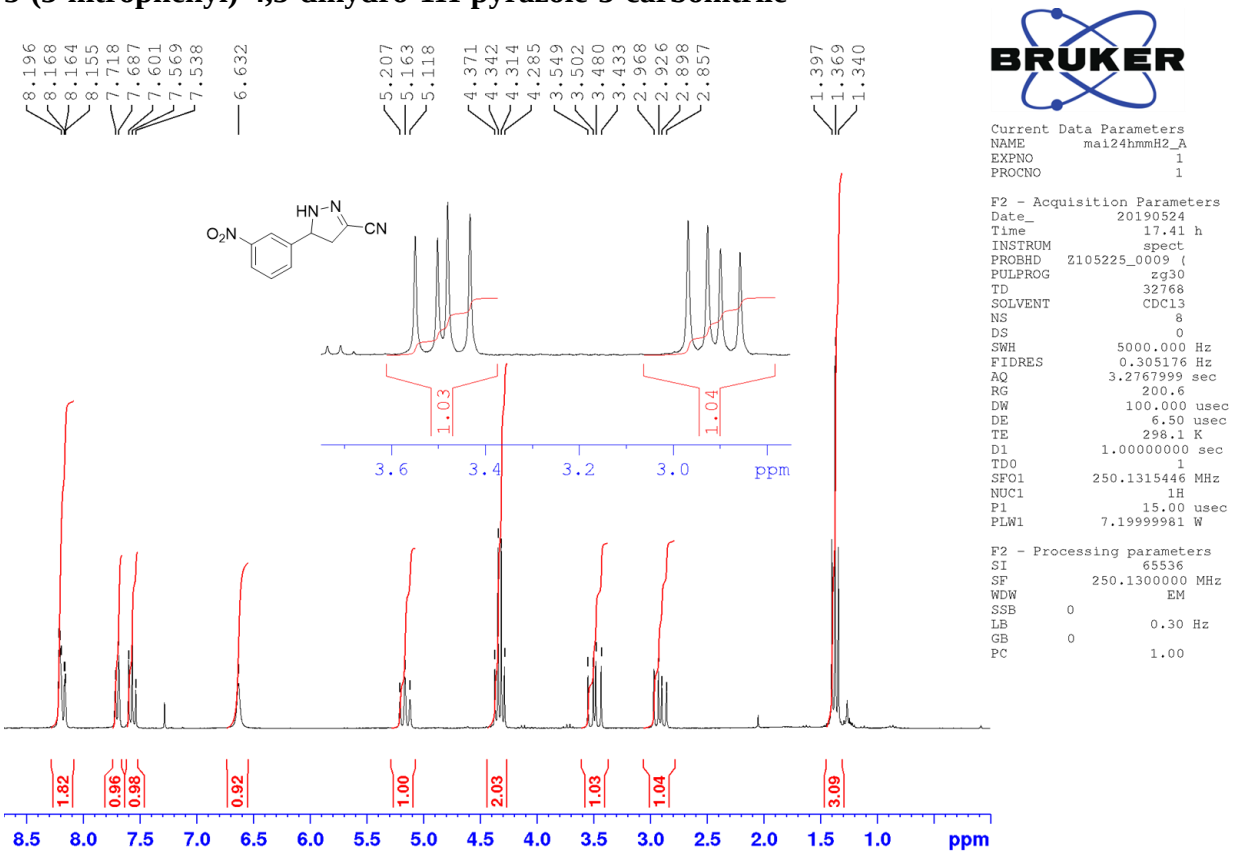

```
Current Data Parameters
NAME        mai24hmmH2_A
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190524
Time               22.42 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           15120.968 Hz
FIDRES         0.922911 Hz
AQ             1.0835285 sec
RG                200.6
DW               33.067 usec
DE               15.00 usec
TE               298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                   1
SFO1          62.9015281 MHz
NUC1                 13C
P1                10.00 usec
PLW1         27.00000000 W
SFO2         250.1310005 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2          7.19999981 W
PLW12         0.20000000 W
PLW13         0.10044000 W

F2 - Processing parameters
SI                32768
SF           62.8952385 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **2**

5-(3-nitrophenyl)-4,5-dihydro-1H-pyrazole-3-carbonitrile

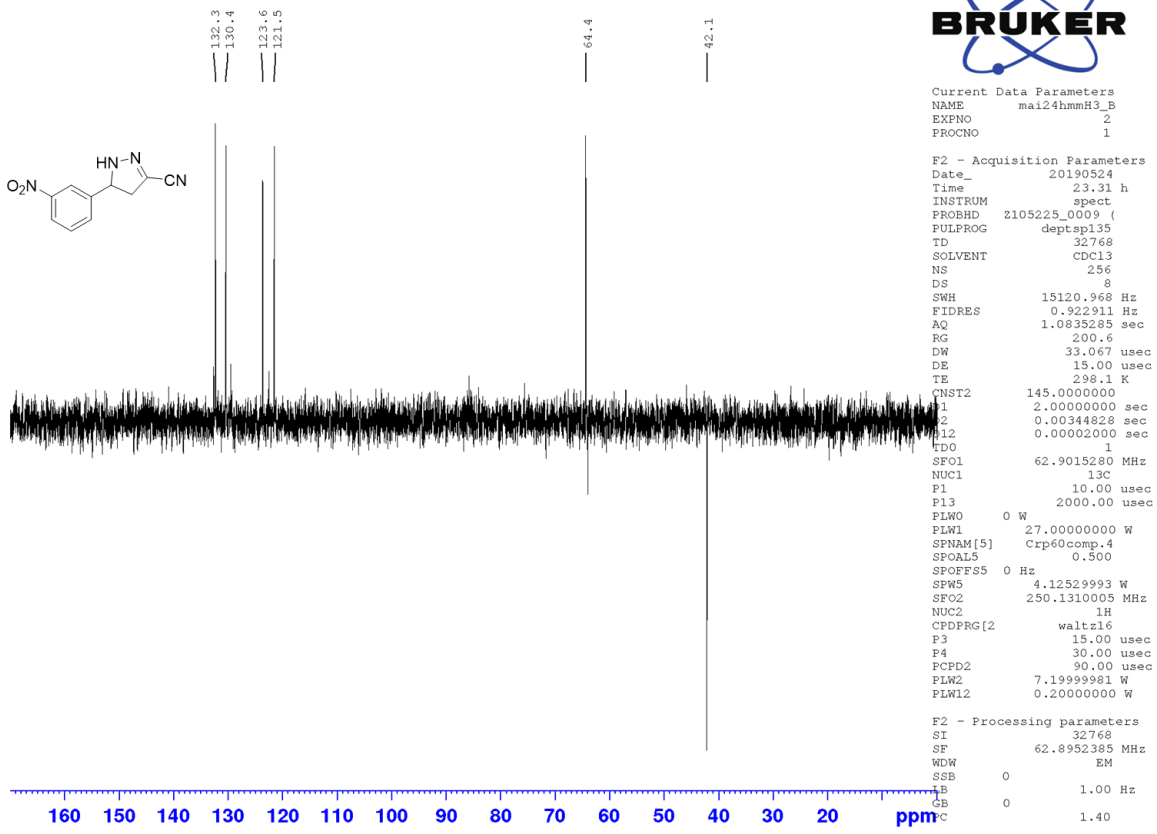



```
Current Data Parameters
NAME        mai24hmmH2_A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190524
Time               17.41 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             5000.000 Hz
FIDRES             0.305176 Hz
AQ              3.2767999 sec
RG                 200.6
DW                 100.000 usec
DE                   6.50 usec
TE                 298.1 K
D1              1.00000000 sec
TD0                    1
SFO1           250.1315446 MHz
NUC1                  1H
P1                  15.00 usec
PLW1           7.19999981 W

F2 - Processing parameters
SI                 65536
SF            250.1300000 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **7**

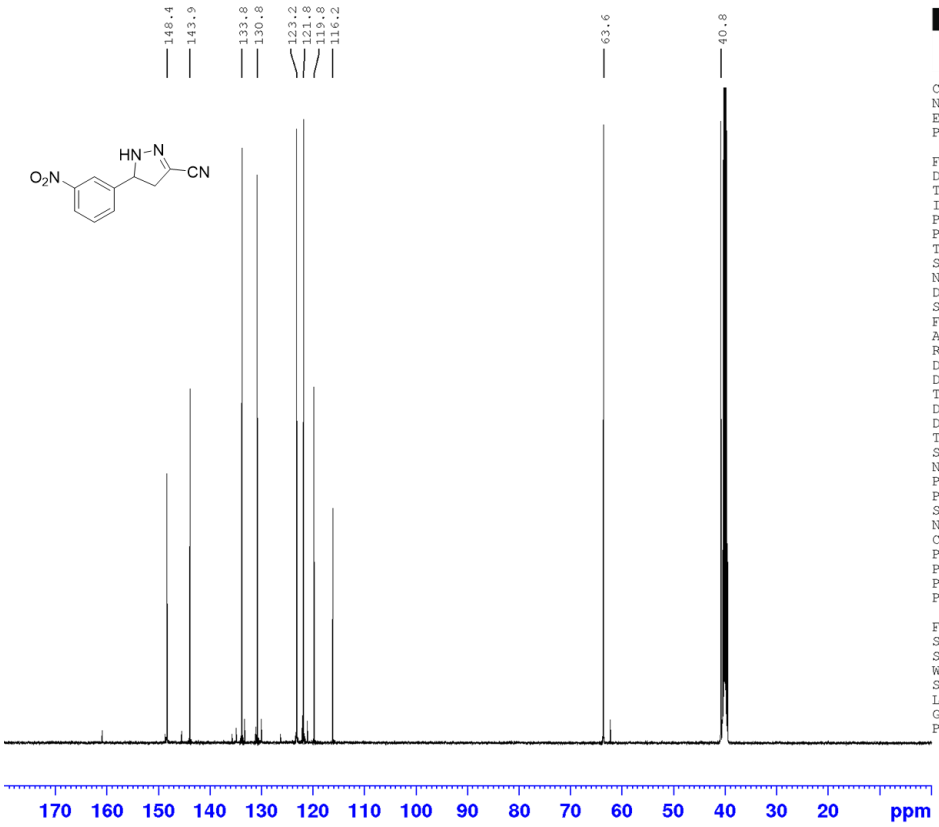



```
Current Data Parameters
NAME        mai24hmmH3_B
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190524
Time               23.31 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG         deptsp135
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     8
SWH            15120.968 Hz
FIDRES             0.922911 Hz
AQ              1.0835285 sec
RG                 200.6
DW                 33.067 usec
DE                 15.00 usec
TE                 298.1 K
CNST2          145.0000000
P1              2.00000000 sec
P2              0.00344828 sec
P12             0.00002000 sec
TD0                    1
SFO1           62.9015280 MHz
NUC1                  13C
P1                 10.00 usec
P13              2000.00 usec
PLW0       0 W
PLW1        27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5            4.12529993 W
SFO2           250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
P3                 15.00 usec
P4                 30.00 usec
PCPD2              90.00 usec
PLW2            7.19999981 W
PLW12           0.20000000 W

F2 - Processing parameters
SI                 32768
SF             62.8952385 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **7**

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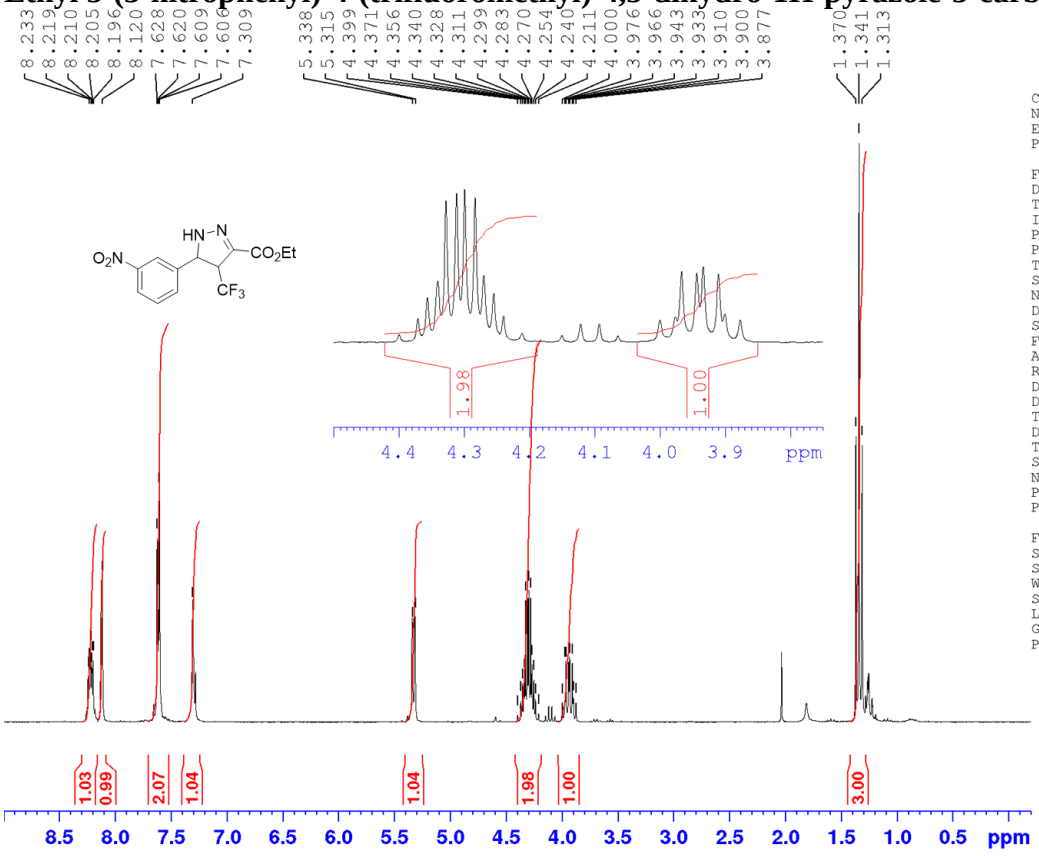
Current Data Parameters
NAME          ago07hmmH1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190808
Time               2.54 h
INSTRUM            spect
PROBHD   Z113652_0120 (
PULPROG          zgpg30
TD                32768
SOLVENT            DMSO
NS                 4200
DS                    0
SWH           32894.738 Hz
FIDRES         2.007735 Hz
AQ            0.4980736 sec
RG                 2050
DW               15.200 usec
DE               10.00 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        125.7062372 MHz
NUC1                13C
P1                10.00 usec
PLW1        85.00000000 W
SFO2        499.8719995 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2             80.00 usec
PLW2        26.85300064 W
PLW12        0.57928002 W
PLW13        0.29137000 W

F2 - Processing parameters
SI                32768
SF          125.6924110 MHz
WDW                 EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

^{13}C NMR spectrum in DMSO-d_6, 125 MHz, of compound **7**

Ethyl 5-(3-nitrophenyl)-4-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-3-carboxylate

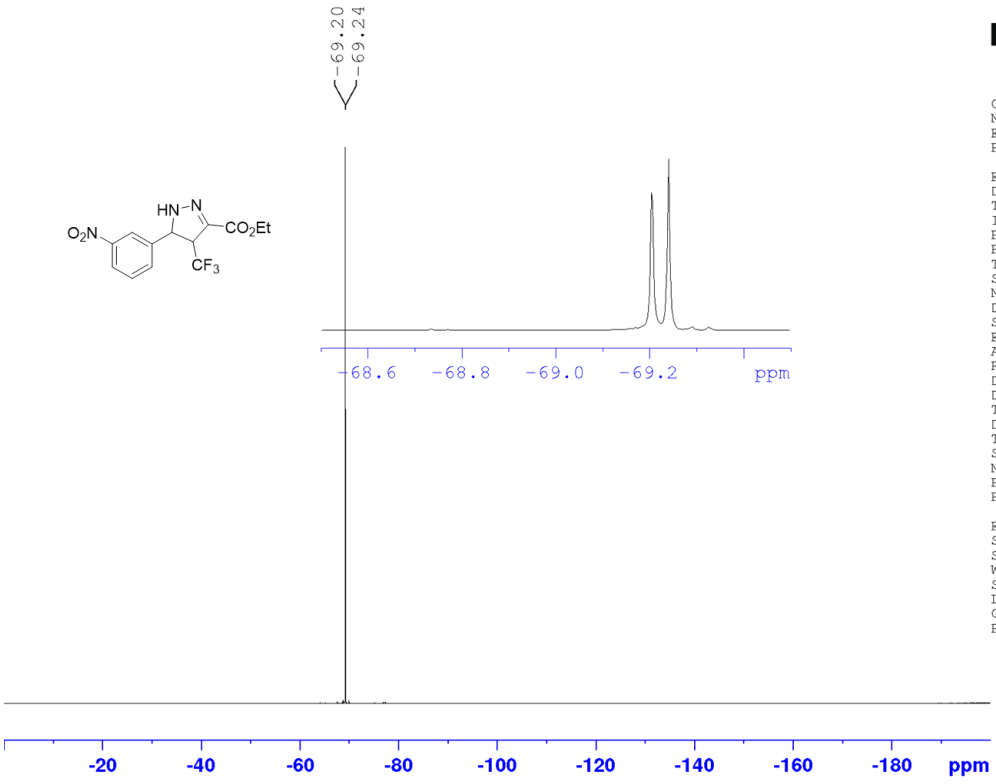



```
Current Data Parameters
NAME         mai24hmmH1_D
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20190524
Time               17.36 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             5000.000 Hz
FIDRES             0.305176 Hz
AQ              3.2767999 sec
RG                 200.6
DW                 100.000 usec
DE                   6.50 usec
TE                 298.2 K
D1              1.00000000 sec
TD0                    1
SFO1           250.1315446 MHz
NUC1                  1H
P1                 15.00 usec
PLW1            7.19999981 W

F2 - Processing parameters
SI                 65536
SF            250.1300000 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **12**

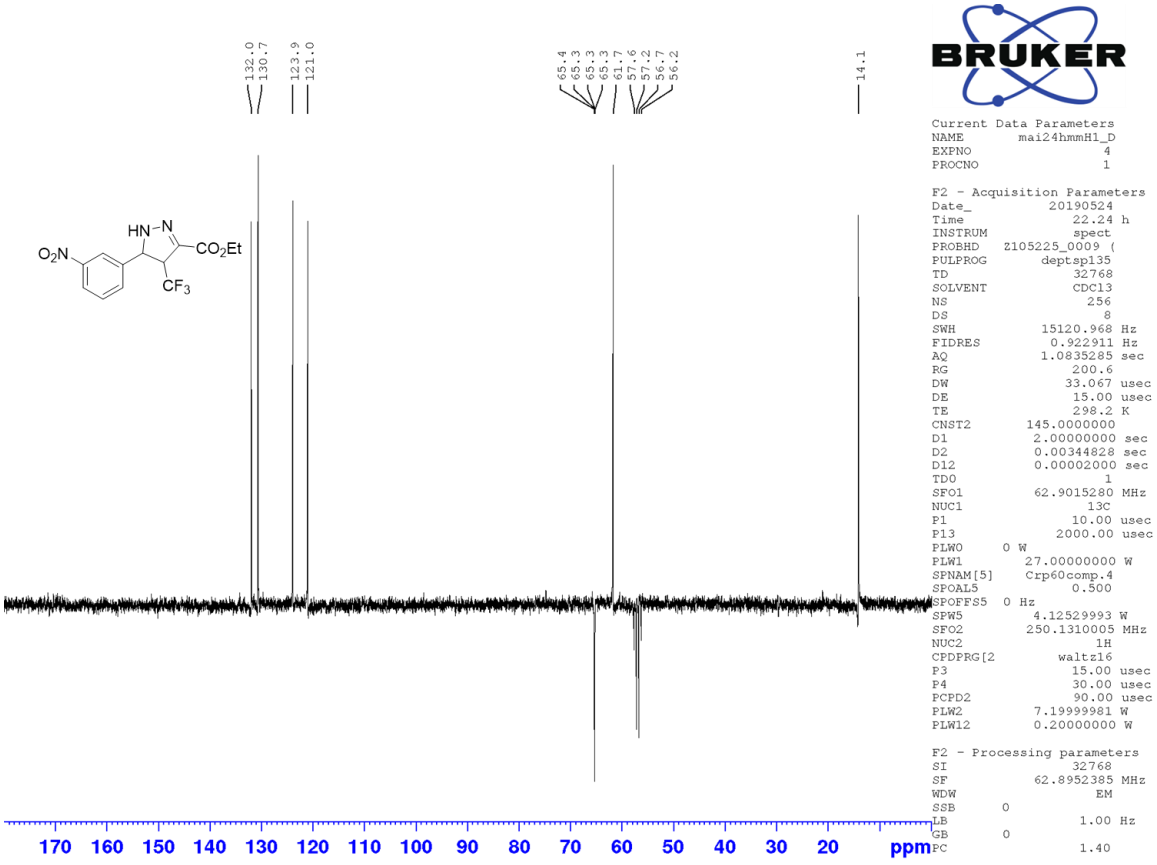



```
Current Data Parameters
NAME         mai24hmmH1_D
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_           20190524
Time               17.38 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG          zgflqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            56818.184 Hz
FIDRES             0.866977 Hz
AQ              1.1534336 sec
RG                 200.6
DW                   8.800 usec
DE                   6.50 usec
TE                 298.1 K
D1              1.00000000 sec
TD0                    1
SFO1           235.3338140 MHz
NUC1                  19F
P1                 15.00 usec
PLW1            6.80000019 W

F2 - Processing parameters
SI                 65536
SF            235.3573497 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

^{19}F NMR spectrum in $CDCl_3$, 235 MHz, of compound **12**

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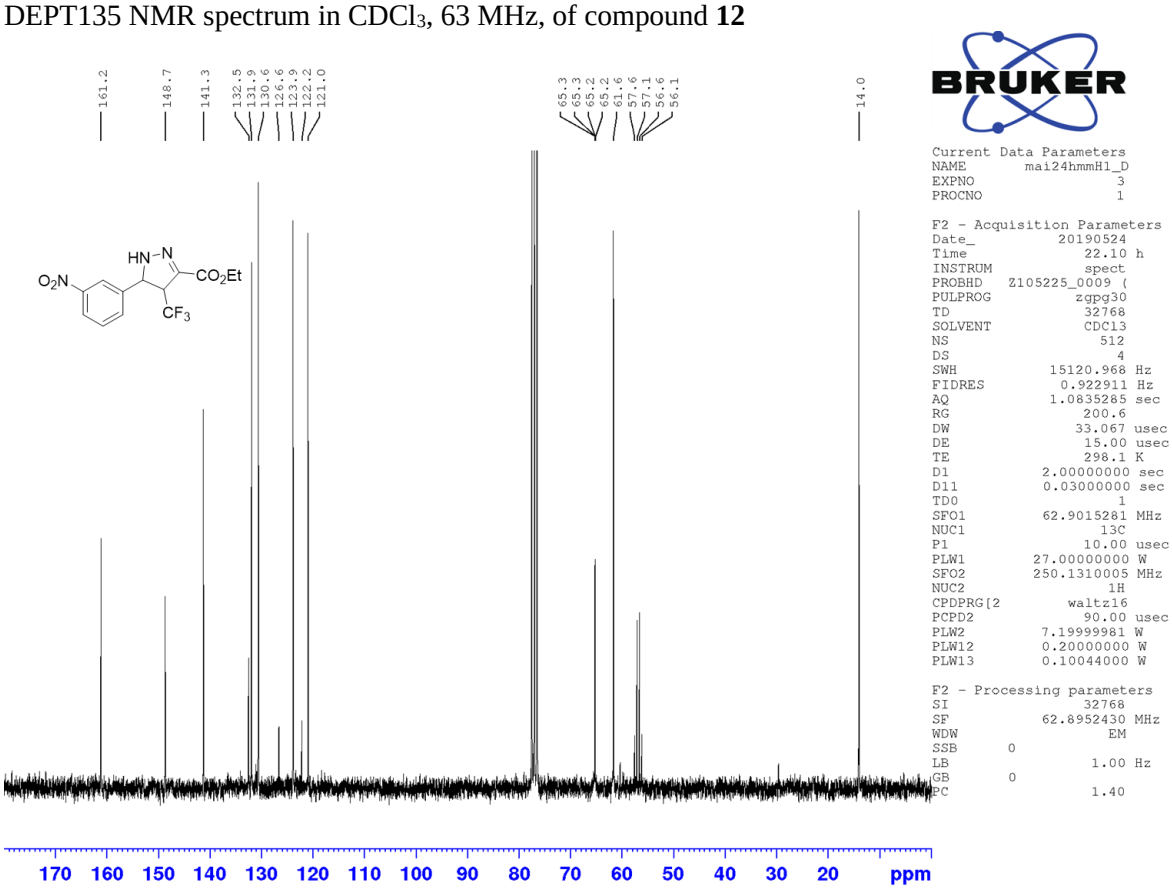
Current Data Parameters
NAME        mai24hmmH1_D
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190524
Time              22.24 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG         deptsp135
TD                 32768
SOLVENT             CDCl3
NS                    256
DS                      8
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.2 K
CNST2        145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1
SFO1           62.9015280 MHz
NUC1                  13C
P1                 10.00 usec
P13              2000.00 usec
PLW0      0 W
PLW1       27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5   0 Hz
SPW5         4.12529993 W
SFO2         250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
P3                 15.00 usec
P4                 30.00 usec
PCPD2              90.00 usec
PLW2           7.19999981 W
PLW12          0.20000000 W

F2 - Processing parameters
SI                 32768
SF            62.8952385 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **12**



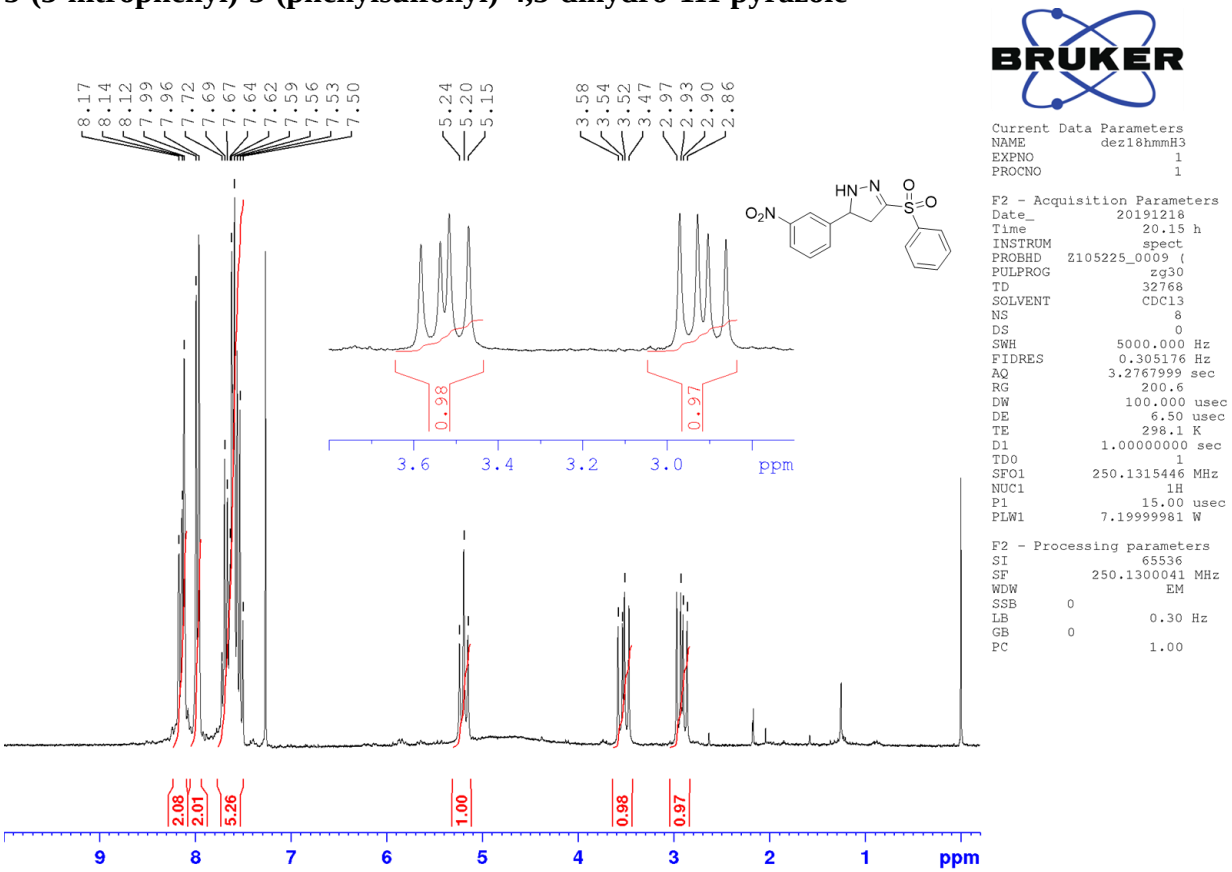

```
Current Data Parameters
NAME        mai24hmmH1_D
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190524
Time              22.10 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG          zgpg30
TD                 32768
SOLVENT             CDCl3
NS                    512
DS                      4
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1           62.9015281 MHz
NUC1                  13C
P1                 10.00 usec
PLW1        27.00000000 W
SFO2         250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2           7.19999981 W
PLW12          0.20000000 W
PLW13          0.10044000 W

F2 - Processing parameters
SI                 32768
SF            62.8952430 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
```

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **12**

5-(3-nitrophenyl)-3-(phenylsulfonyl)-4,5-dihydro-1H-pyrazole

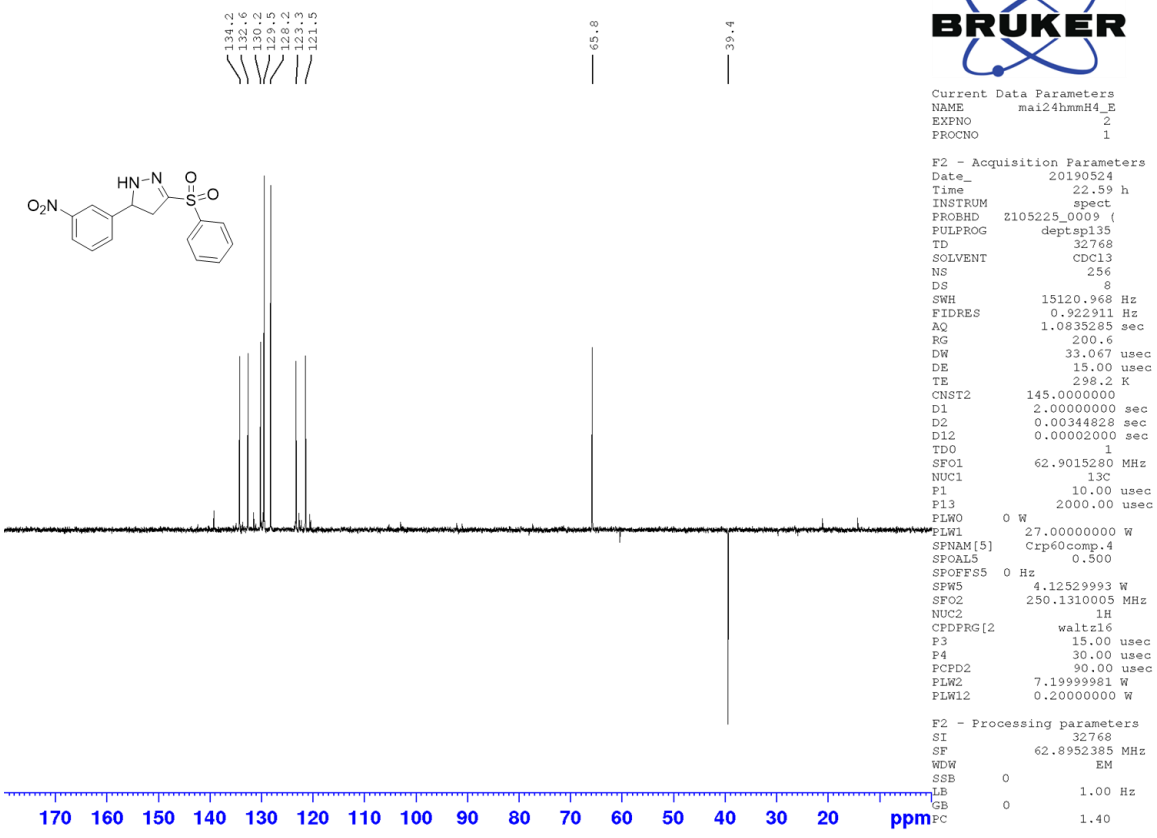


Current Data Parameters
NAME dez18hmmH3
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191218
Time 20.15 h
INSTRUM spect
PROBHD Z105225_0009 (
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 5000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 200.6
DW 100.000 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
SFO1 250.1315446 MHz
NUC1 1H
P1 15.00 usec
PLW1 7.19999981 W

F2 - Processing parameters
SI 65536
SF 250.1300041 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **17**

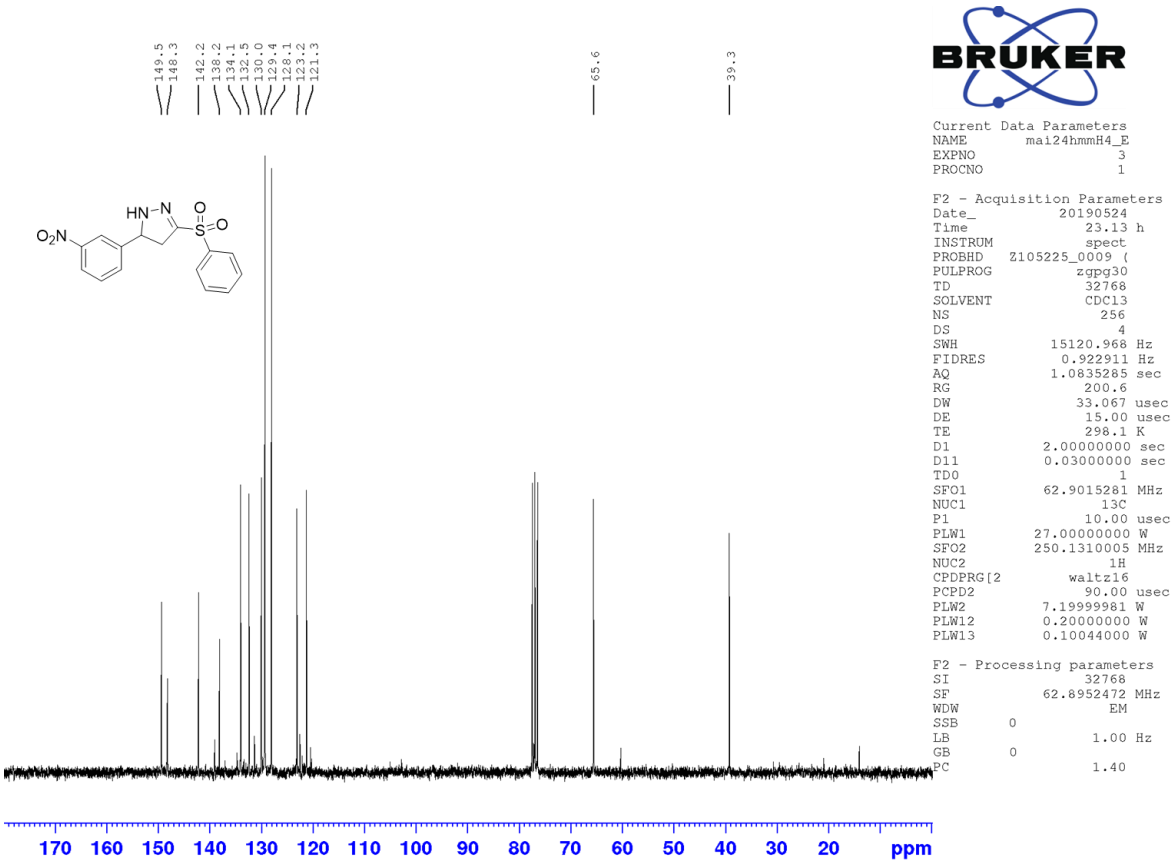


Current Data Parameters
NAME mai24hmmH4_E
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190524
Time 22.59 h
INSTRUM spect
PROBHD Z105225_0009 (
PULPROG deptsp135
TD 32768
SOLVENT CDCl3
NS 256
DS 8
SWH 15120.968 Hz
FIDRES 0.922911 Hz
AQ 1.0835285 sec
RG 200.6
DW 33.067 usec
DE 15.00 usec
TE 298.2 K
CNST2 145.0000000
D1 2.00000000 sec
D2 0.00344828 sec
D12 0.00002000 sec
TD0 1
SFO1 62.9015280 MHz
NUC1 13C
P1 10.00 usec
P13 2000.00 usec
PLW0 0 W
PLW1 27.00000000 W
SPNAM[5] Crp60comp.4
SPOAL5 0.500
SPOFFS5 0 Hz
SPW5 4.12529993 W
SFO2 250.1310005 MHz
NUC2 1H
CPDPRG[2 waltz16
P3 15.00 usec
P4 30.00 usec
PCPD2 90.00 usec
PLW2 7.19999981 W
PLW12 0.20000000 W

F2 - Processing parameters
SI 32768
SF 62.8952385 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **17**



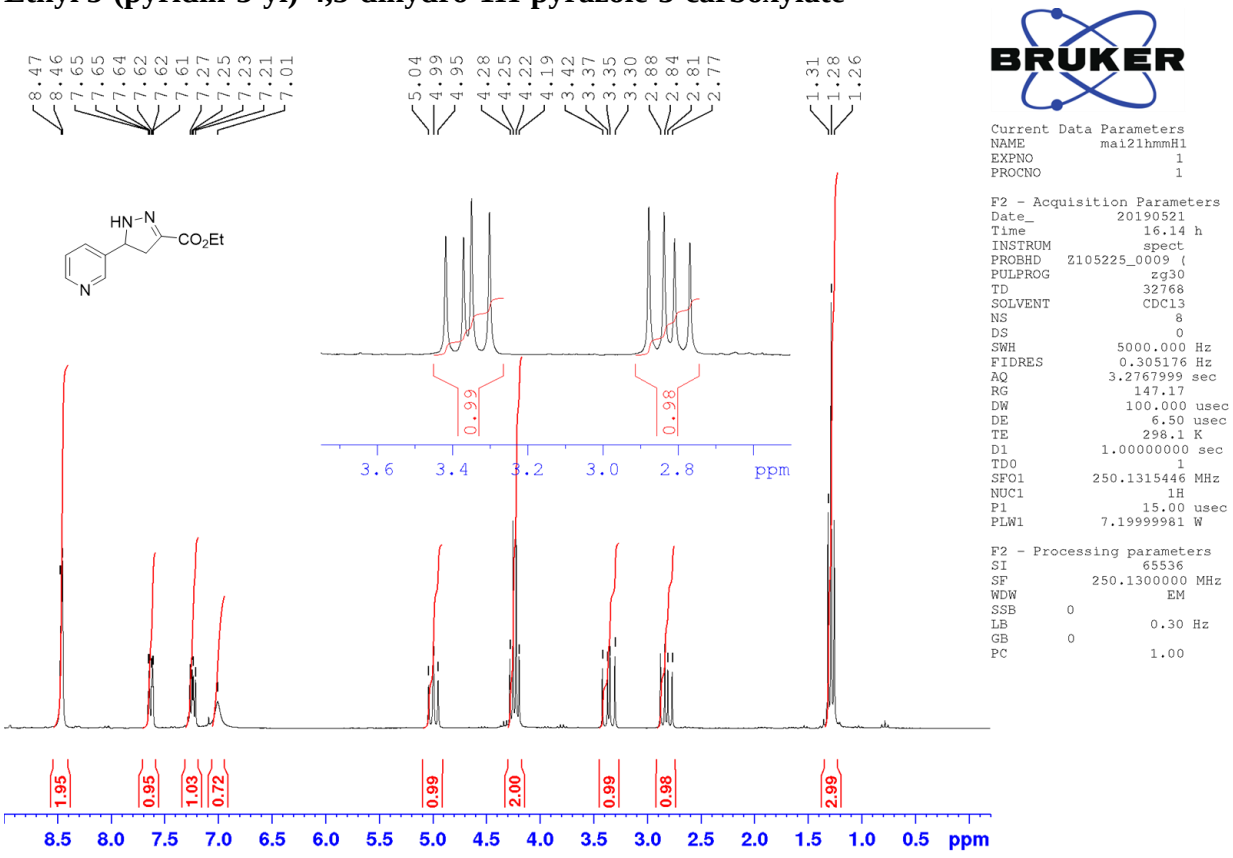

```
Current Data Parameters
NAME        mai24hmmH4_E
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190524
Time              23.13 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           15120.968 Hz
FIDRES         0.922911 Hz
AQ             1.0835285 sec
RG                200.6
DW               33.067 usec
DE                15.00 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1         62.9015281 MHz
NUC1                13C
P1                10.00 usec
PLW1        27.00000000 W
SFO2        250.1310005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         7.19999981 W
PLW12        0.20000000 W
PLW13        0.10044000 W

F2 - Processing parameters
SI                32768
SF           62.8952472 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **17**

Ethyl 5-(pyridin-3-yl)-4,5-dihydro-1H-pyrazole-3-carboxylate

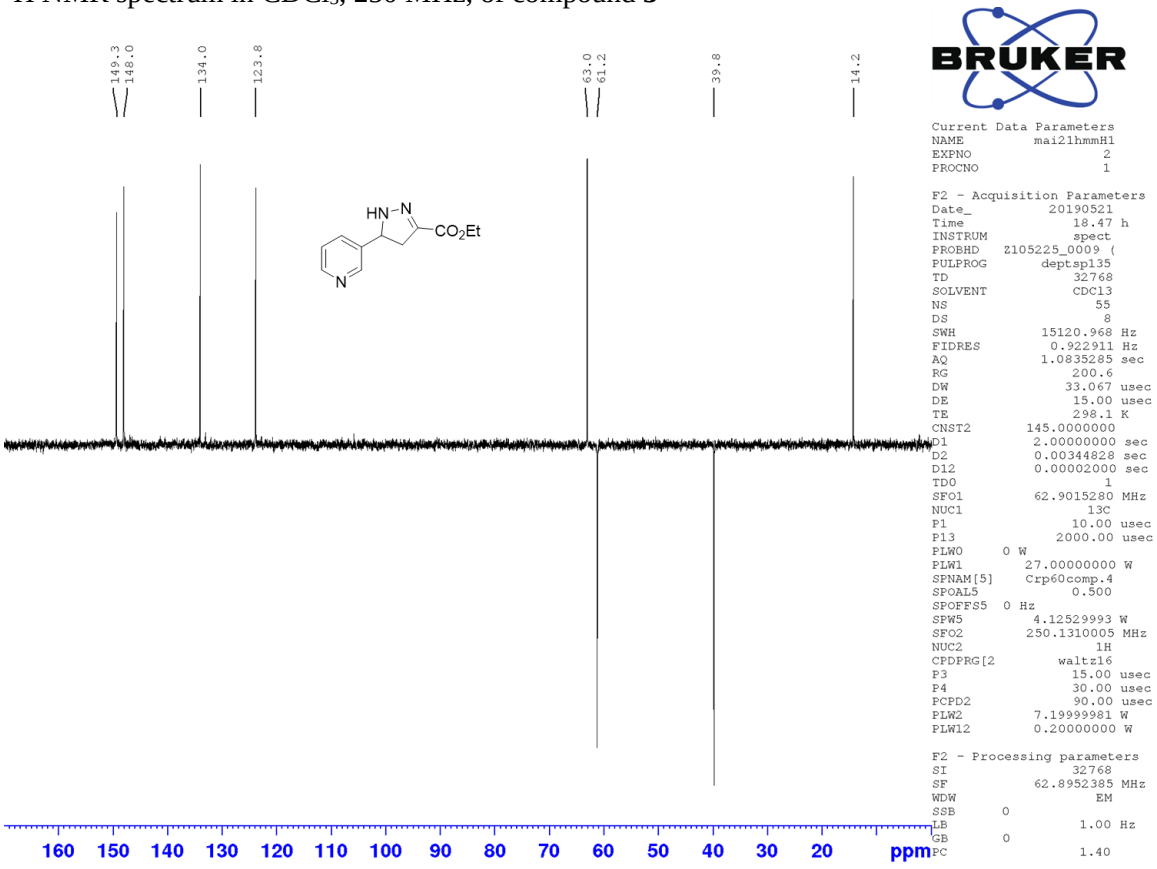



```
Current Data Parameters
NAME          mai21hmmH1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190521
Time              16.14 h
INSTRUM           spect
PROBHD   Z105225_0009 (
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                   8
DS                   0
SWH           5000.000 Hz
FIDRES        0.305176 Hz
AQ           3.2767999 sec
RG              147.17
DW            100.000 usec
DE              6.50 usec
TE              298.1 K
D1          1.00000000 sec
TD0                  1
SFO1        250.1315446 MHz
NUC1                 1H
P1              15.00 usec
PLW1         7.19999981 W

F2 - Processing parameters
SI                65536
SF          250.1300000 MHz
WDW                  EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **3**

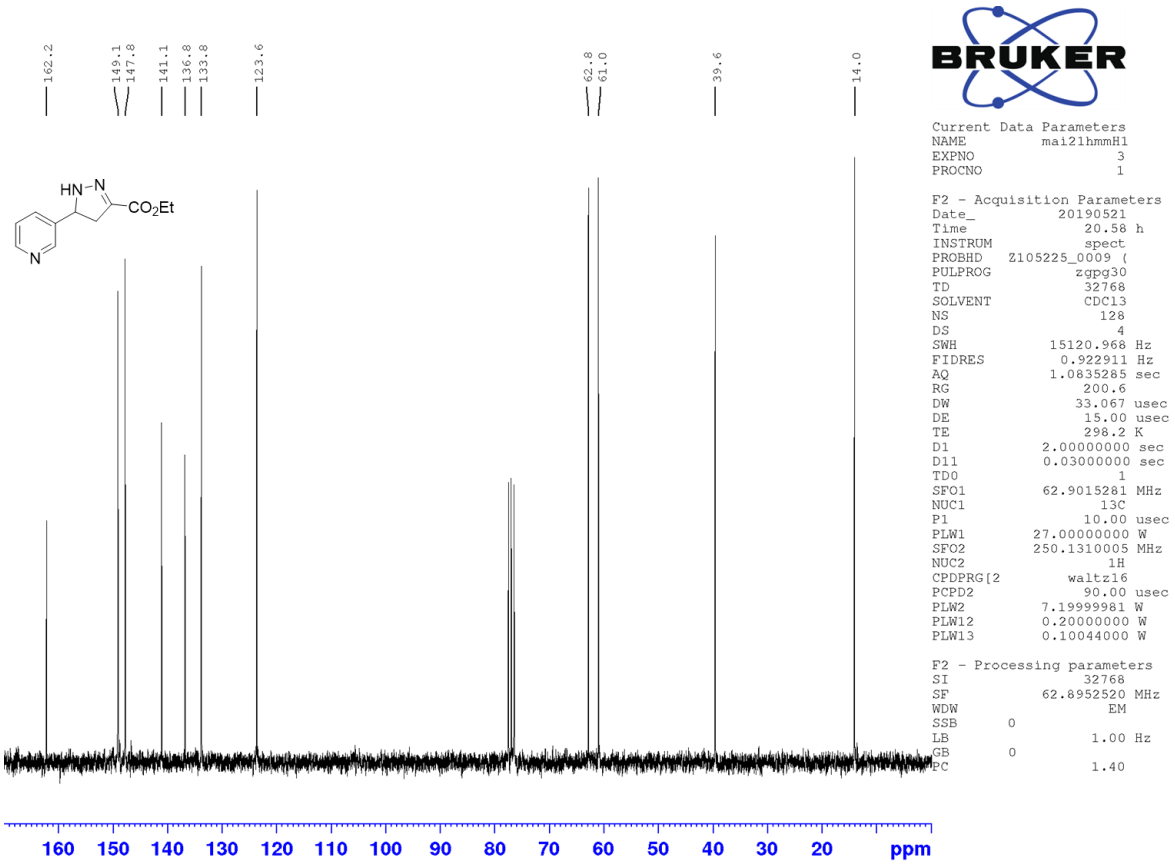



```
Current Data Parameters
NAME          mai21hmmH1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190521
Time              18.47 h
INSTRUM           spect
PROBHD   Z105225_0009 (
PULPROG       deptsp135
TD               32768
SOLVENT          CDCl3
NS                  55
DS                   8
SWH          15120.968 Hz
FIDRES        0.922911 Hz
AQ           1.0835285 sec
RG                200.6
DW             33.067 usec
DE              15.00 usec
TE              298.1 K
CNST2       145.0000000
D1          2.00000000 sec
D2          0.00344828 sec
D12         0.00002000 sec
TD0                  1
SFO1        62.9015280 MHz
NUC1                13C
P1              10.00 usec
P13           2000.00 usec
PLW0      0 W
PLW1     27.00000000 W
SPNAM[5]    Crp60comp.4
SPOAL5            0.500
SPOFFS5   0 Hz
SPW5         4.12529993 W
SFO2        250.1310005 MHz
NUC2                 1H
CPDPRG[2         waltz16
P3              15.00 usec
P4              30.00 usec
PCPD2           90.00 usec
PLW2         7.19999981 W
PLW12        0.20000000 W

F2 - Processing parameters
SI                32768
SF          62.8952385 MHz
WDW                  EM
SSB       0
LB              1.00 Hz
GB        0
PC              1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **3**



BRUKER

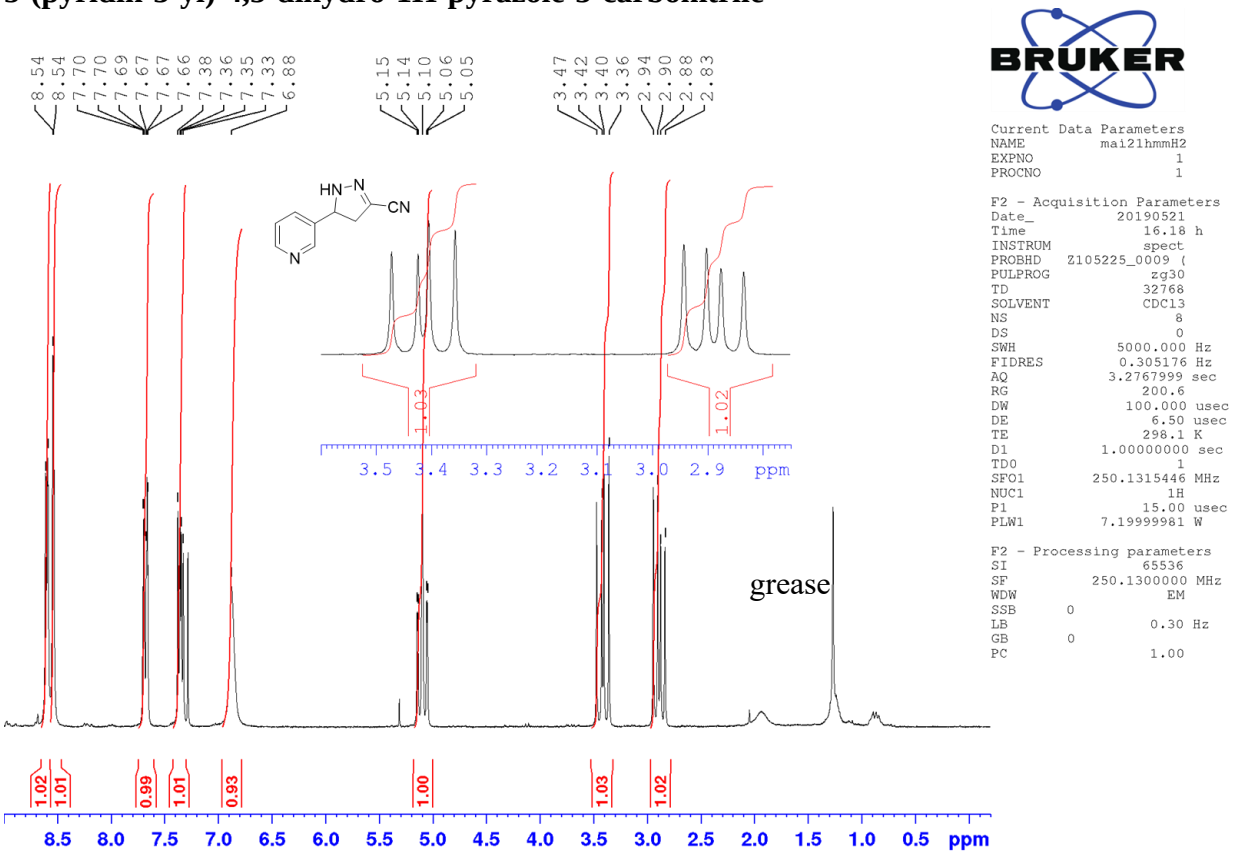
Current Data Parameters
NAME mai21hmmH1
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190521
Time 20.58 h
INSTRUM spect
PROBHD Z105225_0009 (
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 128
DS 4
SWH 15120.968 Hz
FIDRES 0.922911 Hz
AQ 1.0835285 sec
RG 200.6
DW 33.067 usec
DE 15.00 usec
TE 298.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
SFO1 62.9015281 MHz
NUC1 13C
P1 10.00 usec
PLW1 27.00000000 W
SFO2 250.1310005 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 90.00 usec
PLW2 7.19999981 W
PLW12 0.20000000 W
PLW13 0.10044000 W

F2 - Processing parameters
SI 32768
SF 62.8952520 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **3**

5-(pyridin-3-yl)-4,5-dihydro-1H-pyrazole-3-carbonitrile



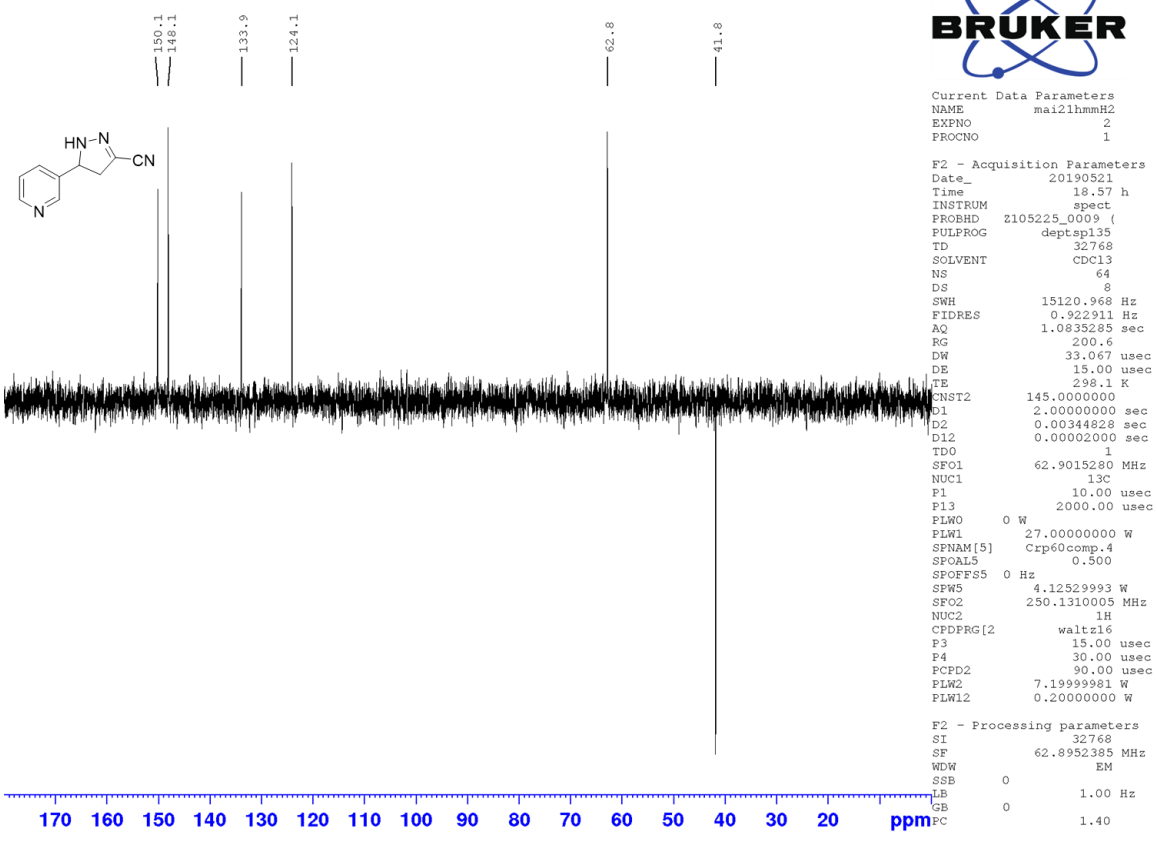
BRUKER

```
Current Data Parameters
NAME          mai21hmmH2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190521
Time              16.18 h
INSTRUM           spect
PROBHD   Z105225_0009 (
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                    8
DS                    0
SWH            5000.000 Hz
FIDRES         0.305176 Hz
AQ            3.2767999 sec
RG                200.6
DW              100.000 usec
DE                6.50 usec
TE                298.1 K
D1            1.00000000 sec
TD0                   1
SFO1          250.1315446 MHz
NUC1                 1H
P1                15.00 usec
PLW1           7.19999981 W

F2 - Processing parameters
SI                65536
SF           250.1300000 MHz
WDW                  EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **8**



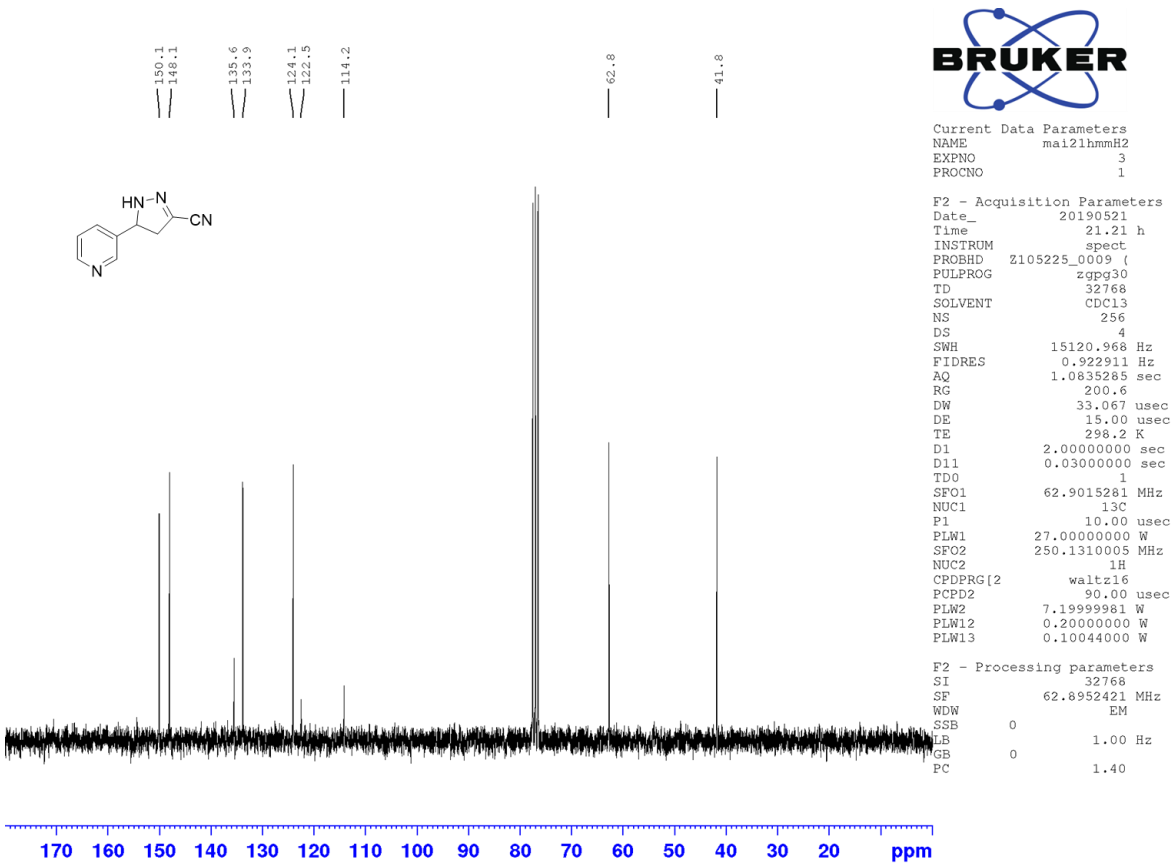
BRUKER

```
Current Data Parameters
NAME          mai21hmmH2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190521
Time              18.57 h
INSTRUM           spect
PROBHD   Z105225_0009 (
PULPROG        deptsp135
TD                32768
SOLVENT           CDCl3
NS                   64
DS                    8
SWH           15120.968 Hz
FIDRES         0.922911 Hz
AQ            1.0835285 sec
RG                200.6
DW              33.067 usec
DE                15.00 usec
TE                298.1 K
CNST2        145.0000000
D1            2.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                   1
SFO1          62.9015280 MHz
NUC1                 13C
P1                10.00 usec
P13             2000.00 usec
PLW0      0 W
PLW1     27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5            0.500
SPOFFS5   0 Hz
SPW5          4.12529993 W
SFO2          250.1310005 MHz
NUC2                 1H
CPDPRG[2          waltz16
P3                15.00 usec
P4                30.00 usec
PCPD2             90.00 usec
PLW2           7.19999981 W
PLW12          0.20000000 W

F2 - Processing parameters
SI                32768
SF            62.8952385 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **8**



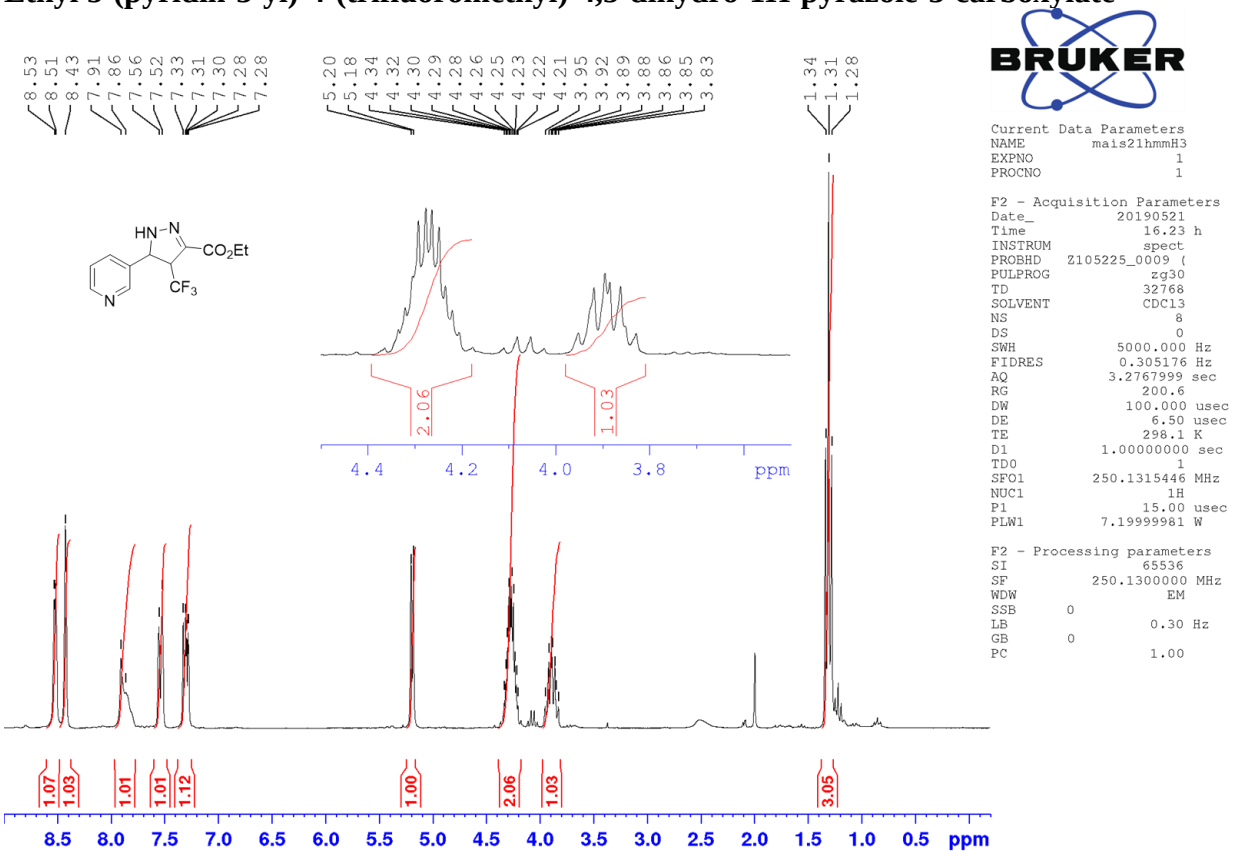

```
Current Data Parameters
NAME          mai21hmmH2
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190521
Time              21.21 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  256
DS                    4
SWH           15120.968 Hz
FIDRES         0.922911 Hz
AQ            1.0835285 sec
RG                200.6
DW               33.067 usec
DE               15.00 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1         62.9015281 MHz
NUC1                13C
P1                10.00 usec
PLW1        27.00000000 W
SFO2        250.1310005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         7.19999981 W
PLW12        0.20000000 W
PLW13        0.10044000 W

F2 - Processing parameters
SI                32768
SF           62.8952421 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **8**

Ethyl 5-(pyridin-3-yl)-4-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-3-carboxylate

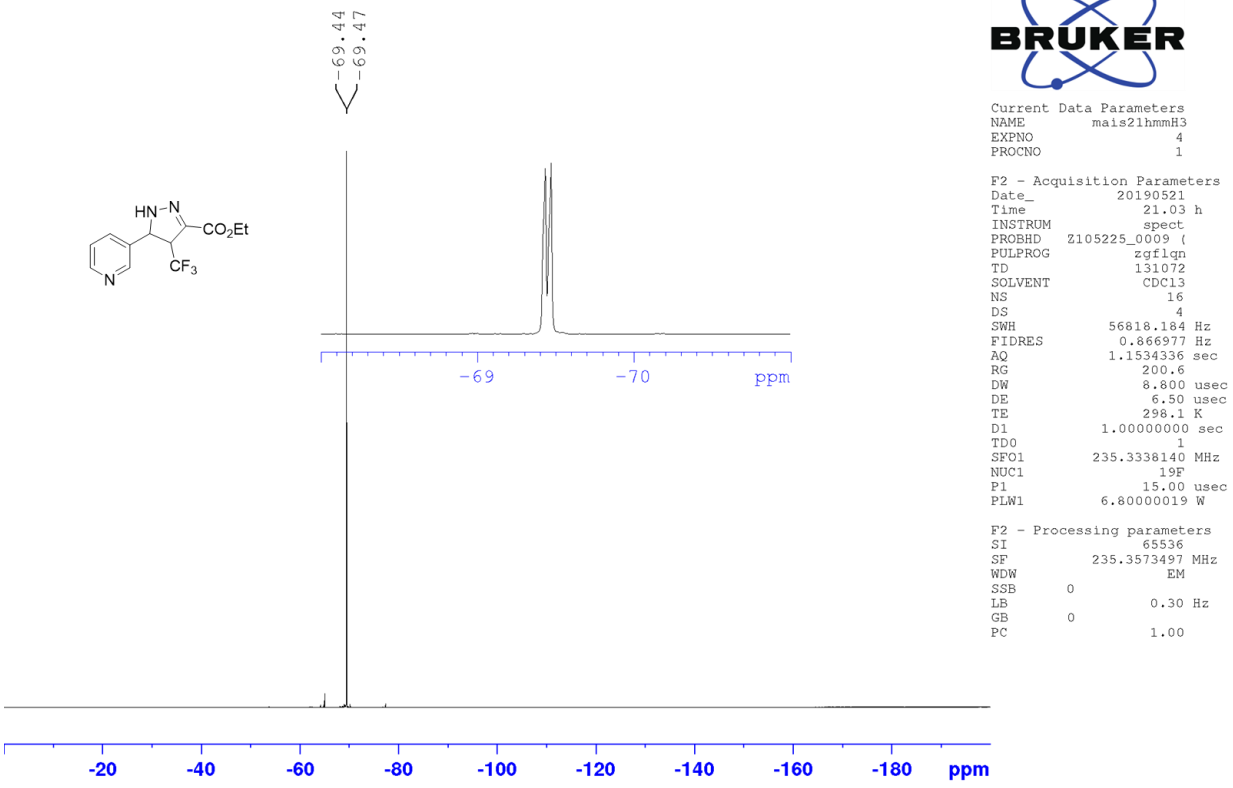



```
Current Data Parameters
NAME         mais21hmmH3
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190521
Time              16.23 h
INSTRUM           spect
PROBHD   Z105225_0009 (
PULPROG           zg30
TD               32768
SOLVENT           CDCl3
NS                   8
DS                   0
SWH           5000.000 Hz
FIDRES          0.305176 Hz
AQ            3.2767999 sec
RG                200.6
DW              100.000 usec
DE                6.50 usec
TE                298.1 K
D1            1.00000000 sec
TD0                  1
SFO1         250.1315446 MHz
NUC1                 1H
P1                15.00 usec
PLW1          7.19999981 W

F2 - Processing parameters
SI               65536
SF           250.1300000 MHz
WDW                 EM
SSB      0
LB               0.30 Hz
GB       0
PC               1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **13**

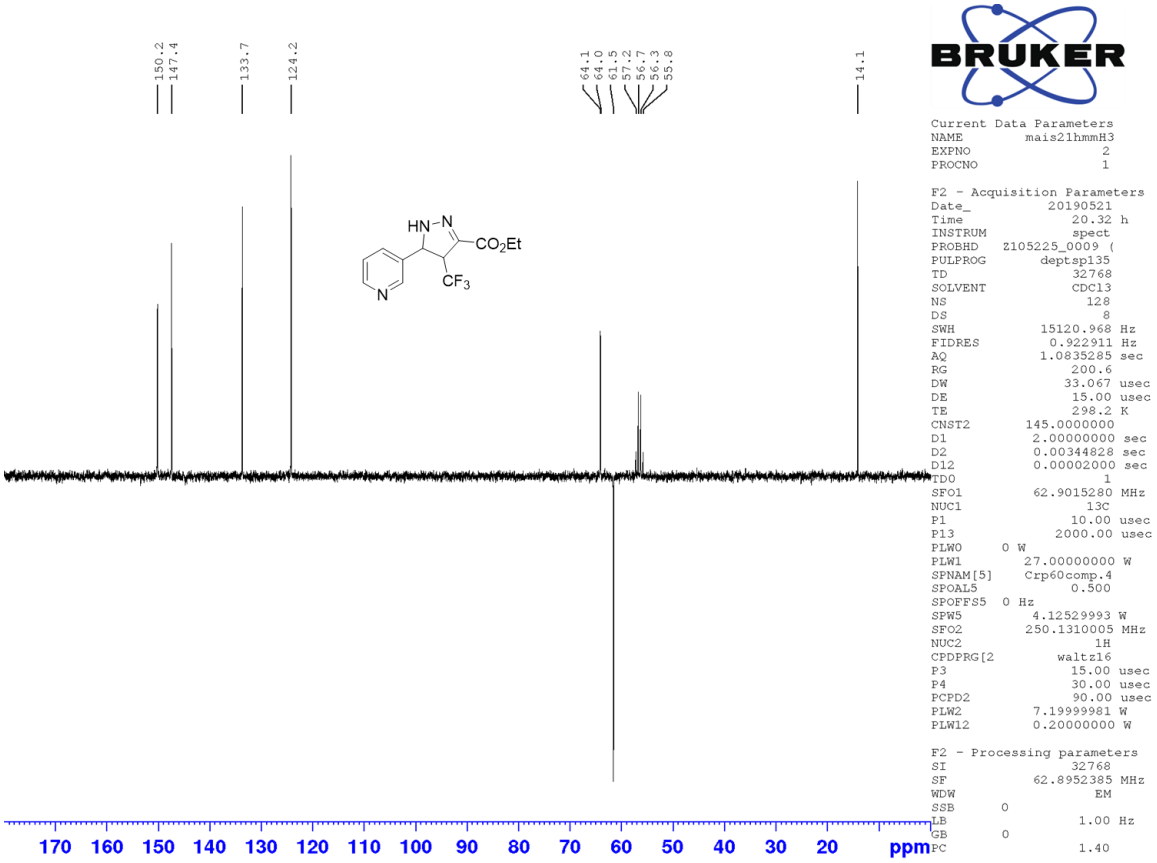



```
Current Data Parameters
NAME         mais21hmmH3
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190521
Time              21.03 h
INSTRUM           spect
PROBHD   Z105225_0009 (
PULPROG          zgflqn
TD              131072
SOLVENT           CDCl3
NS                  16
DS                   4
SWH          56818.184 Hz
FIDRES         0.866977 Hz
AQ            1.1534336 sec
RG                200.6
DW                8.800 usec
DE                6.50 usec
TE                298.1 K
D1            1.00000000 sec
TD0                  1
SFO1         235.3338140 MHz
NUC1                19F
P1                15.00 usec
PLW1          6.80000019 W

F2 - Processing parameters
SI               65536
SF           235.3573497 MHz
WDW                 EM
SSB      0
LB               0.30 Hz
GB       0
PC               1.00
```

^{19}F NMR spectrum in $CDCl_3$, 235 MHz, of compound **13**

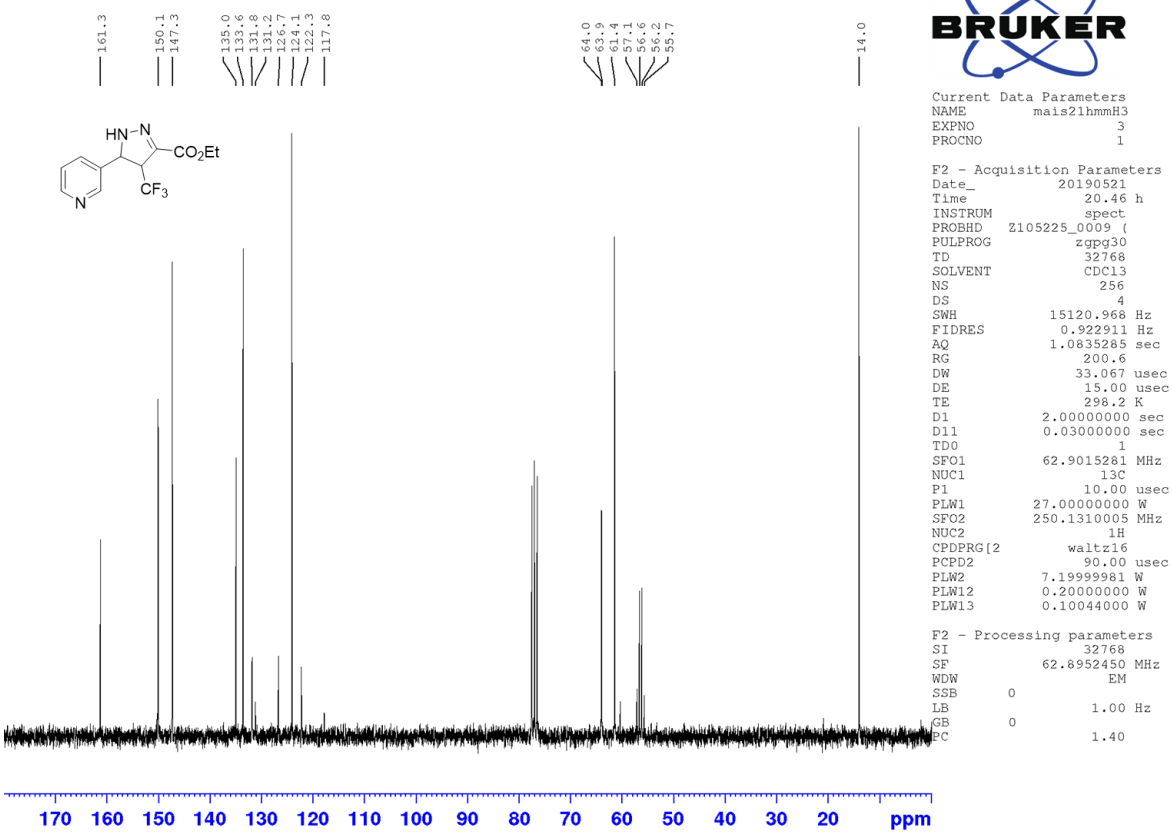



```
Current Data Parameters
NAME         mais21hmmH3
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190521
Time              20.32 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG        deptsp135
TD                 32768
SOLVENT            CDCl3
NS                   128
DS                     8
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.2 K
CNST2        145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1
SFO1          62.9015280 MHz
NUC1                 13C
P1                10.00 usec
P13             2000.00 usec
PLW0      0 W
PLW1       27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5   0 Hz
SPW5          4.12529993 W
SFO2         250.1310005 MHz
NUC2                 1H
CPDPRG[2          waltz16
P3                15.00 usec
P4                30.00 usec
PCPD2             90.00 usec
PLW2          7.19999981 W
PLW12         0.20000000 W

F2 - Processing parameters
SI                 32768
SF            62.8952385 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **13**



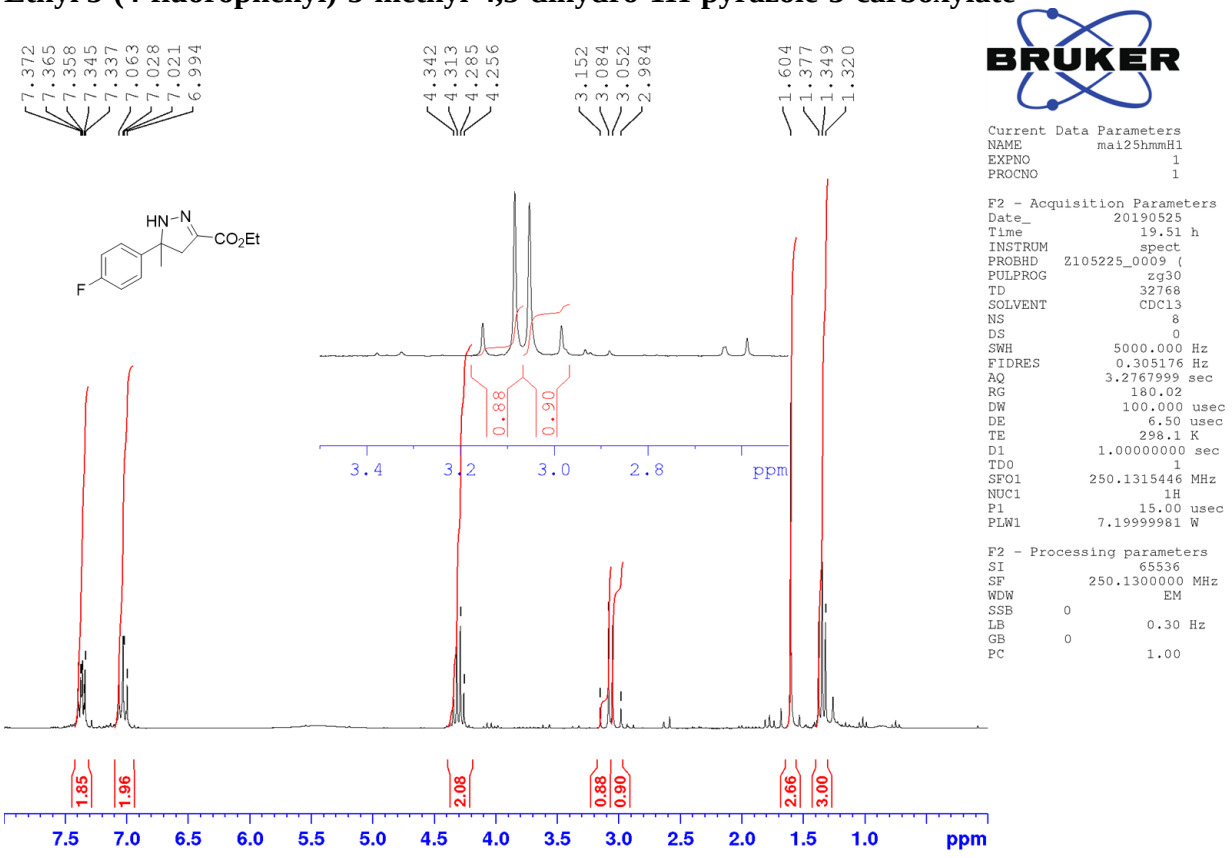

```
Current Data Parameters
NAME         mais21hmmH3
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190521
Time              20.46 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG          zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     4
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1          62.9015281 MHz
NUC1                 13C
P1                10.00 usec
PLW1       27.00000000 W
SFO2         250.1310005 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2          7.19999981 W
PLW12         0.20000000 W
PLW13         0.10044000 W

F2 - Processing parameters
SI                 32768
SF            62.8952450 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **13**

Ethyl 5-(4-fluorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-3-carboxylate

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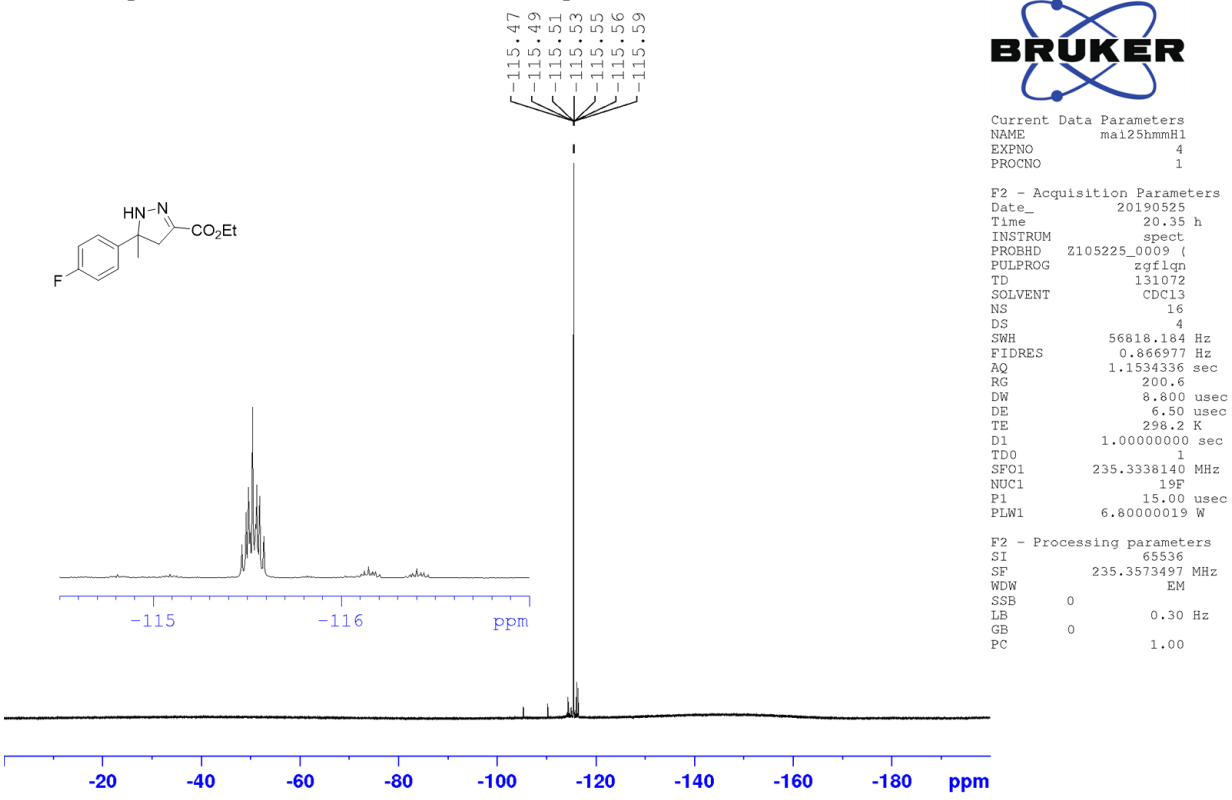
Current Data Parameters
NAME          mai25hmmH1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190525
Time              19.51 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG             zg30
TD                 32768
SOLVENT             CDCl3
NS                     8
DS                     0
SWH           5000.000 Hz
FIDRES          0.305176 Hz
AQ            3.2767999 sec
RG                180.02
DW              100.000 usec
DE                6.50 usec
TE                298.1 K
D1            1.00000000 sec
TD0                    1
SFO1         250.1315446 MHz
NUC1                  1H
P1                15.00 usec
PLW1          7.19999981 W

F2 - Processing parameters
SI                 65536
SF           250.1300000 MHz
WDW                   EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **4**

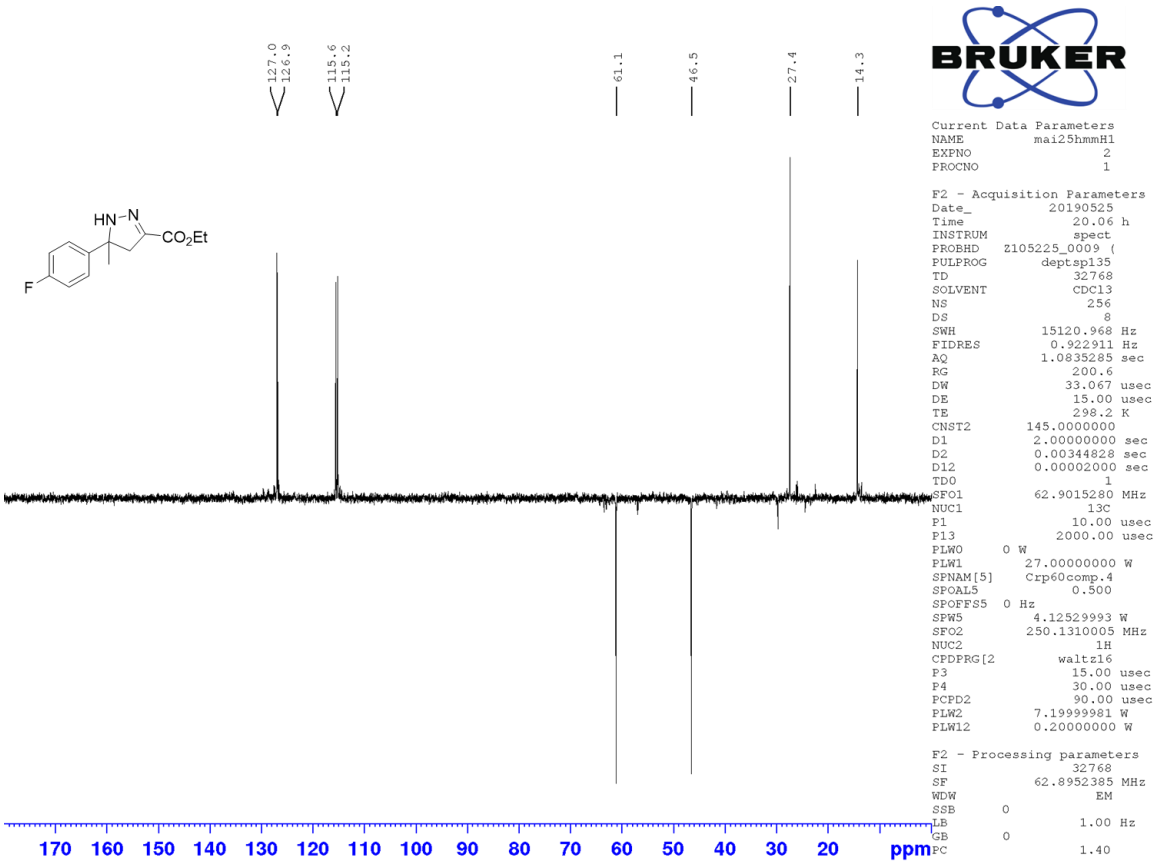



```
Current Data Parameters
NAME          mai25hmmH1
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190525
Time              20.35 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG           zgflqn
TD                131072
SOLVENT             CDCl3
NS                    16
DS                     4
SWH           56818.184 Hz
FIDRES          0.866977 Hz
AQ            1.1534336 sec
RG                200.6
DW                8.800 usec
DE                6.50 usec
TE                298.2 K
D1            1.00000000 sec
TD0                    1
SFO1         235.3338140 MHz
NUC1                 19F
P1                15.00 usec
PLW1          6.80000019 W

F2 - Processing parameters
SI                 65536
SF           235.3573497 MHz
WDW                   EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```

^{19}F NMR spectrum in $CDCl_3$, 235 MHz, of compound **4**

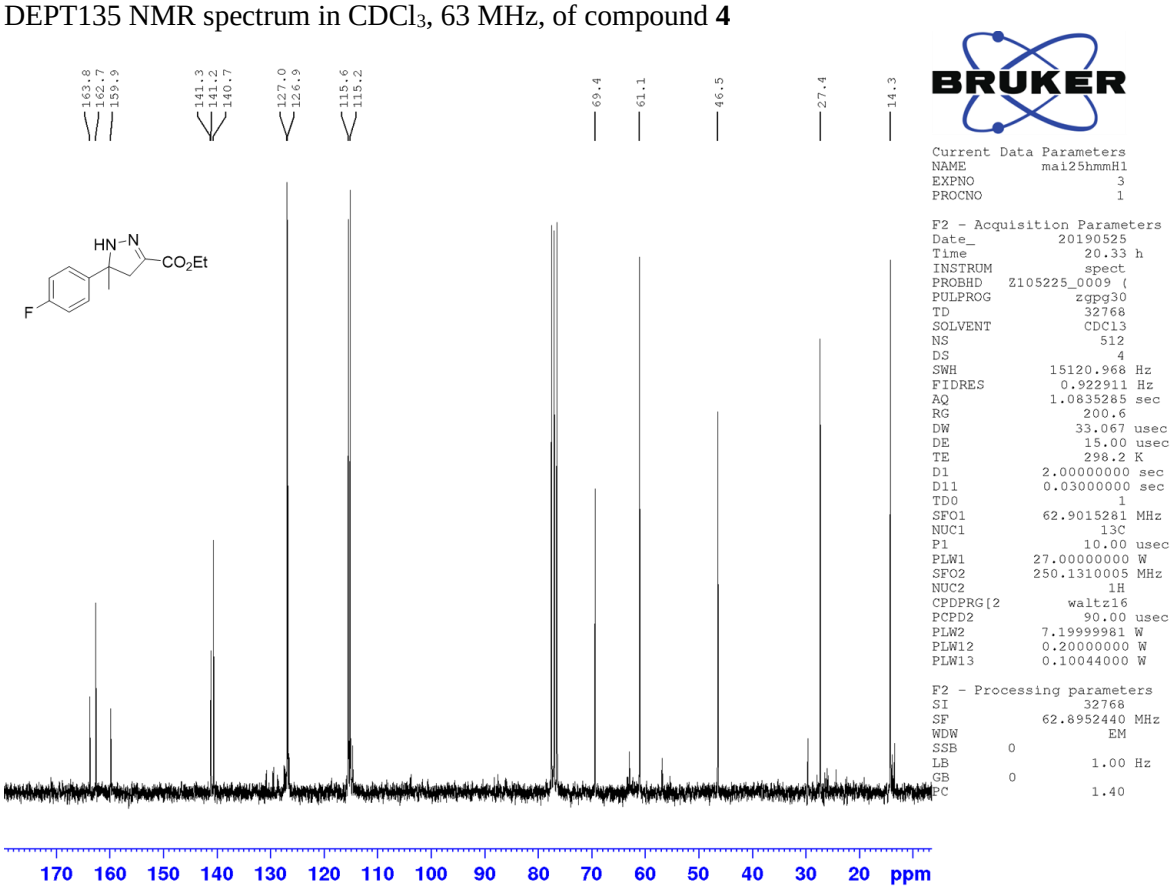



```
Current Data Parameters
NAME          mai25hmmH1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190525
Time              20.06 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG        deptsp135
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     8
SWH           15120.968 Hz
FIDRES         0.922911 Hz
AQ            1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.2 K
CNST2        145.0000000
D1            2.00000000 sec
D2            0.00344828 sec
D12           0.00002000 sec
TD0                    1
SFO1          62.9015280 MHz
NUC1                 13C
P1                10.00 usec
P13             2000.00 usec
PLW0      0 W
PLW1        27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5   0 Hz
SPW5          4.12529993 W
SFO2         250.1310005 MHz
NUC2                 1H
CPDPRG[2          waltz16
P3                15.00 usec
P4                30.00 usec
PCPD2             90.00 usec
PLW2          7.19999981 W
PLW12         0.20000000 W

F2 - Processing parameters
SI                 32768
SF            62.8952385 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **4**



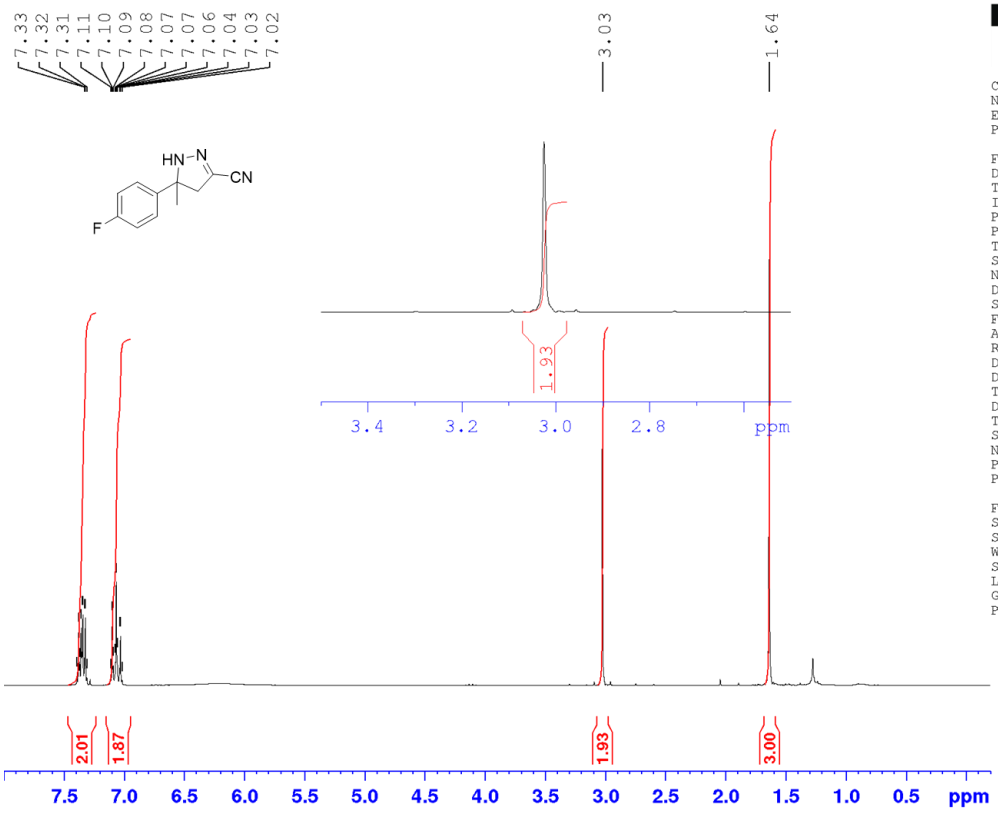

```
Current Data Parameters
NAME          mai25hmmH1
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190525
Time              20.33 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   512
DS                     4
SWH           15120.968 Hz
FIDRES         0.922911 Hz
AQ            1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1          62.9015281 MHz
NUC1                 13C
P1                10.00 usec
PLW1        27.00000000 W
SFO2         250.1310005 MHz
NUC2                 1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2          7.19999981 W
PLW12         0.20000000 W
PLW13         0.10044000 W

F2 - Processing parameters
SI                 32768
SF            62.8952440 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **4**

5-(4-fluorophenyl)-5-methyl-4,5-dihydro-1H-pyrazole-3-carbonitrile

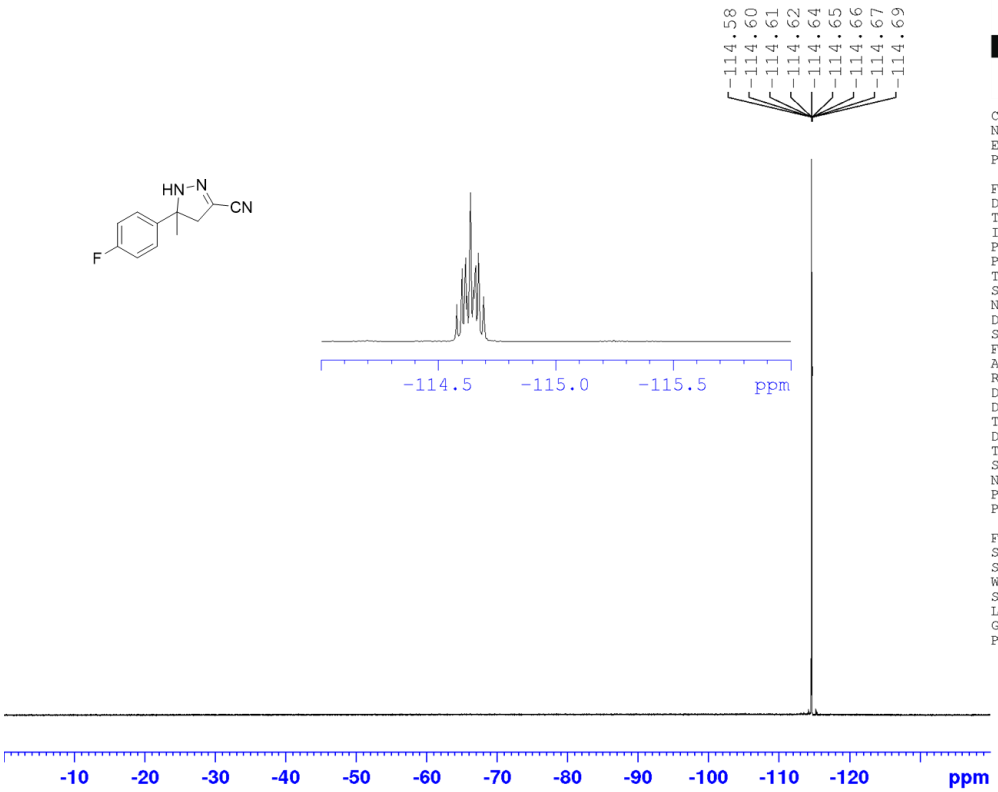



```
Current Data Parameters
NAME          mai25hmmH2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190525
Time               21.15 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             5000.000 Hz
FIDRES             0.305176 Hz
AQ              3.2767999 sec
RG                 180.02
DW                 100.000 usec
DE                   6.50 usec
TE                 298.1 K
D1              1.00000000 sec
TD0                    1
SFO1           250.1315446 MHz
NUC1                  1H
P1                  15.00 usec
PLW1            7.19999981 W

F2 - Processing parameters
SI                 65536
SF            250.1300000 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **9**

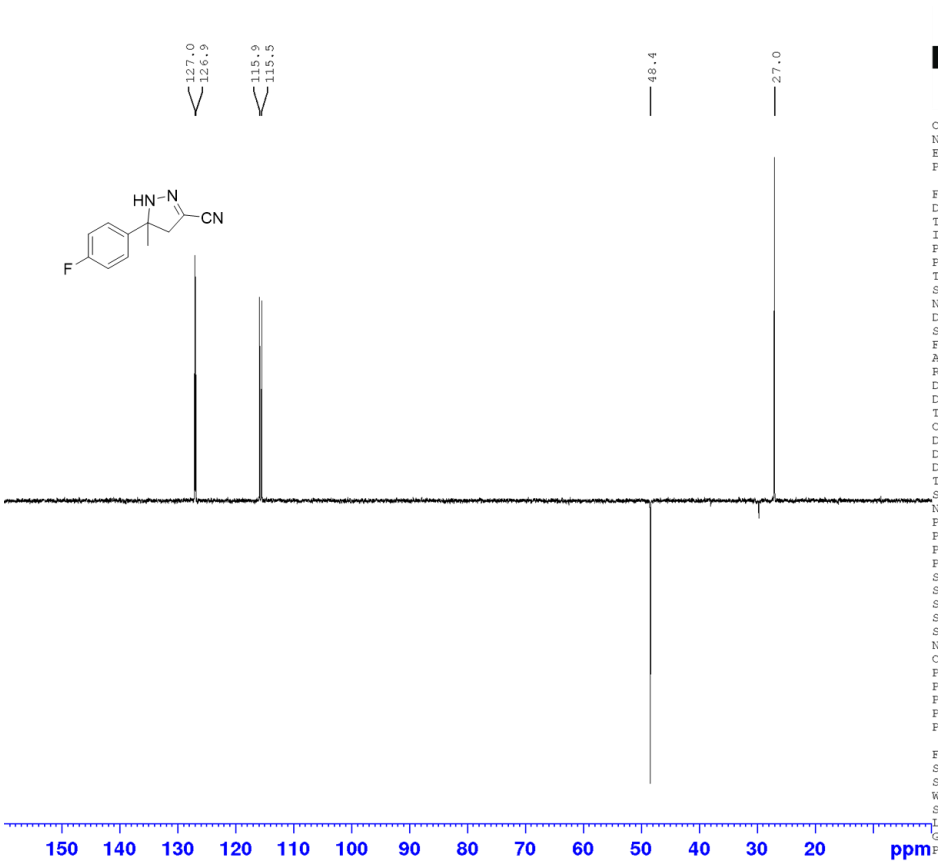



```
Current Data Parameters
NAME          mai25hmmH2
EXPNO                  4
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190525
Time               21.58 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG          zgflqn
TD                131072
SOLVENT            CDCl3
NS                    16
DS                     4
SWH            56818.184 Hz
FIDRES             0.866977 Hz
AQ              1.1534336 sec
RG                 200.6
DW                   8.800 usec
DE                   6.50 usec
TE                 298.2 K
D1              1.00000000 sec
TD0                    1
SFO1           235.3338140 MHz
NUC1                  19F
P1                  15.00 usec
PLW1            6.80000019 W

F2 - Processing parameters
SI                 65536
SF            235.3573497 MHz
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
```

^{19}F NMR spectrum in $CDCl_3$, 235 MHz, of compound **9**

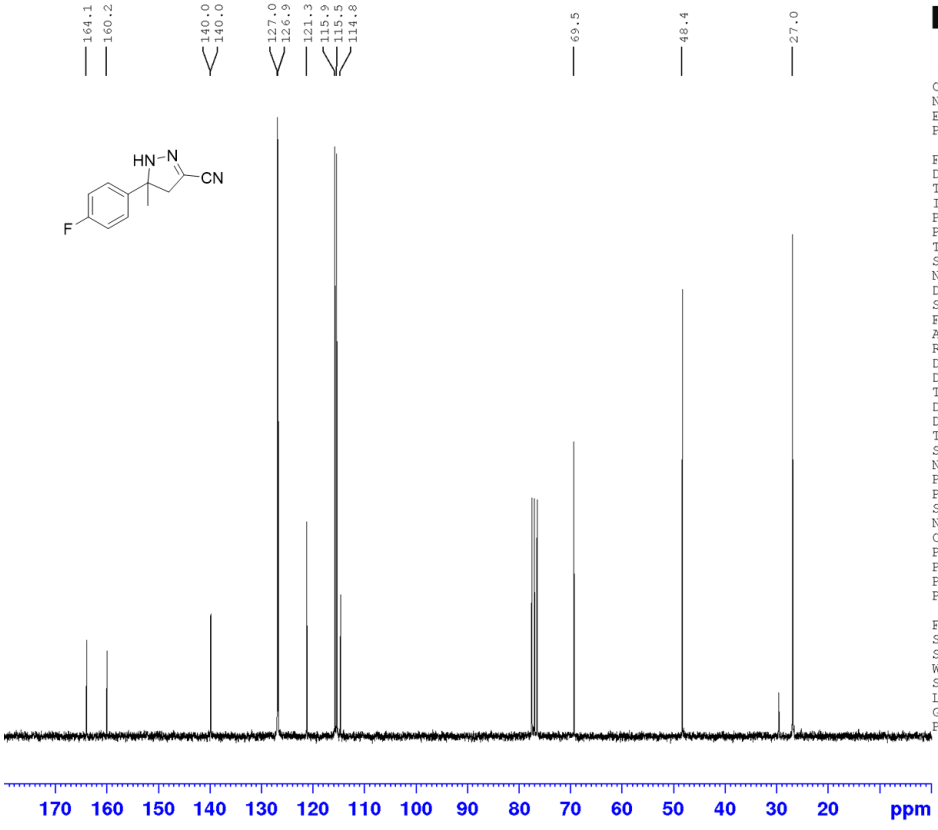



```
Current Data Parameters
NAME          mai25hmmH2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190525
Time              21.29 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG        deptsp135
TD                 32768
SOLVENT             CDCl3
NS                    256
DS                      8
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.1 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1
SFO1           62.9015280 MHz
NUC1                  13C
P1                 10.00 usec
P13              2000.00 usec
PLW0      0 W
PLW1        27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5           4.12529993 W
SFO2          250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
P3                 15.00 usec
P4                 30.00 usec
PCPD2              90.00 usec
PLW2           7.19999981 W
PLW12          0.20000000 W

F2 - Processing parameters
SI                 32768
SF            62.8952385 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **9**



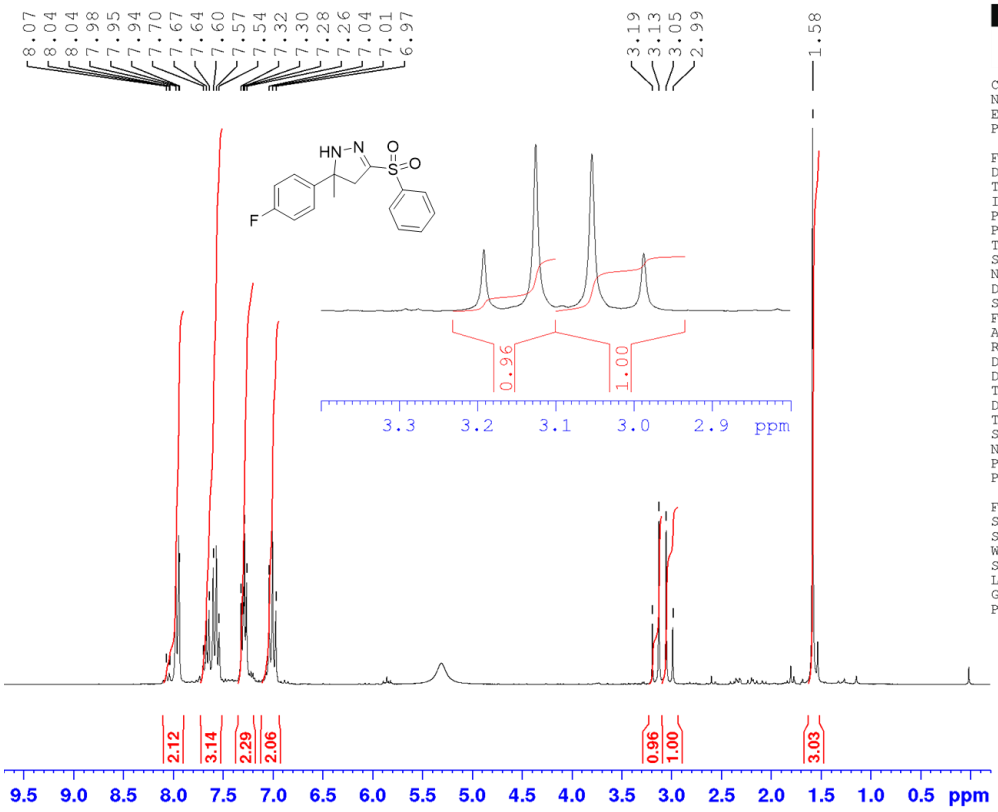

```
Current Data Parameters
NAME          mai25hmmH2
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190525
Time              21.56 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG           zgpg30
TD                 32768
SOLVENT             CDCl3
NS                    512
DS                      4
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1           62.9015281 MHz
NUC1                  13C
P1                 10.00 usec
PLW1        27.00000000 W
SFO2          250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2           7.19999981 W
PLW12          0.20000000 W
PLW13          0.10044000 W

F2 - Processing parameters
SI                 32768
SF            62.8952465 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **9**

5-(4-fluorophenyl)-5-methyl-3-(phenylsulfonyl)-4,5-dihydro-1H-pyrazole

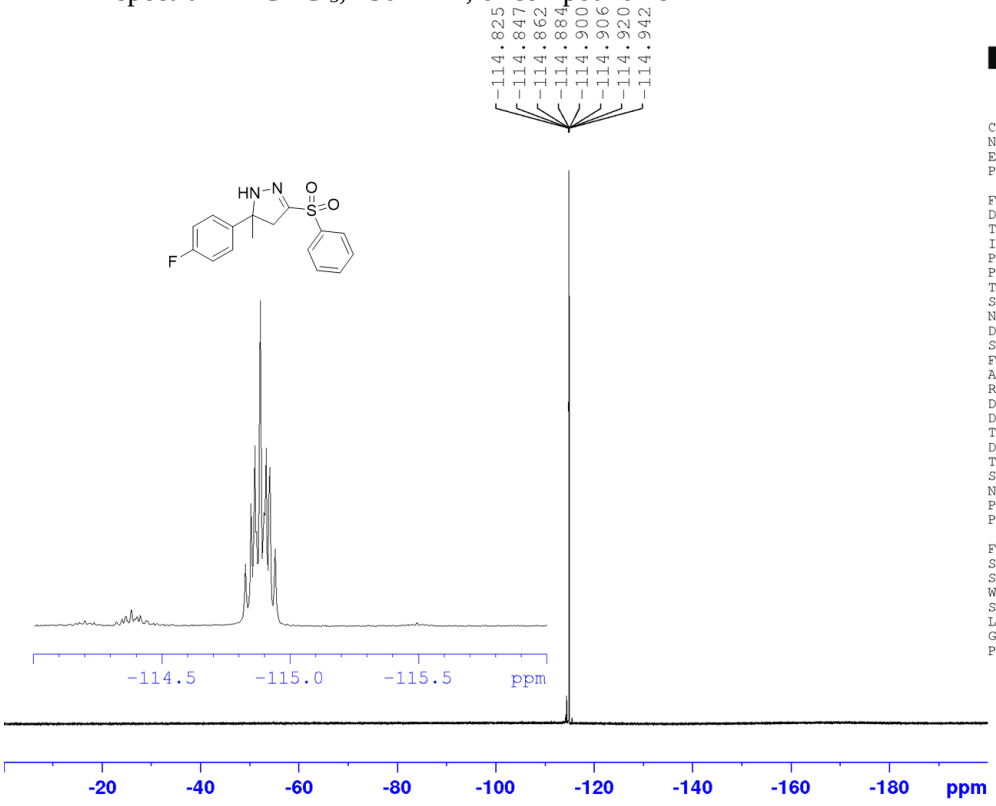


Current Data Parameters
NAME dez18hmmH2
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20191218
Time 20.11 h
INSTRUM spect
PROBHD Z105225_0009 (
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 8
DS 0
SWH 5000.000 Hz
FIDRES 0.305176 Hz
AQ 3.2767999 sec
RG 200.6
DW 100.000 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
SFO1 250.1315446 MHz
NUC1 1H
P1 15.00 usec
PLW1 7.19999981 W

F2 - Processing parameters
SI 65536
SF 250.1300000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **19**

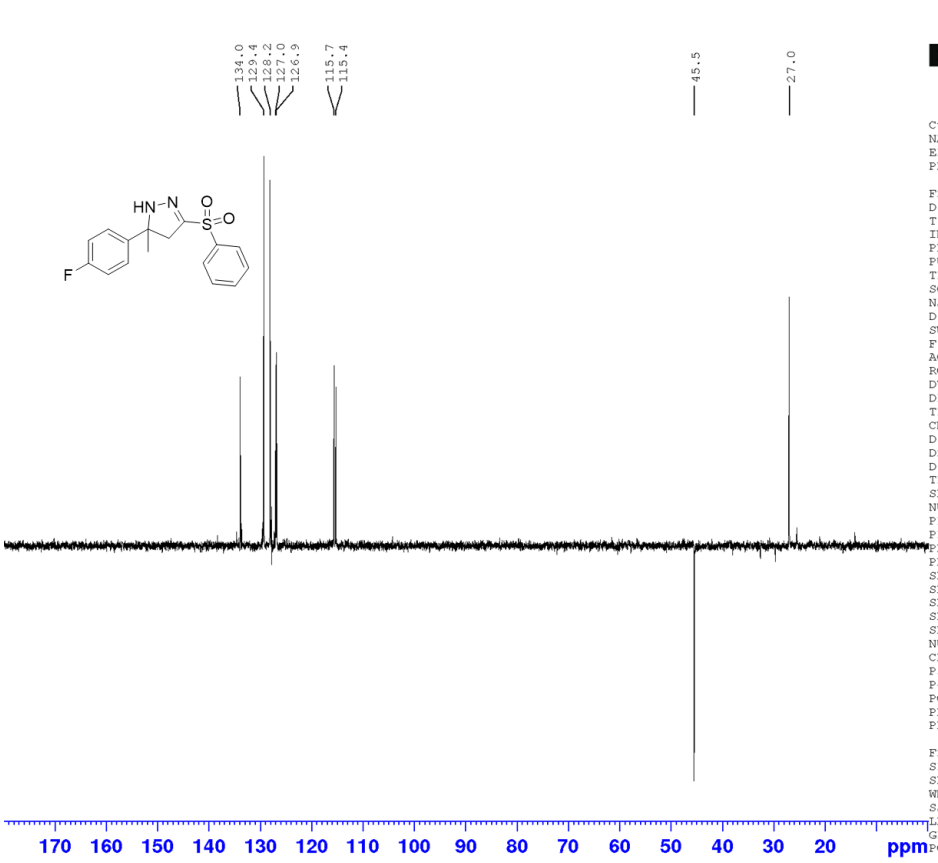


Current Data Parameters
NAME mai25hmmH5
EXPNO 4
PROCNO 1

F2 - Acquisition Parameters
Date_ 20190525
Time 19.47 h
INSTRUM spect
PROBHD Z105225_0009 (
PULPROG zgflqn
TD 131072
SOLVENT CDCl3
NS 16
DS 4
SWH 56818.184 Hz
FIDRES 0.866977 Hz
AQ 1.1534336 sec
RG 200.6
DW 8.800 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
SFO1 235.3338140 MHz
NUC1 19F
P1 15.00 usec
PLW1 6.80000019 W

F2 - Processing parameters
SI 65536
SF 235.3573497 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

^{19}F NMR spectrum in $CDCl_3$, 235 MHz, of compound **19**

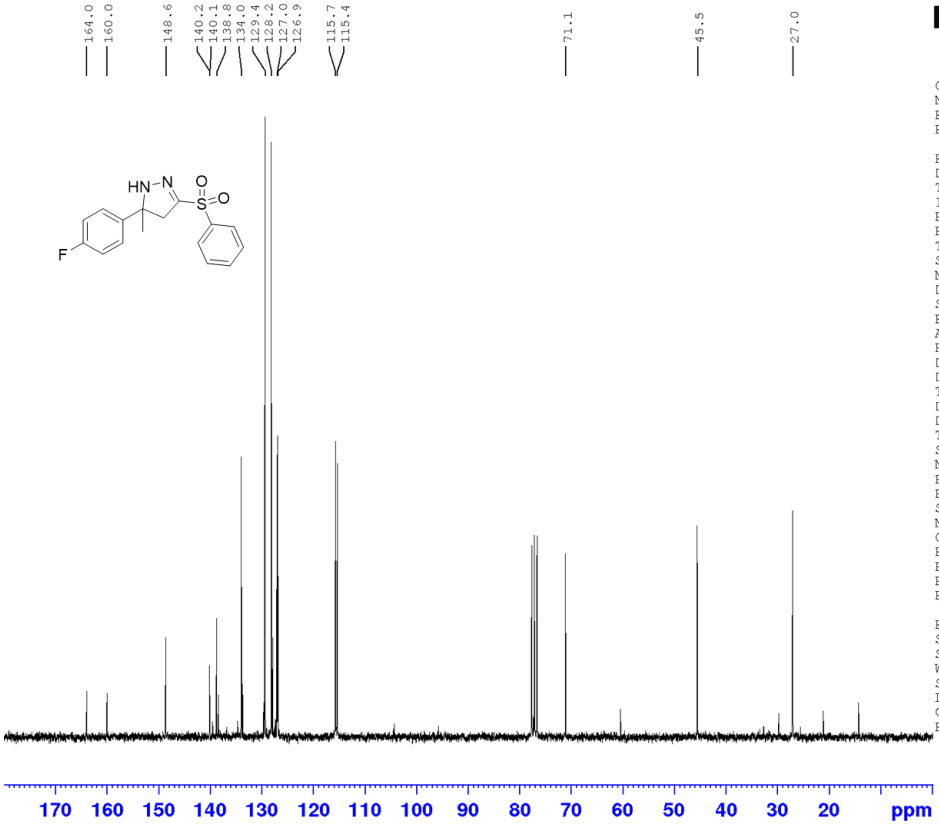



```
Current Data Parameters
NAME          mai25hmmH5
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190525
Time              19.17 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG        deptsp135
TD                 32768
SOLVENT            CDCl3
NS                   128
DS                     8
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.2 K
CNST2        145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1
SFO1           62.9015280 MHz
NUC1                  13C
P1                 10.00 usec
P13              2000.00 usec
PLW0      0 W
PLW1         27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5   0 Hz
SPW5           4.12529993 W
SFO2         250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
P3                 15.00 usec
P4                 30.00 usec
PCPD2              90.00 usec
PLW2           7.19999981 W
PLW12          0.20000000 W

F2 - Processing parameters
SI                 32768
SF            62.8952385 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **19**



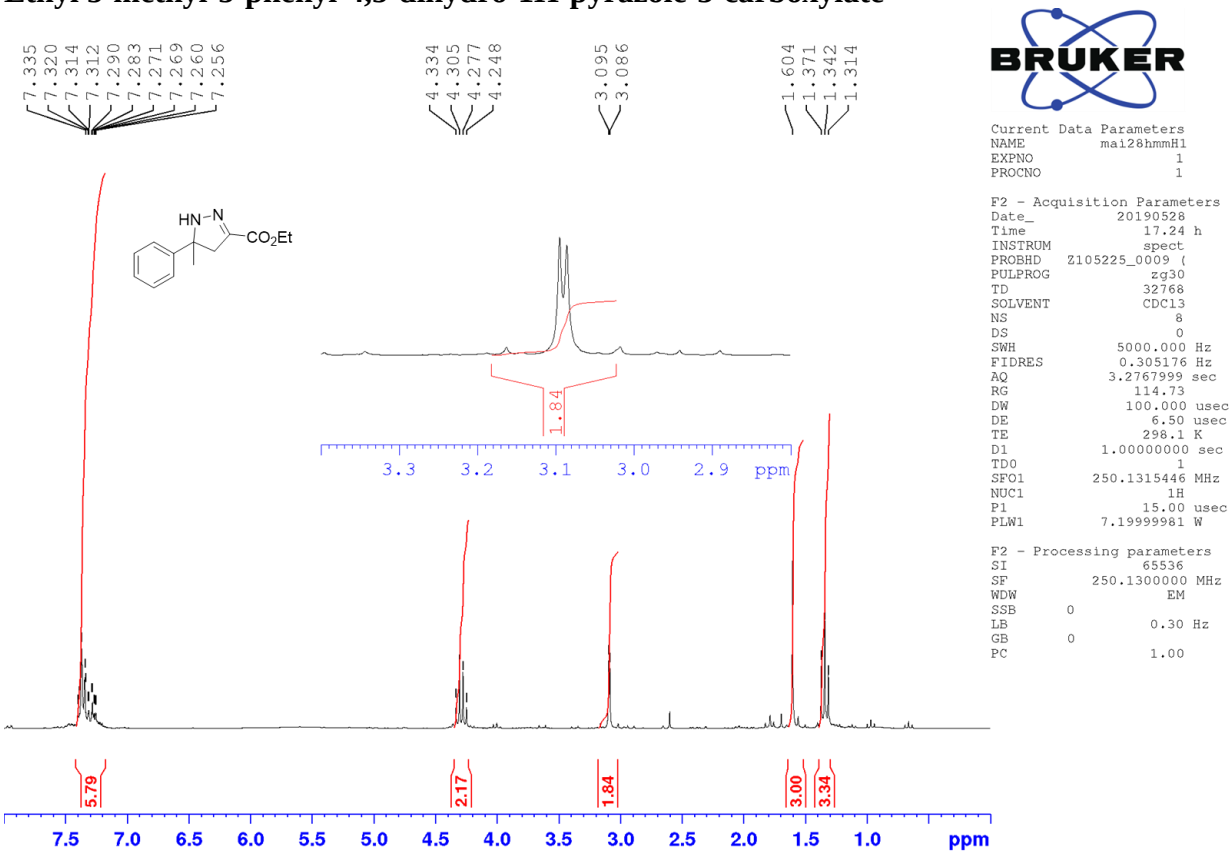

```
Current Data Parameters
NAME          mai25hmmH5
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190525
Time              19.45 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   512
DS                     4
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1
SFO1           62.9015281 MHz
NUC1                  13C
P1                 10.00 usec
PLW1         27.00000000 W
SFO2         250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2              90.00 usec
PLW2           7.19999981 W
PLW12          0.20000000 W
PLW13          0.10044000 W

F2 - Processing parameters
SI                 32768
SF            62.8952385 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **19**

Ethyl 5-methyl-5-phenyl-4,5-dihydro-1H-pyrazole-3-carboxylate

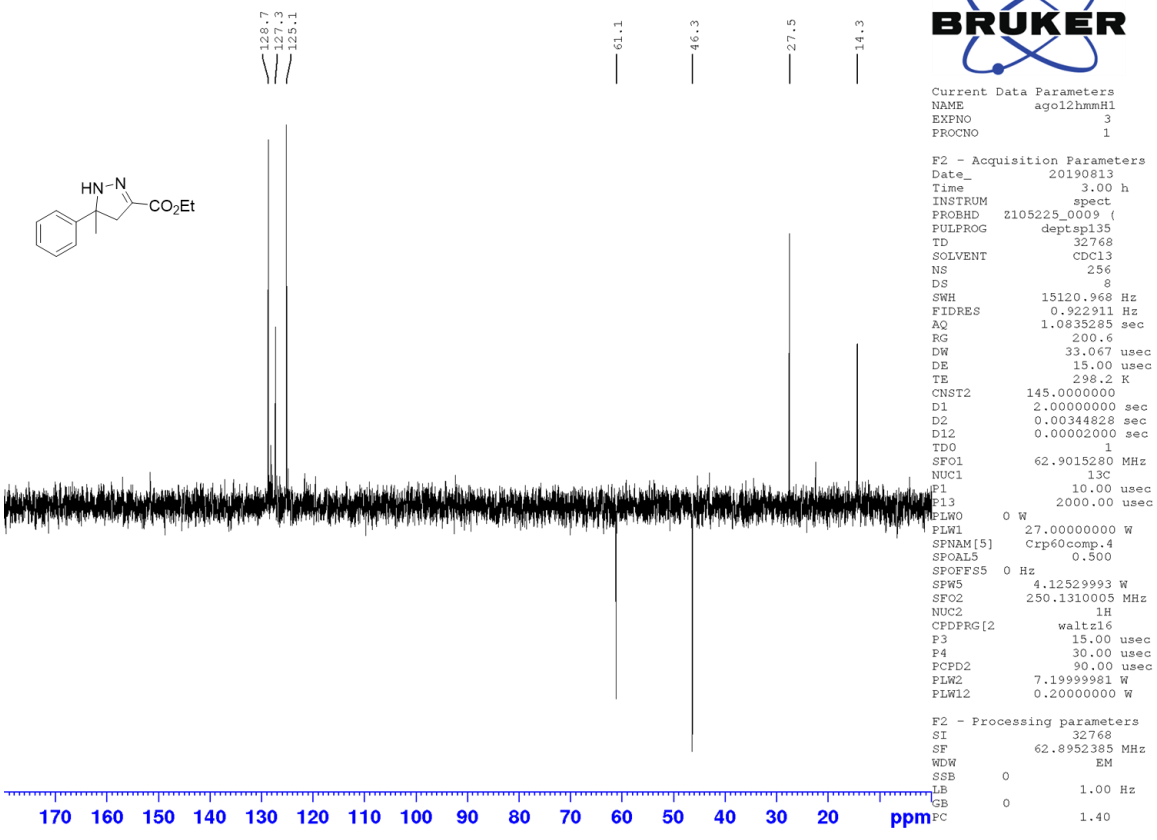



```
Current Data Parameters
NAME          mai28hmmH1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190528
Time               17.24 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             5000.000 Hz
FIDRES             0.305176 Hz
AQ              3.2767999 sec
RG                 114.73
DW                 100.000 usec
DE                   6.50 usec
TE                 298.1 K
D1              1.00000000 sec
TD0                    1
SFO1            250.1315446 MHz
NUC1                  1H
P1                   15.00 usec
PLW1            7.19999981 W

F2 - Processing parameters
SI                 65536
SF            250.1300000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **14**

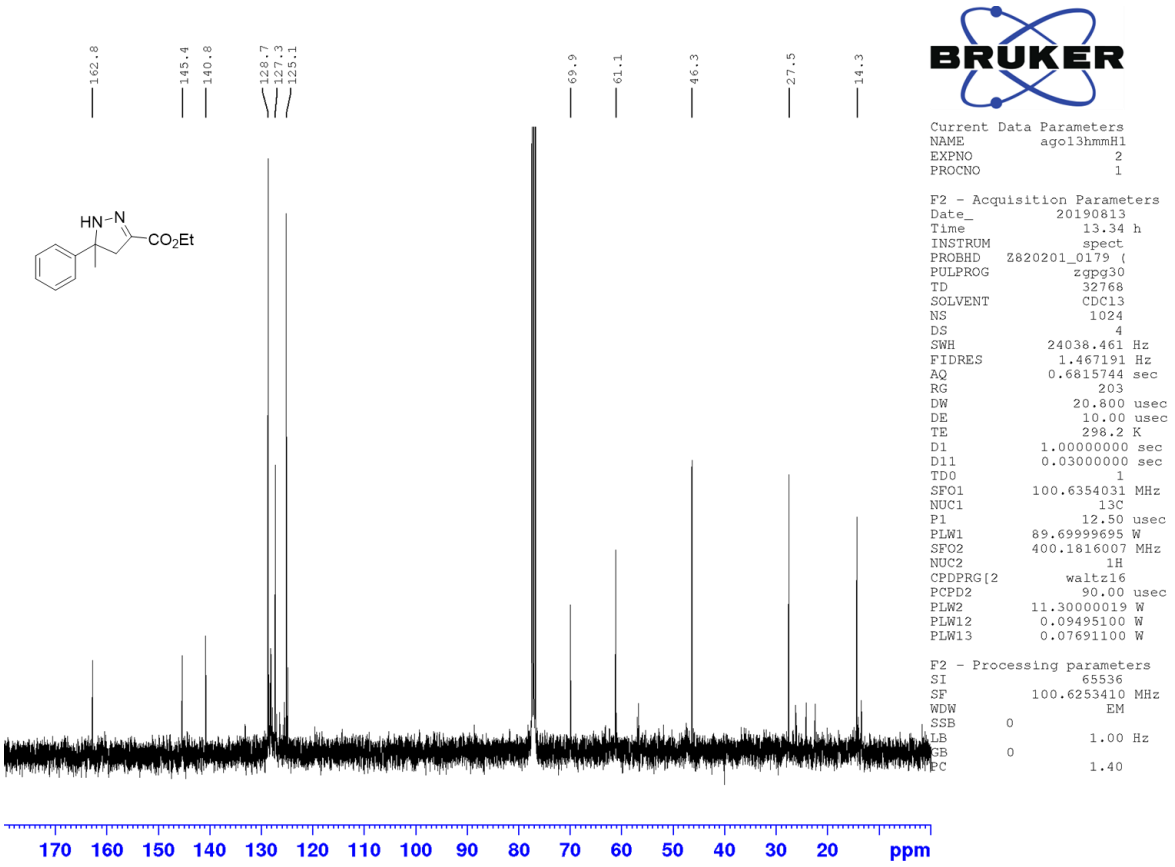



```
Current Data Parameters
NAME          ago12hmmH1
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190813
Time               3.00 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG         deptsp135
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     8
SWH            15120.968 Hz
FIDRES             0.922911 Hz
AQ              1.0835285 sec
RG                 200.6
DW                 33.067 usec
DE                 15.00 usec
TE                 298.2 K
CNST2          145.0000000
D1              2.00000000 sec
D2              0.00344828 sec
D12             0.00002000 sec
TD0                    1
SFO1            62.9015280 MHz
NUC1                  13C
P1                 10.00 usec
P13              2000.00 usec
PLW0      0 W
PLW1       27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5            4.12529993 W
SFO2            250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
P3                 15.00 usec
P4                 30.00 usec
PCPD2              90.00 usec
PLW2            7.19999981 W
PLW12           0.20000000 W

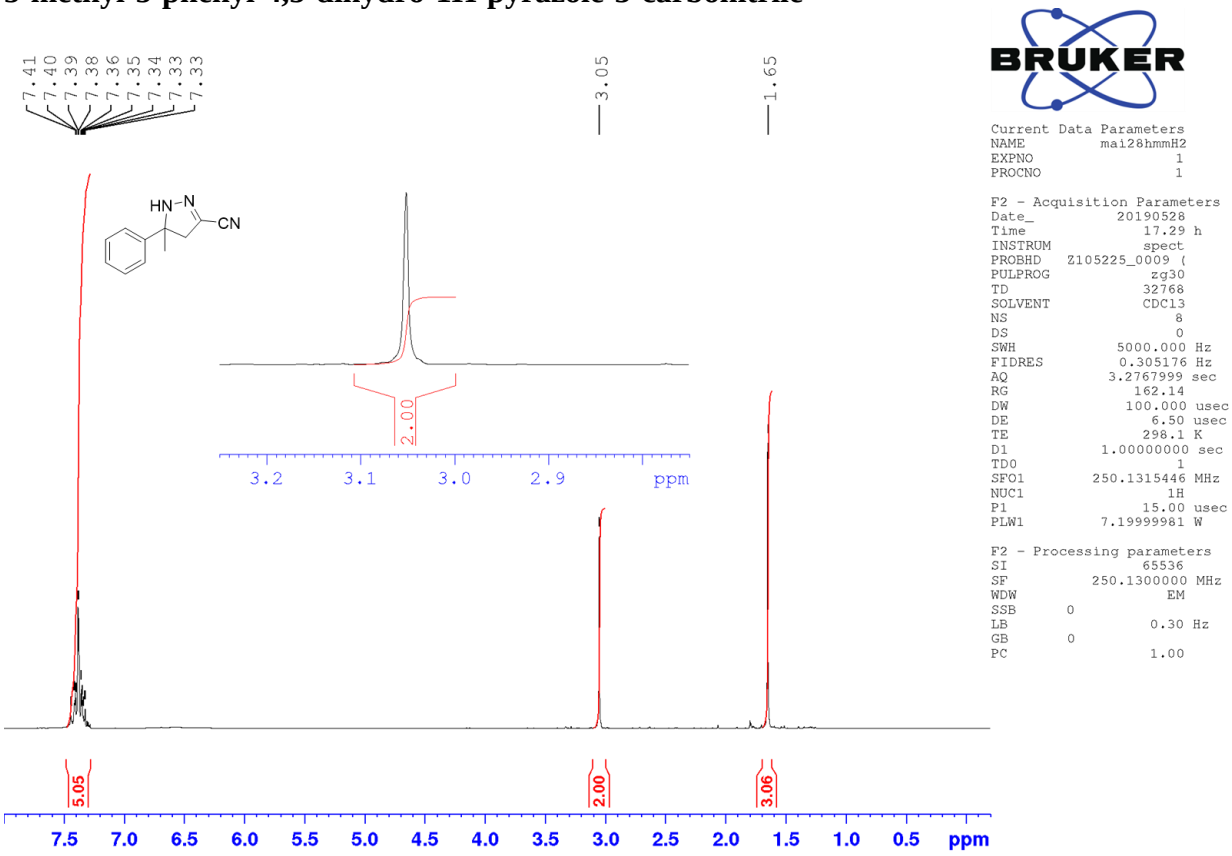
F2 - Processing parameters
SI                 32768
SF              62.8952385 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **14**



^{13}C NMR spectrum in $CDCl_3$, 100 MHz, of compound **14**

5-methyl-5-phenyl-4,5-dihydro-1H-pyrazole-3-carbonitrile

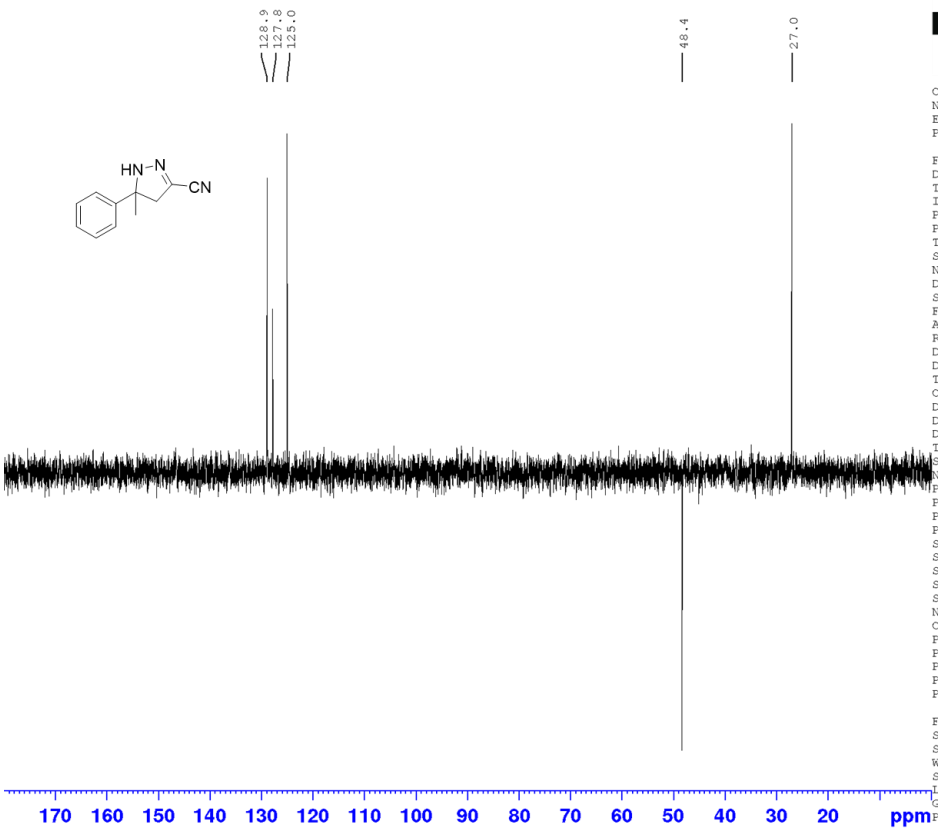



```
Current Data Parameters
NAME          mai28hmmH2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190528
Time               17.29 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                     8
DS                     0
SWH             5000.000 Hz
FIDRES             0.305176 Hz
AQ              3.2767999 sec
RG                 162.14
DW                 100.000 usec
DE                   6.50 usec
TE                 298.1 K
D1              1.00000000 sec
TD0                    1
SFO1           250.1315446 MHz
NUC1                  1H
P1                   15.00 usec
PLW1            7.19999981 W

F2 - Processing parameters
SI                 65536
SF            250.1300000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **18**

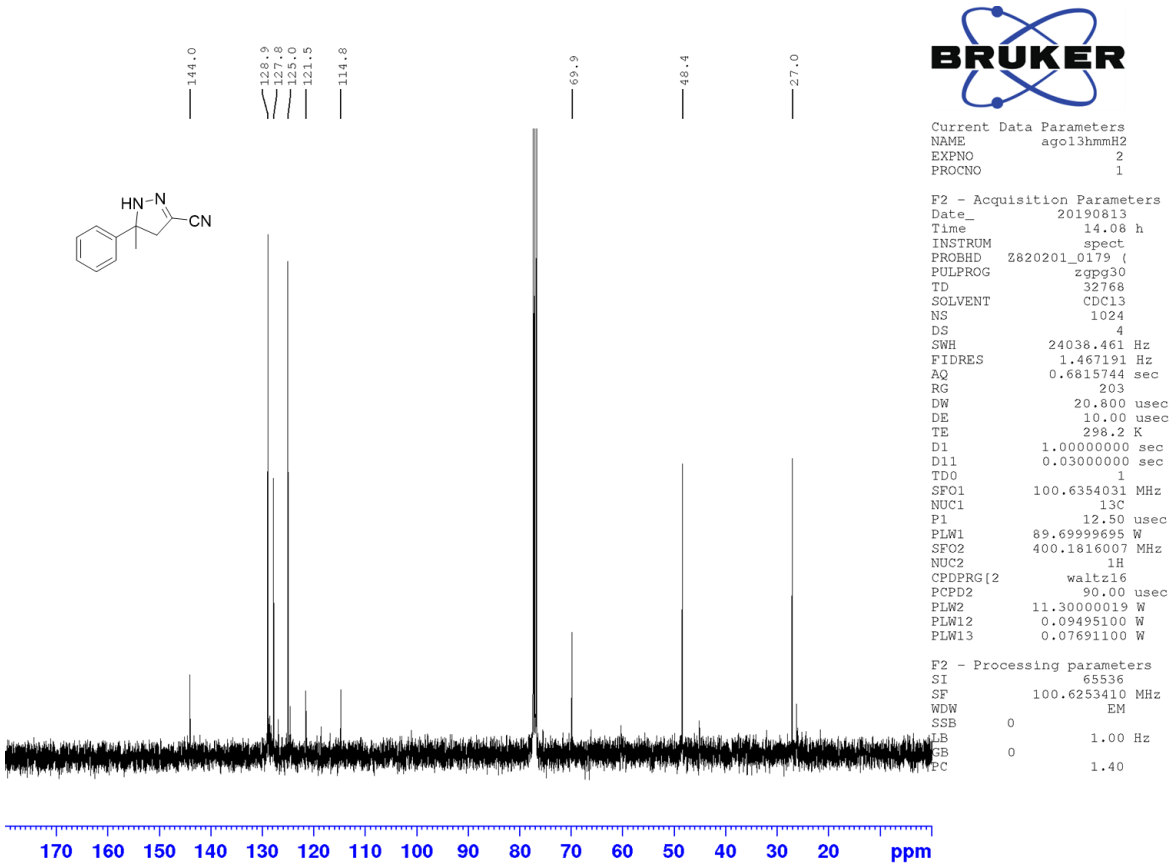



```
Current Data Parameters
NAME          ago12hmmH2
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190813
Time               3.47 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG         deptsp135
TD                 32768
SOLVENT            CDCl3
NS                   256
DS                     8
SWH            15120.968 Hz
FIDRES             0.922911 Hz
AQ              1.0835285 sec
RG                 200.6
DW                 33.067 usec
DE                 15.00 usec
TE                 298.2 K
CNST2         145.0000000
D1              2.00000000 sec
D2              0.00344828 sec
D12             0.00002000 sec
TD0                    1
SFO1           62.9015280 MHz
NUC1                  13C
P1                 10.00 usec
P13              2000.00 usec
PLW0       0 W
PLW1        27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5            4.12529993 W
SFO2           250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
P3                 15.00 usec
P4                 30.00 usec
PCPD2              90.00 usec
PLW2            7.19999981 W
PLW12           0.20000000 W

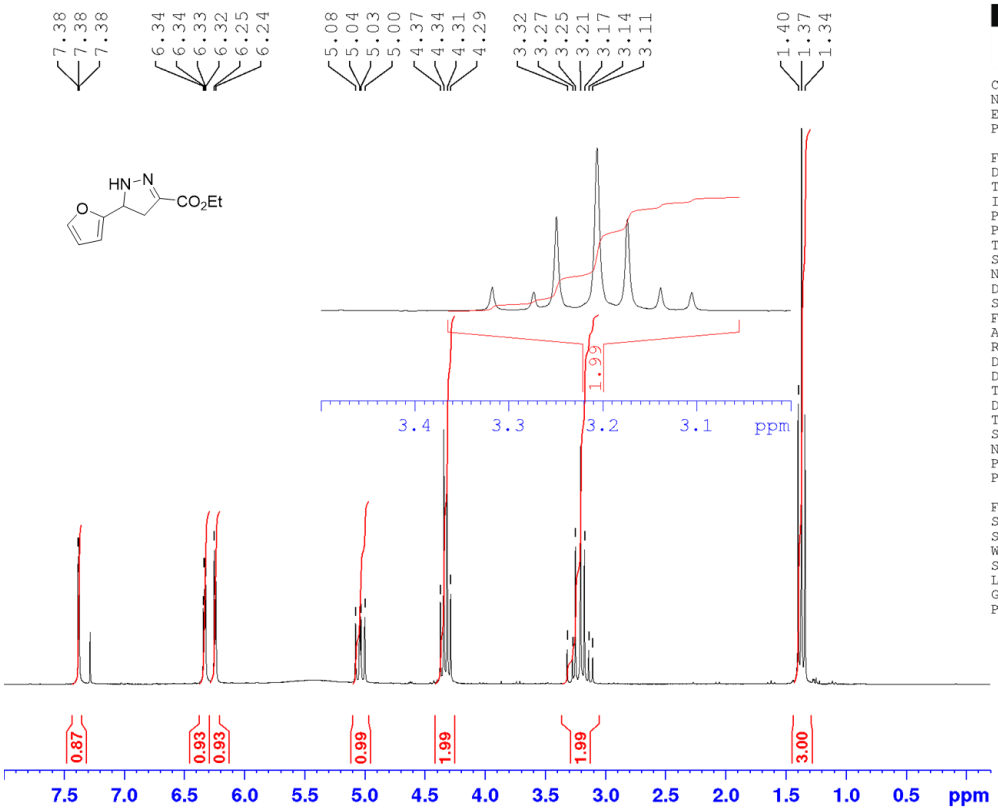
F2 - Processing parameters
SI                 32768
SF             62.8952385 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **18**



^{13}C NMR spectrum in $CDCl_3$, 100 MHz, of compound **18**

Ethyl 5-(furan-2-yl)-4,5-dihydro-1H-pyrazole-3-carboxylate

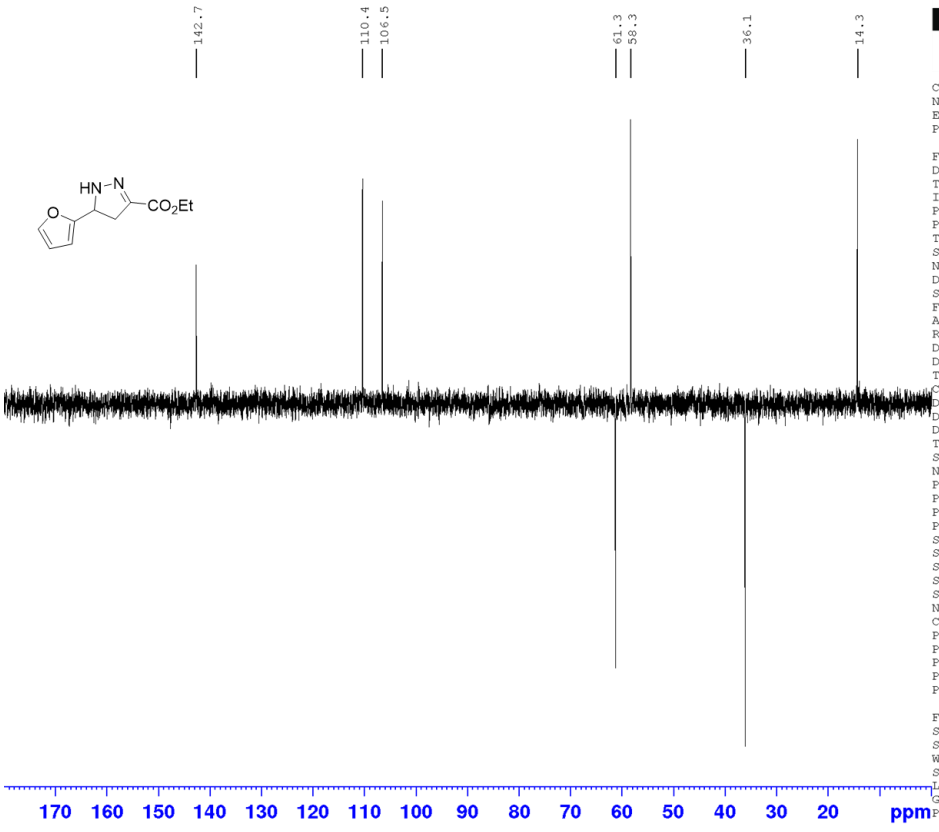



```
Current Data Parameters
NAME        jul13hmmH1_A
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190713
Time              19.05 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             5000.000 Hz
FIDRES          0.305176 Hz
AQ             3.2767999 sec
RG                 200.6
DW               100.000 usec
DE                 6.50 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1
SFO1          250.1315446 MHz
NUC1                  1H
P1                 15.00 usec
PLW1           7.19999981 W

F2 - Processing parameters
SI                 65536
SF           250.1300000 MHz
WDW                   EM
SSB       0
LB                0.30 Hz
GB        0
PC                1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **5**

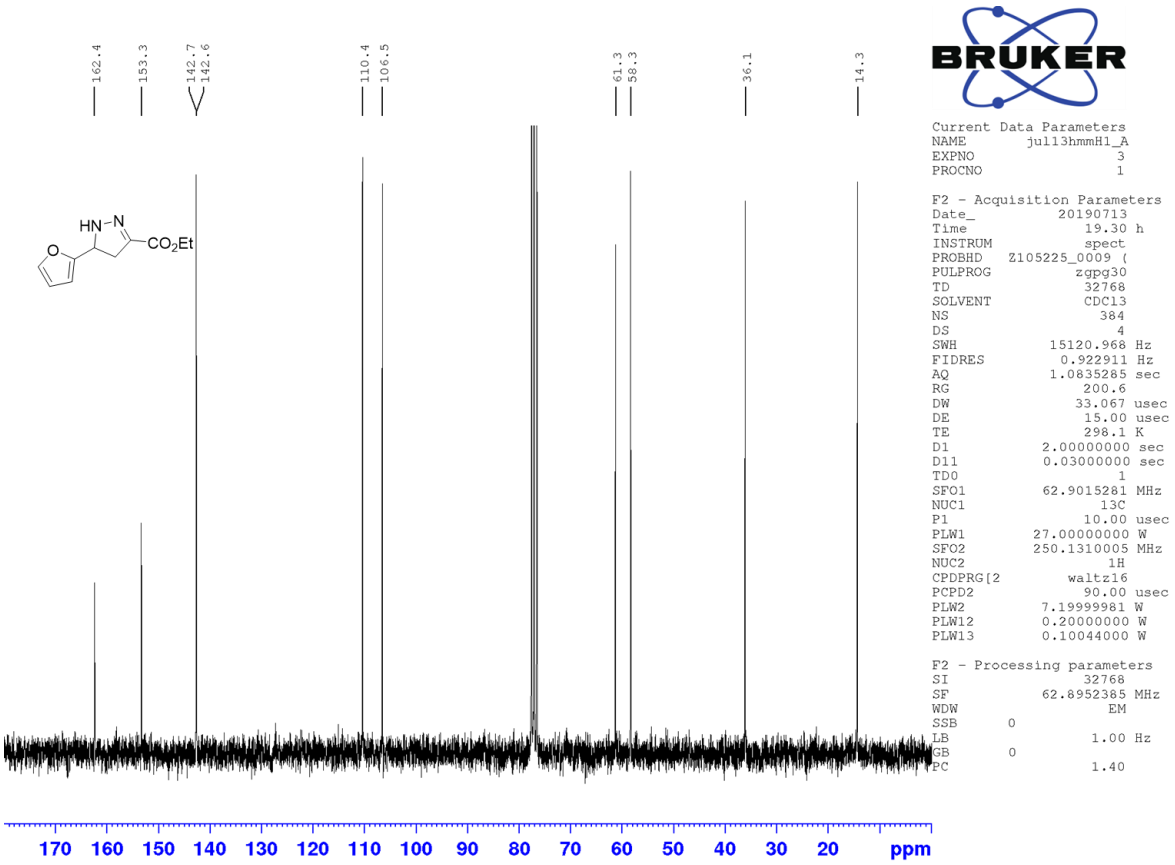



```
Current Data Parameters
NAME        jul13hmmH1_A
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190713
Time              19.09 h
INSTRUM             spect
PROBHD   Z105225_0009 (
PULPROG         deptsp135
TD                 32768
SOLVENT            CDCl3
NS                    64
DS                     8
SWH            15120.968 Hz
FIDRES          0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.2 K
CNST2         145.0000000
D1             2.00000000 sec
D2             0.00344828 sec
D12            0.00002000 sec
TD0                    1
SFO1          62.9015280 MHz
NUC1                  13C
P1                10.00 usec
P13             2000.00 usec
PLW0       0 W
PLW1      27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5   0 Hz
SPW5           4.12529993 W
SFO2          250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
P3                15.00 usec
P4                30.00 usec
PCPD2             90.00 usec
PLW2           7.19999981 W
PLW12          0.20000000 W

F2 - Processing parameters
SI                 32768
SF            62.8952385 MHz
WDW                   EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **5**



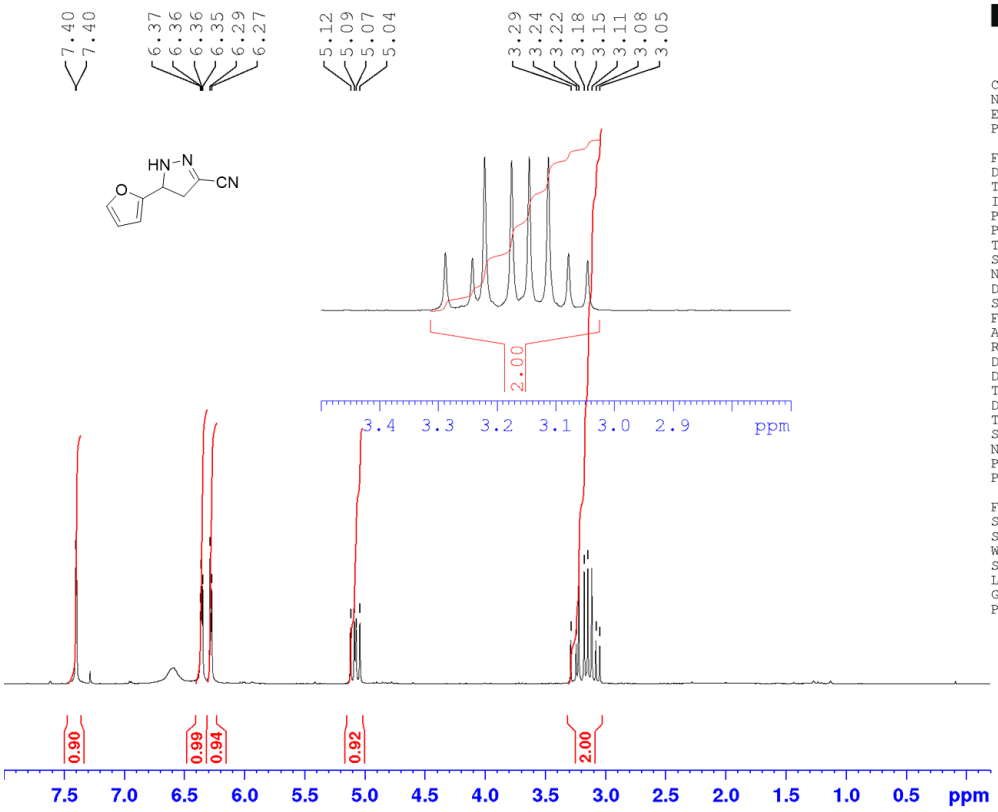

```
Current Data Parameters
NAME        jul13hmmH1_A
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190713
Time              19.30 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG           zgpg30
TD                 32768
SOLVENT            CDCl3
NS                   384
DS                     4
SWH           15120.968 Hz
FIDRES         0.922911 Hz
AQ            1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1
SFO1          62.9015281 MHz
NUC1                  13C
P1                10.00 usec
PLW1         27.00000000 W
SFO2         250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2          7.19999981 W
PLW12         0.20000000 W
PLW13         0.10044000 W

F2 - Processing parameters
SI                 32768
SF            62.8952385 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **5**

5-(furan-2-yl)-4,5-dihydro-1H-pyrazole-3-carbonitrile

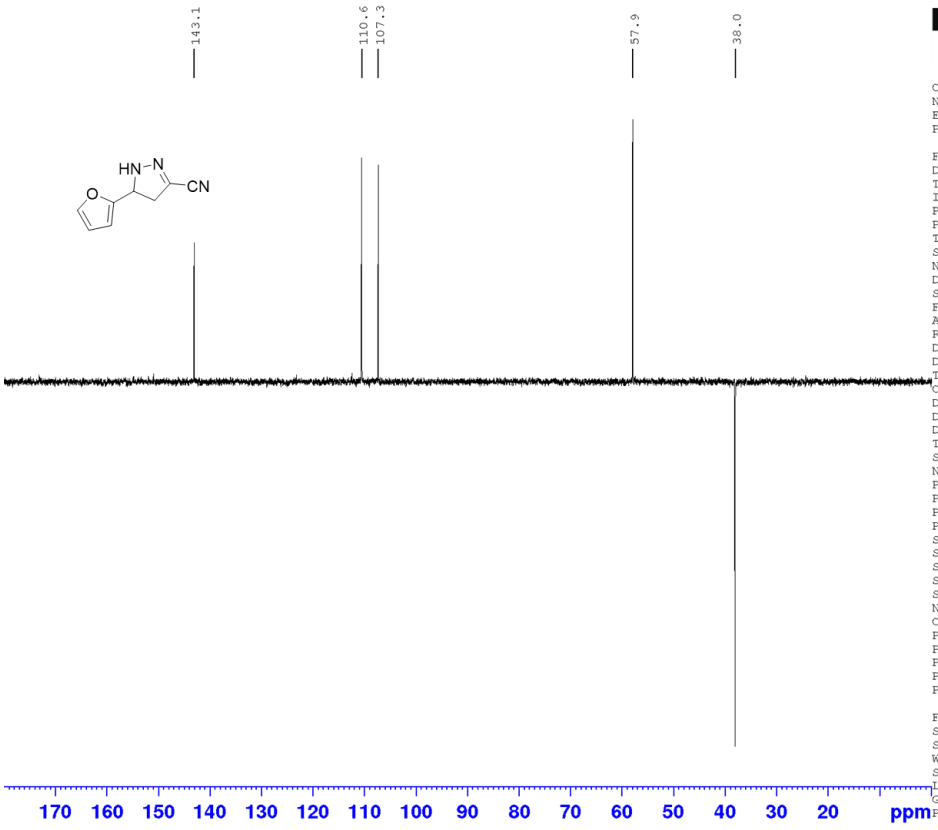



```
Current Data Parameters
NAME        jul13hmmH2_B
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190713
Time              19.35 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             5000.000 Hz
FIDRES             0.305176 Hz
AQ              3.2767999 sec
RG                 200.6
DW                100.000 usec
DE                  6.50 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1
SFO1           250.1315446 MHz
NUC1                  1H
P1                 15.00 usec
PLW1           7.19999981 W

F2 - Processing parameters
SI                 65536
SF            250.1300000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **10**

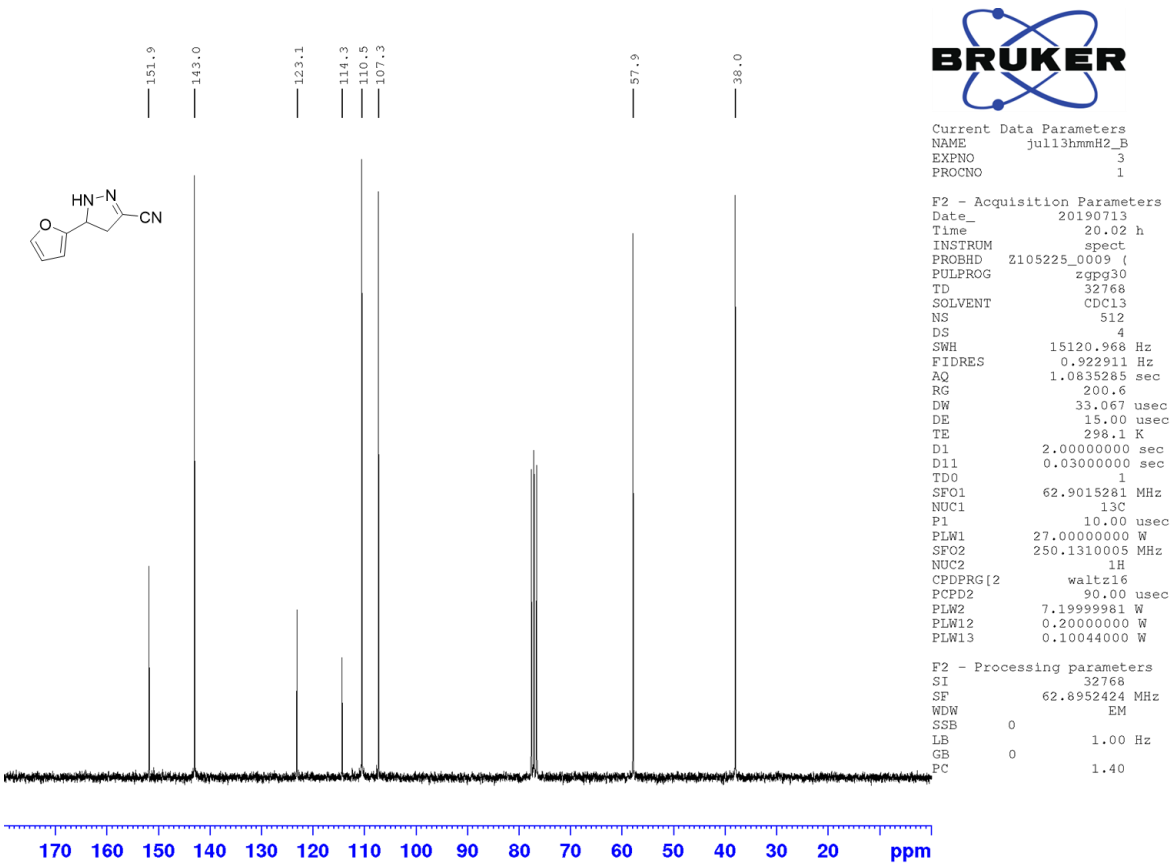



```
Current Data Parameters
NAME        jul13hmmH2_B
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190713
Time              20.10 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG         deptsp135
TD                 32768
SOLVENT            CDCl3
NS                   128
DS                     8
SWH            15120.968 Hz
FIDRES             0.922911 Hz
AQ              1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                 15.00 usec
TE                298.1 K
CNST2          145.0000000
D1              2.00000000 sec
D2              0.00344828 sec
D12             0.00002000 sec
TD0                    1
SFO1           62.9015280 MHz
NUC1                  13C
P1                 10.00 usec
P13              2000.00 usec
PLW0       0 W
PLW1        27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5            4.12529993 W
SFO2           250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
P3                 15.00 usec
P4                 30.00 usec
PCPD2              90.00 usec
PLW2            7.19999981 W
PLW12           0.20000000 W

F2 - Processing parameters
SI                 32768
SF             62.8952385 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **10**



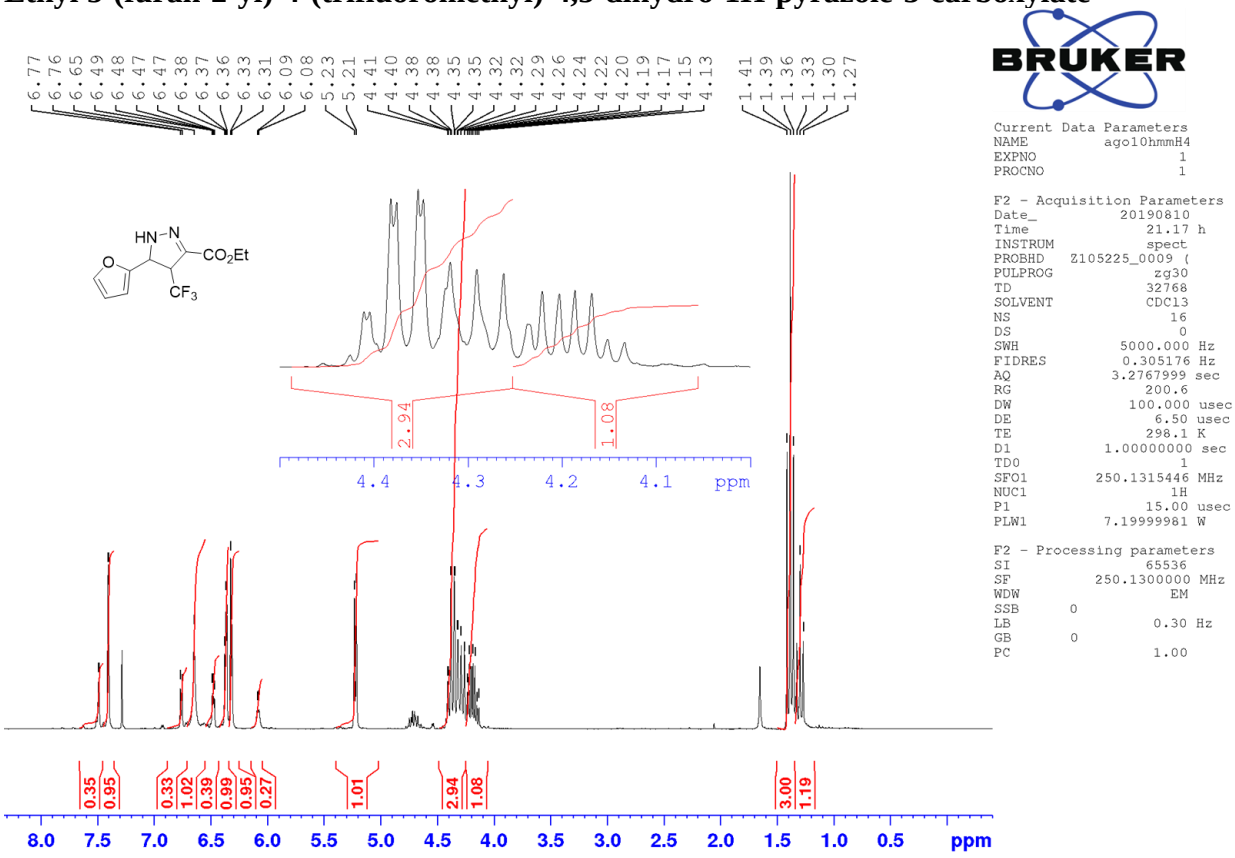

```
Current Data Parameters
NAME        jul13hmmH2_B
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190713
Time              20.02 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG          zgpg30
TD                32768
SOLVENT           CDCl3
NS                  512
DS                    4
SWH           15120.968 Hz
FIDRES         0.922911 Hz
AQ            1.0835285 sec
RG                200.6
DW               33.067 usec
DE               15.00 usec
TE                298.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1          62.9015281 MHz
NUC1                 13C
P1                10.00 usec
PLW1         27.00000000 W
SFO2         250.1310005 MHz
NUC2                 1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2          7.19999981 W
PLW12         0.20000000 W
PLW13         0.10044000 W

F2 - Processing parameters
SI                32768
SF           62.8952424 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **10**

Ethyl 5-(furan-2-yl)-4-(trifluoromethyl)-4,5-dihydro-1H-pyrazole-3-carboxylate

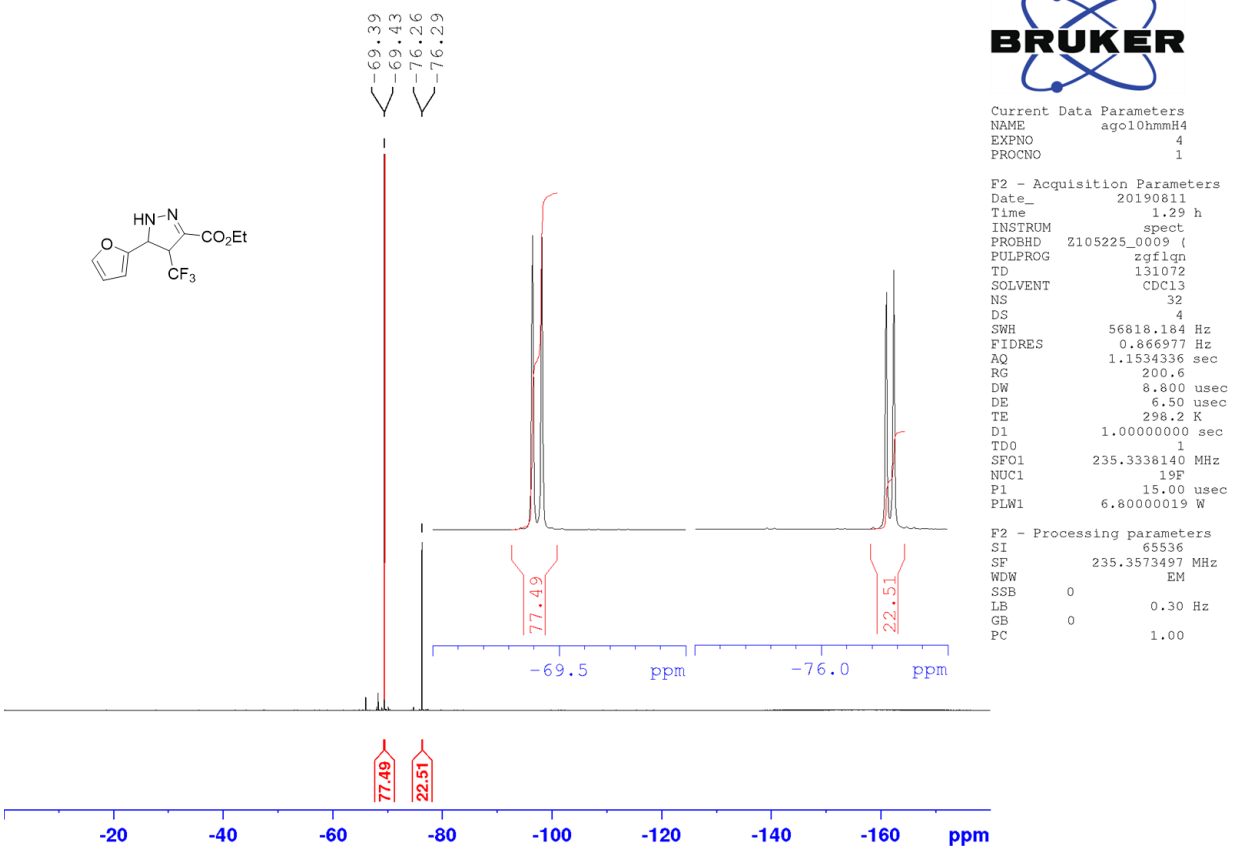



```
Current Data Parameters
NAME            ago10hmmH4
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_          20190810
Time             21.17 h
INSTRUM           spect
PROBHD    Z105225_0009 (
PULPROG           zg30
TD               32768
SOLVENT          CDCl3
NS                  16
DS                   0
SWH           5000.000 Hz
FIDRES          0.305176 Hz
AQ            3.2767999 sec
RG                200.6
DW              100.000 usec
DE                6.50 usec
TE                298.1 K
D1            1.00000000 sec
TD0                  1
SFO1         250.1315446 MHz
NUC1                1H
P1                15.00 usec
PLW1           7.19999981 W

F2 - Processing parameters
SI                65536
SF           250.1300000 MHz
WDW                  EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **15** (mixture of diastereoisomers)

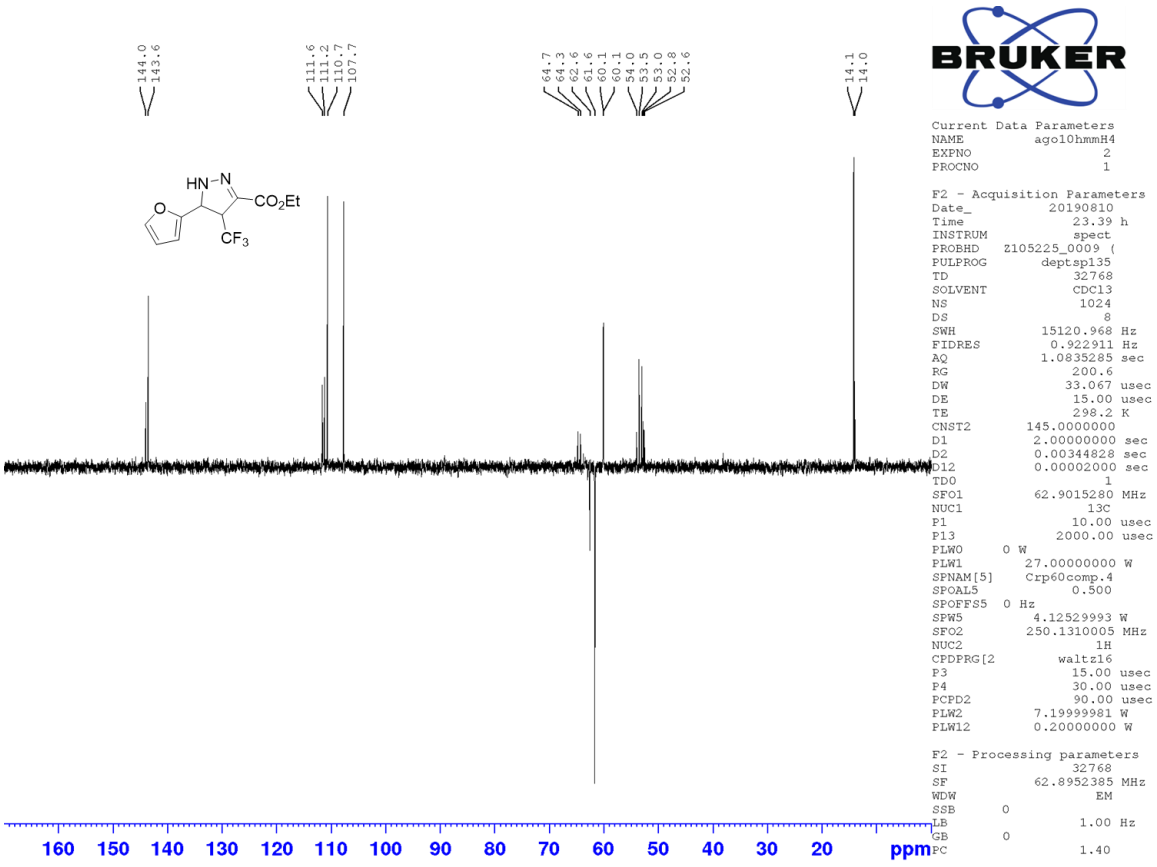



```
Current Data Parameters
NAME            ago10hmmH4
EXPNO                    4
PROCNO                   1

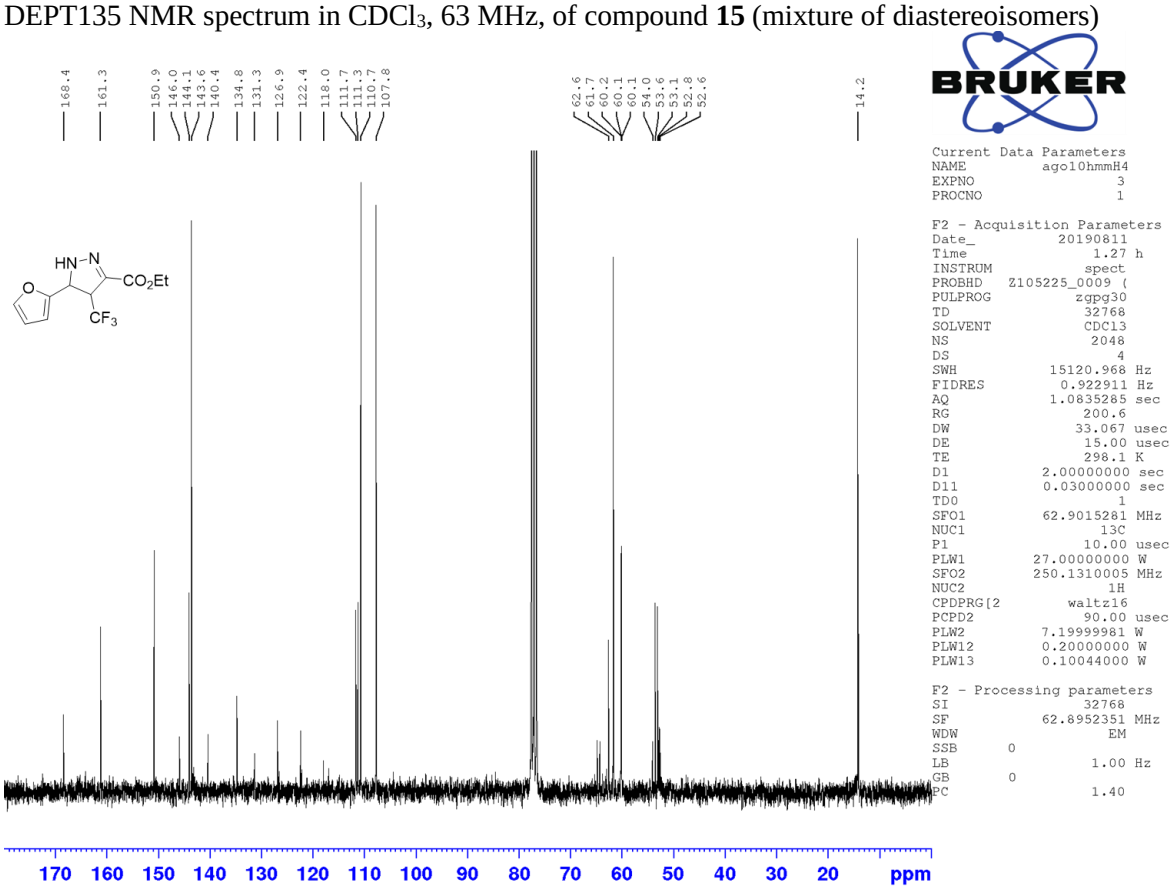
F2 - Acquisition Parameters
Date_          20190811
Time             1.29 h
INSTRUM           spect
PROBHD    Z105225_0009 (
PULPROG          zgflqn
TD              131072
SOLVENT          CDCl3
NS                  32
DS                   4
SWH          56818.184 Hz
FIDRES          0.866977 Hz
AQ            1.1534336 sec
RG                200.6
DW                8.800 usec
DE                6.50 usec
TE                298.2 K
D1            1.00000000 sec
TD0                  1
SFO1         235.3338140 MHz
NUC1                19F
P1                15.00 usec
PLW1           6.80000019 W

F2 - Processing parameters
SI                65536
SF           235.3573497 MHz
WDW                  EM
SSB       0
LB              0.30 Hz
GB        0
PC              1.00
```

^{19}F NMR spectrum in $CDCl_3$, 235 MHz, of compound **15** (mixture of diastereoisomers)

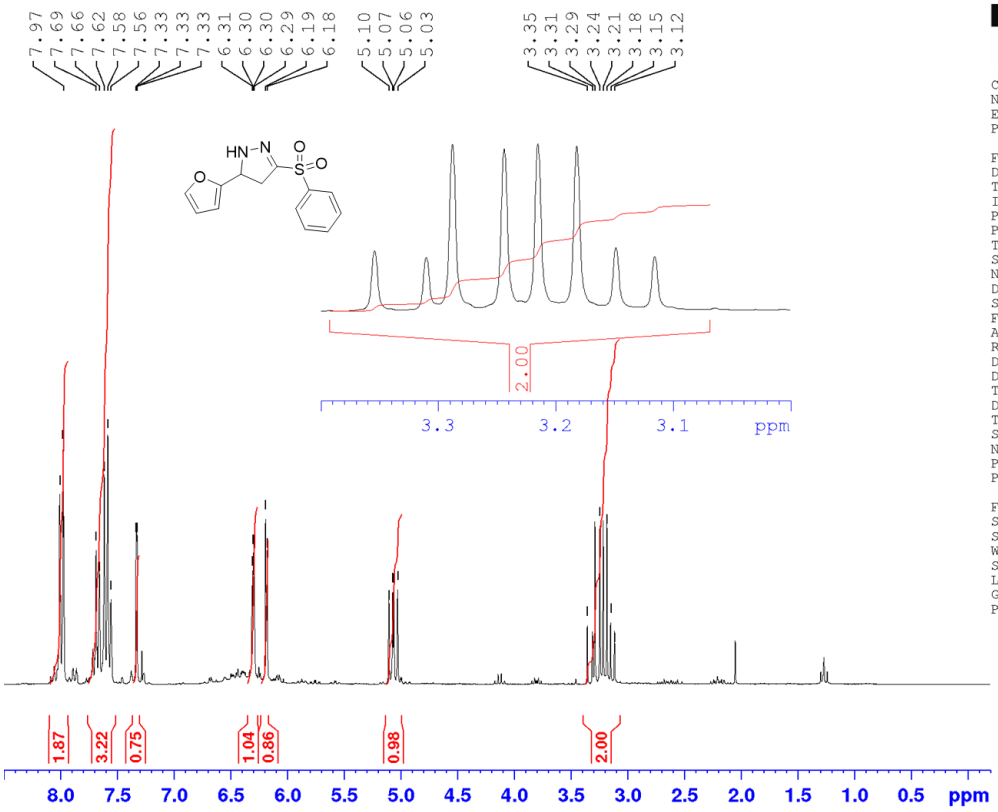


DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **15** (mixture of diastereoisomers)



^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **15** (mixture of diastereoisomers)

5-(furan-2-yl)-3-(phenylsulfonyl)-4,5-dihydro-1H-pyrazole

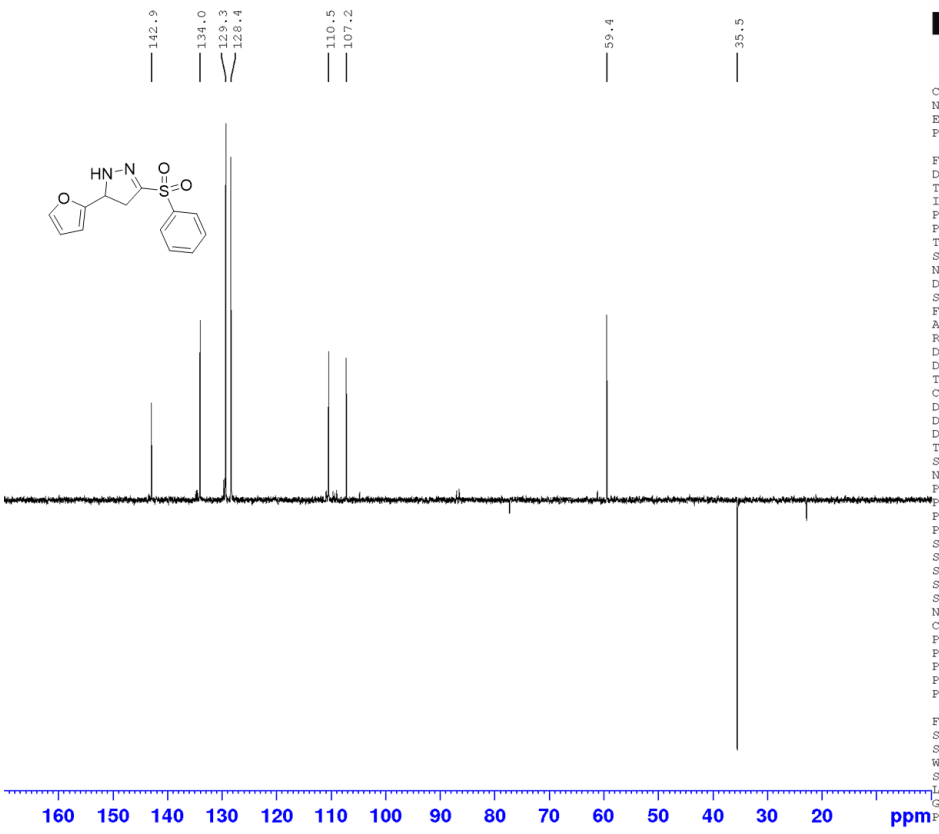



```
Current Data Parameters
NAME          ago10hmmH5
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190811
Time                1.35 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     0
SWH             5000.000 Hz
FIDRES             0.305176 Hz
AQ              3.2767999 sec
RG                  200.6
DW                100.000 usec
DE                  6.50 usec
TE                298.1 K
D1             1.00000000 sec
TD0                    1
SFO1           250.1315446 MHz
NUC1                  1H
P1                 15.00 usec
PLW1           7.19999981 W

F2 - Processing parameters
SI                 65536
SF            250.1300000 MHz
WDW                   EM
SSB       0
LB                 0.30 Hz
GB        0
PC                 1.00
```

^{1}H NMR spectrum in $CDCl_3$, 250 MHz, of compound **20**

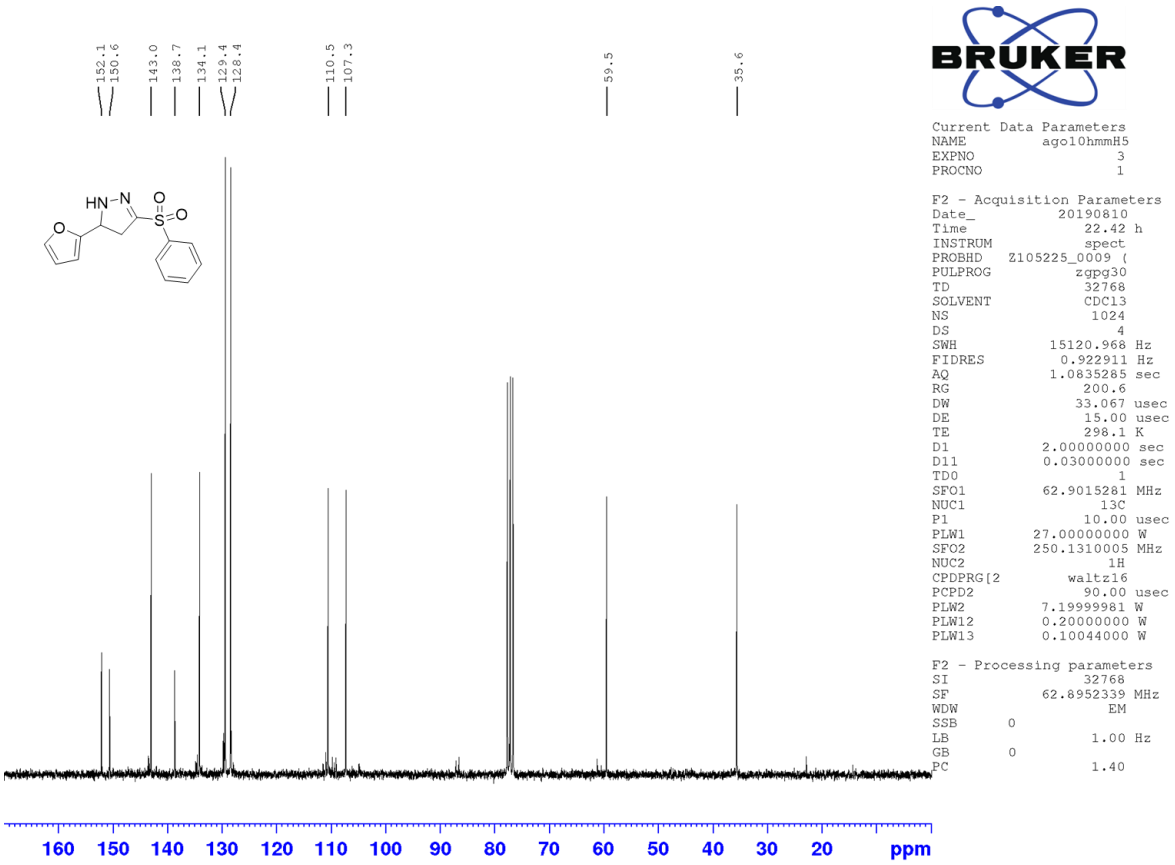



```
Current Data Parameters
NAME          ago10hmmH5
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190810
Time               21.48 h
INSTRUM            spect
PROBHD   Z105225_0009 (
PULPROG         deptsp135
TD                 32768
SOLVENT            CDCl3
NS                   512
DS                     8
SWH            15120.968 Hz
FIDRES             0.922911 Hz
AQ              1.0835285 sec
RG                  200.6
DW                33.067 usec
DE                  15.00 usec
TE                298.2 K
CNST2          145.0000000
D1              2.00000000 sec
D2              0.00344828 sec
D12             0.00002000 sec
TD0                    1
SFO1           62.9015280 MHz
NUC1                  13C
P1                 10.00 usec
P13              2000.00 usec
PLW0       0 W
PLW1        27.00000000 W
SPNAM[5]     Crp60comp.4
SPOAL5             0.500
SPOFFS5  0 Hz
SPW5            4.12529993 W
SFO2           250.1310005 MHz
NUC2                  1H
CPDPRG[2           waltz16
P3                 15.00 usec
P4                 30.00 usec
PCPD2              90.00 usec
PLW2            7.19999981 W
PLW12           0.20000000 W

F2 - Processing parameters
SI                 32768
SF             62.8952385 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

DEPT135 NMR spectrum in $CDCl_3$, 63 MHz, of compound **20**




```
Current Data Parameters
NAME          ago10hmmH5
EXPNO                  3
PROCNO                 1

F2 - Acquisition Parameters
Date_           20190810
Time               22.42 h
INSTRUM             spect
PROBHD    Z105225_0009 (
PULPROG          zgpg30
TD                 32768
SOLVENT            CDCl3
NS                  1024
DS                     4
SWH           15120.968 Hz
FIDRES         0.922911 Hz
AQ             1.0835285 sec
RG                 200.6
DW                33.067 usec
DE                15.00 usec
TE                298.1 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1          62.9015281 MHz
NUC1                  13C
P1                10.00 usec
PLW1         27.00000000 W
SFO2         250.1310005 MHz
NUC2                  1H
CPDPRG[2          waltz16
PCPD2             90.00 usec
PLW2          7.19999981 W
PLW12         0.20000000 W
PLW13         0.10044000 W

F2 - Processing parameters
SI                 32768
SF            62.8952339 MHz
WDW                   EM
SSB       0
LB                 1.00 Hz
GB        0
PC                 1.40
```

^{13}C NMR spectrum in $CDCl_3$, 63 MHz, of compound **20**

References

[1] N. M. Roda, D. N. Tran, C. Battilocchio, R. Labes, R. J. Ingham, J. M. Hawkins, S. V. Ley, *Org. Biomol. Chem.* **2015**, *13*, 2550–2554.