Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Aromatic guanidines as highly active binary catalyst system for the fixation of CO_2 into cyclic carbonates under mild conditions

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Table of Contents

Experimental Section

General Procedures. Reagent-grade solvents were obtained from E. Merck. Toluene was distilled from benzophenone ketyl, The compounds aniline, 1,4-diaminobencene, *N,N′*-Diisopropylcarbodiimide, 4-(trifluoromethyl)aniline, 4-aminobenzonitrile, *N,N′*-Dicyclohexylcarbodiimide, 2,4,6-trimethylaniline, $ZnEt_2$, $Zn(OTf)_2$, $B(C_6F_5)_3$, epoxides, Bu_4NBr, Bu_4NI, Bu_4NCl, Bu_4NF, PPNCl and DMAP were purchased and used as received. The guanidines **1a–e** were prepared according to published procedures.[1–3]

The following instruments were used for the physical characterization of the compounds. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer. Chemical shifts and the coupling constants are reported in parts per million ($SiMe_4$ as standard) and Hertz, respectively. Most of the NMR assignments were supported by additional 2D experiments and the numbers of scans used for ^{13}C NMR ranged from 0.5 to 2 K depending on the sample concentration. FT-IR spectra were recorded on a Bruker Vector-22 spectrophometer using KBr pellets and the infrared frequencies are reported in cm^{-1}. Mass spectra were acquired using a Micro Tof (Bruker) or a Clarus SQ 8T GC/MS (PerkinElmer). Elemental analysis data were recorded on a Foss-Heraeus CHNO-Rapid analyzer.

General procedure for the synthesis of guanidines catalysed by $ZnEt_2$, $Zn(Otf)_2$ and $B(C_6F_5)_3$

In a glovebox, a solution of amine (6.00 mmol) in toluene (20 mL) was added to a solution of the catalyst [$ZnEt_2$, $Zn(OTf)_2$ or $B(C_6F_5)_3$] (0.09 mmol) in toluene (5 mL) in a Schlenk tube. The carbodiimide (6.00 mmol) was then added to the above reaction mixture. The Schlenk tube was taken outside the glovebox, and the reaction was carried out at 50 ºC for 2 h. The solvent was removed under reduced pressure, and the residue was extracted with diethyl ether and filtered throughout silica to give a clear solution, and silica was washed with additional diethyl ether. The solvent was removed under vacuum, and the residue was recrystallised from ether to provide the solid guanidine products.

General procedure for catalyst screening at 1 bar pressure

Styrene oxide **2a** (1.66 mmol), aromatic monoguanidines **1a–e** (33.2 μmol) and bis(guanidines) **1f–i** (16.6 μmol) and TBAI (33.2 μmol) were placed in an individual glass reaction tubes with a magnetic stirrer bar in a multi-point reactor Carousel 12 Place Reaction Station under constant pressure of 1bar of CO_2. The reaction mixture was stirred at 70 ºC for 24 h, then the conversion of styrene oxide **2a** into styrene carbonate **3a** was determined by analysis of a sample by ^1H NMR spectroscopy.

General procedure for catalyst screening at 10 bar pressure

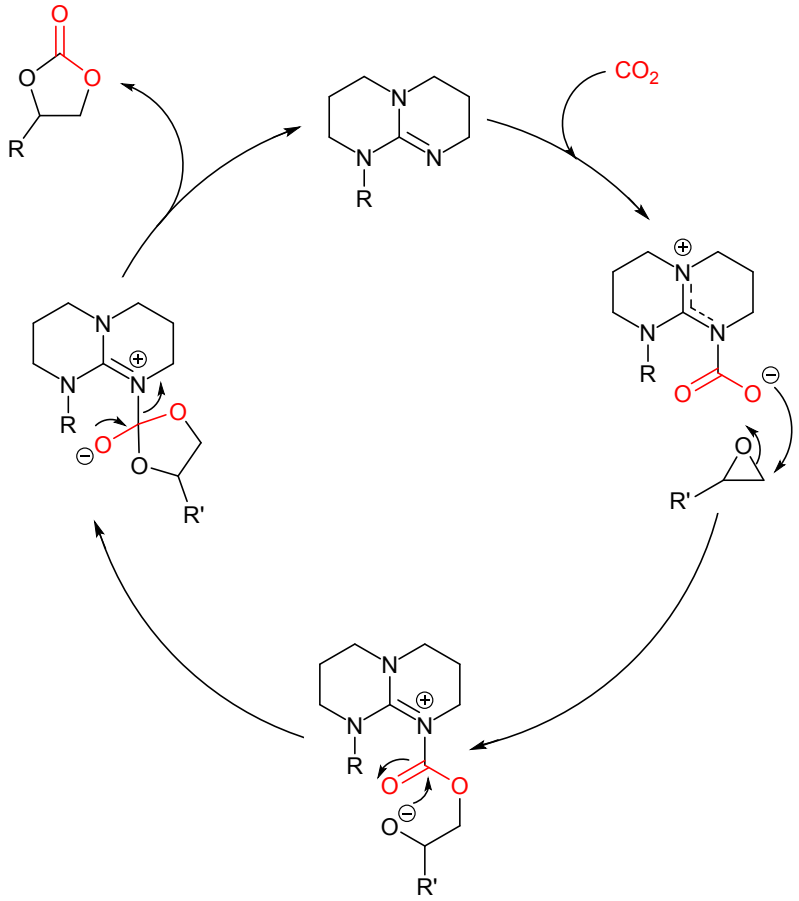
Cyclohexene oxide **4a** (1.66 mmol), bis(guanidine) **1f** (16.6–33.2 μmol) and TBAI (33.2–66.4 μmol) were placed in a stainless steel reactor with a magnetic stirrer bar and it was pressurized to 10 bar. The reaction mixture was stirred at 70–85 ºC for 24 h, then the conversion of cyclohexene oxide **4a** into cyclohexene carbonate **5a** was determined by analysis of a sample by ^1H NMR spectroscopy.

General procedure for the synthesis of cyclic carbonates at 1 bar pressure

An epoxide **2a–k** (1.66 mmol), guanidine **1f** (16.6 μmol) and TBAI (33.2 μmol) were placed an individual glass reaction tubes with a magnetic stirrer bar in a multi-point reactor under constant pressure of 1 bar of CO_2. The reaction mixture was stirred at 70 ºC for 24 h. The conversion of epoxide to cyclic carbonate was then determined by analysis of a sample by ^1H 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 **3a–k** are all known compounds and the spectroscopic data for samples prepared using bis(guanidine) **1f** were consistent with those reported in the literature.[6–9]

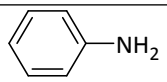
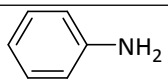
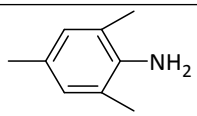
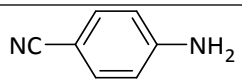
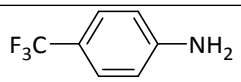
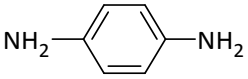
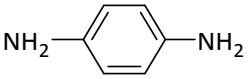
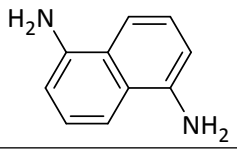
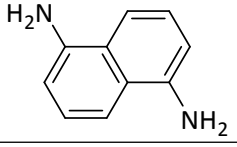
General procedure for the synthesis of cyclic carbonates at 10 bar pressure

The synthesis an purification of cyclic carbonates **5a–d** were carried out in a manner identical than cyclic carbonates **3a–k** using guanidine **1f** (33.2 μmol) and TBAI (66.4 μmol) as binary catalyst system. The reaction mixture was placed in a stainless steel reactor with a magnetic stirrer bar. Cyclic carbonates **5a–d** are all known compounds and the spectroscopic data for samples prepared using bis(guanidine) **1f** were consistent with those reported in the literature.[6–8]



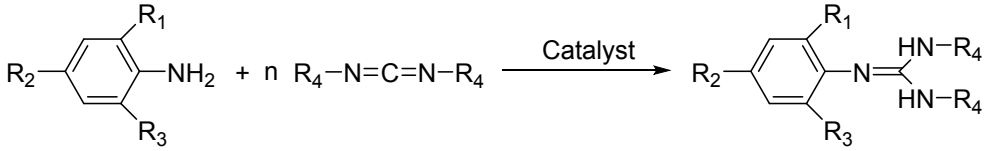
Scheme 1. Plausible and general mechanism for the synthesis of cyclic carbonates through activation of CO_2 molecule by guanidines.

Table S1. Synthesis of guanidines **1a–i** by reaction of aromatic amines with carbodiimides.[a]

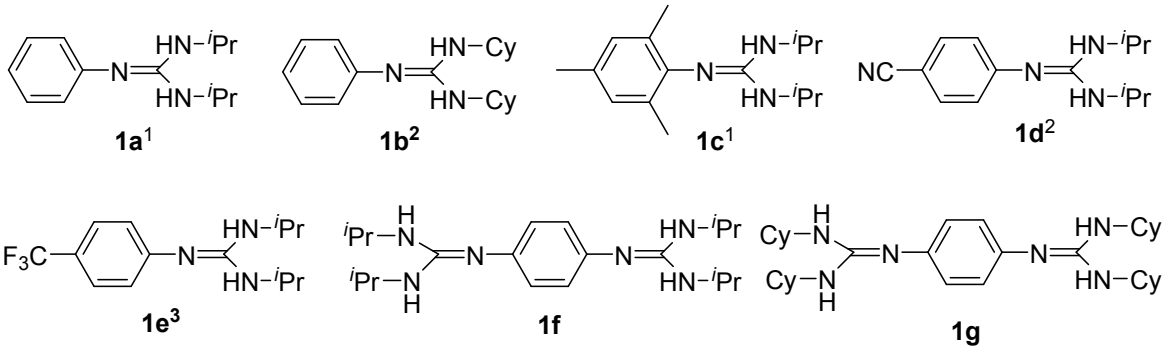
Entry	Cat.	Amine	R-N=C=N-R (n, equiv)	Guanidine (Conv. %)[b]
1[1]	$ZnEt_2$		R = ^{i}Pr (1)	**1a** (>99)
2[2]	$Zn(OTf)_2$		R = Cy (1)	**1b** (96)
3[1]	$ZnEt_2$		R = ^{i}Pr (1)	**1c** (>99)
4[2]	$Zn(OTf)_2$		R = ^{i}Pr (1)	**1d** (92)
5[3]	$B(C_6F_5)_3$		R = ^{i}Pr (1)	**1e** (27)
6[c]	$ZnEt_2$		R = ^{i}Pr (2)	**1f** (95)[d,e]
7[c]	$ZnEt_2$		R = Cy (2)	**g** (>99)[e]
8[c]	$ZnEt_2$		R = ^{i}Pr (2)	**1h** (>99)[e]
9[c]	$ZnEt_2$		R = Cy (2)	**1i** (93)[e]

[a] Conditions: amine (1 mmol) and carbodiimide (1 or 2 mmol). [b] Conversion were determined by ^{1}H NMR spectroscopy. [c] Reactions were carried out at 50 ^{0}C in toluene for 1 h. [d] Product also obtained in reference 4. [e] Product also obtained in reference 5.

Synthesis of guanidines 1a–g

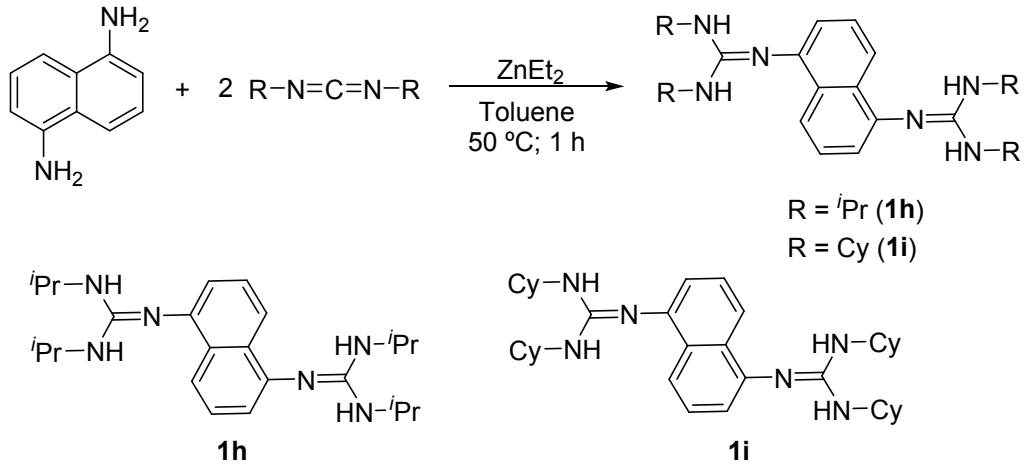


$R_1 = R_2 = R_3 = H$; $R_4 = {}^{i}Pr$; n =1 (**1a**)
$R_1 = R_2 = R_3 = H$; $R_4 = Cy$; n =1 (**1b**)
$R_1 = R_2 = R_3 = Me$; $R_4 = {}^{i}Pr$; n = 1 (**1c**)
$R_1 = R_3 = H$; $R_2 = CN$; $R_4 = {}^{i}Pr$; n =1 (**1d**)
$R_1 = R_3 = H$; $R_2 = CF_3$; $R_4 = {}^{i}Pr$; n = 1 (**1e**)
$R_1 = R_3 = H$; $R_2 = NH_2$; $R_4 = {}^{i}Pr$; n = 2 (**1f**)
$R_1 = R_3 = H$; $R_2 = NH_2$; $R_4 = Cy$; n = 2 (**1g**)



[1]Prepared according to published procedures (ref 1); [2]Prepared according to published procedures (ref 2); [3]Prepared according to published procedures (ref 3).

Synthesis of guanidines 1h and 1i



R = ${}^{i}Pr$ (**1h**)
R = Cy (**1i**)

Scheme 2. Synthesis of aromatic guanidines **1a–i**

NMR data for guanidines 1f–i

Synthesis of 2,2'-(1,4-phenylene)bis(1,3-diisopropylguanidine) (1f). In a 250 mL round bottom flask, *p*-phenylenediamine (0.65 g, 6.0 mmol) was dissolved in dry toluene (50 mL). N,N′-diisopropylcarbodiimide (1.51 g, 12.0 mmol) and a solution of $ZnEt_2$ (1 M in hexane, 0.09 mL, 0.09 mmol) was added and the mixture was heated to 50 ºC and stirred for 1 h. Then, the solvent was removed under vacuum, and the product **1f** was obtained as a white solid. Yield 95 % (2.05 g). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 6.75 (s, 2H, Ar-H), 3.72 (brs, 2H, CH-*i*Pr), 3.52 (brs, 2H, NH), 1.13 ppm (d, $^3J_{HH}$ = 6.1 Hz, 12H, CH_3-*i*Pr); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 297 K): δ = 150.8 (C=N), 144.2 (Ar-C), 124.6 (Ar-CH), 43.3 (CH-*i*Pr), 23.5 ppm (CH_3-*i*Pr); IR (FTIR): 3332–3232 (NH), 1612 (C=N) cm^{-1}. HRMS (ESI) for $C_{10}H_{35}N_6$ $[M+H]^+$: m/z calcd: 360.551, found: 360.562.

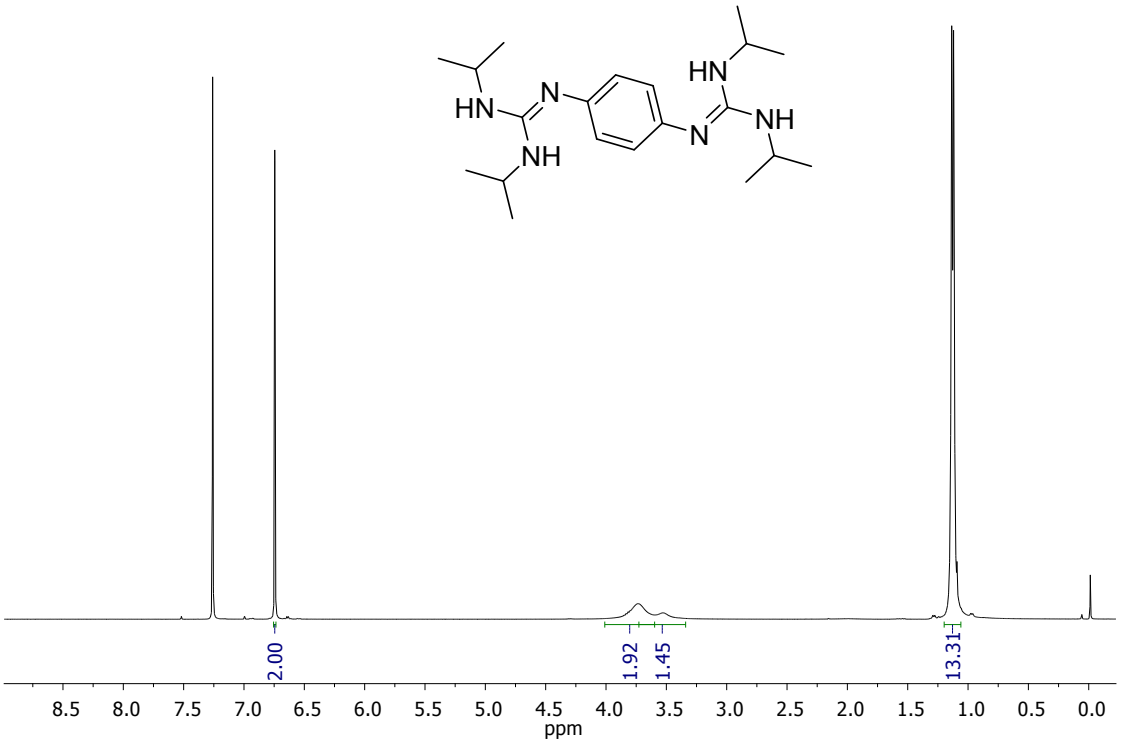
Synthesis of 2,2'-(1,4-phenylene)bis(1,3-dicyclohexylguanidine) (1g). The synthesis of compound **1g** was carried out in a manner identical with that for **1f**, using *p*-phenylenediamine (0.65 g, 6.0 mmol), N, N'- dicyclohexylcarbodiimide (2,48 g, 12.0 mmol) and a solution of $ZnEt_2$ (1 M in hexane, 0.09 mL, 0.09 mmol). The product **1g** was obtained as a white solid. Yield: 99 % (3.09 g). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 6.71 (s, 2H, Ar-H), 3.67–3.16 (brs, 4H, NH, CH-Cy), 2.07–1.87 (m, 4H, CH_2-Cy), 1.70–1.48 (m, 6H, CH_2-Cy), 1.38–1.21 (m, 4H, CH_2-Cy), 1.20–0.95 ppm (m, 6H, CH_2-Cy); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 297 K): δ = 150.6 (C=N), 144.3 (Ar-C), 124.6 (Ar-CH), 50.2 (CH-Cy), 33.8 (CH_2-Cy), 25.8 (CH_2-Cy), 25.0 ppm (CH_2-Cy); IR (FTIR): 3368–3067 (NH), 1604 (C=N) cm^{-1}. HRMS (ESI) for $C_{32}H_{52}N_6$ $[M+H]^+$: m/z calcd: 521.432, found: 521.428.

Synthesis 2,2'-(naphthalene-1,5-diyl)bis(1,3-diisopropylguanidine) (1h). The synthesis of compound **1h** was carried out in a manner identical with that for **1f**, using p- 1,5-diaminonaphthalene (0,95 g, 6.0 mmol), N,N′-diisopropylcarbodiimide (1.51 g, 12.0 mmol) and a solution of $ZnEt_2$ (1 M in hexane, 0.09 mL, 0.09 mmol). the product **1h** was obtained as a white solid. Yield: 99 % (2.49 g). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 7.66 (d, $^3J_{HH}$ = 8.3 Hz, 1H, Ar-H), 7.29 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar-H), 6.87 (d, $^3J_{HH}$ = 7.2 Hz, 1H, Ar-H), 3.85 (m, 2H, CH-*i*Pr), 3.56 (brs, 2H, NH), 1.15 ppm (d, $^3J_{HH}$ = 6.4 Hz, 12H, CH_3-*i*Pr); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 297 K): δ = 150.2 (C=N), 146.5 (Ar-C), 130.9 (Ar-C), 125.4 (Ar-CH), 118.3 (Ar-CH), 118.2 (Ar-CH), 43.5 (CH-*i*Pr),

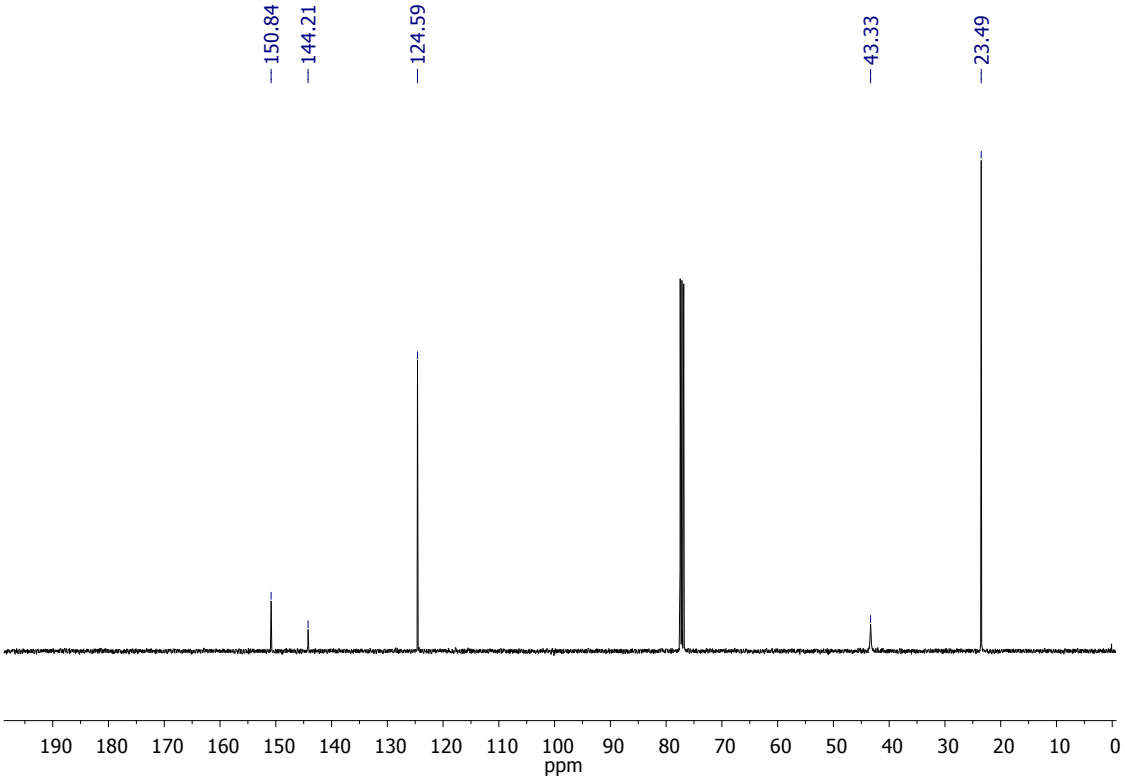
23.6 ppm (CH_3-^{i}Pr); IR (FTIR): 3313–3259 (NH), 1649 (C=N) cm^{-1}. HRMS (ESI) for $C_{24}H_{38}N_6$ $[M+H]^+$: m/z calcd: 411.125, found: 411.132.

Synthesis of 2,2'-(naphthalene-1,5-diyl)bis(1,3-dicyclohexylguanidine) (1i). The synthesis of compound **1i** was carried out in a manner identical with that for **1f**, using p-1,5-diaminonaphthalene (0,95 g, 6.0 mmol), N, N'- dicyclohexylcarbodiimide (2,48 g, 12.0 mmol) and a solution of $ZnEt_2$ (1 M in hexane, 0.09 mL, 0.09 mmol). the product **1i** was obtained as a white solid. Yield: 93 % (3.41 g).^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ = 7.63 (d, $^3J_{HH}$ = 8.4 Hz, 1H, Ar-H), 7.26 (t, $^3J_{HH}$ = 7.8 Hz, 1H, Ar-H), 6.86 (d, $^3J_{HH}$ = 6.8 Hz, 1H, Ar-H), 3.65–3.17 (brs, 4H, NH, CH-Cy), 2.07–1.95 (m, 4H, CH_2-Cy), 1.70–1.51 (m, 6H, CH_2-Cy), 1.41–1.21 (m, 4H, CH_2-Cy), 1.17–0.95 ppm (m, 6H, CH_2-Cy); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 297 K): δ = 149.9 (C=N), 146.6 (Ar-C), 130.9 (Ar-C), 125.3 (Ar-CH), 118.4 (Ar-CH), 118.1 (Ar-CH), 50.3 (CH-Cy), 34.0 (CH_2-Cy), 25.8 (CH_2-Cy), 25.0 ppm (CH_2-Cy); IR (FTIR): 3354–3293 (NH), 1621 (C=N) cm^{-1}. HRMS (ESI) for $C_{36}H_{54}N_6$ $[M+H]^+$: m/z calcd: 571.448, found: 571.442.

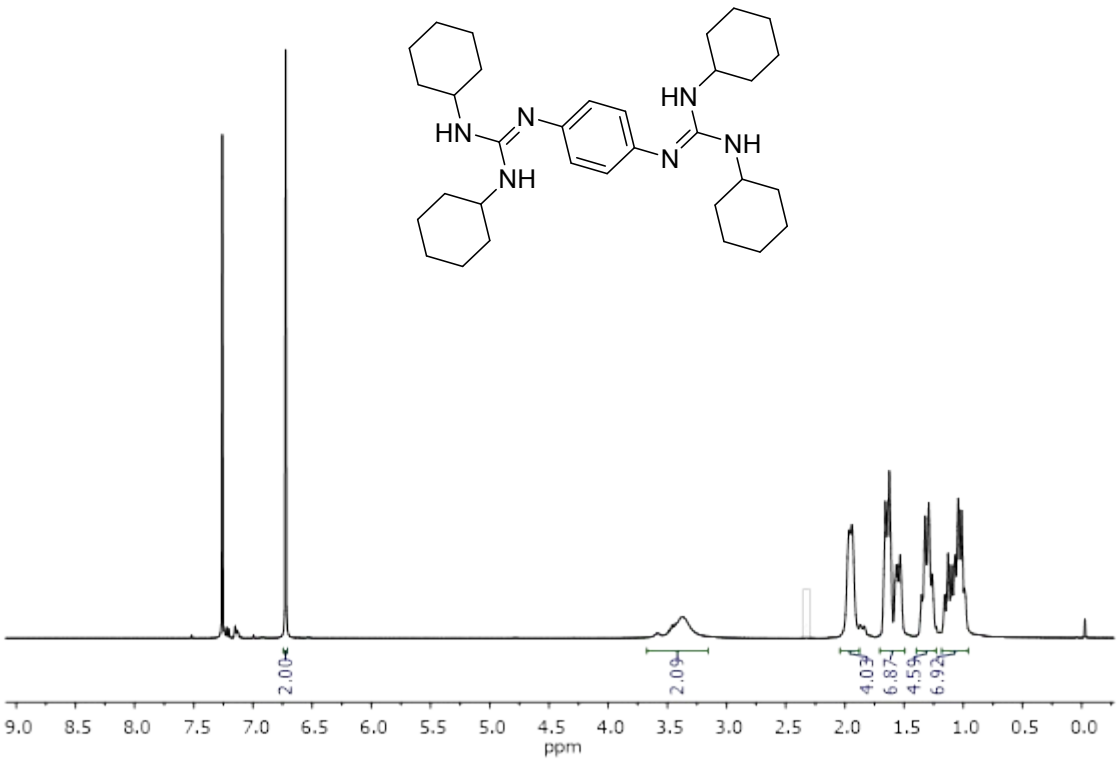
^{1}H-NMR of 2,2'-(1,4-phenylene)bis(1,3-diisopropylguanidine) (**1f**) in $CDCl_3$



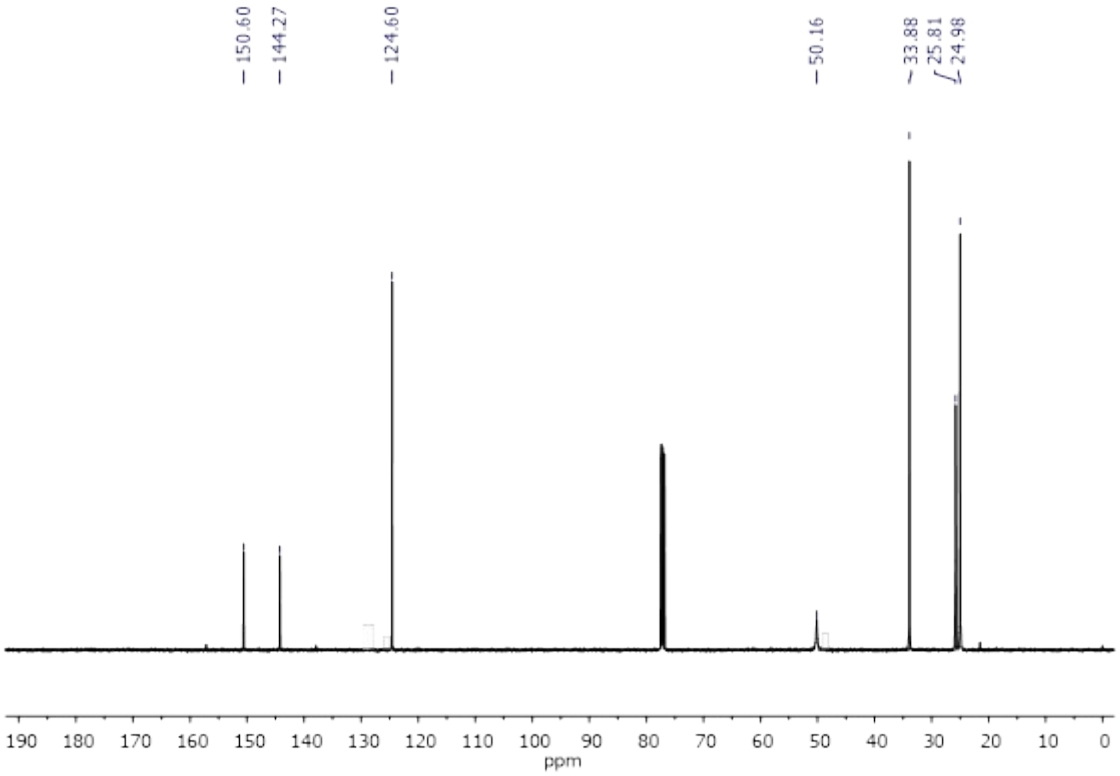
^{13}C-{^{1}H}-NMR of 2,2'-(1,4-phenylene)bis(1,3-diisopropylguanidine) (**1f**) in $CDCl_3$



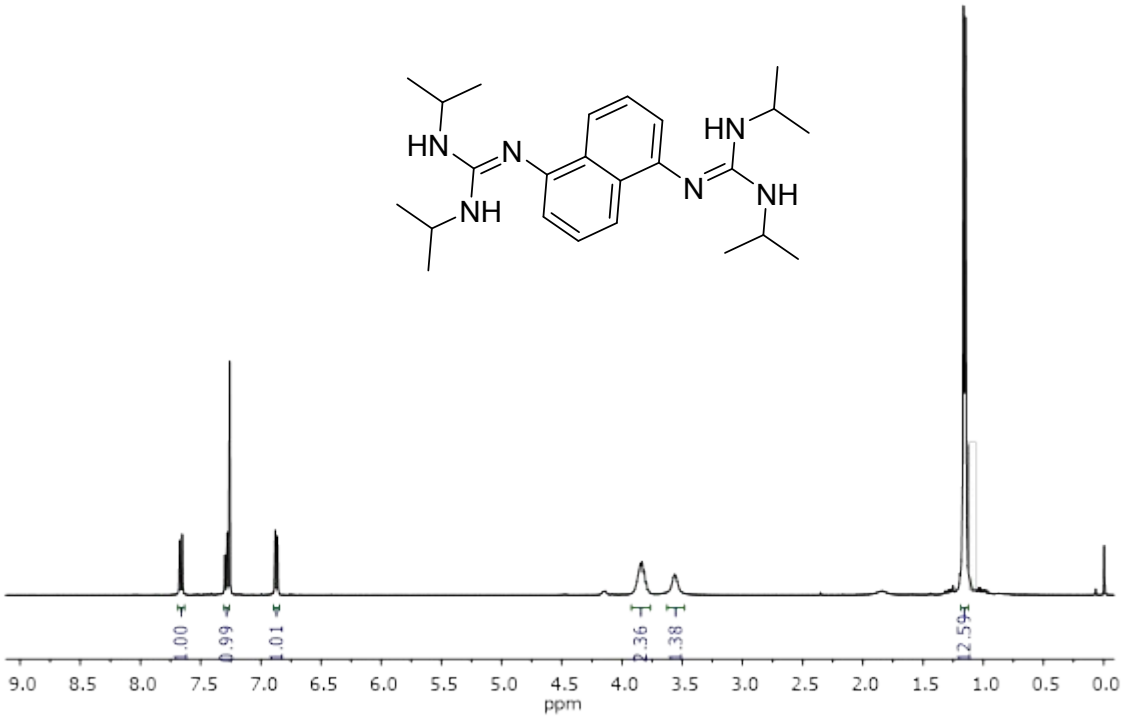
^{1}H-NMR of 2,2'-(1,4-phenylene)bis(1,3-dicyclohexylguanidine) (**1g**) in $CDCl_3$



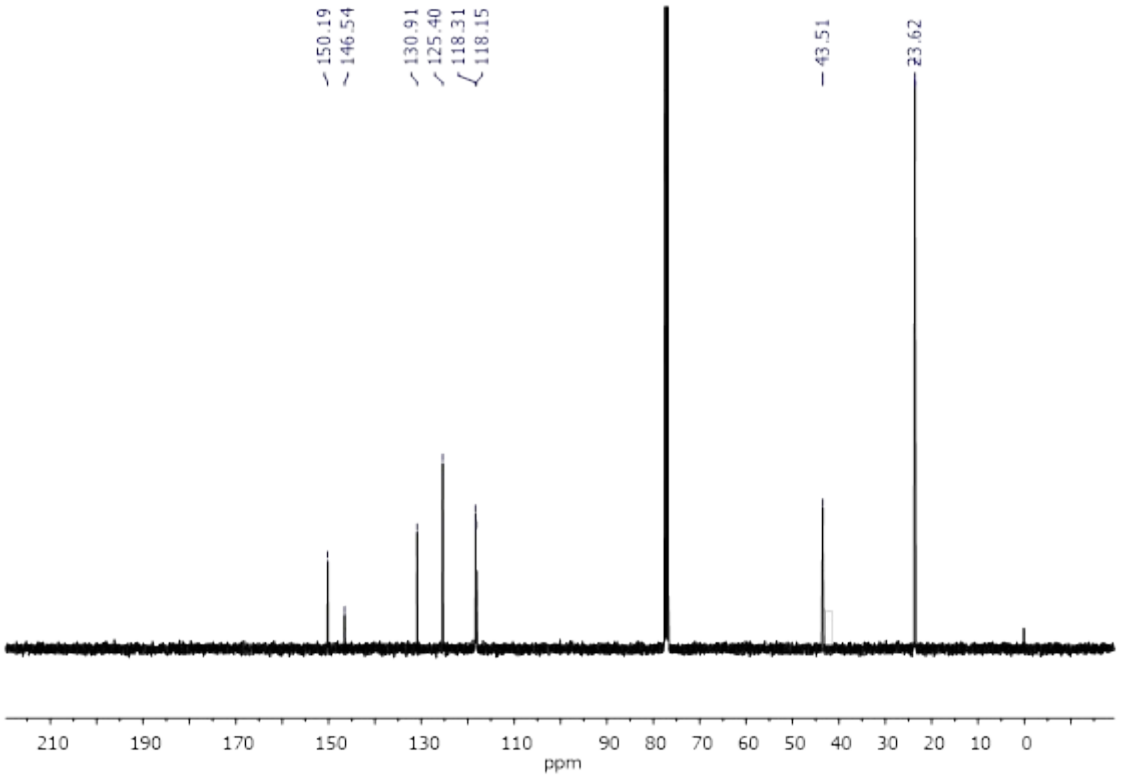
^{13}C-{^{1}H}-NMR of 2,2'-(1,4-phenylene)bis(1,3-dicyclohexylguanidine) (**1g**) in $CDCl_3$



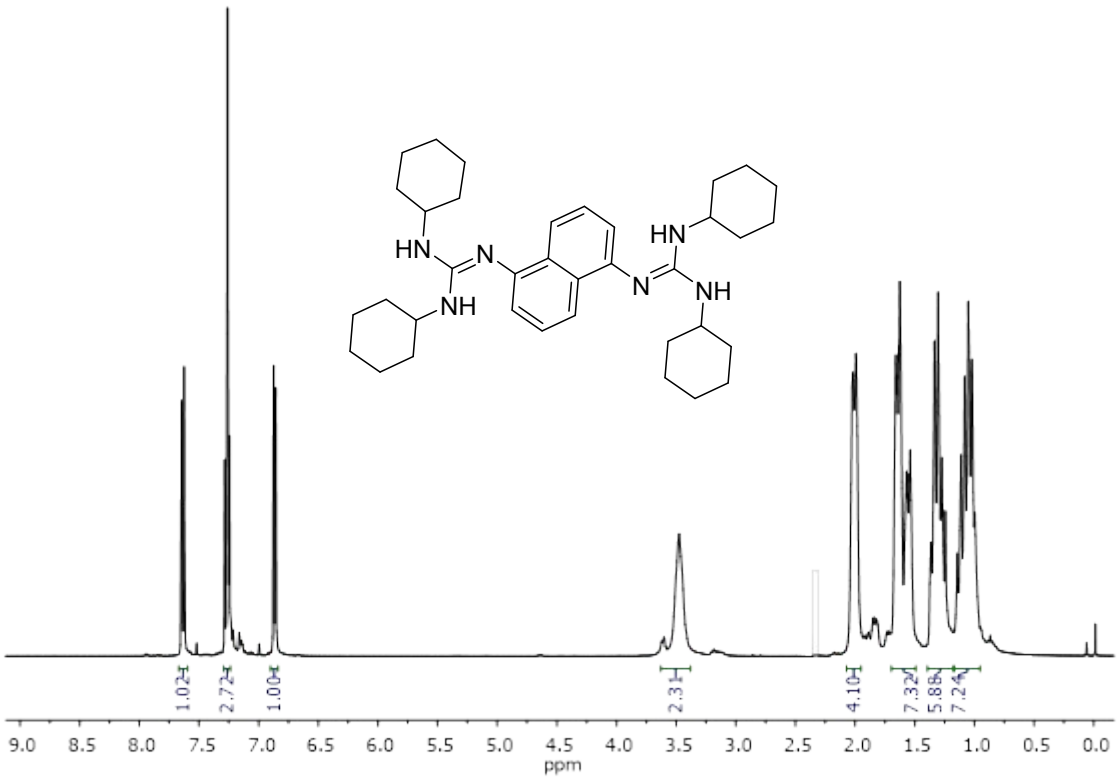
^{1}H-NMR of 2,2'-(naphthalene-1,5-diyl)bis(1,3-diisopropylguanidine) (**1h**) in $CDCl_3$



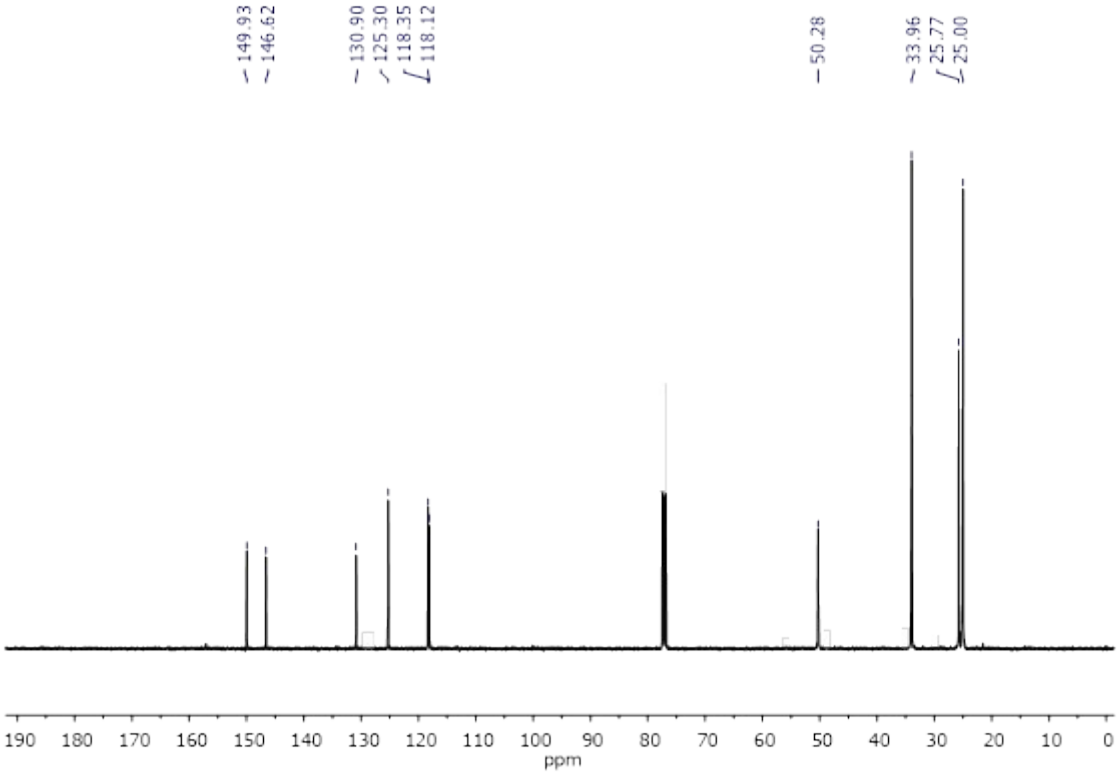
^{13}C-{^{1}H}-NMR of 2,2'-(naphthalene-1,5-diyl)bis(1,3-diisopropylguanidine) (**1h**) in $CDCl_3$



^{1}H-NMR of 2,2'-(naphthalene-1,5-diyl)bis(1,3-dicyclohexylguanidine) (**1i**) in $CDCl_3$



^{13}C-{^{1}H}-NMR of 2,2'-(naphthalene-1,5-diyl)bis(1,3-dicyclohexylguanidine) (**1i**) in $CDCl_3$



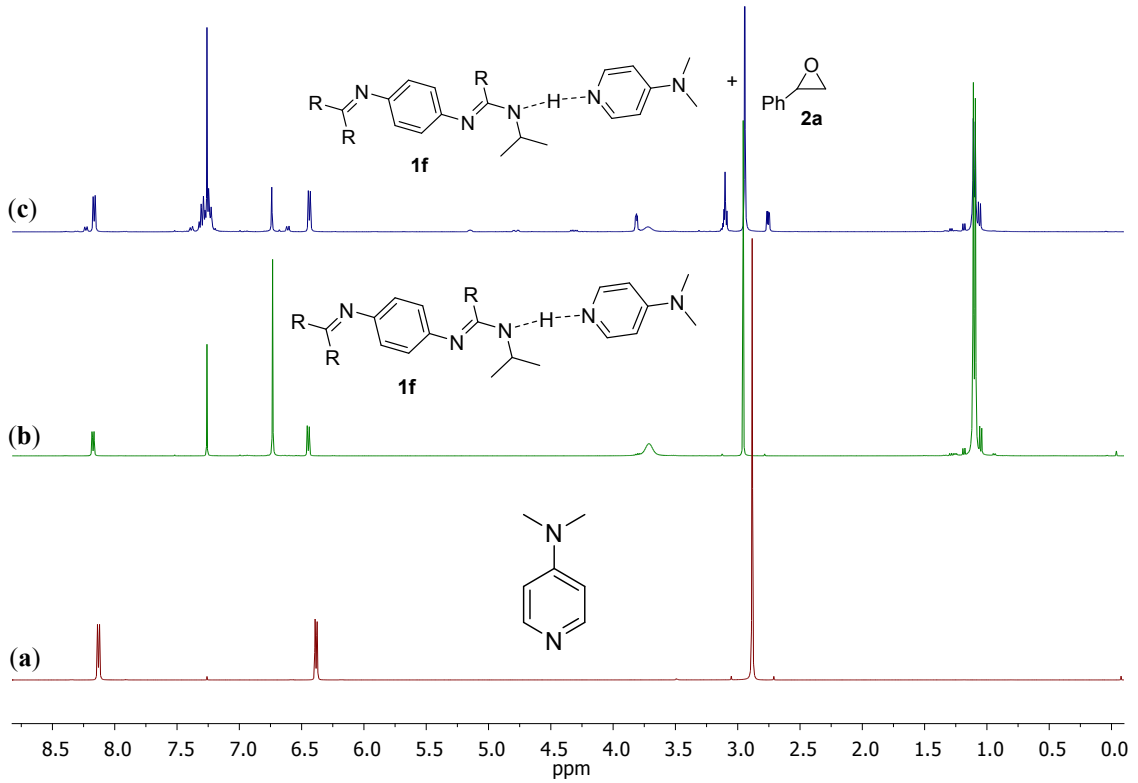


Figure S1. (**a**) ^{1}H NMR spectrum of DMAP in $CDCl_3$. (**b**) ^{1}H NMR spectrum of compound **1f** and DMAP in a molar ratio 1:1 (**1f**:DMAP) at 70 ºC for one hour in $CDCl_3$. (c) ^{1}H NMR spectrum of compound **1f**, DMAP and styrene oxide **2a**, in a molar ratio 1:1:1 (**1f**:DMAP:**2a**) at 70 ºC for one hour in $CDCl_3$.

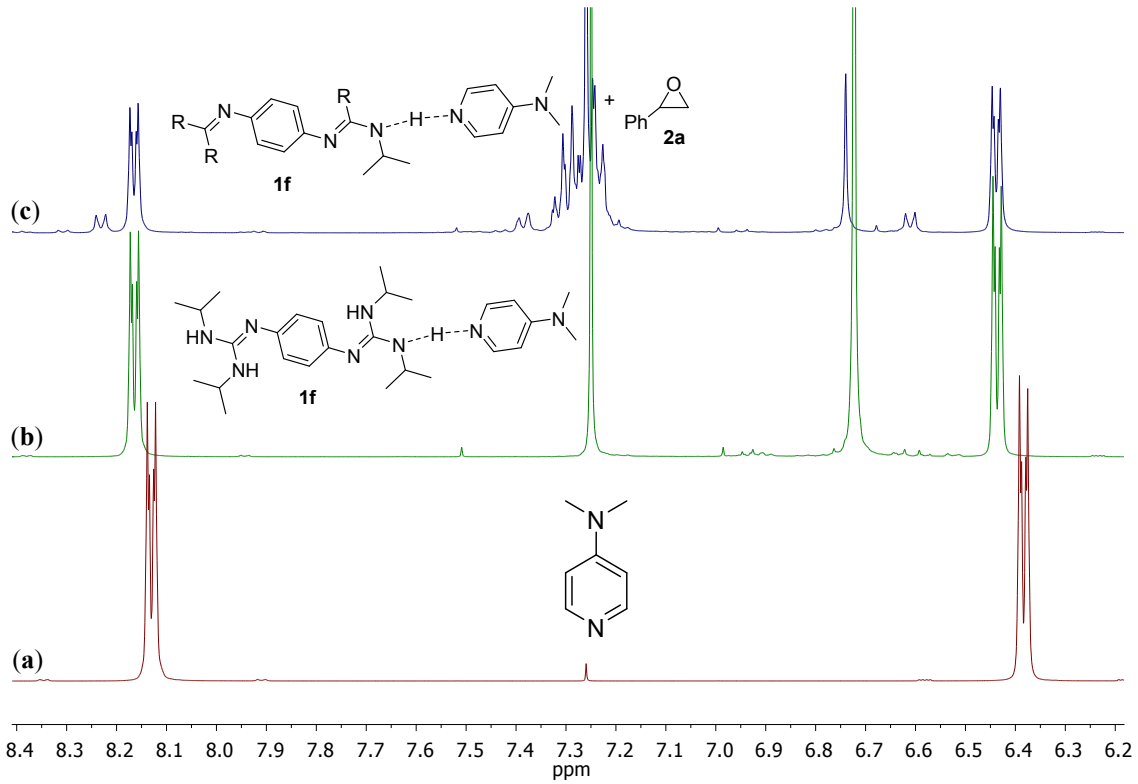


Figure S2. ^{1}H NMR range 6.2–8.4 ppm (**a**) ^{1}H NMR spectrum of DMAP in $CDCl_3$. (**b**) ^{1}H NMR spectrum of compound **1f** and DMAP in a molar ratio 1:1 (**1f**:DMAP) at 70 ºC for one hour in $CDCl_3$. (**c**) ^{1}H NMR spectrum of compound **1f**, DMAP and styrene oxide **2a**, in a molar ratio 1:1:1 (**1f**:DMAP:**2a**) at 70 ºC for one hour in $CDCl_3$.

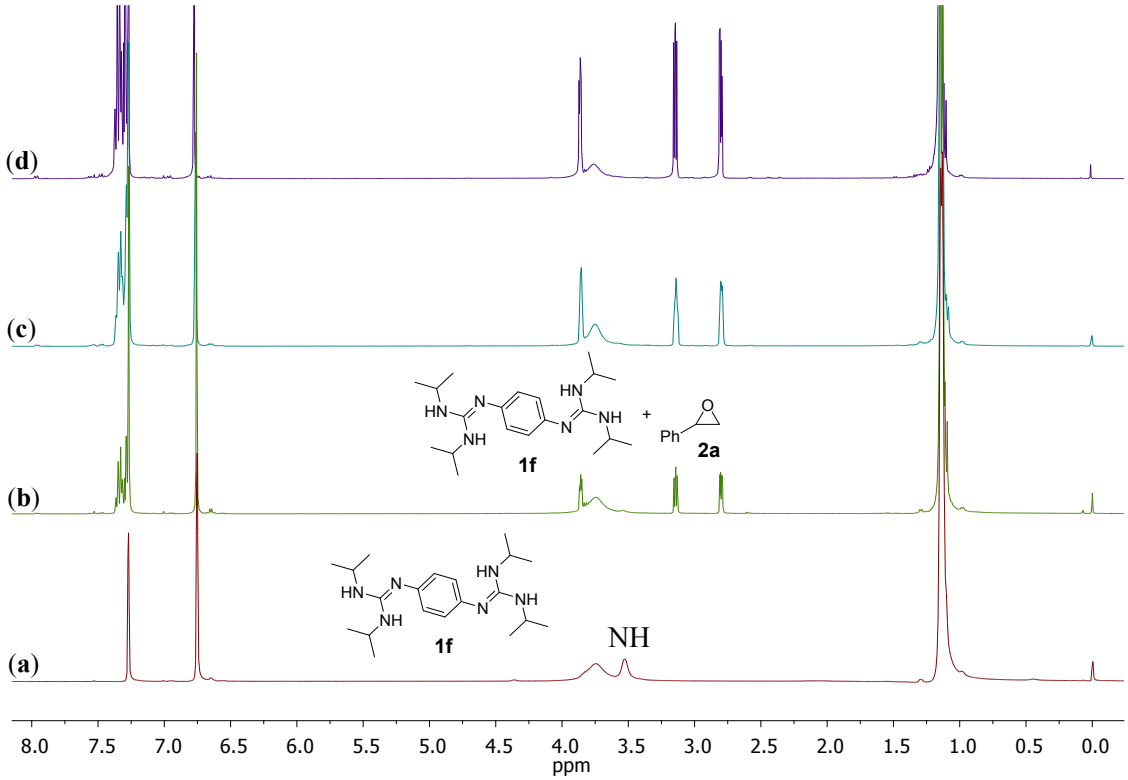


Figure S3. (**a**) ^{1}H NMR spectrum of compound **1f** in $CDCl_3$. (**b**) ^{1}H NMR spectrum of compound **1f** and styrene oxide **2a** in a molar ratio 1:1 (**1f**:**2a**) at 70 ºC for one hour in $CDCl_3$. (c) ^{1}H NMR spectrum of compound **1f** and styrene oxide **2a**, in a molar ratio 1:2 (**1f**:**2a**) at 70 ºC for one hour in $CDCl_3$. (**d**) ^{1}H NMR spectrum of compound **1f** and styrene oxide **2a**, in a molar ratio 1:4 (**1f**:**2a**) at 70 ºC for one hour in $CDCl_3$

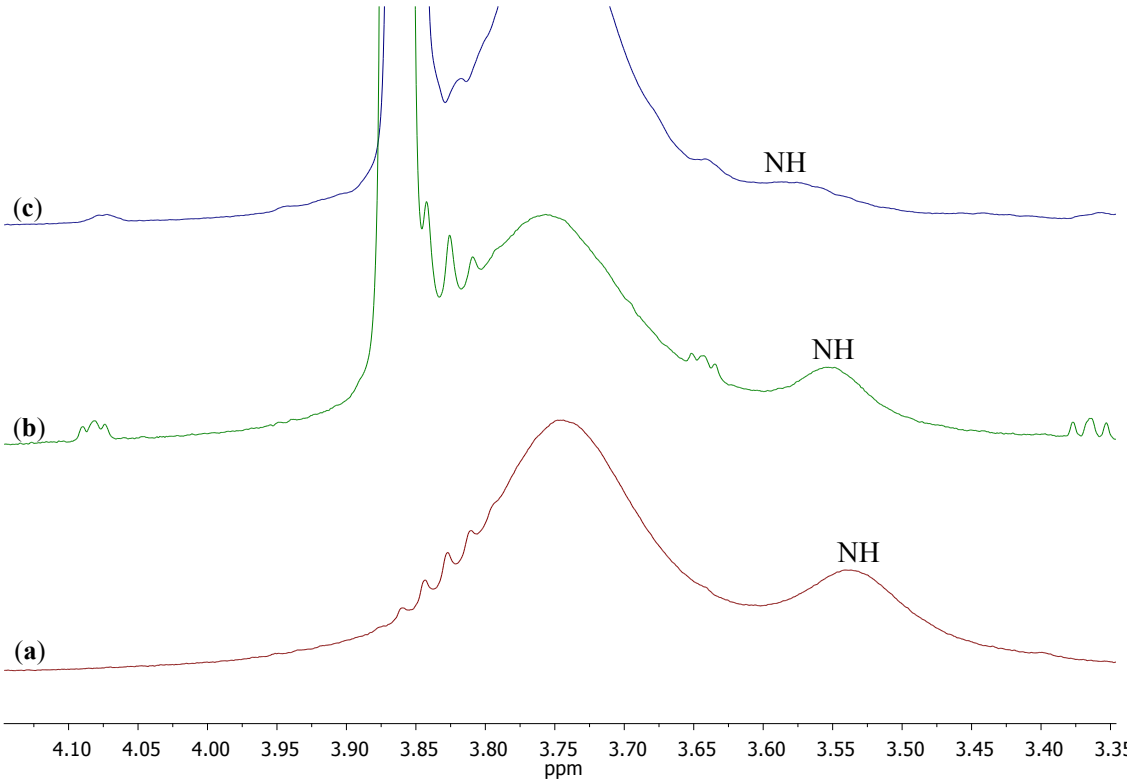


Figure S4. ^{1}H NMR range 3.35–4.20 ppm (**a**) ^{1}H NMR spectrum of compound **1f** in $CDCl_3$. (**b**) ^{1}H NMR spectrum of compound **1f** and styrene oxide **2a** in a molar ratio 1:1 (**1f**:**2a**) at 70 ºC for one hour in $CDCl_3$. (**c**) ^{1}H NMR spectrum of compound **1f** and styrene oxide **2a**, in a molar ratio 1:2 (**1f**:**2a**) at 70 ºC for one hour in $CDCl_3$.

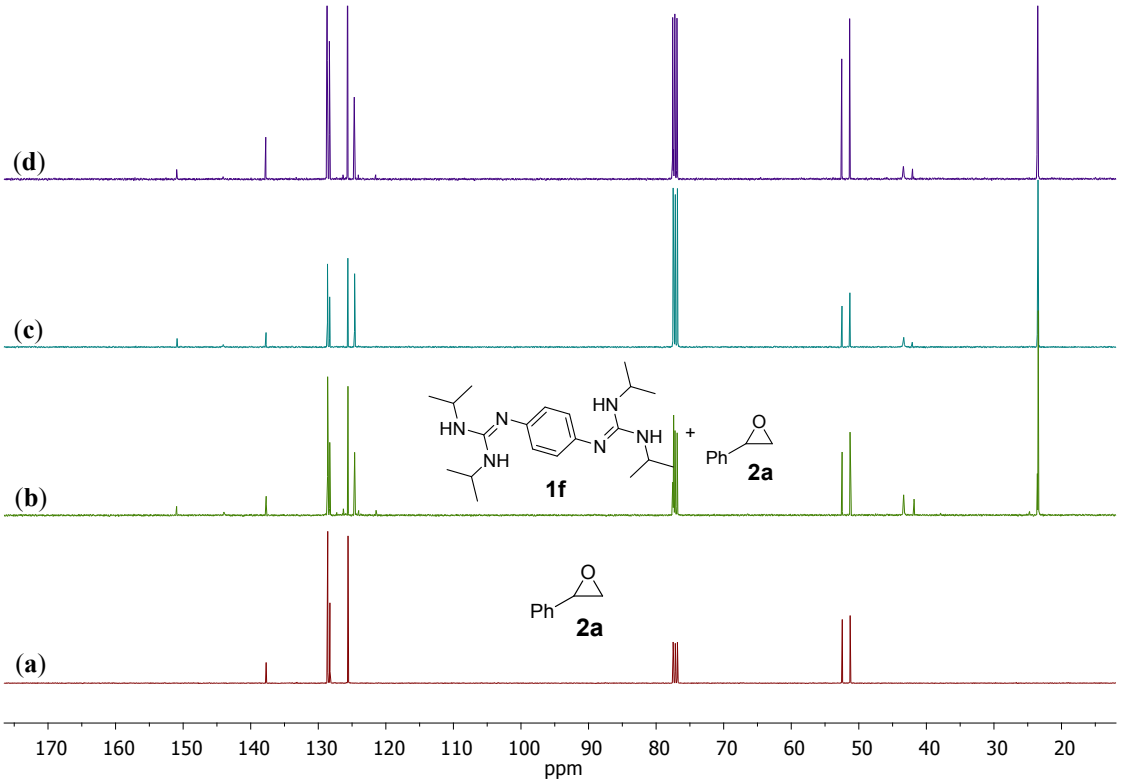


Figure S5. (**a**) $^{13}C\{^{1}H\}$ NMR spectrum of styrene oxide **2a** in $CDCl_3$. (**b**) $^{13}C\{^{1}H\}$ NMR spectrum of compound **1f** and styrene oxide **2a** in a molar ratio 1:1 (**1f**:**2a**) at 70 ºC for one hour in $CDCl_3$. (c) $^{13}C\{^{1}H\}$ NMR spectrum of compound **1f** and styrene oxide **2a**, in a molar ratio 1:2 (**1f**:**2a**) at 70 ºC for one hour in $CDCl_3$. (**d**) $^{13}C\{^{1}H\}$ NMR spectrum of compound **1f** and styrene oxide **2a**, in a molar ratio 1:4 (**1f**:**2a**) at 70 ºC for one hour in $CDCl_3$.

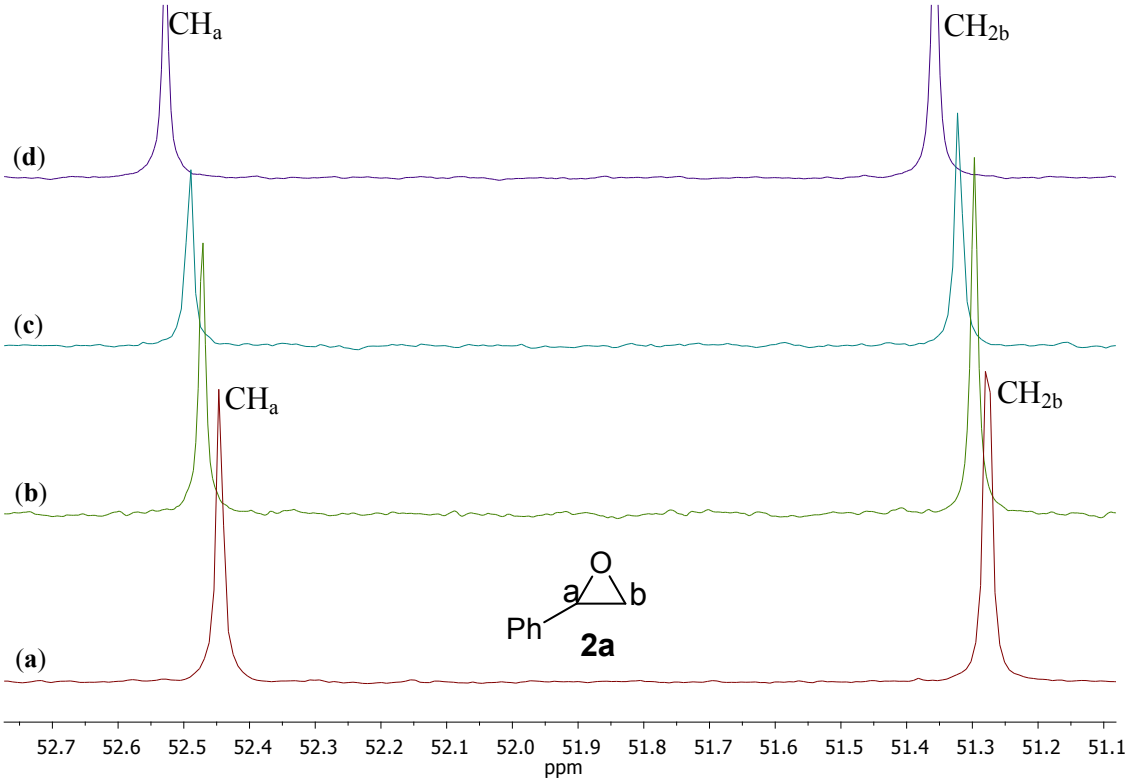


Figure S6. $^{13}C\{^{1}H\}$ NMR range 51.1–52.8 ppm (**a**) $^{13}C\{^{1}H\}$ NMR spectrum of styrene oxide **2a** in $CDCl_3$. (**b**) $^{13}C\{^{1}H\}$ NMR spectrum of compound **1f** and styrene oxide **2a** in a molar ratio 1:1 (**1f**:**2a**) at 70 ºC for one hour in $CDCl_3$. (c) $^{13}C\{^{1}H\}$ NMR spectrum of compound **1f** and styrene oxide **2a**, in a molar ratio 1:2 (**1f**:**2a**) at 70 ºC for one hour in $CDCl_3$. (**d**) $^{13}C\{^{1}H\}$ NMR spectrum of compound **1f** and styrene oxide **2a**, in a molar ratio 1:4 (**1f**:**2a**) at 70 ºC for one hour in $CDCl_3$.

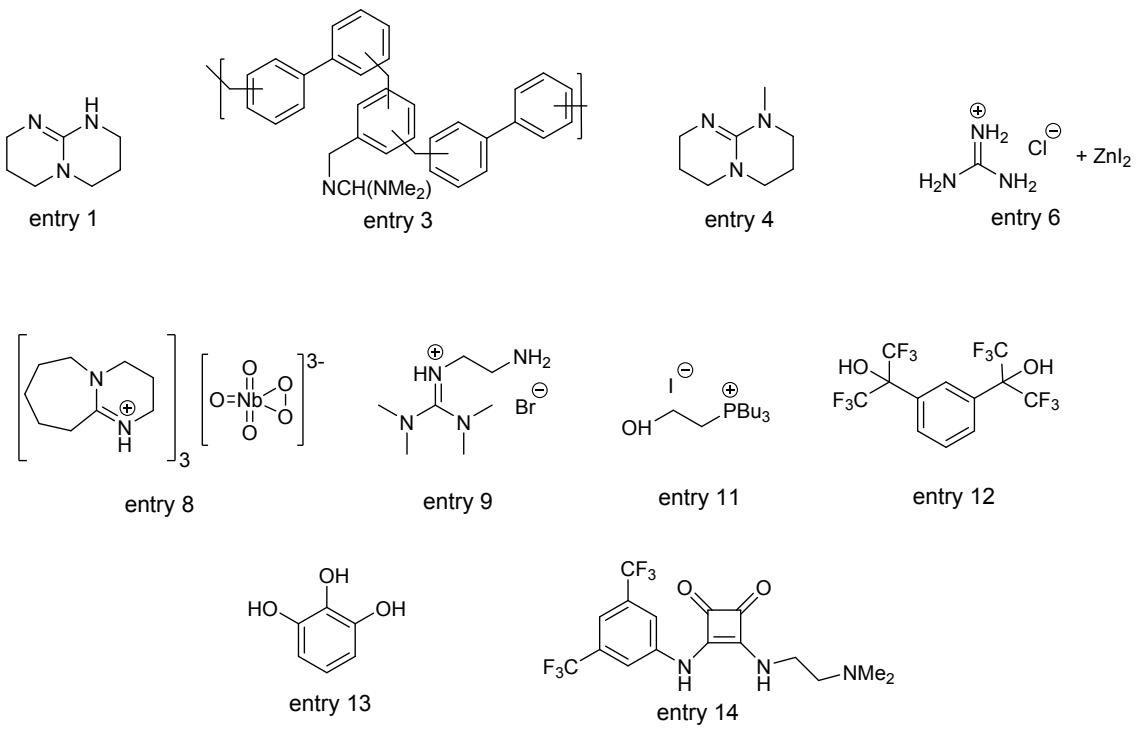


Figure S7. Structure of the different organocatalysts employed in the comparison of catalytic results (Table 4 on the Main Article)

NMR of cyclic carbonates

Styrene carbonate (3a): Obtained as a white solid. (210.6 mg, 88 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.43–7.47 (m, 3H, ArH), 7.32–7.36 (m, 2H, ArH), 5.66 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, PhCHO), 4.79 (t, $^{3}J_{HH}$ =8.5 Hz, 1H, OCH_2), 4.32 ppm (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, OCH_2); $^{13}C\{^{1}H\}$ NMR (100 MHz, CDCl3, 298 K): δ = 155.1, 136.1, 129.9, 129.4, 126.1, 78.2, 71.4 ppm.

Propylene carbonate (3b): Obtained as a colourless liquid (159.3 mg, 94 %); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 4.79–4.88 (m, 1H, OCH), 4.53 (t, , $^{3}J_{HH}$ = 8.0 Hz, OCH_2), 4.00 (t, $^{3}J_{HH}$ = 7.5 Hz, OCH_2), 1.46 ppm (d, , $^{3}J_{HH}$ = 6.5 Hz, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 155.0, 73.6, 70.6, 19.4 ppm.

1,2-Butylene carbonate (3c): Obtained as a colourless liquid (179.3 mg, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 4.62–4.70 (m, 1H, OCH), 4.52 (t, $^{3}J_{HH}$ = 8.5 Hz, 1H, OCH_2), 4.08 (t, $^{3}J_{HH}$ = 8.5 Hz, 1H, OCH_2), 1.70–1.86 (m, 2H, CH_2), 1.03 ppm (t, $^{3}J_{HH}$ = 7.5 Hz, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 155.2, 78.1, 69.1, 27.0, 8.6 ppm.

1,2-Hexylene carbonate (3d): Obtained as a colourless liquid (215.4 mg, 90 %); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 4.65–4.73 (m, 1H, OCH), 4.52 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, OCH_2), 4.06 (dd, $^{3}J_{HH}$ = 8.5, 7.0 Hz, 1H, OCH_2), 1.76–1.86 (m, 1H, CH_2), 1.63–1.73 (m, 1H, CH_2), 1.31–1.49 (m, 4H, $2OCH_2$), 0.92 ppm (t, $^{3}J_{HH}$ = 7.0 Hz, 3H, CH_3); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 155.0, 77.0, 69.4, 33.5, 26.4, 22.2, 13.8 ppm.

Glycerol carbonate (3e): Obtained as a colourless liquid (178.4 mg, 91 %); ^{1}H NMR (400 MHz, $[D_6]$DMSO, 298 K): δ = 5.23 (t, $^{3}J_{HH}$ = 5.5 Hz, 1H, OH), 4.74–4.80 (m, 1H, OCH), 4.47 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, CH_2O), 4.26 (dd, $^{3}J_{HH}$ = 8.0, 5.5 Hz, 1H, CH_2O), 3.60–3.68 (m, 1H, CH_2OH), 3.45–3.52 ppm (m, 1H, CH_2OH); $^{13}C\{^{1}H\}$ NMR (100 MHz, $[D_6]$DMSO, 298 K): δ = 155.6, 77.6, 66.3, 61.0 ppm.

3-Phenoxyproplylene carbonate (3f): Obtained as a white solid. (268.3 mg, 83 %); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.27–7.33 (m, 2H, 2OArH), 7.02 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, ArH), 6.88–6.94 (m, 2H, 2OArH), 4.99–5.06 (m, 1H, OCH), 4.61 (t, $^{3}J_{HH}$ = 8.5 Hz, 1H, OCH_2), 4.55 (dd, $^{3}J_{HH}$ = 9.0, 6.0 Hz, 1H, OCH_2), 4.24 (dd, $^{3}J_{HH}$ = 10.5, 4.5 Hz, 1H, CH_2OPh), 4.15 ppm (dd, $^{3}J_{HH}$ = 10.5, 3.5 Hz, 1H, CH_2OPh); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 157.8, 154.6, 129.7, 122.0, 114.6, 74.1, 66.9, 66.2 ppm.

3-Chloropropylene carbonate (3g): Obtained as a colourless liquid. (210.8 mg, 93 %); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 4.92–5.01 (m, 1H, OCH), 4.59 (t, $^{3}J_{HH}$ = 8.5 Hz, 1H, CH_2Cl), 4.42 (dd, $^{3}J_{HH}$ = 8.5, 5.5 Hz, 1H, CH_2Cl), 3.78 (dd, $^{3}J_{HH}$ = 12.0, 5.5 Hz, 1H, CH_2O), 3.74 ppm (dd, $^{3}J_{HH}$ = 12.5, 3.5 Hz, CH_2O); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.7, 74.8, 67.5, 44.2 ppm.

4-Chlorostyrene carbonate (3h): Obtained as a white solid. (300.0 mg, 91 %); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.36–7.42 (m, 2H, ArH), 7.27–7.33 (m, 2H, ArH), 5.65 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, OCH), 4.79 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, OCH), 4.29 ppm (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, OCH_2); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.5, 135.8, 134.3, 129.4, 127.3, 77.2, 71.0 ppm.

4-Bromostyrene carbonate (3i): Obtained as a white solid. (360.5 mg, 89 %) ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 7.31–7.36 (m, 2H, ArH), 7.20–7.26 (m, 2H, ArH), 5.62 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, OCH), 4.77 (t, $^{3}J_{HH}$ = 8.0 Hz, 1H, OCH_2), 4.34 ppm (dd, $^{3}J_{HH}$ = 8.8, 7.6 Hz, 1H, OCH_2); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.5, 135.7, 134.3, 129.5, 127.3, 77.2, 70.0 ppm.

4-((2,2,3,3-Tetrafluoropropoxy)methyl)-1,3-dioxolan-2-one (3j). Obtained as a colourless liquid (350.6 mg, 91 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 5.83 (tt, $^{3}J_{HH}$ = 52.8, 4.8 Hz, 1H, $CHCF_2$), 4.76–4.81 (m, 1H, OCH), 4.45 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, OCH_2), 4.29 (dd, $^{3}J_{HH}$ = 7.6, 6.0 Hz, 1H, OCH_2), 3.87 (dt, $^{3}J_{HH}$ = 12.8, 2.0 Hz, 2H OCH_2CF_2), 3.80 (dd, $^{3}J_{HH}$ = 11.2, 3,2 Hz, 1H, O*CH*$_2$CH), 3.70 ppm (dd, $^{3}J_{HH}$ = 11.2, 4.0 Hz, 1H, O*CH*$_2$CH); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 159.9 (C=O), 113.9 (tt, $^{3}J_{CF}$ = 994.0, 107.6 Hz, CH*CF*$_2$), 108.2 (tt, $^{3}J_{CF}$ = 991.6, 138.8 Hz, CF_2), 77.4 (CH), 70,4 (CH_2), 67.4 (t, $^{3}J_{CF}$ = 112.4 Hz, CF_2*CH*$_2$), 64.9 ppm (CH_2). ^{19}F NMR (400 MHz, $CDCl_3$, 298 K): δ = (−139.3)–(−139.4) (m, 2F), (−125.1)–(−125.0) ppm (m, 2F).

4-(((2,2,3,3,4,4,5,5-Octafluoropentyl)oxy)methyl)-1,3-dioxolan- 2-one (3k). Obtained as a colourless liquid. (512.8 mg, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 6.01 (tt, $^{3}J_{HH}$ = 52.0, 5.6 Hz, 1H, CHF_2), 4.75–4.83 (m, 1H, OCH), 4.46 (t, $^{3}J_{HH}$ = 8.8 Hz, 1H, OCH_2), 4.31 (dd, $^{3}J_{HH}$ = 8.4, 6.0 Hz, 1H, OCH_2), 3.90–4.10 (m, 2H, OCH_2CF_2), 3.83 (dd, $^{3}J_{HH}$ = 11.2, 3,2 Hz, 1H, O*CH*$_2$CH), 3.75 ppm (dd, $^{3}J_{HH}$ = 11.2, 3.6 Hz, 1H, O*CH*$_2$CH); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 153.8 (C=O), 103.9–117.2 (m, 3 x CF_2), 106.7 (tt, $^{3}J_{CF}$ = 1009.2, 123.2 Hz, $CHCF_2$), 73.8 (CH), 70,6 (CH_2), 67.3 (t, $^{3}J_{CF}$ = 102.8 Hz, CH_2), 64.8 ppm (CH_2).^{19}F NMR (400 MHz, $CDCl_3$, 298 K): δ = (−137.6)–(−136.7) (m, 2F), (−130.4)–(−129.5) (m, 2F), (−125.6)–(−125.7) (m, 2F), (−120.0)– (−120.1) ppm (m, 2F).

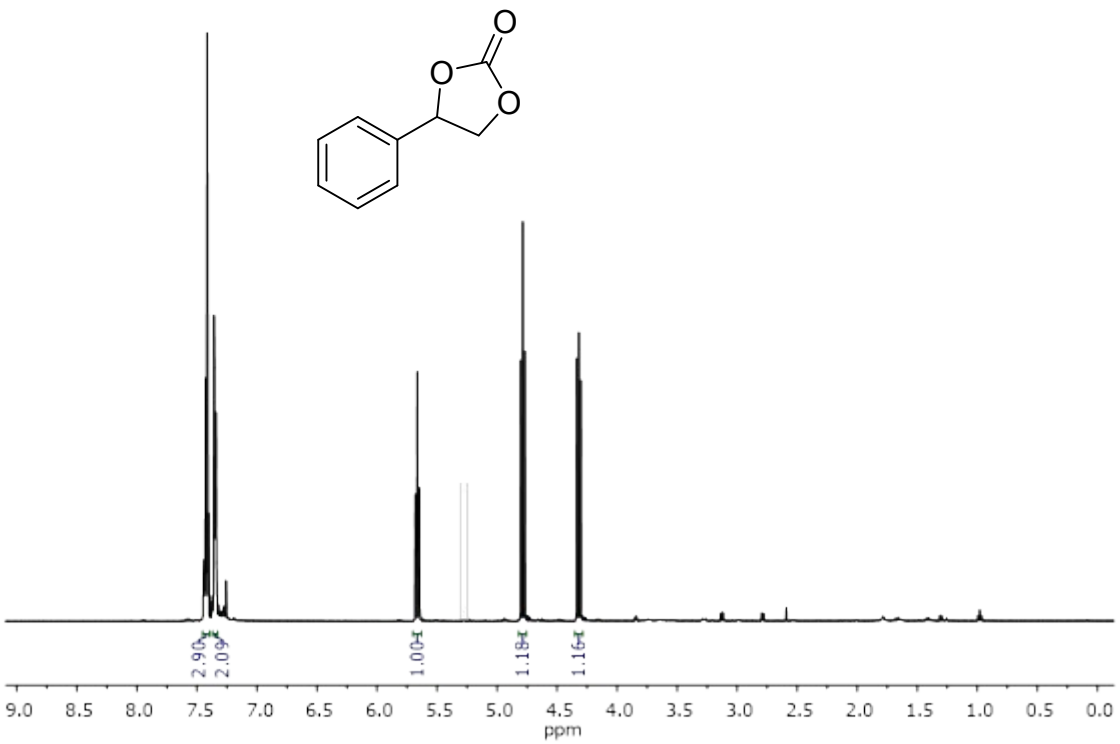
***cis*-1,2-Cyclohexene carbonate** (**5a**): Obtained as a white solid. (191.9 mg, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 4.71–4.64 (m, 2H, CHO), 1.94–1.85 (m, 4H, 2 x CH_2CHO), 1.68–1.57 (m, 2H, CH_2), 1.46–1.37 ppm (m, 2H, CH_2); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 155.3, 75.7, 26.8, 19.1 ppm.

***cis*-1,2-Cyclopentene carbonate** (**5b**): Obtained as a white solid. (163.3 mg, 77 %); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 5.12–5.08 (m, 2H, CHO), 2.19–2.12 (m, 2H, CH_2), 1.85–1.73 (m, 2H, CH_2), 1.71–1.61 ppm (m, 2H, CH_2); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 155.4, 81.8, 33.1, 21.6.

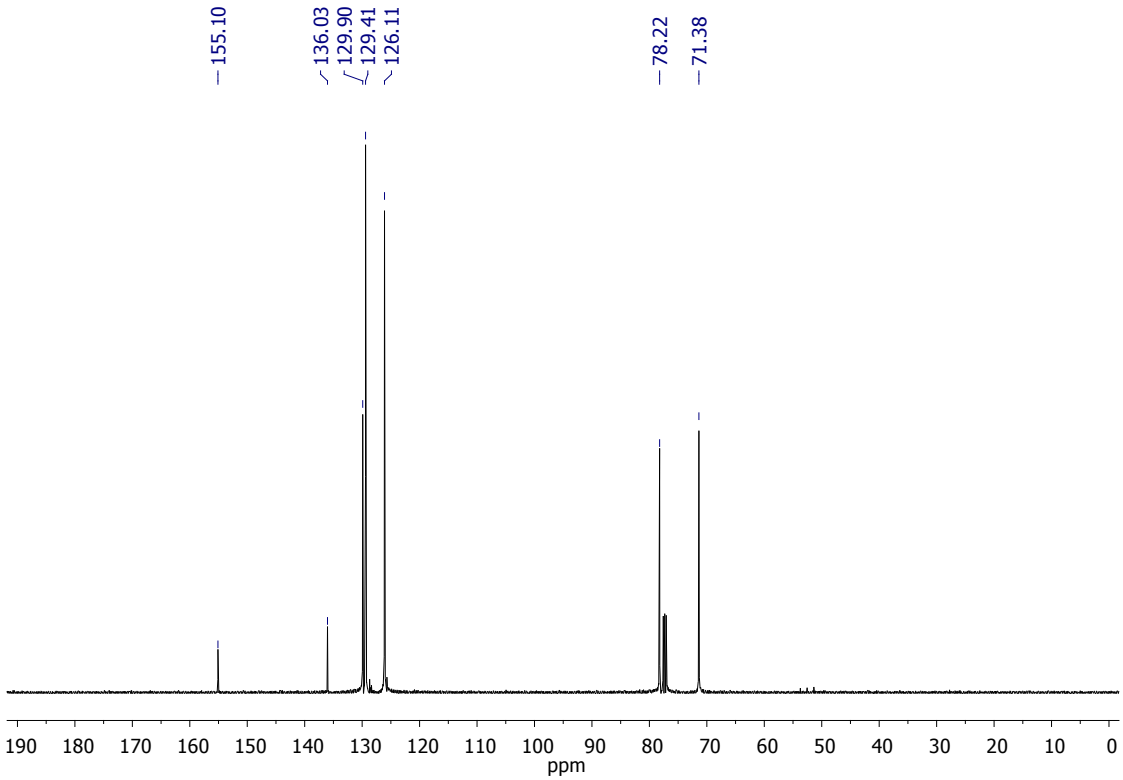
***cis*-2,3-Butene carbonate** (**5c**): Obtained colourless liquid in a 94:6 mixture of *cis*- and *trans*-isomers (114.3 mg, 59 %); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 4.85–4.77 (m, 2H, CH_{cys}), 4.34–4.28 (m, CH_{trans}), 1.43 (d, J = 6.2 Hz, CH_{3trans}), 1.35 ppm (d, J = 6.2 Hz, 6H, CH_{3cis}); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.6, 79.9 (*trans*), 76.1, 18.3 (*trans*), 14.5 ppm.

***trans*-2,3-Butene carbonate** (**4d**): Obtained as a white solid (128.6 mg, 67 %); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ = 4.86–4.79 (m, CH_{cis}), 4.36–4.28 (m, 2H, CH_{trans}), 1.44 (d, J = 5.9 Hz, 6H, CH_{3trans}), 1.35 ppm (d, J = 5.9 Hz, CH_{3cis}); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 298 K): δ = 154.5, 79.9, 18.4, 14.4 (*cis*) ppm.

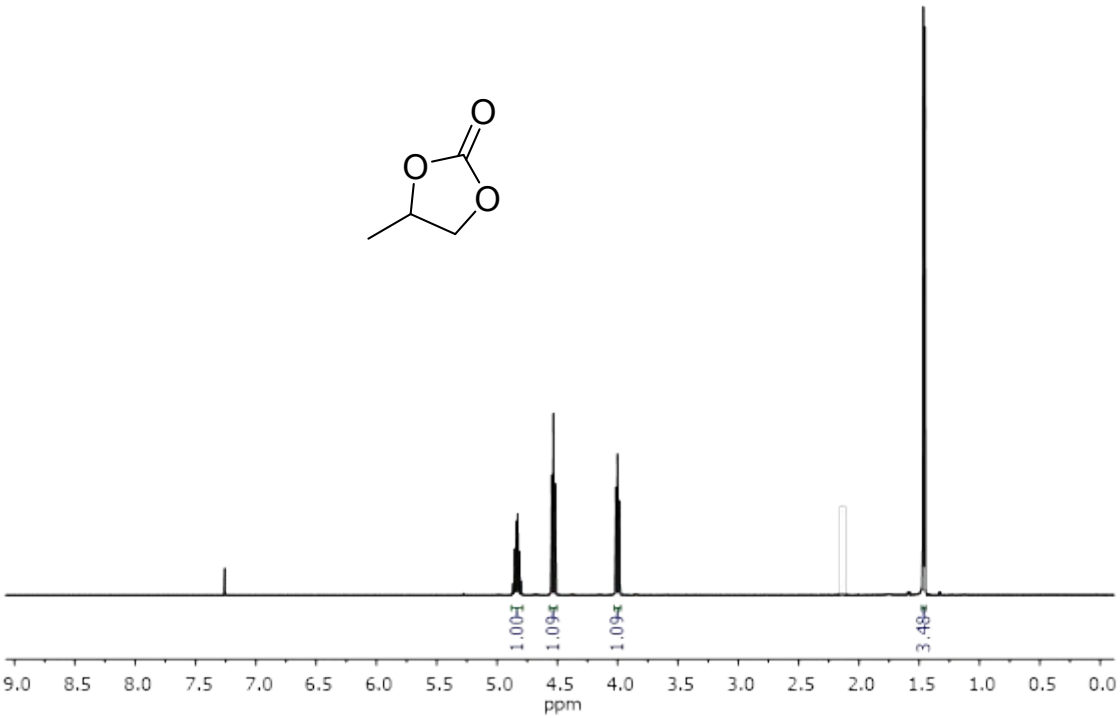
^{1}H-NMR of styene carbonate (**3a**) in $CDCl_3$



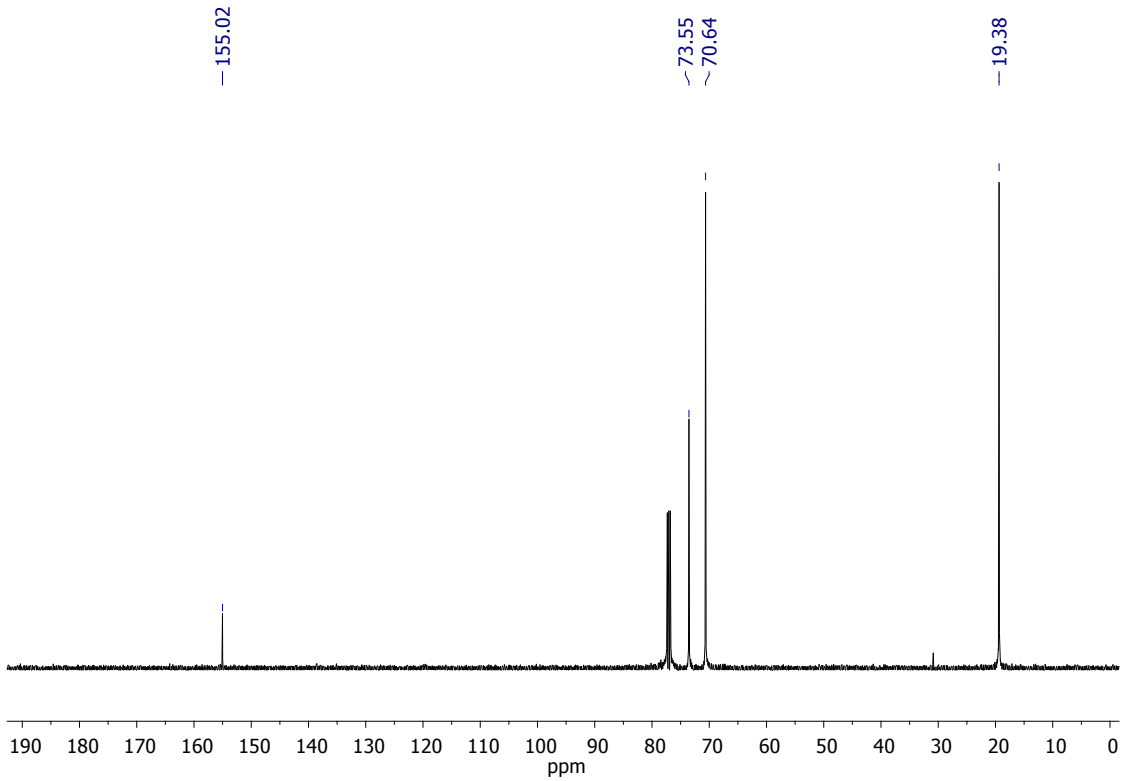
^{13}C-{^{1}H}-NMR of styene carbonate (**3a**) in $CDCl_3$



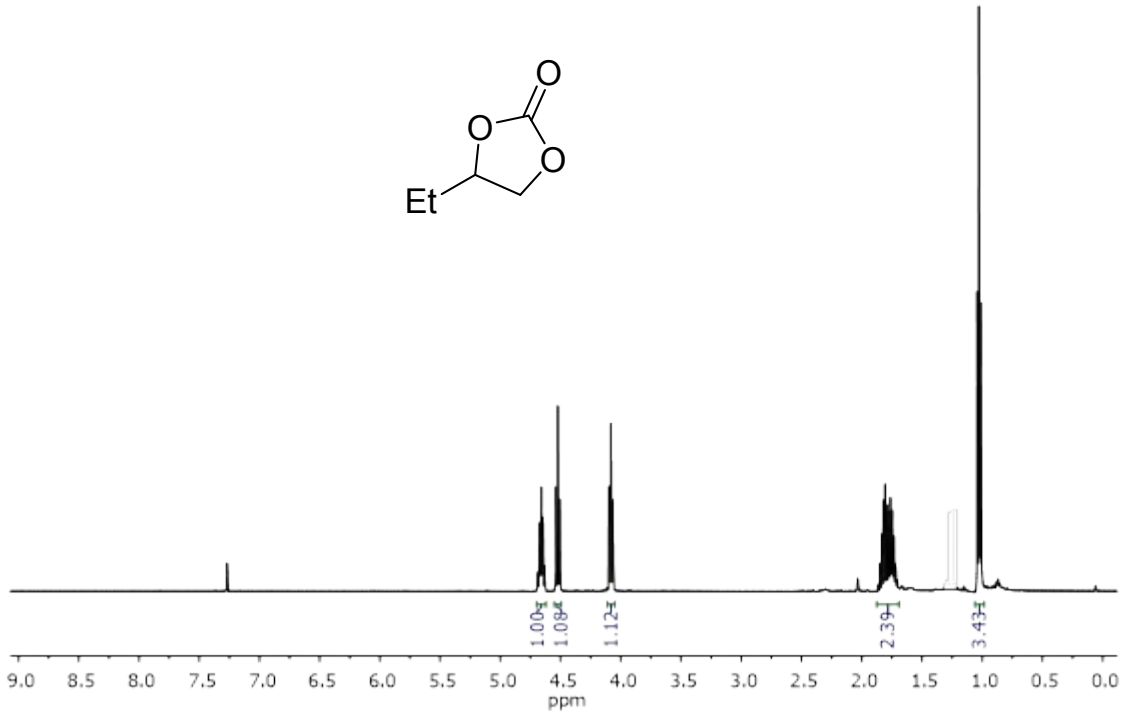
^{1}H-NMR of propylene carbonate (**3b**) in $CDCl_3$



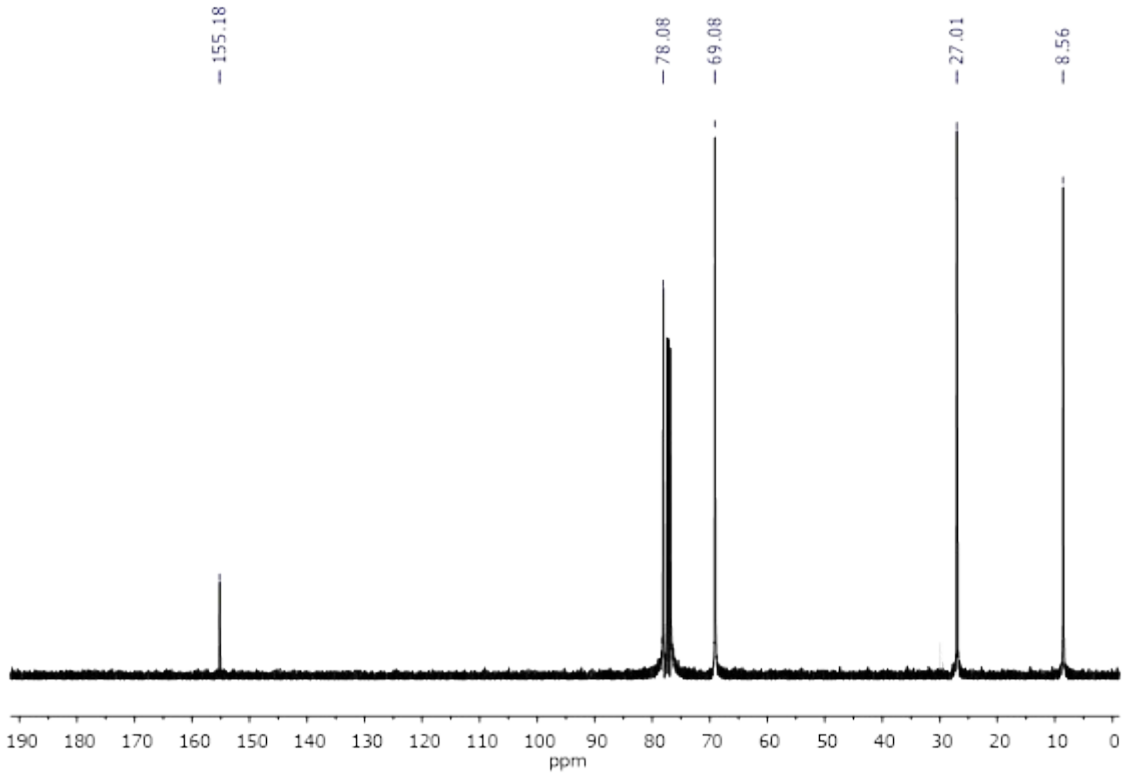
^{13}C-{^{1}H}-NMR of propylene carbonate (**3b**) in $CDCl_3$



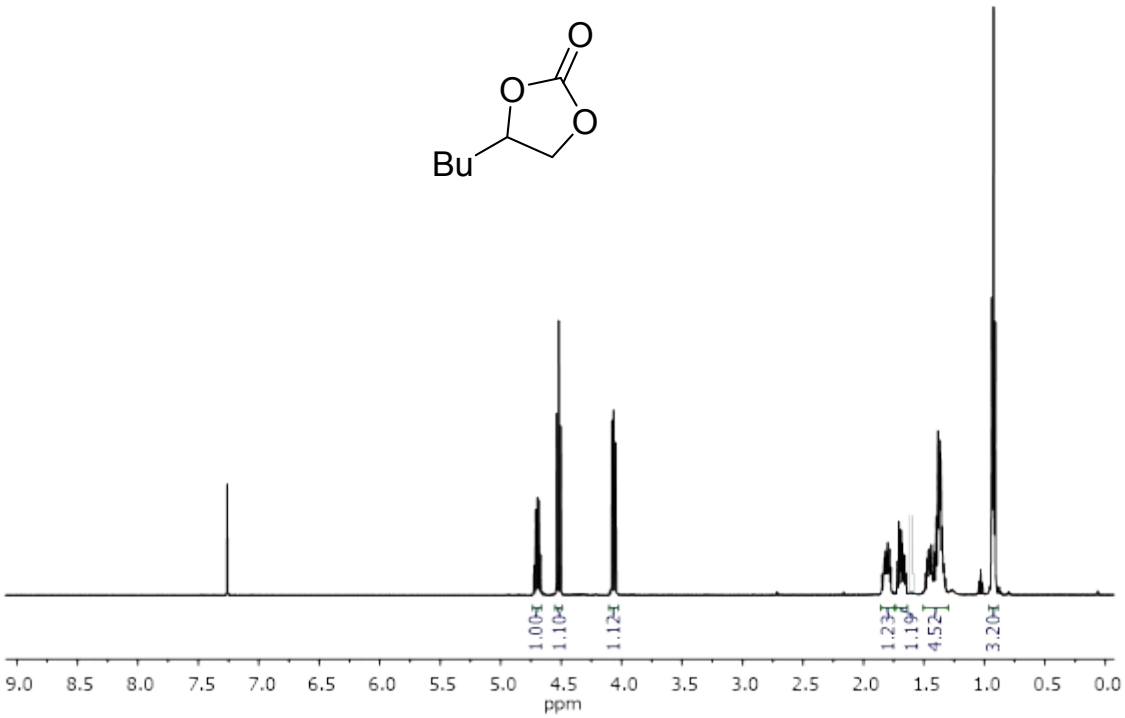
^{1}H-NMR of 1,2-butylene carbonate (**3c**) in $CDCl_3$



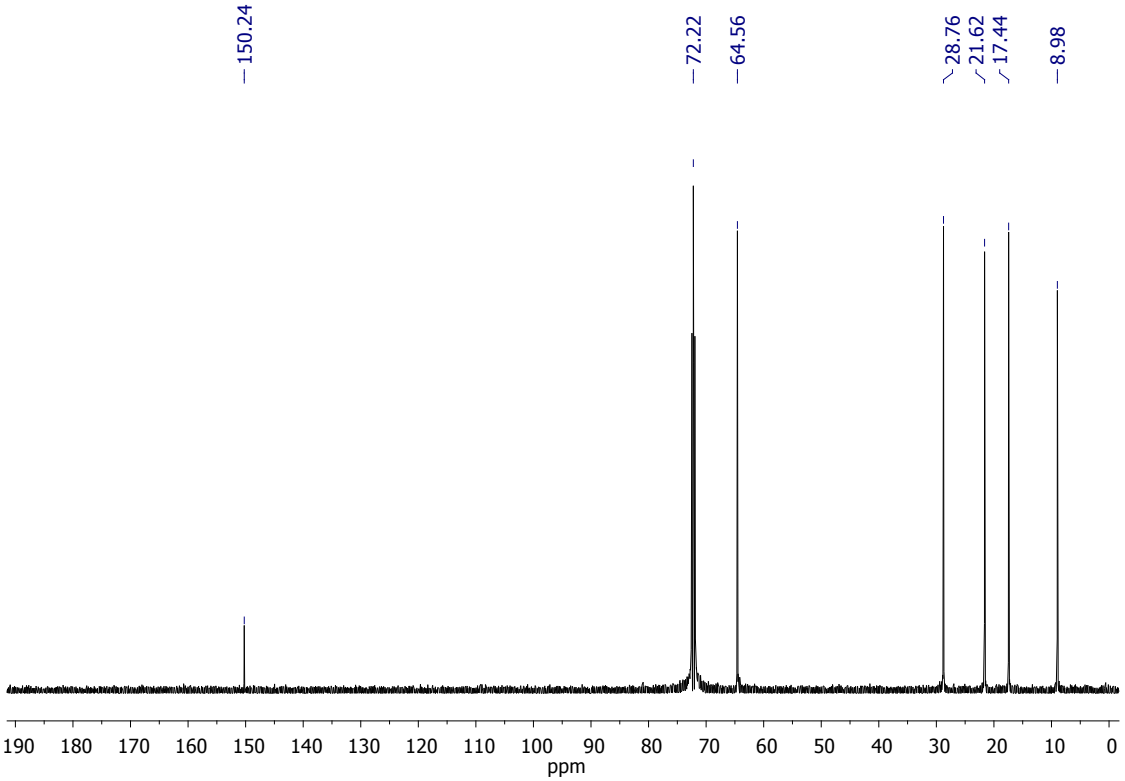
^{13}C-{^{1}H}-NMR of 1,2-butylene carbonate (**3c**) in $CDCl_3$



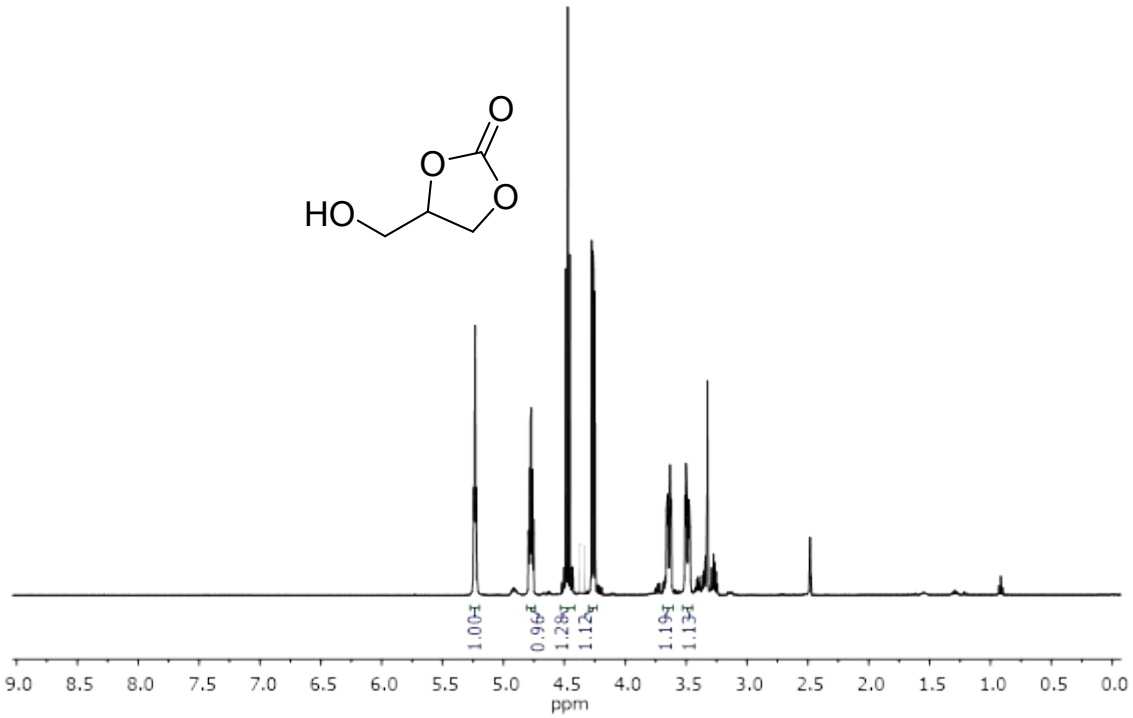
^{1}H-NMR of 1,2-hexylene carbonate (**3d**) in $CDCl_3$



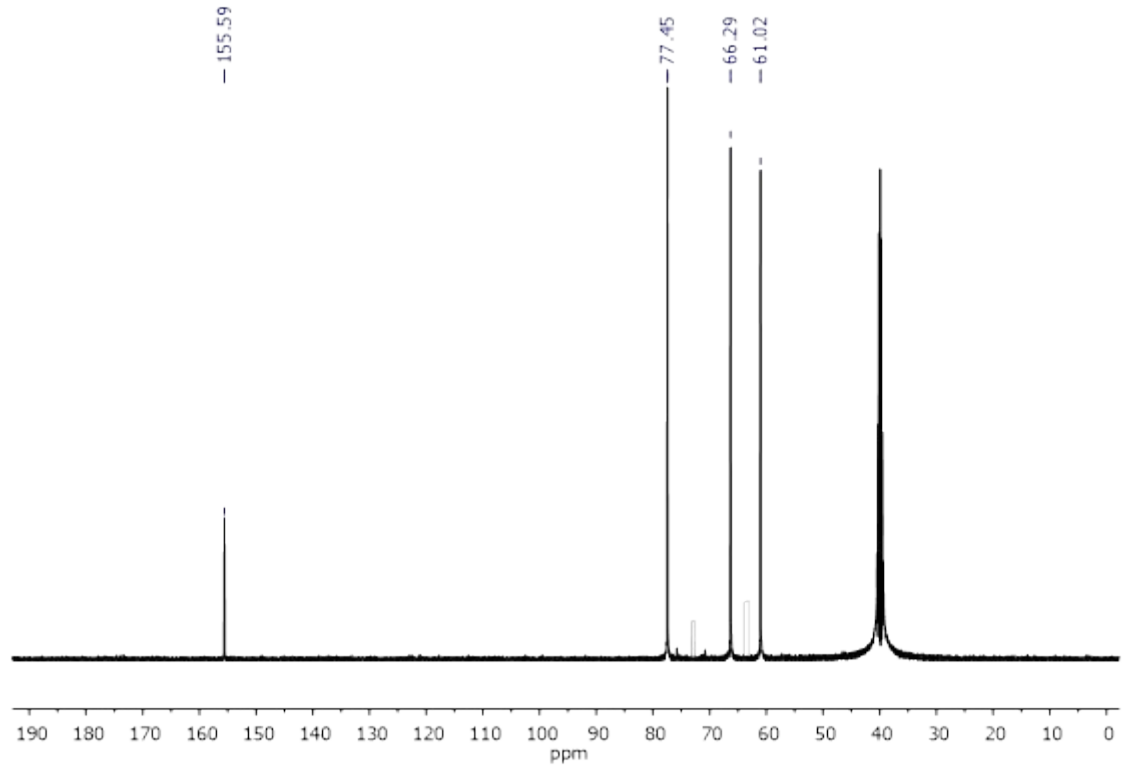
^{13}C-{^{1}H}-NMR of 1,2-hexylene carbonate (**3d**) in $CDCl_3$



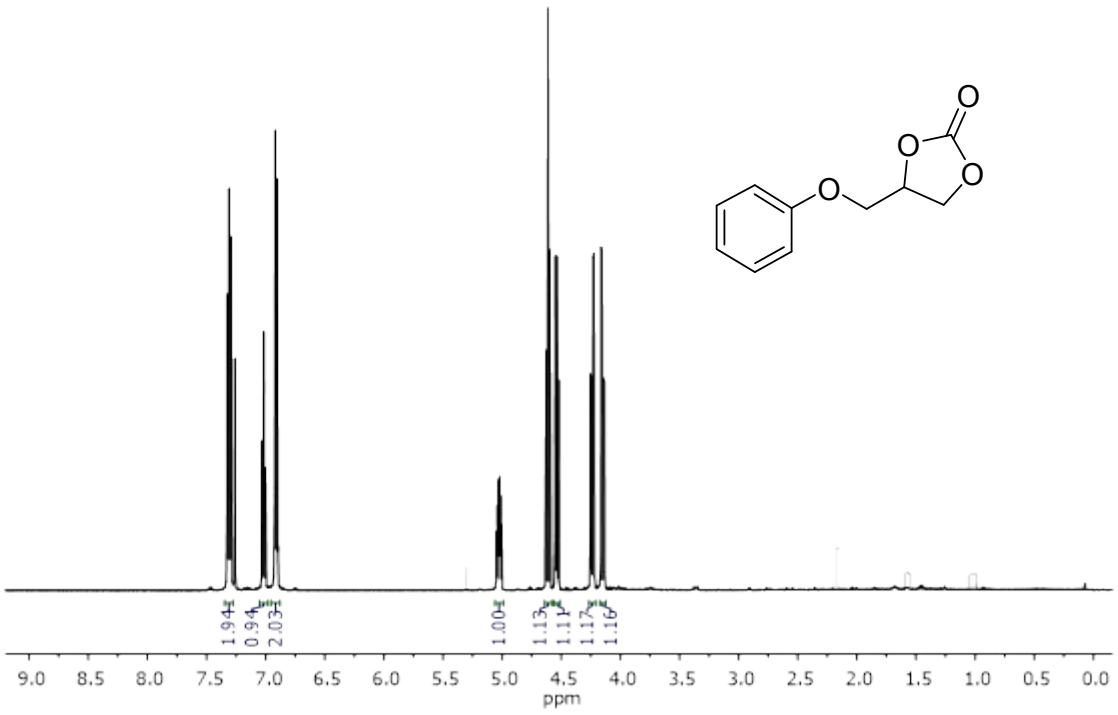
^{1}H-NMR of glycerol carbonate (**3e**) in [D_6]DMSO



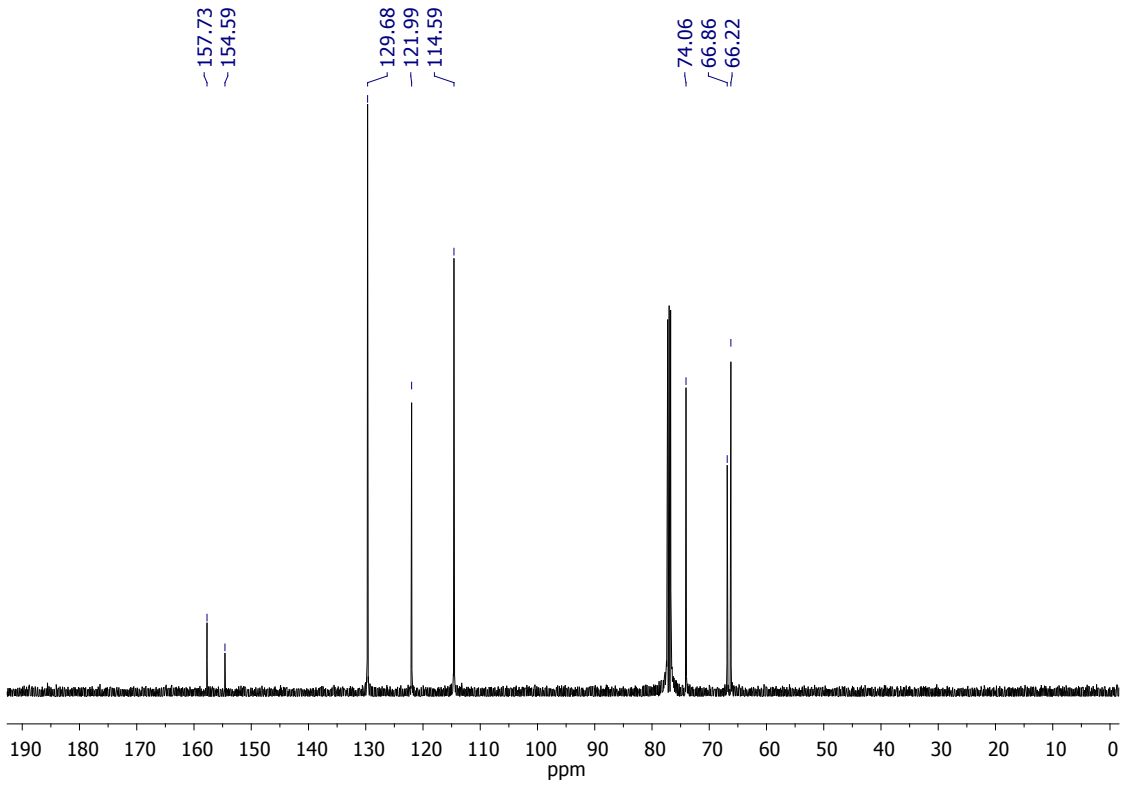
^{13}C-{^{1}H}-NMR of glycerol carbonate (**3e**) in [D_6]DMSO



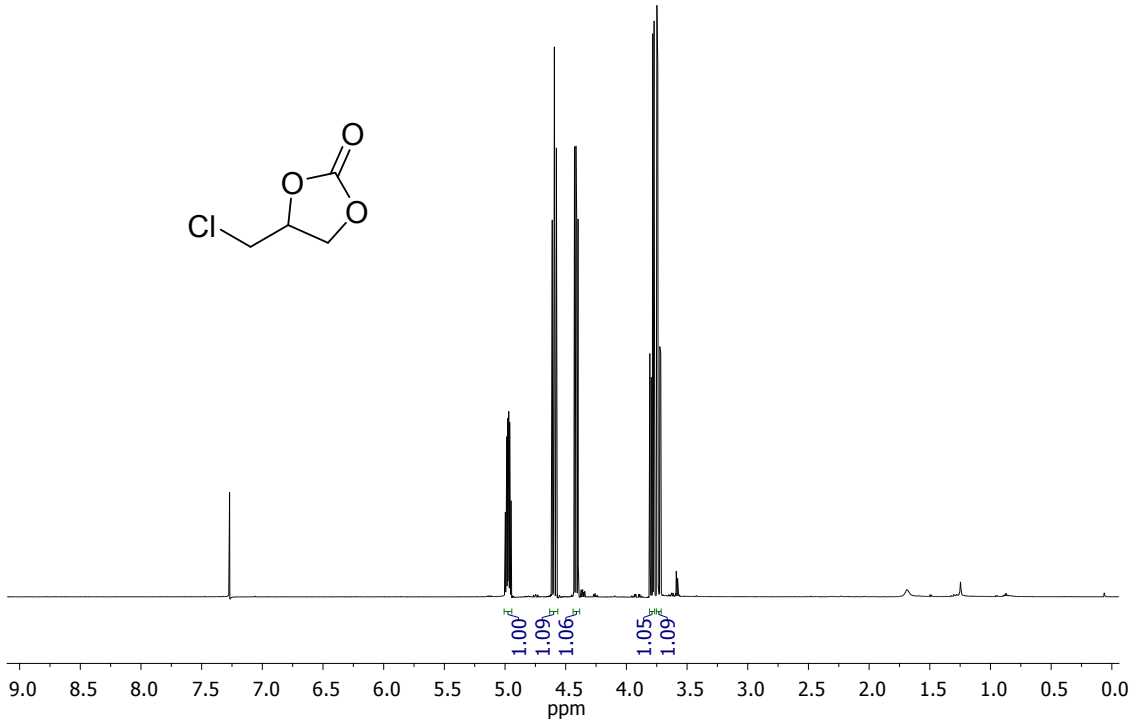
^{1}H-NMR of 3-Phenoxyproplylene carbonate (**3f**) in $CDCl_3$



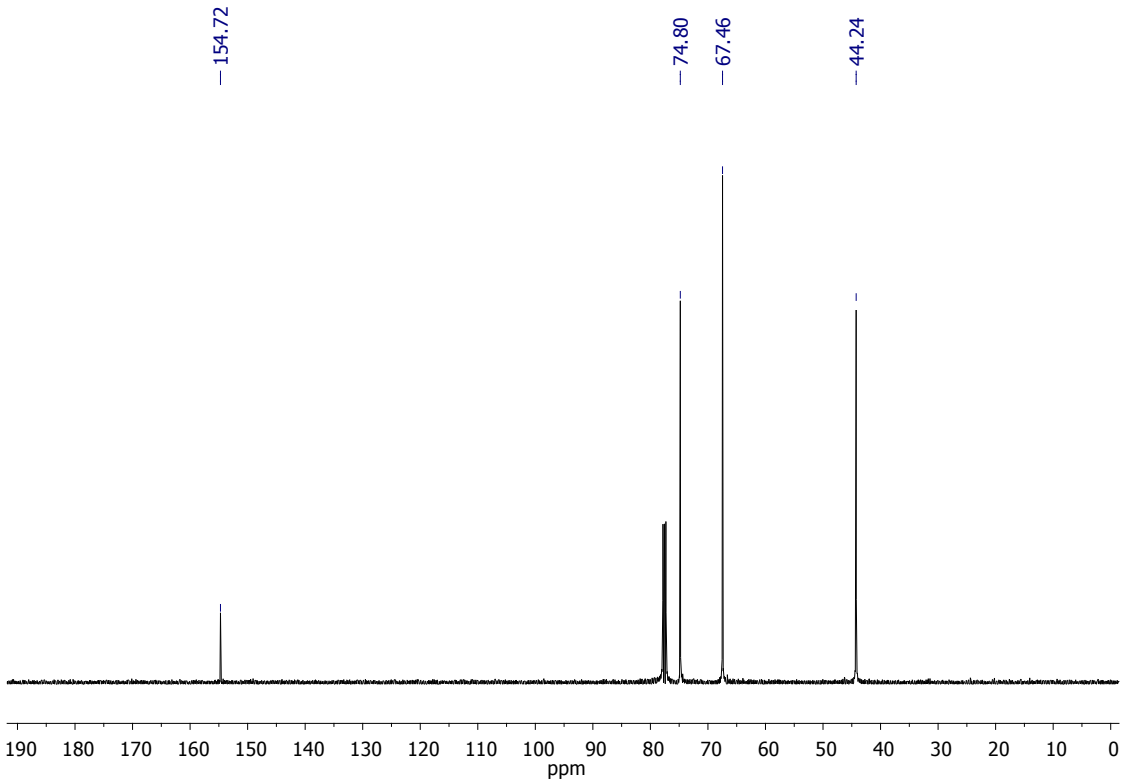
^{13}C-{^{1}H}-NMR of 3-Phenoxyproplylene carbonate (**3f**) in $CDCl_3$



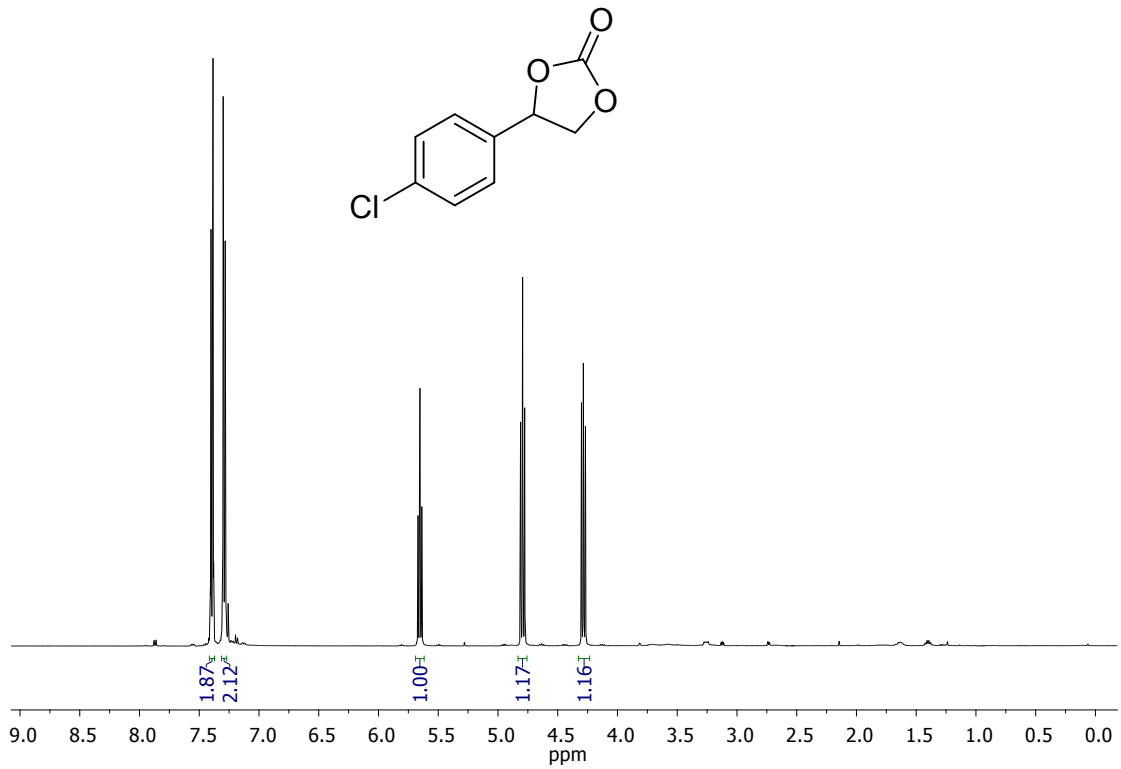
^{1}H-NMR of 3-chloroproplylene carbonate (**3g**) in $CDCl_3$



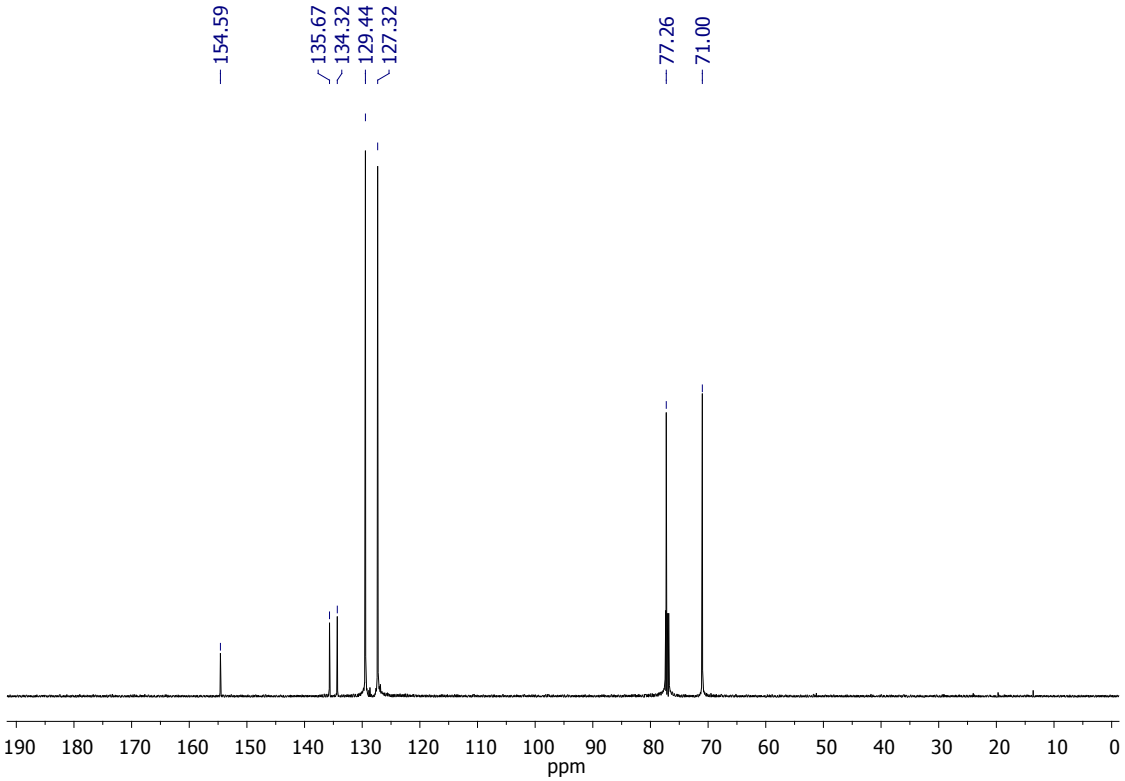
^{13}C-{^{1}H}-NMR of 3-chloroproplylene carbonate (**3g**) in $CDCl_3$



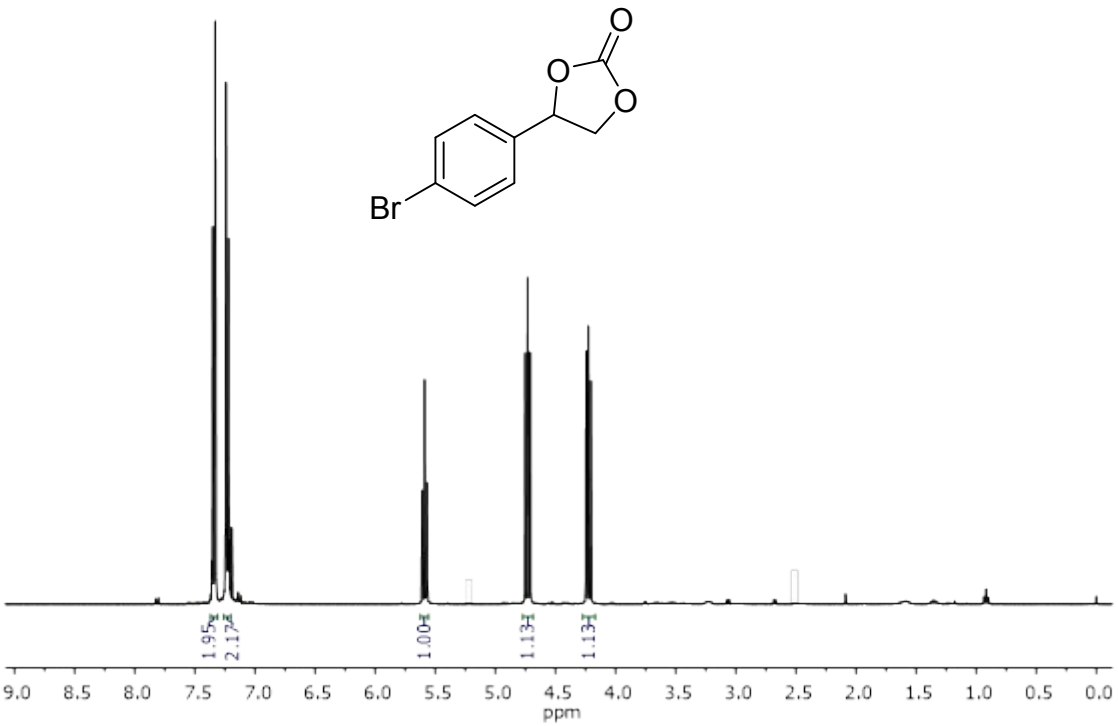
^{1}H-NMR of 4-chlorostyrene carbonate (**3h**) in $CDCl_3$



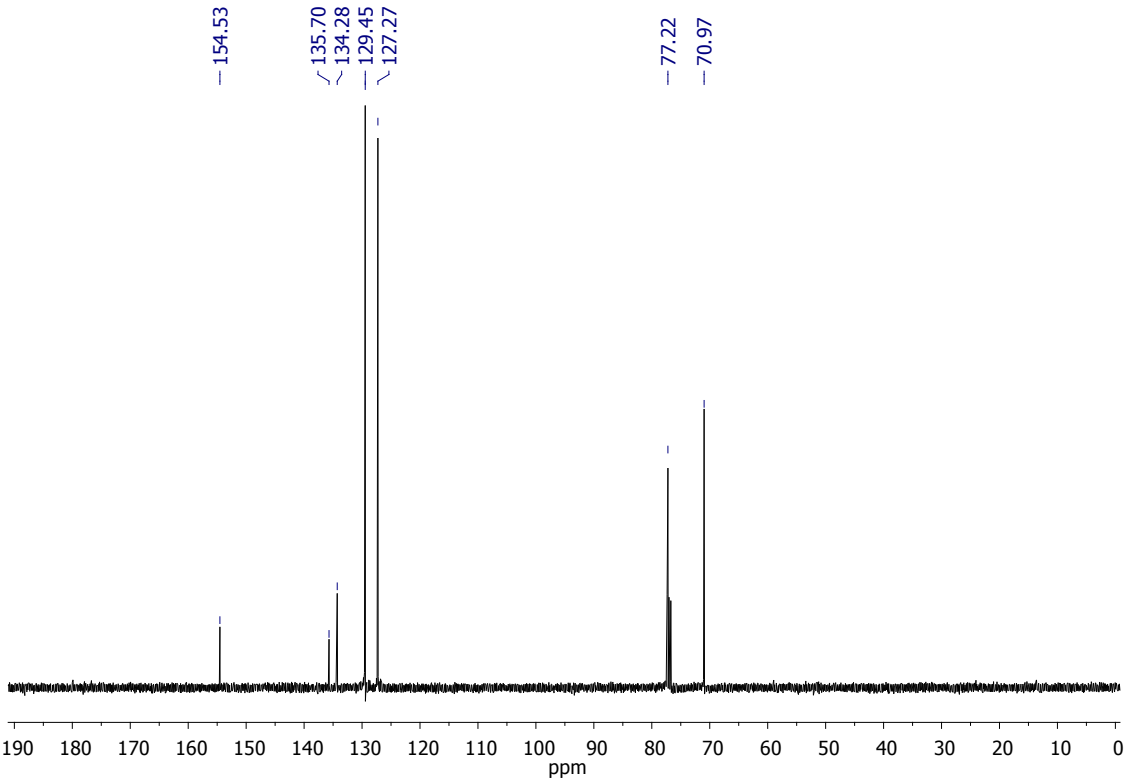
^{13}C-{^{1}H}-NMR of 4-chlorostyrene carbonate (**3h**) in $CDCl_3$



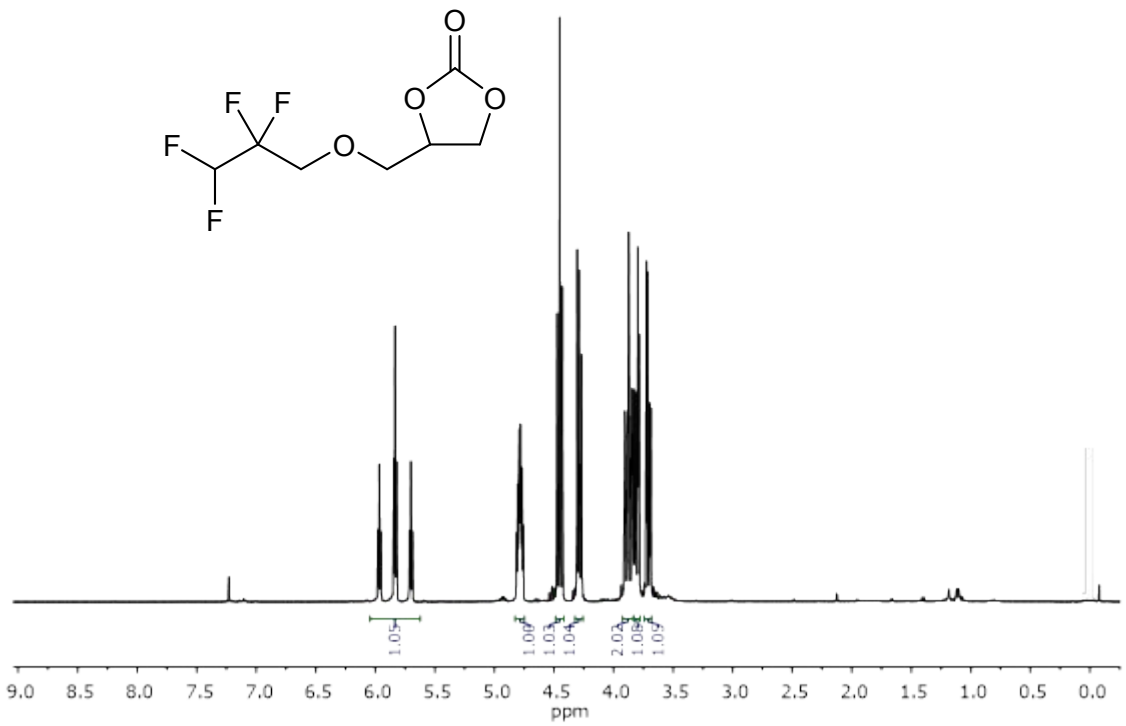
^{1}H-NMR of 4-bromrostyrene carbonate (**3i**) in $CDCl_3$



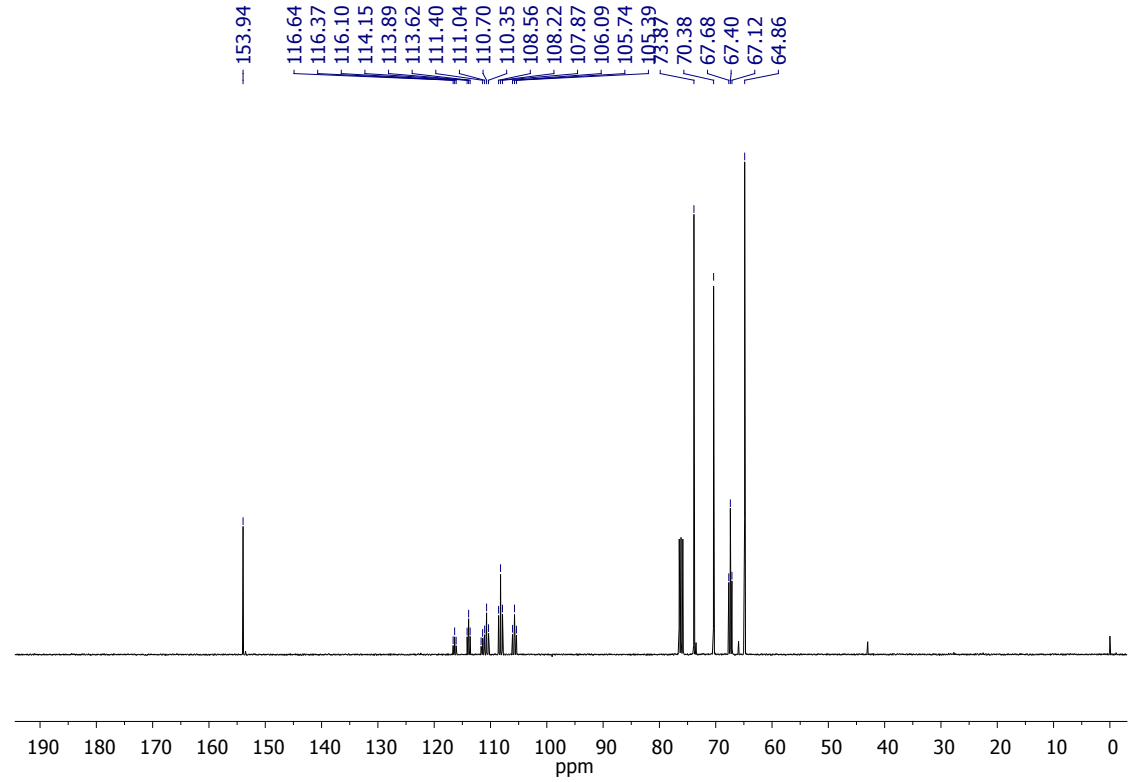
^{13}C-{^{1}H}-NMR of 4-bromorostyrene carbonate (**3i**) in $CDCl_3$



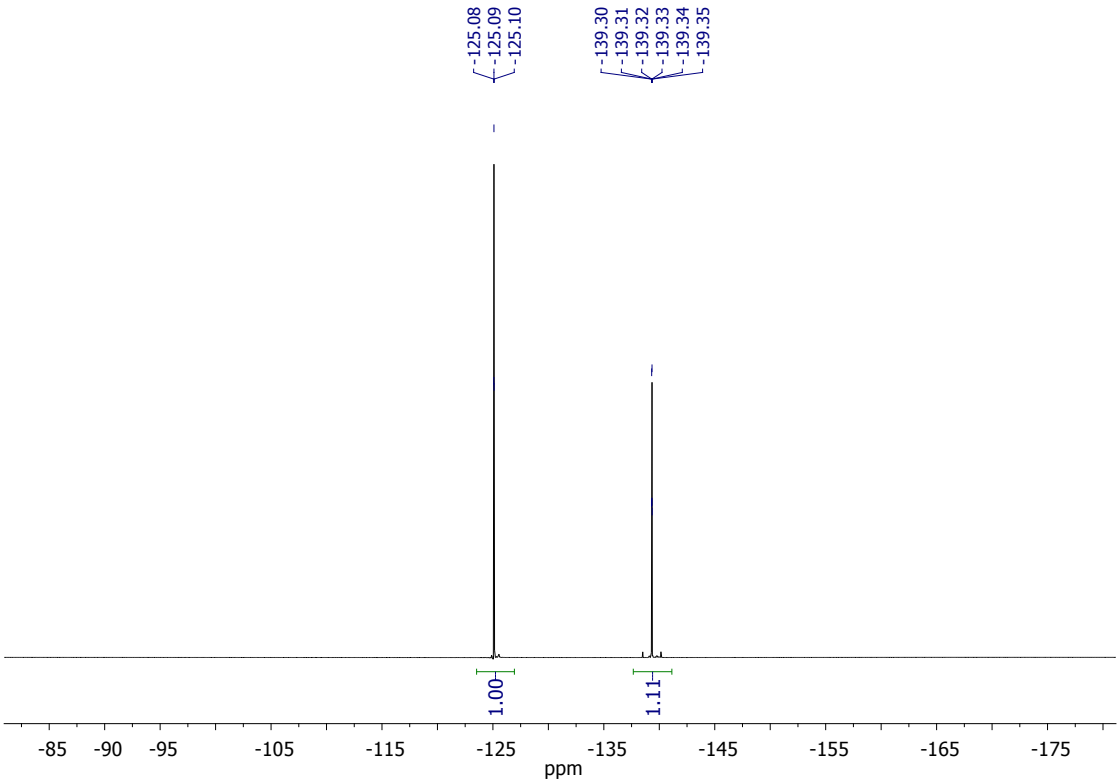
^{1}H-NMR of 4-((2,2,3,3-Tetrafluoropropoxy)methyl)-1,3-dioxolan-2-one (**3j**) in $CDCl_3$



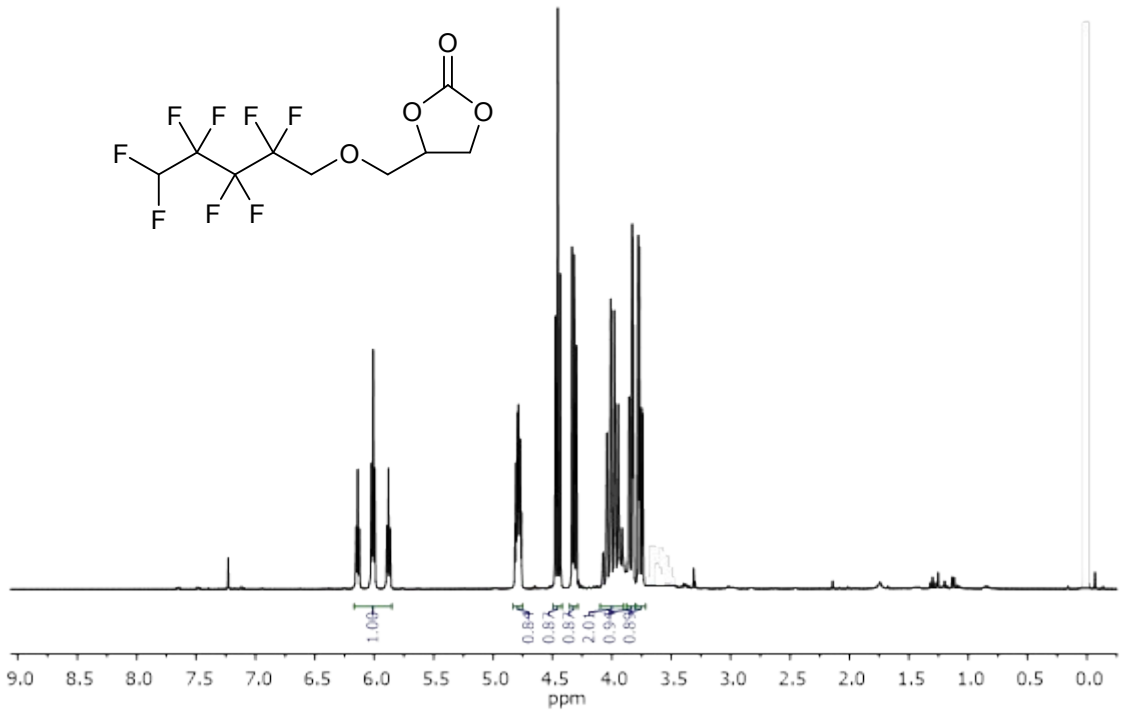
^{13}C-{^{1}H}-NMR of 4-((2,2,3,3-Tetrafluoropropoxy)methyl)-1,3-dioxolan-2-one (**3j**) in $CDCl_3$



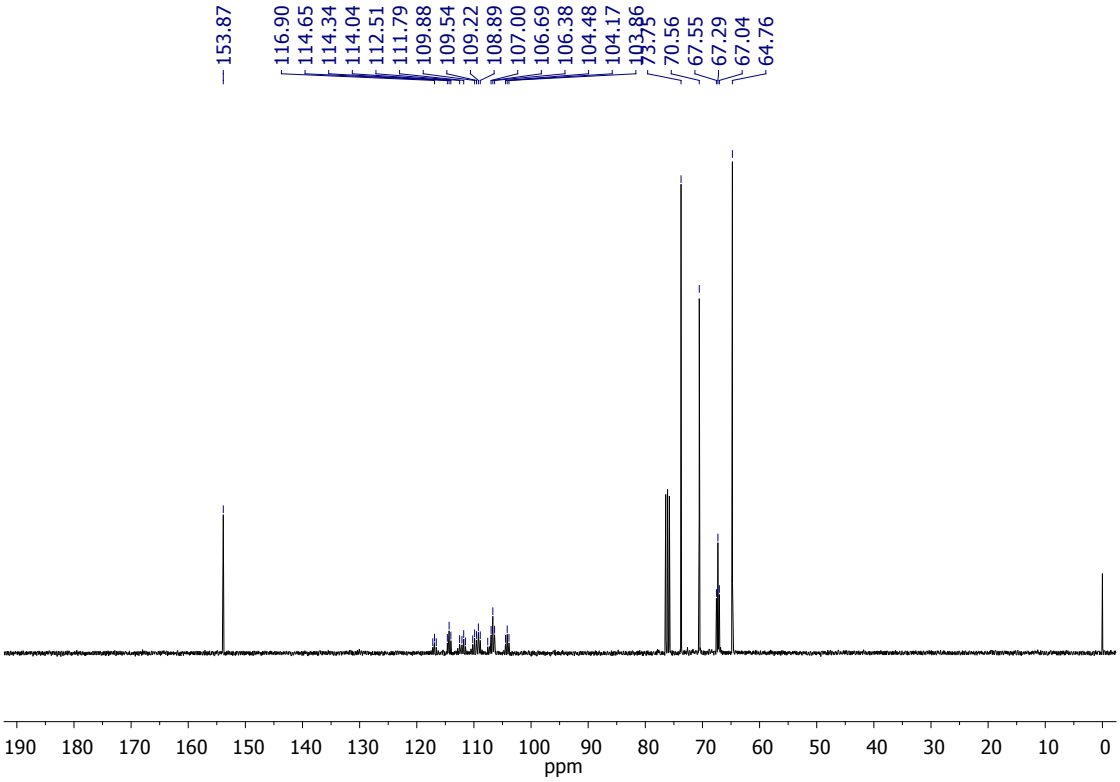
^{19}F-NMR of 4-((2,2,3,3-Tetrafluoropropoxy)methyl)-1,3-dioxolan-2-one (**3j**) in $CDCl_3$



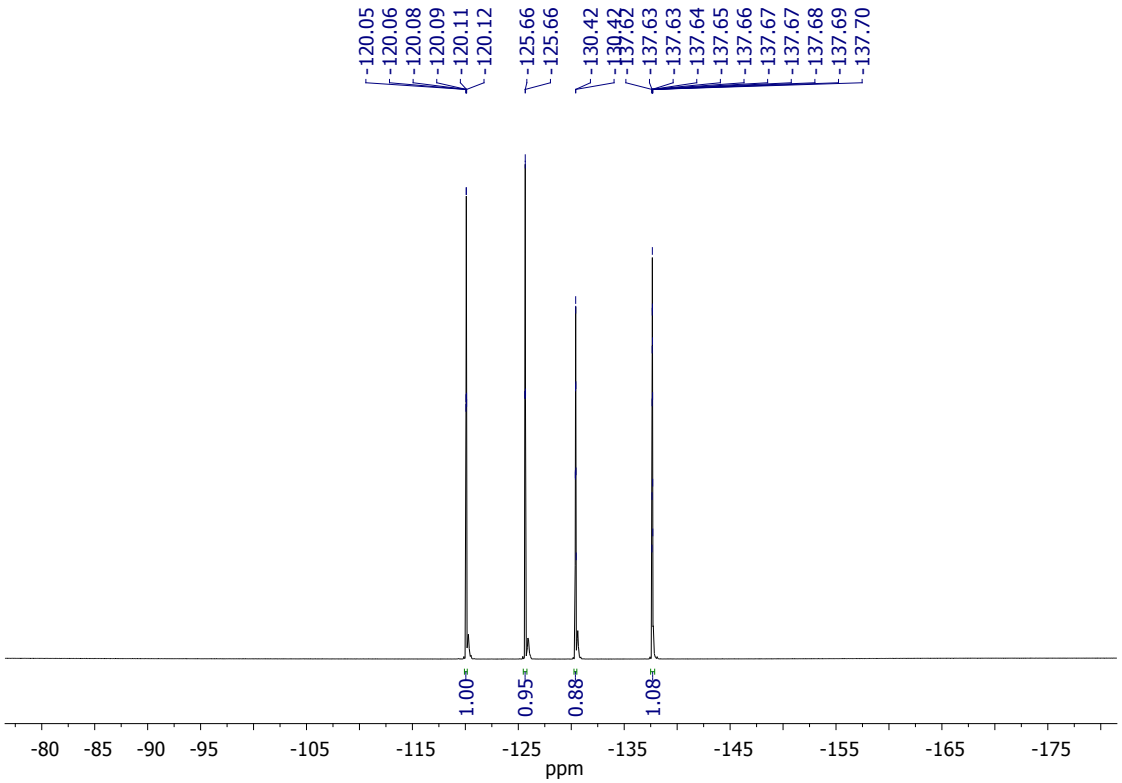
^{1}H-NMR of 4-(((2,2,3,3,4,4,5,5-Octafluoropentyl)oxy)methyl)-1,3-dioxolan- 2-one (**3k**) in $CDCl_3$



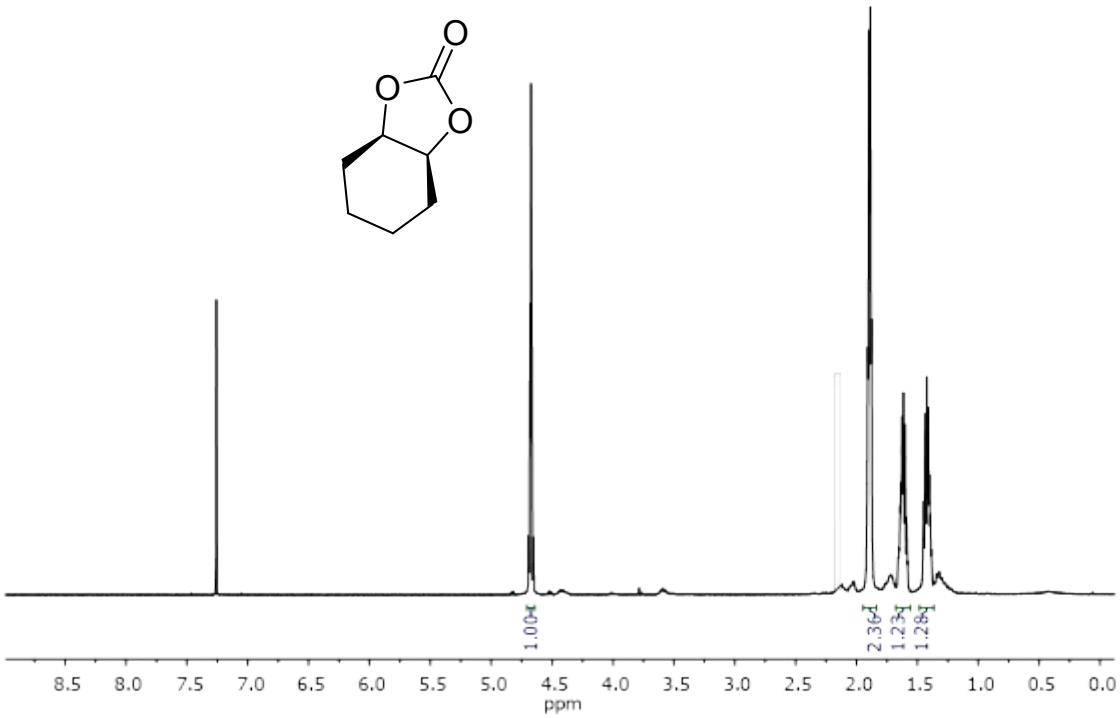
^{13}C-{^{1}H}-NMR of 4-(((2,2,3,3,4,4,5,5-Octafluoropentyl)oxy)methyl)-1,3-dioxolan- 2-one (**3k**) in $CDCl_3$



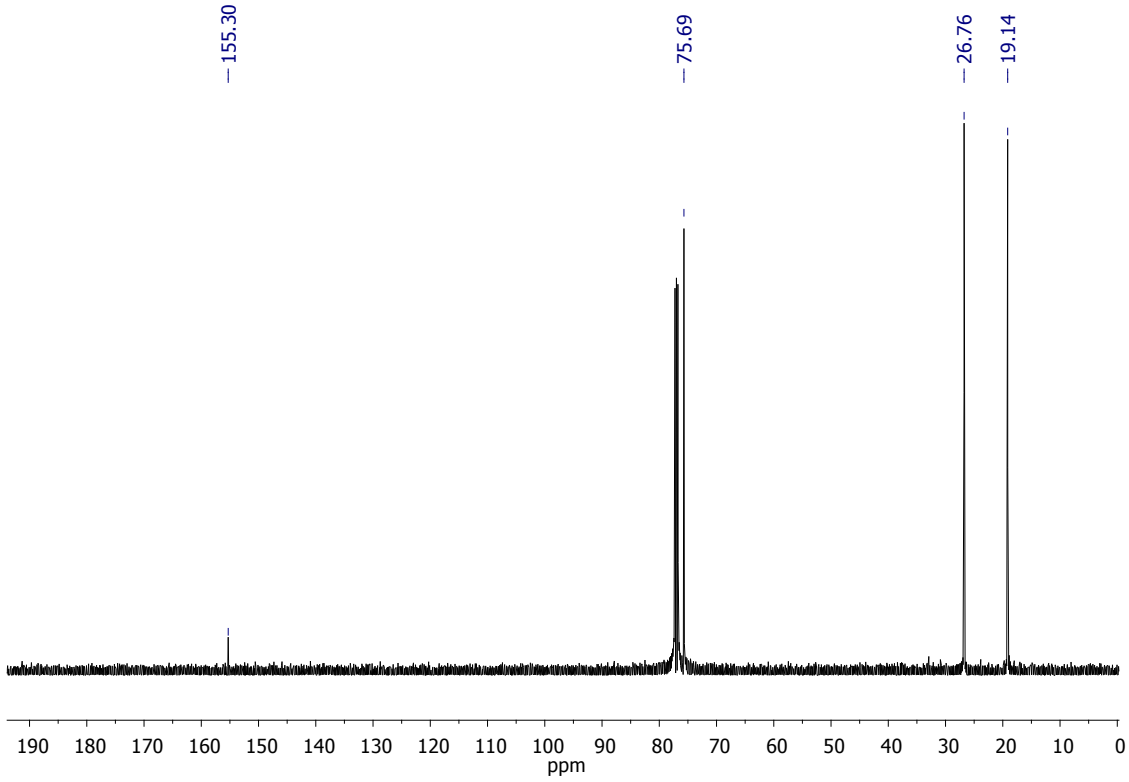
^{19}F-NMR of 4-(((2,2,3,3,4,4,5,5-Octafluoropentyl)oxy)methyl)-1,3-dioxolan- 2-one (**3k**) in $CDCl_3$



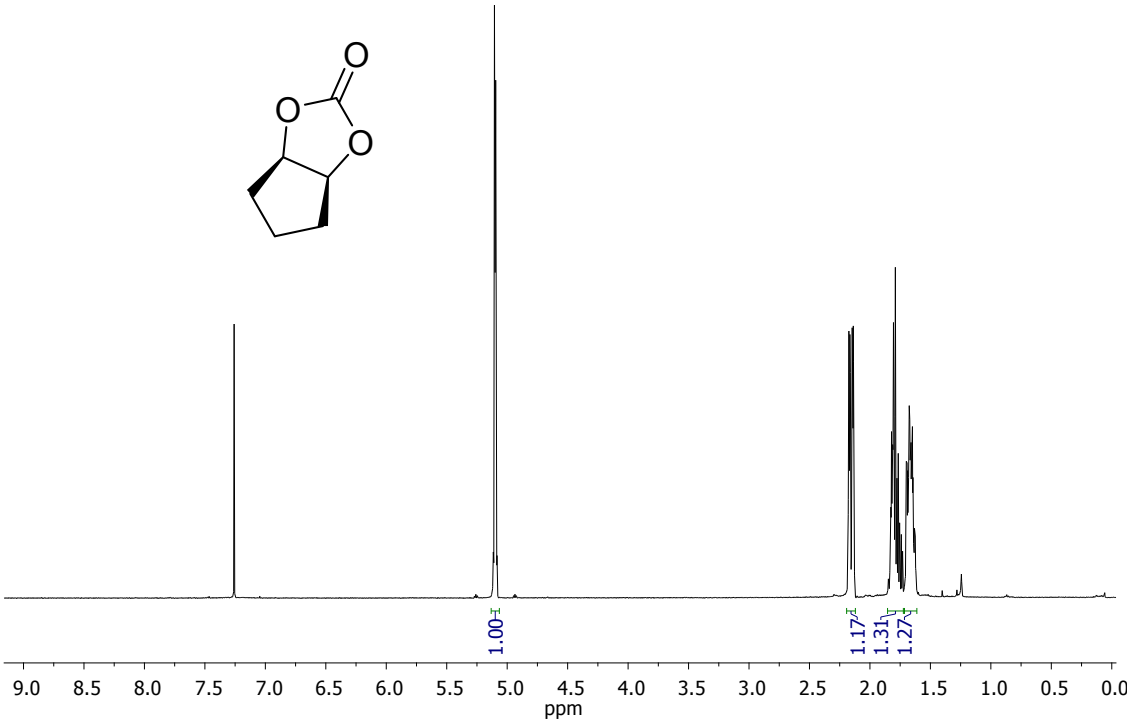
^{1}H-NMR of *cis*-1,2-cyclohexene carbonate (**5a**) in $CDCl_3$



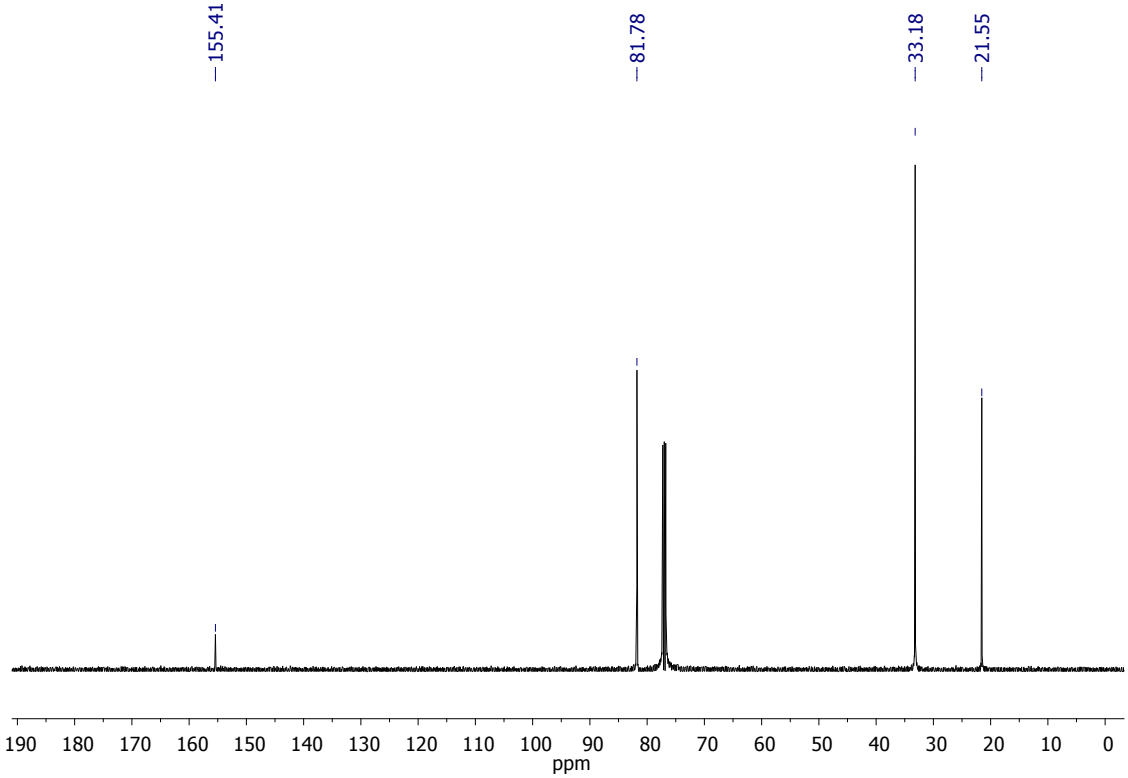
^{13}C-{^{1}H}-NMR *cis*-1,2-cyclohexene carbonate (**5a**) in $CDCl_3$



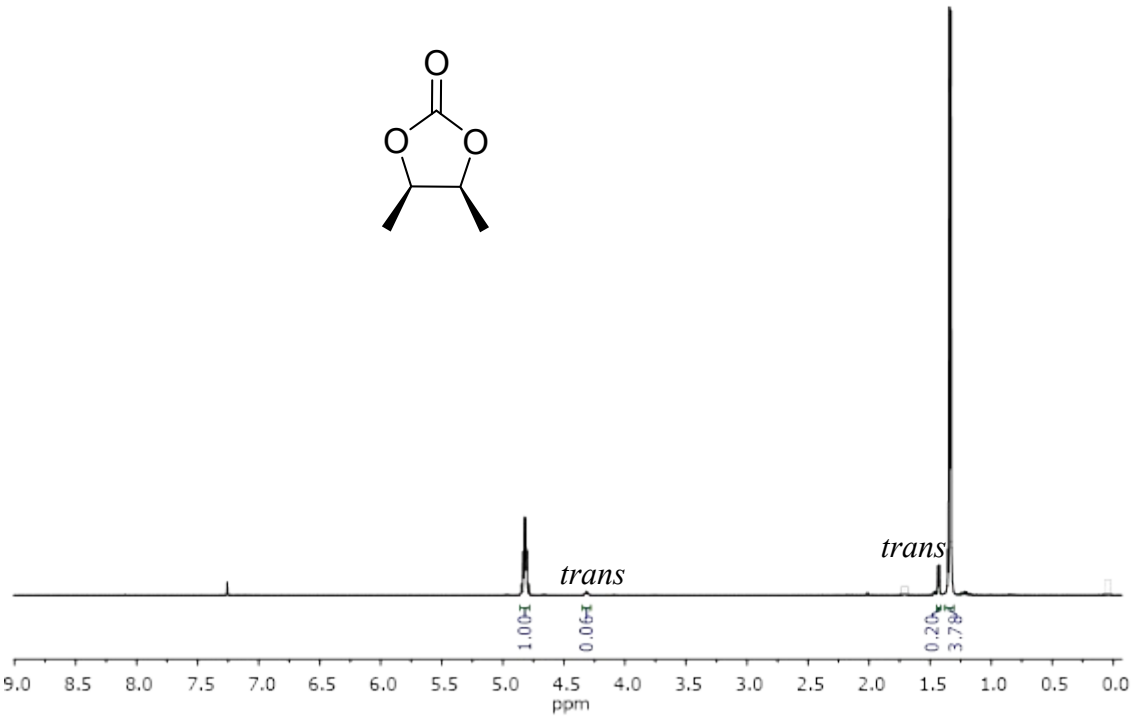
^{1}H-NMR of *cis*-1,2-cyclopentane carbonate (**5b**) in $CDCl_3$



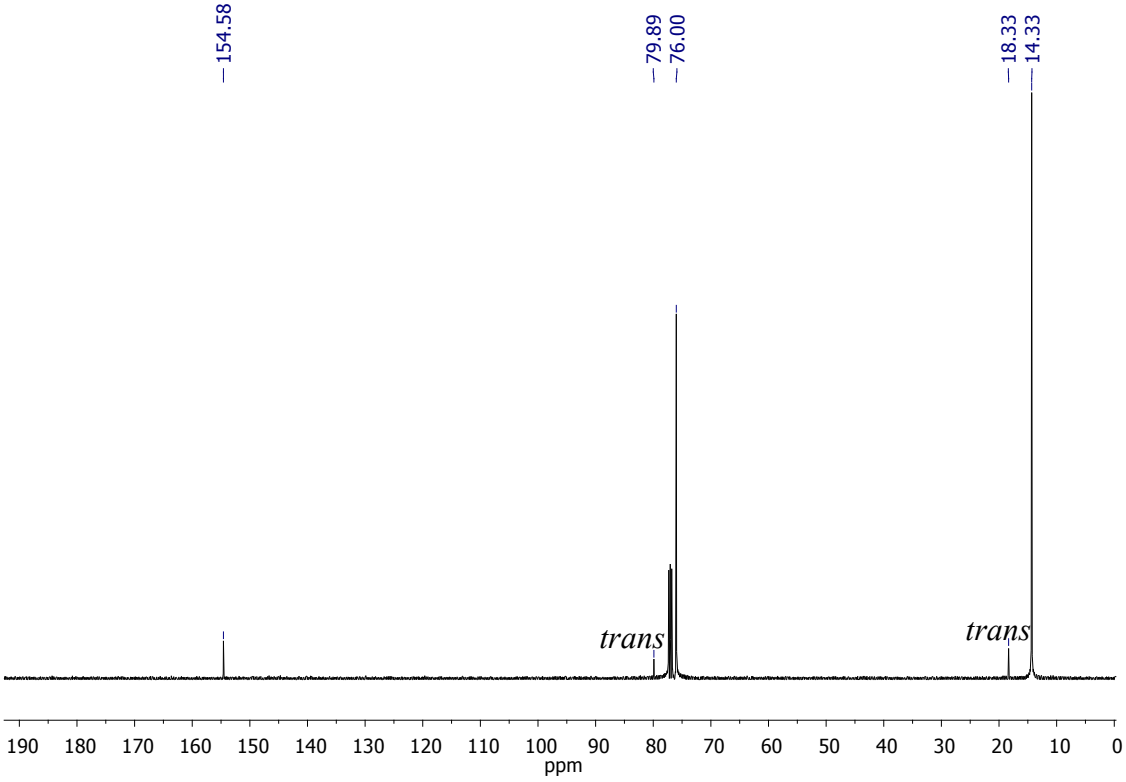
^{13}C-{^{1}H}-NMR *cis*-1,2-cyclopentane carbonate (**5b**) in $CDCl_3$



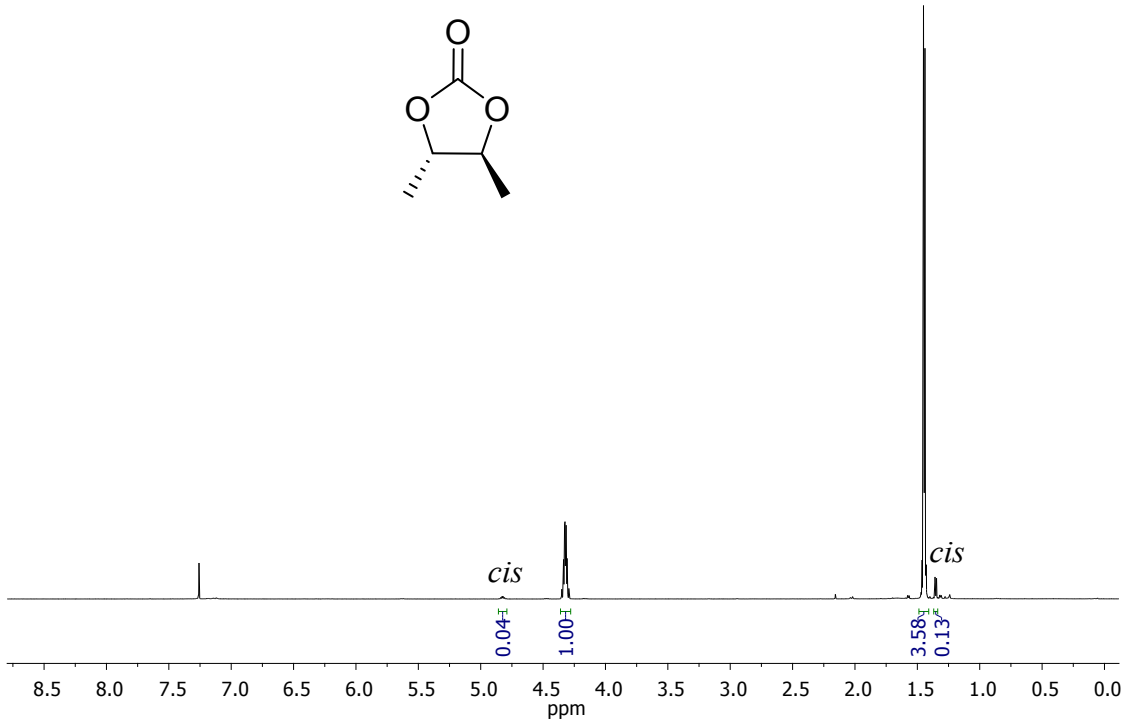
^{1}H-NMR of *cis*-2,3-Butene carbonate (**5c**) in $CDCl_3$



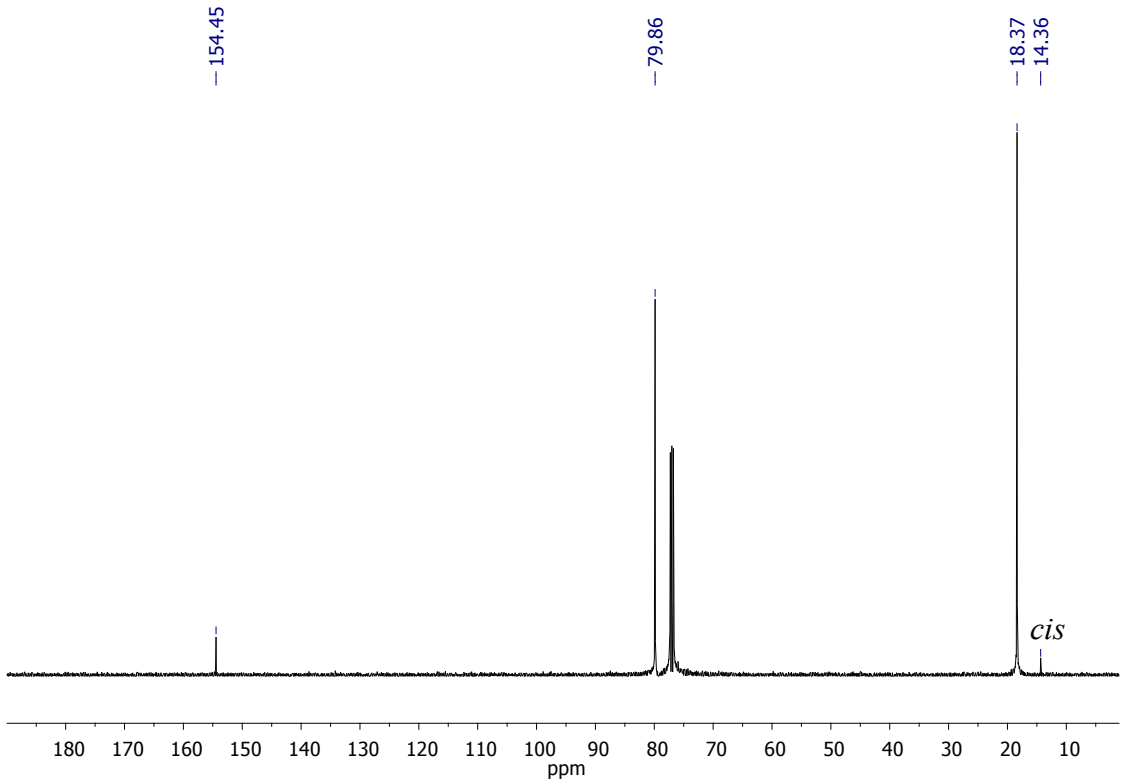
^{13}C-{^{1}H}-NMR *cis*-2,3-Butene carbonate (**5c**) in $CDCl_3$



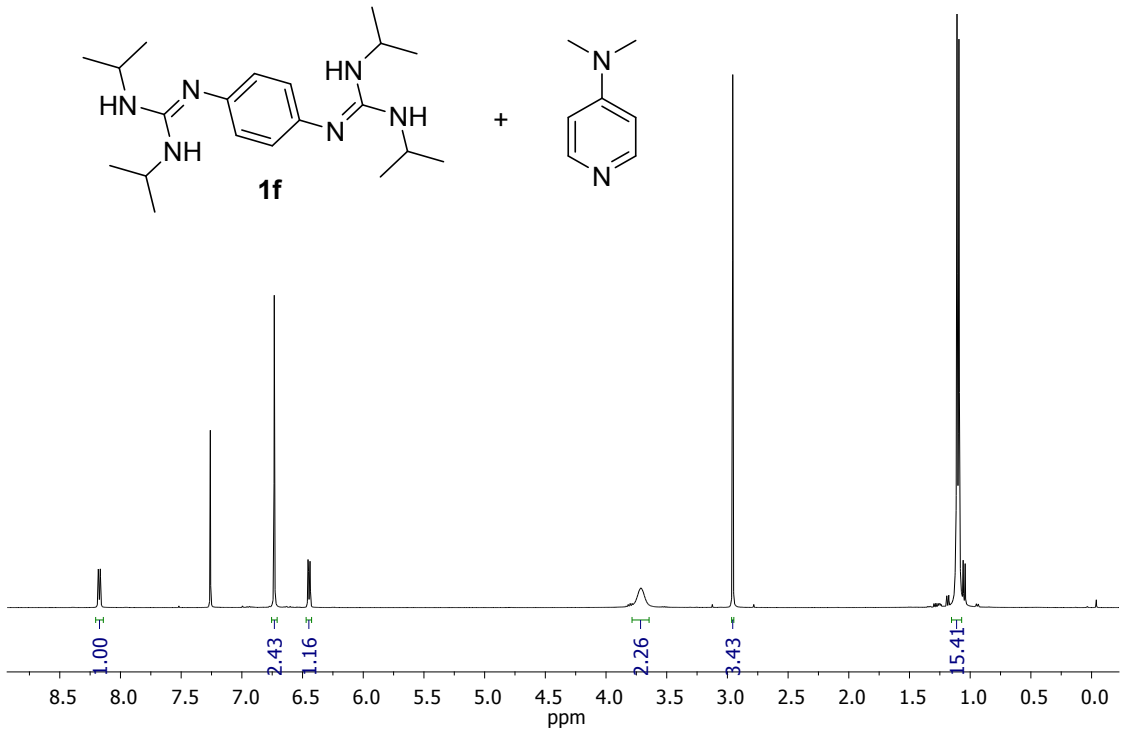
^{1}H-NMR of *trans*-2,3-Butene carbonate (**5d**) in $CDCl_3$



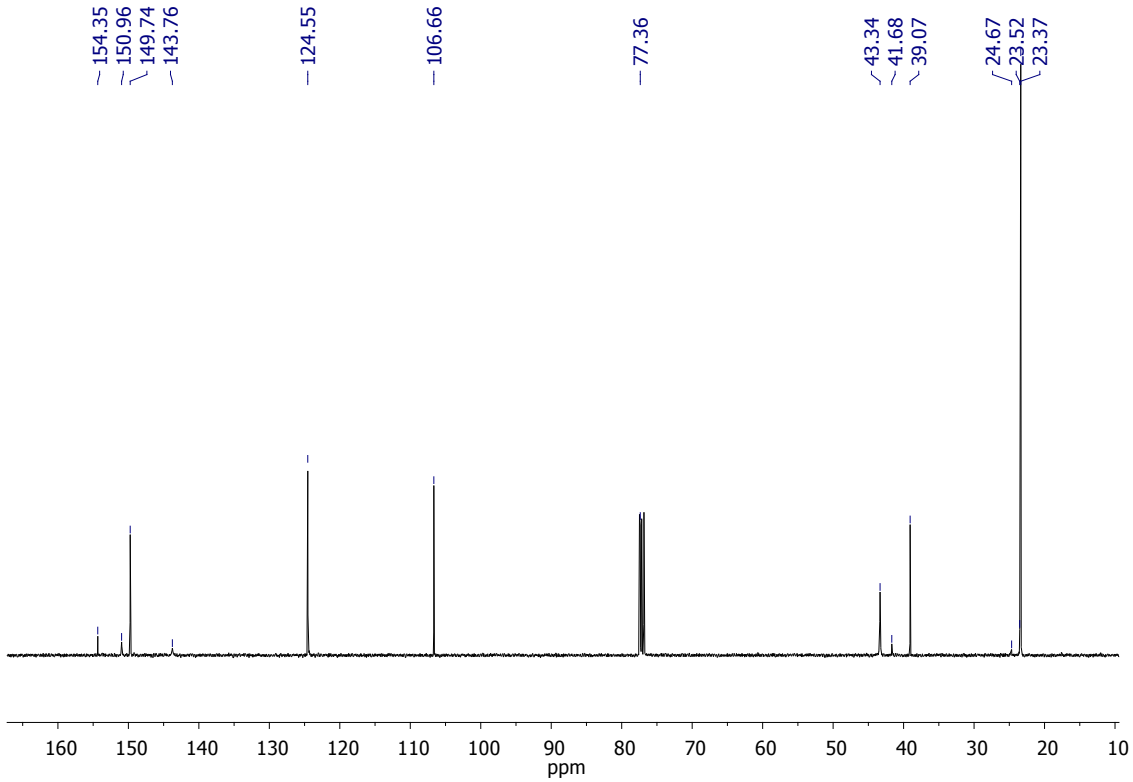
^{13}C-{^{1}H}-NMR *trans*-2,3-Butene carbonate (**5d**) in $CDCl_3$



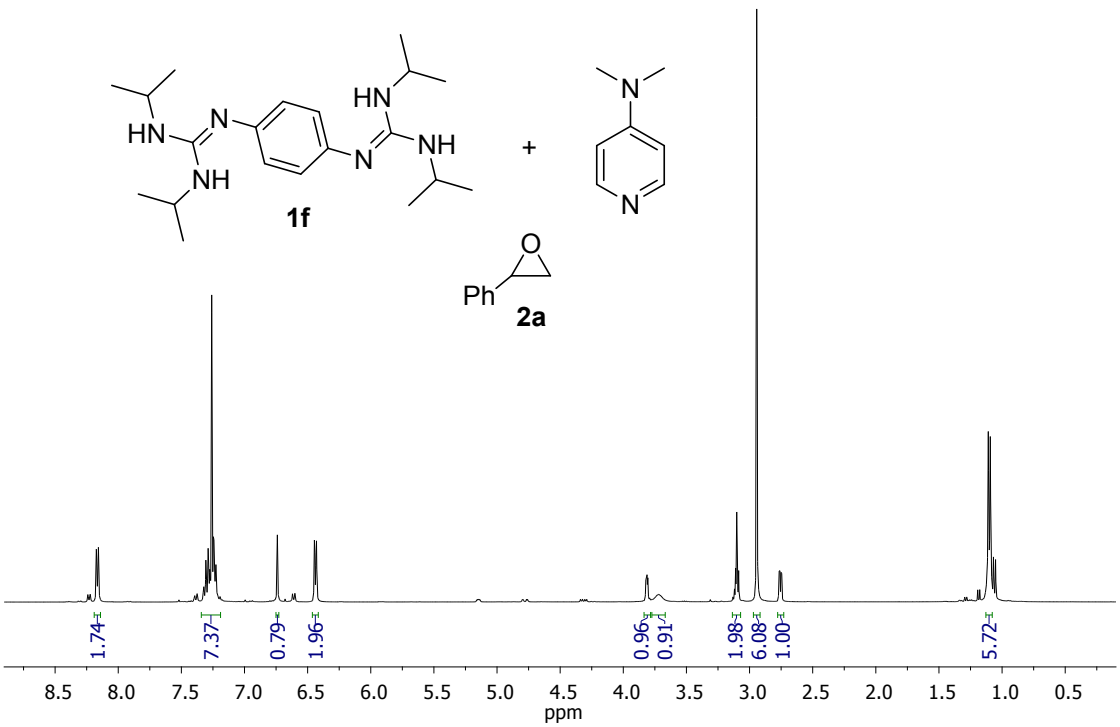
^{1}H-NMR spectrum of compound **1f** and DMAP in a molar ratio 1:1 (**1f**:DMAP) at 70 ºC for one hour in $CDCl_3$



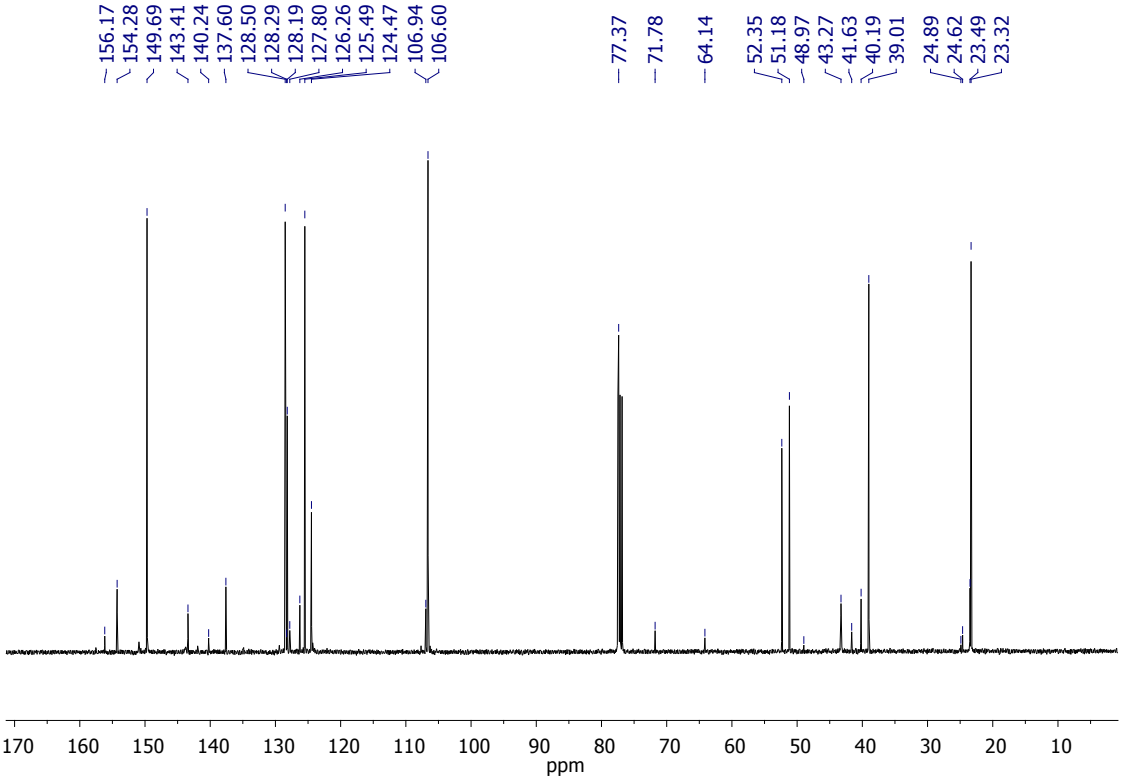
$^{13}C\{^{1}H\}$-NMR spectrum of compound **1f** and DMAP in a molar ratio 1:1 (**1f**:DMAP) at 70 ºC for one hour in $CDCl_3$



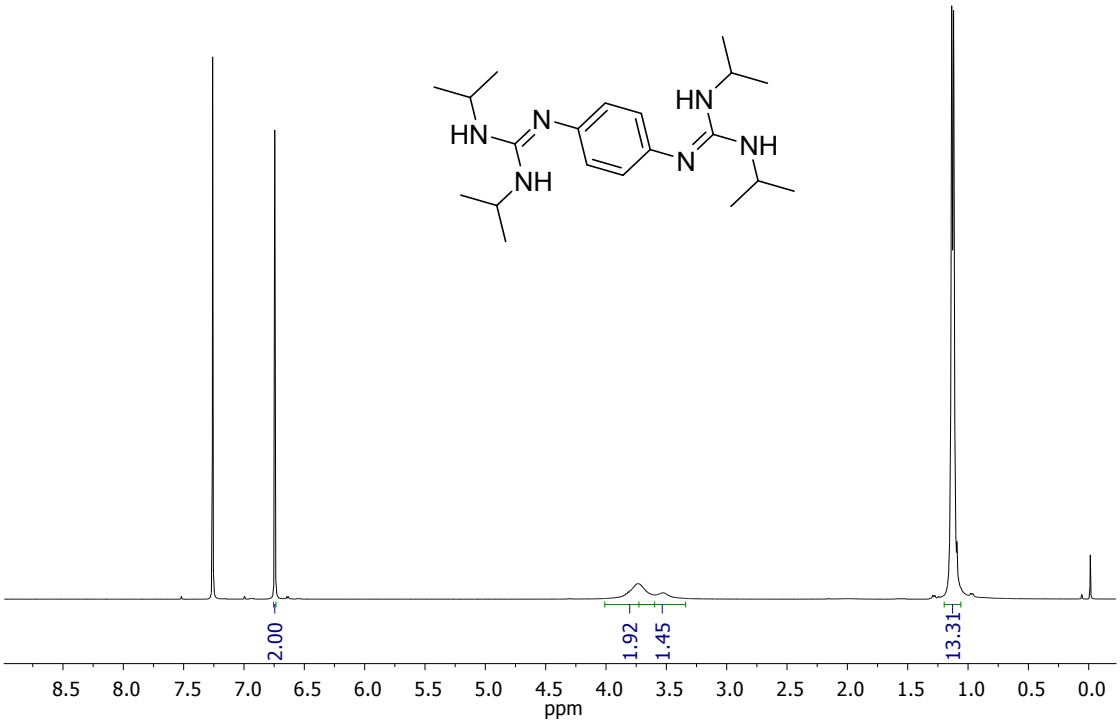
^{1}H-NMR spectrum of compound **1f**, DMAP and styrene oxide **2a** in a molar ratio 1:1:1 (**1f**:DMAP:**2a**) at 70 ºC for one hour in $CDCl_3$



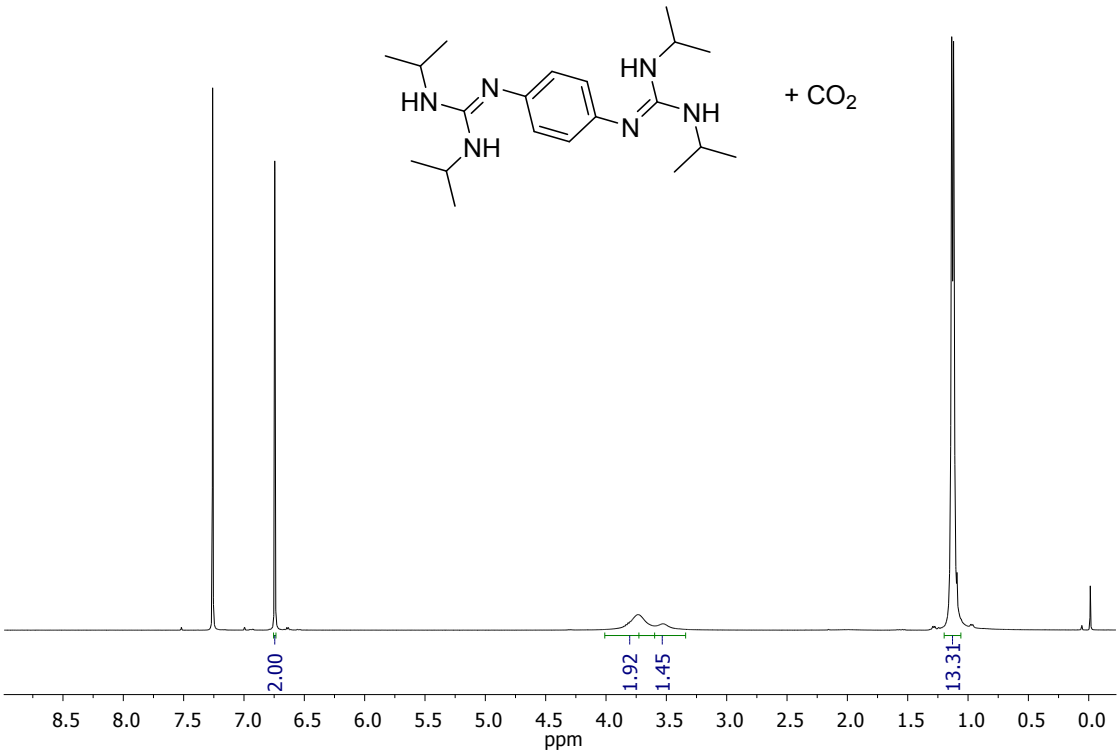
$^{13}C\{^{1}H\}$-NMR spectrum of compound **1f**, DMAP and styrene oxide **2a** in a molar ratio 1:1:1 (**1f**:DMAP:**2a**) at 70 ºC for one hour in $CDCl_3$



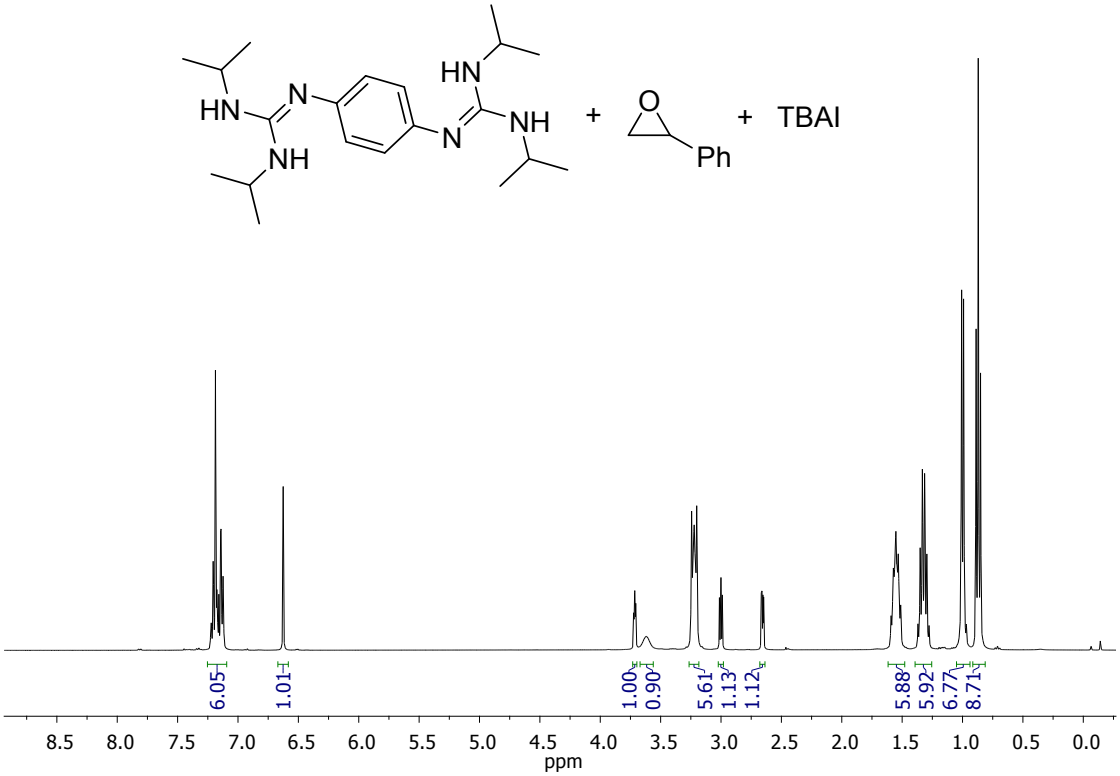
^{1}H NMR spectrum of compound **1f** in $CDCl_3$



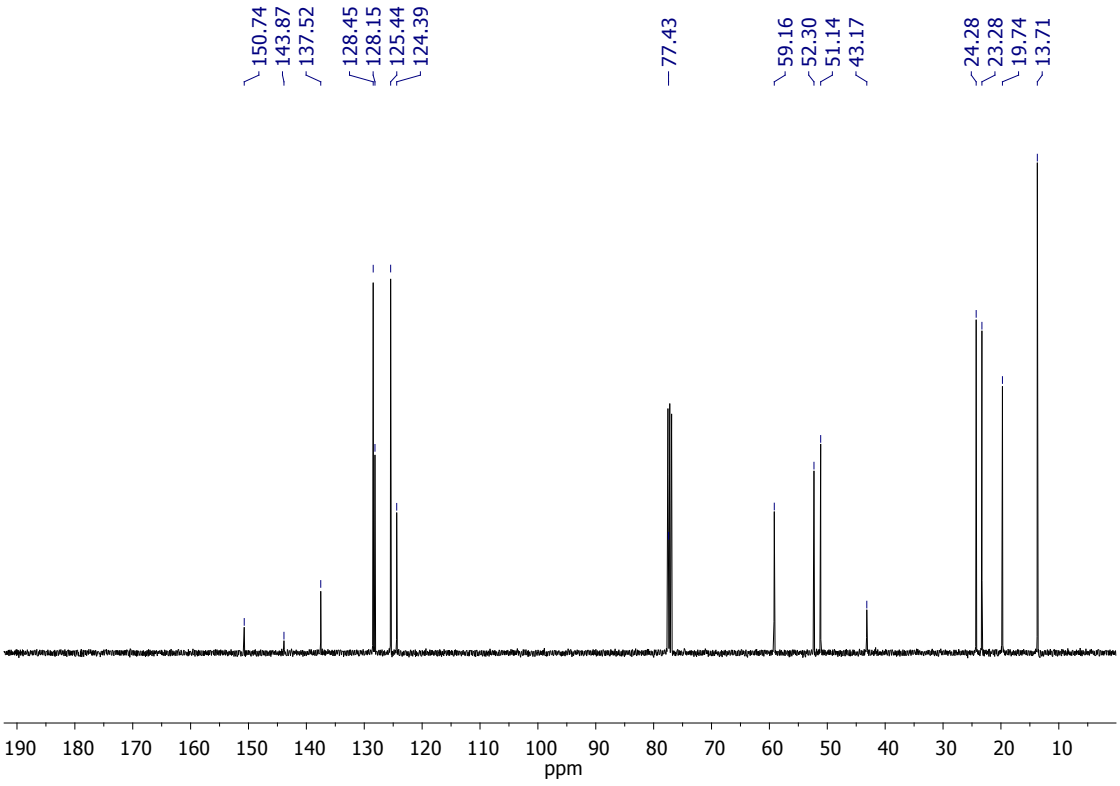
^{1}H NMR spectrum of compound **1f** and CO_2 at 70 ºC for 24 hours in $CDCl_3$



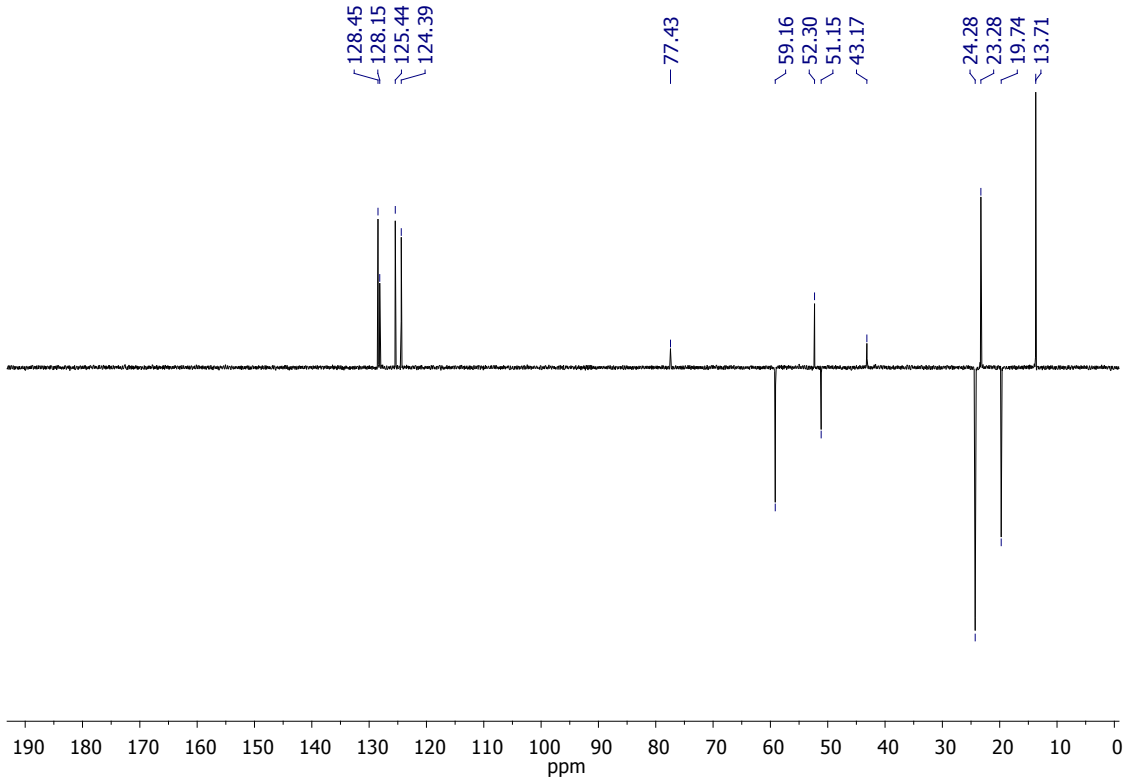
^{1}H-NMR spectrum of compound **1f**, styrene oxide **2a** and TBAI in a molar ratio 1:4:2 (**1f**:**2a**:TBAI) at 70 ºC for one hour in $CDCl_3$



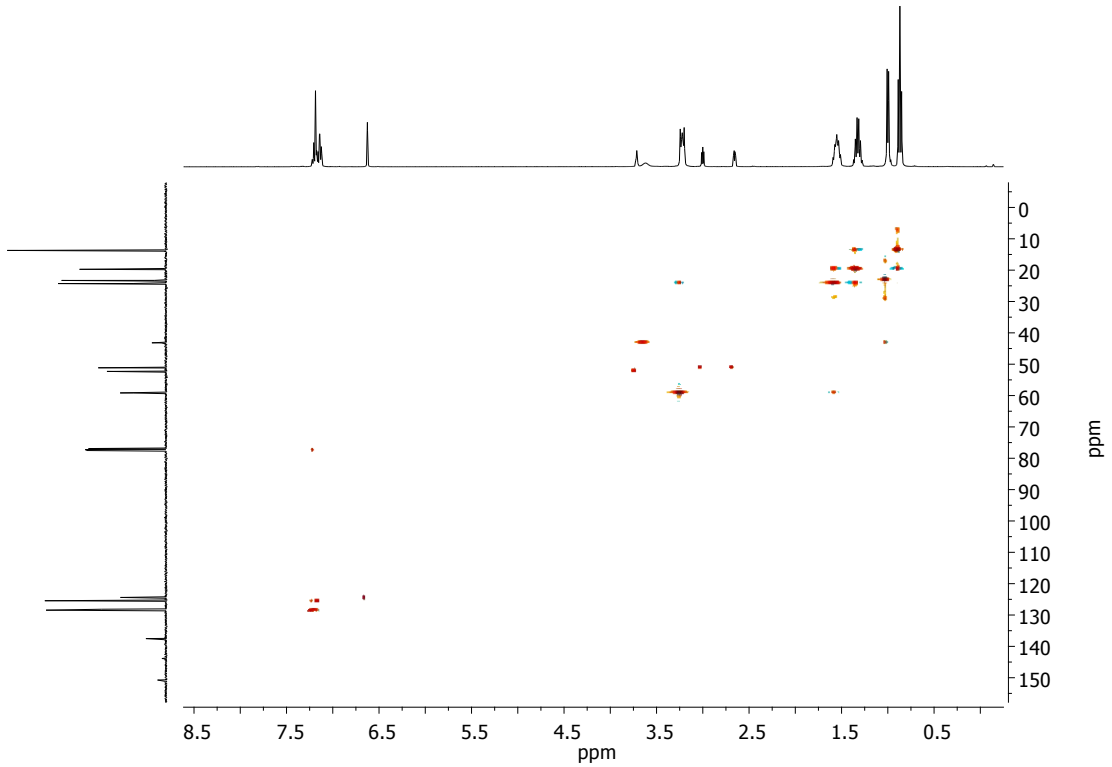
^{13}C-{^{1}H}-NMR spectrum of compound **1f**, styrene oxide **2a** and TBAI in a molar ratio 1:4:2 (**1f**:**2a**:TBAI) at 70 ºC for one hour in $CDCl_3$



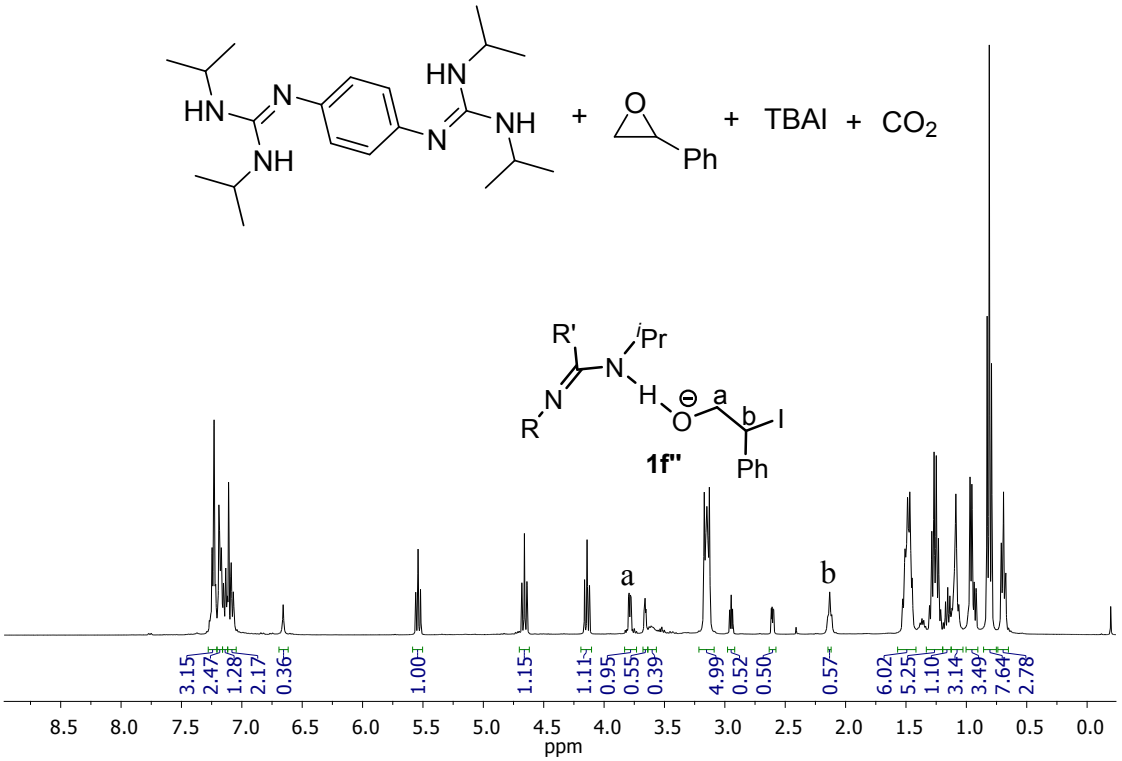
DEPT-135 spectrum of compound **1f**, styrene oxide **2a** and TBAI in a molar ratio 1:4:2 (**1f**:**2a**:TBAI) at 70 ºC for one hour in $CDCl_3$



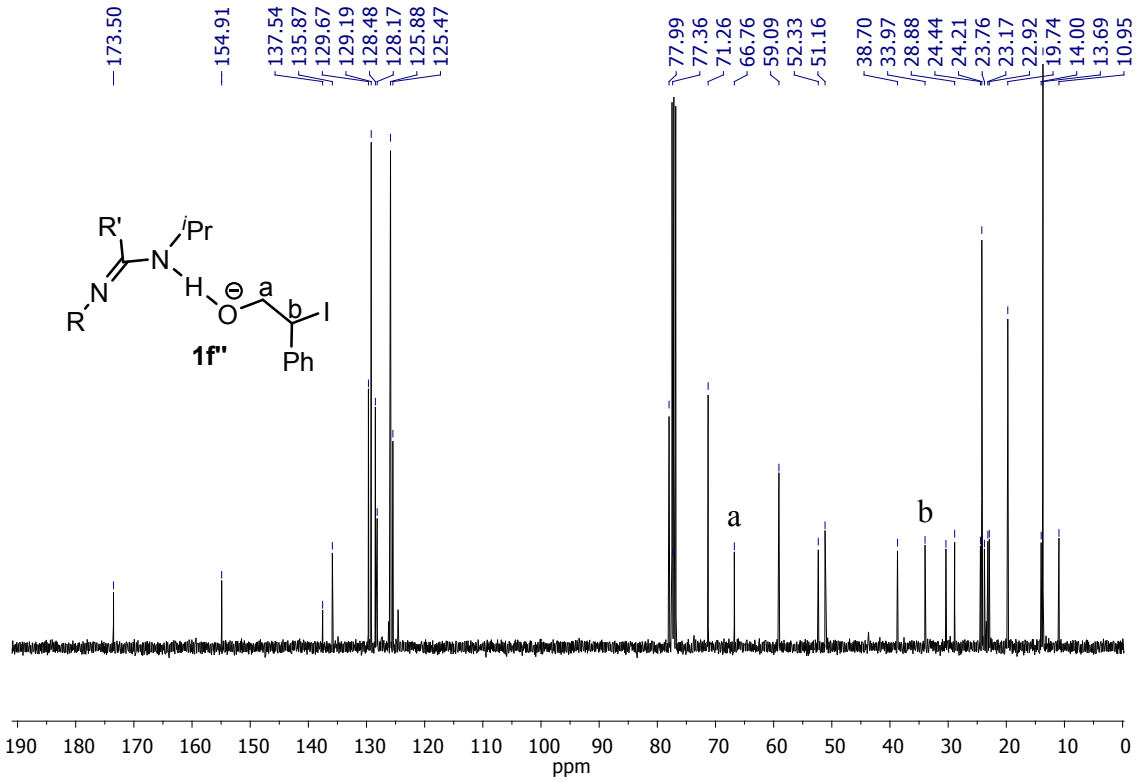
g-HSQC spectrum of compound **1f**, styrene oxide **2a** and TBAI in a molar ratio 1:4:2 (**1f**:**2a**:TBAI) at 70 ºC for one hour in $CDCl_3$



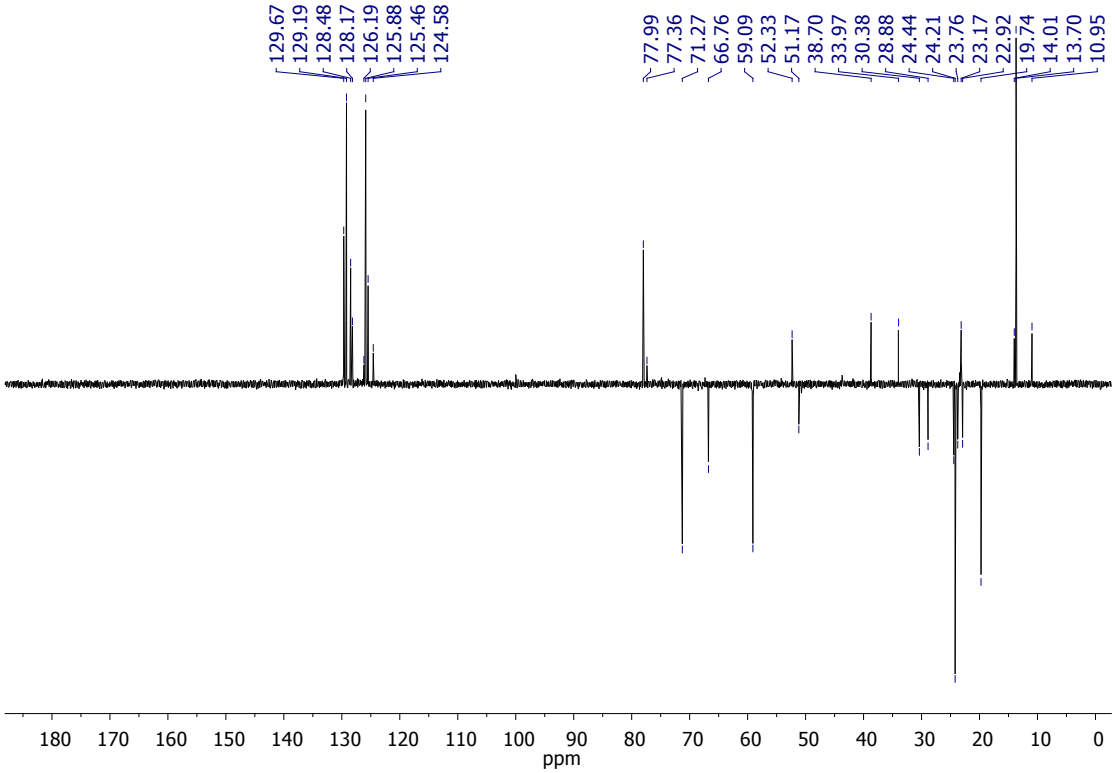
^{1}H NMR spectrum of compound **1f**, styrene oxide **2a**, TBAI and CO_2 in a molar ratio 1:4:2 (**1f**:**2a**:TBAI) at 70 ºC for two hour in $CDCl_3$



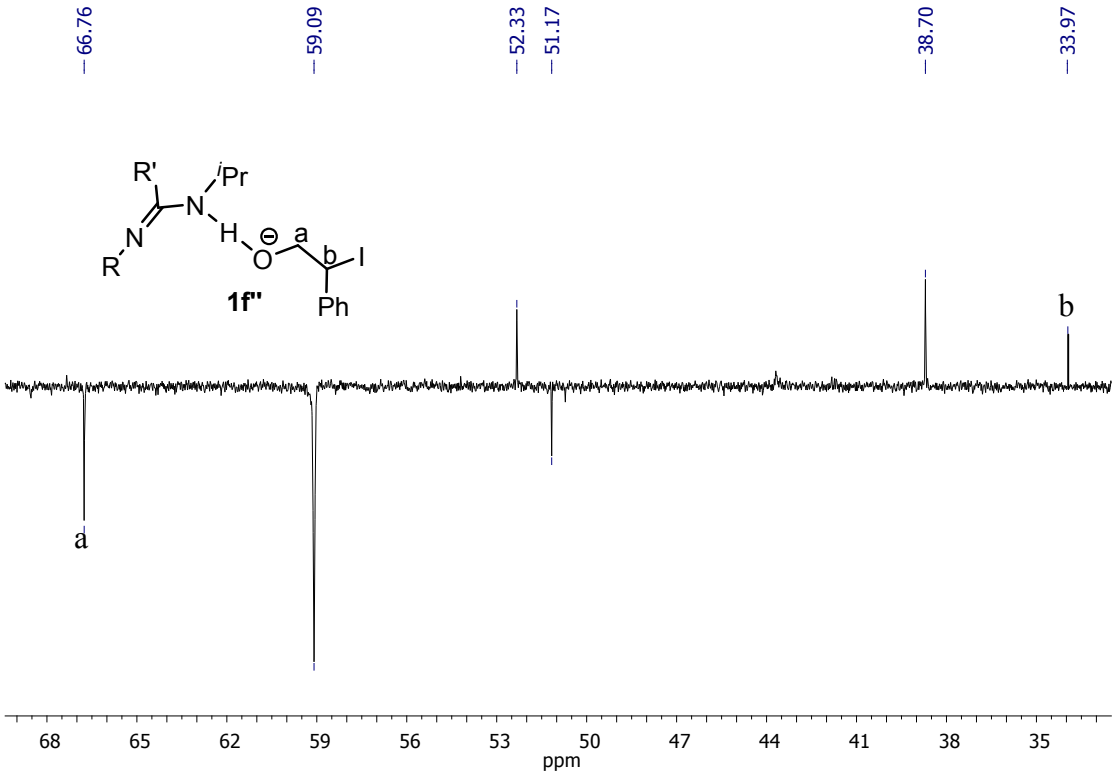
^{13}C{^{1}H} NMR spectrum of compound **1f**, styrene oxide **2a**, TBAI and CO_2 in a molar ratio 1:4:2 (**1f**:**2a**:TBAI) at 70 ºC for two hour in $CDCl_3$



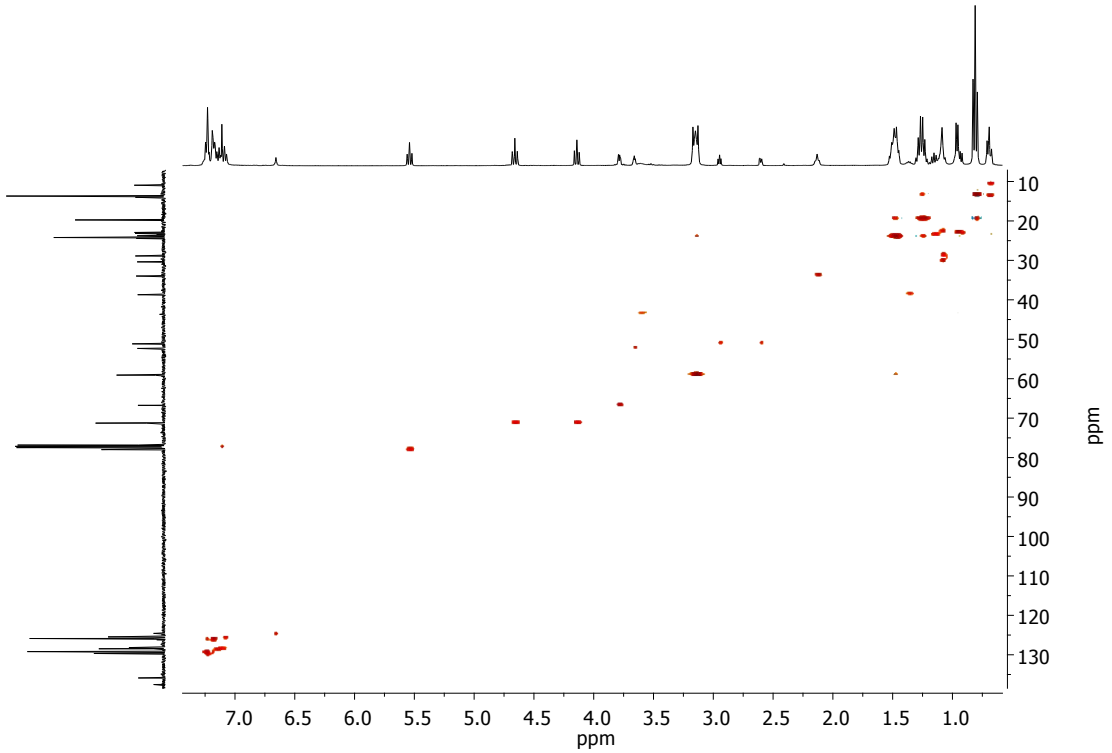
DEPT-135 spectrum of compound **1f**, styrene oxide **2a**, TBAI and CO_2 in a molar ratio 1:4:2 (**1f**:**2a**:TBAI) at 70 ºC for two hour in $CDCl_3$



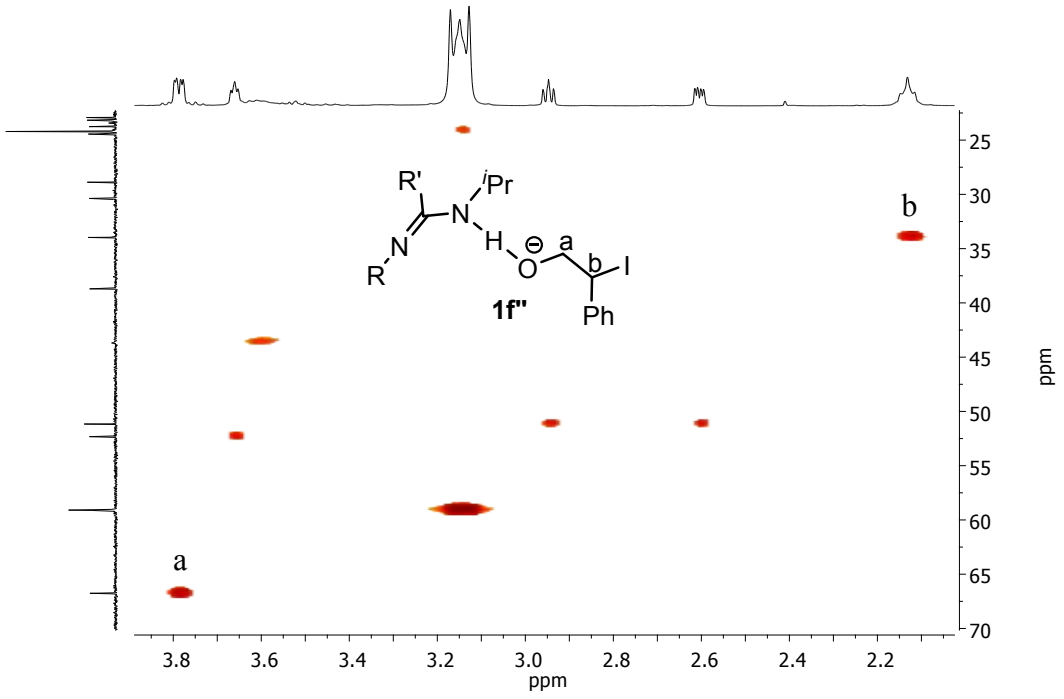
DEPT-135 spectrum of compound **1f**, styrene oxide **2a**, TBAI and CO_2 in a molar ratio 1:4:2 (**1f**:**2a**:TBAI) at 70 ºC for two hour in $CDCl_3$ (range 70.0–32.0 ppm)



g-HSQC spectrum of compound **1f**, styrene oxide **2a**, TBAI and CO_2 in a molar ratio 1:4:2 (**1f**:**2a**:TBAI) at 70 ºC for two hour in $CDCl_3$



g-HSQC spectrum of compound **1f**, styrene oxide **2a**, TBAI and CO_2 in a molar ratio 1:4:2 (**1f**:**2a**:TBAI) at 70 ºC for two hour in $CDCl_3$ (range 4.0–2.0 in ^{1}H-NMR and 70.0-20.0 ppm in ^{13}C-NMR.



References:

[1] C. Alonso-Moreno, F. Carrillo-Hermosilla, A. Garcés, A. Otero, I. López-Solera, A. M. Rodríguez and A. Antiñolo, *Organometallics*, 2010, **29**, 2789–2795.

[2] D. Li, J. Guang, W.-X. Zhang, Y. Wanga and Z. Xi, *Org. Biomol. Chem.,* 2010, **8**, 1816–1820.

[3] A. Antiñolo, F. Carrillo-Hermosilla, R. Fernández-Galán, J. Martínez-Ferrer, C. Alonso-Moreno, I. Bravo, S. Moreno-Blázquez, M. Salgado, E. Villaseñor and J. Albaladejo, *Dalton Trans.,* 2016, **45**, 10717–10729.

[4] Z. Li, M. Xue, H. Yao, H. Sun, Y. Zhang and Q. Shen, *J. Organomet. Chem.,* 2012, **713**, 27–34.

[5] X. Zhang, C. Wang, C. Qian, F. Han, F. Xu and Q. Shen, *Tetrahedron*, 2011, **67**, 8790–8799.

[6] J. A. Castro-Osma, M. North and X. Wu, *Chem. Eur. J.,* 2016, **22**, 2100–2107.

[7] J. Rintjema and A. W. Kleij,. *ChemSusChem,* 2017, **10**, 1274–1282.

[8] D. O. Meléndez, A. Lara-Sánchez, J. Martínez, X. Wu, A. Otero, J. A. Castro-Osma, M. North and R. S. Rojas, *ChemCatChem,* 2018, **10**, 2271–2277.

[9] Y. R Yepes, C. Quintero, D. O. Meléndez, C. G. Daniliuc, J. Martínez and R. S. Rojas, *Organometallics,* 2019, **38**, 469−478.