Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

3D Printed Tetrakis(triphenylphosphine)palladium (0) Impregnated Stirrer Devices for Suzuki-Miyaura Cross-Coupling Reactions

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Supplementary Contents

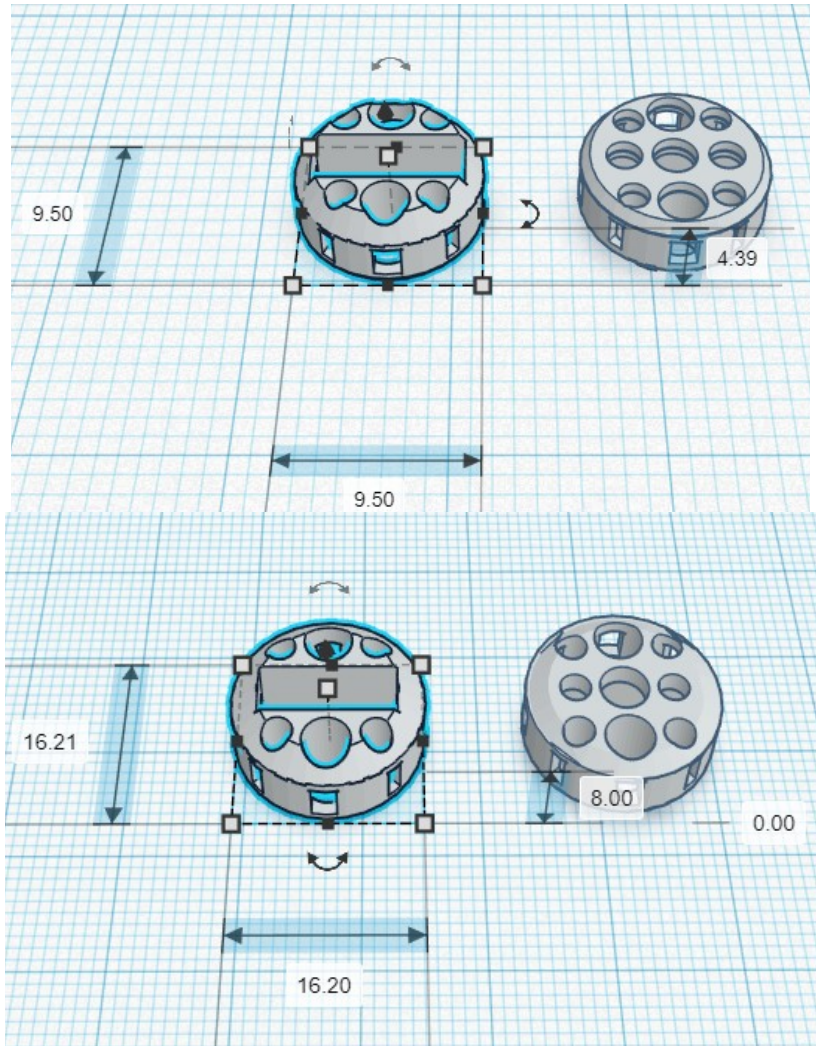
S1.0. General experimental and analysis

All reactions were carried out under an atmosphere of nitrogen and all glassware was pre-dried in an oven (110 °C) and cooled under nitrogen prior to use. Stirring was by internal magnetic follower unless otherwise stated. All reagents and solvents were purchased from Sigma-Aldrich, Fluka or VWR and used without further purification. Analytical TLC was carried out on Merck silica gel 60 F_{254} pre-coated plastic plates. Short wave UV (245 nm) or $KMnO_4$ were used to visualize components. ^{1}H and ^{13}C NMR data were recorded on a Bruker AV400, Bruker AV500 and AV600 spectrometers. Spectra were recorded in deuterochloroform and referenced to residual $CHCl_3$ (^{1}H, 7.26 ppm; ^{13}C, 77.16 ppm). ^{1}H, and ^{13}C spectral data were visualized and processed using MestReNova software. Chemical shifts were expressed in ppm (δ) relative to the standard and coupling constants (J) in Hz. High resolution mass spectra were recorded by the National Mass Spectrometry Facility at Swansea University on a LTQ Orbitrap XL utilizing nanospray ionization (NSI) or Xevo G2-S Atmospheric Solids Analysis Probe (ASAP). Infrared spectra were recorded on a Bruker Alpha IR spectrophotometer. Melting points were determined using open glass capillaries on a Stuart Scientific SMP3 apparatus and are uncorrected.

S2.0. 3D Printing of $Pd(PPh_3)_4$ Impregnated Stirrers

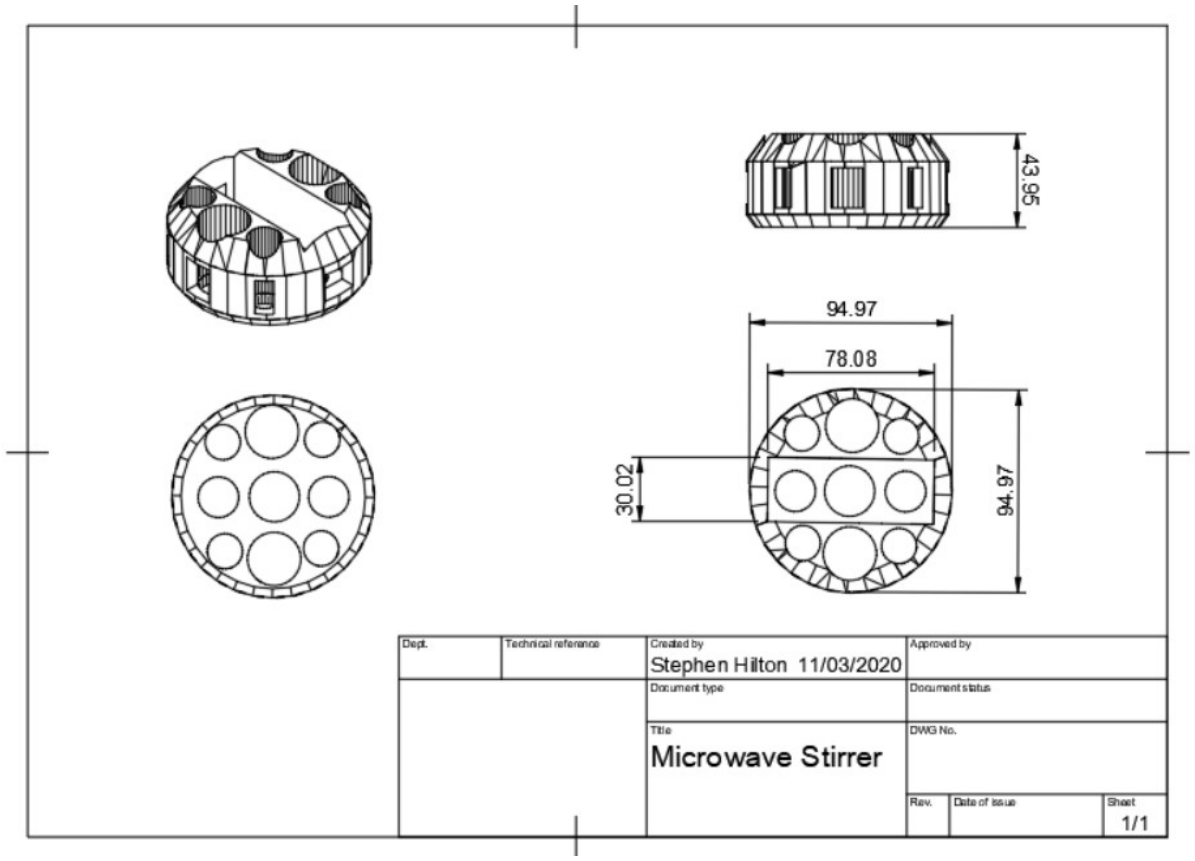
S2.1. Design of 3D Printed Stirrers

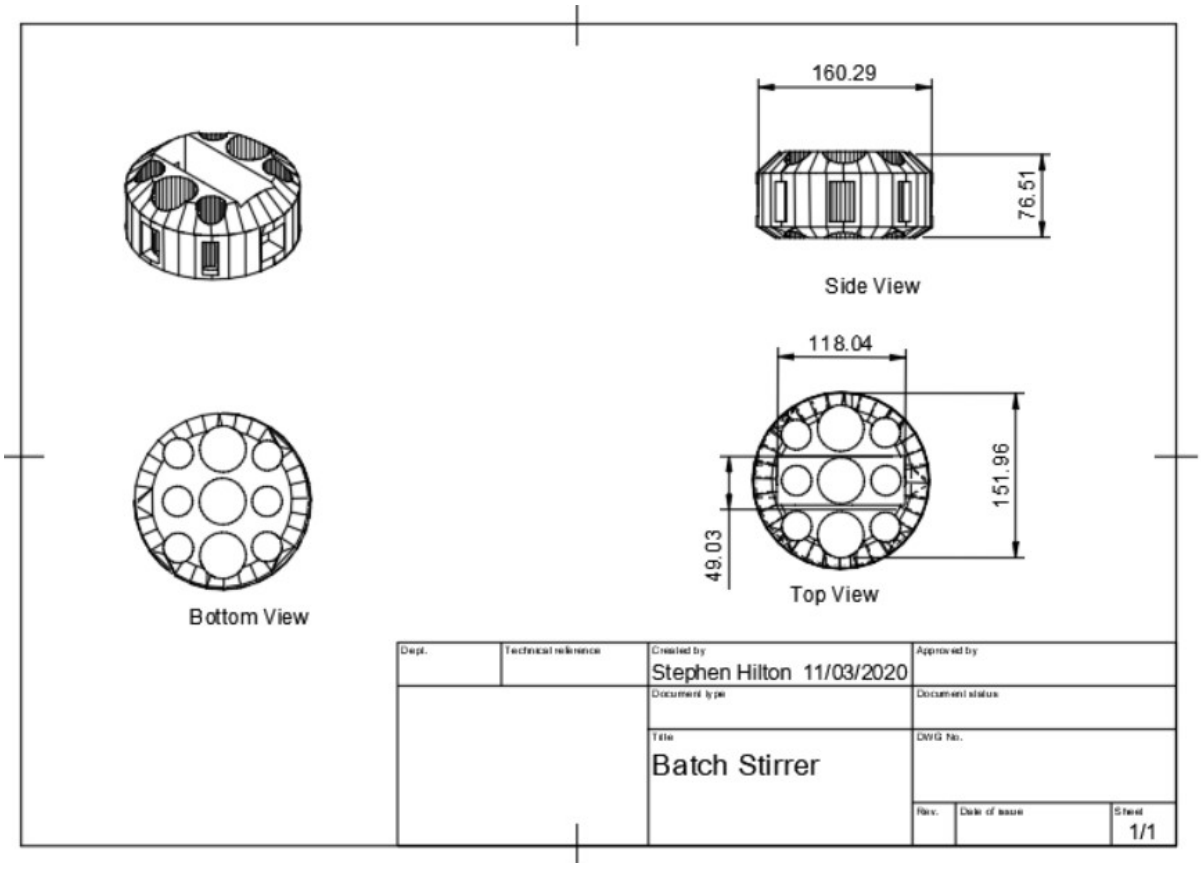
The microwave and batch stirrer devices were designed using the freeware web-based application - Tinkercad (Autodesk) software (Supp. Fig. 1), which were exported as STL (standard tessellation language) files. Designs were based on those previously reported and further optimised for fitting in a Radleys Carousel reactor tube and also for use within a Biotage microwave vial.[1,2]



Supplementary Figure 1. Design size and shape of the microwave and Batch Stirrer Devices from Tinkercad.

S.2.2. Design and Shape of Batch and Microwave Stirrers

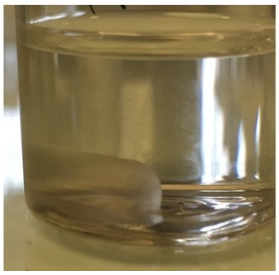
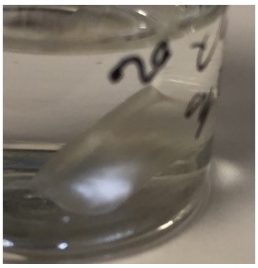
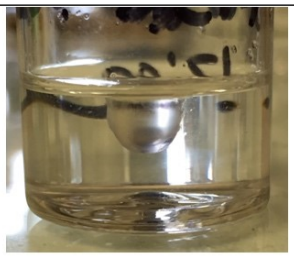
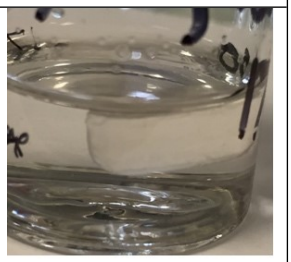




S2.3. Solvent Compatibility of 3D Printed Resin

Most resin formulations that are used for 3D printing display poor stability in organic solvent once printed. 3D printed parts exposed to solvents such as acetonitrile, ethanol and methanol are usually fairly robust and do not display structural damage on short exposure times to organic solvent. However, use of solvents such as acetone, THF and dioxane lead to rapid structural decomposition as shown below (Supplementary table 1). Exposure of a standard 3D printed tablet shape to both THF and dichloromethane leads to very rapid destruction of the 3D printed shape after 12 hours. However, use of the solvent resistant formulation,[2] shows retention of shape even after 48 hours of exposure to solvent.

Supplementary Table 1: Solvent Compatibility

Solvent	Standard Resin Exposure Time	Chemically Resistant Resin Exposure Time	
	12 hours	*18 hours*	*48 hours*
THF			
Dichloromethane			

In order to quantify the solvent compatibility of the 3D printed resin, we printed a number of 3-dimensional cubes (1.5 cm x 1.0 cm x 1.0cm) and challenged their structural integrity by exposure to solvent for differing time periods. The dimensions of the 3D printed shape were measured both before and after using Vernier callipers as well as the mass and the degree of swelling quantified.

Supplementary Table 2: General 3D Printed Resin Solvent Compatibility (24 Hours)

Following exposure of the cubes to solvent, it was shown that their volume changes were minimal for a 24-hour exposure across an array of solvents indicating good solvent compatibility with good mass retention and lack of solvent uptake.

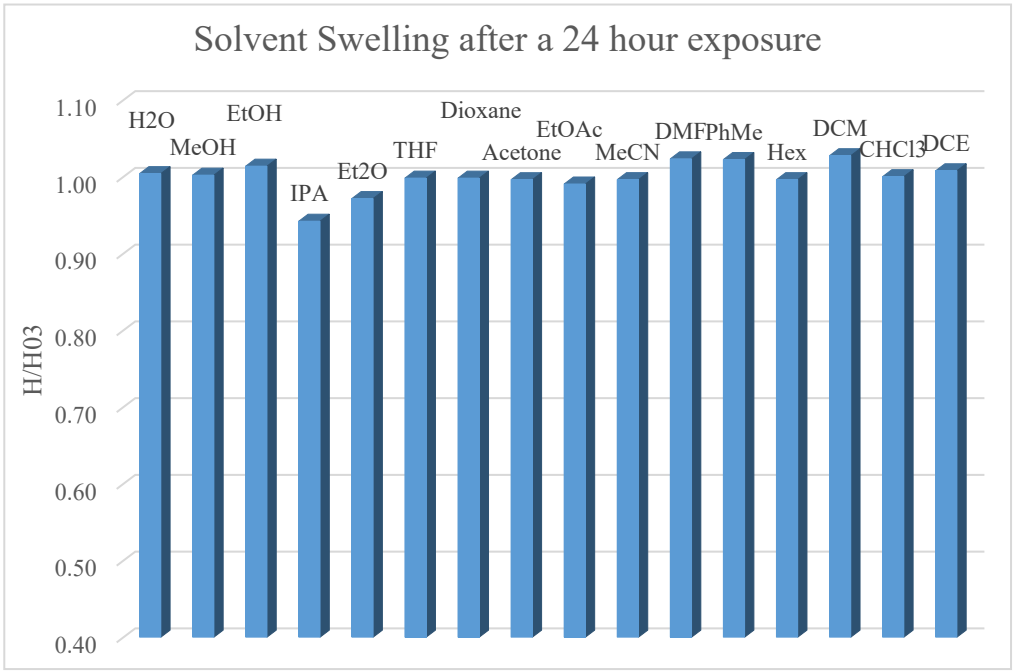
Solvent Swelling Test 24 Hours

Solvent	Height				Width			Depth			Mass			Observations	
	Before	After	H03	% Difference	Before	After	% Difference	Before	After	% Difference	Before	After	% Difference	24 h	1 week
H_2O	15.22	15.24	1.00	0%	9.95	9.97	0%	10.08	10.09	0%	1.95	1.96	0%	N/HD	N
MeOH	15.28	15.29	1.00	0%	9.99	10.01	0%	10.16	10.20	0%	2.12	2.12	0%	N/HD	N
EtOH	15.42	15.49	1.01	0%	10.05	10.04	0%	10.08	10.08	0%	2.04	2.03	0%	N/HD	N
IPA	15.71	15.40	0.94	-2%	10.00	10.00	0%	10.03	10.02	0%	2.08	2.07	0%	N/HD	N
Et_2O	14.58	14.44	0.97	-1%	10.07	10.05	0%	10.20	10.18	0%	1.96	1.95	0%	N/HD	N
THF	15.81	15.80	1.00	0%	10.06	10.02	0%	10.00	9.93	-1%	2.02	2.02	0%	N/HD	N
Dioxane	15.54	15.53	1.00	0%	10.06	10.22	2%	10.05	10.03	0%	2.00	2.00	0%	N/HD	N
Acetone	15.16	15.14	1.00	0%	10.07	10.06	0%	10.14	10.14	0%	2.02	2.02	0%	N/HD	N
EtOAc	15.63	15.58	0.99	0%	9.99	10.03	0%	10.11	10.10	0%	2.05	2.05	0%	N/HD	N
MeCN	15.45	15.43	1.00	0%	9.97	10.05	1%	10.14	10.19	0%	2.00	2.02	1%	N/HD	N
DMF	15.62	15.74	1.02	1%	10.06	9.95	-1%	10.10	9.96	-1%	2.02	2.03	0%	N/HD	N
PhMe	14.89	15.00	1.02	1%	9.90	10.00	1%	10.01	10.04	0%	1.92	1.92	0%	N/HD	N
Hex	15.36	15.34	1.00	0%	9.87	9.96	1%	10.10	10.18	1%	1.94	1.94	0%	N/HD	N
DCM	15.52	15.66	1.03	1%	9.92	10.14	2%	10.01	10.19	2%	2.00	2.10	5%	L	H
$CHCl_3$	15.21	15.21	1.00	0%	10.08	10.24	2%	10.20	10.30	1%	2.14	2.16	1%	L	H
DCE	15.67	15.71	1.01	0%	10.05	10.13	1%	9.96	9.97	0%	2.02	2.04	1%	N/HD	L

Solvent Swelling Test via Heating at Reflux

Solvent	Height				Width			Depth			Mass			Observations	
	Before	After	H03	% Difference	Before	After	% Difference	Before	After	% Difference	Before	After	% Difference	24 h	1 week
Et_3N	15.32	15.49	1.03	1%	10.08	10.09	0%	9.9	9.9	0%	1.98	1.97	0%	N	L
AcOH	14.04	14.16	1.03	1%	10.03	10.05	0%	10.11	10.1	0%	1.81	1.82	0%	L	L
6M HCl	14.94	14.97	1.01	0%	10.01	10.03	0%	10.07	10.06	0%	1.98	1.93	-2%	N	N
PhMe	12.81	12.87	1.01	0%	10.05	10.09	0%	9.92	9.95	0%	1.63	1.63	0%	L	
THF	10.69	10.81	1.03	1%	10.3	10.27	0%	9.93	9.95	0%	1.41	1.41	0%	L	
DCE	12.00	12.24	1.06	2%	10.26	10.32	1%	10.06	10.13	1%	1.59	1.63	3%	L	

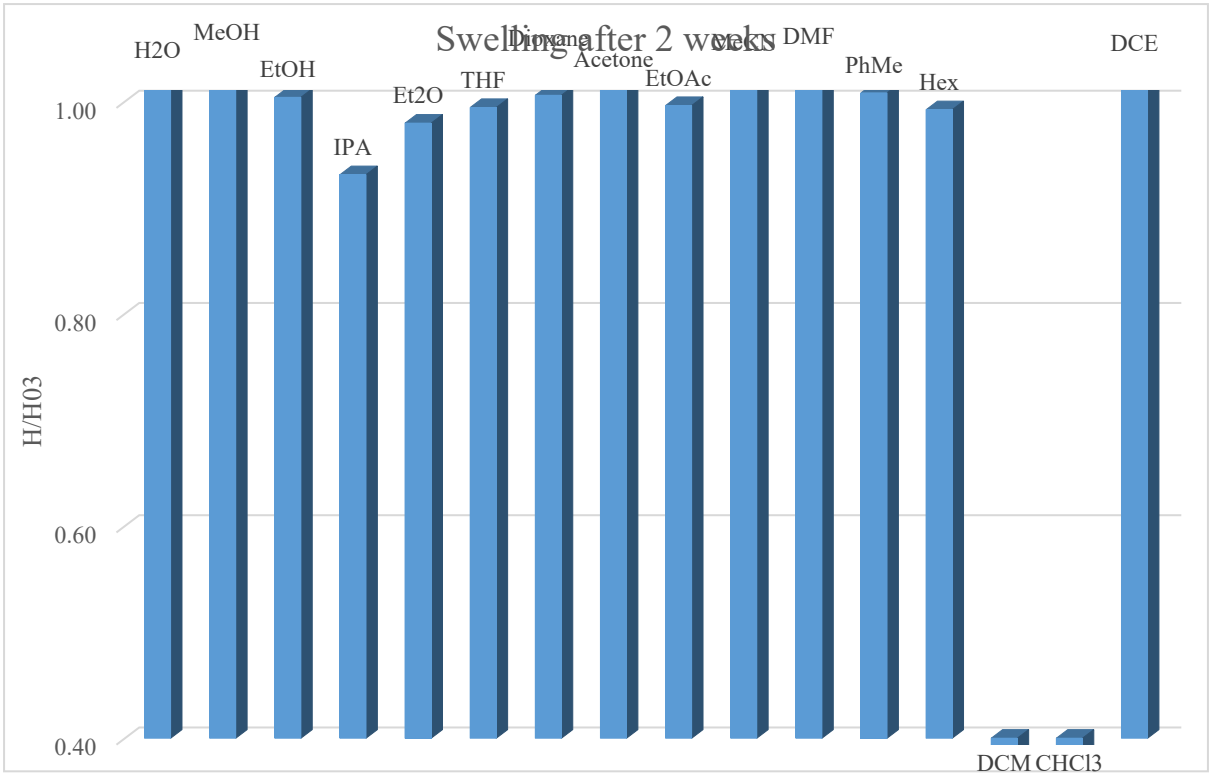
Key to observations	
N	No observed degradation
L*	Low degradation due to thin parts from print defects/rough, powdery ed
L	Low degradation
H	High degradation
D	Disintegrated
HD	Hard to touch
S	Soft to touch
T	Tacky



Supplementary Table 3: General 3D Printed Resin Solvent Compatibility (336 hours)

Further exposure of the 3D printed cubes to solvent for 2 weeks gave good results for their structural integrity except in the case of exposure to DCM and chloroform, where ablation of the top printed layers was observed.

Solvent Swelling Test 2 Weeks															
Solvent	Height				Width			Depth			Mass				
	Before	After	H03	% Difference	Before	After	% Difference	Before	After	% Difference	Before	After	% Difference		
H_2O	15.22	15.33	1.02	1%	9.95	10.00	1%	10.08	10.13	0%	1.95	1.98	1%		
MeOH	15.28	15.38	1.02	1%	9.99	10.21	2%	10.16	10.27	1%	2.12	2.15	1%		
EtOH	15.42	15.44	1.00	0%	10.05	10.04	0%	10.08	10.15	1%	2.04	2.04	0%		
IPA	15.71	15.34	0.93	-2%	10.00	9.99	0%	10.03	10.04	0%	2.08	2.07	0%		
Et_2O	14.58	14.48	0.98	-1%	10.07	10.16	1%	10.20	10.18	0%	1.96	1.96	0%		
THF	15.81	15.78	0.99	0%	10.06	10.06	0%	10.00	9.92	-1%	2.02	2.03	0%		
Dioxane	15.54	15.57	1.01	0%	10.06	10.09	0%	10.05	10.03	0%	2.00	2.01	0%		
Acetone	15.16	15.23	1.01	0%	10.07	10.03	0%	10.14	10.16	0%	2.02	2.04	1%		
EtOAc	15.63	15.61	1.00	0%	9.99	10.03	0%	10.11	10.06	0%	2.05	2.06	1%		
MeCN	15.45	15.6	1.03	1%	10.17	10.05	-1%	10.14	10.35	2%	2.00	2.06	3%		
DMF	15.62	15.8	1.03	1%	10.06	10.04	0%	10.10	9.96	-1%	2.02	2.04	1%		
PhMe	14.89	14.93	1.01	0%	9.90	9.90	0%	10.01	9.98	0%	1.92	1.93	0%		
Hex	15.36	15.32	0.99	0%	9.87	9.90	0%	10.10	10.08	0%	1.94	1.95	0%		
DCM	15.52	n/a	n/a	n/a	9.92	10.14	2%	10.01	10.19	2%	2.00	2.10	5%		
$CHCl_3$	15.21	n/a	n/a	n/a	10.08	10.24	2%	10.20	10.30	1%	2.14	2.16	1%		
DCE	15.67	15.82	1.03	1%	10.05	10.22	2%	9.96	10.17	2%	2.02	2.08	3%		



S2.4. Preparation of $Pd(PPh_3)_4$ containing Resin for Printing

Tetrakis(triphenylphosphine)palladium(0) (0.17 g, 0.5% w/w) and photoinitiator (0.5 g) were dissolved in resin (33.3 g) at room temperature according to the published procedure and left to stir for 30 minutes in the absence of light.[2]

S.2.5. Printing and Preparation of Stirrer Devices

Once the designs had been exported as .stl files, they were uploaded to FormLabs PreForm Software (version 2.10.3) before printing. Support structures to aid printing were automatically generated using PreForm Software. The resin formulation containing the $Pd(PPh_3)_4$ catalyst was poured into the tray of a Form1+ 3D Printer. The device designs were then uploaded to the printer and multiple copies printed at 100-micron layer height with a print time of approximately 30 minutes (100 layers).[2]

Supplementary Figure 2. Design on the FormLabs software, printed on the build plate and with support and removed support from the batch-based stirrer devices.

Following printing, designs were removed from the print bed, washed (isopropanol), and post-cured under UV light *in vacuo* for 30 minutes. Supports were carefully removed from each object and devices stored at room temperature. Stirrer beads were inserted into the central cavity of each device prior to reaction.

S.2.6. Analysis of Palladium Content per Device

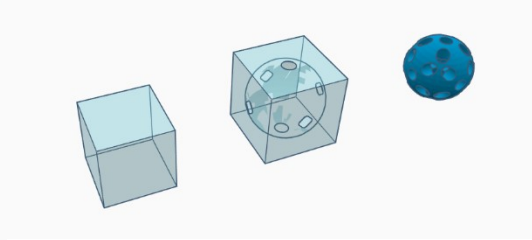
Following printing and support removal, the stirrer devices were weighed in order to determine the amount of $Pd(PPh_3)_4$ catalyst present within each device. Weights are reported as averages over 5 devices and following analysis, it was estimated that the microwave-based stirrer devices contained 9 mg of catalyst and that the batch-based device contained 48 mg of catalyst.

Supplementary Table 4: Estimation of $Pd(PPh_3)_4$ content per device

Stirrer Type	Loading of $Pd(PPh_3)_4$ [%]	Mass of Stirrer [g]	Mass of catalyst Per device [mg]	Mmol of Catalyst Per device [Mmol]
Microwave	0.5	0.18	9	0.0075
Batch	0.5	0.97	48	0.041

n=5

S.2.7. Estimation of $Pd(PPh_3)_4$ Content at Device Surface Available for Catalysis



Supplementary Figure 3: Structures used for Surface Area / Volume calculations

Whilst the devices themselves contain catalyst evenly spread throughout their entire structure, it is likely that not all the catalyst in is available for reaction. Considering recent reports in the literature and the resistance of the 3D printed parts to swelling in organic solvent, it is pertinent to assume that only a fraction of the catalyst is available for reaction. From the literature, estimates of penetration of solvent have been reported for 3D printed devices of 70 microns.[3] Hence, calculations for the estimation of catalyst availability were carried out based on the first 100 microns. The amount available for reaction therefore relies heavily on the surface area/ volume (SA/V) ratio, with larger values equating to more catalyst available for reaction. In order to estimate the amount of catalyst available within the first 100 microns of the device, a series of 3-dimensional shapes with a range of surface areas and volumes were analysed for their volumes lost on ablation of the first 100 microns of their surfaces both internally and externally. The shapes used in this study were a cube, a cube with a hollow sphere and a sphere with large internal channels. As can be seen from the table, increasing SA/V values lead to increasing percentages of volume lost from the shapes as a whole.

Supplementary Table 5

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Entry	Type [mm]	Surface area	Volume	SA/V	V/SA	Volume loss Layer	Volume loss Cumulative	Percentage loss Layer	Percentage loss Cumulative	microns lost	Object
1	Cube 10.00 x 10.00	600.00	1000.00	0.6	1.667	0.000	0.00	0.00%	0.00%	0	
2	Cube 9.90 x 9.90	588.00	970.30	0.6	1.650	29.701	29.70	2.97%	2.97%	100	
3	Cube 9.80 x 9.80	576.00	941.19	0.6	1.634	29.109	58.81	3.00%	5.88%	100	
4	Cube 9.70 x 9.70	564.54	912.67	0.6	1.617	28.517	87.33	3.03%	8.73%	100	
5	Cube 9.60 x 9.60	552.96	884.74	0.6	1.600	27.937	115.26	3.06%	11.53%	100	
6	Cube+hollow 10.00 x 10.00	892.712769	451.195892	2.0	0.505	0.000	0.00	0.00%	0.00%	0	
7	Cube+hollow 9.90 x 9.90	851.707153	407.715942	2.1	0.479	43.480	43.48	9.64%	9.64%	100	
8	Cube+hollow 9.80 x 9.80	804.895386	366.381317	2.2	0.455	41.335	84.81	10.14%	18.80%	100	
9	Cube+hollow 9.70 x 9.70	760.893066	327.297394	2.3	0.430	39.084	123.90	10.67%	27.46%	100	
10	Cube+hollow 9.60 x 9.60	718.258118	290.411621	2.5	0.404	36.886	160.78	11.27%	35.64%	100	
11	Cube+hollow 11.50 x 11.50	1180.616089	686.212708	1.7	0.581	0.000	0.00	0.00%	0.00%	0	
12	Cube+hollow 11.40 x 11.40	1133.658691	628.570557	1.8	0.554	57.642	57.64	8.40%	8.40%	100	
13	Cube+hollow 11.30 x 11.30	1081.724854	573.334167	1.9	0.530	55.236	112.88	8.79%	16.45%	100	
14	Cube+hollow 11.20 x 11.20	1027.979937	520.714478	2.0	0.507	52.620	165.50	9.18%	24.12%	100	
15	Cube+hollow 11.10 x 11.10	979.739319	470.602142	2.1	0.480	50.112	215.61	9.62%	31.42%	100	
16	Sphere+holes 10.00 x 10.00	671.438838	223.975708	3.0	0.334	0.000	0.00	0.00%	0.00%	0	
17	Sphere+holes 9.90 x 9.90	614.599915	191.087219	3.2	0.311	32.888	32.89	14.68%	14.68%	100	
18	Sphere+holes 9.80 x 9.80	553.298096	162.817322	3.4	0.294	28.270	61.16	14.79%	27.31%	100	
19	Sphere+holes 9.70 x 9.70	496.450073	136.857635	3.6	0.276	25.960	87.12	15.94%	38.90%	100	
20	Sphere+holes 9.60 x 9.60	441.648621	113.310623	3.9	0.257	23.547	110.67	17.21%	49.41%	100	
16	Sphere+holes 9.40 x 9.40	567.420898	170.573837	3.3	0.301	0.000	0.00	0.00%	0.00%	0	
17	Sphere+holes 9.30 x 9.30	520.804504	142.691895	3.6	0.274	27.882	27.88	16.35%	16.35%	100	
18	Sphere+holes 9.20 x 9.20	472.807861	118.656624	4.0	0.251	24.035	51.92	16.84%	30.44%	100	
19	Sphere+holes 9.10 x 9.10	419.812042	96.380684	4.4	0.230	22.276	74.19	18.77%	43.50%	100	
20	Sphere+holes 9.00 x 9.00	368.371033	76.779678	4.8	0.208	19.601	93.79	20.34%	54.99%	100	
21	**Generation 1 Stirrer**	1382.567017	815.066284	1.7	0.590	0.000	0.00	0.00%	0.00%	0	
22	*Generation 1 Stirrer (est loss)*	*1327.264336*	*746.600716*	*1.8*	*0.563*	*68.466*	*68.47*	*8.40%*		100	
23	**Generation 2 Carousel Stirrer**	1266.610474	646.114136	2.0	0.510	0.000	0.00	0.00%	0.00%	0	
24	*Generation 2 Carousel Stirrer (est loss)*	1203.27995	583.828733	2.1	0.485	*62.285*	*62.29*	*9.64%*		100	
25	**Generation 2 Microwave Stirrer**	508.346527	109.222298	4.7	0.215	0.000	0.00	0.00%	0.00%	0	
26	*Generation 2 Microwave Stirrer (est loss)*	447.3449438	87.3778384	5.1	0.195	*21.844*	*21.84*	*20.00%*		100	

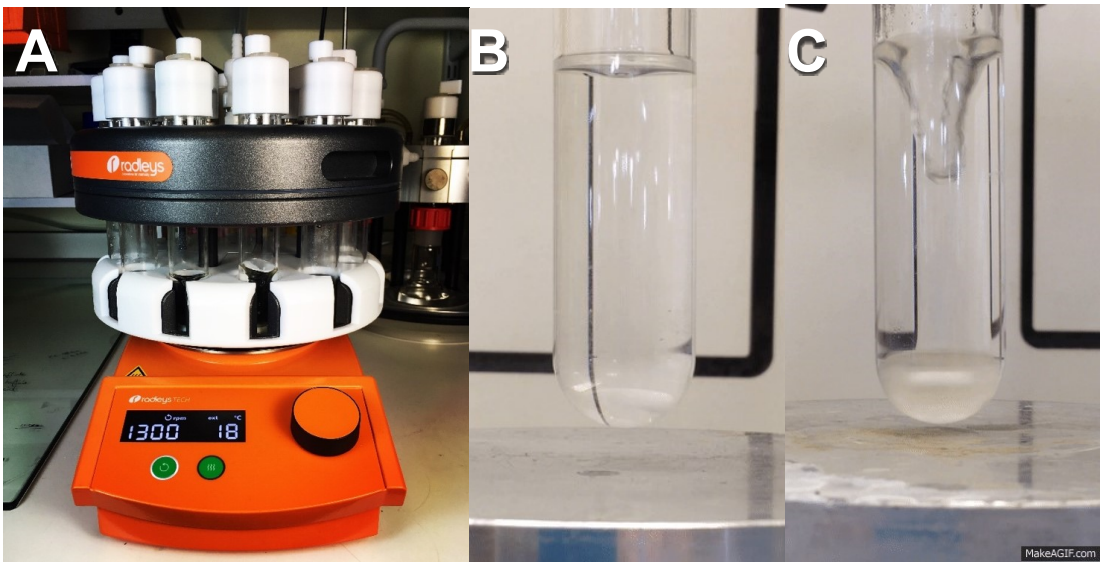
The surface area/ volume ratio of the microwave stirrer device is 4.7 mm^{-1} calculated using Meshlab 64bit v2020.02 and the corresponding batch stirrer 2.0 mm^{-1}. As seen from the surface area ablation results table, comparable entries 19 and 14 provide a good indication of the volume lost from the first 100 microns of the surface of the devices. In the microwave stirrer with a higher SA/V value, we see an estimation of 20% of the catalyst being available for reaction, whilst in the 2nd generation stirrer device, only 9.6% of the catalyst is available for reaction, equating to 1.8 mg and 4.6 mg of catalyst available for reaction for each device respectively. Whilst these results are simple estimations, they provide good approximations for the actual amount that is available for reaction as shown below (Supplementary Table 6).

Supplementary Table 6: Calculation of $Pd(PPh_3)_4$ Content Relating to Solvent Exposure

Stirrer Type	Microwave	Batch
Mass of catalyst per device [mg]	9	48
Mmol of catalyst per device [mmol]	0.075	0.041
Volume [mm^3]	109.22	646.11
Surface Area [mm^2]	508.35	1266.61
Surface Area/ Volume ratio [mm^{-1}]	4.7	2.0
Surface loss Estimate [microns]	100	100
Volume in 100 microns (est.)	21.84	62.29
Percentage volume in 100 microns (est.)	20	9.6
Mass of catalyst per device in first 100 microns [mg]	***1.8***	***4.6***
Mmol of catalyst per device in first 100 microns [mmol]	***0.0016***	***0.0039***

S.2.8. Carousel Based Stirrer Device

Carousel based stirrer Beads were designed to fit the Radleys carousel 12 reaction station (20 mL vials) as shown below. The enhanced mixing of the stirrer bead when compared to the same stirrer bead without the 3D printed housing is shown below (Supplementary Figure 4). Both Stirrers (conventional and 3D printed) are run at the same (1300 rpm) speed in the comparison pictures highlighting the rapid mass transfer of compound over the device itself.



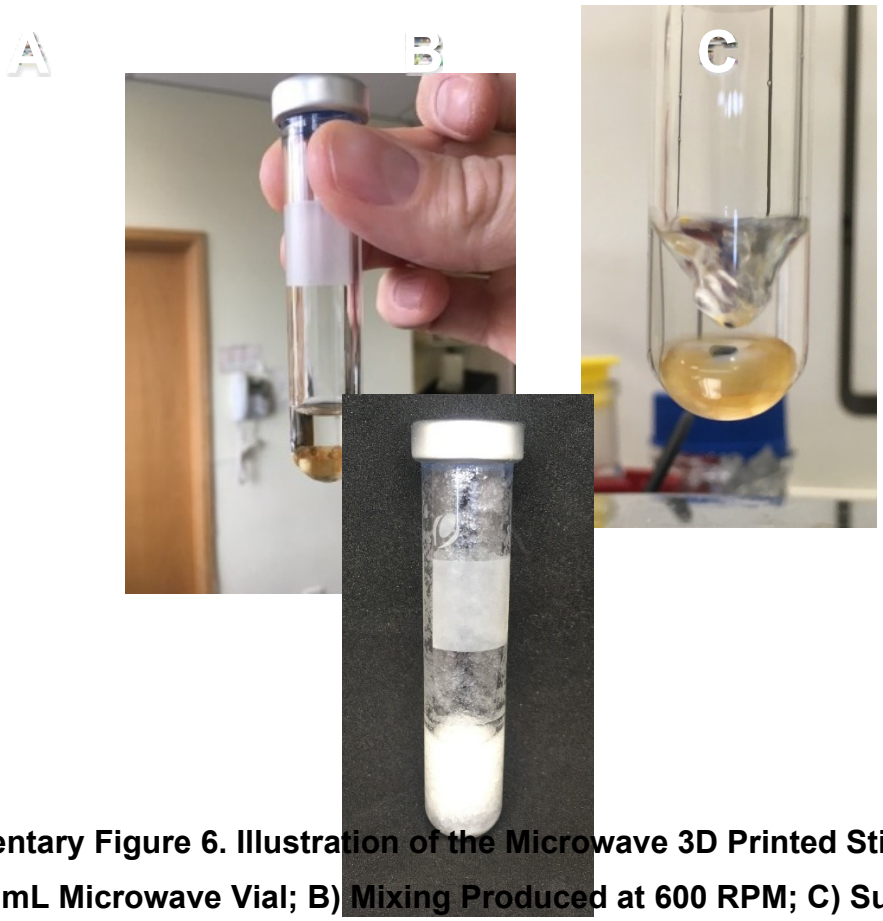
Supplementary Figure 4. Demonstration of Vortex Formation by the 3D Printed Stirrer: A) Placement in the Radleys Carousel; B) Normal Stirrer Bead Mixing at 1300 RPM; C) 3D Printed Stirrer Bead Mixing at 1300 RPM.

Following reaction, the stirrer bead was removed from the reaction and washed with solvent. The colour change is clear from the picture below, indicative of palladium being maintained in the device and not leached into solution.

Supplementary Figure 5. 3D Printed Stirrer Bead Colouration Post Reaction.

S.2.9. Microwave Based Stirrer Device

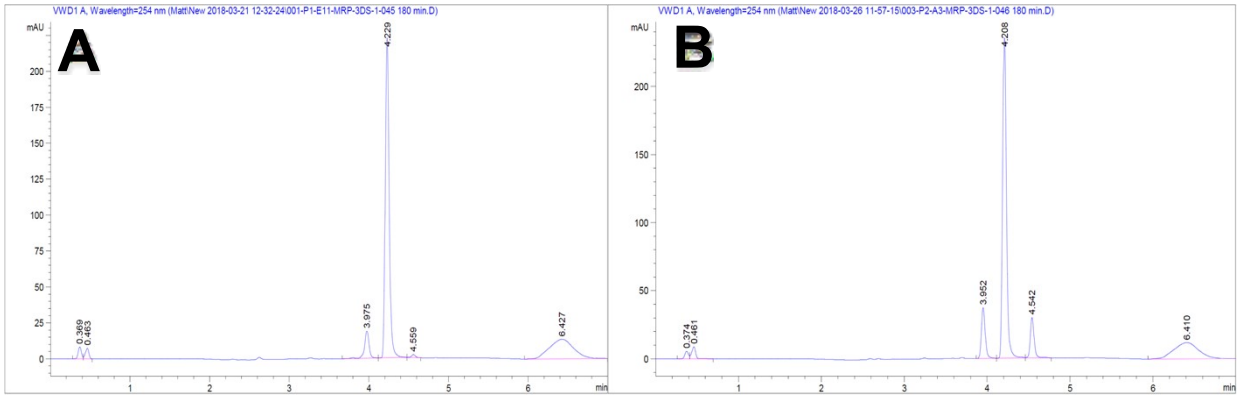
Stirrer Beads were designed to fit the 2-5 mL Biotage vial sizes as shown below. The final bead is shown in a comparative vial and reactions were stirred at 600 rpm in the Biotage microwave reaction cavity. As can be seen below, stirring is enhanced by the stirrer device in an analogous manner to that of the carousel-based device. The post reaction picture (Supplementary Figure 6, Image C), shows that the palladium is retained in the device, obviating the classic palladium coating observed with traditional microwave-based palladium reactions.



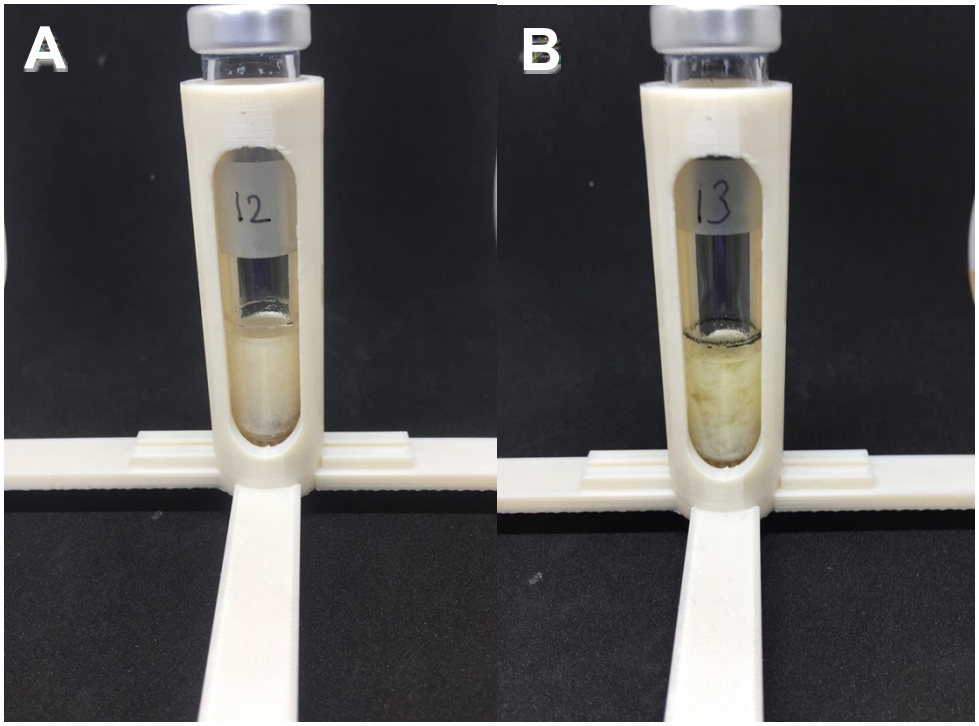
Supplementary Figure 6. Illustration of the Microwave 3D Printed Stirrer Bead: A) In the 2-5 mL Microwave Vial; B) Mixing Produced at 600 RPM; C) Suzuki-Miyaura Reaction after Heating.

S.2.10. Purity of Reaction

Illustration of the reaction purity obtained when using the $Pd(PPh_3)_4$ impregnated stirrer (A) versus a conventional batch based reaction (B). The product peak is at 4.2 mins and as can clearly be seen, by-products are greatly diminished.



Supplementary Figure 7. HPLC trace of crude reactions catalysed by: A) 3D printed $Pd(PPh_3)_4$ impregnated stirrer and B) Solution based $Pd(PPh_3)_4$.



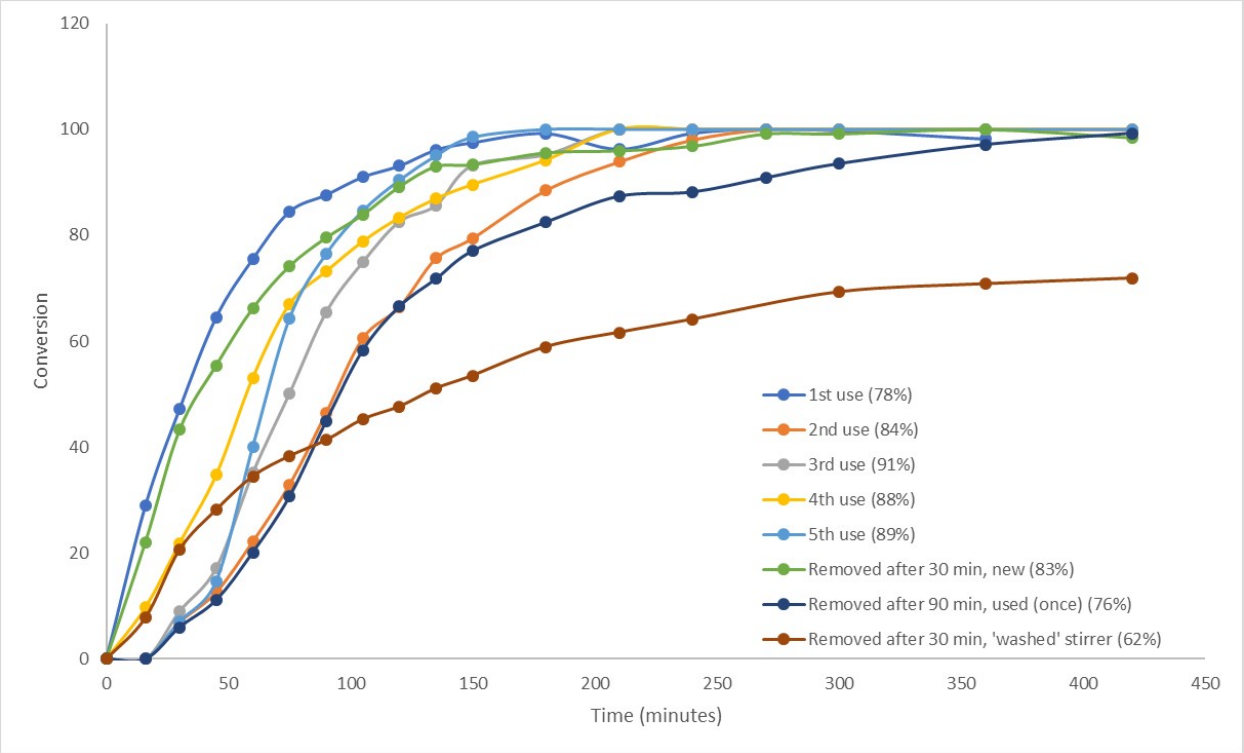
Supplementary Figure 8. Image of crude microwave based reactions catalysed by: A) 3D printed $Pd(PPh_3)_4$ impregnated stirrer and B) Solution based $Pd(PPh_3)_4$.

Analysis of repeated uses

Carousel reactions were carried out as described below. A 10 μL aliquot was taken at various time intervals and diluted with methanol (490 μL) and the sample analysed by HPLC. When the reaction was complete, the stirrer was removed, washed with a small amount of MeOH, dried and stored under N_2. After the 3rd use, the stirrer was washed with a small amount of CH_2Cl_2.

Where applicable, the 3D printed stirrer was removed at a particular time and replaced with a magnetic stir bar.

The 'washed' stirrer was subjected to heating at 65 °C in EtOH (8 mL) and DI water (2 mL) for 7 h and then removed, dried and stored under N_2.

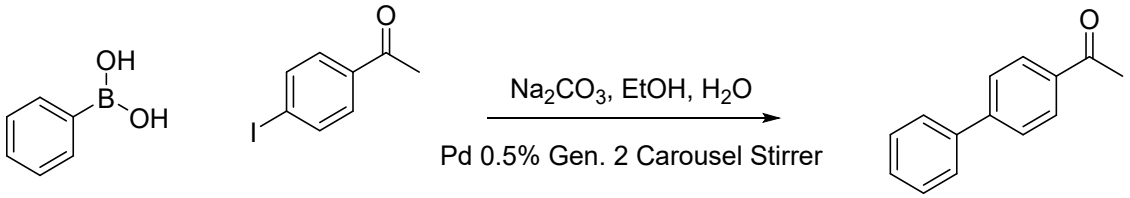


Supplementary Figure 9: Reaction profiles for repeated uses

S.3.0. General Procedures

S.3.1. General Procedure A:

1-([1,1'-Biphenyl]-4-yl)ethanone (3)[4]

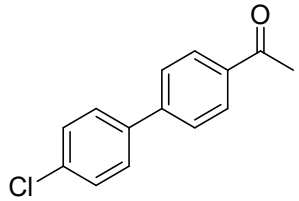


Chemical Formula: $C_{14}H_{12}O$
Molecular Weight: 196.25

1 **2** **3**

Phenylboronic acid (**1**) (0.071 g, 0.59 mmol) and 1-(4-iodophenyl)ethanone (**2**) (0.13 g, 0.53 mmol) were added to a solution of sodium carbonate (0.11 g, 1.07 mmol) in ethanol (8 mL) and water (2 mL) and a 0.5%Pd impregnated stirrer bead and the resulting mixture heated at 65 °C for 18 hours in a Radleys carousel reactor at 800 rpm. The stirrer was washed with DCM and the combined mixture concentrated under reduced pressure. The crude mixture was partitioned between water (15 mL) and DCM (15 mL) and the aqueous phase extracted with DCM (3 x 15 mL) and the combined organic extracts dried ($MgSO_4$), filtered and solvent removed under reduced pressure to give 1-([1,1'-biphenyl]-4-yl)ethanone (**3**) as a colorless solid (0.101 g, 99%); mp 119.4-120.1 °C (lit. 115-117 °C[4]); v_{max} (neat) 3069, 2921 (C–H), 1676 (C=O); ν_{max} (neat) 3069 (CH), 2921 (CH), 1676 (C=O); δ_H (400 MHz, $CDCl_3$) 8.04 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.69 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.65 – 7.62 (2H, m, Ar**H**), 7.48 (2H, t, *J* = 7.5 Hz, Ar**H**), 7.41 (1H, t, *J* = 7.4 Hz, Ar**H**), 2.64 (3H, s, COC**H**$_3$); δ_C (101 MHz, $CDCl_3$) 197.8, 145.9, 139.9, 135.9, 129.1, 129.0, 128.3, 127.4, 127.3, 26.7; HRMS m/z (NSI) 197.0961 ([M+H]+ $C_{14}H_{13}O$ requires 197.0960).

1-(4'-Chloro-[1,1'-biphenyl]-4-yl)ethanone (4)[5]

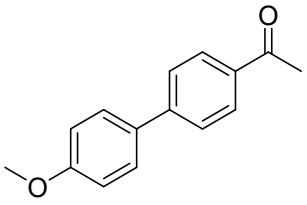


Chemical Formula: $C_{14}H_{11}ClO$
Molecular Weight: 230.69

According to general procedure **A** compound **4** was obtained as a colorless solid (0.088 g, 85%); mp 94.0-95.3 °C (lit. 102-103 °C[5]); ν_{max} (neat) 2922 (CH), 1669 (C=O), 850 (CH); δ_H (400 MHz, $CDCl_3$) 8.01 (1H, d, *J* = 8.3 Hz, Ar**H**), 7.63 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.53 (2H, d, *J* = 8.5 Hz, Ar**H**), 7.42 (2H, d, *J* = 8.5 Hz, Ar**H**), 2.62 (3H, s, COC**H**$_3$); δ_C (101 MHz, $CDCl_3$)

197.6, 144.5, 138.3, 136.2, 134.5, 129.2, 129.1, 128.6, 127.1, 26.7; HRMS m/z (NSI) 231.0571 ([M+H]+ $C_{14}H_{12}ClO$ requires 231.0572).

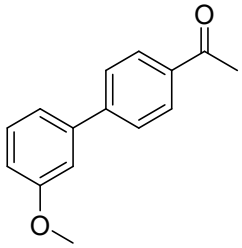
1-(4'-Methoxy-[1,1'-biphenyl]-4-yl)ethanone (5)[6]



Chemical Formula: $C_{15}H_{14}O_2$
Molecular Weight: 226.27

According to general procedure **A** compound **5** was obtained as a colorless solid (0.099 g, 98%); mp 152.0-153.1 °C (lit. 158-159 °C[6]); ν_{max} (neat) 2957 (CH), 1672 (C=O), 813 (CH); δ_H (400 MHz, $CDCl_3$) 8.00 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.63 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.59 – 7.55 (2H, m, Ar**H**), 7.01 – 6.97 (2H, m, Ar**H**), 3.85 (3H, s, OC**H**$_3$), 2.62 (3H, s, COC**H**$_3$); δ_C (101 MHz, $CDCl_3$) 197.7, 160.0, 145.4, 135.4, 132.3, 129.0, 128.4, 126.7, 114.5, 55.4, 26.6; HRMS m/z (NSI) 227.1067 ([M+H]$^+$ $C_{15}H_{15}O_2$ requires 227.1068).

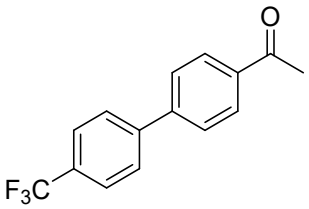
1-(3'-Methoxy-[1,1'-biphenyl]-4-yl)ethanone (6)[7]



Chemical Formula: $C_{15}H_{14}O_2$
Molecular Weight: 226.27

According to general procedure **A** compound **6** was obtained as a colorless solid (0.094 g, 93%); mp 52.6-53.0 °C (lit. 35.2-36.2 °C[7]); ν_{max} (neat) 2996 (CH), 1673 (C=O), 864 (CH); δ_H (400 MHz, $CDCl_3$) 8.03 – 8.00 (2H, m, Ar**H**), 7.68 – 7.65 (2H, m, Ar**H**), 7.38 (1H, t, *J* = 7.9 Hz, Ar**H**), 7.21 (1H, d, *J* = 7.7 Hz, Ar**H**), 7.17 – 7.14 (1H, m, Ar**H**), 6.97 – 6.92 (1H, m, Ar**H**), 3.87 (3H, s, OC**H**$_3$), 2.63 (3H, s, COC**H**$_3$); δ_H (125 MHz, $CDCl_3$) 197.8, 160.2, 145.7, 141.4, 136.1, 130.1, 128.9, 127.3, 119.8, 113.6, 113.2, 55.4, 26.7; HRMS m/z (NSI) 227.1067 ([M+H]+ $C_{15}H_{15}O_2$ requires 227.106).

1-(4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-yl)ethanone (7)[8]

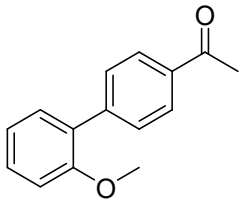


Chemical Formula: $C_{15}H_{11}F_3O$
Molecular Weight: 264.25

According to general procedure **A** compound **7** was obtained as a colorless solid (0.113 g, 96%); mp 118.9-120.1 °C (lit. 120.6-121.4°C[8]); ν_{max} (neat) 2924 (CH), 1683 (C=O), 820 (CH); δ_H (400 MHz, $CDCl_3$) 8.06 (2H, d, *J* = 8.3 Hz, Ar**H**), 7.72 (4H, s, Ar**H**), 7.69 (2H, d, *J* = 8.3 Hz, Ar**H**), 2.65 (3H, s, COC**H**$_3$); δ_C (101 MHz, $CDCl_3$) 197.7, 163.1, 144.8, 136.1, 135.9, 129.1,

128.9, 127.1, 115.9, 26.7; HRMS m/z (NSI) 265.0840 ([M+H]+ $C_{15}H_{12}F_3O$ requires 265.0845);

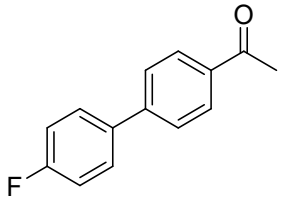
1-(2'-Methoxy-[1,1'-biphenyl]-4-yl)ethanone (8)[4]



Chemical Formula: $C_{15}H_{14}O_2$
Molecular Weight: 226.27

According to general procedure **A** compound **8** was obtained as a colorless solid (0.061 g, 60%); mp 106.8-107.3 °C (lit. 102-103 °C[4]); ν_{max} (neat) 3000 (CH), 1669 (C=O), 750 (CH); δ_H (400 MHz, $CDCl_3$) 8.01 (2H, d, *J* = 8.3 Hz, Ar**H**), 7.65 (2H, d, *J* = 8.3 Hz, Ar**H**), 7.40 – 7.32 (2H, m, Ar**H**), 7.06 (1H, t, *J* = 7.5 Hz, Ar**H**), 7.02 (1H, d, *J* = 8.2 Hz, Ar**H**), 3.83 (3H, s, OC**H**$_3$), 2.64 (3H, s, COC**H**$_3$); δ_H (101 MHz, $CDCl_3$) 197.9, 156.6, 143.7, 135.6, 130.8, 129.8, 129.6, 128.2, 121.1, 111.5, 55.6, 26.7; HRMS m/z (NSI) 227.1067 ([M+H]+ $C_{15}H_{15}O_2$ requires 227.1067).

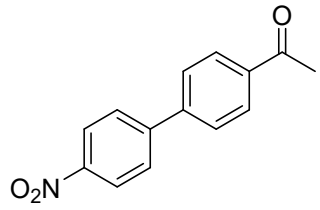
1-(4'-Fluoro-[1,1'-biphenyl]-4-yl)ethanone (9)[6]



Chemical Formula: $C_{14}H_{11}FO$
Molecular Weight: 214.24

According to general procedure **A** compound **9** was obtained as a colorless solid (0.09 g, 99%); mp 100.1-101.8 °C (lit. 105-106 °C[6]); ν_{max} (neat) 2921 (CH), 1679 (C=O), 815 (CH); δ_H (400 MHz, $CDCl_3$) 8.02 (2H, d, *J* = 8.3 Hz, Ar**H**), 7.62 (2H, d, *J* = 8.5 Hz, Ar**H**), 7.60 – 7.56 (2H, m, Ar**H**), 7.18 – 7.12 (2H, m, Ar**H**), 2.63 (3H, s, COC**H**$_3$); δ_C (101 MHz, $CDCl_3$) 197.67, 163.0, 144.7, 135.9, 135.9, 128.9, 128.9, 127.1, 115.9, 26.6; HRMS *m/z* (NSI) Found 215.0872 ([M+H]$^+$ $C_{14}H_{12}FO$ requires 215.0800).

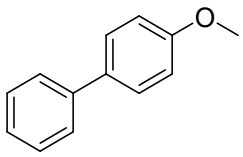
1-(4'-Nitro-[1,1'-biphenyl]-4-yl)ethanone (10)[8]



Chemical Formula: $C_{14}H_{11}NO_3$
Molecular Weight: 241.25

According to general procedure **A** compound **10** was obtained as a colorless solid (0.104 g, 94%); mp 151.6-152.2 °C (lit. 150.2-152.1 °C[8]); ν_{max} (neat) 3012 (CH), 1679 (C=O), 1595 (NO_2); δ_H (400 MHz, $CDCl_3$) 8.31 (2H, d, *J* = 8.6 Hz, Ar**H**), 8.07 (2H, d, *J* = 8.2 Hz, Ar**H**), 7.77 (2H, d, *J* = 8.6 Hz, Ar**H**), 7.71 (2H, d, *J* = 8.2 Hz, Ar**H**), 2.65 (3H, s, COC**H**$_3$); δ_C (101 MHz, $CDCl_3$) 197.5, 147.7, 146.3, 143.2, 137.2, 129.2, 128.2, 127.7, 124.3, 26.8; HRMS m/z (NSI) 242.0817 ([M+H]+ $C_{14}H_{12}NO_3$ requires 242.0817).

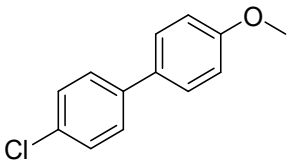
4-Methoxy-1,1'-biphenyl (11)[4]



Chemical Formula: $C_{13}H_{12}O$
Molecular Weight: 184.24

According to general procedure **A** compound **11** was obtained as a colorless solid (0.078 g, 99%); mp 86.5-87.2 °C (lit. 85-86 °C[4]); ν_{max} (neat) 3064 (CH), 1246 (OCH_3), 832 (CH); δ_H (400 MHz, $CDCl_3$) 7.62 – 7.55 (4H, m, Ar**H**), 7.46 (2H, dd, *J* = 10.5, 4.8 Hz, Ar**H**), 7.37 – 7.31 (1H, m, Ar**H**), 7.05 – 6.98 (2H, m, Ar**H**), 3.88 (3H, s, O**CH**$_3$); δ_C (101 MHz, $CDCl_3$) 159.3, 140.9, 133.9, 128.9, 128.3, 126.9, 126.8, 114.3, 55.5; HRMS m/z (NSI) 185.0966 ($[M+H]^+$ $C_{13}H_{13}O$ requires 185.0958).

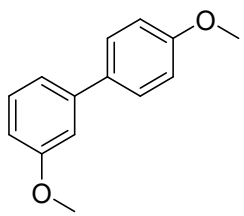
4-Chloro-1,1'-biphenyl (12)[5]



Chemical Formula: $C_{13}H_{11}ClO$
Molecular Weight: 218.68

According to general procedure **A** compound **12** was obtained as a colorless solid (0.088 g, 94%); mp 108.3-110.8 °C (lit. 112-113 °C[5]); ν_{max} (neat) 3010 (CH), 1287 (OCH_3), 809 (CH); δ_H (400 MHz, $CDCl_3$) 7.53 – 7.46 (4H, m, Ar**H**), 7.42 – 7.37 (2H, m, Ar**H**), 7.01 – 6.96 (2H, m, Ar**H**), 3.86 (3H, s, O**CH**$_3$); δ_C (101 MHz, $CDCl_3$) 159.5, 139.4, 132.8, 132.6, 128.9, 128.1, 128.0, 114.5, 55.5; HRMS *m/z* (ASAP) Found 218.0498 ($[M]^+$ $C_{13}H_{11}OCl$ requires 218.0497).

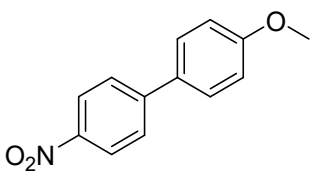
3,4'-Dimethoxy-1,1'-biphenyl (13)[9]



Chemical Formula: $C_{14}H_{14}O_2$
Molecular Weight: 214.26

According to general procedure **A** compound **13** was obtained as a colorless solid (0.080 g, 87%); mp 55.9-57.7 °C (lit. 57-58 °C[9]); ν_{max} (neat) 3010 (CH), 1217 (OCH_3), 826 (CH); δ_H (400 MHz, $CDCl_3$) 7.60 – 7.54 (2H, m, Ar**H**), 7.37 (1H, t, *J* = 7.9 Hz, Ar**H**), 7.19 (1H, dt, *J* = 7.7, 1.3 Hz, Ar**H**), 7.14 (1H, t, *J* = 2.1 Hz, Ar**H**), 7.04 – 6.98 (2H, m, Ar**H**), 6.90 (1H, dd, *J* = 8.1, 2.5 Hz, Ar**H**), 3.89 (3H, s, O**CH**$_3$), 3.87 (3H, s, O**CH**$_3$); δ_C (101 MHz, $CDCl_3$) 160.1, 159.4, 142.5, 133.7, 129.8, 128.3, 119.4, 114.3, 112.7, 112.1, 55.4, 55.4; HRMS m/z (NSI) 215.1072 ($[M+H]^+$ $C_{14}H_{15}O_2$ requires 215.1070).

4-Methoxy-4'-nitro-1,1'-biphenyl (14)[10]

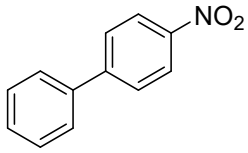


Chemical Formula: $C_{13}H_{11}NO_3$
Molecular Weight: 229.24

According to general procedure **A** compound **14** was obtained as a yellow solid (0.030 g, 30%); mp 108.3-109.6 °C (lit. 104-105 °C[10]); ν_{max} (neat) 3062 (CH), 1595 (NO_2), 858 (CH); δ_H (400 MHz, $CDCl_3$) 8.29 – 8.24 (2H, m, Ar**H**), 7.72 – 7.66 (2H, m, Ar**H**), 7.61 – 7.55 (2H, m, Ar**H**), 7.04 – 6.99 (2H, m, Ar**H**), 3.88 (3H, s, OC**H**$_3$); δ_C (101 MHz, $CDCl_3$) 160.6, 147.4, 146.7, 131.2, 128.7, 127.2, 124.3, 114.8, 55.6; HRMS m/z (NSI) 230.0812 ($[M+H]^+$ $C_{13}H_{12}NO_3$ requires 230.0805).

According to general procedure **A** using 1-iodo-4-nitrobenzene and (4-methoxyphenyl)boronic acid, compound **14** was obtained as a colorless solid (0.089 g, 97%); Spectral data obtained is in good agreement with that reported above.

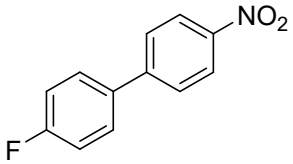
4-Nitro-1,1'-biphenyl (15)[11]



Chemical Formula: $C_{12}H_9NO_2$
Molecular Weight: 199.21

According to general procedure **A** compound **15** was obtained as a colorless solid (0.058 g, 73%); mp 110.2-112.3 °C (lit. 112-113 °C[11]); ν_{max} (neat) 3074 (CH), 1592 (NO_2), 850 (CH); δ_H (400 MHz, $CDCl_3$) 8.32 – 8.26 (2H, m, Ar**H**), 7.77 – 7.70 (2H, m, Ar**H**), 7.66 – 7.60 (2H, m, Ar**H**), 7.54 – 7.42 (3H, m, OC**H**$_3$); δ_C (101 MHz, $CDCl_3$) 147.7, 147.2, 138.9, 129.3, 129.0, 127.9, 127.5, 124.2; HRMS m/z (NSI) 200.0712 ($[M+H]^+$ $C_{12}H_{10}NO_2$ requires 200.0715);

4-Fluoro-4'-nitro-1,1'-biphenyl (16)[12]

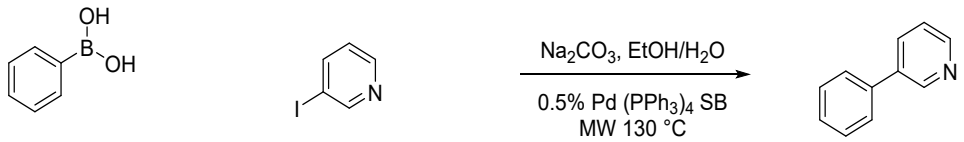


Chemical Formula: $C_{12}H_8FNO_2$
Molecular Weight: 217.20

According to general procedure **A** compound **16** was obtained as a colorless solid (0.070 g, 81%); mp 125.5-126.1 °C (lit. 122-124 °C[12]; ν_{max} (neat) 3073 (CH), 1595 (NO_2), 830 (CH); δ_H (400 MHz, $CDCl_3$) 8.32 – 8.26 (2H, m, Ar**H**), 7.72 – 7.66 (2H, m, Ar**H**), 7.63 – 7.56 (2H, m, Ar**H**), 7.22 – 7.15 (2H, m, Ar**H**); δ_C (101 MHz, $CDCl_3$) 163.5, 147.2, 146.7, 135.1, 129.3, 127.8, 124.3, 116.3; HRMS m/z (NSI) 218.0617 ($[M+H]^+$ $C_{12}H_9FNO_2$ requires 218.0623).

General Procedure B:

3-Phenylpyridine (17)[4]



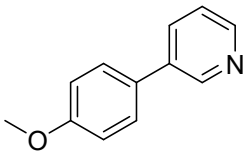
Chemical Formula: $C_6H_7BO_2$
Molecular Weight: 121.93

Chemical Formula: C_5H_4IN
Molecular Weight: 205.00

Chemical Formula: $C_{11}H_{9N}$
Molecular Weight: 155.20

Phenylboronic acid (0.065 g, 0.54 mmol) and 3-iodopyridine (0.10 g, 0.49 mmol) were combined in a reaction vial containing a 0.5% *w/w* $Pd(PPh_3)_4$ microwave stirrer bead. Ethanol (2 mL) was added, followed by a solution of sodium carbonate (0.10 g, 0.98 mmol) in water (1 mL). The resulting mixture was heated at 130 °C for 20 minutes in the microwave. The stirrer was washed with DCM and the residue was concentrated under reduced pressure. The crude mixture was partitioned between water (15 mL) and DCM (15 mL) and the aqueous phase extracted with DCM (3 x 15 mL). The combined organic extracts dried ($MgSO_4$), filtered and solvent removed under reduced pressure to give the crude material. The residue was purified *via* Biotage (9:1 Hex/EtOAc; Zip 10 g column) to give 3-phenylpyridine **17** (0.052 g, 69%) as a colorless oil; ν_{max} (neat) 3030 (C–H), 1336 (C–N); δ_H (500 MHz, $CDCl_3$) 8.85 (1H, d, *J* = 2.3 Hz, NC**H**), 8.59 (1H, dd, *J* = 4.8, 1.6 Hz, NC**H**), 7.87 (1H, dt, *J* = 7.9, 2.0 Hz, Ar**H**), 7.60 - 7.55 (2H, m, Ar**H**), 7.48 (2H, dd, *J* = 8.4, 6.9 Hz, Ar**H**), 7.43 - 7.38 (1H, m, Ar**H**), 7.36 (1H, dd, *J* = 7.9, 4.8 Hz, Ar**H**); δ_C (126 MHz, $CDCl_3$) 148.6, 148.4, 137.9, 136.7, 134.4, 129.2, 128.2, 127.2, 123.6; HRMS *m/z* (NSI) Found 156.0808 ($[M+H]^+$ $C_{11}H_{10}N$ requires 156.0811).

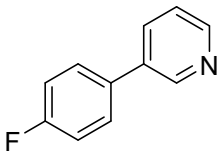
3-(4-Methoxyphenyl)pyridine (18)[7]



Chemical Formula: $C_{12}H_{11}NO$
Molecular Weight: 185.23

According to general procedure **B** compound **18** was obtained as a colorless semi-solid (0.062 g, 69%); ν_{max} (neat) 3008 (CH), 1281 (C=N), 836 (CH); δ_H (500 MHz, $CDCl_3$) 8.81 (1H, d, *J* = 2.5 Hz, NC**H**), 8.54 (1H, dd, *J* = 4.8 Hz, 1.7, NC**H**), 7.81 (1H, dt, *J* = 7.9 Hz, 2.0, Ar**H**), 7.56 - 7.45 (2H, m, Ar**H**), 7.32 (1H, dd, *J* = 7.9, 4.8 Hz, Ar**H**), 7.04 - 6.95 (2H, m, Ar**H**), 3.85 (3H, s, OC**H**$_3$); δ_C (126 MHz, $CDCl_3$) 159.8, 148.1, 147.9, 136.3, 133.9, 130.3, 128.3, 123.6, 114.6, 55.5; HRMS m/z (NSI) 186.0913 ([M+H]+ $C_{12}H_{12}NO$ requires 186.0910).

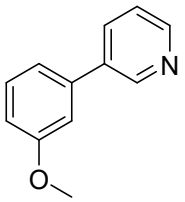
3-(4-Fluorophenyl)pyridine (19)[13]



Chemical Formula: $C_{11}H_8FN$
Molecular Weight: 173.19

According to general procedure **B** compound **19** was obtained as a colorless oil (0.062 g, 73%); ν_{max} (neat) 3043 (CH), 1336 (C=N), 840 (CH); δ_H (500 MHz, $CDCl_3$) 8.80 (1H, d, *J* = 2.3 Hz, NC**H**), 8.58 (1H, dd, *J* = 4.8, 1.6 Hz, NC**H**), 7.82 (1H, dt, *J* = 7.9, 2.0 Hz, Ar**H**), 7.57 - 7.49 (2H, m, Ar**H**), 7.35 (1H, dd, *J* = 8.0, 4.9 Hz, Ar**H**), 7.16 (2H, t, *J* = 8.6 Hz, Ar**H**); δc (126 MHz, $CDCl_3$) 163.0, 148.4, 135.8, 134.3, 134.0, 128.9, 123.7, 116.3, 116.1; HRMS m/z (NSI) 174.0714 ([M+H]+ $C_{11}H_9FN$ requires 174.0710).

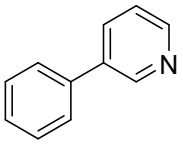
3-(3-Methoxyphenyl)pyridine (20)[7]



Chemical Formula: $C_{12}H_{11}NO$
Molecular Weight: 185.23

According to general procedure **B** compound **20** was obtained as a colorless oil (0.070 g, 77%); ν_{max} (neat) 3031 (CH), 1299 (C=N), 809 (CH); δ_H (500 MHz, $CDCl_3$) 8.84 (1H, d, *J* = 2.3 Hz, NC**H**), 8.59 (1H, dd, *J* = 4.9, 1.6 Hz, NC**H**), 7.88 - 7.78 (1H, m, Ar**H**), 7.39 (1H, t, *J* = 8.0 Hz, Ar**H**), 7.35 (1H, dd, *J* = 7.9, 4.8 Hz, Ar**H**), 7.16 (1H, dt, *J* = 7.6, 1.2 Hz, Ar**H**), 7.10 (1H, t, *J* = 2.1 Hz, Ar**H**), 6.94 (1H, dd, *J* = 8.2, 2.5 Hz, Ar**H**), 3.86 (3H, s, OC**H**$_3$); δ_C (126 MHz, $CDCl_3$) 160.2, 148.7, 148.4, 139.4, 136.6, 134.5, 130.2, 123.6, 119.7, 113.5, 113.0, 55.4; HRMS m/z (NSI) 186.0913 ([M+H]+ $C_{12}H_{12}NO$ requires 186.0909).

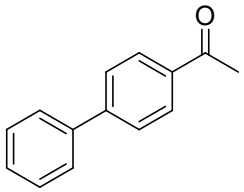
3-Phenylpyridine (17)



Chemical Formula: $C_{11}H_9N$
Molecular Weight: 155.20

According to general procedure **B** compound **17** was also obtained using 3-bromopyridine in 120 minutes (0.032 g, 33%). Spectral data obtained is in good agreement with that reported above.

1-([1,1'-Biphenyl]-4-yl)ethanone (3)

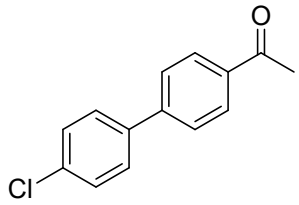


Chemical Formula: $C_{14}H_{12}O$
Molecular Weight: 196.24

According to general procedure **B** compound **3** was also obtained using 1-(4-bromophenyl)ethanone by heating in a microwave at 120

°C for 40 minutes (0.080 g, 99%). Spectral data obtained is in good agreement with that reported above.

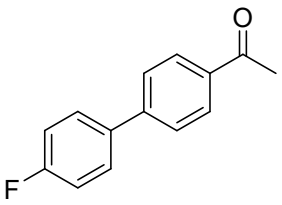
1-(4'-Chloro-[1,1'-biphenyl]-4-yl)ethanone (4)



Chemical Formula: $C_{14}H_{11}ClO$
Molecular Weight: 230.69

According to general procedure **B** compound **4** was also obtained using 1-(4-bromophenyl)ethanone by heating in a microwave at 120 °C for 60 minutes (0.112 g, 97%). Spectral data obtained is in good agreement with that reported above.

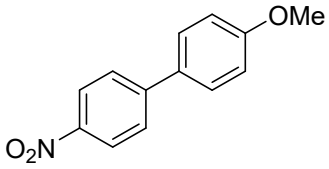
1-(4'-Fluoro-[1,1'-biphenyl]-4-yl)ethanone (9)



Chemical Formula: $C_{14}H_{11}FO$
Molecular Weight: 214.23

According to general procedure **B** compound **9** was also obtained using 1-(4-bromophenyl)ethanone by heating in a microwave at 120 °C for 60 minutes (0.100 g, 93%). Spectral data obtained is in good agreement with that reported above.

4-Methoxy-4'-nitro-1,1'-biphenyl (14)

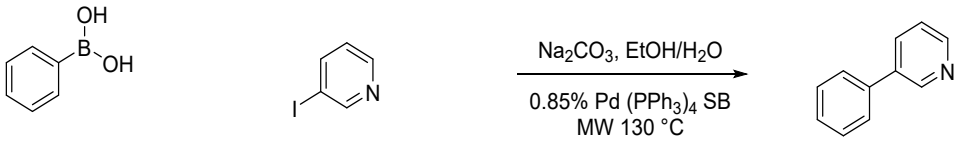


Chemical Formula: $C_{13}H_{11}NO_3$
Molecular Weight: 229.23

According to general procedure **B** compound **14** was also obtained using 1-iodo-4-methoxybenzene by heating in the microwave at 120 °C for 40 minutes (0.081 g, 83%) as a yellow solid. Spectral data obtained is in good agreement with that reported above.

General Procedure C

3-Phenylpyridine (17)[4]



Chemical Formula: $C_6H_7BO_2$
Molecular Weight: 121.93

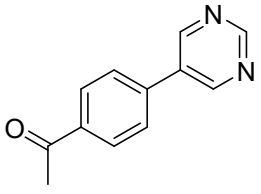
Chemical Formula: C_5H_4IN
Molecular Weight: 205.00

Chemical Formula: $C_{11}H_{9N}$
Molecular Weight: 155.20

Phenylboronic acid (0.054 g, 0.44 mmol) and 3-iodopyridine (0.082 g, 0.4 mmol) were combined in a reaction vial containing a 0.85% *w/w* $Pd(PPh_3)_4$ microwave stirrer bead. Ethanol (2 mL) was added, followed by a solution of sodium carbonate (0.10 g, 0.98 mmol) in water (1 mL). The resulting mixture was heated at 130 °C for 20 minutes in the microwave. The stirrer was washed with DCM and the residue was concentrated under reduced pressure. The crude mixture was partitioned between water (15 mL) and DCM (15 mL) and the aqueous phase extracted with DCM (3 x 15 mL). The combined organic extracts dried ($MgSO_4$), filtered and solvent removed under reduced pressure to give the crude material. The residue was purified *via* Biotage (9:1 Hex/EtOAc; Zip 10 g column) to give 3-phenylpyridine **17** (0.051 g, 82%) as a colorless oil. Spectral data obtained is in good agreement with that reported above.

According to general procedure **C** compound **17** was also obtained using 3-bromopyridine (0.027 g, 44%). Spectral data obtained is in good agreement with that reported above.

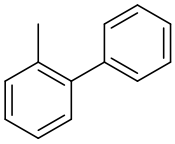
1-(4-(Pyrimidin-5-yl)phenyl)ethanone (21)[14]



Chemical Formula: $C_{12}H_{10}N_2O$
Molecular Weight: 198.23

According to general procedure C after heating for 60 minutes compound **21** was obtained as a colorless solid (0.011 mg, 14%); mp: 135-136 °C (lit. 121-123 °C[14]) ; ν_{max} (neat) 2952, 2922, 2848, 1679, 1605, 1395, 1350, 1265; δ_H (400 MHz, $CDCl_3$) 9.26 (1H, s, Ar**H**), 8.99 (2H, s, Ar**H**), 8.11 (2H, d, *J* = 8.2 Hz, Ar**H**), 7.70 (2H, d, *J* = 8.3 Hz, Ar**H**), 2.66 (3H, s, COC**H$_3$**); δ_C (101 MHz, $CDCl_3$) 197.3, 158.2, 155.0, 138.7, 137.3, 133.29, 129.4, 127.2; Spectral data obtained is in good agreement with reported data.[14]

2-Methylbiphenyl (22)[15]

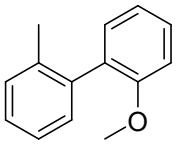


Chemical Formula: $C_{13}H_{12}$
Molecular Weight: 168.24

According to general procedure C compound **22** was obtained from 2-iodotoluene and phenylboronic acid as a colorless oil (0.050 g, 74%); ν_{max} (neat) 3059, 3020, 1478, 1439, 1010; δ_H (400 MHz, $CDCl_3$) 7.47-7.43 (2H, m, Ar**H**), 7.39-7.35 (3H, m, Ar**H**), 7.32-7.38 (4H, m, Ar**H**), 2.32 (3H, s, C**H$_3$**); δ_C (101 MHz, $CDCl_3$) 142.0, 141.9, 135.4, 130.3, 129.8, 129.2, 128.1, 127.3, 126.8, 125.8, 20.5; Spectral data obtained is in good agreement with reported data.[15]

According to general procedure C compound **22** was also obtained using 2-bromotoluene (0.026 g, 39%). Spectral data obtained is in good agreement with that reported above.

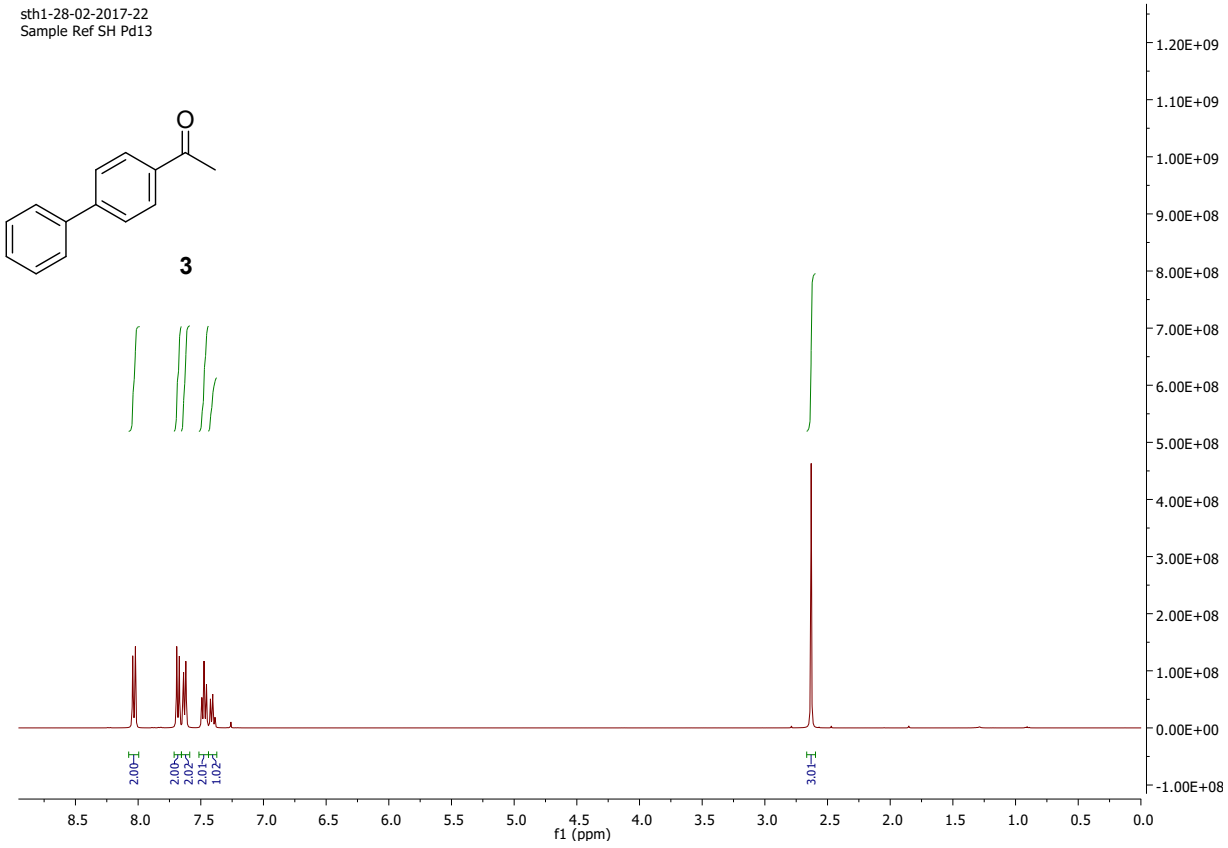
2-Methoxy-2'-methylbiphenyl (23)[16]

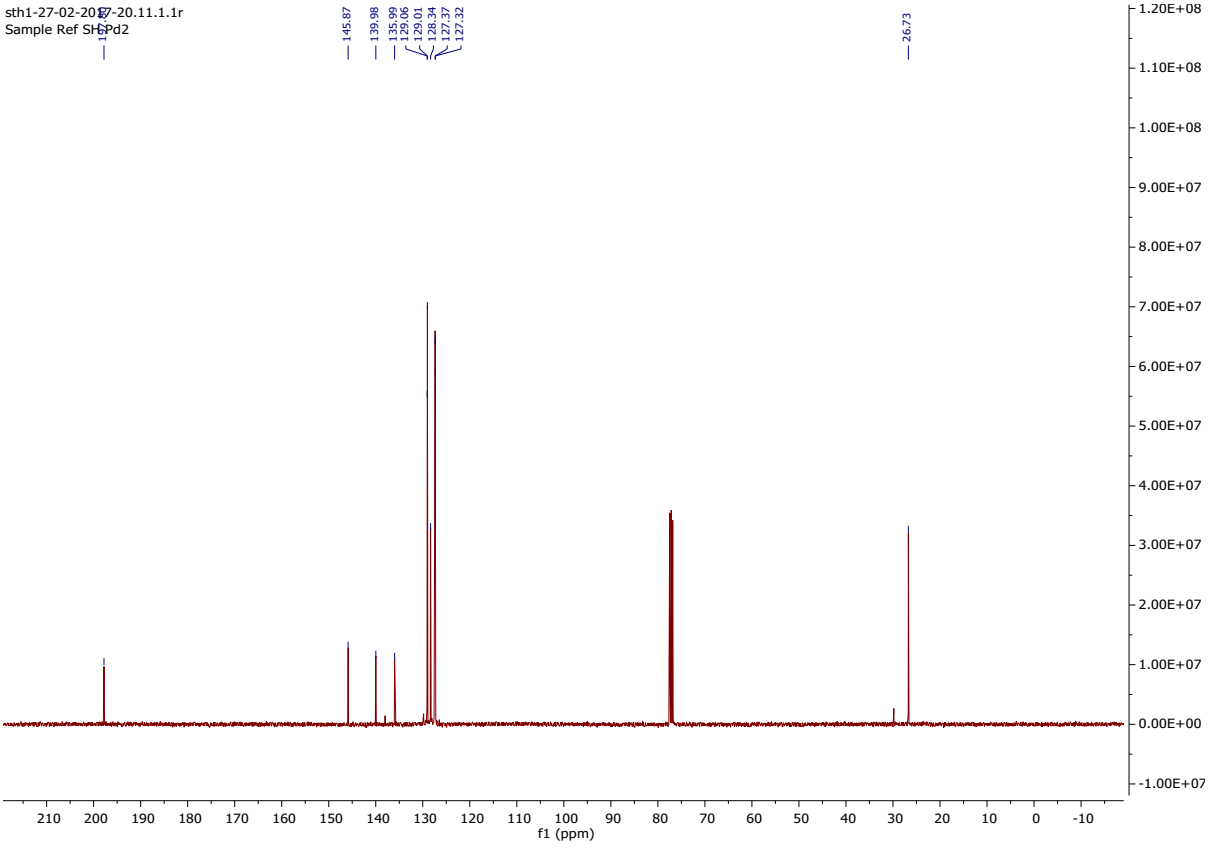


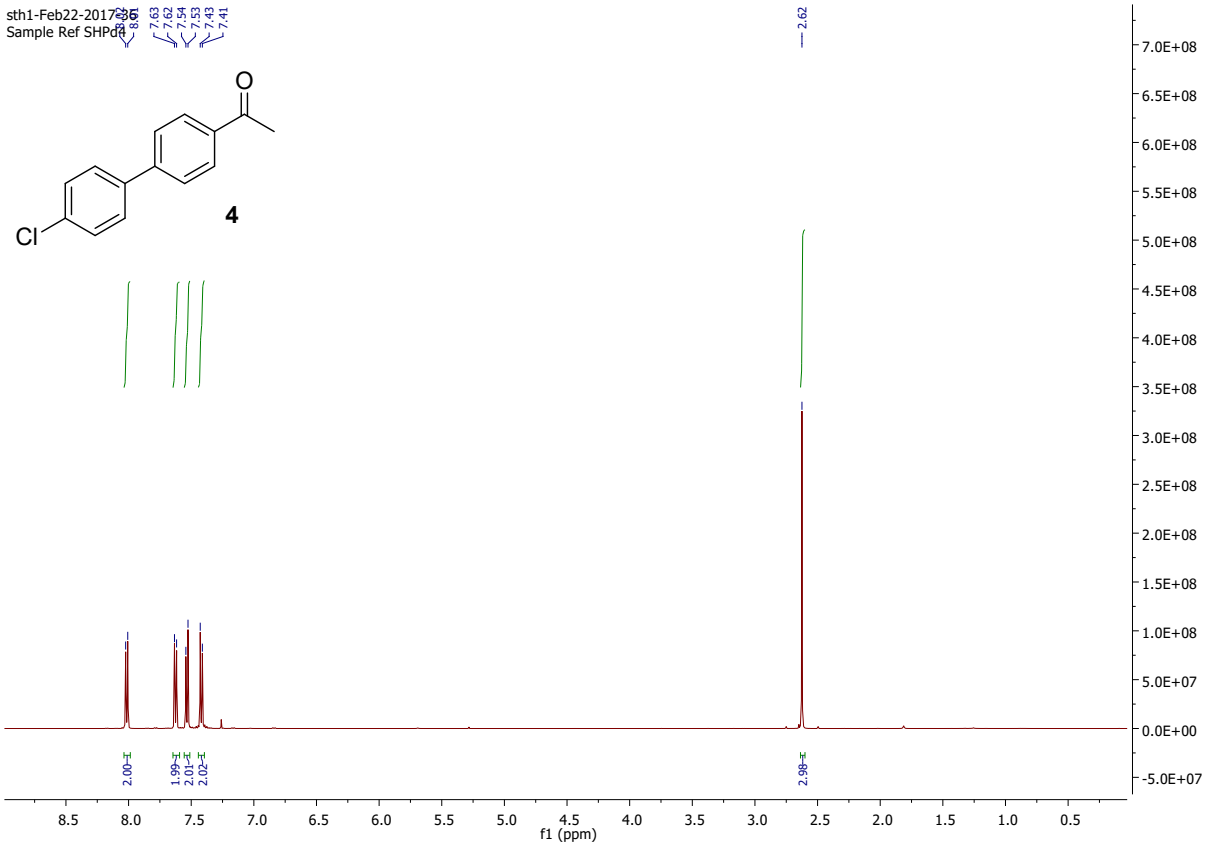
Chemical Formula: $C_{14}H_{14}O$
Molecular Weight: 198.26

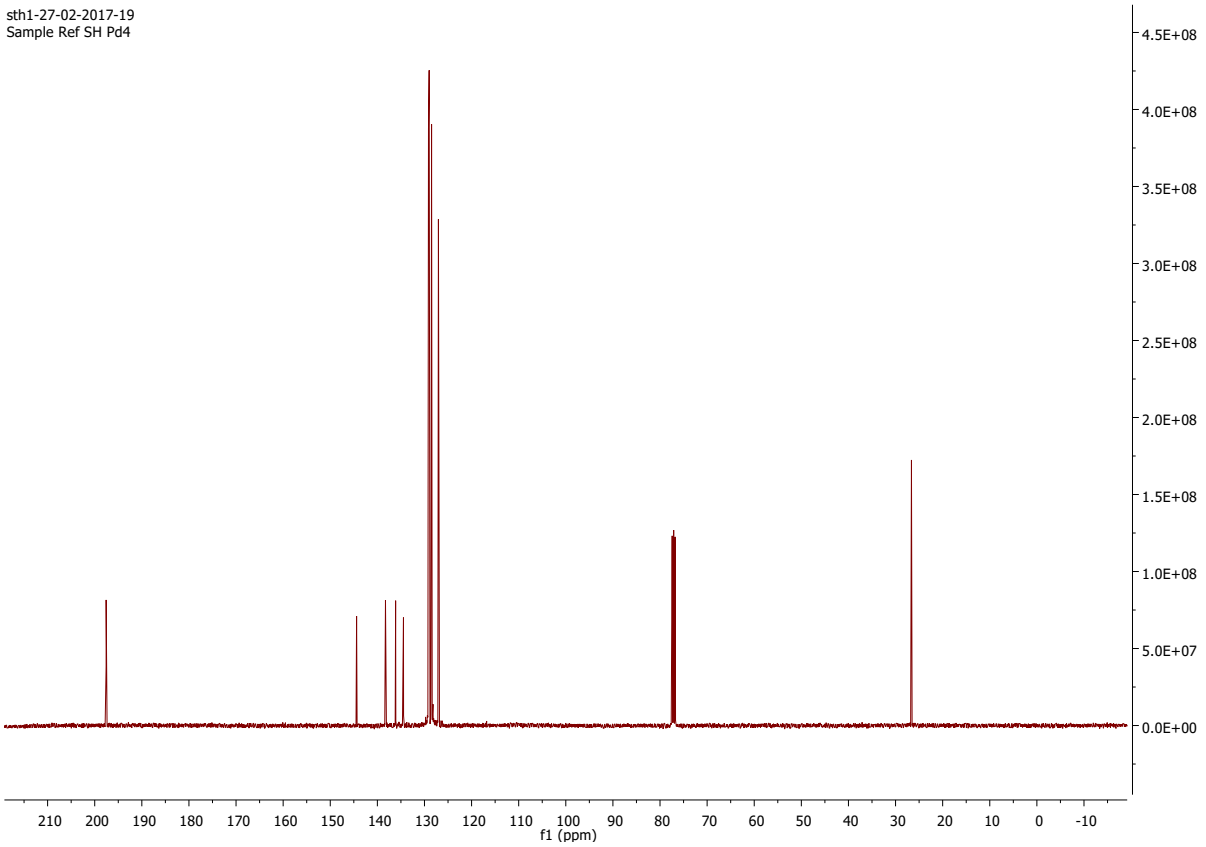
According to general procedure C compound **22** was obtained from 2-bromotoluene and 2-methoxybenzenboronic acid as a colorless solid (0.050 g, 74%); mp: 38-40 °C ν_{max} (neat) 3061, 3018, 2955, 1482, 1261, 1233; δ_H (400 MHz, $CDCl_3$) 7.35 (1H, t, *J* = 7.8 Hz, Ar**H**), 7.28-7.15 (5H, m, Ar**H**), 7.02 (1H, t, *J* = 7.4 Hz, Ar**H**), 6.97 (1H, d, *J* = 8.2 Hz, Ar**H**), 3.77 (3H, s, OCH_3), 2.15 (3H, s, ArC**H$_3$**); δ_C (101 MHz, $CDCl_3$) 156.7, 138.7, 136.8, 131.0, 130.9, 130.0, 129.6, 128.6, 127.3, 125.5, 120.5, 110.7, 55.4, 19.9; Spectral data obtained is in good agreement with reported data [16]

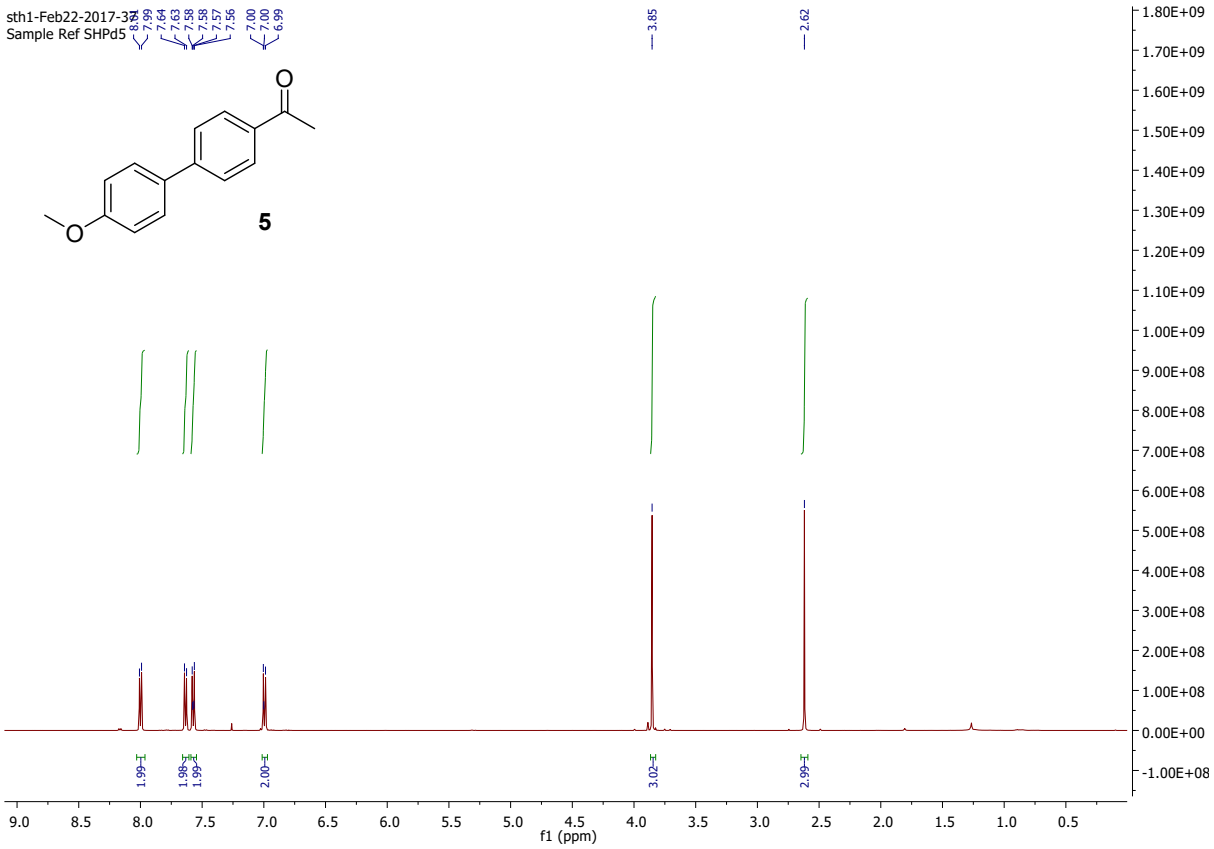
S.4.0. NMR Spectra

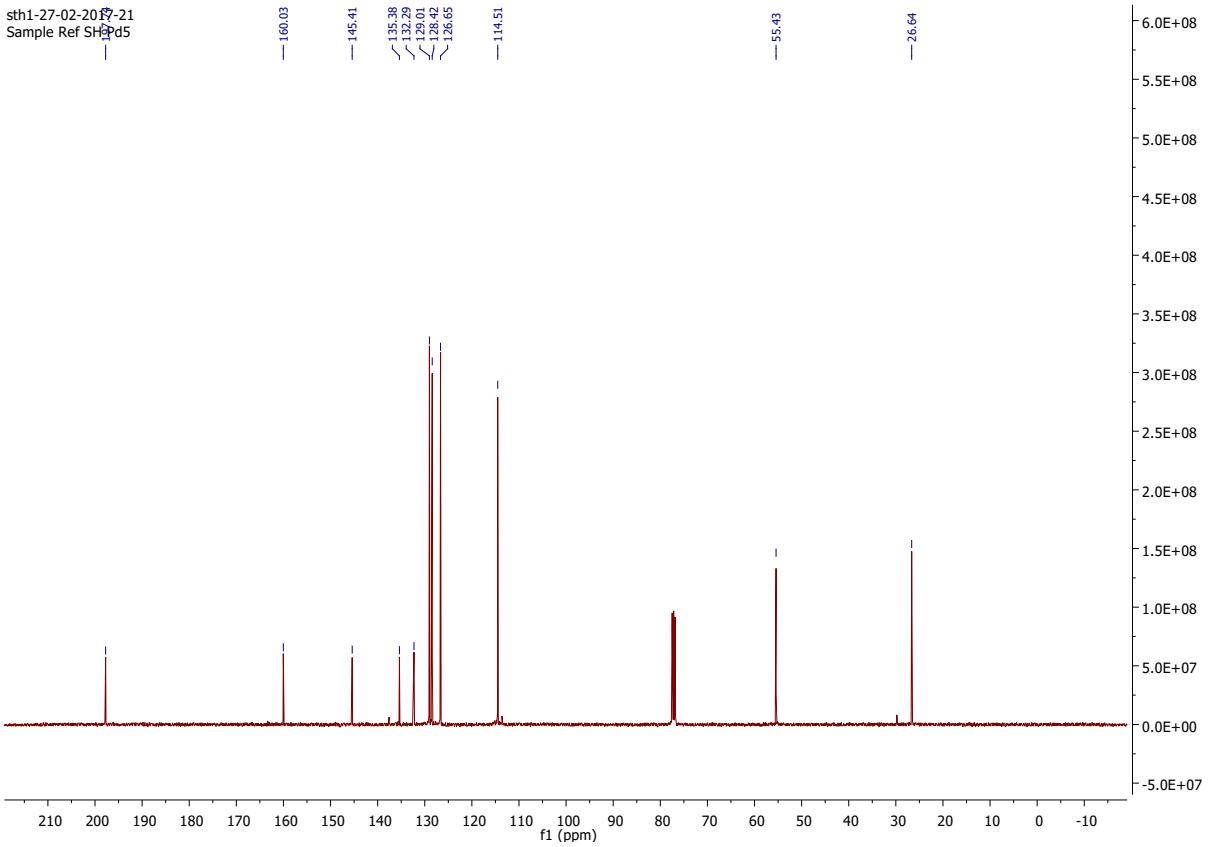


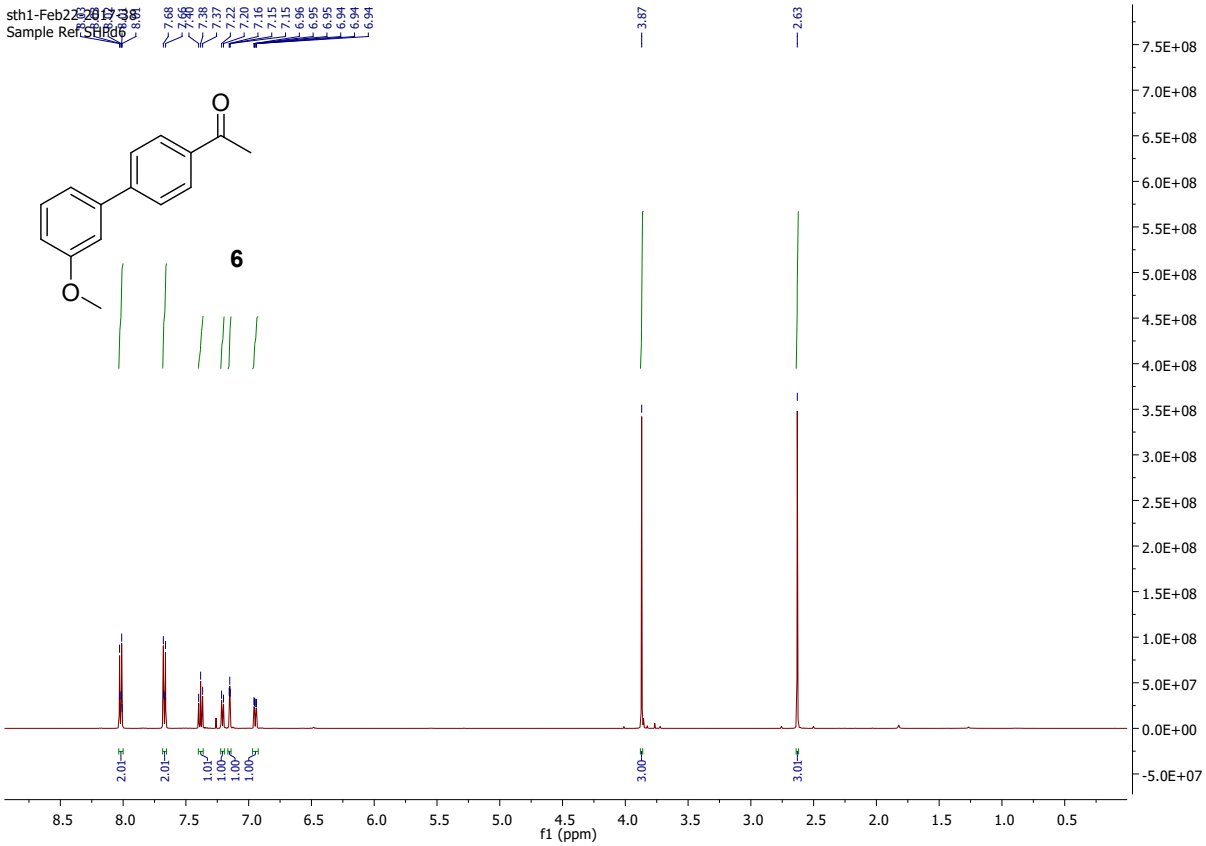


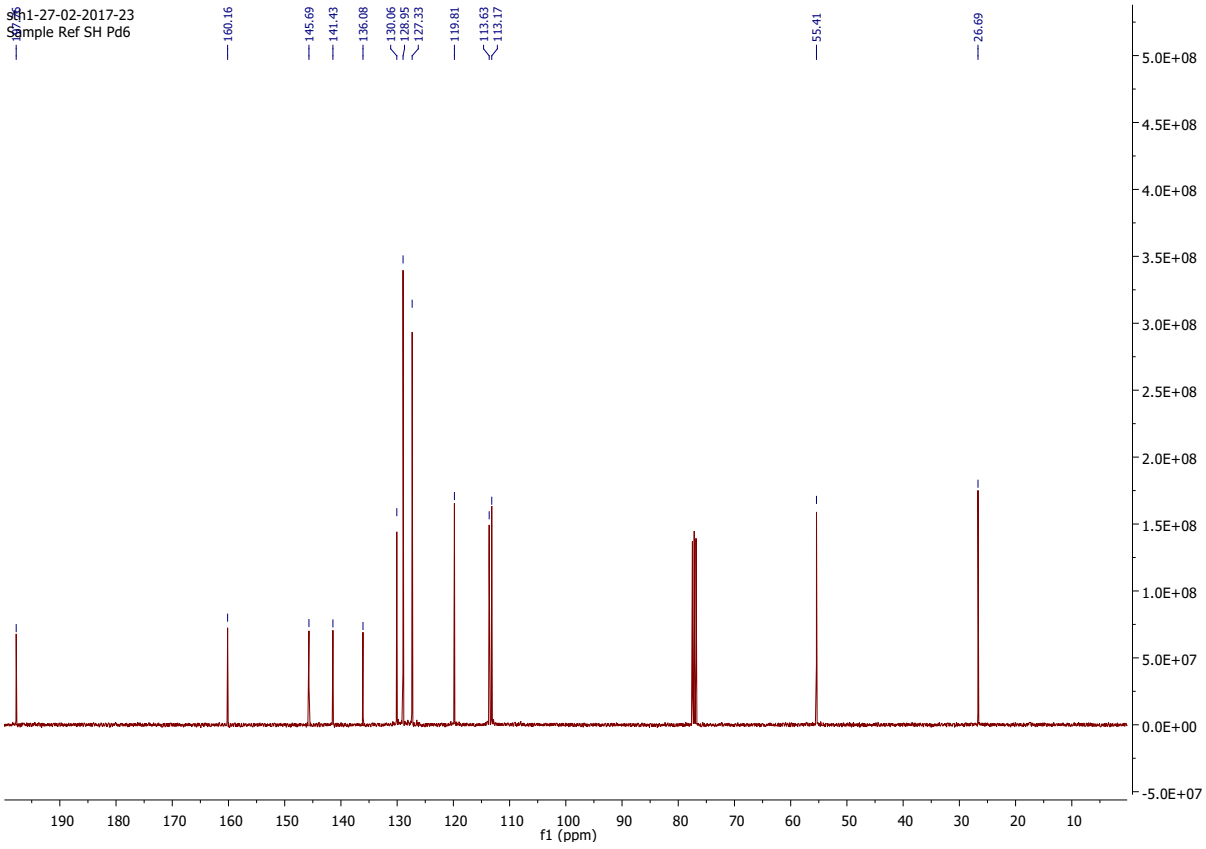

sth1-Feb22-2017-36
Sample Ref SHPd4
8.01
7.63
7.62
7.54
7.53
7.43
7.41
2.62
O
Cl
4
2.00
1.99
2.01
2.02
2.98
f1 (ppm)

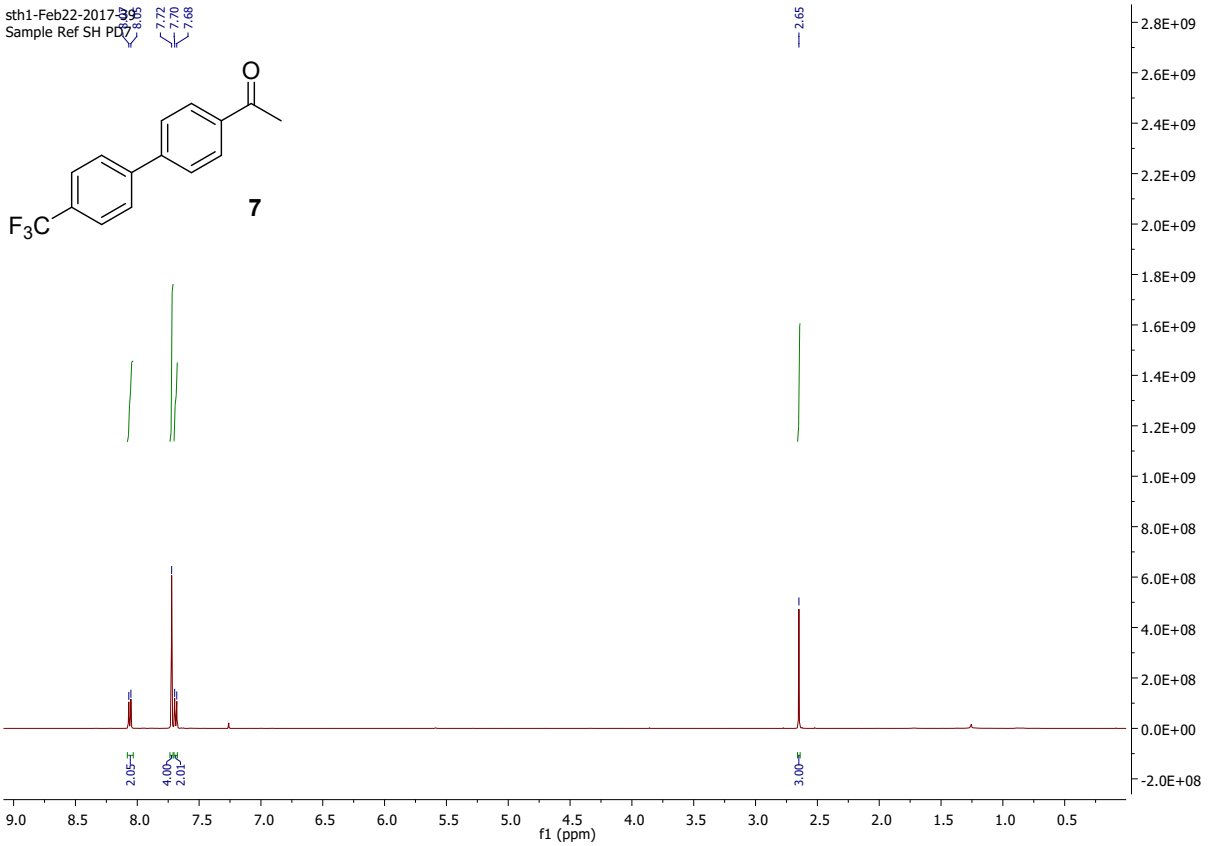

sth1-27-02-2017-19
Sample Ref SH Pd4
f1 (ppm)

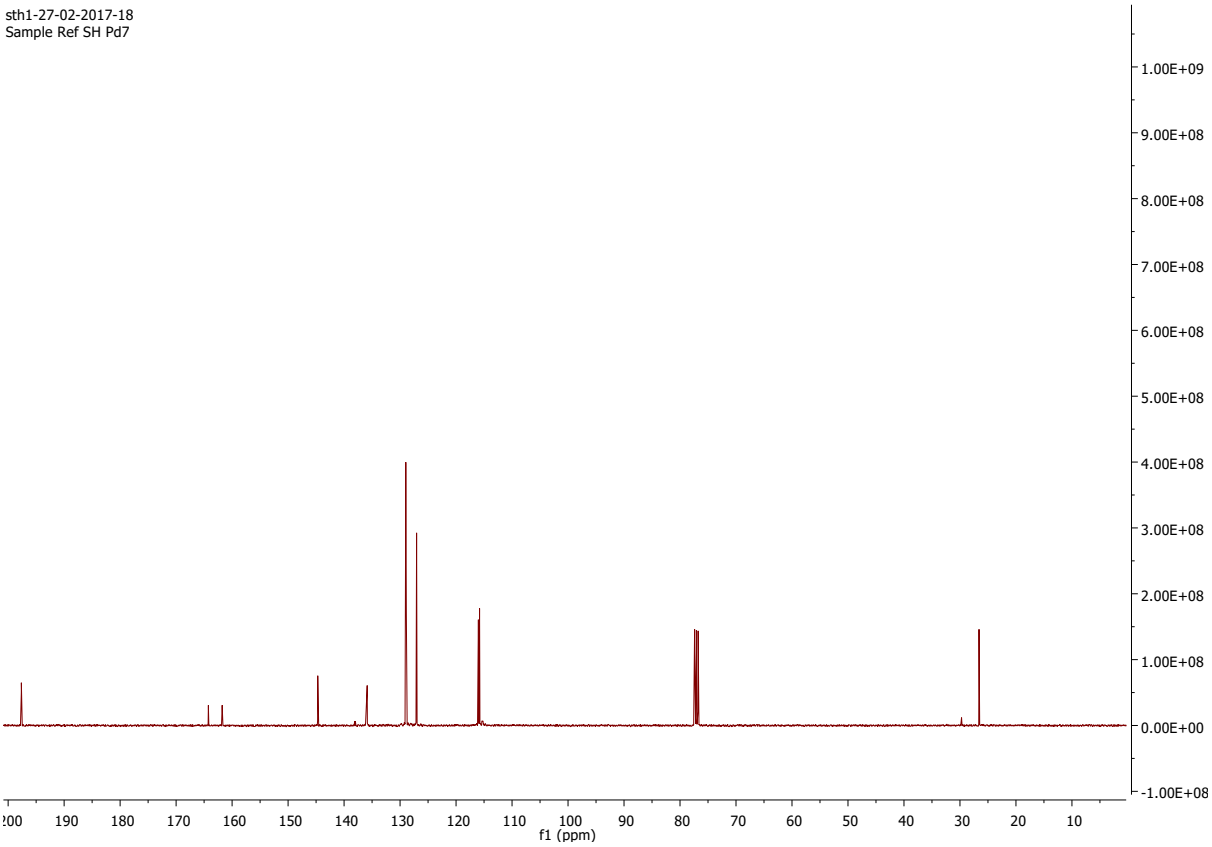

sth1-Feb22-2017-3
Sample Ref SHPd5
8.04
7.99
7.64
7.63
7.58
7.58
7.57
7.56
7.00
7.00
6.99
3.85
2.62
O
O
5
1.99
1.98
1.99
2.00
3.02
2.99
f1 (ppm)

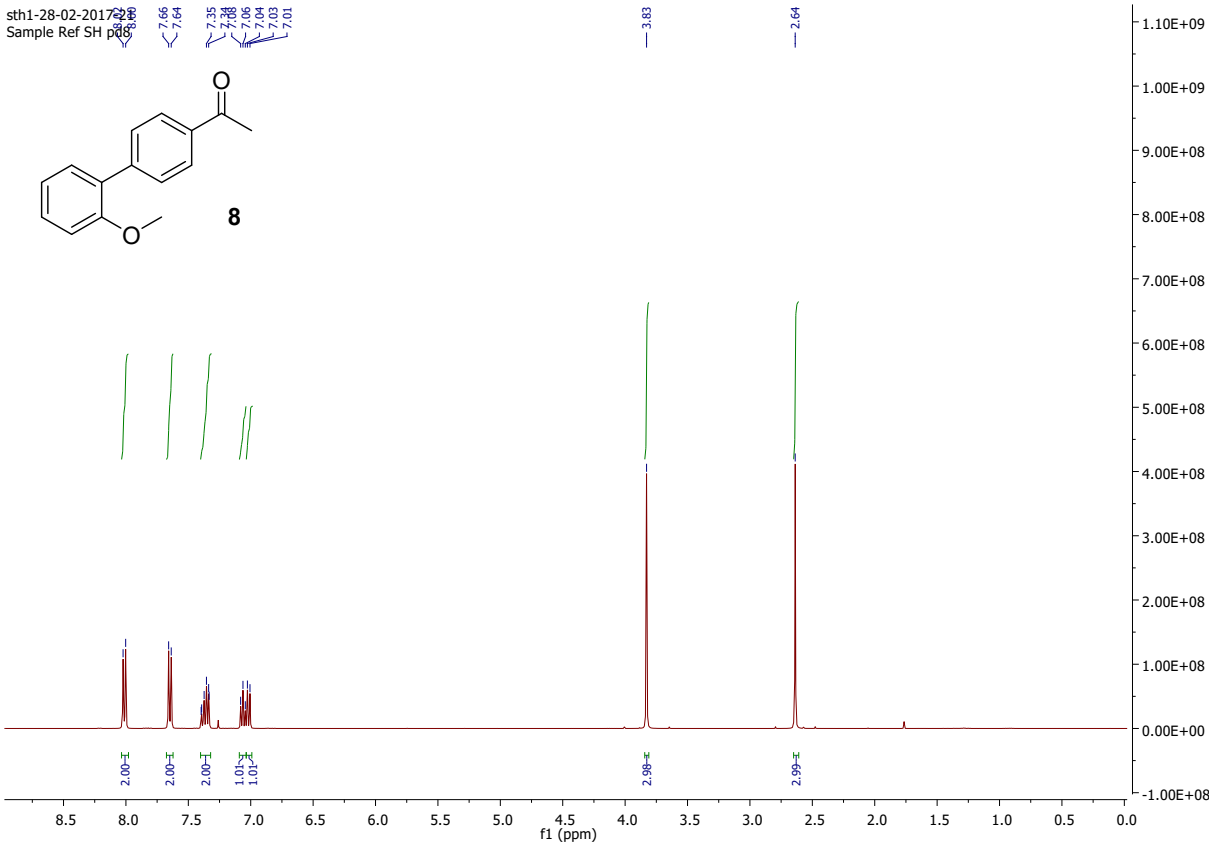

sth1-27-02-2017-21
Sample Ref SHPd5
160.03
145.41
135.38
132.29
129.01
128.42
126.65
114.51
55.43
26.64
f1 (ppm)


sth1-Feb22-2017-38
Sample Ref SHPd6
7.68
7.66
7.66
7.38
7.37
7.22
7.20
7.16
7.15
7.15
6.96
6.95
6.95
6.94
6.94
6.94
3.87
2.63
O
O
6
2.01
2.01
1.01
1.00
1.00
1.00
3.00
3.01
f1 (ppm)


sth1-27-02-2017-23
Sample Ref SH Pd6
160.16
145.69
141.43
136.08
130.06
128.95
127.33
119.81
113.63
113.17
55.41
26.69
f1 (ppm)


sth1-Feb22-2017-39
Sample Ref SH Pd7
8.05
7.72
7.70
7.68
2.65
O
F3C
7
2.05
4.00
2.01
3.00
f1 (ppm)


sth1-27-02-2017-18
Sample Ref SH Pd7
f1 (ppm)


sth1-28-02-2017-21
Sample Ref SH pd8
7.66
7.64
7.35
7.34
7.08
7.06
7.04
7.03
7.01
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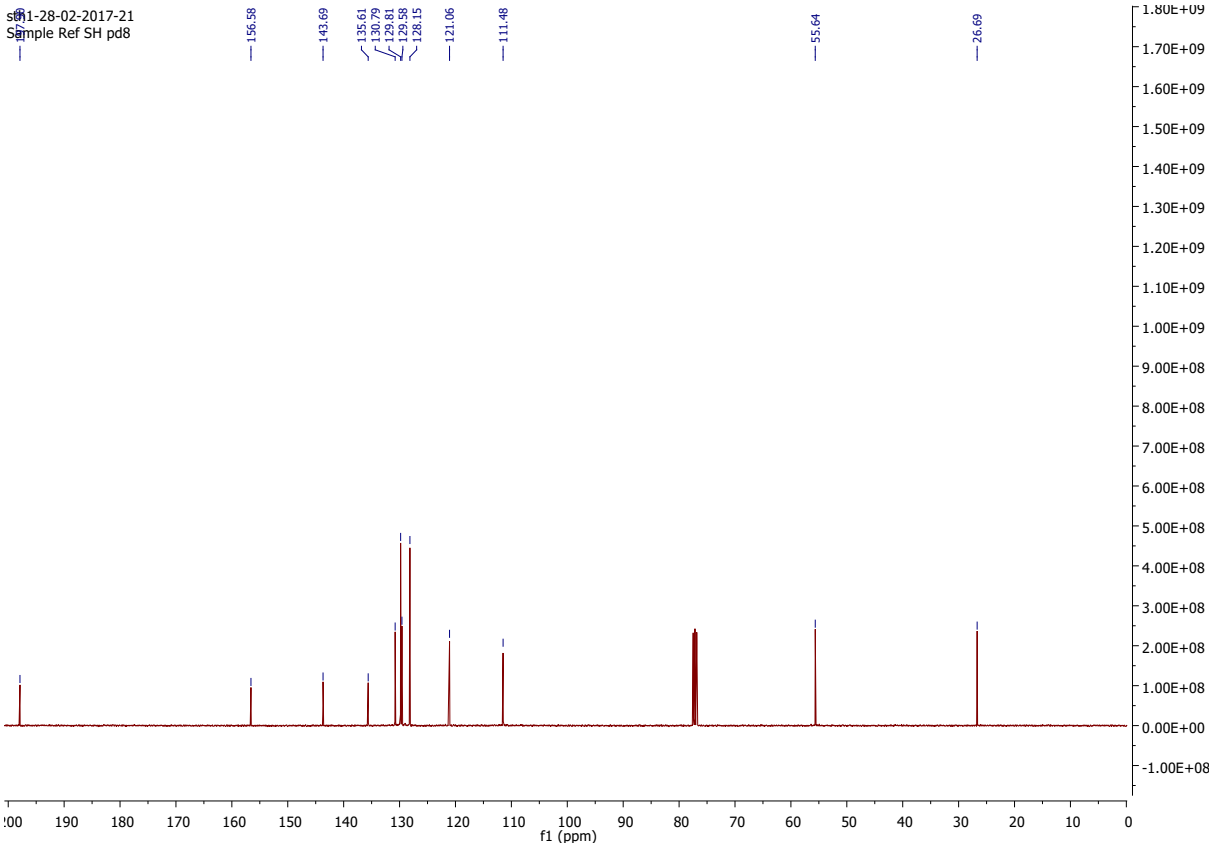
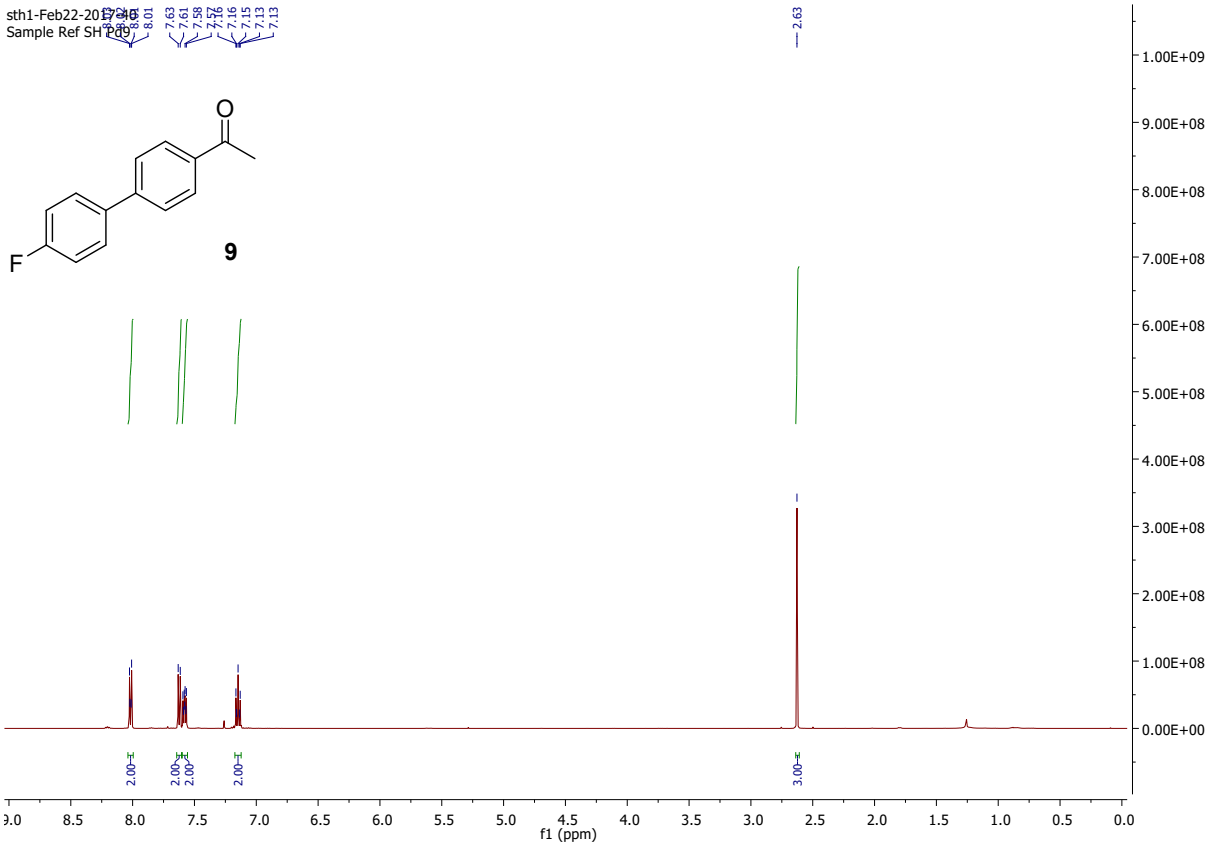
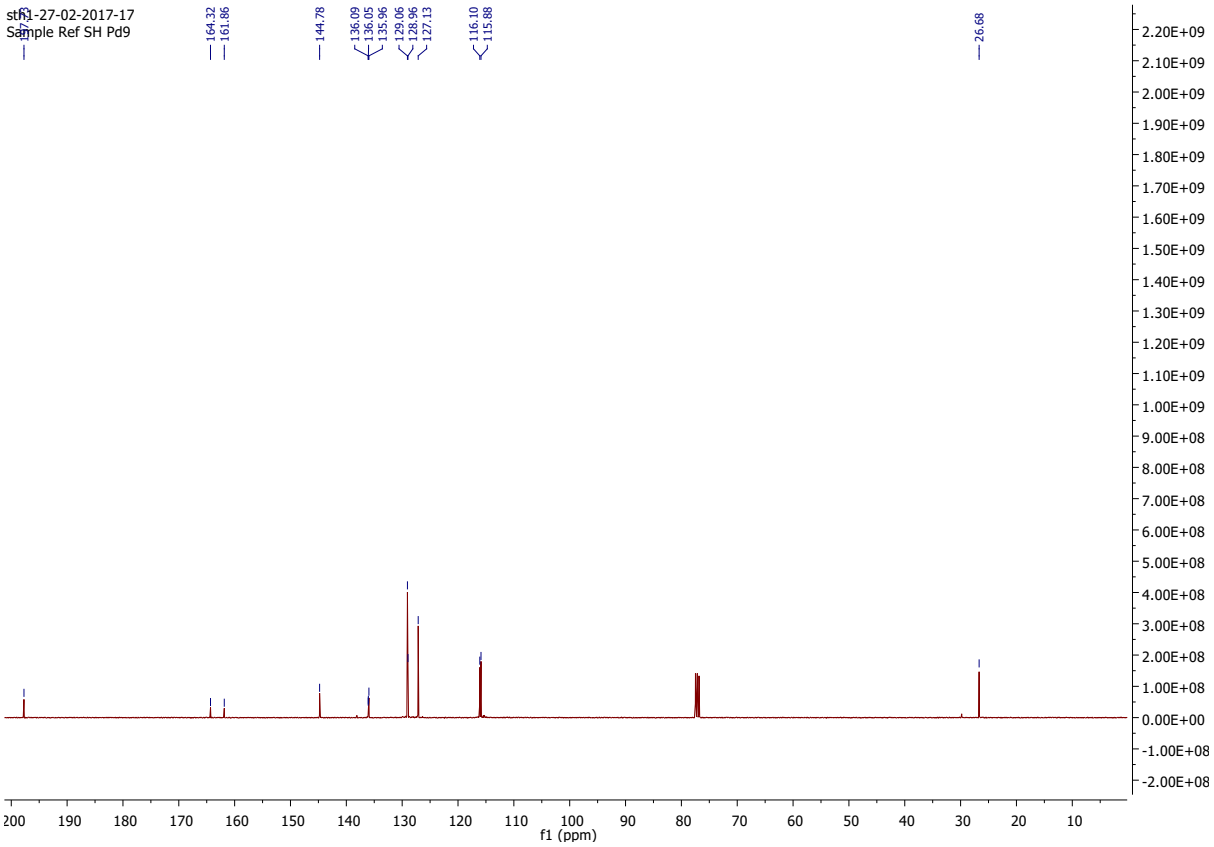
O
O
8
2.00
2.00
2.00
1.01
1.01
2.98
2.99
f1 (ppm)


sth1-28-02-2017-21
Sample Ref SH pd8
156.58
143.69
135.61
130.79
129.81
129.38
128.15
121.06
111.48
55.64
26.69
f1 (ppm)


sth1-Feb22-2017-46
Sample Ref SH Pd9
8.01
7.63
7.61
7.58
7.57
7.16
7.15
7.13
2.63
O
F
9
2.00
2.00
2.00
2.00
3.00
f1 (ppm)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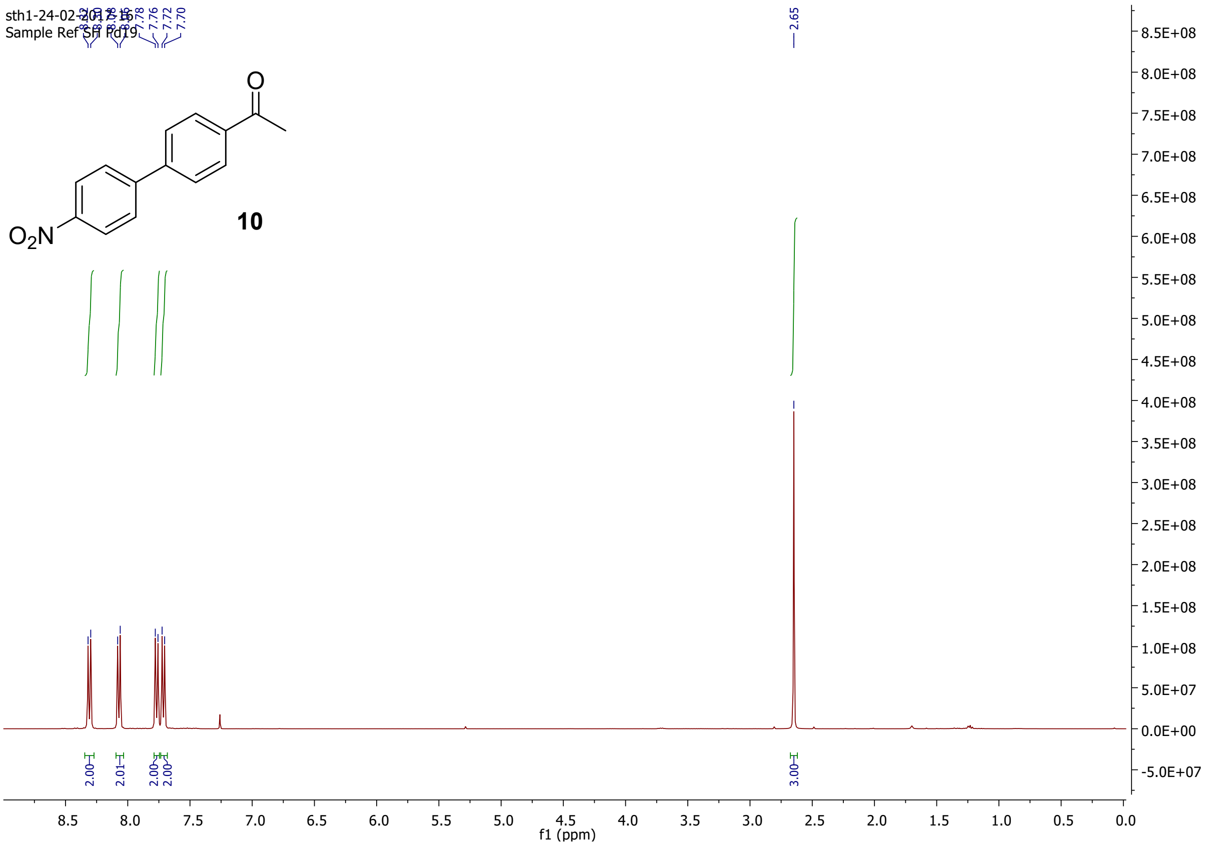
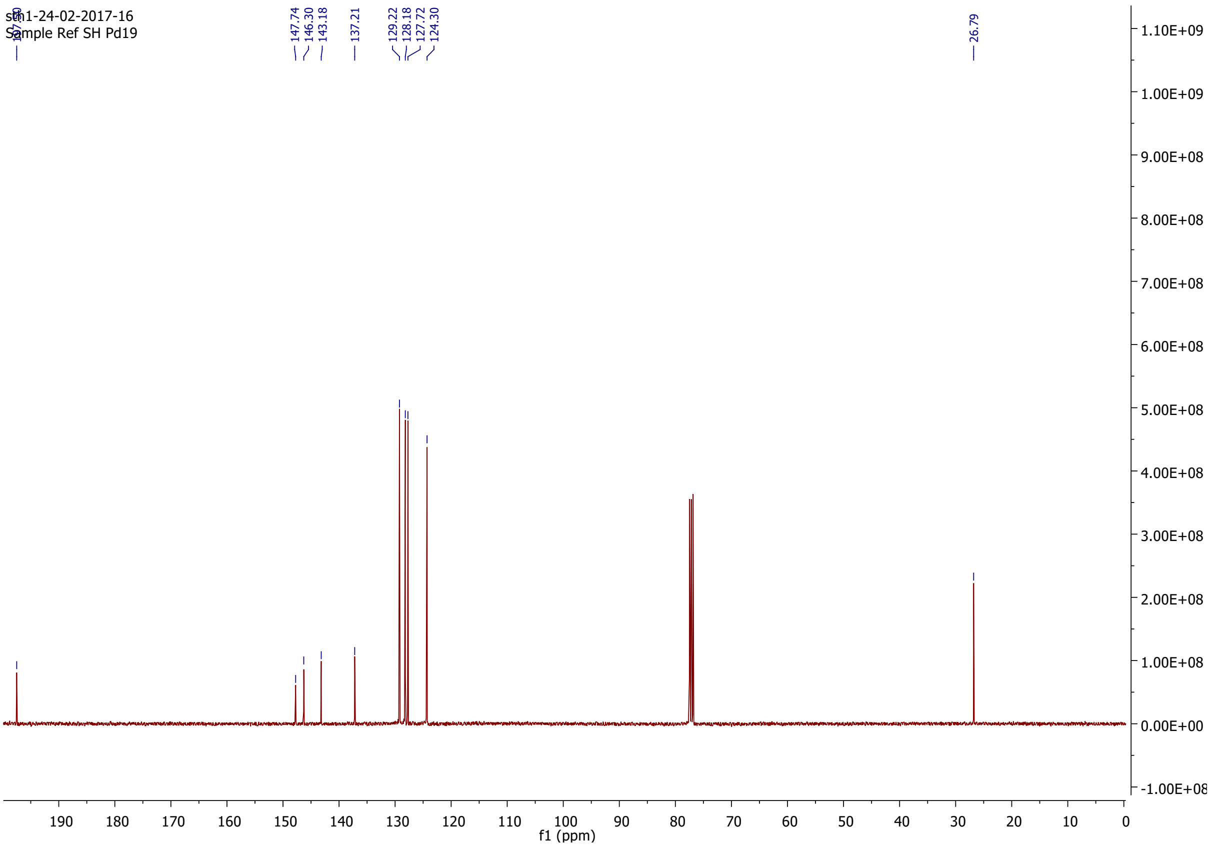
Sample Ref SH Pd9
164.32
161.86
144.78
136.09
136.05
135.96
129.06
128.96
127.13
116.10
115.88
26.68
f1 (ppm)


sth1-24-02-2017-16
Sample Ref SH Pd19
7.78
7.76
7.72
7.70
2.65
O
O_2N
10
2.00
2.01
2.00
2.00
3.00
f1 (ppm)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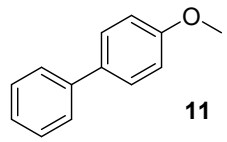
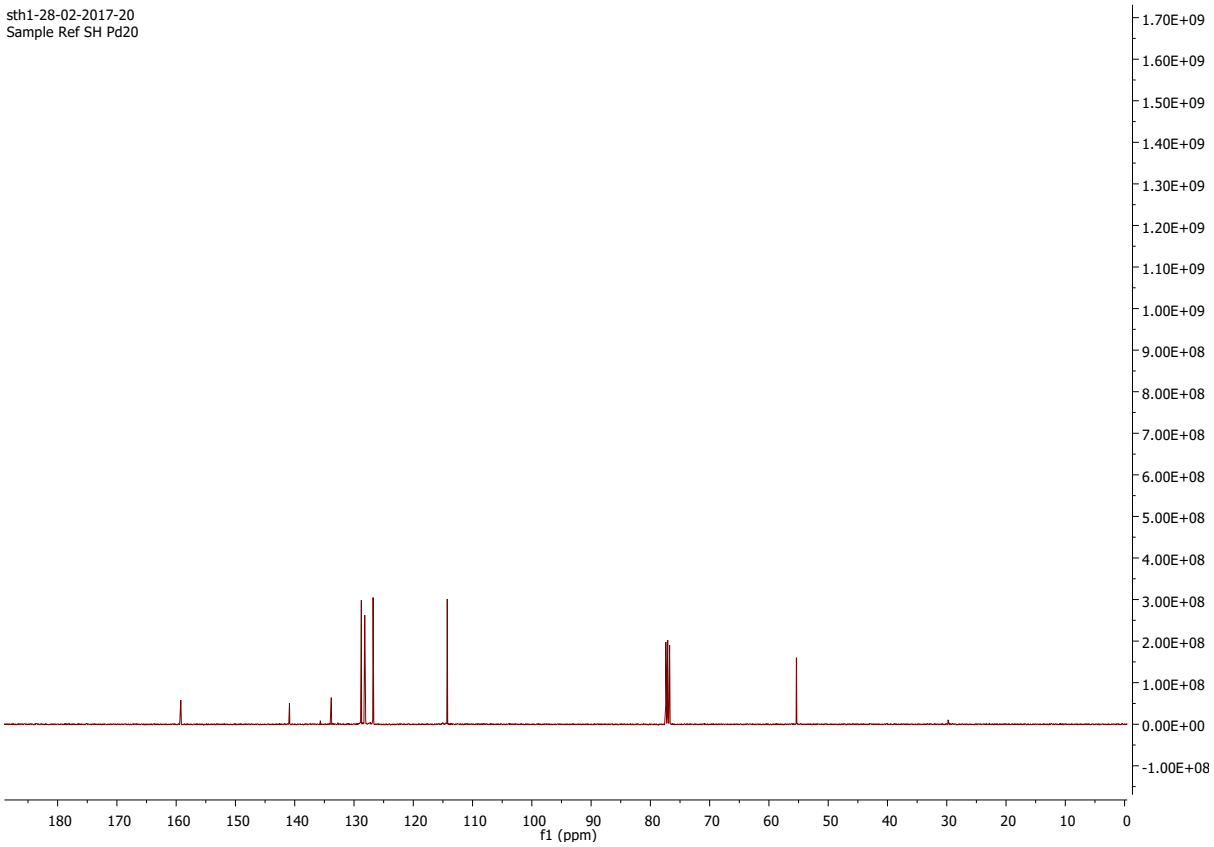
Sample Ref SH Pd19
147.74
146.30
143.18
137.21
129.22
128.18
127.72
124.30
26.79
f1 (ppm)

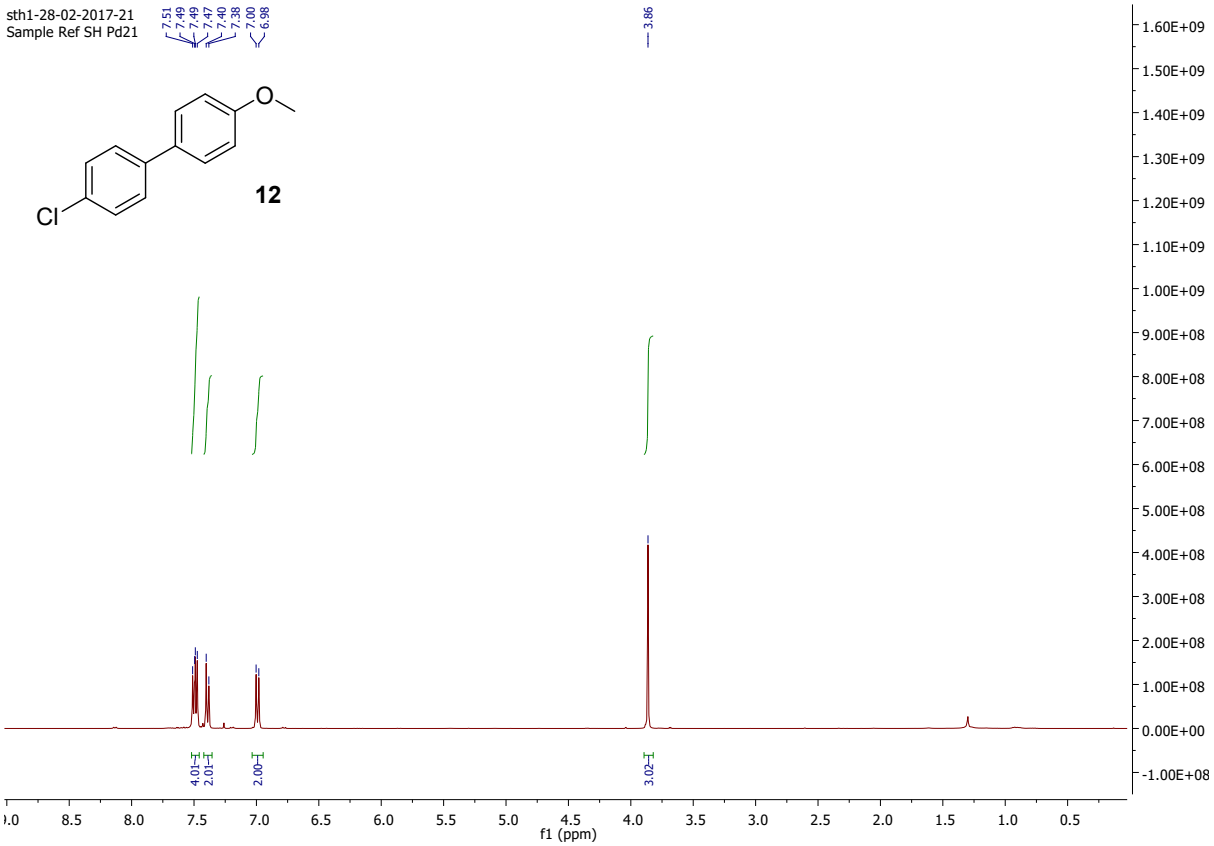
sth1-28-02-2017-25
Sample Ref SH Pd20 crude

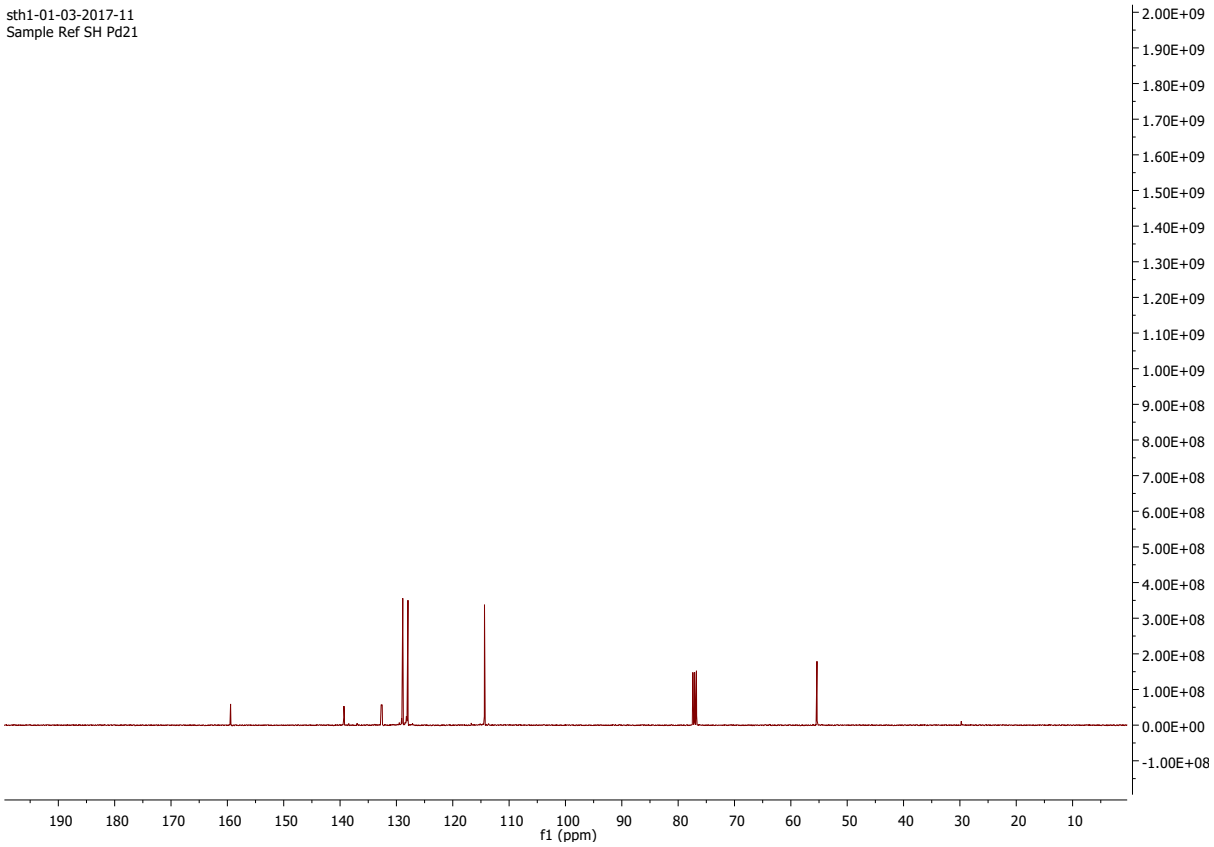


11

sth1-28-02-2017-20
Sample Ref SH Pd20




sth1-28-02-2017-21
Sample Ref SH Pd21
7.51
7.49
7.49
7.47
7.40
7.38
7.00
6.98
3.86
Cl
O
12
4.01
2.01
2.00
3.02
f1 (ppm)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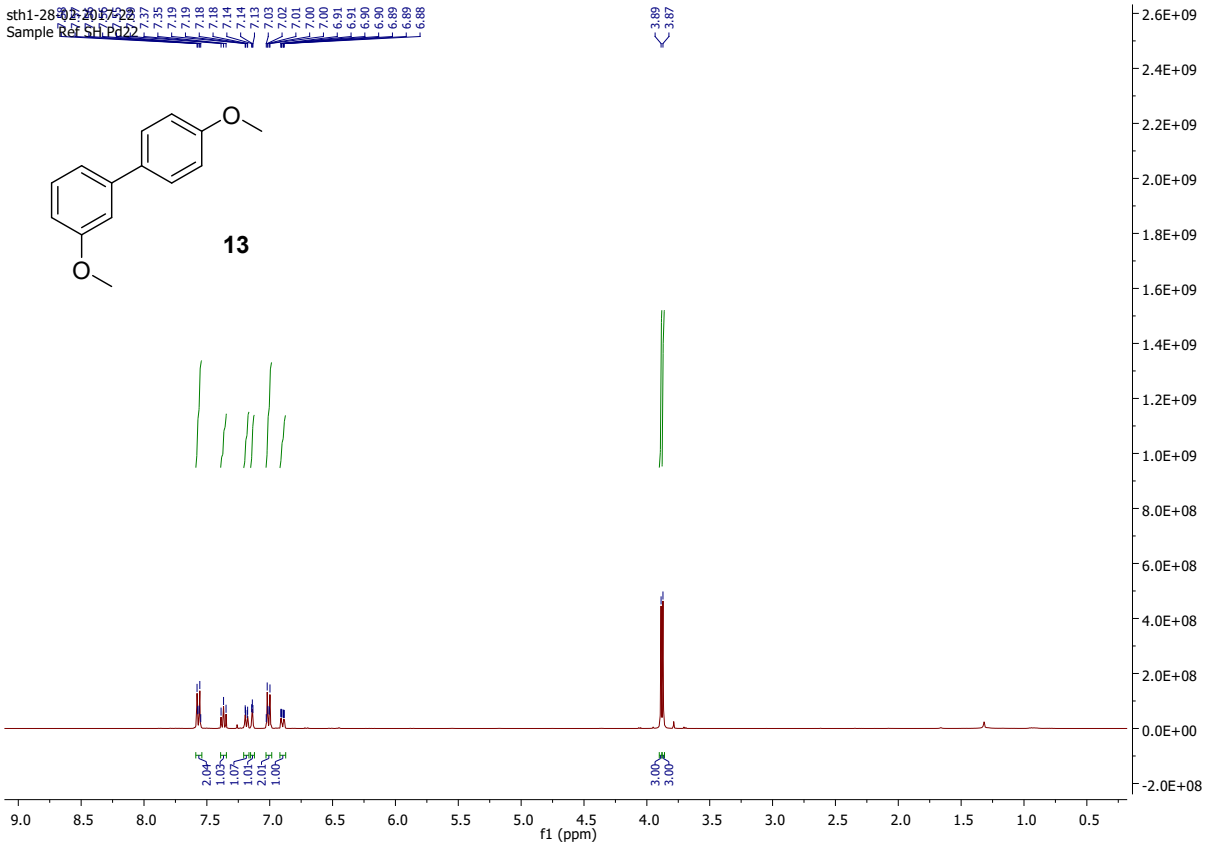
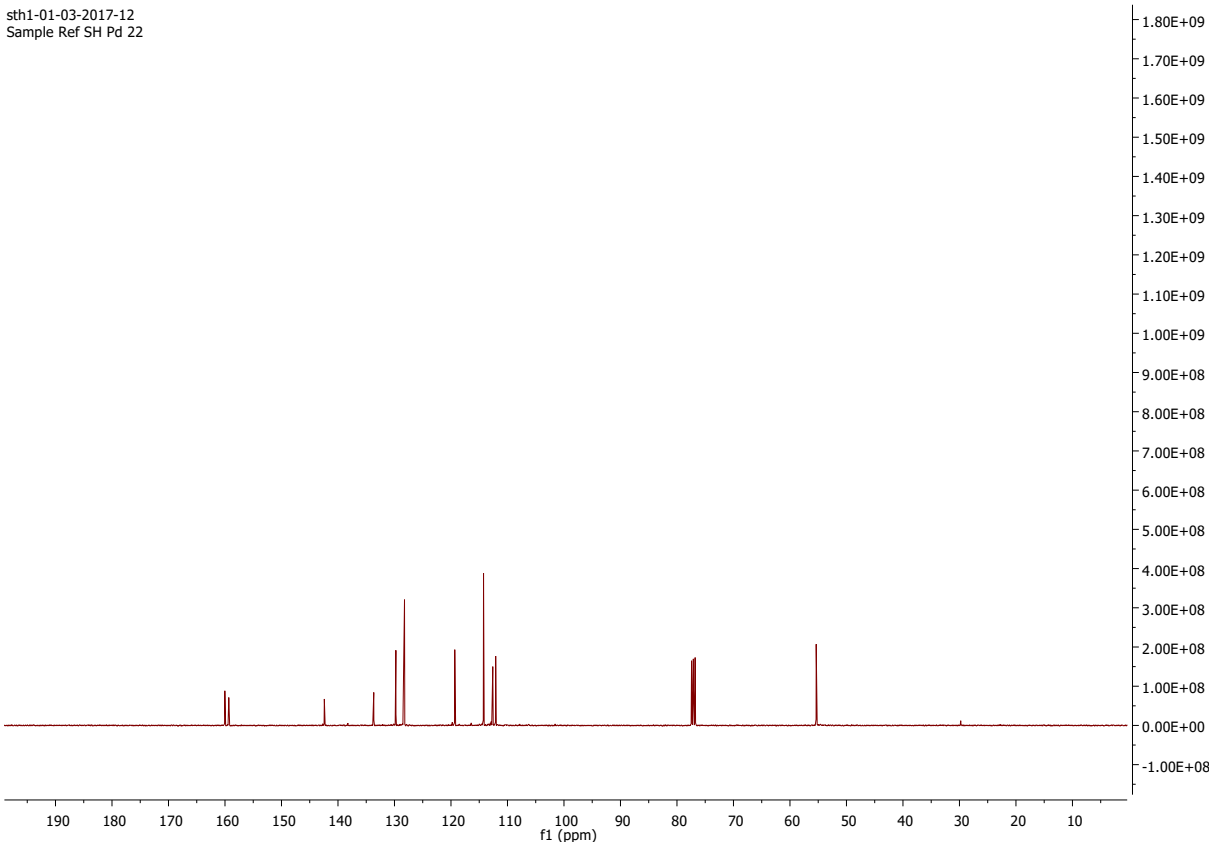
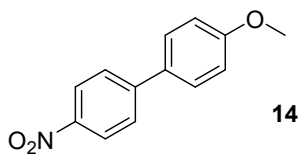
Sample Ref SH Pd21
f1 (ppm)


sth1-28-02-2017-22
Sample Ref SH Pd22
7.37
7.35
7.19
7.18
7.18
7.14
7.14
7.13
7.03
7.02
7.01
7.00
7.00
6.91
6.91
6.90
6.90
6.89
6.89
6.88
3.89
3.87
O
O
13
2.04
1.03
1.07
1.01
2.01
1.00
3.00
3.00
f1 (ppm)

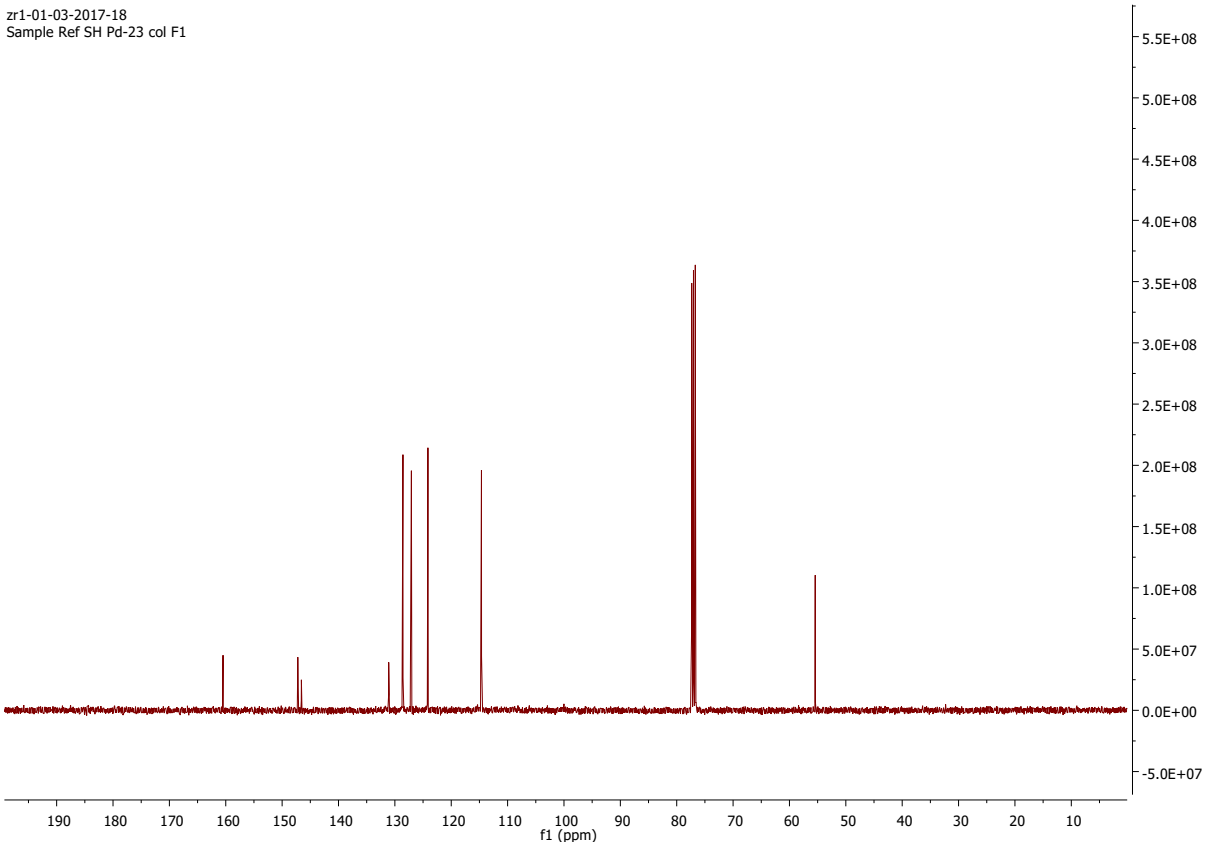

sth1-01-03-2017-12
Sample Ref SH Pd 22
f1 (ppm)

zr1-01-03-2017-34
Sample Ref SH Pd-23 col F1

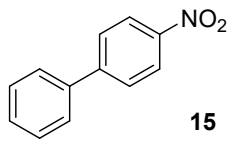


14

zr1-01-03-2017-18
Sample Ref SH Pd-23 col F1

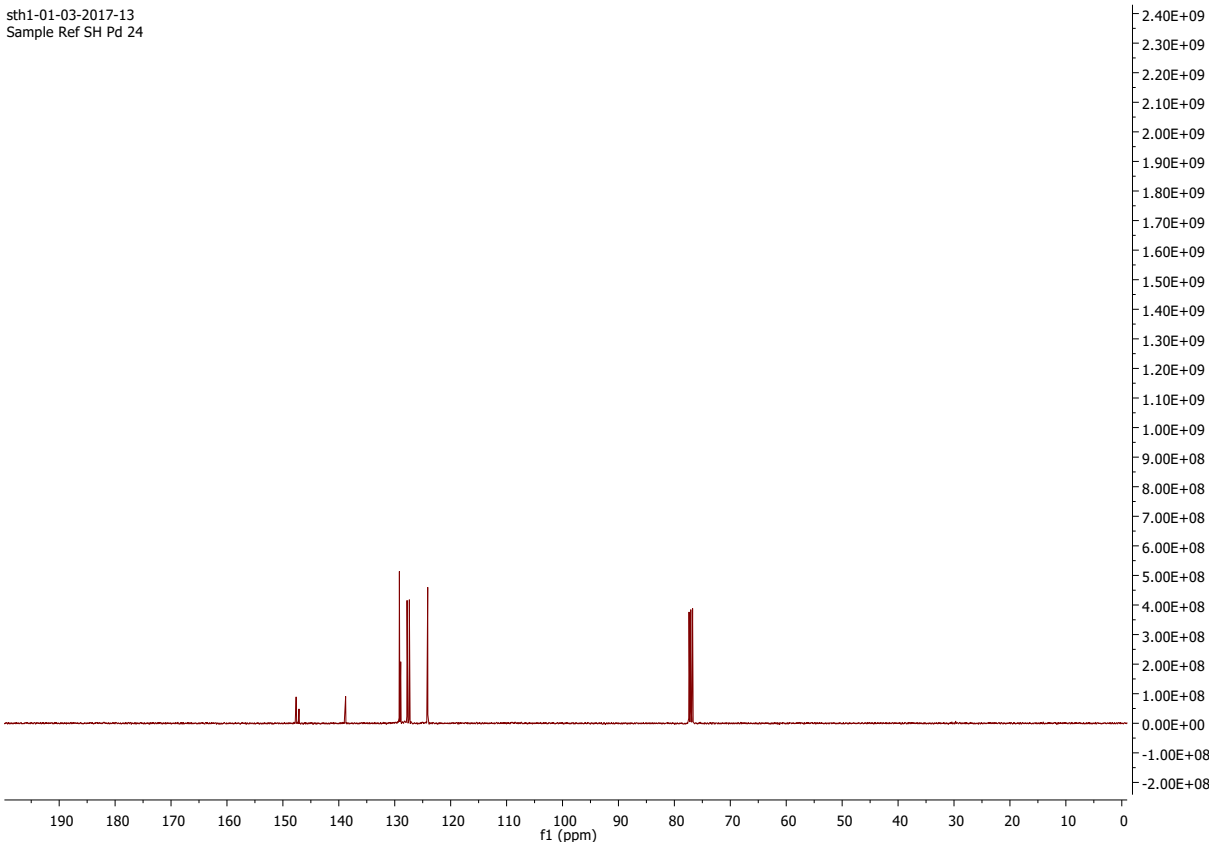


sth1-28-02-2017-24
Sample Ref SH Pd24

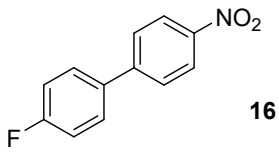


15

sth1-01-03-2017-13
Sample Ref SH Pd 24

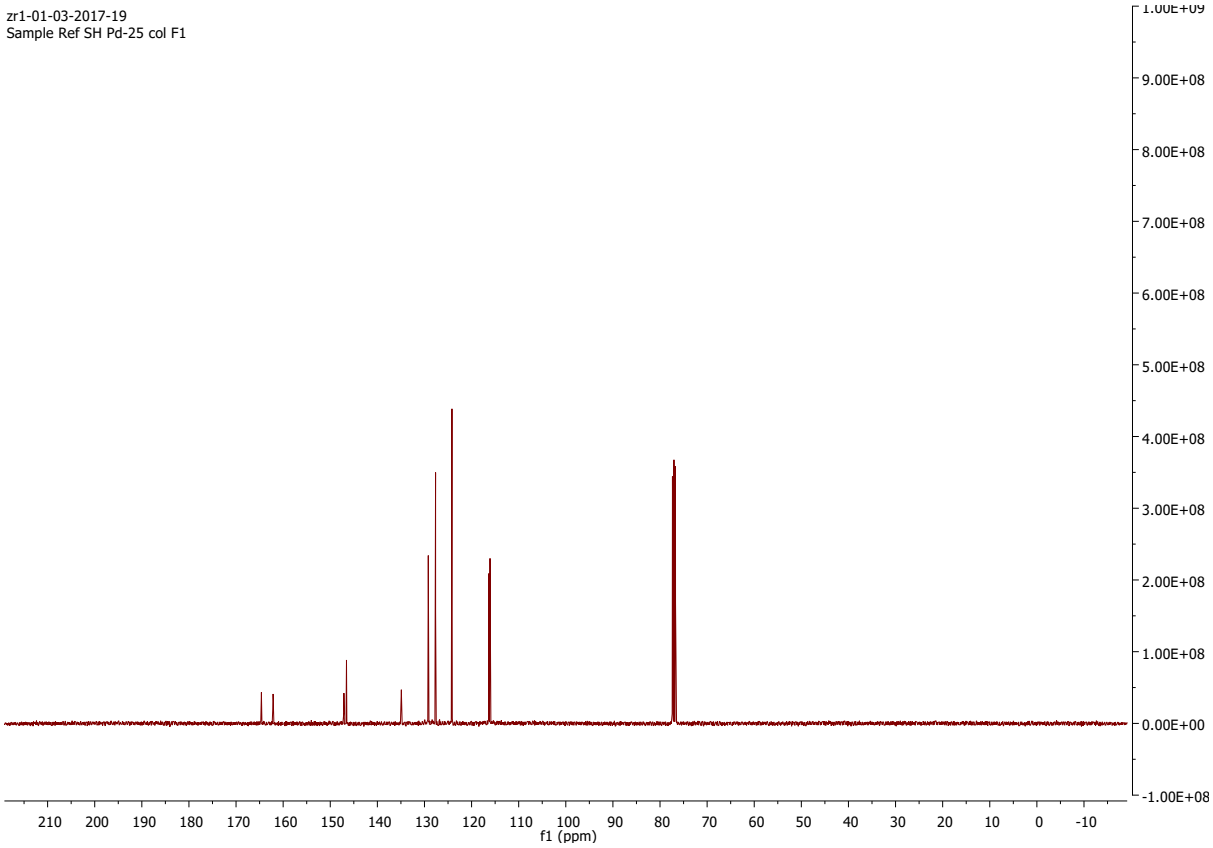


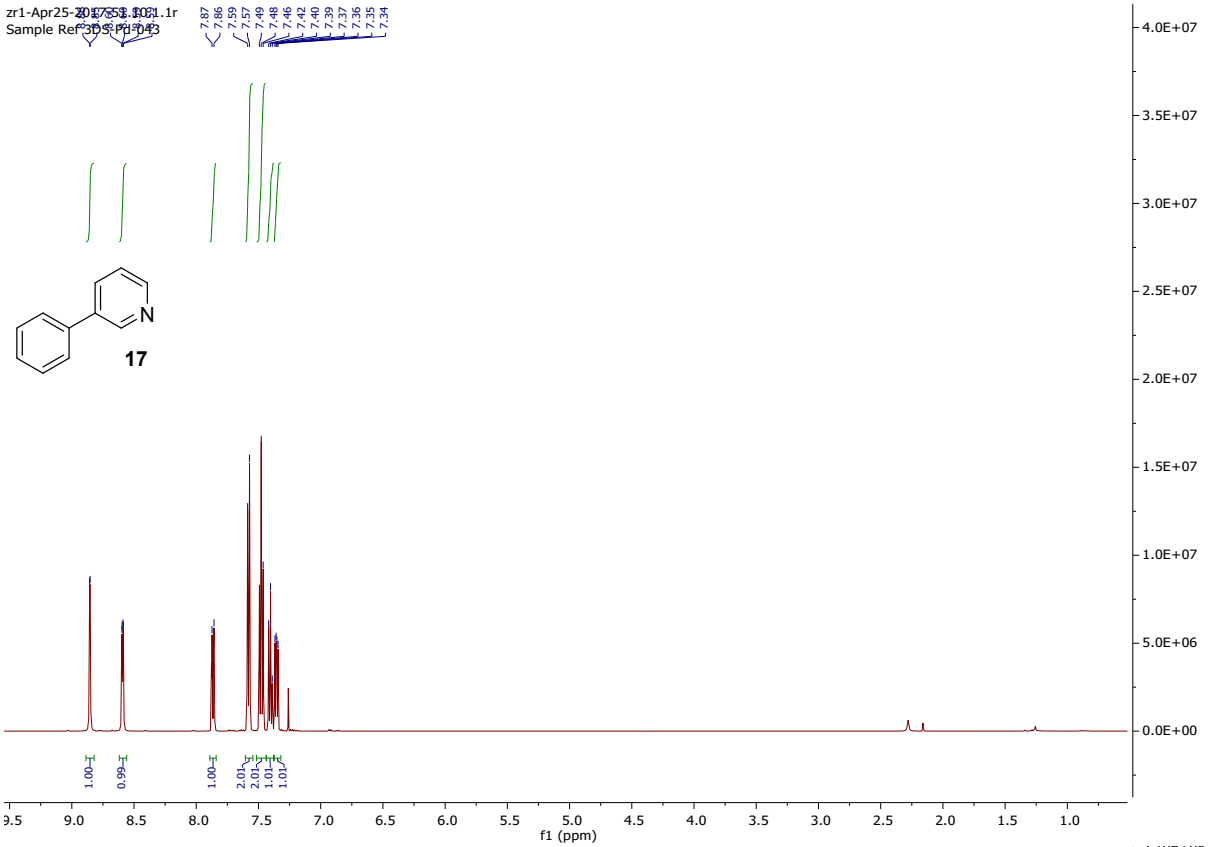
zr1-01-03-2017-35
Sample Ref SH Pd-25 col F1

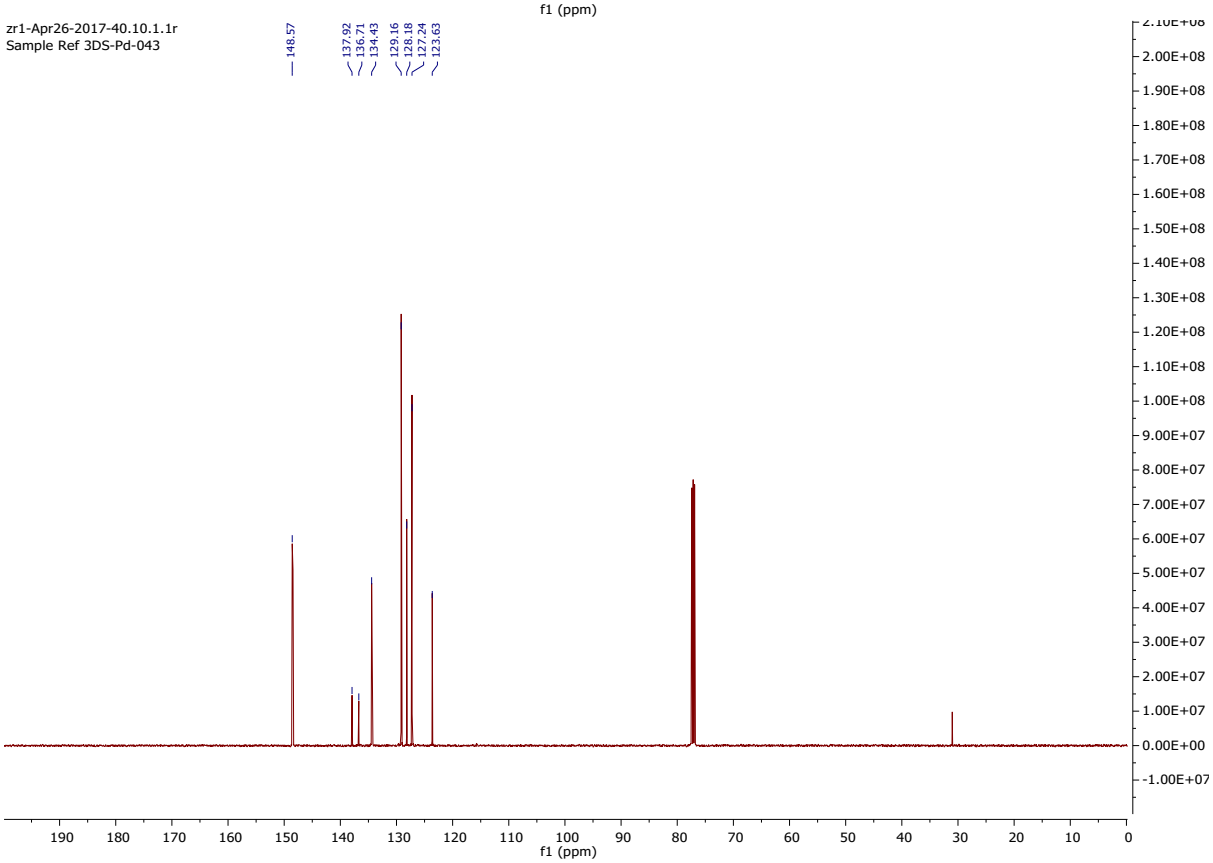


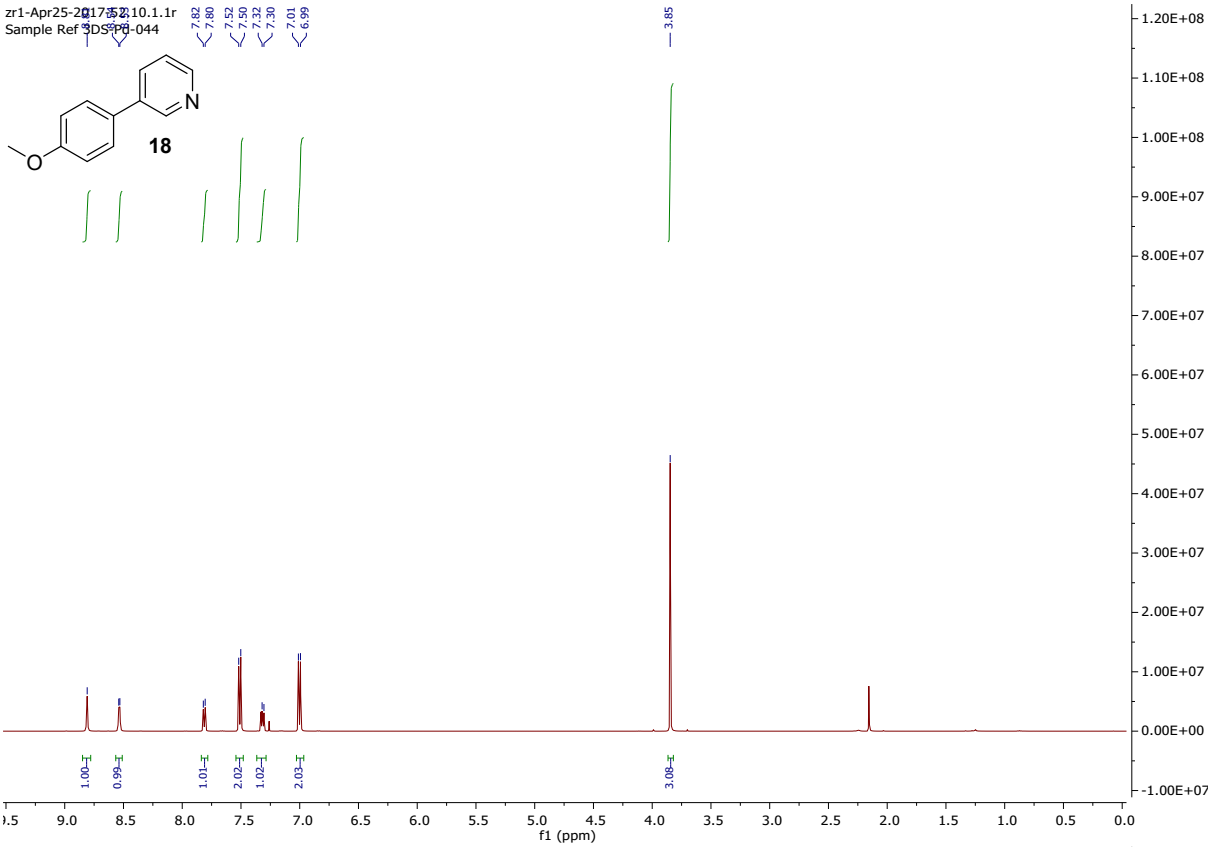
16

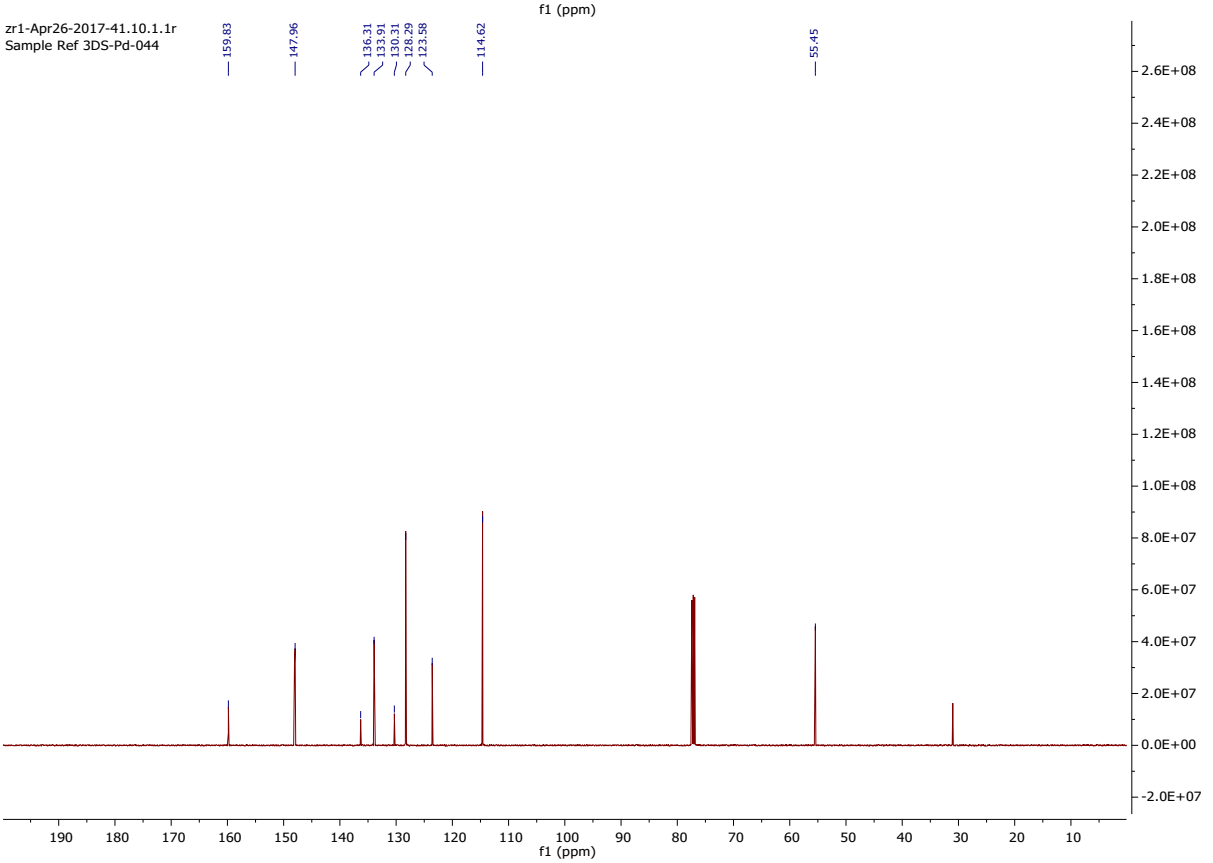
zr1-01-03-2017-19
Sample Ref SH Pd-25 col F1




zr1-Apr25-2017-53.10.1.1r
Sample Ref 3DS-Pd-043
7.87
7.86
7.59
7.57
7.49
7.48
7.46
7.42
7.40
7.39
7.37
7.36
7.35
7.34
N
17
1.00
0.99
1.00
2.01
2.01
1.01
1.01
f1 (ppm)


zr1-Apr26-2017-40.10.1.1r
Sample Ref 3DS-Pd-043
148.57
137.92
136.71
134.43
129.16
128.18
127.24
123.63
f1 (ppm)


zr1-Apr25-2017-52.10.1.1r
Sample Ref 3DS-Pd-044
7.82
7.80
7.52
7.50
7.32
7.30
7.01
6.99
3.85
N
O
18
1.00
0.99
1.01
2.02
1.02
2.03
3.08
f1 (ppm)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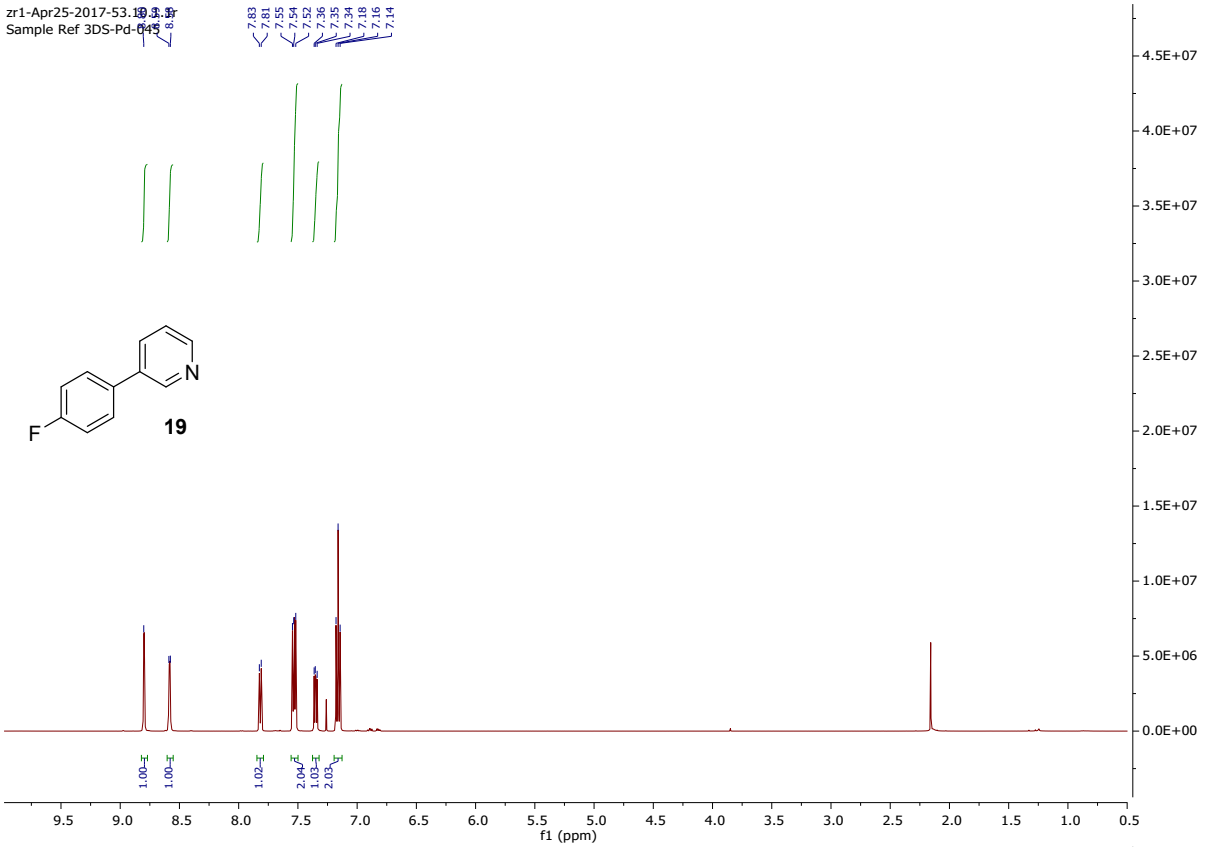
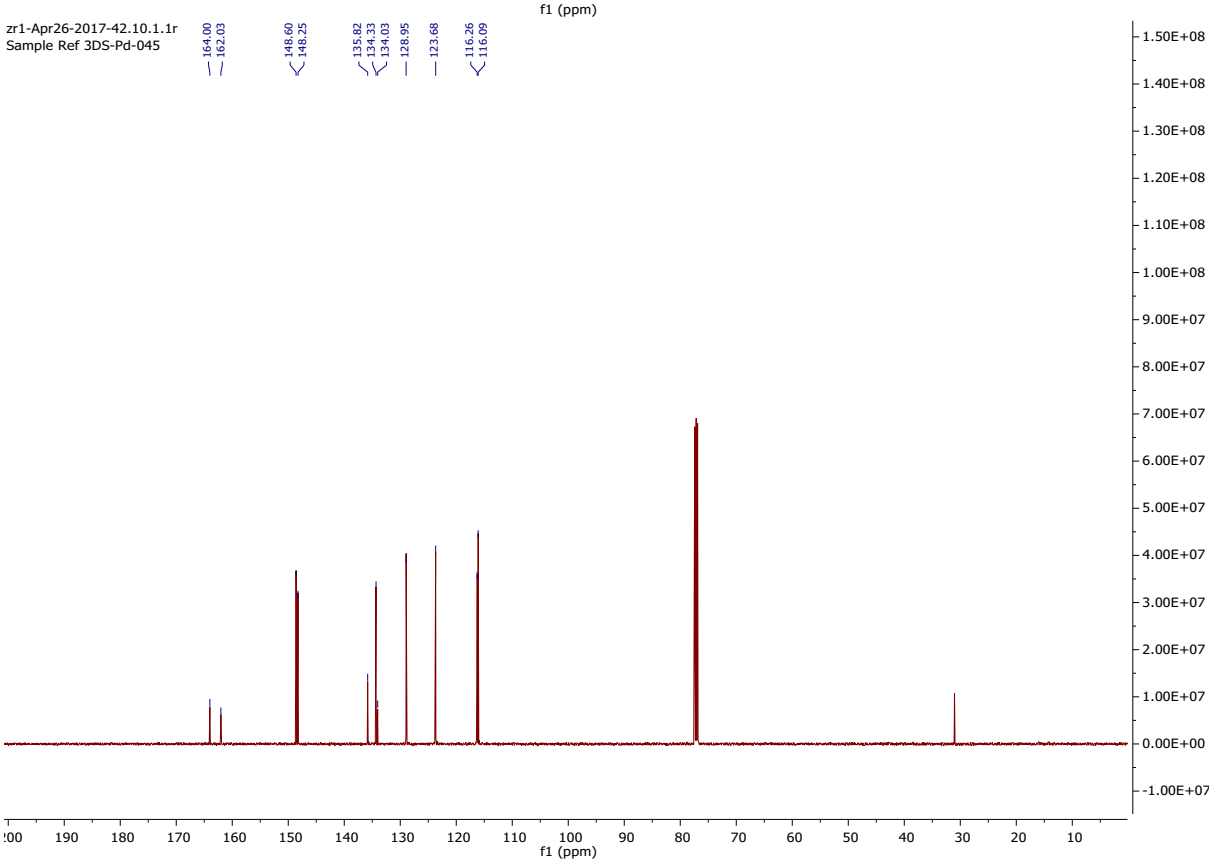
Sample Ref 3DS-Pd-044
159.83
147.96
136.31
133.91
130.31
128.29
123.58
114.62
55.45
f1 (ppm)


zr1-Apr25-2017-53.10.1.1r
Sample Ref 3DS-Pd-045
7.83
7.81
7.55
7.54
7.52
7.36
7.35
7.34
7.18
7.16
7.14
N
F
19
1.00
1.00
1.02
2.04
1.03
2.03
f1 (ppm)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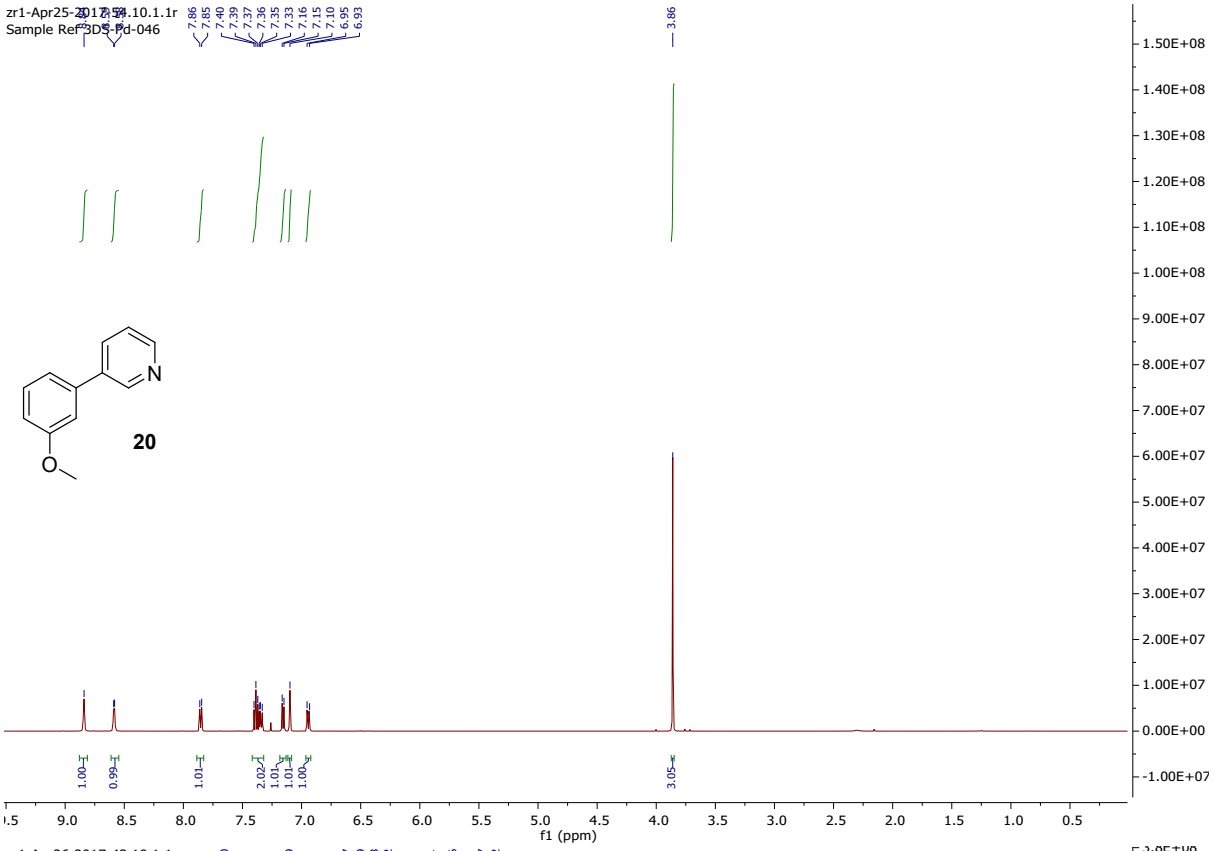
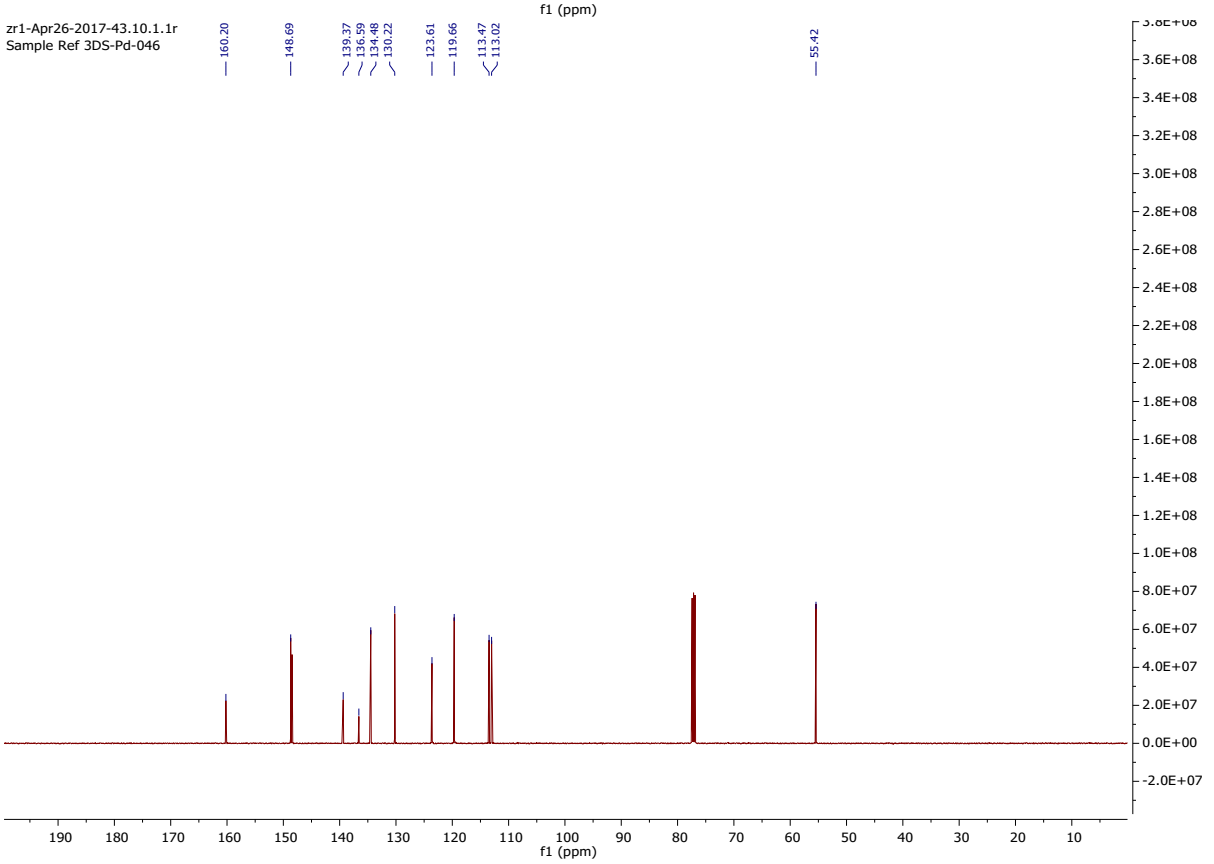
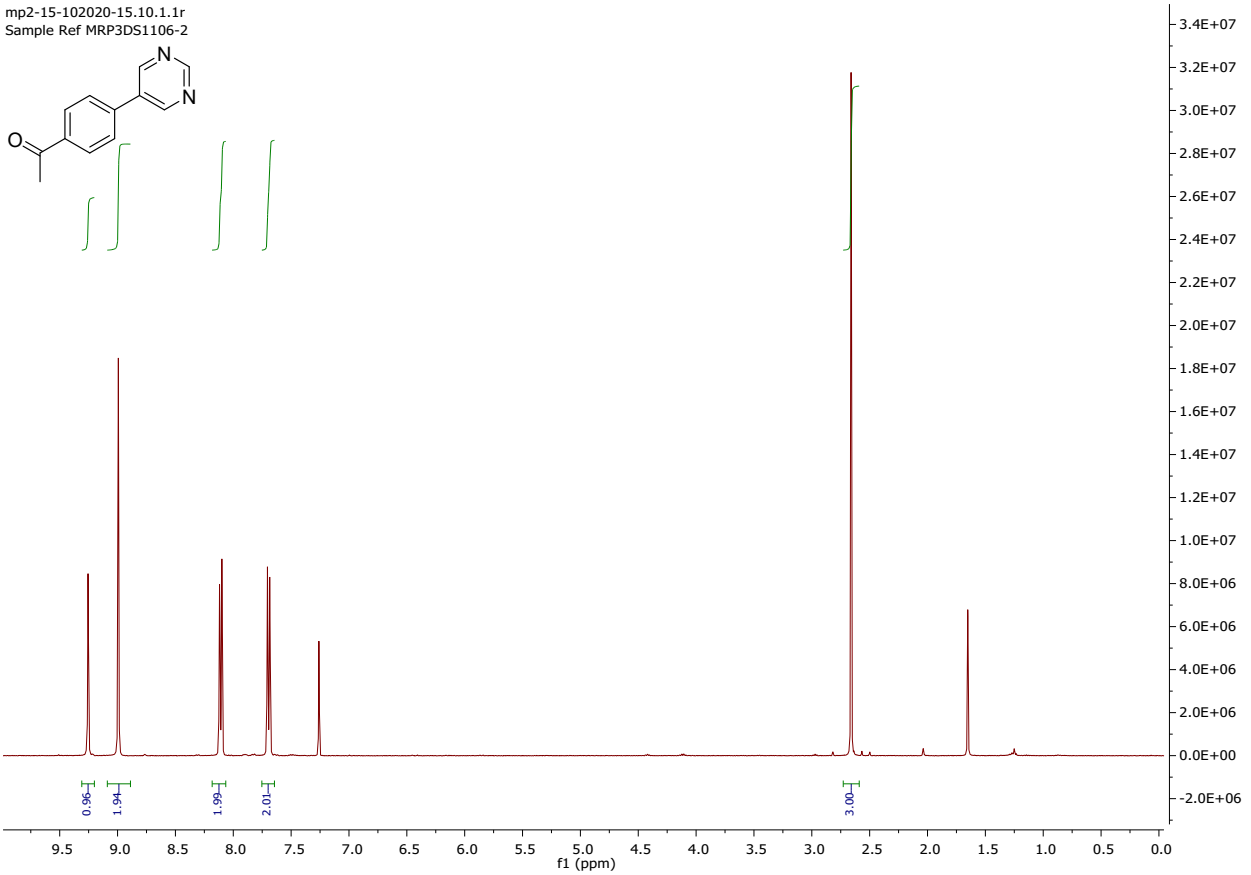
Sample Ref 3DS-Pd-045
164.00
162.03
148.60
148.25
135.82
134.33
134.03
128.95
123.68
116.26
116.09
f1 (ppm)


zr1-Apr25-2017-54.10.1.1r
Sample Ref 3DS-Pd-046
7.86
7.85
7.40
7.39
7.37
7.36
7.35
7.33
7.16
7.15
7.10
6.95
6.93
3.86
N
O
20
1.00
0.99
1.01
2.02
1.01
1.01
1.00
3.05
f1 (ppm)


zr1-Apr26-2017-43.10.1.1r
Sample Ref 3DS-Pd-046
160.20
148.69
139.37
136.59
134.48
130.22
123.61
119.66
113.47
113.02
55.42
f1 (ppm)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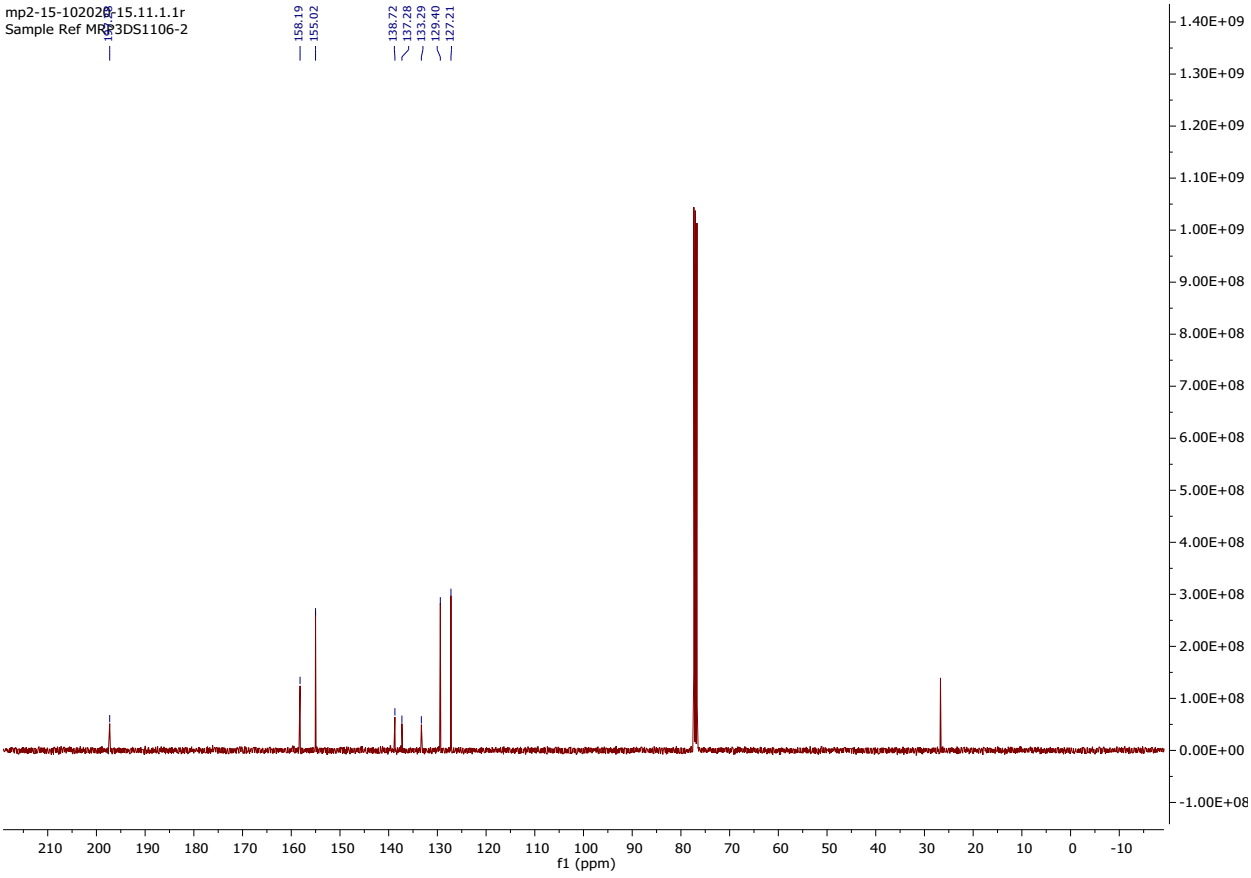
Sample Ref MRP3DS1106-2
0.96
1.94
1.99
2.01
3.00
f1 (ppm)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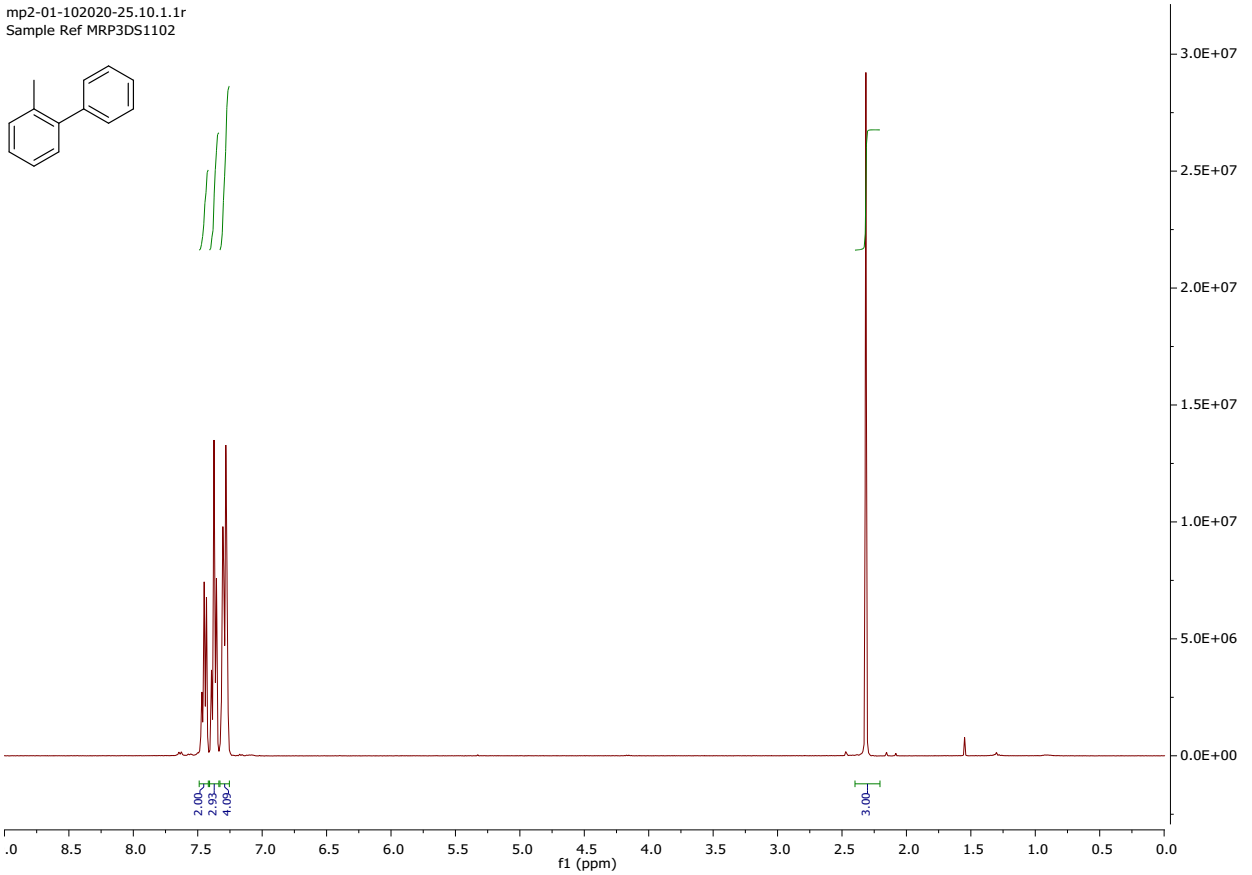
158.19
155.02
138.72
137.28
133.29
129.40
127.21
f1 (ppm)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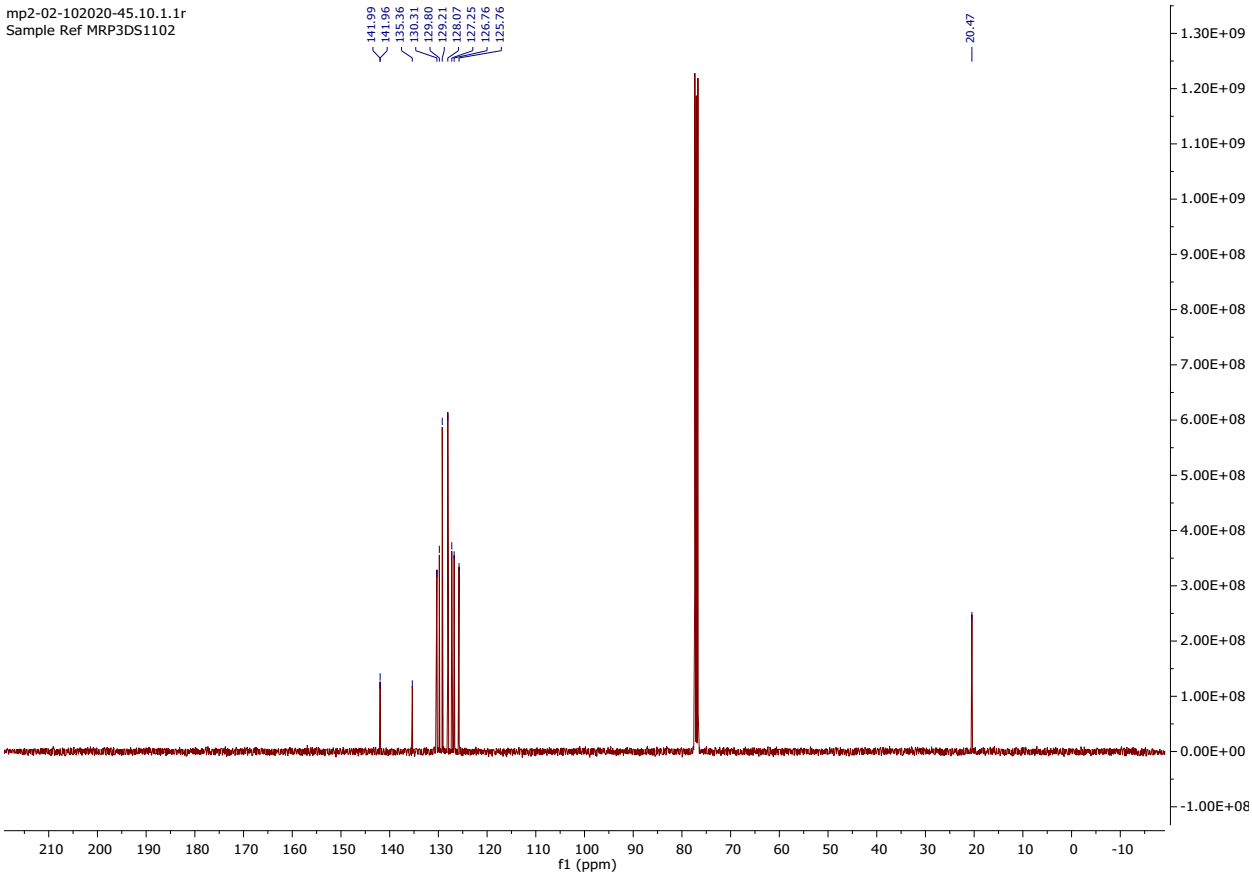
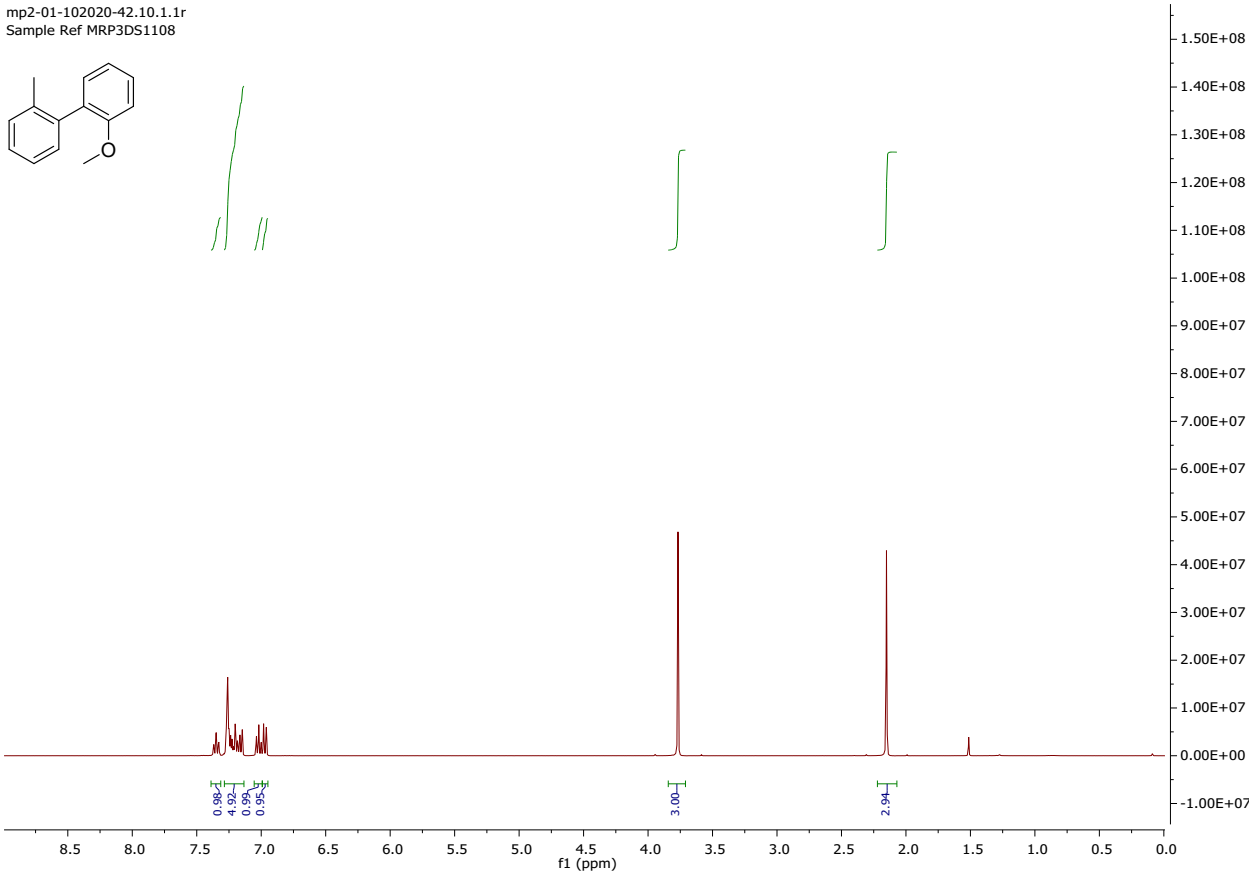
Sample Ref MRP3DS1102
3.0E+07
2.5E+07
2.0E+07
1.5E+07
1.0E+07
5.0E+06
0.0E+00
2.00
2.93
4.09
3.00
f1 (ppm)


mp2-02-102020-45.10.1.1r
Sample Ref MRP3DS1102
141.99
141.96
135.36
130.31
129.80
129.21
128.07
127.25
126.76
125.76
20.47
1.30E+09
1.20E+09
1.10E+09
1.00E+09
9.00E+08
8.00E+08
7.00E+08
6.00E+08
5.00E+08
4.00E+08
3.00E+08
2.00E+08
1.00E+08
0.00E+00
-1.00E+08
f1 (ppm)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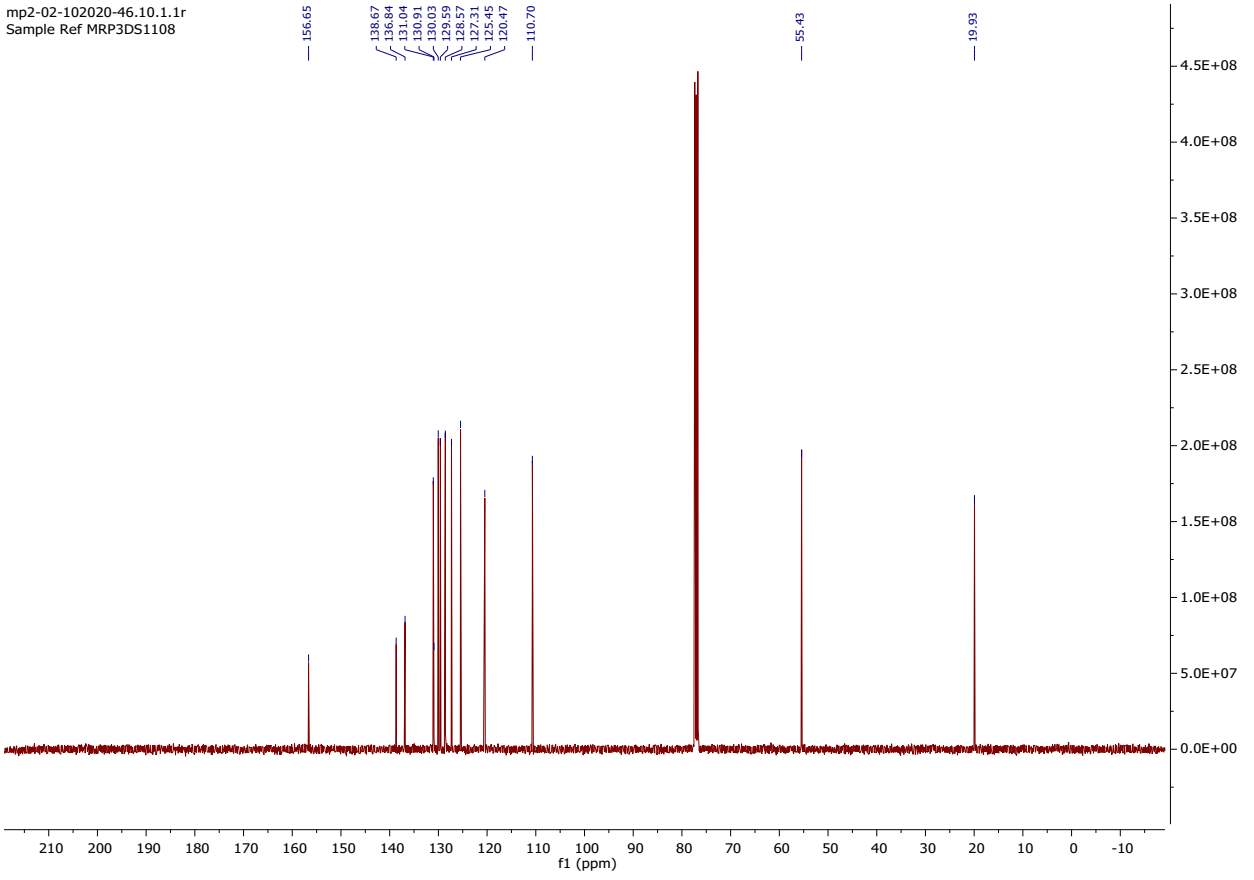
Sample Ref MRP3DS1108
O
0.98
4.92
0.99
0.95
3.00
2.94
f1 (ppm)


mp2-02-102020-46.10.1.1r
Sample Ref MRP3DS1108
156.65
138.67
136.84
131.04
130.91
130.03
129.59
128.57
127.31
125.45
120.47
110.70
55.43
19.93
f1 (ppm)

S.5.0. References

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