Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Carbene Insertion into N-H Bonds with Size-Selectivity Induced by a Microporous Ruthenium-Porphyrin Metal-Organic Framework

Lianfen Chen,[#a] Hao Cui,[#a] Yanhu Wang,[a] Xiang Liang,[a] Li Zhang*[a] and Cheng-Yong Su*[a,b]

[a]MOE Laboratory of Bioinorganic and Synthetic Chemistry, Lehn Institute of Functional Materials, School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China. [b]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China.

Fax: (+86) 20-8411-5178

E-mail: zhli99@mail.sysu.edu.cn; cesscy@mail.sysu.edu.cn

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Captions for Figures and Tables

1. Crystal Structure Data

Table S1. Crystal data and structure refinement parameters for Ru-PMOF-**1**(Hf).

Identification code	Ru-PMOF-**1**(Hf)
Empirical formula	$C_{141}H_{72}N_{12}O_{55}Hf_{12}Ru_3$
Formula weight	5259.19
Temperature/K	150(2)
Crystal system	cubic
Space group	*I*m-3m
a/Å	38.4253(3)
b/Å	38.4253(3)
c/Å	38.4253(3)
α/°	90
β/°	90
γ/°	90
Volume/Å3	56735.2(12)
Z	4
ρ_{calc}g/cm3	0.616
μ/mm-1	4.738
F(000)	9752
Crystal size/mm3	0.18 × 0.17 × 0.16
Radiation	CuKα (λ = 1.54184)
2θ angel or data collection/°	7.276 to 131.914
Index ranges	-21 ≤ h ≤ 44, -43 ≤ k ≤ 12, -30 ≤ l ≤ 12
Reflections collected	17091
Independent reflections	4555 [Rint = 0.0698, Rsigma = 0.0664]
Data/restraints/parameters	4555/48/142
Goodness-of-fit on F2	1.071
Final R indexes [I>=2σ (I)]	R1 = 0.0890, wR2 = 0.2288
Final R indexes [all data]	R1 = 0.1118, wR2 = 0.2399
Largest diff. peak/hole / e Å^{-3}	1.16/-1.41

Table S2. Selected bond lengths (Å) and bond Angles (º) for Ru-PMOF-**1**(Hf).

Ru-PMOF-**1**(Hf)			
Hf1-O4	2.188(6)	O4-Hf1-O31	114.0(4)
Hf1-O33	2.473(15)	O4-Hf1-O1	142.1(2)
Hf1-O31	2.065(6)	O4-Hf1-O15	142.1(2)
Hf1-O3	2.065(6)	O31-Hf1-Hf13	90.7(2)
Hf1-O15	2.193(7)	O31-Hf1-Hf14	90.7(2)
Hf1-O1	2.193(7)	O34-Hf1-O4	68.6(3)
Hf1-O5	2.200(17)	O3-Hf1-O4	68.6(3)
Hf1-O55	2.199(17)	O3-Hf1-O31	79.4(4)
Ru1-N16	2.121(9)	O34-Hf1-O31	79.4(4)
Ru1-N17	2.121(9)	O3-Hf1-O34	118.0(6)
Ru1-N18	2.121(9)	O34-Hf1-O1	147.1(4)
Ru1-N1	2.121(9)	O3-Hf1-O1	78.3(3)
Ru1-C138	1.98(4)	O3-Hf1-O15	147.1(4)
Ru1-C13	1.98(4)	O34-Hf1-O15	78.3(3)
N1-C48	1.329(17)	O3-Hf1-O5	77.1(5)
N1-C410	1.329(17)	O1-Hf1-Hf11	109.1(3)
C1-C19	1.33(5)	O15-Hf1-Hf13	163.9(2)
C1-C2	1.45(3)	O15-Hf1-Hf11	73.9(2)
C1-C410	1.69(3)	O1-Hf1-Hf12	73.9(2)
C1-C58	1.44(2)	O15-Hf1-Hf12	109.1(3)
C1-C510	0.73(2)	O15-Hf1-Hf14	110.63(18)
C3-C310	0.57(7)	O1-Hf1-Hf14	163.9(2)
C3-C210	1.67(3)	O1-Hf1-Hf13	110.63(18)
C3-C2	1.31(4)	O55-Hf1-Hf12	172.0(3)
C3-C610	1.499(17)	O5-Hf1-Hf12	117.5(4)
C3-C410	1.36(6)	O55-Hf1-Hf11	117.5(4)
C2-C310	1.67(3)	C13-Ru1-C138	180
C2-C410	0.76(2)	C2-N1-Ru1	122.0(9)
C2-C510	1.63(3)	C29-N1-Ru1	122.0(9)
C6-C310	1.499(17)	C2-N1-C29	101.4(18)
C6-C610	0.77(2)	C410-N1-Ru1	119.0(8)
O4-Hf11	2.188(6)	C48-N1-Ru1	119.0(8)
O4-Hf14	2.188(6)	C410-C3-C4	115.2(19)
O3-Hf14	2.065(6)	C1-C2-C310	122(2)
O3-Hf12	2.473(15)	O2-C13-Ru1	180

Symmetry transformations used to generate equivalent atoms:
[1]+Z,+X,+Y; [2]1/2-Z,1/2-X,1/2-Y; [3]1/2-Y,1/2-Z,1/2-X; [4]+Y,+Z,+X; [5]+X,+Z,+Y; [6]1-X,-Y,+Z; [7]1/2-Y,-1/2+X,1/2-Z; [8]1/2+Y,1/2-X,1/2-Z; [9]1-X,+Y,+Z; [10]1/2-Y,1/2-X,1/2-Z; [11]+X,-Y,+Z

2. Physical Characterizations of Ru-PMOF-1(Hf).

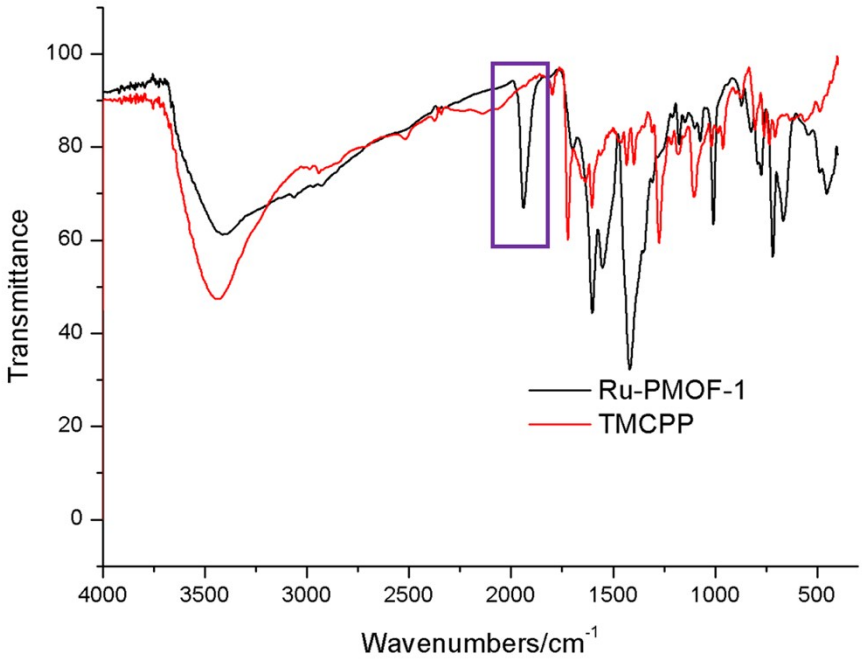


Figure S1. FT-IR spectrum of Ru-PMOF-**1**(Hf). The characteristic peak is placed in the purple rectangle.

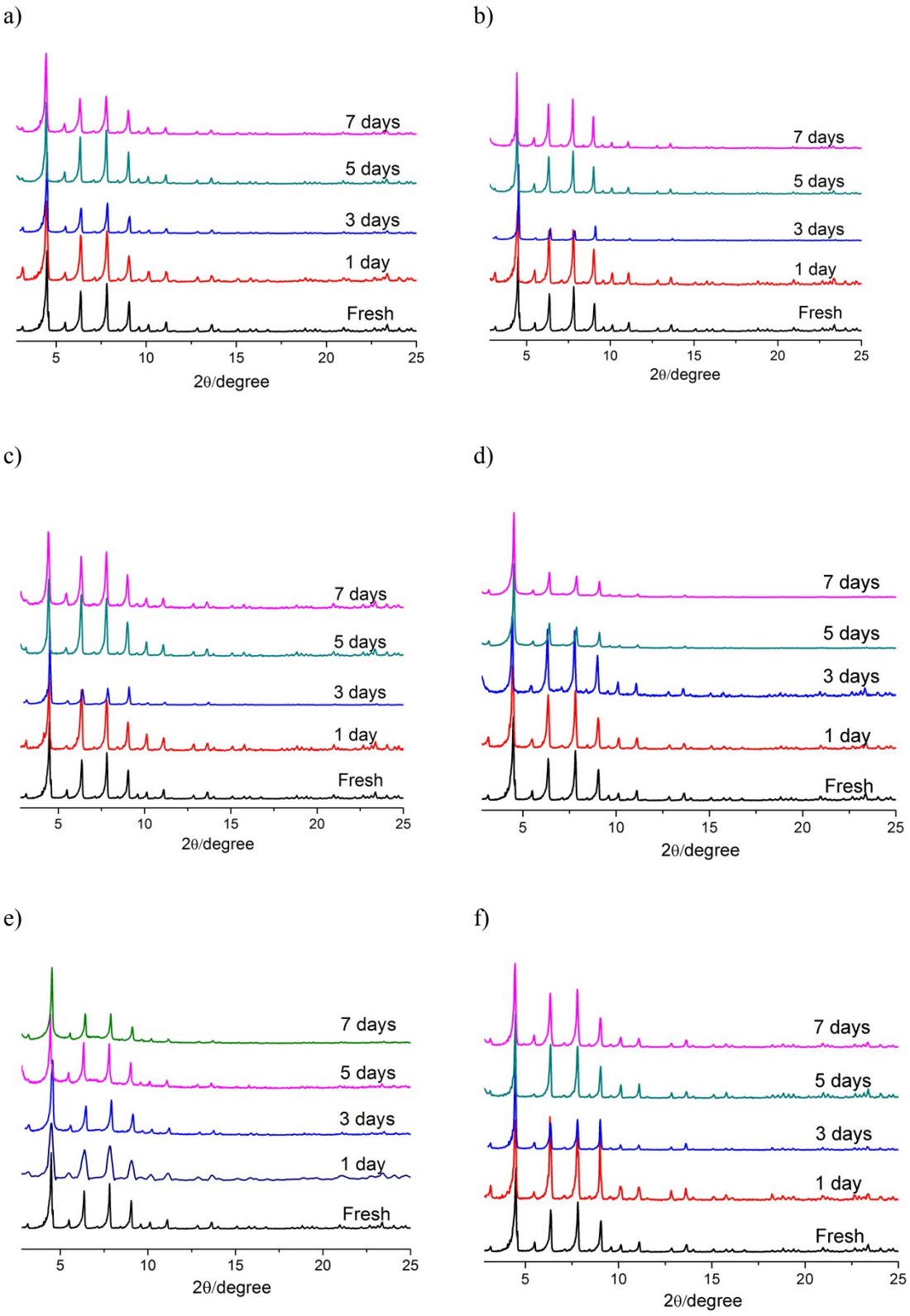


Figure S2. The PXRD patterns of Ru-PMOF-**1**(Hf) upon treatments in different solvents for 1, 3, 5 and 7 days: a) acetone; b) methylene chloride; c) ethyl acetate; d) acetonitrile; e) methanol; and f) tetrahydrofuran.

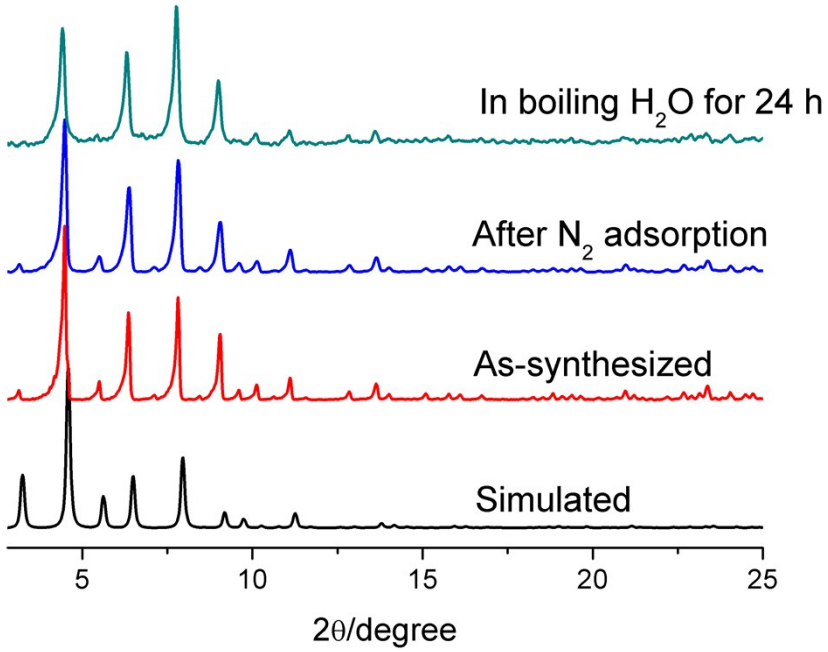


Figure S3. The PXRD patterns of Ru-PMOF-**1**(Hf) upon different treatments.

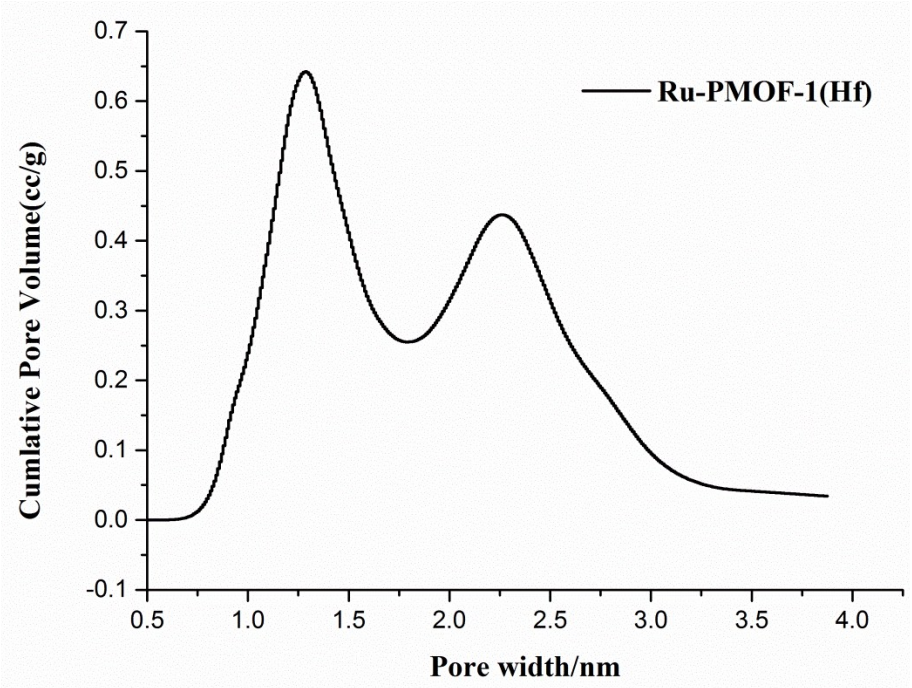


Figure S4. Pore size distribution of Ru-PMOF-**1**(Hf) calculated by SF method

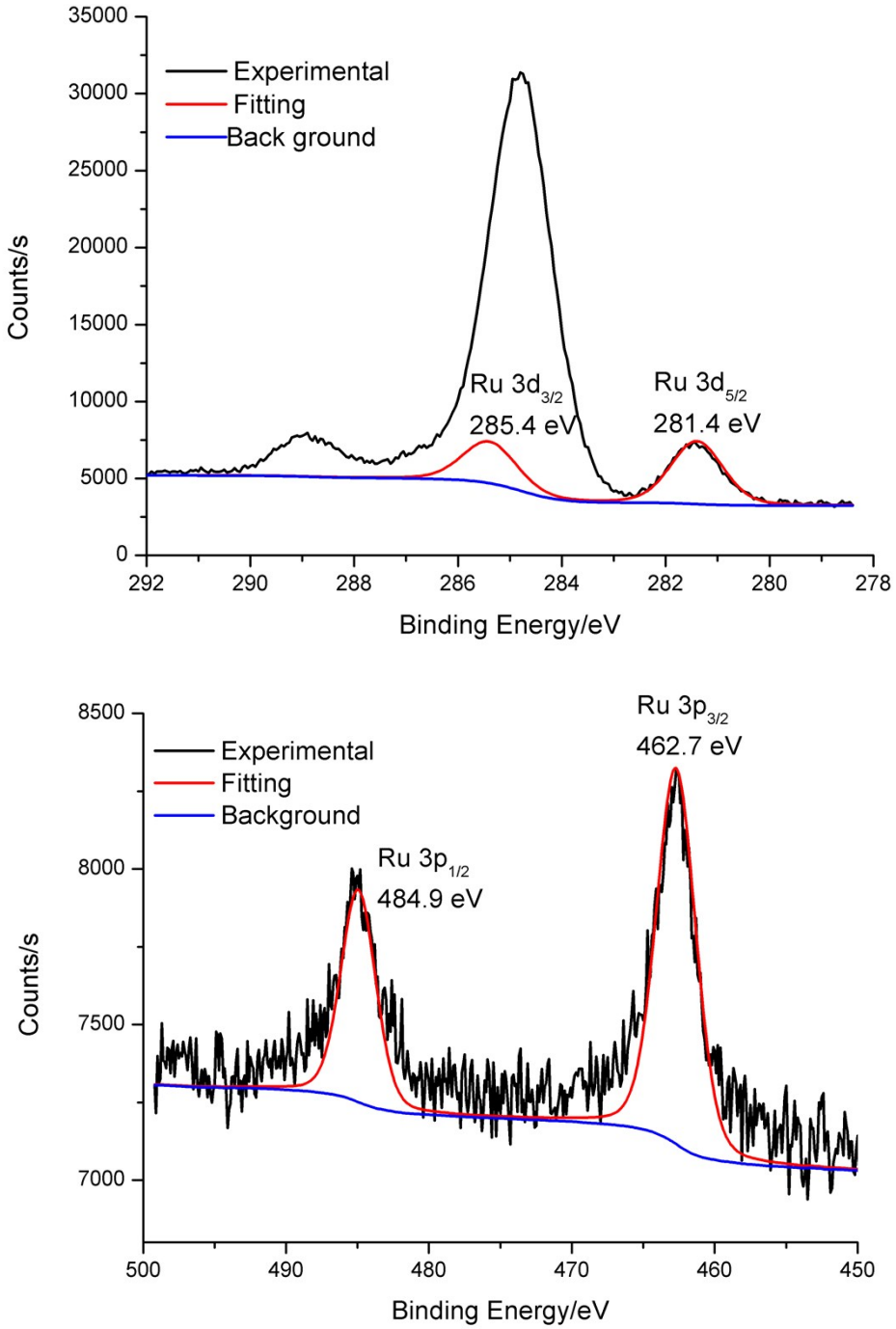
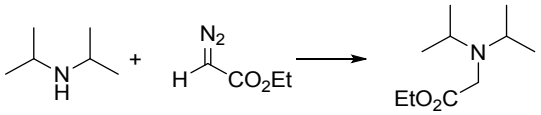


Figure S5. XPS spectra of C 1s, Ru 3d (up) and Ru 3p (down) of Ru-PMOF-**1**(Hf).

3. Comparison of Different Catalysts

A mixture of EDA (0.3 mmol, 34.2 mg, 1 eq) and amine (0.6 mmol, 2 eq) in CH_2Cl_2 (0.5 mL) was added slowly to the solution of different catalyst (1 mol %) in CH_2Cl_2 (1.5 mL). The addition process needs around 10 min. The resulting mixture was stirred for another 20 min until no EDA was detected by TLC. The catalyst was centrifuged and washed with CH_2Cl_2 (5 mL× 3). The combined supernatant was evaporated to dryness and the conversion of the reaction was tested by ^{1}H NMR spectroscopy.

Table S3. Comparison of catalytic results of different catalysts in N-H insertion.[a]

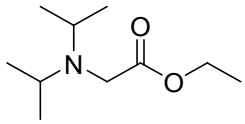


Entry	Catalyst	Yield/%
1	Ru-PMOF-**1**(Hf)	92
2	Ru(TMCPP)(CO)	93
3	Ir-PMOF-**1**(Zr)	7
4	Ir-PMOF-**1**(Hf)	2
5	Rh-PMOF-**1**(Zr)	<1
6	$Rh_2(OAc)_4$	22
7	MOC-Rh-**1**	8
8	$Cu(OTf)_2$	<1
9	none	<1

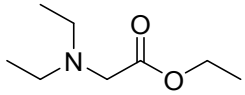
[a]The yields are based on the conversions of diazoacetates into N-H insertion products.

4. Catalytic N-H Insertion Reaction.

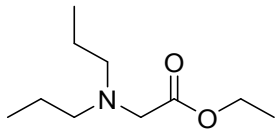
A mixture of EDA (0.3 mmol, 34.2 mg, 1 eq) and amine (0.6 mmol, 2 eq) in CH_2Cl_2 (0.5 mL) was added slowly to the solution of different catalyst (1 mol %) in CH_2Cl_2 (1.5 mL). The addition process needs around 10 min. The resulting mixture was stirred for another 20 min until no EDA was detected by TLC. The catalyst was centrifuged and washed with CH_2Cl_2 (5 mL× 3). The combined supernatant was evaporated to dryness and the conversion of the reaction was tested by ^{1}H NMR spectroscopy.



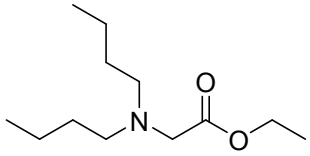
Ethyl diisopropylglycinate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (q, J = 7.1 Hz, 2H), 3.20 (s, 2H), 3.06 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H), 1.00 (d, J = 6.5 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.1, 60.3, 50.0, 47.9, 20.5, 14.2 ppm.



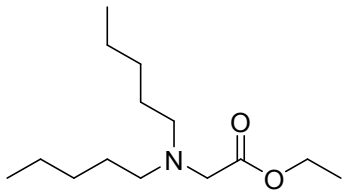
Ethyl diethylglycinate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (q, J = 7.1 Hz, 2H), 3.30 (s, 2H), 2.64 (q, J = 7.2 Hz, 4H), 1.25 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 60.3, 54.3, 47.7, 14.3, 12.1 ppm.



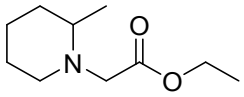
Ethyl dipropylglycinate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (q, J = 7.1 Hz, 2H), 3.32 (s, 2H), 2.53 (m, 4H), 1.47 (dq, J = 14.9, 7.4 Hz, 4H), 1.26 (t, J = 7.1 Hz, 3H), 0.88 (t, J = 7.3 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 60.2, 56.5, 55.2, 20.6, 14.3, 11.8 ppm.



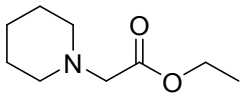
Ethyl dibutylglycinate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (q, J = 7.1 Hz, 2H), 3.29 (s, 2H), 2.61 – 2.44 (m, 4H), 1.49 – 1.36 (m, 4H), 1.34 – 1.20 (m, 7H), 0.89 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 60.2, 55.2, 54.2, 29.6, 20.5, 14.3, 14.0 ppm.



Ethyl dipentylglycinate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (q, J = 7.1 Hz, 2H), 3.29 (s, 2H), 2.63 – 2.43 (m, 4H), 1.43 (dt, J = 9.9, 7.5 Hz, 4H), 1.39 – 1.17 (m, 11H), 0.87 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.4, 60.2, 55.2, 54.5, 29.6, 27.1, 22.6, 14.3, 14.1 ppm.



Ethyl 2-(2-methylpiperidin-1-yl)acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 (q, J = 7.1 Hz, 2H), 3.14 (s, 2H), 2.54 – 2.42 (m, 4H), 1.60 (m, 4H), 1.46 – 1.36 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.61 (s), 60.40 (s), 54.29 (s), 25.76 (s), 23.86 (s), 14.24 (s) ppm.



Ethyl 2-(piperidin-1-yl)acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.15 (q, J = 7.1 Hz, 2H), 3.41 – 3.27 (m, 2H), 2.86-2.82 (m, 1H), 2.56 – 2.42 (m, 2H), 1.71 – 1.46 (m, 4H), 1.33 – 1.18 (m, 5H), 1.06 (d, J = 6.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 60.2, 55.7, 55.5, 53.6, 34.7, 26.2, 24.3, 19.8, 14.3 ppm.

5. Size-Selective Catalysis

Before the catalytic reactions, the Ru-PMOF-**1**(Hf) sample was filtered with a sieve (0.01 mm), followed by another one (0.054 mm). The samples with particle sizes distributed in 0.054-0.1 mm or smaller than 0.054 mm were collected separately for the catalysis. The following procedure is similar: A mixture of EDA (0.3 mmol, 34.2 mg, 1 eq) and amine (0.6 mmol, 2 eq) in CH_2Cl_2 (0.5 mL) was added slowly to the solution of Ru-PMOF-**1**(Hf) (1 mol [Ru]%) in CH_2Cl_2 (1.5 mL). The addition process needs around 10 min. The resulting mixture was stirred for another 5 min. The catalyst was centrifuged and washed with CH_2Cl_2 (5 mL× 3). The combined supernatant was evaporated to dryness and the conversion of the reaction was tested by ^{1}H NMR spectroscopy.

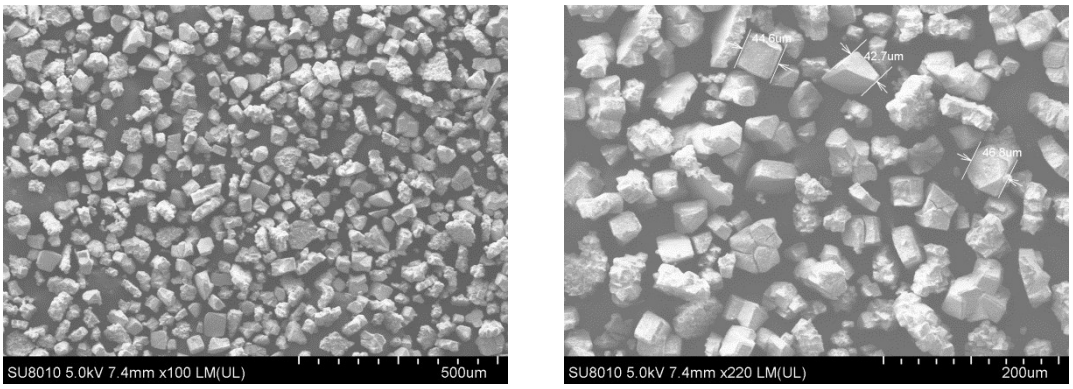
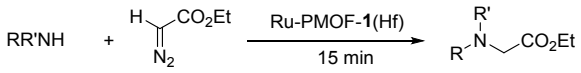
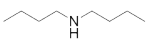
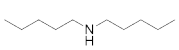
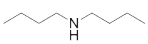
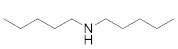


Figure S6. The TEM graphs of Ru-PMOF-**1**(Hf) with sizes smaller than 0.054 mm

Table S4. Size-Selective Catalysis.[a]



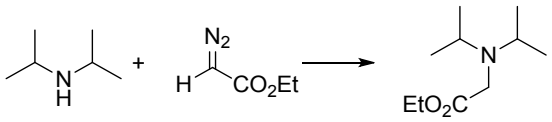
Entry	Substrate	Catalyst Sizes (mm)	Yield (%)
1		< 0.054	75
2		< 0.054	63
3		< 0.054	23
4		0.054 – 0.1	73
5		0.054 – 0.1	66
6		0.054 – 0.1	28

[a]Reaction conditions: 1 mol [Ru]% of the catalyst, R. T., the yields are based on the conversions of EDA to the N-H insertion products by NMR studies.

6. Filtration Experiment

A solution of EDA (0.3 mmol, 34.2 mg, 1 eq) in CH_2Cl_2 (0.5 mL) was added slowly to the mixture of diisopropylamine (0.6 mmol, 60.6 mg, 2 eq) and activated Ru-PMOF-**1**(Hf) (5.5 mg, 0.003 mmol, 1 mol [Ru]%) in CH_2Cl_2 (1.5 mL). The addition process needs around 10 min. The resulting mixture was stirred for another 20 min, and then filtrated with membrane filter. To the filtrate was added a new bunch of EDA (0.3 mmol) and diisopropylamine (0.6 mmol), and then the reaction mixture was stirred for 30 min. Afterwards, a small amount of which was taken for ^{1}H NMR spectroscopy test and the remaining part was allowed to stir for 30 min before being tested by ^{1}H NMR spectroscopy.

Table S5. Filtration experiments.[a]



t/min	yield/%
0	42
30	42

[a] Reaction conditions: The yields are based on the conversions of diazoacetates into N-H insertion products.

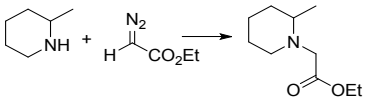
7. ICP Spectrometric Evaluation

A solution of EDA (3 mmol, 342 mg, 1 eq) in CH_2Cl_2 (2 mL) was added slowly to the mixture of 2-methylpiperidine (6 mmol, 594 mg, 2 eq) and activated Ru-PMOF-**1**(Hf) (55 mg, 0.03 mmol, 1 mol %, containing ca 3.03 mg of Ru) in CH_2Cl_2 (18 mL). The addition process needs around 10 min. The mixture was stirred for 2 h, filtrated with membrane filter (0.22 μm) followed by sand core funnel (G5) with a pad of celite, and washed with CH_2Cl_2 (5 mL × 3). The combined solvent was concentrated before a small amount of pure water and triethylamine was added to the sample to destroy the structure, and then the solvent was removed on heating. The resulting sample was treated with nitric acid (2 mL) and hydrochloric acid (6 mL), kept stayed at room temperature for 3 h, and then was heated at 150 °C to remove most of the solvent. Afterward, the remaining mixture was added with nitric acid (6 mL) and aqueous hydrogen dioxide (30 wt%, 1 mL), stayed at room temperature for 3 h and then concentrated to 1 mL. The digestion procedure was repeated five times. The resulting mixture was diluted volumetrically with an aqueous solution of nitric acid (2%) to 25 mL, to obtain a colorless solution, which was then measured by inductively coupled plasma optical emission spectrometer (ICP-OES) for Ru contents. The Ru content was evaluated based on calibration curves, which were obtained with a series of calibration standard solutions with different Ru concentration. The measured Ru content was 0.05 ppm (0.00125 mg), and the leached Ru% should be 0.04%, using the calculation equation “100% (0.00125 mg / 3.03 mg)”.

8. Recycling Experiments

A solution of EDA (3 mmol, 342 mg, 1 eq) in CH_2Cl_2 (2 mL) was added slowly to the mixture of 2-methylpiperidine (6 mmol, 594 mg, 2 eq) and activated Ru-PMOF-**1**(Hf) (55 mg, 0.03 mmol, 1 mol [Ru]%) in CH_2Cl_2 (18 mL). The addition process needs around 10 min. The mixture was stirred for 2 h until no EDA was detected by TLC. The catalyst was centrifuged, washed with CH_2Cl_2 (5 mL× 3) and acetone (5 mL), and dried under vacuum at room temperature for 2h, before it was reused in the consecutive runs. The conversion of the reaction was monitored by ^{1}H NMR spectroscopy.

Table S6. Recycling experiments of N-H insertion.



Run	Yield/%
1	93
2	94
3	93
4	89
5	89
6	89
7	92
8	89
9	81
10	85

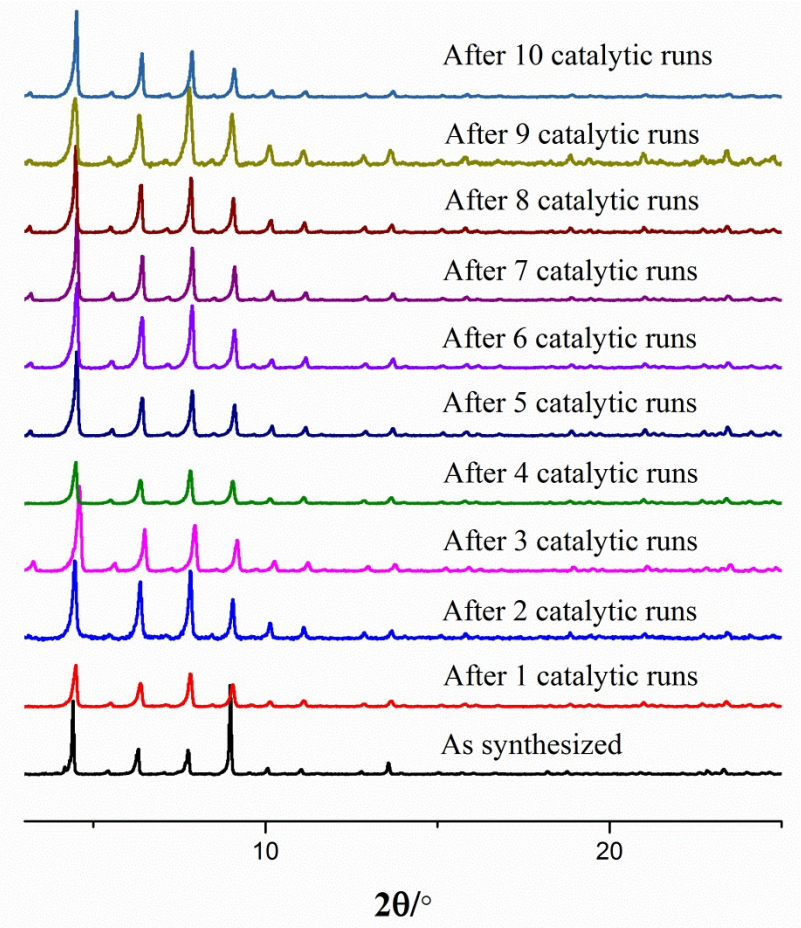


Figure S7. PXRD patterns of the recycled samples after each run and as-synthesized samples.

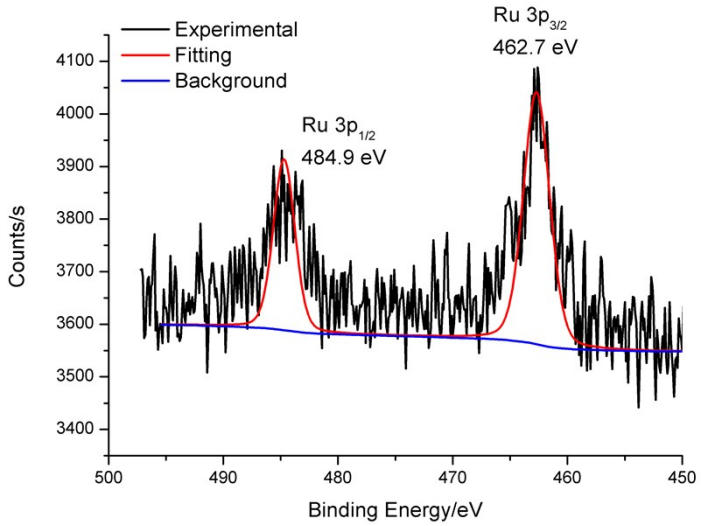


Figure S8. XPS spectrum of C Ru 3p for the recycled Ru-PMOF-**1**(Hf) sample.

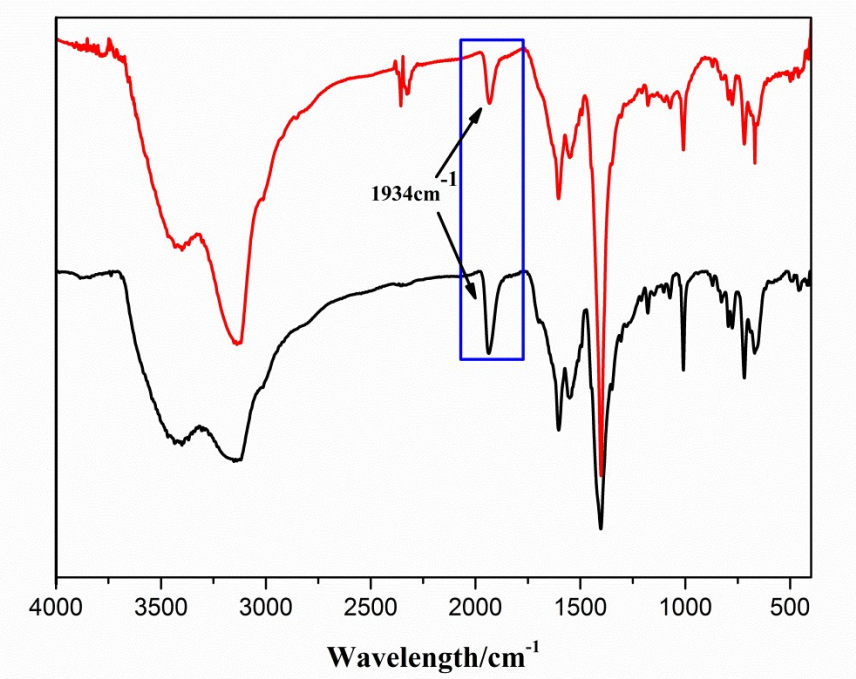


Figure S9. FT-IR spectra of Ru-PMOF-**1**(Hf) before (black) and after (red) catalysis. The characteristic peak is placed in the blue rectangle.

Appendix

^{1}H and ^{13}C NMR Spectra of the Products

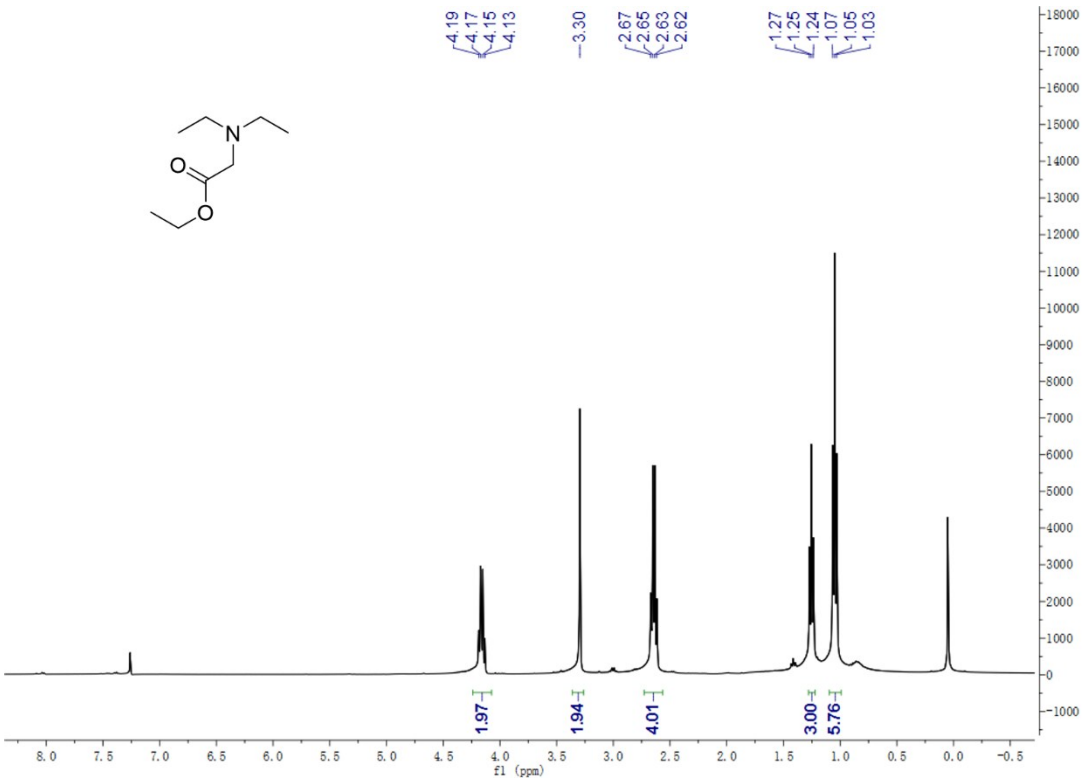


Figure S10a. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of ethyl diethylglycinate.

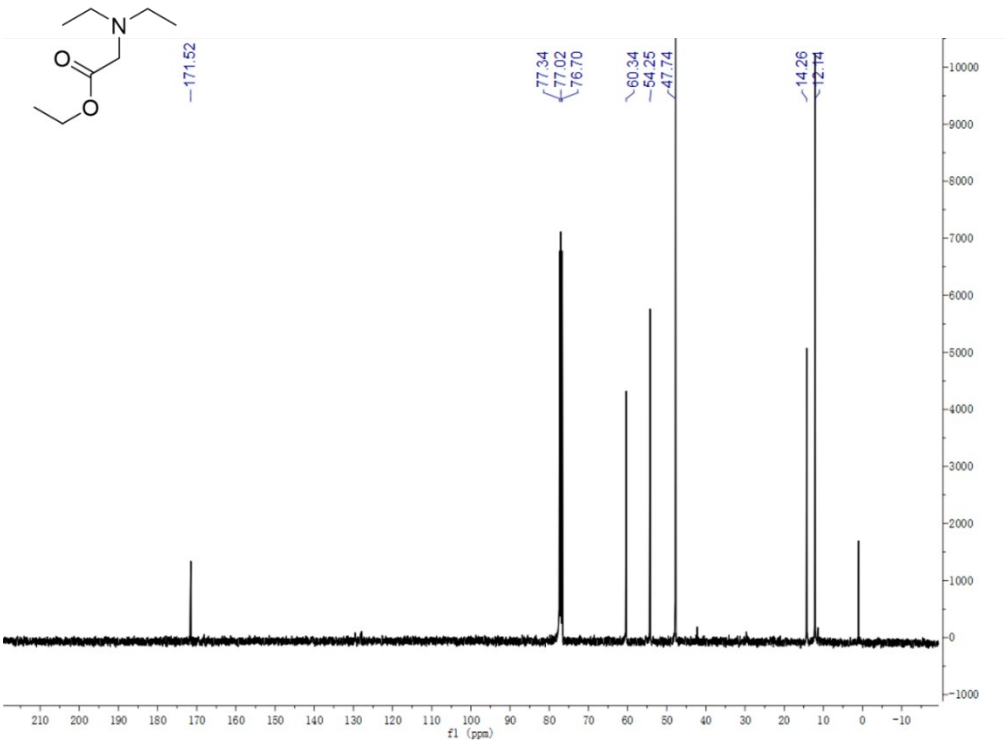


Figure S10b. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of ethyl diethylglycinate.

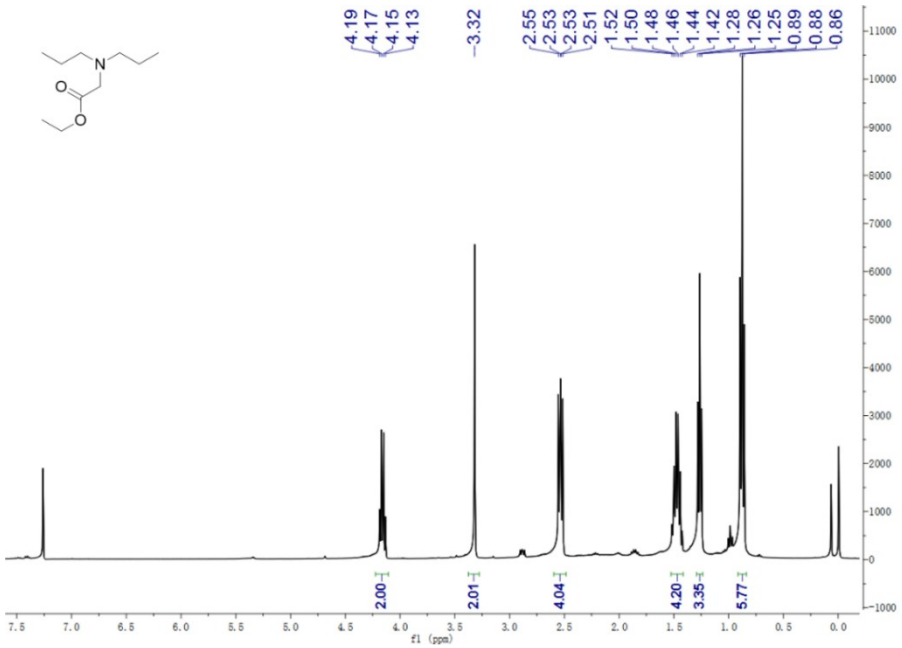


Figure S10c. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of ethyl dipropylglycinate.

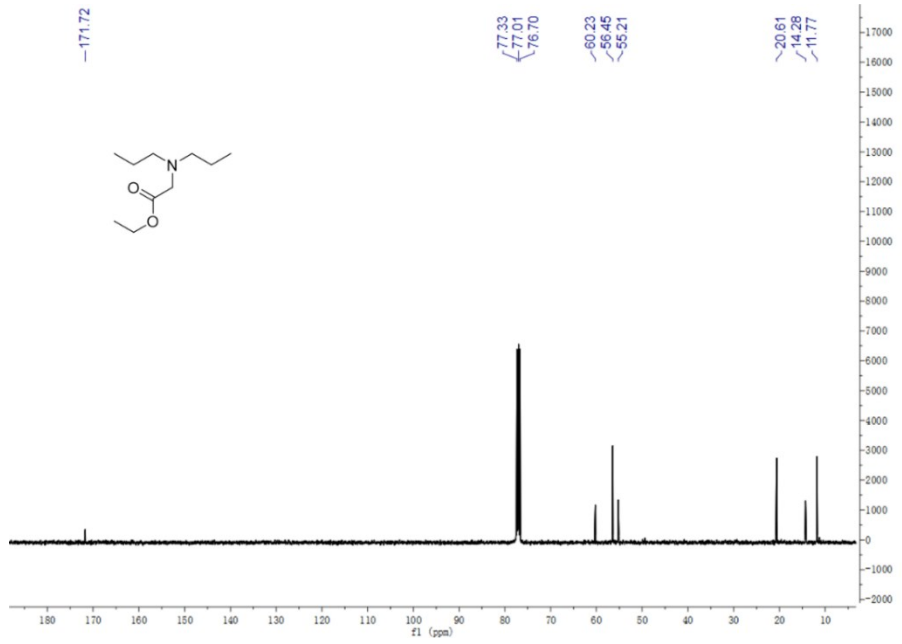


Figure S10d. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of ethyl dipropylglycinate.

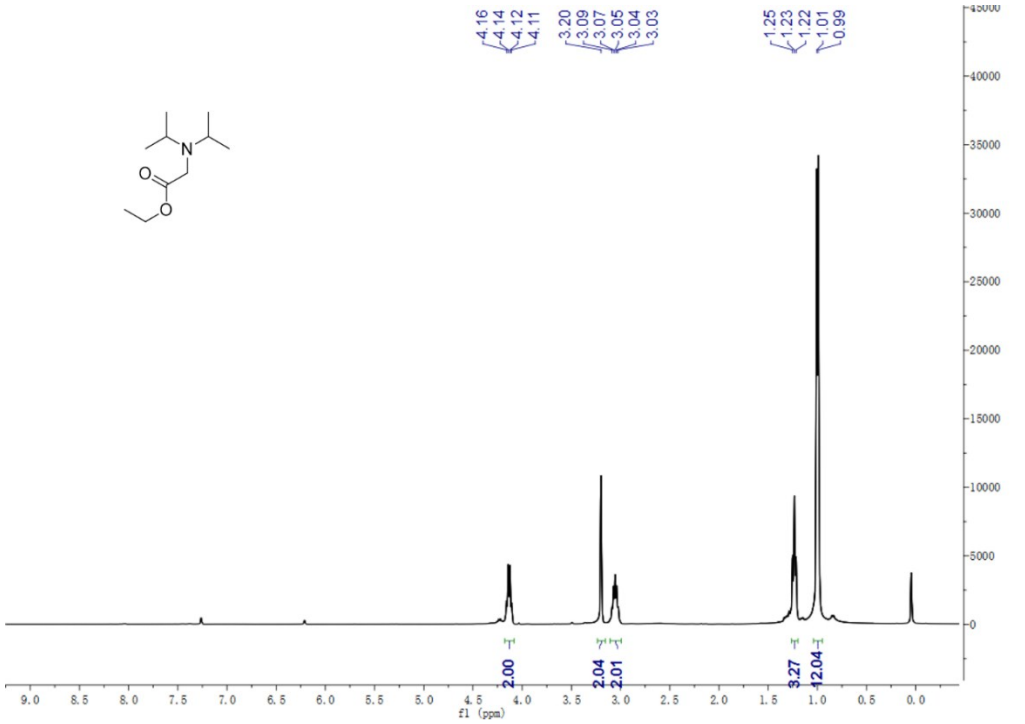


Figure S10e. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of ethyl diisopropylglycinate.

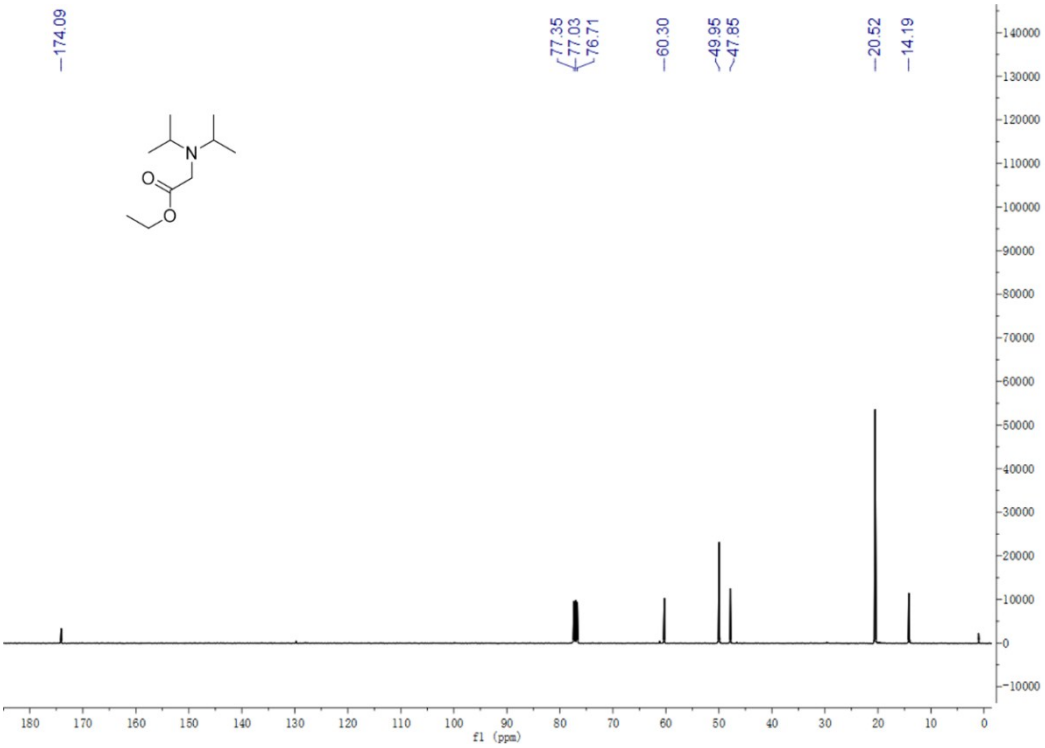


Figure S10f. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of ethyl diisopropylglycinate.

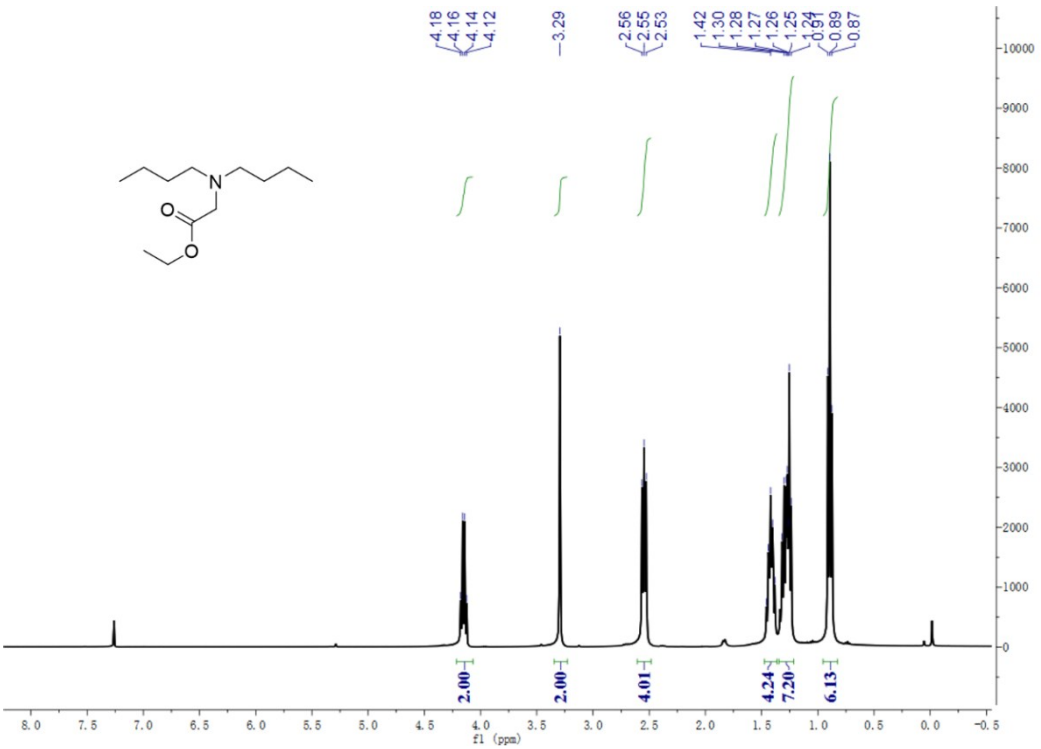


Figure S10g. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of ethyl dibutylglycinate.

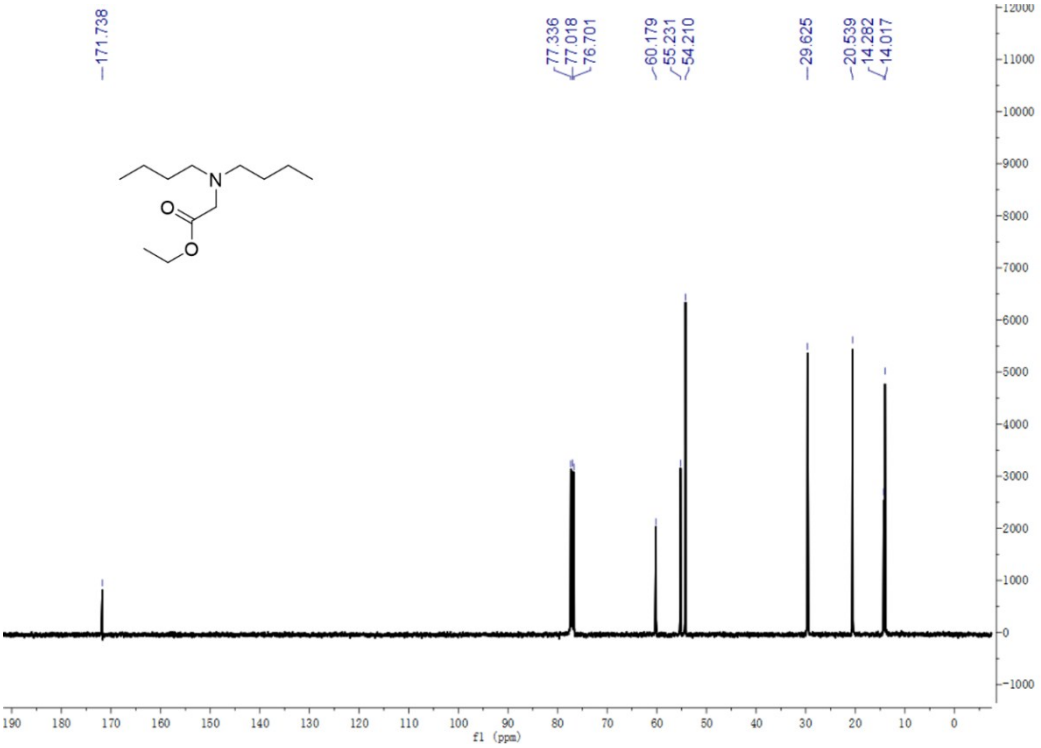


Figure S10h. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of ethyl dibutylglycinate.

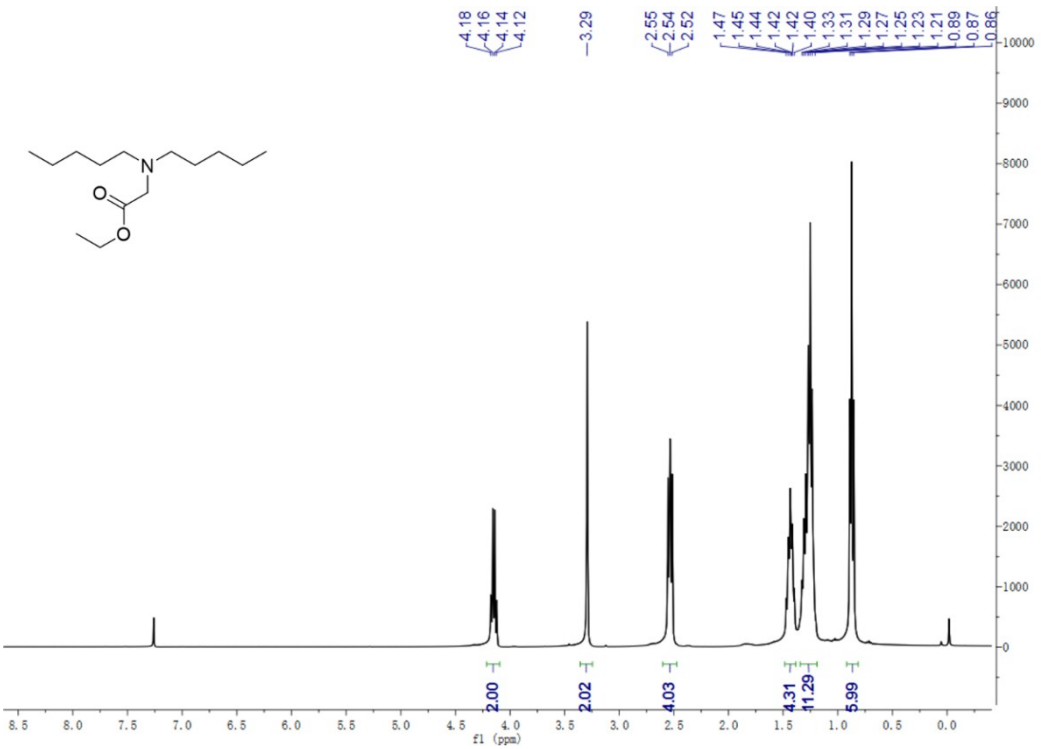


Figure S10i. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of ethyl dipentylglycinate.

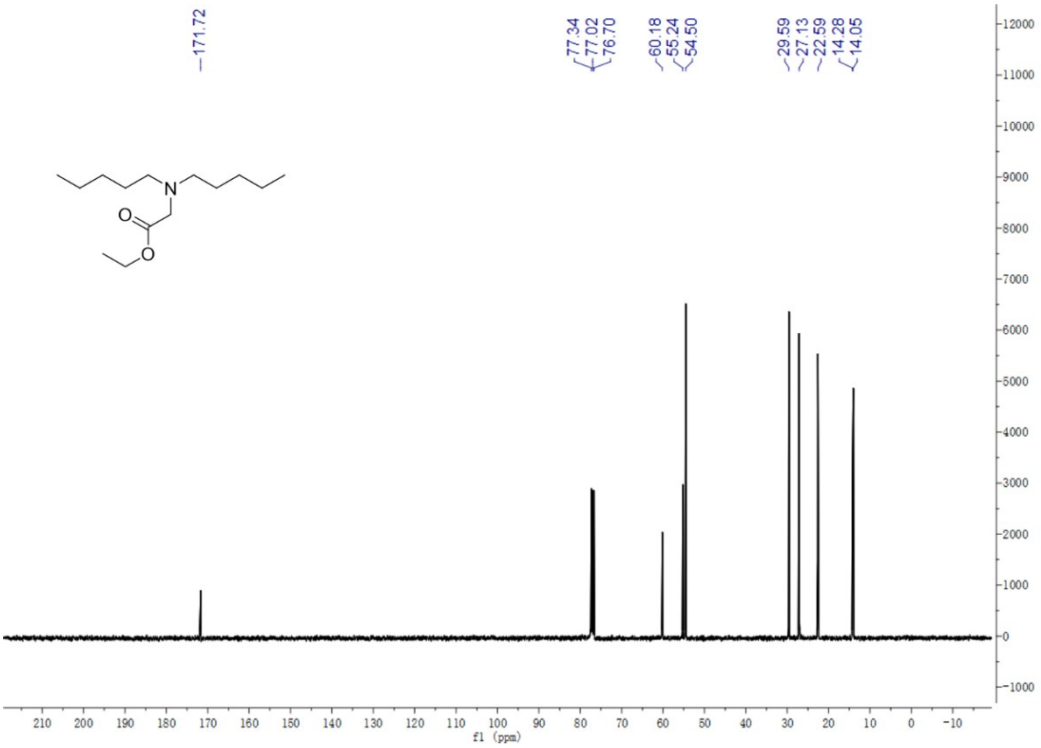


Figure S10j. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of ethyl dipentylglycinate.

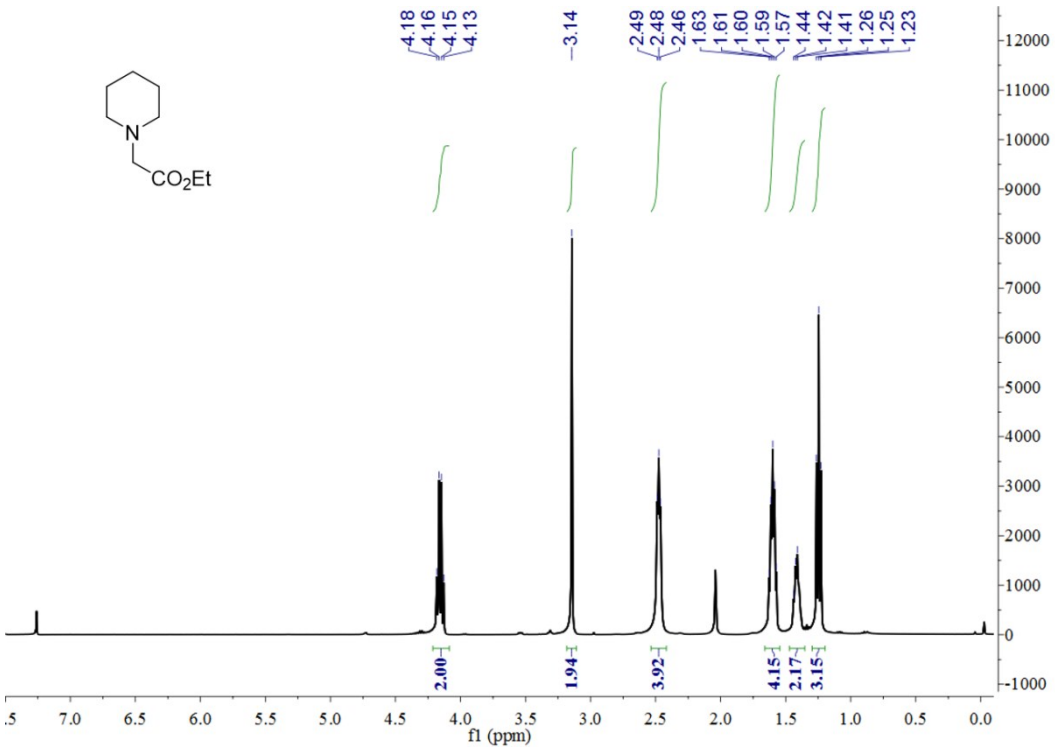


Figure S10k. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of ethyl 2-(piperidin-1-yl) acetate.

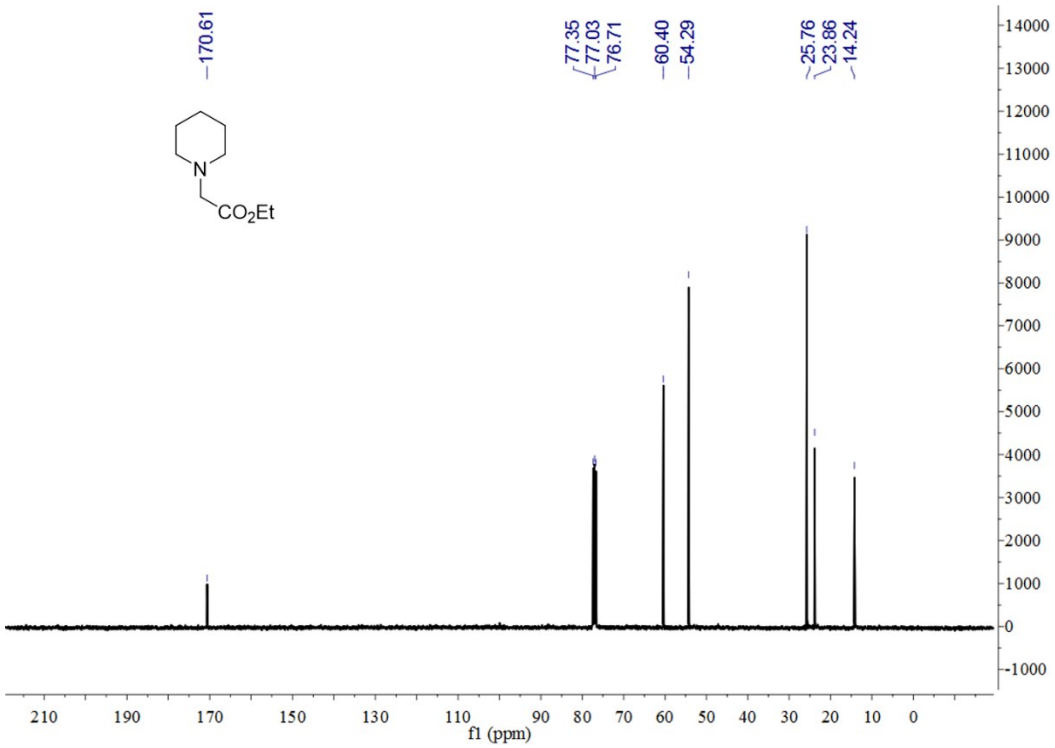


Figure S10l. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of ethyl 2-(piperidin-1-yl) acetate.

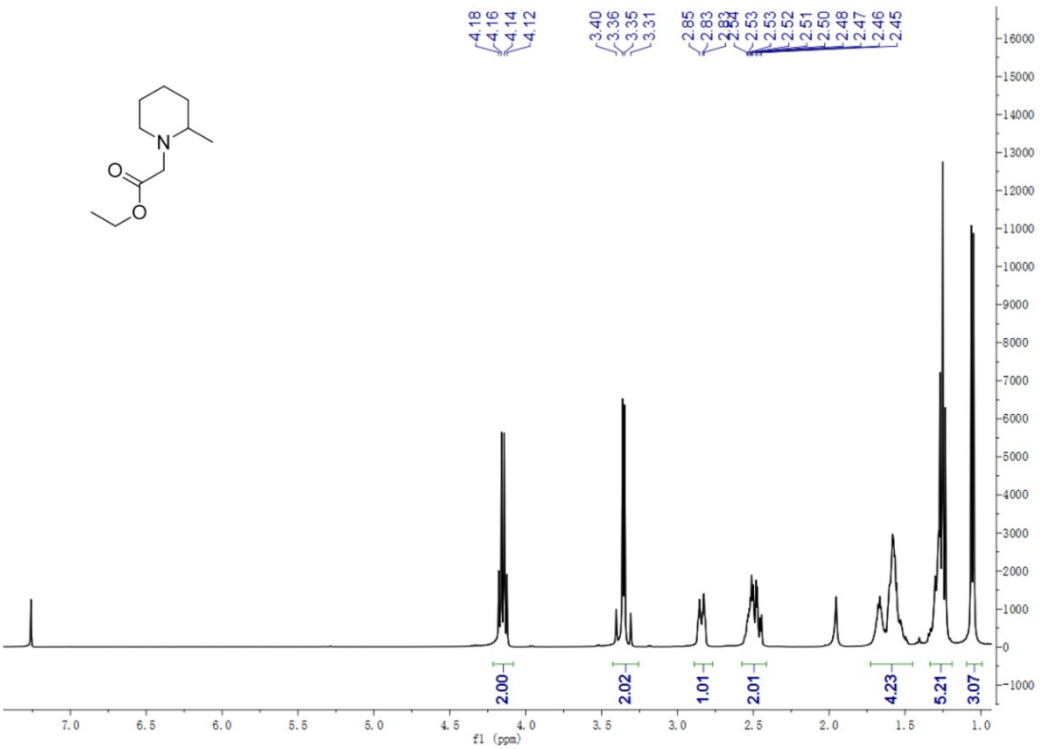


Figure S10m. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of ethyl 2-(2-methylpiperidin-1-yl) acetate.

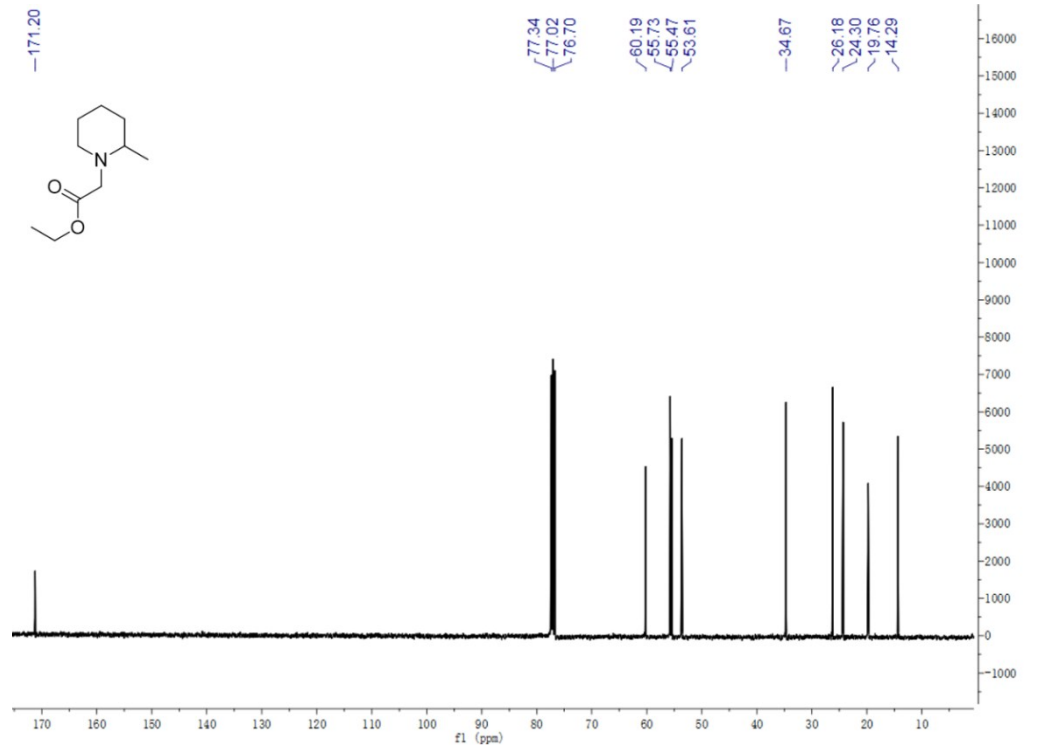


Figure S10n. ^{13}C NMR ($CDCl_3$, 100 MHz) spectrum of ethyl 2-(2-methylpiperidin-1-yl) acetate.