Supporting Information

Efficient single-component nickel catalysts with tetradentate aminopyridine ligands for cycloaddition reactions of CO_2 and epoxides under mild conditions

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1. Crystal information of L1-NiBr$_2$

Table S1 Data collection and structure refinement for **L1-NiBr$_2$**

Name	Data
Empirical formula	$C_{20}H_{28}Br_2N_4Ni$
Formula weight	542.99
Space group	P 43 21 2
a, Å	9.1561(3)
b, Å	9.1561(3)
c, Å	23.8743(13)
α, deg	90
β, deg	90
γ, deg	90
V, Å^3	2001.48(17)
Z	4
temp, K	100.01(10)
λ (Mo $K\alpha$), Å	0.71073
D, g cm^{-3}	1.802
Final R indices [I>2sigma(I)]	R1=0.0379, wR2=0.0662
R indices (all data)	R1=0.0443, wR2=0.0685

Table S2 Selected bond distances (Å) and angles (º) for **L1-NiBr$_2$**

Bond Distances (Å)	
N1-Ni1	2.107(4)
N2-Ni1	2.158(4)
Ni1-Br1	2.5866(7)
Ni1-N1	2.107(4)
Ni1-N2	2.158(4)
Bond Angles (º)	
Br1-Ni1-Br1	91.68(3)
N1-Ni1-Br1	88.62(10)
N1-Ni1-Br1	96.56(10)
N1-Ni1-Br1	88.61(10)
N1-Ni1-Br1	96.55(10)
N1-Ni1-N1	172.6(2)
N1-Ni1-N2	78.52(14)
N1-Ni1-N2	78.52(14)
N1-Ni1-N2	95.84(14)
N1-Ni1-N2	95.84(14)
N2-Ni1-Br1	93.30(10)
N2-Ni1-Br1	172.90(10)
N2-Ni1-Br1	93.30(9)
N2-Ni1-Br1	172.90(10)
N2-Ni1-N2	82.20(19)

2. Part screening reaction conditions for catalytic coupling reactions between 1a and CO_2

Table S3 Catalytic coupling reactions between **1a** and CO_2 in different solvent[a]

Entry	Catalyst	Solvent	Conversion (%)[b]	Yield (%)[b]	Selectivity (%)[b]
1	**L1-NiBr$_2$**	MeCN	95	94	99
2	**L1-NiBr$_2$**	DCE	93	91	98
3	**L1-NiBr$_2$**	Toluene	77	74	97
4	**L1-NiBr$_2$**	MeOH	93	58	62
5	**L1-NiBr$_2$**	DMC	87	76	88
6	**L1-NiBr$_2$**	DMF	95	93	99
7	**L1-NiBr$_2$**	THF	87	80	92
8	**L1-NiBr$_2$**	-	98	98	100

[a] Reaction conditions: **1a** (1 mmol), solvent (2 mL), CO_2 (2.5 MPa), 80 °C, 8 h, 5 mol% **L1-NiBr$_2$**. [b] Gas chromatography is used to determine the conversion rate and yield of cyclic carbonates, with biphenyl as the internal standard.

Table S4 Catalytic coupling reactions between **1a** and CO_2 at different reaction temperature[a]

Entry	Catalyst	T (°C)	Conversion (%)[b]	Yield (%)[b]	Selectivity (%)[b]
1	**L1-NiBr$_2$**	60	59	56	95
2	**L1-NiBr$_2$**	70	88	88	100
3	**L1-NiBr$_2$**	80	98	98	100
4	**L1-NiBr$_2$**	90	98	98	100

[a] Reaction conditions: **1a** (1 mmol); CO_2 (2.5 MPa); 8 h; solvent-free; 5 mol% **L1-NiBr$_2$**. [b] Gas chromatography is used to determine the conversion rate and yield of cyclic carbonates, with biphenyl as the internal standard.

3. TGA and IR spectra of L1-NiBr$_2$

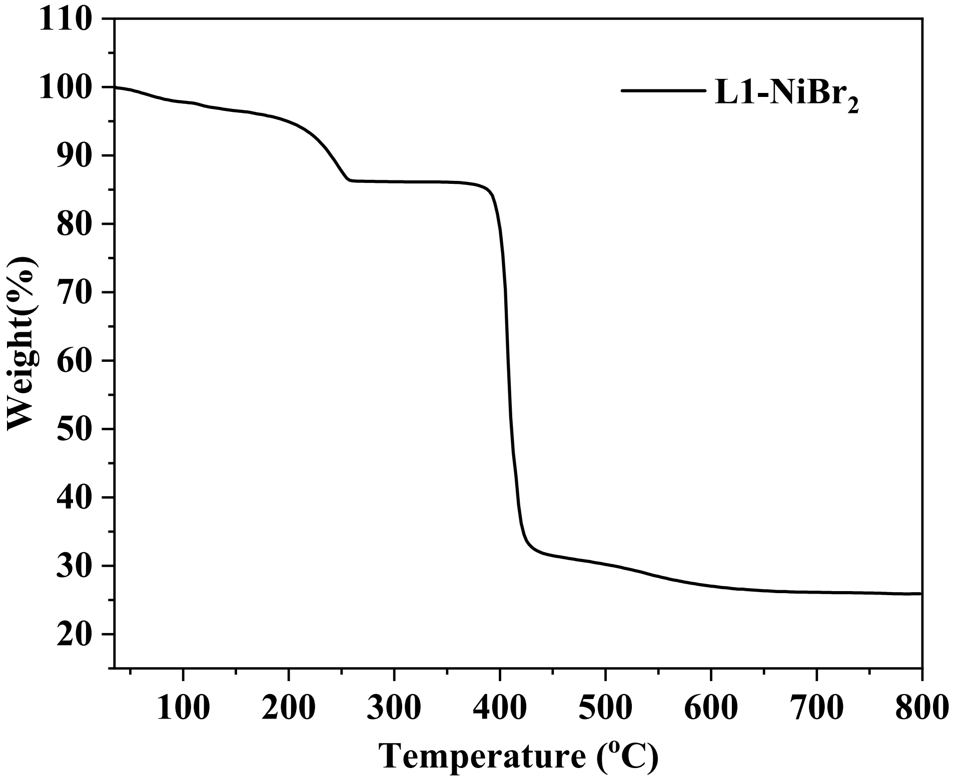


Fig. S1 TGA (Thermogravimetric Analysis) of **L1-NiBr$_2$**.

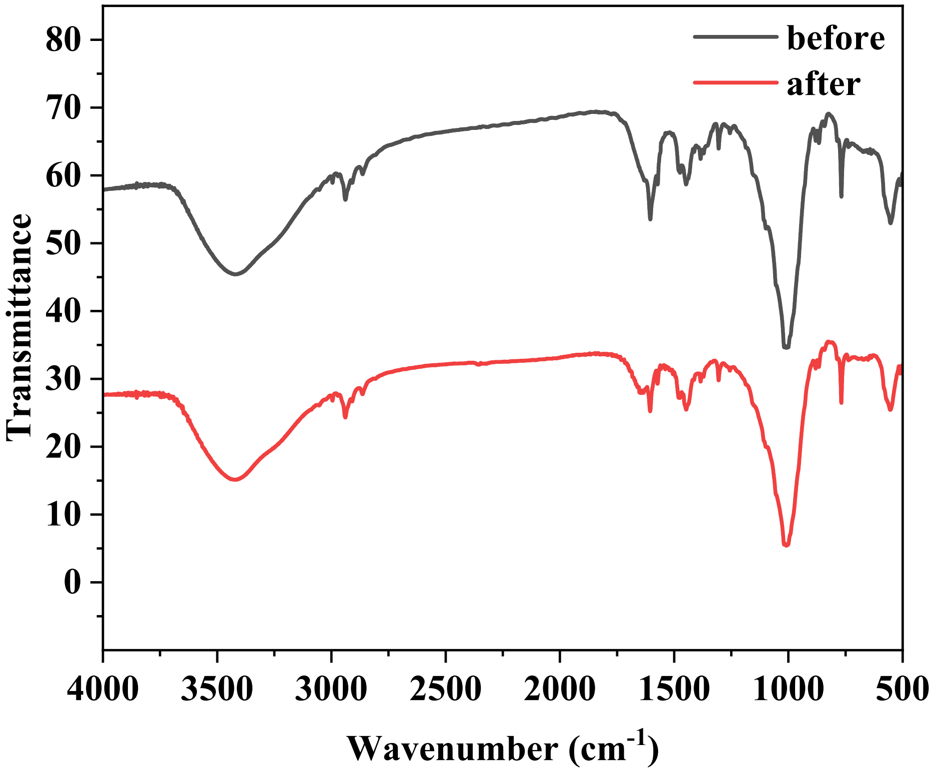


Fig. S2 The IR spectra of **L1-NiBr$_2$** before and after cyclic experiments**.**

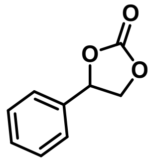
4. NMR data of ligands and products

L1: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (dt, *J* = 4.9, 1.4 Hz, 2H), 7.58 (dd, *J* = 3.7, 1.5 Hz, 4H), 7.12 (td, *J* = 5.1, 3.3 Hz, 2H), 3.92 (d, *J* = 14.5 Hz, 2H), 3.80 (d, *J* = 14.6 Hz, 2H), 2.72 – 2.60 (m, 2H), 2.29 (s, 6H), 2.07 – 1.94 (m, 2H), 1.83 – 1.72 (m, 2H), 1.34 – 1.24 (m, 2H), 1.24 – 1.11 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.4, 148.6, 136.3, 122.9, 121.6, 64.5, 60.5, 36.6, 25.84, 25.80.

L2: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 – 8.42 (m, 2H), 7.90 (d, *J* = 7.9 Hz, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.65 – 7.58 (m, 3H), 7.55 (td, *J* = 7.6, 1.8 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27(m, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 1H), 7.10 (m, 2H), 5.12 (s, 1H), 4.98 (s, 1H), 2.57 (m, 1H), 2.47 (m, 1H), 2.17 (d, *J* = 5.0 Hz, 6H), 1.88 (m, 2H), 1.53 (s, 2H), 1.04 (t, *J* = 7.1 Hz, 2H), 0.78 (t, *J* = 10.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.9, 149.0, 148.7, 143.1, 141.2, 136.7, 136.3, 129.1, 128.5, 128.4, 128.3, 127.3, 127.0, 123.4, 122.3, 121.9, 75.2, 74.7, 60.4, 59.9, 34.5, 34.4, 25.7, 25.4, 25.1, 24.5.

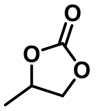
L3: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.57 – 8.51 (m, 6H), 7.80 (t, *J* = 7.6 Hz, 4H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.64 (td, *J* = 7.7, 1.8 Hz, 2H), 7.50 – 7.41 (m, 6H), 7.09 (ddd, *J* = 7.4, 5.0, 1.1 Hz, 2H), 5.91 (s, 2H), 2.70 (d, *J* = 9.2 Hz, 2H), 2.31 (s, 3H), 2.10 (s, 6H), 1.99 (d, *J* = 12.8 Hz, 2H), 1.45 (d, *J* = 7.8 Hz, 2H), 1.12 (d, *J* = 9.2 Hz, 2H), 0.66 (t, *J* = 9.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.4, 148.6, 138.1, 136.4, 133.9, 131.8, 128.8, 127.5, 126.9, 126.0, 125.7, 125.3, 123.9, 123.5, 121.8, 69.2, 60.3, 35.5, 25.4, 24.6.

2a, 4-phenyl-1,3-dioxolan-2-one



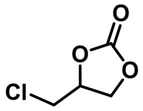
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.39 (m, 3H), 7.35 (dd, *J* = 7.4, 2.4 Hz, 2H), 5.67 (t, *J* = 8.0 Hz, 1H), 4.79 (t, *J* = 8.4 Hz, 1H), 4.32 (t, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.0, 135.9, 129.8, 129.3, 126.0, 78.1, 71.3.

2b, 4-methyl-1,3-dioxolan-2-one



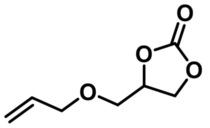
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.97 – 4.83 (m, 1H), 4.59 (t, J = 8.1 Hz, 1H), 4.06 (dd, J = 8.5, 7.2 Hz, 1H), 1.50 (d, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.2, 73.8, 70.7, 19.3.

2c, 4-(chloromethyl)-1,3-dioxolan-2-one



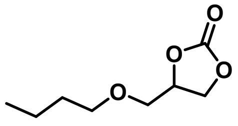
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.99 (dtd, J = 8.7, 5.3, 3.5 Hz, 1H), 4.58 (t, J = 8.6 Hz, 1H), 4.38 (dd, J = 8.9, 5.7 Hz, 1H), 3.80 (dd, J = 12.2, 4.9 Hz, 1H), 3.71 (dd, J = 12.3, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.5, 74.5, 67.0, 44.1.

2d, 4-((allyloxy)methyl)-1,3-dioxolan-2-one



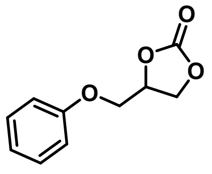
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.85 (ddt, J = 16.4, 10.9, 5.6 Hz, 2H), 5.28 (s, 1H), 5.26 – 5.16 (m, 3H), 4.82 (tdd, J = 9.2, 4.2, 2.3 Hz, 2H), 4.38 (t, J = 7.3 Hz, 2H), 4.10 – 3.97 (m, 4H), 3.59 (dd, J = 11.1, 3.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.1, 133.7, 117.9, 117.9, 75.1, 75.1, 72.6, 68.8, 66.3.

2e, 4-(butoxymethyl)-1,3-dioxolan-2-one



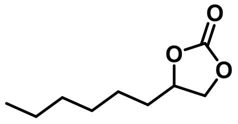
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.80 (dtd, J = 9.2, 4.9, 4.3, 2.4 Hz, 1H), 4.49 (t, J = 8.3 Hz, 1H), 4.42 – 4.34 (m, 1H), 3.66 (dd, J = 11.0, 3.8 Hz, 1H), 3.58 (dd, J = 11.0, 3.6 Hz, 1H), 3.49 (t, J = 6.5 Hz, 2H), 1.59 – 1.48 (m, 2H), 1.34 (h, J = 7.4 Hz, 2H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.1, 75.1, 71.9, 69.6, 66.3, 31.5, 19.2, 13.9.

2f, 4-(phenoxymethyl)-1,3-dioxolan-2-one



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.25 (m, 2H), 7.06 – 6.96 (m, 1H), 6.95 – 6.86 (m, 2H), 5.01 (ddt, J = 8.2, 5.9, 3.7 Hz, 1H), 4.59 (t, J = 8.4 Hz, 1H), 4.51 (dd, J = 8.6, 5.9 Hz, 1H), 4.22 (dd, J = 10.7, 3.9 Hz, 1H), 4.12 (dd, J = 10.6, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.8, 154.8, 129.7, 122.0, 114.6, 74.3, 66.9, 66.3.

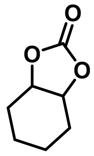
2g, 4-hexyl-1,3-dioxolan-2-one



^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.69 (qd, J = 7.5, 5.4 Hz, 1H), 4.56 – 4.43 (m, 1H), 4.05 (dd, J = 8.4, 7.2 Hz, 1H), 1.79 (dddd, J = 12.8, 9.7, 7.6, 5.2 Hz, 1H), 1.73 – 1.60 (m, 1H), 1.45 (dd, J =

11.1, 6.2 Hz, 1H), 1.35 (ddd, *J* = 18.1, 8.8, 4.3 Hz, 3H), 1.28 (dt, *J* = 7.7, 4.4 Hz, 4H), 0.91 – 0.82 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.2, 77.1, 69.4, 33.9, 31.5, 28.8, 24.3, 22.45, 14.0.

2h, hexahydrobenzo[d][1,3]dioxol-2-one



^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.72 (t, *J* = 4.2 Hz, 2H), 1.91 (dq, *J* = 9.3, 4.9 Hz, 4H), 1.61 (dt, *J* = 14.6, 6.2 Hz, 2H), 1.44 (dq, *J* = 8.5, 5.4, 3.8 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.5, 75.9, 26.8, 19.2.

5. Copies of ^{1}H-NMR and ^{13}C-NMR spectra

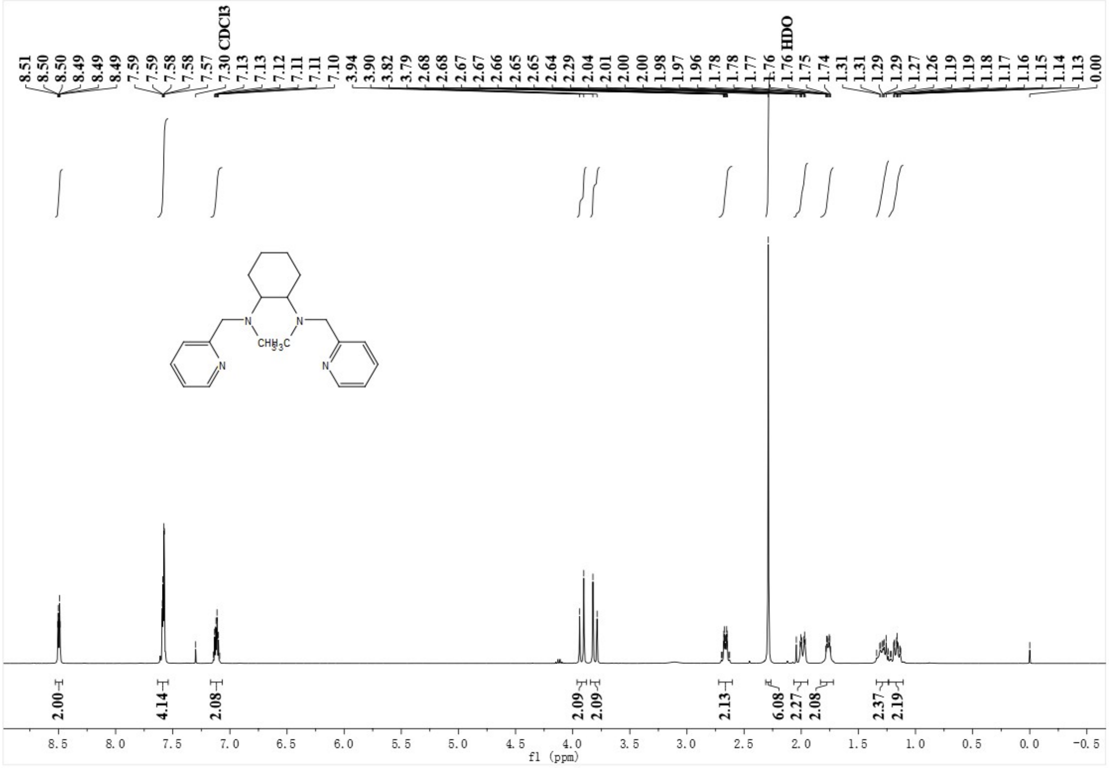


Fig. S3 ^{1}H NMR spectrum of **L1**

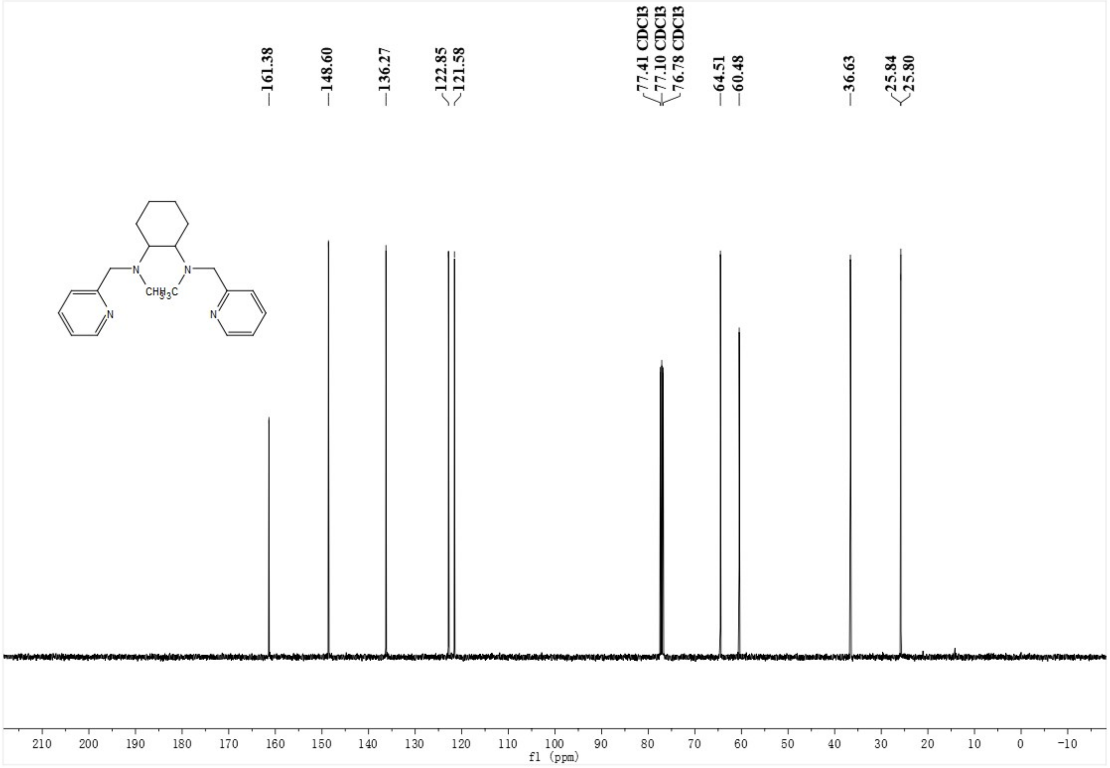


Fig. S4 ^{13}C NMR spectrum of **L1**

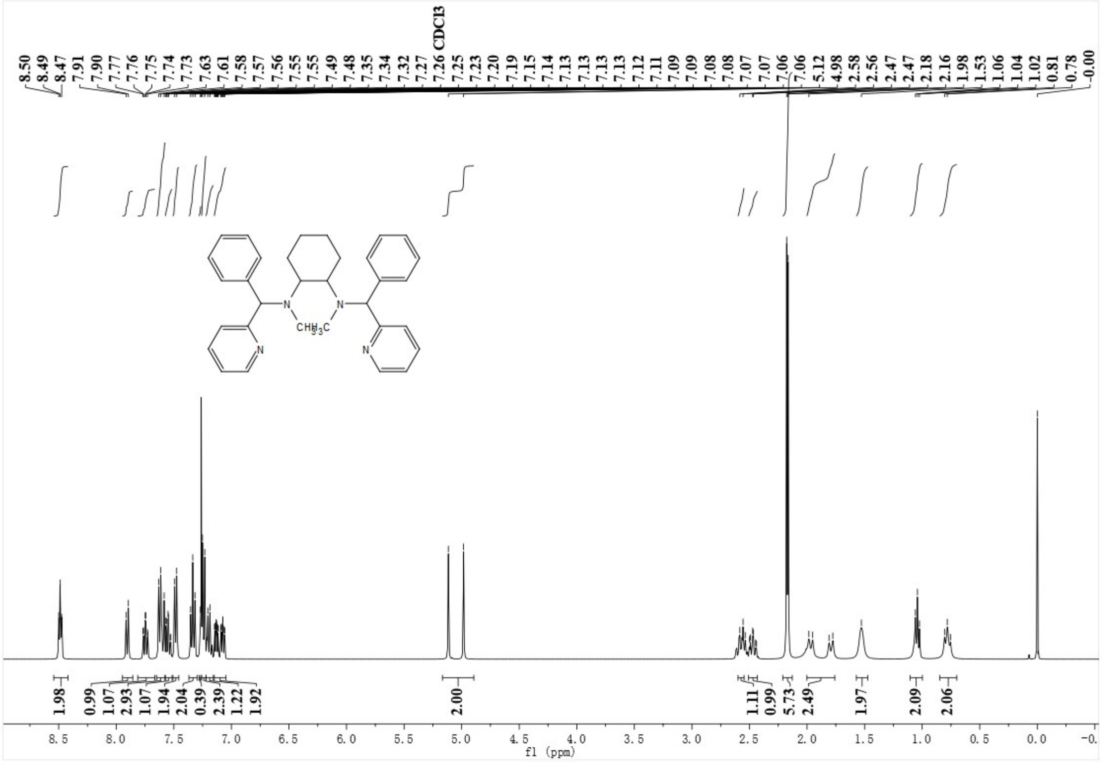


Fig. S5 ^{1}H NMR spectrum of **L2**

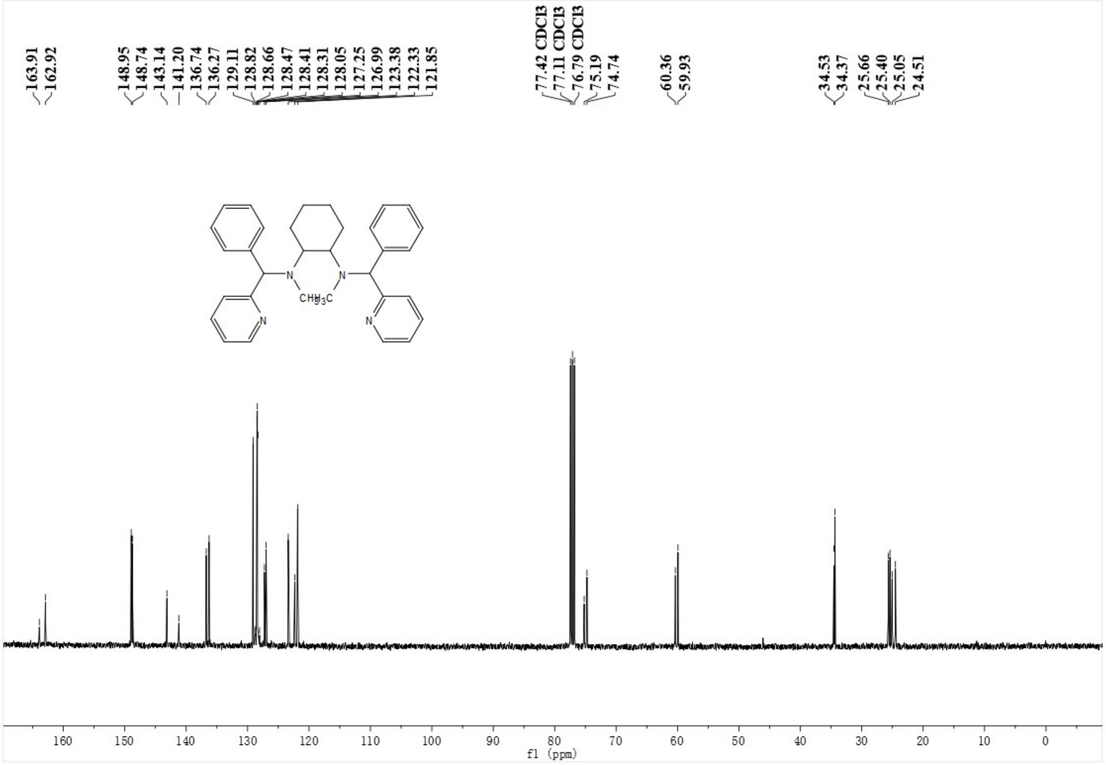


Fig. S6 ^{13}C NMR spectrum of **L2**

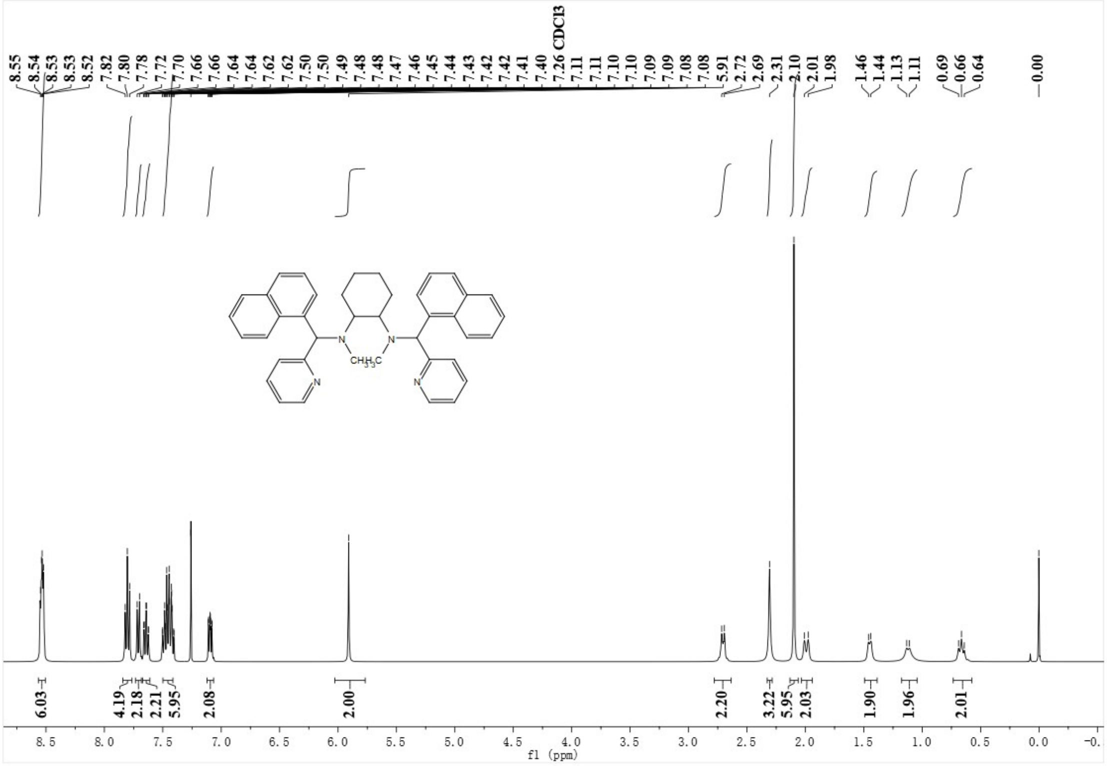


Fig. S7 ^{1}H NMR spectrum of **L3**

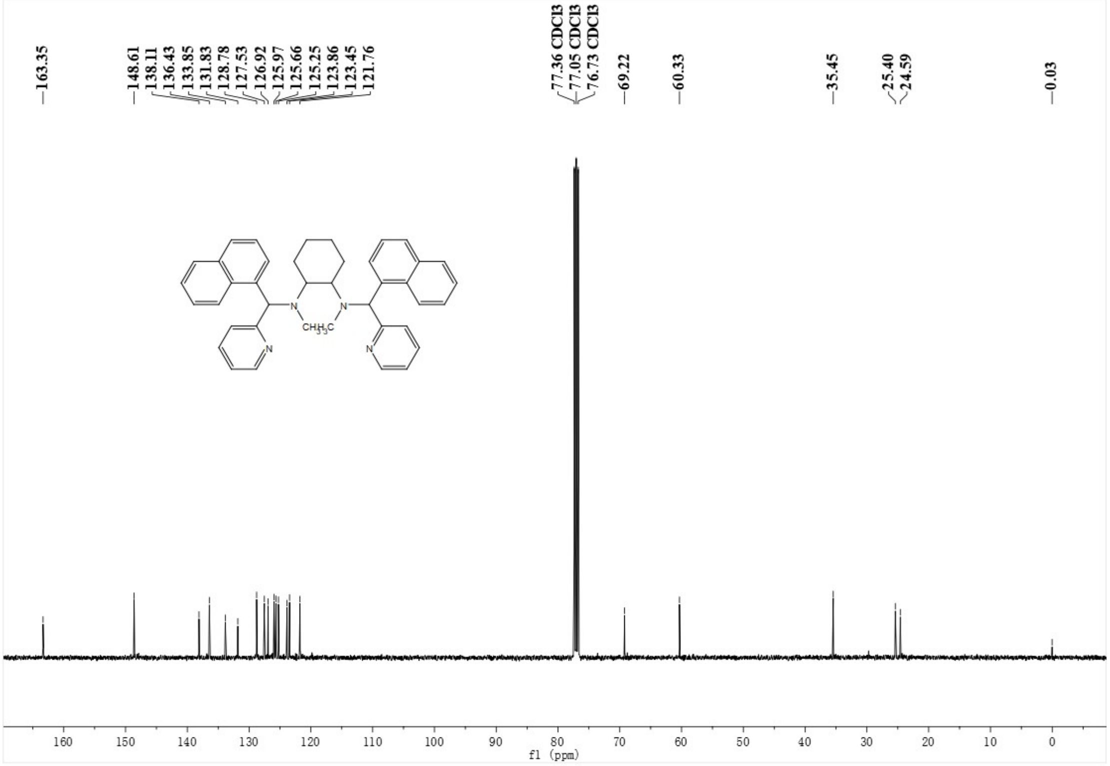


Fig. S8 ^{13}C NMR spectrum of **L3**

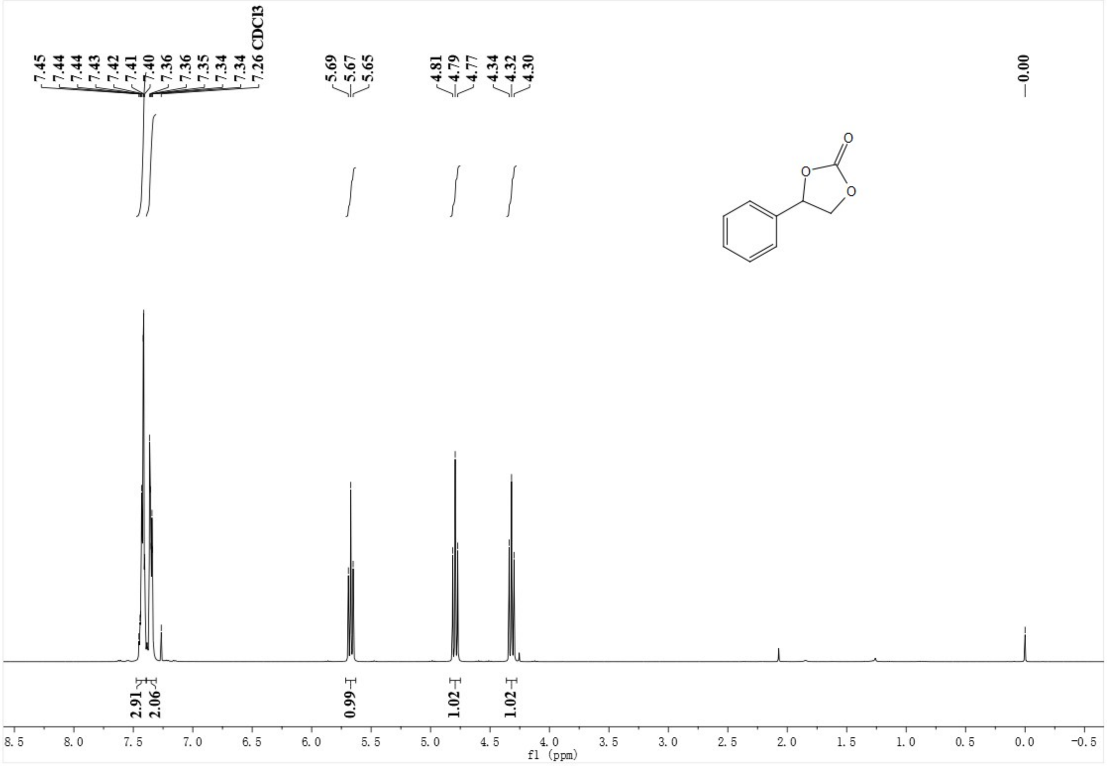


Fig. S9 ^{1}H NMR spectrum of **2a**

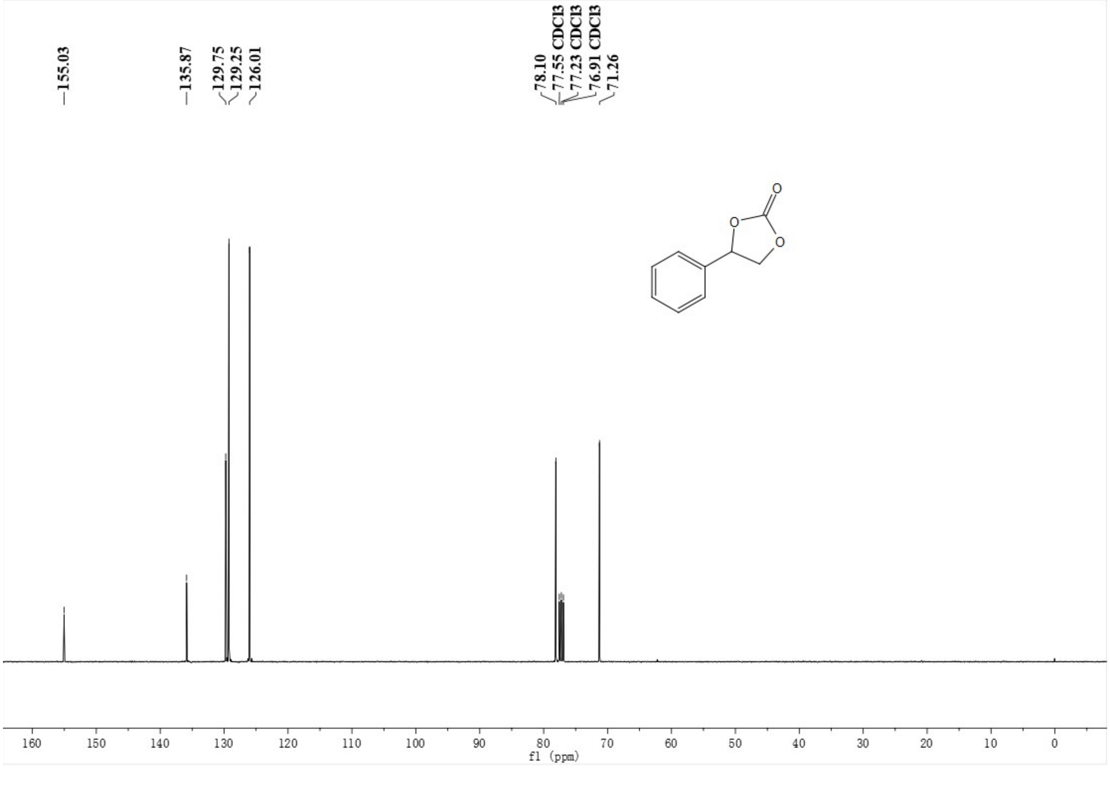


Fig. S10 ^{13}C NMR spectrum of **2a**

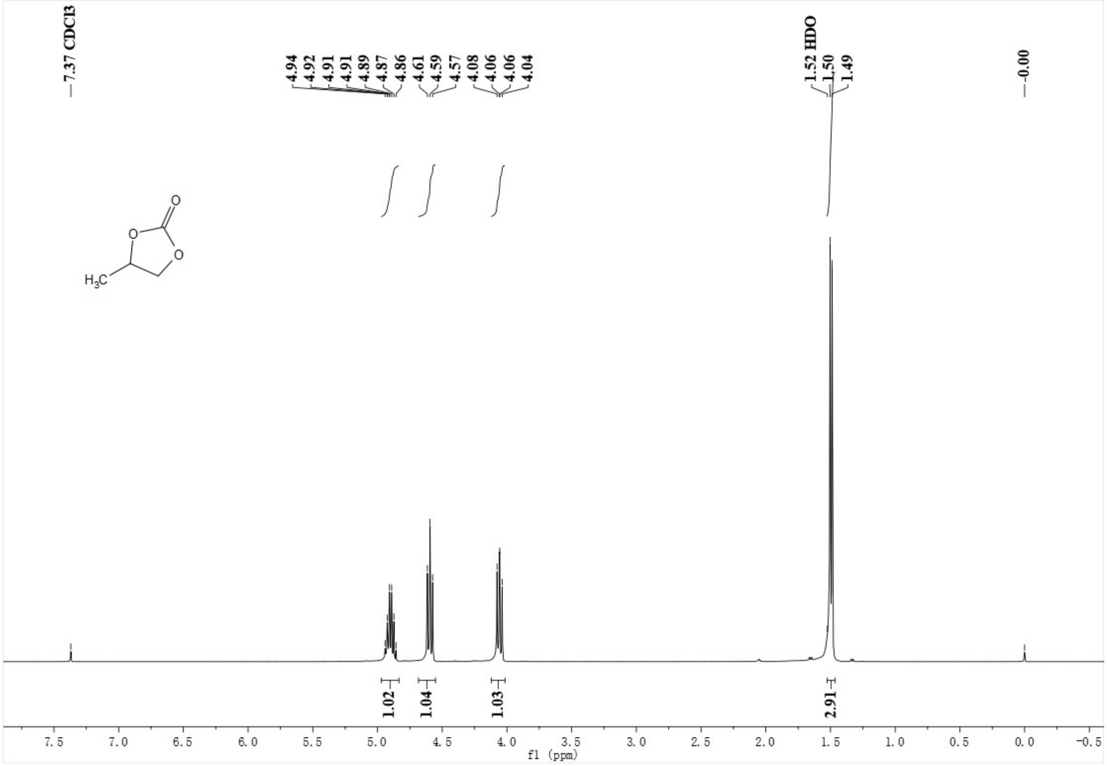


Fig. S11 ^{1}H NMR spectrum of **2b**

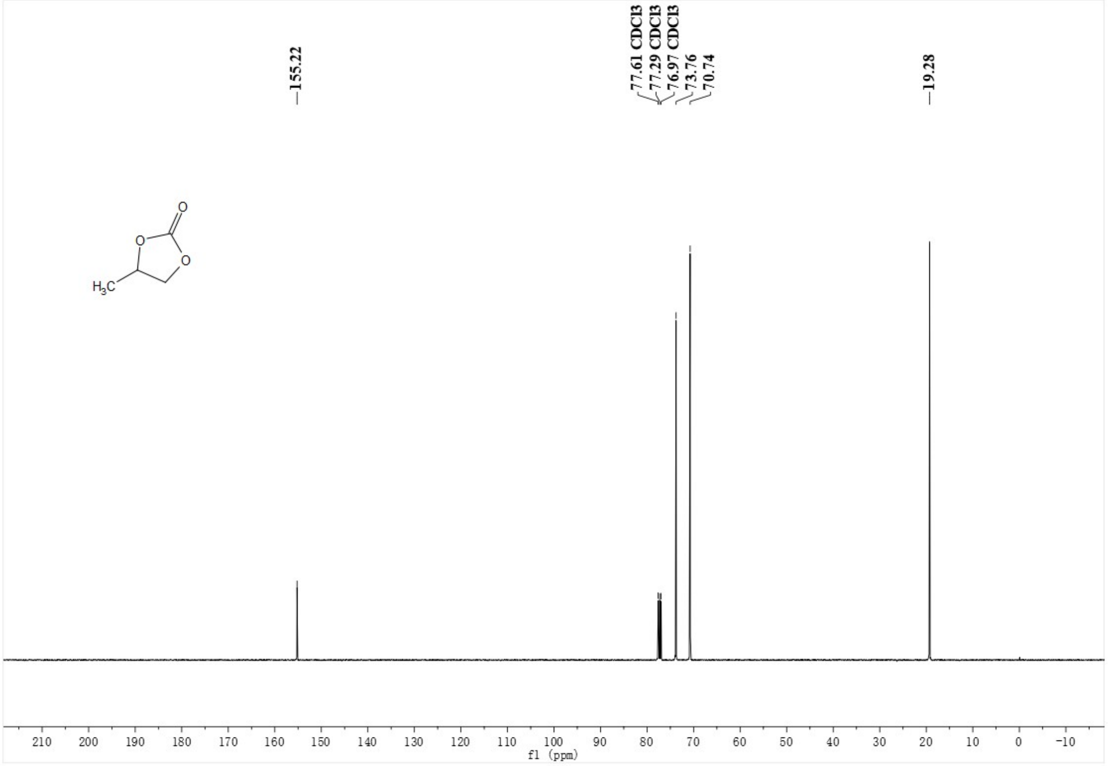


Fig. S12 ^{13}C NMR spectrum of **2b**

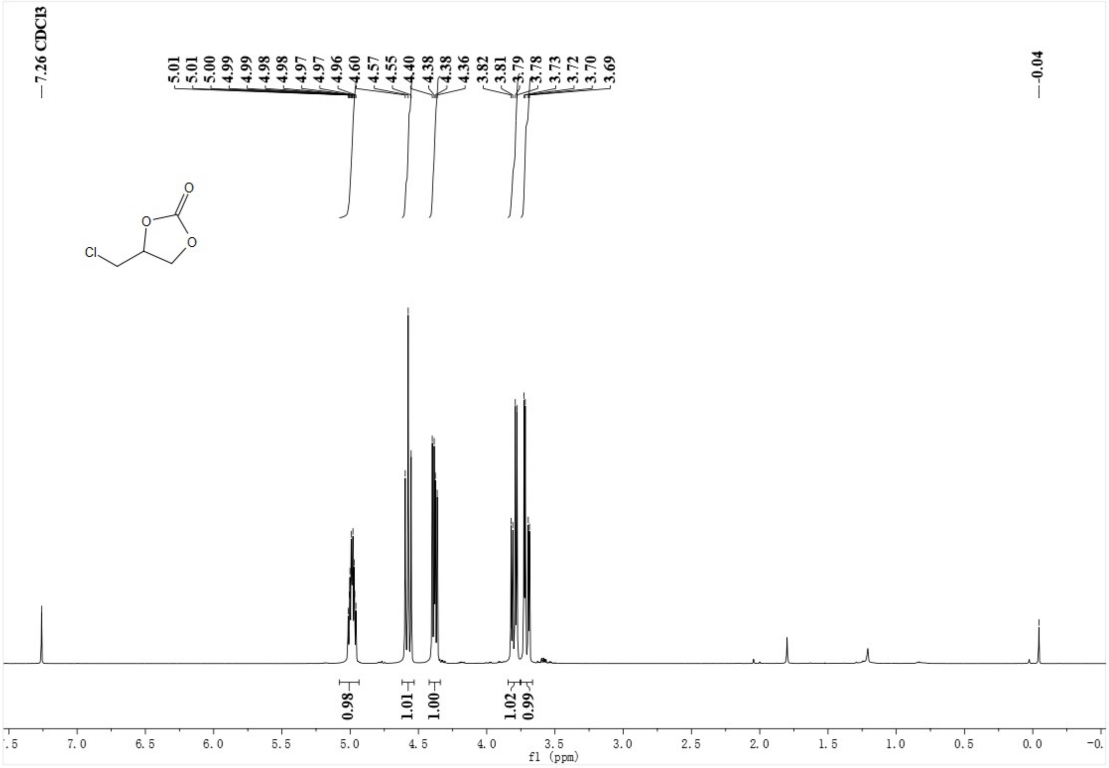


Fig. S13 ^{1}H NMR spectrum of **2c**

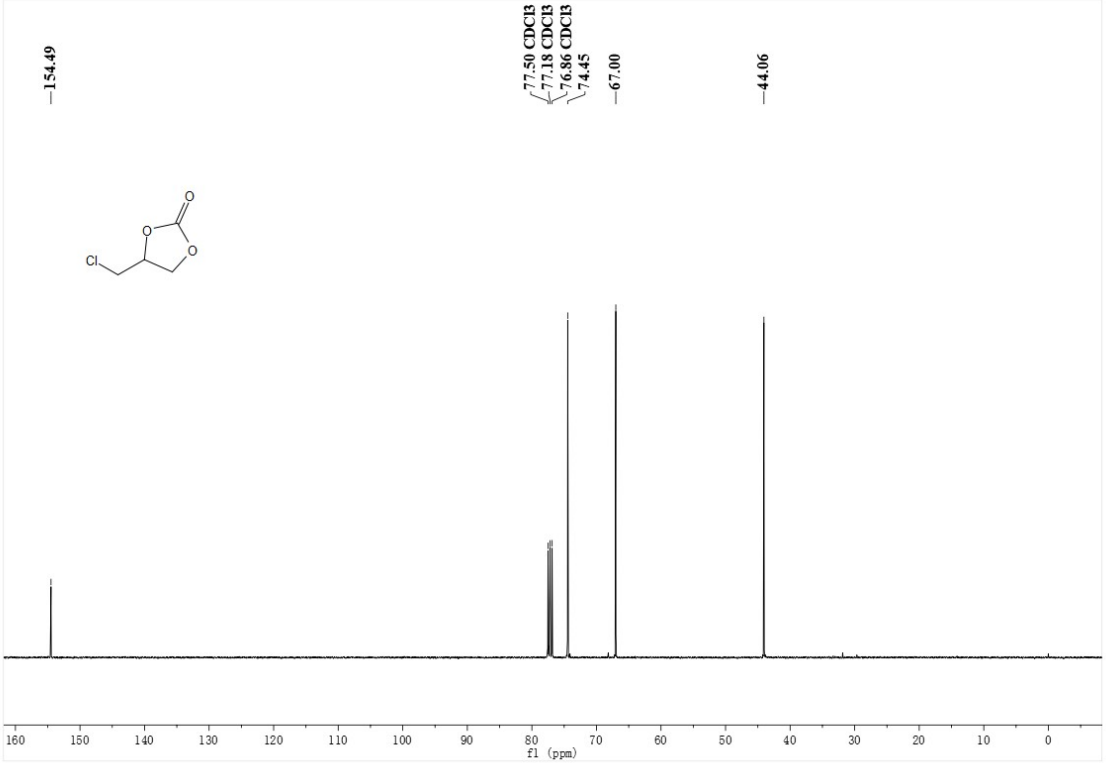


Fig. S14 ^{13}C NMR spectrum of **2c**

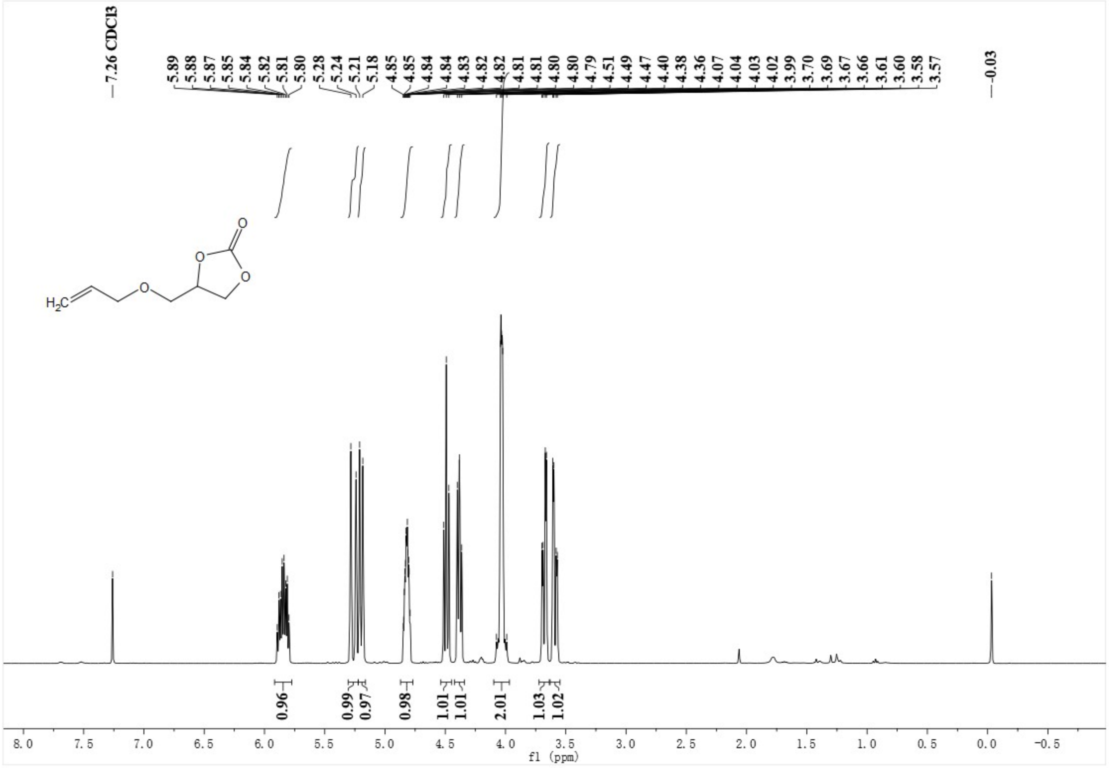


Fig. S15 ^{1}H NMR spectrum of **2d**

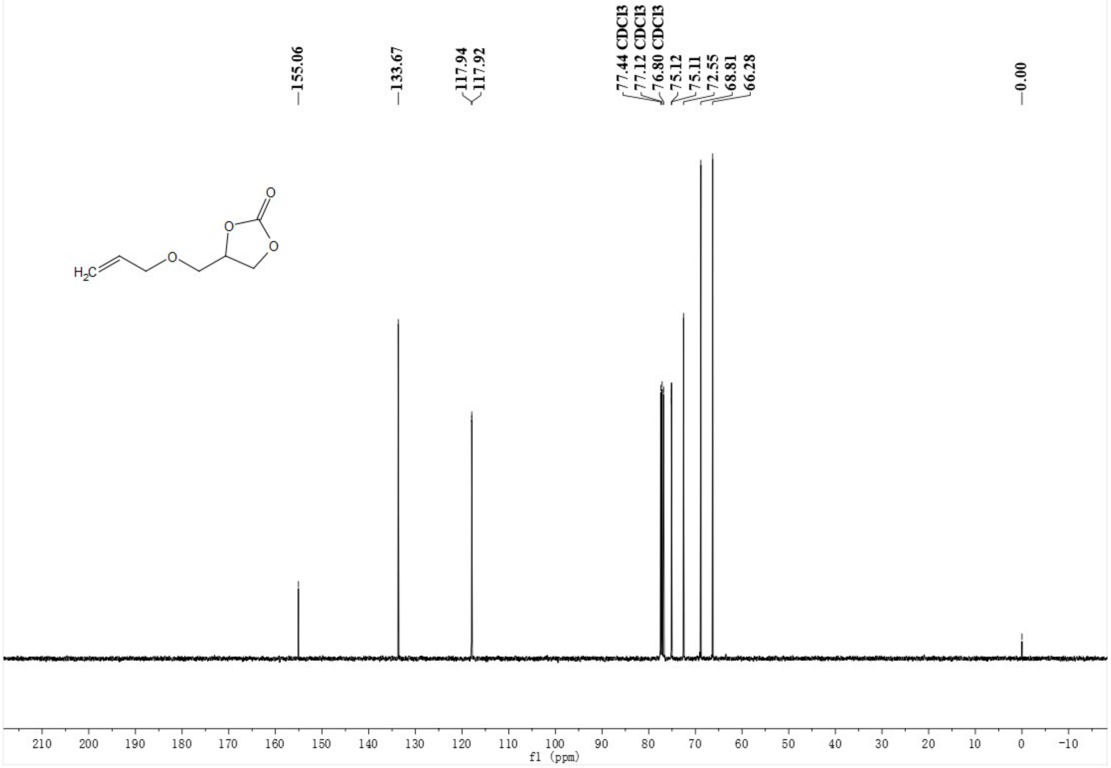


Fig. S16 ^{13}C NMR spectrum of **2d**

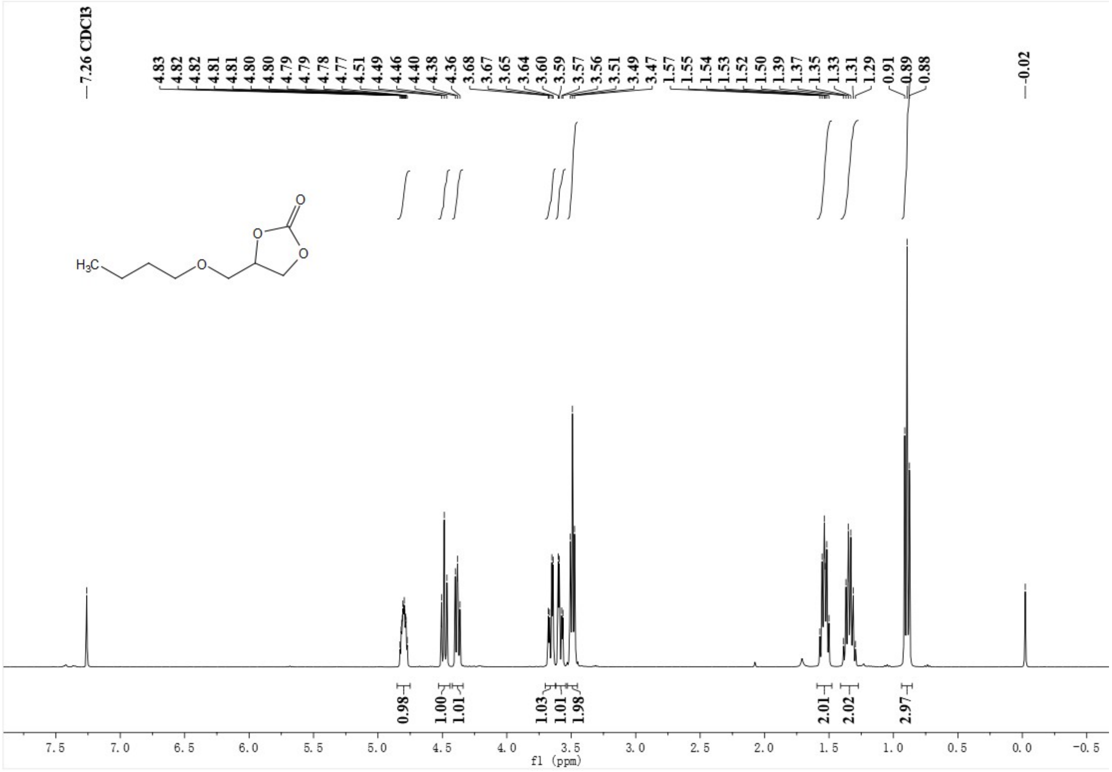


Fig. S17 ^{1}H NMR spectrum of **2e**

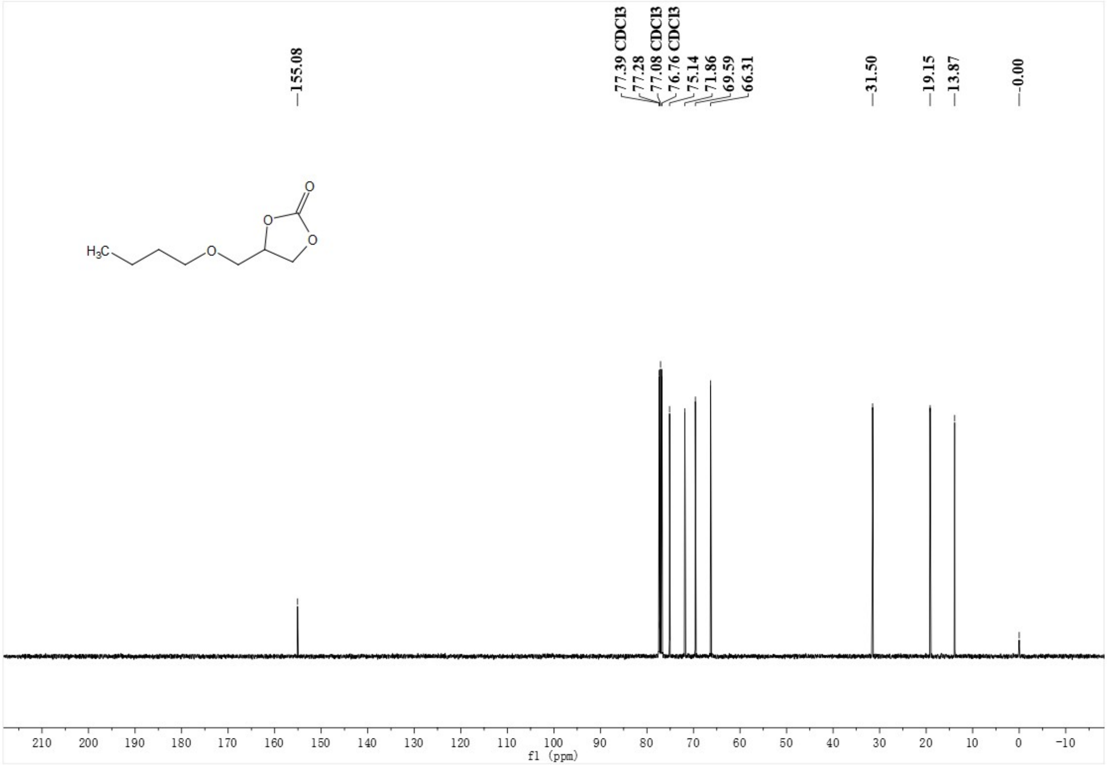


Fig. S18 ^{13}C NMR spectrum of **2e**

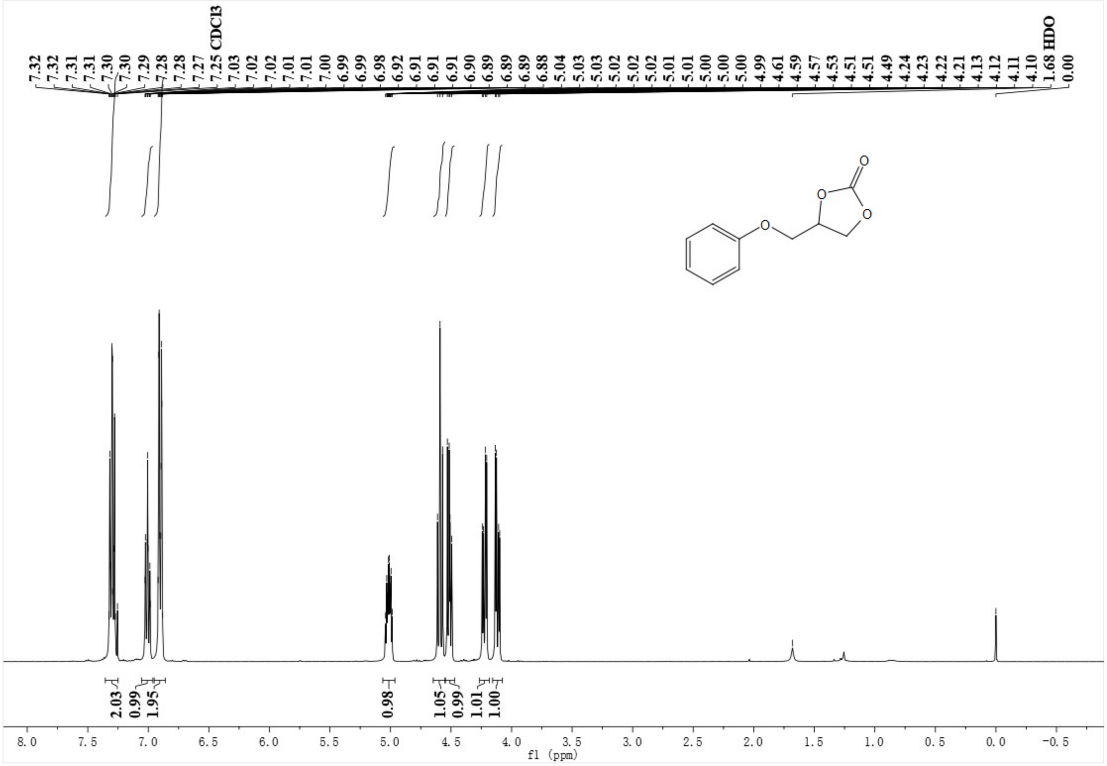


Fig. S19 ^{1}H NMR spectrum of **2f**

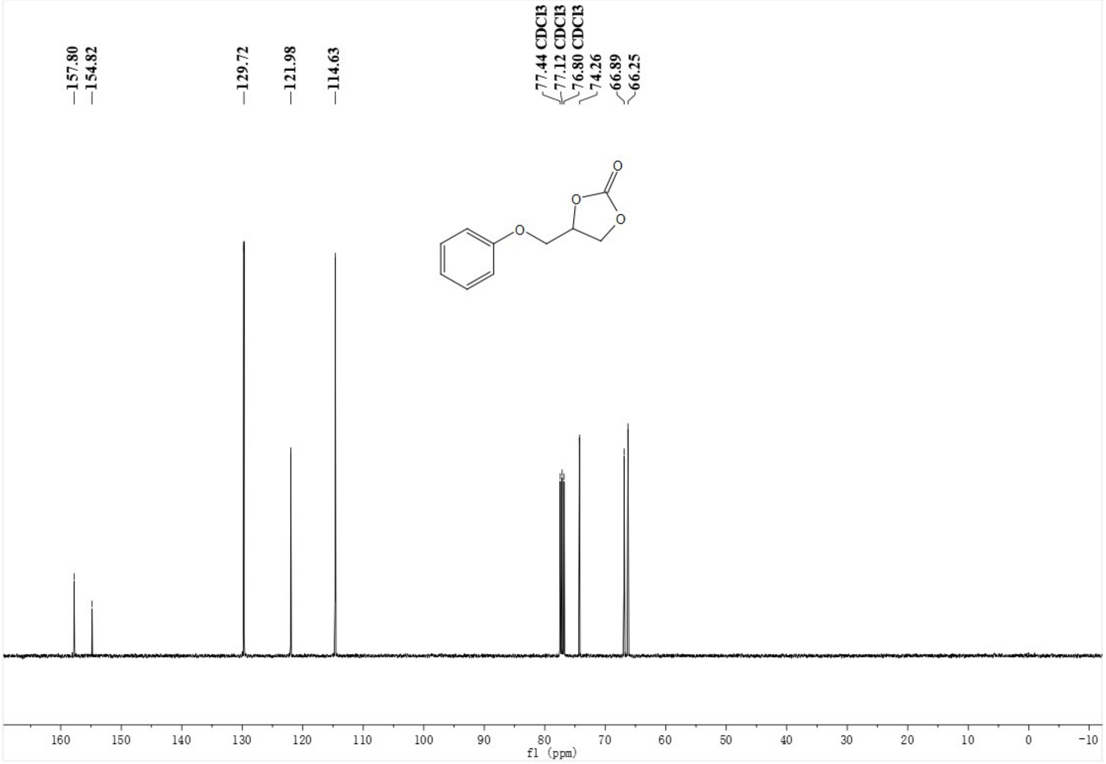


Fig. S20 ^{13}C NMR spectrum of **2f**

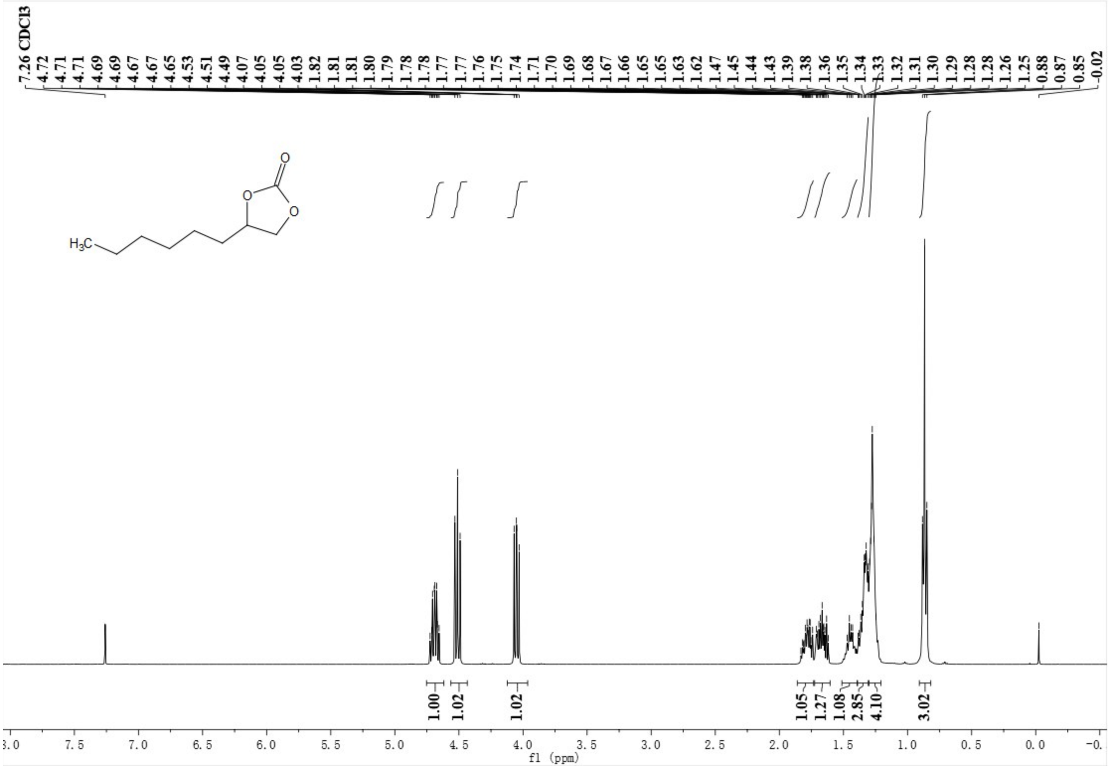


Fig. S21 ^{1}H NMR spectrum of **2g**

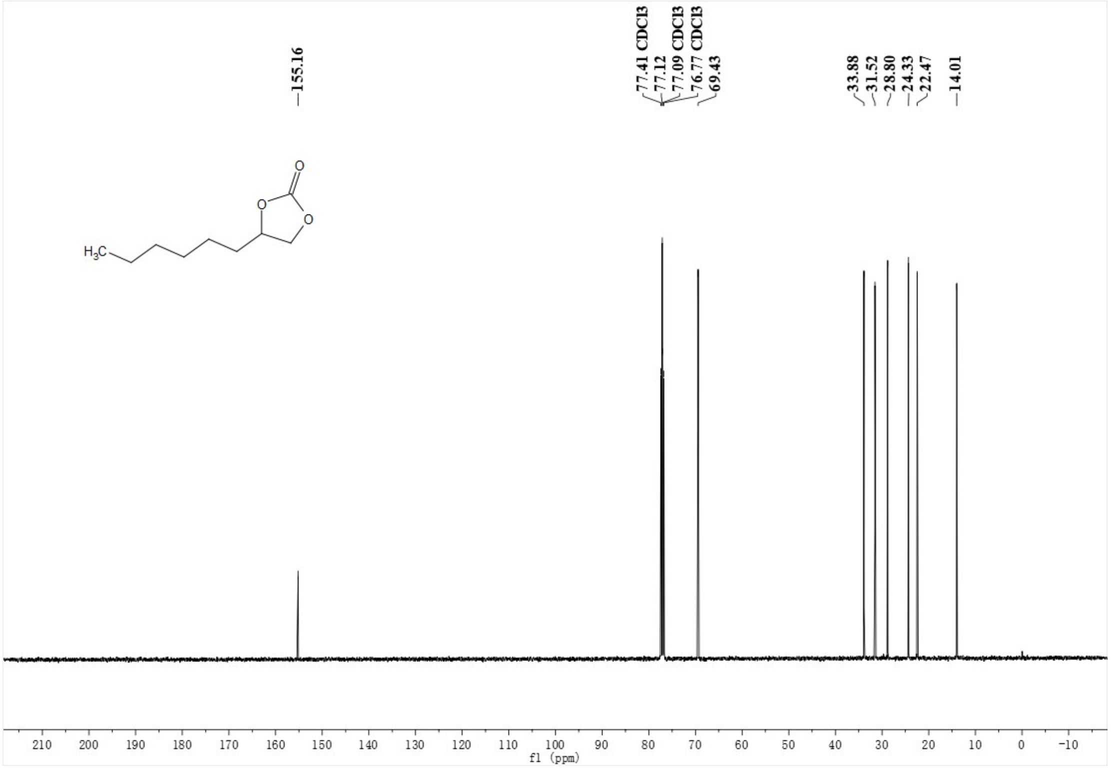


Fig. S22 ^{13}C NMR spectrum of **2g**

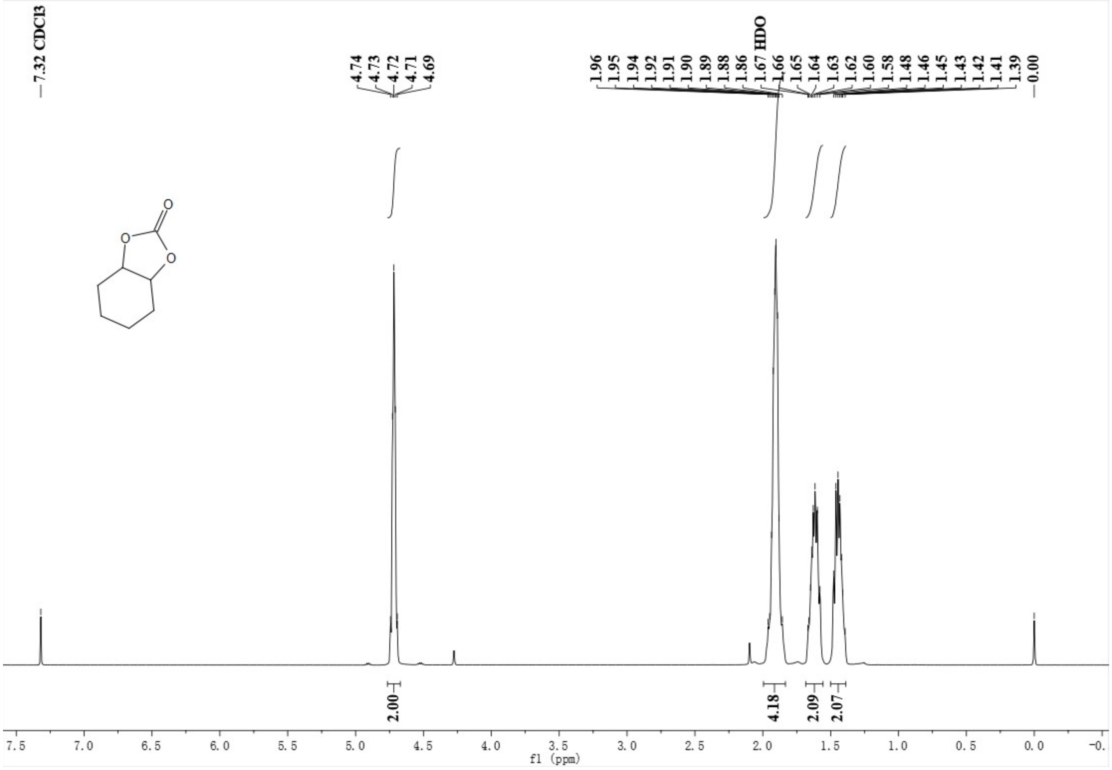


Fig. S23 ^{1}H NMR spectrum of **2h**

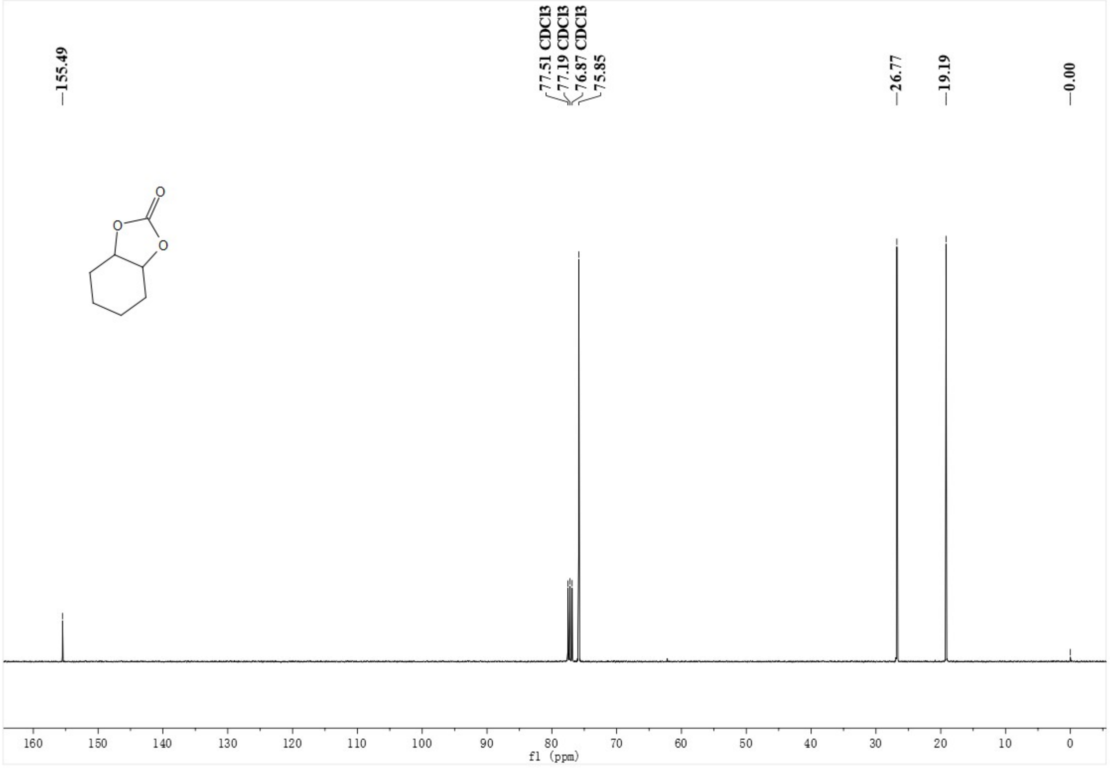


Fig. S24 ^{13}C NMR spectrum of **2h**

6. Computational methods

Geometric optimizations and frequency calculations were performed with Gaussian 16 C01.[S1] TPSSh functional[S2] was used. The def2-TZVP basis sets were used for the Co and Br atoms, and the def2-SVP basis sets were used for the other atoms.[S3-S5] Grimme's dispersion correction[S4] with Becke-Johnson damping[S6] was applied. Grimme's quasi-harmonic approximation was applied to correct the entropy contribution from low-frequency vibrational modes by A single-point energy on the optimized gas phase geometry was calculated with the Model based on Density (SMD).[S7-S8] Since the epoxides were not parametrized in the SMD implementation of Gaussian 16, 1-hexanol was selected as the continuum due to its similar elemental composition and dielectric constant (ethylene oxide: 12.7 at 298.15 K;[S9] 1-hexanol: 12.51, from the Gaussian 16 SCRF definition). The electronic energies were further corrected with a single-point gas phase calculation at the PWPB95-D4[S10-S11]/def2-TZVPP level using ORCA 5.0.4.[S12] Resolution of identity (RI) approximation was applied to accelerate the computation, and the def2-TZVPP/C auxiliary basis sets[S13] were used. A −1.89 kcal/mol molar correction on the Gibbs free energy was applied to each solvated species.

7. The calculation formula

Conversion = [1 - (molar mass of unreacted **1**/all added molar mass of **1**)]*100% (1)

Yield = (molar mass of produced **2**/theoretical molar mass of produced **2**)*100% (2)

Selectivity = Yield/Conversion*100% (3)

TON = molar mass of produced **2**/molar mass of catalyst **L1-NiBr$_2$** (4)

In formula (2) "theoretical molar mass of produced **2**" = "all added molar mass of **1**".

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