Electronic Supplementary Information

Construction of Biomass-Based Amines by Ir-Mediated *N*-Alkylation: Kinetic Analysis

Meixiang Liang,[a] Zhongmou Xu,[a] Tianhao Zhou,[a] Limin Chen,[b,*] and Jinzhu Chen[a,*]

[a]*College of Chemistry and Materials Science, Jinan University, Guangzhou 511443, China.*

[b]*School of Environment and Energy, South China University of Technology. Guangzhou 510006, China.*

**Corresponding author, E-mail address: liminchen@scut.edu.cn (L. Chen), chenjz@jnu.edu.cn (J. Chen), Tel.: (+86)-20-3733-1547 (J. Chen), Fax: (+86)-20-3733-1547 (J. Chen).*

Total number of pages: 49
Total number of Tables: 21 (pages S5-S19)
Total number of Schemes: 3 (pages S20-S23)
Total number of Figures: 25 (pages S24-S48)

Table of contents

S3. References

S1. Experimental procedures

S1.1. Materials

Unless otherwise stated, all chemicals in this work were commercially available and used without further purification. 3-Aminobenzonitrile, furfuryl alcohol, sodium formate (HCOONa) were purchased from Aladdin Reagent (Shanghai, P.R. China). Dichloromethane, tetrahydrofuran (THF), acetonitrile and ethanol were purchased from Kutai Trade Co. Ltd. (Guangzhou P.R. China). Toluene and acetone were purchased from Xinhong Trading Co. Ltd. (Guangzhou P.R. China). Dichloro(pentamethyl-cyclopentadienyl)iridium(III) dime, 4-aminobenzonitrile, 2,6-pyridinedicarbonitrile, 5-methyl-2-furanmethanol, (4-methoxyphenyl)methanol, 3,4,5-trimethoxybenzalcohol, cinnamyl alcohol, 1-butanol, benzyl alcohol, (4-fluorophenyl)methanol, (4-chlorophenyl)methanol, (4-bromophenyl)methanol, pyridin-3-ylmethanol, (4-methoxyphenyl)methanamine, (3,4,5-trimethoxyphenyl)methanamine, 4-fluorobenzylamine, 4-chlorobenzylamine, 4-bromobenzylamine were purchased from Bide Pharmaceutical Technology Co. Ltd. (Shanghai, P.R. China). $ZnCl_2$, 2-furfurylamine, 5-methyl-2-furanmethanamine were purchased from Macklin Reagent (Shanghai, P.R. China). Tetrahydrofurfurylamine was purchased from Energy Chemical (Anhui, P.R. China). Paragormaldehyde was purchased from Damao Chemical Reagent Factory (Tianjin, P.R. China). High purity gases including H_2 (≥99.999%), N_2 (≥ 99.999%), dry air and liquid nitrogen were purchased from Guangzhou Shengying Gas Co. Ltd. (Guangzhou, P.R. China).

S1.2. Preparation of catalyst

Synthesis of compound 12 (Scheme S1): To a stirred solution of paraformaldehyde (0.98 g, 33 mmol) in toluene (50 mL) was added 4-aminobenzonitrile (7.72 g, 65.2 mmol) and aqueous glyoxal [40% (v/v), 4.74 g, 32.6 mmol] followed by the dropwise addition of HCl [37% (v/v), 3.72 mL, 32.6 mmol]. The mixture was refluxed until ca. 6.5 mL of water was recovered via a Dean-Stark apparatus. The solvent was removed in vacuum and the resulting oil was triturated with acetonitrile to yield a pale-brown powder (4.01 g).[1]

Synthesis of compound 13 (Scheme S1): **13** (4.01 g) was prepared with the same synthetic procedure of **12**, except that 4-aminobenzonitrile (7.72 g, 65.2 mmol) was replaced by 3-aminobenzonitrile (7.72 g, 65.2 mmol) as nitrile-source.

The substrate conversions and produce yields in the *N*-alkylation were calculated using the following equation:

$$\text{Conversion (\%)} = \frac{\text{mole of substrate consumed}}{\text{mole of initial substrate}} \times 100\%$$

$$\text{Yield (\%)} = \frac{\text{mole of product formed}}{\text{mole of initial substrate}} \times 100\%$$

S1.3. Catalyst characterization

X-ray photoelectron spectra (XPS) and Auger electron spectroscopy were made on a Thermal Fisher system employing an Al Kα radiation source. The binding energies for each spectrum were calibrated with a C 1*s* spectrum of 284.5 eV.

The morphological analysis and elemental distribution were carried out by using Transmission Electron Microscopy (TEM, Jem 2100F) with an acceleration voltage of 200 kV.

The metal content in catalyst was analyzed with an Optima 2000 DV inductively coupled plasmaoptical emission spectrometer (ICP-OES, Perkin Elmer, USA).

The BET specific surface area measurements were performed with N_2 adsorption-desorption isotherms at liquid-nitrogen temperature (77 K) using automatic volumetric adsorption equipment (Quantachrome Instruments).

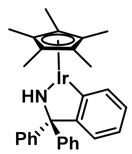
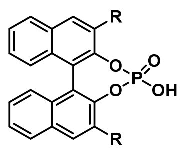
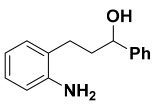
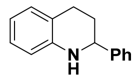
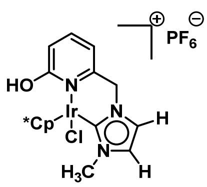
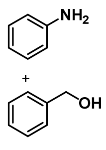
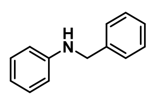
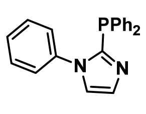
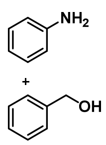
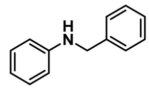
The conversion rate of the reactant and the yield of the product were measured by an external standard method with Gas Chromatography (GC). The GC analysis was performed with a Fuli 9790 (Type II) Gas Chromatography from Fuli Instruments, using an FID detector and capillary column (KB-5, 0.32 mm × 30 m) with high purity N_2 as carrier gas for analysis. The pressures of various gases were all 0.1 MPa for N_2, H_2 and air.

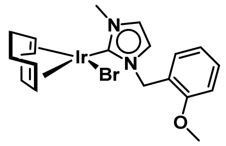
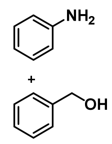
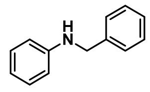
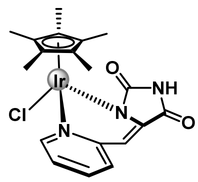
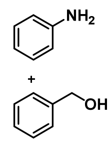
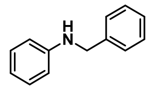
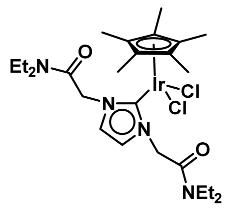
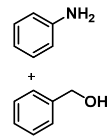
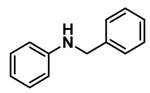
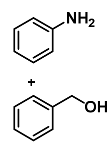
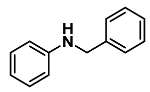
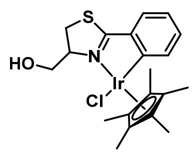
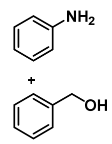
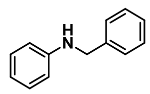
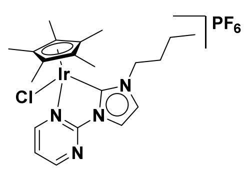
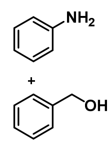
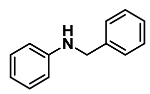
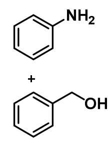
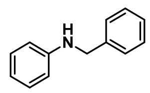
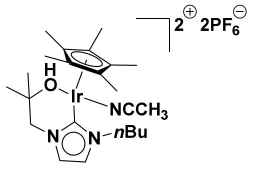
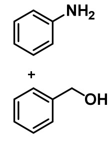
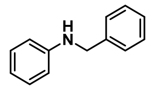
^{1}H and ^{13}C {^{1}H} NMR spectra of products were recorded on Bruker AV III 300 at 25 °C.

S2. Results and discussion

S2.1. Supplementary Tables

Table S1 Reported Ir catalysts for *N*-alkylation amines with alcohols.

Catalyst	Substrate	Reaction condition	Product Yield [%]	Ref.
 3d  4f R=2,4,6-$Cy_3C_6H_2$		3d (5 mol%), 4f (1 mol%), DMC, 4 Å molecular sieves, 80 °C, 18 h.	 92	*Angew. Chem. Int. Ed.*, 2017, **56**, 7176–7180
		amine (0.5 mmol), alcohol (0.5 mmol), catalyst (1 mol%), H_2O (1 mL), 110 °C, 48 h.	 93.5	*Green Chem.*, 2019, **21**, 219–224
[Ir(COD)Cl]$_2$ 		amine (0.5 mmol), alcohol (0.5 mmol), *t*-BuOK (3.5 mmol), diglyme (2 mL), 120 °C, 4 h.	 92	*Green Chem.*, 2017, **19**, 1109–1116

		amine (3.0 mmol), alcohol (3.0 mmol), catalyst (0.03 mmol, 1 mol%), *t*-BuOK (1.5 mmol), toluene (0.3 mL), 110 °C, 5 h.	 98	*Catal. Sci. Technol.*, 2018, **8**, 2381–2393
		amine (0.5 mmol), alcohol (1.0 mmol), K_2CO_3 (1 mmol.), catalyst (1 mol%), TFE (2.6 mL), 100 °C, 7 h.	 94	*Appl. Organomet. Chem.*, 2020, **34**, e6003
		amine (1 mmol), benzyl alcohol (1 mmol), catalyst (2 mol%), water (0.25 mL), 110 °C, 16 h.	 99	*ChemCatChem*, 2017, **9**, 3912–3917
[Ir(dpyx-*N,C,N*)Cl(μ-Cl)]$_2$ (dpyx: 1,3-di(2-pyridyl)-4,6-dimethylbenzene)		amine (0.5 mmol), benzyl alcohol (0.6 mmol), catalyst (1 mol% Ir), Cs_2CO_3 (0.1 mmol), *tert*-amyl alcohol (1 mL), reflux, under air, 12 h.	 86	*J. Org. Chem.*, 2017, **82**, 1943–1950
		amine (0.5 mmol), alcohol (0.5 mmol), catalyst (1 mol%), *t*-BuOK (0.25 mmol), toluene (50 μL), 110 °C, 16 h.	 96	*Appl. Organomet. Chem.*, 2020, **34**, e5970
		amine (1.0 mmol), alcohol (1.0 mmol), catalyst (1 mol%), $NaHCO_3$ (0.5 mmol), 4 Å molecular sieves, toluene (0.2 mL), 110 °C, 45 h.	 98	*Organometallics*, 2009, **28**, 321–325
Zr-[LIr]BF_4		amine (1.0 mmol), alcohol (40 mL), catalyst (0.20 mol% Ir), 150 °C, 2.5 h, microwave reactor.	 90	*ChemCatChem*, 2014, **6**, 1794–1800
		amine (1.0 mmol), alcohol (1.0 mmol), catalyst (1 mol% Ir), toluene (0.5 mL), 110 °C, 2 h.	 99	*Chem. Eur. J.*, 2012, **18**, 14510–14519

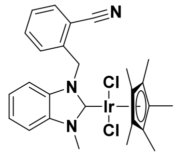
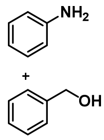
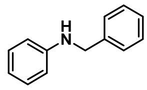
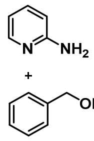
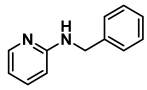
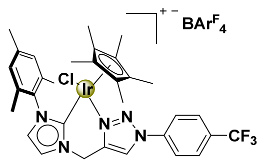
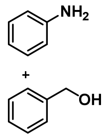
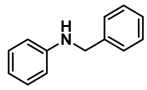
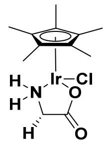
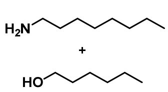
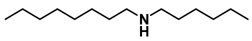
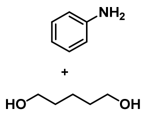
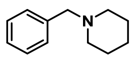
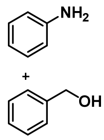
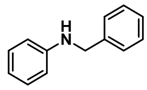
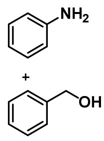
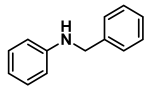
		amine (1.0 mmol), alcohol (1.5 mmol), catalyst (1.0 mol%), *t*-BuOK (1.5 mmol), 120 °C, 24 h.	 93	*ACS Omega*, 2023, **8**, 5332–5348
$[Ir(cod)Cl]_2$ $Py_2NP\textit{i}Pr_2$		amine (1.0 mmol), alcohol (1.1 mmol), $[IrCl(cod)]_2$ (0.05 mol%), $Py_2NP\textit{i}Pr_2$ (0.1 mol%), *t*-BuOK (1.1 mmol), diglyme (0.2 mL), 70 °C, 24 h.	 93	*Chem. Eur. J.*, 2009, **15**, 3790–3799
		amine (1.0 mmol), alcohol (1.1 mmol), catalyst (0.5 mol%), *t*-BuOK (1.1 mmol), toluene-d_8, 100 °C, 6 h.	 93	*Green Chem.*, 2017, **19**, 3142–3151
		amine (1.0 mmol), alcohol (1.0 mmol), catalyst (2 mol%), toluene (0.3 mL), 95°C, 24 h.	 94	*Org. Lett.*, 2013, **15**, 266–269
$[Cp^*IrCl_2]_2$		amine (3.0 mmol), diol (2.0 mmol), $[Cp^*IrCl_2]_2$ (0.01 mmol, 1.0 % Ir), $NaHCO_3$ (0.02 mmol), toluene (1 mL), 90 °C, 17 h.	 99	*Org. Lett.*, 2004, **6**, 3525–3528
$[Cp^*IrCl_2]_2$		aniline (1.0 mmol), benzyl alcohol (1.0 mmol), catalyst (5.0 mol% Ir), K_2CO_3 (0.050 mmol), toluene (0.5 mL), 110 °C, 17 h.	 99	*Tetrahedron Lett.*, 2003, **44**, 2687–2690
$[Cp^*IrCl_2]_2$		amine (1.0 mmol), alcohol (1.0 mmol), $[Cp^*IrCl_2]_2$ (0.005 mmol, 1.0 mol% Ir), $NaHCO_3$ (0.01 mmol), toluene (0.1 mL), 110 °C, 17 h.	 94	*Tetrahedron*, 2008, **64**, 1943–1954

Table S2 The calculated data from Fig. 6d for linear fitting of k_1' (at 130 °C) in Fig. 7a.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{2a}]_{t_1}\times10^3$ [M]	$[\mathbf{2a}]_{t_2}\times10^3$ [M]	$[\ln([\mathbf{2a}]_{t_1}/[\mathbf{2a}]_{t_2})]$ /	t_2-t_1 [h]
20.00→20.60	13.99214	13.4774	0.03748	0.70
20.00→21.20	13.99214	12.98963	0.07434	1.40
20.00→21.80	13.99214	12.52742	0.11058	2.10
20.00→22.40	13.99214	12.08942	0.14617	2.80
20.00→23.00	13.99214	11.67436	0.1811	3.50
20.00→23.60	13.99214	11.28105	0.21537	4.20
20.00→24.20	13.99214	10.90835	0.24897	4.90
20.00→24.80	13.99214	10.55517	0.28188	5.60
20.00→25.40	13.99214	10.22049	0.3141	6.30
20.00→26.00	13.99214	9.90335	0.34562	7.00
20.00→26.60	13.99214	9.60282	0.37644	7.70
20.00→27.20	13.99214	9.31803	0.40654	8.40
20.00→27.80	13.99214	9.04817	0.43593	9.10
20.00→28.40	13.99214	8.79244	0.4646	9.80
20.00→29.00	13.99214	8.55011	0.49255	10.50
20.00→29.60	13.99214	8.32048	0.51978	11.20
20.00→30.20	13.99214	8.10287	0.54628	11.90
20.00→30.80	13.99214	7.89667	0.57205	12.60
20.00→31.40	13.99214	7.70127	0.59711	13.30
20.00→32.00	13.99214	7.51611	0.62145	14.00

Table S3 The calculated data from Fig. 6c for linear fitting of k_1' (at 140 °C) in Fig. 7a.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{2a}]_{t_1}\times10^3$ [M]	$[\mathbf{2a}]_{t_2}\times10^3$ [M]	$[\ln([\mathbf{2a}]_{t_1}/[\mathbf{2a}]_{t_2})]$ /	t_2-t_1 [h]
7.0→7.25	26.92684	26.47033	0.0171	0.25
7.0→7.50	26.92684	26.02095	0.03422	0.50
7.0→7.75	26.92684	25.5786	0.05137	0.75
7.0→8.00	26.92684	25.14317	0.06854	1.00
7.0→8.25	26.92684	24.71455	0.08573	1.25
7.0→8.50	26.92684	24.29264	0.10295	1.50
7.0→8.75	26.92684	23.87732	0.12019	1.75
7.0→9.00	26.92684	23.4685	0.13746	2.00
7.0→9.25	26.92684	23.06607	0.15476	2.25
7.0→9.50	26.92684	22.66993	0.17208	2.50
7.0→9.75	26.92684	22.27999	0.18943	2.75
7.0→10.00	26.92684	21.89615	0.20681	3.00
7.0→10.25	26.92684	21.51832	0.22422	3.25
7.0→10.50	26.92684	21.14639	0.24165	3.50
7.0→10.75	26.92684	20.78028	0.25912	3.75
7.0→11.00	26.92684	20.41989	0.27661	4.00
7.0→11.25	26.92684	20.06514	0.29414	4.25
7.0→11.50	26.92684	19.71594	0.3117	4.50
7.0→11.75	26.92684	19.3722	0.32928	4.75
7.0→12.00	26.92684	19.03383	0.34691	5.00

Table S4 The calculated data from Fig. 6b for linear fitting of k_1' (at 150 °C) in Fig. 7a.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{2a}]_{t_1}\times10^3$ [M]	$[\mathbf{2a}]_{t_2}\times10^3$ [M]	$[\ln([\mathbf{2a}]_{t_1}/[\mathbf{2a}]_{t_2})]$ /	t_2-t_1 [h]
8.00→8.40	23.56355	22.83776	0.03129	0.40
8.00→8.80	23.56355	22.12011	0.06321	0.80
8.00→9.20	23.56355	21.41052	0.09582	1.20
8.00→9.60	23.56355	20.70889	0.12914	1.60
8.00→10.00	23.56355	20.01513	0.16321	2.00
8.00→10.40	23.56355	19.32916	0.19809	2.40
8.00→10.80	23.56355	18.65088	0.23381	2.80
8.00→11.20	23.56355	17.98022	0.27043	3.20
8.00→11.60	23.56355	17.31708	0.30801	3.60
8.00→12.00	23.56355	16.66138	0.34661	4.00
8.00→12.40	23.56355	16.01304	0.3863	4.40
8.00→12.80	23.56355	15.37198	0.42715	4.80
8.00→13.20	23.56355	14.73811	0.46926	5.20
8.00→13.60	23.56355	14.11135	0.51272	5.60
8.00→14.00	23.56355	13.49162	0.55763	6.00
8.00→14.40	23.56355	12.87885	0.60411	6.40
8.00→14.80	23.56355	12.27295	0.6523	6.80
8.00→15.20	23.56355	11.67386	0.70235	7.20
8.00→15.60	23.56355	11.08148	0.75443	7.60
8.00→16.00	23.56355	10.49576	0.80873	8.00

Table S5 The calculated data from Fig. 6a for linear fitting of k_1' (at 160 °C) in Fig. 7a.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{2a}]_{t_1}\times10^3$ [M]	$[\mathbf{2a}]_{t_2}\times10^3$ [M]	$[\ln([\mathbf{2a}]_{t_1}/[\mathbf{2a}]_{t_2})]$ /	t_2-t_1 [h]
11.00→11.25	14.46597	13.97607	0.03445	0.25
11.00→11.50	14.46597	13.50081	0.06905	0.50
11.00→11.75	14.46597	13.03976	0.1038	0.75
11.00→12.00	14.46597	12.59248	0.1387	1.00
11.00→12.25	14.46597	12.15857	0.17376	1.25
11.00→12.50	14.46597	11.73762	0.209	1.50
11.00→12.75	14.46597	11.32925	0.24441	1.75
11.00→13.00	14.46597	10.93309	0.28	2.00
11.00→13.25	14.46597	10.54876	0.31579	2.25
11.00→13.50	14.46597	10.17592	0.35177	2.50
11.00→13.75	14.46597	9.81422	0.38797	2.75
11.00→14.00	14.46597	9.46332	0.42438	3.00
11.00→14.25	14.46597	9.12291	0.46101	3.25
11.00→14.50	14.46597	8.79268	0.49788	3.50
11.00→14.75	14.46597	8.47231	0.535	3.75
11.00→15.00	14.46597	8.16151	0.57237	4.00
11.00→15.25	14.46597	7.86	0.61001	4.25
11.00→15.5	14.46597	7.5675	0.64794	4.50
11.00→15.75	14.46597	7.28374	0.68615	4.75
11.00→16.00	14.46597	7.00847	0.72468	5.00

Table S6 The calculated data from Fig. 6d for linear fitting of k_3' (at 130 °C) in Fig. 7b.

$t_1 \rightarrow t_2$ [h]	$t_1 \rightarrow t_3$ [h]	$[\mathbf{5a}]_{t_1}\times10^3$ [M]	$[\mathbf{5a}]_{t_2}\times10^3$ [M]	$[\mathbf{5a}]_{t_3}\times10^3$ [M]	$([\mathbf{5a}]_{t_2}-[\mathbf{5a}]_{t_1})\times10^3$ [M]	$([\mathbf{5a}]_{t_3}-[\mathbf{5a}]_{t_1})\times10^3$ [M]	$\mathbf{5a}_{t_1\rightarrow t_2}\times10^3$ [M h]	$\mathbf{5a}_{t_1\rightarrow t_3}\times10^3$ [M h]	$\mathbf{4a}_{t_1\rightarrow t_2}\times10^3$ [M h]	$\mathbf{4a}_{t_1\rightarrow t_3}\times10^3$ [M h]	**H** [M^2 h]	**I** [M^2 h^2]
10.00→10.30	10.00→10.60	13.69727	14.28874	14.86754	0.59146	1.17027	4.1979	8.57134	3.97378	7.88415	0.15698	0.96371
10.00→10.60	10.00→10.90	13.69727	14.86754	15.43395	1.17027	1.73668	8.57134	13.11657	7.88415	11.73117	0.46421	2.86116
10.00→10.90	10.00→11.20	13.69727	15.43395	15.98824	1.73668	2.29097	13.11657	17.8299	11.73117	15.51486	0.91519	5.66381
10.00→11.20	10.00→11.50	13.69727	15.98824	16.53066	2.29097	2.83339	17.8299	22.70773	15.51486	19.23526	1.50362	9.34447
10.00→11.50	10.00→11.80	13.69727	16.53066	17.06148	2.83339	3.3642	22.70773	27.74655	19.23526	22.89242	2.22342	13.87725
10.00→11.80	10.00→12.10	13.69727	17.06148	17.58092	3.3642	3.88365	27.74655	32.94291	22.89242	26.48637	3.06869	19.2375
10.00→12.10	10.00→12.40	13.69727	17.58092	18.08925	3.88365	4.39198	32.94291	38.29344	26.48637	30.01716	4.03373	25.40181
10.00→12.40	10.00→12.70	13.69727	18.08925	18.5867	4.39198	4.88943	38.29344	43.79483	30.01716	33.48481	5.11302	32.3479
10.00→12.70	10.00→13.00	13.69727	18.5867	19.0735	4.88943	5.37623	43.79483	49.44386	33.48481	36.88936	6.30123	40.05464
10.00→13.00	10.00→13.30	13.69727	19.0735	19.54988	5.37623	5.8526	49.44386	55.23737	36.88936	40.23087	7.5932	48.50195
10.00→13.30	10.00→13.60	13.69727	19.54988	20.01606	5.8526	6.31879	55.23737	61.17226	40.23087	43.50936	8.98395	57.6708
10.00→13.60	10.00→13.90	13.69727	20.01606	20.47226	6.31879	6.77499	61.17226	67.24551	43.50936	46.72486	10.46865	67.54315
10.00→13.90	10.00→14.20	13.69727	20.47226	20.9187	6.77499	7.22142	67.24551	73.45415	46.72486	49.87743	12.04265	78.10191
10.00→14.20	10.00→14.50	13.69727	20.9187	21.35558	7.22142	7.6583	73.45415	79.7953	49.87743	52.9671	13.70144	89.33091
10.00→14.50	10.00→14.80	13.69727	21.35558	21.78311	7.6583	8.08583	79.7953	86.2661	52.9671	55.99391	15.44067	101.21487
10.00→14.80	10.00→15.10	13.69727	21.78311	22.20148	8.08583	8.50421	86.2661	92.86379	55.99391	58.95789	17.25613	113.73936
10.00→15.10	10.00→15.40	13.69727	22.20148	22.6109	8.50421	8.91363	92.86379	99.58564	58.95789	61.85908	19.14377	126.89075
10.00→15.40	10.00→15.70	13.69727	22.6109	23.01156	8.91363	9.31428	99.58564	106.42901	61.85908	64.69752	21.09966	140.6562
10.00→15.70	10.00→16.00	13.69727	23.01156	23.40364	9.31428	9.70636	106.42901	113.39129	64.69752	67.47326	23.12002	155.02363
10.00→16.00	/			/		/		/		/	/	/

Table S7 The calculated data from Fig. 6c for linear fitting of k_3' (at 140 °C) in Fig. 7b.

$t_1 \rightarrow t_2$ [h]	$t_1 \rightarrow t_3$ [h]	$[\mathbf{5a}]_{t_1}\times10^3$ [M]	$[\mathbf{5a}]_{t_2}\times10^3$ [M]	$[\mathbf{5a}]_{t_3}\times10^3$ [M]	$([\mathbf{5a}]_{t_2}-[\mathbf{5a}]_{t_1})\times10^3$ [M]	$([\mathbf{5a}]_{t_3}-[\mathbf{5a}]_{t_1})\times10^3$ [M]	$\mathbf{5a}_{t_1\rightarrow t_2}\times10^3$ [M h]	$\mathbf{5a}_{t_1\rightarrow t_3}\times10^3$ [M h]	$\mathbf{4a}_{t_1\rightarrow t_2}\times10^3$ [M h]	$\mathbf{4a}_{t_1\rightarrow t_3}\times10^3$ [M h]	**H** [M^2 h]	**I** [M^2 h^2]
10.0→10.5	10.0→11.0	17.49043	18.53493	19.55427	1.0445	2.06384	9.00634	18.52864	5.17661	10.23052	0.76558	3.77591
10.0→11.0	10.0→11.5	17.49043	19.55427	20.54904	2.06384	3.05862	18.52864	28.55446	10.23052	15.16768	2.25985	11.09075
10.0→11.5	10.0→12.0	17.49043	20.54904	21.51985	3.05862	4.02943	28.55446	39.07169	15.16768	19.9937	4.44726	21.71722
10.0→12.0	10.0→12.5	17.49043	21.51985	22.46727	4.02943	4.97684	39.07169	50.06847	19.9937	24.71397	7.29352	35.43752
10.0→12.5	10.0→13.0	17.49043	22.46727	23.39186	4.97684	5.90143	50.06847	61.53325	24.71397	29.33359	10.76562	52.04318
10.0→13.0	10.0→13.5	17.49043	23.39186	24.29417	5.90143	6.80374	61.53325	73.45475	29.33359	33.85741	14.83176	71.33491
10.0→13.5	10.0→14.0	17.49043	24.29417	25.17474	6.80374	7.68432	73.45475	85.82198	33.85741	38.29007	19.46129	93.12238
10.0→14.0	10.0→14.5	17.49043	25.17474	26.0341	7.68432	8.54367	85.82198	98.62419	38.29007	42.63597	24.62469	117.22399
10.0→14.5	10.0→15.0	17.49043	26.0341	26.87274	8.54367	9.38232	98.62419	111.8509	42.63597	46.89929	30.29357	143.46665
10.0→15.0	10.0→15.5	17.49043	26.87274	27.69119	9.38232	10.20076	111.8509	125.49188	46.89929	51.08403	36.44055	171.68555
10.0→15.5	10.0→16.0	17.49043	27.69119	28.48991	10.20076	10.99948	125.49188	139.53716	51.08403	55.19398	43.03931	201.7239
10.0→16.0	10.0→16.5	17.49043	28.48991	29.26939	10.99948	11.77896	139.53716	153.97698	55.19398	59.23276	50.06451	233.43268
10.0→16.5	10.0→17.0	17.49043	29.26939	30.03008	11.77896	12.53966	153.97698	168.80185	59.23276	63.20379	57.49178	266.67039
10.0→17.0	10.0→17.5	17.49043	30.03008	30.77245	12.53966	13.28203	168.80185	184.00248	63.20379	67.11035	65.29764	301.30279
10.0→17.5	10.0→18.0	17.49043	30.77245	31.49693	13.28203	14.00651	184.00248	199.56983	67.11035	70.95555	73.45956	337.20264
10.0→18.0	10.0→18.5	17.49043	31.49693	32.20396	14.00651	14.71353	199.56983	215.49505	70.95555	74.74237	81.95584	374.24945
10.0→18.5	10.0→19.0	17.49043	32.20396	32.89395	14.71353	15.40352	215.49505	231.76953	74.74237	78.47361	90.76563	412.32923
10.0→19.0	10.0→19.5	17.49043	32.89395	33.56731	15.40352	16.07689	231.76953	248.38484	78.47361	82.15196	99.86889	451.3342
10.0→19.5	10.0→20.0	17.49043	33.56731	34.22445	16.07689	16.73403	248.38484	265.33278	82.15196	85.77997	109.24637	491.1626
10.0→20.0	/			/		/		/		/	/	/

Table S8 The calculated data from Fig. 6b for linear fitting of k_3' (at 150 °C) in Fig. 7b.

$t_1 \to t_2$ [h]	$t_1 \to t_3$ [h]	$[\mathbf{5a}]_{t_1}\times10^3$ [M]	$[\mathbf{5a}]_{t_2}\times10^3$ [M]	$[\mathbf{5a}]_{t_3}\times10^3$ [M]	$([\mathbf{5a}]_{t_2}-[\mathbf{5a}]_{t_1})\times10^3$ [M]	$([\mathbf{5a}]_{t_3}-[\mathbf{5a}]_{t_1})\times10^3$ [M]	$\mathbf{5a}_{t_1\to t_2}\times10^3$ [M h]	$\mathbf{5a}_{t_1\to t_3}\times10^3$ [M h]	$\mathbf{4a}_{t_1\to t_2}\times10^3$ [M h]	$\mathbf{4a}_{t_1\to t_3}\times10^3$ [M h]	**H** [M^2 h]	**I** [M^2 h^2]
12.00→12.25	12.00→12.50	24.9993	25.53462	26.06048	0.53532	1.06118	6.31674	12.76613	2.10797	4.18418	0.13079	0.48031
12.00→12.50	12.00→12.75	24.9993	26.06048	26.57704	1.06118	1.57774	12.76613	19.34582	4.18418	6.22998	0.38774	1.41363
12.00→12.75	12.00→13.00	24.9993	26.57704	27.08447	1.57774	2.08517	19.34582	26.05351	6.22998	8.24669	0.76635	2.77385
12.00→13.00	12.00→13.25	24.9993	27.08447	27.58293	2.08517	2.58363	26.05351	32.88693	8.24669	10.23556	1.26225	4.53598
12.00→13.25	12.00→13.50	24.9993	27.58293	28.07258	2.58363	3.07328	32.88693	39.84387	10.23556	12.1978	1.87116	6.67618
12.00→13.50	12.00→13.75	24.9993	28.07258	28.55357	3.07328	3.55427	39.84387	46.92214	12.1978	14.13455	2.58893	9.17165
12.00→13.75	12.00→14.00	24.9993	28.55357	29.02606	3.55427	4.02676	46.92214	54.11959	14.13455	16.04691	3.41153	12.00061
12.00→14.00	12.00→14.25	24.9993	29.02606	29.49019	4.02676	4.49089	54.11959	61.43413	16.04691	17.93594	4.33502	15.14231
12.00→14.25	12.00→14.50	24.9993	29.49019	29.94613	4.49089	4.94683	61.43413	68.86367	17.93594	19.80264	5.35559	18.57692
12.00→14.50	12.00→14.75	24.9993	29.94613	30.394	4.94683	5.3947	68.86367	76.40618	19.80264	21.64797	6.4695	22.28554
12.00→14.75	12.00→15.00	24.9993	30.394	30.83395	5.3947	5.83465	76.40618	84.05967	21.64797	23.47285	7.67314	26.25016
12.00→15.00	12.00→15.25	24.9993	30.83395	31.26612	5.83465	6.26682	84.05967	91.82218	23.47285	25.27817	8.96299	30.45362
12.00→15.25	12.00→15.50	24.9993	31.26612	31.69066	6.26682	6.69136	91.82218	99.69178	25.27817	27.06477	10.33563	34.87956
12.00→15.50	12.00→15.75	24.9993	31.69066	32.10769	6.69136	7.10839	99.69178	107.66658	27.06477	28.83346	11.78773	39.51244
12.00→15.75	12.00→16.00	24.9993	32.10769	32.51735	7.10839	7.51805	107.66658	115.74471	28.83346	30.585	13.31603	44.33744
12.00→16.00	12.00→16.25	24.9993	32.51735	32.91976	7.51805	7.92046	115.74471	123.92434	30.585	32.32015	14.91741	49.34047
12.00→16.25	12.00→16.50	24.9993	32.91976	33.31507	7.92046	8.31576	123.92434	132.2037	32.32015	34.0396	16.5888	54.50814
12.00→16.50	12.00→16.75	24.9993	33.31507	33.70338	8.31576	8.70408	132.2037	140.581	34.0396	35.74403	18.32722	59.82773
12.00→16.75	12.00→17.00	24.9993	33.70338	34.08483	8.70408	9.08553	140.581	149.05453	35.74403	37.4341	20.12977	65.28714
12.00→17.00	/			/		/		/		/	/	/

Table S9 The calculated data from Fig. 6a for linear fitting of k_3' (at 160 °C) in Fig. 7b.

$t_1 \rightarrow t_2$ [h]	$t_1 \rightarrow t_3$ [h]	$[\mathbf{5a}]_{t_1}\times10^3$ [M]	$[\mathbf{5a}]_{t_2}\times10^3$ [M]	$[\mathbf{5a}]_{t_3}\times10^3$ [M]	$([\mathbf{5a}]_{t_2}-[\mathbf{5a}]_{t_1})\times10^3$ [M]	$([\mathbf{5a}]_{t_3}-[\mathbf{5a}]_{t_1})\times10^3$ [M]	$\mathbf{5a}_{t_1\rightarrow t_2}\times10^3$ [M h]	$\mathbf{5a}_{t_1\rightarrow t_3}\times10^3$ [M h]	$\mathbf{4a}_{t_1\rightarrow t_2}\times10^3$ [M h]	$\mathbf{4a}_{t_1\rightarrow t_3}\times10^3$ [M h]	**H** [M^2 h]	**I** [M^2 h^2]
8.00→8.25	8.00→8.50	22.00007	22.78713	23.543	0.78706	1.54293	5.5984	11.38967	1.97071	3.88655	0.32641	0.68722
8.00→8.50	8.00→8.75	22.00007	23.543	24.26892	1.54293	2.26884	11.38967	17.36616	3.88655	5.74979	0.95336	2.00627
8.00→8.75	8.00→9.00	22.00007	24.26892	24.96607	2.26884	2.96599	17.36616	23.52053	5.74979	7.56258	1.85651	3.9051
8.00→9.00	8.00→9.25	22.00007	24.96607	25.63559	2.96599	3.63551	23.52053	29.84574	7.56258	9.32701	3.013	6.33478
8.00→9.25	8.00→9.50	22.00007	25.63559	26.27858	3.63551	4.2785	29.84574	36.33501	9.32701	11.04504	4.40132	9.24936
8.00→9.50	8.00→9.75	22.00007	26.27858	26.89609	4.2785	4.89601	36.33501	42.98184	11.04504	12.7186	6.00129	12.60574
8.00→9.75	8.00→10.00	22.00007	26.89609	27.48912	4.89601	5.48905	42.98184	49.77999	12.7186	14.34951	7.79395	16.36347
8.00→10.00	8.00→10.25	22.00007	27.48912	28.05866	5.48905	6.05859	49.77999	56.72347	14.34951	15.93953	9.76151	20.48462
8.00→10.25	8.00→10.50	22.00007	28.05866	28.60563	6.05859	6.60555	56.72347	63.8065	15.93953	17.49032	11.8873	24.93368
8.00→10.50	8.00→10.75	22.00007	28.60563	29.13092	6.60555	7.13085	63.8065	71.02357	17.49032	19.00352	14.15569	29.67737
8.00→10.75	8.00→11.00	22.00007	29.13092	29.6354	7.13085	7.63532	71.02357	78.36936	19.00352	20.48065	16.55203	34.68458
8.00→11.00	8.00→11.25	22.00007	29.6354	30.11988	7.63532	8.11981	78.36936	85.83877	20.48065	21.9232	19.06263	39.92619
8.00→11.25	8.00→11.50	22.00007	30.11988	30.58517	8.11981	8.58509	85.83877	93.4269	21.9232	23.3326	21.67466	45.37504
8.00→11.50	8.00→11.75	22.00007	30.58517	31.03201	8.58509	9.03194	93.4269	101.12905	23.3326	24.71021	24.37615	51.00572
8.00→11.75	8.00→12.00	22.00007	31.03201	31.46115	9.03194	9.46108	101.12905	108.94069	24.71021	26.05733	27.1559	56.79457
8.00→12.00	8.00→12.25	22.00007	31.46115	31.87328	9.46108	9.87321	108.94069	116.8575	26.05733	27.37521	30.00346	62.71952
8.00→12.25	8.00→12.50	22.00007	31.87328	32.26908	9.87321	10.26901	116.8575	124.87529	27.37521	28.66506	32.9091	68.76002
8.00→12.50	8.00→12.75	22.00007	32.26908	32.6492	10.26901	10.64913	124.87529	132.99008	28.66506	29.92804	35.86374	74.89696
8.00→12.75	8.00→13.00	22.00007	32.6492	33.01425	10.64913	11.01418	132.99008	141.19801	29.92804	31.16523	38.85894	81.11259
8.00→13.00	/			/		/		/		/	/	/

Table S10 The calculated data from Fig. 6d for linear fitting of k'_{-3} (at 130 °C) in Fig. 7c.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{5a}]_{t_1}\times10^3$ [M]	$[\mathbf{5a}]_{t_2}\times10^3$ [M]	$([\mathbf{5a}]_{t_1}-[\mathbf{5a}]_{t_2})\times10^3$ [M]	$\mathbf{4a}_{t_1\rightarrow t_2}\times10^3$ [M h]	J [M]	$\mathbf{5a}_{t_1\rightarrow t_2}\times10^3$ [M h]
10.00→10.30	13.69727	14.28874	-0.59146	3.97378	0.00321	4.1979
10.00→10.60	13.69727	14.86754	-1.17027	7.88415	0.0096	8.57134
10.00→10.90	13.69727	15.43395	-1.73668	11.73117	0.01889	13.11657
10.00→11.20	13.69727	15.98824	-2.29097	15.51486	0.03083	17.8299
10.00→11.50	13.69727	16.53066	-2.83339	19.23526	0.04517	22.70773
10.00→11.80	13.69727	17.06148	-3.3642	22.89242	0.06165	27.74655
10.00→12.10	13.69727	17.58092	-3.88365	26.48637	0.08004	32.94291
10.00→12.40	13.69727	18.08925	-4.39198	30.01716	0.10009	38.29344
10.00→12.70	13.69727	18.5867	-4.88943	33.48481	0.12157	43.79483
10.00→13.00	13.69727	19.0735	-5.37623	36.88936	0.14427	49.44386
10.00→13.30	13.69727	19.54988	-5.8526	40.23087	0.16795	55.23737
10.00→13.60	13.69727	20.01606	-6.31879	43.50936	0.19239	61.17226
10.00→13.90	13.69727	20.47226	-6.77499	46.72486	0.21739	67.24551
10.00→14.20	13.69727	20.9187	-7.22142	49.87743	0.24273	73.45415
10.00→14.50	13.69727	21.35558	-7.6583	52.9671	0.26822	79.7953
10.00→14.80	13.69727	21.78311	-8.08583	55.99391	0.29366	86.2661
10.00→15.10	13.69727	22.20148	-8.50421	58.95789	0.31884	92.86379
10.00→15.40	13.69727	22.6109	-8.91363	61.85908	0.34358	99.58564
10.00→15.70	13.69727	23.01156	-9.31428	64.69752	0.3677	106.42901
10.00→16.00	13.69727	23.40364	-9.70636	67.47326	0.39101	113.39129

Table S11 The calculated data from Fig. 6c for linear fitting of k'_{-3} (at 140 °C) in Fig. 7c.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{5a}]_{t_1}\times10^3$ [M]	$[\mathbf{5a}]_{t_2}\times10^3$ [M]	$([\mathbf{5a}]_{t_1}-[\mathbf{5a}]_{t_2})\times10^3$ [M]	$\mathbf{4a}_{t_1\rightarrow t_2}\times10^3$ [M h]	J [M]	$\mathbf{5a}_{t_1\rightarrow t_2}\times10^3$ [M h]
10.00→10.50	17.49043	18.53493	-1.0445	5.17661	0.10377	9.00634
10.00→11.00	17.49043	19.55427	-2.06384	10.23052	0.20549	18.52864
10.00→11.50	17.49043	20.54904	-3.05862	15.16768	0.30588	28.55446
10.00→12.00	17.49043	21.51985	-4.02943	19.9937	0.40558	39.07169
10.00→12.50	17.49043	22.46727	-4.97684	24.71397	0.50521	50.06847
10.00→13.00	17.49043	23.39186	-5.90143	29.33359	0.60534	61.53325
10.00→13.50	17.49043	24.29417	-6.80374	33.85741	0.70651	73.45475
10.00→14.00	17.49043	25.17474	-7.68432	38.29007	0.80919	85.82198
10.00→14.50	17.49043	26.0341	-8.54367	42.63597	0.91384	98.62419
10.00→15.00	17.49043	26.87274	-9.38232	46.89929	1.02088	111.8509
10.00→15.50	17.49043	27.69119	-10.20076	51.08403	1.1307	125.49188
10.00→16.00	17.49043	28.48991	-10.99948	55.19398	1.24365	139.53716
10.00→16.50	17.49043	29.26939	-11.77896	59.23276	1.36005	153.97698
10.00→17.00	17.49043	30.03008	-12.53966	63.20379	1.48021	168.80185
10.00→17.50	17.49043	30.77245	-13.28203	67.11035	1.60439	184.00248
10.00→18.00	17.49043	31.49693	-14.00651	70.95555	1.73285	199.56983
10.00→18.50	17.49043	32.20396	-14.71353	74.74237	1.86582	215.49505
10.00→19.00	17.49043	32.89395	-15.40352	78.47361	2.00349	231.76953
10.00→19.50	17.49043	33.56731	-16.07689	82.15196	2.14606	248.38484
10.00→20.00	17.49043	34.22445	-16.73403	85.77997	2.29369	265.33278

Table S12 The calculated data from Fig. 6b for linear fitting of k'_{-3} (at 150 °C) in Fig. 7c.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{5a}]_{t_1}\times10^3$ [M]	$[\mathbf{5a}]_{t_2}\times10^3$ [M]	$([\mathbf{5a}]_{t_1} - [\mathbf{5a}]_{t_2})\times10^3$ [M]	$\mathbf{4a}_{t_1\rightarrow t_2}\times10^3$ [M h]	J [M]	$\mathbf{5a}_{t_1\rightarrow t_2}\times10^3$ [M h]
12.00→12.25	24.9993	25.53462	-0.53532	2.10797	0.11259	6.31674
12.00→12.50	24.9993	26.06048	-1.06118	4.18418	0.22487	12.76613
12.00→12.75	24.9993	26.57704	-1.57774	6.22998	0.3371	19.34582
12.00→13.00	24.9993	27.08447	-2.08517	8.24669	0.44953	26.05351
12.00→13.25	24.9993	27.58293	-2.58363	10.23556	0.56237	32.88693
12.00→13.50	24.9993	28.07258	-3.07328	12.1978	0.67584	39.84387
12.00→13.75	24.9993	28.55357	-3.55427	14.13455	0.79013	46.92214
12.00→14.00	24.9993	29.02606	-4.02676	16.04691	0.90542	54.11959
12.00→14.25	24.9993	29.49019	-4.49089	17.93594	1.0219	61.43413
12.00→14.50	24.9993	29.94613	-4.94683	19.80264	1.13971	68.86367
12.00→14.75	24.9993	30.394	-5.3947	21.64797	1.25902	76.40618
12.00→15.00	24.9993	30.83395	-5.83465	23.47285	1.37997	84.05967
12.00→15.25	24.9993	31.26612	-6.26682	25.27817	1.50267	91.82218
12.00→15.50	24.9993	31.69066	-6.69136	27.06477	1.62727	99.69178
12.00→15.75	24.9993	32.10769	-7.10839	28.83346	1.75386	107.66658
12.00→16.00	24.9993	32.51735	-7.51805	30.585	1.88256	115.74471
12.00→16.25	24.9993	32.91976	-7.92046	32.32015	2.01346	123.92434
12.00→16.50	24.9993	33.31507	-8.31576	34.0396	2.14665	132.2037
12.00→16.75	24.9993	33.70338	-8.70408	35.74403	2.28221	140.581
12.00→17.00	24.9993	34.08483	-9.08553	37.4341	2.42022	149.05453

Table S13 The calculated data from Fig. 6a for linear fitting of k'_{-3} (at 160 °C) in Fig. 7c.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{5a}]_{t_1}\times10^3$ [M]	$[\mathbf{5a}]_{t_2}\times10^3$ [M]	$([\mathbf{5a}]_{t_1} - [\mathbf{5a}]_{t_2})\times10^3$ [M]	$\mathbf{4a}_{t_1\rightarrow t_2}\times10^3$ [M h]	J [M]	$\mathbf{5a}_{t_1\rightarrow t_2}\times10^3$ [M h]
8.00→8.25	22.00007	22.78713	-0.78706	1.97071	0.15683	5.5984
8.00→8.50	22.00007	23.543	-1.54293	3.88655	0.31858	11.38967
8.00→8.75	22.00007	24.26892	-2.26884	5.74979	0.48508	17.36616
8.00→9.00	22.00007	24.96607	-2.96599	7.56258	0.65618	23.52053
8.00→9.25	22.00007	25.63559	-3.63551	9.32701	0.83175	29.84574
8.00→9.50	22.00007	26.27858	-4.2785	11.04504	1.01163	36.33501
8.00→9.75	22.00007	26.89609	-4.89601	12.7186	1.19569	42.98184
8.00→10.00	22.00007	27.48912	-5.48905	14.34951	1.38379	49.77999
8.00→10.25	22.00007	28.05866	-6.05859	15.93953	1.57581	56.72347
8.00→10.50	22.00007	28.60563	-6.60555	17.49032	1.77161	63.8065
8.00→10.75	22.00007	29.13092	-7.13085	19.00352	1.97108	71.02357
8.00→11.00	22.00007	29.6354	-7.63532	20.48065	2.17409	78.36936
8.00→11.25	22.00007	30.11988	-8.11981	21.9232	2.38053	85.83877
8.00→11.50	22.00007	30.58517	-8.58509	23.3326	2.59029	93.4269
8.00→11.75	22.00007	31.03201	-9.03194	24.71021	2.80326	101.12905
8.00→12.00	22.00007	31.46115	-9.46108	26.05733	3.01934	108.94069
8.00→12.25	22.00007	31.87328	-9.87321	27.37521	3.23842	116.8575
8.00→12.50	22.00007	32.26908	-10.26901	28.66506	3.46041	124.87529
8.00→12.75	22.00007	32.6492	-10.64913	29.92804	3.68521	132.99008
8.00→13.00	22.00007	33.01425	-11.01418	31.16523	3.91272	141.19801

Table S14 The calculated data from Fig. 9d for linear fitting of k_1'' (at 110 °C) in Fig. 10a.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{2a}]_{t_1}\times 10^3$ [M]	$[\mathbf{2a}]_{t_2}\times 10^3$ [M]	$[\ln([\mathbf{2a}]_{t_1}/[\mathbf{2a}]_{t_2})]$ /	$t_2 - t_1$ [h]
8.00→8.40	40.00854	39.73389	0.00689	0.40
8.00→8.80	40.00854	39.42871	0.0146	0.80
8.00→9.20	40.00854	39.12354	0.02237	1.20
8.00→9.60	40.00854	38.81836	0.0302	1.60
8.00→10.00	40.00854	38.51318	0.03809	2.00
8.00→10.40	40.00854	38.20801	0.04605	2.40
8.00→10.80	40.00854	37.93335	0.05326	2.80
8.00→11.20	40.00854	37.62817	0.06134	3.20
8.00→11.60	40.00854	37.323	0.06948	3.60
8.00→12.00	40.00854	37.01782	0.07769	4.00
8.00→12.40	40.00854	36.71265	0.08597	4.40
8.00→12.80	40.00854	36.40747	0.09432	4.80
8.00→13.20	40.00854	36.13281	0.10189	5.20
8.00→13.60	40.00854	35.82764	0.11037	5.60
8.00→14.00	40.00854	35.52246	0.11893	6.00
8.00→14.40	40.00854	35.21729	0.12756	6.40
8.00→14.80	40.00854	34.91211	0.13626	6.80
8.00→15.20	40.00854	34.60693	0.14504	7.20
8.00→15.60	40.00854	34.33228	0.15301	7.60
8.00→16.00	40.00854	34.0271	0.16194	8.00

Table S15 The calculated data from Fig. 9c for linear fitting of k_1'' (at 120 °C) in Fig. 10a.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{2a}]_{t_1}\times 10^3$ [M]	$[\mathbf{2a}]_{t_2}\times 10^3$ [M]	$[\ln([\mathbf{2a}]_{t_1}/[\mathbf{2a}]_{t_2})]$ /	$t_2 - t_1$ [h]
20.00→20.60	23.00404	22.51193	0.02162	0.60
20.00→21.20	23.00404	22.03439	0.04307	1.20
20.00→21.80	23.00404	21.57099	0.06432	1.80
20.00→22.40	23.00404	21.12129	0.08539	2.40
20.00→23.00	23.00404	20.68491	0.10627	3.00
20.00→23.60	23.00404	20.26143	0.12695	3.60
20.00→24.20	23.00404	19.85049	0.14744	4.20
20.00→24.80	23.00404	19.45171	0.16773	4.80
20.00→25.40	23.00404	19.06473	0.18783	5.40
20.00→26.00	23.00404	18.68921	0.20772	6.00
20.00→26.60	23.00404	18.32479	0.22741	6.60
20.00→27.20	23.00404	17.97117	0.2469	7.20
20.00→27.80	23.00404	17.628	0.26618	7.80
20.00→28.40	23.00404	17.29499	0.28525	8.40
20.00→29.00	23.00404	16.97184	0.30411	9.00
20.00→29.60	23.00404	16.65825	0.32276	9.60
20.00→30.20	23.00404	16.35393	0.3412	10.20
20.00→30.80	23.00404	16.05863	0.35942	10.80
20.00→31.40	23.00404	15.77206	0.37743	11.40
20.00→32.00	23.00404	15.49398	0.39522	12.00

Table S16 The calculated data from Fig. 9b for linear fitting of k_1'' (at 130 °C) in Fig. 10a.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{2a}]_{t_1} \times 10^3$ [M]	$[\mathbf{2a}]_{t_2} \times 10^3$ [M]	$[\ln([\mathbf{2a}]_{t_1}/[\mathbf{2a}]_{t_2})]$ /	$t_2 - t_1$ [h]
20.00→20.60	13.99214	13.4774	0.03748	0.60
20.00→21.20	13.99214	12.98963	0.07434	1.20
20.00→21.80	13.99214	12.52742	0.11058	1.80
20.00→22.40	13.99214	12.08942	0.14617	2.40
20.00→23.00	13.99214	11.67436	0.1811	3.00
20.00→23.60	13.99214	11.28105	0.21537	3.60
20.00→24.20	13.99214	10.90835	0.24897	4.20
20.00→24.80	13.99214	10.55517	0.28188	4.80
20.00→25.40	13.99214	10.22049	0.3141	5.40
20.00→26.00	13.99214	9.90335	0.34562	6.00
20.00→26.60	13.99214	9.60282	0.37644	6.60
20.00→27.20	13.99214	9.31803	0.40654	7.20
20.00→27.80	13.99214	9.04817	0.43593	7.80
20.00→28.40	13.99214	8.79244	0.4646	8.40
20.00→29.00	13.99214	8.55011	0.49255	9.00
20.00→29.60	13.99214	8.32048	0.51978	9.60
20.00→30.20	13.99214	8.10287	0.54628	10.20
20.00→30.80	13.99214	7.89667	0.57205	10.80
20.00→31.40	13.99214	7.70127	0.59711	11.40
20.00→32.00	13.99214	7.51611	0.62145	12.00

Table S17 The calculated data from Fig. 9a for linear fitting of k_1'' (at 140 °C) in Fig. 10a.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{2a}]_{t_1} \times 10^3$ [M]	$[\mathbf{2a}]_{t_2} \times 10^3$ [M]	$[\ln([\mathbf{2a}]_{t_1}/[\mathbf{2a}]_{t_2})]$ /	$t_2 - t_1$ [h]
7.00→7.25	26.38988	25.96854	0.01609	0.25
7.00→7.50	26.38988	25.54762	0.03244	0.50
7.00→7.75	26.38988	25.12712	0.04903	0.75
7.00→8.00	26.38988	24.70703	0.06589	1.00
7.00→8.25	26.38988	24.28736	0.08302	1.25
7.00→8.50	26.38988	23.8681	0.10044	1.50
7.00→8.75	26.38988	23.44926	0.11814	1.75
7.00→9.00	26.38988	23.03083	0.13615	2.00
7.00→9.25	26.38988	22.61282	0.15446	2.25
7.00→9.50	26.38988	22.19521	0.1731	2.50
7.00→9.75	26.38988	21.77803	0.19208	2.75
7.00→10.00	26.38988	21.36125	0.2114	3.00
7.00→10.25	26.38988	20.94489	0.23109	3.25
7.00→10.50	26.38988	20.52893	0.25115	3.50
7.00→10.75	26.38988	20.11339	0.27159	3.75
7.00→11.00	26.38988	19.69826	0.29245	4.00
7.00→11.25	26.38988	19.28354	0.31373	4.25
7.00→11.50	26.38988	18.86923	0.33545	4.50
7.00→11.75	26.38988	18.45534	0.35763	4.75
7.00→12.00	26.38988	18.04184	0.38029	5.00

Table S18 The calculated data from Fig. 9d for linear fitting of k_3'' (at 110 °C) in Fig. 10b.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{5a}]_{t_1}$×10^3 [M]	$[\mathbf{5a}]_{t_2}$×10^3 [M]	$([\mathbf{5a}]_{t_2} - [\mathbf{5a}]_{t_1})$×10^3 [M]	$\mathbf{4a}_{t_1 \rightarrow t_2}$×10^3 [M h]
6.00→6.20	3.51003	4.18845	0.67842	0.58547
6.00→6.40	3.51003	4.82009	1.31005	1.13707
6.00→6.60	3.51003	5.40817	1.89813	1.65597
6.00→6.80	3.51003	5.95569	2.44566	2.14329
6.00→7.00	3.51003	6.46546	2.95543	2.60012
6.00→7.20	3.51003	6.94008	3.43004	3.02751
6.00→7.40	3.51003	7.38196	3.87193	3.42648
6.00→7.60	3.51003	7.79338	4.28334	3.79801
6.00→7.80	3.51003	8.17642	4.66639	4.14304
6.00→8.00	3.51003	8.53305	5.02302	4.46248
6.00→8.20	3.51003	8.86509	5.35505	4.75722
6.00→8.40	3.51003	9.17423	5.66419	5.02811
6.00→8.60	3.51003	9.46205	5.95201	5.27597
6.00→8.80	3.51003	9.73002	6.21999	5.50159
6.00→9.00	3.51003	9.97952	6.46948	5.70575
6.00→9.20	3.51003	10.21181	6.70177	5.88918
6.00→9.40	3.51003	10.42808	6.91805	6.05259
6.00→9.60	3.51003	10.62944	7.1194	6.19668
6.00→9.80	3.51003	10.81691	7.30688	6.32211
6.00→10.00	3.51003	10.99145	7.48142	6.42952

Table S19 The calculated data from Fig. 9c for linear fitting of k_3'' (at 120 °C) in Fig. 10b.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{5a}]_{t_1}$×10^3 [M]	$[\mathbf{5a}]_{t_2}$×10^3 [M]	$([\mathbf{5a}]_{t_2} - [\mathbf{5a}]_{t_1})$×10^3 [M]	$\mathbf{4a}_{t_1 \rightarrow t_2}$×10^3 [M h]
5.000→5.125	5.72471	6.14816	0.42345	0.31575
5.000→5.250	5.72471	6.55029	0.82559	0.61153
5.000→5.375	5.72471	6.93219	1.20748	0.88816
5.000→5.500	5.72471	7.29485	1.57015	1.1464
5.000→5.625	5.72471	7.63926	1.91456	1.38699
5.000→5.750	5.72471	7.96634	2.24163	1.61065
5.000→5.875	5.72471	8.27694	2.55224	1.81804
5.000→6.000	5.72471	8.57191	2.84721	2.00983
5.000→6.125	5.72471	8.85204	3.12733	2.18665
5.000→6.250	5.72471	9.11806	3.39335	2.34908
5.000→6.375	5.72471	9.37069	3.64598	2.49772
5.000→6.500	5.72471	9.6106	3.88589	2.63312
5.000→6.625	5.72471	9.83844	4.11373	2.7558
5.000→6.750	5.72471	10.0548	4.33009	2.86628
5.000→6.875	5.72471	10.26028	4.53557	2.96506
5.000→7.000	5.72471	10.45541	4.7307	3.05259
5.000→7.125	5.72471	10.64071	4.91601	3.12934
5.000→7.250	5.72471	10.81669	5.09198	3.19573
5.000→7.375	5.72471	10.98381	5.2591	3.25219
5.000→7.500	5.72471	11.14252	5.41781	3.29911

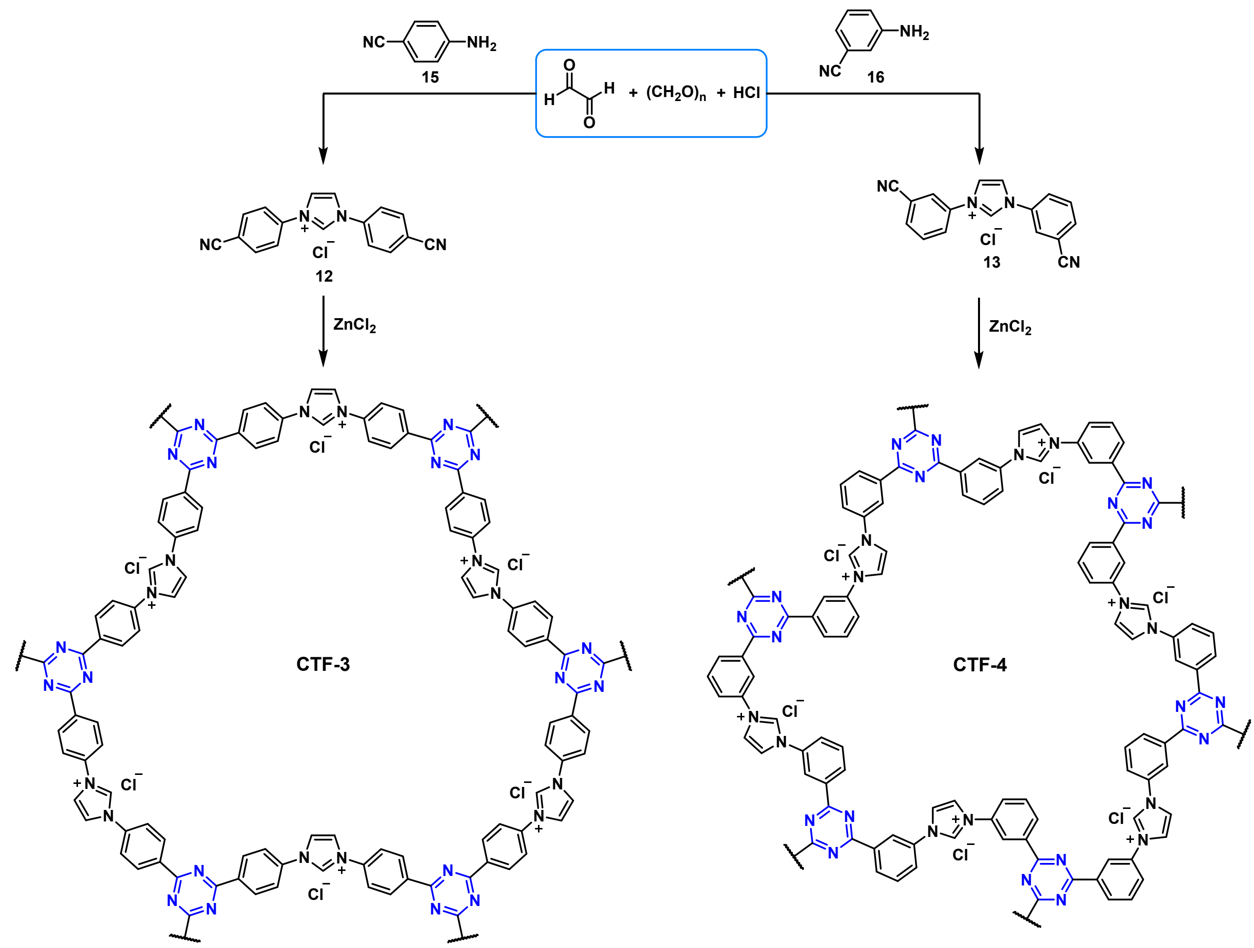
Table S20 The calculated data from Fig. 9b for linear fitting of k_3'' (at 130 °C) in Fig. 10b.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{5a}]_{t_1}$×10^3 [M]	$[\mathbf{5a}]_{t_2}$×10^3 [M]	$([\mathbf{5a}]_{t_2} - [\mathbf{5a}]_{t_1})$×10^3 [M]	$\mathbf{4a}_{t_1\rightarrow t_2}$×10^3 [M h]
4.000→4.075	11.40206	11.74619	0.34413	0.16081
4.000→4.150	11.40206	12.07291	0.67085	0.31325
4.000→4.225	11.40206	12.3831	0.98104	0.45751
4.000→4.300	11.40206	12.6776	1.27554	0.59381
4.000→4.375	11.40206	12.9572	1.55514	0.72234
4.000→4.450	11.40206	13.22265	1.82059	0.8433
4.000→4.525	11.40206	13.47467	2.07261	0.95686
4.000→4.600	11.40206	13.71394	2.31188	1.06321
4.000→4.675	11.40206	13.94111	2.53905	1.16253
4.000→4.750	11.40206	14.15679	2.75473	1.255
4.000→4.825	11.40206	14.36155	2.95949	1.34078
4.000→4.900	11.40206	14.55595	3.15389	1.42003
4.000→4.975	11.40206	14.74052	3.33846	1.49293
4.000→5.050	11.40206	14.91575	3.51369	1.55962
4.000→5.125	11.40206	15.08211	3.68005	1.62026
4.000→5.200	11.40206	15.24006	3.838	1.67501
4.000→5.275	11.40206	15.39002	3.98796	1.72399
4.000→5.350	11.40206	15.53239	4.13033	1.76737
4.000→5.425	11.40206	15.66755	4.26549	1.80527
4.000→5.500	11.40206	15.79588	4.39382	1.83783

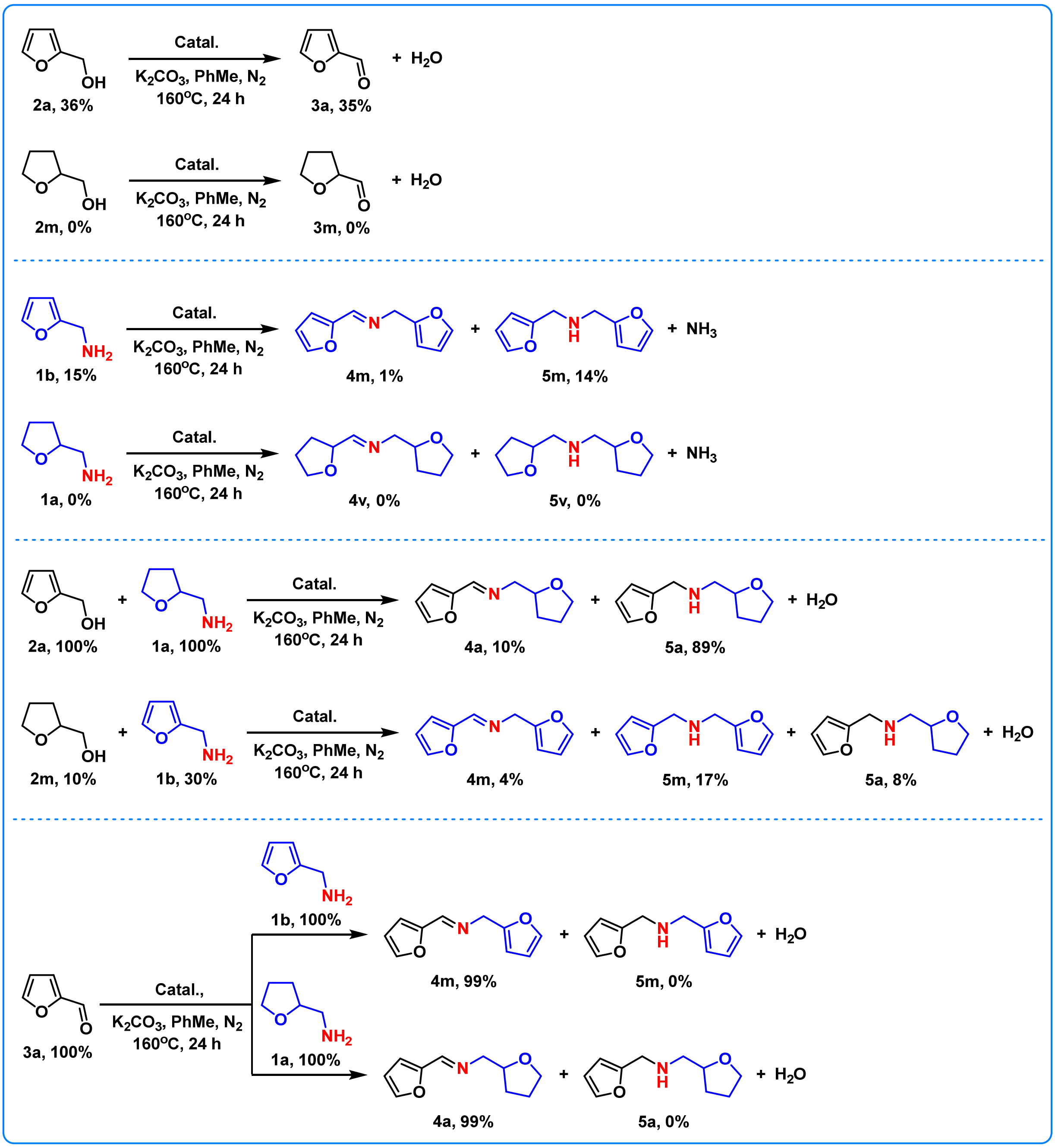
Table S21 The calculated data from Fig. 9a for linear fitting of k_3'' (at 140 °C) in Fig. 10b.

$t_1 \rightarrow t_2$ [h]	$[\mathbf{5a}]_{t_1}$×10^3 [M]	$[\mathbf{5a}]_{t_2}$×10^3 [M]	$([\mathbf{5a}]_{t_2} - [\mathbf{5a}]_{t_1})$×10^3 [M]	$\mathbf{4a}_{t_1\rightarrow t_2}$×10^3 [M h]
0.500→0.550	0.50057	0.90524	0.40467	0.14761
0.500→0.600	0.50057	1.30094	0.80037	0.2904
0.500→0.650	0.50057	1.68789	1.18732	0.42834
0.500→0.700	0.50057	2.06627	1.5657	0.56137
0.500→0.750	0.50057	2.43627	1.9357	0.68945
0.500→0.800	0.50057	2.79808	2.29751	0.81254
0.500→0.850	0.50057	3.15188	2.65131	0.93058
0.500→0.900	0.50057	3.49785	2.99728	1.04352
0.500→0.950	0.50057	3.83616	3.33559	1.15132
0.500→1.000	0.50057	4.16698	3.66641	1.25393
0.500→1.05	0.50057	4.49047	3.9899	1.3513
0.500→1.100	0.50057	4.8068	4.30623	1.44337
0.500→1.150	0.50057	5.11613	4.61556	1.5301
0.500→1.200	0.50057	5.41861	4.91804	1.61144
0.500→1.250	0.50057	5.7144	5.21383	1.68733
0.500→1.300	0.50057	6.00363	5.50306	1.75772
0.500→1.350	0.50057	6.28647	5.7859	1.82257
0.500→1.400	0.50057	6.56304	6.06247	1.8818
0.500→1.450	0.50057	6.83349	6.33291	1.93539
0.500→1.500	0.50057	7.09795	6.59738	1.98325

S2.2. Supplementary Schemes and Figs.



Scheme S1 Synthetic route to CTF-3 and CTF-4



Scheme S2 Control experiments. Reaction conditions: 1.8%-Ir/CTF-1 (15 mg), K_2CO_3 (26 mg, 0.19 mmol), PhMe (2.0 mL), P_{N_2} (1.0 MPa), 160 °C, 24 h, **1a**, **1b**, **2a**, **2m** and **3a** (0.1 mmol).

$$\frac{\mathrm{d}[\mathbf{2a}]}{\mathrm{d}t} = -k_1[\mathbf{2a}][\mathrm{Cat}] + k_{-1}[\mathbf{3a}][\mathrm{Cat}\cdot\mathrm{H_2}] \tag{8}$$

$$\frac{\mathrm{d}[\mathbf{1a}]}{\mathrm{d}t} = -k_2[\mathbf{3a}][\mathbf{1a}] + k_{-2}[\mathbf{4a}][\mathrm{H_2O}] \tag{9}$$

$$\frac{\mathrm{d}[\mathbf{3a}]}{\mathrm{d}t} = +k_1[\mathbf{2a}][\mathrm{Cat}] - k_{-1}[\mathbf{3a}][\mathrm{Cat}\cdot\mathrm{H_2}] - k_2[\mathbf{3a}][\mathbf{1a}] + k_{-2}[\mathbf{4a}][\mathrm{H_2O}] \tag{10}$$

$$\frac{\mathrm{d}[\mathbf{4a}]}{\mathrm{d}t} = +k_2[\mathbf{3a}][\mathbf{1a}] - k_{-2}[\mathbf{4a}][\mathrm{H_2O}] - k_3[\mathbf{4a}][\mathrm{Cat}\cdot\mathrm{H_2}] + k_{-3}[\mathbf{5a}][\mathrm{Cat}] \tag{11}$$

$$\frac{\mathrm{d}[\mathbf{5a}]}{\mathrm{d}t} = +k_3[\mathbf{4a}][\mathrm{Cat}\cdot\mathrm{H_2}] - k_{-3}[\mathbf{5a}][\mathrm{Cat}] \tag{12}$$

$$[\mathrm{Cat}]_0 = [\mathrm{Cat}] + [\mathrm{Cat}\cdot\mathrm{H_2}] \tag{13}$$

$$\frac{\mathrm{d}[\mathbf{2a}]}{\mathrm{d}t} = -k'_1[\mathbf{2a}] + k'_{-1}[\mathbf{3a}] \tag{14}$$

$$\frac{\mathrm{d}[\mathbf{3a}]}{\mathrm{d}t} = +k'_1[\mathbf{2a}] - k'_{-1}[\mathbf{3a}] - k_2[\mathbf{3a}][\mathbf{1a}] + k_{-2}[\mathbf{4a}][\mathrm{H_2O}] \tag{15}$$

$$\frac{\mathrm{d}[\mathbf{4a}]}{\mathrm{d}t} = +k_2[\mathbf{3a}][\mathbf{1a}] - k_{-2}[\mathbf{4a}][\mathrm{H_2O}] - k'_3[\mathbf{4a}] + k'_{-3}[\mathbf{5a}] \tag{16}$$

$$\frac{\mathrm{d}[\mathbf{5a}]}{\mathrm{d}t} = +k'_3[\mathbf{4a}] - k'_{-3}[\mathbf{5a}] \tag{17}$$

$$k'_1 = k_1[\mathrm{Cat}] \tag{18}$$

$$k'_{-1} = k_{-1}[\mathrm{Cat}\cdot\mathrm{H_2}] \tag{19}$$

$$k'_3 = k_3[\mathrm{Cat}\cdot\mathrm{H_2}] \tag{20}$$

$$k'_{-3} = k_{-3}[\mathrm{Cat}] \tag{21}$$

$$r_{\mathbf{2a}} = -\left(\frac{\mathrm{d}[\mathbf{2a}]}{\mathrm{d}t}\right) = +k'_1[\mathbf{2a}] \tag{22}$$

$$\frac{\mathrm{d}[\mathbf{3a}]}{\mathrm{d}t} = +k'_1[\mathbf{2a}] - k_2[\mathbf{3a}][\mathbf{1a}] + k_{-2}[\mathbf{4a}][\mathrm{H_2O}] = 0 \tag{23}$$

$$r_{\mathbf{3a}} = \frac{\mathrm{d}[\mathbf{3a}]}{\mathrm{d}t} = -\left(\frac{\mathrm{d}[\mathbf{2a}]}{\mathrm{d}t}\right) + \left(\frac{\mathrm{d}[\mathbf{1a}]}{\mathrm{d}t}\right) = r_{\mathbf{2a}} - r_{\mathbf{1a}} = 0 \tag{24}$$

$$r_{\mathbf{1a}} = r_{\mathbf{2a}} \tag{25}$$

$$r_1 = r_{\mathbf{2a}} = +k'_1[\mathbf{2a}] \tag{26}$$

$$r_2 = r_{\mathbf{1a}} = r_{\mathbf{2a}} = +k'_1[\mathbf{2a}] \tag{27}$$

$$r_3 = +k'_3[\mathbf{4a}] \tag{28}$$

$$r_{-3} = +k'_{-3}[\mathbf{5a}] \tag{29}$$

$$\mathbf{G}_{t_1\to t_2} = \int_{t_1}^{t_2}[\mathbf{G}]\mathrm{d}t \tag{30}$$

$$\int_{[\mathbf{2a}]_{t_1}}^{[\mathbf{2a}]_{t_2}} \mathrm{d}[\mathbf{2a}] = -k'_1\int_{t_1}^{t_2}[\mathbf{2a}]\mathrm{d}t \tag{31}$$

$$\int_{[\mathbf{2a}]_{t_1}}^{[\mathbf{2a}]_{t_2}} \frac{\mathrm{d}[\mathbf{2a}]}{[\mathbf{2a}]} = -k'_1\int_{t_1}^{t_2}\mathrm{d}t \tag{32}$$

$$\ln\left(\frac{[\mathbf{2a}]_{t_1}}{[\mathbf{2a}]_{t_2}}\right) = k_1'(t_2 - t_1) \tag{33}$$

$$k_1' = \frac{\ln\left(\frac{[\mathbf{2a}]_{t_1}}{[\mathbf{2a}]_{t_2}}\right)}{t_2 - t_1} \tag{34}$$

$$\int_{[\mathbf{5a}]_{t_1}}^{[\mathbf{5a}]_{t_2}} \mathrm{d}[\mathbf{5a}] = +k_3' \int_{t_1}^{t_2} [\mathbf{4a}]\mathrm{d}t - k_{-3}' \int_{t_1}^{t_2} [\mathbf{5a}]\mathrm{d}t \tag{35}$$

$$[\mathbf{5a}]_{t_2} - [\mathbf{5a}]_{t_1} = +k_3' \mathbf{4a}_{t_1\to t_2} - k_{-3}' \mathbf{5a}_{t_1\to t_2} \tag{36}$$

$$[\mathbf{5a}]_{t_3} - [\mathbf{5a}]_{t_1} = +k_3' \mathbf{4a}_{t_1\to t_3} - k_{-3}' \mathbf{5a}_{t_1\to t_3} \tag{37}$$

$$k_3' = \frac{\mathbf{5a}_{t_1\to t_3}([\mathbf{5a}]_{t_2} - [\mathbf{5a}]_{t_1}) - \mathbf{5a}_{t_1\to t_2}([\mathbf{5a}]_{t_3} - [\mathbf{5a}]_{t_1})}{\mathbf{4a}_{t_1\to t_2}\mathbf{5a}_{t_1\to t_3} - \mathbf{4a}_{t_1\to t_3}\mathbf{5a}_{t_1\to t_2}} = \frac{\mathbf{H}}{\mathbf{I}} \tag{38}$$

$$k_{-3}' = \frac{([\mathbf{5a}]_{t_1} - [\mathbf{5a}]_{t_2}) + k_3' \mathbf{4a}_{t_1\to t_2}}{\mathbf{5a}_{t_1\to t_2}} = \frac{\mathbf{J}}{\mathbf{5a}_{t_1\to t_2}} \tag{39}$$

$$k_1'' = \frac{\ln\left(\frac{[\mathbf{2a}]_{t_1}}{[\mathbf{2a}]_{t_2}}\right)}{t_2 - t_1} \tag{40}$$

$$\int_{[\mathbf{5a}]_{t_1}}^{[\mathbf{5a}]_{t_2}} \mathrm{d}[\mathbf{5a}] = +k_3'' \int_{t_1}^{t_2} [\mathbf{4a}]\mathrm{d}t \tag{41}$$

$$k_3'' = \frac{[\mathbf{5a}]_{t_2} - [\mathbf{5a}]_{t_1}}{\mathbf{4a}_{t_1\to t_2}} \tag{42}$$

$$\frac{\mathrm{d}[\mathbf{4a}]}{\mathrm{d}t} = +k_2[\mathbf{3a}][\mathbf{1a}] - k_{-2}[\mathbf{4a}][\mathrm{H_2O}] - k_3''[\mathbf{4a}] + k_{-3}''[\mathbf{5a}] = 0 \tag{43}$$

$$\frac{\mathrm{d}[\mathbf{4a}]}{\mathrm{d}t} = -\left(\frac{\mathrm{d}[\mathbf{1a}]}{\mathrm{d}t}\right) - \left(\frac{\mathrm{d}[\mathbf{5a}]}{\mathrm{d}t}\right) = r_{\mathbf{1a}} - r_{\mathbf{5a}} = 0 \tag{44}$$

$$r_{\mathbf{1a}} = r_{\mathbf{5a}} \tag{45}$$

Scheme S3 Kinetic equations for **1a**/**2a**-to-**5a** *N*-alkylation

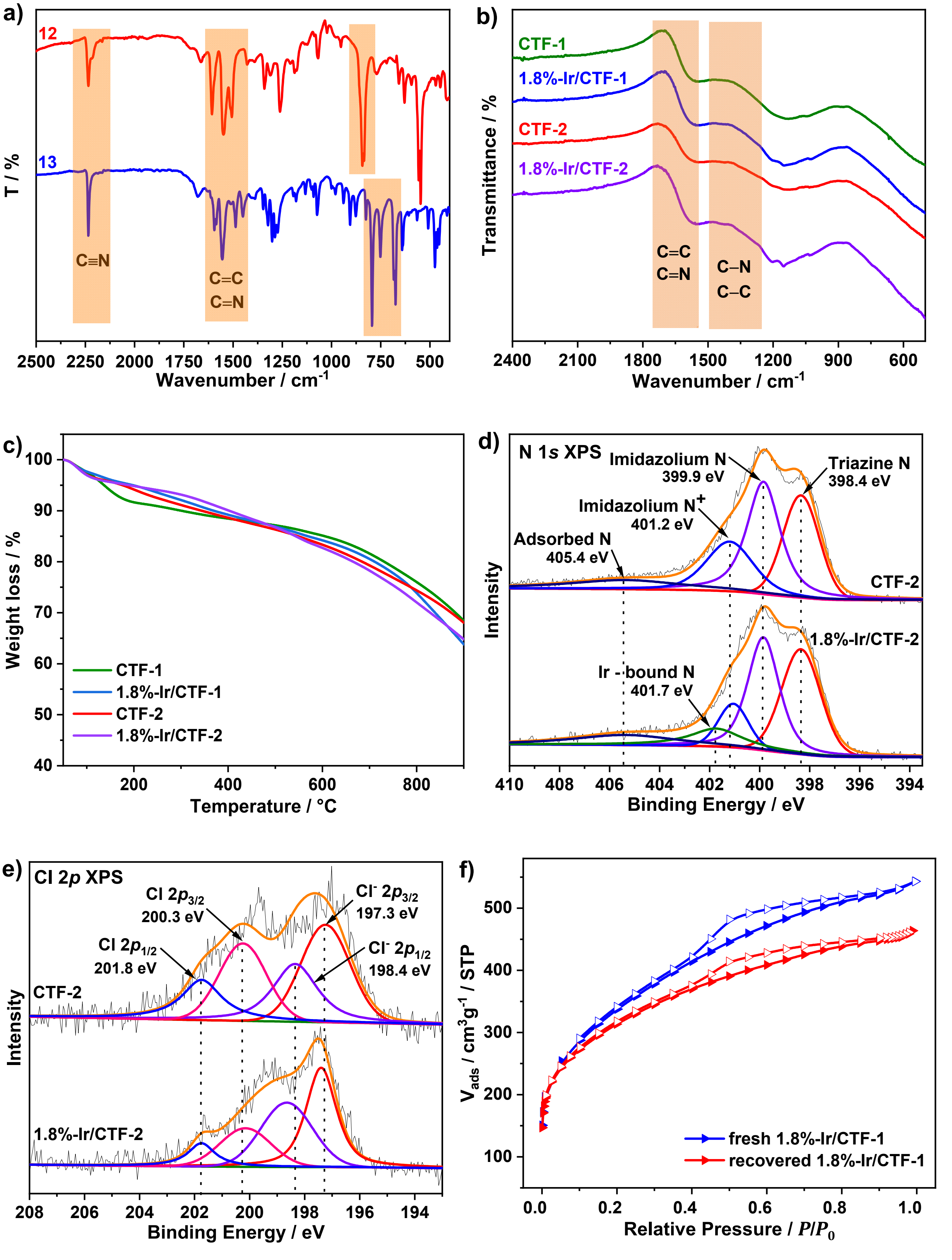


Fig. S1 (a) IR spectra of **12** and **13**. CTF and Ir/CTF serial samples: (b) IR spectra, (c) TGA plots. CTF-2 and 1.8%-Ir/CTF-2: (d) N 1*s* XPS, (e) Cl 2*p* XPS. (f) Nitrogen sorption isotherms of fresh and recovered 1.8%-Ir/CTF-1.

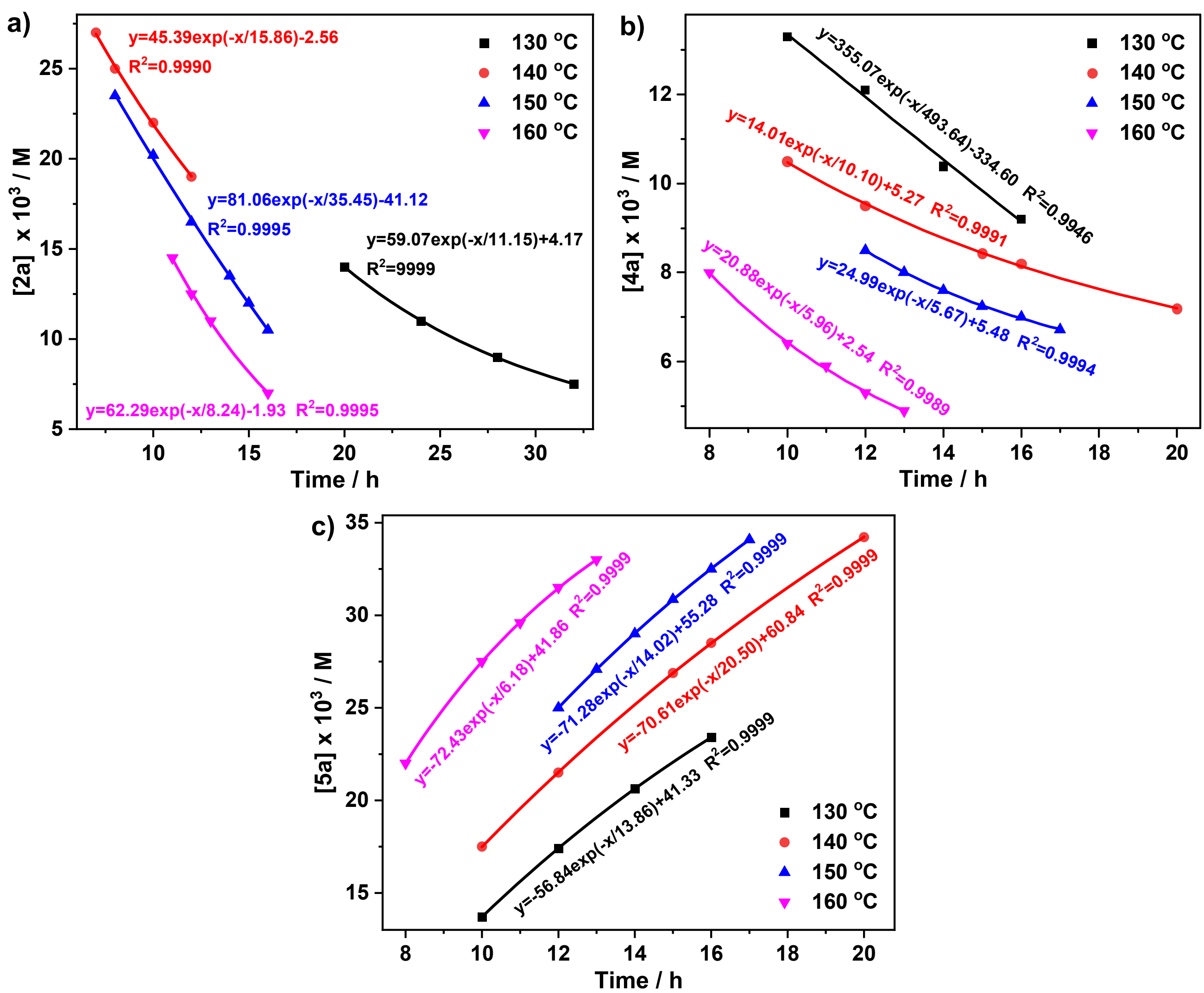


Fig. S2 Nonlinear fittings of concentration–time curves at the specified reaction-time intervals (corresponding to Fig. 6 and Tables S2–13): (a) [**2a**]~t, (b) [**4a**]~t, (c) [**5a**]~t. Reaction conditions: 1.8%-Ir/CTF-1 (15 mg, 1.4 mol% Ir relative to **2a**), **1a** (10 mg, 0.10 mmol), **2a** (10 mg, 0.10 mmol), K_2CO_3 (26 mg, 0.19 mmol), PhMe (2 mL), P_{N_2} (1.0 MPa), specified reaction temperature.

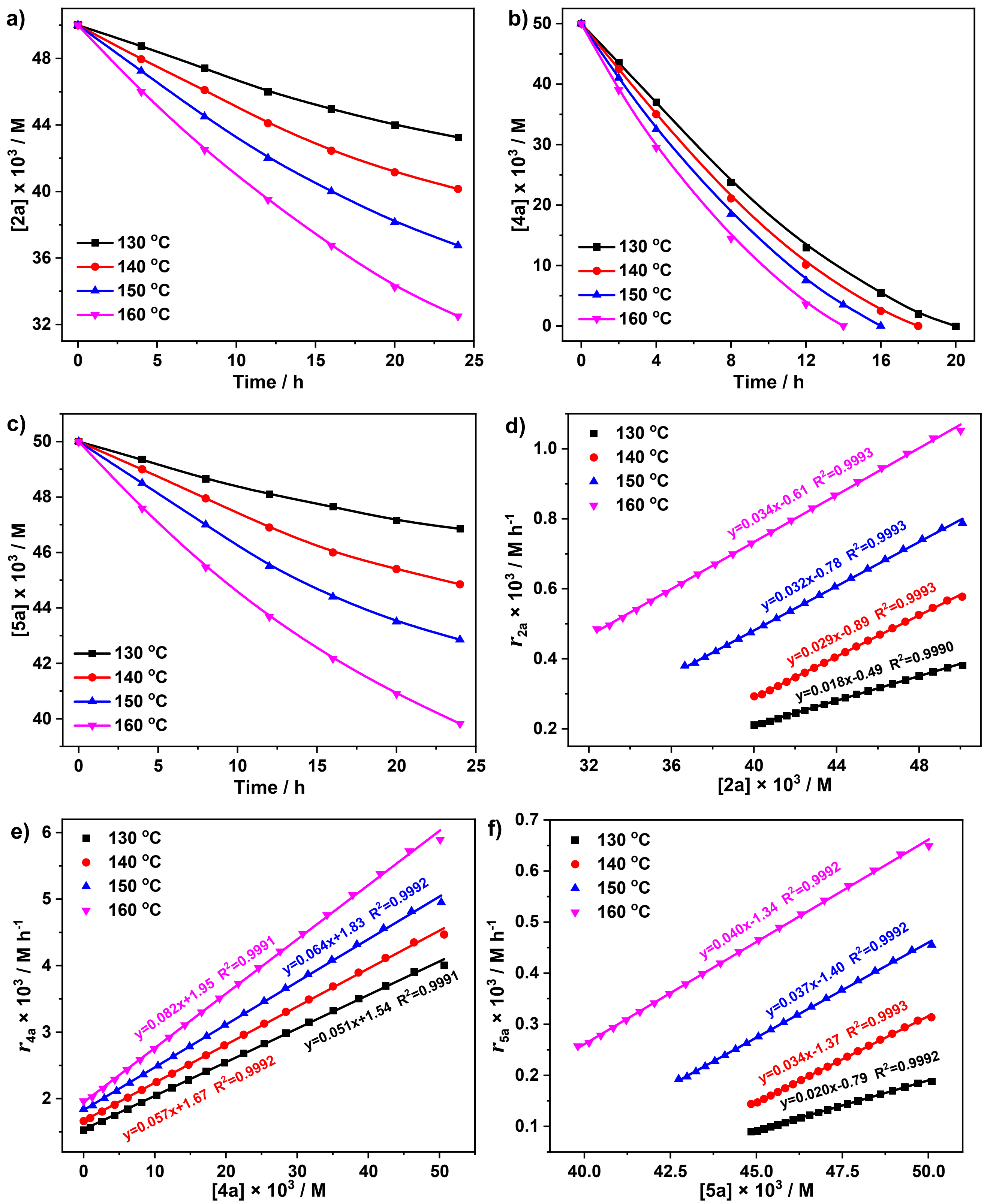


Fig. S3 The concentration–time curves at the specified reaction-time intervals: (a) $[\mathbf{2a}] \sim t$, (b) $[\mathbf{4a}] \sim t$, (c) $[\mathbf{5a}] \sim t$. And plots of: (d) r_{2a} against $[\mathbf{2a}]$, (e) r_{4a} against $[\mathbf{4a}]$, (f) r_{5a} against $[\mathbf{5a}]$. Reaction conditions: 1.8%-Ir/CTF-1 (15 mg), K_2CO_3 (26 mg, 0.19 mmol), PhMe (2.0 mL), P_{N_2} (1.0 MPa), [**2a** (0.10 mmol) for panel (a)], [**4a** (0.10 mmol) and HCOONa (17 mg, 0.25 mmol) for panel (b)], [**5a** (0.10 mmol) for panel (c)].

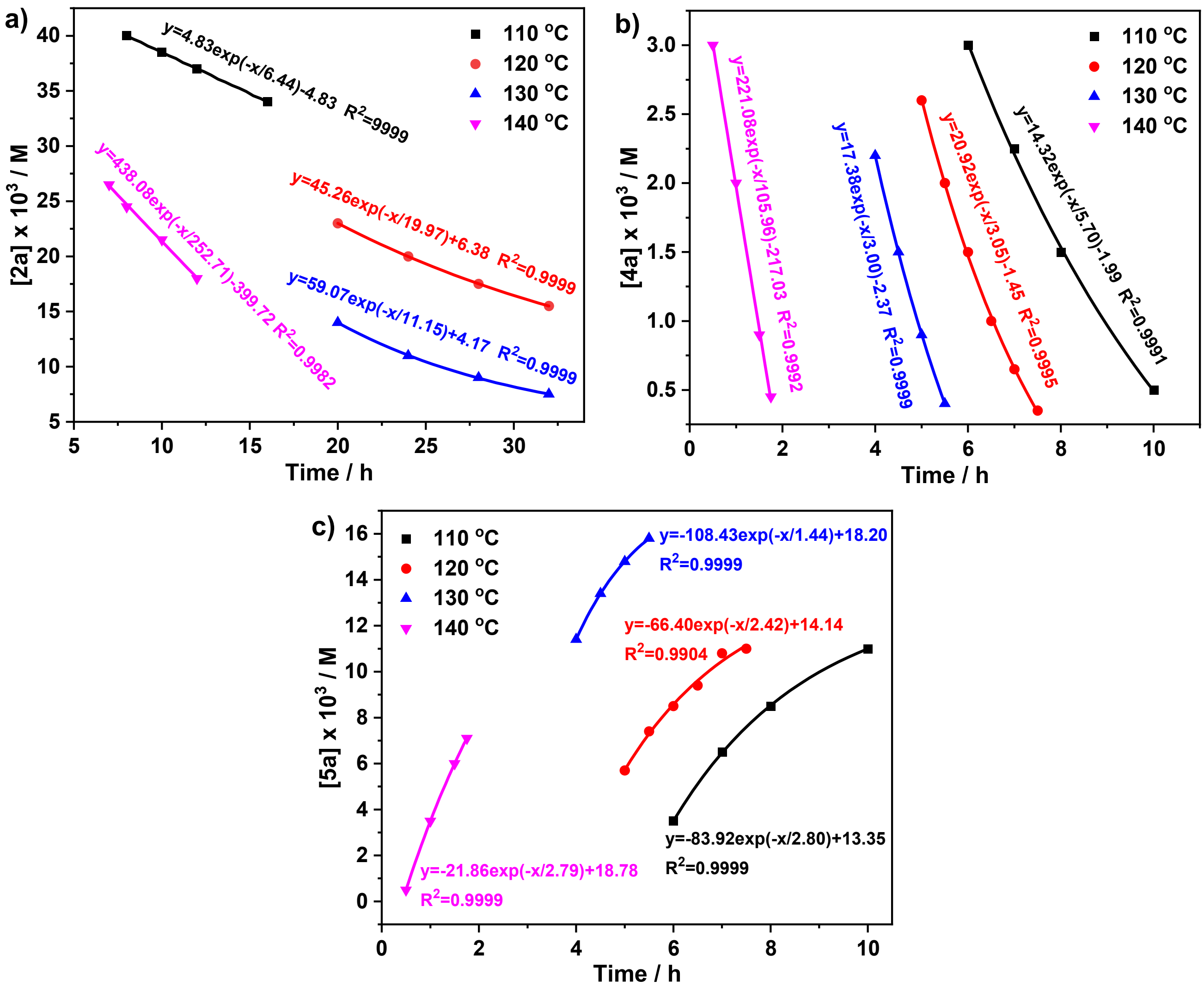


Fig. S4 Nonlinear fittings of concentration–time curves at the specified reaction-time intervals (corresponding to Fig. 9 and Tables S14–21): (a) [**2a**]$\sim t$, (b) [**4a**]$\sim t$, (c) [**5a**]$\sim t$. Reaction conditions: 1.8%-Ir/CTF-1 (15 mg, 1.4 mol% Ir relative to **2a**), **1a** (10 mg, 0.10 mmol), **2a** (10 mg, 0.10 mmol), K_2CO_3 (26 mg, 0.19 mmol), HCOONa (17 mg, 0.25 mmol), PhMe (2.0 mL), P_{N_2} (1.0 MPa), specified reaction temperature.

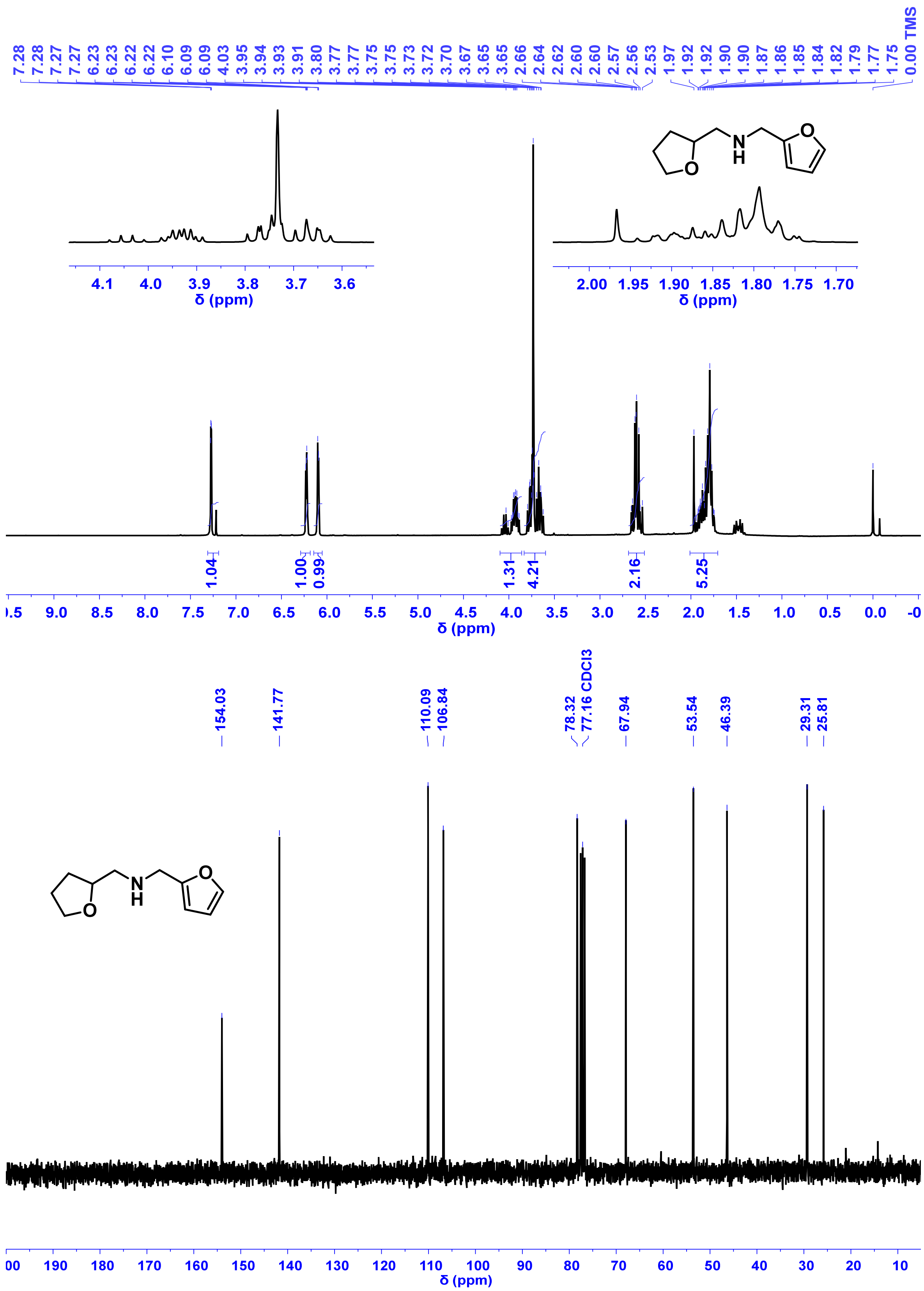
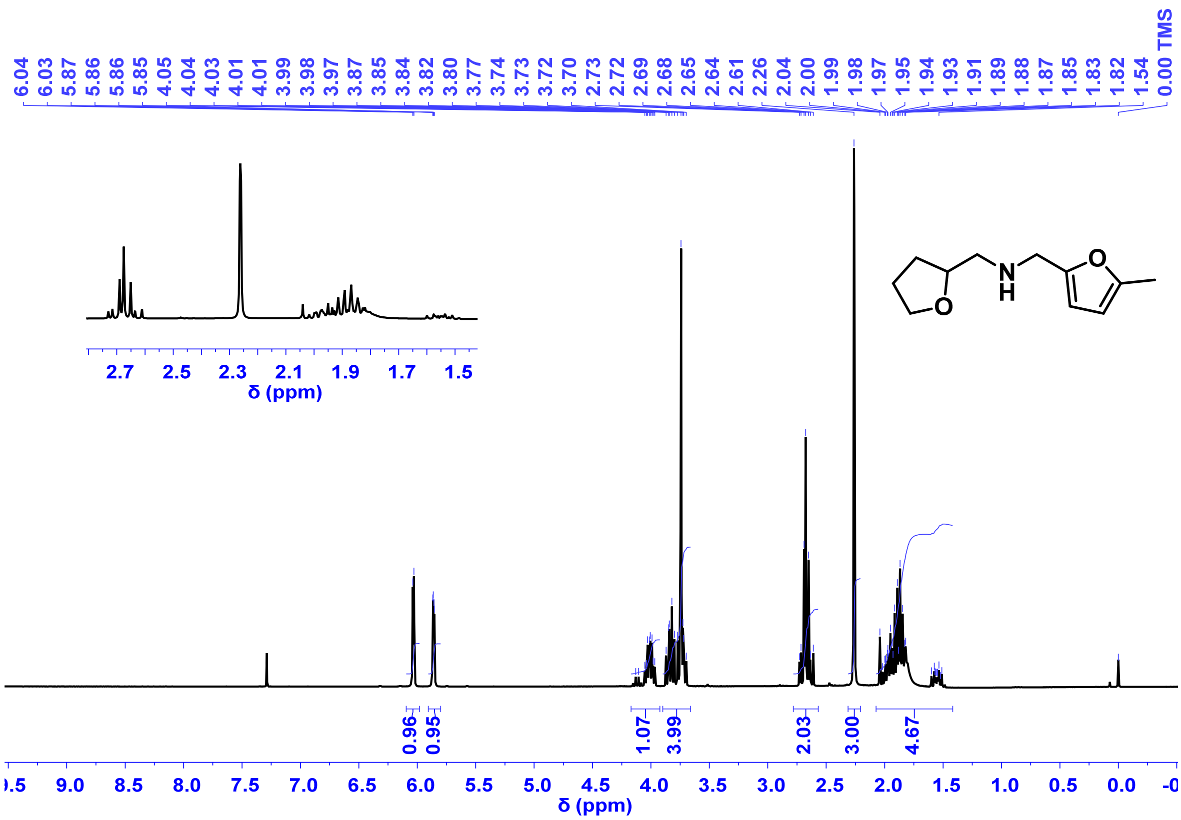


Fig. S5 ^{1}H and ^{13}C {^{1}H} NMR of *N*-[(tetrahydro-2-furanyl)methyl]-2-furanmethanamine **5a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.22 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.18 – 6.05 (m, 1H), 4.11 – 3.86 (m, 1H), 3.86 – 3.60 (m, 4H), 2.69 – 2.51 (m, 2H), 1.99 – 1.72 (m, 5H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 154.03, 141.77, 110.09, 106.84, 78.32, 67.94, 53.54, 46.39, 29.31, 25.81.



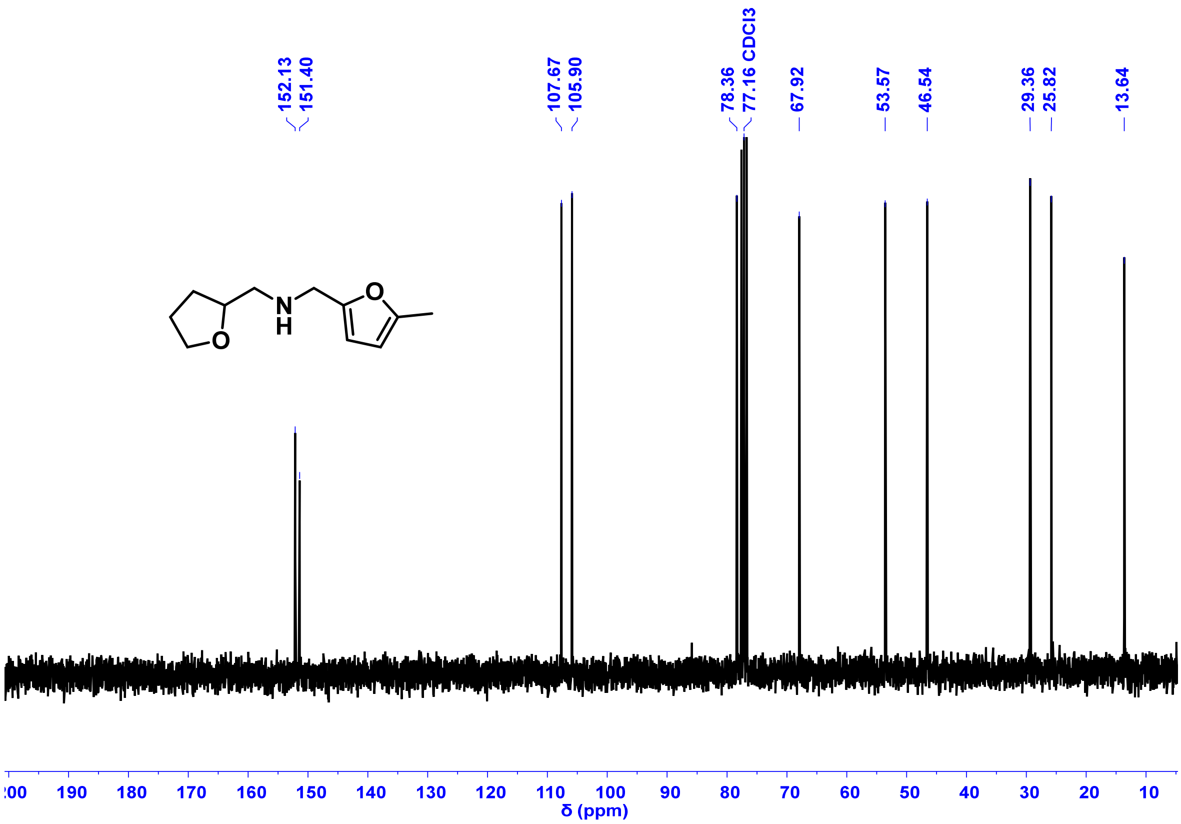


Fig. S6 ^{1}H and ^{13}C {^{1}H} NMR of 5-Methyl-*N*-[(tetrahydro-2-furanyl)methyl]-2-furanmethanamine **5b**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.03 (d, *J* = 3.0 Hz, 1H), 5.86 (dd, *J* = 3.0, 1.0 Hz, 1H), 4.17 – 3.92 (m, 1H), 3.90 – 3.66 (m, 4H), 2.78 – 2.57 (m, 2H), 2.26 (s, 3H), 2.07 – 1.42 (m, 5H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 152.13, 151.40, 107.67, 105.90, 78.36, 67.92, 53.57, 46.54, 29.36, 25.82, 13.64.

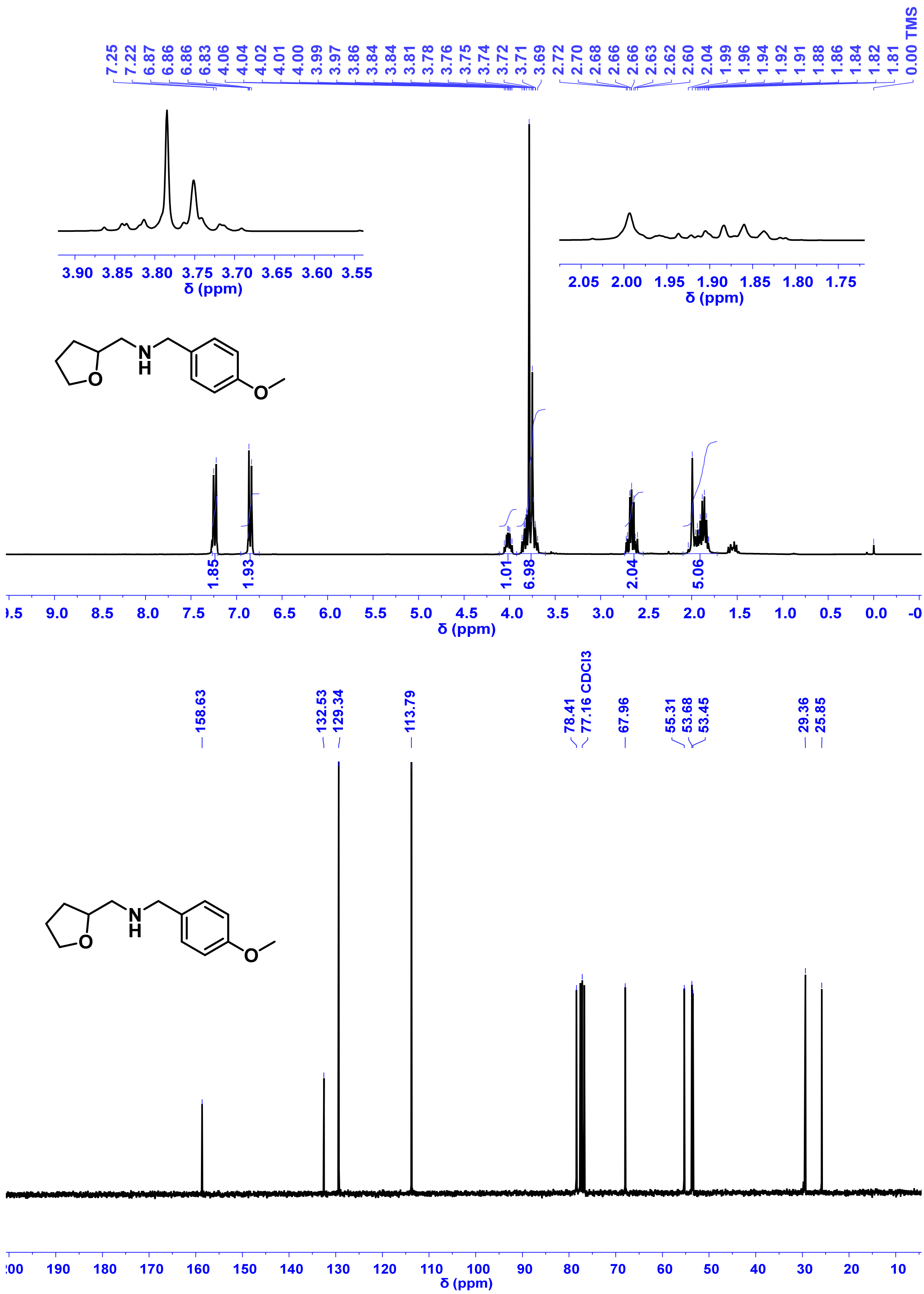
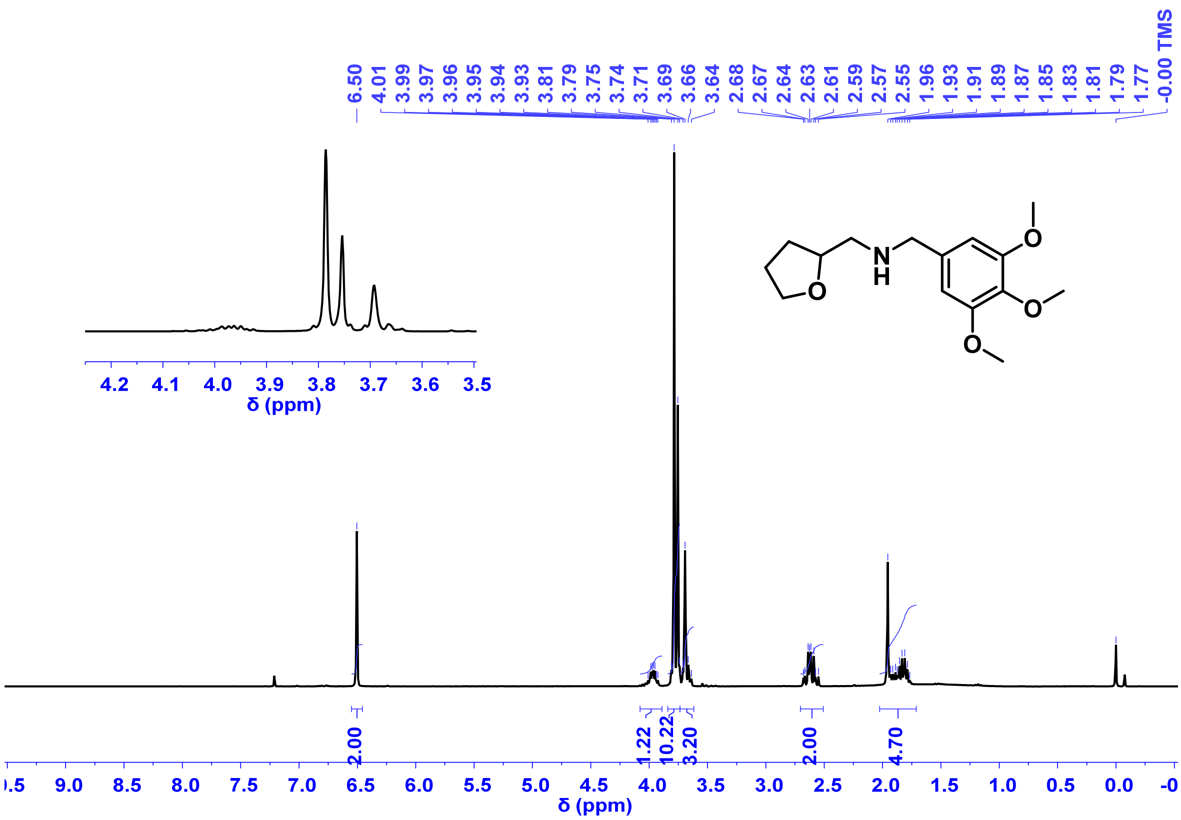


Fig. S7 ^{1}H and ^{13}C {^{1}H} NMR of tetrahydro-*N*-[(4-methoxyphenyl)methyl]-2-furanmethanamine **5c**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 8.5 Hz, 2H), 6.95 – 6.75 (m, 2H), 4.01 (tt, J = 7.3, 4.2 Hz, 1H), 3.92 – 3.61 (m, 7H), 2.74 – 2.53 (m, 2H), 2.10 – 1.72 (m, 5H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 158.63, 132.53, 129.34, 113.79, 78.41, 67.96, 55.31, 53.68, 53.45, 29.36, 25.85.



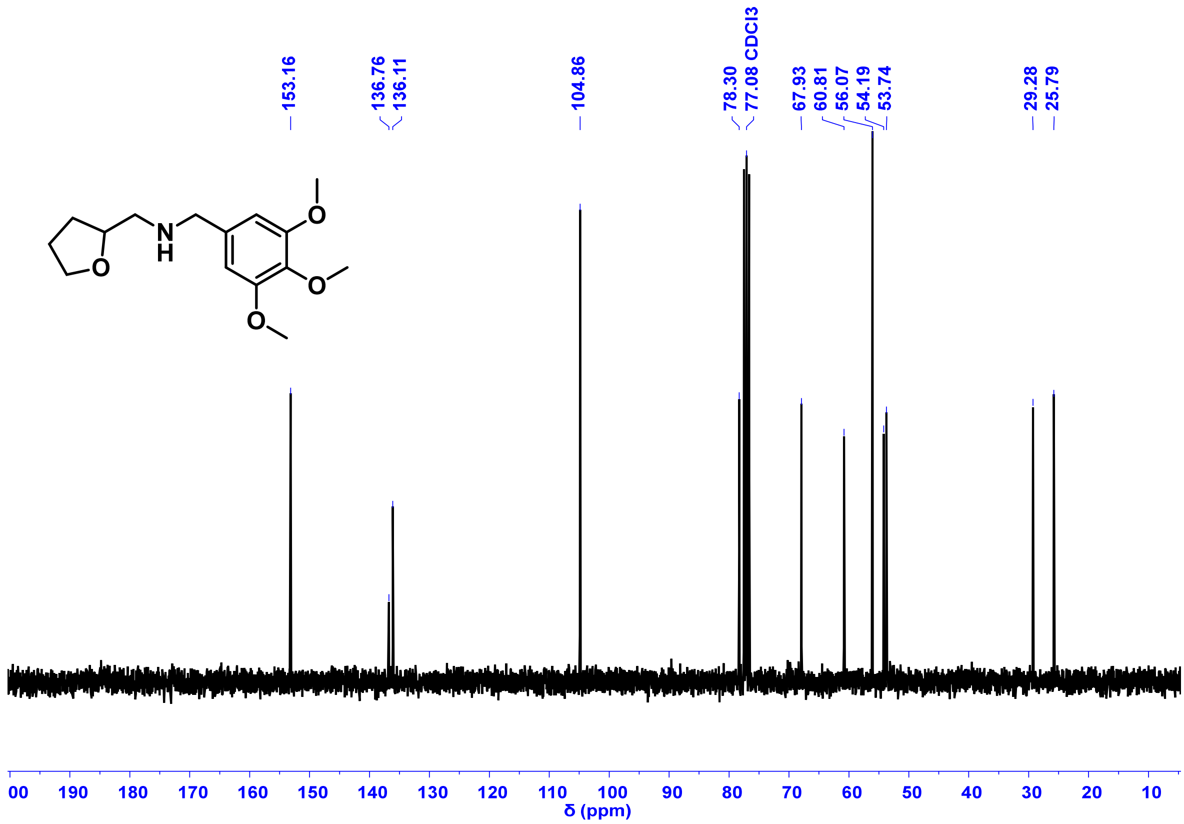
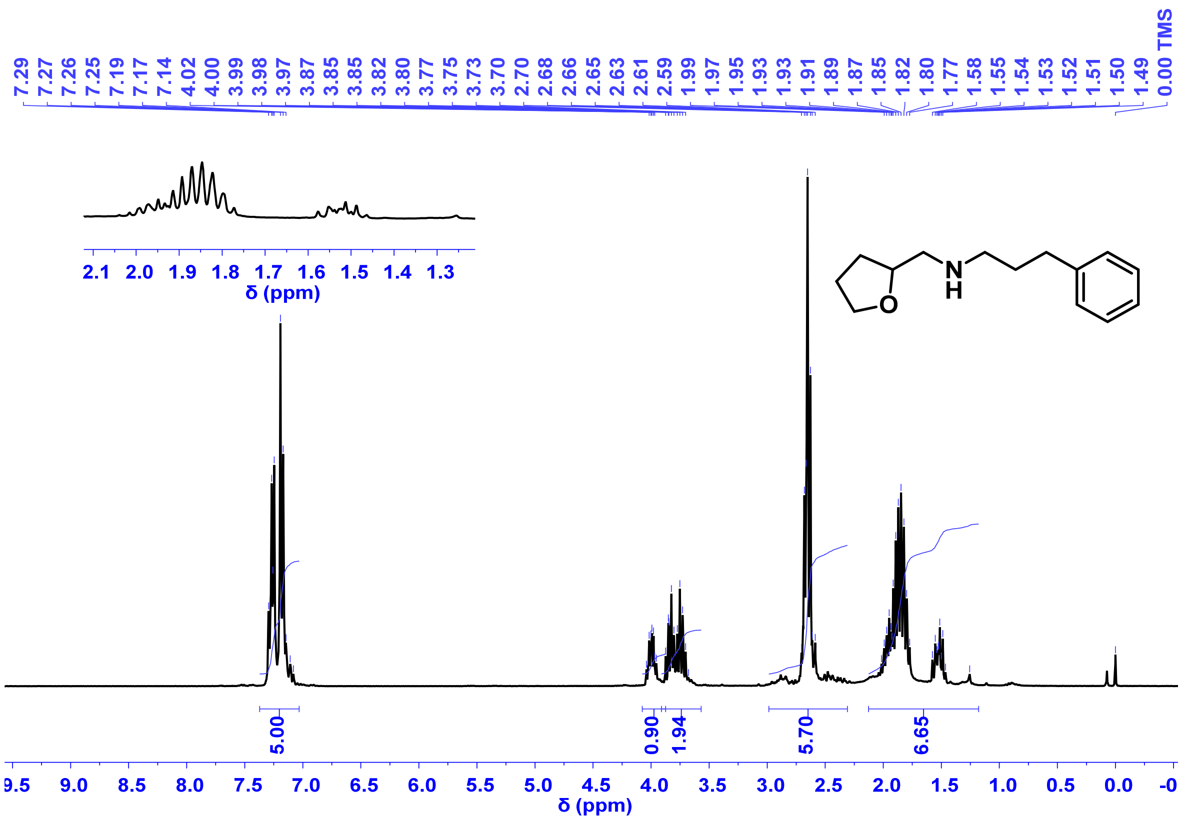


Fig. S8 ^{1}H and ^{13}C {^{1}H} NMR of tetrahydro-*N*-[(3,4,5-trimethoxyphenyl)methyl]-2-furanmethanamine **5d**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.50 (s, 2H), 3.96 (td, J = 7.2, 4.0 Hz, 1H), 3.77 (d, J = 9.5 Hz, 10H), 3.68 (d, J = 8.4 Hz, 3H), 2.70 – 2.51 (m, 2H), 2.02 – 1.71 (m, 5H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.16, 136.76, 136.11, 104.86, 78.30, 67.93, 60.81, 56.07, 54.19, 53.74, 29.28, 25.79.



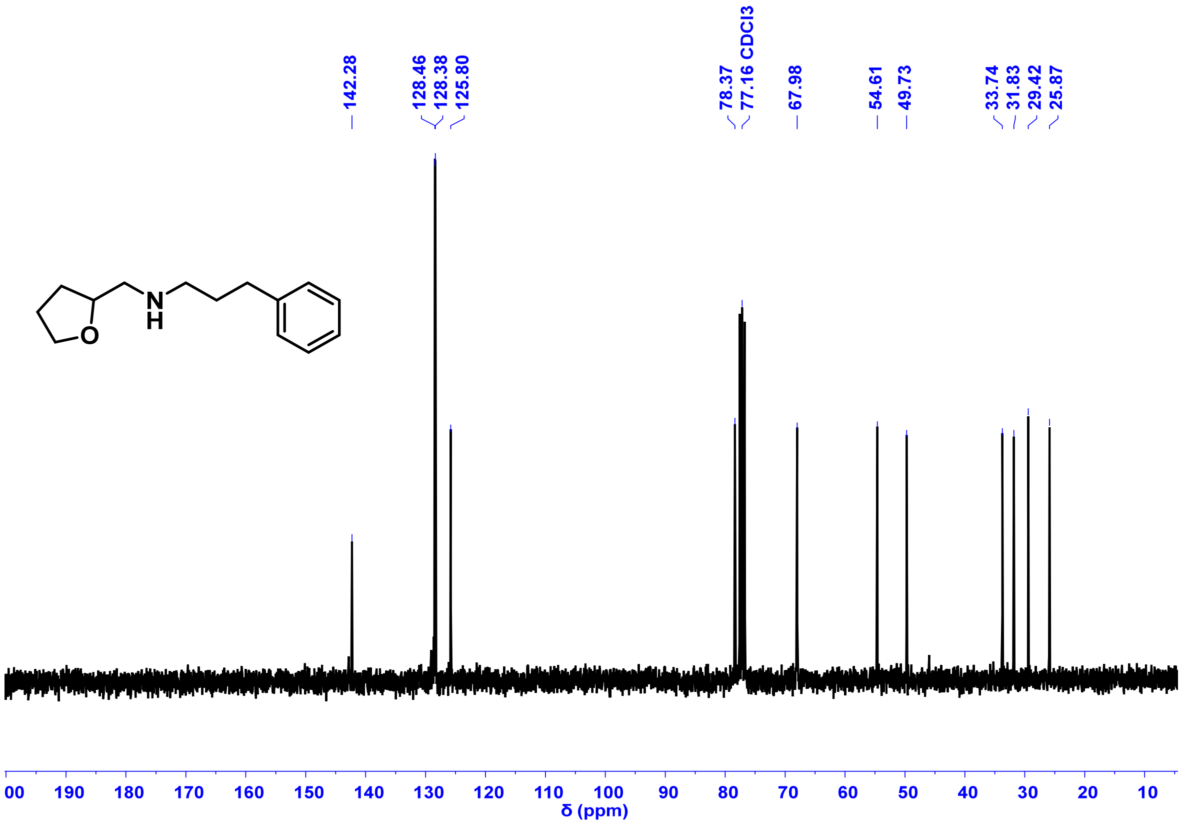
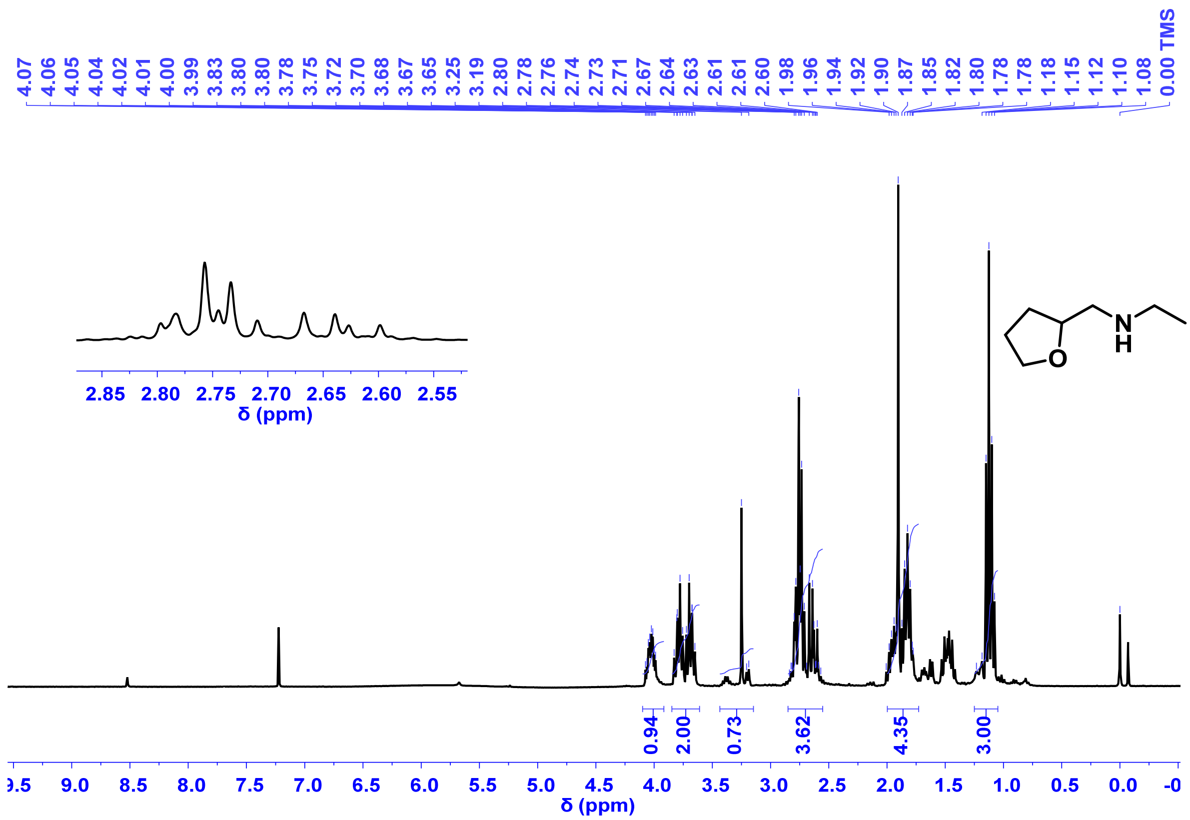


Fig. S9 ^{1}H and ^{13}C {^{1}H} NMR of 3-phenyl-*N*-((2-tetrahydrofuranyl)methyl)propan-1-amine **5e**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.03 (m, 5H), 3.99 (td, *J* = 7.2, 4.2 Hz, 1H), 3.91 – 3.57 (m, 2H), 2.99 – 2.31 (m, 6H), 2.13 – 1.18 (m, 7H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.28, 128.46, 128.38, 125.80, 78.37, 67.98, 54.61, 49.73, 33.74, 31.83, 29.42, 25.87.



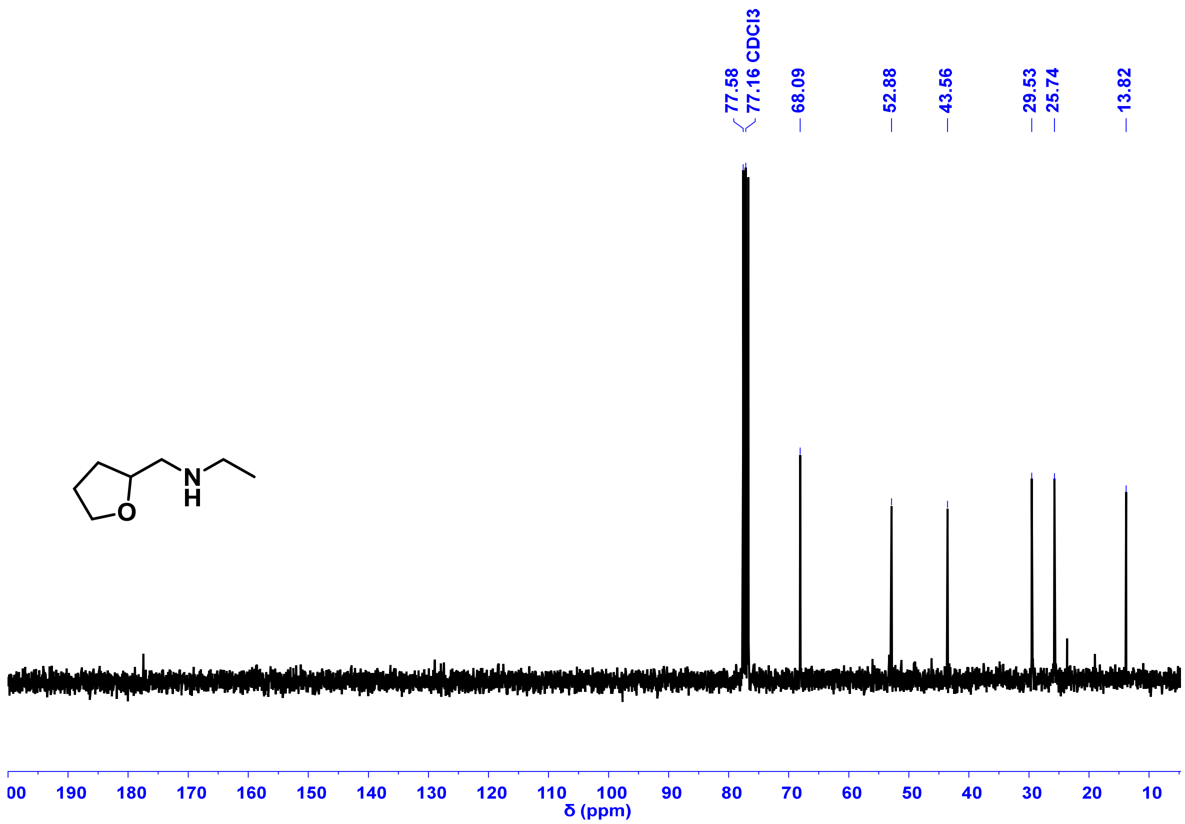
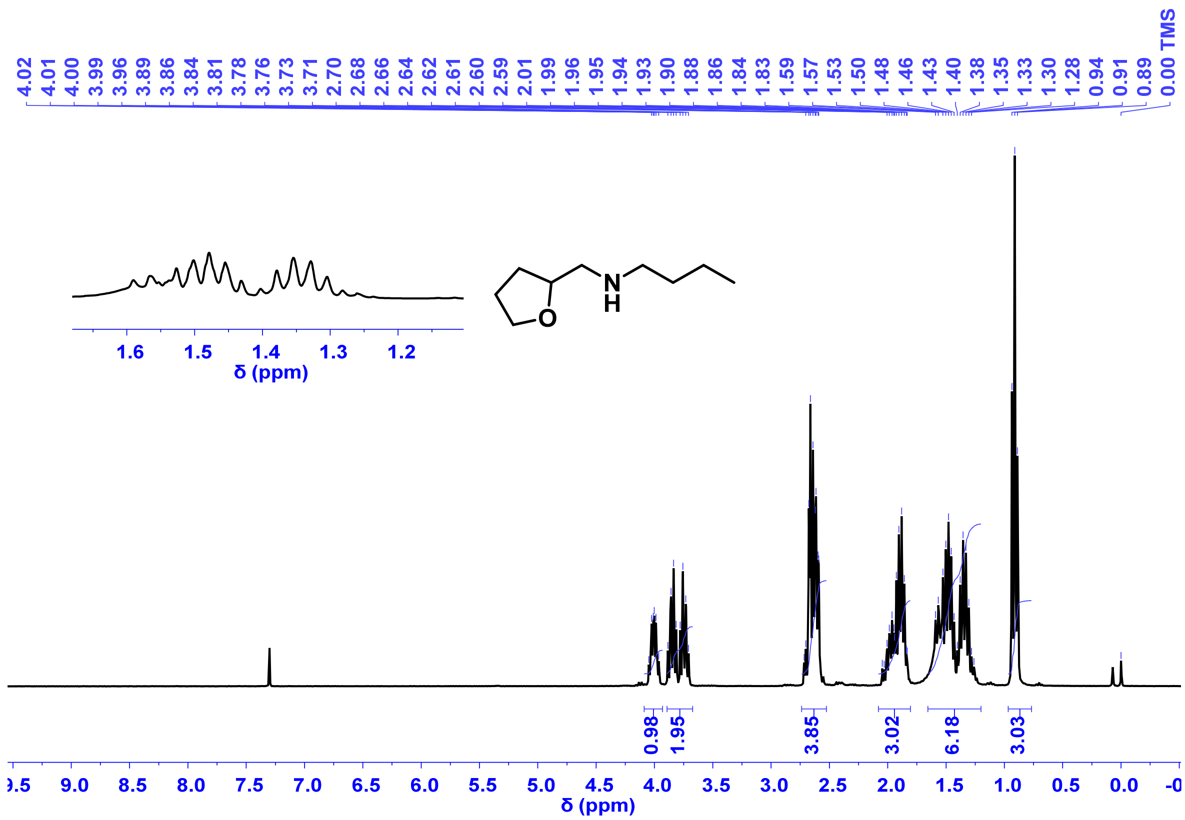


Fig. S10 ^{1}H and ^{13}C {^{1}H} NMR of *N*-ethyltetrahydro-2-furanmethanamine **5f**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (ddt, *J* = 10.8, 7.3, 3.5 Hz, 1H), 3.85 – 3.61 (m, 2H), 3.25 (s, 1H), 2.85 – 2.55 (m, 4H), 2.00 – 1.73 (m, 4H), 1.11 (q, *J* = 7.1 Hz, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 77.58, 68.09, 52.88, 43.56, 29.53, 25.74, 13.82.



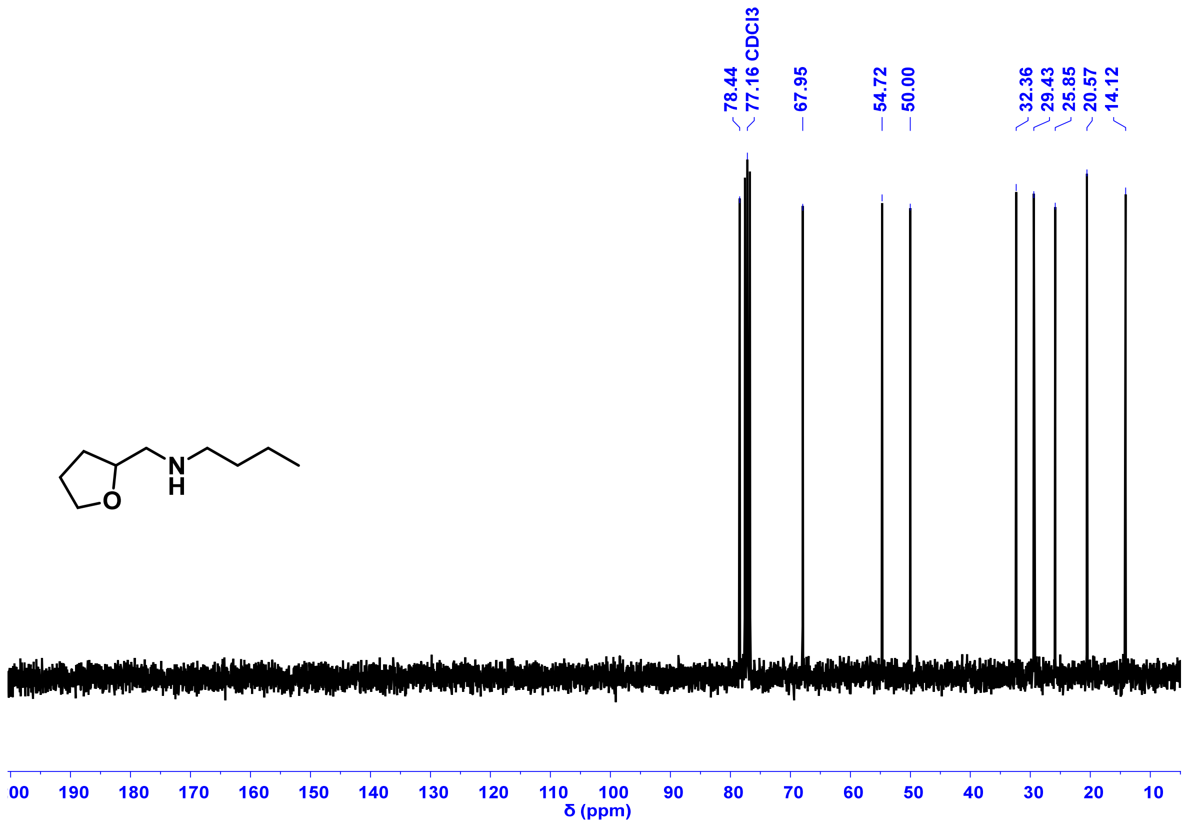


Fig. S11 ^{1}H and ^{13}C {^{1}H} NMR of *N*-butyltetrahydro-2-furanmethanamine **5g**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.00 (dt, *J* = 11.5, 5.7 Hz, 1H), 3.80 (dq, *J* = 31.9, 7.6, 7.0 Hz, 2H), 2.74 – 2.53 (m, 4H), 2.08 – 1.81 (m, 3H), 1.42 (dtt, *J* = 42.7, 13.2, 6.9 Hz, 6H), 0.91 (t, *J* = 7.2 Hz, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 78.44, 67.95, 54.72, 50.00, 32.36, 29.43, 25.85, 20.57, 14.12.

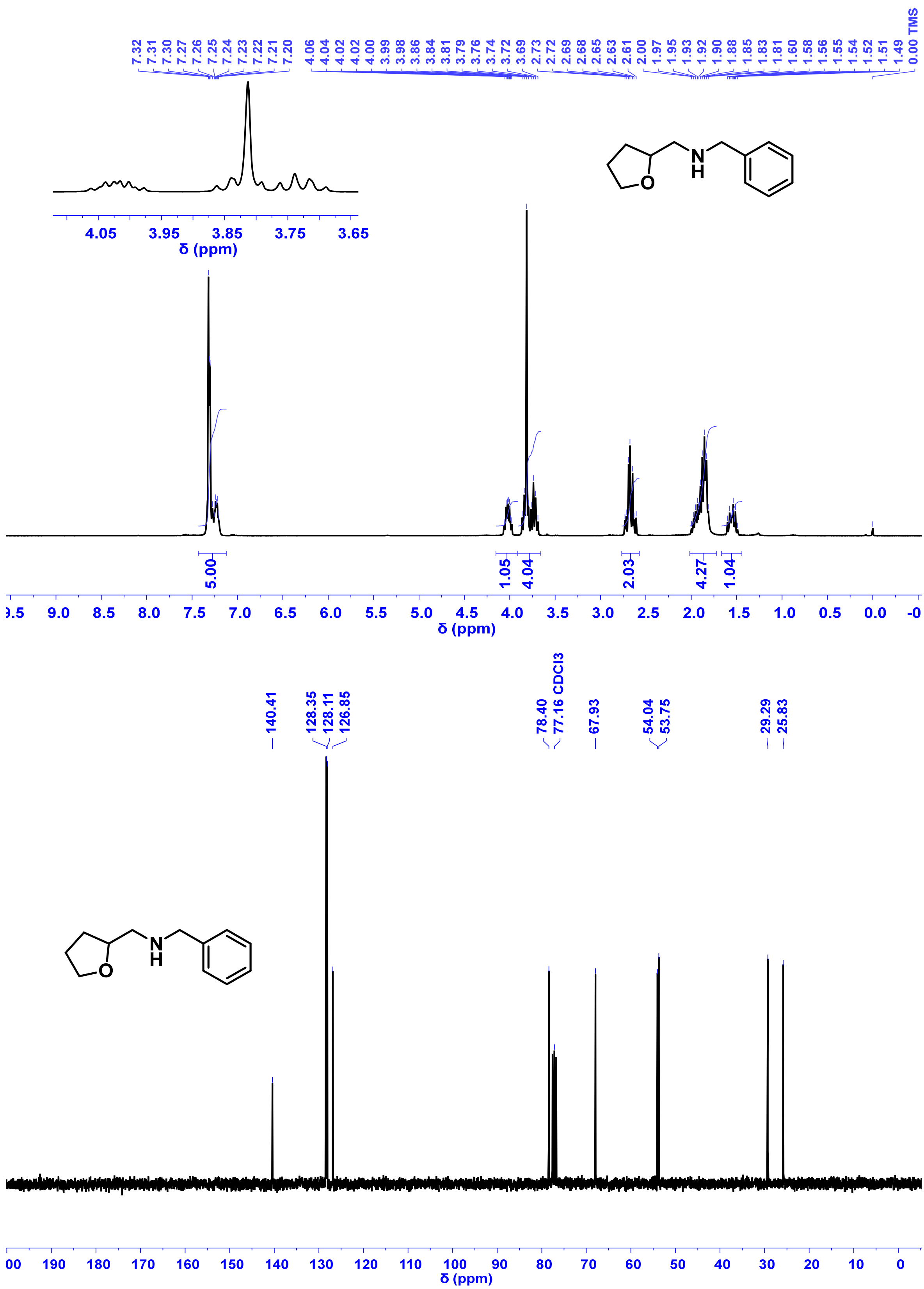
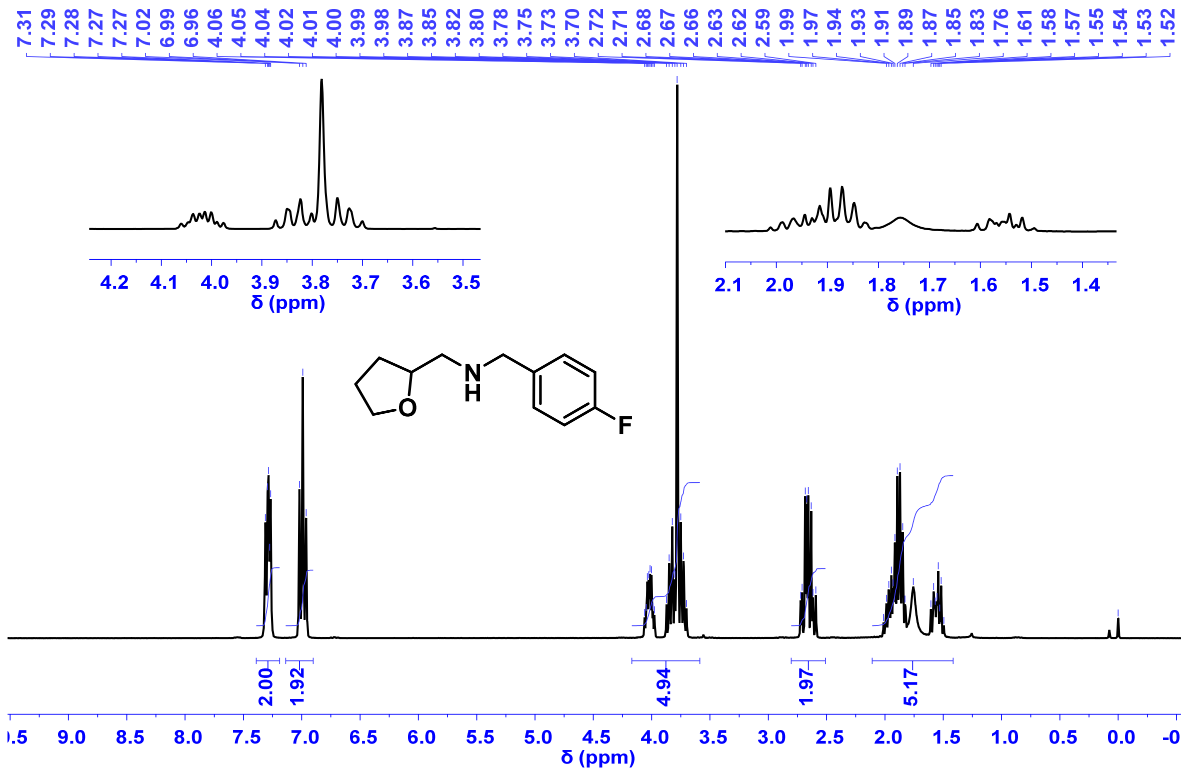


Fig. S12 ^{1}H and ^{13}C {^{1}H} NMR of tetrahydro-*N*-(phenylmethyl)-2-furanmethanamine **5h**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.12 (m, 5H), 4.01 (td, J = 7.1, 4.1 Hz, 1H), 3.91 – 3.66 (m, 4H), 2.77 – 2.57 (m, 2H), 1.89 (ddt, J = 25.9, 12.5, 6.2 Hz, 4H), 1.54 (dq, J = 10.6, 7.2 Hz, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 140.41, 128.35, 128.11, 126.85, 78.40, 67.93, 54.04, 53.75, 29.29, 25.83.



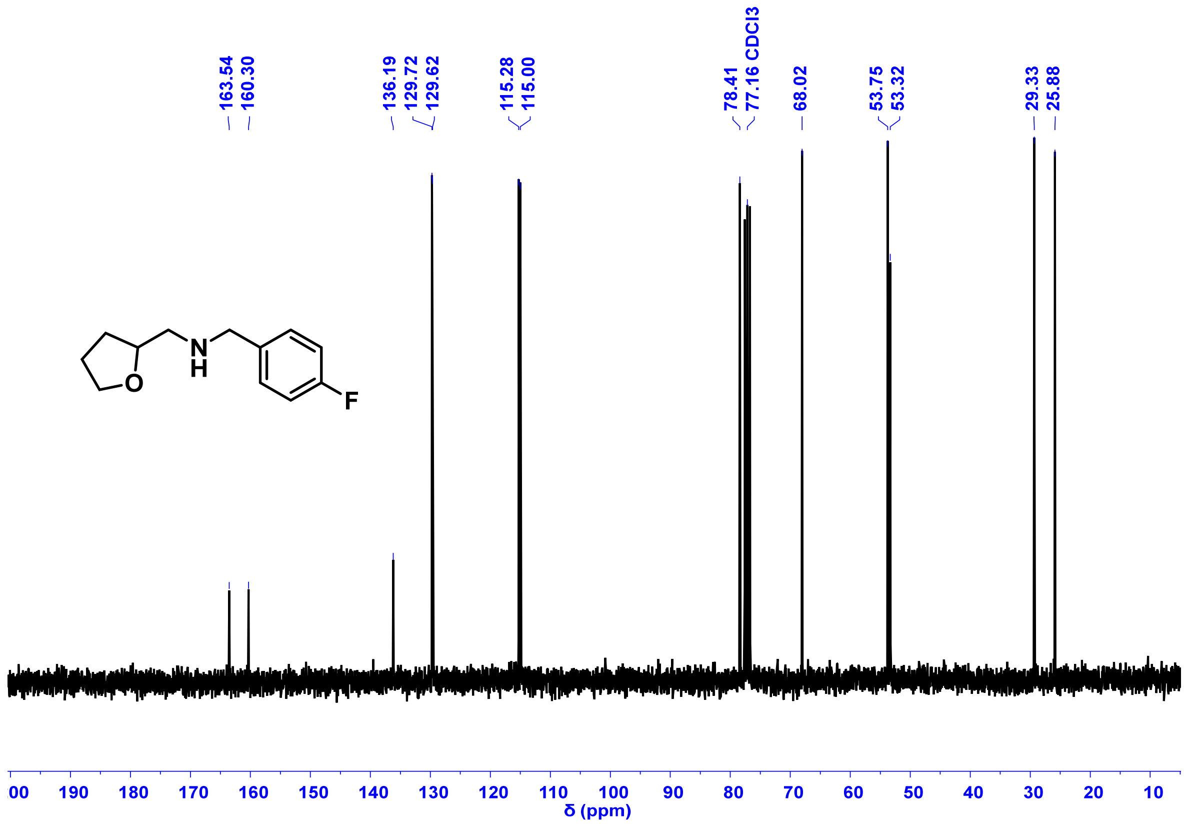
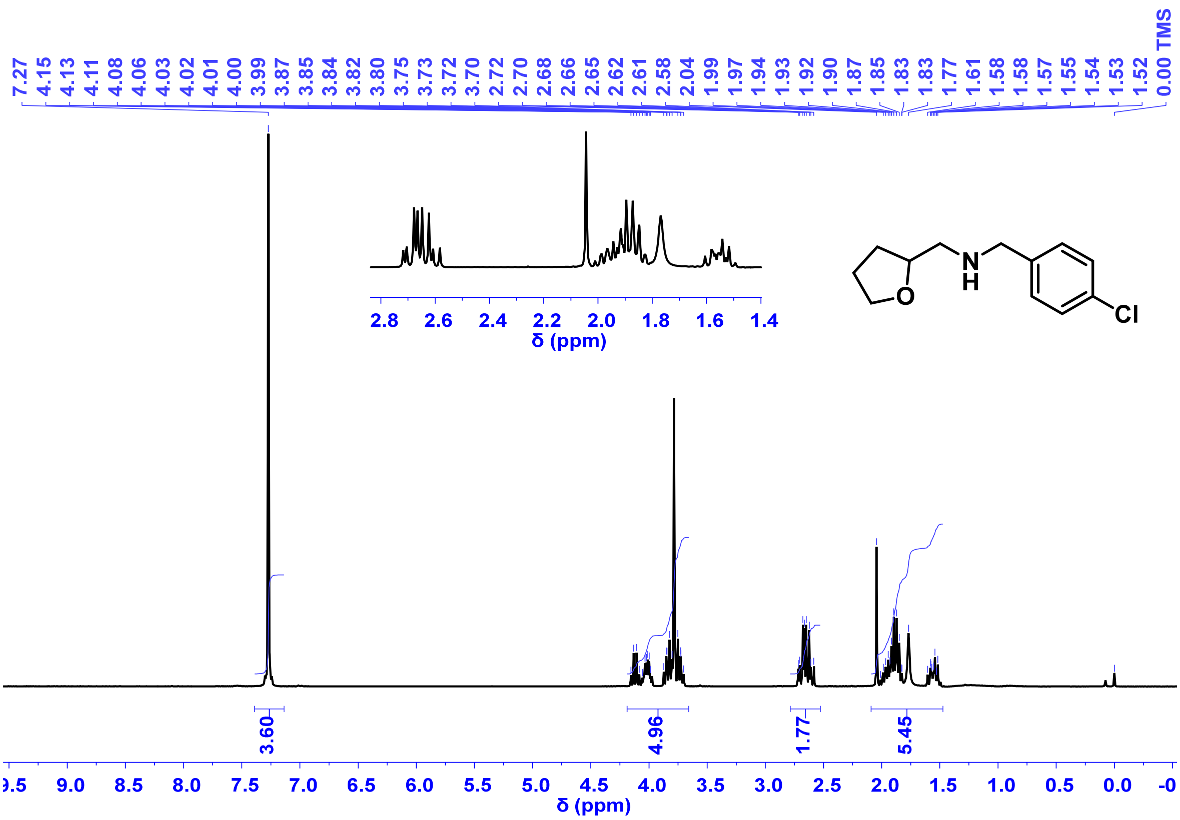


Fig. S13 ^{1}H and ^{13}C {^{1}H} NMR of *N*-[(4-fluorophenyl)methyl]tetrahydro-2-furanmethanamine **5i**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.19 (m, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 4.17 – 3.59 (m, 5H), 2.66 (qd, *J* = 11.9, 5.7 Hz, 2H), 2.11 – 1.41 (m, 5H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.54, 160.30, 136.19, 129.72, 129.62, 115.28, 115.00, 78.41, 68.02, 53.75, 53.32, 29.33, 25.88.



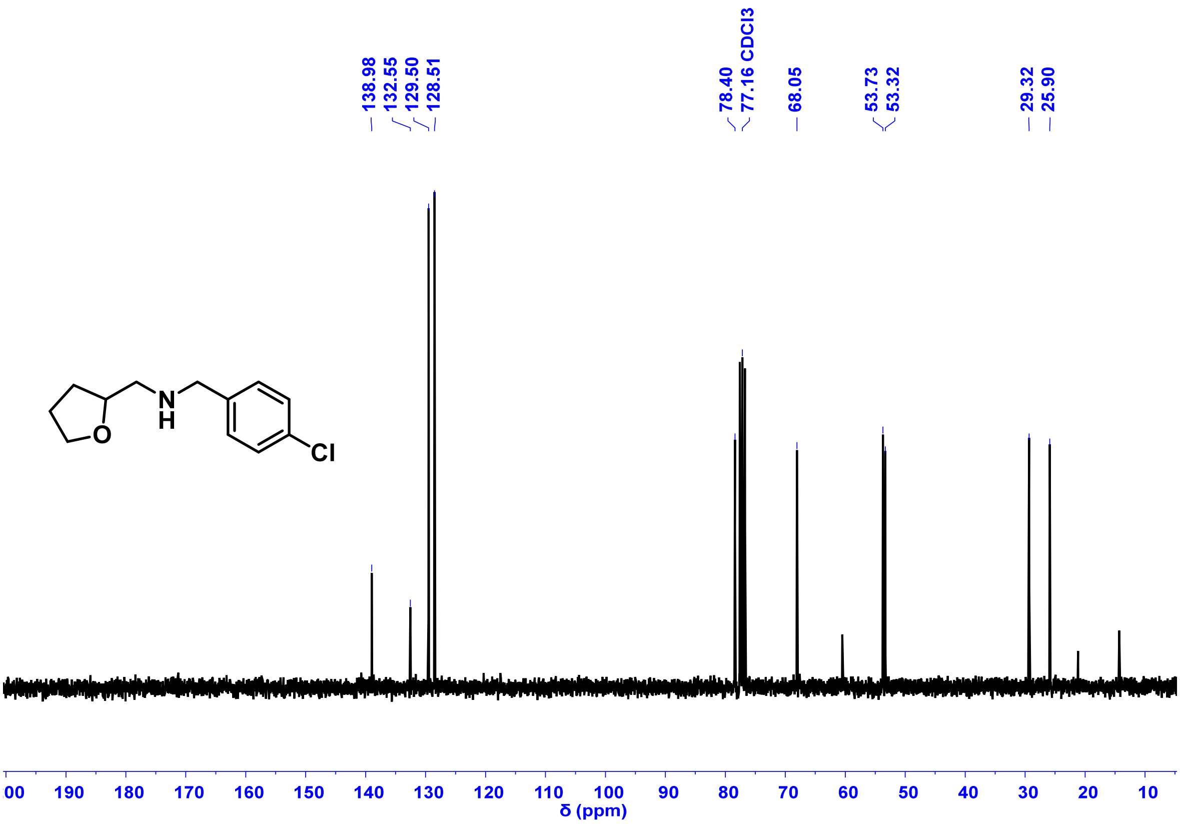


Fig. S14 ^{1}H and ^{13}C {^{1}H} NMR of *N*-[(4-chlorophenyl)methyl]tetrahydro-2-furanmethanamine **5j**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (s, 4H), 4.19 – 3.66 (m, 5H), 2.65 (qd, *J* = 11.9, 5.7 Hz, 2H), 2.09 – 1.47 (m, 5H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 138.98, 132.55, 129.50, 128.51, 78.40, 68.05, 53.73, 53.32, 29.32, 25.90.

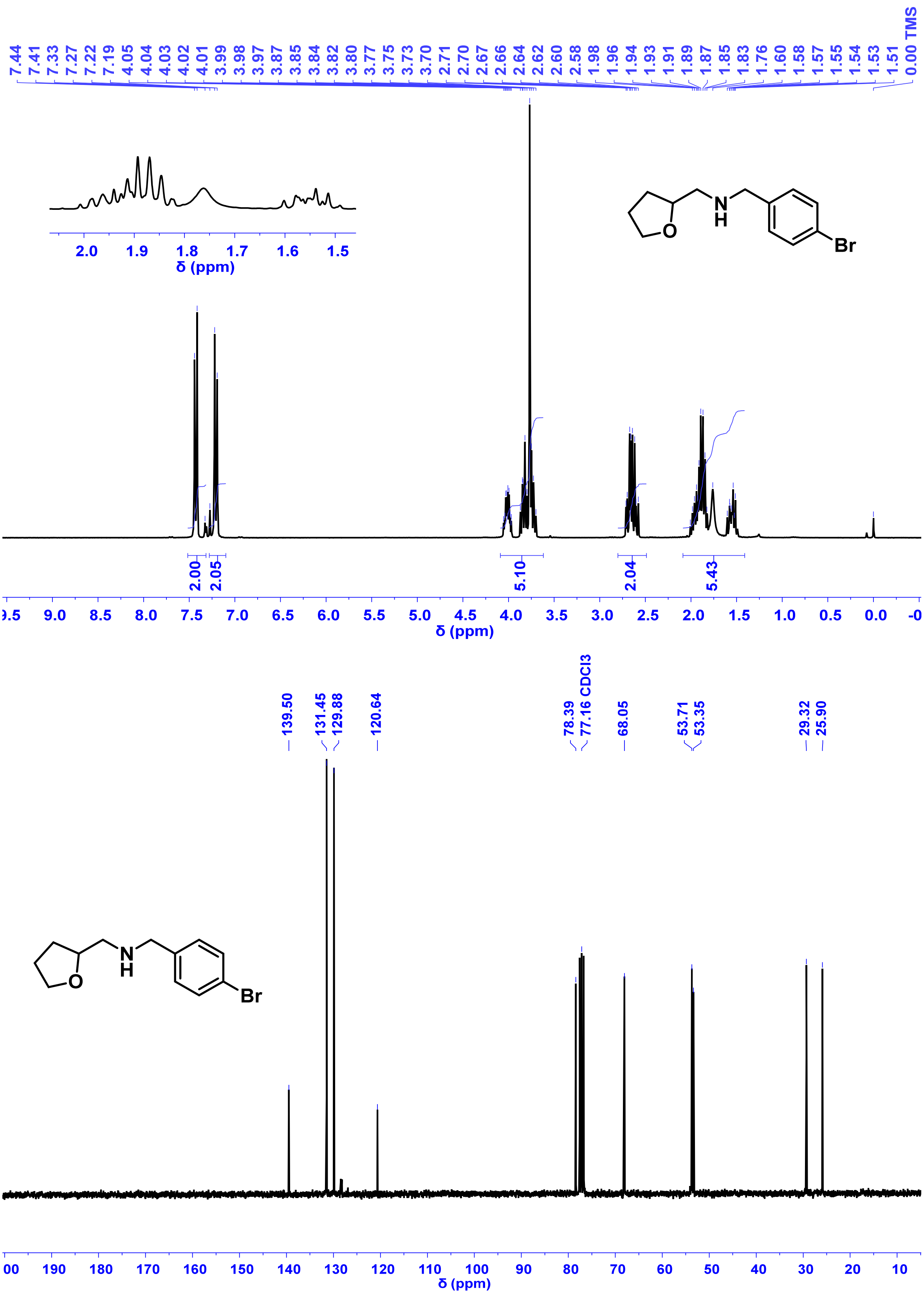


Fig. S15 ^{1}H and ^{13}C {^{1}H} NMR of *N*-[(4-bromophenyl)methyl]tetrahydro-2-furanmethanamine **5k**. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.43 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 4.09 – 3.62 (m, 5H), 2.65 (qd, *J* = 11.9, 5.7 Hz, 2H), 2.09 – 1.41 (m, 5H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ = 139.50, 131.45, 129.88, 120.64, 78.39, 68.05, 53.71, 53.35, 29.32, 25.90.

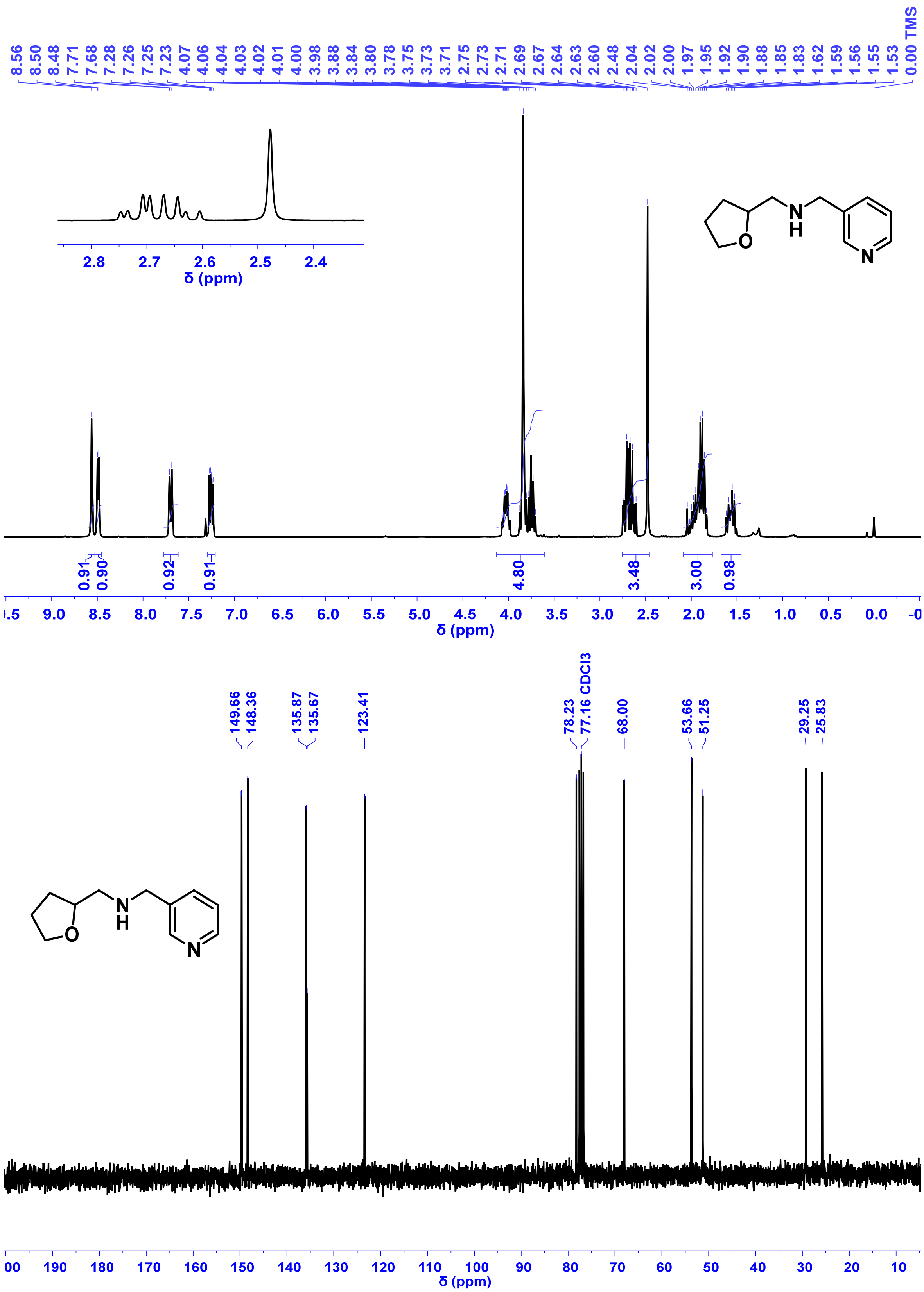


Fig. S16 ^{1}H and ^{13}C {^{1}H} NMR of *N*-[(tetrahydro-2-furanyl)methyl]-3-pyridinemethanamine **5l**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.49 (d, *J* = 4.7 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.25 (dd, *J* = 7.7, 4.8 Hz, 1H), 4.13 – 3.61 (m, 5H), 2.75 – 2.46 (m, 3H), 1.94 (dh, *J* = 26.6, 7.2, 6.5 Hz, 3H), 1.67 – 1.45 (m, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.66, 148.36, 135.87, 135.67, 123.41, 78.23, 68.00, 53.66, 51.25, 29.25, 25.83.

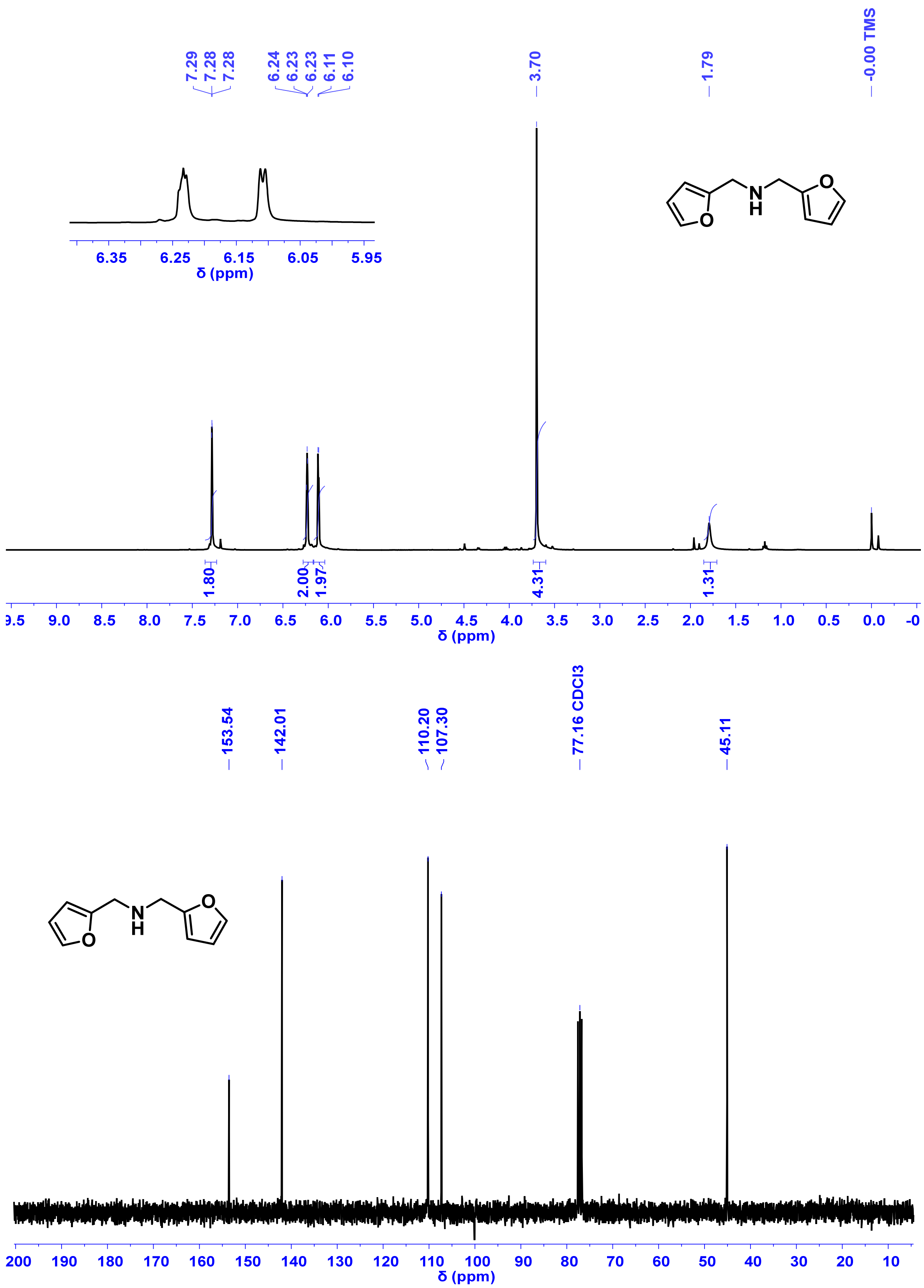
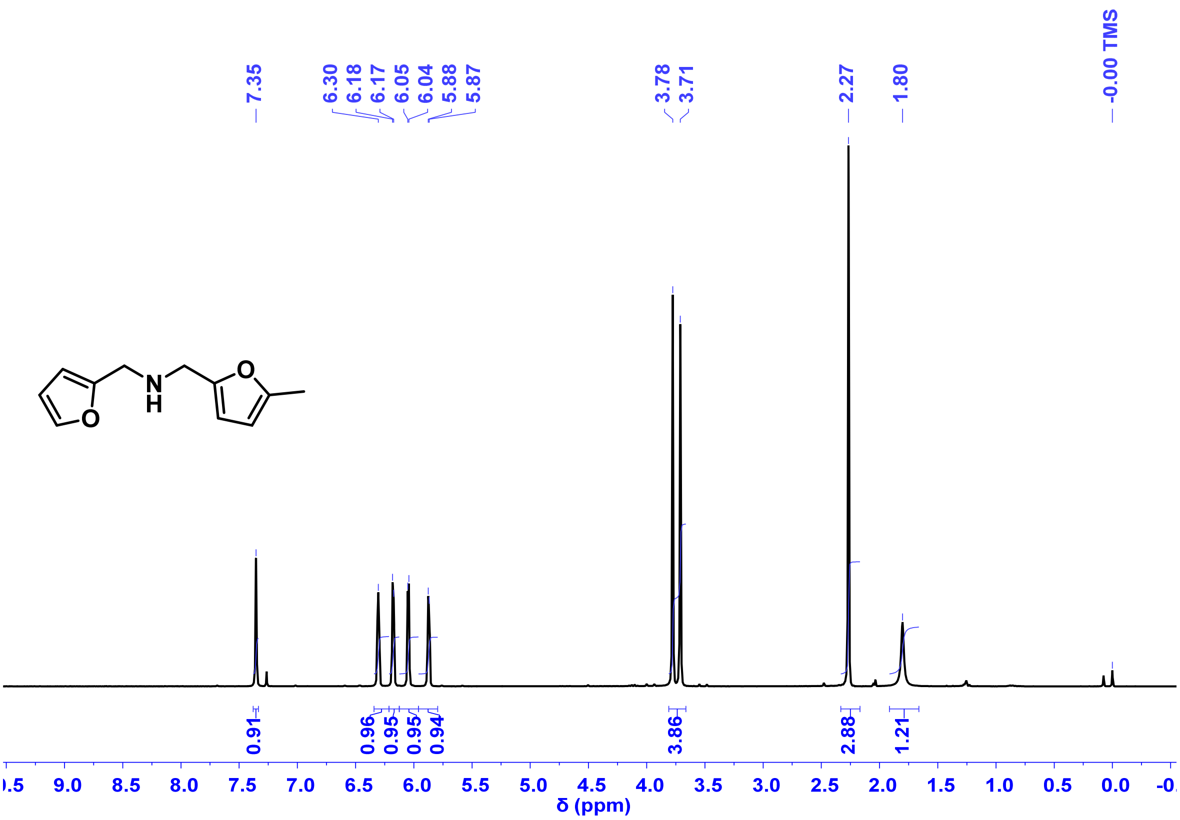


Fig. S17 ^{1}H and ^{13}C {^{1}H} NMR of *N*-(2-furanylmethyl)-2-furanmethanamine **5m**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.23 (m, 2H), 6.28 – 6.17 (m, 2H), 6.11 (d, J = 3.0 Hz, 2H), 3.70 (s, 4H), 1.79 (s, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.54, 142.01, 110.20, 107.30, 45.11.



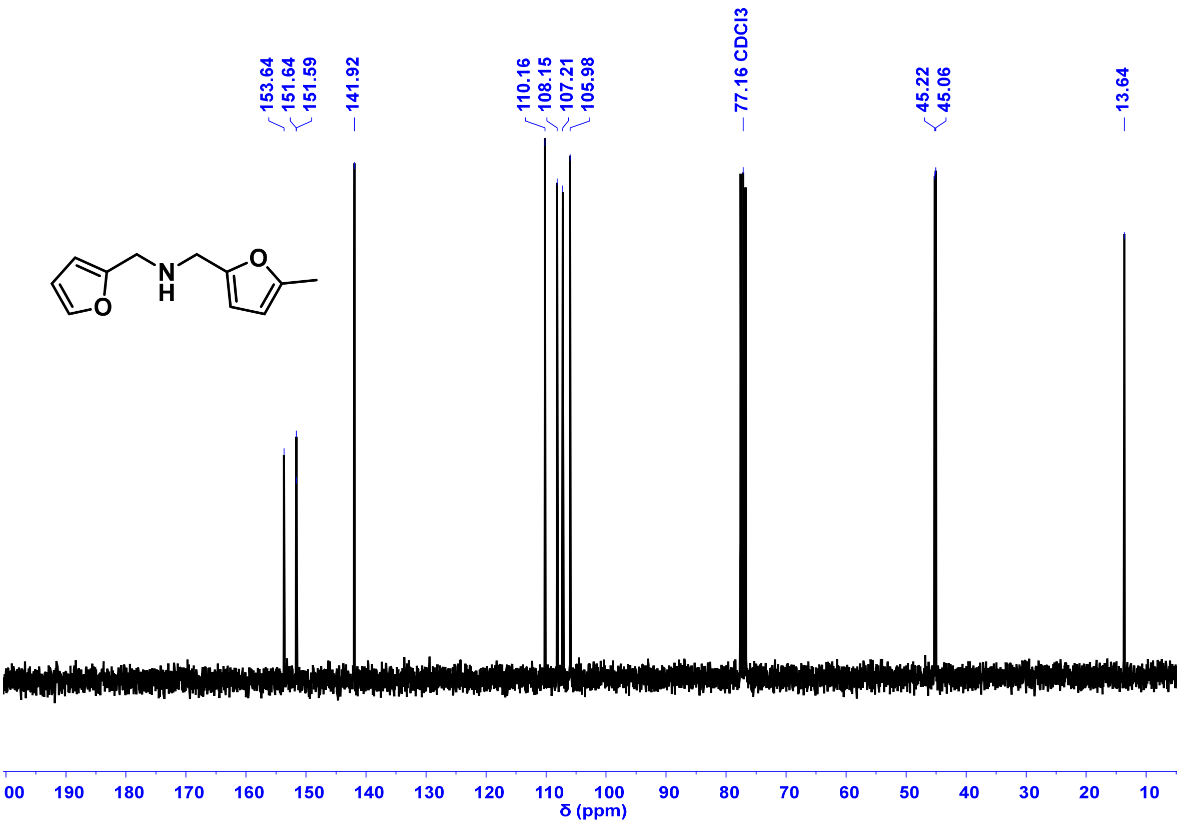


Fig. S18 [1]H and [13]C {[1]H} NMR of *N*-(2-furanylmethyl)-5-methyl-2-furanmethanamine **5n**. [1]H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 1H), 6.30 (s, 1H), 6.18 (d, J = 3.0 Hz, 1H), 6.05 (d, J = 2.9 Hz, 1H), 5.87 (d, J = 2.6 Hz, 1H), 3.74 (d, J = 19.6 Hz, 4H), 2.27 (s, 3H), 1.80 (s, 1H). [13]C {[1]H} NMR (75 MHz, $CDCl_3$) δ 153.64, 151.64, 151.59, 141.92, 110.16, 108.15, 107.21, 105.98, 45.22, 45.06, 13.64.

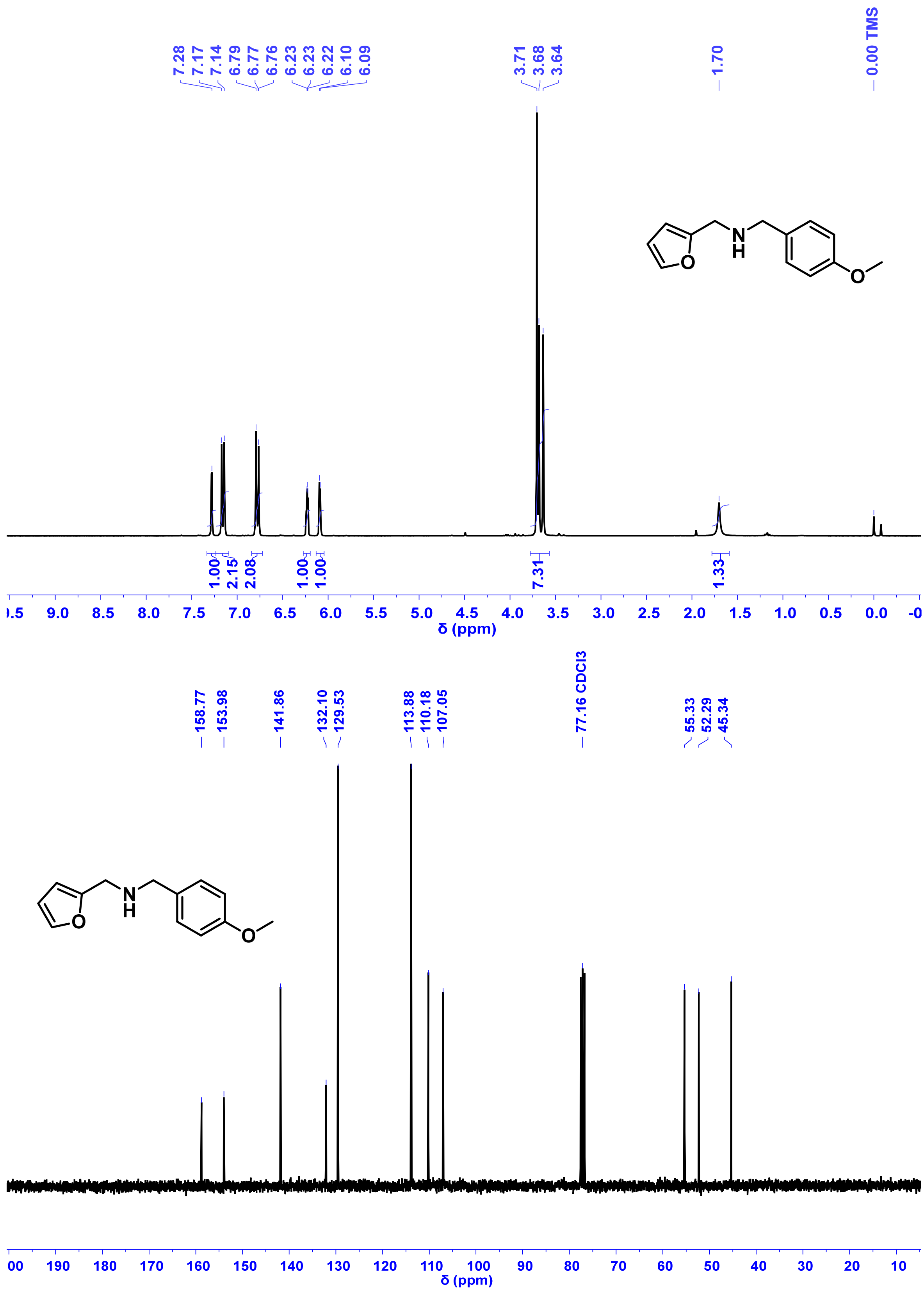


Fig. S19 [1]H and [13]C {[1]H} NMR of *N*-[(4-methoxyphenyl)methyl]-2-furanmethanamine **5o**. [1]H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.84 – 6.72 (m, 2H), 6.27 – 6.20 (m, 1H), 6.09 (d, *J* = 3.1 Hz, 1H), 3.78 – 3.57 (m, 7H), 1.70 (s, 1H). [13]C {[1]H} NMR (75 MHz, $CDCl_3$) δ 158.77, 153.98, 141.86, 132.10, 129.53, 113.88, 110.18, 107.05, 55.33, 52.29, 45.34.

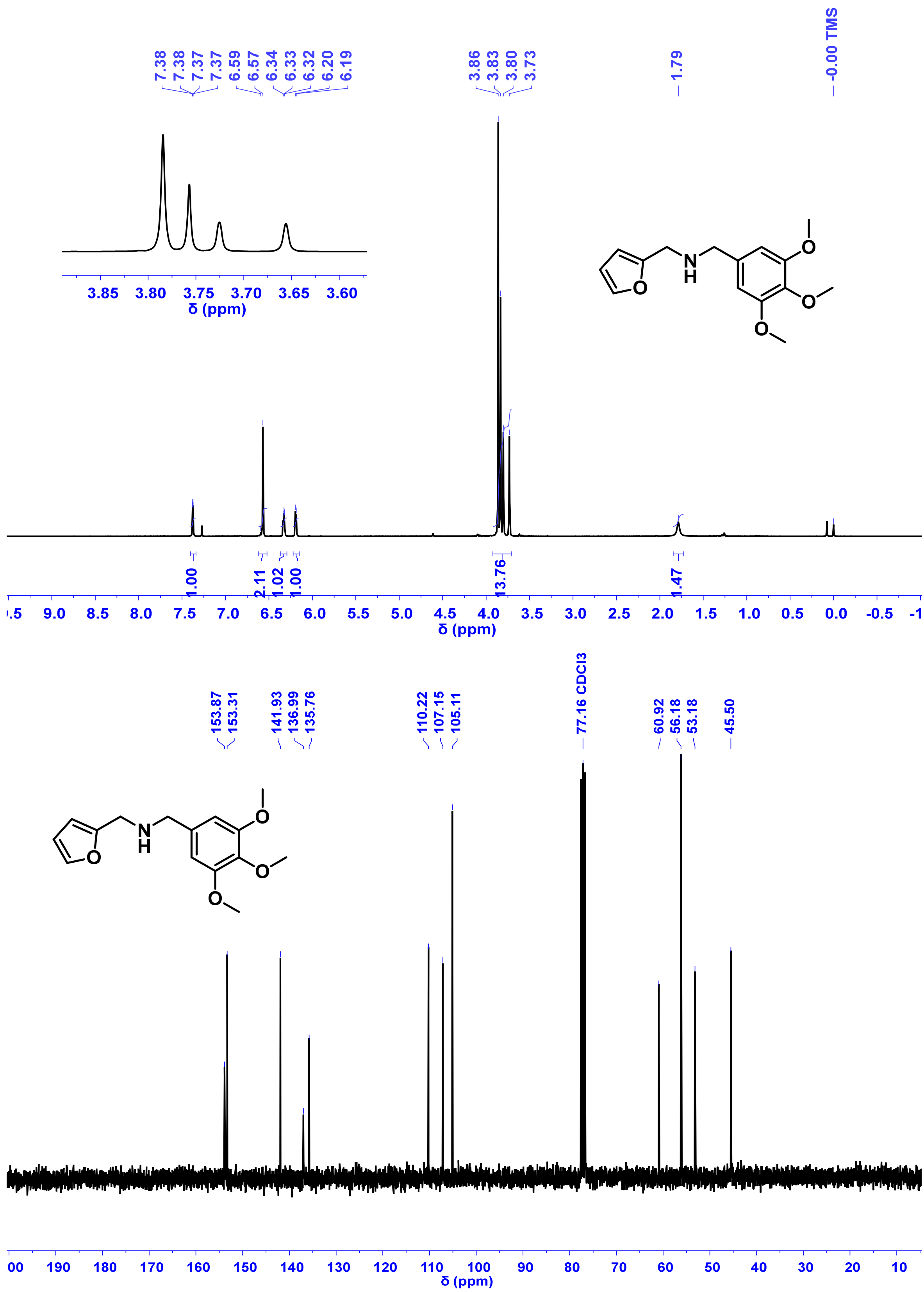
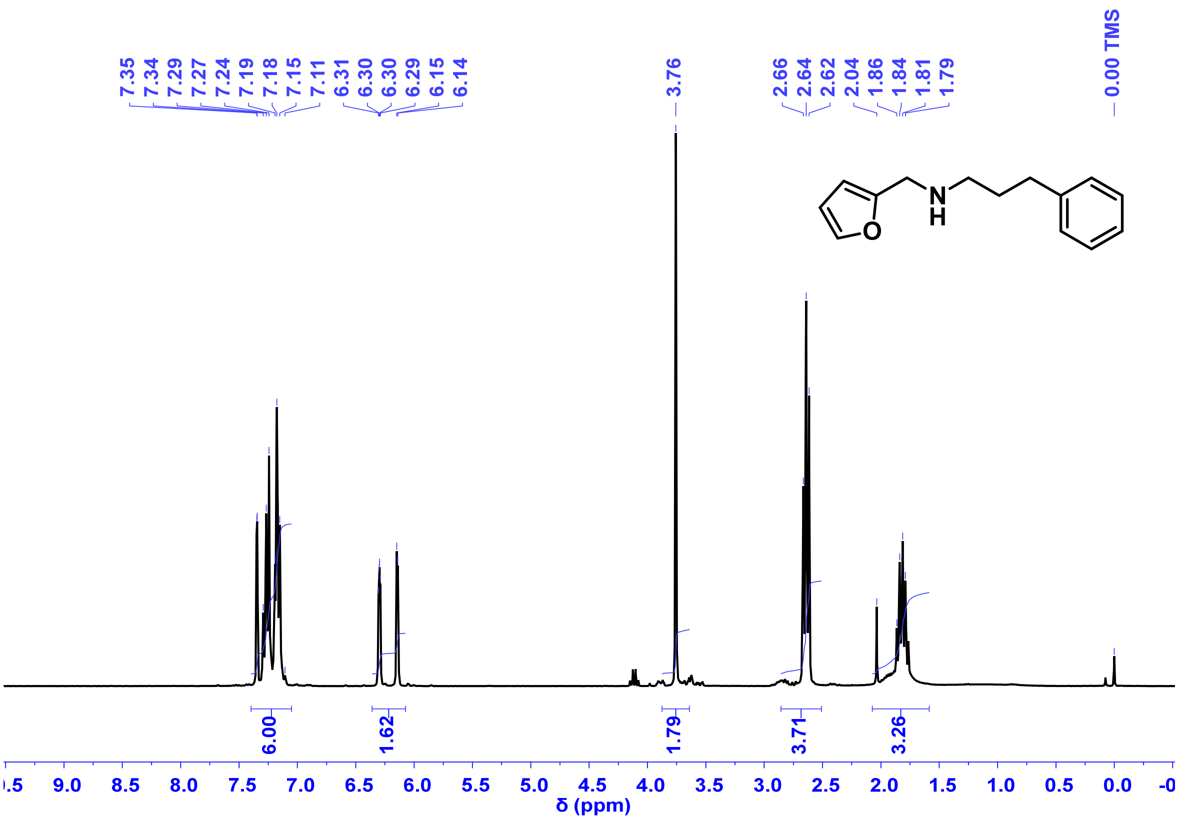


Fig. S20 ^{1}H and ^{13}C {^{1}H} NMR of *N*-[(3,4,5-trimethoxyphenyl)methyl]-2-furanmethanamine **5p**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 1.8, 0.7 Hz, 1H), 6.57 (s, 2H), 6.37 – 6.29 (m, 1H), 6.19 (d, *J* = 3.1 Hz, 1H), 3.92 – 3.71 (m, 14H), 1.79 (s, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.87, 153.31, 141.93, 136.99, 135.76, 110.22, 107.15, 105.11, 60.92, 56.18, 53.18, 45.50.



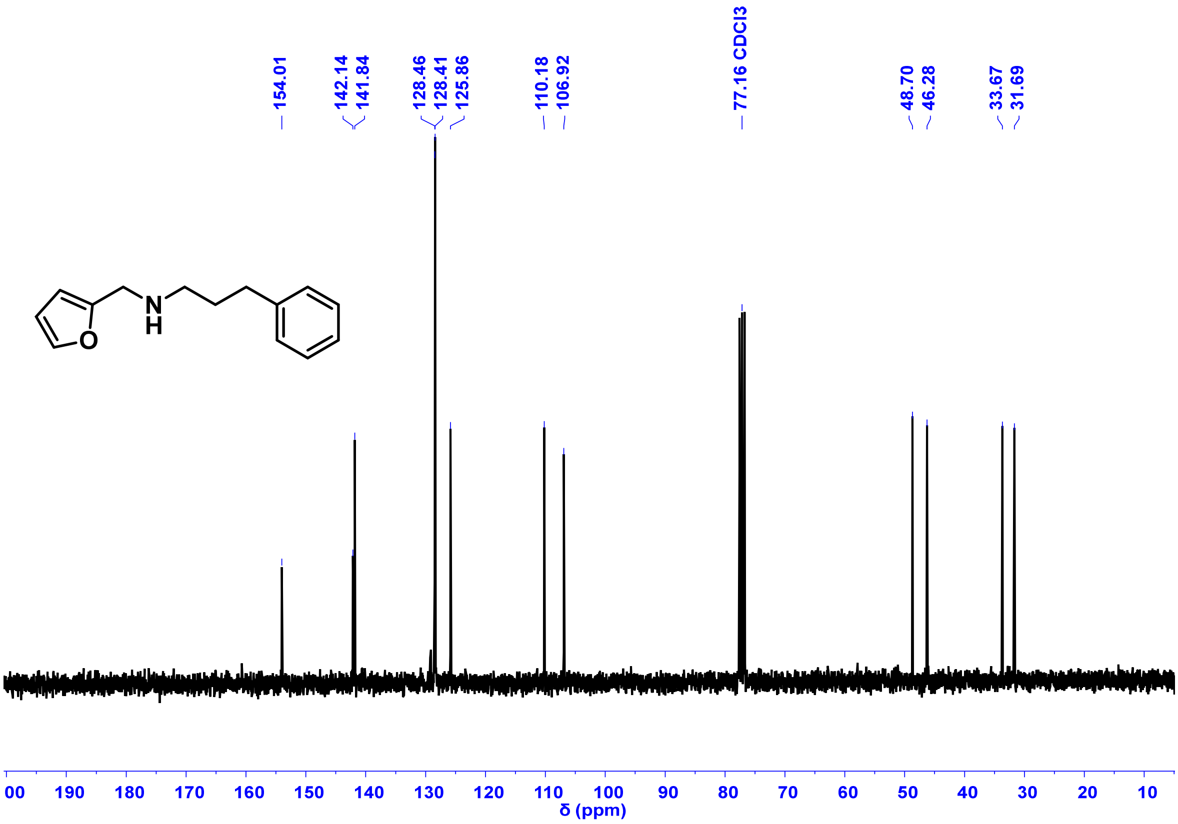
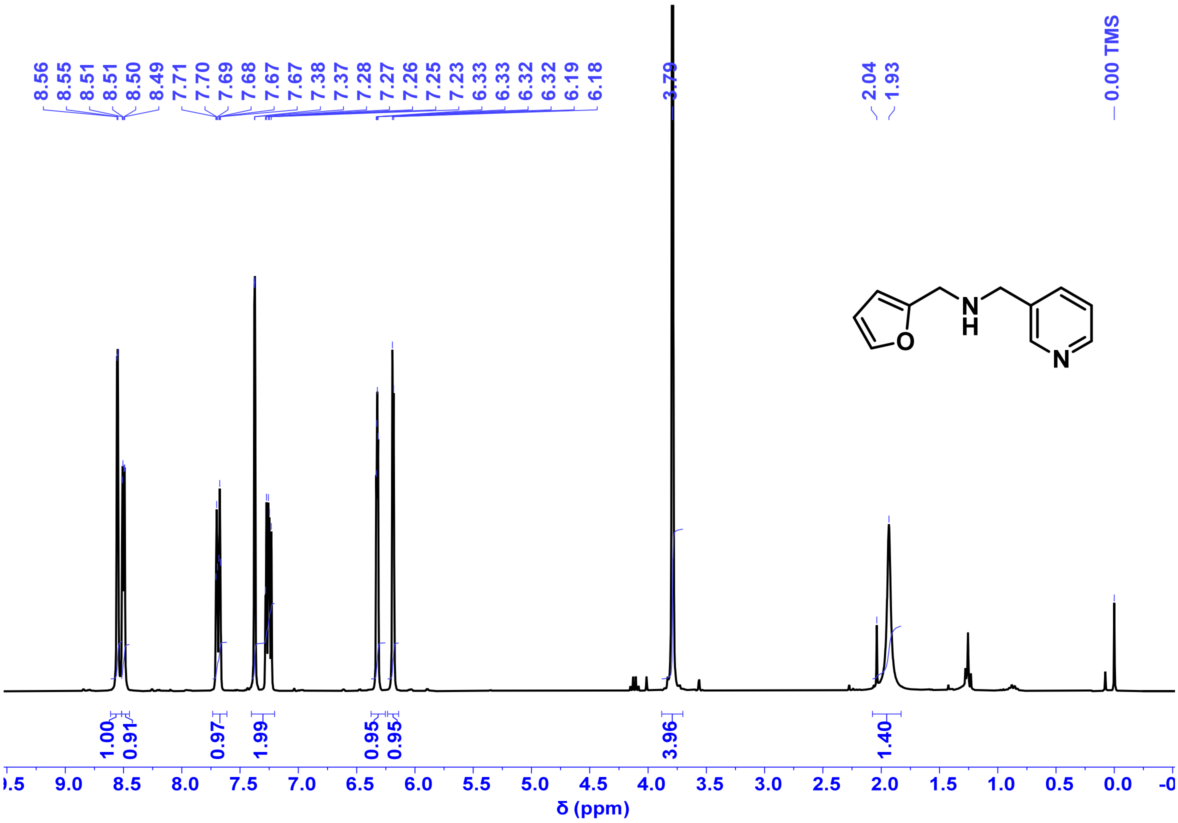


Fig. S21 ^{1}H and ^{13}C {^{1}H} NMR of *N*-(3-phenylpropyl)-2-furanmethanamine **5q**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.05 (m, 6H), 6.36 – 6.07 (m, 2H), 3.76 (s, 2H), 2.64 (t, J = 7.3 Hz, 4H), 2.07 – 1.59 (m, 3H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 154.01, 142.14, 141.84, 128.46, 128.41, 125.86, 110.18, 106.92, 48.70, 46.28, 33.67, 31.69.



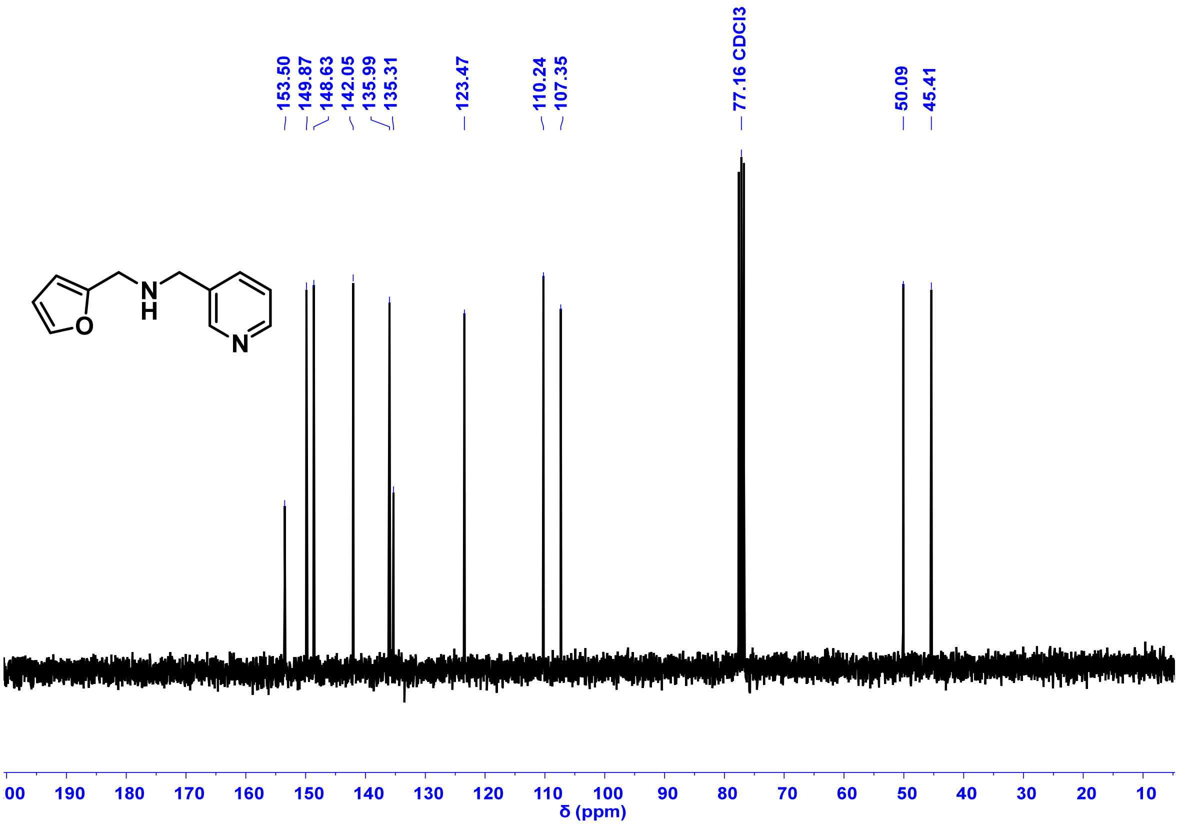
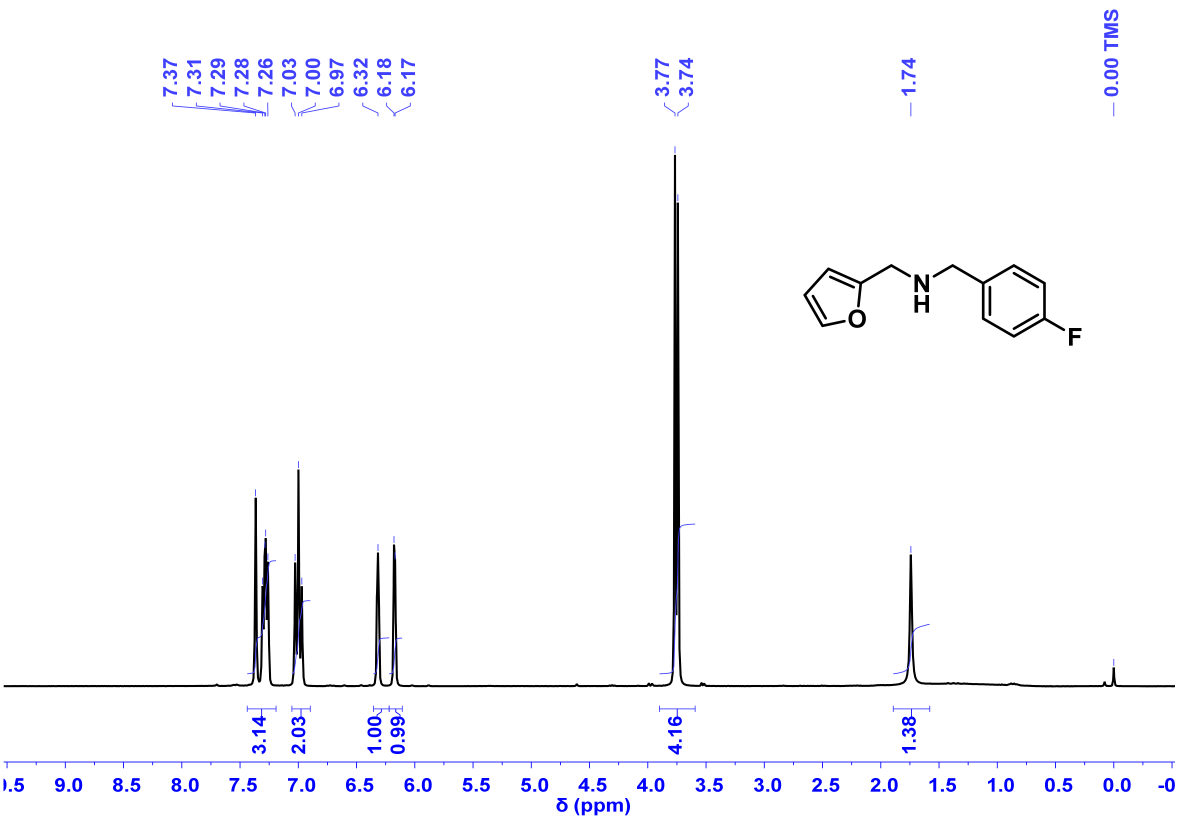


Fig. S22 ^{1}H and ^{13}C {^{1}H} NMR of *N*-(2-furanylmethyl)-3-pyridinemethanamine **5r**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.2 Hz, 1H), 8.50 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.69 (dt, *J* = 7.9, 2.0 Hz, 1H), 7.40 – 7.20 (m, 2H), 6.32 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.19 (d, *J* = 3.2 Hz, 1H), 3.79 (s, 4H), 1.99 (d, *J* = 31.3 Hz, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 153.50, 149.87, 148.63, 142.05, 135.99, 135.31, 123.47, 110.24, 107.35, 50.09, 45.41.



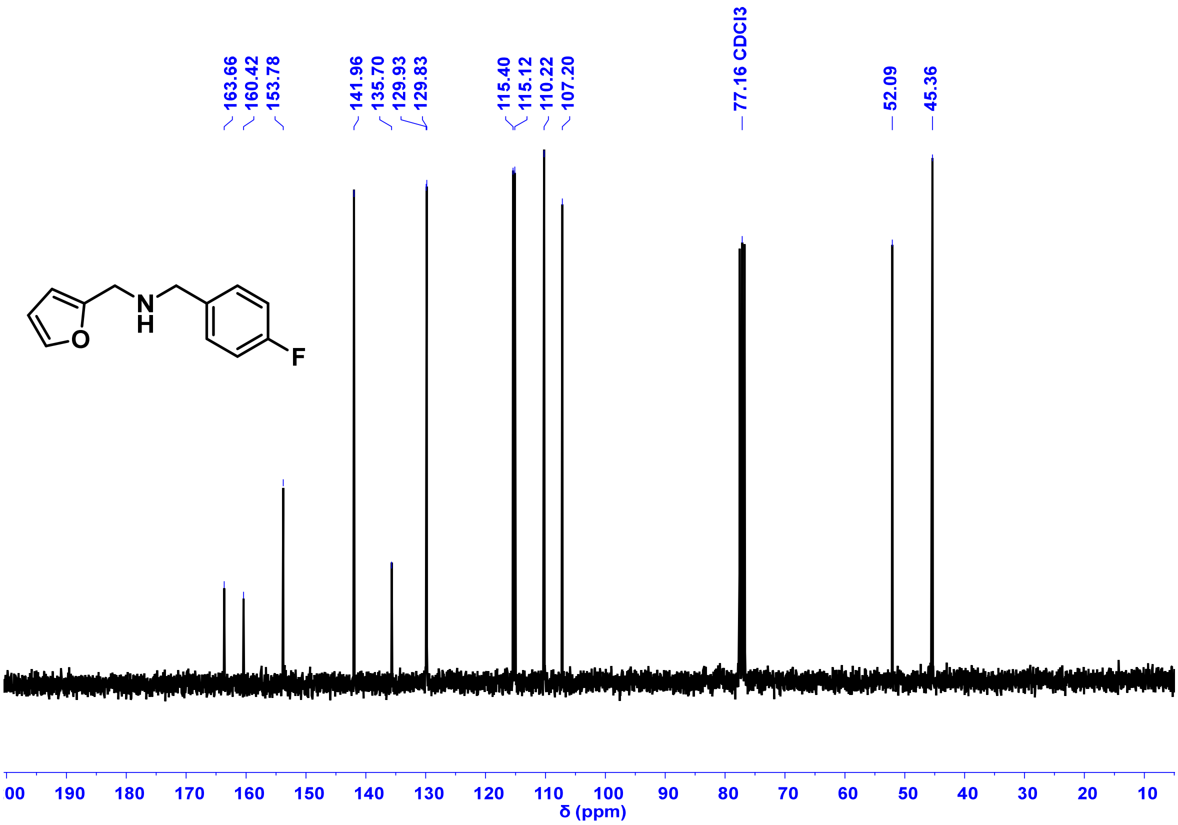
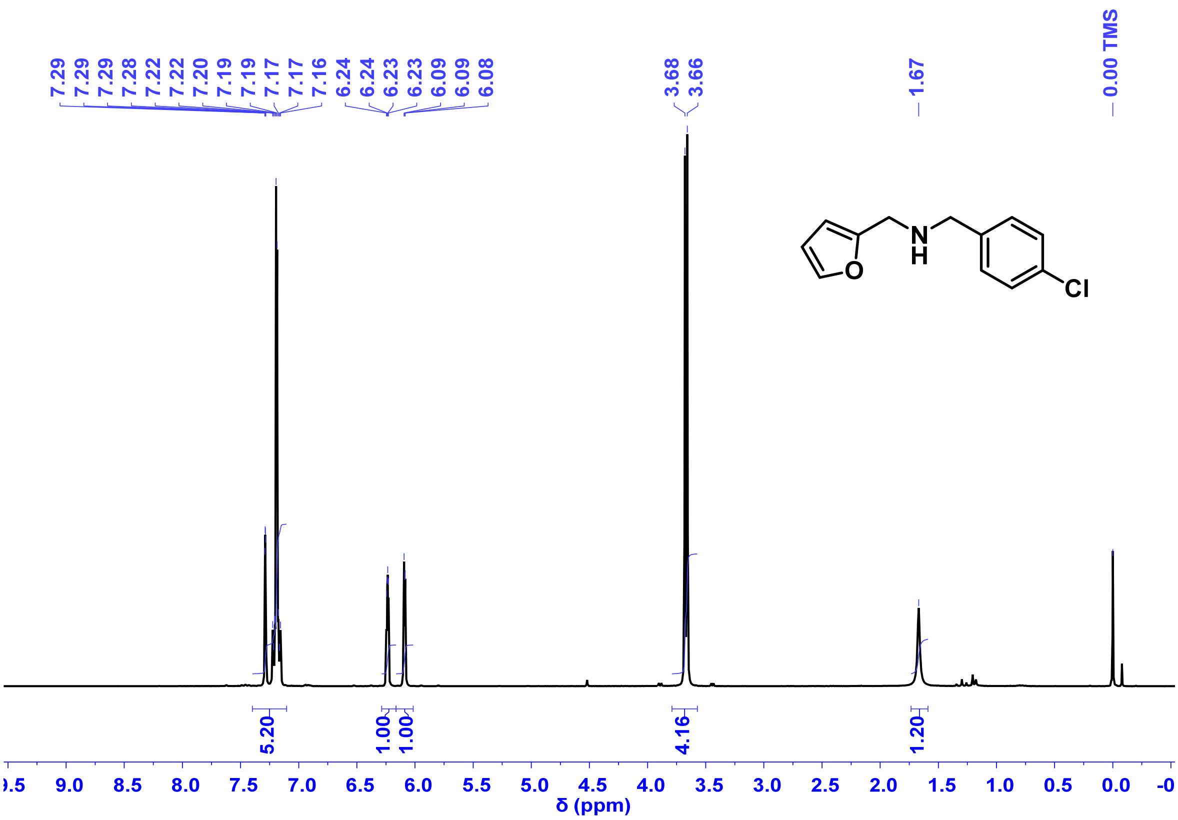


Fig. S23 ^{1}H and ^{13}C {^{1}H} NMR of *N*-[(4-fluorophenyl)methyl]-2-furanmethanamine **5s**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.19 (m, 3H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.32 (s, 1H), 6.17 (d, *J* = 2.9 Hz, 1H), 3.75 (d, *J* = 7.6 Hz, 4H), 1.74 (s, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.66, 160.42, 153.78, 141.96, 135.70, 129.93, 129.83, 115.40, 115.12, 110.22, 107.20, 52.09, 45.36.



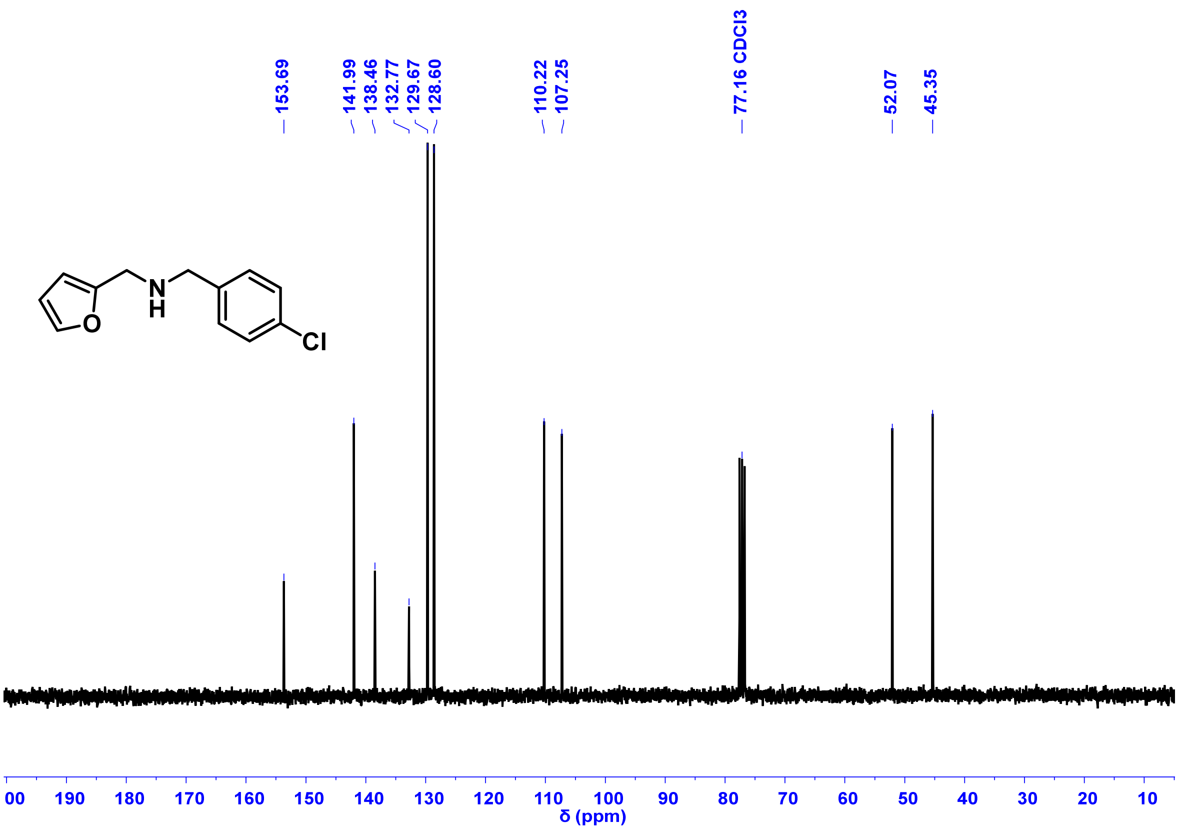
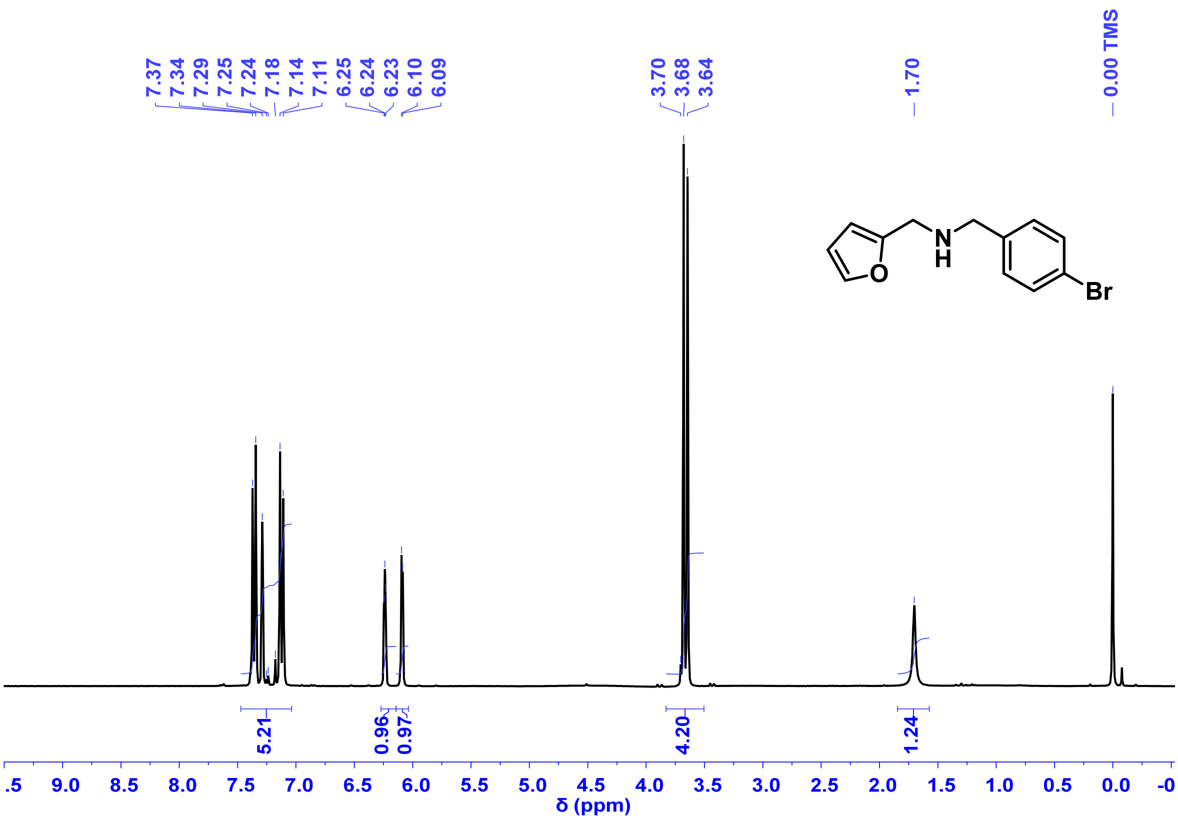


Fig. S24 [1]H and [13]C {[1]H} NMR of *N*-[(4-chlorophenyl)methyl]-2-furanmethanamine **5t**. [1]H NMR (300 MHz, $CDCl_3$) δ = 7.40 – 7.10 (m, 5H), 6.24 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.16 – 6.02 (m, 1H), 3.67 (d, *J* = 6.1 Hz, 4H), 1.67 (s, 1H). [13]C {[1]H} NMR (75 MHz, $CDCl_3$) δ = 153.69, 141.99, 138.46, 132.77, 129.67, 128.60, 110.22, 107.25, 52.07, 45.35.



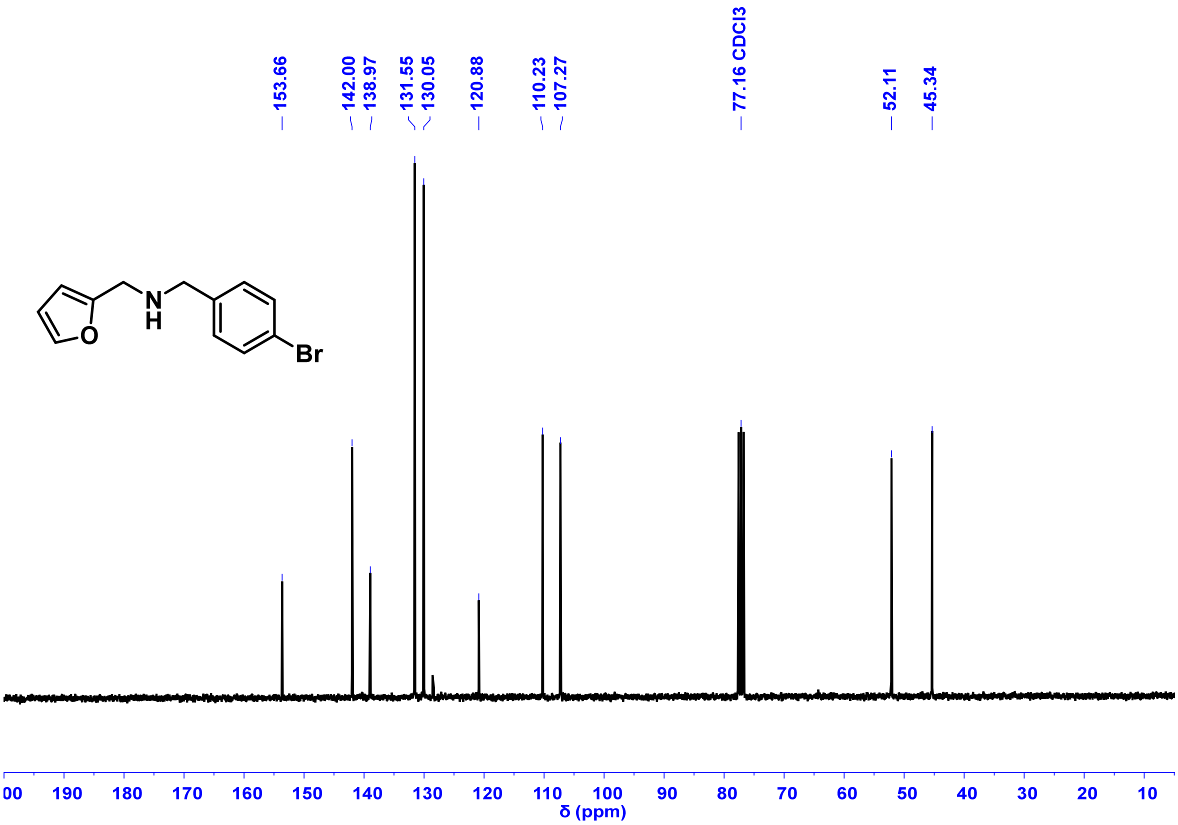


Fig. S25 ^{1}H and ^{13}C {^{1}H} NMR of *N*-[(4-bromophenyl)methyl]-2-furanmethanamine **5u**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.04 (m, 5H), 6.27 – 6.14 (m, 1H), 6.09 (d, *J* = 3.1 Hz, 1H), 3.66 (d, *J* = 10.1 Hz, 4H), 1.70 (s, 1H). ^{13}C {^{1}H} (75 MHz, $CDCl_3$) δ 153.66, 142.00, 138.97, 131.55, 130.05, 120.88, 110.23, 107.27, 52.11, 45.34.

S3. References

1 R. S. Crees, M. L. Cole, L. R. Hanton and C. J. Sumby, *Inorg. Chem.*, 2010, **49**, 1712–1719.