Electronic Supplementary Material (ESI) for Green Chemistry.

Single-reactor tandem oxidation-amination process for the synthesis of furan-derived secondary diamines from 5-hydroxymethylfurfural

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Experimental Section

Chemicals

5-Hydroxymethyl-2-furaldehyde (HMF, purity 98%) was purchased from Accela ChemBio. Furan-2,5-dicarbaldehyde (DFF, purity > 99%), 2,5-bis-(butylamino-methyl)-furan (BAF, purity > 99%), 2,5-bis-(butyliminomethyl) furan (BIF, purity > 99%) and 2,5-bis-(butylaminomethyl) tetrahydrofuran (BATHF, purity > 99%), (5-((butylamino)methyl)furan-2-yl)methanol (BUFM, purity > 99%) were supplied by Shanghai ChemPartner. 1,4-dioxane (purity > 99.5%), 1-butylamine (purity > 97%) was supplied by Sinopharm Chemical Reagent Co., Ltd. H_2 was supplied by Air Liquide. 5%Rh/Al_2O_3, 5%Pd/C and 5%Ru/C were procured from Johnson Matthey. 5%Ru/Al_2O_3 was obtained from Evonik. $Pd(NO_3)_2 \cdot 2H_2O$ (~40 wt% Pd basis) and $RuCl_3 \cdot xH_2O$ (99.98 wt% trace metals basis) were purchased from Sigma-Aldrich. Activated carbon (G60) was provided by Cabot Corporation.

Bimetallic Ru-Pd catalyst preparation

A Pd(Ru/C)_IWI catalyst was prepared by the incipient wetness impregnation (IWI) method using an aqueous solution of $Pd(NO_3)_2.2H_2O$.[S1] In a typical procedure, the desired amount of the precursor was dissolved into 50 mL of deionized water, and 0.5 g of commercial 5%Ru/C was added to the solution under stirring. The Ru/Pd molar ratio between was 2.8. After stirring for 2 h, the sample was first dried in a rotary evaporator at 40 °C for 3 h, and later at 60 °C overnight under vacuum, and then calcined at 400 °C (5 ºC/min to 400 °C and then hold for 2 h) under H_2 before use.

A second series of catalysts was prepared by the precipitation-reduction method using $Pd(NO_3)_2.2H_2O$ and $RuCl_3 \cdot xH_2O$ precursors.[S2] Briefly, an aqueous solution of the given precursor was added into 10 mL of an aqueous solution containing 0.5 g of 5%Ru/C, 5%Pd/C or activated carbon and then deonized water was added until a total volume of 60 mL. The resulting slurry was stirred vigorously at room temperature for 1 h. Then, 5 mL of an aqueous solution of $NaBH_4$ (0.1 M) was added dropwise to reduce the ionic precursor. The as-obtained bimetallic catalyst was centrifuged, washed with deionized water until no chloride traces were detected using a 1 wt% $AgNO_3$ solution, and dried at 60 °C overnight under vacuum. The Ru/Pd molar ratio was also kept at 2.8. The catalysts were denoted as Ru(Pd/C), Pd(Ru/C) and (Ru+Pd)/C for Ru deposited over 5%Pd/C, Pd deposited over 5%Ru/C and Ru and Pd deposited over activated carbon, respectively.

Catalyst characterization

Temperature-programmed reduction (H_2-TPR) and CO-chemisorption (CO-DOSE) were carried out on a Micromeritics AutoChem II 2920 system equipped with a thermal conductivity detector (TCD) to monitor the changes in the gas composition, a CryoCooler for sub-ambient (-100 °C) measurements, and a cold trap before the detector. The H_2-TPR profiles were measured using a heating rate of 10 °C/min under a 10% H_2/Ar flow (40 mL(STP) /min). Catalysts were reduced before CO-DOSE test. Measured flow rate of CO was 40.12 mL(STP) /min. The operation temperature was 45 °C. Active Loop volume at 110.8 °C was 0.03422 mL STP. The chemisorption was repeated 20 times or until no more change of the TCD signal before stopping.

Thermogravimetric analysis (TGA) was conducted using a TA Instruments SDT 2960 apparatus equipped with a flow gas system. The catalyst was treated from room temperature to 105 °C using a heating rate of 5 °C/min under N_2 with a flow rate of 100 mL(STP)/min for 4 h. Approximately 10 mg of sample was heated in an open alumina crucible.

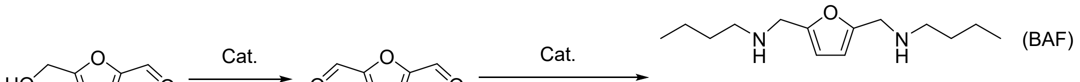
Accelerating Rate Calorimeter (ARC) is used to determine the time, temperature, and pressure relationships of any exothermal reaction in a confined adiabatic environment. This data can be applied to assess the thermal and pressure hazard potentials of a reaction, and is used for specifying plant protection measures including emergency relief system design.

Catalytic tests

The catalytic tests (oxidation, reductive amination, single-reactor) were conducted in a-30 mL stainless steel autoclave (TVS-N2, Taiatsu) equipped with a pressure gauge and a safety valve. In a typical oxidation experiment, the reactor was charged with 2 mL HMF solution and a given amount of catalyst. The reactor was sealed, flushed with O_2 for six times, charged to the desired pressure, and placed on a hot plate equipped with a holder pre-heated to the desired temperature and a magnetic stirrer at the desired temperature. The reaction solution reached the desired temperature within 1 min. In all the experiments, the temperature difference between the reaction solution inside the autoclave and the holder was lower than 3 °C. After the reaction, the autoclave was removed from the holder and placed into the cold ice water solution, and the reaction was quenched within 20 s.

In a typical reductive amination experiment, 2 mL DFF solution, 1-butylamine and a given amount of catalyst were charged to the reactor before sealing. The reactor was flushed with H_2 for six times, evacuated by applying a vacuum followed by charging H_2 (40 bar), and placed on a hot plate equipped with a magnetic stirrer at the desired temperature. The single-reactor reaction was conducted by combining both steps starting from HMF (Scheme S1).

After the reaction, all the reaction solution was filtered, and the reactants and products were analysed and quantified by gas chromatography using an Agilent 7890A GC equipped with HP-5 capillary column (30 m x 0.320 mm x 0.25 µm) and a FID detector with an external standard method. Additional analysis by ^1H and ^{13}C NMR was performed on Bruker 300 UltraShield equipment to identify and quantify the reaction products. The products were separated using a chromatographic column employing different solvents such as n-hexane, ethyl acetate, and chloroform. Two of the solvents were mixed together at different volume ratios. The actual ratio between the solvents was measured by thin-layer chromatography (TLC) method. Then a chromatographic column filled with silica gel was used to separate the different products using the best solvent mixture, the solvent mixture was evaporated and the residue was dissolved in $CDCl_3$ before conducting NMR analysis.



Scheme S1. Cascade HMF oxidation and followed by reductive amination.

The recyclability tests were carried out for the 5%Ru/C+5%Pd/C catalyst mixture and the Pd(Ru/C)_IWI bimetallic catalyst. After each run, the reaction solution was centrifuged before analysis. The remaining catalyst was washed with 10 mL water and 10 mL acetone. Then it was dried at 80 °C under vacuum for 6 h before the next run, and weighted to assess for any possible loss. The catalyst was added to the autoclave in the presence of fresh reactant and solvent, and the next run was conducted according to the experimental conditioned indicated above.

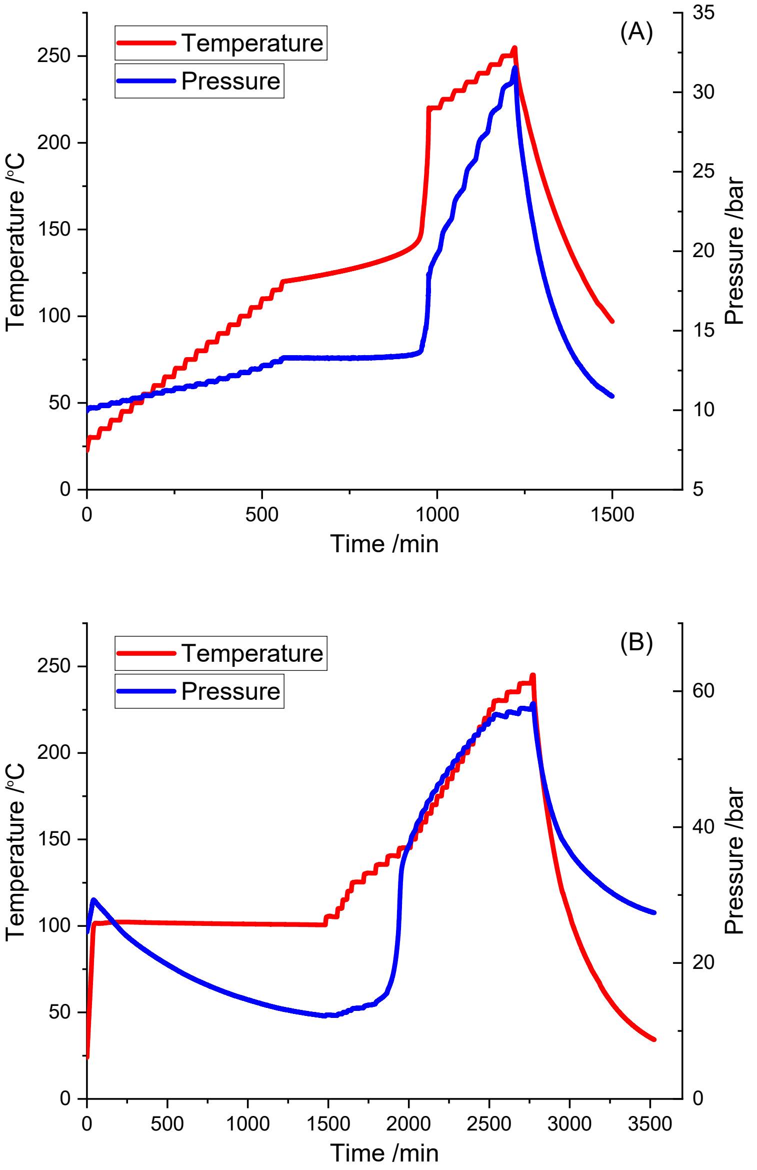


Fig. S1 Simulation of reaction condition with accelerated rate calorimeter (ARC). (A) 3%HMF in 1,4-dioxane without catalyst, 10 bar O_2, increase temperature from 30 to 300 ºC, (B) 3%HMF in 1,4-dioxane with catalyst, 25 bar O_2, isothermal 100 ºC for 24 h then rise up to 300 ºC.

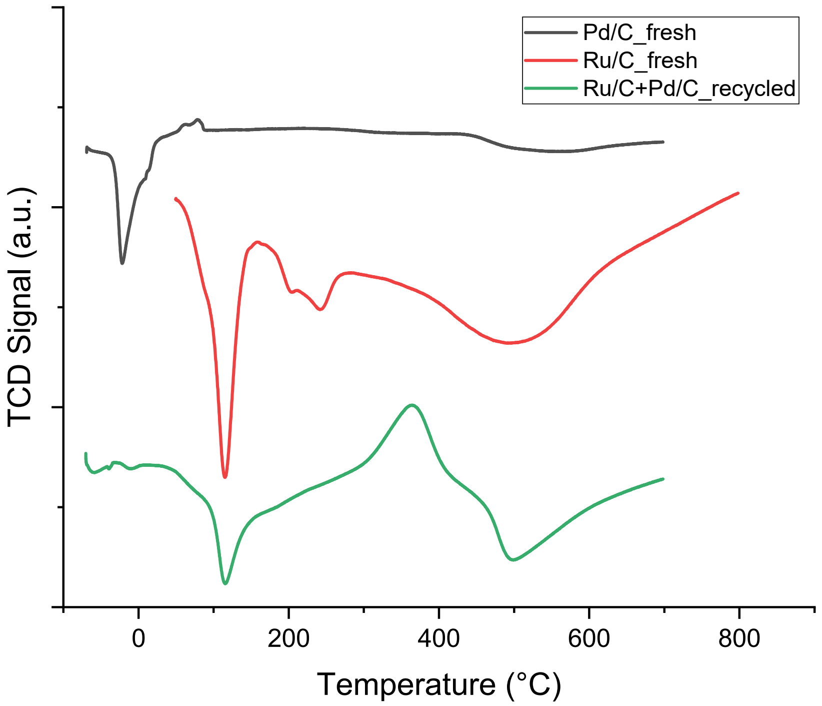


Fig. S2. H_2-TPR profiles in the temperature range from -100 °C to 800 °C for 5%Ru/C, 5%Pd/C and recycled 5%Ru/C + 5%Pd/C catalysts after the single-reactor reaction.

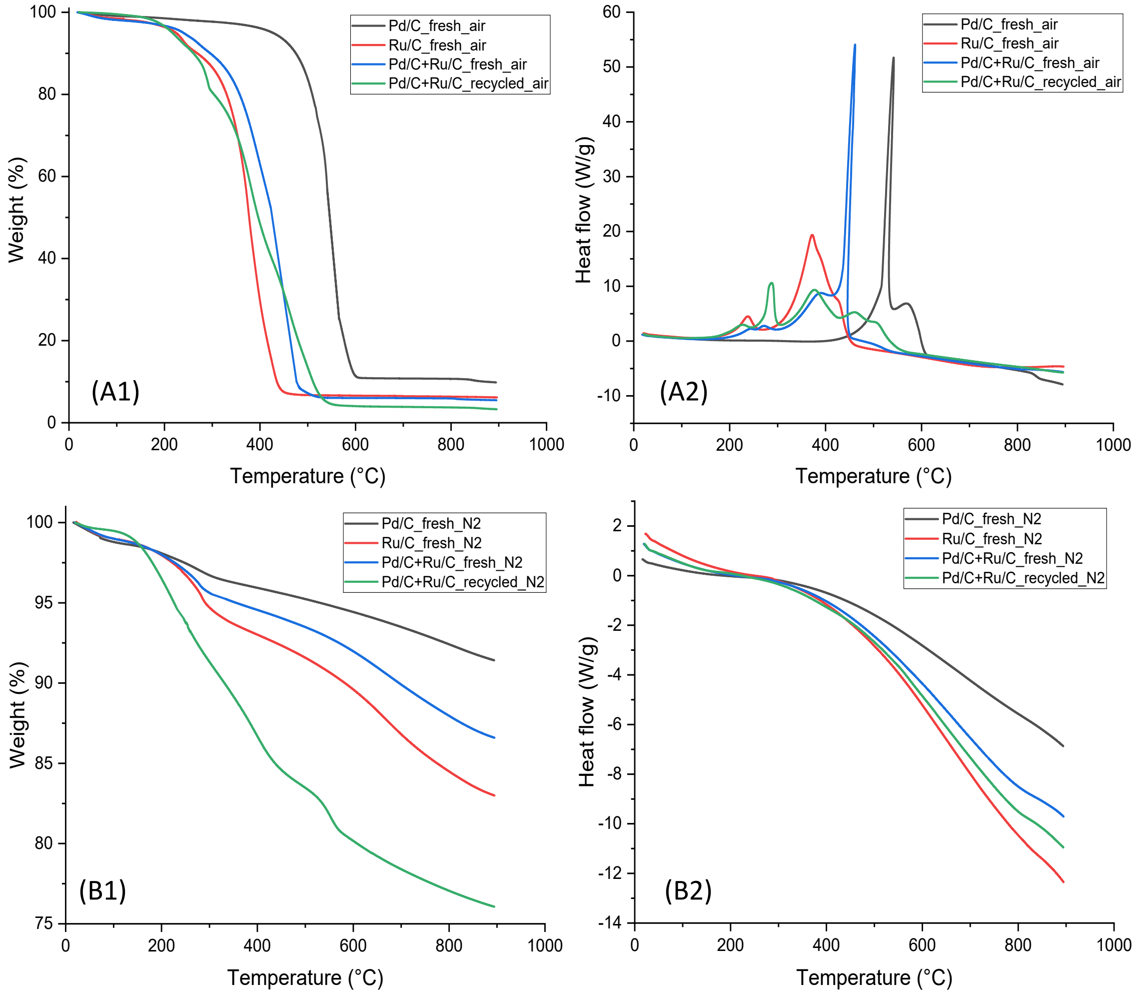


Fig. S3. TGA and DTG profiles in the temperature range from room temperature to 900 °C of fresh, recycled 5%Ru/C, 5%Pd/C and combined 5%Ru/C + 5%Pd/C catalysts under air (A1, A2) and N2 (B1, B2).

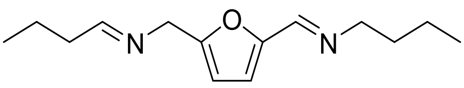
Table S1. Metal property of catalyst given by CO-chemisorption

Catalyst	Metal dispersion %	Particle size /nm
5%Ru/C	13.4	8.2
5%Pd/C	8.1	13.8

Table S2. ICP tests of fresh and used catalysts

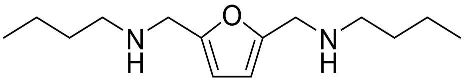
Sample	Pd (wt.%)	Ru(wt.%)
fresh catalyst	1.67	3.17
used catalyst	1.60	2.97

Characterization of products



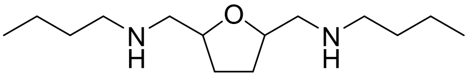
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (s, 1H), 6.69 (s, 1H), 3.43 (t, J = 6.9 Hz, 2H), 1.65 – 1.35 (m, 2H), 1.19 (dq, J = 14.6, 7.3 Hz, 2H), 0.76 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.65 (s), 149.55 (s), 113.44 (s), 61.49 (s), 32.52 (s), 20.09 (s), 13.57 (s).



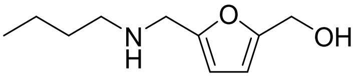
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.87 (s, 1H), 3.54 (s, 2H), 2.48 – 2.29 (m, 2H), 1.37 – 1.05 (m, 5H), 0.71 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.93 (s), 106.92 (s), 48.50 (s), 46.09 (s), 31.80 (s), 20.12 (s), 13.65 (s).



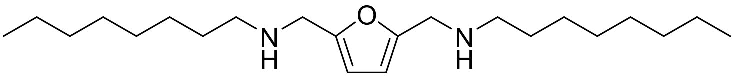
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.11 – 3.87 (m, 1H), 2.75 – 2.44 (m, 4H), 2.01 – 1.74 (m, 1H), 1.65 – 1.47 (m, 2H), 1.47 – 1.34 (m, 2H), 1.26 (dq, J = 14.0, 7.0 Hz, 2H), 0.84 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 78.79 (s), 78.15 (s), 77.58 (s), 77.16 (s), 76.74 (s), 54.96 (s), 49.92 (s), 32.24 (s), 29.20 (s), 20.50 (s), 14.04 (s).



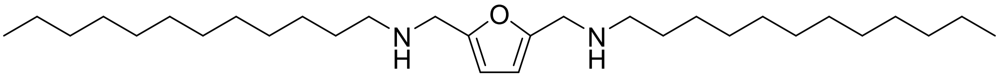
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.05 (dd, J = 7.4, 3.1 Hz, 1H), 4.49 (s, 1H), 4.40 (s, 1H), 3.65 (s, 1H), 2.58 – 2.41 (m, 1H), 1.81 (s, 1H), 1.55 – 1.30 (m, 1H), 1.29 – 1.09 (m, 1H), 0.81 (td, J = 7.2, 3.2 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 154.44 (s), 152.04 (s), 108.26 (s), 107.73 (s), 56.53 (s), 48.27 (s), 45.55 (s), 31.23 (s), 20.27 (s), 13.83 (s).



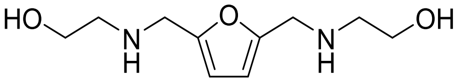
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.04 (s, 1H), 3.70 (s, 2H), 2.55 (t, J = 7.2 Hz, 2H), 1.61 – 1.36 (m, 3H), 1.23 (s, 11H), 0.84 (t, J = 6.4 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.30 (s), 107.36 (s), 49.28 (s), 46.47 (s), 31.90 (s), 30.06 (s), 29.46 (d, J = 19.2 Hz), 27.42 (s), 22.73 (s), 14.17 (s).



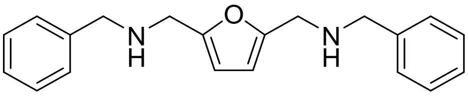
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.01 (s, 1H), 3.68 (s, 2H), 2.53 (t, J = 7.2 Hz, 2H), 1.71 – 1.33 (m, 3H), 1.20 (s, 19H), 0.82 (t, J = 6.6 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.24 (s), 107.29 (s), 49.23 (s), 46.43 (s), 31.94 (s), 30.02 (s), 29.88 – 29.24 (m), 27.37 (s), 22.71 (s), 14.14 (s).



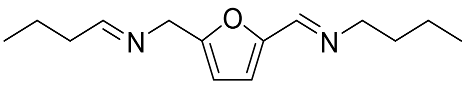
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.00 (s, 1H), 3.63 (s, 2H), 3.58 – 3.34 (m, 4H), 2.72 – 2.50 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 152.60 (s), 107.79 (s), 60.41 (s), 50.49 (s), 45.76 (s).



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.43 – 7.20 (m, 6H), 6.14 (s, 1H), 3.80 (d, J = 7.9 Hz, 4H), 1.88 (s, 1H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 153.06 (s), 139.86 (s), 128.35 (d, J = 10.7 Hz), 127.02 (s), 107.73 (s), 52.81 (s), 45.51 (s).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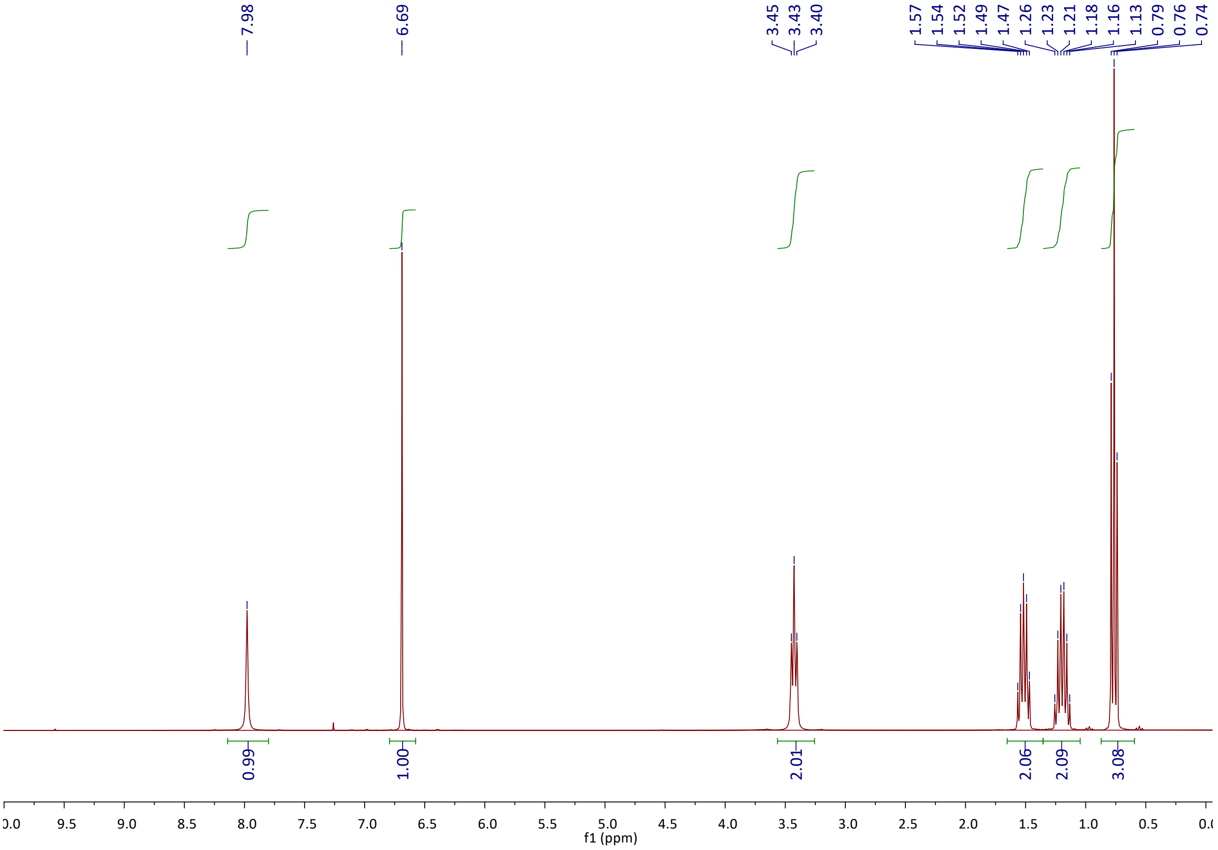
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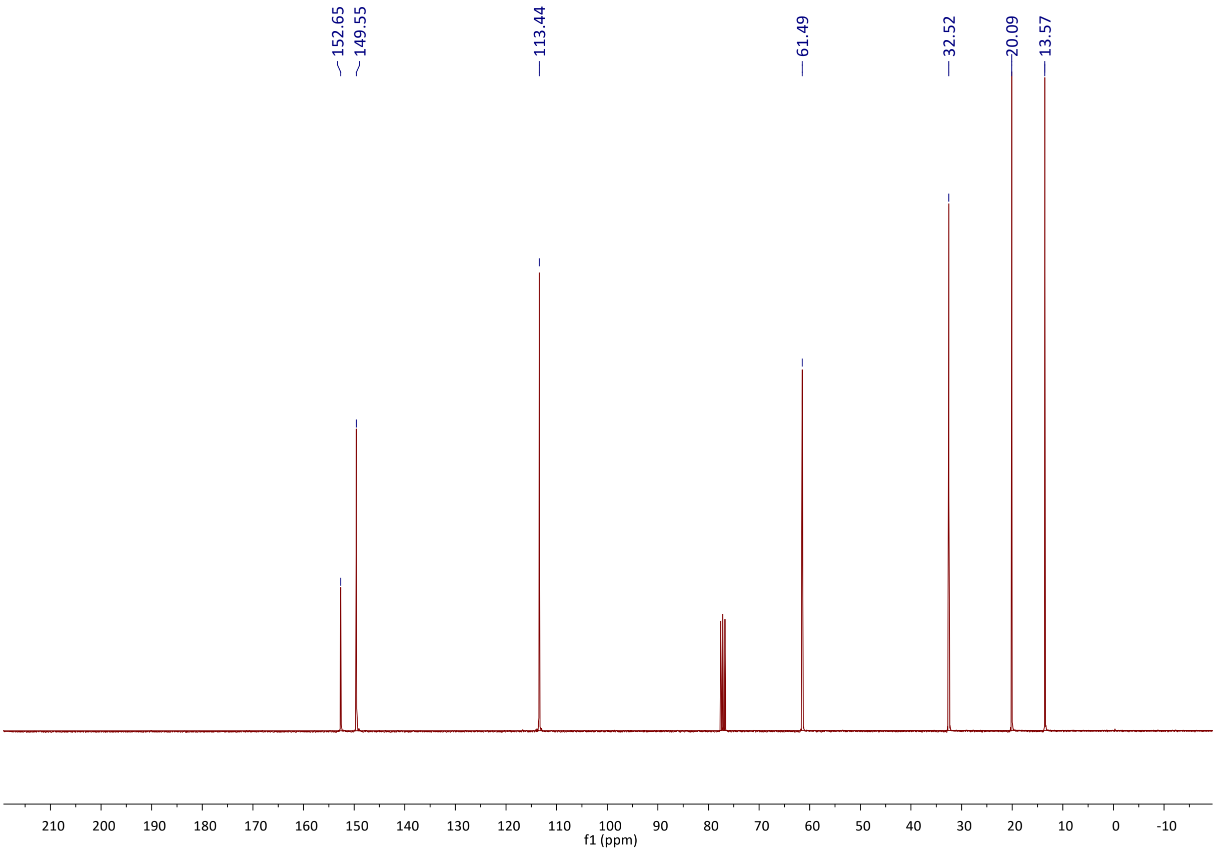
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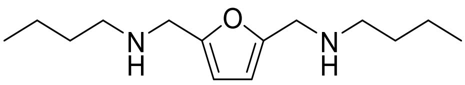
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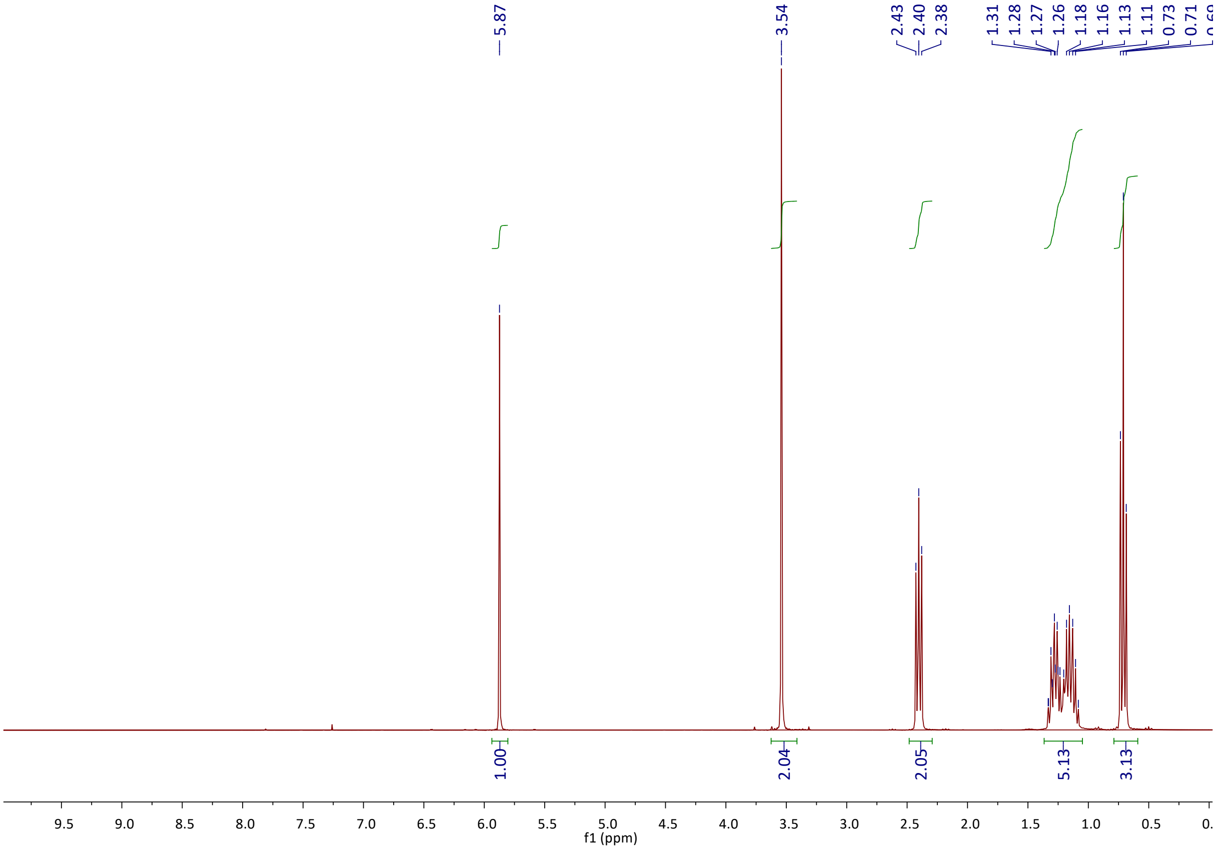
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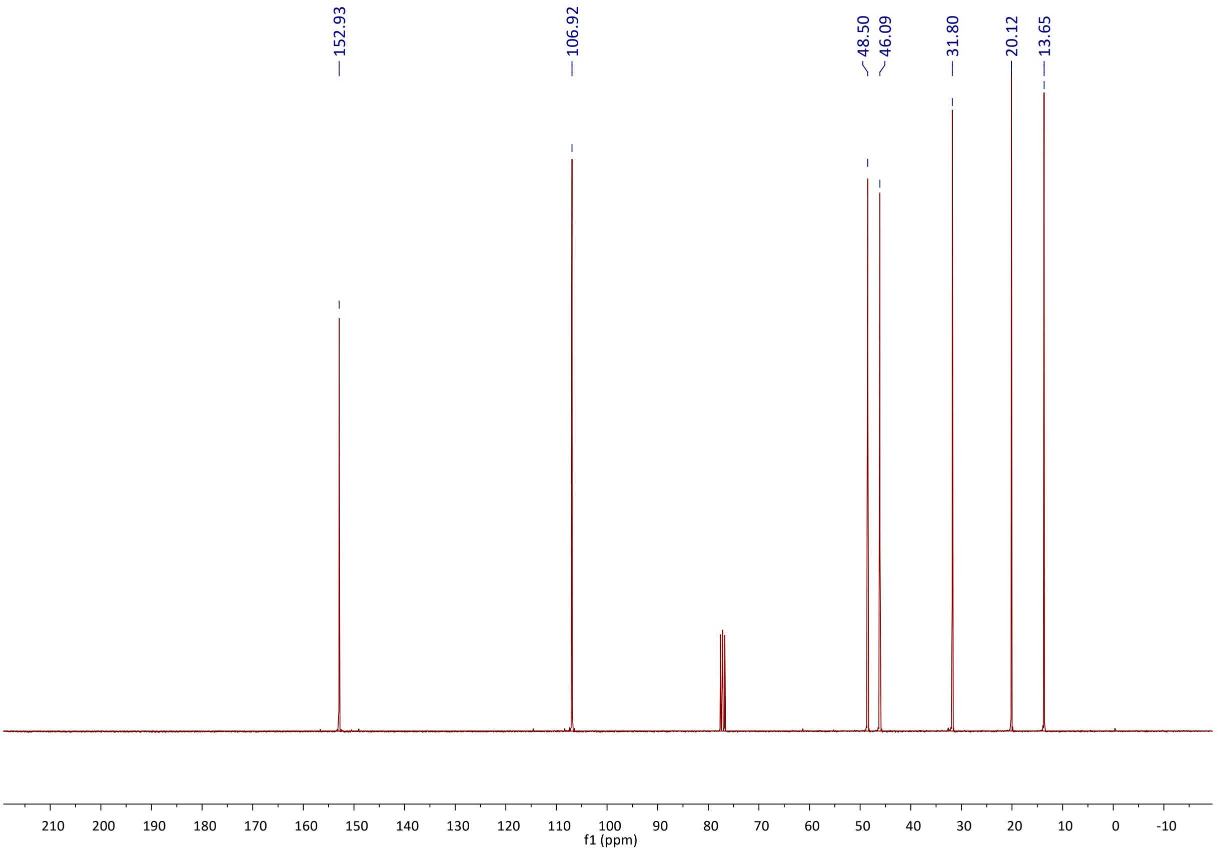
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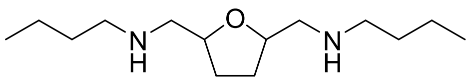
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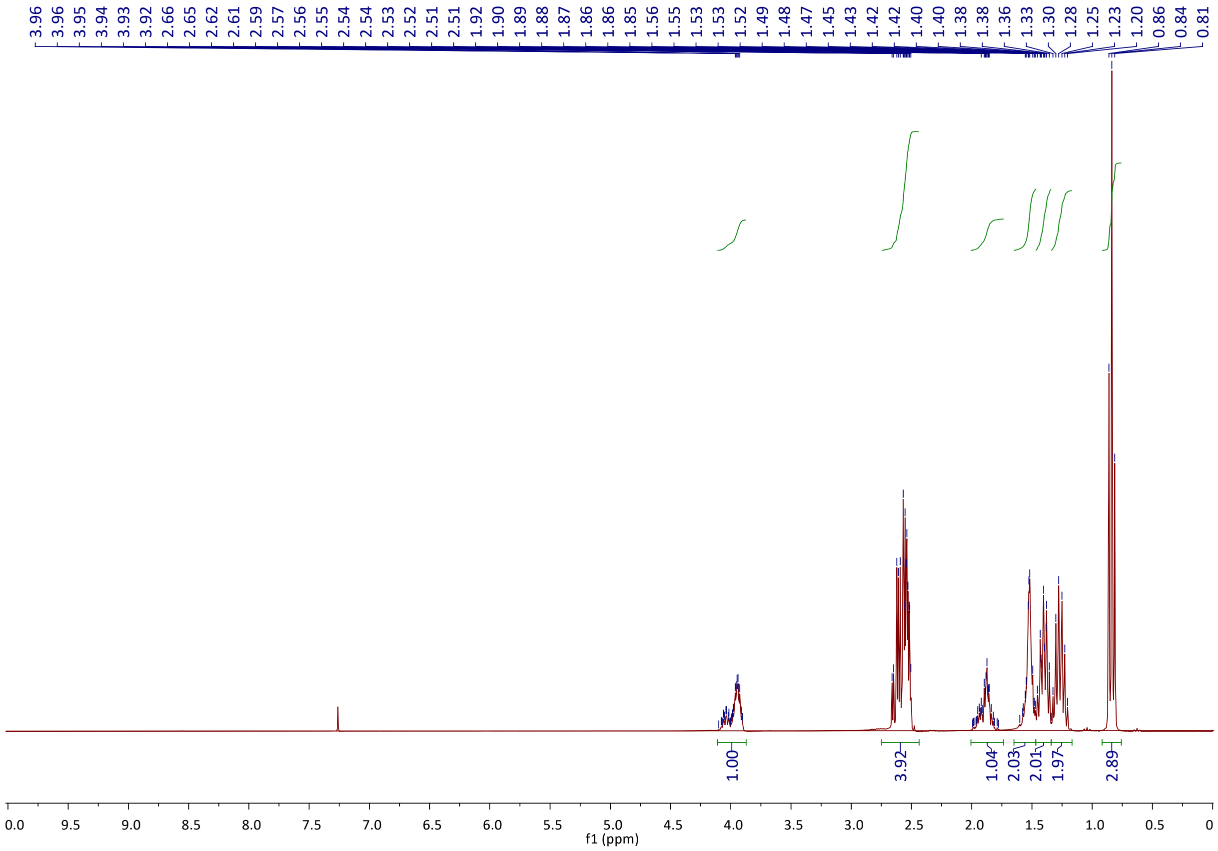
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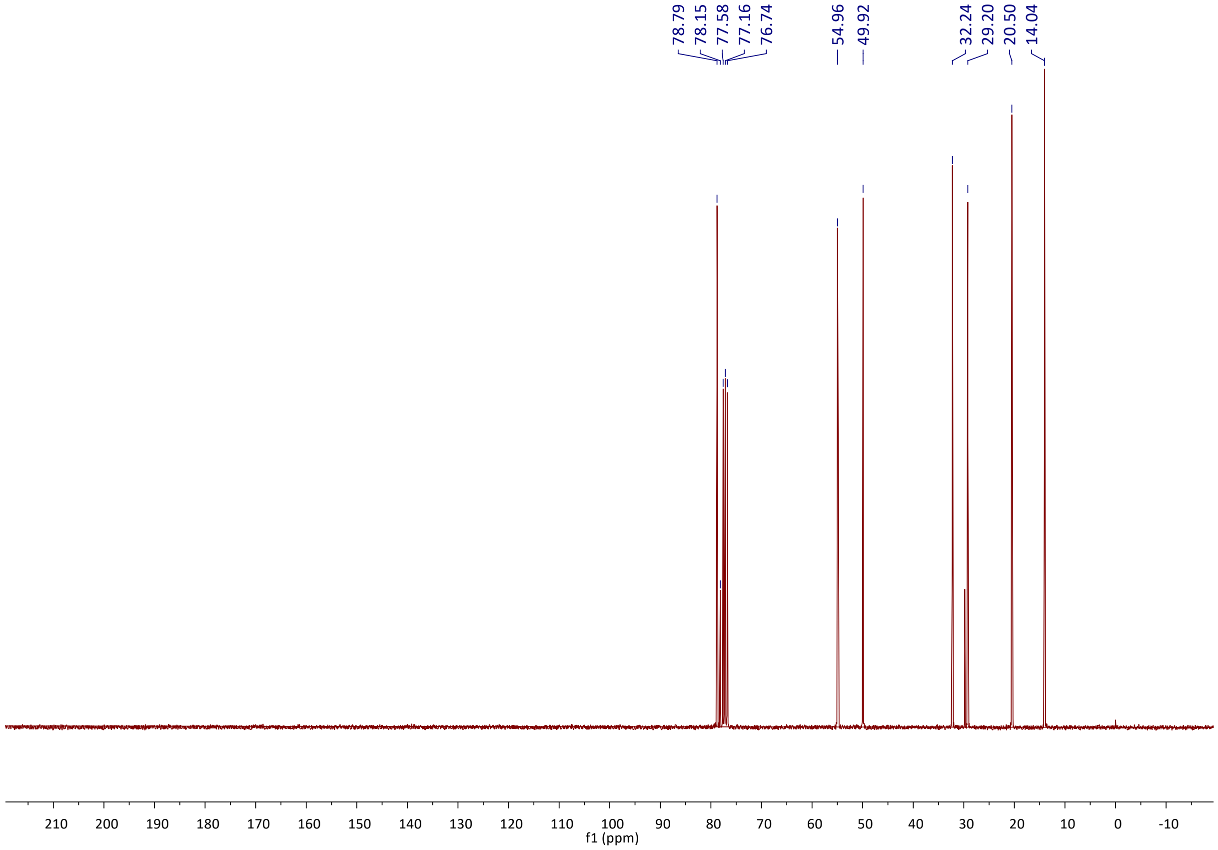
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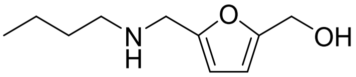
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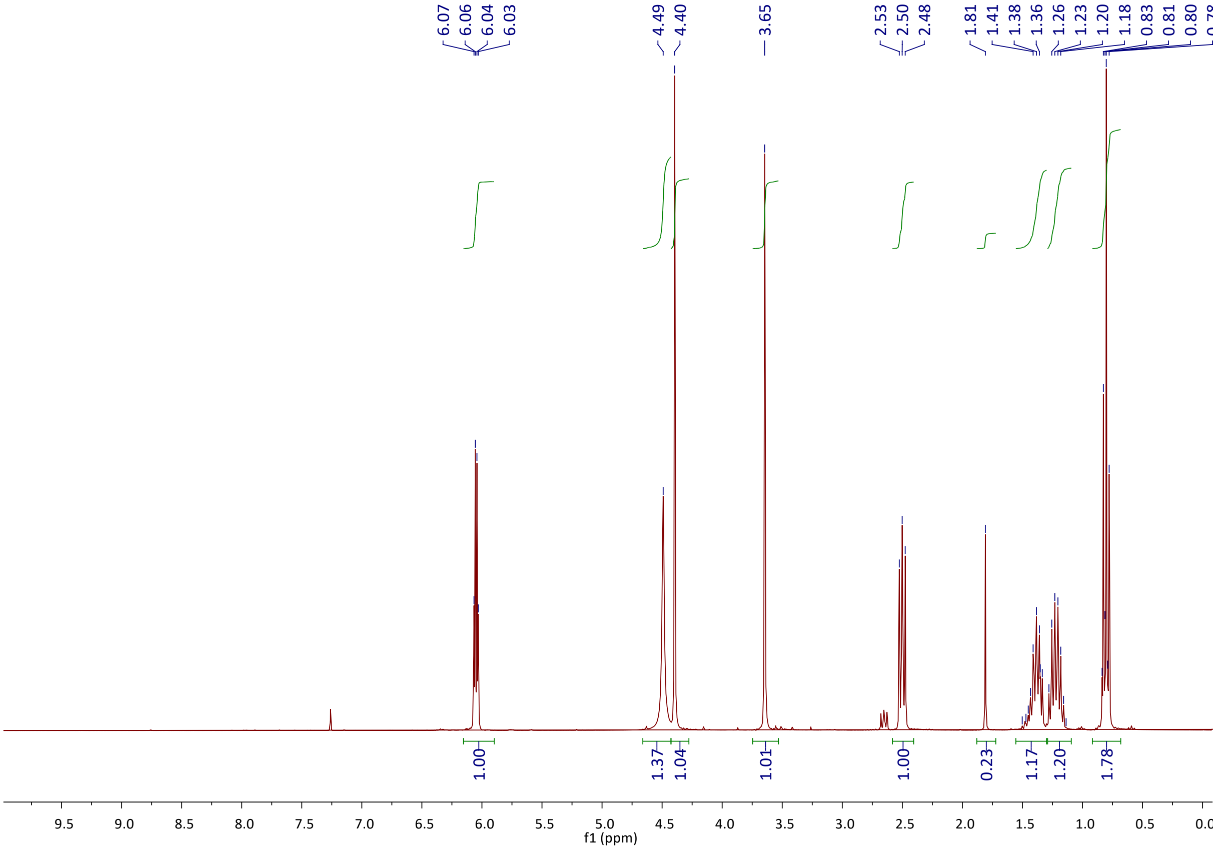
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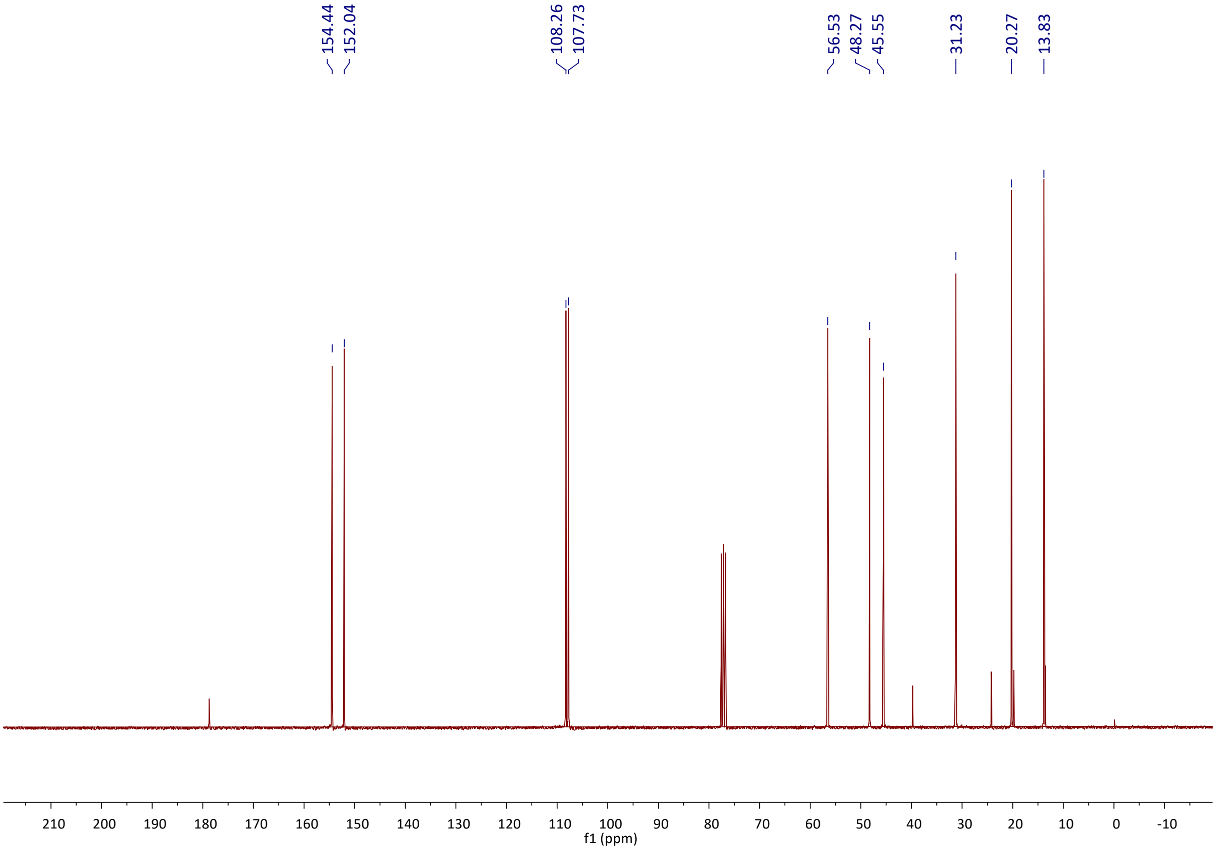
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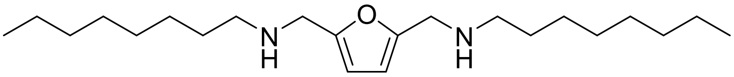
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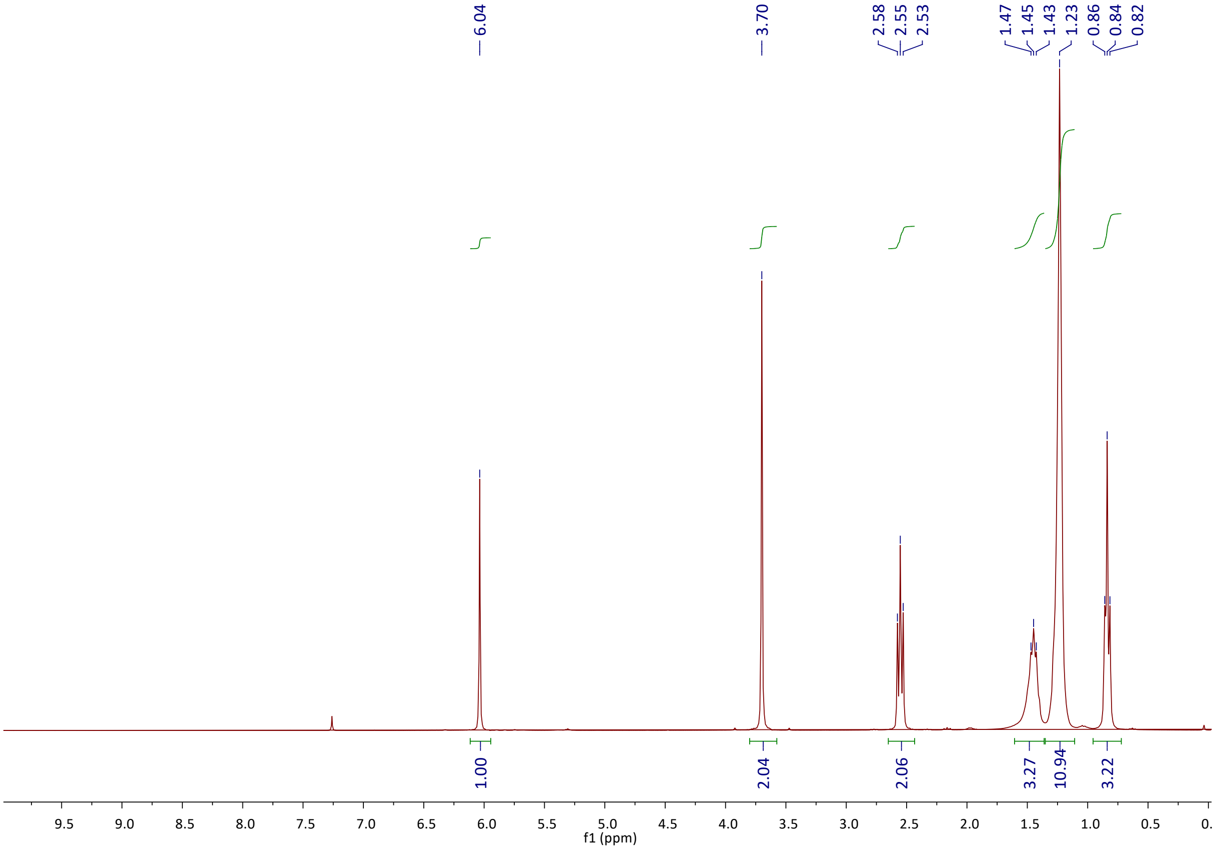
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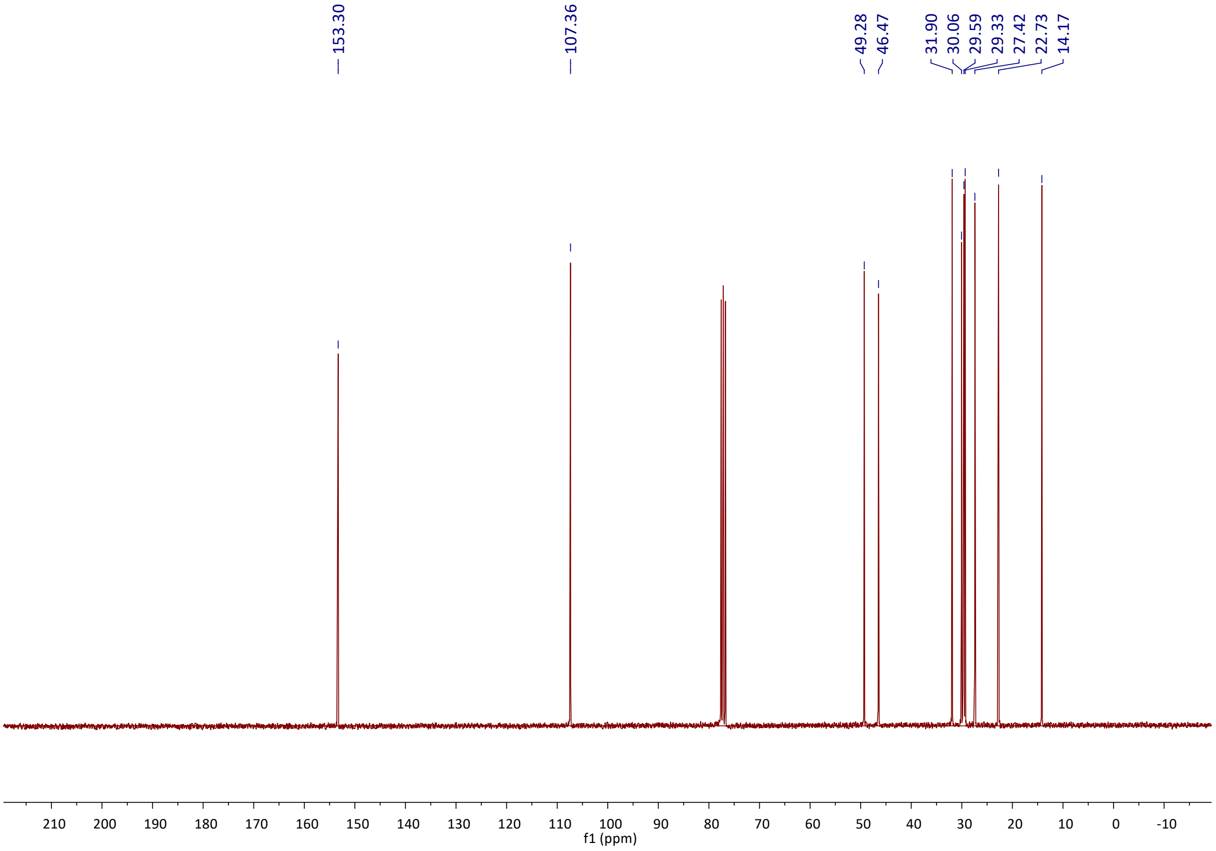
f1 (ppm)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49.28
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30.06
29.59
29.33
27.42
22.73
14.17
210
200
190
180
170
160
150
140
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110
100
90
80
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40
30
20
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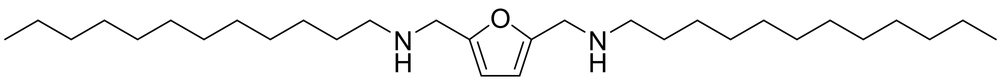
0
-10
f1 (ppm)


O
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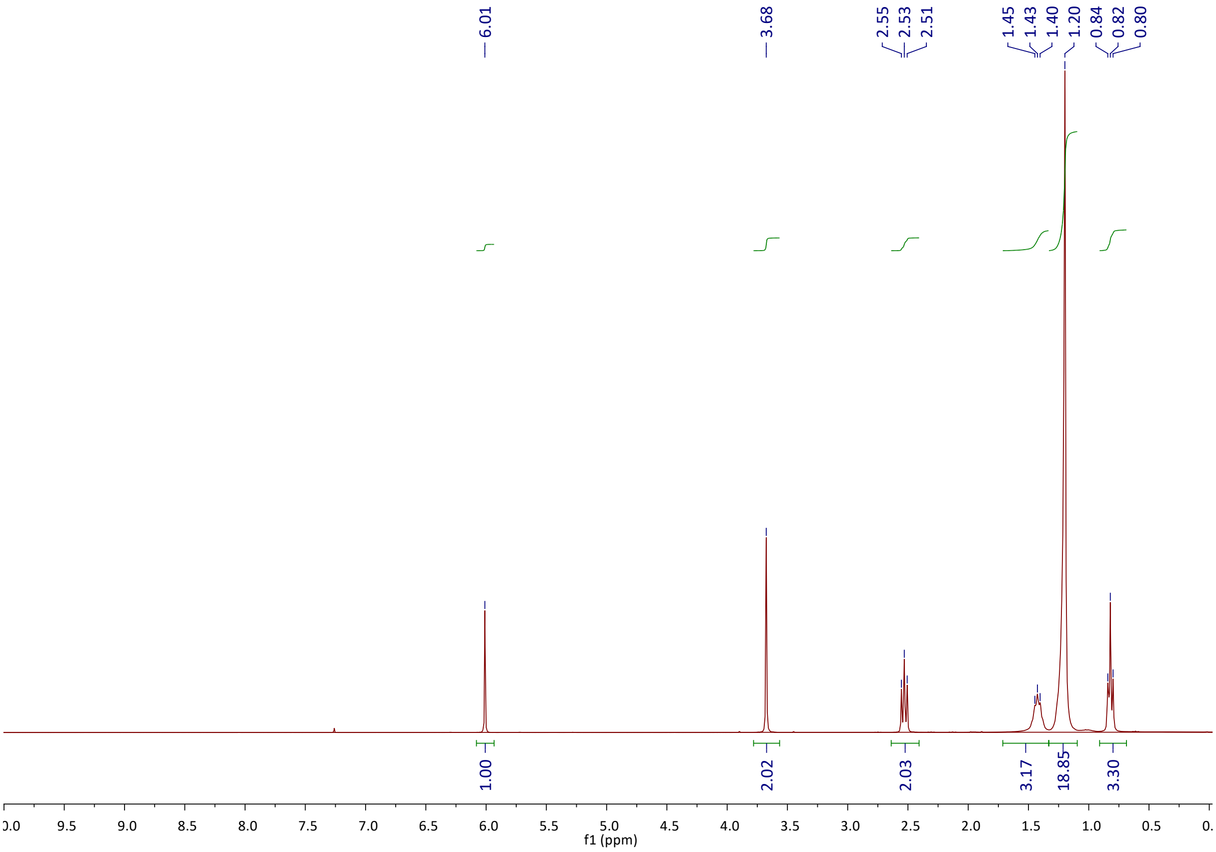
H
N
H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1.00
2.02
2.03
3.17
18.85
3.30
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
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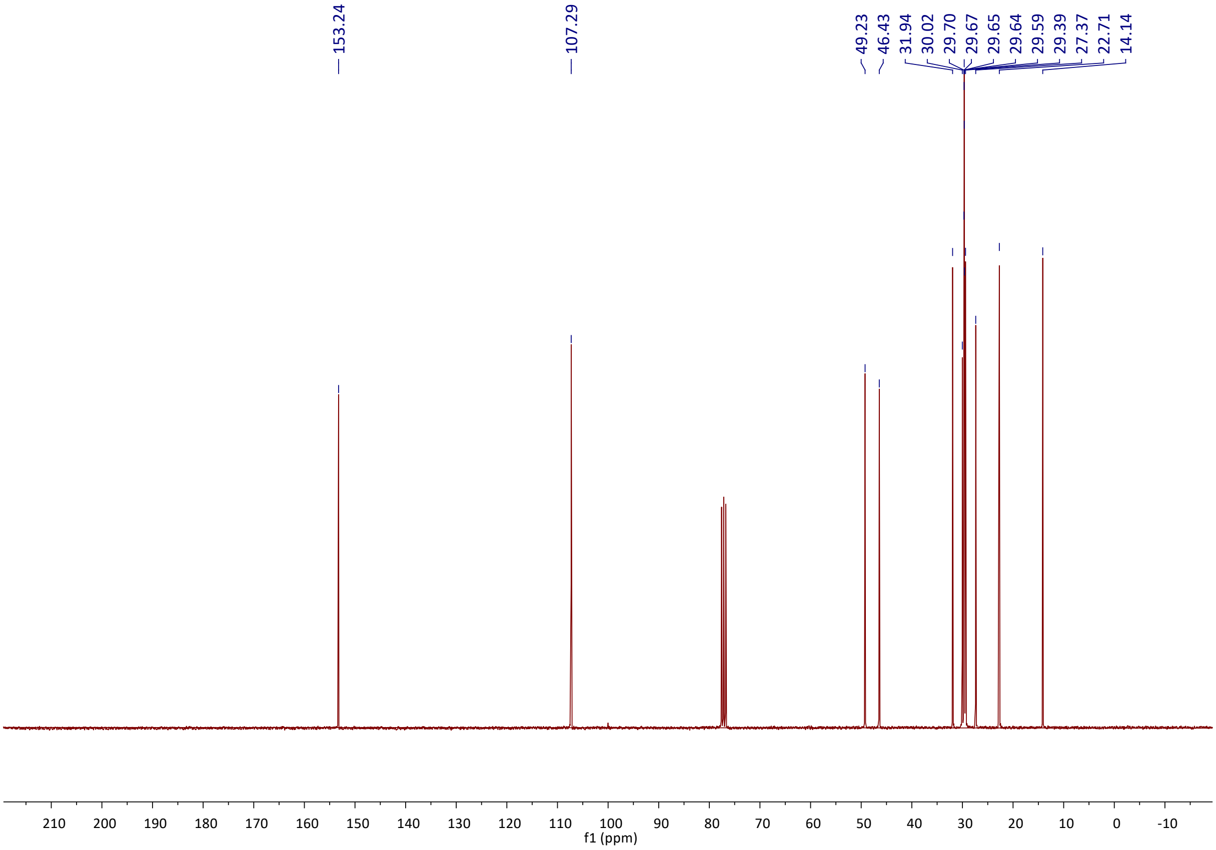
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)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29.67
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29.64
29.59
29.39
27.37
22.71
14.14
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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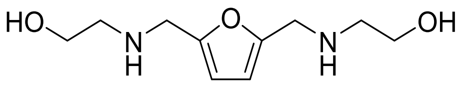
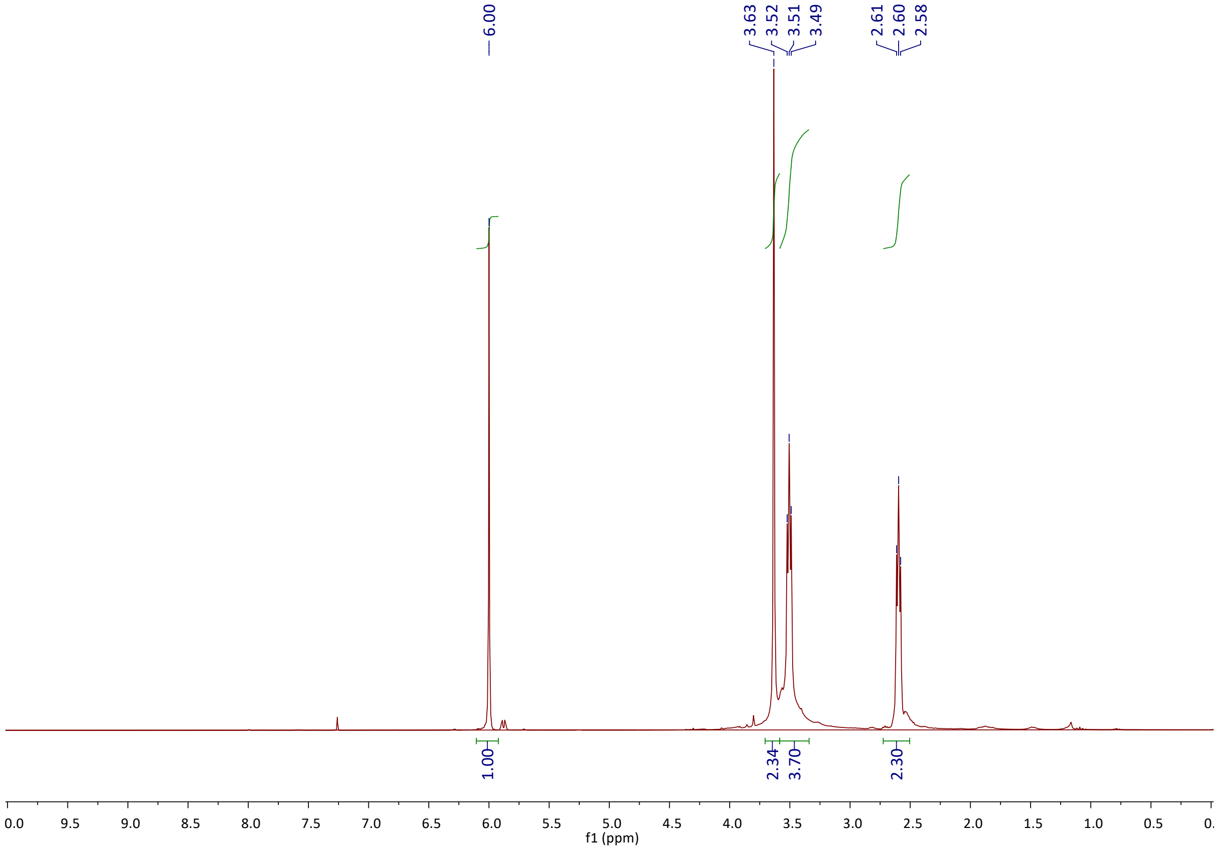
60
50
40
30
20
10
0
-10
f1 (ppm)


HO
N
H
O
N
H
OH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3.49
2.61
2.60
2.58
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2.34
3.70
2.30
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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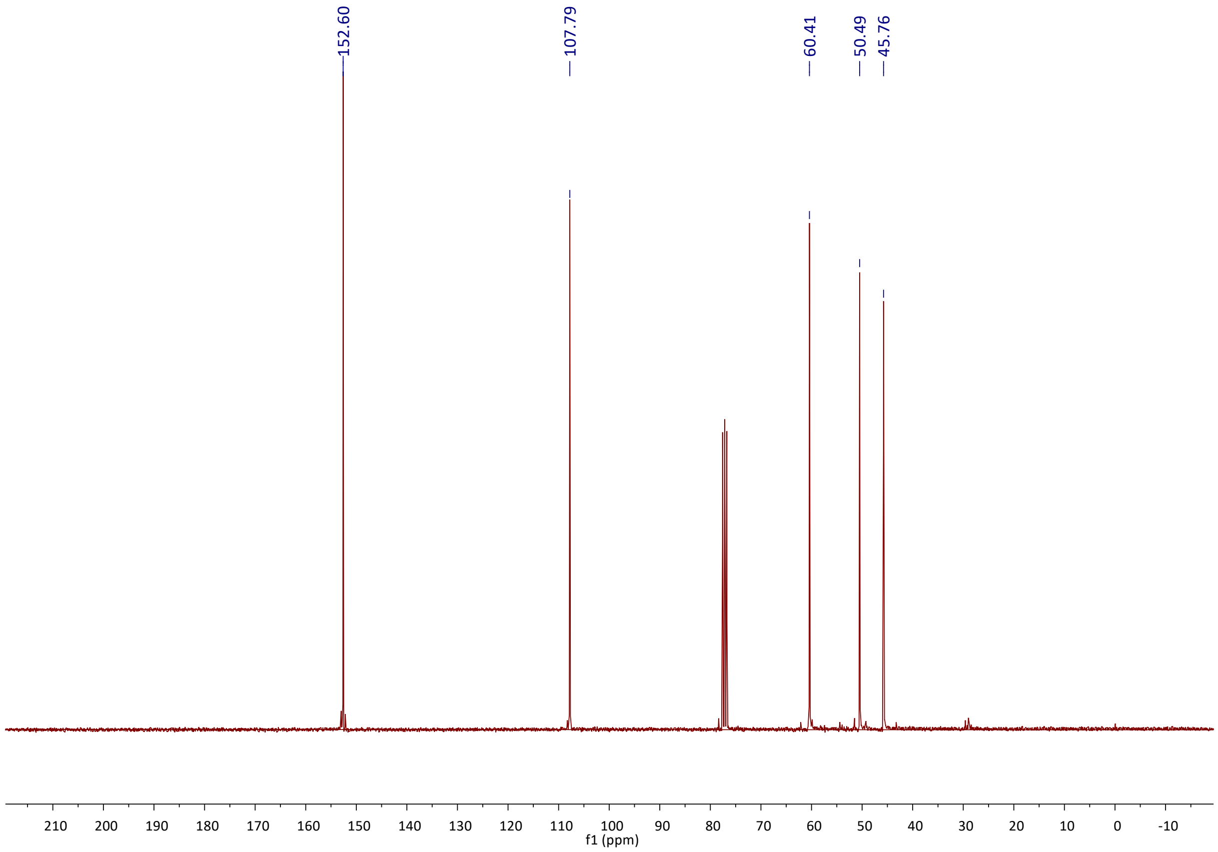
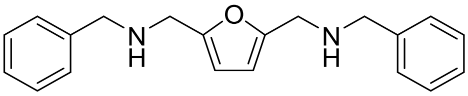
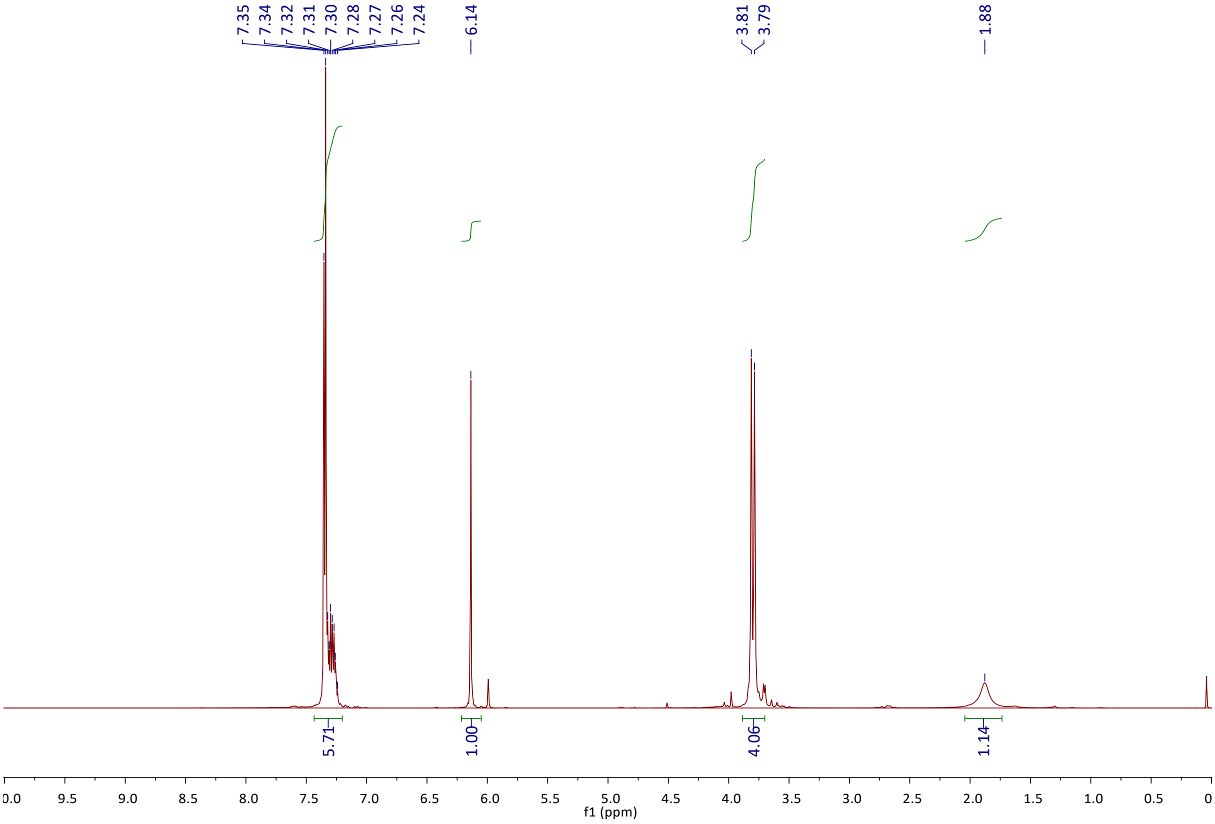
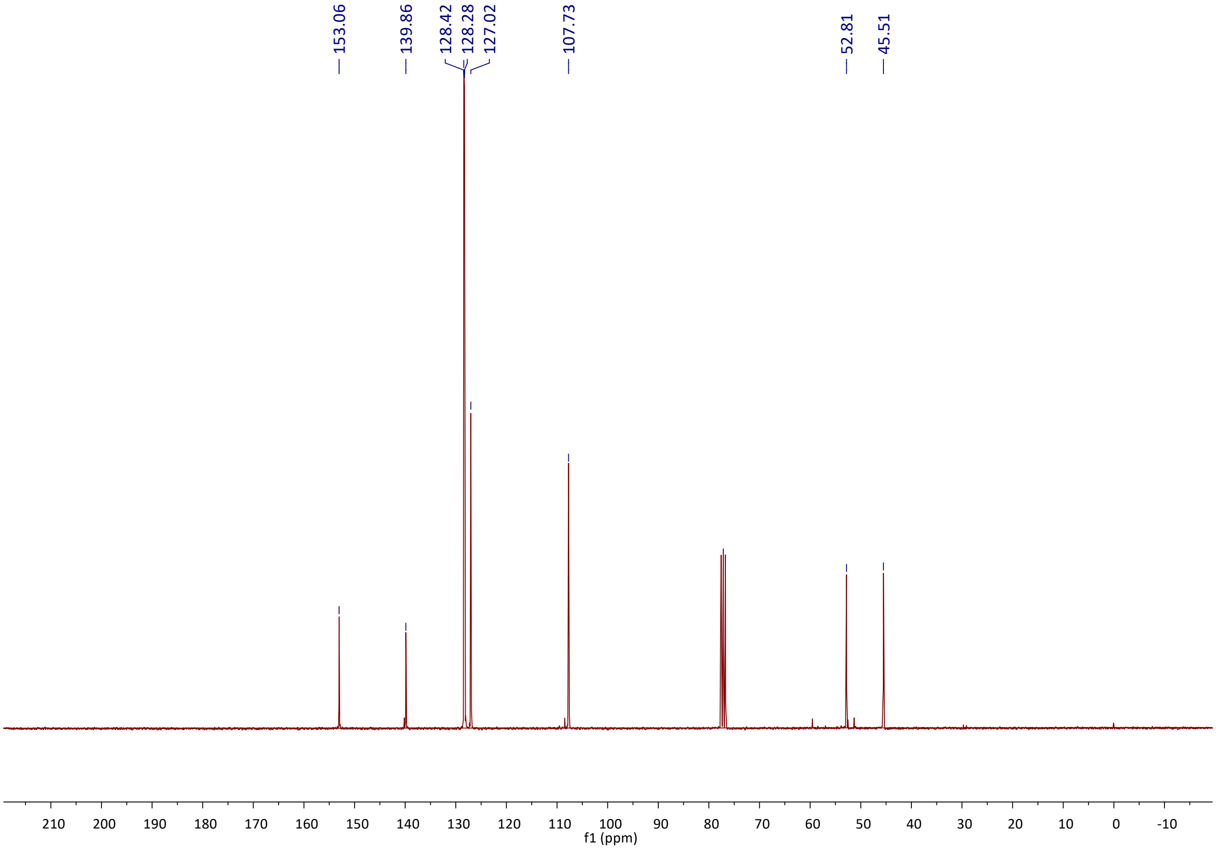
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.
f1 (ppm)


152.60
107.79
60.41
50.49
45.76
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


N
H
O
N
H


7.35
7.34
7.32
7.31
7.30
7.28
7.27
7.26
7.24
6.14
3.81
3.79
1.88
5.71
1.00
4.06
1.14
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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139.86
128.42
128.28
127.02
107.73
52.81
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210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

References

1. Z. Yan, A. Tomer, G. Perrussel, M. Ousmane, B. Katryniok, F. Dumeignil, A. Ponchel, A. Liebens and M. Pera-Titus, *ChemCatChem*, 2016, **8**, 3347.
2. J. Sha, E.-J. Zheng, W.-J. Zhou, A. Liebens and M. Pera-Titus, *J. Catal.*, 2016, **337**, 199.