Electronic Supplementary Information

Straightforward synthesis and catalytic applications of rigid N,O-type calixarene ligands

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1. General Information

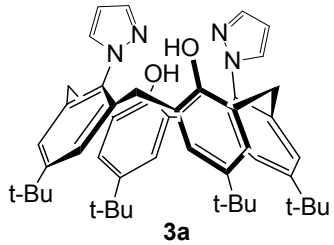
The synthetic manipulations involving air-sensitive compounds were performed in a nitrogen-filled Innovative Technology glove box. All solvents were degassed and stored under high-purity nitrogen and activated 4Å molecular sieves. All deuterated solvents were stored under high-purity nitrogen on 3Å molecular sieves. Commercially available reagents (Aldrich, Strem and Fluka) were used as received. The NMR spectra were recorded on Bruker Avance 400MHz spectrometer. All measurements were performed at 22ºC in C_6D_6 unless stated otherwise. Mass Spectra were recorded on a VG-Autospec M-250 instrument.

2. Experimental Section

2.1. General experimental procedure for amination of 1,3-bis(triflate)-*p-tert*-butylcalix[4]arene (1):

The reaction was carried out under an inert atmosphere of pure nitrogen. To a stirred suspension of copper (I) trifluoromethanesulfonate toluene complex (56 mg, 0.108 mmol), K_3PO_4 (460 mg, 2.16 mmol) and 1,3-bis(triflate)-*p-tert*-butylcalix[4]arene **1** (500 mg, 0.54 mmol) in ^{i}PrOH (15 mL) were added cyclic secondary amines (2.16 mmol) and ethylene glycol (0.09 mL, 1.62 mmol). The reaction mixture was then stirred at 80ºC for 12 h. The solvent was evaporated and the resulting crude product was dissolved in EtOAc (50 mL), washed with water (5 ml x 2), brine and dried over anhydrous $MgSO_4$. Removal of solvent under reduced pressure and column chromatographic purification with $CHCl_3$/Hexane (2:1 v/v) gave pure compounds (**3a-f**) in 46-68% yields.

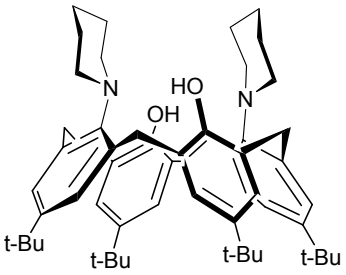
1,3-Bis(pyrazole)-*p-tert*-butylcalix[4]arene (3a):



3a

Yield: 235 mg (58% yield); white solid; **^{1}H NMR** (C_6D_6): 1.06 (s, 18 H, t-Bu), 1.38 (s, 18 H, t-Bu), 3.25 (d, $^2J_{HH}$ = 13.2 Hz, 4 H, CH_2), 4.16 (d, $^2J_{HH}$ = 13.2 Hz, 4 H, CH_2), 6.10 (s, 2 H, Ar-H), 6.97 (s, 4 H, Ar-H), 7.01 (s, 2 H, Ar-H), 7.13 (s, 4 H, Ar-H, merging with solvent residual peak), 7.56 (s, 2H, Ar-H) and 11.47 (br s, 2 H, OH); **^{13}C NMR** (100 MHz, C_6D_6): δ 30.9 (t-Bu), 31.9 (t-Bu), 33.7 (CH_2), 34.1 (C), (all aromatics): 105.3, 125.6, 128.5, 132.8, 134.6, 135.8, 137.0, 139.4, 149.5 and 152.8; **HRMS** (ESI) calcd for $C_{50}H_{60}N_4O_2$ $[M]^+$ 748.4716; found 748.4672.

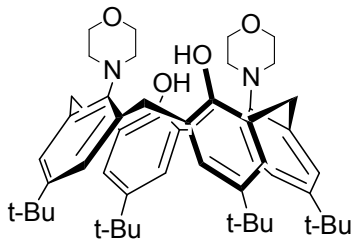
1,3-Bis(piperidine)-*p-tert*-butylcalix[4]arene (3b):



3b

Yield: 288 mg (68% yield); white solid; **^{1}H NMR** (C_6D_6): 1.12 (s, 18 H, t-Bu), 1.40 (s, 22 H, t-Bu, CH_2), 1.50 (m, 8 H, CH_2), 2.85 (m, 4 H, CH_2-N), 3.14 (m, 4 H, CH_2-N), 3.62 (d, $^2J_{HH}$ = 14.5 Hz, 4 H, CH_2), 4.34 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, CH_2), 6.56 (br s, 2 H, OH), 7.06 (s, 4 H, Ar-H) and 7.16 (s, 4 H, Ar-H); **^{13}C NMR** (100 MHz, $CDCl_3$): 24.7 (CH_2), 27.1 (CH_2), 27.5 (CH_2), 31.2 (t-Bu), 31.9 (t-Bu), 33.8 (C), 33.9 (C), 37.1 (CH_2), 53.2 (CH_2-N), 56.6 (CH_2-N), (all aromatics): 125.8, 128.4, 136.8, 140.7, 145.9, 146.4 and 152.6; **HRMS** (ESI) calcd for $C_{54}H_{74}N_2O_2$ $[M]^+$ 782.5750; found 782.5681.

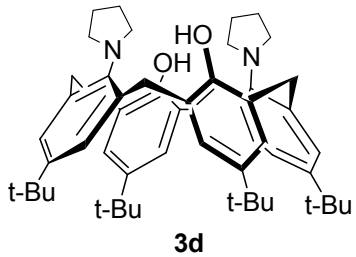
1,3-Bis(morpholine)-*p-tert*-butylcalix[4]arene (3c):



3c

Yield: 242 mg (57% yield); white solid; **^{1}H NMR** ($CDCl_3$): δ 1.03 (s, 18 H, t-Bu), 1.37 (s, 18 H, t-Bu), 2.99 (m, 8 H, CH_2-N), 3.50 (m, 4 H, CH_2-O), 3.64 (d, $^2J_{HH}$ = 14.7 Hz, 4 H, CH_2), 3.81 (m, 4 H, CH_2-O), 4.23 (d, $^2J_{HH}$ = 14.7 Hz, 4 H, CH_2), 6.01 (br s, 2 H, OH), 6.91 (s, 4 H, Ar-H) and 7.10 (s, 4 H, Ar-H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 31.0 (t-Bu), 31.7 (t-Bu), 33.7 (C), 33.9 (C), 36.9 (CH_2), 52.5 (CH_2-N), 54.8 (CH_2-N), 68.0 (CH_2-O), (all aromatics): 125.7, 127.7, 128.0, 136.6, 141.4, 144.4, 146.9 and 151.8; **HRMS** (ESI) calcd for $C_{52}H_{70}N_2O_4$ $[M]^+$ 786.5336; found 786.5307.

1,3-Bis(pyrrolidine)-*p-tert*-butylcalix[4]arene (3d):

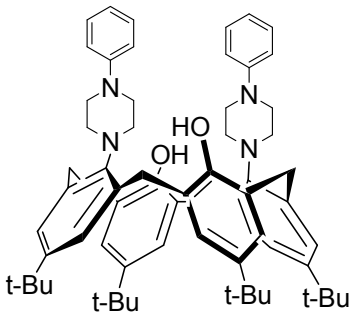


3d

Yield: 216 mg (53% yield), white solid; **^{1}H NMR** (C_6D_6): δ 1.10 (s, 18 H, t-Bu), 1.37 (s, 18 H, t-Bu), 1.66 (m, 8 H, CH_2), 3.11 (m, 8 H, CH_2-N), 3.61 (d, $^2J_{HH}$ = 14.1 Hz, 4 H, CH_2), 4.25 (d, $^2J_{HH}$ = 14.4 Hz, 4 H, CH_2), 6.10 (br s, 2 H, OH), 7.08 (s, 4 H, Ar-H) and 7.14 (s, 4 H, Ar-H); **^{13}C NMR** (100 MHz, C_6D_6): δ 25.3 (CH_2), 31.2 (t-Bu), 31.5 (C), 31.8 (t-Bu), 33.7 (C), 36.7 (CH_2),

53.0 (CH_2-N), (all aromatics): 125.9, 127.2, 128.7, 138.6, 141.1, 142.5, 146.7 and 152.4; **HRMS** (ESI) calcd for $C_{52}H_{70}N_2O_2$ $[M]^+$ 754.5437; found 754.5402.

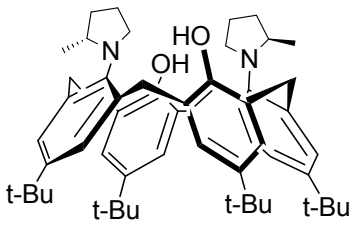
1,3-Bis(1-phenylpiperazine)-*p-tert*-butylcalix[4]arene (3e):



3e

Yield: 253 mg (50% yield); white solid; **^{1}H NMR** (C_6D_6): δ 1.14 (s, 18 H, t-Bu), 1.37 (s, 18 H, t-Bu), 2.9-3.14 (m, 12 H, CH_2-N), 3.39-3.43 (m, 4 H, CH_2-N), 3.65 (d, $^2J_{HH}$ = 14.9 Hz, 4 H, CH_2), 4.36 (d, $^2J_{HH}$ = 14.9 Hz, 4 H, CH_2), 6.32 (br s, 2 H, OH), 6.84-6.91(m, 6H, Ph), 6.91 (s, 4 H, Ar-H), 7.10 (s, 4 H, Ar-H) and 7.18-7.23 (m, 4H, Ph); **^{13}C NMR** (100 MHz, C_6D_6): δ 31.1 (t-Bu), 31.7 (t-Bu), 33.80 (C), 33.85 (C), 37.0 (CH_2), 50.2 (CH_2-N), 53.1 (CH_2-N), (all aromatics): 116.1, 119.7, 125.9, 128.3, 129.2, 136.9, 141.3, 144.9, 146.7. 151.9 and 152.3; **HRMS** (ESI) calcd for $C_{64}H_{80}N_4O_2$ $[M]^+$ 936.6281; found 936.6191.

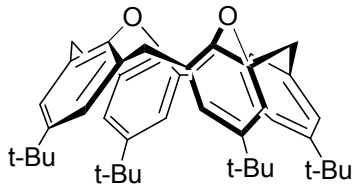
1,3-Bis[(*R*)-2-methylpyrrolidine]-*p-tert*-butylcalix[4]arene (3f):



3f

Yield: 195 mg (46% yield); white solid; $[\alpha]_D$ ^{25} +20.1 (c 1.0, $CHCl_3$); **^{1}H NMR** (C_6D_6): δ 0.83 (d, $^2J_{HH}$ = 5.9 Hz, 6 H, CH_3), 1.12 (s, 18 H, t-Bu), 1.36 (s, 20 H, t-Bu + CH_2), 1.60-1.69 (m, 4 H, CH_2), 1.88-1.90 (m, 2 H, CH_2), 3.03-3.13 (m, 4 H, CH_2-N), 3.41-3.46 (q, $^2J_{HH}$ = 6.0, 12.1 Hz, 2H, CH-N), 3.64 (dd, $^2J_{HH}$ = 7.0, 7.5, 15.3 Hz, 4 H, CH_2), 4.05 (d, $^2J_{HH}$ = 13.9 Hz, 2 H, CH_2), 4.49 (d, $^2J_{HH}$ = 13.9 Hz, 2 H, CH_2), 5.00 (br s, 2 H, OH), 7.10 (s, 4 H, Ar-H) and 7.13 (s, 4 H, Ar-H); **^{13}C NMR** (100 MHz, C_6D_6): δ 20.7 (CH_3), 24.7 (CH_2), 31.2(t-Bu), 31.7 (t-Bu), 33.8 (C), 33.9 (C), 37.1 (CH_2), 37.4 (CH_2), 50.9 (CH_2-N), 59.3 (CH-N), (all aromatics): 125.5, 126.4, 126.5, 127.2, 128.6, 129.5, 140.1, 141.5, 142.2, 142.6, 147.5 and 152.3; **HRMS** (ESI) calcd for $C_{54}H_{74}N_2O_2$ $[M+H]^+$ 783.5829; found 783.5831.

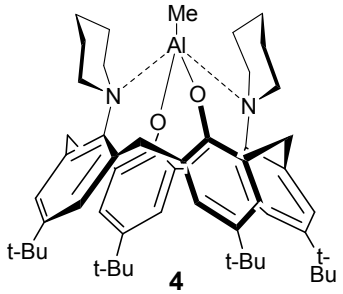
Bis-(xanthene):



white solid; **^{1}H NMR** (C_6D_6): δ 1.29 (s, 36 H, t-Bu), 3.26 (d, $^2J_{HH}$ = 13.6 Hz, 2 H, CH_2), 3.46 (d, $^2J_{HH}$ = 13.6 Hz, 2 H, CH_2), 3.56 (d, $^2J_{HH}$ = 13.6 Hz, 2 H, CH_2), 3.56 (d, $^2J_{HH}$ = 13.6 Hz, 2 H, CH_2), 5.38 (d, $^2J_{HH}$ = 13.6 Hz, 2 H, CH_2), 6.84 (s, 4 H, Ar-H), 7.41 (s, 4 H, Ar-H); **^{13}C NMR** (100 MHz, C_6D_6): δ 29.7 (C), 29.9 (C), 31.5 (t-Bu), 34.1 (CH_2), (all aromatics): 122.2, 123.1, 125.6, 129.1, 145.1 and 148.9; **HRMS** (ESI) calcd for $C_{44}H_{53}O_2$ $[M]^+$ 612.3967; found 612.3964.

2.2. Synthesis of metal complexes

Al-complex of 1,3-Bis(piperidine)-*p-tert*-butylcalix[4]arene (4):

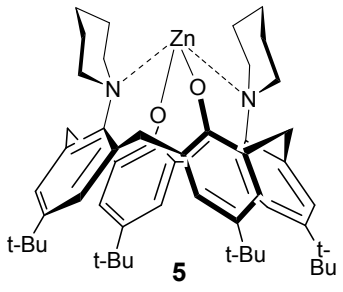


4

1,3-Bis(piperidine)-*p*-*tert*-butylcalix[4]arene **3b** (20 mg, ~0.026 mmol) was dissolved in about 4ml of dry toluene and $AlMe_3$ (5 µL, 0.052 mmol) was added. The resulting mixture was stirred for 12 h at 110 °C followed by solvent evaporation to give the crude product. After precipitation from pentane (2 ml of pentane), pure complex was obtained in 73%.

Yield: 16 mg (73 % yield); white solid; **^{1}H NMR** (C_6D_6): δ -0.18 (s, 3 H, CH_3), 0.99 (s, 18 H, t-Bu), 1.19-1.21 (m, 8 H, CH_2), 1.44 (s, 24 H, t-Bu + CH_2), 3.51 (m, 8 H, CH_2-N), 3.59 (d, $^2J_{HH}$ = 13.6 Hz, 4 H, CH_2), 4.56 (d, $^2J_{HH}$ = 13.6 Hz, 4 H, -CH_2), 6.82 (s, 4 H, Ar-H) and 7.22 (s, 4 H, Ar-H); **^{13}C NMR** (100 MHz, C_6D_6): δ 24.4 (CH_2), 25.3 (CH_2), 31.1 (t-Bu), 31.8 (t-Bu), 33.5 (C), 33.7 (C), 39.1(CH_2), 55.6 (CH_2) (all aromatics): 125.9, 131.6, 134.5, 139.4, 145.3, and 153.2; **HRMS** (ESI) calcd for $C_{55}H_{75}AlN_2O_2$ $[M+H]^+$ 823.5722; found 823.5726.

Zn-complex of 1,3-Bis(piperidine)-*p*-*tert*-butylcalix[4]arene (5):



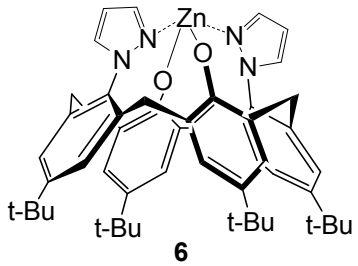
5

1,3-Bis(piperidine)-*p*-*tert*-butylcalix[4]arene **3b** (20 mg, ~0.026 mmol) was dissolved in about 4ml of dry toluene and 0.05 mL of $Zn(HMDS)_2$ (0.13 mmol) was added. The resulting mixture

was stirred at 110 °C for 12 h and the solvent was evaporated giving the crude product. After precipitation from pentane (2ml), pure product was obtained.

Yield: 17 mg (77 % yield); white solid; **^{1}H NMR** (C_6D_6): δ 0.91 (s, 18 H, t-Bu), 1.16-1.28 (m, 5H), 1.38 (s, 20 H, t-Bu + -CH_2), 1.47-1.52 (m, 6H), 1.47-1.52 (m, 8H), 3.36 (d, $^{2}J_{HH}$ = 12.9 Hz, 4 H, -CH_2), 4.84 (d, $^{2}J_{HH}$ = 12.7 Hz, 4 H, -CH_2), 6.93 (s, 4 H, Ar-H), 7.25 (s, 4 H, Ar-H); **^{13}C NMR** (100 MHz, C_6D_6): 25.0 (CH_2), 27.9 (CH_2), 30.6 (t-Bu), 31.2 (C), 31.8 (C), 32.0 (t-Bu), 33.7 (CH_2), 33.9 (CH_2), 34.2 (CH_2-N), 35.1 (CH_2-N), (all aromatics): 125.4, 125.8, 126.5, 127.7, 128.3, 128.4, 129.1, 131.7, 136.7, 138.9, 139.6, 145.9, 148.8, 152.6 and 161.4; **HRMS** (ESI) calcd for $C_{54}H_{72}N_2O_2Zn$ $[M+H]^+$ 845.4963; found 845.4941.

Zn-complex of 1,3-Bis(pyrazole)-*p-tert*-butylcalix[4]arene (6):



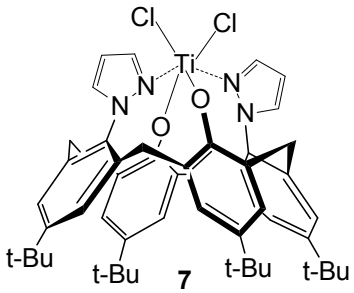
6

1,3-Bis(pyrazole)-*p-tert*-butylcalix[4]arene **3a** (20 mg, 0.026 mmol) was dissolved in about 4ml of dry toluene and 0.05 mL of $Zn(HMDS)_2$ (0.13 mmol) was added. The resulting mixture was stirred at 110 °C for 12 h after which the solvent was evaporated giving the crude product. After precipitation from pentane (2ml), 19 mg of pure product was obtained.

Yield: 19 mg (90% yield) from $Zn(HMDS)_2$; white solid; **^{1}H NMR** (C_6D_6): δ 1.09 (s, 18 H, t-Bu), 1.43 (s, 18 H, t-Bu), 3.37 (d, $^{2}J_{HH}$ = 13.6 Hz, 4 H, CH_2), 3.49 (d, $^{2}J_{HH}$ = 13.6 Hz, 4 H, CH_2), 5.83 (s, 2 H, Ar-H), 6.75 (s, 2 H, Ar-H), 7.09 (s, 2 H, Ar-H), 7.18 (s, 4H, Ar-H) and 7.26 (d, 4 H, Ar-H); **^{13}C NMR** (100 MHz, C_6D_6): δ 31.1 (t-Bu), 32.2 (t-Bu), 33.8 (C), 34.3 (CH_2), (all

aromatics): 105.8, 124.7, 125.3, 127.2, 128.5, 129.1, 130.1, 132.6, 134.9, 135.3, 137.9, 140.9, 152.1 and 161.9; **HRMS** (ESI) calcd for $C_{50}H_{58}N_4O_2Zn$ $[M+H]^+$ 811.3929; found 811.3935.

Ti-complex of 1,3-Bis(pyrazole)-*p-tert*-butylcalix[4]arene (7):



7

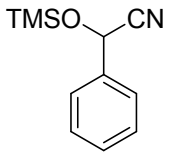
1,3-Bis(pyrazole)-*p-tert*-butylcalix[4]arene **3a** (20 mg, 0.026 mmol) and DIPEA (7 mg, 0.0546 mmol) was dissolved in about 4ml of dry toluene and 30 µL of a $TiCl_4$ solution in toluene (1.0 M, 0.030 mmol) was added. The resulting red mixture was heated at 110 °C for 12 h, after which the reaction mixture was cooled to room temperature followed by solvent evaporation giving the crude product. After precipitation from pentane (2ml), 17 mg of pure product **7** was obtained.

Yield: 17 mg (75 % yield); red solid; **^{1}H NMR** (C_6D_6): δ 1.00 (s, 18 H, t-Bu), 1.29 (s, 18 H, t-Bu), 2.99 (d, $^2J_{HH}$ = 14.2 Hz, 4 H, CH_2), 3.53 (d, $^2J_{HH}$ = 13.7 Hz, 4 H, CH_2), 5.93 (t, $^2J_{HH}$ = 2.4 Hz, 2 H, Ar-H), 6.43 (d, $^2J_{HH}$ = 2.2 Hz, 2 H, Ar-H), 6.74 (s, 4 H, Ar-H), 6.94 (s, 4H, Ar-H) and 9.53 (d, $^2J_{HH}$ = 2.5 Hz, 2 H, Ar-H); **^{13}C NMR** (100 MHz, C_6D_6): δ 30.7 (t-Bu), 31.2 (t-Bu), 33.7 (C), 34.1 (CH_2), (all aromatics): 106.3, 123.5, 126.3, 128.9, 131.5, 132.8, 134.7, 139.4, 142.6, 148.4, and 152.4; **HRMS** (ESI) calcd for $C_{50}H_{58}Cl_2N_4O_2Ti$ $[M-Cl]^+$ 829.3728; found 829.3732.

2.3. General experimental procedure for cyanosilylation of benzaldehyde:

In a vial, 1 mol% of complex **7** (21.6 mg) was dissolved in 4 ml of CH_2Cl_2 under nitrogen and benzaldehyde (266 mg, 2.5 mmol) and trimethylsilylcyanide (274 mg, 2.8 mmol) were added

with syringe via rubber septum. The solution was stirred for 4 hours and the solvent evaporated. To the crude product, about 2ml of methanol were added to remove the catalyst. The combined solvent was evaporated giving the product.



^{1}H NMR ($CDCl_3$): δ 0.24 (s, 9 H, CH_3), 5.50 (s, 1 H, CH), 7.39-7.49 (m, 5 H, Ar-H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ -0.1 (CH_3), 63.8 (CH_2), (all aromatics): 126.6, 129.3, 129.7.

General procedure for competitive cyanosilylation of benzaldehyde:

In a vial, 1 mol% catalyst (26.2 mg of **2-Ti** or 21.6 mg of complex **7**) dissolved in 4 ml of CD_2Cl_2 under nitrogen and benzaldehyde (266 mg, 2.5 mmol) and trimethylsilylcyanide (274 mg, 2.8 mmol) were added with syringe via rubber septum. To compare the catalysts, the reaction progress was monitored by ^{1}H NMR spectroscopy of small aliquots which were periodically withdrawn from solution and analyzed immediately (Table S1).

Table S1: Ti(IV)-catalyzed cyanosilylation of benzaldehyde

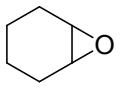
Entry	Catalyst	Time (hour)	conversion (%)[b]
1	Cl_2Ti-1,3-	1	28
	bis(triazole)calixarene	2	44
	(**2-Ti**)	3	53
		4	68
2	Cl_2Ti-1,3-	1	71
	bis(pyrazole)calixarene (**7**)	2	91

		3	99
		4	100
3	Bis pyrazole	1	nr[c]

Reaction conditions: [a] benzaldehyde (2.5 mmol), catalyst (1 mol%), TMSCN (2.8 mmol), CD_2Cl_2 (4 mL), 25 C; [b]Calculated by ^{1}H-NMR as the number of moles of product cyanohydrin per mole of benzaldehyde × 100.; [c] nr = no reaction. See **Figure S13**.

2.4. General experimental procedure for the epoxidation of cyclohexene:

To a stirred suspension of powdered 4 Å molecular sieves (100 mg) in dry CH_2Cl_2 (5 mL), cyclohexene (164 mg, 2 mmol), Cl_2Ti-complex **7** (17.4 g, 1 mol %), *tert*-butyl hydroperoxide 5-6 molar solution in decane (1.1 mL, 6 mmol) was added under nitrogen atmosphere. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with 1M NaOH (1 mL) with further stirring for 1 h at 0 ºC. The organic layer was then separated, washed with brine solution, dried over anhyd. Na_2SO_4 and concentrated under reduced pressure to get the product as slightly yellow liquid.



^{1}H NMR ($CDCl_3$): δ 1.18-1.20 (m, 2 H, CH_2), 1.39-1.42 (m, 2H, CH_2), 1.78-1.82 (m, 2 H, CH_2), 1.91-1.96 (m, 2 H, CH_2), 3.12 (s, 2 H, CH); **^{13}C NMR** (100 MHz, $CDCl_3$): δ 19.5 (CH_2), 24.5 (CH_2), 52.2 (CH).

General procedure for competitive epoxidation of cyclohexene:

To a stirred suspension of powdered 4 Å molecular sieves (100 mg) in dry CD_2Cl_2 (5 mL), cyclohexene (164 mg, 2 mmol), 1 mol % catalyst [16 mg of Cl_2Ti-dimethoxy calixarene **8**, 21 mg of Cl_2Ti-bis(triazole) calixarene (**2-Ti**) or 17.4 mg of complex **7**], *tert*-butyl hydroperoxide 5-

6 molar solution in decane (1.1 mL, 6 mmol) was added under nitrogen atmosphere. To compare the catalysts, the reaction progress was monitored by ^{1}H NMR spectroscopy of small aliquots which were periodically withdrawn from solution and analyzed immediately (Table S2).

Table S2: Ti(IV)-catalyzed epoxidation of cyclohexene[a]

Entry	Catalyst	Time (hour)	Conversion (%)[b]
1	Cl_2Ti-1,3-dimethoxycalixarene (**8**)	1	1
		3	8
		5	20
		7	27
2	Cl_2Ti-1,3-bis(triazole)calixarene (**2-Ti**)	1	4
		3	17
		5	38
		7	45
4	Cl_2Ti-1,3-bis(pyrazole)calixarene (**7**)	1	21
		3	50
		5	71
		7	98

Reaction conditions: [a] Cyclohexene (2 mmol), TBHP (3 equiv., 5.5 M in decane), Catalyst (1 mol%), 4 A MS (100 mg), CD_2Cl_2 (5 ml), RT; [b] Calculated by ^{1}H NMR as the number of moles of product Cyclohexene oxide per mole of cyclohexene × 100. See **Figure S16**.

2.5. Polymerization of 1-hexene:

Preparation of poly-1-hexene with 7 activated by $B(C_6F_5)_3$.

$B(C_6F_5)_3$ (1.3 – 1.6 equiv) was dissolved in 1 mL of 1-hexene and added to a stirred solution of a complex **7** (7 mg, 10 μmol) in 4 mL 1-hexene. The resulting mixture was stirred for 24 h. The remaining olefin was removed under vacuum yielding poly-1-hexene as an yellow gum.

Preparation of poly(1-hexene) with 7 activated by MAO.

Dichlorotitanium complex **7** (7 mg, 10 μmol) was dissolved in 1 mL of 1-hexene and added to a stirred solution of MAO (500 equiv) in 4 mL 1-hexene. The resulting mixture was stirred until the resulting polymer solution had become viscous (12 hrs). The polymer was treated with acidified methanol solution (5% HCl solution) and extracted with chloroform. The organic solvent was removed under vacuum yielding poly-1-hexene as a yellow gum.

2.6. Polymerization of styrene:

Neat polymerization:

In typical polymerizations, the complex **7** (7 mg, 10 μmol) was dissolved in 1 mL of styrene and added to a stirred solution of MAO (500 equiv) in 1 mL styrene. The resulting mixture was stirred for 3 hours, during which the solution became viscous. The polymer was treated with acidified methanol solution (5 % HCl solution). The insoluble polymer was obtained by filtration and was dried in air.

Toluene polymerization:

In typical polymerizations, the complex **7** (7 mg, 10 μmol) was dissolved in 10 mL of toluene and added to a stirred solution of MAO (500 equiv), 2 mL styrene in 10 mL of toluene. The resulting mixture was stirred for 12 hours and stopped by adding acidified methanol solution (5 % HCl solution). The insoluble polymer was filtered and dried in air.

3. Spectra

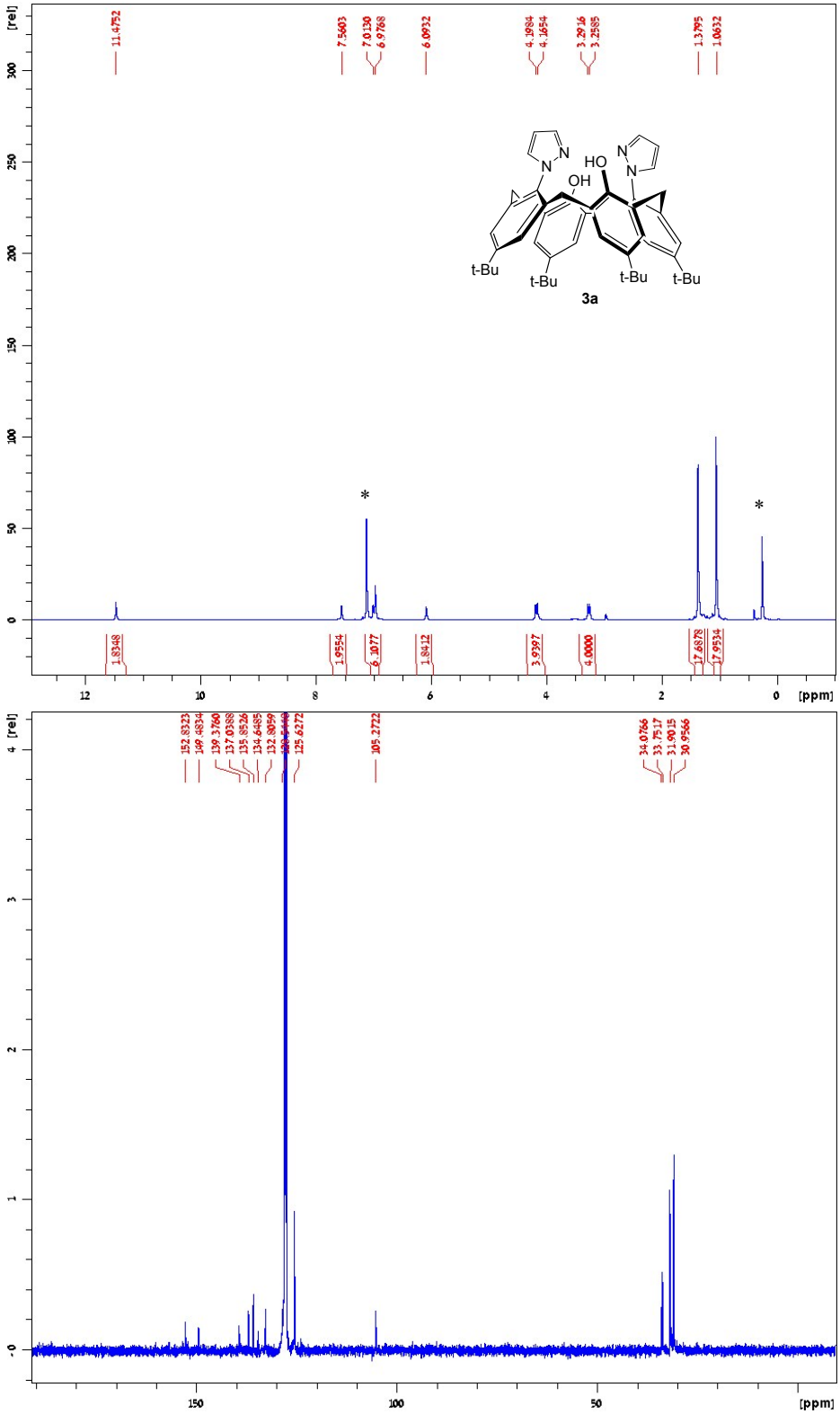


Figure S1: ^{1}H and ^{13}C NMR spectra of 1,3-Bis(pyrazole)-*p*-*tert*-butylcalix[4]arene **3a** in C_6D_6. * indicate peaks due to residual protons and silicone grease.

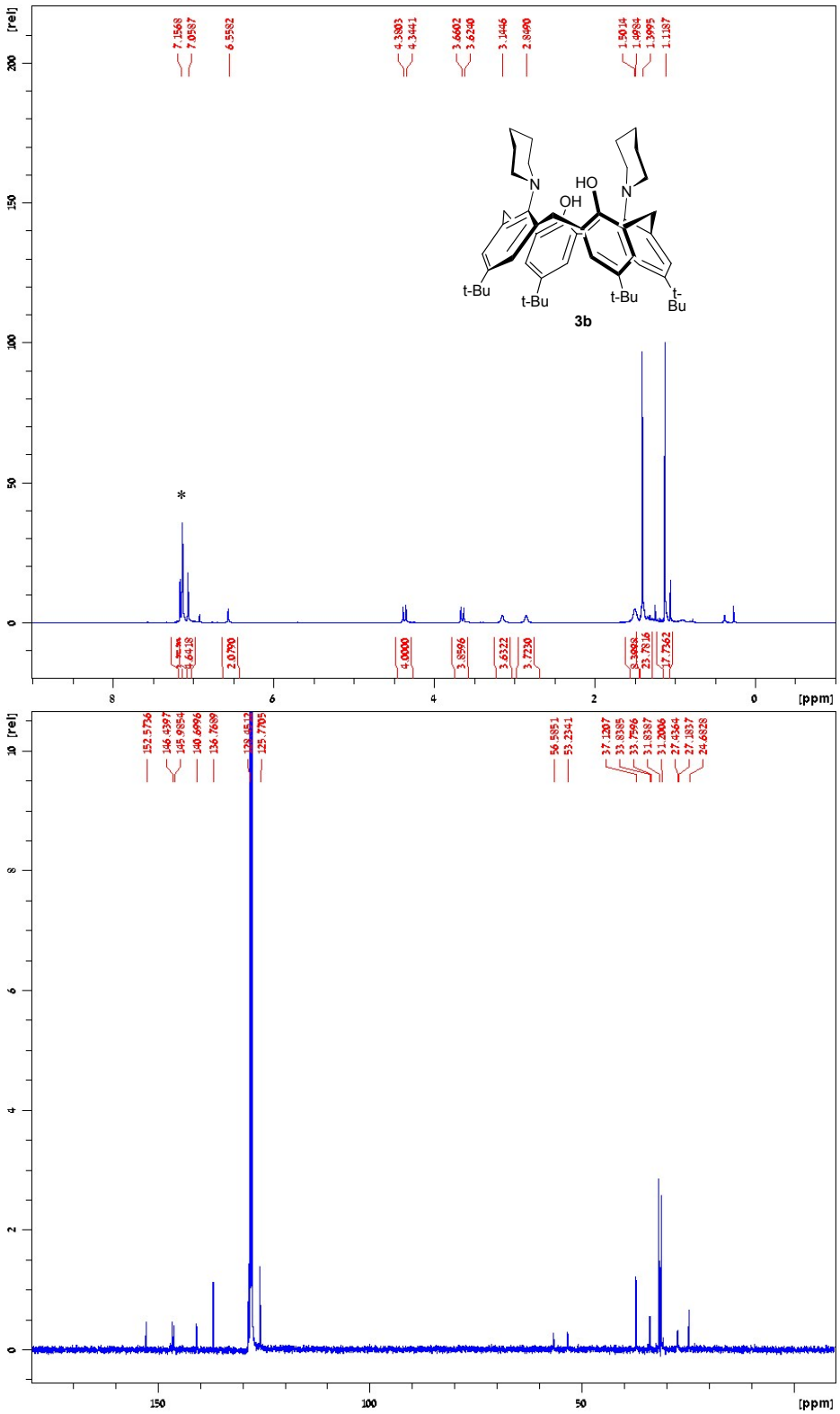


Figure S2: ^{1}H and ^{13}C NMR spectra of 1,3-Bis(piperidine)-*p*-*tert*-butylcalix[4]arene **3b** in C_6D_6. * indicate peak due to residual protons.

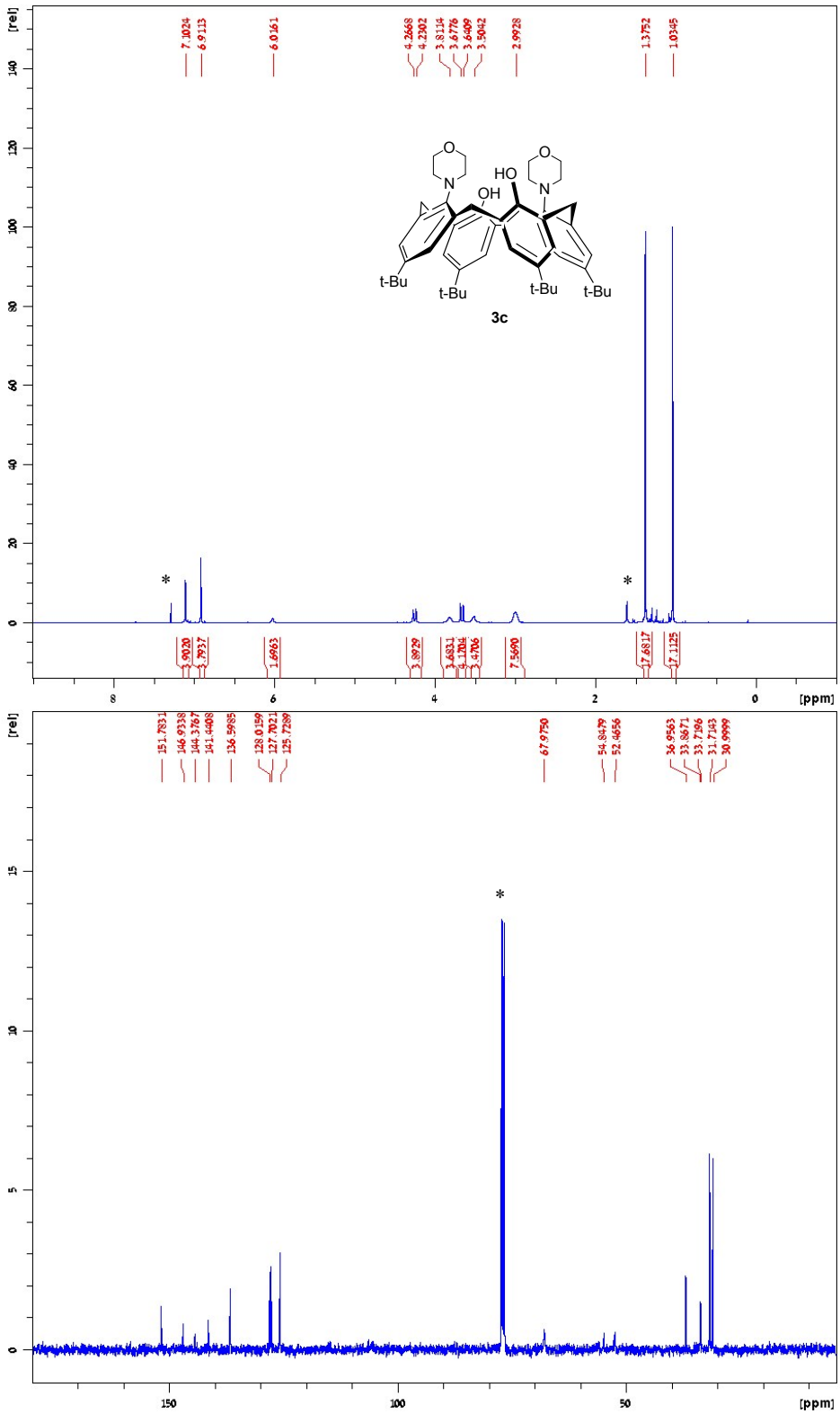


Figure S3: ^{1}H and ^{13}C NMR spectra of 1,3-Bis(morpholine)-*p-tert*-butylcalix[4]arene **3c** in $CDCl_3$. * indicate peaks due to residual protons and H_2O.

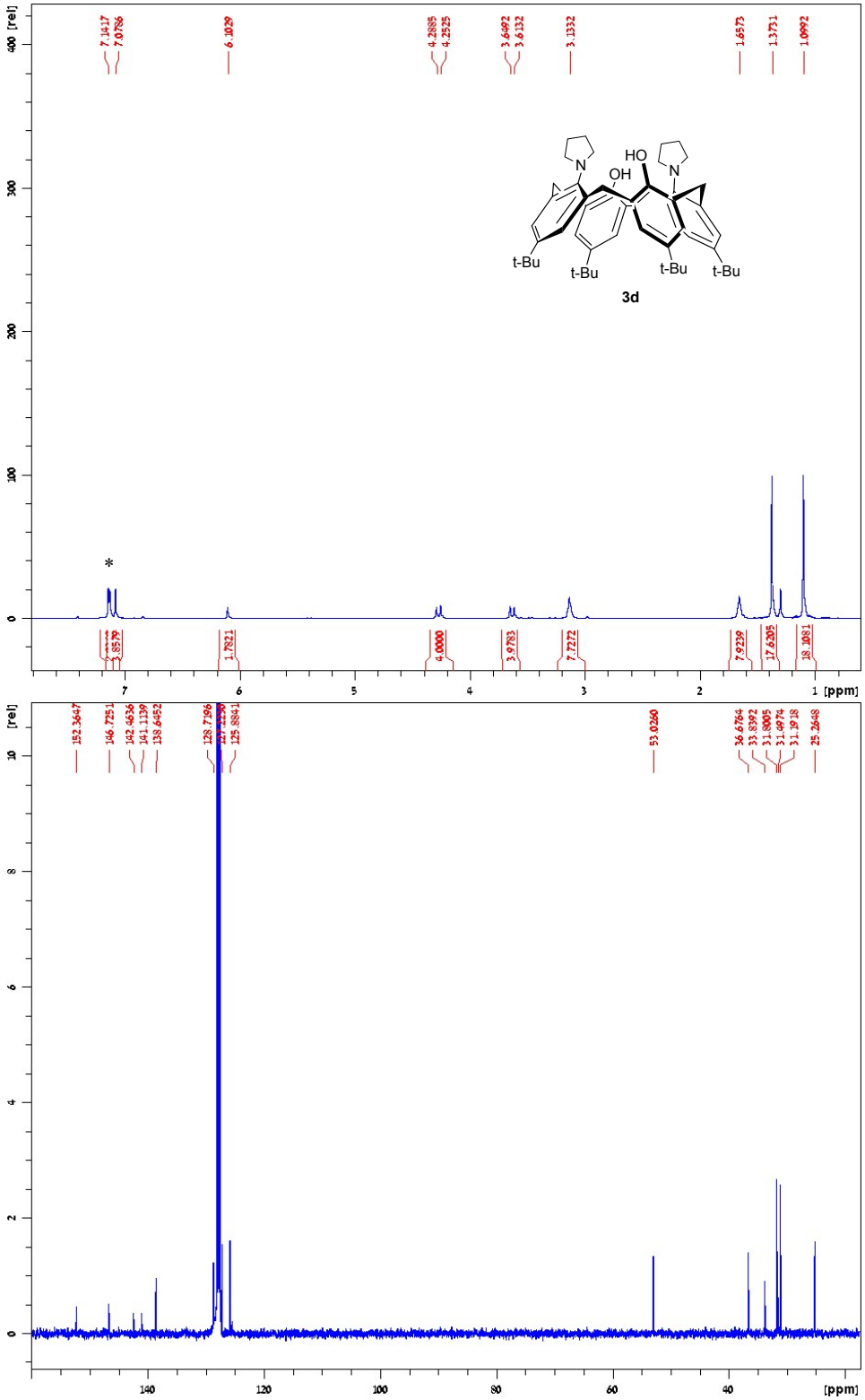


Figure S4: ^{1}H and ^{13}C NMR spectra of 1,3-Bis(pyrrolidine)-*p*-*tert*-butylcalix[4]arene **3d** in C_6D_6. * indicate peaks due to residual protons and grease.

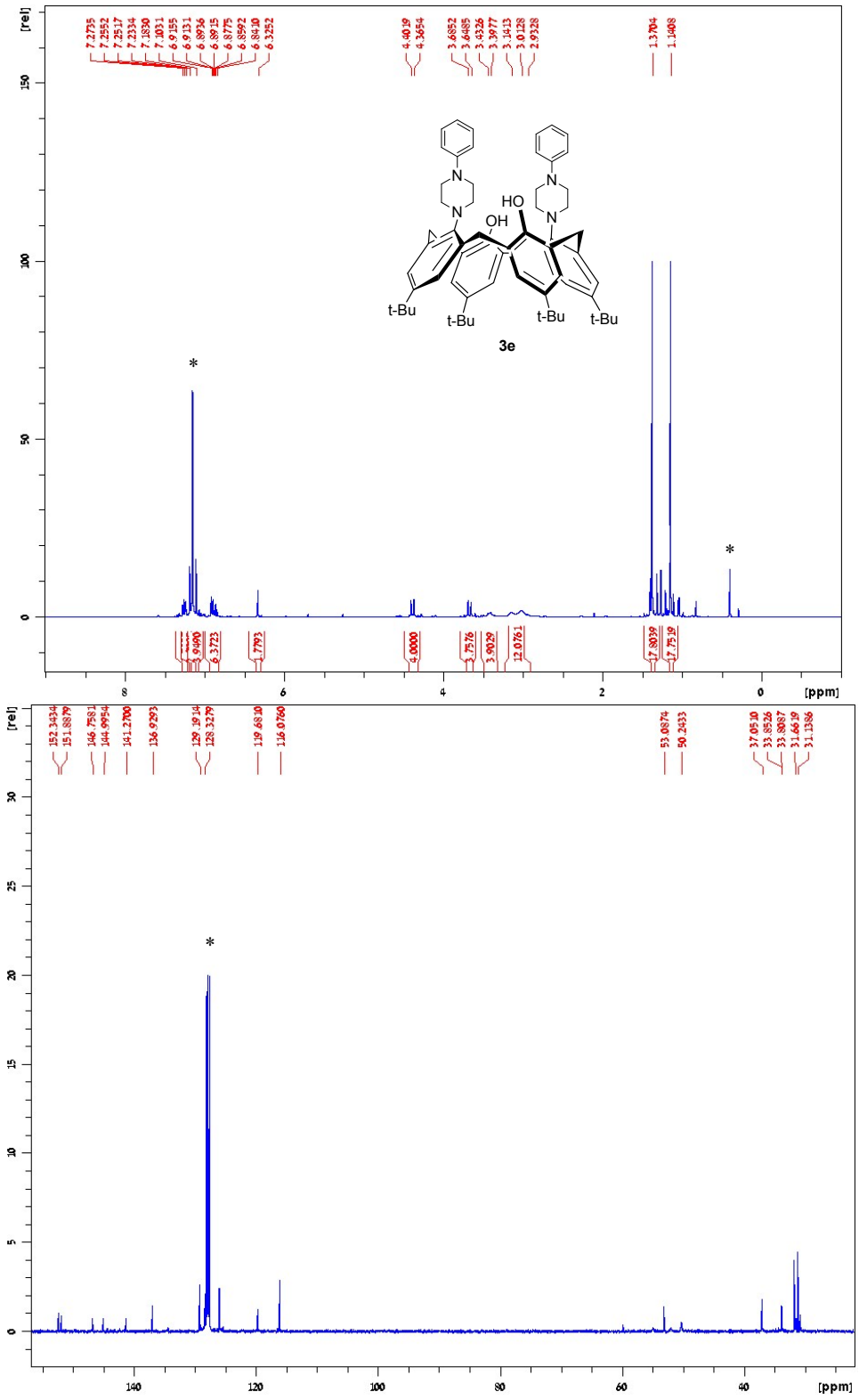


Figure S5: ^{1}H and ^{13}C NMR spectra of 1,3-Bis(1-phenylpiperazine)-*p*-*tert*-butylcalix[4]arene **3e** in C_6D_6. * indicate peaks due to residual protons, hexane and grease.

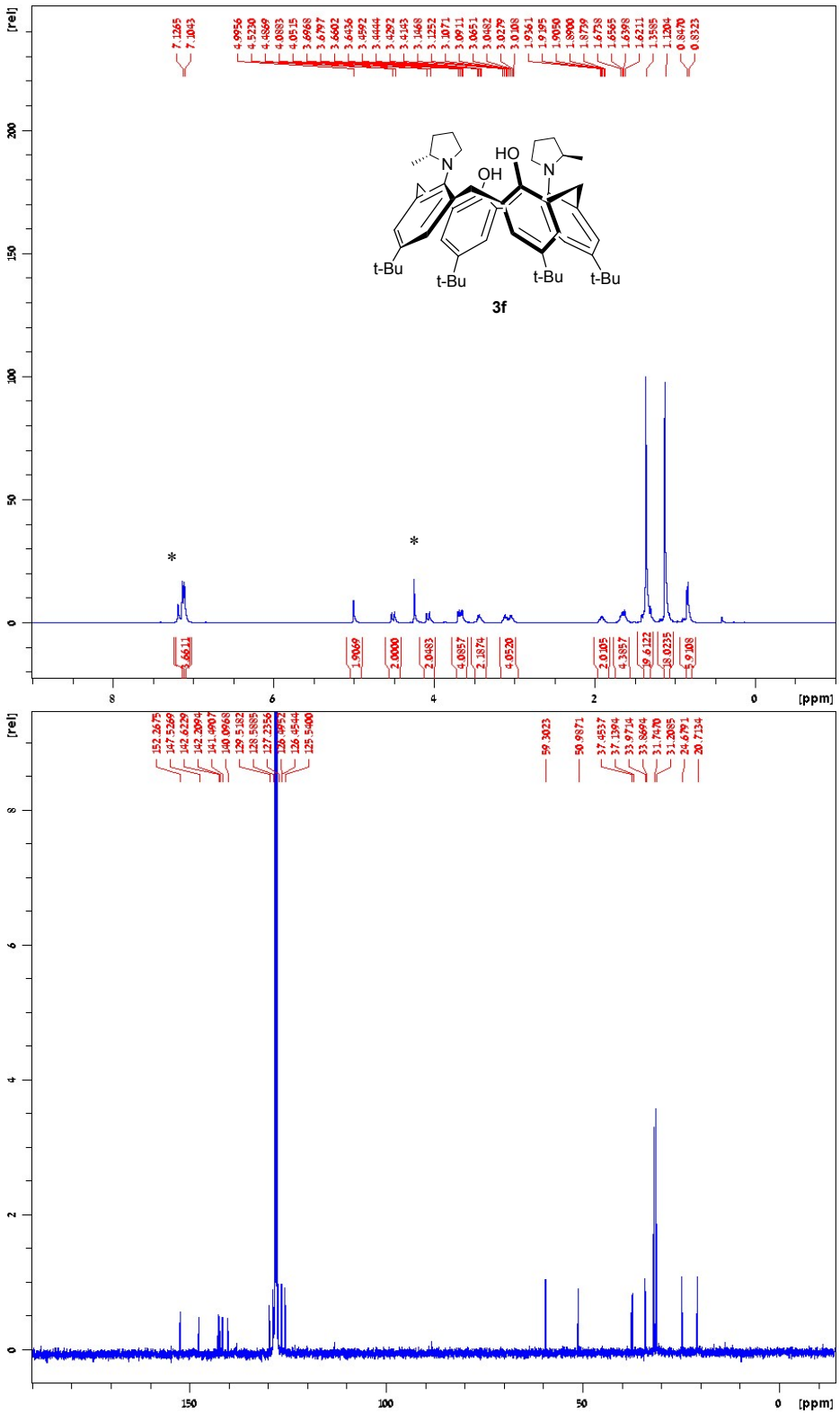


Figure S6: ^{1}H and ^{13}C NMR spectra of 1,3-Bis[(*R*)-2-methylpyrrolidine]-*p*-*tert*-butylcalix[4]arene **3f** in C_6D_6. * indicate peaks due to residual protons and CH_2Cl_2.

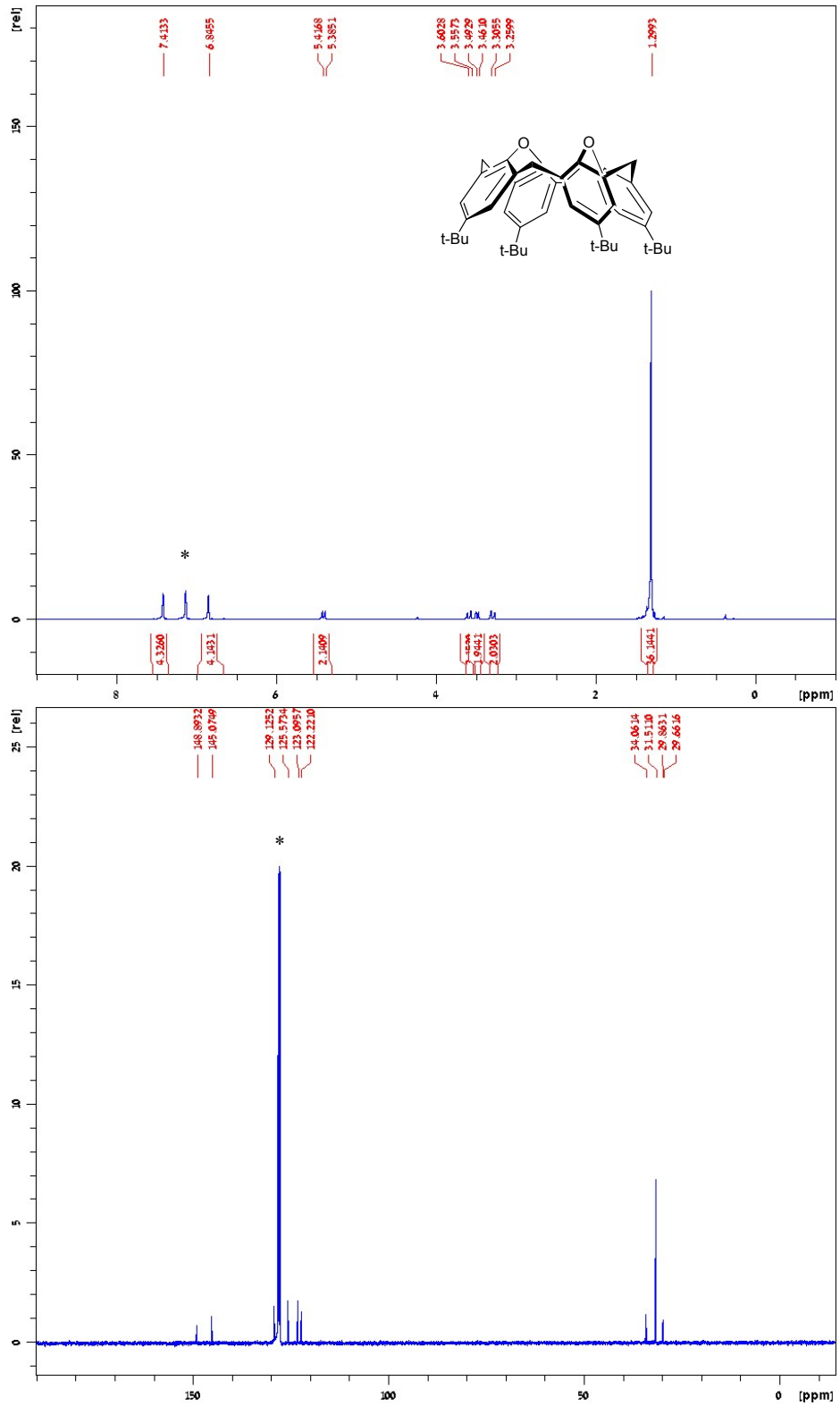


Figure S7: ^{1}H and ^{13}C NMR spectra of side product Bis-(xanthene) in C_6D_6. * indicate peak due to residual protons.

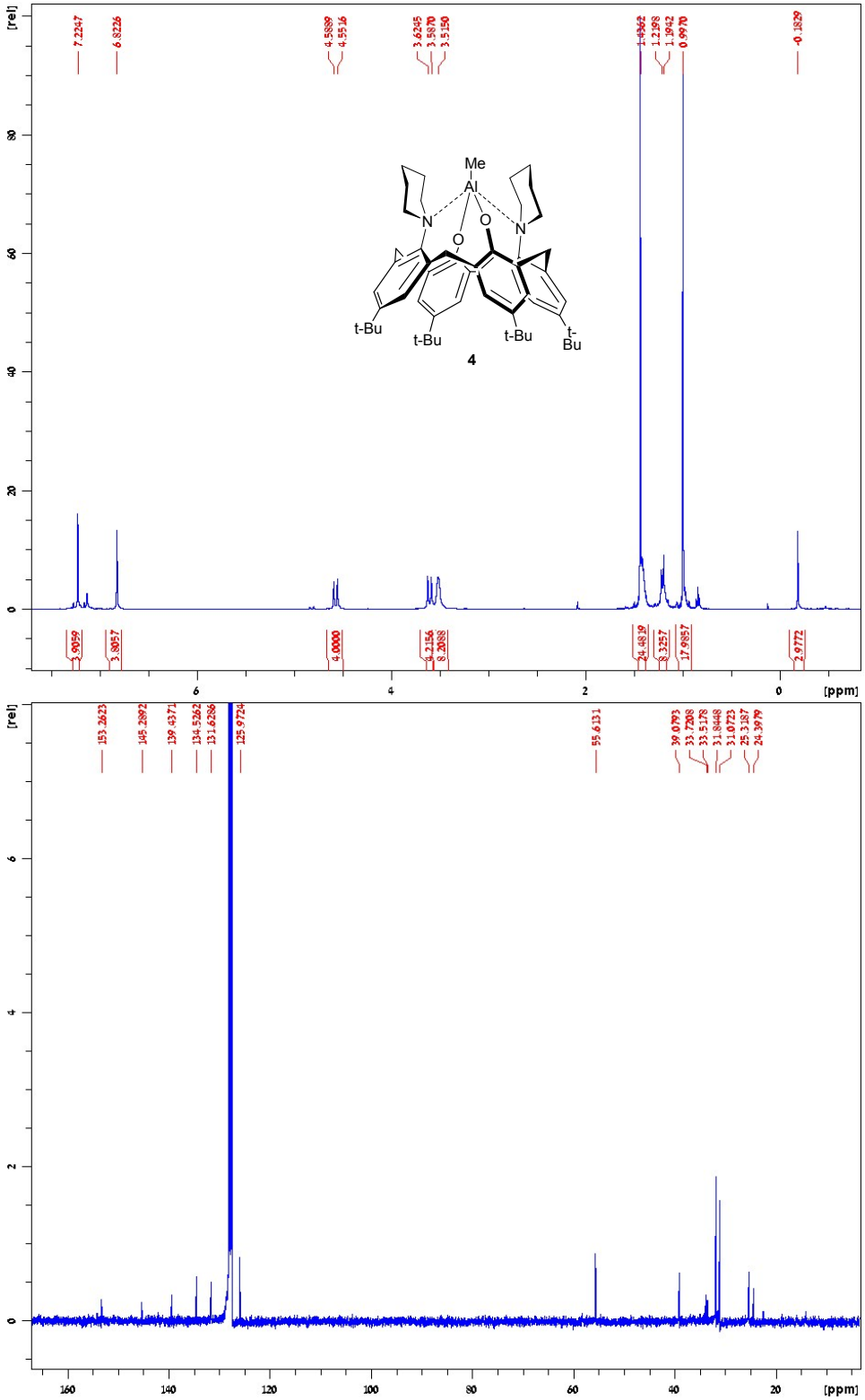


Figure S8: ^{1}H and ^{13}C NMR spectra of Me-Al-bis(piperidine)-p-tert-butylcalix[4]arene **4** in C_6D_6. * indicate peaks due to residual proton and pentane.

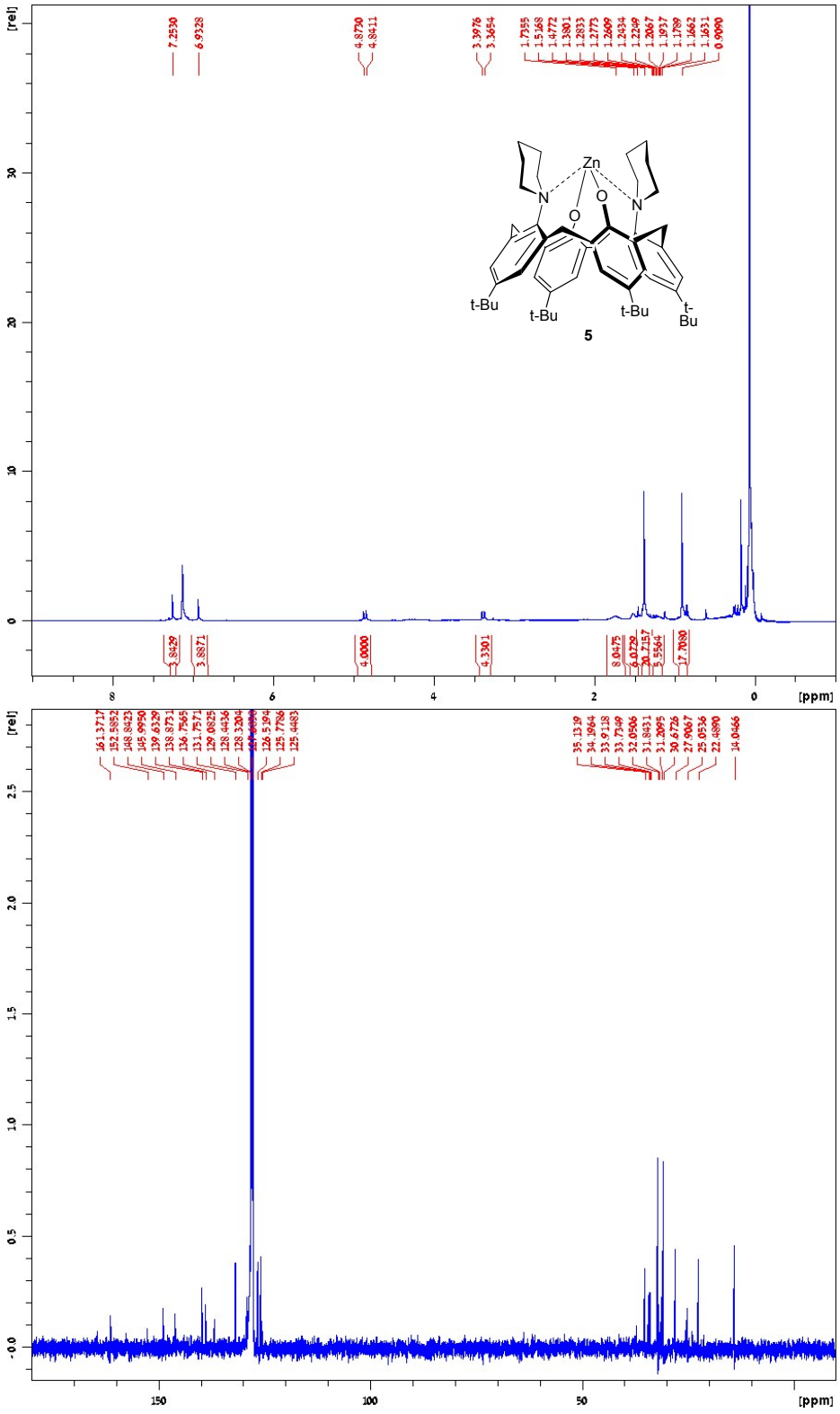


Figure S9: ^{1}H and ^{13}C NMR spectra of Zn-bis(piperidine)-p-tert-butylcalix[4]arene **5** in C_6D_6. * indicate peaks due to HMDS and pentane.

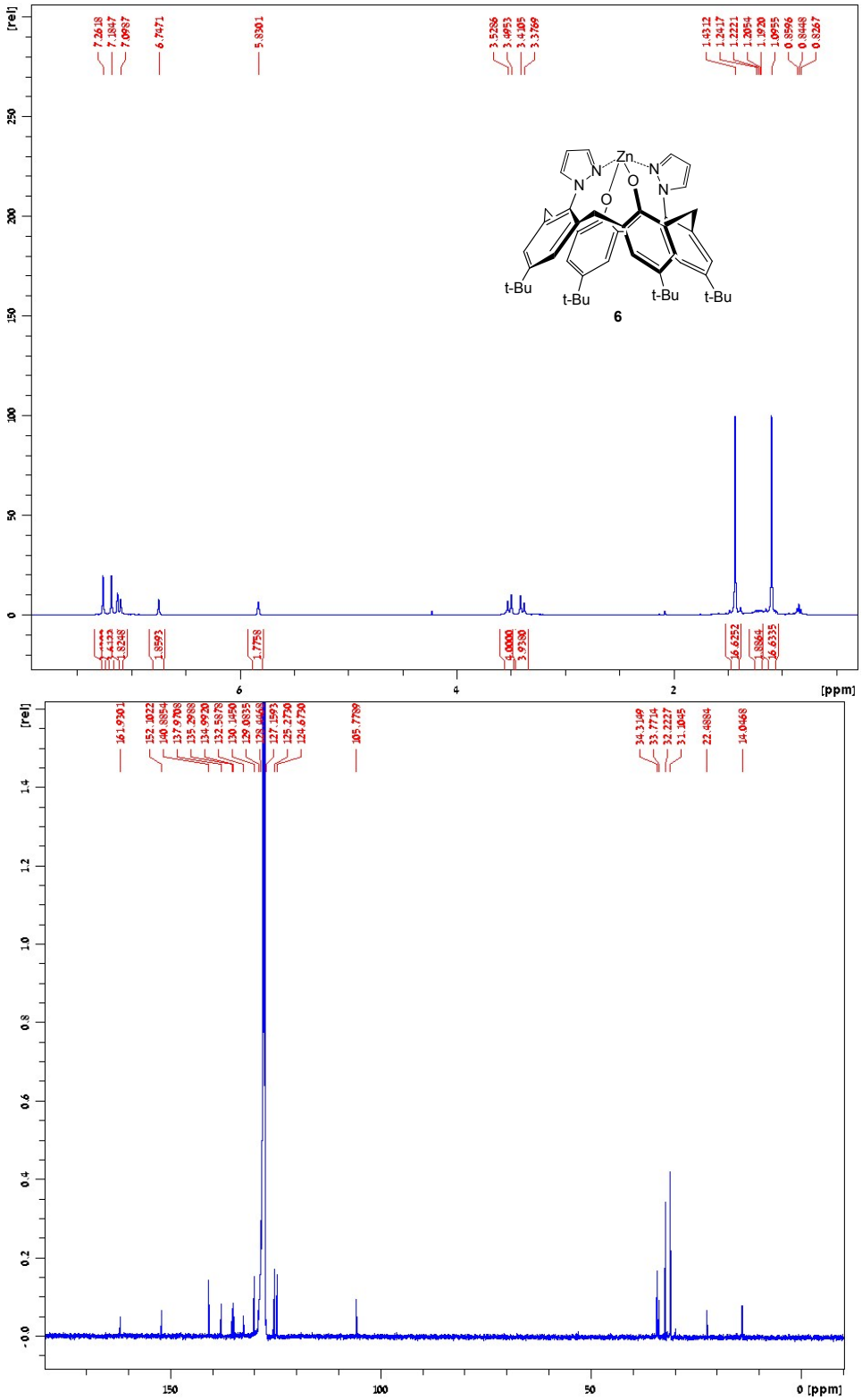


Figure S10: ^{1}H and ^{13}C NMR spectra of Zn-bis(pyrazole)-p-tert-butylcalix[4]arene **6** in C_6D_6. * indicate peaks due to residual protons and pentane.

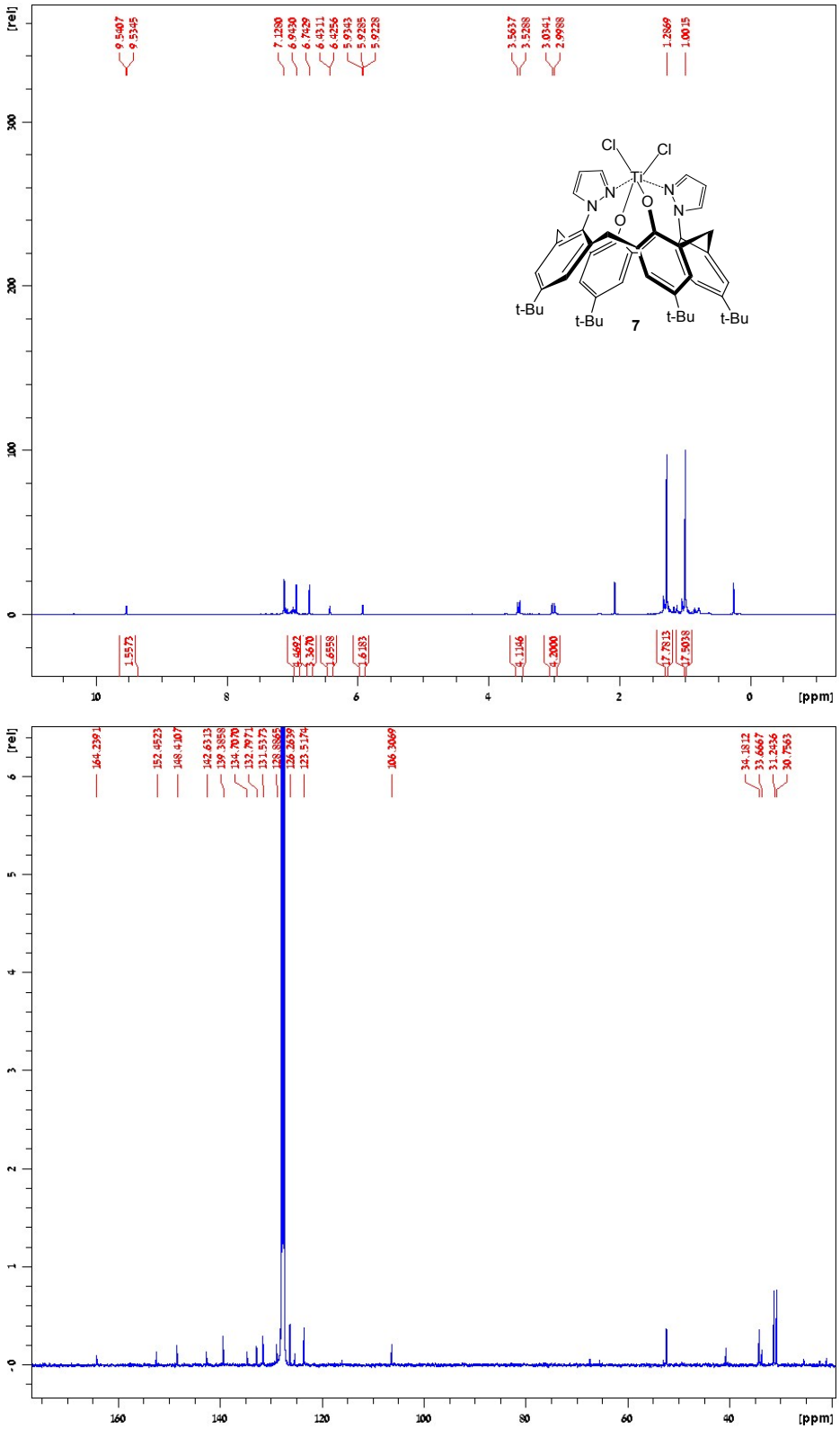


Figure S11: ^{1}H and ^{13}C NMR spectra Cl_2Ti-complex **7** in C_6D_6. * indicate peak due to residual protons, trace amount of DIPEA and silicon grease.

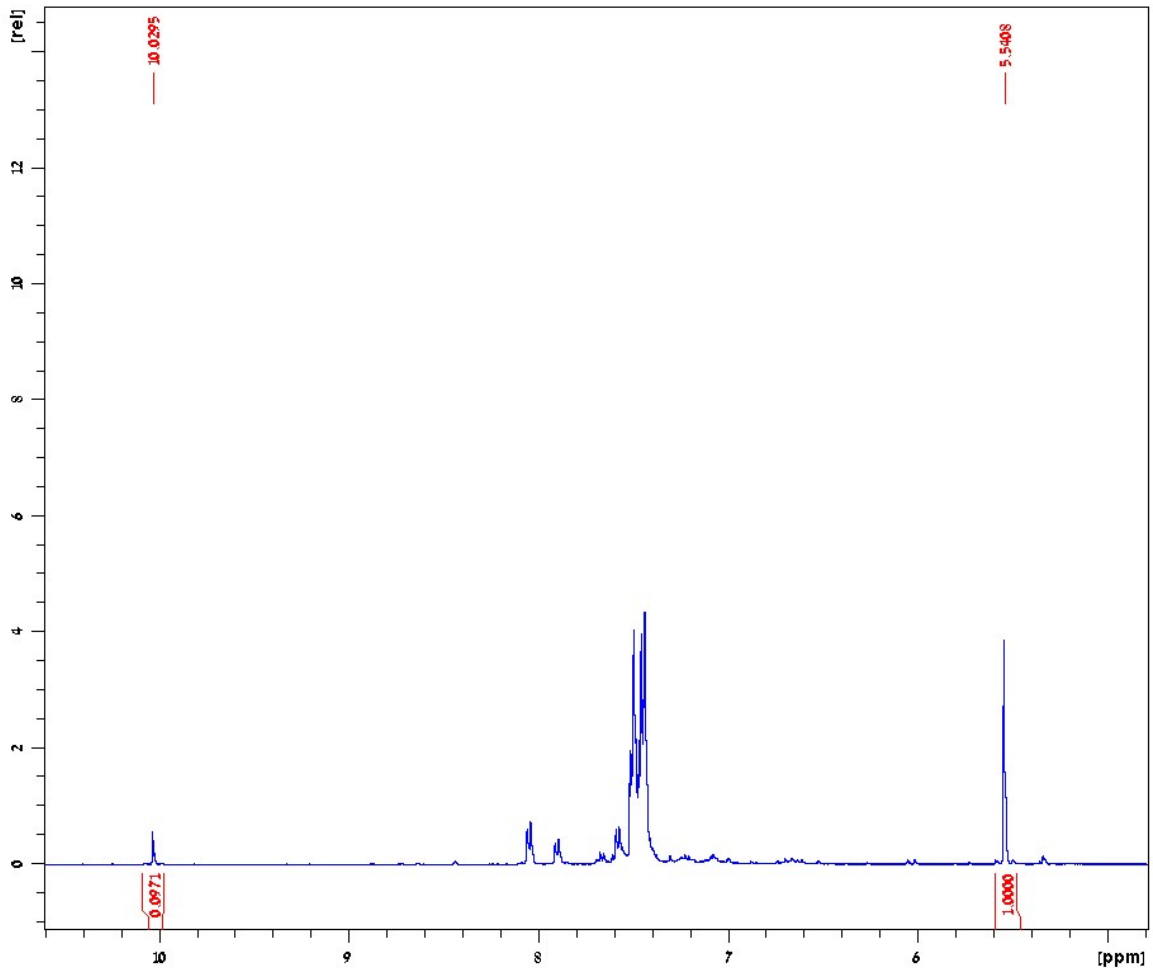


Figure S12: Calculation of relative conversion in the cyanosilylation reaction: **Table S1, Entry 2**.

After 2 h; the CH peak corresponding to unreacted aldehyde peak (reactant) appears at 10.02 ppm and the CH peak corresponding to cyanohydrin (product) appears at 5.50 ppm.

Total amount: unreacted benzaldehyde (0.1) + cyanohydrin (1) = 1.1

Percentage of conversion into cyanohydrin: 100/1.1 = 90.91%

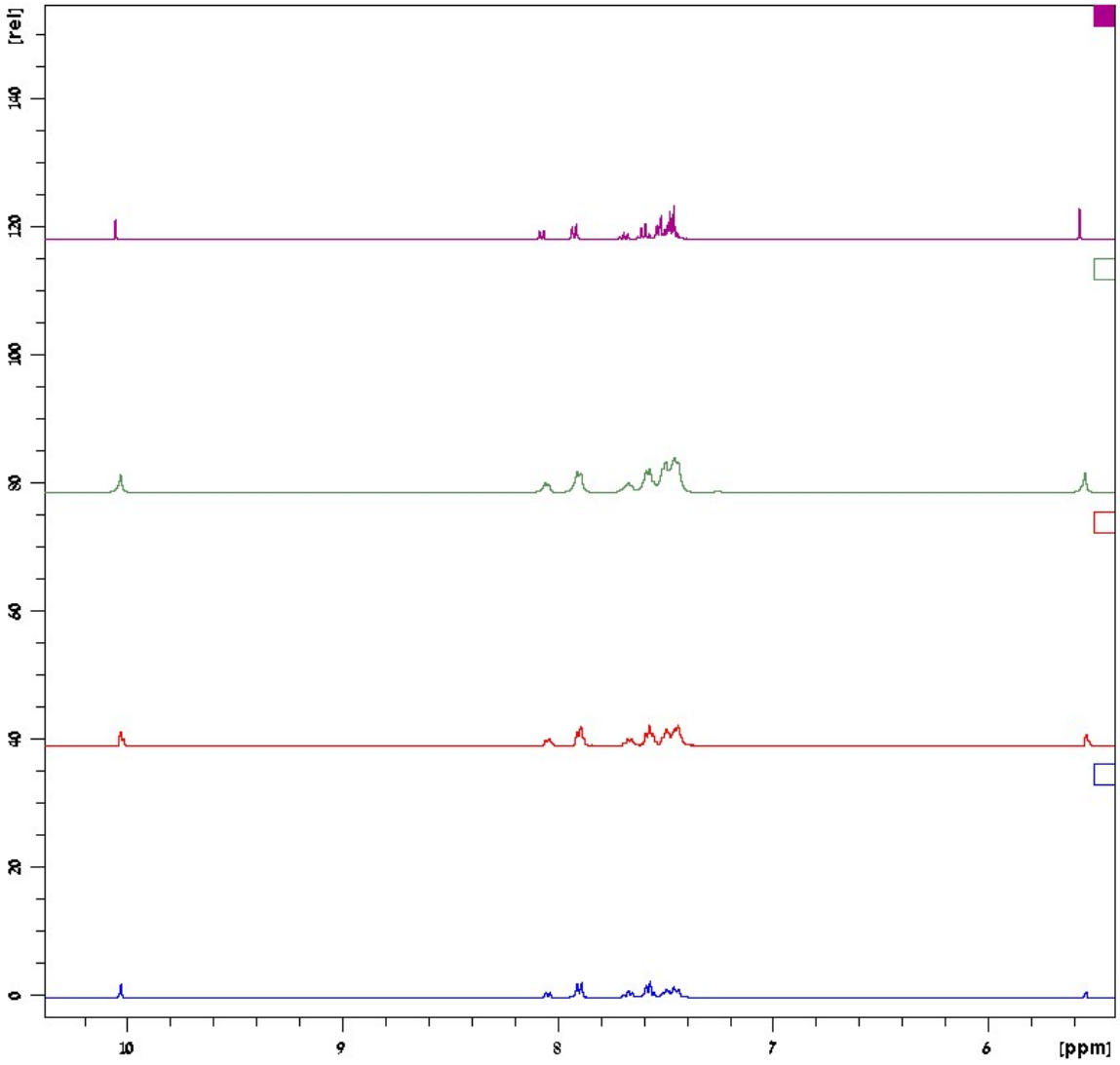


Figure S13: Representative ^{1}H NMR spectra of cyanosilylation reaction solution at definite time interval (1, 2, 3, 4 h) with **2-Ti** as catalyst; **Table S1, Entry 1**.

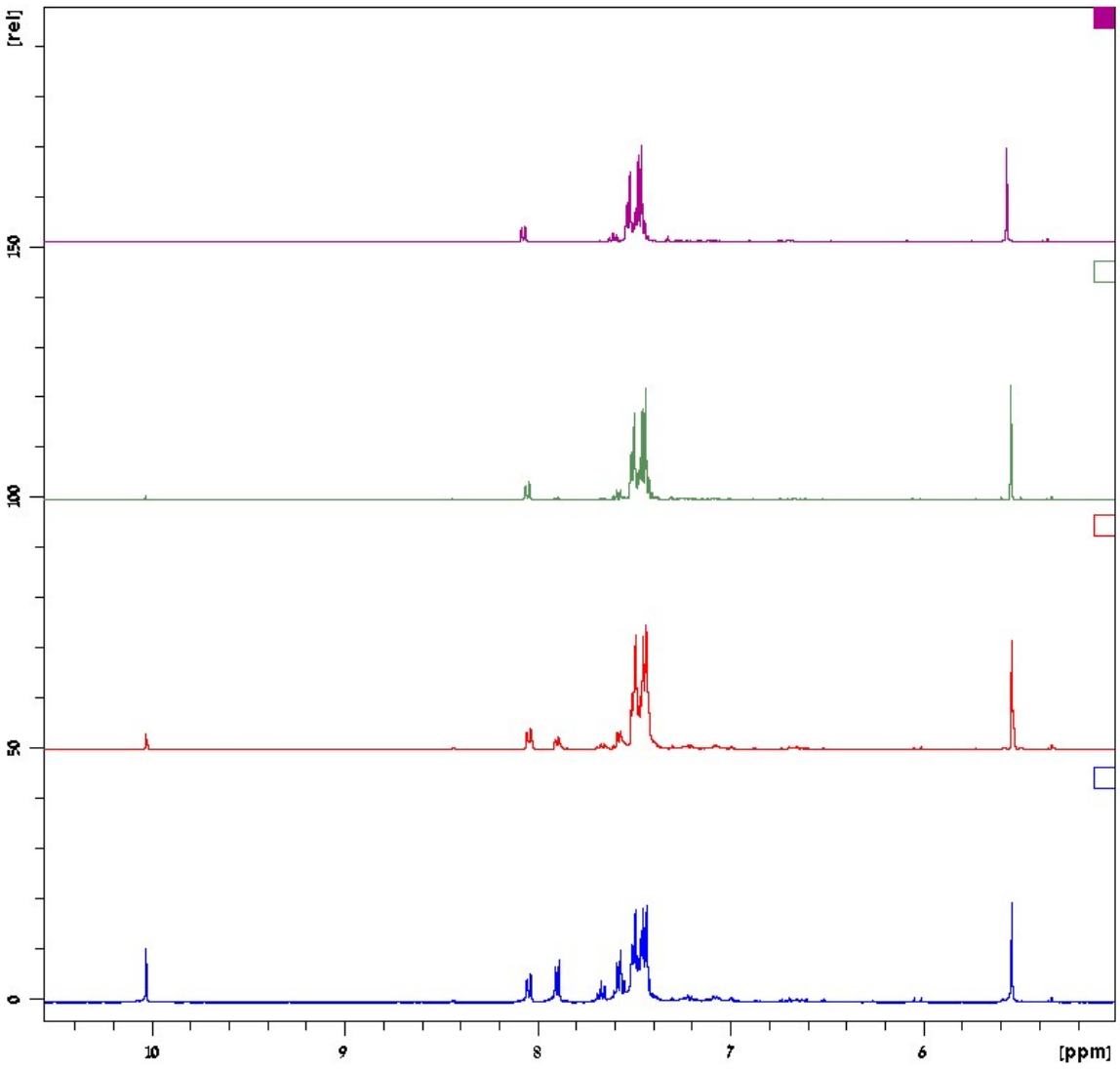


Figure S14: Representative ^{1}H NMR spectra of cyanosilylation reaction solution at definite time interval (1, 2, 3, 4 h) with **7** as catalyst; **Table S1, Entry 2**.

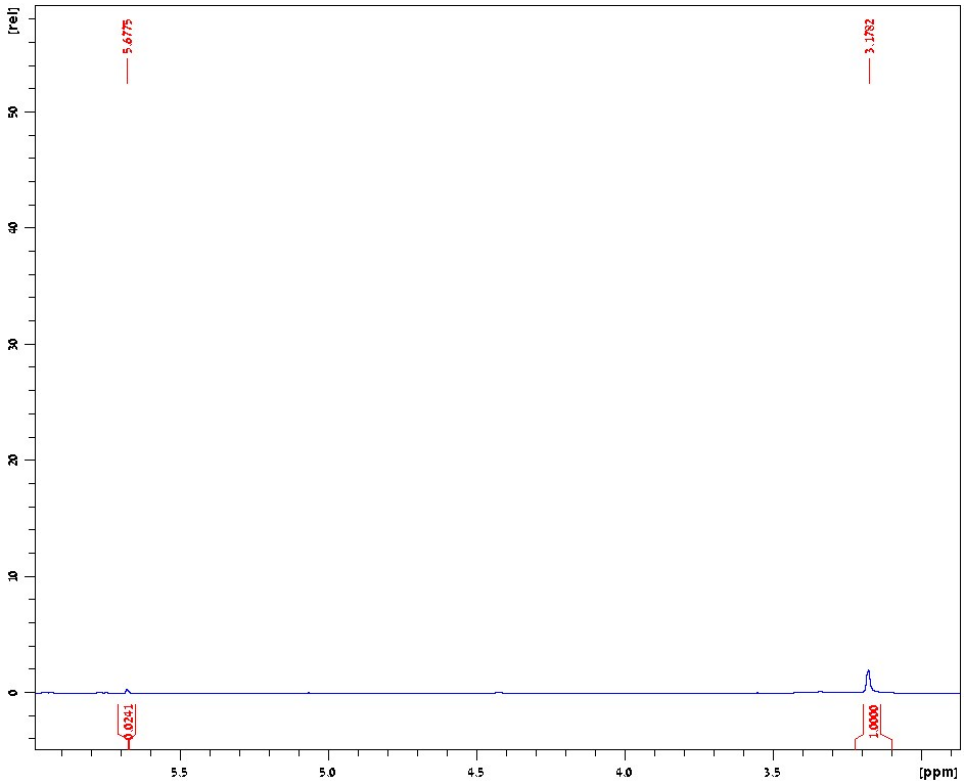


Figure S15: Calculation of relative conversion in the epoxidation reaction: **Table S2, Entry 3**.

The CH peak corresponding to olefinic protons of cyclohexene (reactant) appears at 5.68 ppm and the CH peak corresponding to epoxide protons of cyclohexene oxide (product) appears at 3.18 ppm.

Total amount: unreacted cyclohexene (0.02) + cyclohexene oxide (1) = 1.02

Percentage of conversion into cyclohexene oxide: 100/1.02 = 98.0%

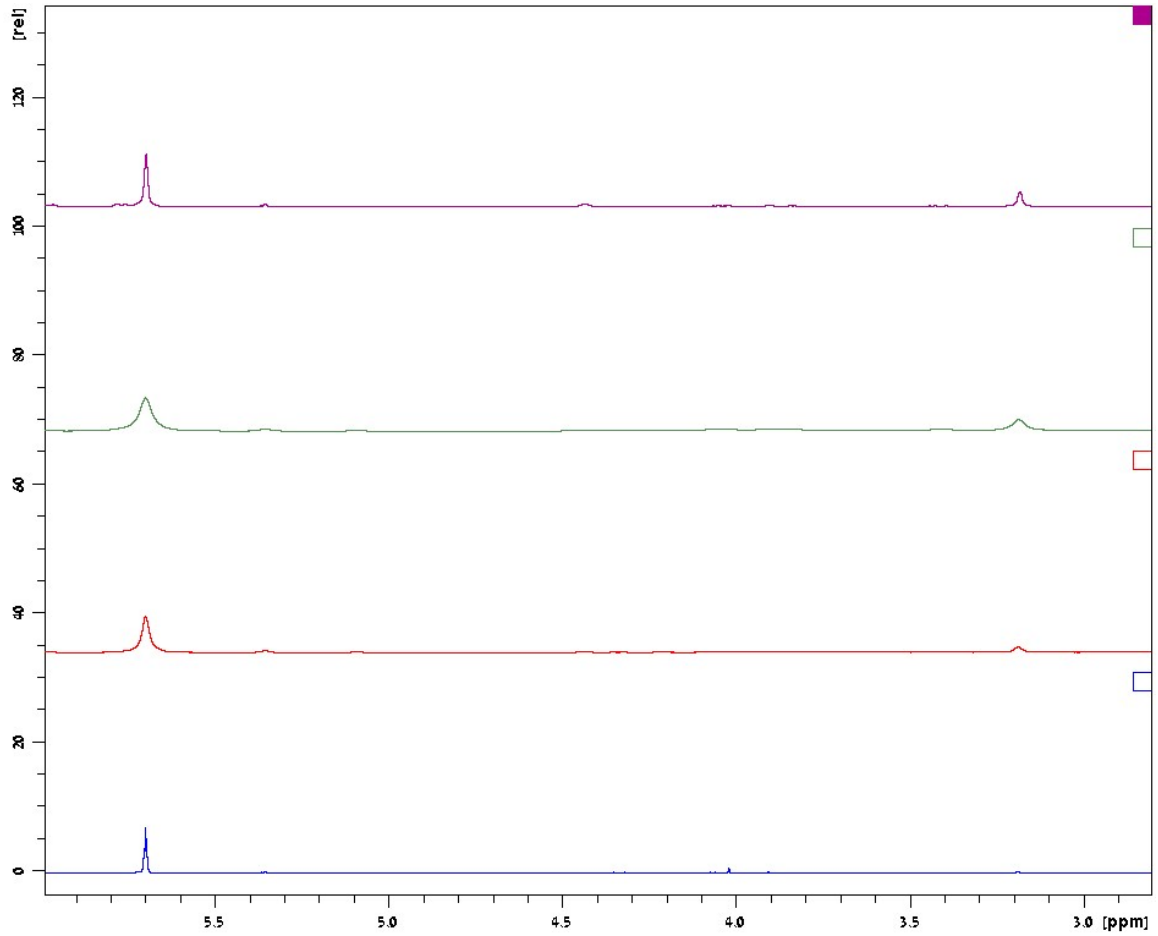


Figure S16: Representative ^{1}H NMR spectra of epoxidation reaction solution at definite time intervals (1, 3, 5, 7 h) with Cl_2Ti-1,3-dimethoxycalixarene **8** as catalyst; **Table S2, Entry 1**.

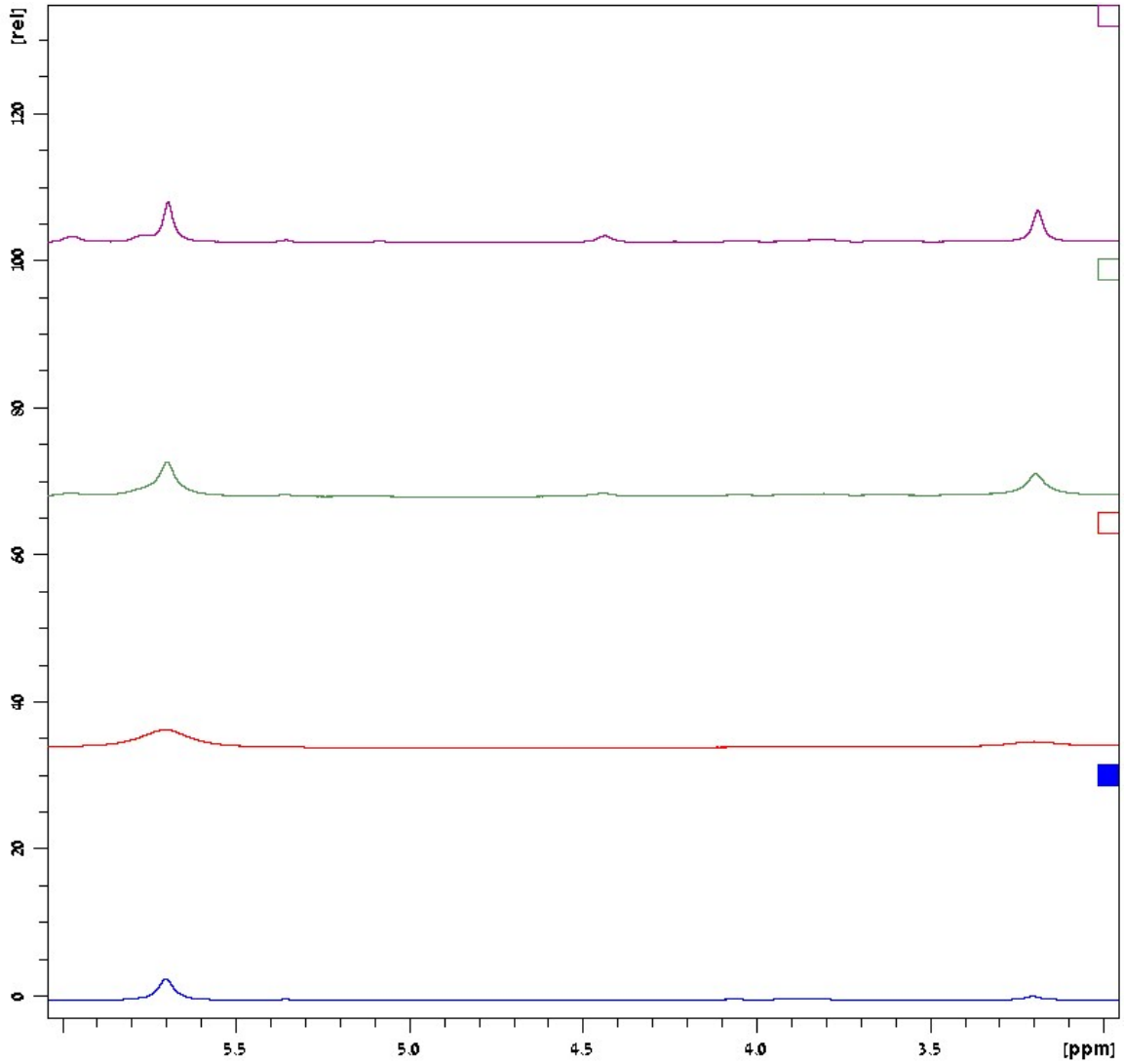


Figure S17: Representative ^{1}H NMR spectra of epoxidation reaction solution at definite time intervals (1, 3, 5, 7 h) with **2-Ti** as catalyst; **Table S2, Entry 2**.

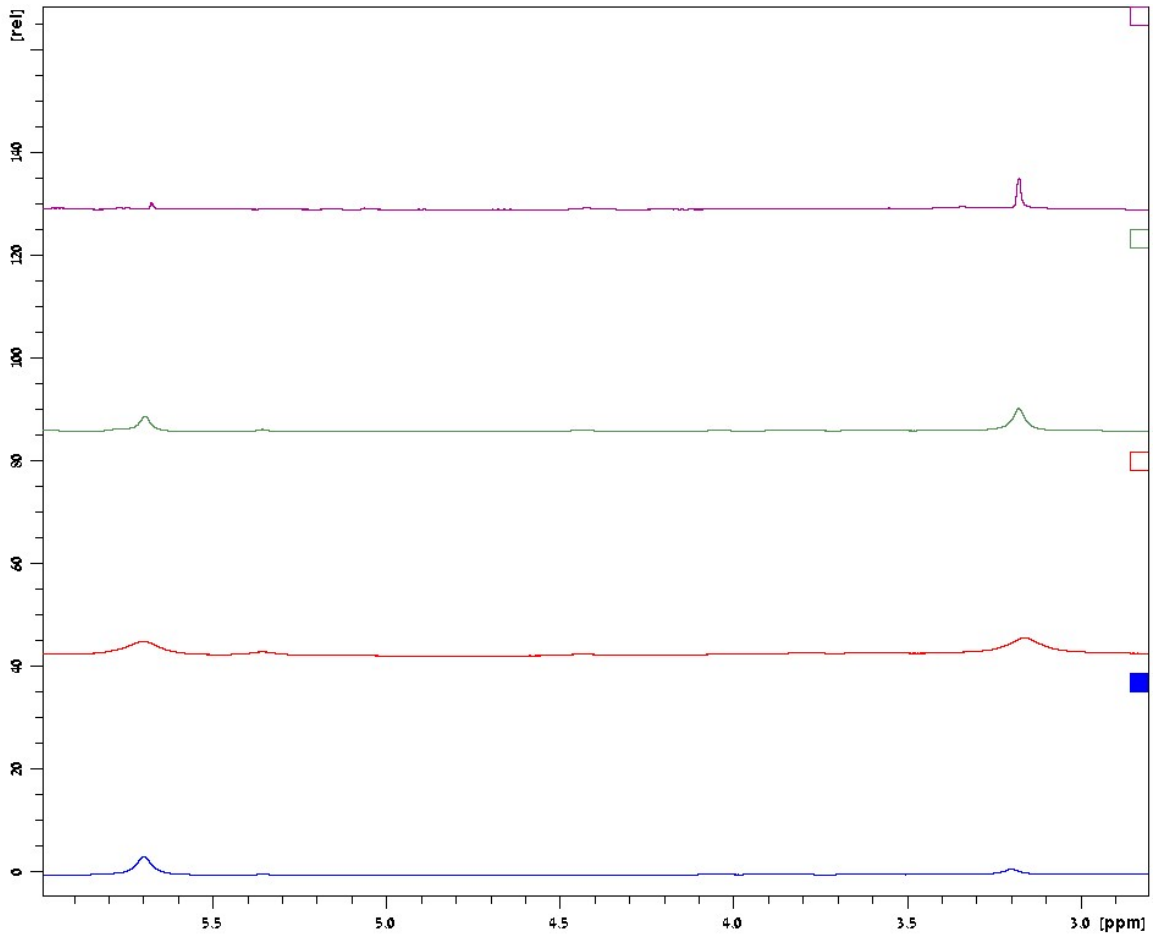


Figure S18: Representative ^{1}H NMR spectra of epoxidation reaction solution at definite time intervals (1, 3, 5, 7 h) with **7** as catalyst; **Table S2, Entry 3**.

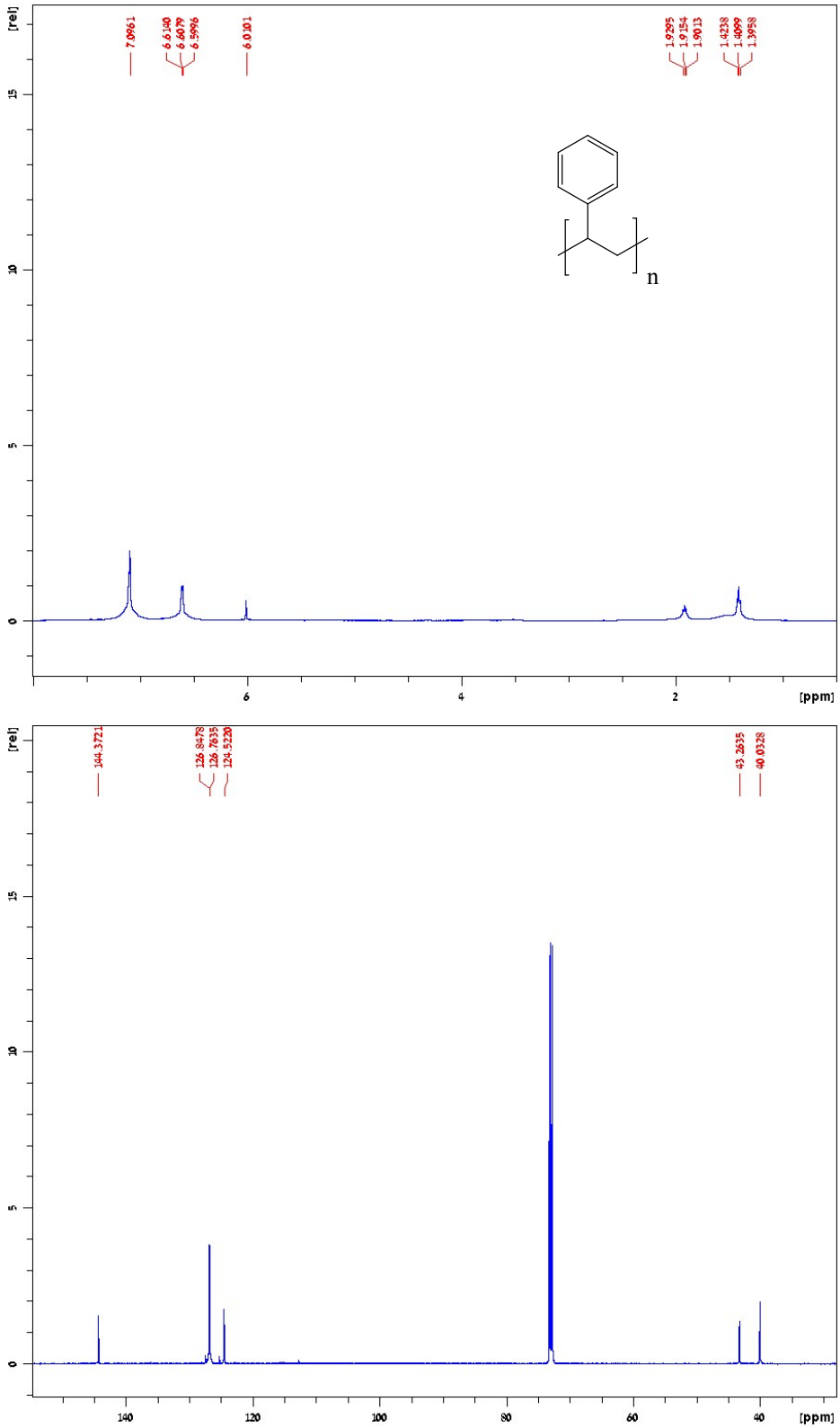


Figure S19: ^{1}H and ^{13}C NMR spectra of polystyrene with **7** activated by MAO in $CDCl_2$

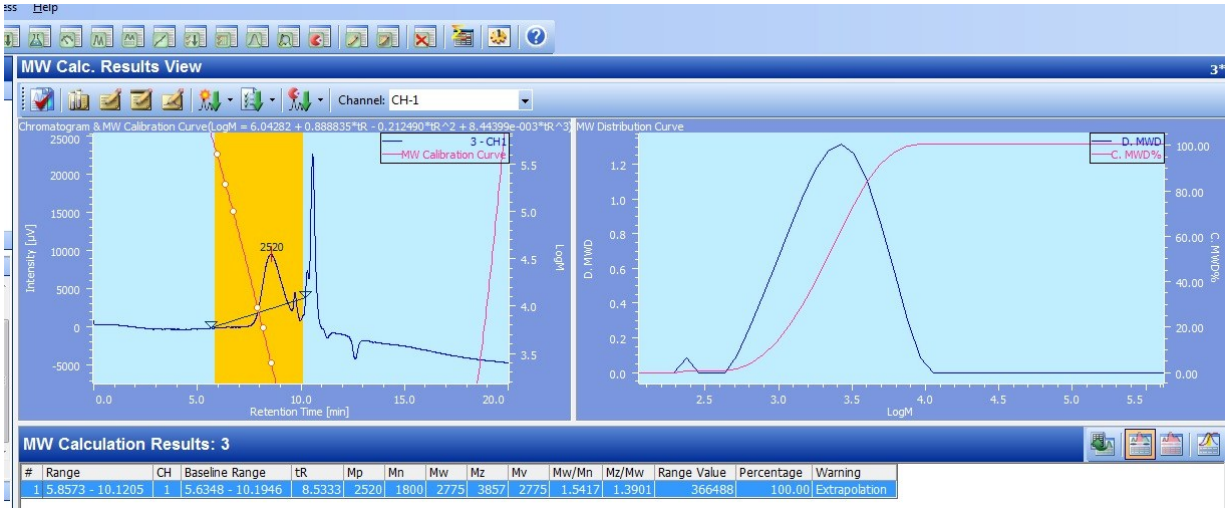


Figure S20: GPC trace of poly-1-hexene with **7** activated by $B(C_6F_5)_3$

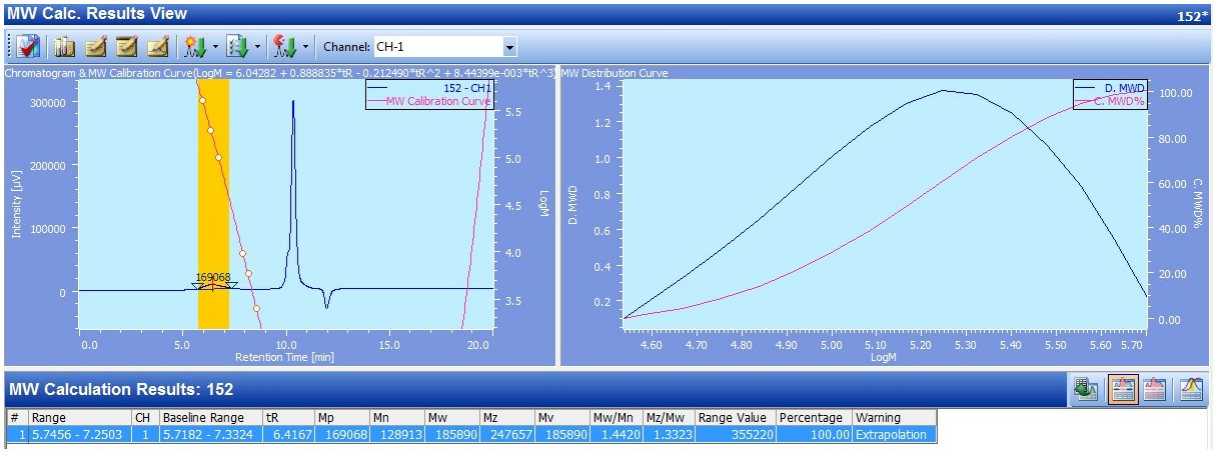


Figure S21: GPC trace of poly-1-hexene with **7** activated by MAO