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Supporting Information for:

Hf^{4+}-exchanged montmorillonite-boosted Pd-catalyzed reductive aminolysis of aryl ethers to efficiently synthesize cyclohexylamines

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Experimental Procedures

Chemicals and materials. Unless otherwise stated, all chemicals in this work were commercially available and used without further purification. Na^+-MMT was purchased from Zhejiang Sanding Co., Ltd. Hafnium dichloride oxide octahydrate (98%), and cyclooctylamine (>97%) were purchased from ALFA. Benzyl phenyl ether (98%), dodecylamine (97%), cyclohexylamine (99%), cycloheptylamine (99%), n-dodecane (99.5%), phenol (99.5%), cyclopentylamine (99%), and cyclohexanone (99.8%) were provided by TCI. Palladium on carbon (Pd/C, Pd wt% 10%, reduced, anhydrous), palladium (II) acetate (99%, Pd wt% 46.0-48.0%), *p*-xylene (99%), benzylamine (99%), butylamine (99%), 3-phenylpropylamine (98%), n-heptylamine (98%), and n-octylamine (98%) were obtained from INNOCHEM. Amylamine (99%), hexylamine (99%), and phenethoxybenzene (98%) were purchased from ALADDIN. 4-Phenylbutan-2-amine (>97%) was purchased from ACCELA. Ethanol (99.9%) was obtained from Sinopharm. The compounds of 1b-1k were synthesized according to the literatures.[S1,S2]

Synthesis of Pd/Hf-MMT. The Pd/Hf-MMT catalyst was prepared based on the procedures reported previously. Typically, 1.5 g of Na^+-MMT was dispersed in 50 mL of aqueous solution of $HfOCl_2$ (1.5 g) under sonication to form a stable suspension and stirred at 90 ^oC for 24 h. Subsequently, the treated MMT was separated via centrifugation, washed with distilled water several times to remove the unabsorbed $HfOCl_2$, and finally washed with ethanol. Then, this slurry was dried at 60 ^oC in vacuum overnight and ground to powder, which was denoted as Hf-MMT. The resultant Hf-MMT was dispersed in the $Pd(OAc)_2$ ethanol solution and stirred at room temperature for 12 h. The slurry was centrifuged and washed with distilled water three times, which was then dried at 60 ^oC in vacuum overnight, followed by reduction using hydrogen (5 °C/min) at 300 ^oC for 6 h, resulting in brown-yellow Pd/Hf-MMT powder. The loading content of Pd in Pd/Hf-MMT was 2 wt% as determined by ICP-AES. For comparison, Pd/MMT was prepared via dispersing MMT in the $Pd(OAc)_2$ ethanol solution to adsorb Pd^{2+} onto the MMT support, followed by hydrogen reduction at 300 ^oC for 6 h.

Reductive aminolysis of aryl ethers. In a typical experiment, aryl ether (0.5 mmol), amine (1 mmol), Pd/Hf-MMT (1 mol% Pd metal based on aryl ether), and *p*-xylene (2 mL) were added into a stainless-steel reactor of 15 mL with a Teflon coating. After the air in the autoclave was replaced by hydrogen (three times), the autoclave was pressurized to the desired pressure with H_2. Then, the autoclave was placed into a constant-temperature air bath and heated to the desired temperature, and the reactions were conducted with a stirring rate of 800 rpm for the desired reaction time. After the reaction was completed, the products were analyzed quantitatively using n-dodecane as the internal standard by gas chromatography (GC) and gas chromatography coupled with mass spectroscopy (GC-MS). In addition, to ensure the reliability of the obtained results, each experiment was repeated three times under the same reaction conditions.

Recyclability of Pd/Hf-MMT. To test the recyclability of Pd/Hf-MMT, the catalyst was separated from the reaction system by filtration, washed with ethanol for 5 times, and then dried under oven at 60 ^oC for 12 h. The sample was collected and transferred into a ceramic boat, and was reduced in a tubular furnace under H_2/Ar atmosphere (containing 90% Ar) with a flow rate of 100 mL min^{-1}. The sample was heated with a heating rate of 5 ^oC min^{-1} from room temperature to 300 ^oC and held at this temperature for 6 h. Afterwards, the tubular furnace was cooled down to room temperature. Finally, the catalyst was reused in the next catalytic cycle.

Synthesis of the standard products. Because there were no commercial resources, we pre-synthesized the products as the standards. Taking the synthesis of *N*-dodecyl cyclohexylamine as an example, benzyl phenyl ether (0.5 mmol), dodecylamine (1 mmol), Pd/Hf-MMT (1 mol% Pd metal based on benzyl phenyl ether), and *p*-xylene (2 mL) were added into a stainless-steel reactor of 15 mL with a Teflon coating. After the air in the autoclave was replaced by hydrogen (three times), the autoclave was pressurized to the desired pressure with H_2 (0.3 MPa). Then, the autoclave was placed into a constant-temperature air bath and heated to the desired temperature (90 ^oC), and the reactions were conducted with a stirring rate of 800 rpm for the desired reaction time

(4 h). After the reaction, pure *N*-dodecyl cyclohexylamine was obtained by column chromatography (silica gel) using petroleum ether/EtOAc (1:1, 500 mL), and subsequently pure EtOAc as the elution solvent. Additionally, similar routes were employed to prepare other standard products.

Instruments. Conversions and yields were determined by a gas chromatography (Agilent 8890B) with the FID detector and a HP-5 column (30 m x 320 μm x 0.25μm). ^{1}H, and ^{13}C NMR data were recorded on a Bruker ARX 400 and Bruker ARX 500 spectrometers using DMSO-d_6 or CD_3OD solvents. X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer using Cu Kα radiation at 35 kV and 25 mA (λ = 1.5405 Å) over a 2θ ranging from 5 to 90 ^{o}C at a scanning speed of 5°/min. X-ray photoelectron spectroscopy (XPS) was worked with Al kα (*hv* = 1486.36 eV) radiation with a Thermo Scientific K-Alpha spectrometer. The crystal morphology and size were determined by scanning electron microscopy (SEM) on a Hitachi S-4800 microscope and transmission electron microscopy (TEM) on a JEOL JEM-2100F microscope at an accelerating voltage of 200 kV. The scanning electron microscopy (SEM) was performed on a German ZEISS Sigma 300. The Pd and Hf contents were quantified by inductively coupled plasma emission spectrometer (ICP-OES) on an Optima 8300. Nitrogen sorption isotherms were obtained at 77 K by using a BEL-SORP-MAX instrument after degassing the samples for 8 h under vacuum at 473 K. The specific surface area was measured using the Brunauer-Emmett-Teller (BET) analysis method. Temperature programmed desorptionon was conducted on AutoChem Discovery and AutoChem 2920.

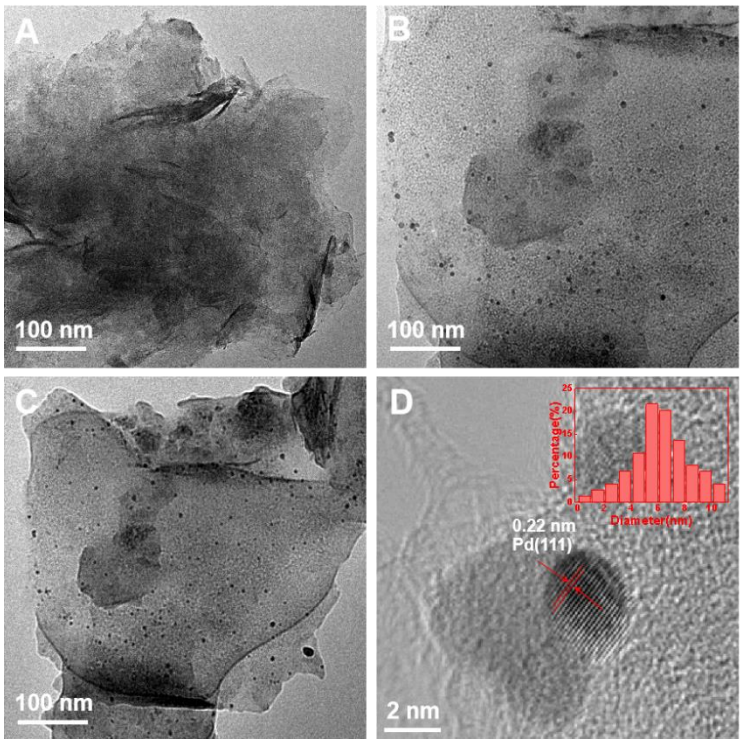


Fig. S1. TEM images of (A) MMT, (B) Pd/MMT, and (C and D) Pd/Hf-MMT.

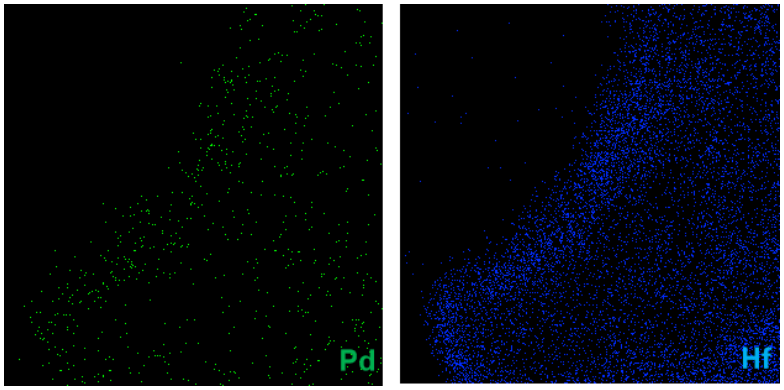


Fig. S2. Elemental distribution mapping of Pd/Hf-MMT.

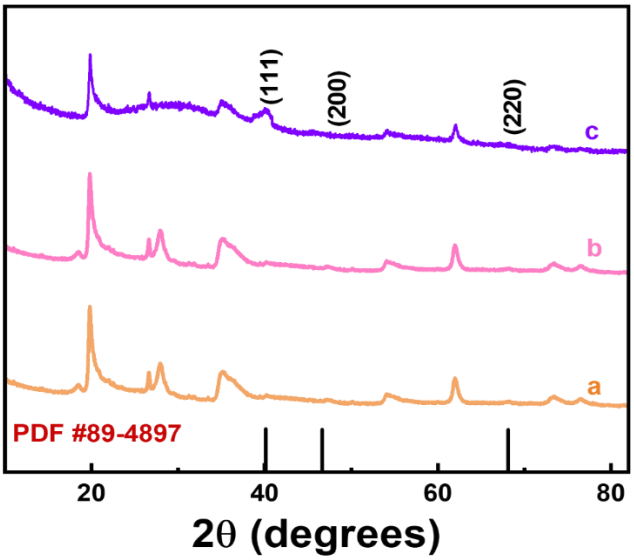


Fig. S3. Powder XRD patterns. (a) MMT, (b) Pd/MMT, and (c) Pd/Hf-MMT.

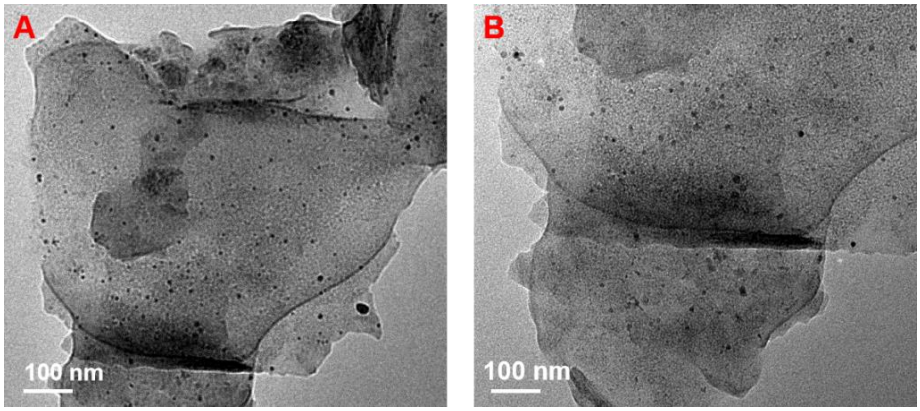


Fig. S4. TEM image of (A) the fresh Pd/Hf-MMT, and (B) the recovered Pd/Hf-MMT.

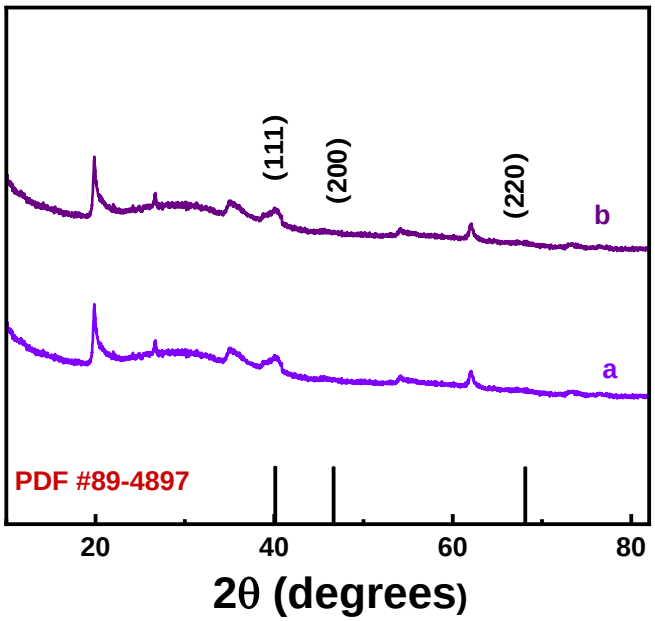


Fig. S5. Powder XRD patterns. (a) The fresh Pd/Hf-MMT, and (b) the recovered Pd/Hf-MMT.

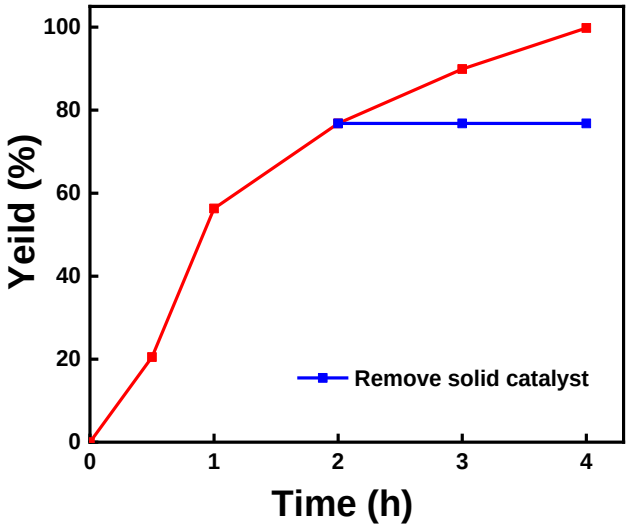


Fig. S6. Time-yield plots for reductive amination of benzyl phenyl ether with Pd/Hf-MMT (Red line) or removing Pd/Hf-MMT after 2 h (Blue line). Reaction conditions: benzyl phenyl ether, 0.5 mmol; dodecylamine, 1 mmol; *p*-xylene, 2 mL; 90 °C; 4 h; Pd/Hf-MMT, 25 mg; H_2, 0.3 MPa.

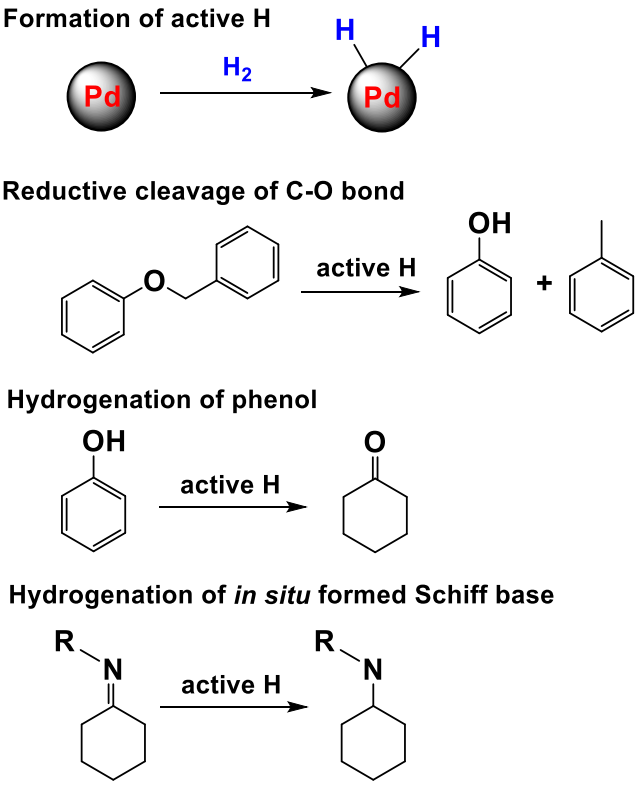


Fig. S7. Reductive steps in the conversion process.

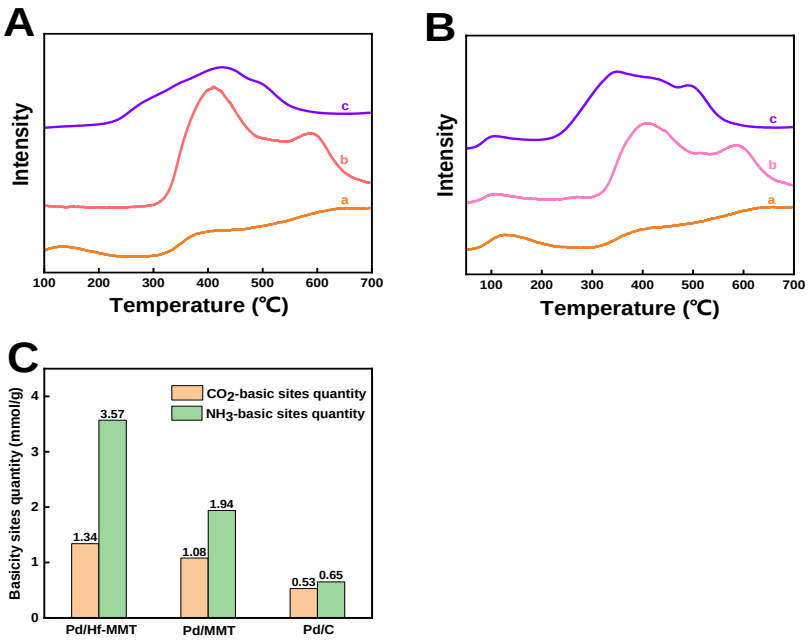


Fig. S8. (A) CO_2-TPD profile, (B) NH_3-TPD profile, and (C) quantity of acidic or basic sites in different catalysts. In A and B, a, b, and c represented MMT, Pd/MMT, and Pd/Hf-MMT, respectively.

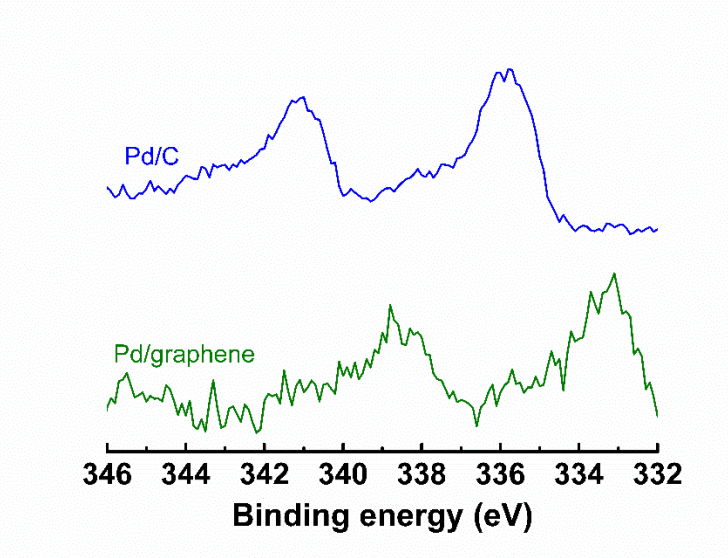


Fig. S9. XPS spectra of Pd 3d in Pd/C and Pd/graphene.

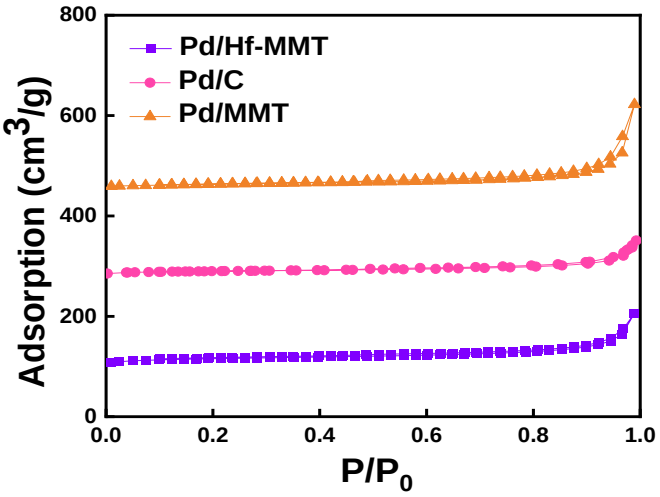


Fig. S10. N_2 adsorption-desorption isotherms of different materials.

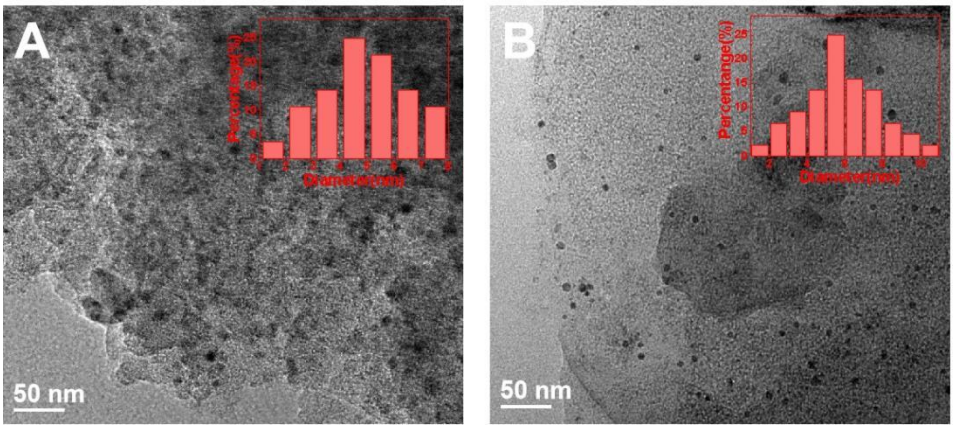
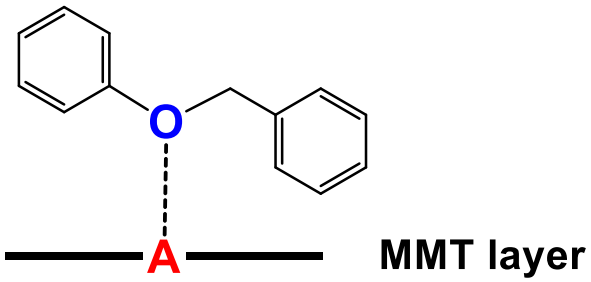


Fig. S11. TEM images and particle size distribution of (A) Pd/C, and (B) Pd/MMT.



A: acidic sites on MMT

Scheme S1. The interaction between the acidic sites on MMT and the O atom of the benzyl phenyl ether.

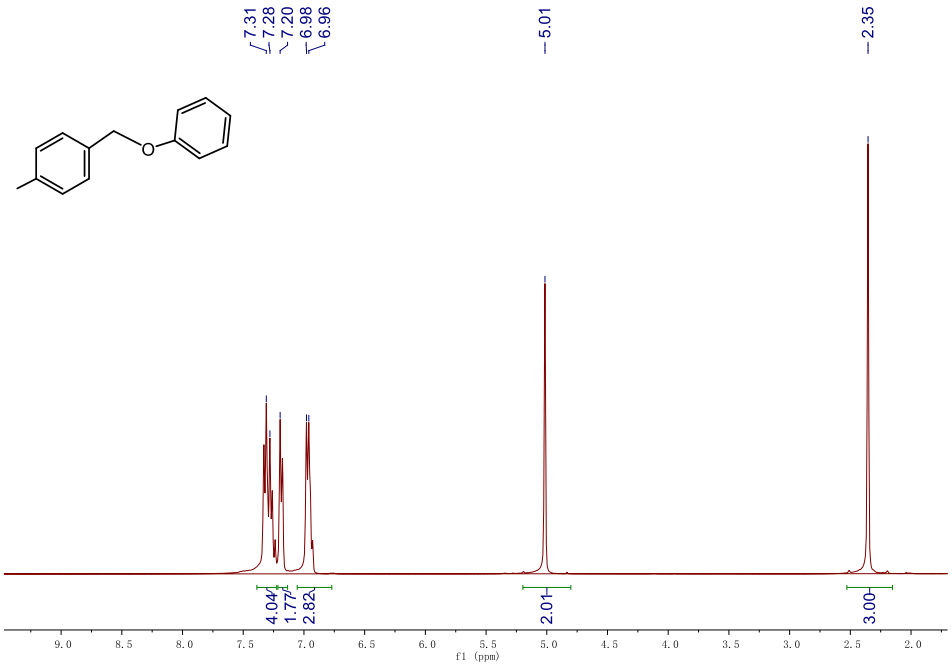
Table S1. ICP-OES analysis of different catalysts.

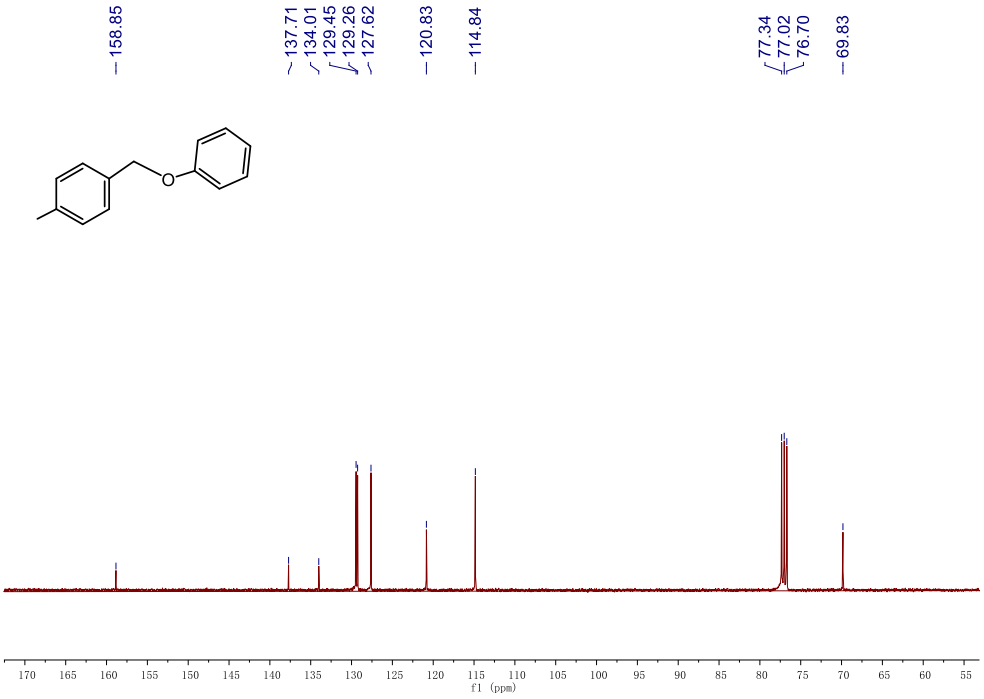
Entry	Catalyst	Pd (wt%)	Hf (wt%)
1	Pd/MMT	2	0
2	Pd/Hf-MMT	2	10.2
3	Pd/Hf-MMT (used)	1.9	10
4	Reaction solution	0	0

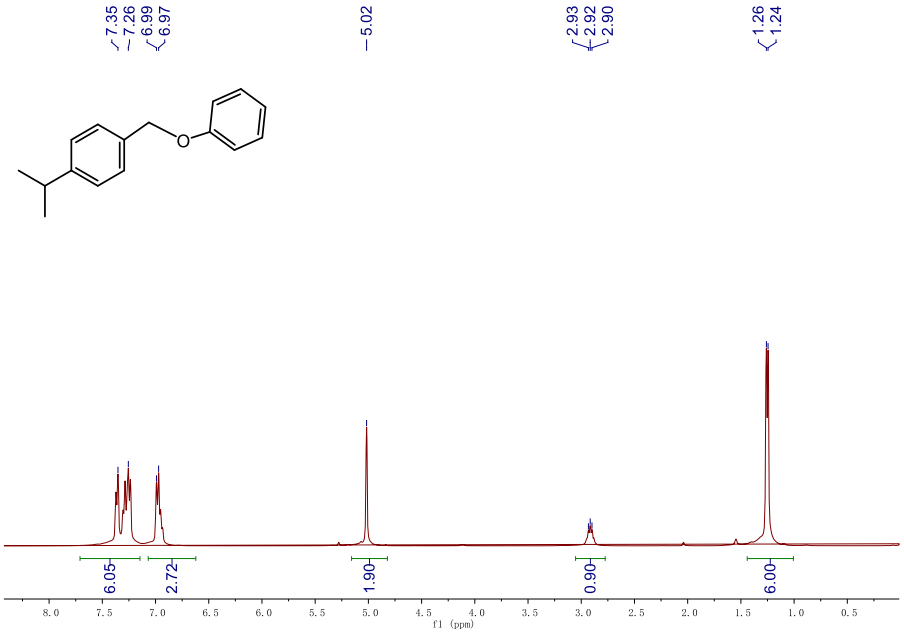
Table S2. Summary of the results from N_2 adsorption-desorption.

Entry	Catalyst	BET surface area (m^2g^{-1})
1	Pd/MMT	35.1
2	Pd/C	112.4
3	Pd/Hf-MMT	78.1

^{1}H NMR and ^{13}C NMR Data



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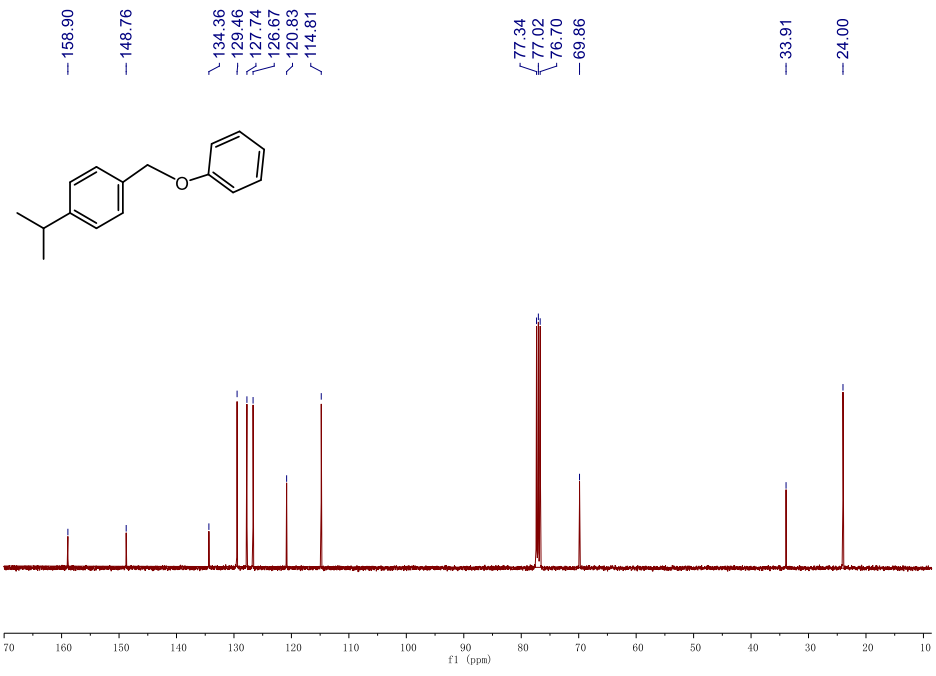
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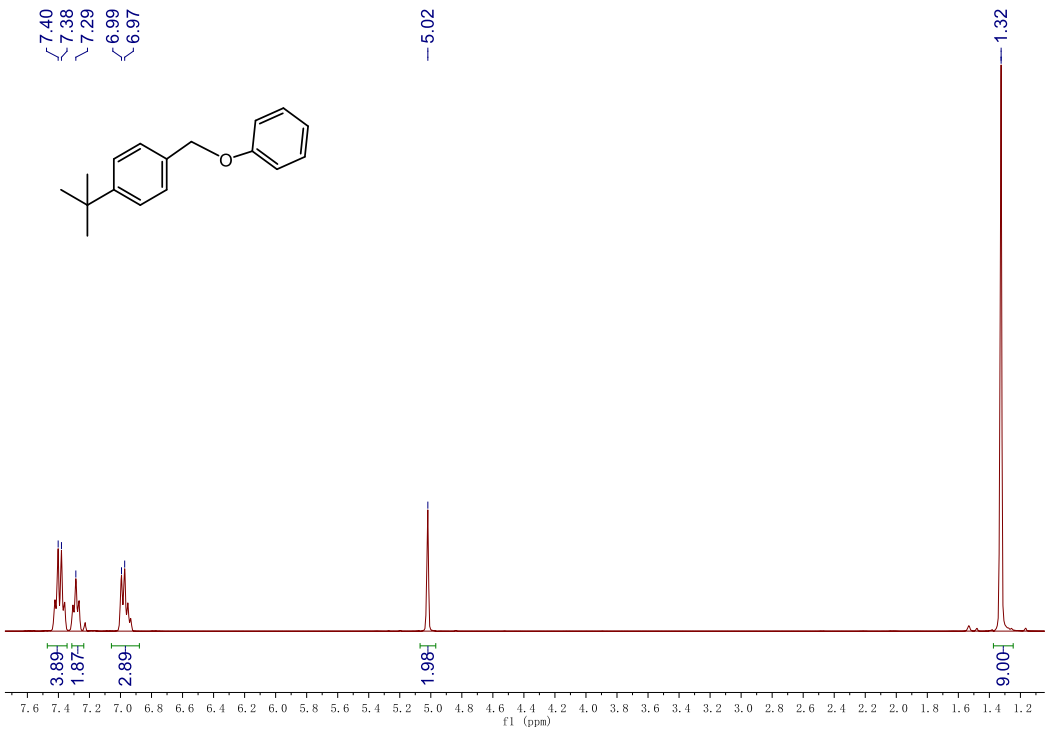
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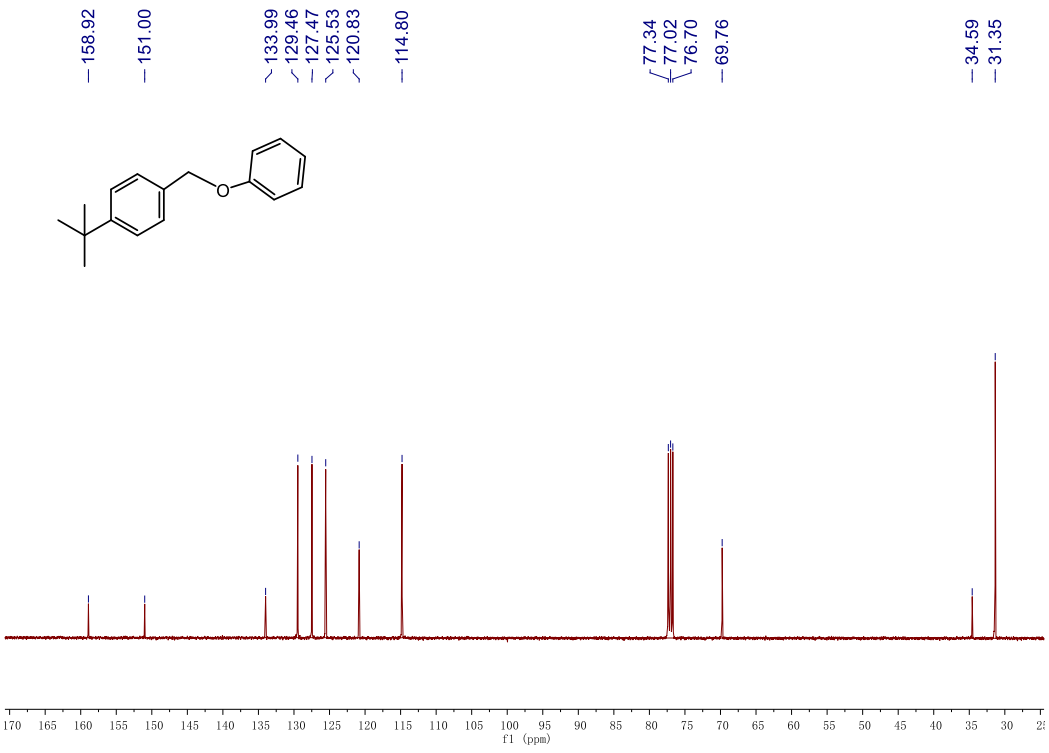
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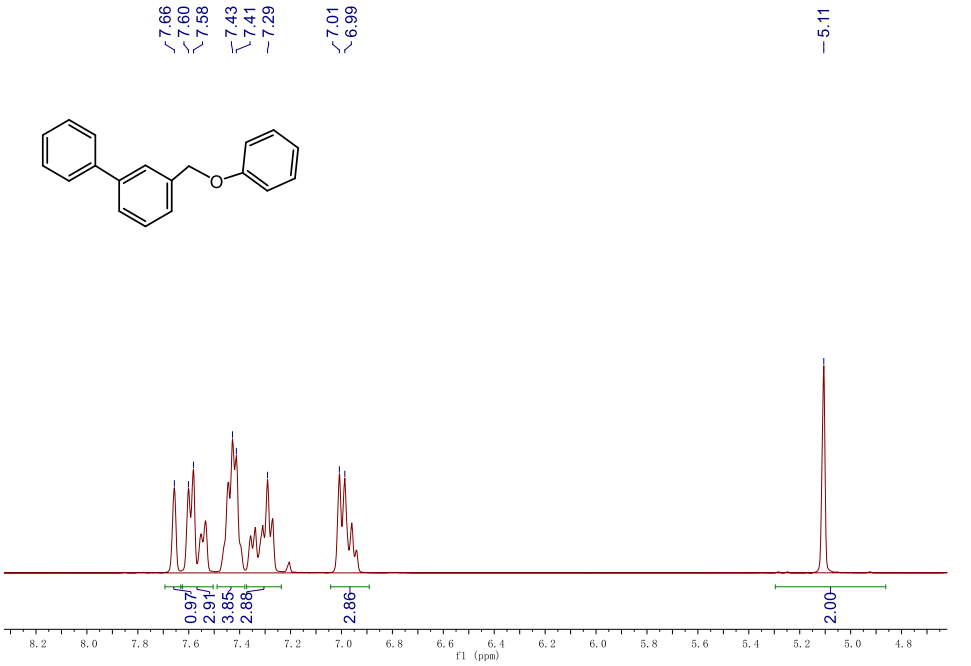
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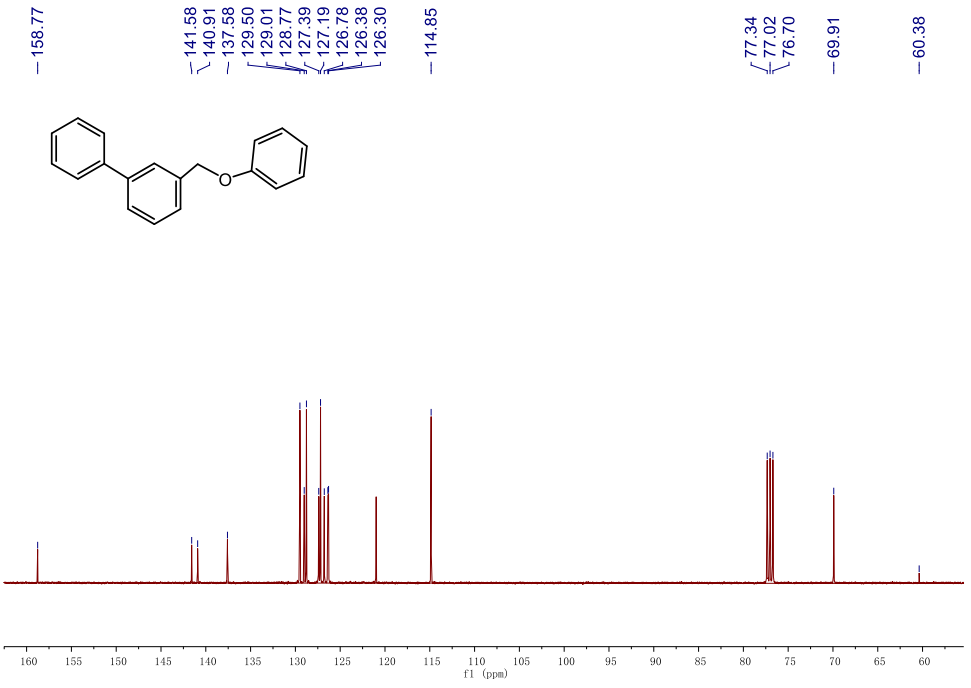
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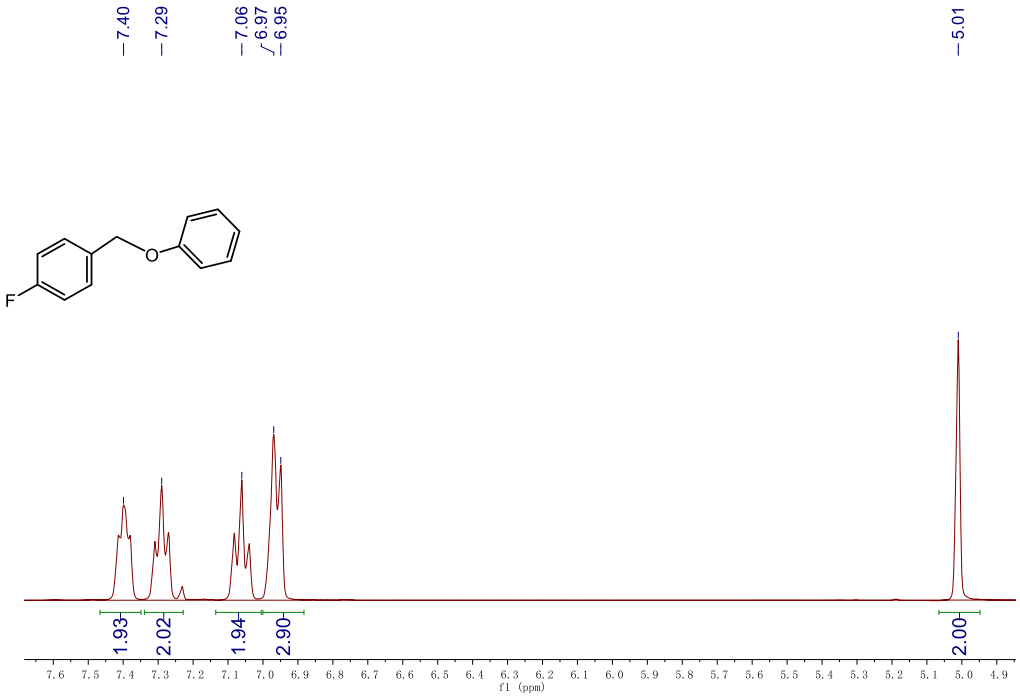
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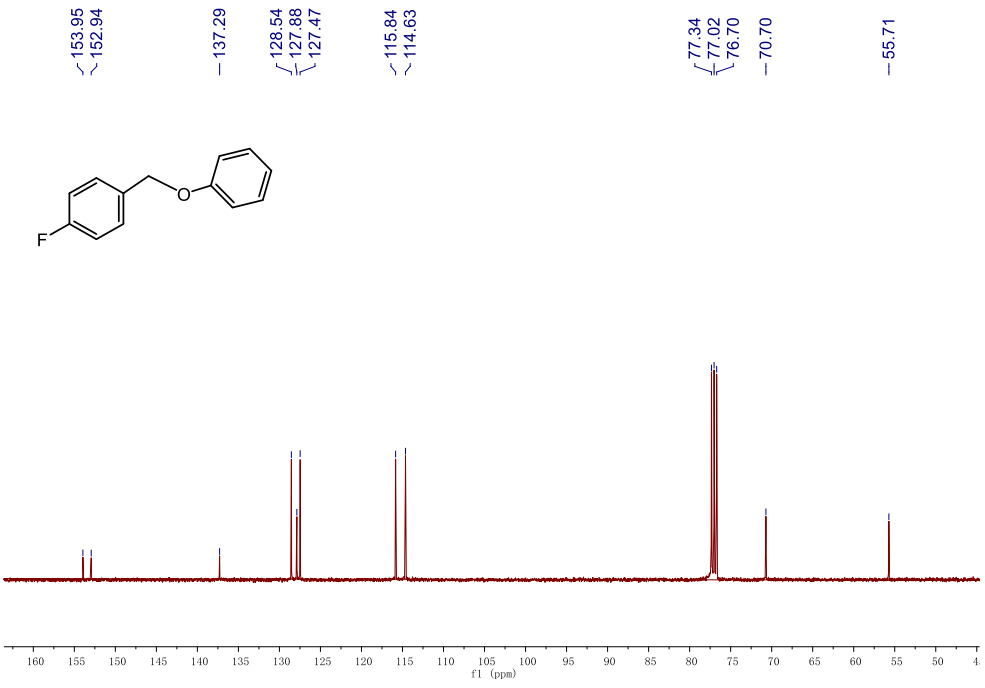
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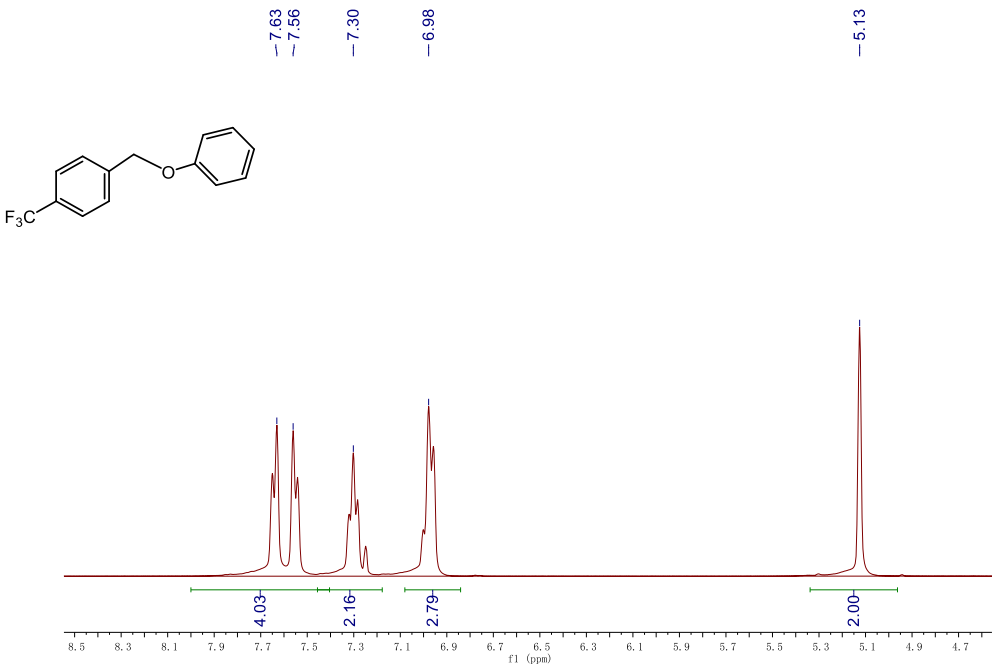
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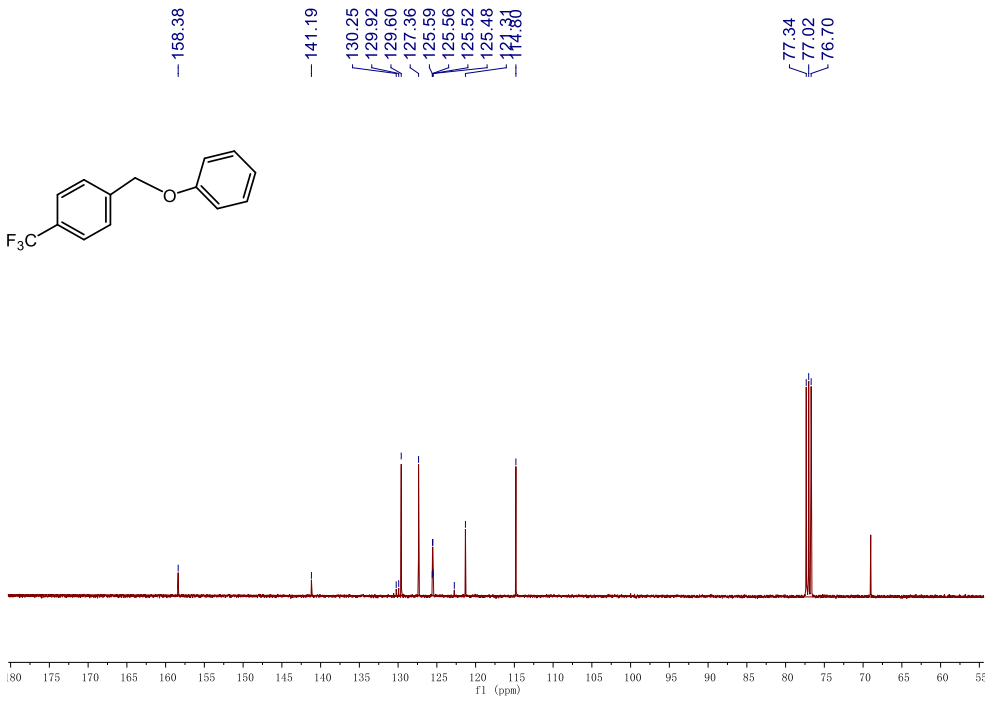
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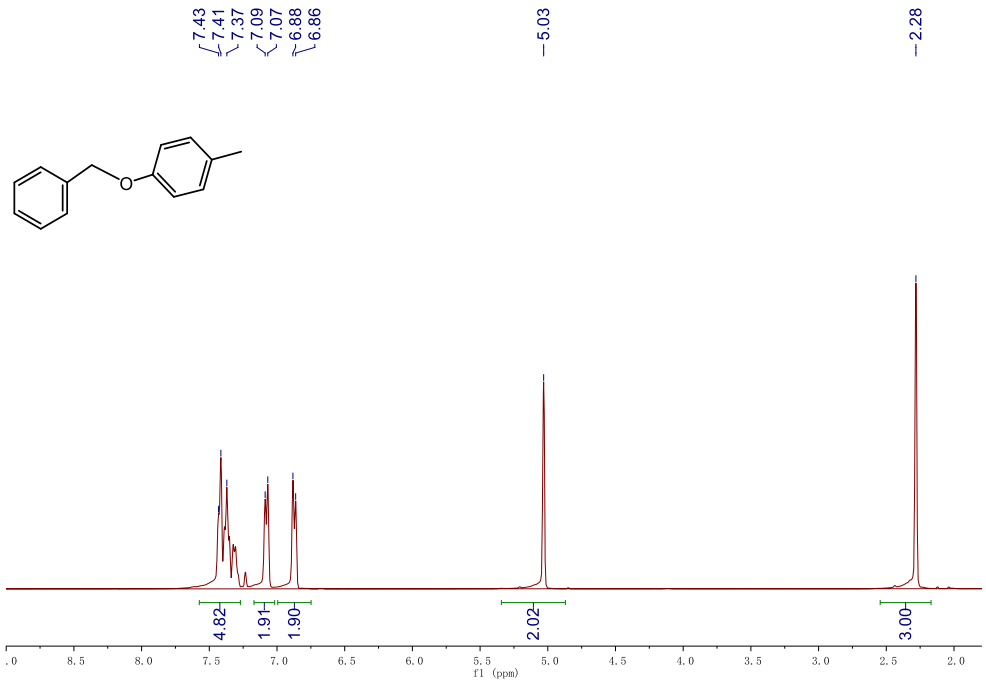
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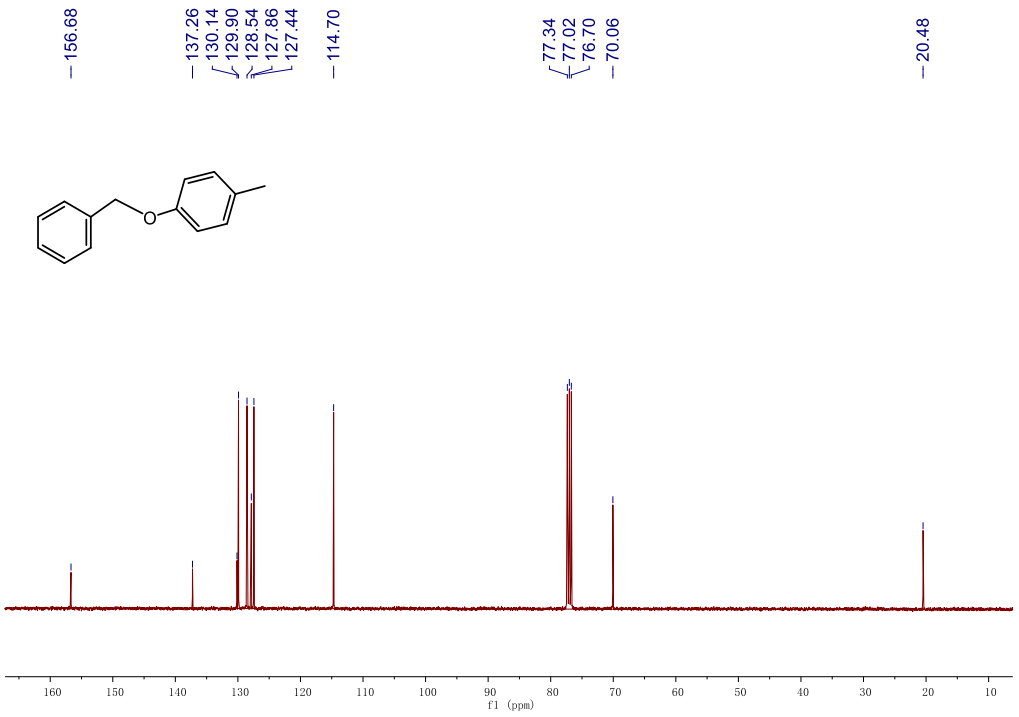
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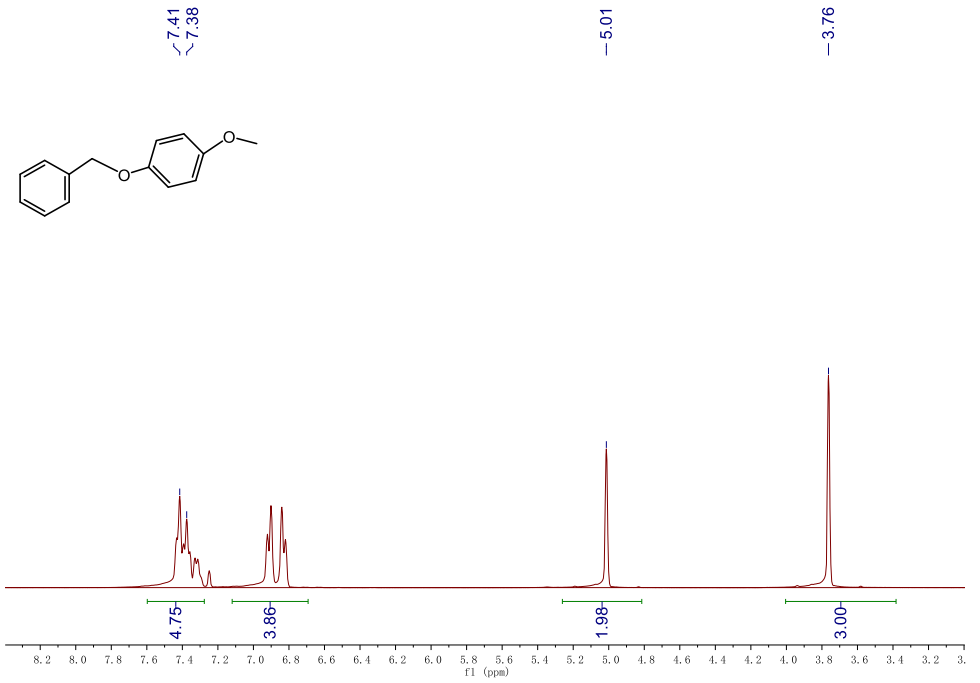
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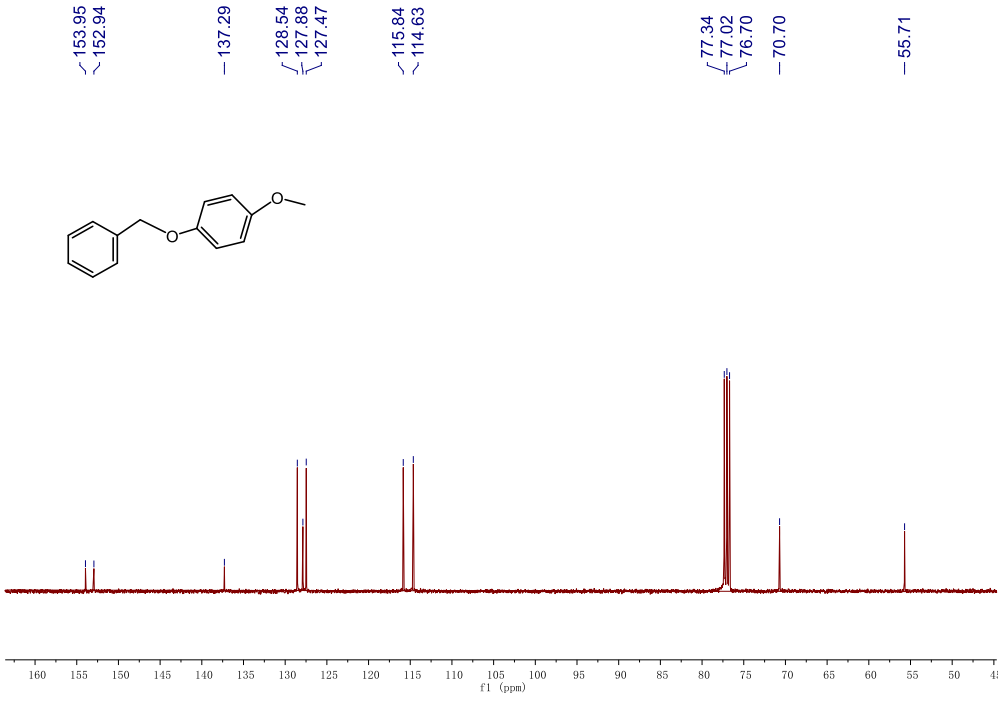
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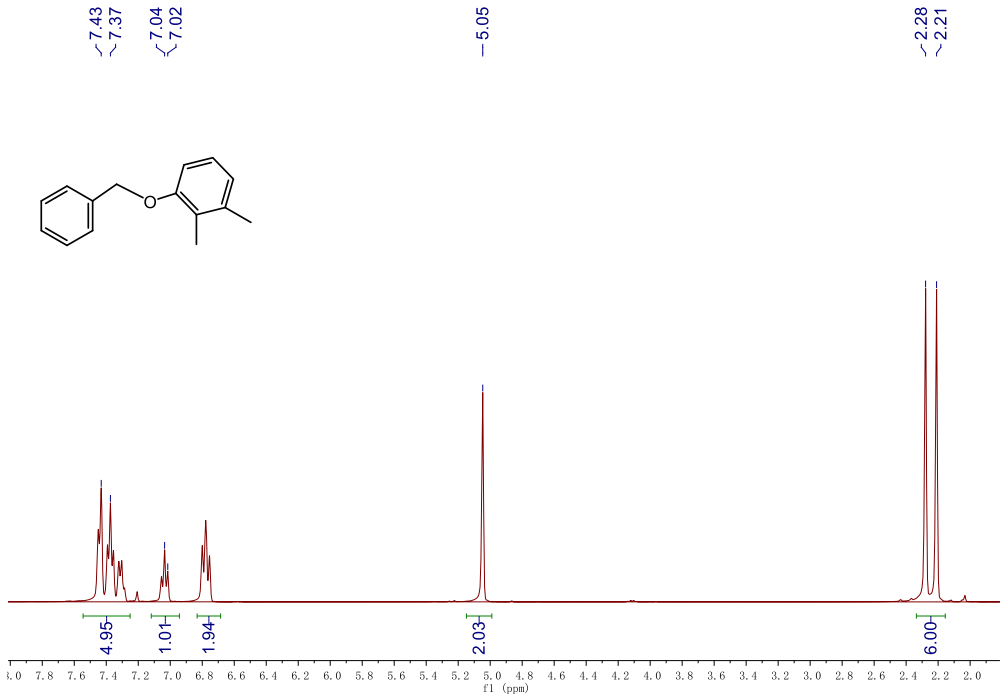
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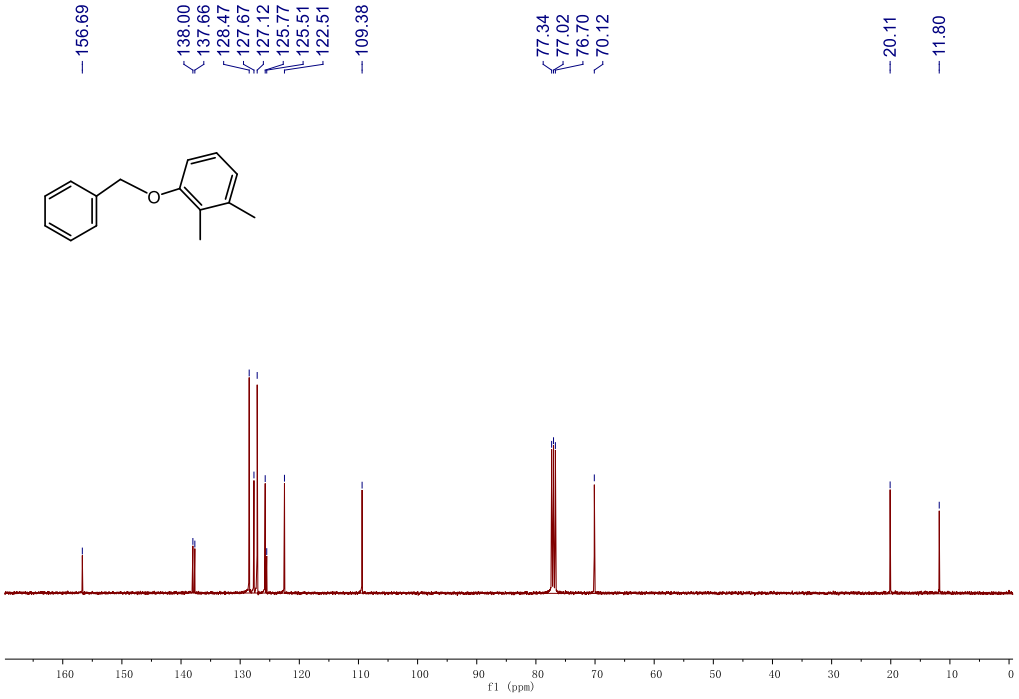
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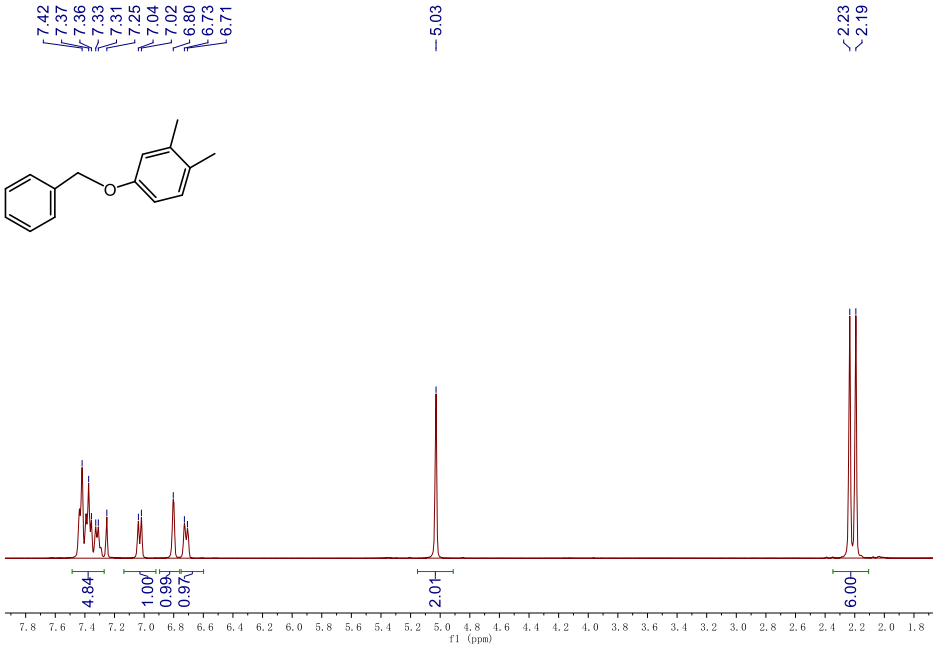
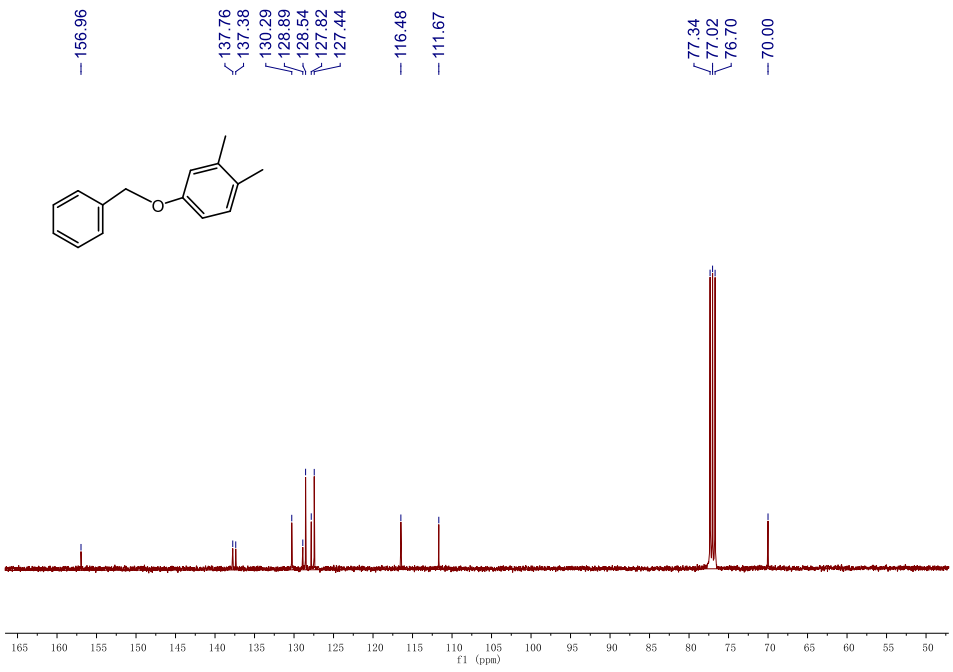
127.67
127.12
125.77
125.51
122.51
109.38
77.34
77.02
76.70
70.12
20.11
11.80
O
f1 (ppm)


7.42
7.37
7.36
7.33
7.31
7.25
7.04
7.02
6.80
6.73
6.71
5.03
2.23
2.19
O
4.84
1.00
0.99
0.97
2.01
6.00
f1 (ppm)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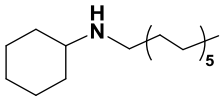
137.76
137.38
130.29
128.89
128.54
127.82
127.44
116.48
111.67
77.34
77.02
76.70
70.00
O
f1 (ppm)

2.47
2.46
2.30
1.79
1.76
1.66
1.62
1.56
1.52
1.46
1.32
1.29
1.27
1.24
1.18
1.14
1.10
0.87
0.85
0.84


H
N
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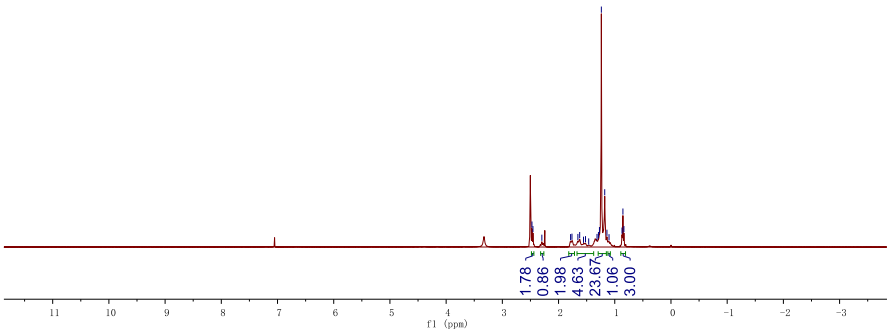
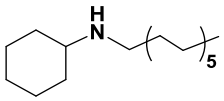

1.78
0.86
1.98
4.63
23.67
1.06
3.00
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
−3
f1 (ppm)

56.69
46.88
33.57
31.77
30.52
29.51
29.48
29.18
27.41
26.43
24.95
22.57
14.43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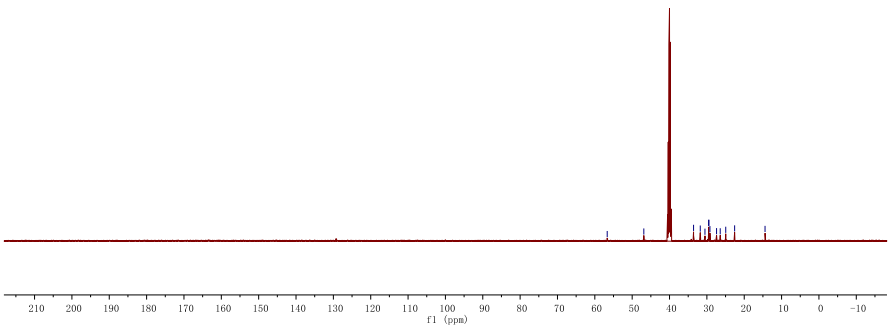
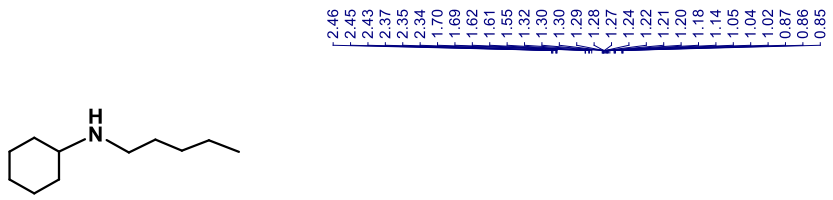
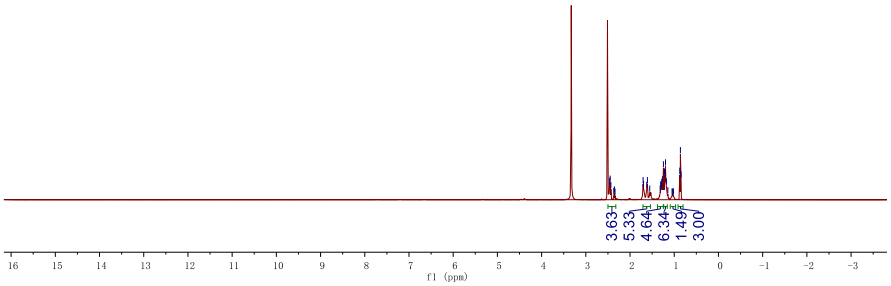
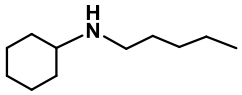
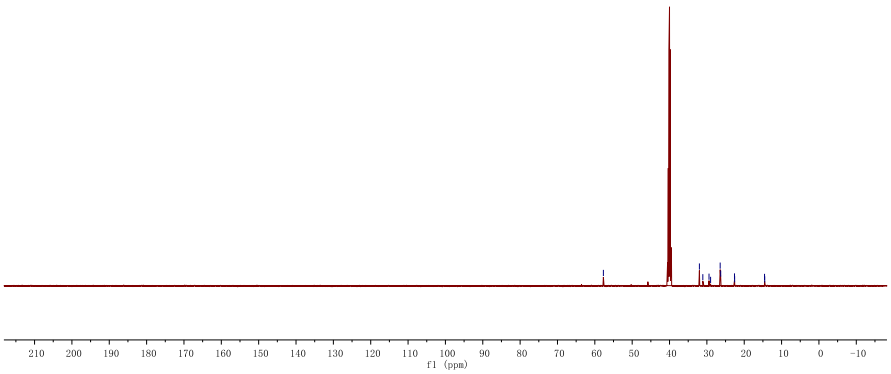

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

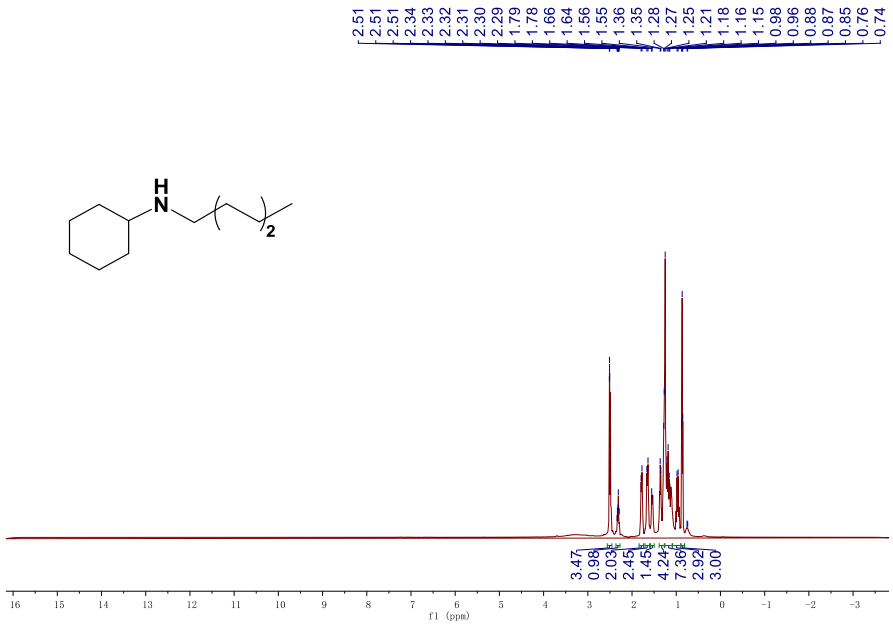

2.46
2.45
2.43
2.37
2.35
2.34
1.70
1.69
1.62
1.61
1.55
1.32
1.30
1.30
1.29
1.28
1.27
1.24
1.22
1.21
1.20
1.18
1.14
1.05
1.04
1.02
0.87
0.86
0.85

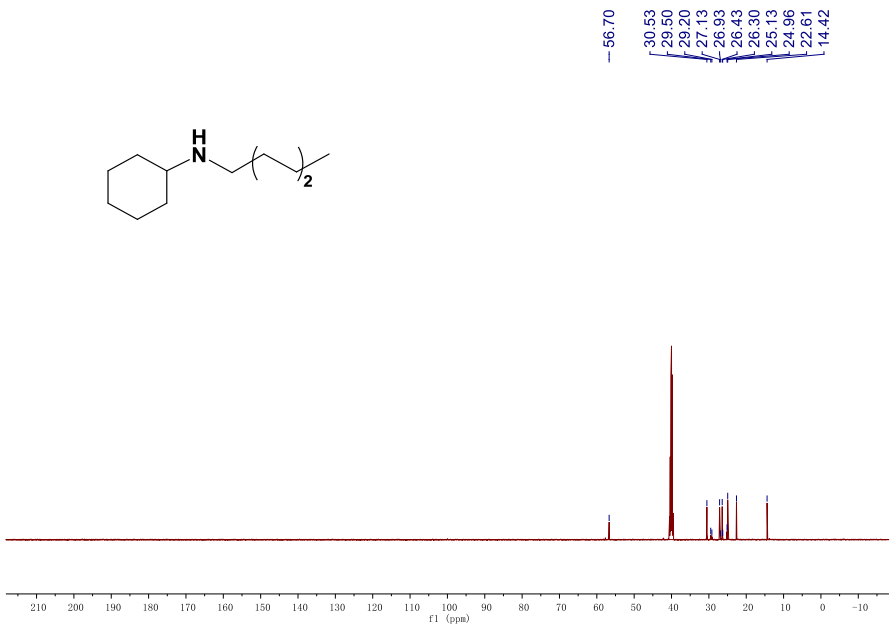

3.63
5.33
4.64
6.34
1.49
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3
f1 (ppm)

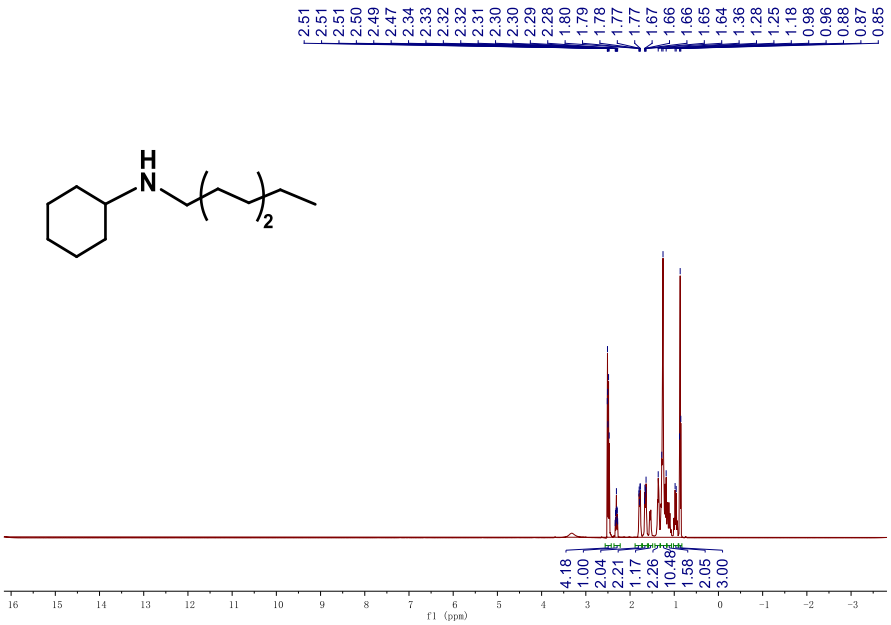
57.71
32.00
31.09
29.43
29.01
26.44
26.30
22.61
22.57
14.56
14.51

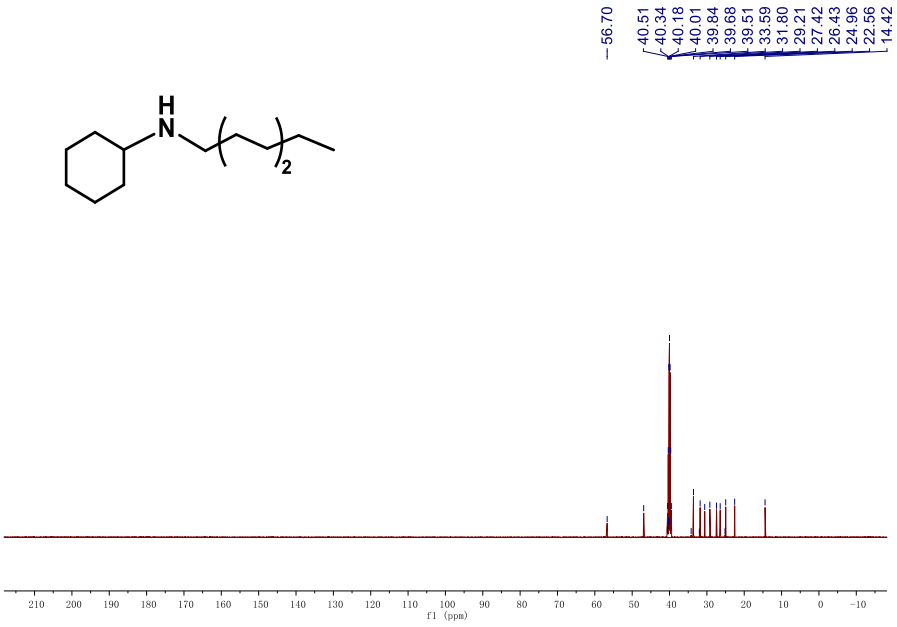


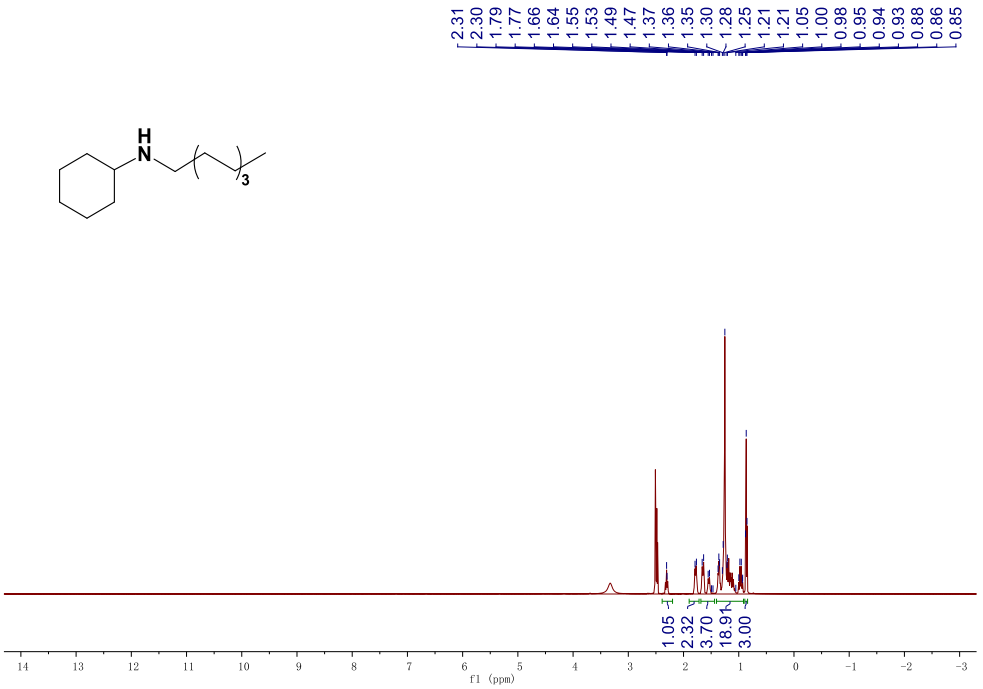

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

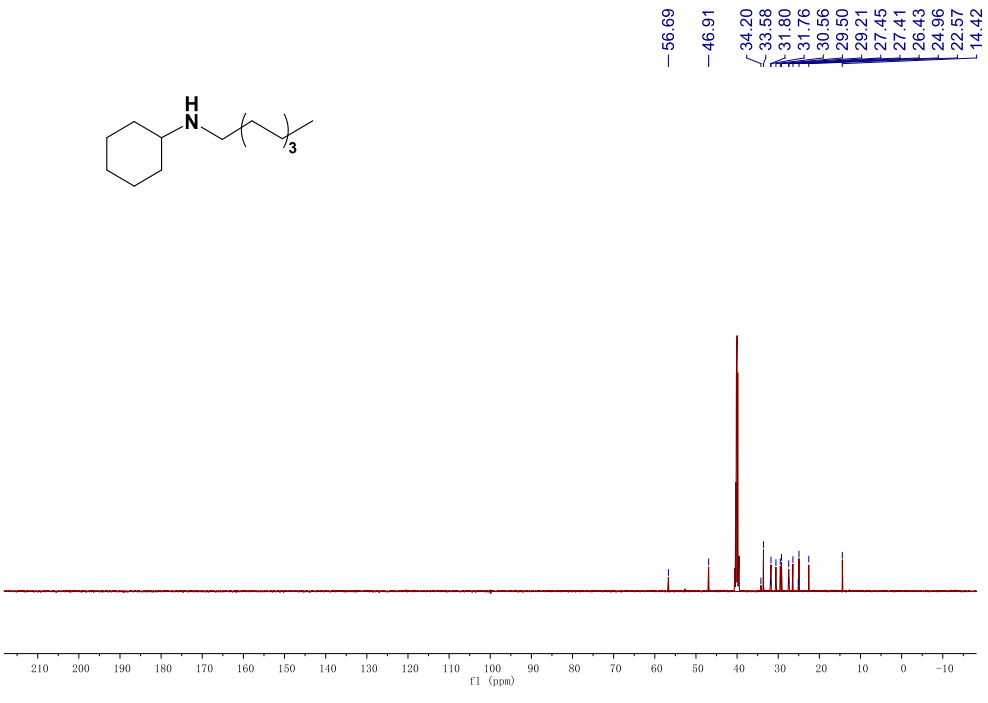

2.51
2.51
2.51
2.34
2.33
2.32
2.31
2.30
2.29
1.79
1.78
1.66
1.64
1.56
1.55
1.36
1.35
1.28
1.27
1.25
1.21
1.18
1.16
1.15
0.98
0.96
0.88
0.87
0.85
0.76
0.74
H
N
2
3.47
0.98
2.03
2.45
1.45
4.24
7.36
2.92
3.00
f1 (ppm)

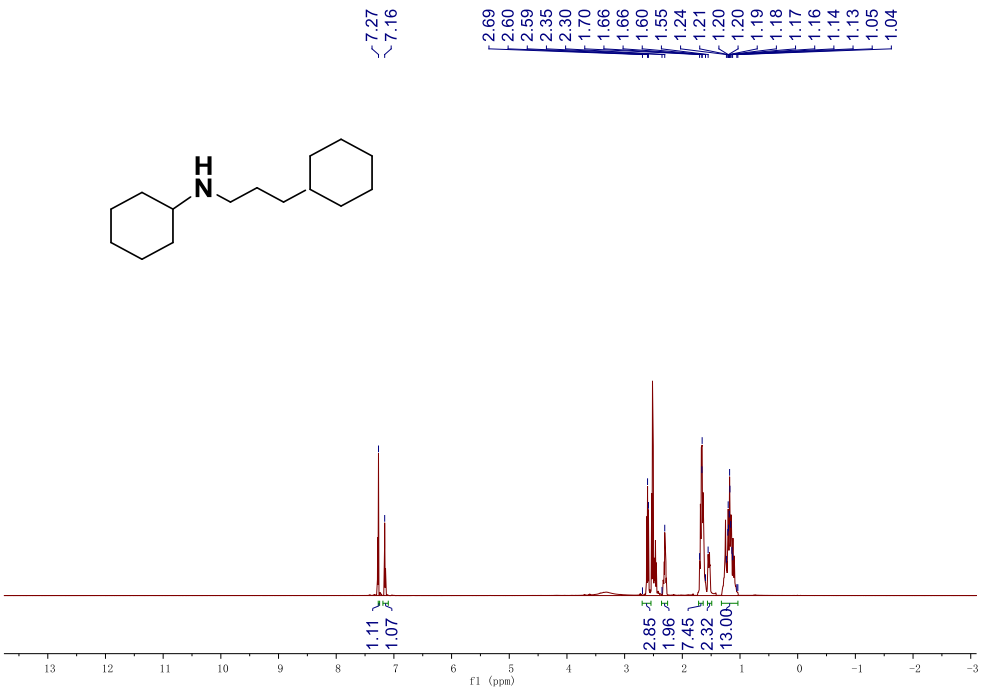

56.70
30.53
29.50
29.20
27.13
26.93
26.43
26.30
25.13
24.96
22.61
14.42
H
N
2
f1 (ppm)


2.51
2.51
2.51
2.50
2.49
2.47
2.34
2.33
2.32
2.32
2.31
2.30
2.30
2.29
2.28
1.80
1.79
1.78
1.77
1.77
1.67
1.66
1.66
1.65
1.64
1.36
1.28
1.25
1.18
0.98
0.96
0.88
0.87
0.85
H
N
2
4.18
1.00
2.04
2.21
1.17
2.26
10.48
1.58
2.05
3.00
f1 (ppm)


56.70
40.51
40.34
40.18
40.01
39.84
39.68
39.51
33.59
31.80
29.21
27.42
26.43
24.96
22.56
14.42
H
N
2
f1 (ppm)


2.31
2.30
1.79
1.77
1.66
1.64
1.55
1.53
1.49
1.47
1.37
1.36
1.35
1.30
1.28
1.25
1.21
1.21
1.05
1.00
0.98
0.95
0.94
0.93
0.88
0.86
0.85
H
N
3
1.05
2.32
3.70
18.91
3.00
f1 (ppm)


56.69
46.91
34.20
33.58
31.80
31.76
30.56
29.50
29.21
27.45
27.41
26.43
24.96
22.57
14.42
H
N
3
f1 (ppm)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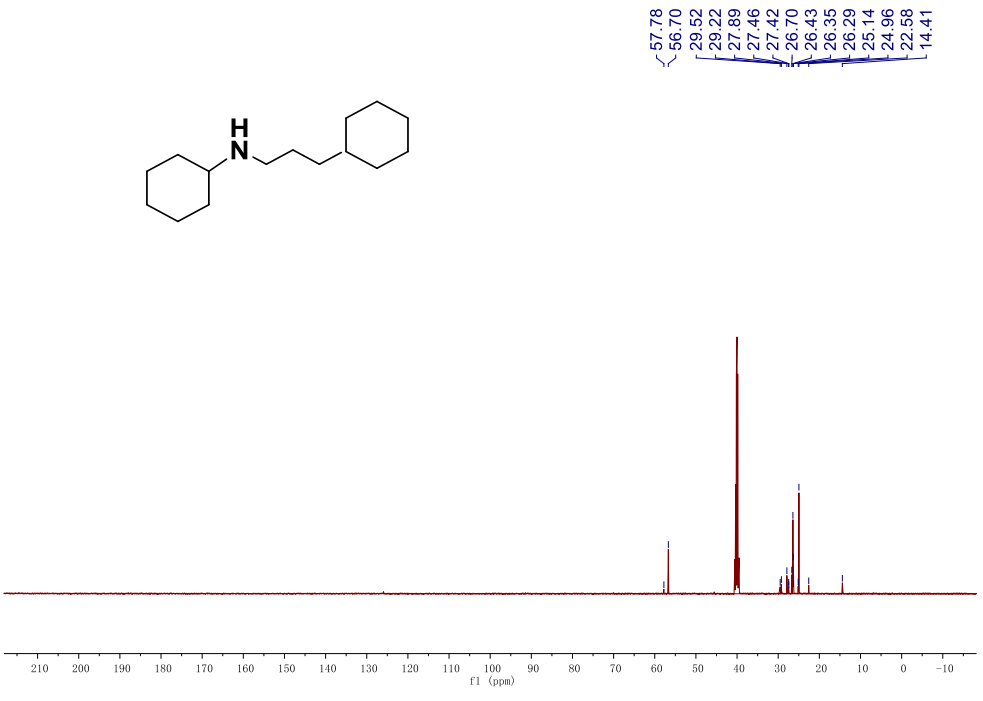
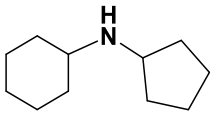
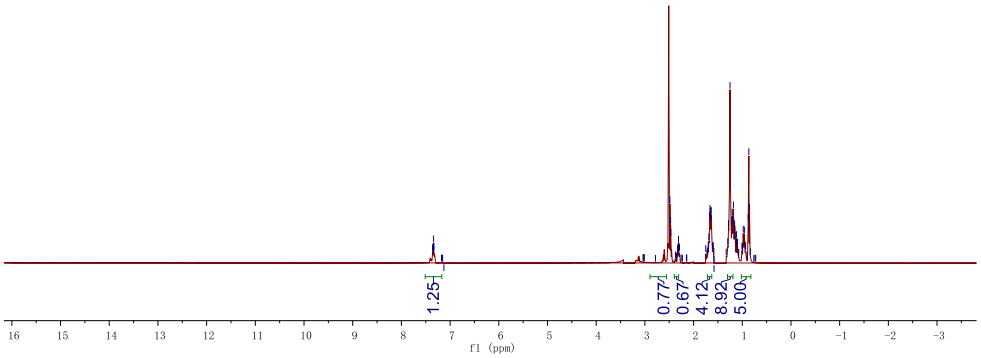
7.16
2.69
2.60
2.59
2.35
2.30
1.70
1.66
1.66
1.60
1.55
1.24
1.21
1.20
1.20
1.19
1.18
1.17
1.16
1.14
1.13
1.05
1.04
H
N
1.11
1.07
2.85
1.96
7.45
2.32
13.00
f1 (ppm)

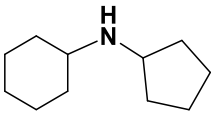

57.78
56.70
29.52
29.22
27.89
27.46
27.42
26.70
26.43
26.35
26.29
25.14
24.96
22.58
14.41
H
N
f1 (ppm)

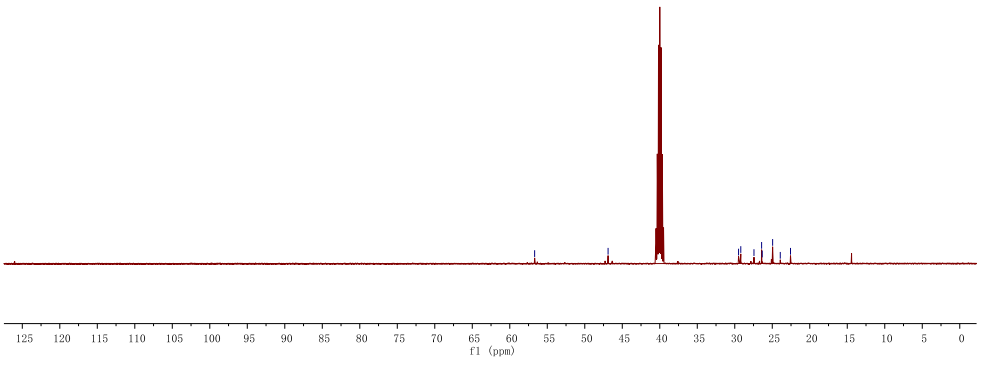
7.36
7.35
7.35
7.34
7.33
2.49
2.47
2.47
2.33
2.32
2.32
2.31
2.30
2.29
1.75
1.71
1.70
1.68
1.67
1.66
1.65
1.64
1.64
1.61
1.60
1.60
1.30
1.28
1.25
1.21
1.21
1.19
1.18
1.16
1.16
1.15
1.14
1.13
1.12
1.10
1.10
1.01
1.00
0.98
0.96
0.94
0.93
0.88
0.86
0.85

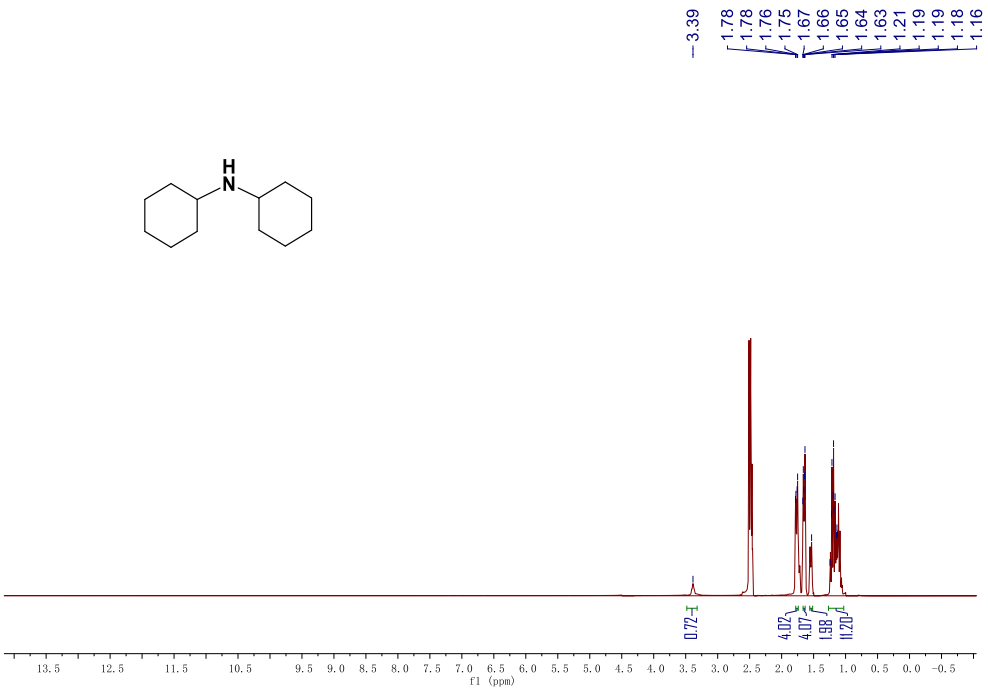

H
N

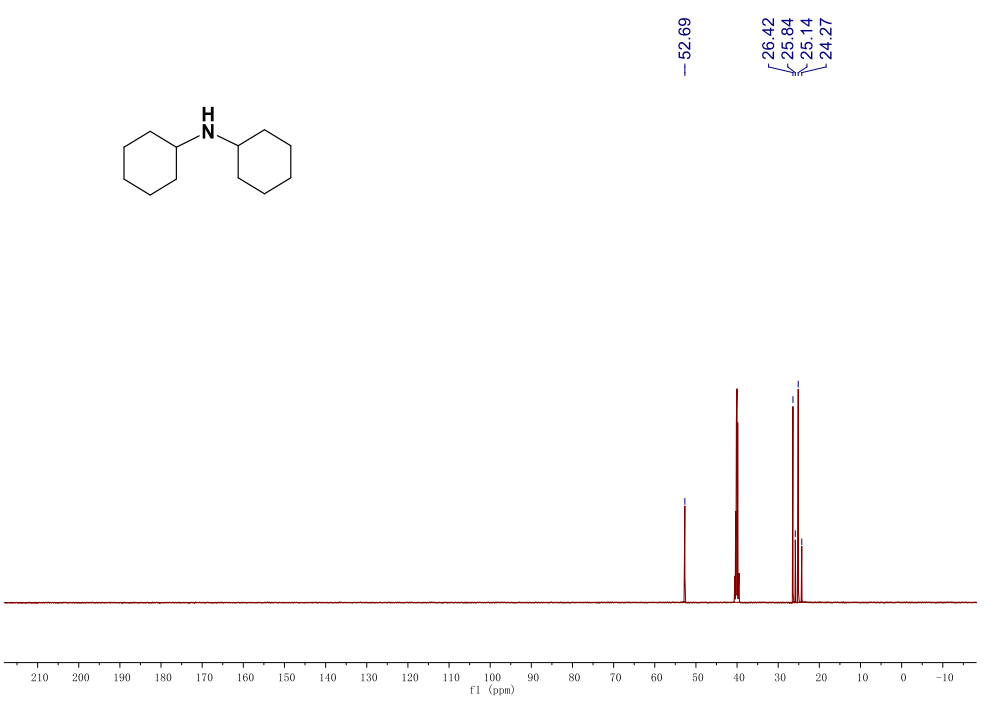

1.25
0.77
0.67
4.12
8.92
5.00
f1 (ppm)

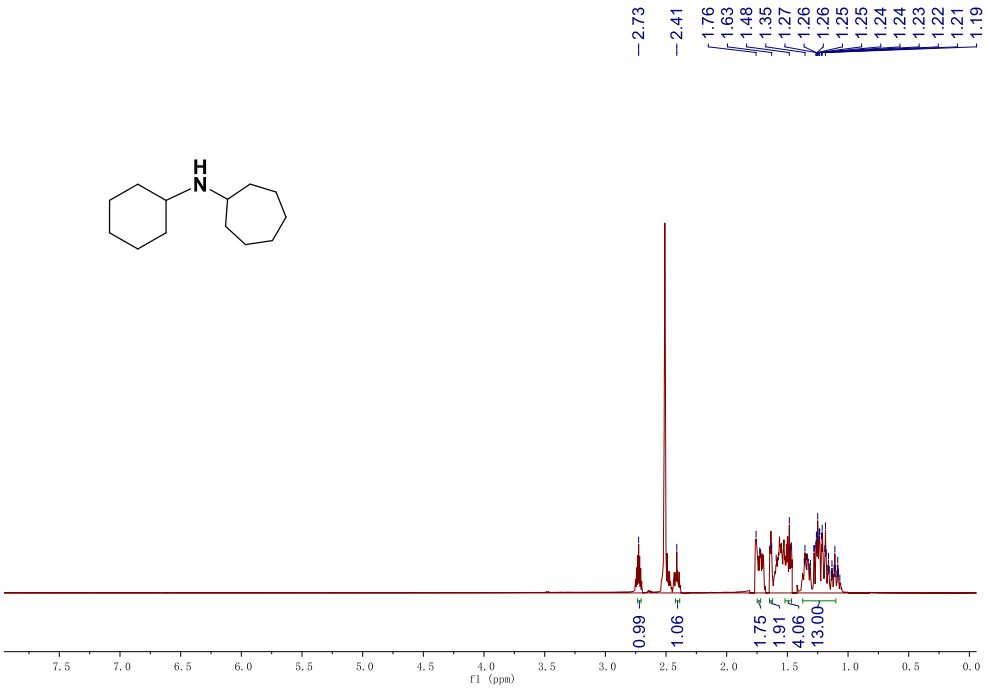
56.69
46.89
29.49
29.20
27.44
26.42
26.34
24.95
23.93
22.57

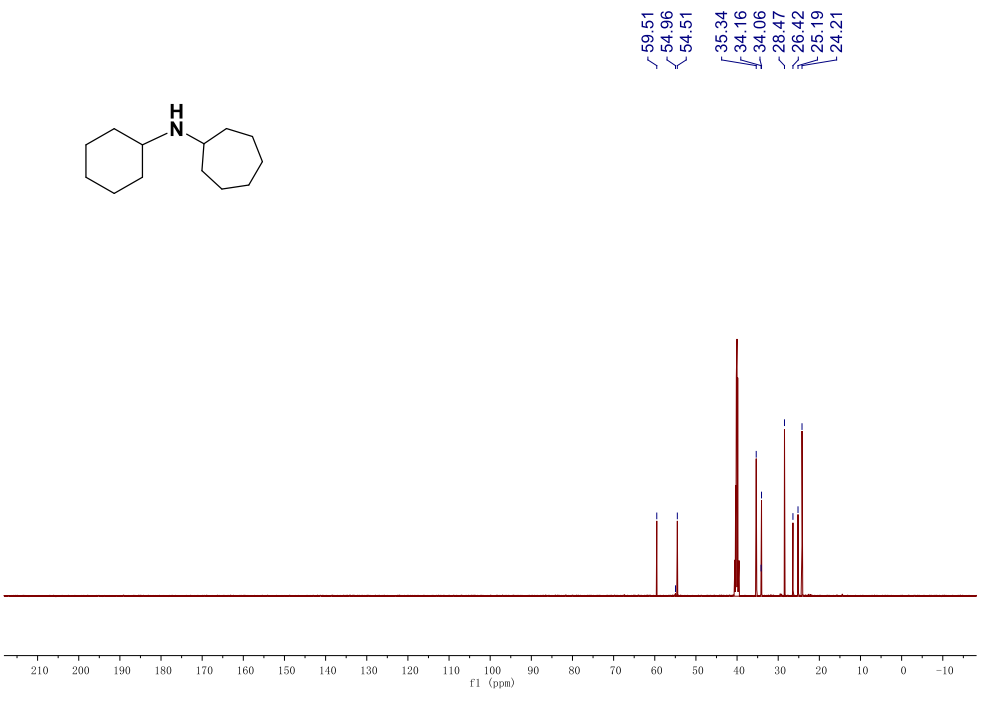

H
N


f1 (ppm)


3.39
1.78
1.78
1.76
1.75
1.67
1.66
1.65
1.64
1.63
1.21
1.19
1.19
1.18
1.16
0.72
4.02
4.07
1.98
11.20
f1 (ppm)


52.69
26.42
25.84
25.14
24.27
f1 (ppm)


2.73
2.41
1.76
1.63
1.48
1.35
1.27
1.26
1.26
1.25
1.25
1.24
1.24
1.23
1.22
1.21
1.19
0.99
1.06
1.75
1.91
4.06
13.00
f1 (ppm)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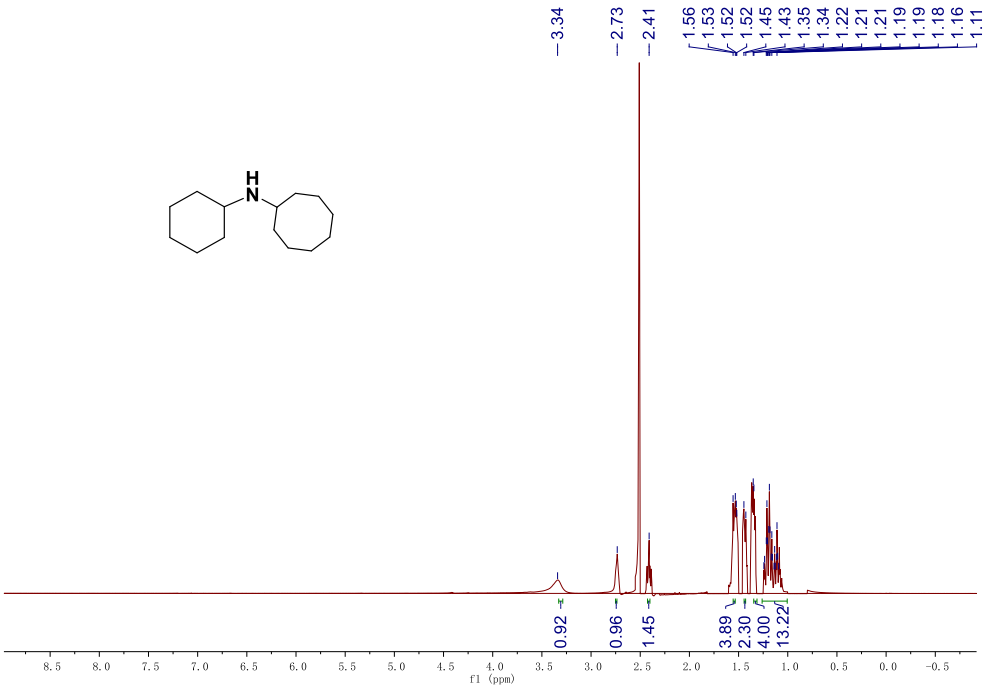
54.51
35.34
34.16
34.06
28.47
26.42
25.19
24.21
f1 (ppm)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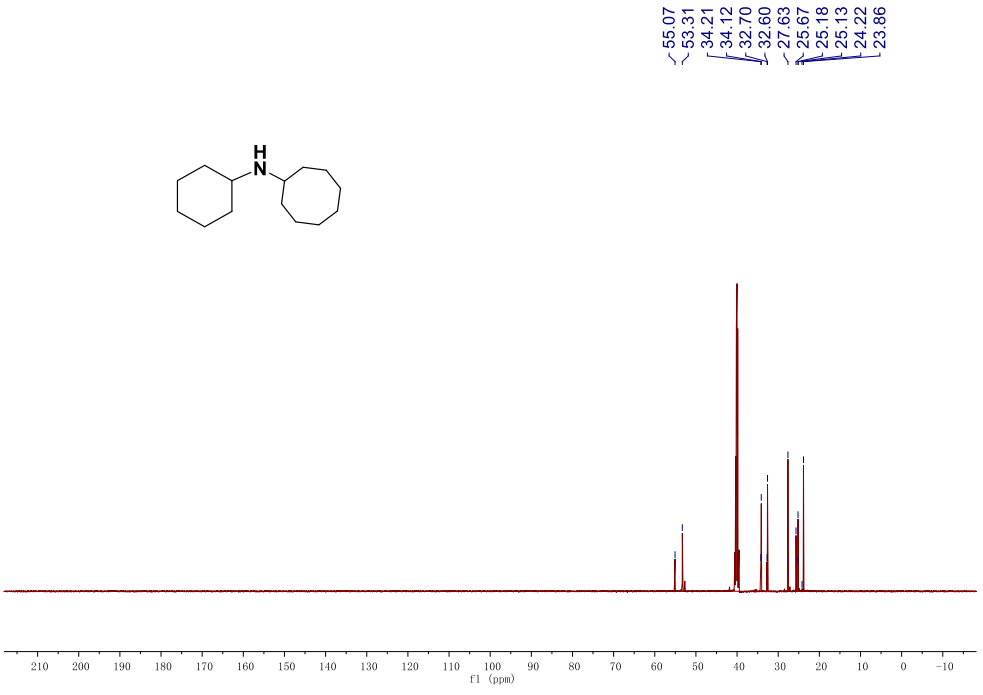
2.73
2.41
1.56
1.53
1.52
1.52
1.45
1.43
1.35
1.34
1.22
1.21
1.21
1.19
1.19
1.18
1.16
1.11
0.92
0.96
1.45
3.89
2.30
4.00
13.22
f1 (ppm)


55.07
53.31
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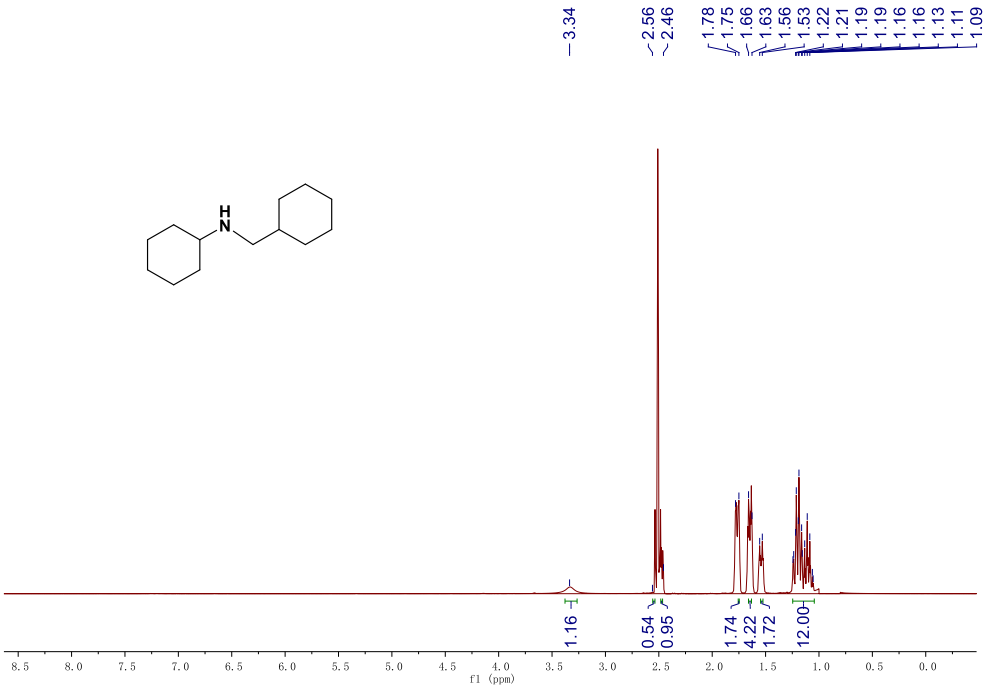
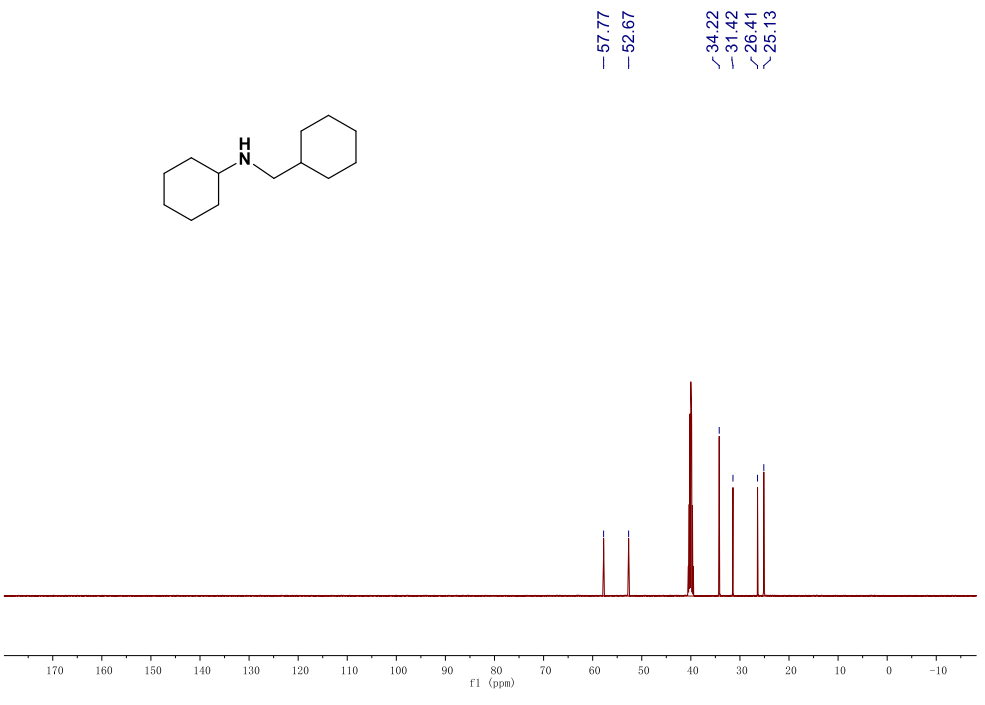
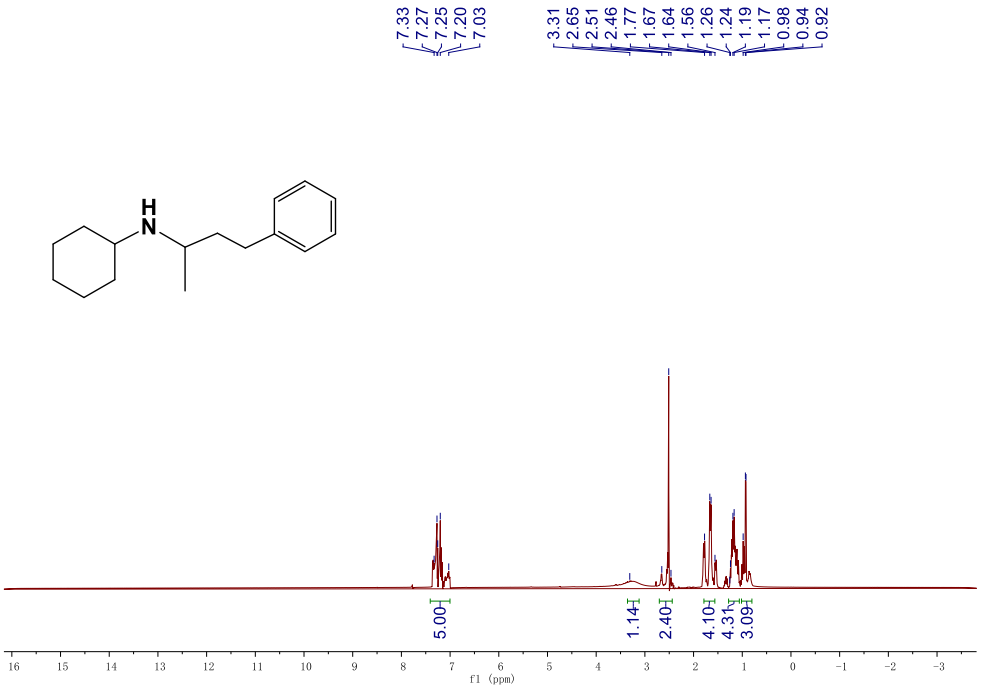
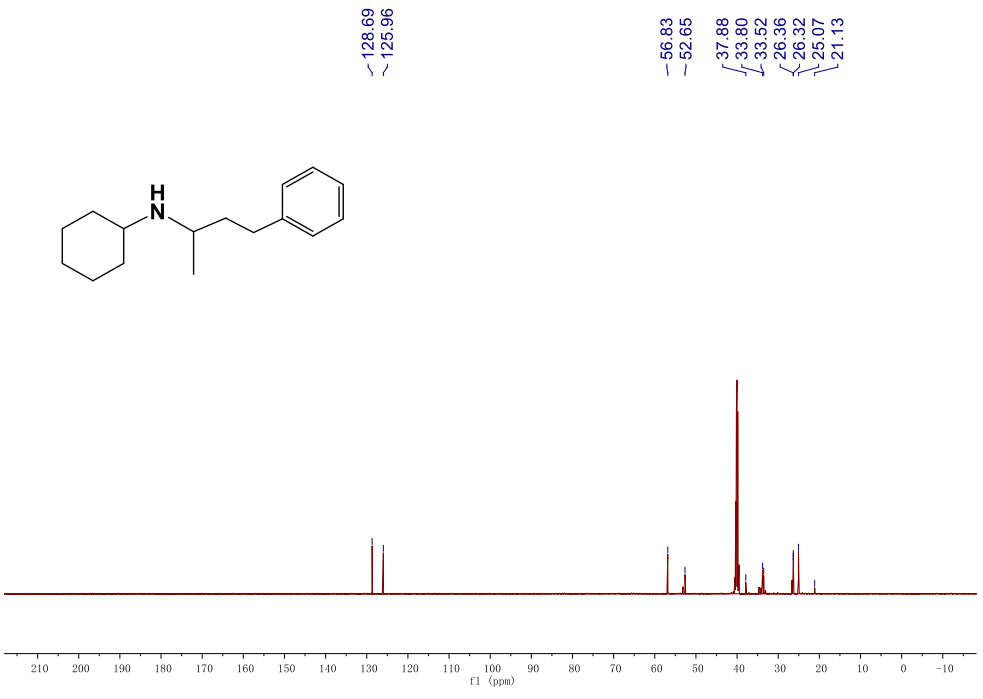
27.63
25.67
25.18
25.13
24.22
23.86
f1 (ppm)


3.34
2.56
2.46
1.78
1.75
1.66
1.63
1.56
1.53
1.22
1.21
1.19
1.19
1.16
1.13
1.11
1.09
1.16
0.54
0.95
1.74
4.22
1.72
12.00
f1 (ppm)


57.77
52.67
34.22
31.42
26.41
25.13
f1 (ppm)


7.33
7.27
7.25
7.20
7.03
3.31
2.65
2.51
2.46
1.77
1.67
1.64
1.56
1.26
1.24
1.19
1.17
0.98
0.94
0.92
H
N
5.00
1.14
2.40
4.10
4.31
3.09
f1 (ppm)


128.69
125.96
56.83
52.65
37.88
33.80
33.52
26.36
26.32
25.07
21.13
H
N
f1 (ppm)

3.07
3.02
2.98
2.96
2.89
2.84
2.78
2.70
2.67
2.57
2.51
2.09
1.99
1.97
1.91
1.86
1.80
1.73
1.70
1.66
1.37
1.32
1.11
0.96
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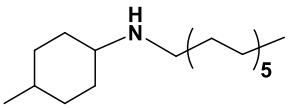
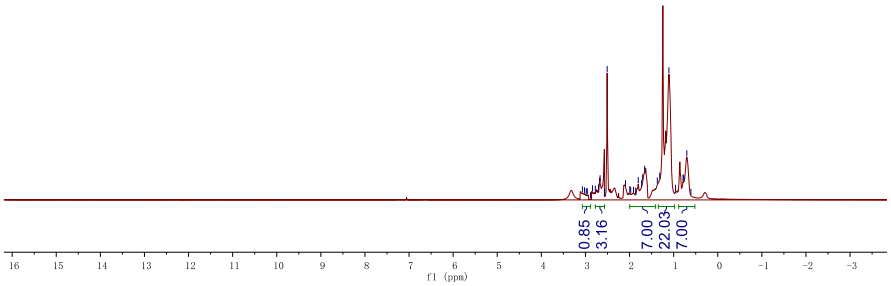
0.70
0.61


H
N
5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22.03
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46.96
34.02
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27.44
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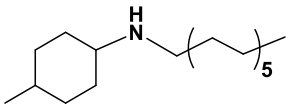
13.83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N
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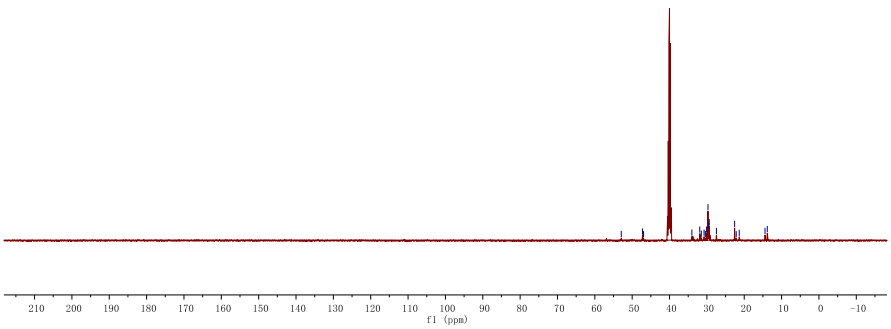
f1 (ppm)

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2.06
1.99
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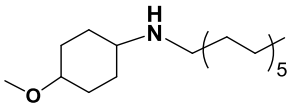
0.72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O
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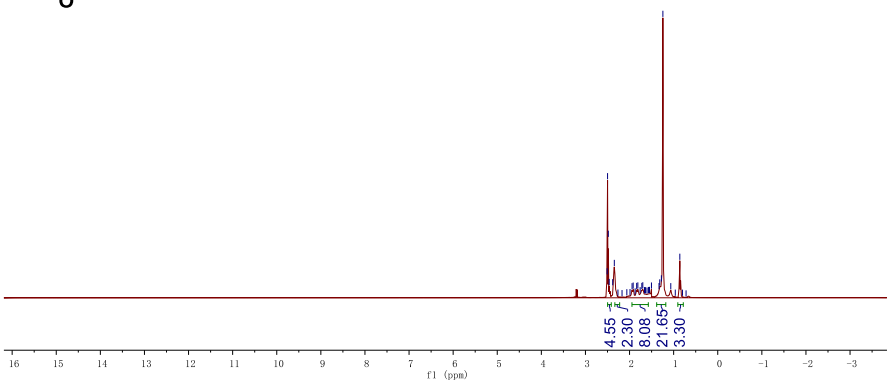
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3.30
f1 (ppm)

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30.53
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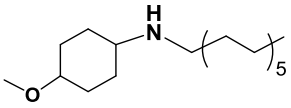
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O
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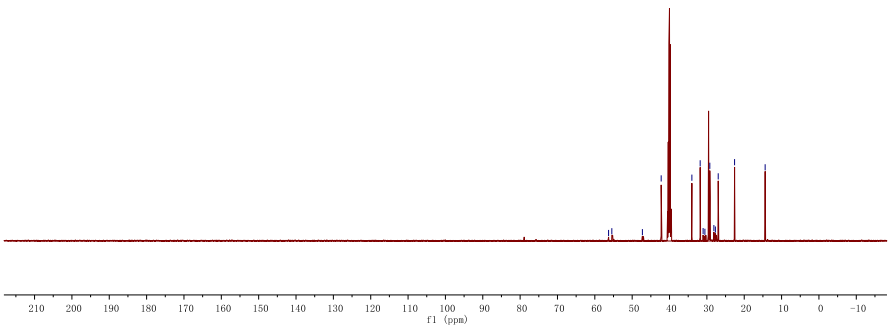
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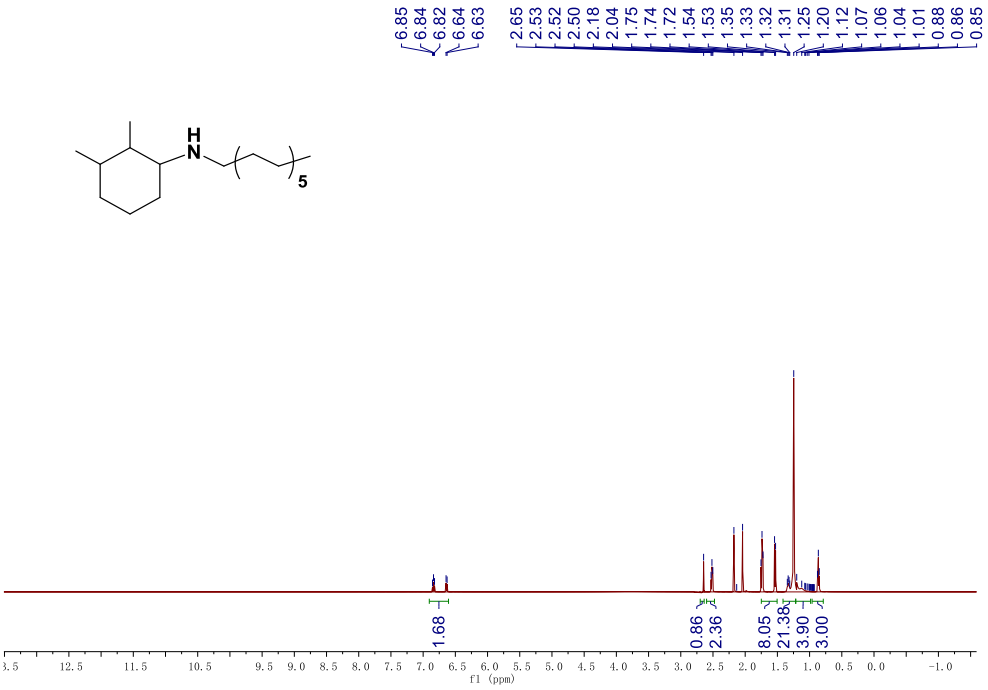
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2.18
2.04
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1.33
1.32
1.31
1.25
1.20
1.12
1.07
1.06
1.04
1.01
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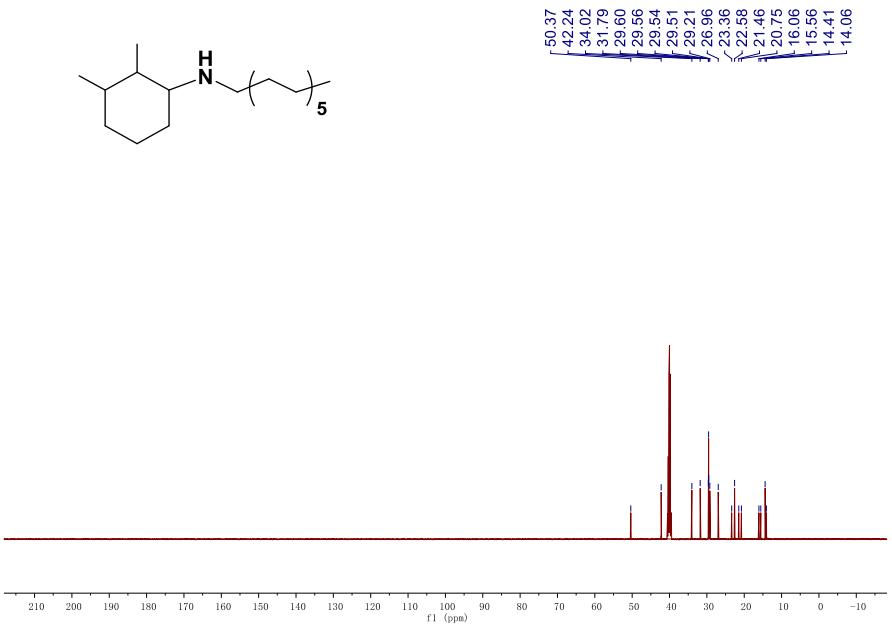
3.00
f1 (ppm)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20.75
16.06
15.56
14.41
14.06
H
N
5
f1 (ppm)

2.50
2.49
2.46
1.80
1.78
1.77
1.75
1.73
1.71
1.69
1.65
1.61
1.48
1.44
1.32
1.31
1.25
1.16
1.16
1.15
1.15
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1.03
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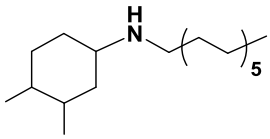
0.83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N
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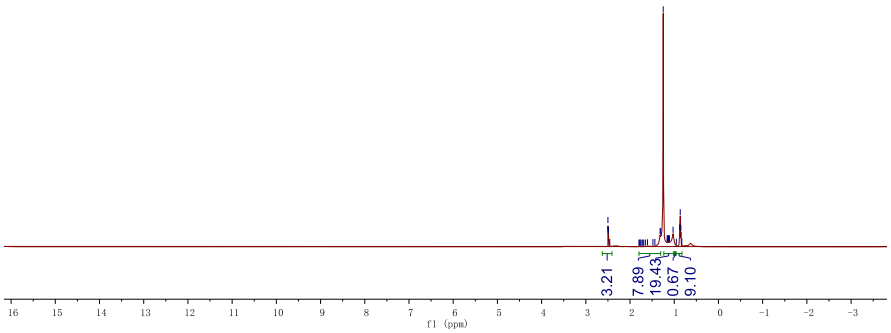
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f1 (ppm)

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34.02
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29.53
29.51
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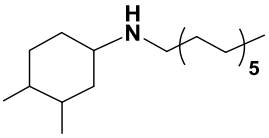
22.58
14.41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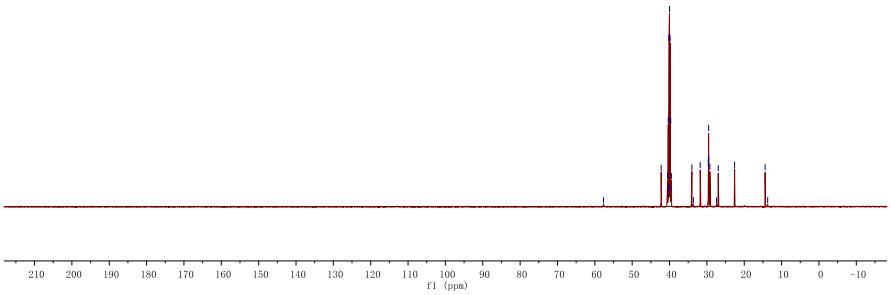

f1 (ppm)

HR-MS Data.

HR-MS for compound 3a

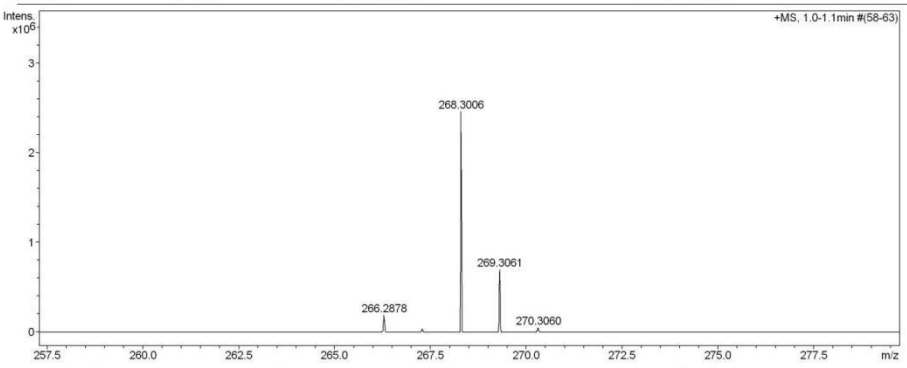
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-1_41_01_4882.d	Acquisition Date	2/10/2023 1:16:04 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-1	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
268.3006	1	C 18 H 38 N	268.2999	-2.5	-4.3	0.5	ok	even	47.04	0.0733	0.0015	0.0290	0.0022	0.8427

HR-MS for compound 3b

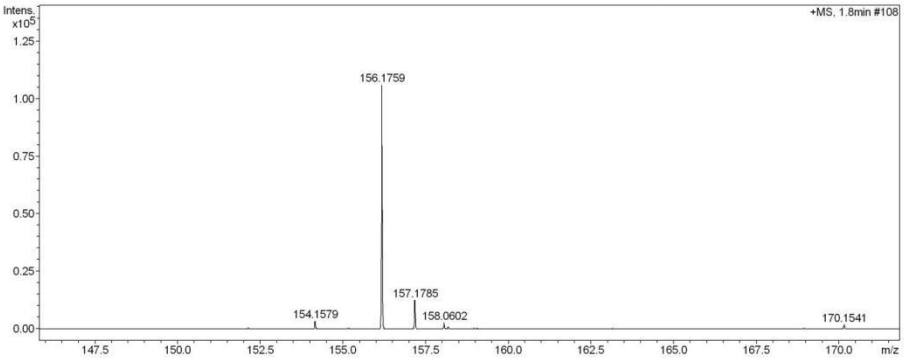
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-6_47_01_4888.d	Acquisition Date	2/10/2023 1:43:27 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-6	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
156.1759	1	C 10 H 22 N	156.1747	-8.1	-7.5	0.5	ok	even	5.11	0.0093	0.0012	0.0052	0.0008	0.8427

HR-MS for compound 3c

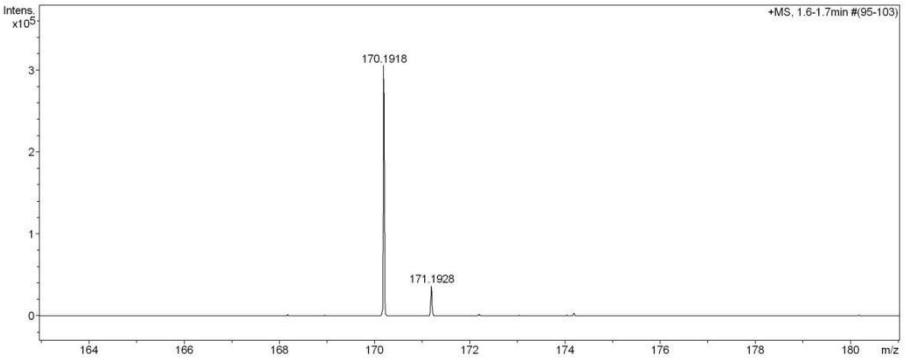
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-7_48_01_4889.d	Acquisition Date	2/10/2023 1:48:05 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-7	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
170.1918	1	C 11 H 24 N	170.1903	-8.7	-7.1	0.5	ok	even	1.47	0.0025	0.0014	0.0012	0.0023	0.8427

HR-MS for compound 3d

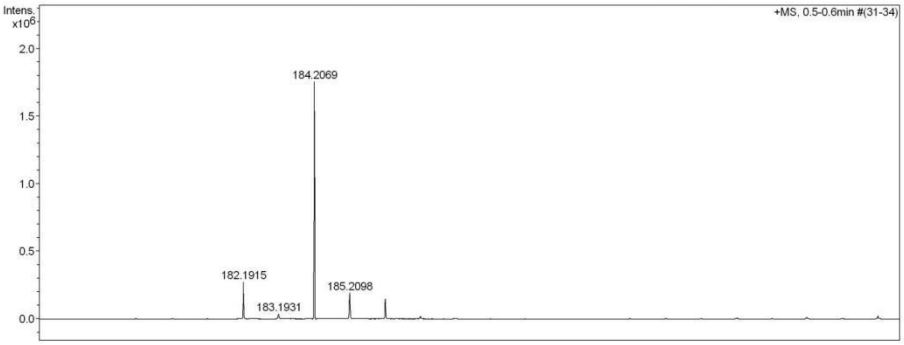
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-8_49_01_4891.d	Acquisition Date	2/10/2023 1:57:14 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-8	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
184.2069	1	C 12 H 26 N	184.2060	-5.1	-7.7	0.5	ok	even	46.78	0.0796	0.0024	0.0550	0.0005	0.8427

HR-MS for compound 3e

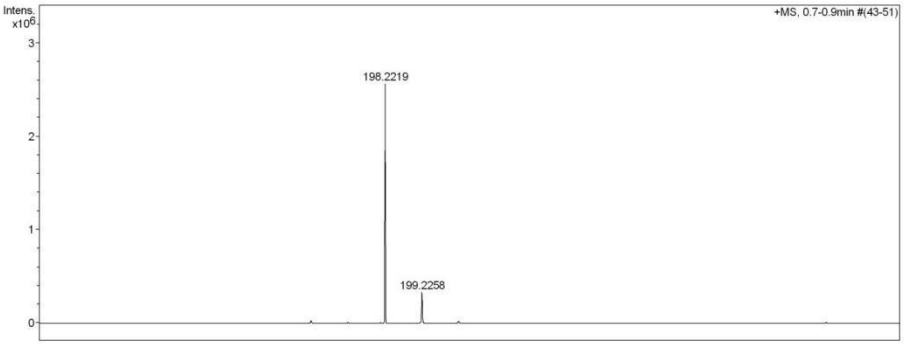
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-9_50_01_4892.d	Acquisition Date	2/10/2023 2:01:52 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-9	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
198.2219	1	C 13 H 28 N	198.2216	-1.2	-1.4	0.5	ok	even	8.16	0.0160	0.0004	0.0065	0.0006	0.8427

HR-MS for compound 3f

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-10_51_01_4893.d	Acquisition Date	2/10/2023 2:06:23 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-10	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
212.2387	1	C 14 H 30 N	212.2373	-6.9	-8.5	0.5	ok	even	22.96	0.0362	0.0023	0.0257	0.0006	0.8427

HR-MS for compound 3g

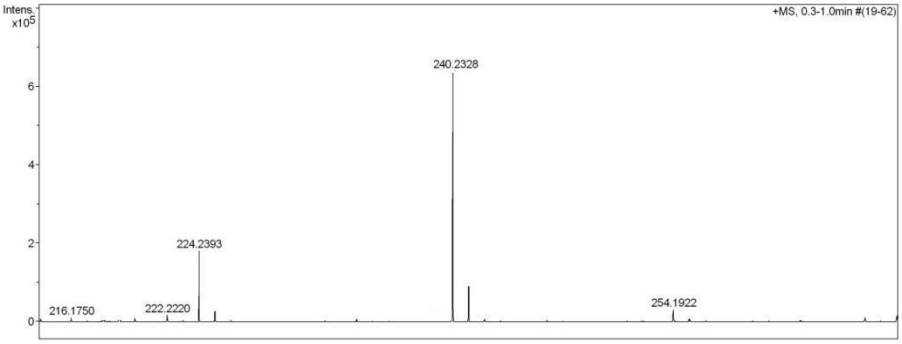
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-11_52_01_4894.d	Acquisition Date	2/10/2023 2:11:00 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-11	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
240.2328	1	C 16 H 34 N	240.2999	-2.5	-4.3	0.5	ok	even	47.04	0.0733	0.0015	0.0290	0.0022	0.8427

HR-MS for compound 3h

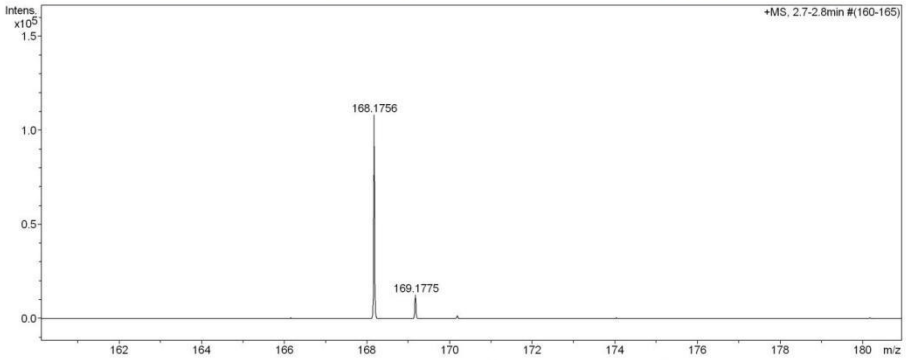
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-12_53_01_4895.d	Acquisition Date	2/10/2023 2:15:34 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-12	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e¯ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
168.1756	1	C 11 H 22 N	168.1747	-5.5	-4.9	1.5	ok	even	5.97	0.0093	0.0010	0.0065	0.0014	0.8427

HR-MS for compound 3i

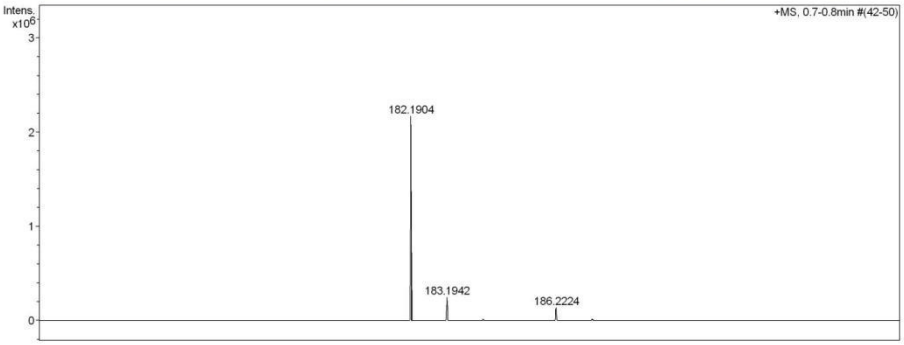
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-13_54_01_4898.d	Acquisition Date	2/10/2023 2:29:17 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-13	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
182.1904	1	C 12 H 24 N	182.1903	-0.6	-0.8	1.5	ok	even	11.09	0.0216	0.0002	0.0089	0.0004	0.8427

HR-MS for compound 3j

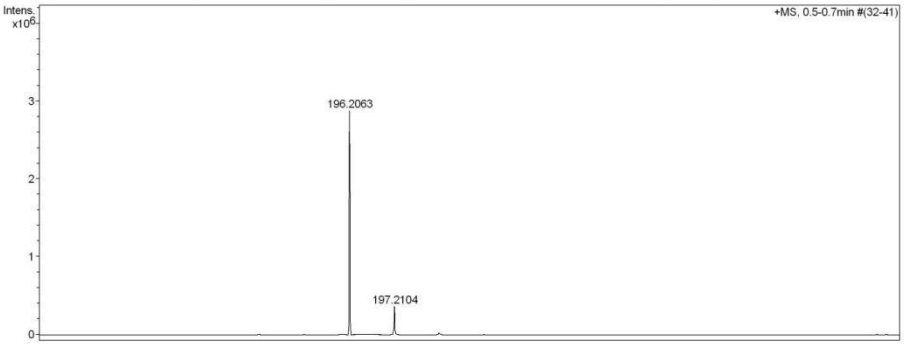
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-14_55_01_4899.d	Acquisition Date	2/10/2023 2:33:51 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-14	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
196.2063	1	C 13 H 26 N	196.2060	-1.9	-2.2	1.5	ok	even	11.35	0.0224	0.0006	0.0091	0.0007	0.8427

HR-MS for compound 3k

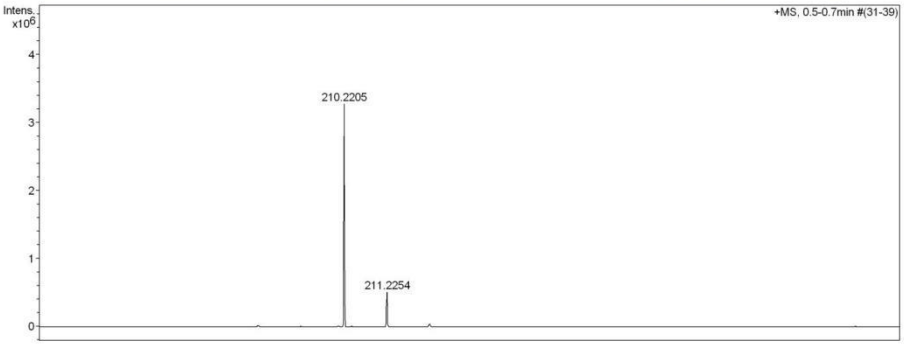
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-15_56_01_4900.d	Acquisition Date	2/10/2023 2:38:27 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-15	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
210.2205	1	C 14 H 28 N	210.2216	5.5	4.6	1.5	ok	even	0.63	0.0009	0.0011	0.0006	0.0016	0.8427

HR-MS for compound 3l

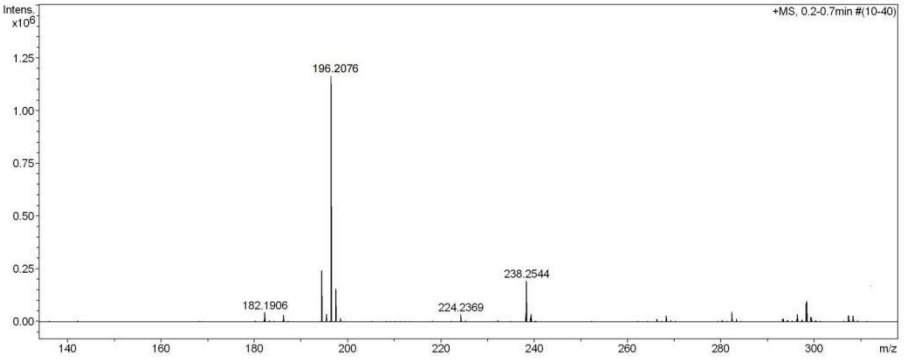
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-16_57_01_4901.d	Acquisition Date	2/10/2023 2:43:04 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-16	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
196.2076	1	C 13 H 26 N	196.2060	-7.2	-5.4	4.5	ok	even	2.47	0.0036	0.0016	0.0022	0.0025	0.4646

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HR-MS for compound 3m

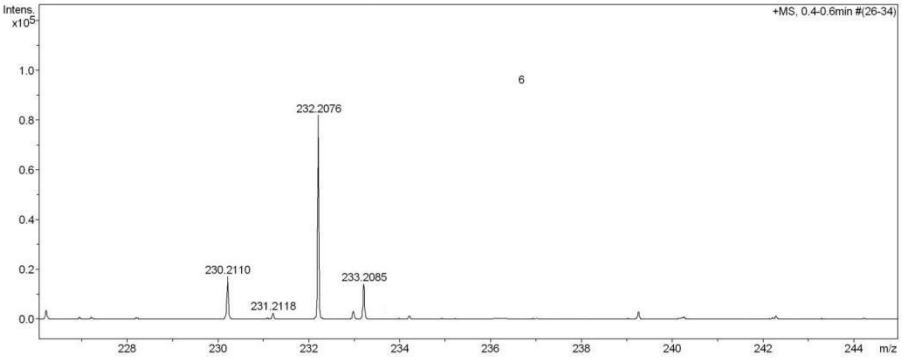
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-17_58_01_4902.d	Acquisition Date	2/10/2023 2:47:43 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-17	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e¯ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
232.2076	1	C 16 H 26 N	232.2060	-7.2	-5.4	4.5	ok	even	2.47	0.0036	0.0016	0.0022	0.0025	0.4646

HR-MS for compound 3n

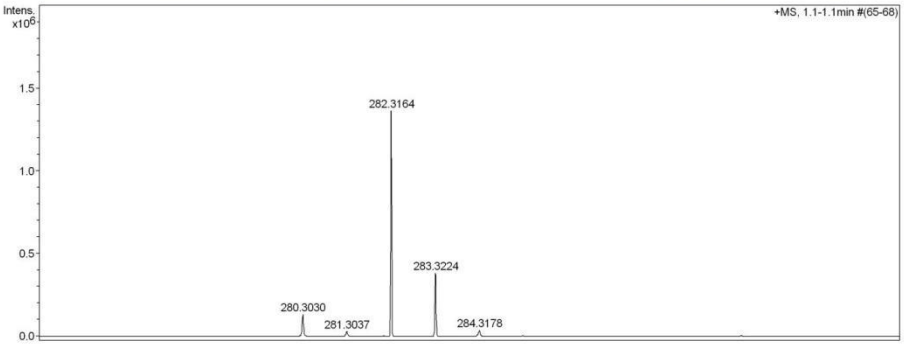
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-2_42_01_4883.d	Acquisition Date	2/10/2023 1:20:36 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-2	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
282.3164	1	C 19 H 40 N	282.3155	-3.0	-4.6	0.5	ok	even	38.14	0.0602	0.0019	0.0238	0.0027	0.8427

HR-MS for compound 3o

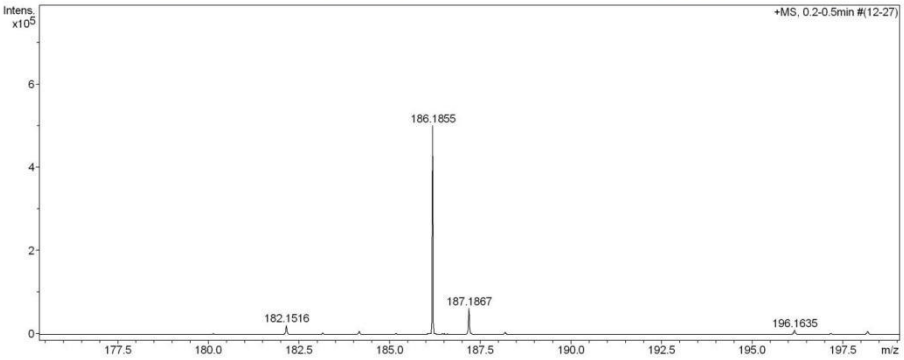
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-3_43_01_4920.d	Acquisition Date	2/10/2023 4:10:56 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-3	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
186.1855	1	C 11 H 24 N O	186.1852	-1.5	-0.0	0.5	ok	even	1.23	0.0029	0.0008	0.0014	0.0022	0.8427

HR-MS for compound 3p

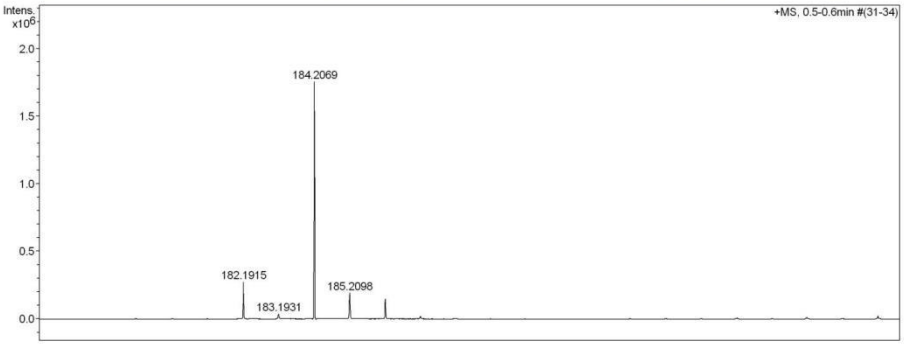
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-8_49_01_4891.d	Acquisition Date	2/10/2023 1:17:14 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-4	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
184.2069	1	C 12 H 26 N	184.2060	-5.1	-7.7	0.5	ok	even	46.78	0.0796	0.0024	0.0550	0.0005	0.8427

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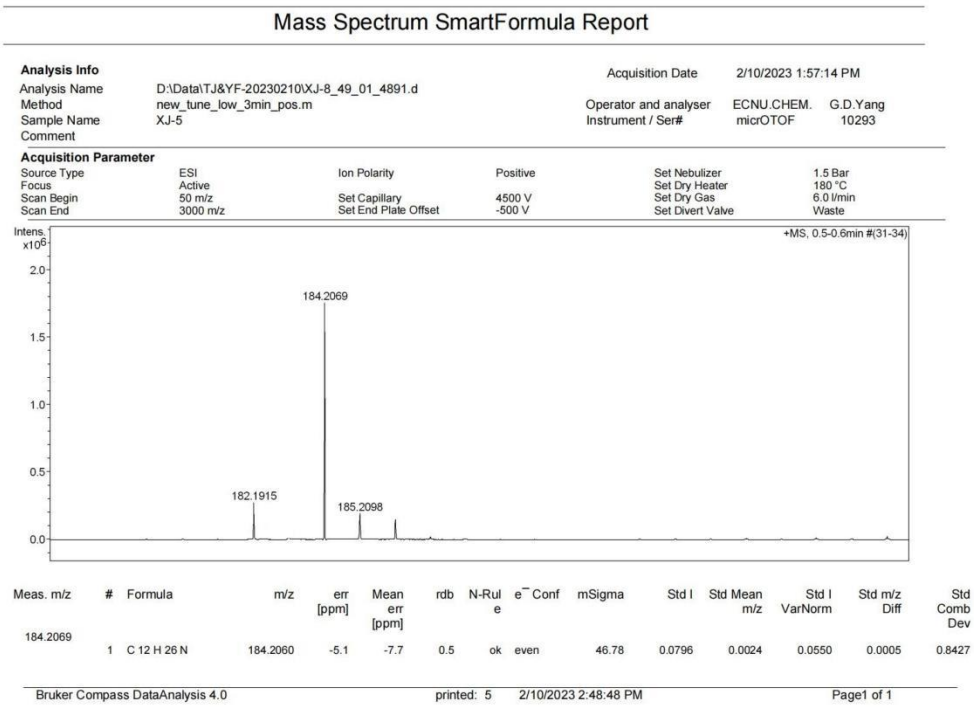
HR-MS for compound 3q



Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\TJ&YF-20230210\XJ-8_49_01_4891.d	Acquisition Date	2/10/2023 1:57:14 PM
Method	new_tune_low_3min_pos.m	Operator and analyser	ECNU.CHEM. G.D.Yang
Sample Name	XJ-5	Instrument / Ser#	micrOTOF 10293
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.5 Bar
Focus	Active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	6.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste

Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
184.2069	1	C 12 H 26 N	184.2060	-5.1	-7.7	0.5	ok	even	46.78	0.0796	0.0024	0.0550	0.0005	0.8427

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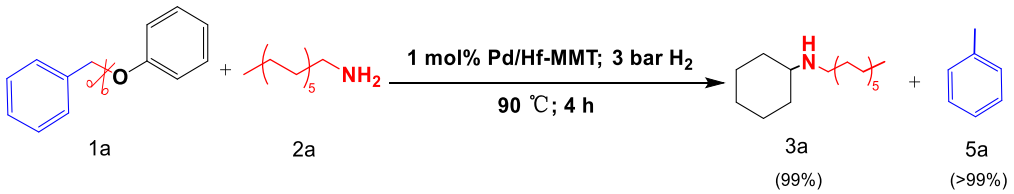
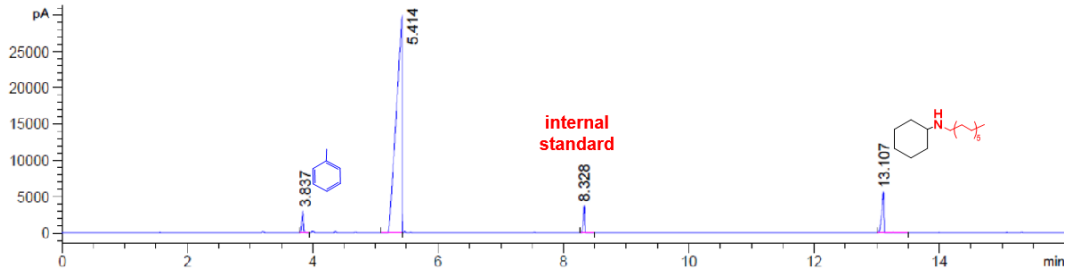
Chromatograms for GC-measurements

Reaction 1





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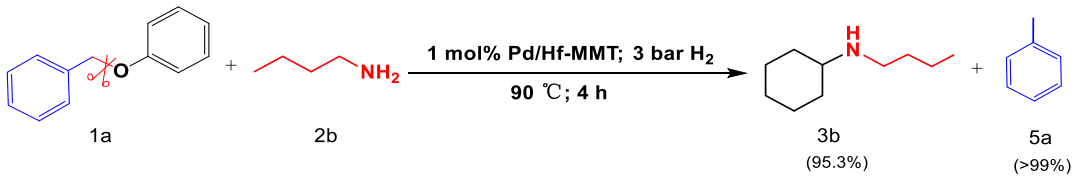
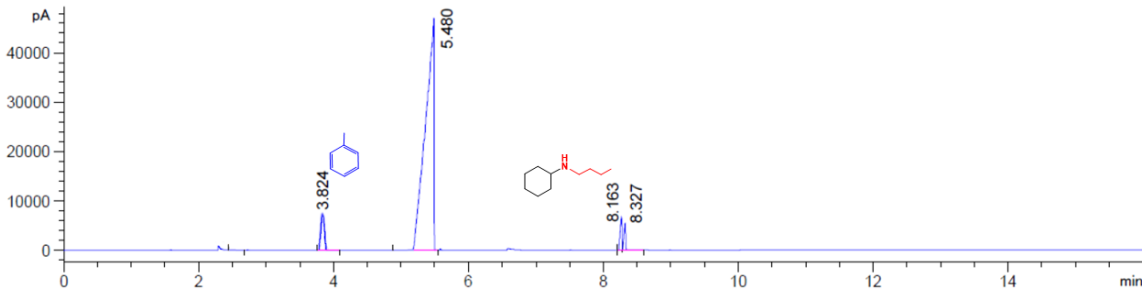
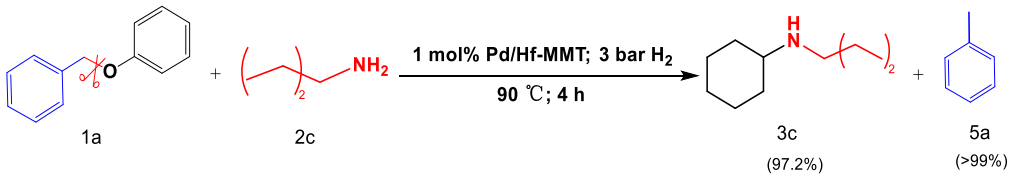
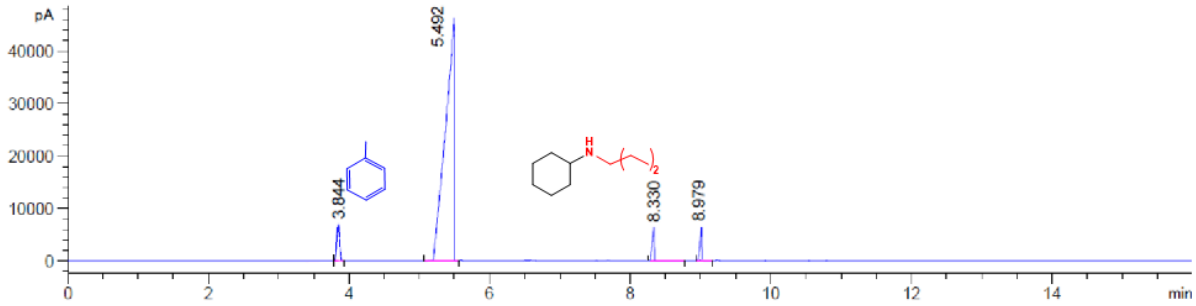




Reaction 3





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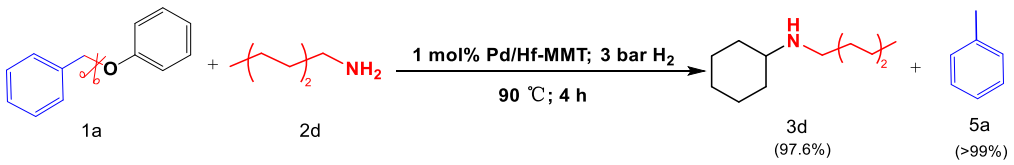

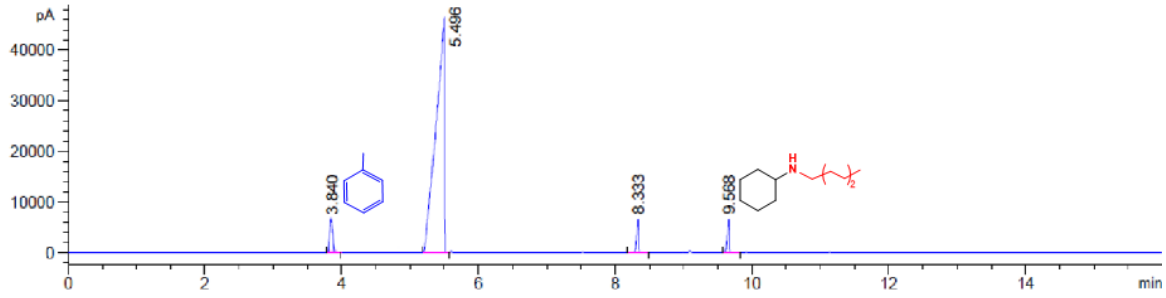

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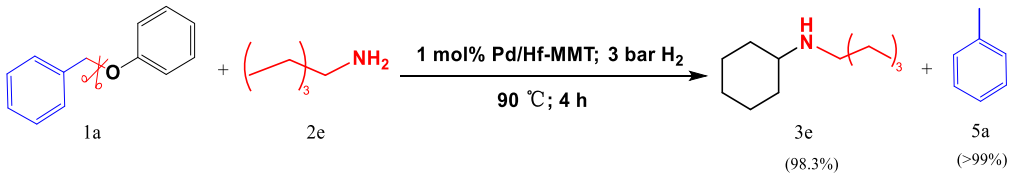
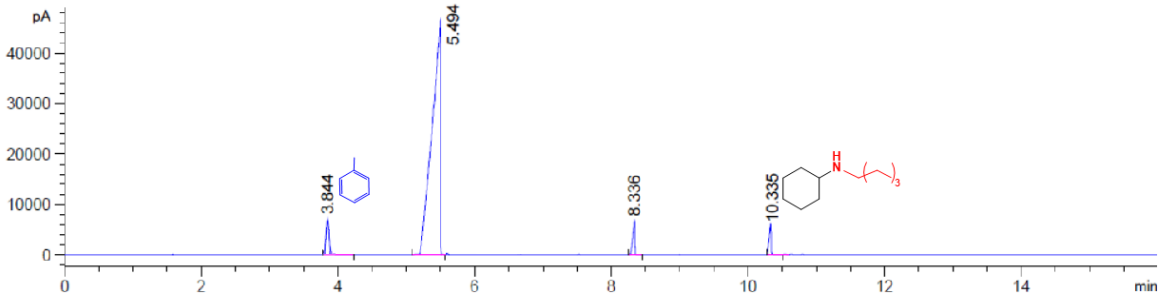
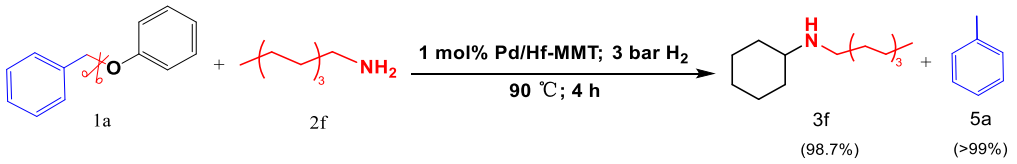


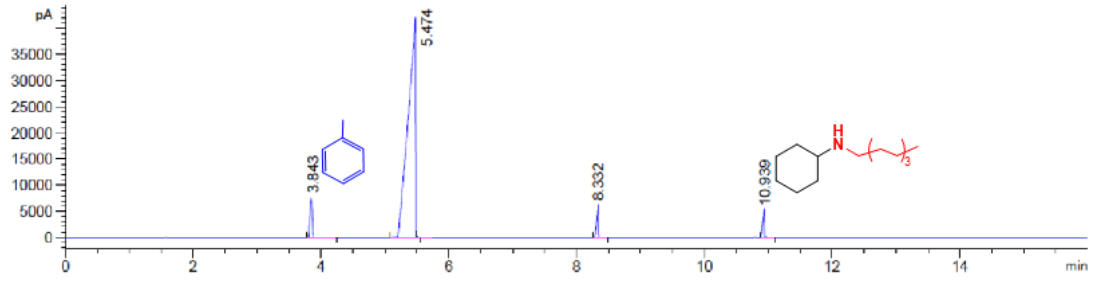
1a 2e 3e (98.3%) 5a (>99%)



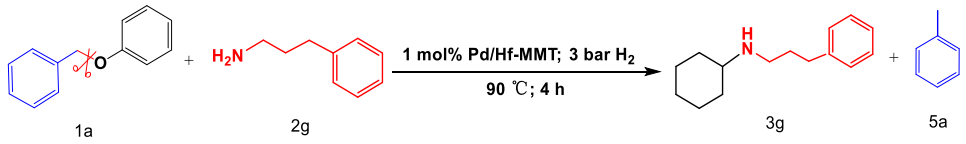
Reaction 6



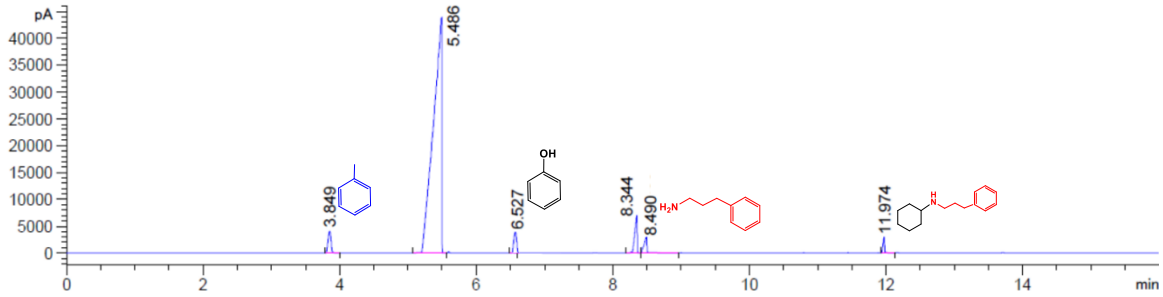
1a 2f 3f (98.7%) 5a (>99%)



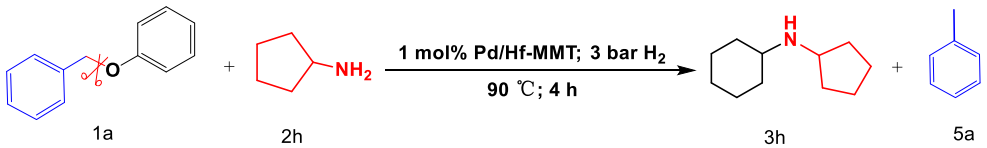
Reaction 7



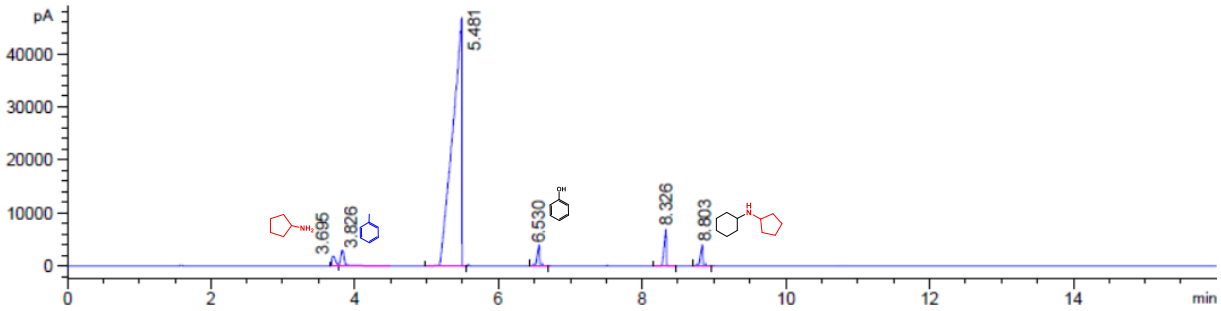
1a + 2g → 3g (67.8%) + 5a (>99%)



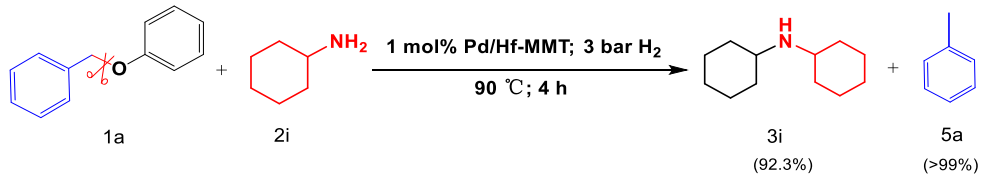
Reaction 8



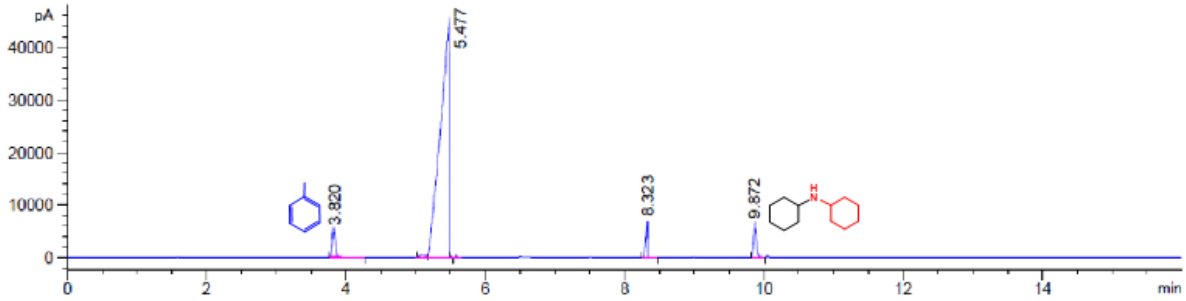
1a + 2h → 3h (75.8%) + 5a (>99%)



Reaction 9



1a 2i 3i (92.3%) 5a (>99%)



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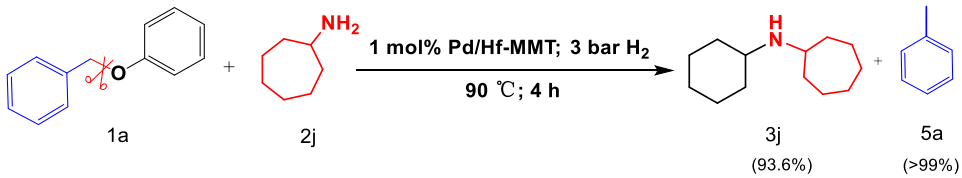
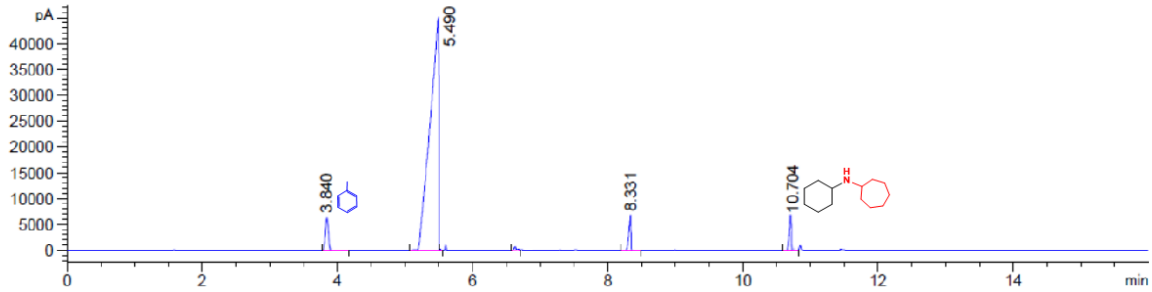


1a 2j 3j (93.6%) 5a (>99%)



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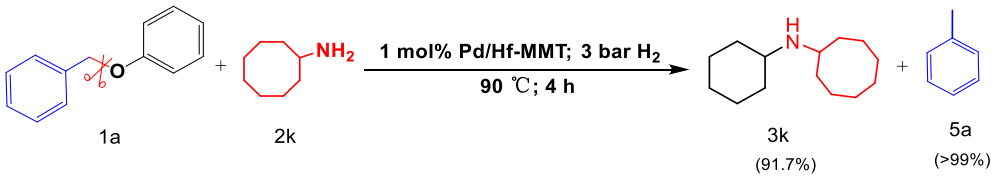
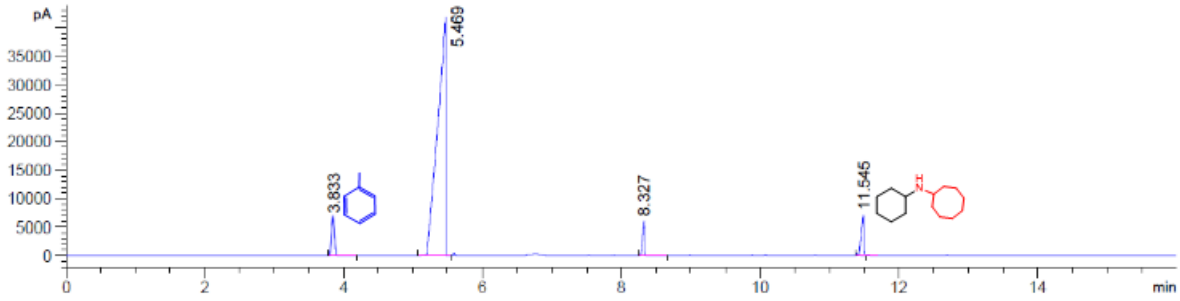
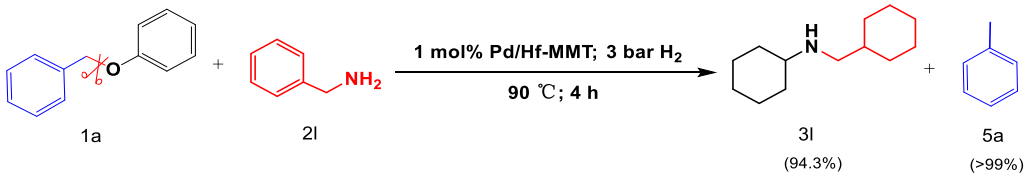


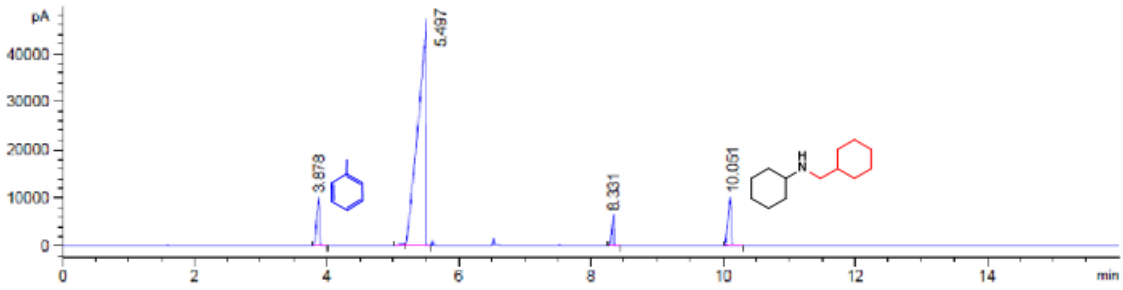
1a 2k 3k (91.7%) 5a (>99%)



Reaction 12



1a 2l 3l (94.3%) 5a (>99%)



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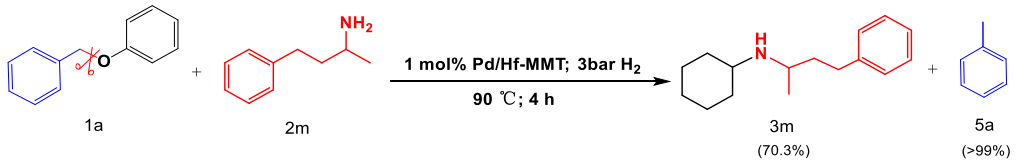
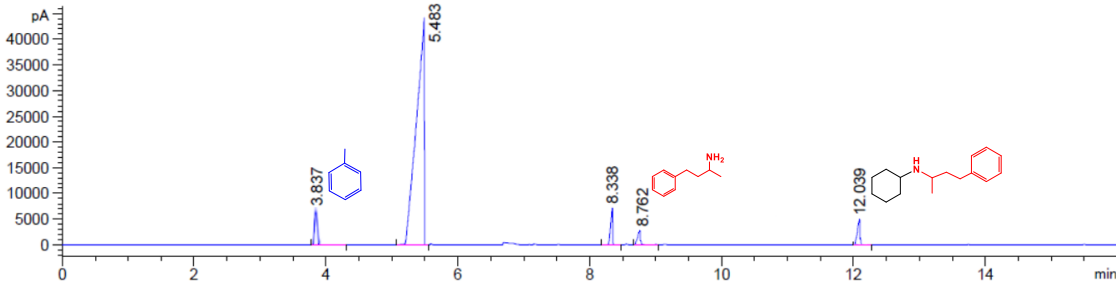
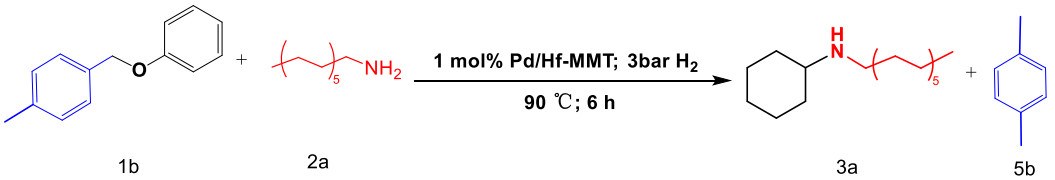


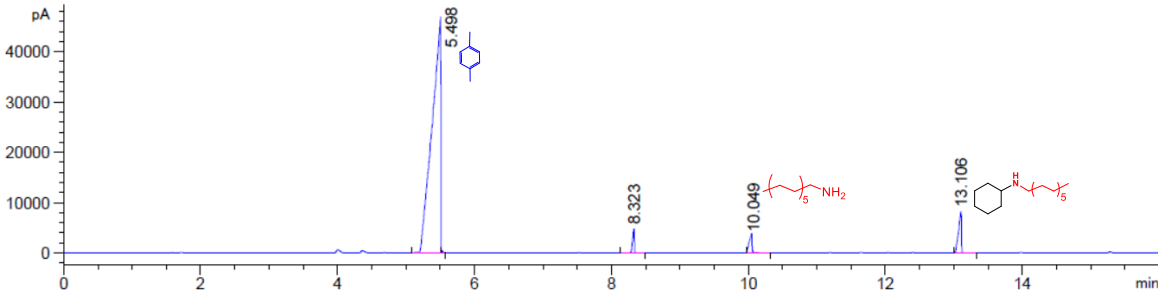
1a + 2m → 3m (70.3%) + 5a (>99%)



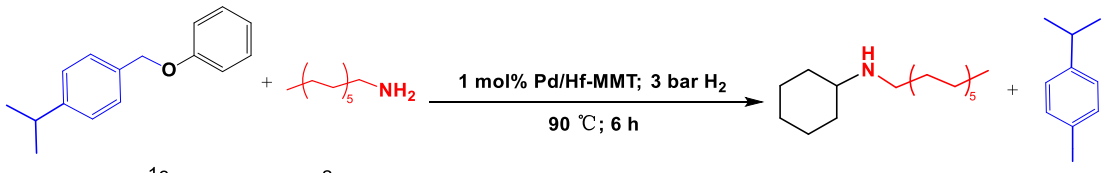
Reaction 14



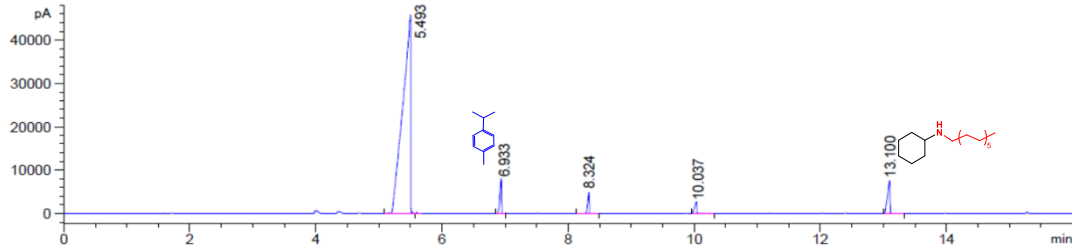
1b + 2a → 3a (85.3%) + 5b (>99%)



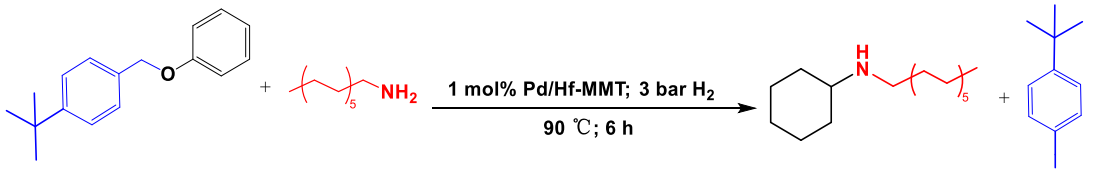
Reaction 15



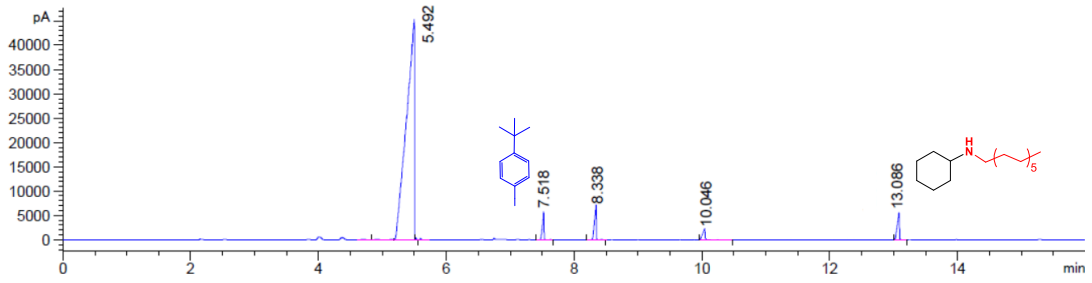
1c + 2a → 3a (84.7%) + 5c (>99%)



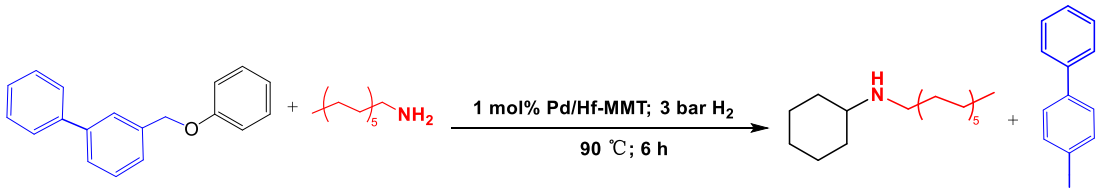
Reaction 16



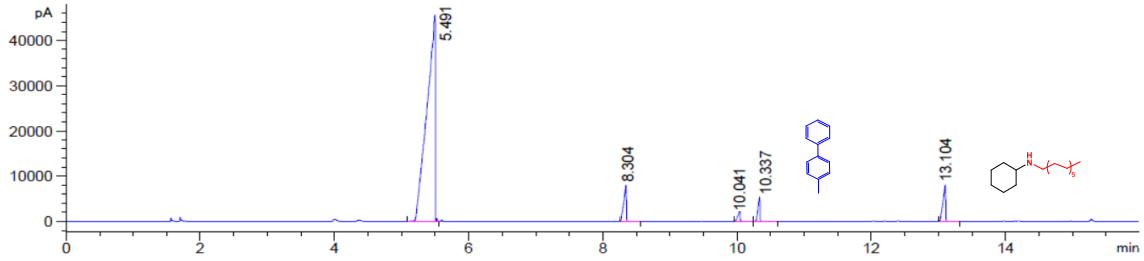
1d + 2a → 3a (90.3%) + 5d (>99%)



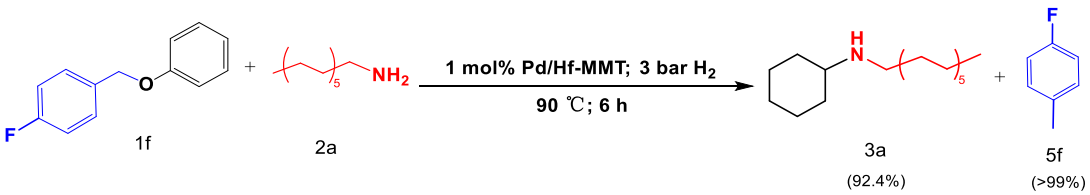
Reaction 17



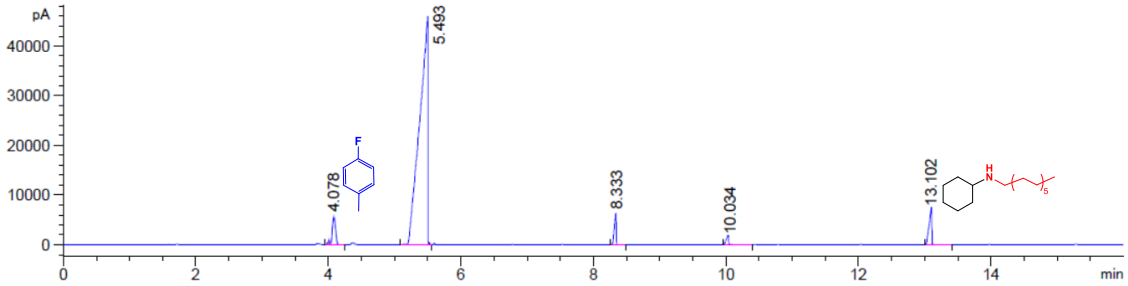
1e + 2a → 3a (88.6%) + 5e (>99%)



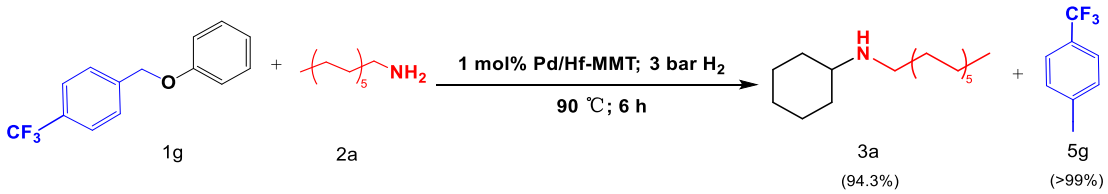
Reaction 18



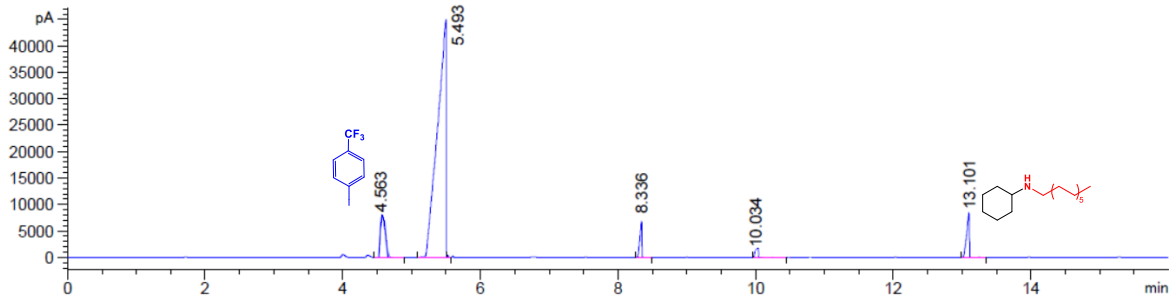
1f + 2a → 3a (92.4%) + 5f (>99%)



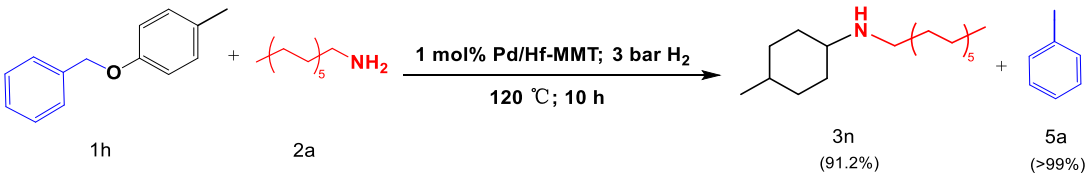
Reaction 19



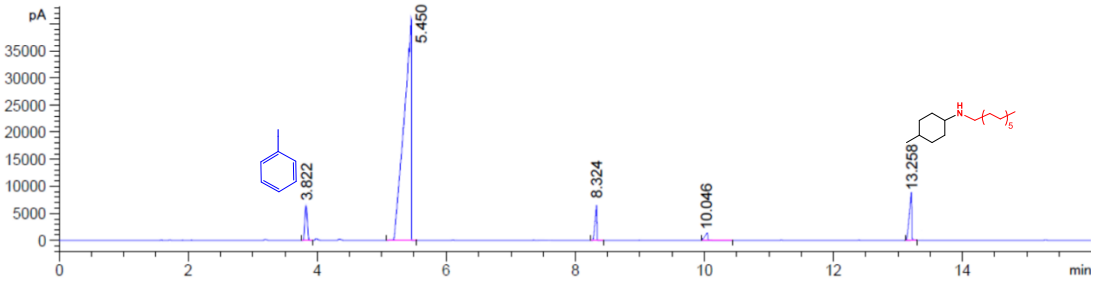
1g 2a 3a (94.3%) 5g (>99%)



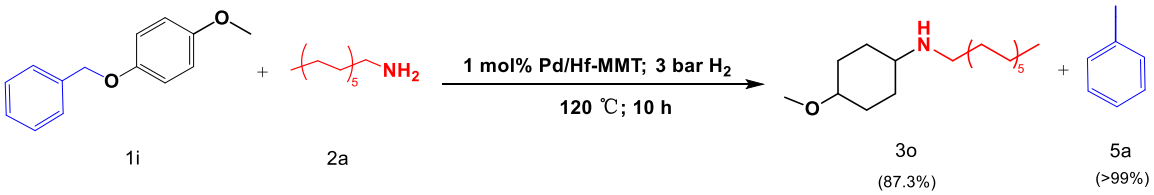
Reaction 20



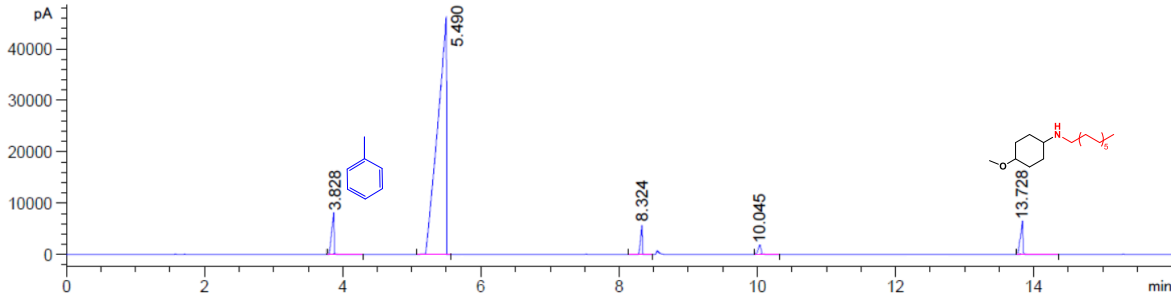
1h 2a 3n (91.2%) 5a (>99%)



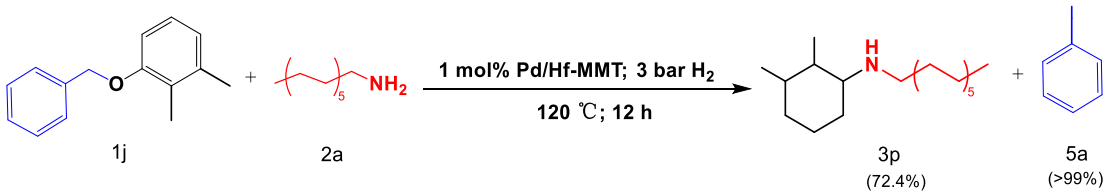
Reaction 21



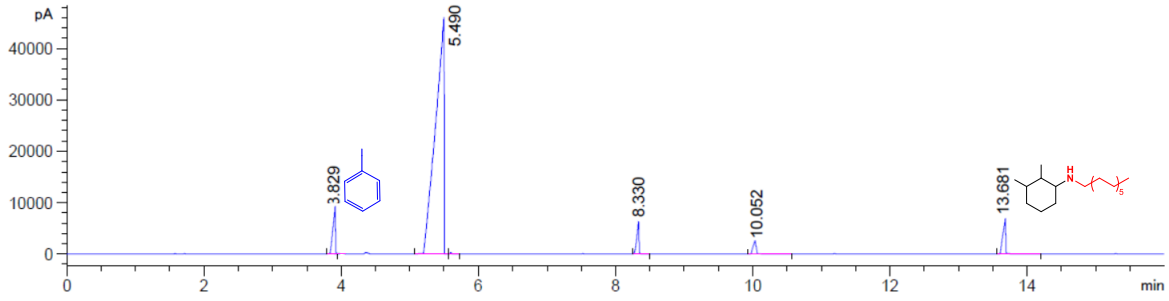
1i + 2a → 3o (87.3%) + 5a (>99%)



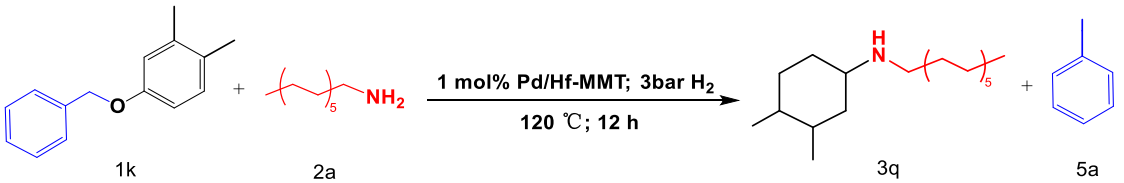
Reaction 22

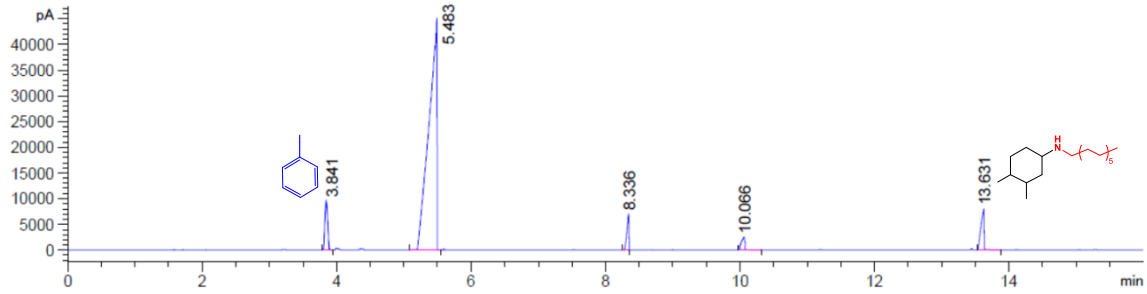


1j + 2a → 3p (72.4%) + 5a (>99%)

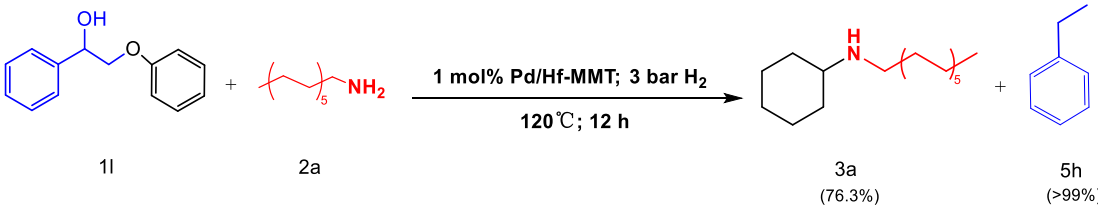


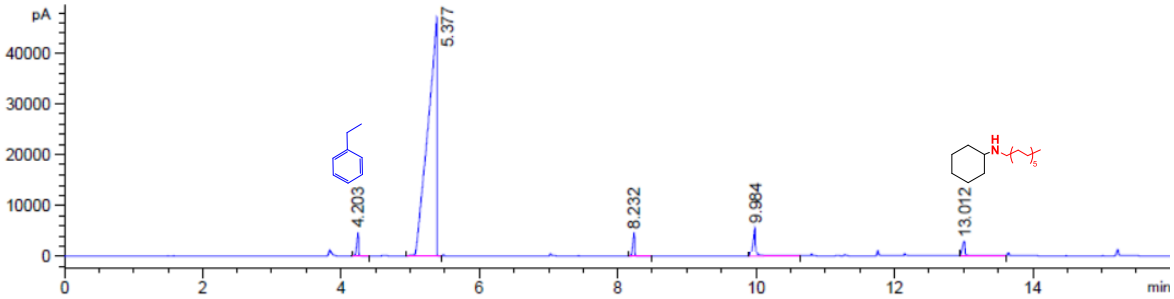
Reaction 23



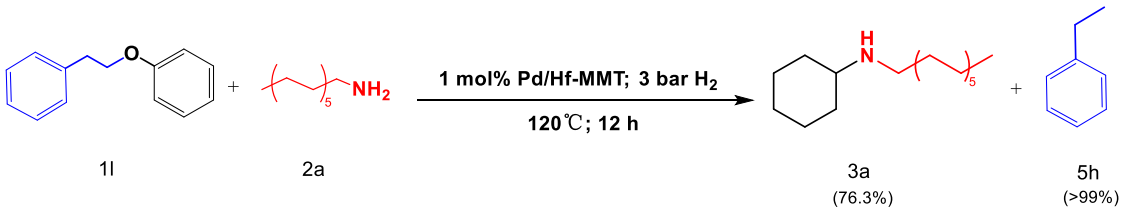


Reaction 24

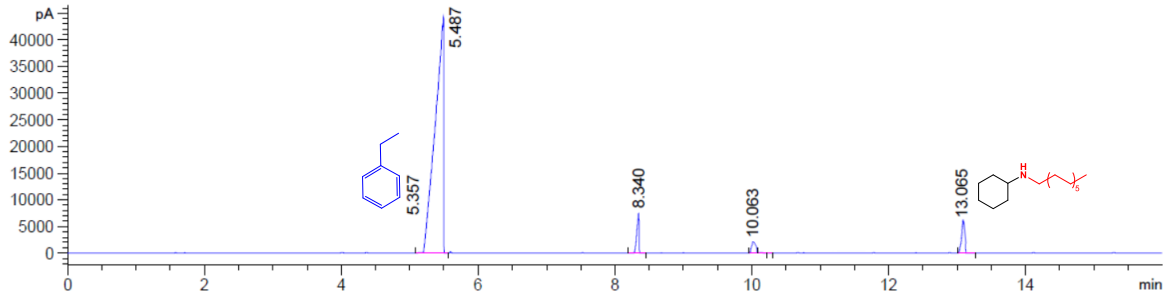




Reaction 25



1l 2a 3a (76.3%) 5h (>99%)



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