SUPPORTING INFORMATION

Visible Light Promoted Synthesis of Ureas and Formamides from Amines and CO_2

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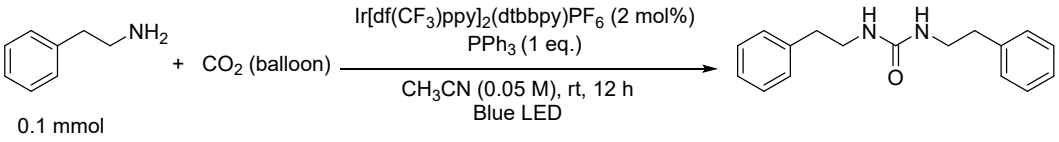
Contents

1. General experimental methods

All reagents were purchased from commercial suppliers without further purification. Experiments were monitored by thin layer chromatography (TLC) and the TLC was performed on precoated silica gel plates. Visualization was accomplished with UV light (254 nm) and exposure to phosphomolybdic acid (PMA) or potassium perm anganate solution followed by heating. Photocatalytic synthesis of formamides were carried out using a high pressure photoreactor from WATTCAS. The NMR spectra were recorded at room temperature on a Bruker Avance III 500 MHz. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR and DMSO-d_6: 2.50 ppm ^{1}H NMR, 39.52 ppm ^{13}C NMR). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), brs (broad singlet). The high resolution mass spectra (HRMS) were measured on AB Sciex Triple TOF 4600 mass spectrometer by ESI. Column chromatography was carried out over 200-300 mesh silica gel.

2. General procedures.

2.1 General procedure A: synthesis of ureas.



0.1 mmol

A 25-mL Schlenk sealing tube was charged with phenethylamine (0.1 mmol, 12.5 uL), $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ (2 mol%, 2.3 mg), PPh_3 (1.0 eq., 26.2 mg). The atmosphere was exchanged by applying vacuum and backfilling with CO_2 (this process was conducted a total of three times). Under CO_2 atmosphere, CH_3CN (0.05 M) was added via syringe. Then the reaction was placed under a blue LED (wavelength 440 nm, 40 W) with an CO_2 balloon and irradiated for 12 h at room temperature. After the reaction was completed, 10 mL water was added and extracted with ethyl acetate for 3 times. The organic layer was washed with water, brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixture was purified by column chromatography on silica gel (eluent: PE: EA = 1:1) to give the product as a white solid in 81% yield (10.8 mg).

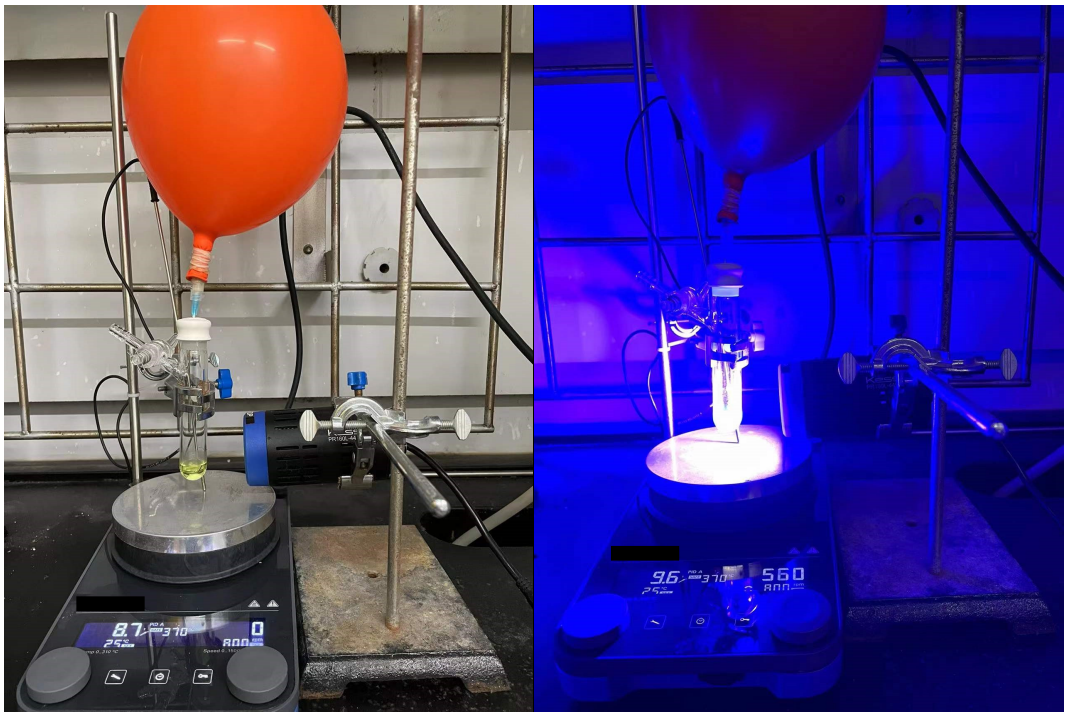
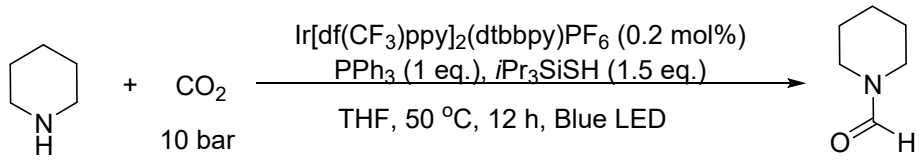


Figure S1. Devices for the photocatalytic reactions for synthesis ureas.

2.2 General procedure B: synthesis of formamides.



3a

A 25 mL vial tube equipped with a magnetic stir was charged with piperidine (0.2 mmol), Ir[df(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.2 mol%), triisopropylsilanethiol (1.5 eq., 0.3 mmol), triphenylphosphine (1 eq., 0.2 mmol), anhydrous THF (2 mL). After evacuated and backfilled CO_2 three times, it was filled with 10 bar of CO_2. The reaction mixture was then irradiated with a 10 W blue LED lamp with heating from circulating liquid (ethylene glycol: H_2O = 1:1) for 12 h at 50 °C. After the reaction was completed, 10 mL water was added and extracted with ethyl acetate for 3 times. The organic layer was washed with water, brine, dried with anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude reaction mixture was purified by column chromatography on silica gel (eluent: PE: EA = 1:1) to give the product to as a yellow oil in 80% yield (18.1 mg).

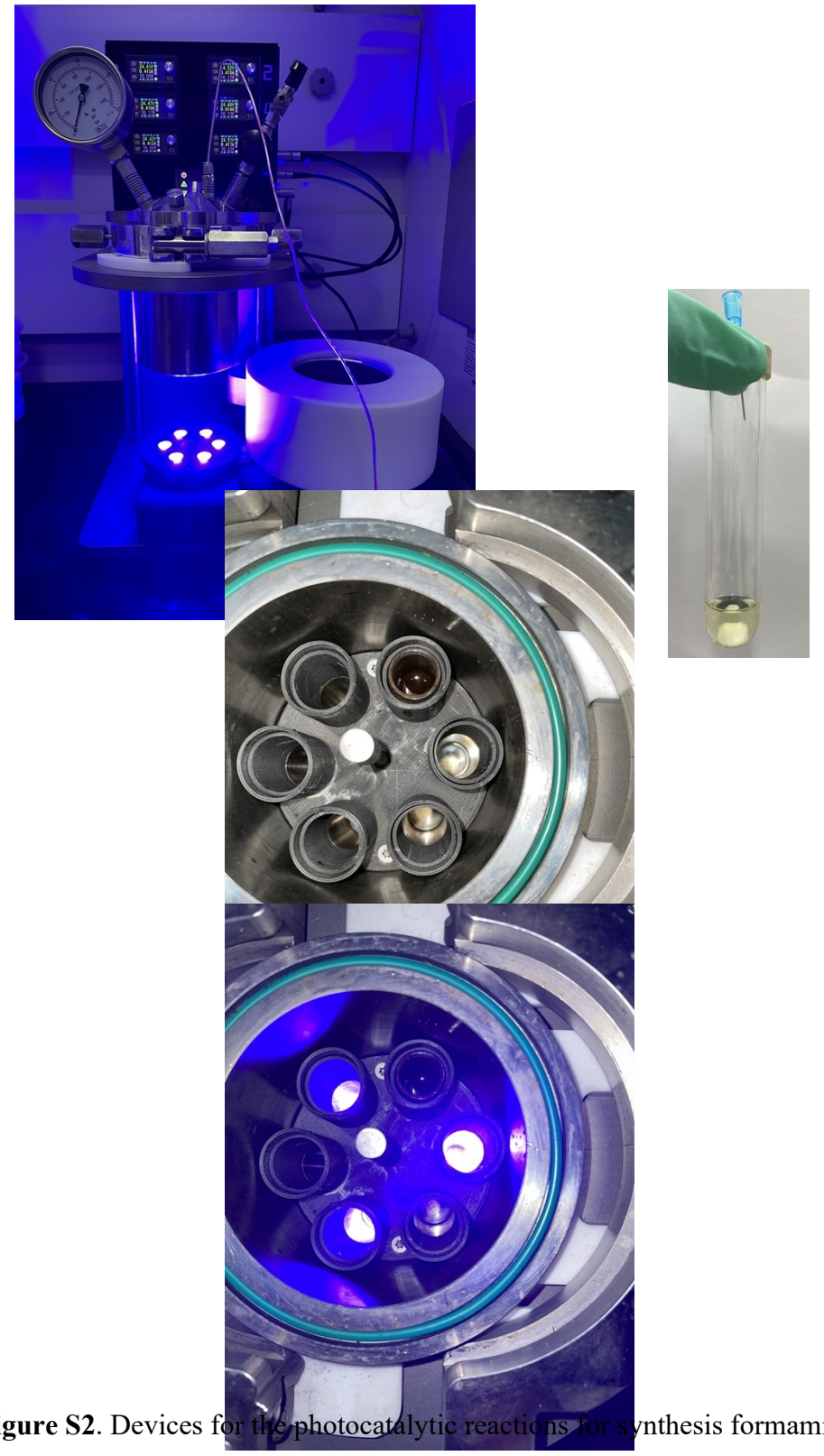
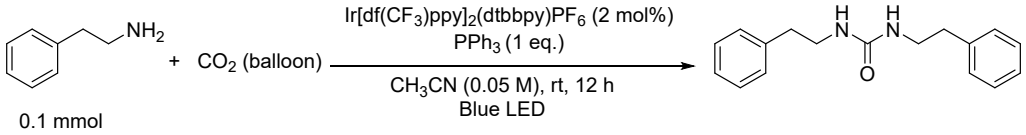


Figure S2. Devices for the photocatalytic reactions for synthesis formamides.

3. Investigation of the key reaction parameters.

Table S1. Control reactions for synthesis of ureas [a]

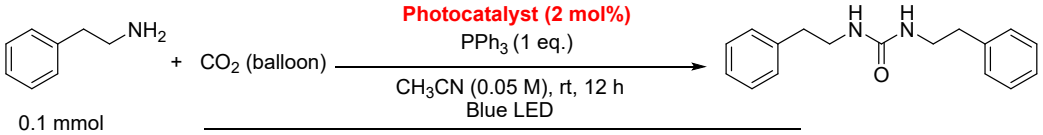


0.1 mmol

entry	deviation	Yield[b] (%)
1	Without $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$	10
2	Without PPh_3	<5
3	Without light	ND

[a]General conditions,unless otherwise noted: amine (0.1 mmol), $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ (2 mol%), PPh_3 (0.1 mmol), CH_3CN (2 mL), blue LED, CO_2 (balloon), 12 h. [b]Yields determined by ^1H NMR spectroscopy using trimethoxybenzene as an internal standard. [c]Isolated yield.

Table S2. Photocatalysts optimization for synthesis of ureas [a]

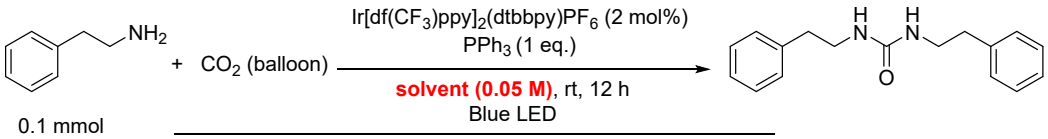


0.1 mmol

Entry	Photocatalyst	yield[b] (%)
1	**$Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$**	**82 (81[c])**
2	4CzIPN	30
3	$[Ir(ppy)_2(dtbpy)][PF_6]$	42
4	Acridinium dye	33
5	$[Ru(bpy)_3][PF_6]_2$	9
6	$[Ru(bpy)_3]Cl_2$	8
7	Eosin Y	25
8	$Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ (0.2 mol%)	30

[a]General conditions,unless otherwise noted: amine (0.1 mmol), PPh_3 (0.1 mmol), CH_3CN (2 mL), blue LED, CO_2 (balloon), 12 h. [b]Yields determined by ^1H NMR spectroscopy using trimethoxybenzene as an internal standard. [c]Isolated yield.

Table S3. Solvents optimization for synthesis of ureas [a]

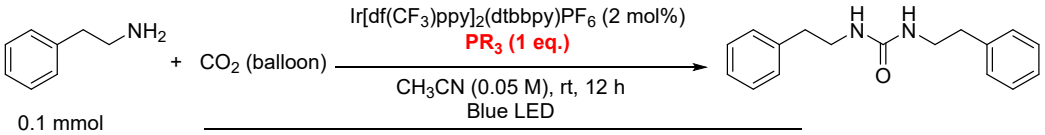


0.1 mmol

Entry	Solvent	yield[b] (%)
1	**CH_3CN**	**82 (81[c])**
2	toluene	44
3	Acetone	ND
4	CH_2Cl_2	ND
5	THF	41
6	DMSO	ND
7	1,4-dioxane	46
8	CH_3CN (0.1 M)	65
9	CH_3CN (0.025 M)	57
10	CH_3CN (use freeze pump thaw to remove oxygen)	36

[a]General conditions,unless otherwise noted: amine (0.1 mmol), $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ (2 mol%), PPh_3 (0.1 mmol), blue LED, CO_2 (balloon), 12 h. [b]Yields determined by ^1H NMR spectroscopy using trimethoxybenzene as an internal standard. [c]Isolated yield.

Table S4. Phosphine optimization for synthesis of ureas [a]

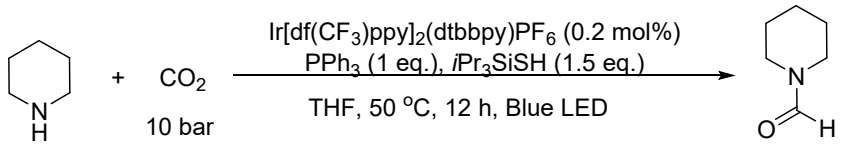


0.1 mmol

Entry	Phosphine	yield[b] (%)
1	**PPh_3**	**82 (81[c])**
2	$P(Cy)_3$	42
3	$Ph_2PCH_2CH_2PPh_2$	72
4	Ph_2POEt	69
5	$P(OEt)_3$	ND
6	PPh_3 (0.5 eq.)	45
7	PPh_3 (1.5 eq.)	82

[a]General conditions,unless otherwise noted: amine (0.1 mmol), $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ (2 mol%), PR_3 (1 eq.), CH_3CN (2 mL), blue LED, CO_2 (balloon), 12 h. [b]Yields determined by ^1H NMR spectroscopy using trimethoxybenzene as an internal standard. [c]Isolated yield.

Table S5. Control reactions for synthesis of formamides [a]

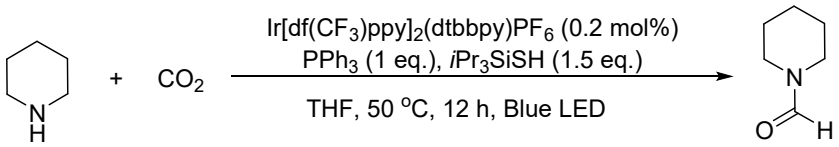


3a

entry	deviation	Yield[b] (%)
1	Without $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$	trace
2	Without PPh_3	trace
3	Without iPr_3SiSH	trace
4	Without light	trace

[a]General conditions,unless otherwise noted: amine (0.2 mmol), triisopropylsilanethiol (0.3 mmol), PPh_3 (0.2 mmol), $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ (0.2 mol%), THF (2 mL), 50 °C, blue LED, CO_2 (10 bar), 12 h. [b]Yields determined by ^1H NMR spectroscopy using trimethoxybenzene as an internal standard.

Table S6. Pressure optimization for synthesis of formamides [a]

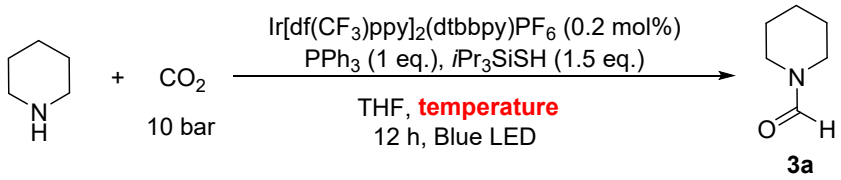


3a

Entry	pressure	yield[b] (%)
1	CO_2 (balloon)	44
2	**10 bar**	**84 (80[c])**

[a]General conditions,unless otherwise noted: amine (0.2 mmol), triisopropylsilanethiol (0.3 mmol), PPh_3 (0.2 mmol), $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ (0.2 mol%), THF (2 mL), 50 °C, blue LED, 12 h. [b]Yields determined by ^1H NMR spectroscopy using trimethoxybenzene as an internal standard. [c]Isolated yield.

Table S7. Temperature optimization for synthesis of formamides [a]

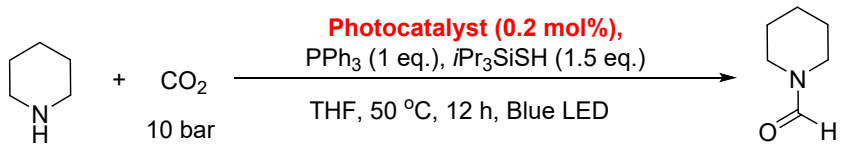


3a

Entry	temperature (°C)	yield[b] (%)
1	30	83
2	**50**	**84 (80[c])**
3	70	63

[a]General conditions,unless otherwise noted: amine (0.2 mmol), triisopropylsilanethiol (0.3 mmol), PPh_3 (0.2 mmol), $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ (0.2 mol%), THF (2 mL), blue LED, CO_2 (10 bar), 12 h. [b]Yields determined by ^1H NMR spectroscopy using trimethoxybenzene as an internal standard. [c]Isolated yield.

Table S8. Photocatalysts optimization for synthesis of formamides [a]

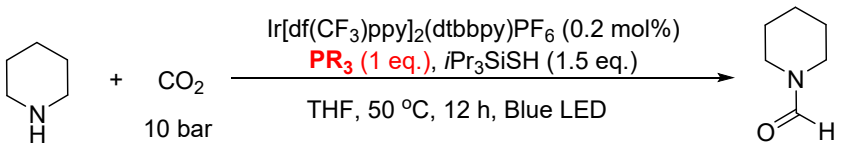


3a

Entry	Photocatalyst	yield[b] (%)
1	**$Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$**	**84 (80[c])**
2	4CzIPN	trace
3	$[Ir(ppy)_2(dtbpy)][PF_6]$	84
4	Acridinium dye	trace
5	$[Ru(bpy)_3][PF_6]_2$	32
6	$[Ru(bpy)_3]Cl_2$	trace
7	Eosin Y	trace
8	$Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ (2 mol%)	64

[a]General conditions,unless otherwise noted: amine (0.2 mmol), triisopropylsilanethiol (0.3 mmol), PPh_3 (0.2 mmol), THF (2 mL), 50 °C, blue LED, CO_2 (10 bar), 12 h. [b]Yields determined by ^1H NMR spectroscopy using trimethoxybenzene as an internal standard. [c]Isolated yield.

Table S9. Phosphine optimization for synthesis of formamides [a]

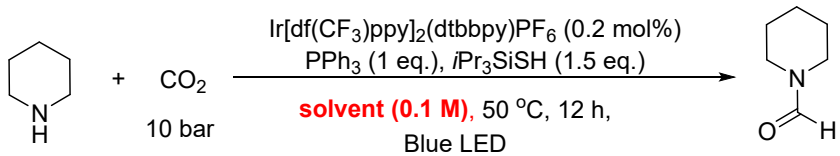


3a

Entry	PR_3	yield[b] (%)
1	**Ph_3P**	**84 (80[c])**
2	$PhP(OEt)_2$	62
3	Ph_2POEt	84
4	Cy_3P	48
5	$Ph_2PCH_2CH_2PPh_2$	75
6	Ph_3P (1.5 eq)	84
7	Ph_3P (0.5 eq)	45

[a]General conditions,unless otherwise noted: amine (0.2 mmol), triisopropylsilanethiol (0.3 mmol), $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ (0.2 mol%), THF (2 mL), 50 °C, blue LED, CO_2 (10 bar), 12 h. [b]Yields determined by ^1H NMR spectroscopy using trimethoxybenzene as an internal standard. [c]Isolated yield.

Table S10. Solvent optimization for synthesis of formamides [a]

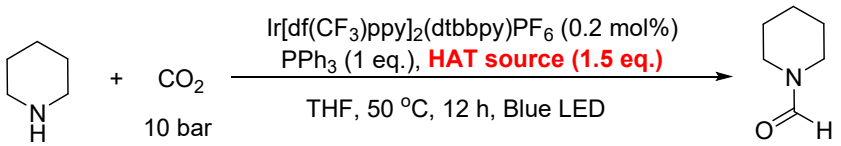


3a

Entry	solvent	yield[b] (%)
1	**THF**	**84 (80[c])**
2	CH_3CN	64
3	DMSO	trace
5	1,4-dixoane	trace
6	DCE	58
7	EA	42
8	THF (0.2 M)	81
9	THF (use freeze pump thaw to remove oxygen)	80[c]

[a]General conditions,unless otherwise noted: amine (0.2 mmol), triisopropylsilanethiol (0.3 mmol), PPh_3 (0.2 mmol), $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ (0.2 mol%), 50 °C, blue LED, CO_2 (10 bar), 12 h. [b]Yields determined by ^1H NMR spectroscopy using trimethoxybenzene as an internal standard. [c]Isolated yield.

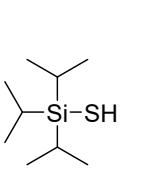
Table S11. HAT source optimization for synthesis of formamides [a]



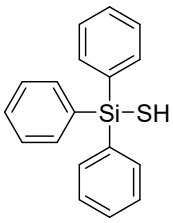
3a

Entry	HAT source	yield[b] (%)
1	**A**	**84 (80[c])**
2	**B**	18
3	**C**	ND
4	**D**	ND
5	**E**	ND
6	**F**	ND
7	**G**	ND
8	**H**	ND
9	1,4-Cyclohexadiene	ND
10	Hantzsch ester	ND
11	(p-OMeC$_6$H$_4$)$_2$S$_2$	ND
12	**A** (1 eq)	77
13	**A** (0.8 eq)	67
14	**A** (0.5 eq)	42
15	**A** (0.3 eq)	30

[a]General conditions,unless otherwise noted: amine (0.2 mmol), PPh_3 (0.2 mmol), Ir[df(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.2 mol%), THF (2 mL), 50 °C, blue LED, CO_2 (10 bar), 12 h. [b]Yields determined by ^{1}H NMR spectroscopy using trimethoxybenzene as an internal standard. [c]Isolated yield.



A



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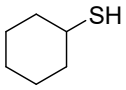

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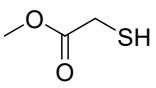

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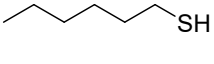

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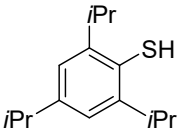

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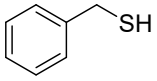

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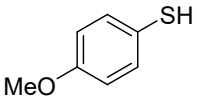
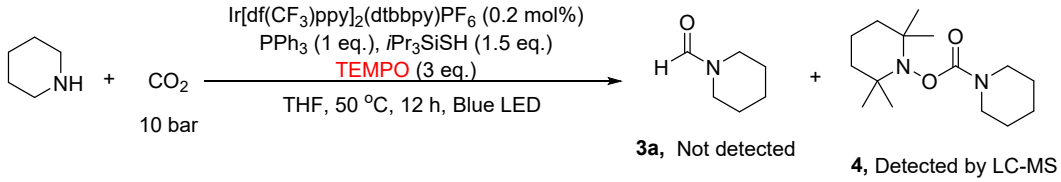


H

4. Mechanistic studies

4.1 Radical trapping experiment



A 25 mL vial tube equipped with a magnetic stir was charged with piperidine (**1a**) (0.2 mmol), Ir[df(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.2 mol%), triisopropylsilanethiol (1.5 eq., 0.3 mmol), triphenylphosphine (1 eq., 0.2 mmol), TEMPO (3 eq., 0.6 mmol), anhydrous THF (2 mL). After evacuated and backfilled CO_2 three times, it was filled with 10 bar of CO_2. The reaction mixture was then irradiated with a 10 W blue LED lamp with heating from circulating liquid (ethylene glycol: H_2O = 1:1) for 12 h at 50 °C. After the reaction was completed, the mixture was detected by LC-MS, the formation of **3a** was completely inhibited and 2,2,6,6-tetramethylpiperidin-1-yl piperidine-1-carboxylate (**4**) was detected by LC-MS.

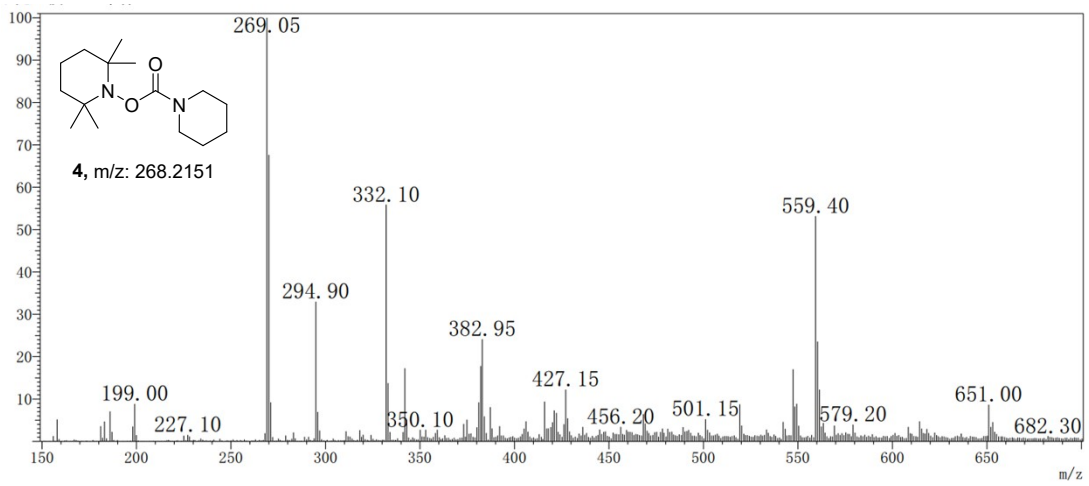


Figure S3. LC-MS spectrum of 2,2,6,6-tetramethylpiperidin-1-yl piperidine-1-carboxylate (**4**).

4.2 Stern–Volmer quenching studies

A solution of Ir[df(CF_3)ppy]$_2$(dtbbpy)PF_6 in anhydrous CH_3CN (0.01 mM) was added with an appropriate amount of PPh_3 in a quartz cuvette. Then the emission of the sample was collected. The emission intensity at 380 nm was collected with excited wavelength of 474 nm.

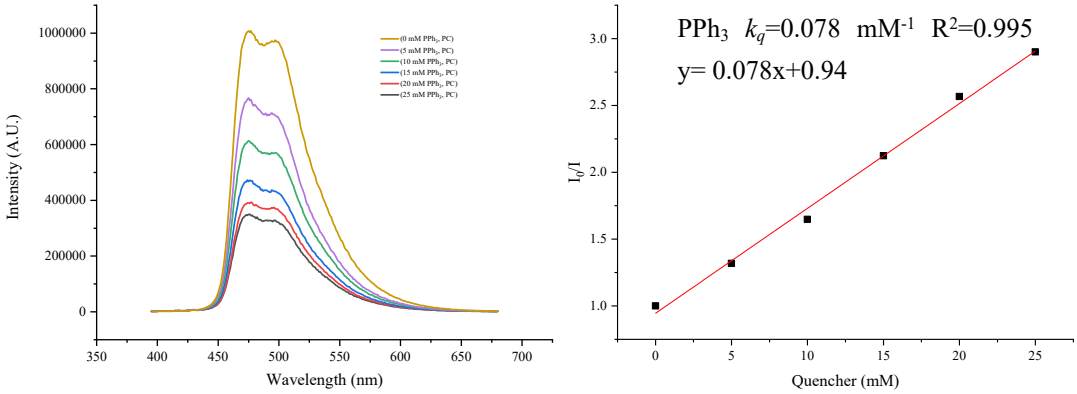


Figure S4. Stern-Volmer quenching by PPh_3.

A solution of $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ in anhydrous CH_3CN (0.01 mM) was added with an appropriate amount of phenethylamine in a quartz cuvette. Then the emission of the sample was collected. The emission intensity at 380 nm was collected with excited wavelength of 474 nm.

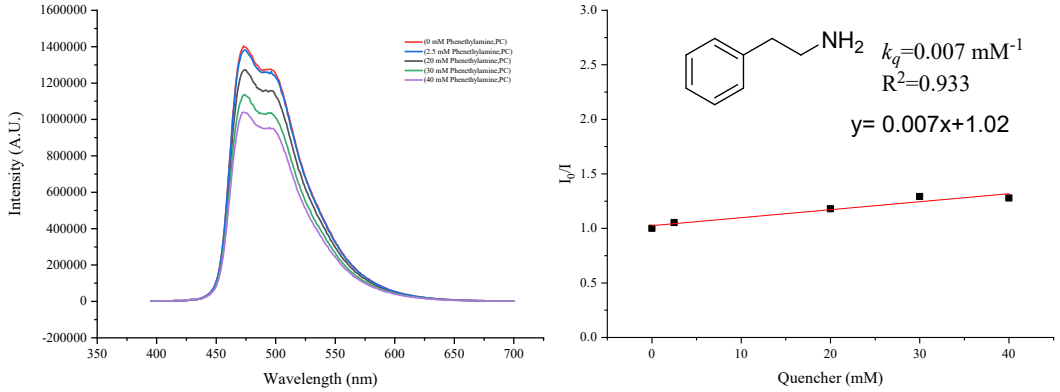


Figure S5 Stern-Volmer quenching by phenethylamine

A solution of $Ir[df(CF_3)ppy]_2(dtbbpy)PF_6$ in anhydrous THF (0.01 mM) was added with an appropriate amount of piperidine in a quartz cuvette. Then the emission of the sample was collected. The emission intensity at 378 nm was collected with excited wavelength of 479 nm.

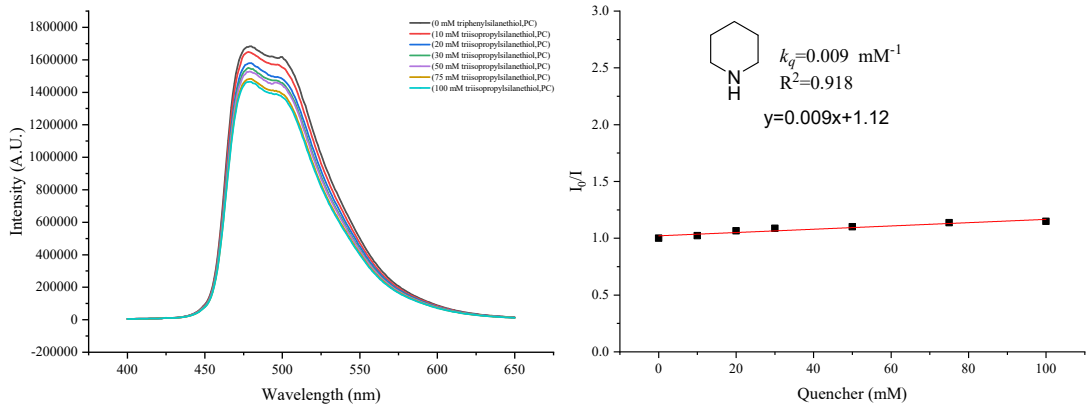


Figure S6 Stern-Volmer quenching by piperidine.

4.3 Proposed mechanism for synthesis of ureas via energy transfer

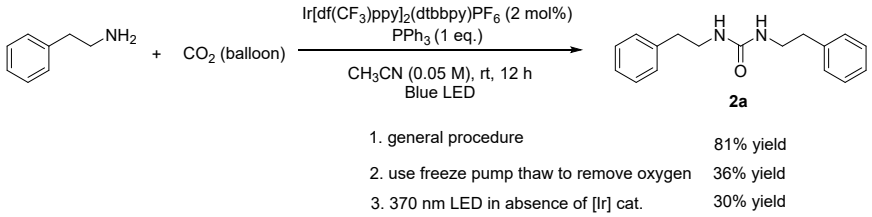


Figure S7 Control experiments

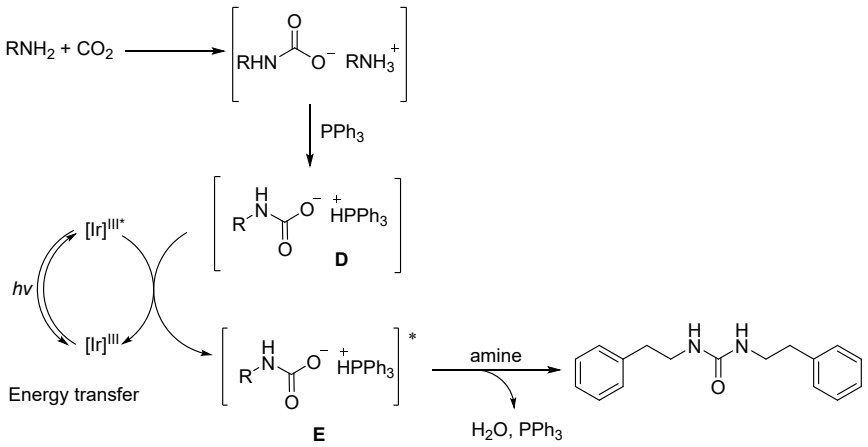
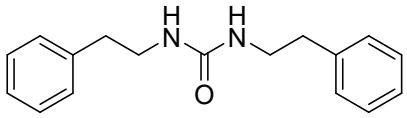


Figure S8 Proposed mechanism for synthesis of ureas via energy transfer

We found that **2a** could also be obtained under this condition indicating that another way may exist for the generation of ureas. When we used 370 nm LED instead of 440 nm LED, **2a** could be obtained in 30% yield in absence of photocatalyst. According to these results, we think that the generation of **2a** may also be promoted by energy transfer process (Figure S8). Since PPh_3 was essential for the reaction, we proposed that excited carbamate anion (**E**) may react with amine to produce the corresponding urea.

5. Characterization data

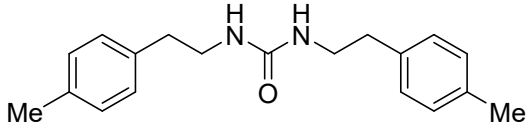
1,3-diphenethylurea (2a) [1]



2a

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (10.9 mg, 81%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 4H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.18 – 7.14 (m, 4H), 4.51 (t, *J* = 5.9 Hz, 2H), 3.37 (q, *J* = 6.6 Hz, 4H), 2.76 (t, *J* = 6.9 Hz, 4H).

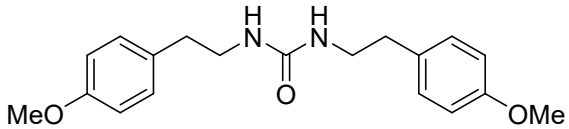
1,3-bis(4-methylphenethyl)urea (2b)



2b

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (11.4 mg, 77%); Mp: 183 - 185 ℃
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.8 Hz, 4H), 7.05 (d, *J* = 7.8 Hz, 4H), 4.44 (t, *J* = 5.9 Hz, 2H), 3.36 (q, *J* = 6.6 Hz, 4H), 2.72 (t, *J* = 6.9 Hz, 4H), 2.32 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 136.1, 136.0, 129.4, 128.8, 41.9, 36.0, 21.1.
HRMS : m/z calcd. for $C_{19}H_{25}N_2O$ $[M+H]^+$: 297.1961; found: 297.1957.

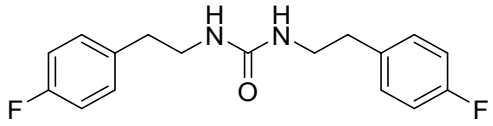
1,3-bis(4-methoxyphenethyl)urea (2c) [2]



2c

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (13.1 mg, 80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.6 Hz, 4H), 6.82 (d, *J* = 8.6 Hz, 4H), 4.44 (t, *J* = 5.9 Hz, 2H), 3.77 (s, 6H), 3.34 (q, *J* = 6.7 Hz, 4H), 2.70 (t, *J* = 6.9 Hz, 4H).

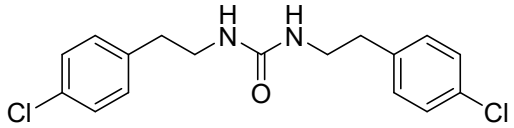
1,3-bis(4-fluorophenethyl)urea (2d)



2d

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (7.3 mg, 48%);
Mp: 127 - 129 ℃
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (dd, *J* = 8.4, 5.5 Hz, 4H), 6.97 (t, *J* = 8.7 Hz, 4H), 4.30 (t, *J* = 6.0 Hz, 2H), 3.37 (q, *J* = 6.6 Hz, 4H), 2.75 (t, *J* = 6.9 Hz, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 161.7 (d, *J* = 244.7 Hz), 158.0, 134.8 (d, *J* = 3.2 Hz), 130.3 (d, *J* = 7.9 Hz), 115.5 (d, *J* = 21.2 Hz), 41.8, 35.7.
^{19}F NMR (470 MHz, $CDCl_3$) δ -116.64
HRMS: m/z calcd. for $C_{17}H_{19}F_2N_2O$ $[M+H]^+$: 305.1460; found: 305.1455.

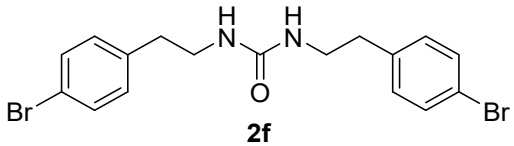
1,3-bis(4-chlorophenethyl)urea (2e)



2e

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (8.9 mg, 53%);
Mp: 141 - 143 ℃
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7 Hz, 4H), 7.09 (d, *J* = 8.4 Hz, 4H), 4.32 (t, *J* = 5.9 Hz, 2H), 3.37 (q, *J* = 6.6 Hz, 4H), 2.74 (t, *J* = 6.9 Hz, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8, 137.6, 132.3, 130.2, 128.7, 41.5, 35.8.
HRMS: m/z calcd. for $C_{17}H_{19}Cl_2N_2O$ $[M+H]^+$: 337.0869; found: 337.0861.

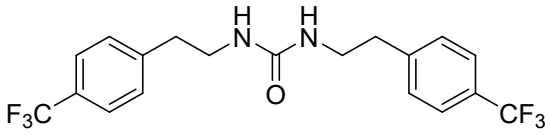
1,3-bis(4-bromophenethyl)urea (2f)[3]



2f

The title compound was prepared according to the General procedure A and yields determined by ^{1}H NMR spectroscopy using trimethoxybenzene as an internal standard (71%);
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.46 (d, *J* = 8.3 Hz, 4H), 7.14 (d, *J* = 8.4 Hz, 4H), 5.83 (t, *J* = 5.8 Hz, 2H), 3.19 (q, *J* = 6.8 Hz, 5H), 2.63 (t, *J* = 7.0 Hz, 5H).
HRMS: m/z calcd. for $C_{17}H_{19}Br_2O$ $[M+H]^+$: 424.9859; found: 424.9859.

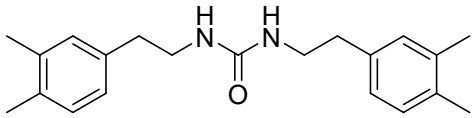
1,3-bis(4-(trifluoromethyl)phenethyl)urea (2g)



2g

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (12.5 mg, 62%);
Mp: 124 - 126 ℃
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.63 (d, J = 8.0 Hz, 4H), 7.40 (d, J = 7.9 Hz, 4H), 5.87 (t, J = 5.8 Hz, 2H), 3.25 (q, J = 6.7 Hz, 4H), 2.76 (t, J = 7.0 Hz, 4H).
^{13}C NMR (126 MHz, DMSO-d_6) δ 157.8, 144.8, 129.5, 126.9, 125.0 (q, J = 3.9, 3.5 Hz), 123.4, 40.3, 35.8.
^{19}F NMR (470 MHz, DMSO-d_6) δ -60.8.
HRMS: m/z calcd. for $C_{19}H_{19}F_6N_2O$ [M+H]$^+$: 405.1396; found: 405.1389.

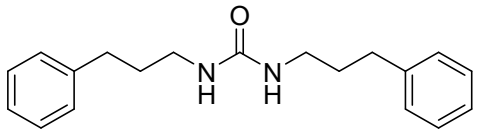
1,3-bis(3,4-dimethylphenethyl)urea (2h)



2h

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (12.3 mg, 76%);
Mp: 149 - 151 ℃
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, J = 7.6 Hz, 2H), 6.95 (s, 2H), 6.90 (d, J = 7.5 Hz, 2H), 4.24 (t, J = 5.8 Hz, 2H), 3.37 (q, J = 6.6 Hz, 4H), 2.71 (t, J = 6.9 Hz, 4H), 2.23 (s, 12H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 136.9, 136.6, 134.7, 130.3, 129.9, 126.3, 41.9, 36.0, 19.9, 19.4.
HRMS: m/z calcd. for $C_{21}H_{29}N_2O$ [M+H]$^+$: 325.2274; found: 325.2267.

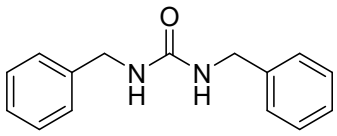
1,3-bis(3-phenylpropyl)urea (2i) [2]



2i

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (11.4 mg, 77%);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 4H), 7.17 (dd, J = 7.3, 5.7 Hz, 6H), 4.42 (s, 2H), 3.15 (q, J = 6.4 Hz, 4H), 2.63 (t, J = 7.7 Hz, 4H), 1.80 (m, 4H).

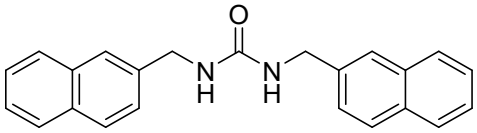
1,3-dibenzylurea (2j) [4]



2j

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (9.0 mg, 75%);
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 4H), 7.25 – 7.21 (m, 6H), 4.88 (brs, 2H), 4.32 (d, *J* = 5.7 Hz, 4H).

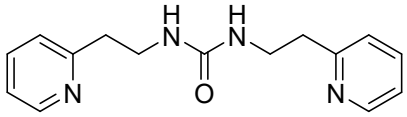
1,3-bis(naphthalen-2-ylmethyl)urea (2k) [5]



2k

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (4.4 mg, 26%);
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.88 (t, *J* = 7.8 Hz, 6H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.73 (s, 2H), 7.52 – 7.41 (m, 6H), 6.63 (t, *J* = 6.1 Hz, 2H), 4.42 (d, *J* = 6.0 Hz, 4H).

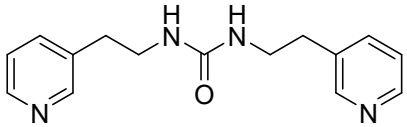
1,3-bis(2-(pyridin-2-yl)ethyl)urea (2l)



2l

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (8.5 mg, 63%);
Mp: 265 - 267 ℃
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.9 Hz, 2H), 7.64 – 7.50 (m, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.06 (m, 2H), 5.25 (s, 2H), 3.55 (q, *J* = 6.2 Hz, 4H), 2.95 (t, *J* = 6.5 Hz, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.9, 158.4, 149.2, 136.7, 123.7, 121.6, 39.9, 38.1.
HRMS: m/z calcd. For $C_{15}H_{19}N_4O$ $[M+H]^+$: 271.1553; found: 271.1556.

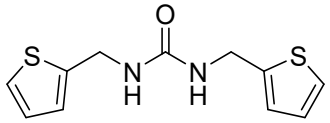
1,3-bis(2-(pyridin-3-yl)ethyl)urea (2m)



2m

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (8.9 mg, 66%);
Mp: 261-263 ℃
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (d, *J* = 4.4 Hz, 2H), 8.34 – 8.30 (m, 2H), 7.50 (dd, *J* = 7.9, 2.1 Hz, 2H), 7.19 (dd, *J* = 7.8, 4.8 Hz, 2H), 4.91 (t, *J* = 5.9 Hz, 2H), 3.43 (q, *J* = 6.4 Hz, 4H), 2.78 (t, *J* = 6.8 Hz, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.2, 150.1, 147.8, 136.6, 135.0, 123.7, 41.2, 33.8.
HRMS: m/z calcd. For $C_{15}H_{19}N_4O$ $[M+H]^+$: 271.1553; found:271.1560.

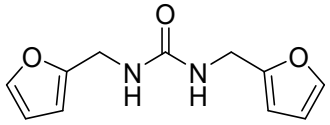
1,3-bis(thiophen-2-ylmethyl)urea (2n) [4]



2n

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a yellow solid (11.3 mg, 90%);
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.30 (dd, *J* = 4.5, 1.8 Hz, 2H), 6.88 (d, *J* = 4.6 Hz, 4H), 6.47 (t, *J* = 6.1 Hz, 2H), 4.33 (d, *J* = 6.0 Hz, 4H).

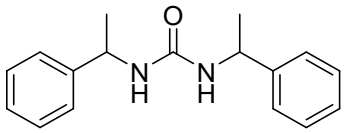
1,3-bis(furan-2-ylmethyl)urea (2o) [5]



2o

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a yellow solid (9.8 mg, 89%);
^{1}H NMR (500 MHz, DMSO-d_6) δ 7.55 (s, 2H), 6.39 – 6.31 (m, 4H), 6.18 (d, *J* = 3.2 Hz, 2H), 4.20 (d, *J* = 5.8 Hz, 4H).

1,3-bis(1-phenylethyl)urea(2p) [4]

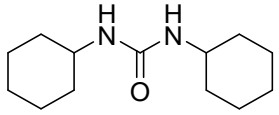


2p

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (5.5 mg, 41%, rotamers ratio 52:48);;
The presence of two rotamers (ratio 52:48) were observed in the NMR spectra.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 16.57H), 7.15 – 7.09 (m, 4.15H), 4.88 – 4.67 (m, 8H), 1.37 (d, *J* = 6.7 Hz, 6H), 1.33 (d, *J* = 6.45 Hz, 7H).

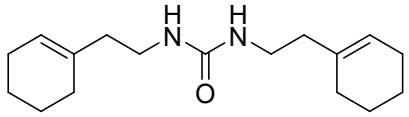
1,3-dicyclohexylurea (2q) [1]



2q

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (9.0 mg, 80%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.47 – 3.39 (m, 2H), 1.95 – 1.88 (m, 4H), 1.70 (m, 4H), 1.80 – 1.50 (m, 2H), 1.41 – 1.29 (m, 4H), 1.19 – 1.05 (m, 6H).

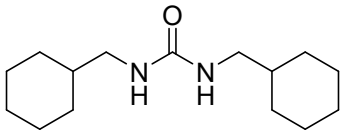
1,3-bis(2-(cyclohex-1-en-1-yl)ethyl)urea (2r) [2]



2r

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a yellow solid (8.8 mg, 64%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (s, 2H), 4.33 (t, *J* = 5.4 Hz, 2H), 3.21 (td, *J* = 6.8, 5.2 Hz, 4H), 2.12 (t, *J* = 6.8 Hz, 4H), 2.01 – 1.96 (m, 4H), 1.92 – 1.88 (m, 4H), 1.63 – 1.58 (m, 4H), 1.57 – 1.52 (m, 4H).

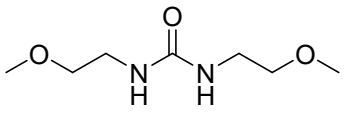
1,3-bis(cyclohexylmethyl)urea (2s) [5]



2s

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (8.1 mg, 64%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.61 (s, 2H), 2.98 (t, *J* = 6.3 Hz, 4H), 1.77 – 1.56 (m, 10H), 1.43 – 1.39 (m, 2H), 1.31 – 1.06 (m, 6H), 0.94 – 0.82 (m, 4H).

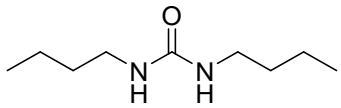
1,3-bis(2-methoxyethyl)urea (2t) [6]



2t

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (6.4 mg, 73%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87 (s, 2H), 3.46 (t, *J* = 4.98 Hz, 4H), 3.38 – 3.35 (m, 10H).

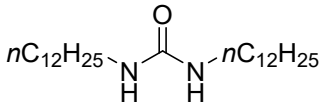
1,3-dibutylurea (2u) [5]



2u

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (5.9 mg, 69%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.62 (s, 2H), 3.16 – 3.12 (m, 4H), 1.49 – 1.43 (m, 4H), 1.37 – 1.31 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H).

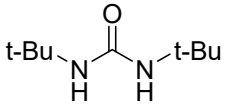
1,3-didodecylurea (2v) [2]



2v

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (5.3 mg, 28%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.17 (brs, 2H), 3.14 (q, *J* = 6.6 Hz, 4H), 1.48 (t, *J* = 7.1 Hz, 4H), 1.25 (m, 36H), 0.88 (t, *J* = 6.8 Hz, 6H).

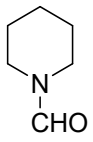
1,3-di-tert-butylurea (2w) [1]



2w

The title compound was prepared according to the General procedure A and purified by flash column chromatography to give the product as a white solid (1.3 mg, 15%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.29 (s, 2H), 1.38 (s, 18H).

piperidine-1-carbaldehyde (3a) [7]

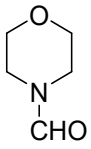


3a

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a yellow oil (18.1 mg, 80%);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 3.46 (t, *J* = 5.71 Hz, 2H), 3.29 (t, *J* = 5.60 Hz, 2H), 1.66 (q, *J* = 6.19 Hz, 2H), 1.54 (m, 4H).

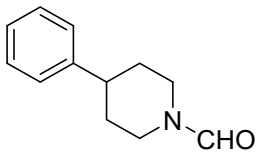
morpholine-4-carbaldehyde (3b) [7]



3b

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a yellow oil (12.7 mg, 55%);
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 3.70 (t, *J* = 4.84 Hz, 2H), 3.66 (t, *J* = 4.92 Hz, 2H), 3.57 (t, *J* = 4.88 Hz, 2H), 3.39 (t, *J* = 4.83 Hz, 2H).

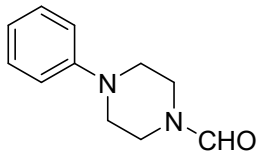
4-phenylpiperidine-1-carbaldehyde (3c) [8]



3c

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a yellow solid (30.3 mg, 80%);
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.32 (t, *J* = 7.52 Hz, 2H), 7.21 (dd, *J* = 21.94, 7.42 Hz, 3H), 4.57 (d, *J* = 13.29 Hz, 0H), 3.73 (d, *J* = 13.26 Hz, 0H), 3.20 (t, *J* = 11.46 Hz, 1H), 2.85 – 2.66 (m, 2H), 2.01 – 1.86 (m, 1H), 1.69 – 1.51 (m, 2H).

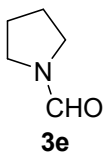
4-phenylpiperazine-1-carbaldehyde (3d)[8]



3d

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a yellow solid (22.1 mg, 58%);
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.29 (m, 2H), 6.96 – 6.92 (m, 3H), 3.73 – 3.70 (m, 2H), 3.60 – 3.50 (m, 2H), 3.23 – 3.17 (m, 2H), 3.17 – 3.13 (m, 2H).

pyrrolidine-1-carbaldehyde (3e)[9]

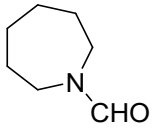


3e

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a colorless oil (15.9 mg, 80%);

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (s, 1H), 3.49 (t, *J* = 6.30 Hz, 2H), 3.42 (t, *J* = 6.70 Hz, 2H), 1.91 (p, *J* = 7.19 Hz, 4H).

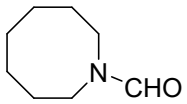
azepane-1-carbaldehyde (3f)[9]



3f

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a colorless oil (13.7 mg, 54%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 3.47 – 3.42 (m, 2H), 3.41 – 3.35 (m, 2H), 1.73 (t, *J* = 6.24 Hz, 4H), 1.61 – 1.51 (m, 4H).

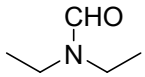
azocane-1-carbaldehyde (3g)[10]



3g

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a colorless oil (7.6 mg, 27%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 3.41 (t, *J* = 6.18 Hz, 2H), 3.32 (t, *J* = 5.94 Hz, 2H), 1.80 – 1.67(m, 4H), 1.60 – 1.56 (m, 2H), 1.55 – 1.49 (m, 4H).

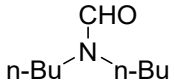
***N,N*-diethylformamide (3h) [9]**



3h

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a yellow oil (10.1 mg, 50%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 3.35 (q, *J* = 7.21 Hz, 2H), 3.26 (q, *J* = 7.18 Hz, 2H), 1.18 (t, *J* = 7.19 Hz, 3H), 1.12 (t, *J* = 7.20 Hz, 3H).

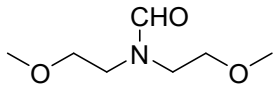
***N,N*-dibutylformamide (3i) [9]**



3i

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a brown oil (21.4 mg, 68%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 3.30 – 3.24 (m, 2H), 3.18 (t, *J* = 7.17 Hz, 2H), 1.54 – 1.47 (m, 4H), 1.35 – 1.25(m, 4H), 0.94 – 0.91 (m, 6H).

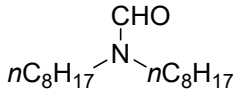
***N,N*-bis(2-methoxyethyl)formamide (3j)[9]**



3j

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a brown oil (12.2 mg, 38%);
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (s, 1H), 3.54 – 3.50 (m, 4H), 3.46 – 3.45 (m, 4H), 3.32 (d, *J* = 2.73 Hz, 6H).

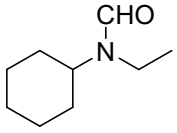
***N,N*-dioctylformamide (3k)[9]**



3k

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a brown oil (32.3 mg, 60%);
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 3.26 (t, *J* = 7.65 Hz, 2H), 3.17 (t, *J* = 7.16 Hz, 2H), 1.51 (q, *J* = 6.72 Hz, 4H), 1.27 (m, 20H), 0.87 (td, *J* = 6.82, 2.85 Hz, 6H).

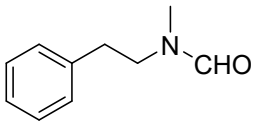
***N*-cyclohexyl-*N*-ethylformamide (3l)[9]**



3l

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a yellow oil (9.3 mg, 30%);
The presence of two rotamers (ratio 73:27) were observed in the NMR spectra.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 0.73H), 8.08 (s, 0.27H), 3.29 (q, *J* = 7.15 Hz, 2H), 3.22 (m, 1H), 1.90 – 1.63 (m, 6H), 1.50 (dd, *J* = 12.49, 3.37 Hz, 2H), 1.29 – 1.18 (m, 2H), 1.15 (t, *J* = 7.13 Hz, 3H).

***N*-methyl-*N*-phenethylformamide (3m)[11]**

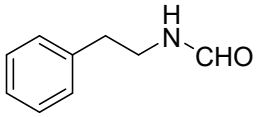


3m

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a yellow oil (27.1 mg, 83%);
The presence of two rotamers (ratio 63:37) were observed in the NMR spectra.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 0.37H), 7.83 (s, 0.63H), 7.37 – 7.31 (m, 2H), 7.29 – 7.24 (m, 2H), 7.21 – 7.15 (m, 1H), 3.65 – 3.56 (m, 0.74H), 3.50 (t, *J* = 7.02 Hz,

1.26H), 2.96 – 2.81 (m, 5H).

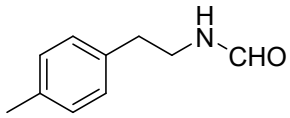
_N_-phenethylformamide (3n)[12]



3n

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a yellow oil (18.8 mg, 63%);
The presence of two rotamers (ratio 82:18) were observed in the NMR spectra.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, J = 1.76 Hz, 0.83H), 7.93 (d, J = 12.02 Hz, 0.17H), 7.41 – 7.18 (m, 5H), 5.99 – 5.74 (brs, 1H), 3.61 (q, J = 6.68 Hz, 1.66H), 3.51 (q, J = 6.72 Hz, 0.34H), 2.87 (dt, J = 13.70, 6.87 Hz, 2H).

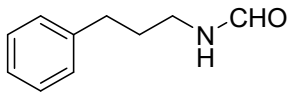
_N_-(4-methylphenethyl)formamide (3o) [13]



3o

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a yellow oil (17.6 mg, 54%);
The presence of two rotamers (ratio 83:17) were observed in the NMR spectra.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, J = 1.79 Hz, 0.82H), 7.86 (d, J = 11.91 Hz, 0.18H), 7.17 – 6.97 (m, 5H), 5.92 (brs, 1H), 3.52 (q, J = 6.71 Hz, 1.64H), 3.42 (q, J = 6.72 Hz, 0.36H), 2.77 (m, 3H), 2.32 (s, 3H).

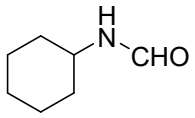
_N_-(3-phenylpropyl)formamide (3p)[8]



3p

The title compound was prepared according to the General procedure B and yields determined by ^{1}H NMR spectroscopy using trimethoxybenzene as an internal standard (78%);
The presence of two rotamers (ratio 82:18) were observed in the NMR spectra.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (s, 0.82H), 8.04 (d, J = 11.94 Hz, 0.18H), 7.32 (t, J = 7.59 Hz, 2H), 7.22 (m, 3H), 6.04 – 5.84 (m, 1H), 3.35 (q, J = 6.76 Hz, 1.64H), 3.24 (q, J = 6.76 Hz, 0.36H), 2.69 (t, J = 7.69 Hz, 2H), 1.92 – 1.86 (m, 3H).

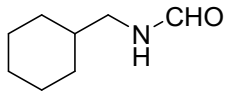
_N_-cyclohexylformamide (3q)[14]



3q

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a brown oil (24.5 mg, 75%);
The presence of two rotamers (ratio 86:14) were observed in the NMR spectra.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 0.14H), 8.09 (s, 0.86H), 5.73 (brs, 0.2H), 5.50 (brs, 0.8H), 3.85 (m, 0.84H), 3.71 (q, *J* = 7.02 Hz, 0.15H), 2.16 – 1.53 (m, 6H), 1.41 – 1.00 (m, 5H).

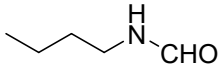
***N*-(cyclohexylmethyl)formamide (3r)[15]**



3r

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a white solid (20.9 mg, 74%);
The presence of two rotamers (ratio 77:23) were observed in the NMR spectra.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 0.77H), 7.97 (d, *J* = 11.91 Hz, 0.23H), 5.94 (brs, 0.23H), 5.82 (brs, 0.77H), 3.12 (t, *J* = 6.52 Hz, 1.54), 3.02 (t, *J* = 6.61 Hz, 0.46H), 1.89 – 1.61 (m, 6H), 1.43 (m, 1H),1.37 – 1.07 (m, 3H), 1.01 – 0.80 (m, 2H).

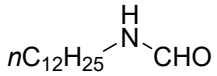
***N*-butylformamide (3s)[16]**



3s

The title compound was prepared according to the General procedure B and yields determined by ^{1}H NMR spectroscopy using trimethoxybenzene as an internal standard (71%);
The presence of two rotamers (ratio 77:23) were observed in the NMR spectra.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (s, 0.77H), 8.07 (d, *J* = 12.09 Hz, 0.23H), 5.98 (brs, 023H), 5.76 (brs, 0.77H), 3.53 – 3.19 (m, 2H), 1.54 (m 2H), 1.48 – 1.24 (m, 2H), 0.96 (q, *J* = 11.73, 9.55 Hz, 3H)

***N*-(dodecyl)formamide (3t)[12]**



3t

The title compound was prepared according to the General procedure B and purified by flash column chromatography to give the product as a gray solid (29.8mg, 70%);
The presence of two rotamers (ratio 77:23) were observed in the NMR spectra.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 0.81), 8.00 (d, *J* = 11.96 Hz, 0.19H), 5.95 (brs, 0.19H), 5.89 (brs, 0.81H), 3.26 (q, *J* = 6.83 Hz, 1.6H), 3.17 (t, *J* = 6.83 Hz, 0.4H), 1.49 (q, *J* = 7.19 Hz, 3H), 1.25 (m, 18H), 0.85 (t, *J* = 6.80 Hz, 3H).

6. Reference.

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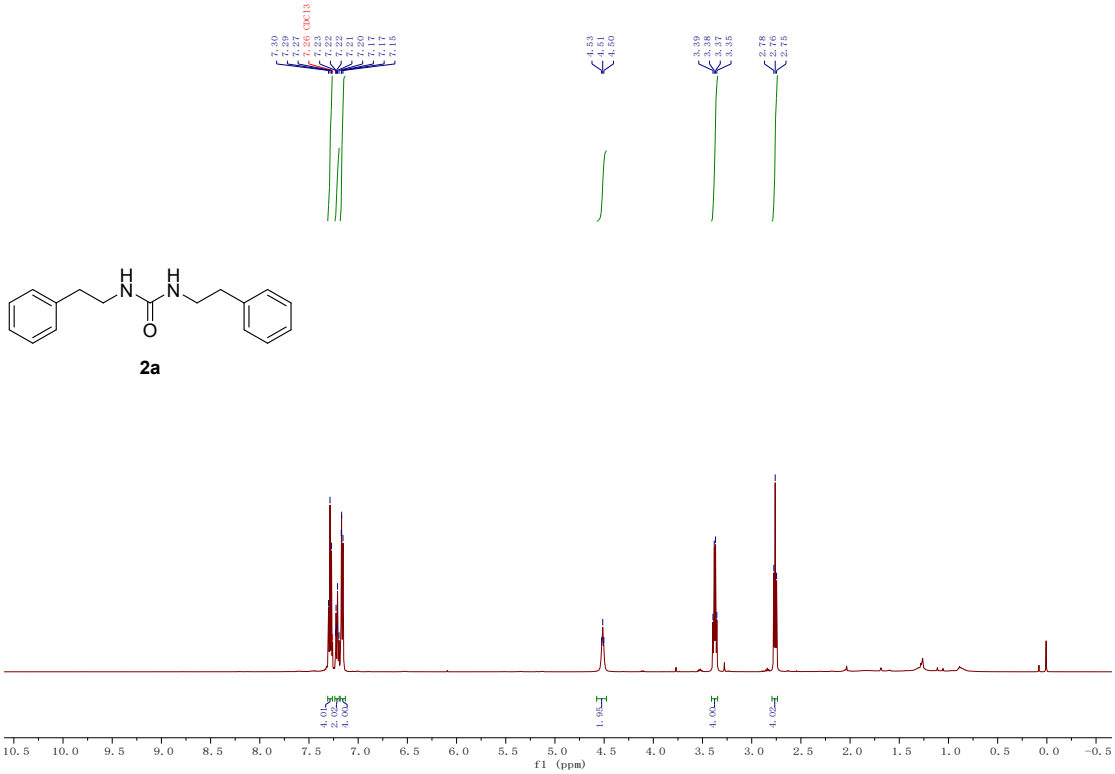
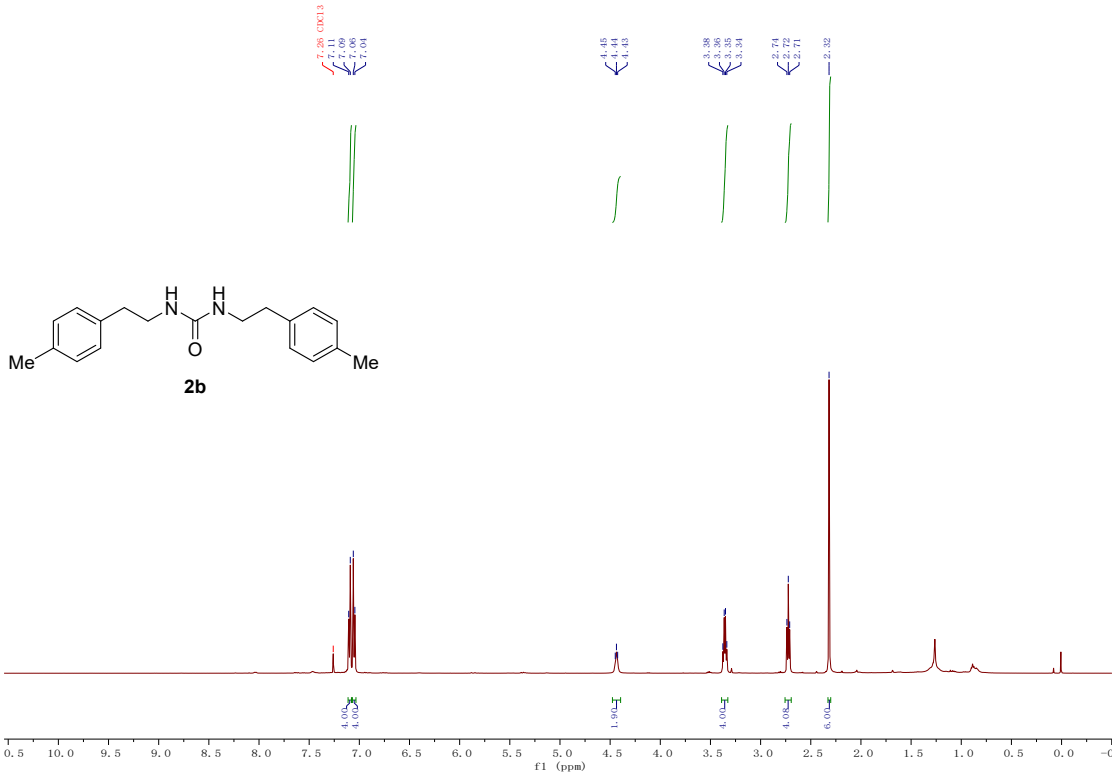
7. NMR spectra

^{1}H NMR spectrum of **2a** in $CDCl_3$ at 500 MHz



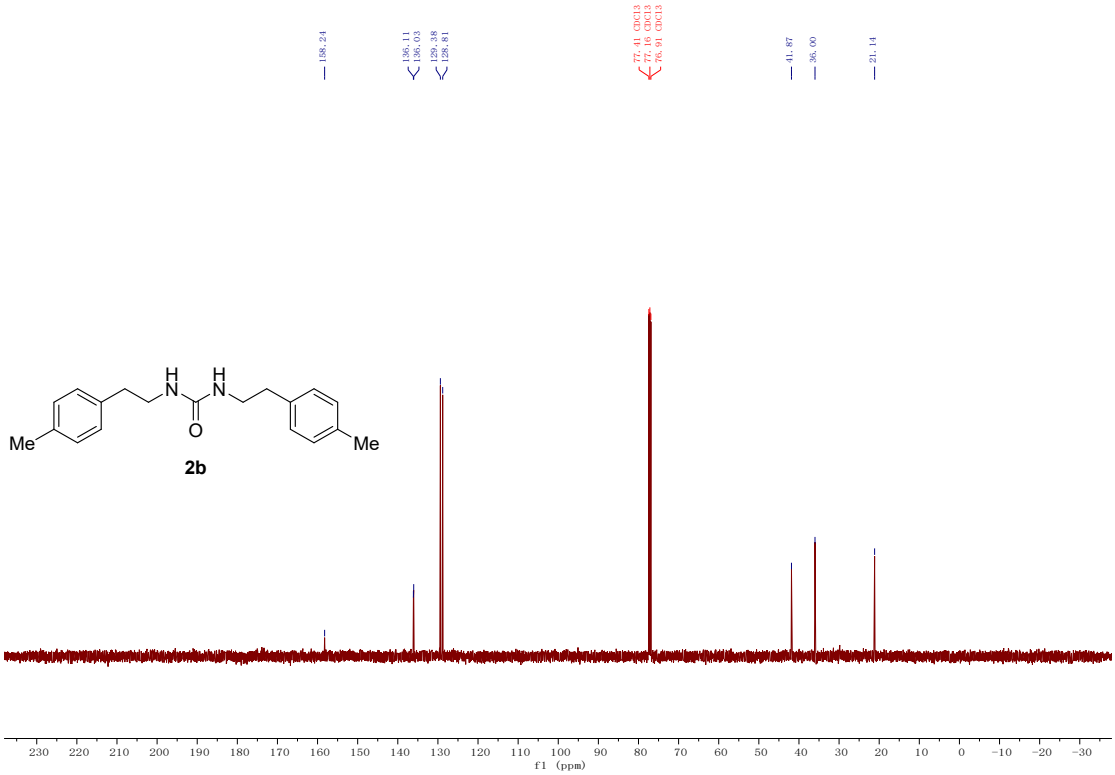
2a

^{1}H NMR spectrum of **2b** in $CDCl_3$ at 500 MHz

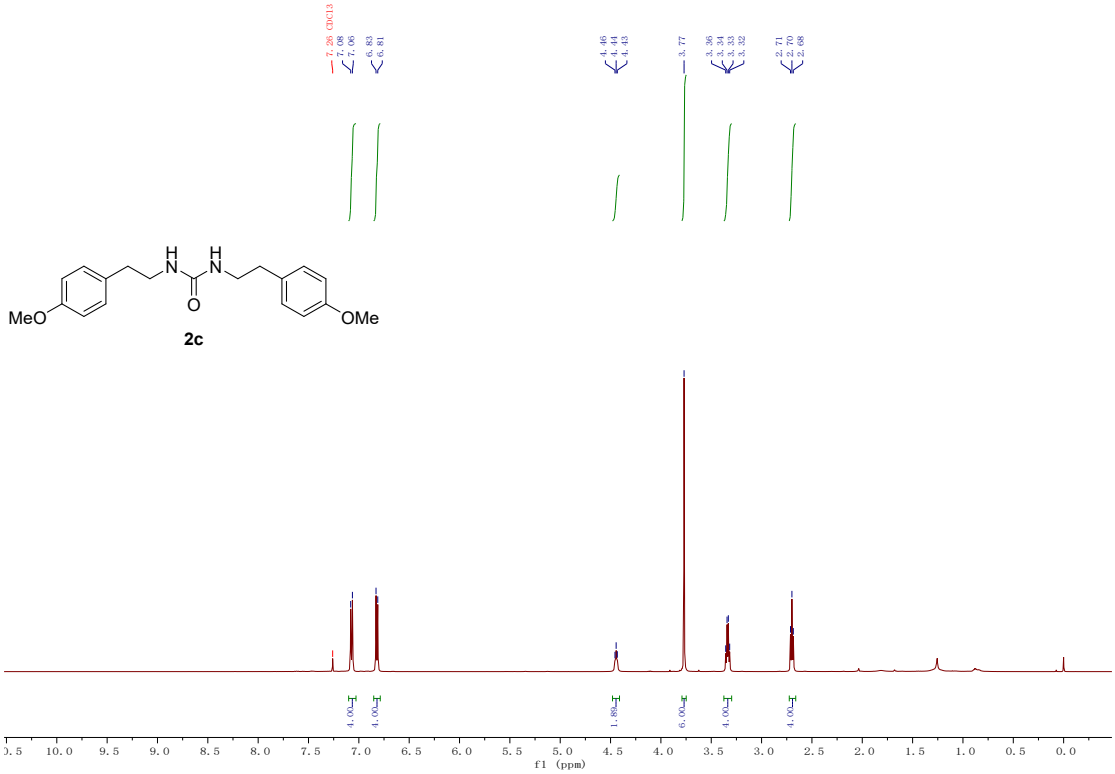


2b

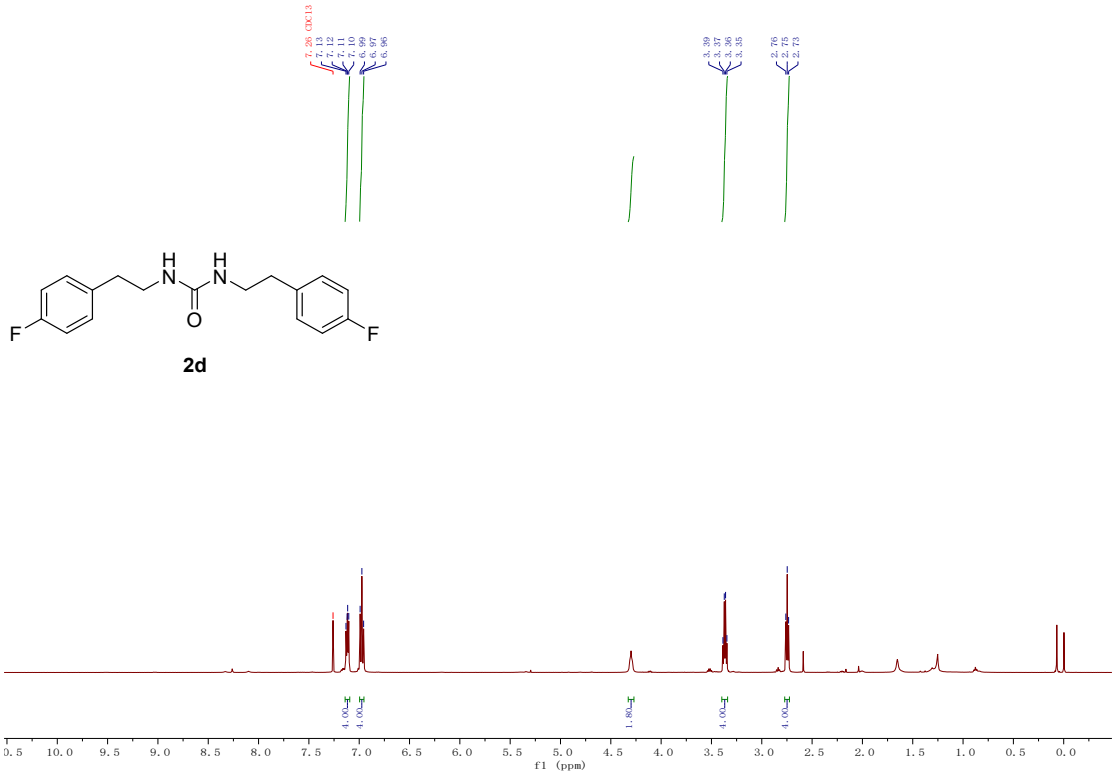
^{13}C NMR spectrum of **2b** in $CDCl_3$ at 126 MHz



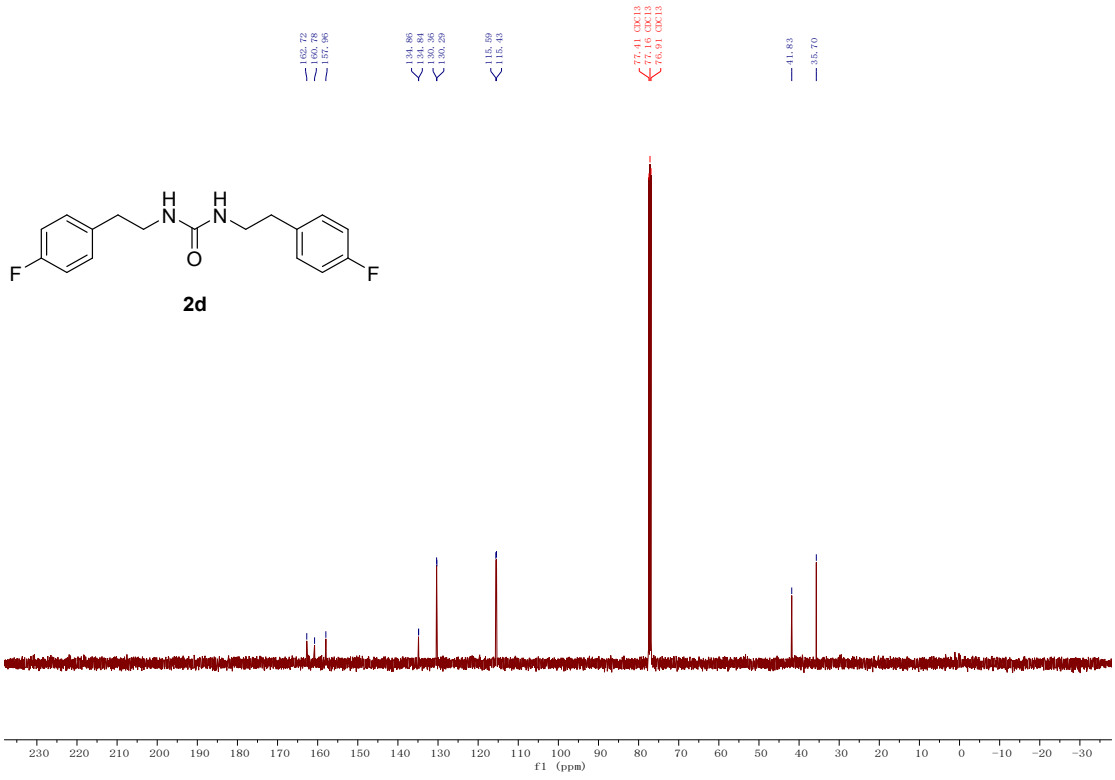
^{1}H NMR spectrum of **2c** in $CDCl_3$ at 500 MHz



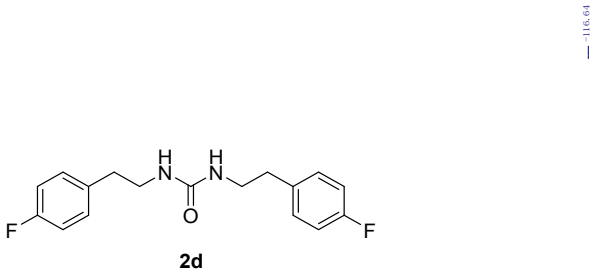
^{1}H NMR spectrum of **2d** in $CDCl_3$ at 500 MHz



^{13}C NMR spectrum of **2d** in $CDCl_3$ at 126 MHz

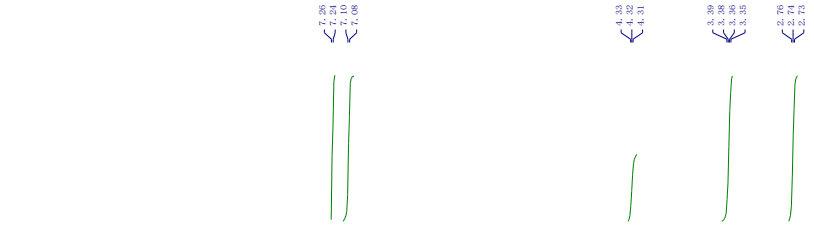


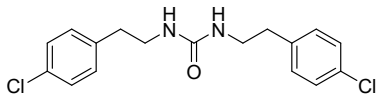
^{19}F NMR spectrum of **2d** in $CDCl_3$ at 475 MHz



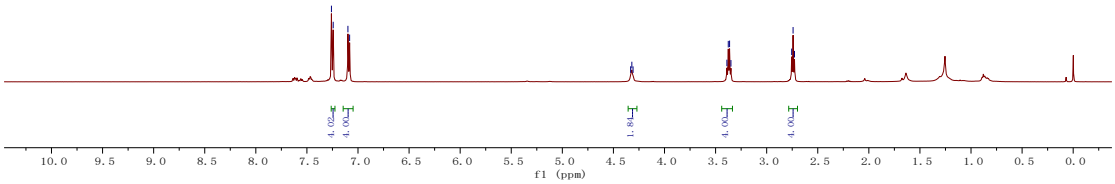
2d

^{1}H NMR spectrum of **2e** in $CDCl_3$ at 500 MHz

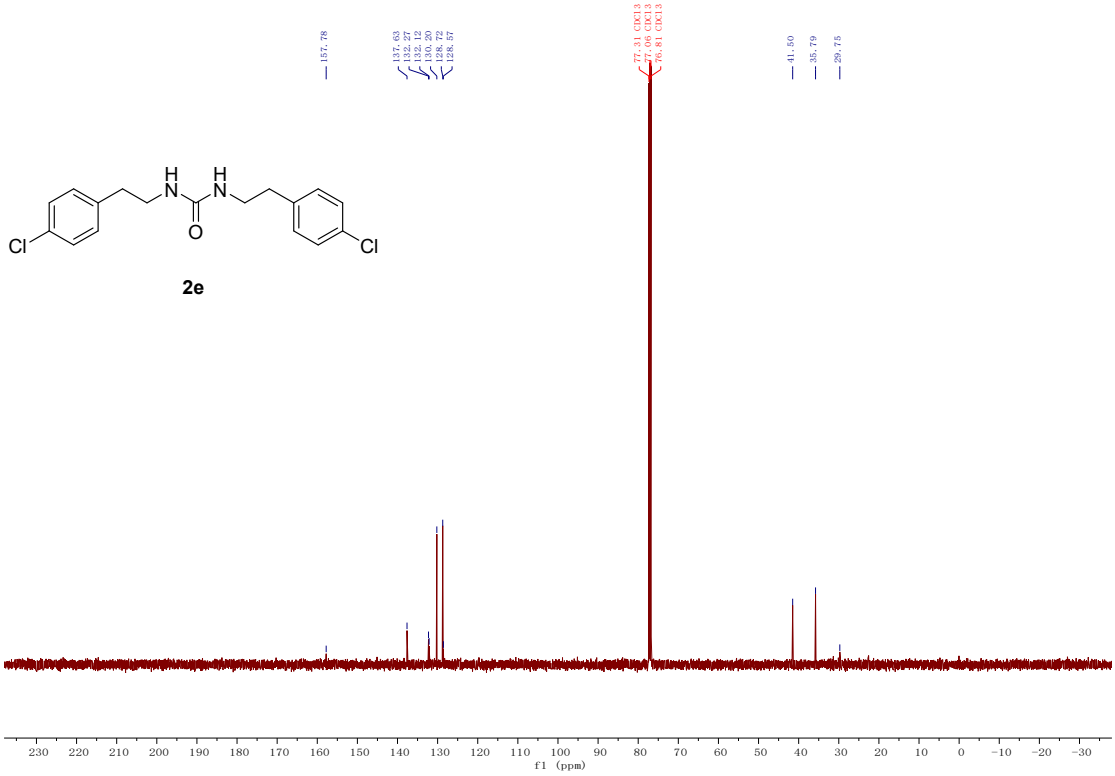




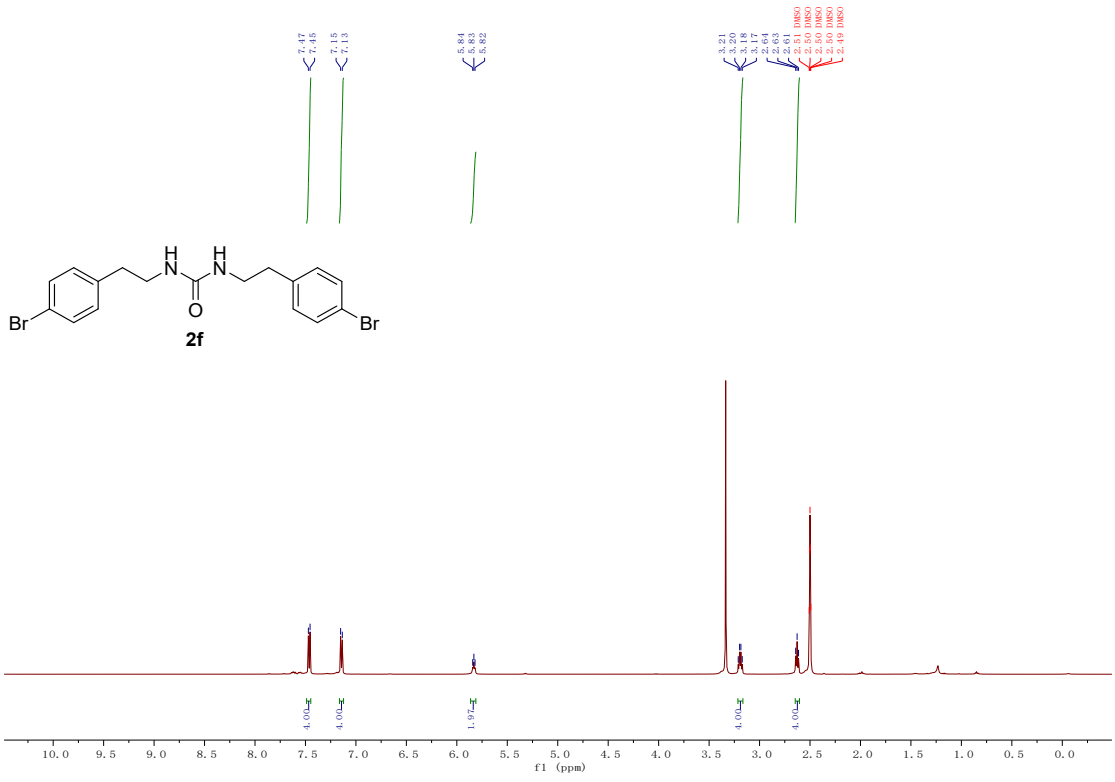
2e



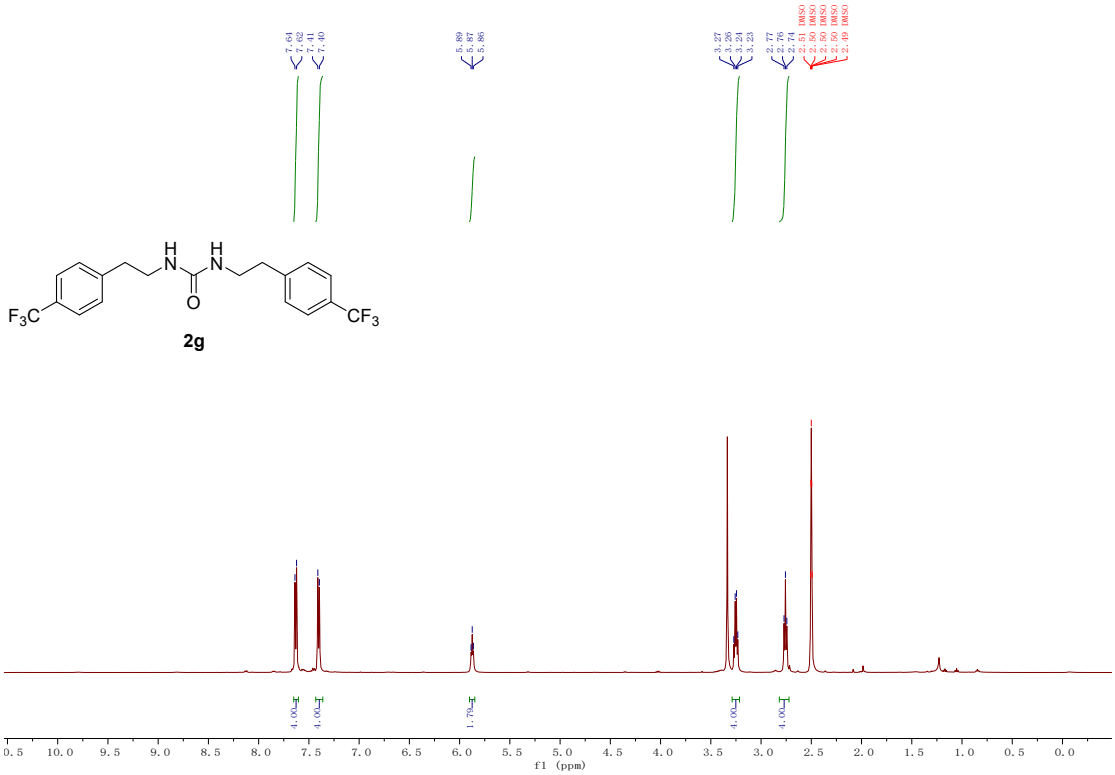
^{13}C NMR spectrum of **2e** in $CDCl_3$ at 126 MHz



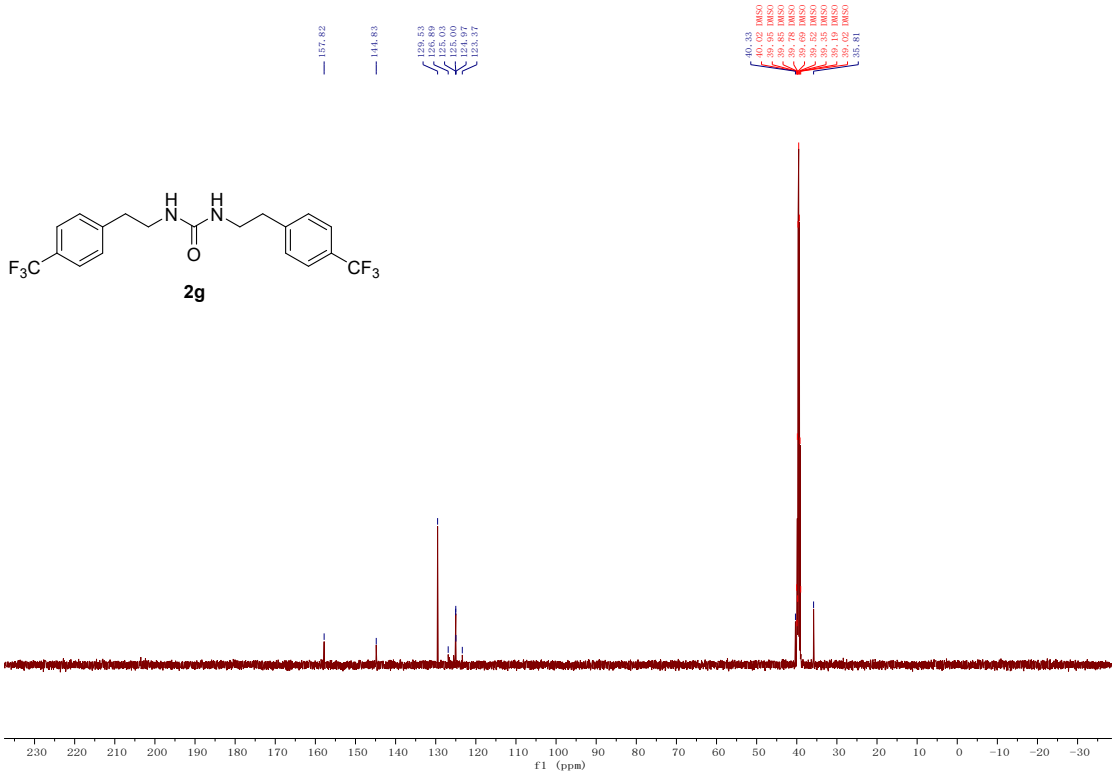
^{1}H NMR spectrum of **2f** in DMSO-d_6 at 500 MHz



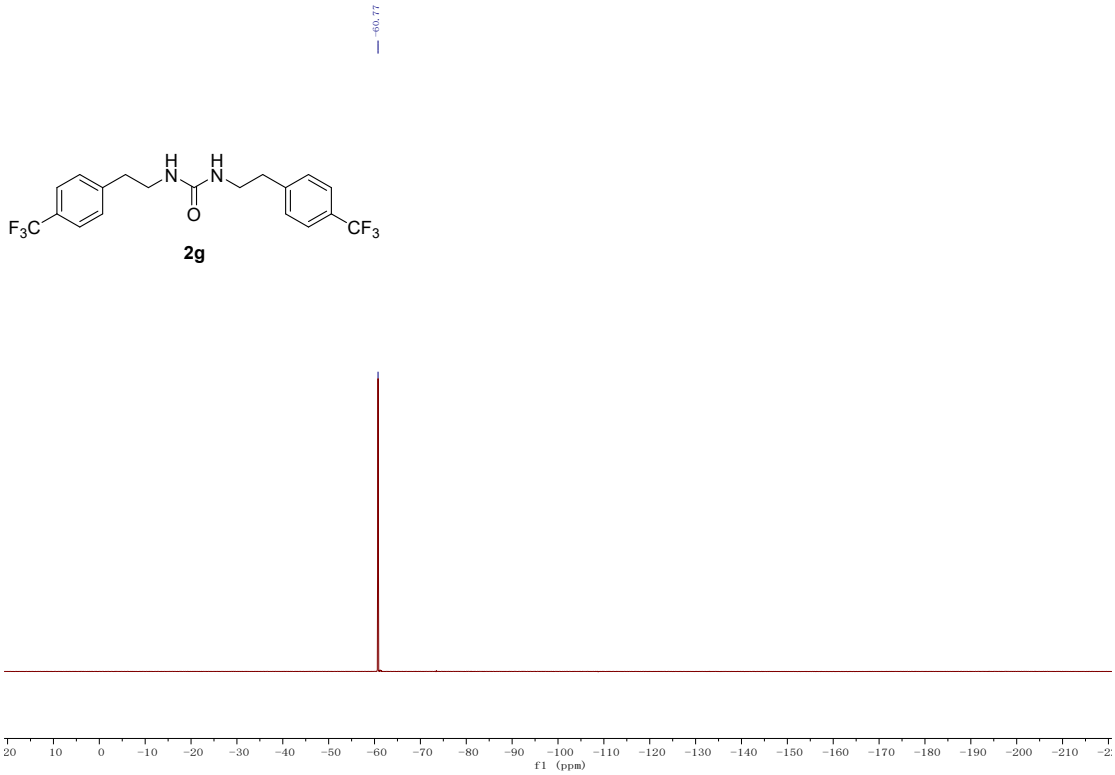
^{1}H NMR spectrum of **2g** in DMSO-d_6 at 500 MHz



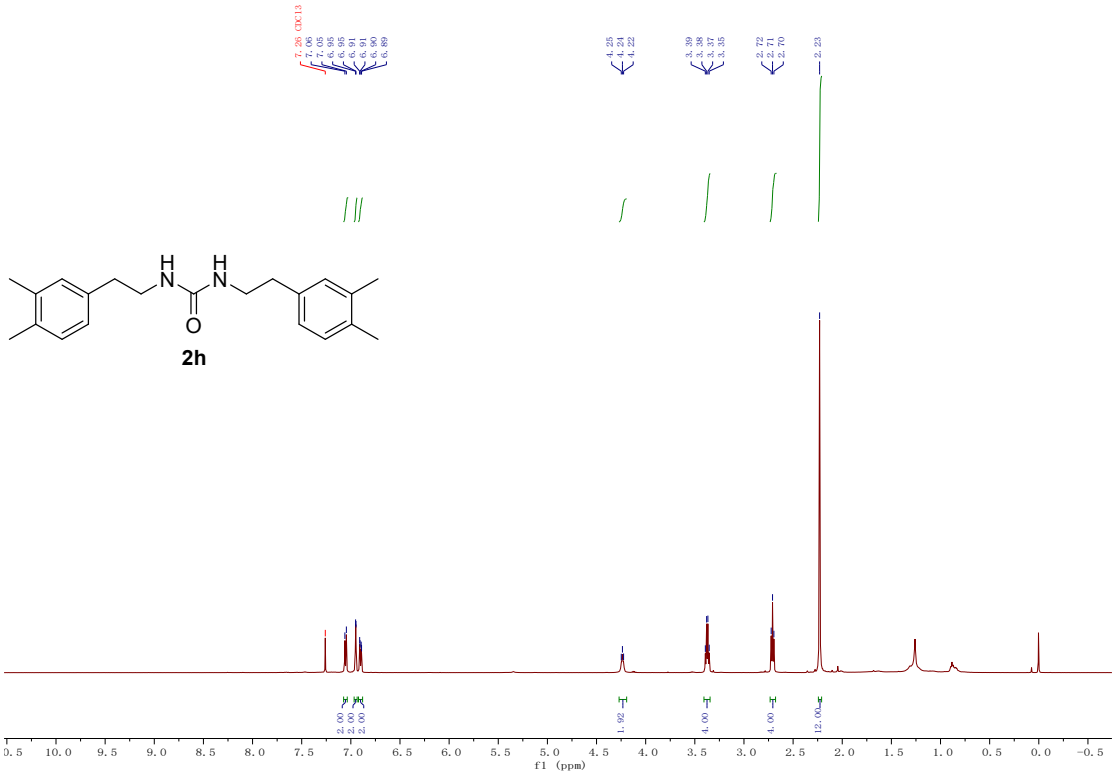
^{13}C NMR spectrum of **2g** in DMSO-d_6 at 126 MHz



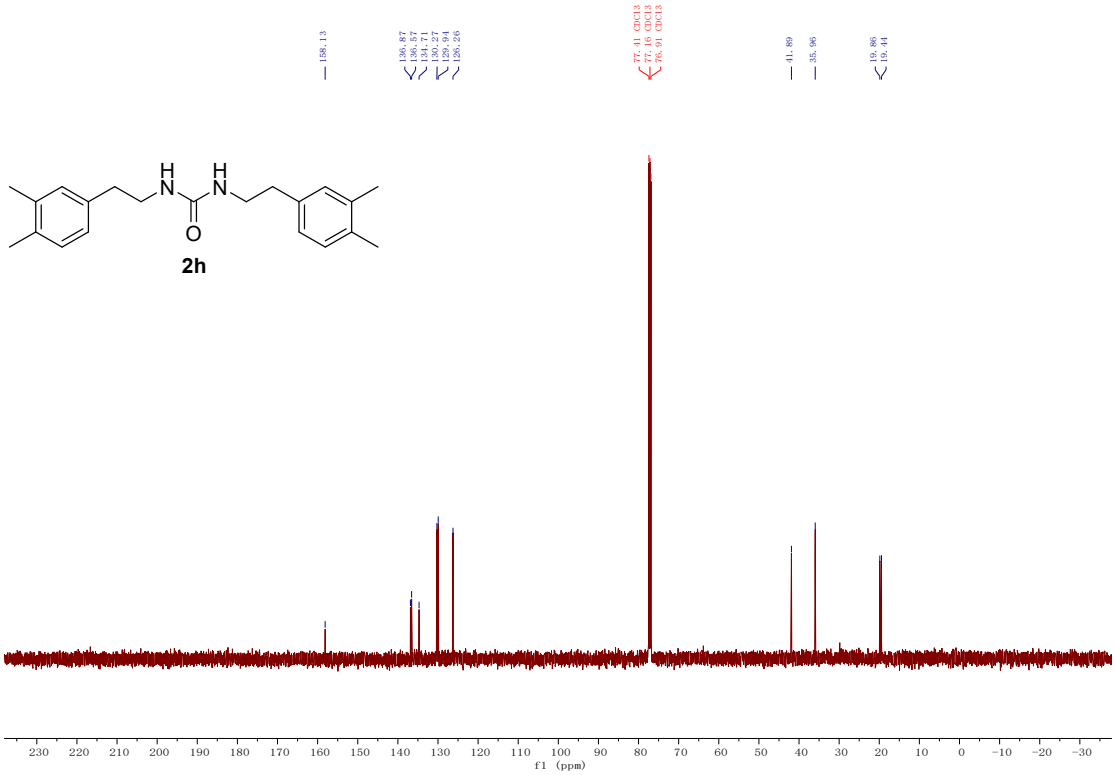
^{19}F NMR spectrum of **2g** in DMSO-d_6 at 470 MHz



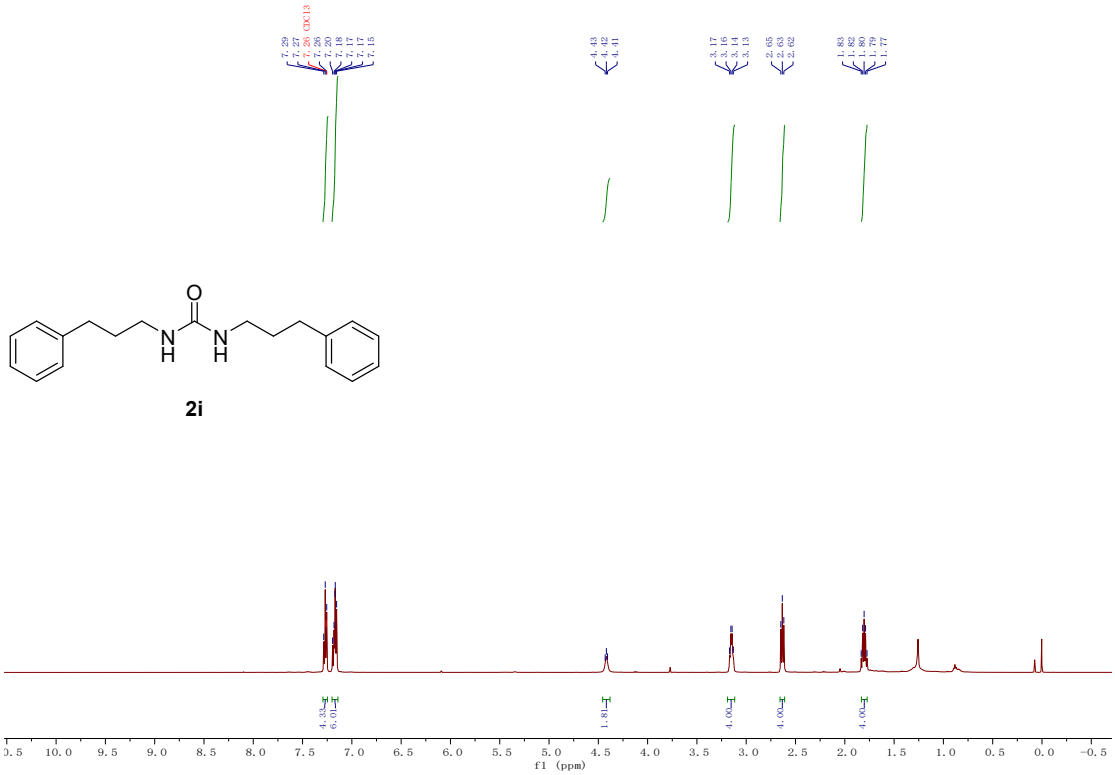
^{1}H NMR spectrum of **2h** in $CDCl_3$ at 500 MHz



^{13}C NMR spectrum of **2h** in $CDCl_3$ at 126 MHz

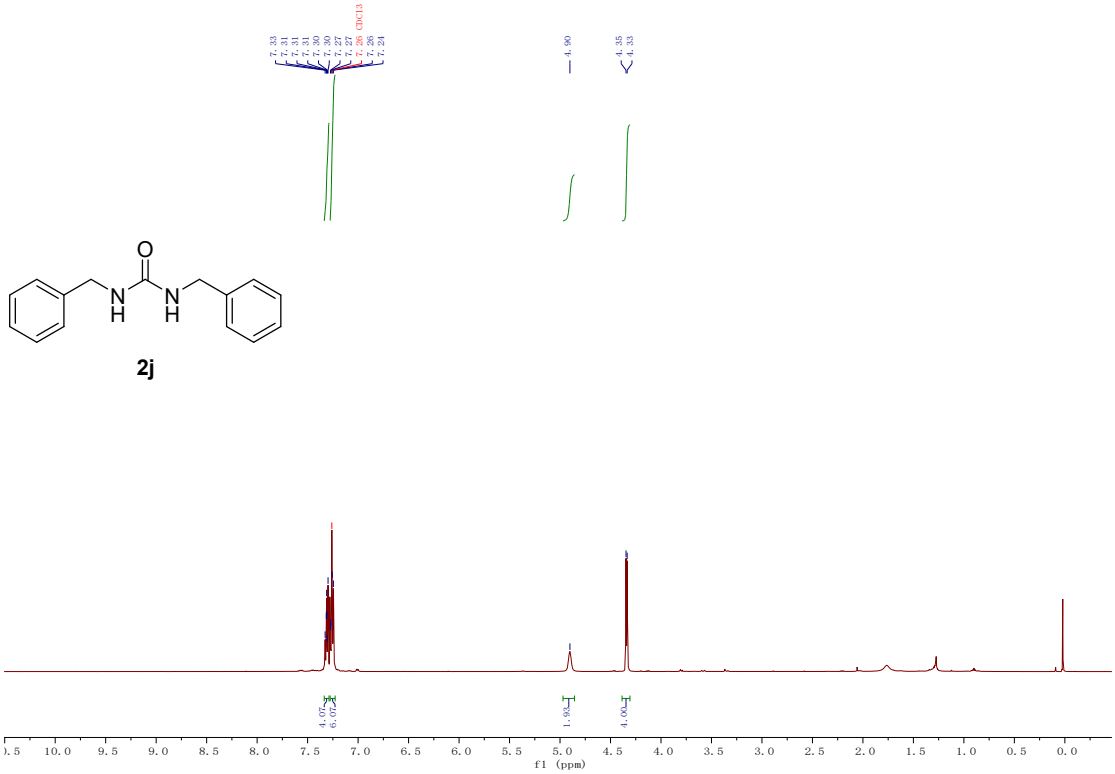


^{1}H NMR spectrum of **2i** in $CDCl_3$ at 500 MHz



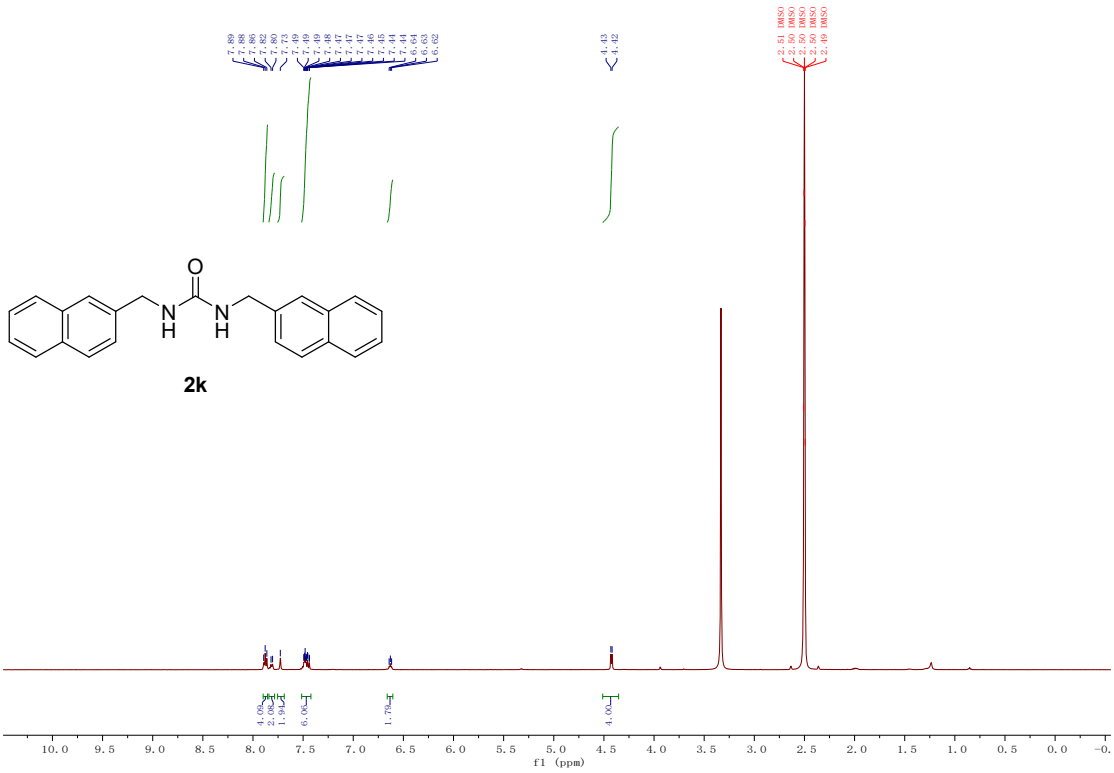
2i

^{1}H NMR spectrum of **2j** in $CDCl_3$ at 500 MHz

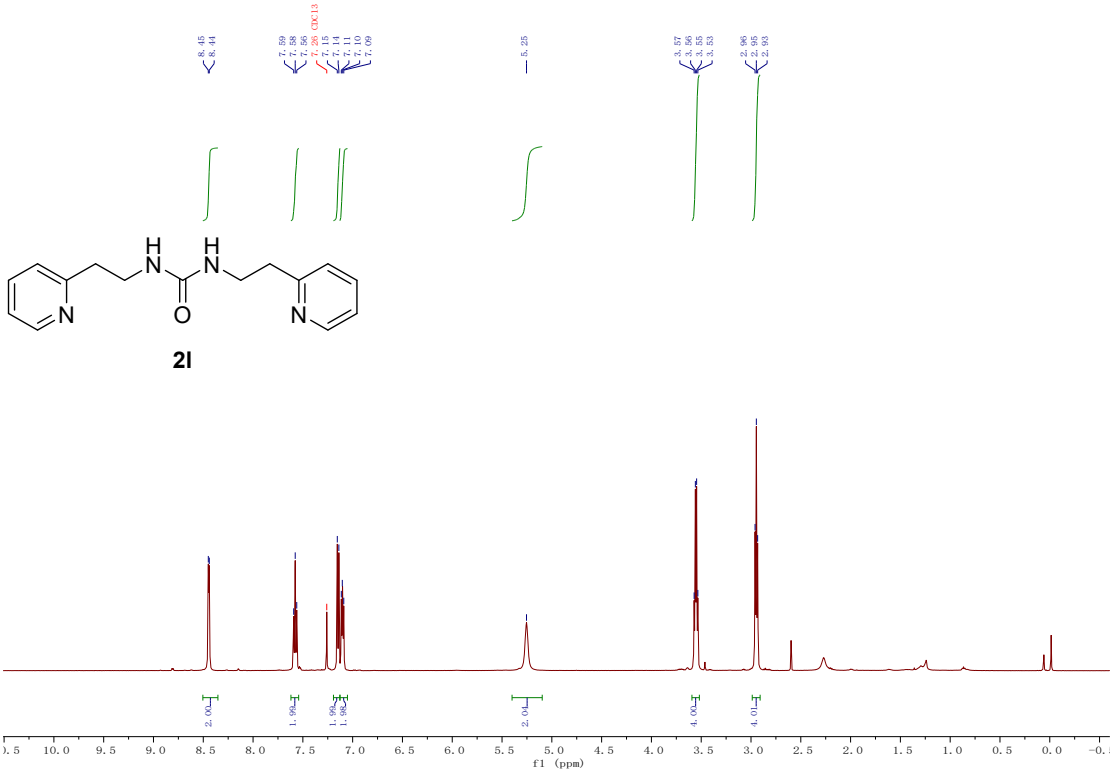


2j

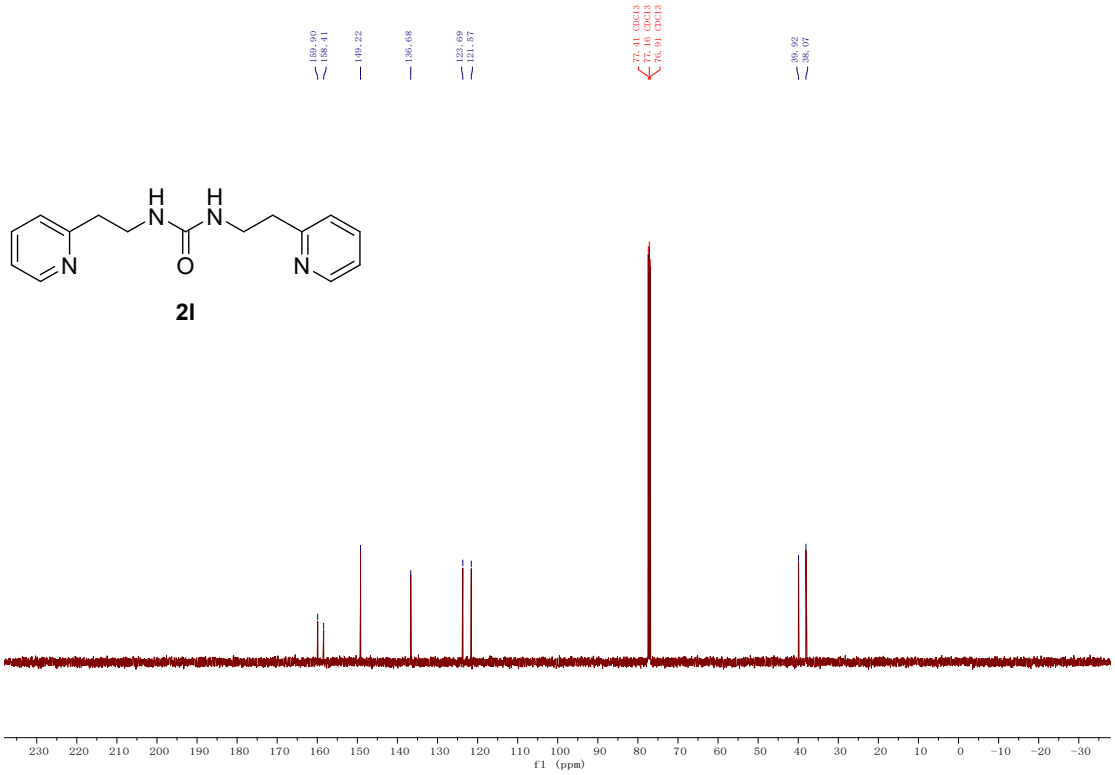
^{1}H NMR spectrum of **2k** in DMSO-d_6 at 500 MHz



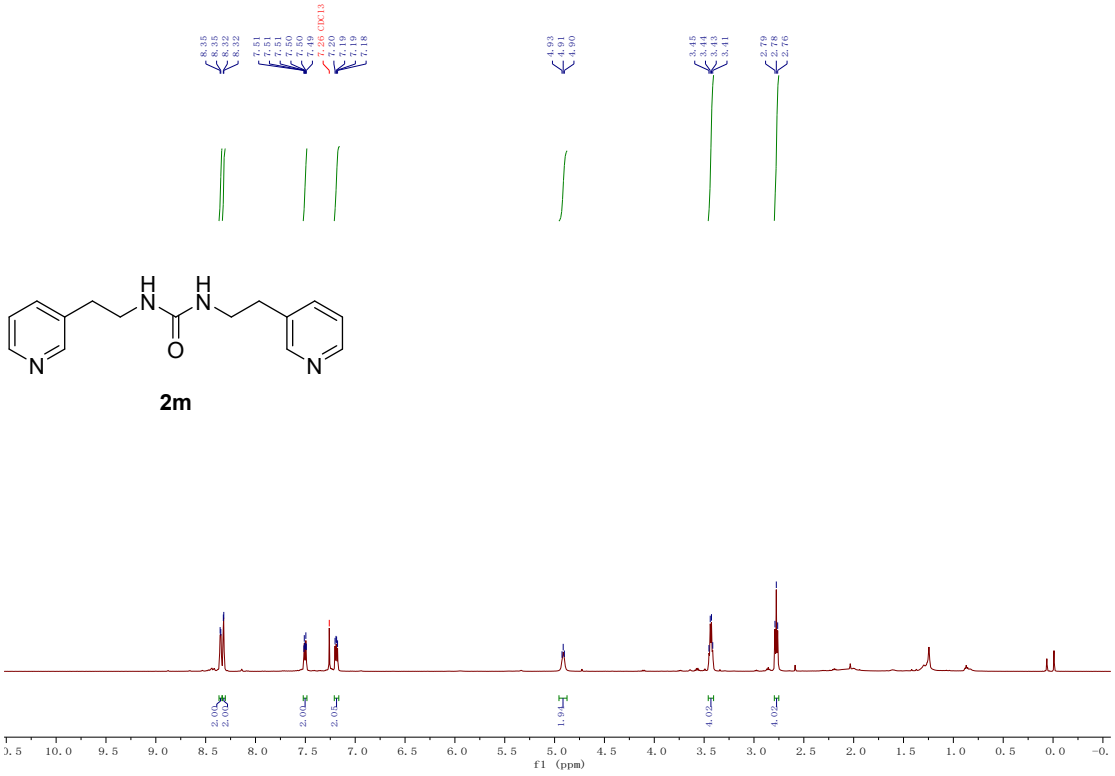
^{1}H NMR spectrum of **2l** in $CDCl_3$ at 500 MHz



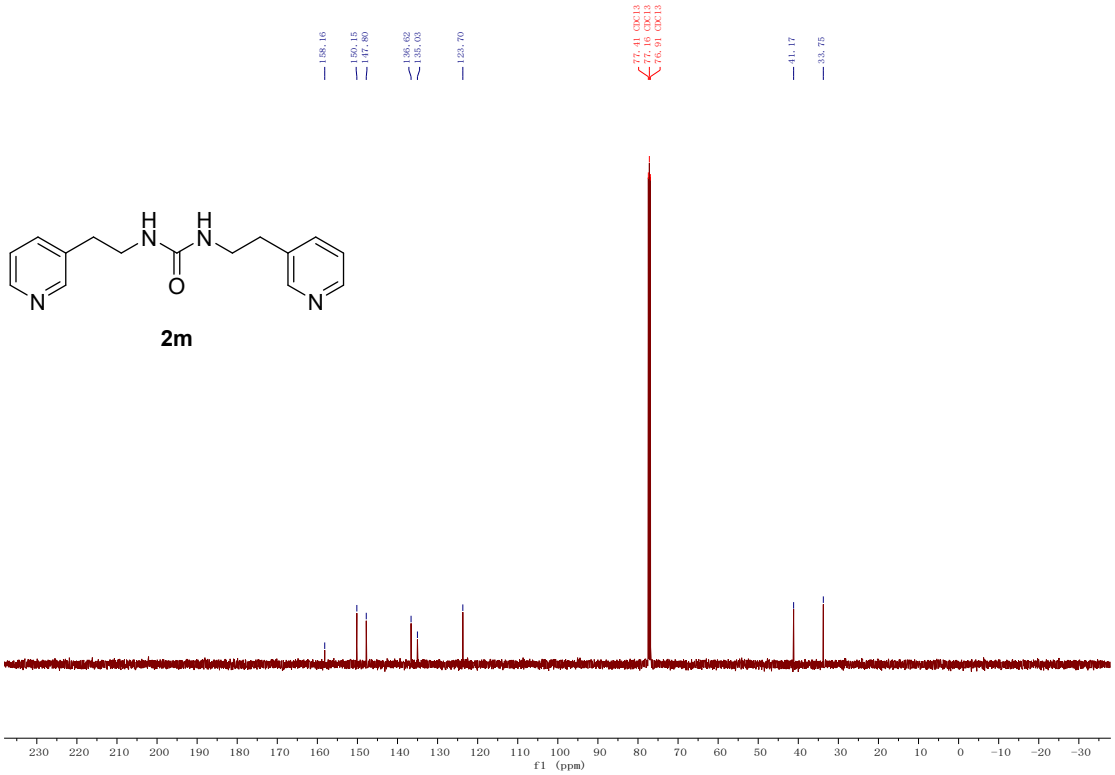
^{13}C NMR spectrum of **2l** in $CDCl_3$ at 126 MHz



^{1}H NMR spectrum of **2m** in $CDCl_3$ at 500 MHz

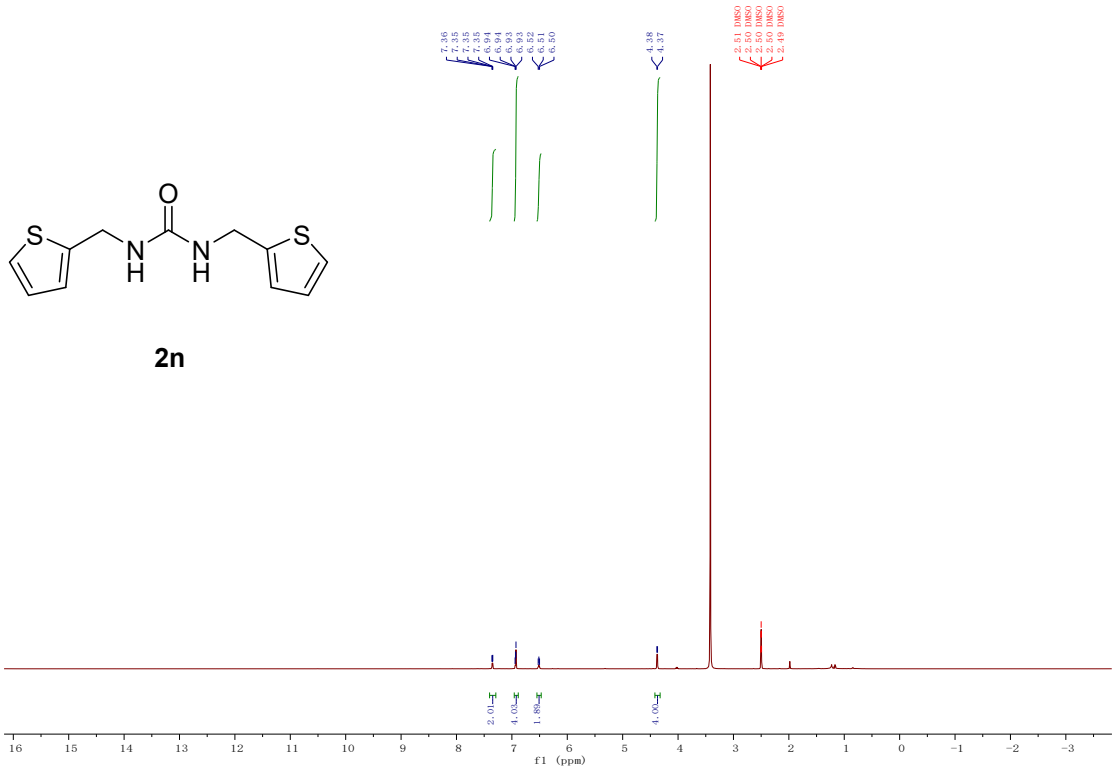


^{13}C NMR spectrum of **2m** in $CDCl_3$ at 126 MHz



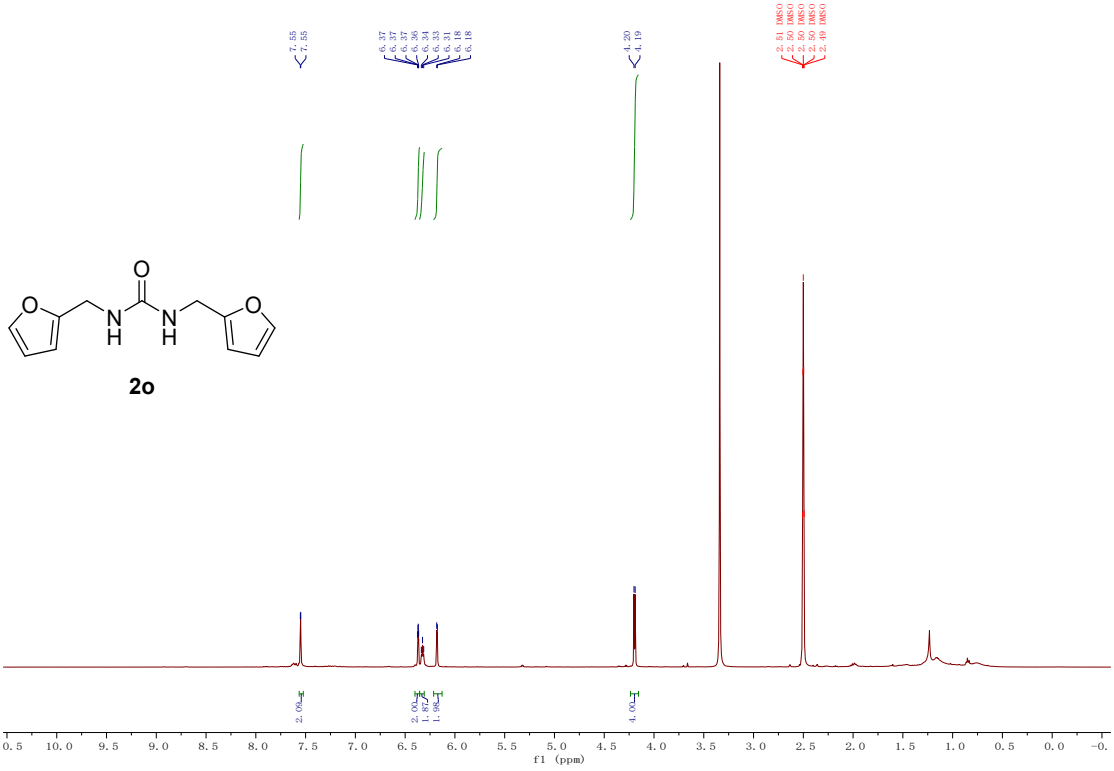
2m

^{1}H NMR spectrum of **2n** in DMSO-d_6 at 500 MHz



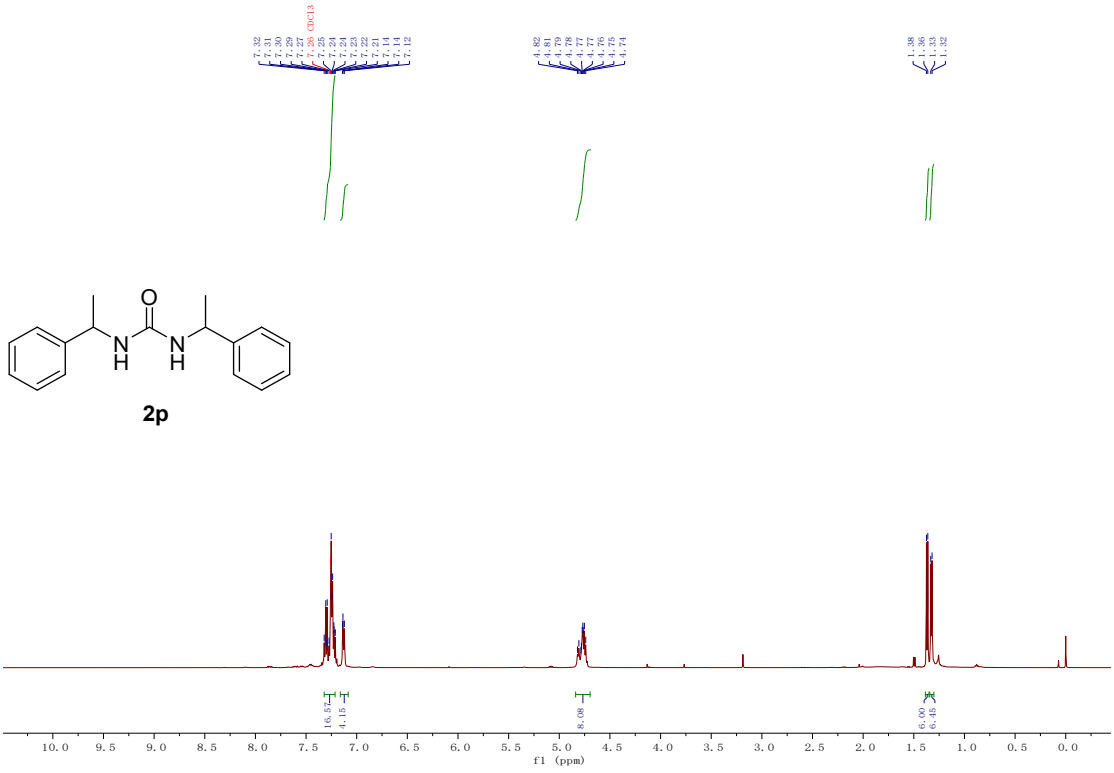
2n

^{1}H NMR spectrum of **2o** in DMSO-d_6 at 500 MHz



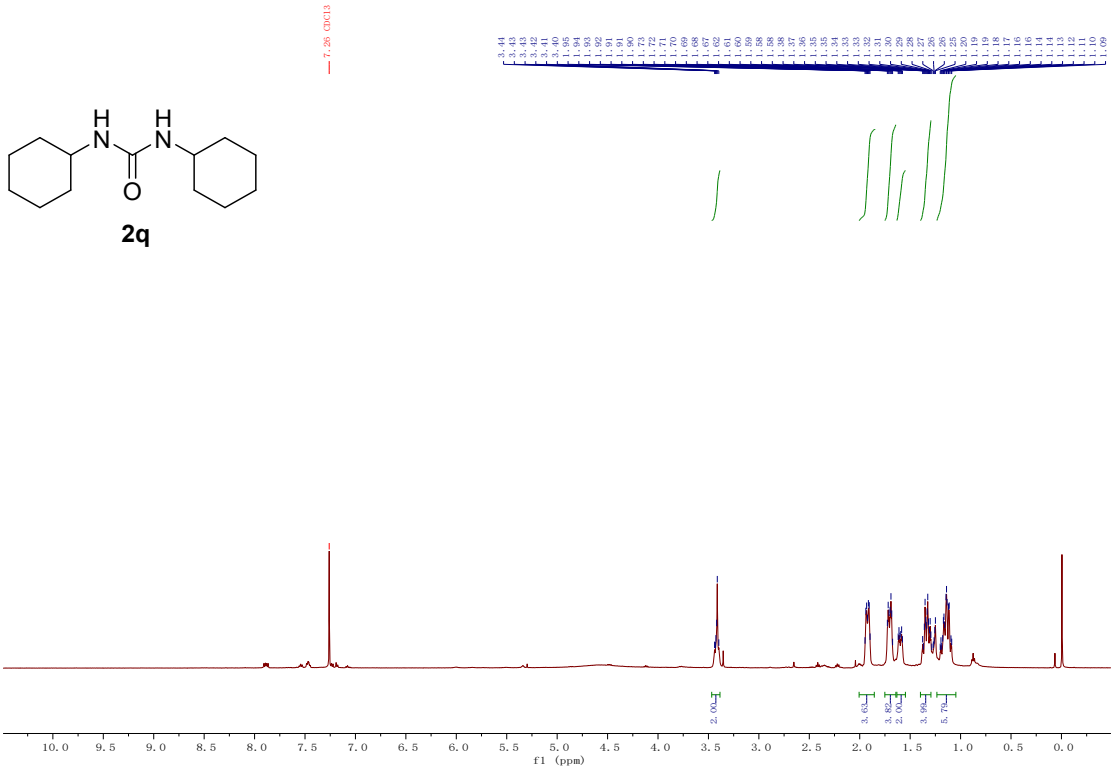
2o

^{1}H NMR spectrum of **2p** in $CDCl_3$ at 500 MHz

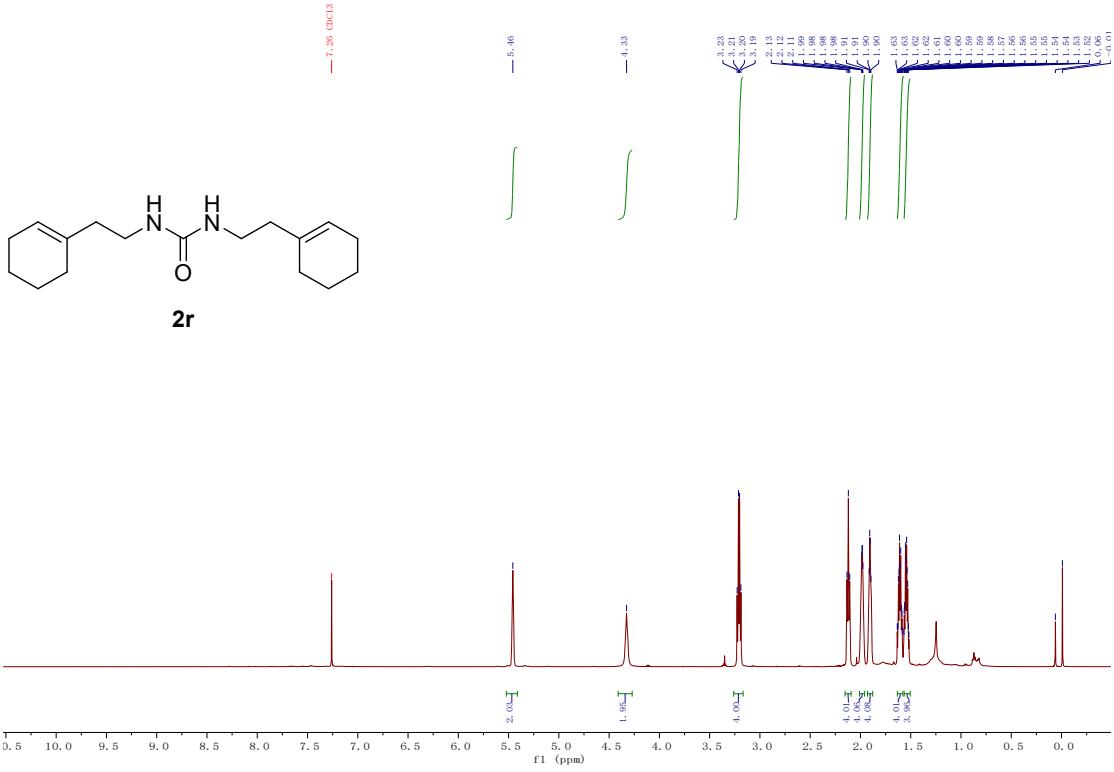


2p

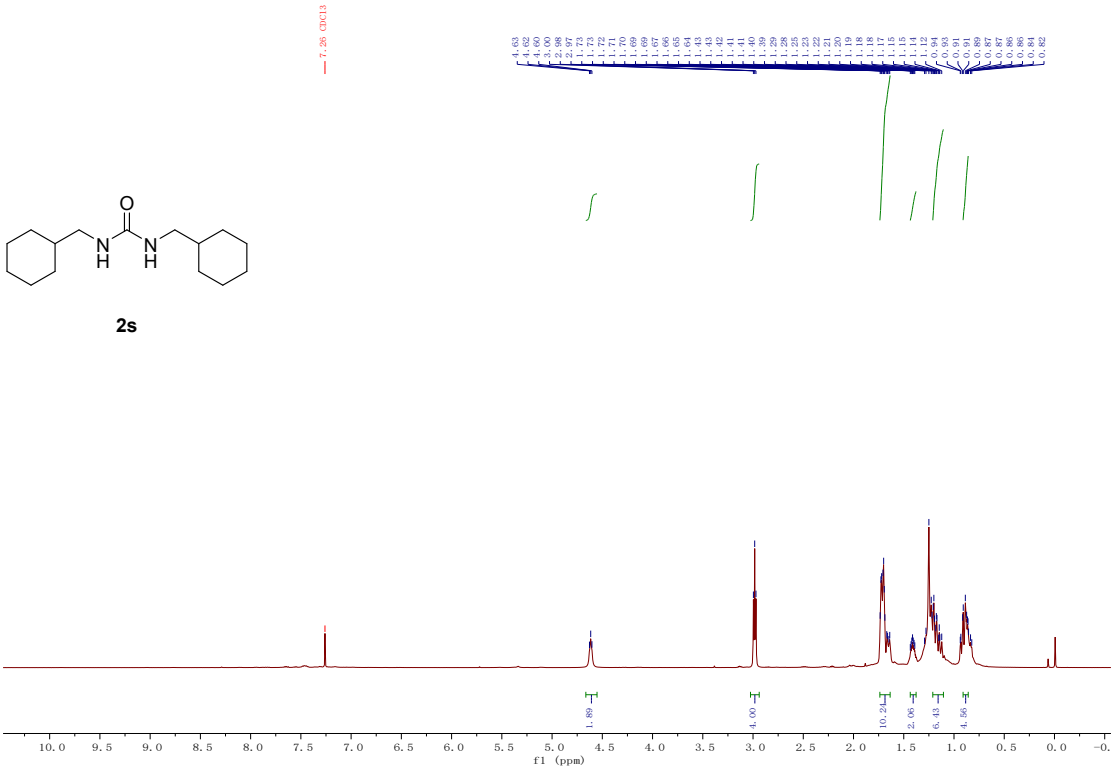
^{1}H NMR spectrum of **2q** in $CDCl_3$ at 500 MHz



^{1}H NMR spectrum of **2r** in $CDCl_3$ at 500 MHz

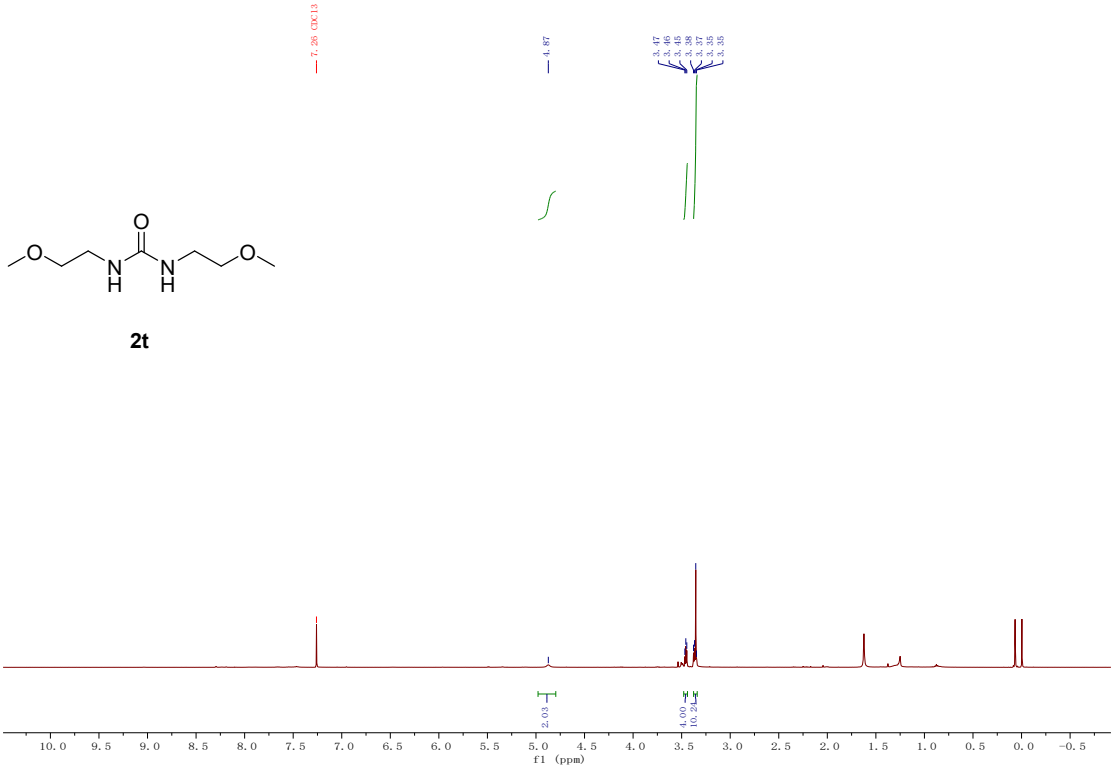


^{1}H NMR spectrum of **2s** in $CDCl_3$ at 126 MHz



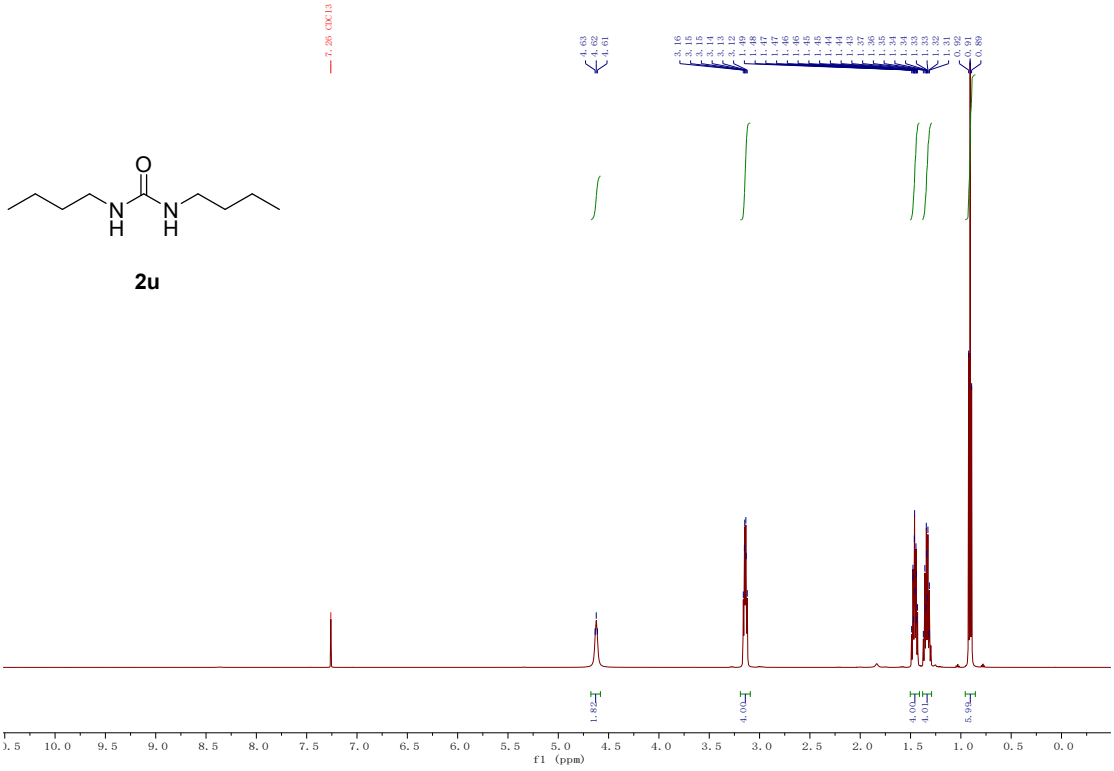
2s

^{1}H NMR spectrum of **2t** in $CDCl_3$ at 500 MHz



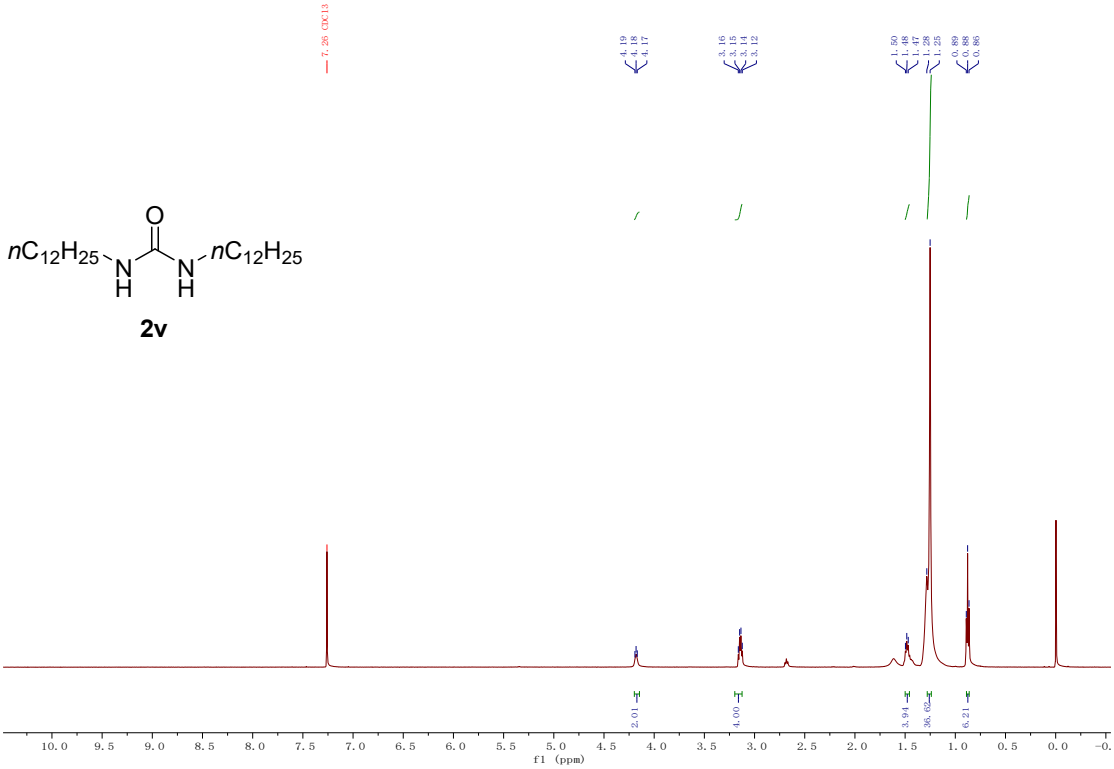
2t

^{1}H NMR spectrum of **2u** in $CDCl_3$ at 500 MHz



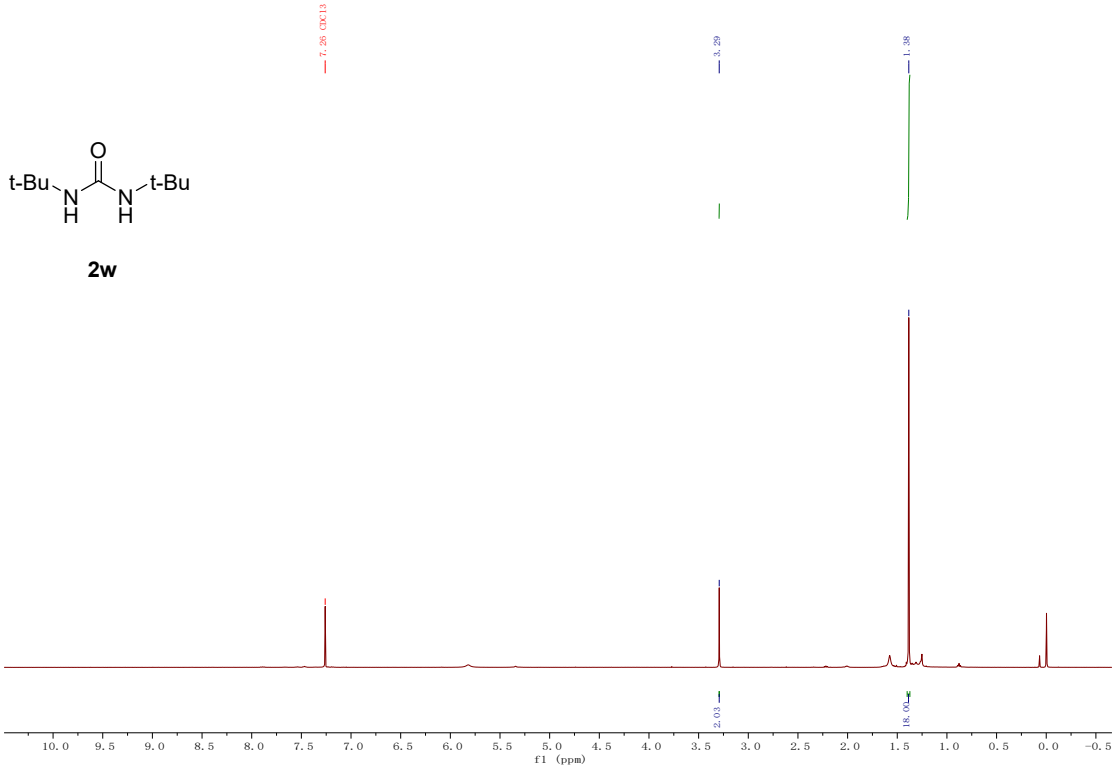
2u

^{1}H NMR spectrum of **2v** in $CDCl_3$ at 500 MHz

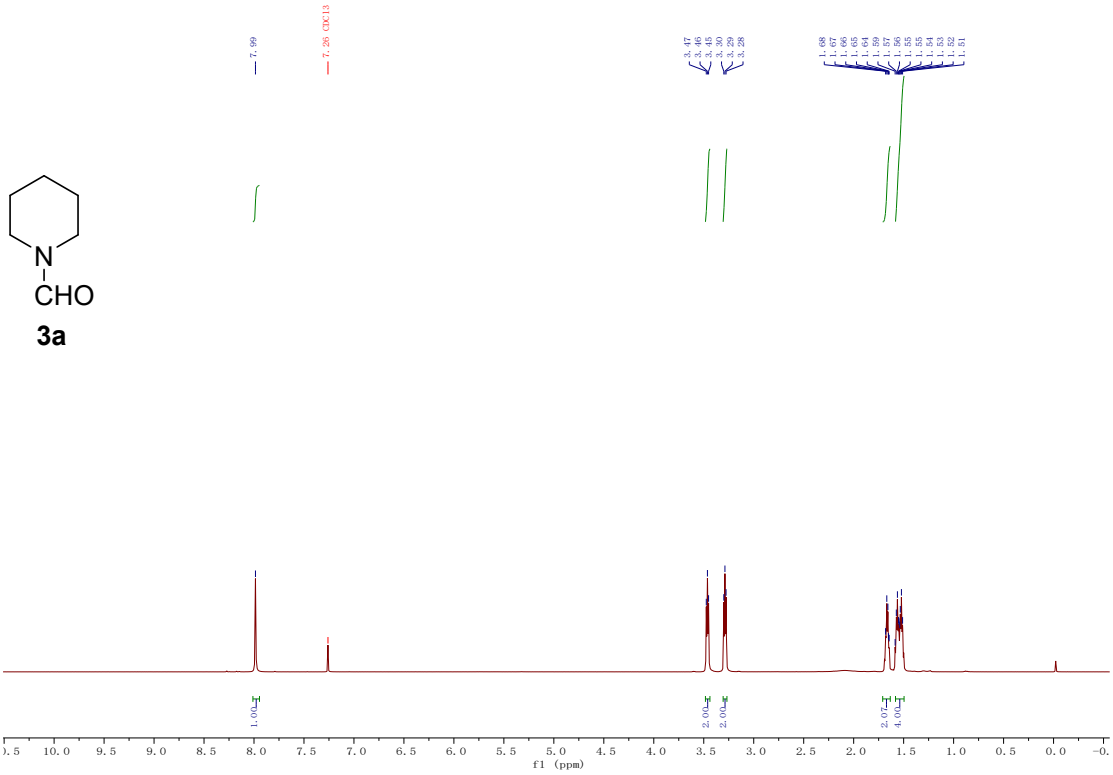


2v

^{1}H NMR spectrum of **2w** in $CDCl_3$ at 500 MHz

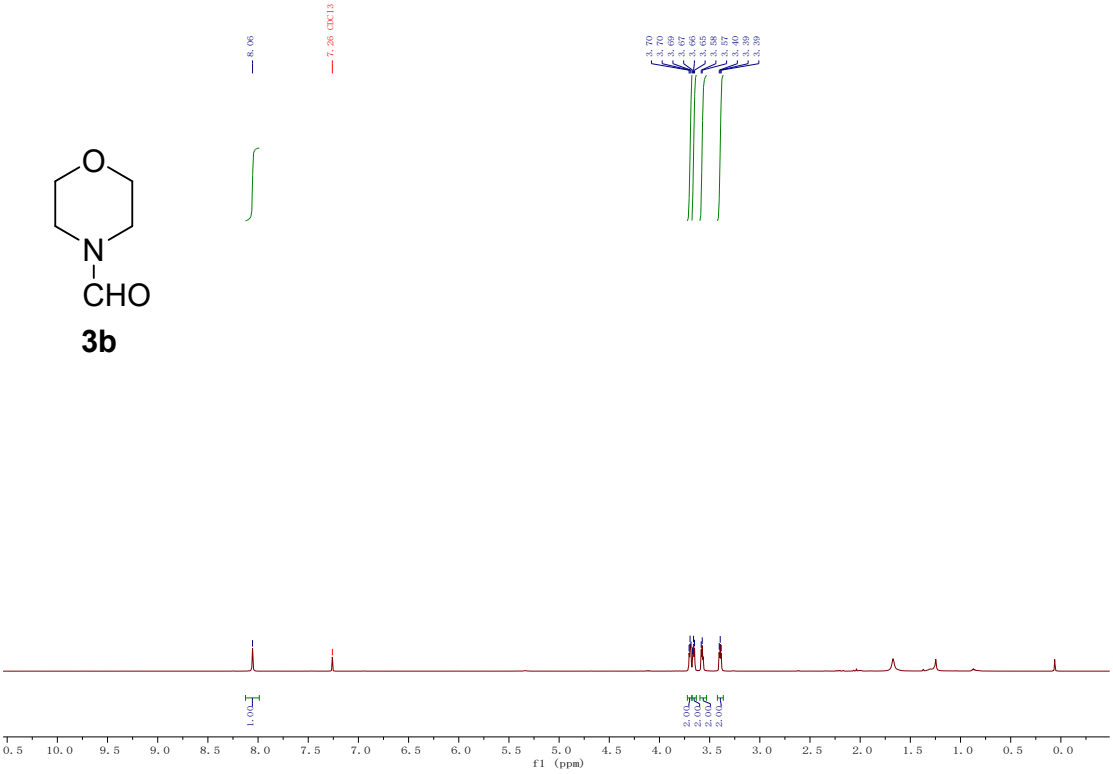


^{1}H NMR spectrum of **3a** in $CDCl_3$ at 500 MHz



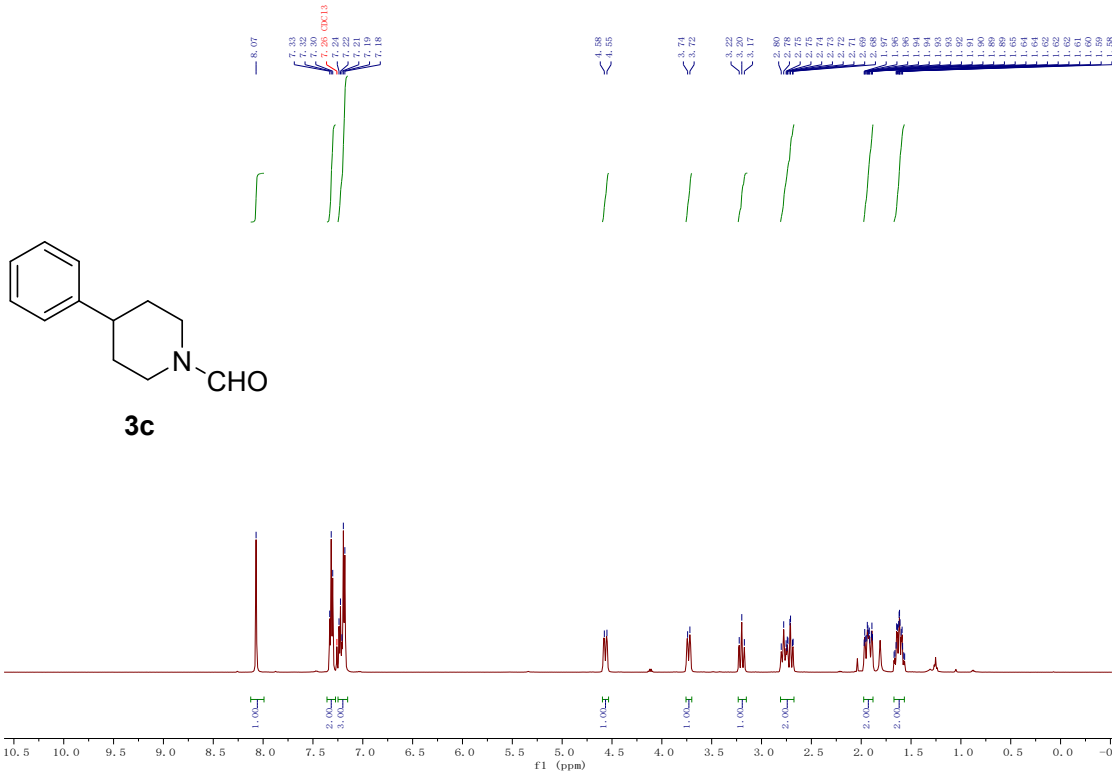
3a

^{1}H NMR spectrum of **3b** in $CDCl_3$ at 500 MHz



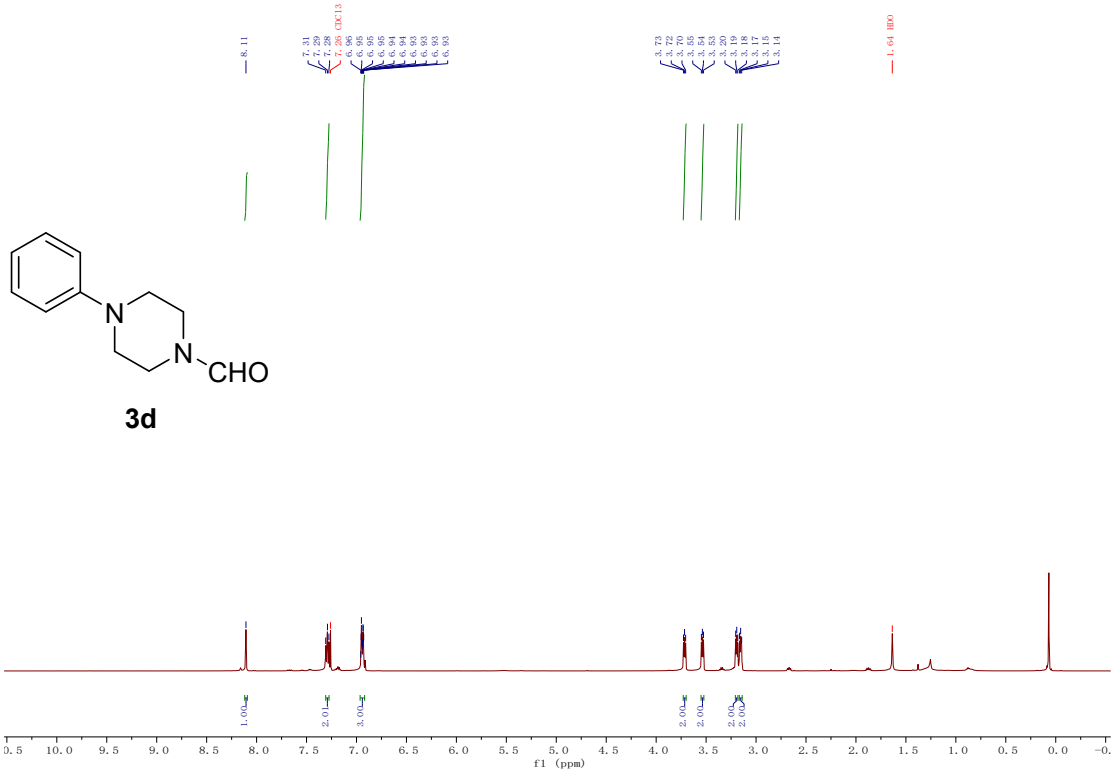
3b

^{1}H NMR spectrum of **3c** in $CDCl_3$ at 500 MHz



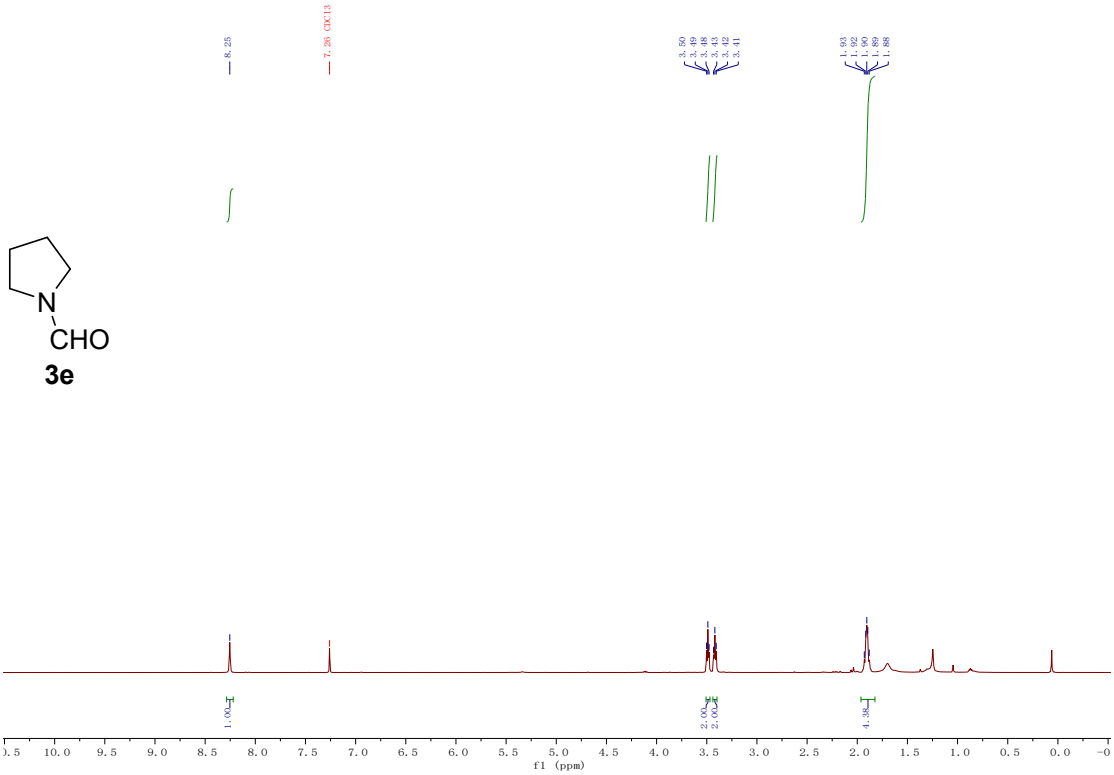
3c

^{1}H NMR spectrum of **3d** in $CDCl_3$ at 500 MHz

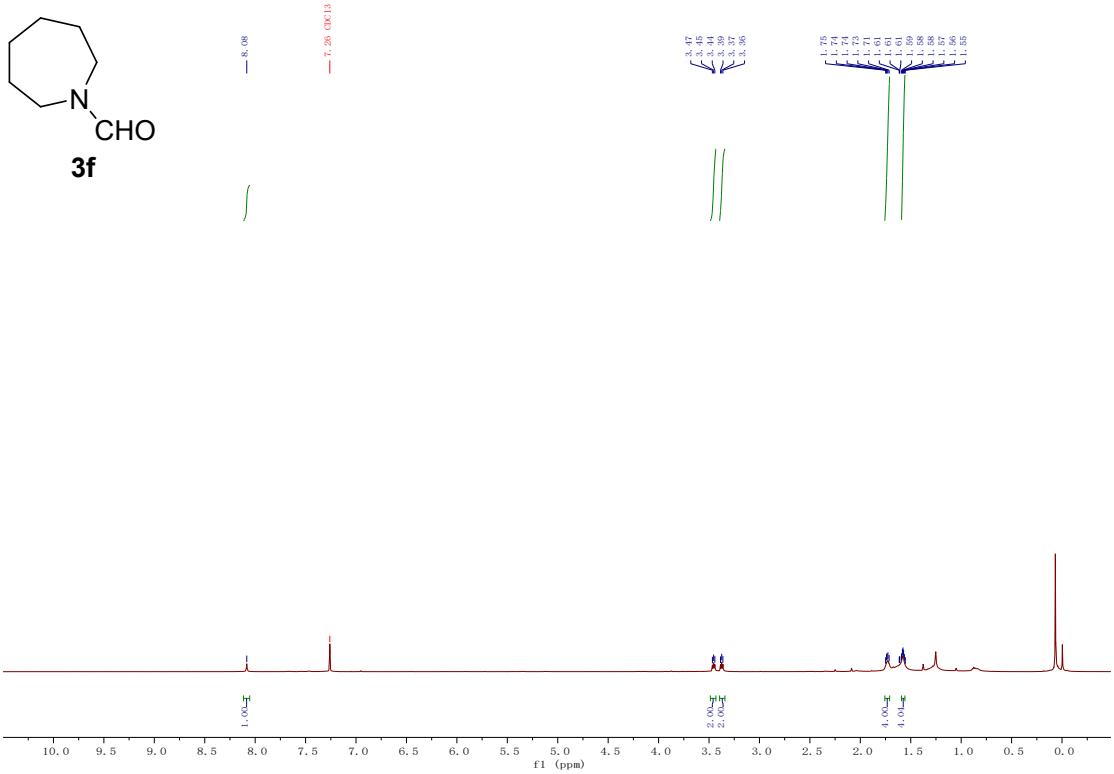


3d

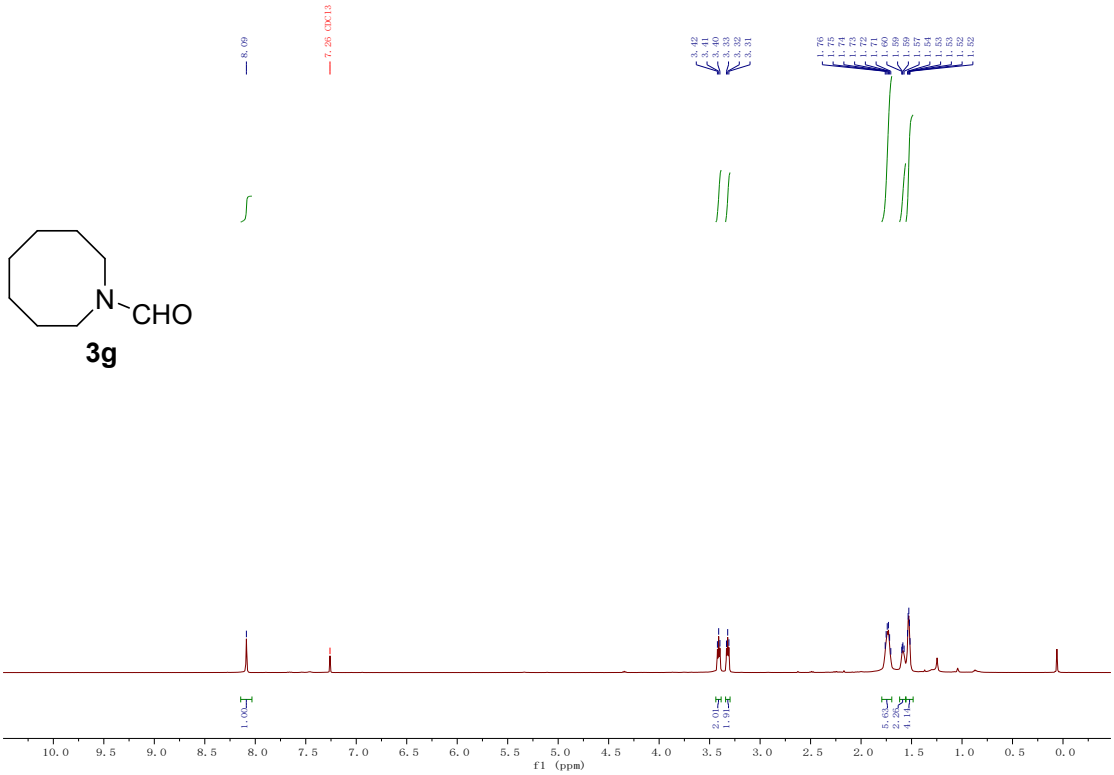
^{1}H NMR spectrum of **3e** in $CDCl_3$ at 500 MHz



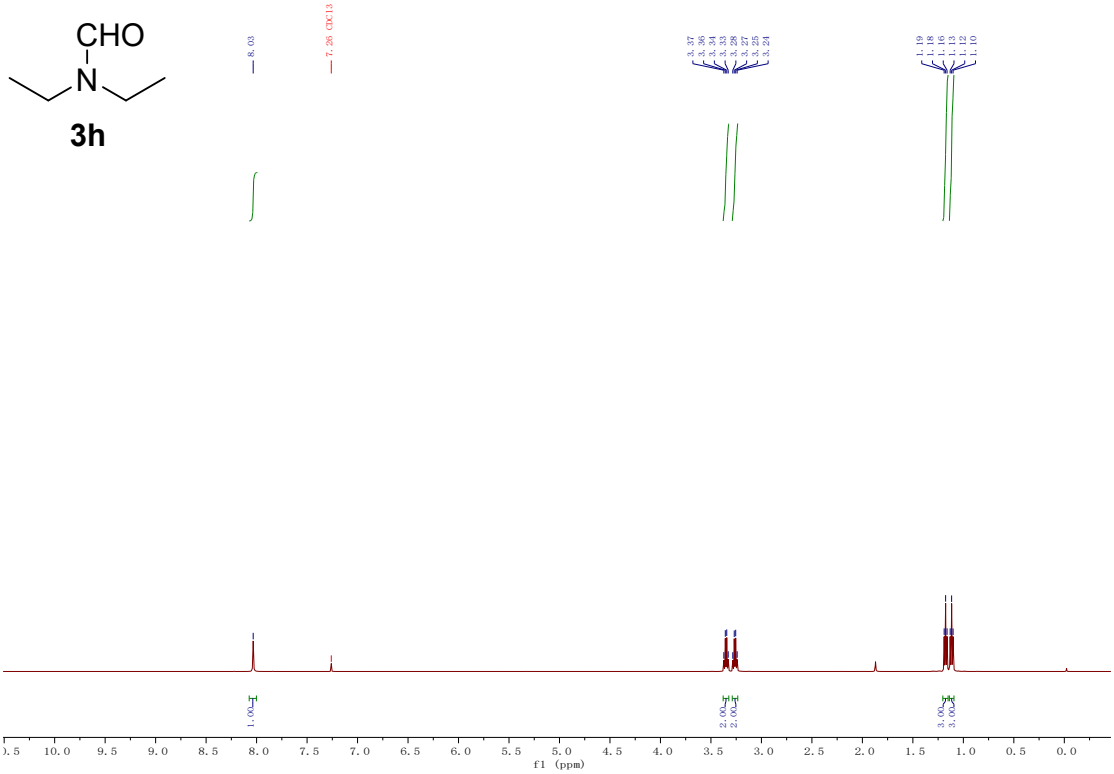
^{1}H NMR spectrum of **3f** in $CDCl_3$ at 500 MHz



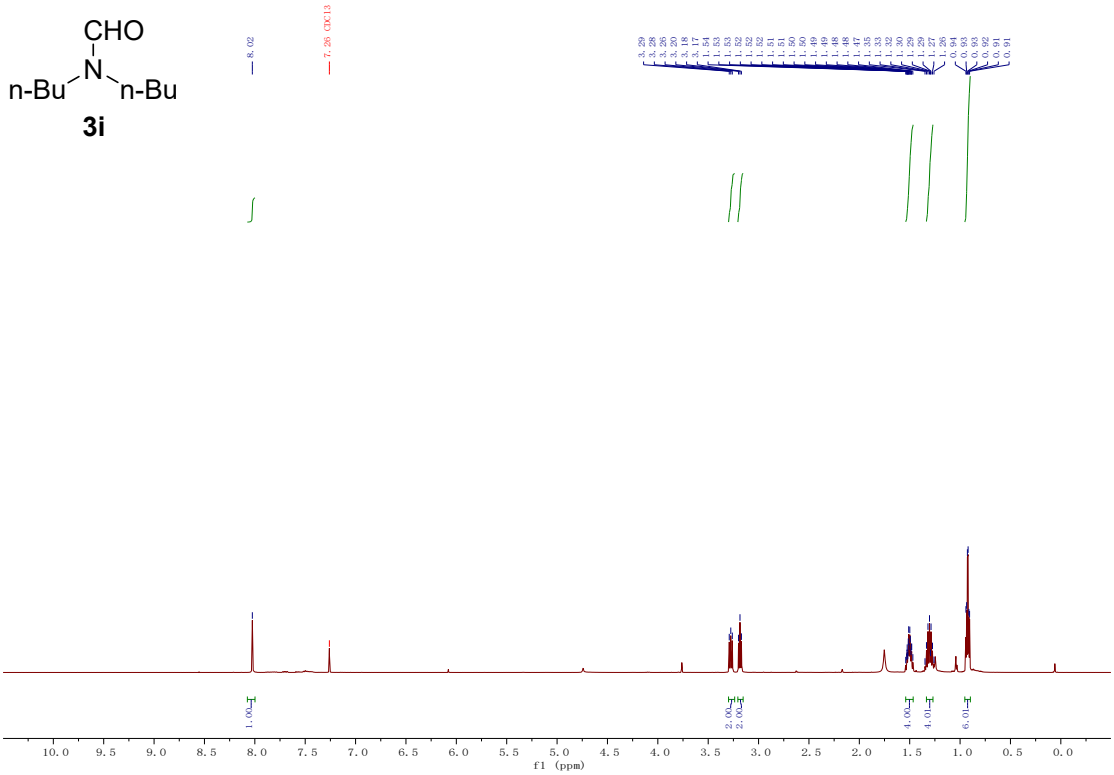
^{1}H NMR spectrum of **3g** in $CDCl_3$ at 500 MHz



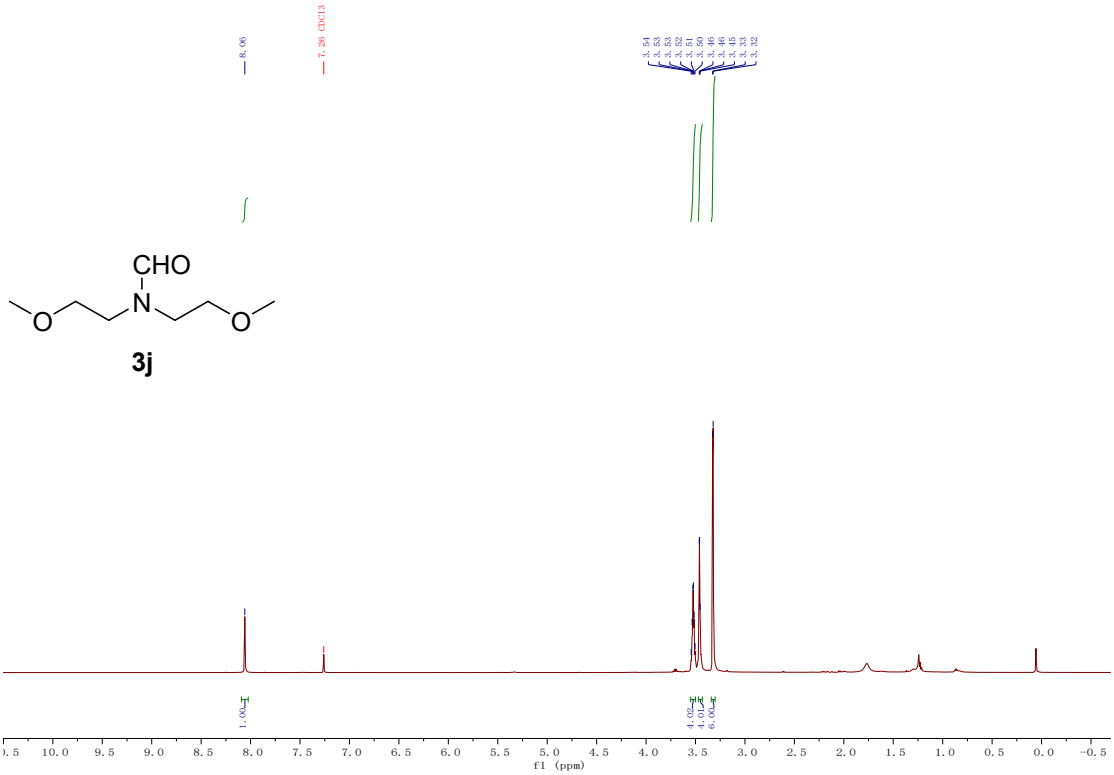
^{1}H NMR spectrum of **3h** in $CDCl_3$ at 500 MHz



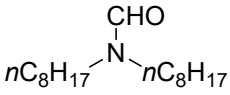
^{1}H NMR spectrum of **3i** in $CDCl_3$ at 500 MHz



^{1}H NMR spectrum of **3j** in $CDCl_3$ at 500 MHz

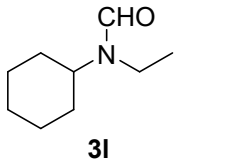


^{1}H NMR spectrum of **3k** in $CDCl_3$ at 500 MHz



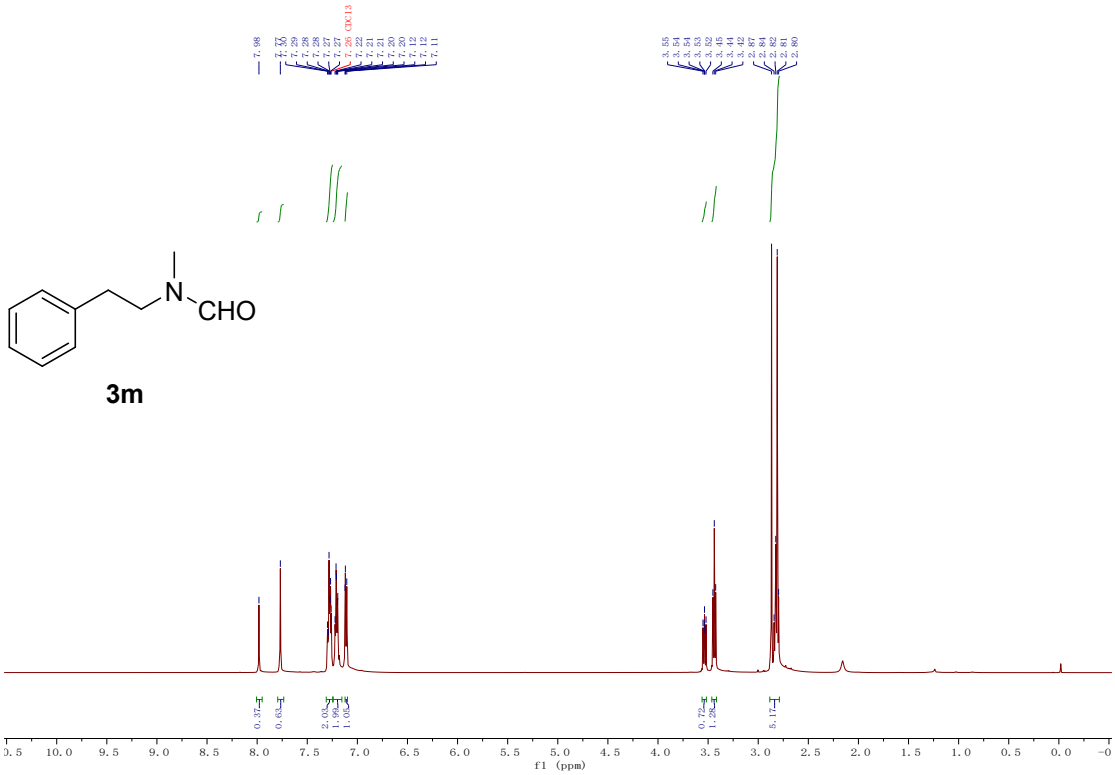
3k

^{1}H NMR spectrum of **3l** in $CDCl_3$ at 500 MHz



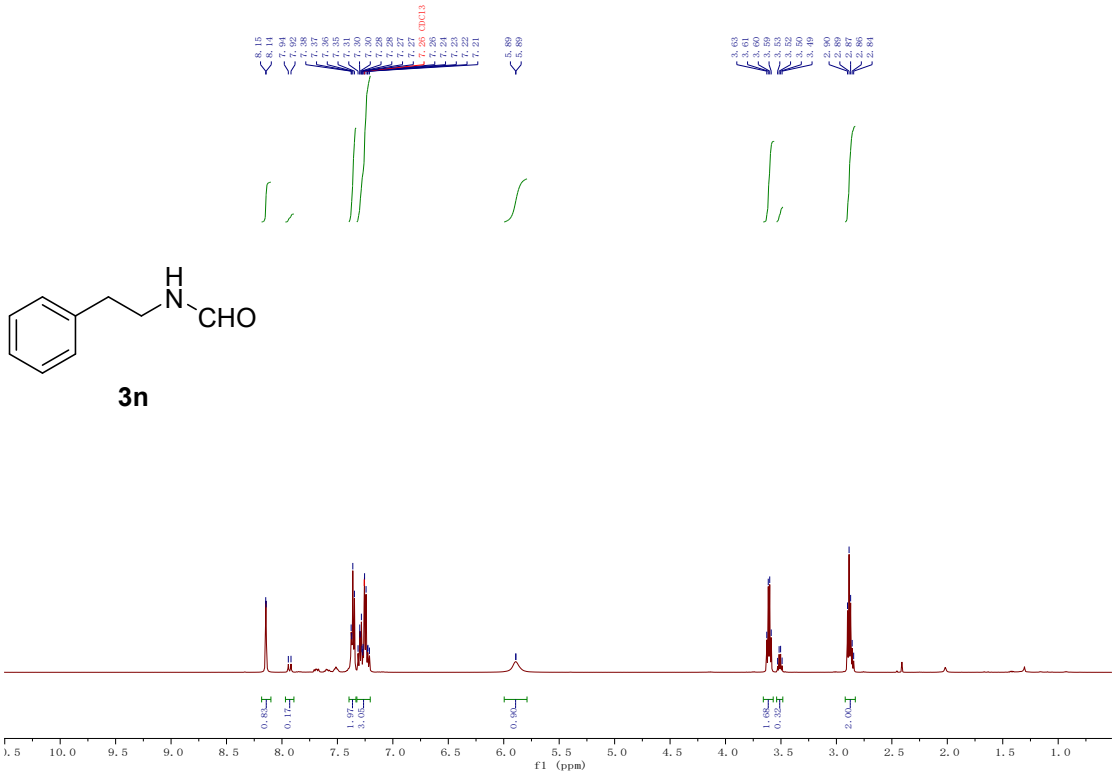
3l

^{1}H NMR spectrum of **3m** in $CDCl_3$ at 500 MHz



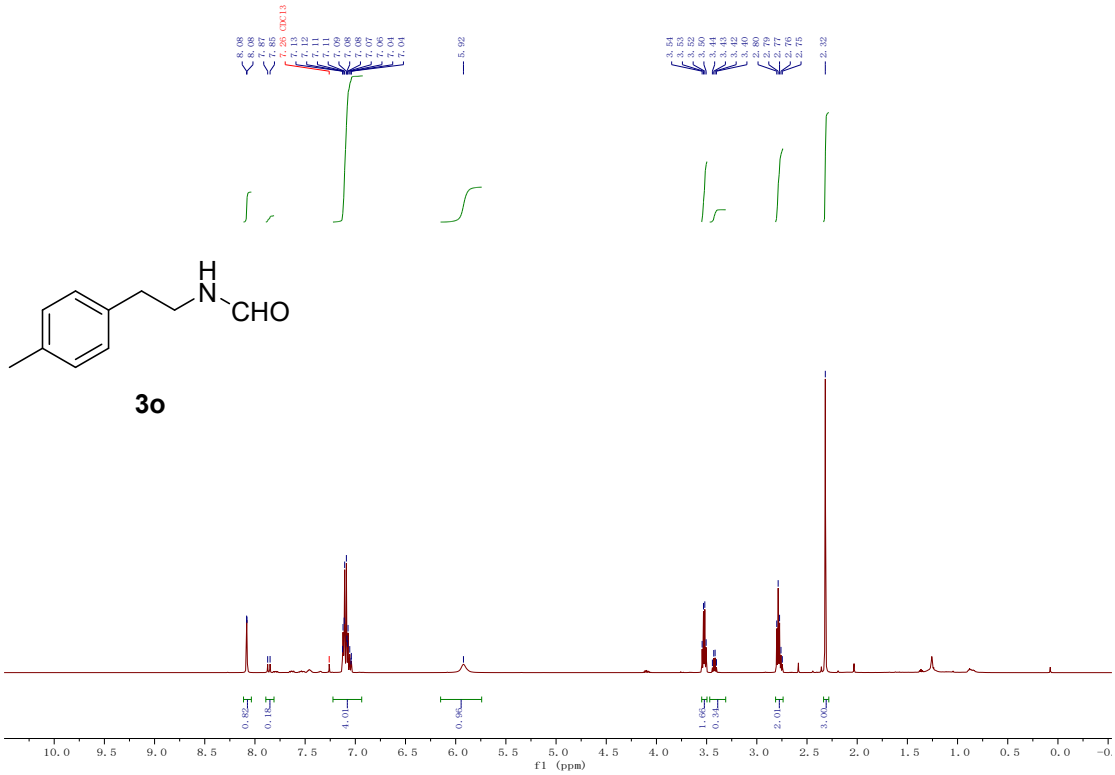
3m

^{1}H NMR spectrum of **3n** in $CDCl_3$ at 500 MHz



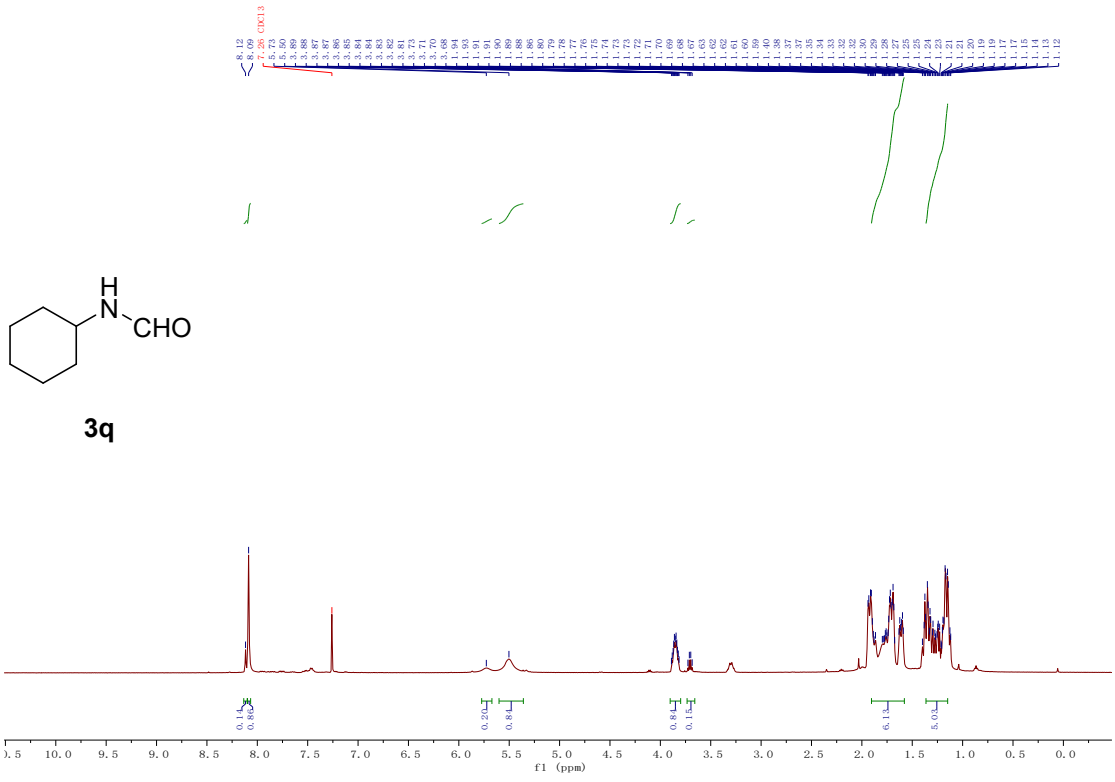
3n

^{1}H NMR spectrum of **3o** in $CDCl_3$ at 500 MHz



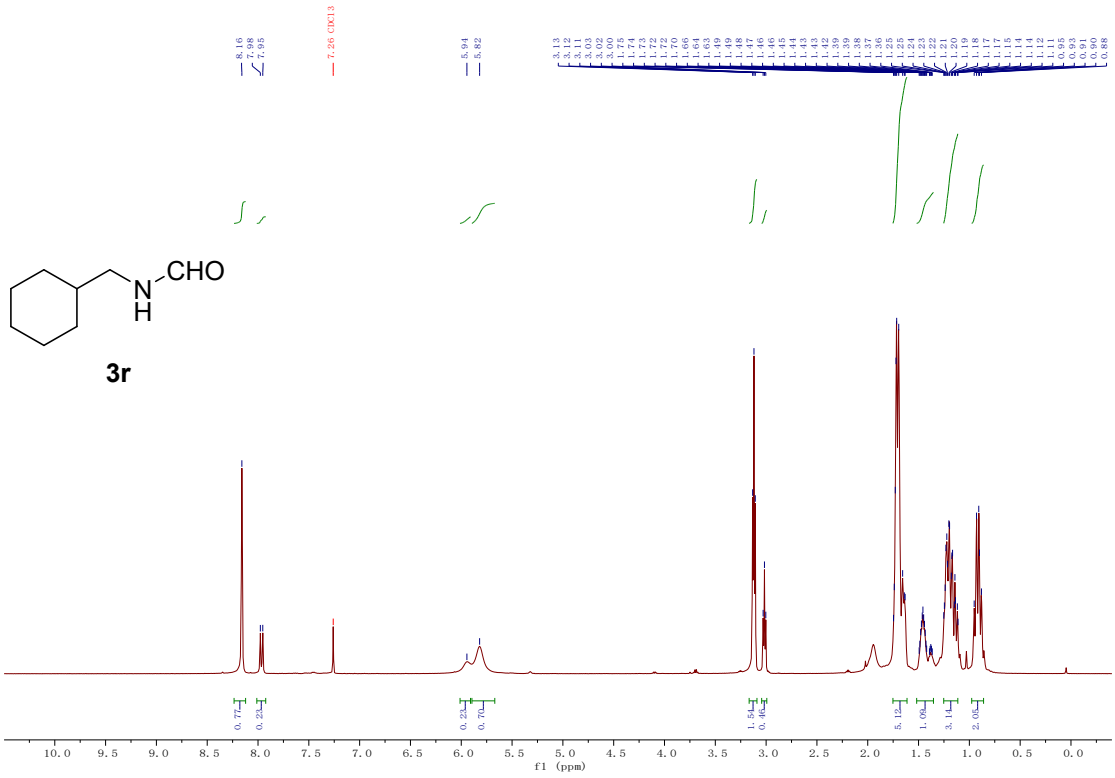
3o

^{1}H NMR spectrum of **3q** in $CDCl_3$ at 500 MHz



3q

^{1}H NMR spectrum of **3r** in $CDCl_3$ at 500 MHz



^{1}H NMR spectrum of **3t** in $CDCl_3$ at 500 MHz