Organic ligand and solvent free oxidative carbonylation of amine over Pd/TiO_2 with unprecedented activity

Shujuan Liu,[a,b] Xingchao Dai,[a,b] Hongli Wang,[a] and Feng Shi[a]*

[a]*State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, No.18, Tianshui Middle Road, Lanzhou, 730000, China;*

E-mail: fshi@licp.cas.cn

[b]*University of Chinese Academy of Sciences, No. 19A, Yuquanlu, Beijing, 100049, China*

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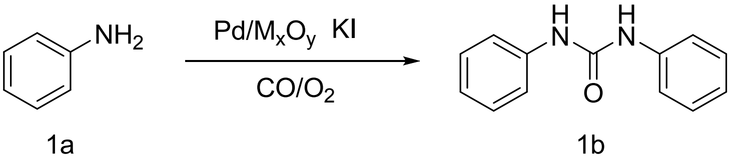
1. Optimization of the reaction conditions.

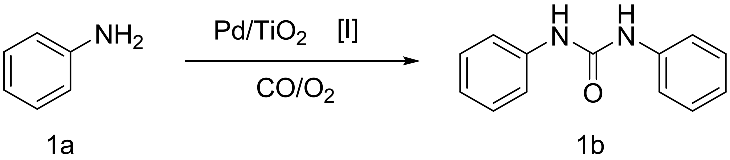
Table S1 Reaction condition optimization for oxidative carbonylation of aniline [a]



Entry	Catalyst	Metal content (wt%)[b]	Yield /%[b]	TON	TOF/h^{-1}
1	Pd/TiO_2	0.004	54	572000	72000
2	Pd/Al_2O_3	0.002	21	222000	37000
3	Pd/SiO_2	0.002	35	742000	92750
4	Pd/Fe_2O_3	0.004	29	154000	25667

[a] Reaction conditions: 1a (20 mmol), catalyst (50 mg), KI (1 mol %), CO (35 bar), O_2 (5 bar), solvent free, 92 ± 2 °C, 8 h, TON was defined as mol aniline converted per mol Pd and TOF as mol aniline converted per mol Pd per h; [b] Determined by isolated yield.

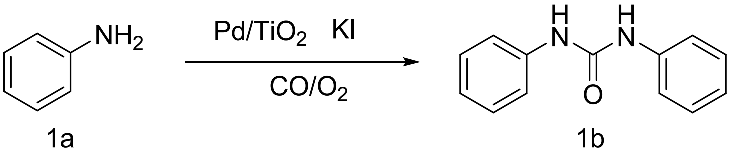
Table S2. Screening of the [I] for the carbonylation of aniline [a].



Entry	[I]	Yield /%[b]	TON	TOF/h^{-1}
1	KI	54	572000	72000
2	I_2	36	382000	48000
3	NaI	27	286000	36000
4	(n-Bu)$_4$NI	11	116000	15000

[a] Reaction conditions: 1a (20 mmol), catalyst (50 mg), [I] (1 mol %), CO (35 bar), O_2 (5 bar), solvent free, 92 ± 2 °C, 8 h, TON was defined as mol aniline converted per mol Pd and TOF as mol aniline converted per mol Pd per h; [b] Determined by isolated yield.

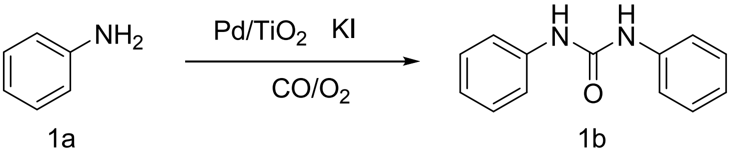
Table S3. Screening of the amount of KI for the carbonylation of aniline [a].



Entry	[KI]	Yield /%[b]	TON	TOF/h^{-1}
1	0.2 mol %	38	402000	50000
2	0.5 mol %	40	424000	53000
3	1 mol %	54	572000	72000

[a] Reaction conditions: 1a (20 mmol), catalyst (50 mg), CO (35 bar), O_2 (5 bar), solvent free, 92 ± 2 °C, 8 h, TON was defined as mol aniline converted per mol Pd and TOF as mol aniline converted per mol Pd per h; [b] Determined by isolated yield.

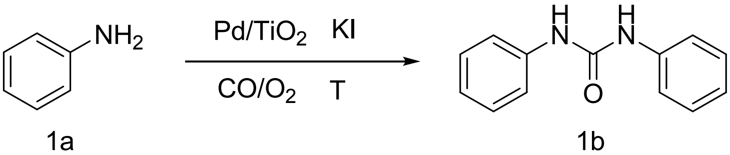
Table S4. Screening of the pressure of CO and O_2 for the carbonylation of aniline [a].



Entry	CO (bar)	O_2 (bar)	Yield /%[b]	TON	TOF/h^{-1}
1	1	0.1	28	296000	37000
2	2	0.1	36	382000	48000
3	3	0.1	41	434000	54000
4	3.5	0.1	46	488000	61000
6	2.5	0.5	39	414000	52000
7	3.5	0.5	54	572000	72000

[a] Reaction conditions: 1a (20 mmol), catalyst (50 mg), KI (1 mol %), solvent free, 92 ± 2 °C, 8 h, TON was defined as mol aniline converted per mol Pd and TOF as mol aniline converted per mol Pd per h; [b] Determined by isolated yield.

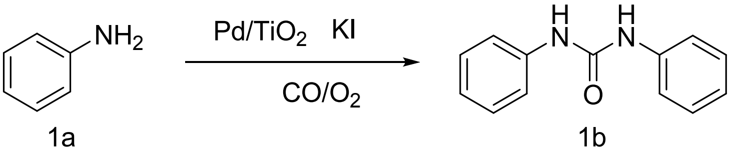
Table S5. Screening of the temperature for the carbonylation of aniline [a].



Entry	T (℃)	Yield /%[b]	TON	TOF/h^{-1}
1	105(92)	10	402000	50000
2	120(108)	54	572000	72000
3	135(122)	55	584000	73000

[a] Reaction conditions: 1a (20 mmol), catalyst (50 mg), KI (1 mol %), CO (35 bar), O_2 (5 bar), solvent free, 8 h, TON was defined as mol aniline converted per mol Pd and TOF as mol aniline converted per mol Pd per h; [b] Determined by isolated yield.

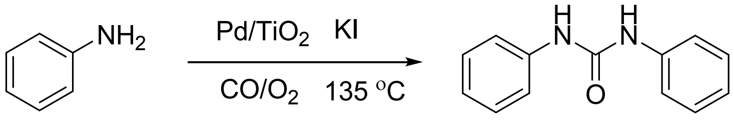
Table S6. Screening of the solvent for the carbonylation of aniline [a].



Entry	solvent	Yield /%[b]	TON	TOF/h^{-1}
1	--	55	584000	73000
2	toluene	53	564000	70000
3	NMP	50	534000	67000
4	CH_3CN	48	514000	64000
5	cyclohexane	41	430000	54000
6	dioxane	38	400000	50000
7	DMF	12	132000	17000
8[c]	CH_3CN	5	52000	7000

[a] Reaction conditions: 1a (20 mmol), catalyst (50 mg), KI (1 mol %), CO (35 bar), O_2 (5 bar), solvent (3 mL), 122 ± 2 °C, 8 h, TON was defined as mol aniline converted per mol Pd and TOF as mol aniline converted per mol Pd per h; [b] Determined by isolated yield; [c] CH_3CN (15 mL).

Table S7. Screening of the time for the carbonylation of aniline [a].



1a 1b

Entry	Time /h	Yield/%[b]	TON	TOF/h^{-1}
1	1	24	254000	254000
2	2	30	322000	161000
3	4	47	500000	125000
4	6	54	578000	96000
5	8	55	584000	73000
6	24	59	624000	26000

[a] Reaction conditions: 1a (20 mmol), catalyst (50 mg), KI (1 mol %), CO (35 bar), O_2 (5 bar), solvent free, 122 ± 2 °C; TON was defined as mol aniline converted per mol Pd and TOF as mol aniline converted per mol Pd per h [b] Determined by isolated yield.

2. Characterization results of catalysts

Table S8. The physicochemical properties of catalysts.

Entry	Catalyst	SA[a] (m^2 g^{-1})	APR[a] (nm)	PV[a] (cm^3 g^{-1})
1	Pd/TiO_2	103.0	18.8	0.97

[a] Determined by an IQ2 automated gas sorption analyser. SA: BET surface area; APS: average pore radius; PV: pore volume.

Table S9. Reuse of the catalyst.

entry	Time	actual metal loading [b]	Yield/%[c]	TON	TOF/h^{-1}
1	1	0.002 wt %	85	450000	225000
2	2	0.002 wt %	84	444000	222000
3	3	0.002 wt %	87	460000	250000

Reaction conditions: benzylamine (5 mmol), 0.004 wt% Pd/TiO_2 (35 mg), CO (35 bar), O_2 (5 bar), KI (1 mol %), toluene (2 mL), 122 ± 2 °C, 2 h. TON was defined as mol aniline converted per mol Pd and TOF as mol aniline converted per mol Pd per h; [b] Determined by ICP-AES; [c] Determined by isolated yield.

Fig. S1 XRD patterns of prepared catalysts.

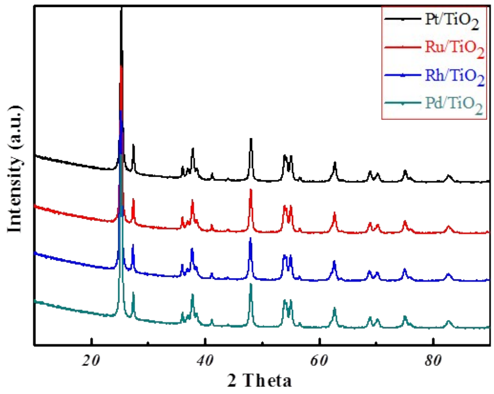


Fig. S2 TEM patterns of prepared catalysts. 0.274 wt% Pd/TiO_2 catalyst (a, b, c), 0.004 wt% Pd/TiO_2 fresh catalyst (d, e), 0.004 wt% Pd/TiO_2 fresh catalyst used three times (f, g).

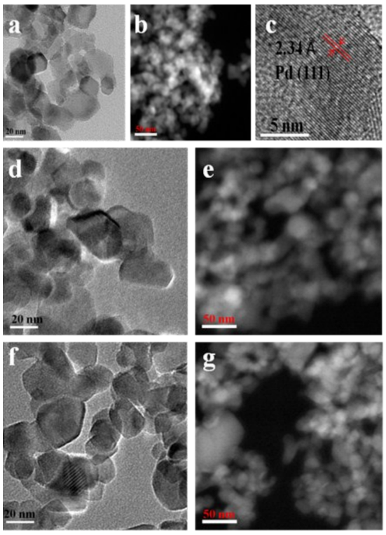
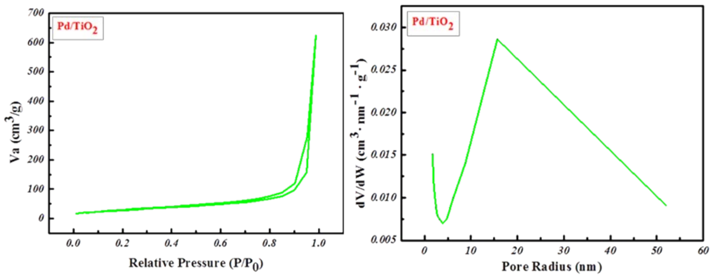
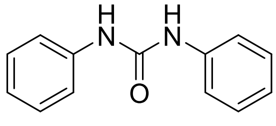


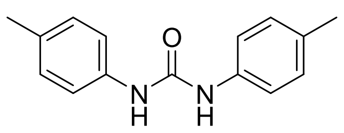
Fig. S3 BJH Desorption patterns of prepared catalysts



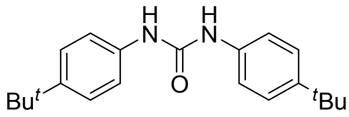
3. Characterization data for products



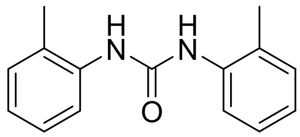
1b 1,3-diphenylurea[1]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a white solid; mp: 227-232℃; **^{1}H NMR** (400 MHz, DMSO-d6) δ 8.67 (brs, 2H), 7.41-7.43 (m, 4H), 7.26-7.30 (m, 4H), 6.99-7.03 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d6) δ 148.9, 131.9, 121.3, 115.3, 111.9.



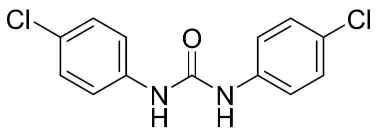
2b 1,3-Bis(4-methylphenyl)urea[1]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was white solid; mp: 266-267℃; **^{1}H NMR** (400 MHz, DMSO-d6) δ 8.48 (brs, 2H), 7.32 (d, 4.8 MHz, 4H), 7.07 (d, 5.2 MHz, 4H), 2.24 (s, 6H); **^{13}C NMR** (100 MHz, DMSO-d6) δ 152.6, 137.2, 130.5, 129.1, 118.2, 20.3.



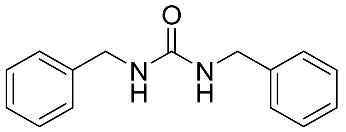
3b 1,3-bis(4-tert-butylphenyl)urea[2]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a black sticky oil; **^{1}H NMR** (400 MHz, DMSO-d6) δ 8.53 (brs, 2H), 7.35 (d, 8.8 MHz, 4H), 7.28 (d, 8.4 MHz, 4H), 1.25 (s, 18H); **^{13}C NMR** (100 MHz, DMSO-d6) δ 146.8, 138.8, 126.2, 118.9, 114.6, 40.0, 32.4.



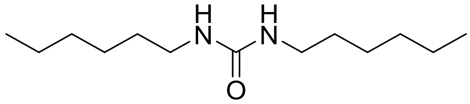
4b 1,3-dio-tolylurea[3]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a black sticky oil; **^{1}H NMR** (400 MHz, DMSO-d6) δ 8.27 (brs, 2H), 7.80-7.82 (m, 2H), 7.12-7.18 (m, 4H), 6.92-6.96 (m, 2H), 2.26 (s, 6H); **^{13}C NMR** (100 MHz, DMSO-d6) δ 147.3, 130.8, 127.3, 121.9, 117.0, 114.9, 18.3.



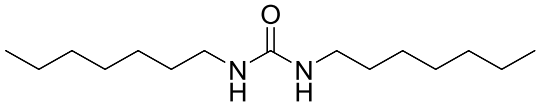
5b 1,3-Bis(4-chlorophenyl)urea[1]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a brown solid; mp: 278-280℃; **^{1}H NMR** (400 MHz, DMSO-d6) δ 8.89 (brs, 2H), 7.48 (d, 8.0 MHz, 4H), 7.33 (d, 8.4 MHz, 4H); **^{13}C NMR** (100 MHz, DMSO-d6) δ 152.3, 138.5, 128.6, 125.5, 119.8.



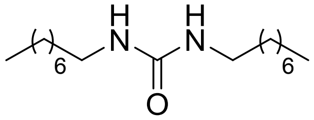
6b 1,3-Dibenzylurea[1]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was light brown solid; mp: 209-210℃; **^{1}H NMR** (400 MHz, DMSO-d6) δ 7.24-7.31 (m, 10H), 6.44 (brs , 2H), 4.23 (s, 4H); **^{13}C NMR** (100 MHz, DMSO-d6) δ 158.1, 140.9, 128.2, 127.0, 126.5, 40.0.



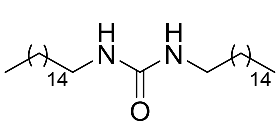
7b 1,3-dihexylurea[1]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a brown sticky oil; **^{1}H NMR** (400 MHz, DMSO-d6) δ 5.72 (brs, 2H), 3.50 (s, 2H), 2.92-3.11 (m, 3H), 1.24-1.44 (m, 16H), 0.84-0.86 (m, 6H); **^{13}C NMR** (100 MHz, DMSO-d6) δ 158.1, 39.2, 31.1, 30.0, 26.1, 22.1, 13.9.



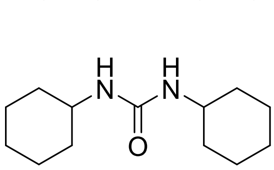
8b 1,3-diheptylurea[1]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a yellow sticky solid; mp: 65℃; **^{1}H NMR** (400 MHz, DMSO-d6) δ 5.73 (brs, 2H), 2.95-3.11 (m, 4H), 1.24-2.02 (m, 20H), 0.86 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.7, 40.5, 31.7, 30.3, 29.0, 26.9, 22.5, 14.0.



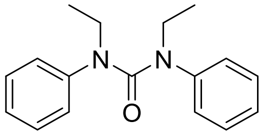
9b 1,3-dioctylurea[4]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a yellow sticky solid; **^{1}H NMR** (400 MHz, DMSO-d6) δ 8.01 (brs, 2H), 3.03-3.34 (m, 2H), 1.28 (m, 26H), 0.88-0.89 (m, 6H); **^{13}C NMR** (100 MHz, DMSO-d6) δ 161.7, 38.0, 32.2, 30.0, 29.6, 27.3, 23.1, 14.9.



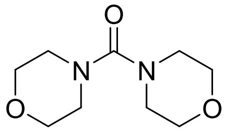
10b 1,3-dicetylurea: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a yellow solid; **^{1}H NMR** (400 MHz, DMSO-d6) δ 1.28 (m, 56H), 0.89 (t, 4.4 MHz, 6H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.2, 40.7, 31.9, 29.7, 29.6 29.4, 22.7, 14.1.



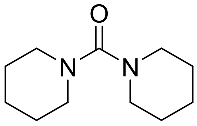
11b 1,3-dicyclohexylurea[1]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a light grey solid; mp: 209-210℃; ^{1}**HNMR** (400 MHz, CDCl$_3$) δ 3.46-3.41 (m, 2H) 1.10-1.95 (m, 20H) ; ^{13}**C NMR** (100 MHz, CDCl$_3$) δ 156.7, 49.1, 33.9, 25.6, 24.9.



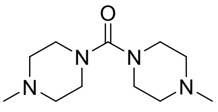
12b 1,3-diethyl-1,3-diphenylurea: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a black sticky oil; ^{1}**H NMR** (400 MHz, DMSO-d6) δ 8.45 (brs, 2H), 7.11-7.14 (m, 4H), 6.57-6.63 (m, 4H), 3.05-3.09 (m, 4H), 1.21 (t, 4.6 MHz, 6H); ^{13}**C NMR** (100 MHz, DMSO-d6) δ 149.9, 149.3, 129.7, 116.3, 112.8, 38.2, 15.3.



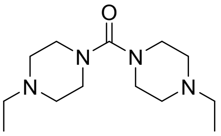
13b dimorpholinomethanone[1]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a brown sticky oil; ^{1}**H NMR** (400 MHz, DMSO-d6) δ 3.13-3.57 (m, 16H); ^{13}**C NMR** (100 MHz, DMSO-d6) δ 162.6, 66.2, 65.9, 65.7, 46.8, 45.8, 40.6.



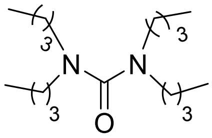
14b 4,4'-Carbonyldimorpholine[5]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a brown sticky oil; ^{1}**H NMR** (400 MHz, DMSO-d6) δ 3.04-3.48 (m, 8H), 1.27-1.63 (m, 12H); ^{13}**C NMR** (100 MHz, CDCl$_3$) δ 163.2, 46.8, 41.4, 26.1, 25.0, 24.0.



15b bis(4-methylpiperazin-1-yl)methanone[6]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a black sticky oil; ^{1}**H NMR** (400 MHz, DMSO-d6) δ 8.02 (brs, 2H), 3.36-3.39 (m, 8H), 2.17-2.32 (m, 14H); ^{13}**C NMR** (100 MHz, DMSO-d6) δ 161.6, 56.0, 54.8, 46.6, 45.6, 35.1.



16b bis(4-ethylpiperazin-1-yl)methanone: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a black sticky oil; ^{1}**H NMR** (400 MHz, DMSO-d6) δ 8.02 (brs, 2H), 3.37-3.40 (m, 8H), 2.30-2.36 (m, 12H), 1.00-1.02 (m, 6H); ^{13}**C NMR** (100 MHz, DMSO-d6) δ 161.4, 53.8, 52.6, 52.5, 45.7, 12.7.



17b 1,1,3,3-tetraethylurea[7]: The title compound was prepared according to the general procedure and purified by heating to remove the reactant to give the desired product which was a black sticky oil;

^{1}**H NMR** (400 MHz, DMSO-d6) δ 3.22-3.23 (m, 2H), 1.44-1.49 (m, 4H), 1.25-1.28 (m, 4H), 0.89-0.92 (m, 6H); ^{13}C **NMR** (100 MHz, DMSO-d6) δ 163.2, 46.9, 29.8, 20.4, 14.4.

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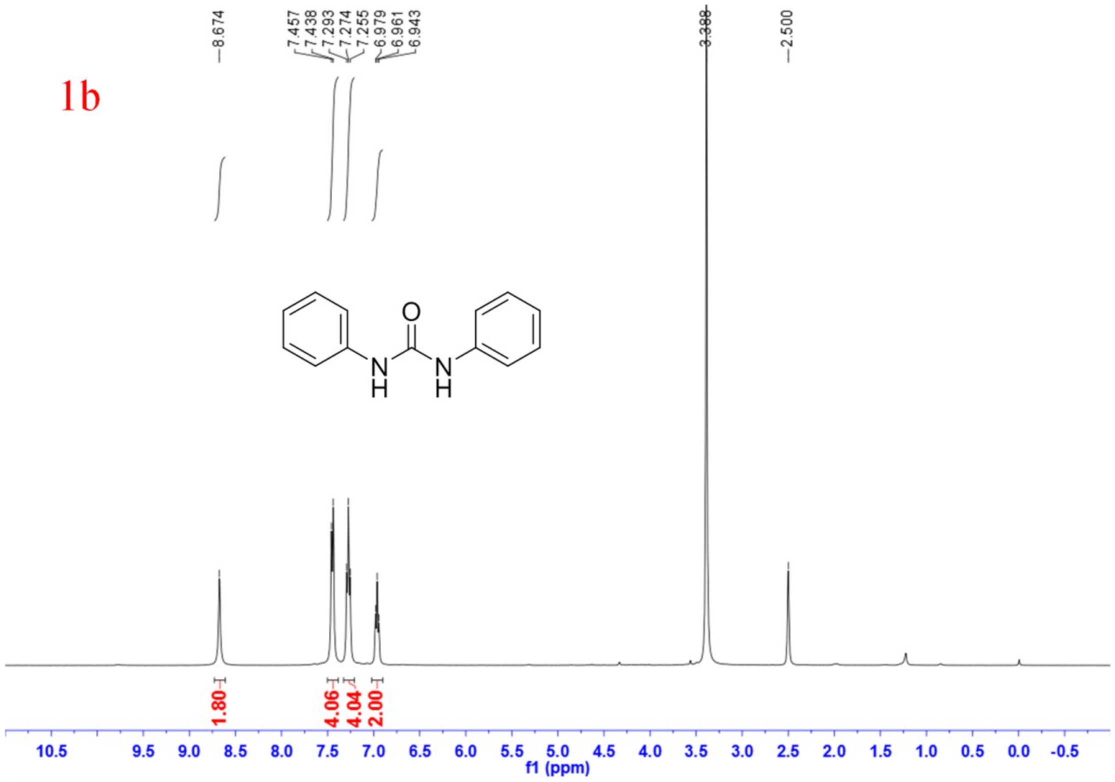
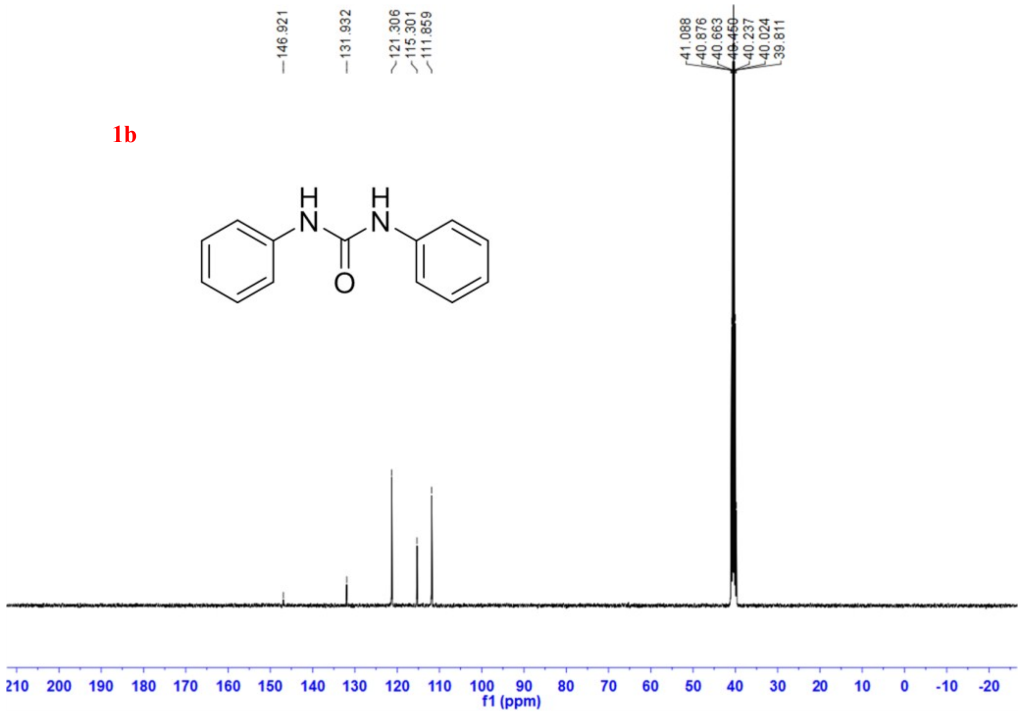
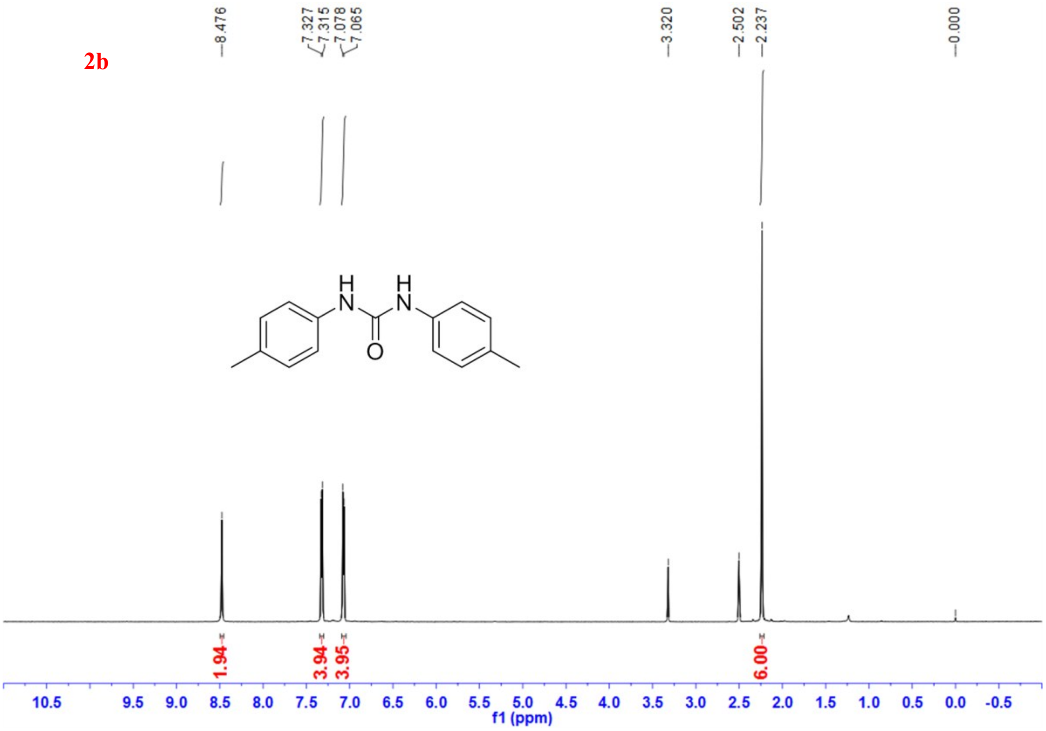
4. NMR spectra of the products





2b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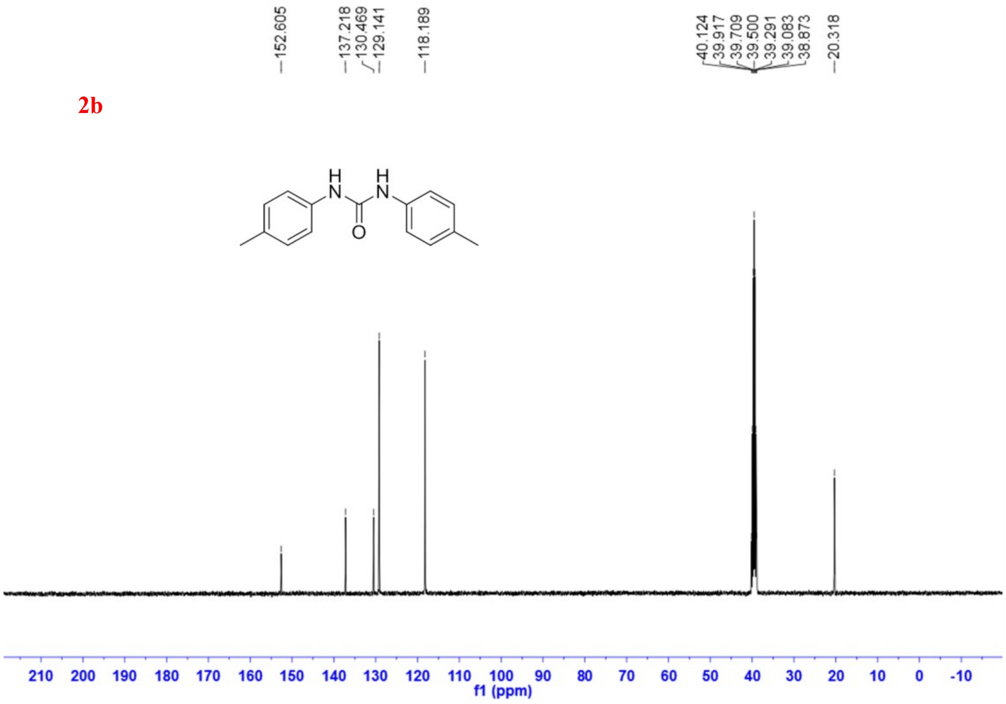
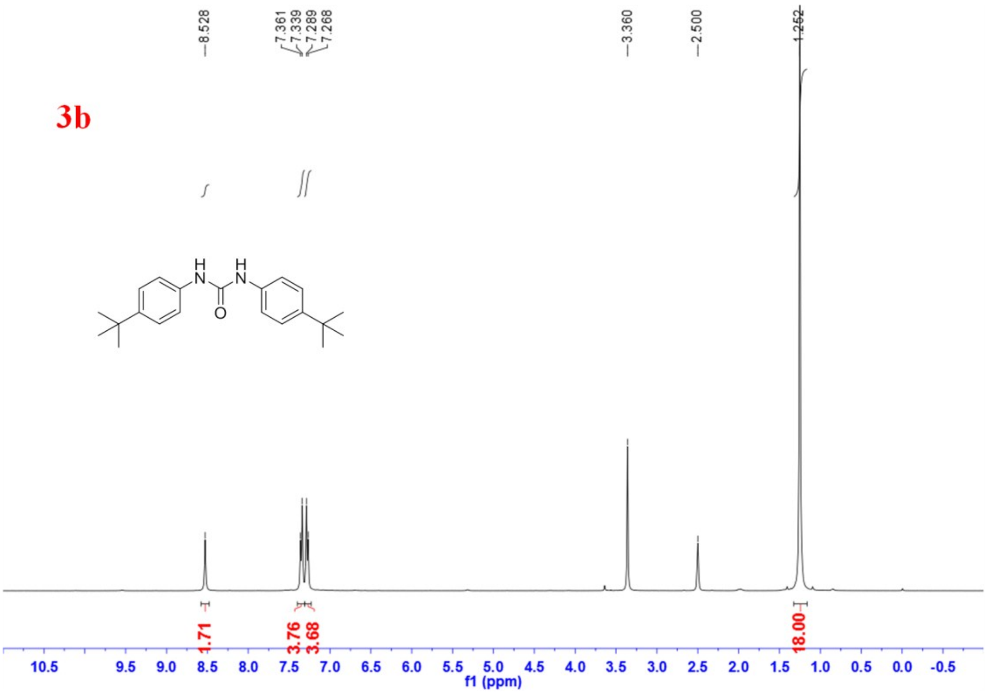
f1 (ppm)

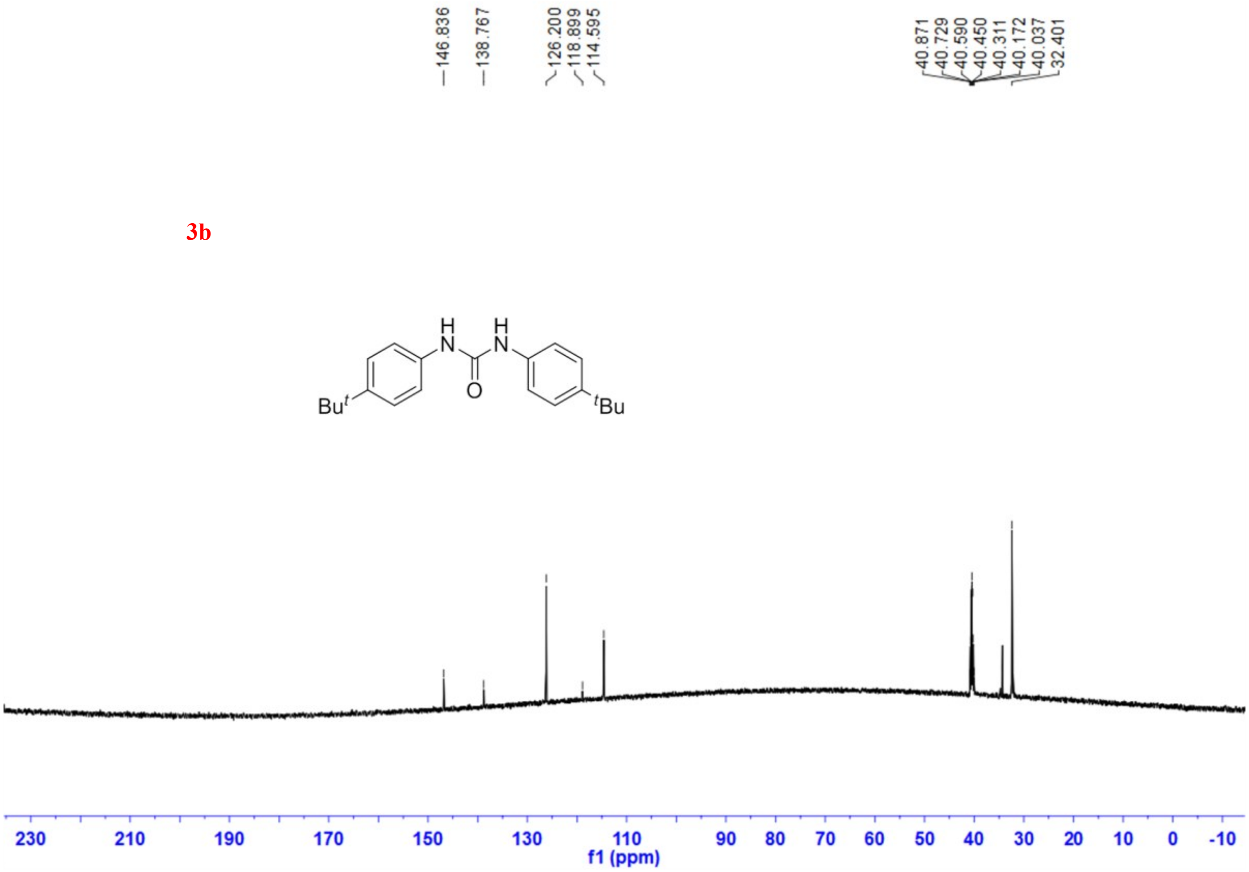
2b


152.605
137.218
130.469
129.141
118.189
40.124
39.917
39.709
39.500
39.291
39.083
38.873
20.318
H
N
H
N
O
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)

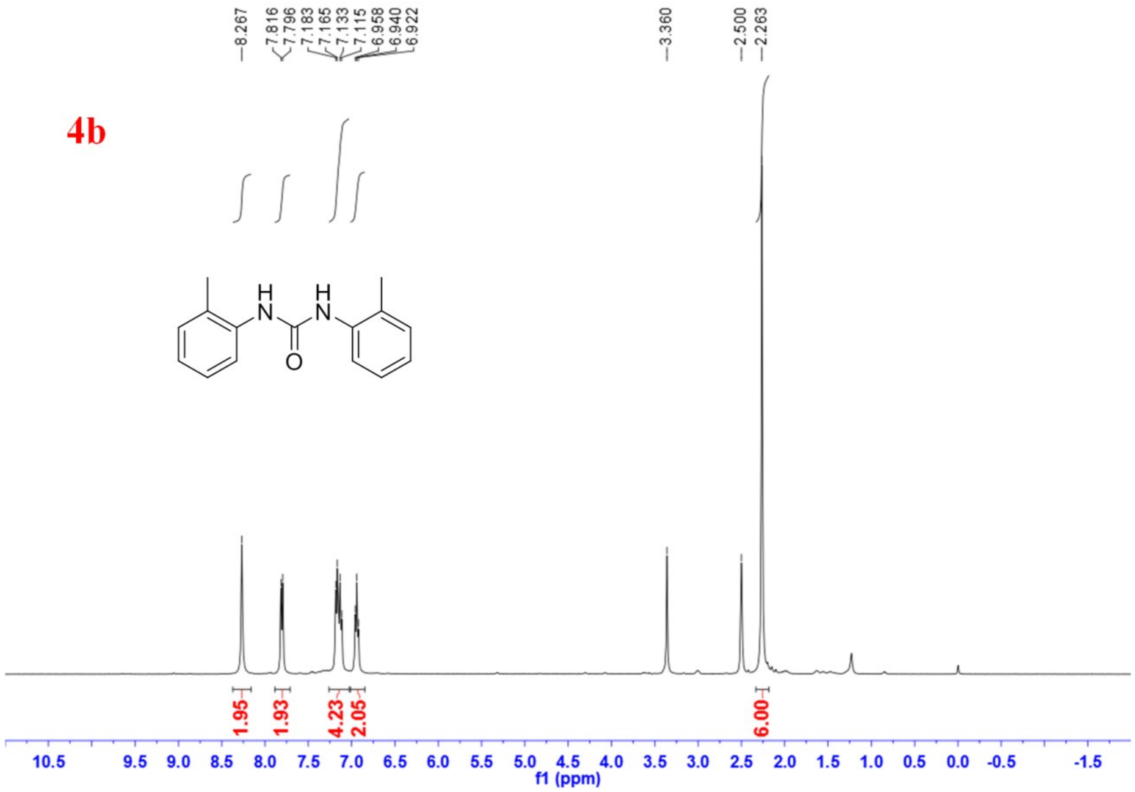
3b


8.528
7.361
7.339
7.289
7.268
3.360
2.500
1.252
H
N
H
N
O
1.71
3.76
3.68
18.00
10.5
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
0.0
-0.5
f1 (ppm)

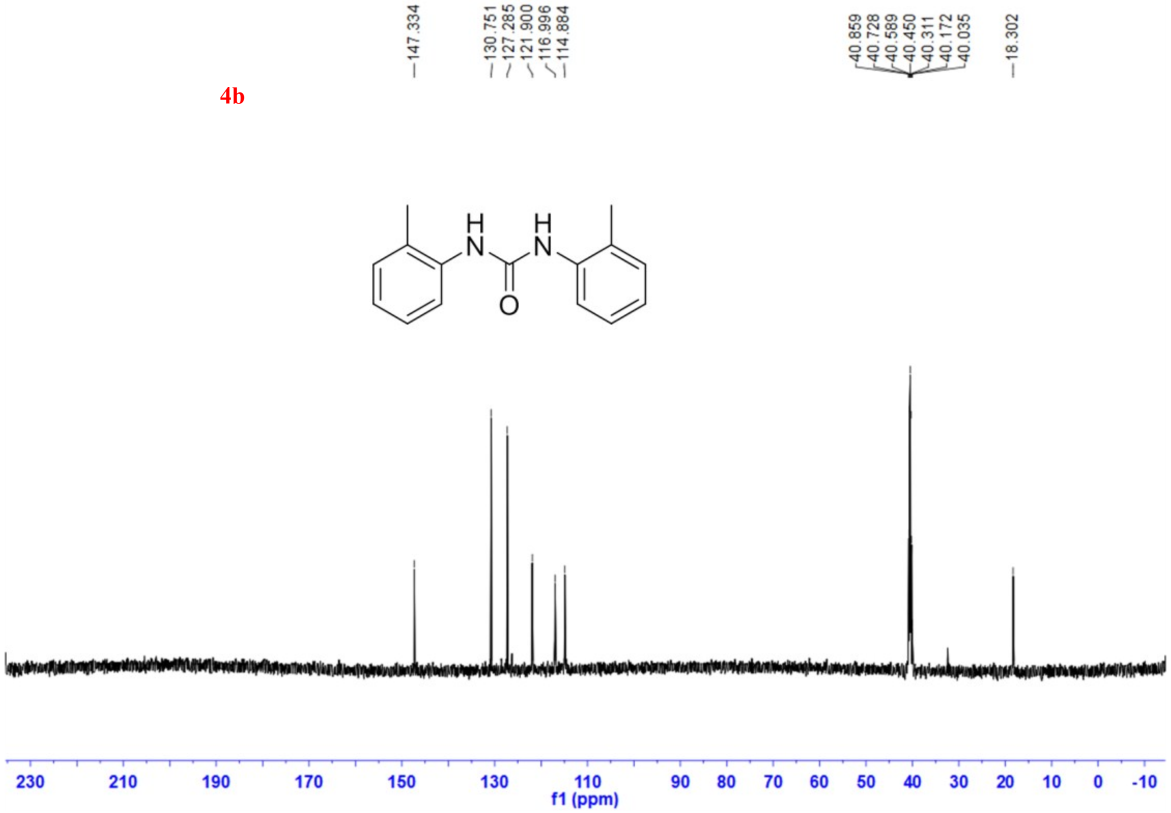
3b


146.836
138.767
126.200
118.899
114.595
40.871
40.729
40.590
40.450
40.311
40.172
40.037
32.401
H
N
H
N
O
Bu^t
^{t}Bu
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

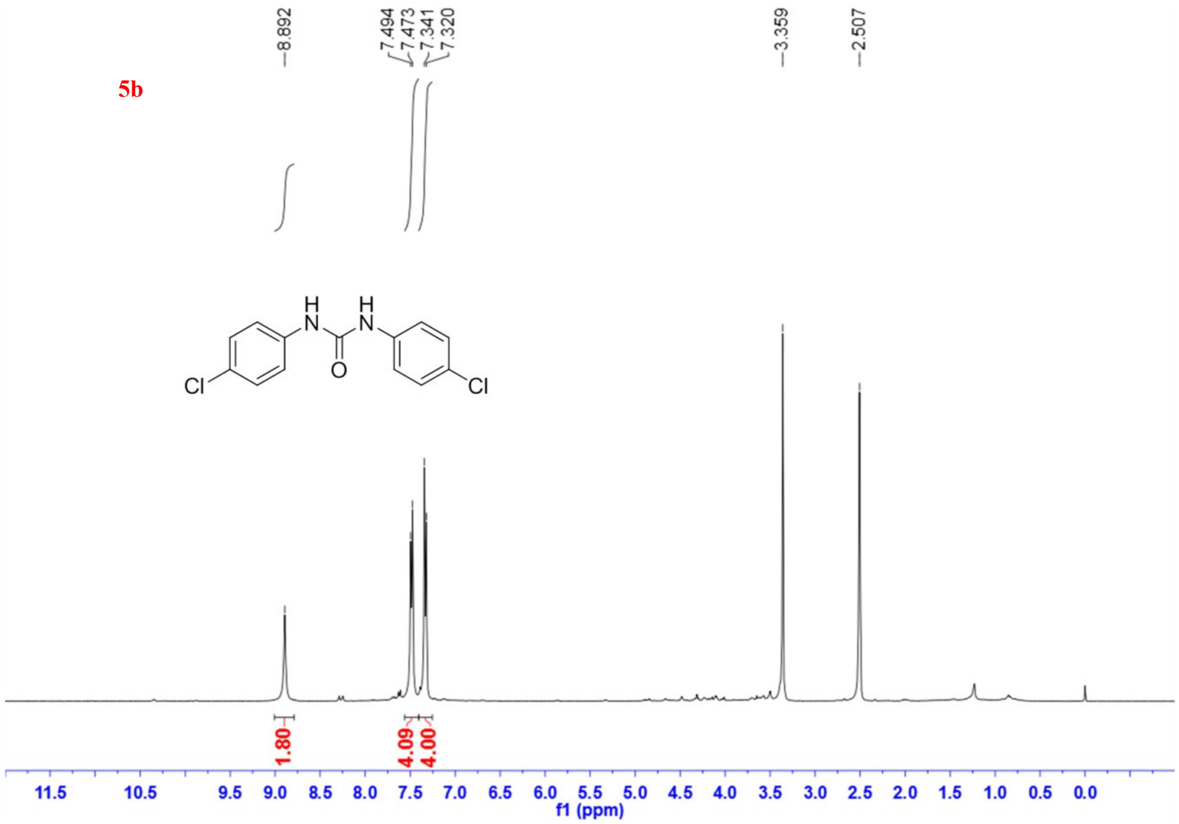
4b


8.267
7.816
7.796
7.183
7.165
7.133
7.115
6.958
6.940
6.922
3.360
2.500
2.263
H
N
H
N
O
1.95
1.93
4.23
2.05
6.00
10.5
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
0.0
-0.5
-1.5
f1 (ppm)

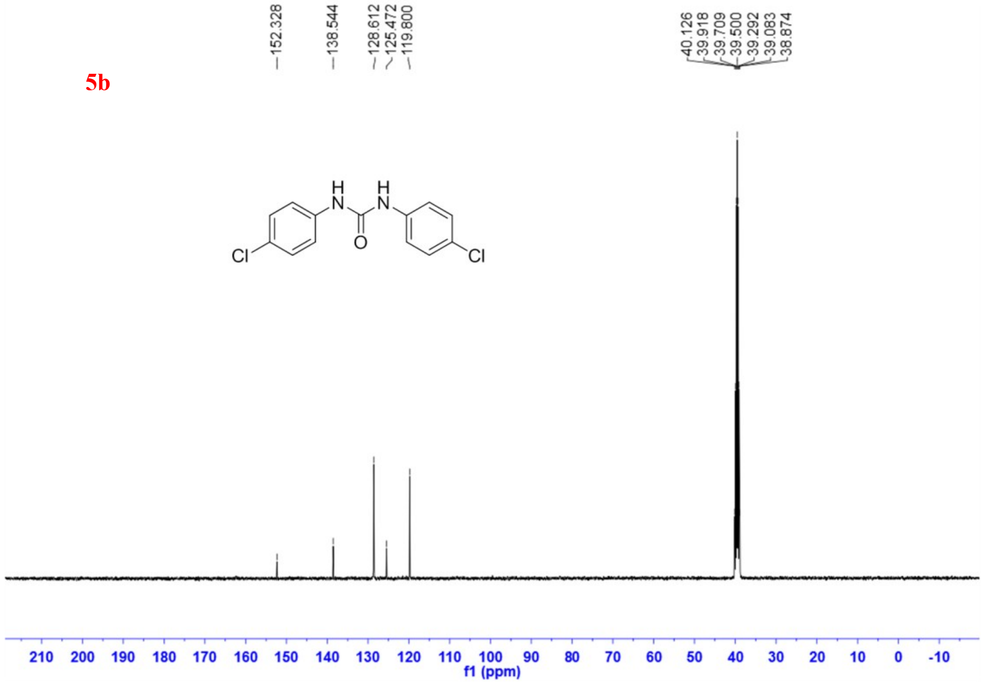
4b


147.334
130.751
127.285
121.900
116.996
114.884
40.859
40.728
40.589
40.450
40.311
40.172
40.035
18.302
H
N
H
N
O
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

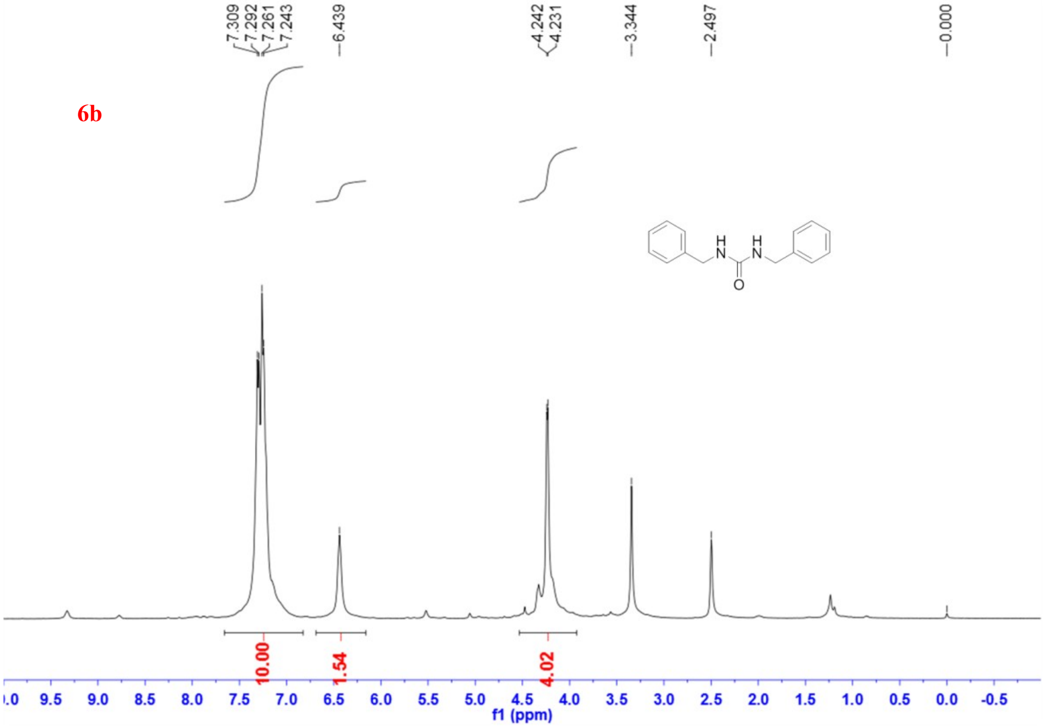
5b


8.892
7.494
7.473
7.341
7.320
3.359
2.507
H
N
H
N
Cl
O
Cl
1.80
4.09
4.00
11.5
10.5
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
0.0
f1 (ppm)

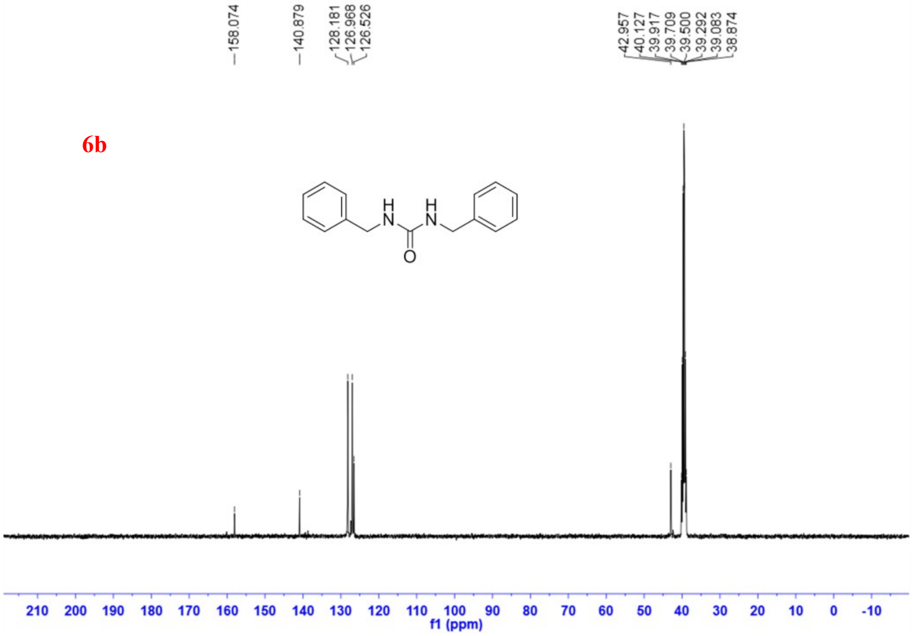
5b


152.328
138.544
128.612
125.472
119.800
40.126
39.918
39.709
39.500
39.292
39.083
38.874
H
N
H
N
Cl
O
Cl
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)

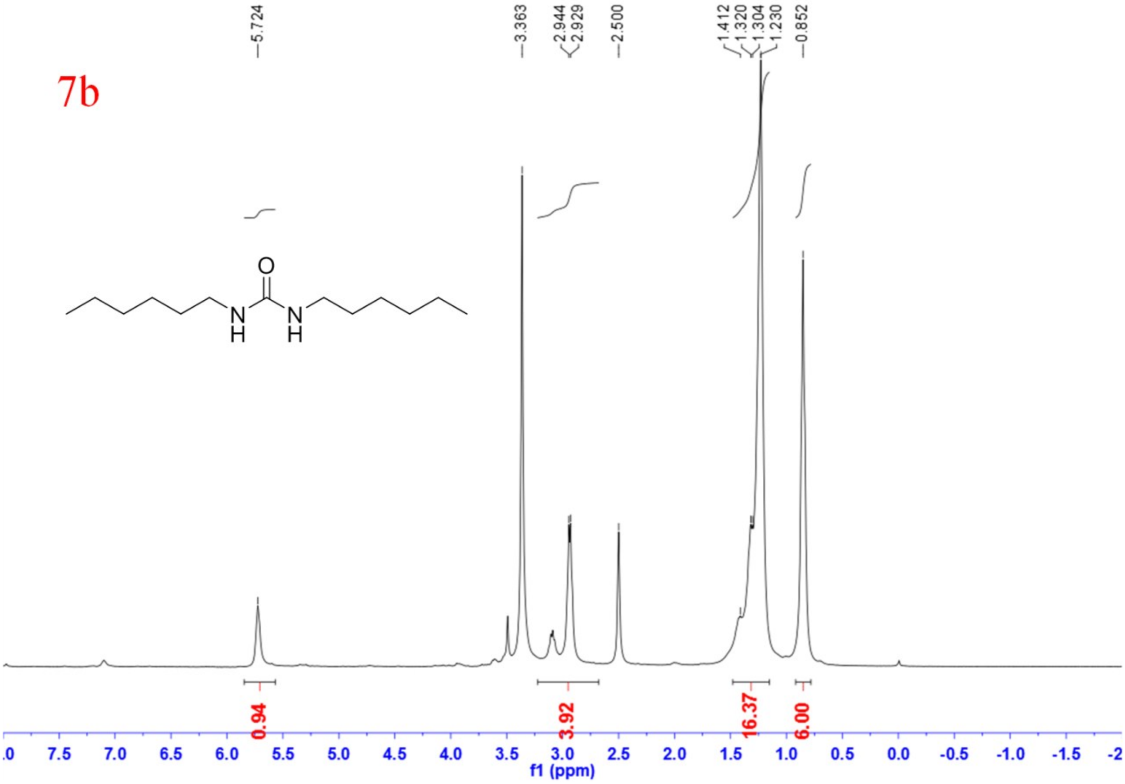
6b


7.309
7.292
7.261
7.243
6.439
4.242
4.231
3.344
2.497
0.000
H
N
H
N
O
10.00
1.54
4.02
.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 0.0 -0.5
f1 (ppm)

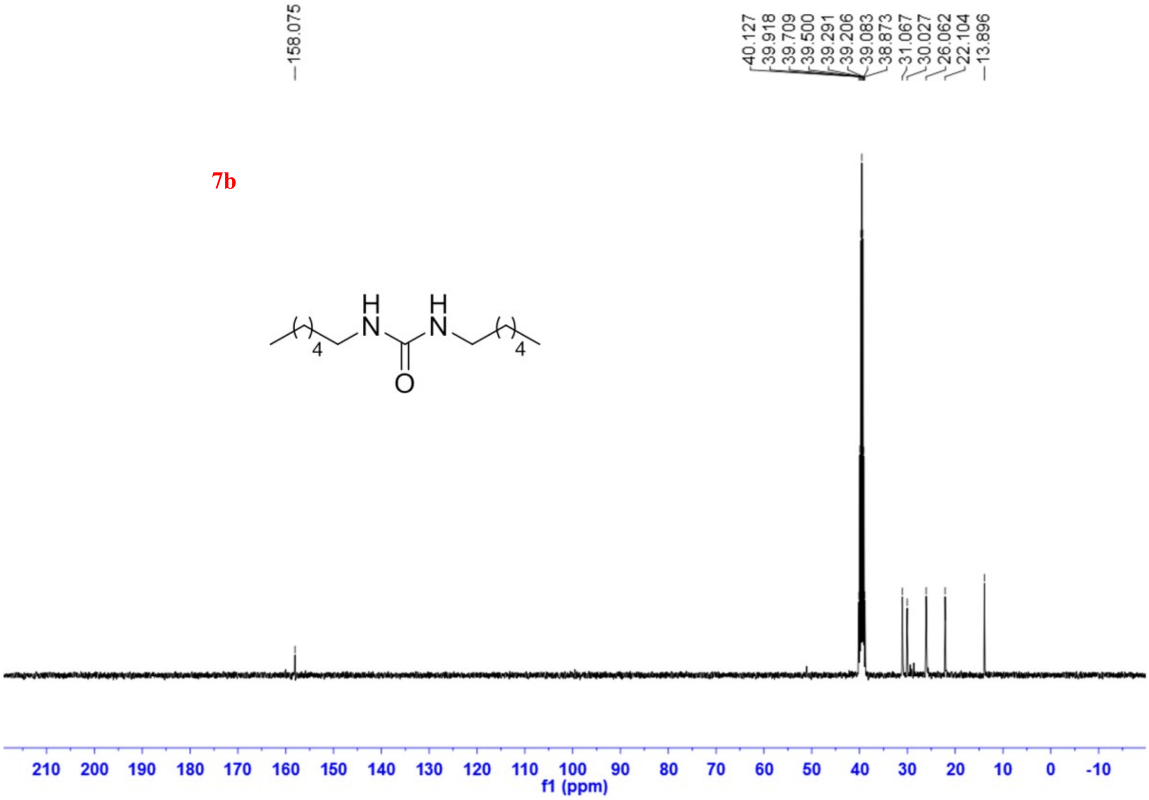
6b


158.074
140.879
128.181
126.968
126.526
42.957
40.127
39.917
39.709
39.500
39.292
39.083
38.874
H
N
H
N
O
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)

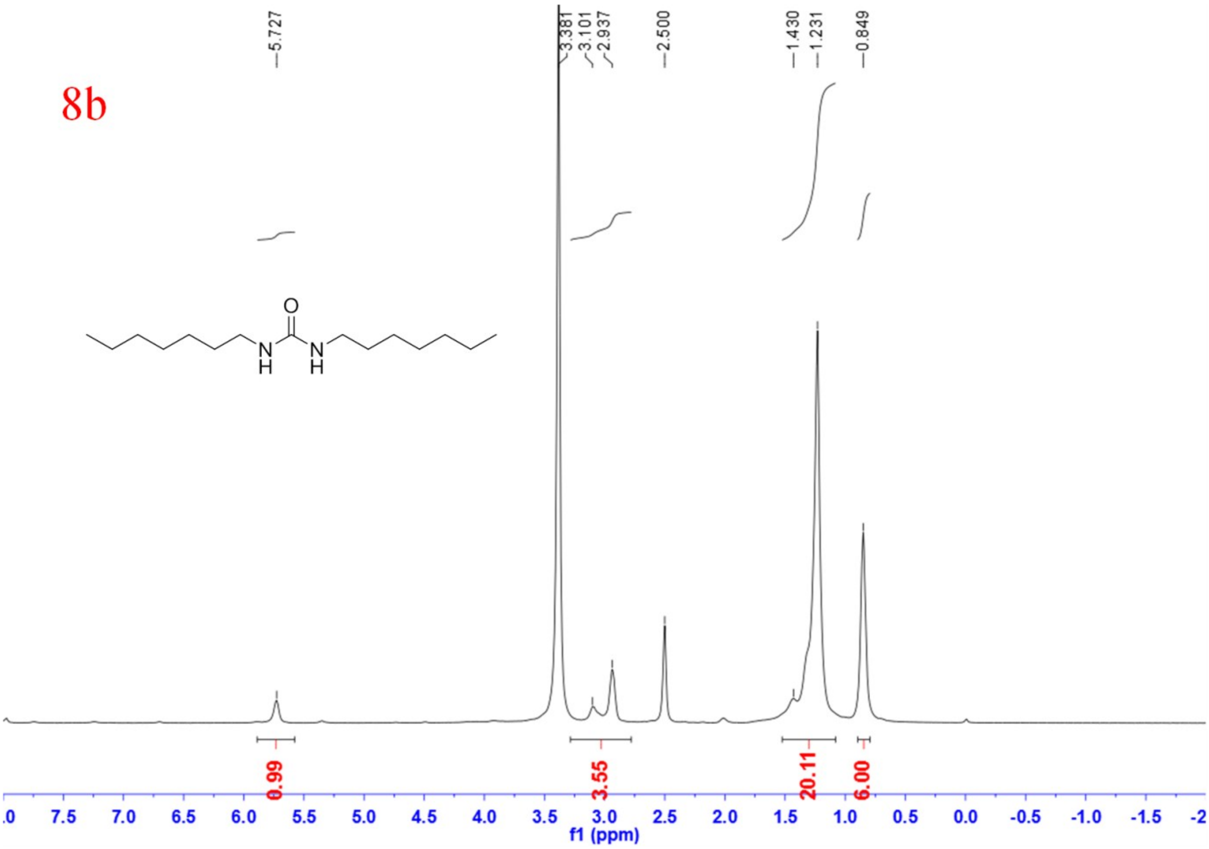
7b


5.724
3.363
2.944
2.929
2.500
1.412
1.320
1.304
1.230
0.852
O
N
H
N
H
0.94
3.92
16.37
6.00
.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 0.0 -0.5 -1.0 -1.5 -2
f1 (ppm)

7b

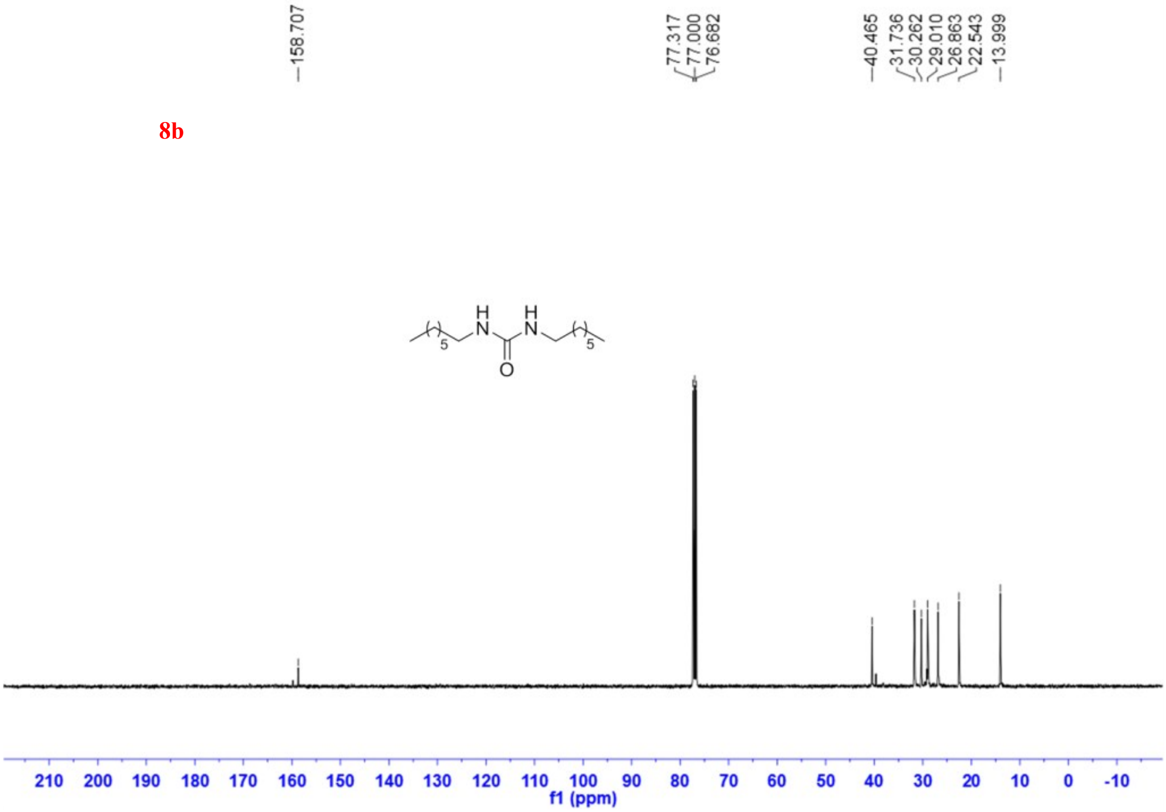

158.075
40.127
39.918
39.709
39.500
39.291
39.206
39.083
38.873
31.067
30.027
26.062
22.104
13.896
H
N
H
N
4
4
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

8b



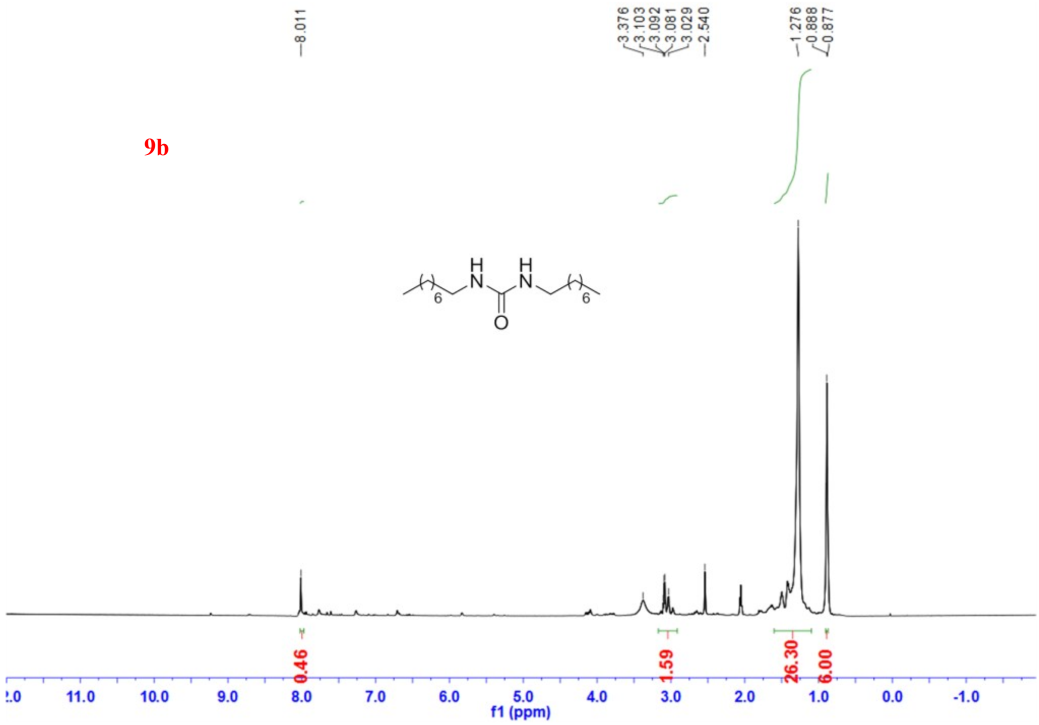
5.727
3.381
3.101
2.937
2.500
1.430
1.231
0.849
O
N
H
N
H
0.99
3.55
20.11
6.00
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2
f1 (ppm)

8b

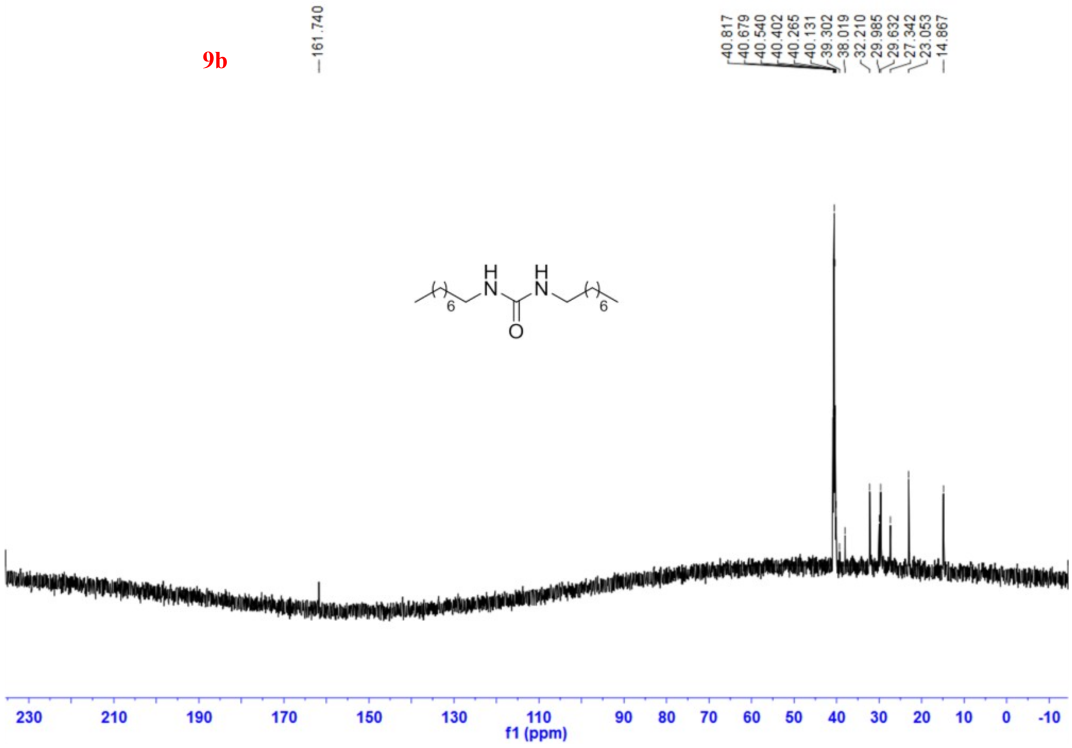


158.707
77.317
77.000
76.682
40.465
31.736
30.262
29.010
26.863
22.543
13.999
H
N
H
N
O
5
5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

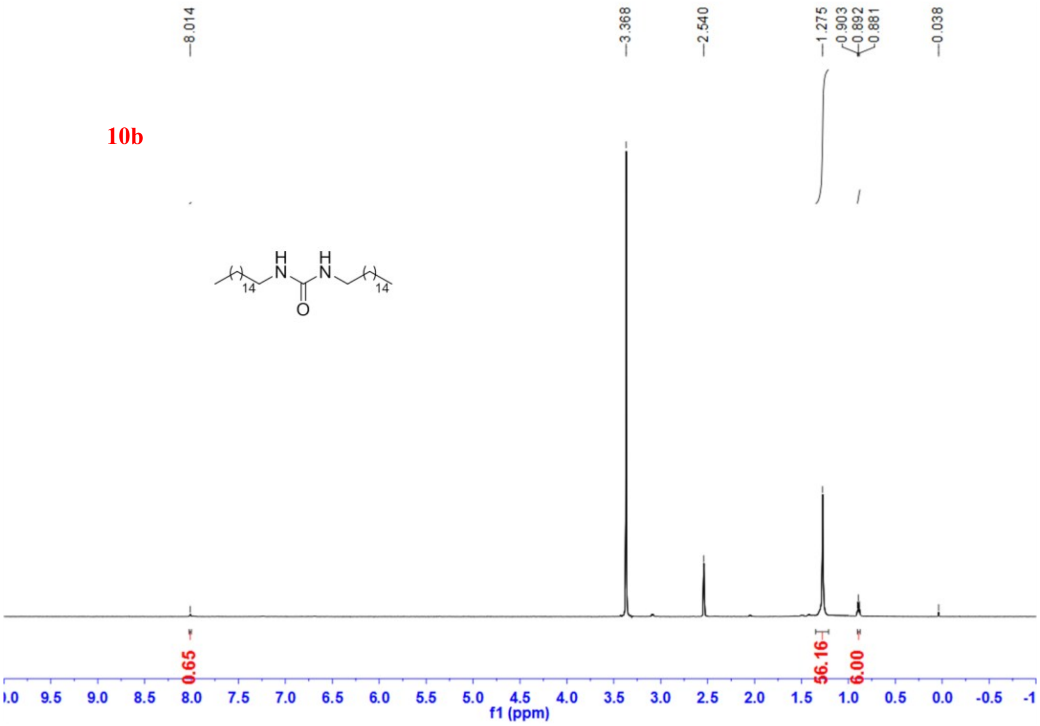
9b


8.011
3.376
3.103
3.092
3.081
3.029
2.540
1.276
0.888
0.877
H
N
H
N
6
6
O
0.46
1.59
26.30
6.00
2.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

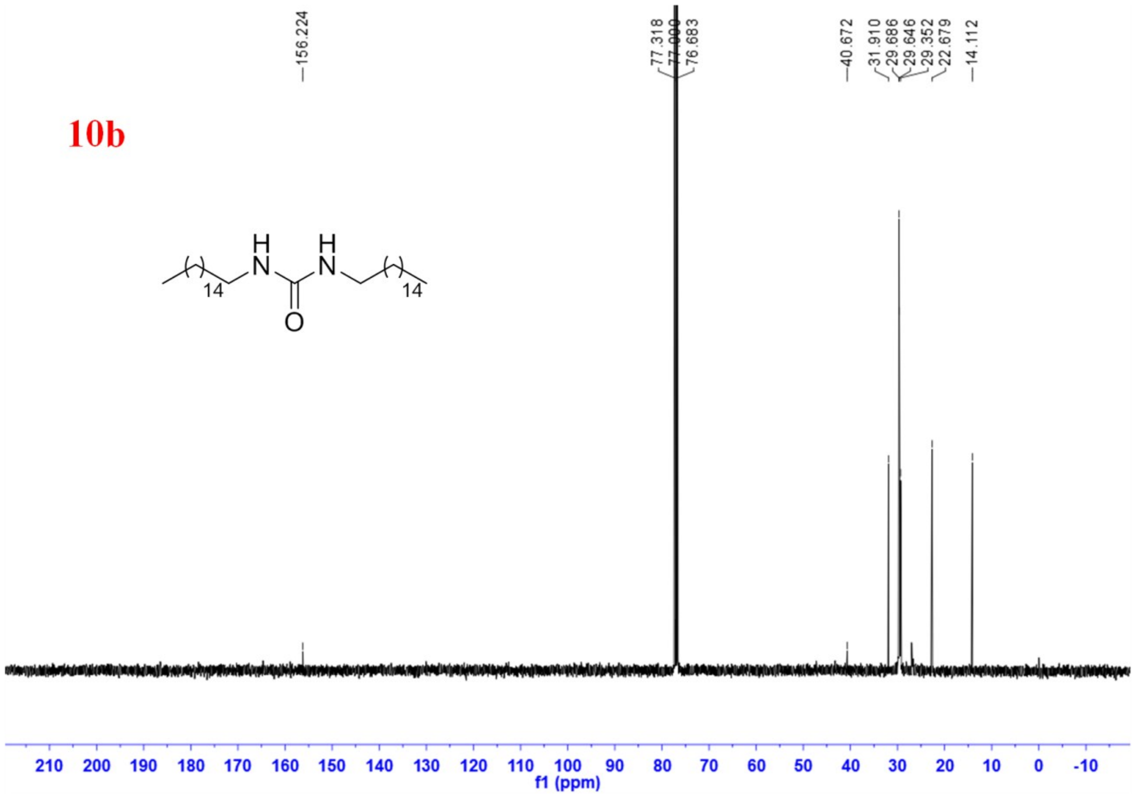
9b


161.740
40.817
40.679
40.540
40.402
40.265
40.131
39.302
38.019
32.210
29.985
29.632
27.342
23.053
14.867
H
N
H
N
6
6
O
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

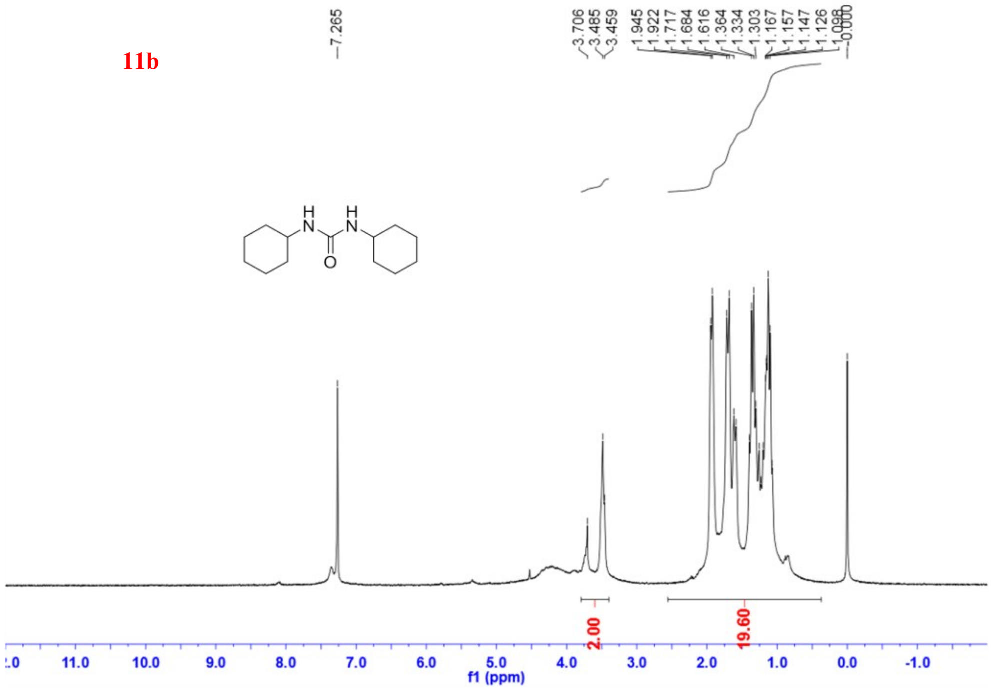
10b


8.014
3.368
2.540
1.275
0.903
0.892
0.881
0.038
H
N
H
N
14
14
O
0.65
56.16
6.00
.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 0.0 -0.5 -1
f1 (ppm)

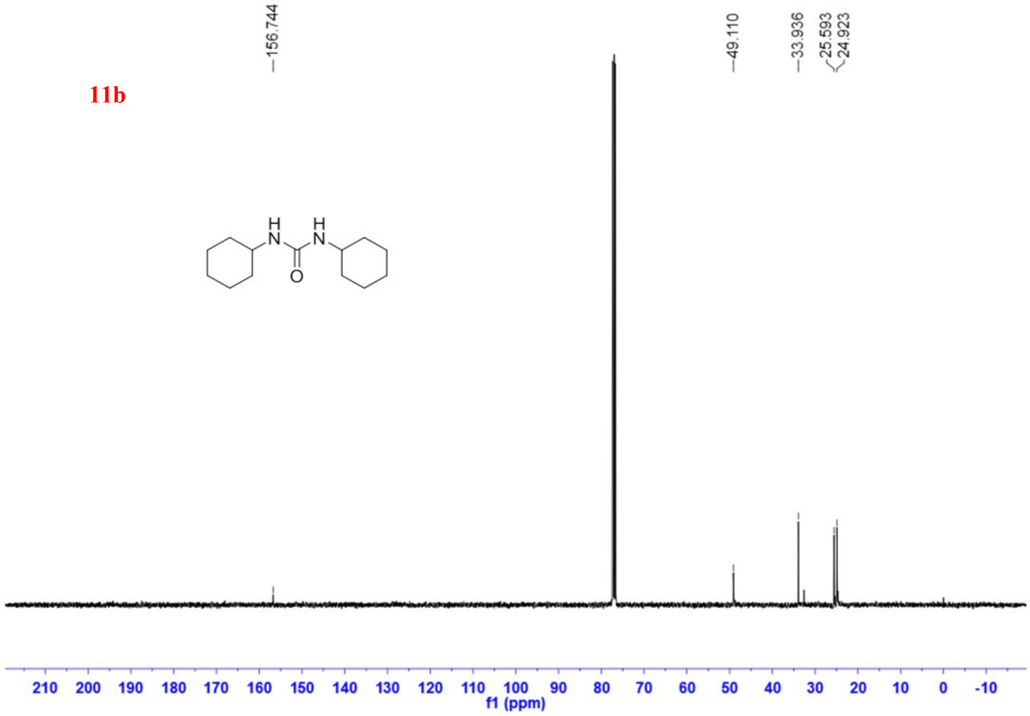
10b


156.224
77.318
77.000
76.683
40.672
31.910
29.686
29.646
29.352
22.679
14.112
H
N
H
N
14
14
O
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)

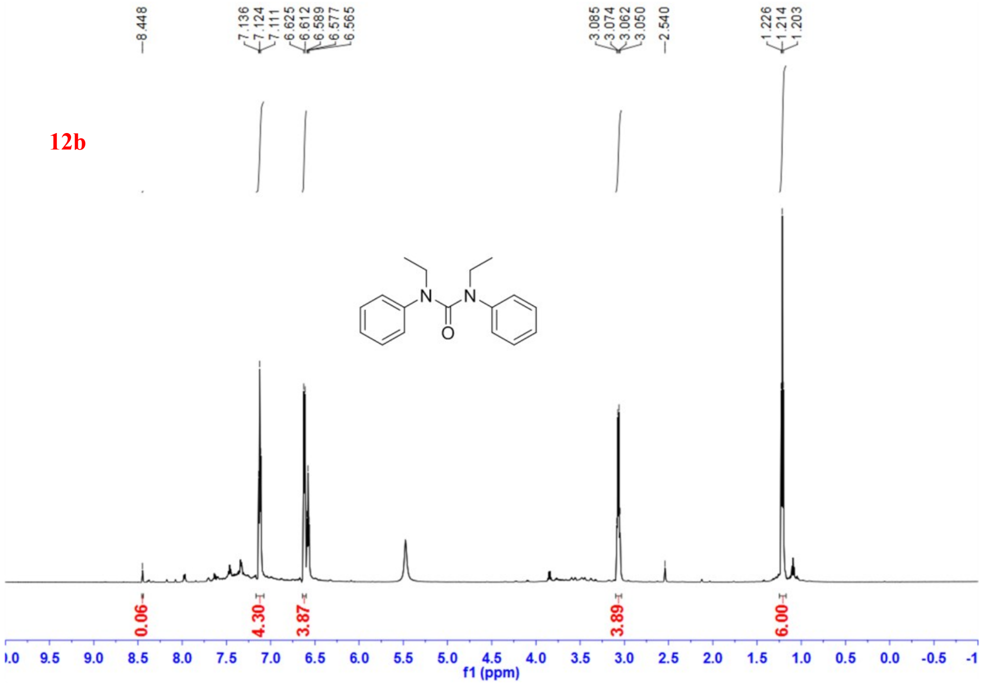
11b


7.265
3.706
3.485
3.459
1.945
1.922
1.717
1.684
1.616
1.364
1.334
1.303
1.167
1.157
1.147
1.126
1.098
0.000
H
N
H
N
O
2.00
19.60
.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

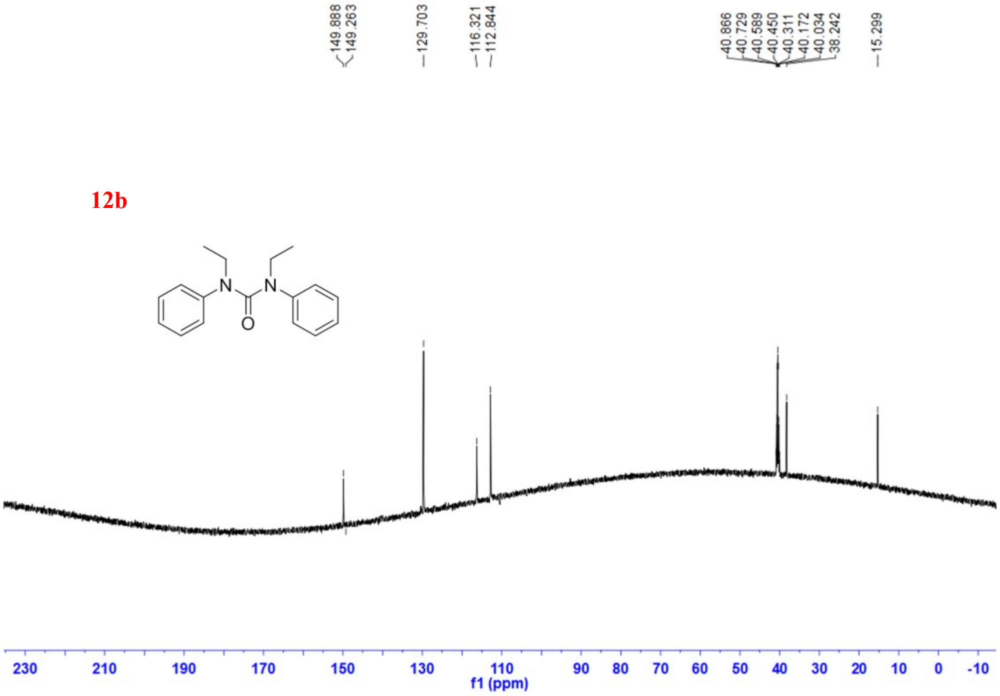
11b


156.744
49.110
33.936
25.593
24.923
H
N
H
N
O
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)

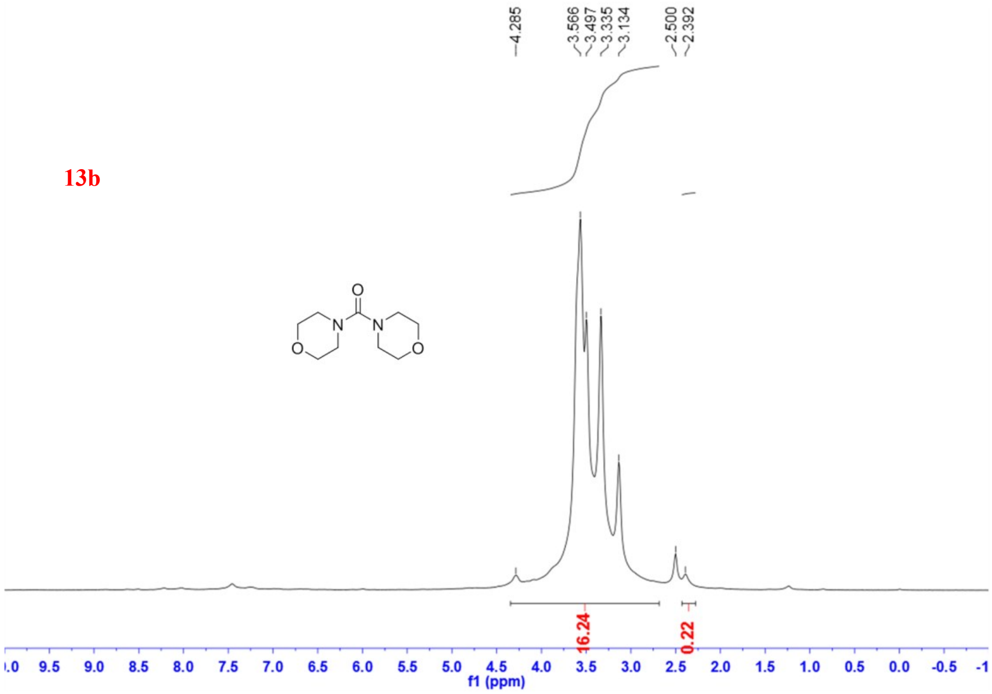
12b


8.448
7.136
7.124
7.111
6.625
6.612
6.589
6.577
6.565
3.085
3.074
3.062
3.050
2.540
1.226
1.214
1.203
N
N
O
0.06
4.30
3.87
3.89
6.00
10.0
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
0.0
-0.5
-1
f1 (ppm)

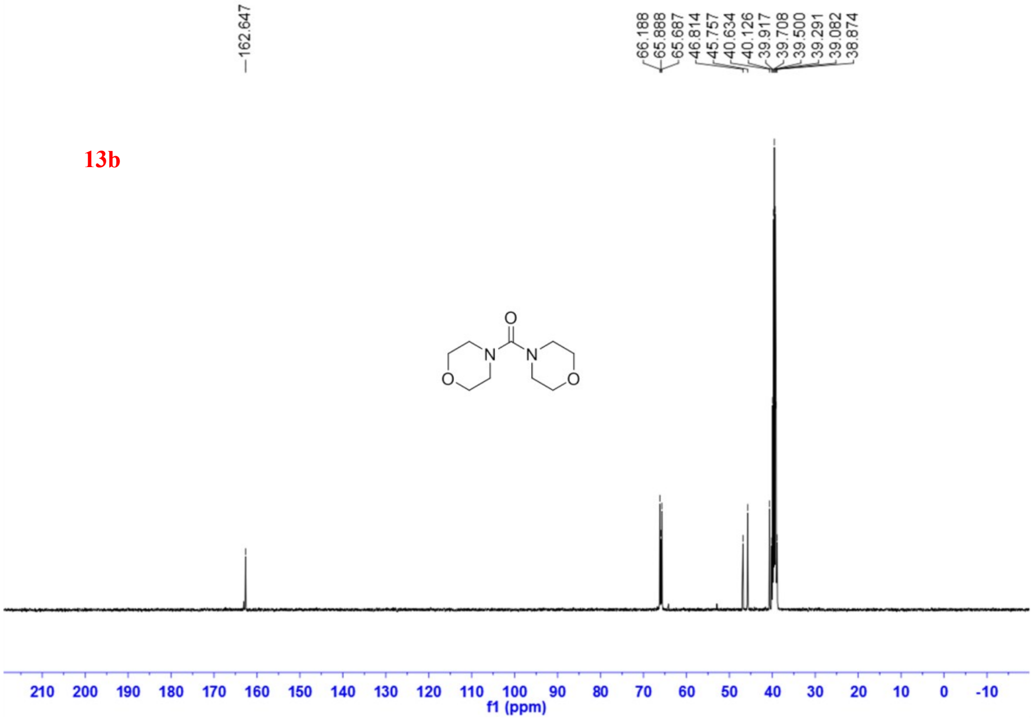
12b


149.888
149.263
129.703
116.321
112.844
40.866
40.729
40.589
40.450
40.311
40.172
40.034
38.242
15.299
N
N
O
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

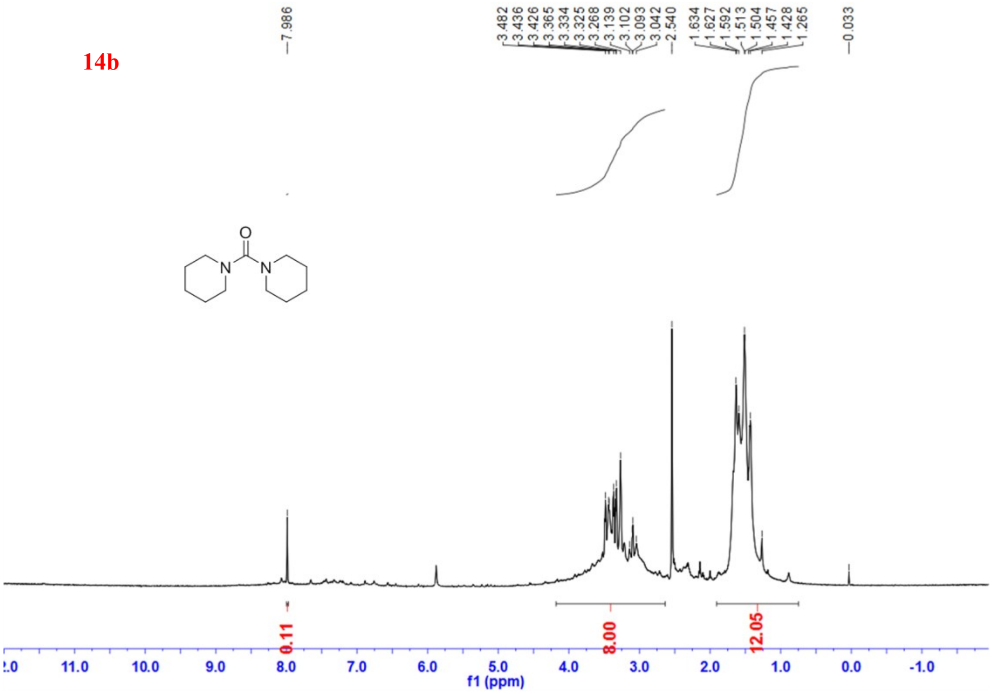
13b


4.285
3.566
3.497
3.335
3.134
2.500
2.392
O
N
N
O
O
16.24
0.22
.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 0.0 -0.5 -1
f1 (ppm)

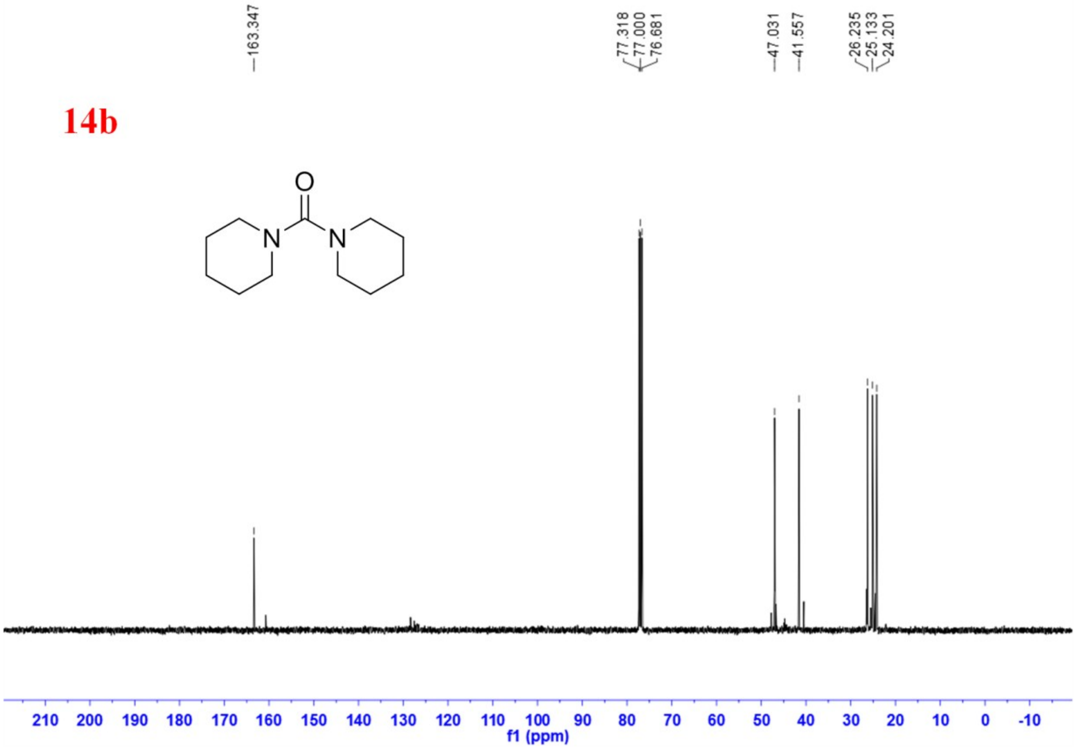
13b


162.647
66.188
65.888
65.687
46.814
45.757
40.634
40.126
39.917
39.708
39.500
39.291
39.082
38.874
O
N
N
O
O
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)

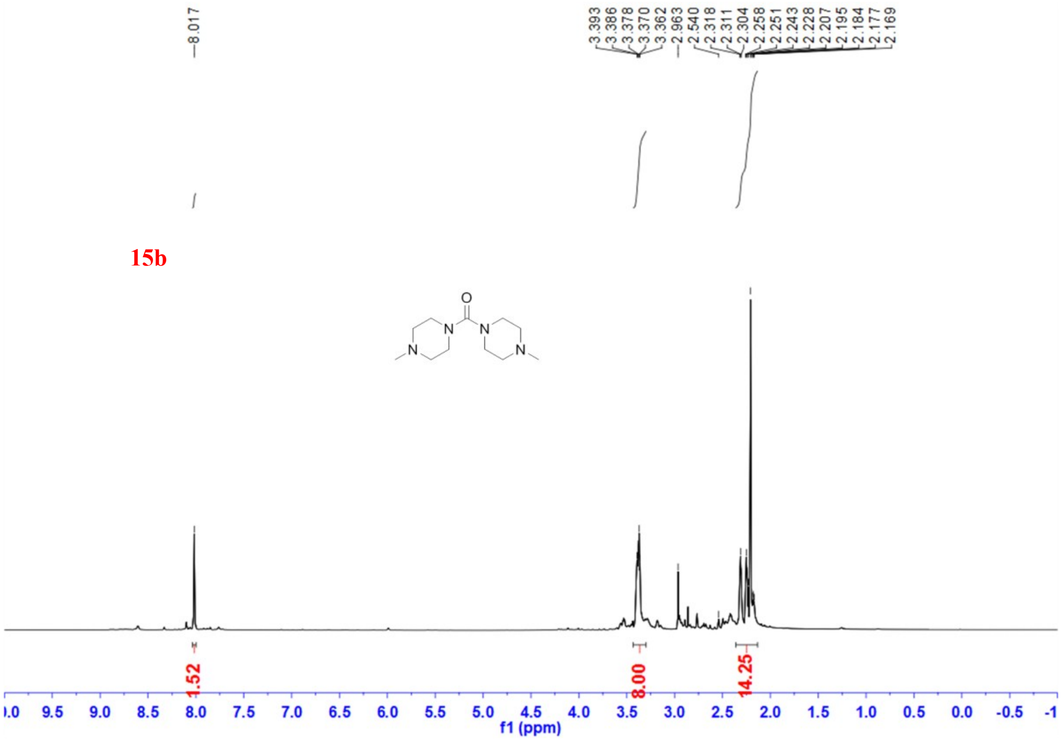
14b


7.986
3.482
3.436
3.426
3.365
3.334
3.325
3.268
3.139
3.102
3.093
3.042
2.540
1.634
1.627
1.592
1.513
1.504
1.457
1.428
1.265
0.033
O
N
N
0.11
8.00
12.05
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

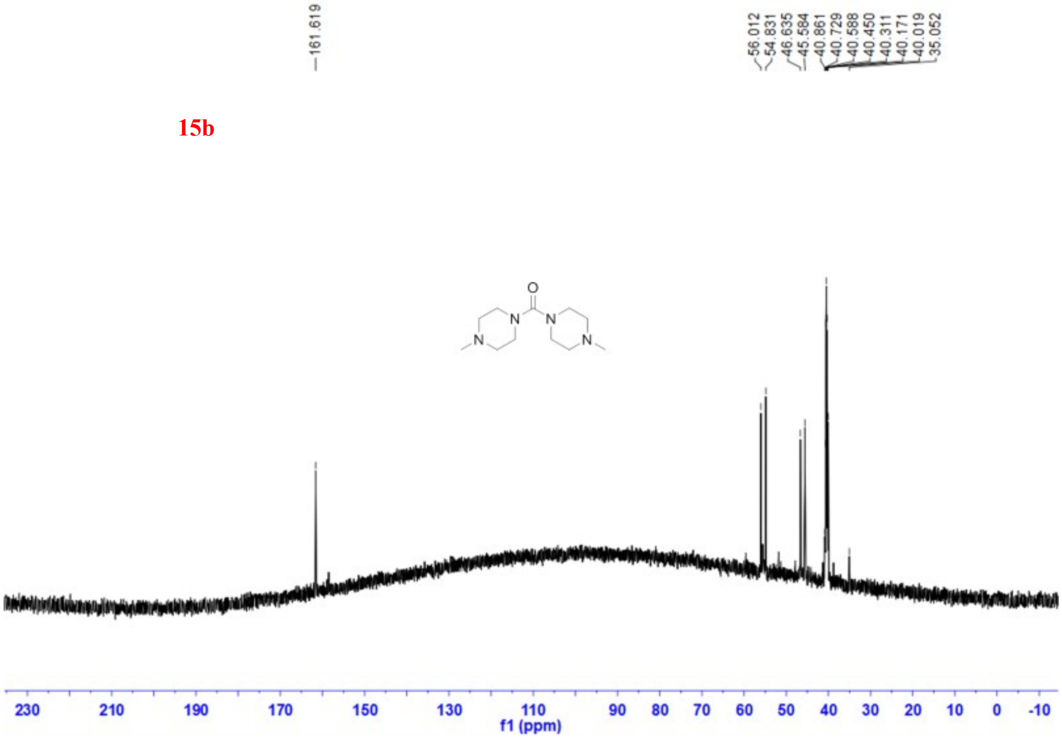
14b


163.347
77.318
77.000
76.681
47.031
41.557
26.235
25.133
24.201
O
N
N
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)

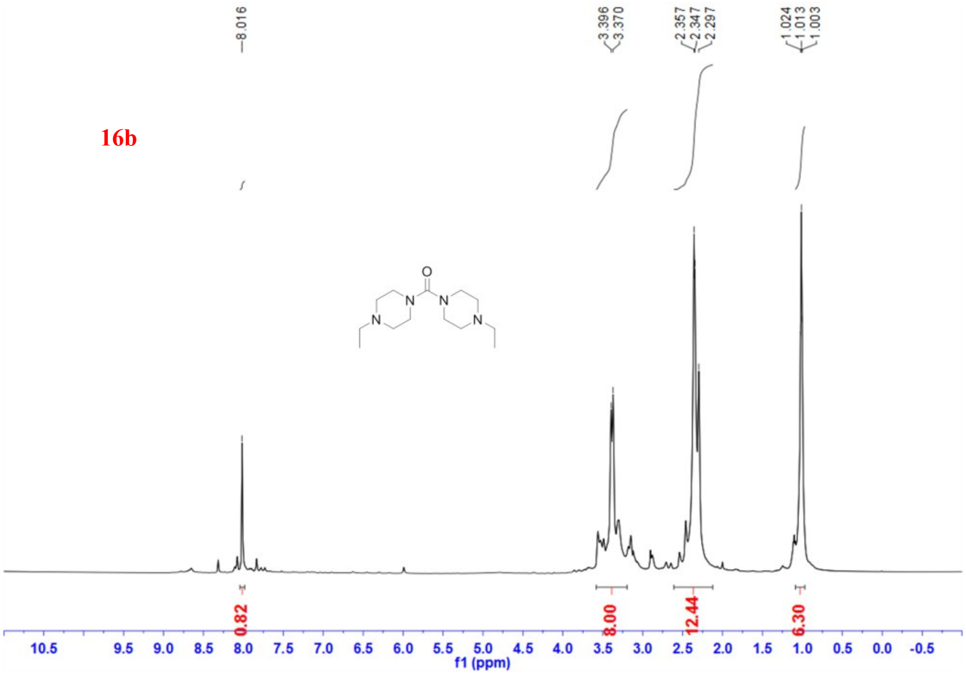
15b


8.017
3.393
3.386
3.378
3.370
3.362
2.963
2.540
2.318
2.311
2.304
2.258
2.251
2.243
2.228
2.207
2.195
2.184
2.177
2.169
O
N
N
N
N
1.52
8.00
14.25
10.0
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
0.0
-0.5
-1
f1 (ppm)

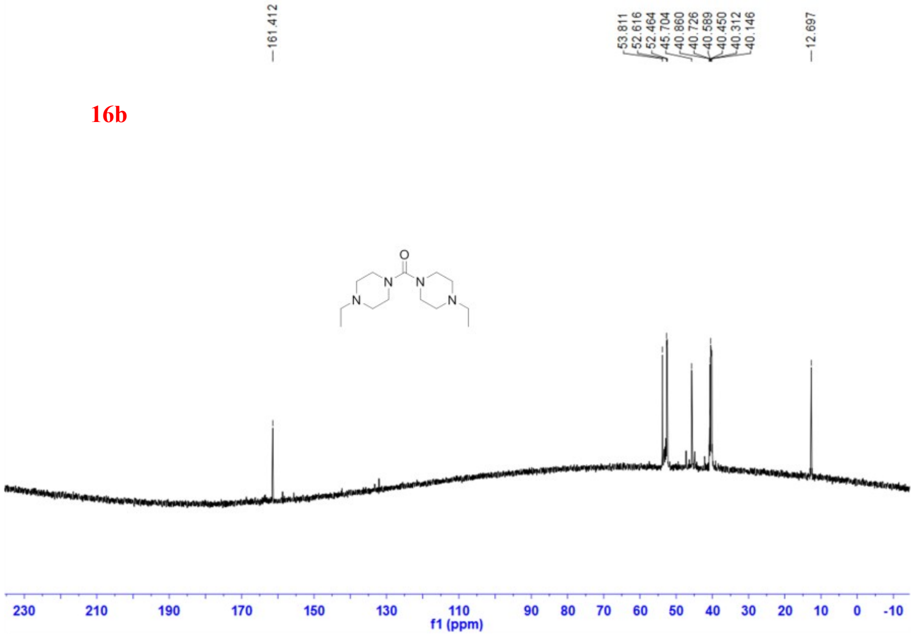
15b


161.619
56.012
54.831
46.635
45.584
40.861
40.729
40.588
40.450
40.311
40.171
40.019
35.052
O
N
N
N
N
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

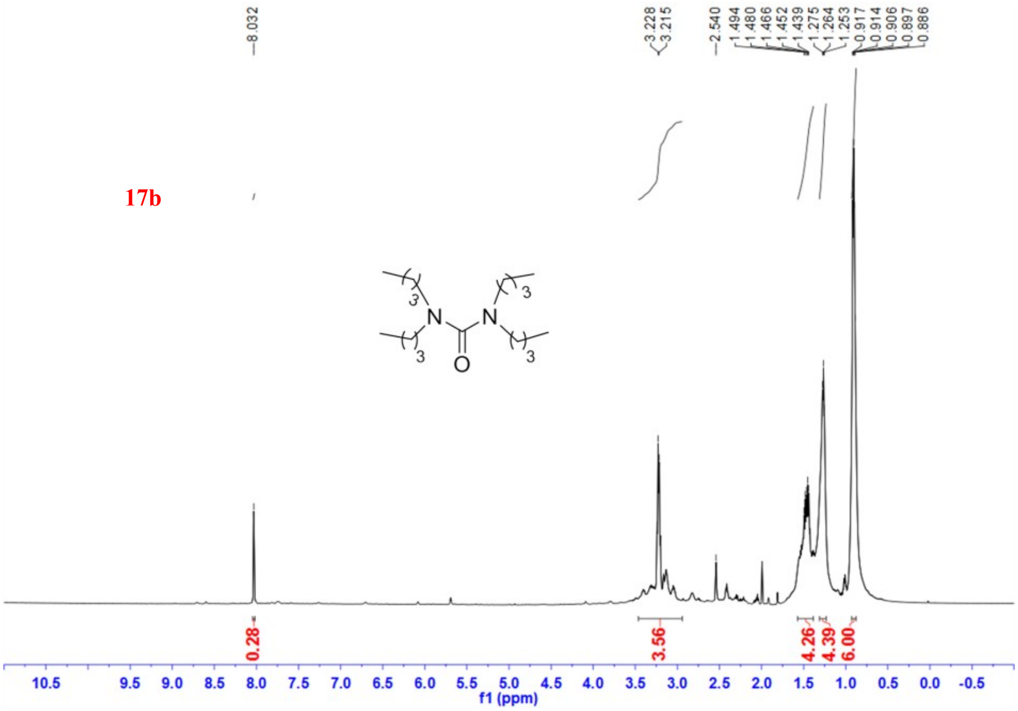
16b


8.016
3.396
3.370
2.357
2.347
2.297
1.024
1.013
1.003
O
N
N
N
N
0.82
8.00
12.44
6.30
10.5
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
0.0
-0.5
f1 (ppm)

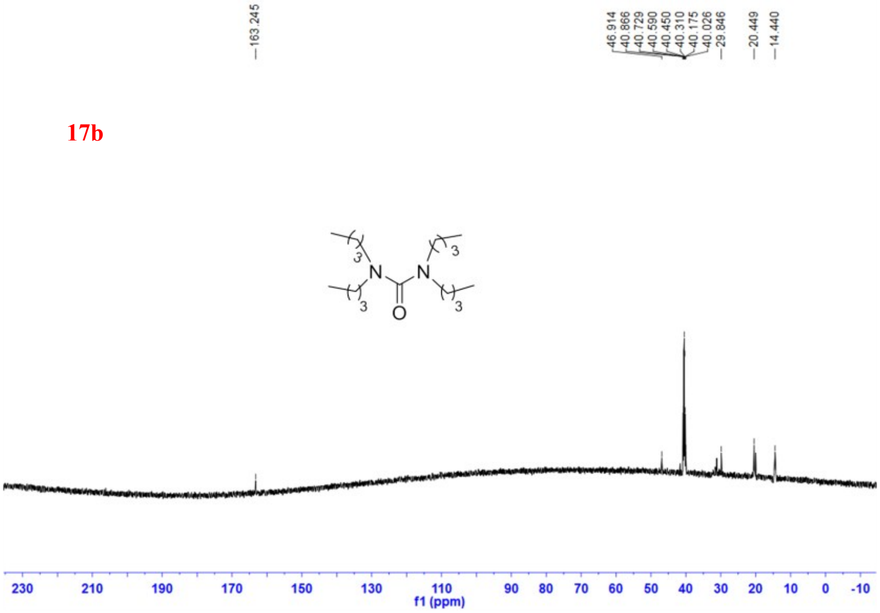
16b


161.412
53.811
52.616
52.464
45.704
40.860
40.726
40.589
40.450
40.312
40.146
12.697
O
N
N
N
N
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

17b



17b



5. References

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