

Electronic supplementary information for *Dalton Trans.*

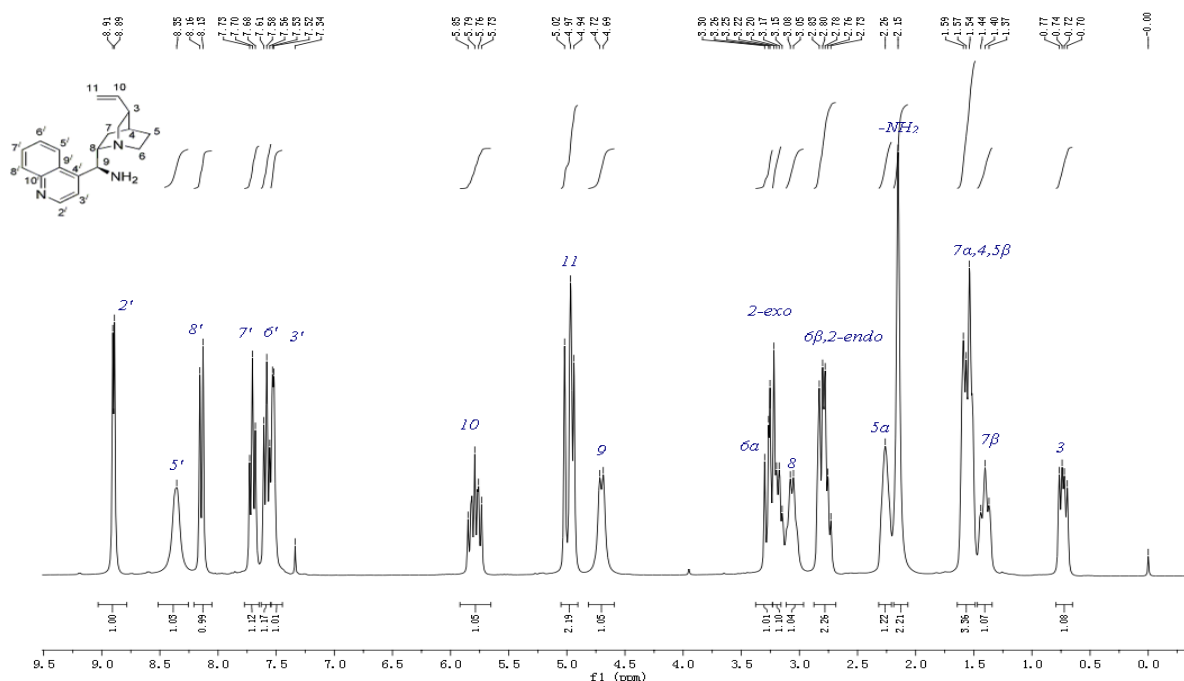
Preparation and confinement effect of heterogeneous 9-amino-9-deoxy-epi-cinchonine organocatalyst for asymmetric aldol addition in aqueous medium

Wei Wang, Xuebing Ma,* Jun Cao, Jingwei Wan, Qian Tang

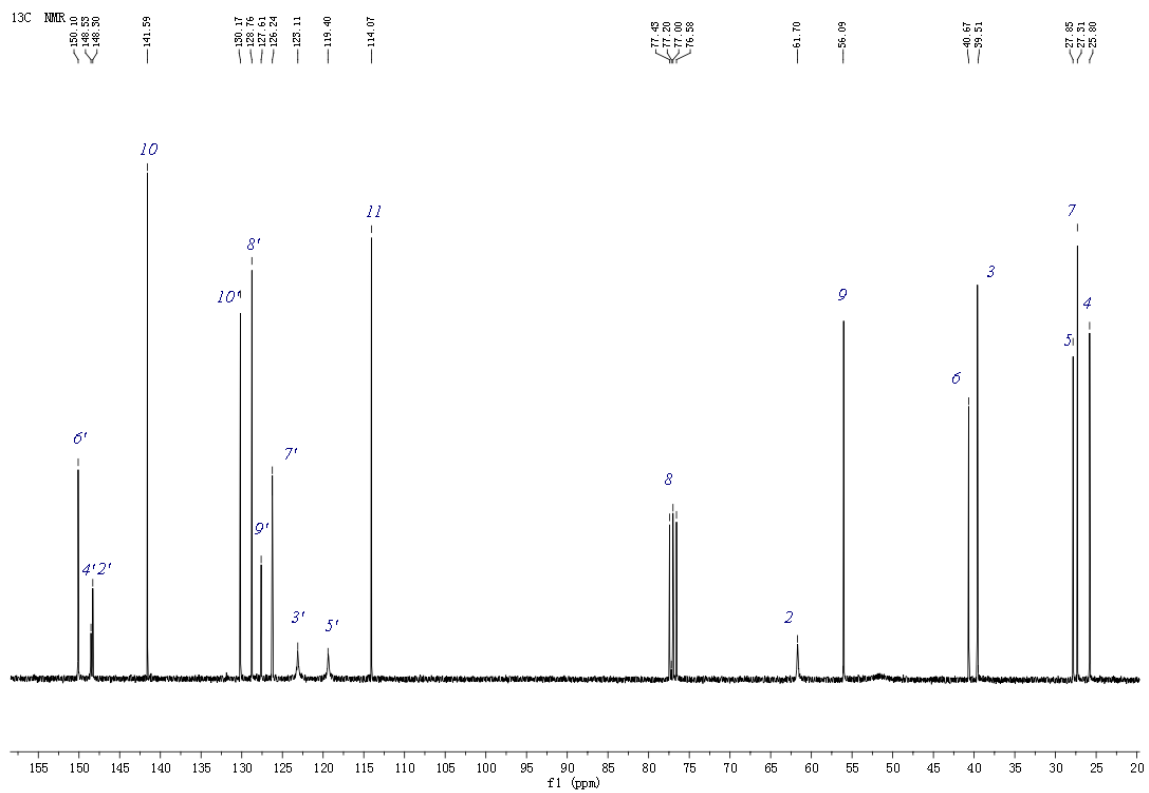
College of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, P. R. China

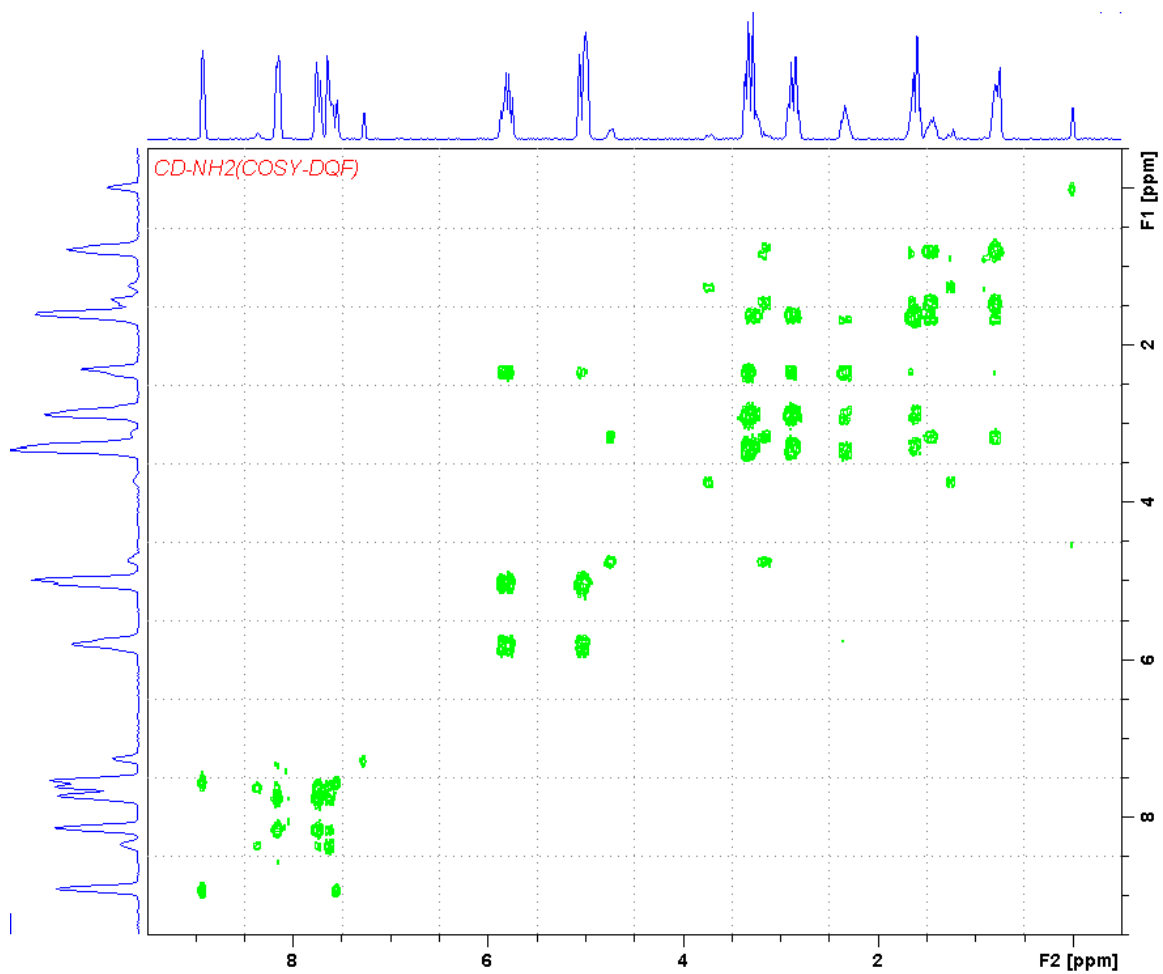
1. NMR spectra of 1a-e and 9-amino-9-deoxy-epi-cinchonine

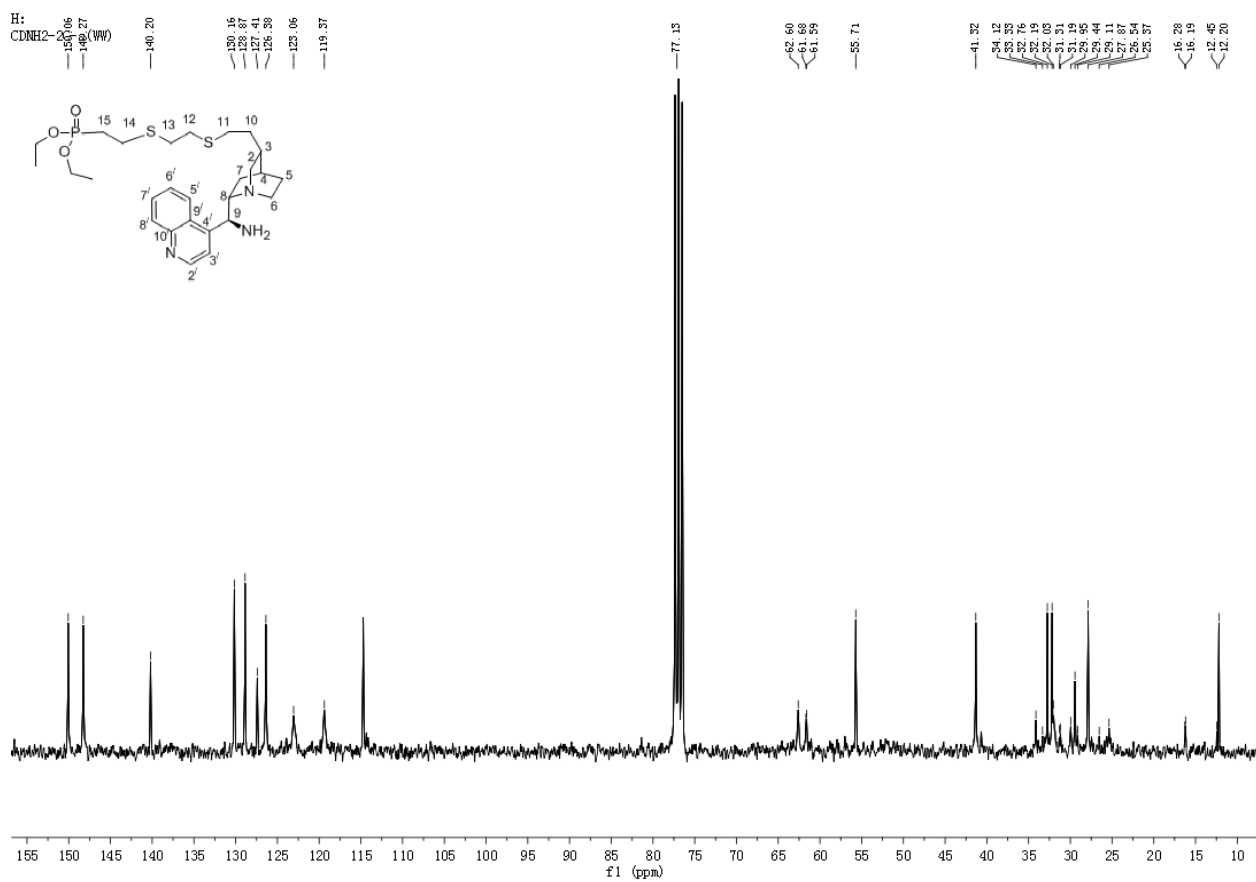
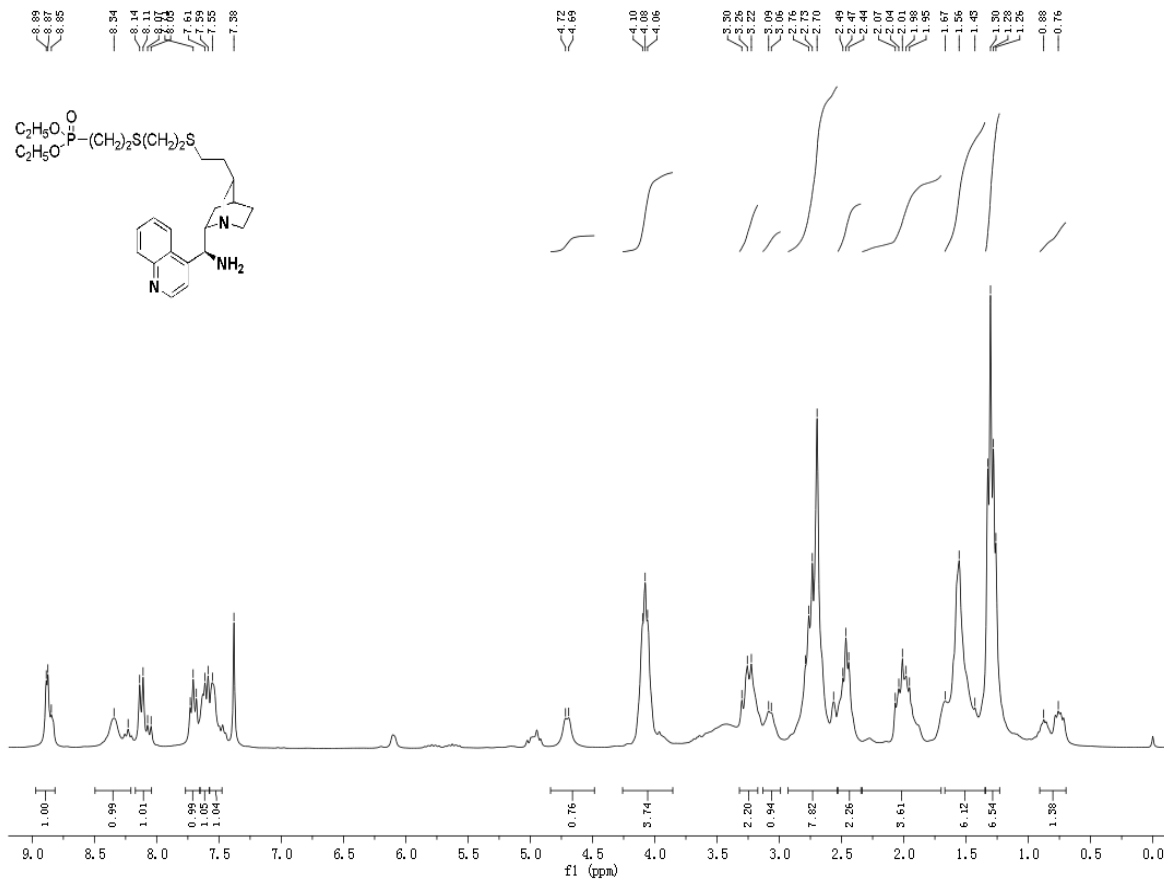
9-amino-9-deoxy-epi-cinchonine:

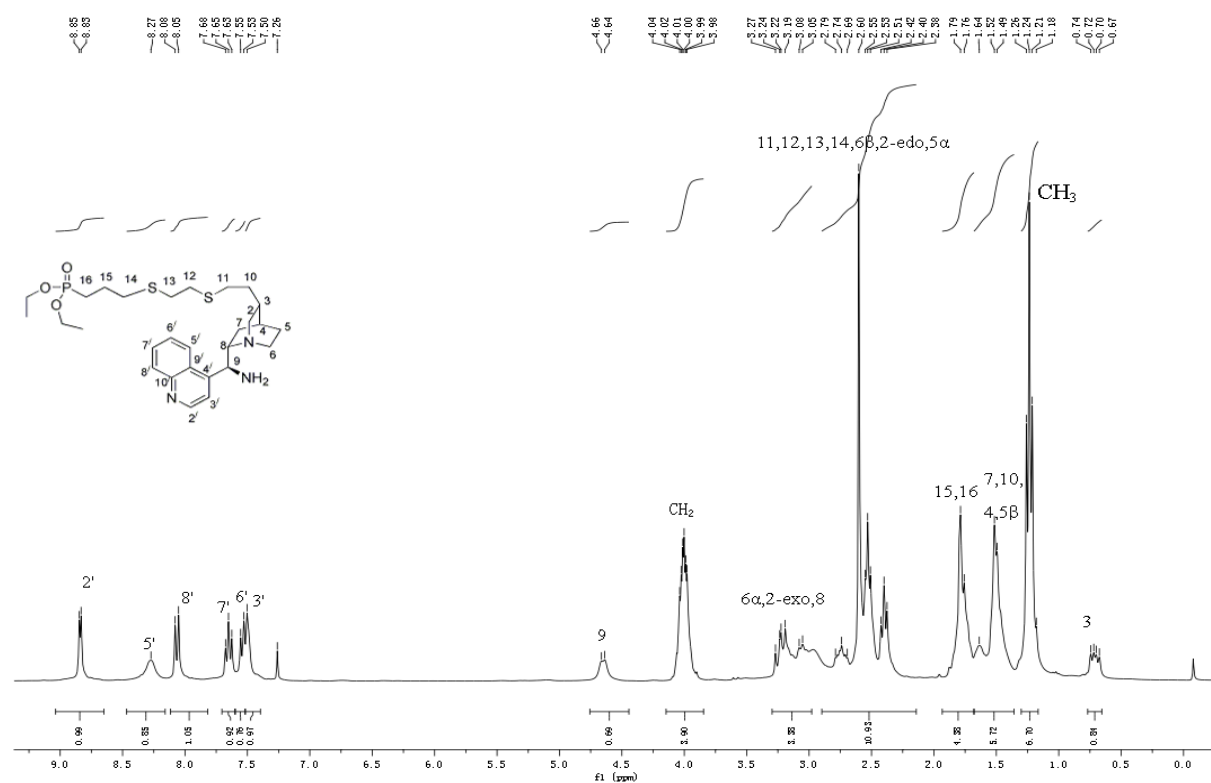
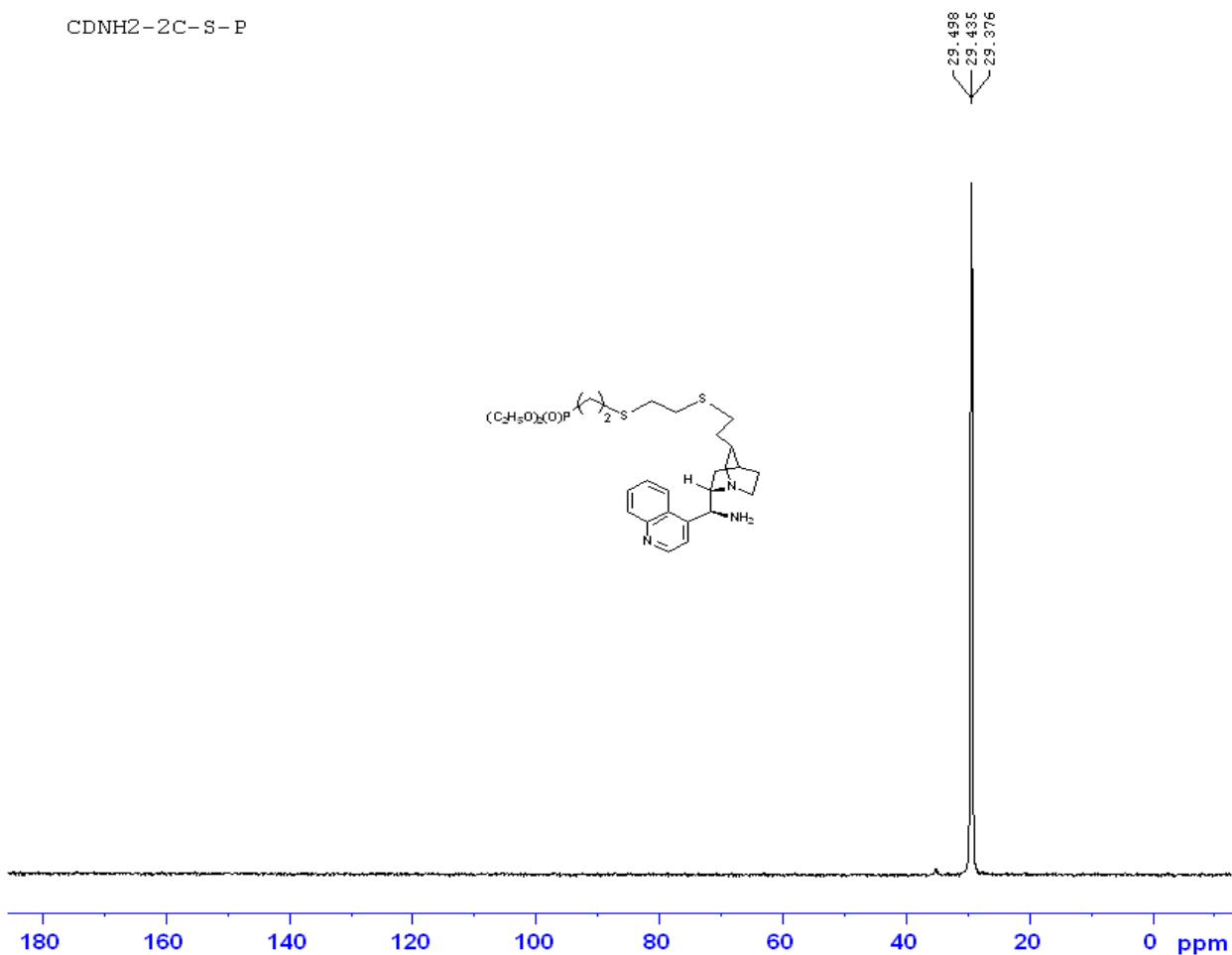


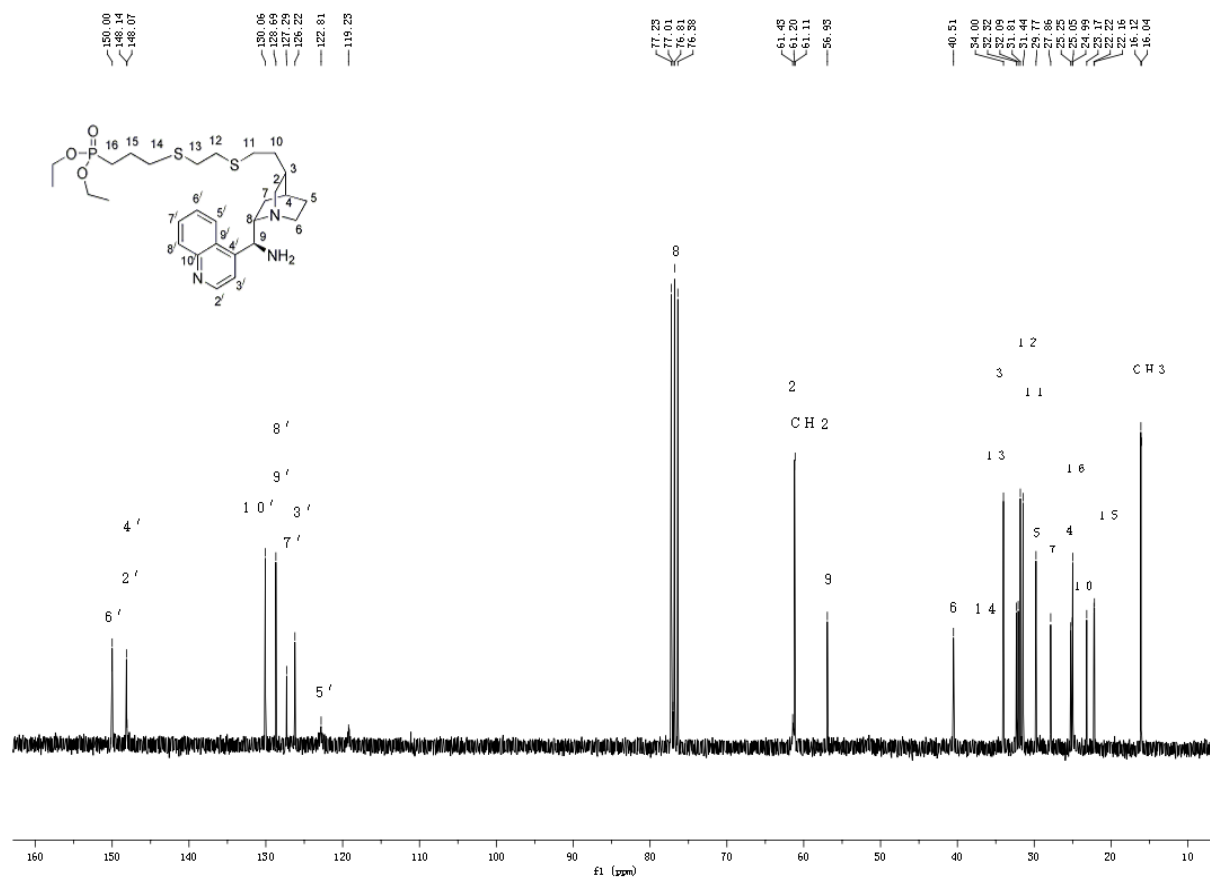
^1H NMR (300M Hz, CDCl_3 , TMS): δ 8.90 (H-2', 1 H, d, $^3J=6.0$ Hz), 8.35 (H-5', 1 H, br s, $^3J=9.0$ Hz), 8.15 (H-8', 1 H, d, $^3J=3.0$ Hz), 7.70 (H-7', 1 H, t, $^3J=6.0$ Hz), 7.58 (H-6', 1 H, t, $^3J=6.0$ Hz), 7.52 (H-3', 1 H, d, $^3J=2.0$ Hz), 5.78 (H-10, 1 H, ddd), 4.94-5.02 (H-11, 2 H, m), 4.70 (H-9, 1 H, d, $^3J=9.0$ Hz), 3.26 (H-6 α , dd, 1 H), 3.17 (H-2-exo, q, 1 H), 3.06 (H-8, 1 H, d, $^3J=9.0$ Hz), 2.73-2.83 (H-6 β , H-2-endo, 2 H), 2.26 (H-5 α , s, 1 H), 2.15 (-NH $_2$, s, 2 H), 1.57-1.59 (H-3, H-4, H-5 β , 3 H), 1.40 (H-7 β , 1 H), 0.73 (H-7 α , dd, 1 H). ^{13}C NMR (75M Hz, CDCl_3 , TMS): δ 150.1 (C-6'), 148.5 (C-4'), 148.3 (C-2'), 141.6 (C-10), 130.2 (C-10'), 128.8 (C-8'), 127.6 (C-9'), 126.2 (C-7'), 123.1 (C-3'), 119.4 (C-5'), 114.1 (C-11), 77.2 (C-8), 61.7 (C-2), 56.1 (C-9), 40.7 (C-6), 39.5 (C-3), 27.9 (C-5), 27.3 (C-7), 25.8 (C-4).



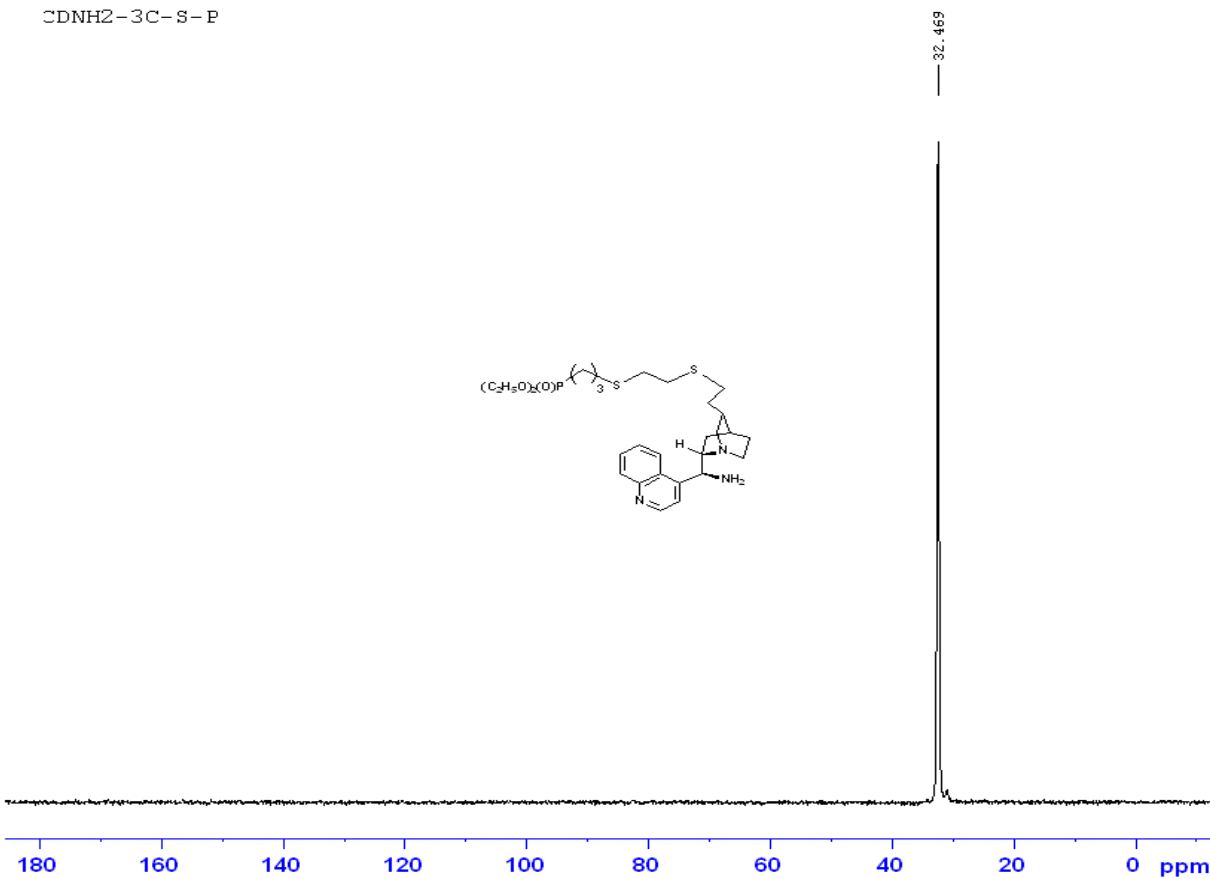


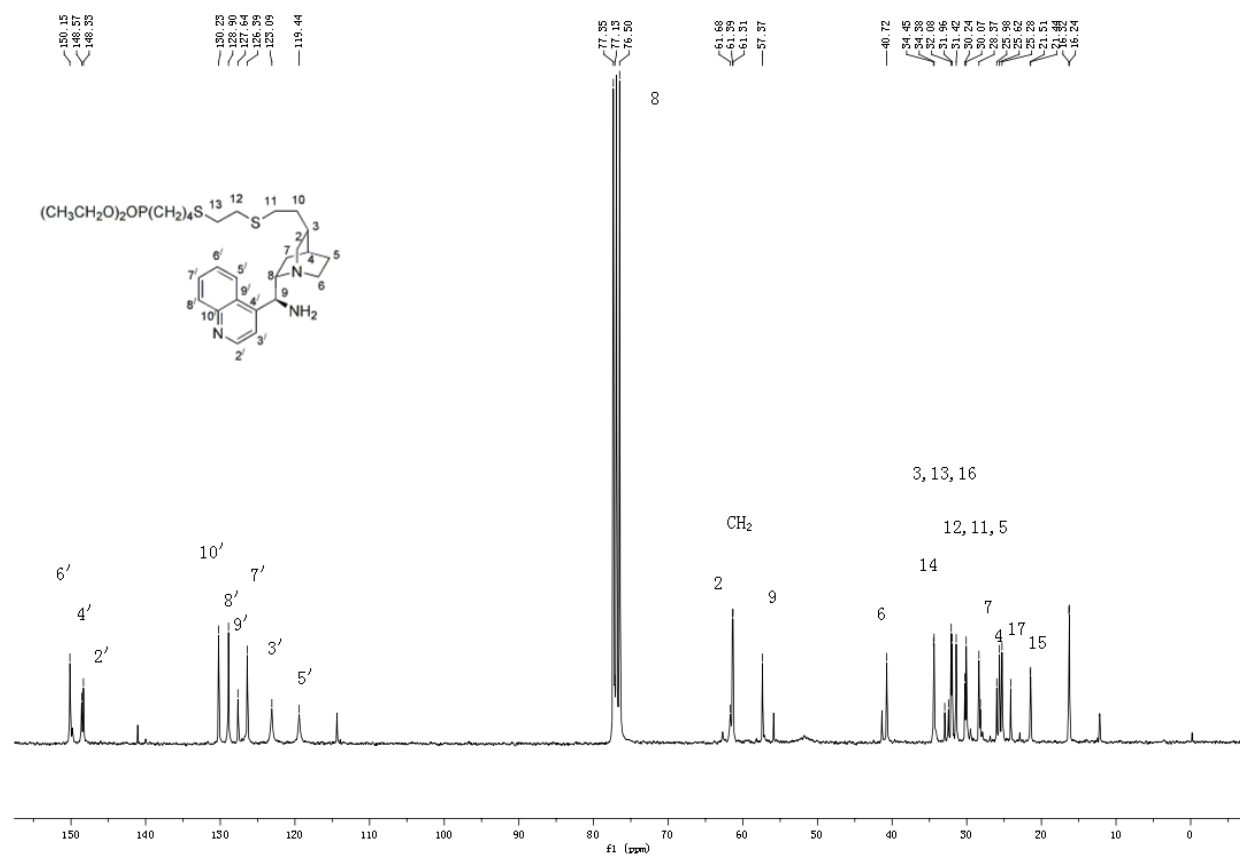
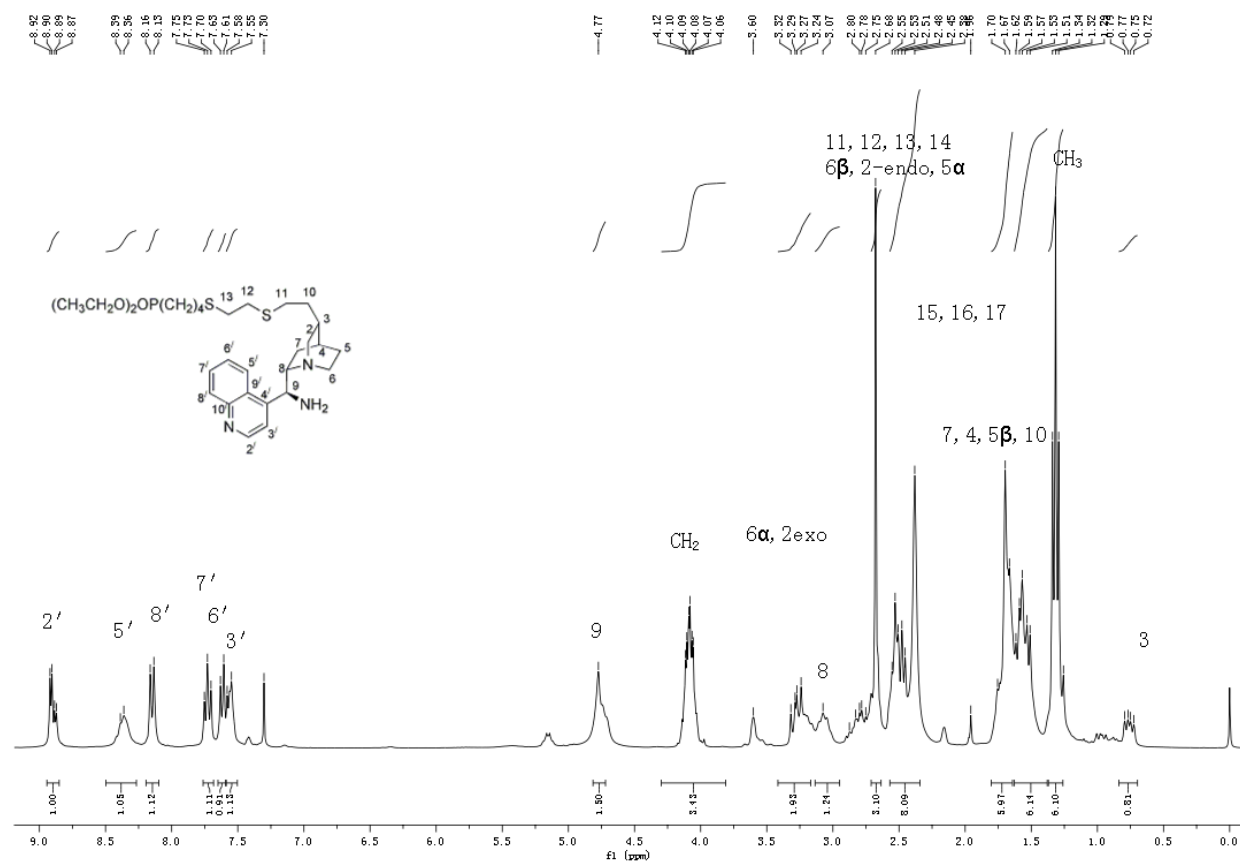




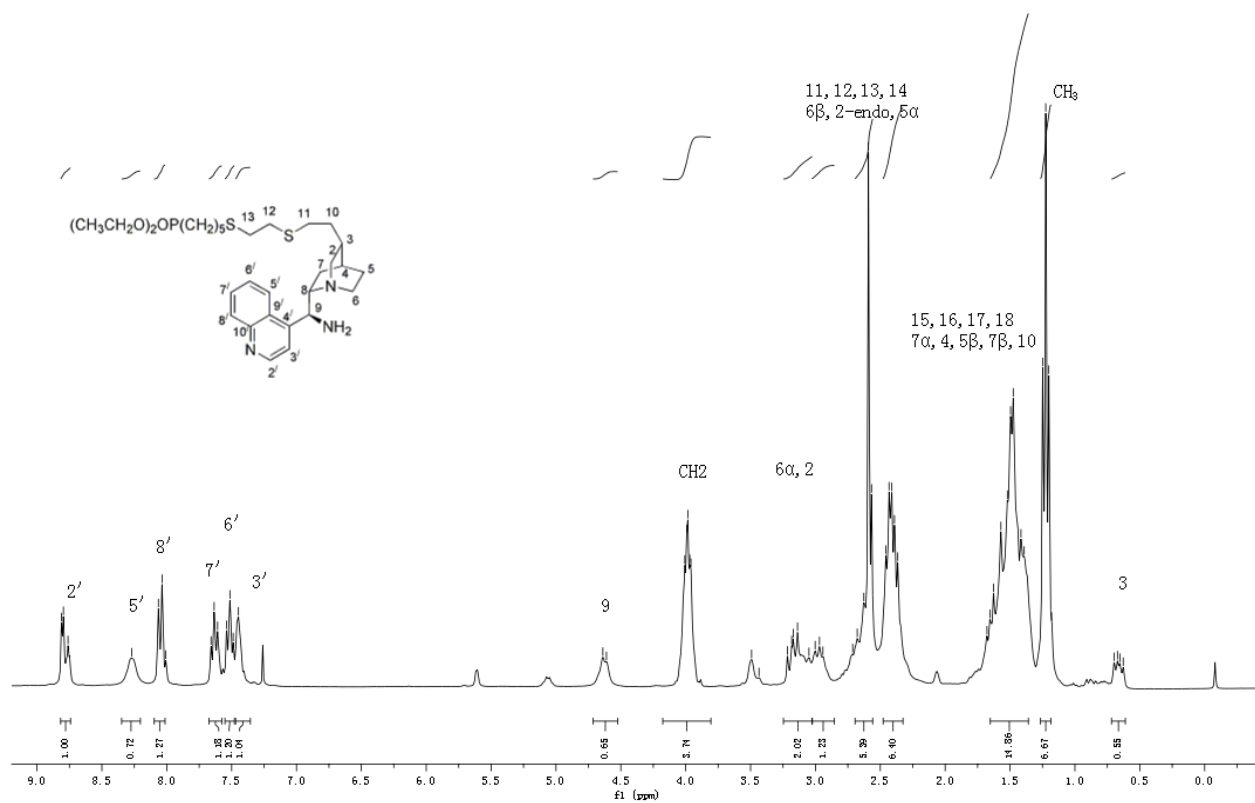
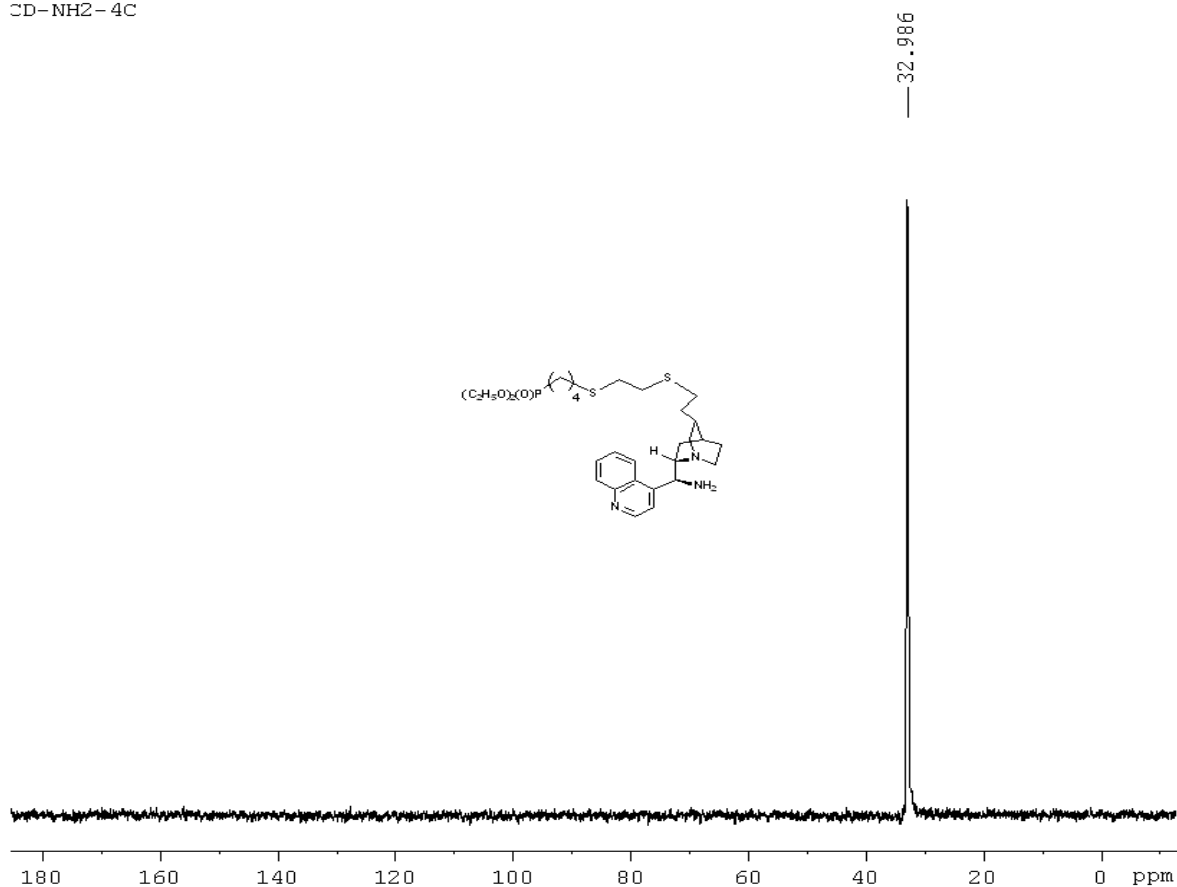


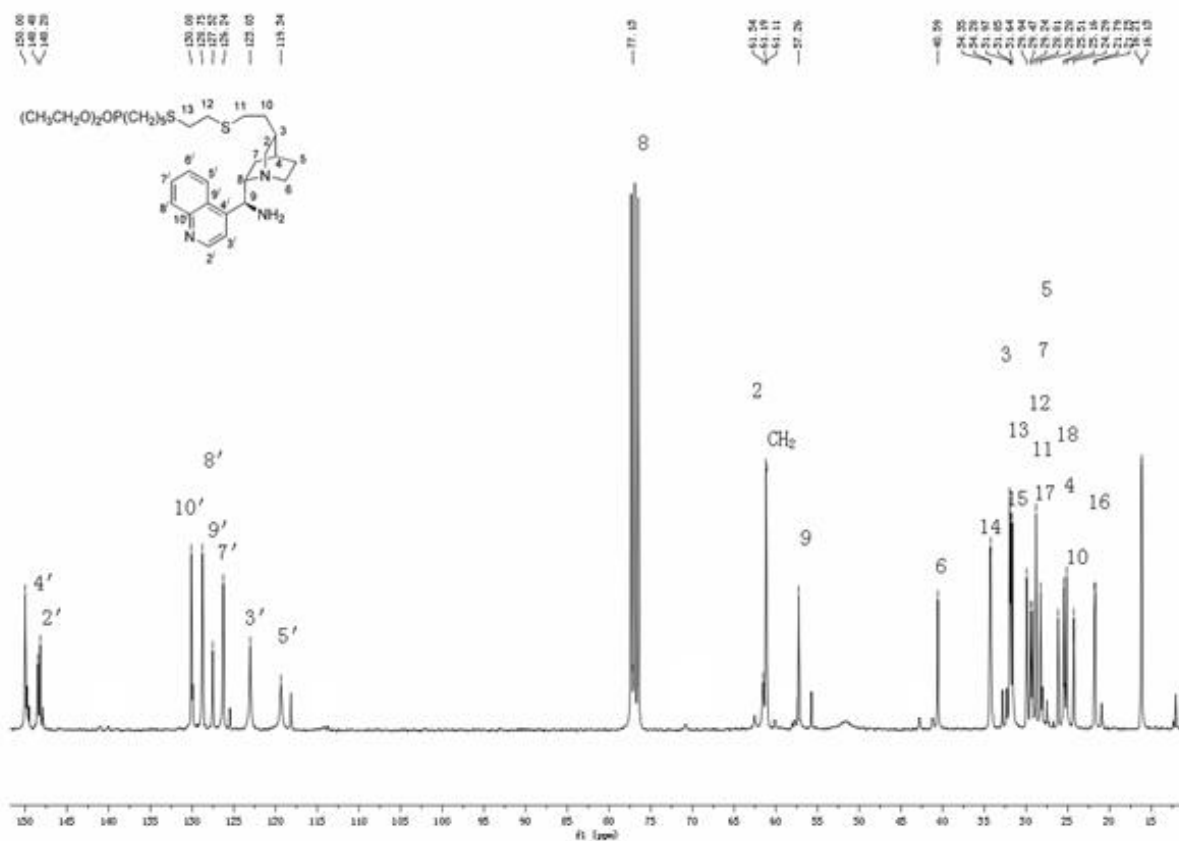
CDNH2-3C-S-P





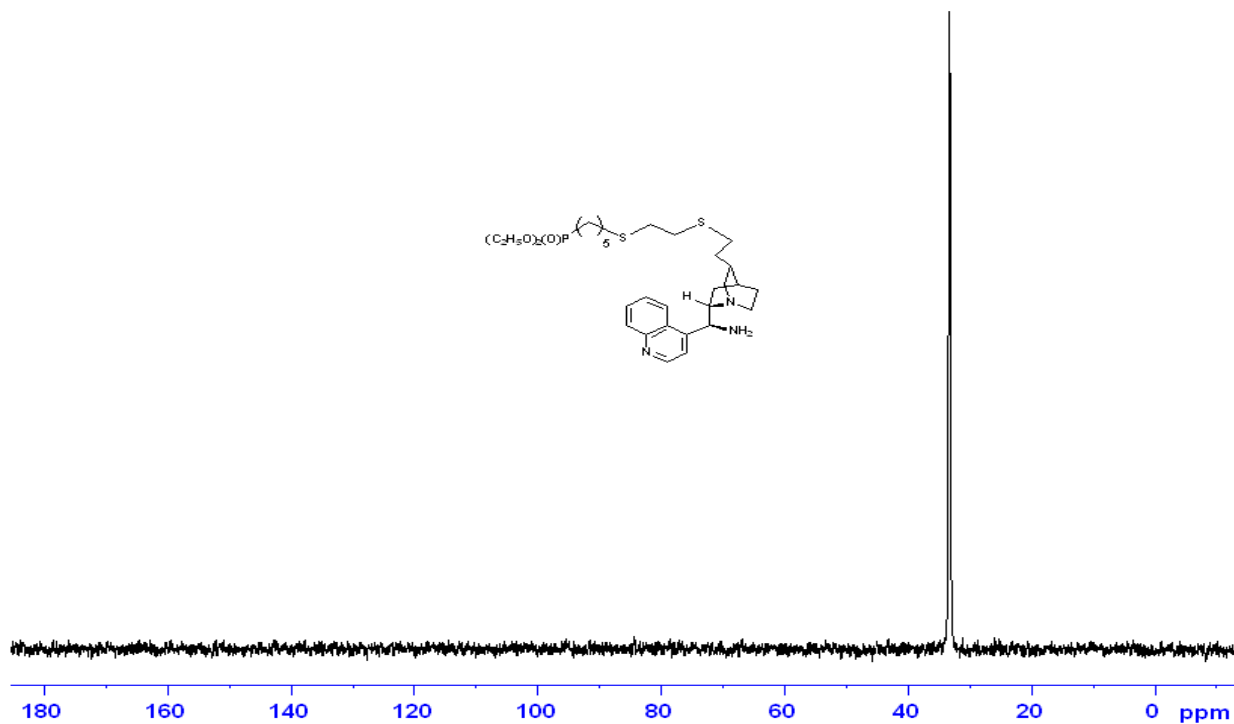
CD-NH2-4C

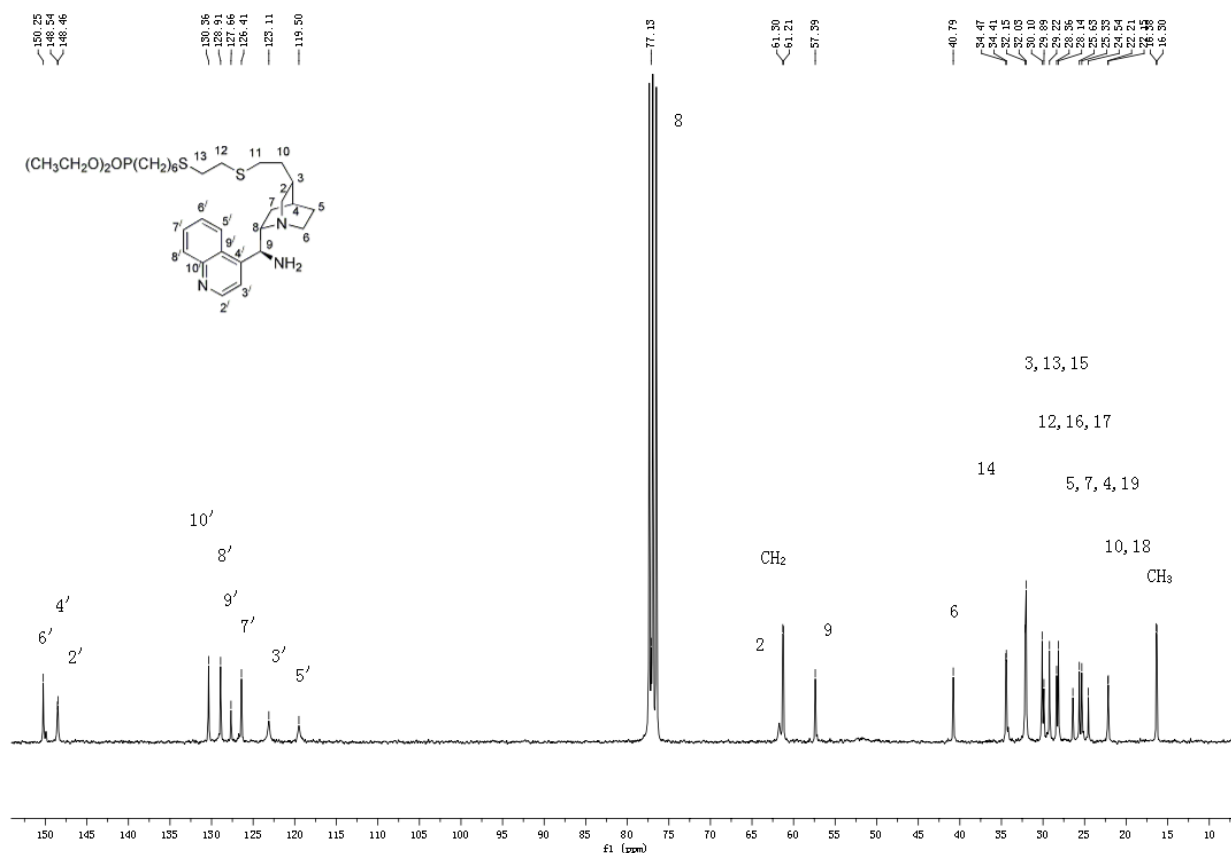
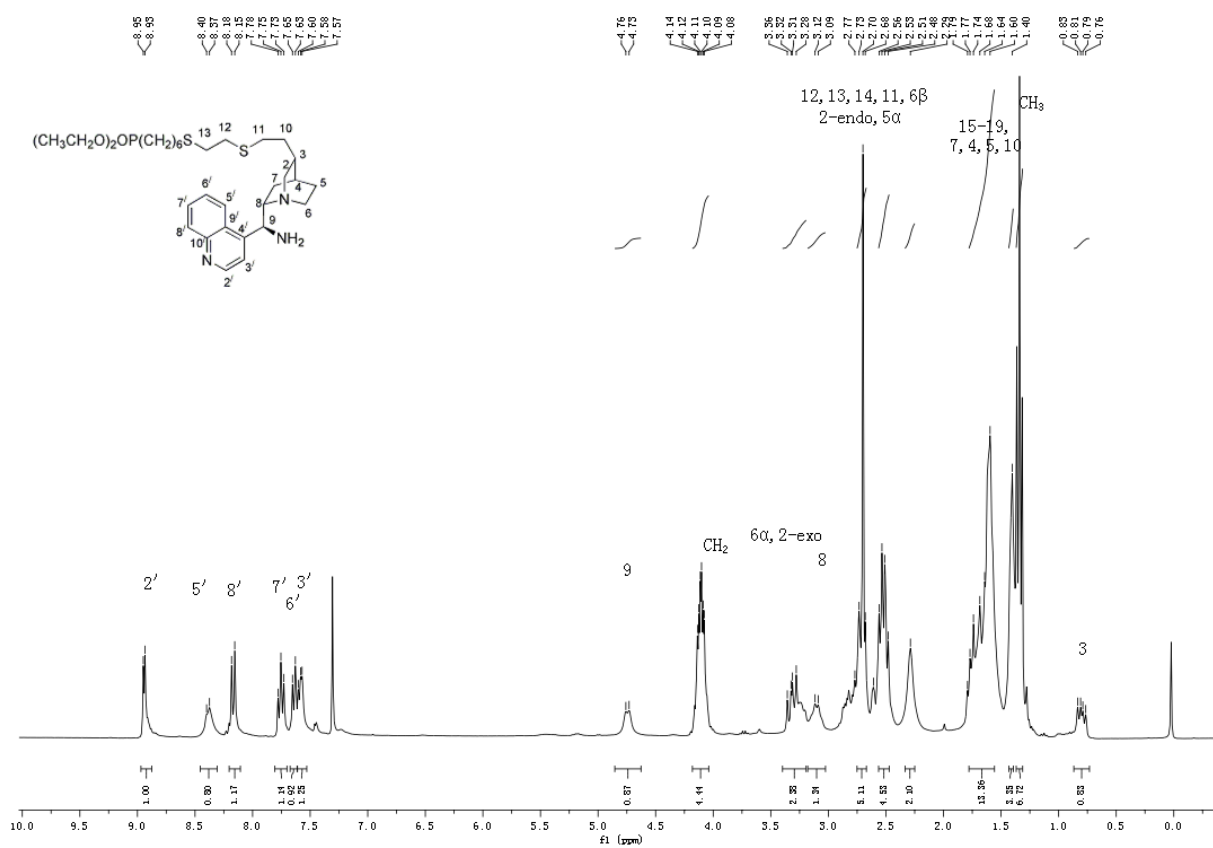


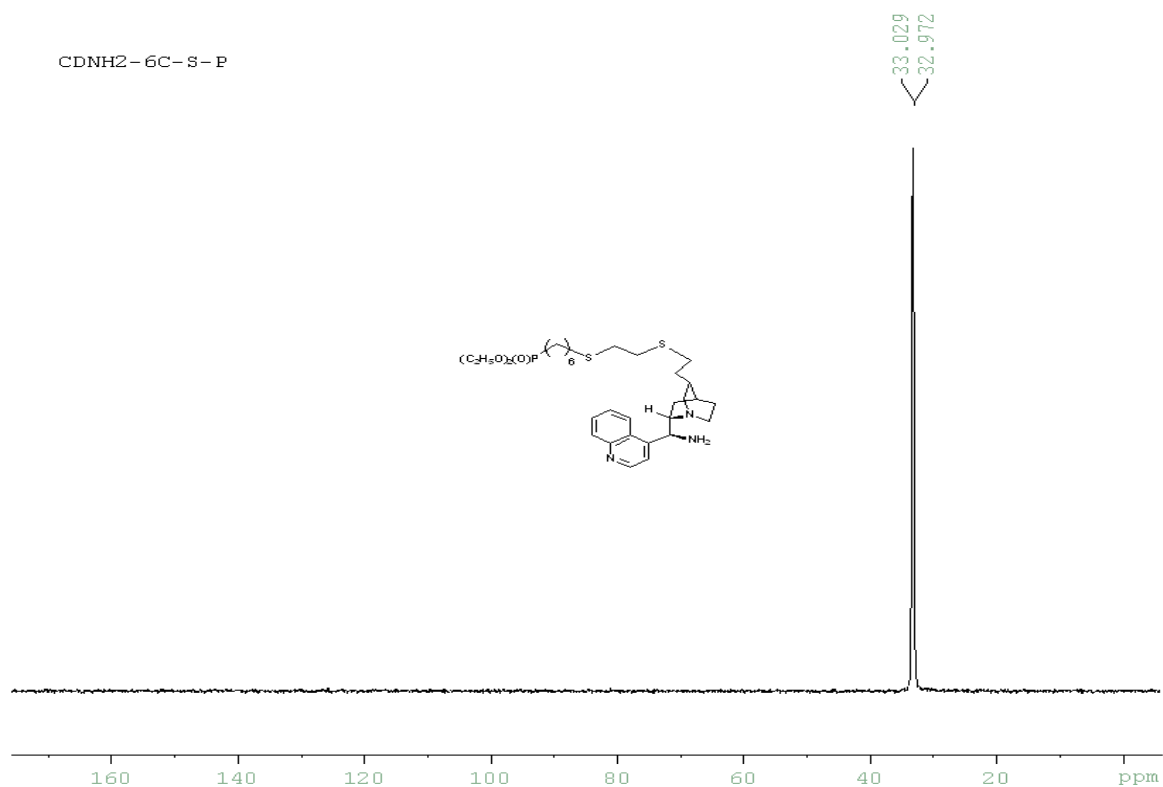


CD-NH2-5C

33.366
33.239
33.133



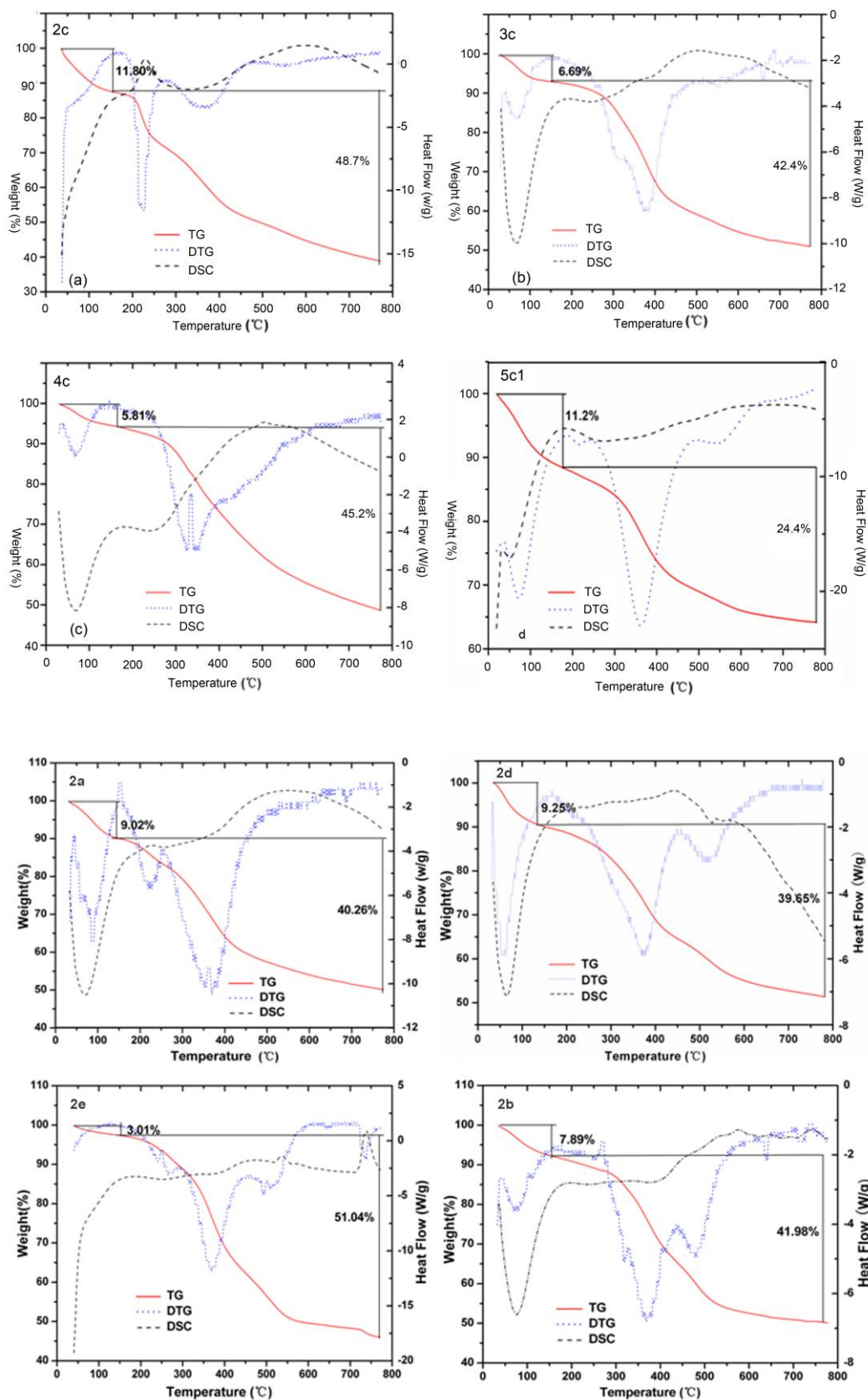




2. Elemental analysis of 2a–e

Catalyst	Molecular formula	Calcd.(Found) (%)		
		C	H	N
2a	Zr(OH) _{3.18} (O ₃ PR) _{0.41} ·1.98H ₂ O	29.24 (29.01)	6.29 (6.46)	4.44 (4.23)
2b	Zr(OH) _{3.14} (O ₃ PR) _{0.43} ·1.76H ₂ O	30.64 (30.23)	6.41 (6.59)	4.53 (4.34)
2c	Zr(OH) _{2.88} (O ₃ PR) _{0.56} ·2.89H ₂ O	34.31 (33.98)	7.02 (7.43)	4.80 (4.59)
2d	Zr(OH) _{3.26} (O ₃ PR) _{0.37} ·2.02H ₂ O	30.07 (30.12)	6.52 (6.61)	4.05 (4.21)
2e	Zr(OH) _{3.04} (O ₃ PR) _{0.48} ·2.28H ₂ O	34.46 (34.12)	7.00 (7.37)	4.46 (4.51)
3b	Zr(OH) _{3.18} (O ₃ PR) _{0.41} ·1.12H ₂ O	35.00 (35.24)	6.95 (7.21)	5.10 (4.88)
3c	Zr(OH) _{3.22} (O ₃ PR) _{0.39} ·1.47H ₂ O	30.83 (30.38)	6.35 (6.89)	4.31 (4.10)
4c	Zr(OH) _{3.12} (O ₃ PR) _{0.44} ·1.41H ₂ O	32.61 (32.68)	6.46 (6.51)	4.56 (4.46)
5c₁	Zr(O ₃ POH) _{1.71} (O ₃ PR) _{0.29} ·2.14H ₂ O	19.43 (19.40)	4.31 (4.44)	2.72 (2.43)
5c₂	Zr(O ₃ POH) _{1.78} (O ₃ PR) _{0.22} ·1.54H ₂ O	16.24 (16.09)	3.68 (3.92)	2.27 (2.26)
5c₃	Zr(O ₃ POH) _{1.81} (O ₃ PR) _{0.19} ·1.21H ₂ O	14.71 (14.54)	3.34 (4.02)	2.06 (1.91)

3. TGA analysis



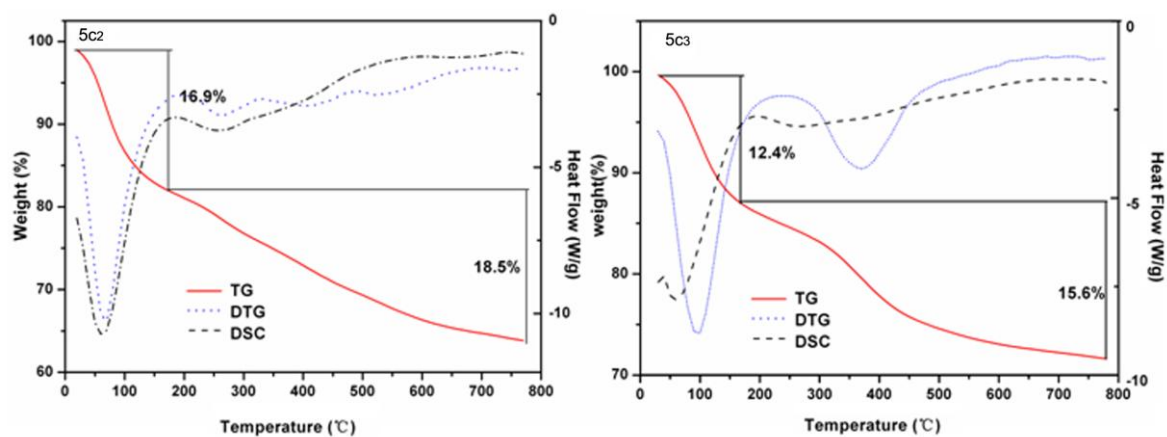


Fig.S1

4. IR spectra

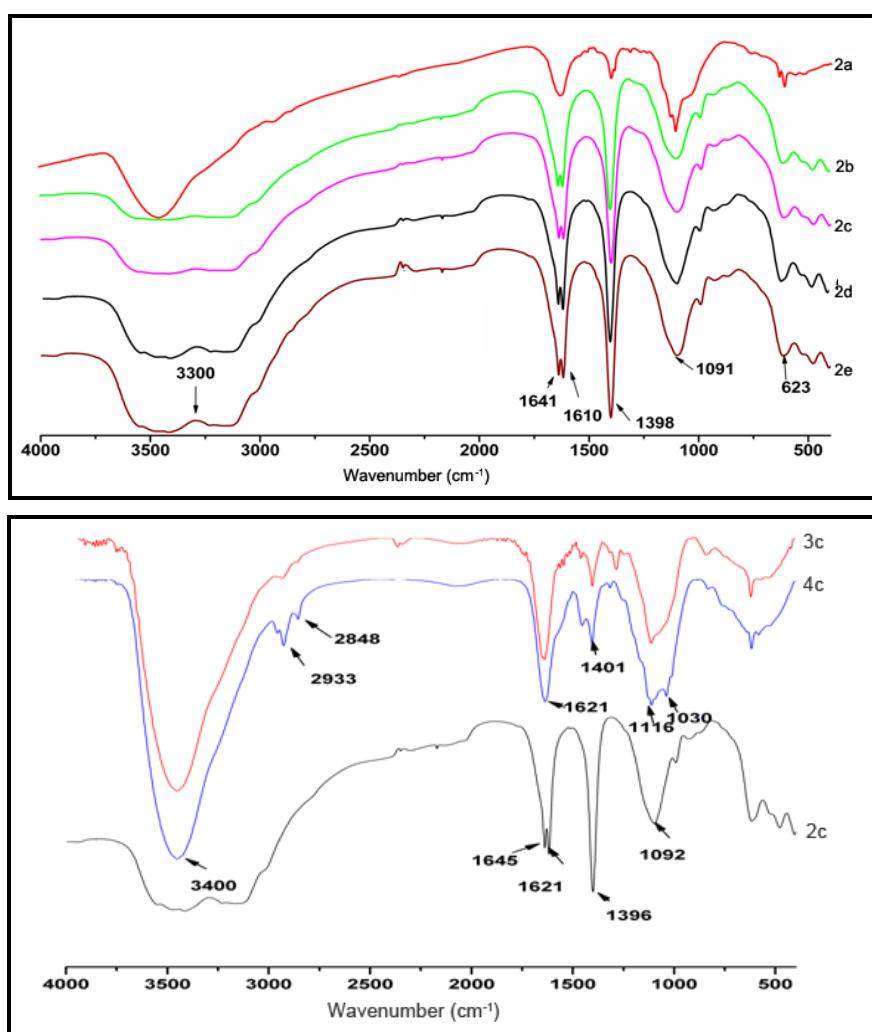


Fig.S2

5. XRD spectra

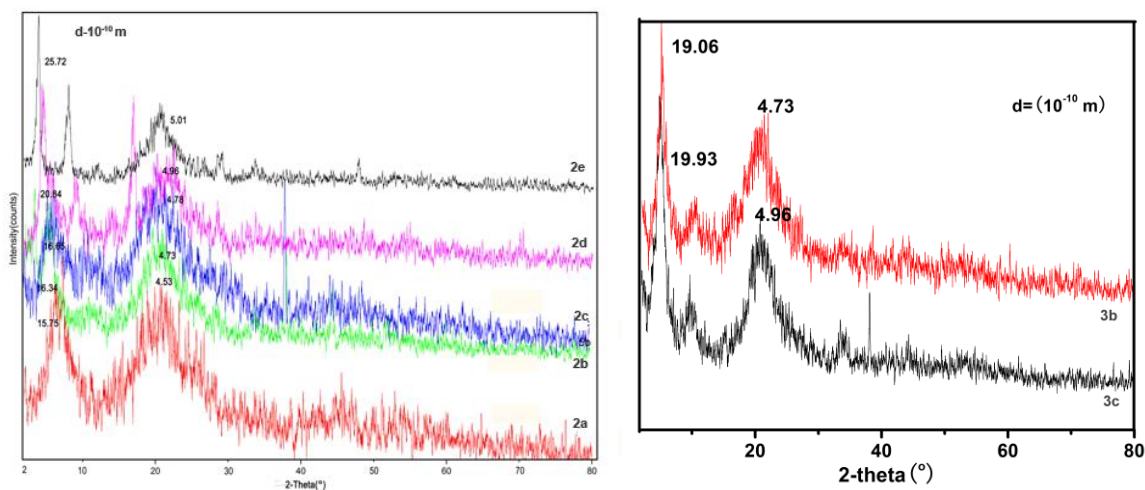
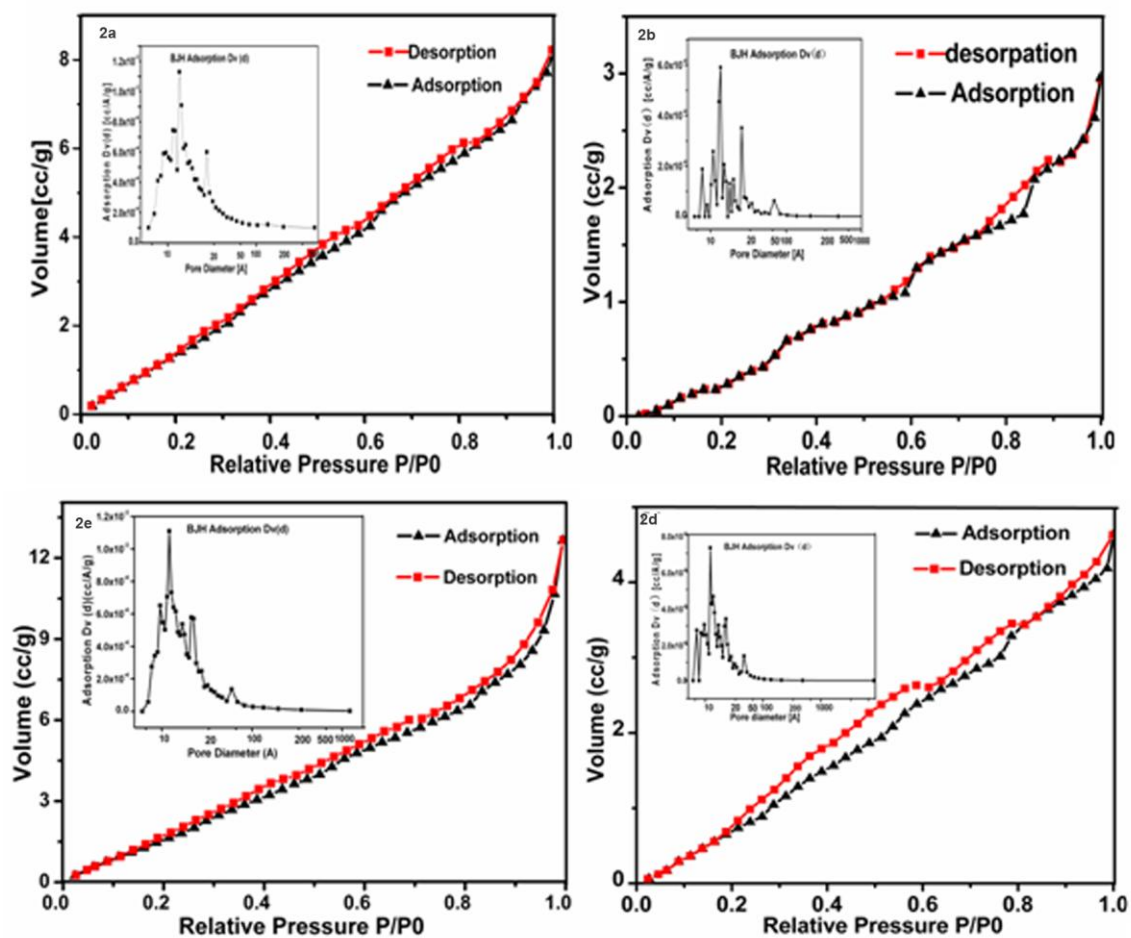


Fig.S3 The powder XRD patterns of zirconium phosphonates 2a-e and 3b, c

6. Nitrogen adsorption–adsorption isotherms



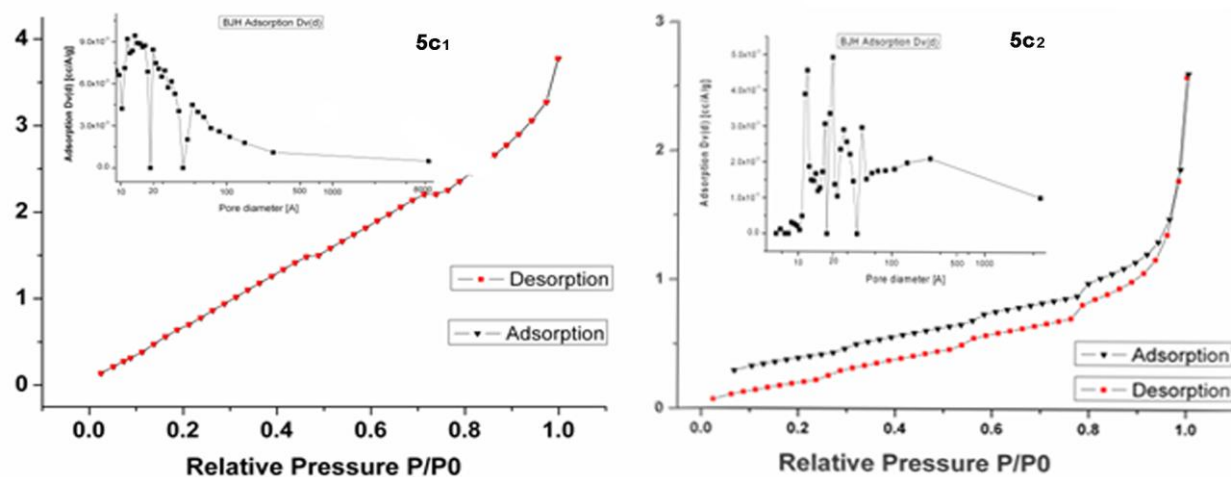
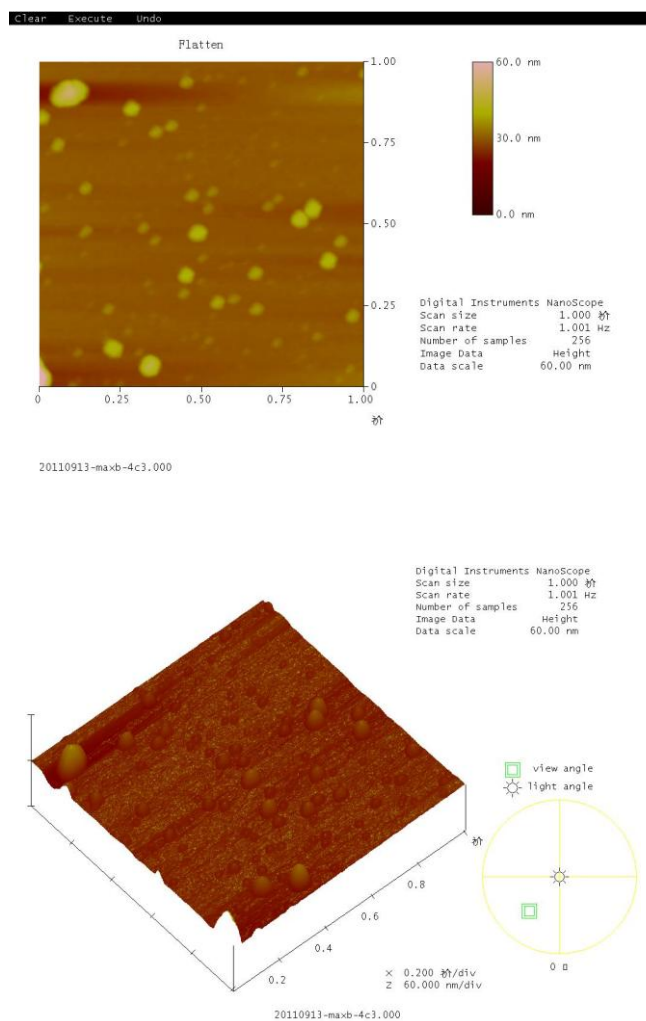


Fig.S4 Nitrogen adsorption–desorption isotherm plots

7.AFM images

(1) Zirconium phosphonate 3c



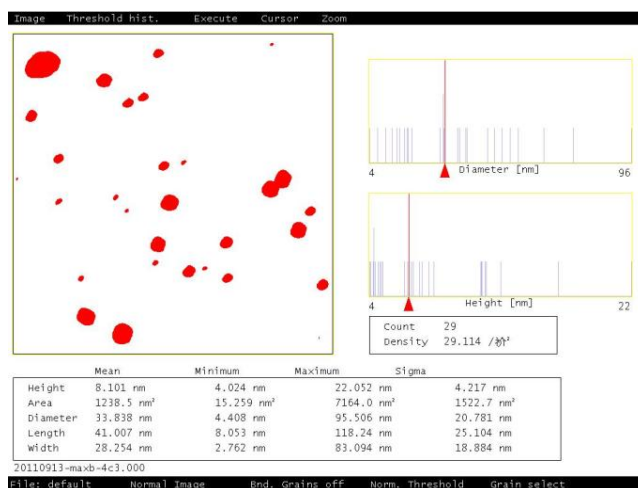
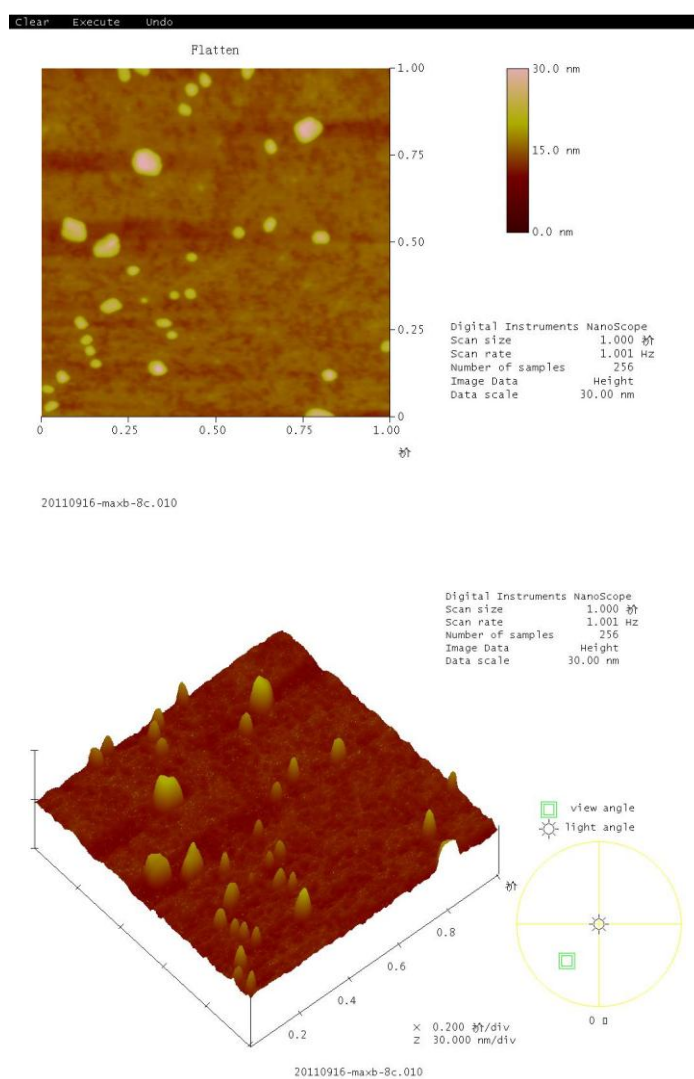


Fig.S 5 AFM images of zirconium phosphonate **3c**

(2) Zirconium phosphonate **4c**



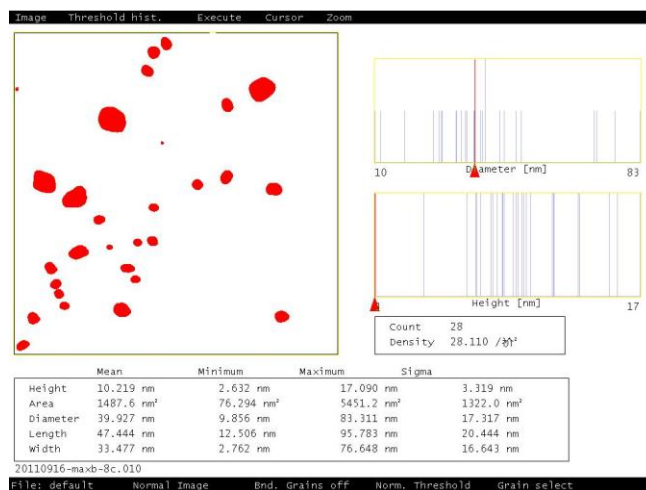
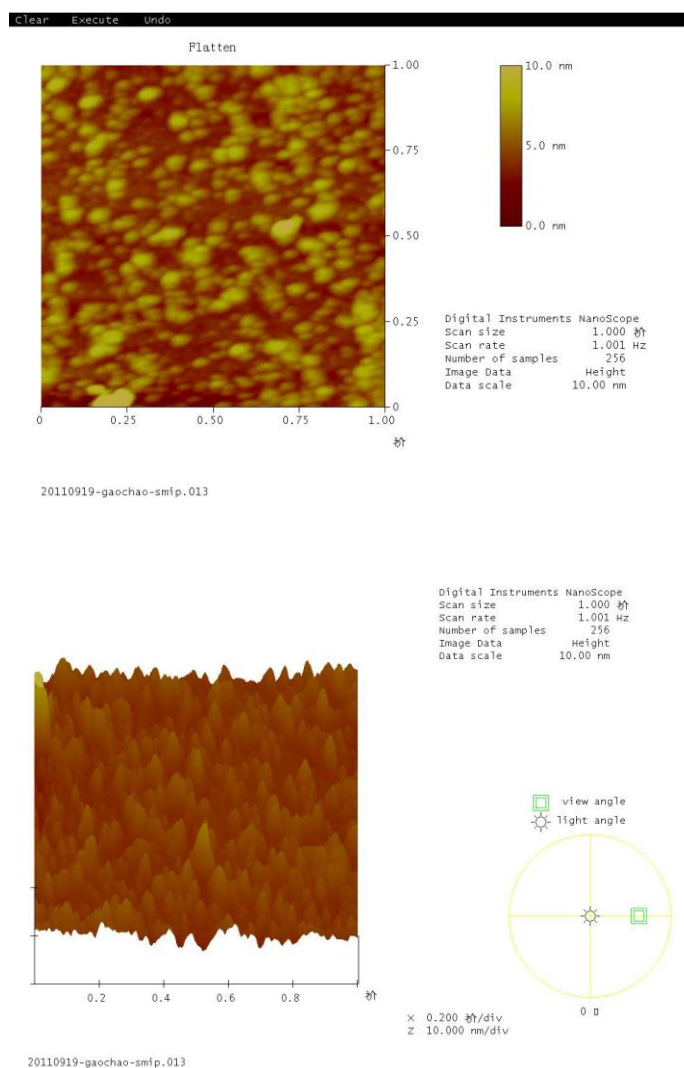


Fig.S6 AFM images of zirconium phosphonate **4c**

(3) Zirconium phosphonate **5c₁**



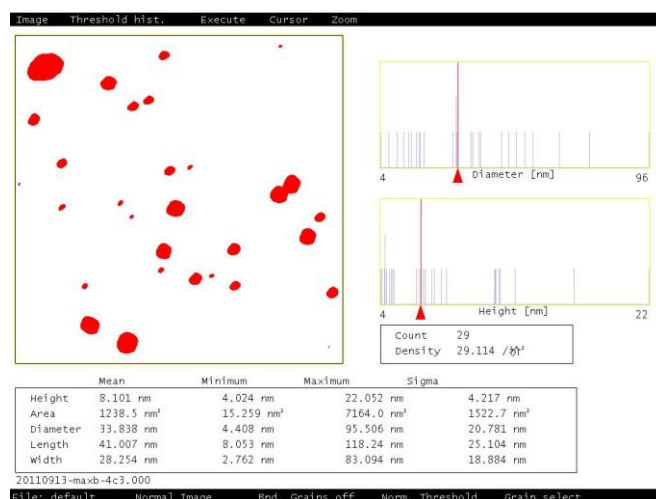


Fig.S7 AFM images of zirconium phosphonate **5c₁**

8. Influence of other factors on the catalytic properties

(1) The acidic additives

Table S1.

The direct asymmetric aldol reaction of 4-nitrobenzaldehyde and cyclohexanone in water^a

Entry	additive	Yield (%) ^b	ee(anti) ^c	ee (%) (syn) ^c	dr(anti/syn)
1	<i>P</i> -TsOH	45	9	17	56/44
2	HOAc	71	78	47	65/35
3	HCl	90	90	7	77/23
4	4-NO ₂ PhCOOH	94	90	2	79/21
5	TFA	64	85	29	73/27
6	(<i>S</i>)-NCM	47	69	23	63/37
7	PhCOOH	76	92	44	84/16
8	(<i>S</i>)-NCM ^d	18	47	15	58/42
9	TfOH	98	96	25	80/20

^a Reaction conditions: 4-nitrobenzaldehyde (0.25 mmol), cyclohexanone (0.39 mmol), catalyst **3c** (0.025 mmol, 10 mol%), 25 °C, 96 h, 1 mL of water, acidic additive (3.75×10⁻³ mmol).

^b Isolated yield.

^c Determined by chiral HPLC.

^d With out catalyst **3c**, NCM=1,1'-bi-2-naphthol cyclic monophosphate.

(2) Solvents

Table S2.

The direct asymmetric aldol reaction of 4-nitrobenzaldehyde and cyclohexanone in water^a

Entry	Solvent	Yield (%) ^b	ee(anti) ^c	ee (%) (syn) ^c	dr(anti/syn)
1	H ₂ O	96	96	27	85/15
2	THF	19	48	9	38/62
3	DMF	15	31	8	43/57
4	C ₂ H ₅ OH	11	83	5	60/40
5	C ₆ H ₅ CH ₃	59	5	15	34/66
6	CH ₃ CN	26	15	0	37/63

7	DMSO	21	9	7	31/69
8	CHCl ₃	29	75	64	72/28

^a Reaction conditions: 4-nitrobenzaldehyde (0.25 mmol), cyclohexanone (0.39 mmol), catalyst **3c** (0.025 mmol, 10 mol%), 25 °C, 96 h, 1 mL of solvent, acidic additive (3.75×10⁻³ mmol).

^b Isolated yield.

^c Determined by chiral HPLC.

(3) Temperature, used amount of water and zirconium phosphonate

Table S3.

The direct asymmetric aldol reaction of 4-nitrobenzaldehyde and cyclohexanone in water ^a

Entry	Catalyst (mol%)	Temp.	Water (mL)	Yield (%) ^b	ee(%) (anti) ^c	ee (%) (syn) ^c	dr(anti/syn)
1	10	10	1	76	97	87	64/36
2	10	20	1	92	96	47	80/20
3	10	25	1	98	96	26	81/19
4	10	30	1	94	95	30	77/23
5	10	40	1	93	90	19	83/17
6	10	25	0.2	81	92	17	86/14
7	10	25	0.5	86	94	13	78/22
8	10	25	1	97	95	14	85/15
9	10	25	2	98	93	-21	74/26
10	10	25	3	91	92	-27	88/12
11	5	25	1	77	91	47	78/22
12	10	25	1	98	96	32	83/17
13	15	25	1	93	93	-38	81/19
14	20	25	1	92	94	-10	77/23
15	30	25	1	90	92	-26	72/28

^a Reaction conditions: 4-nitrobenzaldehyde (0.25 mmol), cyclohexanone (0.39 mmol), catalyst **3c**, 96 h, 1 mL of water, acidic additive (3.75×10⁻³ mmol).

^b Isolated yield.

^c Determined by chiral HPLC.

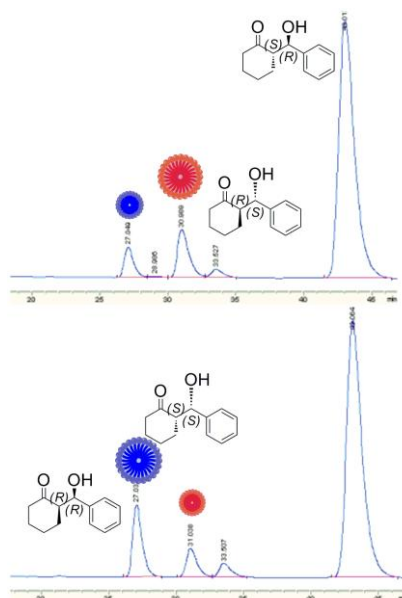
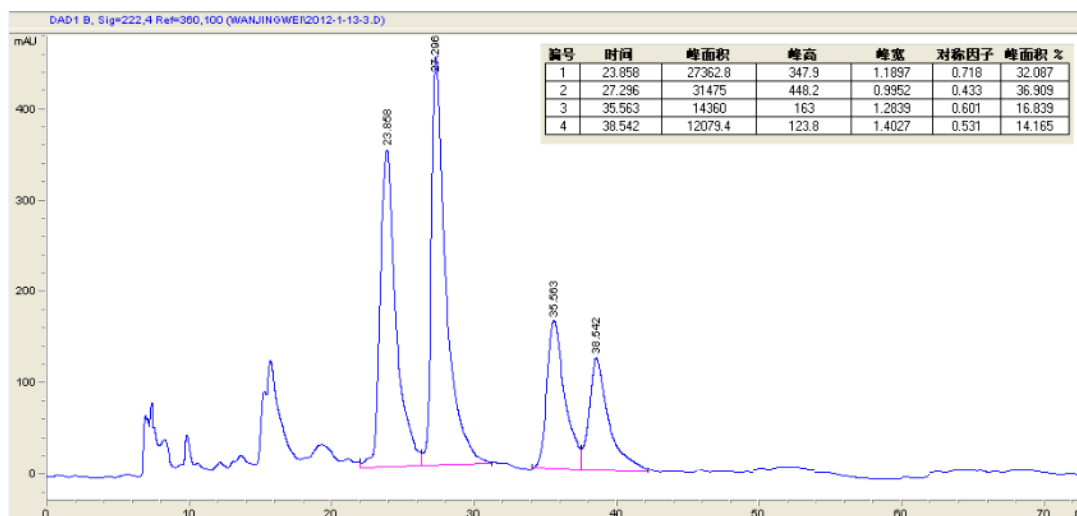


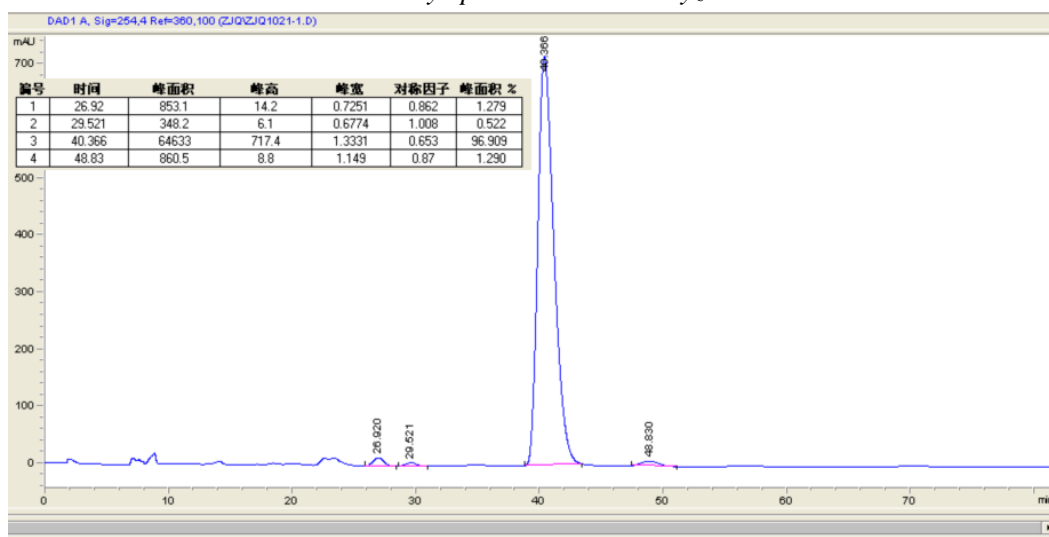
Fig.S8 The influence of used amounts of supported-catalyst **3c** on catalytic performance (5 and 15 mol%)
9. HPLC spectra for some compounds

(1) The aldol adducts of *o*-nitrobenzaldehyde to cyclohexanone

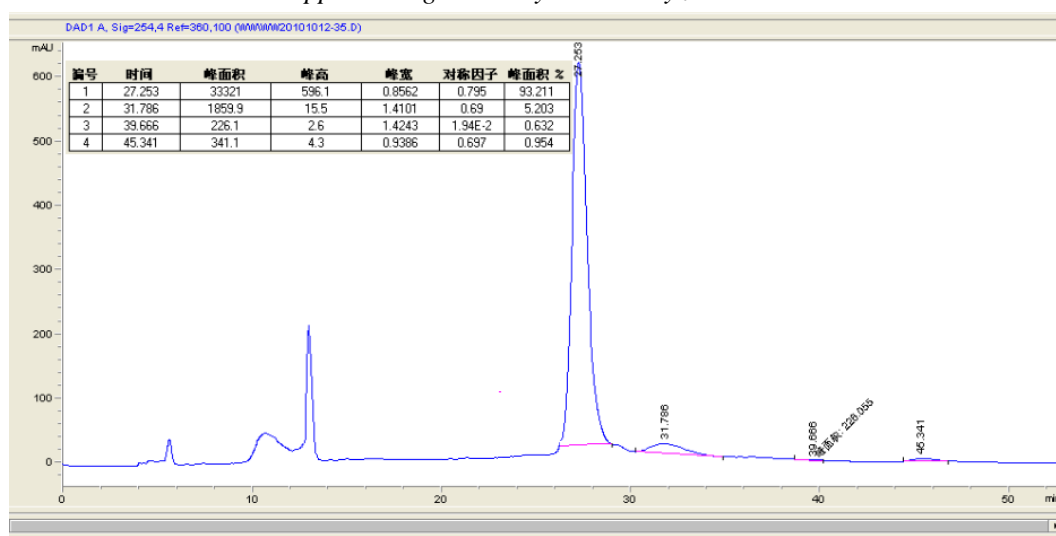
Racemic compounds



9-amino-9-deoxy-epi-cinchonine-catalyzed adducts

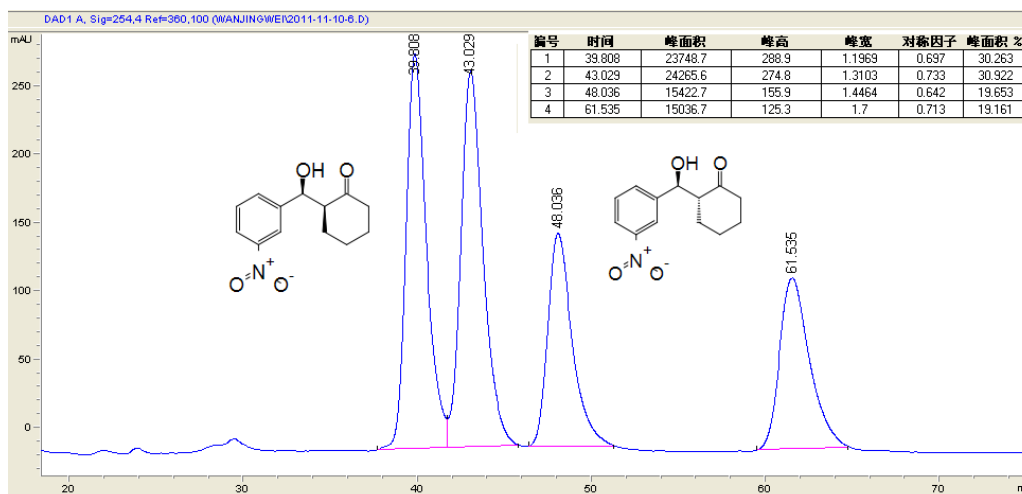


Supported organocatalyst 3c-catalyzed adducts

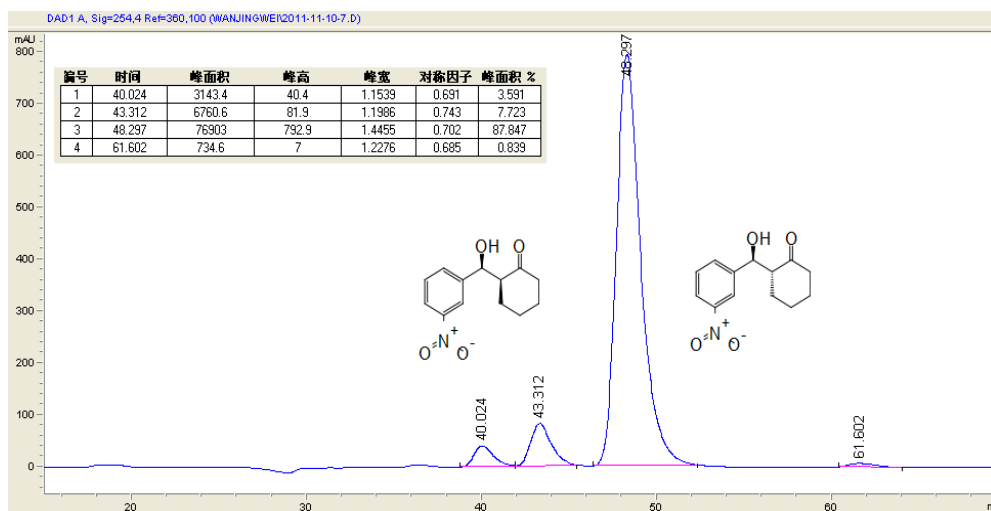


(2) The aldol adducts of *m*-nitrobenzaldehyde to cyclohexanone

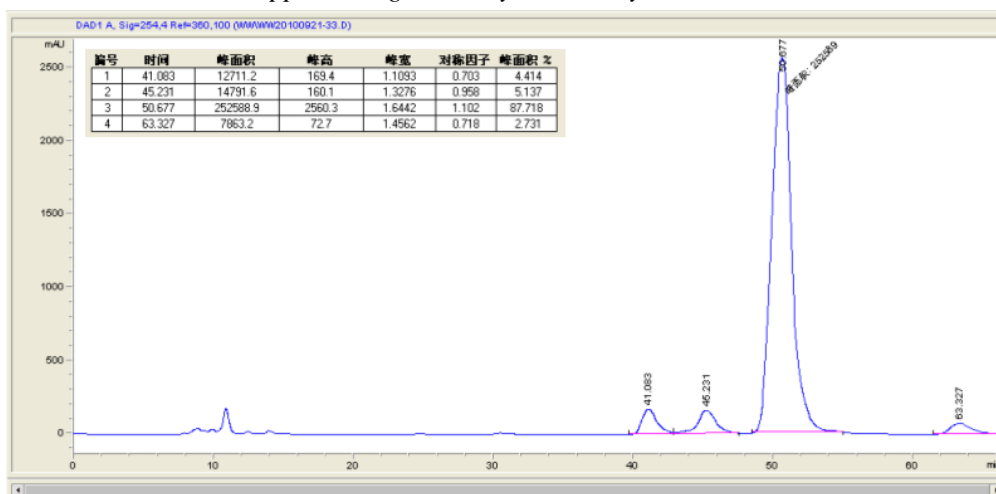
Racemic compounds



9-amino-9-deoxy-*epi*-cinchonine-catalyzed adducts

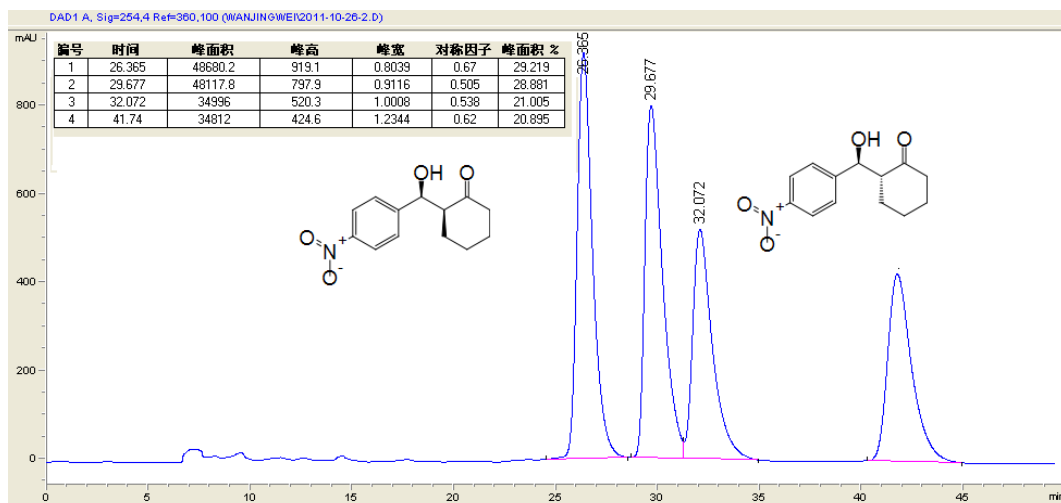


Supported organocatalyst **3c**-catalyzed adducts

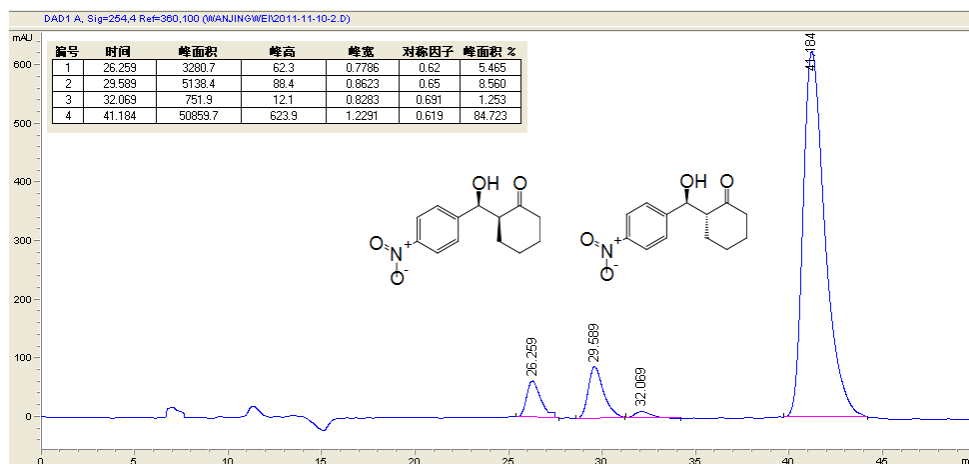


(3) The aldol adducts of *m*-nitrobenzaldehyde to cyclohexanone

Racemic compounds



9-amino-9-deoxy-*epi*-cinchonine-catalyzed adducts



Supported organocatalyst **3c**-catalyzed adducts

