Electronic Supplementary Material (ESI) for Dalton Transactions.

ELECTRONIC SUPPLEMENTARY INFORMATION

Efficient CO_2 Fixation into Cyclic Carbonates Catalyzed by NNO-Scorpionate Zinc Complexes

Sonia Sobrino,[a] *Marta Navarro,*[b] *Juan Fernández-Baeza,**[a] *Luis F. Sánchez-Barba,**[b] *Andrés Garcés,*[b] *Agustín Lara-Sánchez*[a] *and José A. Castro-Osma,*[c]

[a] Dr. Juan Fernández-Baeza, Dr. Agustín Lara-Sánchez, Sonia Sobrino

Universidad de Castilla-La Mancha, Departamento de Química Inorgánica, Orgánica y Bioquímica, Centro de Innovación en Química Avanzada (ORFEO-CINQA) Campus Universitario, 13071-Ciudad Real, Spain.

E-mail: juan.fbaeza@uclm.es;

[b] Dr. Luis F. Sánchez-Barba, Dr. Andrés Garcés, Marta Navarro

Universidad Rey Juan Carlos, Departamento de Biología y Geología, Física y Química Inorgánica, Móstoles-28933-Madrid, Spain.

E-mail: luisfernando.sanchezbarba@urjc.es

[c] Dr. José A. Castro-Osma

Universidad de Castilla-La Mancha, Departamento de Química Inorgańica, Orgańica y Bioquímica, Centro de Innovación en Química Avanzada (ORFEO−CINQA), Facultad de Farmacia, Universidad de Castilla-La Mancha, 02071 Albacete, Spain.

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

Table of Contents

3) ^{1}H NMR experiment for adduct stability on complex **11** with a donor solvent:

4) ^{1}H NMR experiment in ($CDCl_3$, 25 ºC) to show conservation of the alkyl groups bonded to the zinc centers during the cycloaddition reaction:

5) Kinetic studies to determine the order with respect the catalyst and cocatalyst:

6) NMR characterization for the cyclic carbonates **16a-16m**:

7) NMR characterization for the ligand compounds **3**, **17** and **18**:

8) NMR characterization for the complexes **19-24**:

10) NMR characterization for the cyclic carbonates **16l-16m** obtained using catalyst **22**:

General procedure for catalyst screening at 1 bar pressure

Styrene oxide **15a** (1.66 mmol), catalyst (83.0 μmol) and Bu_4NBr (27 mg, 83.0 μmol, when required) 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 room temperature for 24 h, then the conversion of styrene oxide **15a** to styrene carbonate **16a** was determined by analysis of a sample by ^{1}H-NMR spectroscopy.

General procedure for synthesis of cyclic carbonates 16a–16m at 10 bar pressure

An epoxide **15a**–**15m** (1.66 mmol) and the bicomponent system catalyst **11** (22 mg, 42 μmol)/Bu_4NBr (14 mg, 42.0 μmol), or the one-component catalyst **22** (22 mg, 42 μmol) were placed in a multipoint reactor with a magnetic stirrer bar. The reaction mixture was stirred for 15 h at 50ºC. For epoxides **15a**–**15m**, the conversion of epoxide to cyclic carbonate was then 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 in vacuo 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 system of first hexane, then hexane/EtOAc (9:1), then hexane/EtOAc (6:1), then hexane/EtOAc (3:1), then EtOAc to give the pure cyclic carbonate. Cyclic carbonates **16a**–**16m** are all known compounds and the spectroscopic data for samples prepared using catalyst **22** were consistent with those reported in the literature.[1]

Styrene carbonate (16a). Obtained as a white solid (236.6 mg, 87%). δ_H ($CDCl_3$) 4.18 (1H, t, J=8.6 Hz, OCH_2), 4.62 (1H, t, J=8.4 Hz, OCH_2), 5.51 (1H, t, J=8.0 Hz, $Ph\underline{CH}O$), 7.15–7.30 (5H, m, ArH); δ_C ($CDCl_3$) 71.0 (OCH_2), 78.1 ($Ph\underline{C}HO$), 126.0, 129.4, 129.8 (Ph), 136.0 (C^{ipso}), 154.8 (C=O).

1,2-Hexylene carbonate (16b). Obtained as a colourless liquid (208.2 mg, 87%). δ_H ($CDCl_3$) 0.91 (3H, t, J=7.1 Hz, CH_3), 1.20–1.50 (4H, m, 2 × CH_2), 1.60–1.90 (2H, m, CH_2), 4.10 (1H, dd, J=8.4, 7.2 Hz,

OCH_2), 4.54 (1H, t, J=8.1 Hz, OCH_2), 4.69 (1H, dq, J=7.5, 5.4 Hz, OCH); δ_C ($CDCl_3$) 13.9 (-CH_3), 22.0 (-CH_2-), 26.1 (-CH_2-), 33.8 (-CH_2-), 69.3 (OCH_2), 77.0 (OCH), 154.8 (C=O).

3-Phenoxypropylene carbonate (16c). Obtained as a white solid (315.9 mg, 98%). δ_H ($CDCl_3$) 4.11 (1H, dd, J=10.6, 3.6 Hz, CH_2OPh), 4.22 (1H, dd, J=10.6, 4.2 Hz, CH_2OPh), 4.50–4.70 (2H, m, OCH_2), 4.90–5.10 (1H, m, OCH), 6.90 (2H, m, 2 × ArH), 7.00 (1H, t, J=7.5 Hz, ArH), 7.20–7.30 (2H, m, 2 × ArH); δ_C ($CDCl_3$) 66.0 (-$\underline{CH_2}$OPh), 67.1 (OCH), 74.0 (OCH_2), 114.7, 122.0, 129.9 (Ph), 154.3 (C^{ipso}), 157.9 (C=O).

3-Allyloxypropylene carbonate (16d). Obtained as a white solid (259.9 mg, 99%). δ_H ($CDCl_3$) 3.58 (1H, dd, J=10.6, 3.6 Hz, CH_2OPh), 3.63 (1H, dd, J=10.6, 4.2 Hz, CH_2O-Allyl), 4.00 (2H, m, =CH-$\underline{CH_2}$O), 4.30–4.50 (2H, m, OCH_2), 4.80 (1H, m, OCH), 5.10-5.30 (2H, m, =CH_2), 5.80-5.90 (1H, m, -CH=). δ_C ($CDCl_3$), 66.1 (CH_2O-Allyl), 69.0 (OCH_2), 72.2 (=CH-$\underline{C}H_2$O), 75.0 (OCH), 118.0 (C=C), 134.0 (C=C), 155.1 (C=O).

1,2-Decylene carbonate (16e). Obtained as a colourless liquid (326.8 mg, 98%). δ_H ($CDCl_3$) 0.84 (3H, t, J=6.8 Hz, CH_3), 1.20–1.50 (12H, m, 6 × CH_2), 1.60–1.90 (2H, m, CH_2), 4.03 (1H, dd, J=8.4, 7.8 Hz, OCH_2), 4.50 (1H, dd, J=8.4, 7.8 Hz, OCH_2), 4.70 (1H, m, OCH); δ_C ($CDCl_3$) 14.0 (-CH_3), 22.3 (-CH_2-), 24.2 (-CH_2-), 29.2 (-CH_2-), 29.3 (-CH_2-), 29.5 (-CH_2-), 31.9 (-CH_2-), 33.9 (R-$\underline{C}H_2$-), 69.6 (OCH_2), 77.0 (OCH), 155.2 (C=O).

3-Chloropropylene carbonate (16f). Obtained as a colorless liquid (224.9 mg, 99%). δ_H ($CDCl_3$) 3.70–3.80 (2H, m, CH_2Cl), 4.40 (1H, dd, J=9.0, 8.7 Hz, OCH_2), 4.60 (1H, t, J=8.5 Hz, OCH_2), 4.90–5.00 (1H, m, OCH); δ_C ($CDCl_3$) 43.9 (CH_2Cl), 67.0 (OCH_2), 74.1 (OCH), 154.4 (C=O).

Glycerol carbonate (16g). Obtained as a colourless liquid (194.3 mg, 99%). δ_H ($CDCl_3$) 3.60 (1H, dd, J=12.6, 3.2 Hz, CH_2OH), 3.80-4.00 (1H, dd, J=12.6, 2.6 Hz, CH_2OH), 4.35 (1H, dd, J=8.1, 5.8 Hz, CH_2O), 4.40-4.60 (1H, t, J=8.3 Hz, CH_2O), 4.80–4.90 (1H, m, OCH), 5.29 (1H, br, OH); δ_C ($CDCl_3$) 60.8 (CH_2OH), 65.9 (OCH_2), 77.9 (OCH), 154.3 (C=O).

Propylene carbonate (16h). Obtained as a colourless liquid (170.0 mg, 100%). δ_H ($CDCl_3$) 1.48 (3H, d, J=6.3 Hz, CH_3), 4.05 (1H, dd, J=8.3 Hz, 7.4 Hz, OCH_2), 4.58 (1H, t, J=8.3 Hz, OCH_2), 4.80–4.90 (1H, m, OCH); δ_C ($CDCl_3$) 19.4 (CH_3), 70.6 (OCH_2), 73.6 (OCH), 155.2 (C=O).

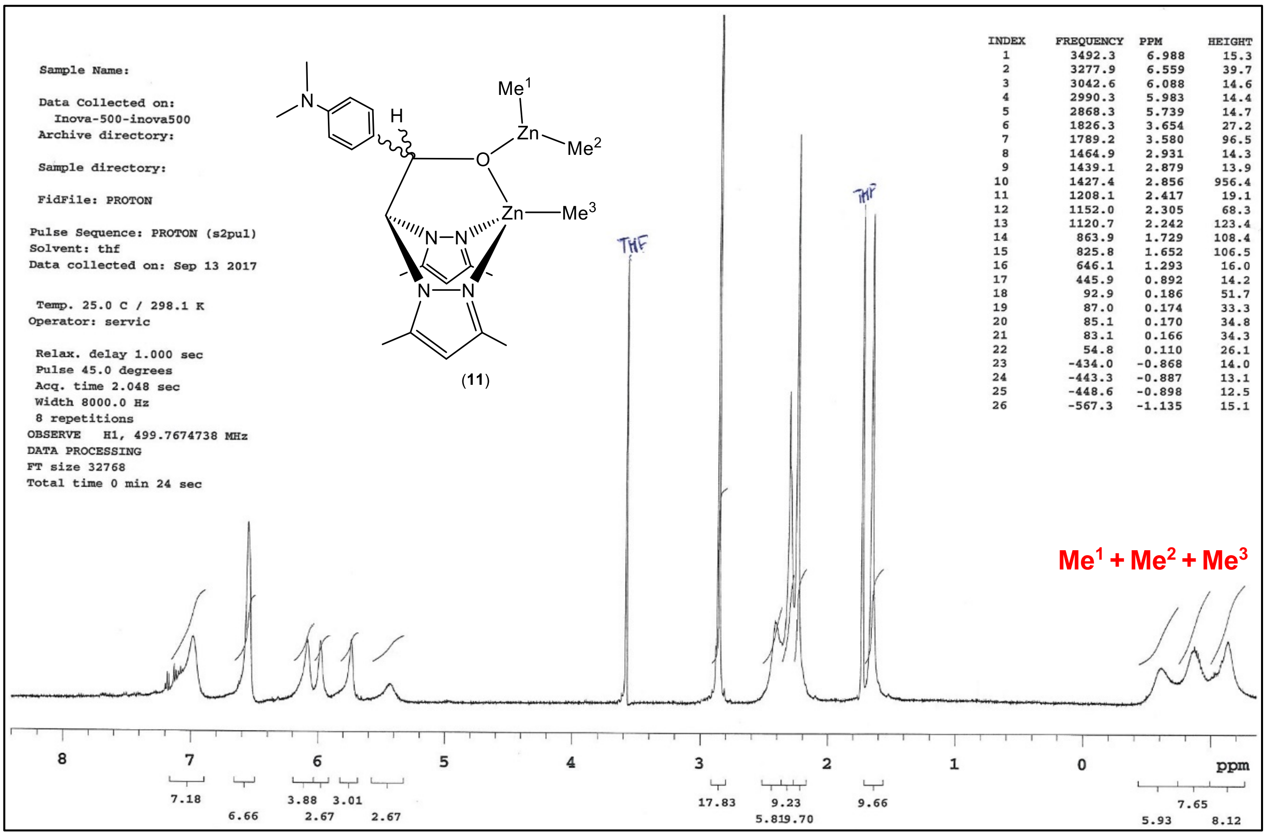
1,2-Butylene carbonate (16i). Obtained as a colourless liquid (188.9 mg, 98%). δ_H ($CDCl_3$) 1.02 (3H, t, J=7.1 Hz, CH_3), 1.60–1.90 (2H, m, CH_2), 4.10 (1H, dd, J=6.3, 5.3 Hz, OCH_2), 4.50 (1H, t, J=8.1 Hz, OCH_2), 4.60–4.70 (1H, m, OCH); δ_C ($CDCl_3$) 8.2 (CH_3), 26.9 (CH_2), 69.1 (OCH_2), 78.0 (OCH), 154.9 (C=O).

4-Bromostyrene carbonate (16j). Obtained as a white solid (371.6 mg, 92%). δ_H ($CDCl_3$) 4.32 (1H, t, J=8.2 Hz, OCH_2), 4.80 (1H, t, J=8.4 Hz, OCH_2), 5.65 (1H, t ,J=8.0 Hz, OCH), 7.23 (2H, dd, J=8.4, 1.8 Hz, ArH), 7.58 (2H, dd, J=8.1, 2.0 Hz, ArH); δ_C ($CDCl_3$) 70.5 (OCH_2), 77.2 (OCH), 123.9, 127.8, 132.2 (Ph), 134.9 (C^{ipso}), 154.2 (C=O).

4-Chlorostyrene carbonate (16k). Obtained as a white solid (318.2 mg, 97%). δ_H ($CDCl_3$) 4.29 (1H, t, J=7.8 Hz, OCH_2), 4.79 (1H, t, J=8.4 Hz, OCH_2), 5.64 (1H, t, J=7.9 Hz, OCH), 7.30 (2H, d, J=8.5 Hz, ArH), 7.41 (2H, d, J=8.5 Hz, ArH); δ_C ($CDCl_3$) 70.7 (OCH2), 77.0 (OCH), 127.2, 129.7, 134.2 (Ph), 135.6 (C^{ipso}), 154.1 (C=O).

***cis*-1,2-Cyclohexene carbonate (16l).** Obtained as a white solid (149.4 mg, 63%). δ_H ($CDCl_3$) 1.30–1.40 (2H, m, CH_2), 1.50–1.70 (2H, m, CH_2), 1.80–2.00 (4H, m, 2 × CH_2), 4.60–4.70 (2H, m); δ_C ($CDCl_3$) 19.2 (CH_2), 26.2 (CH_2), 75.8 (OCH), 155.8 (C=O).

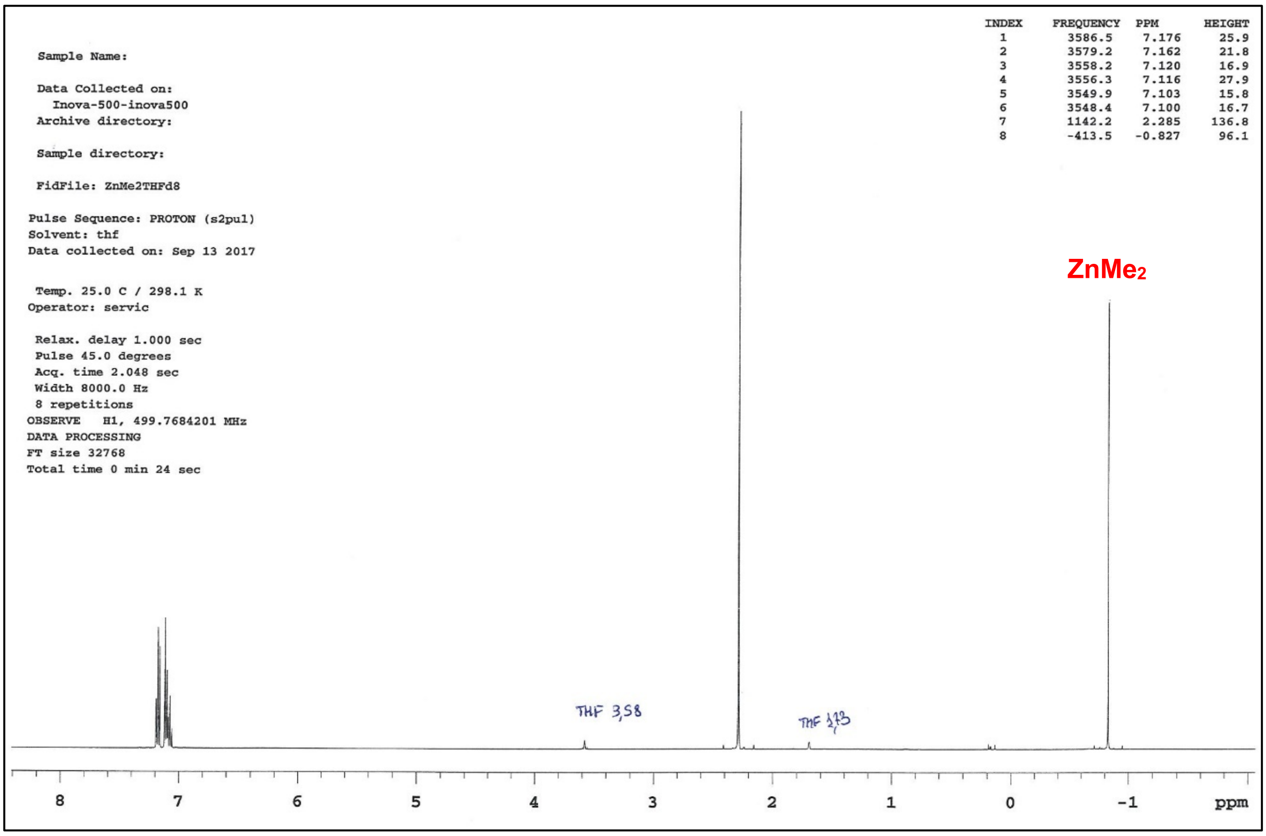
***cis*-1,2-Cyclopentene carbonate (16m).** Obtained as a white solid (122.8 mg, 58%). δ_H ($CDCl_3$) 1.60–1.70 (2H, m, CH_2), 1.70–1.80 (2H, m, CH_2), 2.10–2.20 (2H, m, CH_2), 5.10 (2H, m, OCH); δ_C ($CDCl_3$) 21.8 (CH), 33.6 (CH_2), 81.7 (OCH), 155.5 (C=O).



```
Sample Name:

Data Collected on:
  Inova-500-inova500
Archive directory:

Sample directory:

FidFile: PROTON

Pulse Sequence: PROTON (s2pul)
Solvent: thf
Data collected on: Sep 13 2017

Temp. 25.0 C / 298.1 K
Operator: servic

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
8 repetitions
OBSERVE   H1, 499.7674738 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 24 sec
```

```
INDEX   FREQUENCY   PPM      HEIGHT
  1       3492.3    6.988     15.3
  2       3277.9    6.559     39.7
  3       3042.6    6.088     14.6
  4       2990.3    5.983     14.4
  5       2868.3    5.739     14.7
  6       1826.3    3.654     27.2
  7       1789.2    3.580     96.5
  8       1464.9    2.931     14.3
  9       1439.1    2.879     13.9
 10       1427.4    2.856    956.4
 11       1208.1    2.417     19.1
 12       1152.0    2.305     68.3
 13       1120.7    2.242    123.4
 14        863.9    1.729    108.4
 15        825.8    1.652    106.5
 16        646.1    1.293     16.0
 17        445.9    0.892     14.2
 18         92.9    0.186     51.7
 19         87.0    0.174     33.3
 20         85.1    0.170     34.8
 21         83.1    0.166     34.3
 22         54.8    0.110     26.1
 23       -434.0   -0.868     14.0
 24       -443.3   -0.887     13.1
 25       -448.6   -0.898     12.5
 26       -567.3   -1.135     15.1
```

(a)

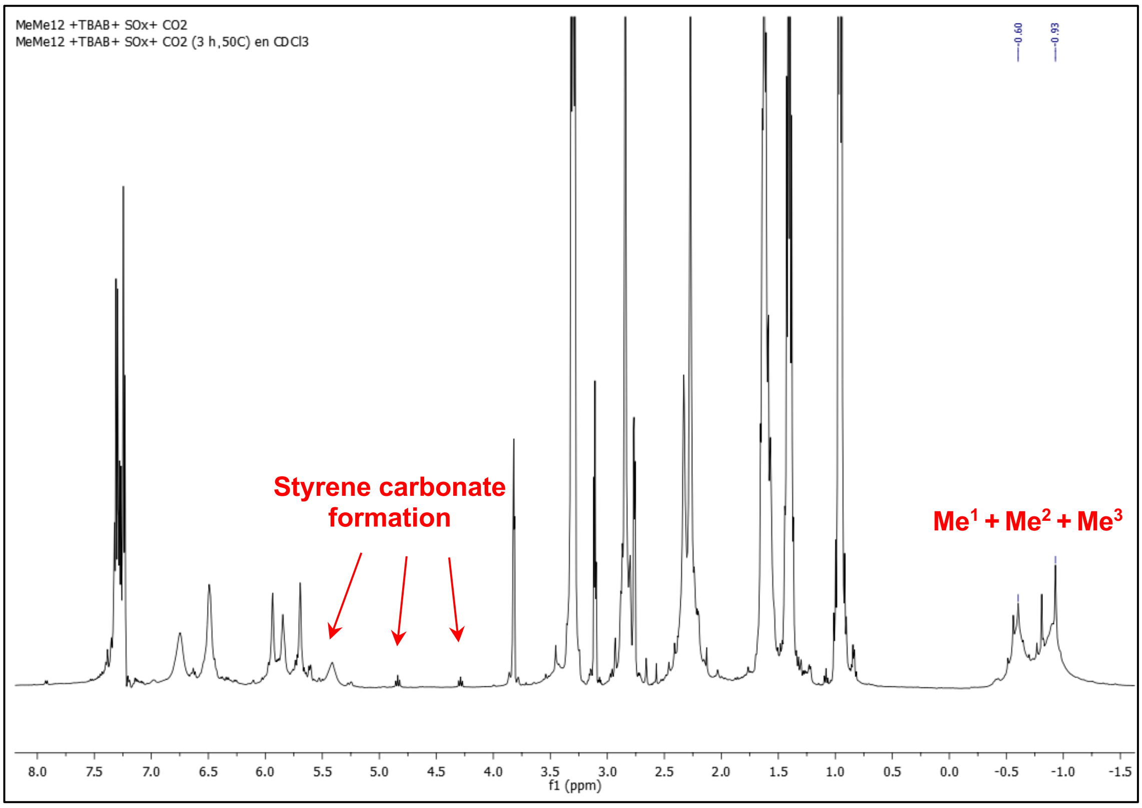


```
Sample Name:

Data Collected on:
  Inova-500-inova500
Archive directory:

Sample directory:

FidFile: ZnMe2THFd8

Pulse Sequence: PROTON (s2pul)
Solvent: thf
Data collected on: Sep 13 2017

Temp. 25.0 C / 298.1 K
Operator: servic

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
8 repetitions
OBSERVE   H1, 499.7684201 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 24 sec
```

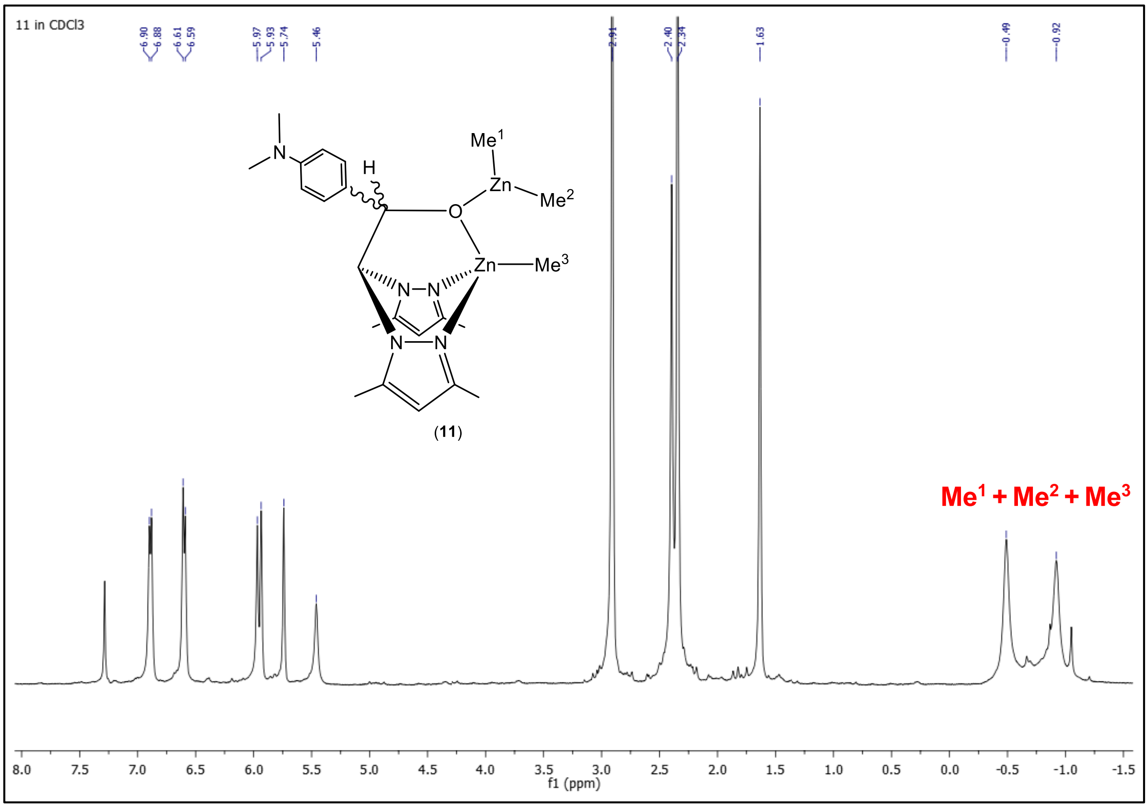
```
INDEX   FREQUENCY   PPM      HEIGHT
  1       3586.5    7.176     25.9
  2       3579.2    7.162     21.8
  3       3558.2    7.120     16.9
  4       3556.3    7.116     27.9
  5       3549.9    7.103     15.8
  6       3548.4    7.100     16.7
  7       1142.2    2.285    136.8
  8       -413.5   -0.827     96.1
```

(b)

Figure S1. ^{1}H NMR spectra (thf-d_8, 25ºC) for (*a*) complex [Zn(Me)(bpzampe)Zn(Me)$_2$] (**11**) and (*b*) commercial ZnMe$_2$ in toluene 2M.



(b)



(a)

Figure S2. ^{1}H NMR spectra ($CDCl_3$, 25ºC) for *(a)* complex [Zn(Me)(bpzampe)Zn(Me)$_2$] (**11**), *(b)* the stoichiometric reaction of complex **11** with styrene oxide **15a** and Bu_4NBr as co-catalyst in the presence of 1 bar CO_2 pressure in a Young tube, after 3 h at 50 ºC.

Typical kinetic experiment procedure

Styrene oxide **15a** (0.28 mL, 2.48 mmol, 8.86 M), complex **11** (50 mg, 99.2 µmol) and Bu_4NBr (33 mg, 99.2 µmol) were placed in a sample vial fitted with a magnetic stirred bar. The sample vial was placed in a large conical flask fitted with a rubber stopper pierced by a deflated balloon. Cardice pellets were added to the conical flask and placed in an oil bath preheated to 50 °C. The reaction mixture was stirred at this temperature during 2.5 hours. Samples of the mixture were withdrawn at different time intervals and the conversion of the epoxide to cyclic carbonate was determined by ^1H NMR analysis.

Similar experimental procedures were followed for additional runs but employing the corresponding amount of each substance according to the established loading for catalyst and/or co-catalyst (from 1% to 4%) and extending the time as needed.

Kinetics analysis

Kinetics measurements as a function of catalyst and co-catalyst loading were performed at early stages of the cycloaddition reaction. Under these conditions, the epoxide acts as both substrate and solvent and its concentration does not change significantly, and therefore it can be considered as pseudo-constant.

The reaction also proceeds in the presence of a large excess of CO_2, and therefore its concentration can be considered constant.

Accordingly, the general rate equation for this reaction, shown in equation 1, can be written as equation 2.

$$\text{Rate} = k\,[\mathbf{15a}]^a[\mathrm{CO_2}]^b[\mathbf{11}]^c[\mathrm{TBAB}]^d \qquad [1]$$

$$\text{Rate} = k_{\text{obs.}}\,[\mathbf{11}]^c[\mathrm{TBAB}]^d\text{, where } k_{\text{obs.}} = k\,[\mathbf{15a}]^a[\mathrm{CO_2}]^b \qquad [2]$$

From equation 2, it is possible to determine the order with respect catalyst and co-catalyst by carrying out two sets of reactions at different concentrations of **11** or TBAB and maintaining the other catalyst component constant, respectively.

Initially, for determining the order with respect the catalyst, the amount of TBAB was fixed to 4 mol % with respect the epoxide, whilst concentration of complex **11** was varied from 1% to 4%. Concentration of epoxide **15a** was plotted against time for the four runs (Figure S3a).

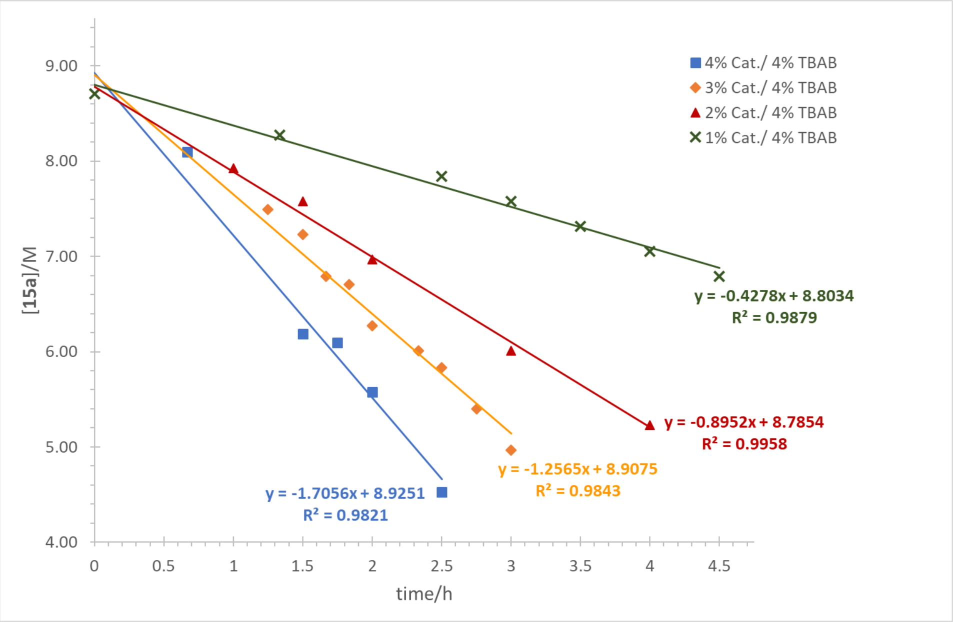


Figure S3a

Equation 2 can be rewritten as:

$$\text{Rate} = k'_{\text{obs.}}\,[\mathbf{11}]^{c}, \text{ where } k'_{\text{obs.}} = k\,[\mathbf{15a}]^{a}[\text{CO}_2]^{b}[\text{TBAB}]^{d} \qquad [3]$$

By plotting log $k'_{0,\text{ obs.}}$ against log [**11**] is possible to determine the order with respect the catalyst from the slope of the curve (Figure S3b).

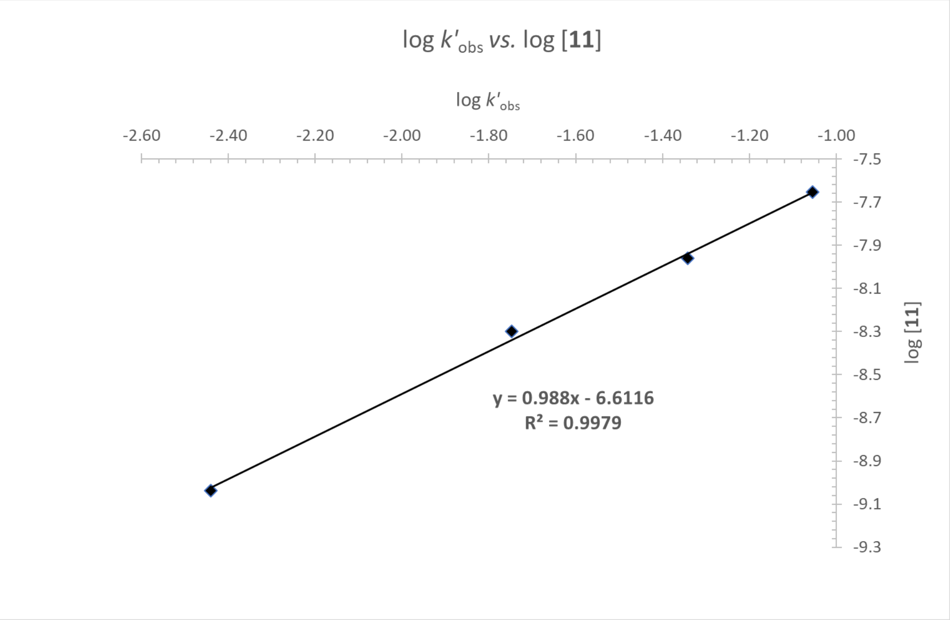


Figure S3b

The order with respect co-catalyst was determined following a similar procedure, but keeping concentration of complex **11** constant, 4% of the initial epoxide concentration, and varying the concentration of TBAB from 1% to 4%. Concentration of epoxide **15a** was plotted against time for the four runs (Figure S3c).

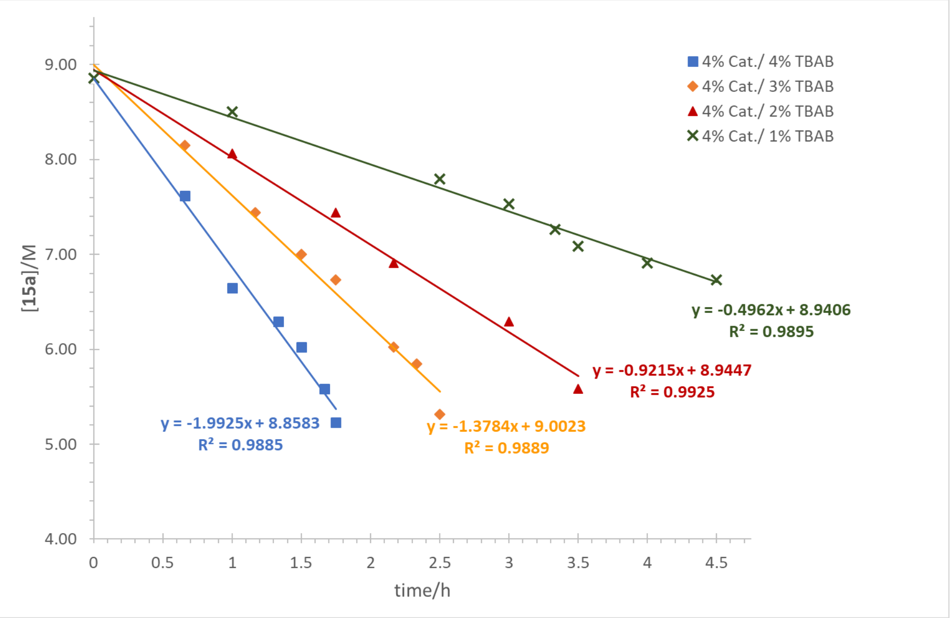


Figure S3c

In this case, Equation 2 can be rewritten as:

$$\text{Rate} = k''_{\text{obs.}}\,[\text{TBAB}]^{d}, \text{ where } k''_{\text{obs.}} = k\,[\mathbf{15a}]^{a}[\text{CO}_2]^{b}[\mathbf{11}]^{d} \qquad [4]$$

By plotting log $k''_{0,\text{ obs.}}$ against log [TBAB] is possible to determine the order with respect the co-catalyst from the slope of the curve (Figure S3d).

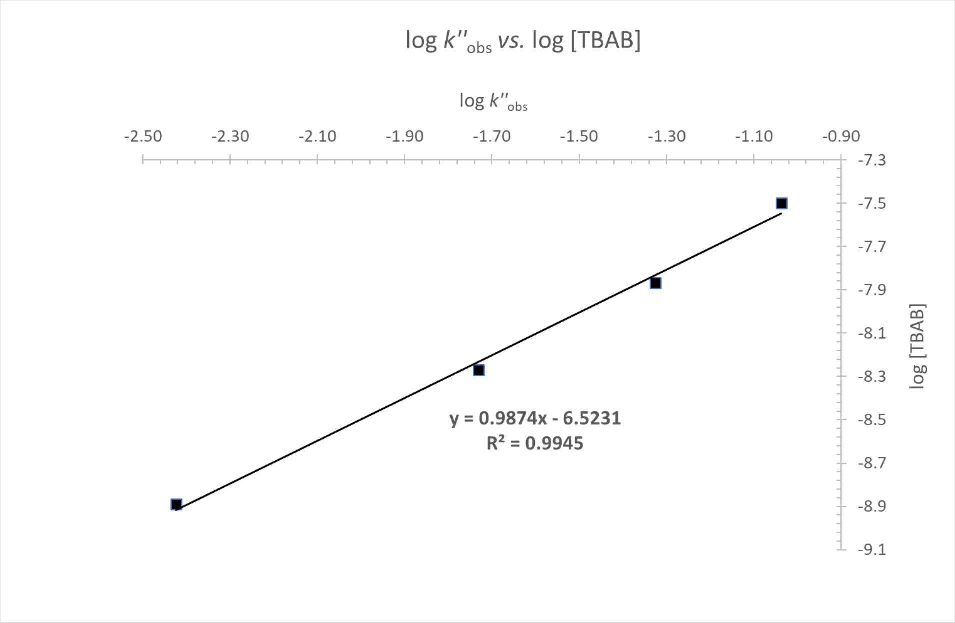


Figure S3d

Complete set of kinetic data are summarized in Tables S1a and S1b with the corresponding associated error.

Table S1a

Conc. (mM)	$k'_{\text{obs.}}$ (h^{-1})	Error (h^{-1})	$k'_{\text{obs.}}$ (s^{-1})	Error (s^{-1})	$k'_{\text{obs.}}$ (s^{-1}) × 10^4	Error (s^{-1})× 10^4	$k'_{\text{obs.}}$ ± error (s^{-1}) × 10^4
87	0.428	6.06E-02	1.188E-04	1.68E-05	1.2	0.2	1.2 ± 0.2
174	0.895	6.06E-02	2.487E-04	1.68E-05	2.5	0.2	2.5 ± 0.2
261	1.257	5.62E-02	3.490E-04	1.56E-05	3.5	0.2	3.5 ± 0.2
348	1.706	1.15E-01	4.738E-04	3.20E-05	4.7	0.3	4.7 ± 0.3

Reaction order with respect [**11**] = 0.99 ± 0.03

Table S1b

Conc. (mM)	$k''_{\text{obs.}}$ (h^{-1})	Error (h^{-1})	$k''_{\text{obs.}}$ (s^{-1})	Error (s^{-1})	$k''_{\text{obs.}}$ (s^{-1}) × 10^4	Error (s^{-1})× 10^4	$k''_{\text{obs.}}$ ± error (s^{-1}) × 10^4
89	0.496	4.02E-02	1.378E-04	1.12E-05	1.4	0.1	1.4 ± 0.1
177	0.921	4.02E-02	2.560E-04	1.12E-05	2.6	0.1	2.6 ± 0.1
266	1.378	5.96E-02	3.829E-04	1.66E-05	3.8	0.2	3.8 ± 0.2
354	1.992	9.61E-02	5.535E-04	2.67E-05	5.5	0.3	5.5 ± 0.3

Reaction order with respect [TBAB] = 0.99 ± 0.05

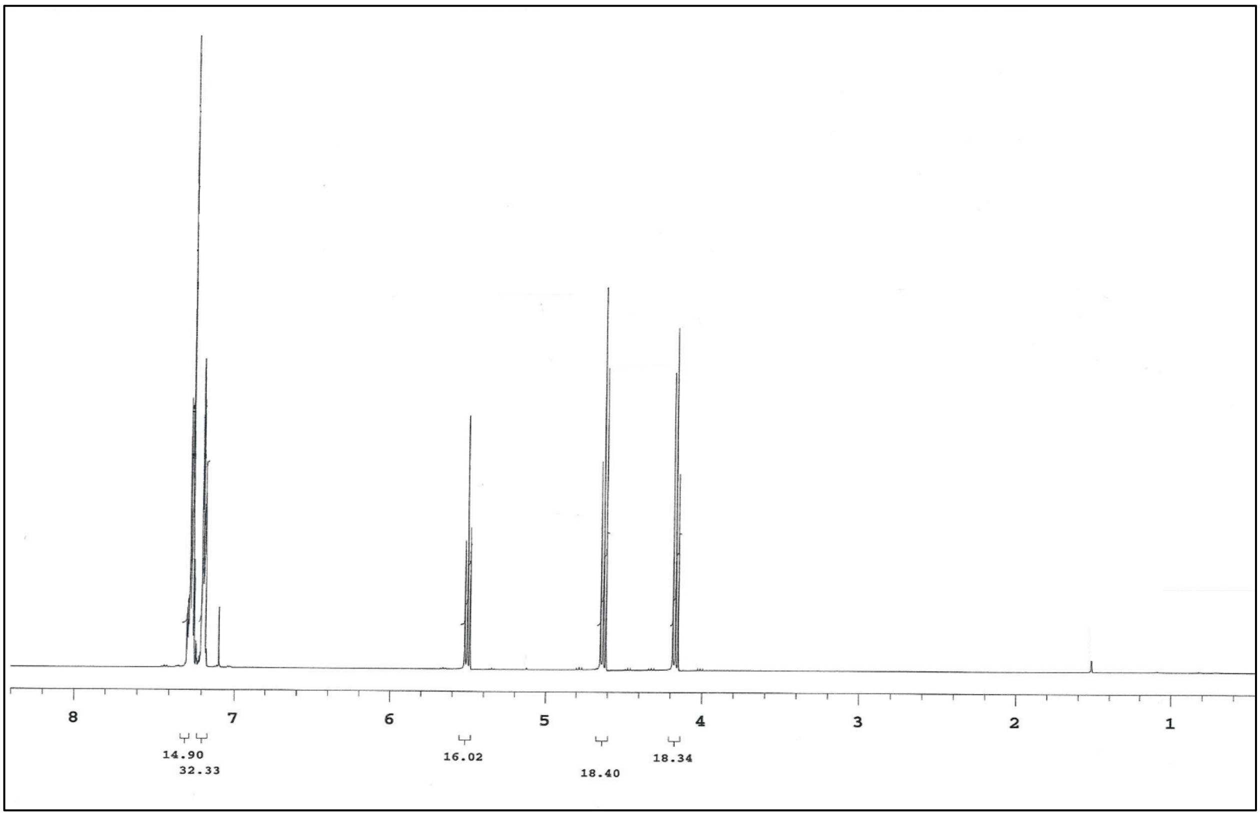


Figure S4a. ^{1}H NMR spectrum (500 MHz, 297 K, CDCl$_3$) of styrene carbonate **(16a)**.

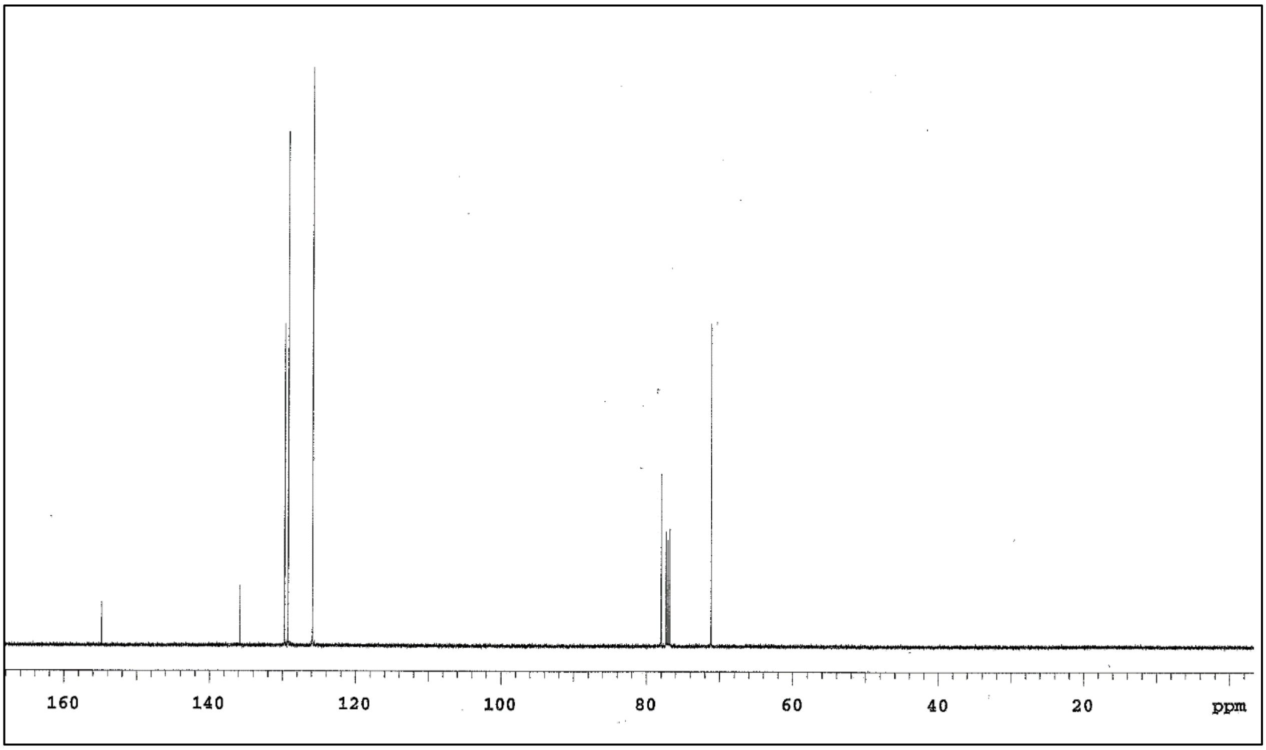


Figure S4b. ^{13}C{^{1}H} NMR spectrum (125 MHz, 297 K, CDCl$_3$) of styrene carbonate **(16a)**.

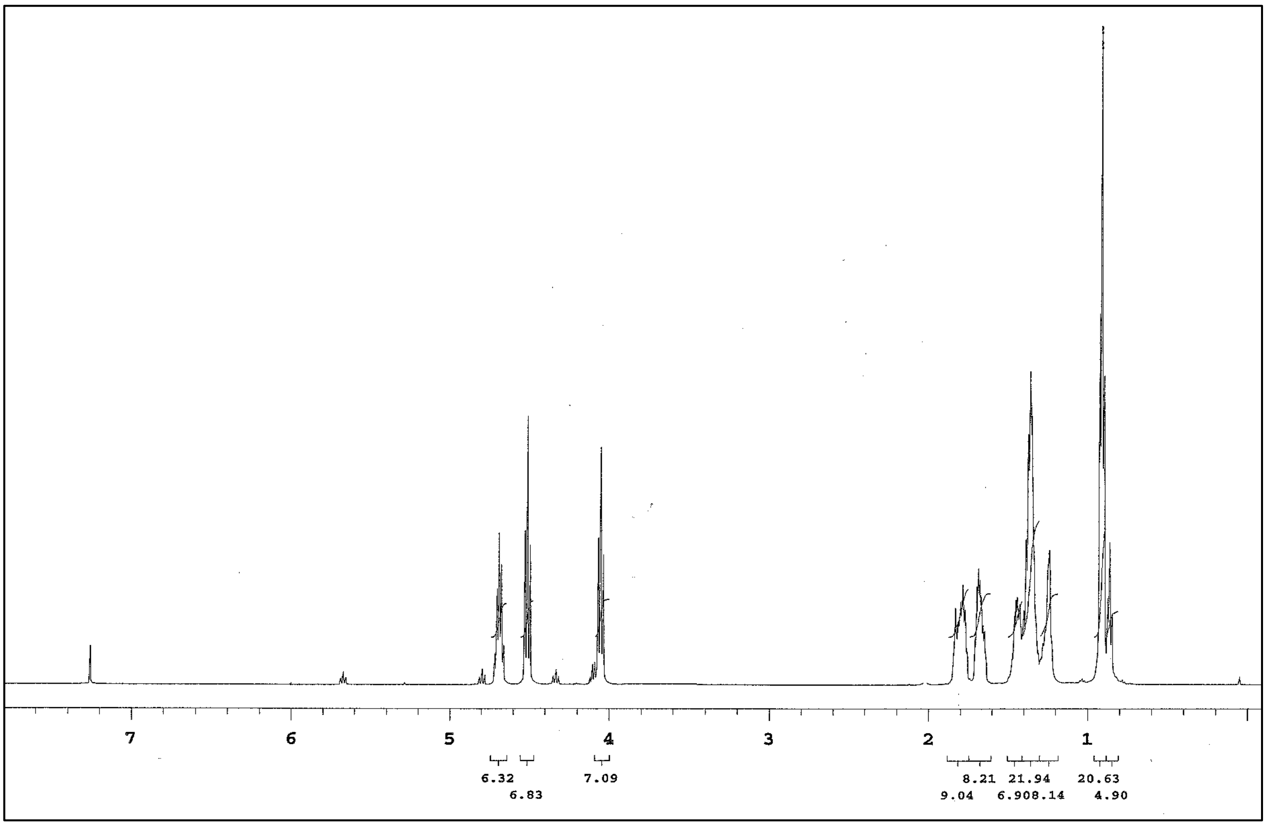


Figure S5a. ^{1}H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of 1,2-hexylene carbonate **(16b)**.

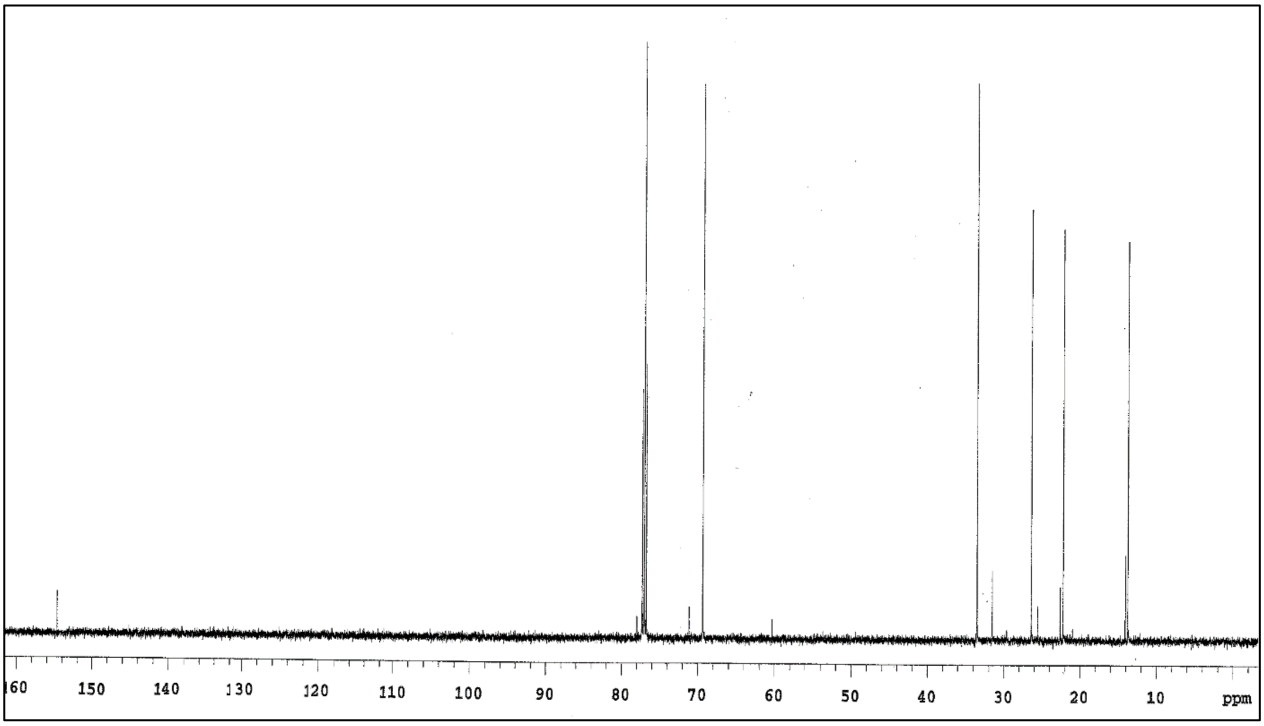


Figure S5b. ^{13}C{^{1}H} NMR spectrum (125 MHz, 297 K, $CDCl_3$) of 1,2-hexylene carbonate **(16b)**.

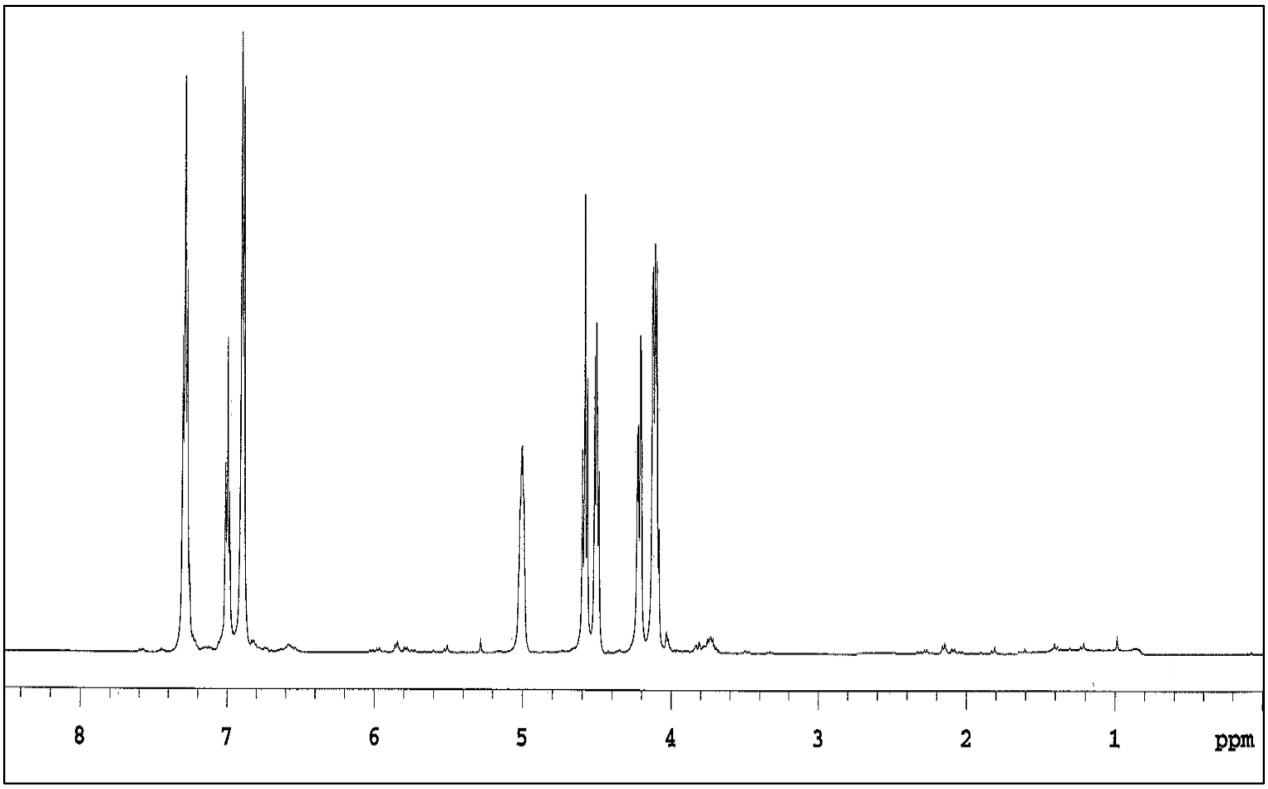


Figure S6a. ^{1}H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of 3-phenoxypropylene carbonate **(16c)**.

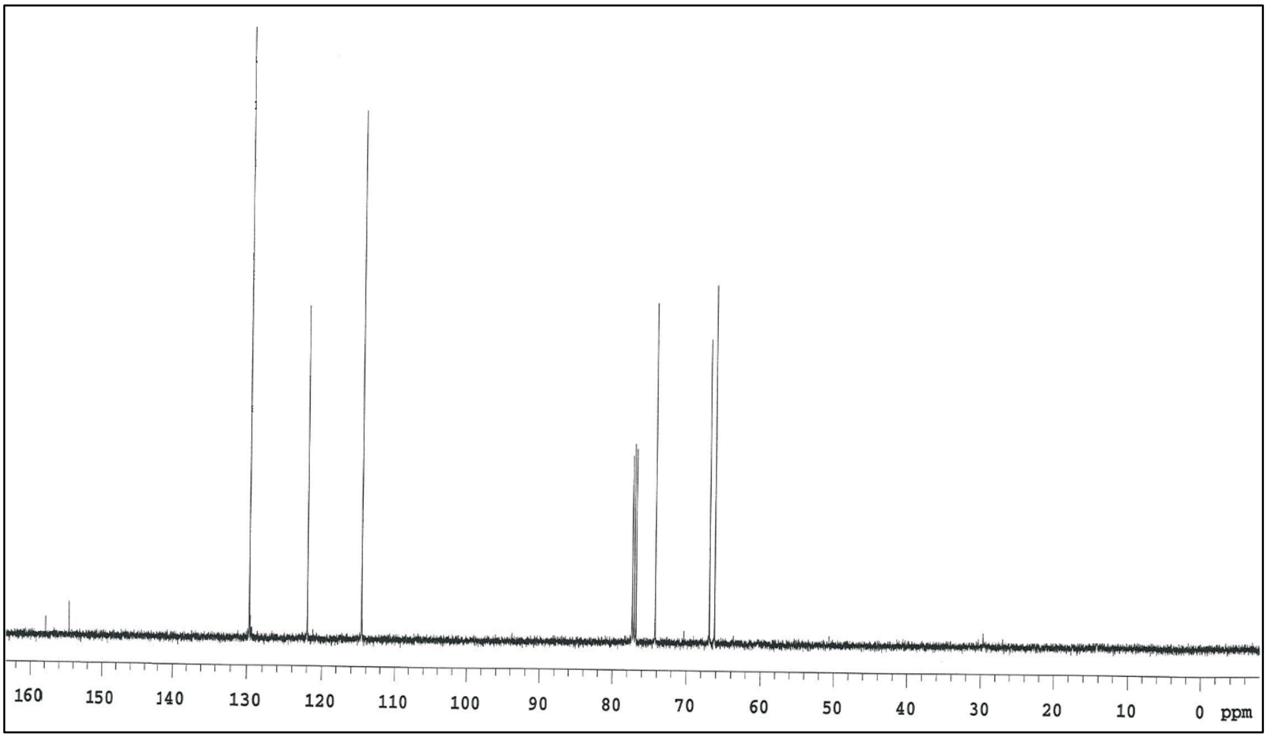


Figure S6b. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 297 K, $CDCl_3$) of 3-phenoxypropylene carbonate **(16c)**.

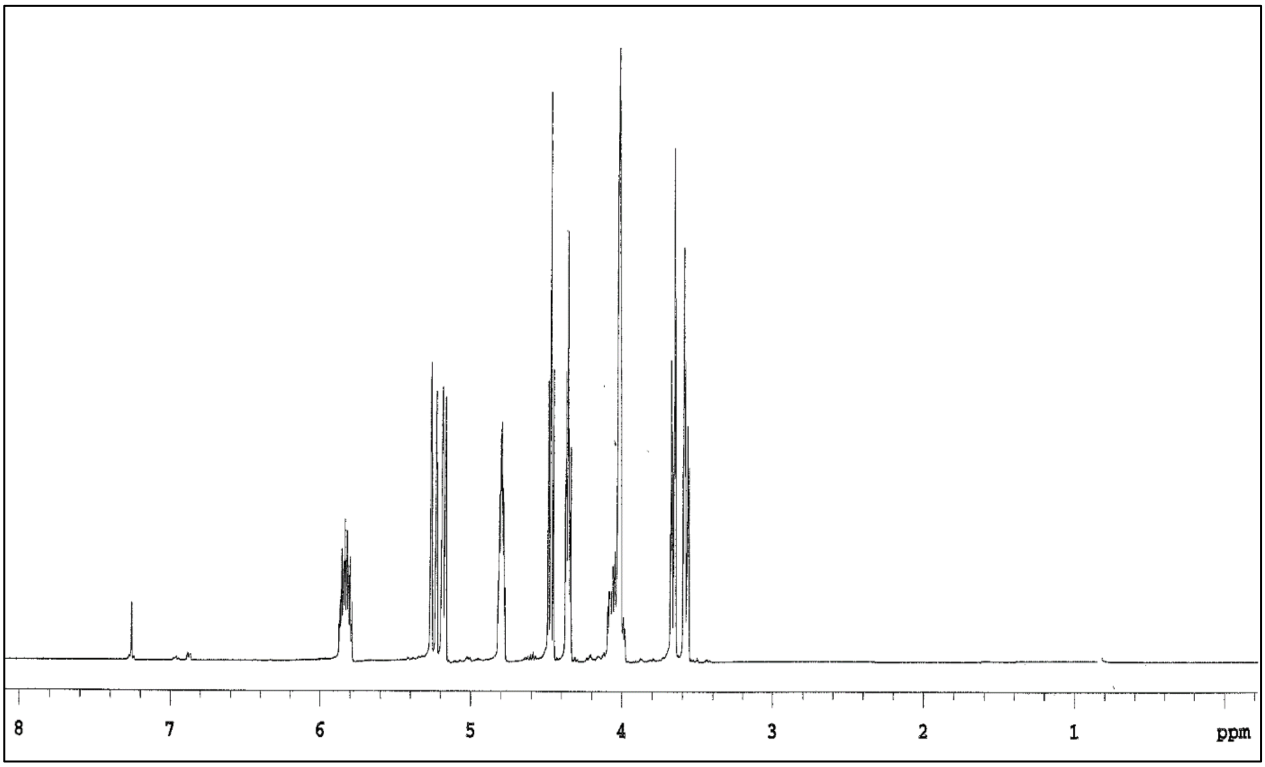


Figure S7a. ^1H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of 3-allyloxypropylene carbonate **(16d)**.

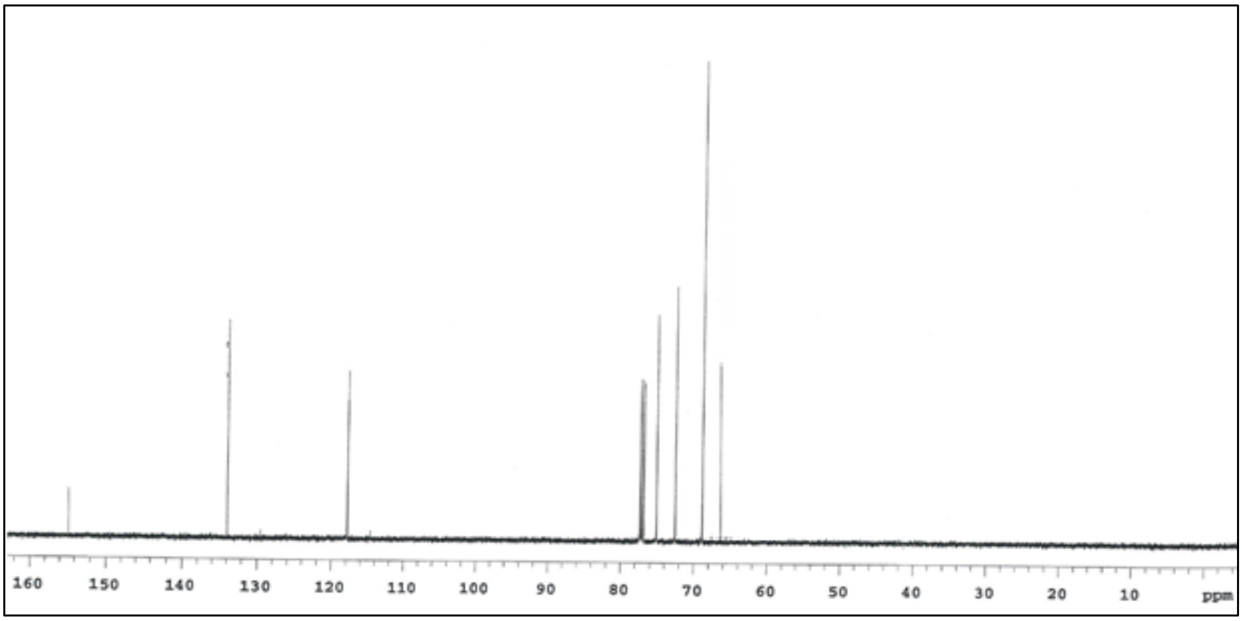


Figure S7b. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 297 K, $CDCl_3$) of 3-allyloxypropylene carbonate **(16d)**.

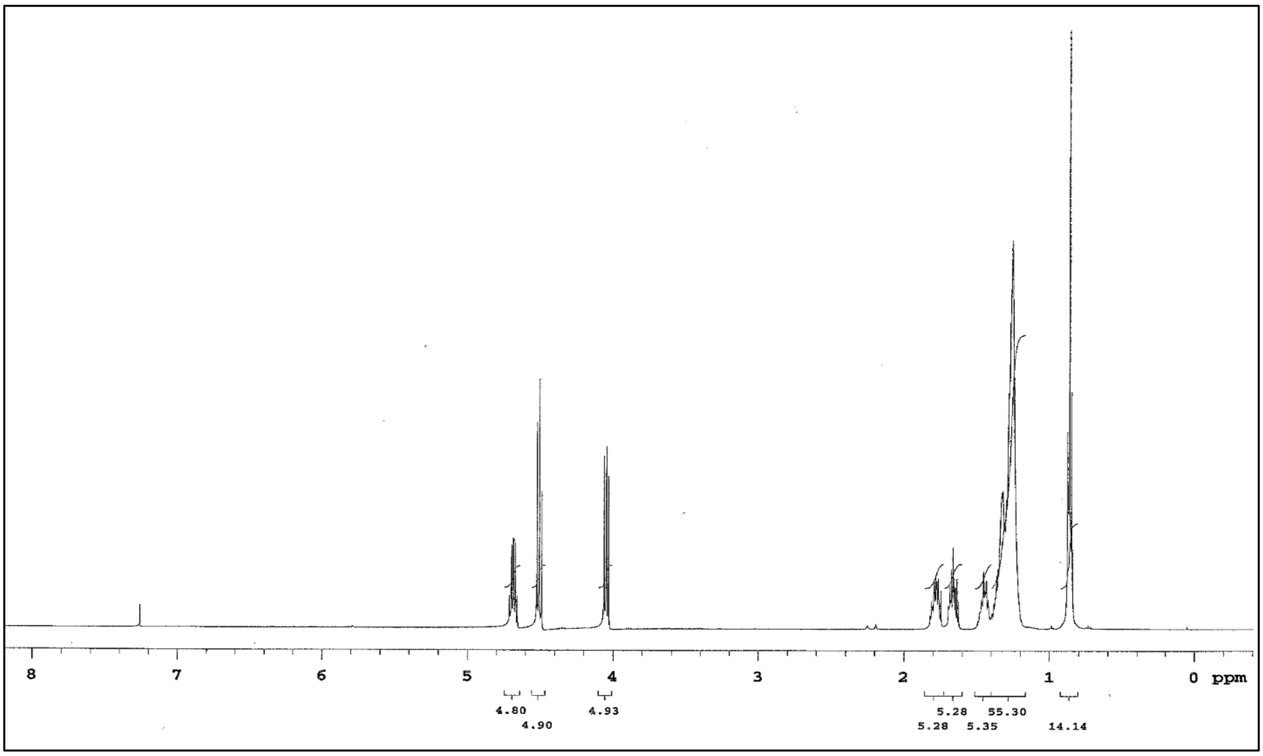


Figure S8a. ^{1}H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of 1,2-decylene carbonate **(16e)**.

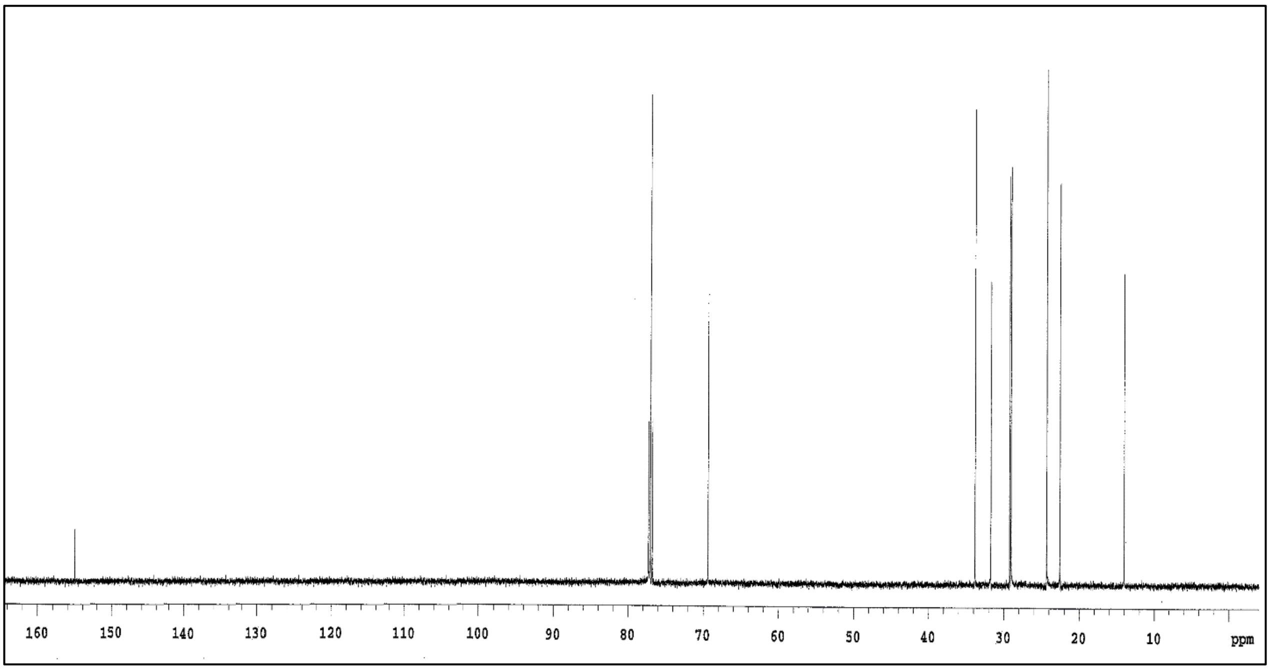


Figure S8b. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 297 K, $CDCl_3$) of 1,2-decylene carbonate **(16e)**.

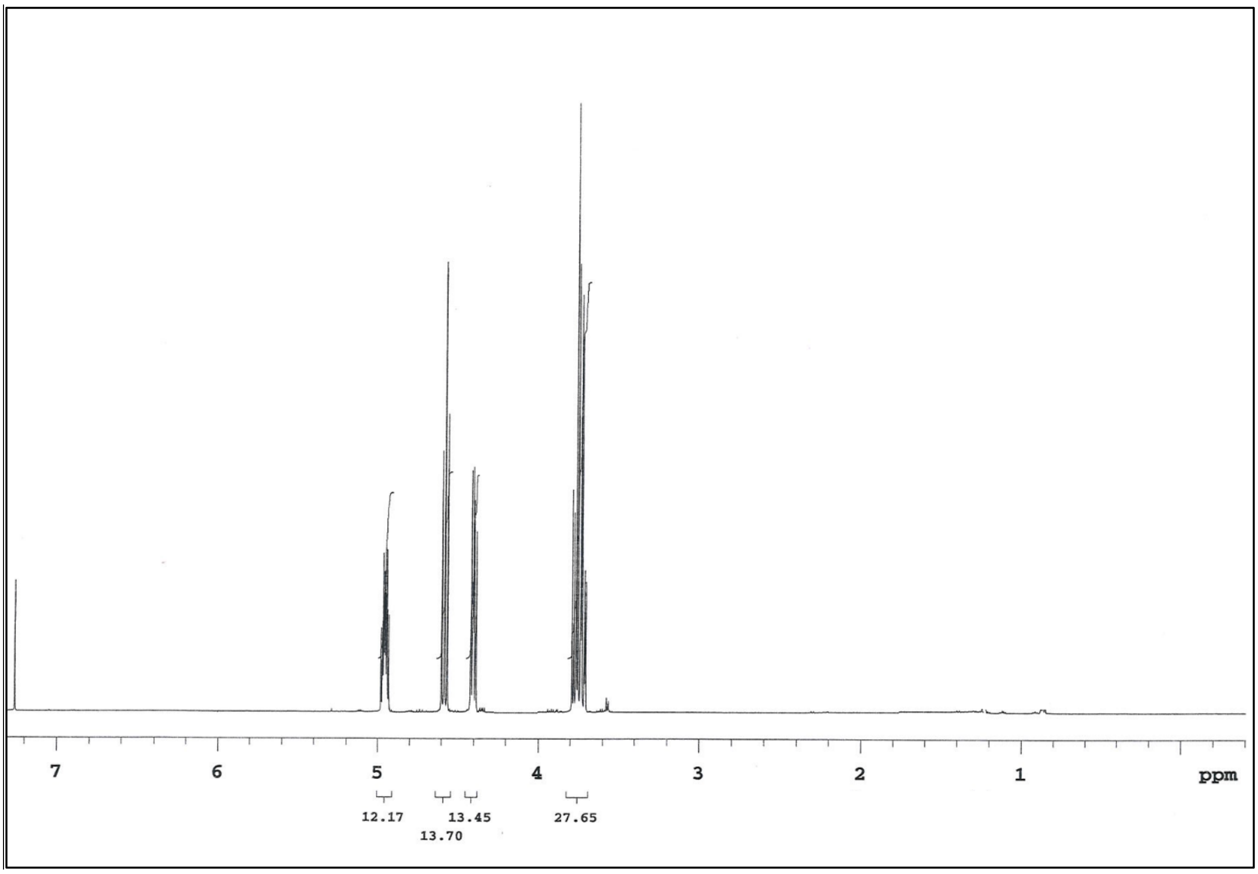


Figure S9a. ^{1}H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of 3-chloropropylene carbonate **(16f)**.

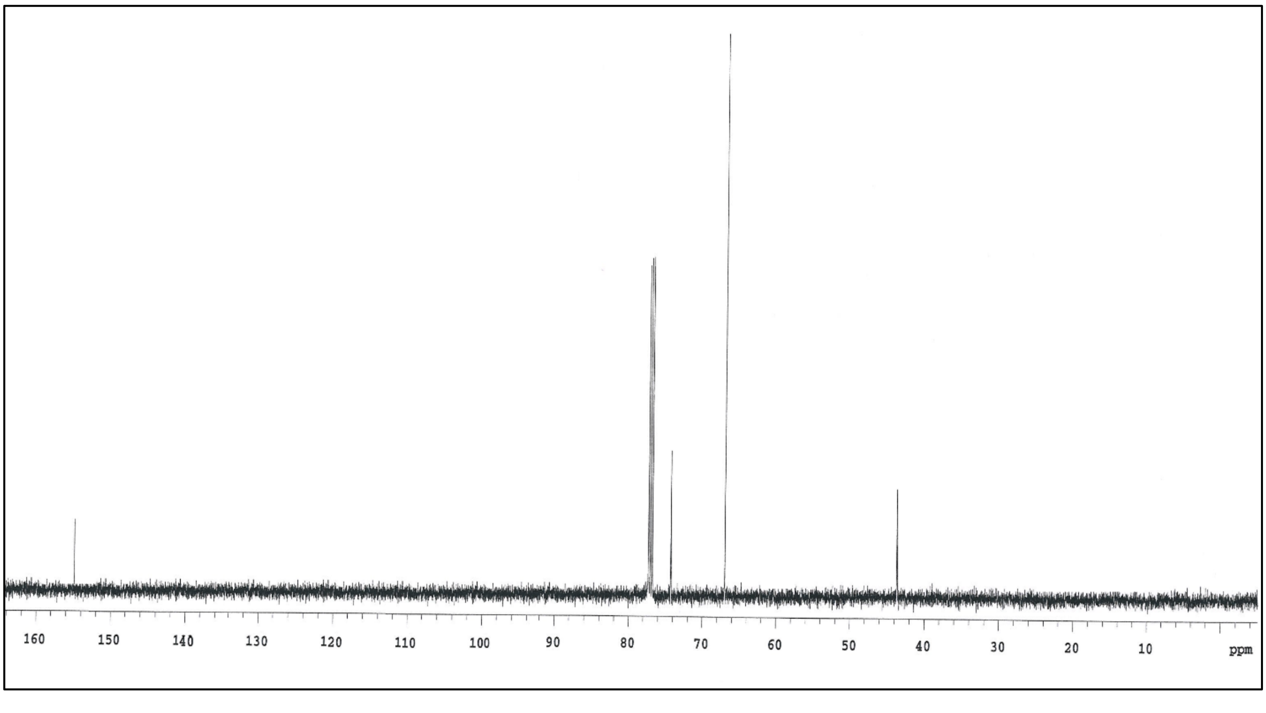


Figure S9b. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 297 K, $CDCl_3$) of 3-chloropropylene carbonate **(16f)**.

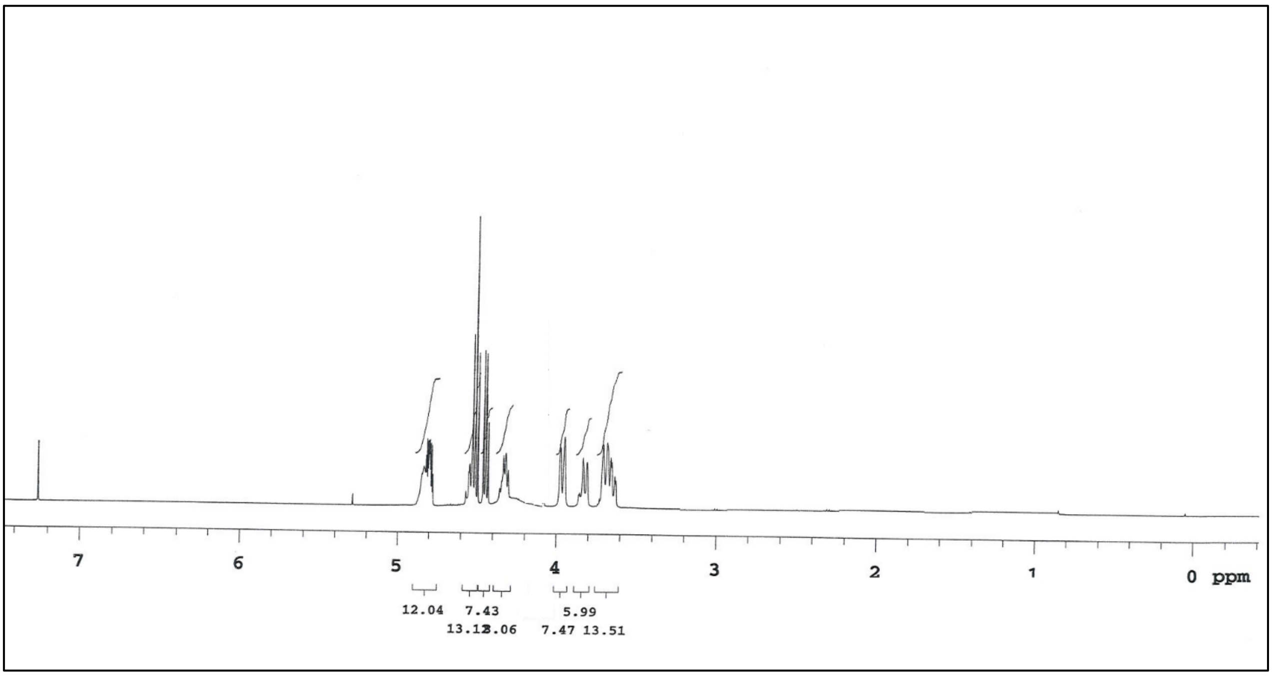


Figure S10a. ^{1}H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of glycerol carbonate **(16g)**.

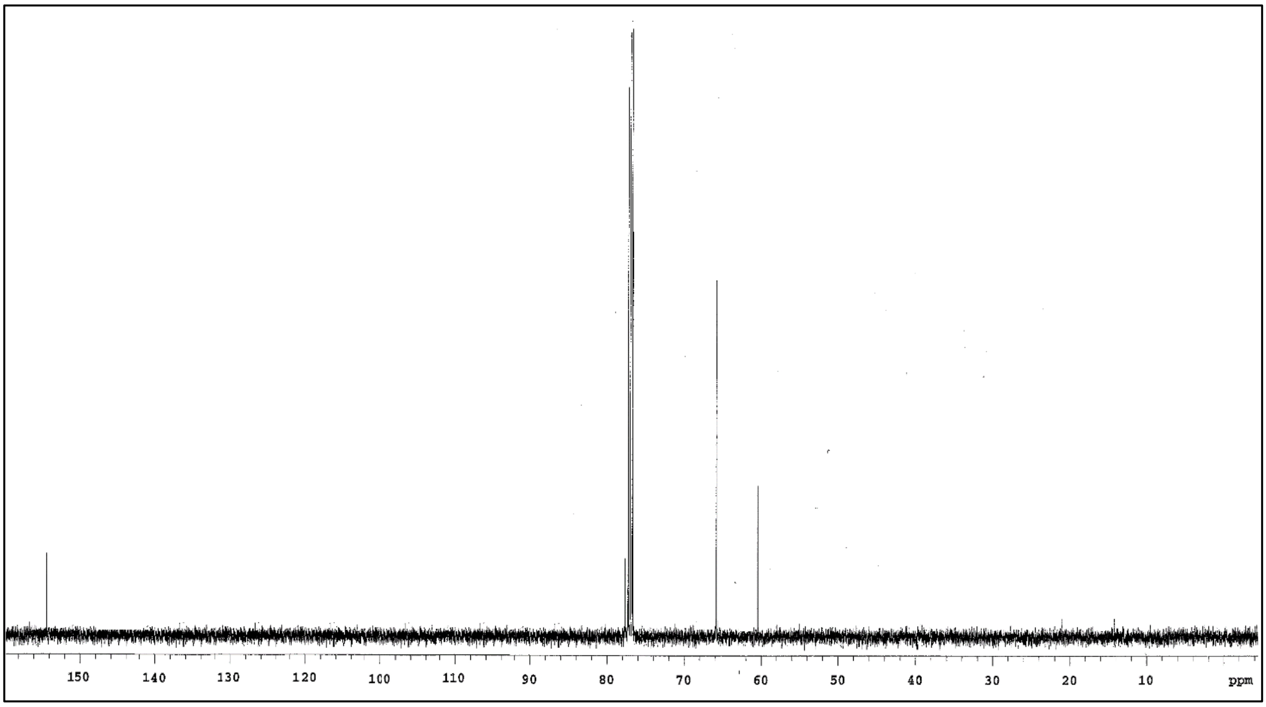


Figure S10b. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 297 K, $CDCl_3$) of glycerol carbonate **(16g)**.

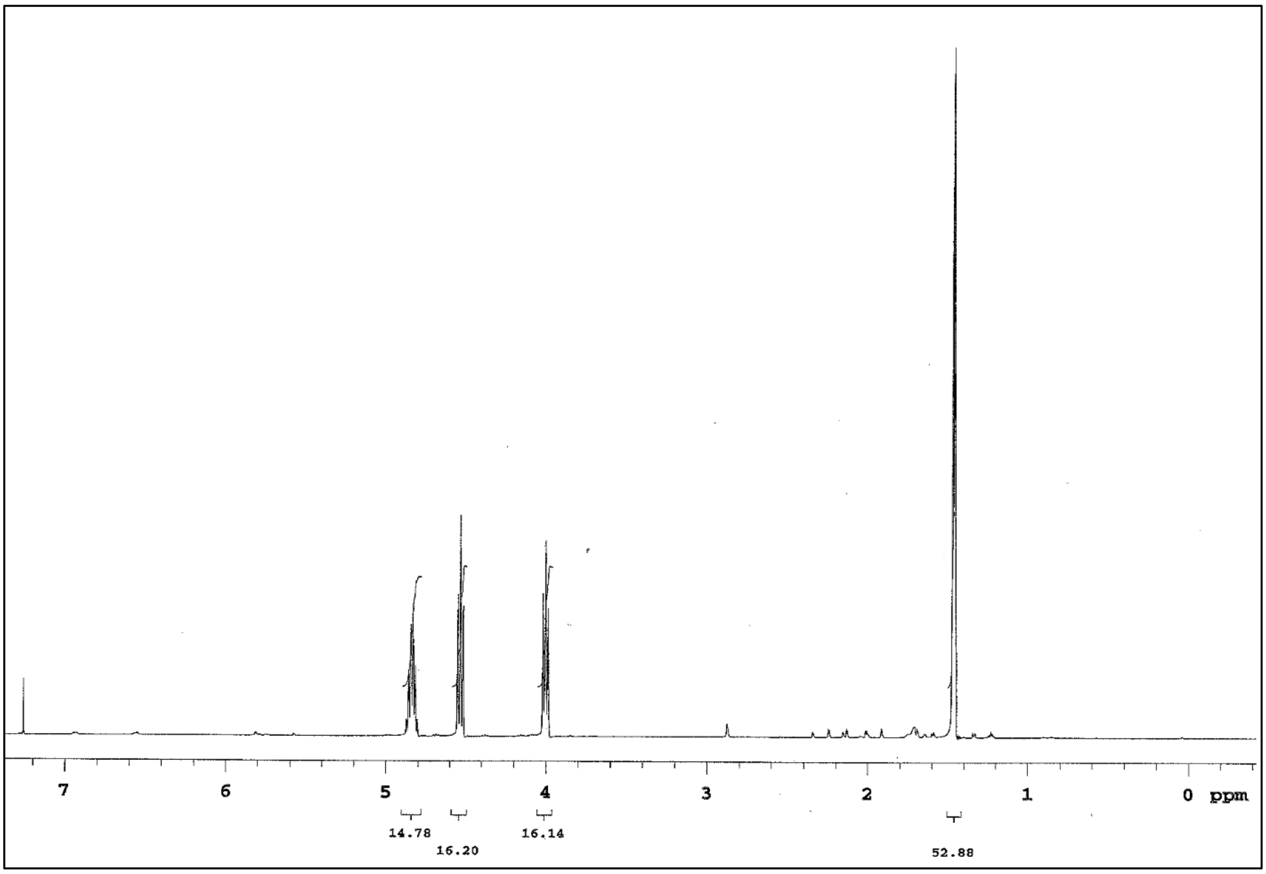


Figure S11a. ^{1}H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of propylene carbonate **(16h)**.

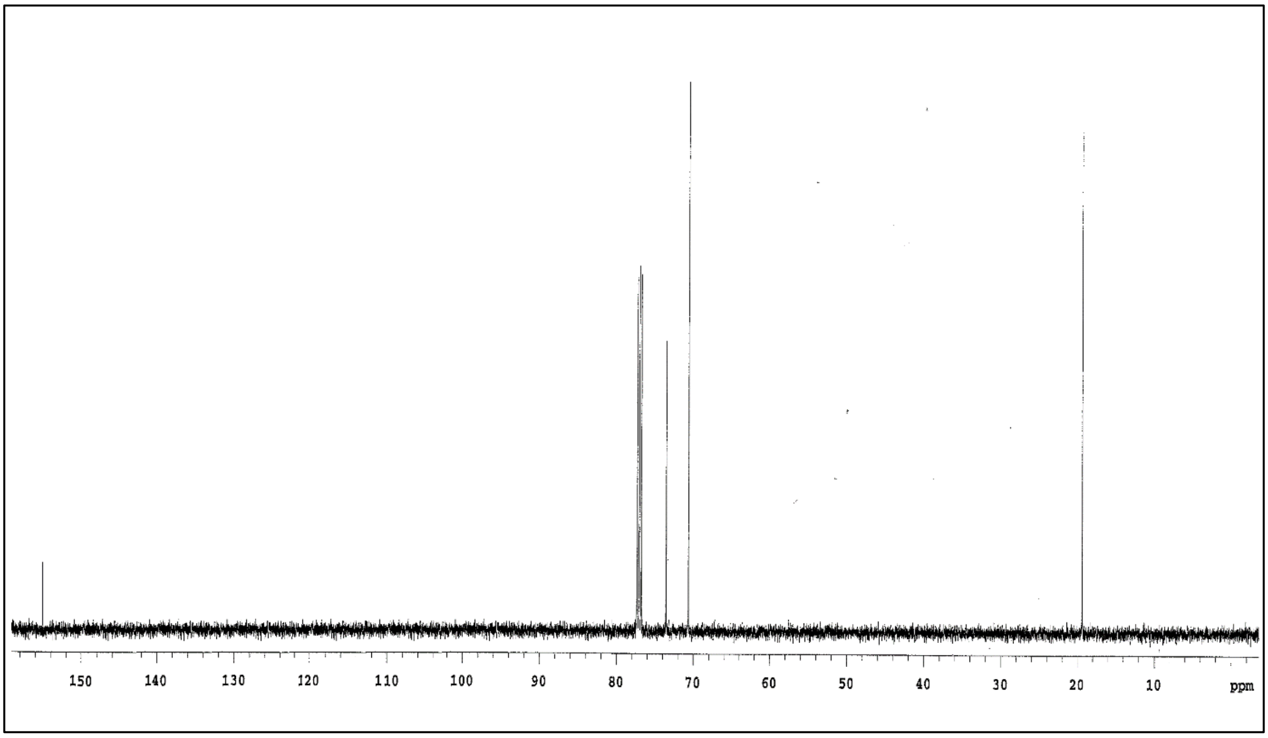


Figure S11b. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 297 K, $CDCl_3$) of propylene carbonate **(16h)**.

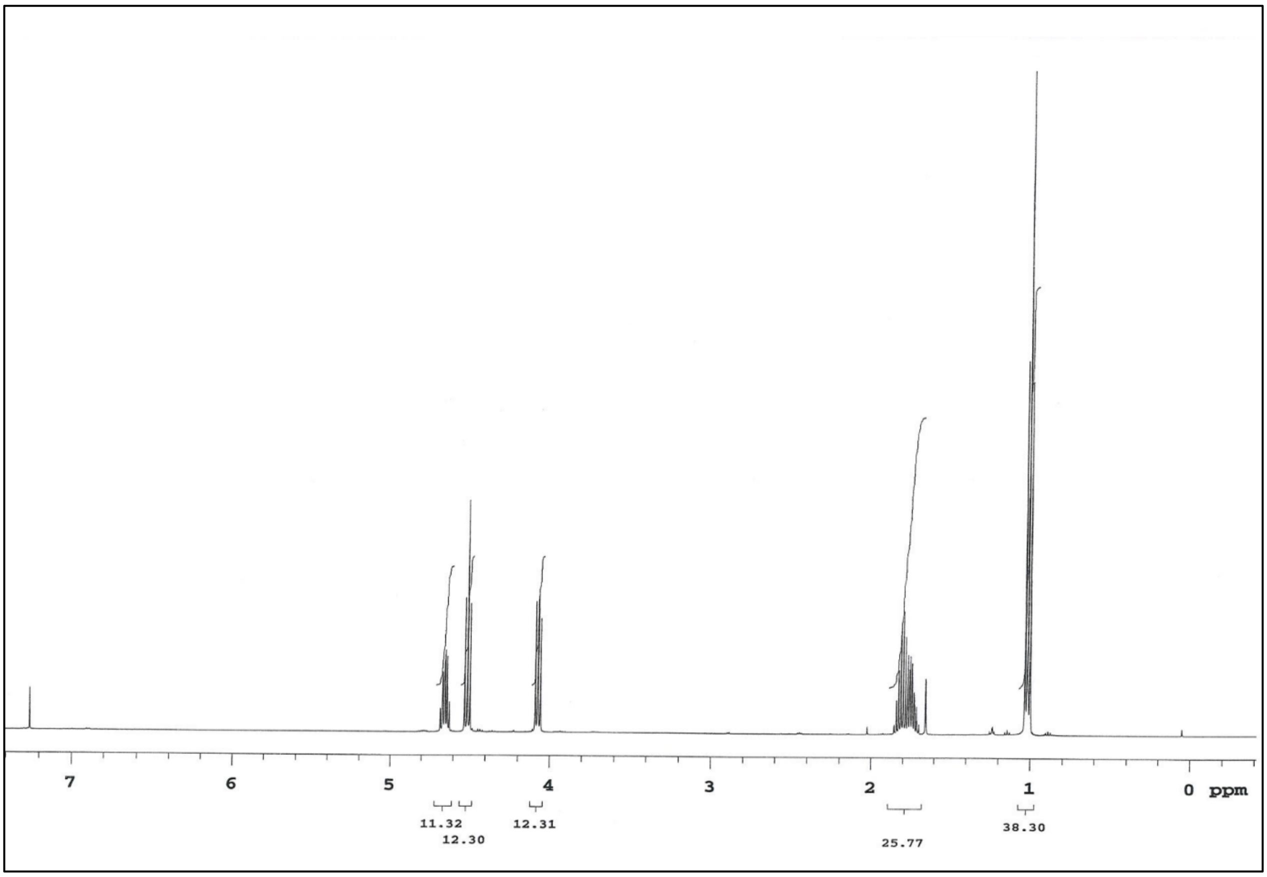


Figure S12a. ^{1}H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of 1,2-butylene carbonate **(16i)**.

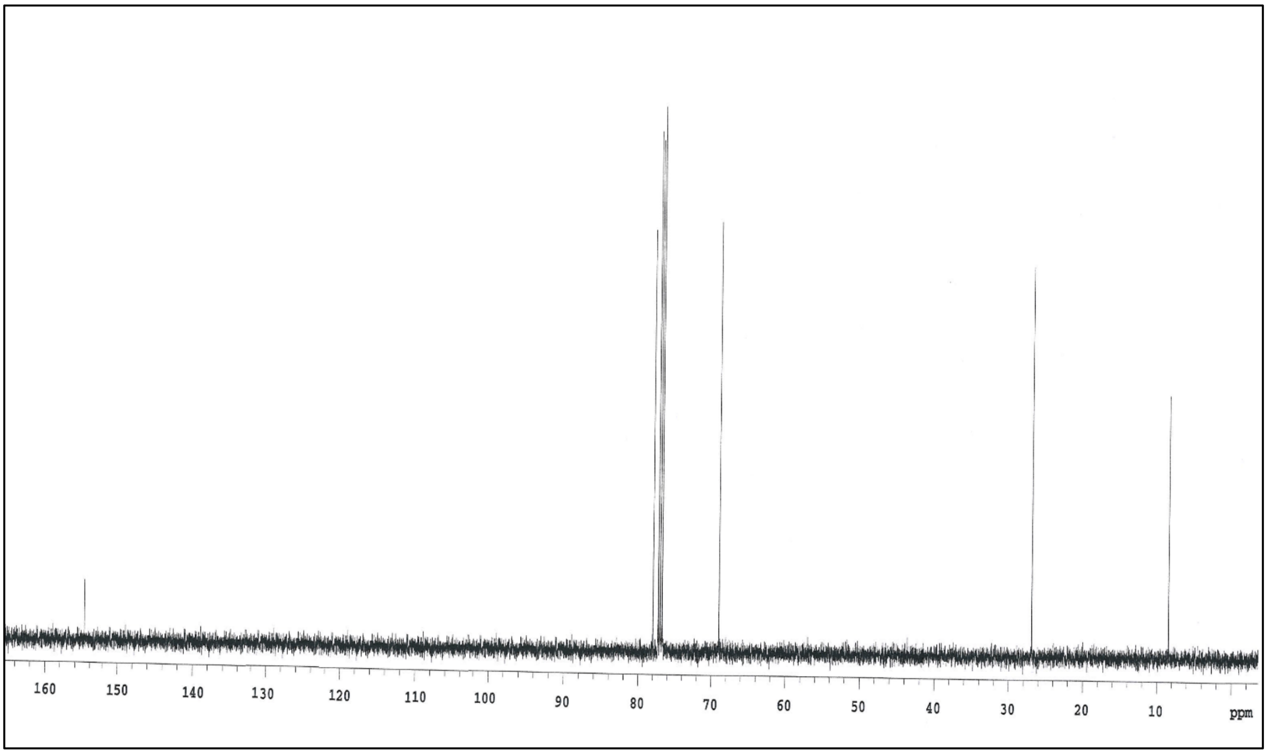


Figure S12b. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 297 K, $CDCl_3$) of 1,2-butylene carbonate **(16i)**.

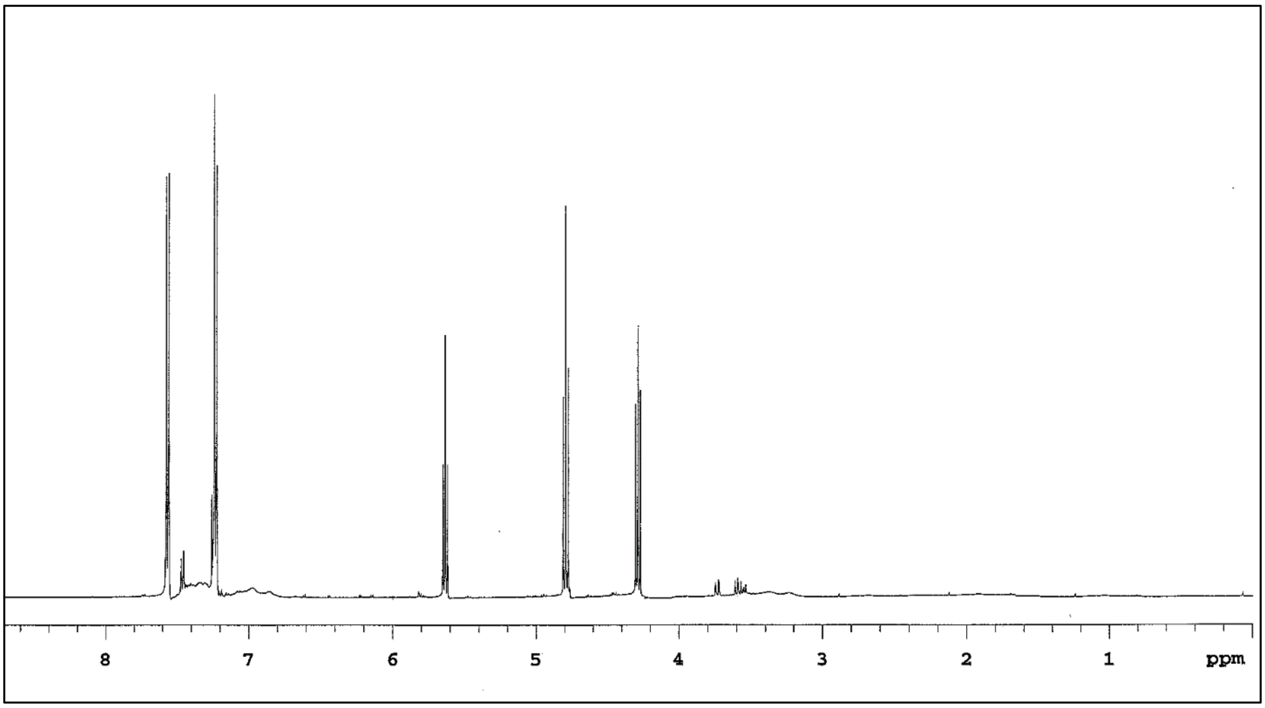


Figure S13a. ^{1}H NMR spectrum (500 MHz, 297 K, CDCl$_3$) of 4-bromostyrene carbonate **(16j)**.

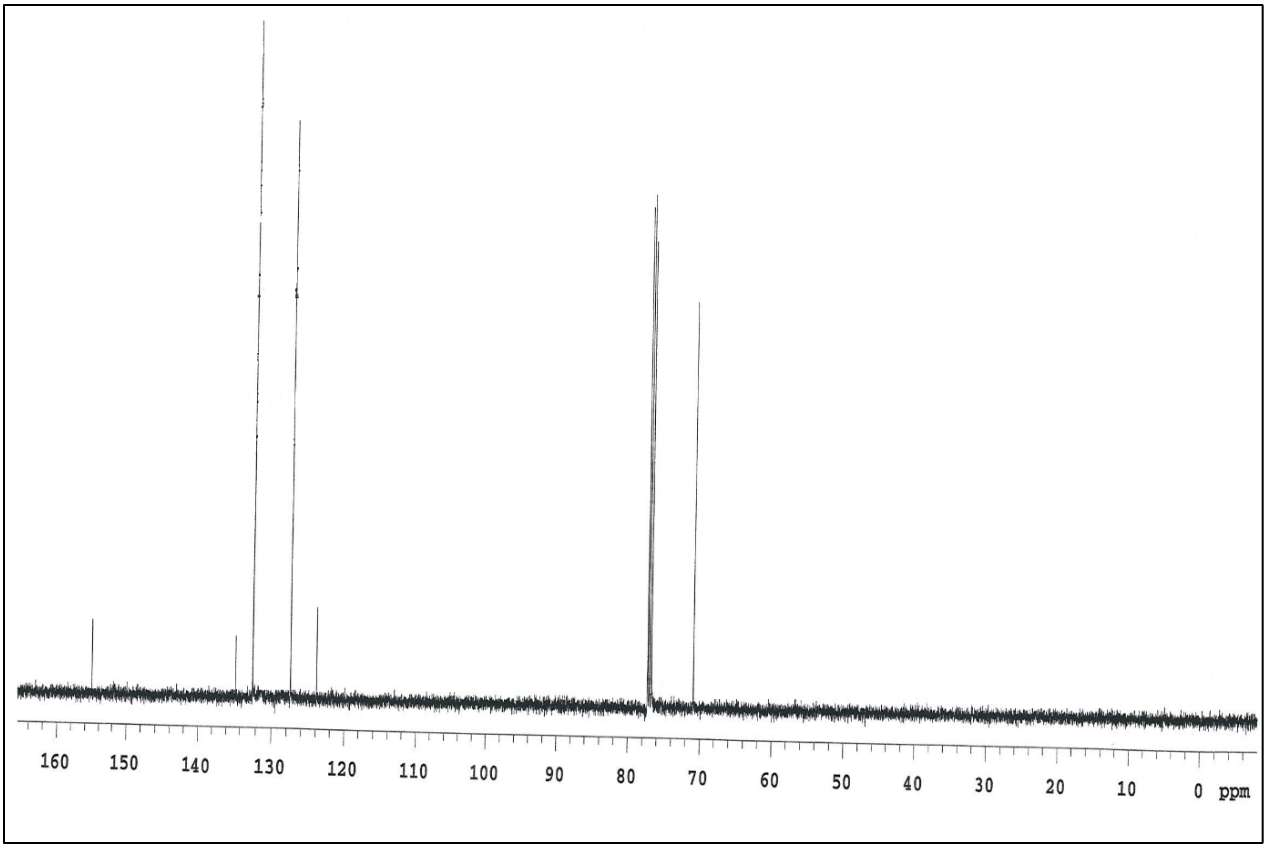


Figure S13b. ^{13}C{^{1}H} NMR spectrum (125 MHz, 297 K, CDCl$_3$) of 4-bromostyrene carbonate **(16j)**.

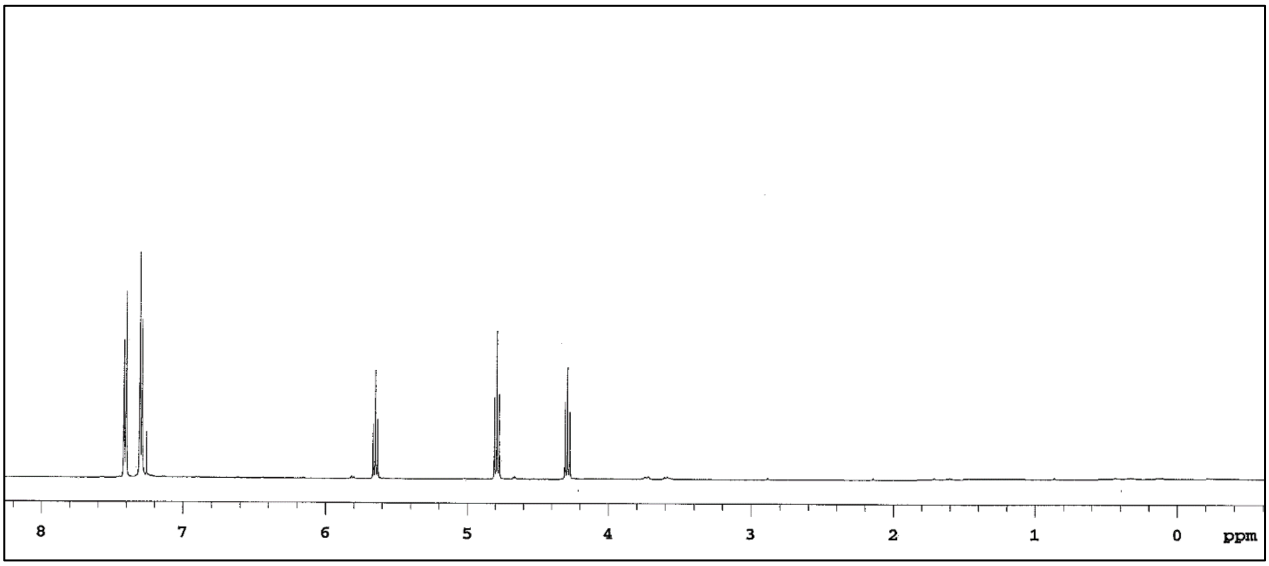


Figure S14a. ^{1}H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of 4-chlorostyrene carbonate **(16k)**.

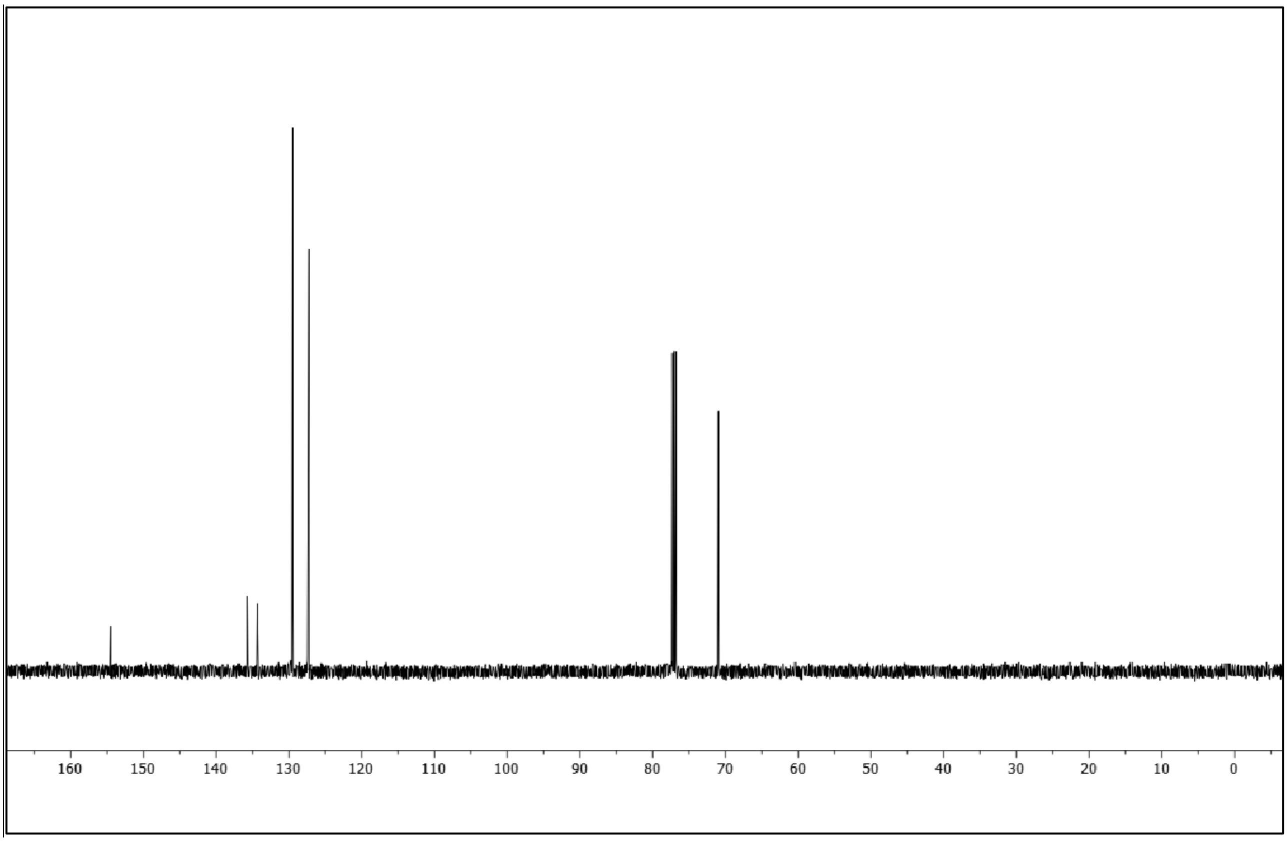


Figure S14b. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 297 K, $CDCl_3$) of 4-chlorostyrene carbonate **(16k)**.

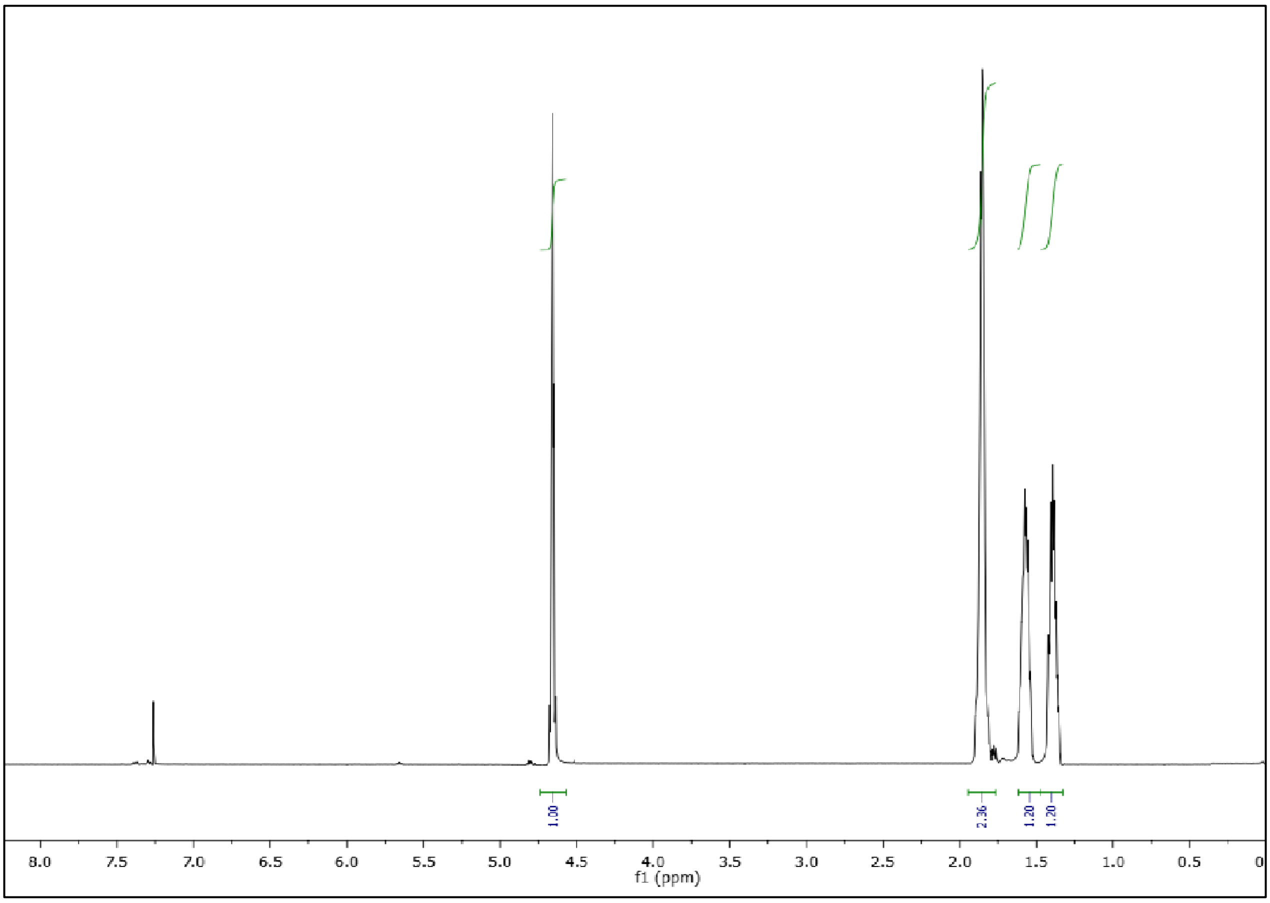


Figure S15a. ^{1}H NMR spectrum (500 MHz, 297 K, CDCl$_3$) of cyclohexene carbonate **(16l)**.

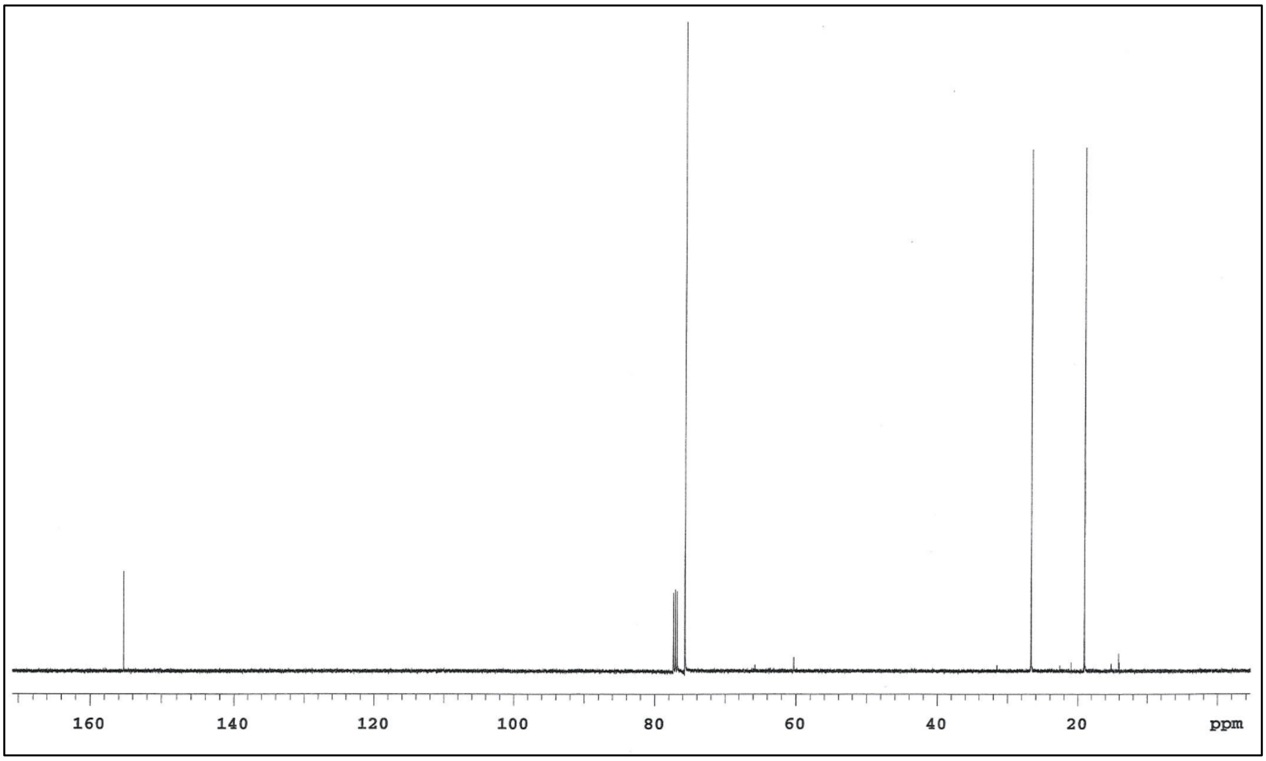


Figure S15b. ^{13}C{^{1}H} NMR spectrum (125 MHz, 297 K, CDCl$_3$) of cyclohexene carbonate **(16l)**.

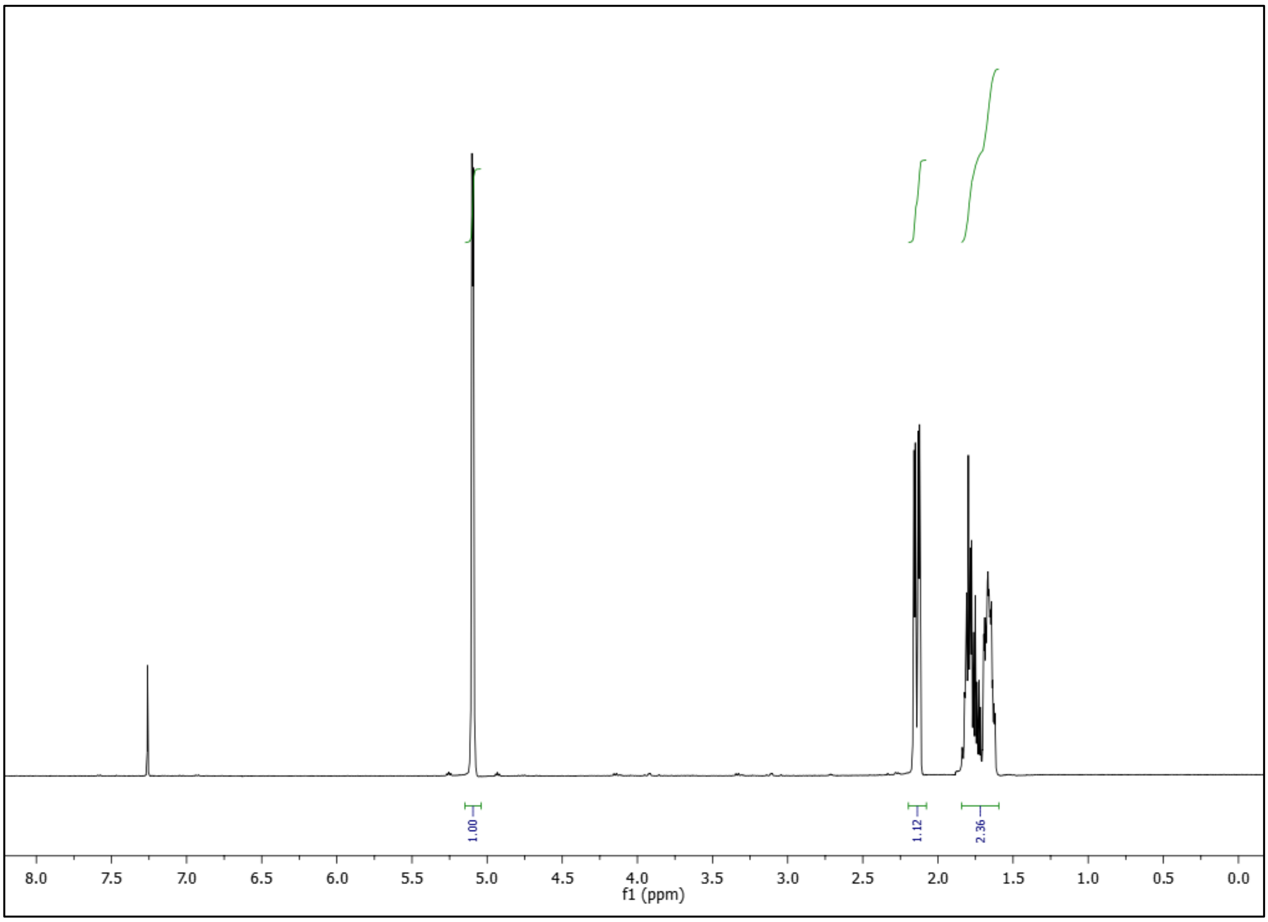


Figure S16a. ^{1}H NMR spectrum (500 MHz, 297 K, CDCl$_3$) of cyclopentene carbonate **(16m)**.

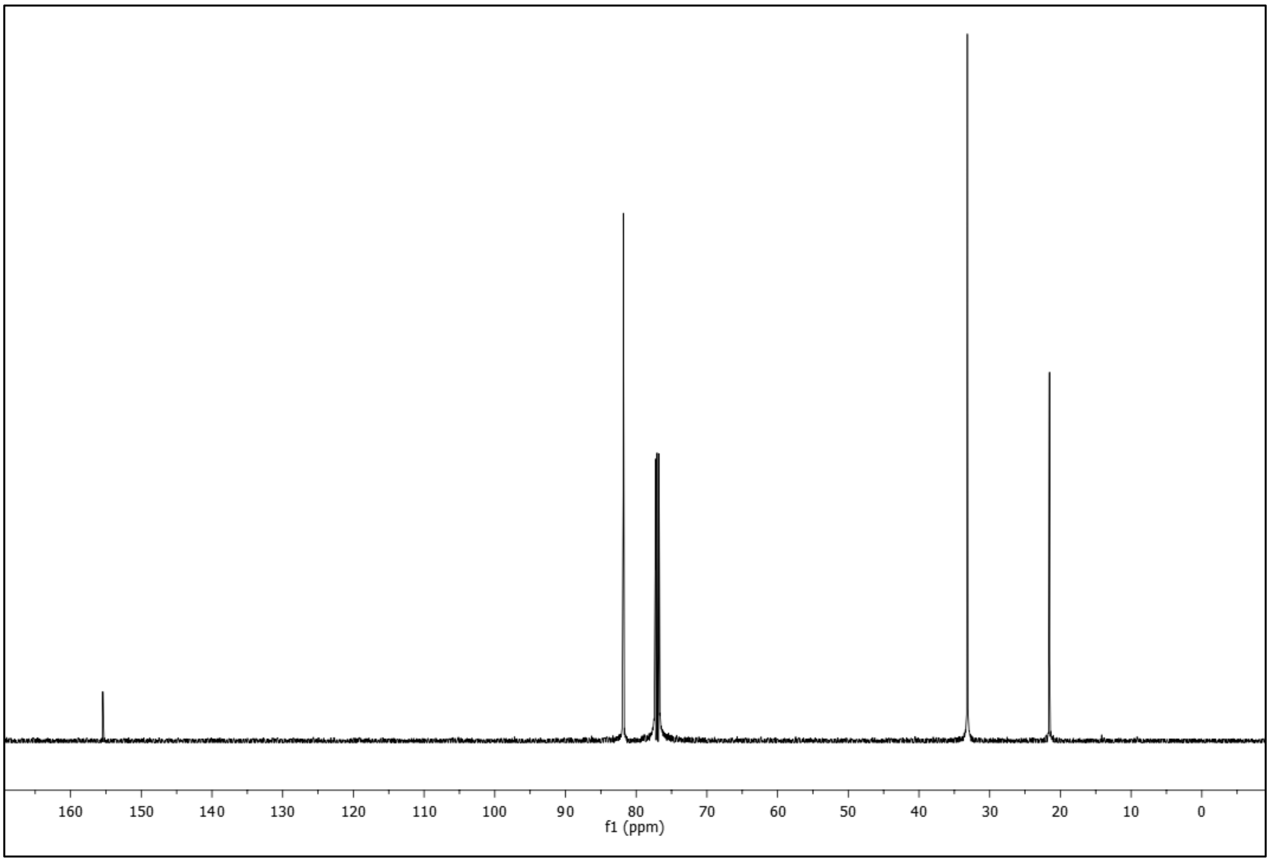


Figure S16b. ^{13}C{^{1}H} NMR spectrum (125 MHz, 297 K, CDCl$_3$) of cyclopentene carbonate **(16m)**.

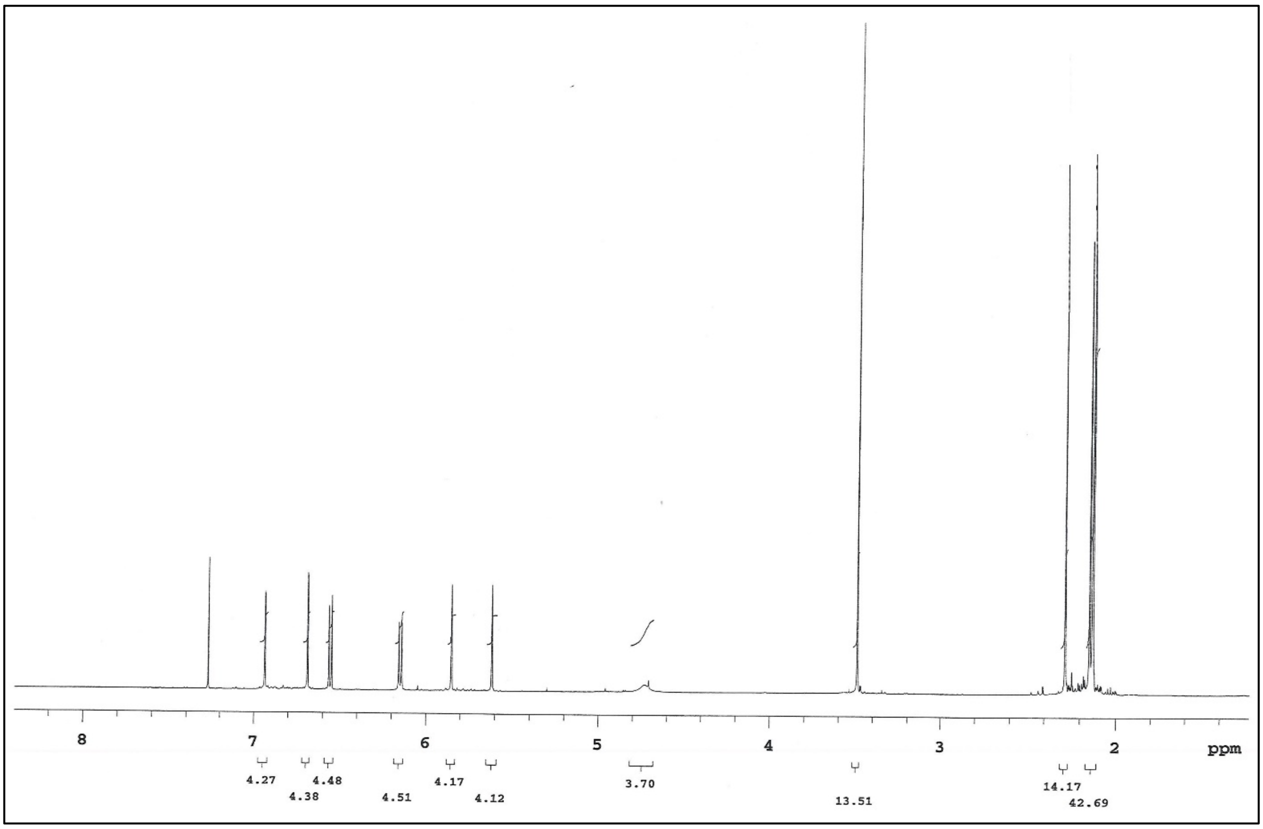


Figure S17a. ^{1}H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of compound bpzimeH (**3**).

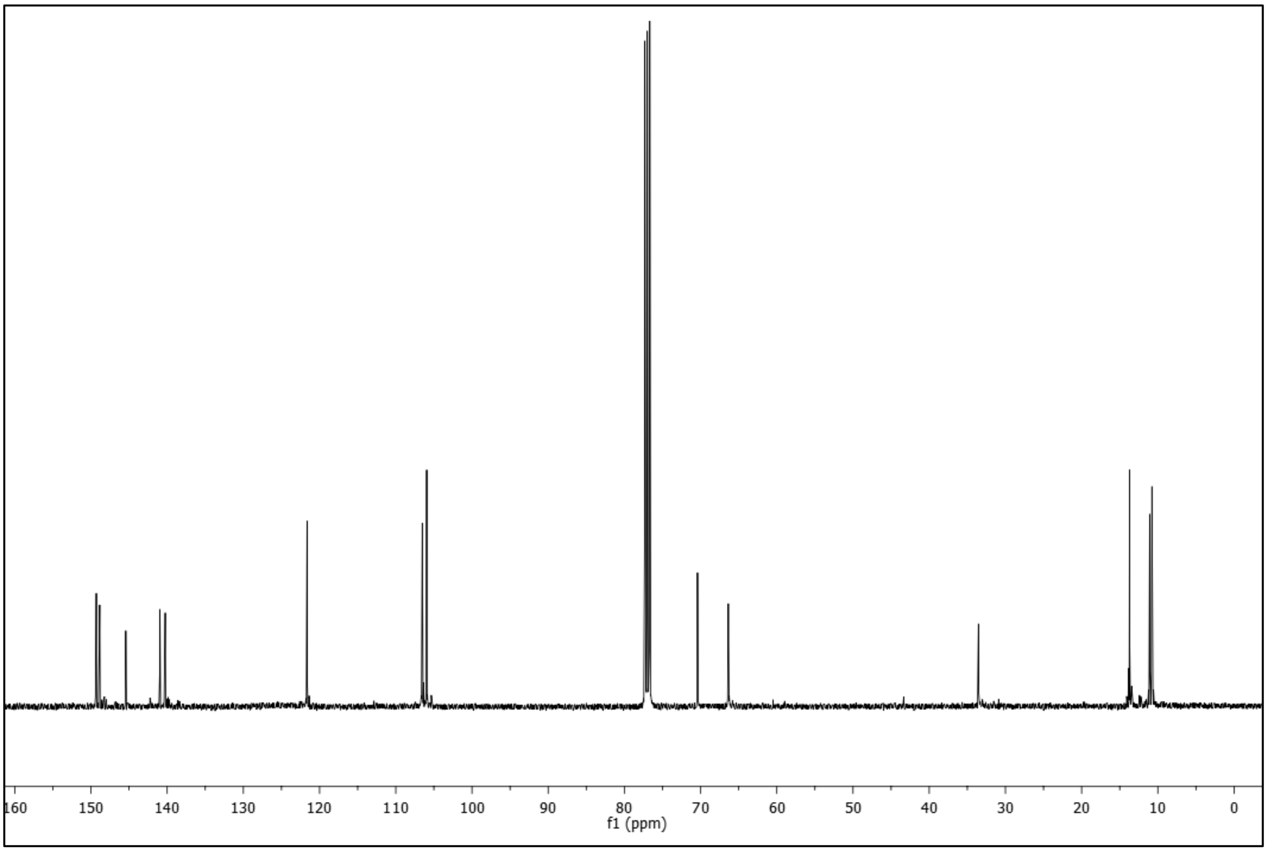


Figure S17b. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 297 K, $CDCl_3$) of compound bpzimeH (**3**).

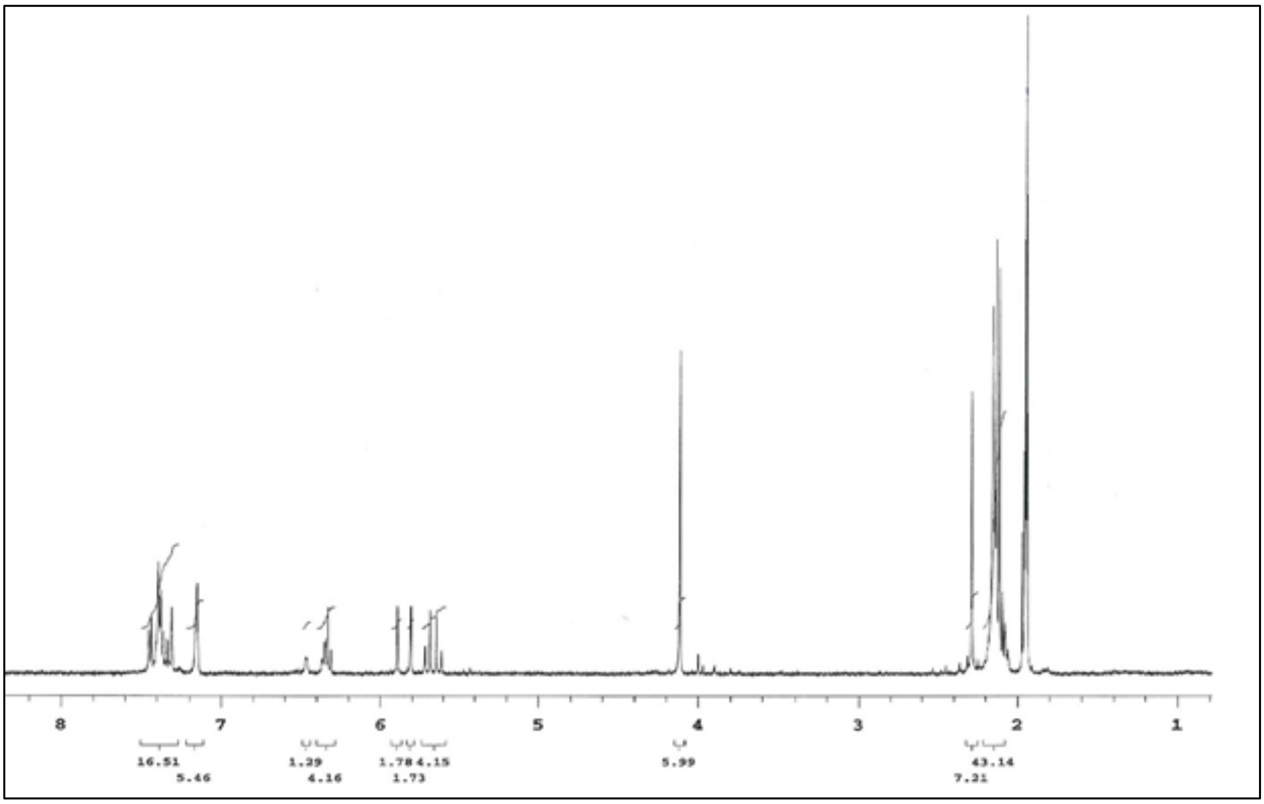


Figure S18a. ^{1}H NMR spectrum (500 MHz, 297 K, CD_3CN) of compound [(bzbpzimeH)Br] (**17**).

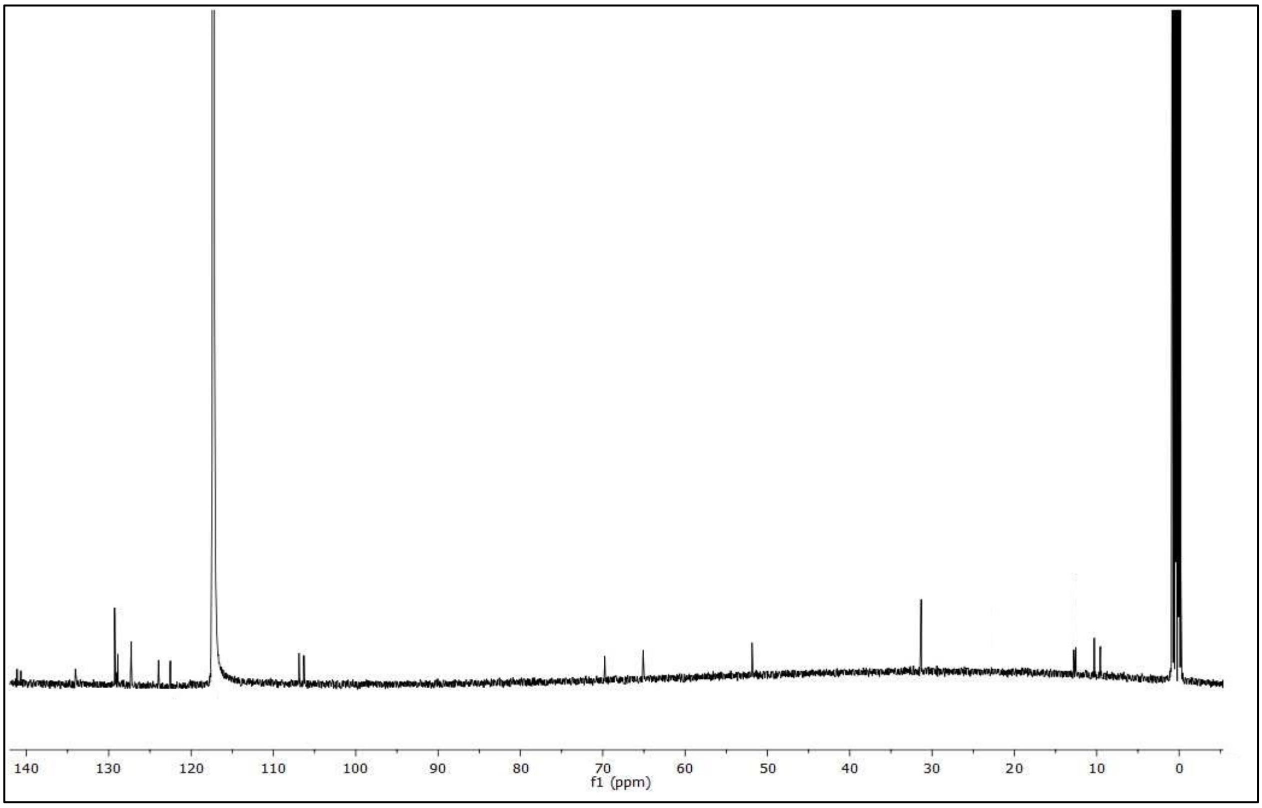


Figure S18b. ^{13}C{^{1}H} NMR spectrum (125 MHz, 297 K, CD_3CN) of compound [(bzbpzimeH)Br] (**17**).

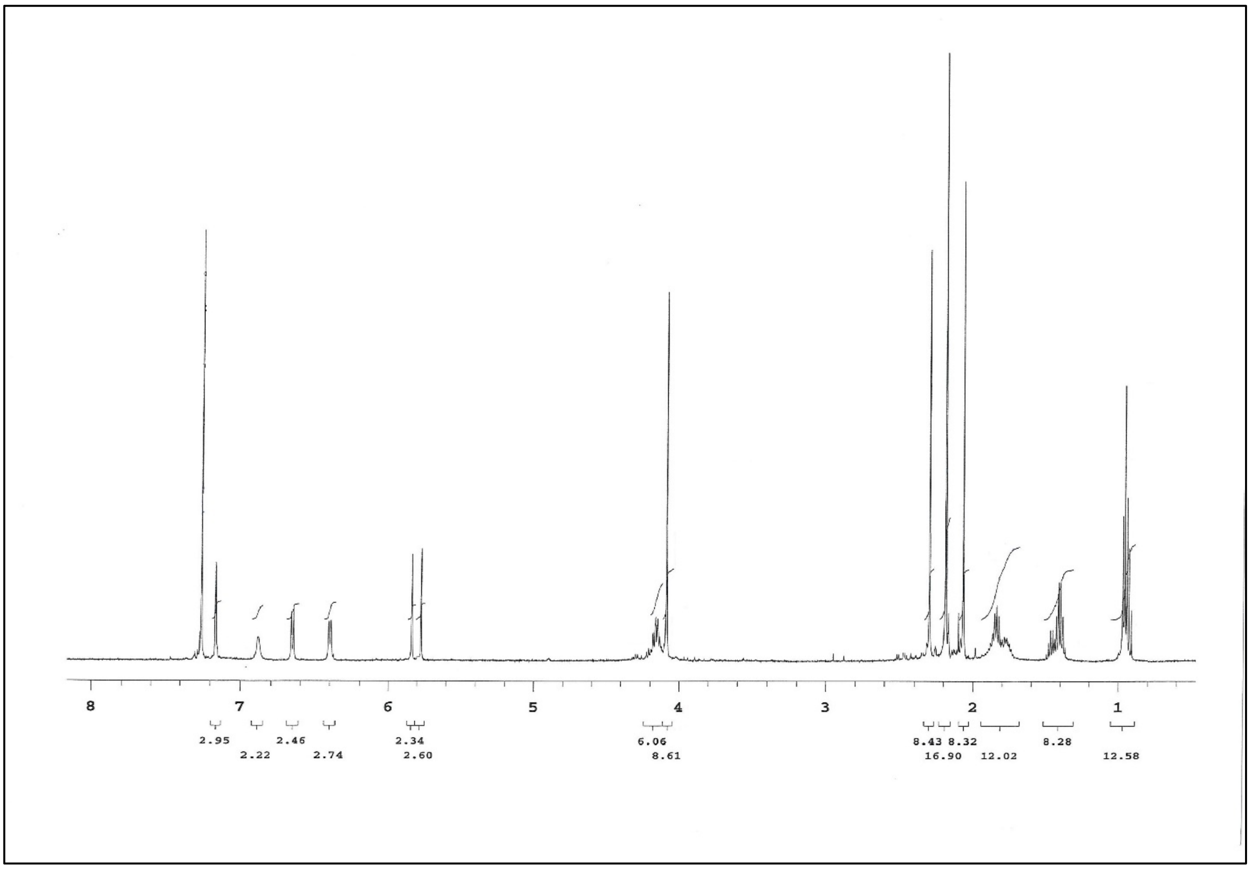


Figure S19a. ^{1}H NMR spectrum (500 MHz, 297 K, CDCl$_3$) of compound [(bubpzimeH)Br] (**18**).

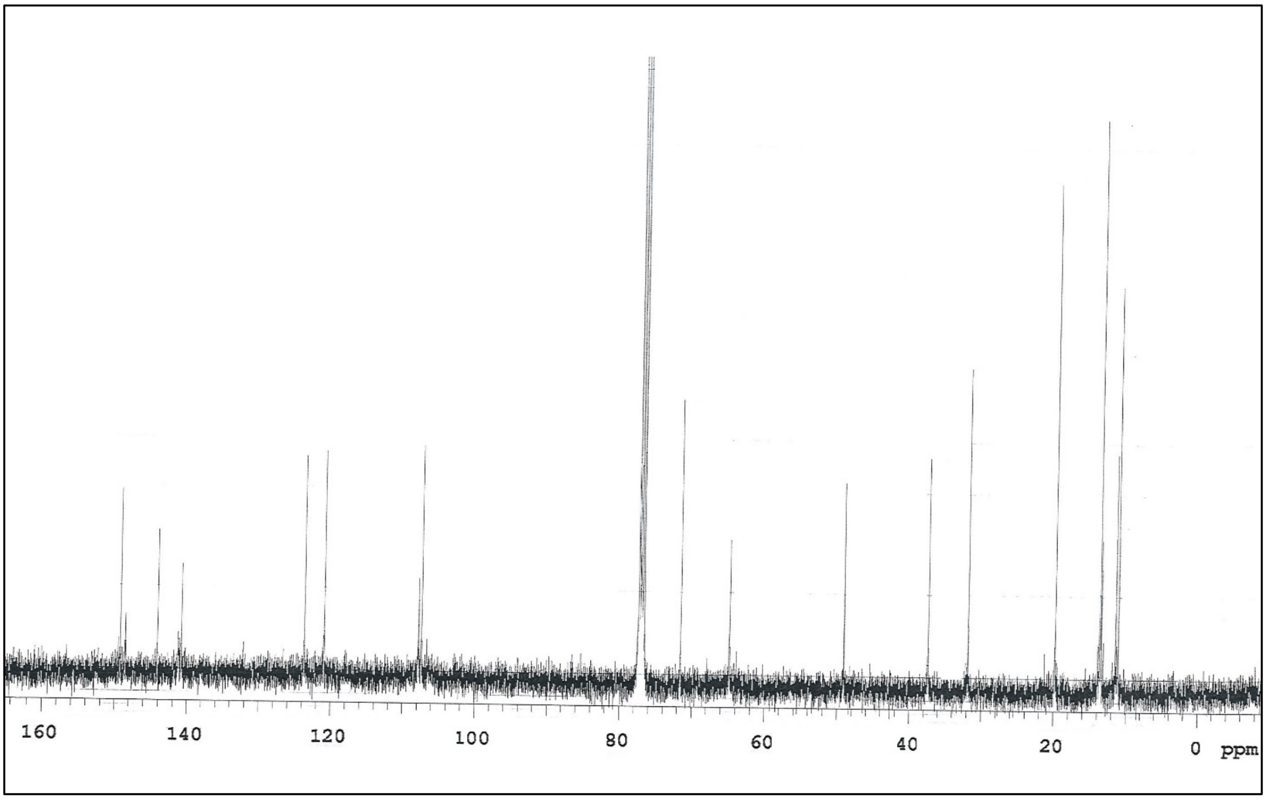


Figure S19b. ^{13}C{^{1}H} NMR spectrum (125 MHz, 297 K, CDCl$_3$) of compound [(bubpzimeH)Br] (**18**).

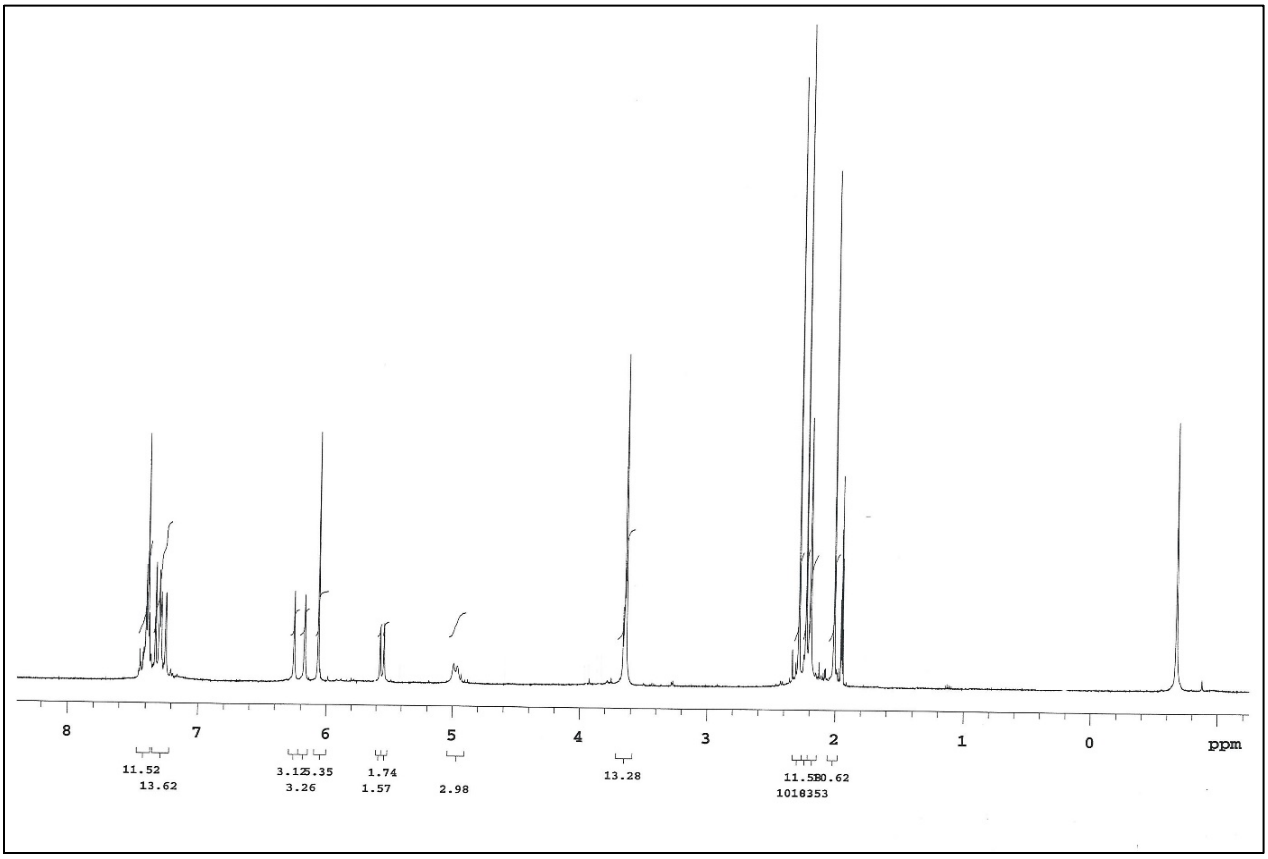


Figure S20a. ^{1}H NMR spectrum (500 MHz, 297 K, CD_3CN) of complex [Zn(Me)(bzbpzime)]Br (**19**).

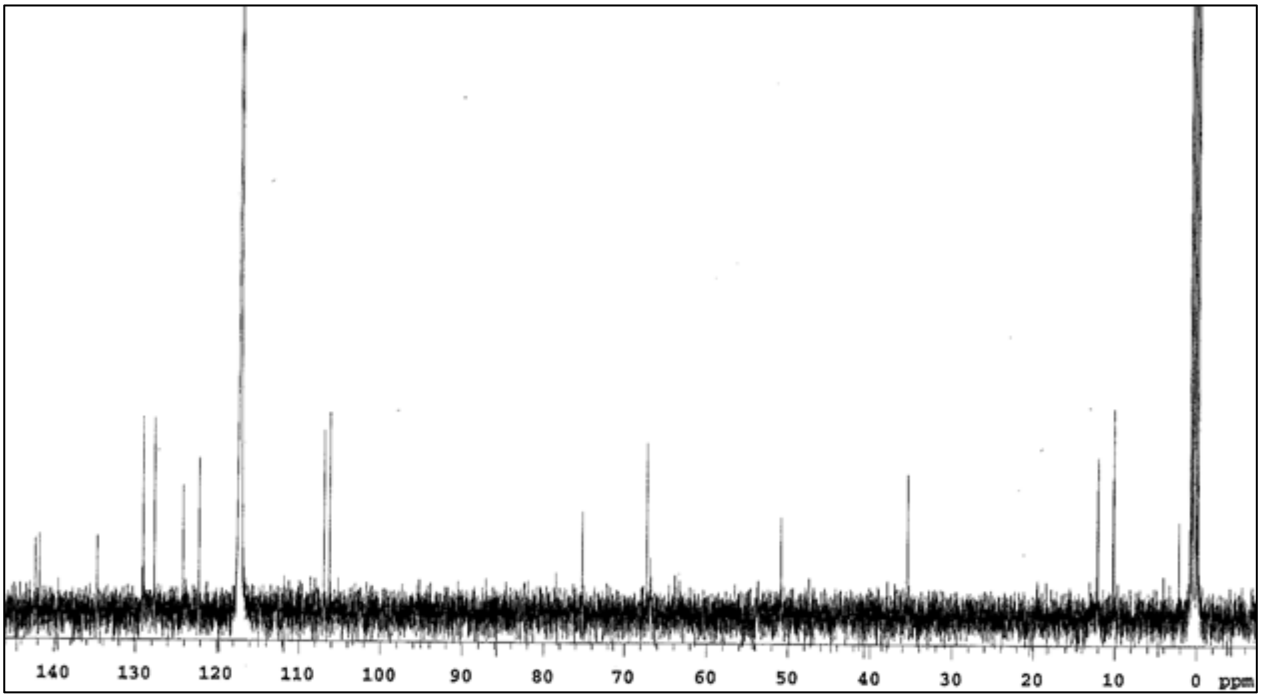


Figure S20b. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 297 K, CD_3CN) of complex [Zn(Me)(bzbpzime)]Br (**19**).

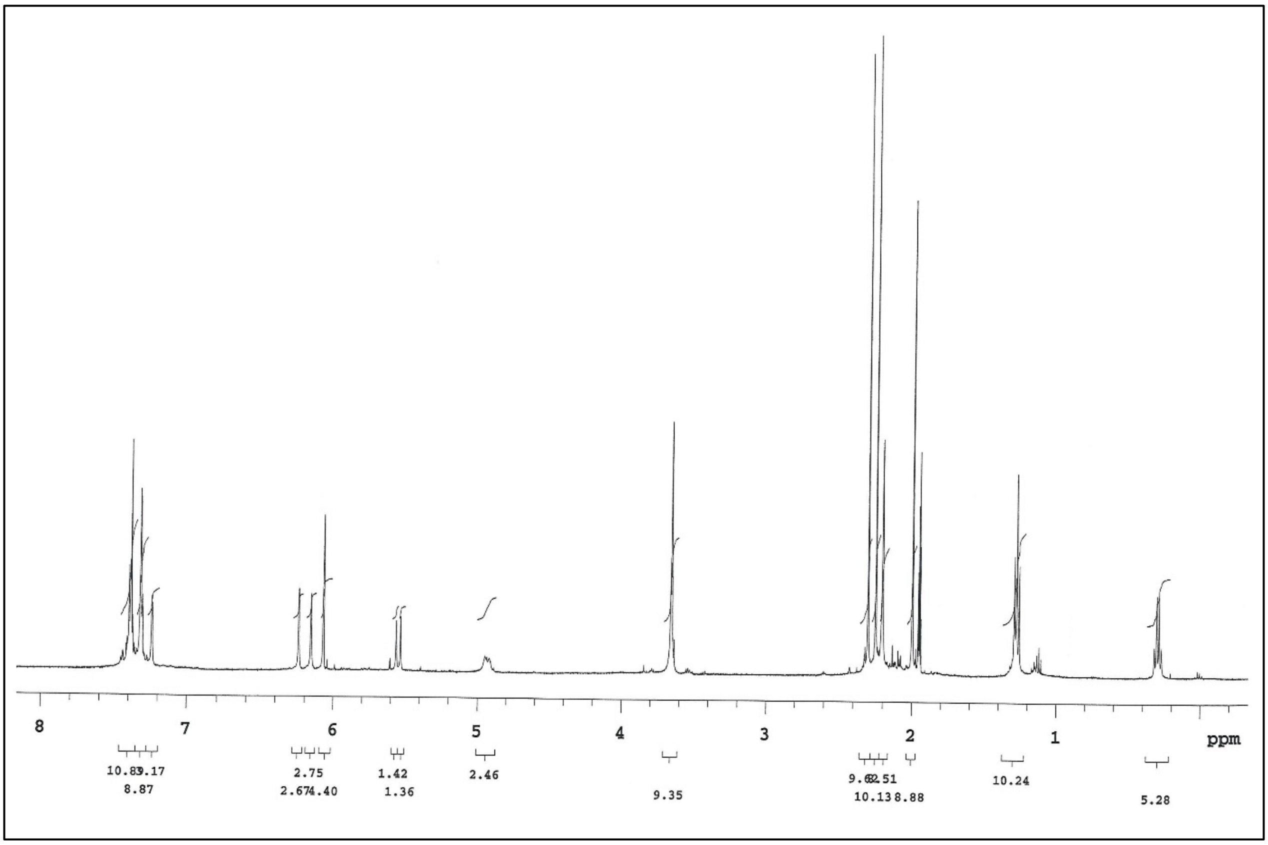


Figure S21a. ^{1}H NMR spectrum (500 MHz, 297 K, CD_3CN) of complex [Zn(Et)(bzbpzime)]Br (**20**).

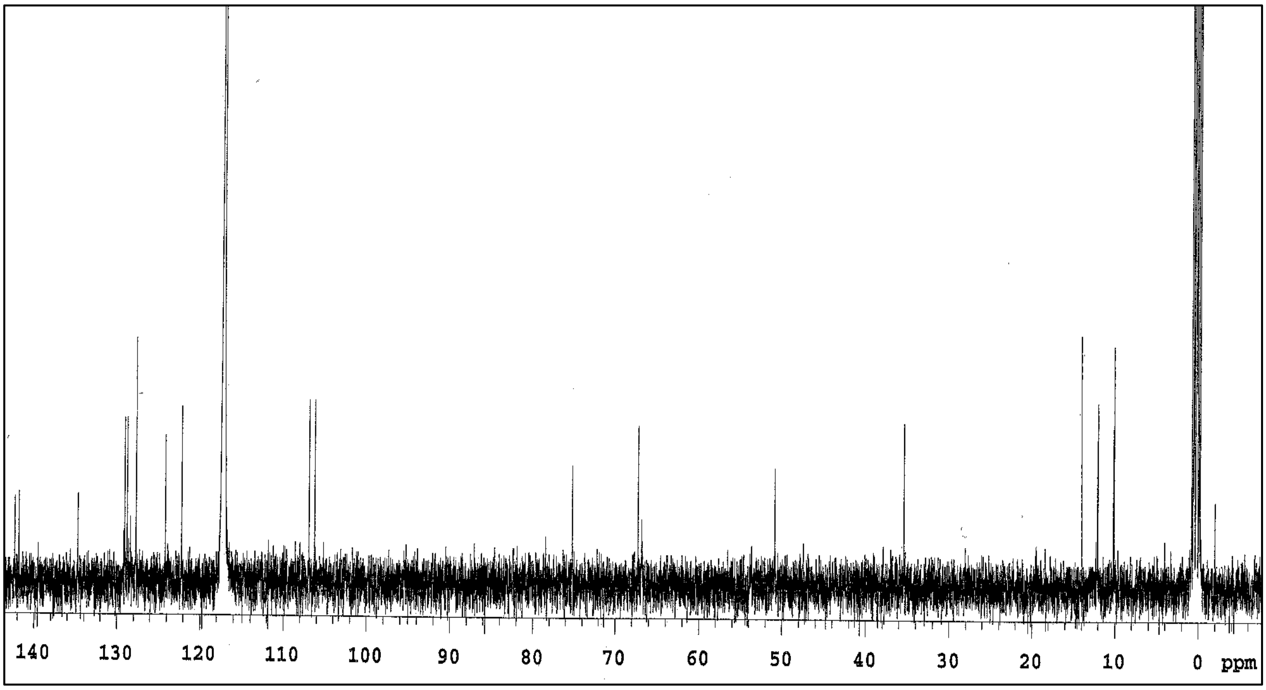


Figure S21b. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 297 K, CD_3CN) of complex [Zn(Et)(bzbpzime)]Br (**20**).

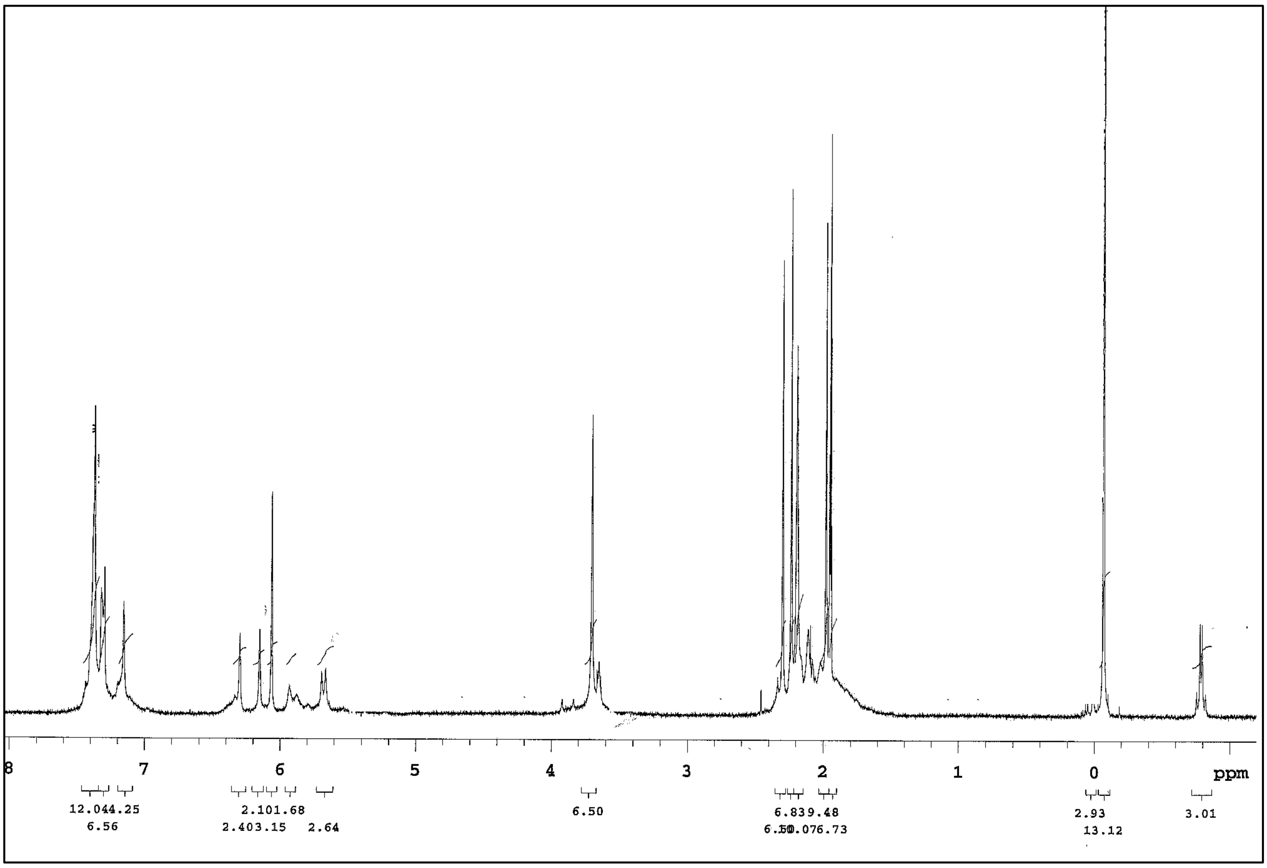


Figure S22a. ^{1}H NMR spectrum (500 MHz, 297 K, CD_3CN) of complex $[Zn(CH_2SiMe_3)(bzbpzime)]Br$ (**21**).

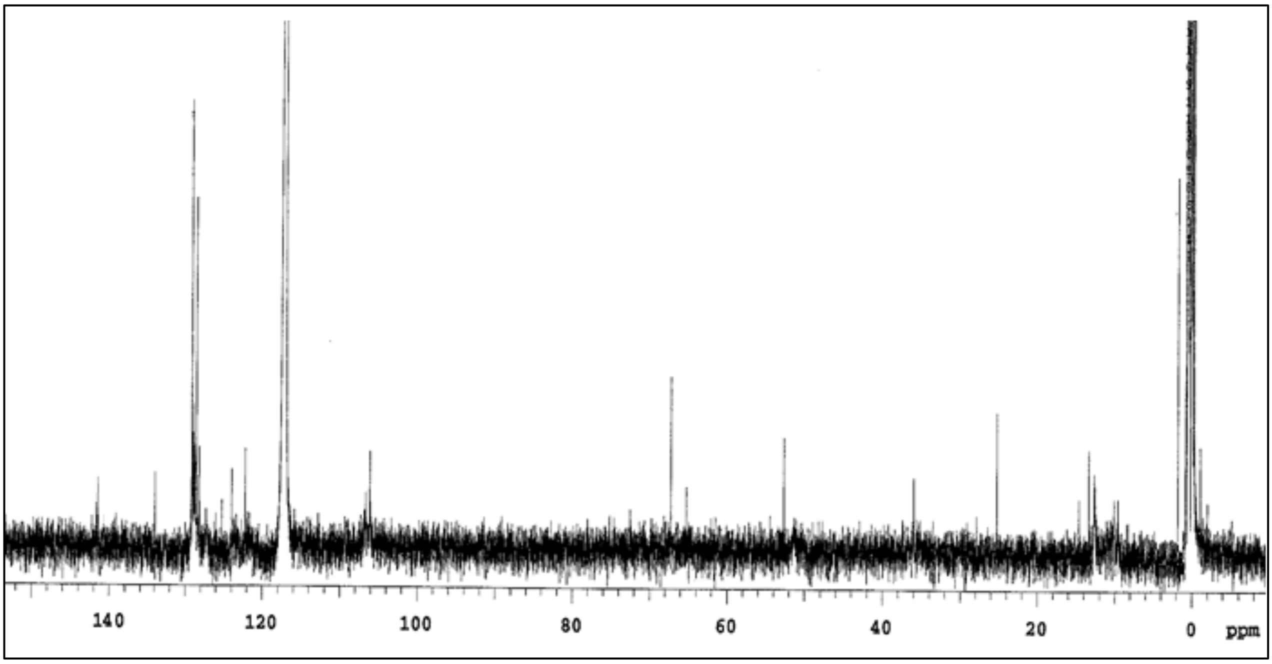


Figure S22b. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 297 K, CD_3CN) of complex $[Zn(CH_2SiMe_3)(bzbpzime)]Br$ (**21**).

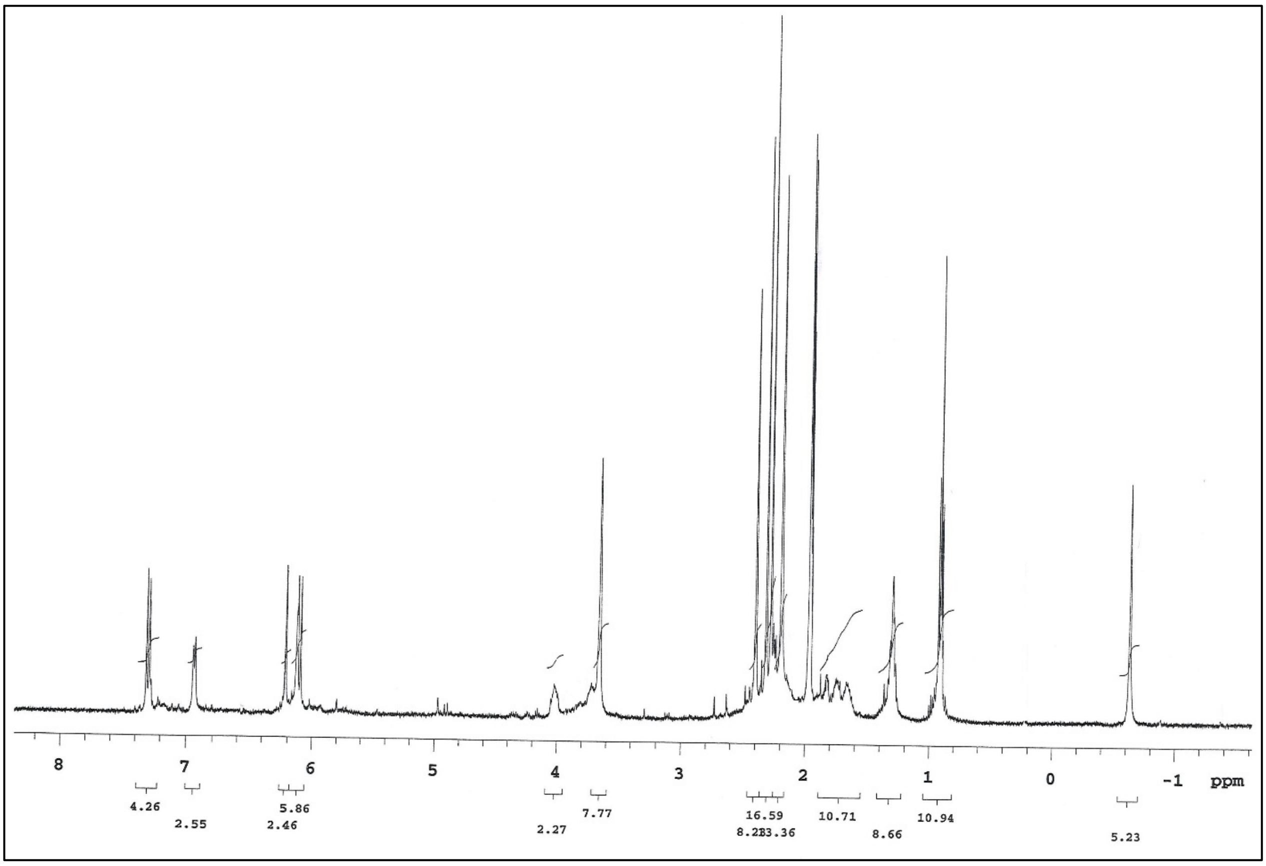


Figure S23a. ^{1}H NMR spectrum (500 MHz, 297 K, CD_3CN) of complex [Zn(Me)(bubpzime)]Br (**22**).

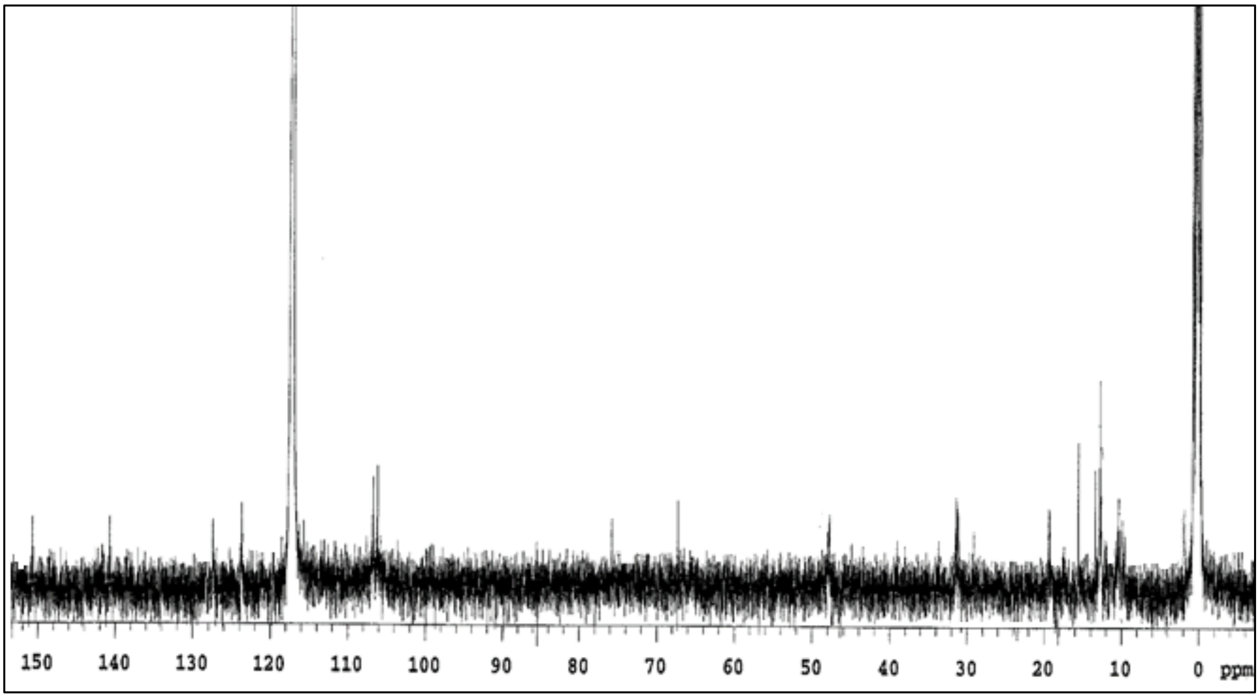


Figure S23b. $^{13}C\{^1H\}$ NMR spectrum (125 MHz, 297 K, CD_3CN) of complex [Zn(Me)(bubpzime)]Br (**22**).

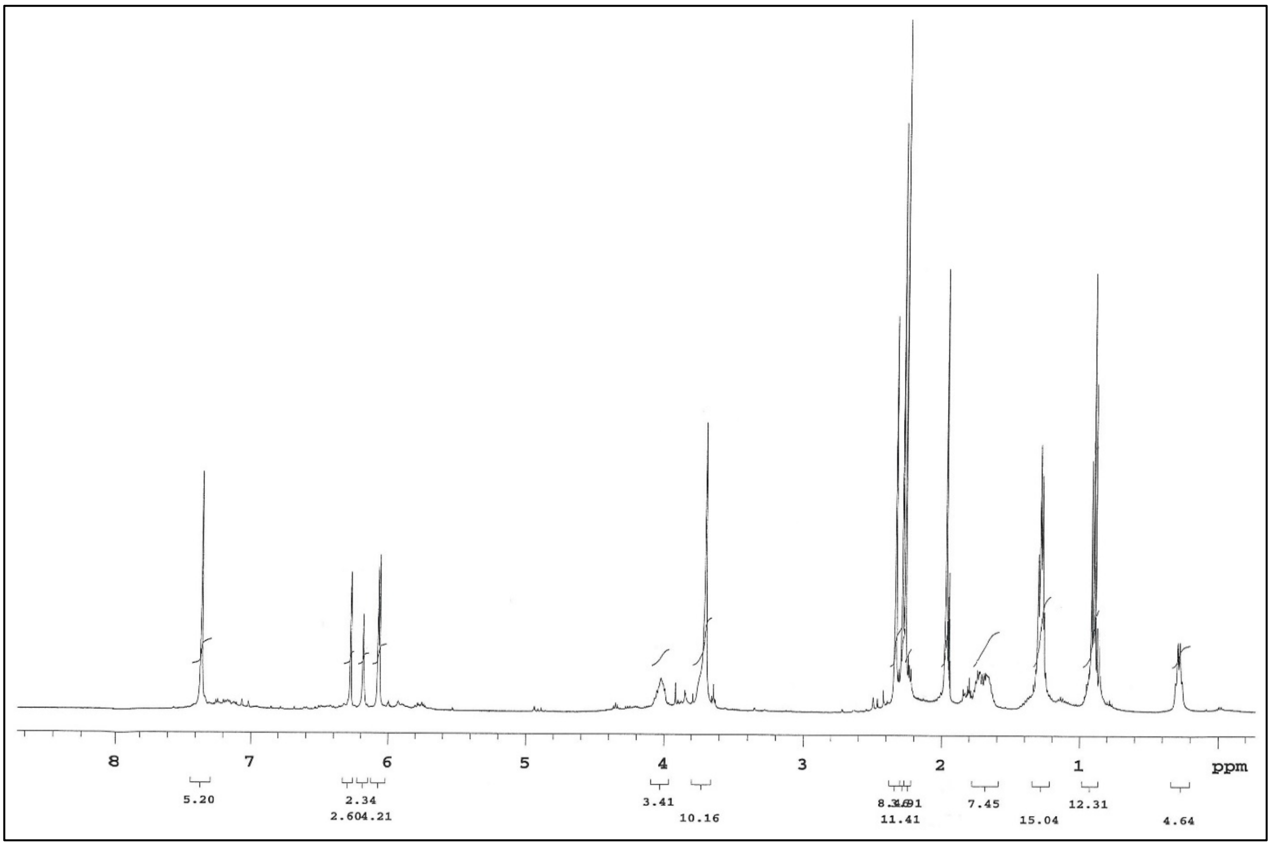


Figure S24a. ^{1}H NMR spectrum (500 MHz, 297 K, CD_3CN) of complex [Zn(Et)(bubpzime)]Br (**23**).

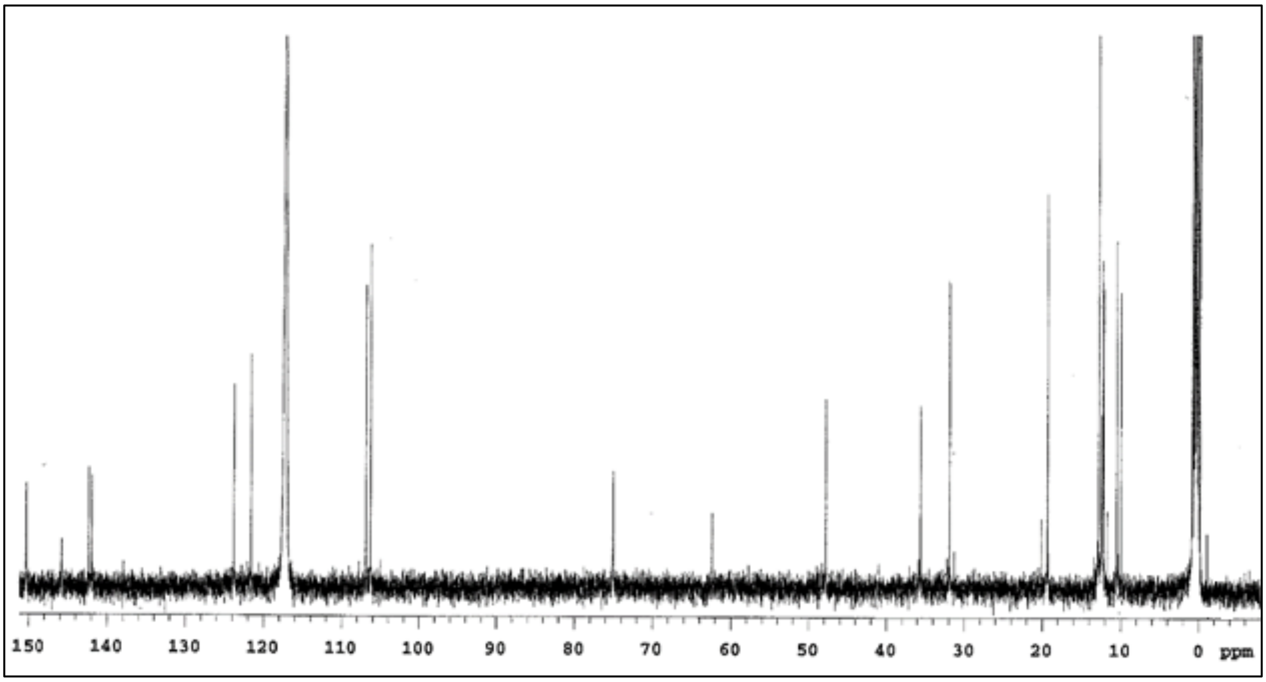


Figure S24b. $^{13}C\{^{1}H\}$ NMR spectrum (125 MHz, 297 K, CD_3CN) of complex [Zn(Et)(bubpzime)]Br (**23**).

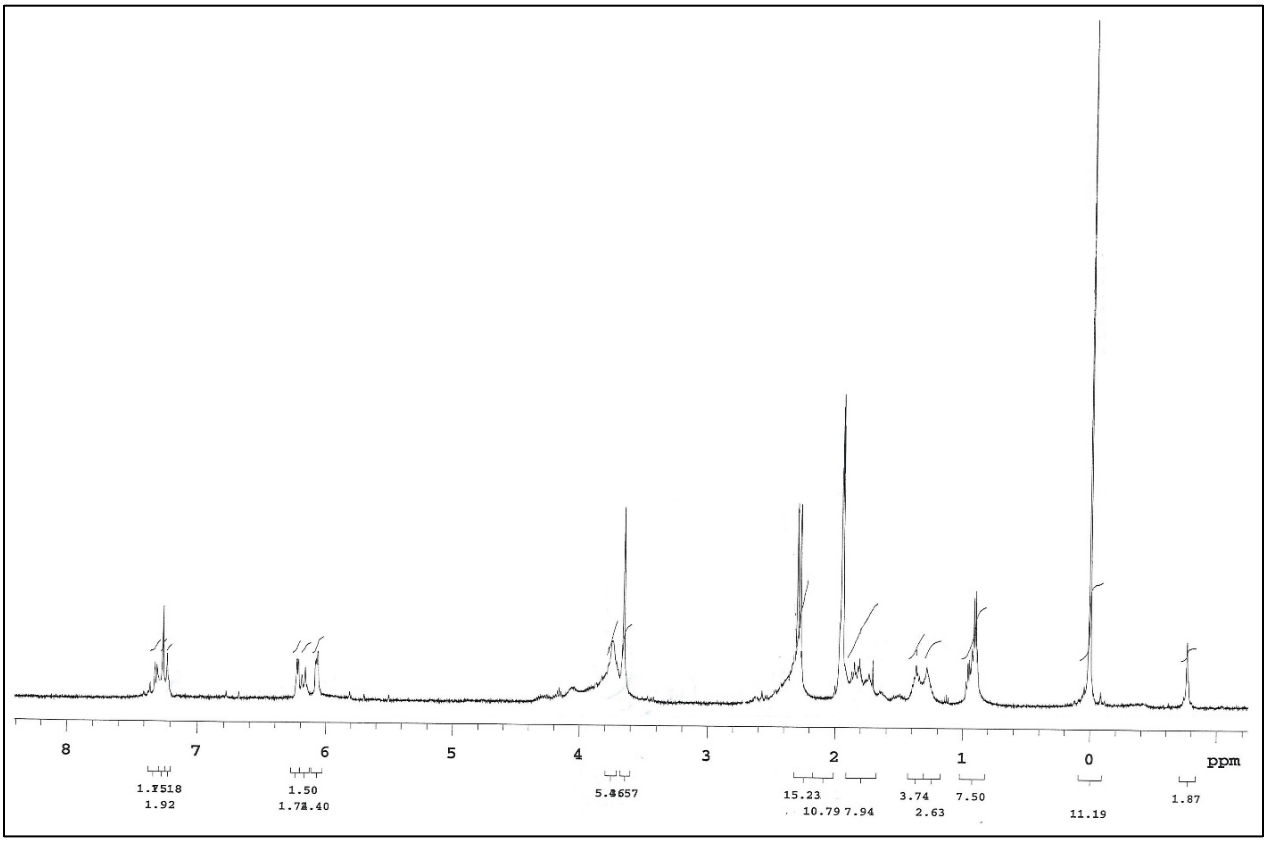


Figure S25a. ^{1}H NMR spectrum (500 MHz, 297 K, CD_3CN) of complex [Zn(CH_2SiMe_3)(bubpzime)]Br (**24**).

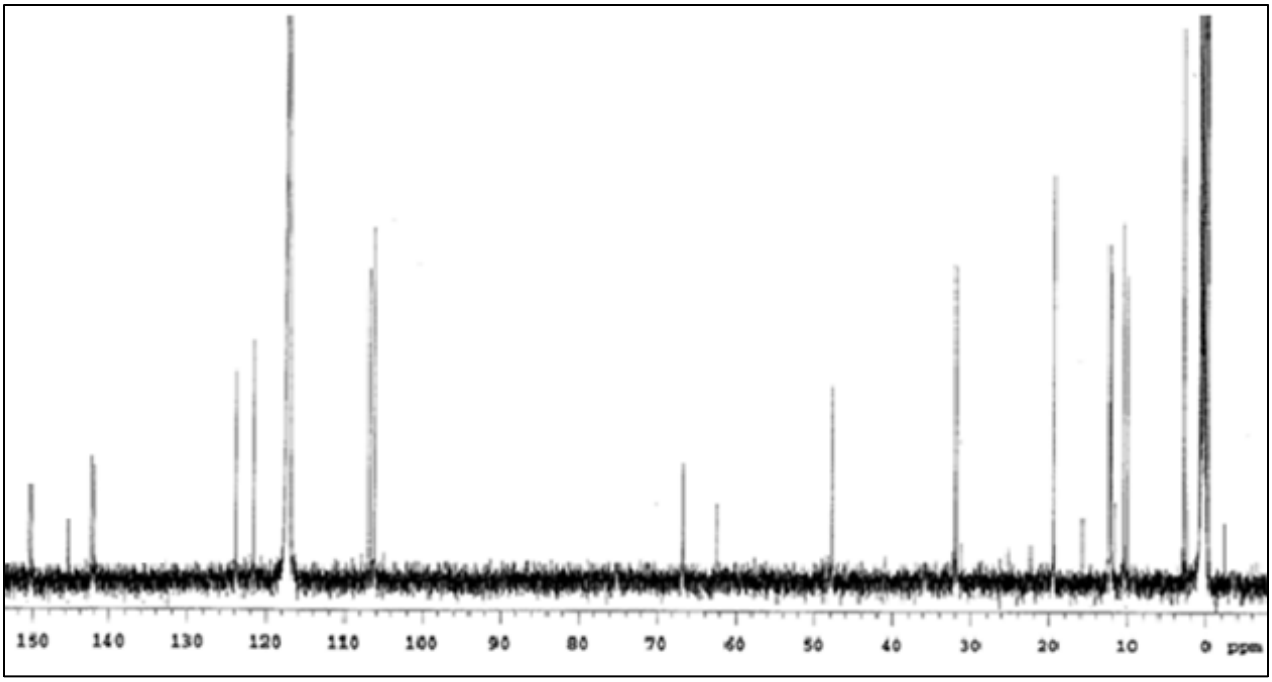


Figure S25b. ^{13}C{^{1}H} NMR spectrum (125 MHz, 297 K, CD_3CN) of complex [Zn(CH_2SiMe_3)(bubpzime)]Br (**24**).

Table S2. Optimization of the synthesis of styrene carbonate **16a** using catalyst **22**[a]

Entry	**22 (mol %)**	**conv.**[b] **(%)**	**TOF**[c] **(h^{-1})**
	1	51	5.10
	2.5	76	3.44
	5	86	1.72
	7.5	95	1.27

[a] Reactions carried out at 50 ºC and 10 bar CO_2 pressure for 10 h using catalyst **22** unless specified otherwise. [b] Determined by ^1H NMR spectroscopy of the crude reaction mixture. [c] TOF = moles of product/(moles of catalyst·time).

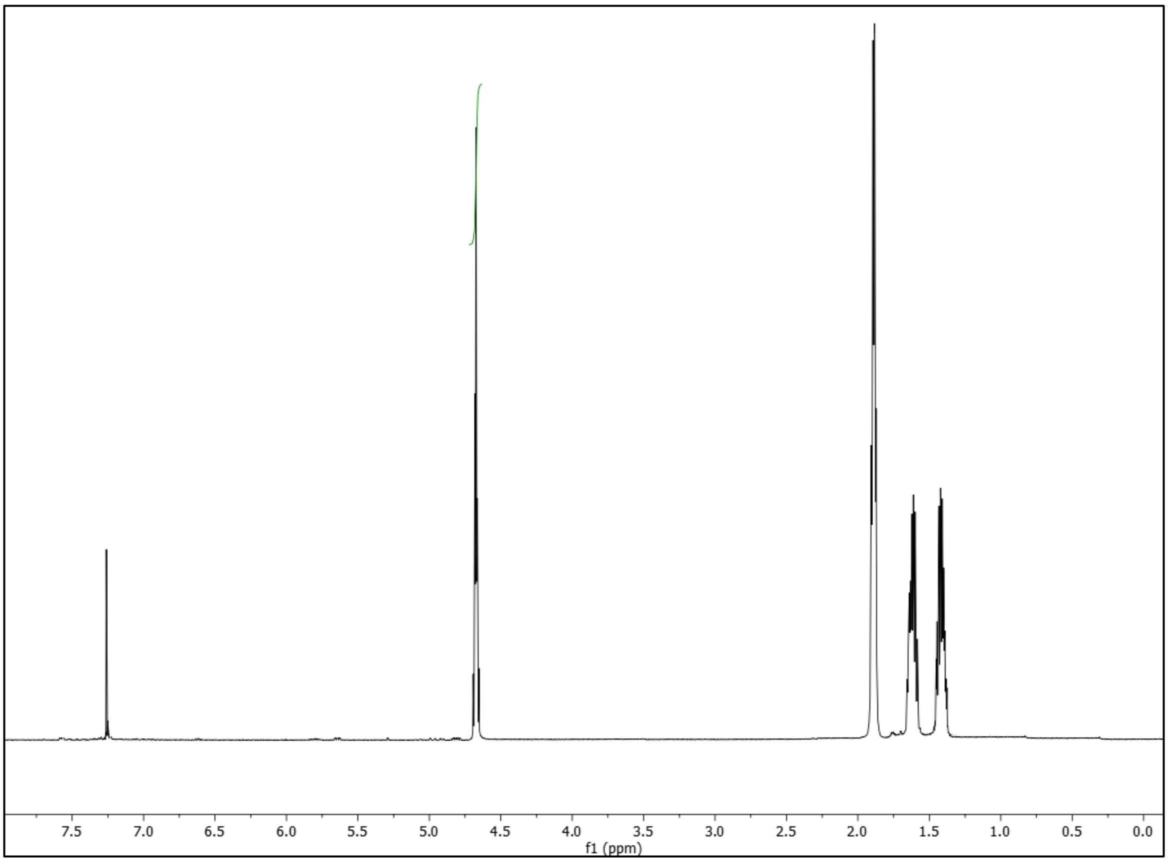


Figure S26. ^{1}H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of cyclohexene carbonate **(16l)** obtained using catalyst **22**.

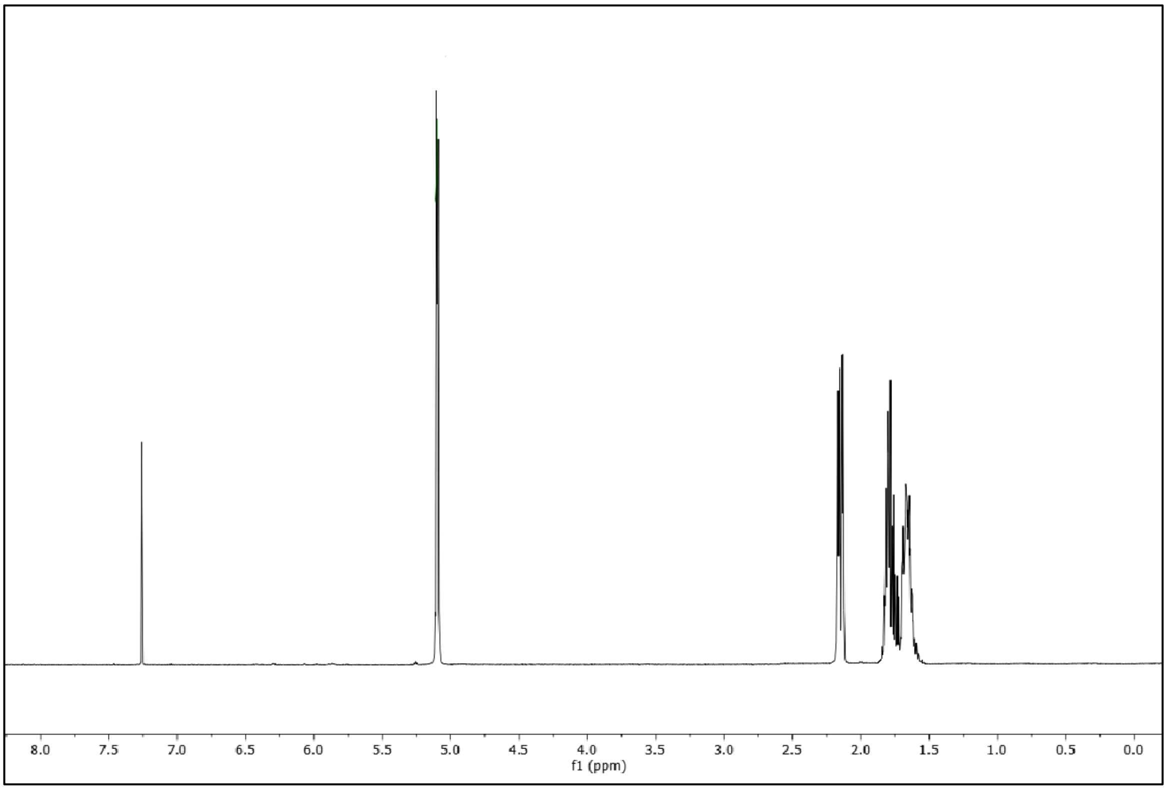


Figure S27. ^{1}H NMR spectrum (500 MHz, 297 K, $CDCl_3$) of cyclopentene carbonate **(16m)** obtained using catalyst **22.**

References

[1] J. A. Castro-Osma, A. Lara-Sánchez, M. North, A. Otero and P. Villuendas, *Catal. Sci. Technol.*, 2012, **2**, 1021–1026.