Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information (ESI)

for

Blue light mediated C-H arylation of heteroarenes using TiO_2 as immobilized photocatalyst in a continuous-flow microreactor

David C. Fabry,[a] Yee Ann Ho,[a] Ralf Zapf,[b] Wolfgang Tremel,[c] Martin Panthöfer,[c] Magnus Rueping,[a*] and Thomas. H. Rehm[b*]

[a] RWTH Aachen University, Institute of Organic Chemistry, Landoltweg 1, 52074 Aachen, Germany;
e-mail: magnus.rueping@rwth-aachen.de

[b] Fraunhofer ICT-IMM, Carl-Zeiss-Straße 18-20, 55129 Mainz, Germany;
e-mail : thomas.rehm@imm.fraunhofer.de

[c] Johannes Gutenberg University Mainz, Institute of Inorganic Chemistry and Analytical Chemistry, Duesbergweg 10-14, 55128 Mainz, Germany.

1. Microstructured falling film reactor

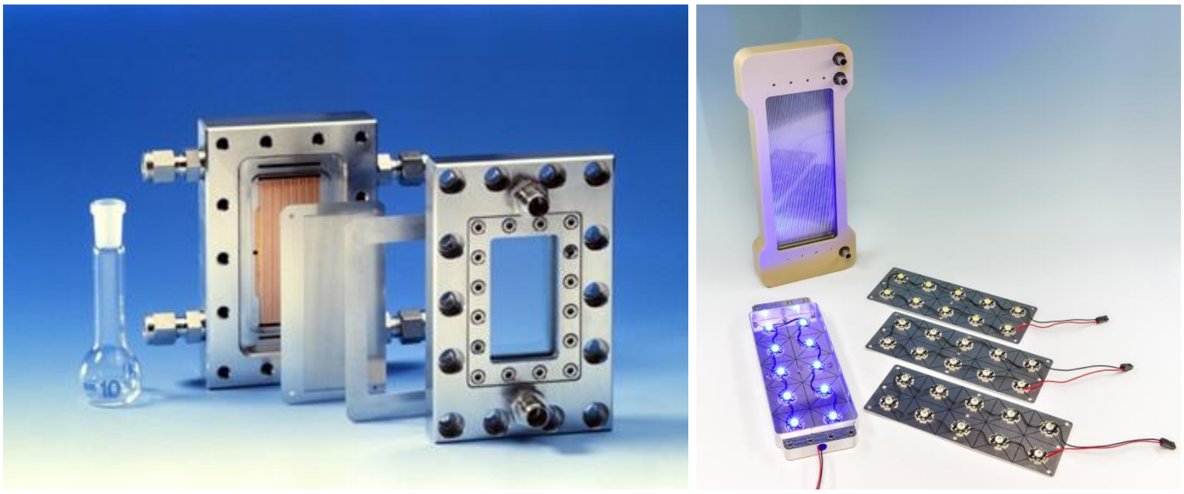


Figure S1 Fully disassembled FFMR-Standard (left) and FFMR-Large for scale-up (right; both © Fraunhofer ICT-IMM).

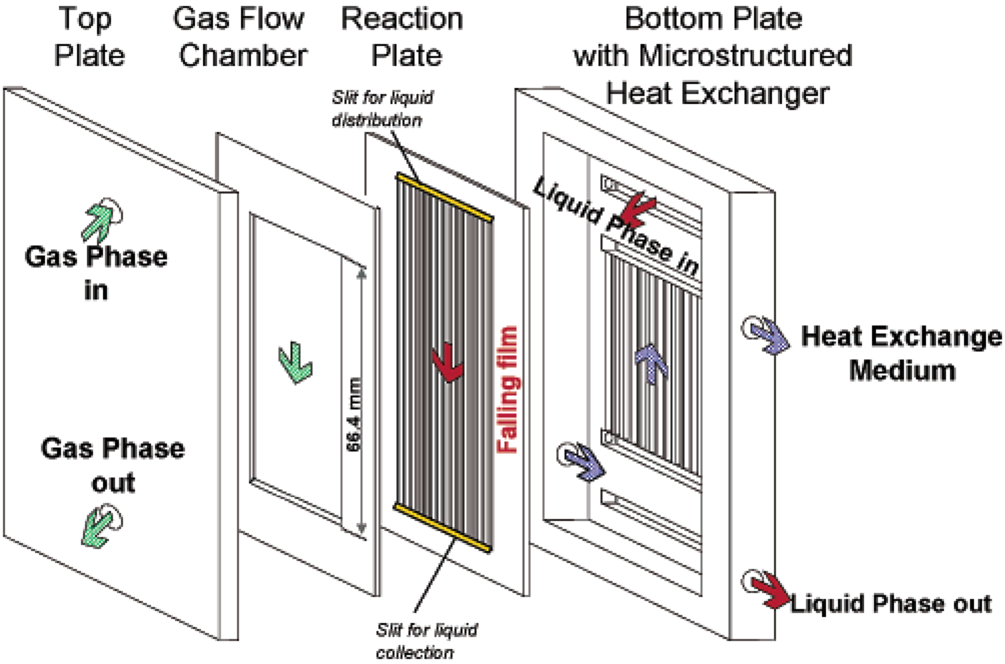


Figure S2 Working principle of the FFMR class. Reprinted (adapted) with permission from *Ind. Eng. Chem. Res.* 2005, *44,* 1742-1751. Copyright (2005) American Chemical Society.

2. Catalyst preparation and immobilisation

A slurry-washcoat process was used for the immobilization of catalyst material on the FFMR reaction plates. The preparation of TiO_2, ZnO and Bi_2O_3 washcoats was done according to literature procedures.[1,2] The method is exemplified here for TiO_2. 2.5 g of *poly*(vinyl alcohol) (PVA) used as a binder (SIGMA ALDRICH, Mowiol 40-88) were mixed with 42.5 mL of distilled water and stirred at 65 °C until PVA was completely dissolved (approx. 2-3 h). 5 g of ZnO (Alfa Aesar, 45603) and 0.375 g concentrated acetic acid were added to the solution and stirred for 3 h at 65 °C, and finally at room temperature for 2-3 days, until the suspension became homogeneous and dense.

All reaction plates were cleaned in a citric acid solution (10 wt% in water) under ultrasound treatment. After rinsing the cleaned plates with distilled water, they were heated in an oven at 800 °C. Prior to the deposition of the washcoat in the microchannels, the area on the reaction plate not to be coated with catalyst was covered with an adhesive tape. Afterwards the microchannels were completely filled with the prepared suspension and the excess of suspension was wiped off. After drying at room temperature in air, the coated plates were calcined at 450 °C for 6 h.

3. Roughness measurement

Surface roughness of the catalyst layer inside the microchannels was measured with a NanoFocus AF 2000.

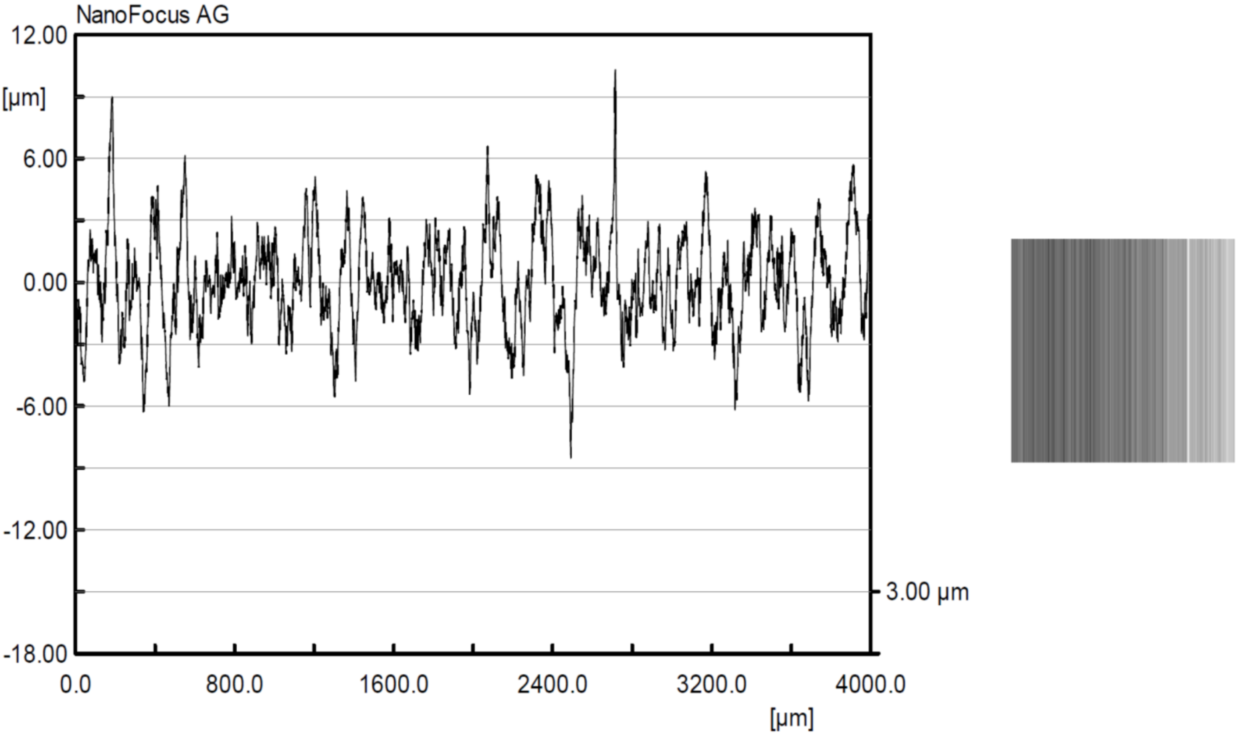
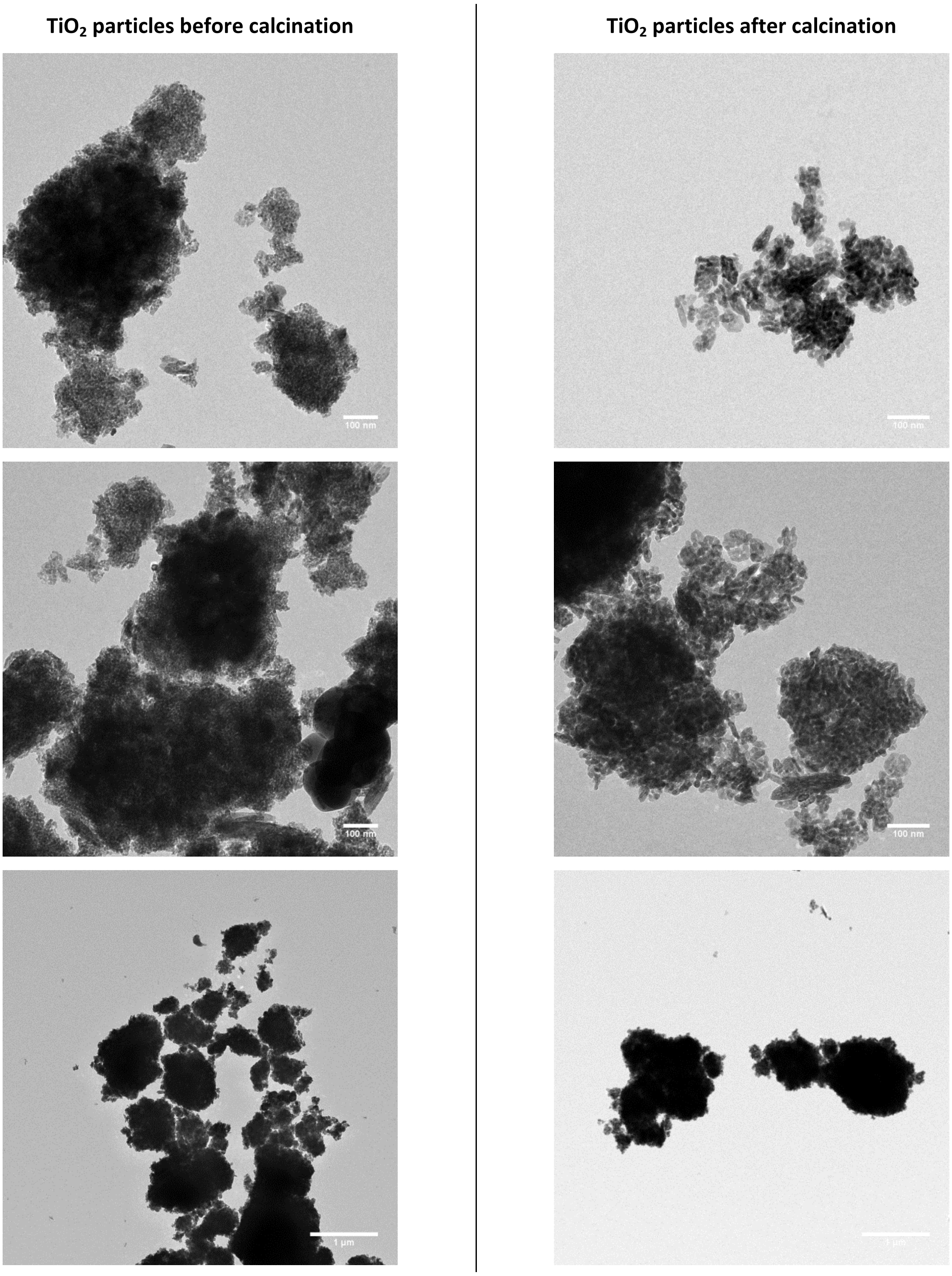


Figure S3 Surface roughness of TiO_2 catalyst material inside microchannel before use in the microreactor.

4. Transmission electron microscopy (TEM)

TEM images were recorded with a Zeiss Libra® 120 using a LaB6 cathode with 120 kV acceleration voltage. CF-300 CU copper grids with a carbon thin film were used for sample preparation.

Suspensions of TiO_2 catalyst material were prepared with ethanol as solvent (approx. 3 mg mL^{-1}) and sonicated for one minute. A drop of the suspension was placed on a copper grid. Residual suspension was removed with filter paper. As-prepared copper grids were left drying at room temperature for four hours.


TiO_2 particles before calcination

TiO_2 particles after calcination

Figure S4 TEM images of TiO_2 surface in the microchannels before (left) and after (right) calcination.

5. Low-temperature nitrogen physisorption

The specific surface area was determined by nitrogen sorption using a Sorptomatic 1990 (Carlo Erba Instruments) automatic apparatus and calculated with the BET model.

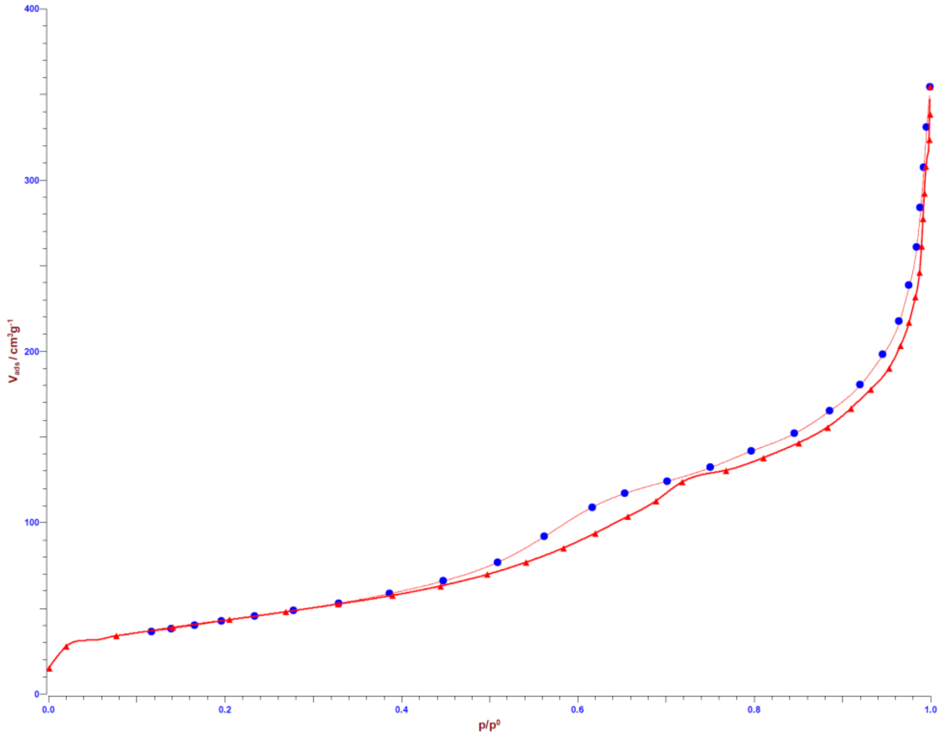


Figure S5 Nitrogen adsorption-desorption isotherm of TiO_2 sample (m_{TiO2} = 326 mg) before calcination.

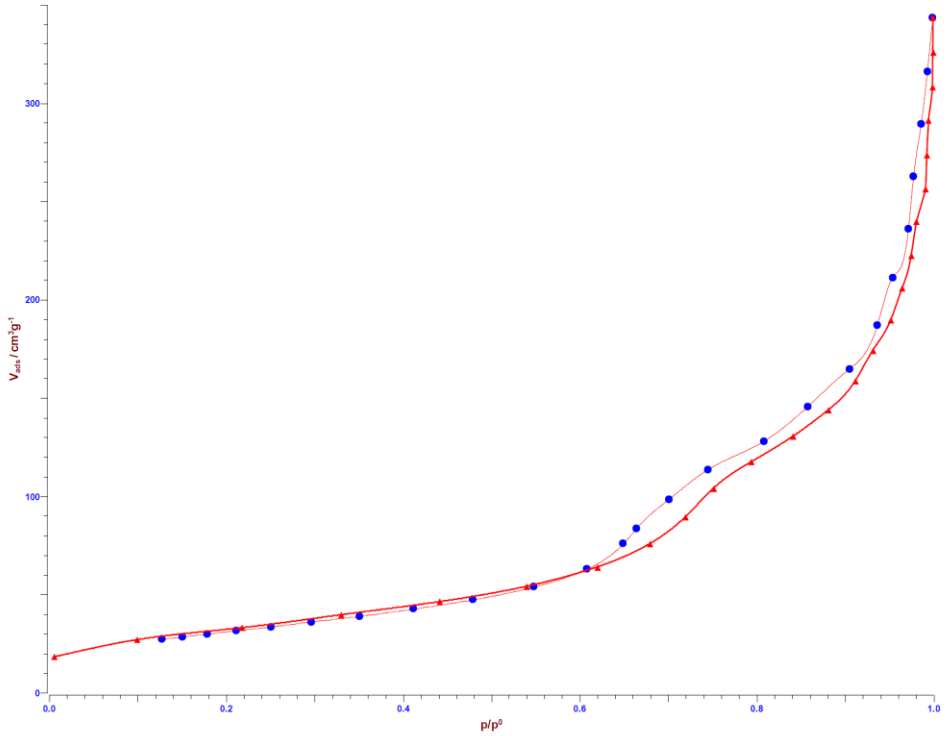


Figure S6 Nitrogen adsorption-desorption isotherm of TiO_2 sample (m_{TiO2}=558 mg) after calcination at 450 °C for 6 h.

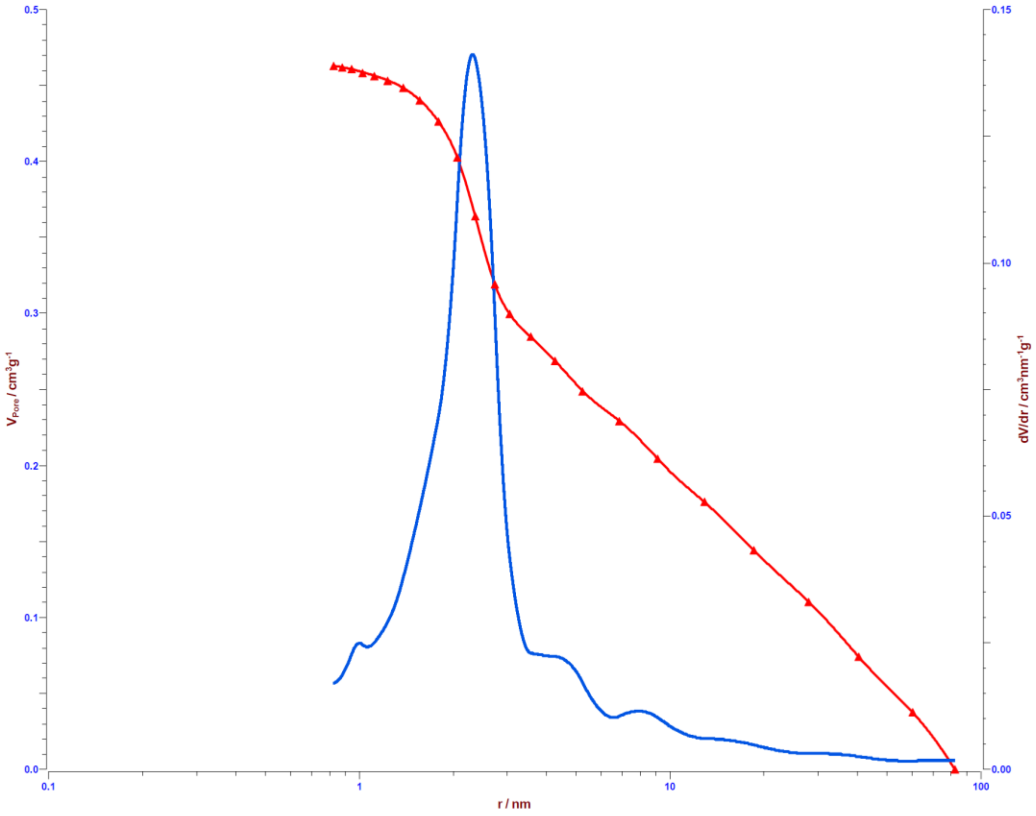


Figure S7 Pore size distribution of TiO_2 sample before calcination

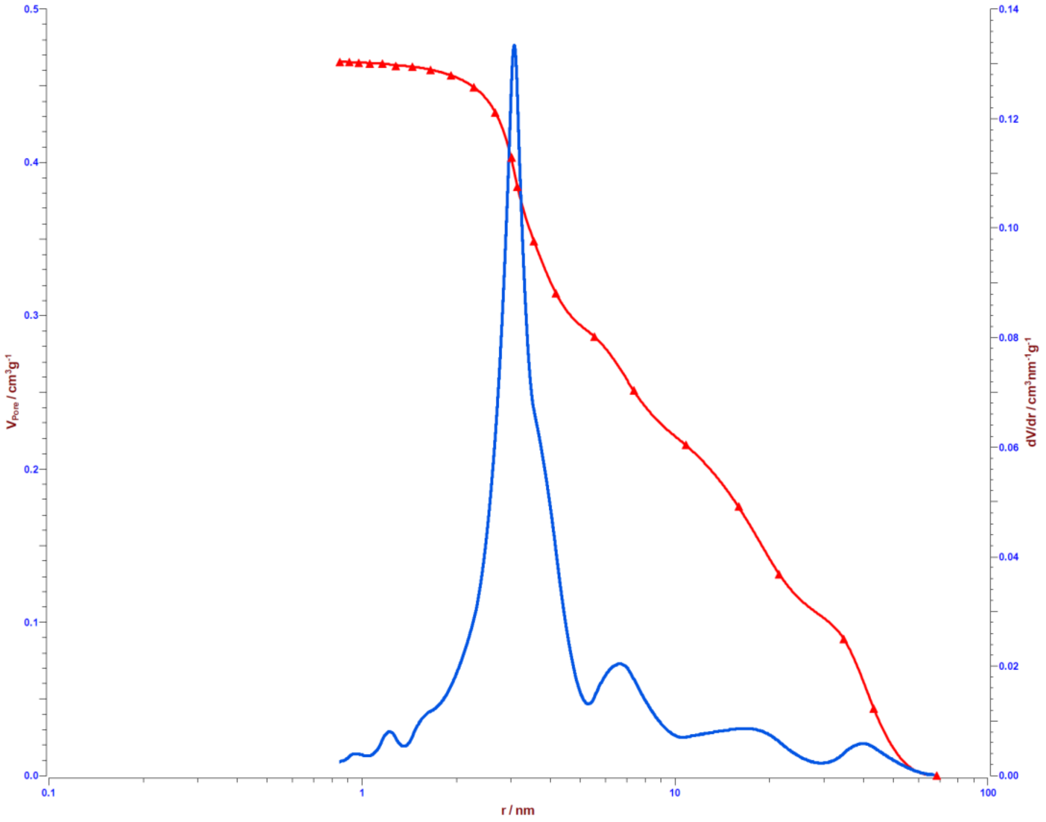


Figure S8 Pore size distribution of TiO_2 sample after calcination

6. X-Ray diffraction (XRD)

X-ray powder diffraction patterns were recorded from powders prepared between two stripes of 3m Scotch tape using a Siemens D5000 equipped with a Ge (111) monochromator (Huber 611 Guinier monochromator) and a Braun M50 position sensitive detector in transmission mode.

Full pattern fits were performed according to the Rietveld method using TOPAS Academic V6[3] applying the fundamental parameter approach[4] for profile generation. Structure models were taken from Pearson's Crystal database.[5]

Table S1 Measurement parameters for x-ray diffraction analysis.

Diffractometer	Siemens D5000, Cu-anode, Ge(111) monochromator
Sample preparation	Fine powder between two Scotch ® stripes
Measuring mode	Transmission
Wavelength / Å	1.540596
Measuring range	$10 \leq 2\Theta/° \leq 95$, $0.71 \leq Q·Å \leq 5.54$
Refinement range	$17.5 \leq 2\Theta/° \leq 85$, $1.24 \leq Q·Å \leq 5.51$
Step size /°	0.025
Step time /s	4s
Temperature /K	298K
Profile Fit	Rietveld refinement according to reported crystal structure models
Background	Chebyshev
Profile function	Fundamental Parameters Approach
Program	TOPAS Academic V6

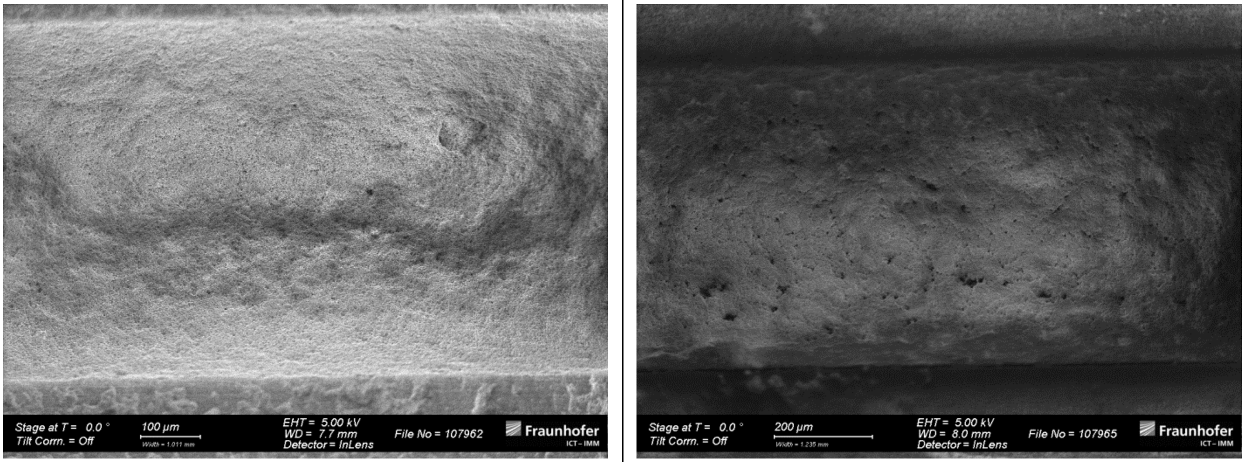
Table S2 Measurement and refinement parameters of the x-ray diffraction pattern of TiO_2 catalyst material before and after sintering process.

	before sintering	**after sintering**
Total No. of Parameters / Background	23 / 12	23 / 12
R_{wp}	2.1	2.7
GoF	1.24	1.15
TiO_2 – Anatase – *tI*12 (major)		
Space group	$I4_1/amd$	
Cell parameters /Å	a = 3.7923(4) c = 9.518(1)	
Crystallite size / nm	19(1)	25(1)
Weight fraction / %	88.9(6)	92.7(14)
Atomic parameters	Ti: 0, 0.25, 0.375 O: 0, 0.25, 0.1686	
TiO_2 – Anatase – *tI*12 (minor)		
Crystallite size / nm	> 100	> 100
Weight fraction / %	6.3(6)	4.8(13)
TiO_2 – Rutile – *tP*6		
Space group	$P4_2$/mnm	
Cell parameters /Å	a = 4.595(2) c = 2.960(3)	a = 4.595(2) c = 2.960(3)
Crystallite size / nm	> 100	> 100
Weight fraction / %	4.9(3)	2.5(4)
Atomic parameters	Ti: 0,0,0 O: 0.3056, 0.3056, 0	

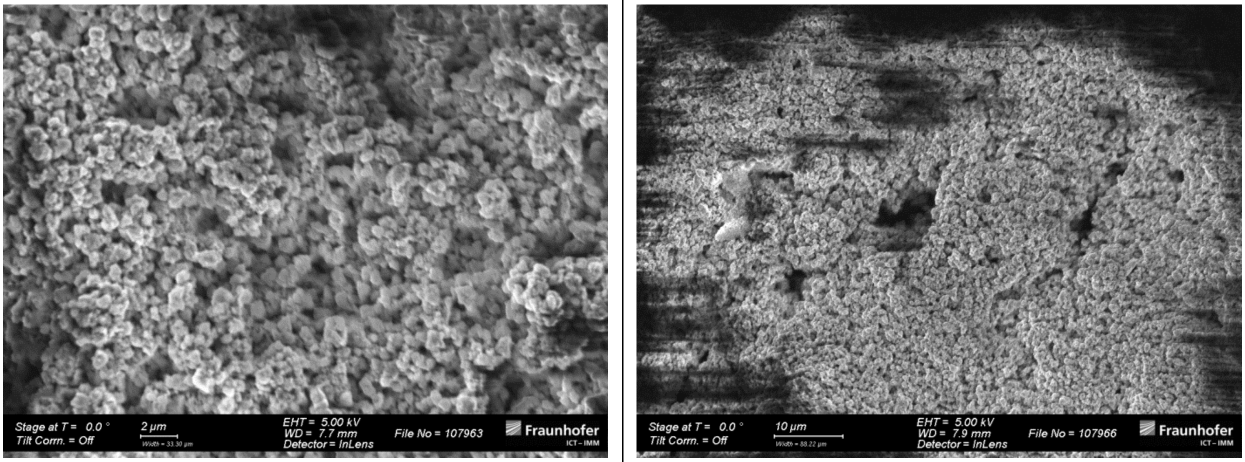
7. Scanning electron microscopy (SEM)

SEM images were taken with a ZEISS Leo 1550 VP Field Emission Scanning Electron Microscope. The reaction plates containing TiO_2 as immobilized photocatalyst were scanned without any sample preparation. Acceleration voltage was 5.00 kV, working distance was between 7.7 and 8.0 mm.

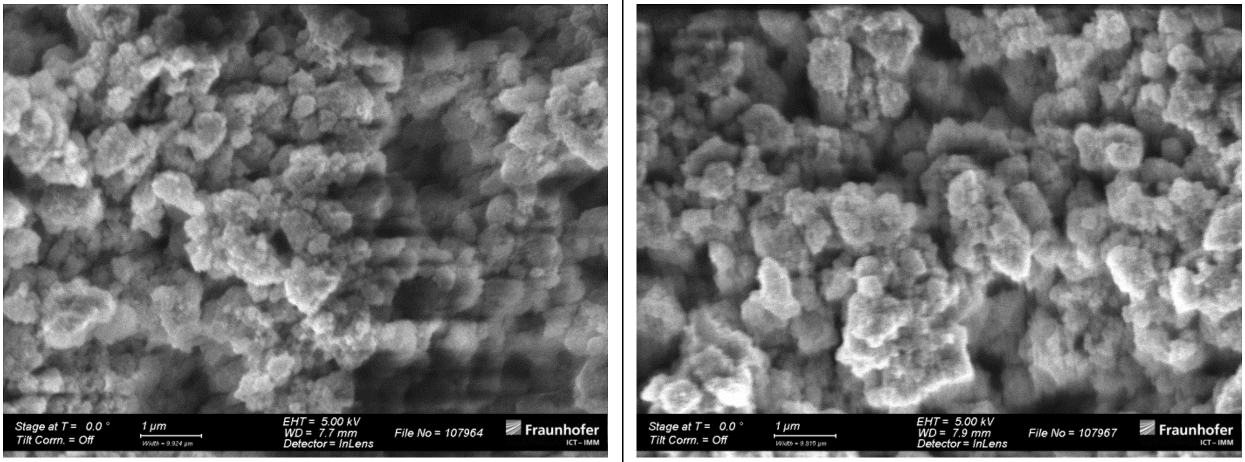
Fresh catalyst on reaction plate | **Used catalyst on reaction plate**



Magnification: 297 | Magnification: 243



Magnification: 9010 | Magnification: 3401

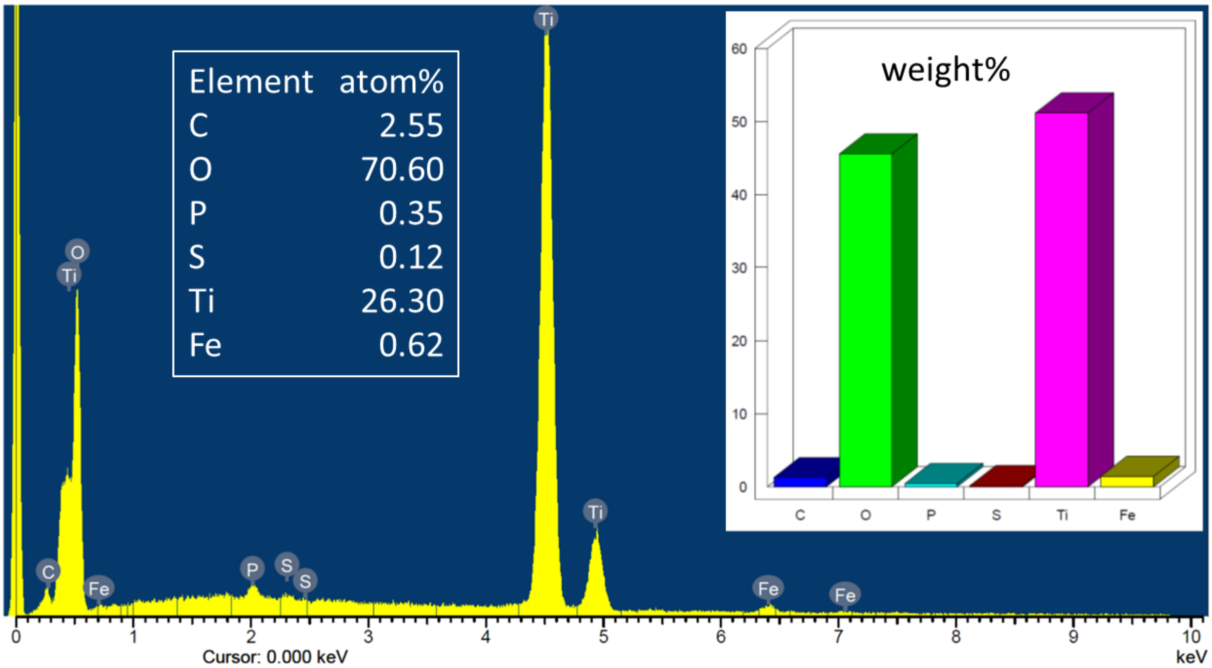


Magnification: 30229 | Magnification: 30567

Figure S9 SEM images of TiO_2 surface in the microchannels before (left) and after (right) calcination.

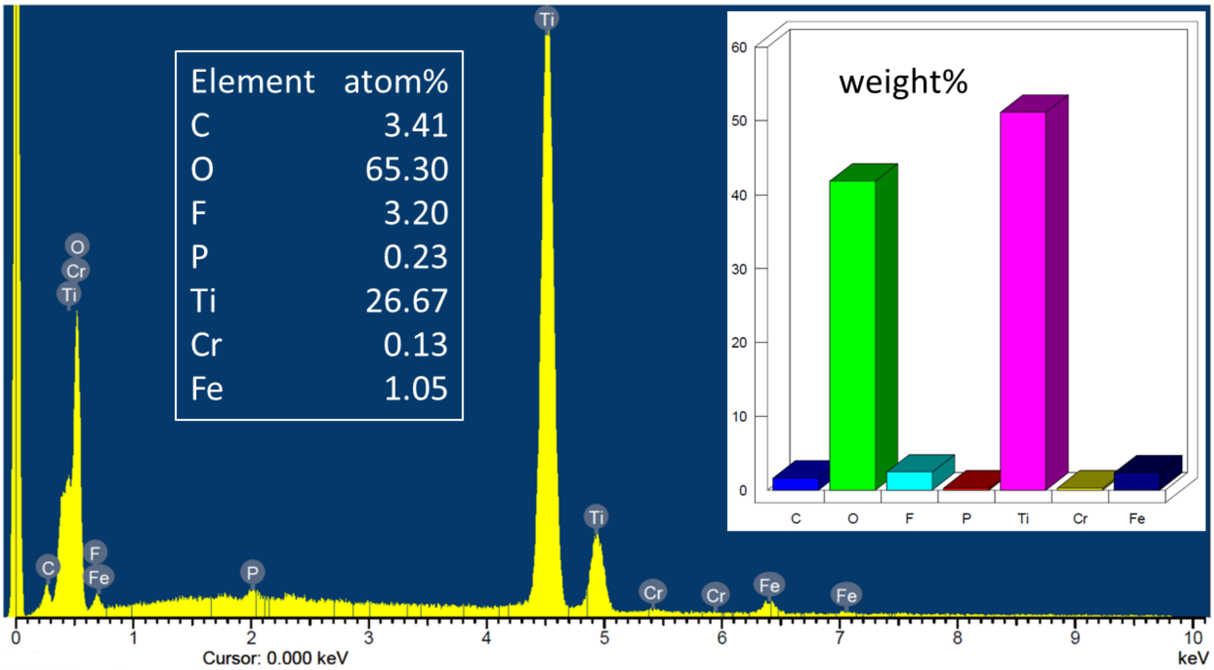
8. Energy Dispersive X-ray (EDX) analysis

Energy Dispersive X-ray (EDX) analysis was performed with an Oxford INCA II setup.



Element	atom%
C	2.55
O	70.60
P	0.35
S	0.12
Ti	26.30
Fe	0.62

Figure S10 EDX spectrum of catalyst material calcined inside a microchannel before use in the FFMR.

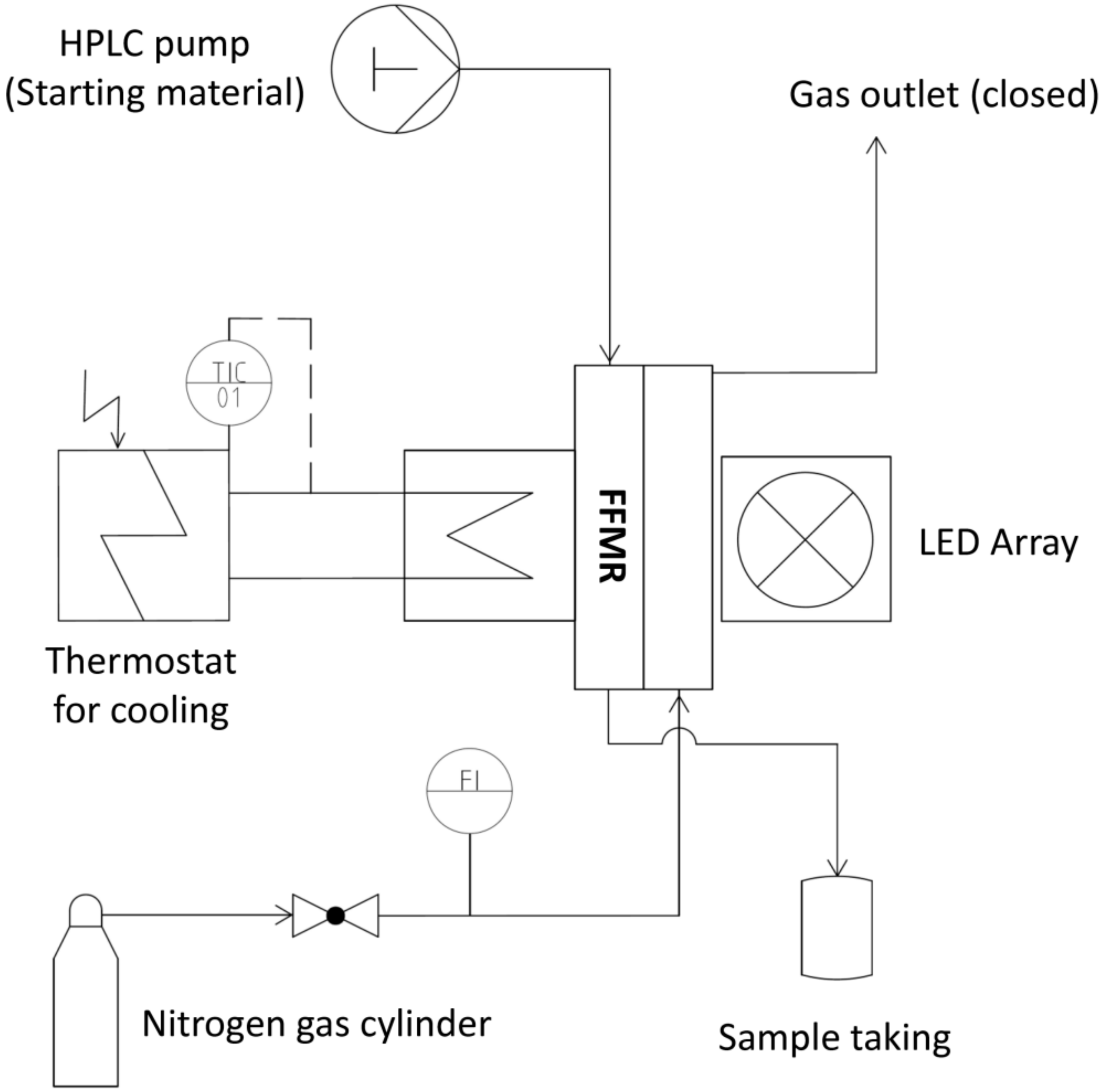


Element	atom%
C	3.41
O	65.30
F	3.20
P	0.23
Ti	26.67
Cr	0.13
Fe	1.05

Figure S11 EDX spectrum of catalyst material calcined inside a microchannel after use in the FFMR.

9. Lab plant description and flow chart

The heat exchanger of the FFMR is connected to a water-filled thermostat (Huber CC304/CC1) for maintaining the temperature of the reactor at 20 °C. The starting material solution is pumped with a HPLC pump (Knauer K-501) into the reactor with a flow rate of f_{liq} = 0.5 mL min^{-1}. A nitrogen gas stream is fed from the in-house installed gas line via a pressure regulator to a mechanical rotameter with a final gas flow rate of approx. f_{gas} = 10 mL min^{-1}. Actinic blue (λ_{max} = 410 nm), royal-blue (λ_{max} = 455 nm) and cold-white (6500 K) LEDs (GeTian Opto-Electronics CO., LTD) are installed on an aluminium heat sink, which can be fixed magnetically in front of the inspection window of the FFMR. Current and voltage for the LED array were adjusted with a standard power supply (Basetech BT-305) and fixed at I = 350 mA and U = 6.8 V.



Scheme S1 Simplified flow chart of FFMR lab plant used for photochemically catalyzed C-H arylations of heteroarenes.

10. General procedure for the synthesis of aryldiazonium salts

The corresponding aniline (50 mmol) was dissolved in a mixture of deionized water (20 mL) and 50% tetrafluoroboric acid (1 eq). The reaction mixture was cooled to 0 °C and sodium nitrite (1 eq in deionized water) was added drop wise over a period of 10 min. Afterwards, the mixture was stirred for 40 min, the resulting precipitate was filtered off, dissolved in acetone and recrystallized by addition of diethyl ether. The resulting solid was washed with diethyl ether and dried in vacuo.

11. Procedure for the synthesis of dantrolene

1-Aminohydantoin (1.1 mmol, 1.1 equiv.) in 0.67 M HCl was added to a solution of 5-(4-nitrophenyl)furan-2-carbaldehyde (1 equiv, 1.0 mmol) in DMF (5 mL) at 0 °C and the mixture was stirred for 1 h at room temperature. Water (10 mL) was added and the formed precipitate filtered and washed with water (50 mL). The collected solid was dried under reduced pressure to give dantrolene (301 mg, 96%).

12. ^{19}F NMR analysis during long-term run

^{19}F NMR spectra (256 scans) were recorded with a NMReady 60e© benchtop NMR spectrometer from Nanalysis Corporation. Spectra were handled with ACD/NMR Processor Academic Edition V12.01.

Long-term run

The long-term run was performed with 4-trifluoromethylbenzene diazonium salt (50 mM) in EtOH and pyridine as heteroarene (1/1, v/v). Samples (600 µL) of the reaction solution were directly taken from the reactor outlet and mixed with the internal standard (4-trifluoromethylbenzyl alcohol, 50 µL, 1 M in DMSO-d_6).

Internal standard 4-trifluoromethylbenzyl alcohol: ^{19}F NMR (56 MHz) δ = -65.99; s, 3F
Intermediate diazoether of **1e** with EtOH: ^{19}F NMR (56 MHz) δ = -66.28; s
Product 2-(4-(trifluoromethyl)phenyl)pyridine **7e**: ^{19}F NMR (56 MHz) δ = -66.44; s

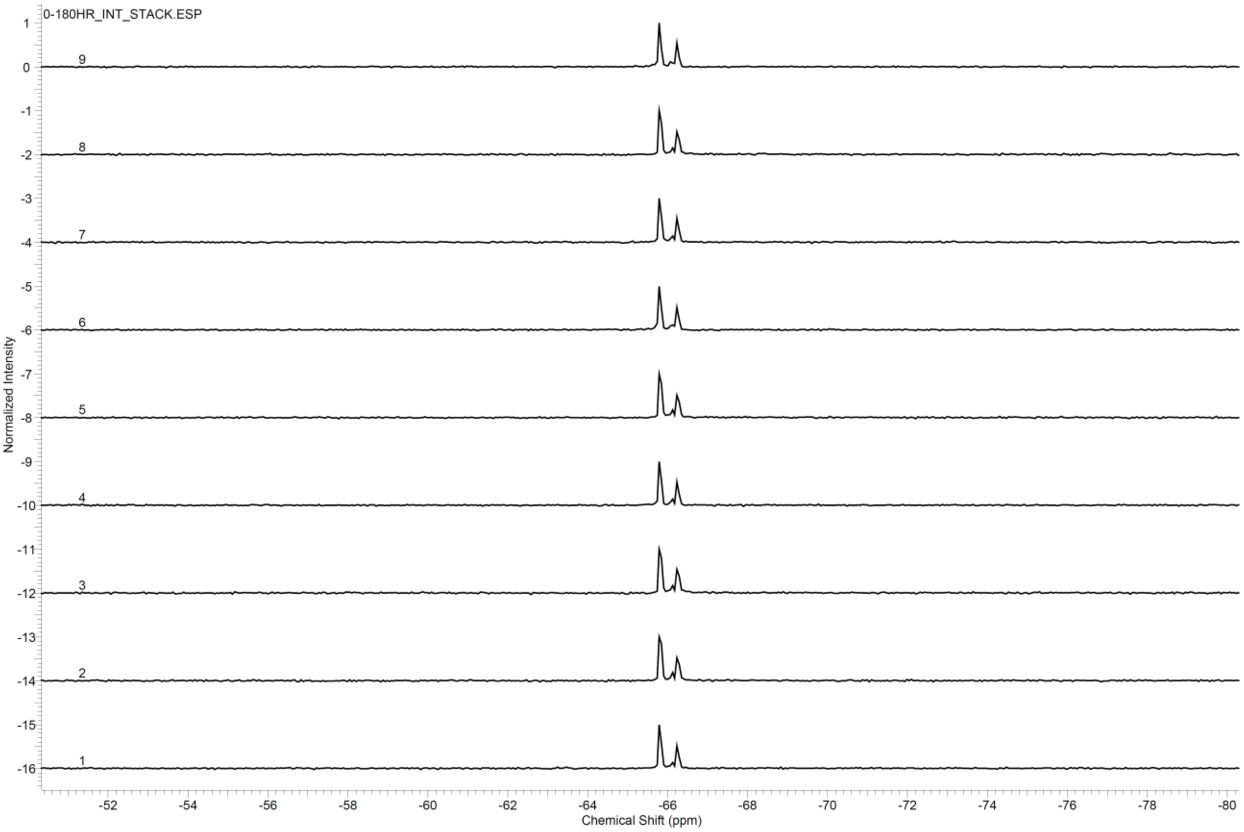
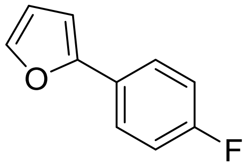


Figure S12 Stacked plot of ^{19}F NMR spectra from long-term run (time from bottom to top: 1, 10, 20, 30, 60, 90, 120, 150, 180 minutes).

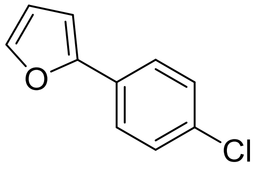
13. Product characterization

2-(4-fluorophenyl)furan[6]



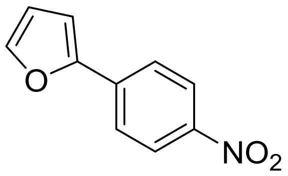
colourless solid; ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.64 (ddd, J = 8.9, 5.6, 2.9 Hz, 2H), 7.46 (d, J = 1.2 Hz, 1H), 7.10-7.06 (m, 2H), 6.58 (d, J = 3.3 Hz, 1H), 6.47 (dd, J = 3.2, 1.8 Hz, 1H); ^{13}C NMR (151 MHz; $CDCl_3$): δ 162.1 (d, J = 243.86 Hz), 153.1, 142.0, 127.3 (d, J = 2.26 Hz), 125.5 (d, J = 8.40 Hz), 115.7 (d, J = 21.94 Hz), 111.7, 104.6; ^{19}F NMR (564 MHz; $CDCl_3$): δ -114.5.

2-(4-chlorophenyl)furan[6]



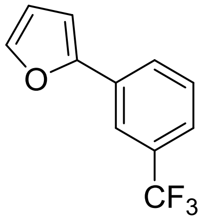
colourless solid; ^{1}H-NMR (400 MHz; $CDCl_3$): δ 7.60-7.56 (m, 2H), 7.45 (dd, J = 1.8, 0.6 Hz, 1H), 7.35-7.31 (m, 2H), 6.63-6.62 (m, 1H), 6.46 (dd, J = 3.4, 1.8 Hz, 1H); ^{13}C NMR (151 MHz; $CDCl_3$): δ 152.9, 142.3, 132.9, 129.3, 128.8, 125.0, 111.7, 105.4.

2-(4-nitrophenyl)furan[6]



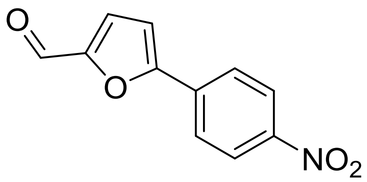
yellow solid; ^{1}H-NMR (400 MHz; $CDCl_3$): δ 8.25-8.22 (m, 2H), 7.80-7.76 (m, 2H), 7.56 (t, J = 0.9 Hz, 1H), 6.86 (dd, J = 3.5, 0.6 Hz, 1H), 6.54 (dd, J = 3.5, 1.8 Hz, 1H); ^{13}C NMR (151 MHz; $CDCl_3$): δ 151.7, 146.4, 144.1, 136.4, 124.3, 123.9, 112.4, 108.9.

2-(3-trifluoromethylphenyl)furan[7]



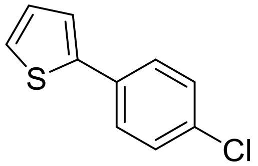
colourless solid; ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.92 (s, 1H), 7.84-7.83 (m, 1H), 7.51-7.48 (m, 3H), 6.74 (d, J = 3.3 Hz, 1H), 6.51 (dd, J = 3.4, 1.8 Hz, 1H); ^{13}C NMR (151 MHz; $CDCl_3$): δ 152.4, 142.8, 131.5, 131.0 (t, J = 32.87 Hz), 129.1, 126.7, 124.0 (q, J = 272.24 Hz), 123.7 (q , J = 3.71 Hz), 120.5 (q, J = 3.77 Hz), 111.9, 106.3; ^{19}F NMR (564 MHz; $CDCl_3$): δ -62.9.

5-(4-nitrophenyl)furan-2-carbaldehyde[6]



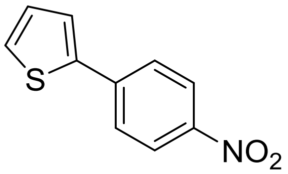
yellow oil; ^{1}H-NMR (600 MHz; $CDCl_3$): δ 9.74 (s, 1H), 8.32 (d, J = 8.8 Hz, 2H), 7.98 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 3.7 Hz, 1H), 7.04 (d, J = 3.8 Hz, 1H); ^{13}C NMR (151 MHz; $CDCl_3$): δ 177.6, 156.3, 153.0, 134.5, 124.4, 115.0, 110.6, 83.1.

2-(4-chlorophenyl)thiophen[6]



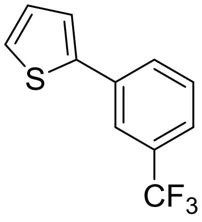
colourless solid; ^{1}H-NMR (600 MHz; $CDCl_3$): δ 7.55-7.52 (m, 2H), 7.37-7.33 (m, 2H), 7.29 (dd, J = 4.3, 1.8 Hz, 2H), 7.08 (dd, J = 4.8, 3.9 Hz, 1H); ^{13}C NMR (151 MHz; $CDCl_3$): δ 143.1, 133.2, 132.9, 129.0, 128.1, 127.1, 125.2, 123.4.

2-(4-nitrophenyl)thiophen[6]



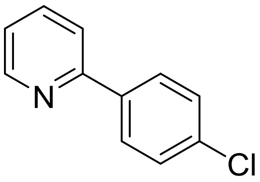
colourless solid; ^{1}H-NMR (600 MHz; CDCl$_3$): δ 8.24 (dd, *J* = 9.1, 2.1 Hz, 2H), 7.75-7.73 (m, 2H), 7.48 (d, *J* = 3.7 Hz, 1H), 7.45-7.44 (m, 1H), 7.15 (dd, *J* = 5.0, 3.7 Hz, 1H); ^{13}C NMR (151 MHz; CDCl$_3$): δ 141.6, 140.6, 128.7, 127.7, 126.0, 125.7, 124.4.

2-(3-trifluoromethylphenyl)thiophen[8]



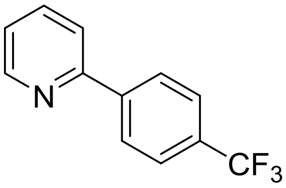
colourless solid; ^{1}H-NMR (400 MHz; CDCl$_3$): δ 7.84 (d, *J* = 4.8 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.51-7.48 (m, 2H), 7.36 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.33 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.10 (dd, *J* = 5.1, 3.6 Hz, 1H).; ^{13}C NMR (151 MHz; CDCl$_3$): δ 142.6 ,135.2 (d, *J* = 32.17 Hz), 129.3, 129.1, 128.2, 128.0 (q, *J* = 248 Hz), 125.8, 124.1, 123.9 (q, *J* = 4.01 Hz), 122.5 (q, *J* = 3.94 Hz); ^{19}F NMR (564 MHz; CDCl$_3$): δ -62.8.

2-(4-chlorophenyl)pyridine[6]



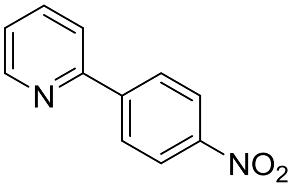
colourless solid; ^{1}H-NMR (400 MHz; CDCl$_3$): δ 8.65 (d, *J* = 4.7 Hz, 1H), 7.92-7.90 (m, 2H), 7.70 (td, *J* = 7.6, 1.7 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.42-7.40 (m, 2H), 7.20 (ddd, *J* = 7.2, 4.9, 1.2 Hz, 1H); ^{13}C NMR (101 MHz; CDCl$_3$): δ 156.1, 149.7, 137.8, 136.8, 135.0, 128.9, 128.1, 122.3, 120.2.

2-(4-(trifluoromethyl)phenyl)pyridine[9]



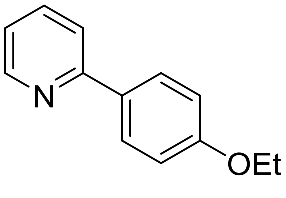
off-white solid; ^{1}H-NMR (400 MHz; CDCl$_3$): δ 8.71 (ddd, *J* = 4.8, 1.6, 1.1 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 2H), 7.80-7.70 (m, 4H), 7.28 (ddd, *J* = 6.9, 5.0, 1.8 Hz, 1H); ^{13}C NMR (101 MHz; CDCl$_3$): δ 155.8, 149.9, 142.6, 136.9, 130.6 (q, *J* = 32 Hz), 127.1, 125.6 (q, *J* = 4 Hz), 122.9, 120.8; ^{19}F NMR (376 MHz; CDCl$_3$): δ -62.6.

2-(4-nitrophenyl)pyridine[6]



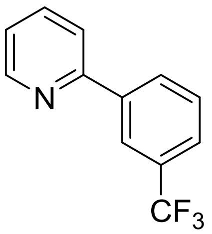
yellow solid; ^{1}H-NMR (400 MHz; CDCl$_3$): δ 8.71 (ddd, *J* = 4.8, 1.6, 1.1 Hz, 1H), 8.09 (d, *J* = 8.1 Hz, 2H), 7.80-7.70 (m, 4H), 7.28 (ddd, *J* = 6.9, 5.0, 1.8 Hz, 1H); ^{13}C NMR (101 MHz; CDCl$_3$): δ 154.8, 150.1, 148.1, 145.2, 137.1, 127.7, 124.0, 123.5, 121.2

2-(4-ethoxyphenyl)pyridine[10]



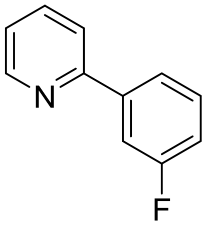
colourless solid; ^{1}H-NMR (400 MHz; CDCl$_3$): δ 8.63 (dd, *J* = 4.8, 1.0 Hz, 1H), 7.93-7.90 (m, 2H), 7.71-7.63 (m, 2H), 7.15 (ddd, *J* = 7.0, 4.9, 1.5 Hz, 1H), 6.98-6.95 (m, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz; CDCl$_3$): δ 159.8, 157.1, 149.5, 136.6, 131.8, 128.1, 121.3, 119.7, 114.7, 114.6, 63.5, 14.8.

2-(3-(trifluoromethyl)phenyl)pyridine[10]



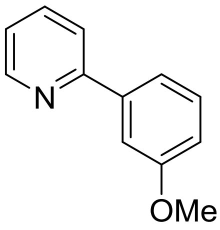
colourless solid; ^{1}H-NMR (400 MHz; CDCl$_3$): δ 8.71 (d, *J* = 4.8 Hz, 1H), 8.27 (s, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.80-7.73 (m, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.27 (ddd, *J* = 6.8, 5.0, 1.6 Hz, 1H); ^{13}C NMR (101 MHz; CDCl$_3$): δ 155.8, 149.8, 140.1, 137.0, 131.2 (q, *J* = 32.00 Hz), 130.0, 129.2, 123.8 (q, *J* = 3.89 Hz), 125.5 (q, *J* = 3.94 Hz), 122.8, 120.6; ^{19}F NMR (376 MHz; CDCl$_3$): δ -62.7.

2-(3-fluorophenyl)pyridine[11]



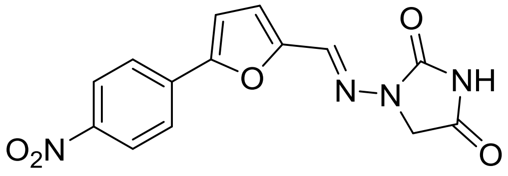
colourless solid; ^{1}H-NMR (400 MHz; CDCl$_3$): δ 8.68 (d, *J* = 4.5 Hz, 1H), 7.78-7.68 (m, 4H), 7.41 (td, *J* = 7.9, 6.0 Hz, 1H), 7.26-7.23 (m, 1H), 7.09 (td, *J* = 8.3, 2.2 Hz, 1H); ^{13}C NMR (101 MHz; CDCl$_3$): δ 163.2 (d, *J* = 248.55 Hz), 155.9 (d, *J* = 2.50 Hz), 149.5, 141.4 (d, *J* = 7.40 Hz), 137.0, 130.2 (d, *J* = 8.15 Hz), 122.7, 122.4 (d, *J* = 2.55 Hz), 120.6, 115.8 (d, *J* = 21.48 Hz), 113.9 (d, *J* = 22.85 Hz); ^{19}F NMR (376 MHz; CDCl3): δ -113.0.

2-(3-methoxyphenyl)pyridine[12]



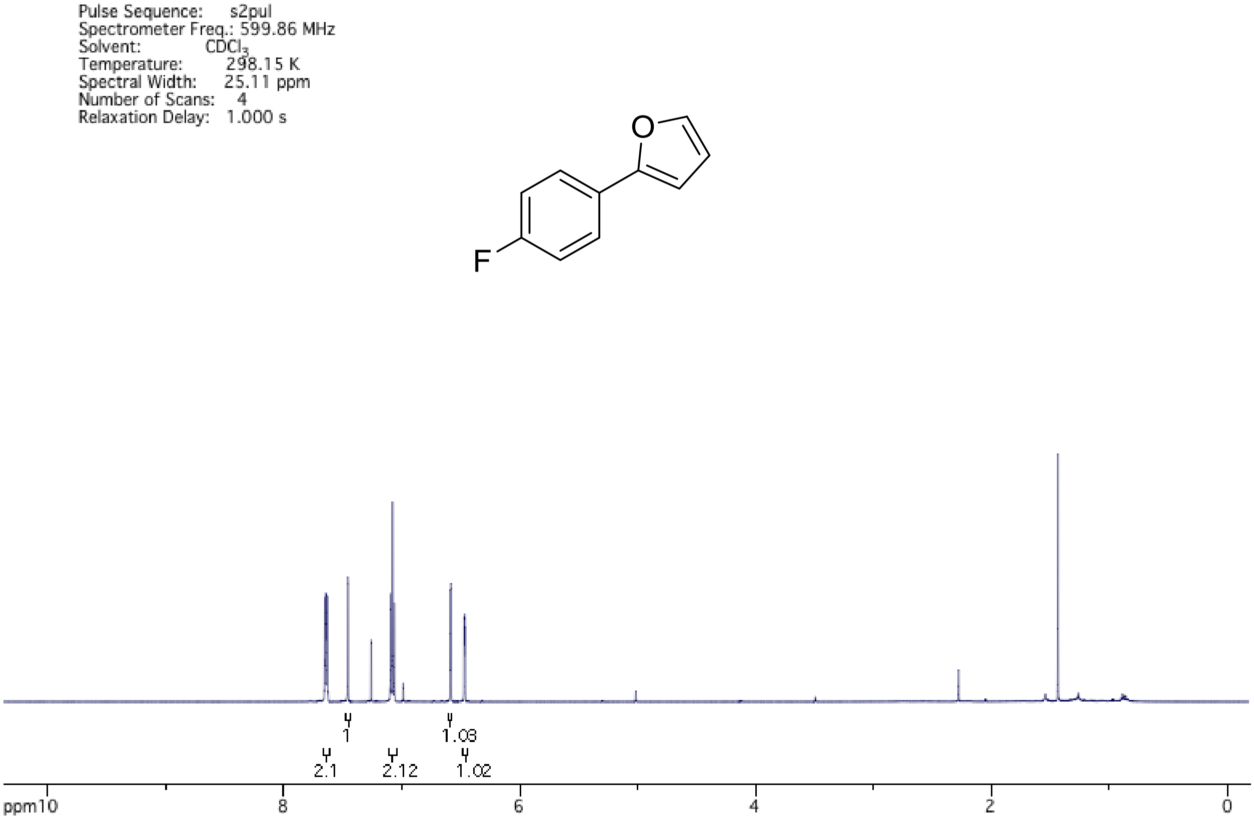
colourless solid; ^{1}H-NMR (400 MHz; CDCl$_3$): δ 8.68 (d, *J* = 4.7 Hz, 1H), 7.73-7.69 (m, 2H), 7.57 (d, *J* = 2.2 Hz, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.24-7.20 (m, 1H), 6.95 (dd, *J* = 8.2, 1.9 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR (151 MHz; CDCl$_3$): δ 160.1, 157.2, 149.6, 140.9, 136.7, 129.7, 122.2, 120.7, 119.3, 115.1, 112.0, 55.4.

Dantrolene[6]

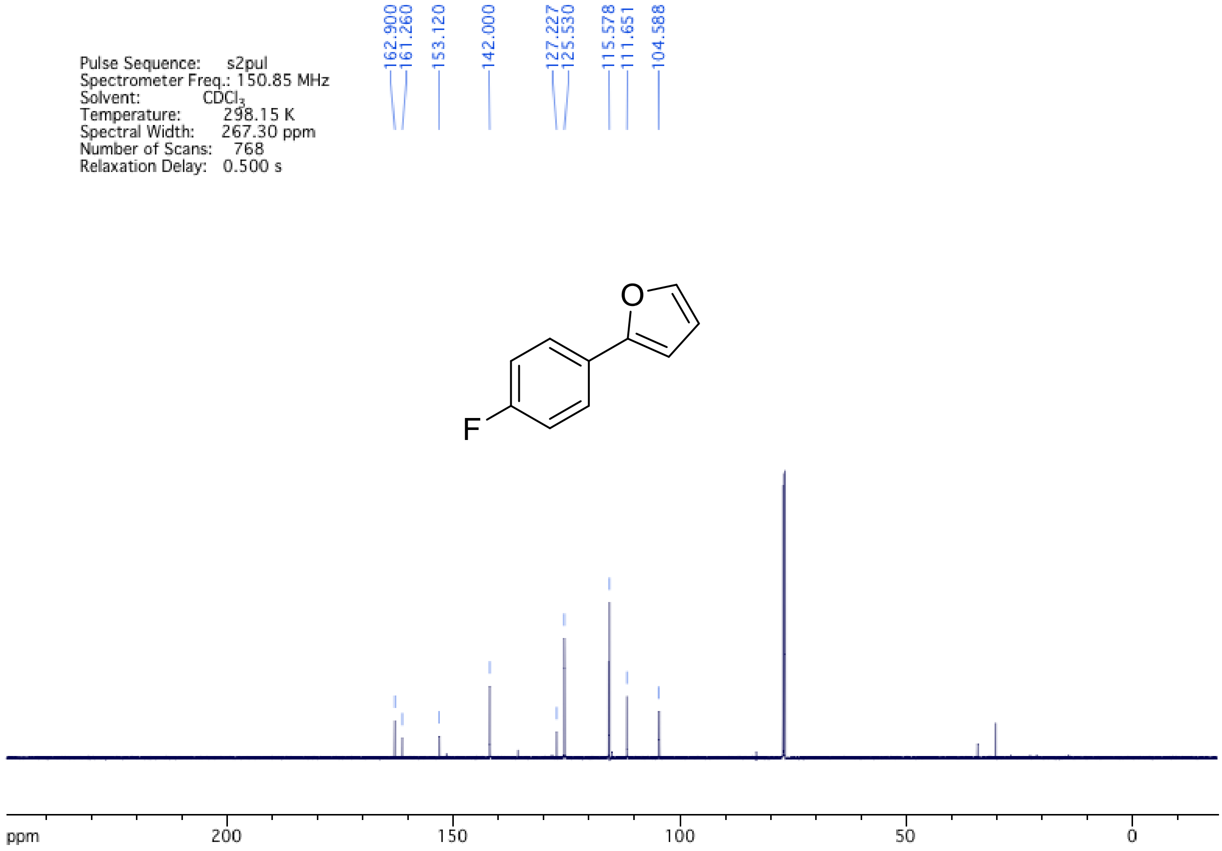


yellow solid; ^{1}H-NMR (600 MHz; DMSO-d$_6$): δ 8.31 (d, *J* = 8.7 Hz, 2H), 8.00 (d, *J* = 8.7 Hz, 2H), 7.75 (s, 1H), 7.45 (d, *J* = 3.5 Hz, 1H), 7.03 (d, *J* = 3.5 Hz, 1H), 4.34 (s, 2H); ^{13}C NMR (151 MHz; CDCl$_3$): 169.3, 153.7, 152.5, 151.5, 146.7, 135.6, 133.0, 125.02, 124.95, 116.0, 112.9, 49.4.

14. ^{1}H-, ^{13}C-, ^{19}F-NMR spectra

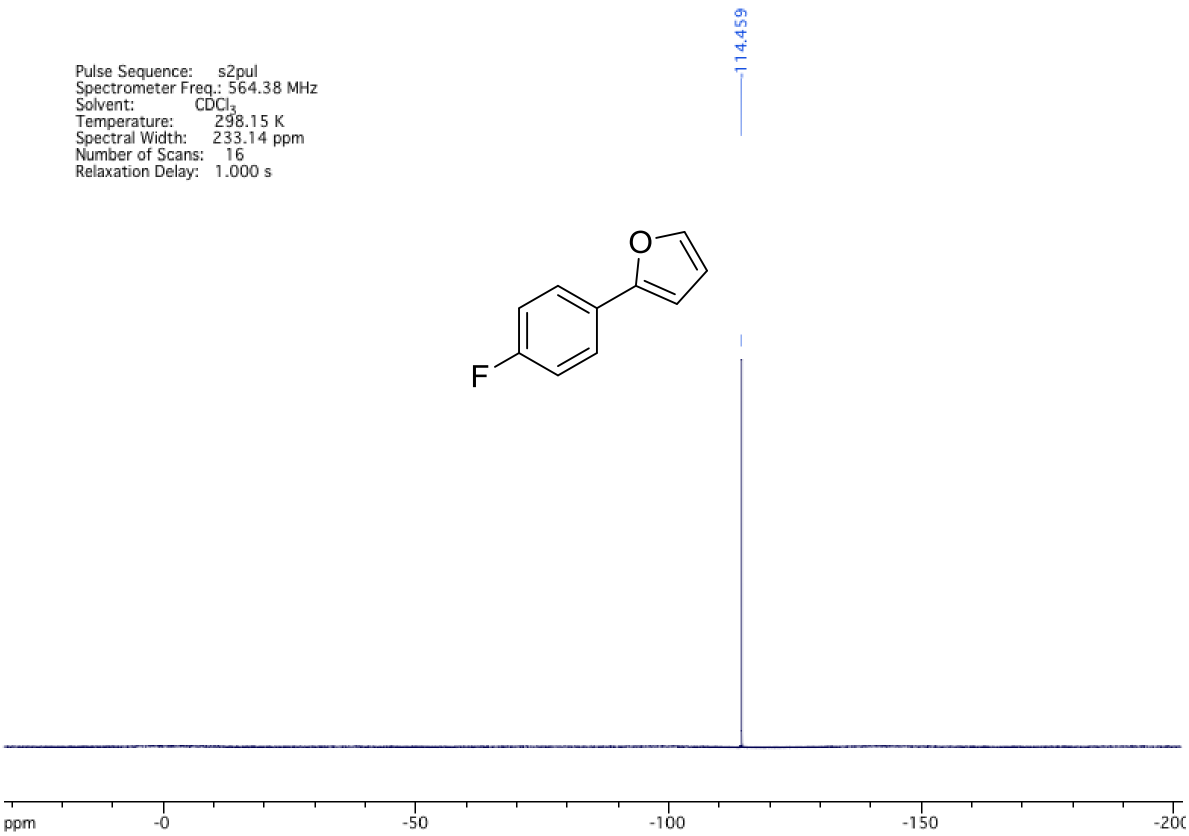


Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 25.11 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s

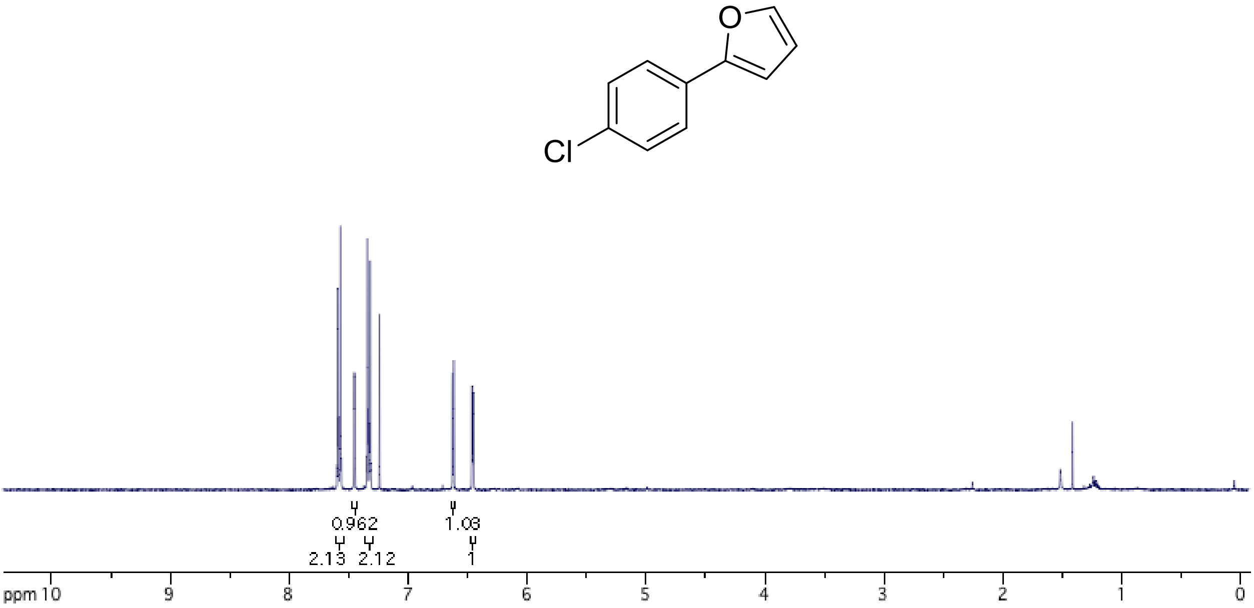


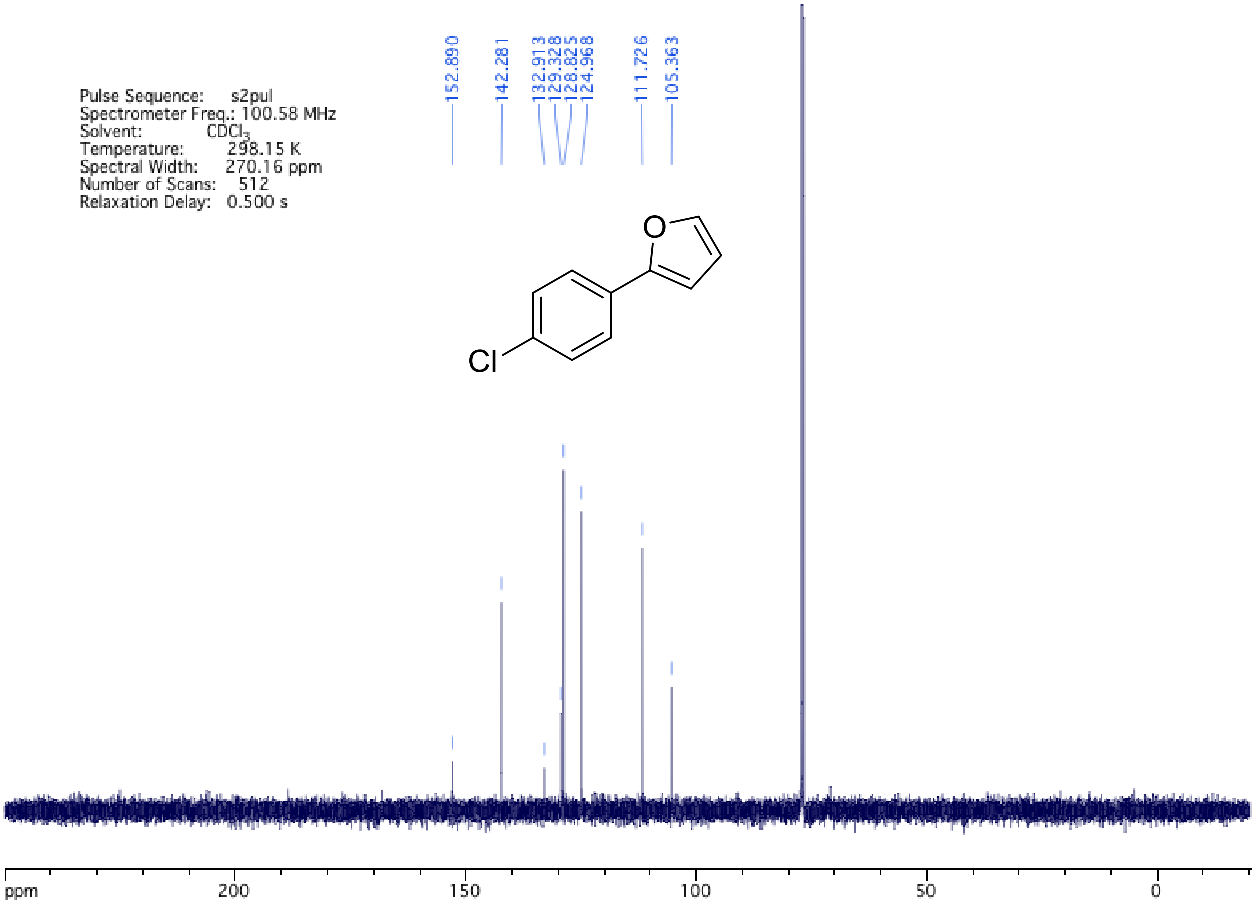
Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 267.30 ppm
Number of Scans: 768
Relaxation Delay: 0.500 s

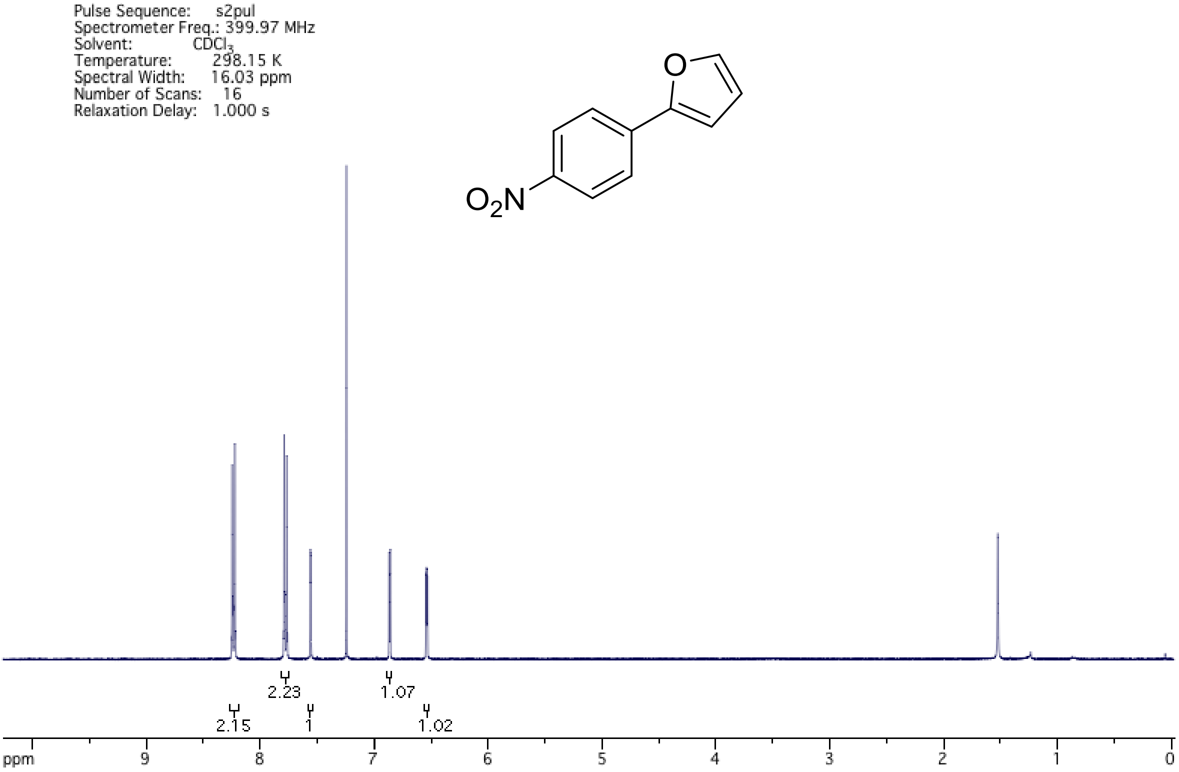
Pulse Sequence: s2pul
Spectrometer Freq.: 564.38 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 233.14 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s



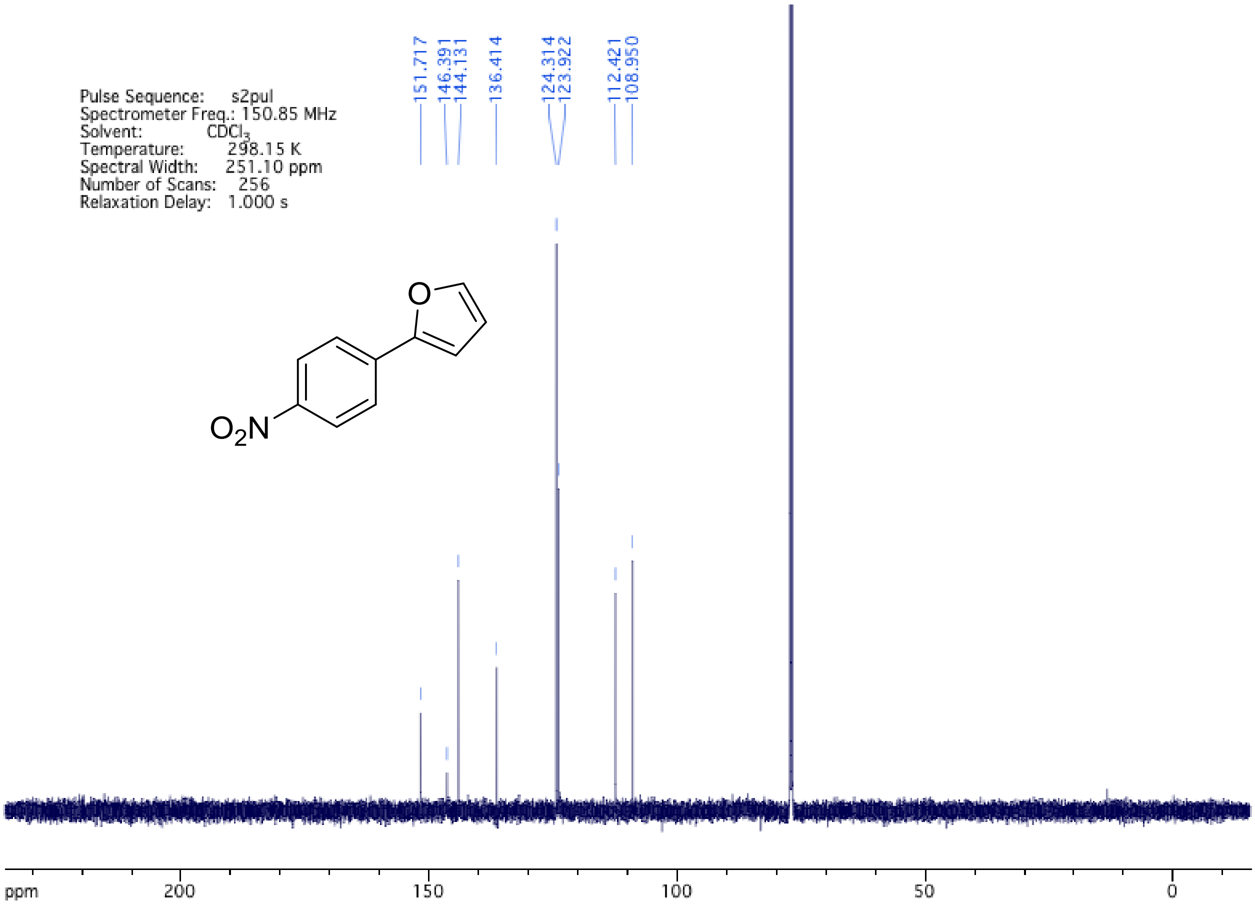
Pulse Sequence: s2pul
Spectrometer Freq.: 399.97 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 16.03 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s



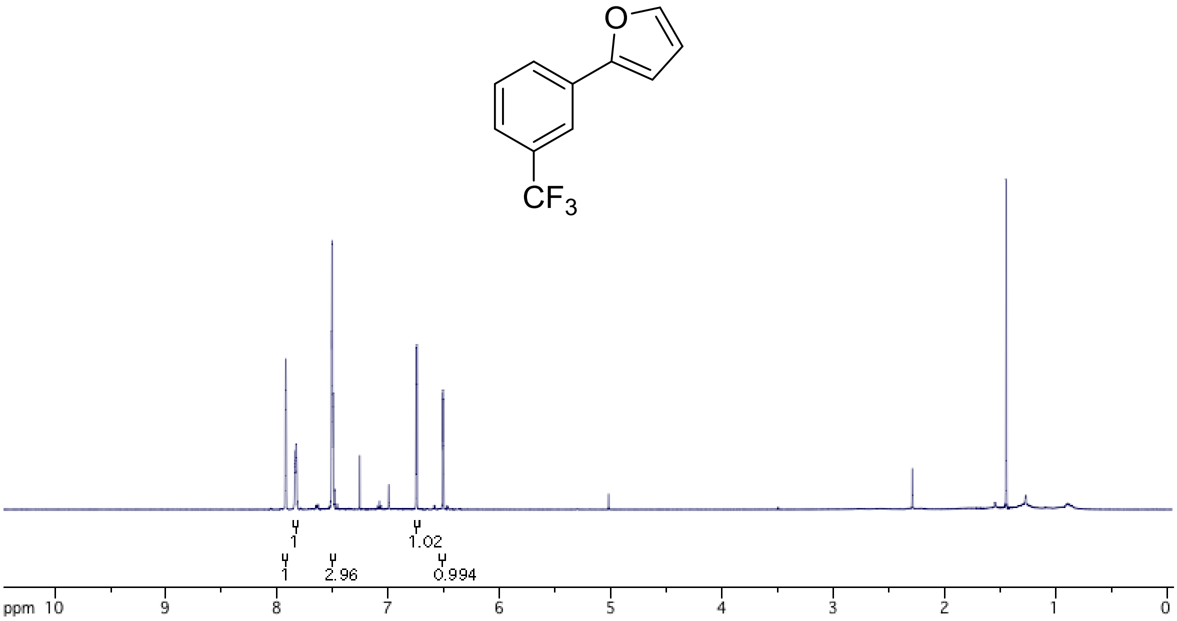

Pulse Sequence: s2pul
Spectrometer Freq.: 100.58 MHz
Solvent: CDCl$_3$
Temperature: 298.15 K
Spectral Width: 270.16 ppm
Number of Scans: 512
Relaxation Delay: 0.500 s
152.890
142.281
132.913
129.328
128.825
124.968
111.726
105.363
O
Cl
ppm
200
150
100
50
0

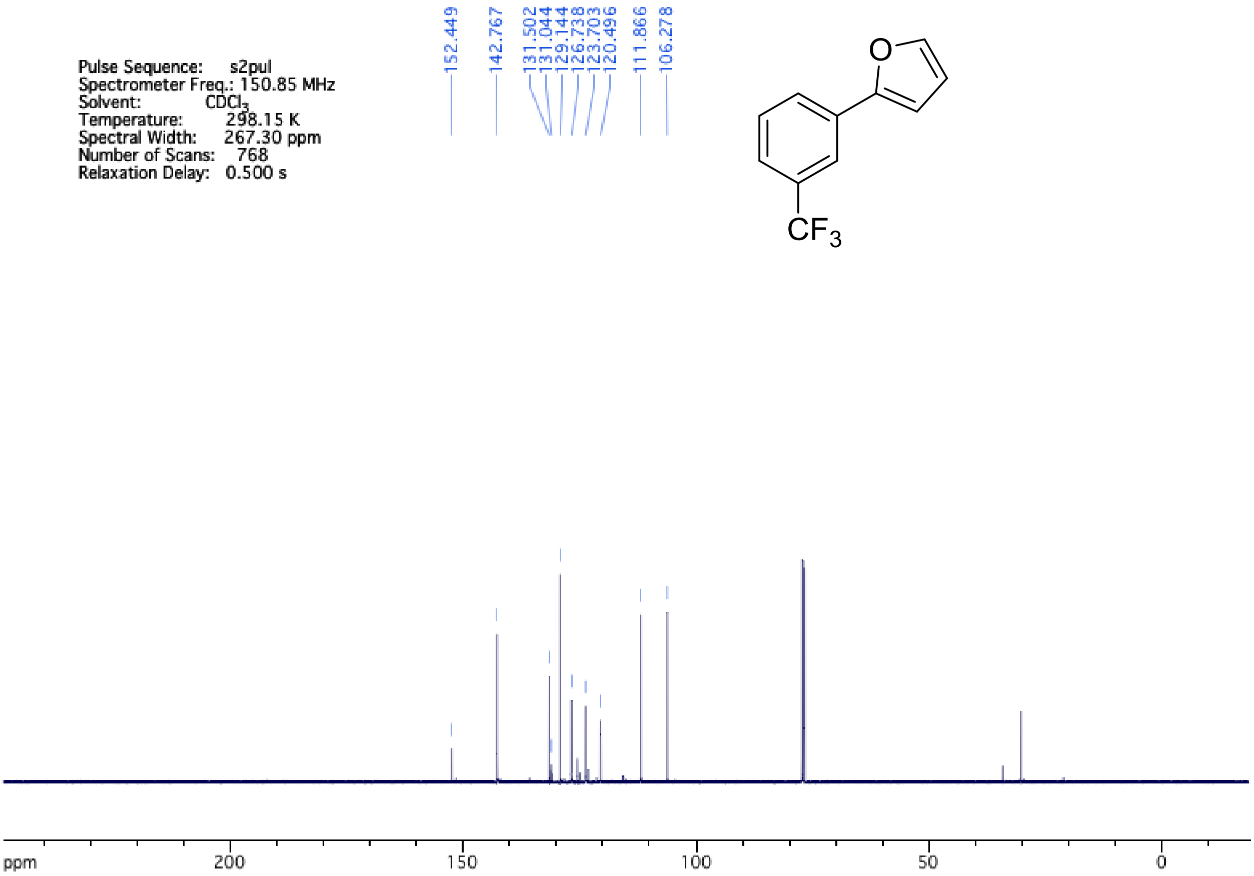

Pulse Sequence: s2pul
Spectrometer Freq.: 399.97 MHz
Solvent: CDCl$_3$
Temperature: 298.15 K
Spectral Width: 16.03 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s
O
O$_2$N
2.23
1.07
2.15
1
1.02
ppm
9
8
7
6
5
4
3
2
1
0

Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 251.10 ppm
Number of Scans: 256
Relaxation Delay: 1.000 s

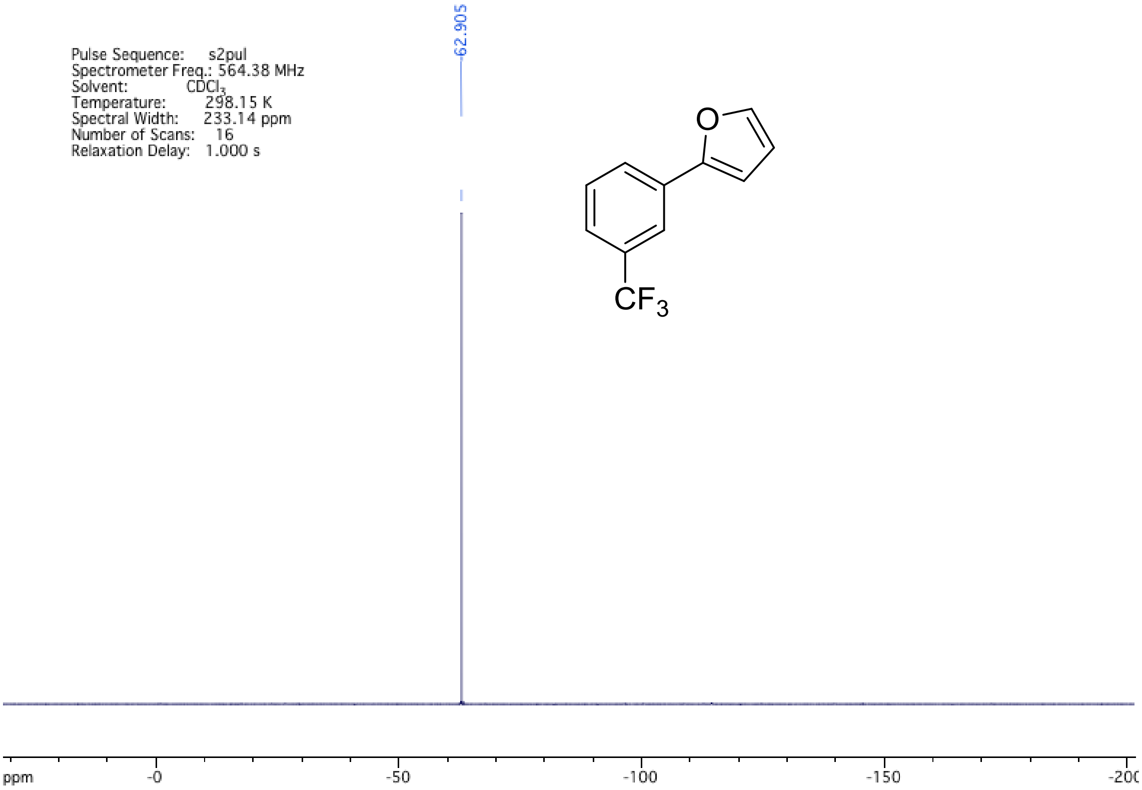


Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 25.11 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s

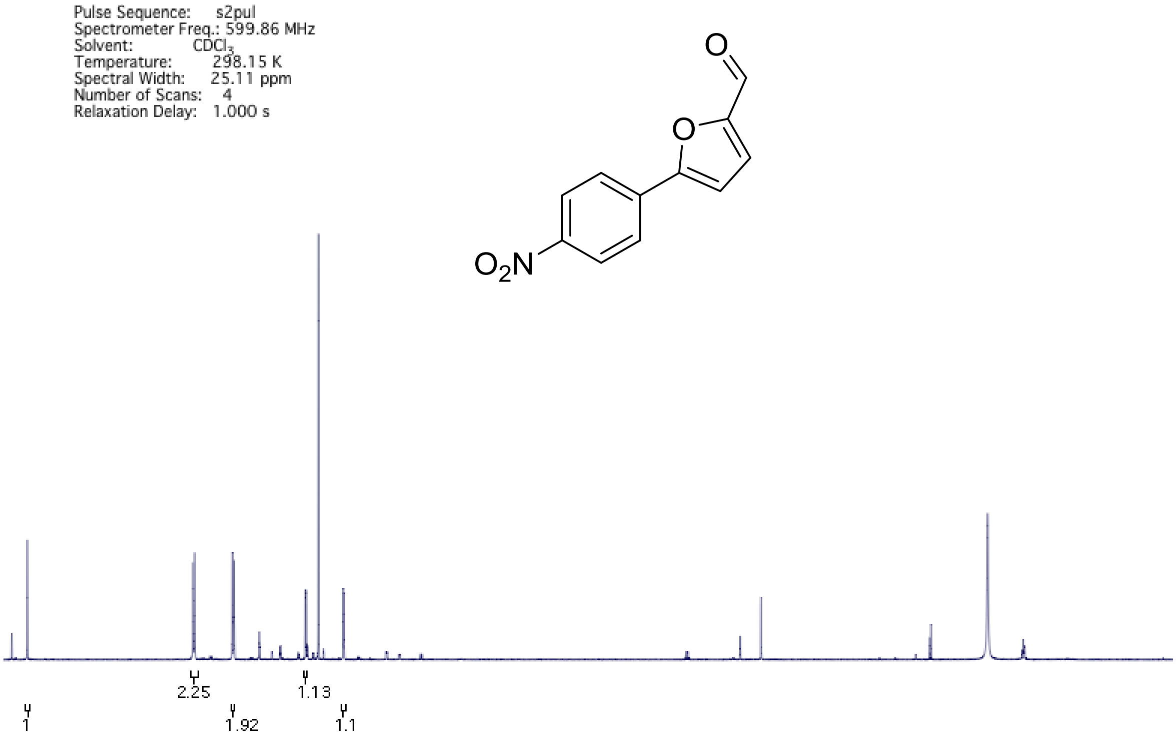


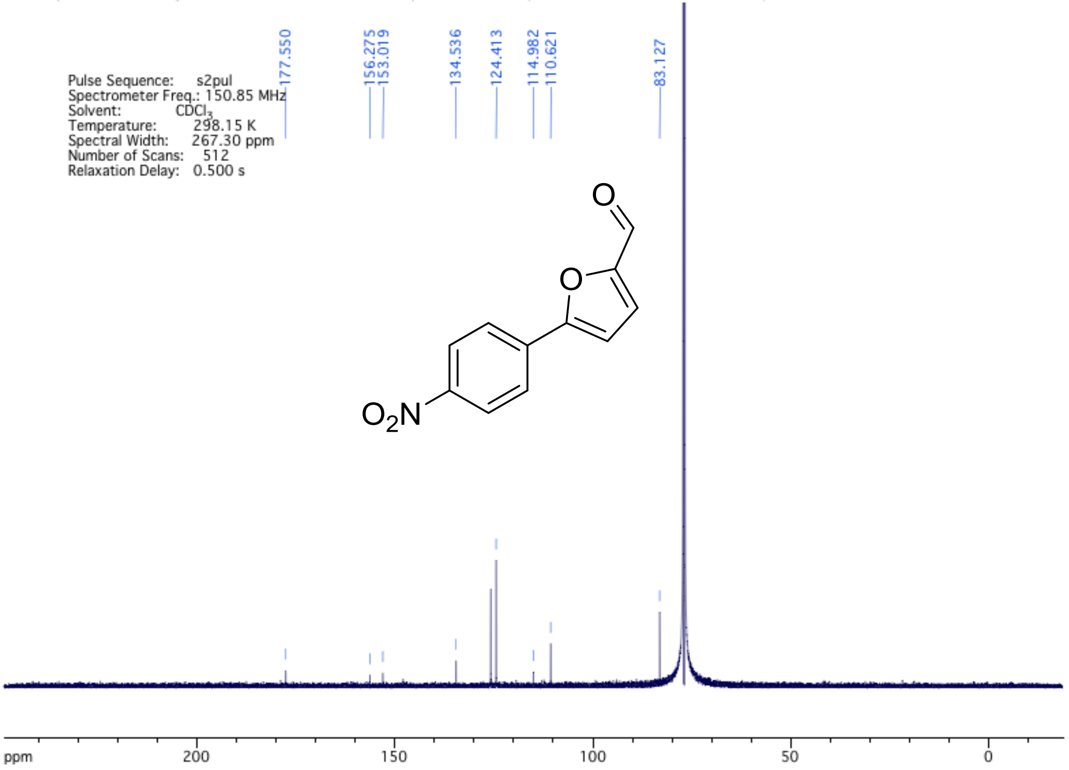


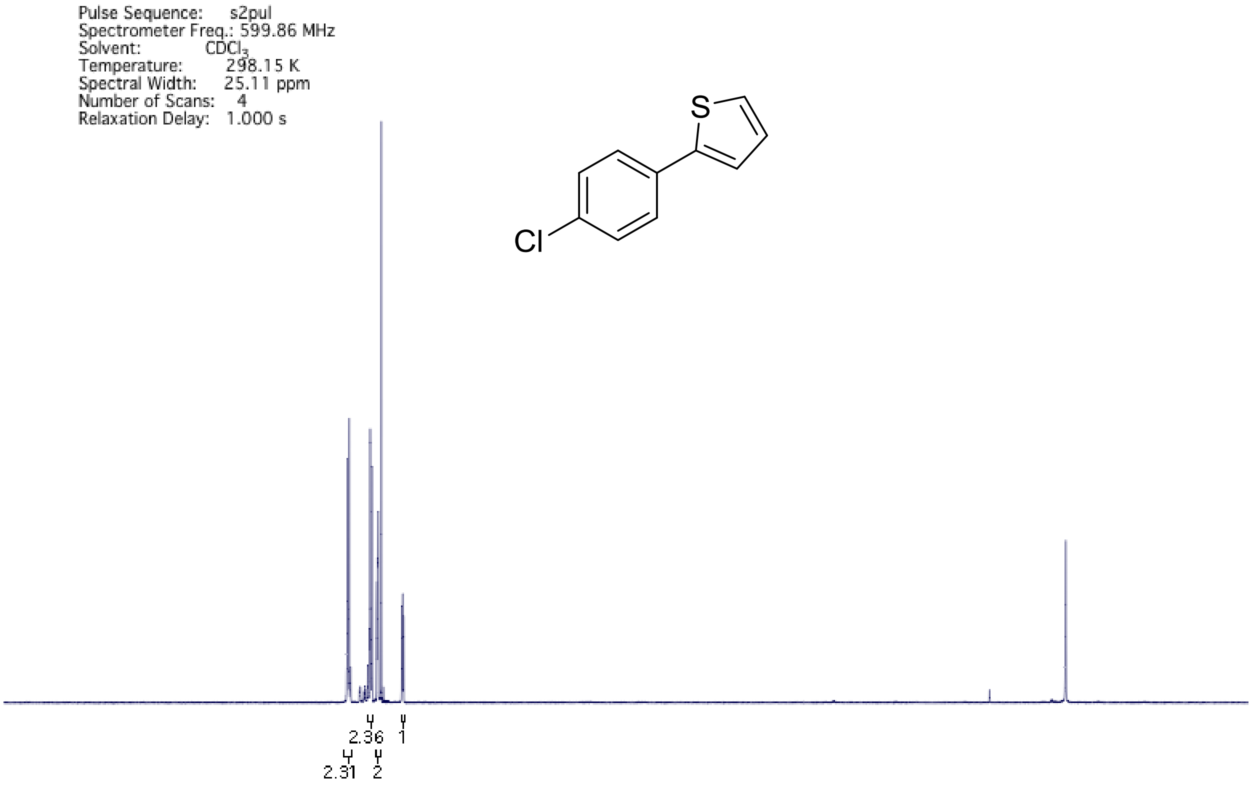
Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 267.30 ppm
Number of Scans: 768
Relaxation Delay: 0.500 s

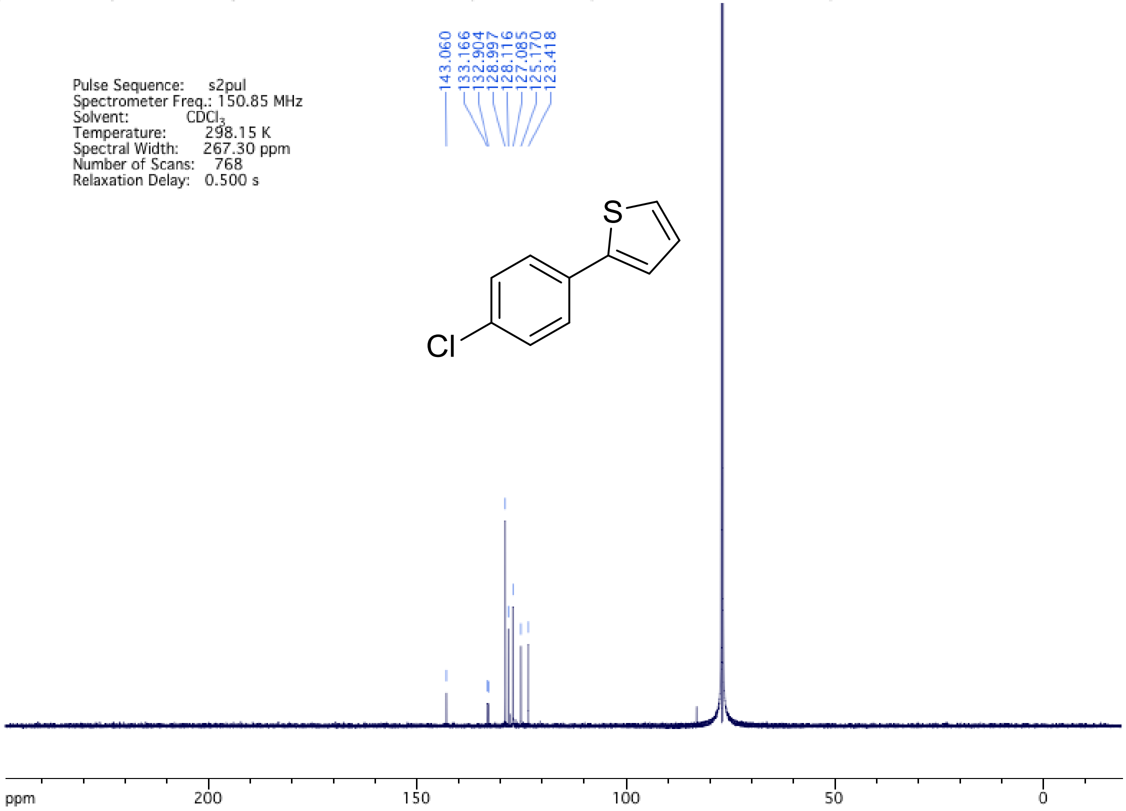


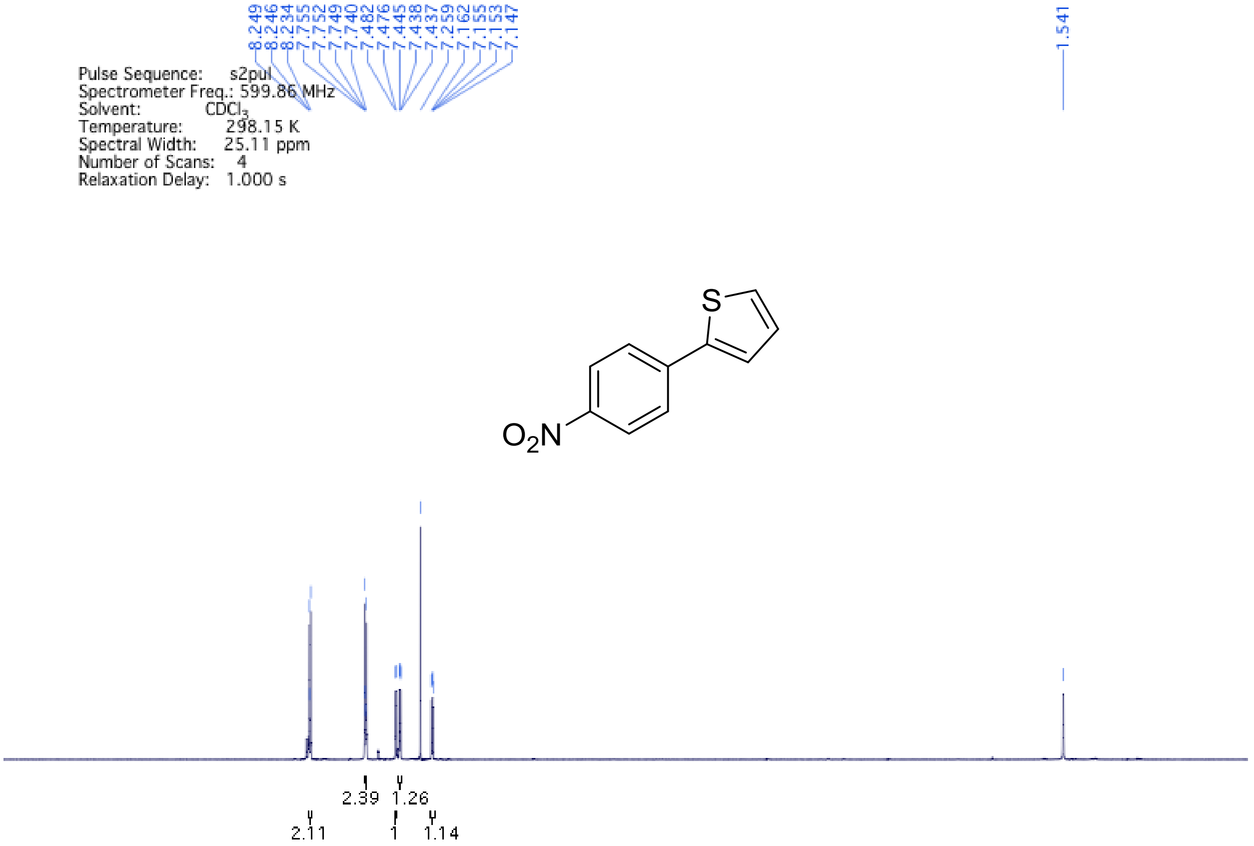
Pulse Sequence: s2pul
Spectrometer Freq.: 564.38 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 233.14 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s


Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: CDCl$_3$
Temperature: 298.15 K
Spectral Width: 25.11 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s
O
O
O$_2$N
2.25
1.13
1
1.92
1.1
ppm
9
8
7
6
5
4
3
2
1
0

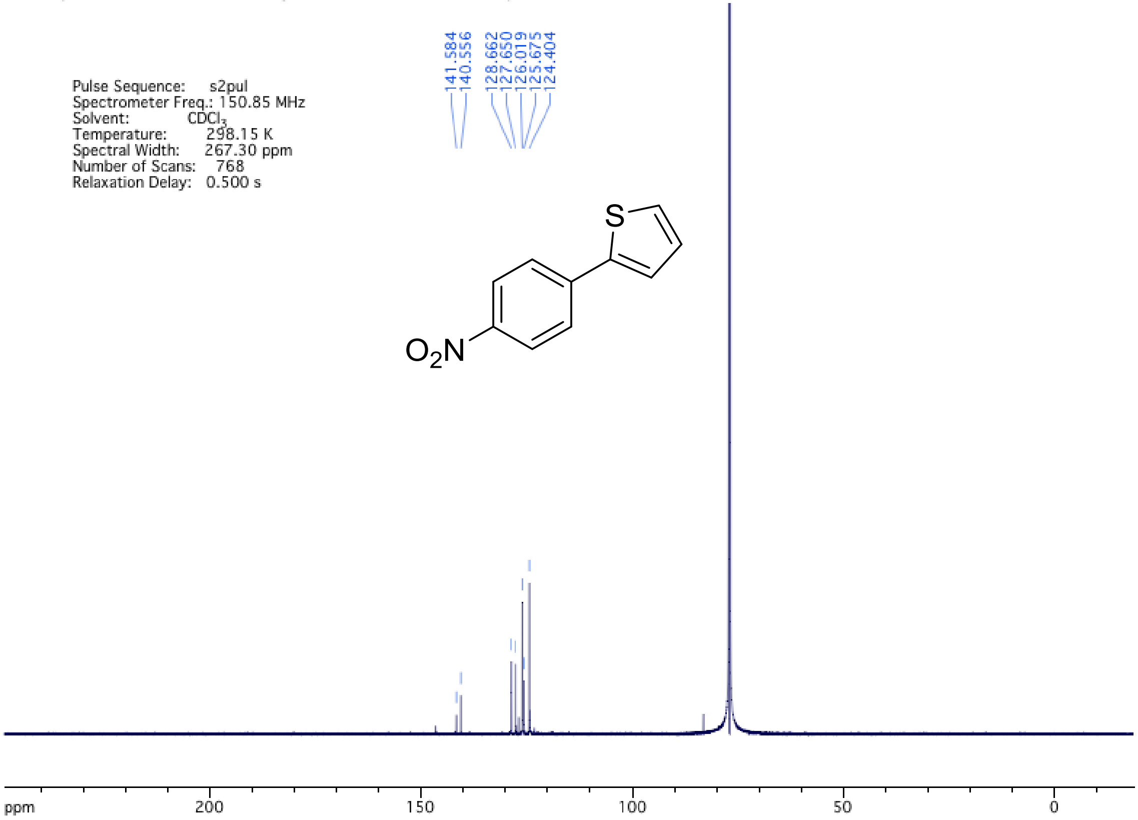

177.550
156.275
153.019
134.536
124.413
114.982
110.621
83.127
Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: CDCl$_3$
Temperature: 298.15 K
Spectral Width: 267.30 ppm
Number of Scans: 512
Relaxation Delay: 0.500 s
O
O
O$_2$N
ppm
200
150
100
50
0


Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 25.11 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s
S
Cl
2.31
2.36
2
1
ppm 10
9
8
7
6
5
4
3
2
1


143.060
133.166
132.904
128.997
128.116
127.085
125.170
123.418
Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 267.30 ppm
Number of Scans: 768
Relaxation Delay: 0.500 s
S
Cl
ppm
200
150
100
50
0

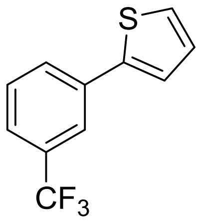


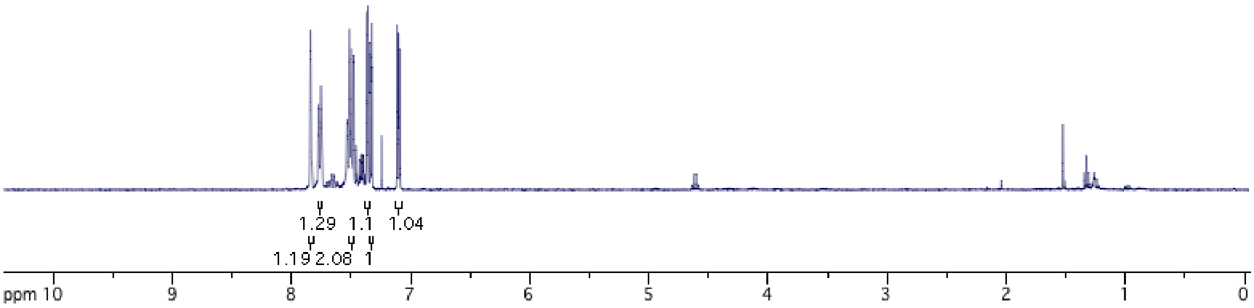
Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 25.11 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s



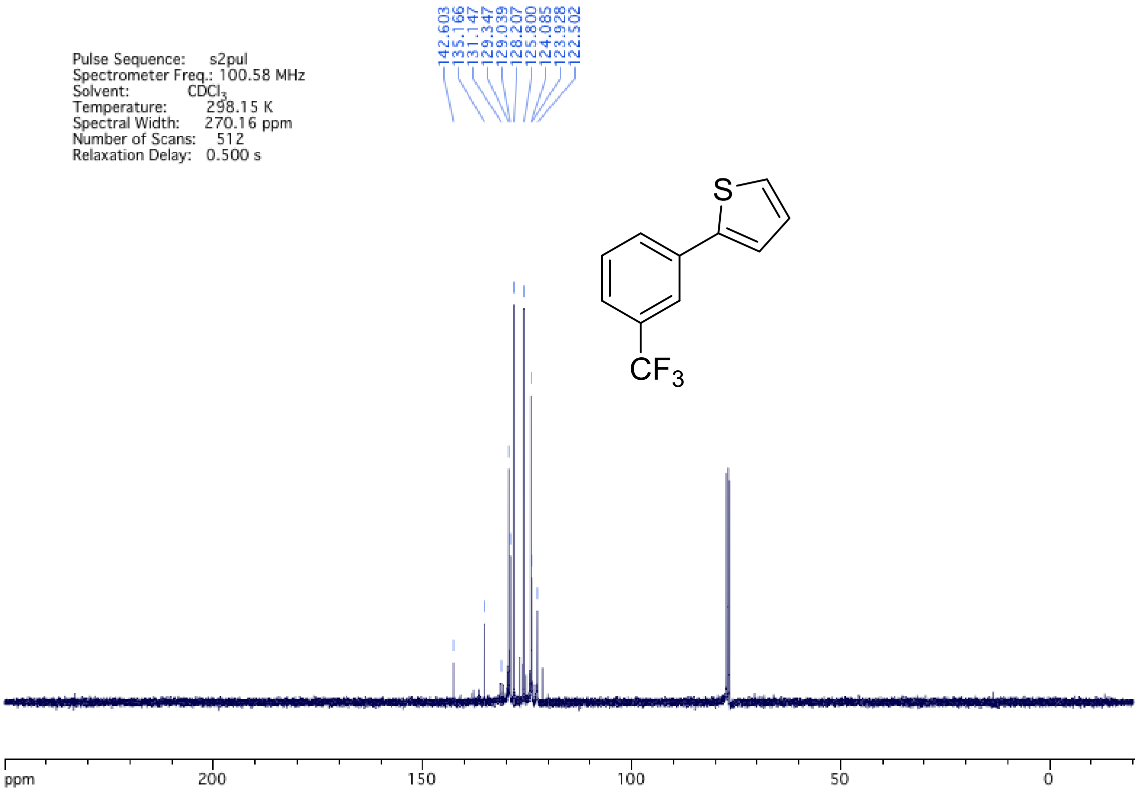
Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 267.30 ppm
Number of Scans: 768
Relaxation Delay: 0.500 s

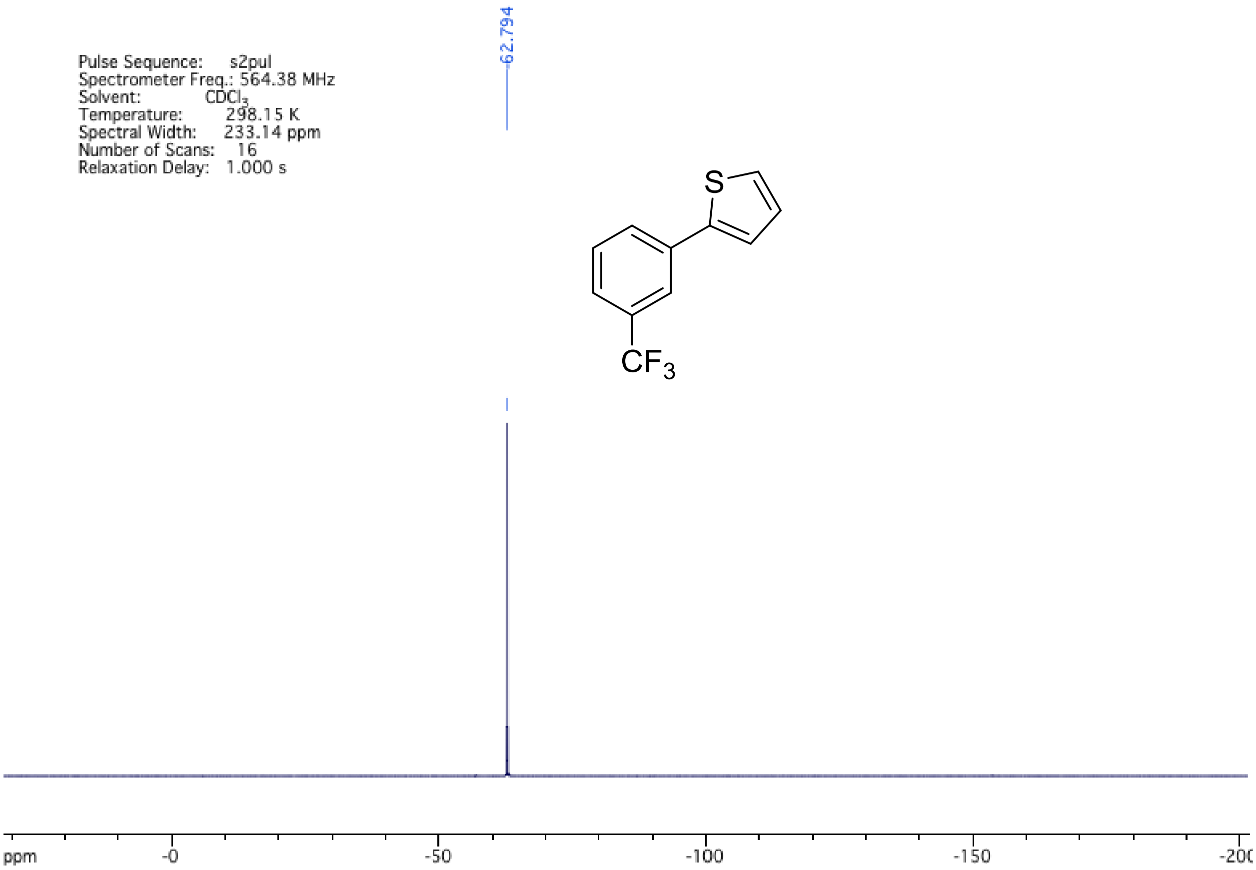
Pulse Sequence: s2pul
Spectrometer Freq.: 399.97 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 16.03 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s



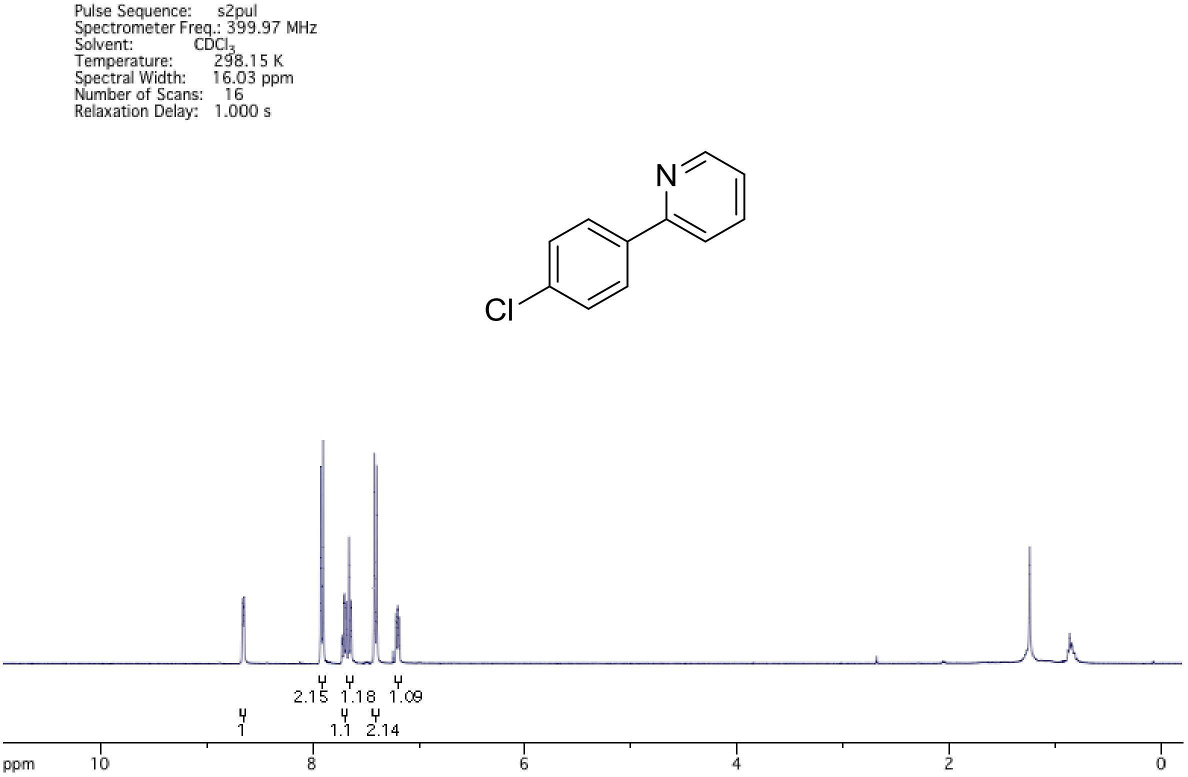


Pulse Sequence: s2pul
Spectrometer Freq.: 100.58 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 270.16 ppm
Number of Scans: 512
Relaxation Delay: 0.500 s

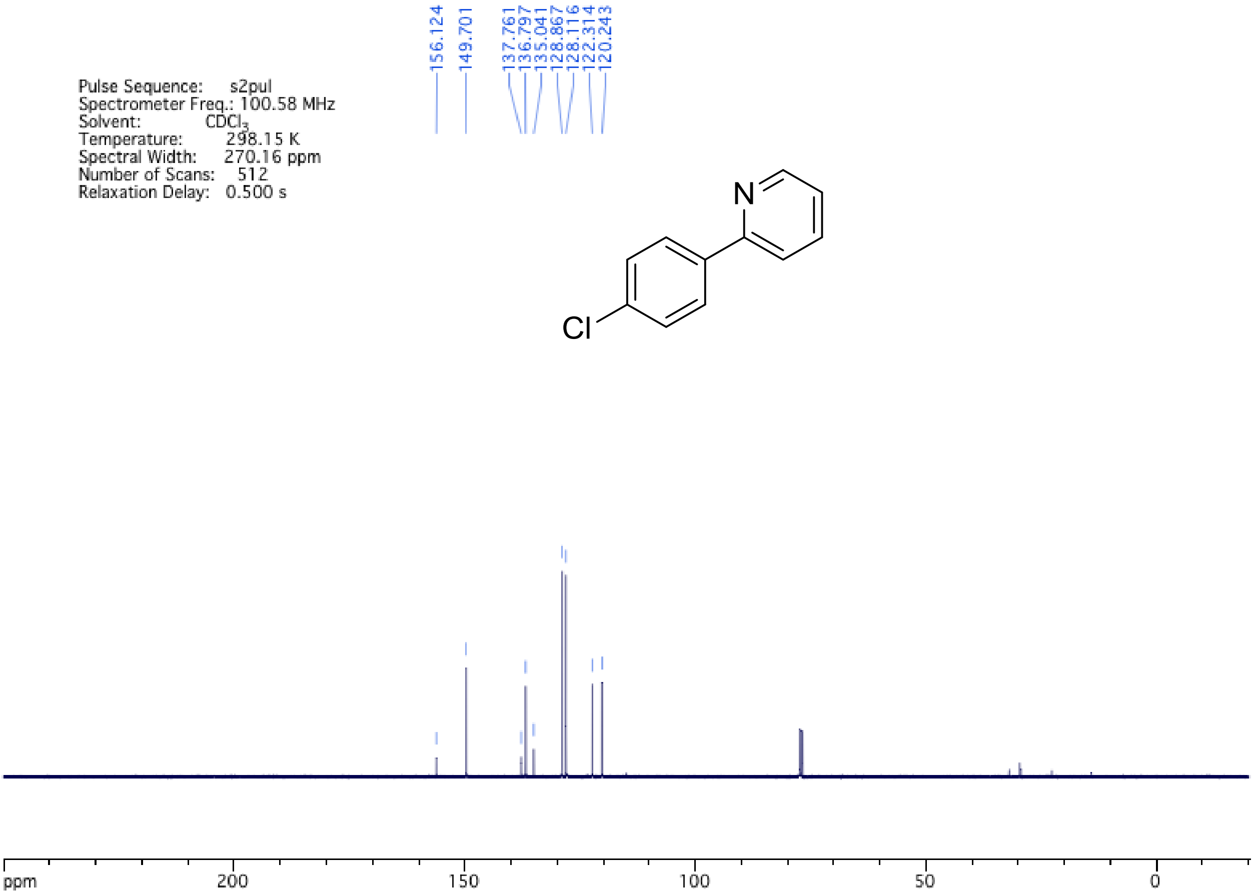




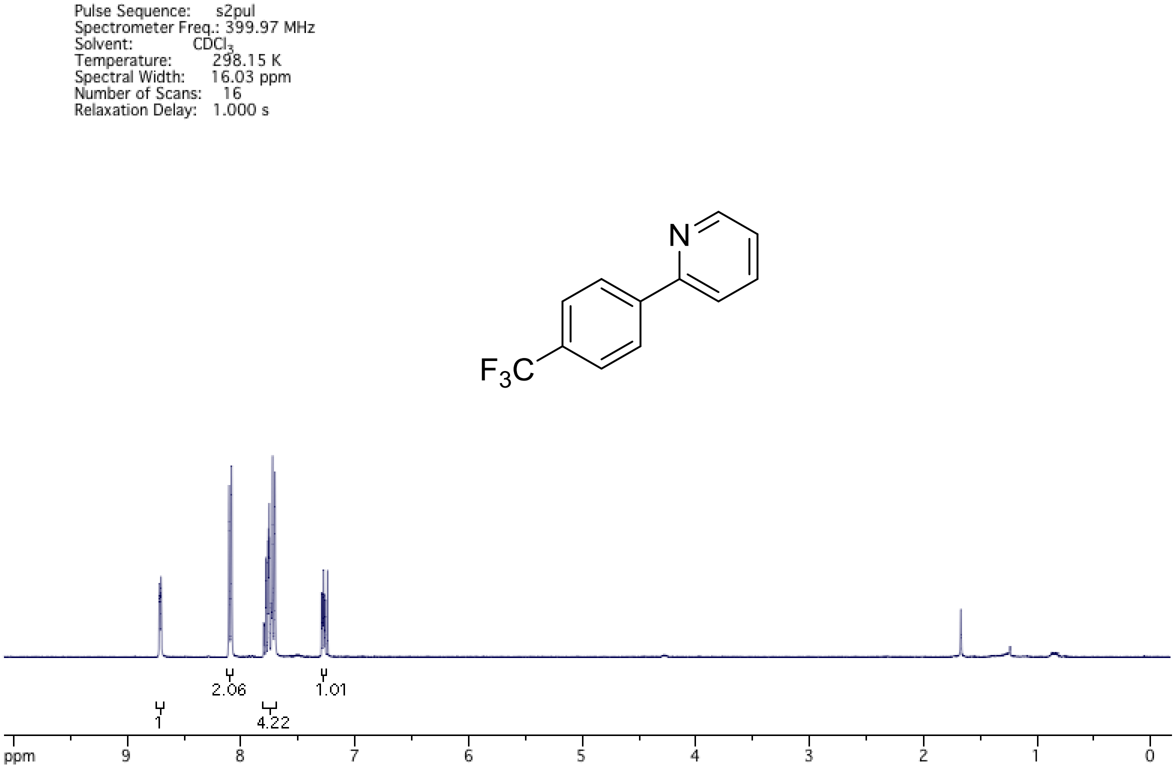
Pulse Sequence: s2pul
Spectrometer Freq.: 564.38 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 233.14 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s



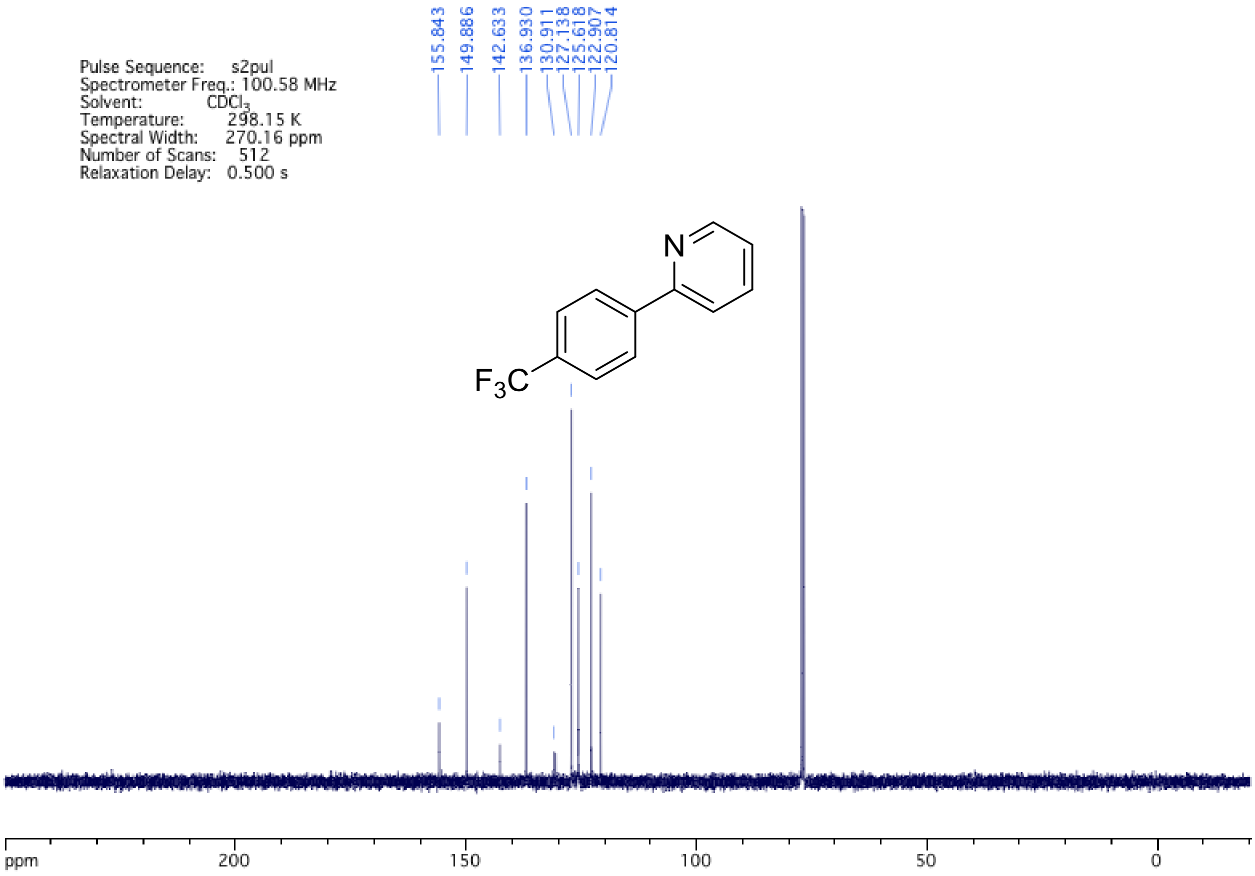
Pulse Sequence: s2pul
Spectrometer Freq.: 399.97 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 16.03 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s

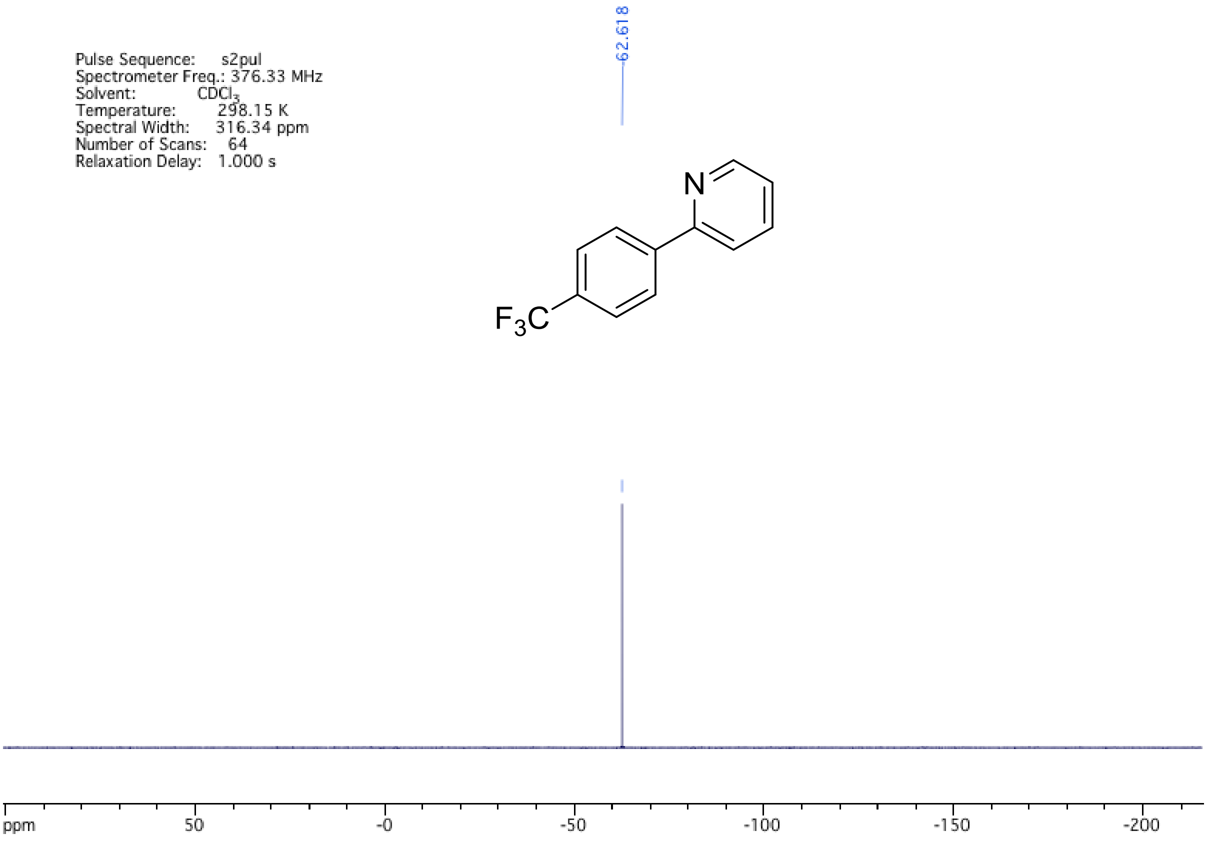


Pulse Sequence: s2pul
Spectrometer Freq.: 100.58 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 270.16 ppm
Number of Scans: 512
Relaxation Delay: 0.500 s

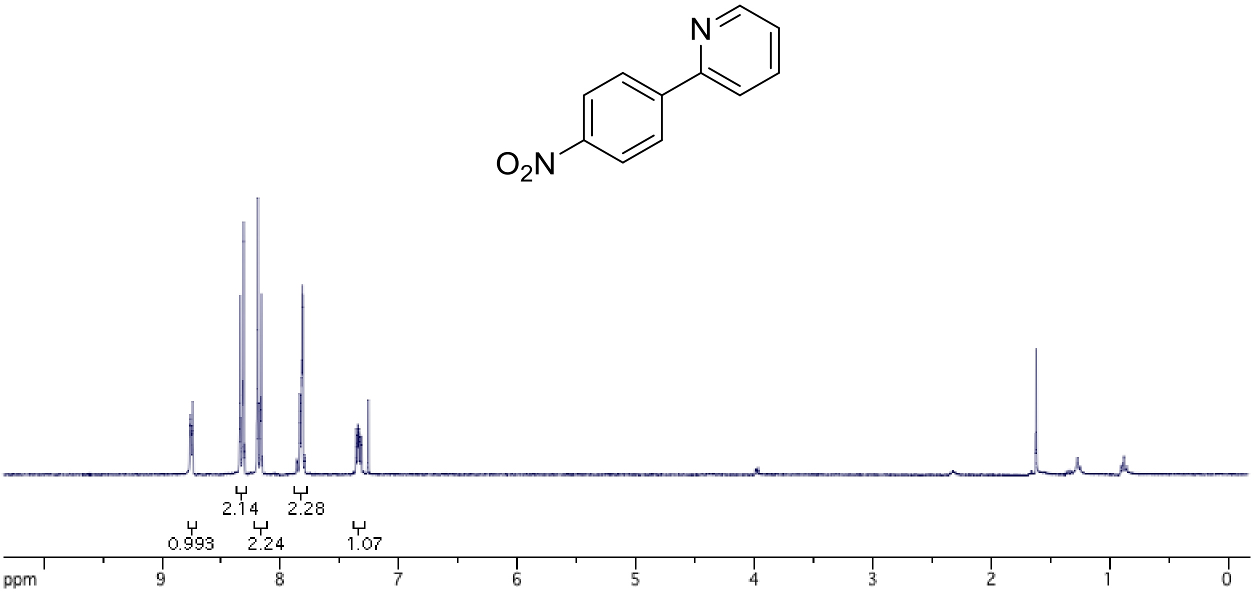


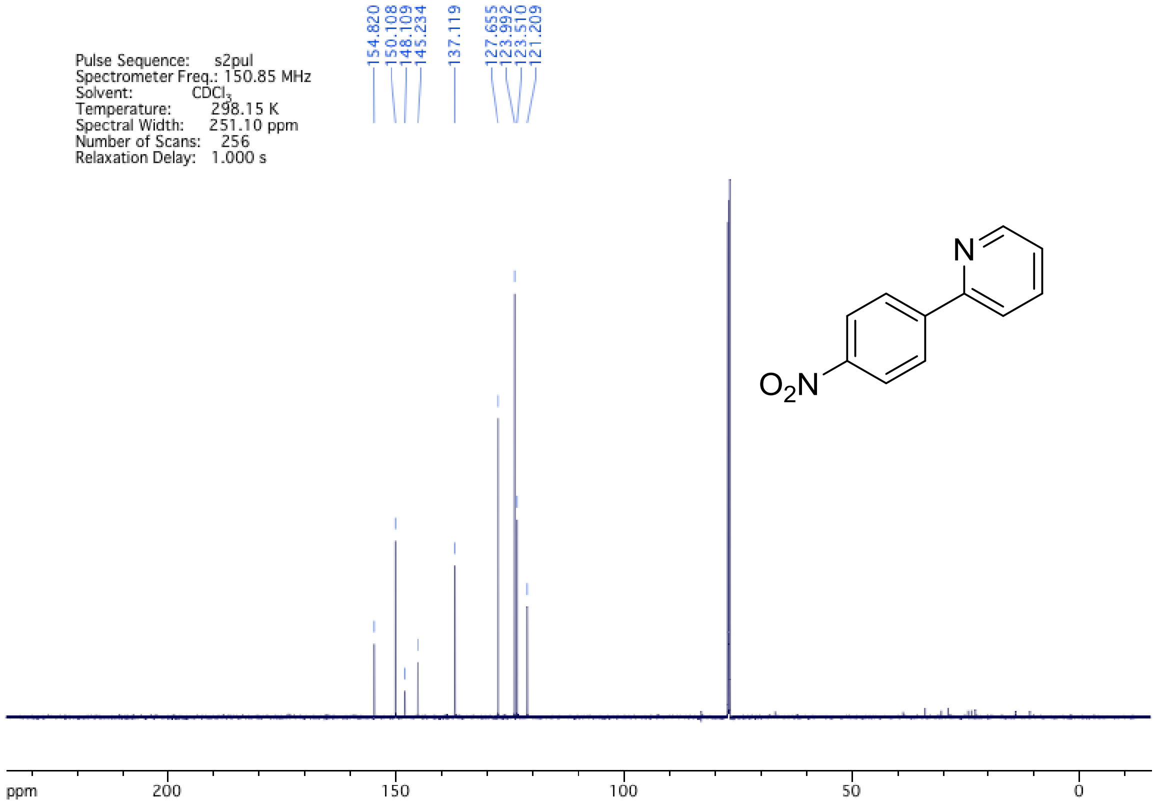
Pulse Sequence: s2pul
Spectrometer Freq.: 399.97 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 16.03 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s


Pulse Sequence: s2pul
Spectrometer Freq.: 100.58 MHz
Solvent: CDCl3
Temperature: 298.15 K
Spectral Width: 270.16 ppm
Number of Scans: 512
Relaxation Delay: 0.500 s
155.843
149.886
142.633
136.930
130.911
127.138
125.618
122.907
120.814
N
F3C
ppm
200
150
100
50
0


Pulse Sequence: s2pul
Spectrometer Freq.: 376.33 MHz
Solvent: CDCl3
Temperature: 298.15 K
Spectral Width: 316.34 ppm
Number of Scans: 64
Relaxation Delay: 1.000 s
-62.618
N
F3C
ppm
50
-0
-50
-100
-150
-200

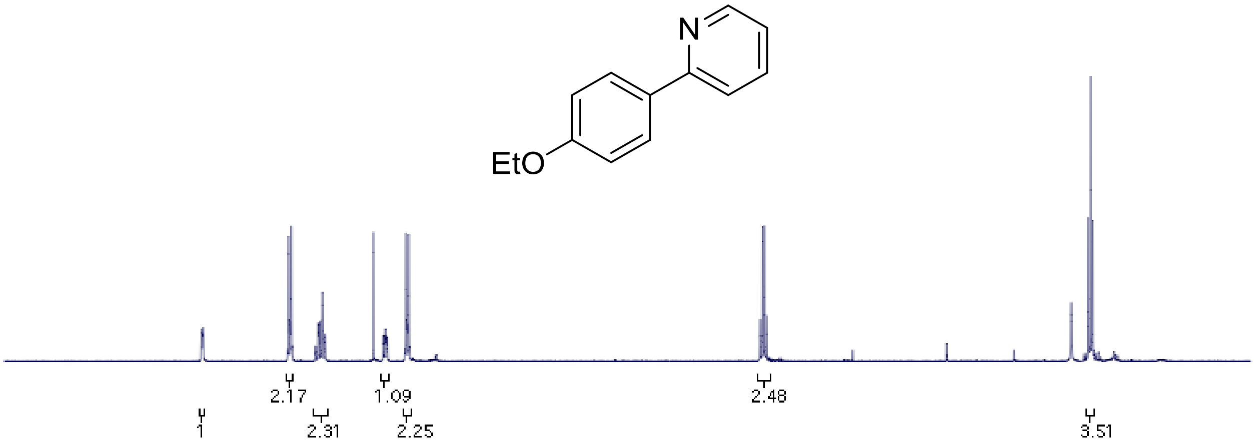
Pulse Sequence: s2pul
Spectrometer Freq.: 300.03 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 27.01 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s



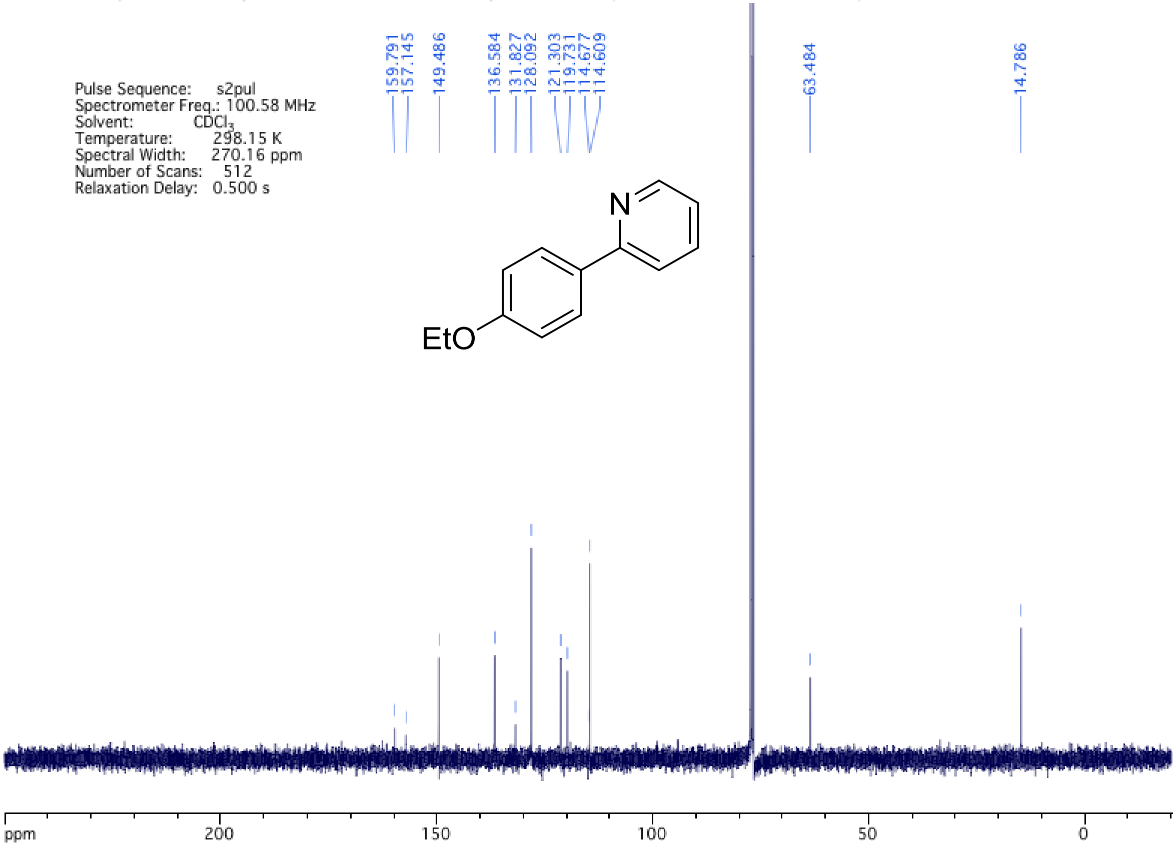


Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 251.10 ppm
Number of Scans: 256
Relaxation Delay: 1.000 s

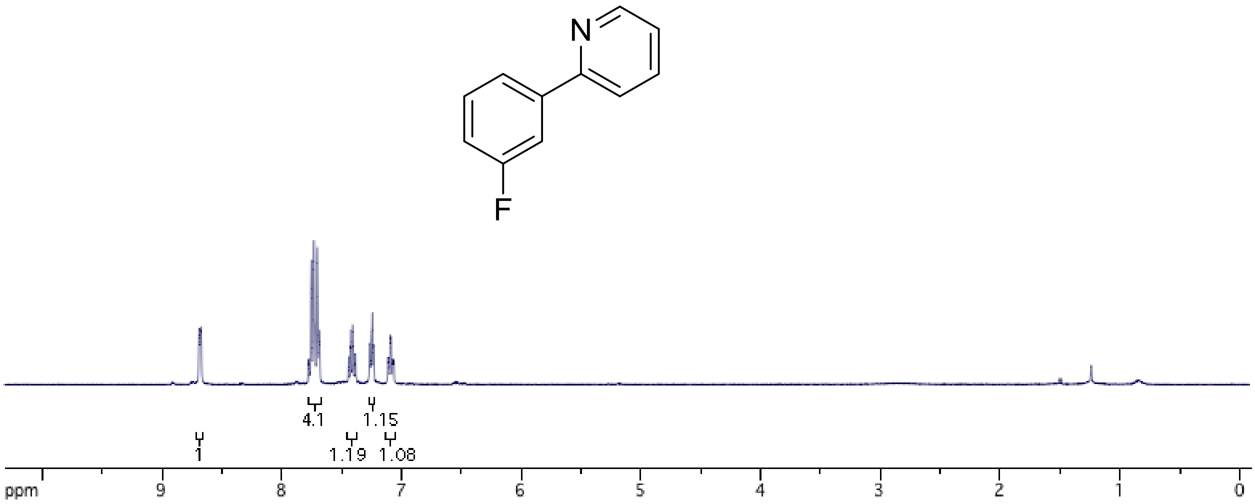
Pulse Sequence: s2pul
Spectrometer Freq.: 399.97 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 16.03 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s



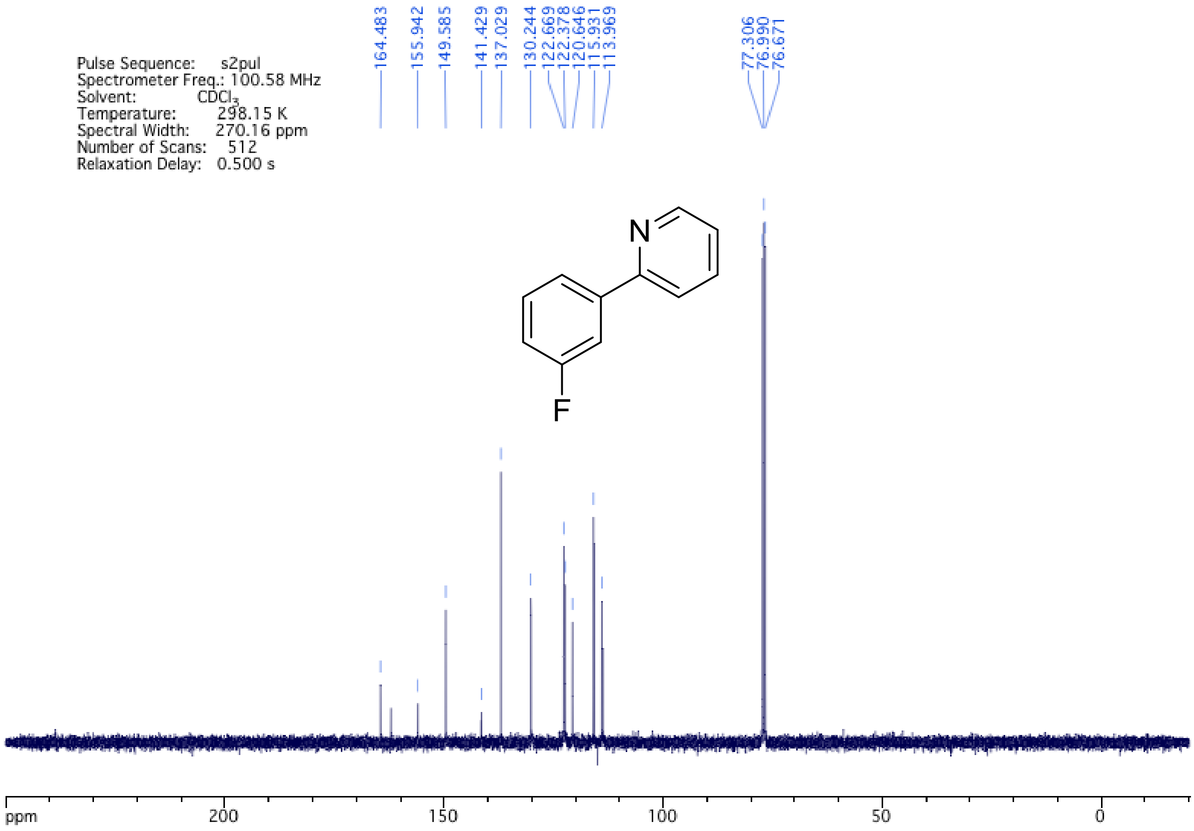
Pulse Sequence: s2pul
Spectrometer Freq.: 100.58 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 270.16 ppm
Number of Scans: 512
Relaxation Delay: 0.500 s



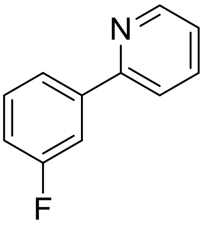
Pulse Sequence: s2pul
Spectrometer Freq.: 399.97 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 16.03 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s

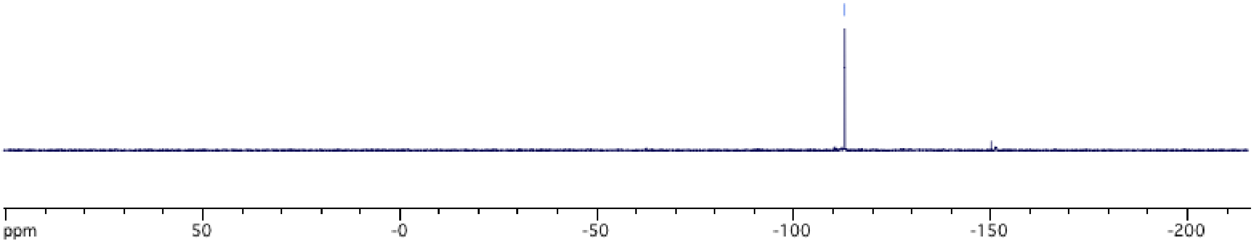


Pulse Sequence: s2pul
Spectrometer Freq.: 100.58 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 270.16 ppm
Number of Scans: 512
Relaxation Delay: 0.500 s

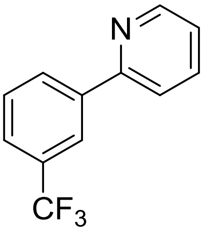


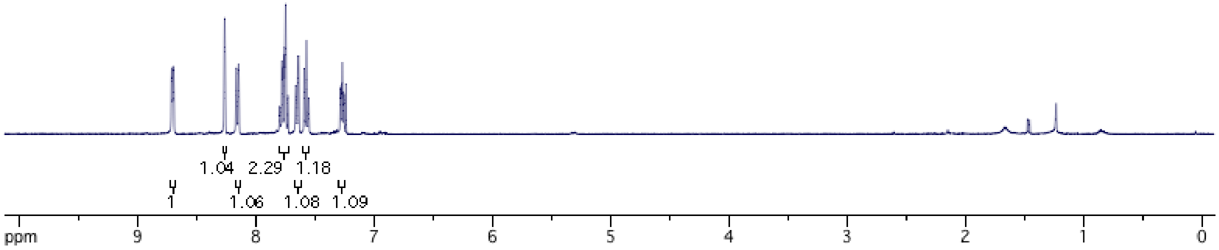
Pulse Sequence: s2pul
Spectrometer Freq.: 376.33 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 316.34 ppm
Number of Scans: 64
Relaxation Delay: 1.000 s



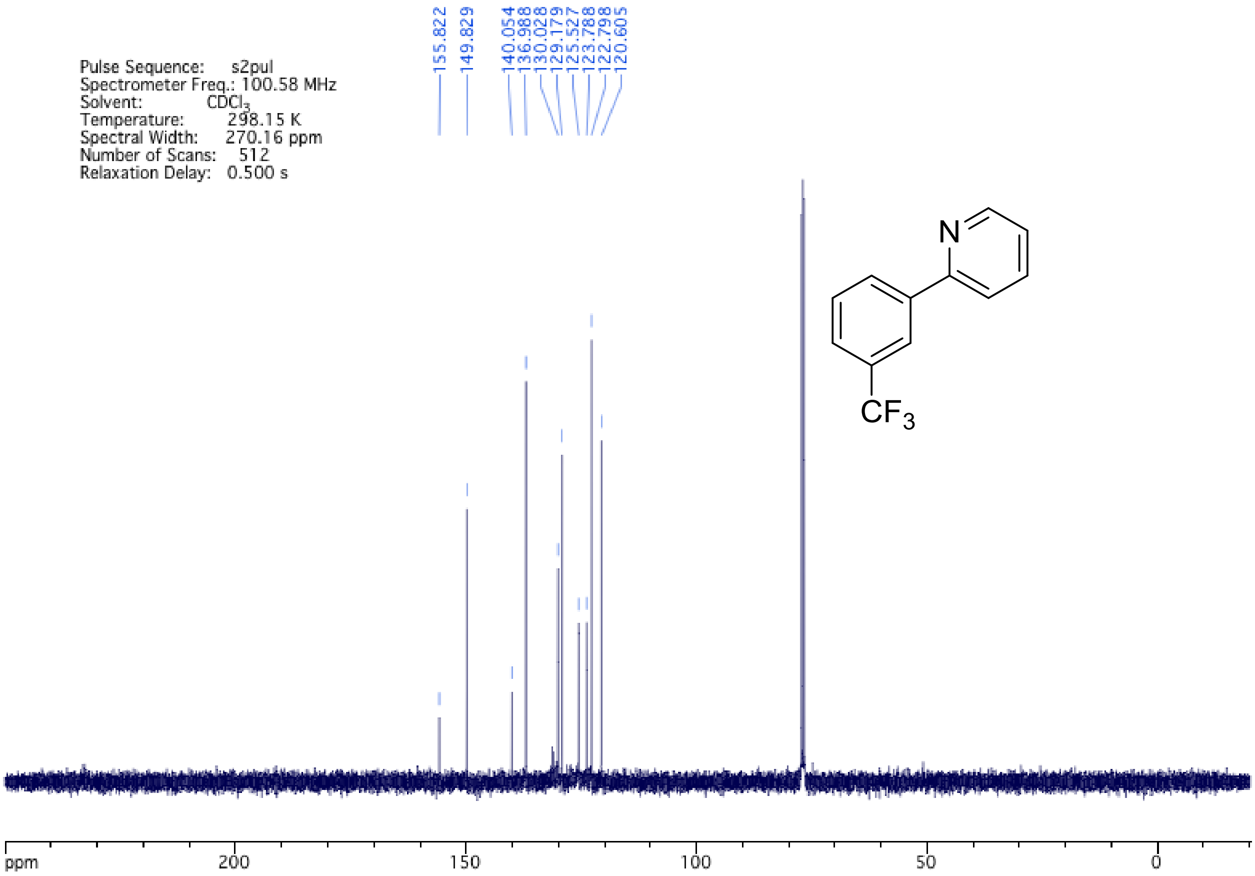


Pulse Sequence: s2pul
Spectrometer Freq.: 399.97 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 16.03 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s

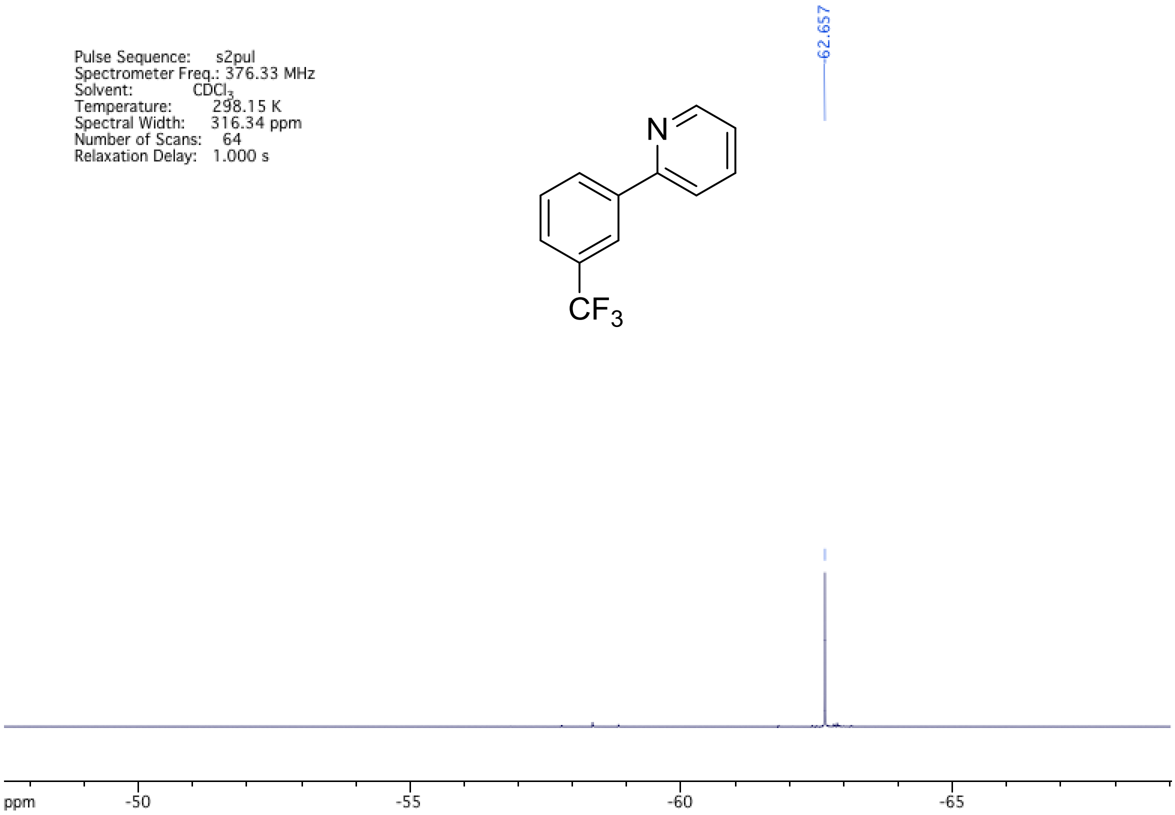




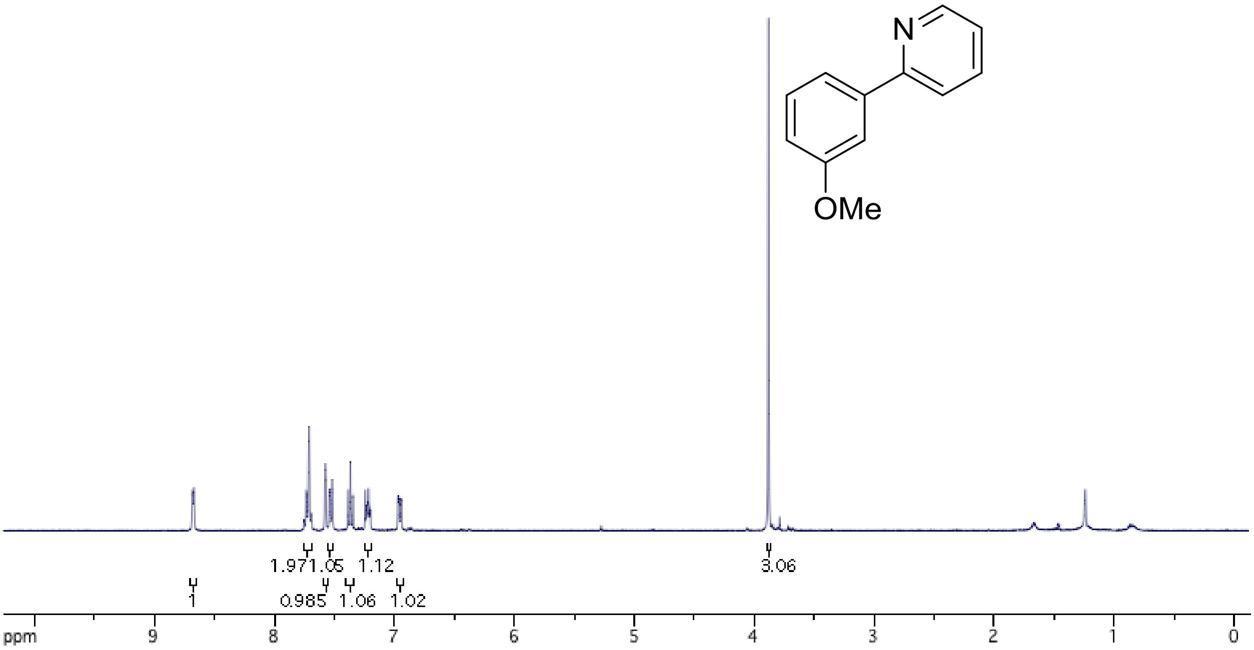
Pulse Sequence: s2pul
Spectrometer Freq.: 100.58 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 270.16 ppm
Number of Scans: 512
Relaxation Delay: 0.500 s



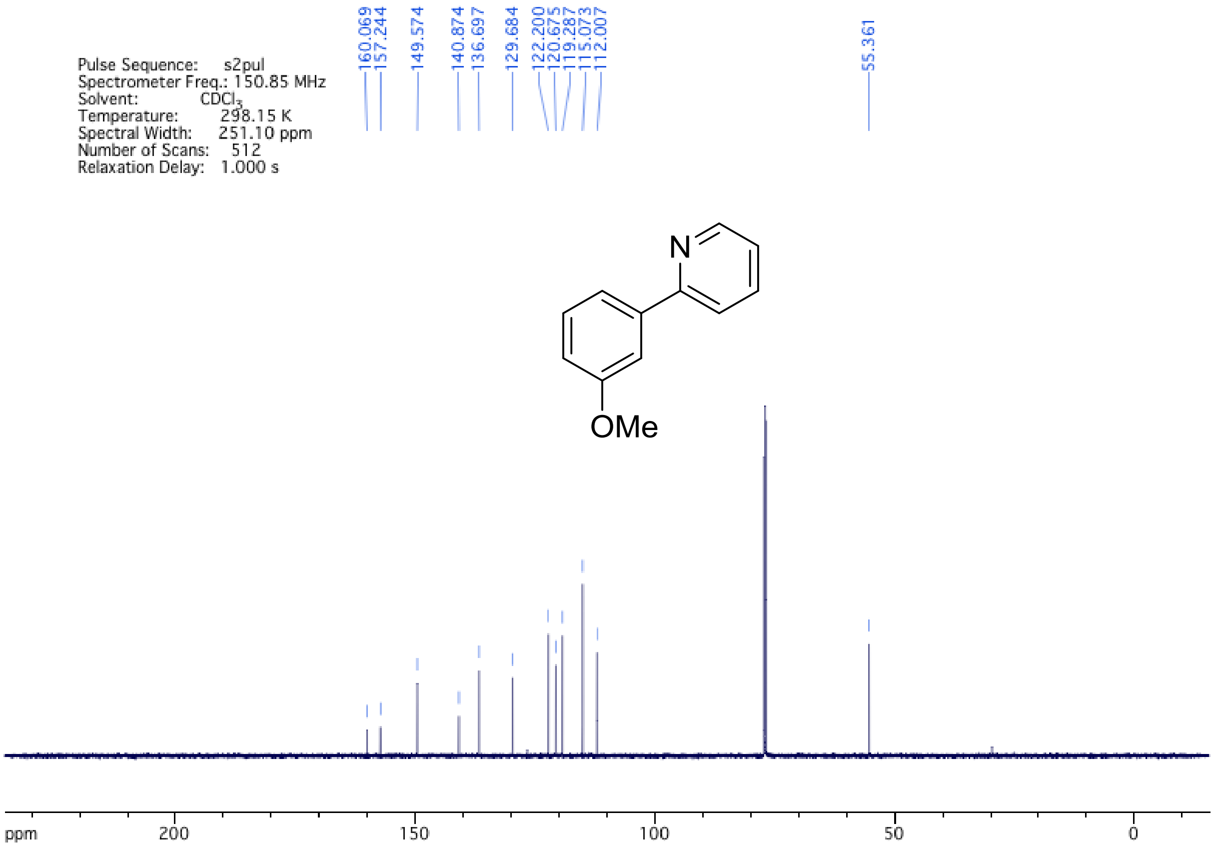
Pulse Sequence: s2pul
Spectrometer Freq.: 376.33 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 316.34 ppm
Number of Scans: 64
Relaxation Delay: 1.000 s

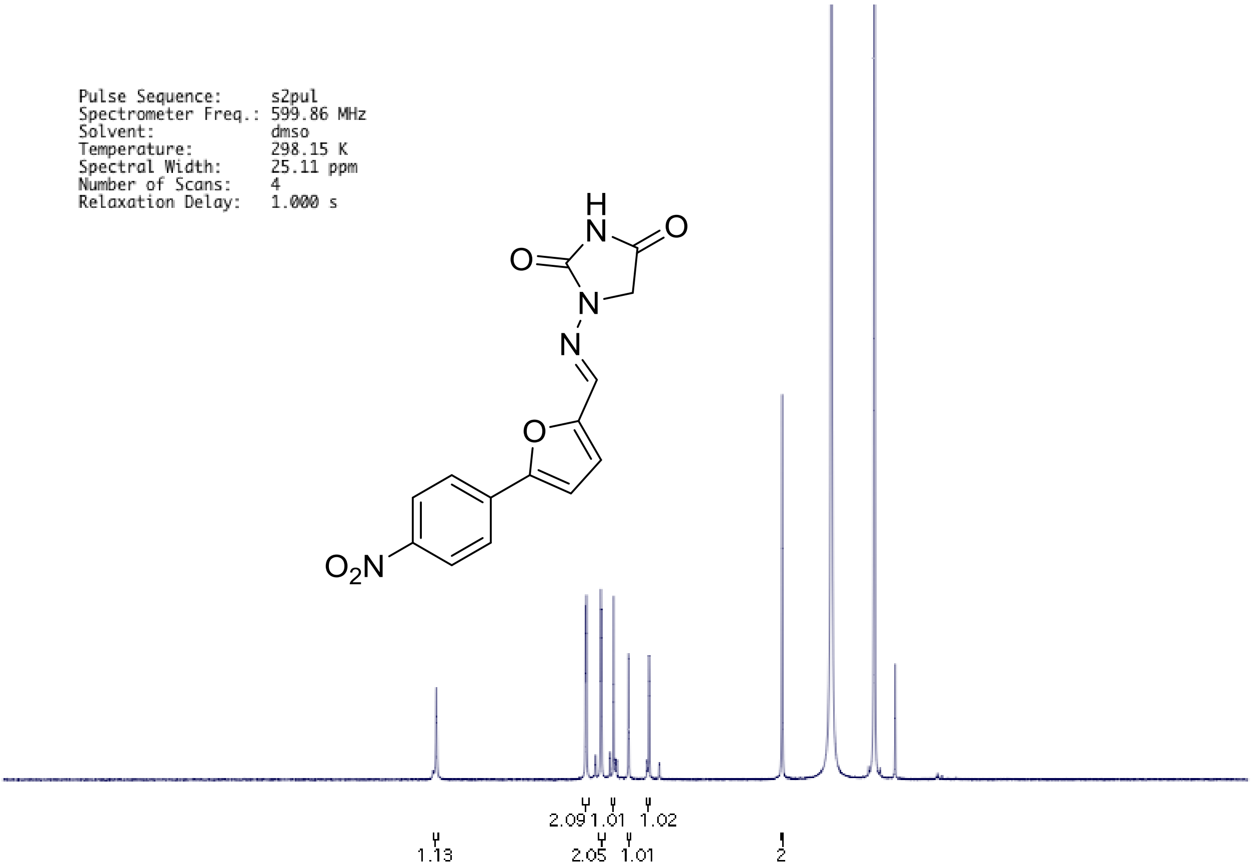


Pulse Sequence: s2pul
Spectrometer Freq.: 399.97 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 16.03 ppm
Number of Scans: 16
Relaxation Delay: 1.000 s

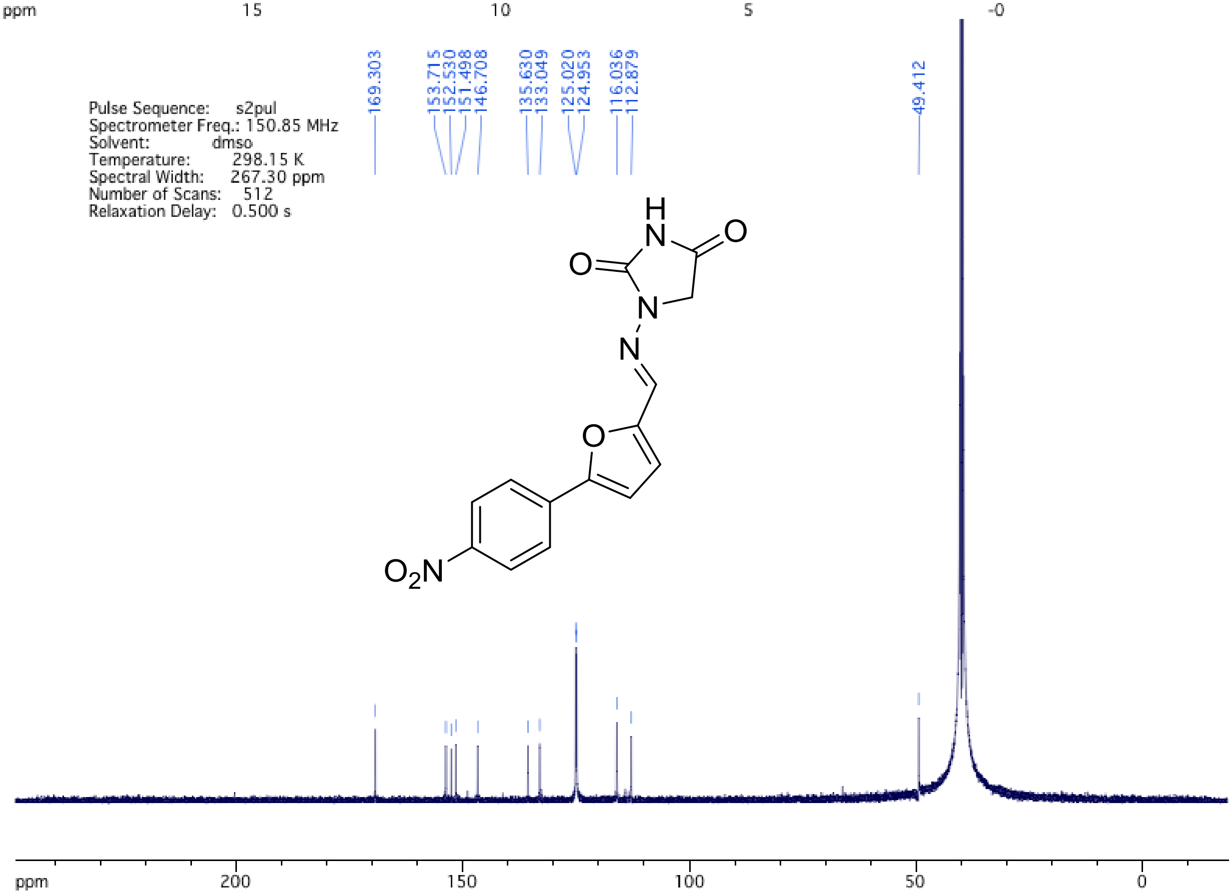


Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: $CDCl_3$
Temperature: 298.15 K
Spectral Width: 251.10 ppm
Number of Scans: 512
Relaxation Delay: 1.000 s





Pulse Sequence: s2pul
Spectrometer Freq.: 599.86 MHz
Solvent: dmso
Temperature: 298.15 K
Spectral Width: 25.11 ppm
Number of Scans: 4
Relaxation Delay: 1.000 s



Pulse Sequence: s2pul
Spectrometer Freq.: 150.85 MHz
Solvent: dmso
Temperature: 298.15 K
Spectral Width: 267.30 ppm
Number of Scans: 512
Relaxation Delay: 0.500 s

15. Literature

1 R. Zapf, C. Becker-Willinger, K. Berresheim, H. Bolz, H. Gnaser, V. Hessel, G. Kolb, A.-K. Pannwitt, A. Ziogas *Trans IChemE* 2003, **81A**, 721–729.

2 R. Zapf, G. Kolb, H. Pennemann, V. Hessel *Chem. Eng. Technol.* 2006, **29**, 1509–1512.

3 TOPAS-Academic V6, Coelho Software, Brisbane (AUS) **2016**.

4 R.W. Cheary, A. Coelho *J. Appl. Cryst.* **1992**, *25*, 109–121.

5 Perason's Crystal Data, Release **2009/10**, P. Villars, K. Cenzual, ASM International Materials Park, Ohio (US).

6 J. Zoller, D. C. Fabry, M. Rueping *ACS Catal.*, **2015**, *5*, 3900–3904.

7 S. Shaaban, A. Jolit, D. Petkova, N. Maulide *Chem. Commun.,* **2015**, *51*, 13902–13905.

8 A. Yokooji, T. Satoh, M. Miura, M. Nomura *Tetrahedron,* **2004**, *60*, 6757–6763.

9 S. Wübbolt, M. Oestreich *Angew. Chem. Int. Ed.*, **2015**, *54*, 15876–15879.

10 M. L. N. Rao, R. J. Dhanorkar, *Eur. J. Org. Chem.*, **2014**, *2014*, 5214–5228.

11 J. Xu, G. Cheng, D. Su, Y. Liu, X. Wang, Y. Hu, *Chem. Eur. J,* **2009,** *15*, 13105–13110.

12 C. Xu, Q. Shen, *Org. Lett.*, **2014**, *16*, 2046–2049.