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Exploring Enantiopure Zinc-Scorpionates as Catalysts for the Preparation of Polylactides, Cyclic Carbonates, and Polycarbonates

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1) Materials and Methods

General Procedures

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques or a glovebox. Solvents were predried over sodium wire and distilled under nitrogen from sodium (toluene and *n*-hexane) or sodium-benzophenone (THF and diethyl ether). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze-thaw cycles. The starting materials $ZnMe_2$, $ZnCl_2$, (-)-*cis*-myrtanylamine, (*R*)-(+)-bornylamine, diphenylacetyl chloride, Et_3N, ^nBuLi, $Li(CH_2SiMe_3)$, KO^tBu and 3,5-dimethylpyrazole were used as purchased, and the and PPh_3Br_2[1] were prepared as described in the literature. *rac*-Lactide was sublimed twice, recrystallized from THF and finally sublimed again prior to use.

Instruments and Measurements

NMR spectra were recorded on a Bruker Advance Neo 500 (^{1}H NMR 500 MHz and ^{13}C NMR 125 MHz) spectrometer and were referenced to the residual deuterated solvent signal. Microanalyses were performed with a Perkin-Elmer 2400 CHN analyser. Mass spectra were recorded on a VG Autospec instrument using the FAB technique and nitrobenzyl alcohol as matrix. The specific rotation $[\alpha]_D^{25}$ was measured at a concentration of 0.1% w/v in toluene at 22 °C on a JASCO P2000 Polarimeter equipped with a sodium lamp operating at 589 nm with a light path length of 10 cm. The molecular weights (M_n) and the molecular mass distributions (M_w/M_n) of polymer samples were measured by Gel Permeation Chromatography (GPC) performed on a Shimadzu LC-20AD GPC equipped with a TSK-GEL G3000Hxl column and an ELSD-LTII light-scattering detector. The GPC column was eluted with THF at 40 °C at 1 mL/min and was calibrated using eight monodisperse polystyrene standards in the range 580–483 000 Da. MALDI-ToF MS data were acquired with a Bruker Autoflex II ToF/ToF spectrometer, using a nitrogen laser source (337 nm, 3 ns) in linear mode with a positive acceleration voltage of 20 kV. Samples were prepared as follows: PLA (20 mg) was dissolved in HPLC quality THF with matrix and NaI in a 100:5:5 ratio. Before evaporation, 10 μL of the mixture

solution was deposited on the sample plate. External calibration was performed by using Peptide Calibration Standard II (covered mass range: 700–3 200 Da) and Protein Calibration Standard I (covered mass range: 5 000–17 500 Da). All values are the average of two independent measurements. The microstructures of PLA samples were determined by examination of the methine region in the homodecoupled ^{1}H NMR spectrum of the polymers recorded at room temperature in $CDCl_3$ on a Bruker Advance Neo 500 spectrometer with concentrations in the range 1.0 to 2.0 mg/mL.

2) Preparation of compounds 1–6c and complexes 7–9

Synthesis of phosphanimine (1). In a 250 cm^3 Schlenk tube, (-)-*cis*-myrtanylamine (5.00 cm^3, 4.58 g, 29.85 mmol) was dissolved in dry THF (30 cm^3). A solution of PPh_3Br_2[1] (12.60 g, 29.85 mmol) in THF (50 cm^3) was added. To the yellow-colored mixture was added Et_3N (4,16 mL, 29.85 mmol), leaving the reaction at room temperature during 4 h. After this time, a solution of KO^tBu (3.51 g, 31.29 mmol) in THF (30 cm^3) was added, the reaction mixture was stirred for overnight and the resulting yellow suspension was filtered. The solvent of the solution obtained was removed under reduced pressure to yield **1** as a yellow oil. Yield: 11.20 g, 91%. Anal. Calcd. for $C_{28}H_{32}NP$: C, 81.32; H, 7.80; N, 3.39. Found: C, 81.23; H, 7.82; N, 3.41. ^1H NMR (C_6D_6, 297 K), δ 7.85 (m, 6H, Ph^o), 7.08 (m, 6H, Ph^m), 7.00 (m, 3H, Ph^p), 3.40 (m, 2H, N-$\underline{CH_2}^{Myr}$), 2.75 (m, 1H, H^c), 2.63 (m, 1H, H^b), 2.50, 2.17 (m, 2H, H^d), 1.95 (m, 2H, H^e), 1.65 (m, 1H, H^f), 1.21, 0.94 (s, 6H, Me^g), 1.96, 1.11 (d, 2H, H^h). ^{13}C-{^1H} NMR (C_6D_6, 297 K), δ 134.0 ($C^{Ph,i}$), 129.5 ($C^{Ph,o}$), 128.0 ($C^{Ph,m}$), 126.0 ($C^{Ph,p}$), 58.0 (N-$\underline{CH_2}^{Myr}$), 44.2 (C^b), 42.8 (C^c), 41.9 (C^e), 38.7 (C^h), 28.0, 23.9 (Me^g), 26.1 (C^d), 20.1 (C^f). $[\alpha]_D^{25}$ = -7.3 (*c* 1.00, EtOH).

Synthesis of phosphanimine (2). The synthesis of **2** was carried out in an identical manner to **1**, using (*R*)-(+)-bornylamine (5 mL, 4.58 g, 29.85 mmol) to give **2** as a white solid. Yield: (11.25 g, 91%). Anal. Calcd. for $C_{28}H_{32}NP$: C, 81.32; H, 7.80; N, 3.39. Found: C, 81.33; H, 7.82; N, 3.42. ^1H NMR (C_6D_6, 297 K), δ 7.79 (m, 6H, Ph^o), 7.07 (m, 6H, Ph^m), 7.06 (m, 3H, Ph^p), 3.72 (m, 1H, H^b), 3.31, 1.64 (m, 2H, H^d), 2.26, 1.73 (m, 2H, H^g), 1.93 (m, 1H, H^f), 1.52, 1.26 (m, 2H, H^e), 1.00, 0.95 (s, 6H, $Me^{h,i}$), 0,92 (s, 3H, Me^c). ^{13}C-{^1H} NMR (C_6D_6, 297 K), δ 134.0 ($C^{Ph,i}$), 129.5 ($C^{Ph,o}$), 128.0 ($C^{Ph,m}$), 126.0 ($C^{Ph,p}$), 44.5 (C^b), 41.9 (C^d), 28.7 (Me^c), 26.1 (C^e), 22.1 (C^f), 21.9 (C^g), 21.3, 21.2 ($Me^{h,i}$). $[\alpha]_D^{25}$ = -14.6 (*c* 1.00, EtOH).

Synthesis of ketenimine (3). In a 250 cm^3 Schlenk tube, phosphanimine (**1**) **(**10 g, 24.18 mmol) was dissolved in dry THF (50 cm^3). A solution of diphenylketene[2] (4.7 g, 24.18 mmol) in THF (30 cm^3) was added, the reaction mixture was stirred for 4 h at room temperature and a orange suspension was obtained. The solvent was removed under reduced pressure to yield an orange oil. 100 cm^3 of n-hexane

was added and the new suspension was leaved to -26 °C overnight to favor the precipitation of triphenylphosfine oxide. The mixture of reaction was filtered, and the solution dried under reduced pressure to yield **3** as an orange oil. Yield: 7.49 g, 94%. Anal. Calcd. for $C_{24}H_{27}N$: C, 87.49; H, 8.26; N, 4.25. Found: C, 87.63; H, 8.09; N, 4.28. ^{1}H NMR (C_6D_6, 297 K), δ 7.42 (m, 4H, Ph^{o}), 7.17 (m, 4H, Ph^{m}), 7.01 (m, 2H, Ph^{p}), 3.40 (m, 2H, N-$\underline{CH_2}^{Myr}$), 2.39 (m, 1H, H^{c}), 2.22, 1.80 (m, 2H, H^{d}), 1.96 (m, 1H, H^{b}), 1.70 (m, 2H, H^{e}), 1.37 (m, 1H, H^{f}), 1.05, 0,81 (s, 6H, Me^{g}), 1.78, 0.79 (d, 2H, H^{h}). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K), δ 185.9, 185.0 (C=C), 136.0 ($C^{Ph,i}$), 129.0 ($C^{Ph,o}$), 128.0 ($C^{Ph,m}$), 126.0 ($C^{Ph,p}$), 59.2 (N-$\underline{CH_2}^{Myr}$), 44.0 (C^{b}), 42.3 (C^{c}), 41.8 (C^{g}), 38.8 (C^{e}), 33.2 (C^{h}), 28.0, 23,8 (Me^{g}), 26.0 (C^{d}), 20.0 (C^{f}). $[\alpha]_D^{25}$ = -22.0 (*c* 1.00, EtOH).

Synthesis of ketenimine (4). The synthesis of **4** was carried out in an identical manner to **3**, using phosphanimine **(2) (**10 g, 24.2 mmol) to give **4** as a white solid. Yield: (7.49 g, 94%). Anal. Calcd. for $C_{24}H_{27}N$: C, 87.49; H, 8.26; N, 4.25. Found: C, 87.53; H, 8.19; N, 4.22. ^{1}H NMR (C_6D_6, 297 K), δ 7.78 (m, 4H, Ph^{o}), 7.46 (m, 4H, Ph^{m}), 7.06 (m, 2H, Ph^{p}), 3.77 (m, 1H, H^{b}), 2.08, 1.60 (m, 2H, H^{d}), 1.98 (m, 1H, H^{f}), 1.46, 0.96 (m, 2H, H^{g}), 1.39, 0.97 (dd, 2H, H^{e}), 0.88, 0.72 (s, 6H, $Me^{h,i}$), 0.67 (s, 3H, Me^{g}). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K), δ 185.9, 185.0 (C=C), 136.0 ($C^{Ph,i}$), 129.0 ($C^{Ph,o}$), 128.0 ($C^{Ph,m}$), 126.0 ($C^{Ph,p}$), 46.3 (C^{b}), 41.8 (C^{d}), 28.6 (Me^{c}), 25.9 (C^{e}), 22.2 (C^{f}), 21.7 (C^{g}), 20.9, 20.7 ($Me^{h,i}$). $[\alpha]_D^{25}$ = -22.0 (*c* 1.00, EtOH).

Synthesis of (-)-*cis*-bpmyH (5a) and (-)-*cis*-bpmy'H (5b). In a 250 cm^3 Schlenk tube bis(3,5-dimethylpyrazol-1-yl)methane (bdmpzm)[3] (1 g, 4.89 mmol) was dissolved in dry THF (50 mL) and cooled to around –70 º C (acetone/liquid nitrogen). ^{n}BuLi (2.5 M in n-hexane) (1.95 cm^3, 4.89 mmol) was added dropwise, maintaining the reaction temperature at –70 °C for 1 h to give a yellow suspension. A pre-cooled solution (salt/ice at 0 °C) of ketenimine **3** (1.61 g, 4.89 mmol) in THF (20 mL) was added dropwise to the suspension. The resulting mixture was allowed to reach 0 °C and was maintained at this temperature for one hour. After this time a saturated solution of NH_4Cl in water (40 mL) was added to the mixture and the organic layer is decanted into a 250 mL separatory funnel. The resulting organic phase was dried over $MgSO_4$ and solvent was removed under vacuum to give a

yellow oil. The product were purified using a plug of silica, eluting with a mixture of AcOEt/*n*-hexane (1:9) to give compound **5** yellow oil as two tautomers mixture (**5a**, **5b**) (1:1). Tautomer **5a** was separated by crystallization at -26 ° C in a hexane solution, while from mother liquor after several recrystallizations, tautomer **5b** was obtained as the majority product. Yield of mixture: 1.77 g, 68%. Anal. Calcd. for $C_{35}H_{43}N_5$: C, 78.76; H, 8.12; N, 13.12. Found: C, 78.45; H, 8.17; N, 13.42. **(-)-*cis*-bpmyH** (**5a**): ^{1}H NMR (C_6D_6, 297 K), δ 7.42 (m, 4H, Ph^o), 7.15 (m, 4H, Ph^m), 7.01 (m, 2H, Ph^p), 6.78 (s, 1H, CH^a), 5.70, 5.69 (s, 1H, $H^{4,4'}$), 5.36 (t,1H, -NH-CH_2^{Myr}), 3.17 (m, 2H, NH-CH_2^{Myr}), 2.5-2.4 (m, 1H, H^c), 2.3 (m, 1H, H^b), 2.21, 1.19 (s, 6H, $Me^{3,3'}$), 1.90 (m, 2H, H^d), 1.80 (m, 2H, H^e), 1.73, 1.70 (s, 6H, $Me^{5,5'}$), 1.60 (m, 1H, H^f), 1.17, 0.91 (s, 6H, Me^g), 2.22, 0.90 (d, 2H, H^h). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K), δ 148.5, 146.4 (C=C), 148.4 ($C^{Ph,i}$), 148.1, 142.7, 139.7, 139.5 ($C^{3,3',5,5'}$), 129.2 ($C^{Ph,o}$), 128.5 ($C^{Ph,m}$), 126.9 ($C^{Ph,p}$), 126.3 (C^g), 106.5, 106.0 ($C^{4,4'}$), 59.4 (CH^a), 54.1 (N-CH_2^{Myr}), 44.5 (C^f), 42.0 (C^d), 41.8 (C^e), 41.7 (C^c), 38.2 (C^h), 31.8 (C^b), 27.8, 23.1 (Me^g), 13.8, 11.7 ($Me^{3,3'}$), 10.0, 9.9 ($Me^{5,5'}$). $[\alpha]_D^{25}$ = -7.2 (*c* 1.00, EtOH). **(-)-*cis*-bpmy'H** (**5b**): ^{1}H NMR (C_6D_6, 297 K), δ 7.40 (m, 4H, Ph^o), 7.17 (m, 4H, Ph^m), 7.03 (m, 2H, Ph^p), 7.00 (s, 1H, CH^a), 5.65, 5.60 (s, 2H, $H^{4,4'}$), 5.38 (s, 1H, $CHPh_2$), 3.28 (m, 2H, N-CH_2^{Myr}), 2.60 (m, 1H, H^c), 2.60, 2,28 (s, 6H, $Me^{3,3'}$), 2.20 (m, 1H, H^b), 2.21, 1.19 (s, 6H, $Me^{5,5'}$), 1.80, 1.70 (m, 2H, H^d), 1.65 (m, 2H, H^e), 1.50 (m, 1H, H^f), 1.05, 0.80 (s, 6H, Me^g), 0.61, 0.29 (d, 2H, H^h). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K), δ 143.4, 143.3 (C=C), 148.4 ($C^{Ph,i}$), 148.0, 140.8, 133.5, 133.4 ($C^{3,3',5,5'}$), 129.3 ($C^{Ph,o}$), 128.6 ($C^{Ph,m}$), 126.9 ($C^{Ph,p}$), 125.4 (C^g), 105.0, 104.5 ($C^{4,4'}$), 69.1 (CH^a), 54.7 (N-CH_2^{Myr}), 52.5 ($CHPh_2$), 49.1 (C^c), 44.0 (C^f), 41.6 (C^d), 38.1 (C^e), 33.7 (C^b), 33.0 (C^h), 27.9, 23.0 (Me^g), 13.9, 11.9 ($Me^{3,3'}$), 13.8, 11.7 ($Me^{5,5'}$). $[\alpha]_D^{25}$ = -5.1 (*c* 1.00, EtOH).

Synthesis of (*R*)-(+)-bpmbnH (6c). The synthesis of **6c** was carried out in an identical manner to **5**, using bis(3,5-dimethylpyrazol-1-yl)methane (1 g, 4.89 mmol) and ketenimine **4** (1.61 g, 4.89 mmol), to give **6c** as a white solid as a white solid and as a single tautomer (imine). Colourless crystals corresponding to **6c** suitable for study by X-ray diffraction were obtained in a THF solution at -26 °C. Yield: (1.77 g, 70%). Anal. Calcd. for $C_{35}H_{43}N_5$: C, 78.76; H, 8.12; N, 13.12. Found; C, 78.82; H, 8.13; N, 13.22. ^{1}H NMR (C_6D_6, 297 K), δ 7.49 (m, 4H, Ph^o), 7.13 (m, 4H, Ph^m), 7.02 (m, 2H, Ph^p), 7.12 (s,

1H, CH^a), 5.66, 5.61 (s, 2H, $H^{4,4'}$), 5.40 (s,1H, -$\underline{C}HPh_2$), 2.95 (m, 1H, H^b), 2.55, 2.26 (s, 6H, $Me^{3,3'}$), 2.23, 2.14 (s, 6H, $Me^{5,5'}$), 1.88 (m, 1H, H^f), 1.43, 0.75 (m, 2H, H^g), 1.35, 0.96 (m, 2H, H^d), 1.05, 0.79 (m, 2H, H^e), 0.64 (s, 6H, $Me^{i,j}$), 0.62 (s, 3H, Me^g). ^{13}C-{^1H} NMR (C_6D_6, 297 K), δ 147.5, 146.8 (C=C), 148.7 ($C^{Ph,i}$), 148.3, 143.0, 139.0, 138.5 ($C^{3,3',5,5'}$), 128.9 ($C^{Ph,o}$), 128.7 ($C^{Ph,m}$), 125.9 ($C^{Ph,p}$), 105.6, 105.3 ($C^{4,4'}$), 71.0 (C^a), 48.3 ($\underline{C}HPh_2$) 46.2 (C^b), 41.7 (C^d), 28.8 (Me^c), 24.5 (C^e), 23.6 (C^f), 22.9 (C^g), 20.1, 19.8 ($Me^{h,i}$), 13.4, 12.1 ($Me^{3,3'}$), 10.1, 9.8 ($Me^{5,5'}$) $[\alpha]_D^{25}$ = -11.2 (*c* 1.00, EtOH).

Synthesis of [ZnMe(κ³-(-)-*cis*-bpmy)] (7). In a 250 cm^3 Schlenk tube the scorpionate ligand **5** (1.0 g, 1.87 mmol) was dissolved in dry toluene. $ZnMe_2$ (0.94 mL, 1.87 mmol, 2.0 M in toluene) was added and the mixture was heated at 80 °C for 72 h. The crude reaction mixture was dried under reduced pressure, resulting a sticky orange solid corresponding to **7**. Yield: 1.07 g, 93%. Anal. Calcd. for $C_{36}H_{45}N_5Zn$: C, 70.52; H, 7.40; N, 11.42; Found: C, 70.53; H, 7.27; N, 11.38. mp 134-136 °C. ^1H NMR (C_6D_6, 297 K), δ 7.30 (m, 4H, Ph^o), 7.10 (m, 4H, Ph^m), 7.02 (s, 1H, CH^a), 7.00 (m, 2H, Ph^p), 5.32, 5.29 (s, 2H, $H^{4,4'}$), A 3.23, B 3.18, X 2.89 [ABX, J_{AB} = 13.4, J_{AX} = 7.4, J_{BX} = 8.3 Hz (N-$\underline{CH_2}^{Myr}$, H^c)] 2.30 (m, 1H, H^b), 2.10 (s, 6H, $Me^{3,3'}$), 1.90 (m, 2H, H^d), 1.80 (m, 2H, H^e), 1.70, 1.62 (s, 6H, $Me^{5,5'}$), 1.25 (m, 1H, H^f), 1.70, 1.11 (d, 2H, H^h), 1.09, 0.89 (s, 6H, Me^g), 0.11 (s, 1H, Zn-Me). ^{13}C-{^1H} NMR (C_6D_6, 297 K), δ 152.0, 148.0 (C=C), 148.0, 140.0, 132.0, 131.0 ($C^{3,3',5,5'}$), 139.1 ($C^{Ph,i}$), 130.0 ($C^{Ph,o}$), 129.0 ($C^{Ph,m}$), 124.2 ($C^{Ph,p}$), 105.5 ($C^{4,4'}$), 66.5 (CH^a), 61.0 (N-$\underline{CH_2}^{Myr}$), 44.0 (C^b), 42.0 (C^c), 38.5 (C^e), 33.5 (C^h), 28.1, 23.0 (Me^g), 26.0 (C^d), 20.1 (C^f), 12.5 ($Me^{3,3'}$), 10.2, 9.8 ($Me^{5,5'}$), -16.0 (ZnMe). $[\alpha]_D^{25}$ = -9.1 (*c* 1.00, EtOH). Mass spectrum (FAB): (*m*/*z* assignment, % intensity): 612,3 $[ZnMe(bpmy) + H]^+$, 100.

Synthesis of [Zn(CH_2SiMe_3)(κ³-(-)-*cis*-bpmy)] (8). In a 250 cm^3 Schlenk tube the scorpionate ligand **5** (1.0 g, 1.87 mmol) was dissolved in dry toluene. $Zn(CH_2SiMe_3)_2$ [prepared in situ by reaction of $ZnCl_2$ (0.19 g, 1.87 mmol) and $Li(CH_2SiMe_3)$ 0.7M in hexane (5.34 mL, 3.74 mmol)] was added and the mixture was heated at 80 °C for 72 h. The crude reaction mixture was dried under reduced pressure, resulting a sticky yellow solid corresponding to **8**. Yield: 1.19 g, 93%. Anal. Calcd. for $C_{39}H_{53}N_5SiZn$: C, 68.35; H, 7.80; N, 10.22; Found: C, 68.46; H, 7.87; N, 10.12. ^1H NMR (C_6D_6, 297 K), δ 7.28 (m, 4H, Ph^o), 7.09 (m, 4H, Ph^m), 7.02 (m, 2H, Ph^p), 6.83 (s, 1H, CH^a), 5.31, 5.26 (s, 2H, $H^{4,4'}$), A 3.25, B

3.18, X 2.60 [ABX, J_{AB} = 13.4, J_{AX} = 7.4, J_{BX} = 8.3 Hz (N-$\underline{CH_2}^{Myr}$, H^c)], 2.60 (m, 1H, H^c), 2.29 (m, 1H, H^b), 2.10 (m, 2H, H^d), 2.15, 2.14 (s, 6H, $Me^{3,3'}$), 2.08, 1.10 (d, 2H, H^h), 1.73, 1.58 (s, 6H, $Me^{5,5'}$), 1.61 (m, 2H, H^e), 1.52 (m, 1H, H^f), 1.09, 0.87 (s, 6H, Me^g), 0.51 (s, 9H, Zn-$CH_2Si\underline{Me_3}$), -0.25 (s, 2H, Zn-$\underline{CH_2}SiMe_3$). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K), δ 151.9, 148.0 (C=C), 148.3, 141.2, 132.4, 131.0 ($C^{3,3',5,5'}$), 140.0 ($C^{Ph,i}$), 130.3 ($C^{Ph,o}$), 129.1 ($C^{Ph,m}$), 123.9 ($C^{Ph,p}$), 105.4 ($C^{4,4'}$), 66.0(CH^a), 61.1 (N-$\underline{CH_2}^{Myr}$), 44.2 (C^b), 42.4 (C^c), 38.1 (C^e), 33.1 (C^h), 28.7, 23.2 (Me^g), 26.6 (C^d), 20.5 (C^f), 13.7, 12.9 ($Me^{3,3'}$), 10.0, 9.9 ($Me^{5,5'}$), 3.6 (Zn-$CH_2Si\underline{Me_3}$), -9.9 (Zn$\underline{C}H_2SiMe_3$). $[\alpha]_D^{25}$ = -4.3 (*c* 1.00, EtOH). $[\alpha]_D^{25}$ = -9.1 (*c* 1.00, EtOH). Mass spectrum (FAB): (*m*/*z* assignment, % intensity): 684,3 $[ZnCH_2SiMe_3(bpmy) + H]^+$, 100.

Synthesis of [ZnMe(κ^3-(-)-*cis*-bpmyO)] (9). In a 250 cm^3 Schlenk tube the complex **7** (1.5 g, 2.45 mmol) was dissolved in dry *n*-hexane (25 cm^3). After 72 hours at room temperature in an air atmosphere were obtained pale orange crystals suitable for X-ray diffraction corresponding to **9**. Yield: 0.42 g, 37%. Anal. Calcd. for $C_{23}H_{35}ON_5Zn$: C, 59.67; H, 7.62; N, 15.13. Found: C, 59.75; H, 7.48; N, 15.22. mp 177-179 °C. ^{1}H NMR (C_6D_6, 297 K), δ 6.67 (s, 1H, CH^a), 5.24, 5.23 (s, 2H, $H^{4,4'}$), A 3.89, B 3.67, X 2,83 [ABX, J_{AB} = 12.2, J_{AX} = 7.8, J_{BX} = 8.2 Hz (N-$\underline{CH_2}^{Myr}$, H^c)], 2.39, 2.00 (m, 2H, H^d), 2.24 (m, 1H, H^b), 2.08, 2.04 (s, 6H, $Me^{3,3'}$), 1.80 (m, 2H, H^e), 1.78, 1.77 (s, 6H, $Me^{5,5'}$), 1.70 (m, 1H, H^f), 1.25, 1.22 (s, 6H, Me^g), 2.10, 1.00 (d, 2H, H^h), 0.12 (s, 1H, Zn-Me). ^{13}C-{^{1}H} NMR (C_6D_6, 297 K), δ 166.0 (C=O), 149.0, 141.0, 132.0, 130.0 ($C^{3,3'5,5'}$), 71.0 (CH^a), 51.0 (N-$\underline{CH_2}$), 44.5 (C^b), 43.0 (C^c), 39.0 (C^e), 34.0 (C^h), 31.0, 24.0 (Me^g), 27.0 (C^d), 20.5 (C^f), 14.0, 12.5 ($Me^{3,3'}$), 10.0, 9.9 ($Me^{5,5'}$), -16.0 (ZnMe). $[\alpha]_D^{25}$ = -3.3 (*c* 1.00, EtOH). Mass spectrum (FAB): (*m*/*z* assignment, % intensity): 829,4 $[Zn(bpmyO)_2 + H]^+$, 100; 462,2 $[ZnMe(bpmyO) + H]^+$, 23.

3) Spectroscopy details of compounds 1−6c and complexes 7−9

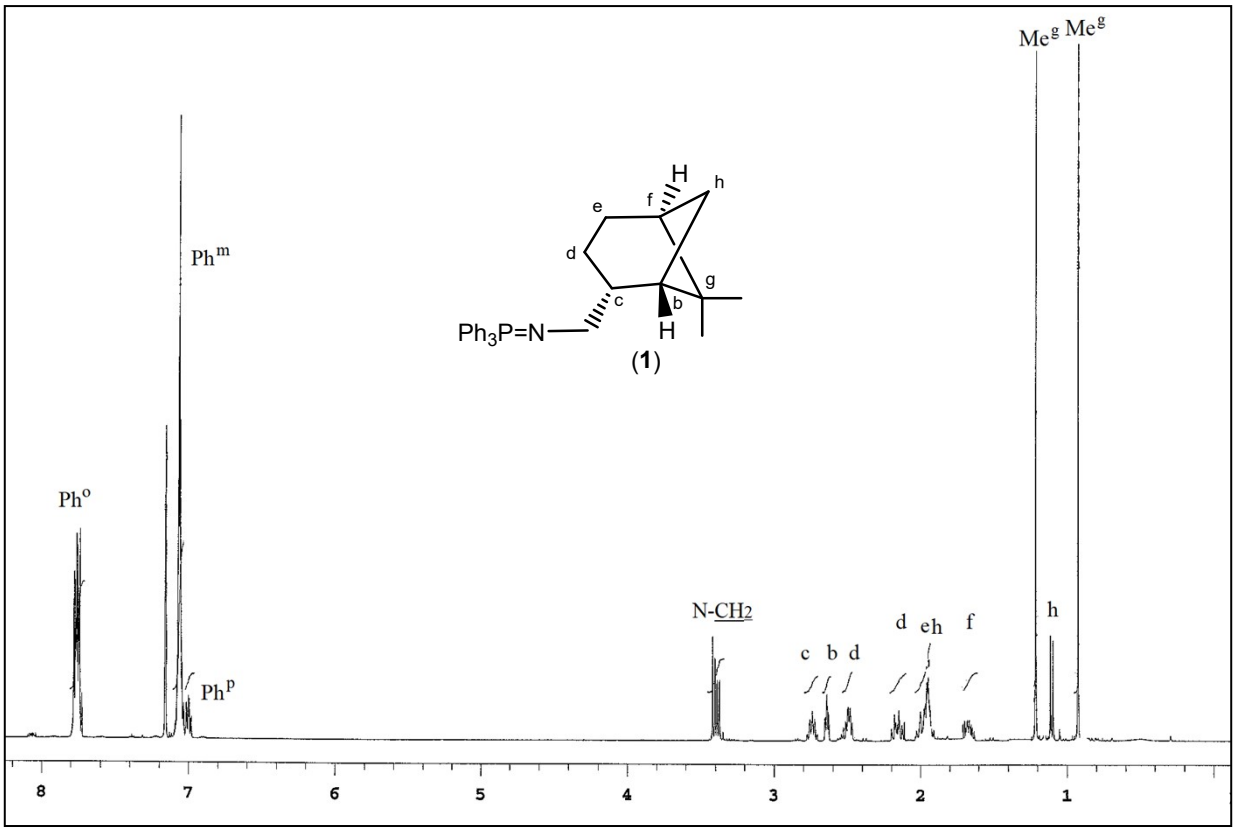


Figure S1a. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **1**.

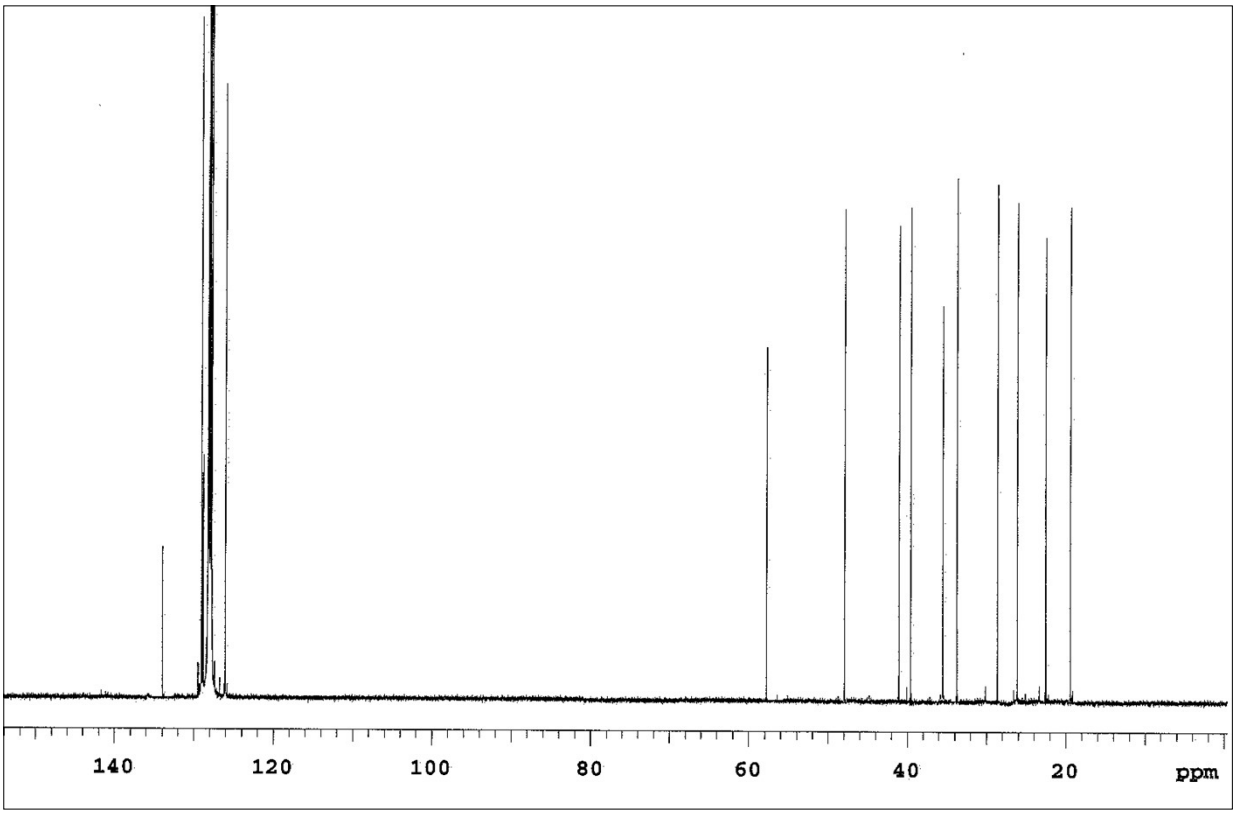


Figure S1b. ^{13}C-{^{1}H} NMR (125 MHz, 298 K, C_6D_6) spectrum of compound **1**.

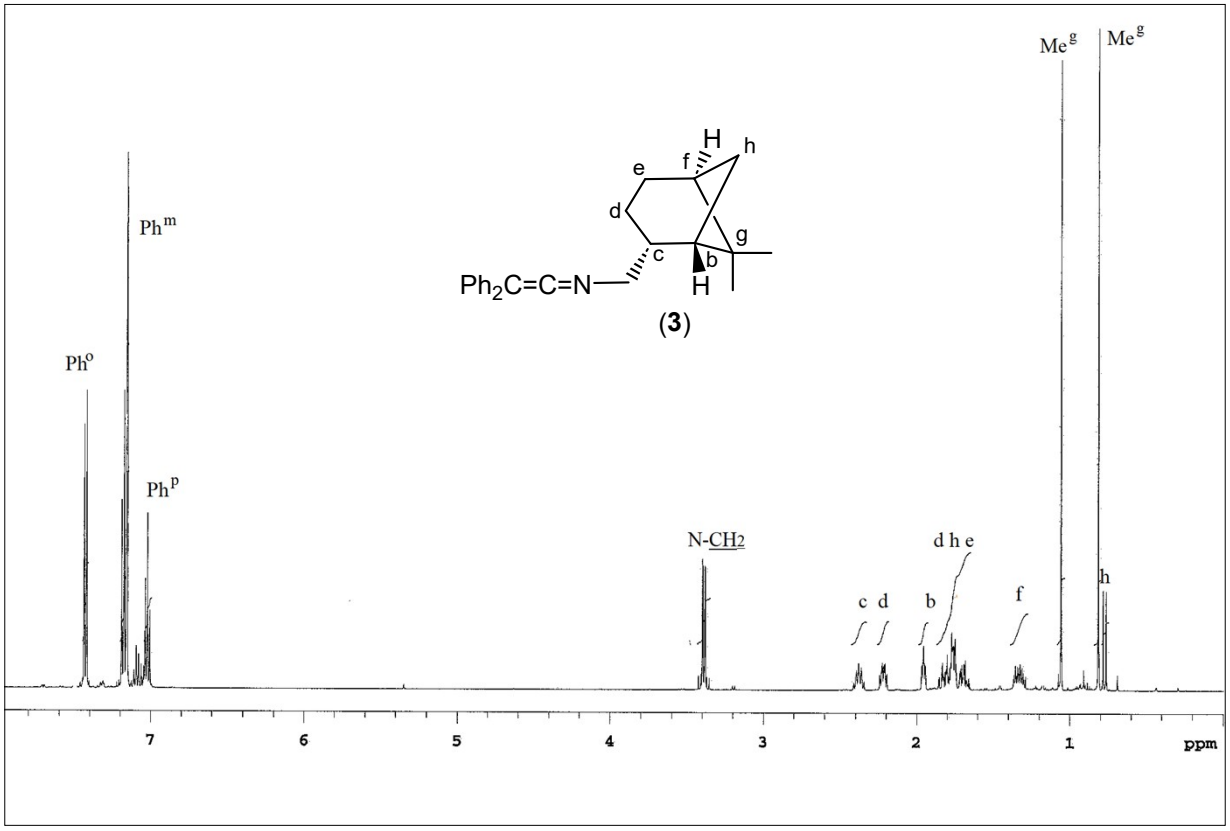


Figure S2a. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **3**.

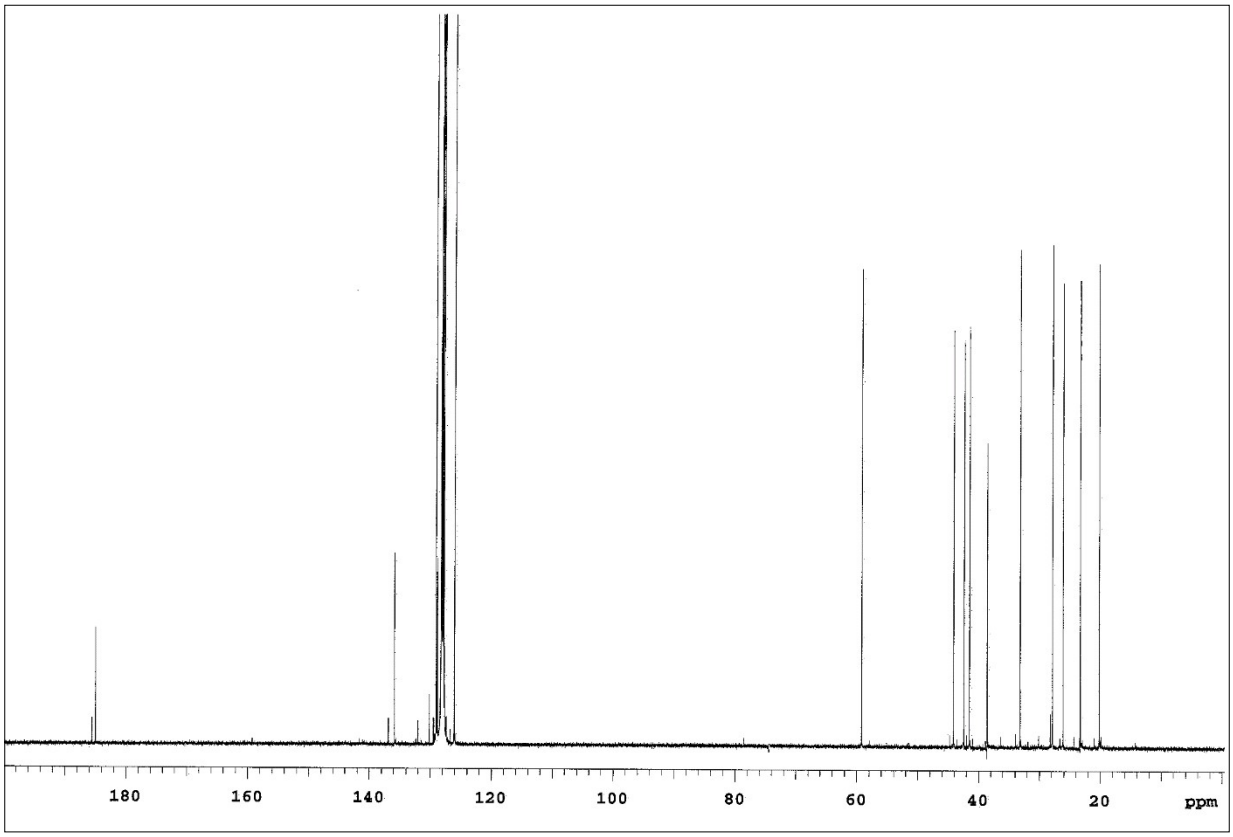


Figure S2b. ^{13}C-{^{1}H} NMR (125 MHz, 298 K, C_6D_6) spectrum of compound **3**.

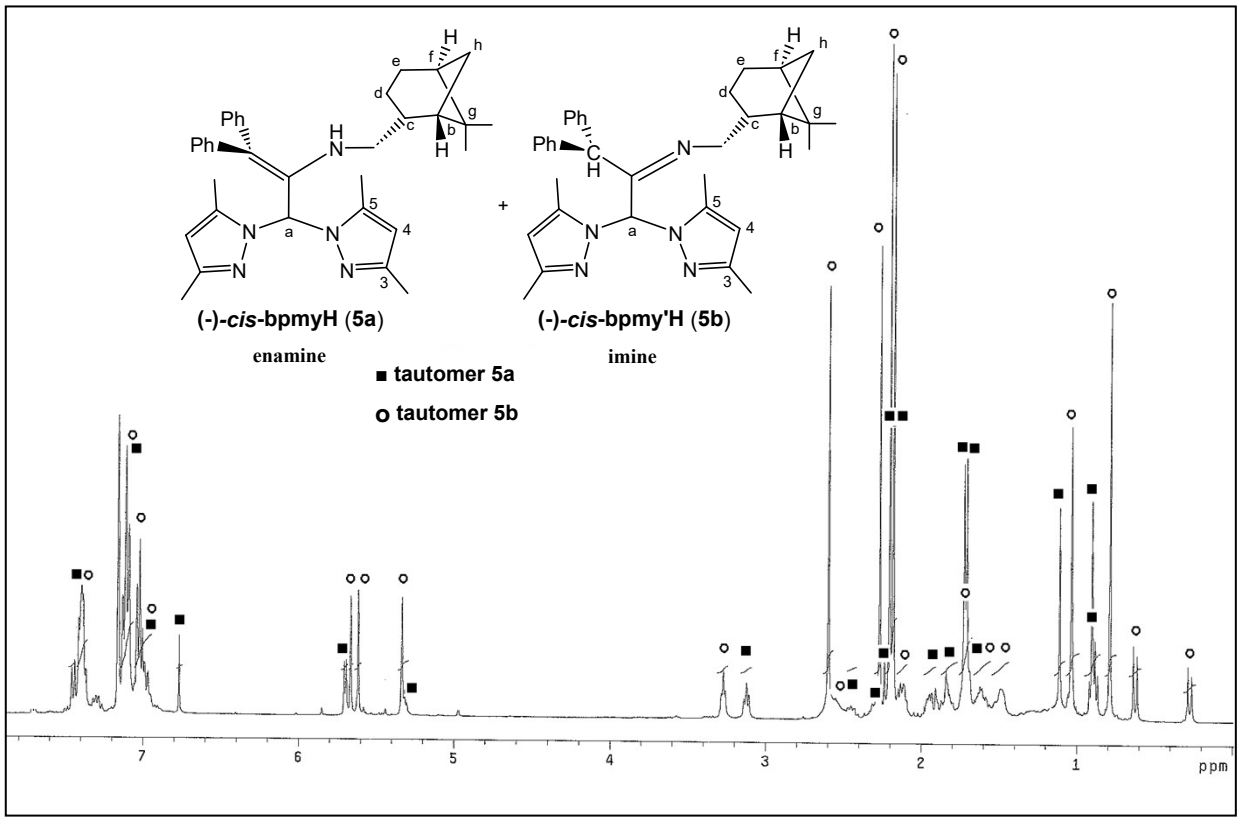


Figure S3a. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **5** (as a mixture of tautomers).

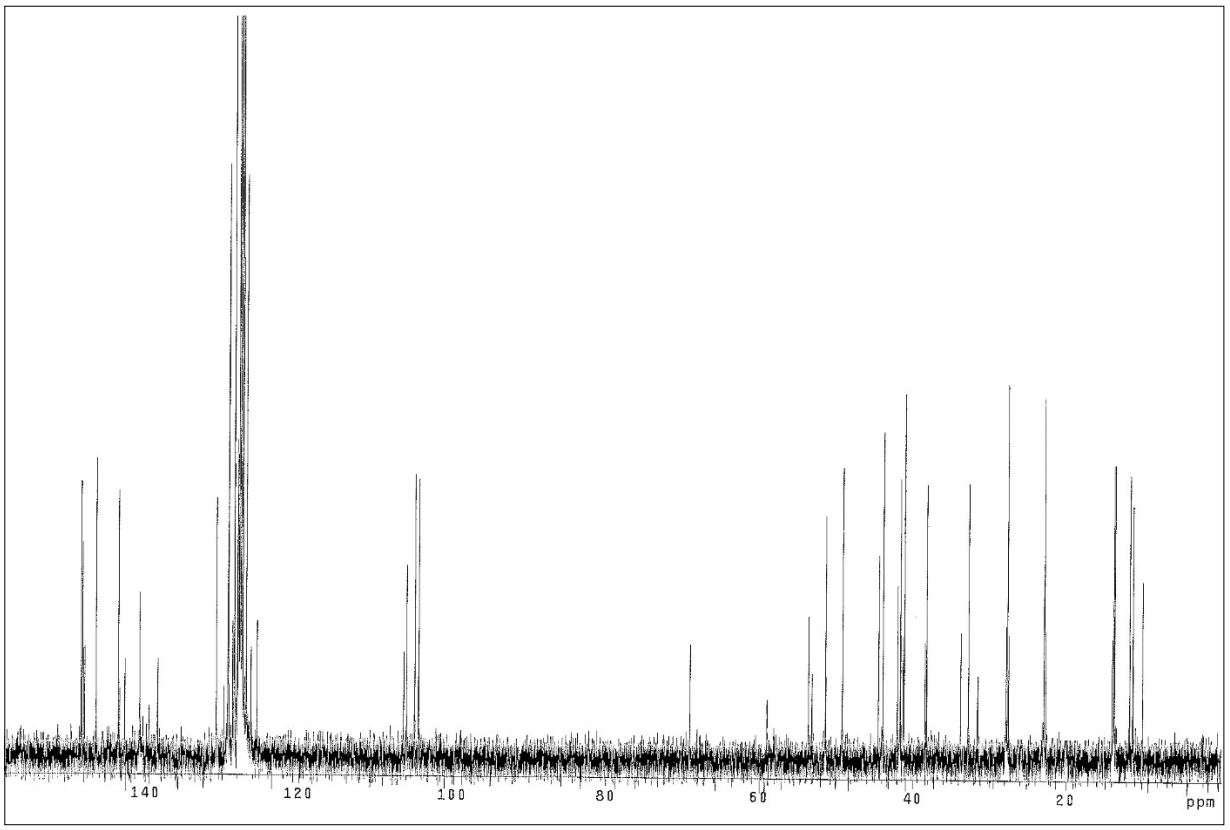


Figure S3b. ^{13}C-{^{1}H} NMR (125 MHz, 298 K, C_6D_6) spectrum of compound **5** (as a mixture of tautomers).

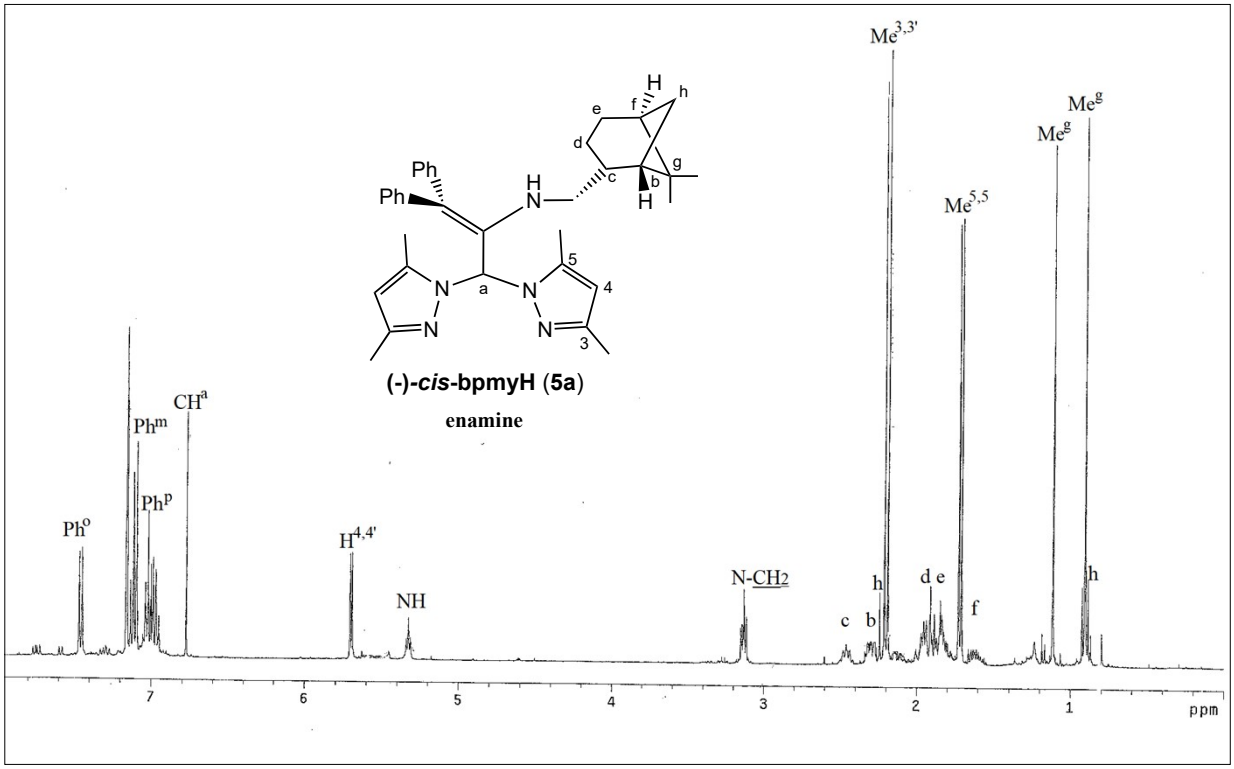


Figure S3c. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **5a**.

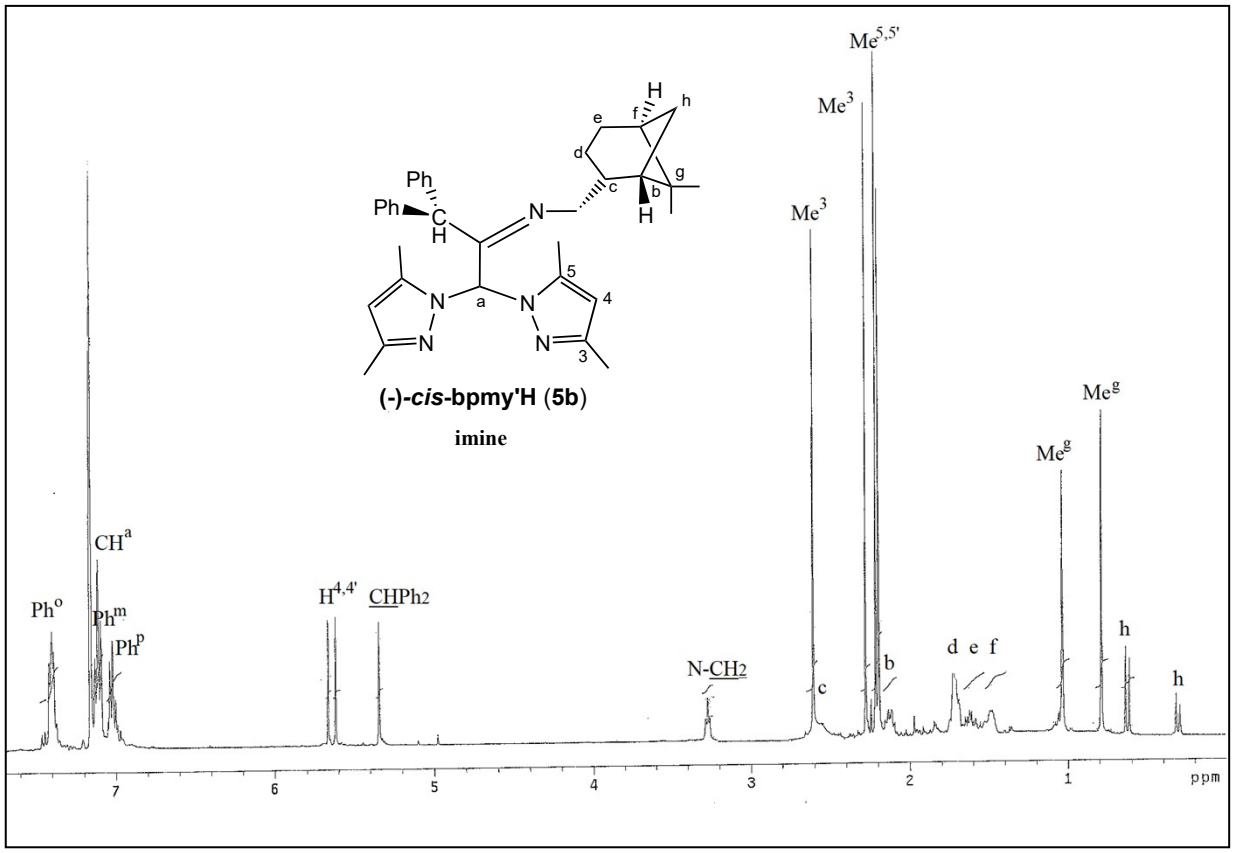


Figure S3d. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **5b**.

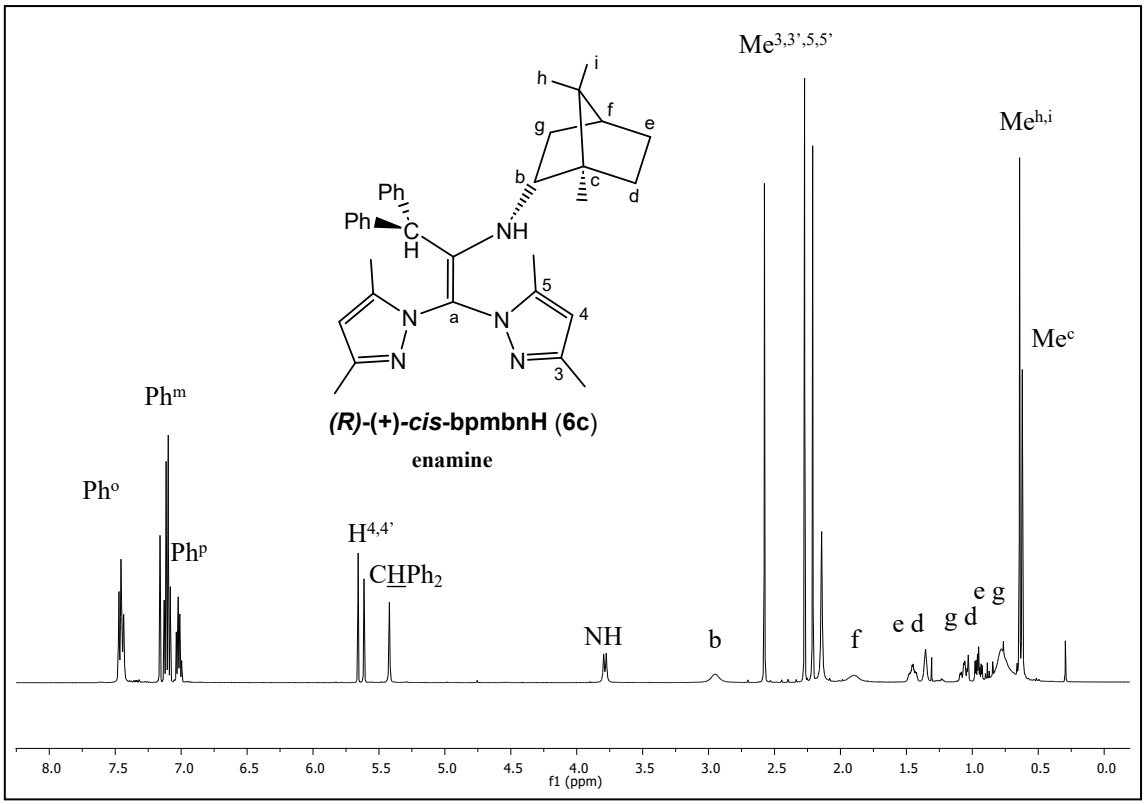


Figure S4a: ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **6c**.

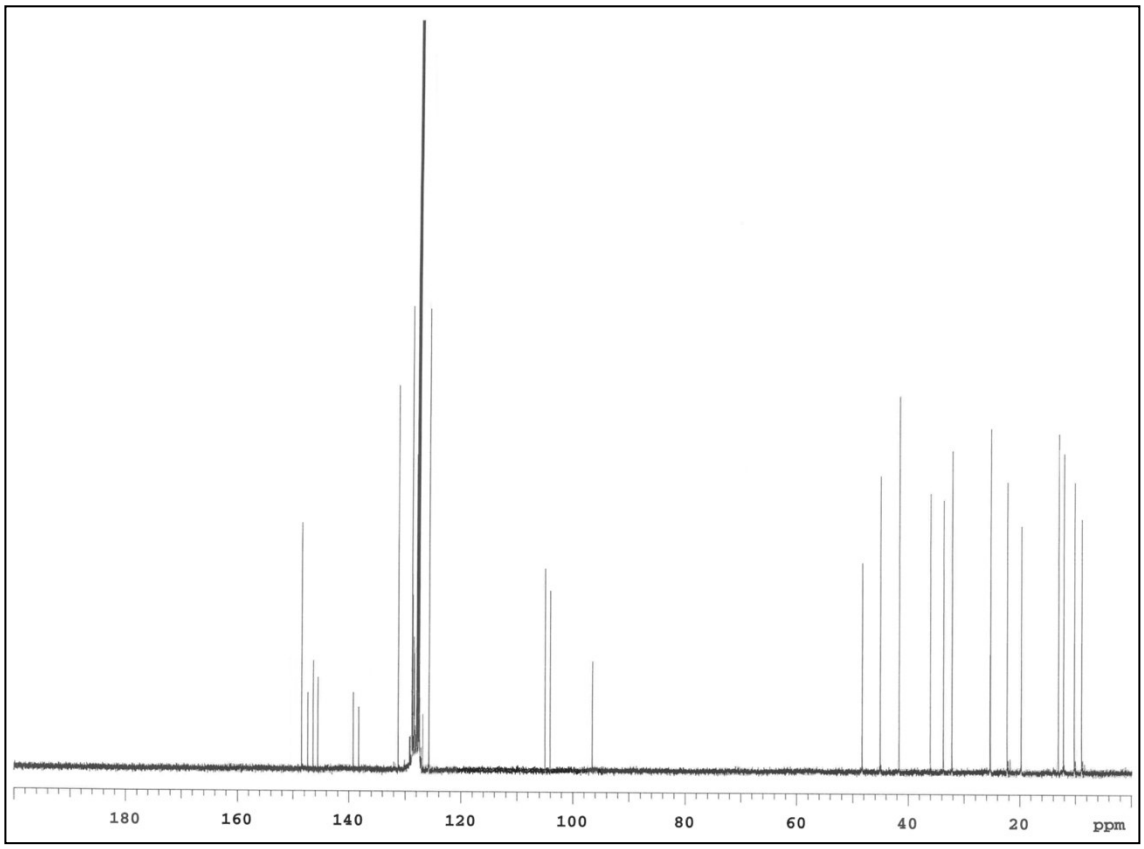


Figure S4b. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **6c**.

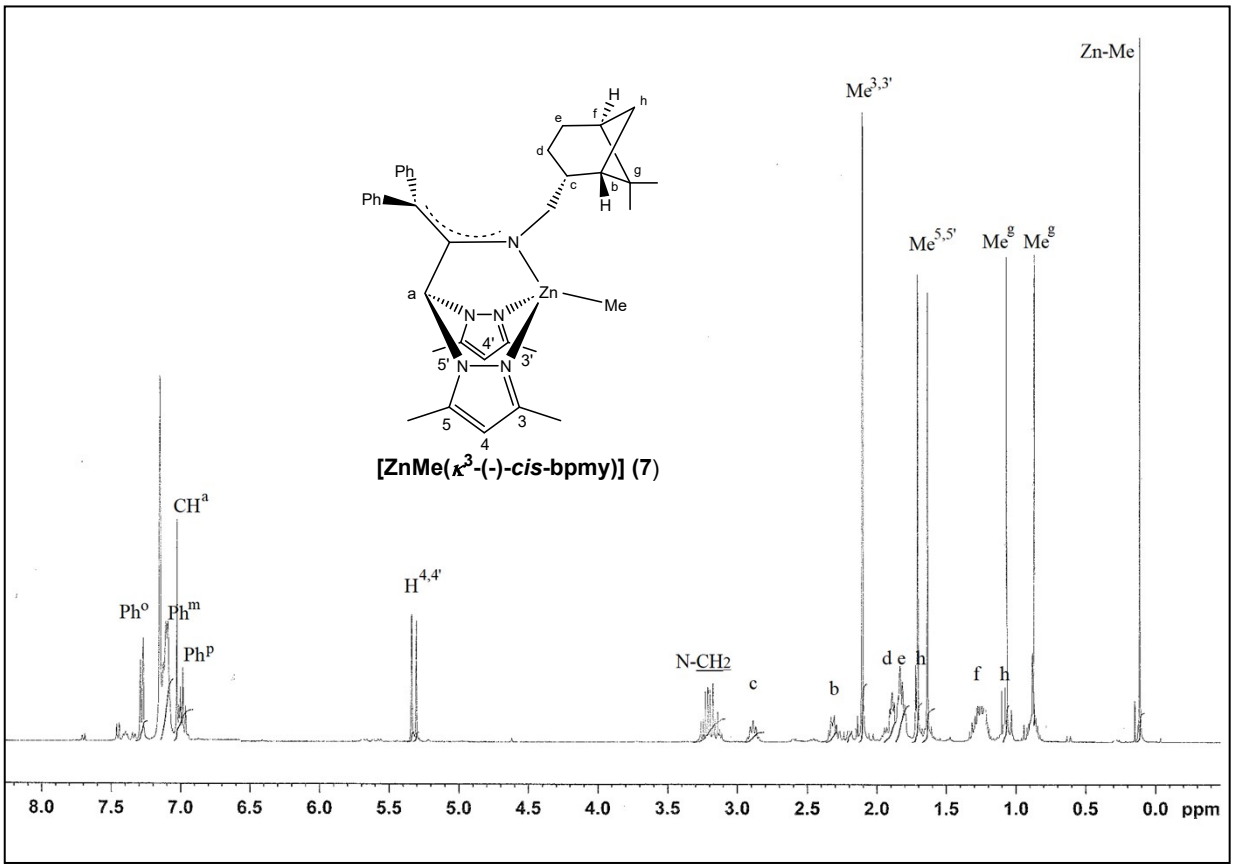


Figure S5a. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **7**.

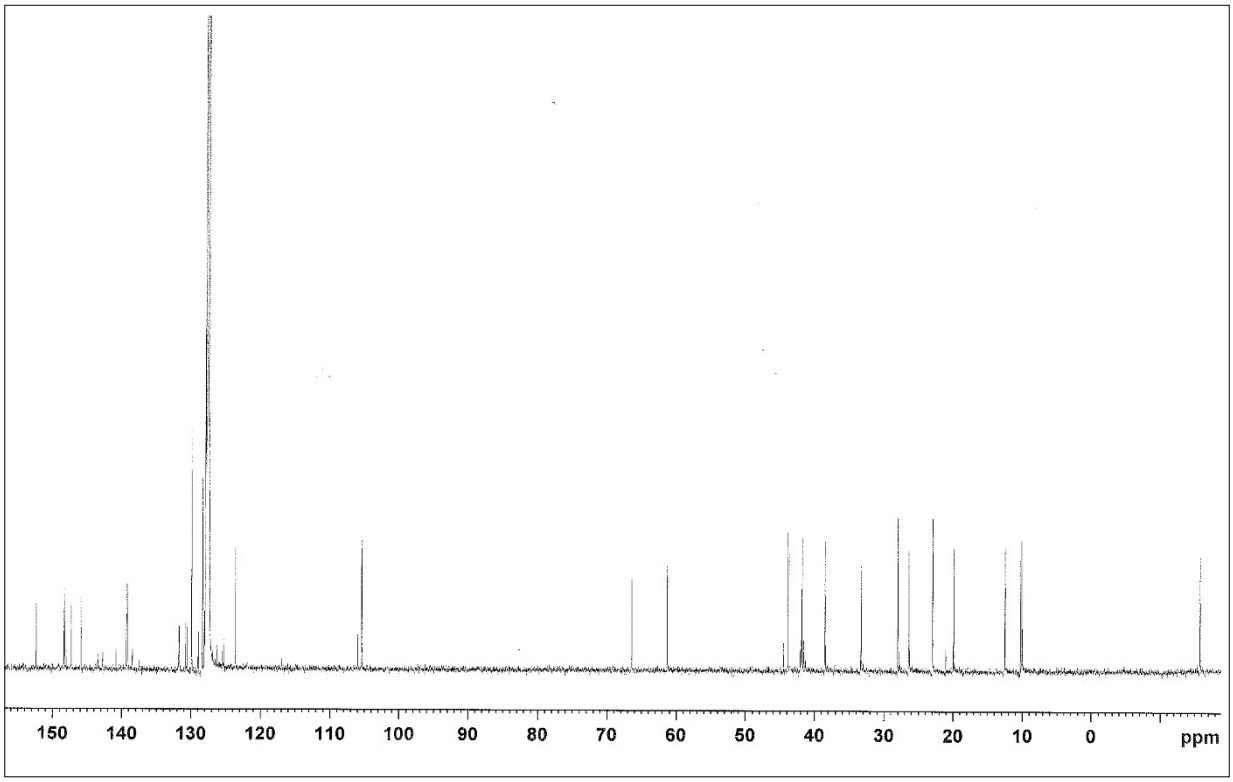


Figure S5b. ^{13}C-{^{1}H} NMR (125 MHz, 298 K, C_6D_6) spectrum of compound **7**.

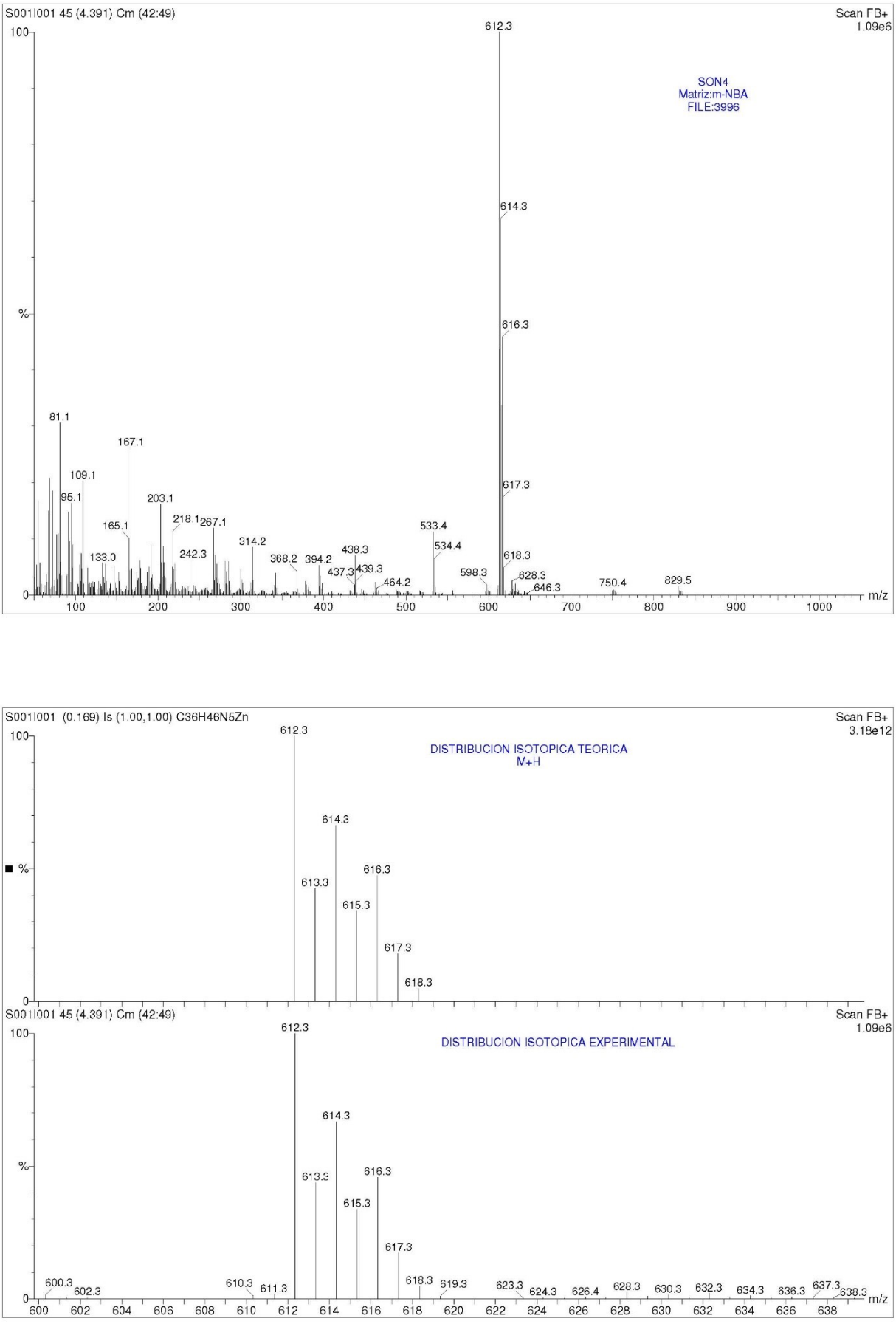


Figure S5c. Mass spectra for compound **7**.

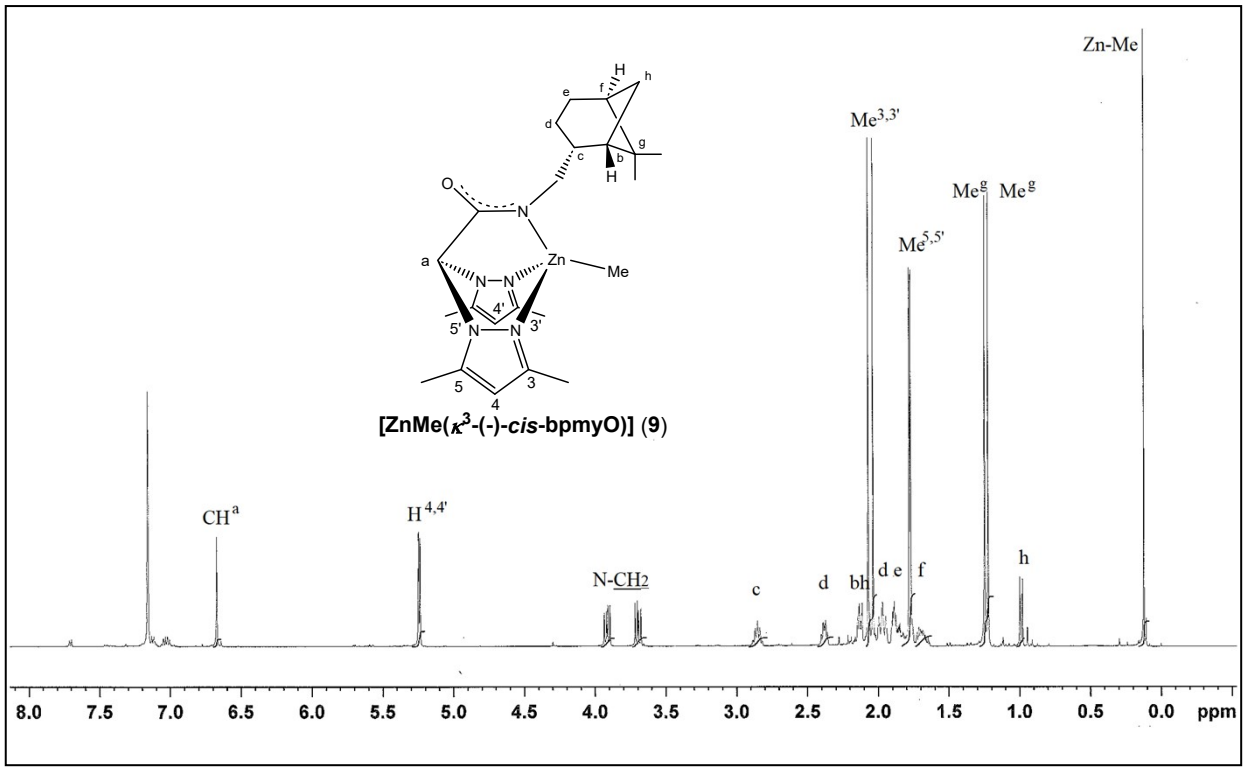


Figure S6a. ^{1}H NMR (500 MHz, 298 K, C_6D_6) spectrum of compound **9**.

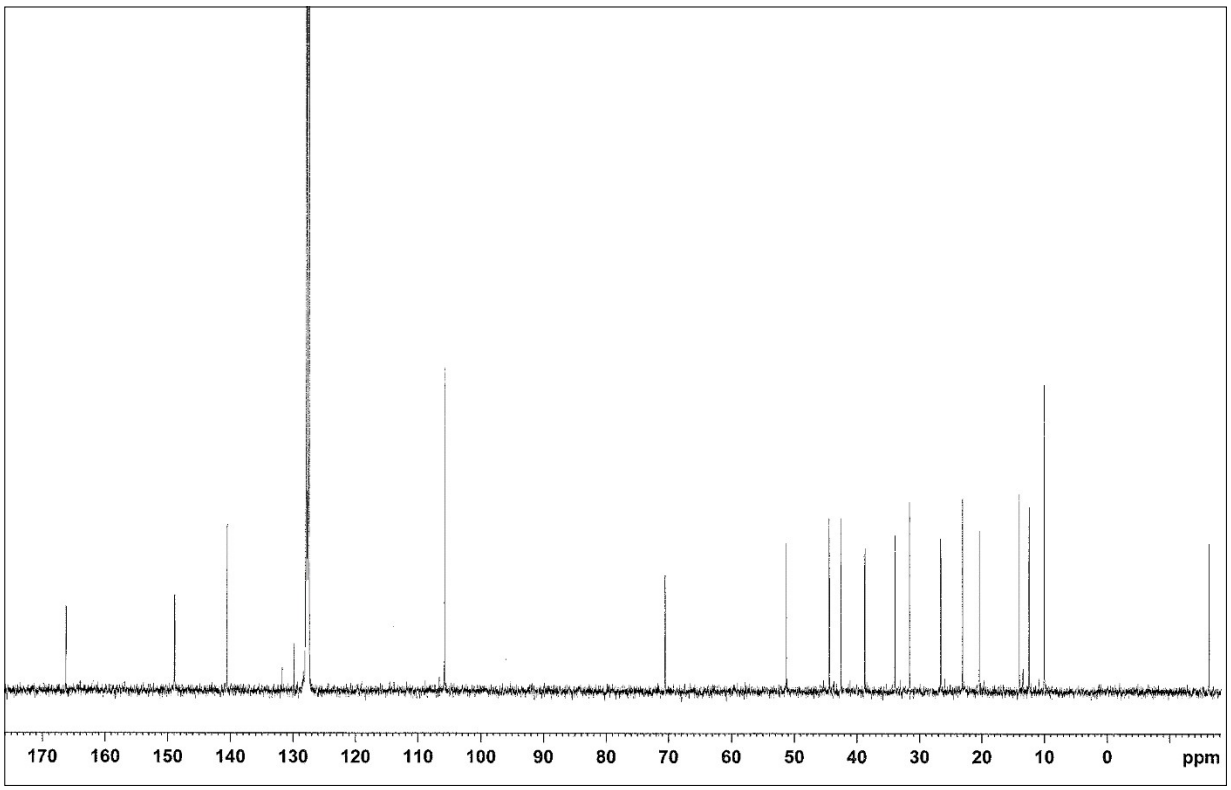
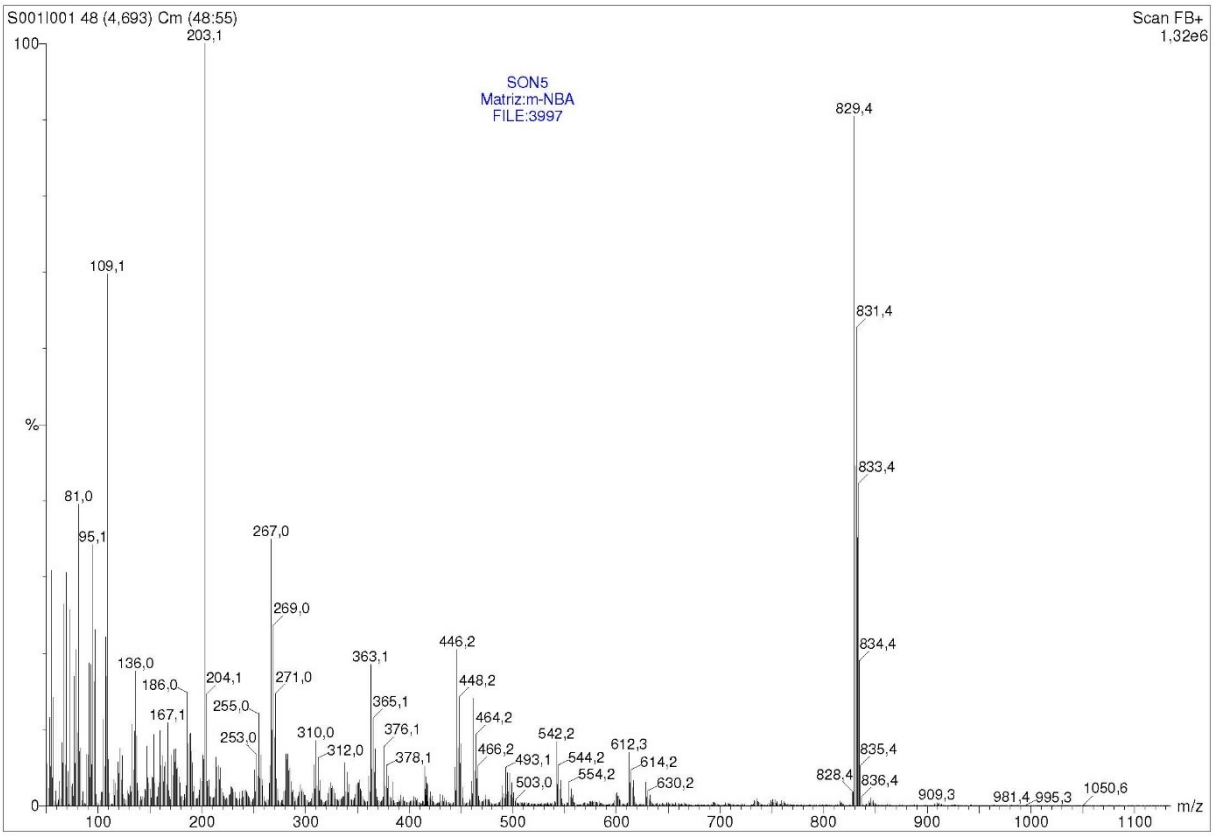


Figure S6b. ^{13}C-{^{1}H} NMR (125 MHz, 298 K, C_6D_6) spectrum of compound **9**.


S001l001 48 (4,693) Cm (48:55)
Scan FB+
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SON5
Matriz:m-NBA
FILE:3997
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109,1
831,4
833,4
81,0
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544,2
614,2
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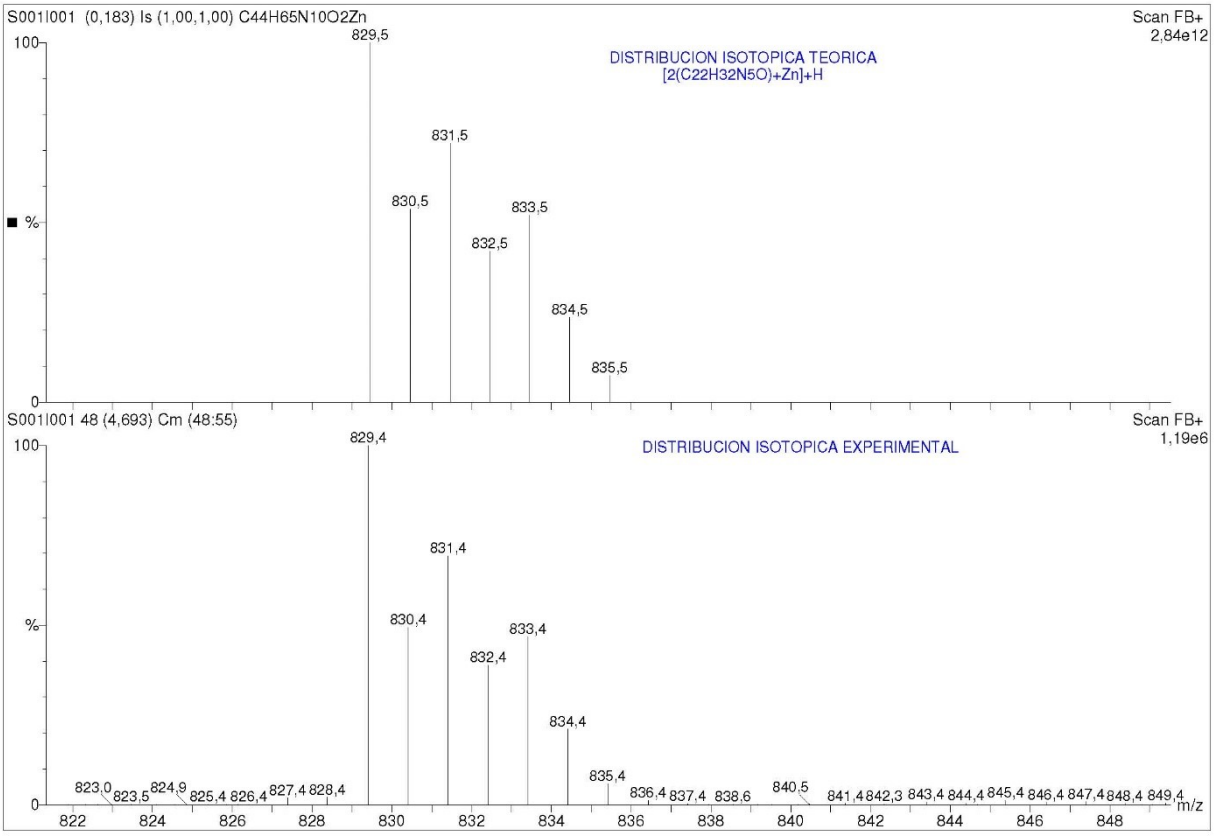
836,4
909,3
981,4
995,3
1050,6
%
m/z


S001l001 (0,183) Is (1,00,1,00) C44H65N10O2Zn
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2,84e12
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DISTRIBUCION ISOTOPICA TEORICA
[2(C22H32N5O)+Zn]+H
831,5
830,5
833,5
832,5
834,5
835,5
%
S001l001 48 (4,693) Cm (48:55)
Scan FB+
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829,4
DISTRIBUCION ISOTOPICA EXPERIMENTAL
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832,4
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838,6
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845,4
846,4
847,4
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%
m/z

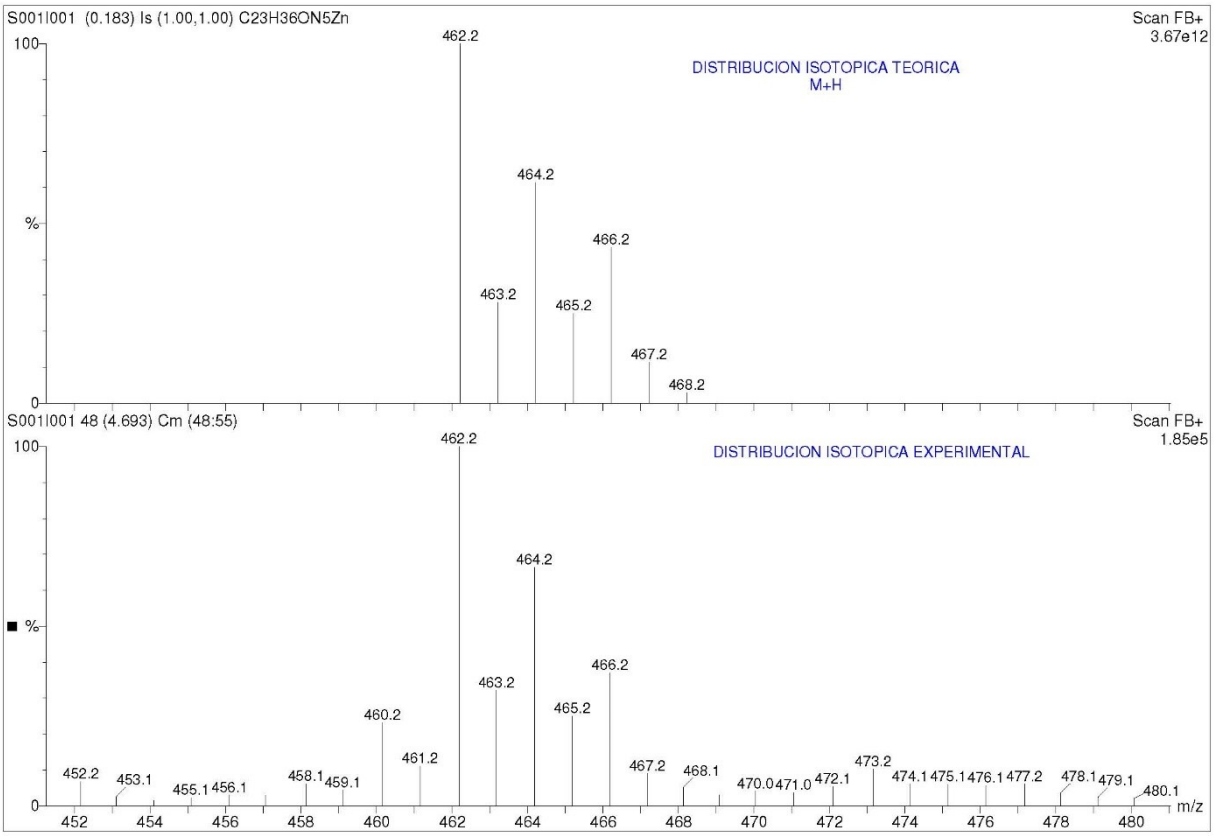


Figure S6c. Mass spectra of compound **9**.

4) X-Ray Diffraction Studies: Crystallographic structure determination for the compound 6c and complex 9.

Details for crystallographic studies

X-ray Crystallography. All diffraction data were collected using a Bruker D8 KAPPA APEX II diffractometer with CCD area-detector system equipped with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 100 K at SCXRD Laboratory (SIdI) at Universidad Autónoma de Madrid. Absorption corrections for all data sets were performed with the multiscan procedure SADABS.[4]; Raw intensity data frames were integrated with the SAINT[5] program, which also applied corrections for Lorentz and polarization effects. Data for complexes **6c** and **9** were deposited in the Cambridge Crystallographic Data Centre under numbers CCDC 2350072 and 1915940, respectively.

The crystals were selected and mounted with inert oil and attached to the tip of a MiTeGen mount.

The software package WINGX[6] was used for structure solution and refinement by full-matrix least-squares methods based on F^2. A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. The complex **9** crystallises with one molecule of hexane in the asymmetric unit disordered over two positions. DFIX restrain and isotropic refinement were necessary for this molecule. All non-hydrogen atoms were refined with anisotropic displacement coefficients unless specified otherwise. All hydrogen atoms were included in the structure factor calculation at idealised positions and were allowed to ride on the neighbouring atoms with relative isotropic displacement coefficients.

Final R(F), wR(F^2) and goodness-of-fit agreement factors, details on the data collection and analysis for **6c** and **9** can be found in Table S1 in this section.

Table S1. Crystal data and structure refinement for **6c** and **9**

Identification code	**6c**	**9**
Empirical formula	C_{35} H_{43} N_5	C_{29} H_{49} N_5 O Zn
Formula weight	533,76	549.12
Temperature	100(2) K	110(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P1	P 2_1
Unit cell dimensions	a = 9.5508(4) Å b = 10.8747(5) Å c = 16.5110(7) Å α= 76.766(2)º β= 84.633(2)º γ = 68.232(2)º	a = 7.9364(9) Å b = 21.825(2) Å c = 17.4095(17) Å α= 90º β= 93.640(6)º γ = 90 º
Volume	1550.22(12) Å	3009.4(5) Å
Z	1	4
Density (calculated)	1.143 Mg/m^3	1.212 Mg/m^3
Absorption coefficient	0.068 mm^{-1}	0.845 mm^{-1}
F(000)	576	1184
Crystal size	0.48 × 0.32 × 0.18 mm^3	0.36 × 0.20 × 0.18 mm^3
Theta range for data collection	2.063 to 26.370°	2.344 to 26.368°
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20	-9 ≤ h ≤9, -27 ≤ k ≤ 24, -21 ≤ l ≤21
Reflections collected	55265	33635
Independent reflections	12570 [R(int) = 0.0348]	11609 [R(int) = 0.0969]
Completeness to theta = 25.242º	99.9 %	99.9 %
Absorption correction	Multi-scan (SADABS)	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.7214	0.745 and 0.577
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	12570 / 3 / 735	11609 / 596 / 652
Goodness-of-fit on F^2	1.024	0.862
Final R indices [I>2sigma(I)]	R_1 = 0.0394, wR_2 = 0.1000	R_1 = 0.0612, wR_2 = 0.1387
R indices (all data)	R_1 = 0.0453, wR_2 = 0.1042	R_1 = 0.1380, wR_2 = 0.1849
Largest diff. peak and hole	0.253 and -0.231 e.$Å^{-3}$	0.389 and -0.656 e.$Å^{-3}$

5) Ring-opening polymerisation of *rac*-lactide details:

Typical polymerization procedures

Polymerisations of *rac*-lactide (LA) were performed on a Schlenk line in a flame-dried Schlenk tube equipped with a magnetic stirrer. The Schlenk tubes were charged in a glovebox with the required amount of LA and initiator, separately, and then attached to the vacuum line. The initiator and LA were dissolved in the appropriate amount of solvent and temperature equilibration was ensured in both Schlenk tubes by stirring the solutions for 15 min in a bath. Next, the appropriate amount of initiator was added by using a syringe and polymerization times were measured from that point. Polymerizations were stopped by injecting a solution of acetic acid in water (0.35 M). Polymers were precipitated in methanol, filtered off, redissolved and reprecipitated in methanol, and dried in vacuo to a constant weight.

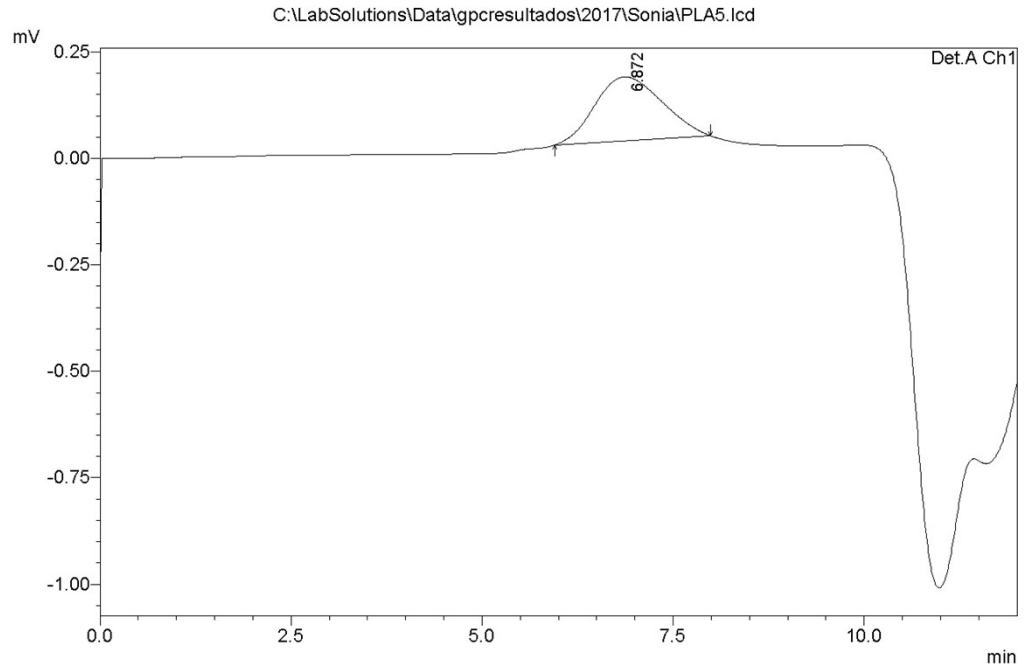
09/03/2019 17:42:48 1 / 2

==== Shimadzu LCsolution Analysis Report ====

C:\LabSolutions\Data\gpcresultados\2017\Sonia\PLA5.lcd

Acquired by	: Admin
Sample Name	: PLA5
Sample ID	: PLA5
Vail #	:
Injection Volume	: 20 uL
Data File Name	: PLA5.lcd
Method File Name	: metodo_2017_Alberto.lcm
Batch File Name	: SingleRun120170425171458.lcb
Report File Name	: Default.lcr
Data Acquired	: 25/04/2017 16:15:34
Data Processed	: 06/03/2019 19:05:28

<Chromatogram>



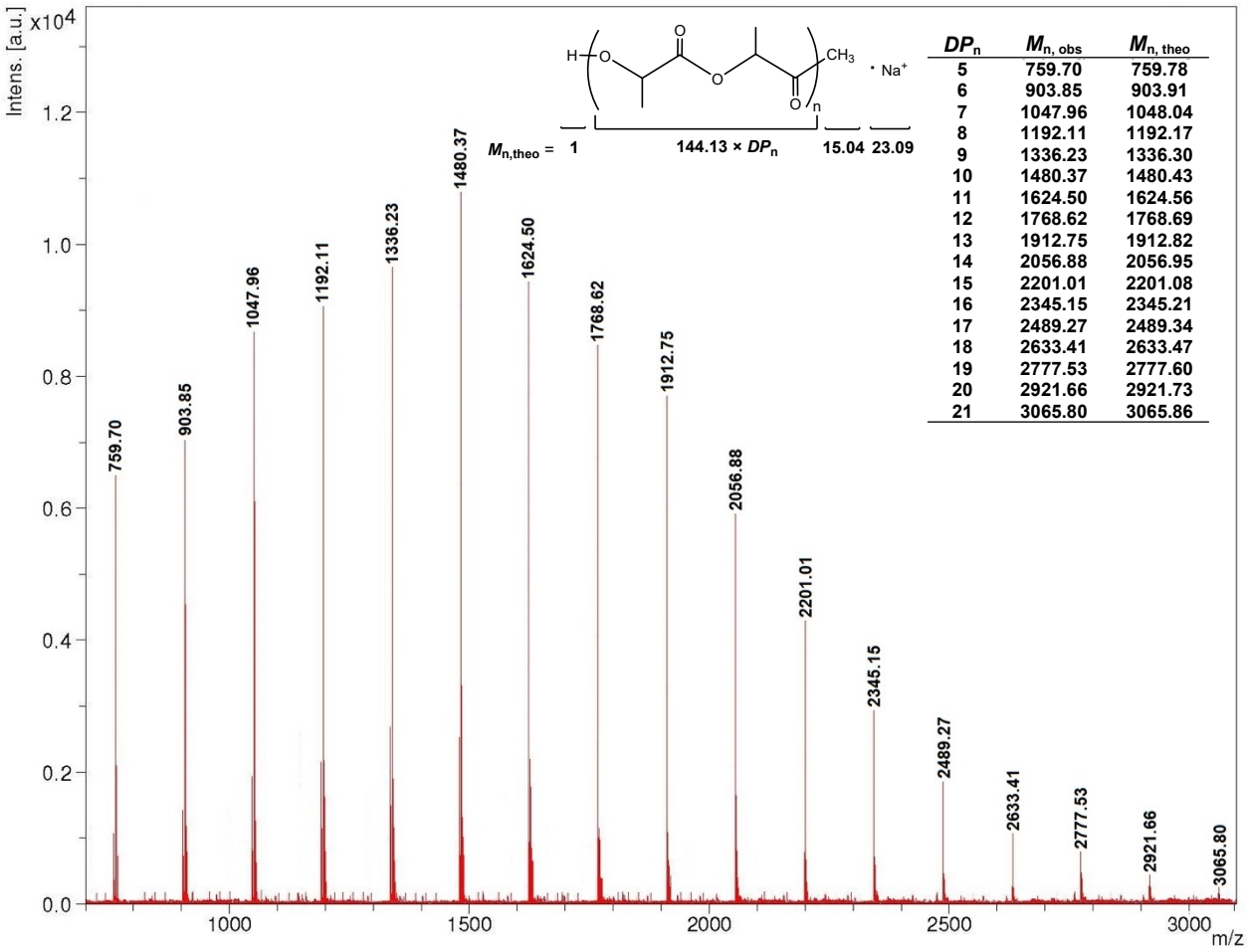
1 Det.A Ch1/

GPC Summary

Chromatogram Det.A Ch1

#	Title	Mn	Mw	Mw/Mn	Intrinsic Viscosity
1	PLA5.lcd	8187	10029	1.22501	1.00000
	Average	8187	10029	1.22501	1.00000
	%RSD	0.000	0.000	0.000	0.000
	Maximum	8187	10029	1.22501	1.00000
	Minimum	8187	10029	1.22501	1.00000
	SD	0	0	0.00000	0.00000

Figure S7. GPC trace corresponding to a poly(*rac*-lactide) (Table 2, entry 7) prepared with catalyst **9**.



DP_n	$M_{n,obs}$	$M_{n,theo}$
5	759.70	759.78
6	903.85	903.91
7	1047.96	1048.04
8	1192.11	1192.17
9	1336.23	1336.30
10	1480.37	1480.43
11	1624.50	1624.56
12	1768.62	1768.69
13	1912.75	1912.82
14	2056.88	2056.95
15	2201.01	2201.08
16	2345.15	2345.21
17	2489.27	2489.34
18	2633.41	2633.47
19	2777.53	2777.60
20	2921.66	2921.73
21	3065.80	3065.86

Figure S8. Selected area of MALDI-ToF mass spectrum of PLA sample obtained with $[rac\text{-LA}]_0/[\mathbf{7}]_0 = 25$; theoretical molecular weights calculated according to the equation: $M_n = (DP_n \times M_{wLA}) + M_{wMeH} + M_{wNa}$, where DP_n is the degree of polymerization, $M_{wLA} = 144.13$, $M_{wMeH} = 16.04$ and $M_{wNa} = 23.09$ g·mol^{-1}.

The distribution in the spectrum indicates the existence of a single family of polymer chains capped by –CH(CH$_3$)OH and CH$_3$–OC–CH(CH$_3$)– *termini*, corresponding to oligomers of formula H(OCHMeCO)$_{2n}$(CH$_3$)·Na$^+$ (n = 5 to 21) with consecutive peaks separated by increments of 144 Da. Moreover, neither intermolecular ester-exchange (transesterification) reactions nor cyclic oligomers were detected.

Model	PsdVoigt1		
Equation	y = y0 + A * (mu * (2/PI) * (w / (4*(x-xc)^2 + w^2)) + (1 - mu) * (sqrt(4*ln(2)) / (sqrt(PI) * w)) * exp(-(4*ln(2)/w^2)*(x-xc)^2))		
Reduced Chi-Sqr	23.94472		
Adj. R-Square	0.9941		
y0	0.61224	–	--
Tetrad		**Value**	**Standard Error**
isi	xc	5.14979	0.00159
	Area	**0.4179**	**0.05602**
	w	0.00537	5.40661E-4
	mu	1.14093	0.15362
iii	xc	5.16042	1.74116E-4
	Area	**3.12286**	**0.0827**
	w	0.00748	8.06226E-5
	mu	0.7948	0.0462
iis	xc	5.1716	0.00295
	Area	**0.17782**	**0.08649**
	w	0.0086	0.00147
	mu	0.19693	0.86038
sii	xc	5.20645	0.00199
	Area	**0.22867**	**0.07449**
	w	0.00789	5.93563E-4
	mu	0.18614	0.68595
sis	xc	5.22105	1,16108E-4
	Area	**0.23957**	**0.04633**
	w	0.00532	4.40167E-4
	mu	0.59822	0.36538

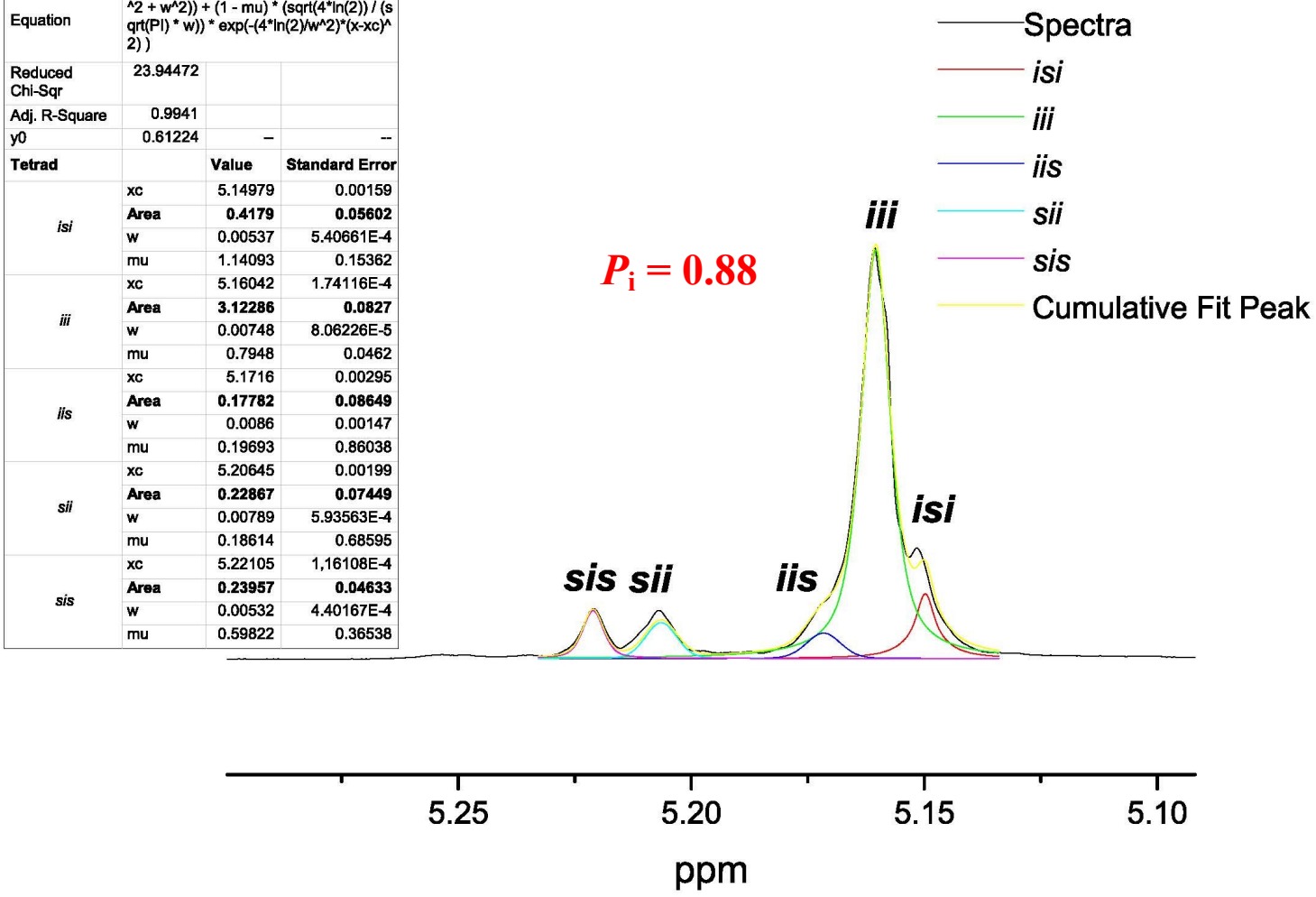


Figure S9. Deconvoluted ^{1}H NMR spectra (500 MHz, 298 K, $CDCl_3$) of the homodecoupled C*H* resonance of poly(*rac*-lactide) prepared employing [ZnMe(κ^3-(-)-*cis*-bpmy)] (**7**) as catalyst in tetrahydrofuran at 50 ºC for 2.5 h. The tacticity of the polymer was assigned using the methine signals with homonuclear decoupling as described by Hillmyer and co-workers.[7]

Table S2: Tetrads area distribution and P_i value calculation.[a]

	sis	*sii*	*iis*	*iii*	*isi*	
	Experimental Normalized Values					
	0.057	0.055	0.042	0.746	0.100	
	Theoretical Values					**Differences of squares**
P_i	$[P_i^2(1-P_i)+P_i(1-P_i)^2]/2$			$[P_i^2(1-P_i)^2+P_i^3+(1-P_i)^3]/2$	$[P_i(1-P_i)+P_i(1-P_i)]/2$	
0.87	0.05655	0.05655	0.05655	0.71725	0.1131	0.046
0.88	0.0528	0.0528	0.0528	0.736	0.1056	0.030
0.89	0.0490	0.0490	0.0490	0.7553	0.0979	0.031

[a] The relative theoretical tetrad proportions are based on an enantiomorphic site control statistics as proposed by Ovitt and Coates.[8] The best experimental P_i value is estimated by minimizing the sum of absolute differences between experimental and predicted squared values.

6) Experimental details for the synthesis of cyclic carbonates

General procedures for catalytic studies

General procedure for catalyst screening at 1 bar pressure

Styrene oxide **10a** (1.24 mmol), complexes **7**−**9** (62 μmol) and TBAB (20 mg, 62 μmol) were placed in a sample vial fitted with a magnetic stirrer bar and placed in a large conical flask. Cardice pellets were added to the conical flask, which was fitted with a rubber stopper pierced by a deflated balloon. The reaction mixture was stirred at 25 ºC for 24 h, then the conversion of styrene oxide **10a** to styrene carbonate **11a** was determined by analysis of a sample by ^{1}H-NMR spectroscopy.

General procedure for the synthesis of cyclic carbonates compounds 11a−11i, 11j−11o and 11p at 10-20 bar pressure

An epoxide **10a**−**10i** or **10j**−**10o**, (24.8-3.10 mmol), catalyst **7** (37.9 mg, 62.0 μmol) and TBAB (20 mg, 62.0 μmol) were placed in stainless steel reactor with a magnetic stirrer bar. The reactor was pressurized to 10−20 bar of carbon dioxide and the reaction mixture was stirred at 50−100 ºC for 1.5−24h. After that, the reactor was cooled down to ambient temperature and depressurized, and the conversion of these epoxides into cyclic carbonates **11a**−**11i** and **11j**−**11o** was determined by analysis of a sample by ^{1}H-NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated *under vacuum* to give either the pure cyclic carbonate or a mixture of cyclic carbonate and unreacted epoxide. In the latter case, the mixture was purified by flash chromatography using a solvent gradient as follows: hexane, hexane-EtOAc (9:1), hexane-EtOAc (6:1), hexane-EtOAc (3:1) and finally EtOAc to give the pure cyclic carbonate. Cyclic carbonates **11a**−**11i** or **11j**−**11o** are all known compounds and the spectroscopic data for samples prepared using catalyst **7** were consistent with those reported in the literature.[9,10]

General procedure for the synthesis of cyclic carbonate 11p

(*R*)-(+)-limonene oxide (*cis* and *trans* mixture) **10p** was previously dried with calcium hydride overnight and distilled under vacuum and stored under nitrogen. Stainless-steel reactor was dried under vacuum at 80 ºC for 18 hours.

In a representative experiment, 0.56 g of (*R*)-(+)-limonene oxide (*cis/trans* mixture) (0.60 mL, 3.68 mmol), catalyst **7** (45.0 mg, 73.6 μmol) and TBAC (61.4 mg, 0.22 mmol) were placed in the dried stainless-steel reactor with a magnetic stirrer bar. The reactor was pressurized to 20 bar of carbon dioxide and the reaction mixture was stirred at 80 ºC for 72 h. After that, the reactor was cooled down to ambient temperature and depressurized, and the conversion of epoxide into cyclic carbonate **11p** was determined by analysis of a sample by ^{1}H-NMR spectroscopy. The remaining sample was filtered through a plug of silica, eluting with CH_2Cl_2 to remove the catalyst. The eluent was evaporated under vacuum and later purified by flash chromatography using a solvent gradient as follows: hexane, hexane-EtOAc (9:1), hexane-EtOAc (6:1), hexane-EtOAc (3:1) and finally EtOAc to give the pure cyclic carbonate. Cyclic carbonate **11p** is a known compound and the spectroscopic data for samples prepared using catalyst **7** were consistent with those reported in the literature.[11]

^{1}H and ^{13}C-{^{1}H} NMR spectroscopic data of compounds 11a−11i, 11j−11o and **11p**

Styrene carbonate (11a). Isolated in 91% yield as a white solid (3.99 g, 98%). ^{1}H NMR ($CDCl_3$, 298 K) δ 7.47-7.33 (m, 5 H, Ar-H), 5.67 (m, 1 H, OC*H*), 4.80 (m, 1 H, OCH_2), 4.34 (m, 1 H, OCH_2). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.8 (*C*=O), 135.7 (C^{ipso}), 129.7, 129.2, 125.8 (Ph), 78.0 (Ph*C*HO), 71.1 (O*C*H_2).

Propylene carbonate (11b). Isolated in 92% yield as a white solid (2.49 g, 99%). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.84 (m, 1 H, OC*H*), 4.54 (m, 1 H, OCH_2), 4.01 (m, 1 H, OCH_2), 1.48 (d, 3 H, $^{3}J_{H-H}$ = 8.0 Hz, OCH_2CH_3). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.0 (O=*C*O), 73.5 (O*C*H), 70.6 (O*C*H_2), 19.3 (OCH_2CH_3).

1,2-Butylene carbonate (11c). Isolated in 93% yield as a colourless liquid (2.84 g, 99 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.70–4.60 (1H, m, OCH), 4.50 (1H, t, $^{3}J_{H-H}$ = 8.1 Hz, OCH_2), 4.10 (1H, dd, $^{3}J_{H-H}$ = 6.3, 5.3 Hz, OCH_2), 1.60–1.90 (2H, m, CH_2), 1.02 (3H, t, $^{3}J_{H-H}$ = 7.1 Hz, CH_3). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.9 (C=O), 78.0 (OCH), 69.1 (OCH_2), 26.9 (CH_2), 8.2 (CH_3).

1,2-Hexylene carbonate (11d). Isolated in 90 % yield as a colourless liquid (3.49 g, 98 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.70 (m, 1 H, OC*H*), 4.52 (m, 1 H, OCH_2), 4.06 (m, 1 H, OCH_2), 1.73 (m, 2 H, CH_2), 1.40 (m, 4 H, CH_2), 0.91 [t, 3 H, $^{3}J_{H-H}$ = 8 Hz, CH_3]. ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.1 (*C*=O), 77.0 (O*C*H), 69.4 (O*C*H_2), 33.6, 26.4, 22.2 (-*C*H_2-),13.8 (*C*H_3).

1,2-Decylene carbonate (11e). Isolated in 90% yield as a colourless liquid (4.70 g, 95 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 4,68 (m, 1 H, OC*H*), 4.50 (m, 1 H, OCH_2), 4.04 (m, 1 H, OCH_2), 1.71 (m, 2 H, CH_2), 1.37 (m, 12 H, CH_2), 0.86 [t, 3 H, $^{3}J_{H-H}$ = 8 Hz, CH_3]. ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.1 (*C*=O), 77.0 (O*C*H), 69.4 (O*C*H_2), 33.9, 31.8, 29.3, 29.2 29.1, 24.3, 22.6 (-*C*H_2-),14.1 (*C*H_3).

3-Chloropropylene carbonate (11f). Isolated in 91% yield as a colourless liquid (3.33 g, 99%). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.94 (m, 1 H, OC*H*), 4.57 (m, 1 H, OCH_2), 4.40 (dd, 1 H, $^{3}J_{H-H}$ = 9 Hz, 8.7 Hz, OCH_2), 3.73 (m, 2 H, CH_2Cl). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.1 (C=O), 74.16 (O*C*H), 66.9 (O*C*H_2), 43.5 (*C*H_2Cl).

Glycerol carbonate (11g). Isolated in 90% yield as a colourless liquid (2.89 g, 99%).^{1}H NMR ($CDCl_3$, 298 K) δ 4.80 (m, 1 H, OC*H*), 4.49 (m, 2 H, OCH_2), 3.99 (m, 1 H, CH_2OH), 3.71 (m, 1 H, CH_2OH), 2.59 (m, 1 H, O*H*). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.0 (*C*=O), 76.7 (O*C*H), 65.7 (O*C*H_2), 61.7 (*C*H_2OH).

3-Phenoxypropylene carbonate (11h). Isolated in 91% yield as a white solid (4.65 g, 97%). ^{1}H NMR ($CDCl_3$, 298 K) δ 7.29 (m, 2 H, Ar-H), 7.00 (m, 1 H, Ar-H), 6.89 (m, 2 H, Ar-H), 5.01 (m, 1 H, OC*H*), 4.60 (m, 1 H, PhOCH_2), 4.52 (m, 1 H, PhOCH_2), 4.22 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 10.6 Hz, 4.2 Hz, OCH_2), 4.12 (dd, 1 H, $^{3}J_{H\text{-}H}$ = 12 Hz, 4 Hz, OCH_2). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 157.7 (OPh^{ipso}), 154.7 (O*C*OO), 129.7, 121.9, 114.5 (Ph), 74.1 (*C*H_2OPh), 66.8 (O*C*H), 66.2 (-*C*H_2O).

4-Chlorostyrene carbonate (11i). Isolated in 90% yield as a white solid (4.41 g, 98%). ^{1}H NMR ($CDCl_3$, 298 K) δ 7.42 (dd, 2 H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, Ar-H), 7.30 (dd, 2 H, $^{3}J_{H\text{-}H}$ = 8.4 Hz, Ar-H), 5.66 (m, 1 H, OC*H*), 4.80 (m, 1 H, OCH_2), 4.29 (m, 1 H, OCH_2). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.5 (*C*=O), 135.7 (C^{ipso}), 134.2, 129.5, 127.2 (Ph), 77.3 (O*C*H), 71.0 (O*C*H_2).

***cis*-1,2-Cyclohexene carbonate (11j).** Isolated in 73% yield as a white solid (0.34 g, 78%). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.65 (m, 2 H, OC*H*), 1.86 (m, 4 H, CH_2), 1.58 (m, 4 H, CH_2),1.39 (m, 4 H, CH_2). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.3 (*C*=O), 75.7 (O*C*H), 26.7 (*C*H_2), 19.1 (*C*H_2).

***cis*-1,2-Cyclopentene carbonate (11k).** Isolated in 70% yield as a white solid (0.29 g, 75%). ^{1}H NMR ($CDCl_3$, 298 K) δ 5.09 (m, 2 H, OC*H*), 2.13 (m, 2 H, CH_2), 1.72 (m, 4 H, CH_2). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 155.5 (*C*=O), 81.8 (O*C*H), 33.2 (*C*H_2), 21.5 (*C*H).

1,2-Isobutylene carbonate (11l) Isolated in 77% yield as a white solid (0.29 g, 82%). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.14 (s, 2H), 1.52 (s, 6H). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.70 (C=O), 81.79, 75.52, 26.20.

***trans*-stilbene carbonate (11m)** Isolated in 67% yield as a white solid (0.54 g, 73%). ^{1}H NMR ($CDCl_3$, 298 K) δ 7.54 – 7.43 (m, 6H), 7.39 – 7.32 (m, 4H), 5.46 (s, 2H). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.08 (C=O), 134.82, 129.80, 129.24, 126.07, 85.37.

***cis*-2,3-butane carbonate (11n)** Isolated in 70% yield as a colourless liquid in a 94:6 mixture of cisand trans-isomers (0.27 g, 76%). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.88 – 4.76 (m, 2H), 1.32 (d, 3 JHH = 5.9 Hz, 6H). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.63 (C=O), 76.06, 14.33.

***trans*-2,3-butane carbonate (11o).** Isolated in 68% yield as a colourless liquid (0.26 g, 74%). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.39 – 4.27 (m, 2H), 1.45 (d, 3 JHH = 5.9 Hz, 6H). ^{13}C {^{1}H} ($CDCl_3$, 298 K) 154.60 (C=O), 80.01, 18.54. IR Neat: 1796 cm^{-1} (C=O).

(*R*)-(+)-Limonene carbonate (11p). Isolated in 58 % yield as a colourless oil in a 6:94 mixture of *cis*- and *trans*-isomers (0.38 g, 63 %). ^{1}H NMR ($CDCl_3$, 298 K) δ 4.69 (m, 1 H, MeC=C$\underline{H_2}$), 4.66 (m, 1 H, MeC=C$\underline{H_2}$), 4.33 (dd, $^{3}J_{HH}$ = 9.6 Hz and 7.0 Hz, 1 H, OC$\underline{H}$), 2.36-2.21 (m, 2 H, -C$\underline{H_2}$-), 1.87 (tt, $^{3}J_{HH}$ = 12.0 Hz and 3.2 Hz, C$\underline{H}$), 1.65 (s, 3 H, -C(*Me*)=CH_2), 1.64-1.55 (m, 2H, -C$\underline{H_2}$-), 1.40 (s, 3H, -COC$\underline{H_3}$), 1.38-1-31 (m, 2H, -C$\underline{H_2}$-). ^{13}C {^{1}H} ($CDCl_3$, 298 K) δ 154.9 (O=$\underline{C}$OO), 147.4 (-$\underline{C}$(CH_3)=CH_2), 110.3 (-C(CH_3)=$\underline{C}H_2$), 82.2 (-$\underline{C}$(O)Me), 80.7 (-$\underline{C}$O), 40.1 ($\underline{C}$-C(CH_3)(=CH_2)), 34.1, 33.2, 25.8 (-$\underline{C}H_2$-), 26.3 (-CO($\underline{C}H_3$)), 20.7 (C-C($\underline{C}H_3$)(=CH_2).

Figures S10–S25. ^{1}H and ^{13}C-{^{1}H} NMR spectra of compounds **11a**−**11i**, **11j**−**11o** and **11p**

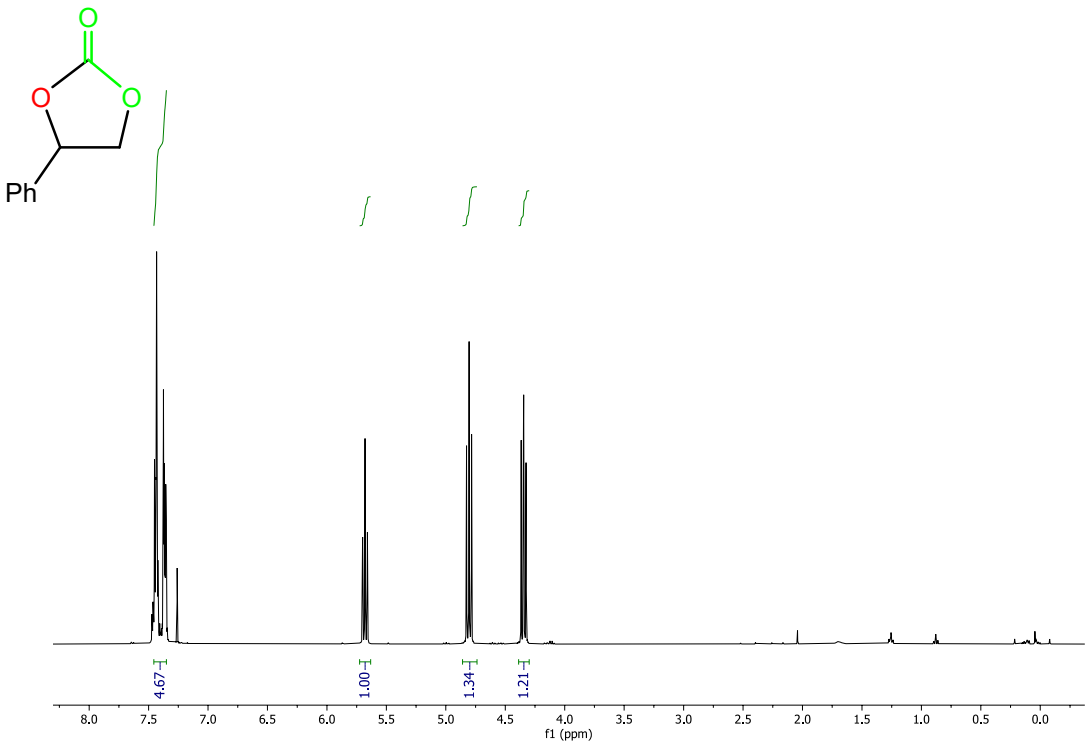


Figure S10a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for styrene carbonate **11a**.

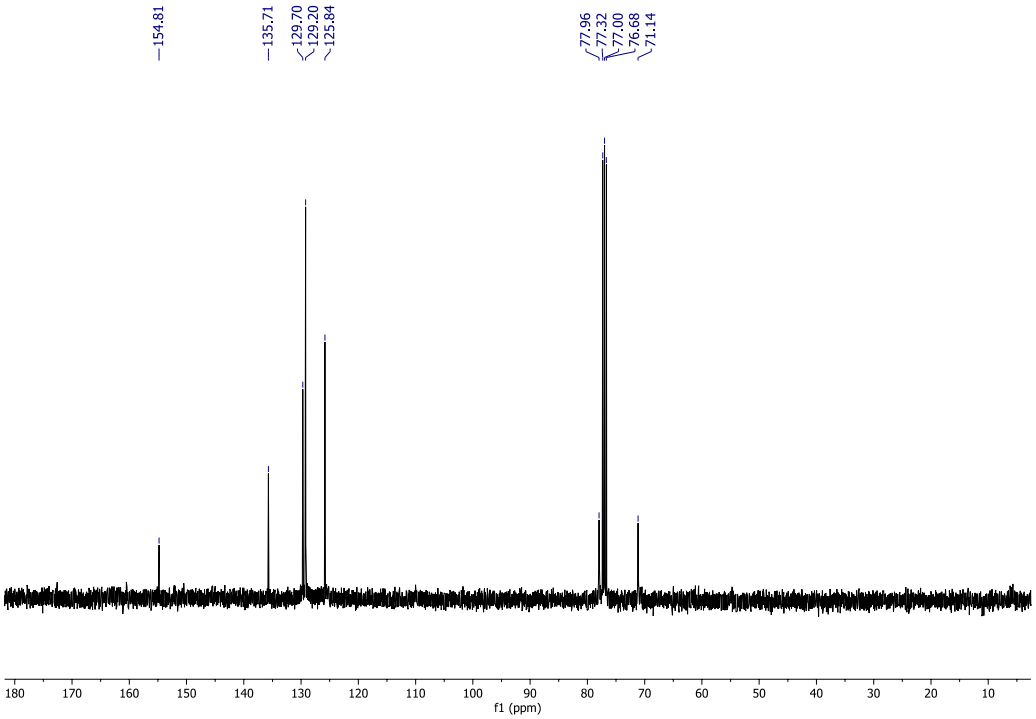


Figure S10b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for styrene carbonate **11a**.

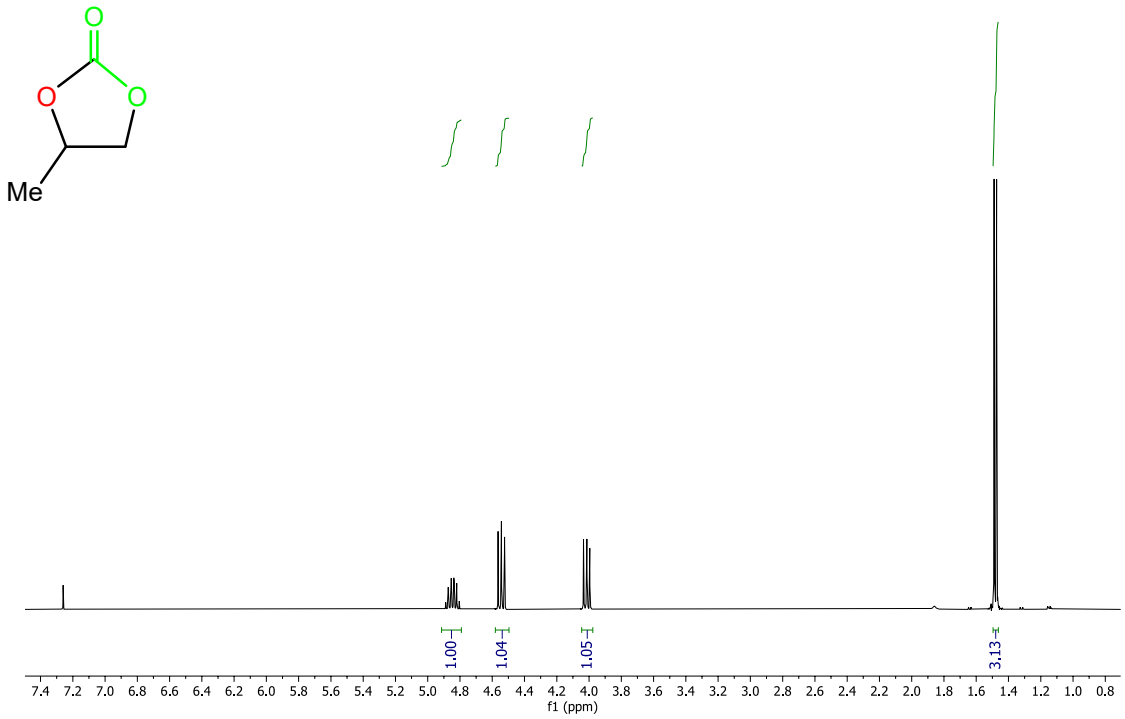


Figure S11a. ^{1}H-NMR spectrum (500 MHz, 297 K, $CDCl_3$) for propylene carbonate **11b**.

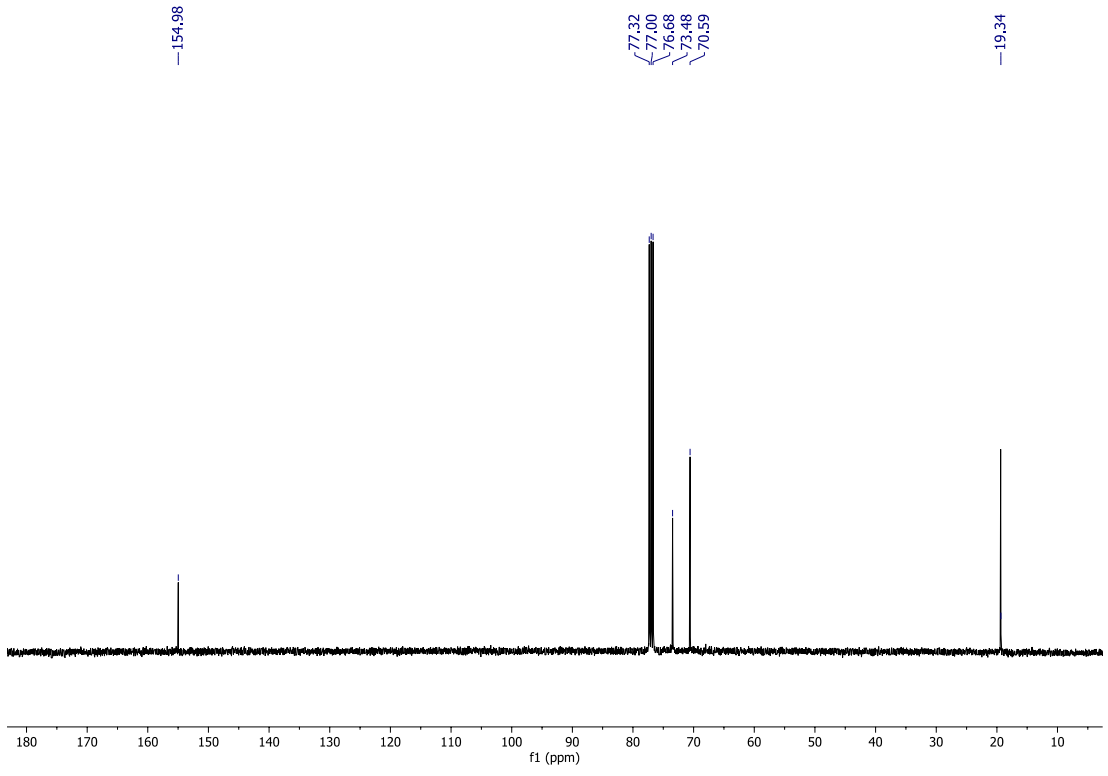


Figure S11b. ^{13}C-{^{1}H}-NMR spectrum (125 MHz, 297 K, $CDCl_3$) for propylene carbonate **11b**.

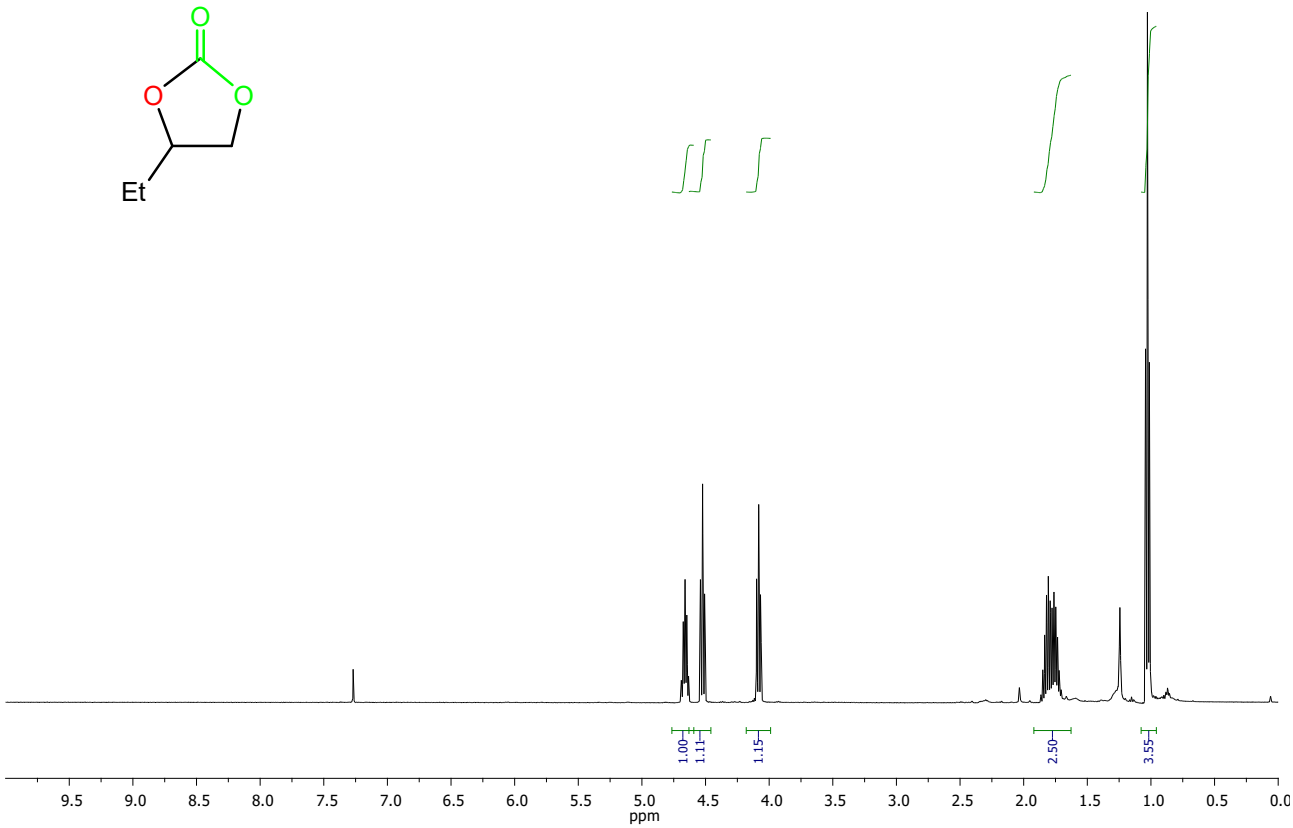


Figure S12a. ^{1}H-NMR spectrum (500 MHz, 297 K, $CDCl_3$) for butylene carbonate **11c**.

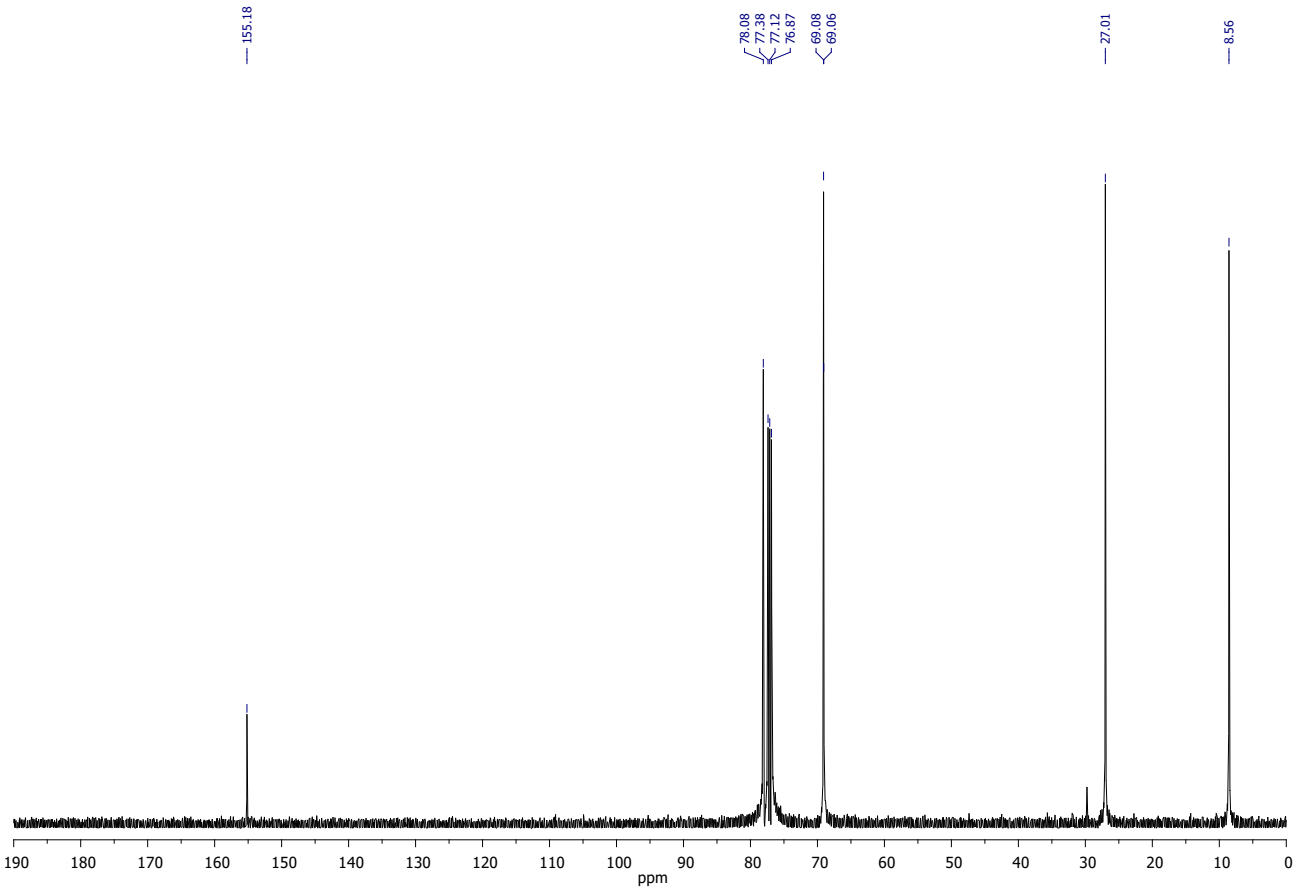


Figure S12b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for butylene carbonate **11c**.

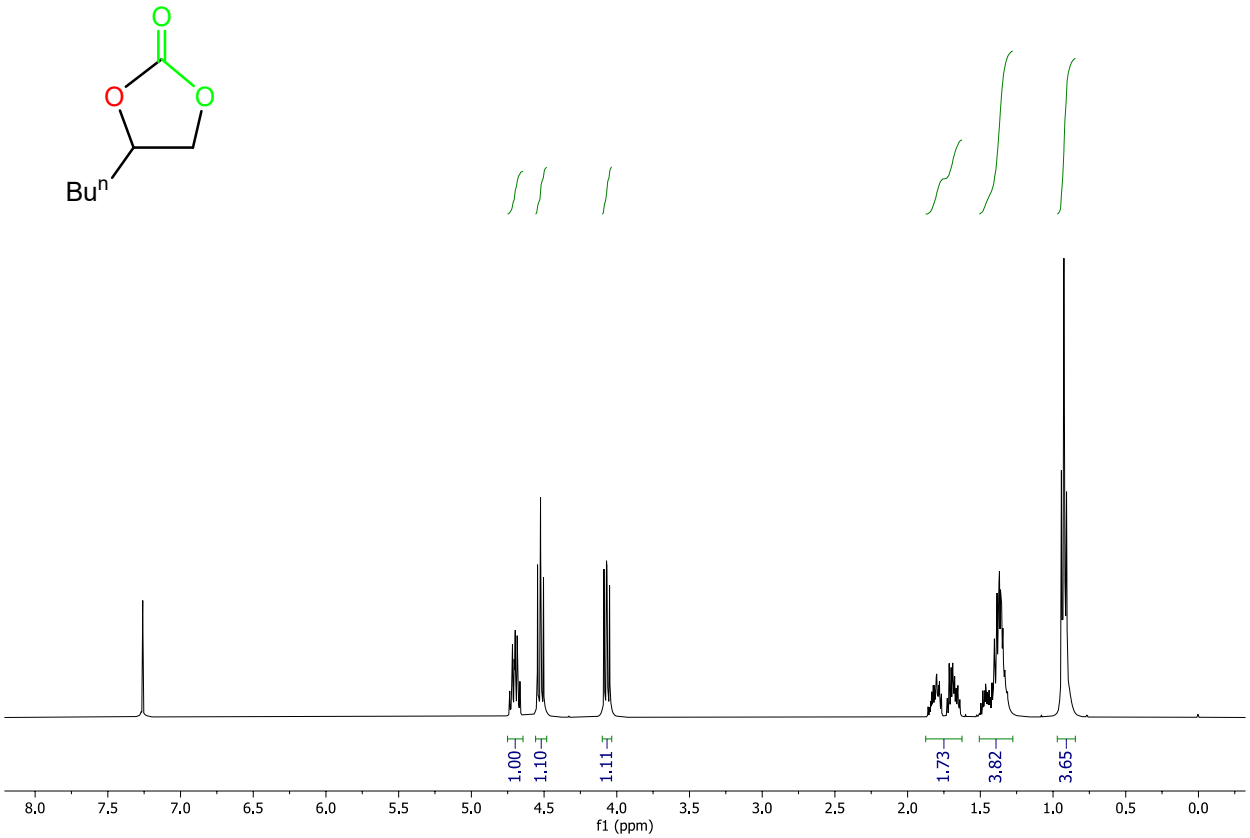


Figure S13a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 1,2-hexylene carbonate **11d**.

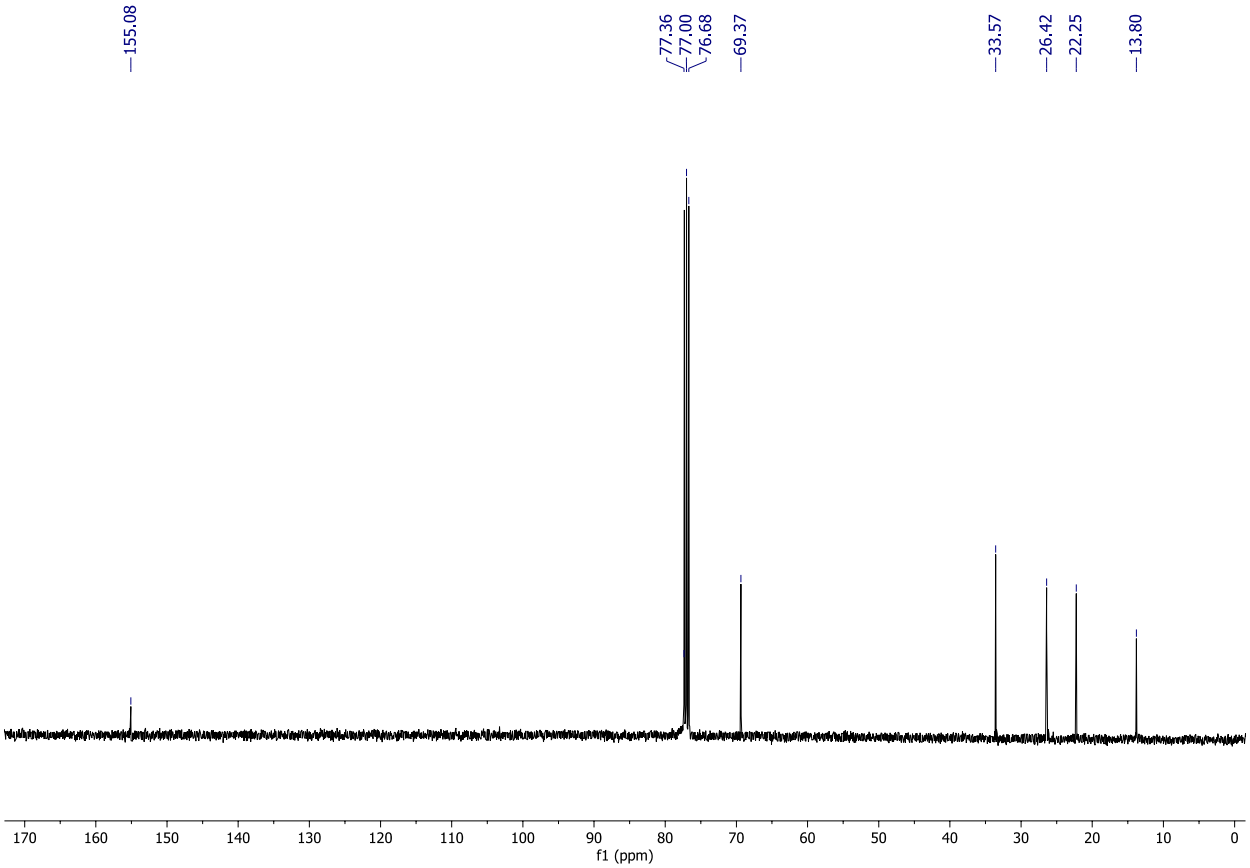


Figure S13b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 1,2-hexylene carbonate **11d**.

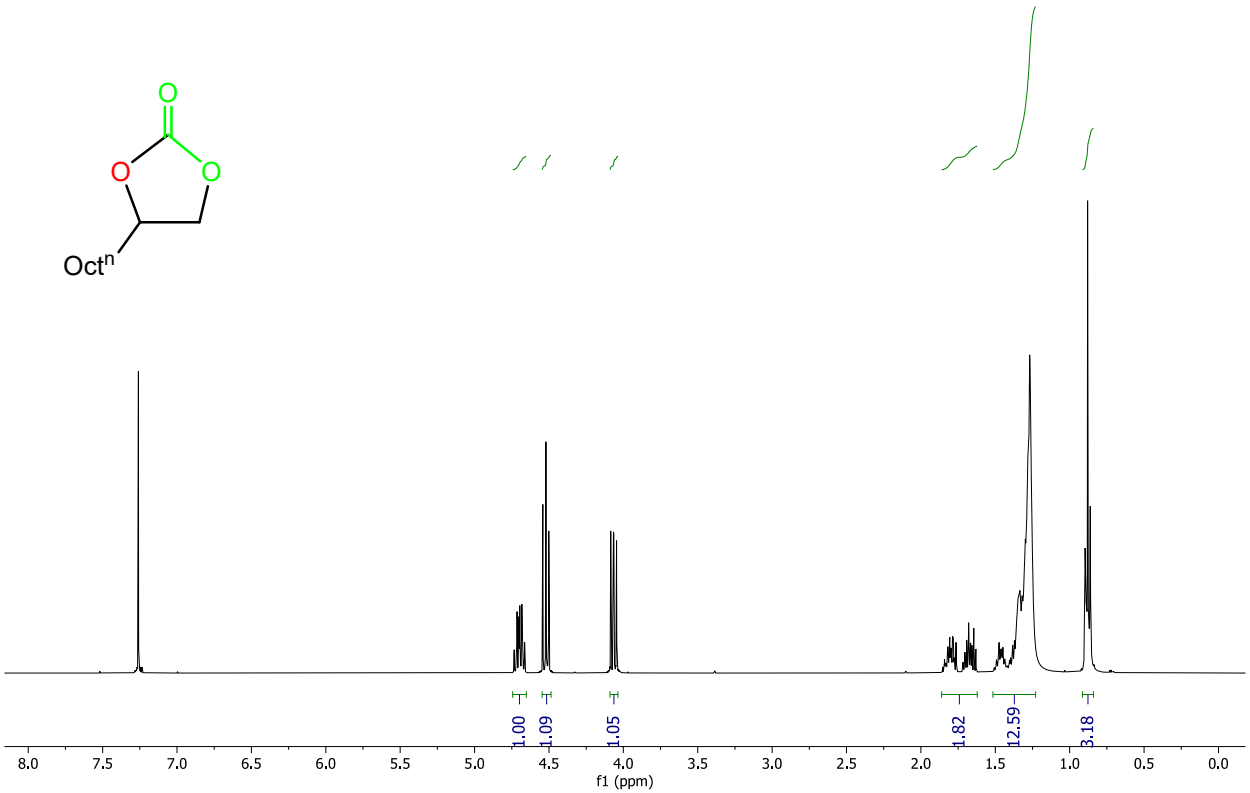


Figure S14a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 1,2-decylene carbonate **11e**.

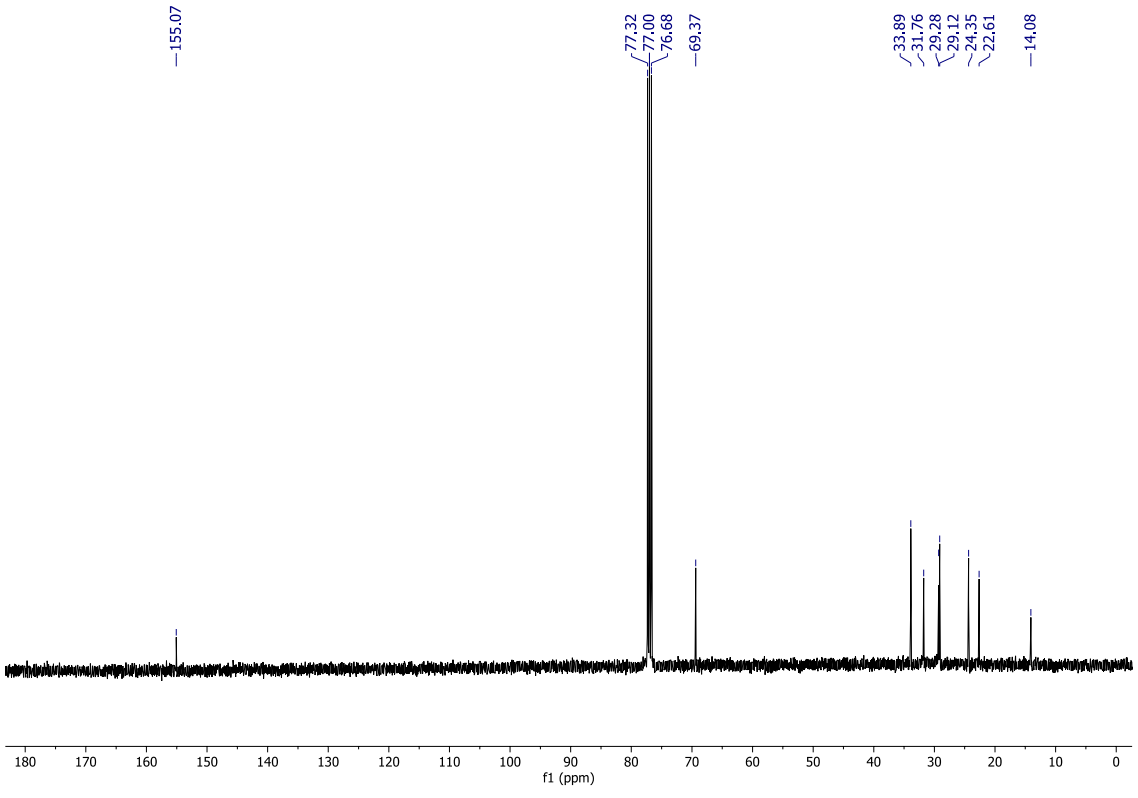


Figure S14b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 1,2-decylene carbonate **11e**.

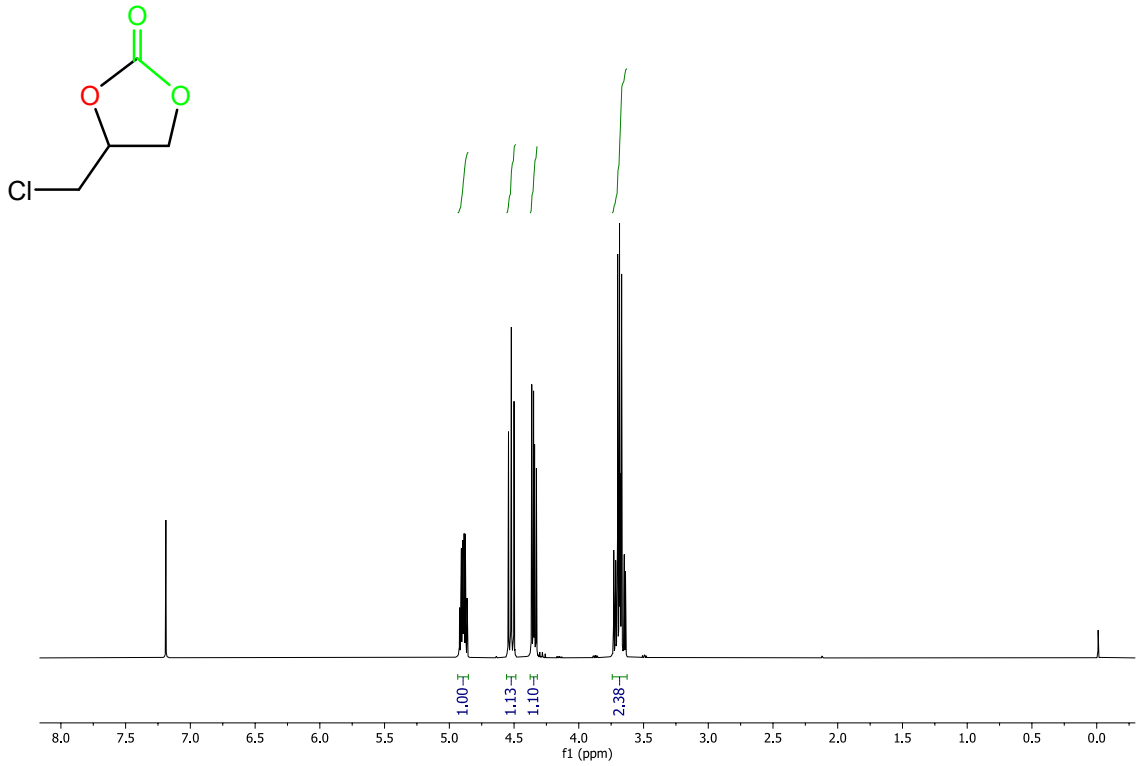


Figure S15a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 3-chloropropylene carbonate **11f**.

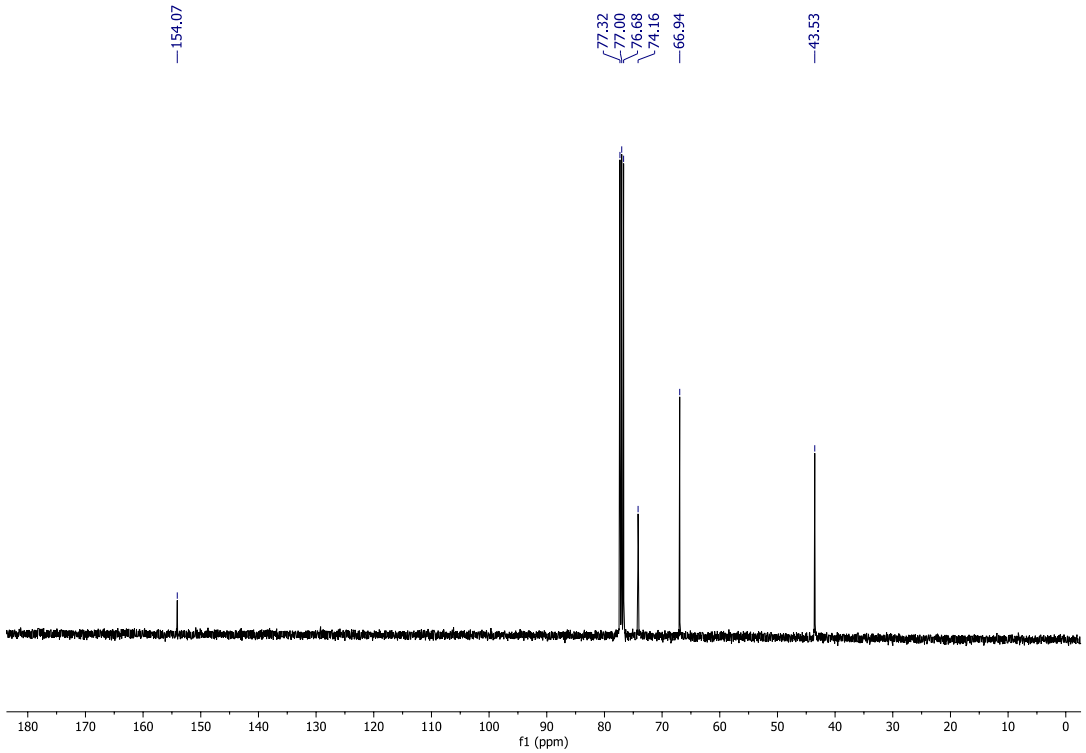


Figure S15b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 3-chloropropylene carbonate **11f**.

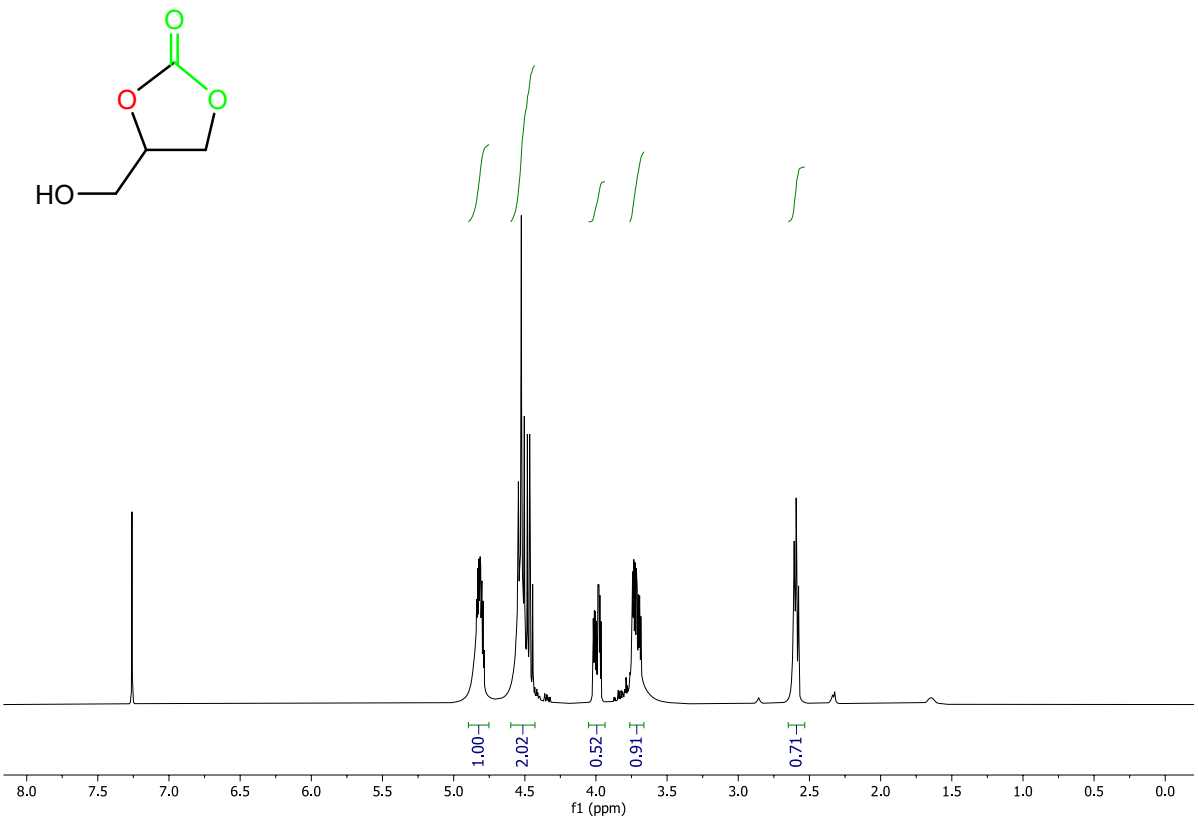


Figure S16a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for glycerol carbonate **11g**.

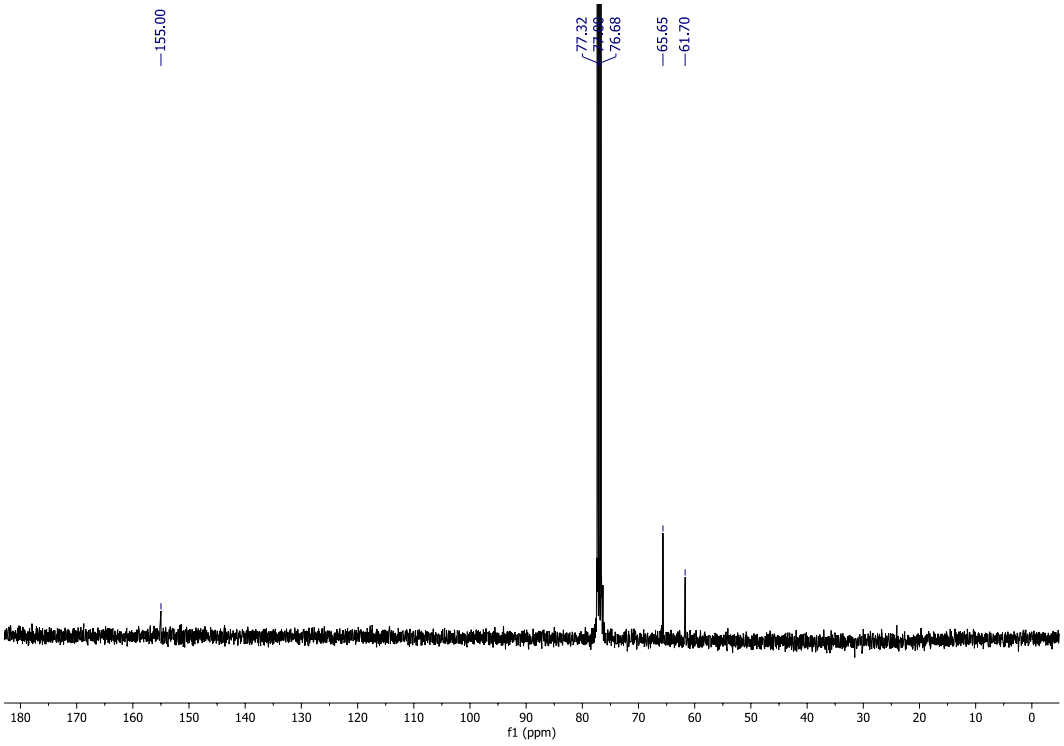


Figure S16b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for glycerol carbonate **11g**.

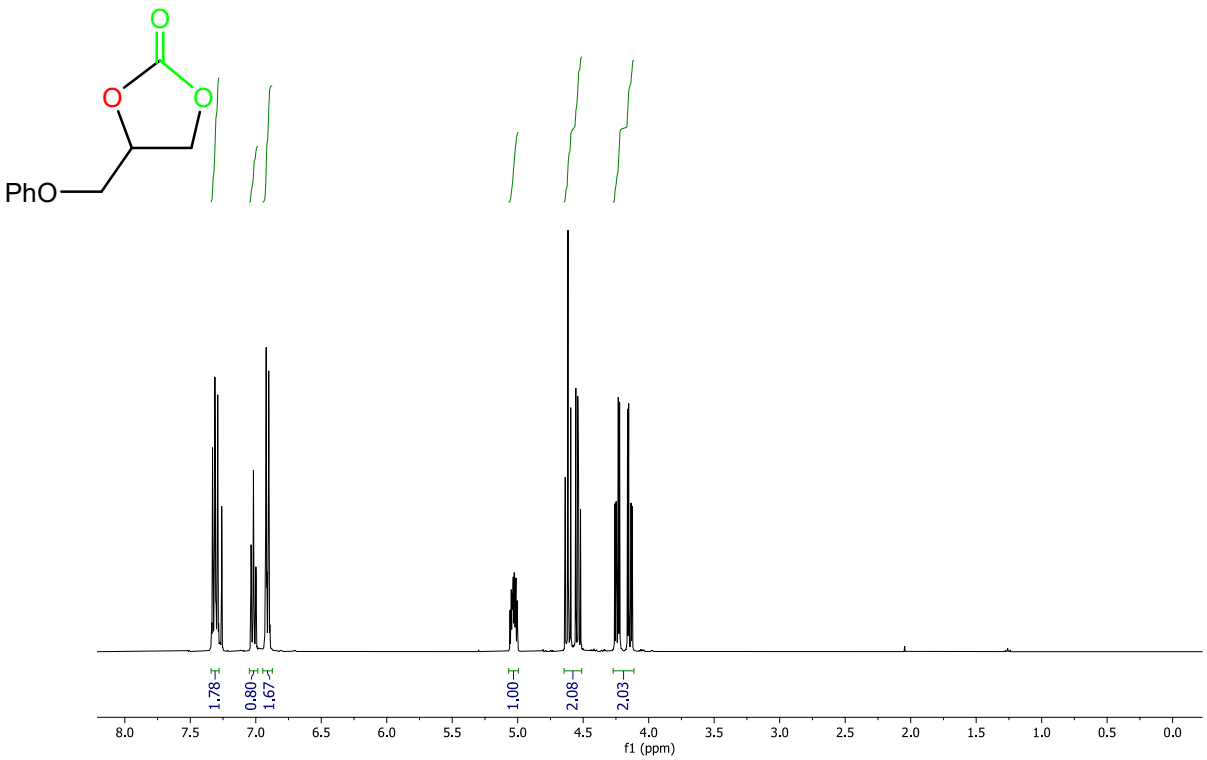


Figure S17a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 3-phenoxypropylene carbonate **11h**.

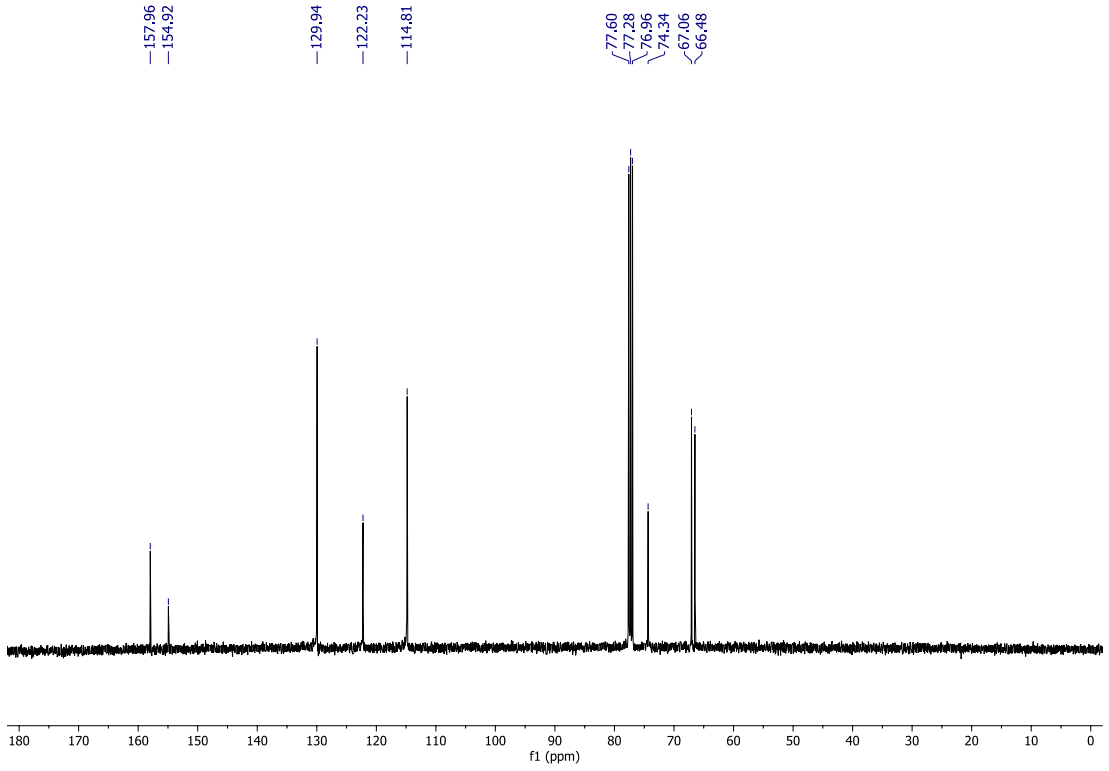


Figure S17b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 3-phenoxypropylene carbonate **11h**.

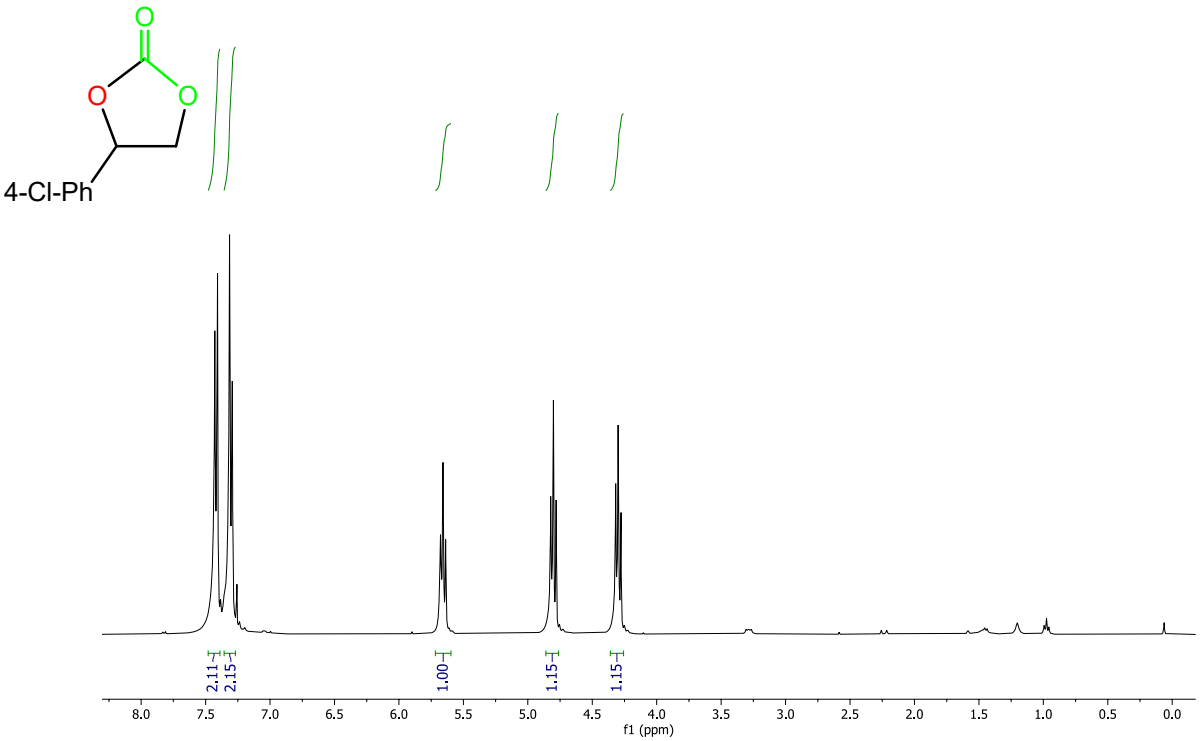


Figure S18a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for 4-chlorostyrene carbonate **11i**.

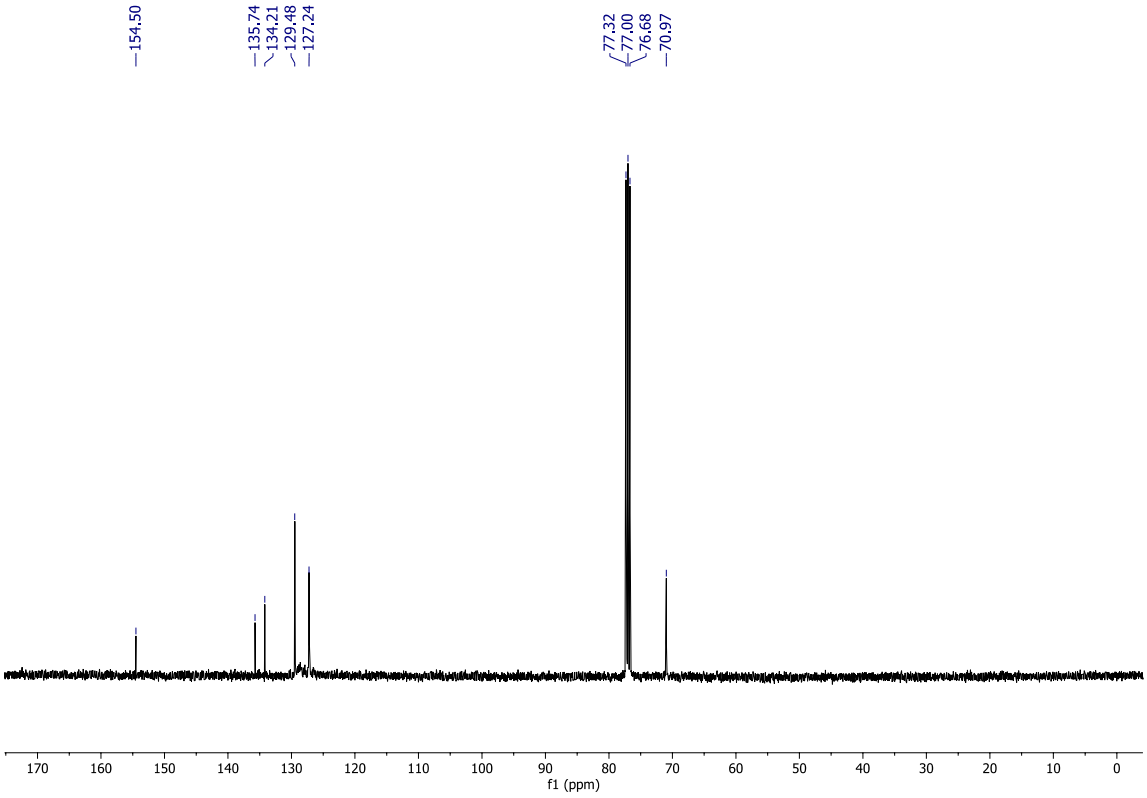


Figure S18b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for 4-chlorostyrene carbonate **11i**.

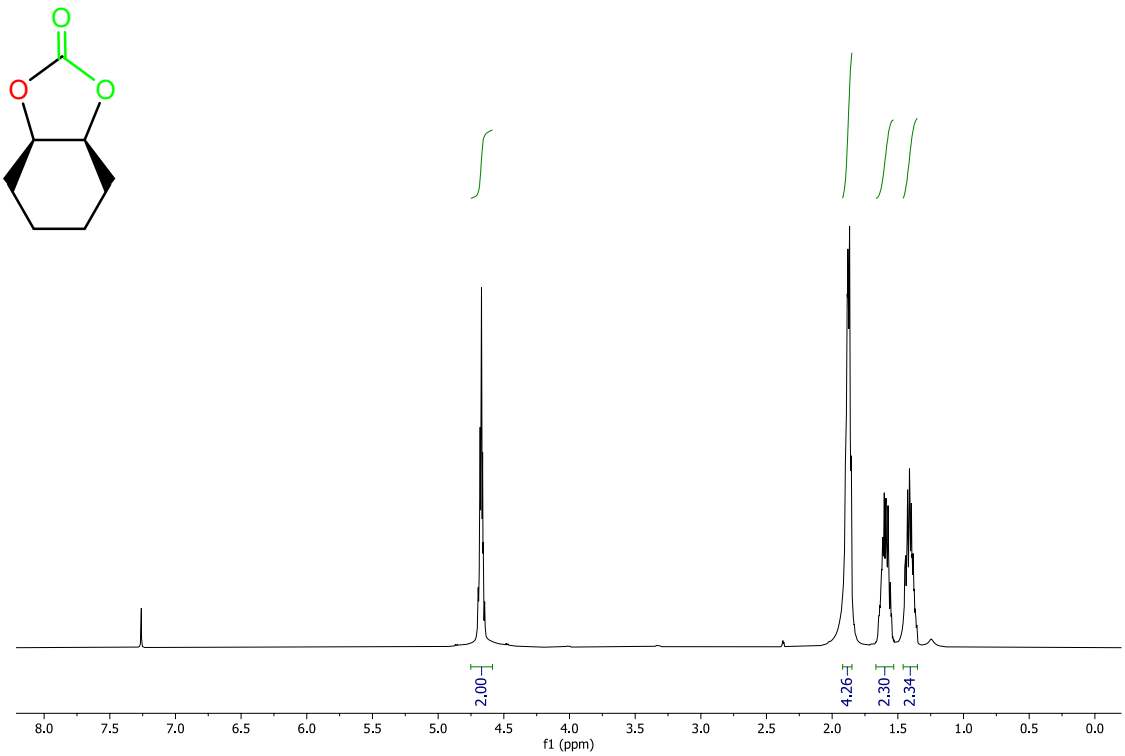


Figure S19a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for *cis*-1,2-cyclohexene carbonate **11j**.

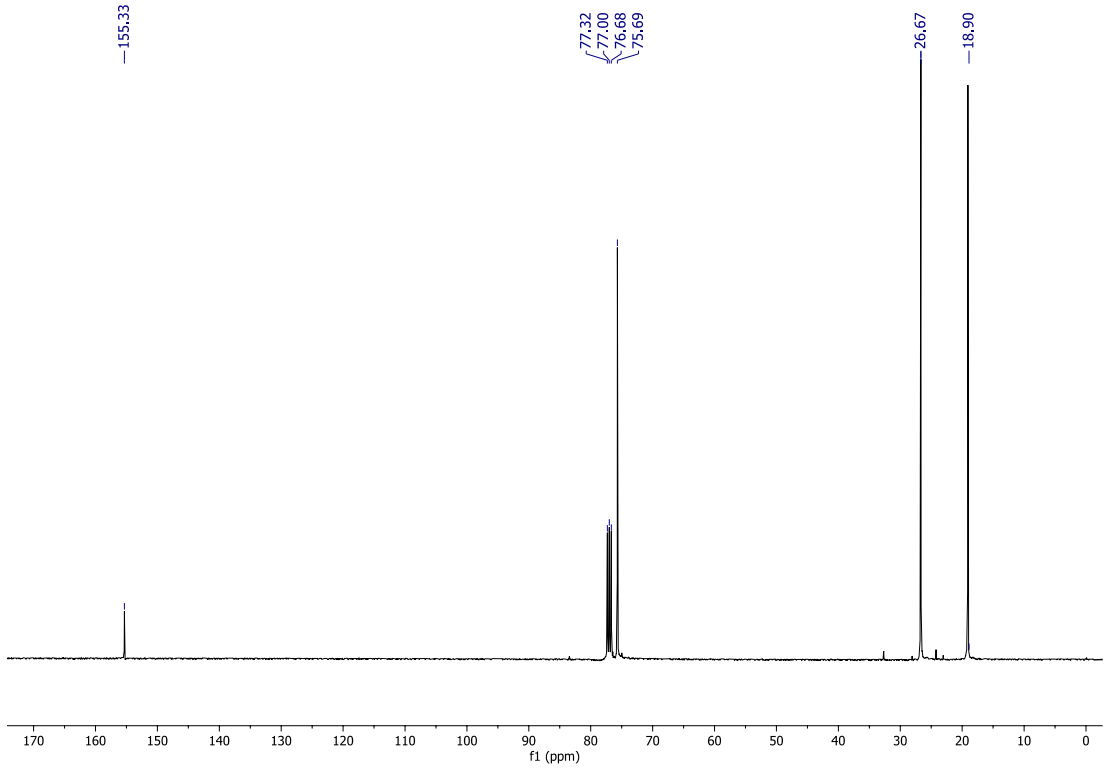


Figure S19b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for *cis*-1,2-cyclohexene carbonate **11j**.

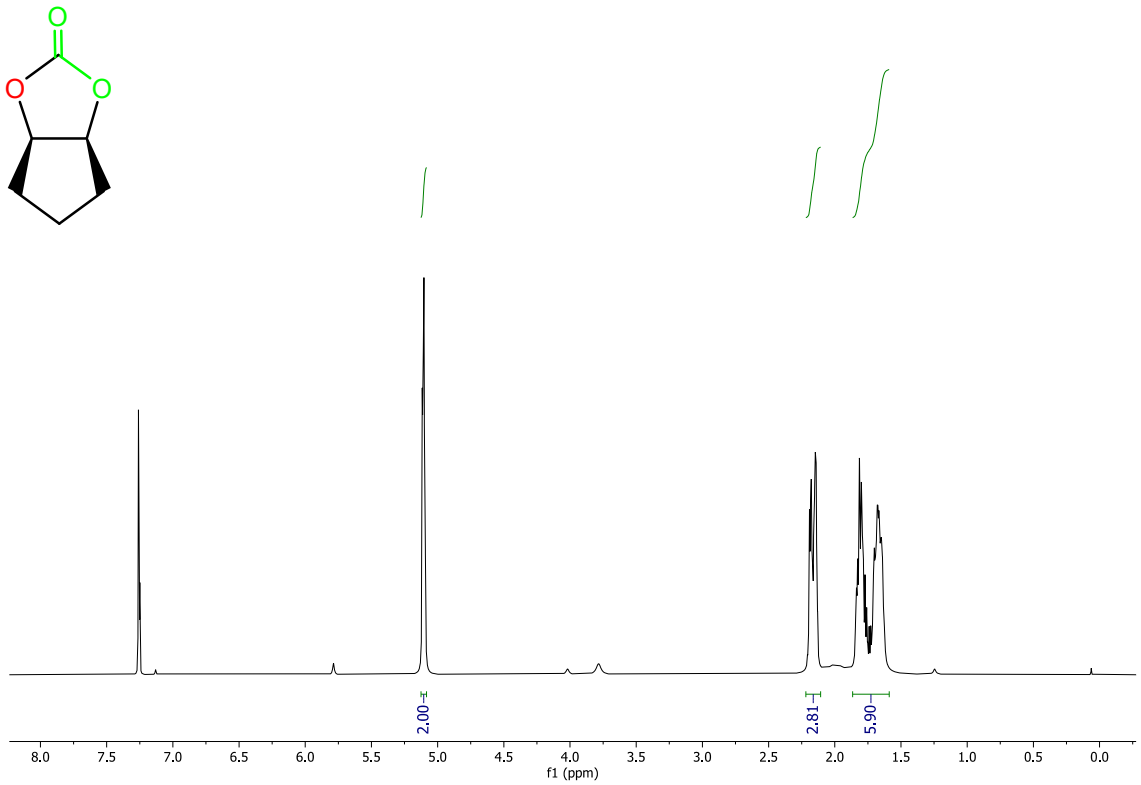


Figure S20a. ^{1}HNMR spectrum (400 MHz, 297 K, $CDCl_3$) for *cis*-1,2-cyclopentene carbonate **11k**.

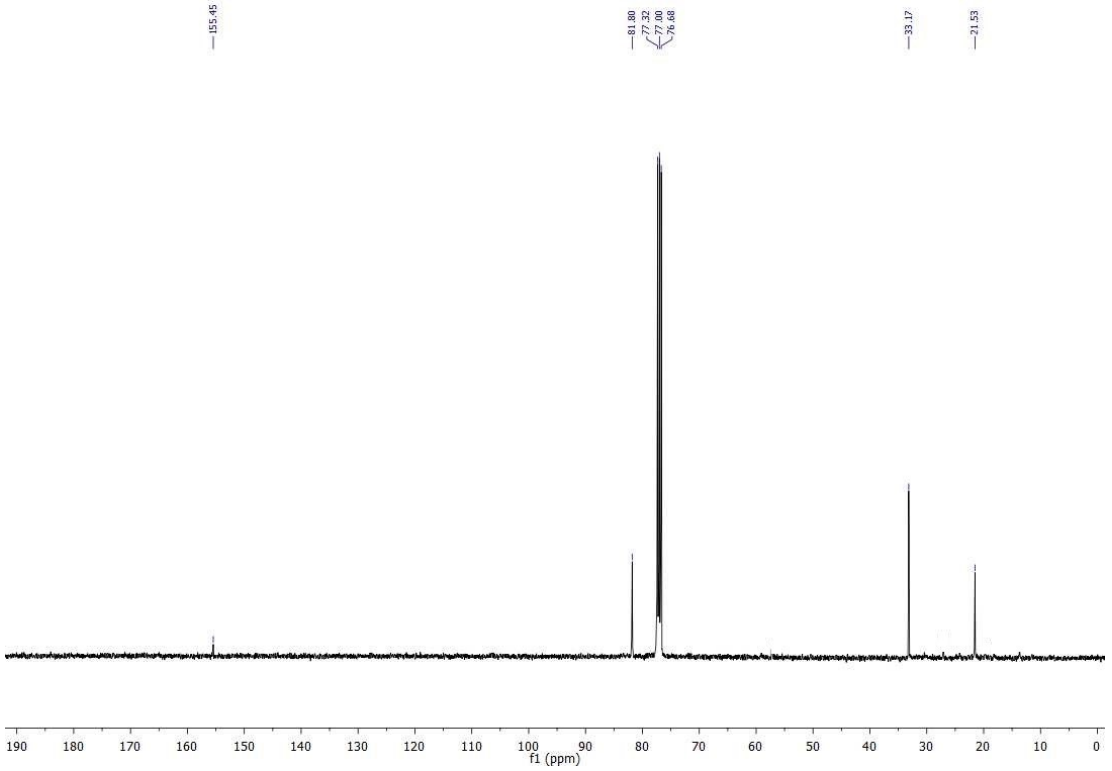


Figure S20b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) for c*is*-1,2-cyclopentene carbonate **11k**.

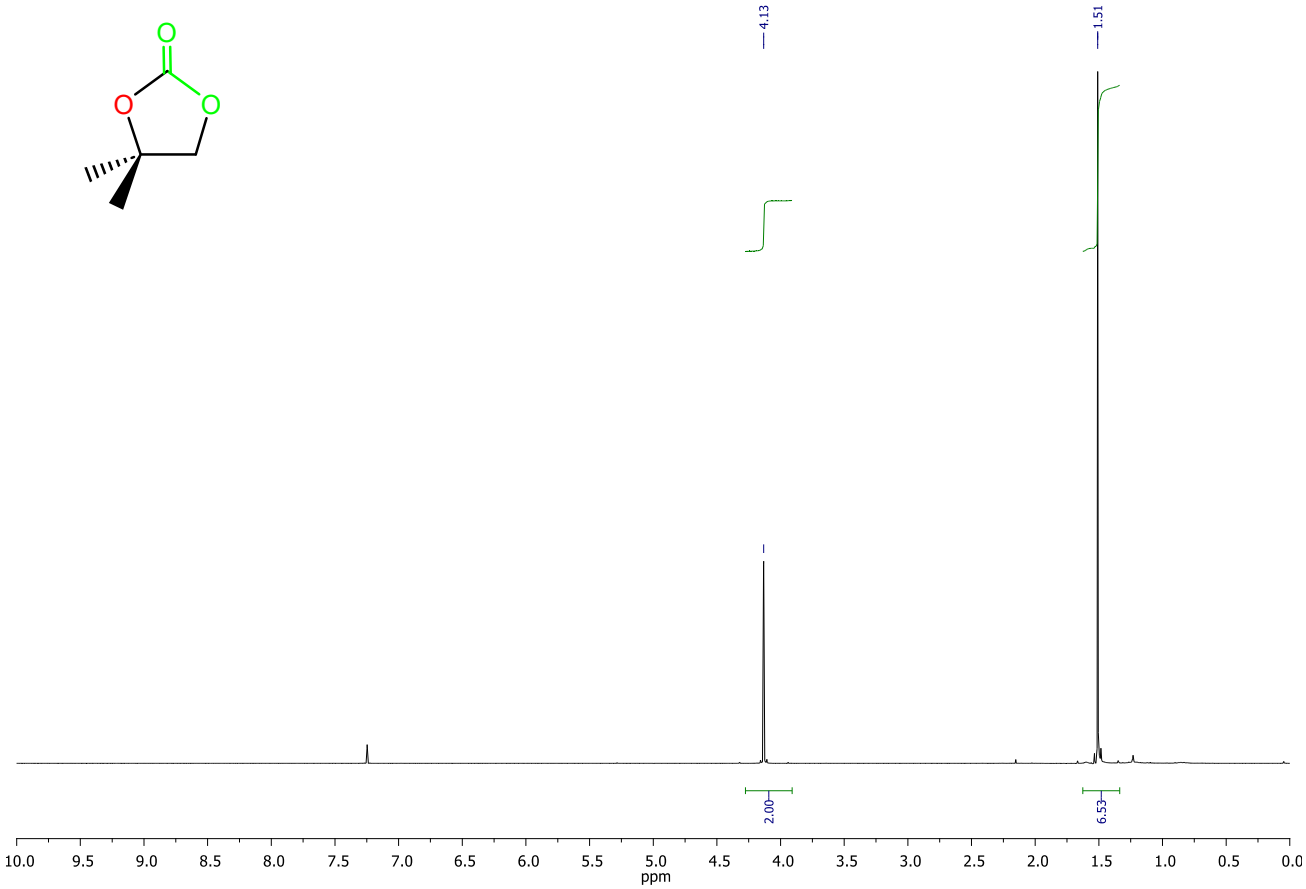


Figure S21a. ^{1}H-NMR spectrum (400 MHz, 297 K, $CDCl_3$) for 1,2-isobutylene carbonate **11l**.

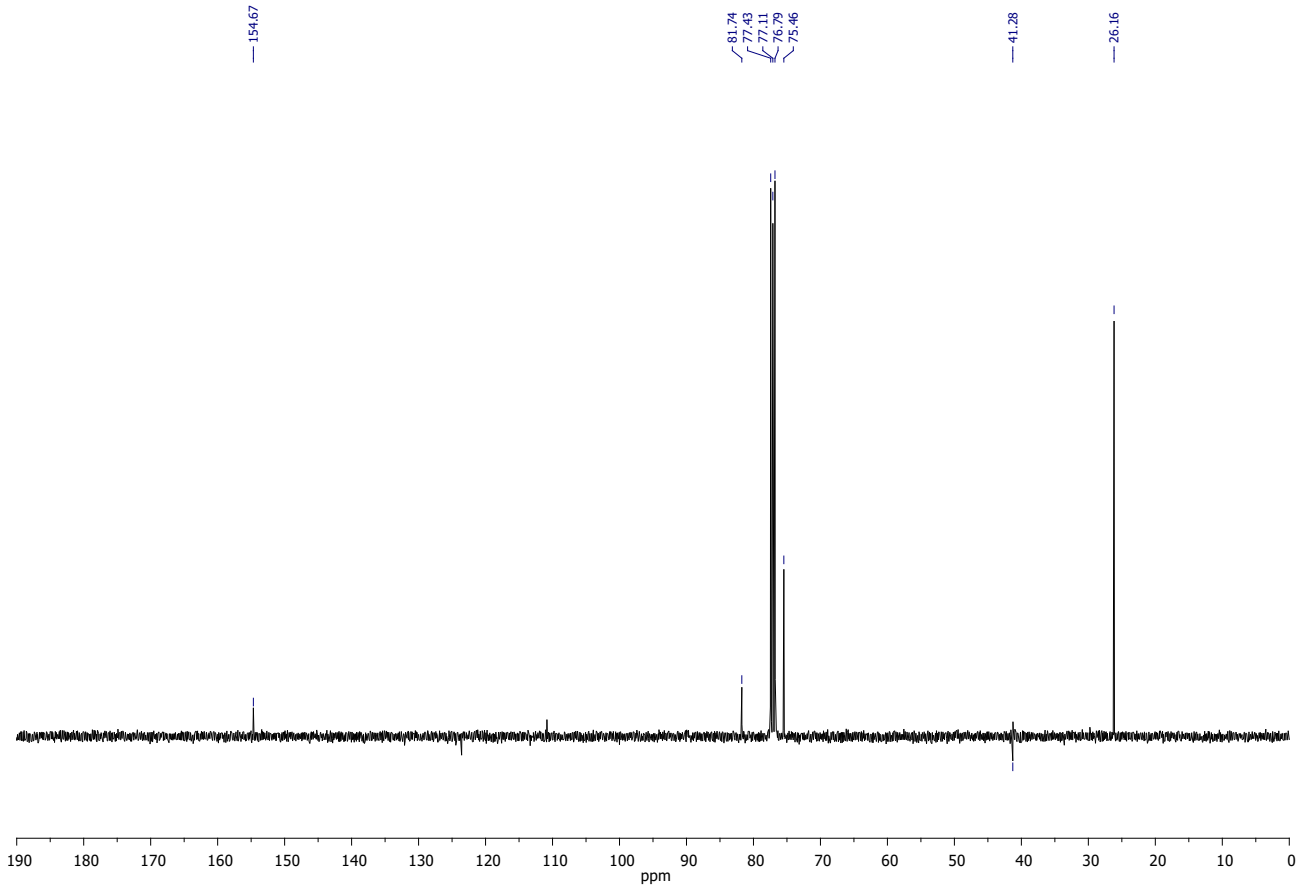


Figure S21b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, $CDCl_3$) 1,2-isobutylene carbonate **11l**.

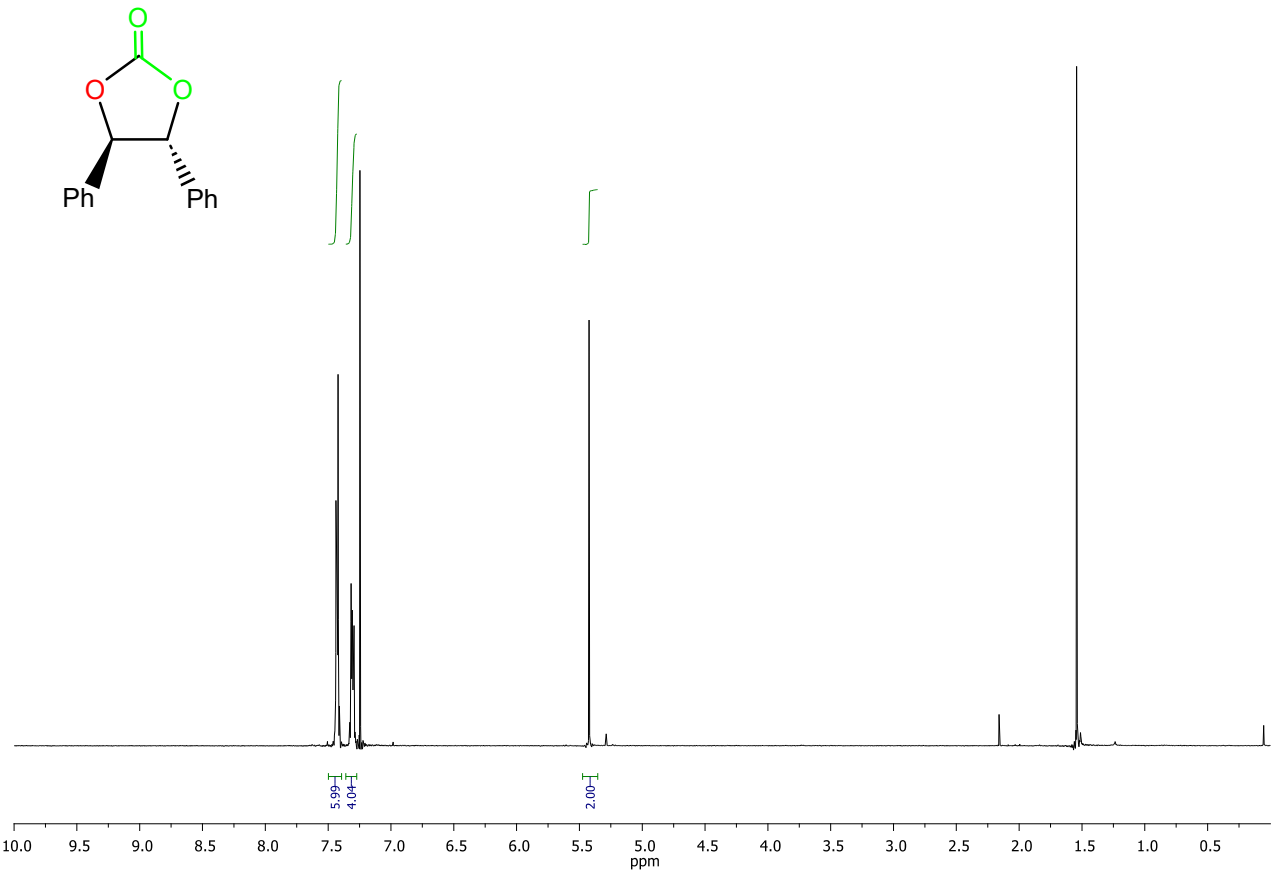


Figure S22a. ^{1}H-NMR spectrum (400 MHz, 297 K, DMSO-d_6) for *trans*-stilbene carbonate **11m**.

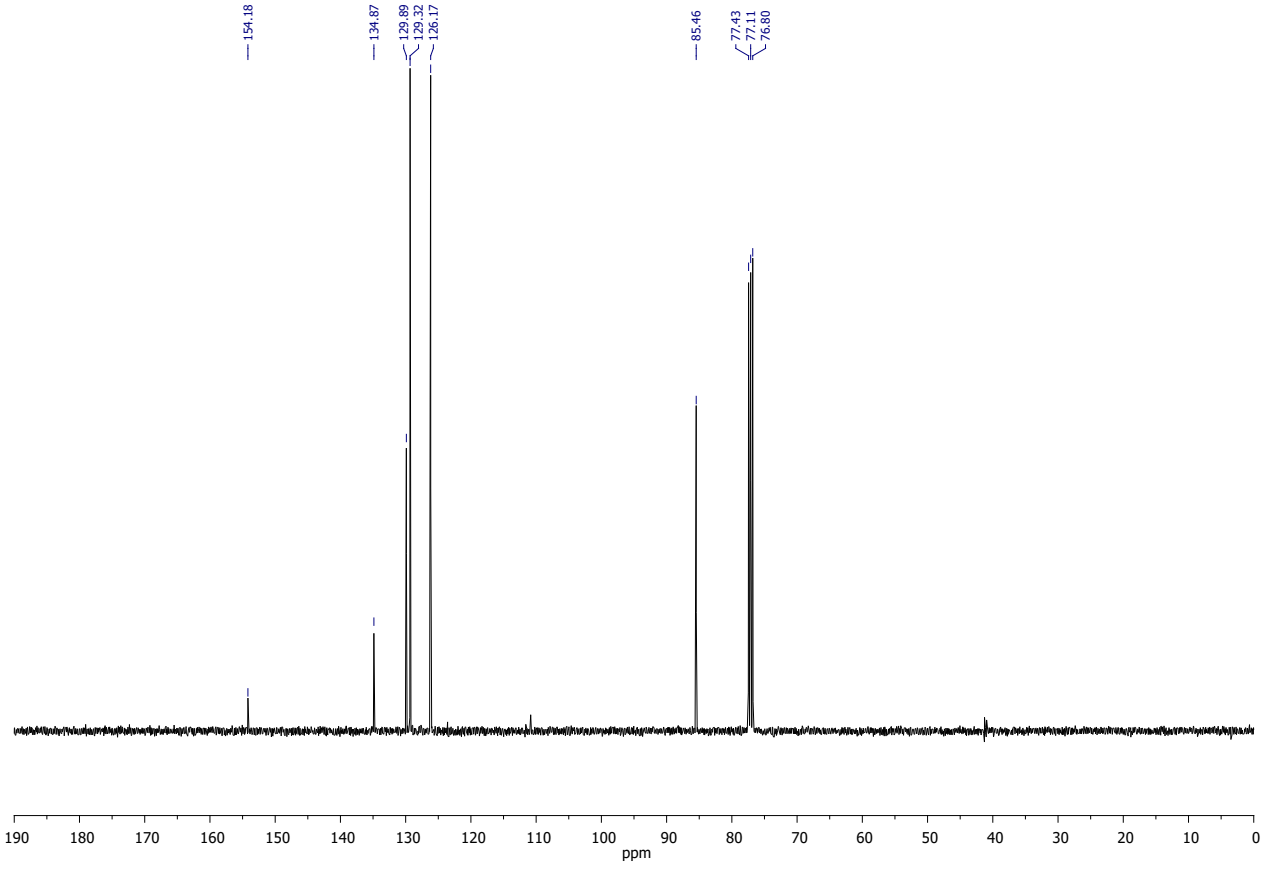


Figure S22b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, DMSO-d_6) for *trans*-stilbene carbonate **11m**.

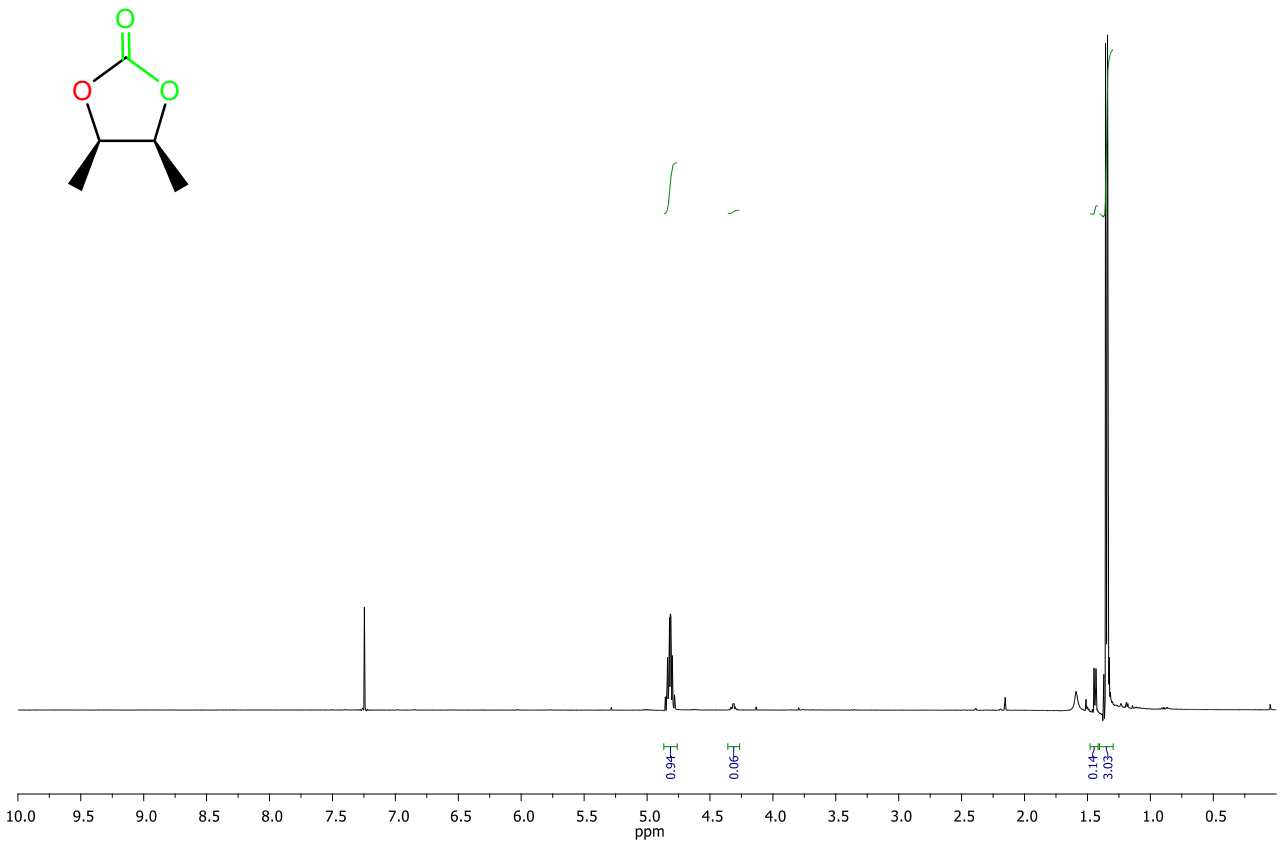


Figure S23a. ^{1}H-NMR spectrum (400 MHz, 297 K, DMSO-d_6) for *cis*-2,3-epoxybutane **11n**.

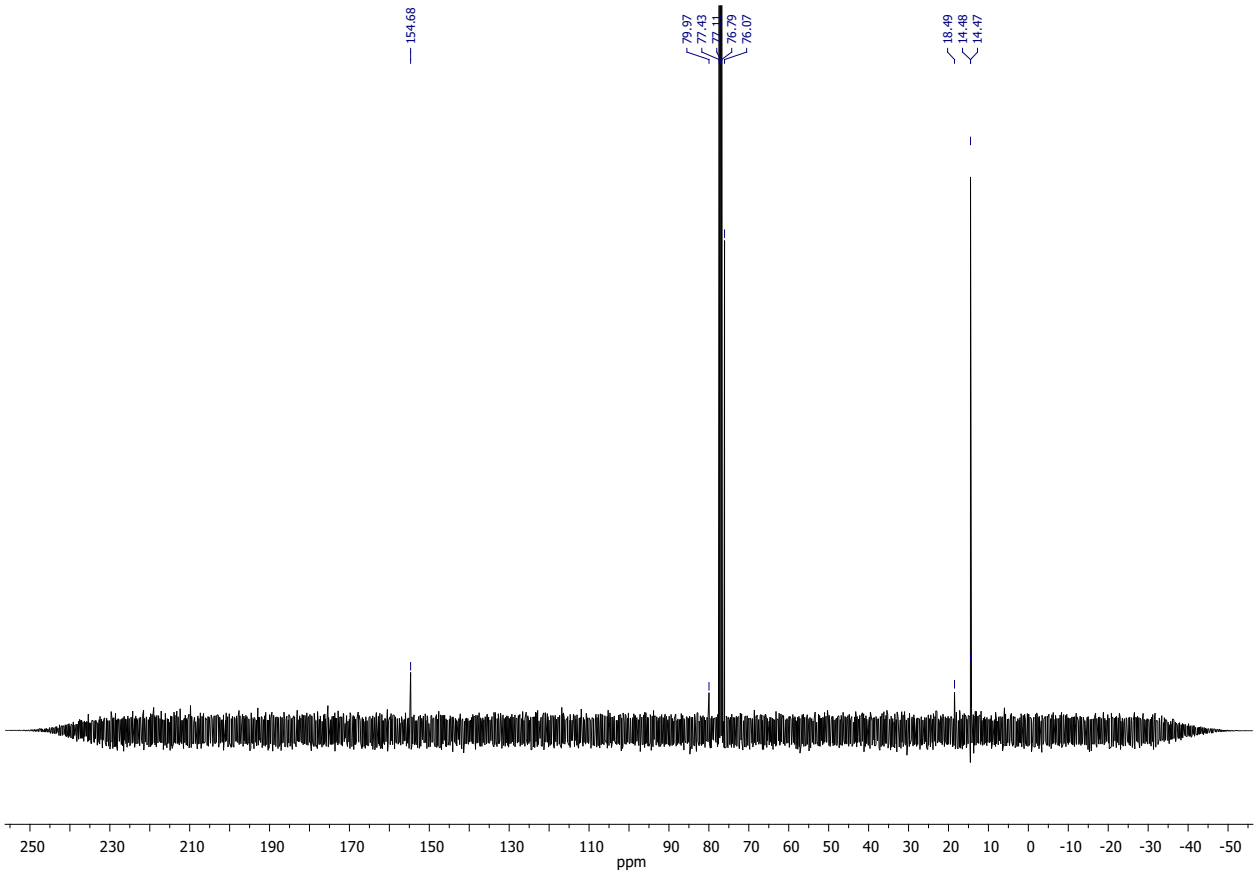


Figure S23b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, DMSO-d_6) for *cis*-2,3-epoxybutane **11n**.

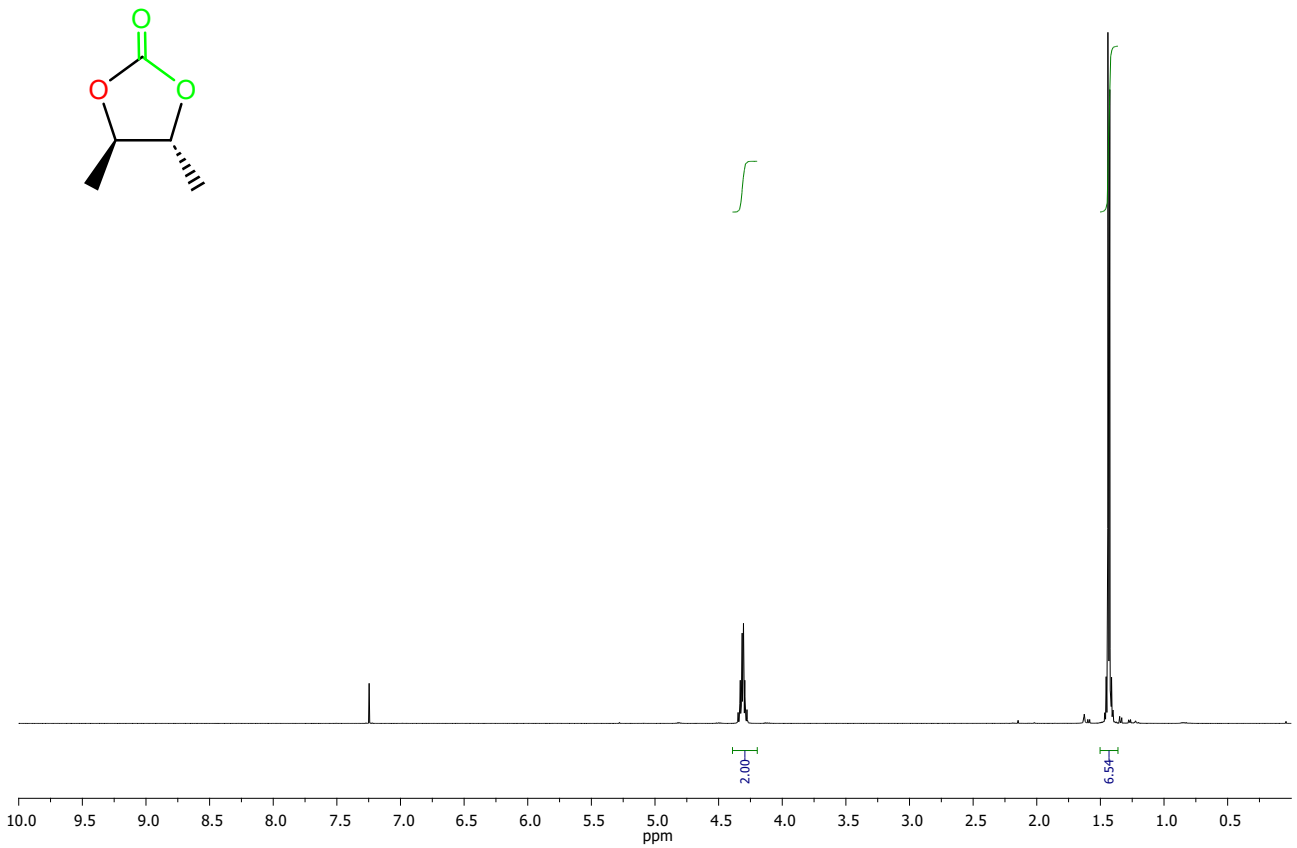


Figure S24a. ^{1}H-NMR spectrum (400 MHz, 297 K, DMSO-d_6) for *trans*-2,3-epoxybutane **11o**.

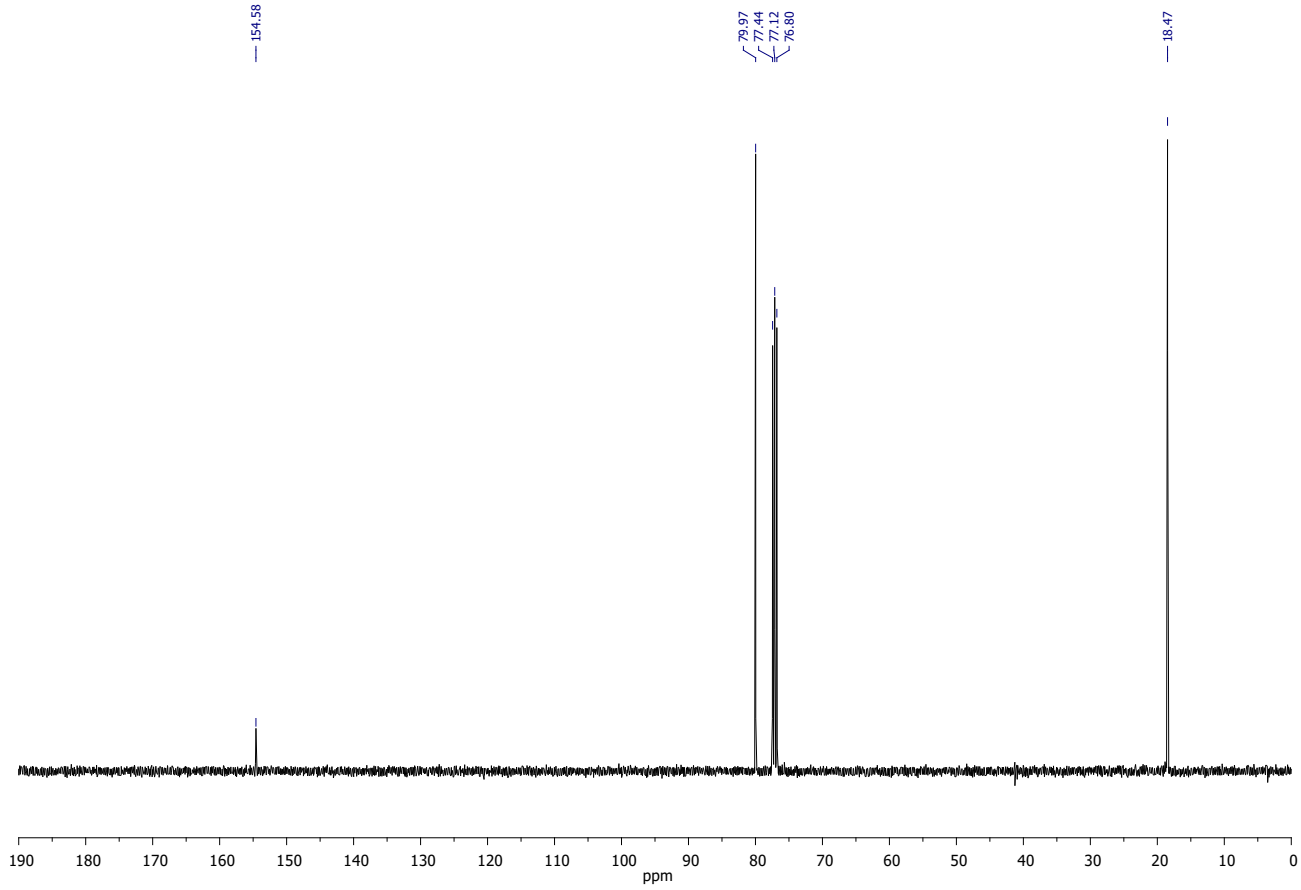


Figure S24b. ^{13}C-{^{1}H}-NMR spectrum (100 MHz, 297 K, DMSO-d_6) for *trans*-2,3-epoxybutane **11o**.

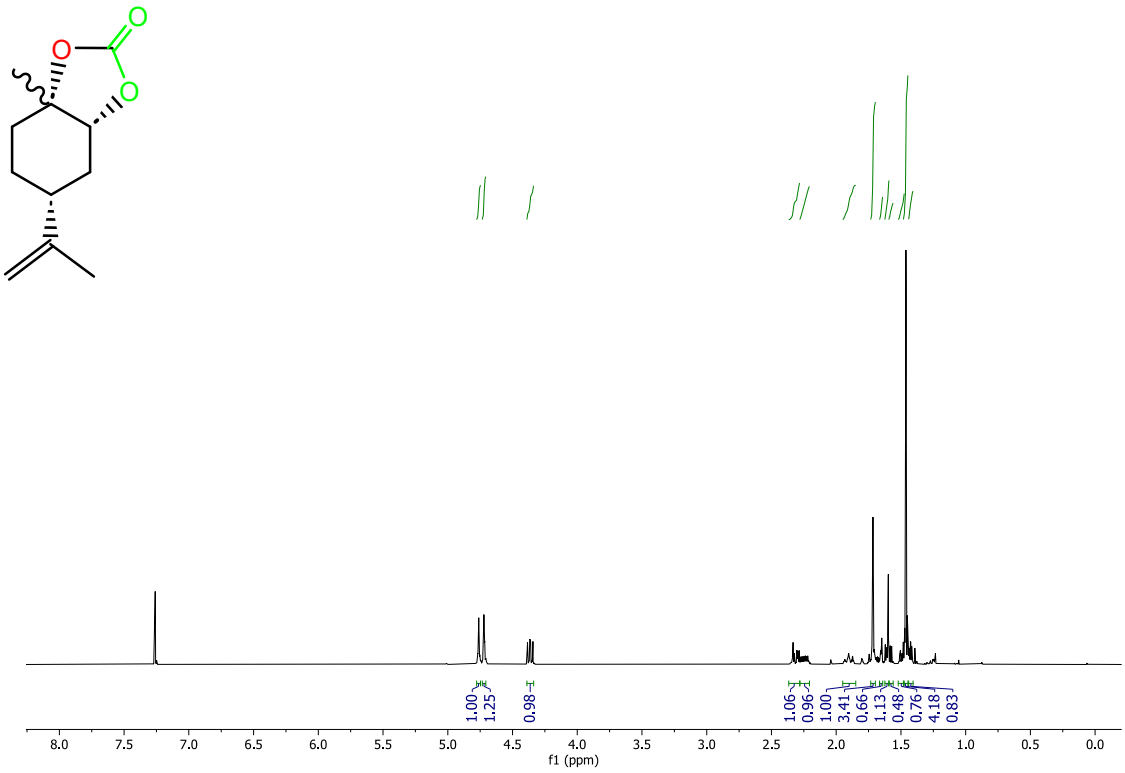


Figure S25a. ^{1}H-NMR spectrum (500 MHz, 297 K, $CDCl_3$) for 3a-methyl-6-(prop-1-en-2-yl)hexahydrobenzo[*d*][1,3]dioxol-2-one **11p**. (*trans* > 99%)

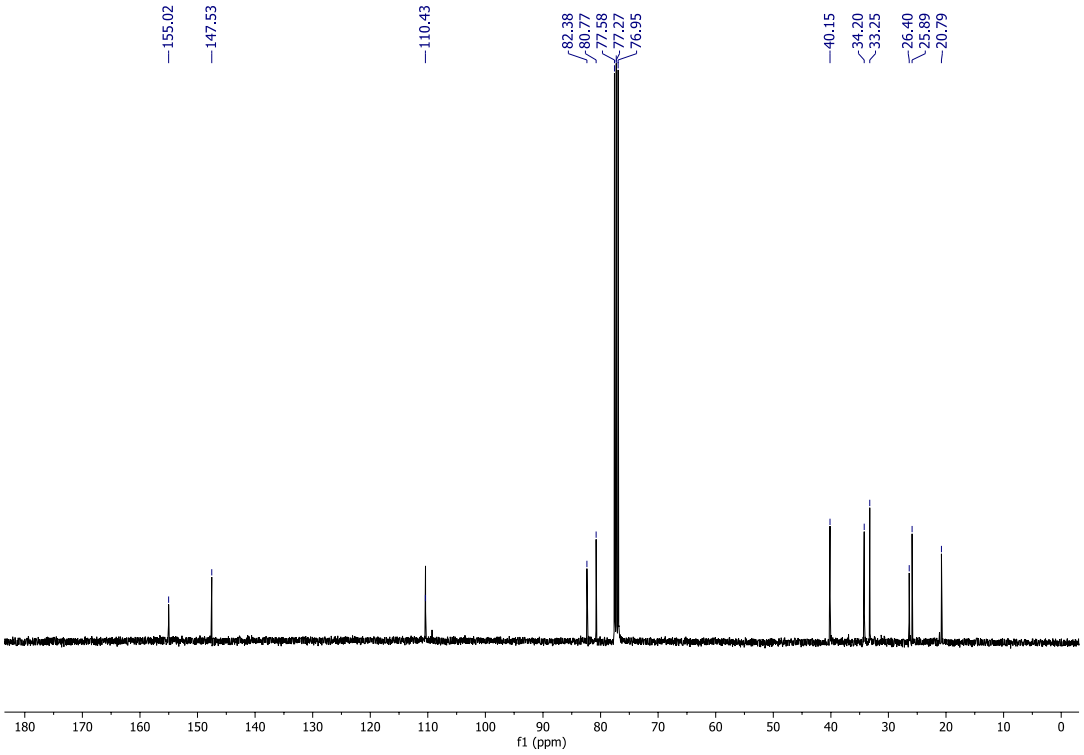


Figure S25b. ^{13}C-{^{1}H}-NMR spectrum (125 MHz, 297 K, $CDCl_3$) for 3a-methyl-6-(prop-1-en-2-yl)hexahydrobenzo[*d*][1,3]dioxol-2-one **11p**. (*trans* > 99%)

7) Experimental details for the synthesis of poly(cyclohexene carbonate)s

General procedure for the Ring Opening Co-Polymerisation of cyclohexene oxide and carbon dioxide at 1 bar CO_2 pressure.

In the glovebox, complex **7** (40.0 mg, 65.4 μmol) was dissolved in 0.64 g of cyclohexene oxide (0.66 mL, 6.54 mmol) under N_2 atmosphere in a Schlenk flask equipped with a stirring bar. The Schlenk flask was sealed, brought outside the glovebox and connected into a vacuum-CO_2 line. The reaction mixture was then purged with three cycles of vacuum-CO_2 and heated at 50 °C under one bar of CO_2 pressure, for 16 h. The conversion of cyclohexene oxide into poly(cyclohexene carbonate) was determined by analysis of the crude reaction mixture by ^{1}H-NMR spectroscopy. Polymers were isolated by precipitation using MeOH to yield white powders. The solid was filtered and dried to constant weight.

General procedure for the Ring Opening Co-Polymerisation of cyclohexene oxide and carbon dioxide at high CO_2 pressure.

In the glovebox, complexes **7**–**9** (65.4 μmol) were dissolved in 0.64 g of cyclohexene oxide (0.66 mL, 6.54 mmol) cyclohexene oxide and placed into a stainless-steel reactor equipped with a magnetic stirrer bar. The autoclave was sealed, pressurised to 5 bar with CO_2, heated to the desired temperature and then pressurised to 10–40 bar with CO_2. The reaction mixture was subsequently stirred at 25–80 °C for 2–16 h. The conversion of cyclohexene oxide **10j** into poly(cyclohexene carbonate) was determined by analysis of the crude reaction mixture by ^{1}H-NMR spectroscopy. Polymers were isolated by precipitation using MeOH to yield white powders. The solid was filtered and dried to constant weight.

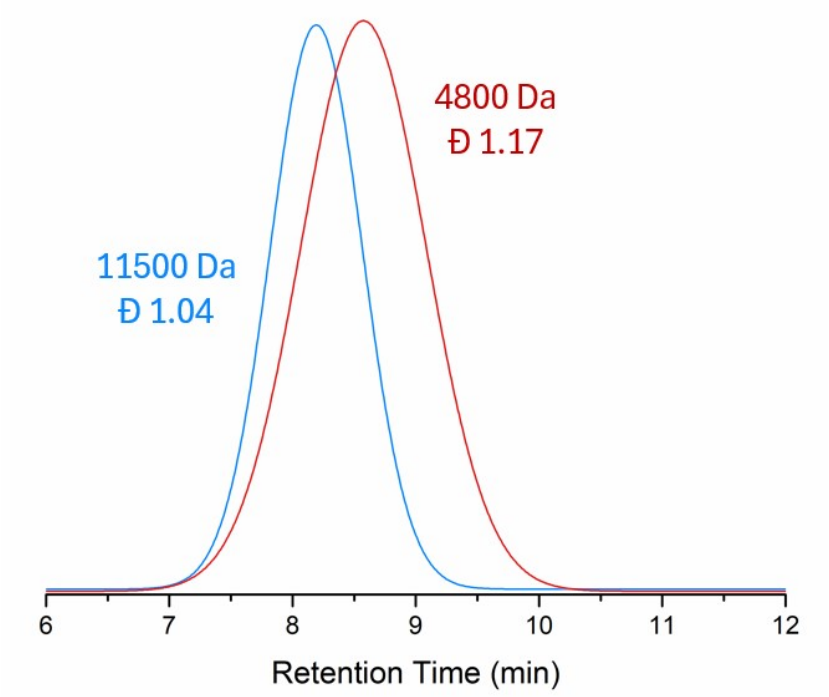


Figure S26. GPC traces of poly(cyclohexene carbonate)s (Table 4, entries 15 and 17, respectively) produced by complex **7** as catalyst at 50 °C and 20 bar CO_2.

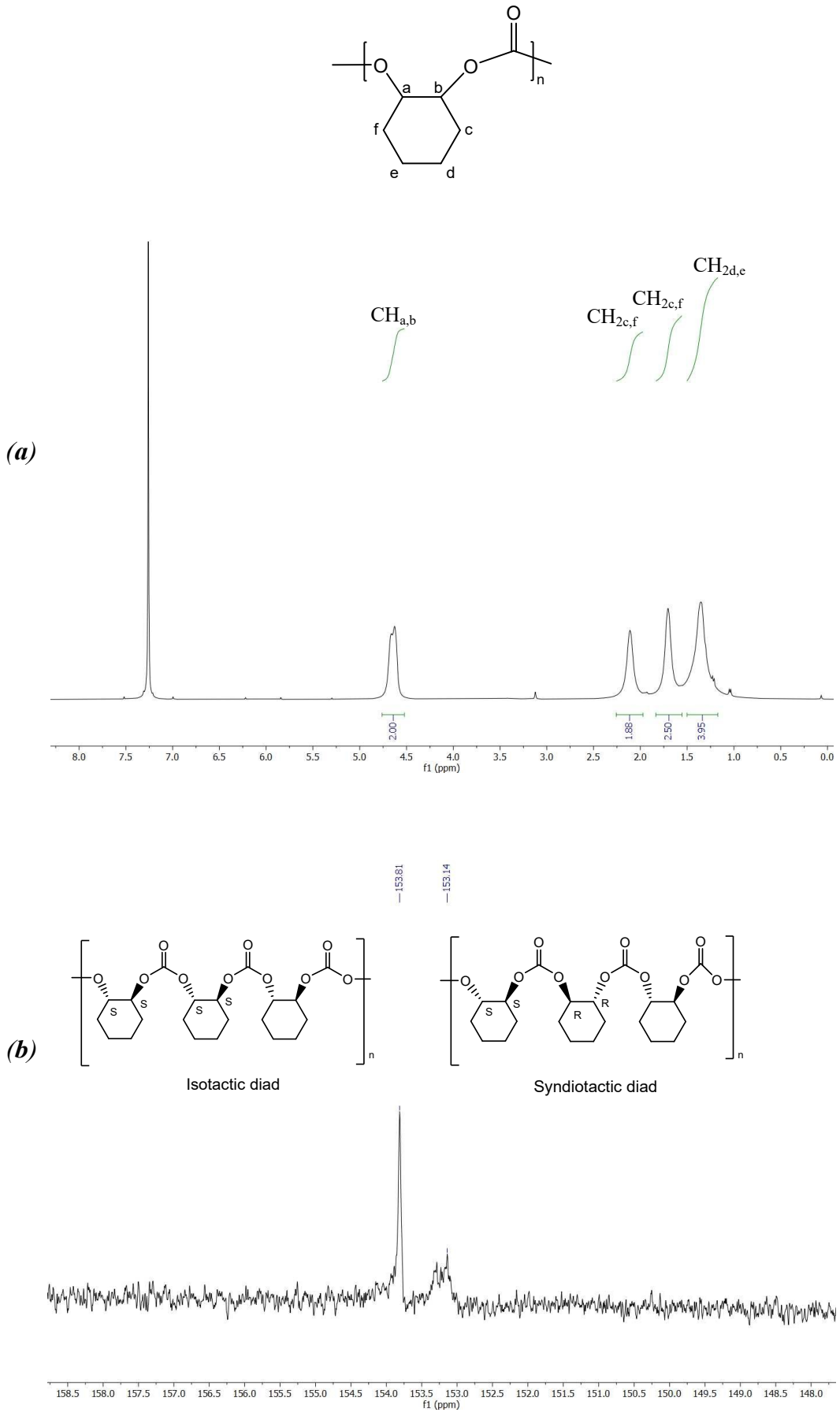
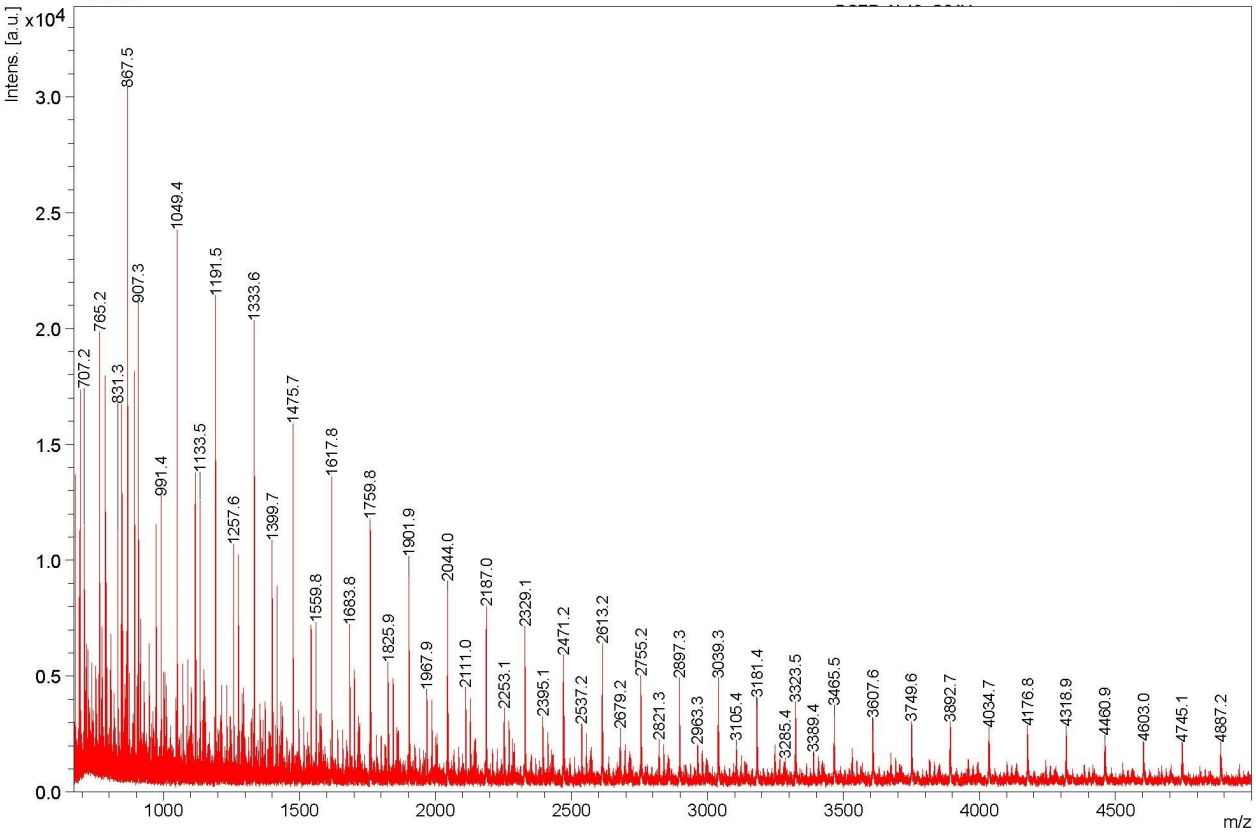
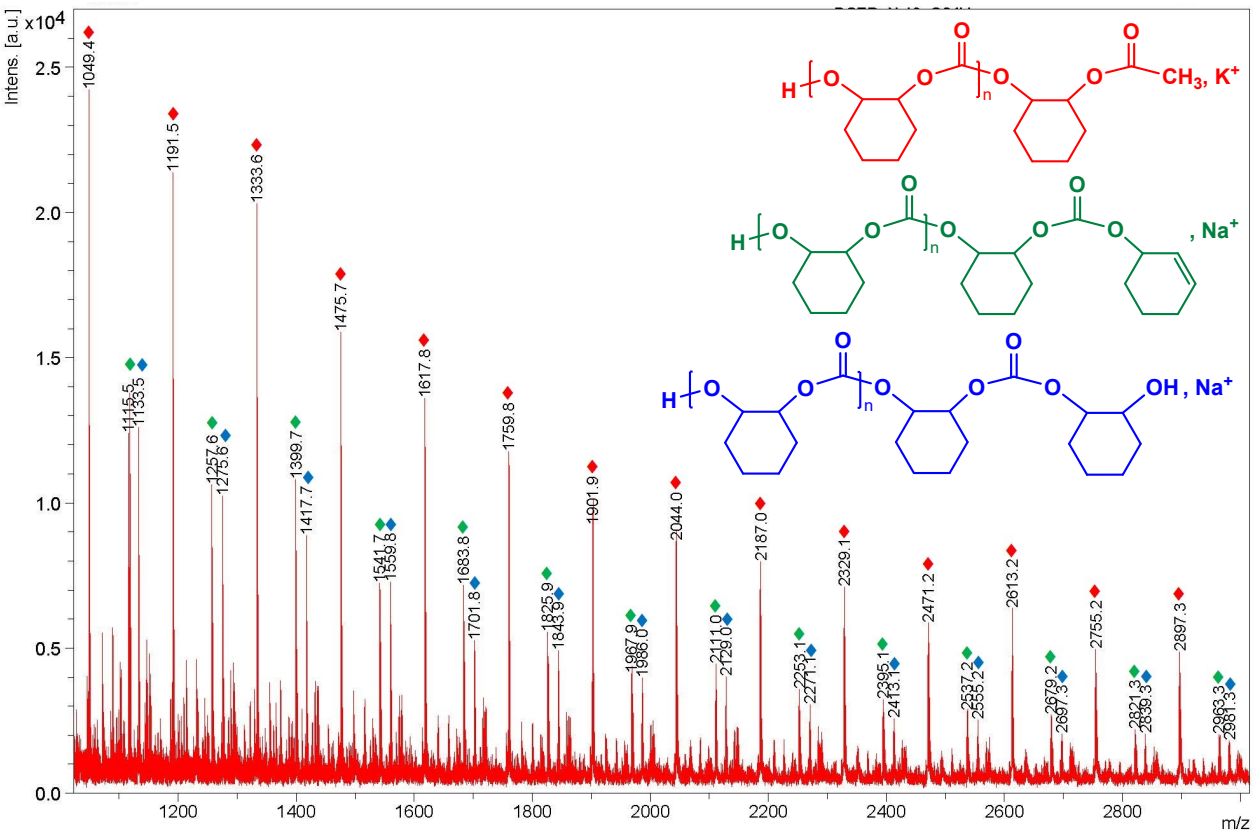


Figure S27. ^{1}H NMR and ^{13}C-{^{1}H} NMR spectra (500 and 125 MHz, 297 K, $CDCl_3$) of a poly(cyclohexene carbonate) sample (Table 4, entry 15) prepared using complex **7** as catalyst at 50 °C and 20 bar CO_2.



(a)



(b)

Figure S28. *(a)* MALDI-ToF mass spectrum of poly(cyclohexene carbonate) sample from Table 4 (entry 15) using zinc complex **7** as catalyst at 50 °C and 20 bar CO_2. *(b)* Expansion of the MALDI-ToF

with the following assignment of peaks: Series ♦ has a repeat unit m/z = 1.01 + (142.07 × DP_{n+1}) + 15.02 + 39.09, where n = 6-19. Series ♦ has a repeat unit m/z = 1.01+ (142.07 × DP_{n+1}) + 115.08 + 22.99, where n = 6-19. Series ♦ has a repeat unit m/z = 1.01+ (142.07 × DP_{n+1}) + 97.07 + 22.99, where n = 6-19.

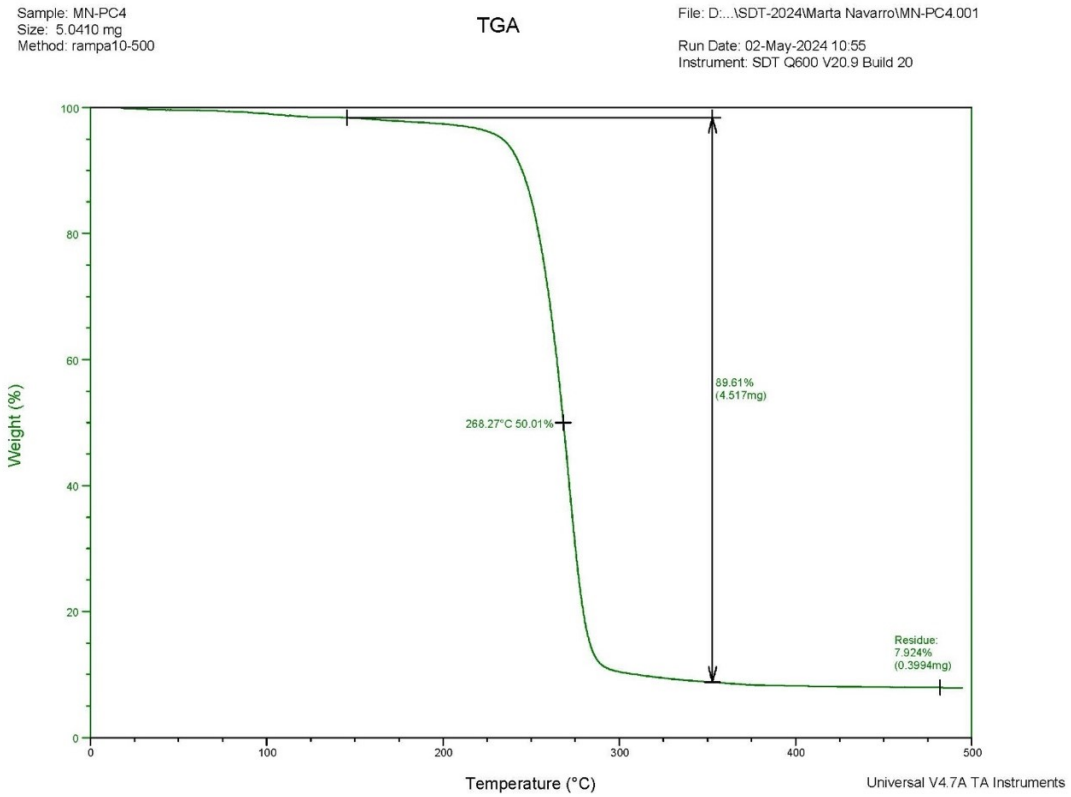


Figure S29. TGA analysis of a poly(cyclohexene carbonate) sample from Table 4 (entry 17) using zinc complex **7** as catalyst at 50 °C and 20 bar CO_2.

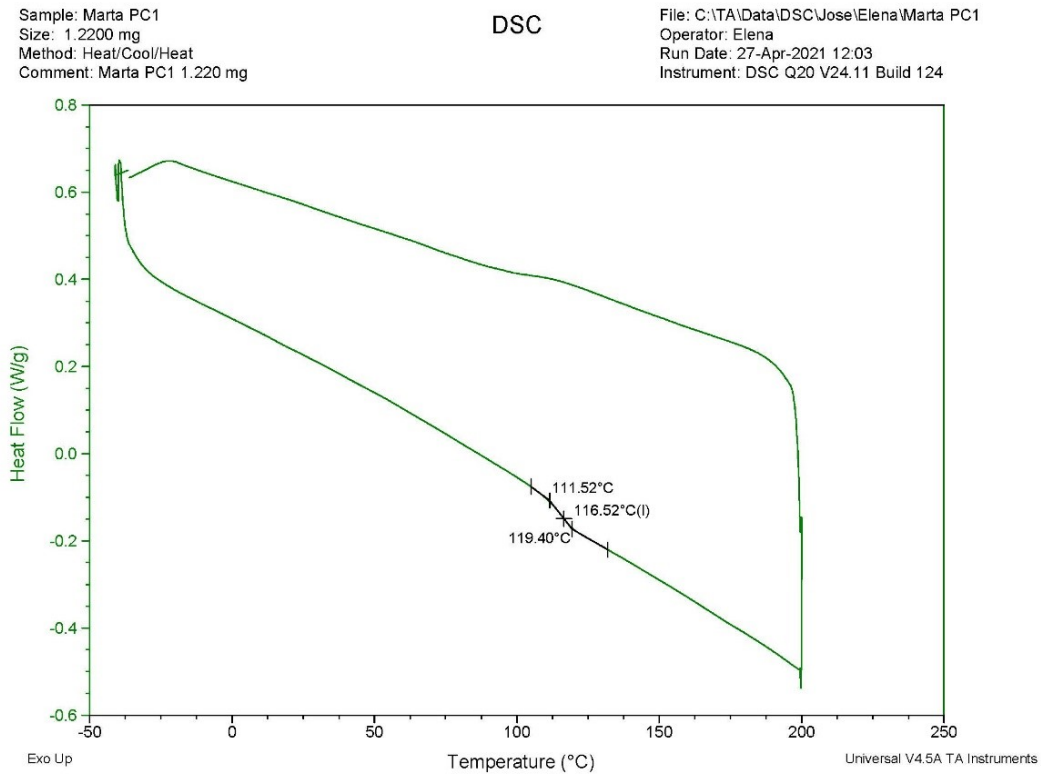


Figure S30. DSC analysis of a poly(cyclohexene carbonate) sample from Table 4 (entry 17) using zinc complex **7** as catalyst at 50 °C and 20 bar CO_2.

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