Supporting Information

Iron-catalyzed oxidative cleavage of C–N Bonds of Tertiary Amines: Syntheses of Unsymmetrical Ureas from Isocyanates

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CONTENT

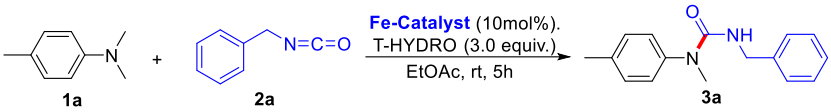
1. General Information

All the solvents and commercial reagents were used without additional purification. Purification of the reaction products was carried out by flash column chromatography using 200-300 mesh silica gel. Visualization on TLC (analytical thin layer chromatography) was achieved by the use of UV light (254 nm). ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded on a Varian Inova 400 NMR spectrometers with solvent resonance as the internal standard (^{1}H NMR: $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm). ^{1}H NMR data are reported as follows: chemical shifts, multiplicity (s = singlet, br s = broad singlet, d = doublet, dd= doublet of doublet, t = triplet, q = quartet, m= multiplet), coupling constant(s) in Hz, integration. High-resolution mass spectrometry (HRMS) was determined on Waters G2-XS Qtof. The melting point was determined using a BÜCHI B-540 melting point apparatus.

2. Experimental section

2. 1 Optimization of reaction conditions

Table S1. Catalyst screening [a,b]

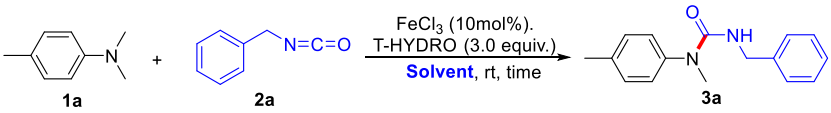


1a 2a 3a

Entry	Catalyst (10 mol%)	Yield (%)[b]
1	**$FeCl_3$**	**75**
2	$FeBr_3$	58
3	$FeCl_2$	74
4	$Fe_2(SO_4)_3$	17
5	$FeSO_4·7H_2O$	10
6	$Fe(OAc)_3$	39
7	$Fe(OAc)_2$	19
8	Fe powder	22
9	$(NH_4)_2Fe(SO_4)_2·6H_2O$	40
10	$NH_4Fe(SO_4)_2·12H_2O$	25
11	$FeCl_3·6H_2O$	70
12	$Fe(NO_3)_3·9H_2O$	42

[a] Reactions were performed with **1a** (0.3 mmol) and **2a** (0.6 mmol) in 1.0 mL ethyl acetate (EtOAc) at room temperature for 5h. [b] Isolated yield.

Table S2. Solvent screening [a,b]



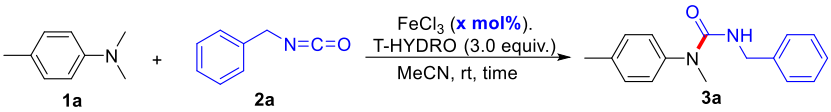
1a 2a 3a

Entry	Solvent	Time (h)	Yield (%)[b]
1	EtOAc	5	75
2	DCM	5	50
3	DCE	5	47
4	THF	5	58
5	**MeCN**	**2.5**	**78**
6	Acetone	2.5	76
7	EtOH	5	0
8	MeOH	5	trace
9	Dioxane	5	60

10	$CHCl_3$	5	40
11	DMSO	5	25
12	DMF	5	23

[a] Reactions were performed with **1a** (0.3 mmol), **2a** (0.6 mmol) and $FeCl_3$ (0.03mmol, 10mol%) in 1.0 mL of solvent. [b] Isolated yield.

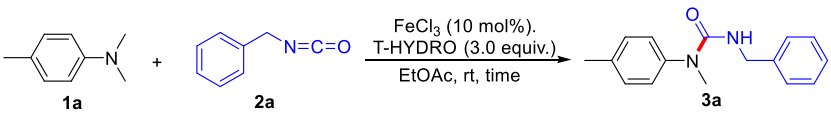
Table S3. The dosage of catalyst screening [a,b]



Entry	$FeCl_3$ (mol%)	Time (h)	Yield (%)[b]
1	5	5	45
2	**10**	**2.5**	**78**
3	15	2	80
4	20	1.5	78

[a] Reactions were performed with **1a** (0.3 mmol) and **2a** (0.6 mmol) in 1.0 mL of acetonitrile (MeCN) at room temperature. [b] Isolated yield.

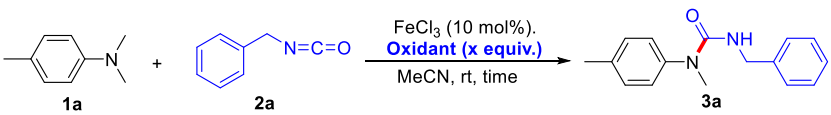
Table S4. The dosage of substrates screening [a,b]



Entry	1a (equiv.)	2a (equiv.)	Yield (%)[b]
1	1	1	59
2	**1**	**2**	**78**
3	2	1	70

[a] Reactions were performed with **1a** (0.3 mmol), **2a** (0.6 mmol) and $FeCl_3$ (0.03mmol, 10mol%) in 1.0 mL of acetonitrile (MeCN) at room temperature for 2.5 h. [b] Isolated yield.

Table S5. The oxidant and dosage screening [a,b]



Entry	Oxidant (equiv.)	Time (h)	Yield (%)[b]
1[c]	T-HYDRO（3.0）	2.5	78
2[d]	TBHP（3.0）	5	66
3[e]	DTBP（3.0）	5	30

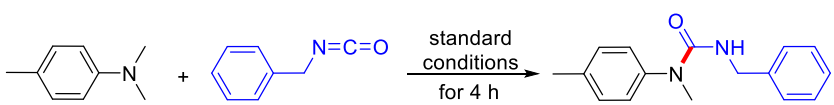
4[f]	H_2O_2（3.0）	5	35
5	O_2 (1.0 atm, ballon)	5	33
6	air (1.0 atm, ballon)	5	21
7	**T-HYDRO（2.0）**	**2.5**	**88**
8	T-HYDRO（2.0）	5	84
9	T-HYDRO（1.0）	11	53
10	N_2 (1.0 atm, ballon)	24	trace

[a] Reactions were performed with **1a** (0.3 mmol), **2a** (0.6 mmol) and $FeCl_3$ (0.03mmol, 10 mol%) in 1.0 mL of acetonitrile (MeCN) at room temperature. [b] Isolated yield. [c] T-HYDRO (70% aqueous tert-butyl hydroperoxide solution). [d] TBHP 5.5 M in decan. [e] DTBP (di-tert-butyl peroxide). [f] H_2O_2 30% aqueous solution.

2.2 General procedure for the synthesis of the ureas 3

A 5 mL reaction vial equipped with a magnetic stir bar was charged with anhydrous $FeCl_3$ (4.9 mg, 0.03mmol, 10 mol%) dissolved in acetonitrile (1 mL). To this solution was sequentially added tertiary aniline (0.3 mmol, 1.0 equiv.), isocyanate (0.6 mmol, 2.0 equiv), and T-HYDRO (78 mg, 0.6 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature and monitored by TLC until completion. The reaction mixture was diluted with ethyl acetate, then transferred to a separatory funnel and washed with distilled water and brine. The aqueous layer was back-extracted with ethyl acetate (3 x 5 mL), and the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure afforded the crude product, which was purified by column chromatography on silica gel column [petroleum ether (PE) / ethyl acetate (EA)] to yield the pure product.

2.3 Scale-Up Experiment



1a
(5 mmol, 0.68 g)

2a
(10 mmol, 1.33 g)

3a (82 %)
(1.04 g)

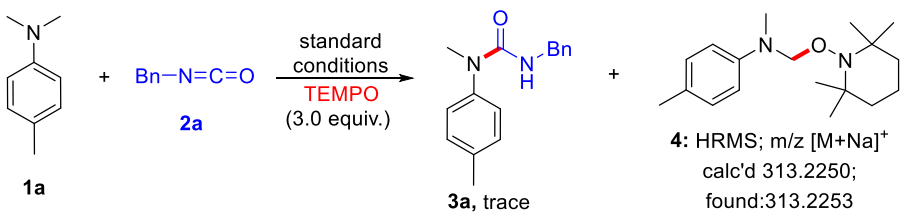
A 25 mL reaction vial equipped with a magnetic stir bar was charged with

anhydrous $FeCl_3$ (82 mg, 10 mol%) dissolved in acetonitrile (15 mL). To this solution was sequentially added *N,N*-dimethyltoluidine (0.68 g, 5.0 mmol, 1.0 equiv.), benzylisocyanate (1.33 g, 10 mmol, 2.0 equiv), and T-HYDRO (1.3 g, 10 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with ethyl acetate 20 mL then transferred to a separatory funnel and washed with distilled water and brine. The aqueous layer was back-extracted with ethyl acetate (3 x 15 mL), and the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure afforded the crude product, which was purified by column chromatography on silica gel column (PE/EA= 3:1) to afford the desired product **3a,** 1.04g (82% yield).

3. The Mechanistic Investigations

3. 1 Control experiments

(1) Radical trapping experiment



A 5 mL reaction vial equipped with a magnetic stir bar was charged with anhydrous $FeCl_3$ (4.9 mg, 0.03mmol, 10 mol%) dissolved in acetonitrile (1 mL). To this solution was sequentially added *N,N*-dimethyltoluidine (41 mg, 0.3 mmol, 1.0 equiv.), benzylisocyanate (80 mg, 0.6 mmol, 2.0 equiv.), T-HYDRO (78 mg, 0.6 mmol, 2.0 equiv) and TEMPO (140 mg, 0.9 mmol, 3.0 equiv.). The resulting mixture was stirred at room temperature for 2.5h. When the reaction mixture was monitored by TLC and found that TEMPO fully inhibited the reaction and trace of **3a** was observed. The reaction mixture was diluted with ethyl acetate and filtered, then analyzed by HRMS (Figures S1).

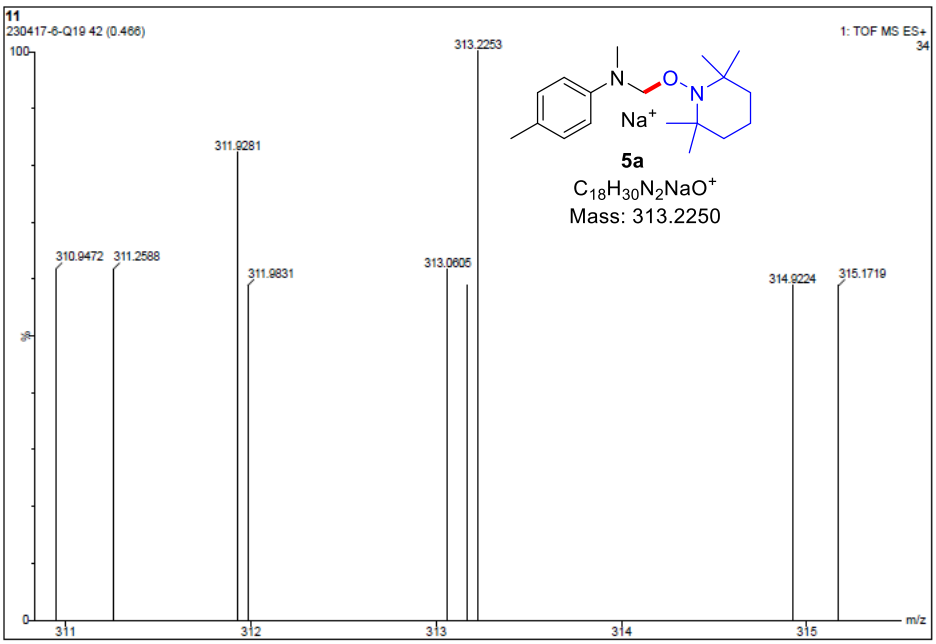
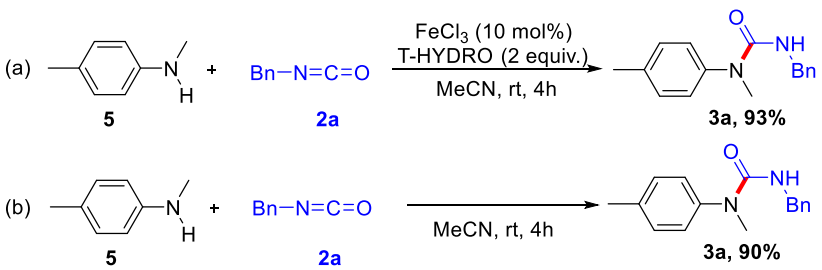


Figure S1. HRMS of the TEMPO adduct **4**

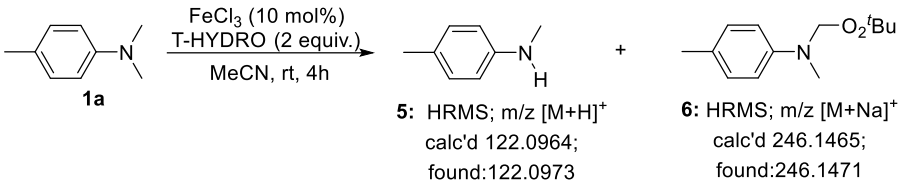
(2) Reactions between *N*-methyl-p-toluidine (**5**) and benzyl isocyanate (**2a**)



Two oven-dried 5 mL reaction vial, each equipped with a stir bar, to one tube, sequentially added $FeCl_3$ (4.9 mg, 0.03mmol, 10 mol%), acetonitrile (1 mL), *N*-methyl-p-toluidine (36 mg, 0.3 mmol, 1.0 equiv.), benzylisocyanate (80 mg, 0.6 mmol, 2.0 equiv), and T-HYDRO (78 mg, 0.6 mmol, 2.0 equiv). To the other reaction vial, *N*-methyl-p-toluidine (36 mg, 0.3 mmol, 1.0 equiv.), benzylisocyanate (80 mg, 0.6 mmol, 2.0 equiv) and acetonitrile (1 mL) was added. The two reactions (*a* and *b*) were stirred at room temperature for 4h. The reaction mixture was diluted with ethyl acetate, then washed with distilled water and brine. The aqueous layer was back-extracted with ethyl acetate (3 x 5 mL), and the combined organic phases were dried over anhydrous

Na_2SO_4, filtered and concentrated under reduced pressure, which was purified by column chromatography on silica gel column, yielding 93% (reaction a) and 90% (reaction b) yields of **3a**, respectively.

(3) Reaction of **1a** under standard conditions in the absence of isocyanate



A 5 mL reaction vial equipped with a magnetic stir bar was charged with anhydrous $FeCl_3$ (4.9 mg, 0.03mmol, 10 mol%) dissolved in acetonitrile (1 mL). To this solution was sequentially added *N,N*-dimethyltoluidine (41 mg, 0.3 mmol, 1.0 equiv.), and T-HYDRO (78 mg, 0.6 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 4h. When the reaction mixture was monitored by TLC and the secondary amine **5** was not observed. The reaction mixture was diluted with ethyl acetate and filtered, then analyzed by HRMS (Figures S2 and S3).

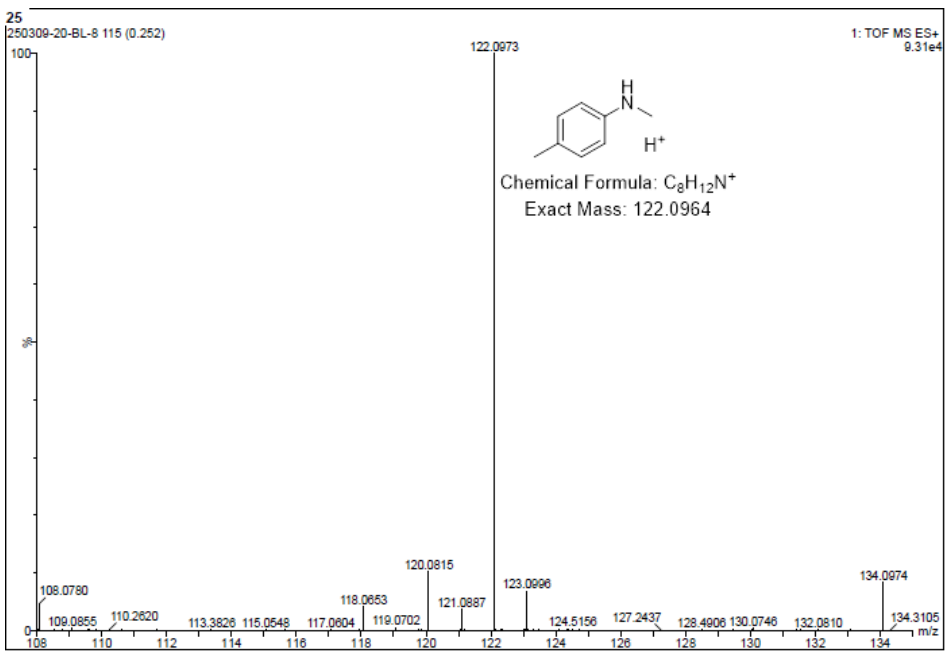


Figure S2. HRMS spectra of intermediate **5**

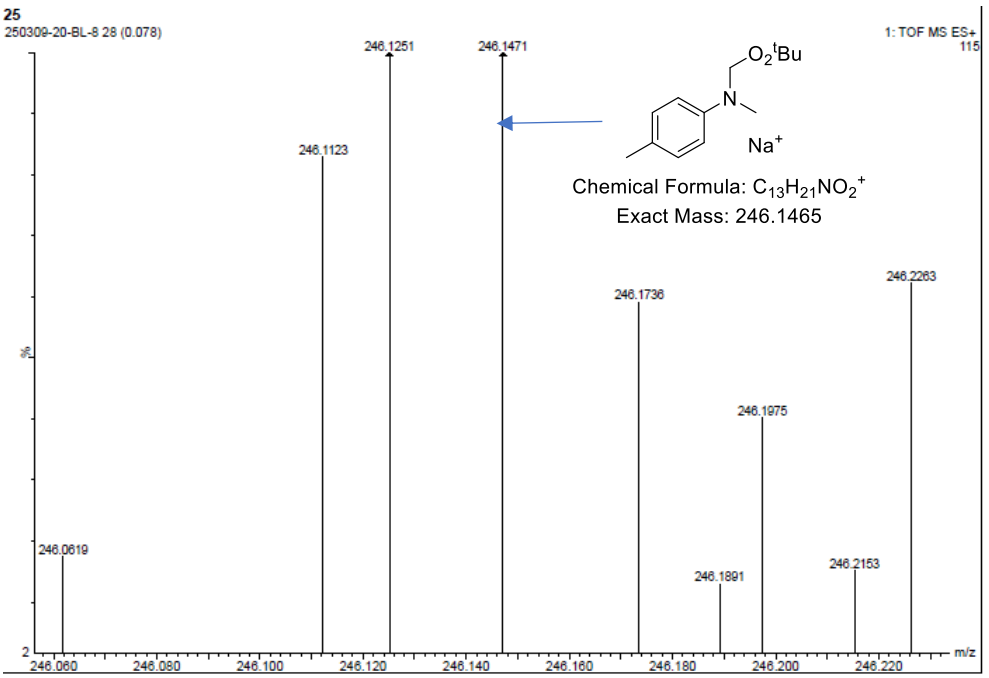
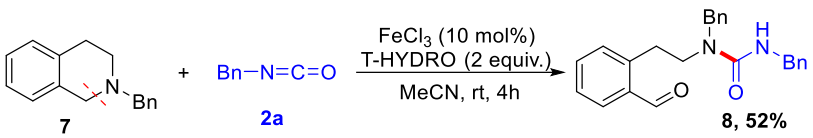


Figure S3. HRMS spectra of intermediate **6**

(4) Reaction of **7** and **2a** under standard conditions



A 5 mL reaction vial equipped with a magnetic stir bar was charged with anhydrous $FeCl_3$ (4.9 mg, 0.03mmol, 10 mol%) dissolved in acetonitrile (1 mL). To this solution was sequentially added *N*-benzyl tetrahydroisoquinoline (76 mg, 0.3 mmol, 1.0 equiv.), benzylisocyanate (80 mg, 0.6 mmol, 2.0 equiv), and T-HYDRO (78 mg, 0.6 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 4h. The reaction mixture was diluted with ethyl acetate, then transferred to a separatory funnel and washed with distilled water and brine. The aqueous layer was back-extracted with ethyl acetate (3 x 5 mL), the combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure, crude product was purified by column chromatography on silica gel column (PE/EA=1:1), yielding the product **8**.

4. Crystal structure of product 3z

The ORTEP diagram (Figure S4) and Crystal Parameters (Table S6) of **3z** where in thermal ellipsoids are drawn at 50% probability level. Suitable crystal of compound **3z** was obtained by slowly evaporating of dichloromethane solution at ambient temperature. The data were collected by a diffractometer Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation (1.54184 Å) by using a w scan mode. Atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC: 2497104).

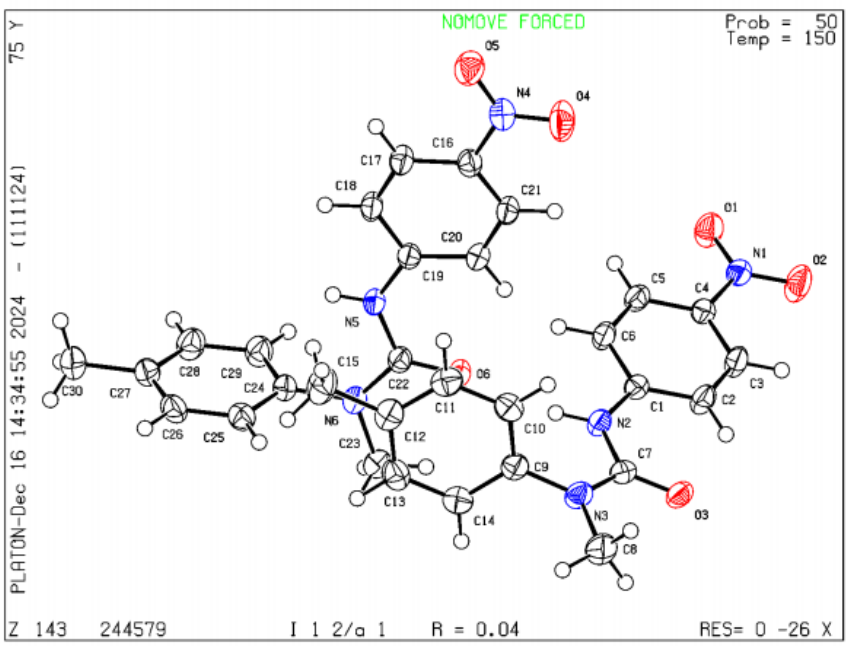
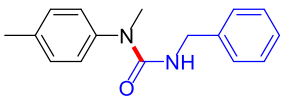


Figure S4. Crystal XRD image of **3z**

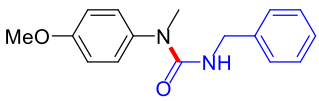
Table S6. Crystal data and structure refinement for 3z

Identification code	244579
Empirical formula	$C_{15}H_{15}N_3O_3$
Formula weight	285.30
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	I2/a
a/Å	15.38200(14)
b/Å	20.5919(2)
c/Å	17.87192(16)
α/°	90
β/°	98.5017(9)
γ/°	90
Volume/Å^3	5598.64(9)
Z	16
ρ_{calc}g/cm^3	1.354
μ/mm^{-1}	0.797
F(000)	2400.0
Crystal size/mm^3	0.16 × 0.12 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.224 to 145.946
Index ranges	-18 ≤ h ≤ 19, -25 ≤ k ≤ 24, -19 ≤ l ≤ 22
Reflections collected	21901
Independent reflections	5361 [R_{int} = 0.0162, R_{sigma} = 0.0146]
Data/restraints/parameters	5361/0/391
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0965
Final R indexes [all data]	R_1 = 0.0395, wR_2 = 0.0990
Largest diff. peak/hole / e Å^{-3}	0.18/-0.23

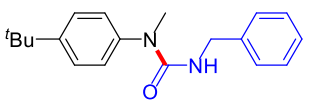
5. Characterization of the products



3-Benzyl-1-methyl-1-(p-tolyl)urea(3a): White solid, m.p.: 88-89 ℃; 67.1 mg, 88% yield, (EA/PE =1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 2H), 7.24 – 7.17 (m, 5H), 7.14 (d, *J* = 8.3 Hz, 2H), 4.64 (s, 1H), 4.38 (d, *J* = 5.8 Hz, 2H), 3.28 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 140.6, 139.7, 137.4, 130.7, 128.5, 127.3, 127.2, 127.0, 44.7, 37.4, 21.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{19}N_2O$, 255.1492; found 255.1495.

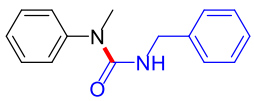


3-Benzyl-1-(4-methoxyphenyl)-1-methylurea(3b): White solid, m.p.: 77-78 ℃; 65.6 mg, 81% yield, (EA/PE =1 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, *J* = 6.8 Hz, 2H), 7.22 (d, *J* = 5.0 Hz, 2H), 7.19 (d, *J* = 4.4 Hz, 2H), 7.16 (s, 1H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.59 (s, 1H), 4.37 (d, *J* = 5.8 Hz, 2H), 3.80 (s, 3H), 3.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.7, 139.7, 135.8, 128.8, 128.5, 127.3, 127.0, 115.3, 55.5, 44.7, 37.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{19}N_2O_2$, 271.1441; found 271.1447.

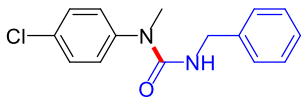


3-Benzyl-1-(4-(tert-butyl)phenyl)-1-methylurea(3c): White solid, m.p.: 83-85 ℃; 72.8 mg, 82% yield, (EA/PE =1 : 5); ^{1}H NMR (400 MHz,$CDCl_3$): δ 7.41 (d, *J* = 8.6 Hz, 2H), 7.30 (dd, *J* = 7.8, 6.6 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 3H), 7.18 (d, *J* = 8.6 Hz, 2H), 4.72 (s, 1H), 4.40 (d, *J* = 5.9 Hz, 2H), 3.29 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 150.5, 140.5, 139.8, 128.5, 127.3, 127.0, 127.0, 126.9, 44.6,

37.4, 34.6, 31.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{25}N_2O$, 297.1961; found 297.1962.



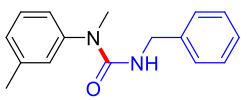
3-Benzyl-1-methyl-1-phenylurea(3d)[1]: Yellow oil, 57.6 mg, 80% yield, (EA/PE =1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.27 (s, 2H), 7.22 (d, *J* = 7.7 Hz, 3H), 4.67 (s, 1H), 4.39 (d, *J* = 5.8 Hz, 2H), 3.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 143.4, 139.6, 130.1, 128.5, 127.4, 127.4, 127.3, 127.1, 44.7, 37.4.



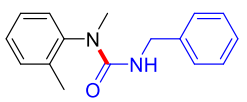
3-Benzyl-1-(4-chlorophenyl)-1-methylurea(3e): White solid, m.p.: 86-88 °C; 65.8 mg, 80% yield, (EA/PE =1 : 5); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.25 – 7.18 (m, 5H), 4.62 (s, 1H), 4.38 (d, *J* = 5.7 Hz, 2H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 141.9, 139.3, 133.0, 130.2, 128.7, 128.6, 127.4, 127.2, 44.8, 37.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}ClN_2O$, 275.0946; found 275.0953.

3-Benzyl-1-(4-bromophenyl)-1-methylurea(3f): White solid, m.p.: 89-91 °C; 70.6 mg, 74% yield, (EA/PE =1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.35 – 7.27 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.7 Hz, 2H), 4.63 (s, 1H), 4.38 (d, *J* = 5.7 Hz, 2H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 142.4, 139.3, 133.2, 129.0, 128.6, 127.4, 127.2, 120.9, 44.8, 37.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}BrN_2O$, 319.0441; found 319.0446.

3-Benzyl-1-(4-iodophenyl)-1-methylurea(3g): Brown solid, m.p.: 109-111 ℃; 65.9 mg, yield 60%, (EA/PE =1 : 2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.6 Hz, 2H), 7.30 (s, 1H), 7.28 (s, 1H), 7.24 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.21 (s, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 4.65 (s, 1H), 4.38 (d, *J* = 5.7 Hz, 2H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 143.2, 139.3, 139.2, 129.2, 128.6, 127.4, 127.2, 92.1, 44.8, 37.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}IN_2O$, 367.0302; found 367.0305.

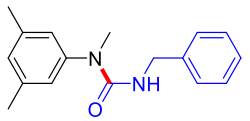


3-Benzyl-1-methyl-1-(m-tolyl)urea(3i): White solid, 54.9 mg, 72% yield, (EA/PE =1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.27 (m, 3H), 7.24 – 7.20 (m, 3H), 7.07 (q, *J* = 7.3 Hz, 3H), 4.68 (s, 1H), 4.39 (d, *J* = 5.8 Hz, 2H), 3.28 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 143.2, 140.2, 139.7, 129.8, 128.5, 128.2, 128.0, 127.3, 127.1, 124.3, 44.7, 37.3, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{19}N_2O$, 255.1492; found 255.1496.

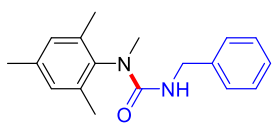


3-Benzyl-1-methyl-1-(o-tolyl)urea(3j): Light yellow oil; 51.8 mg, 68% yield, (EA/PE =1 : 2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (s, 1H), 7.29 – 7.26 (m, 2H), 7.25 (d, *J* = 2.5 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.23 (s, 1H), 7.20 (d, *J* = 2.1 Hz, 2H), 7.18 (s, 1H), 4.45 – 4.40 (m, 1H), 4.39 (s, 2H), 3.22 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 141.2, 139.8, 136.9, 131.8, 129.1, 128.7, 128.5, 127.8, 127.3, 127.0, 44.6, 36.2, 17.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{19}N_2O$, 255.1492; found 255.1497.

3-Benzyl-1-(3-bromophenyl)-1-methylurea(3k): Light yellow oil, 51.5 mg, 54% yield, (EA/PE= 1 : 2); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.39 (m, 2H), 7.33 (d, *J* = 3.7 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 4H), 7.19 (d, *J* = 4.9 Hz, 1H), 4.67 (s, 1H), 4.40 (d, *J* = 5.8 Hz, 2H), 3.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 144.6, 136.1, 133.0, 131.6, 130.9, 130.7, 129.5, 126.2, 123.6, 119.8, 37.5, 20.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}BrN_2O$, 319.0441; found 319.0452.

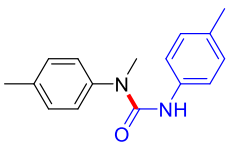


3-Benzyl-1-(3,5-dimethylphenyl)-1-methylurea(3l): Yellow solid, m.p.: 93-94 ℃; 52.3 mg, 65% yield, (EA/PE =1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 2H), 7.23 (d, *J* = 6.1 Hz, 3H), 6.91 (s, 1H), 6.86 (s, 2H), 4.70 (s, 1H), 4.39 (d, *J* = 5.8 Hz, 2H), 3.27 (s, 3H), 2.30 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 143.2, 139.8, 139.8, 129.1, 128.5, 127.3, 127.0, 124.9, 44.7, 37.3, 21.2. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{20}N_2NaO$, 291.1468; found 291.1470.

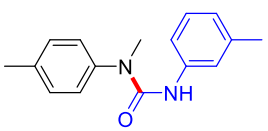


3-Benzyl-1-mesityl-1-methylurea(3m): White solid, m.p.: 82-83 ℃; 35.5 mg, 42% yield, (EA/PE =1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.24 (m, 2H), 7.20 (d, *J* = 7.9 Hz, 3H), 6.91 (s, 2H), 4.45 (s, 1H), 4.37 (d, *J* = 5.8 Hz, 2H), 3.15 (s, 3H), 2.27 (s, 3H), 2.17 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.1, 140.0, 138.1, 136.8, 129.9, 128.5, 127.3, 127.0, 44.6, 34.4, 20.9, 17.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{23}N_2O$, 283.1805; found 283.1812.

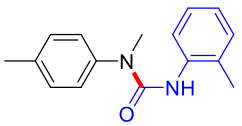
3-Benzyl-1-ethyl-1-(p-tolyl)urea(3n): White solid, m.p.: 61-63 ℃; 23.3 mg, 29% yield,(EA/PE =1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 5H), 7.11 (d, *J* = 8.2 Hz, 2H), 4.48 (s, 1H), 4.37 (d, *J* = 5.8 Hz, 2H), 3.74 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 139.8, 138.7, 137.7, 130.7, 128.7, 128.5, 127.3, 126.99, 44.6, 44.1, 21.1, 13.9. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{20}N_2NaO$, 291.1468; found 291.1469.



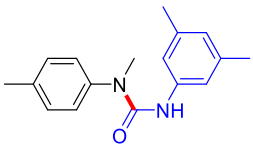
1-Methyl-1,3-di-p-tolylurea(3p)[2]: White solid, m.p.: 114-116 ℃; 57.2 mg, 75% yield, (EA/PE =1 : 8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.2 Hz, 2H), 7.23 – 7.14 (m, 4H)0, 7.03 (d, *J* = 8.1 Hz, 2H), 6.18 (s, 1H), 3.31 (s, 3H), 2.41 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 140.4, 137.8, 136.4, 132.3, 130.9, 129.3, 127.3, 119.4, 37.3, 21.1, 20.7.



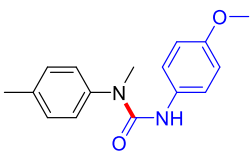
1-methyl-3-(m-tolyl)-1-(p-tolyl)urea(3q): White solid, m.p.: 71-73 ℃; 70.1 mg, 92% yield, (EA/PE =1 : 8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.7 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 7.1 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.20 (s, 1H), 3.31 (s, 3H), 2.41 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 140.2, 138.9, 138.7, 137.9, 130.9, 128.6, 127.3, 123.6, 119.8, 116.2, 37.3, 21.5, 21.1. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{18}N_2NaO$, 277.1311; found 277.1311.



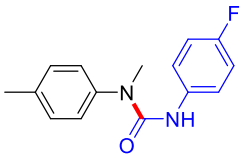
1-Methyl-3-(o-tolyl)-1-(p-tolyl)urea(3r): Yellow solid, m.p.: 57-58 ℃; 67.1 mg, 88% yield, (EA/PE =1 : 8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.12 (s, 1H), 3.33 (s, 3H), 2.40 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 140.4, 138.1, 137.2, 130.9, 130.0, 127.4, 127.0, 126.8, 123.2, 121.0, 37.2, 21.1, 17.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{19}N_2O$, 255.1492; found 255.1495.



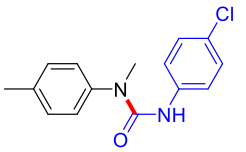
3-(3,5-Dimethylphenyl)-1-methyl-1-(p-tolyl)urea(3s): White solid, m.p.: 57-58 ℃; 72.4 mg, 90% yield, (EA/PE =1 : 8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.92 (s, 2H), 6.63 (s, 1H), 6.16 (s, 1H), 3.31 (s, 3H), 2.41 (s, 3H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 140.3, 138.8, 138.4, 137.8, 130.9, 127.3, 124.5, 116.9, 37.2, 21.3, 21.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{21}N_2O$, 269.1648; found 269.1659.



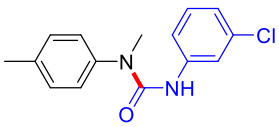
3-(4-Methoxyphenyl)-1-methyl-1-(p-tolyl)urea(3t): White solid, m.p.: 77-78 ℃; 76.8 mg, 95% yield, (EA/PE =1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.11 (s, 1H), 3.76 (s, 3H), 3.31 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.6, 155.0, 140.4, 137.8, 132.1, 130.9, 127.3, 121.5, 114.0, 55.5, 37.3, 21.1. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{18}N_2NaO_2$, 293.1260; found 293.1270.



3-(4-Fluorophenyl)-1-methyl-1-(p-tolyl)urea(3u): White solid, m.p.: 125-126 ℃, 68.9 mg, 89% yield, (EA/PE= 1 : 10); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 4.7 Hz, 1H), 7.22 (d, J = 2.6 Hz, 2H), 7.20 (d, J = 4.1 Hz, 1H), 6.94 – 6.88 (m, 2H), 6.19 (s, 1H), 3.30 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 156.1 ($^{1}J_{C\text{-}F}$ = 279.5 Hz), 140.1, 138.1, 135.0 ($^{4}J_{C\text{-}F}$ = 2.7 Hz), 131.1, 127.4, 121.1 ($^{3}J_{C\text{-}F}$ = 7.7 Hz), 115.3 ($^{2}J_{C\text{-}F}$ = 22.3 Hz), 37.3, 21.1; ^{19}F NMR (376.5 MHz, $CDCl_3$) δ -120.4. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{15}FN_2NaO$, 281.1061; found 281.1055.

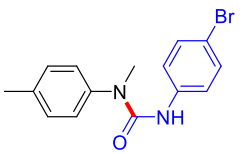


3-(4-chlorophenyl)-1-methyl-1-(p-tolyl)urea(3v) [3]: White solid, m.p.: 108-109 ℃; 75.6 mg, 92% yield, (EA/PE=1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 2H), 7.23 (d, J = 9.0 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.9 Hz, 2H), 6.24 (s, 1H), 3.30 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 139.9, 138.2, 137.6, 131.0, 128.7, 127.6, 127.3, 120.4, 37.3, 21.1.

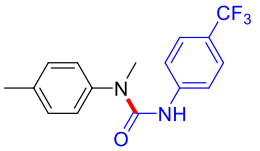


3-(3-Chlorophenyl)-1-methyl-1-(p-tolyl)urea(3w): White solid, m.p.: 71-72 ℃; 70.7 mg, 86% yield, (EA/PE=1 : 10); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 2.0 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.3 Hz, 2H), 7.15 – 7.09 (m, 2H), 6.93 (dt, J = 6.5, 2.2 Hz, 1H), 6.26 (s, 1H), 3.30 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 140.2, 139.8, 138.2, 134.4, 131.1, 129.7, 127.3, 122.7, 119.0, 117.0,

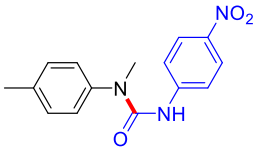
37.3, 21.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}ClN_2O$, 275.0946; found 275.0946.



3-(4-Bromophenyl)-1-methyl-1-(p-tolyl)urea(3x): White solid, m.p.: 122-123 ℃, 89.7 mg, 94% yield, (EA/PE=1 : 10); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, J = 8.9 Hz, 2H), 7.27 (d, J = 8.1 Hz, 2H), 7.18 (dd, J = 8.5, 5.8 Hz, 4H), 6.23 (s, 1H), 3.29 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 139.9, 138.2, 138.1, 131.6, 131.0, 127.3, 120.7, 115.1, 37.3, 21.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}BrN_2O$, 319.0441; found 319.0446.

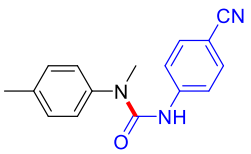


1-Methyl-1-(p-tolyl)-3-(4-(trifluoromethyl)phenyl)urea(3y): White solid, m.p.: 103-105 ℃, 76.7 mg, 83% yield, (EA/PE=1 : 15); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 8.6 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 6.39 (s, 1H), 3.32 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.0, 142.1, 139.7, 138.4, 131.1, 127.3, 126.0 (q, J_{CF} = 3.7 Hz)., 118.3, 37.4, 21.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}F_3N_2O$, 309.1209; found 309.1210.

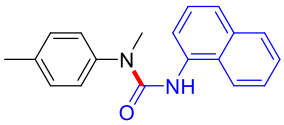


1-Methyl-3-(4-nitrophenyl)-1-(p-tolyl)urea(3z): Yellow solid, m.p.: 147-148 ℃, 49.6 mg, 58% yield, (EA/PE=1 : 6); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 9.2 Hz, 2H), 7.44 (d, J = 9.2 Hz, 2H), 7.31 (d, J = 8.7 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H),

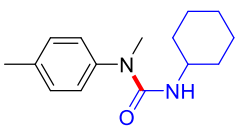
6.60 (s, 1H), 3.33 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 145.1, 142.4, 139.3, 138.8, 131.3, 127.2, 125.0, 117.8, 37.5, 21.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}N_3O_3$, 286.1186; found 286.1189.



3-(4-Cyanophenyl)-1-methyl-1-(p-tolyl)urea(3aa): White solid, m.p.: 140-142 ℃, 51.7 mg, 65% yield, (EA/PE=1 : 8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 8.3 Hz, 2H), 6.47 (s, 1H), 3.31 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.6, 143.2, 139.4, 138.6, 133.1, 131.2, 127.2, 119.2, 118.5, 105.3, 37.4, 21.1. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{16}N_3O$, 266.1288; found 266.1291.



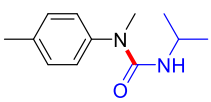
1-Methyl-3-(naphthalen-1-yl)-1-(p-tolyl)urea(3ab): White solid, m.p.: 102-104 ℃, 70.5 mg, 81% yield, (EA/PE=1 : 10); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.5 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.39 – 7.31 (m, 6H), 6.68 (s, 1H), 3.40 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 140.4, 138.2, 134.1, 133.7, 131.1, 128.7, 127.5, 127.0, 126.0, 125.9, 125.6, 124.2, 120.2, 119.2, 37.4, 21.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{19}N_2O$, 291.1492; found 291.1494.



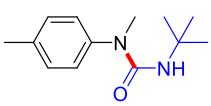
3-Cyclohexyl-1-methyl-1-(p-tolyl)urea(3ad): White solid, m.p.: 44-45 ℃, 50.2 mg, 68% yield, (EA/PE=1 : 6); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.3 Hz, 2H), 4.17 (s, 1H), 3.62 (s, 1H), 3.22 (s, 3H), 2.36 (s, 3H),

1.84 (d, J = 8.7 Hz, 2H), 1.62 – 1.50 (m, 3H), 1.34 – 1.25 (m, 2H), 1.07 (t, J = 11.6 Hz, 1H), 0.95 (q, J = 11.7, 10.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 141.0, 137.0, 130.6, 127.1, 49.3, 37.1, 33.7, 25.6, 24.9, 21.0. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{22}N_2NaO$, 269.1624; found 269.1624.

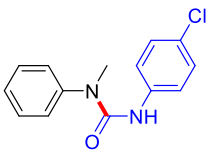
3-Butyl-1-methyl-1-(p-tolyl)urea(3ae): White solid, m.p.: 36-37 ℃, 35 mg, 53% yield, (EA/PE=1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (s, 2H), 7.11 (d, J = 8.3 Hz, 2H), 4.27 (s, 1H), 3.22 (s, 3H), 3.14 (td, J = 7.1, 5.6 Hz, 2H), 2.36 (s, 3H), 1.41 – 1.32 (m, 2H), 1.23 (dd, J = 15.5, 6.9 Hz, 2H), 0.86 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 141.0, 137.1, 130.6, 127.2, 40.5, 37.1, 32.4, 21.0, 20.0, 13.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{13}H_{21}N_2O$, 221.1648; found 221.1652.



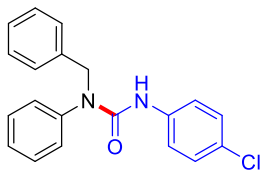
3-Isopropyl-1-methyl-1-(p-tolyl)urea(3af): Yellow oil, 32.1 mg, 52% yield, (EA/PE=1 : 4); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 4.14 (d, J = 7.9 Hz, 1H), 3.98 (h, J = 6.3 Hz, 1H), 3.27 (s, 3H), 2.41 (s, 3H), 1.08 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 140.9, 137.0, 130.6, 127.1, 42.5, 37.1, 23.3, 21.0. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_{18}N_2NaO$, 229.1311; found 229.1311.



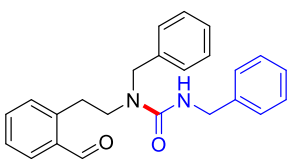
3-(tert-butyl)-1-methyl-1-(p-tolyl)urea(3ag)[4]: Yellow oil, 19.8 mg, 30% yield, (EA/PE =1 : 8); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 8.3 Hz, 2H), 4.22 (s, 1H), 3.18 (s, 3H), 2.34 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.7, 141.3, 136.8, 130.5, 127.0, 50.6, 36.8, 29.4, 21.0.



3-(4-Chlorophenyl)-1-methyl-1-phenylurea(3aj)[5]: Yellow solid, m.p.: 128-129 °C; 18.7 mg, 24% yield, (EA/PE=1 : 3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 9.0 Hz, 2H), 6.24 (s, 1H), 3.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 142.7, 137.5, 130.4, 128.8, 128.1, 127.8, 127.5, 120.5, 37.3.



1-Benzyl-3-(4-chlorophenyl)-1-phenylurea(3ak): Yellow solid, m.p.: 104-105 °C, 46.4 mg, 46% yield, (EA/PE=1 : 8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dt, *J* = 13.9, 7.1 Hz, 4H), 7.23 (s, 5H), 7.19 (s, 2H), 7.18 – 7.11 (m, 3H), 6.18 (s, 1H), 4.92 (s, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 140.9, 138.0, 137.5, 130.3, 128.8, 128.7, 128.6, 128.4, 127.9, 127.4, 120.6, 53.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{20}H_{17}ClN_2NaO$, 336.1029; found 336.1020.



***1,3-Dibenzyl-1-(2-formylphenethyl)urea*(8)**: Colorless oil, 58 mg, 52% yield, (EA/PE=1 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.98 (s, 1H), 7.74 (d, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.34 – 7.28 (m, 6H), 7.25 (d, *J* = 9.1 Hz, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.31 (s, 1H), 4.61 (s, 2H), 4.57 (d, *J* = 5.7 Hz, 2H), 3.37 – 3.29 (m, 2H), 3.18 – 3.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 194.4, 158.1, 140.3, 140.3, 138.7, 136.0, 134.3, 133.9, 132.2, 128.6,

128.4, 127.7, 127.6, 127.4, 127.3, 126.9, 50.8, 48.2, 44.9, 33.0. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{24}H_{25}N_2O_2$, 373.1911; found 373.1922.

6. References

1. J. Li, W. He, P. Lei, J. Song, J. Huo, H. Wei, *Syn. Comm.*, 2021, **51**, 3590-3600.
2. Y. Meng, B. Wang, L. Ren, Q. Zhao, W. Yu, J. Chang, *New J. Chem.*, 2018, **42**, 13790-13796.
3. J. S. Li, P. P. Yang, X.-Y. Xie, S. Jiang, L. Tao, Z. W. Li, W. D. Liu, *Adv. Syn. Catal.*, 2020, **362**, 1977-1981.
4. Q. Zhang, X. Wang, S. W. Chen, M. Tang, Q. Zhang, *Eur. J. Org. Chem.*, 2023, **26**, 1-7.
5. S. Aich, M. Saha, D. Ghosh, S. A. Molla, A. K. Sarkar, D. Bag, D. K. Maiti, *Org. Lett.*, 2024, **26**, 10970-10975.

6. Copies of ^{1}H, ^{13}C NMR and ^{19}F Spectra

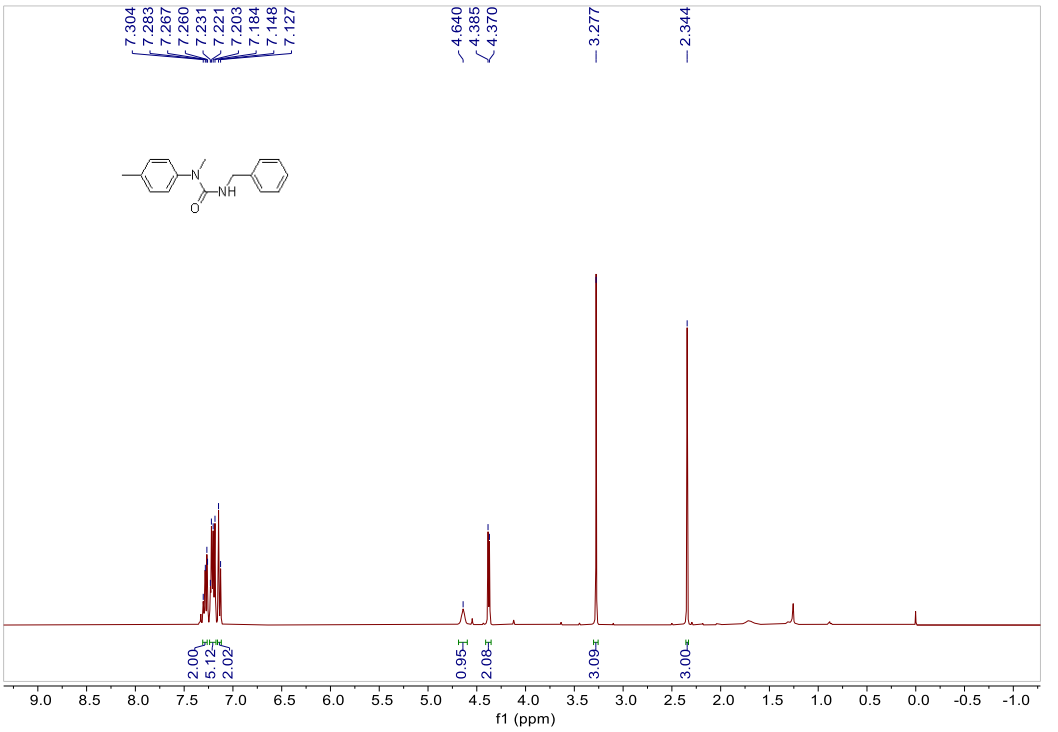


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3a**

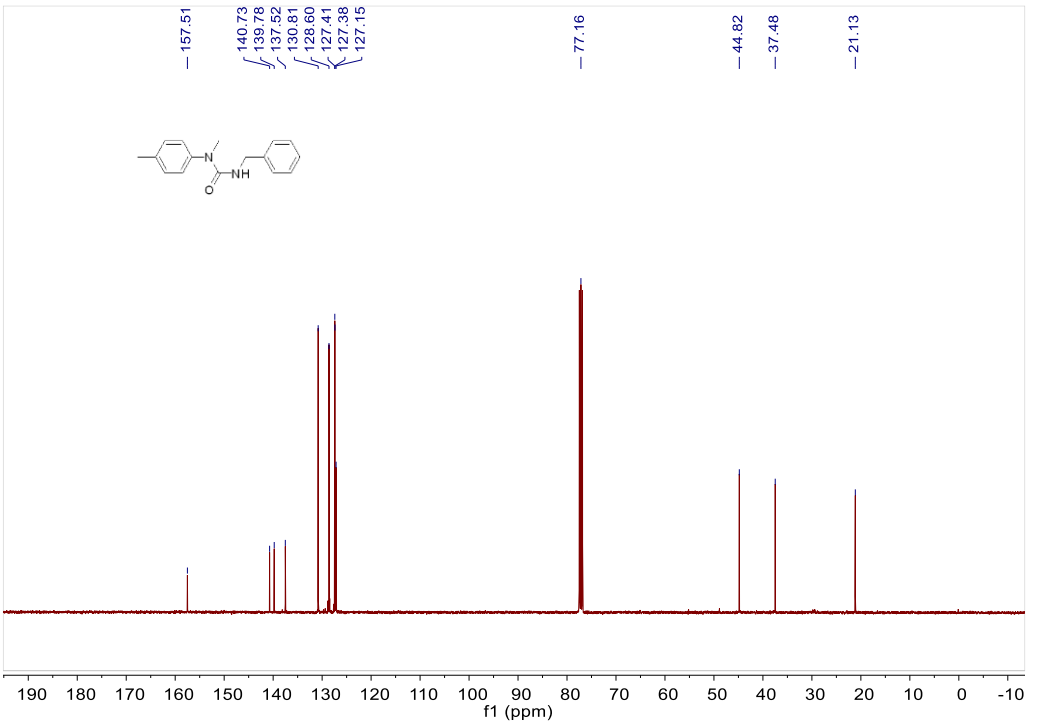


Figure S6. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3a**

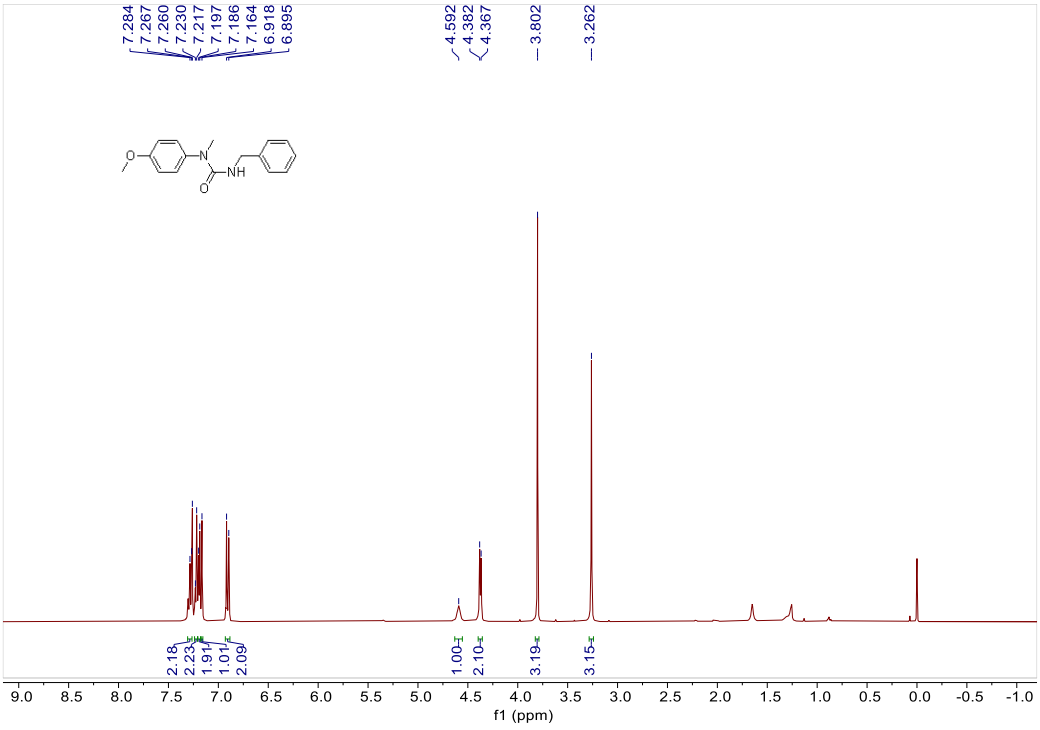


Figure S7. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3b**

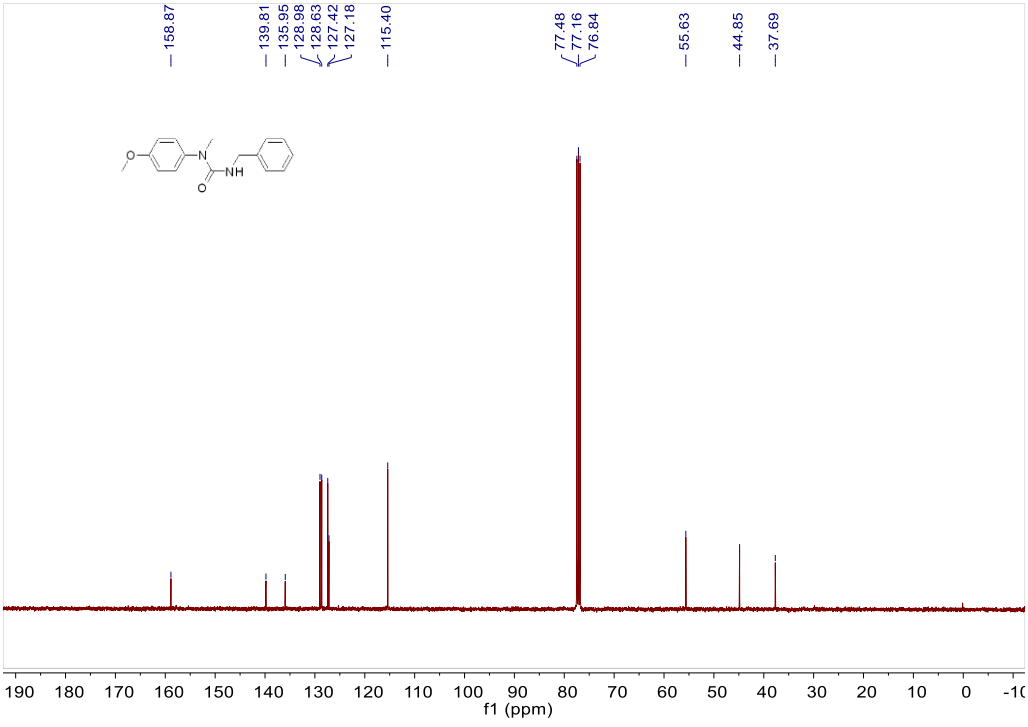


Figure S8. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3b**

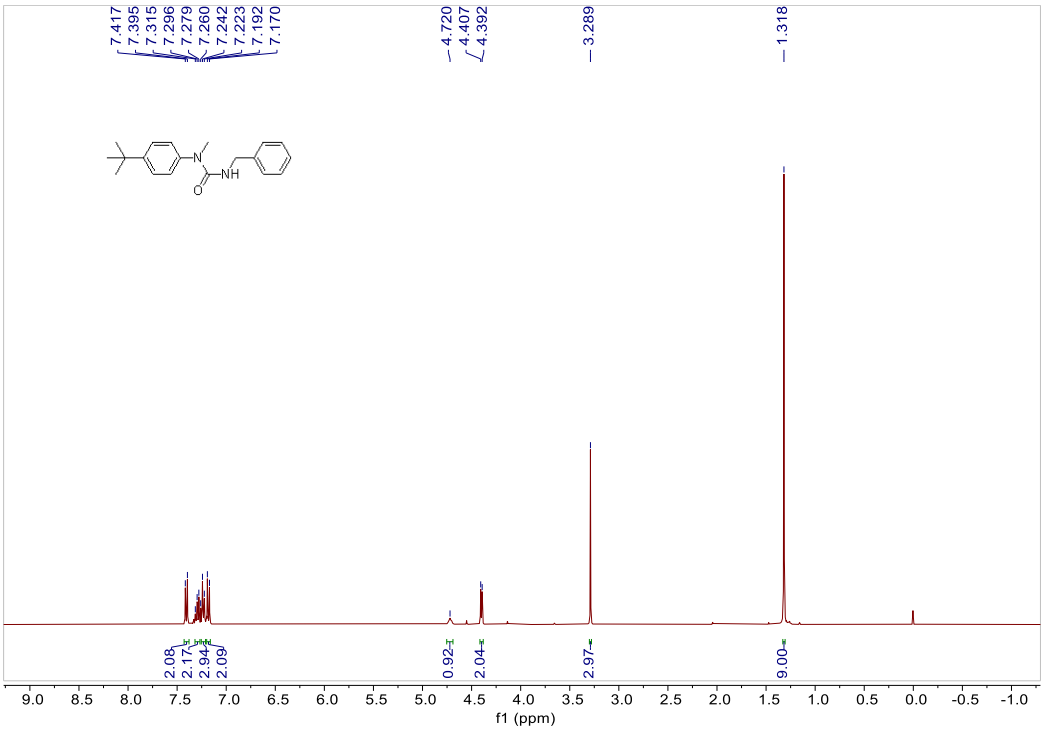


Figure S9. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3c**

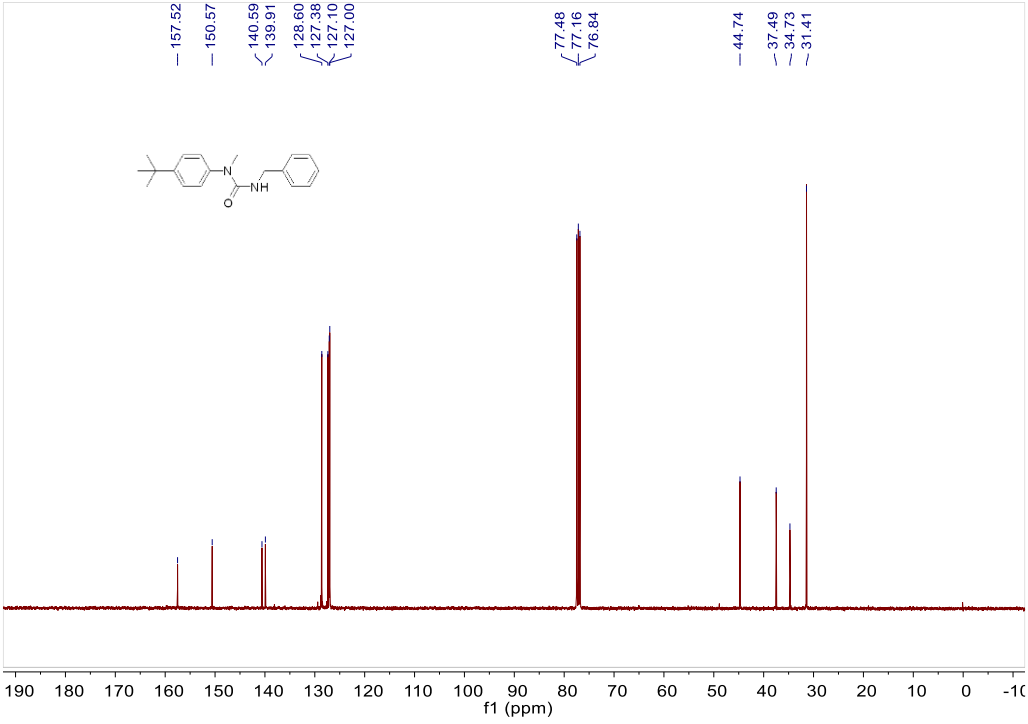


Figure S10. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3c**

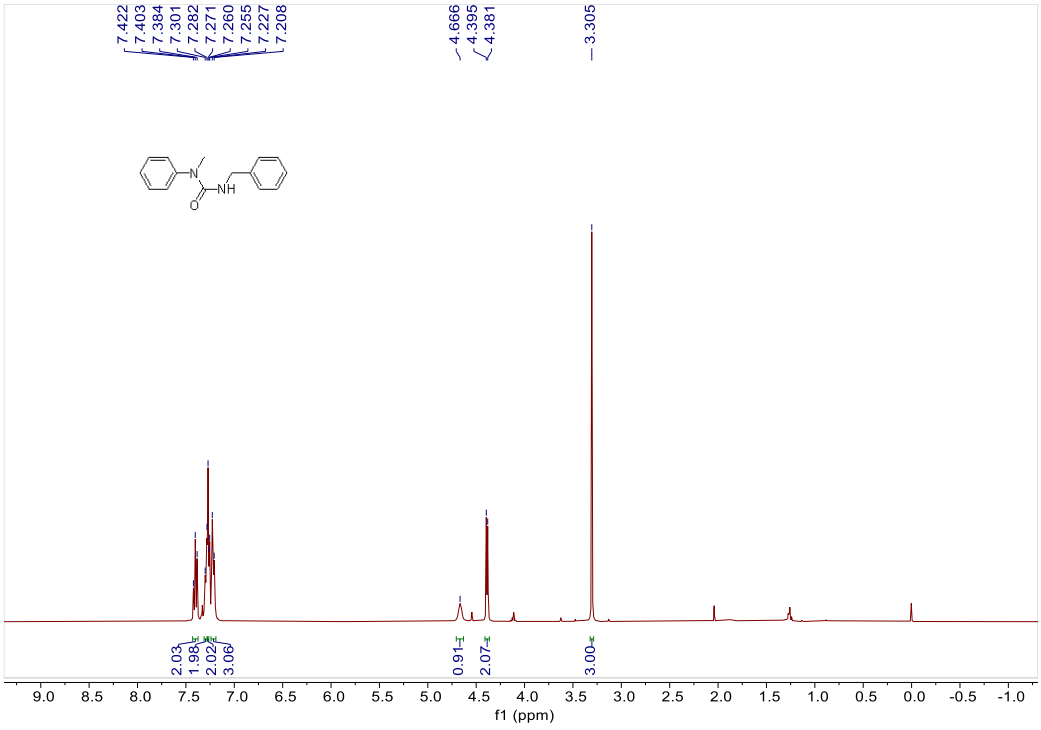


Figure S11. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3d**

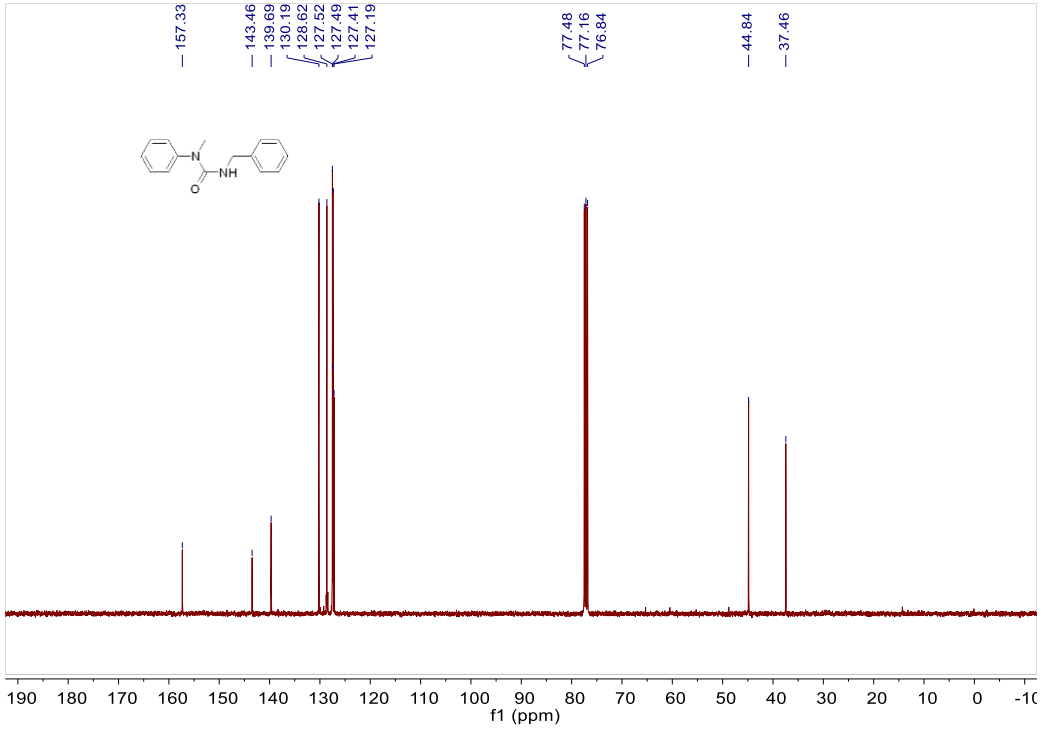


Figure S12. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3d**

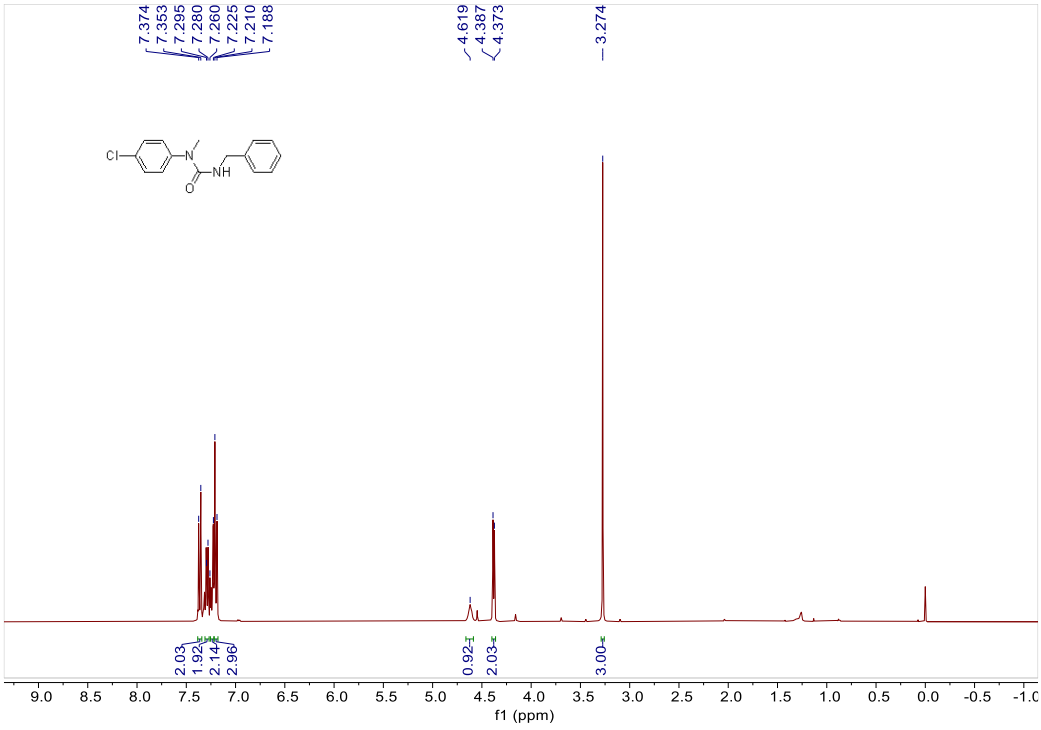


Figure S13. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3e**

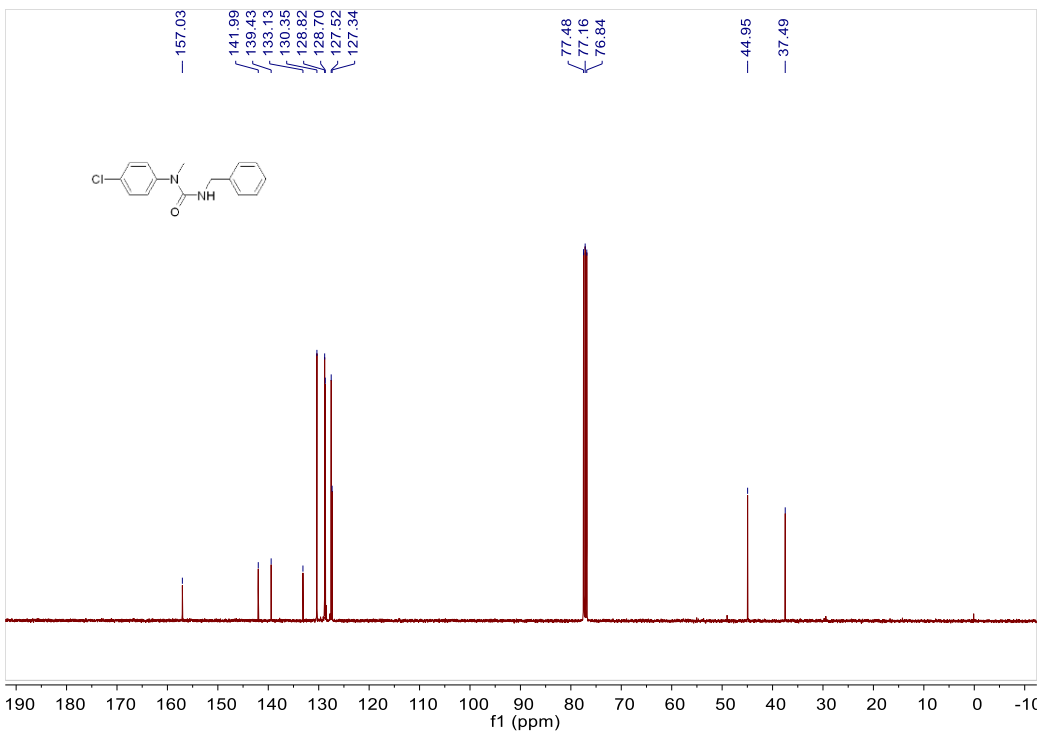


Figure S14. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3e**

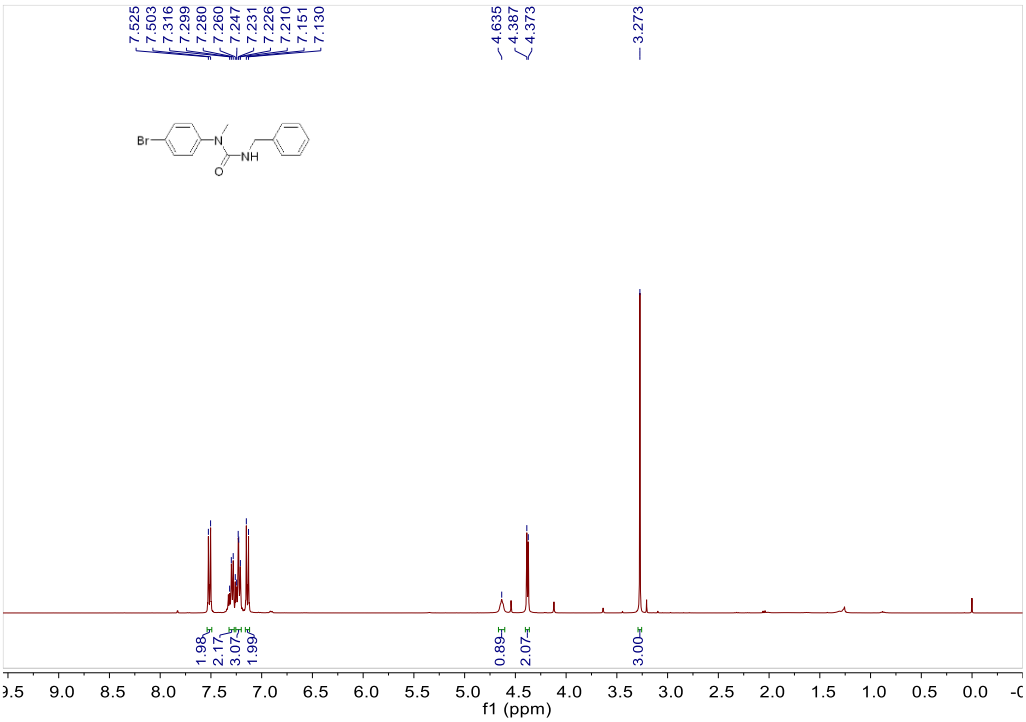


Figure S15. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3f**

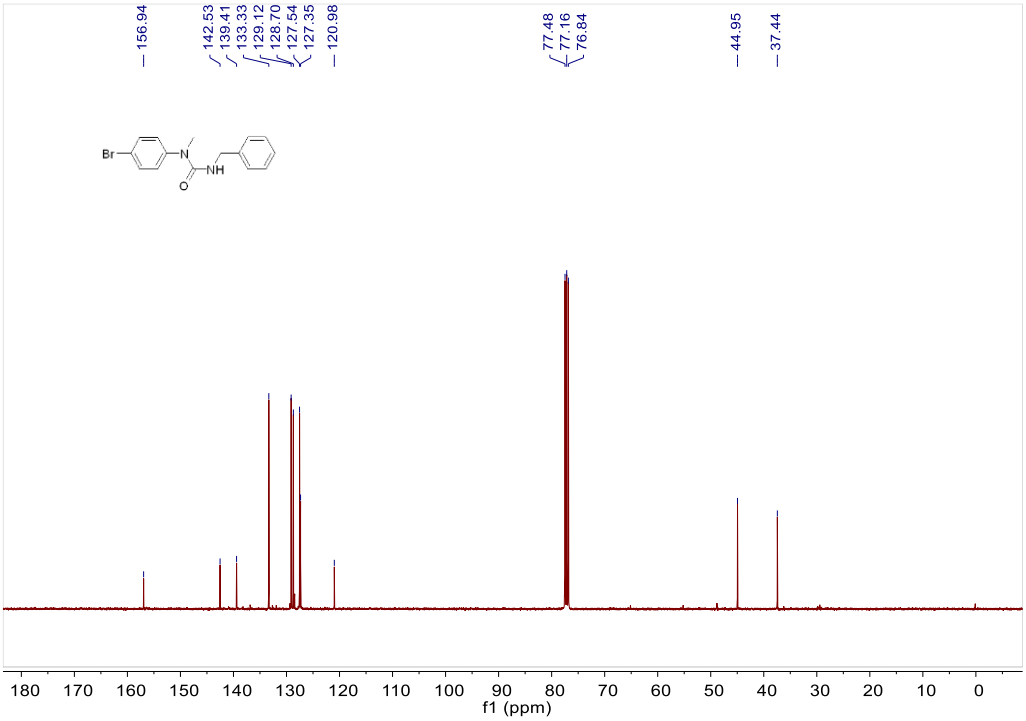


Figure S16. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3f**

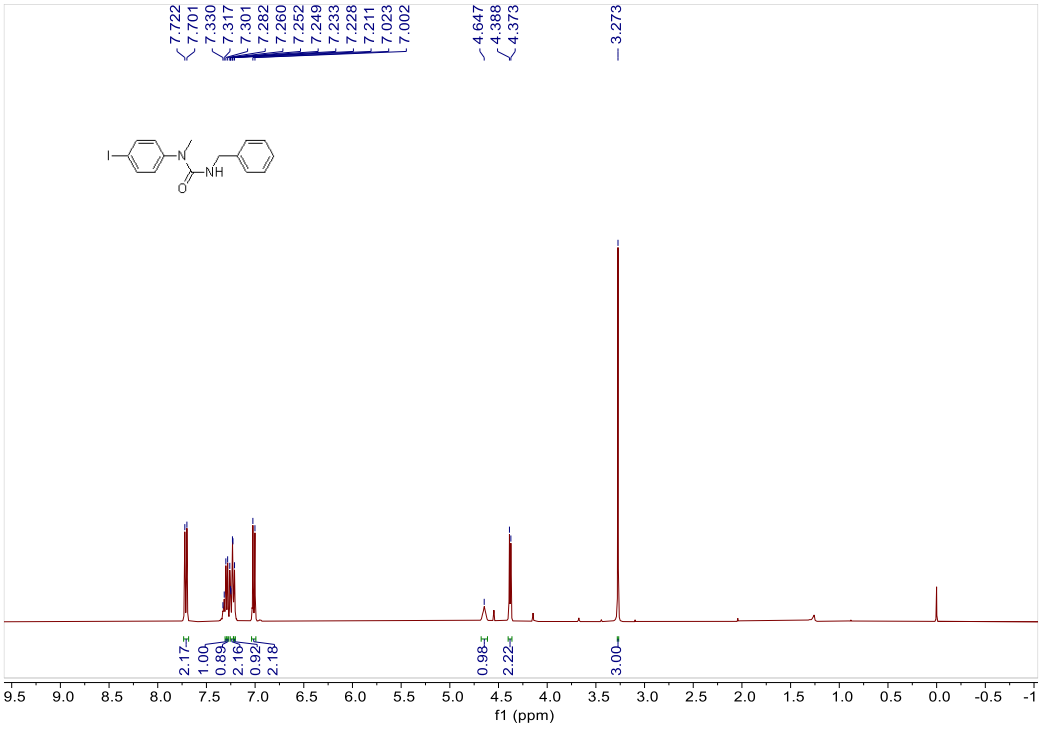


Figure S17. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3g**

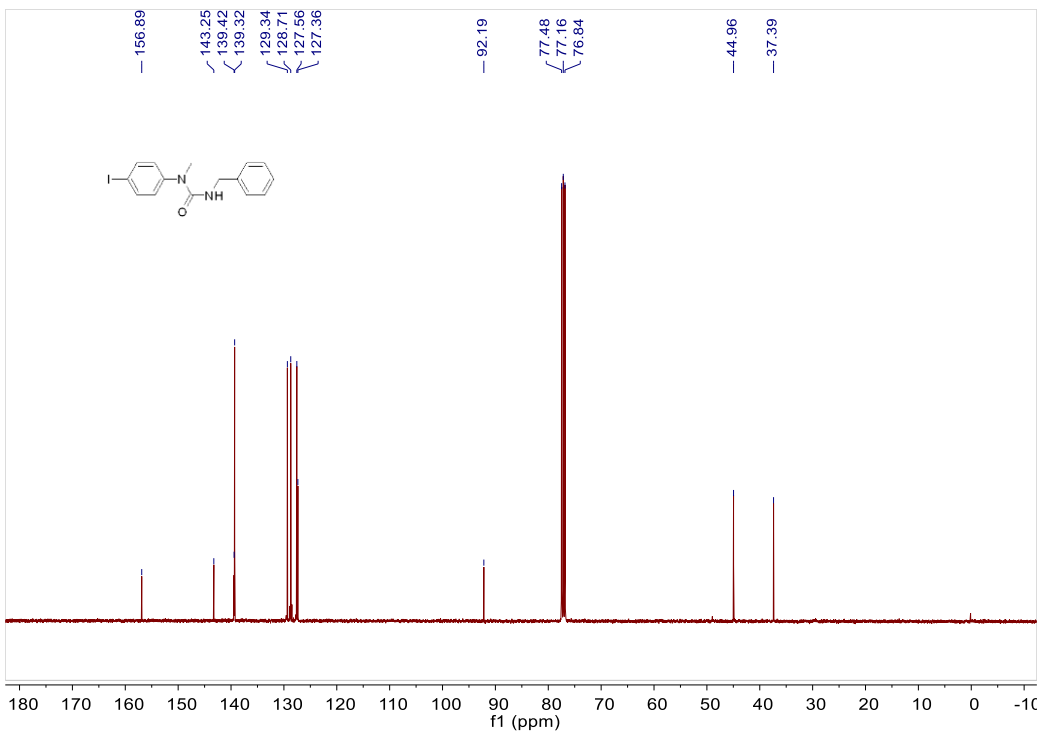


Figure S18. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3g**

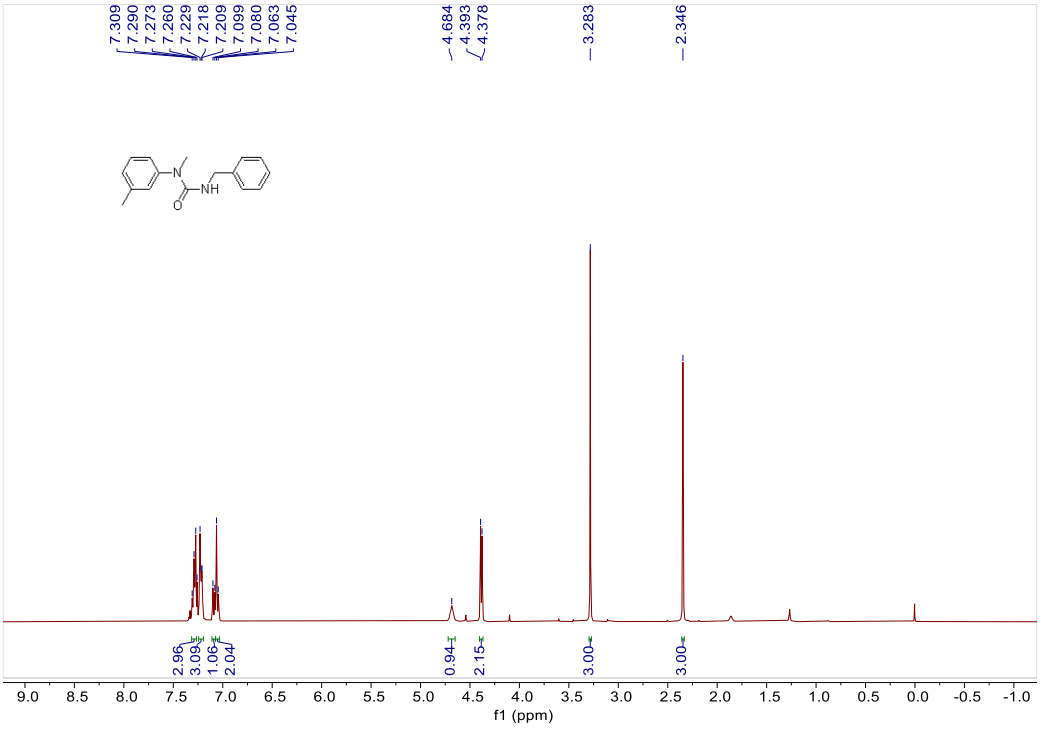


Figure S19. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3i**

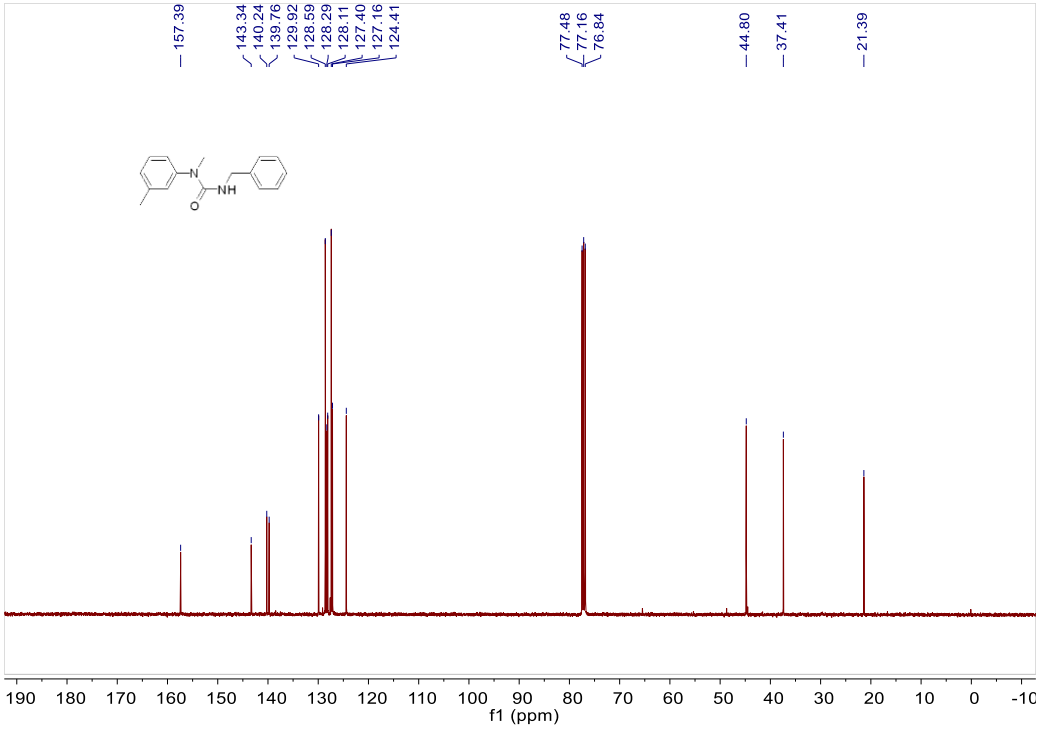


Figure S20. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3i**

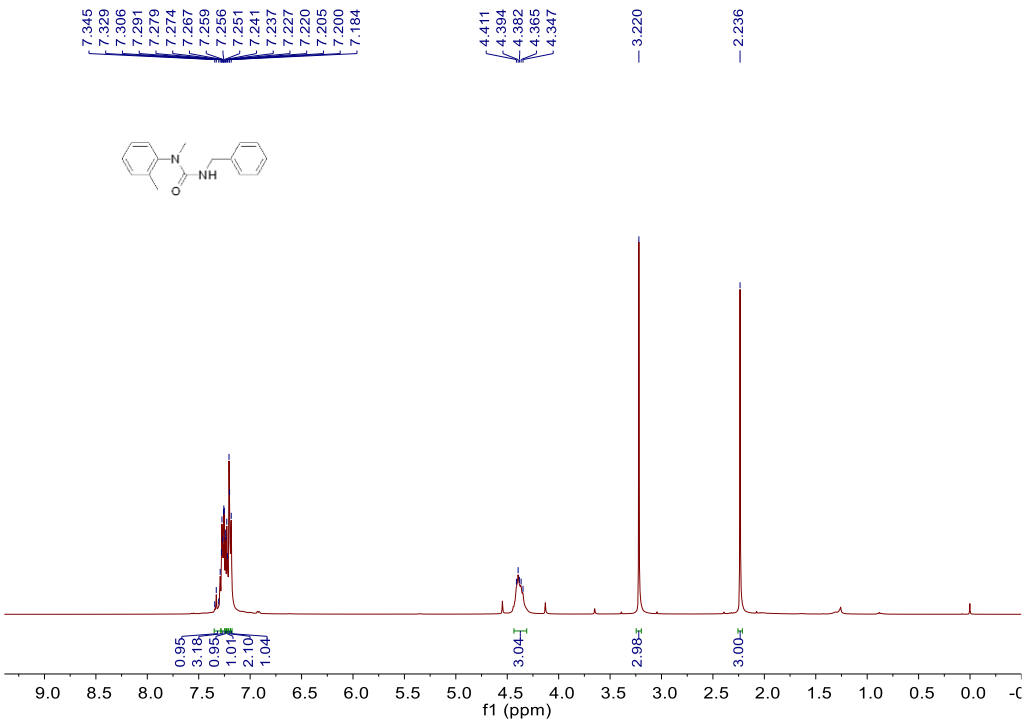


Figure S21. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3j**

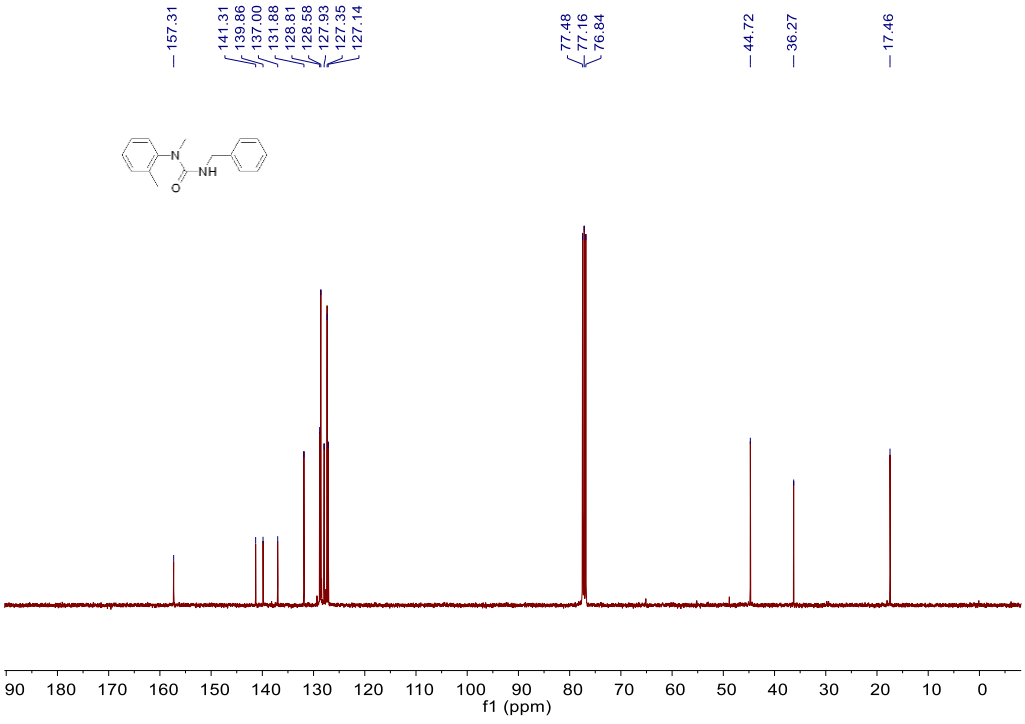


Figure S22. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3j**

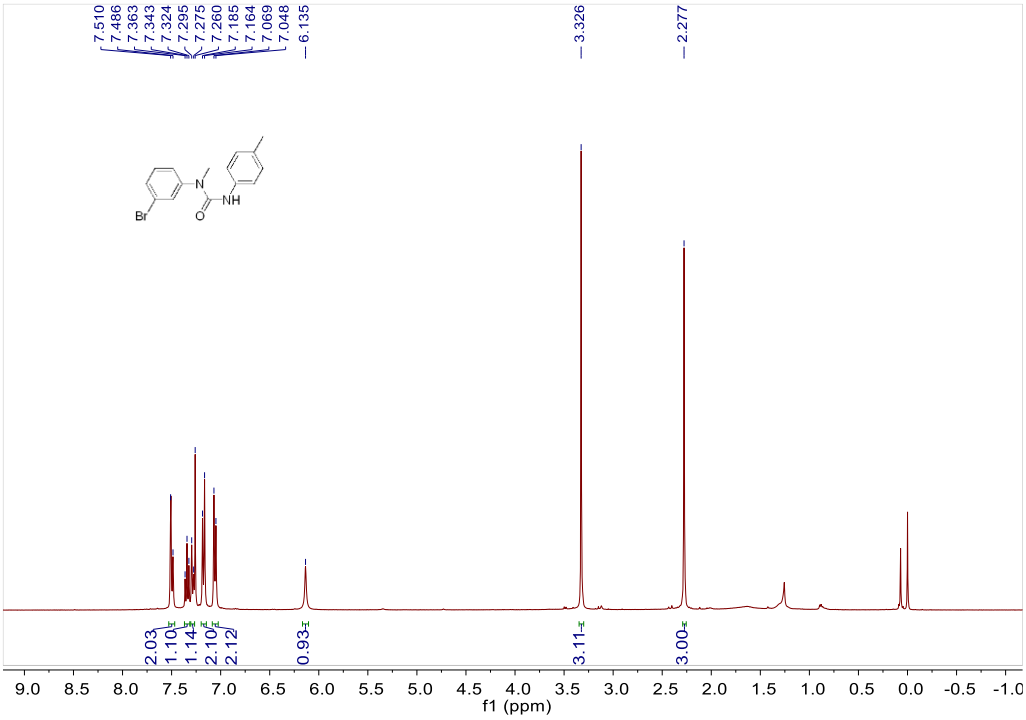


Figure S23. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3k**

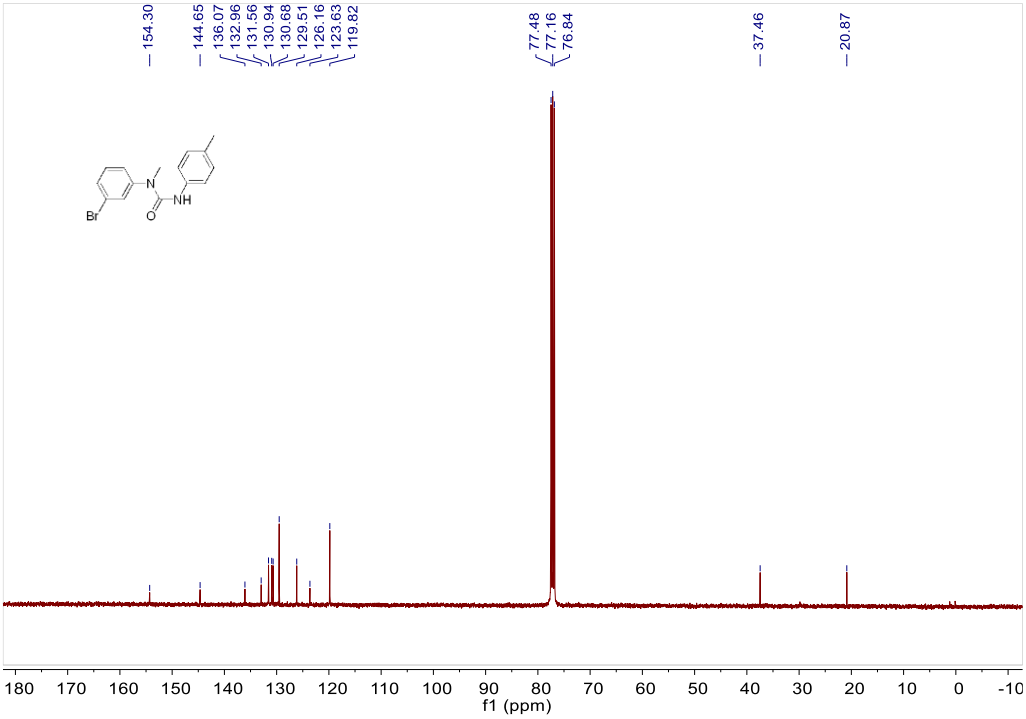


Figure S24. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3k**

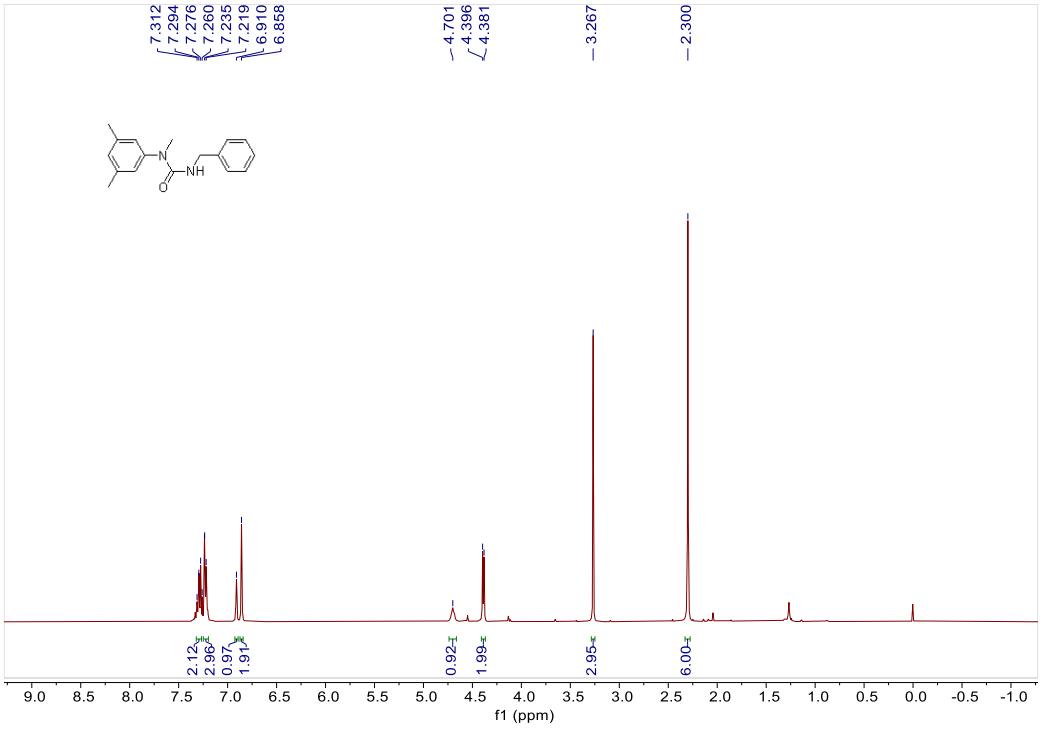


Figure S25. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3l**

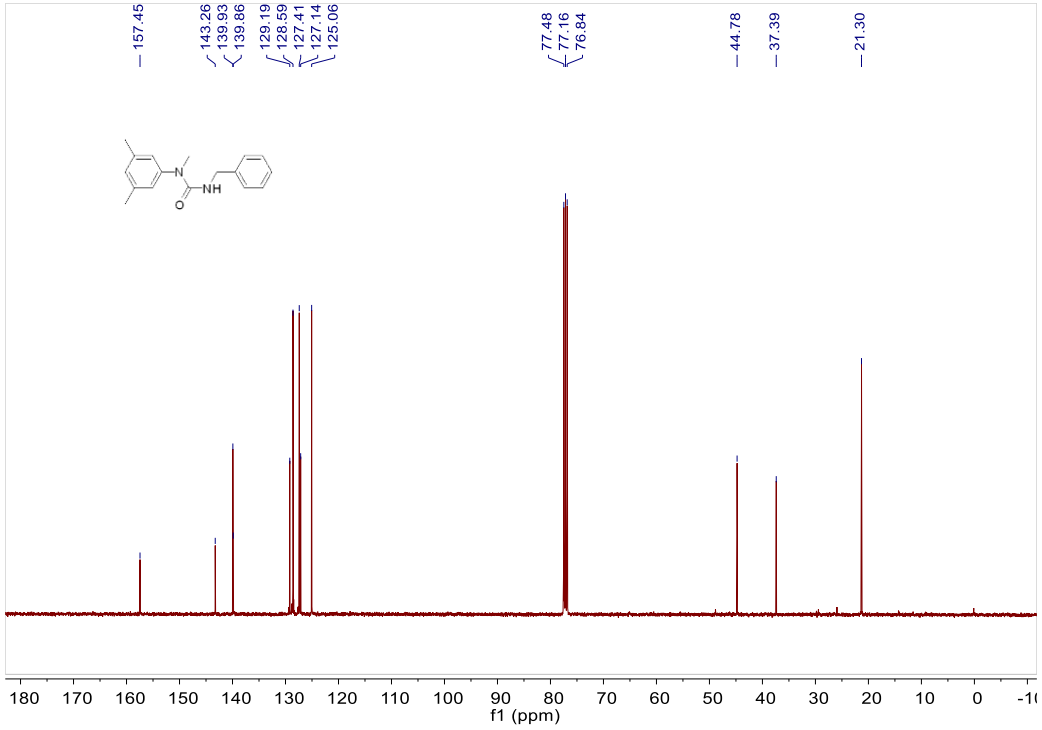


Figure S26. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3l**

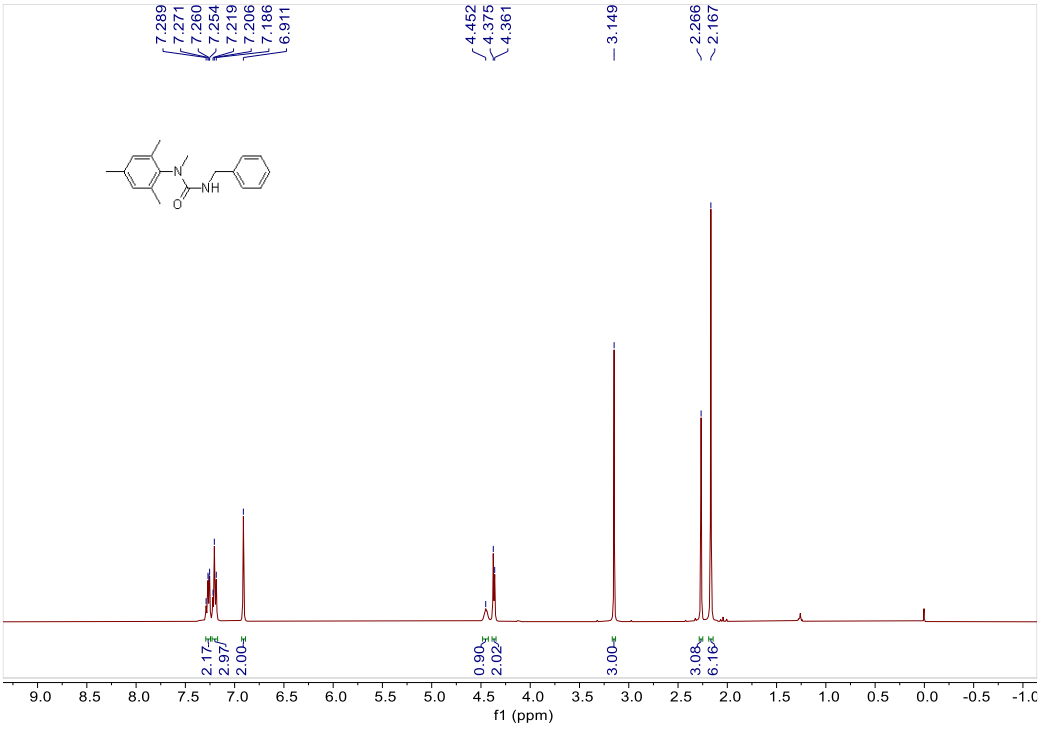


Figure S27. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3m**

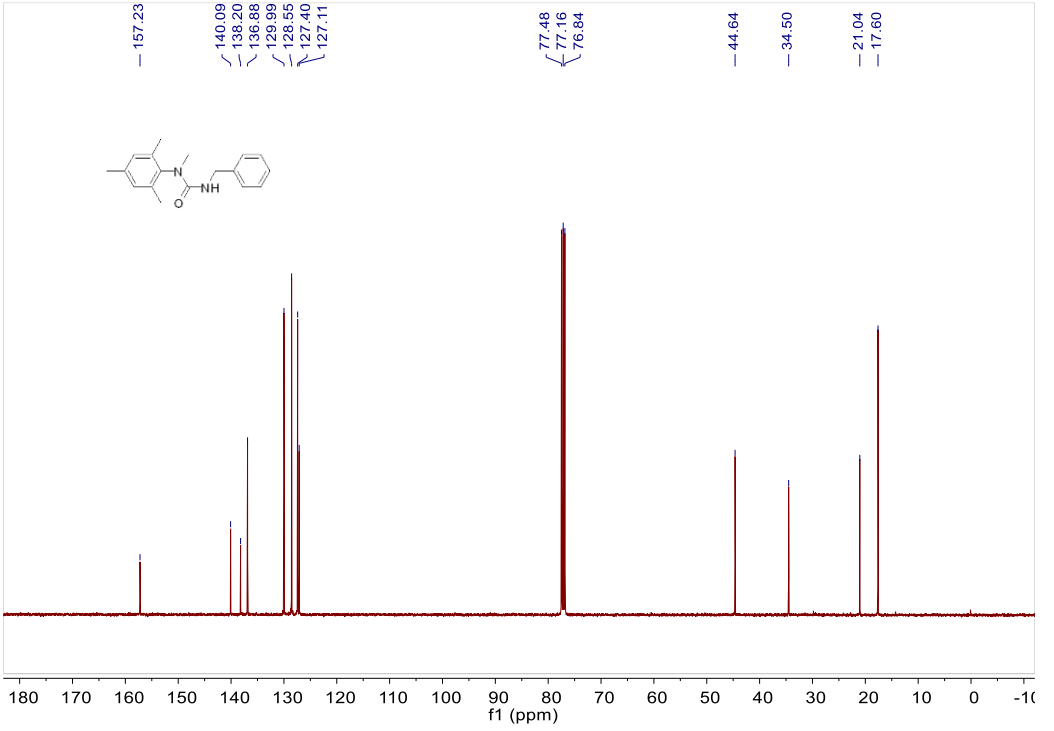


Figure S28. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3m**

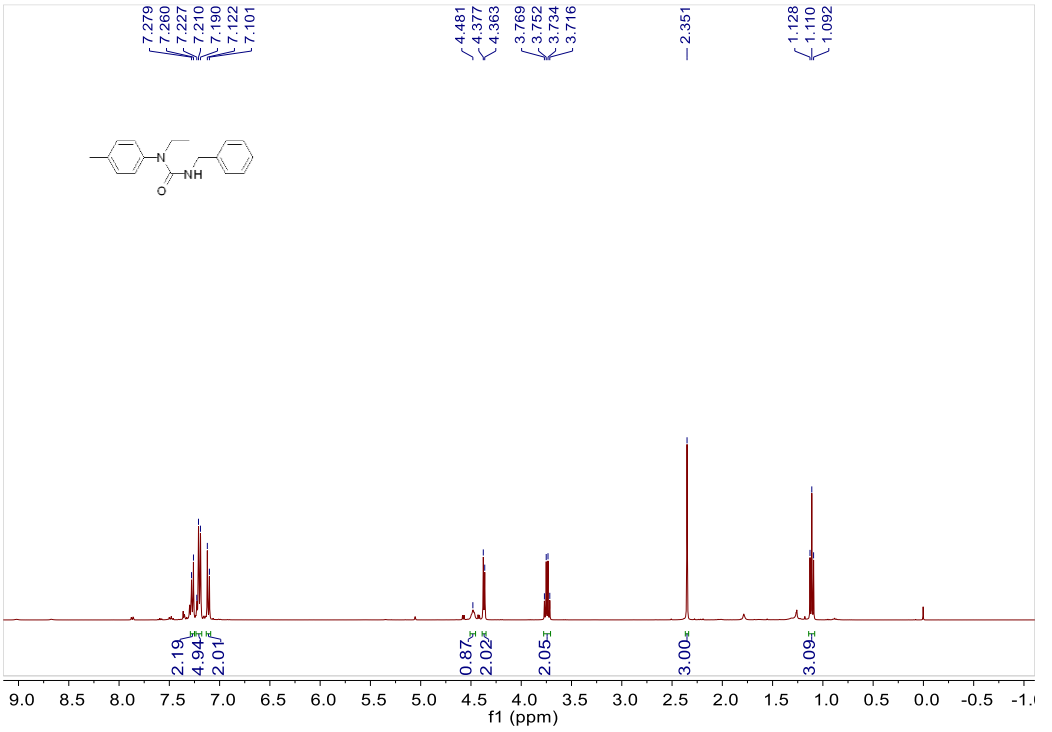


Figure S29. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3n**

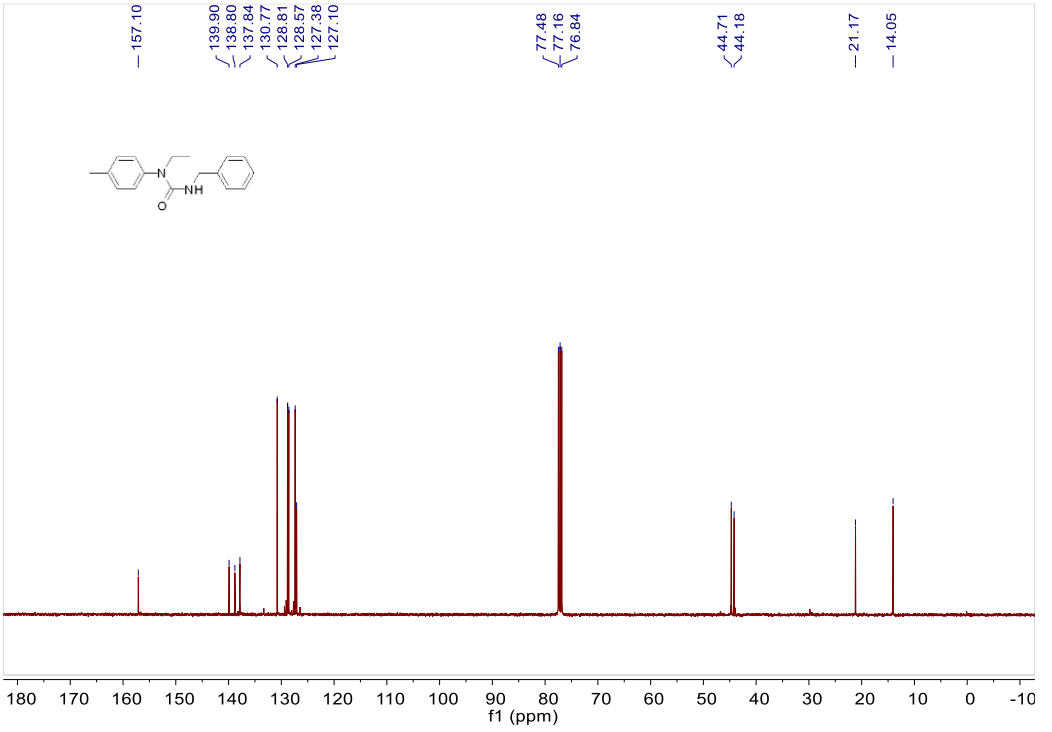


Figure S30. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3n**

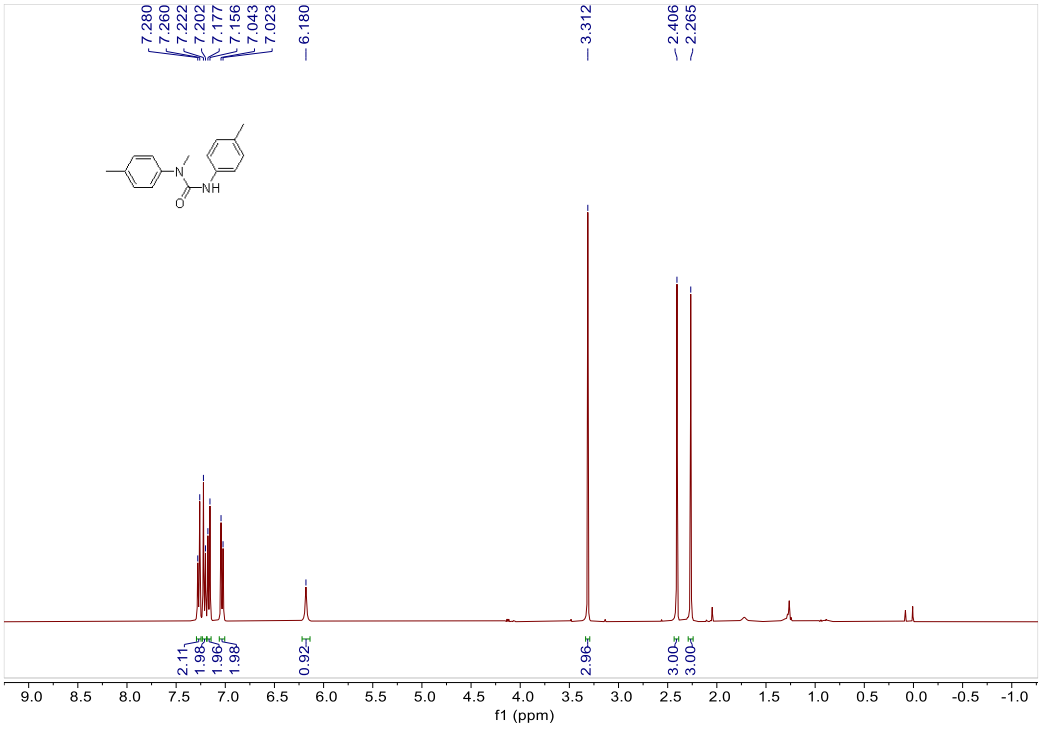


Figure S31. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3p**

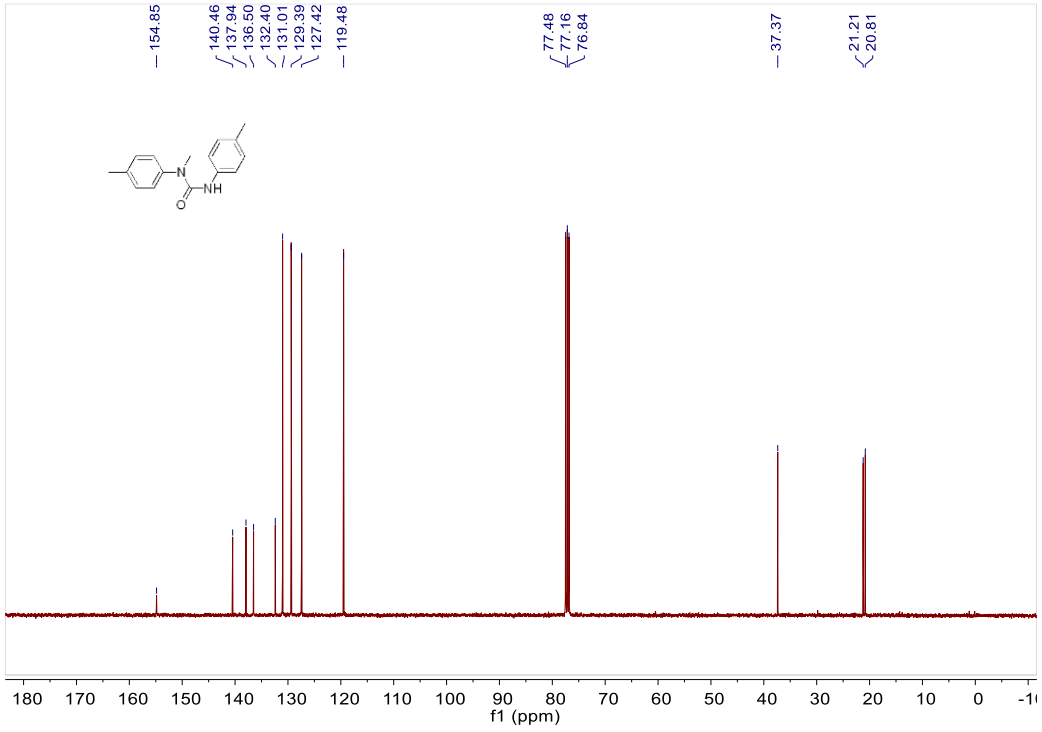


Figure S32. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3p**

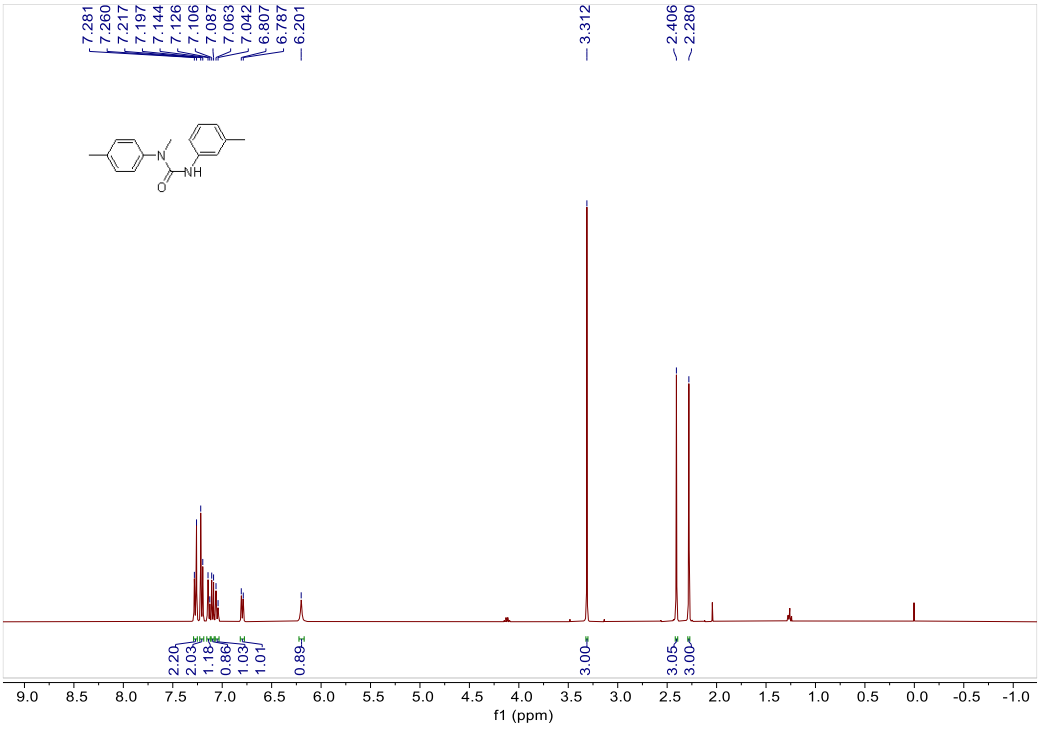


Figure S33. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3q**

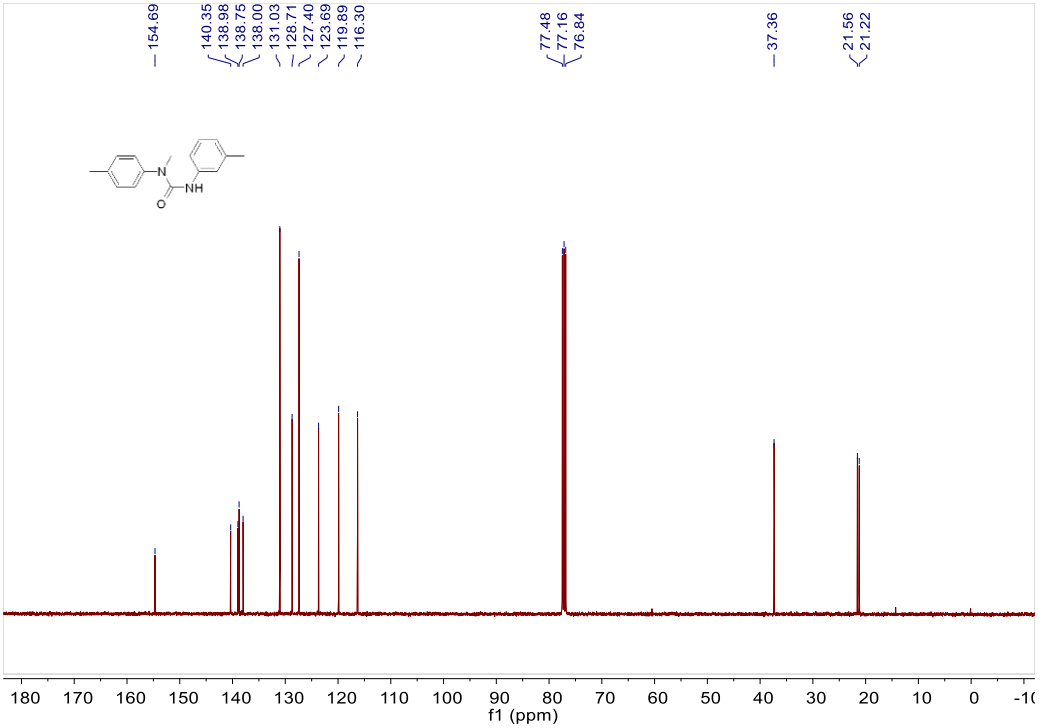


Figure S34. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3q**

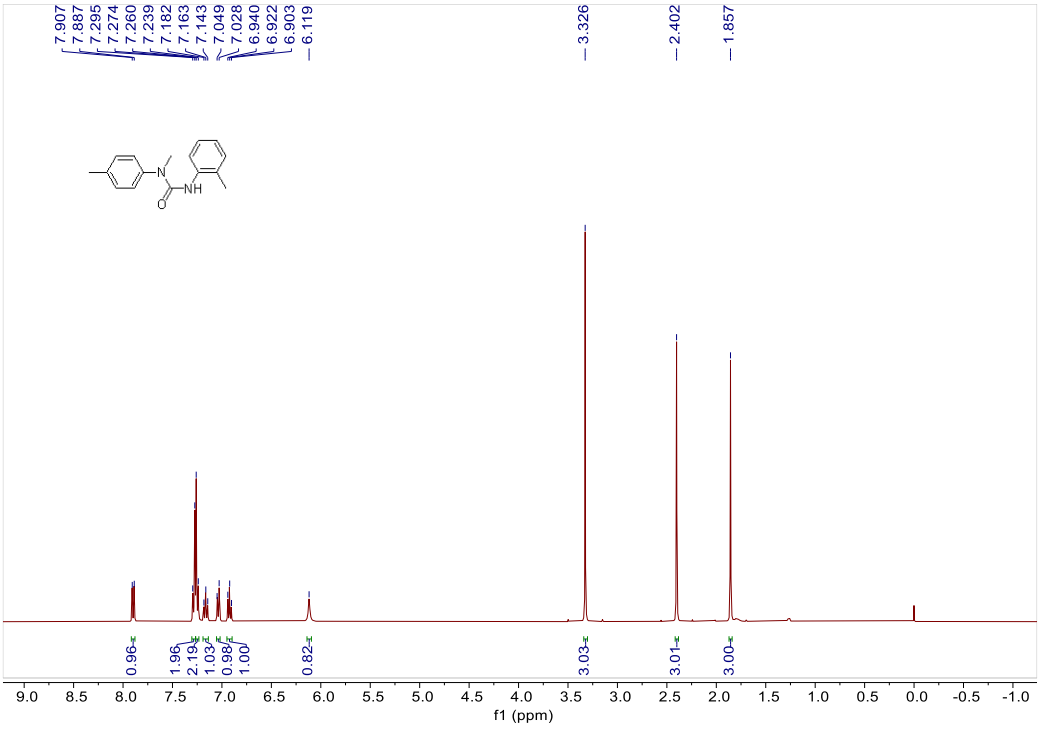


Figure S35. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3r**

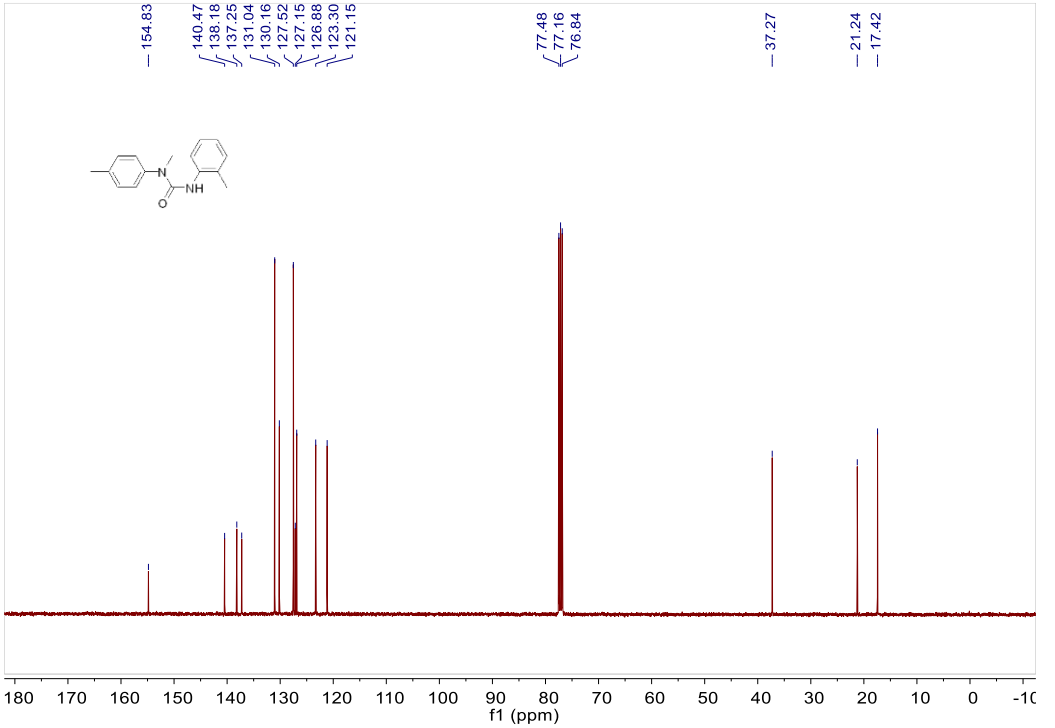


Figure S36. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3r**

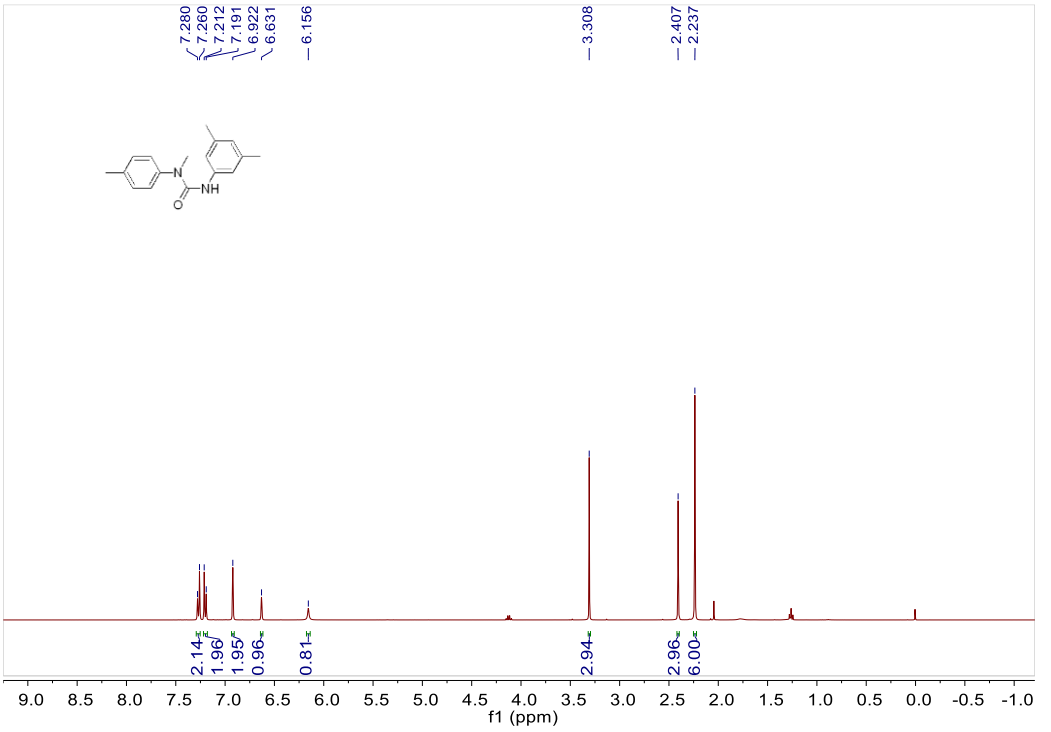


Figure S37. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3s**

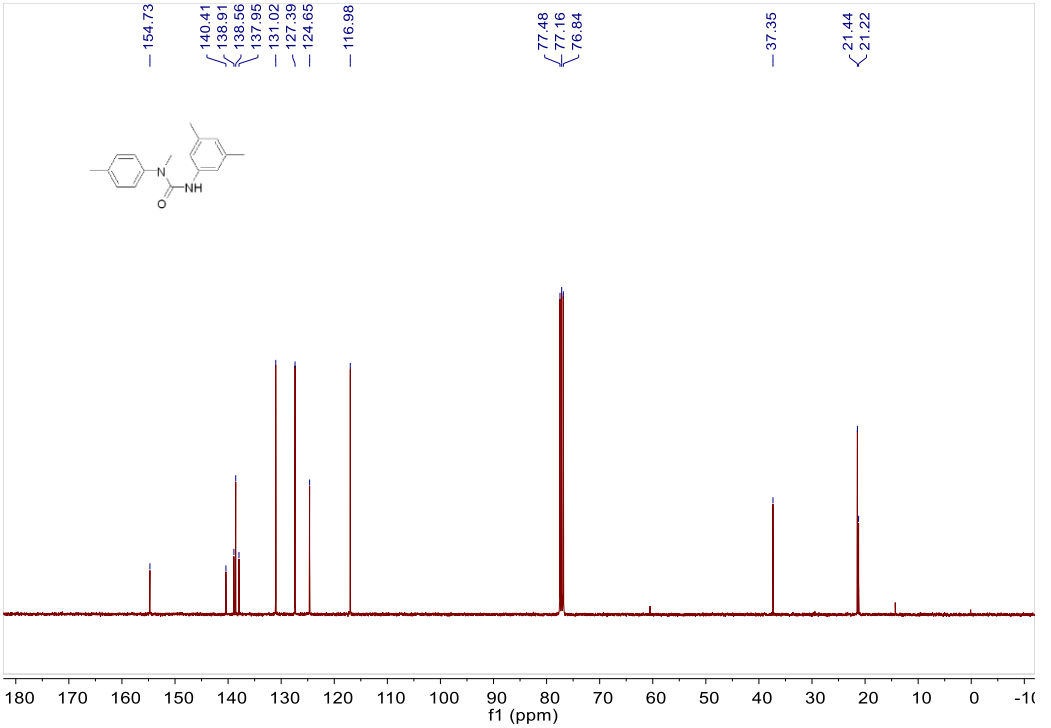


Figure S38. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3s**

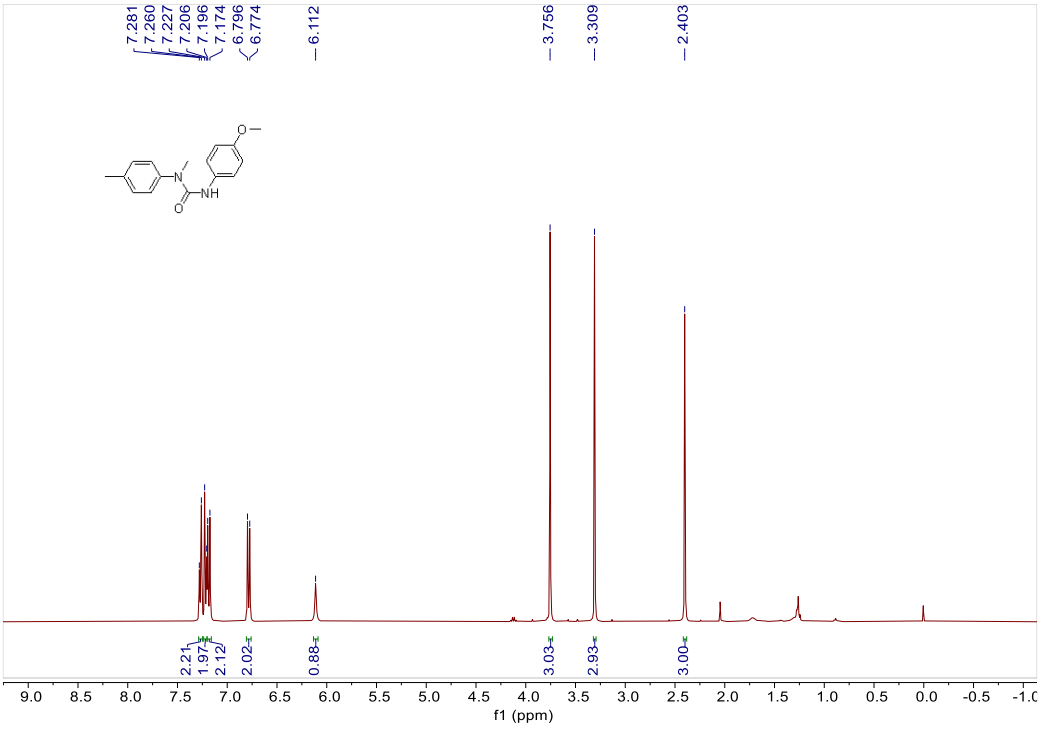


Figure S39. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3t**

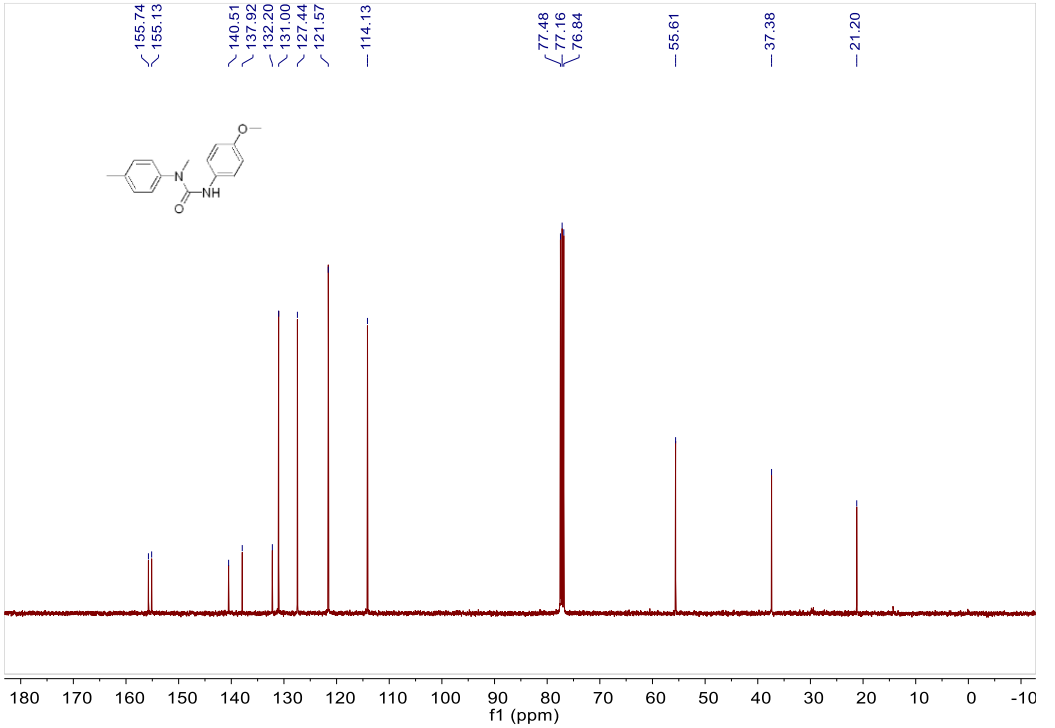


Figure S40. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3t**

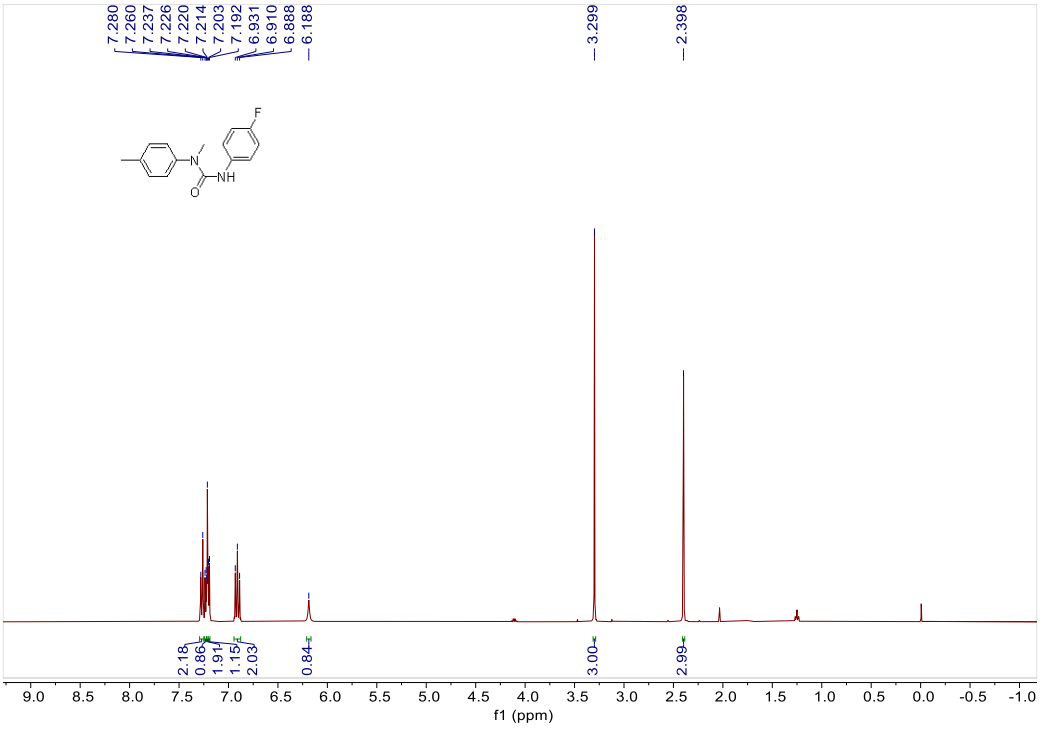


Figure S41. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3u**

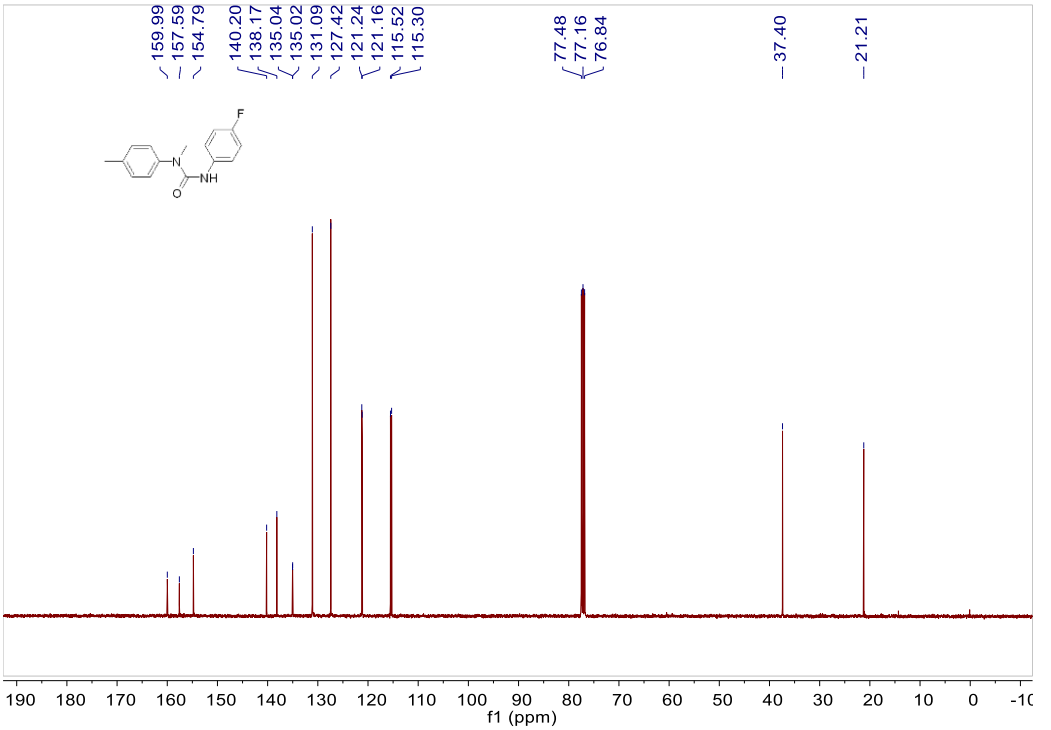


Figure S42. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3u**

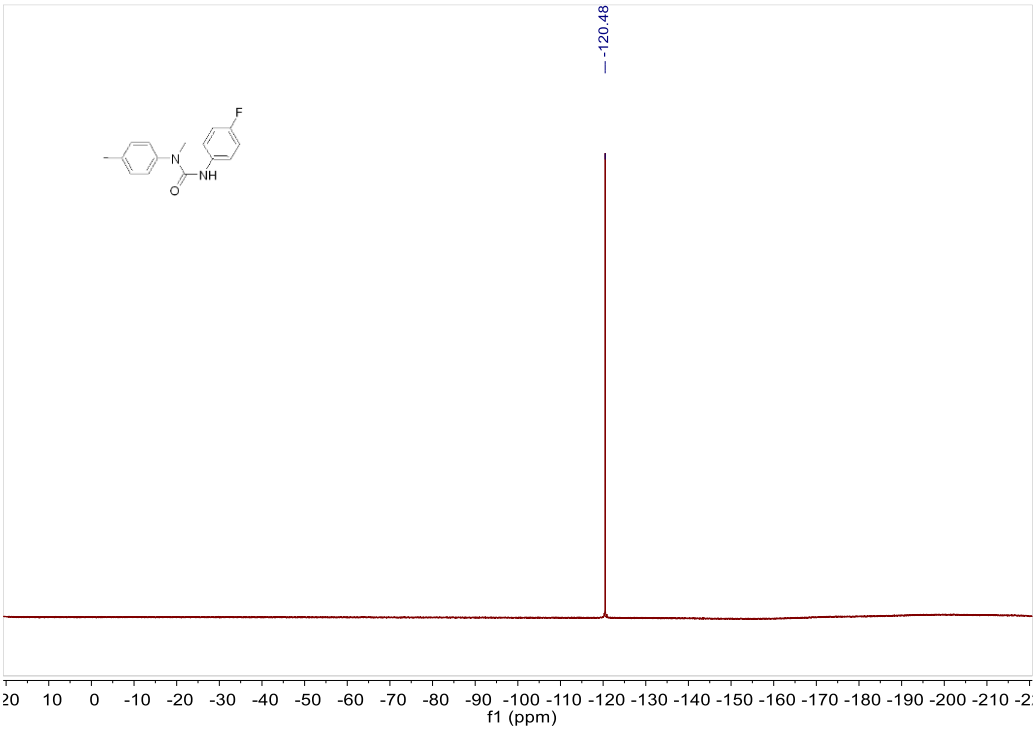


Figure S43. ^{19}F NMR spectrum ($CDCl_3$, 376.5 MHz) of **3u**

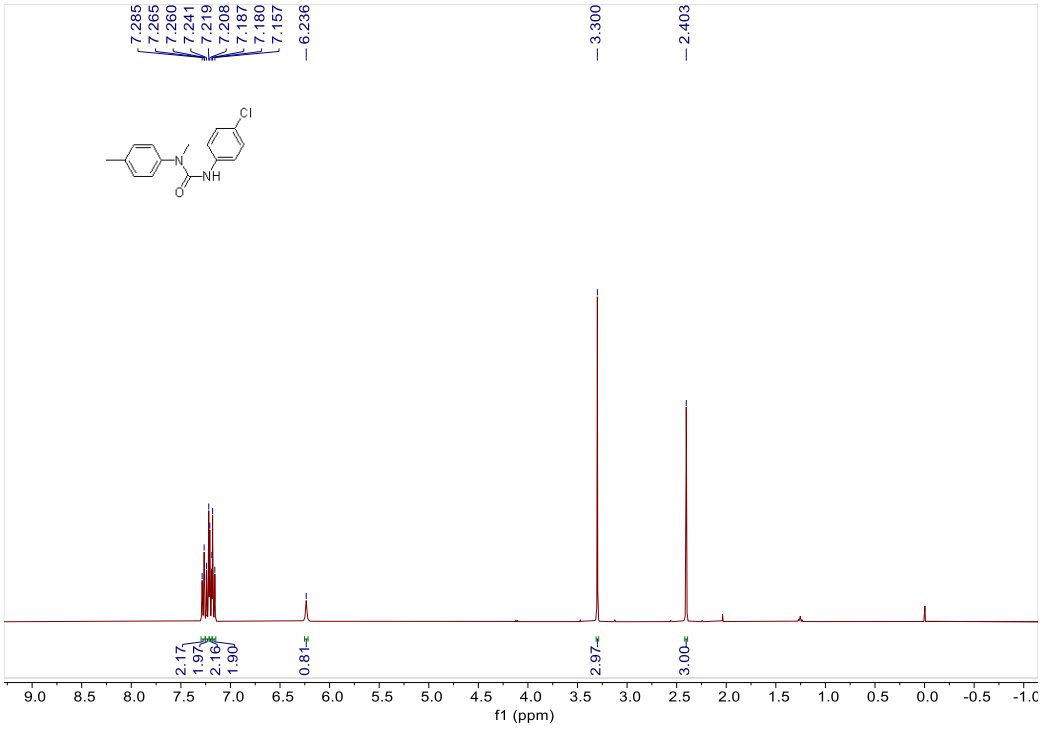


Figure S44. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3v**

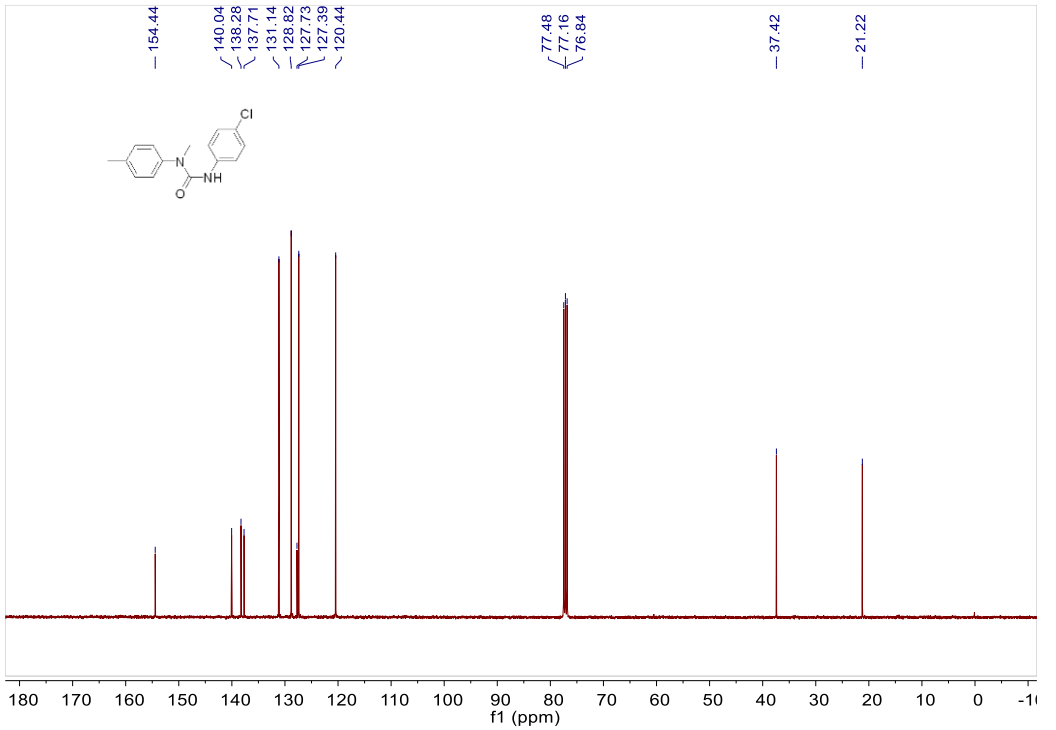


Figure S45. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3v**

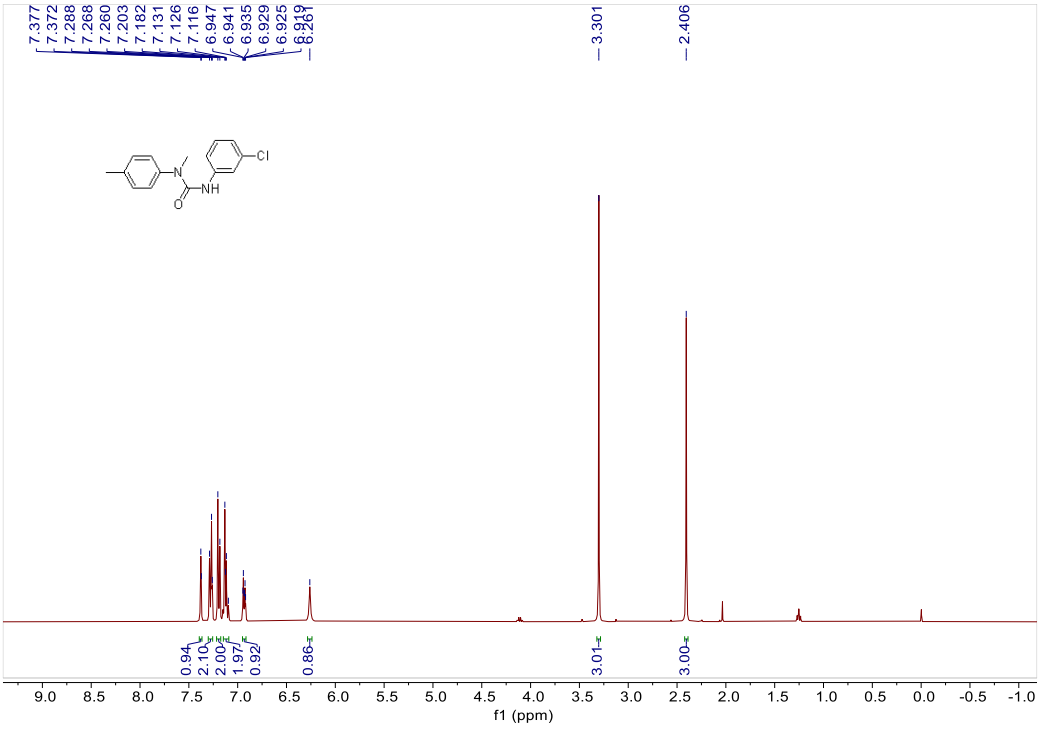


Figure S46. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3w**

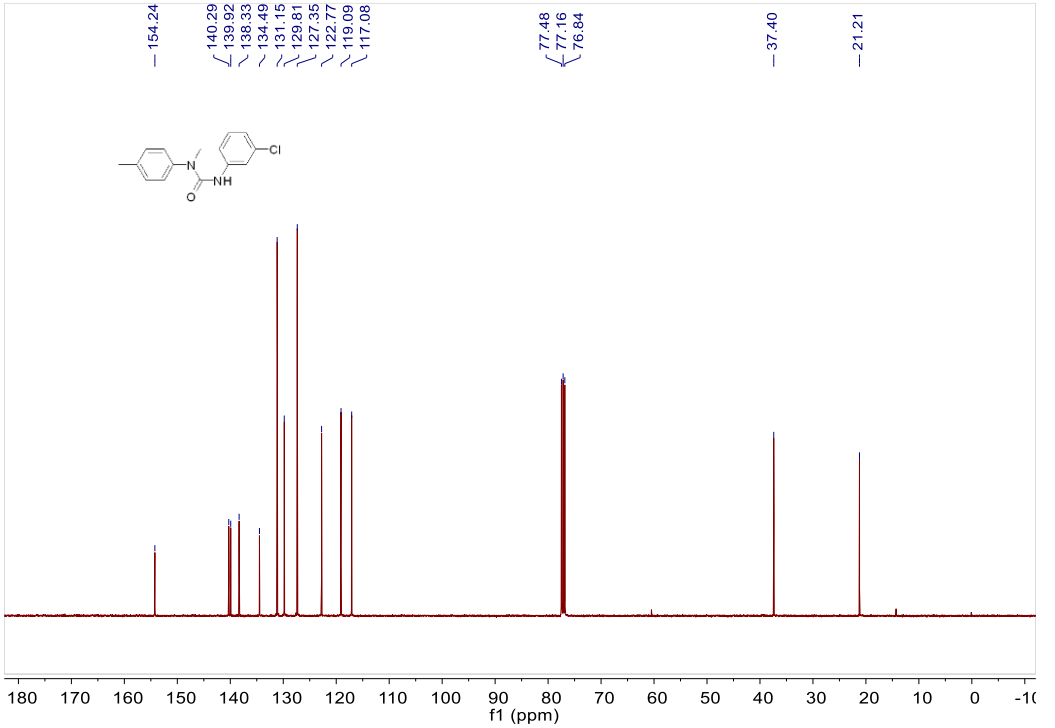


Figure S47. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3w**

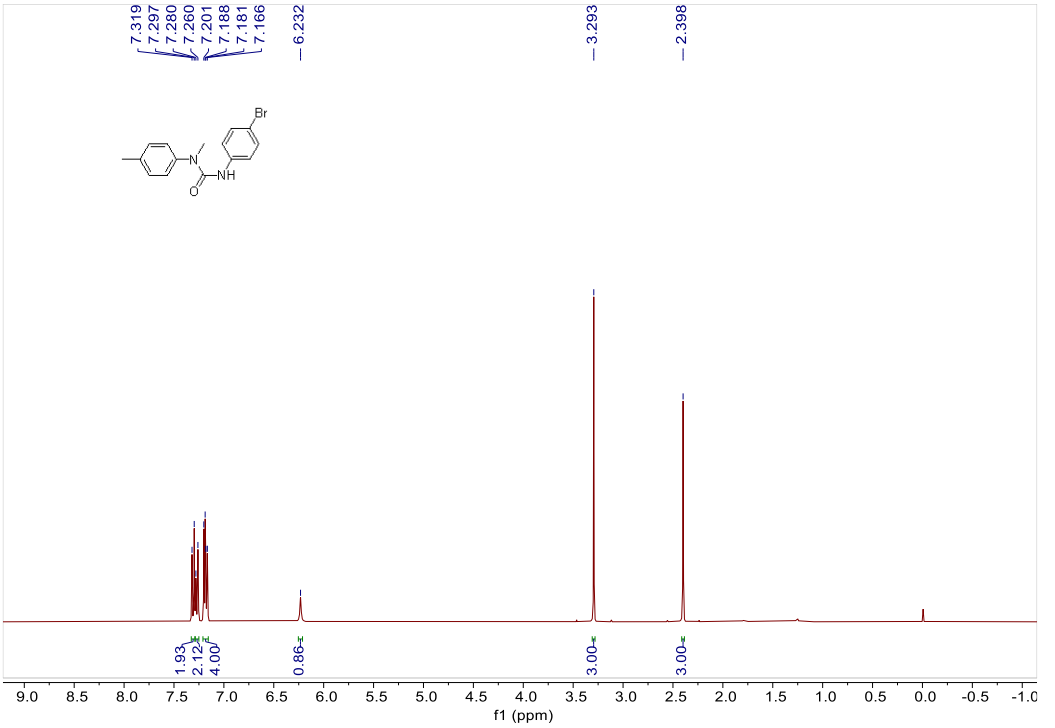


Figure S48. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3x**

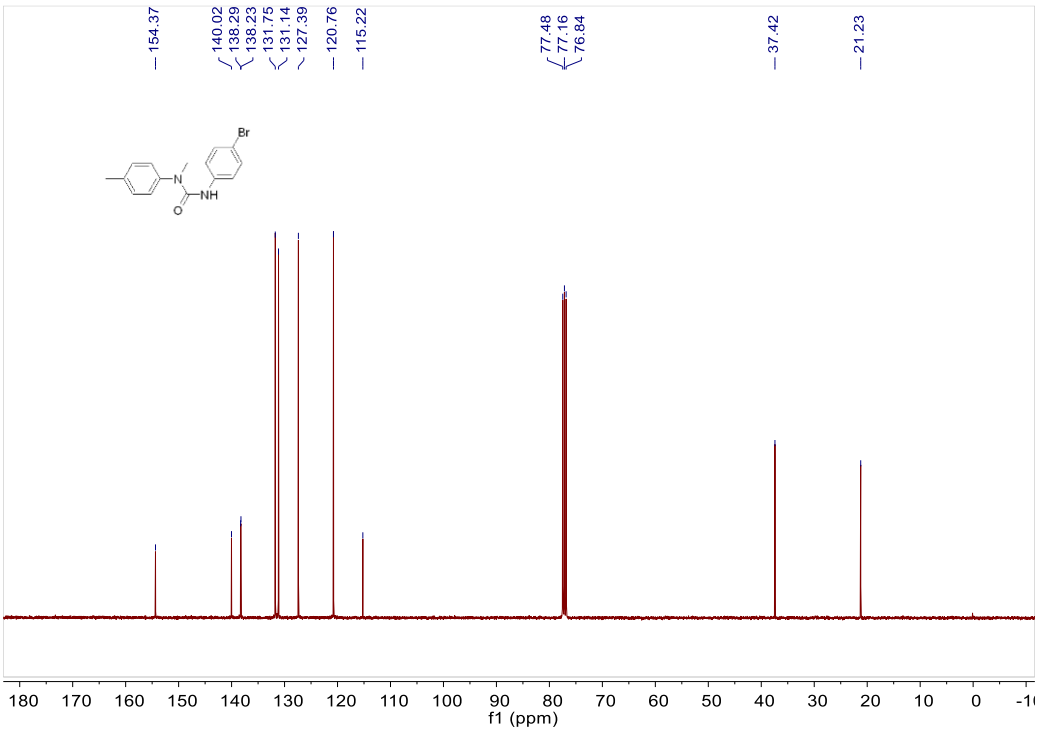


Figure S49. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3x**

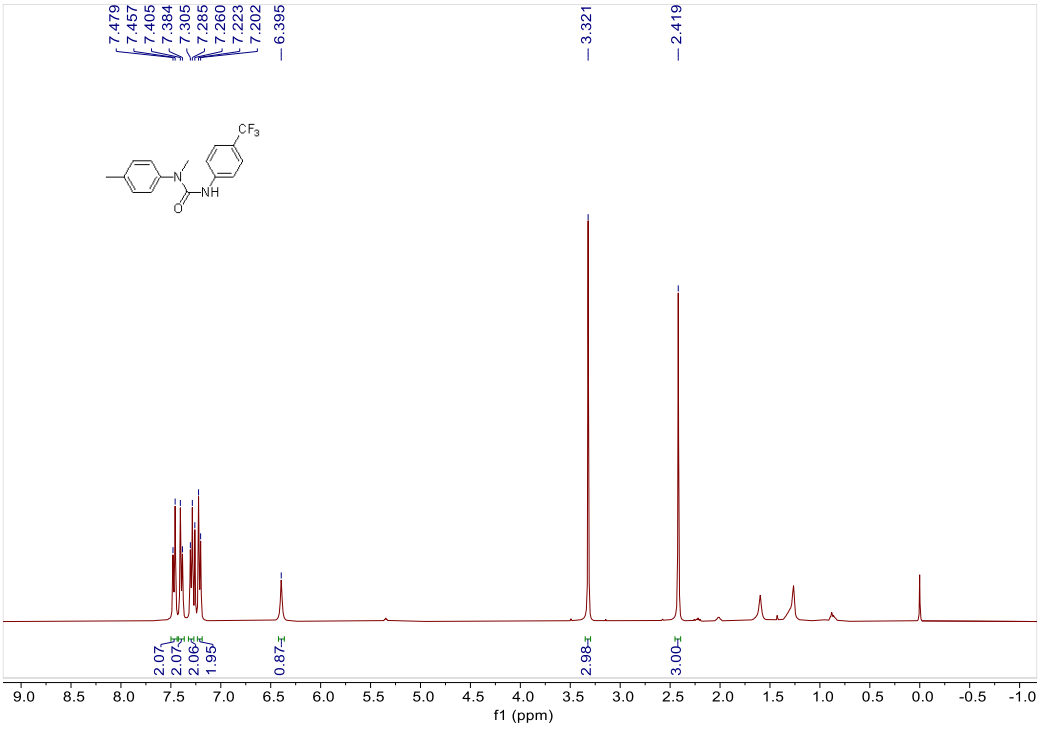


Figure S50. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3y**

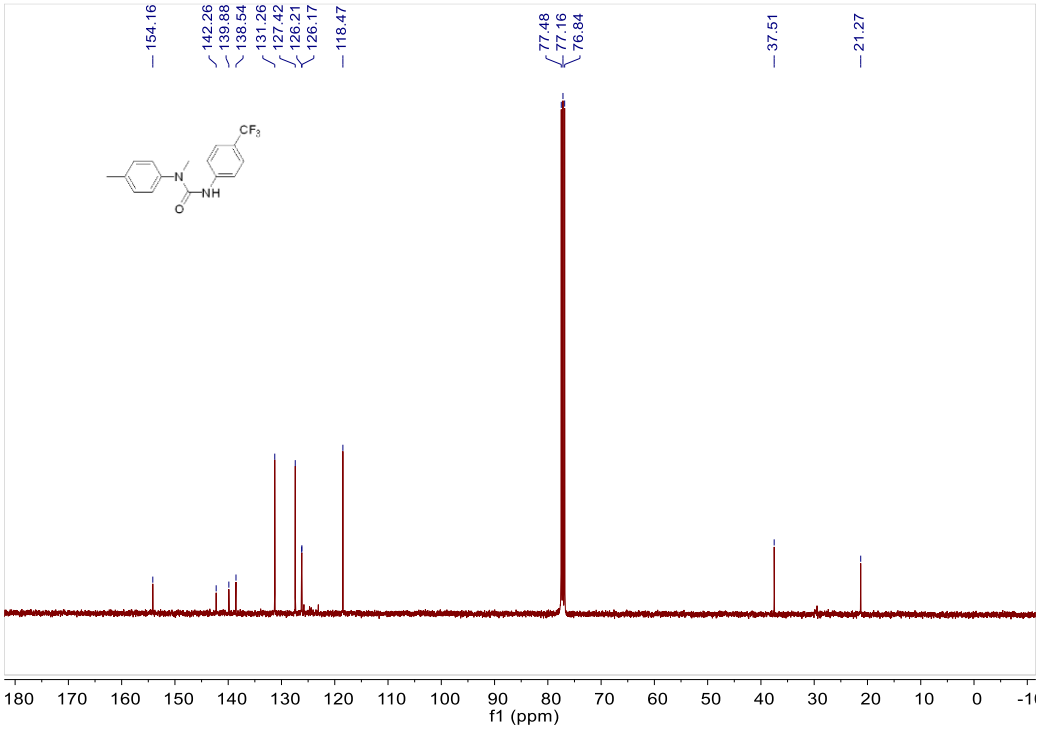


Figure S51. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3y**

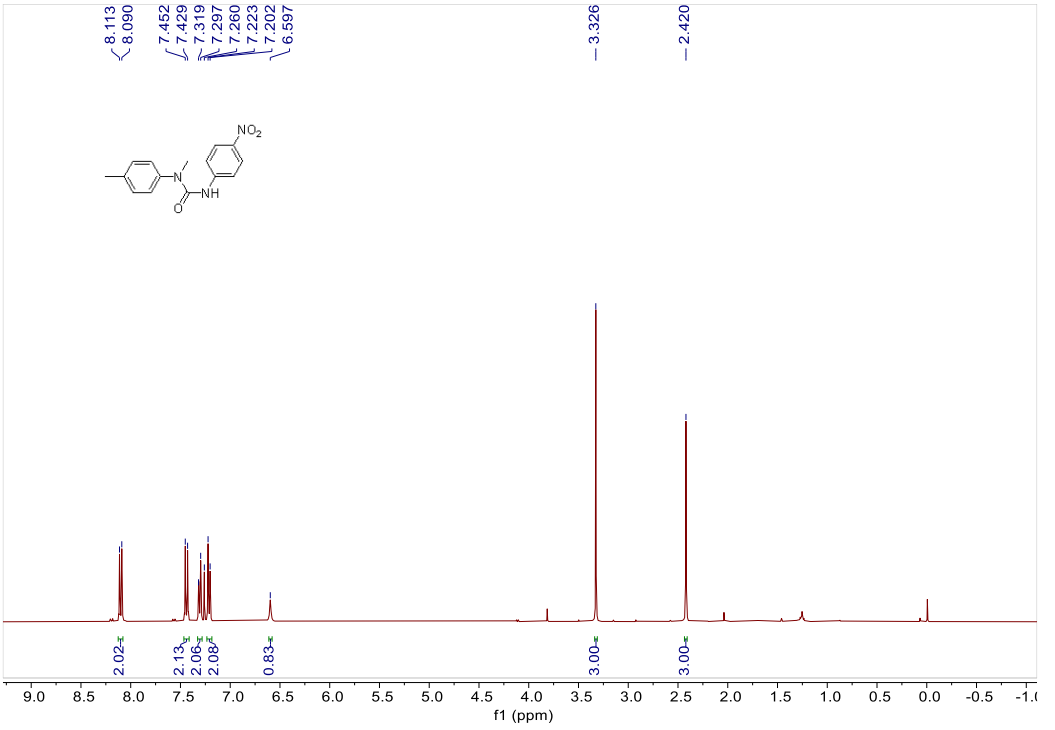


Figure S52. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3z**

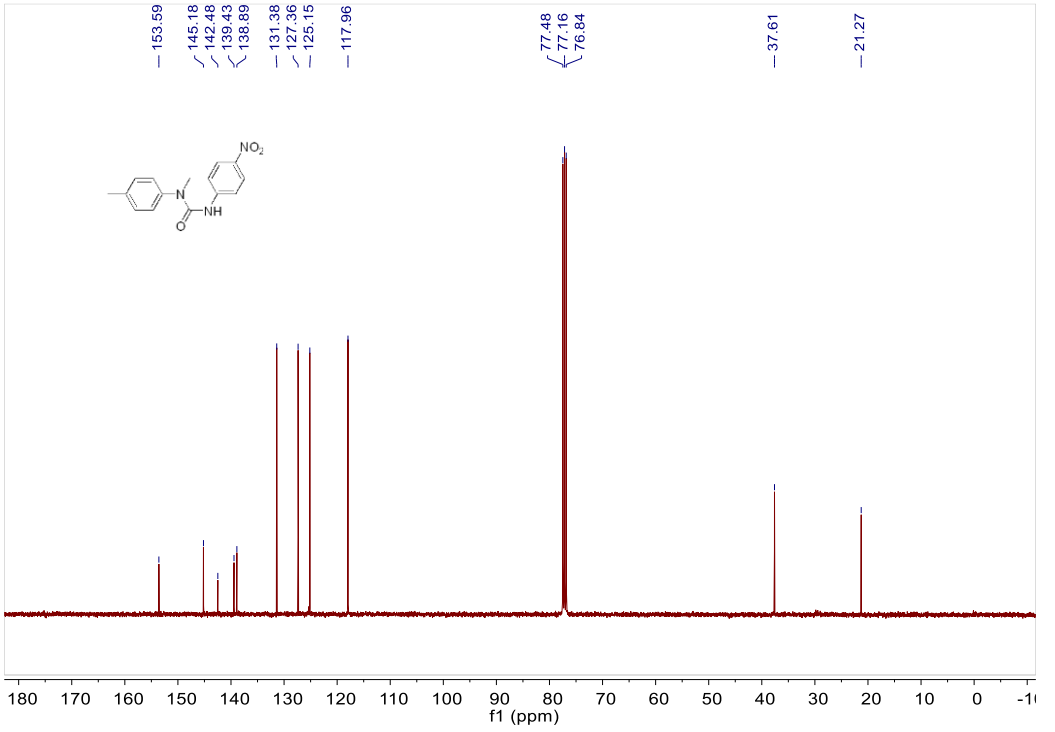


Figure S53. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3z**

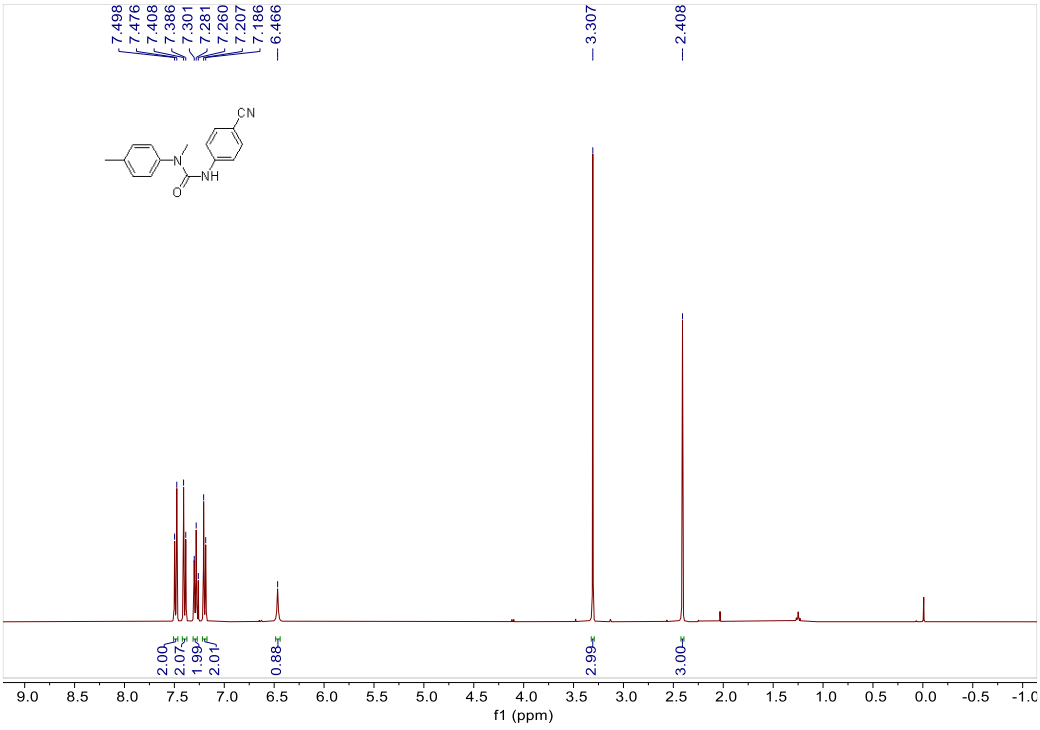


Figure S54. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3aa**

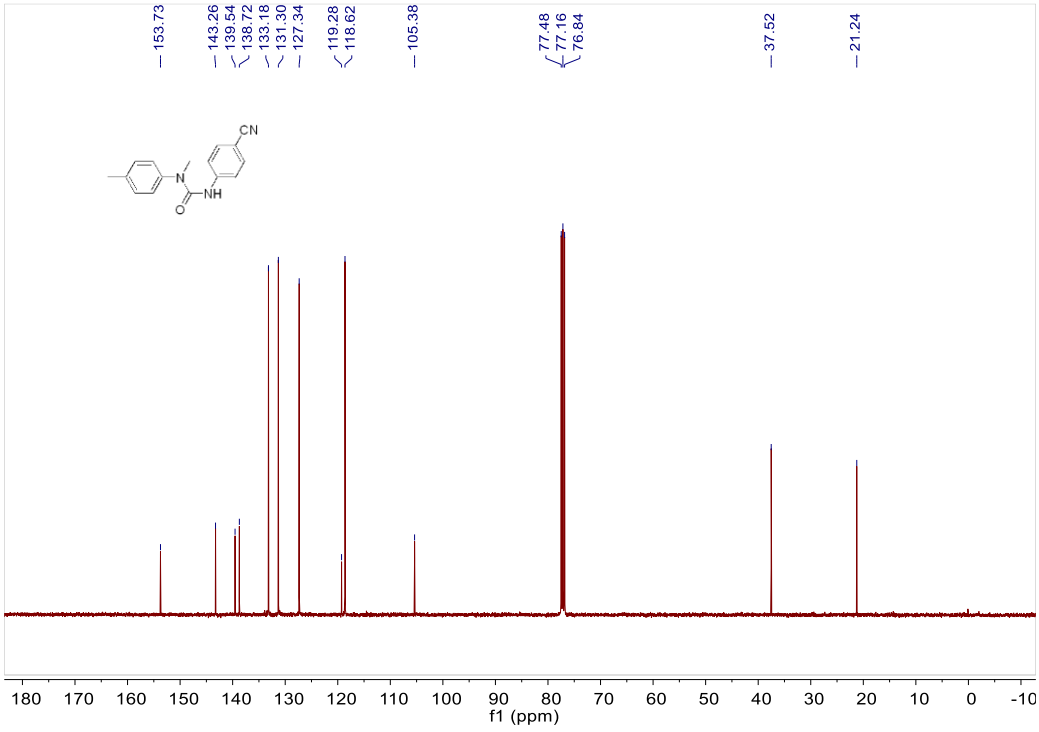


Figure S55. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3aa**

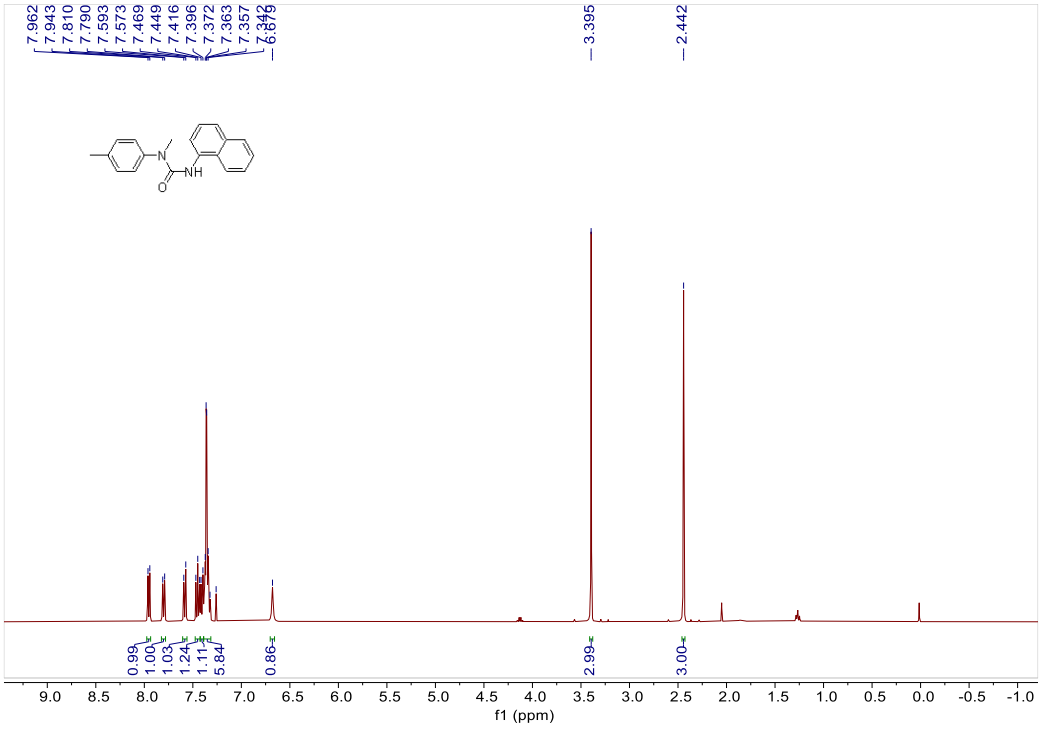


Figure S56. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3ab**

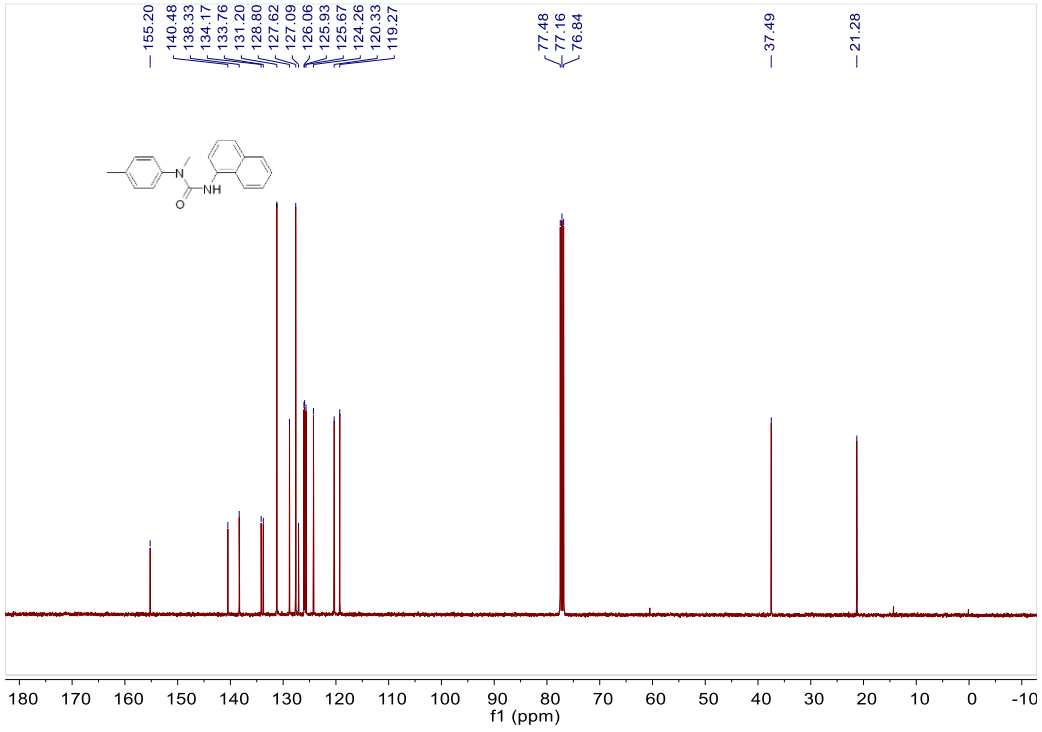


Figure S57. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3ab**

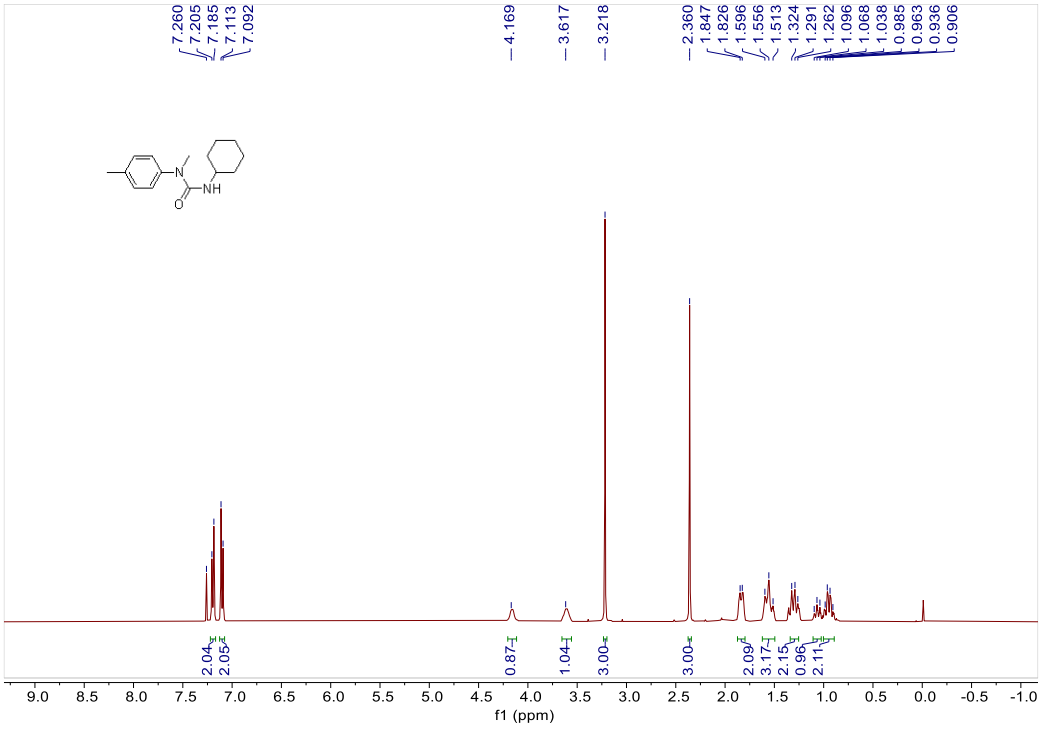


Figure S58. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3ad**

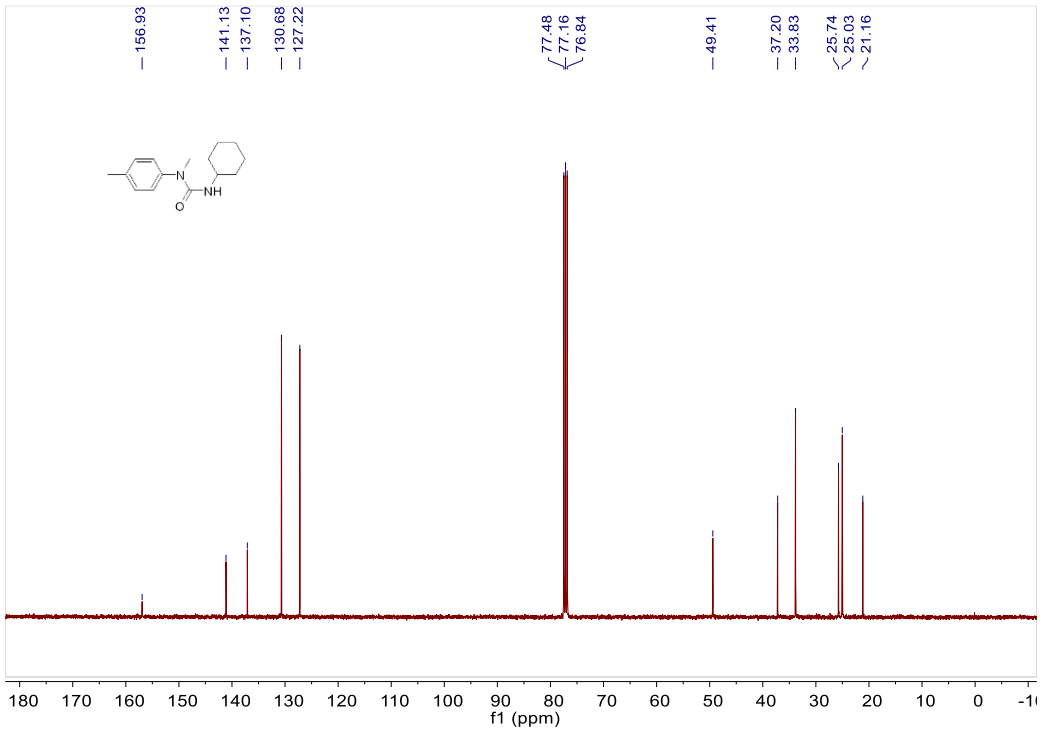


Figure S59. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3ad**

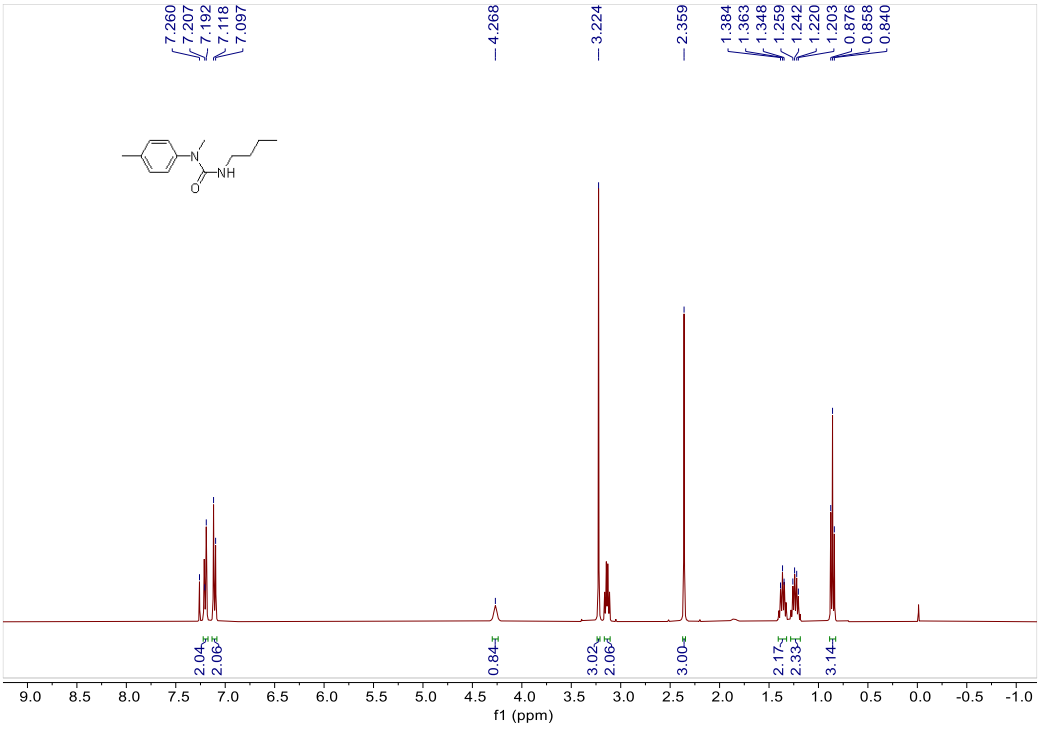


Figure S60. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3ae**

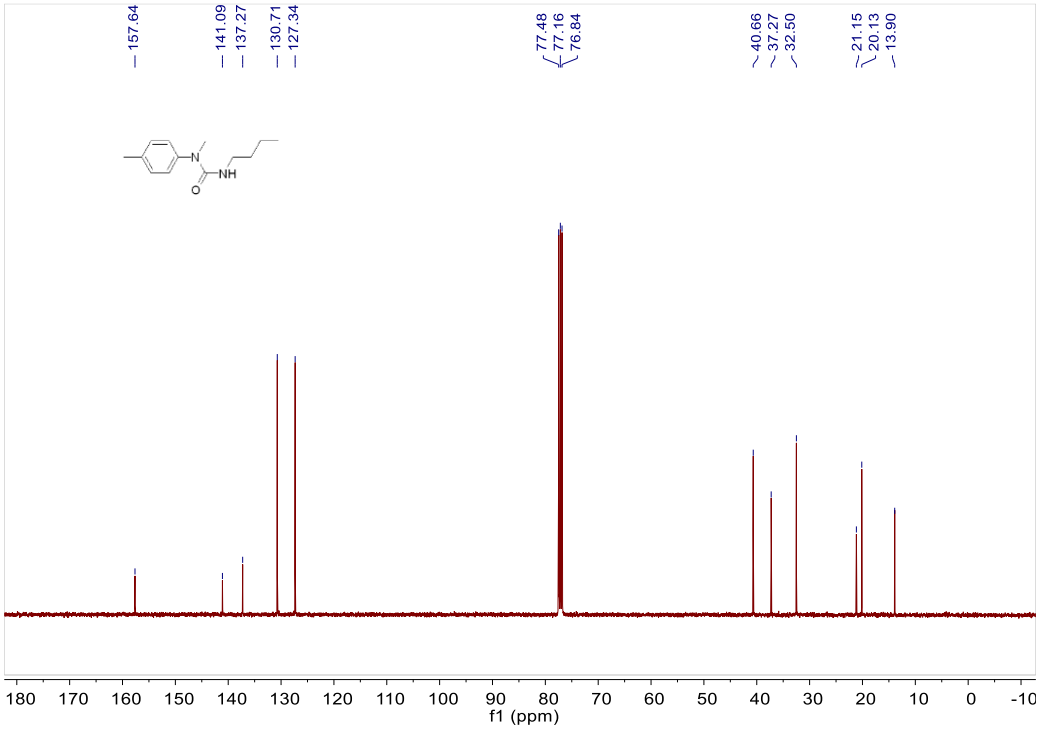


Figure S61. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3ae**

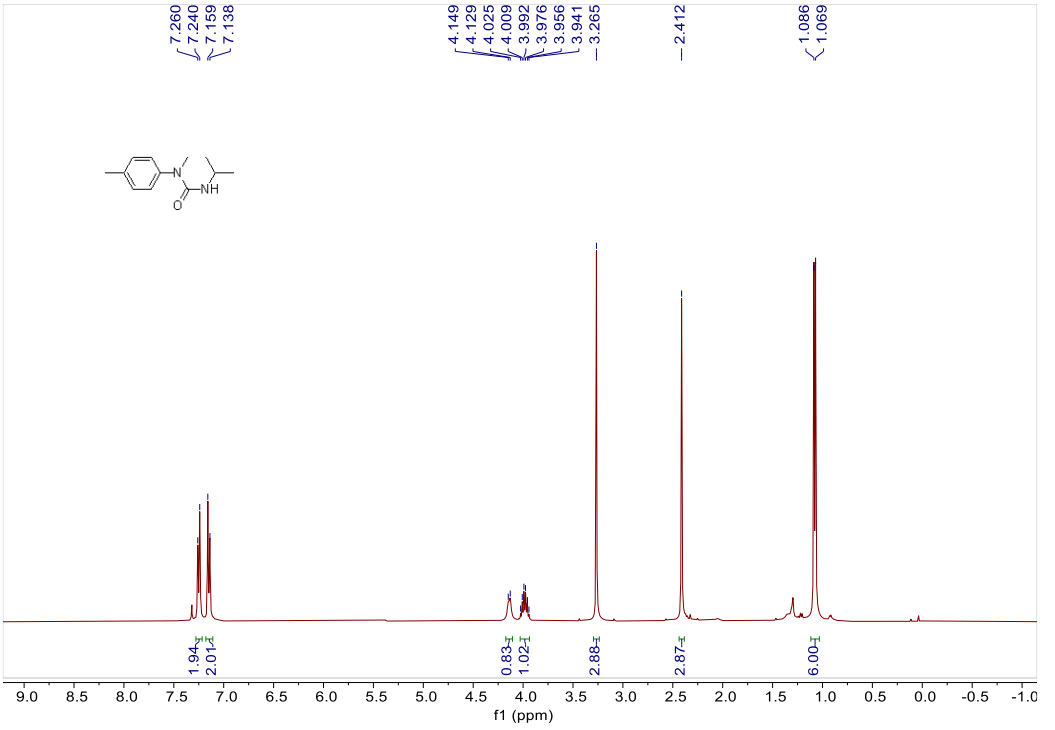


Figure S62. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3af**

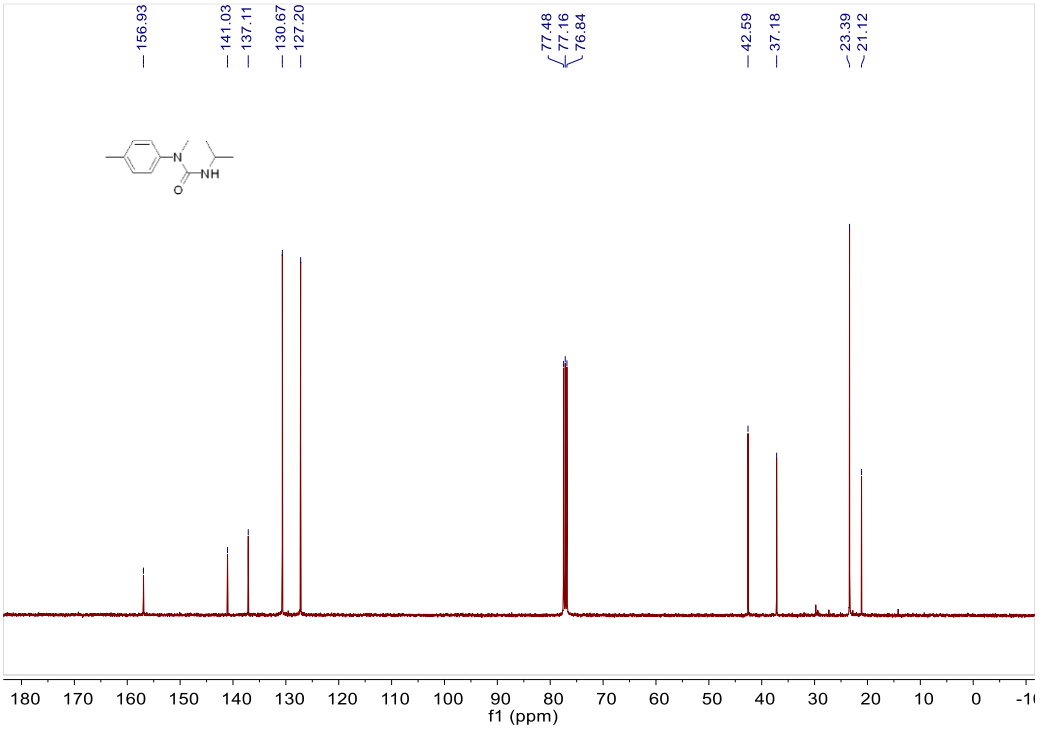


Figure S63. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3af**

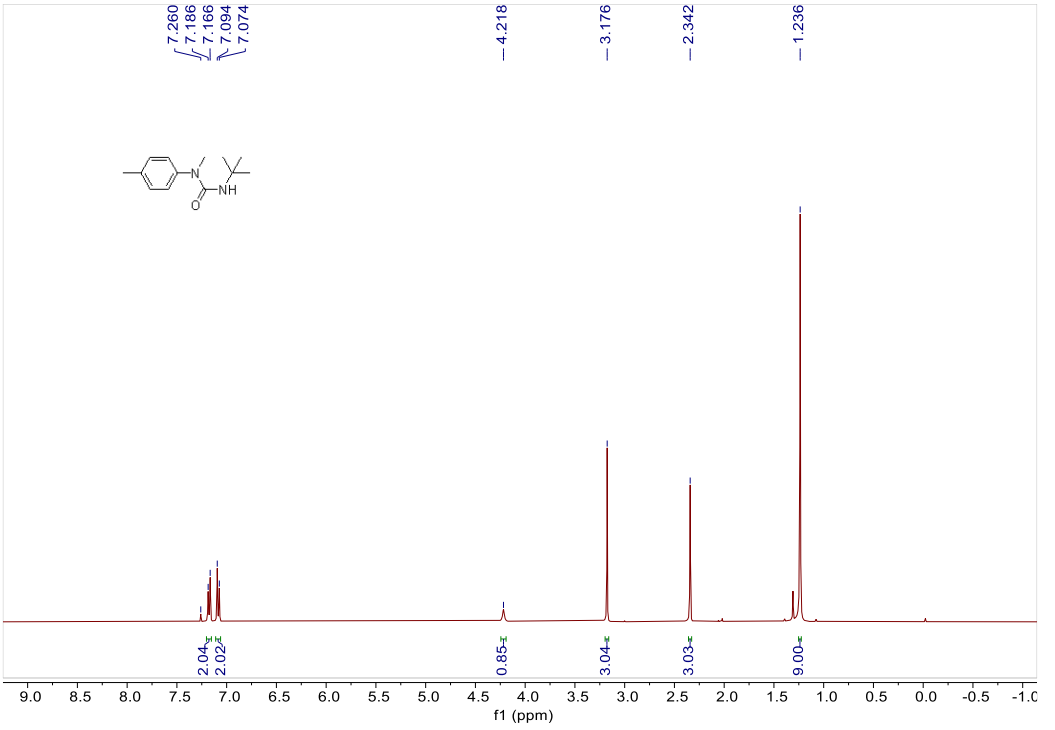


Figure S64. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3ag**

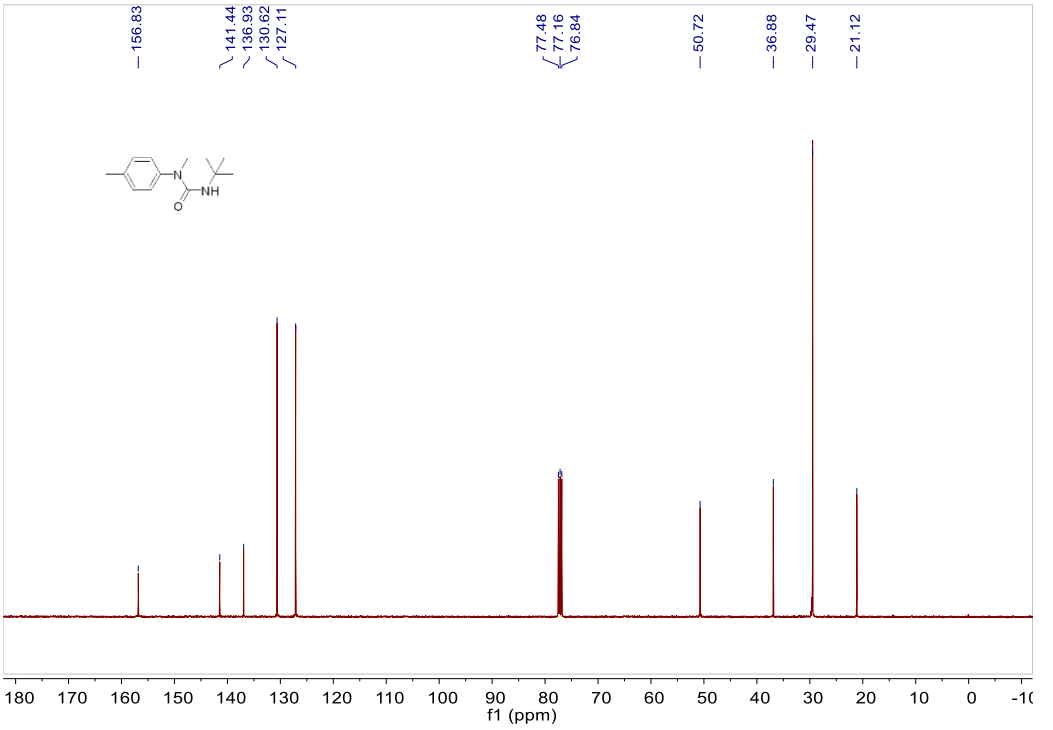


Figure S65. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3ag**

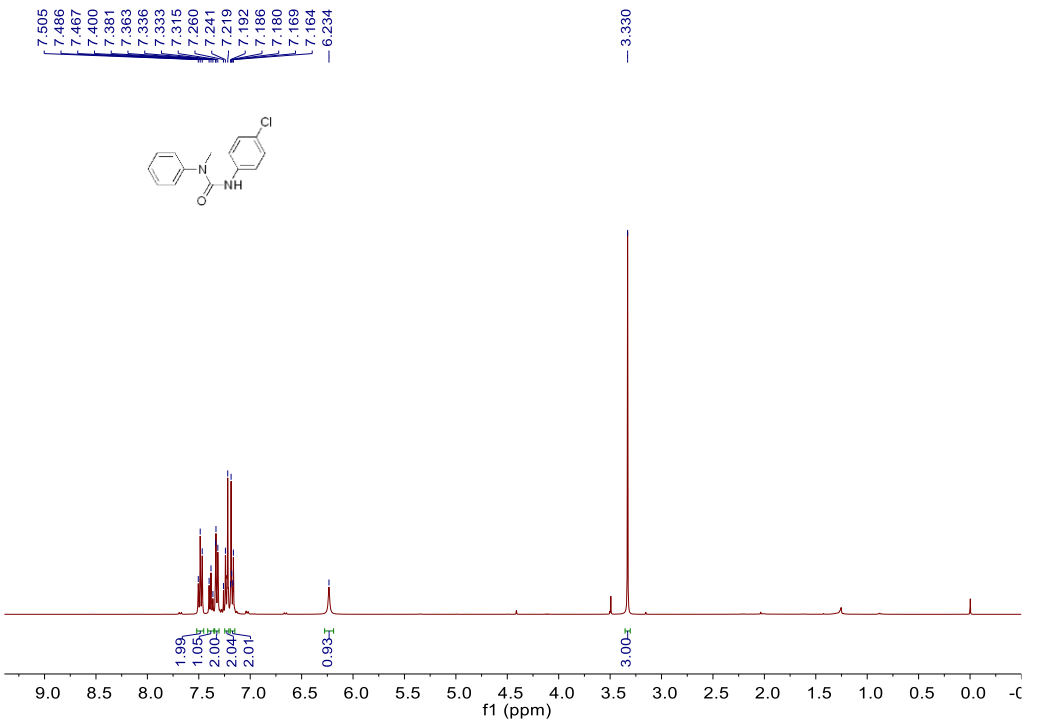


Figure S66. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3aj**

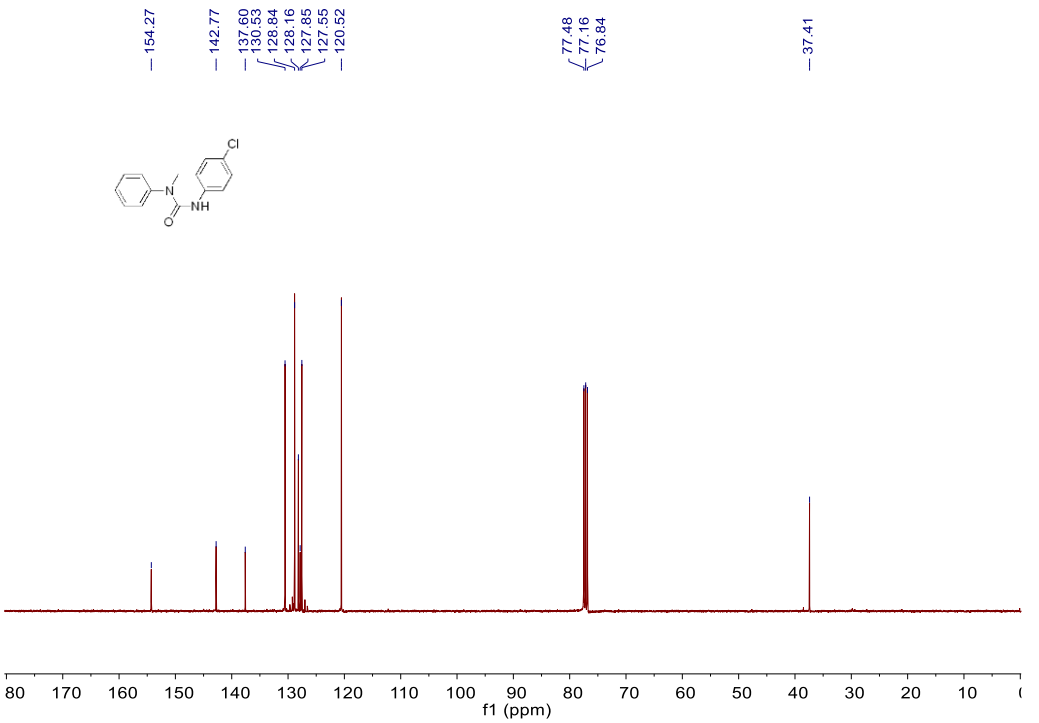


Figure S67. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3aj**

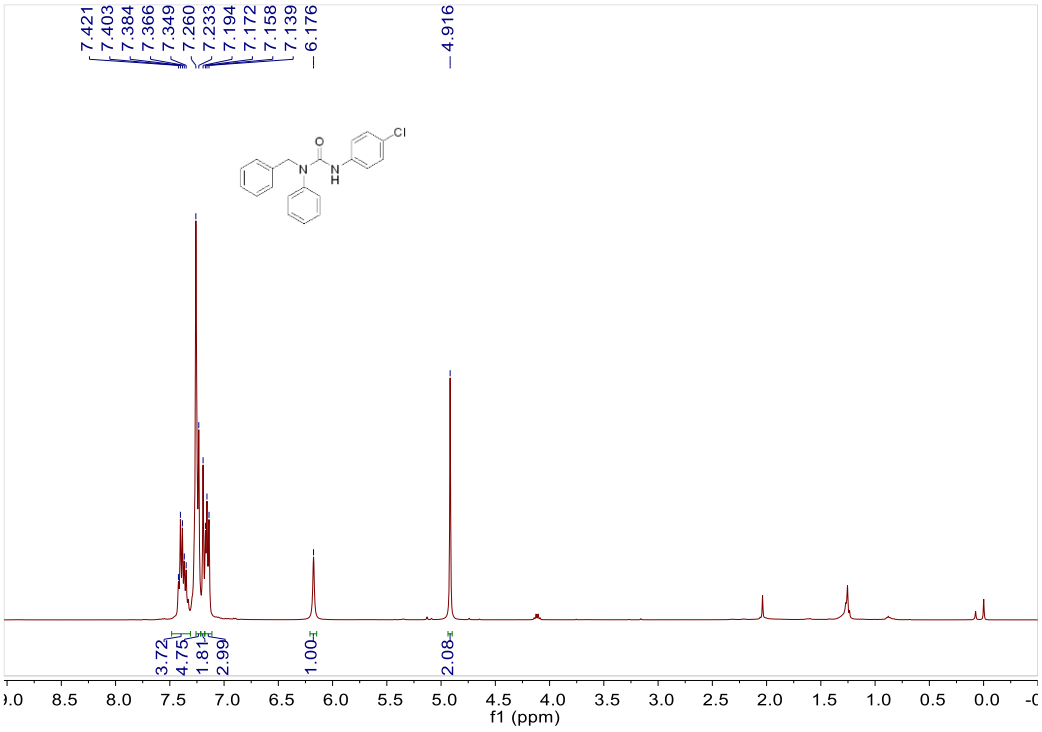


Figure S68. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **3ak**

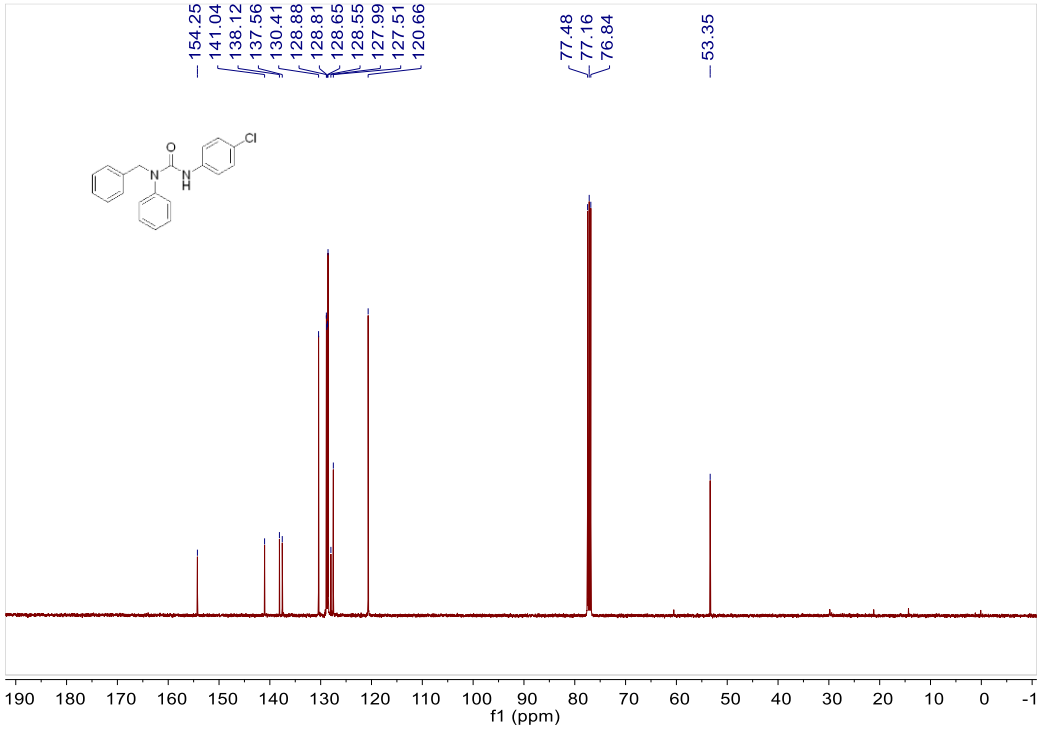


Figure S69. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **3ak**

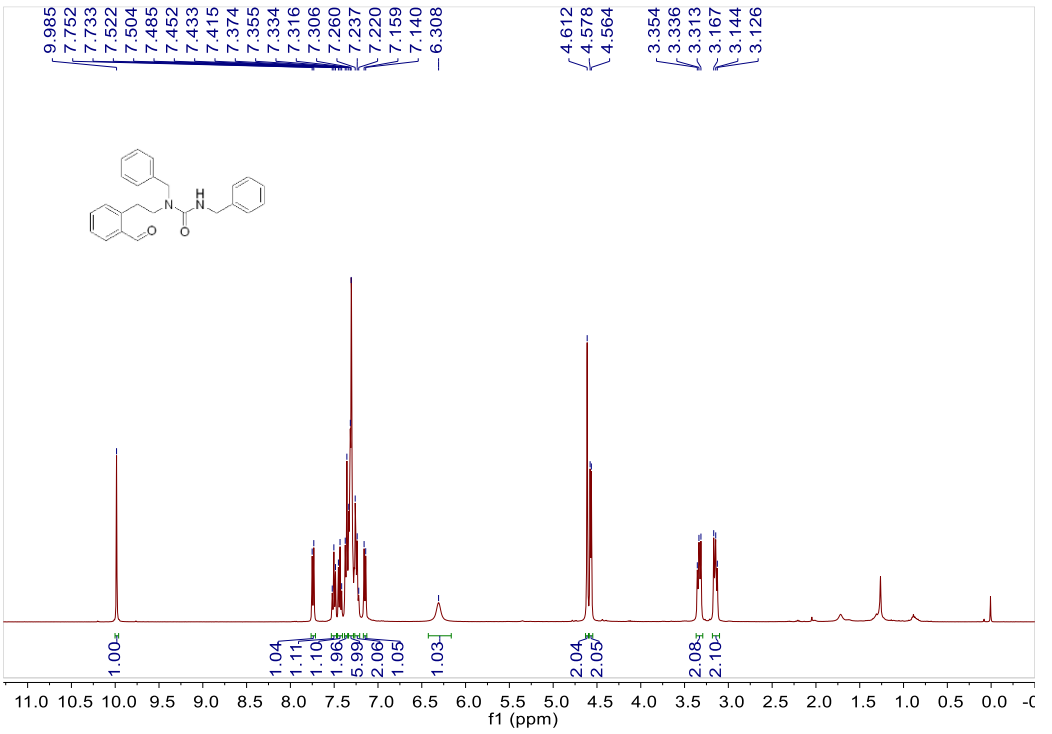


Figure S70. ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of **8**

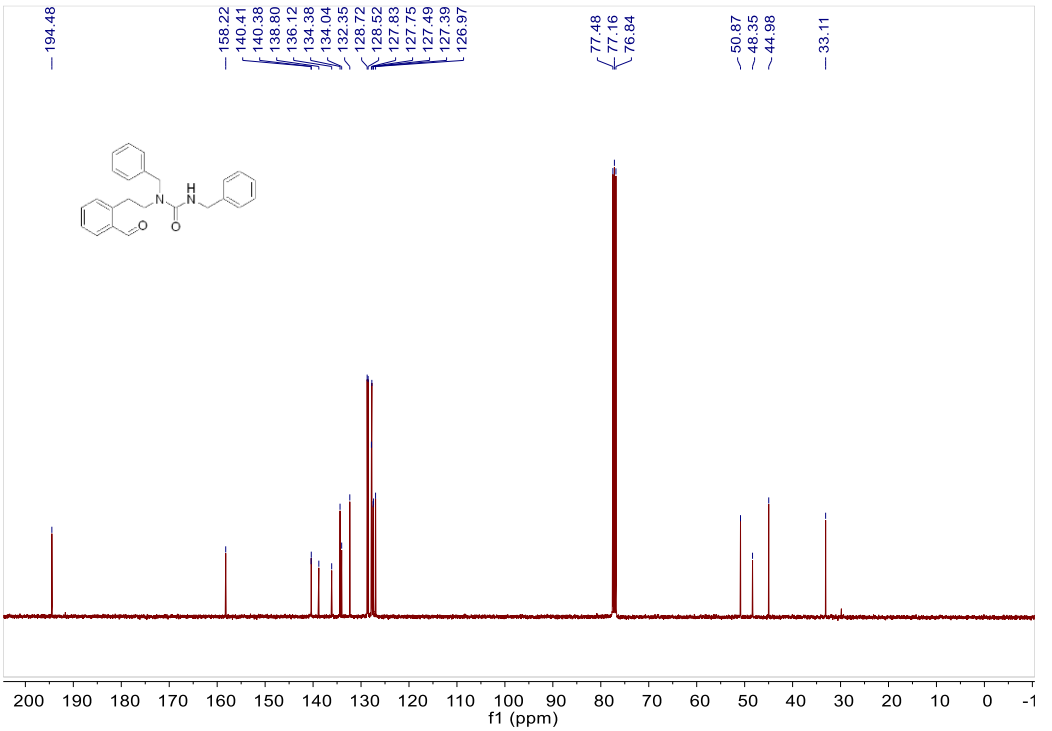


Figure S71. ^{13}C NMR spectrum ($CDCl_3$, 100MHz) of **8**