Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Superior Activity and Selectivity of Heterogenized Cobalt Catalysts for Hydrogenation of Nitroarenes

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1. General Remarks

N_2-Physisorption was performed on an Asap 2000 from Micromeritics. The samples were degassed for 24 hours at 300 °C and afterwards the measurement was performed at -196 °C. Inductively coupled plasma (ICP-OES) analysis was conducted with an instrument of SPECTRO Analytical Instruments, Model SPECTROFLAME. The pore structure and particle distribution of the catalyst samples were investigated via STEM imaging on a Hitachi HD-2700 electron microscope (CS-corrected, 200 kV, Cold FEG, EDX Octane T Ultra W 100 mm^2 SDD TEAM-Software). X-ray diffraction (XRD) was performed on a Siemens D5000 (Radiation/wavelength: Cu K-alpha, 0.15418 nm). Thermogravimetric analysis (TGA) was conducted on a STA 409 cell from Netzsch. X-ray photoelectron spectroscopy (XPS) data were obtained on a Phi5000 VersaProbe II spectrometer (ULVAC-Phi Inc., USA) using AlKα as the excitation source (1.486 keV) and operated at 50 W, 15 kV, 200 µm. Survey spectra were obtained by 187.5 eV energy, 0.8 eV step range, 100 ms/step. High resolution spectra were obtained by 23.5 eV energy, 0.1 eV step, 100 ms/step. The shift of the binding energy was corrected using C 1s level at 285 eV. Furthermore, the quantifications in at% show a relative error of 15% and was indexed to 100% with a Shirley-background and empiric device-optimized sensitivity factor.

Unless otherwise stated, reactions were performed in a 300 mL autoclave from Parr Instrument Company. Solvents were used directly without further purification. NMR-spectra were recorded on Bruker AV 300 and 400 spectrometers. Chemicals shifts (δ) are reported in ppm downfield of tetramethylsilane. The residual solvent signals were used as references for ^1H and ^{13}C NMR spectra ($CDCl_3$: δH = 7.26 ppm, δC = 77.12 ppm; DMSO-*d6*: δH = 2.50 ppm, δC = 39.52 ppm).

2. Procedure for the Preparation of Catalysts

2.1. Synthesis of the hard-template

SBA-15 materials were synthesized according to the procedure of Zhao *et al.*[1] in order to use them as templates for the formation of nanostructured carbon. Ordered mesoporous silica templates were prepared using the surfactant $EO_{20}PO_{70}EO_{20}$ (P123), and TEOS as silica source. P123 (6.0 g) was completely dissolved in 2 M HCl (180 mL) overnight at room temperature. TEOS (12.6 mL) was added to the stirred mixture at 35 °C. The mixture was placed in the oven at 120 °C for 24 h. The white precipitates were filtered by vacuum filtration and washed twice with distilled water and twice with ethanol. The product was dried at 80 °C for 24 h and calcined at 550 °C for 6 h.

2.2. Synthesis of nanostructured carbon (CMK-3-CoPc)

Ordered mesoporous carbon materials (CMK-3) were formed using the same procedure as introduced by Ryoo *et al.*[2] CMK-3 was synthesized with Cobalt phthalocyanine (CoPc) as a carbon source by replicating mesoporous silica SBA-15 (hard-template). The pores of SBA-15 were filled with CoPc via different impregnation methods (see 2.2.1-2.2.3). The mixture was then placed into an oven at 100 °C for 1 h, 350 °C for 1 h and subsequently carbonized at 990°C for 1 h under nitrogen atmosphere. To leach the silica template from the silica-Co-phthalocyanine composite, the resulting black powder was treated with 5 M NaOH solution at 100 °C for 24 h. The solution was then centrifuged at 6000 rpm for 15 minutes, followed by decantation of the supernatant solution. The sediment was dispersed in distilled water. Centrifugation was repeated ten times to ensure a neutral pH of the supernatant solution. The silica leaching step was then repeated. The replica was dried at 100 °C and ordered mesoporous carbon materials denoted as CMK-3-CoPc were obtained (see Scheme S1).

2.2.1 Grinding (solid/solid-impregnation; denoted as GR)

CoPc (1.0 g) was added to SBA-15 (1.0 g) and both materials were physically mixed together thoroughly via pestle and mortar until a homogeneous colored powder was formed.

2.2.2 Wet Impregnation (denoted as WI)

CoPc (1.0 g) was dissolved in ethanol (50 mL) and SBA-15 (1.0 g) was added to the solution. The mixture was heated up to 60 °C for 24 h and stirred until the solution turned colorless. The solvent was evaporated under reduced pressure.

2.2.3. Incipient Wetness Impregnation (denoted as IWI)

SBA-15 (1.0 g) was impregnated with CoPc (1.0 g) dissolved in ethanol (2 mL). The metal solution was added dropwise to SBA-15, thus only wetting the solid template by the incipient wetness principle.

(1) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. Fredrickson, B. Chmelka, G. Stucky, *Science* **1998**, *279*, 548–52.

(2) L. Solovyov, N. Shmakov, V. I. Zaikovskii, S. H. Joo, R. Ryoo, *Carbon* **2002**, *40*, 2477–2481.

3. Characterization of the Catalysts

3.1. Thermogravimetric analysis

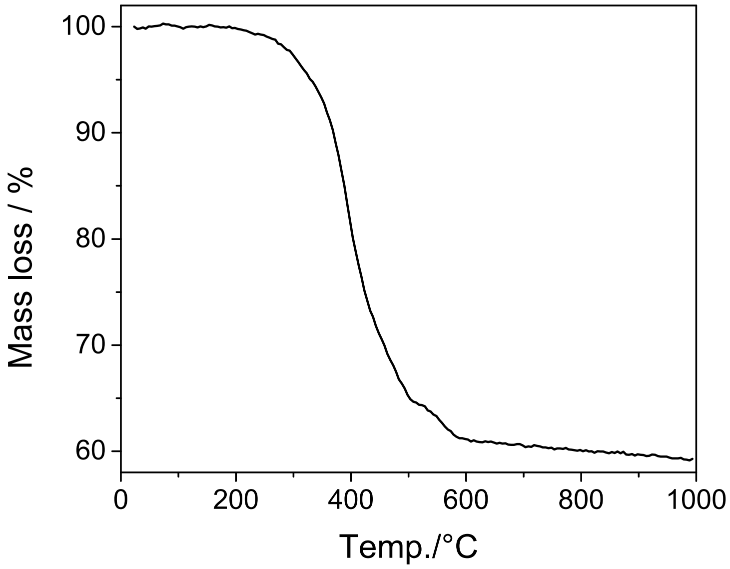


Figure S1. Thermogravimetric analysis (TGA) for CMK-3-CoPc-WI.

3.2. X-ray Photoelectron Spectroscopy (XPS)

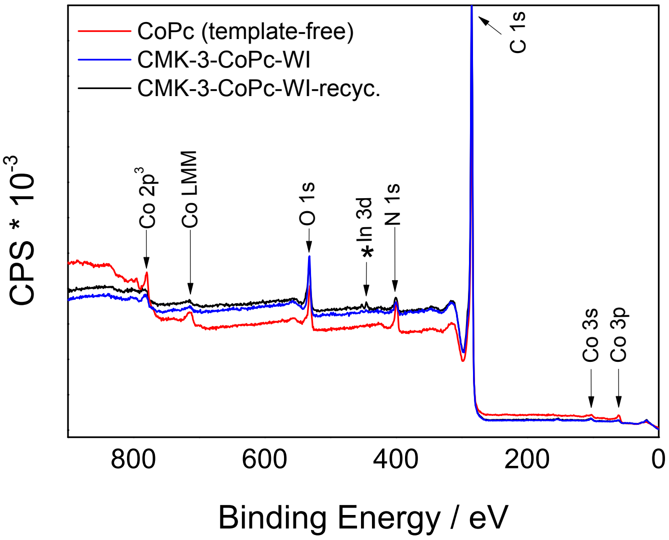


Figure S2. XPS survey scan for CoPc (template-free) and CMK-3-CoPc-WI prior and after 5 catalytic cycles. The survey spectra indicate that no other metallic or inorganic contaminants are present. The In 3d signal (marked by *) originates from the Indium-foil used for fixation of the powder sample.

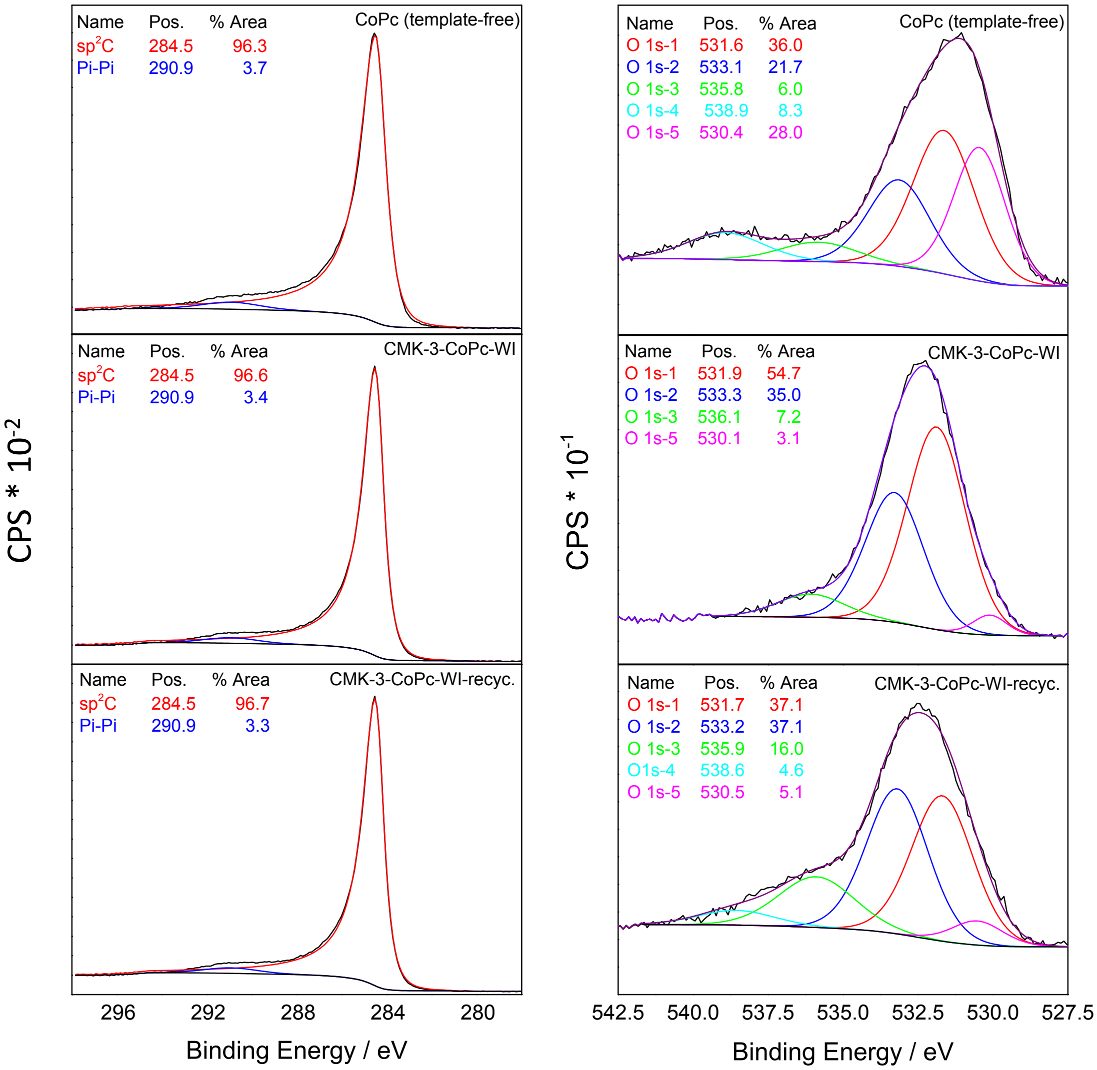


Figure S3. XPS C 1s (left) and O 1s spectra (right) for CoPc (template-free) and CMK-3-CoPc-WI prior and after 5 catalytic cycles; O 1s species can be assigned as follows: (O 1s-1, red) O=C-N, C=O (aromatic); (O 1s-2, blue) C-O-C (aromatic), epoxy-, O-C-O, C=O (aliphatic), H_2O; (O 1s-3, green) H_2O, O_2/C; (O 1s-4, light blue) O_2/C; (O 1s-5, magenta) CoO.

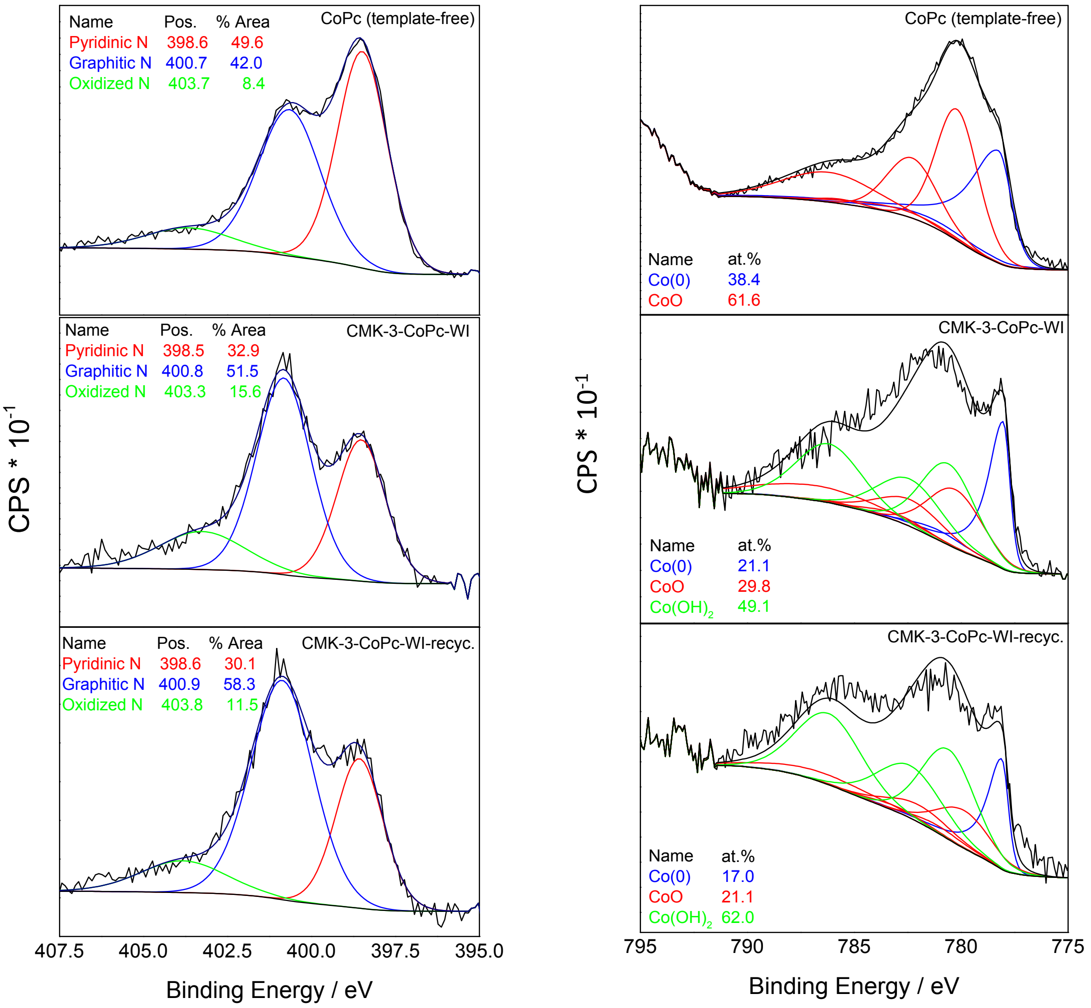


Figure S4. XPS N 1s (left) and Co 2p spectra (right) for CoPc (template-free) and CMK-3-CoPc-WI prior and after 5 catalytic cycles; Co $2p_{3/2}$ spectra were curve fitted based on the literature peak set of CoO and Co_3O_4 multiplets (M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, R. St. C. Smart, *Appl. Surf. Sci.* 2011, **257**, 2717-2730).

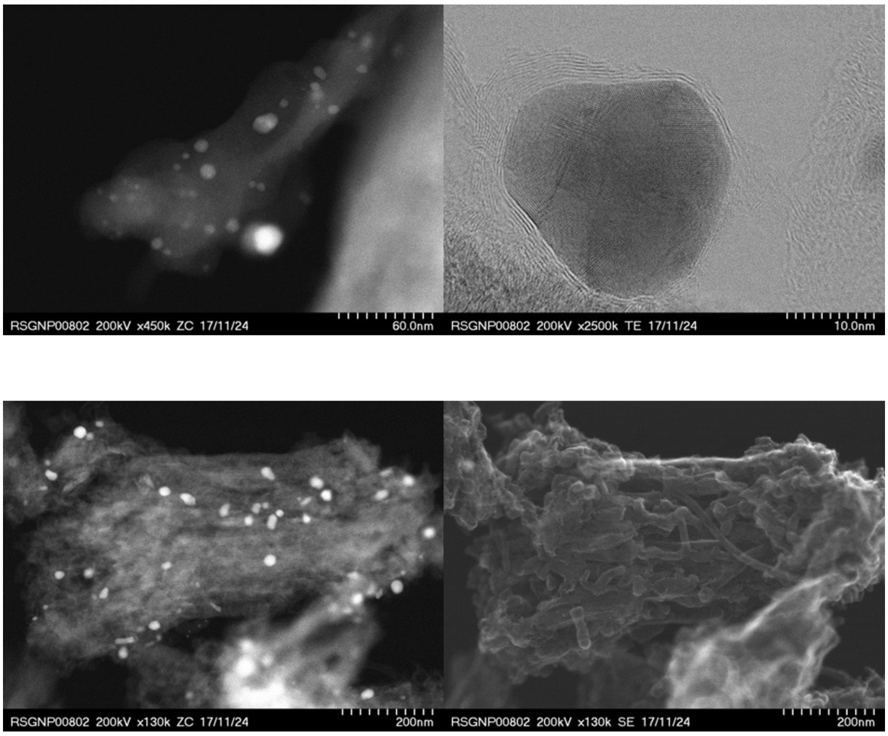


Figure S5. STEM analysis of different regions within the recycled catalyst CMK-3-CoPc-WI-(recyc.) after 5 successive runs.

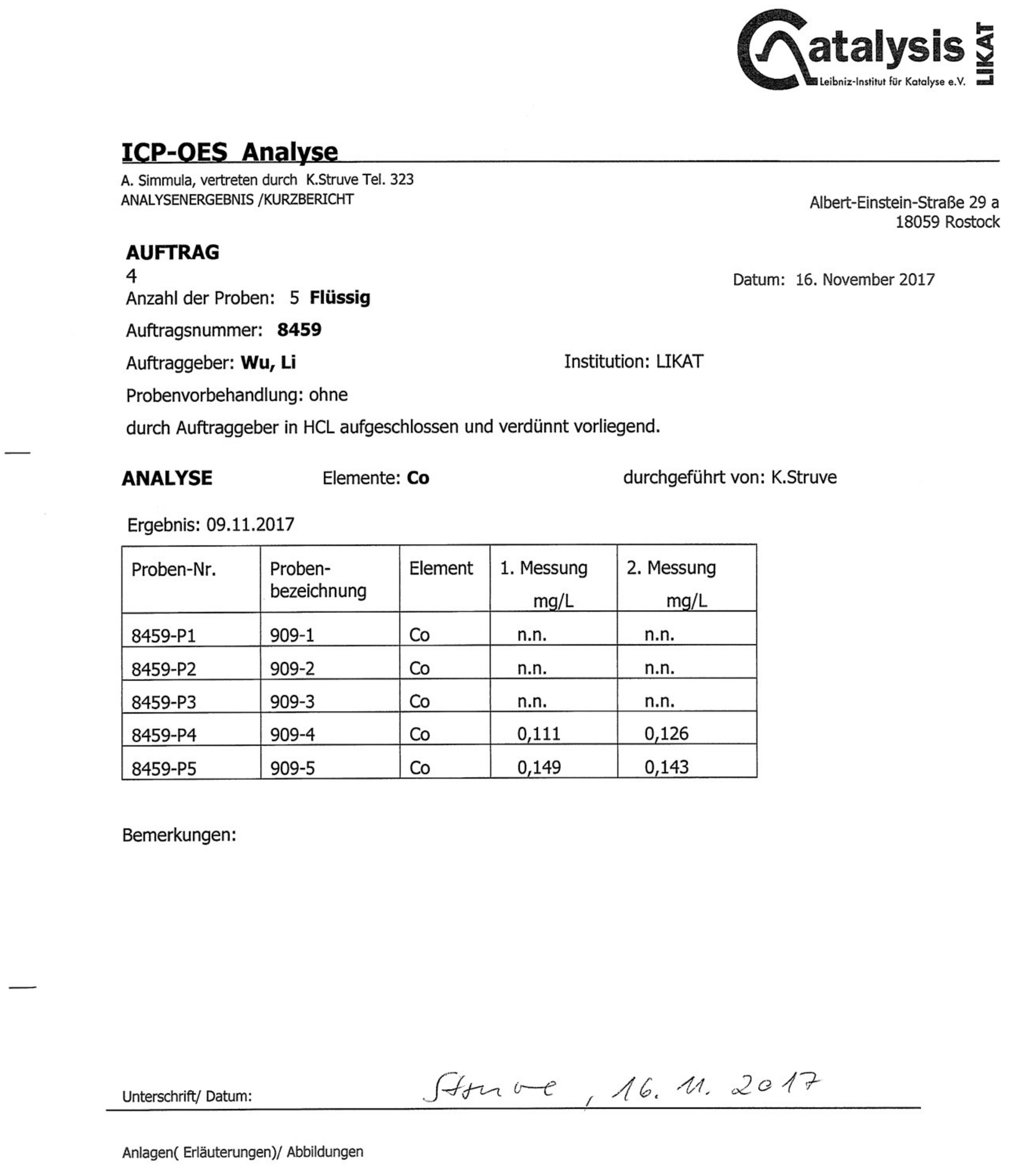
4. General Procedure for the Hydrogenation of nitroarene (GR)

In a 4 mL vial fitted with magnetic stirring bar and septum cap, cobalt catalyst (30 mg) was added. Then, a needle was inserted in the septum which allows gaseous reagents to enter. Solvent (2-methyltetrahydrofuran (MTHF)/H_2O 1.5 mL/0.5 mL) and nitroarene (0.5 mmol) were added, independently. The vials (up to eight) were placed into a 300 mL steel Parr autoclave. The autoclave was flushed with hydrogen 10 times at 20 bar and finally pressurized to the desired value (20 bar). Then it was placed into an aluminium block and heat to the desired temperature (40 ^{o}C) from room temperature. At the end of the reaction, the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, and dodecane (89 mg, 0.52 mmol) was added to the crude reaction mixture as internal standard, then diluted with aceton. The reaction mixture was centrifuged and the liquid was analysed at the GC-FID.

5. Procedure for Catalyst Recycling

In a 4 mL vial fitted with magnetic stirring bar and septum cap, cobalt catalyst (30 mg) was added. Then, a needle was inserted in the septum which allows gaseous reagents to enter. Solvent (MTHF/H_2O 1.5 mL/0.5 mL) and nitroarene (0.5 mmol) were added, independently. The vials (up to eight) were placed into a 300 mL steel Parr autoclave. The autoclave was flushed with hydrogen 10 times at 20 bar and finally pressurized to the desired value (20 bar). Then it was placed into an aluminium block and heat to the desired temperature (40 ^oC) from room temperature. At the end of the reaction, the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, and dodecane (89 mg) was added to the crude reaction mixture as internal standard, and then diluted with aceton. The reaction mixture was centrifuged and the liquid was analysed at the GC-FID. The catalyst was isolated by centrifugation and reused for next reaction.

6. ICP-OES analysis



atalysis LIKAT
Leibniz-Institut für Katalyse e.V.

ICP-OES Analyse

A. Simmula, vertreten durch K.Struve Tel. 323
ANALYSENERGEBNIS /KURZBERICHT

Albert-Einstein-Straße 29 a
18059 Rostock

AUFTRAG
4

Datum: 16. November 2017

Anzahl der Proben: 5 **Flüssig**

Auftragsnummer: **8459**

Auftraggeber: **Wu, Li** Institution: LIKAT

Probenvorbehandlung: ohne

durch Auftraggeber in HCL aufgeschlossen und verdünnt vorliegend.

ANALYSE Elemente: **Co** durchgeführt von: K.Struve

Ergebnis: 09.11.2017

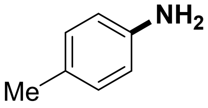
Proben-Nr.	Proben-bezeichnung	Element	1. Messung mg/L	2. Messung mg/L
8459-P1	909-1	Co	n.n.	n.n.
8459-P2	909-2	Co	n.n.	n.n.
8459-P3	909-3	Co	n.n.	n.n.
8459-P4	909-4	Co	0,111	0,126
8459-P5	909-5	Co	0,149	0,143

Bemerkungen:

Unterschrift/ Datum: Struve, 16. 11. 2017

Anlagen(Erläuterungen)/ Abbildungen

7. Characterization Data for the Products

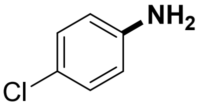


2b 92%

According to **GP**, catalyst (31 mg), 1-methyl-4-nitrobenzene **1b** (68 mg, 0.50 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2b** (49 mg, 0.46 mmol, 92%) was obtained as a solid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.08–6.89 (m, 2H), 6.69–6.54 (m, 2H), 3.32 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.78, 129.87, 128.02, 115.47, 20.58.

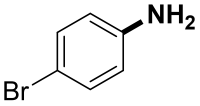


2c 98%

According to **GP**, catalyst (31 mg), 1-chloro-4-nitrobenzene **1c** (79 mg, 0.50 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2c** (63 mg, 0.49 mmol, 98%) was obtained as a solid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.15–7.04 (m, 2H), 6.65–6.53 (m, 2H), 3.55 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.46, 129.62, 123.66, 116.77.

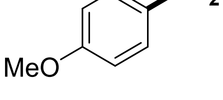


2d 98%

According to **GP**, catalyst (31 mg), 1-bromo-4-nitrobenzene **1d** (100 mg, 0.50 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2d** (83 mg, 0.49 mmol, 98%) was obtained as a solid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.41–7.10 (m, 2H), 6.77– 6.43 (m, 2H), 3.59 (s, 2H).

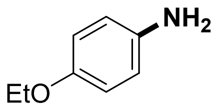
^{13}C NMR (75 MHz, $CDCl_3$) δ 145.52, 132.08, 116.81, 110.24.



2e 99%

According to **GP**, catalyst (30 mg), 1-methoxy-4-nitrobenzene **1e** (80 mg, 0.52 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2e** (65 mg, 0.52 mmol, 99%) was obtained as a liquid.

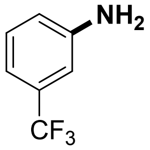
^1H NMR (300 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.9 Hz, 2H), 6.64 (d, *J* = 8.9 Hz, 2H), 3.74 (s, 3H), 3.39 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 152.88, 140.04, 116.50, 114.90, 55.81.



2f 99%

According to **GP**, catalyst (30 mg), 1-ethoxy-4-nitrobenzene **1f** (86 mg, 0.51 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2f** (70 mg, 0.51 mmol, 99%) was obtained as a solid.

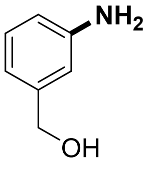
^1H NMR (300 MHz, $CDCl_3$) δ 6.84–6.69 (m, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 3.95 (q, *J* = 7.0 Hz, 2H), 3.34 (s, 2H), 1.37 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 152.16, 139.99, 116.50, 115.75, 64.12, 15.06.



2g 94%

According to **GP**, catalyst (31 mg), 1-nitro-3-(trifluoromethyl)benzene **1g** (95 mg, 0.50 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2g** (75 mg, 0.47 mmol, 94%) was obtained as a solid.

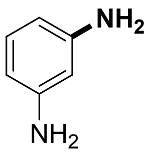
^1H NMR (300 MHz, $CDCl_3$) δ 7.18–7.09 (m, 1H), 6.88 (ddq, *J* = 7.7, 1.6, 0.8 Hz, 1H), 6.78 (ddt, *J* = 2.3, 1.5, 0.7 Hz, 1H), 6.70 (ddq, *J* = 8.0, 2.3, 0.7 Hz, 1H), 3.69 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 146.85, 131.74 (d, *J* = 31.9 Hz), 129.86, 126.14, 122.53, 119.00–116.34(m), 115.12 (q, *J* = 4.0 Hz), 111.43 (q, *J* = 3.9 Hz).



2h 98%

According to **GP**, catalyst (29 mg), (3-nitrophenyl)methanol **1h** (77 mg, 0.50 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2h** (60 mg, 0.49 mmol, 98%) was obtained as a solid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.20–7.05 (m, 1H), 6.76–6.68 (m, 2H), 6.61 (dddt, *J* = 7.9, 2.4, 1.0, 0.4 Hz, 1H), 4.59 (q, *J* = 0.6 Hz, 2H), 2.83 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 146.76, 142.37, 129.65, 117.24, 114.53, 113.71, 65.49.

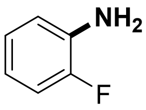


2i 96%

According to **GP**, catalyst (31 mg), 3-nitroaniline **1i** (71 mg, 0.51 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2i** (53 mg, 0.49 mmol, 96%) was obtained as a liquid.

^1H NMR (300 MHz, $CDCl_3$) δ 6.92–6.76 (m, 1H), 6.02 (dd, *J* = 7.9, 2.2 Hz, 2H), 5.91 (td, *J* = 2.2, 0.4 Hz, 1H), 3.42 (s, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.59, 130.20, 105.99, 102.03.

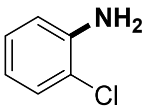


2j 90%

According to **GP**, catalyst (32 mg), 1-fluoro-2-nitrobenzene **1j** (72 mg, 0.51 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2j** (51 mg, 0.46 mmol, 90%) was obtained as a liquid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.06 – 6.89 (m, 2H), 6.87–6.61 (m, 2H), 3.67 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.41, 150.25, 134.59 (d, *J* = 12.6 Hz), 124.54 (d, *J* = 3.6 Hz), 118.73 (d, *J* = 6.8 Hz), 117.04 (d, *J* = 3.5 Hz), 115.44, 115.20.

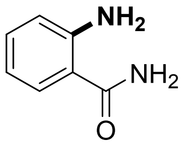


2k 99%

According to **GP**, catalyst (30 mg), 1-chloro-2-nitrobenzene **1k** (82 mg, 0.52 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2k** (66 mg, 0.52 mmol, 99%) was obtained as a liquid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.16 (ddd, *J* = 8.0, 1.5, 0.3 Hz, 1H), 7.02–6.94 (m, 1H), 6.69 (ddd, *J* = 8.0, 1.5, 0.3 Hz, 1H), 6.61 (ddd, *J* = 8.0, 7.3, 1.5 Hz, 1H), 3.58 (t, *J* = 6.1 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 129.55, 127.75, 119.17, 116.01.

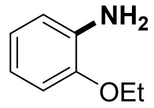


2l 99%

According to **GP**, catalyst (30 mg), 2-nitrobenzamide **1l** (82 mg, 0.49 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2l** (67 mg, 0.49 mmol, 99%) was obtained as a solid.

^1H NMR (400 MHz, DMSO-d_6) δ 7.73 (s, 1H), 7.53 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.20–7.10 (m, 1H), 7.07 (s, 1H), 6.68 (d, *J* = 8.3 Hz, 1H), 6.56 (s, 2H), 6.48 (t, *J* = 7.5 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 171.76, 150.64, 132.35, 129.21, 116.86, 114.83, 114.12.

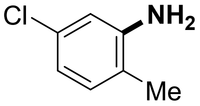


2m 90%

According to **GP**, catalyst (30 mg), 1-ethoxy-2-nitrobenzene **1m** (81 mg, 0.49 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2m** (60 mg, 0.44 mmol, 90%) was obtained as a liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83–6.70 (m, 3H), 4.07 (q, J = 7.0 Hz, 2H), 3.70 (s, 2H), 1.44 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.81, 136.12, 121.05, 118.70, 115.30, 111.57, 63.84, 15.10.

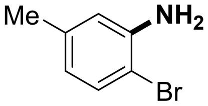


2n >99%

According to **GP**, catalyst (29 mg), 4-chloro-1-methyl-2-nitrobenzene **1n** (85 mg, 0.50 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2n** (70 mg, 0.50 mmol, >99%) was obtained as a liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99–6.88 (m, 1H), 6.67 (d, J = 7.3 Hz, 2H), 3.60 (s, 2H), 2.12 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.69, 132.17, 131.42, 120.72, 118.40, 114.63, 16.91.

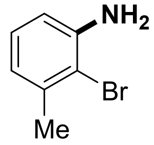


2o >99%

According to **GP**, catalyst (30 mg), 1-bromo-4-methyl-2-nitrobenzene **1o** (105 mg, 0.49 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2o** (90 mg, 0.49 mmol, >99%) was obtained as a liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, J = 8.1 Hz, 1H), 6.68–6.58 (m, 1H), 6.54–6.42 (m, 1H), 3.98 (s, 2H), 2.26 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 143.72, 138.48, 132.30, 120.68, 116.64, 106.30, 21.12.

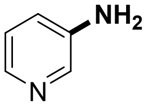


2p 98%

According to **GP**, catalyst (31 mg), 2-bromo-1-methyl-3-nitrobenzene **1p** (106 mg, 0.50 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2p** (90 mg, 0.49 mmol, 99%) was obtained as a solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (t, J = 7.7 Hz, 1H), 6.64 (tdd, J = 7.7, 1.5, 0.8 Hz, 2H), 4.07 (s, 2H), 2.39 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.23, 138.83, 127.53, 120.47, 113.31, 112.34, 23.65.

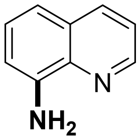


2q 98%

According to **GP**, catalyst (29 mg), 3-nitropyridine **1q** (62 mg, 0.50 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2q** (45 mg, 0.48 mmol, 98%) was obtained as a liquid.

^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (dd, J = 2.8, 0.8 Hz, 1H), 7.96 (dd, J = 4.7, 1.5 Hz, 1H), 7.03 (ddd, J = 8.2, 4.6, 0.8 Hz, 1H), 6.93 (ddd, J = 8.2, 2.8, 1.5 Hz, 1H), 3.61 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 142.76, 139.78, 137.38, 123.82, 121.56.

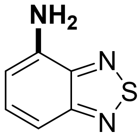


2r 98%

According to **GP**, catalyst (31 mg), 8-nitroquinoline **1r** (87 mg, 0.50 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2r** (71 mg, 0.49 mmol, 98%) was obtained as a solid.

^1H NMR (300 MHz, $CDCl_3$) δ 8.76 (dd, J = 4.2, 1.7 Hz, 1H), 8.06 (ddd, J = 8.3, 1.7, 0.4 Hz, 1H), 7.42–7.28 (m, 2H), 7.15 (dd, J = 8.2, 1.3 Hz, 1H), 6.93 (dd, J = 7.5, 1.3 Hz, 1H), 4.82 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 147.41, 144.01, 138.37, 136.16, 128.94, 127.49, 121.38, 116.08, 110.19.

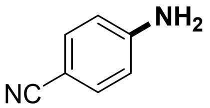


2s >99%

According to **GP**, catalyst (31 mg), 4-nitrobenzo[c][1,2,5]thiadiazole **1s** (97 mg, 0.54 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2s** (80 mg, 0.53 mmol, >99%) was obtained as a solid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.42–7.28 (m, 2H), 6.59 (ddd, J = 6.8, 1.4, 0.5 Hz, 1H), 4.69 (s, 2H).

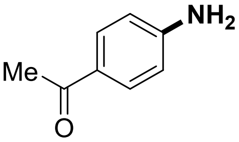
^{13}C NMR (75 MHz, $CDCl_3$) δ 155.87, 147.88, 139.01, 131.30, 110.11, 106.70.



2t >99%

According to **GP**, catalyst (31 mg), 4-nitrobenzonitrile **1t** (76 mg, 0.51 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2t** (60 mg, 0.51 mmol, >99%) was obtained as a solid.

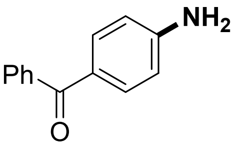
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.5 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 4.20 (s, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 150.66, 133.82, 120.33, 114.48, 99.90.



2u 94%

According to **GP**, catalyst (30 mg), 1-(4-nitrophenyl)ethan-1-one **1u** (84 mg, 0.51 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2u** (65 mg, 0.48 mmol, 94%) was obtained as a solid.

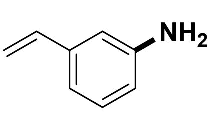
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91–7.62 (m, 2H), 6.75–6.45 (m, 2H), 4.10 (s, 2H), 2.48 (s, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 196.68, 151.43, 130.86, 127.70, 113.75, 26.12.



2v 95%

According to **GP**, catalyst (30 mg), (4-nitrophenyl)(phenyl)methanone **1v** (108 mg, 0.48 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2v** (90 mg, 0.46 mmol, 95%) was obtained as a solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60–7.48 (m, 5H), 6.63 (d, *J* = 8.3 Hz, 2H), 6.19 (s, 2H).
^{13}C NMR (101 MHz, DMSO-d_6) δ 193.88, 154.26, 139.54, 133.06, 131.47, 129.23, 128.63, 124.18, 113.02.

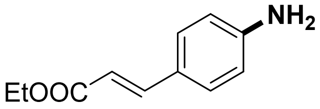


2w >99%

According to **GP**, catalyst (30 mg), 1-nitro-3-vinylbenzene **1w** (75 mg, 0.50 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2w** (60 mg, 0.50 mmol, >99%) was obtained as a liquid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (t, *J* = 7.8 Hz, 1H), 6.84 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.78–6.49 (m, 3H), 5.72 (dd, *J* = 17.6, 1.0 Hz, 1H), 5.22 (dd, *J* = 10.9, 1.0 Hz, 1H), 3.54 (s, 2H).

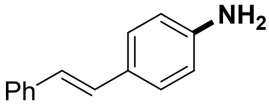
^{13}C NMR (75 MHz, $CDCl_3$) δ 146.59, 138.76, 137.10, 129.51, 117.04, 114.90, 113.71, 112.84.



2x >99%

According to **GP**, catalyst (30 mg), ethyl (E)-3-(4-nitrophenyl)acrylate **1x** (107 mg, 0.48 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2x** (92 mg, 0.48 mmol, 99%) was obtained as a liquid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 15.9 Hz, 1H), 7.40–7.16 (m, 2H), 6.75–6.55 (m, 2H), 6.25 (d, *J* = 15.9 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 167.80, 148.75, 144.97, 129.90, 124.70, 114.92, 113.67, 60.23, 14.43.



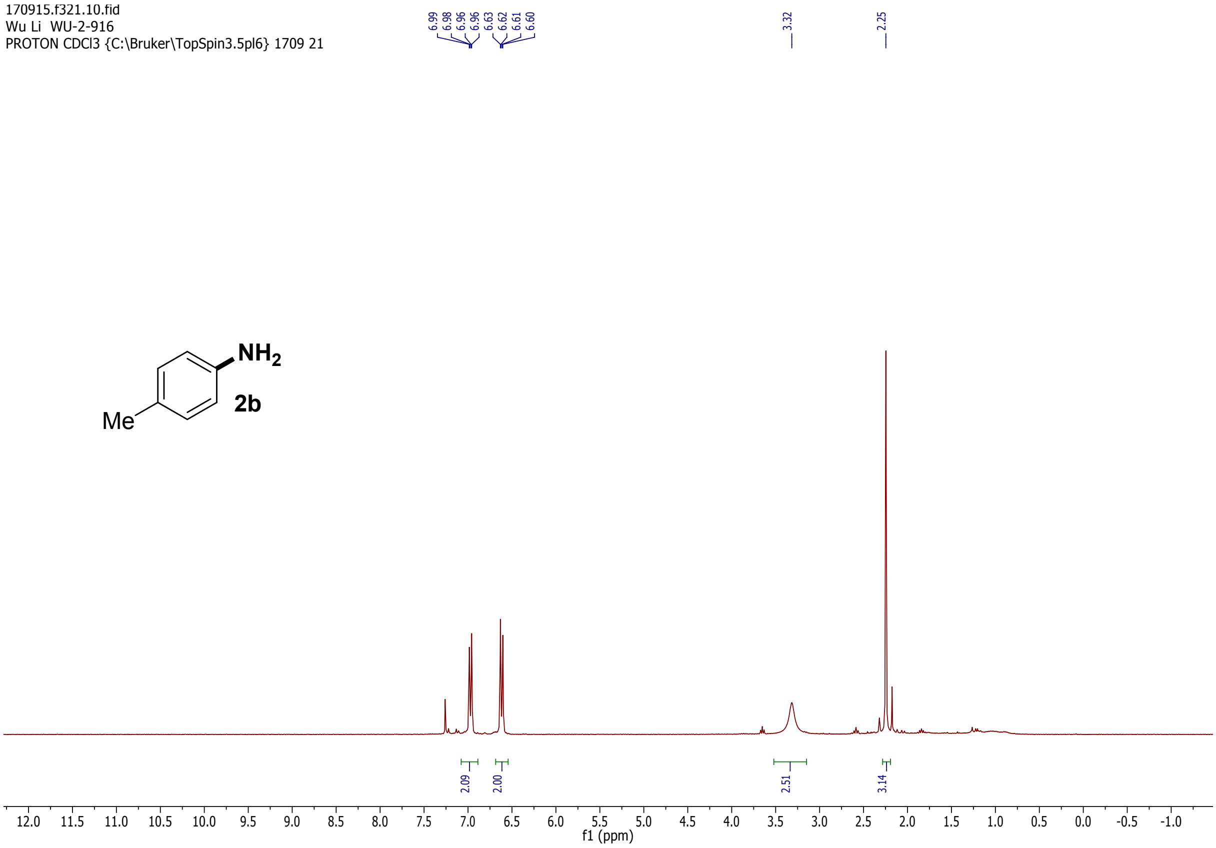
2y 98%

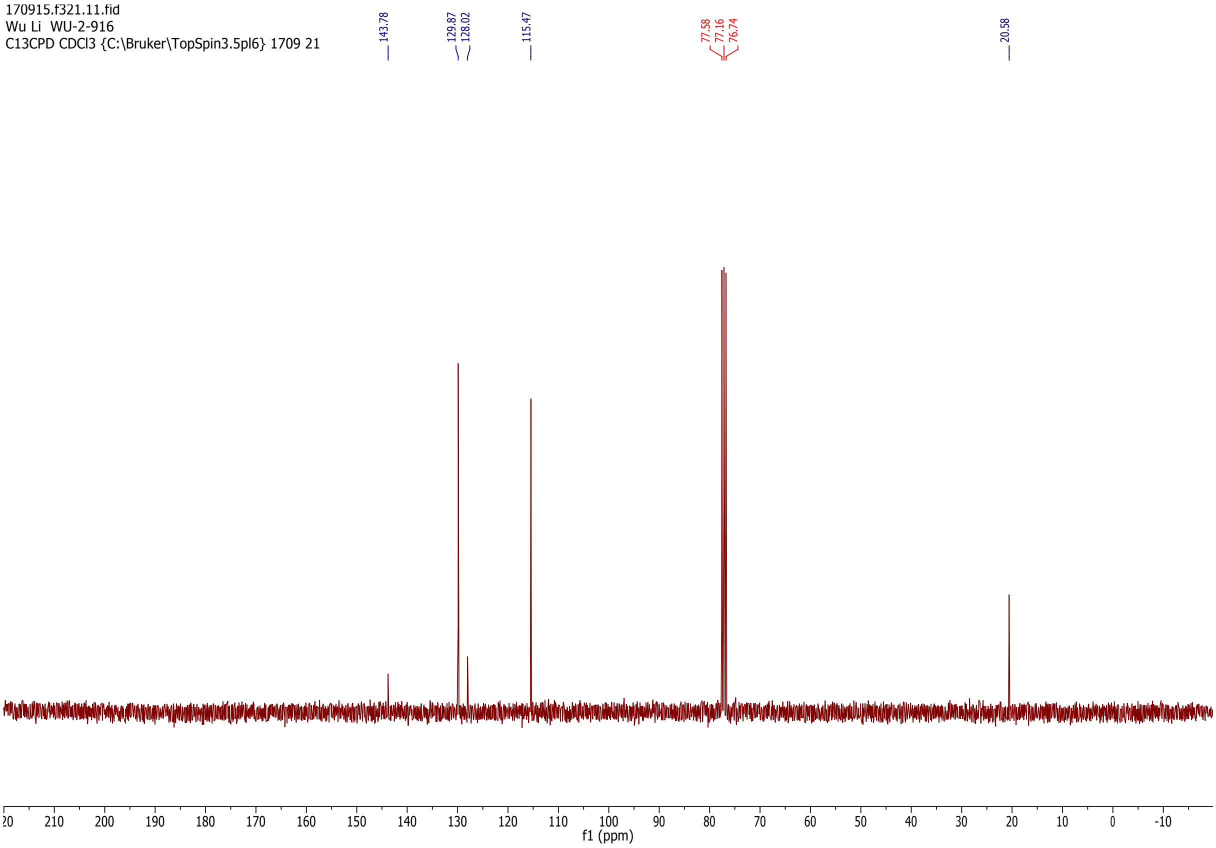
According to **GP**, catalyst (31 mg), (*E)*-1-nitro-4-styrylbenzene **1y** (108 mg, 0.48 mmol), in MTHF/H_2O (1.5 mL/0.5 mL), H_2 (20 bar), at 40 °C for 24 h. The product **2y** (93 mg, 0.47 mmol, 98%) was obtained as a liquid.

^1H NMR (300 MHz, $CDCl_3$) δ 7.58–7.50 (m, 2H), 7.41 (dddd, *J* = 8.1, 4.7, 2.1, 0.7 Hz, 4H), 7.32 – 7.24 (m, 1H), 7.11 (d, *J* = 16.3 Hz, 1H), 6.99 (d, *J* = 16.3 Hz, 1H), 6.76–6.66 (m, 2H), 3.96 – 3.50 (m, 2H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 146.26, 138.04, 128.79, 128.74, 128.05, 127.84, 126.97, 126.19, 125.16, 115.29.

9. ^{1}H NMR and ^{13}C NMR Spectra of Products

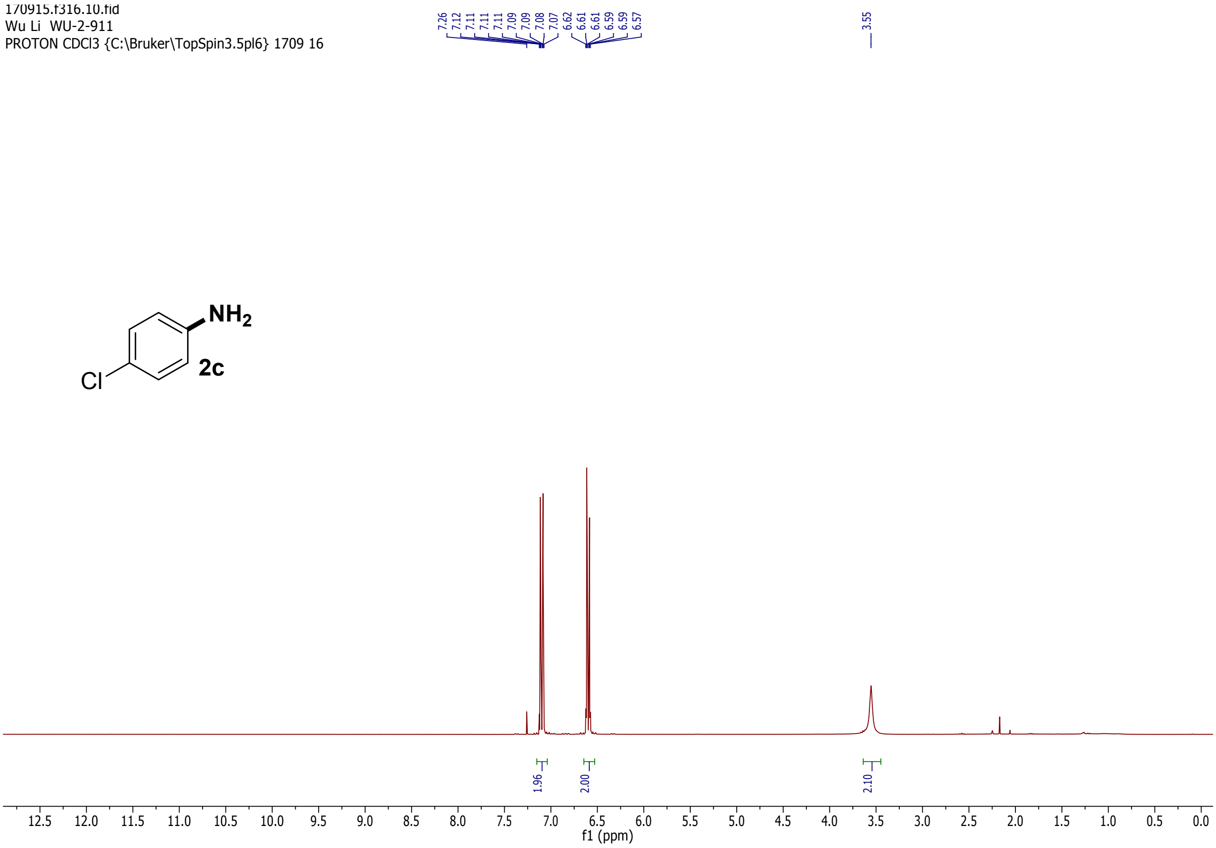
Original spectra for **2b**:



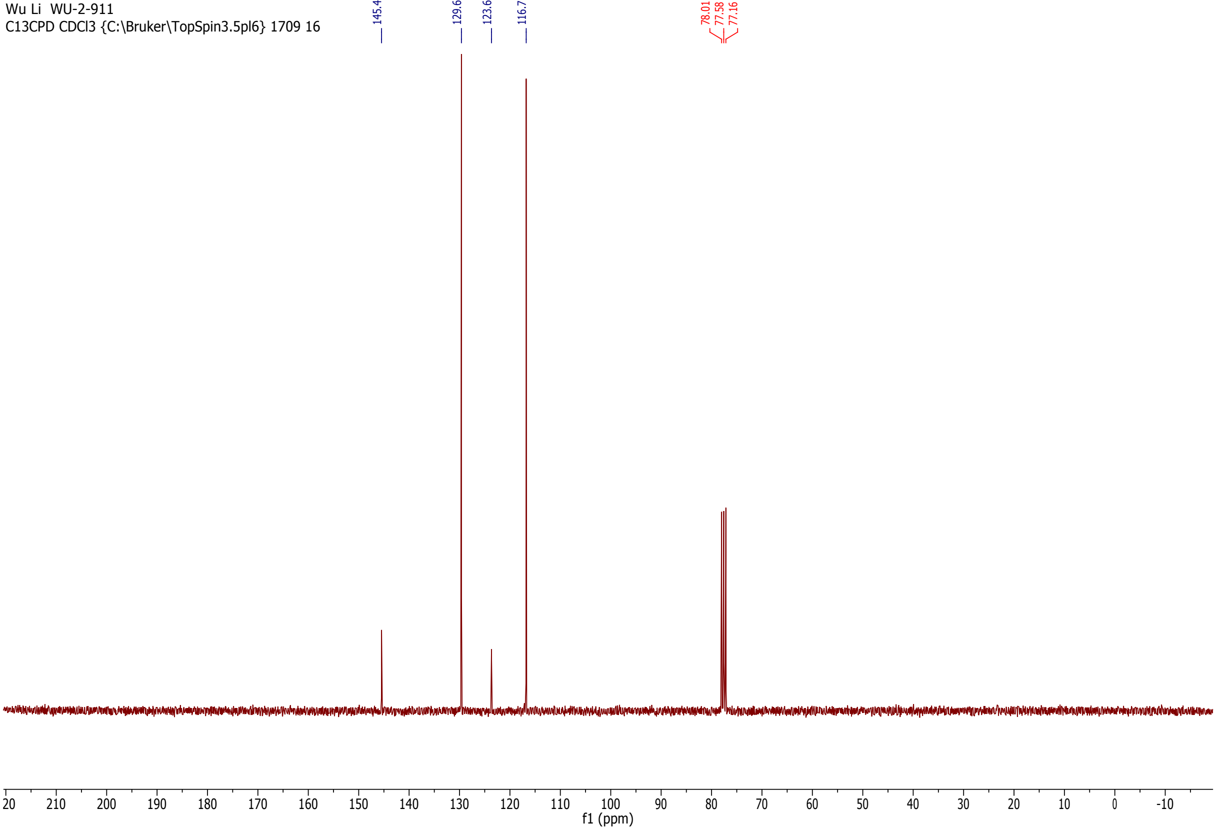


Original spectra for **2c**:

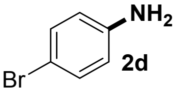
170915.f316.10.fid
Wu Li WU-2-911
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 16



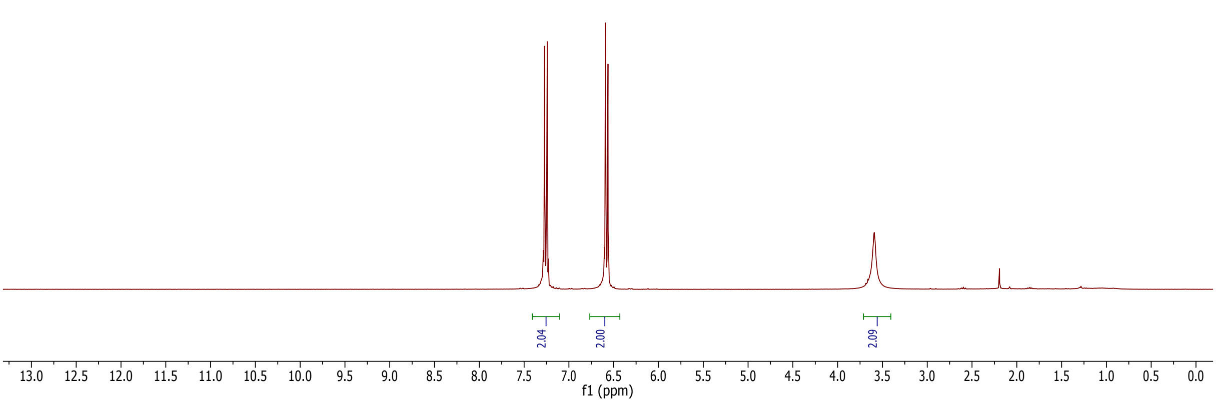
170915.f316.11.fid
Wu Li WU-2-911
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 16

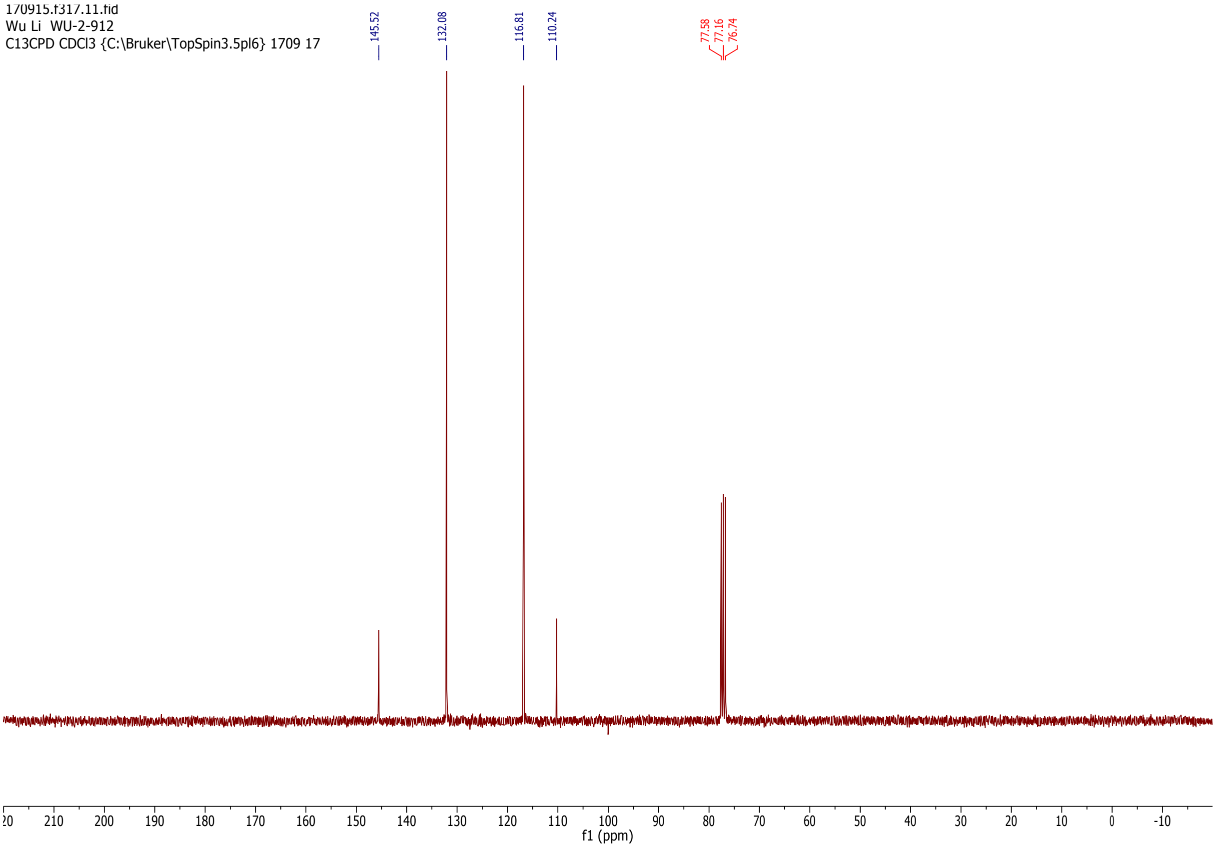


Original spectra for **2d**:



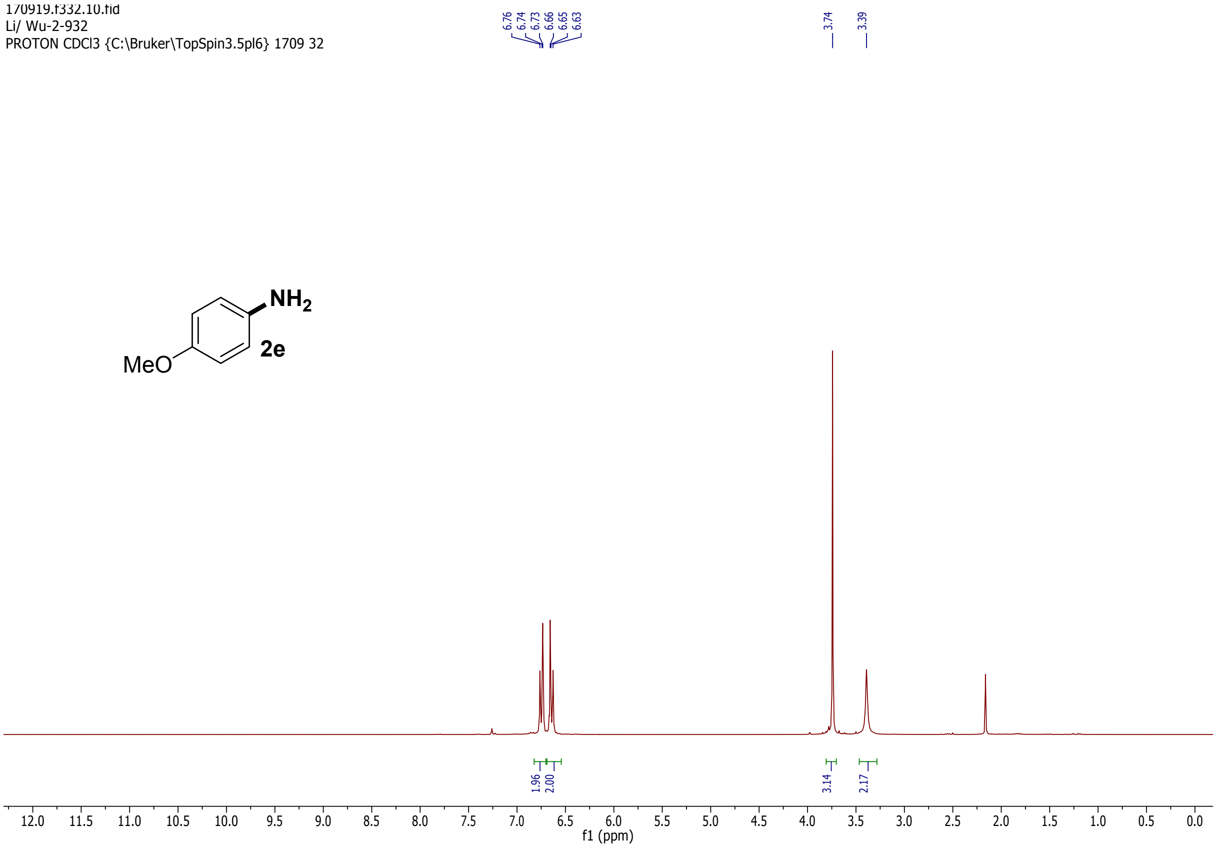
2d



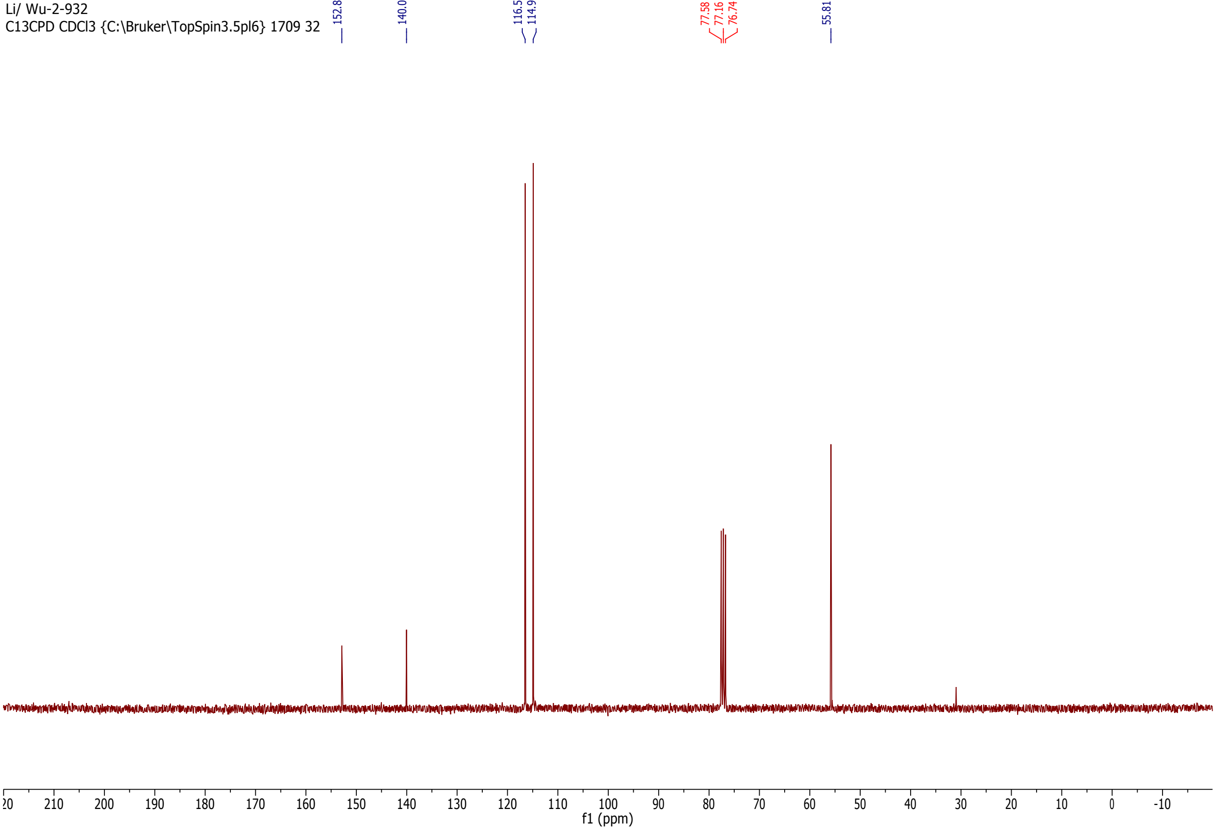


Original spectra for **2e**:

170919.f332.10.fid
Li/ Wu-2-932
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 32

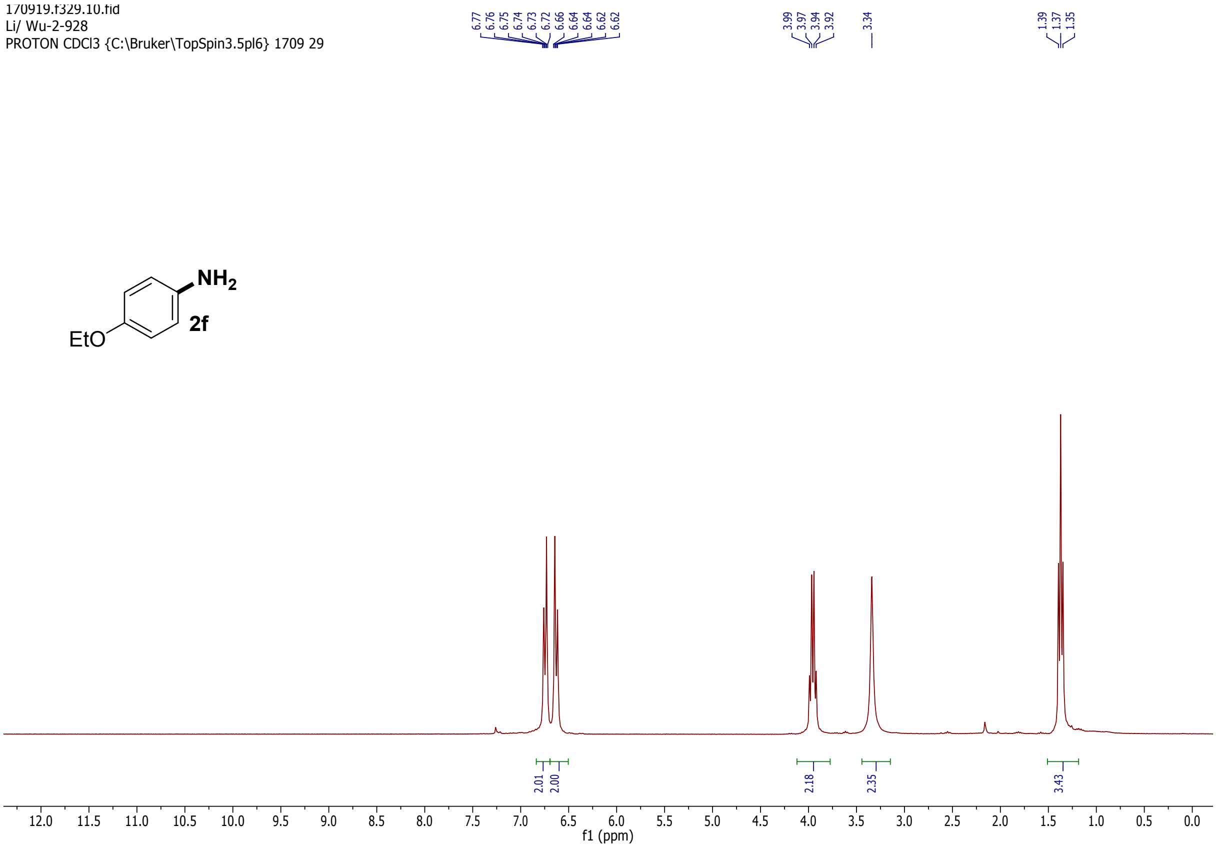


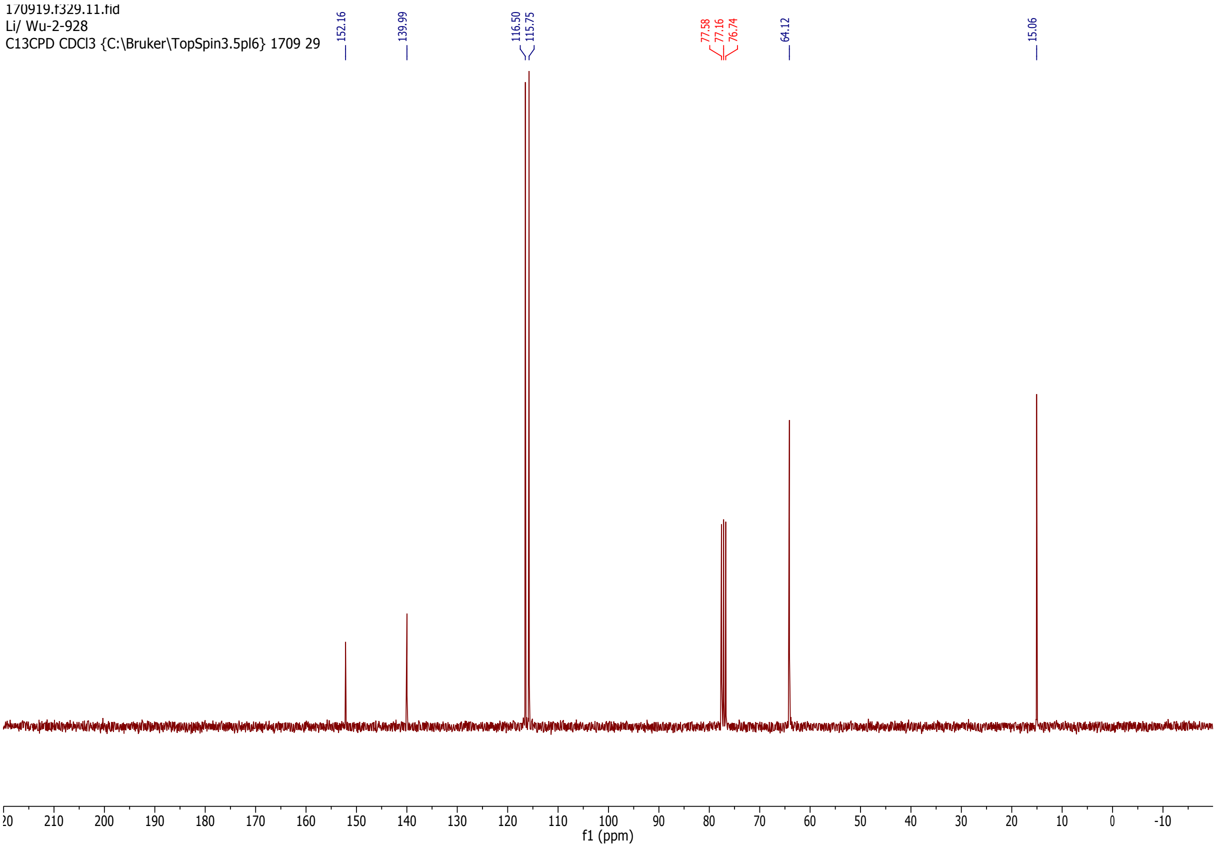
170919.f332.11.fid
Li/ Wu-2-932
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 32



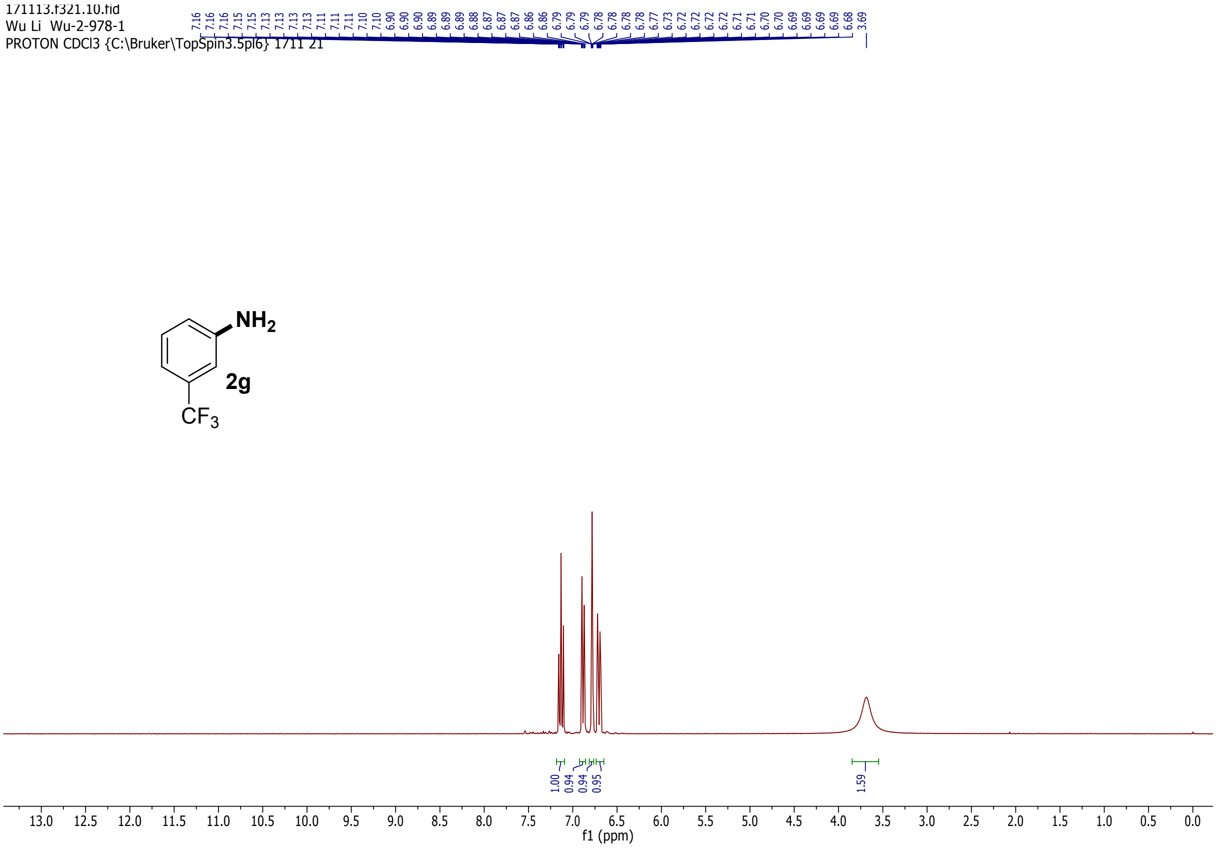
Original spectra for **2f**:

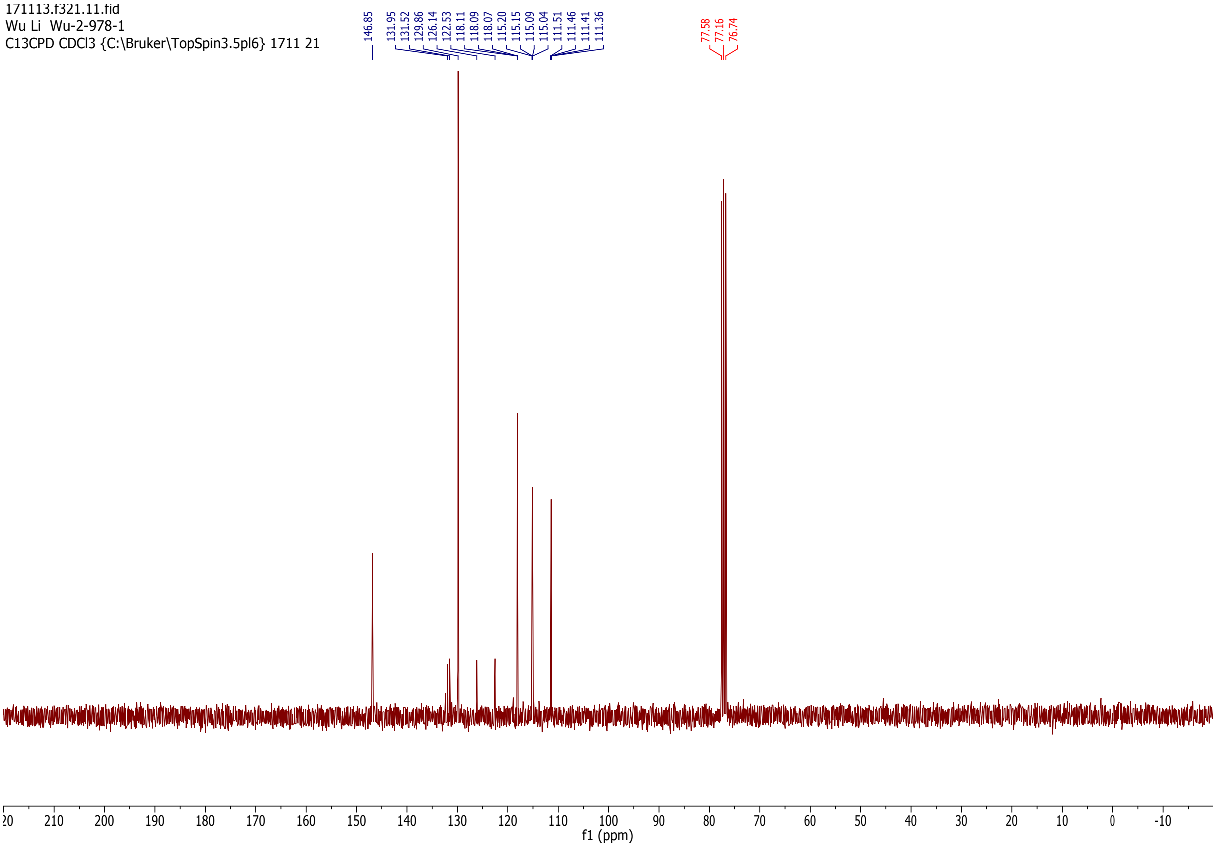
2f



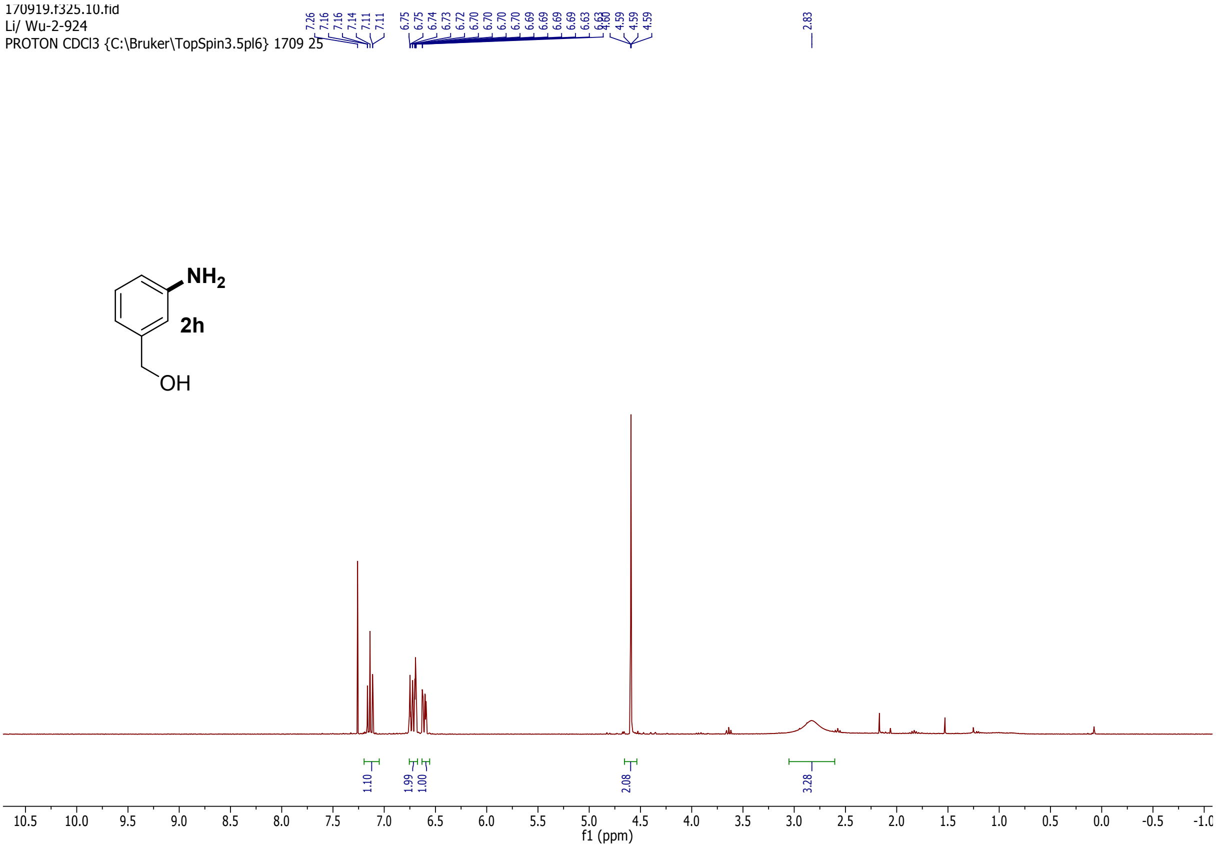


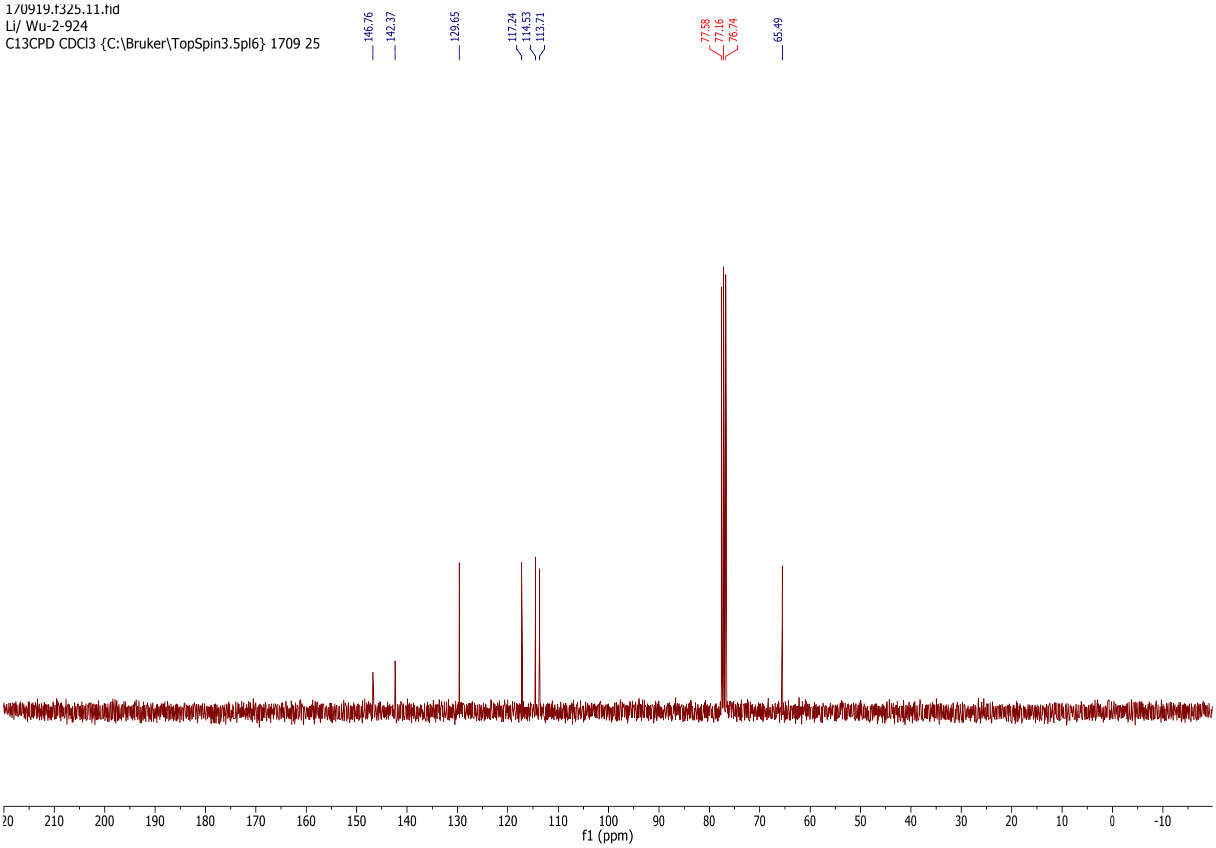
Original spectra for **2g**:





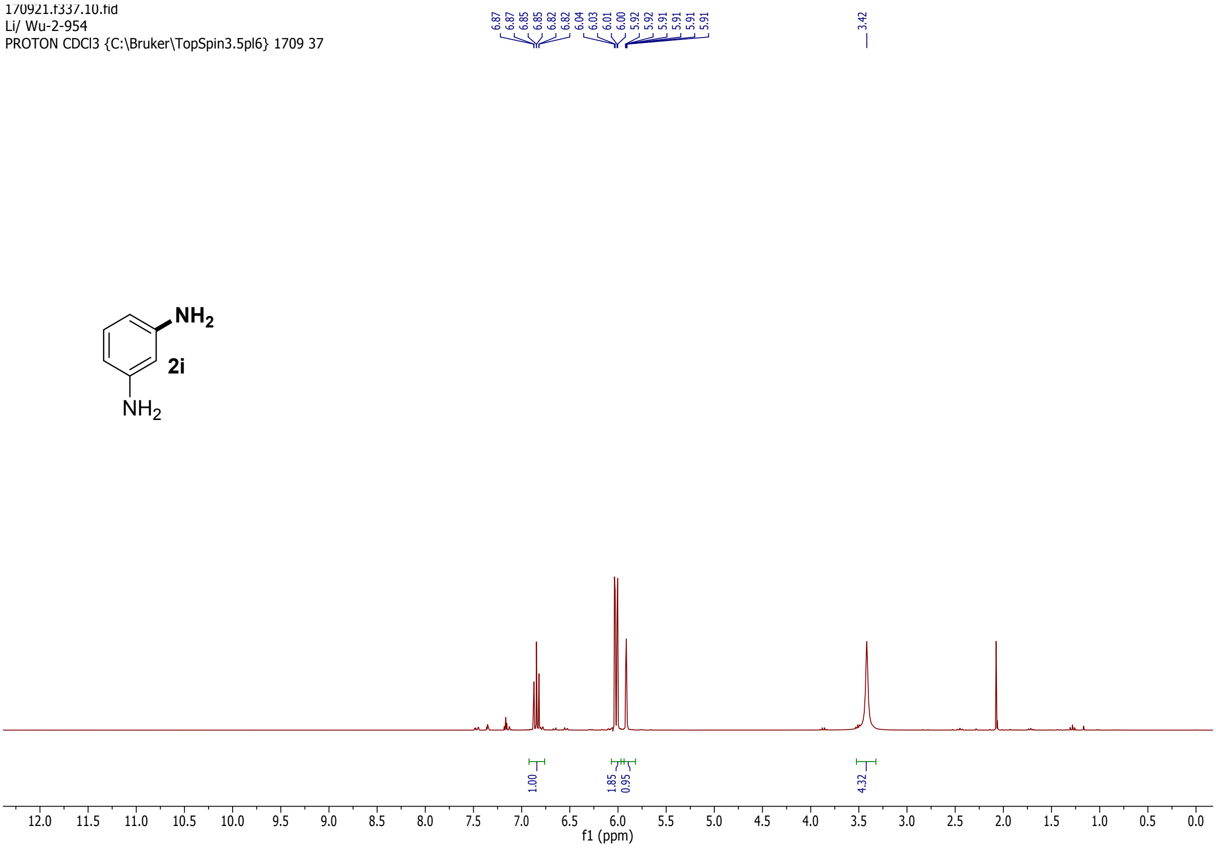
Original spectra for **2h**:



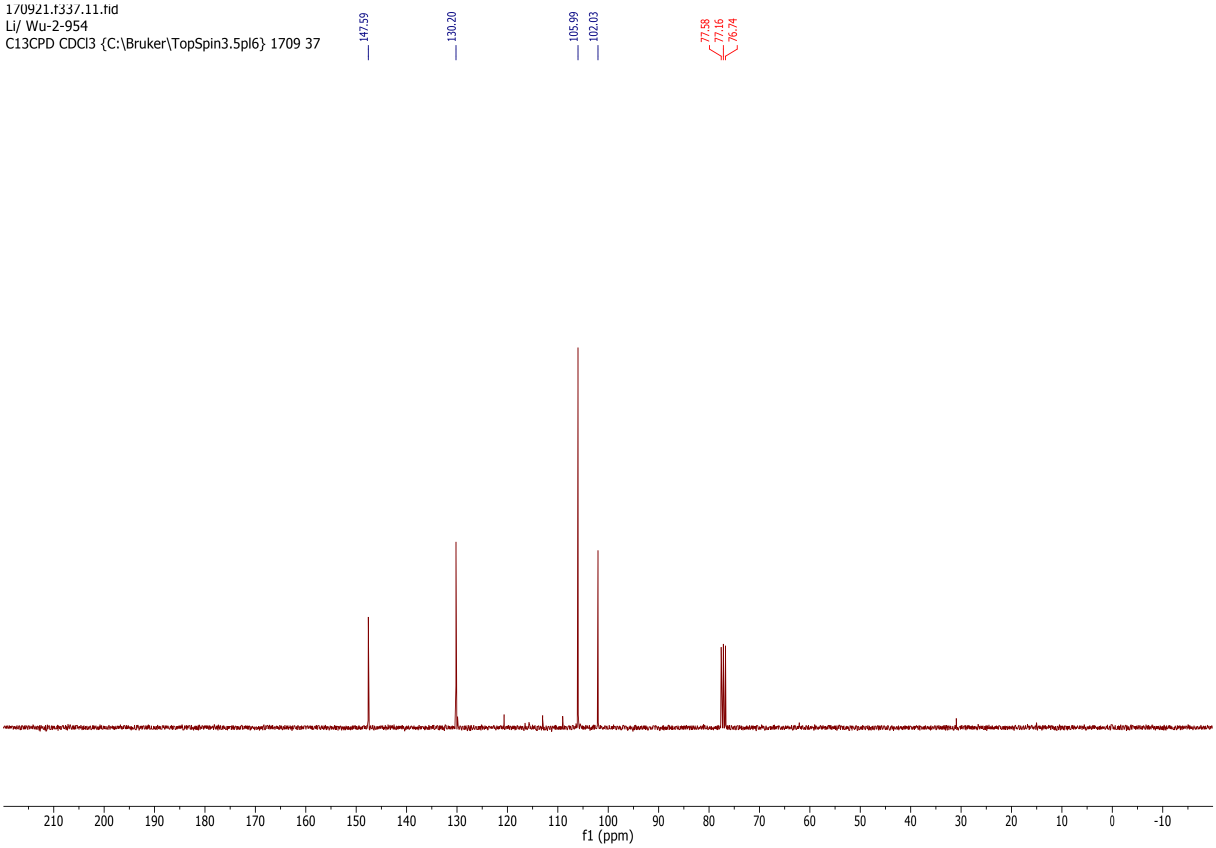


Original spectra for **2i**:

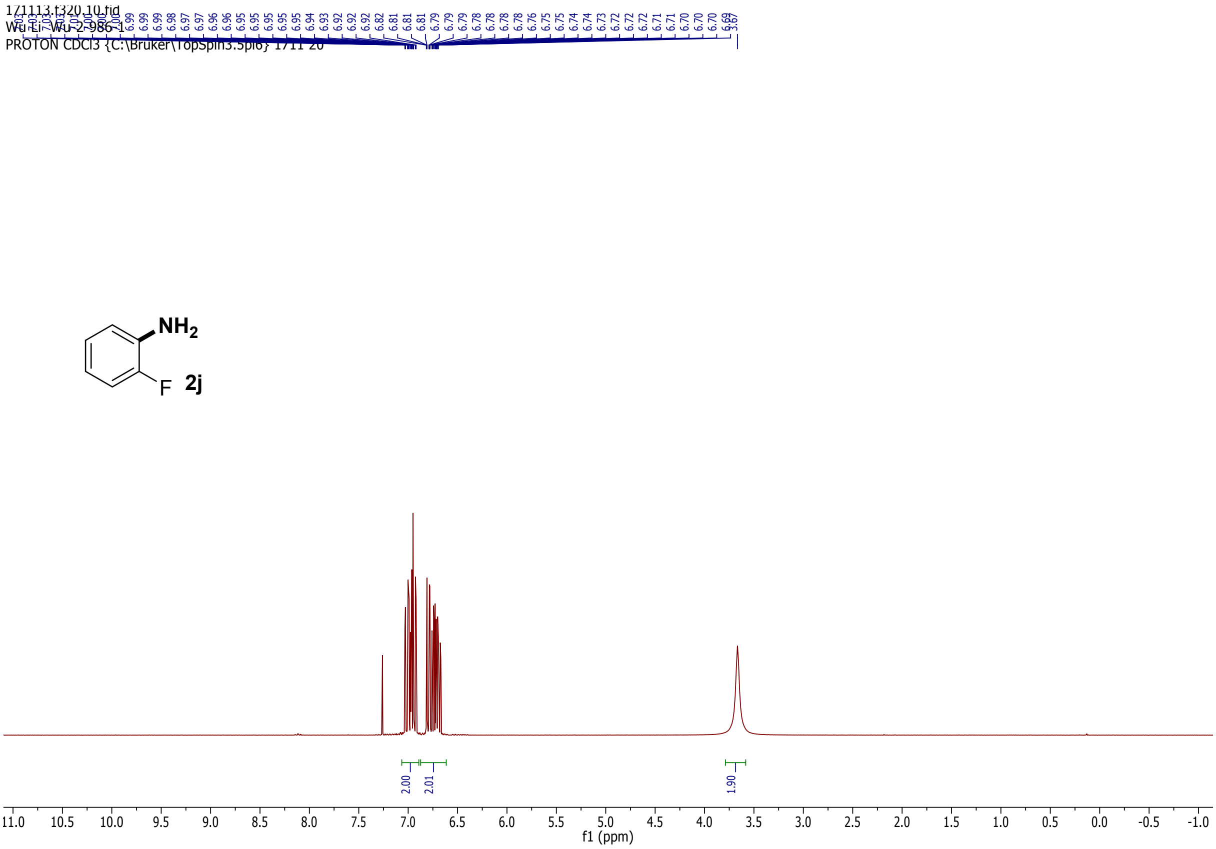
170921.f337.10.fid
Li/ Wu-2-954
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 37

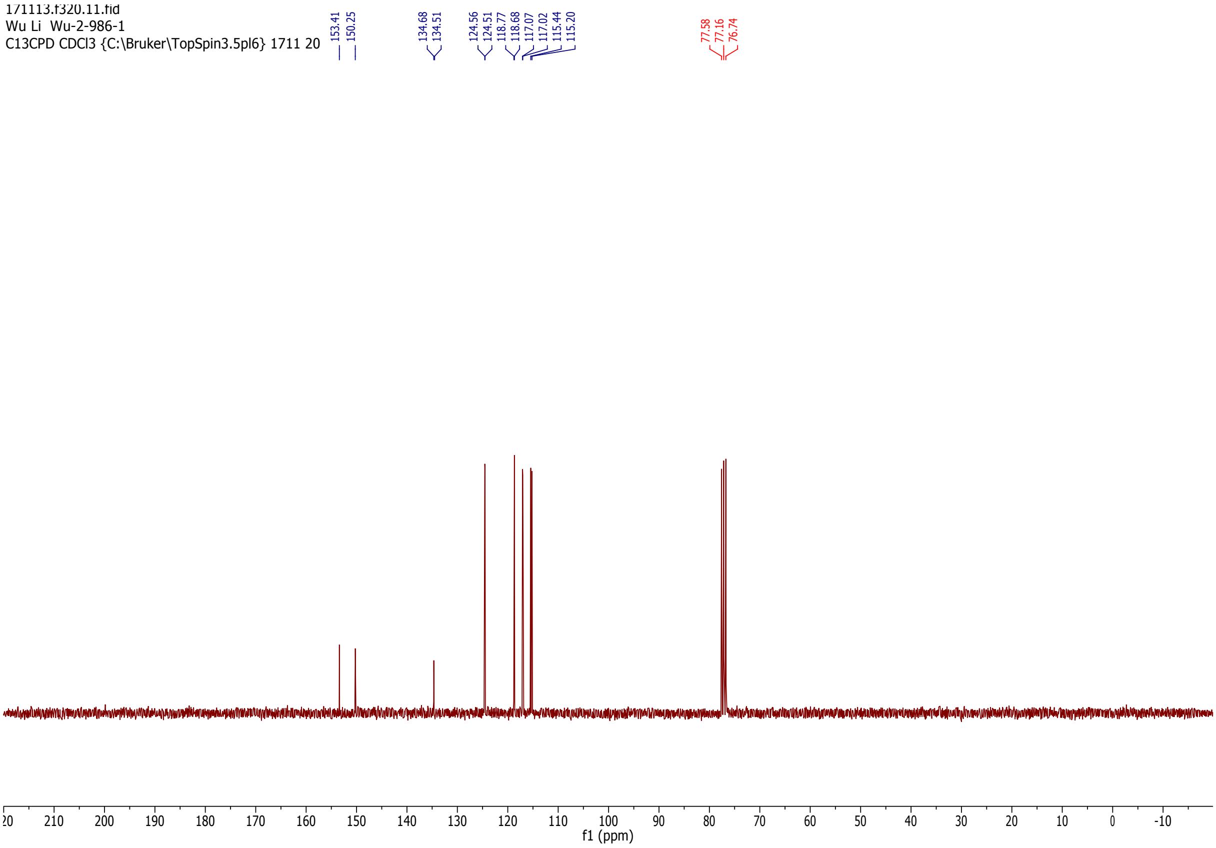


170921.f337.11.fid
Li/ Wu-2-954
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 37



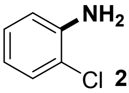
Original spectra for **2j**:



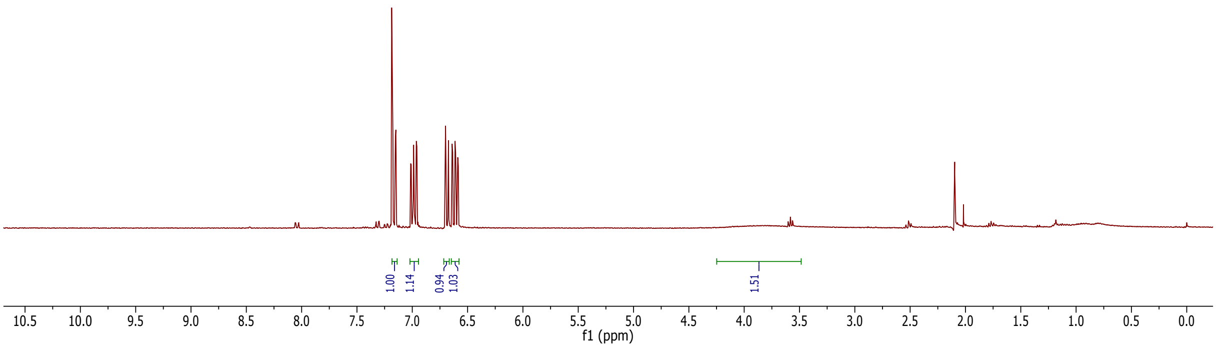


Original spectra for **2k**:

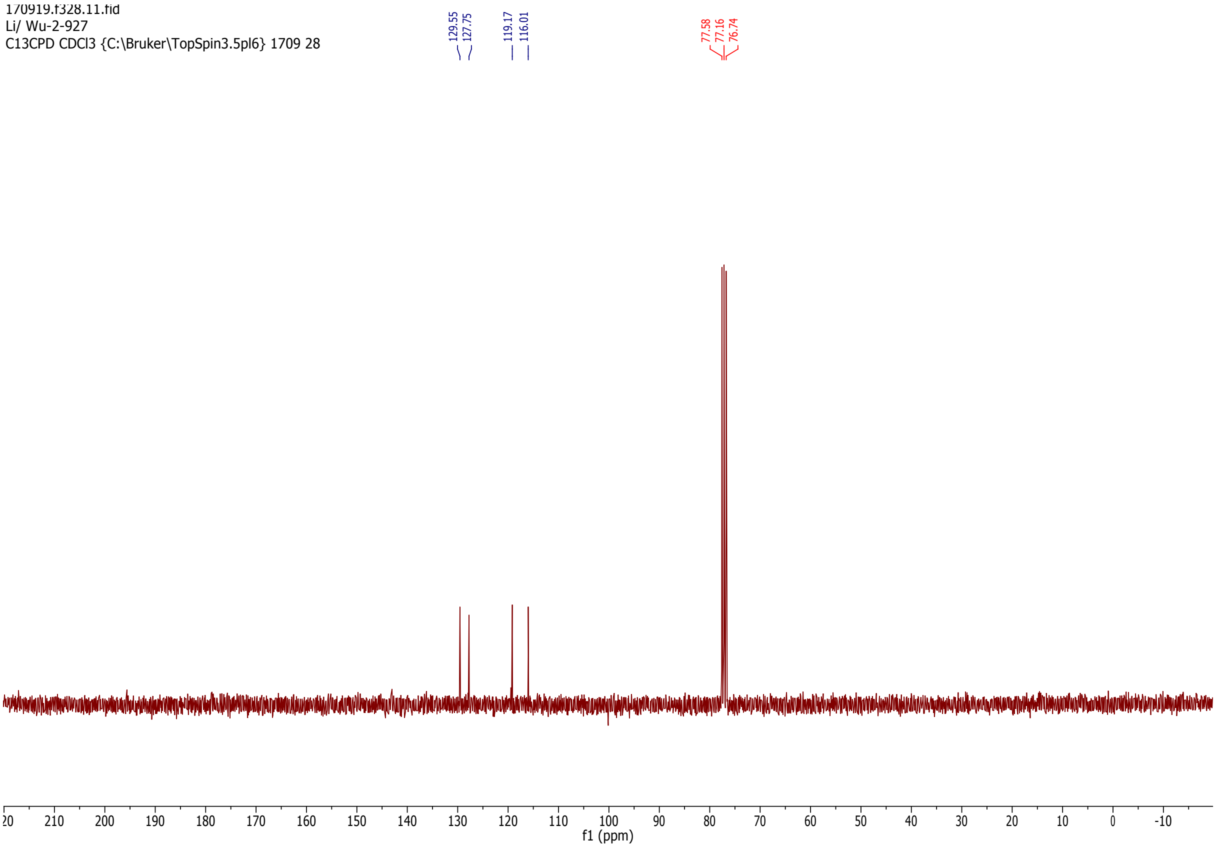
170919.f328.10.fid
Li/ Wu-2-927
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 28



2k

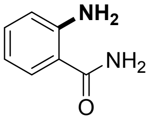


170919.f328.11.fid
Li/ Wu-2-927
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 28

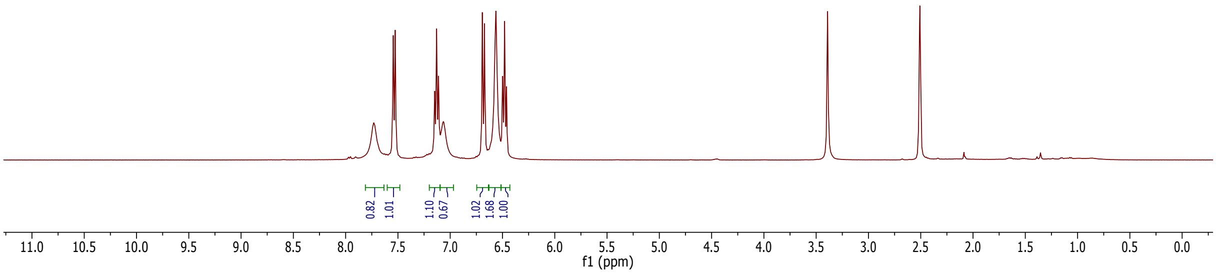


Original spectra for **2l**:

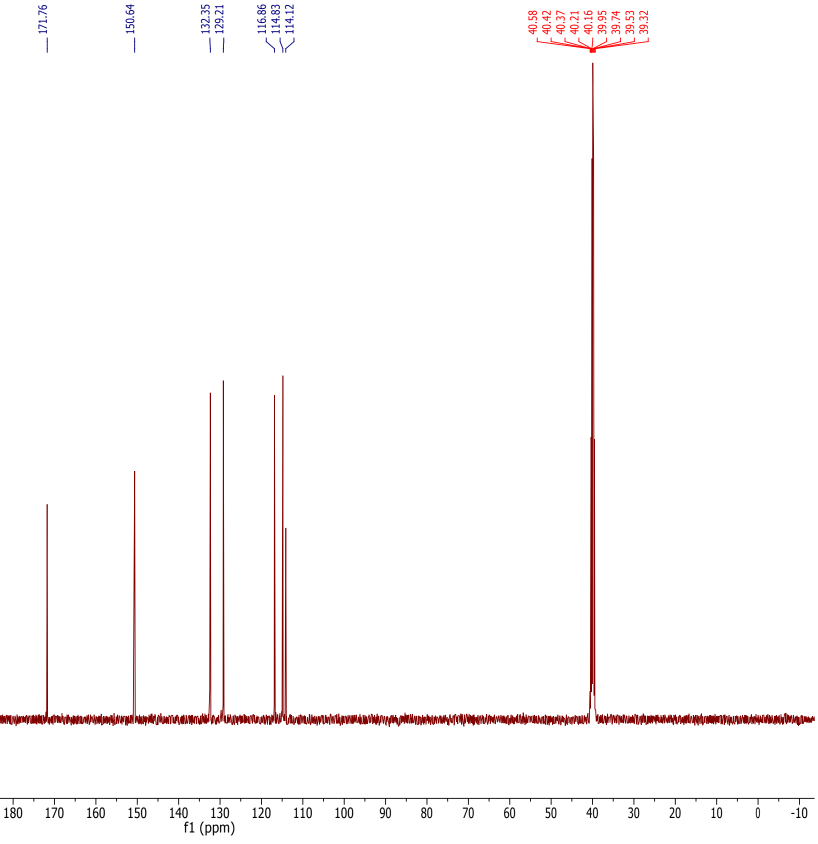
170926.410.10.fid
Wu Li WU-2-976
Au1H DMSO {C:\Bruker\TopSpin3.5pl6} 1709 10



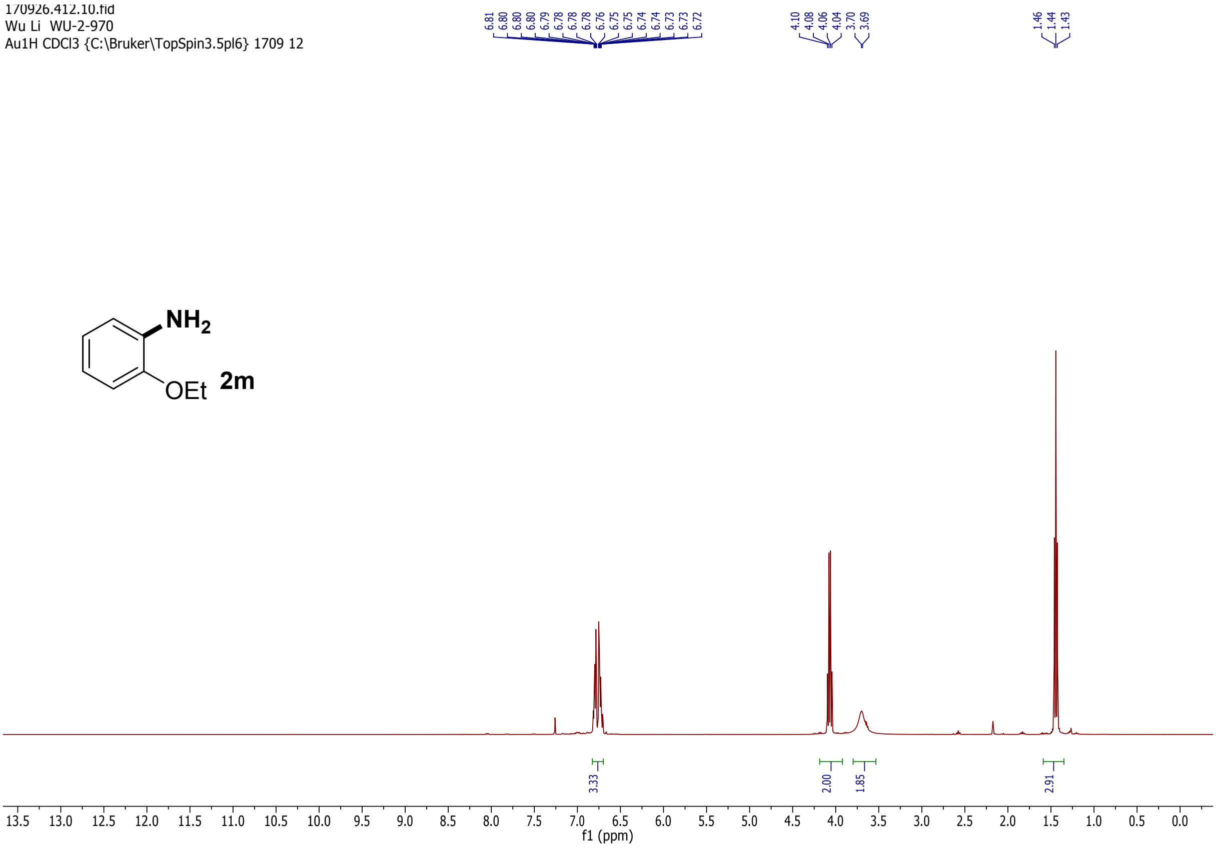
2l

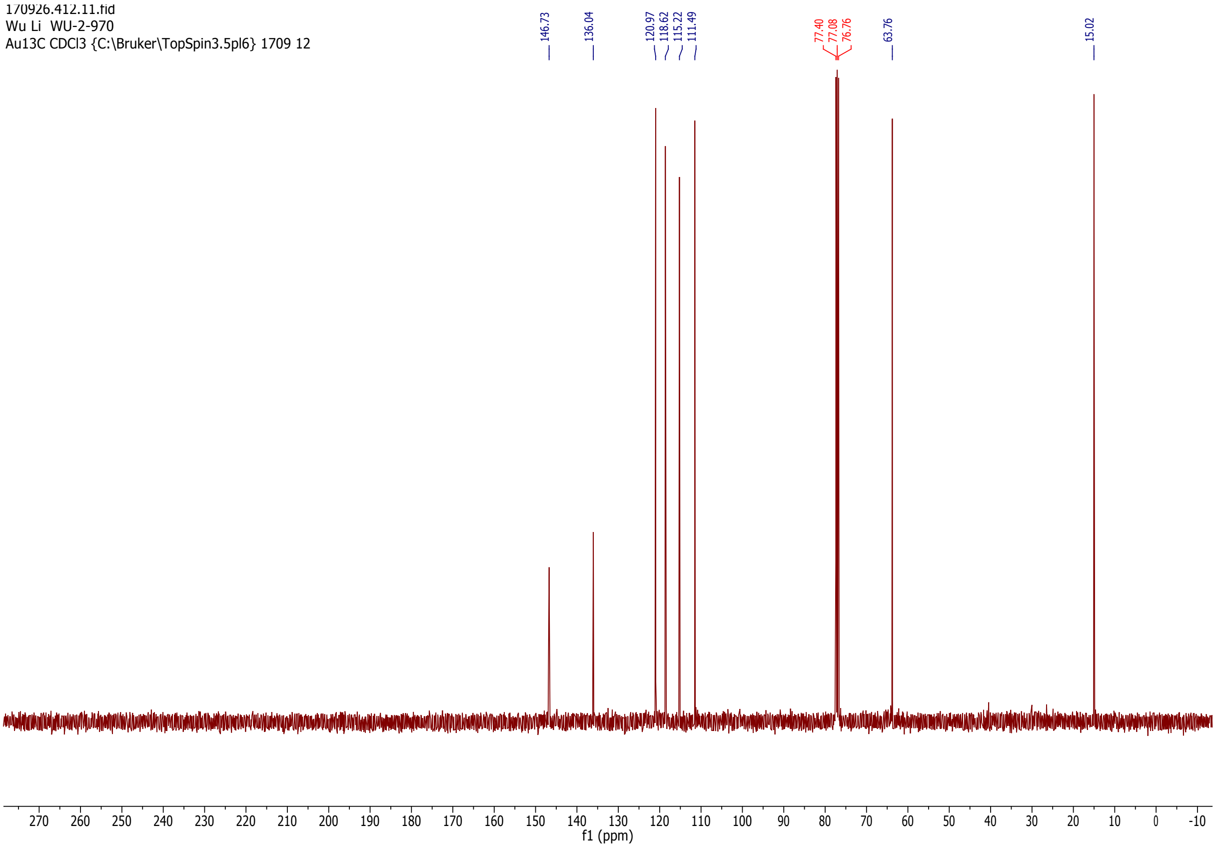


170926.410.11.fid
Wu Li WU-2-976
Au13C DMSO {C:\Bruker\TopSpin3.5pl6} 1709 10

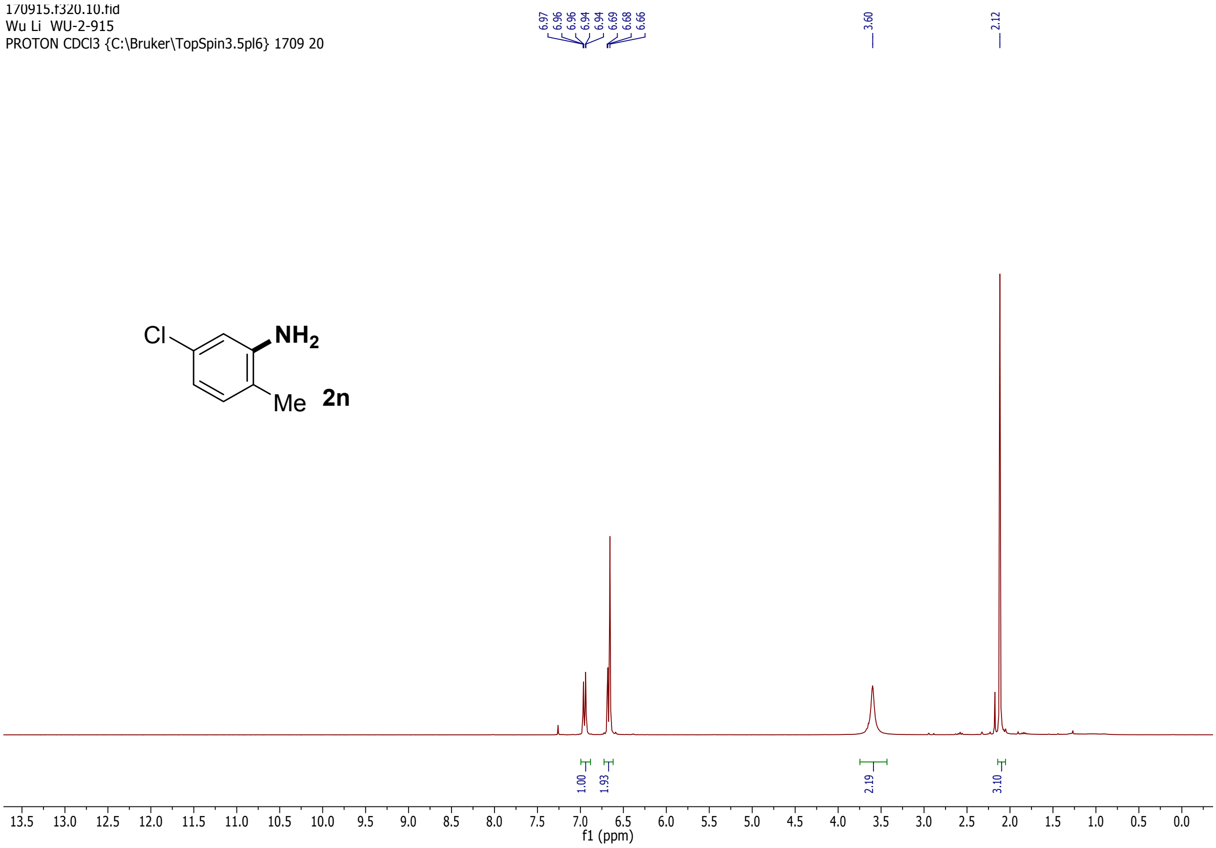


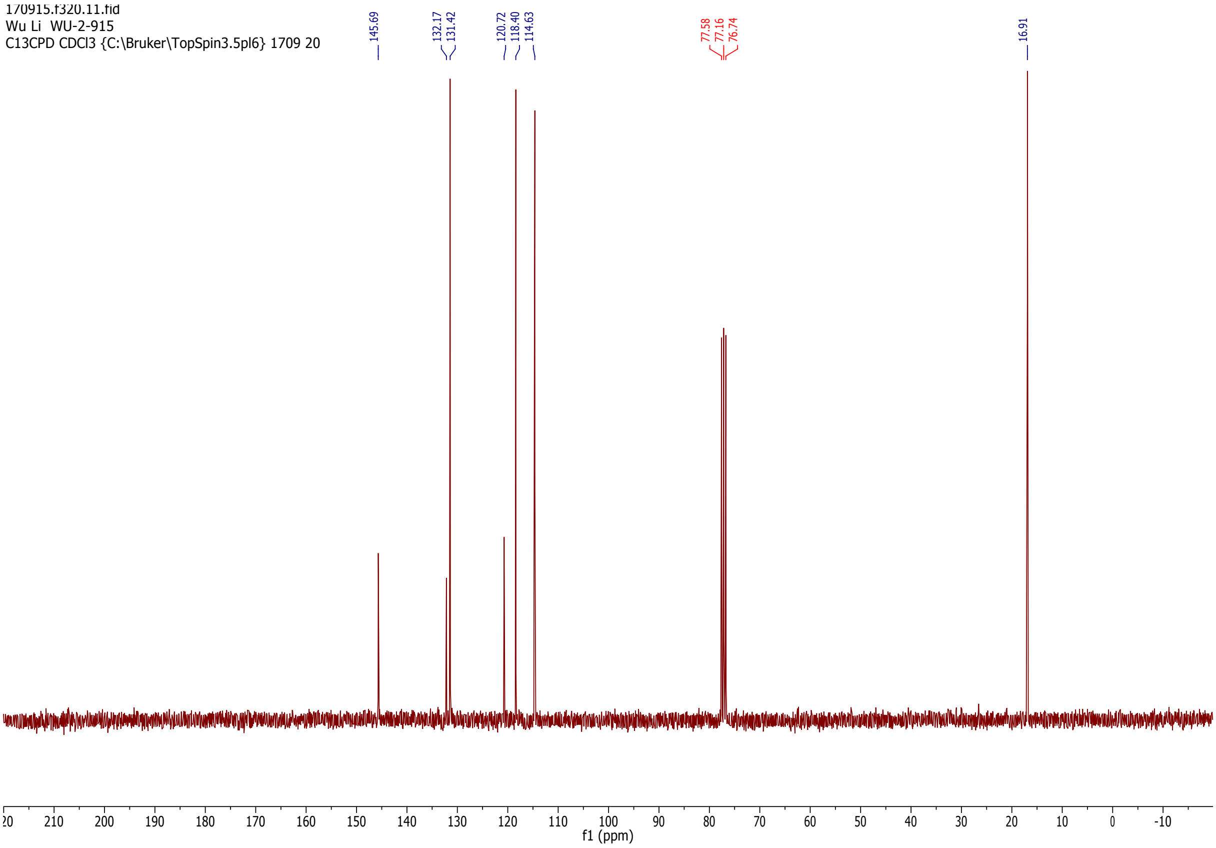
Original spectra for **2m**:



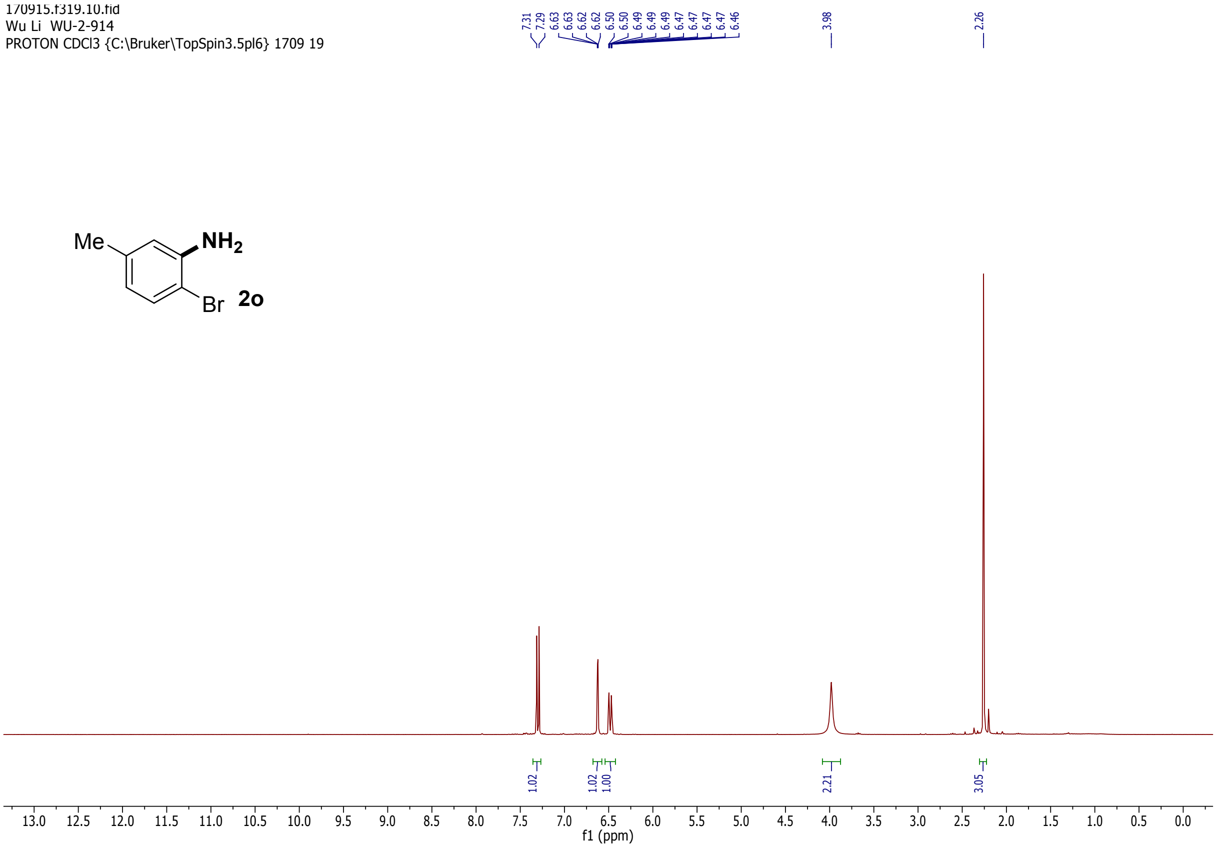


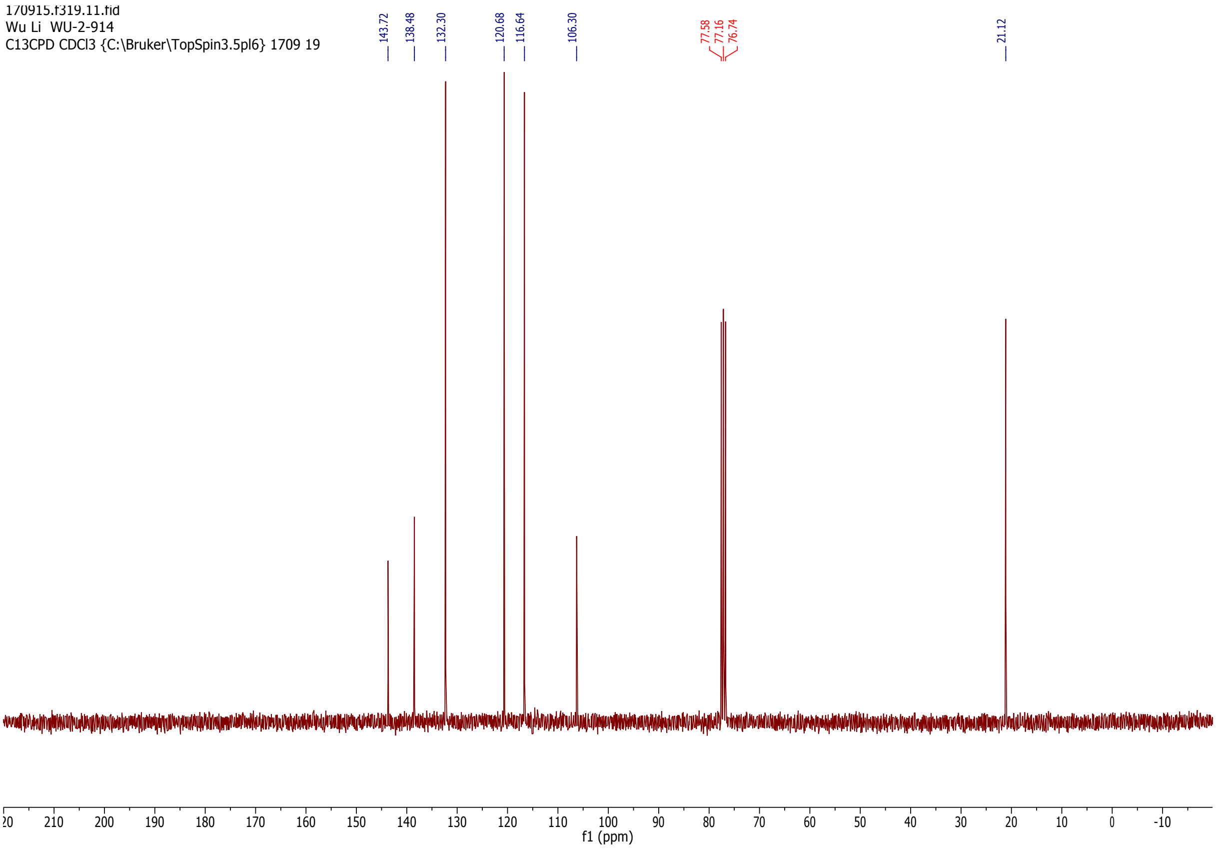
Original spectra for **2n**:





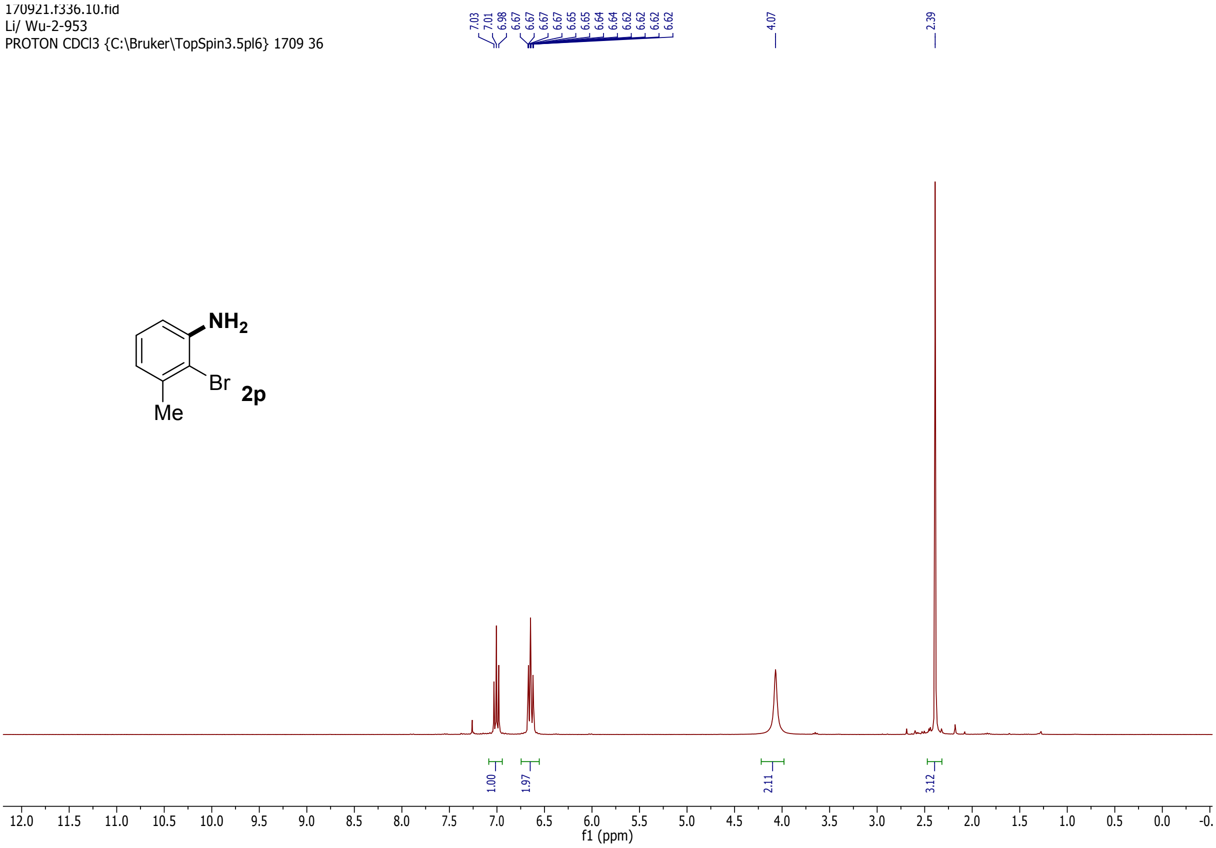
Original spectra for **2o**:



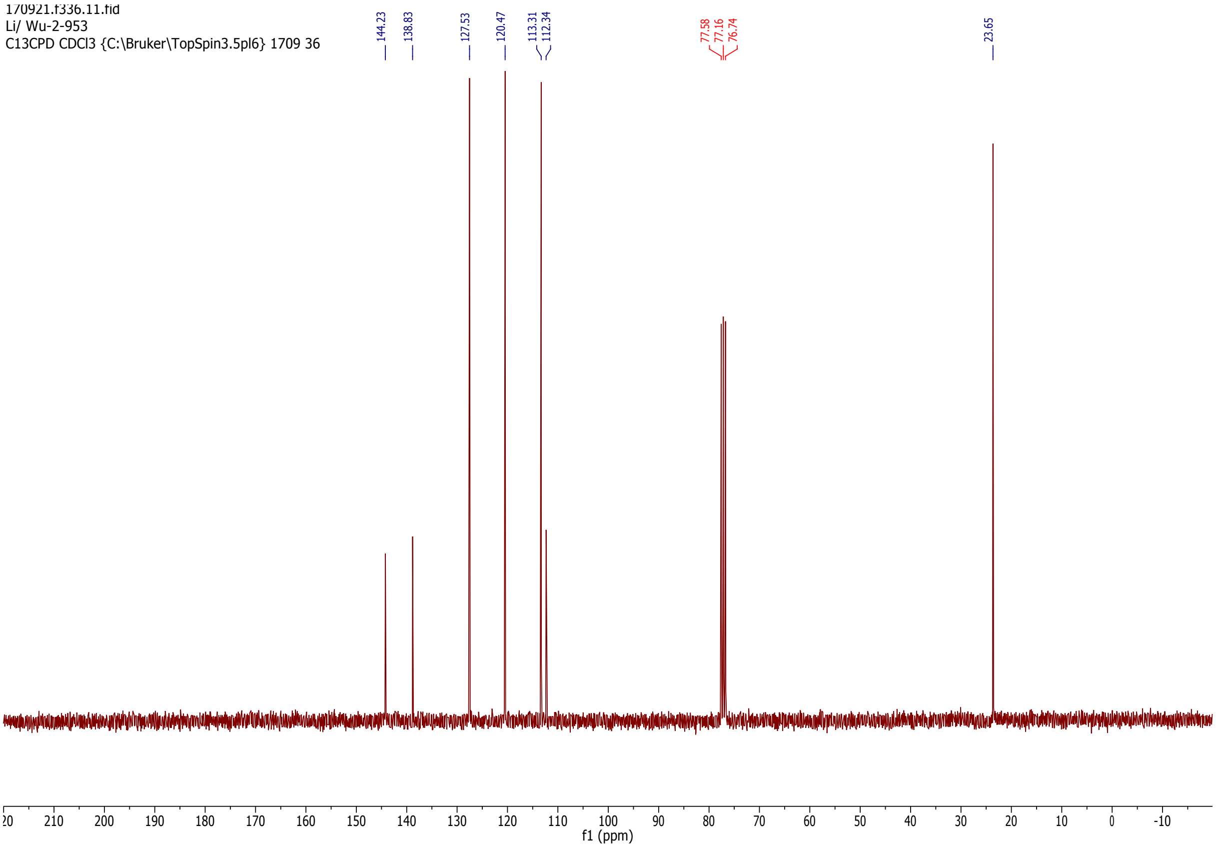


Original spectra for **2p**:

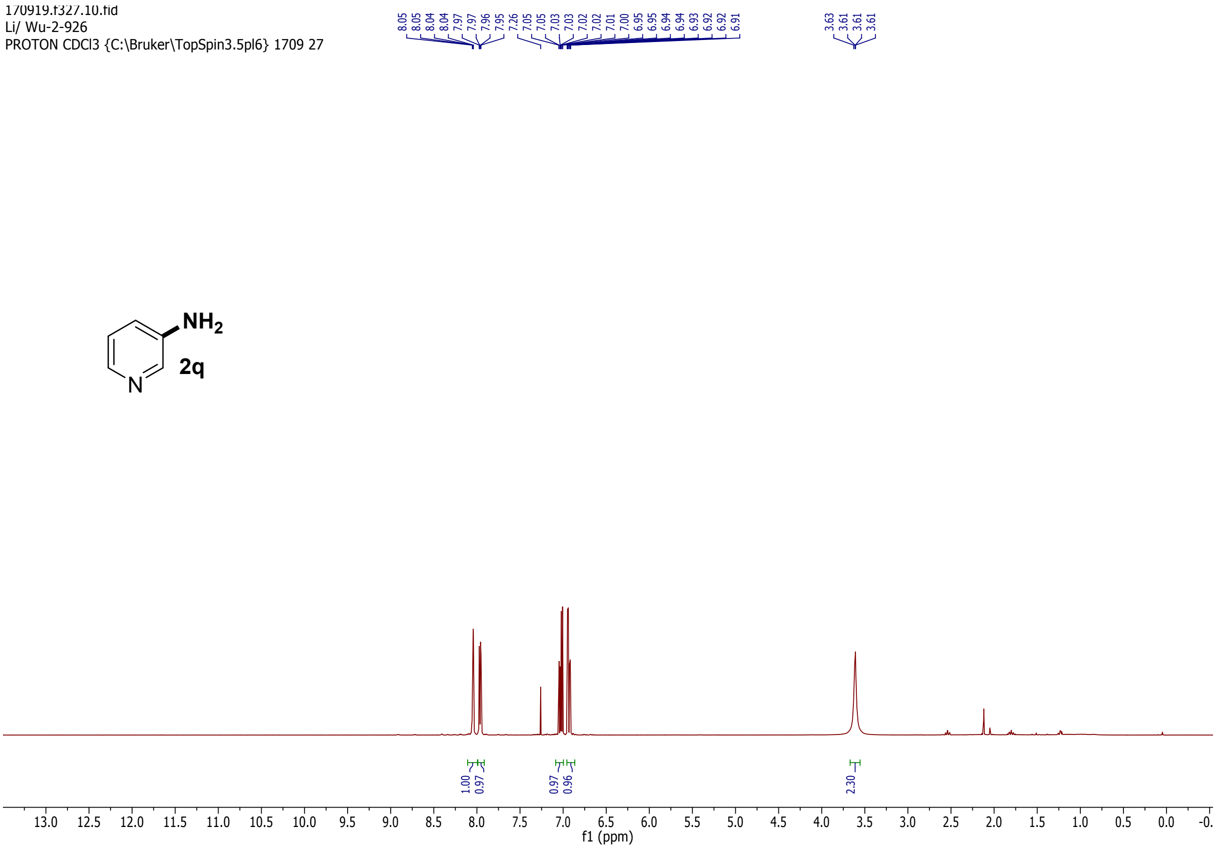
170921.f336.10.fid
Li/ Wu-2-953
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 36

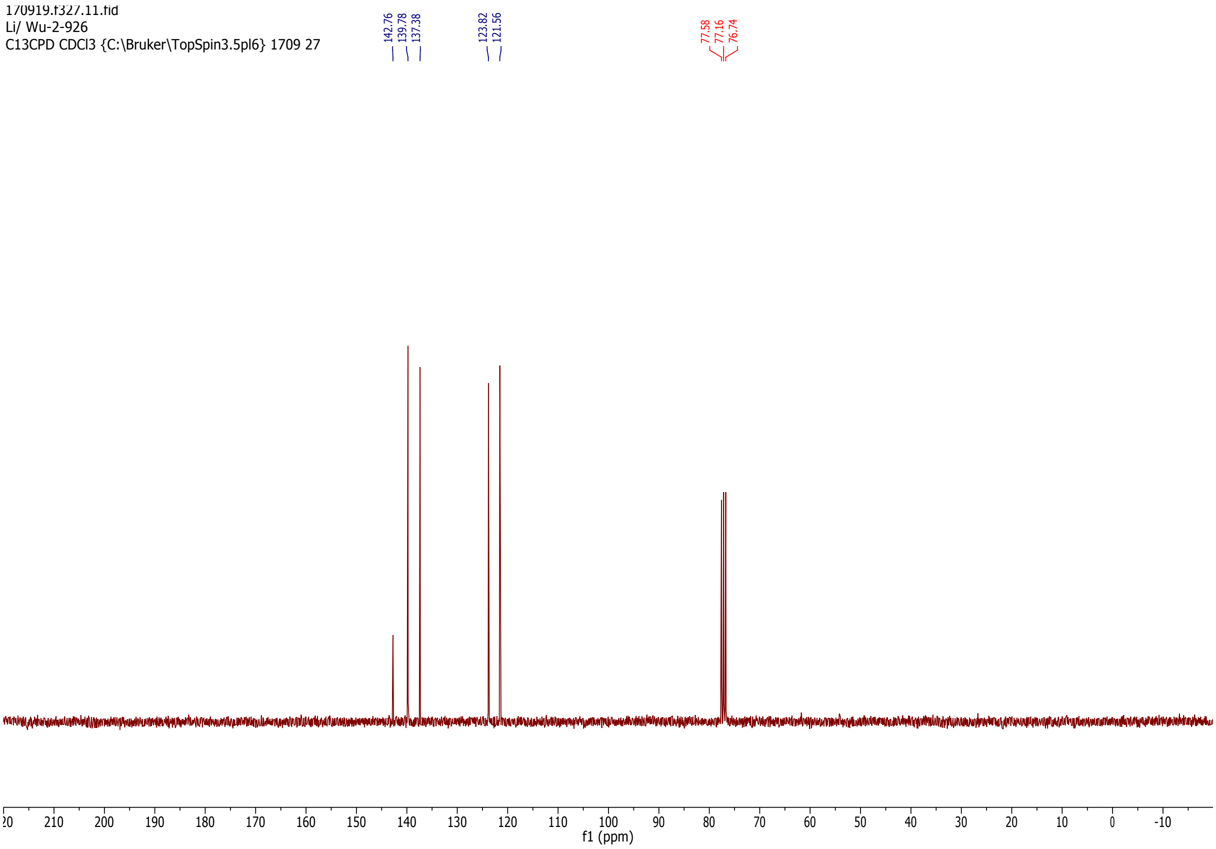


170921.f336.11.fid
Li/ Wu-2-953
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 36

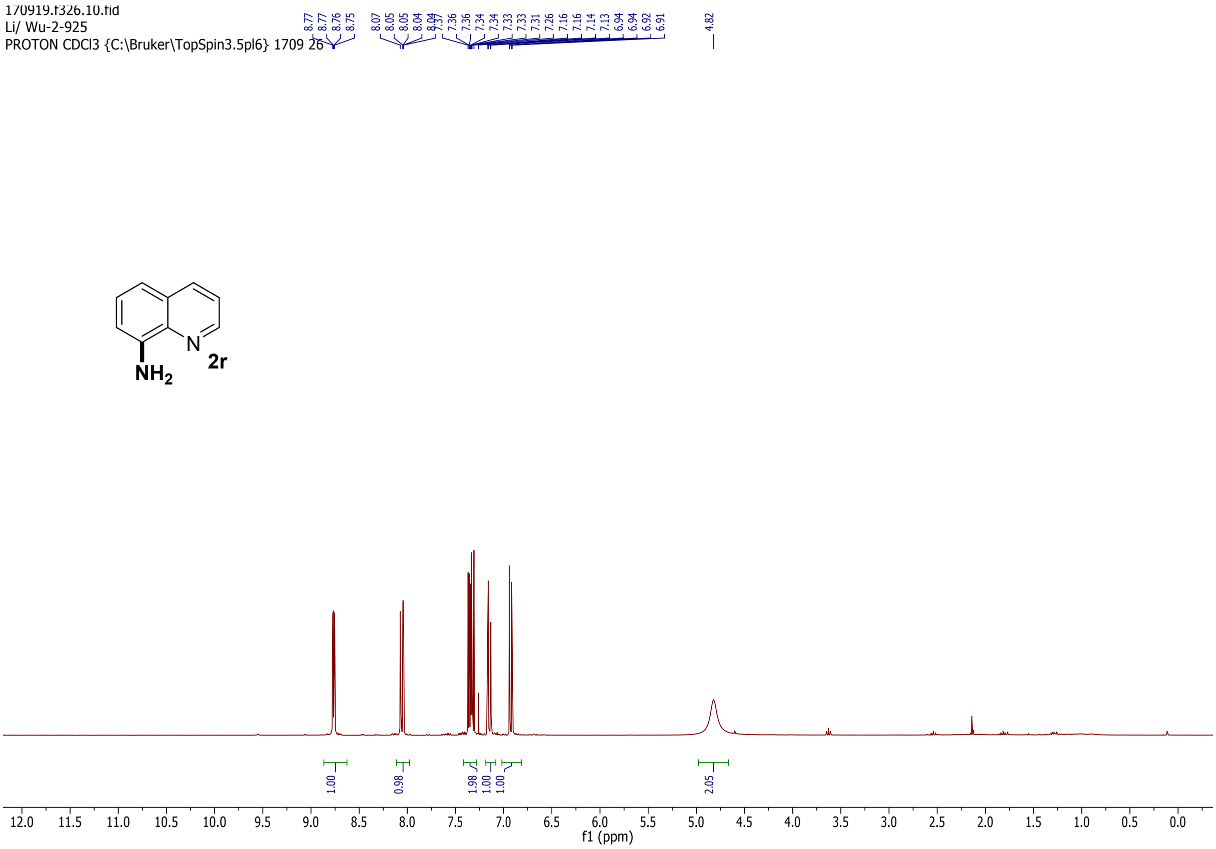


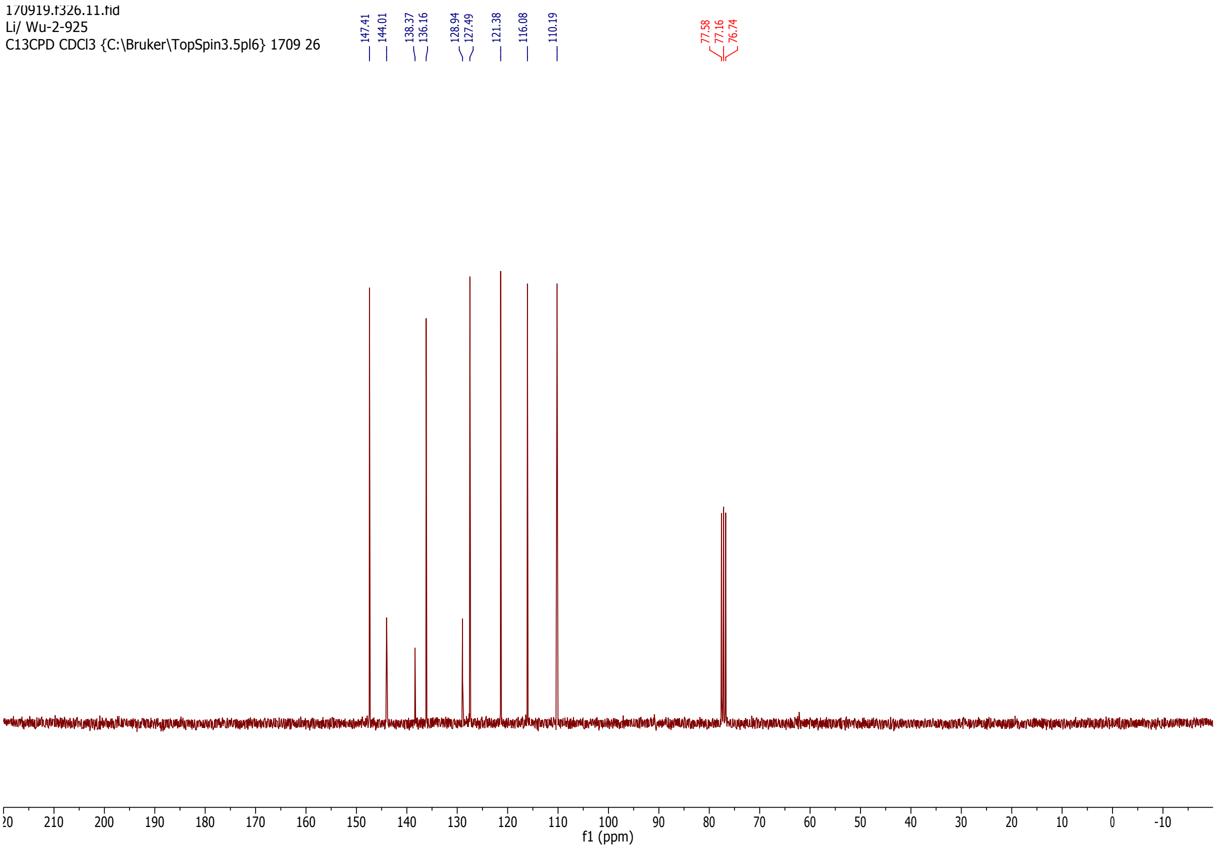
Original spectra for **2q**:





Original spectra for **2r**:





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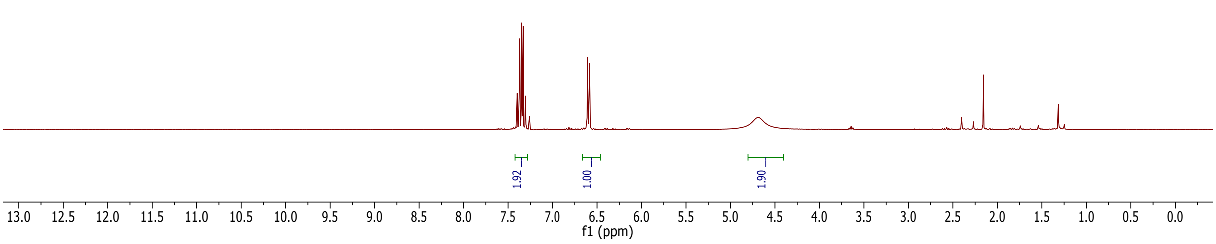
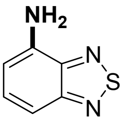
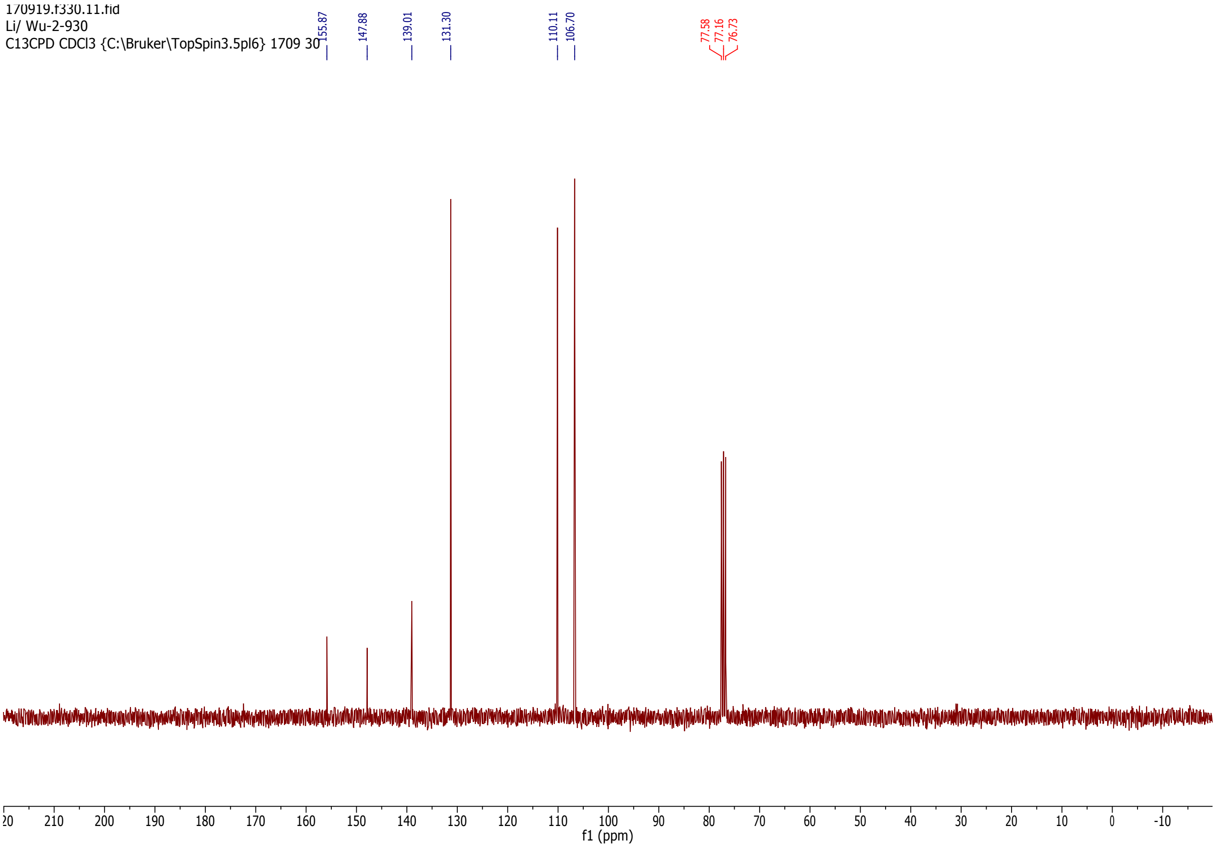




2s



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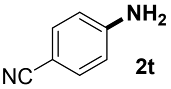
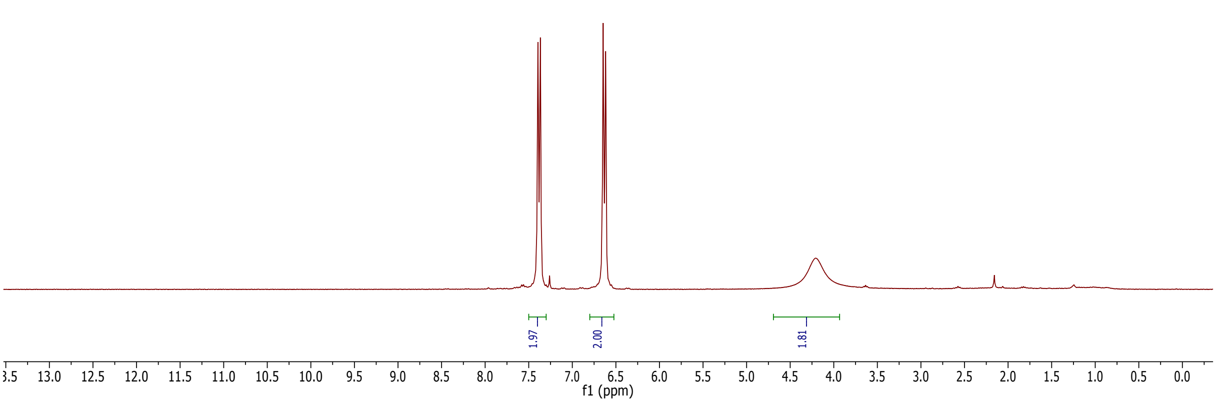


2t

170915.f318.10.fid
Wu Li WU-2-913
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 18



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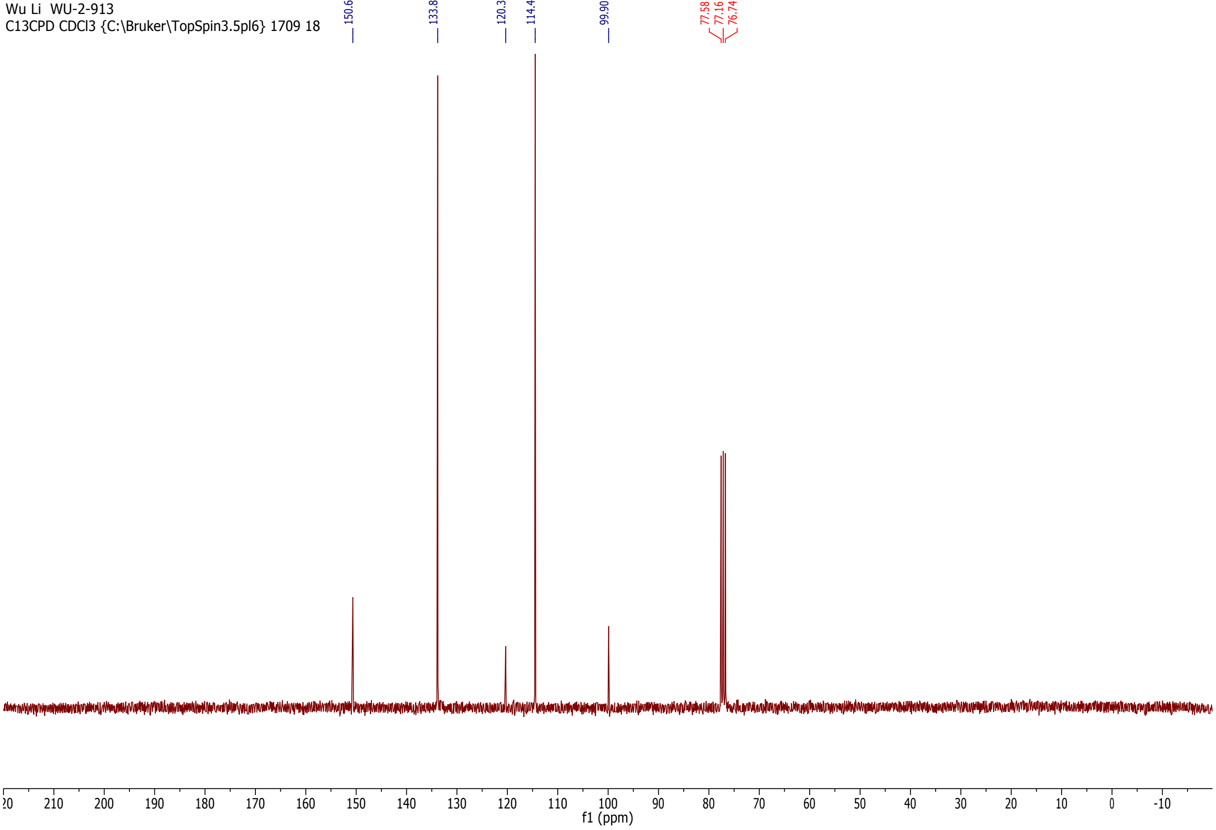
C13CPD CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 18



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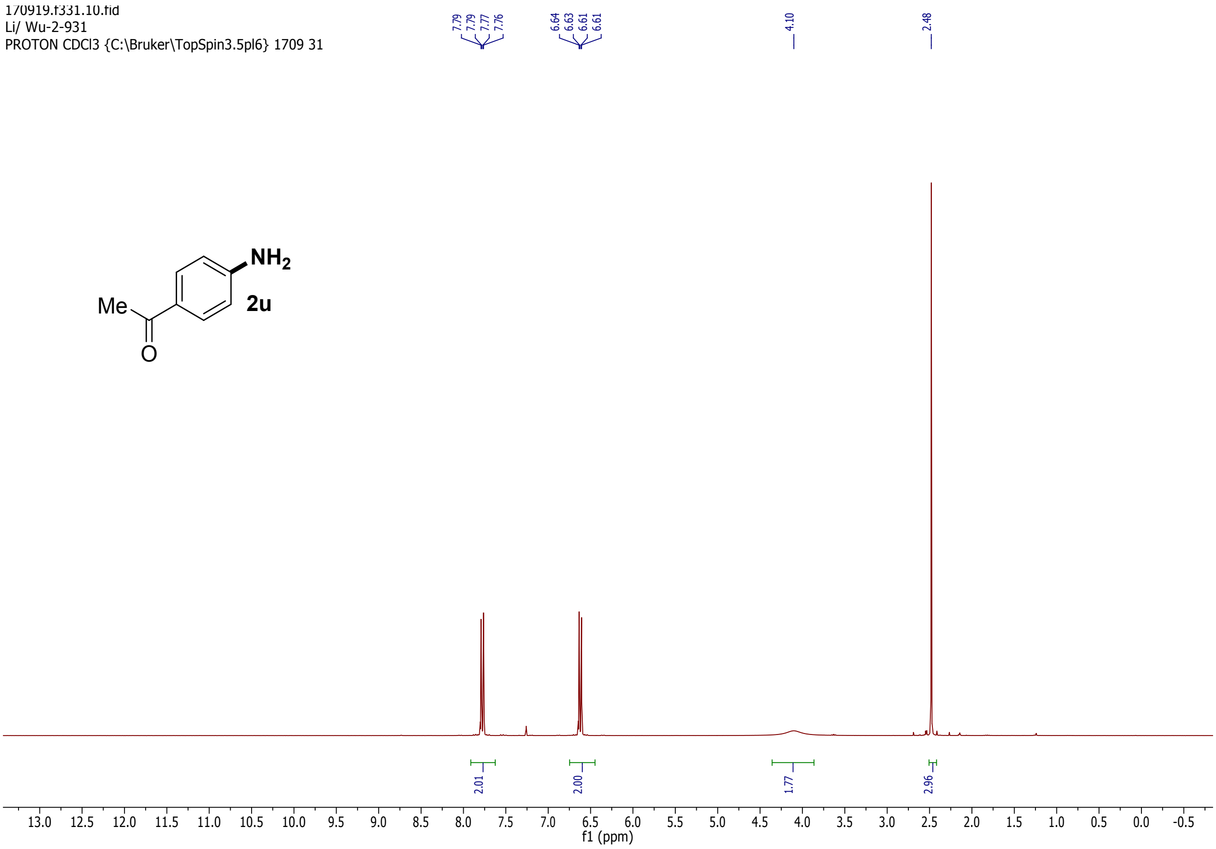
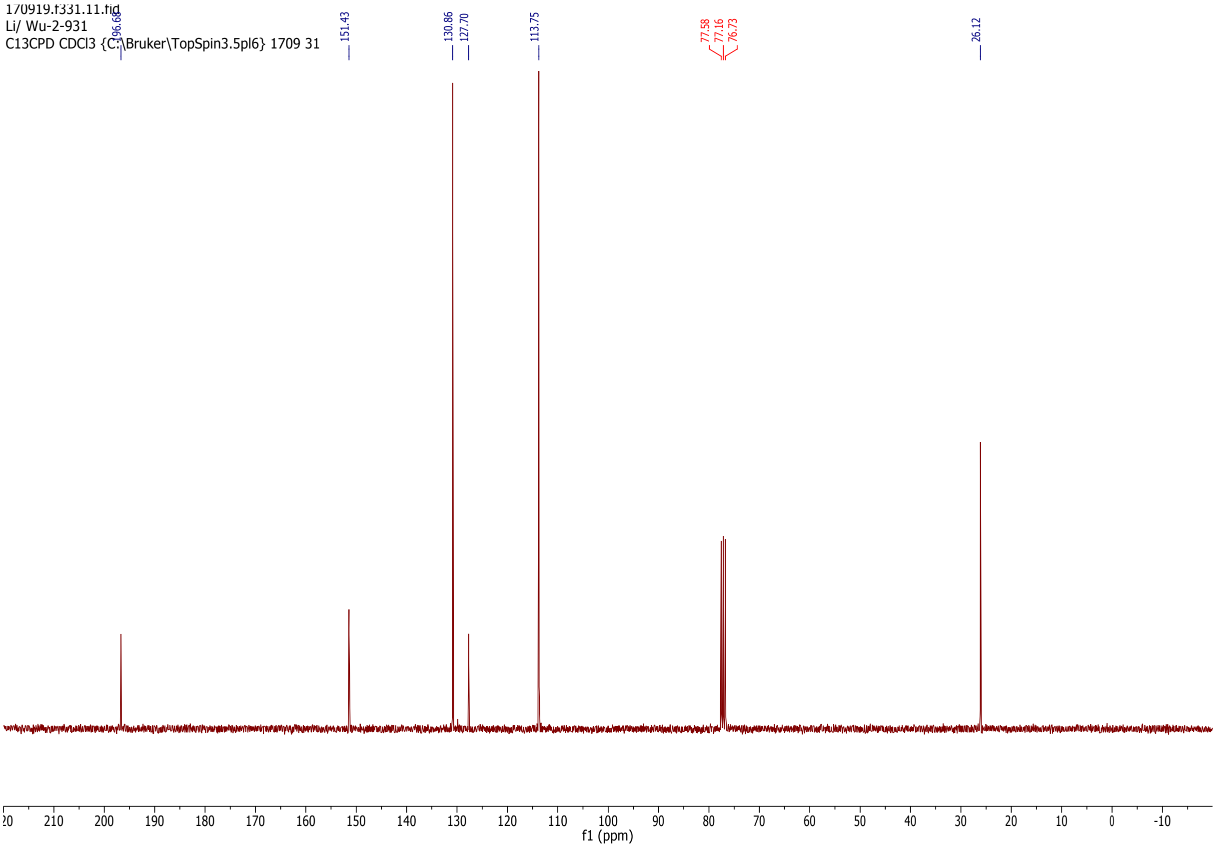
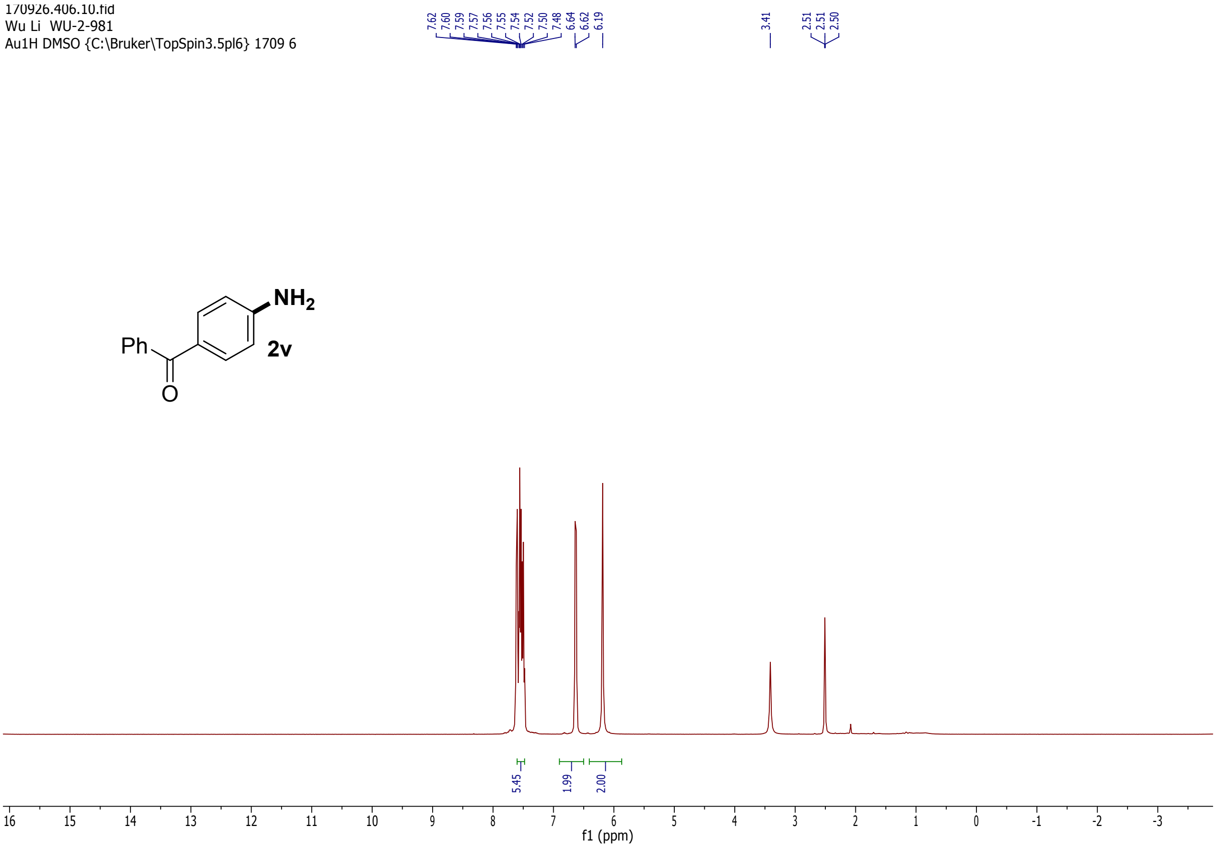
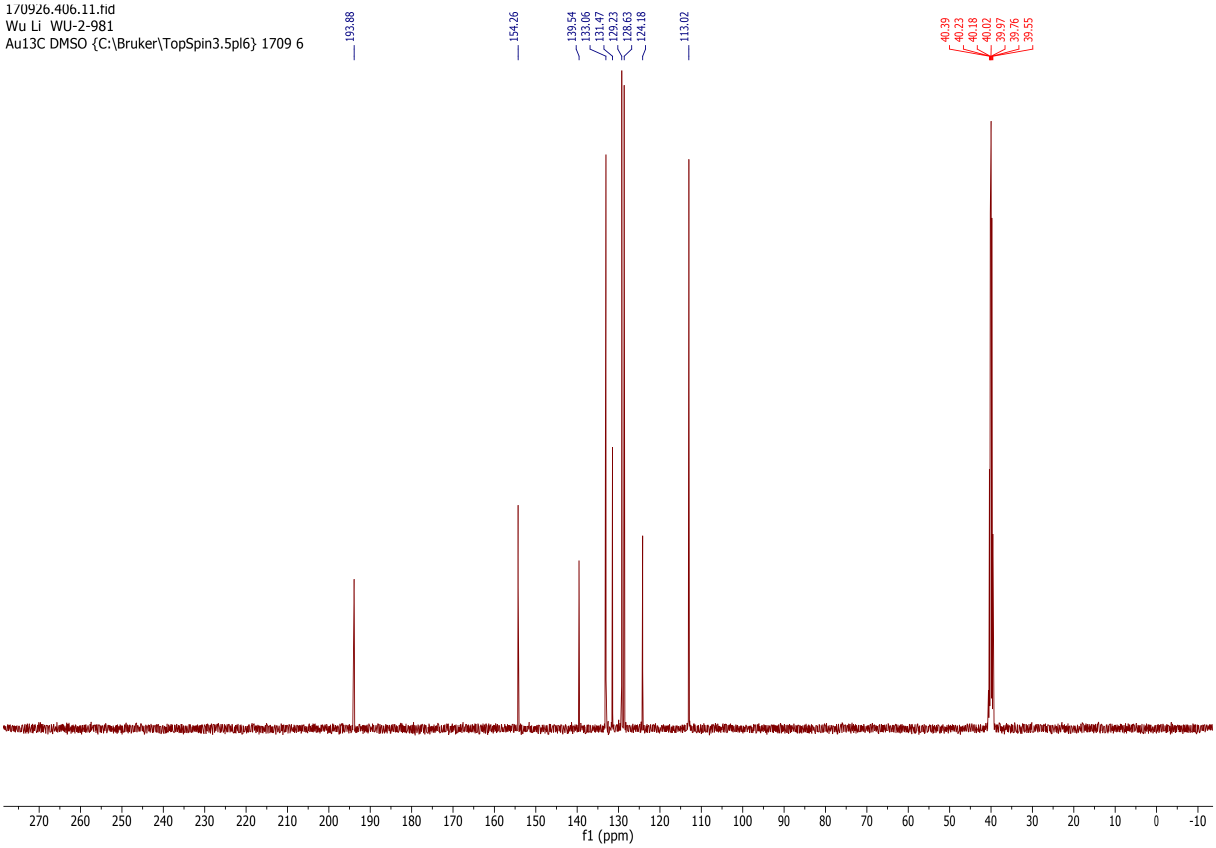




Original spectra for **2v**:





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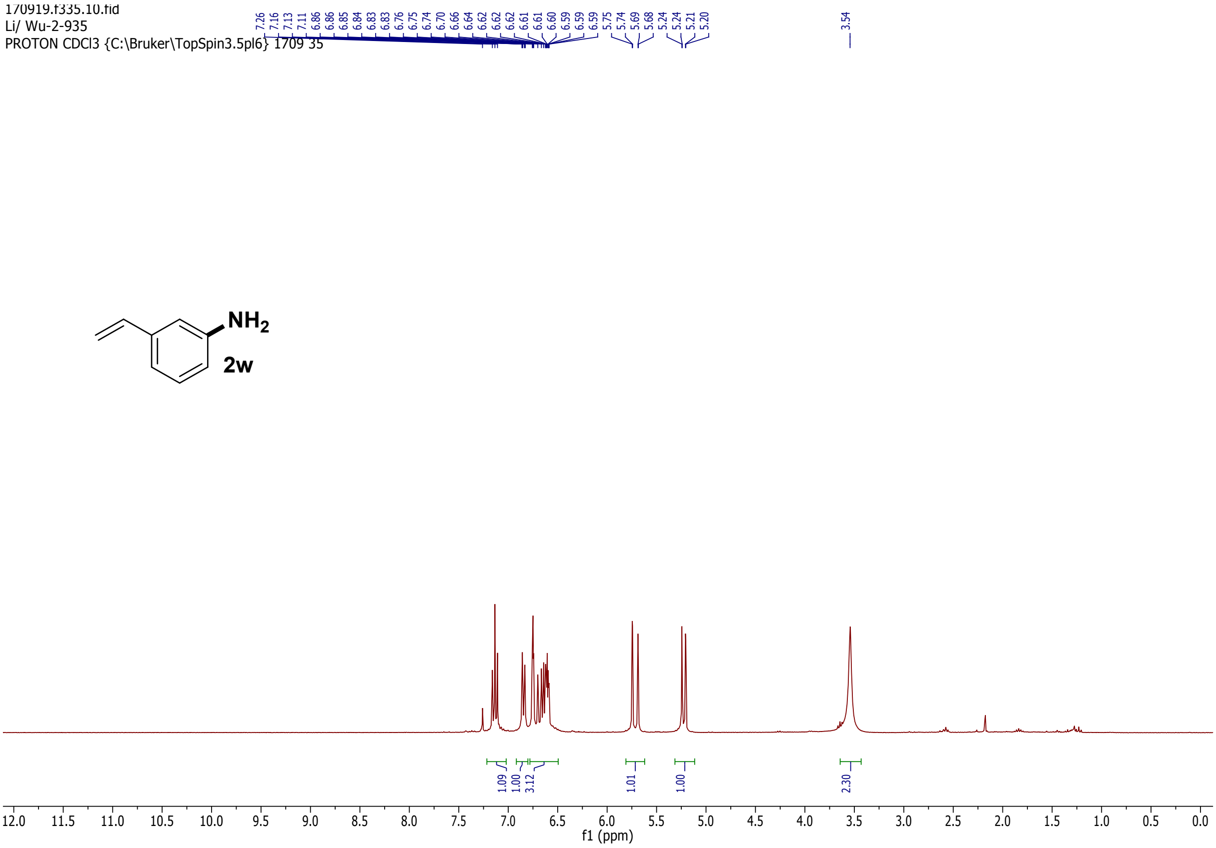
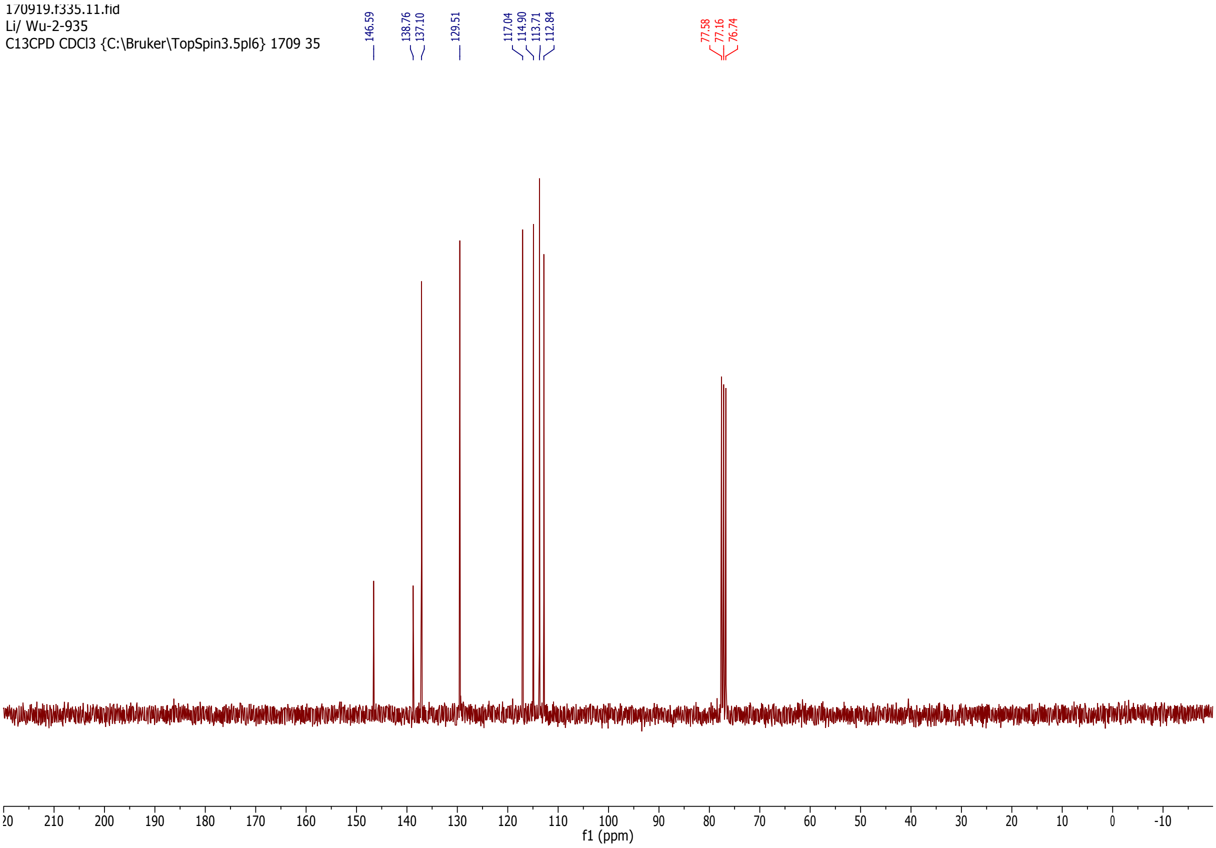

170919.f335.10.fid
Li/ Wu-2-935
PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6} 1709 35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Li/ Wu-2-935
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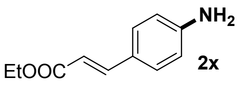
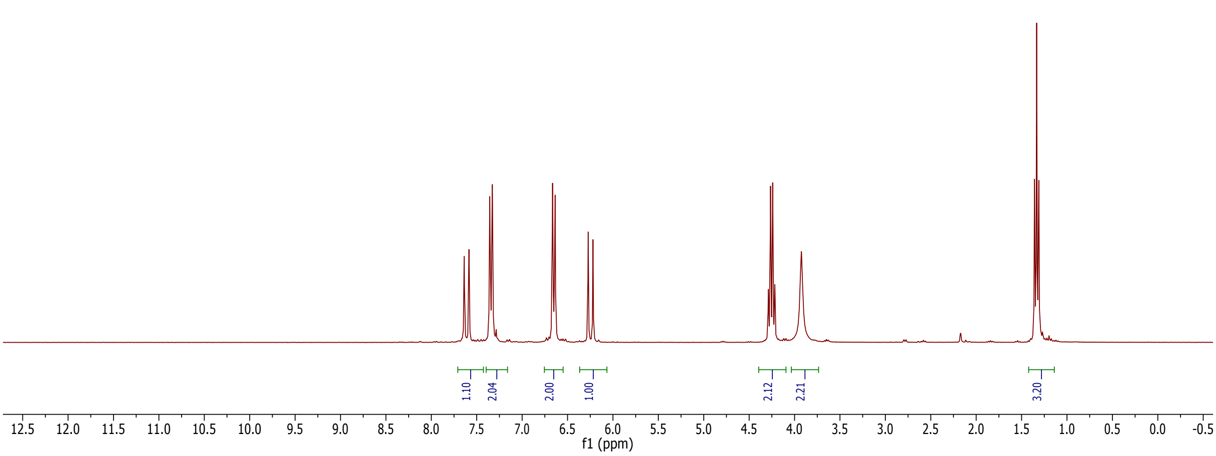
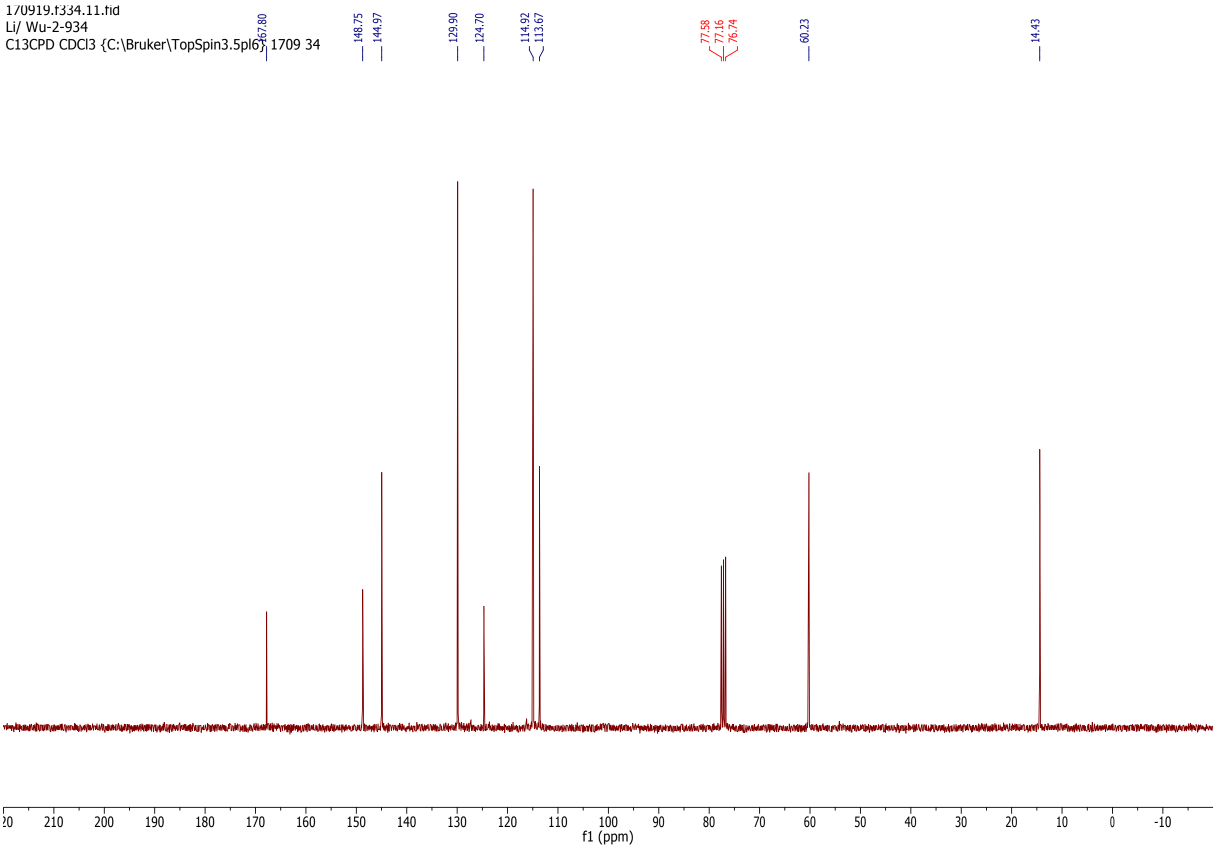
Original spectra for **2x**:



2x





Original spectra for **2y**: