SUPPORTING INFORMATION

Catalyst-Free Synthesis of Unsymmetrical Ureas from COS and Amines: a Strategy for Selectivity Regulation

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1. General Information

All reagents were purchased from Aladdin, Adamas, Macklin, or Bidepharm and directly used without further purification. Column chromatography separations were carried out on silica gel (200–300 mesh). Melting points were determined on a XT4A melting point apparatus and were uncorrected. Molecular weights were determined by high-resolution mass spectra (ESI) of Agilent Technologies LCMS TOF mass spectrometry. The NMR spectra were obtained in $CDCl_3$, DMSO-d_6 or TFA-*d* on an Agilent 500 MHz DD2 spectrometer and referenced to the residual deuterated solvent or TMS. X-ray data for compound **A** were recorded on Bruker D8 VENTURE diffractometer with graphite monochromated Cu-Kα (λ = 1.54178 Å) radiation. All data were collected using the φ- and ω-scan techniques. The molecular configurations were solved by direct methods and refined by full-matrix least squares on F2 using SHELXL-2014.[1] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were added at calculated positions. The bond lengths were restrained with DFIX, followed by additional refinements.

2. Experimental Section

2.1 The Experiment of COS Absorbed by Amines

The interaction between amine and COS was studied using benzylamine (**1a**) and dibenzylamine (**2a**) as model compounds (Figure S1). A 15 mL stainless-steel autoclave equipped with a magnetic stirrer was charged with 25 mmol of either **1a** (2.67g) or **2a** (4.92g). The reactor was then charged with 1.5 MPa COS, and the reaction mixture was stirred at room temperature (25 °C) for the indicated time. After the reaction, the COS gas was released, and the products were weighed. It was found that 25 mmol of **1a** could adsorb 12.5 mmol of COS at room temperature within 20 minutes. Extending the reaction time allowed **1a** to adsorb up to 13.7 mmol of COS, resulting in the formation of a white solid product. This phenomenon indicates that **1a** can completely react with COS to form thiocarbamate salts. In contrast, 25 mmol of **2a** adsorbed only 5 mmol of COS within 20 minutes, and even with prolonged reaction time, it only adsorbed up to 6 mmol of COS, yielding a liquid product. This observation, along with previous research,[2] suggests that an equilibrium exists between **2a** and COS.

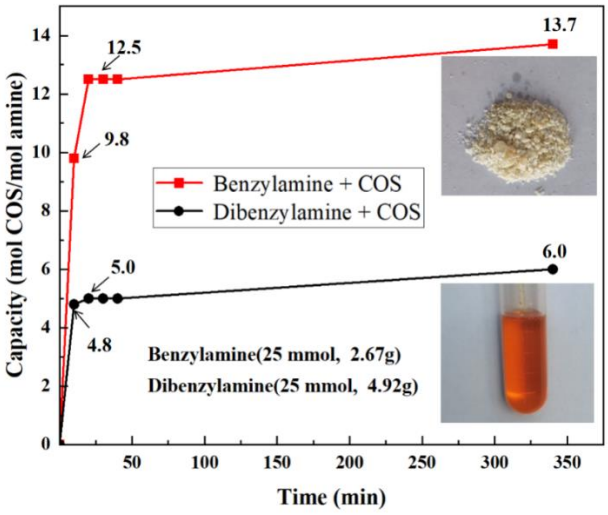


Figure S1. The interaction between amines and COS.

2.2 General Procedure for Preparing Unsymmetrical Ureas

2.2.1 Reaction of aliphatic primary amine, aliphatic secondary amine with COS to synthesize unsymmetrical urea

As an example, the procedure using benzylamine (**1a**) and dibenzylamine (**2a**) as model substrates is described, and similar protocols were applied to other substrates. In a 15 mL stainless-steel autoclave equipped with a magnetic stirrer, **1a** (0.1072 g, 1.0 mmol), **2a** (0.3945 g, 2.0 mmol), and 1 mL of MeCN were added. The reactor was flushed with N_2 to remove air, and then charged with 0.4 MPa COS. The reaction mixture was stirred at a constant temperature for the indicated time during the first stage. In the second stage, the reactor was heated and stirred for the indicated time at a constant temperature. After the reaction was complete, an aqueous HCl solution was added to the reaction mixture, followed by extraction with EtOAc three times. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (PE/EA = 5/1–1/1) to yield the desired product, 1,1,3-tribenzylurea (**3a**). The selectivity was determined by ^{1}H NMR spectroscopy using pyrazine (40 mg) as an internal standard, $CDCl_3$ as solvent (Figure S2).

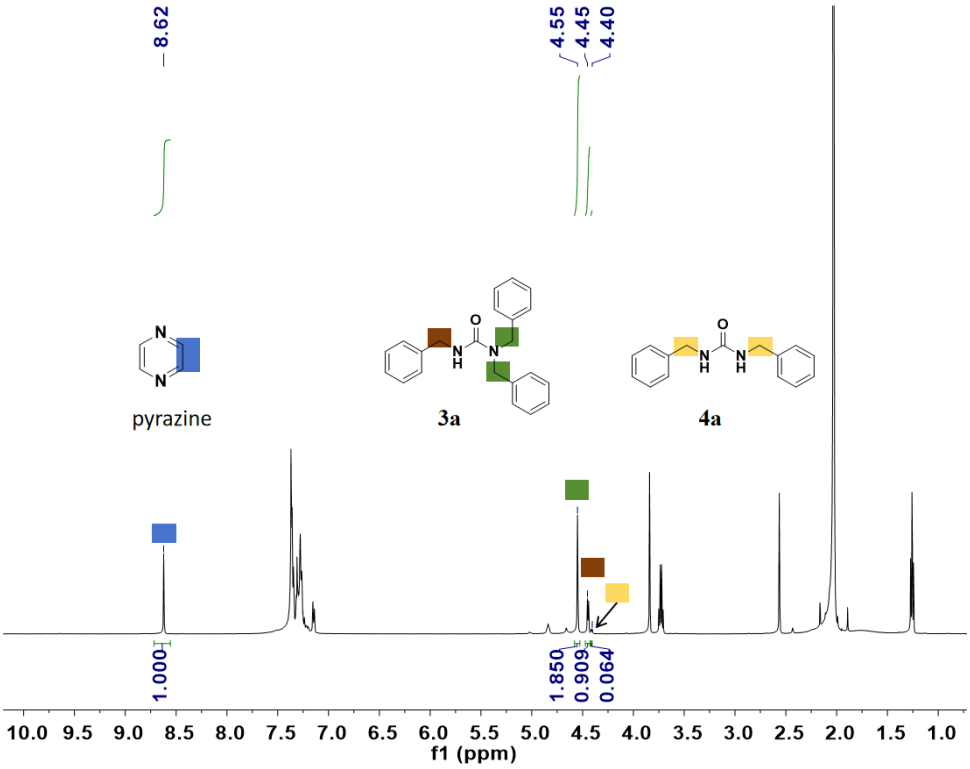


Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) of reaction solution.

According to the nuclear magnetic quantitative formula $m_s = \frac{(A_s/N_s)M_s}{(A_b/N_b)M_b} m_b w_b\%$, $m\ (\mathbf{3a}) = \frac{(1.850/4)\times 330}{(1/4)\times 80} \times 40 \times 9\ 9\% = 305$ mg, the yield of unsymmetrical urea **3a** $= \frac{305}{330} \times 1\ 00\% = 93\%$. $m\ (\mathbf{4a}) = \frac{(0.064/4)\times 240}{(1/4)\times 80} \times 40 \times 99\% = 7.6$ mg, the yield of symmetric urea **4a** $= \frac{7.6}{120} \times 100\% = 6\%$, the selectivity of **3a** $= \frac{93\%}{93\%+6\%} \times 100\% = 94\%$, the selectivity of **4a** $= \frac{6\%}{93\%+6\%} \times 100\% = 6\%$.

2.2.2 Reaction of two kinds of primary amines with COS to synthesize unsymmetrical urea

The procedure using tert-butylamine and aniline as the substrates is described, and similar methods were applied to other substrates. In a 15 mL stainless-steel autoclave equipped with a magnetic stirrer, tert-butylamine (0.735 g, 1.0 mmol), aniline (0.186 g/0.279 g, 2.0 mmol/3mmol), and MeCN (1 mL) were added. The reactor was flushed with N_2 to remove air, and then charged with 0.4 MPa COS. The reaction mixture was stirred at a constant temperature for the indicated time during the first stage. In the second stage, the reactor was heated and stirred for the indicated time at a constant temperature. After the reaction was complete, an aqueous HCl solution was added to the reaction mixture, followed by extraction with EtOAc three times. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was then purified by silica gel column chromatography (PE/EA = 20/1–1/1) to yield the desired product, 1-(tert-butyl)-3-phenylurea (**3ay**), as well as the byproduct symmetric urea (**4d** and **5a**). The selectivity was determined by ^{1}H NMR spectroscopy using pyrazine (20 mg) as an internal standard, DMSO-d_6 as solvent (Figure S3).

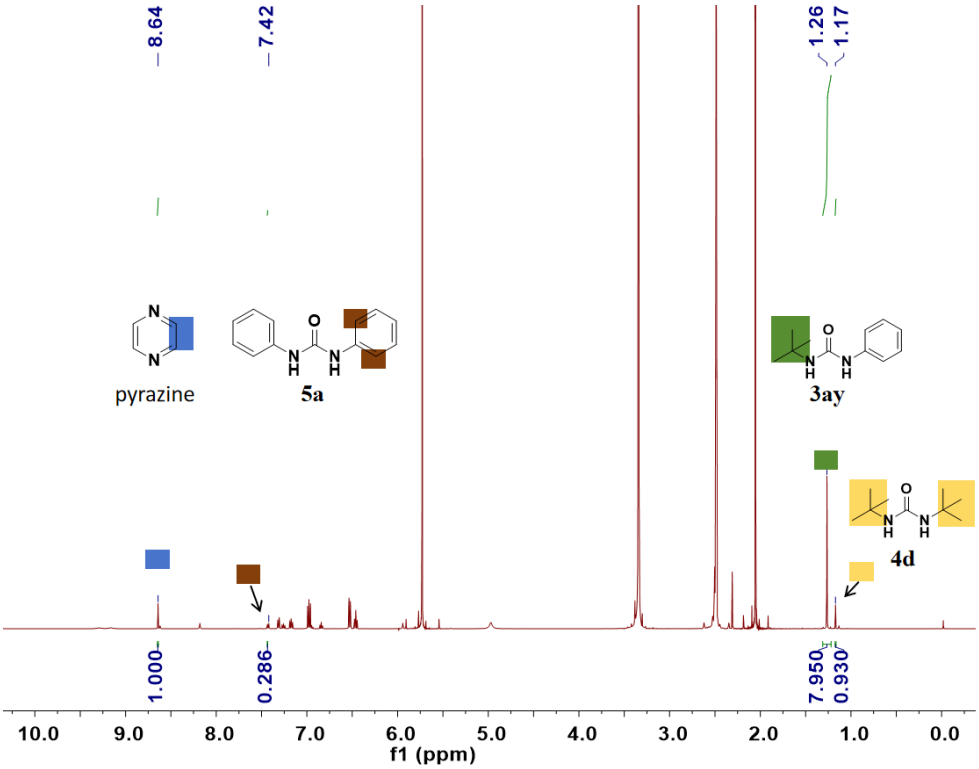


Figure S3. ^{1}H NMR (500 MHz, DMSO-d_6) of reaction solution.

According to the nuclear magnetic quantitative formula $m_s = \frac{(A_s/N_s)M_s}{(A_b/N_b)M_b} m_b w_b\%$, m (**3ay**) = $\frac{(7.950/9)\times 192}{(1/4)\times 80} \times 20 \times 99\% = 170$ mg, the yield unsymmetrical urea **3ay** = $\frac{170}{192} \times 100\% = 88$ %. m (**4d**) = $\frac{(0.930/18)\times 172}{(1/4)\times 80} \times 20 \times 99\% = 8.8$ mg, the yield of symmetric urea **4d** = $\frac{8.8}{86} \times 100\% = 10$ %, the selectivity of **3ay** = $\frac{88\%}{88\%+10\%} \times 100\% = 90$ %, the selectivity of **4d** = $\frac{10\%}{88\%+10\%} \times 100\% = 10$ %. m (**5a**) = $\frac{(0.286/4)\times 212}{(1/4)\times 80} \times 20 \times 99\% = 15$ mg, the yield of symmetric urea **5a** = $\frac{15}{212} \times 100\% = 7$ %.

Caution! Carbonyl sulfur is a colorless, flammable, and toxic gas with an unpleasant odor similar to that of rotten eggs. Therefore, both the reaction process and the post-processing step should be carried out in a fume hood.

2.3 Detailed Optimization of Reaction Conditions

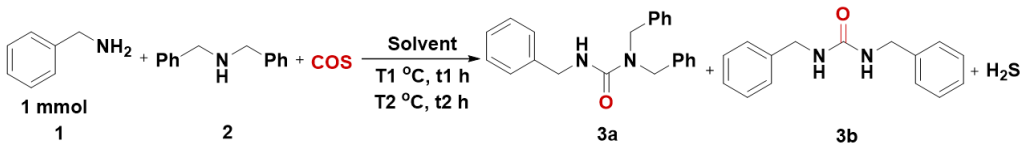


Table S1 Optimization of reaction conditions[a]

Entry	**2a** Amount (equiv.)	P_{COS} (MPa)	T1/°C	T2/°C	Solvent	t1/h	t2/h	**3a** Yield	selectivity
1	1	0.4	25	90	MeCN	12	12	72%	75%
2	1.5	0.4	25	90	MeCN	12	12	81%	84%
3	2	0.4	25	90	MeCN	12	12	94%	97%
4	2.5	0.4	25	90	MeCN	12	12	91%	96%
5	3	0.4	25	90	MeCN	12	12	92%	97%
6	4	0.4	25	90	MeCN	12	12	95%	98%
7	2	0.2	25	90	MeCN	12	12	81%	82%
8	2	0.3	25	90	MeCN	12	12	91%	93%
9	2	0.5	25	90	MeCN	12	12	91%	95%
10	2	0.6	25	90	MeCN	12	12	77%	78%
11	2	0.4	25	90	DMF	12	12	84%	85%
12	2	0.4	25	90	NMP	12	12	70%	71%
13	3	0.4	25	90	--	12	12	96%	98%
14	2	0.4	30	90	MeCN	12	12	93%	96%
15	2	0.4	40	90	MeCN	12	12	91%	93%
16	2	0.4	50	90	MeCN	12	12	87%	89%
17	2	0.4	60	90	MeCN	12	12	82%	82%
18	2	0.4	25	80	MeCN	12	12	96%	98%
19	2	0.4	25	70	MeCN	12	12	95%	98%
20	2	0.4	25	60	MeCN	12	12	90%	95%
21	2	0.4	25	50	MeCN	12	12	42%	89%
22	2	0.4	25	40	MeCN	12	12	36%	88%
23	2	0.4	25	30	MeCN	12	12	28%	85%
24	2	0.4	25	100	MeCN	12	12	80%	83%

25	2	0.4	25	70	MeCN	12	12	95%	98%
26	2	0.4	25	70	MeCN	8	12	91%	96%
27	2	0.4	25	70	MeCN	6	12	97%	99%
28	2	0.4	25	70	MeCN	4	12	93%	96%
29	2	0.4	25	70	MeCN	2	12	87%	89%
30	2	0.4	25	70	MeCN	1	12	84%	88%
31	2	0.4	25	70	MeCN	4	10	94%	96%
32	2	0.4	25	70	MeCN	4	8	94%	97%
33	2	0.4	25	70	MeCN	4	6	92%	94%
34	2	0.4	25	70	MeCN	4	4	71%	94%
35	2	0.4	70	70	MeCN	4	8	79%	80%

[a] Reaction conditions: **1a** (1 mmol), solvent (1 mL), isolated yield based on **1a** after column chromatography, selectivity determined by ^{1}H NMR spectroscopy using pyrazine as an internal standard (selectivity=amount of **1a** consumed by the target product / total substrate **1a** consumption). Based on weighing and flow meter monitoring, a COS of 0.4 MPa is approximately 3-5 mmol.

2.4 Gram-scale Experiment for Preparing Useful Unsymmetrical Urea

A gram-scale reaction was carried out in a 100mL mechanically stirred high-pressure reactor (Figure S4). 2-Phenylpropan-2-amine (10 mmol, 1.36g), *p*-toluidine (20 mmol, 2.15g) and 30 mL of MeCN were loaded into the reactor. The reactor was flushed with N_2 to remove air, and then charged with 0.5 MPa COS (approximately 50 mmol). The reaction mixture was stirred at 25 °C for 4 h, followed by heating and stirring at 70 °C for 8 h. Upon completion of the reaction, dichloromethane (20 mL) was added to the reaction mixture, leading to the precipitation of the target product. The precipitate was filtered to obtain a portion of the unsymmetrical urea products (0.56 g). The filtrate was then concentrated by rotary evaporation, and an aqueous HCl solution was added to remove any remaining amines. The mixture was extracted three times with EtOAc, and the combined organic layers were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed under reduced pressure. The crude product was further purified by silica gel column chromatography (PE/EA = 20/1 to 1/1) to afford the desired product, 1-(tert-butyl)-3-phenylurea (1.72 g). The selectivity of the reaction was determined by ^{1}H NMR spectroscopy using pyrazine as an internal standard.

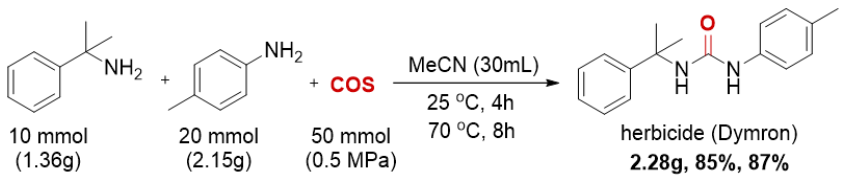
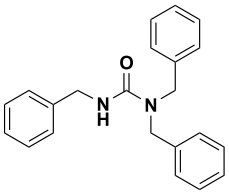
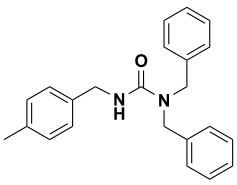


Figure S4. Gram-scale Experiment.

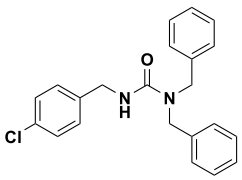
2.5 Characterization of Unsymmetrical Urea Products



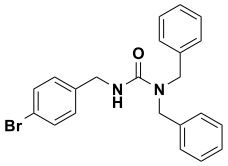
1,1,3-tribenzylurea (3a)[3]: According to general procedure, the crude residue was purified by flash chromatography (PE/EA =5/1-1/1) to give the product as a white solid (323.4mg, 94% yield, 98% selectivity). m.p.=117–119℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.39-7.33 (m, 4H), 7.32-7.21 (m, 9H), 7.14 (d, J = 7.2 Hz, 2H), 4.75 (s, 1H), 4.55 (s, 4H), 4.45 (d, J = 5.4 Hz, 2H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ158.5, 139.5, 137.7, 128.9, 128.6, 127.6, 127.4, 127.4, 127.2, 50.5, 45.1. $[M+H]^+$ Calcd for $C_{22}H_{22}N_2O$ 331.1805; Found 331.1807.



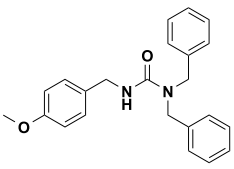
1,1-dibenzyl-3-(4-methylbenzyl)urea(3b): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (330.1mg, 96% yield, 99% selectivity). m.p. = 118-120℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (m, 4H), 7.28 (m, 6H), 7.09 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 4.69 (t, J = 4.7 Hz, 1H), 4.53 (s, 4H), 4.40 (d, J = 5.4 Hz, 2H), 2.33 (s, 3H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.4, 137.6, 136.7, 136.3, 129.2, 128.8, 127.5, 127.3, 127.3, 50.3, 44.8, 21.1. $[M+H]^+$ Calcd for $C_{23}H_{24}N_2O$ 345.1961; Found 345.1963.



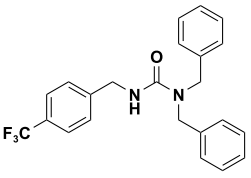
1,1-dibenzyl-3-(4-chlorobenzyl)urea (3c): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (334.9mg, 92% yield, 96% selectivity). m.p. = 128-130℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (m, 4H), 7.31 (d, J = 7.0 Hz, 2H), 7.25 (m, 6H), 7.04 (d, J = 8.6 Hz, 2H), 4.74 (t, J = 5.4 Hz, 1H), 4.54 (s, 4H), 4.38 (d, J = 5.7 Hz, 2H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.4, 138.2, 137.6, 132.9, 129.0, 128.7, 128.7, 127.7, 127.3, 50.6, 44.4. $[M+H]^+$ Calcd for $C_{22}H_{21}ClN_2O$ 365.1415; Found 365.1416.



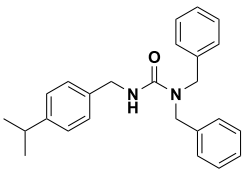
1,1-dibenzyl-3-(4-bromobenzyl)urea (3d): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (388.5mg, 95% yield, 97% selectivity). m.p. = 139-141℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.36 (m, 6H), 7.33 - 7.28 (m, 2H), 7.26 (t, J = 7.8 Hz, 4H), 6.98 (d, J = 7.8 Hz, 2H), 4.74 (t, J = 5.3 Hz, 1H), 4.54 (s, 4H), 4.36 (d, J = 5.7 Hz, 2H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.4, 138.7, 137.6, 131.7, 129.1, 129.0, 127.7, 127.3, 121.0, 50.6, 44.4. $[M+H]^+$ Calcd for $C_{22}H_{21}BrN_2O$ 409.0910; Found 409.0912.



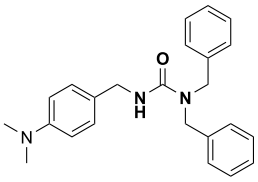
1,1-dibenzyl-3-(4-methoxybenzyl)urea (3e): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (338.4 mg, 94% yield, 98% selectivity). m.p. = 149-151℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.44-7.18 (m, 10H), 7.07 (d, J = 7.9 Hz, 2H), 6.81 (d, J = 7.8 Hz, 2H), 4.68 (s, 1H), 4.53 (s, 4H), 4.37 (d, J = 4.8 Hz, 2H), 3.80 (s, 3H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.7, 158.3, 137.6, 131.5, 128.8, 128.7, 127.5, 127.3, 113.9, 55.3, 50.3, 44.5. $[M+H]^+$ Calcd for $C_{23}H_{24}N_2O_2$ 361.1911; Found 361.1912.



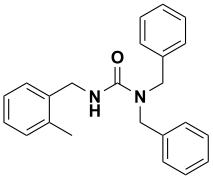
1,1-dibenzyl-3-(4-(trifluoromethyl)benzyl)urea (3f): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (366.2mg, 92% yield, 96% selectivity). m.p. = 141-143℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.51 (d, J = 7.9 Hz, 2H), 7.39 - 7.33 (m, 4H), 7.33 - 7.28 (m, 2H), 7.26 (d, J = 7.2 Hz, 4H), 7.21 (d, J = 7.9 Hz, 2H), 4.85 (t, J = 5.4 Hz, 1H), 4.56 (s, 4H), 4.47 (d, J = 5.7 Hz, 2H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.2, 143.7, 137.4, 129.3 (q, J = 32.8 Hz), 128.9, 127.6, 127.3, 127.2, 125.4 (q, J = 3.8 Hz), 124.2 (q, J = 277.2 Hz), 50.6, 44.4. $[M+H]^+$ Calcd for $C_{23}H_{21}F_3N_2O$ 399.1679; Found 399.1681.



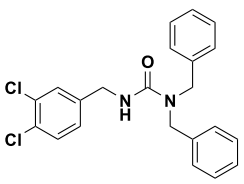
1,1-dibenzyl-3-(4-isopropylbenzyl)urea (3g): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (320.1mg, 86% yield, 90% selectivity). m.p. = 104-106℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (t, J = 7.1 Hz, 4H), 7.29 (m, 6H), 7.14 (d, J = 7.7 Hz, 2H), 7.08 (d, J = 6.8 Hz, 2H), 4.70 (d, J = 5.8 Hz, 1H), 4.54 (s, 4H), 4.42 (d, J = 4.3 Hz, 2H), 2.89 (m, 1H), 1.25 (d, J = 6.4 Hz, 6H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.5, 147.9, 137.7, 136.8, 128.9, 127.6, 127.5, 127.4, 126.7, 50.4, 44.9, 33.9, 24.1. $[M+H]^+$ Calcd for $C_{25}H_{28}N_2O$ 373.2274; Found 373.2277.



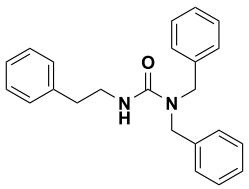
1,1-dibenzyl-3-(4-(dimethylamino)benzyl)urea (3h): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (344.5mg, 93% yield, 98% selectivity). m.p. = 107-109℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (t, J = 7.7 Hz, 4H), 7.28 (m, 6H), 7.05 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.5 Hz, 2H), 4.61 (s, 1H), 4.51 (s, 4H), 4.35 (d, J = 5.1 Hz, 2H), 2.93 (s, 6H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.4, 149.9, 137.6, 128.8, 128.6, 127.4, 127.3, 127.1, 112.7, 50.2, 44.7, 40.7. $[M+H]^+$ Calcd for $C_{24}H_{27}N_3O$ 374.2227; Found 374.2227



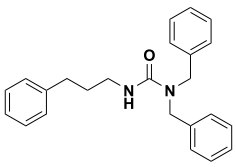
1,1-dibenzyl-3-(2-methylbenzyl)urea (3i): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (299.7 mg, 87% yield, 95% selectivity). m.p. = 137-139℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (t, J = 6.7 Hz, 4H), 7.30 (d, J = 6.3 Hz, 2H), 7.27 (d, J = 7.3 Hz, 4H), 7.18-7.14 (m, 1H), 7.11 (d, J = 7.4 Hz, 2H), 7.05 (d, J = 7.1 Hz, 1H), 4.56 (s, 1H), 4.54 (s, 4H), 4.44 (s, 2H), 2.21 (s, 3H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.2, 137.6, 136.8, 136.2, 130.3, 128.8, 127.8, 127.5, 127.3, 127.3, 126.0, 50.5, 43.2, 18.8. $[M+H]^+$ Calcd for $C_{23}H_{24}N_2O$ 345.1961; Found 345.1963.



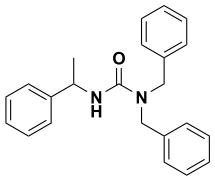
1,1-dibenzyl-3-(3,4-dichlorobenzyl)urea (3j): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (377.3 mg, 95% yield, 98% selectivity). m.p. = 125-127℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.36 (t, J = 6.7 Hz, 4H), 7.33-7.28 (m, 3H), 7.25 (d, J = 7.5 Hz, 4H), 7.17 (s, 1H), 6.93 (d, J = 8.2 Hz, 1H), 5.00 (t, J = 4.5 Hz, 1H), 4.53 (s, 4H), 4.32 (d, J = 5.4 Hz, 2H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.2, 140.1, 137.4, 132.4, 130.8, 130.3, 128.9, 128.8, 127.7, 127.2, 126.5, 50.5, 43.7. $[M+H]^+$ Calcd for $C_{22}H_{20}Cl_2N_2O$ 399.1025; Found 399.1028.



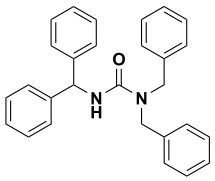
1,1-dibenzyl-3-phenethylurea (3k)[3]: According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (323.4 mg, 94% yield, 96% selectivity). m.p. = 100-102℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.31 (m, 6H), 7.21 (m, 7H), 7.06 (d, J = 5.9 Hz, 2H), 4.43 (m, 5H), 3.52 (t, J = 6.3 Hz, 2H), 2.77 (d, J = 6.6 Hz, 2H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.5, 139.3, 137.7, 128.9, 128.8, 128.6, 127.5, 127.3, 126.3, 50.4, 42.2, 36.4. $[M+H]^+$ Calcd for $C_{23}H_{24}N_2O$ 345.1961; Found 345.1962.



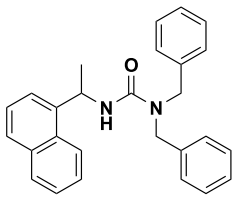
1,1-dibenzyl-3-(3-phenylpropyl)urea (3l): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (336.5 mg, 94% yield, 97% selectivity). m.p. = 68-70℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.36 (m, 4H), 7.34 -7.21 (m, 8H), 7.17 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.5 Hz, 2H), 4.48 (s, 4H), 4.39 (t, J = 5.2 Hz, 1H), 3.27 (q, J = 6.5 Hz, 2H), 2.51 (t, J = 7.7 Hz, 2H), 1.76 (m, 2H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.4, 141.7, 137.7, 128.8, 128.4, 128.3, 127.5, 127.2, 125.8, 50.4, 40.6, 33.2, 31.7. $[M+H]^+$ Calcd for $C_{24}H_{26}N_2O$ 359.2118; Found 359.2120.



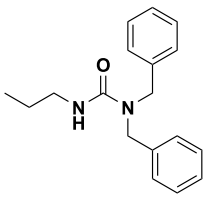
1,1-dibenzyl-3-(1-phenylethyl)urea (3m): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (326 mg, 95% yield, 98% selectivity). m.p. = 116-118℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.29 (m, 13H), 7.12 (d, J = 6.8 Hz, 2H), 5.11 - 4.96 (m, 1H), 4.65 (d, J = 6.3 Hz, 1H), 4.60 - 4.43 (m, 4H), 1.36 (d, J = 6.4 Hz, 3H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 157.6, 144.5, 137.7, 128.8, 128.5, 127.5, 127.3, 126.9, 125.8, 50.5, 50.2, 22.8. $[M+H]^+$ Calcd for $C_{23}H_{24}N_2O$ 345.1961; Found 345.1963.



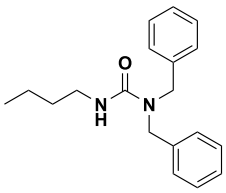
3-benzhydryl-1,1-dibenzylurea (3n)[4]: According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (391.2 mg, 96% yield, 99% selectivity). m.p. = 140-142℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.48-7.16 (m, 16H), 7.05 (d, J = 6.0 Hz, 4H), 6.16 (s, 1H), 5.06 (s, 1H), 4.56 (s, 4H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 157.5, 142.5, 137.7, 128.9, 128.5, 127.6, 127.4, 127.1, 127.1, 58.5, 50.8. $[M+H]^+$ Calcd for $C_{28}H_{26}N_2O$ 407.2118; Found 407.2119.



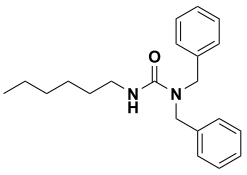
1,1-dibenzyl-3-(1-(naphthalen-1-yl)ethyl)urea (3o): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid (354.5 mg, 90% yield, 96% selectivity). m.p. = 116-118℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 8.19 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.53 (m, 2H), 7.42 - 7.00 (m, 12H), 5.96 - 5.83 (m, 1H), 4.72 (d, J = 7.0 Hz, 1H), 4.50 (s, 4H), 1.56 (d, J = 6.4 Hz, 3H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 157.5, 139.7, 137.6, 133.9, 131.0, 128.8, 128.7, 127.9, 127.5, 127.3, 126.3, 125.6, 125.1, 123.7, 122.1, 50.4, 46.3, 21.8. $[M+H]^+$ Calcd for $C_{27}H_{26}N_2O$ 395.2118; Found 395.2120.



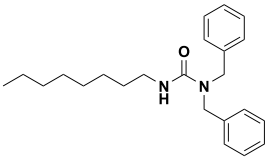
1,1-dibenzyl-3-propylurea (3p): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 5/1-1/1) to give the product as a white solid. (242.5 mg, 86% yield, 89% selectivity). m.p. = 72-74℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 5H), 7.31-7.26 (m, 5H), 4.51 (s, 4H), 4.37 (t, J = 4.7 Hz, 1H), 3.19 (m, 2H), 1.42 (m, 2H), 0.78 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.7, 137.9, 128.9, 127.6, 127.4, 50.5, 42.9, 23.5, 11.3. $[M+H]^+$ Calcd $C_{18}H_{22}N_2O$ 283.1805; Found 283.1804.



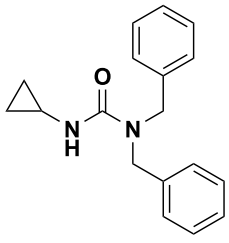
1,1-dibenzyl-3-butylurea(3q): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (245.6 mg, 83% yield, 85% selectivity). m.p. = 65-67℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (t, J = 7.7 Hz, 4H), 7.28 (m, 6H), 4.51 (s, 4H), 4.35 (s, 1H), 3.22 (q, J = 7.2 Hz, 2H), 1.38 (m, 2H), 1.19 (m, 2H), 0.85 (t, J = 8.2 Hz, 3H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.6, 137.8, 128.8, 127.4, 127.2, 50.4, 40.7, 32.2, 19.9, 13.7. $[M+H]^+$ Calcd for $C_{19}H_{24}N_2O$ 297.1961; Found 297.1964.



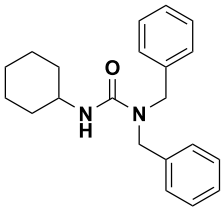
1,1-dibenzyl-3-hexylurea (3r): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (233.4 mg, 72% yield, 81% selectivity). m.p. = 50-52℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (t, J = 7.5 Hz, 4H), 7.32 – 7.18 (m, 6H), 4.51 (s, 4H), 4.36 (s, 1H), 3.22 (q, J = 6.4 Hz, 2H), 1.39 (m, 2H), 1.30 – 1.07 (m, 6H), 0.87 (t, J = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.5, 137.8, 128.8, 127.4, 127.2, 50.4, 41.0, 31.5, 30.1, 26.4, 22.5, 14.0. $[M+H]^+$ Calcd for $C_{21}H_{28}N_2O$ 325.2274; Found 325.2278.



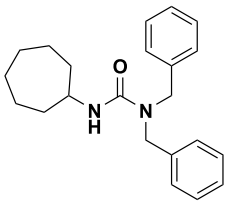
1,1-dibenzyl-3-octylurea (3s): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as colorless oil (246 mg, 70% yield, 71% selectivity). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4H), 7.32-7.25 (m, 6H), 4.51 (s, 4H), 4.33 (t, *J* = 5.2 Hz, 1H), 3.21 (m, 2H), 1.38 (m, 2H), 1.32-1.26 (m, 2H), 1.22 (s, 6H), 1.13 (m, 2H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.5, 137.8, 128.8, 127.4, 127.2, 50.4, 41.0, 31.8, 30.1, 29.24, 29.20, 26.7, 22.6, 14.1. $[M+H]^+$ Calcd for $C_{23}H_{32}N_2O$ 353.2587; Found 353.2589.



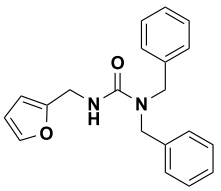
1,1-dibenzyl-3-cyclopropylurea (3t): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (246.4 mg, 88% yield, 99% selectivity). m.p. = 110-113℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (t, J = 7.4 Hz, 4H), 7.31 - 7.27 (m, 2H), 7.24 (d, J = 7.4 Hz, 4H), 4.61 (s, 1H), 4.47 (s, 4H), 2.72 - 2.60 (m, 1H), 0.69 (q, J = 6.0 Hz, 2H), 0.40 - 0.31 (m, 2H). ^{13}C{^{1}H}NMR (126MHz, $CDCl_3$) δ 159.4, 137.5, 128.8, 127.5, 127.3, 50.2, 23.6, 6.9. $[M+H]^+$ Calcd for $C_{18}H_{20}N_2O$ 281.1648; Found 281.1649.



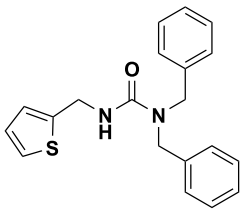
1,1-dibenzyl-3-cyclohexylurea(3u)[5]: According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (280 mg, 87% yield, 99% selectivity). m.p. = 139-142℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (t, J = 7.2 Hz, 4H), 7.34 – 7.19 (m, 6H), 4.49 (s, 4H), 4.23 (d, J = 7.3 Hz, 1H), 3.82 – 3.58 (m, 1H), 1.85 (d, J = 10.2 Hz, 2H), 1.55 (s, 3H), 1.33 (m, 2H), 1.08 (m, 1H), 0.96 (q, J = 10.5 Hz, 2H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 157.8, 137.9, 128.8, 127.4, 127.3, 50.4, 49.3, 33.6, 25.6, 24.7. $[M+H]^+$ Calcd for $C_{21}H_{26}N_2O$ 323.2118; Found 323.2120



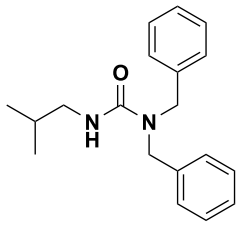
1,1-dibenzyl-3-cycloheptylurea (3v): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (242 mg, 72% yield, 99% selectivity). m.p. = 119-121℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (t, J = 7.6 Hz, 4H), 7.28 (m, 6H), 4.49 (s, 4H), 4.29 (d, J = 7.6 Hz, 1H), 3.89 (m, 1H), 1.83 (m, 2H), 1.62-1.49 (m, 2H), 1.50 - 1.34 (m, 6H), 1.28 (m, 2H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 157.7, 137.9, 128.8, 127.4, 127.3, 51.6, 50.4, 35.5, 27.9, 24.0. $[M+H]^+$ Calcd for $C_{22}H_{28}N_2O$ 337.2274; Found 337.2277



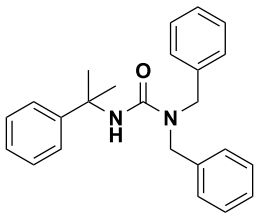
1,1-dibenzyl-3-(furan-2-ylmethyl)urea (3w): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (279.3 mg, 87% yield, 92% selectivity). m.p. = 83-85℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.35 (t, J = 7.7 Hz, 4H), 7.30 (d, J = 6.3 Hz, 2H), 7.28 (s, 1H), 7.25 (d, J = 7.5 Hz, 4H), 6.28 (s, 1H), 6.09 (s, 1H), 4.79 - 4.69 (m, 1H), 4.51 (s, 4H), 4.43 (d, J = 5.5 Hz, 2H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.2, 152.5, 141.8, 137.4, 128.8, 127.5, 127.3, 110.3, 106.6, 50.2, 38.1. $[M+H]^+$ Calcd for $C_{20}H_{20}N_2O_2$ 321.1598; Found 321.1597.



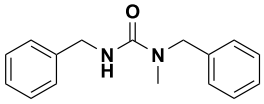
1,1-dibenzyl-3-(thiophen-2-ylmethyl)urea (3x): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (306 mg, 91% yield, 94% selectivity). m.p. = 85-87℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.40 - 7.32 (m, 4H), 7.32-7.22 (m, 6H), 7.19 (d, J = 5.1 Hz, 1H), 6.91 (t, J = 3.5 Hz, 1H), 6.85 (s, 1H), 4.86 - 4.76 (m, 1H), 4.61 (d, J = 5.5 Hz, 2H), 4.52 (s, 4H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 158.1, 142.7, 137.4, 128.8, 127.5, 127.3, 126.7, 125.1, 124.7, 50.2, 40.0. $[M+H]^+$ Calcd for $C_{20}H_{20}N_2OS$ 337.1369; Found 337.1370.



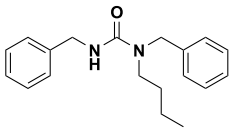
1,1-dibenzyl-3-isobutylurea (3y): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (240.5 mg, 81% yield, 84% selectivity). m.p. = 90-92 ^{o}C ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4H), 7.32-7.25 (m, 6H), 4.52 (s, 4H), 4.41 (s, 1H), 3.13-2.96 (m, 2H), 1.65 (m, 1H), 0.75 (d, *J* = 6.7 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.5, 137.8, 128.8, 127.5, 127.2, 50.6, 48.4, 28.7, 19.9. $[M+H]^+$ Calcd for $C_{19}H_{24}N_2O$ 297.1961; Found 297.1963.



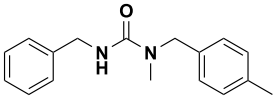
1,1-dibenzyl-3-(2-phenylpropan-2-yl)urea (3z): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (315 mg, 88% yield, 89% selectivity). m.p. = 92-94 ºC ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, 5H), 7.34-7.26 (m, 7H), 7.20 (m, 3H), 4.77 (s, 1H), 4.50 (s, 4H), 1.59 (s, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.0, 147.9, 138.0, 128.8, 128.2, 127.5, 127.4, 126.3 , 124.7, 55.5, 50.7, 29.7. $[M+H]^+$ Calcd for $C_{24}H_{26}N_2O$ 359.2118; Found 359.2124.



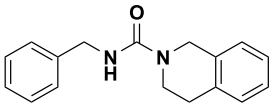
1,1-dibenzyl-3-(1,3-dibenzyl-1-methylurea) (3aa)[6]: According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (252mg, 99% yield, 99% selectivity). m.p. = 101-103 ℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.38 - 7.30 (m, 4H), 7.28 (m, 6H), 4.76 (s, 1H), 4.54 (s, 2H), 4.46 (d, J = 2.3 Hz, 2H), 2.91 (s, 3H). $^{13}C\{^1H\}$ NMR (126MHz, $CDCl_3$) δ 158.3, 139.6, 137.9, 128.7, 128.6, 127.6, 127.3, 127.24, 127.22, 52.3, 45.1, 34.4. $[M+H]^+$ Calcd for $C_{16}H_{18}N_2O$ 225.1492; Found 225.1493.



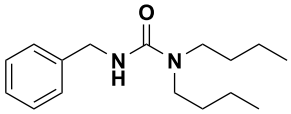
1,3-dibenzyl-1-butylurea (3ab): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (299.9mg, 99% yield, 99% selectivity). m.p. = 58-60 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (m, 2H), 7.28 (m, 6H), 7.21 (d, *J* = 7.5 Hz, 2H), 4.63 (t, *J* = 5.5 Hz, 1H), 4.51 (s, 2H), 4.44 (d, *J* = 5.4 Hz, 2H), 3.37-3.24 (m, 2H), 1.57 (m, 2H), 1.32 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H).$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.0, 139.6, 138.0, 128.8, 128.5, 127.4, 127.4, 127.1, 126.9, 50.5, 47.4, 44.9, 30.5, 20.2, 13.9. $[M+H]^+$ Calcd for $C_{19}H_{24}N_2O$ 297.1961; Found 297.1963.



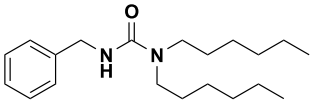
3-benzyl-1-methyl-1-(4-methylbenzyl)urea (3ac): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (249 mg, 93% yield, 95% selectivity). m.p. = 76-78℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.31 (m, 2H), 7.28 (m, 3H), 7.16 (s, 4H), 4.72 (d, *J* = 5.7 Hz, 1H), 4.49 (s, 2H), 4.46 (d, *J* = 5.6 Hz, 2H), 2.91 (s, 3H), 2.35 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.3, 139.6, 137.0, 134.8, 129.4, 128.6, 127.6, 127.2, 127.2, 52.0, 45.0, 34.4, 21.1. $[M+H]^+$ Calcd for $C_{17}H_{20}N_2O$ 269.1648; Found 269.1649.



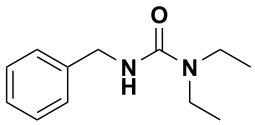
N-benzyl-3,4-dihydroisoquinoline-2(1H)-carboxamide (3ad): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (243mg, 91% yield, 96% selectivity). m.p. = 96-98 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, J = 4.5 Hz, 4H), 7.28 (m, 1H), 7.24 - 7.15 (m, 3H), 7.13 (q, J = 4.3 Hz, 1H), 4.88 (t, J = 5.6 Hz, 1H), 4.58 (s, 2H), 4.49 (d, J = 5.5 Hz, 2H), 3.66 (t, J = 5.9 Hz, 2H), 2.89 (t, J = 5.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.5, 139.5, 135.1, 133.4, 128.6, 128.4, 127.8, 127.3, 126. 7, 126.4, 126.3, 45.6, 45.1, 41.3, 29.1. $[M+H]^+$ Calcd for $C_{17}H_{18}N_2O$ 267.1492; Found 267.1493.



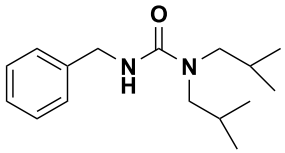
3-benzyl-1,1-dibutylurea (3ae)[7]: According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (257.2mg, 98% yield, 99% selectivity). m.p. = 53-55 ℃; ^{1}H NMR (500MHz, $CDCl_3$) δ 7.62 - 7.06 (m, 5H), 4.59 (m, 1H), 4.45 (d, J = 5.5 Hz, 2H), 3.29 – 3.12 (m, 4H), 1.54 (m, 4H), 1.32 (m, 4H), 0.93 (t, J = 7.4 Hz, 6H). ^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) δ 157.5, 140.0, 128.6, 127.6, 127.1, 47.2, 44.9, 30.8, 20.2, 13.9. $[M+H]^+$ Calcd for $C_{16}H_{26}N_2O$ 263.2118; Found 263.2121.



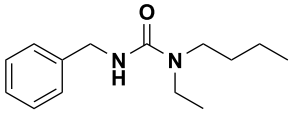
3-benzyl-1,1-dihexylurea(3af): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as colorless oil (295mg, 93%yield, 98% selectivity). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 - 7.29 (m, 4H), 7.28 (m, 1H), 4.59 (t, *J* = 5.1 Hz, 1H), 4.45 (d, *J* = 5.5 Hz, 2H), 3.23 - 3.12 (m, 4H), 1.55 (m, 4H), 1.33-1.22 (m, 12H), 0.92 - 0.84 (m, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.5, 140.0, 128.6, 127.6, 127.1, 47.4, 44.9, 31.6, 28.6, 26.7, 22.6, 14.02. $[M+H]^+$ Calcd for $C_{20}H_{34}N_2O$ 319.2744; Found 319.2746.



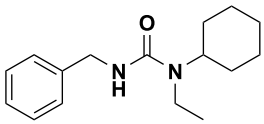
3-benzyl-1,1-diethylurea Chemical Formula(3ag): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (195.5mg, 95% yield, 98% selectivity). m.p. = 42-44 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 4H), 7.29 – 7.25 (m, 1H), 4.65 (t, *J* = 5.8 Hz, 1H), 4.44 (d, *J* = 5.5 Hz, 2H), 3.29 (q, *J* = 7.1 Hz, 4H), 1.15 (t, *J* = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.2, 139.9, 128.6, 127.6, 127.2, 44.9, 41.3, 13.9. $[M+H]^+$ Calcd for $C_{12}H_{18}N_2O$ 207.1492; Found 207.1493.



3-benzyl-1,1-diisobutylurea (3ah): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (244.5mg, 93% yield, 98% selectivity). m.p. = 53-55 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 4H), 7.29 - 7.23 (m, 1H), 4.64 (t, *J* = 5.4 Hz, 1H), 4.45 (s, 2H), 3.07 (d, *J* = 7.5 Hz, 4H), 1.98 (m, 2H), 0.91 (d, *J* = 6.6 Hz, 12H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.1, 140.1, 128.7, 127.6, 127.2, 55.7, 45.1, 27.8, 20.4. $[M+H]^+$ Calcd for $C_{16}H_{26}N_2O$ 263.2118; Found 263.2120.

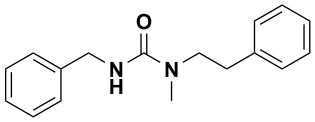


3-benzyl-1-butyl-1-ethylurea （3ai）: According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as colorless oil (222.4mg，95%yield, 98% selectivity). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.30 (m, 4H), 7.27 (m, 1H), 4.59 (s, 1H), 4.46 (d, J = 5.5 Hz, 2H), 3.28 (m, 2H), 3.25-3.17 (m, 2H), 1.54 (m, 2H), 1.34 (m, 2H), 1.15 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.5, 140.0, 128.7, 127.8, 127.3, 46.8, 45.1, 41.9, 31.1, 20.4, 14.0, 13.9. $[M+H]^+$ Calcd for $C_{14}H_{22}N_2O$ 235.1805; Found 235.1807.

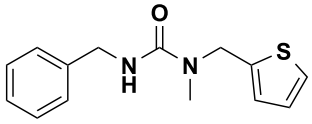


3-benzyl-1-cyclohexyl-1-ethylurea (3aj): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (259.7mg, 99% yield, >99% selectivity). m.p. = 70-72℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.28 (m, 4H), 7.30-

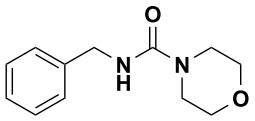
7.24 (m, 1H), 4.62 (s, 1H), 4.47 (d, *J* = 5.5 Hz, 2H), 4.03 (s, 1H), 3.17 (m, 2H), 1.78 (m, 4H), 1.66 (d, *J* = 12.7 Hz, 1H), 1.37 (t, *J* = 9.6 Hz, 4H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.09 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.3, 140.0, 128.6, 127.6, 127.1, 54.5, 45.0, 36.5, 31.5, 26.0, 25.6, 16.1. $[M+H]^+$ Calcd for $C_{16}H_{24}N_2O$ 261.1961; Found 261.1963.



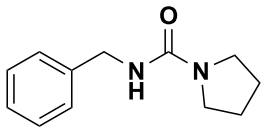
3-benzyl-1-methyl-1-phenethylurea (3ak)[8]: According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as colorless oil (240 mg, 90% yield, 96% selectivity). ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 2H), 7.29 - 7.22 (m, 5H), 7.20 (m, 3H), 4.46 (s, 1H), 4.35 (s, 2H), 3.51 (t, *J* = 7.3 Hz, 2H), 2.85 (m, 2H), 2.82 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.9, 139.6, 139.2, 128.8, 128.6, 128.5, 127.7, 127.2, 126.4, 51.1, 45.0, 34.74, 34.65. $[M+H]^+$ Calcd for $C_{17}H_{20}N_2O$ 269.1648; Found 269.1650.



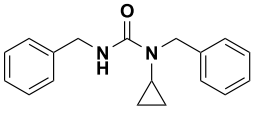
3-benzyl-1-methyl-1-(thiophen-2-ylmethyl)urea (3al): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (258.1mg, 98% yield, 99% selectivity). m.p. = 61-63℃; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 - 7.28 (m, 4H), 7.27 (s, 1H), 7.26 - 7.22 (m, 1H), 6.96 (m, 2H), 4.75 (s, 1H), 4.69 (s, 2H), 4.47 (d, J = 5.5 Hz, 2H), 2.92 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.8, 141.1, 139.5, 128.6, 127.7, 127.3, 126.7, 125.8, 125.2, 47.4, 45.1, 34.1. [M+H]+ Calcd for $C_{14}H_{16}N_2OS$ 269.1648; Found 269.1650.



N-benzylmorpholine-4-carboxamide (3am)[9]: According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (195.6mg, 89% yield, 96% selectivity). m.p. = 118-120 ℃; ^1H NMR (500 MHz, $CDCl_3$) δ 7.31 (m, 5H), 4.80 (t, *J* = 6.0 Hz, 1H), 4.44 (d, *J* = 5.5 Hz, 2H), 3.76 – 3.59 (t, *J* = 5.0 Hz, 4H), 3.44 – 3.30 (t, *J* = 5.5 Hz, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.7, 139.2, 128.7, 127.8, 127.4, 66.5, 45.0, 44.0. $[M+H]^+$ Calcd for $C_{12}H_{16}N_2O_2$ 221.1285; Found 221.1285.

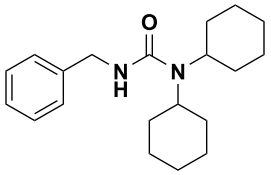


N-benzylpyrrolidine-1-carboxamide(3an)[10]: According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (176.5mg, 87% yield, 96% selectivity). m.p. =115-117 ℃; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 - 7.31 (m, 4H), 7.30 - 7.24 (m, 1H), 4.50 (s, 1H), 4.46 (d, J = 4.7 Hz, 2H), 3.37 (d, J = 6.9 Hz, 4H), 1.91 (t, J = 6.6 Hz, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 156.7, 139.9, 128.6, 127.8, 127.2, 45.6, 44.7, 25.6. $[M+H]^+$ Calcd for $C_{12}H_{16}N_2O$ 205.1335; Found 205.1336.

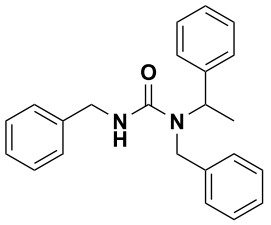


1,3-dibenzyl-1-cyclopropylurea (3ao)[11]: According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (239.4mg, 86% yield, 89% selectivity). m.p. = 60-62 ℃; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41-7.21 (m, 10H), 5.64 (s, 1H), 4.61 (s, 2H), 4.53 (d, J = 5.7 Hz, 2H), 2.38 (m, 1H), 0.78 (d, J = 5.4 Hz, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 159.0, 139.8,

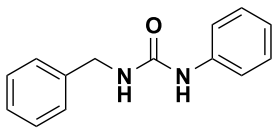
139.0, 128.6, 128.4, 127.9, 127.4, 127.2, 127.0, 50.5, 44.8, 27.7, 8.7. $[M+H]^+$ Calcd for $C_{18}H_{20}N_2O$ 281.1648; Found 281.1650.



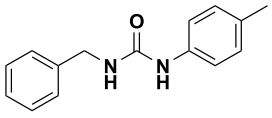
3-benzyl-1,1-dicyclohexylurea (3ap): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (223.1mg, 71% yield, 86% selectivity). m.p. = 131-133 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.29 (m, 4H), 7.29-7.24 (m, 1H), 4.57 (t, J = 4.9 Hz, 1H), 4.46 (d, J = 5.5 Hz, 2H), 3.39 (t, J = 11.7 Hz, 2H), 1.84-1.61 (m, 14H), 1.32 (m, 4H), 1.11 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.4, 140.1, 128.6, 127.5, 127.0, 55.2, 44.8, 31.8, 26.4, 25.5. $[M+H]^+$ Calcd for $C_{20}H_{30}N_2O$ 315.2431; Found 315.2433.



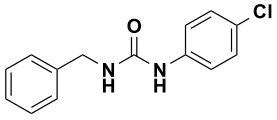
1,3-dibenzyl-1-(1-phenylethyl)urea(3aq): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as colorless oil (200 mg, 58% yield, 93% selectivity). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (m, 4H), 7.33-7.26 (m, 4H), 7.26-7.16 (m, 5H), 7.01 (d, *J* = 7.1 Hz, 2H), 5.89 (m, 1H), 4.57 (t, *J* = 5.2 Hz, 1H), 4.44-4.35 (m, 2H), 4.34-4.18 (m, 2H), 1.57 (d, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.5, 141.8, 139.3, 138.2, 128.9, 128.6, 128.4, 127.41, 127.35, 127.3, 127.1, 127.0, 126.5, 52.8, 47.0, 44.9, 17.4. $[M+H]^+$ Calcd for $C_{23}H_{24}N_2O$ 345.1961; Found 345.1961.



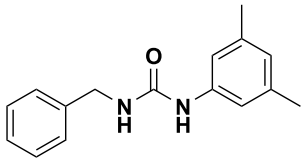
1-benzyl-3-phenylurea (3ar)[12]**:** According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (138.9mg, 61% yield, 63% selectivity). m.p. = 167-169℃; ^{1}H NMR (500MHz, DMSO-d_6) δ 8.54 (s, 1H), 7.40 (d, J = 8.6 Hz, 2H), 7.39 - 7.27 (m, 4H), 7.23 (q, J = 8.6 Hz, 3H), 6.89 (t, J = 7.9 Hz, 1H), 6.60 (s, 1H), 4.30 (d, J = 4.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (126MHz, DMSO-d_6) δ 155.7, 140.9, 140.8, 129.1, 128.8, 127.6, 127.2, 121.5, 118.1, 43.2. $[M+H]^+$ Calcd for $C_{14}H_{14}N_2O$ 227.1179; Found 227.1179.



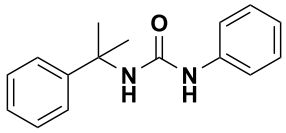
1-benzyl-3-(p-tolyl)urea (3as)[13]**:** According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 20/1-1/1) to give the product as a white solid (158mg, 66% yield, 67% selectivity). m.p. = 182-184℃; ^{1}H NMR (500MHz, DMSO-d_6) δ 8.40 (s, 1H), 7.31 (m, 6H), 7.23 (t, J = 6.9 Hz, 1H), 7.02 (d, J = 7.4 Hz, 2H), 6.53 (t, J = 5.4 Hz, 1H), 4.28 (d, J = 5.4 Hz, 2H), 2.21 (s, 3H). $^{13}C\{^1H\}$ NMR (126MHz, DMSO-d_6) δ 155.7, 140.9, 138.3, 130.2, 129.5, 128.7, 127.6, 127.2, 118.3, 43.2, 20.8. $[M+H]^+$ Calcd for $C_{15}H_{16}N_2O$ 241.1335; Found 241.1336.



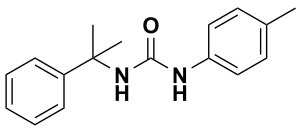
1-benzyl-3-(4-chlorophenyl)urea (3at)[14]**:** According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (156mg, 60% yield, 61% selectivity). m.p. = 210-212℃; ^{1}H NMR (500MHz, DMSO-d_6) δ 8.70 (s, 1H), 7.43 (d, J = 8.9 Hz, 2H), 7.32 (m, 4H), 7.24 (m, 3H), 6.72 - 6.58 (m, 1H), 4.29 (s, 2H). $^{13}C\{^1H\}$ NMR (126MHz, DMSO-d_6) δ 155.5, 140.7, 139.9, 128.9, 128.8, 127.6, 127.2, 125.0, 119.6, 43.2. $[M+H]^+$ Calcd for $C_{14}H_{13}ClN_2O$ 261.0789; Found 261.0789.



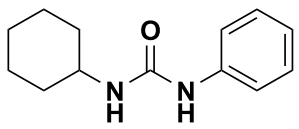
1-benzyl-3-(3,5-dimethylphenyl)urea (3au)[15]**:** According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (155mg, 61% yield, 64% selectivity). m.p. = 176-178℃; ^{1}H NMR (500MHz, DMSO-d_6) δ 8.36 (s, 1H), 7.31 (m, 4H), 7.24 (t, J = 7.0 Hz, 1H), 7.02 (s, 2H), 6.55 (d, J = 8.7 Hz, 2H), 4.28 (d, J = 5.7 Hz, 2H), 2.19 (s, 6H). ^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) δ 155.7, 140.9, 140.7, 138.0, 128.7, 127.6, 127.2, 123.2, 115.9, 43.2, 21.60. $[M+H]^+$ Calcd for $C_{16}H_{18}N_2O$ 255.1492; Found 255.1496.



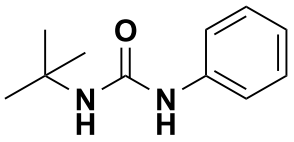
1-phenyl-3-(2-phenylpropan-2-yl)urea (3av)[16]**:** According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 20/1-1/1) to give the product as a white solid (230mg, 90% yield, 91% selectivity). m.p. = 175-177 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.1 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.28 (m, 1H), 7.21 (m, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.52 (s, 1H), 5.37 (s, 1H), 1.65 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.9, 146.6, 138.8, 128.9, 128.7, 127.0, 125.2, 123.0, 119.9, 55.2, 30.1. $[M+H]^+$ Calcd for $C_{16}H_{18}N_2O$ 255.1942; Found 255.1942.



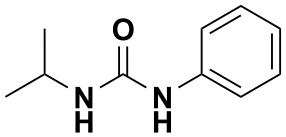
1-(2-phenylpropan-2-yl)-3-(p-tolyl)urea (3aw)[17]**:** According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 20/1-1/1) to give the product as a white solid (243mg, 91% yield, 95% selectivity). m.p. = 185-188 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.5 Hz, 2H), 7.37 (t, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.07 - 6.96 (m, 4H), 6.09 (s, 1H), 5.10 (s, 1H), 2.27 (s, 3H), 1.67 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 154.9, 146.5, 135.8, 133.2, 129.6, 128.7, 127.1, 125.2, 120.8, 55.3, 30.1, 20.7. $[M+H]^+$ Calcd for $C_{17}H_{20}N_2O$ 269.1648; Found 269.1649.



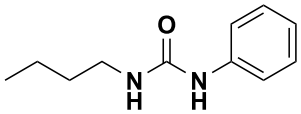
1-cyclohexyl-3-phenylurea (3ax)[18]**:** According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (201mg, 92% yield, 95% selectivity). m.p. = 177-180 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 4H), 7.08 (t, *J* = 6.3 Hz, 1H), 6.57 (s, 1H), 4.85 (m, 1H), 3.76 - 3.56 (m, 1H), 1.96 (d, *J* = 10.1 Hz, 2H), 1.69 (d, *J* = 13.5 Hz, 2H), 1.60 (d, *J* = 10.4 Hz, 1H), 1.36 (m, 2H), 1.13 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.1, 138.7, 129.3, 123.7, 121.0, 49.0, 33.7, 25.5, 24.9. $[M+H]^+$ Calcd for $C_{13}H_{18}N_2O$ 219.1492; Found 219.1492.



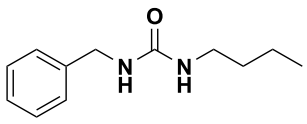
1-(tert-butyl)-3-phenylurea (3ay) [19]**:** According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (169 mg, 88% yield, 90% selectivity). m.p. = 163-165 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (m, 4H), 7.03 (m, 1H), 6.63 (s, 1H), 4.92 (s, 1H), 1.36 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.1, 139.01, 129.2, 123.32, 120.6, 50.76, 29.36. $[M+H]^+$ Calcd for $C_{11}H_{16}N_2O$ 193.1335; Found 193.1336.



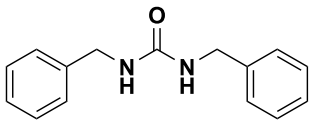
1-isopropyl-3-phenylurea (3az)[20]**:** According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (111mg, 60% yield, 61% selectivity). m.p. = 148-150℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 - 7.27 (m, 4H), 7.06 (m, 1H), 6.75 (s, 1H), 4.91 (d, *J* = 7.1 Hz, 1H), 4.00 (m, 1H), 1.16 (d, *J* = 6.5 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.3, 138.8, 129.2, 123.5, 120.8, 42.2, 23.2. $[M+H]^+$ Calcd for $C_{10}H_{14}N_2O$ 179.1179; Found 179.1179.



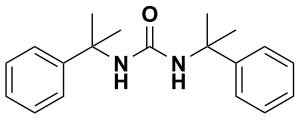
1-butyl-3-phenylurea (3ba)[21]**:** According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (106 mg, 55% yield, 56% selectivity). m.p. = 125-127 ℃; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.35 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 2H), 6.87 (t, *J* = 7.3 Hz, 1H), 6.08 (t, *J* = 5.1 Hz, 1H), 3.07 (m, 2H), 1.41 (m, 2H), 1.31 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 155.6, 141.1, 129.1, 121.3, 118.0, 39.1, 32.3, 20.0, 14.2. $[M+H]^+$ Calcd for $C_{11}H_{16}N_2O$ 193.1335; Found 193.1336.



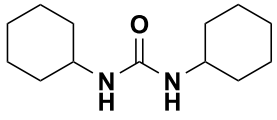
1-benzyl-3-butylurea (3bb): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/1) to give the product as a white solid (136mg, 60% yield, 61% selectivity). m.p. = 70-74 ℃; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.30 (t, *J* = 7.4 Hz, 2H), 7.22 (m, 3H), 6.25 (t, *J* = 5.7 Hz, 1H), 5.88 (t, *J* = 5.5 Hz, 1H), 4.32 - 4.05 (m, 2H), 3.00 (m, 2H), 1.35 (m, 2H), 1.26 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d$_6$) δ 158.5, 141.5, 128.6, 127.4, 127.0, 43.3, 39.5, 32.6, 20.0, 14.2. $[M+H]^+$ Calcd for $C_{12}H_{18}N_2O$ 207.1492; Found 207.1492.



1,3-dibenzylurea (4a): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/5) to give the product as a white solid. m.p. = 158-160 ℃; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.31 (m, 4H), 7.23 (m, 6H), 6.43 (t, *J* = 5.8 Hz, 2H), 4.23 (d, *J* = 6.0 Hz, 4H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 158.5, 141.4, 128.7, 127.4, 127.0, 43.4. $[M+H]^+$ Calcd for $C_{15}H_{16}N_2O$ 241.1335; Found 241.1336.

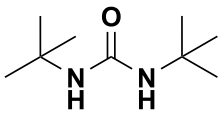


1,3-bis(2-phenylpropan-2-yl)urea (4b): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/5) to give the product as a white solid. m.p. = 226-228 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (m, 8H), 7.24 (m, 2H), 4.49 (s, 2H), 1.53 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 156.2, 146.7, 128.5, 126.9, 125.2, 54.9, 30.0. $[M+H]^+$ Calcd for $C_{19}H_{24}N_2O$ 297.1961; Found 297.1963.

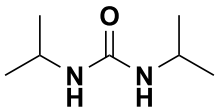


1,3-dicyclohexylurea (4c): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/5) to give the product as a white solid. m.p.=224-226 ℃; ^{1}H NMR (500 MHz, TFA-

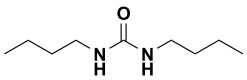
d) δ 5.11 (s, 2H), 3.54 (m, 4H), 3.35 (m, 4H), 3.22 (m, 2H), 2.86 (m, 12H); $^{13}C\{^{1}H\}$ NMR (126 MHz, TFA-*d*) δ 159.9, 55.3, 35.0, 27.3, 26.9. $[M+H]^+$ Calcd for $C_{13}H_{24}N_2O$ 225.1961; Found 225.1962.



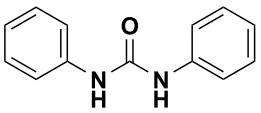
1,3-di-tert-butylurea (4d): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/5) to give the product as a white solid. m.p.=164-167 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.08 (s, 2H), 1.32 (s, 18H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 156.9, 50.3, 29.6. $[M+H]^+$ Calcd for $C_9H_{20}N_2O$ 173.1648; Found 173.1649.



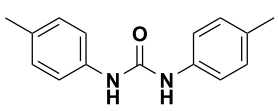
1,3-diisopropylurea (4e): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/5) to give the product as a white solid. m.p.=179-181 ℃; ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.48 (d, J = 6.7 Hz, 2H), 3.73 - 3.53 (m, 2H), 1.00 (d, J = 6.5 Hz, 12H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 157.2, 41.1, 23.8. $[M+H]^+$ Calcd for $C_7H_{16}N_2O$ 145.1335; Found 145.1335.



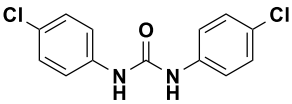
1,3-dibutylurea (4f): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/5) to give the product as a white solid. m.p. = 68-70 ℃; ^{1}H NMR (500 MHz, DMSO-d_6) δ 5.70 (t, J = 5.3 Hz, 2H), 2.95 (m, 4H), 1.32 (m, 4H), 1.25 (m, 4H), 0.86 (t, J = 7.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 158.5, 39.37, 32.7, 20.0, 14.2. $[M+H]^+$ Calcd for $C_9H_{20}N_2O$ 173.1648; Found 173.1649.



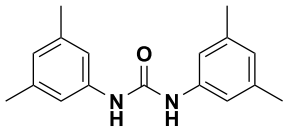
1,3-diphenylurea (5a): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/5) to give the product as a white solid. m.p. = 240-242℃; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.61 (s, 2H), 7.42 (d, J = 6.8 Hz, 4H), 7.24 (t, J = 7.7 Hz, 4H), 6.93 (t, J = 6.8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 153.0, 140.1, 129.2, 122.2, 118.6. $[M+H]^+$ Calcd for $C_{13}H_{12}N_2O$ 213.1022; Found 213.1023.



1,3-di-p-tolylurea (5b): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/5) to give the product as a white solid. m.p. = 248-251℃; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.48 (s, 2H), 7.32 (d, J = 8.4 Hz, 4H), 7.07 (d, J = 8.3 Hz, 4H), 2.23 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 153.1, 137.7, 131.0, 129.6, 118.7, 20.8. $[M+H]^+$ Calcd for $C_{15}H_{16}N_2O$ 241.1335; Found 241.1336.



1,3-bis(4-chlorophenyl)urea (5c): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/5) to give the product as a white solid. m.p. = 244-246 ℃; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.84 (s, 2H), 7.47 (d, J = 8.7 Hz, 4H), 7.32 (d, J = 8.7 Hz, 4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 152.8, 139.0, 129.1, 126.0, 120.3. $[M+H]^+$ Calcd for $C_{13}H_{10}Cl_2N_2O$ 281.0243; Found 281.0242.



1,3-bis(3,5-dimethylphenyl)urea(5d): According to general procedure, the crude residue was purified by flash chromatography (PE/EA = 10/1-1/5) to give the product as a white solid. m.p. = 270-272℃; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.44 (s, 2H), 7.06 (s, 4H), 6.60 (s, 2H), 2.22 (s, 12H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 152.9, 140.0, 138.2, 123.8, 116.3, 21.6. $[M+H]^+$ Calcd for $C_{17}H_{20}N_2O$ 269.1648; Found 269.1649.

3. Control Experiment to Investigate the Reaction Mechanism

3.1 NMR experiments

We attempted to monitor the reaction process using high-pressure NMR tubes with temperature-variable NMR. However, we encountered difficulties due to the poor solubility of thiocarbamate I in deuterated solvents such as $CDCl_3$, CD_3CN, and DMF-d_7, which resulted in very weak NMR signals. Notably, DMSO-d_6 was able to dissolve thiocarbamate salt I, producing visible NMR signals. However, because DMSO-d_6 has oxidizing properties, when it was heated with **1a**, **2a**, and COS, it tended to oxidize either the COS or its reaction intermediates.[22] This oxidation property of DMSO hindered the progress of the reaction, making DMSO-d_6 unsuitable for monitoring the reaction process over extended periods at high temperatures. To address these issues, we conducted the reactions in the absence of solvent, using three separate stainless-steel autoclaves equipped with a magnetic stirrer, each containing the same quantities of **1a** (0.1072 g, 1.0 mmol), **2a** (0.3945 g, 2.0 mmol). The reactor was flushed with N_2 to remove air, and then charged with 0.4 MPa COS. The reactions were carried out under identical conditions, and sampling was performed at different time intervals for NMR analysis.

- In the first reactor, the reaction was allowed to proceed at 25 °C for 4 h, after which the reaction solution was dissolved in DMSO-d_6 for immediate NMR analysis.

- The second reactor followed the same protocol, but after the initial 4 h at 25 °C, the reaction continued for an additional 2 h at 70 °C. The reaction solution was then dissolved in DMSO-d_6 for immediate NMR testing.

- The third reactor was maintained at 25 °C for 4 h, followed by 8 h at 70 °C. The reaction solution was subsequently collected and dissolved in DMSO- d_6 for immediate NMR analysis.

The ^{1}HNMR spectra of **1a**, **2a**, **3a** were acquired when **1a** (6.0 mg), **2a** (10.0 mg) or **3a** (13 mg) were dissolved in the NMR tube containing DMSO-d_6 respectively, which were shown in Figure S5a, Figure S5b and Figure S5g. The ^{1}HNMR spectra for the mixture solution of **1a** (7.2 mg) and **2a** (17.8 mg) were dissolved in the NMR tube containing DMSO-d_6 (0.4 mL), which were shown in Figure S5c. The ^{1}HNMR and ^{13}CNMR spectra for the first reactor mixture solution were acquired when the solution (16.9 mg) dissolved in the NMR tube containing DMSO-d_6 (0.4 mL), which were shown in Figure S5d and Figure S6. The ^{1}HNMR spectra for the second reactor mixture solution were acquired when the solution (16.8 mg) dissolved in the NMR tube containing DMSO-d_6 (0.4 mL), which were shown in Figure S5e. The ^{1}HNMR spectra for the third reactor mixture solution were acquired when the solution (16.5 mg) dissolved in the NMR tube containing DMSO-d_6 (0.4 mL), which were shown in Figure S5f.

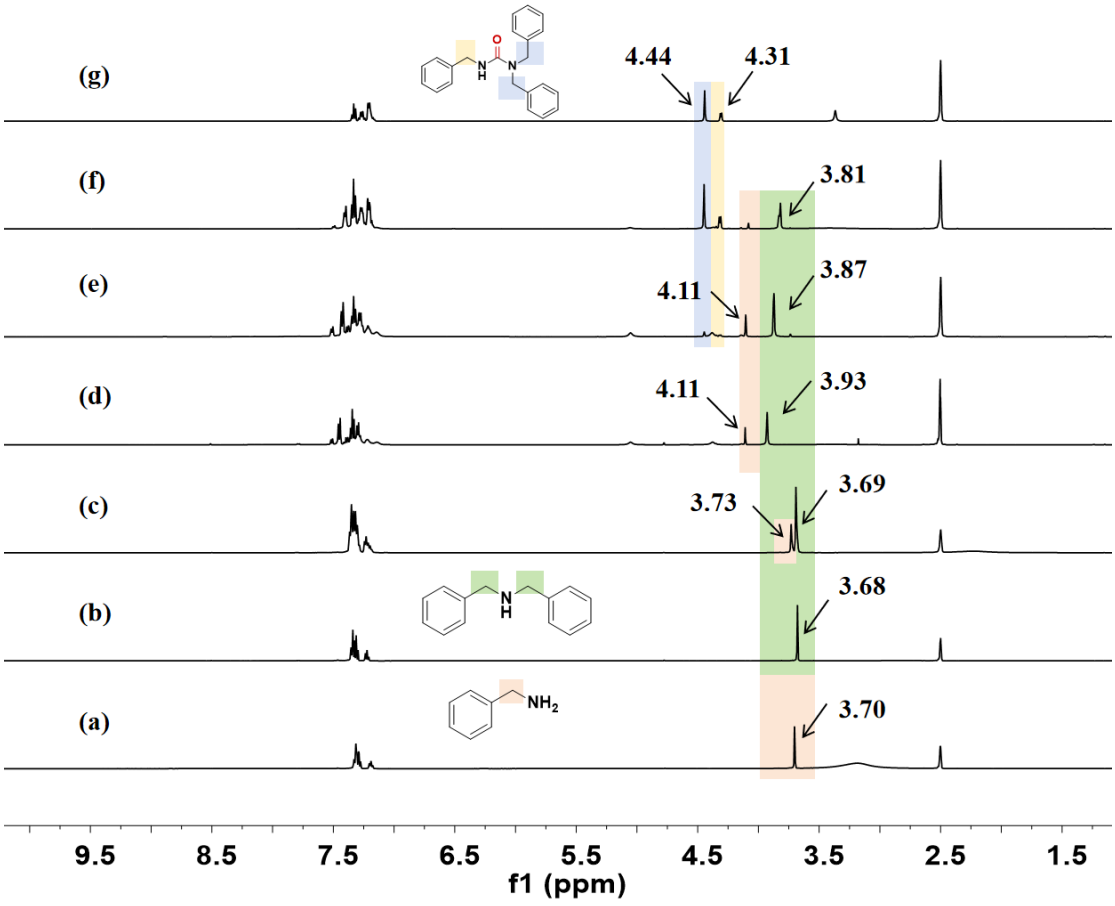


Figure S5. ^{1}H NMR spectra of **1a** (a), **2a** (b), the mixture of **1a** and **2a** (c), the mixture of **1a**, **2a** and COS 25°C for 4 h (d), the mixture of **1a**, **2a** and COS 25°C for 4 h then 70 °C for 2 h (e), the mixture of **1a**, **2a** and COS 25°C for 4 h then 70 °C for 8 h (f), the product **3a** (g) in DMSO-d_6.

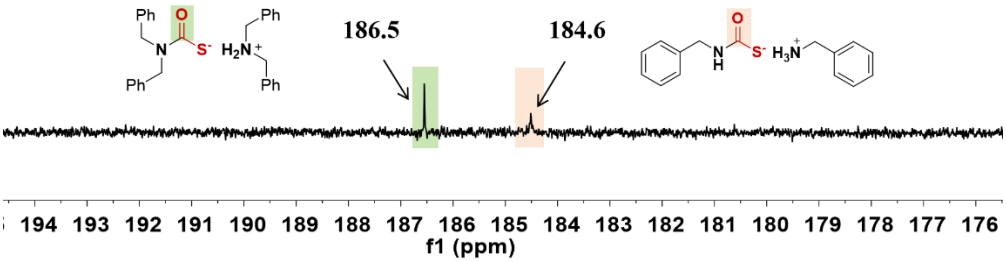
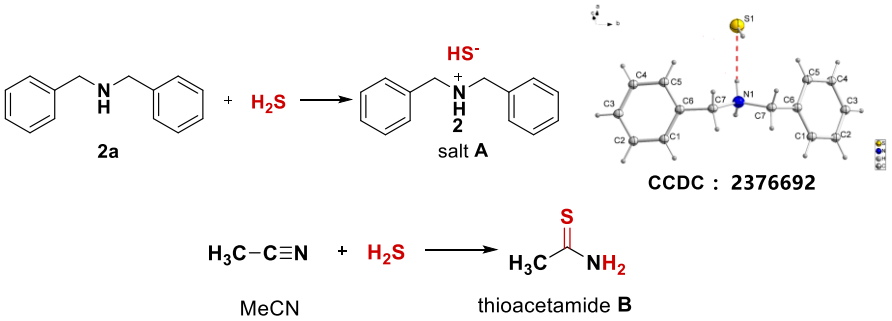


Figure S6. ^{13}C NMR spectra of **1a**, **2a** and COS 25 °C for 4 h in DMSO-d_6.

3.2 Analysis on the composition of the reaction solution

Unsymmetrical urea can be selectively synthesized from two different amines and COS under mild conditions. Notably, only the carbonyl group of COS is utilized in the synthesis of unsymmetrical urea, while the sulfur is not incorporated. To investigate the fate of sulfur in COS, we separated and analyzed all the components in the reaction mixture. In the solvent-free reaction system (Table 1, entry 11), after extraction with ethyl acetate and water, the aqueous layer was collected and evaporated to dryness. The residue was then treated with dichloromethane (5 mL) and petroleum ether (2 mL), followed by slow

evaporation at room temperature, resulting in the formation of crystalline salt **A**. The crystallographic data for salt **A** is shown in Figure S7. Additionally, when the reaction was performed using MeCN as the solvent, the crude mixture was purified by silica gel column chromatography (PE/EA = 10/1 to 1/1), yielding not only the desired unsymmetrical urea product and the symmetric urea byproduct but also a compound **B**. The NMR data for these compounds is presented in section **3.2.2**. Based on the identified structures, we speculate that COS releases H_2S during its reaction with amines. The released H_2S is then absorbed by the substrate **2a** or MeCN, leading to the formation of salt **A** or thioacetamide **B**, as illustrated in Scheme S1.



Scheme S1. Reaction of **2a** or MeCN with H_2S.

3.2.1. X-Ray Crystallography Data of Salt A

The CCDC number of salt **A** is 2376692, the detail information please see salt **A** cif document.

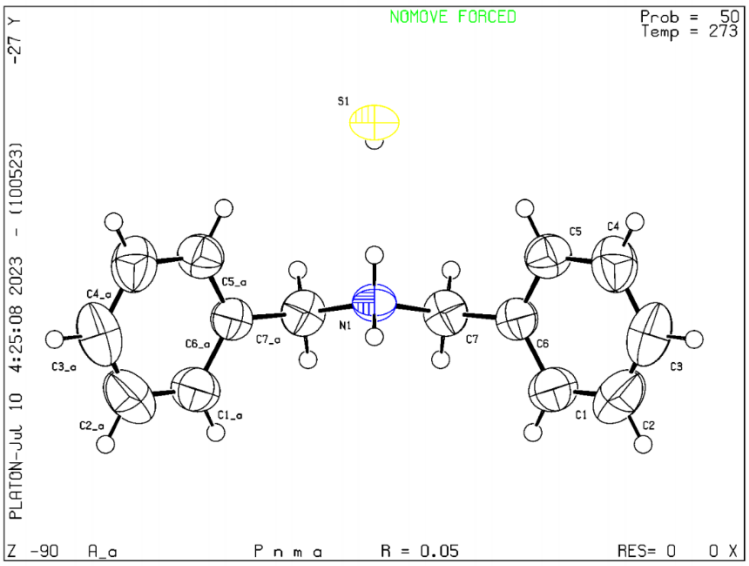


Figure S7. The crystallography structure of salt **A**.

checkCIF/PLATON report

You have not supplied any structure factors. As a result the full set of tests cannot be run.

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

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Temperature:      273 K

                 Calculated                Reported
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Hall group       -P 2ac 2n                 -P 2ac 2n
Moiety formula   C14 H16 N, H S            H S, C14 H16 N
Sum formula      C14 H17 N S               C14 H17 N S
Mr               231.35                    231.36
Dx,g cm-3        1.206                     1.206
Z                4                         4
Mu (mm-1)        2.014                     2.014
F000             496.0                     498.5
F000'            498.41
h,k,lmax         12,30,6                   12,30,6
Nref             1345                      1338
Tmin,Tmax                                  0.443,0.754
Tmin'

Correction method= # Reported T Limits: Tmin=0.443 Tmax=0.754
AbsCorr = MULTI-SCAN

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                                                 0.1636( 1338)
S = 1.003                Npar= 79
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The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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PLAT053_ALERT_1_C	Minimum Crystal Dimension Missing (or Error) ...	Please Check
PLAT054_ALERT_1_C	Medium Crystal Dimension Missing (or Error) ...	Please Check
PLAT055_ALERT_1_C	Maximum Crystal Dimension Missing (or Error) ...	Please Check
PLAT420_ALERT_2_C	D-H Bond Without Acceptor S1 --H1 .	Please Check
PLAT911_ALERT_3_C	Missing FCF Refl Between Thmin & STh/L= 0.600	6 Report
PLAT913_ALERT_3_C	Missing # of Very Strong Reflections in FCF	6 Note

Alert level G

PLAT002_ALERT_2_G	Number of Distance or Angle Restraints on AtSite	3 Note
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PLAT172_ALERT_4_G	The CIF-Embedded .res File Contains DFIX Records	3 Report
PLAT199_ALERT_1_G	Reported _cell_measurement_temperature ..... (K)	273 Check
PLAT200_ALERT_1_G	Reported _diffrn_ambient_temperature ..... (K)	273 Check
PLAT769_ALERT_4_G	CIF Embedded explicitly supplied scattering data	Please Note
PLAT860_ALERT_3_G	Number of Least-Squares Restraints	3 Note
PLAT883_ALERT_1_G	No Info/Value for _atom_sites_solution_primary .	Please Do !
PLAT910_ALERT_3_G	Missing # of FCF Reflection(s) Below Theta(Min).	1 Note
PLAT960_ALERT_3_G	Number of Intensities with I < - 2*sig(I) ...	2 Check
PLAT978_ALERT_2_G	Number C-C Bonds with Positive Residual Density.	0 Info
PLAT982_ALERT_1_G	The C-f'= 0.0192 Deviates from IT-value =	0.0181 Check
PLAT982_ALERT_1_G	The N-f'= 0.0326 Deviates from IT-value =	0.0311 Check
PLAT982_ALERT_1_G	The S-f'= 0.3354 Deviates from IT-value =	0.3331 Check
PLAT983_ALERT_1_G	The S-f"= 0.5513 Deviates from IT-Value =	0.5567 Check

0	**ALERT level A** = Most likely a serious problem - resolve or explain
0	**ALERT level B** = A potentially serious problem, consider carefully
7	**ALERT level C** = Check. Ensure it is not caused by an omission or oversight
15	**ALERT level G** = General information/check it is not something unexpected
11	ALERT type 1 CIF construction/syntax error, inconsistent or missing data
4	ALERT type 2 Indicator that the structure model may be wrong or deficient
5	ALERT type 3 Indicator that the structure quality may be low
2	ALERT type 4 Improvement, methodology, query or suggestion
0	ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

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A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

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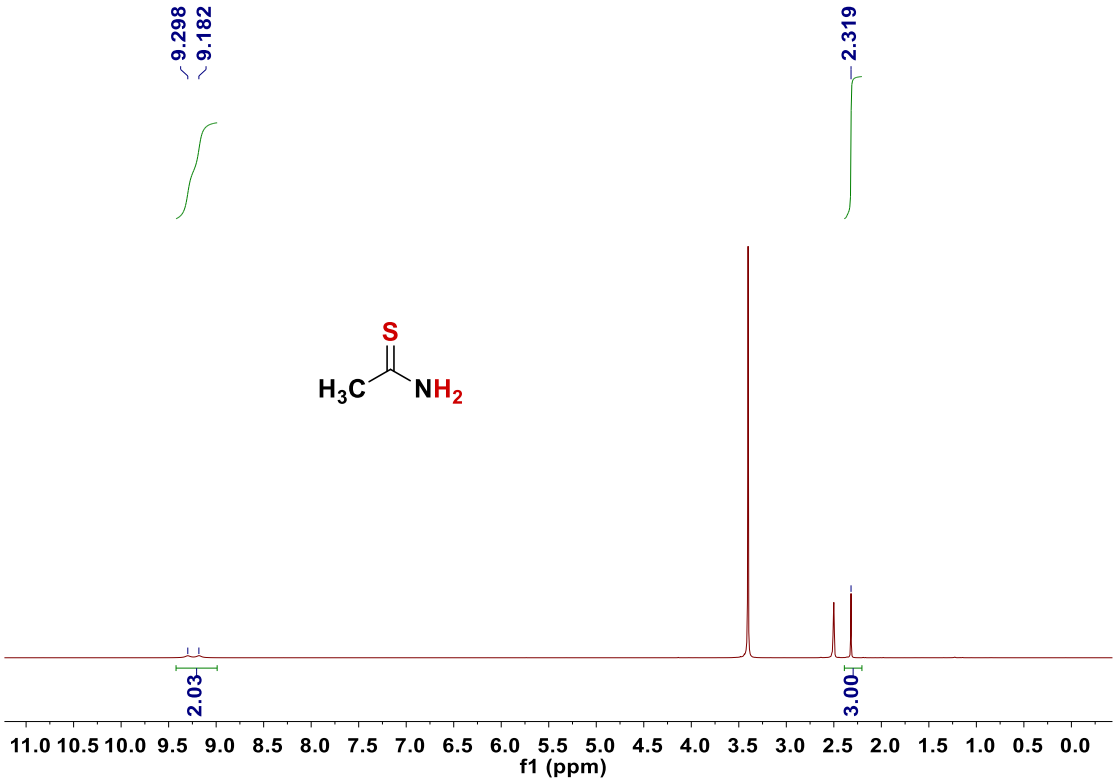
Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

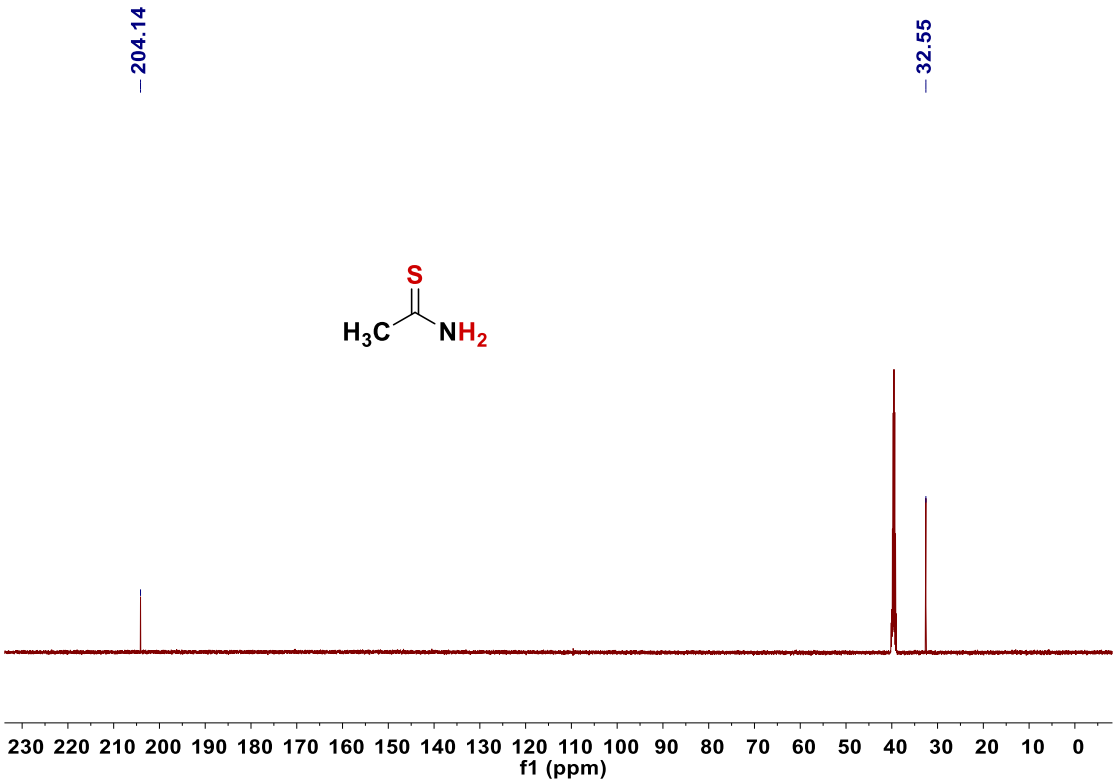
PLATON version of 10/05/2023; check.def file version of 10/05/2023

3.2.2. NMR Data of Thioacetamide B

^{1}H NMR (500 MHz, DMSO-d_6) of thioacetamide B

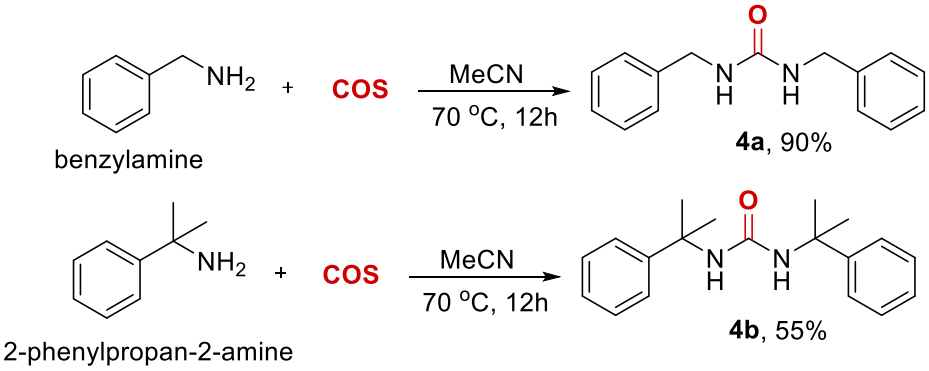


^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) of thioacetamide B



3.2.3 Control experiment for symmetric urea synthesis

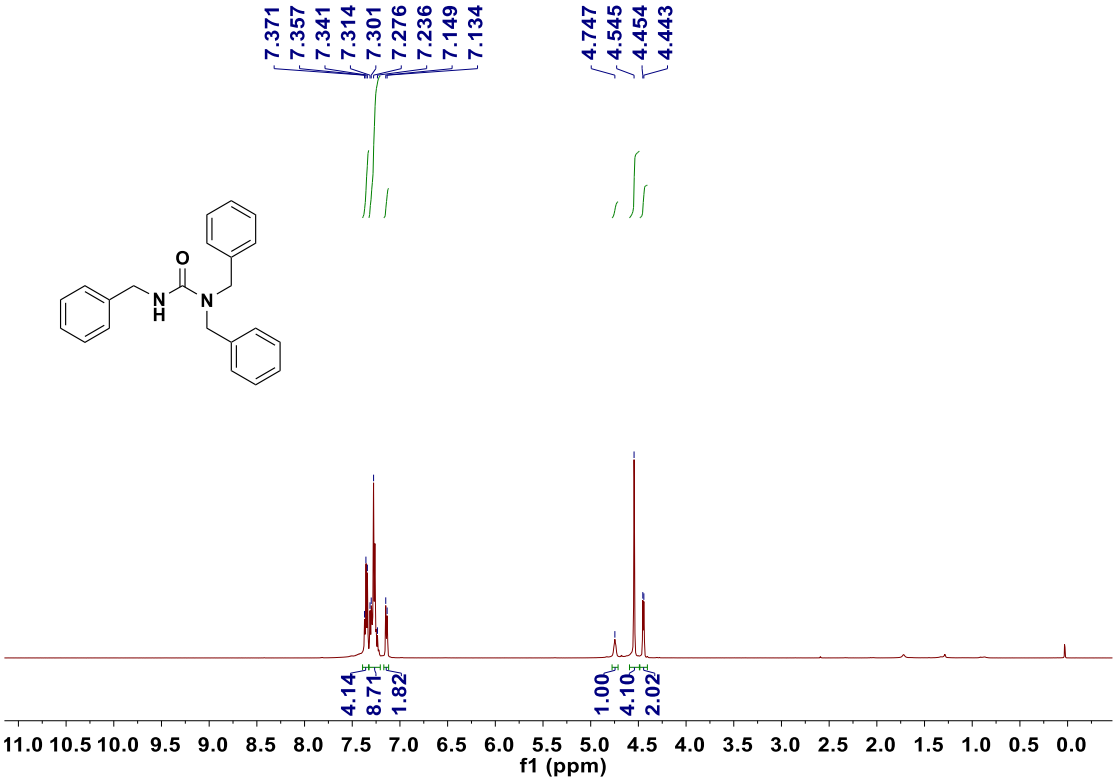
In a 15 mL stainless-steel autoclave equipped with a magnetic stirrer, **1a** (107.2 mg, 1.0 mmol) and 1 mL of MeCN were added. The reactor was flushed with N_2 to remove air, and then charged with 0.4 MPa COS. The reaction mixture was stirred at 70 °C for 12 h. After the reaction was complete, an aqueous HCl solution was added to the reaction mixture, followed by extraction with EtOAc three times. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (PE/EA = 5/1–1/1) to yield the desired product 1,3-dibenzylurea (**4a**, 108.2 mg, 90%). The same procedure to yield the product 1,3-bis(2-phenylpropan-2-yl) urea (**4b**, 81.3 mg, 55%) (Scheme S2).



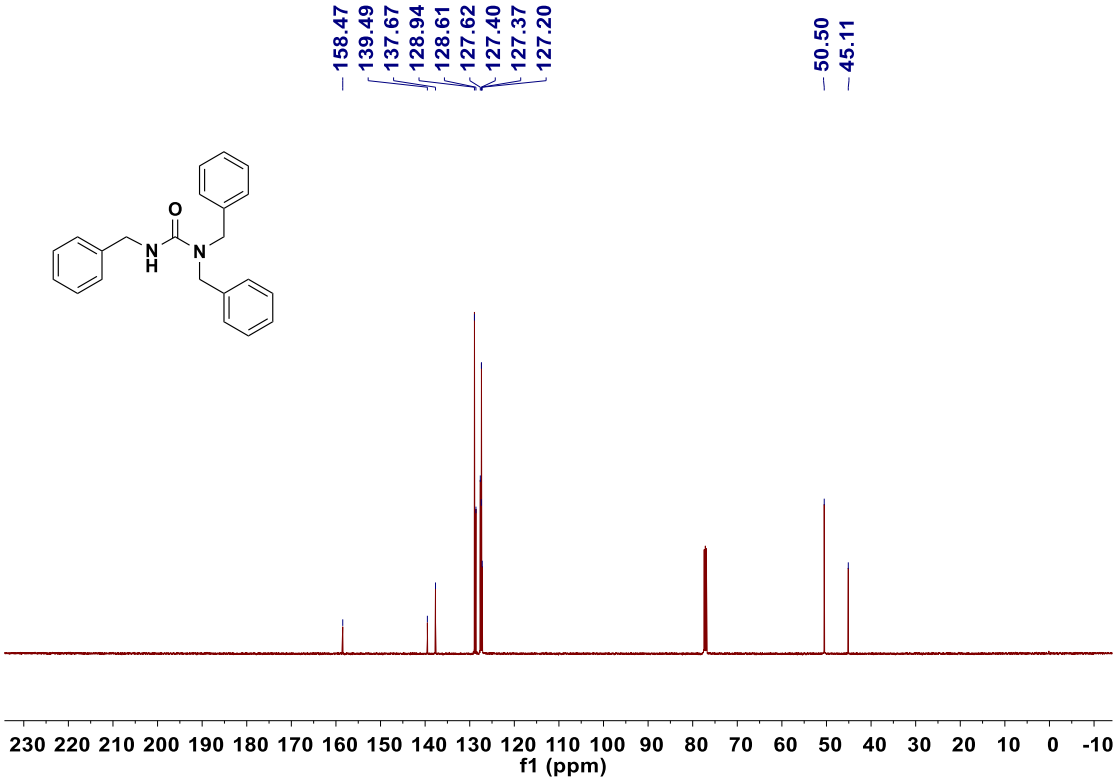
Scheme S2. Reaction of symmetric urea synthesis.

4. NMR Spectra

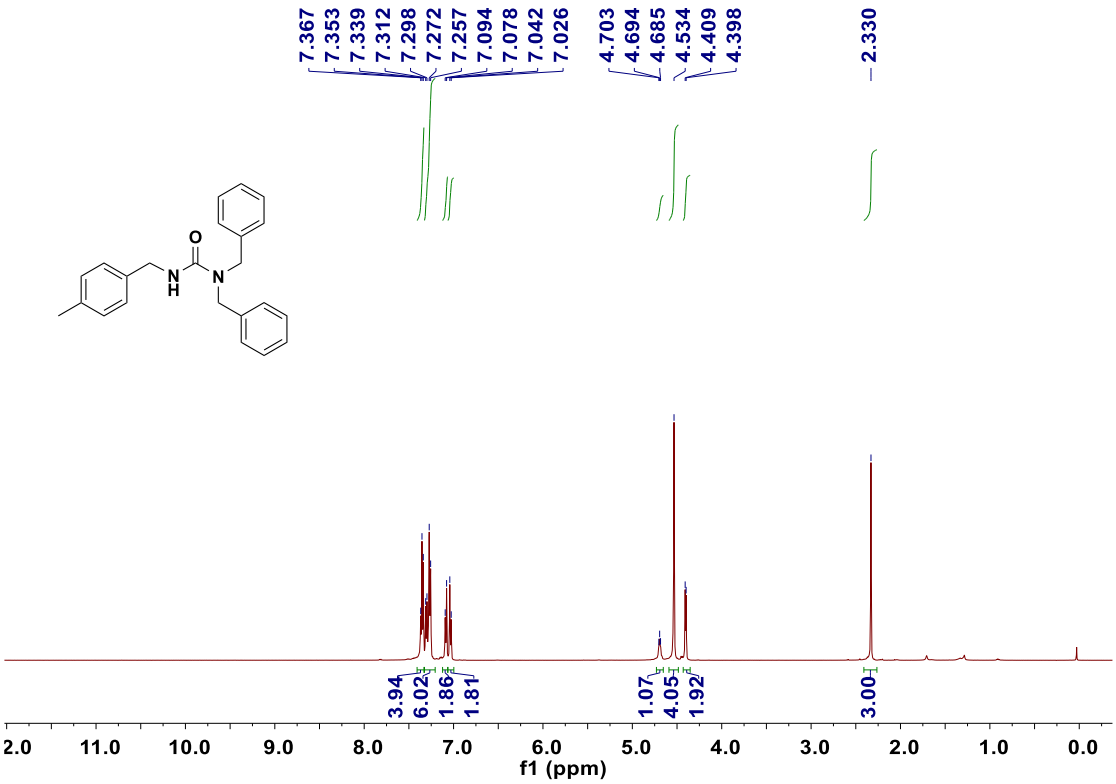
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1,3-tribenzylurea (3a)



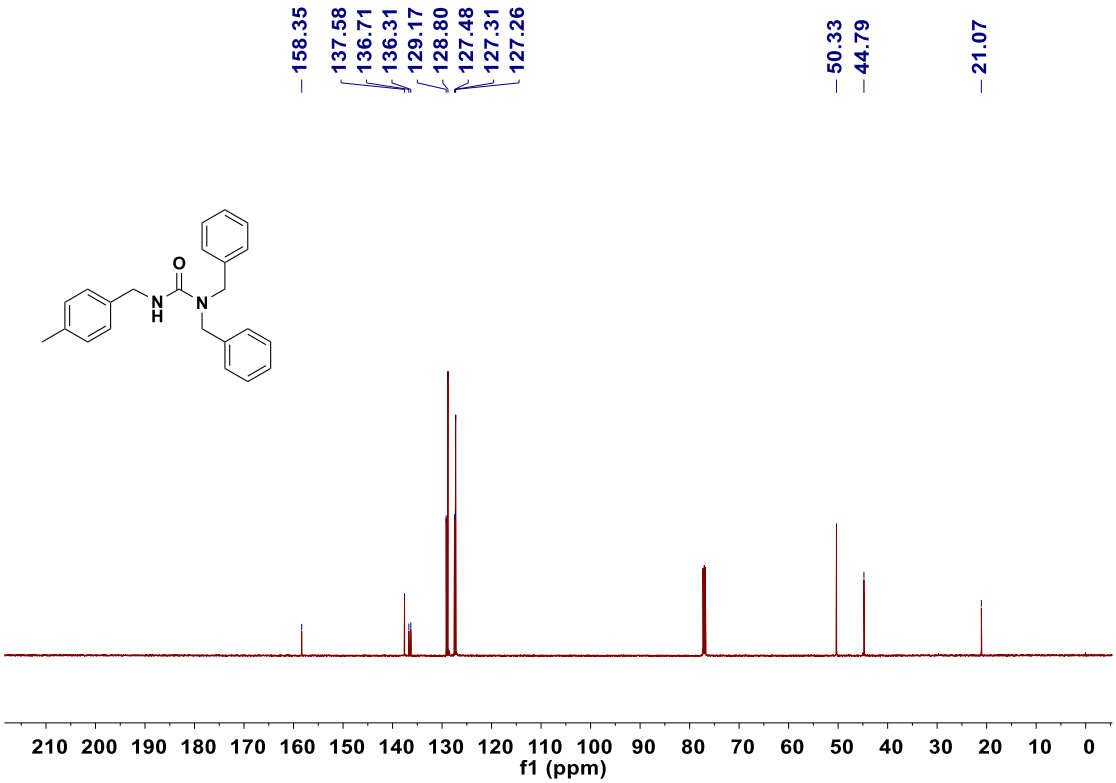
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1,3-tribenzylurea (3a)



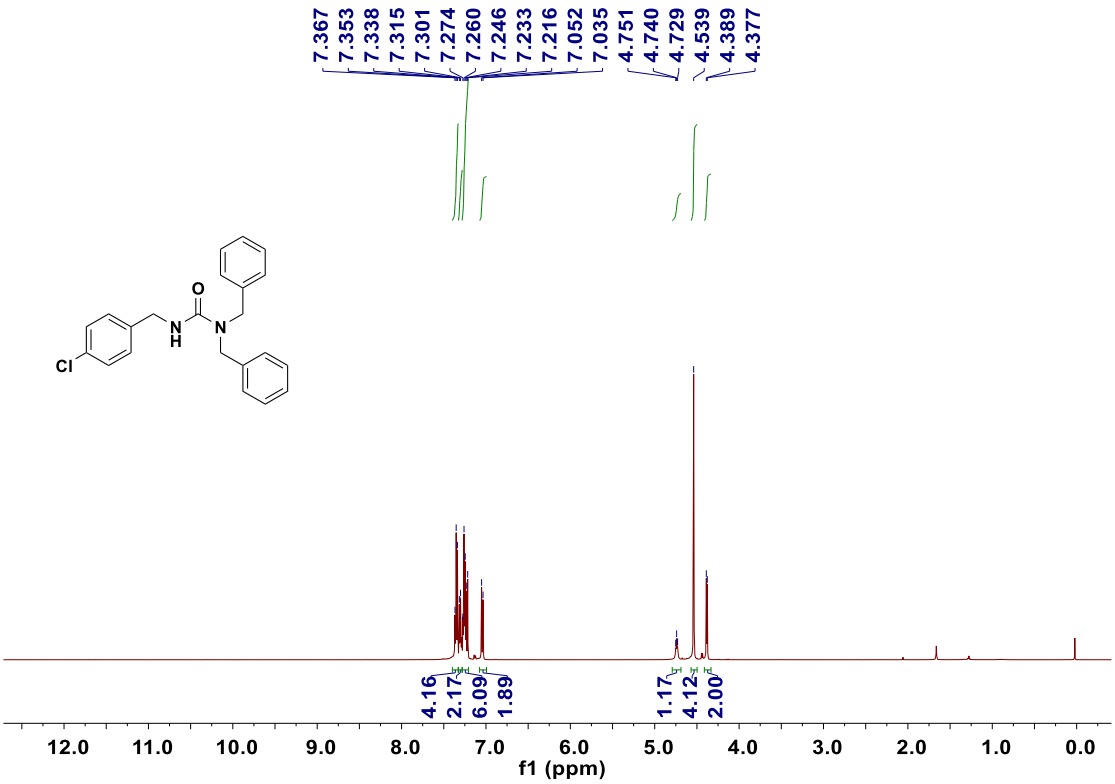
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-methylbenzyl)urea(3b)



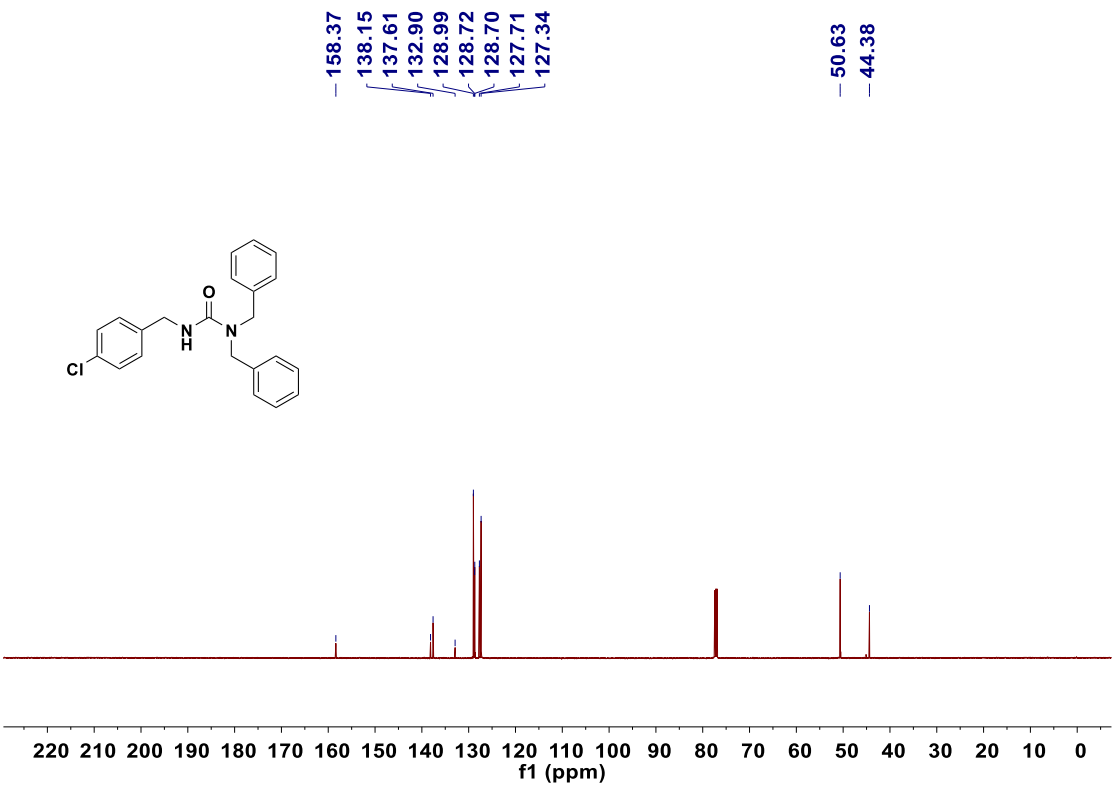
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-methylbenzyl)urea(3b)



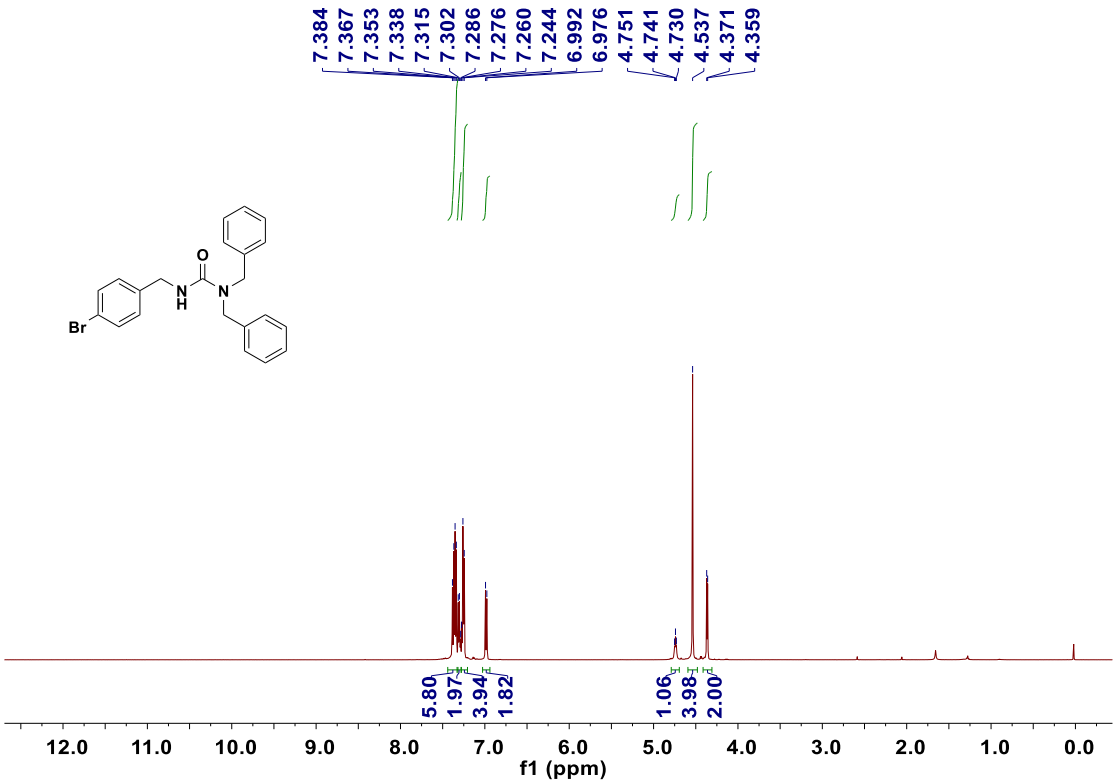
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-chlorobenzyl)urea (3c)



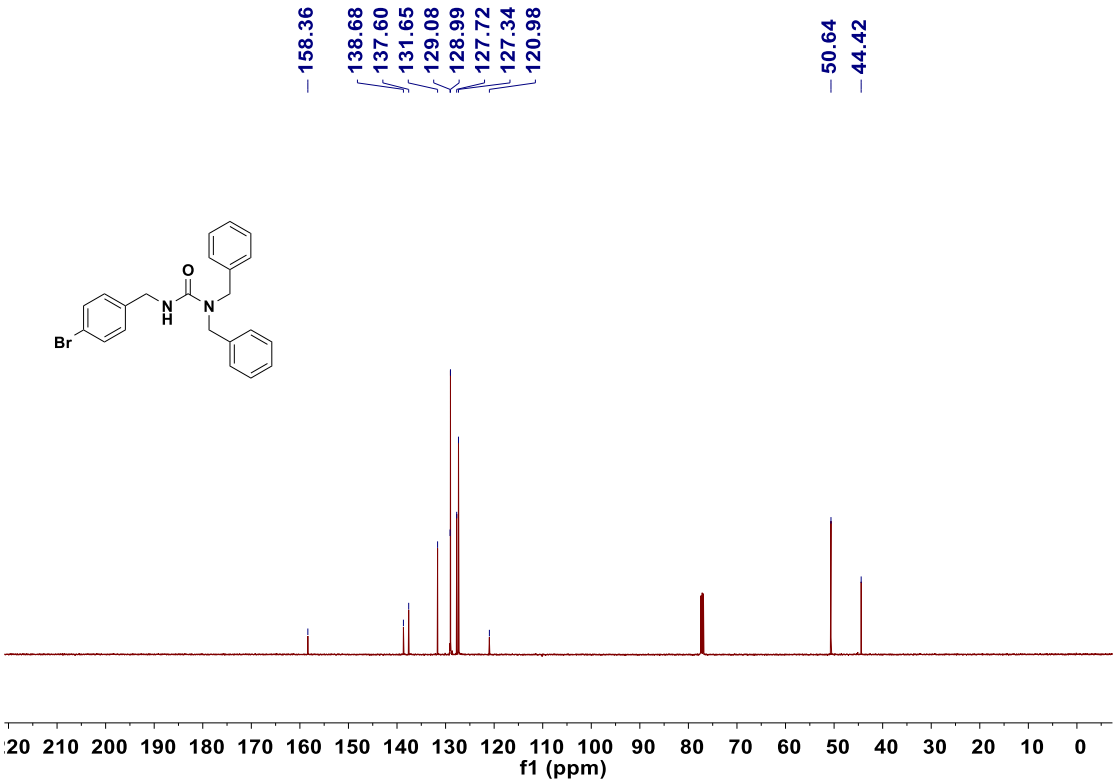
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-chlorobenzyl)urea (3c)



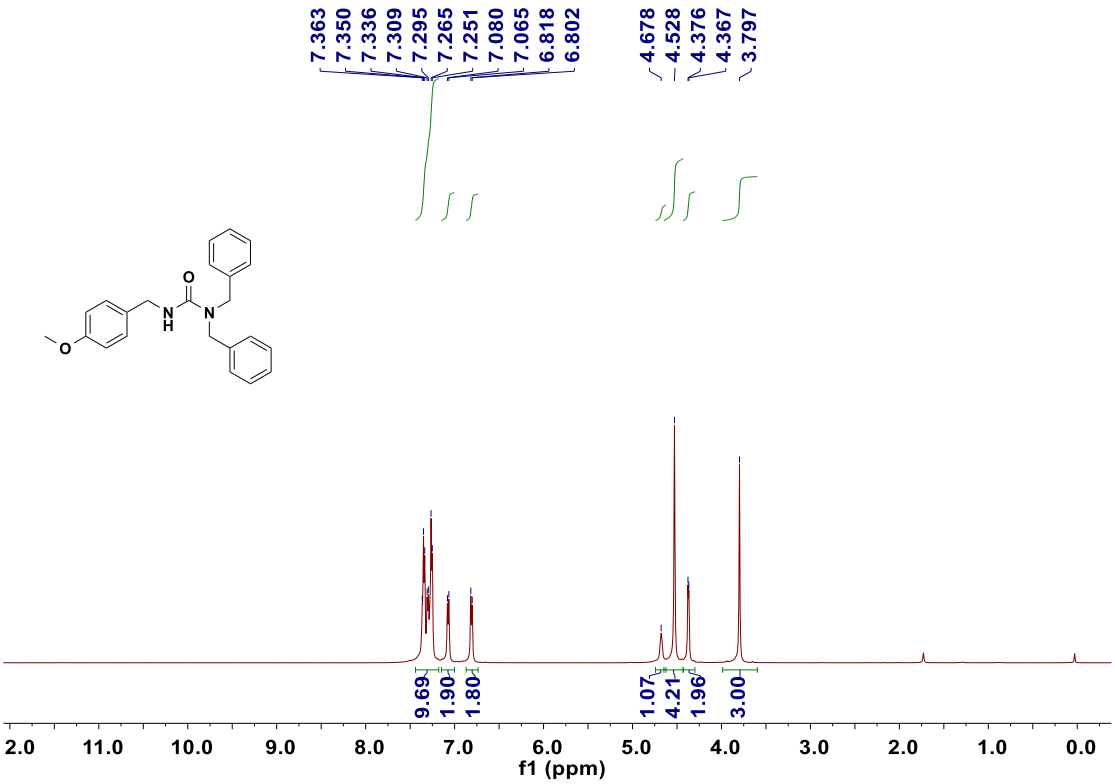
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-bromobenzyl)urea (3d)



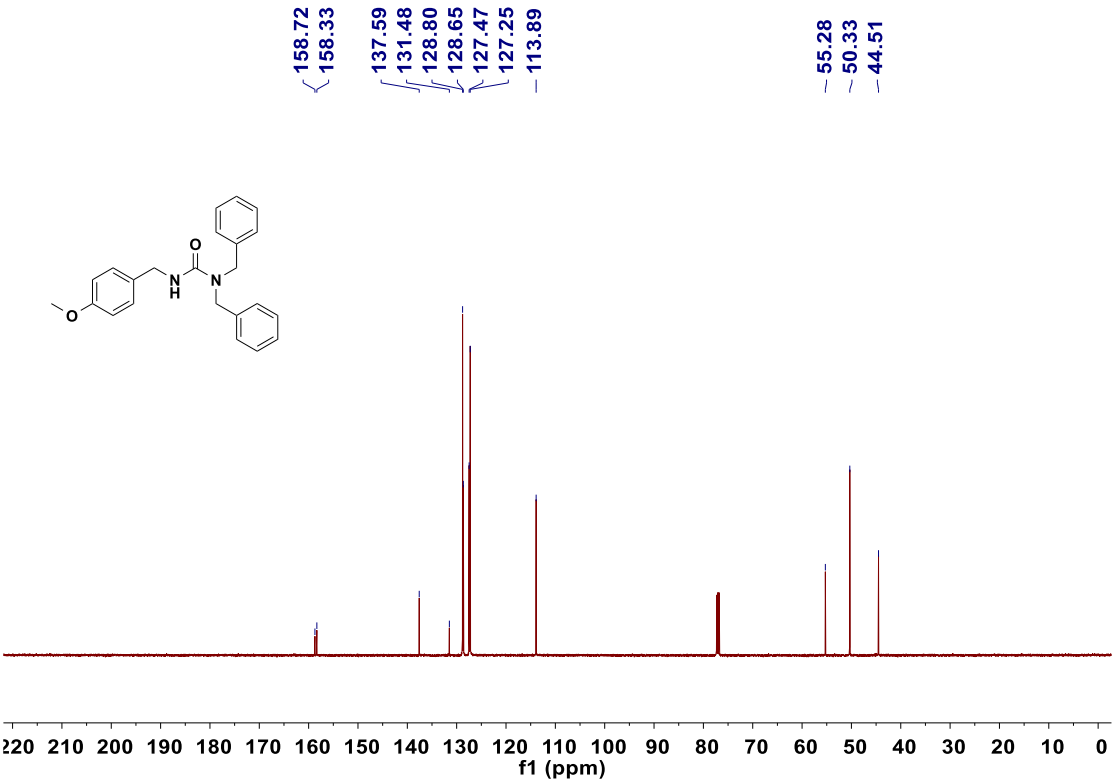
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-bromobenzyl)urea (3d)



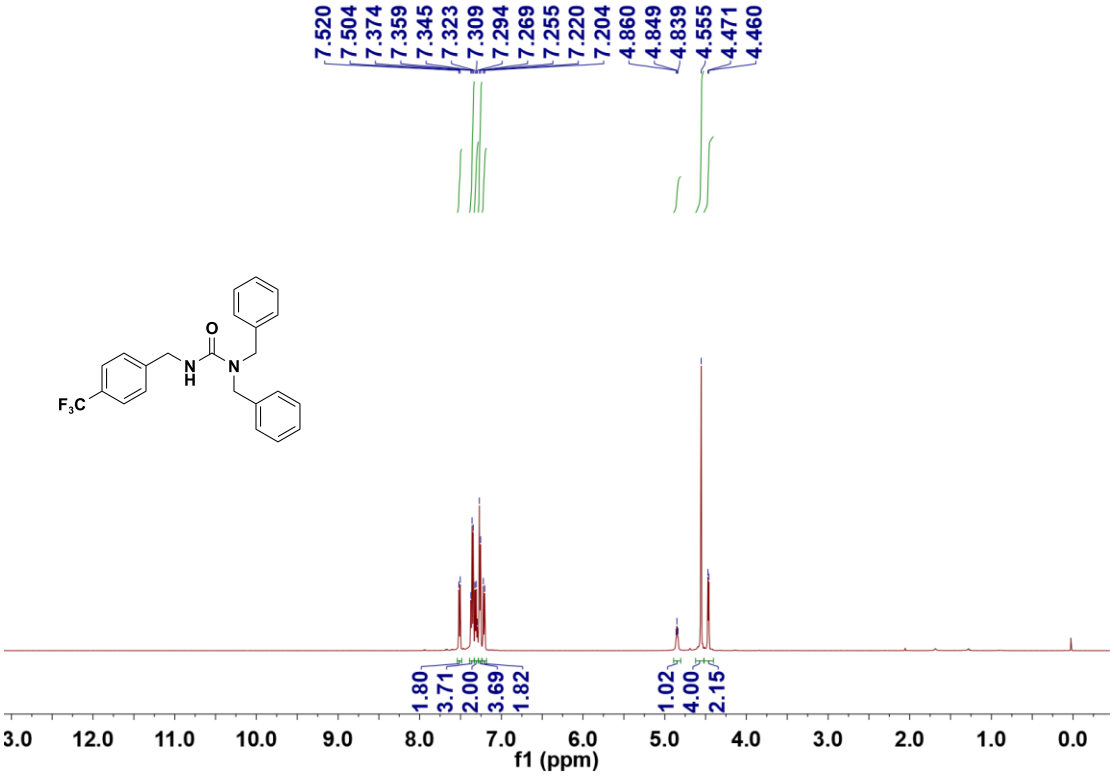
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-methoxybenzyl)urea (3e)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-methoxybenzyl)urea (3e)



^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-(trifluoromethyl)benzyl)urea (3f)



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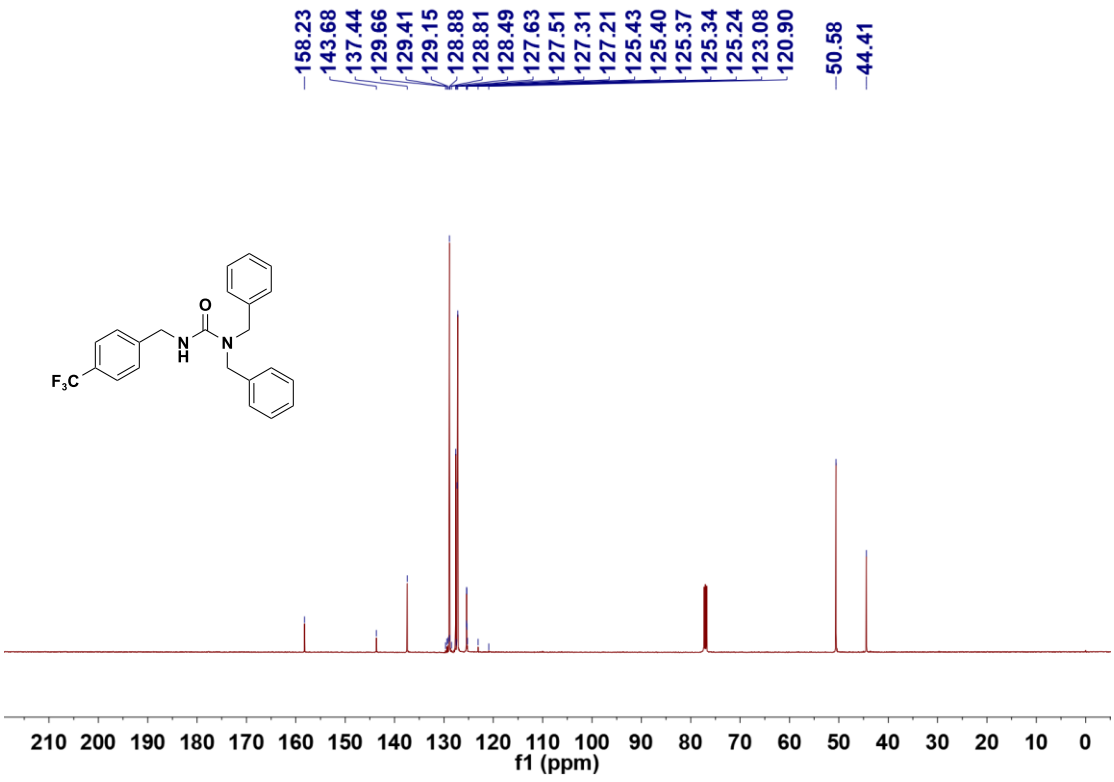
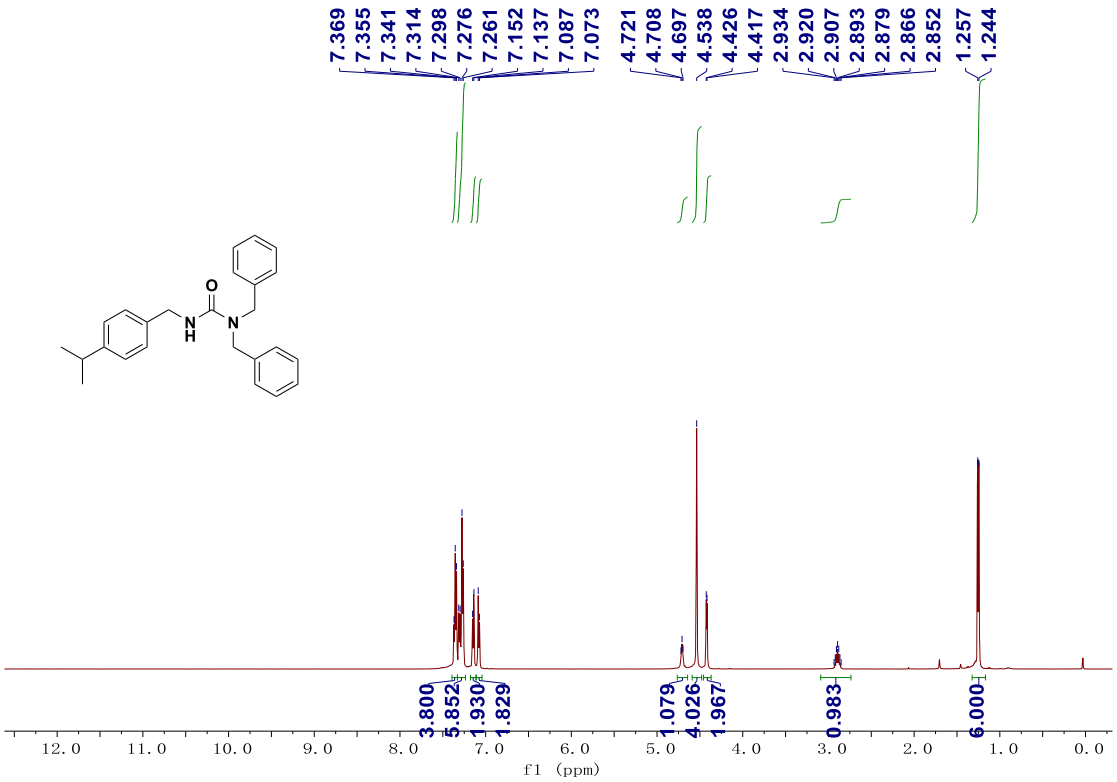
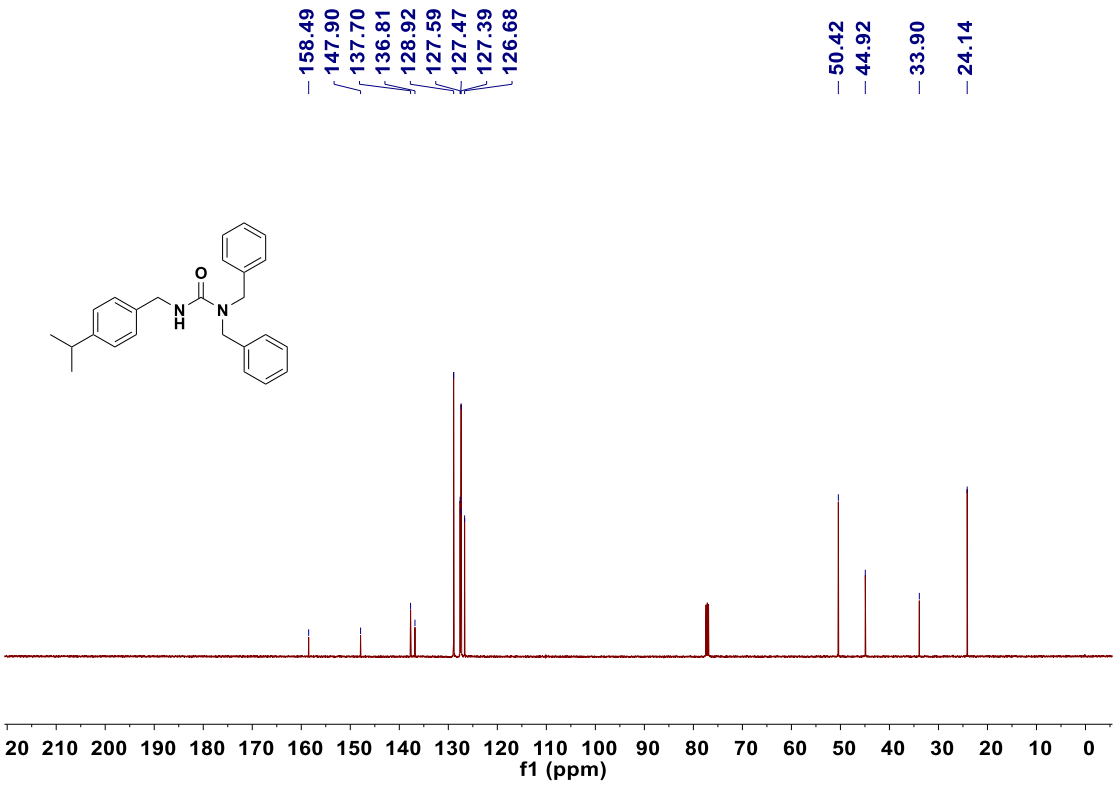


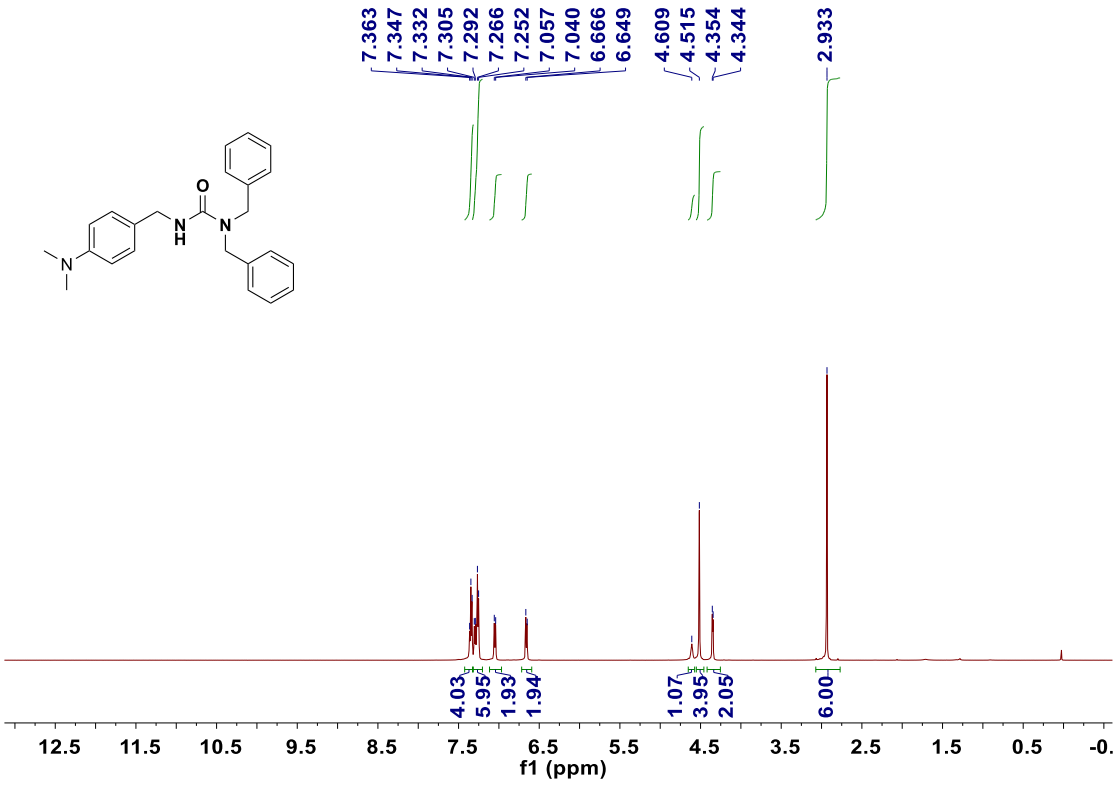
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-isopropylbenzyl)urea (3g)



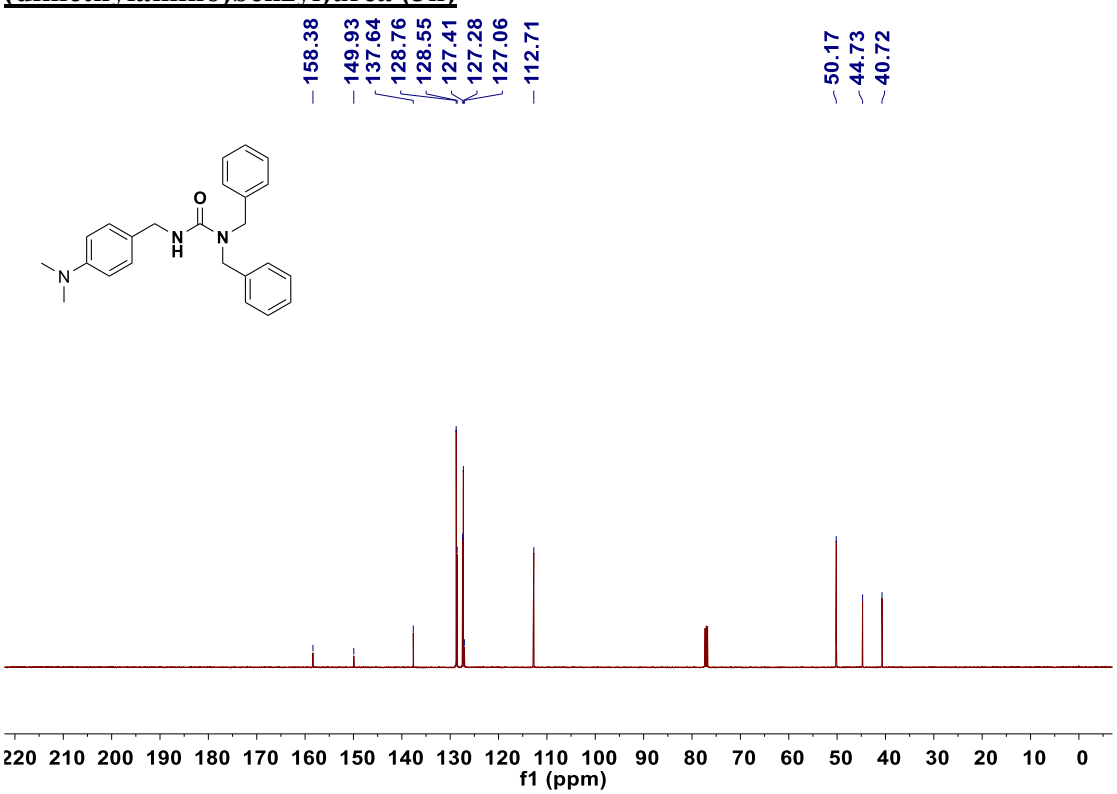
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-isopropylbenzyl)urea (3g)



^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-(dimethylamino)benzyl)urea (3h)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(4-(dimethylamino)benzyl)urea (3h)



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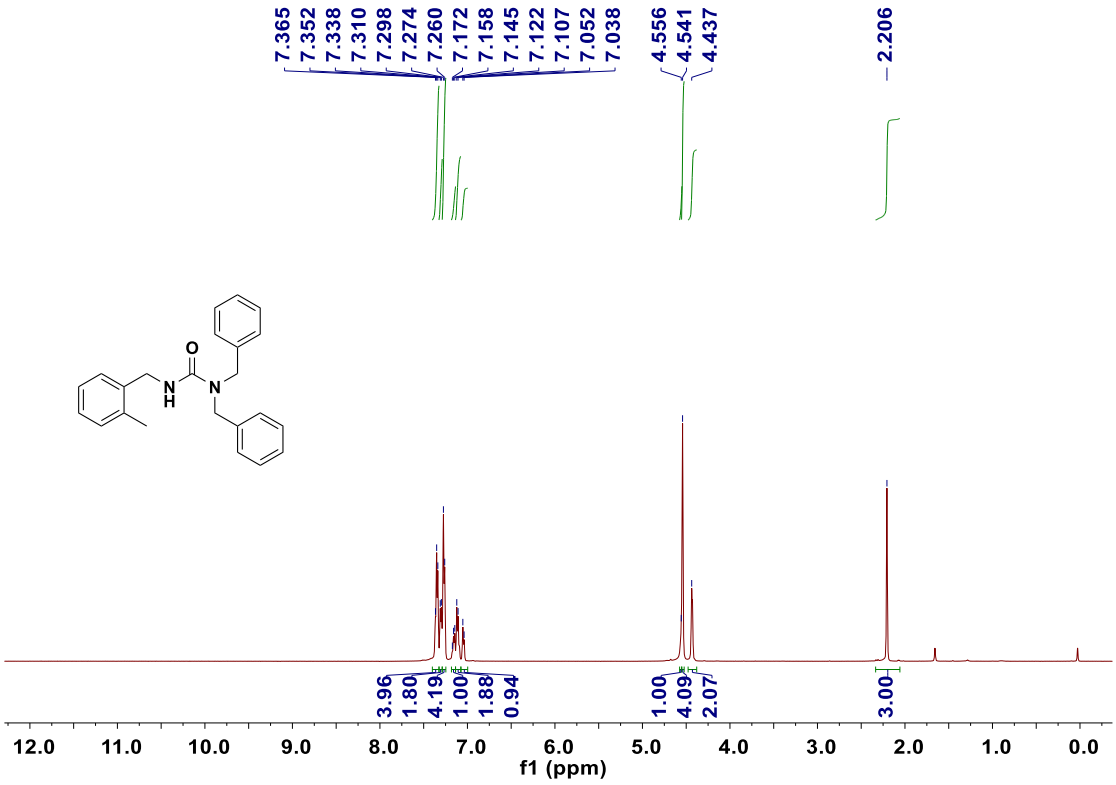
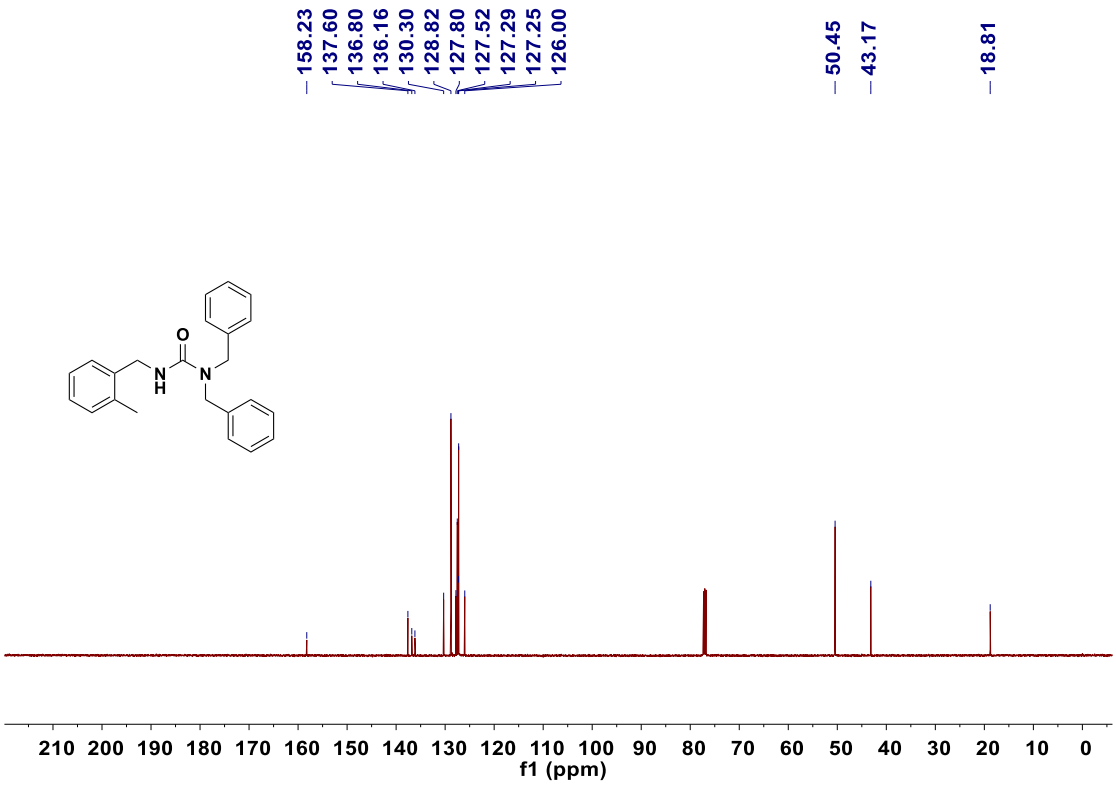
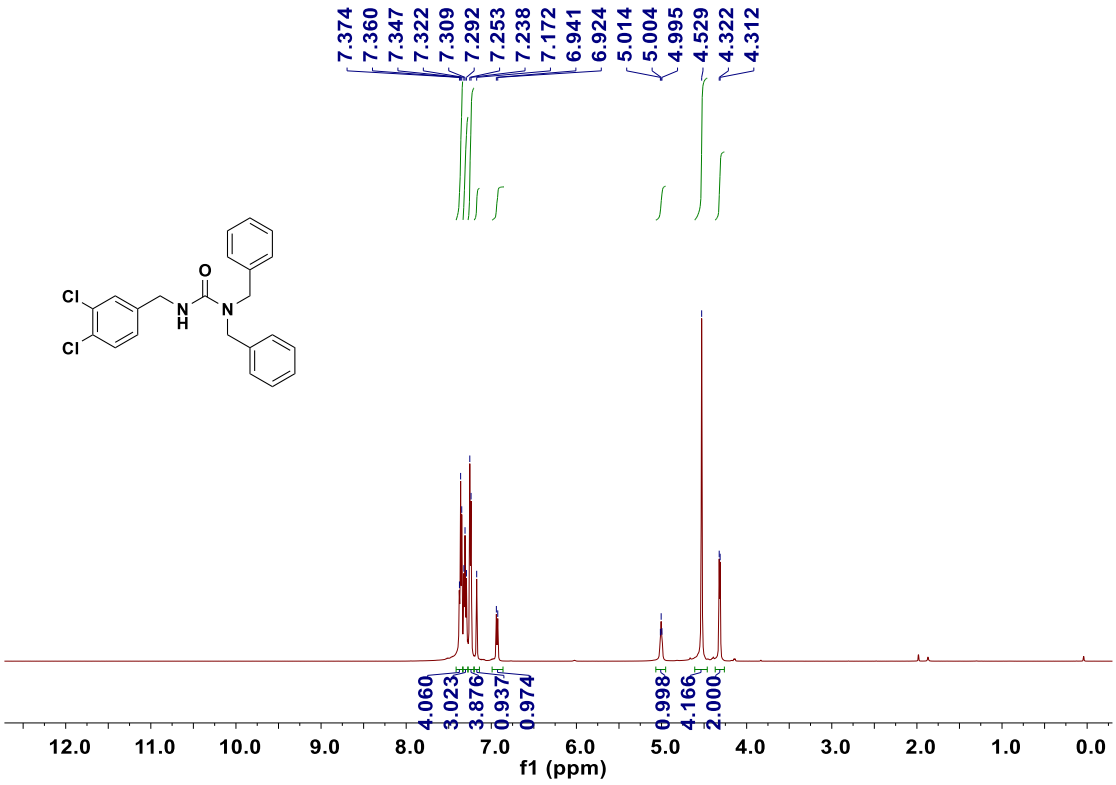


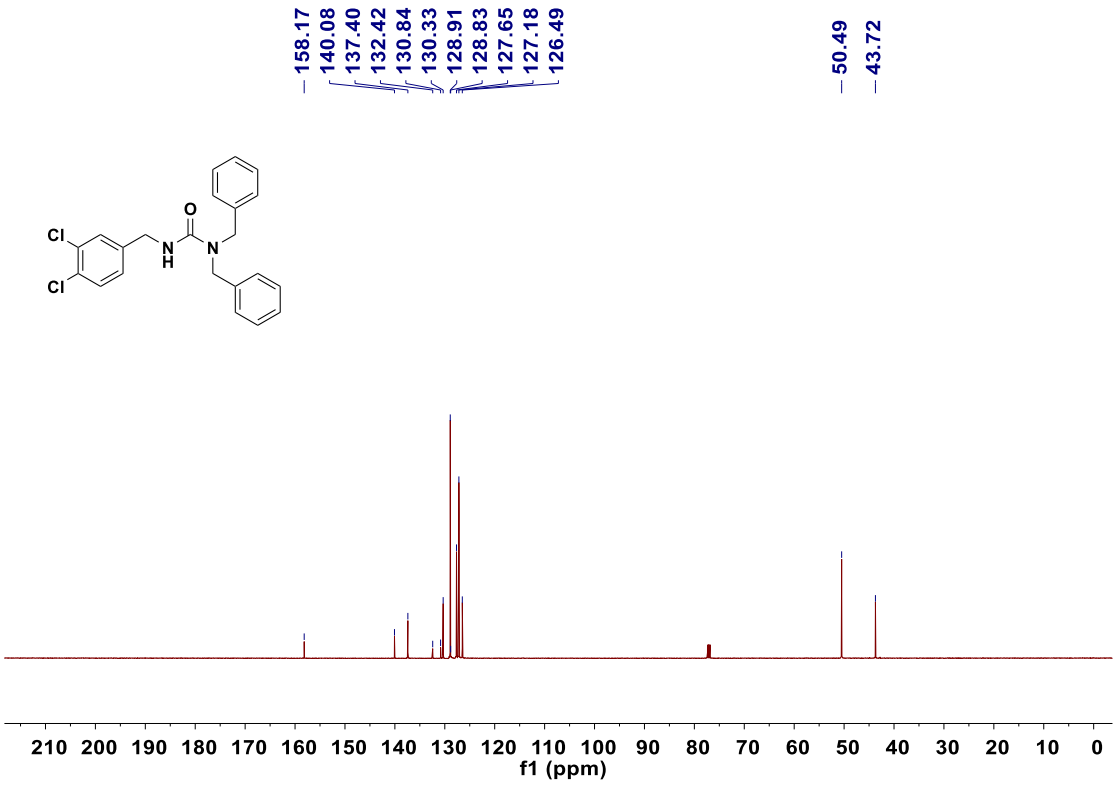
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(2-methylbenzyl)urea (3i)



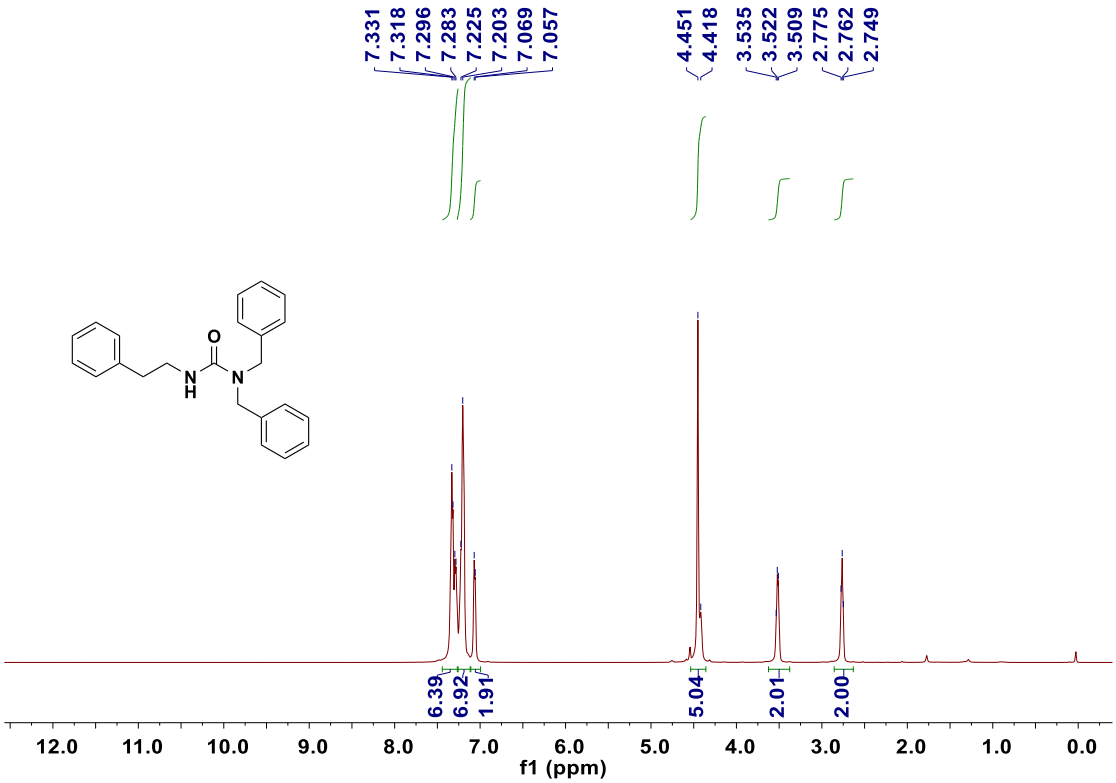
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(3,4-dichlorobenzyl)urea (3j)



^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(3,4-dichlorobenzyl)urea (3j)



^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-phenethylurea (3k)



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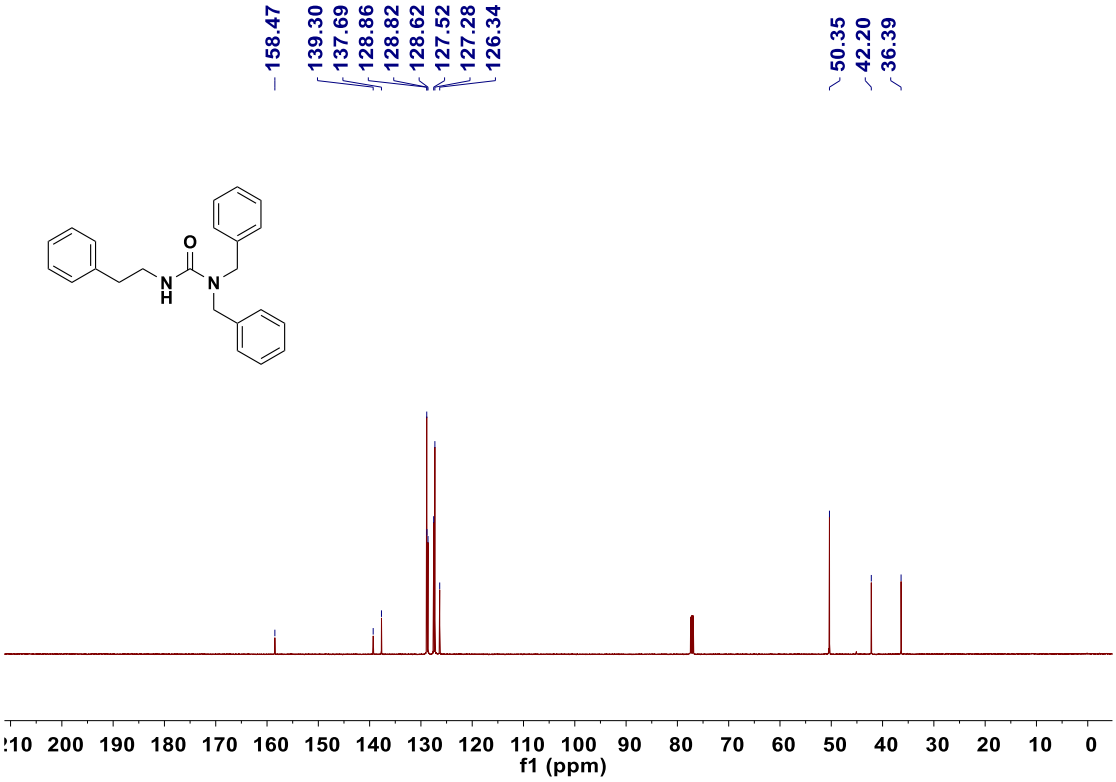
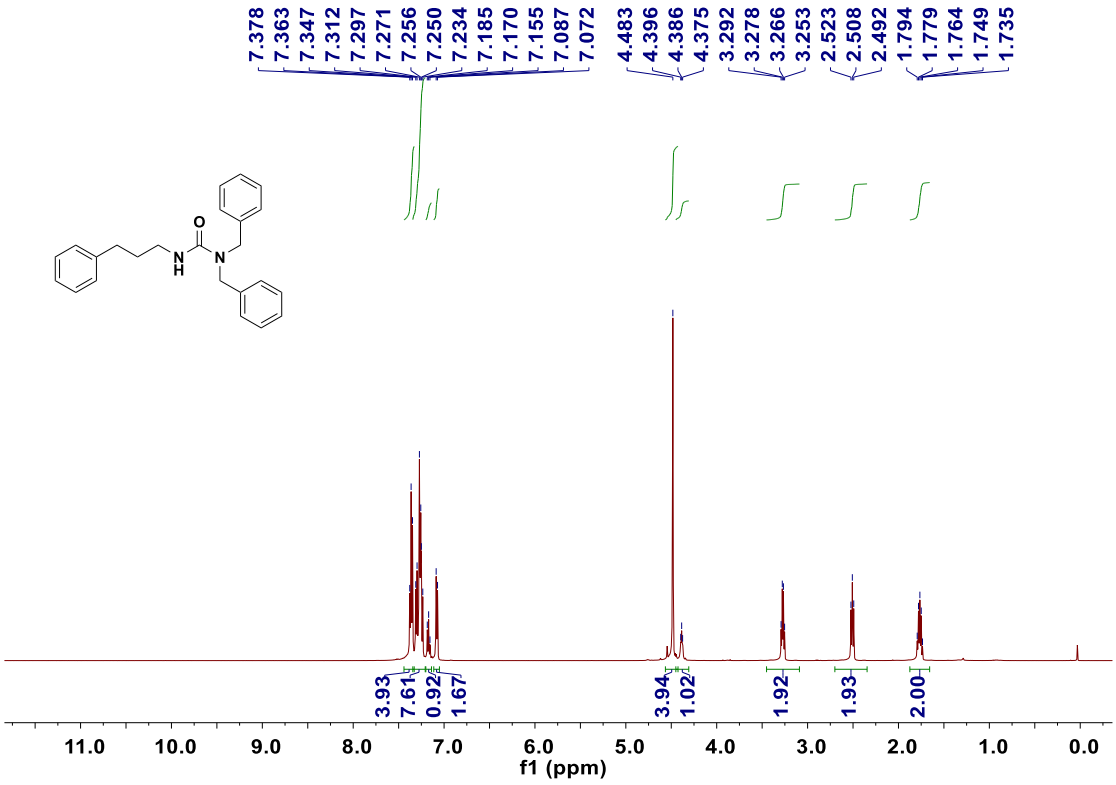
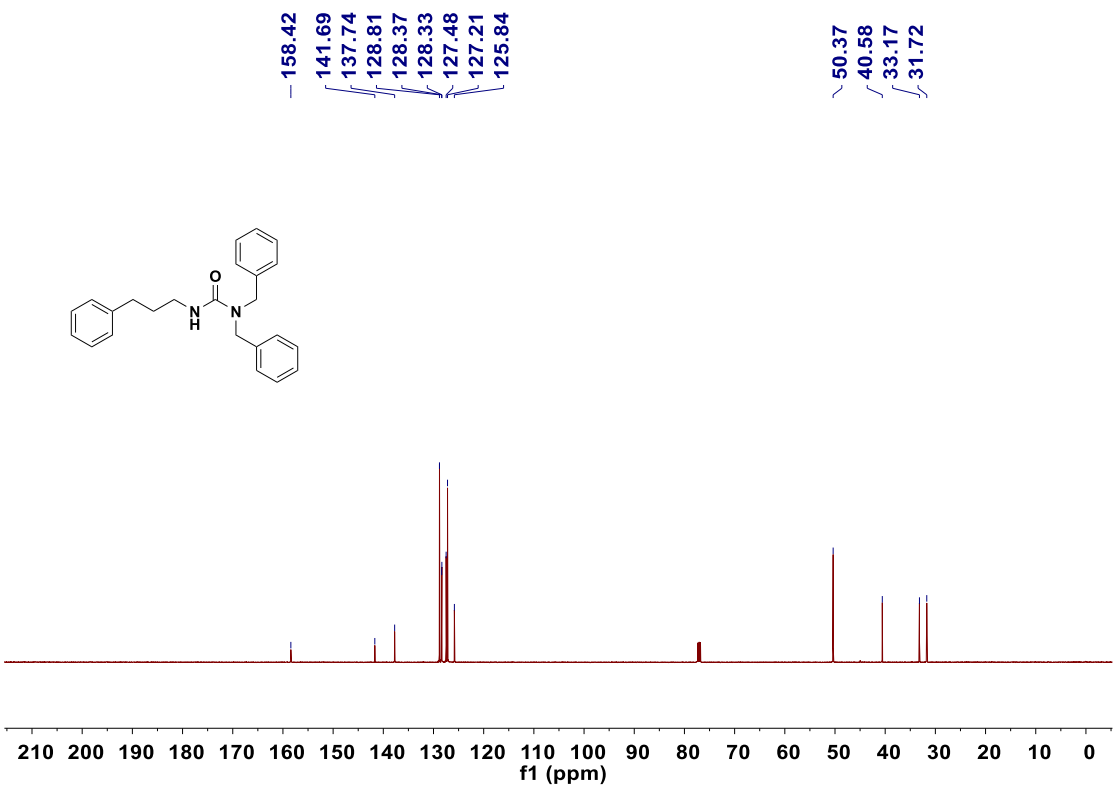


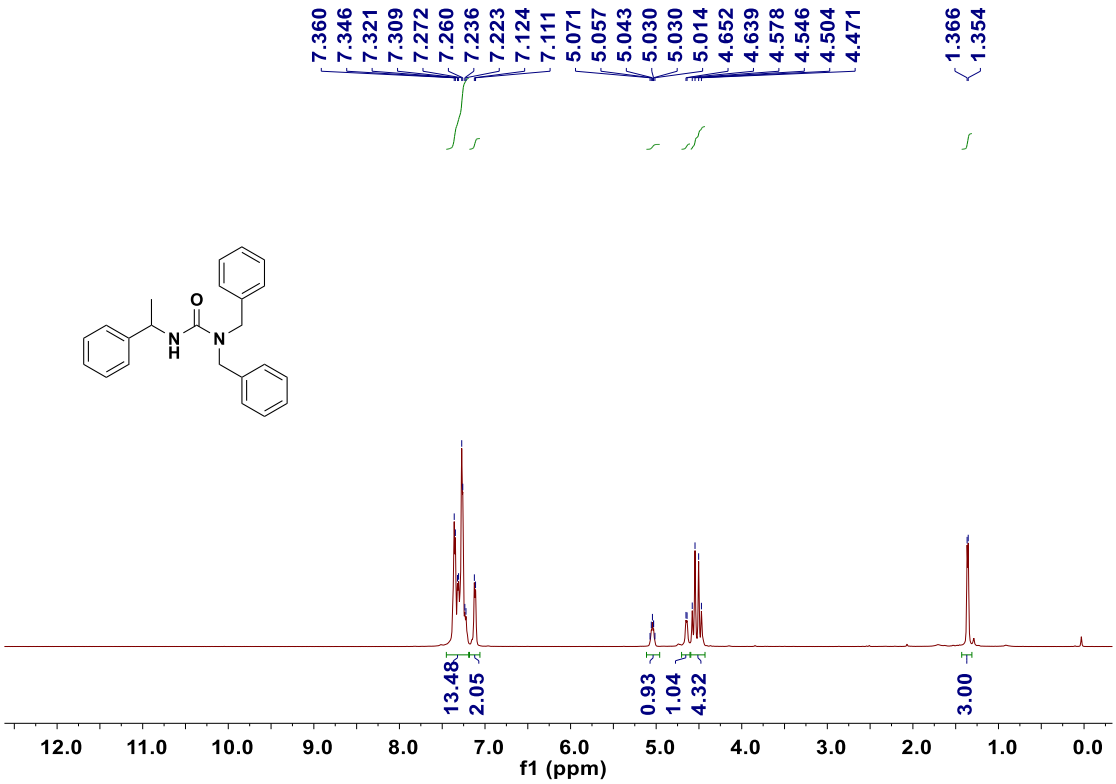
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(3-phenylpropyl)urea (3l)



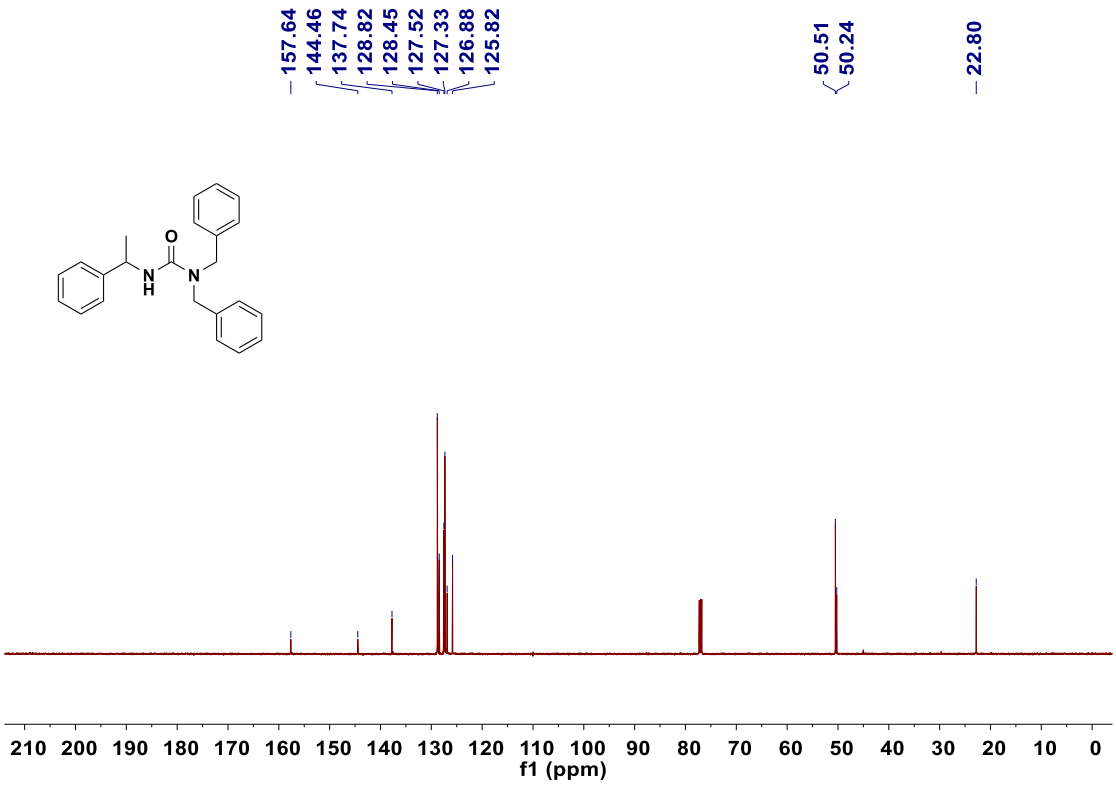
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(3-phenylpropyl)urea (3l)



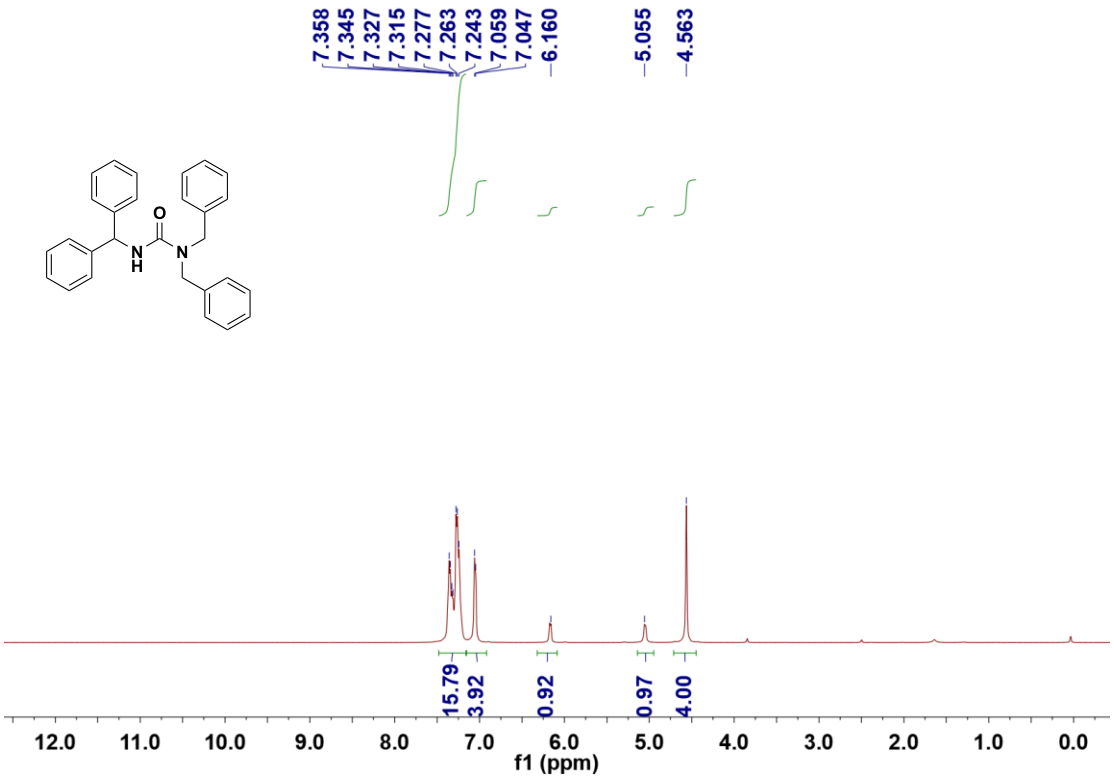
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(1-phenylethyl)urea (3m)



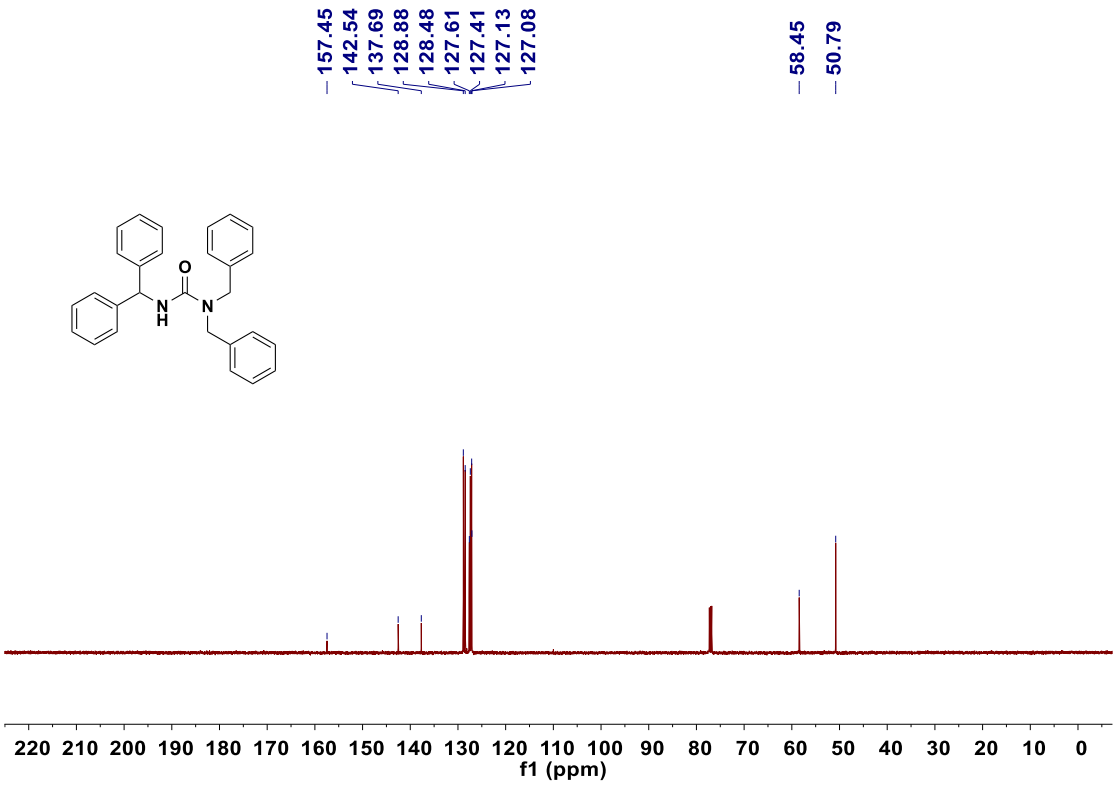
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(1-phenylethyl)urea (3m)



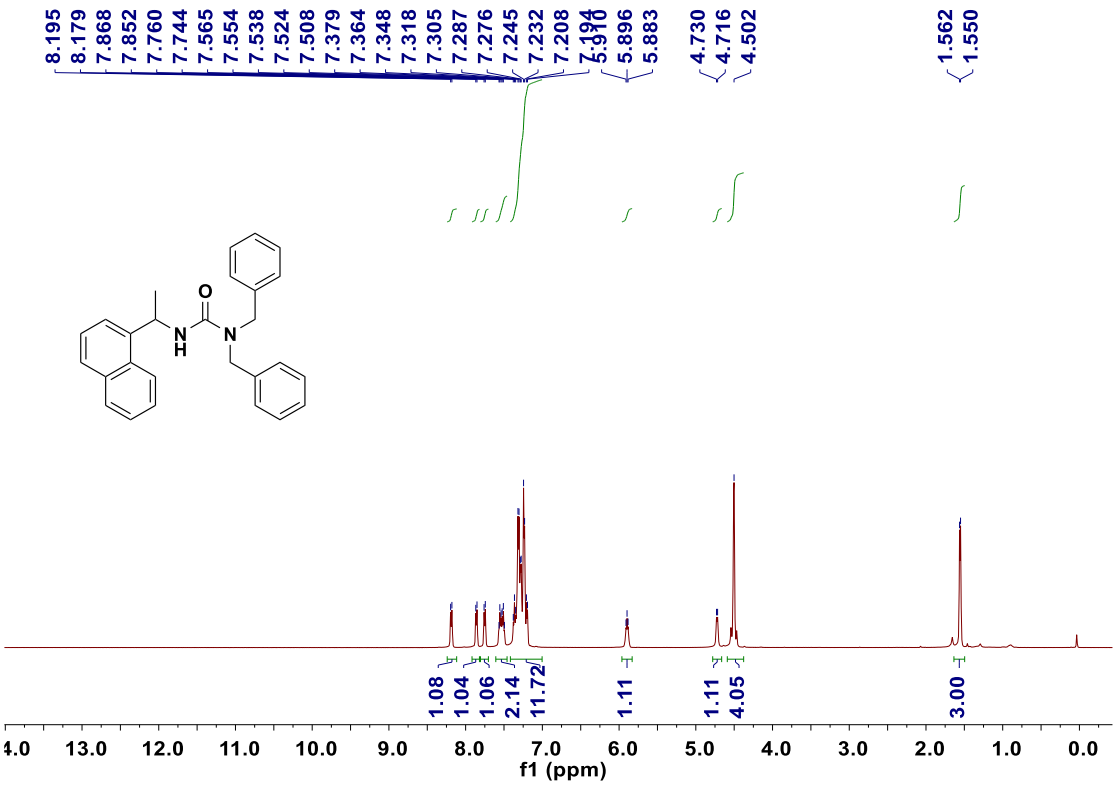
^{1}H NMR (500 MHz, $CDCl_3$) of 3-benzhydryl-1,1-dibenzylurea (3n)



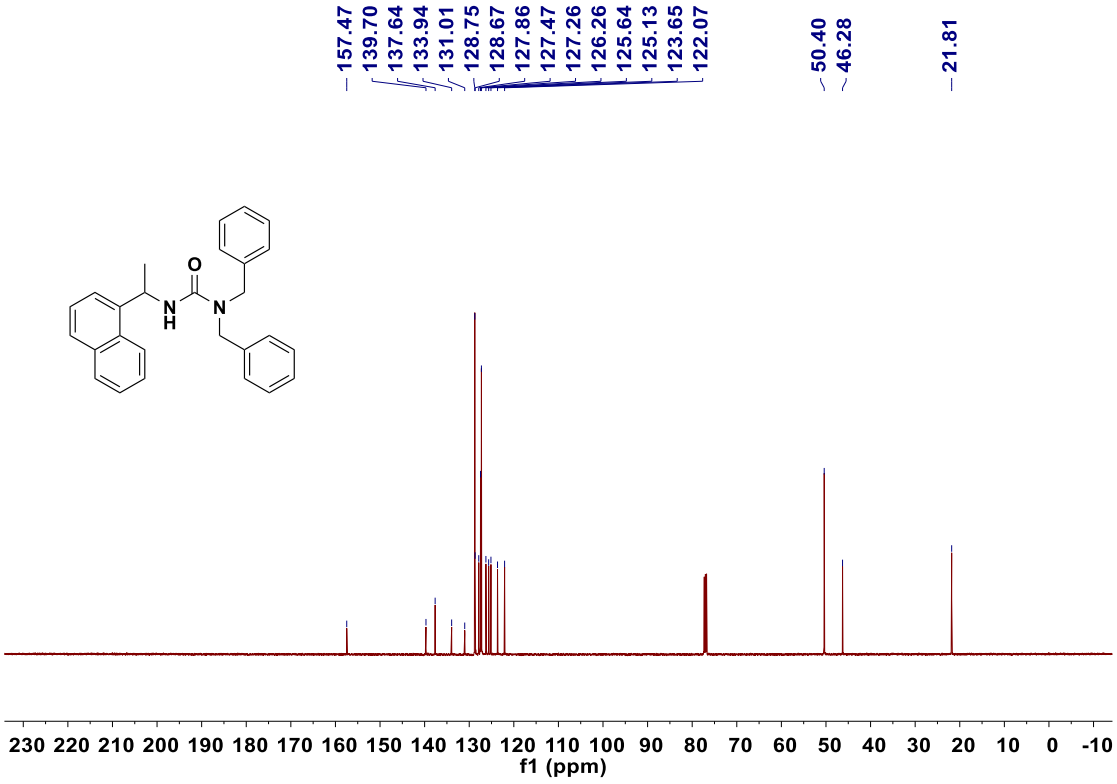
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 3-benzhydryl-1,1-dibenzylurea (3n)



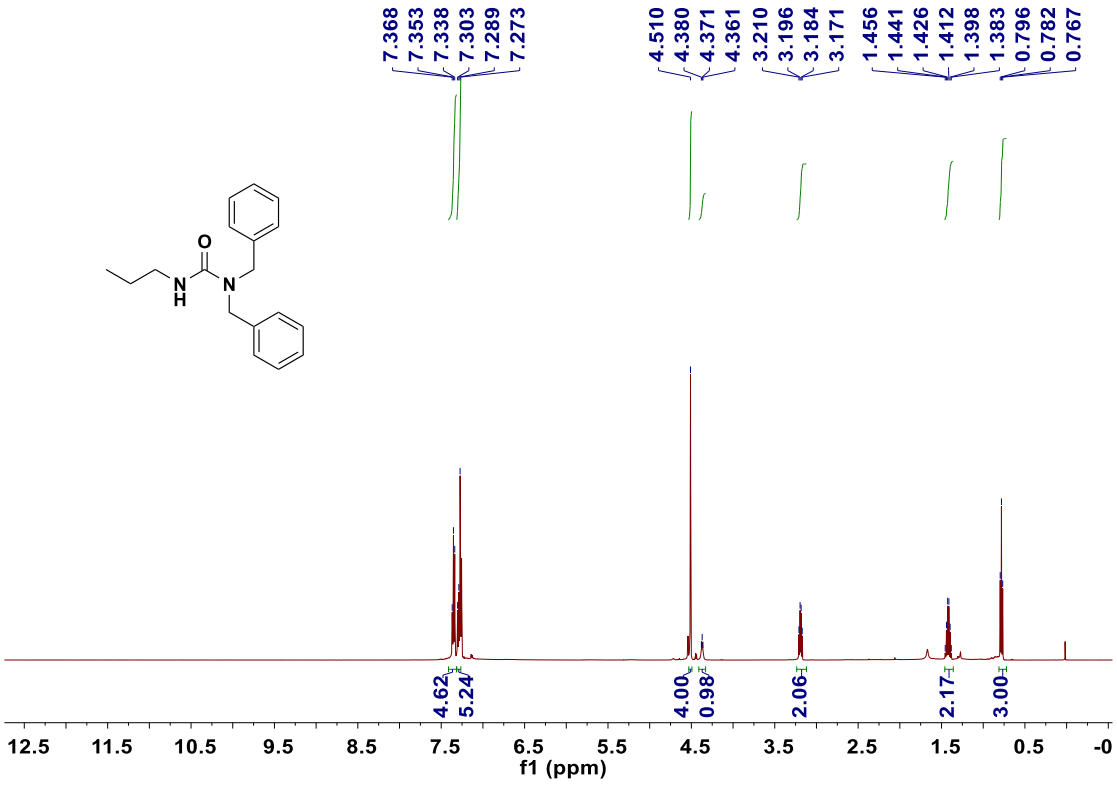
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(1-(naphthalen-1-yl)ethyl)urea (3o)



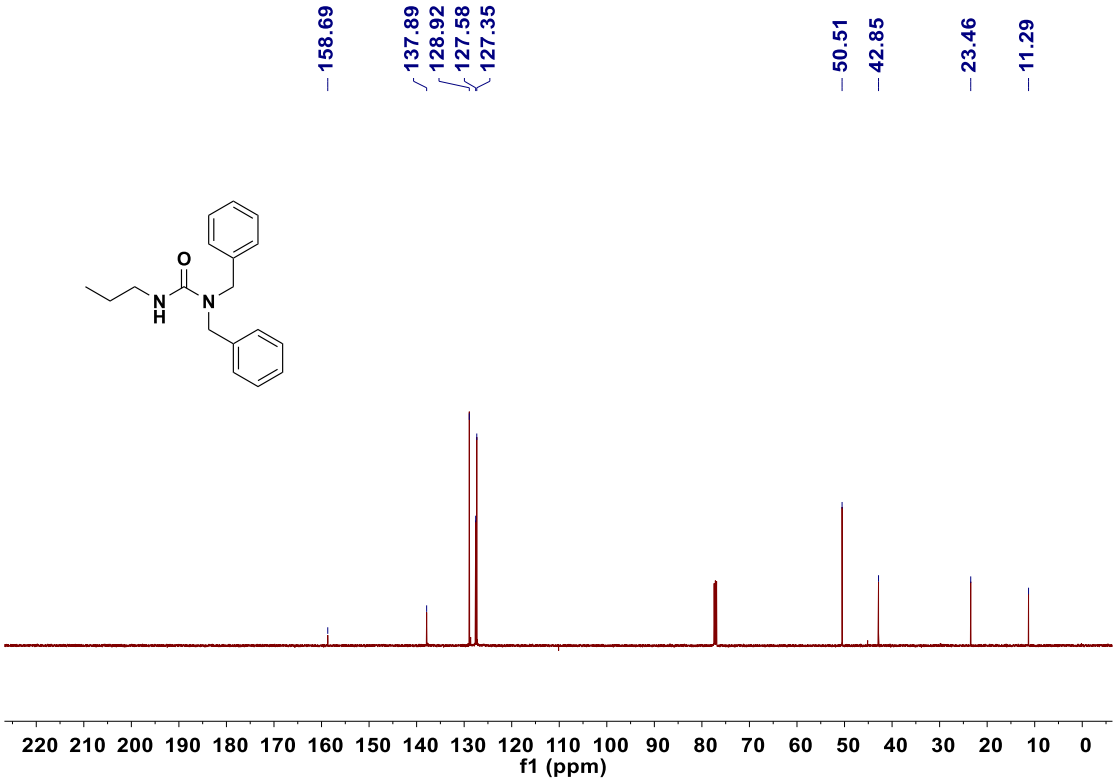
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(1-(naphthalen-1-yl)ethyl)urea (3o)



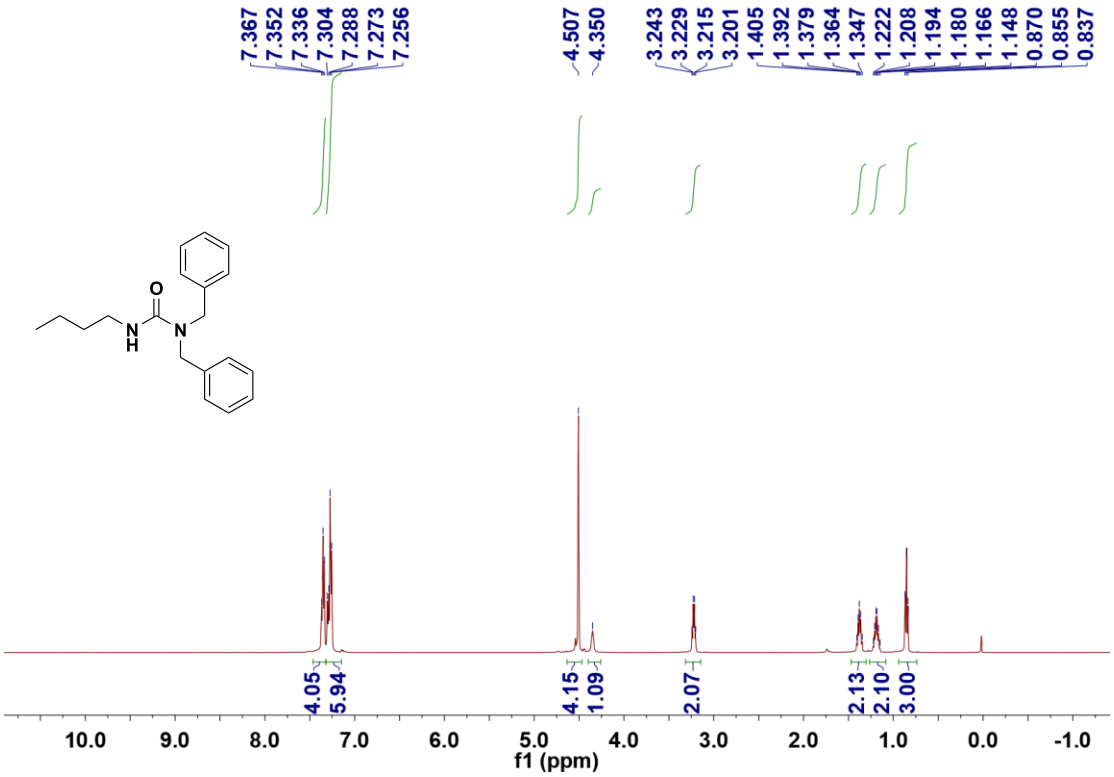
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-propylurea (3p)



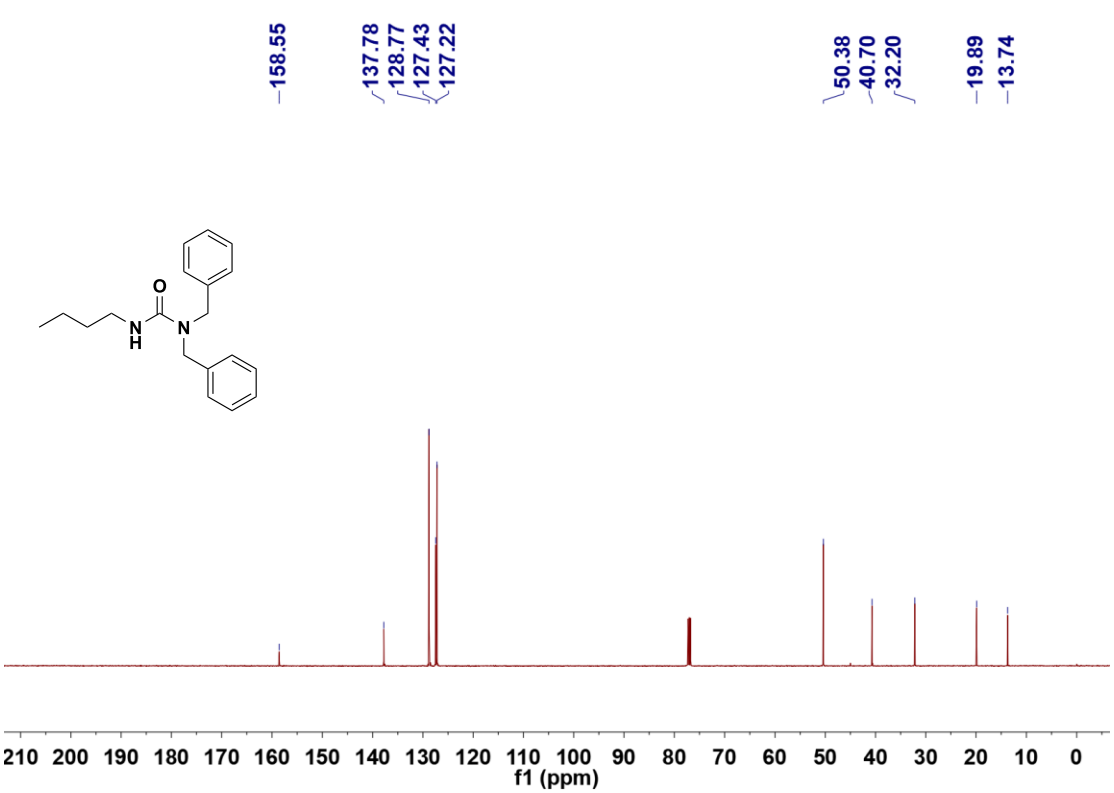
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-propylurea (3p)



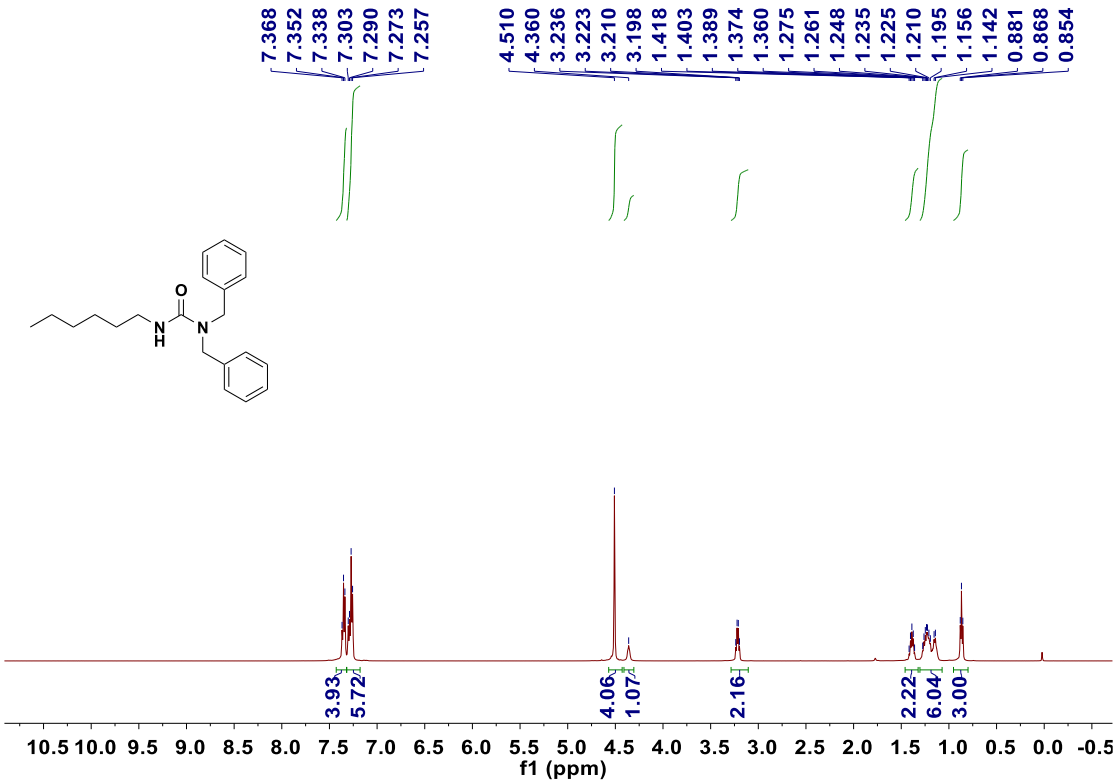
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-butylurea(3q)



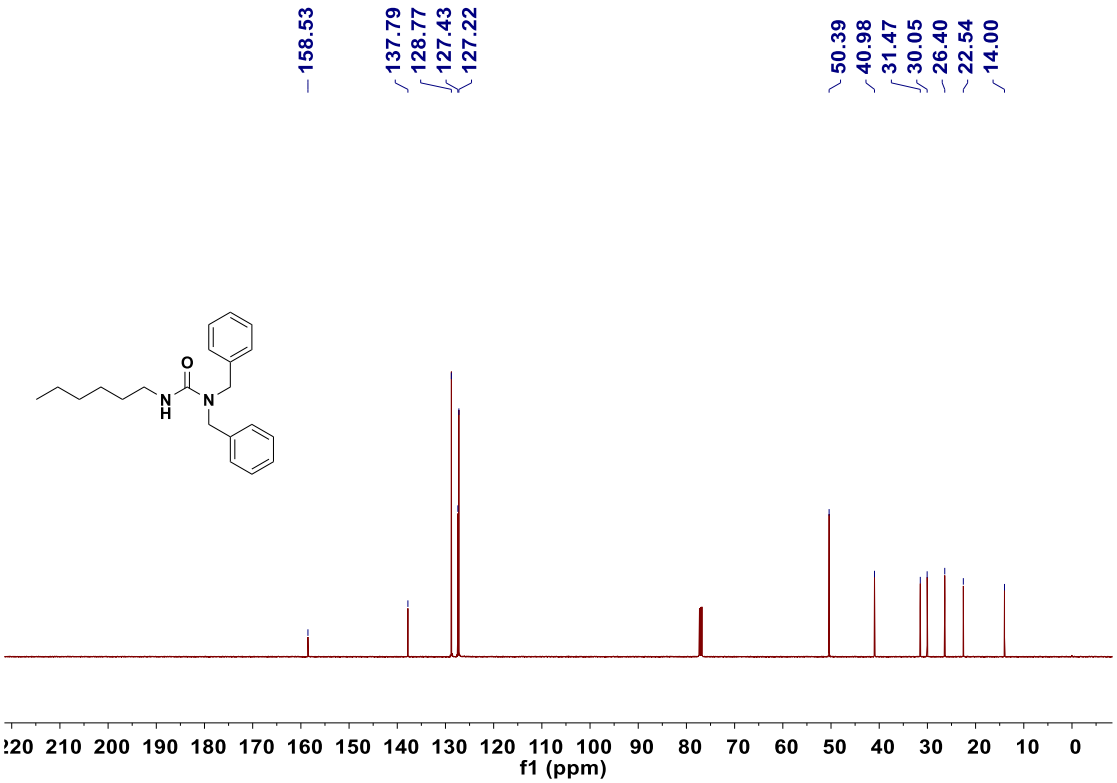
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-butylurea(3q)



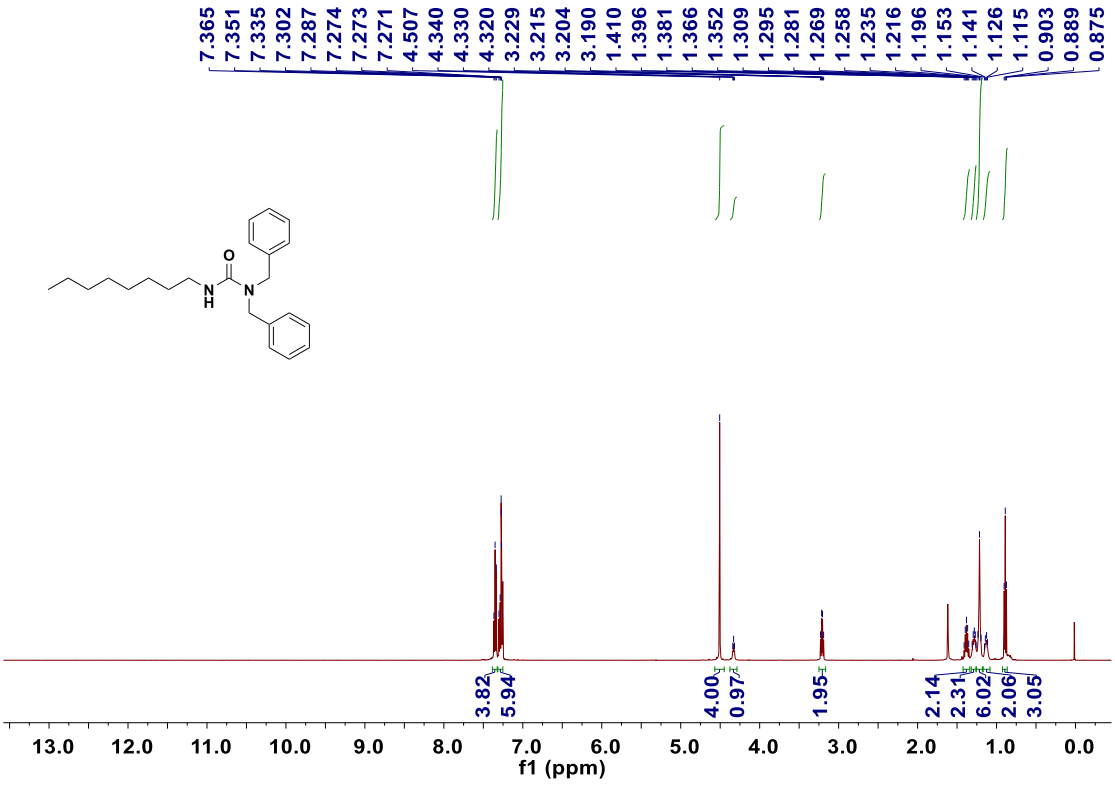
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-hexylurea (3r)



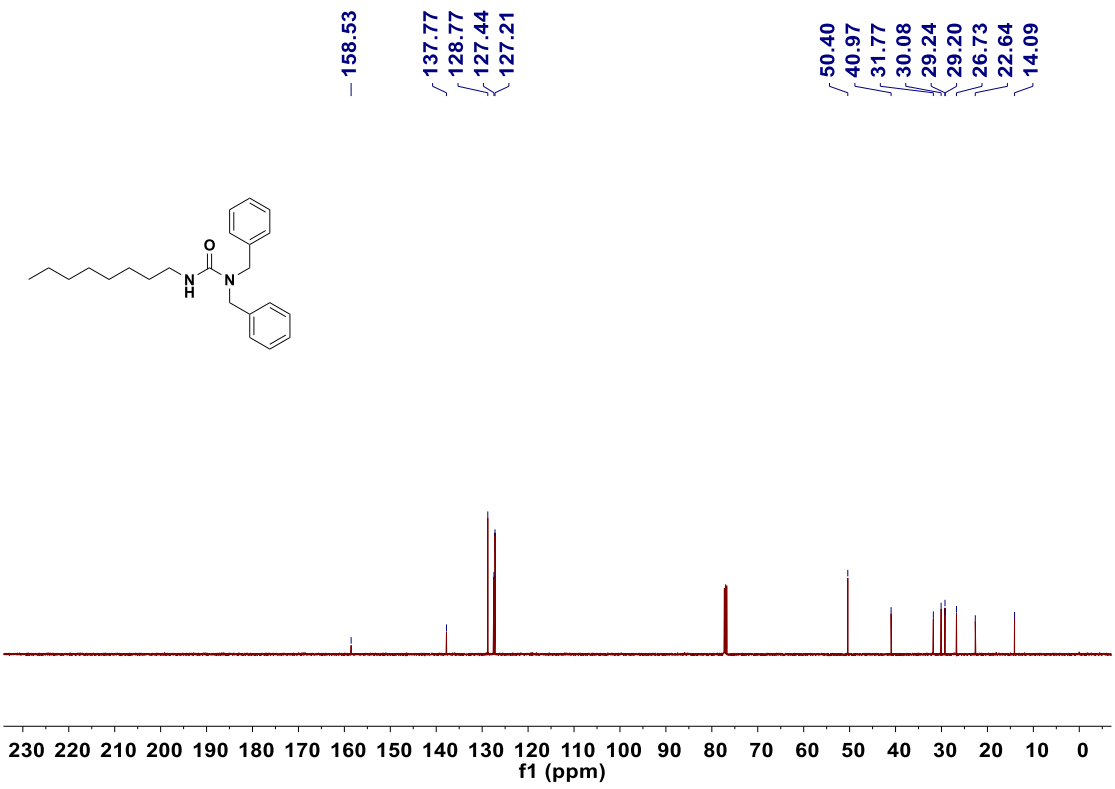
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-hexylurea (3r)



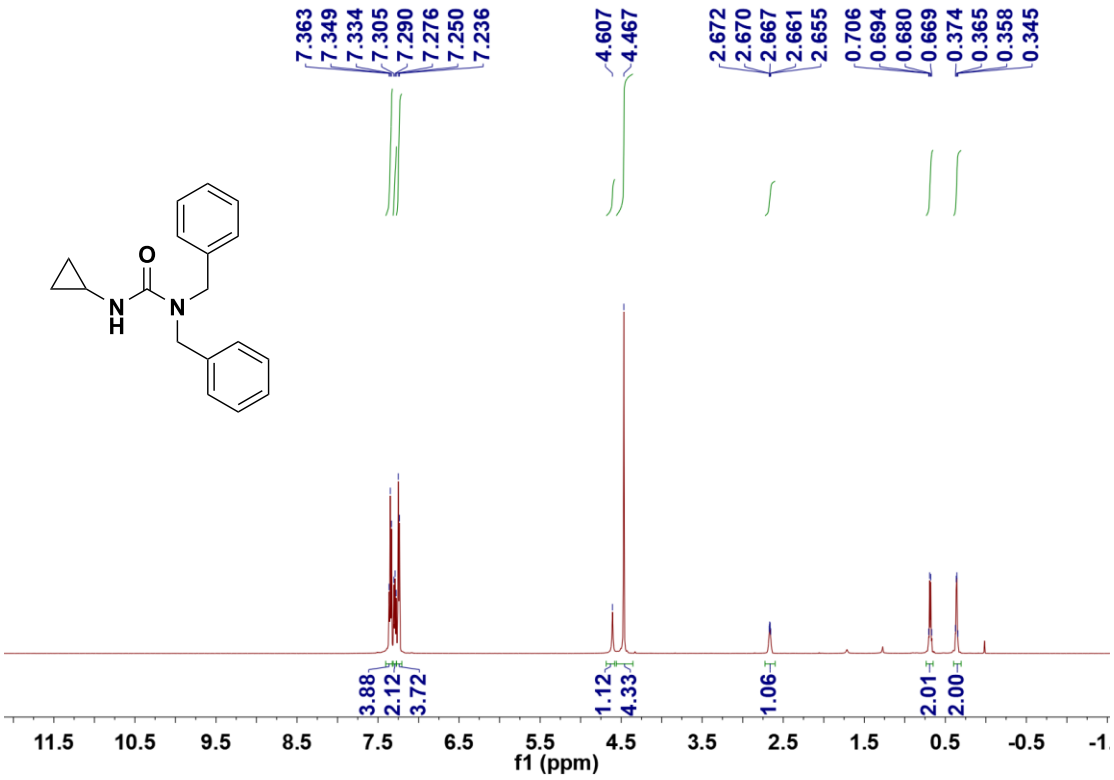
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-octylurea (3s)



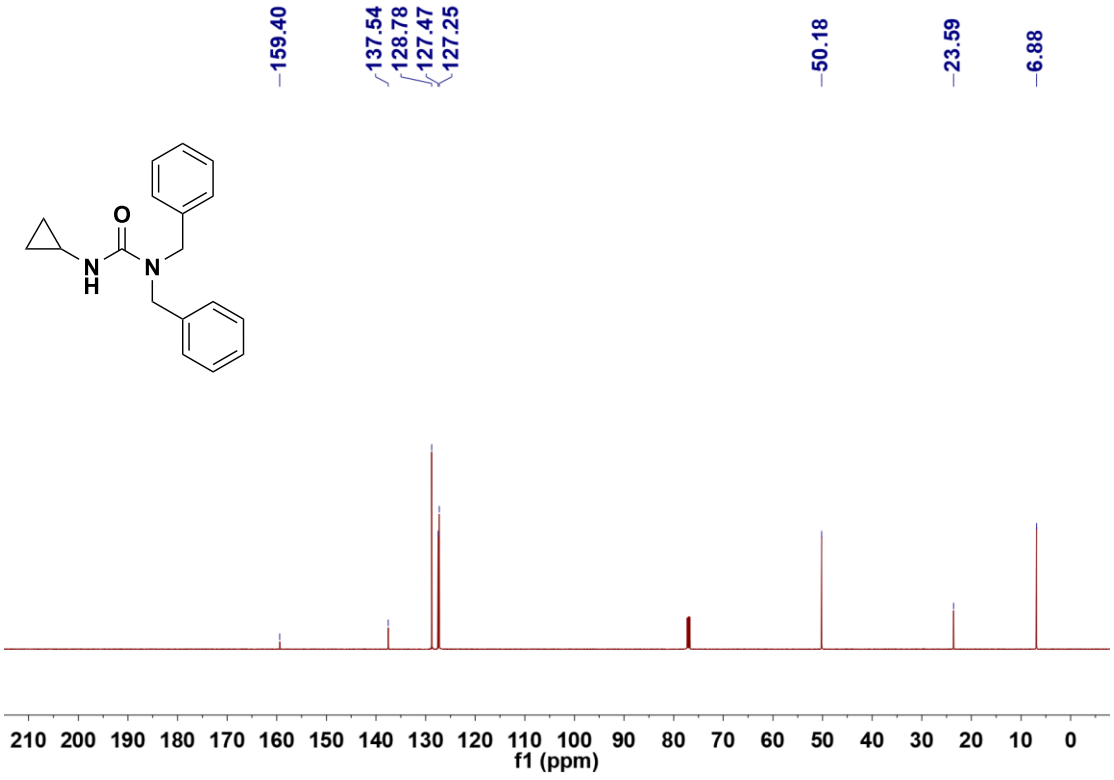
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-octylurea (3s)



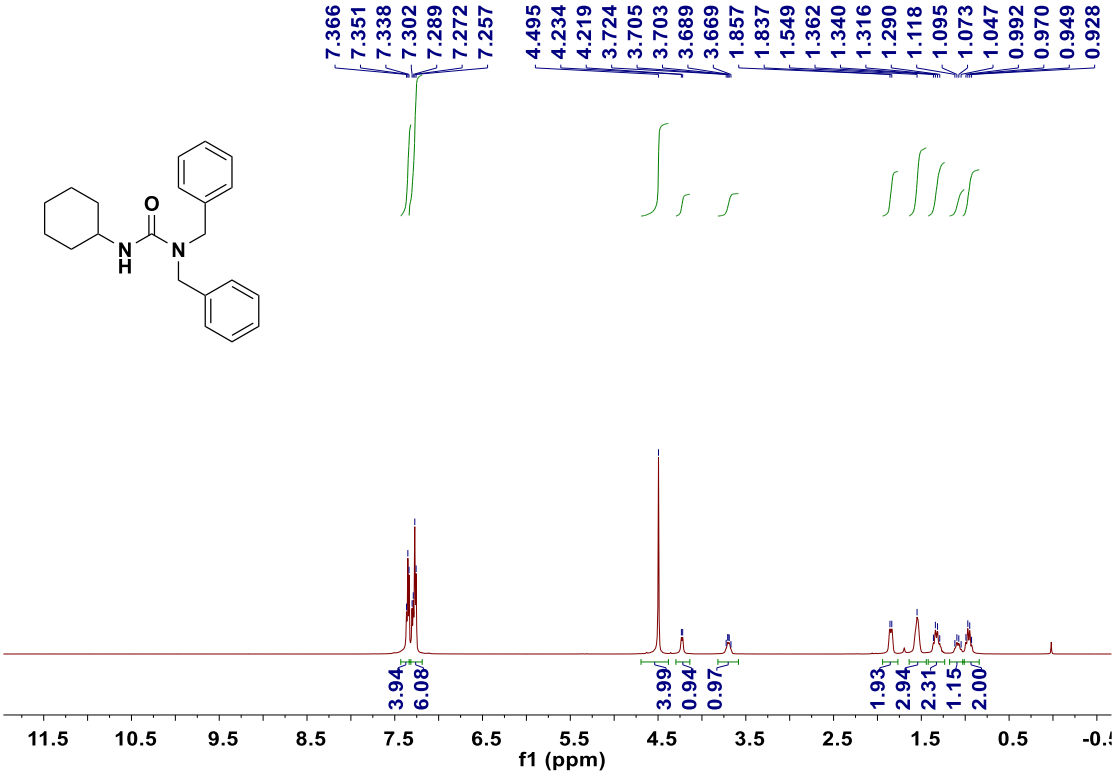
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-cyclopropylurea (3t)



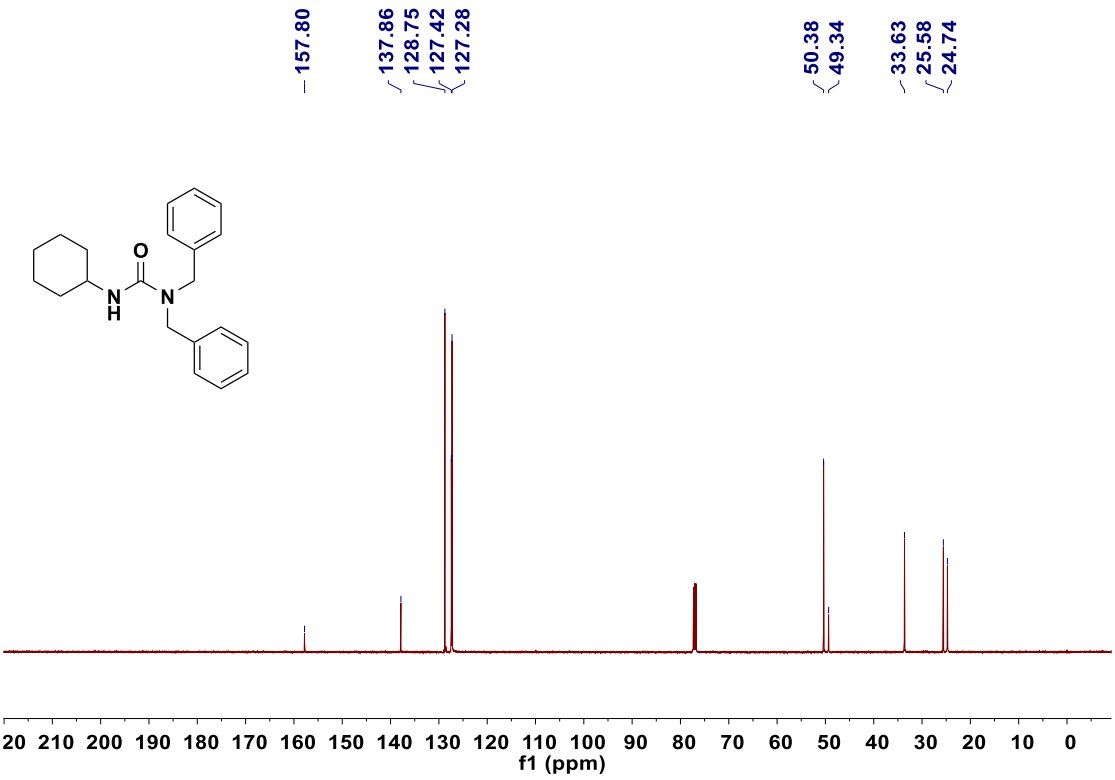
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-cyclopropylurea (3t)



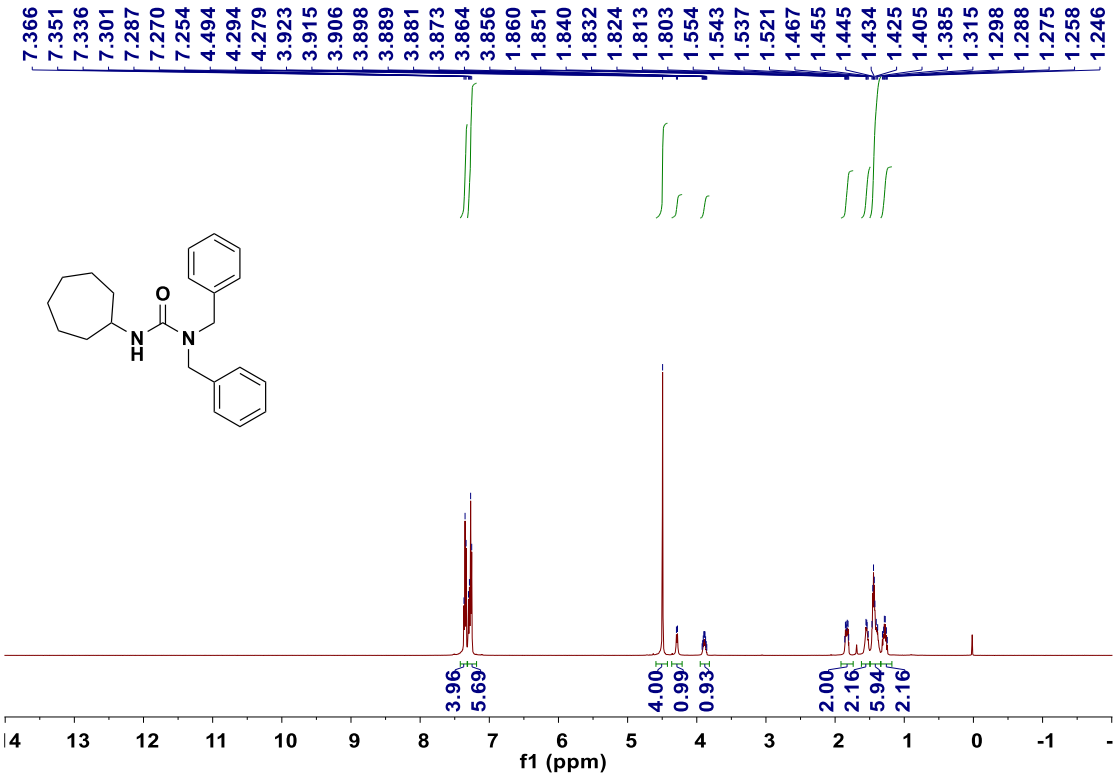
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-cyclohexylurea(3u)



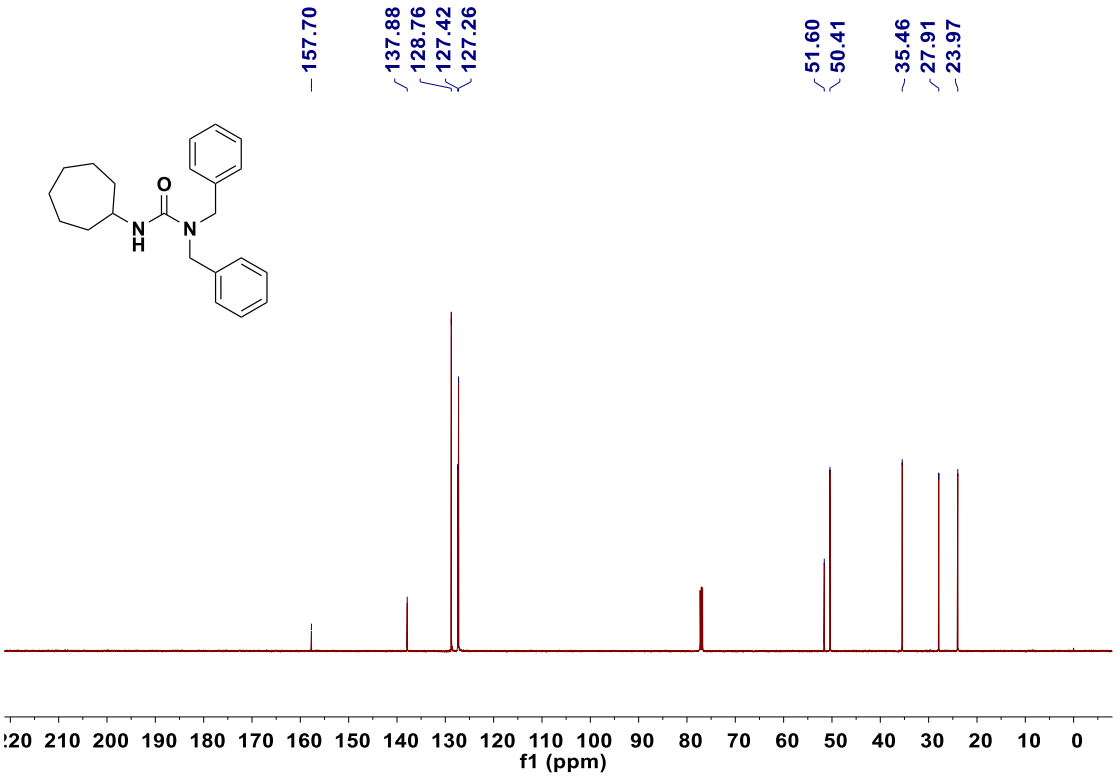
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-cyclohexylurea(3u)



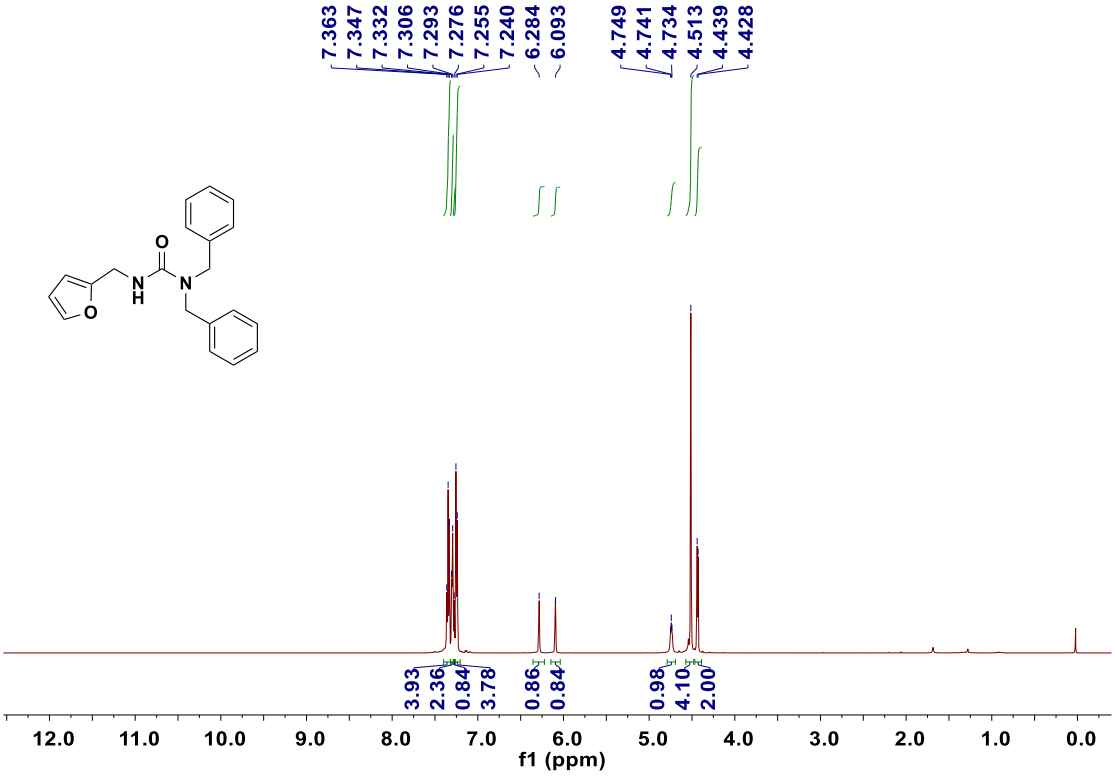
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-cycloheptylurea (3v)



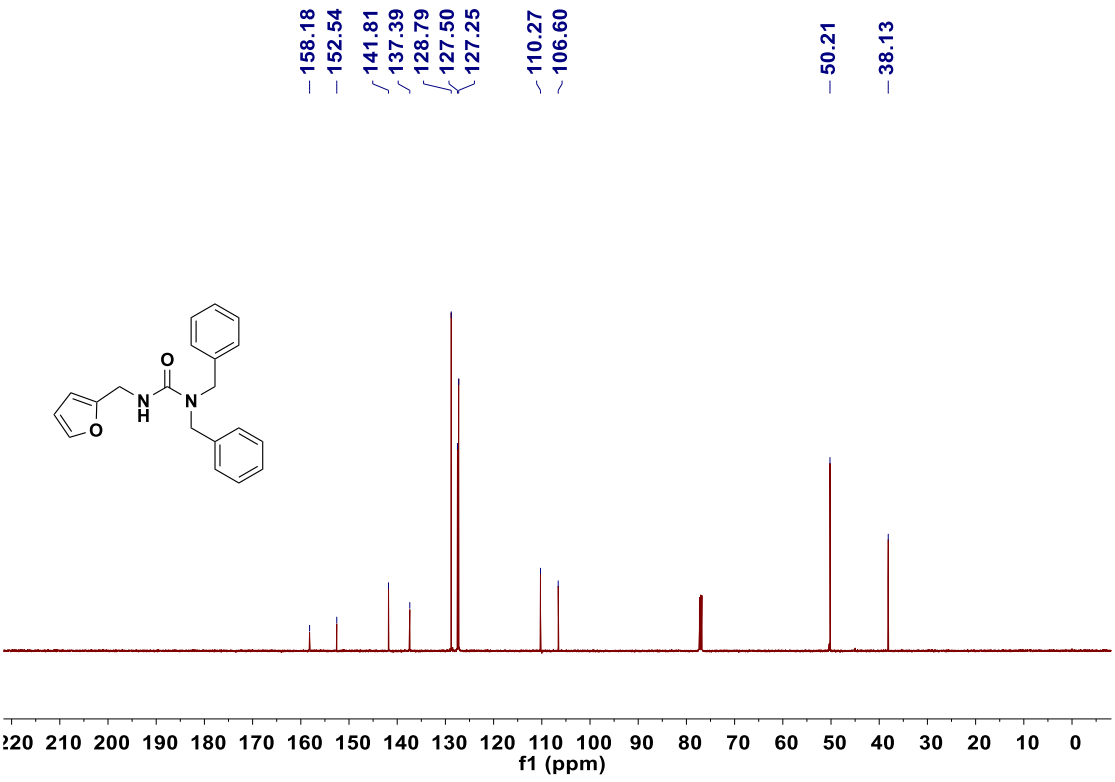
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-cycloheptylurea (3v)



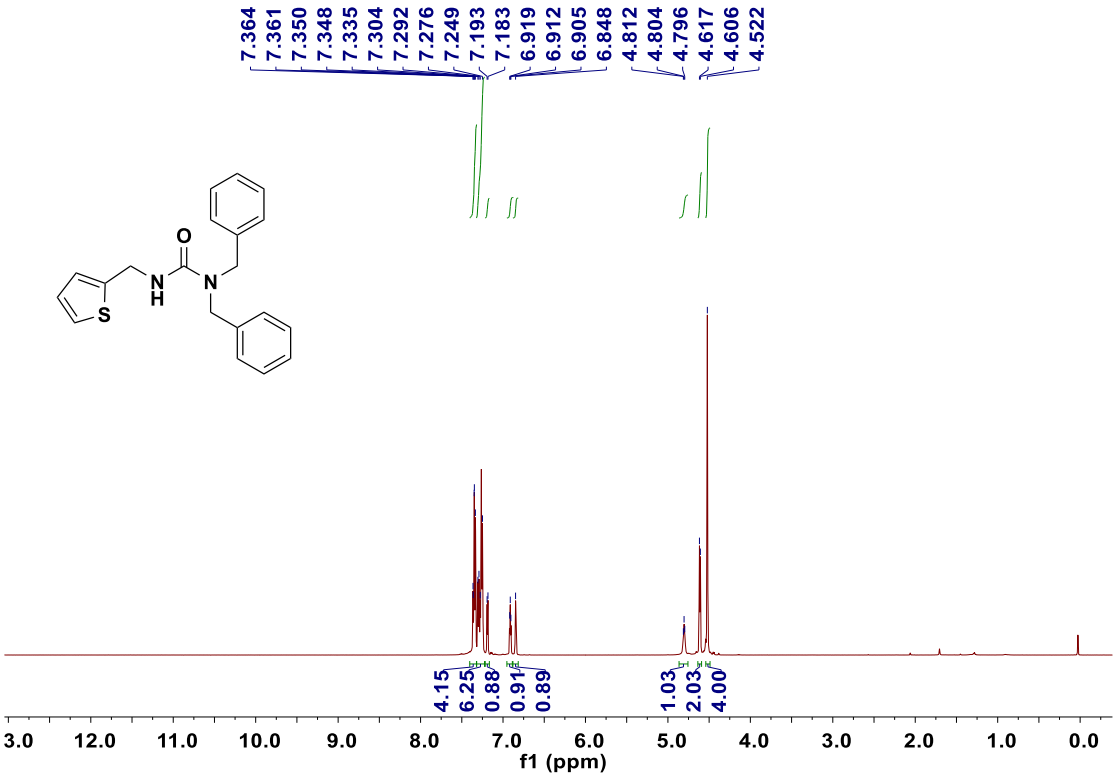
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(furan-2-ylmethyl)urea (3w)



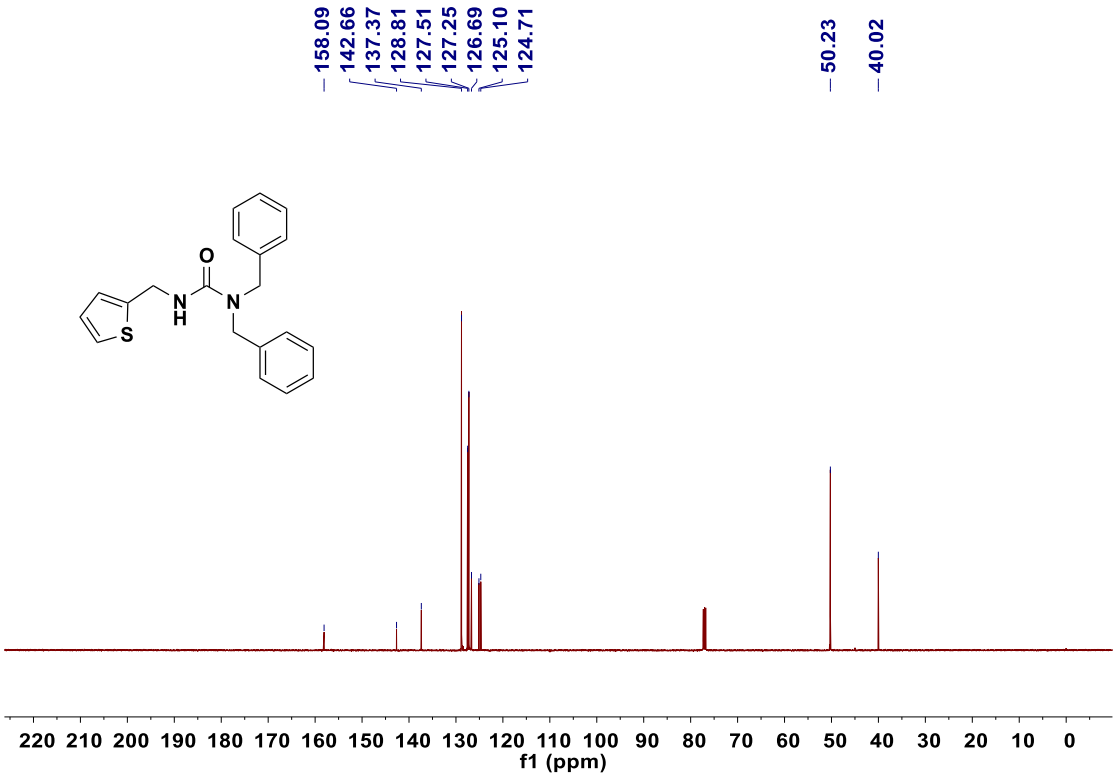
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(furan-2-ylmethyl)urea (3w)



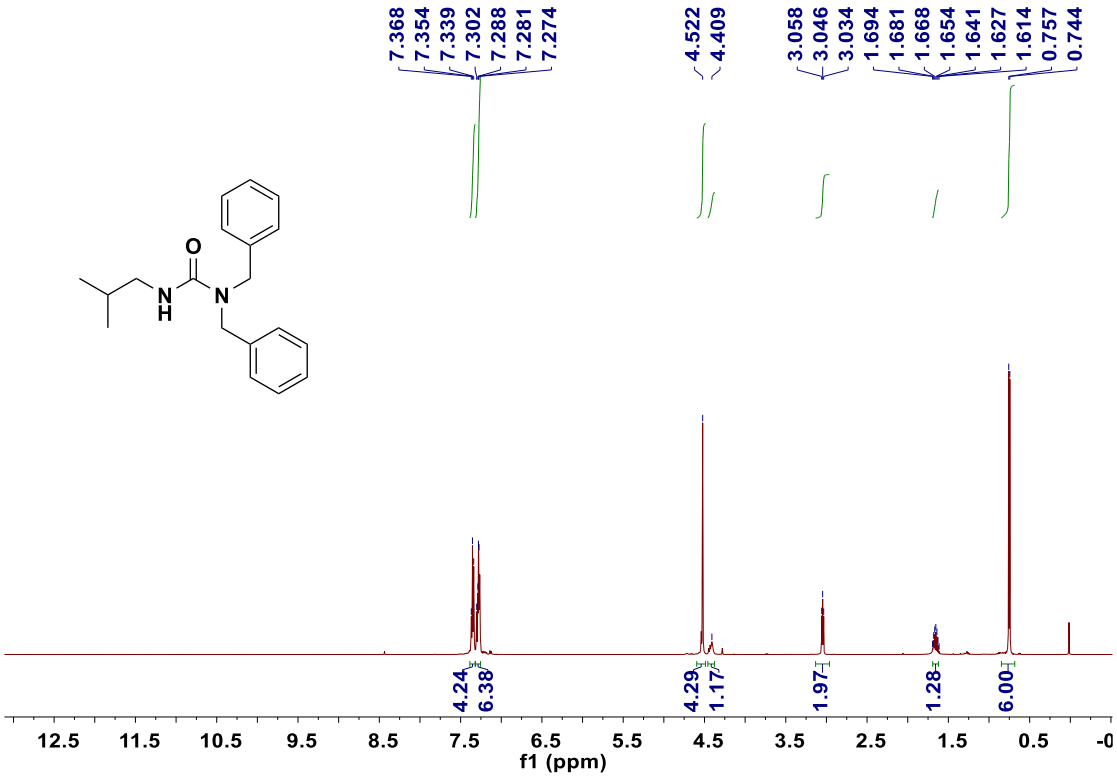
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(thiophen-2-ylmethyl)urea (3x)



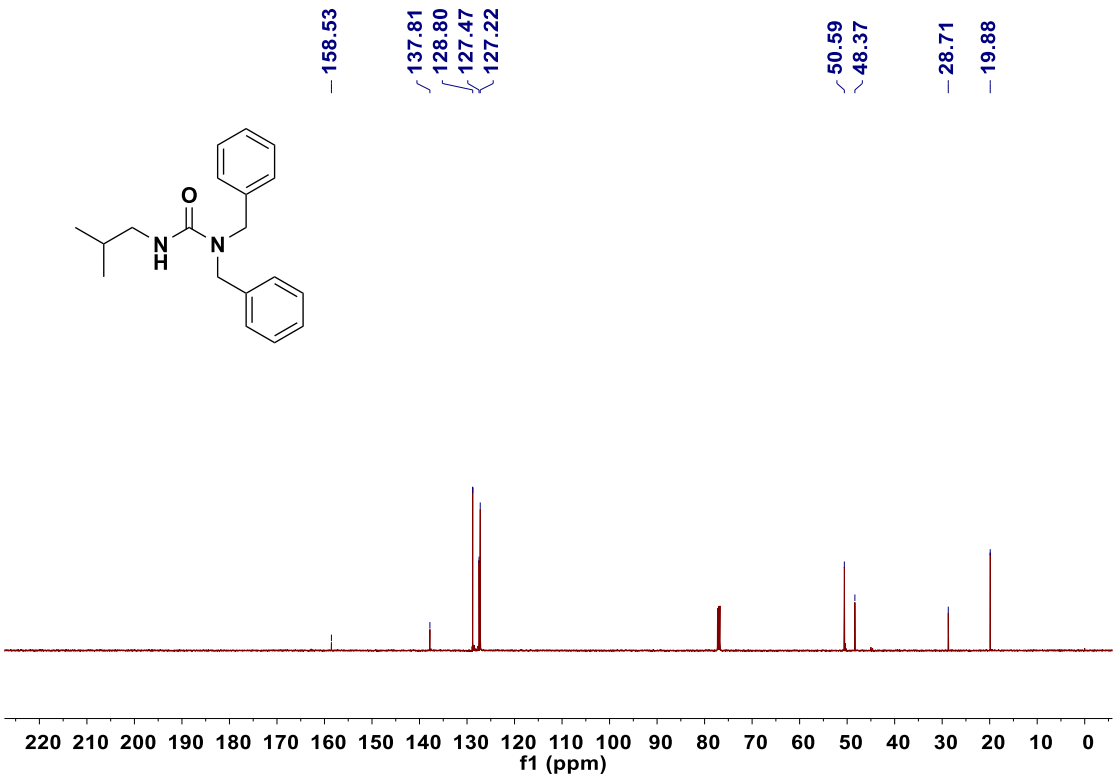
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(thiophen-2-ylmethyl)urea (3x)



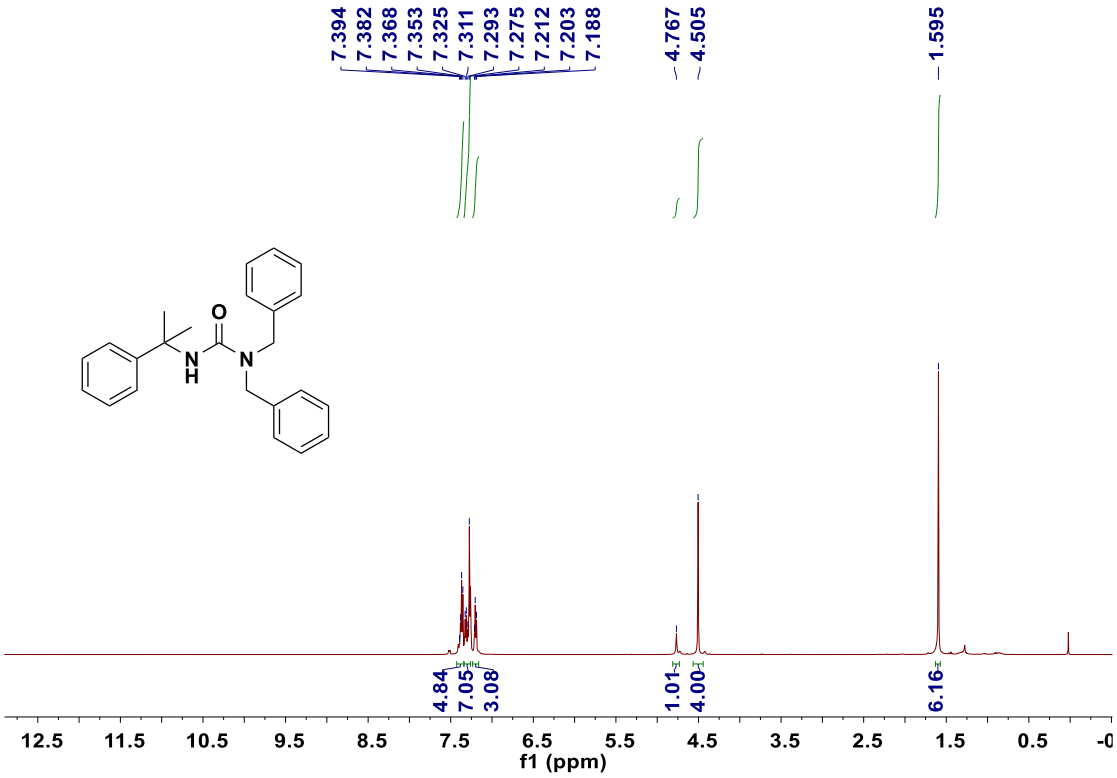
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-isobutylurea (3y)



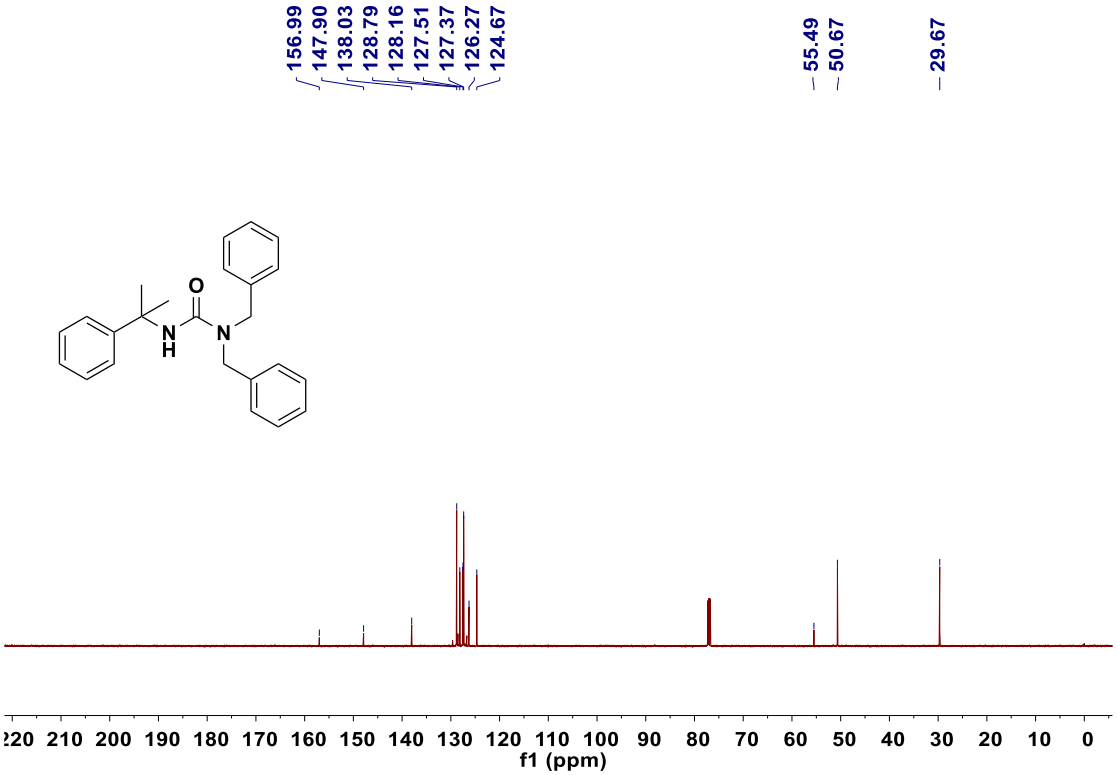
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-isobutylurea (3y)



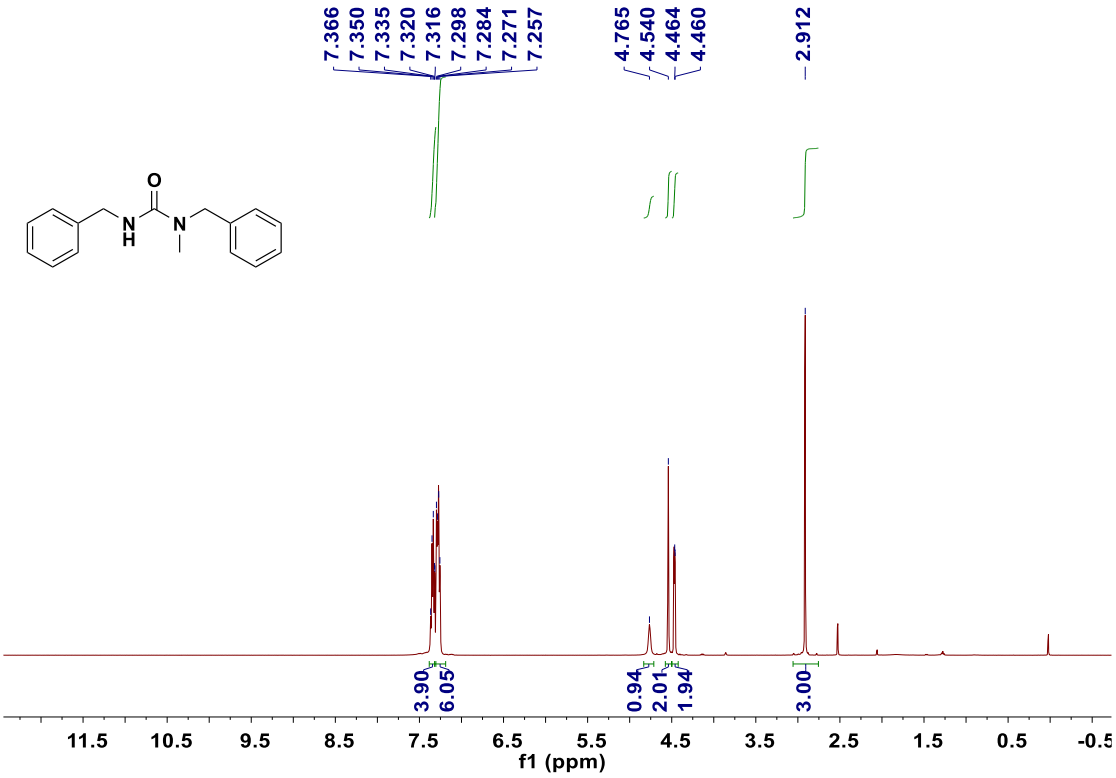
^{1}H NMR (500 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(2-phenylpropan-2-yl)urea (3z)



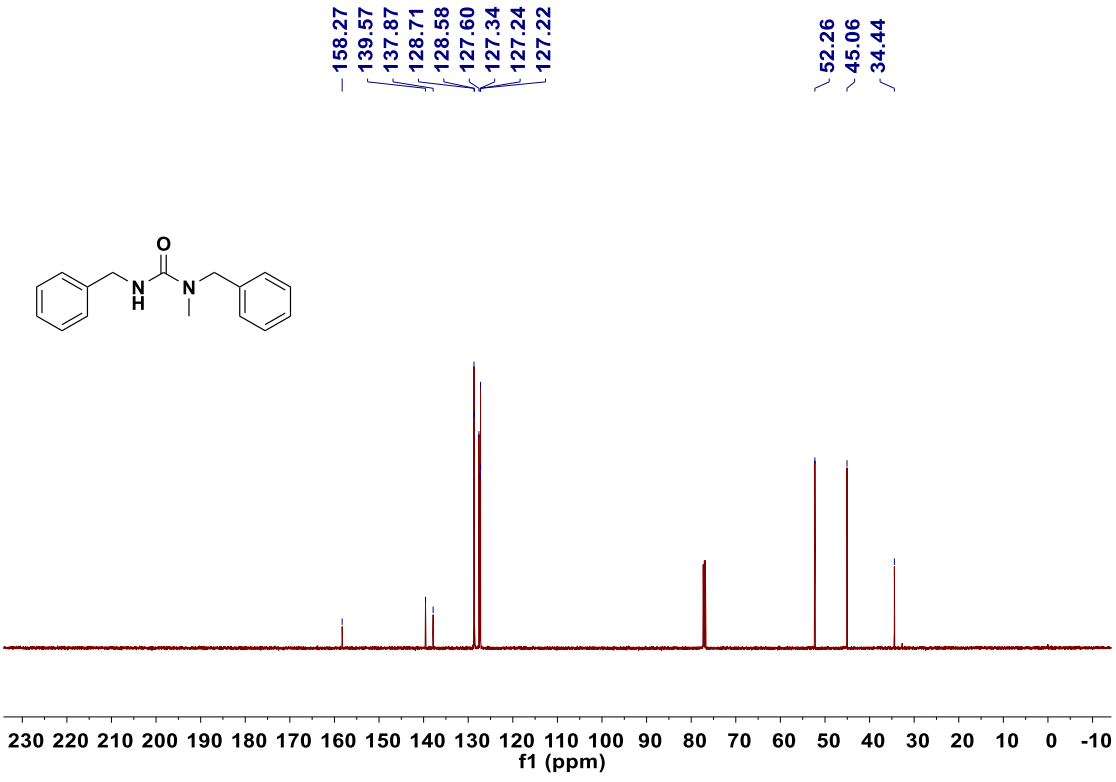
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of 1,1-dibenzyl-3-(2-phenylpropan-2-yl)urea (3z)



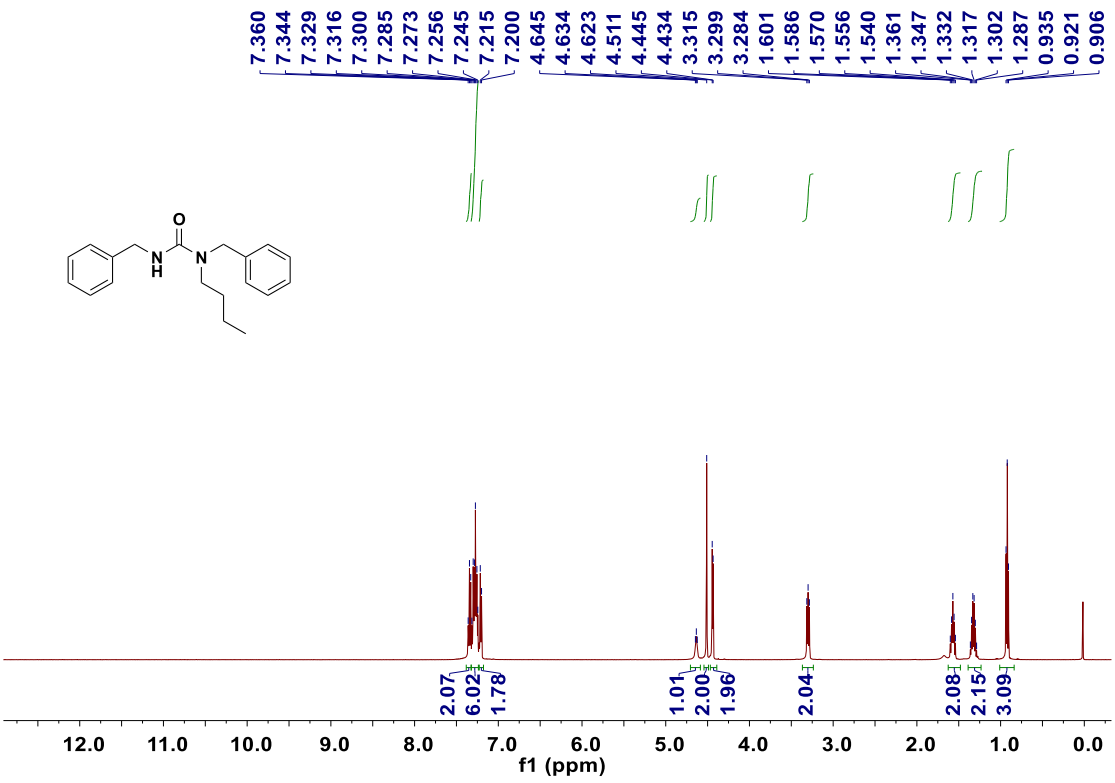
^{1}H NMR (500MHz, $CDCl_3$) of 1,1-dibenzyl-3-(1,3-dibenzyl-1-methylurea)(3aa)



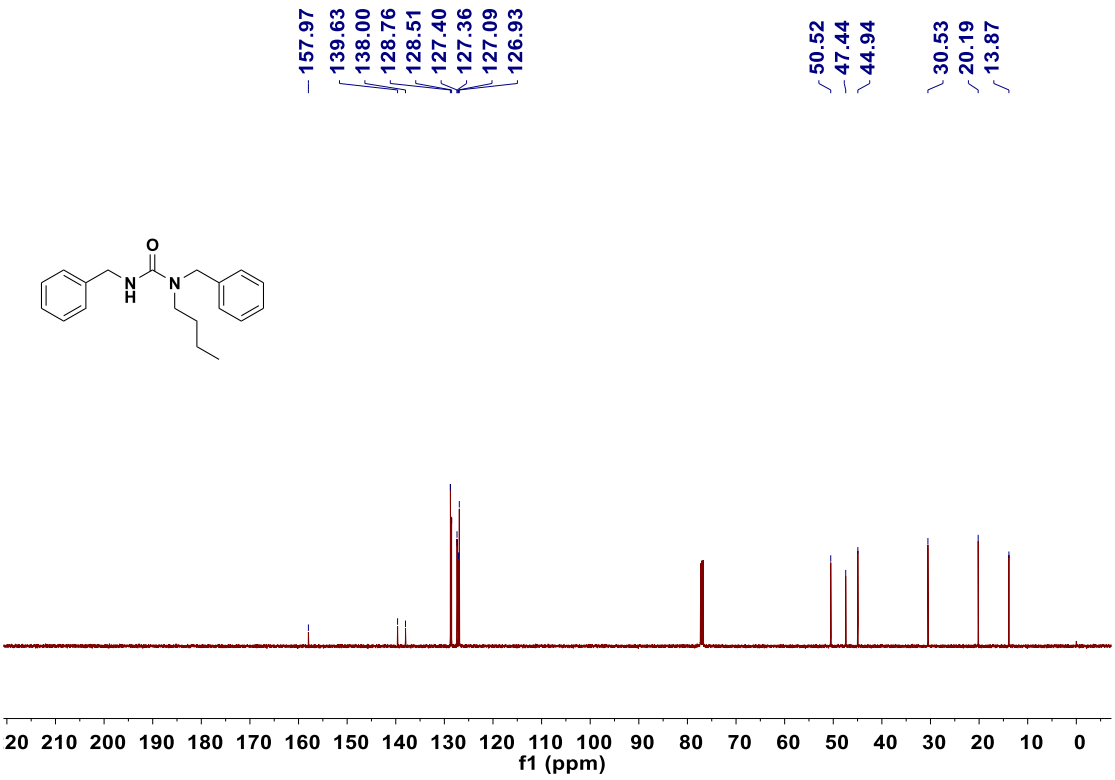
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 1,1-dibenzyl-3-(1,3-dibenzyl-1-methylurea)(3aa)



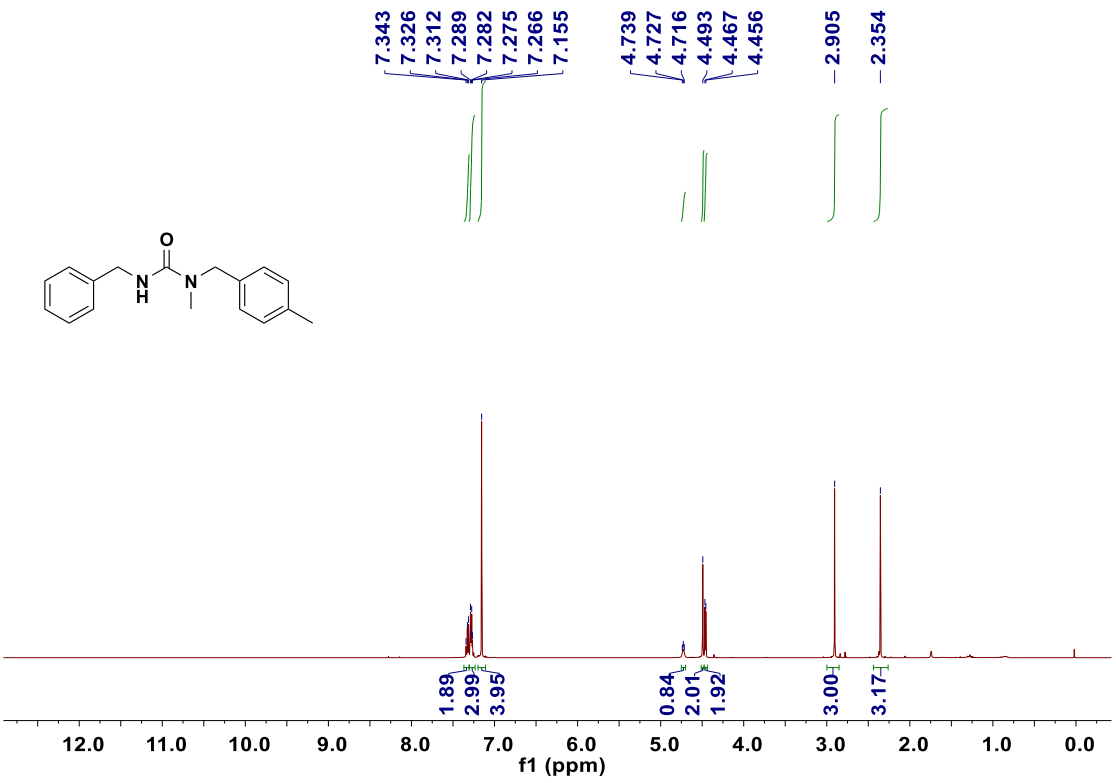
^{1}H NMR (500MHz, $CDCl_3$) of 1,3-dibenzyl-1-butylurea (3ab)



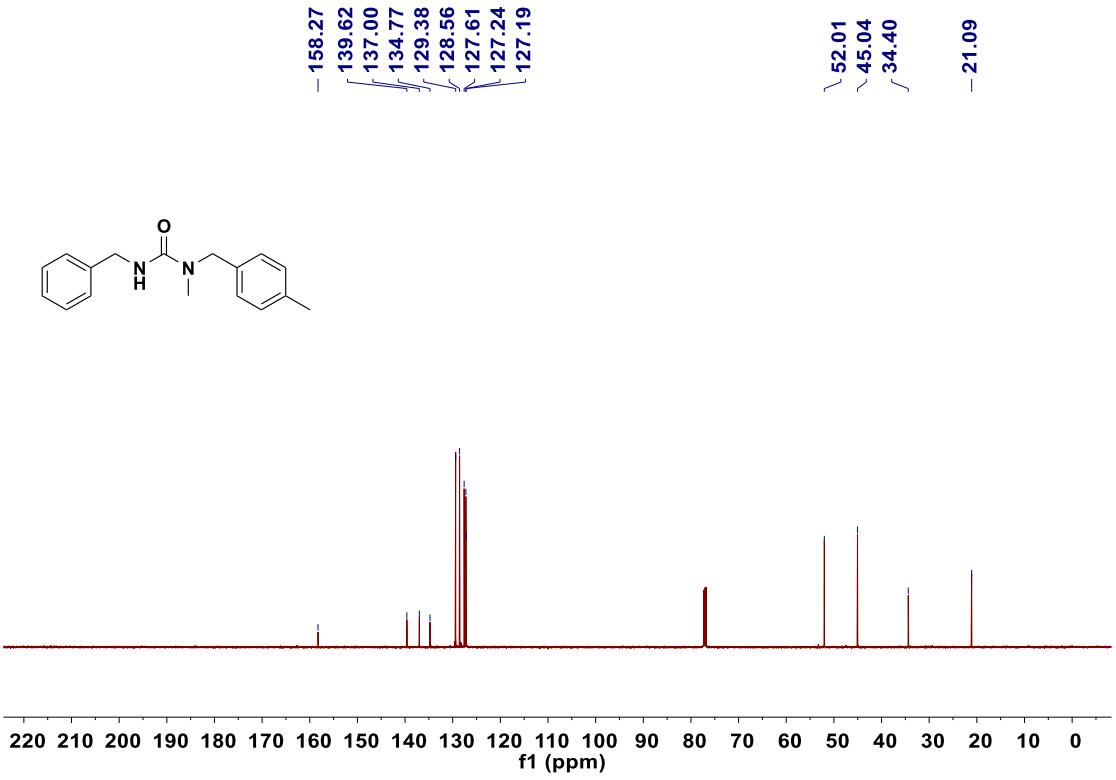
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 1,3-dibenzyl-1-butylurea (3ab)



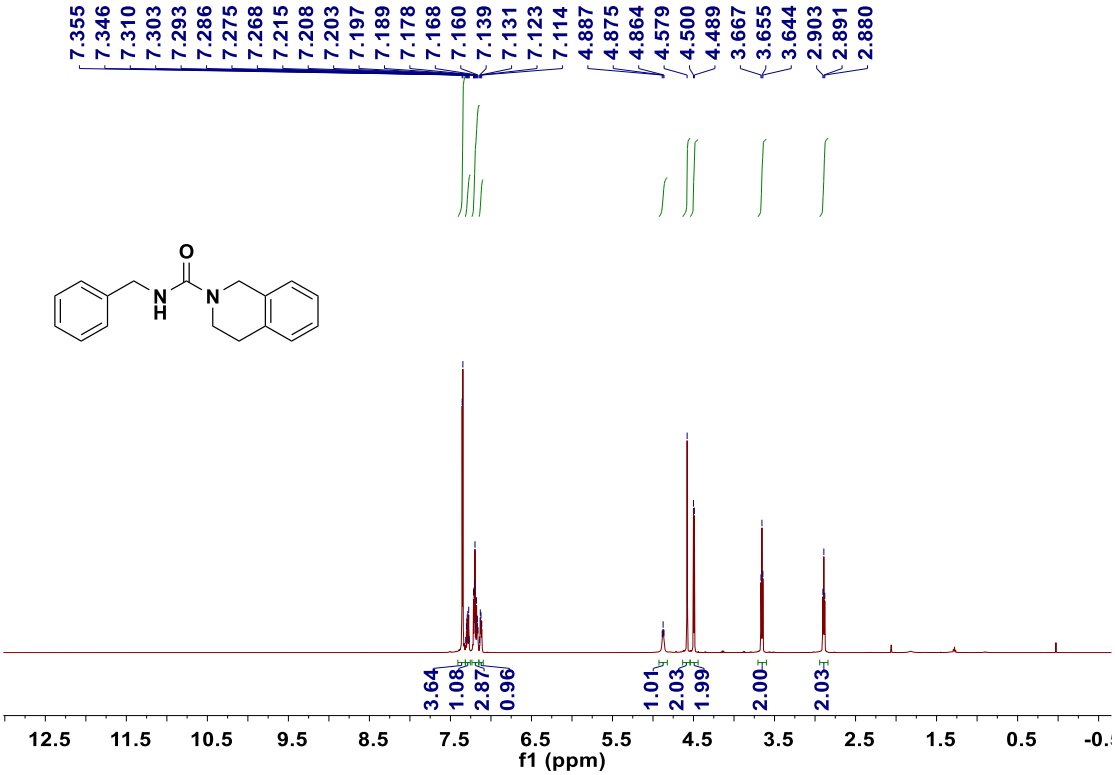
^{1}H NMR (500MHz, $CDCl_3$) of 3-benzyl-1-methyl-1-(4-methylbenzyl)urea (3ac)



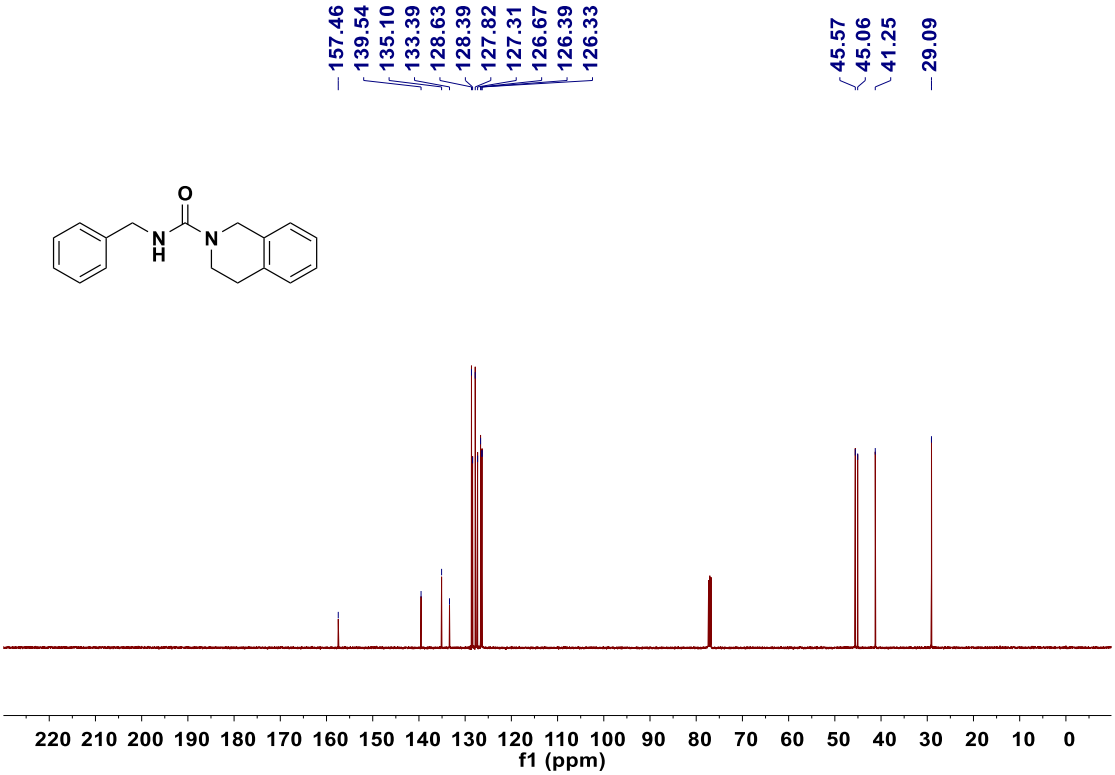
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 3-benzyl-1-methyl-1-(4-methylbenzyl)urea (3ac)



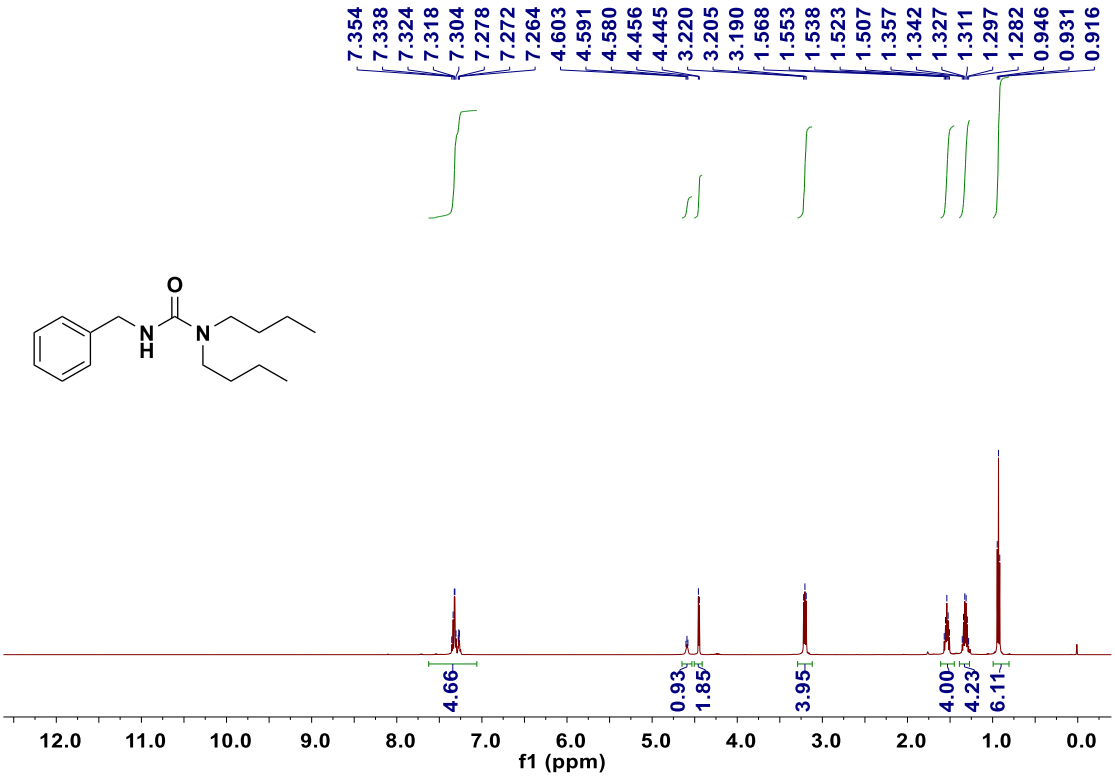
^{1}H NMR (500MHz, $CDCl_3$) of N-benzyl-3,4-dihydroisoquinoline-2(1H)-carboxamide (3ad)



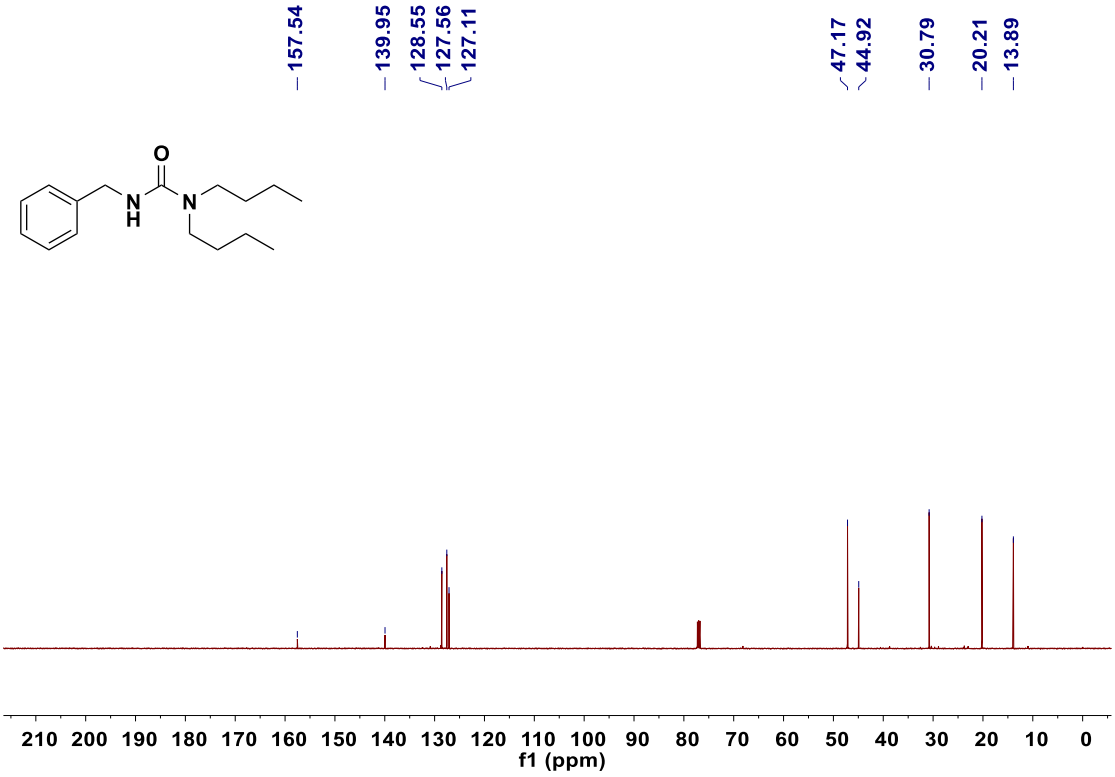
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of N-benzyl-3,4-dihydroisoquinoline-2(1H)-carboxamide (3ad)



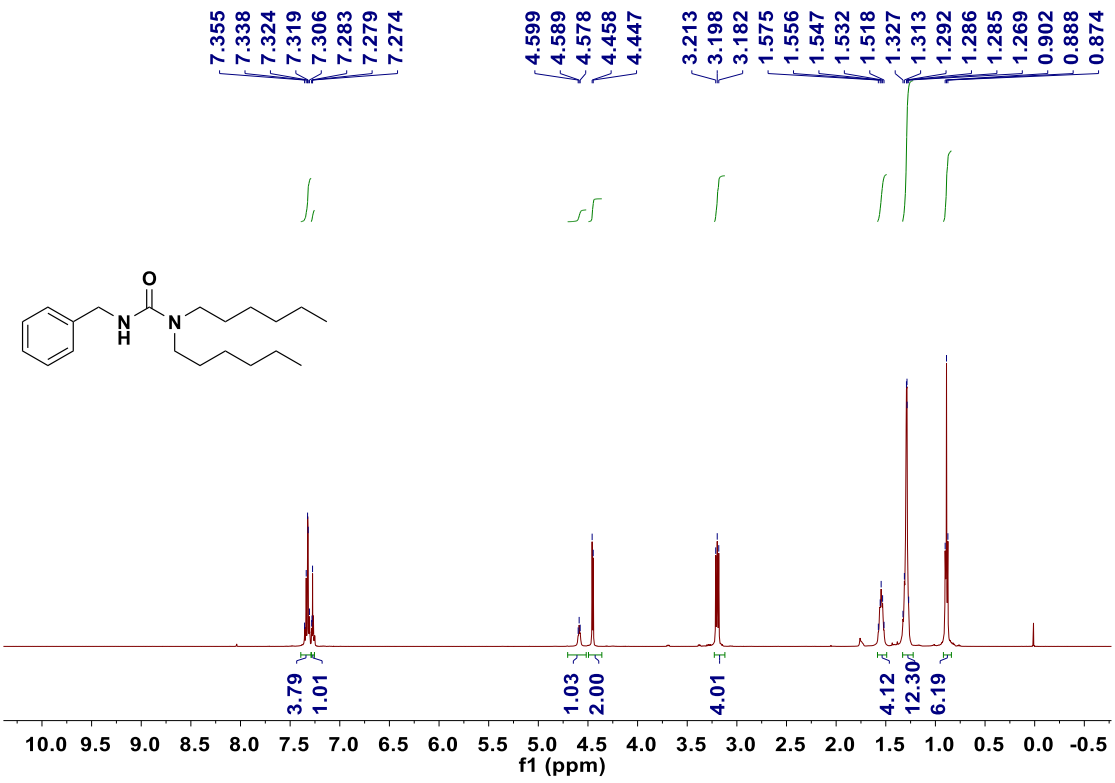
^{1}H NMR (500MHz, $CDCl_3$) of 3-benzyl-1,1-dibutylurea (3ae)



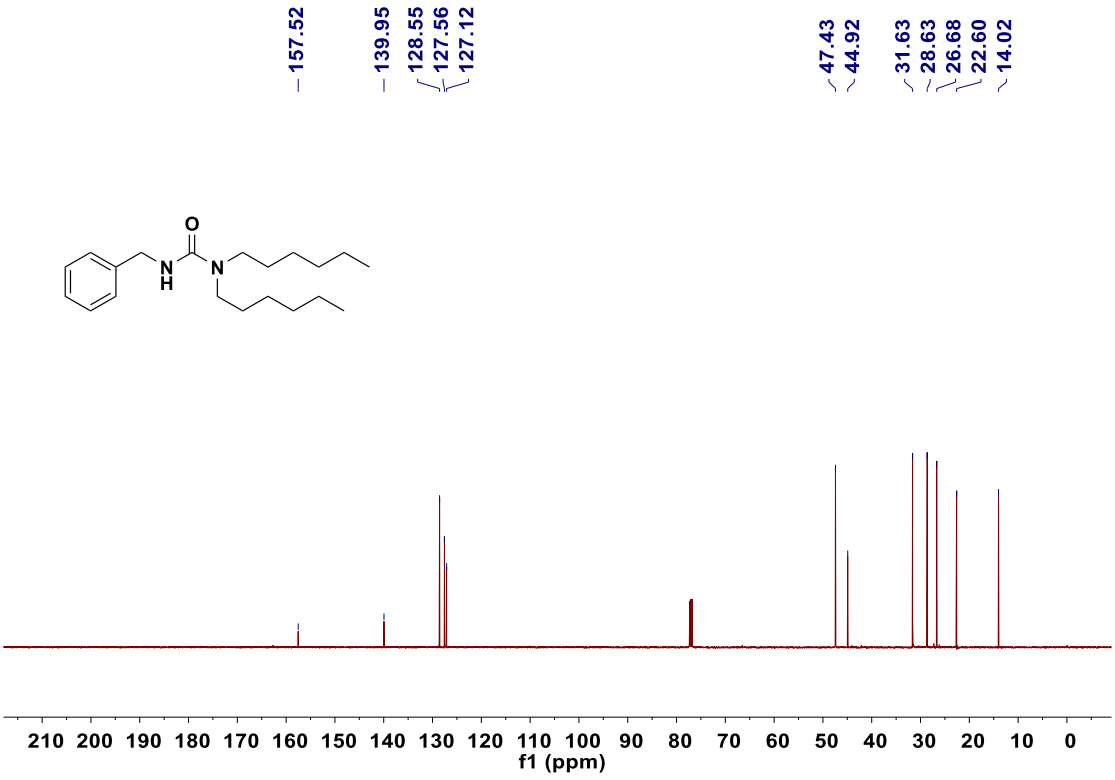
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 3-benzyl-1,1-dibutylurea (3ae)



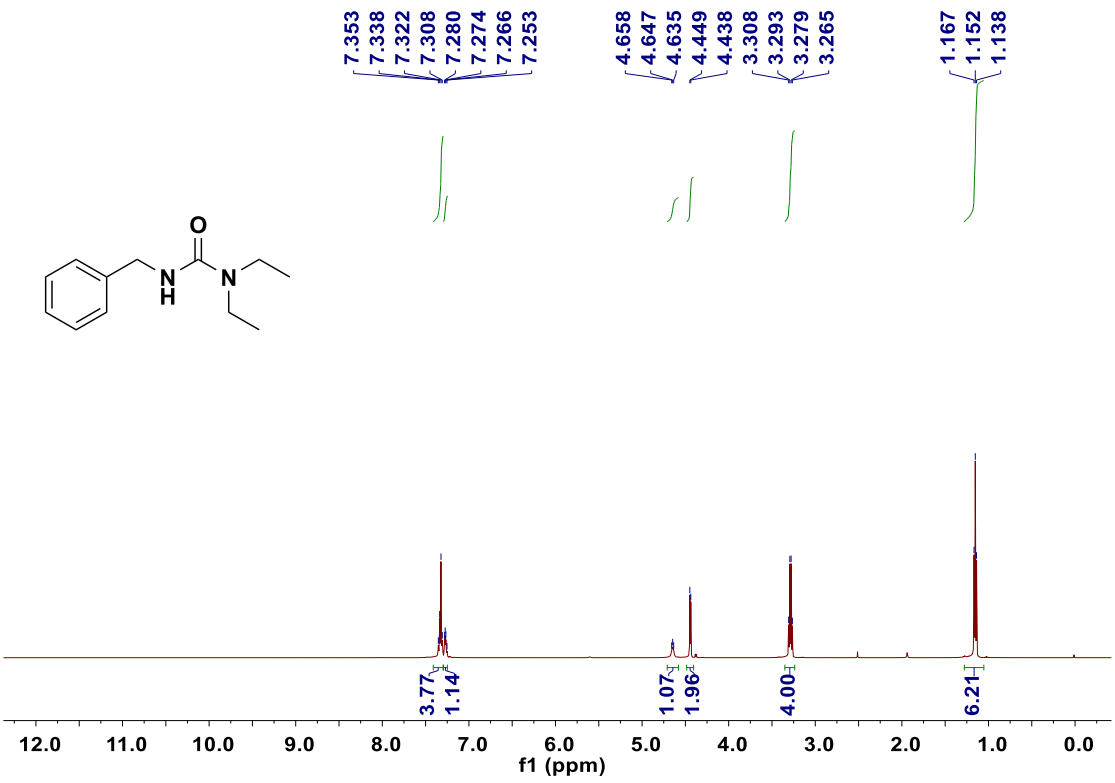
^{1}H NMR (500MHz, $CDCl_3$) of 3-benzyl-1,1-dihexylurea(3af)



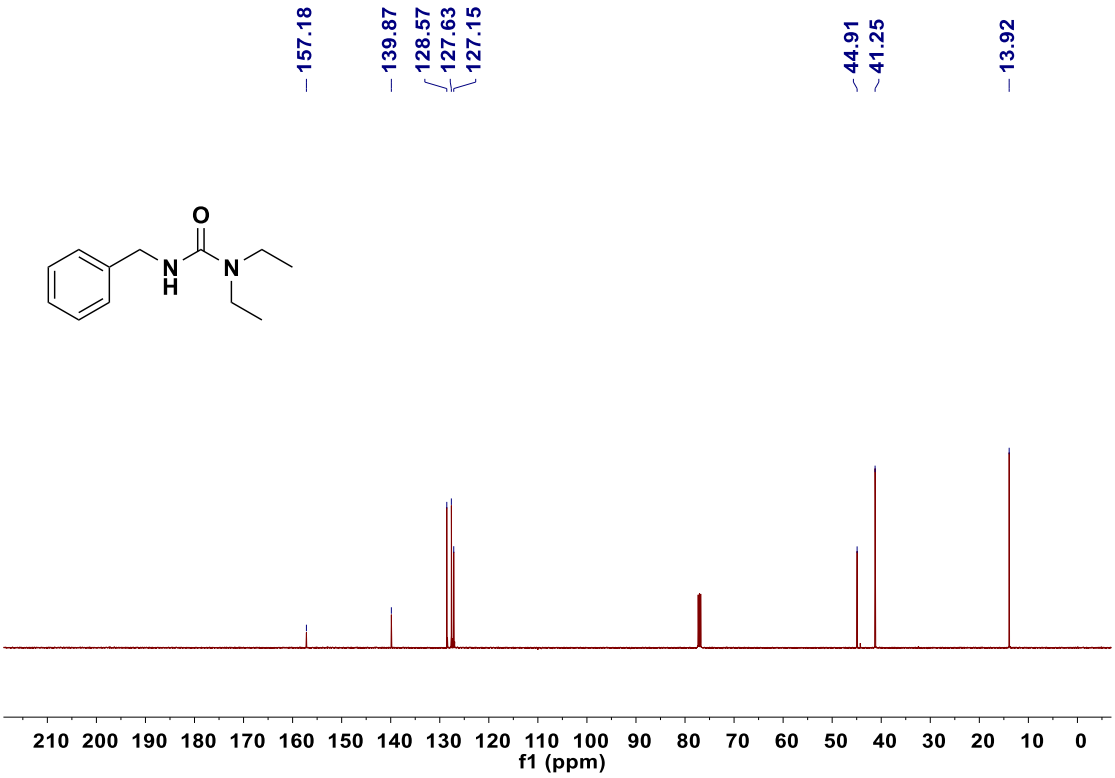
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 3-benzyl-1,1-dihexylurea(3af)



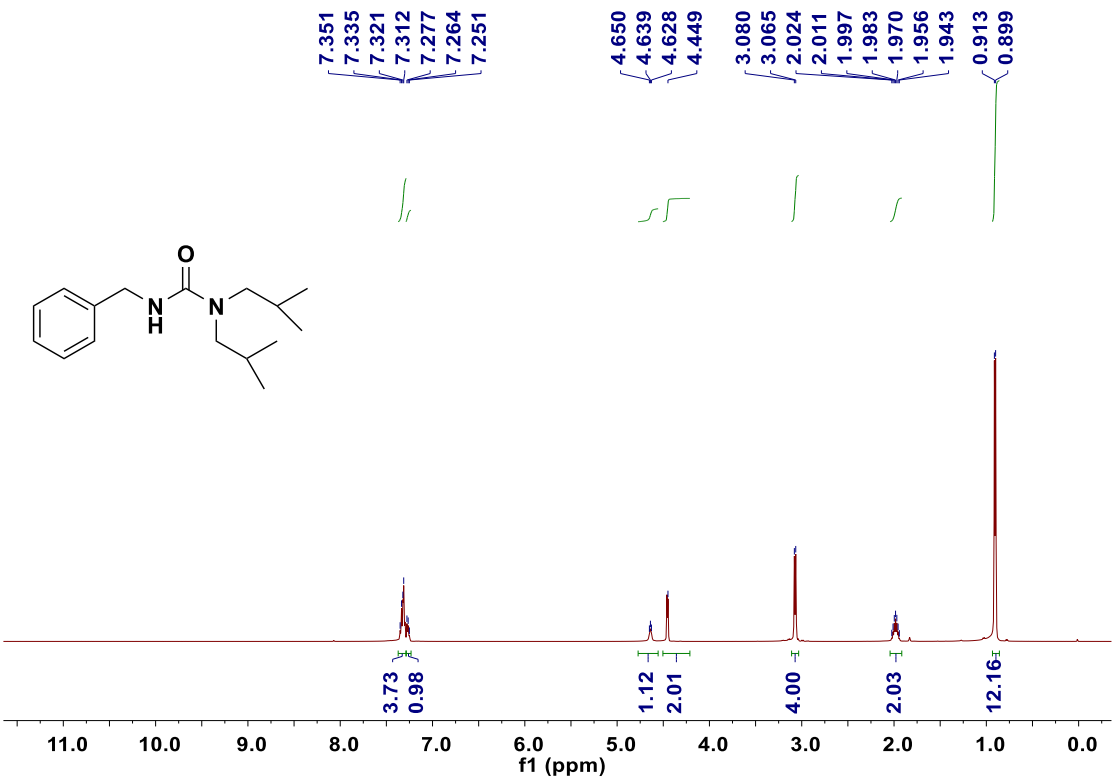
^{1}H NMR (500MHz, $CDCl_3$) of 3-benzyl-1,1-diethylurea Chemical Formula(3ag)



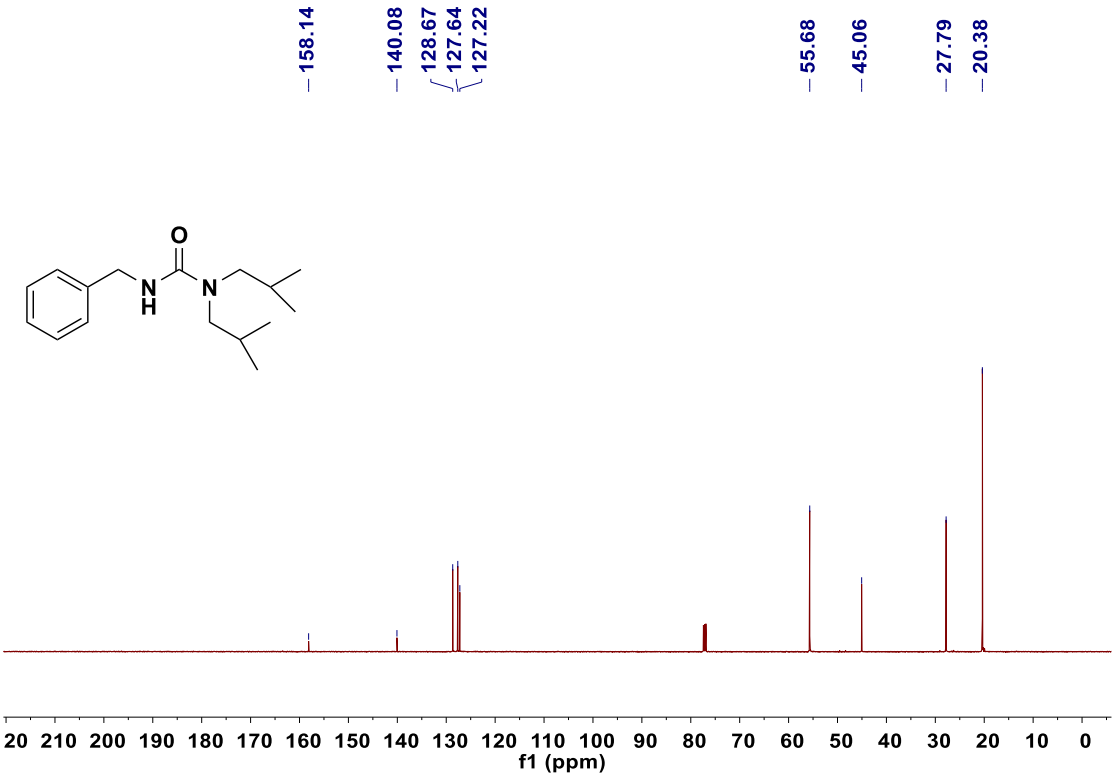
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 3-benzyl-1,1-diethylurea Chemical Formula(3ag)



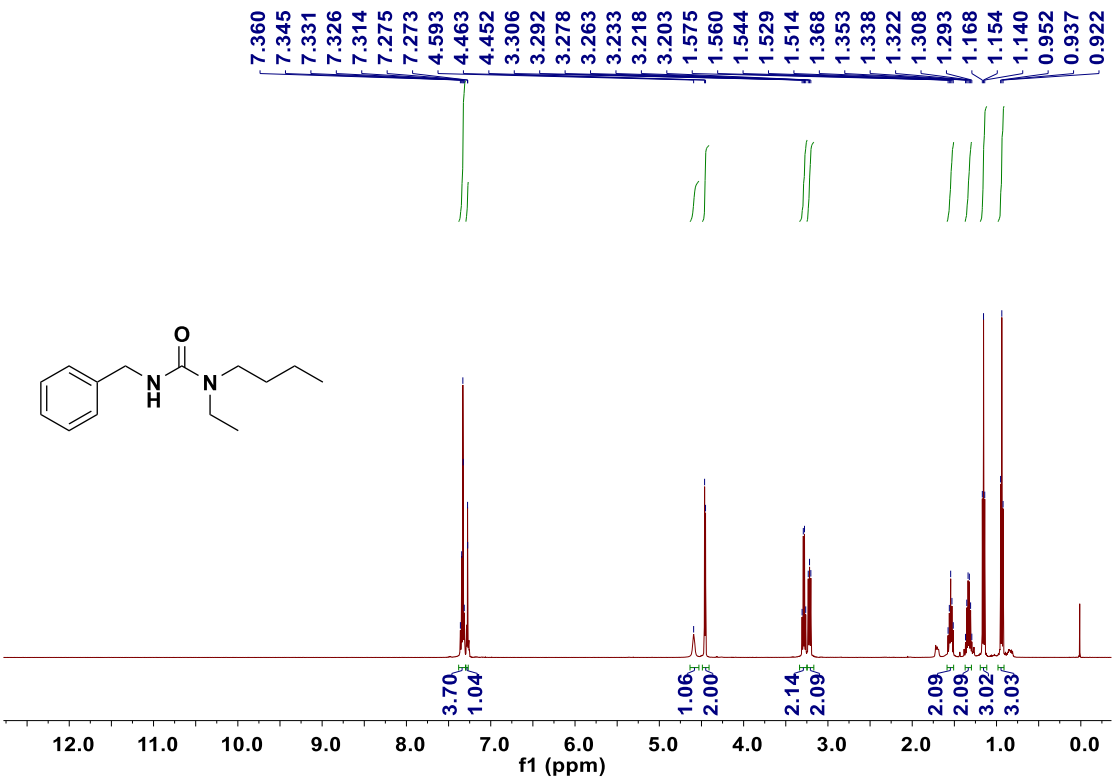
^{1}H NMR (500MHz, $CDCl_3$) of 3-benzyl-1,1-diisobutylurea (3ah)



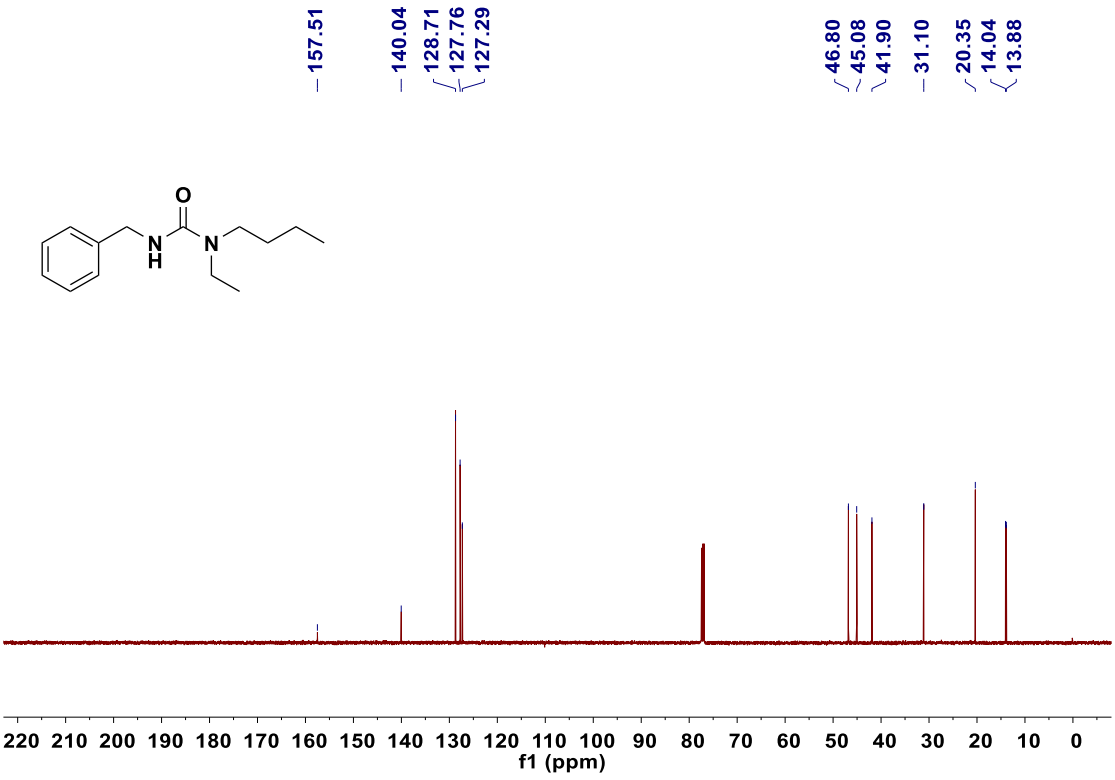
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 3-benzyl-1,1-diisobutylurea (3ah)



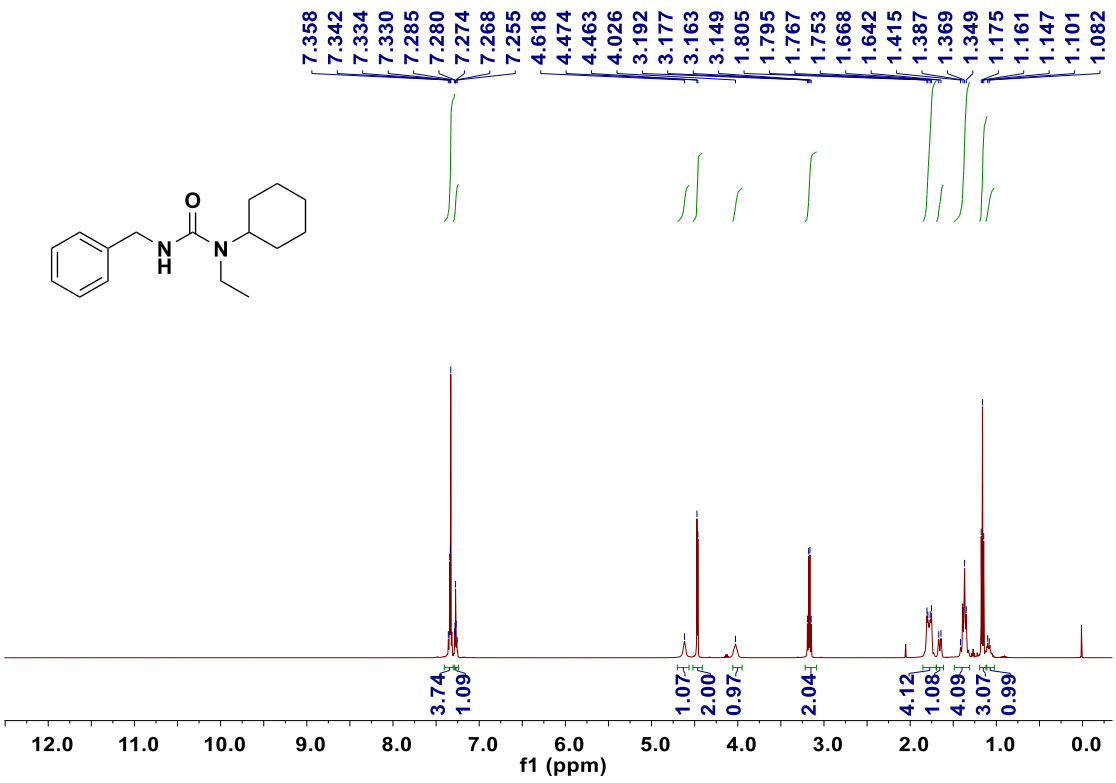
^{1}H NMR (500MHz, $CDCl_3$) of 3-benzyl-1-butyl-1-ethylurea (3ai)



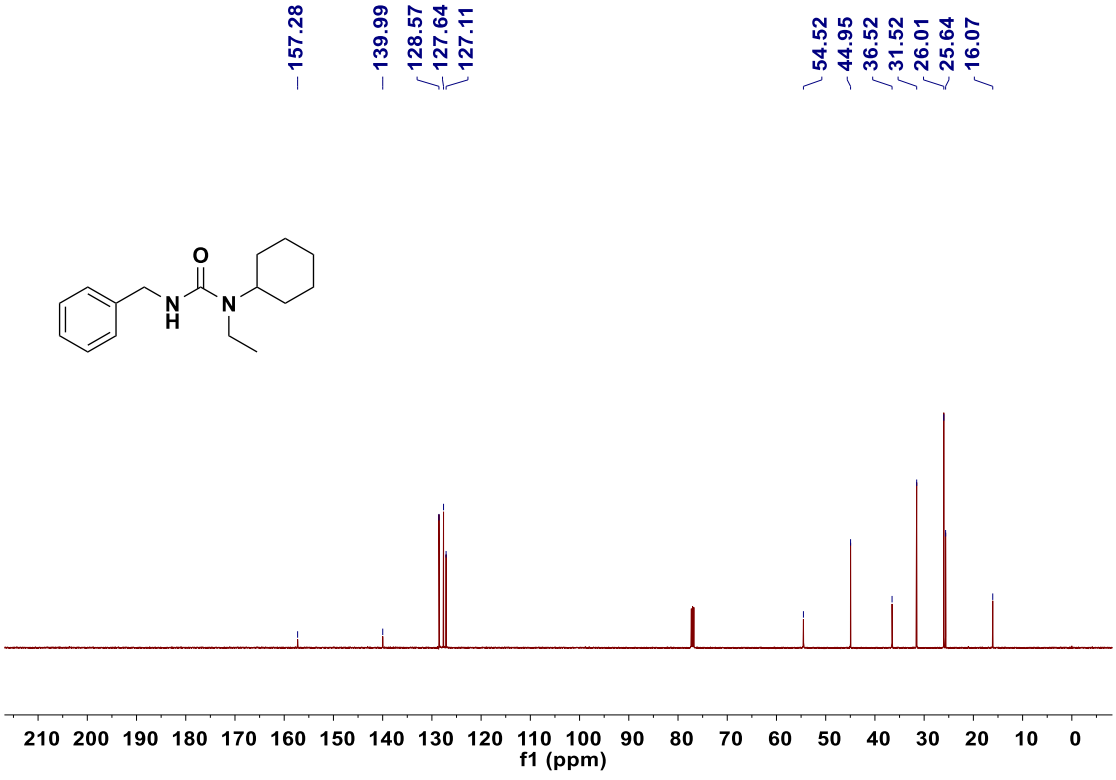
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 3-benzyl-1-butyl-1-ethylurea (3ai)



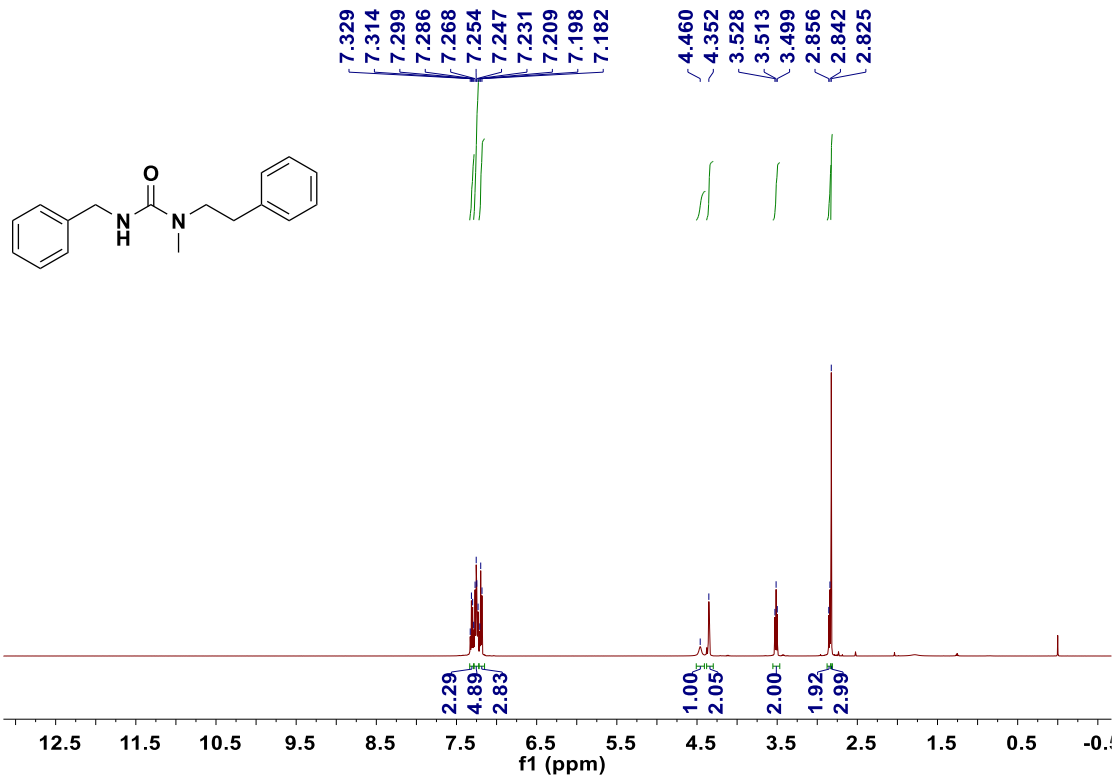
^{1}H NMR (500MHz, $CDCl_3$) of 3-benzyl-1-cyclohexyl-1-ethylurea (3aj)



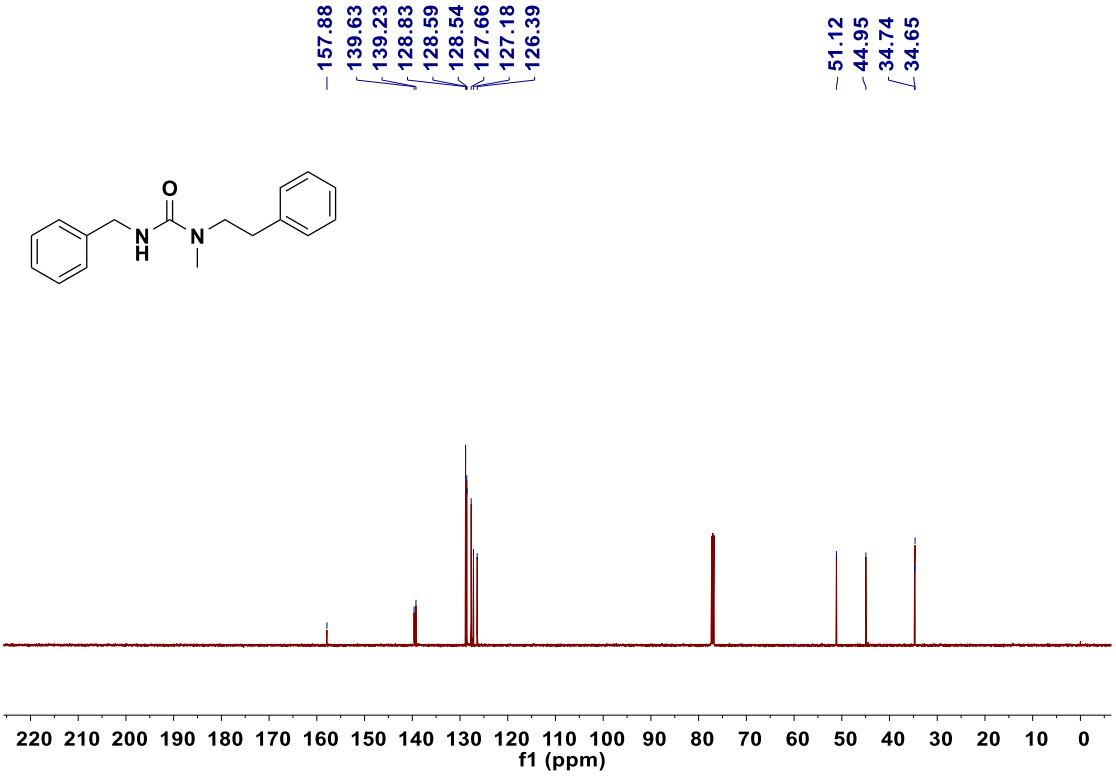
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 3-benzyl-1-cyclohexyl-1-ethylurea (3aj)



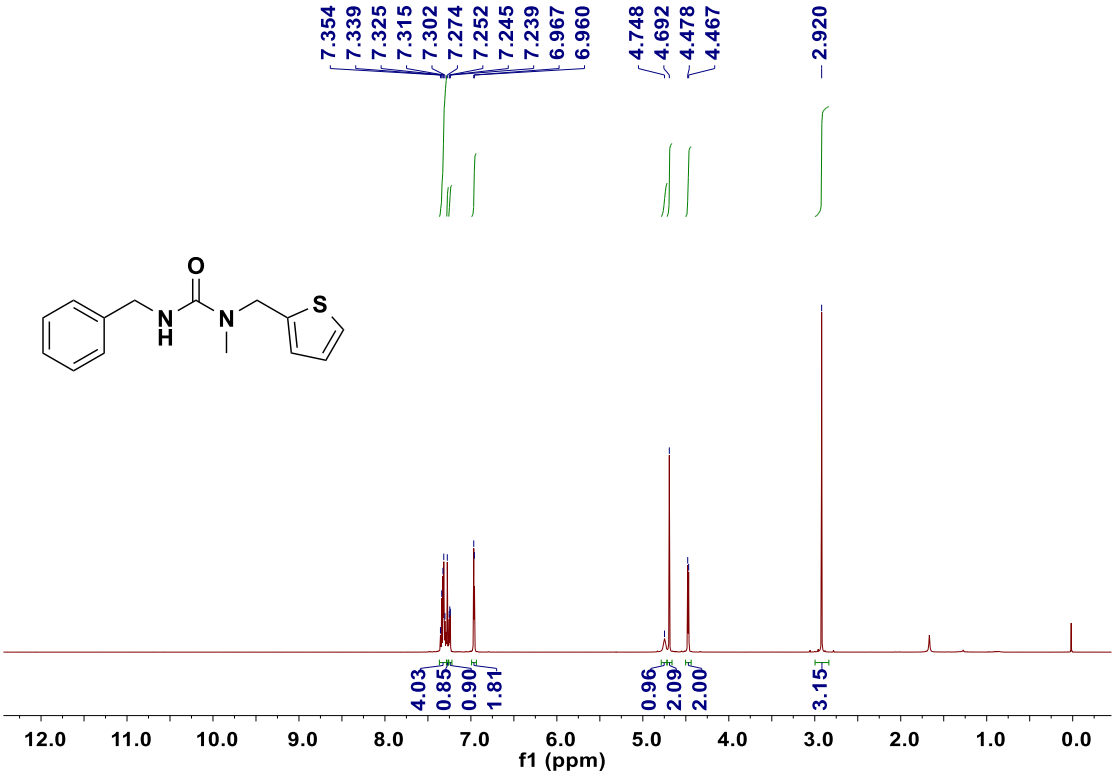
^{1}H NMR (500MHz, $CDCl_3$) of 3-benzyl-1-methyl-1-phenethylurea (3ak)



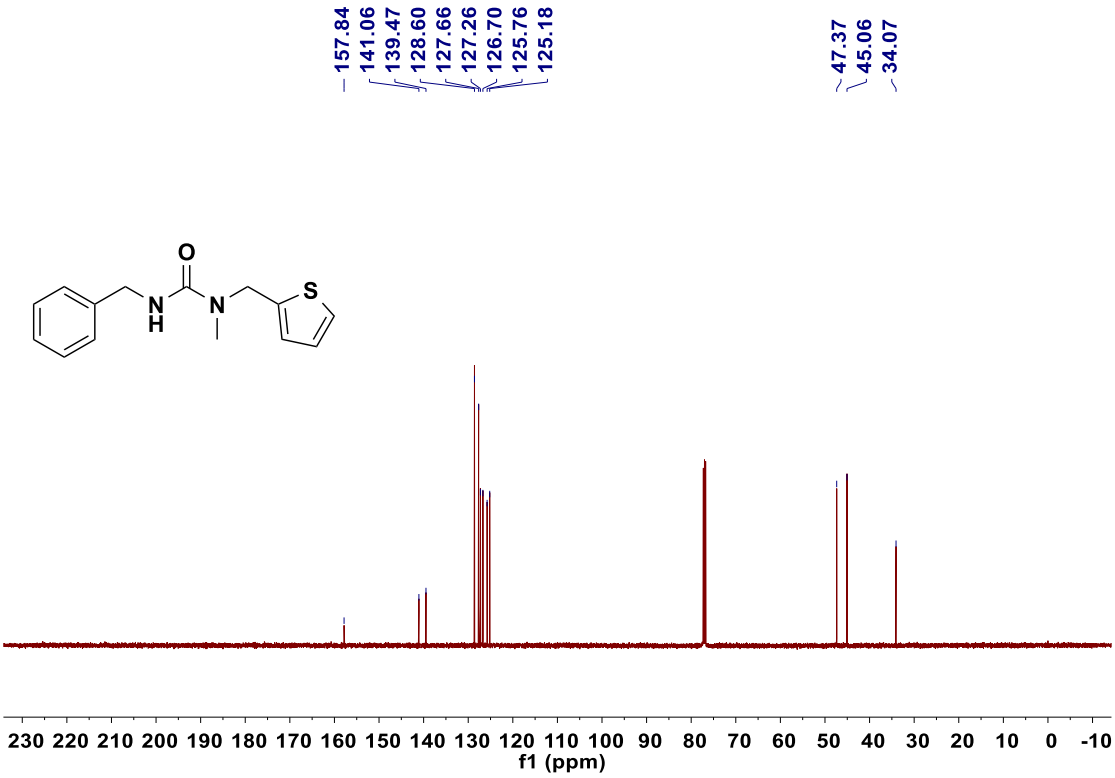
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 3-benzyl-1-methyl-1-phenethylurea (3ak)



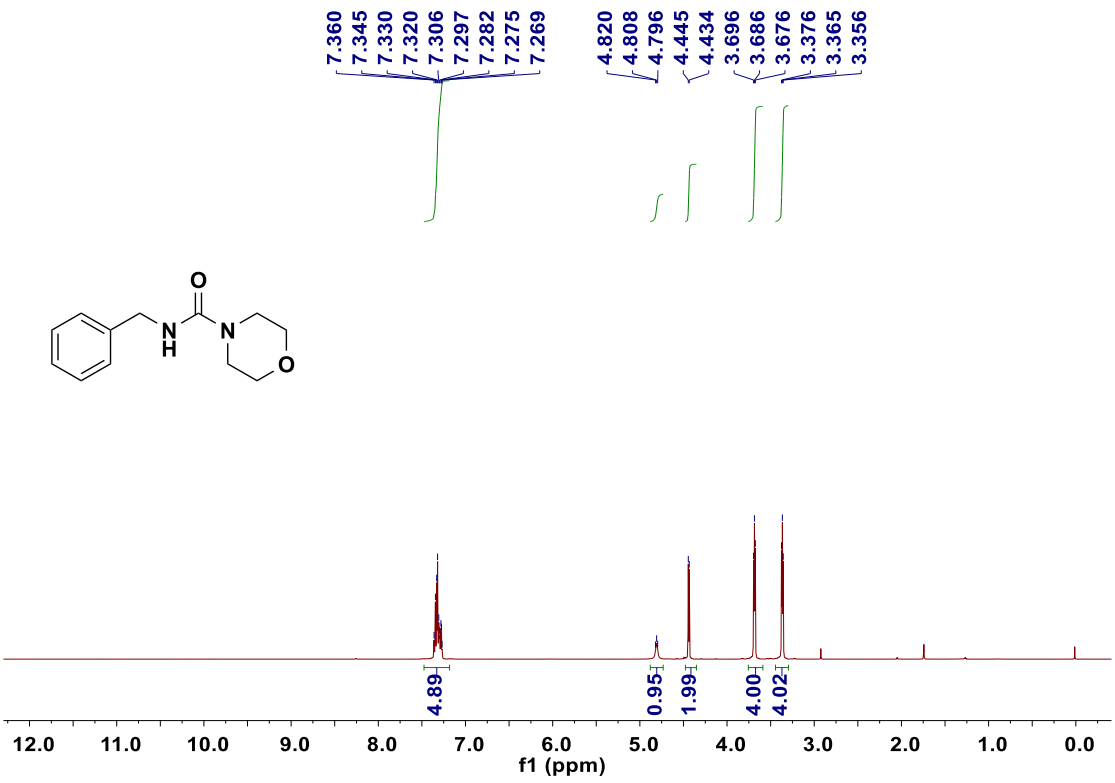
^{1}H NMR (500MHz, $CDCl_3$) of 3-benzyl-1-methyl-1-(thiophen-2-ylmethyl)urea (3al)



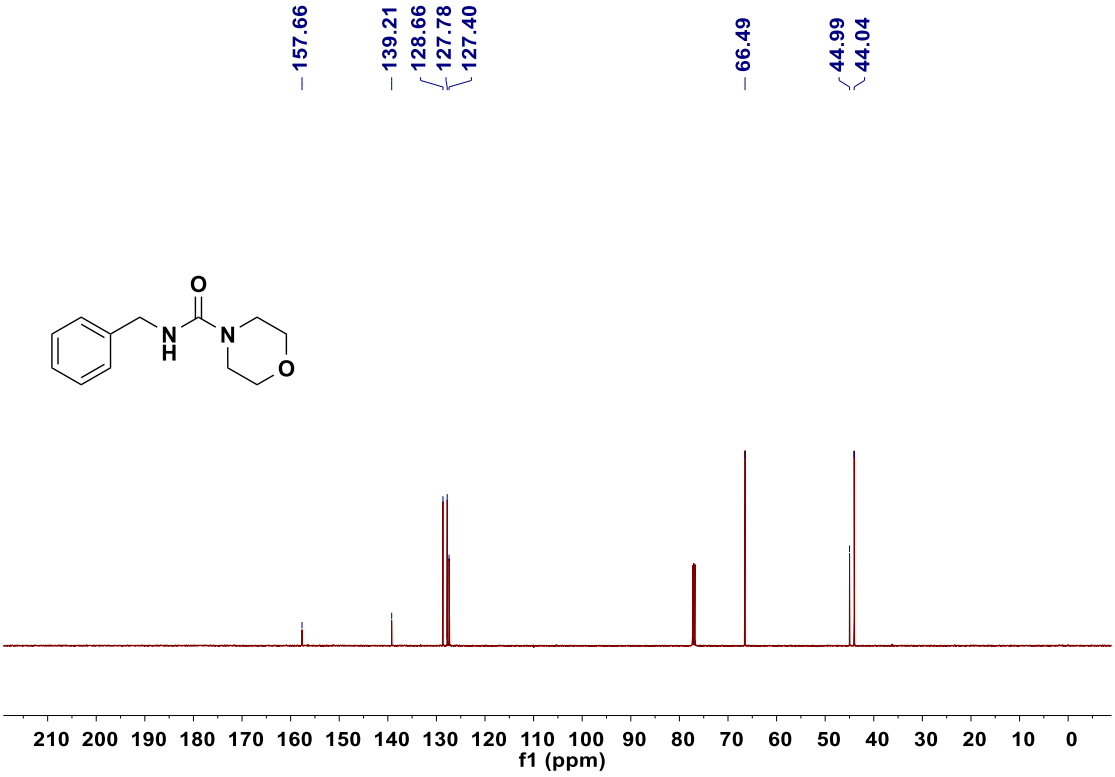
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 3-benzyl-1-methyl-1-(thiophen-2-ylmethyl)urea (3al)



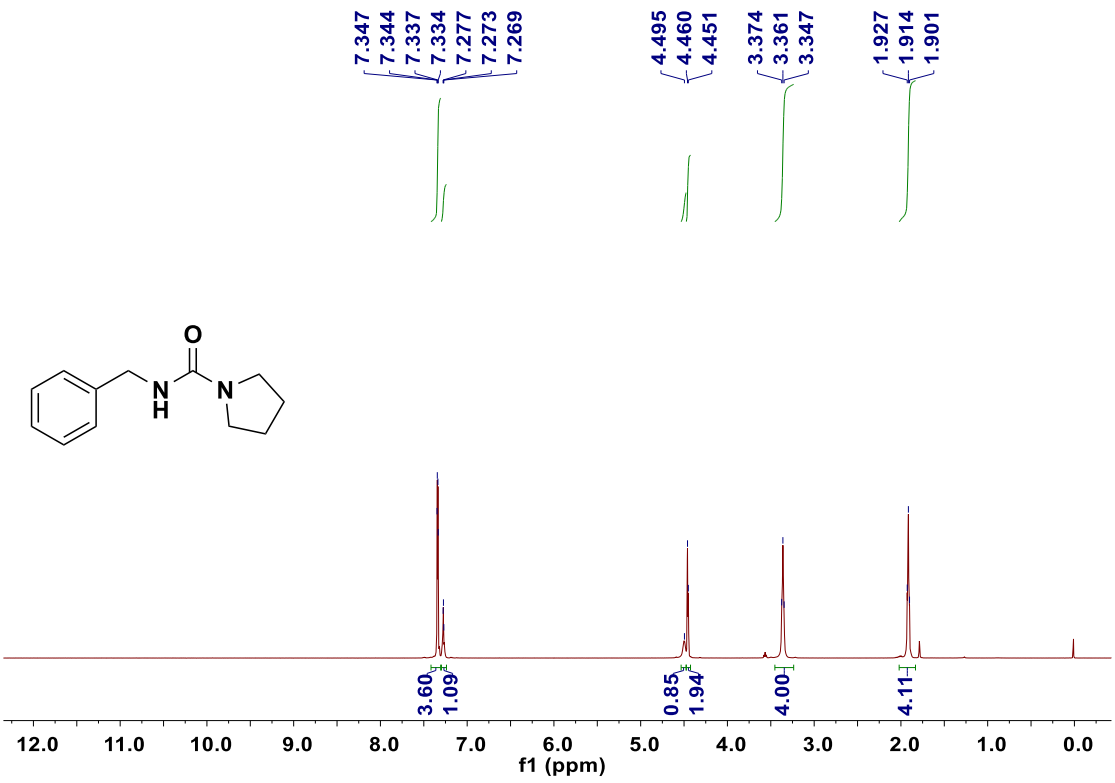
^{1}H NMR (500MHz, $CDCl_3$) of N-benzylmorpholine-4-carboxamide (3am)



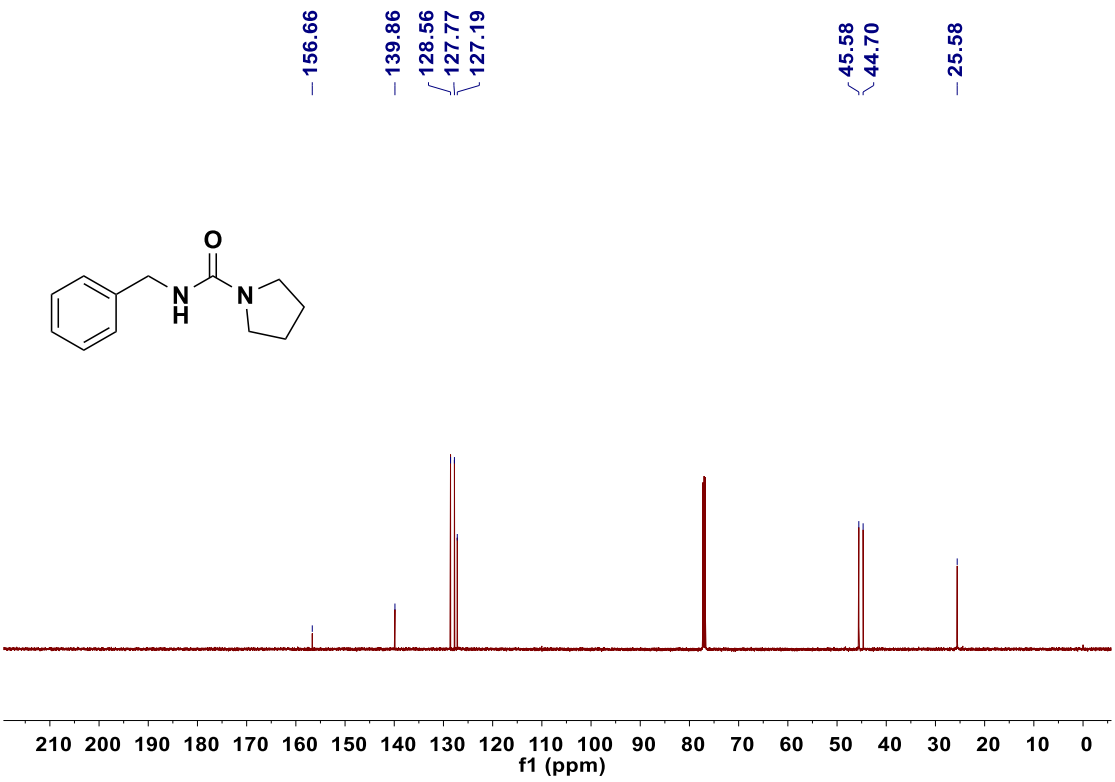
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of N-benzylmorpholine-4-carboxamide (3am)



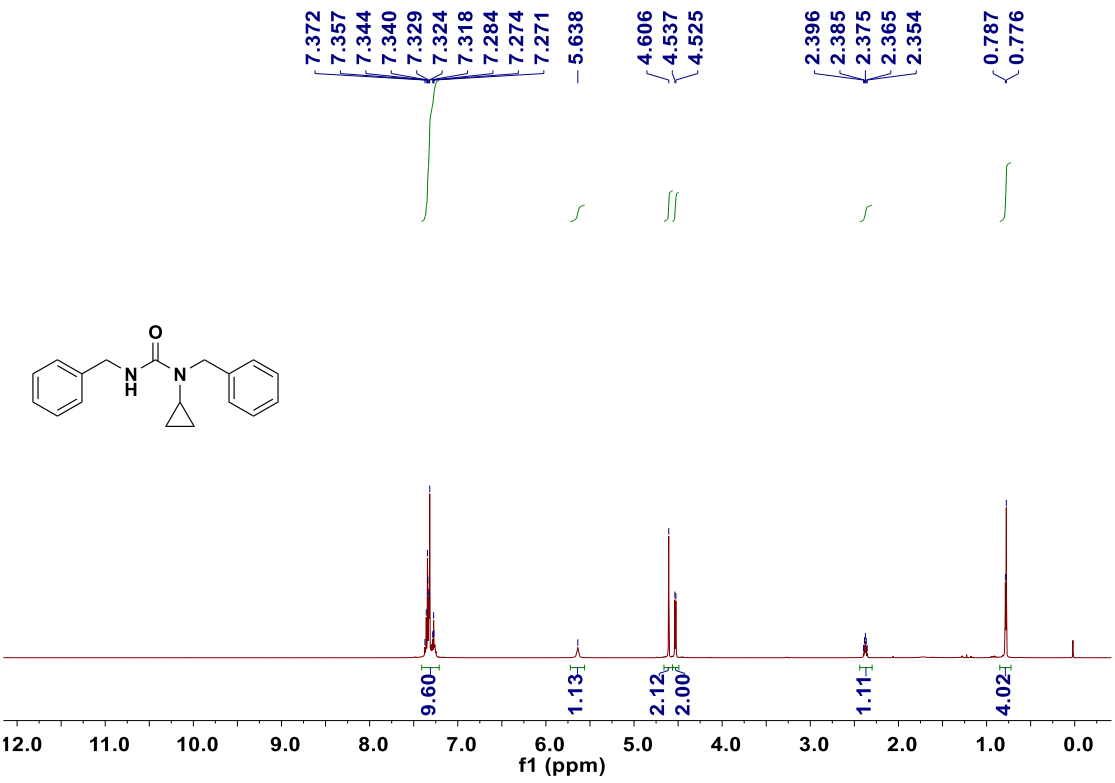
^{1}H NMR (500MHz, $CDCl_3$) of N-benzylpyrrolidine-1-carboxamide(3an)



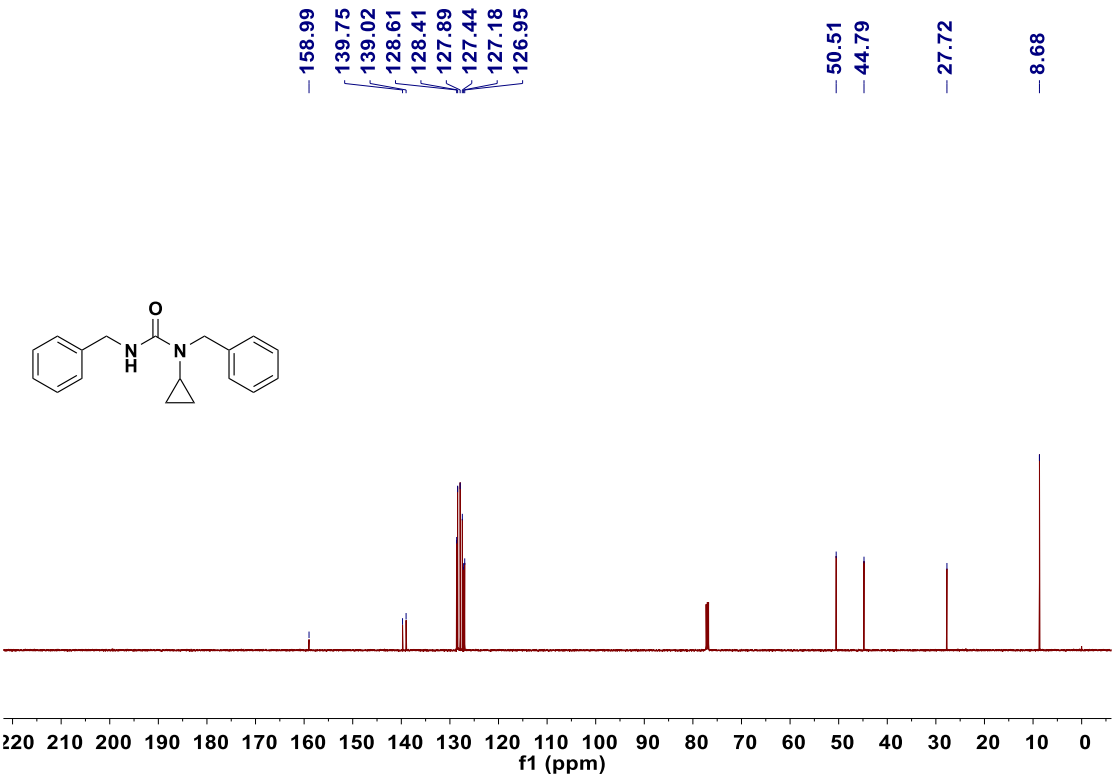
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of N-benzylpyrrolidine-1-carboxamide(3an)



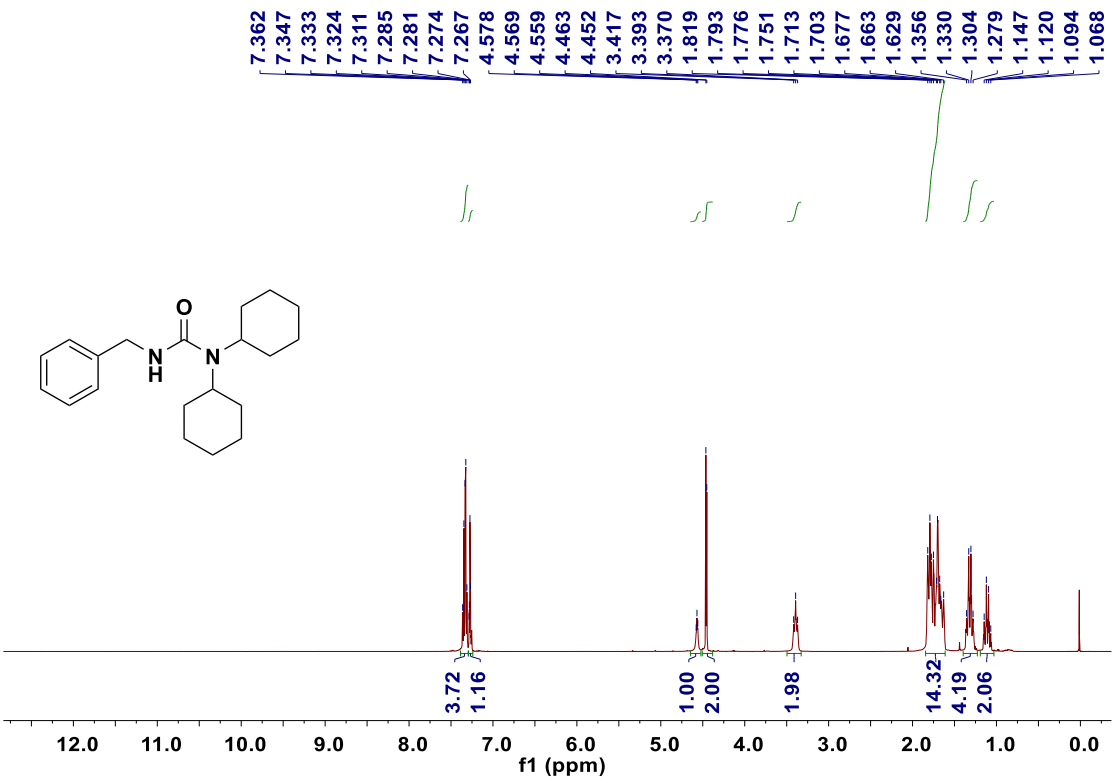
^{1}H NMR (500MHz, $CDCl_3$) of 1,3-dibenzyl-1-cyclopropylurea (3ao)



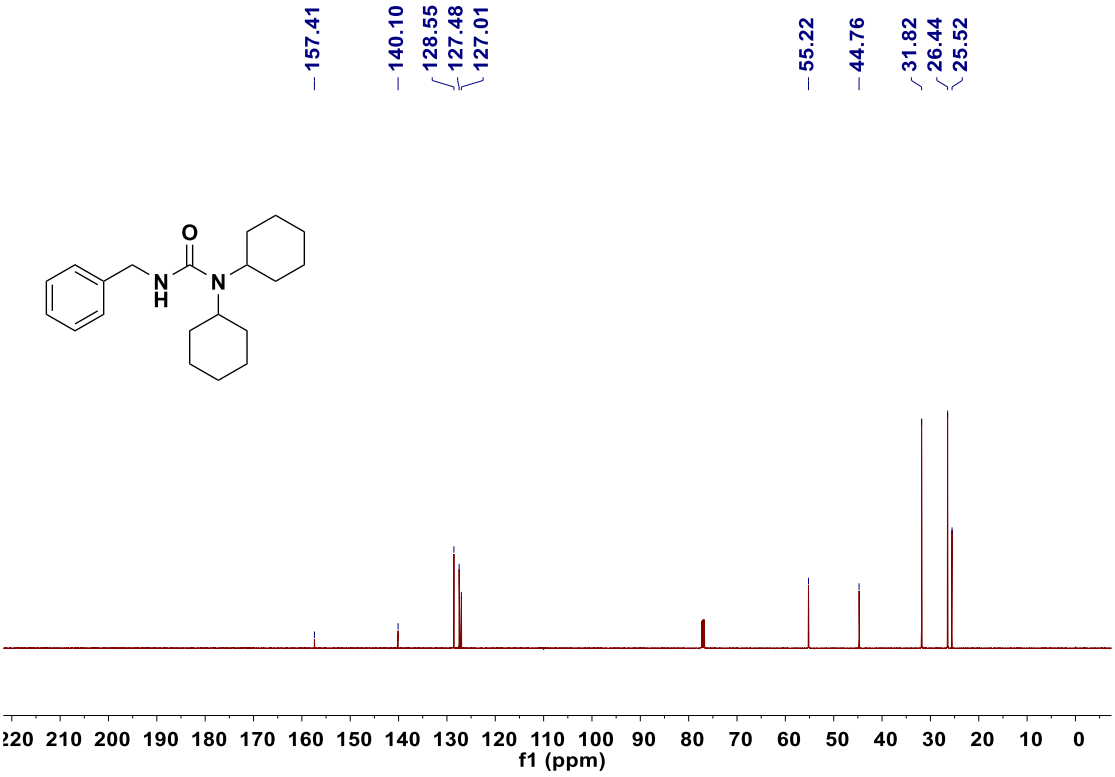
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 1,3-dibenzyl-1-cyclopropylurea (3ao)



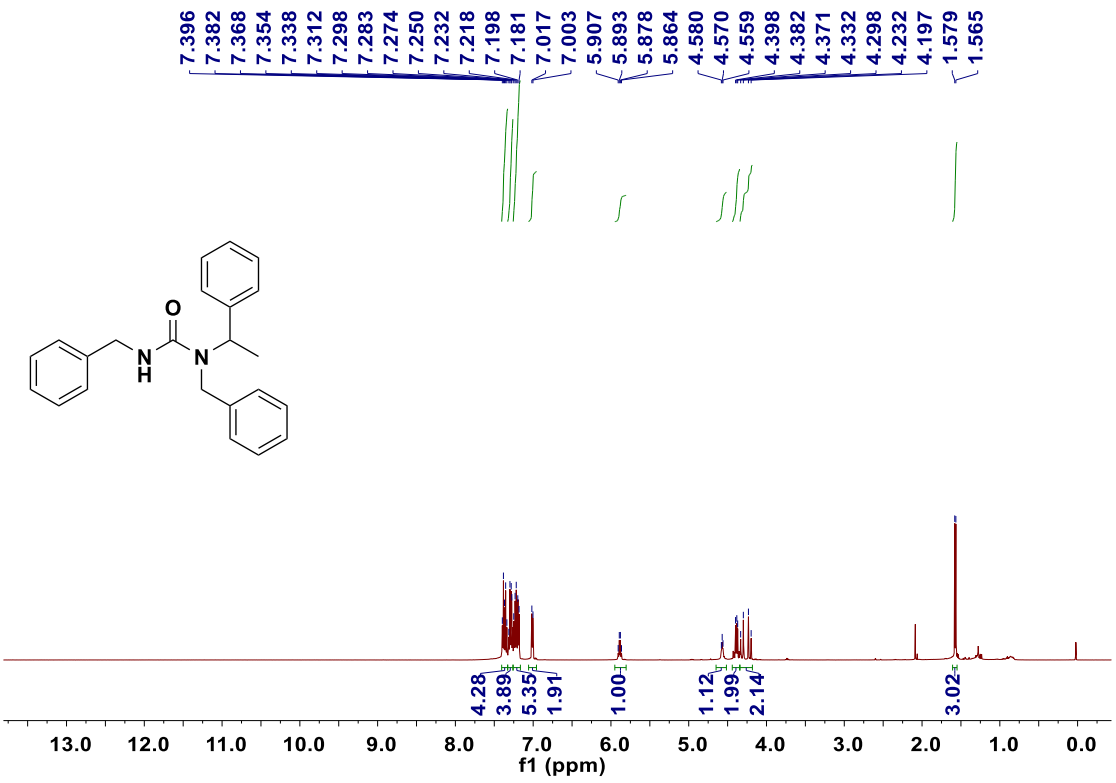
^{1}H NMR (500MHz, $CDCl_3$) of 3-benzyl-1,1-dicyclohexylurea (3ap)



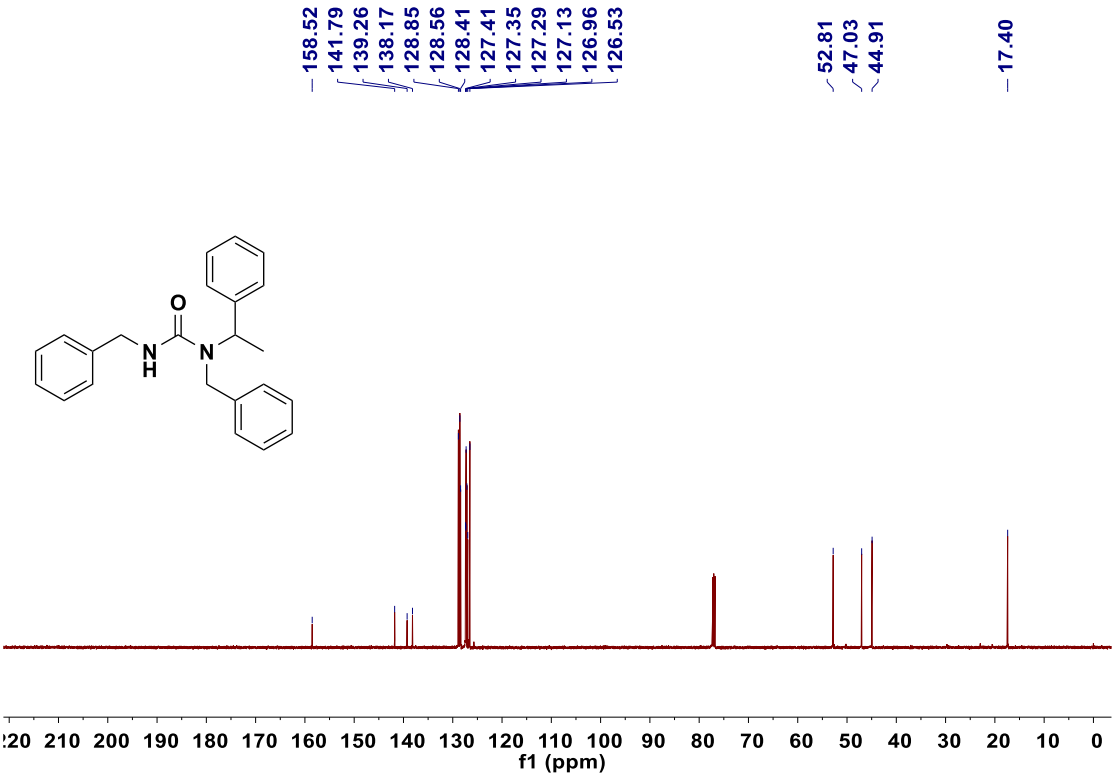
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 3-benzyl-1,1-dicyclohexylurea (3ap)



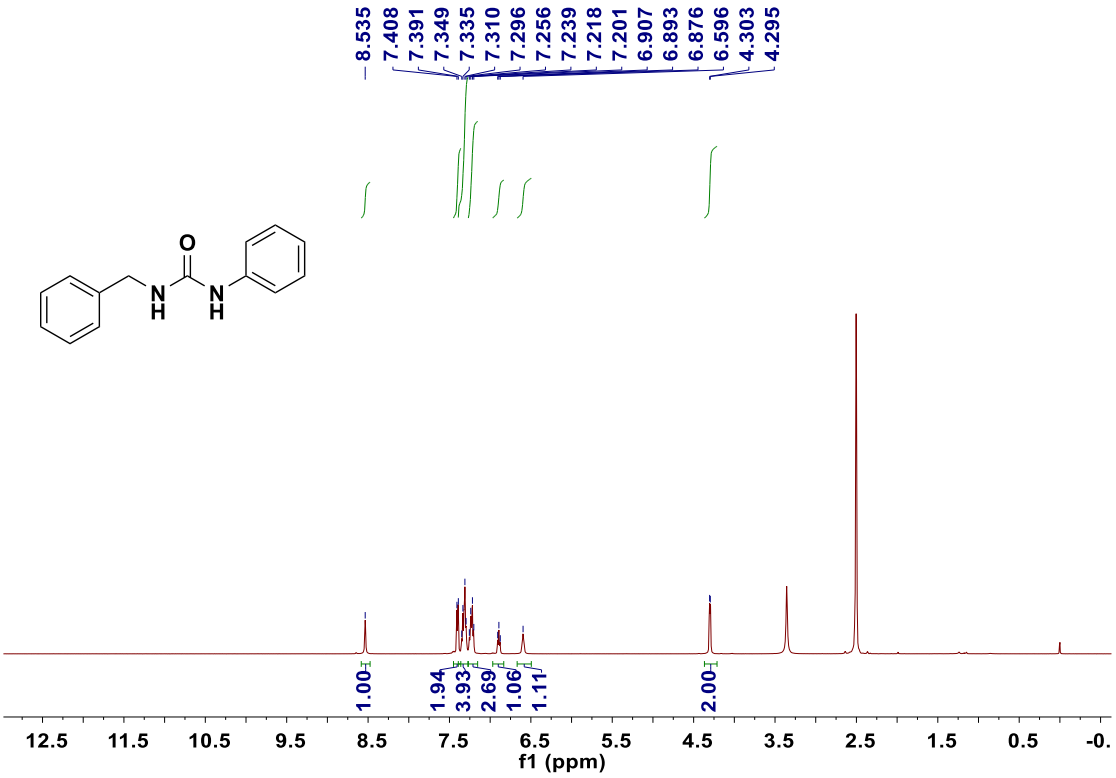
^{1}H NMR (500MHz, $CDCl_3$) of 1,3-dibenzyl-1-(1-phenylethyl)urea(3aq)



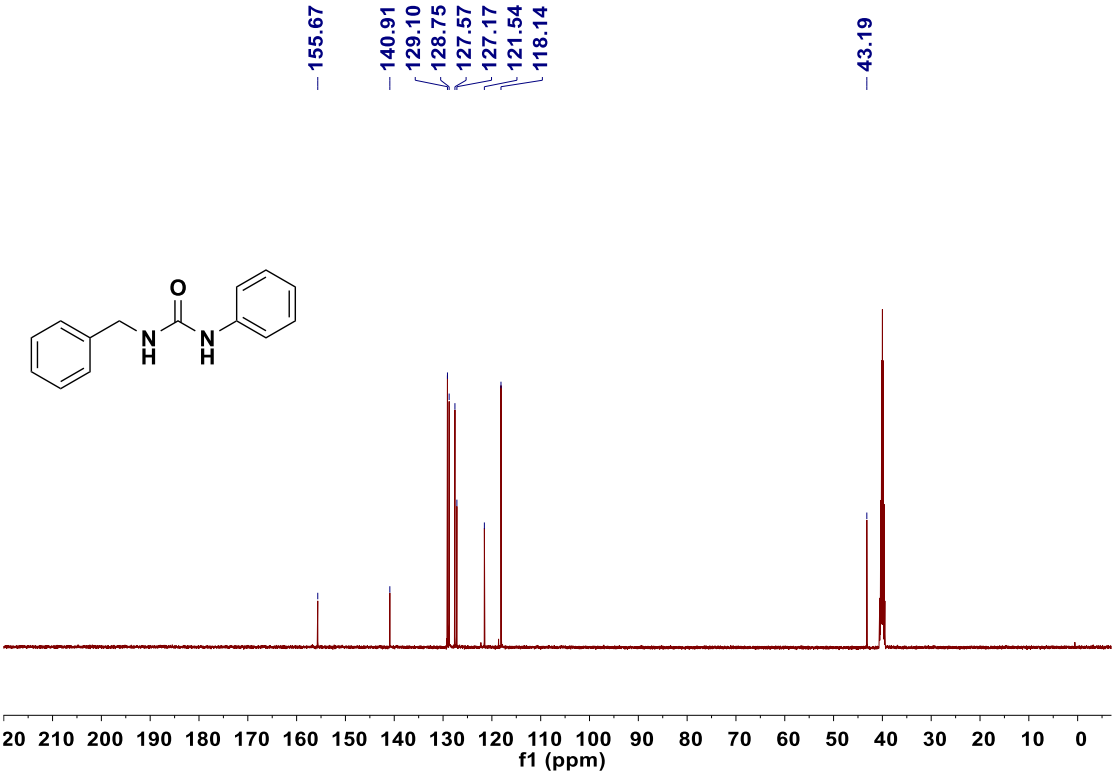
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 1,3-dibenzyl-1-(1-phenylethyl)urea(3aq)



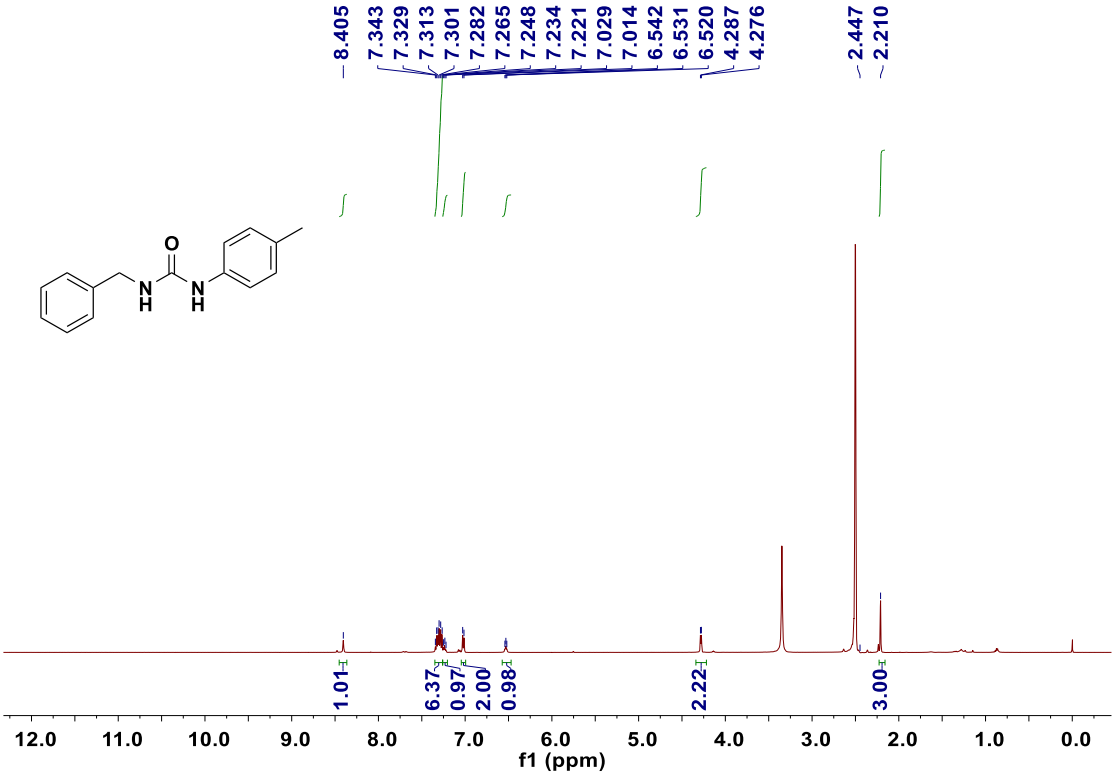
^{1}H NMR (500MHz, DMSO-d_6) of 1-benzyl-3-phenylurea (3ar)



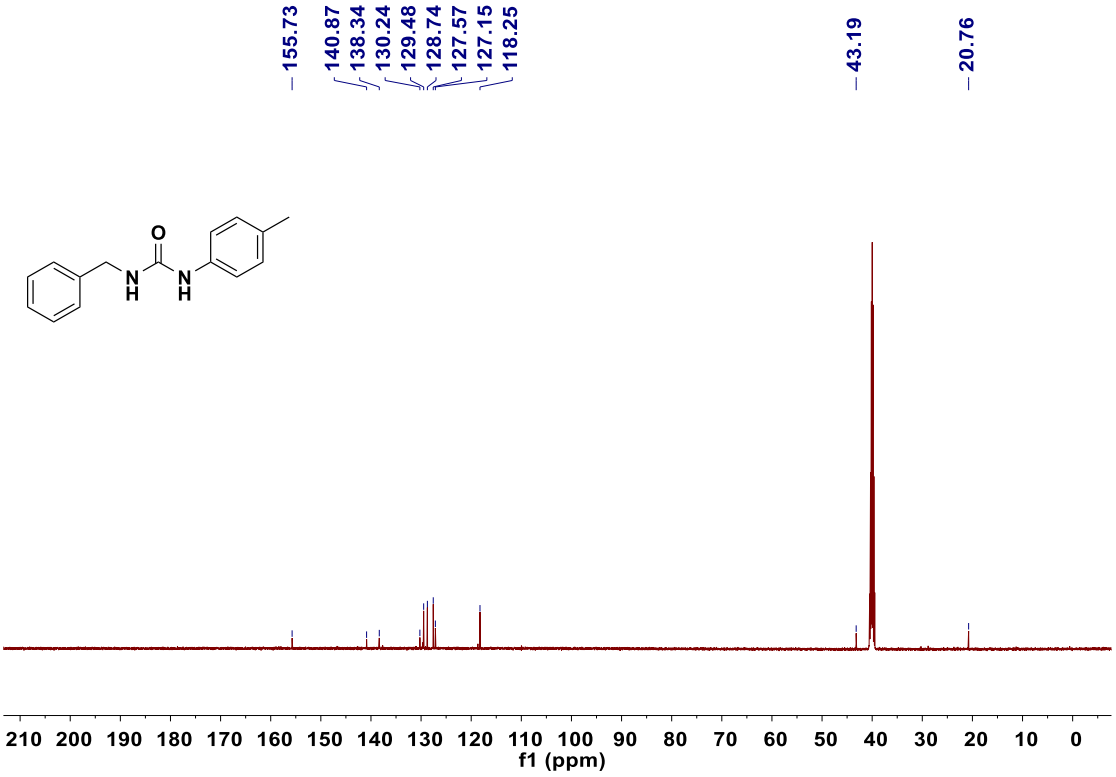
^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1-benzyl-3-phenylurea (3ar)



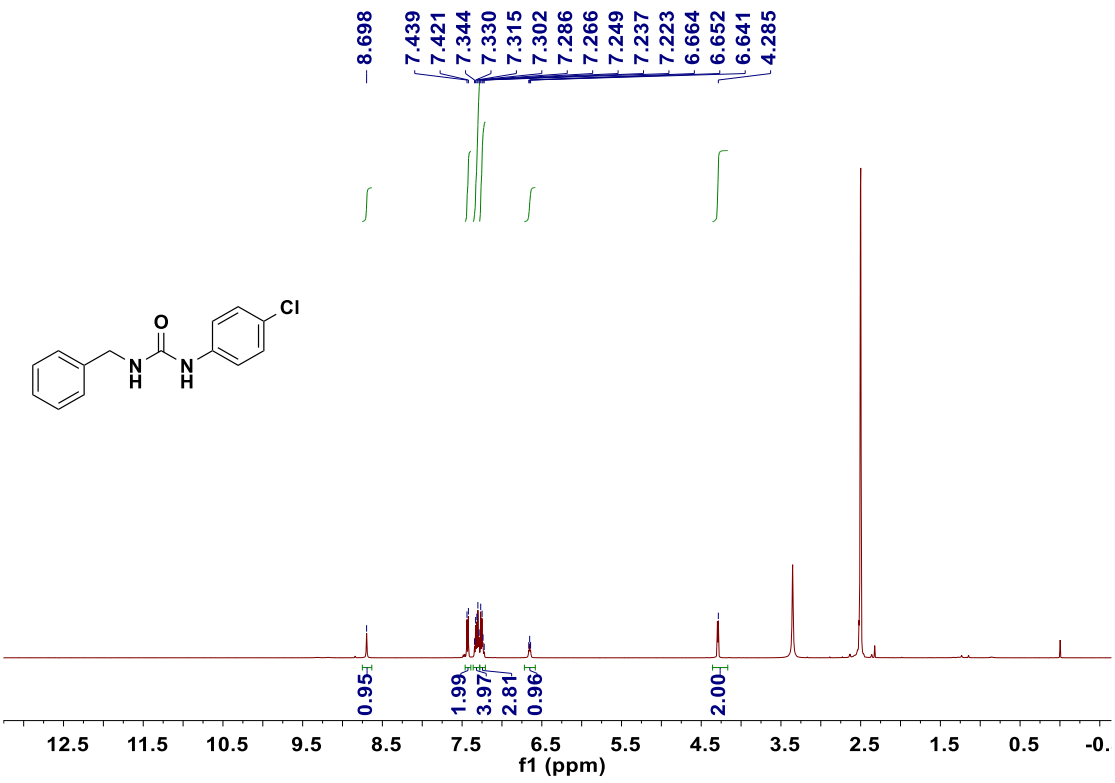
^{1}H NMR (500MHz, DMSO-d_6) of 1-benzyl-3-(p-tolyl)urea (3as)



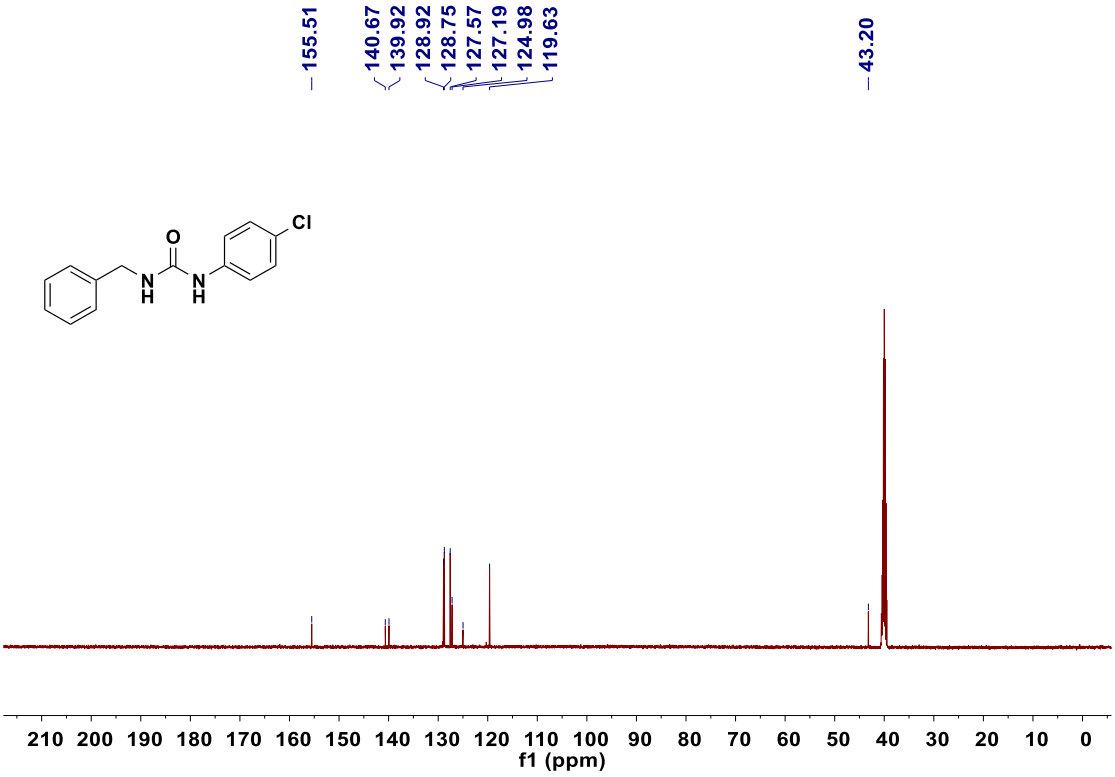
^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1-benzyl-3-(p-tolyl)urea (3as)



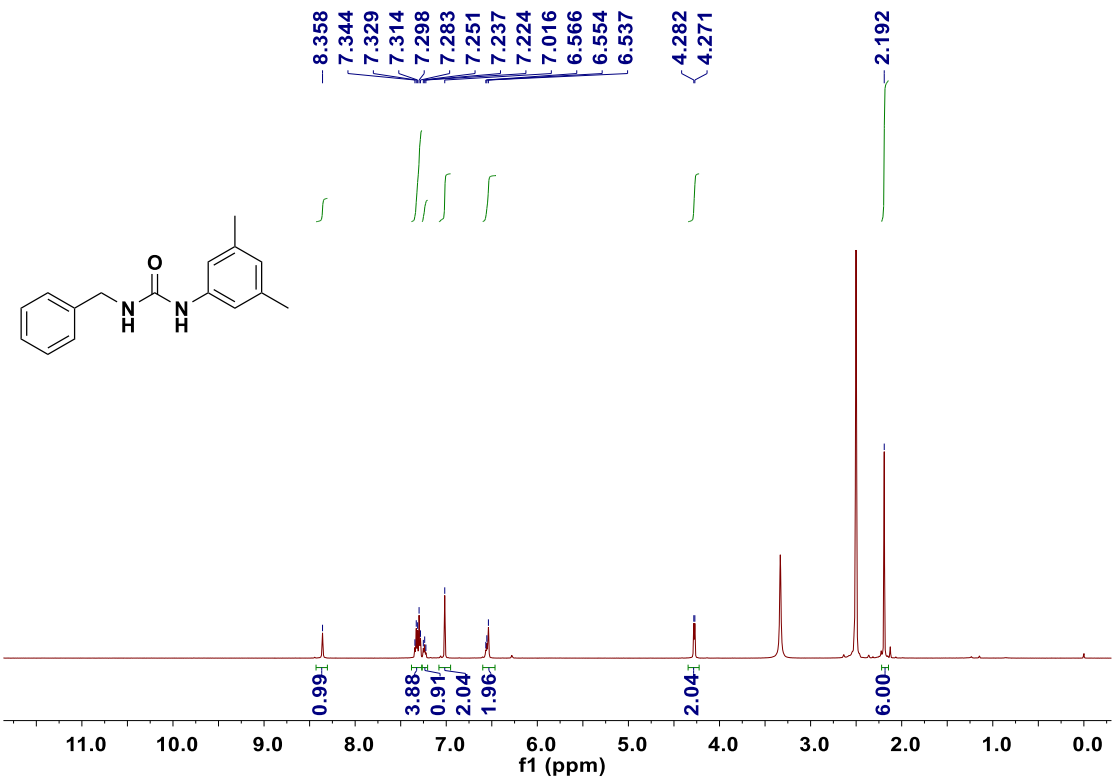
^{1}H NMR (500MHz, DMSO-d_6) of 1-benzyl-3-(4-chlorophenyl)urea (3at)



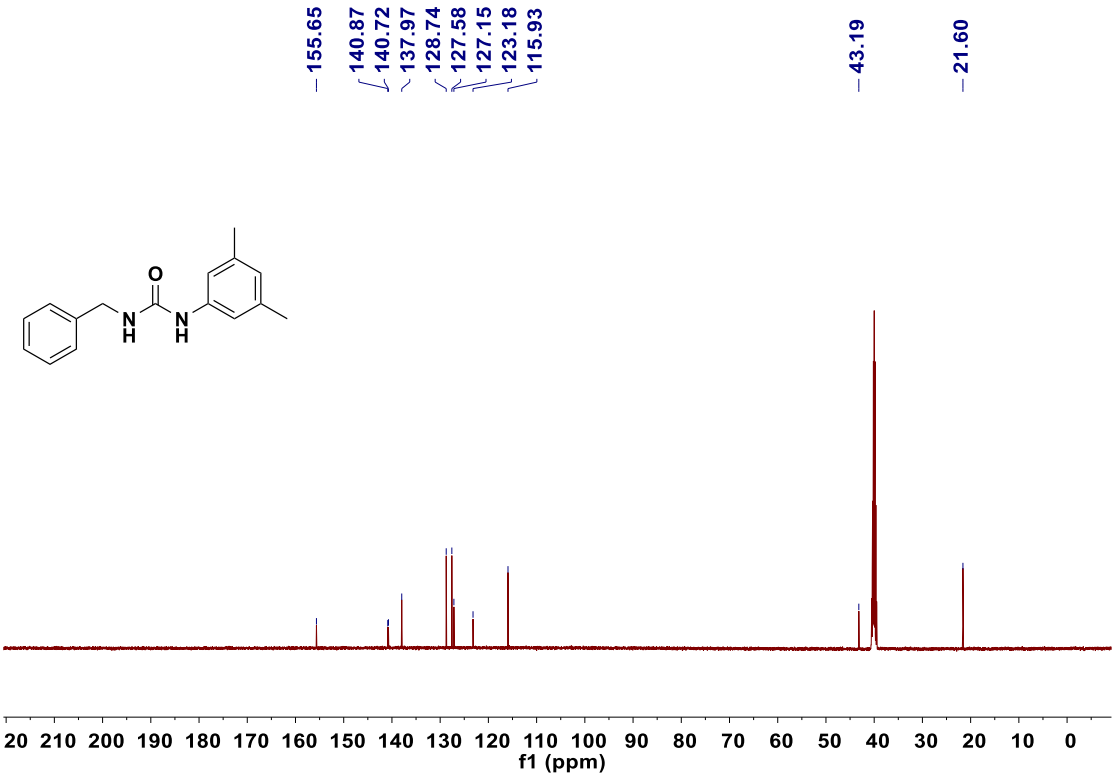
^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1-benzyl-3-(4-chlorophenyl)urea (3at)



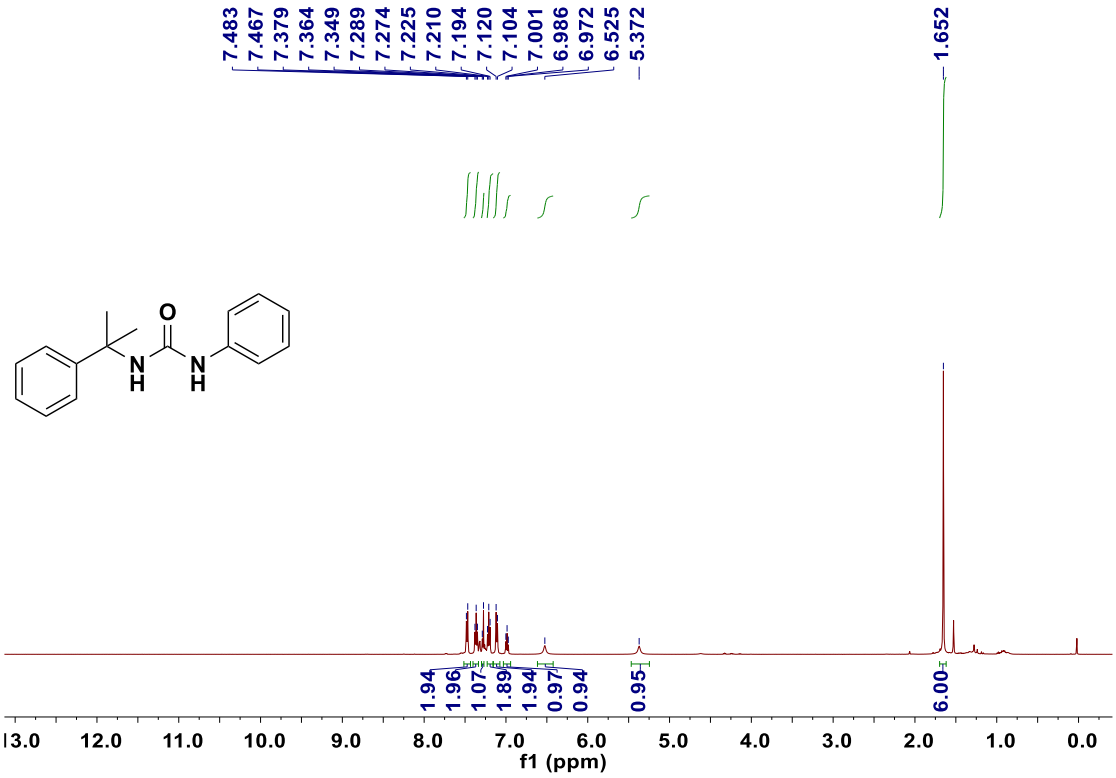
^{1}H NMR (500MHz, DMSO-d_6) of 1-benzyl-3-(3,5-dimethylphenyl)urea (3au)



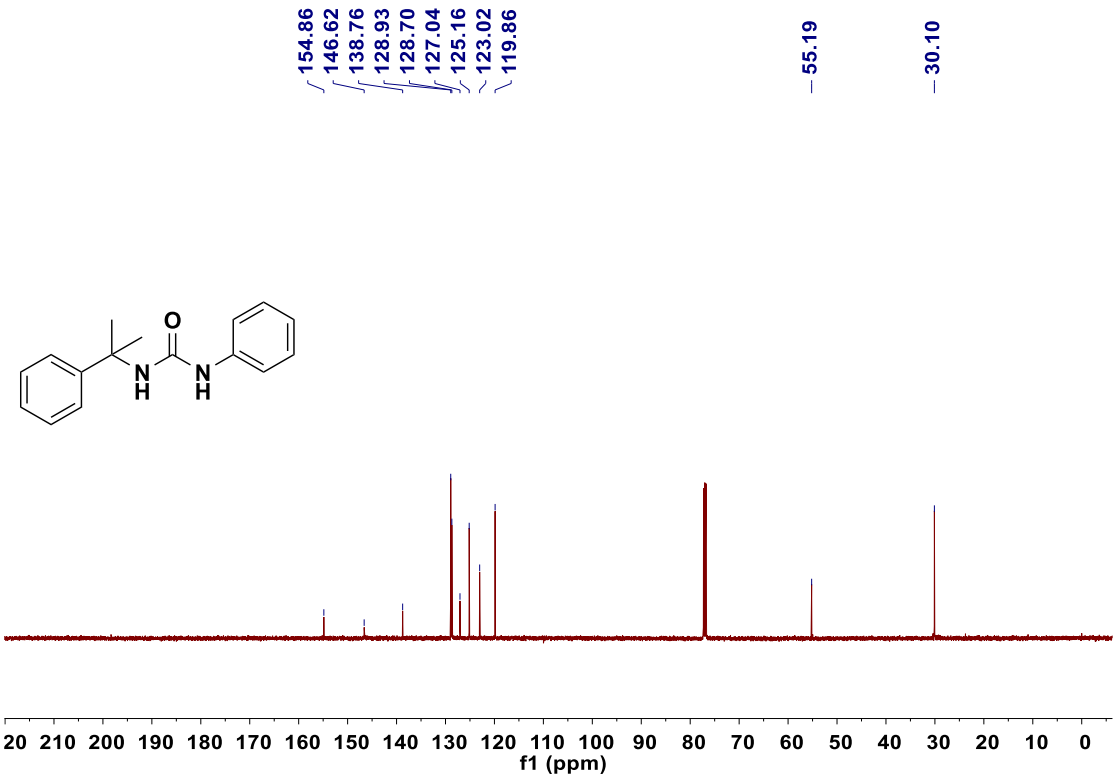
^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1-benzyl-3-(3,5-dimethylphenyl)urea (3au)



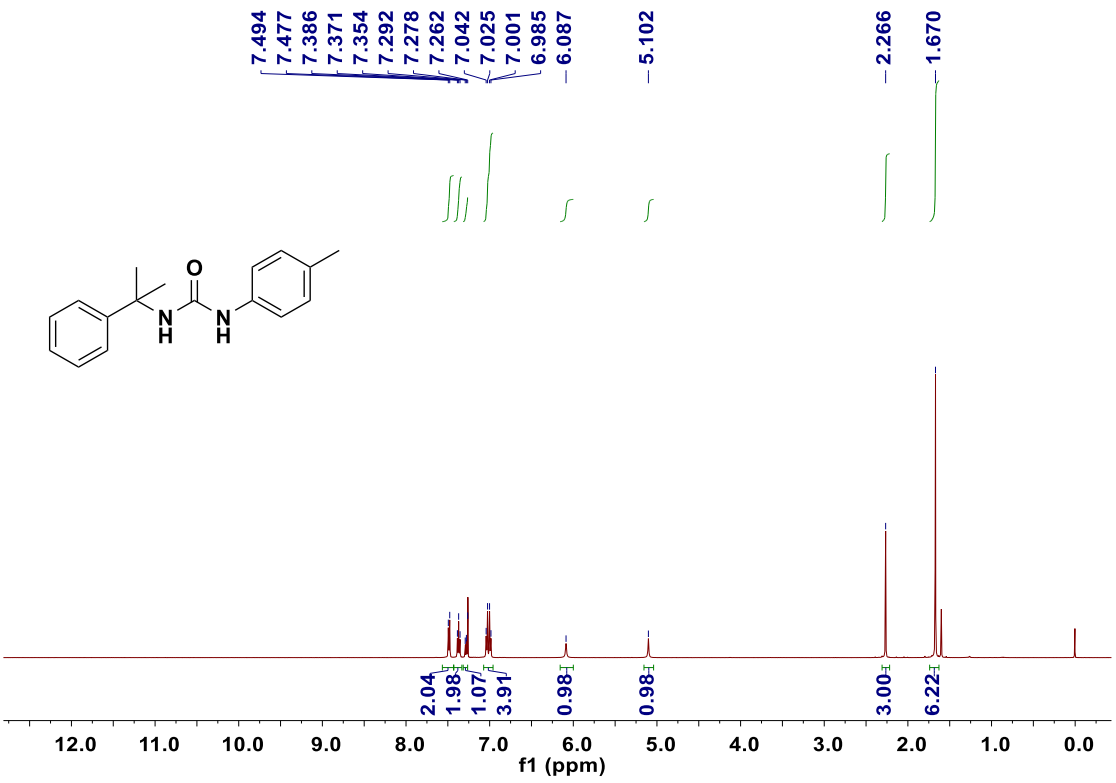
^{1}H NMR (500MHz, $CDCl_3$) of 1-phenyl-3-(2-phenylpropan-2-yl)urea (3av)



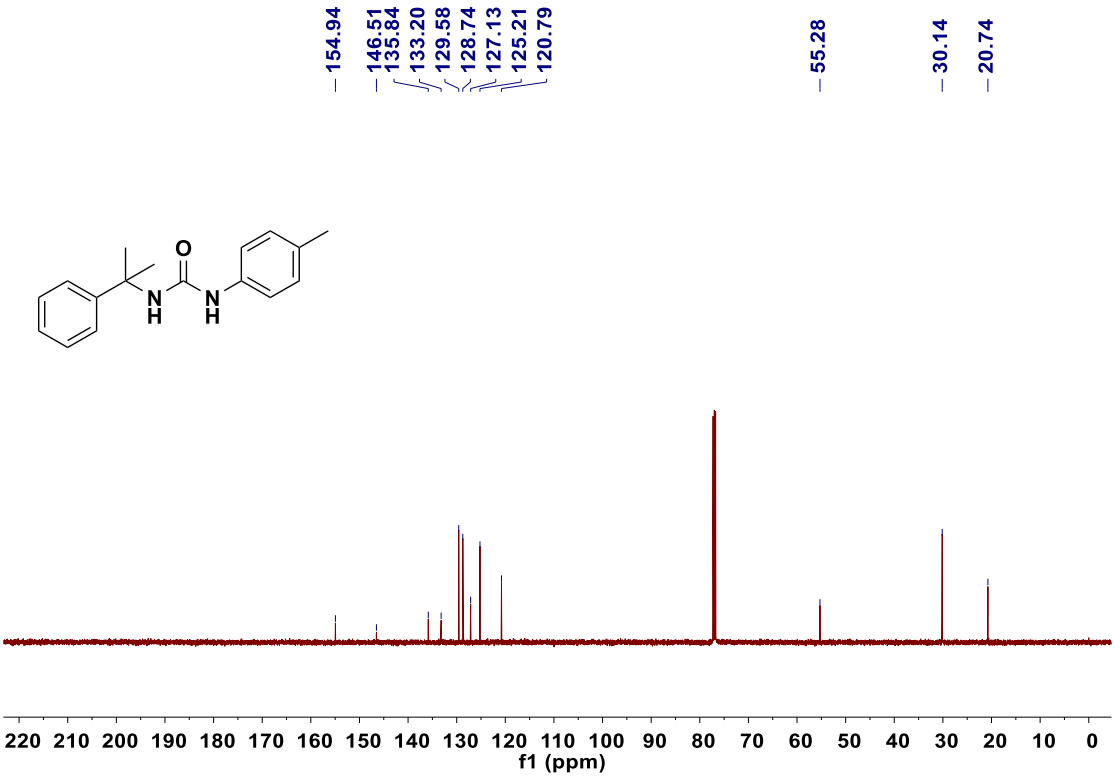
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 1-phenyl-3-(2-phenylpropan-2-yl)urea (3av)



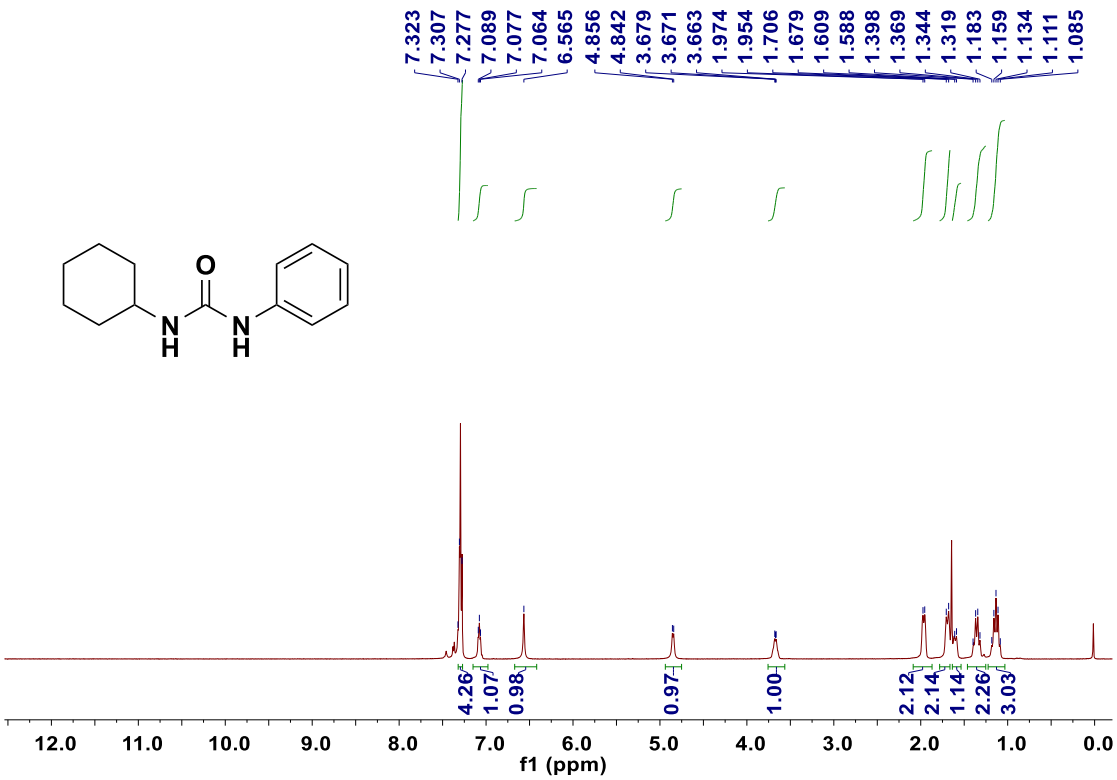
^{1}H NMR (500MHz, $CDCl_3$) of 1-(2-phenylpropan-2-yl)-3-(p-tolyl)urea (3aw)



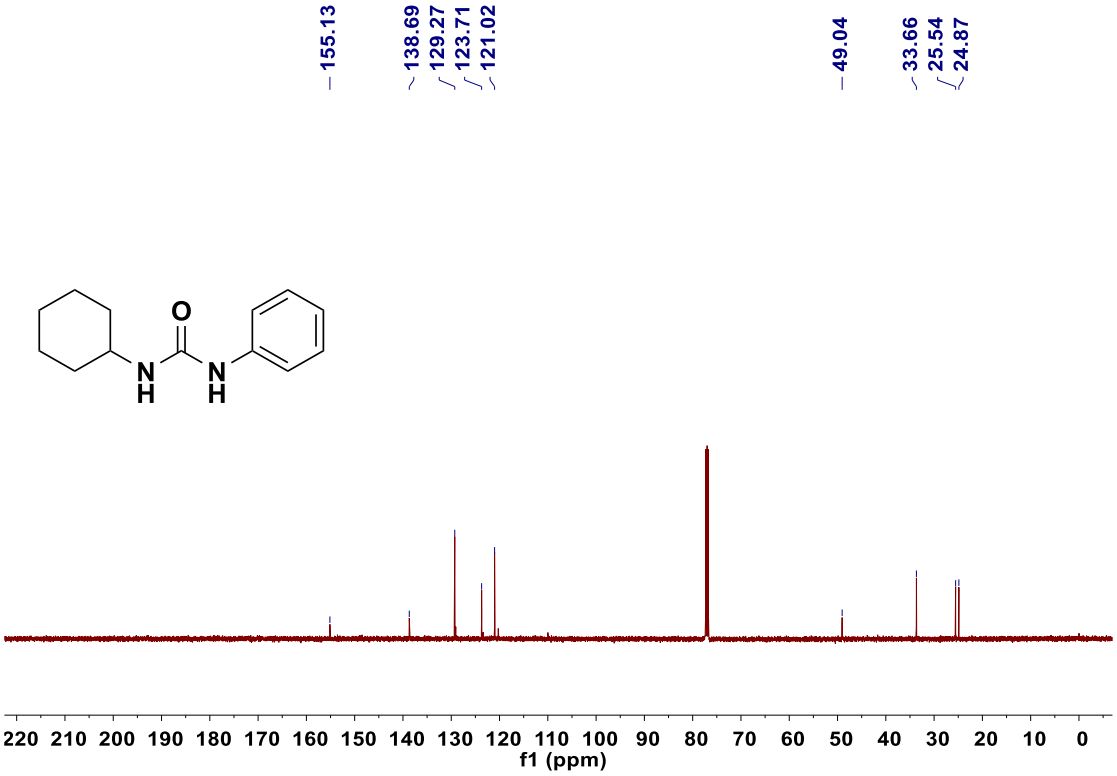
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 1-(2-phenylpropan-2-yl)-3-(p-tolyl)urea (3aw)



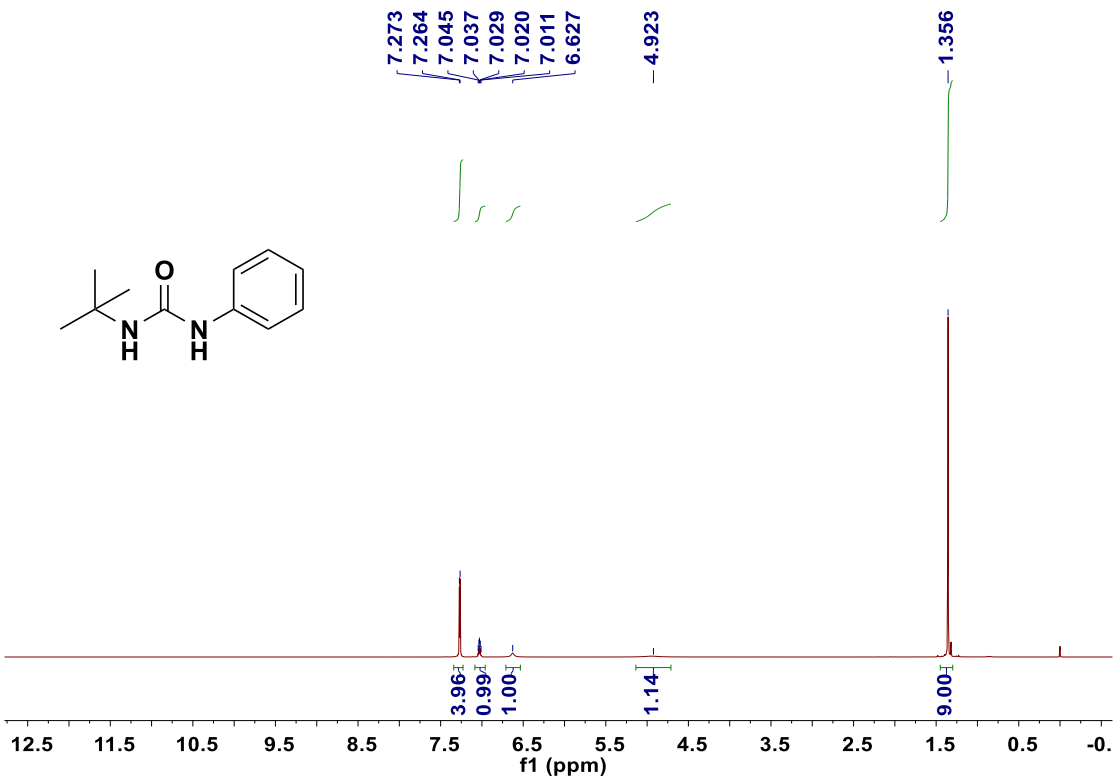
^{1}H NMR (500MHz, $CDCl_3$) of 1-cyclohexyl-3-phenylurea (3ax)



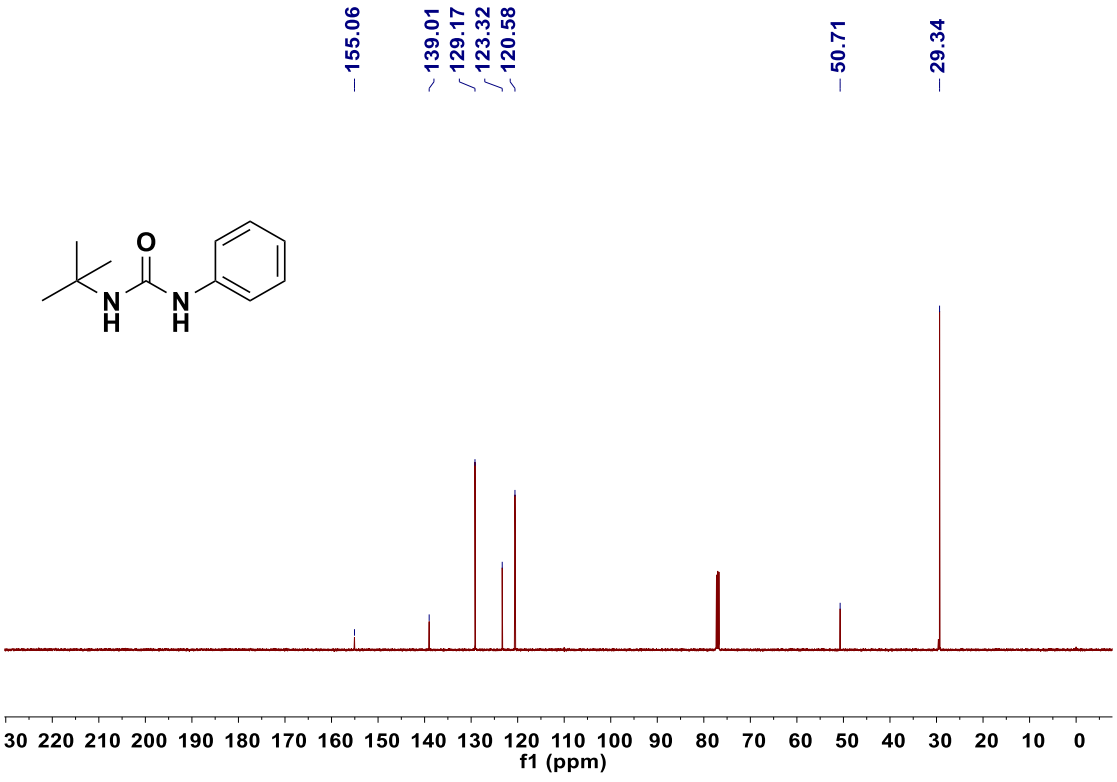
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 1-cyclohexyl-3-phenylurea (3ax)



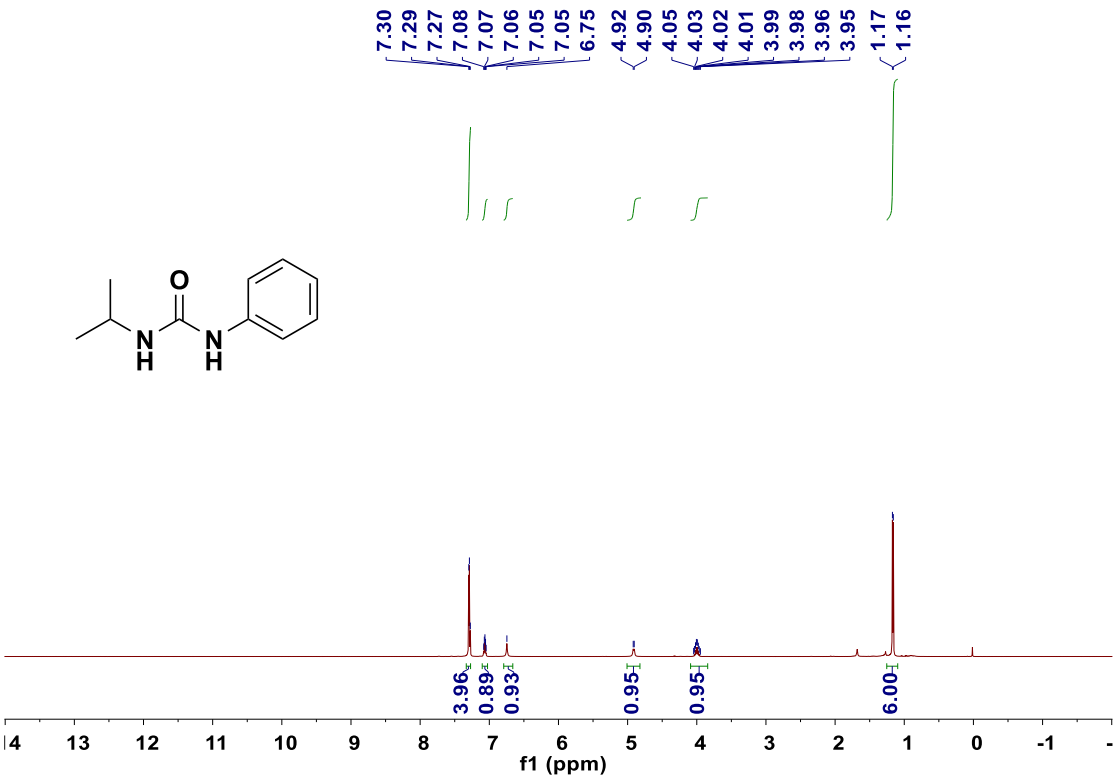
^{1}H NMR (500MHz, $CDCl_3$) of 1-(tert-butyl)-3-phenylurea (3ay)



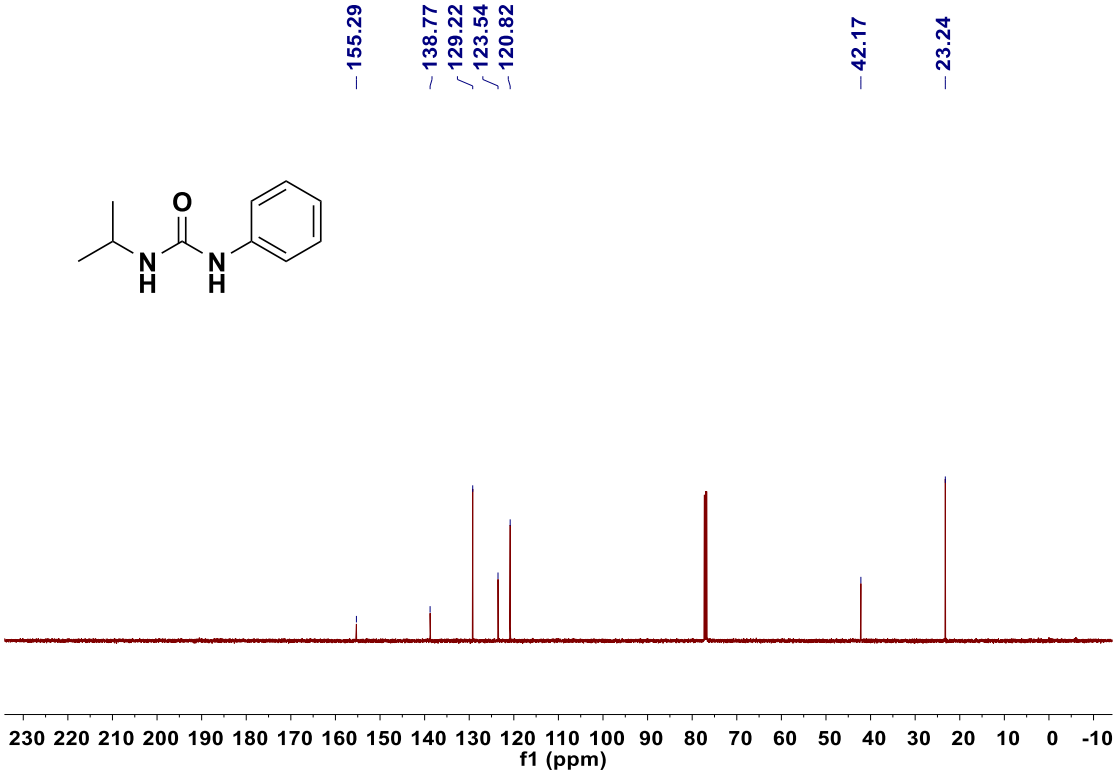
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 1-(tert-butyl)-3-phenylurea (3ay)



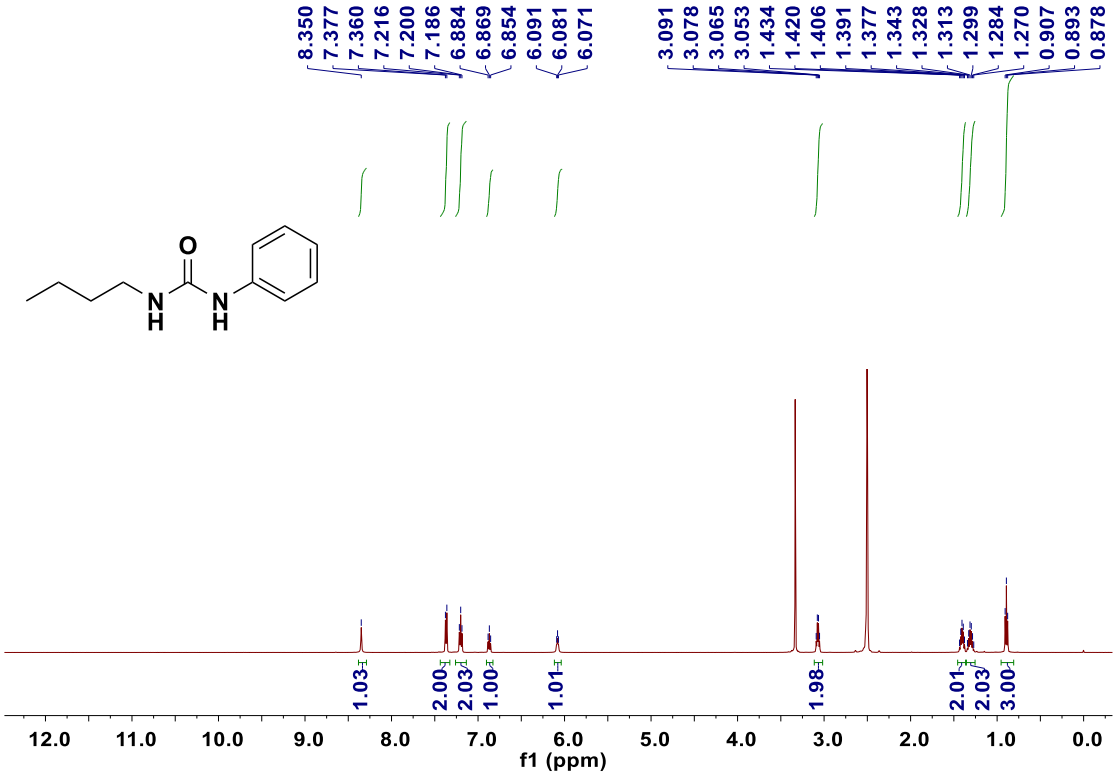
^{1}H NMR (500MHz, $CDCl_3$) of 1-isopropyl-3-phenylurea (3az)



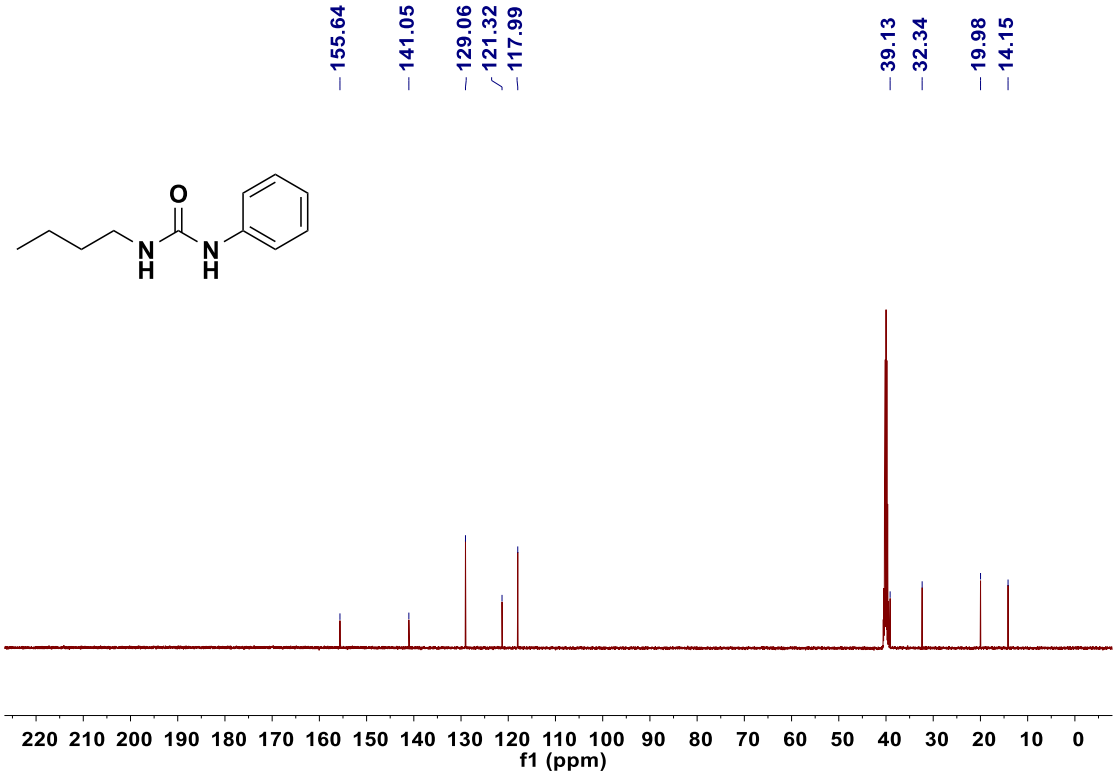
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 1-isopropyl-3-phenylurea (3az)



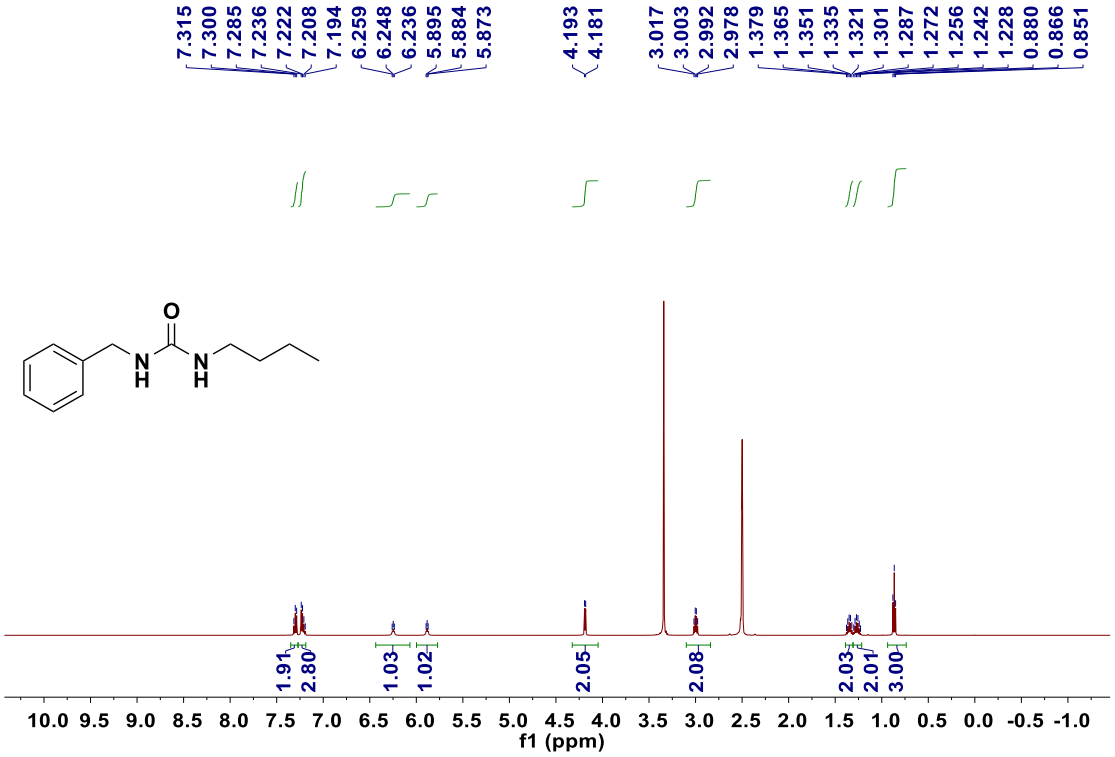
^{1}H NMR (500MHz, DMSO-d$_6$) of 1-butyl-3-phenylurea (3ba)



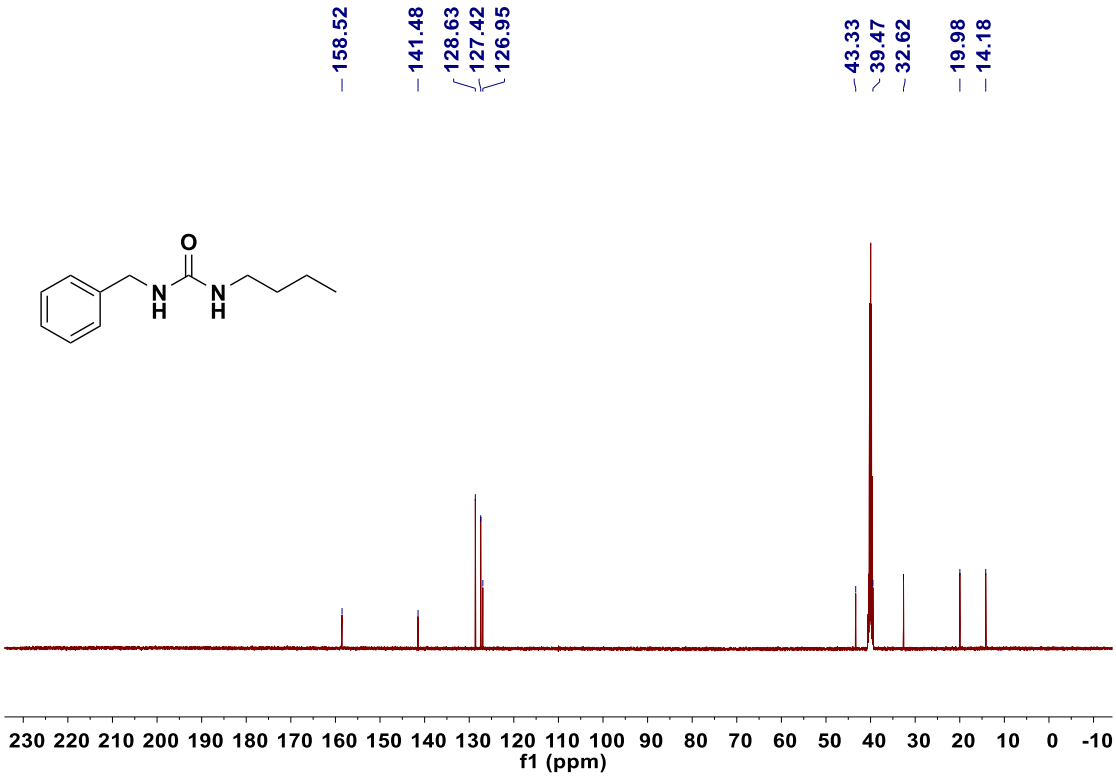
^{13}C{^{1}H} NMR (126MHz, DMSO-d$_6$) of 1-butyl-3-phenylurea (3ba)



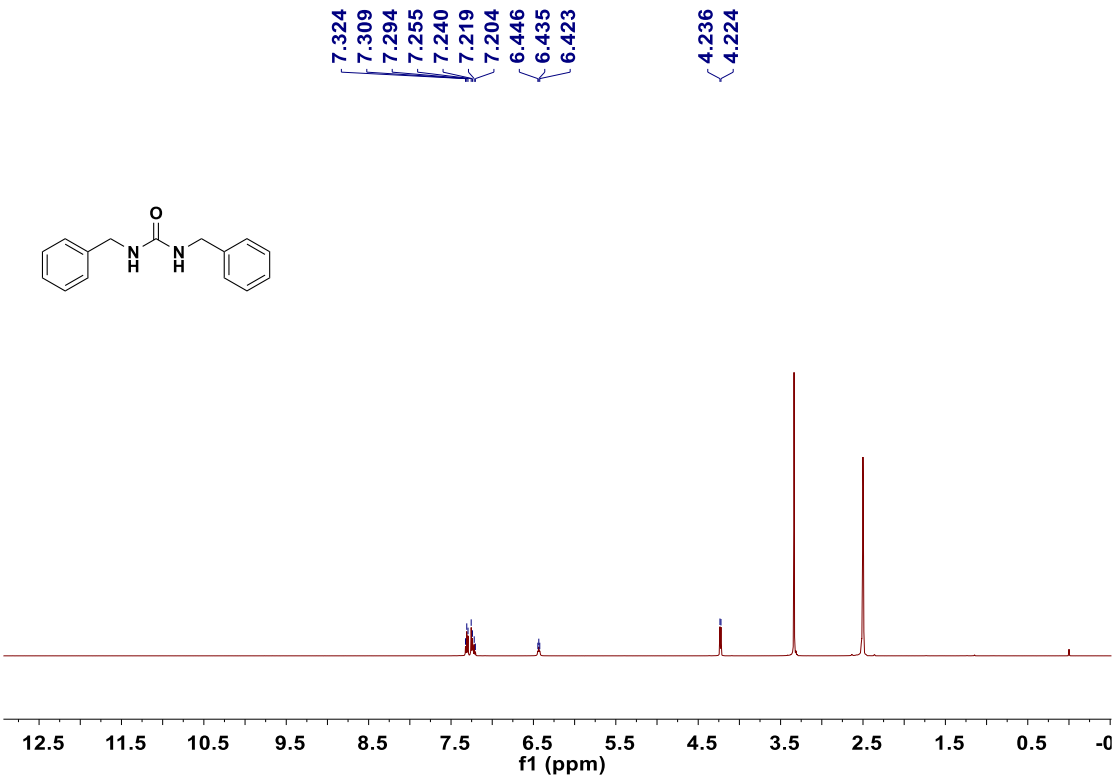
^{1}H NMR (500MHz, DMSO-d_6) of 1-benzyl-3-butylurea (3bb)



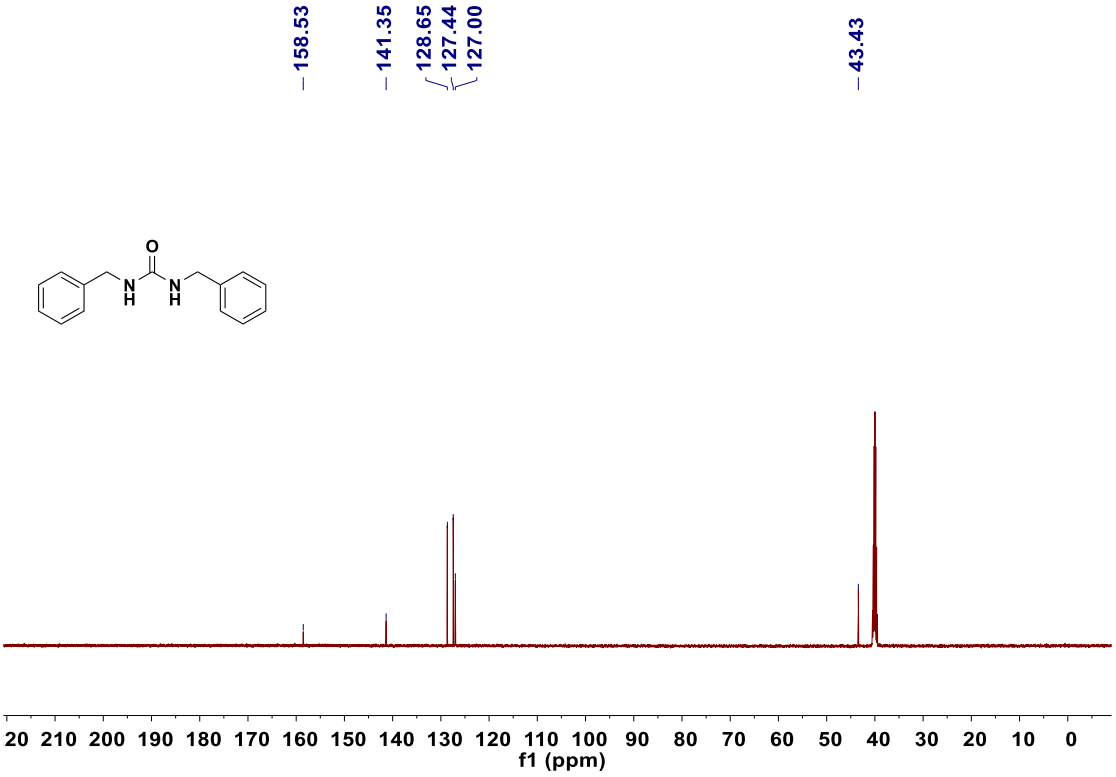
^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1-benzyl-3-butylurea (3bb)



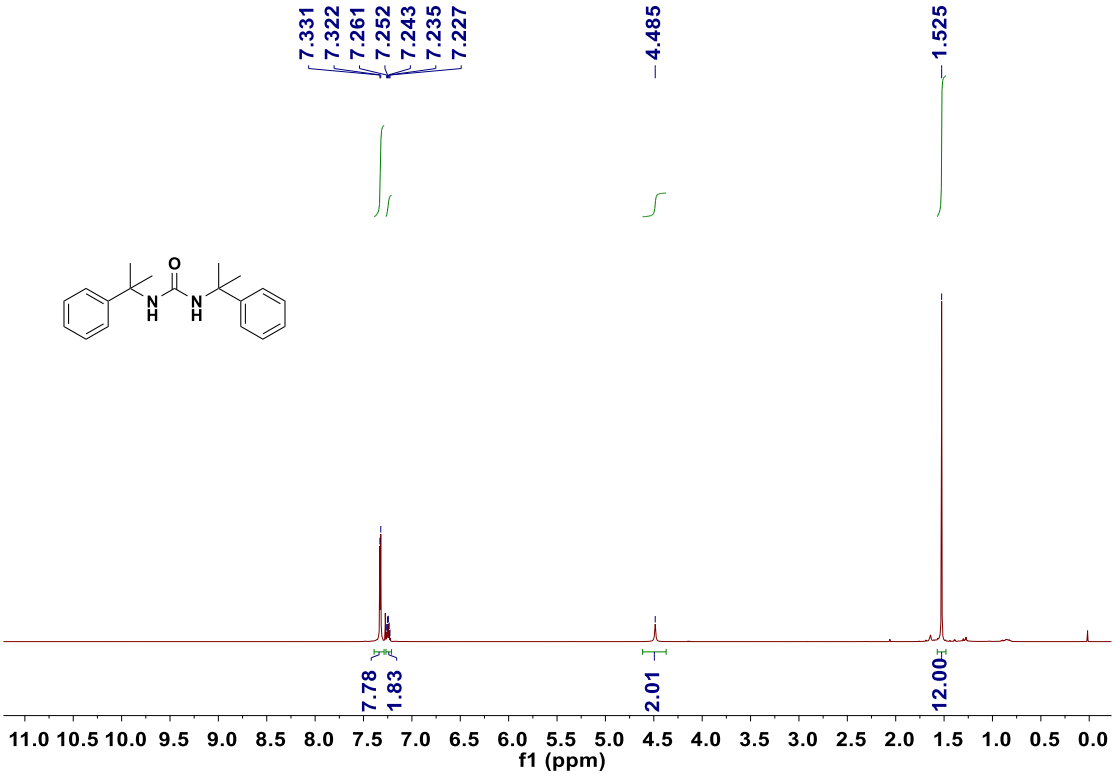
^{1}H NMR (500MHz, DMSO-d_6) of 1,3-dibenzylurea (4a)



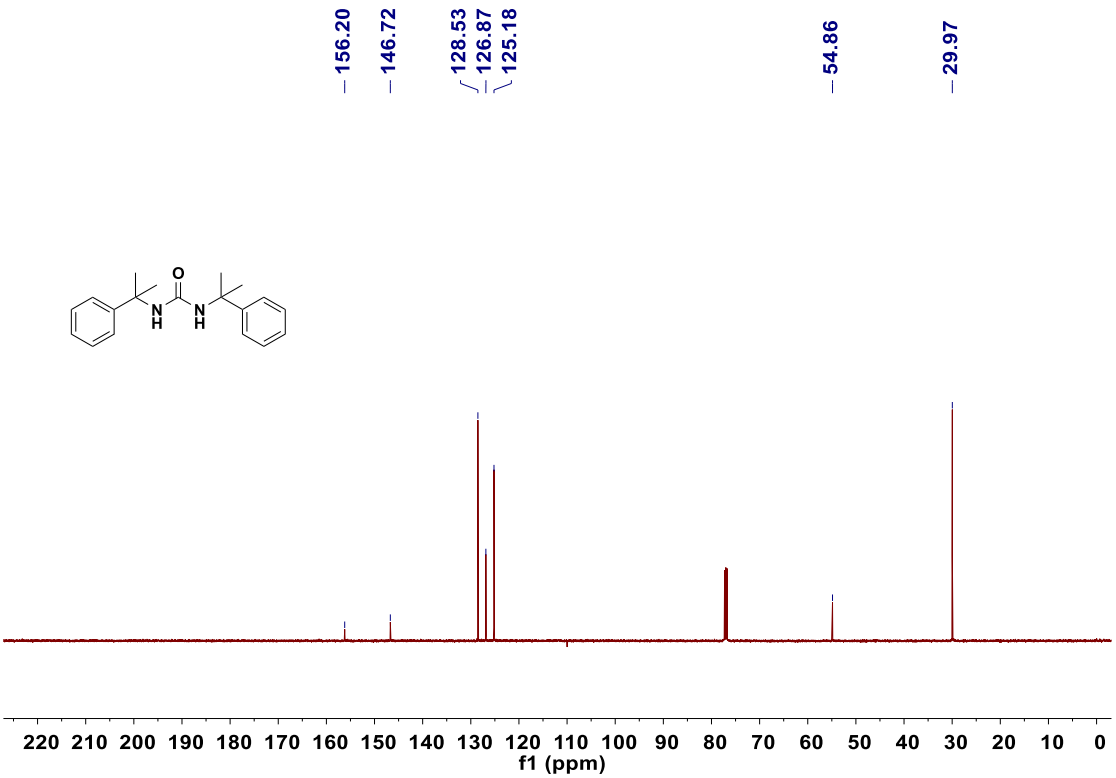
^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1,3-dibenzylurea (4a)



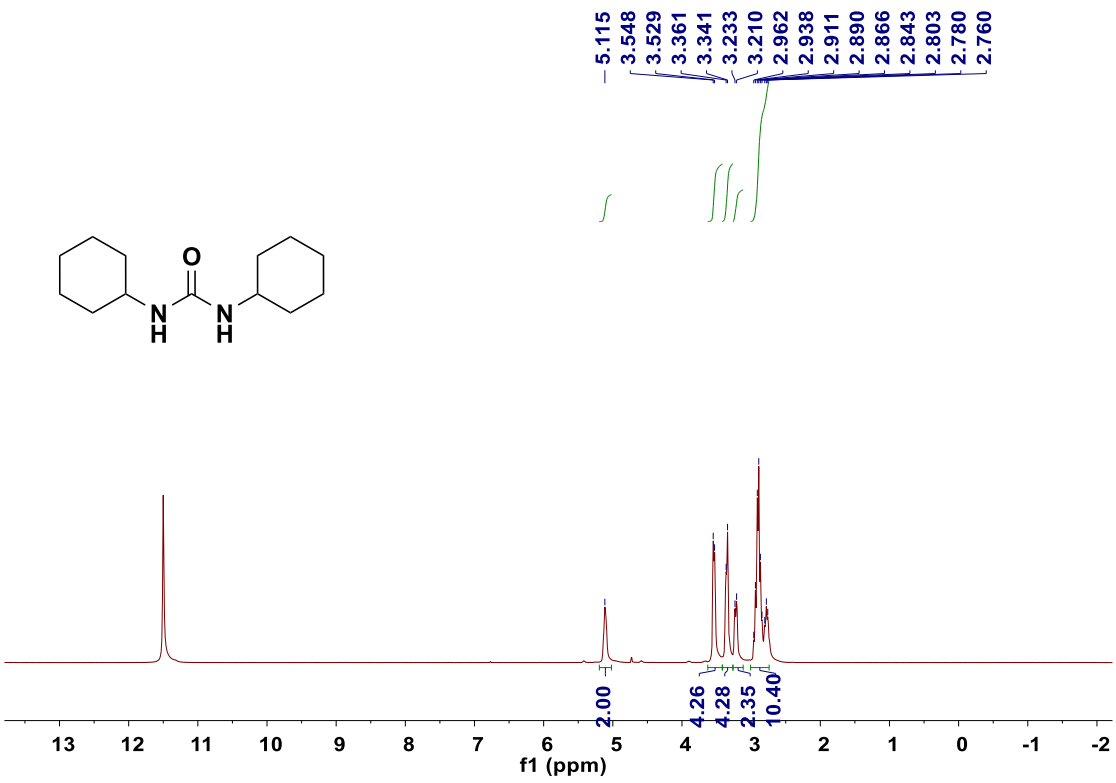
^{1}H NMR (500MHz, $CDCl_3$) of 1,3-bis(2-phenylpropan-2-yl)urea(4b)



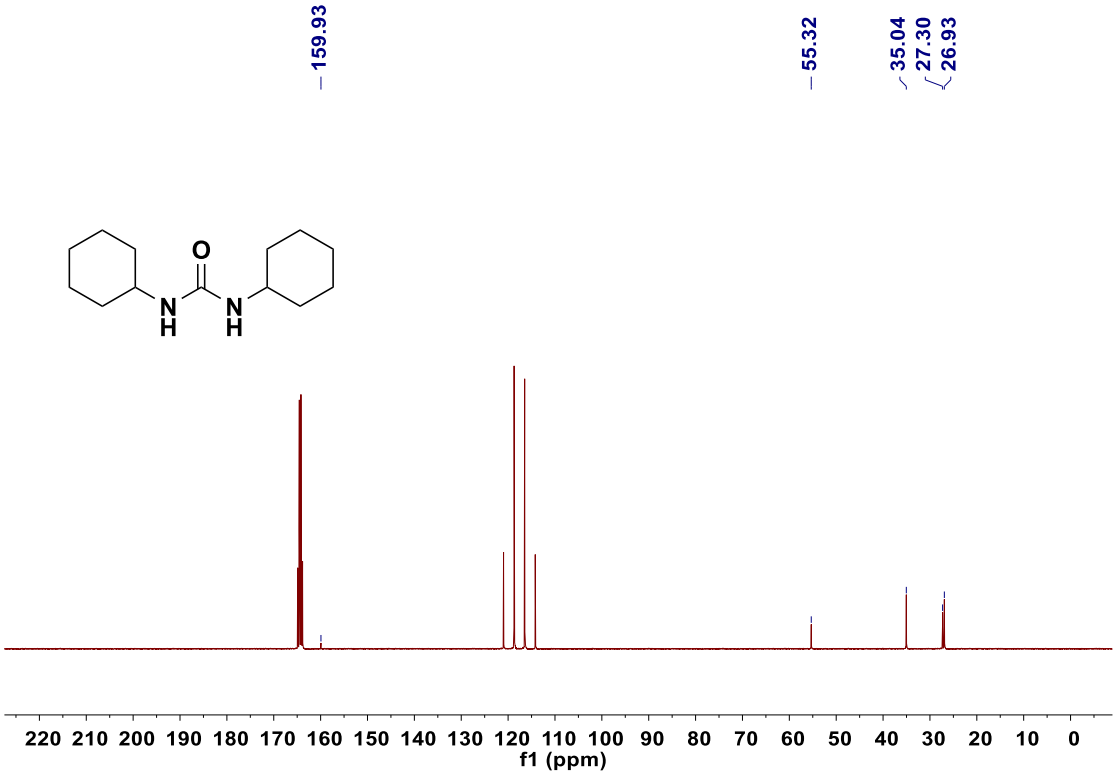
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 1,3-bis(2-phenylpropan-2-yl)urea(4b)



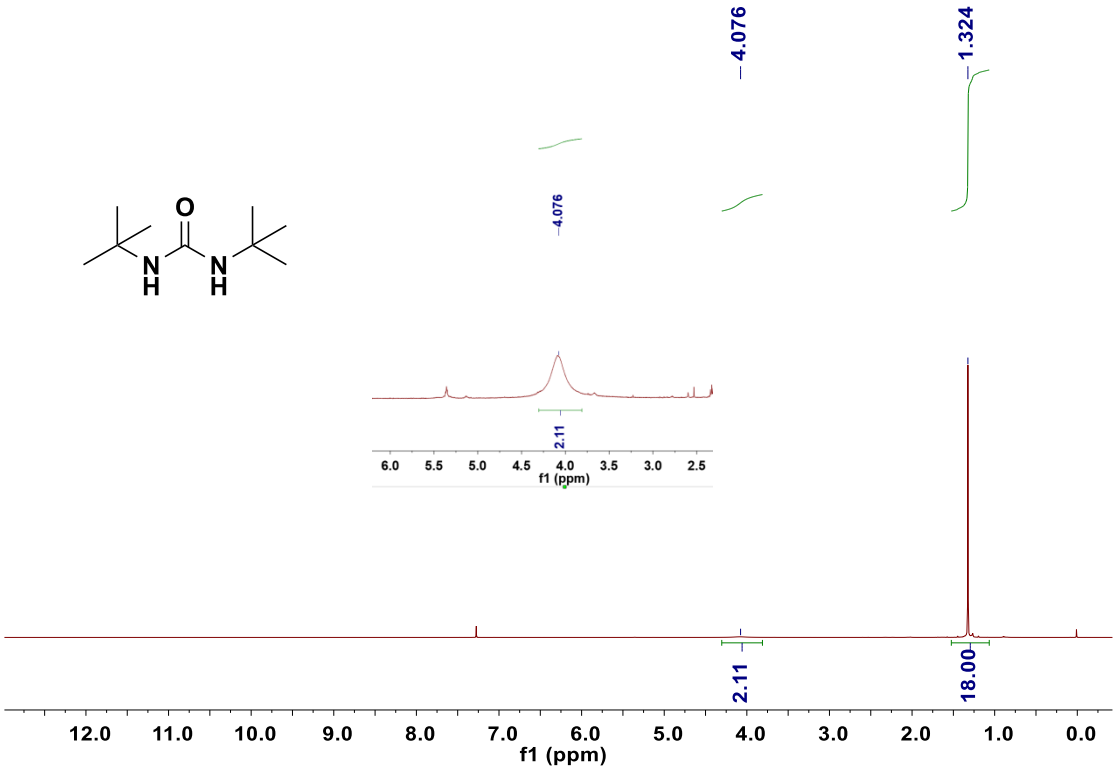
^{1}H NMR (500MHz, TFA-*d*) of 1,3-dicyclohexylurea (4c)



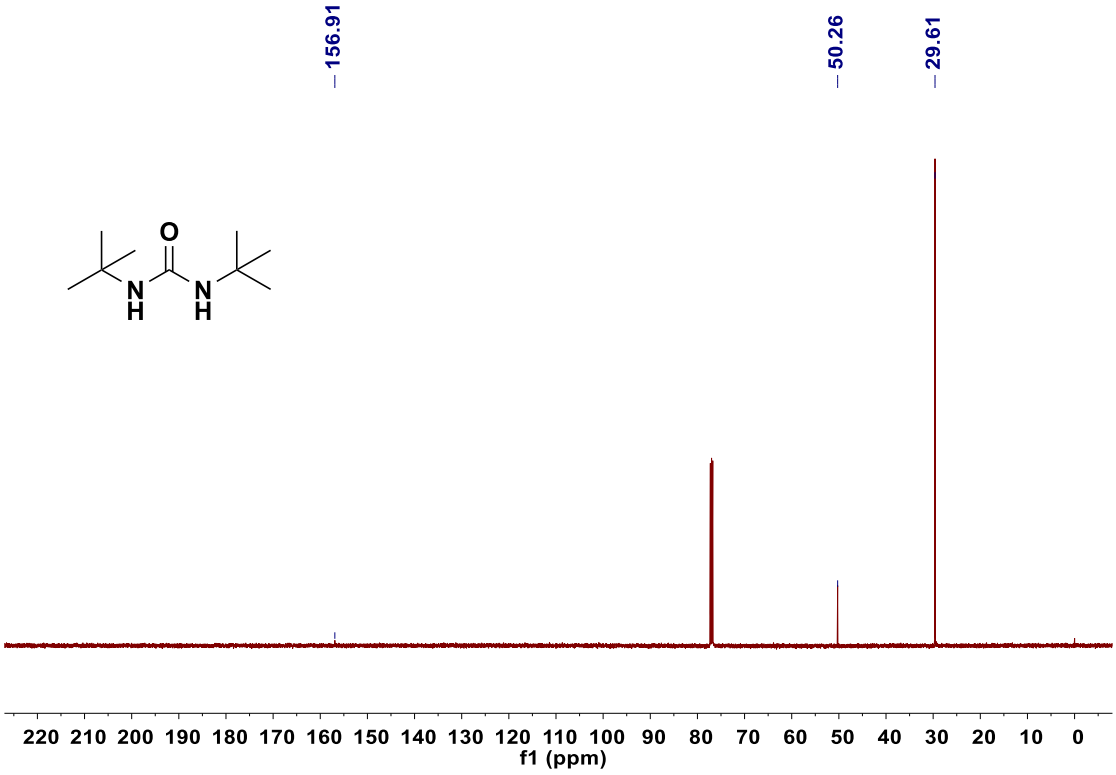
^{13}C{^{1}H} NMR (126MHz, TFA-*d*) of 1,3-dicyclohexylurea (4c)



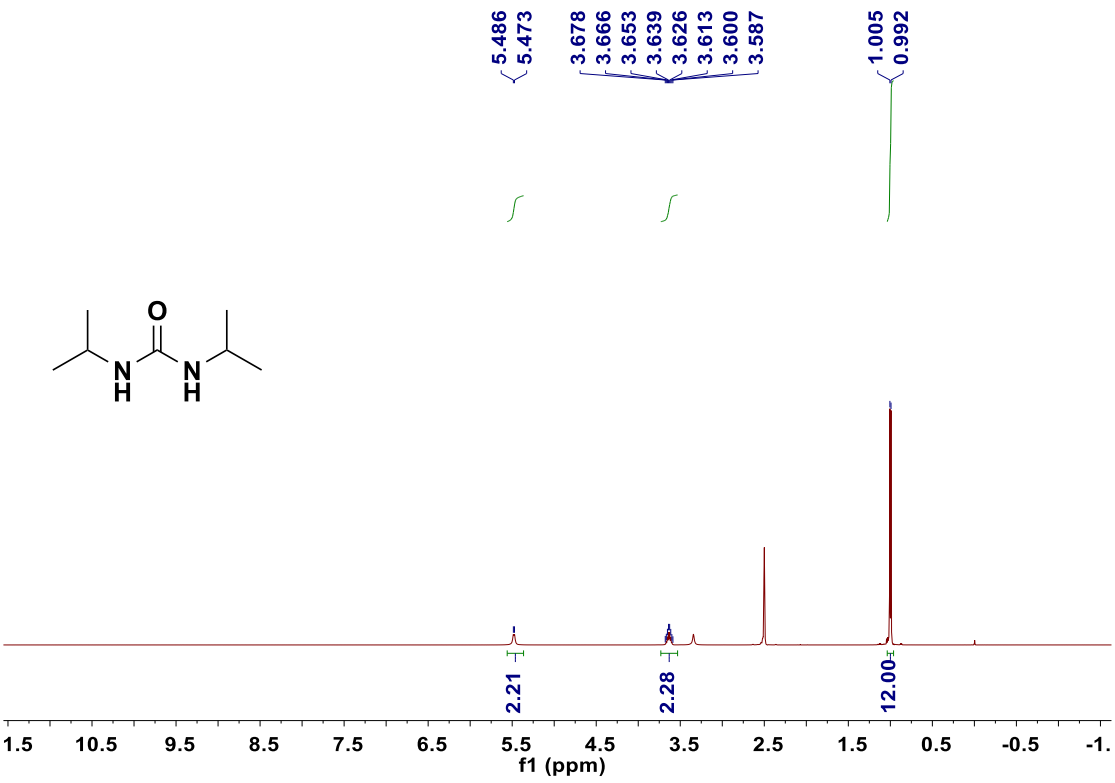
^{1}H NMR (500MHz, $CDCl_3$) of 1,3-di-tert-butylurea (4d)



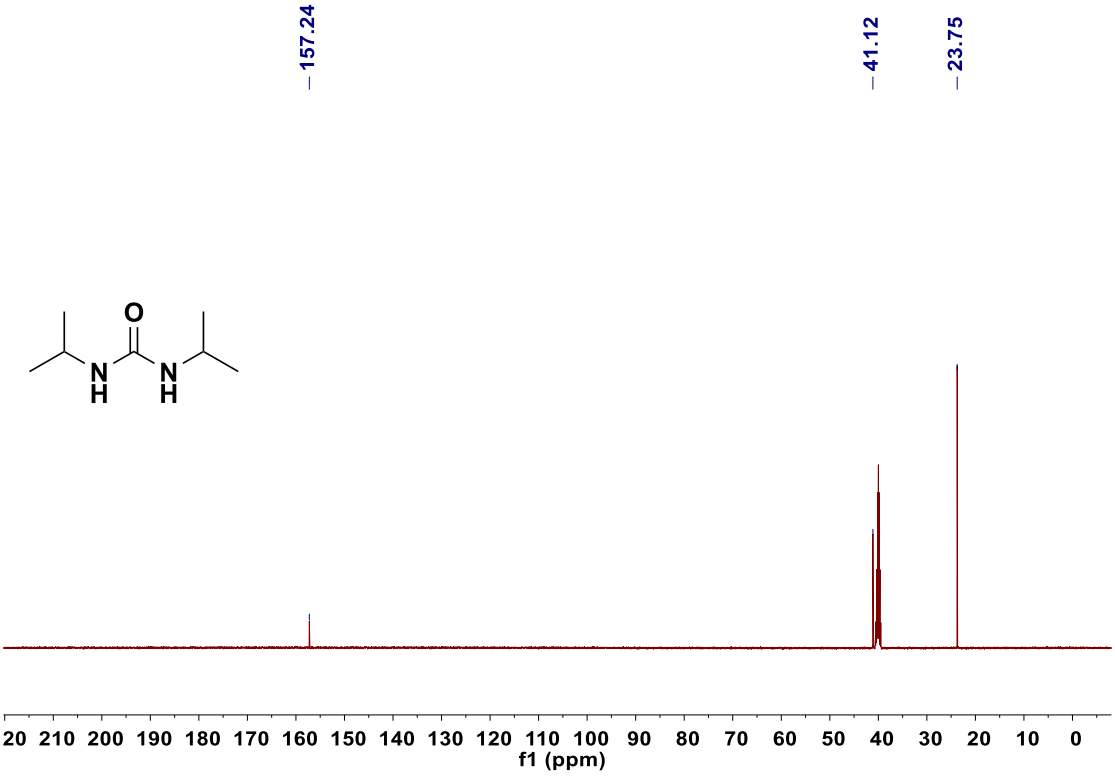
^{13}C{^{1}H} NMR (126MHz, $CDCl_3$) of 1,3-di-tert-butylurea (4d)



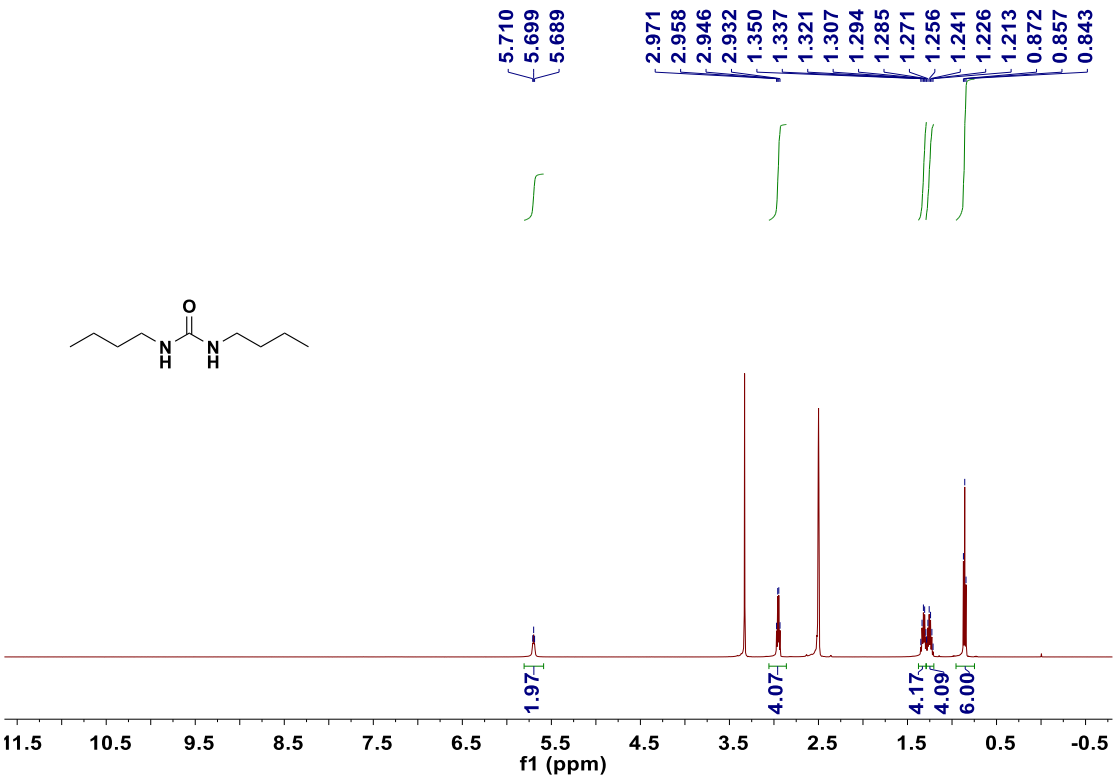
^{1}H NMR (500MHz, DMSO-d_6) of 1,3-diisopropylurea (4e):



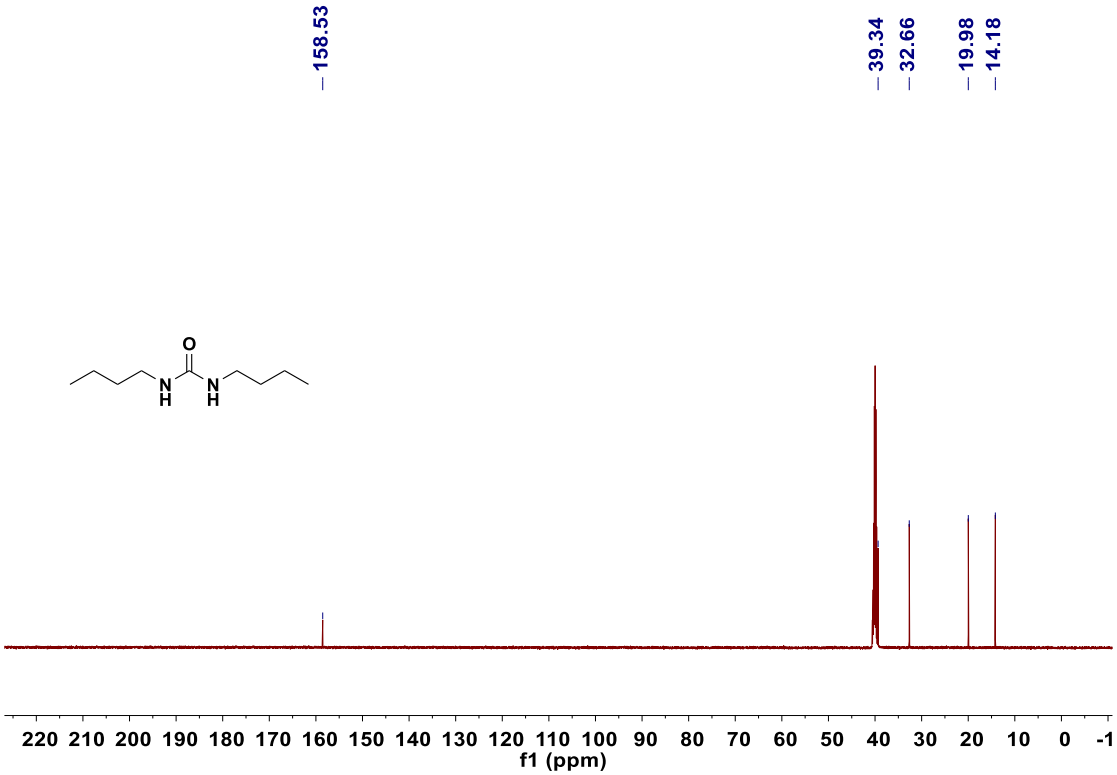
^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1,3-diisopropylurea (4e):



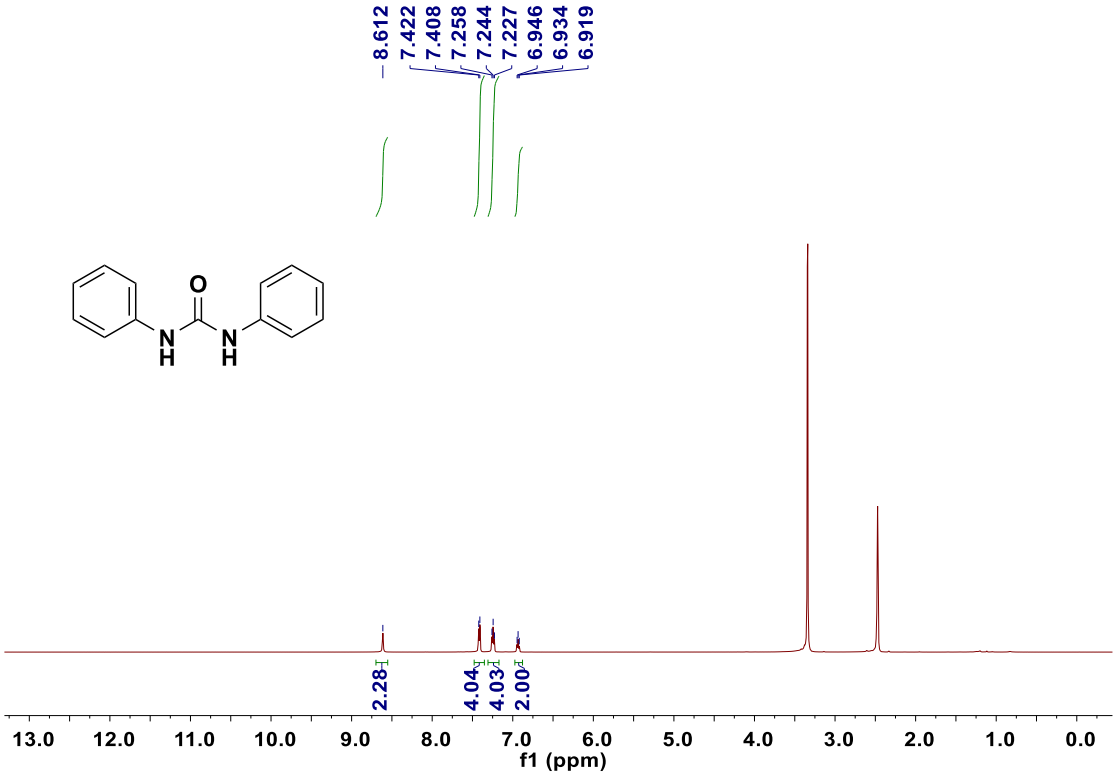
^{1}H NMR (500MHz, DMSO-d_6) of 1,3-dibutylurea (4f)



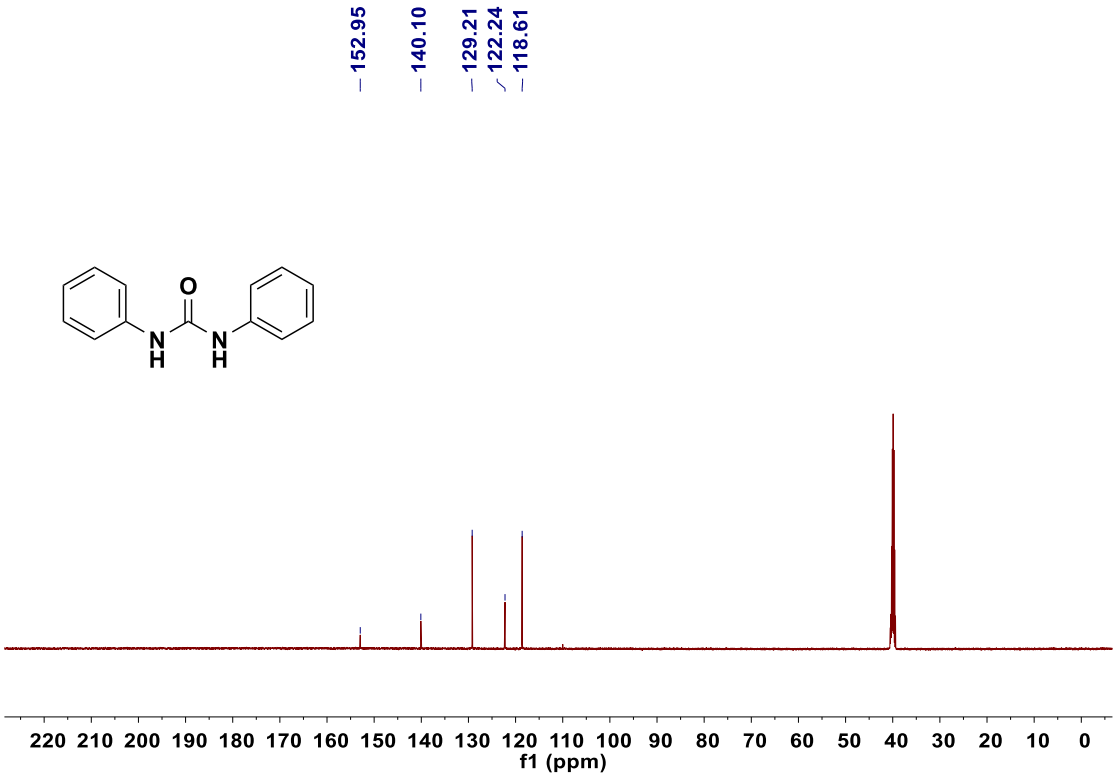
^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1,3-dibutylurea (4f)



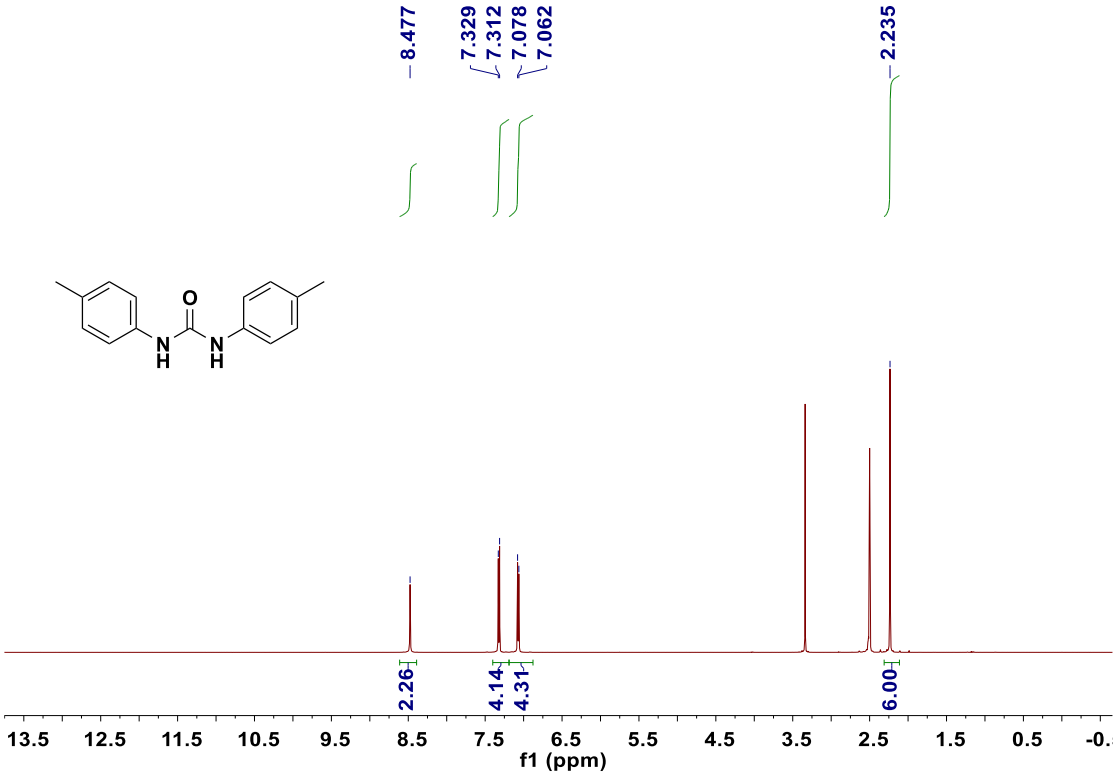
^{1}H NMR (500MHz, DMSO-d_6) of 1,3-diphenylurea (5a)



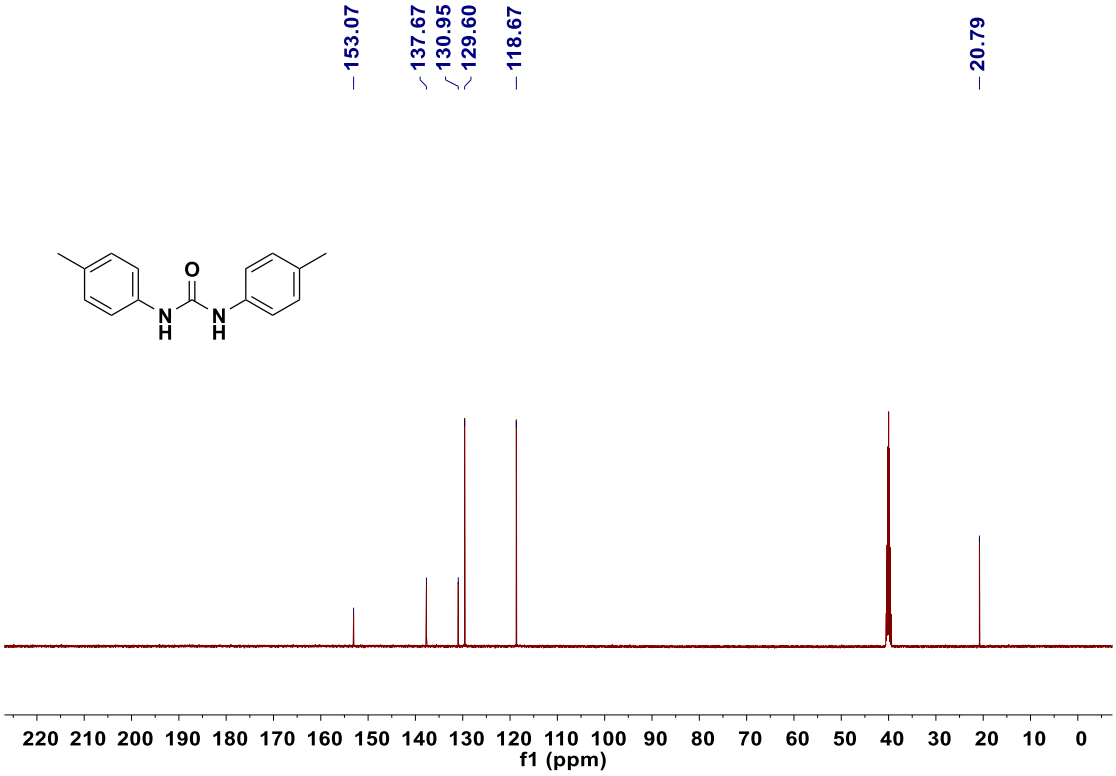
^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1,3-diphenylurea (5a)



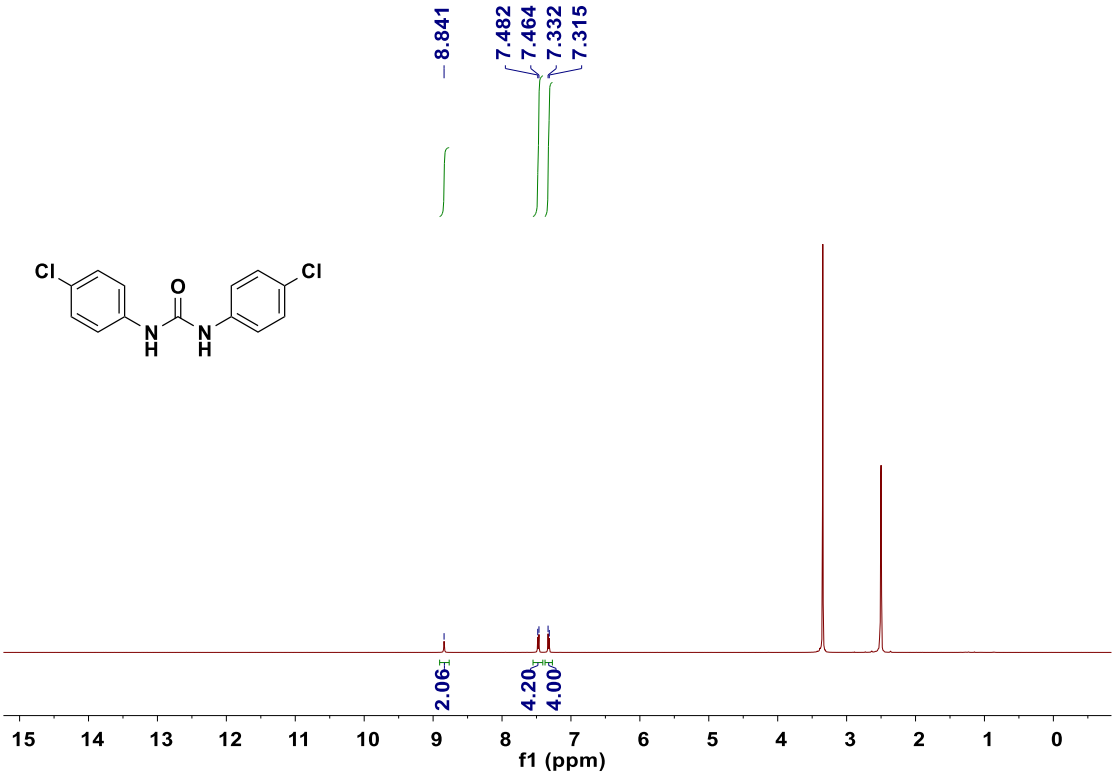
^{1}H NMR (500MHz, DMSO-d_6) of 1,3-di-p-tolylurea (5b)



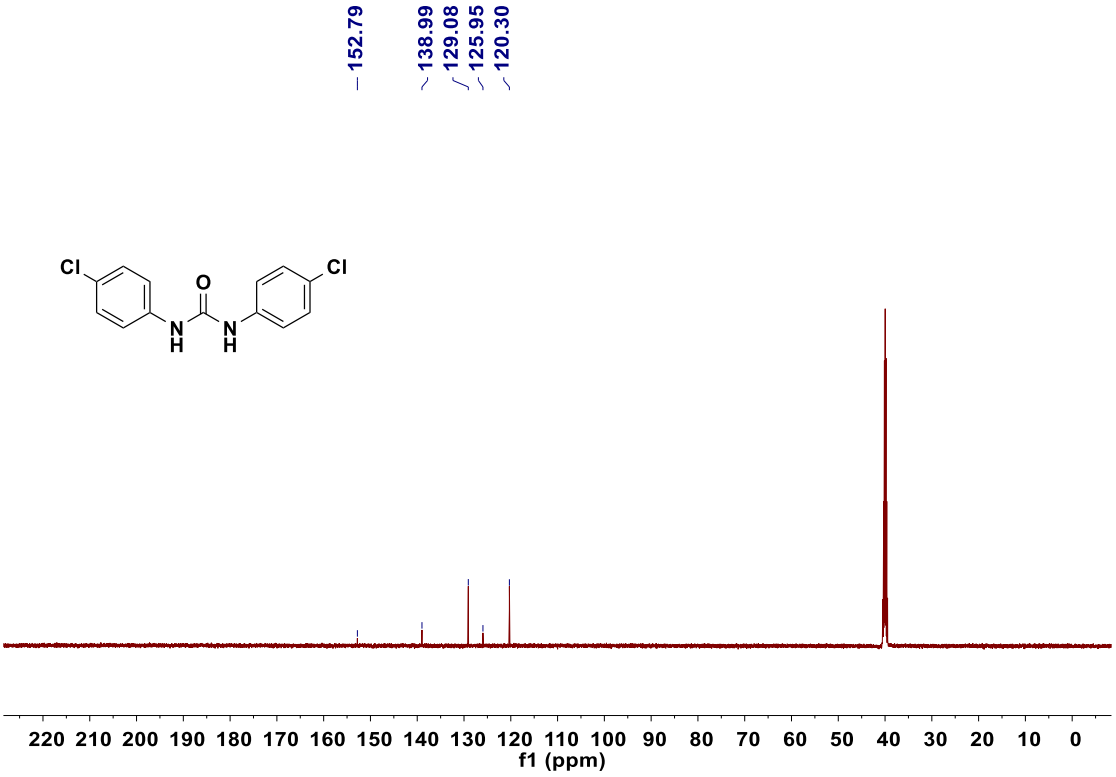
^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1,3-di-p-tolylurea (5b)



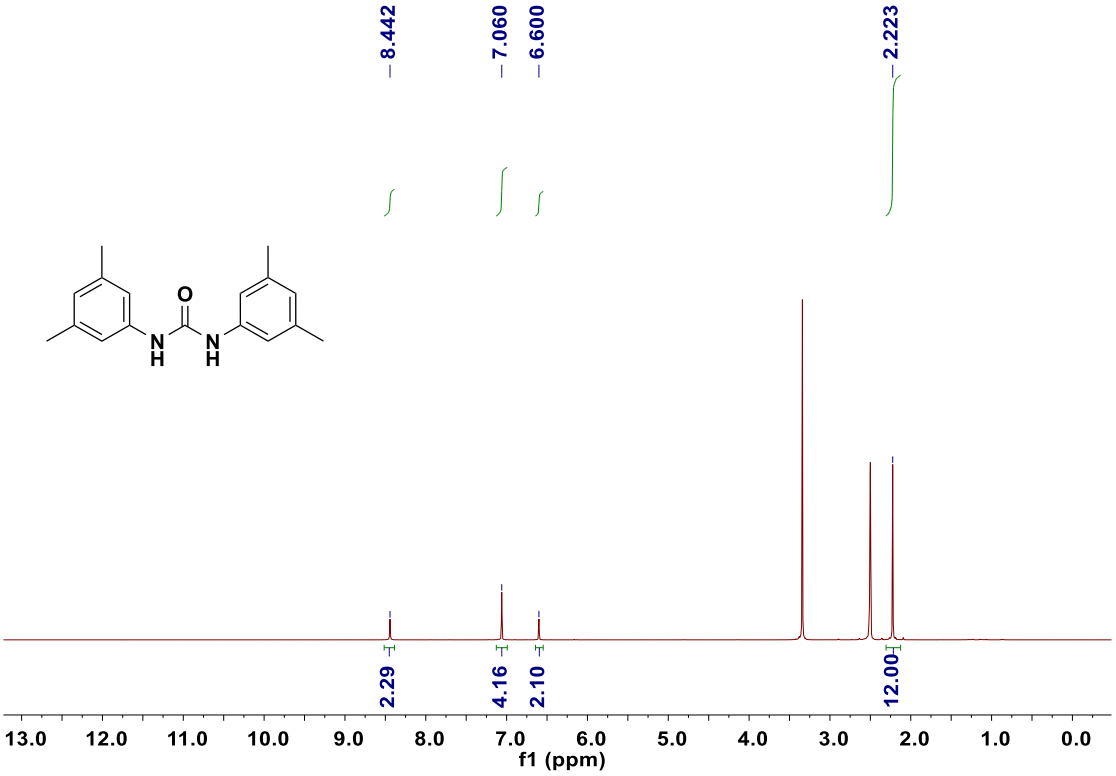
^{1}H NMR (500MHz, DMSO-d_6) of 1,3-bis(4-chlorophenyl)urea (5c)



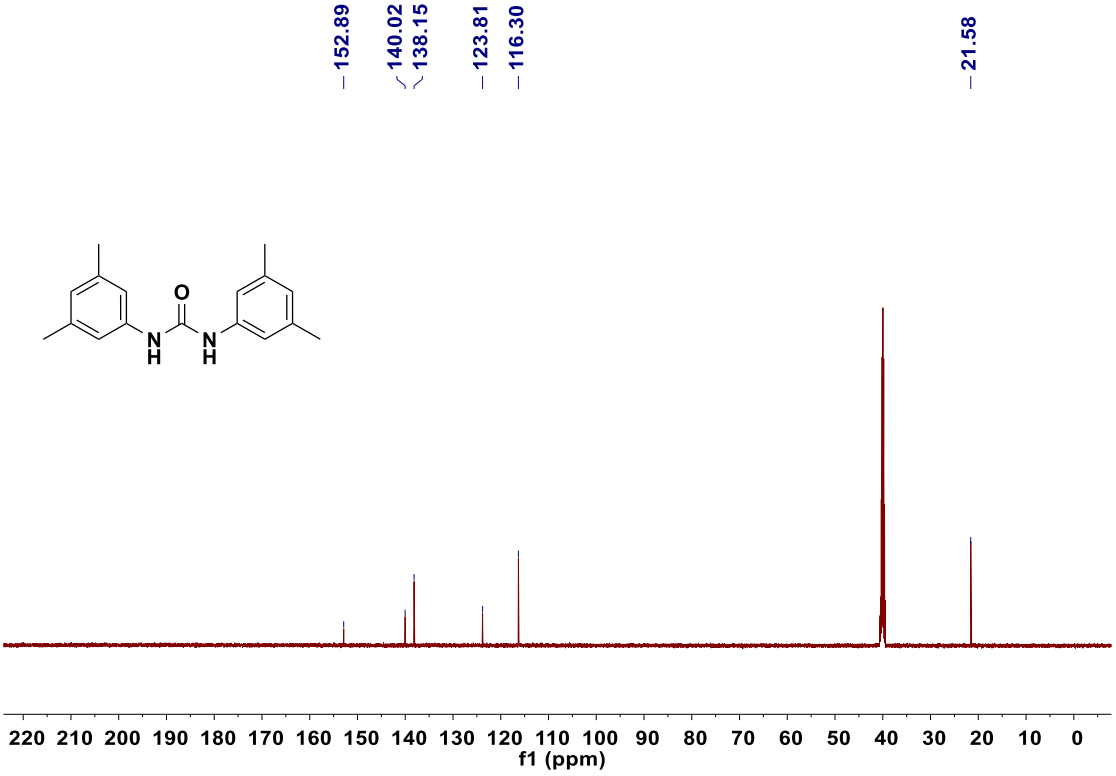
^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1,3-bis(4-chlorophenyl)urea (5c)



^{1}H NMR (500MHz, DMSO-d_6) of 1,3-bis(3,5-dimethylphenyl)urea(5d)



^{13}C{^{1}H} NMR (126MHz, DMSO-d_6) of 1,3-bis(3,5-dimethylphenyl)urea(5d)



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