Electronic supplementary information (ESI) for

Selective hydrogenation of phenols to cyclohexanols catalyzed by robust solid NHC-Rh coordination assemblies in water

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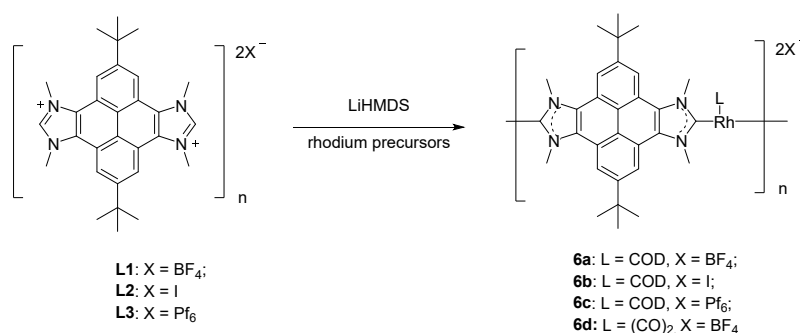
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1. General

All commercial reagents were used directly without further purification unless otherwise stated. Dry *N,N*-dimethylformamide (DMF) was purchased from Alfa Aesar, stored over 4 Å molecular sieves, and handled under N_2 atmosphere. Hydrogen gas (99.99%) was purchased from Dumaoai. All reaction vials were purchased from Beijing Synthware Glass. $CDCl_3$ and D_2O were purchased from Cambridge Isotope Laboratories. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Jeol ECA-400 and Bruker 400 DRX spectrometers. The chemical shifts (δ) for ^{1}H NMR are given in parts per million (ppm) referenced to the residual proton signal of the deuterated solvent ($CHCl_3$ at δ 7.26 ppm, D_2O at δ 4.79 ppm); coupling constants are expressed in hertz (Hz). ^{13}C NMR spectra were referenced to the carbon signal of $CDCl_3$ (77.0 ppm). The following abbreviations are used to describe NMR signals: *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet. Scanning electron microscope (SEM) experiments were carried out on a Philips XL30 microscope operated at 20 kV. Transmission electron microscope (TEM) experiments were carried out on a JEOL JEM 2010 transmission electron microscope. XPS experiments were carried out on PHI 5000C&PHI5300.

2. General procedure for the synthesis of catalyst 6a-d

The self-supported catalysts **6a-d** were synthesized according to the literature reports.[1]

L1: X = BF_4;
L2: X = I
L3: X = Pf_6

6a: L = COD, X = BF_4;
6b: L = COD, X = I;
6c: L = COD, X = Pf_6;
6d: L = $(CO)_2$, X = BF_4

**Scheme S1**. Syntheses of NHC-Rh solid coordination assemblies **6a-d**.

The NHC-Rh solid coordination assemblies **6a-d** were synthesized according to our previous synthetic procedures.[1] The corresponding bis-imidazolium salts (0.2

mmol) and rhodium precursors ([Rh(COD)Cl]$_2$ or Rh(acac)(CO)$_2$, 0.2 mmol) were dissolved in DMF under nitrogen. And then, LiHMDS was added at room temperature. The mixture reacted at 80 °C for 24 hours. The solid product was obtained by centrifugation and then washed three times with DMF, water, and methanol, respectively.

3. Catalytic hydrogenation of phenol and derivatives

3.1 Reaction condition optimization

Table S1. Optimization for hydrogenation of phenol[a]
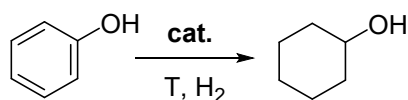
Entry	Cat. (0.5 mol %)	Base (5 mol %)	Solvent (4 mL)	H$_2$ (bar)	Temp. (°C)	Yield (%)
1	5	KOH	THF	20	80	NR
2	5	KOH	i-PrOH	20	80	NR
3	5	KOH	EtOH	20	80	NR
4	5	KOH	CH$_3$CN	20	80	NR
5	5	KOH	1,4-dioxane	20	80	NR
6	5	KOH	H$_2$O	20	80	65%
7	6a	KOH	H$_2$O	20	80	85%
8[b]	6a	KOH	H$_2$O	20	80	68%
9	6a	t-BuONa	H$_2$O	20	80	93%
10	6a	t-BuONa	H$_2$O	20	30	92%
11	6a	t-BuONa	H$_2$O	5	30	94%
12[c]	6a	t-BuONa	H$_2$O	5	30	90%

[a]Reaction conditions: phenol 1.0 mmol, cat 0.5 mol%, base 0.05 mmol, solvent 4 mL for 24 h. Yield was determined based on ^{1}H NMR results by using 1,3,5-trimethoxybenzene as an internal standard. [b]Base 0.1 mmol. [c]Phenol 20 mmol.

3.2 General procedure for the hydrogenation of phenol

The hydrogenation of phenol was carried out in a stainless-steel autoclave (125 mL). In a typical experiment, phenol derivatives (1.0 mmol), **6a** (0.5 mol%) and *t*-BuONa (0.05 mmol) were added to a stainless-steel autoclave with a magnetic stirring bar, and then 4mL deionized water was added. The autoclave was purged thrice with H_2 (10 bar), pressurized to 5-20 bar H_2, and then heated to 30-80 °C. The reactions were stirred for the required time. After the reaction was completed, the autoclave was cooled in an ice water bath for a period of time to room temperature. The remaining hydrogen was discharged. Extracted with dichloromethane several times and collected the organic phase. Then 1,3,5-trimethoxybenzene was added to the organic phase as an internal standard for ^{1}H NMR analysis to determine the yield. And the corresponding products were further purified by column chromatography.

3.3 General procedure for the reuse of catalyst

In a reused experiment, **6a** (0.37 mol%), *t*-BuONa (0.2 mmol) and phenol (4 mmol) were added to a stainless steel autoclave with a magnetic stirring bar, and then 13mL deionized water was added. The autoclave was purged thrice with H_2 (10 bar), pressurized to 5 bar H_2, and then heated to 30 °C. The reactions were stirred for 24h. After the reaction was complete, the autoclave was cooled in an ice water bath for a period of time to room temperature. The remaining hydrogen was discharged. The reaction solution was centrifuged at 10000 rpm for 10 minutes. The upper liquid was poured out carefully. Then extracted with dichloromethane for several times and collected the organic phase. Then 1,3,5-trimethoxybenzene was added to the organic phase as an internal standard for ^{1}H NMR analysis to determine the yield. The precipitates obtained were washed with water, methanol and DCM for three times respectively. Then it was dried at 65 °C, and then used for the next hydrogenation reaction.
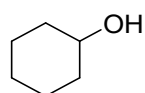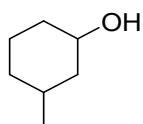

Cyclohexanol (**2**)[2]: colorless oil, yield: 94%

¹H NMR (400 MHz, CDCl₃) δ = 3.63 - 3.57 (m, 1H), 1.95 – 1.81 (m, 2H), 1.79 – 1.65 (m, 3H), 1.59 – 1.47 (m, 1H), 1.29 - 1.22 (m, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 70.3, 35.5, 25.4, 24.1 ppm.
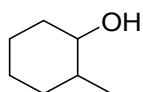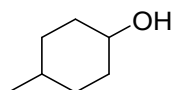

2-Methylcyclohexan-1-ol (**10a**)[2]: colorless oil, yield: 94%

¹H NMR (400 MHz, CDCl₃) δ = 3.87 – 3.00 (m, 1H), 1.78 – 1.64 (m, 2H), 1.63 – 1.46 (m, 2H), 1.45 – 1.33 (m, 2H), 1.28 - 1.05(m, 3H), 1.00-0.91 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 76.4, 71.1, 40.2, 35.8, 35.4, 33.6, 32.4, 28.7, 25.6, 25.2, 24.4, 20.6, 18.5, 16.9 ppm.
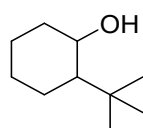

3-Methylcyclohexan-1-ol (**10b**)[2]: colorless oil, yield: 93%

¹H NMR (400 MHz, CDCl₃) δ = 4.06 – 3.54 (m, 1H), 1.97 – 1.93 (m, 1H), 1.81 – 1.68 (m, 1H), 1.62 – 1.58 (m, 2H), 1.46 – 1.20 (m, 3H), 1.18 – 1.03 (m, 1H), 0.93 – 0.89 (m, 3H), 0.88 – 0.70 (m, 1H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 70.9, 44.7, 35.5, 34.1, 31.5, 24.2, 22.4 ppm.


4-Methylcyclohexan-1-ol (**10c**)[2]: colorless oil, yield: 91%

¹H NMR (400 MHz, CDCl₃) δ = 3.93 – 3.43 (m, 1H), 2.06 – 1.85 (m, 1H), 1.80 – 1.63 (m, 2H), 1.63 – 1.50 (m, 1H), 1.52 – 1.43 (m, 1H), 1.40 – 1.16 (m, 3H), 1.07 – 0.92 (m, 1H), 0.90 – 0.86 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ = 70.9, 66.9, 35.6, 33.3, 32.2, 31.7, 31.1, 29.0, 21.9, 21.6 ppm.
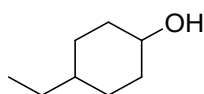
4-Ethylcyclohexane-1-ol (**10d**)[3]: colorless oil, yield: 85%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.30 – 3.34 (m, 1H), 2.00 – 1.92 (m, 1H), 1.72 (m, 2H), 1.61 – 1.42 (m, 2H), 1.39 – 1.16 (m, 5H), 0.98 – 0.83 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 71.2, 67.3, 38.5, 38.0, 35.6, 32.3, 30.9, 29.3, 28.6, 26.6, 11.7, 11.6 ppm.
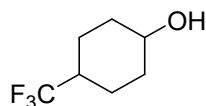
4-Trifluoromethylcyclohexane-1-ol (**10e**)[4]: colorless oil, yield: 91%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.21 – 3.33 (m, 1H), 2.10 – 2.03 (m, 1H), 2.01 – 1.93 (m, 1H), 1.89 – 1.82 (m, 1H), 1.81 – 1.66 (m, 3H), 1.57 – 1.47 (m, 1H), 1.43 – 1.24 (m, 2H) ppm.^{13}C NMR (101 MHz, CDCl$_3$) δ = 128.97, 69.72, 64.88, 41.65 – 40.76 (m), 33.80, 31.18, 23.36 (q, J = 2.5 Hz), 18.79 (q, J = 2.7 Hz). ppm. ^{19}F NMR (376 MHz, CDCl$_3$) δ = -73.54 (dd, J = 94.3, 8.5 Hz) ppm.
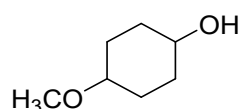
4-Methoxycyclohexane-1-ol: colorless oil (**10f**)[5], yield: 92%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.79 – 3.63 (m, 1H), 3.34 – 3.31 (m, 3H), 3.29 – 3.12 (m, 1H), 2.06 – 1.94 (m, 2H), 1.88 – 1.78 (m, 2H), 1.68 – 1.61 (m, 2H), 1.58 – 1.49 (m, 1H), 1.35 – 1.27 (m, 1H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 69.6, 68.3, 55.9, 55.5, 32.5, 30.3, 28.9, 27.0 ppm.
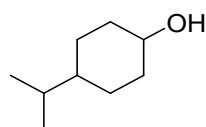
4-Isopropylcyclohexan-1-ol (**10g**)[3]: colorless oil, yield: 90%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.09 – 3.44 (m, 1H), 2.04 – 1.95 (m, 1H), 1.84 – 1.69 (m, 2H), 1.60 – 1.38 (m, 5H), 1.30 – 1.17 (m, 1H), 1.13 – 1.02 (m, 1H), 0.95 – 0.80 (m, 6H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 71.2, 66.7, 43.3, 43.1, 35.8, 32.7, 32.4, 32.0, 27.8, 23.6, 19.9, 19.8 ppm.
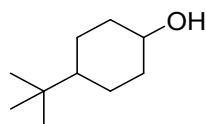
4-(Tert-butyl)cyclohexan-1-ol (**10h**)[2]: white solid, yield: 79%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.20 – 3.41 (m, 1H), 2.07 – 1.99 (m, 1H), 1.89 – 1.76 (m, 1H), 1.61 – 1.46 (m, 2H), 1.42 – 1.17 (m, 3H), 1.09 – 1.02 (m, 2H), 0.88 (d, J = 5.3 Hz, 9H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 71.2, 47.2, 36.1, 33.4, 27.6, 27.5, 25.6, 20.9 ppm.

2-(Tert-butyl)cyclohexan-1-ol (**10i**)[2]: colorless oil, yield: 86%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.29 – 3.41 (m, 1H), 2.36 – 2.05 (m, 2H), 1.98 – 1.76 (m, 2H), 1.68 – 1.38 (m, 5H), 1.02 – 0.92 (m, 12H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 73.5, 67.9, 60.2, 53.7, 51.0, 44.2, 37.9, 35.2, 32.6, 31.9, 29.8, 29.3, 28.6, 27.7, 26.9, 26.0, 25.2, 21.3, 20.0 ppm.
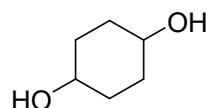
1,4-Dihydroxycyclohexane (**10j**)[6]: colorless oil, yield: 91%

^{1}H NMR (400 MHz, D$_2$O) δ = 3.89 – 3.47 (m, 2H), 1.87 – 1.85 (m, 2H), 1.68 – 1.47 (m, 4H), 1.29 – 1.24 (m, 2H) ppm. ^{13}C NMR (101 MHz, D$_2$O) δ = 69.3, 67.3, 31.8, 29.1 ppm.
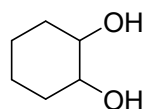
1,2-Dihydroxycyclohexane (**10k**)[5]: colorless oil, yield: 88%

^{1}H NMR (400 MHz, D$_2$O) δ = 3.76 – 3.19 (m, 2H), 1.63 – 1.55 (m, 2H), 1.53 – 1.42 (m, 3H), 1.38 – 1.01 (m, 3H). ^{13}C NMR (101 MHz, D$_2$O) δ = 74.9, 70.5, 32.5, 29.0, 23.6, 21.0 ppm.
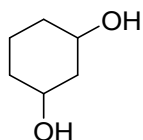
1,3-Dihydroxycyclohexane (**10l**)[6]: colorless oil, yield: 90%

^{1}H NMR (400 MHz, D$_2$O) δ = 4.34 – 3.38 (m, 2H), 2.25 – 2.05 (m, 1H), 1.86 – 1.45 (m, 5H), 1.31 – 1.03 (m, 2H) ppm. ^{13}C NMR (101 MHz, D$_2$O) δ = 68.5, 66.8, 42.9, 40.1, 33.3, 32.3, 20.1, 18.4 ppm.
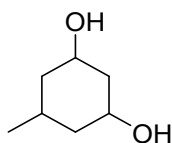
5-Methyl-1,3-dihydroxycyclohexane (**10m**)[7]: colorless oil, yield: 73%

^{1}H NMR (400 MHz, D$_2$O) δ = 4.18 – 3.43 (m, 2H), 2.20 – 0.93 (m, 6H), 0.90 – 0.51 (m, 4H) ppm. ^{13}C NMR (101 MHz, D$_2$O) δ = 67.8, 67.4, 65.9, 42.6, 42.3, 41.9, 39.5, 39.1, 27.0, 24.9, 21.2, 20.9 ppm.
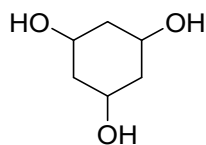
1,3,5-Trihydroxycyclohexane (**10n**)[8]: colorless oil, yield: 72%

^{1}H NMR (400 MHz, D$_2$O) δ = 4.28 – 3.36 (m, 3H), 2.22 – 2.00 (m, 2H), 1.95 – 1.27 (m, 2H), 1.24 – 0.93 (m, 2H) ppm. ^{13}C NMR (101 MHz, D$_2$O) δ = 64.9, 41.9 ppm.
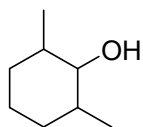
2,6-Dimethylcyclohexan-1-ol (**10o**)[2]: colorless oil, yield: 91%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.52 – 3.32 (m, 1H), 1.75 – 1.58 (m, 2H), 1.58 – 1.42 (m, 2H), 1.34 – 1.21 (m, 4H), 0.98 (dd, J = 17.8, 6.8 Hz, 6H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 75.1, 39.8, 37.2, 34.3, 27.4, 25.9, 19.9, 18.7 ppm.
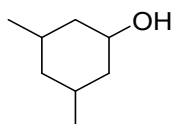
3,5-Dimethylcyclohexan-1-ol (**10p**)[2]: colorless oil, yield: 93%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.07 – 3.51 (m, 1H), 1.95 – 1.85 (m, 2H), 1.82 – 1.47 (m, 3H), 1.47 – 1.31 (m, 1H), 1.05 – 0.95 (m, 1H), 0.85 (dd, J = 19.3, 6.5 Hz, 6H), 0.81 – 0.69 (m, 1H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 70.4, 67.4, 44.1, 43.9, 43.1, 41.1, 30.7, 26.1, 22.5, 22.2 ppm.
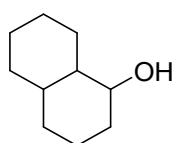
Decahydro-1-naphthalenol (**10q**)[8]: colorless oil, yield: 88%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.86 – 3.61 (m, 1H), 1.97 – 1.73 (m, 3H), 1.72 – 1.21 (m, 13H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 73.5, 42.9, 35.7, 31.8, 29.4, 26.3, 24.4, 24.3, 21.5, 18.9 ppm.
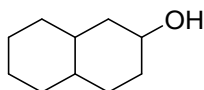
Decahydro-2-naphthalenol (**10r**)[5]: colorless oil, yield: 72%

^{1}H NMR (400 MHz, DMSO-d_6) δ = 4.42 (d, J = 4.4 Hz, 1H), 3.44 – 3.33 (m, 1H), 1.72-1.65 (m, 3H), 1.54 – 1.34 (m, 10H), 1.29 – 1.15 (m, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ = 70.1, 35.8, 35.1, 34.6, 31.9, 30.8, 30.1, 29.6, 26.7, 25.9, 21.2 ppm.
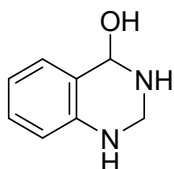
1-Hydroxy-2,3,4,5-tetrahydro-1H-benzo [E] [1,4] diazepine (**10s**): white solid, yield: 72%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.90 – 7.85 (m, 1H), 7.45 (s, 1H), 7.37 – 7.21 (m, 1H), 6.91 – 6.83 (m, 1H), 6.74 – 6.68 (m, 1H), 4.66 (t, J = 2.4 Hz, 2H), 4.47 (s, 1H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$) δ = 165.9, 148.3, 133.7, 128.5, 119.5, 116.8, 115.1, 54.8 ppm.

HR-MS (ESI), *m/z*: [M+H]$^+$ calculated for C$_8$H$_{11}$N$_2$O: 151.0871, found: 151.0859.
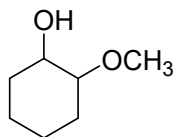
2-Methoxycyclohexanol (**10t**)[9]: colorless oil, yield: 99%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.92 – 3.74 (m, 1H), 3.38 (s, 3H), 3.31 – 3.25 (m, 1H), 1.85 – 1.72 (m, 2H), 1.66 – 1.47 (m, 4H), 1.37 – 1.18 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 80.1, 68.4, 56.0, 30.4, 26.0, 22.0, 21.2 ppm.
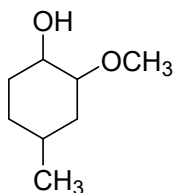
4-Methyl-2-methoxycyclohexanol (**10u**)[9]: colorless oil, yield: XX%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.08 (m, 1H), 3.38 (s, 3H), 3.23-3.06 (m, 1H), 2.01-1.90 (m, 1H), 1.75-1.65 (m, 1H), 1.26 (dd, J = 20.5, 14.6 Hz, 4H), 0.94 (d, J = 5.9 Hz, 4H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 80.7, 65.4, 55.7, 33.8, 30.9, 29.76, 27.6, 22.1 ppm.
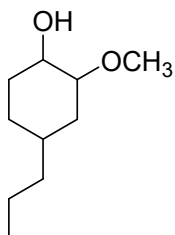
4-Propyl-2-methoxycyclohexanol (**10v**)[9]: colorless oil, yield: 65%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.12-4.06 (m, 1H), 3.38 (s, 3H), 3.24-3.06 (m, 1H), 1.97 (d, J = 12.4 Hz, 1H), 1.72 (dd, J = 18.4, 13.6 Hz, 1H), 1.26 (t, J = 8.3 Hz, 7H), 0.88 (t, J = 7.1 Hz, 5H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 80.8, 65.7, 55.7, 39.1, 35.6, 31.9, 29.7, 25.6, 19.8, 14.2 ppm.
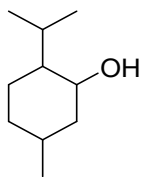
2-Isopropyl-5-methylcyclohexan-1-ol (**10w**)[11]: white solid, yield: 70%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.34 – 3.70 (m, 1H), 1.80 – 1.53 (m, 5H), 1.51 – 1.29 (m, 3H), 1.17 – 0.98 (m, 6H), 0.98 – 0.90 (m, 3H), 0.90 – 0.84 (m, 1H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 71.5, 50.1, 45.0, 34.5, 31.6, 25.8, 23.1, 22.2, 21.0, 16.1 ppm.
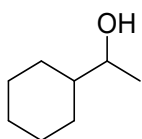
1-Cyclohexane-1-ethanol (**10x**)[9]: colorless oil, yield: 91%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.63 – 3.31 (m, 1H), 1.89 – 1.54 (m, 5H), 1.30 – 1.04 (m, 7H), 1.02 – 0.79 (m, 2H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 72.1, 45.1, 28.6, 28.4, 26.5, 26.2, 26.1, 20.3 ppm.
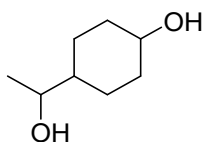
4-Hydroxy-α-methylcyclohexanemethanol (**10y**)[10]: colorless oil, yield: 87%

^{1}H NMR (400 MHz, CDCl$_3$) δ = 4.06 – 3.39 (m, 2H), 2.10 – 1.62 (m, 3H), 1.60 – 1.37 (m, 3H), 1.30 – 1.15 (m, 2H), 1.12 (t, J = 6.7 Hz, 3H), 1.08 – 0.93 (m, 1H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 71.4, 71.1, 70.7, 66.1, 43.9, 43.9, 35.0, 34.9, 32.1, 32.0, 26.7, 26.4, 22.5, 21.6, 20.5, 20.4 ppm.

4 FT-IR, solid-state ^{13}C NMR

4.1 FT-IR spectra of coordination assemblies
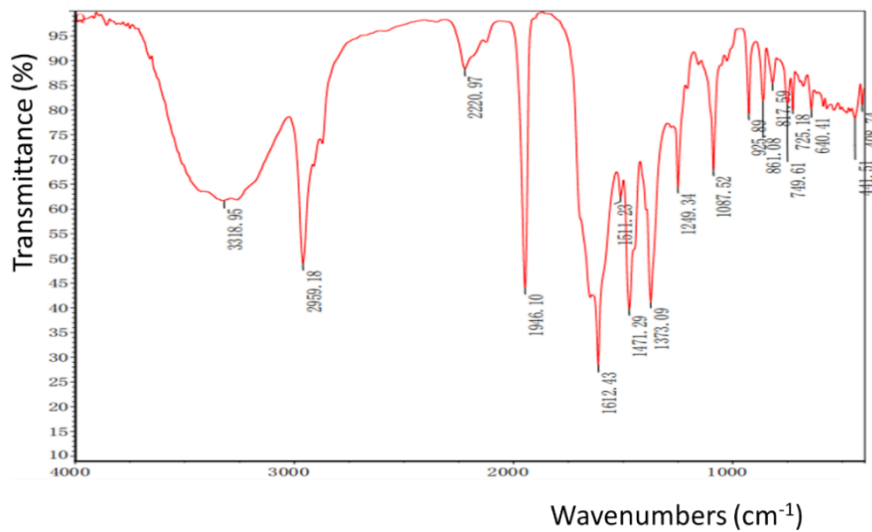
Fig. S1 FT-IR spectrum of freshly prepared NHC-Rh solid catalyst **6a**.
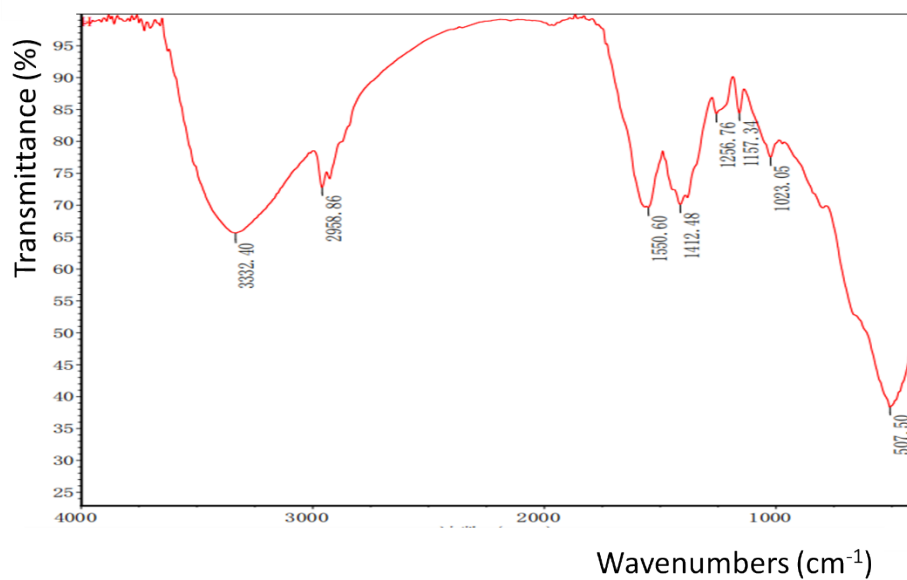
Fig. S2 FT-IR spectrum of recovered NHC-Rh solid catalyst **6a**.

4.2 Solid-state ^{13}C NMR
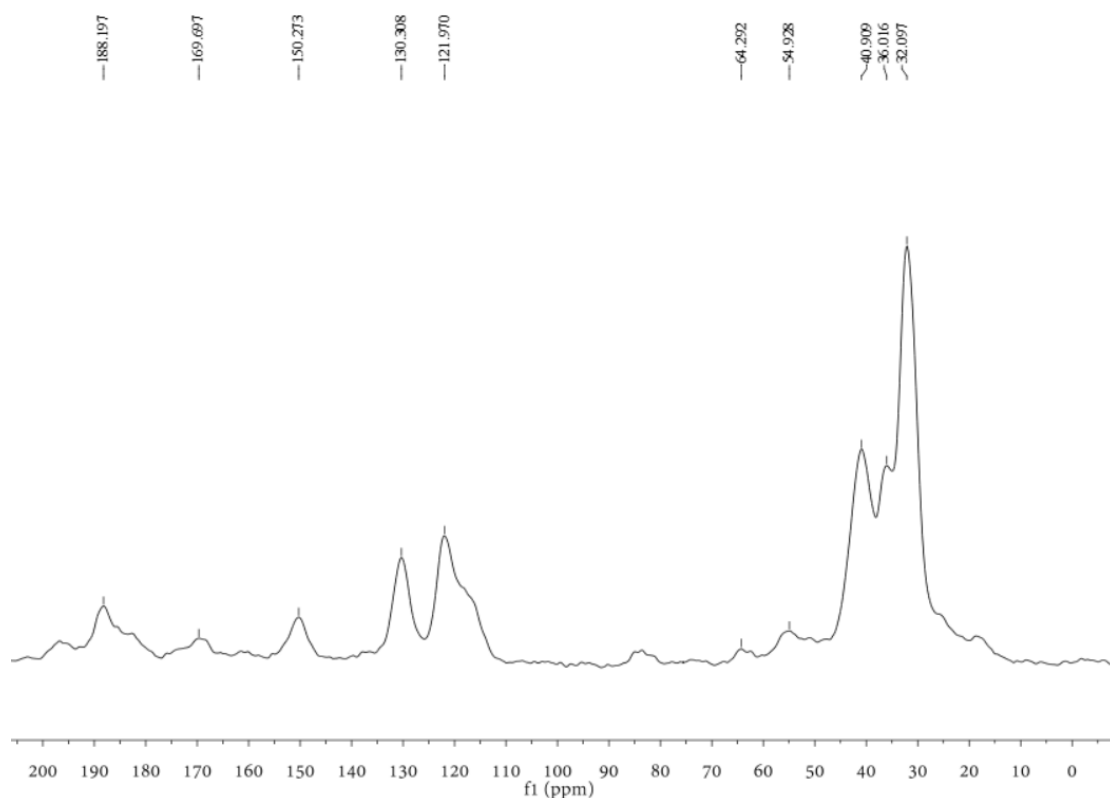
Fig. S3 Solid-state ^{13}C NMR of NHC-Rh solid catalyst **6a**.

5. Leaching tests with ICP-AES

Table S2. Rh and B leaching tests with the filtrates of the reaction mixture after consecutive runs[a] .

Run	Elementary	Concentration(mg/L)[a]	Concentration(mg)
1	Rh	0.0125	<0.005
3	Rh	0.0040	<0.005
5	Rh	0.0063	<0.005
7	Rh	0.0071	<0.005
9	Rh	0.0385	<0.005
1	B	0.0219	<0.005
3	B	0.0625	<0.005
5	B	0.0643	<0.005
7	B	0.0392	<0.005
9	B	0.0553	<0.005

[a]ICP-AES analysis of the reaction filtrates after each consecutive run (reaction was carried at 4 mmol scale with 0.37 mol % **6a**). After filtration, the recovered catalyst was washed with 10 mL dichloromethane then separated with centrifuging. After full

volatilization of the dichloromethane at r.t, the residue was diluted to 50 mL as an alkaline or higher concentration will both cause a flameout of ICP-AES. The corresponding amount of Rh in the original mixture is 0.05 × the concentration measured with ICP-AES (mg).

6. Derivation of cyclohexanol and derivatives

6.1 Preparation of adipic chloride
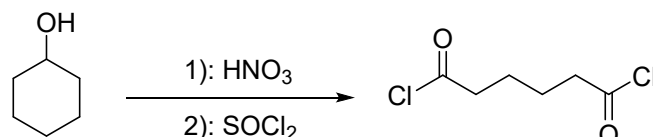
Scheme S2. Preparation of adipic chloride.

Cyclohexanol (0.5 mmol) was added into a round-bottom flask, and then HNO_3 (1 mL) was slowly added in drops. After stirring at 60 °C for 30 min, the resulting reaction mixture was heated to 100 °C and stirred for 5 min. After filtration, white solids were obtained. The obtained solid reacted with $SOCl_2$ under reflux at 85 °C for 15 h. The solvent was removed under vacuum, washed with n-hexane. Colorless oil was obtained (512 mg, 54%).[12,13]
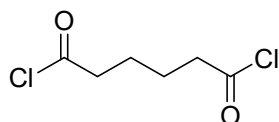
adipic chloride[13]: colorless oil

^{1}H NMR (400 MHz, CDCl$_3$) δ = 3.01 – 2.84 (m, 4H), 1.78-1.72 (m, 4H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 173.3, 46.4, 23.7 ppm.

6.2 Preparation of 1-chloroethylcyclohexyl carbonate
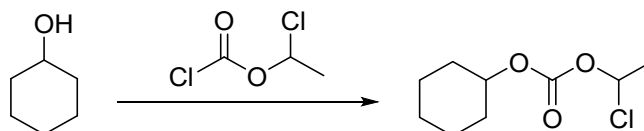
Scheme S3. Preparation of 1-chloroethylcyclohexyl carbonate.

To a solution of Cyclohexanol (5 mmol) and pyridine (5.5 mmol) in dichloromethane (4 mL) was added Chloroacetyl chloride (5.5 mmol) in dichloromethane (1 mL). After stirring at -78 °C for 30 min, the resulting reaction mixture was stirred at room temperature for 12 h. The solvent was washed with water and then purified via column chromatography (PE/EA = 10:1) to give 1-chloroethylcyclohexyl carbonate as colorless oily liquid (976 mg, 95%).[14]
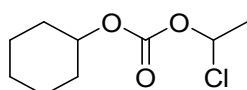
1-chloroethylcyclohexyl carbonate[14]: colorless oil

^{1}H NMR (400 MHz, CDCl$_3$) δ = 6.59 – 6.22 (m, 1H), 4.75 – 4.56 (m, 1H), 1.96-1.85 (m, 2H), 1.81-1.76 (m, 3H), 1.75-1.67 (m, 2H), 1.56 – 1.41 (m, 3H), 1.38-1.19 (m, 3H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 152.2, 84.3, 77.9, 31.3, 31.3, 25.2, 25.1, 23.5 ppm.

6.3 Preparation of monomenthyl succinate
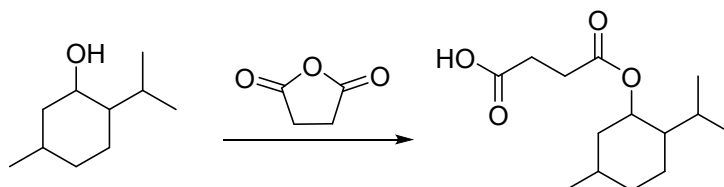
Scheme S4. Preparation of monomenthyl succinate.

A round-bottom flask was charged with menthol (5 mmol), succinic anhydride (10 mmol), DMAP (2.5 mmol) and chloroformand (20 mL), and stirred at 75 °C for 12 h. After reaction completion, solvent was removed under vacuum, and the residue was purified over column chromatography on silica gel to give monomenthyl succinate (998 mg, 78%) as a white solid.[15]
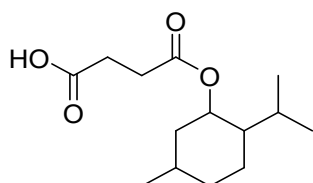
monomenthyl succinate[15]: white solid

^{1}H NMR (400 MHz, CDCl$_3$) δ = 11.59 (s, 1H), 4.70 (m, 1H), 2.71-2.55 (m, 4H), 2.08-1.92 (m, 1H), 1.91 – 1.81 (m, 1H), 1.71-1.61 (m, 2H), 1.53 – 1.31 (m, 2H), 1.12 – 0.94 (m, 2H), 0.89 ((t, J = 6.3 Hz, 6H), 0.87-0.79 (m, 1H), 0.74 (d, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl$_3$) δ = 178.6, 171.7, 74.8, 47.0, 40.8, 34.2, 31.4, 29.2, 29.1, 26.2, 23.4, 22.0, 20.7, 16.2 ppm.

7. ^{1}H, ^{13}C and ^{19}F NMR spectra.
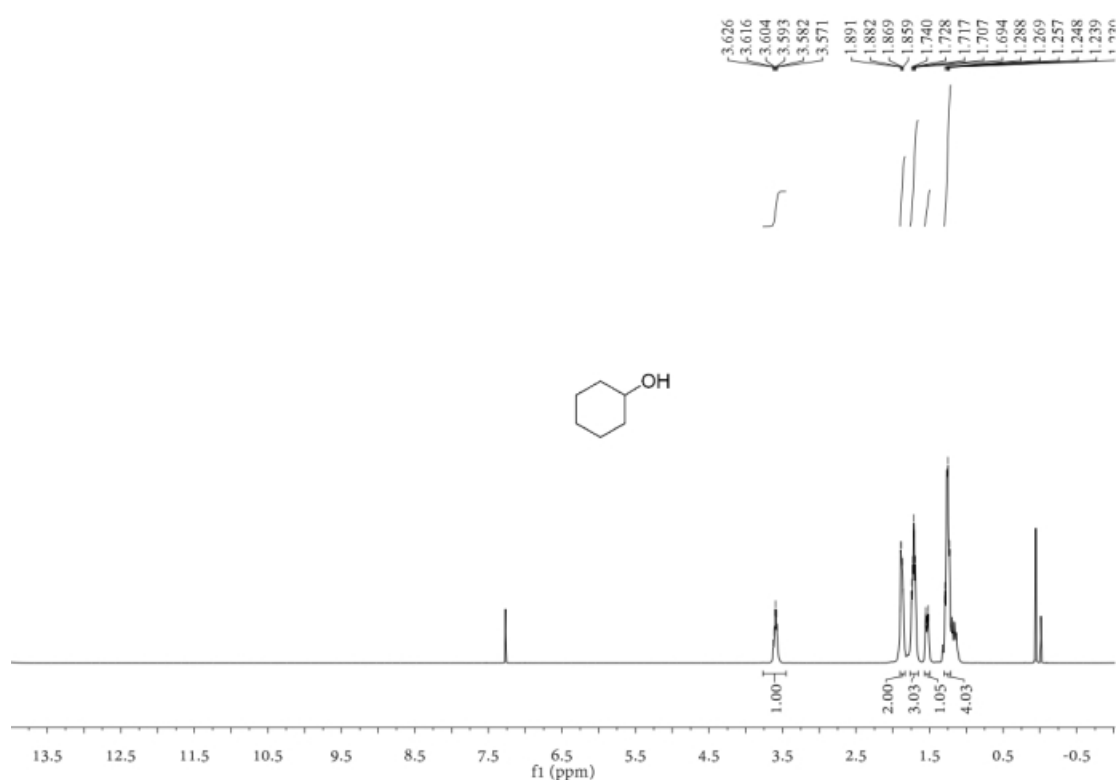
Fig. S4 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **2**.

70.253   35.481   25.405   24.096

Fig. S5 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **2**.

3.774 3.768 3.761 3.755   3.119 3.105 3.095 3.081   1.614 1.515 1.399 1.387 1.376 1.367 1.272 1.244 1.222 1.002 0.986 0.937

1.00   2.07 2.08 2.03 3.03 3.06
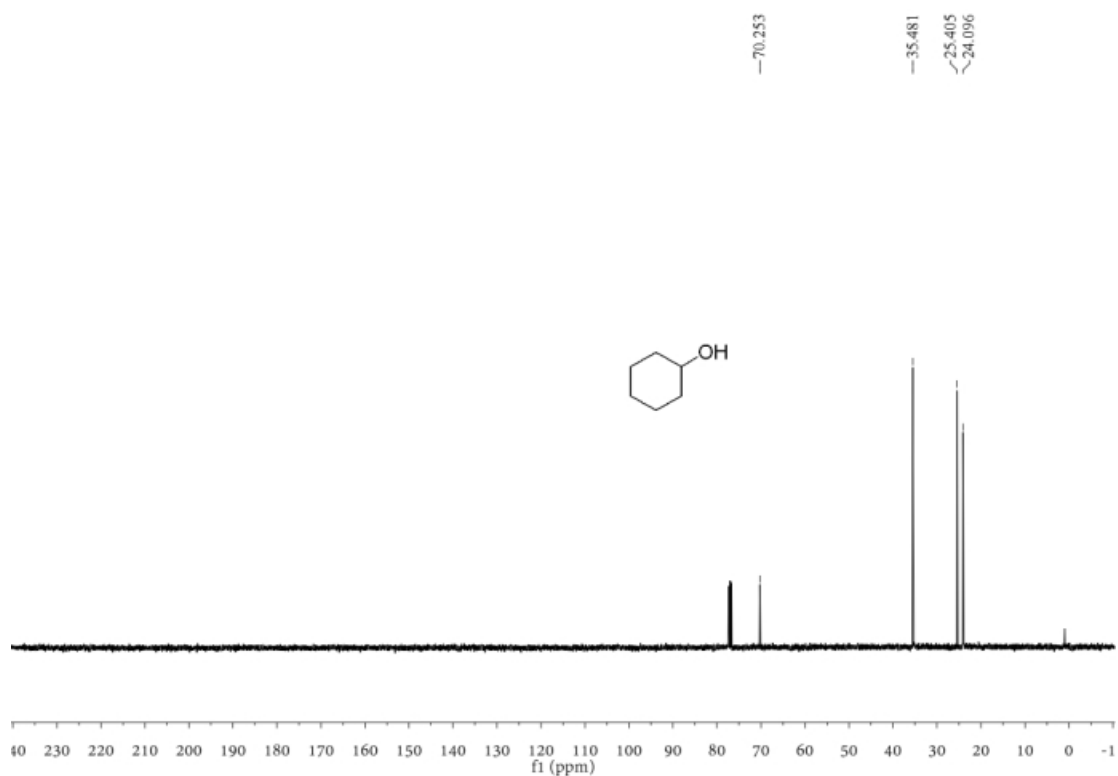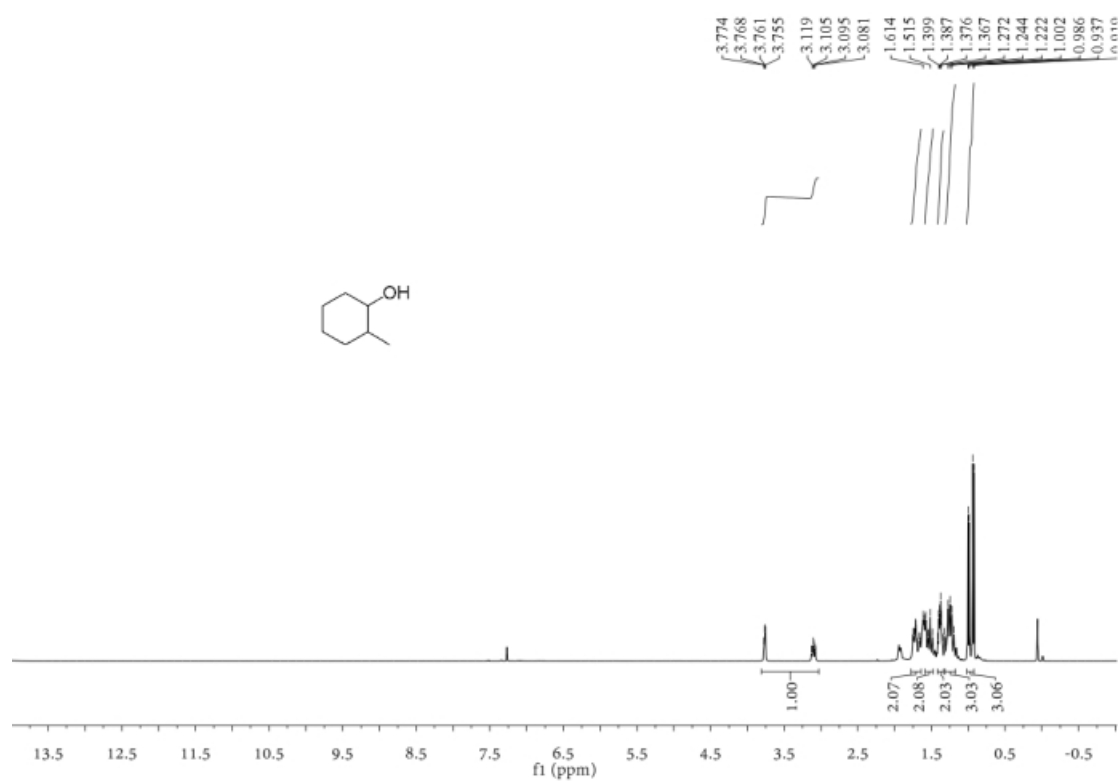
Fig. S6 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10a**.
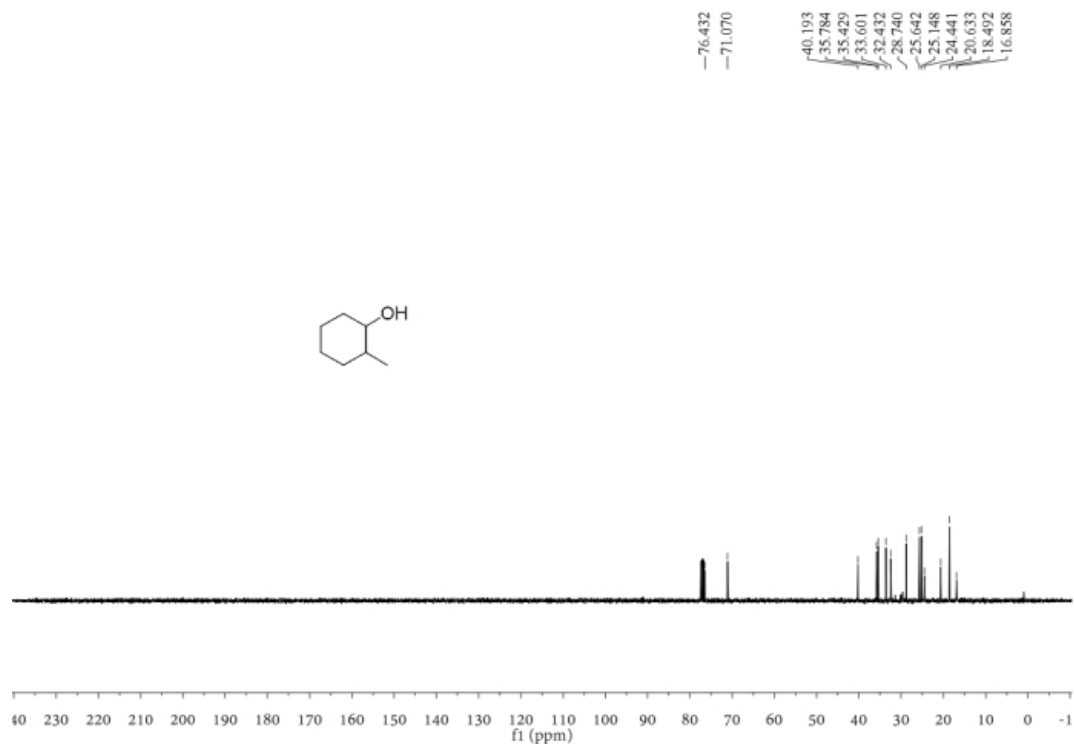
Fig. S7 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10a**.
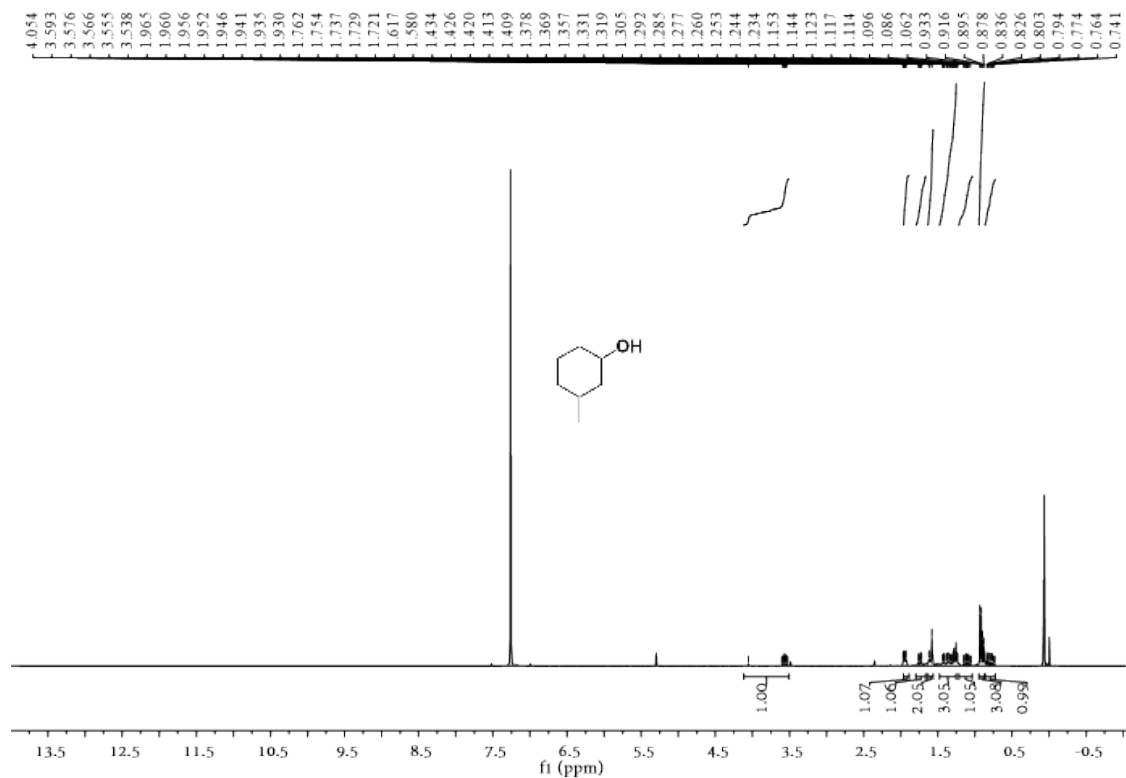
Fig. S8 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10b**.
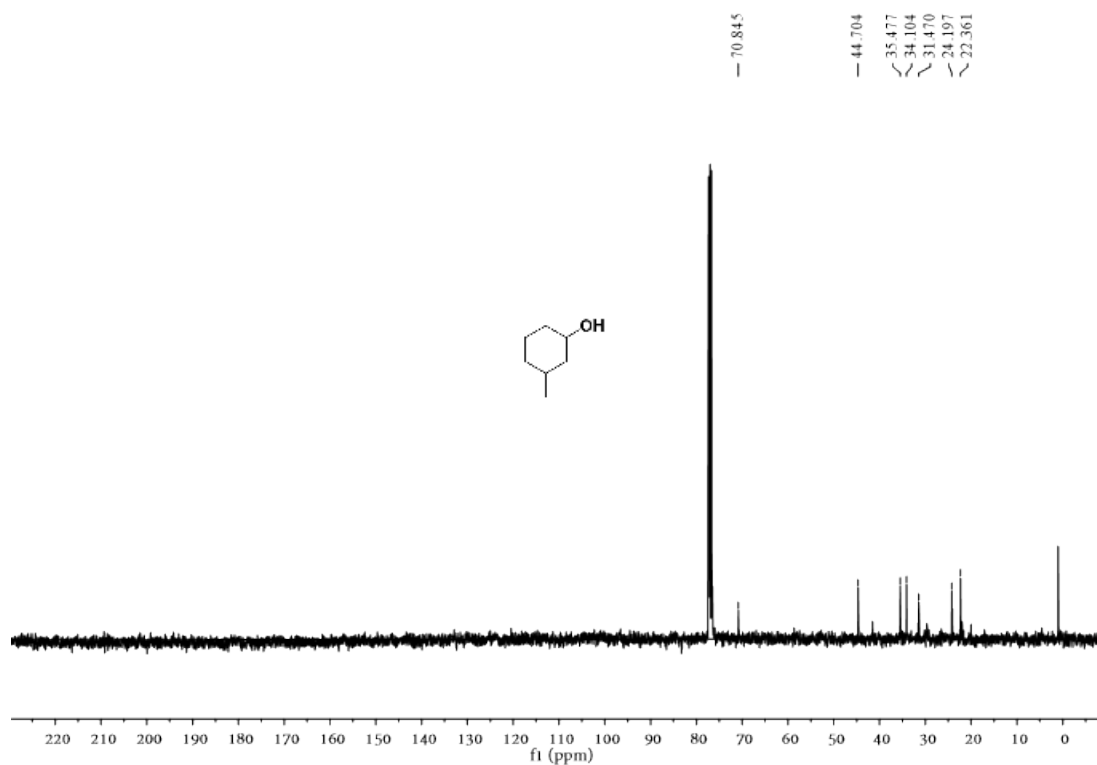
Fig. S9 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10b**.
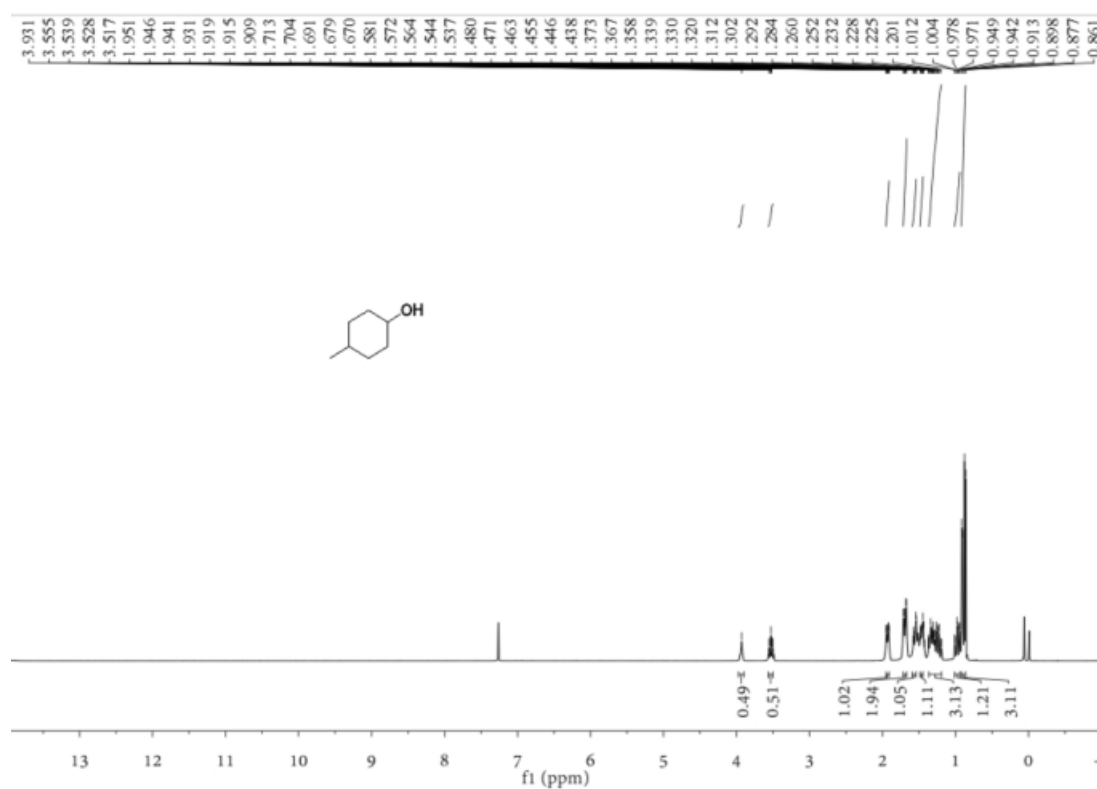
Fig. S10 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10c**.
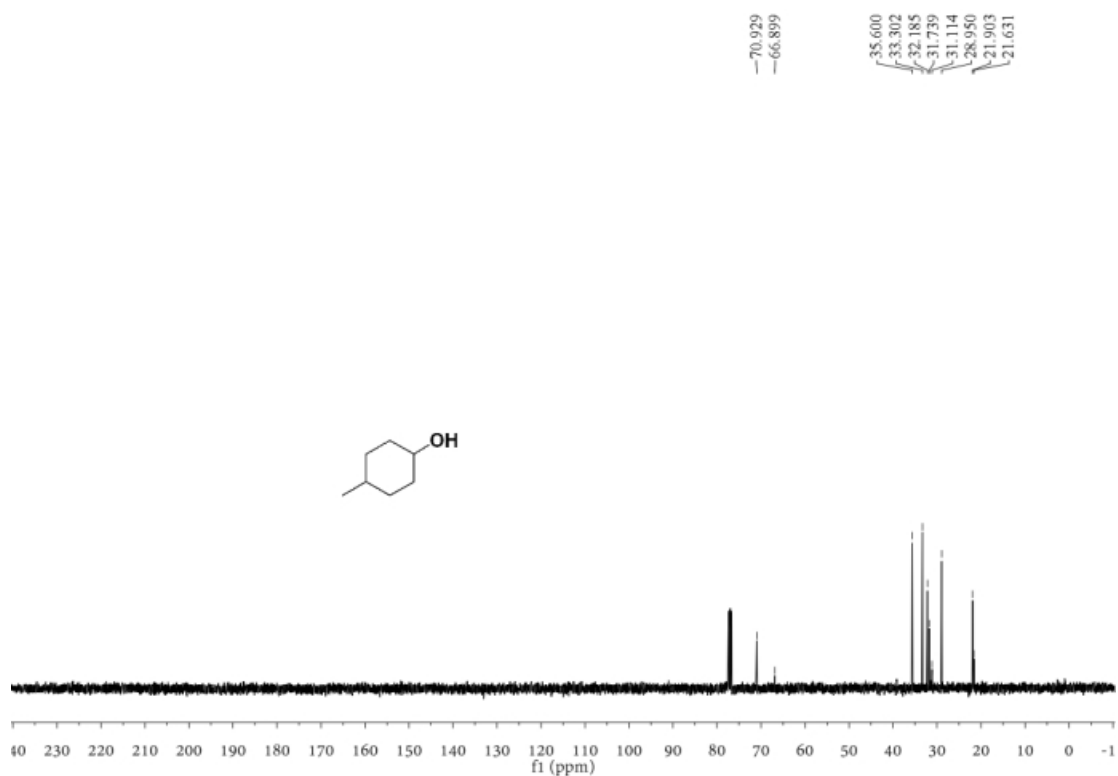
Fig. S11 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10c**.
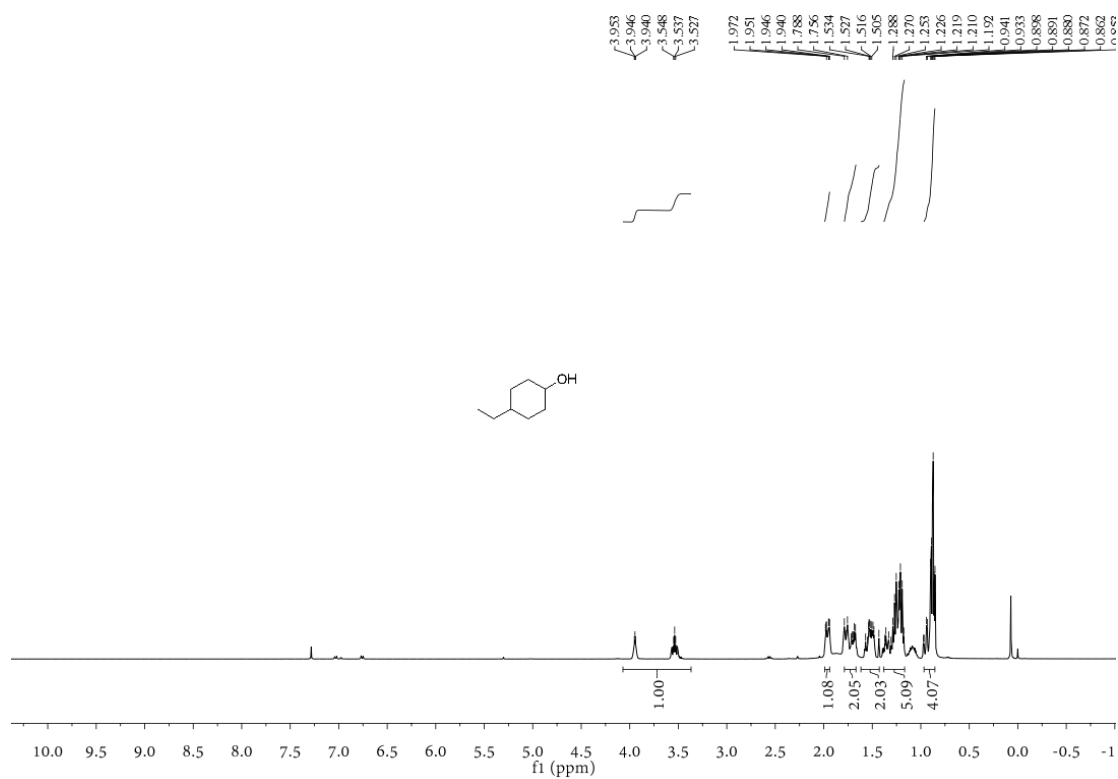
Fig. S12 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10d**.
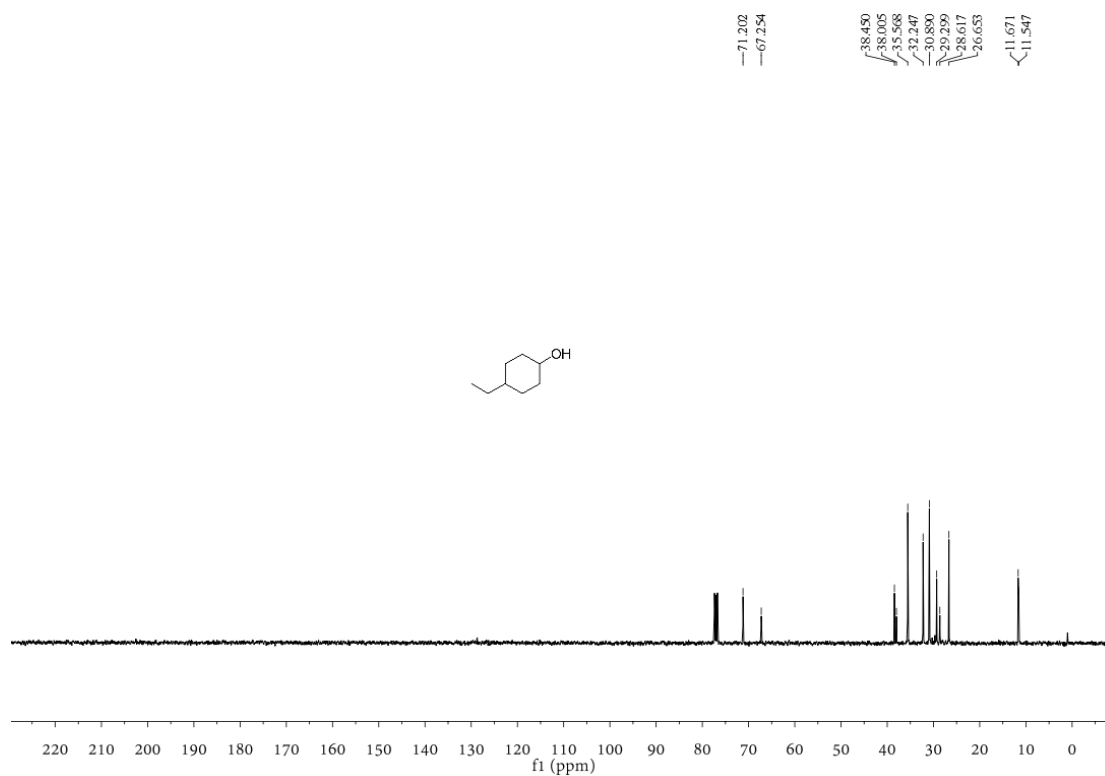
Fig. S13 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10d**.
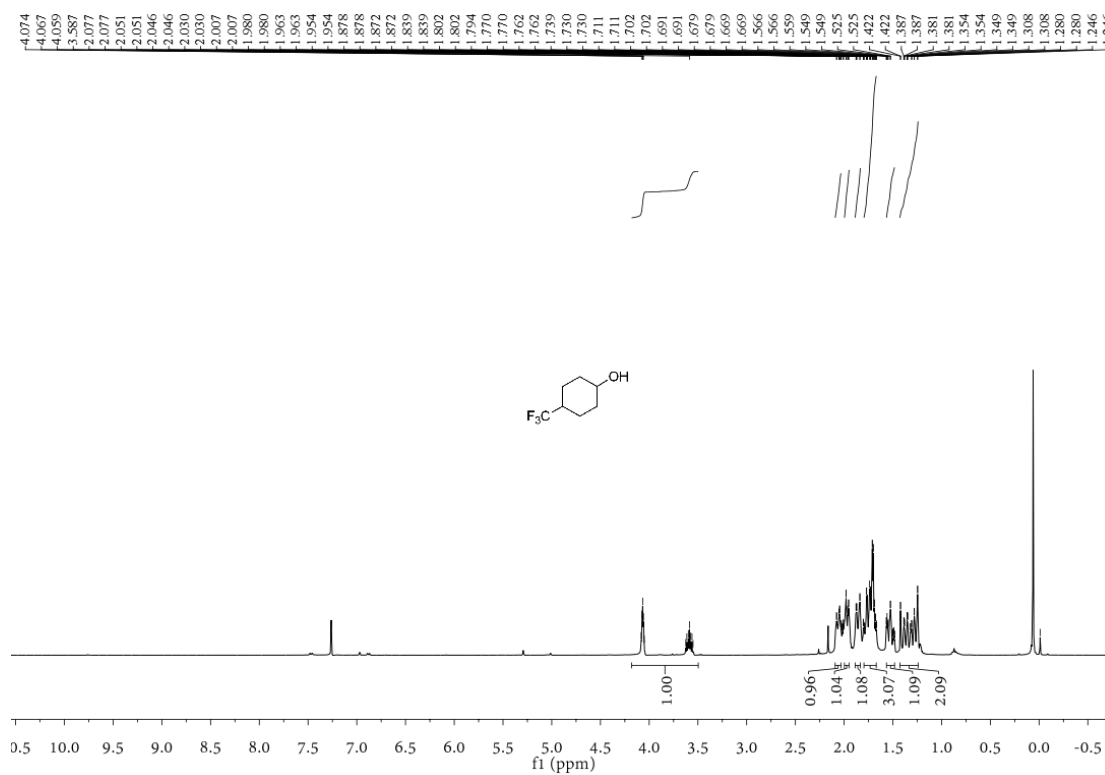
Fig. S14 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10e**.
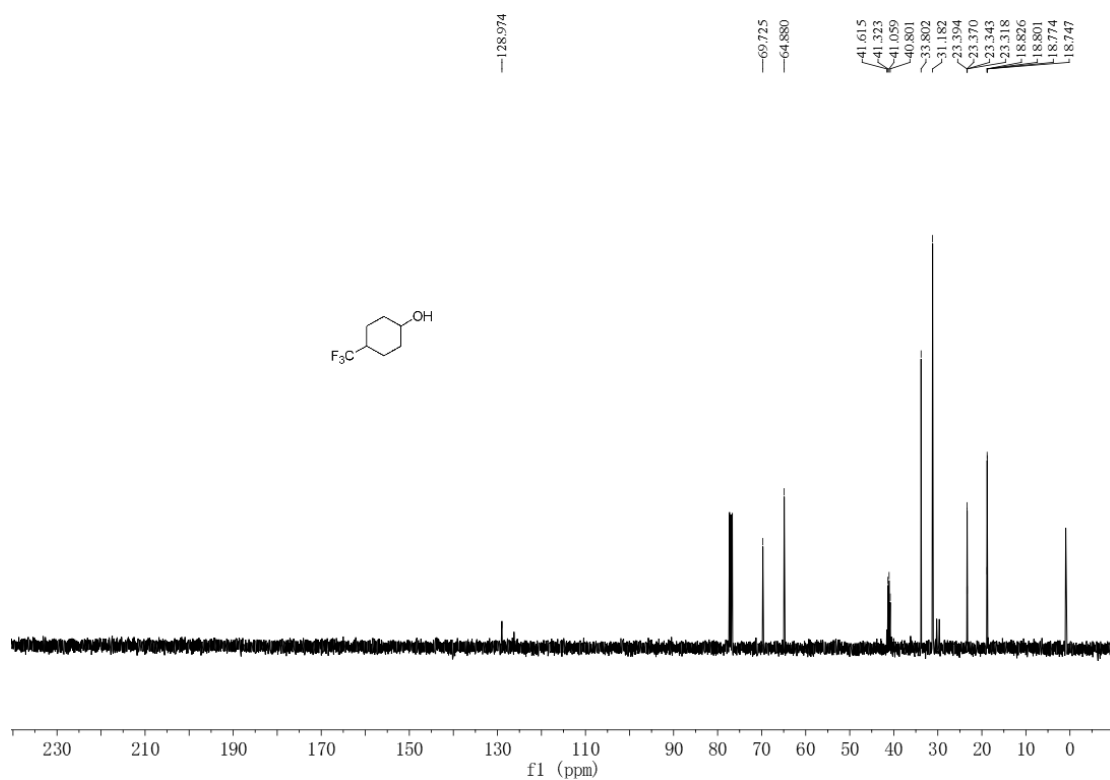
Fig. S15 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10e**.
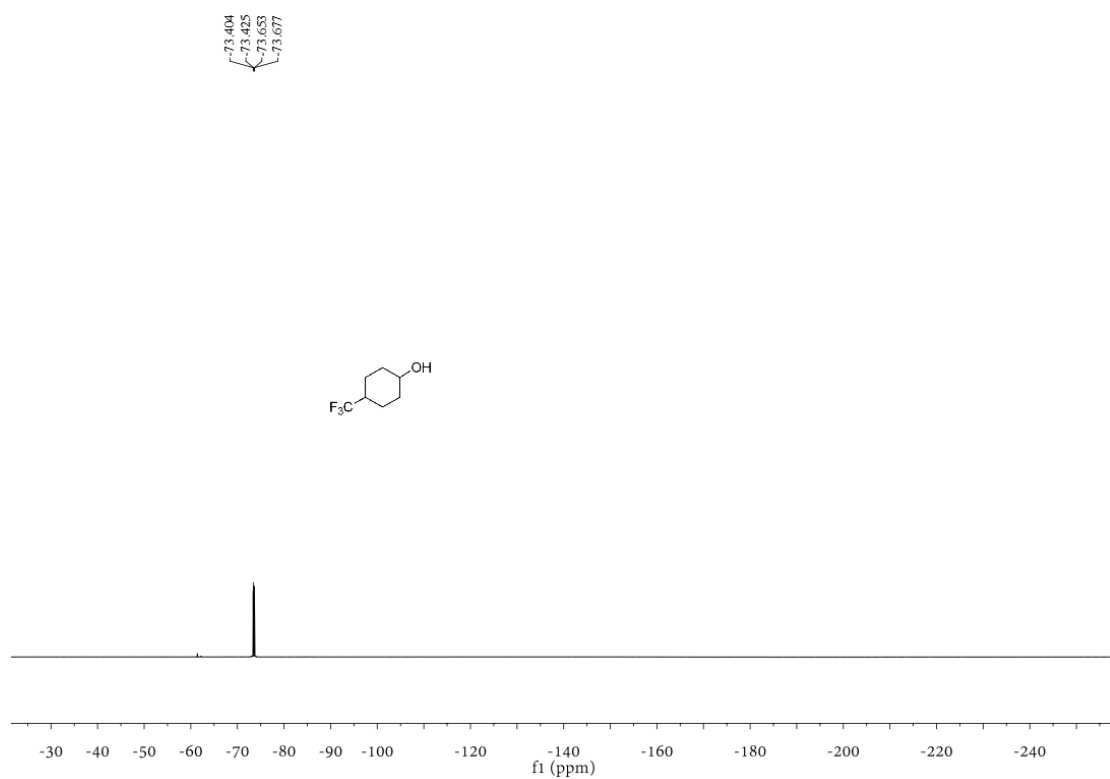
Fig. S16 ^{19}F NMR (376 MHz, CDCl$_3$, 298 K) spectrum of compound **10e**
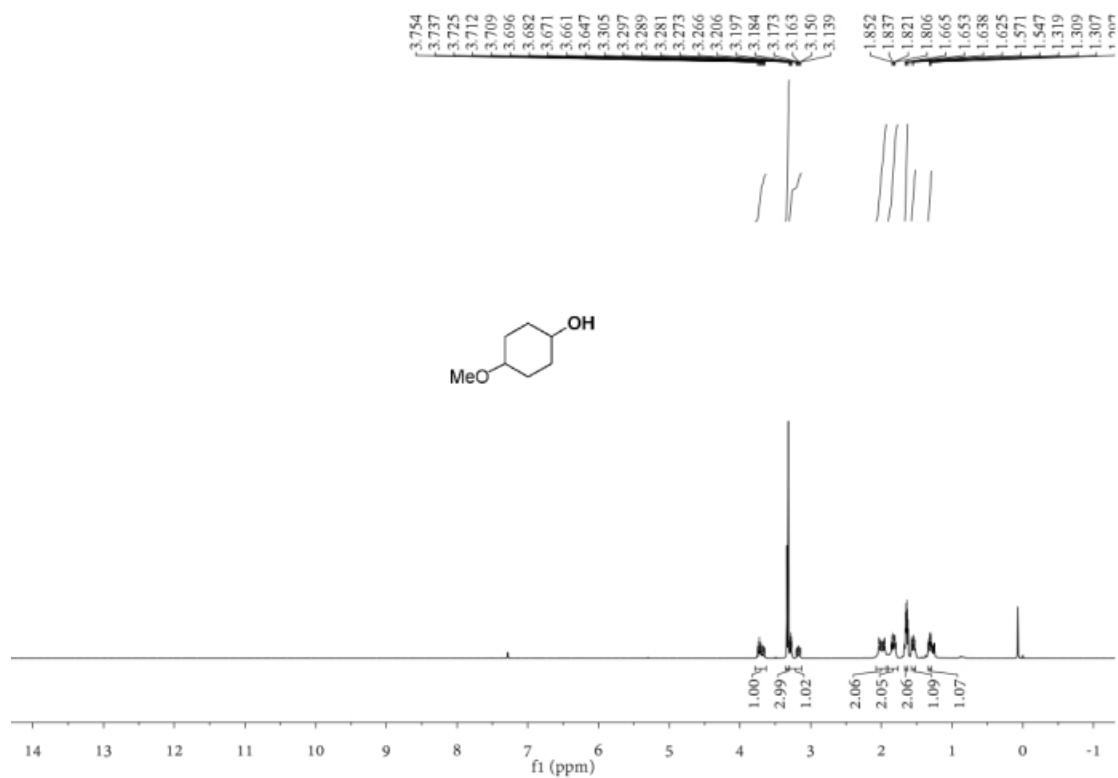
Fig. S17 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10f**.
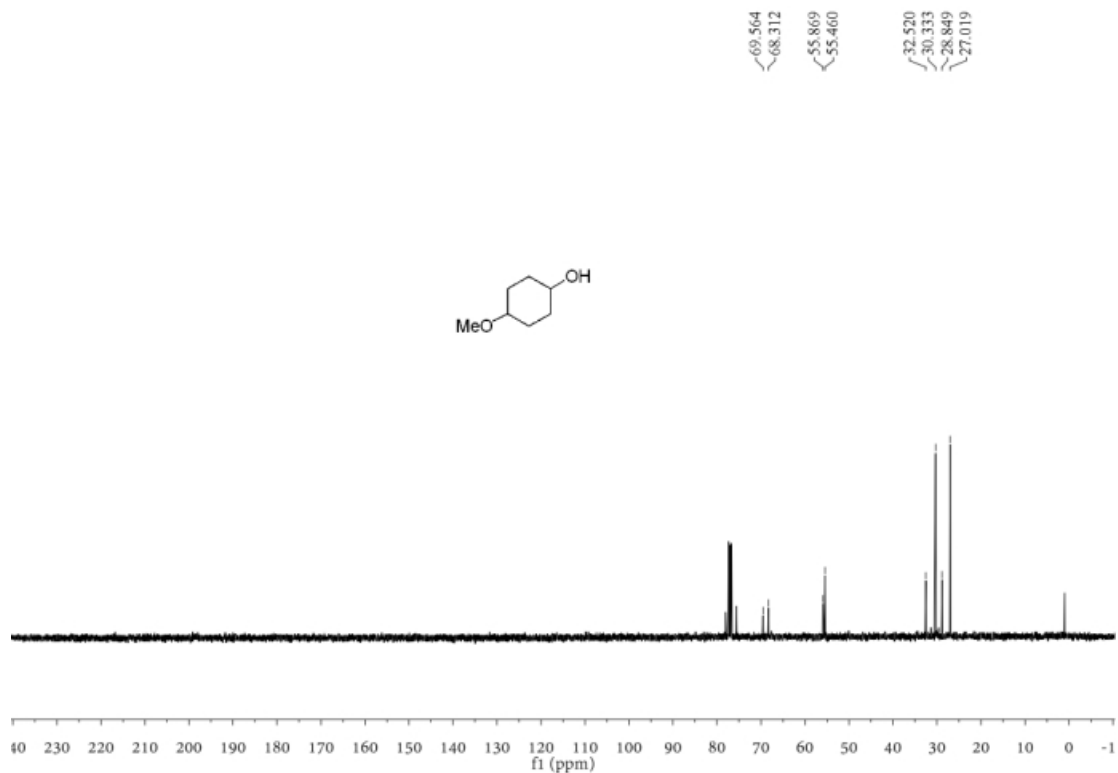
Fig. S18 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10f**.
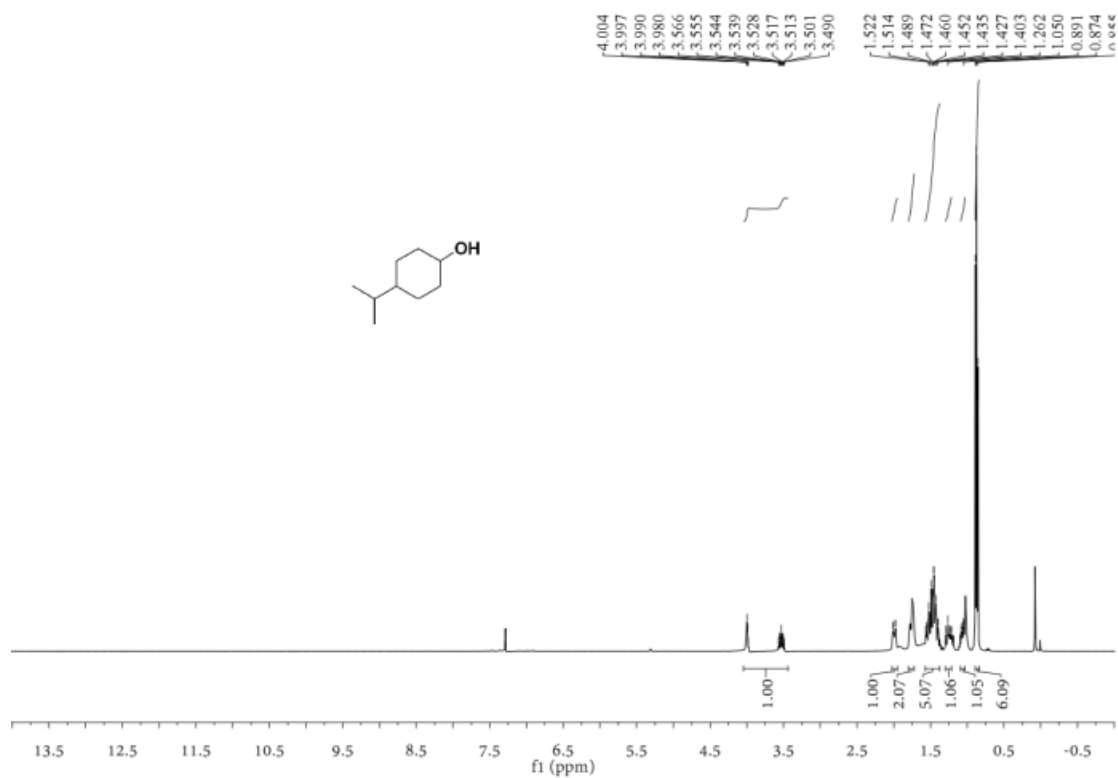
Fig. S19 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10g**.
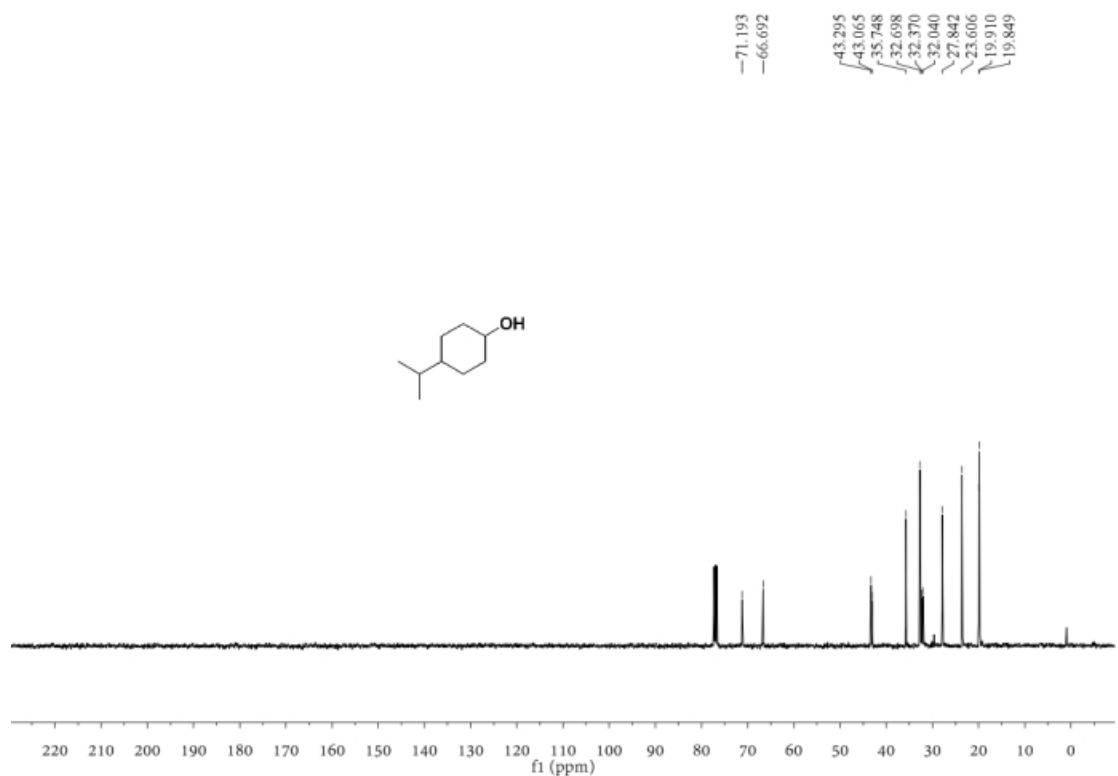
Fig. S20 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10g**.
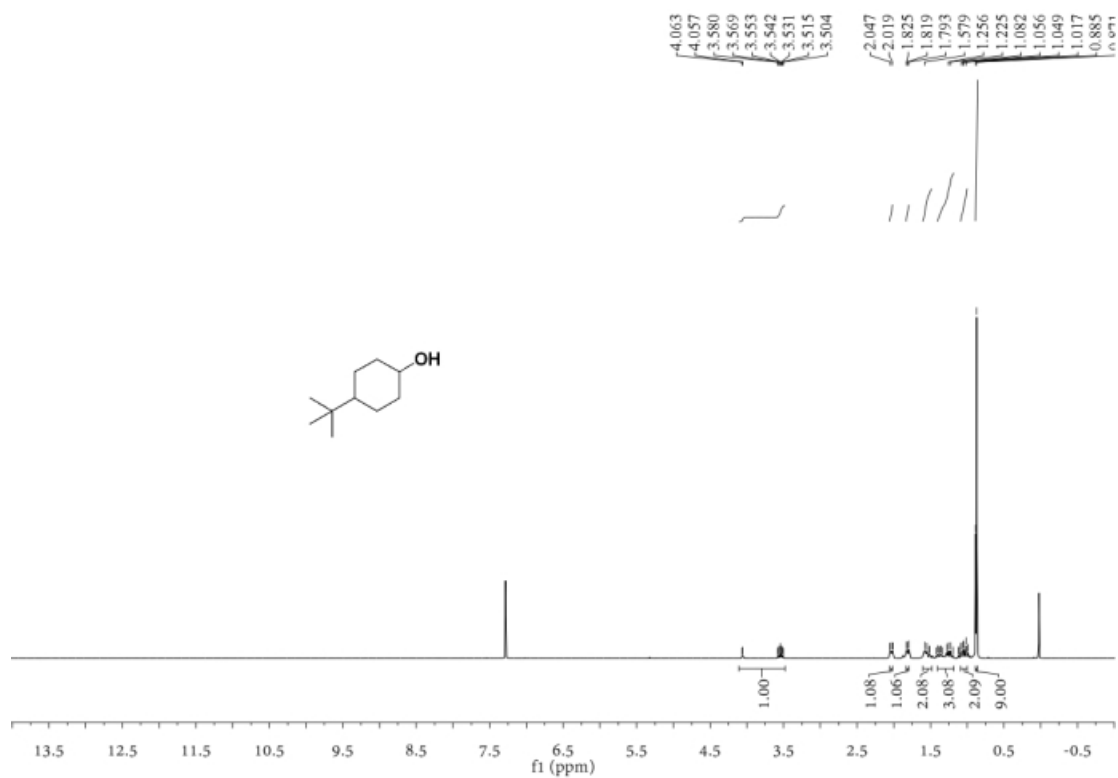
Fig. S21 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10h**.
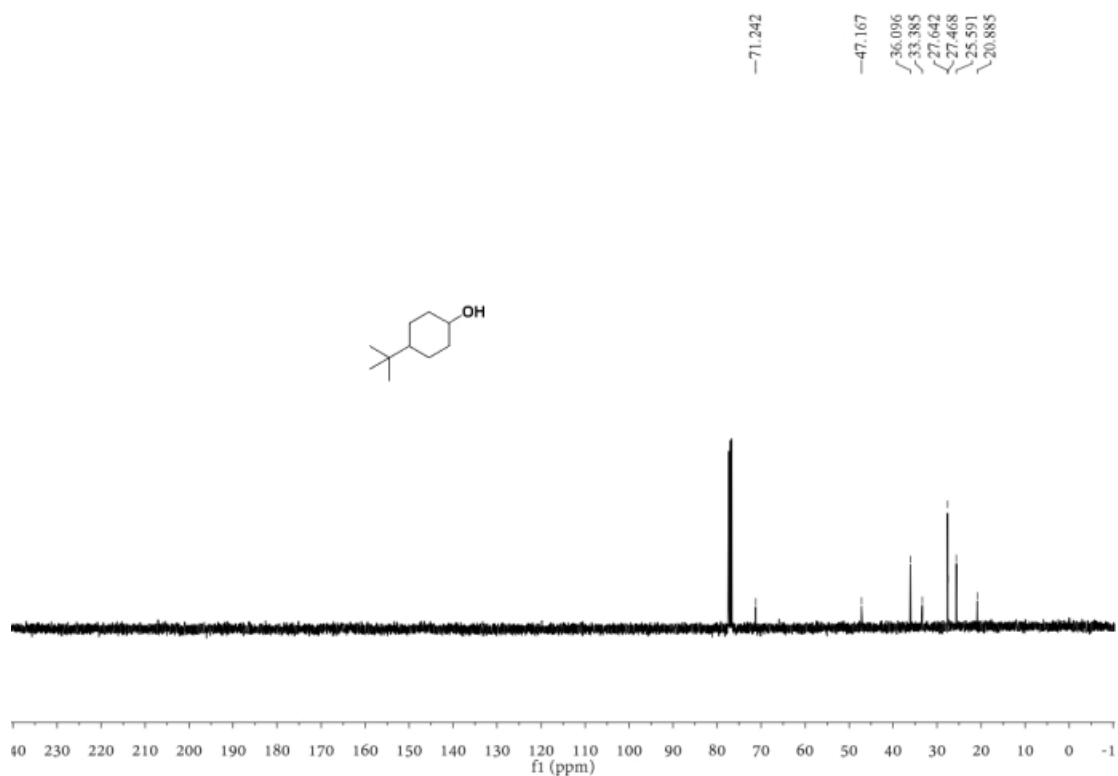
Fig. S22 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10h**.
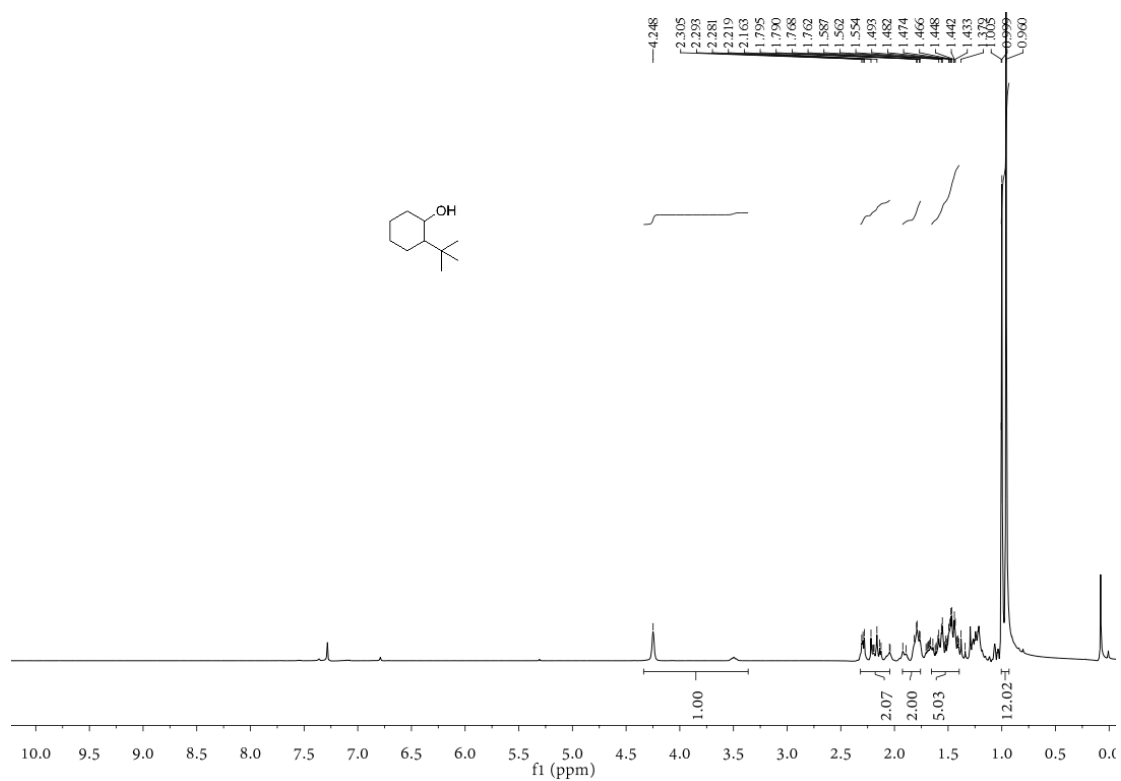
Fig. S23 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10i**.
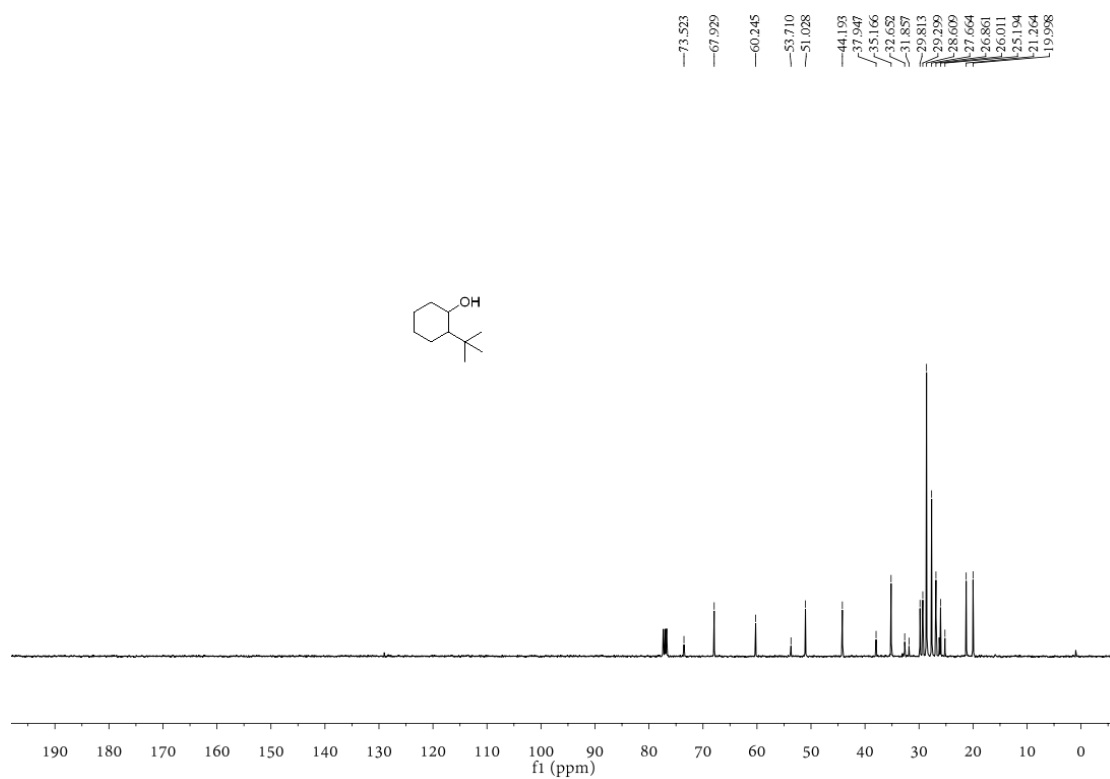
Fig. S24 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10i**.
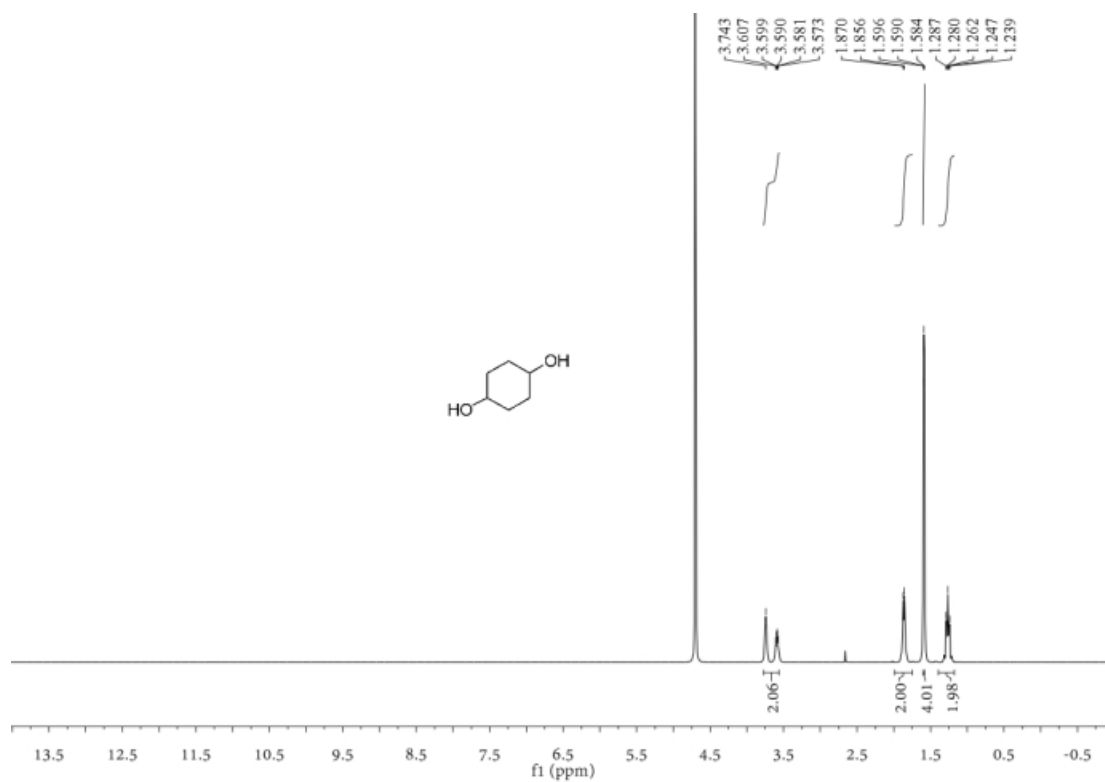
Fig. S25 ^{1}H NMR (400 MHz, D$_2$O, 298 K) spectrum of compound **10j**.
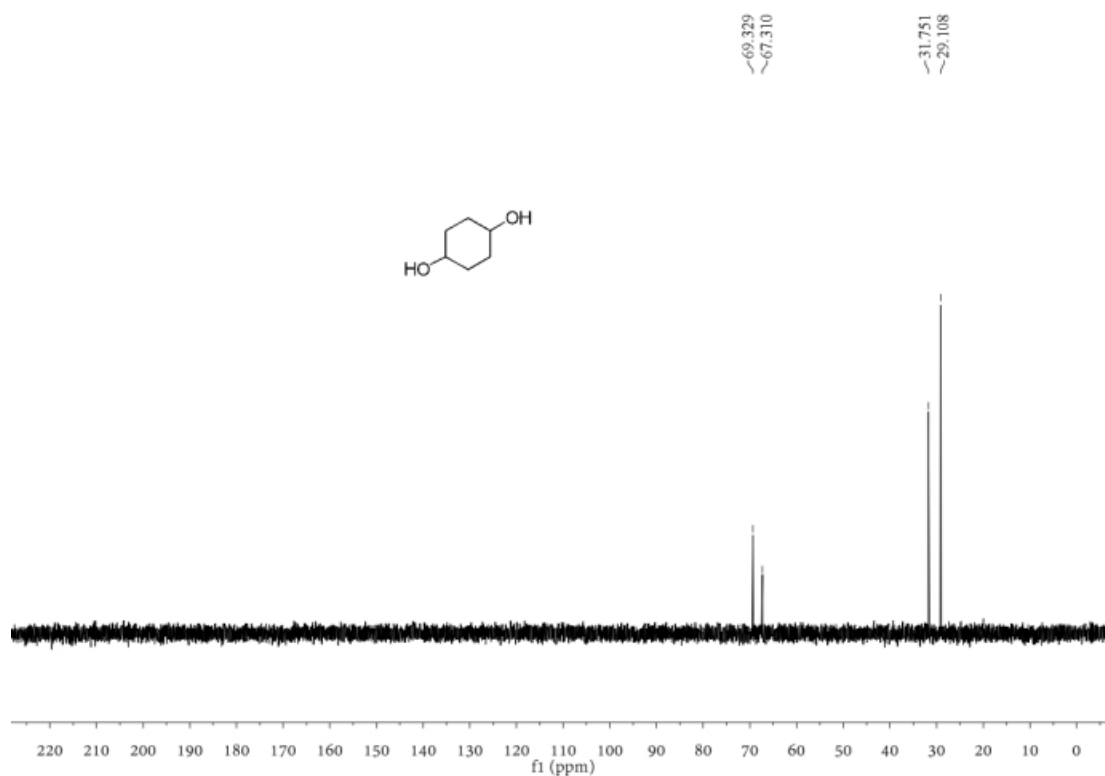
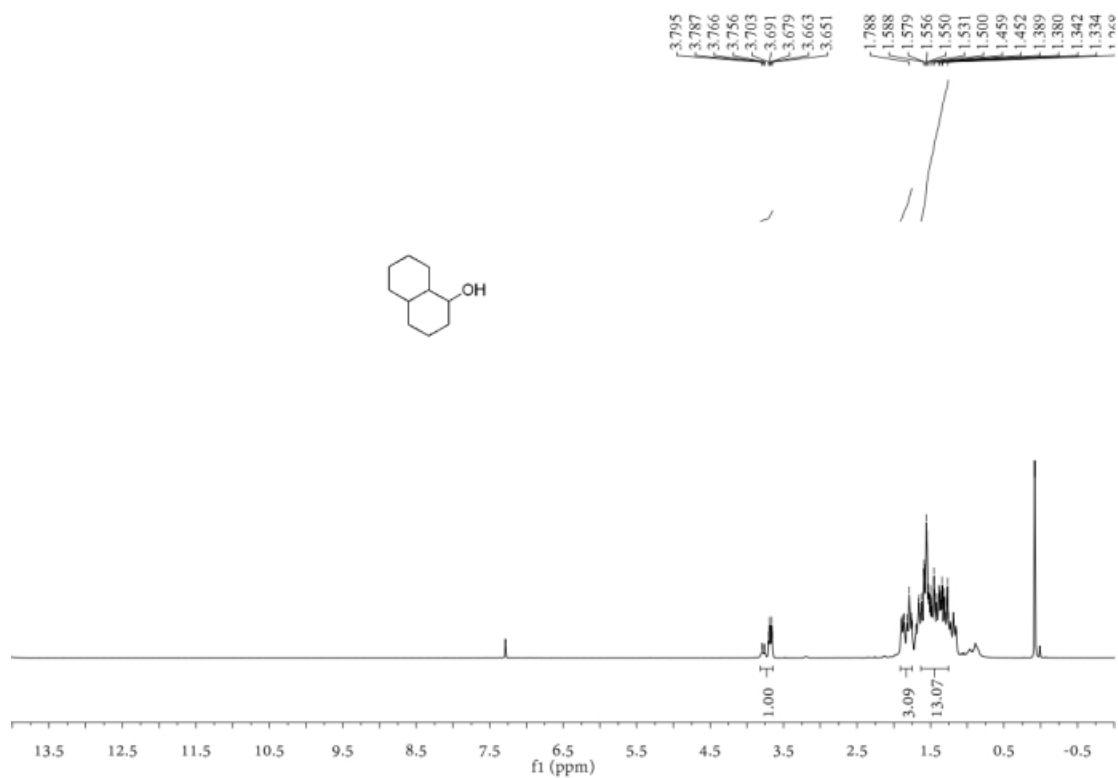**Fig. S26** ^{13}C NMR (101 MHz, D$_2$O, 298 K) spectrum of compound **10j**.
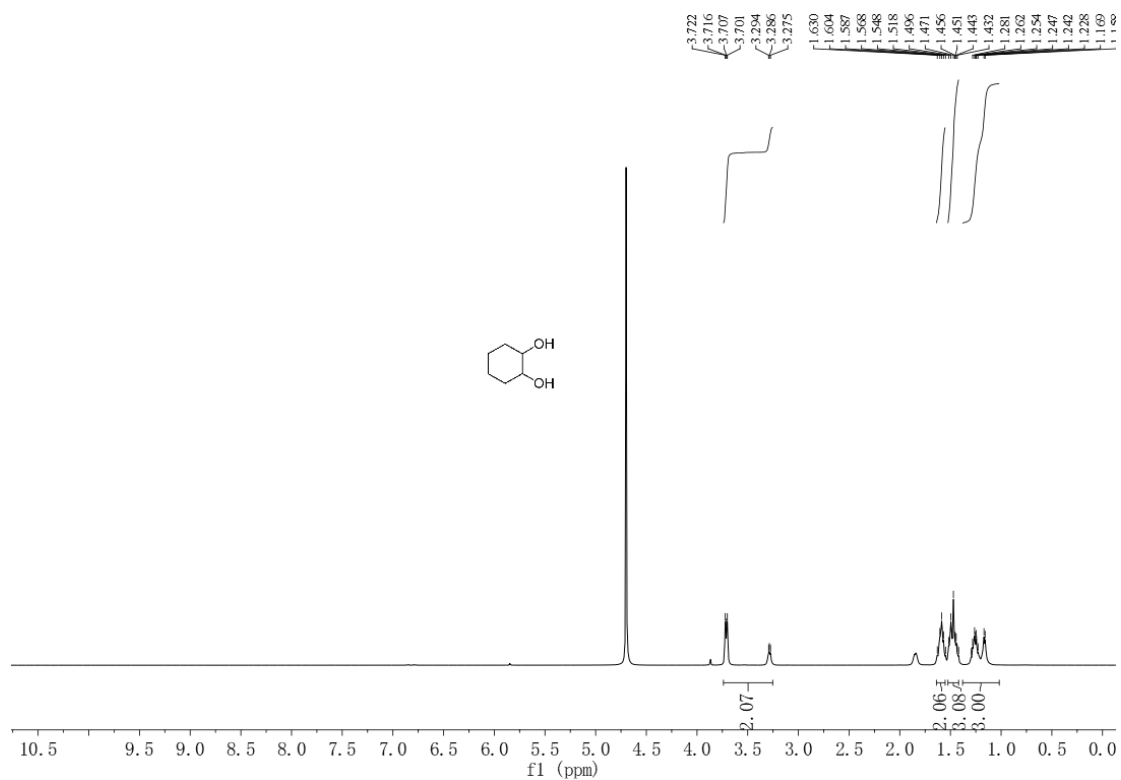
Fig. S27 ¹H NMR (400 MHz, D₂O, 298 K) spectrum of compound **10k**
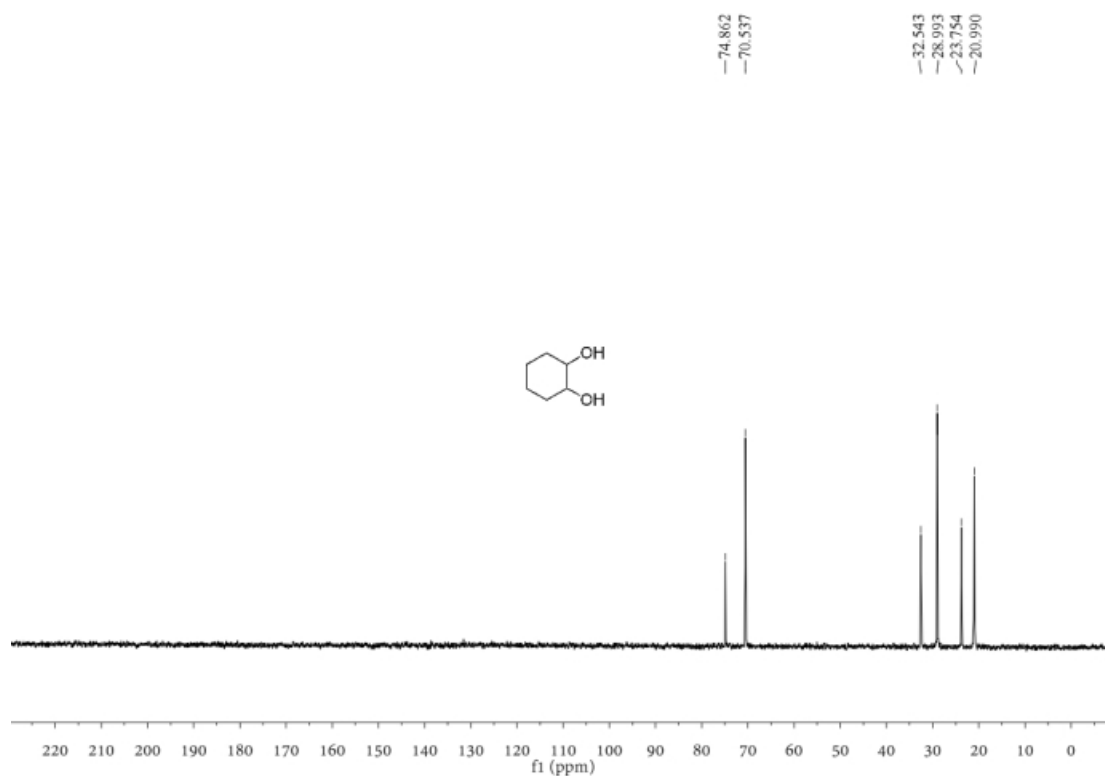
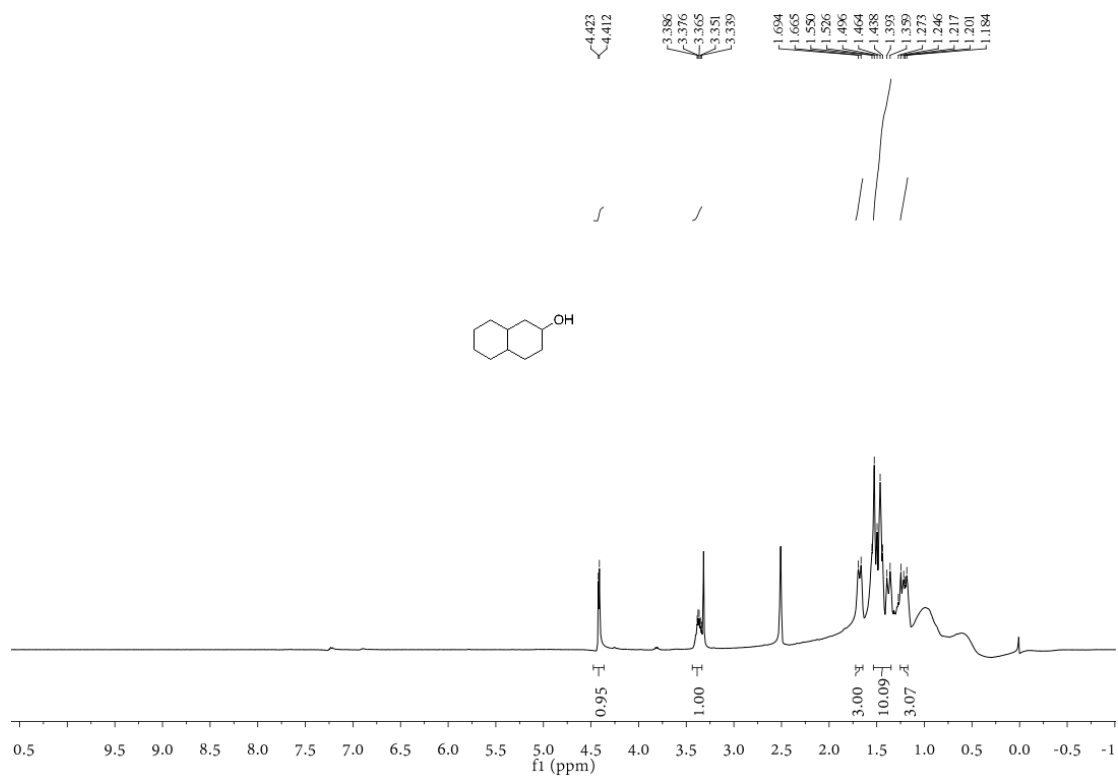**Fig. S28** ¹³C NMR (101 MHz, D₂O, 298 K) spectrum of compound **10k**.
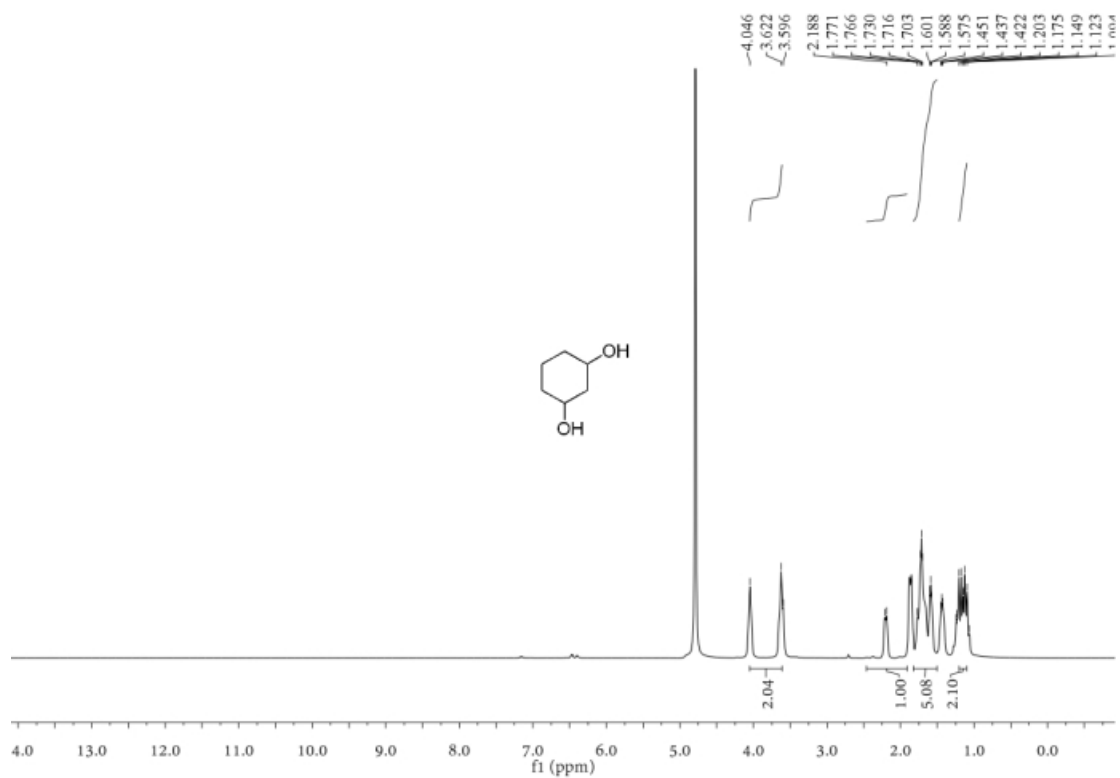
Fig. S29 ^{1}H NMR (400 MHz, D$_2$O, 298 K) spectrum of compound **10l**
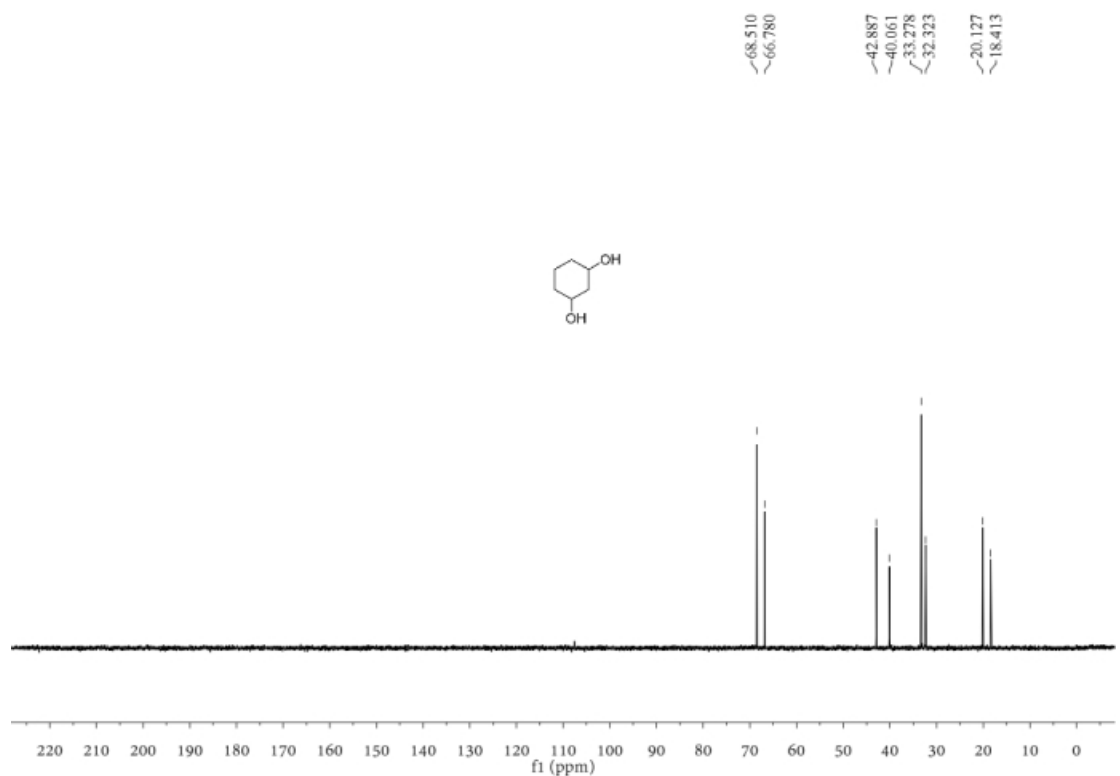
Fig. S30 ^{13}C NMR (101 MHz, D$_2$O, 298 K) spectrum of compound **10l**.
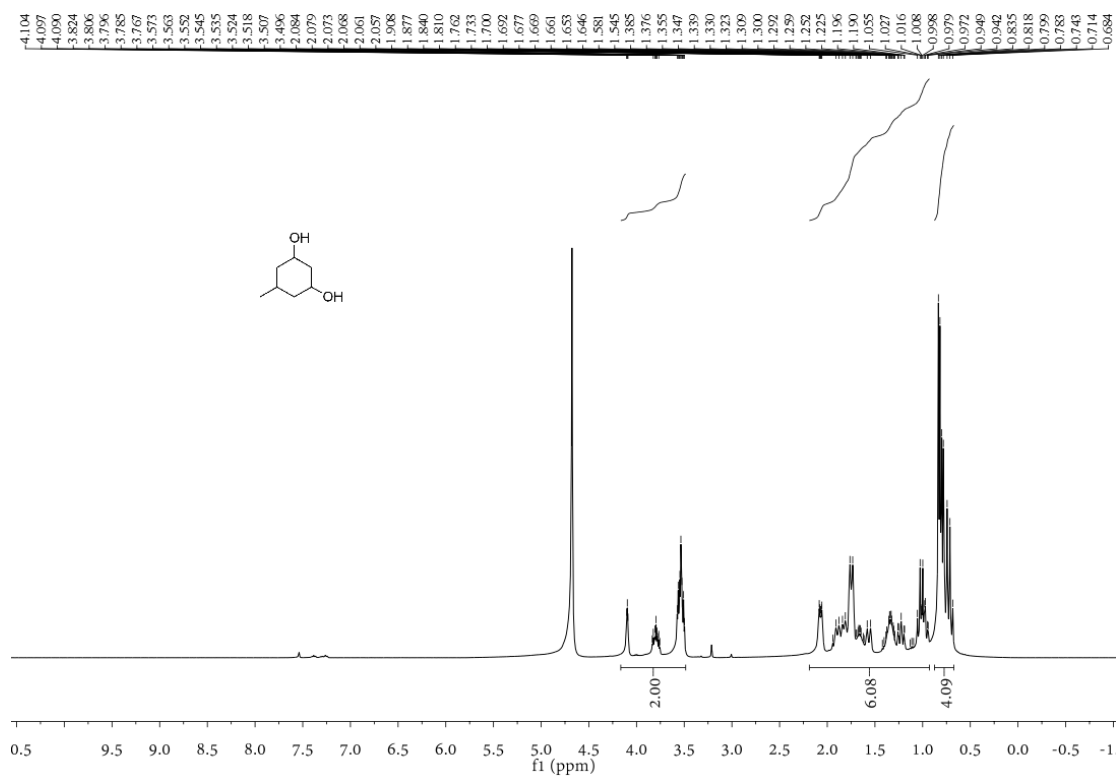
Fig. S31 ^{1}H NMR (400 MHz, D$_2$O, 298 K) spectrum of compound **10m**
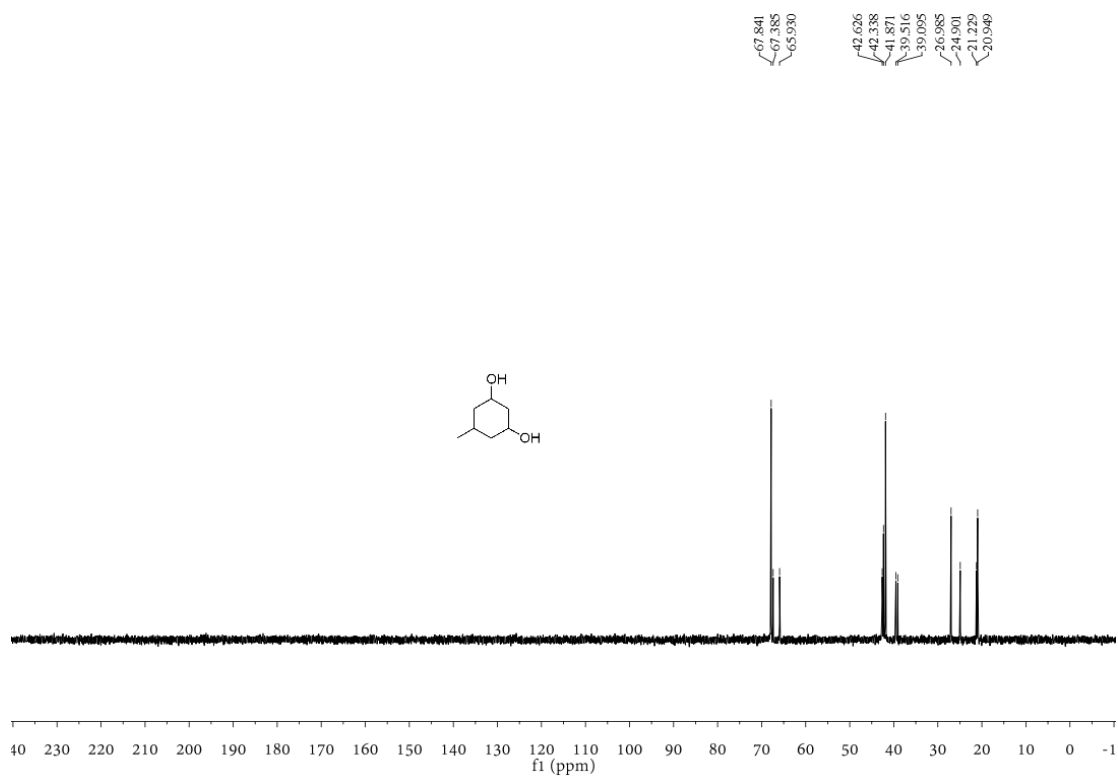
Fig. S32 ^{13}C NMR (101 MHz, D$_2$O, 298 K) spectrum of compound **10m**.
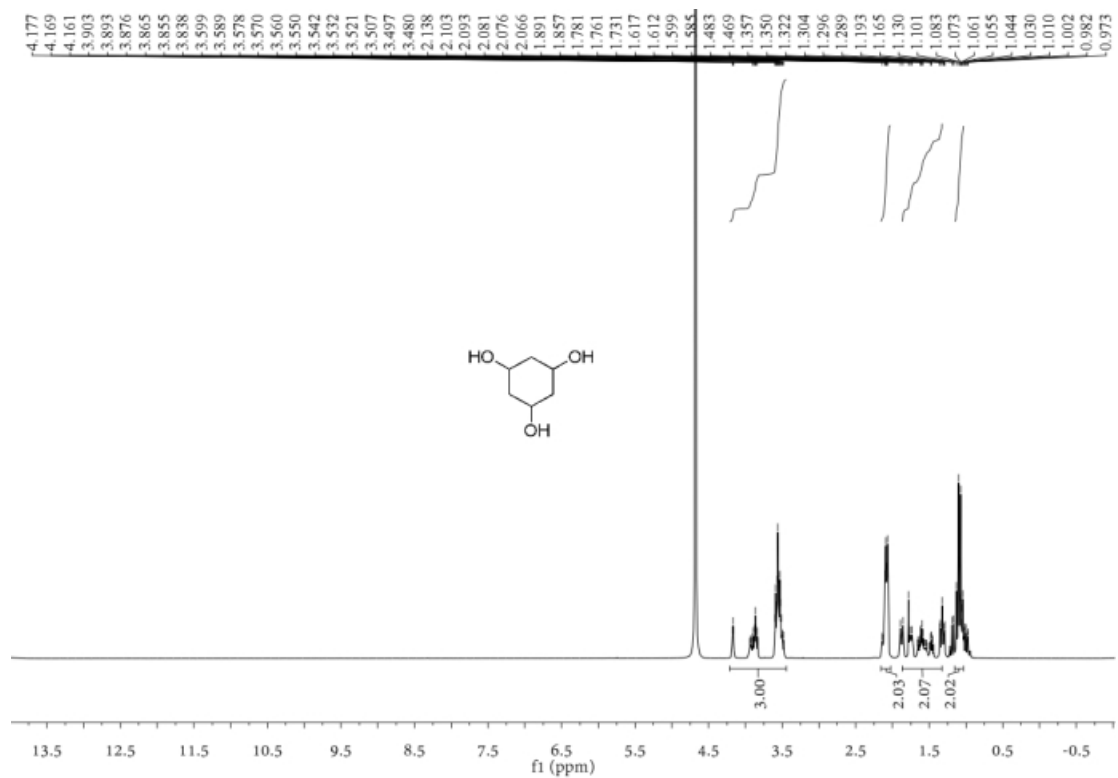
Fig. S33 ^{1}H NMR (400 MHz, D$_2$O, 298 K) spectrum of compound **10n**
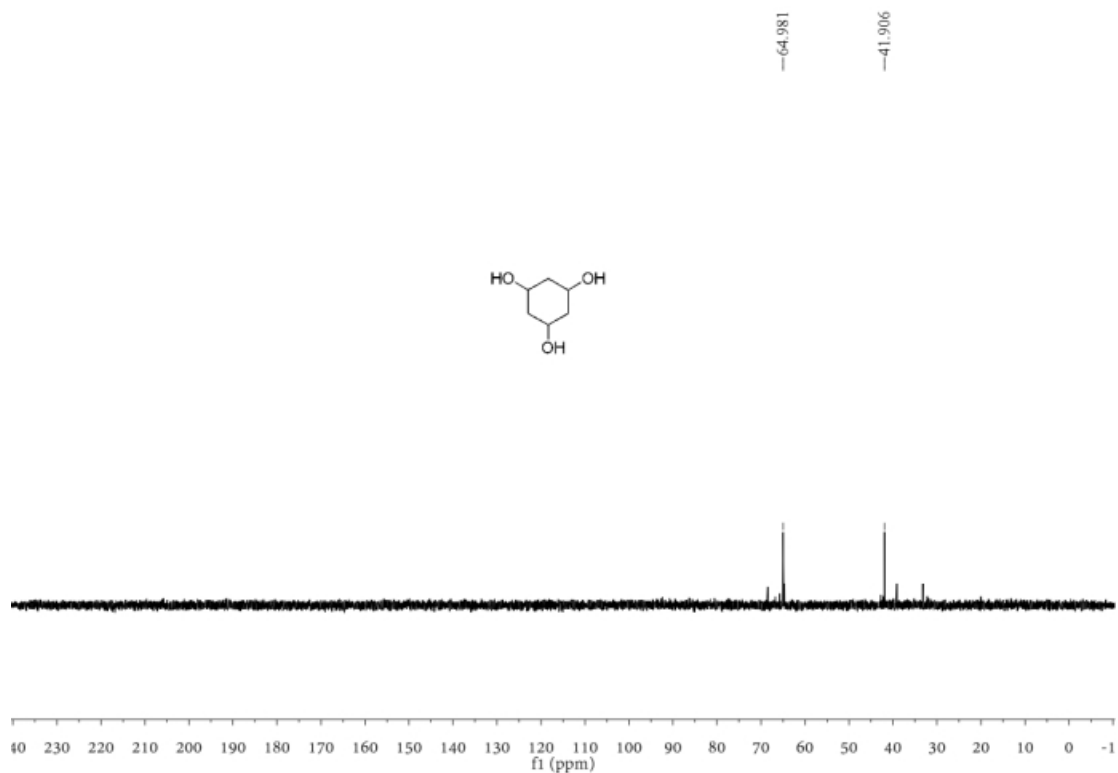
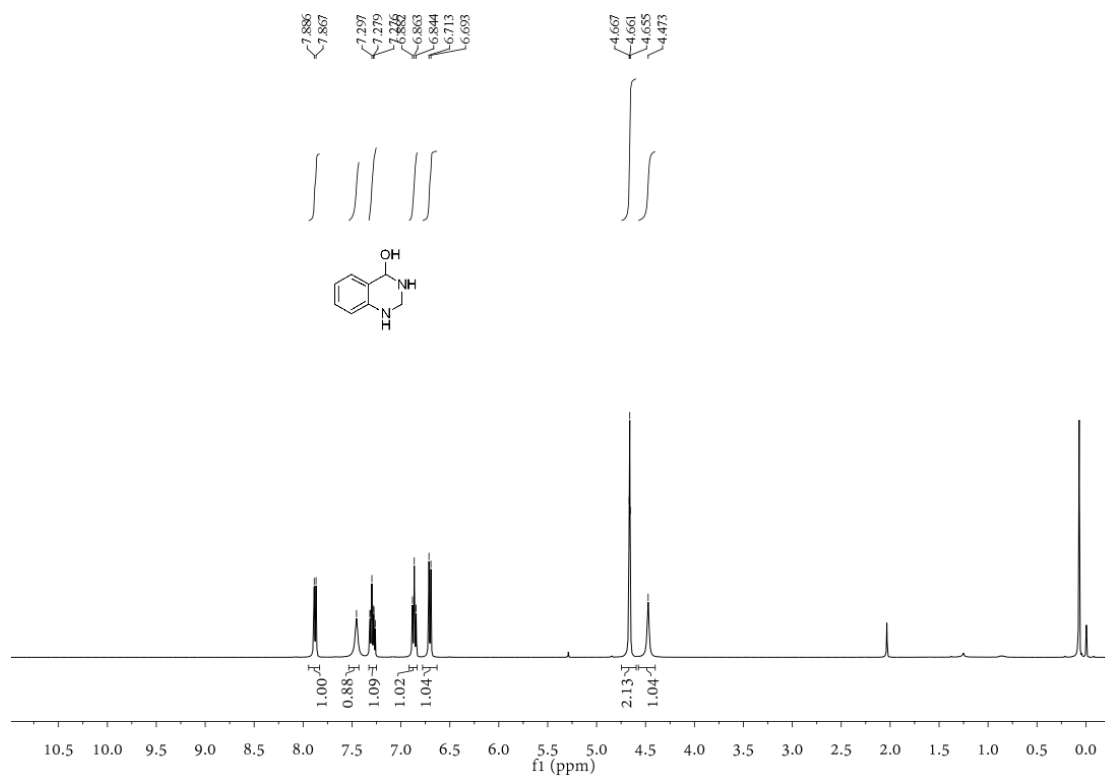**Fig. S34** ^{13}C NMR (101 MHz, D$_2$O, 298 K) spectrum of compound **10n**.
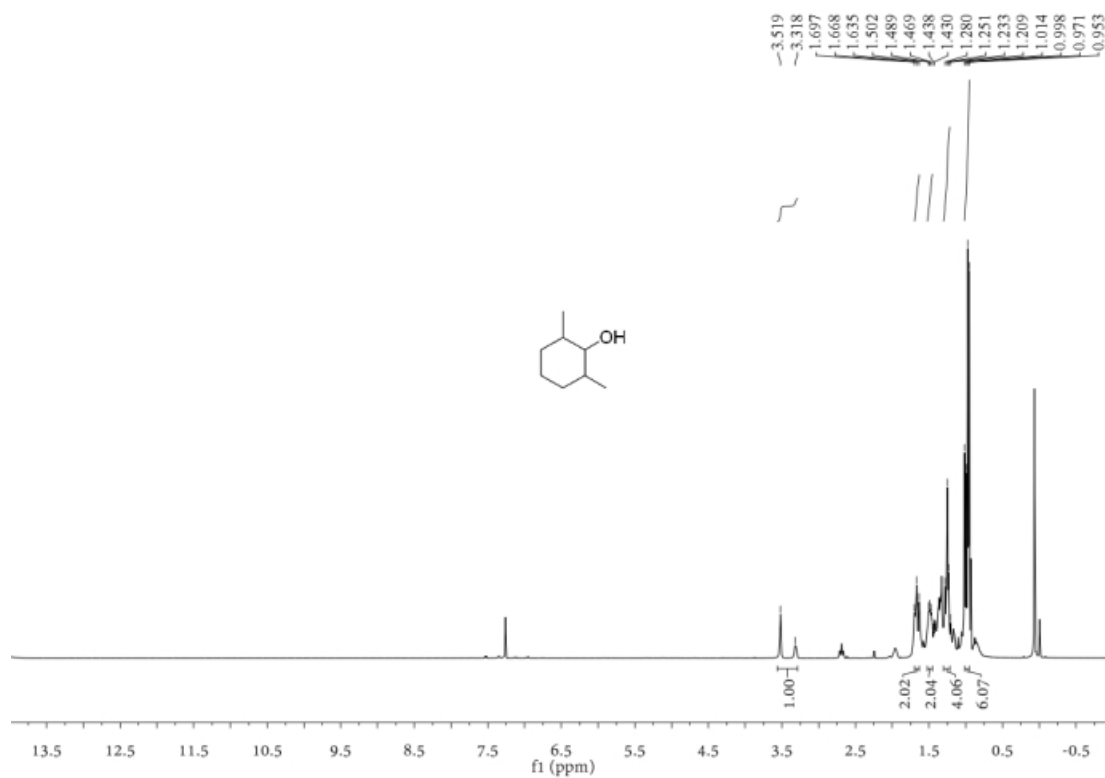
Fig. S35 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10o**
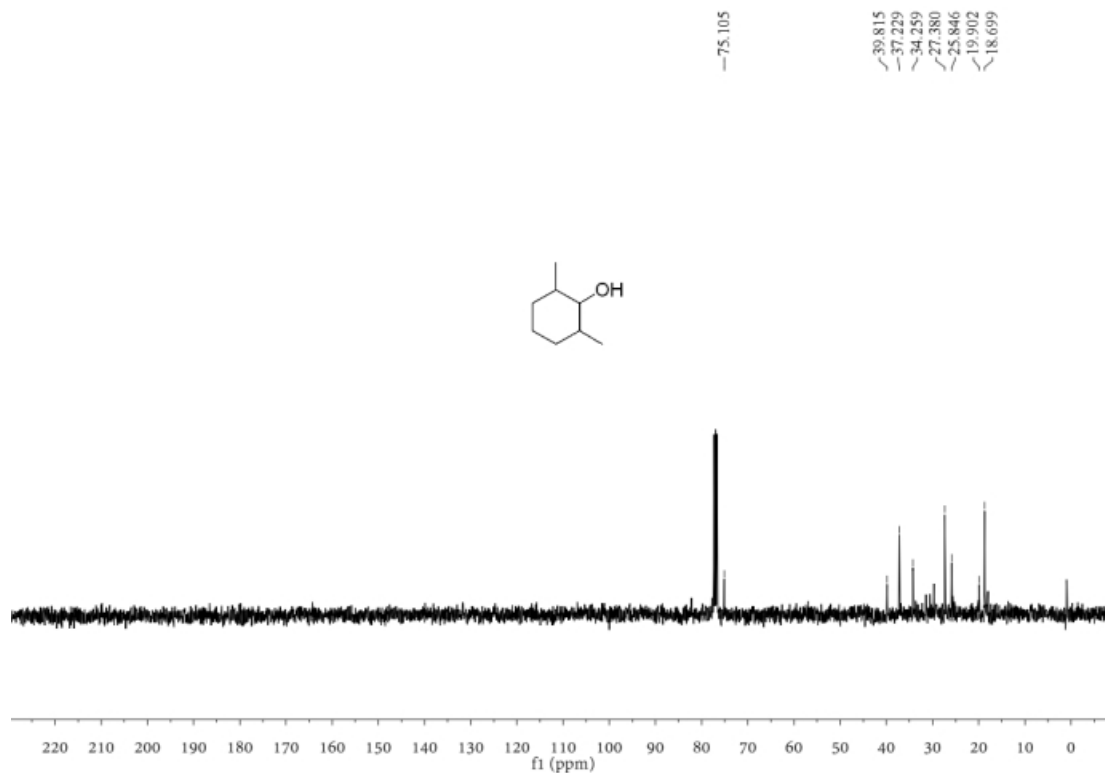
Fig. S36 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10o**.
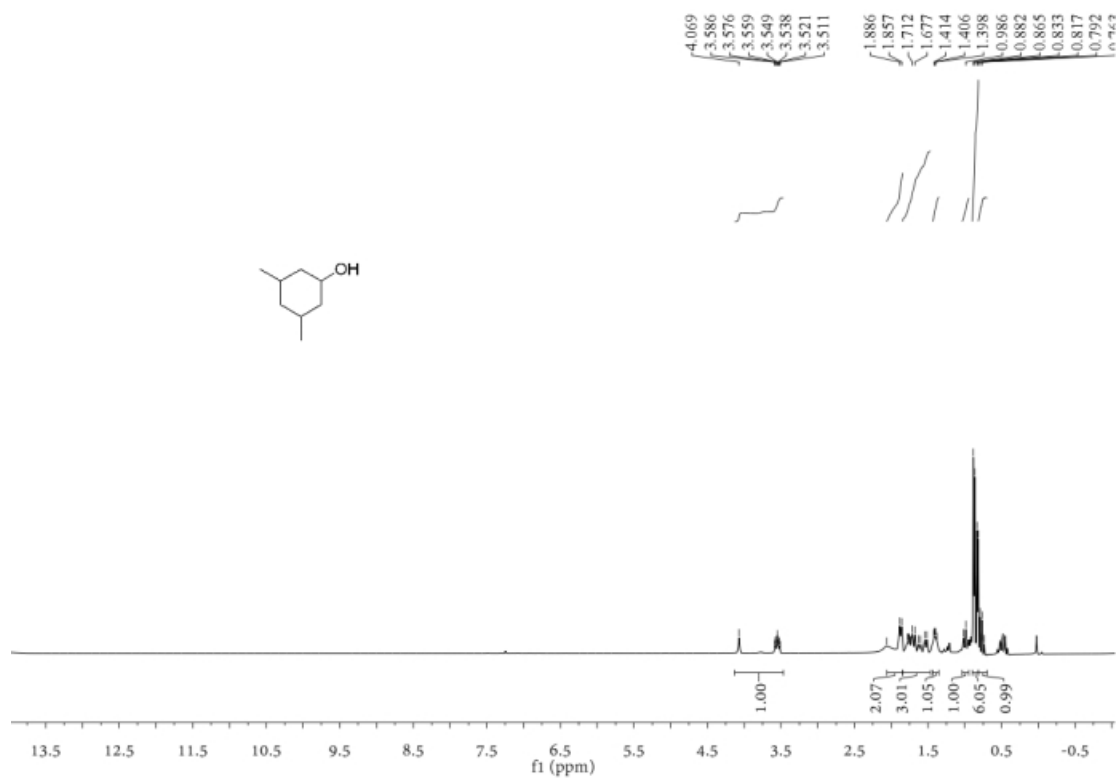
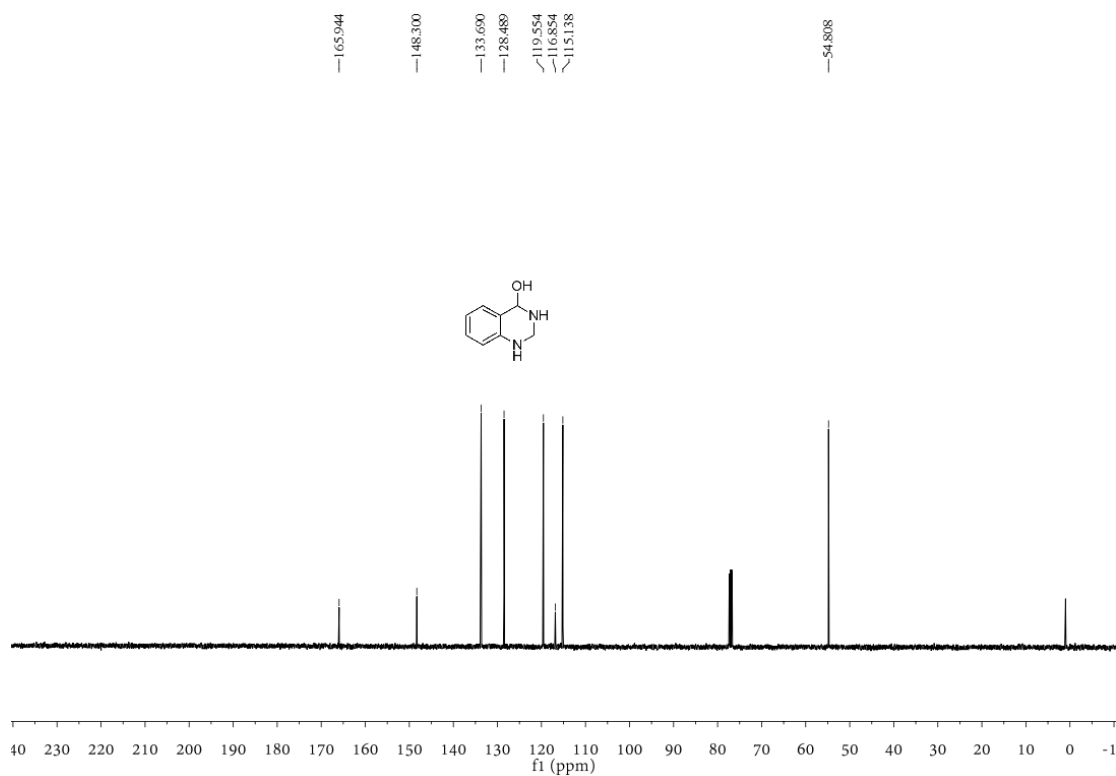**Fig. S37** ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10p**
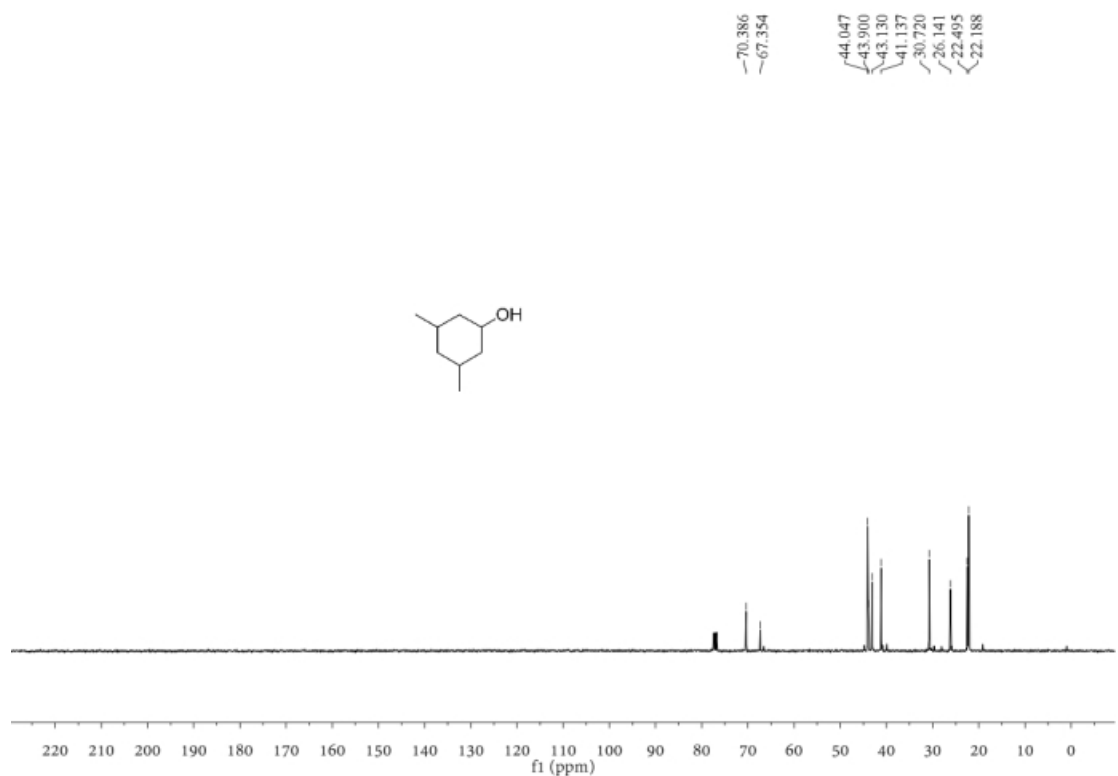
Fig. S38 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10p**.
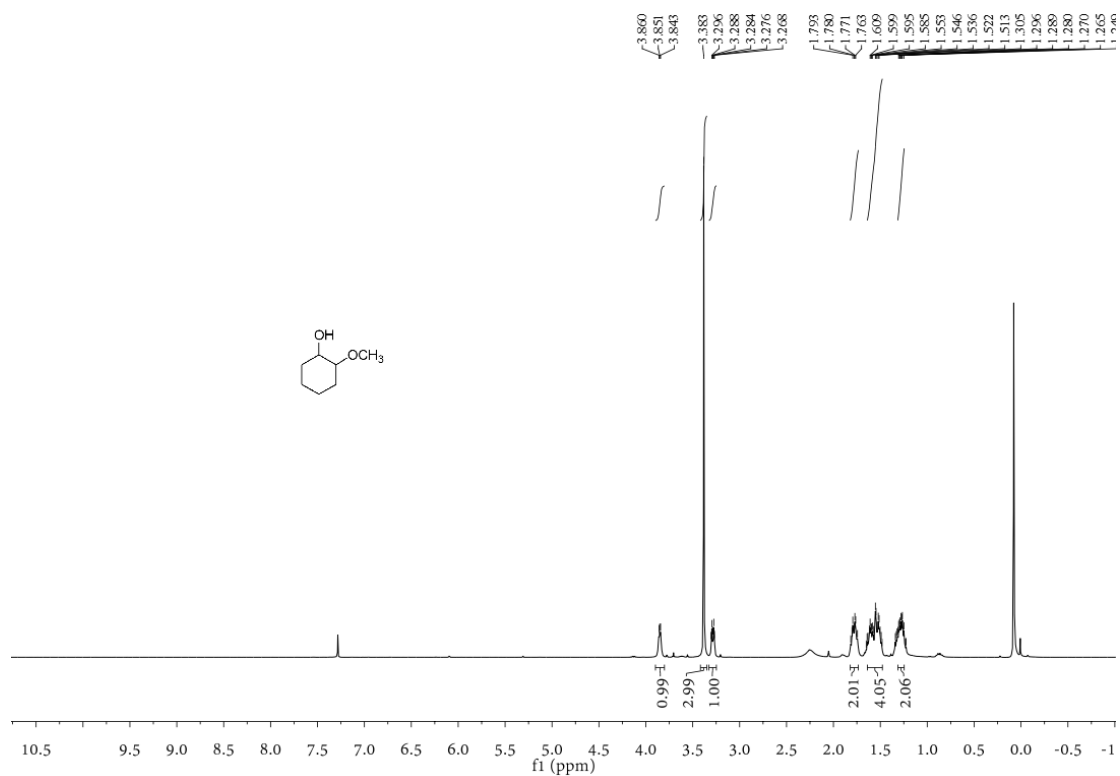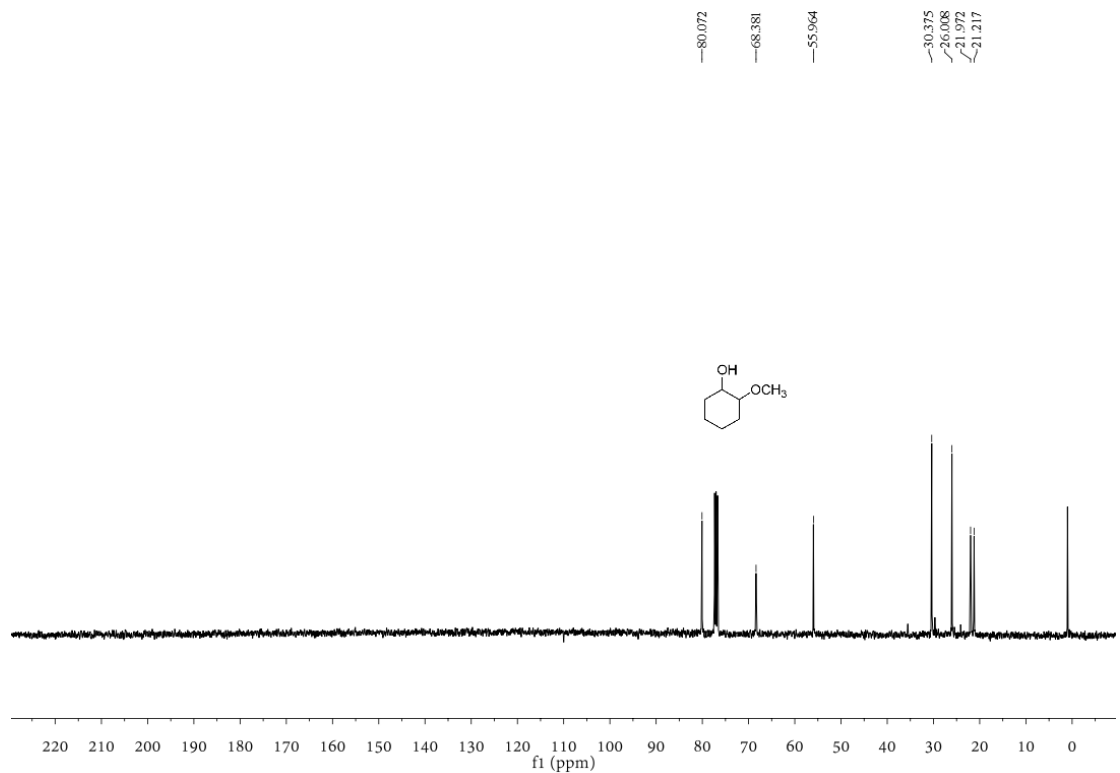
Fig. S39 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10q**
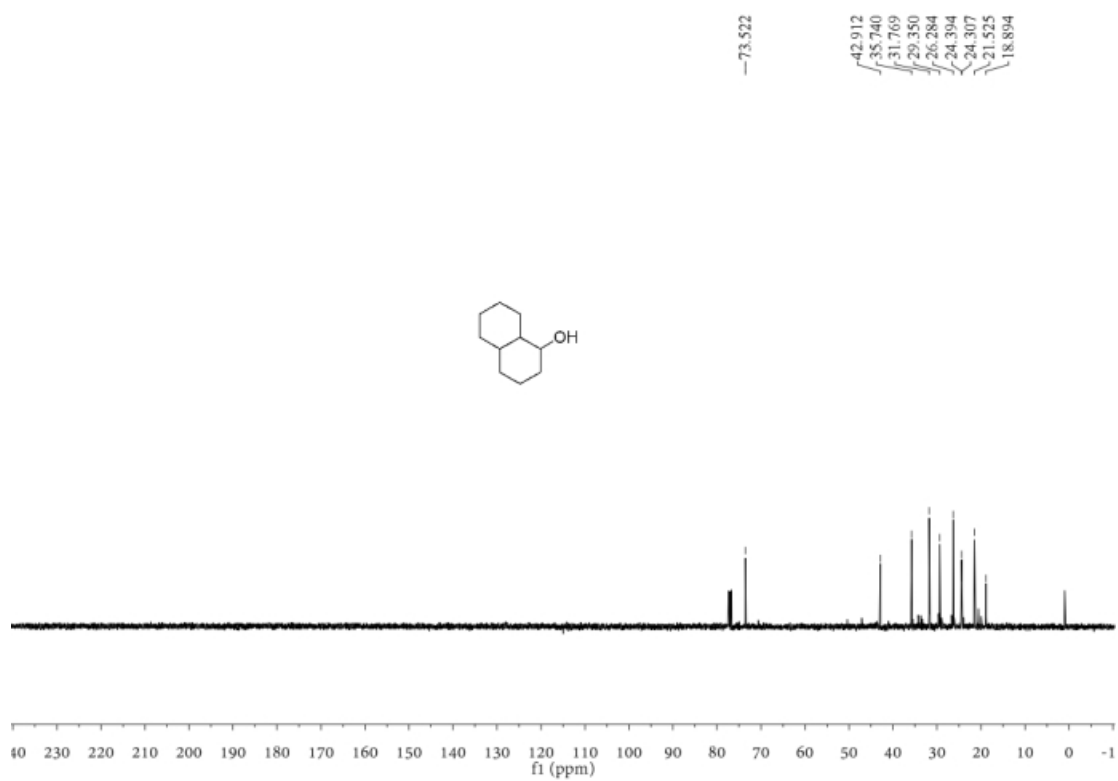
Fig. S40 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10q**.

Fig. S41 ^{1}H NMR (400 MHz, DMSO-d_6, 298 K) spectrum of compound **10r**
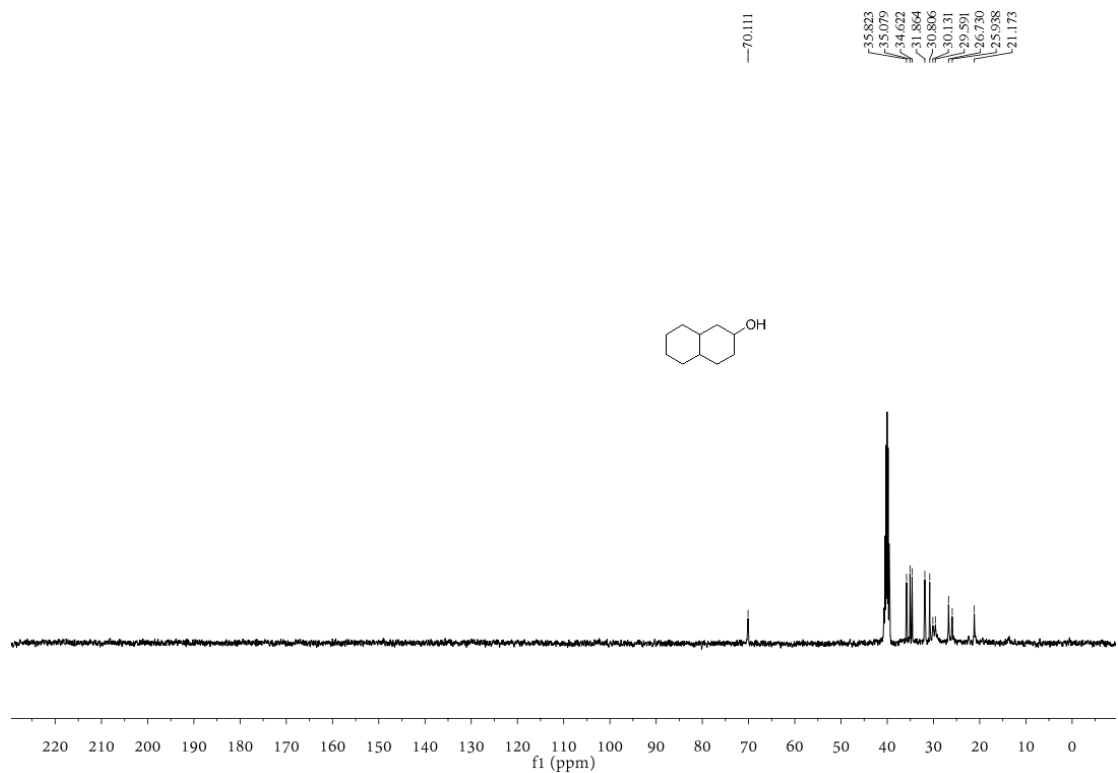
Fig. S42 ^{13}C NMR (101 MHz, DMSO-d_6, 298 K) spectrum of compound **10r**.

Fig. S43 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10s.**

Fig. S44 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10s.**

Fig. S45 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10t.**

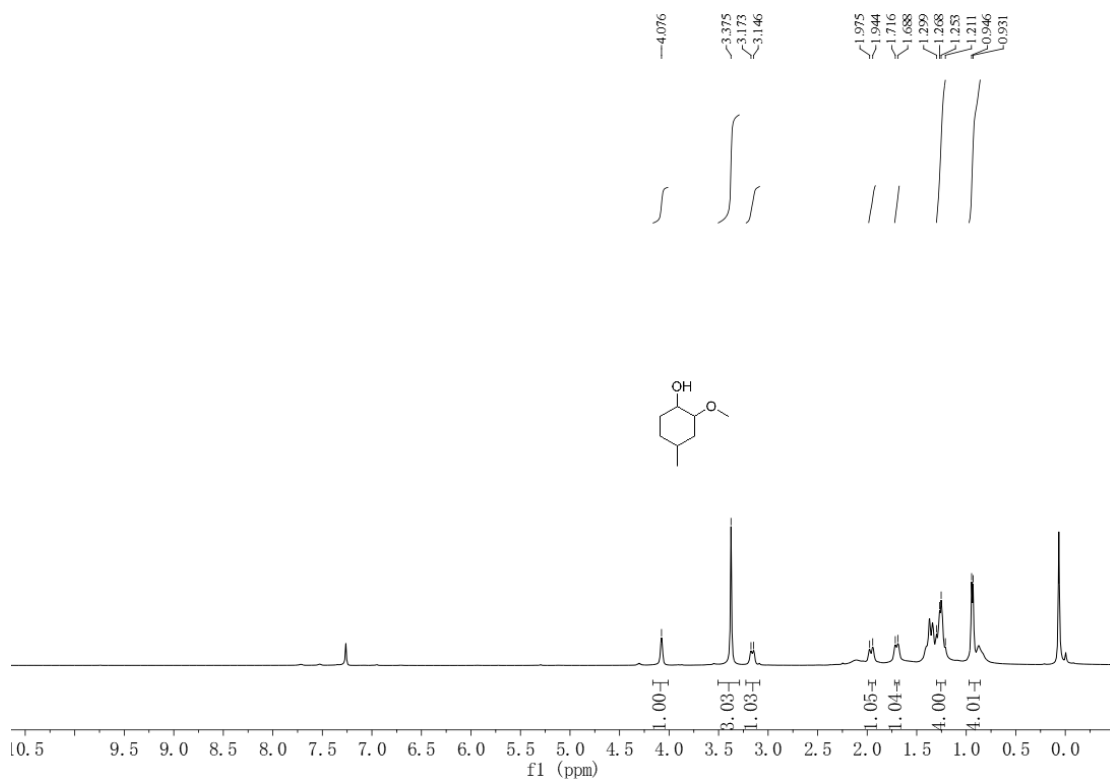**Fig. S46** ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10t.**

Fig. S47 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10u.**
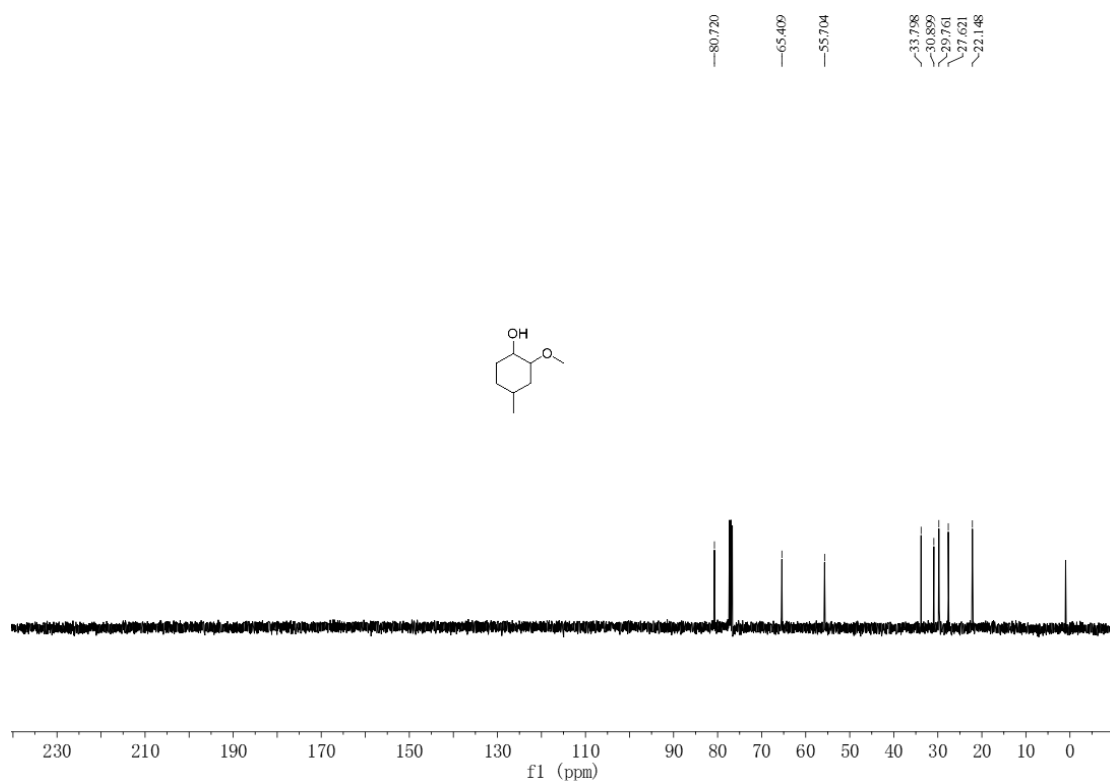

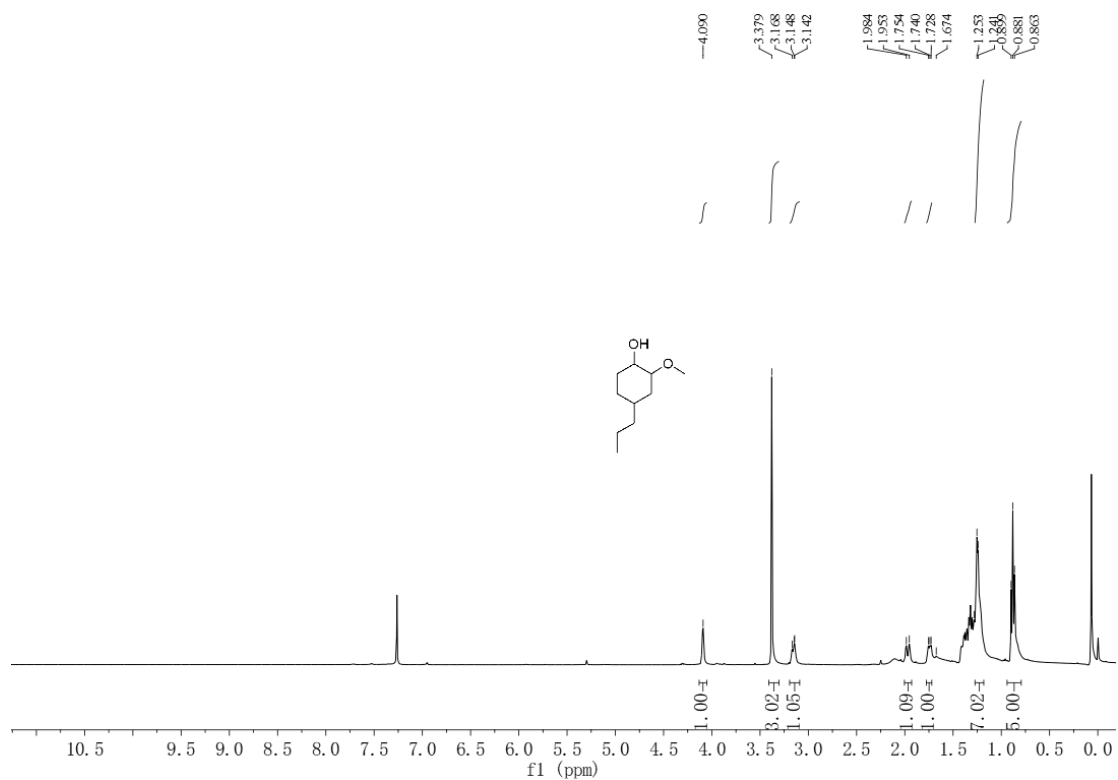**Fig. S48** ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10u**.

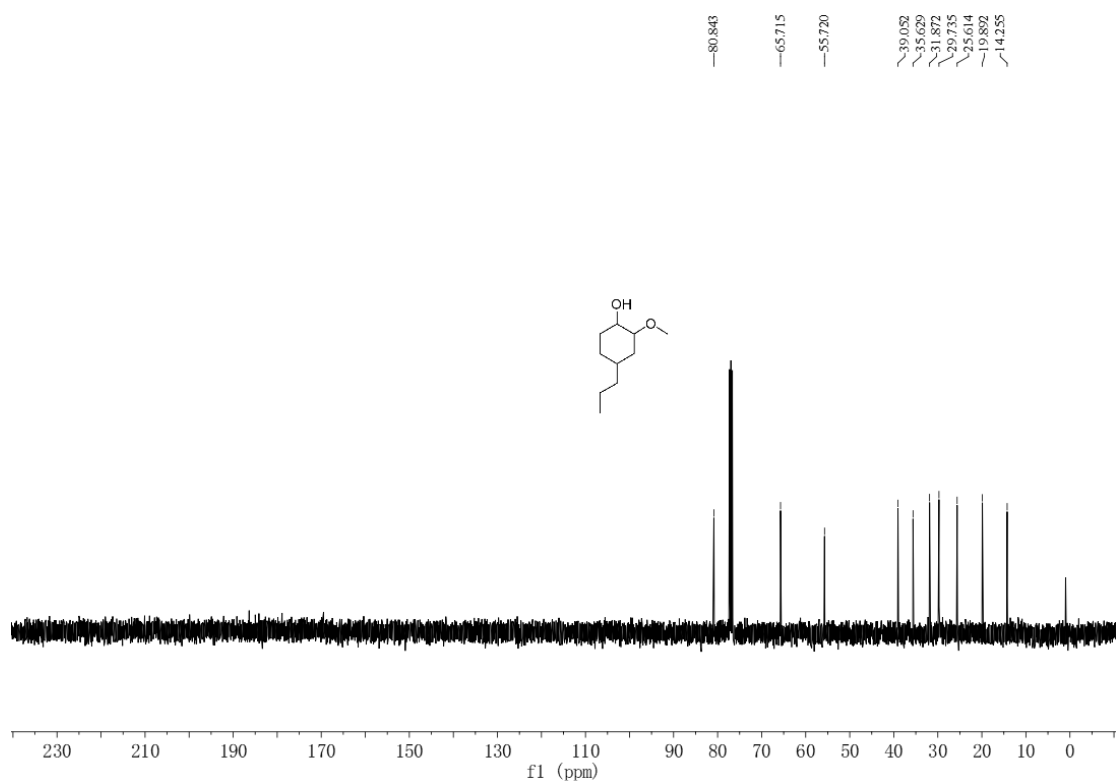**Fig. S49** ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10v.**

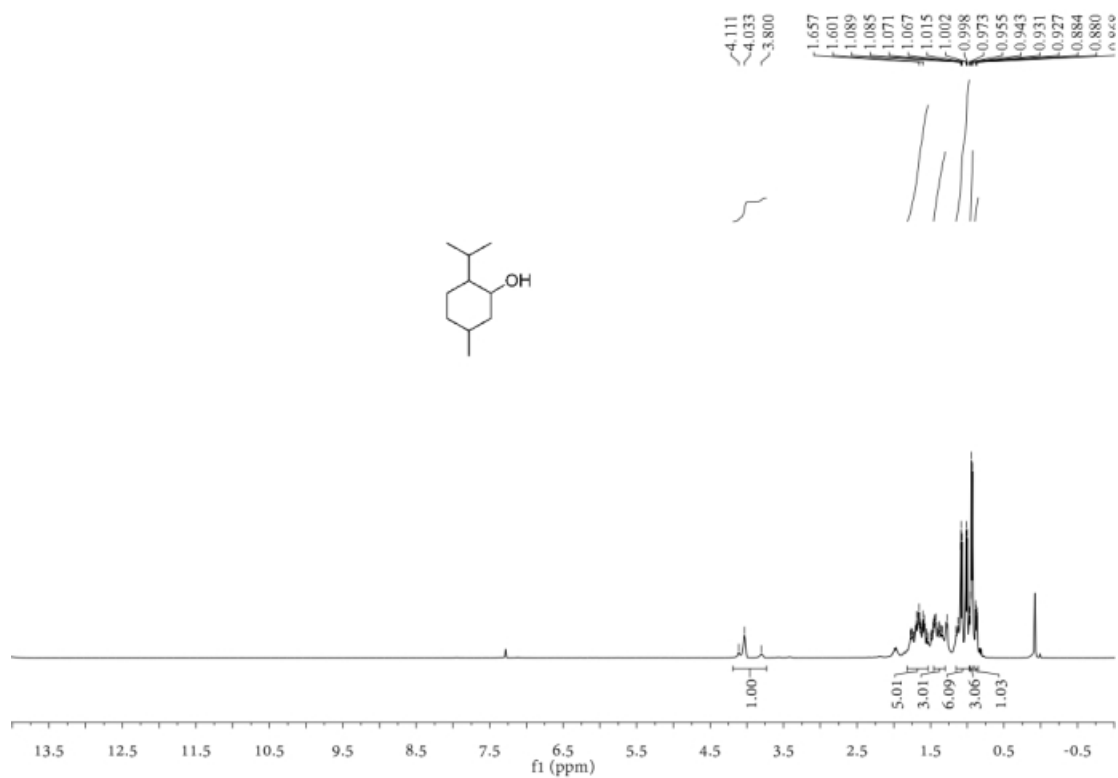**Fig. S50** ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10v.**

Fig. S51 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10w.**
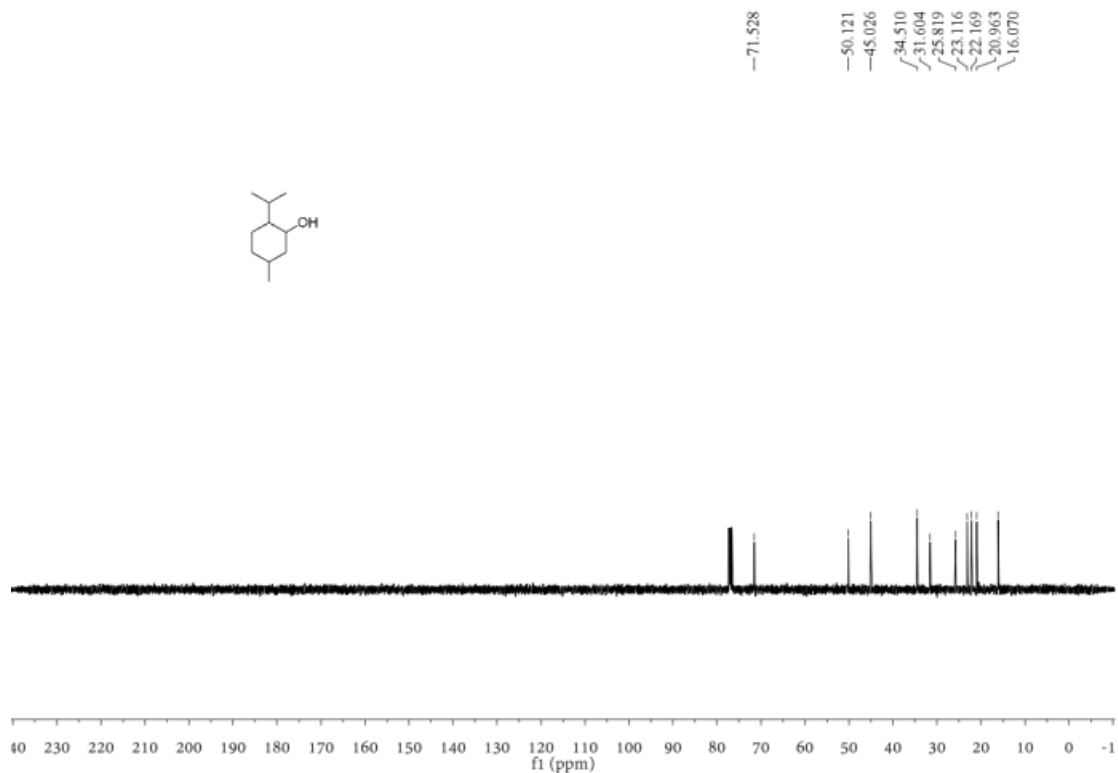

Fig. S52 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10w.**

Fig. S53 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10x.**

Fig. S54 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10x**.
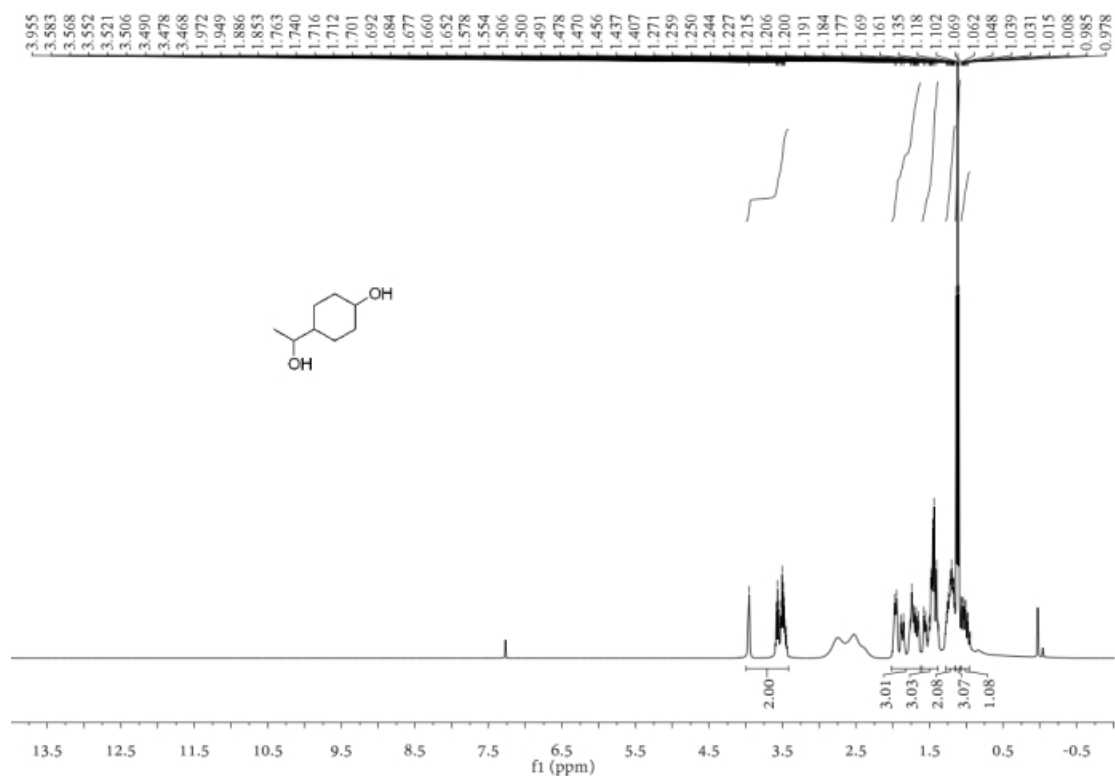
Fig. S55 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of compound **10y.**

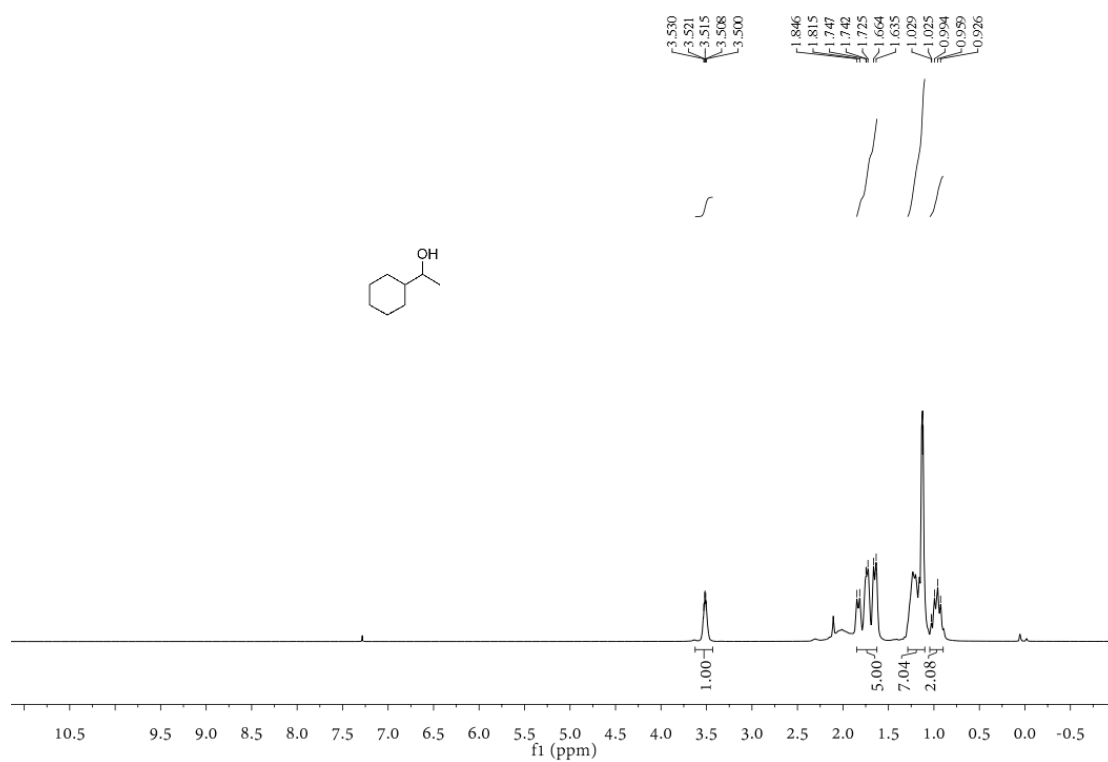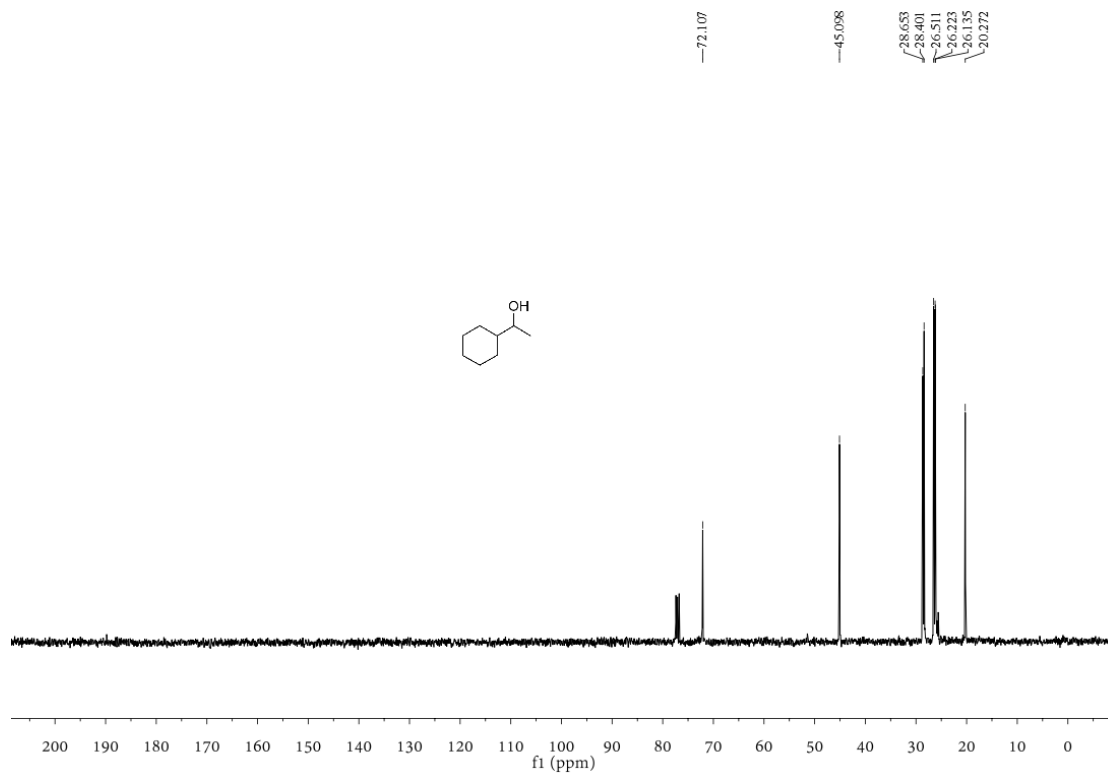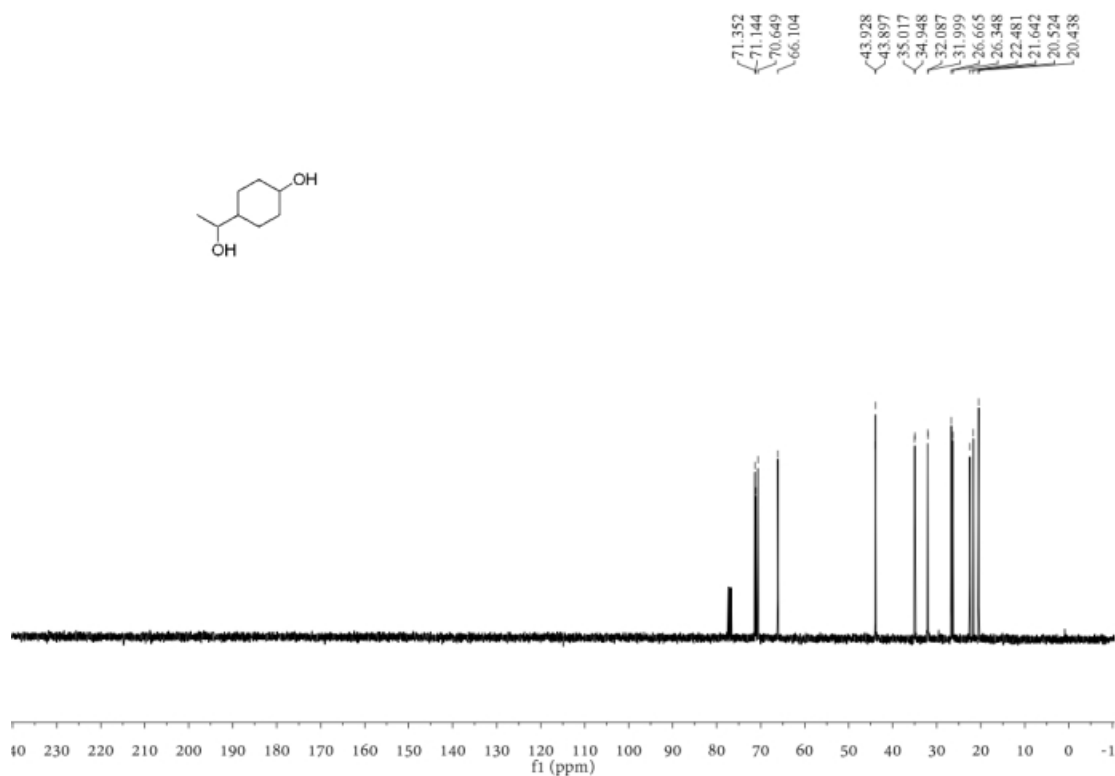**Fig. S56** ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of compound **10y**.

Peak labels: 2.941, 2.929, 2.925, 1.765, 1.757, 1.749, 1.741

Integrations: 4.00, 4.05

f1 (ppm)

Fig. S57 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of adipic chloride

Peak labels: 173.289, 46.356, 23.707
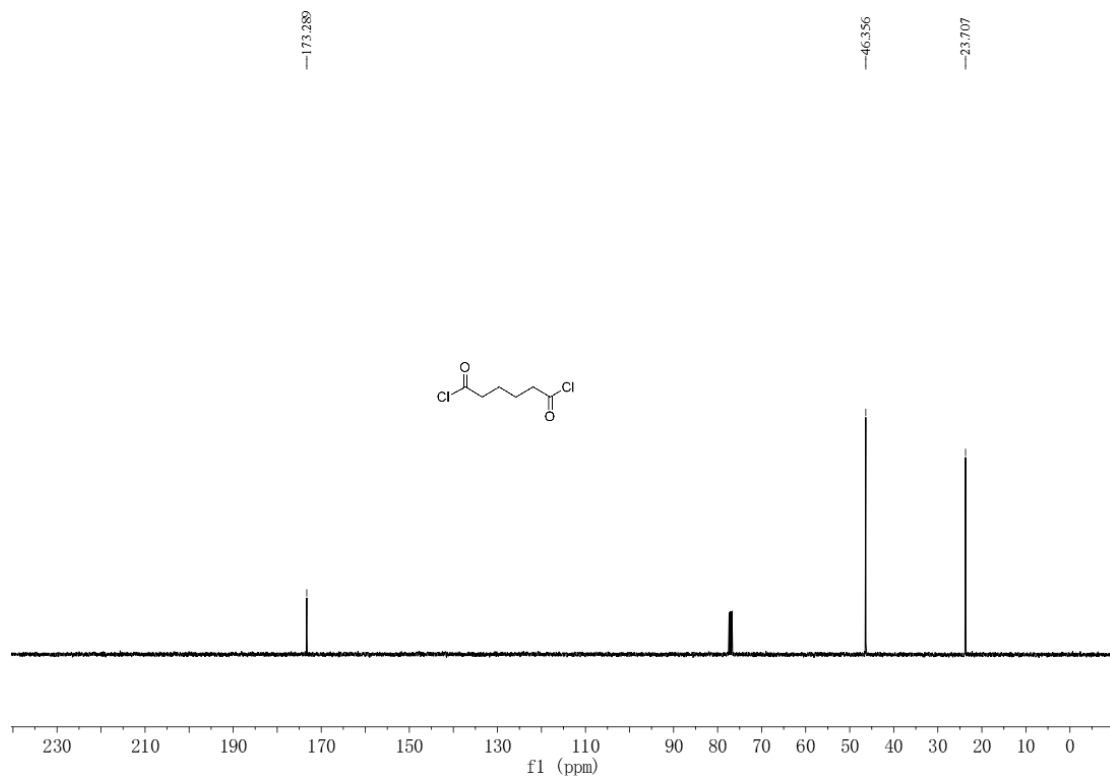
f1 (ppm)
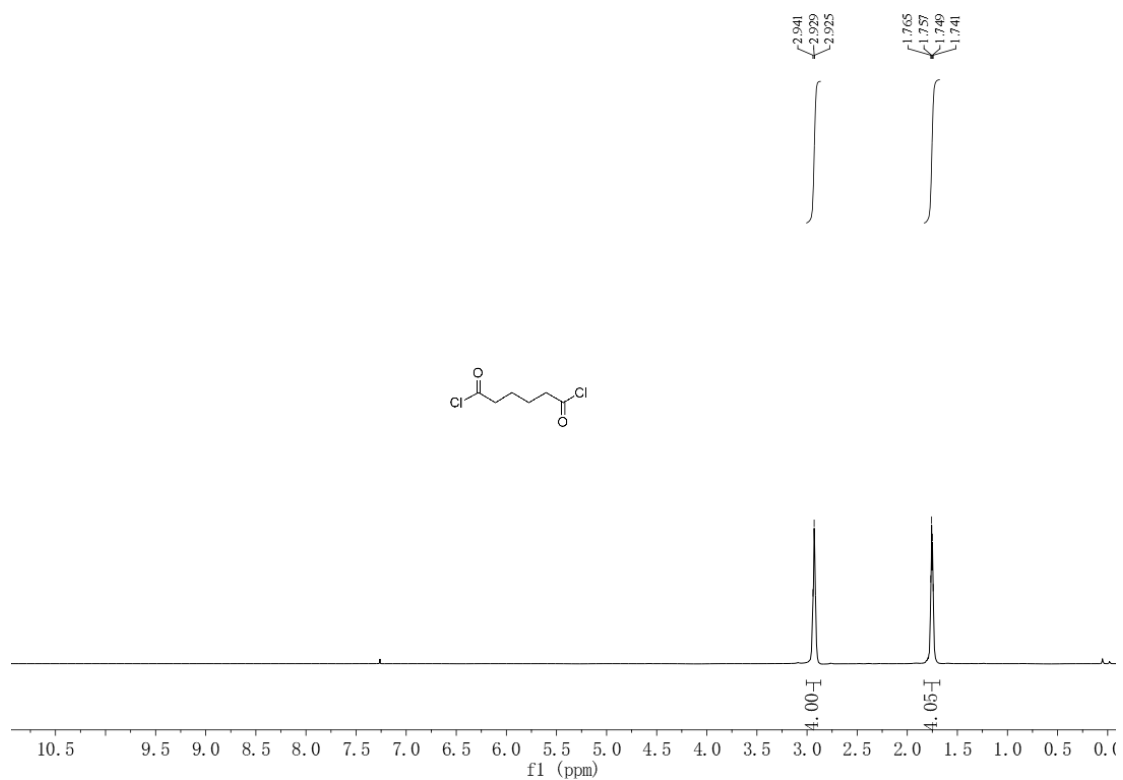
Fig. S58 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of adipic chloride.
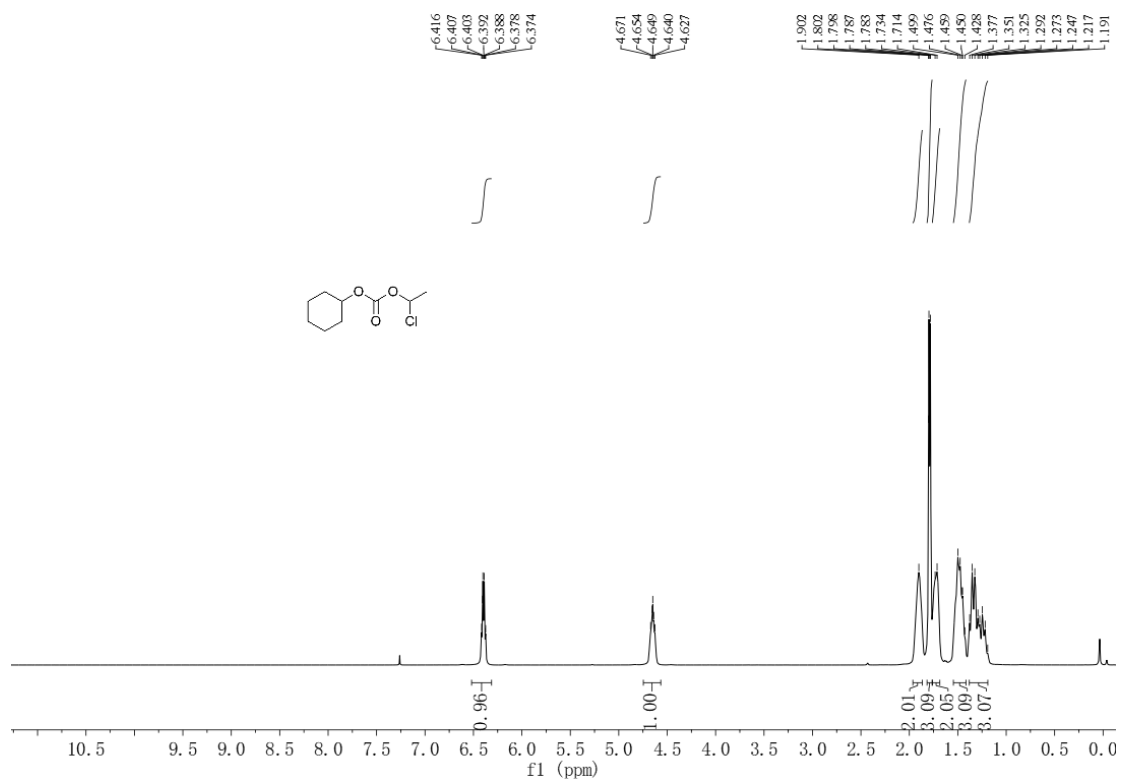
Fig. S59 ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of 1-chloroethylcyclohexyl carbonate
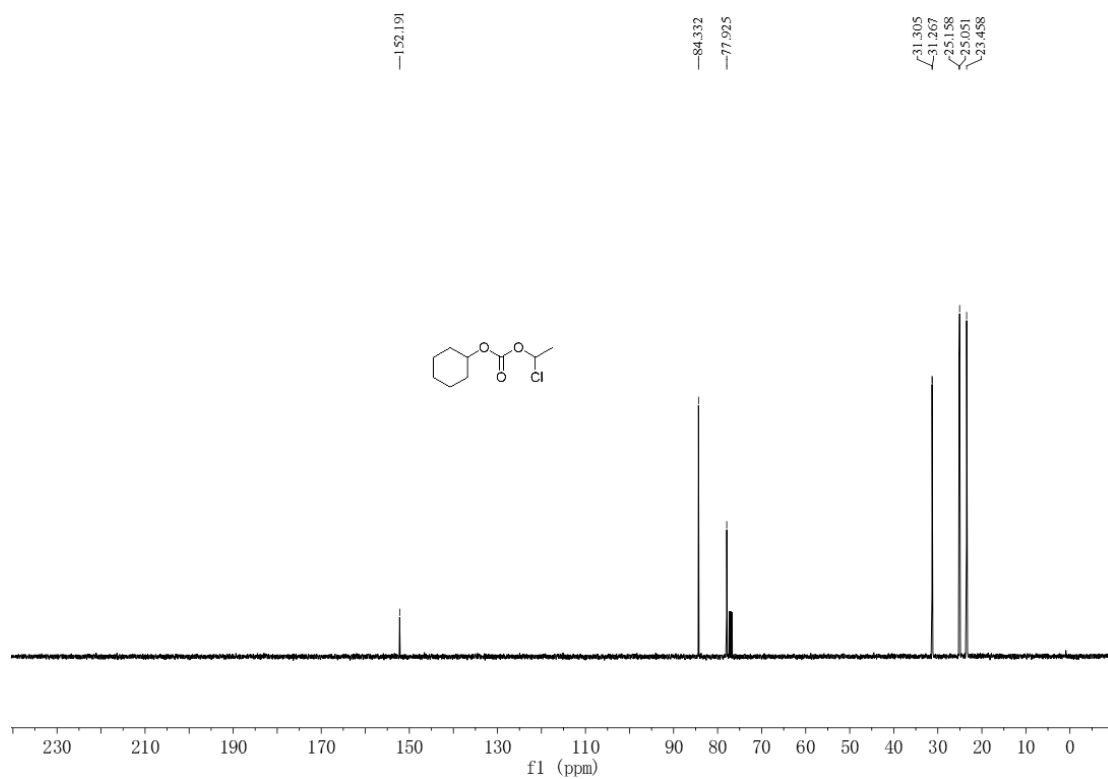

Fig. S60 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of 1-chloroethylcyclohexyl carbonate.
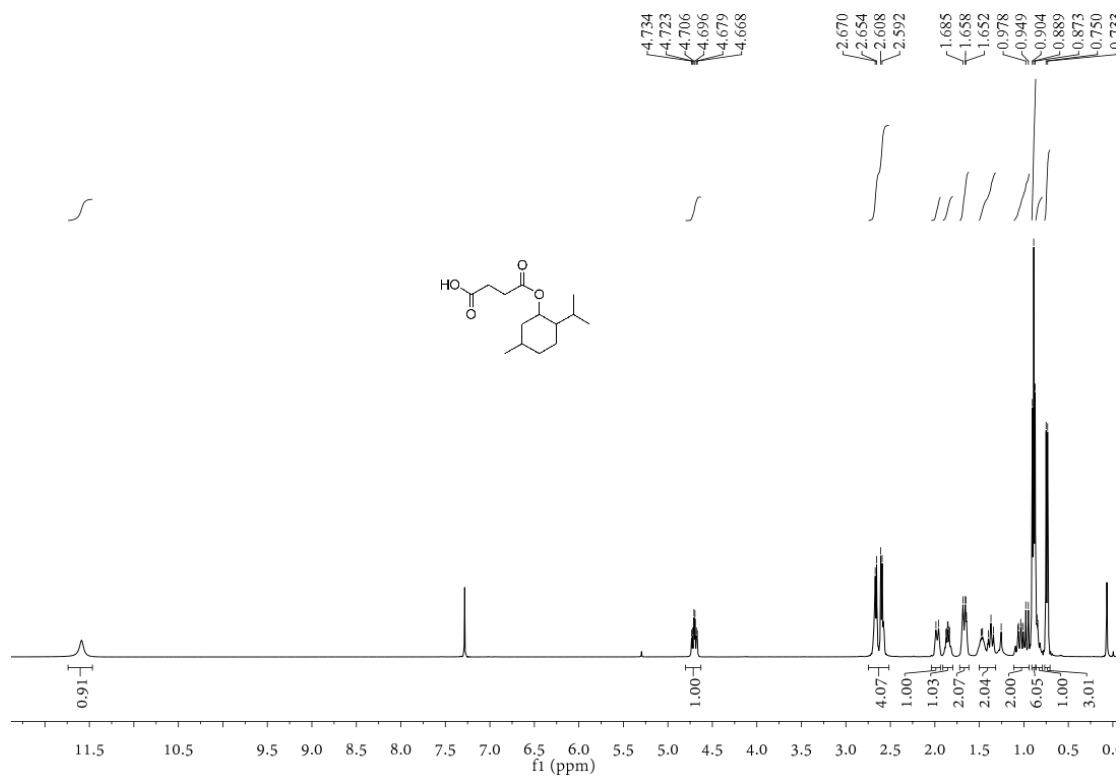
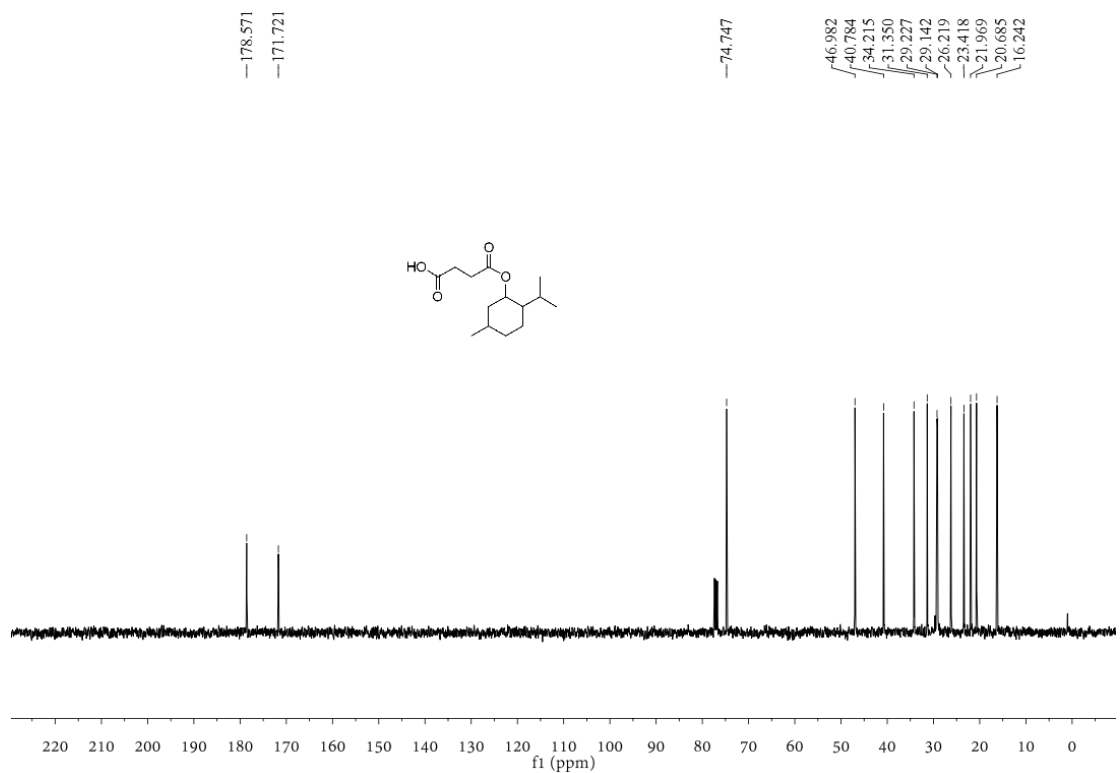**Fig. S61** ^{1}H NMR (400 MHz, CDCl$_3$, 298 K) spectrum of monomenthyl succinate

Fig. S62 ^{13}C NMR (101 MHz, CDCl$_3$, 298 K) spectrum of monomenthyl succinate.

8. References

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