Electronic Supplementary Information

The Impact of Anion Shielding on the Catalytic Activity of CO_2 Fixation into Cyclic Carbonates

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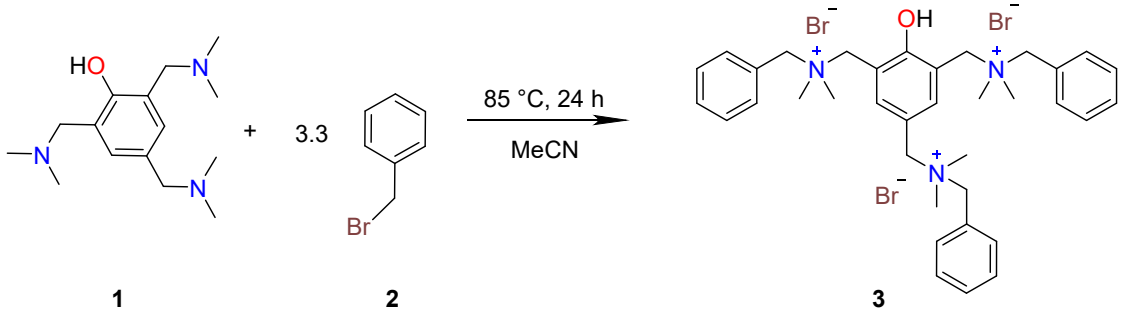
1 Synthesis Part

1.1 Synthesis of the Catalysts

1.1.1 Synthesis of the organocatalyst 3

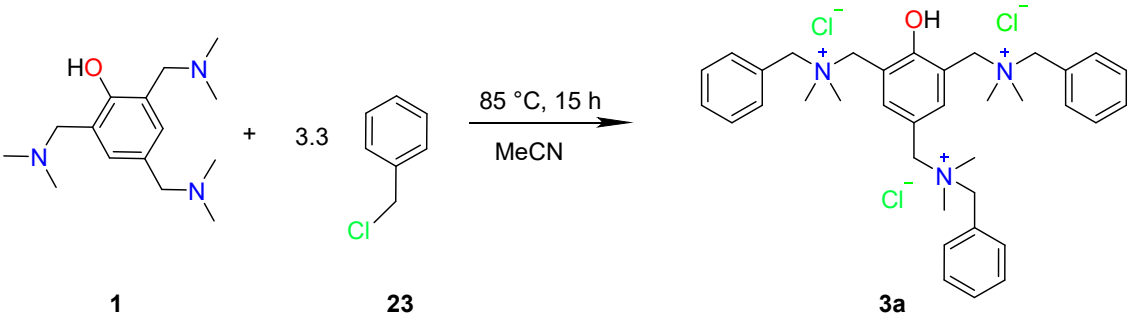


1 **2** **3**

Scheme S1. Synthetic route of **3**.

In the absence of light, **1** (1.0 mL, 3.47 mmol) was added to a solution of freshly distilled benzyl bromide (**2**, 1.4 mL, 11.4 mmol, 3.3 *eq*.) in MeCN (70 mL), and refluxed at 85 °C for 24 h. Turbidity was observed after 5 mins. The pinkish precipitate **3** (1.55 g) was filtered, washed with MeCN (30 mL) and dried under vacuum (Yield: 57%). CP MAS ^{13}C NMR (ppm): δ= 160.7, 152.4, 140.6, 132.4, 123.9, 61.3, 53.5, 44.1. ATR-FTIR (cm^{-1}): 3392, 3006, 2962, 1739, 1612, 1470, 1368, 1300, 1216, 1172, 1133, 1030, 903, 844, 771, 727, 703, 615, 541. TGA: T_{d50} took place at 313.5 °C. Melting point: 164 °C (uncorrected).

1.1.2 Synthesis of the corresponding catalyst 3a



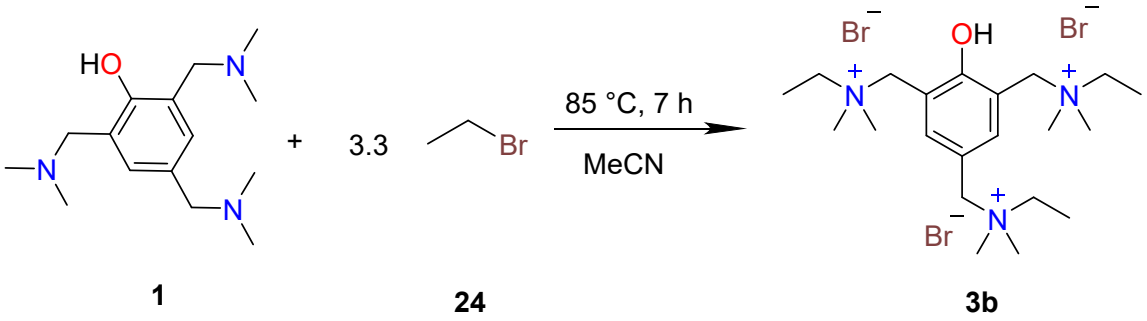
1 **23** **3a**

Scheme S2. Synthetic route of catalyst **3a**.

Solution of **1** (0.73 mL, 1.83 mmol) in 25 mL MeCN was added to a 50 mL RB flask, then benzyl chloride (**23**, 0.71 mL, 6.02 mmol, 3.3 *eq*.) was added dropwise with continuous stirring and refluxed for 15 h at 85 °C. The white precipitate of **3a** (0.81 g) was filtered,

washed with MeCN (3×15 mL), and dried under vacuum. (Yield: 68%). ATR-FTIR (cm^{-1}): 3370, 3007, 2959, 2112, 1613, 1473, 1372, 1343, 1269, 1216, 1174, 1031, 908, 850, 754, 728, 702, 615, 545, 514. TGA: T_{d50} took place at 313 °C.

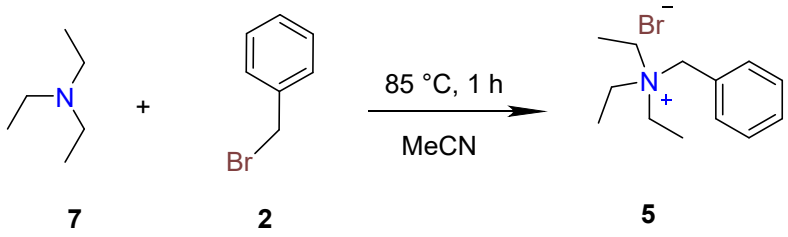
1.1.3 Synthesis of the corresponding catalyst 3b



Scheme S3. Synthetic route of catalyst **3b**.

In a 50 mL RB flask, **1** (1.0 mL, 3.47 mmol, 1 *eq*.) was added to a clear solution of bromoethane (**24**, 0.86 mL, 0.0114 mol, 3.3 *eq*.) in 20 mL MeCN and refluxed at 85 °C for 7 h. Turbidity was observed after 1 h. The white precipitate of **3b** (1.04 g) was filtered, washed with MeCN (3×20 mL), and dried overnight under air. (Yield: 49%). ATR-FTIR (cm^{-1}): 3389, 3007, 2957, 2111, 1612, 1548, 1472, 1372, 1342, 1298, 1271, 1226, 1203, 1172, 1026, 905, 846, 810, 749, 540, 508. TGA: T_{d50} took place at 338 °C.

1.1.4 Synthesis of *N*-benzyl-*N*,*N*-diethylethanammonium bromide (5)

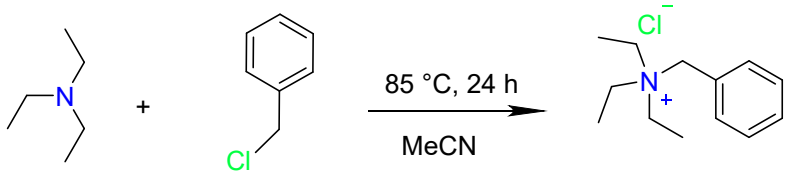


Scheme S4. Synthetic route of **5**.

In the absence of the light, **7** (1.5 mL, 0.011 mol) was added to a solution of **2** (1.3 mL, 0.011 mol, 1 *eq*.) in MeCN (30 mL), and refluxed at 85 °C for 1 h. The white precipitate

of **5** (2.92 g), was filtered, washed with MeCN (3×15 mL), and dried under air (Yield: 97%). ^{1}H NMR: (500 MHz, D_2O, ppm): δ = 7.55 (m, 5H), 4.42 (s, 2H), 3.24 (q, 6H), 1.41 (t, 9H). ^{13}C NMR (125 MHz, D_2O, ppm): δ = 132.4, 130.6, 129.2, 127.1, 59.8, 52.2, 7.0. ATR-FTIR (cm^{-1}): 2973, 2913, 2118, 1577, 1496, 1454, 1402, 1306, 1215, 1187, 1152, 1078, 1036, 1015, 923, 906, 875, 822, 769, 712, 678, 614, 547, 495.

1.1.5 Synthesis of *N*-benzyl-*N*,*N*-diethylethanammonium chloride (5a)

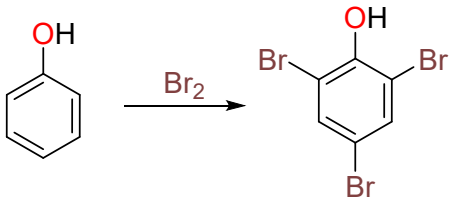


7 **23** **5a**

Scheme S5. Synthetic route of **5a**.

In 50 mL RB flask, **7** (1.53 mL, 0.011 mol) was added to a solution of **23** (1.30 mL, 0.011 mol, 1 *eq*.) in MeCN (30 mL), and refluxed at 85 °C for 24 h. The white precipitate of **5a** was observed upon concentrating the solution to *ca.* 10 mL. The precipitate was filtered, washed with THF (3×15 mL), and dried under air (Yield: 68%). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ = 7.28 (m, 2H), 7.14 (m, 3H), 4.47 (s, 2H), 3.15 (q, 6H), 1.17 (t, 9H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 131.9, 130.0, 128.7, 126.7, 60.5, 52.2, 7.8.

1.1.6 Synthesis of 2,4,6-tribromophenol (6)

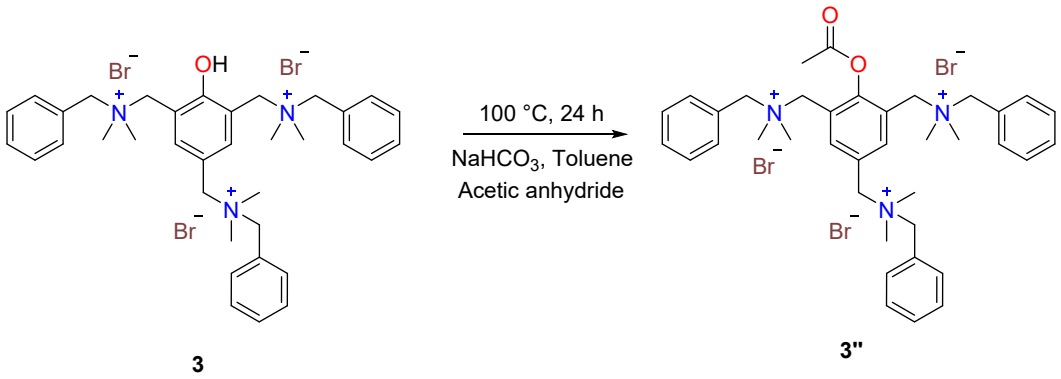


4 **6**

Scheme S6. Synthetic route of **6**.

In 50 mL RB flask, **4** (0.153 g, 1.62 mmol) was dissolved in 20 mL distilled water. Once the solution became clear, concentrated bromine (0.5 mL, 9.70 mmol, 6 *eq.*) was added dropwise with continuous stirring. The white precipitate (**6**) was filtered and washed with copious amount of water. The filtrate was treated with sodium bisulfite to remove and reduce the existing bromine into bromide ions. ATR-FTIR (cm^{-1}): 3445, 3070, 2297, 1611, 1547, 1454, 1379, 1345, 1306, 1267, 1228, 1191, 1144, 1040, 856, 735, 670, 604, 551. Melting point: 94 °C (uncorrected).

1.1.7 Synthesis of the corresponding catalyst 3''



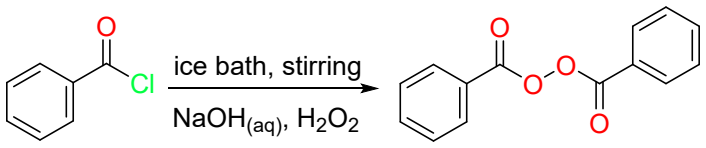
Scheme S7. Synthetic route of the corresponding capped catalyst **3''**.

The target compound **3''** was synthesized according to the published procedure by Lugemwa *et al.*[1] with some modifications: In 50 mL RB flask, **3** (0.10 g, 0.129 mmol) was suspended in 20 mL toluene and heated to 100 °C with continuous stirring. After that, sodium bicarbonate (0.0216 g, 0.257 mmol, 2 *eq.*) and acetic anhydride (0.061 mL, 0.642 mmol, 5 *eq.*) were added. The mixture continued to stir for 24 h. After cooling to room temperature (RT), the precipitate was filtered, washed with acetone (3×10 mL) then distilled water (3×15 mL), respectively. The solid was soaked in distilled water for 3 days with replacement of water daily, then the light-yellow solid of **3''** was filtered using nylon filter paper and dried under air (Yield: 27%). ATR-FTIR (cm^{-1}): 3509, 2969, 2459, 2415,

2255, 2212, 1743, 1679, 1601, 1472, 1402, 1301, 1158, 1039, 969, 925, 861, 768, 678, 649, 614, 567, 541 TGA: the decomposition temperature at 50% weight loss (T_{d50}) took place at 268 °C.

1.2 Synthesis of Monomers, Precursors, Reagents, and polymers catalysts

1.2.1 Synthesis of benzoyl peroxide (18)

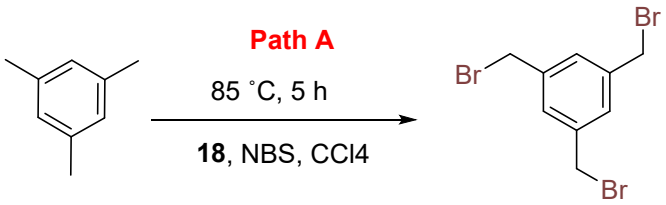


17 **18**

Scheme S8. Synthetic route for the production of **18**.

To a cold solution of benzoyl chloride (**17**, 2.2 mL, 18.6 mmol, 2 *eq.*), a solution of H_2O_2 (0.95 mL, 9.3 mmol, 30%) and 1 M of NaOH (18.6 mL, 18.6 mmol, 2 *eq.*) was added dropwise while stirring. After completion of the addition, the reaction mixture was stirred for further 50 min in an ice bath then the white solid of **18** was filtered and dried under vacuum (Yield: 54%). ^{1}H NMR: (500 MHz, DMSO-d_6, ppm): δ = 8.04 (m, 4H), 7.82 (m, 2H), 7.65 (m, 4H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm): δ = 162.6, 135.1, 129.5, 124.6

1.2.2 1,3,5-tris(bromomethyl)benzene (8, Path A)



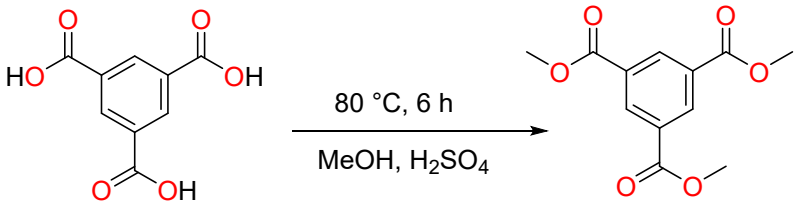
19 **8**

Scheme S9. Synthetic route for the production of **8**, **Path A**.

The target compound **8** was synthesized according to the published procedure by Ponmuthu *et al.*[2] with some modifications: A freshly recrystallized N-bromosuccinimide (NBS) was

dried under vacuum for 30 min before used in the reaction. A solution of mesitylene (**19**, 2.0 mL, 14.38 mmol), NBS (7.68 g, 43.14 mmol, 3 *eq.*), and **18** (0.10 g, 0.431 mmol, 0.03 *eq.*) in a distilled CCl_4 (200 mL) was refluxed at 85 °C for 5 h in the absence of light. The solution became pale-yellow with time, and a white precipitate of succinimide started to form. Next, the mixture was cooled to RT and then cooled to -20 °C till the next day. After that, the precipitate was filtered out, and the solvent was evaporated at 60 °C under reduced pressure to yield a yellow liquid which was diluted with *ca*.5 mL of distilled petroleum ether and adsorbed on a silica column to purify the desired product **8** (eluent is petroleum ether), which was recrystallized -after isolation- from distilled hexane. Yield: 20%, Purity (94% according to ^{1}H NMR). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ = 7.35 (s, 3H), 4.45 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 139.2, 129.7, 32.3. ATR-FTIR (cm^{-1}): 3670, 2970, 2901, 1451, 1436, 1398, 1212, 1164, 1139, 1115, 1066, 974, 892, 857, 701, 579, 551, 527.

1.2.3 Trimethyl benzene-1,3,5-tricarboxylate (21)



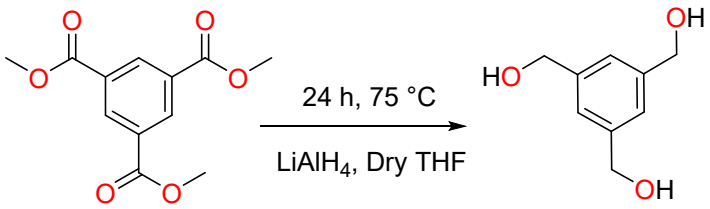
20 **21**

Scheme S10. Synthetic route for the production of **21**.

Compound **21** was synthesized according to the published procedure by Xu *et al.*[3] with some modifications: In a 250 mL round-bottomed flask, trimesic acid (**20**, 8.0 g, 38.1 mmol) was dissolved in a warm MeOH (150 mL), followed by a dropwise addition of concentrated H_2SO_4 (2.5 mL) and the mixture was refluxed for 6 h at 80 °C with continuous

stirring. After cooling to RT, glassy crystals were formed, and the solution was neutralized by dropwise addition of a saturated solution of sodium bicarbonate. The precipitate was separated by gravity filtration and washed with water to get rid of any sodium sulfate (Na_2SO_4) salt. For further purification, the precipitate was dissolved in ethyl acetate while the undissolved species were filtered out. The filtrate was evaporated under reduced pressure to get a white solid of **21** (Yield: 92%). ^{1}H NMR: (500 MHz, DMSO-d_6, ppm): δ = 8.54 (s, 3H), 3.92 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm): δ = 164.5, 133.3, 130.8, 52.8. ATR-FTIR (cm^{-1}): 3093, 3010, 2956, 2848, 2154, 2017, 1973, 1722, 1608, 1443, 1431, 1340, 1230, 1138, 1097, 991, 928, 874, 800, 717. EA ($C_{12}H_{12}O_6$) Calculated: C: 57.14, H: 4.80. Found: C: 57.29, H: 4.99. HRMS ($C_{12}H_{12}O_6$) Calculated for [M+H]: 253.07121. Found: 253.07126

1.2.4 Benzene-1,3,5-triyltrimethanol (22)



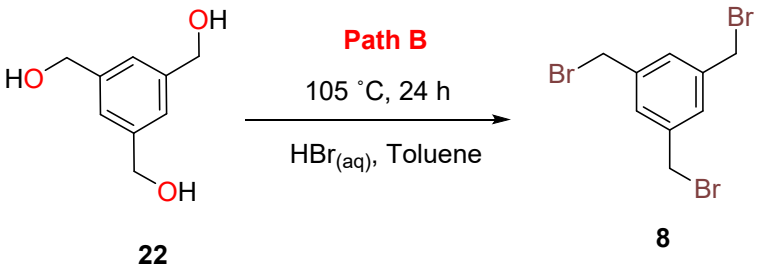
21 **22**

Scheme S11. Synthetic route for the production of **22**.

To a suspended mixture of $LiAlH_4$ (2.85 g, 71.4 mmol, 6 *eq.*) in 30 mL dry THF that cooled in an ice bath, a solution of **21** (3.00 g, 11.9 mmol) in dry THF (25 mL) was added dropwise while stirring under N_2 atmosphere using Schlenk line technique. During the addition, the solution color had been changing from gray to orange, then light green. After the completeness of the addition, the mixture was allowed to stir at RT for 30 min then refluxed at 75 °C for 24 h. The gray color back during the reflux and solid precipitate formed. The workup starts with quenching the excess of $LiAlH_4$ by cooling the flask in an ice bath and

adding slowly water (2.85 mL), 15% NaOH solution (2.85 mL), and water again (8.55 mL), in that order. The flask was allowed to warm to RT, stirred for 15 min, and the solid is filtered out. The filtrate was refiltered again through a celite pad and evaporated to get the first crop of the targeted product (**22**). The filtered solid was suspended and stirred in a mixture of as-received THF/ MeOH (v/v, 1/1) many times to extract as much as possible of the adsorbed product. (Yield: 68%). ^{1}H NMR: (500 MHz, DMSO-d_6, ppm): δ = 6.81 (s, 3H), 4.16 (s, 6H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm): δ = 141.7, 124.9, 63.5. ATR-FTIR (cm^{-1}): 3565, 2834, 2693, 2356, 1679, 1519, 1451, 1383, 1329, 1023, 876, 643, 715, 667, 627.

1.2.5 1,3,5-tris(bromomethyl)benzene (8, Path B)



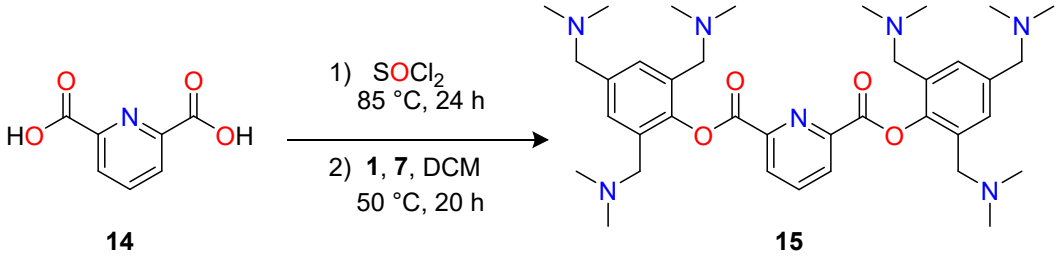
22 **8**

Scheme S12. Synthetic route for the production of **8**, **Path B.**

Similarly to a literature procedure by Lauer *et al.* [4] with slight modifications, compound **22** (1.26 g, 7.49 mmol) was added to a solution of toluene (20 mL) and HBr (12.6 mL, 48% in water) and refluxed at 105 °C for 24 h. After cooled to RT, the aqueous layer was separated, extracted with Et_2O (3×20 mL), and dried by Na_2SO_4. The two fractions of organic solvents were mixed and transferred into the fume hood to evaporate the ether. The rest of the solvent (toluene) was treated with distilled hexane (40 mL) and transferred to the freezer to precipitate the desired product (**8**) as a light-yellow needle crystal (Yield: 55%). ^{1}H NMR: (500 MHz, $CDCl_3$, ppm): δ = 7.35 (s, 3H), 4.46 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$, ppm): δ = 139.0, 129.5, 32.1. ATR-FTIR (cm^{-1}): 3024, 2970, 2857, 2652,

2459, 2419, 2325, 2288, 2114, 1995, 1817, 1798, 1705, 1603, 1580, 1454, 1435, 1387, 1292, 1208, 1166, 1117, 977, 891, 855, 701, 661, 632, 576, 548, 529, 475. EA ($C_9H_9Br_3$) Calculated: C: 30.29, H: 2.54. Found: C: 30.19, H: 2.40.

1.2.6 Synthesis of Bis(2,4,6-tris((dimethylamino)methyl)phenyl)pyridine-2,6-dicarboxylate (15)



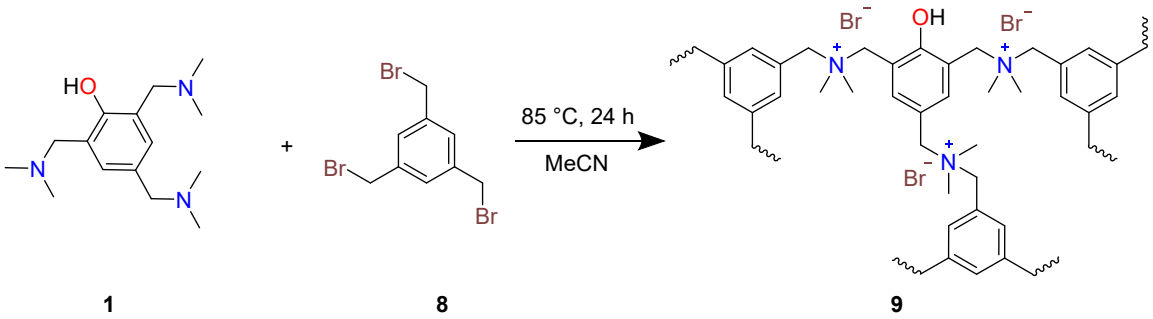
Scheme S13. Synthetic route of **15**.

1. In 50 mL RB flask, pyridine-2,6-dicarboxylic acid (**14**, 3.34 g, 19.6 mmol) was suspended in $SOCl_2$ (30 mL, 0.387 mol) and refluxed in an oil bath at 85 °C while stirring. The solid of **14** dissolved gradually with time. After 24 h, the solution was distilled to get rid of the excess $SOCl_2$ and obtain a pale-yellow solid (2.5 g) of pyridine-2,6-dicarbonyl dichloride. (Yield: 63%).

2. In a previously cooled 250 mL RB flask in an ice bath, triethylamine (**7**, 3.7 mL, 25.7 mmol, 2.1 *eq.*) was added slowly to a clear solution of the diacyl chloride (2.5 g, 12.3 mmol) in 60 mL DCM with continuous stirring. Solid precipitate was formed during the addition. Next, the mixture was added drop-wisely to a stirred solution of 2,4,6-tris((dimethylamino)methyl)phenol (**1**, 7.42 mL, 25.7 mmol, 2.1 *eq.*) in DCM (20 mL), the mixture color was turned from yellow into maroon during the addition. The system was refluxed at 50 °C for 20 h, then the workup starts with an extraction with copious amount of distilled water to get rid of the salt (4×50 mL). After that, the organic layer was dried over Na_2SO_4, and concentrated till 10 mL. A quantitative amount of distilled petroleum

ether (*ca.* 40 mL) was added to the solution to precipitate the target ester linker (**15**) which was filtered, washed with distilled petroleum ether (3×15 mL) and dried to get white solid (3.11 g, Yield: 38%). ^{1}H NMR: (500 MHz, DMSO-d_6, ppm): δ = 8.02 (m, 3H), 7.19 (m, 4H), 3.76 (s, 12H), 2.37 (s, 36H). ^{13}C NMR (125 MHz, DMSO-d_6, ppm): δ = 167.8, 156.7, 152.9, 137.6, 131.7, 129.9, 125.2, 120.8, 60.6, 57.9, 43.3, 42.8, 38.6, 34.7. ATR-FTIR (cm^{-1}): 3392, 2976, 2946, 2814, 2763, 1758, 1606, 1565, 1468, 1416, 1354, 1297, 1230, 1167, 1150, 1075, 1030, 993, 948, 902, 837, 761, 714, 646, 556, 512, 445, 422, 406.

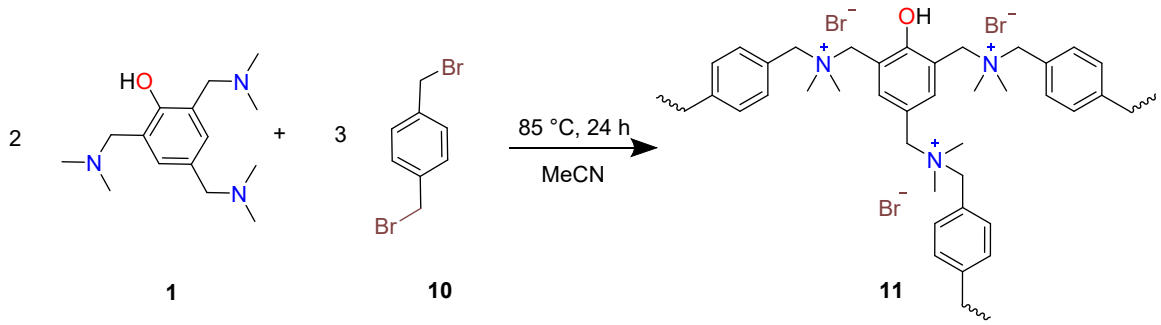
1.2.7 Synthesis of polymer 9



Scheme S14. Synthetic route of polymer **9**.

In a 50 mL RB flask, a solution of **8** (0.75 g, 2.05 mmol) in MeCN (30 mL) was added to the solution of **1** (0.53 mL, 2.05 mmol, 1 *eq.*) in MeCN (20 mL) and refluxed at 85 °C for 24 h. The white precipitate of polymer (**9**, 1.07 g) was filtered, washed with MeCN (30 mL) and dried under vacuum (Yield: 83%). CP MAS ^{13}C NMR (ppm): δ = 159.5, 142.7, 131.2, 120.2, 69.0, 65.4, 51.9, 51.5. ATR-FTIR (cm^{-1}): 3365, 2989, 2692, 1615, 1475, 1411, 1379, 1340, 1296, 1257, 1242, 1225, 1171, 1135, 1046, 1031, 902, 852, 750. TGA: T_{d50} took place at 313.5 °C.

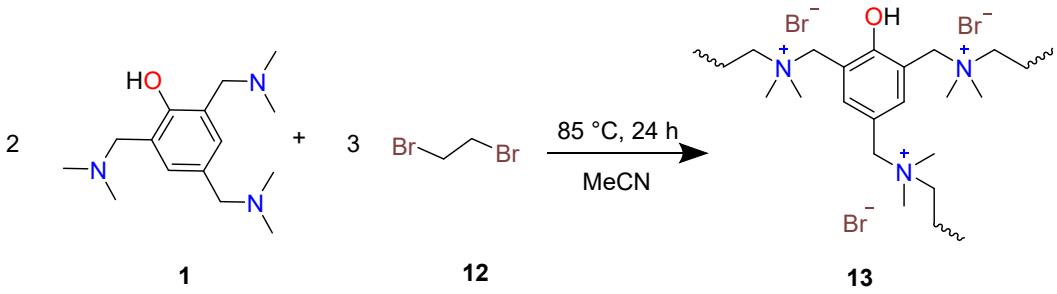
1.2.8 Synthesis of polymer 11



Scheme S15. Synthetic route of polymer **11**.

In a 50 mL RB flask, **1** (0.15 mL, 0.545 mmol) was added to a clear solution of α,α-dibromoxylene (**10**, 0.22 g, 0.82 mmol, 1.5 *eq*.) in 30 mL MeCN and refluxed at 85 °C for 24 h. Turbidity was observed after 5 mins. The white precipitate of **11** (710 mg) was filtered, washed with MeCN (30 mL), and dried under vacuum (Yield: 50%). CP MAS ^{13}C NMR (ppm): δ = 158.8, 141.7, 133.4, 118.3, 66.8, 63.5, 50.8, 47.2. ATR-FTIR (cm^{-1}): 854, 880, 997, 1000, 1137, 1174, 1223, 1302, 1378, 1477, 1616, 2958, 3000, 3393. TGA: T_{d50} took place at 315.8 °C.

1.2.9 Synthesis of polymer 13

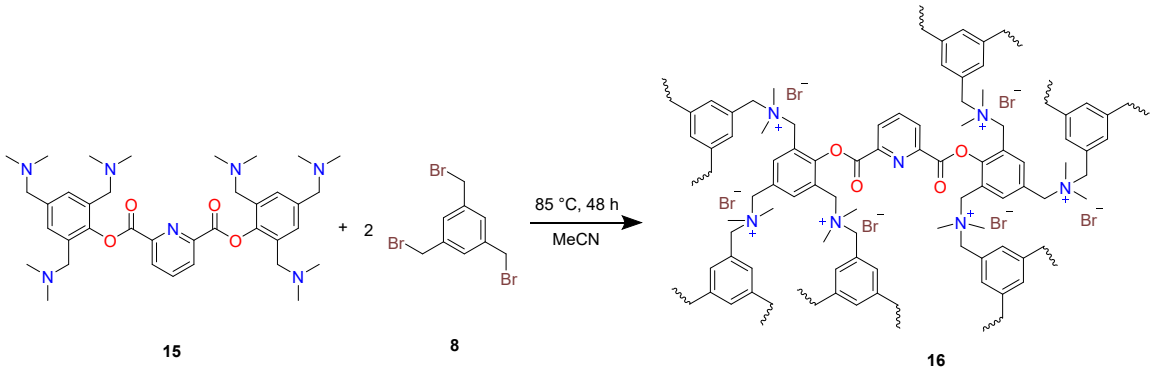


Scheme S16. Synthetic route of polymer **13**.

In a 50 mL RB flask, **1** (1.0 mL, 3.46 mmol) was dissolved in 10 mL MeCN, afterward, 1,2-dibromoethane (**12**, 0.46 mL, 5.2 mmol, 1.5 *eq*.) was added and the reaction mixture was refluxed at 85 °C for 24 h. Turbidity was observed after 30 mins. The white precipitate (**13**, 1.40 g) was filtered, washed with MeCN (30 mL), and dried under air overnight (Yield:

72 %). CP MAS ^{13}C NMR (ppm): δ = 158.8, 146.1, 122.4, 67.8, 66.6, 51.2. ATR-FTIR (cm^{-1}): 3386, 3012, 2968, 2621, 2586, 2564, 2458, 1615, 1507, 1476, 1410, 1374, 1318, 1298, 1231, 1174, 1134, 1061, 1026, 976, 971, 921, 849, 812, 522. TGA: T_{d50} took place at 314.2 °C.

1.2.10 Synthesis of polymer 16



Scheme S17. Synthetic route of polymer **16**.

In 50 mL RB flask, a solution of **15** (0.50 g, 0.76 mmol) in MeOH (5 mL) was added to a solution of **8** (0.55 g, 1.51 mmol, 2 *eq.*) in MeCN (50 mL) and refluxed for 48 h at 85 °C. The white solid of **16** was observed within 15 min. After cooling to RT, the solid was filtered and washed with MeCN (10 mL) to get 800 mg (Yield: 76%). CP MAS ^{13}C NMR (ppm): δ = 170.5, 157.1, 138.7, 129.1, 118.6, 66.4, 63.1, 50.1, 46.0 ATR-FTIR (cm^{-1}): 3386, 3008, 2960, 1701, 1616, 1477, 1377, 1299, 1203, 1176, 1137, 1023, 1031, 906, 856, 750, 522, 474. TGA: T_{d50} took place at 274.1 °C.

2 Characterization

2.1 Characterization of the precursors and monomers

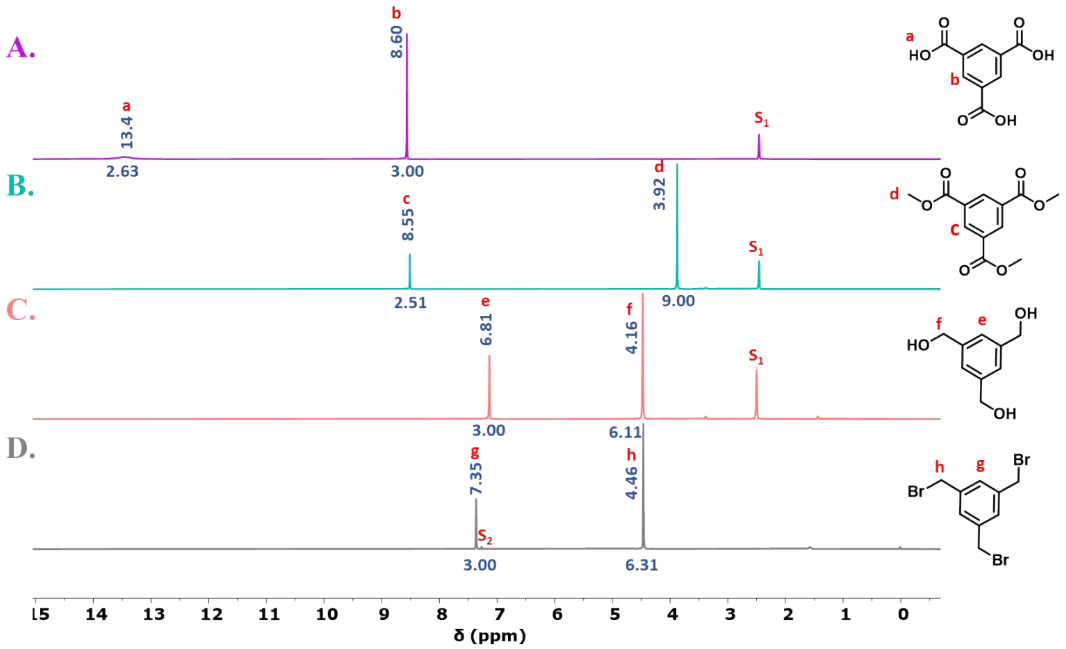


Figure S1. ^{1}H NMR spectra of **A.** trimesic acid **20** (purple trace), **B.** trimethyl benzene-1,3,5-tricarboxylate **21** (dark teal trace), **C.** benzene-1,3,5-triyltrimethanol **22** (rose trace), **D.** 1,3,5-tris(bromomethyl)benzene **8** (gray trace), $\mathbf{S_1}$: DMSO-d_6, $\mathbf{S_2}$: $CDCl_3$.

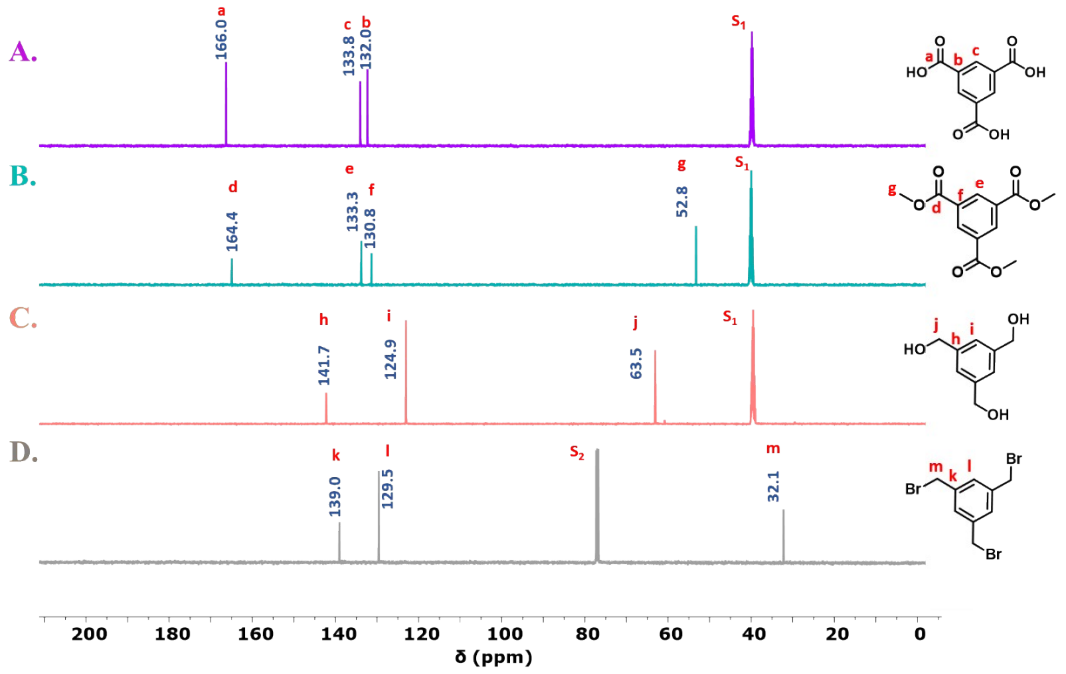


Figure S2. ^{13}C NMR spectra of **A.** trimesic acid **20** (purple trace), **B.** trimethyl benzene-1,3,5-tricarboxylate **21** (dark teal trace), **C.** benzene-1,3,5-triyltrimethanol **22** (rose trace), **D.** 1,3,5-tris(bromomethyl)benzene **8** (gray trace), $\mathbf{S_1}$: DMSO-d_6, $\mathbf{S_2}$: $CDCl_3$.

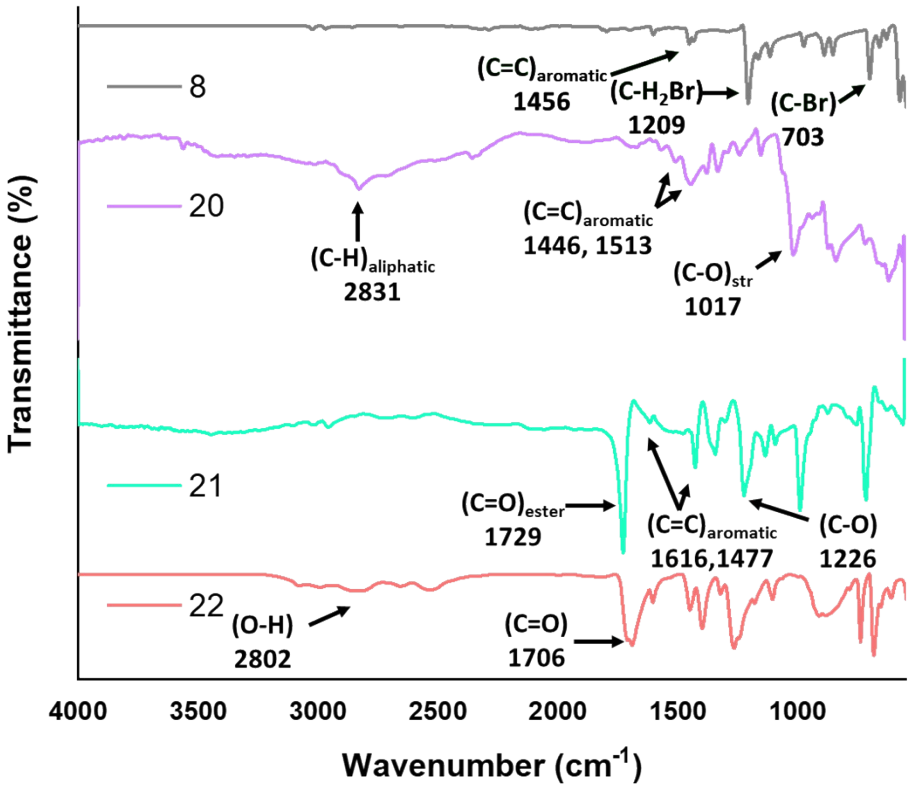


Figure S3. ATR-FTIR spectra of trimesic acid (**20**, purple trace), trimethyl benzene-1,3,5-tricarboxylate (**21**, dark teal trace), benzene-1,3,5-triyltrimethanol (**22**, rose trace), and 1,3,5-tris(bromomethyl)benzene (**8**, gray trace).

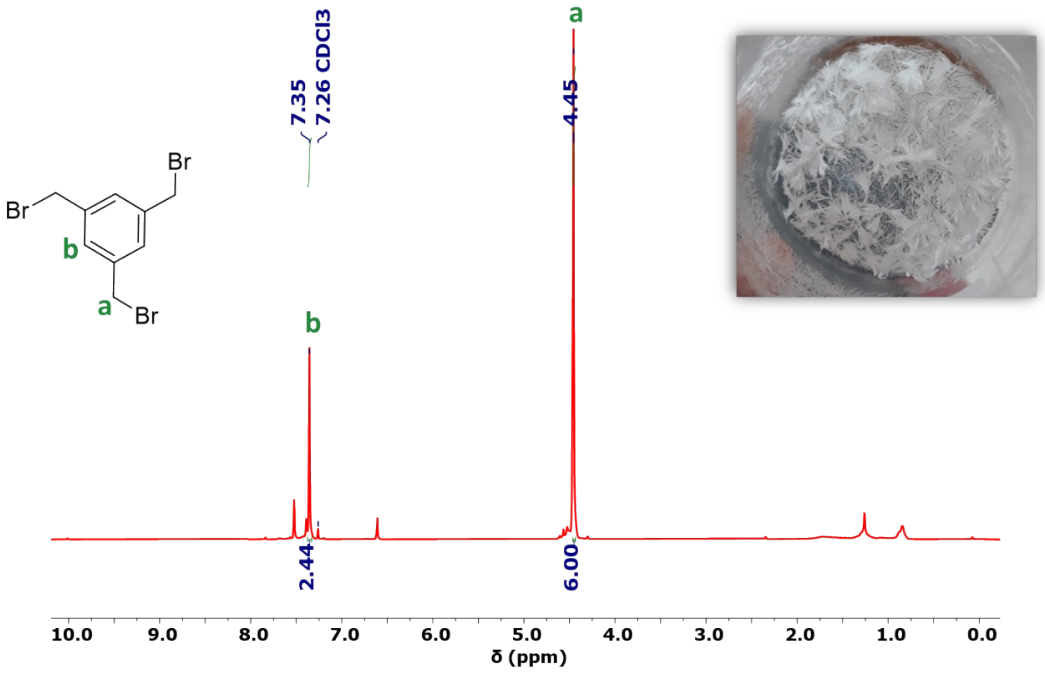


Figure S4. ^{1}H NMR spectrum of isolated **8** from the column, **Path A**

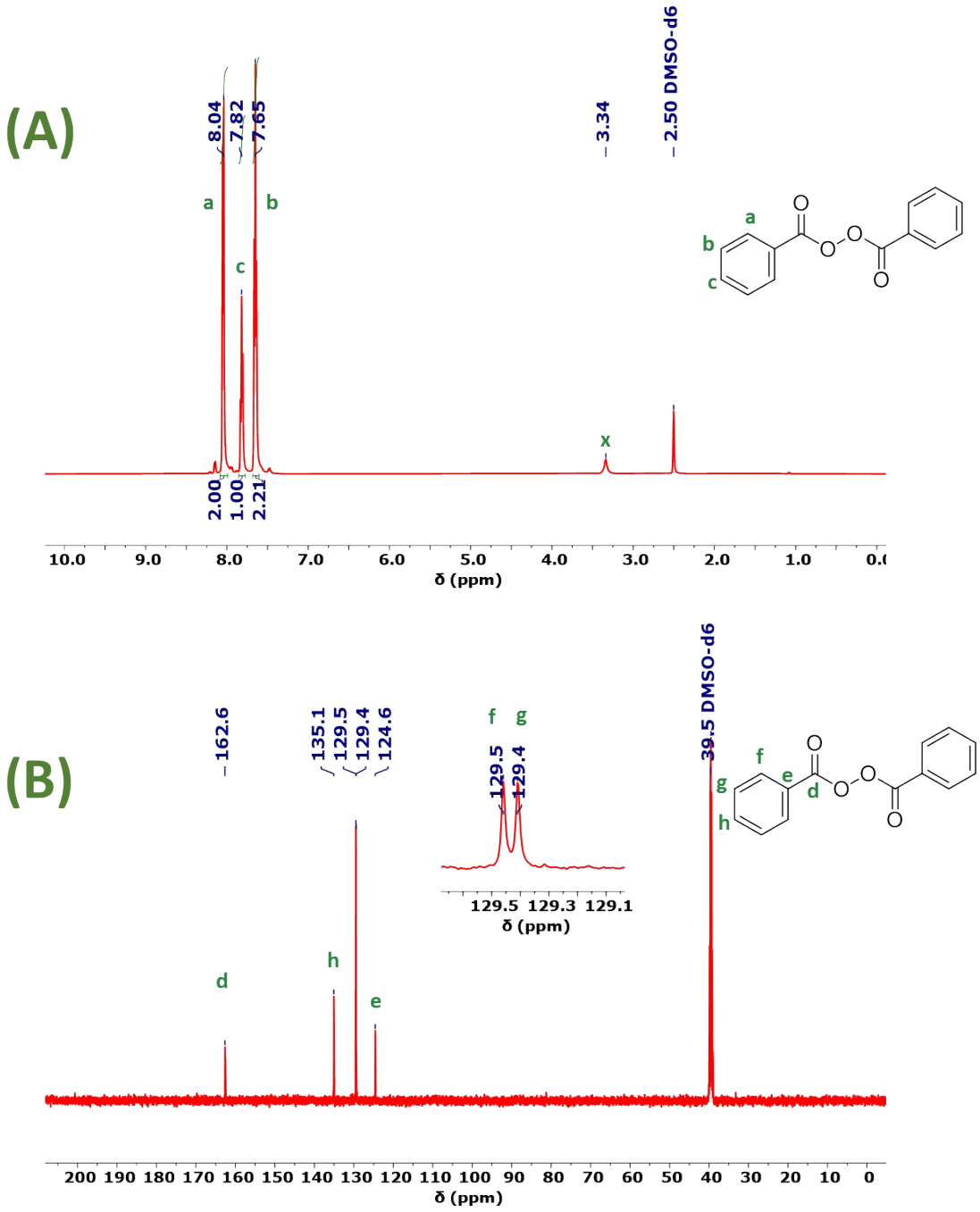


Figure S5. (**A**) ^{1}H NMR and (**B**) ^{13}C NMR spectra of **18**.

2.2 Characterization of the Catalysts

2.2.1 Characterization of catalyst 3

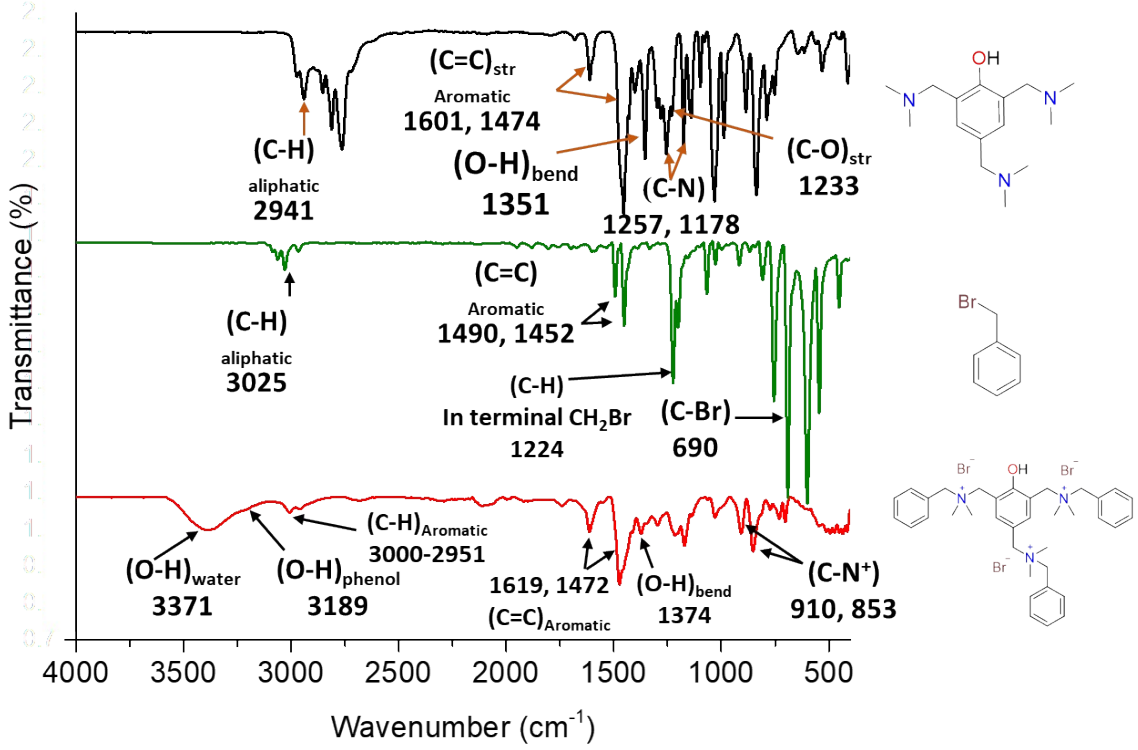


Figure S6. The ATR-FTIR spectra of the starting materials **1** and **2** (black and dark green traces, respectively) as well as the prepared catalyst **3** (red trace).

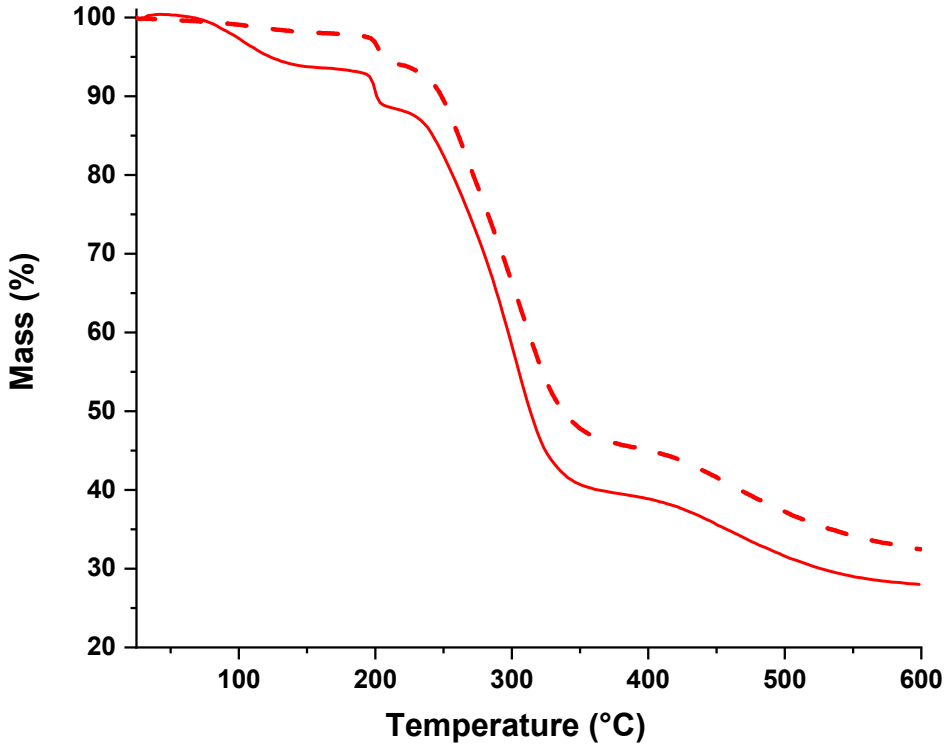


Figure S7. TGA profile for catalyst **3** without drying (red trace), and together with a one-hour fixed isotherm analysis (red dashed trace).

2.2.2 Characterization of the dissected catalysts

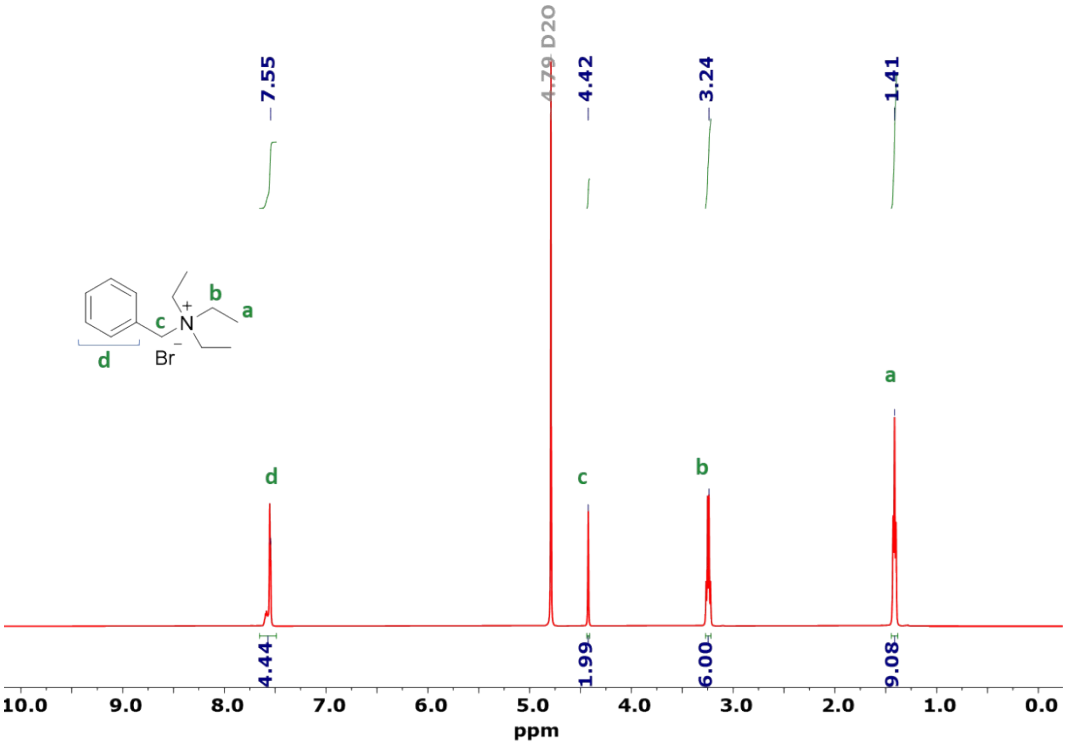


Figure S8. ^{1}H NMR spectrum of **5**.

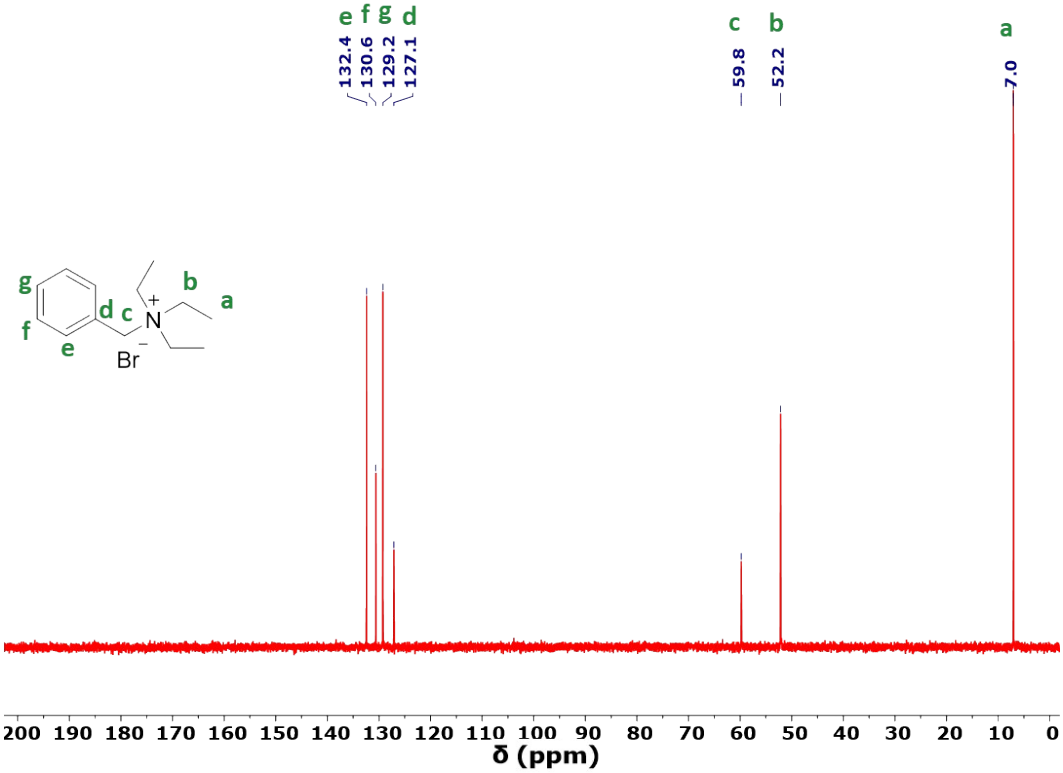


Figure S9. ^{13}C NMR spectrum of **5**.

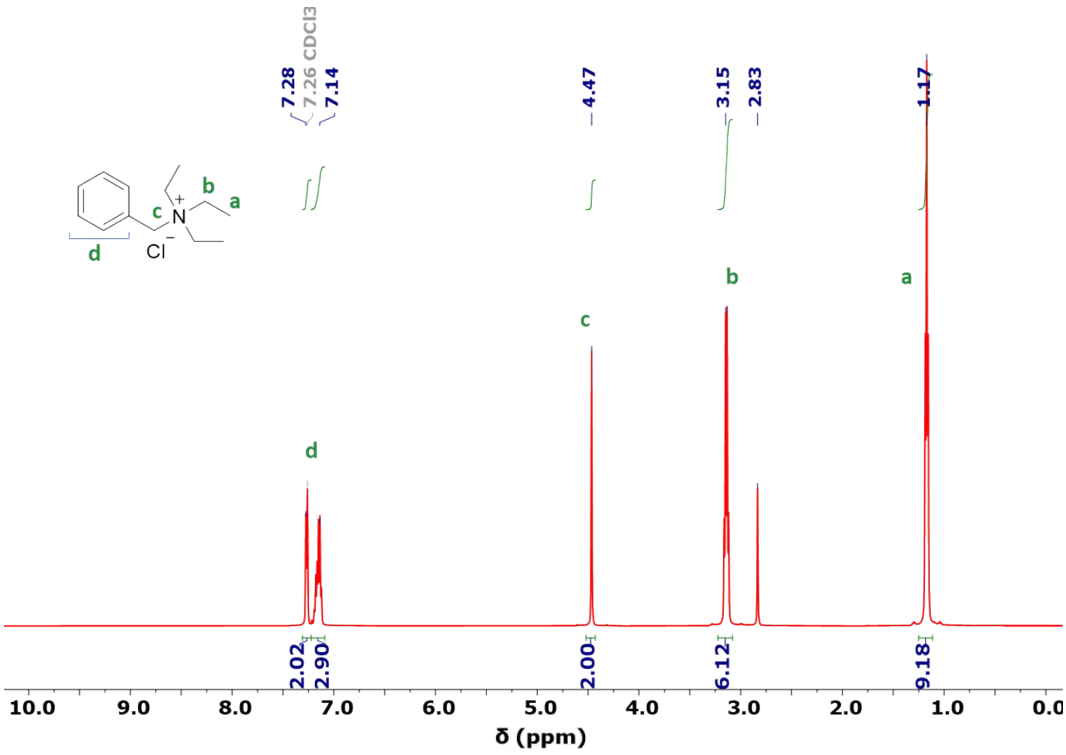


Figure S10. ^{1}H NMR spectrum of **5a**.

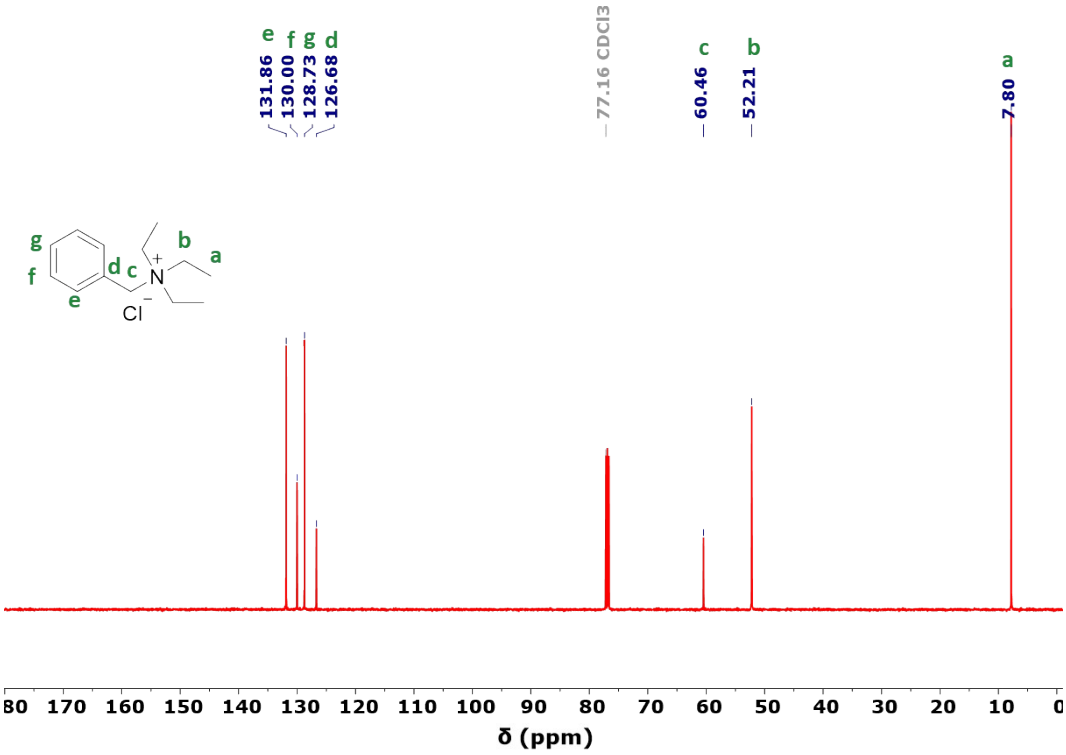


Figure S11. ^{13}C NMR spectrum of **5a**.

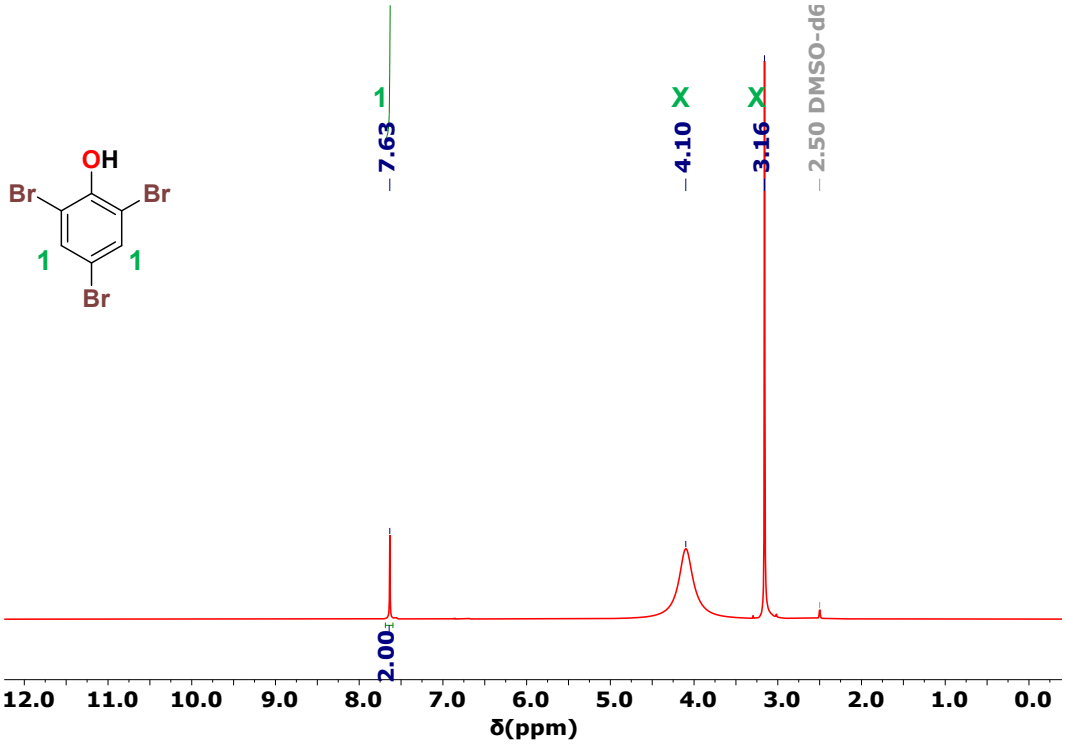


Figure S12. ^{1}H NMR spectrum of **6** in DMSO-d_6. Peaks at 3.16 and 4.10 ppm corresponding to methanol.

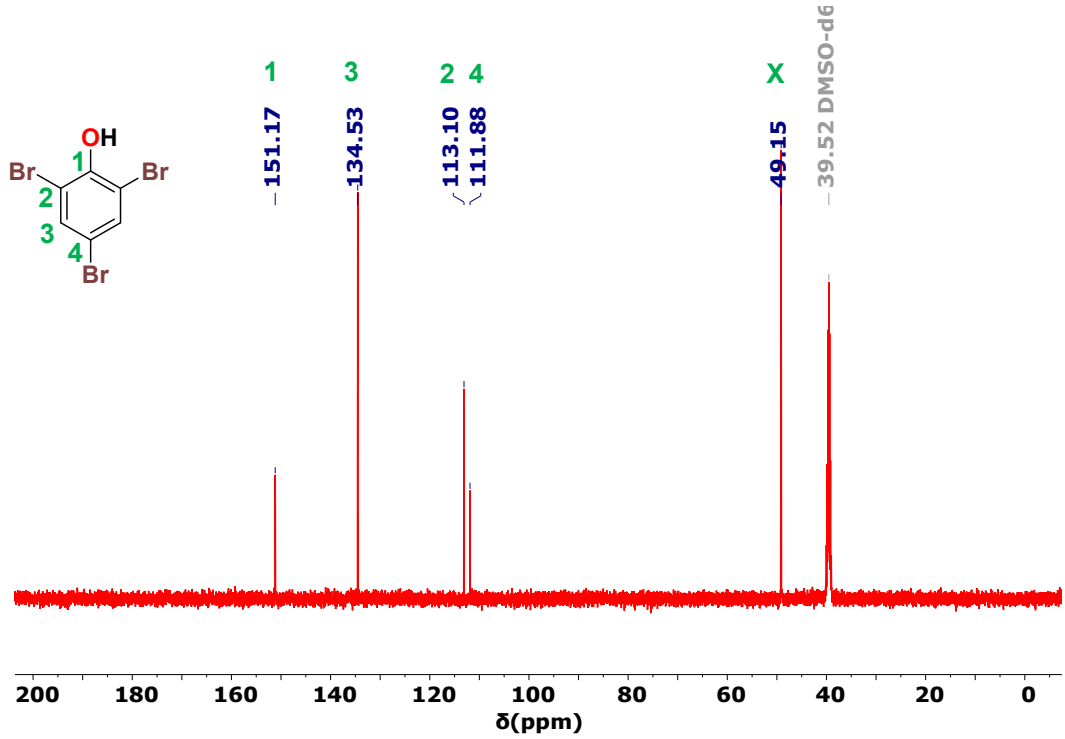


Figure S13. ^{13}C NMR spectrum of **6** in DMSO-d_6. Peak at 49.15 ppm corresponding to methanol.

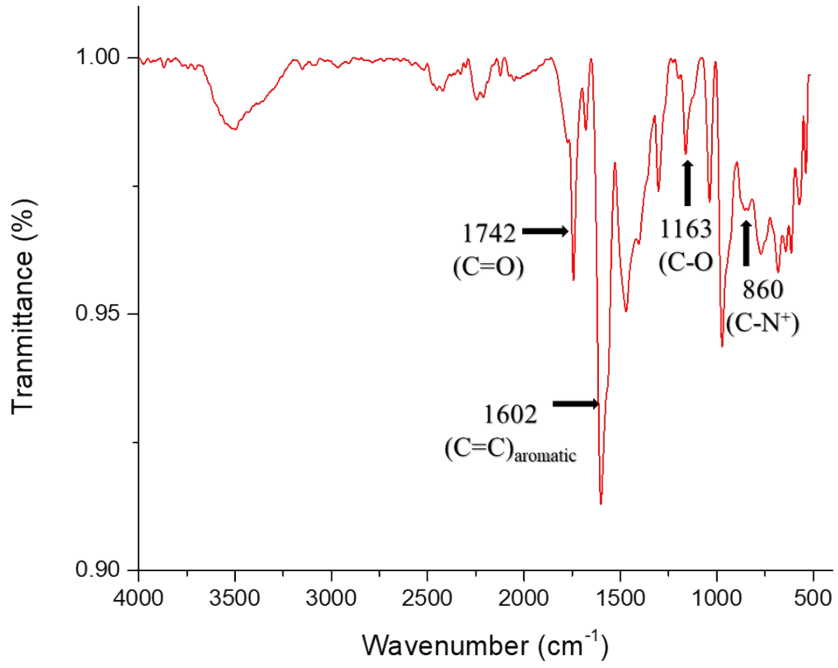


Figure S14. ATR-FTIR spectrum of the corresponding model **3''**.

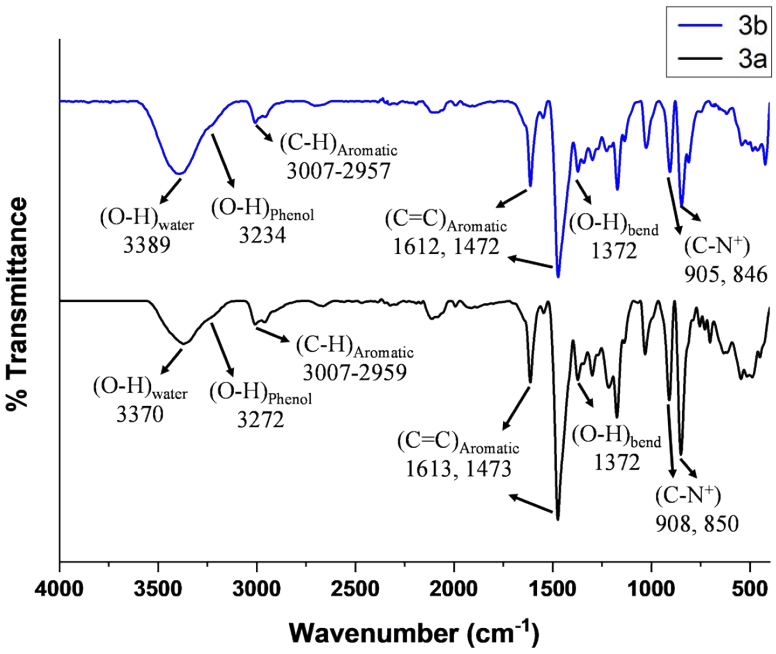


Figure S15. ATR-FTIR spectra of the corresponding model **3a**, and **3b**.

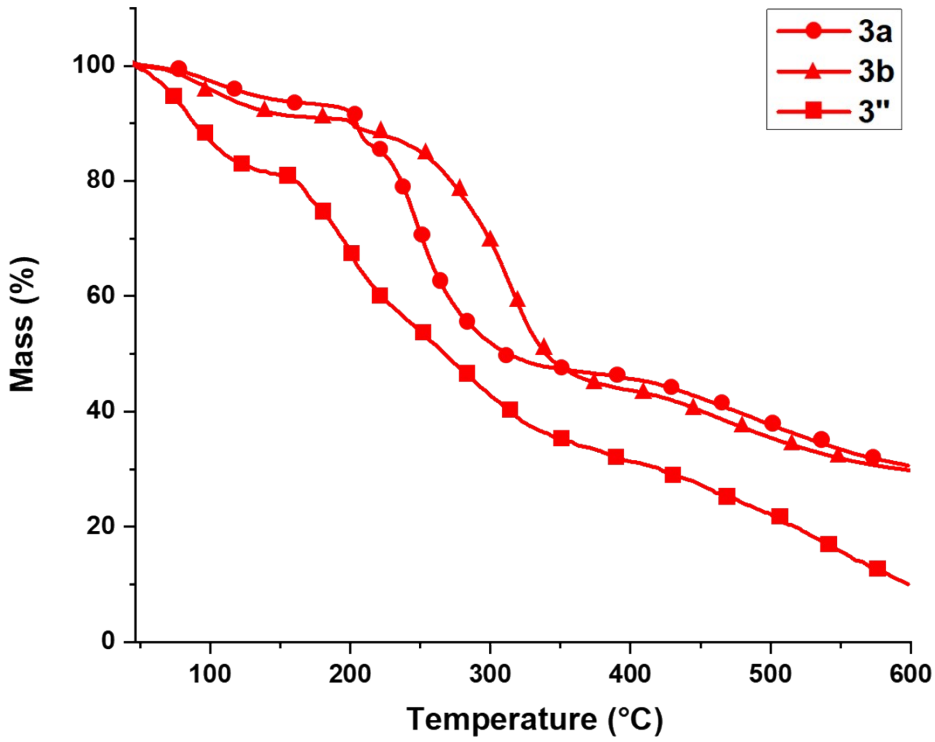


Figure S16. TGA profile for the corresponding model **3a** (circle line), **3b** (triangle line), and **3''** (square line).

2.2.3 Characterization of the polymers (9, 11, 13, and 16)

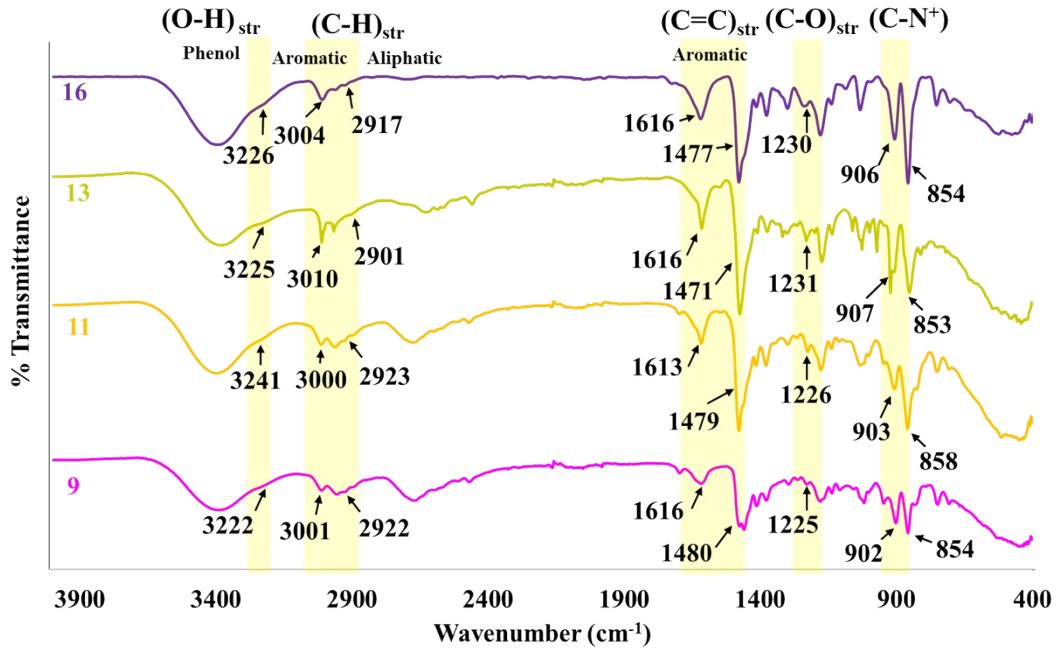


Figure S17. ATR-FTIR spectra of the polymers **9** (pink trace), **11** (orange trace), **13** (yellow trace), and **16** (dark purple trace).

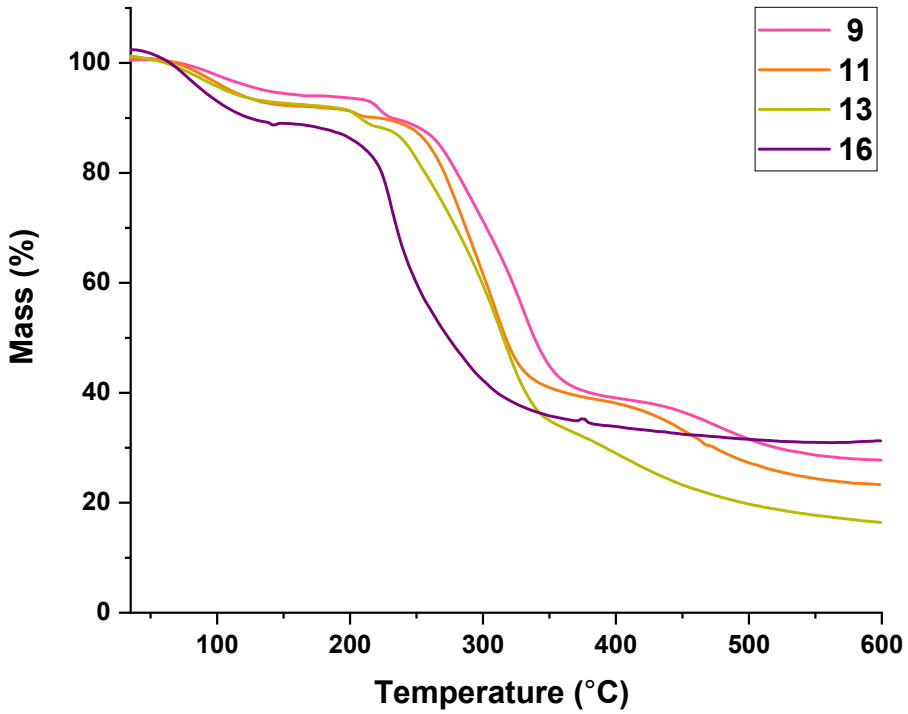


Figure S18. TGA traces of the polymers **9** (pink trace), **11** (orange trace), **13** (yellow trace), and **16** (dark purple trace).

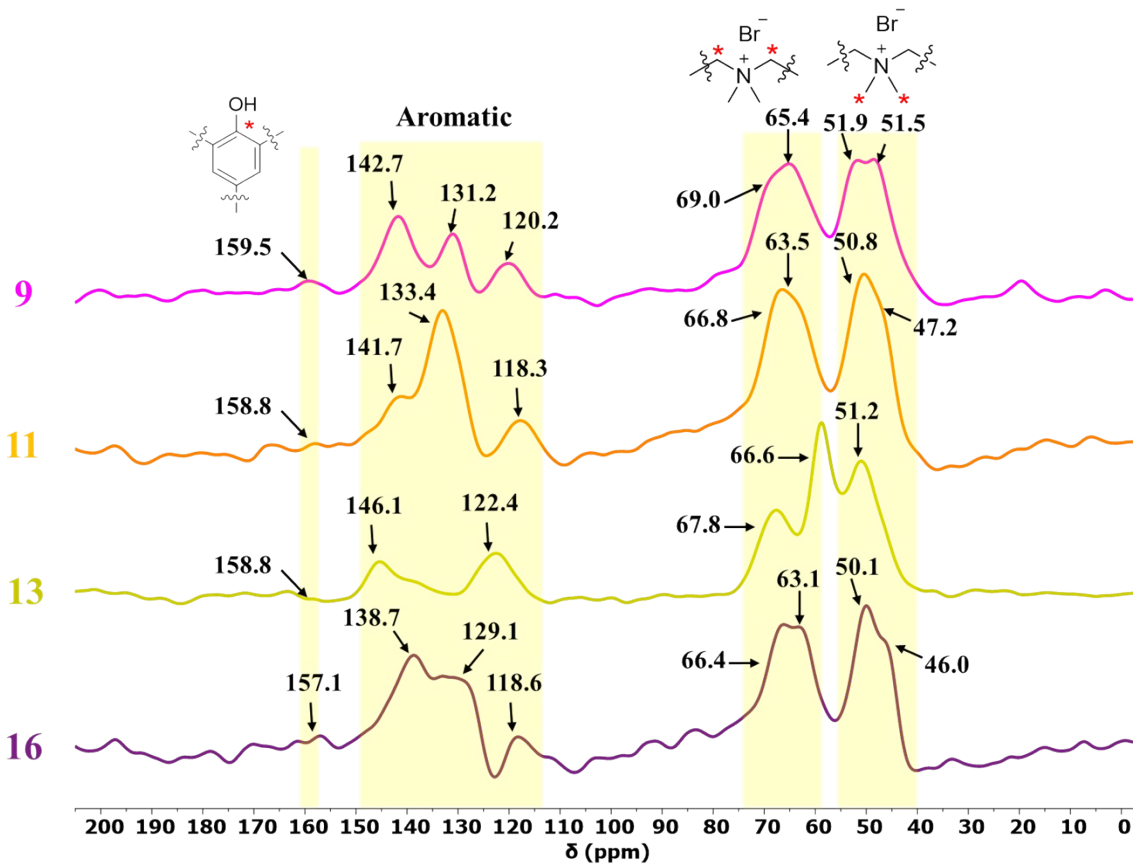


Figure S19. CP MAS ^{13}C NMR spectra of the polymers **9** (pink trace), **11** (orange trace), **13** (yellow trace), and **16** (dark purple trace).

3 ^{1}H NMR spectra of the ECH conversions for recyclability

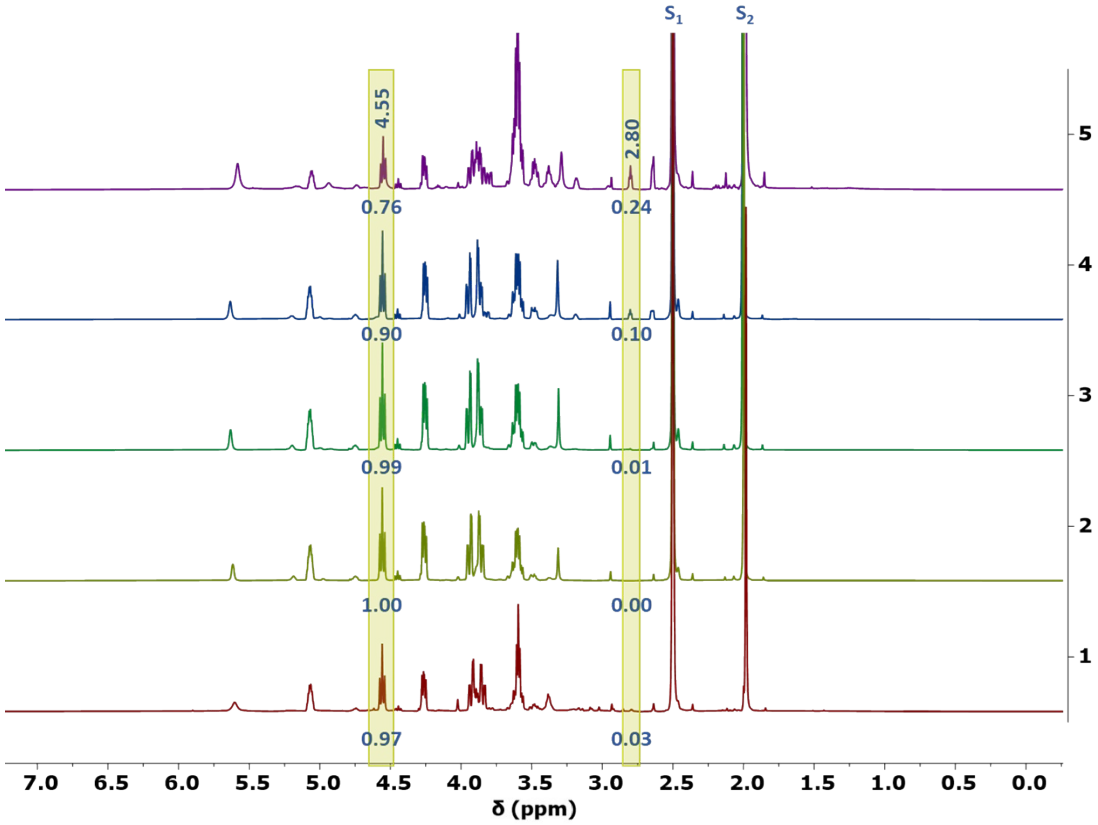


Figure S20. ^{1}H NMR spectra of the ECH conversion to it corresponding CC for 5 runs in testing the recyclability using **3**, first trial. $\mathbf{S_1}$: DMSO-d_6, $\mathbf{S_2}$: MeCN.

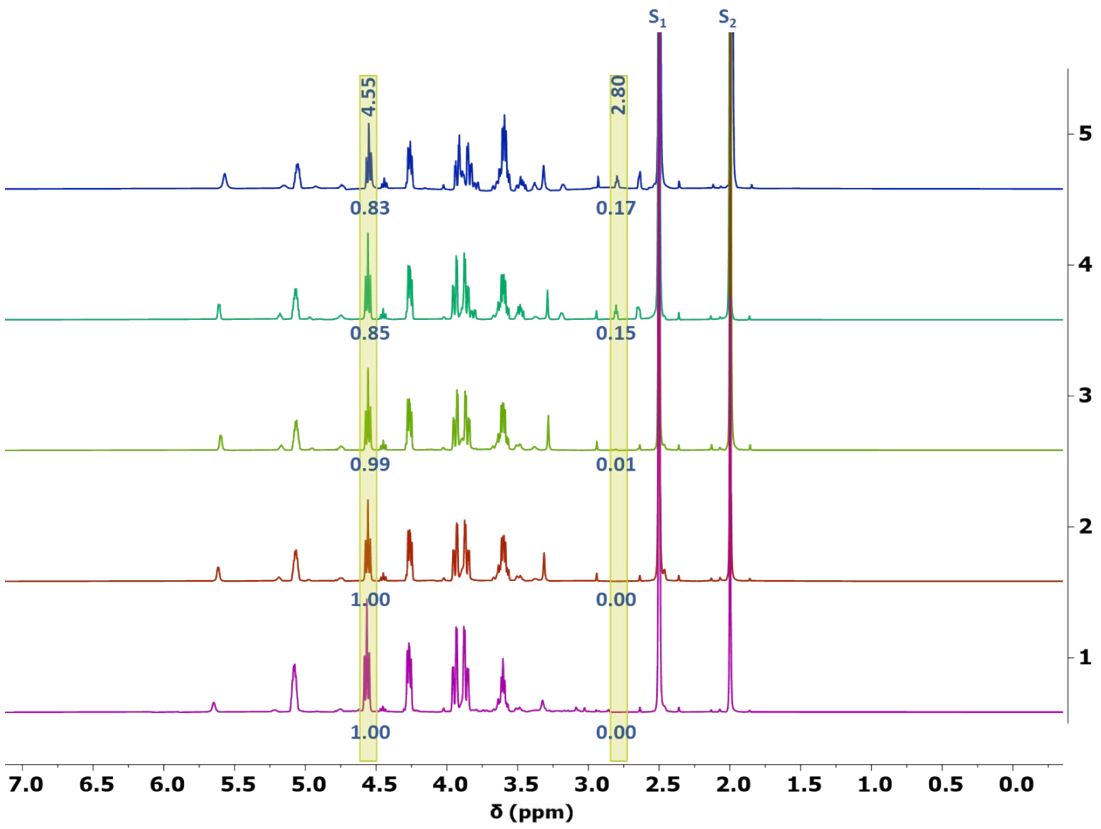


Figure S21. ^{1}H NMR spectra of the ECH conversion to it corresponding CC for 5 runs in testing the recyclability using **3**, second trial. $\mathbf{S_1}$: DMSO-d_6, $\mathbf{S_2}$: MeCN.

4 ^{1}H NMR spectra of the cycloaddition reaction for 8 h

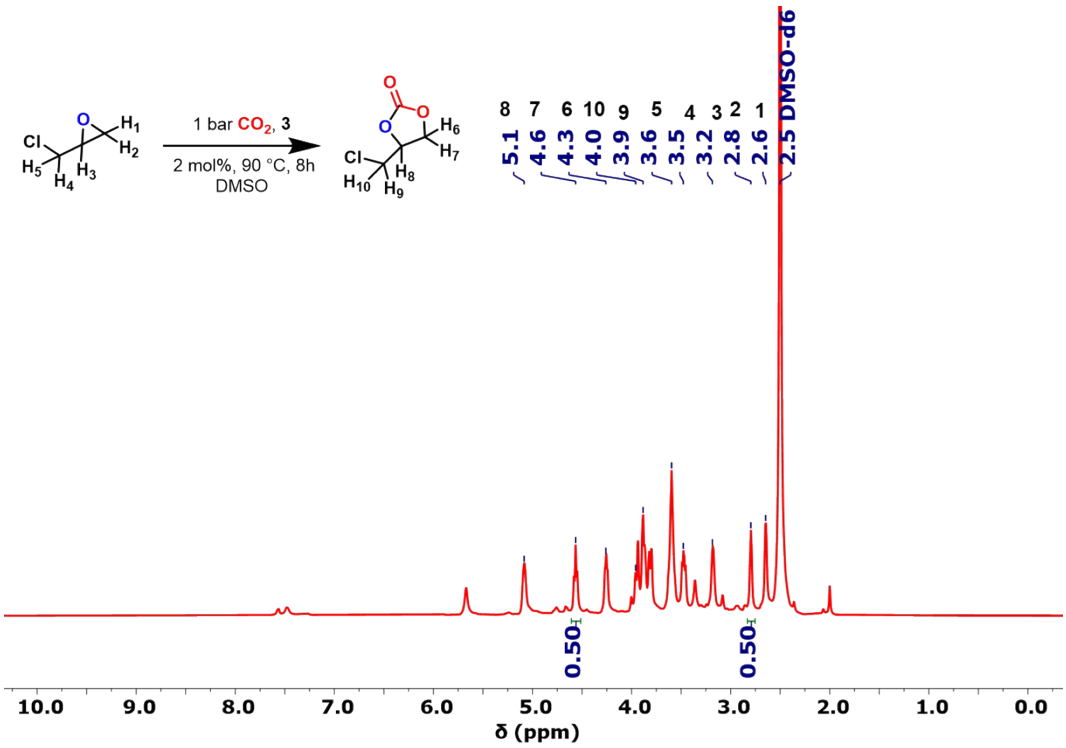


Figure S22. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using 2 mol% of **3** for 8 h.

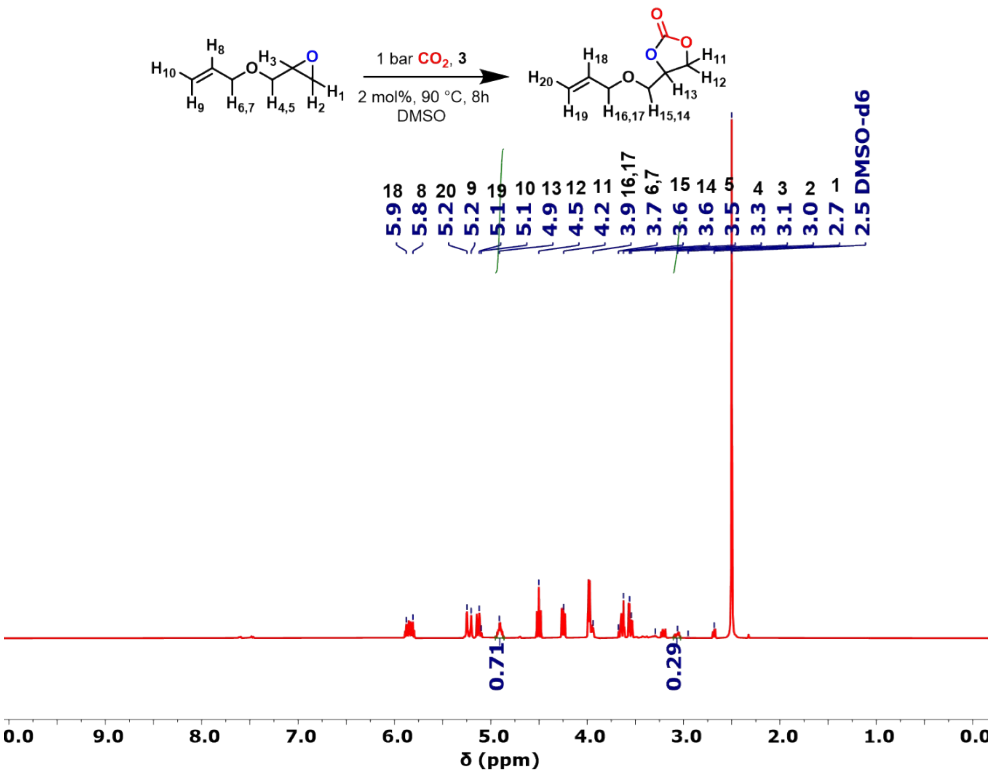


Figure S23. ^{1}H NMR spectrum of allyl glycidyl ether conversion to its corresponding CC in DMSO-d_6 using 2 mol% of **3** for 8 h.

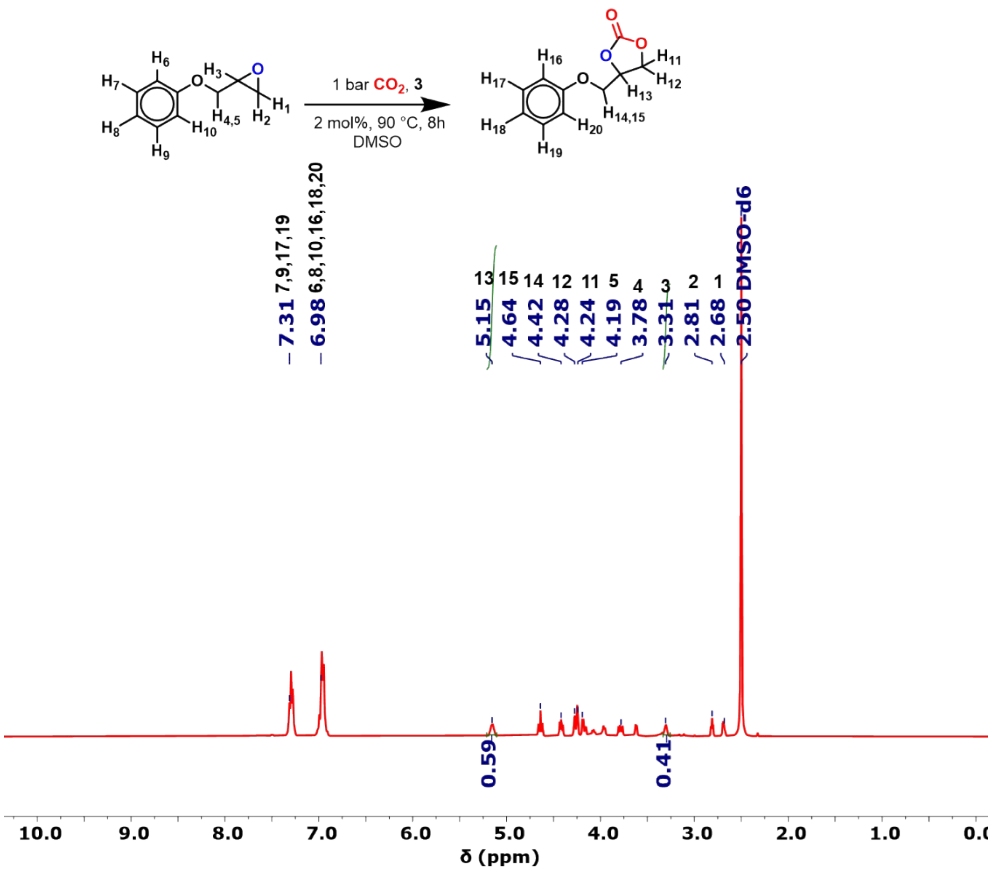


Figure S24. ^{1}H NMR spectrum of 1,2-epoxy-3-phenoxypropane conversion to its corresponding CC in DMSO-d_6 using 2 mol% of **3** for 8 h.

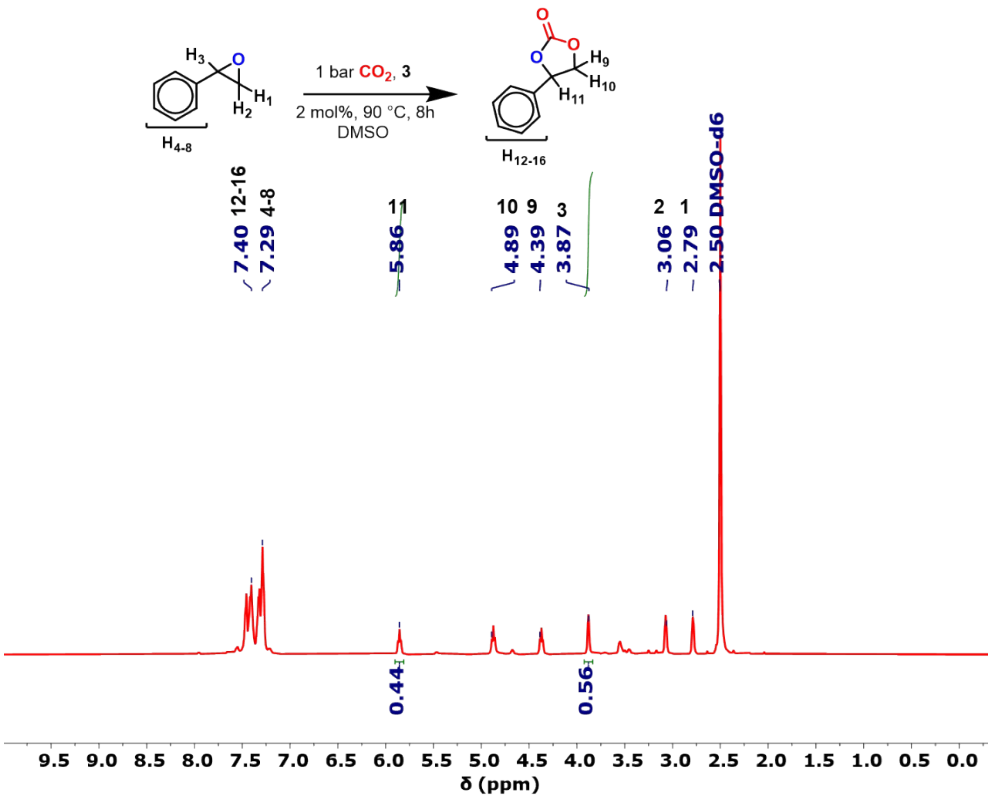


Figure S25. [1]H NMR spectrum of styrene oxide conversion to its corresponding CC in DMSO-d_6 using 2 mol% of **3** for 8 h.

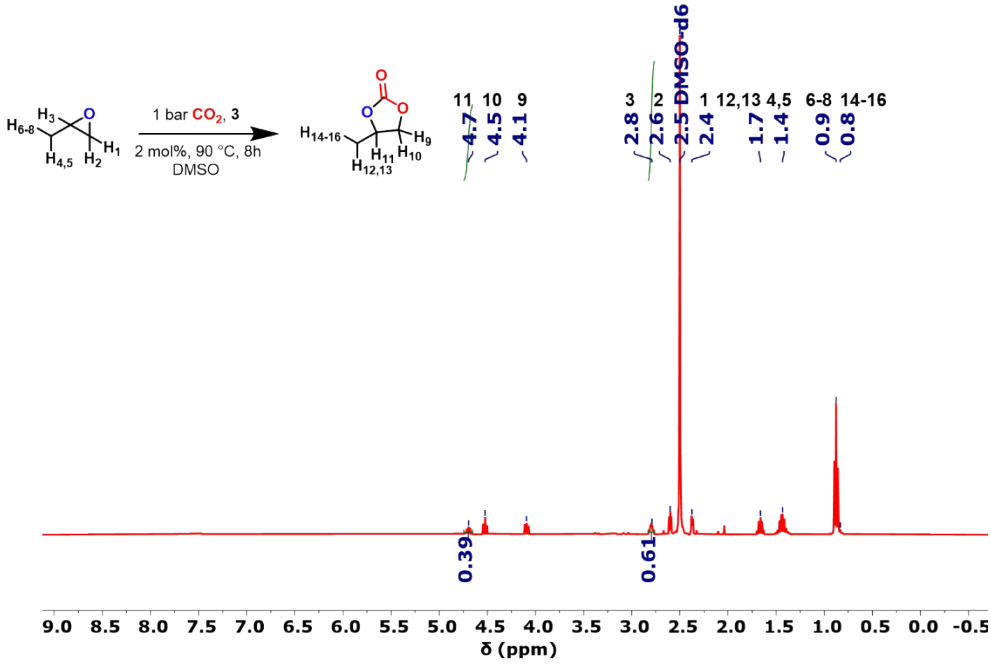


Figure S26. [1]H NMR spectrum of 1,2-epoxybutane conversion to its corresponding CC in DMSO-d_6 using 2 mol% of **3** for 8 h.

5 ^{1}H NMR spectra of the cycloaddition reaction for 24 h

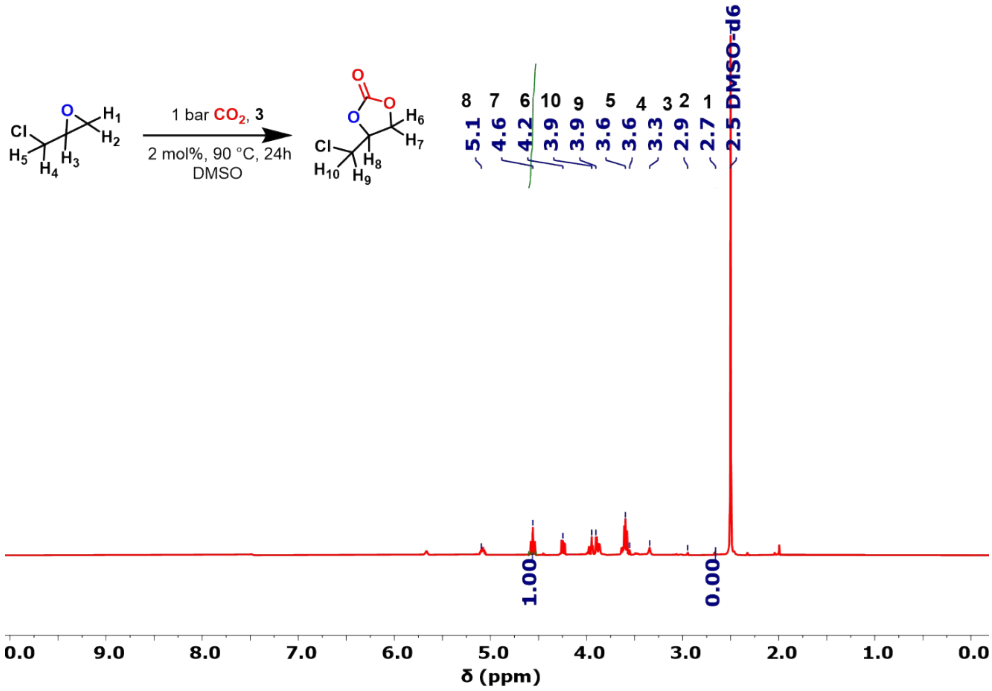


Figure S27. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using 2 mol% of **3** for 24 h.

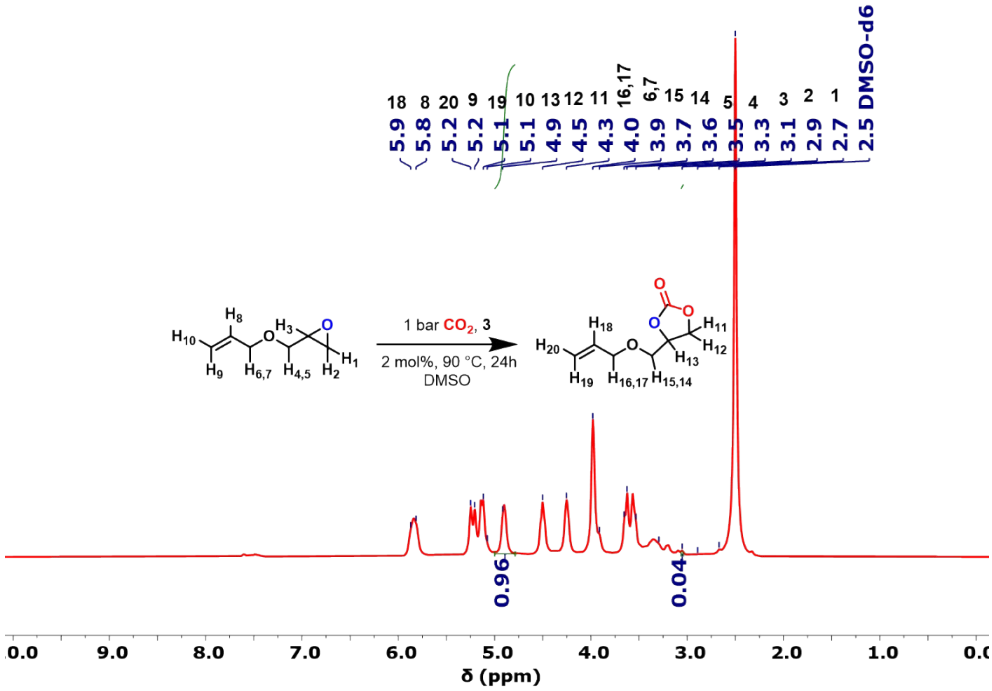


Figure S28. ^{1}H NMR spectrum of allyl glycidyl ether conversion to its corresponding CC in DMSO-d_6 using 2 mol% of **3** for 24 h.

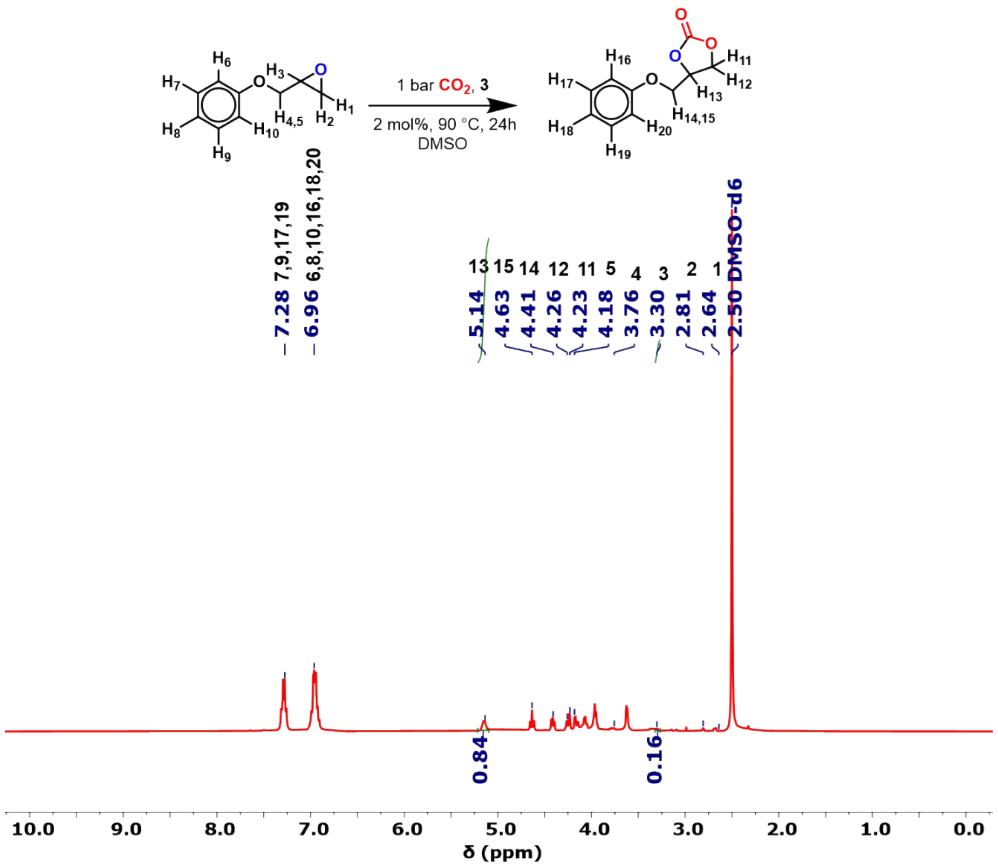


Figure S29. ^{1}H NMR spectrum of 1,2-epoxy-3-phenoxypropane conversion to its corresponding CC in DMSO-d_6 using 2 mol% of **3** for 24 h.

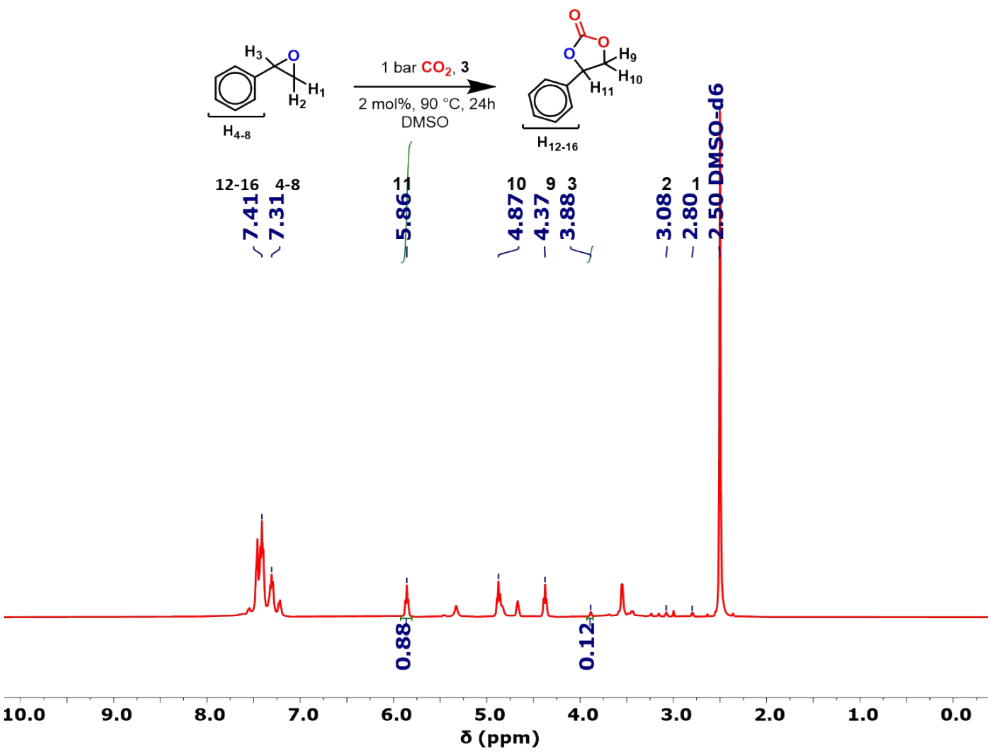


Figure S30. [1]H NMR spectrum of styrene oxide conversion to its corresponding CC in DMSO-d_6 using 2 mol% of **3** for 24 h.

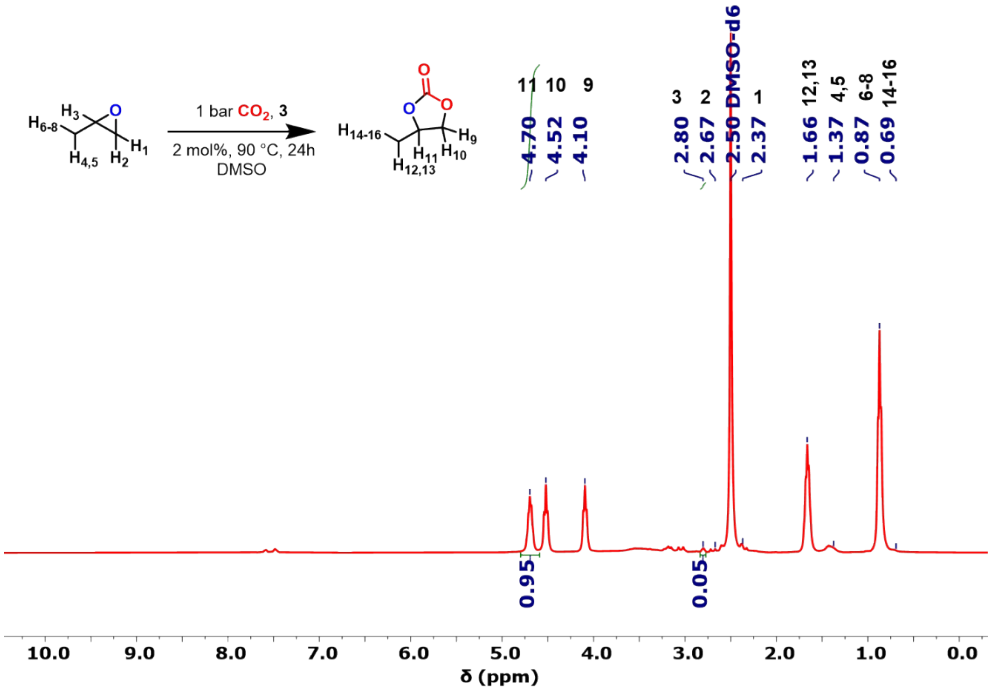


Figure S31. [1]H NMR spectrum of 1,2-epoxybutane conversion to its corresponding CC in DMSO-d_6 using 2 mol% of **3** for 24 h.

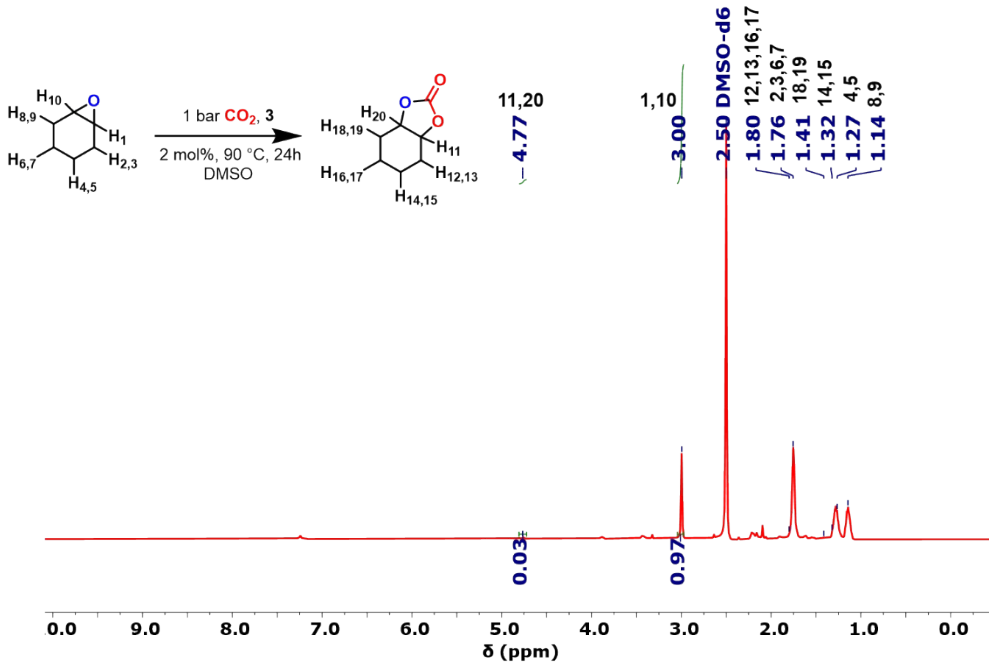


Figure S32. [1]H NMR spectrum of cyclohexene oxide conversion to its corresponding CC in DMSO-d_6 using 2 mol% of **3** for 24 h.

6 Characterization of the isolated CCs

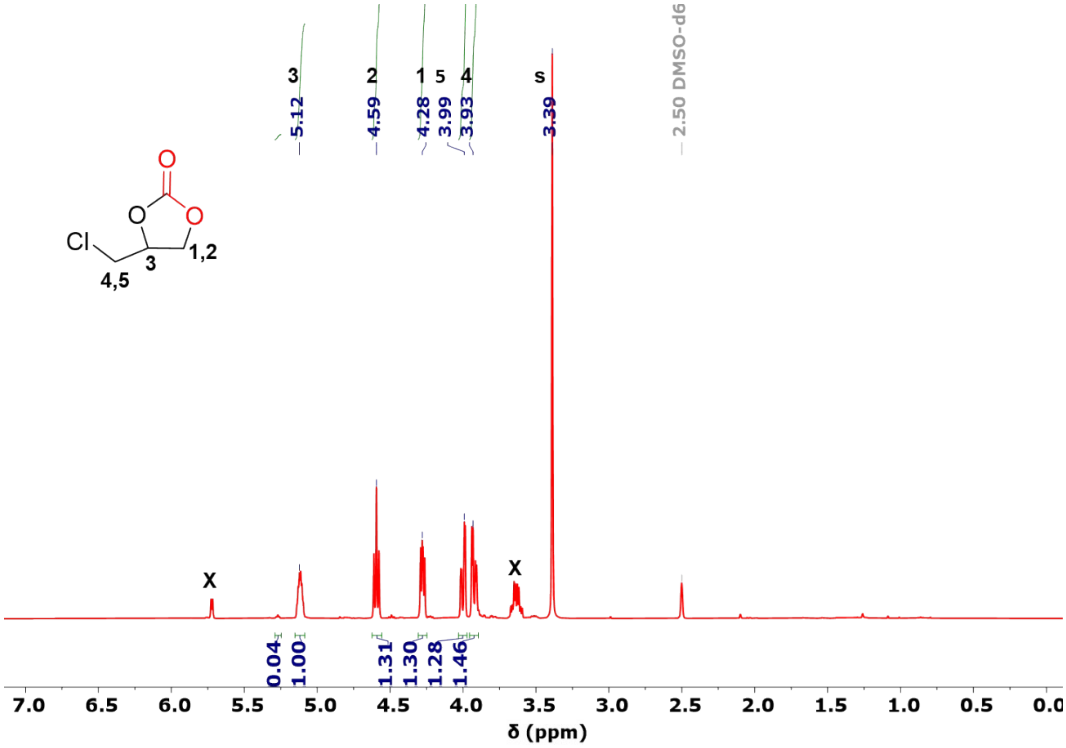


Figure S33. [1]H NMR spectrum of the isolated 4-(chloromethyl)-1,3-dioxolan-2-one in DMSO-d_6. **x**:1,2-diol (from the starting material as supplied by the chemical vendor), **s**: water.

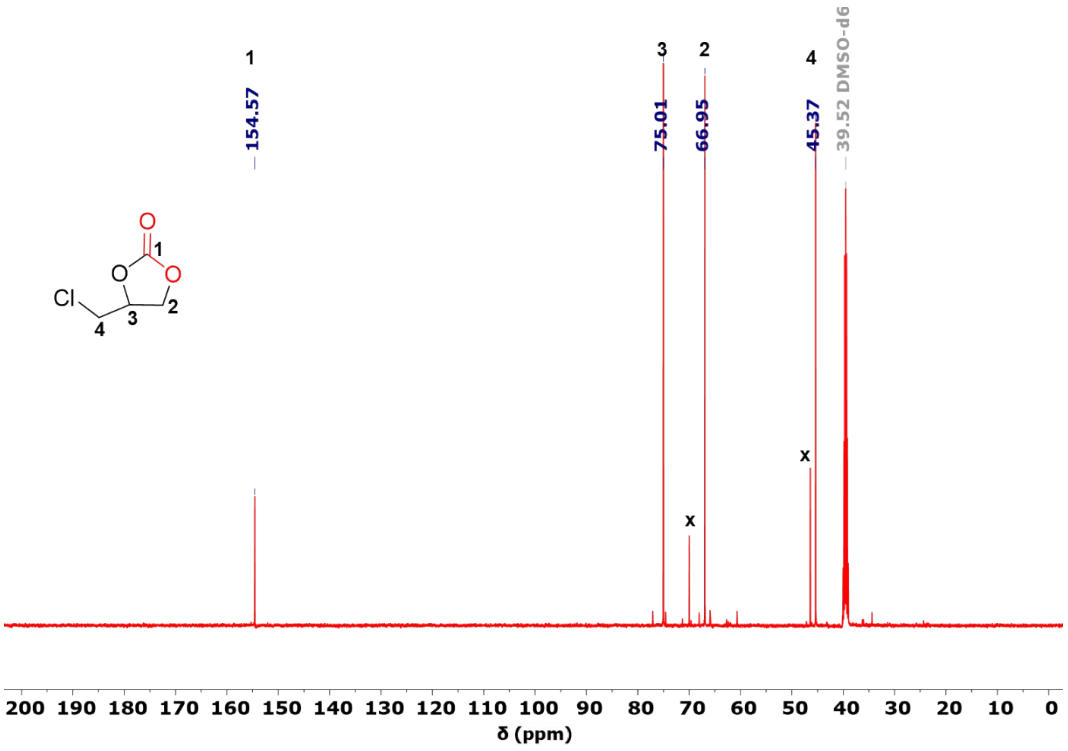


Figure S34.[13]C NMR spectrum of the isolated 4-(chloromethyl)-1,3-dioxolan-2-one in DMSO-d_6. **x**:1,2-diol (from the starting material as supplied by the chemical vendor).

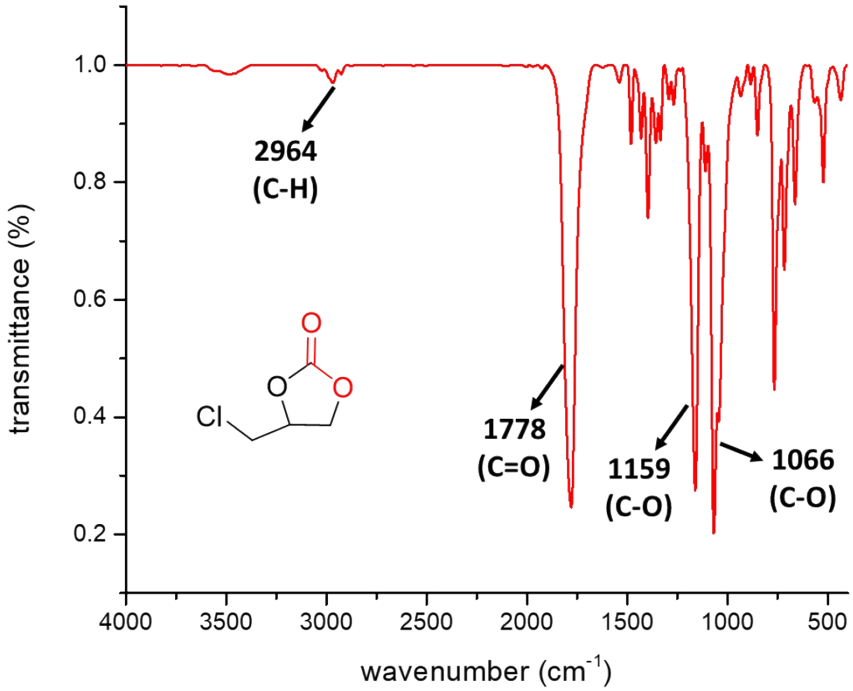


Figure S35. ATR-FTIR spectrum of the isolated 4-(chloromethyl)-1,3-dioxolan-2-one.

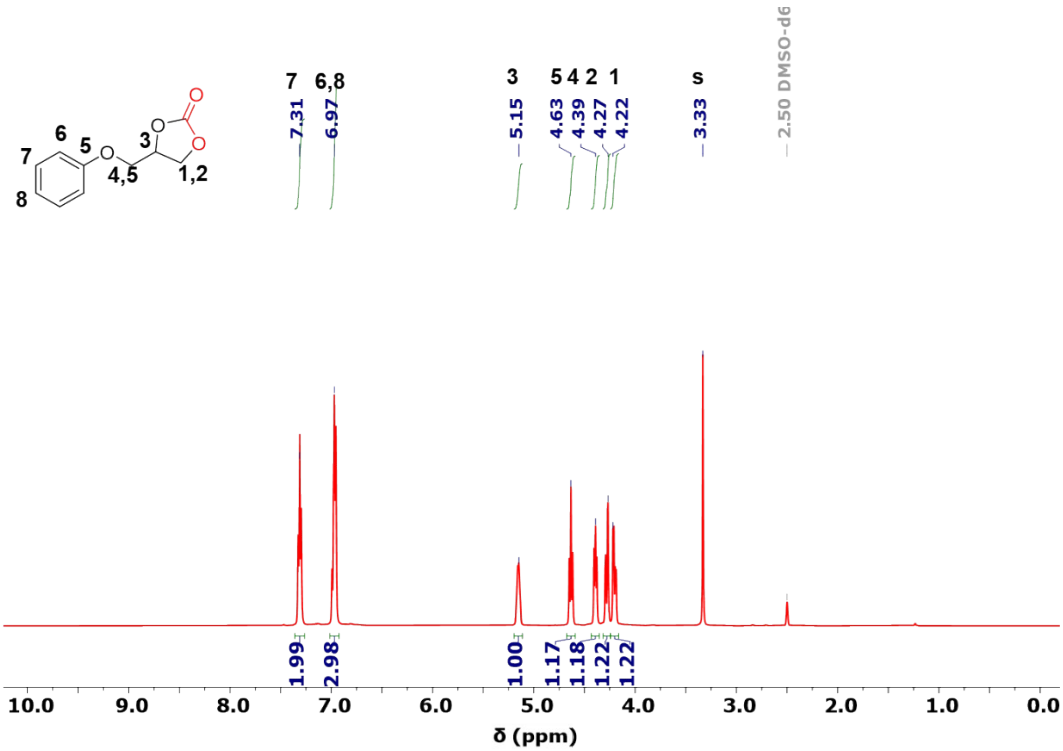


Figure S36. [1]H NMR spectrum of the isolated 4-(phenoxymethyl)-1,3-dioxolan-2-onein DMSO-d_6. **s**: water.

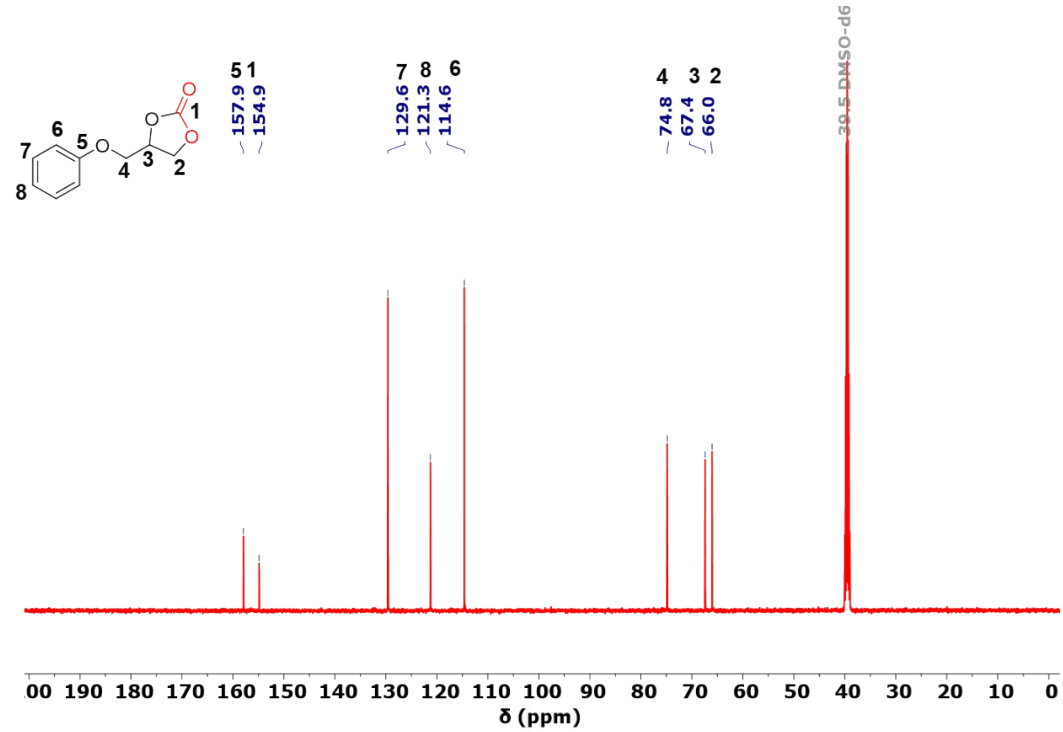


Figure S37.[13]C NMR spectrum of the isolated 4-(phenoxymethyl)-1,3-dioxolan-2-one in DMSO-d_6.

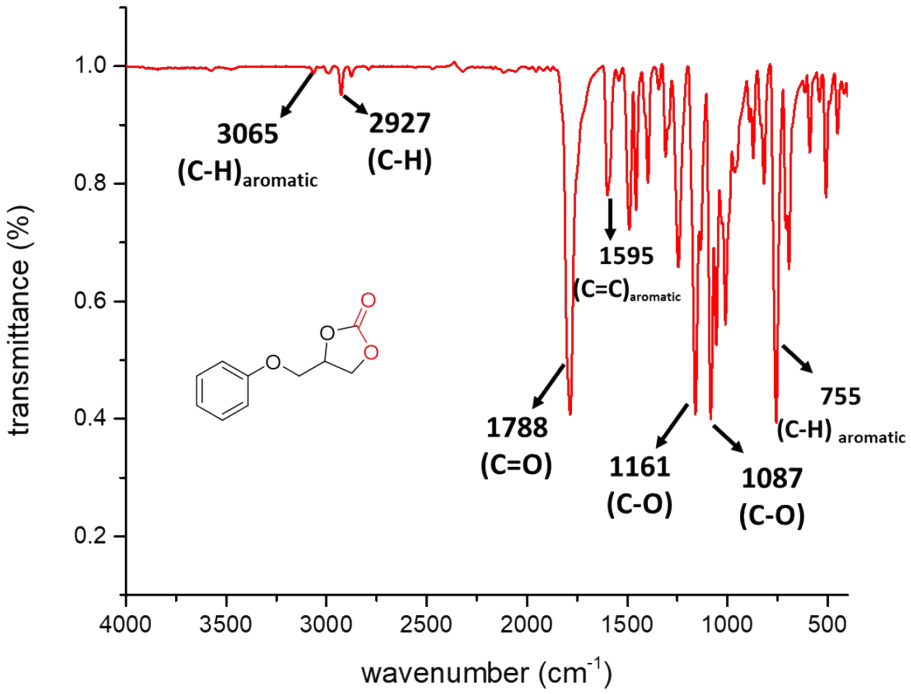


Figure S38. ATR-FTIR spectrum of the isolated 4-(phenoxymethyl)-1,3-dioxolan-2-one.

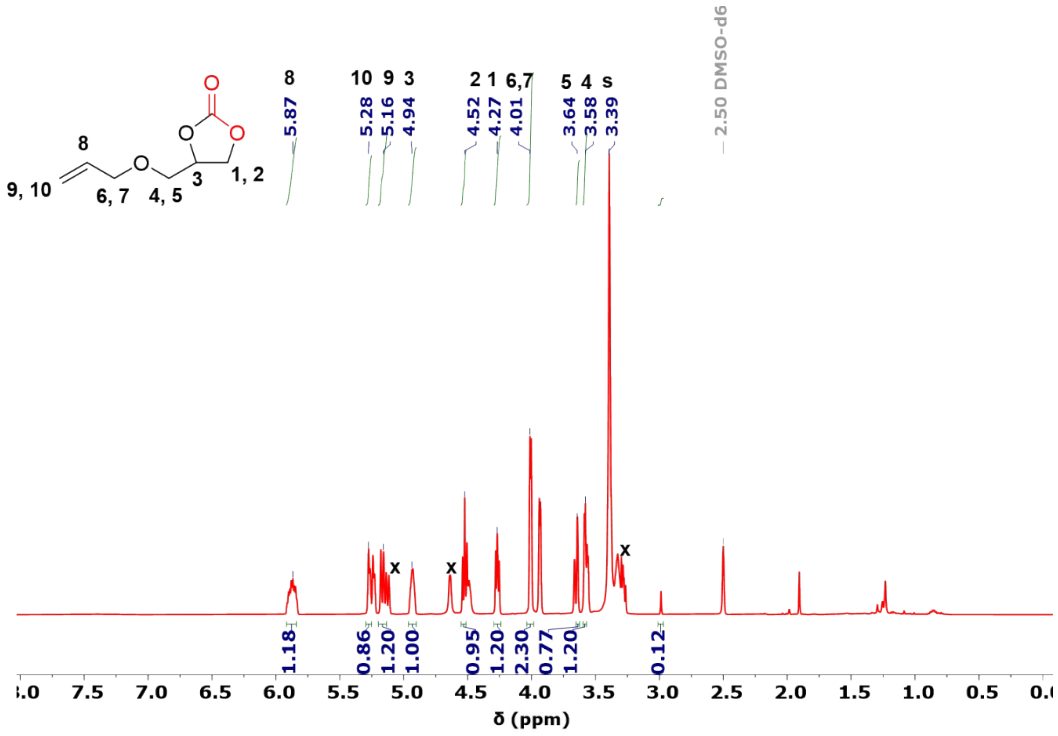


Figure S39. [1]H NMR spectrum of the isolated 4-((allyloxy)methyl)-1,3-dioxolan-2-one in DMSO-d_6. **x**: 1,2-diol (from the starting material as supplied by the chemical vendor), **s**: water.

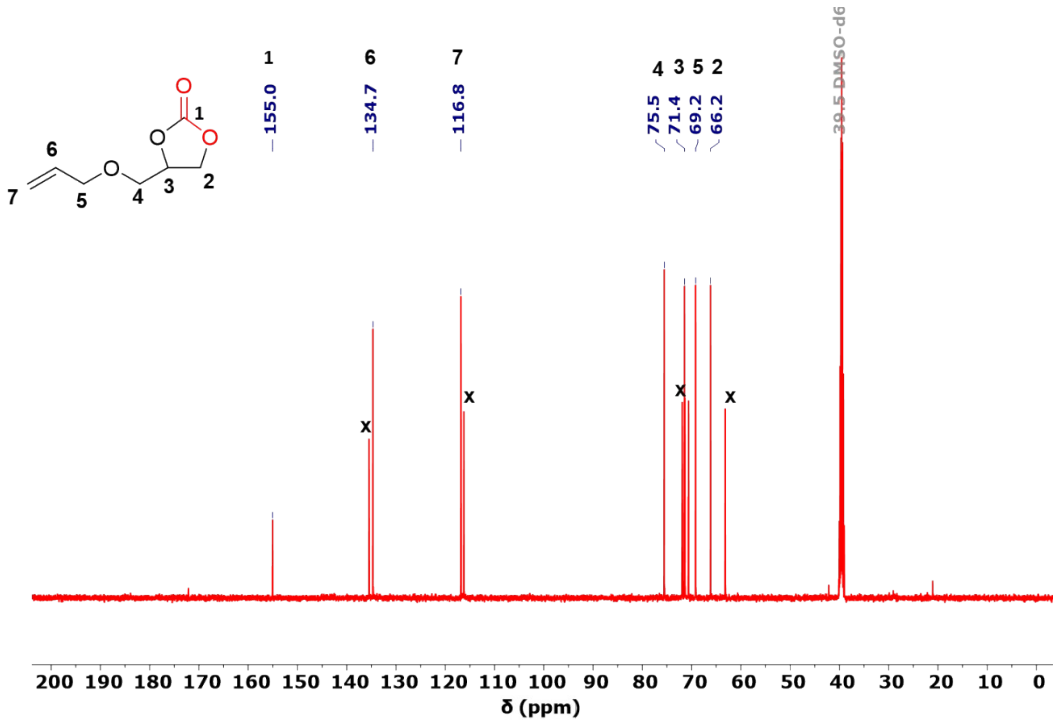


Figure S40.[13]C NMR spectrum of the isolated 4-((allyloxy)methyl)-1,3-dioxolan-2-one in DMSO-d_6.

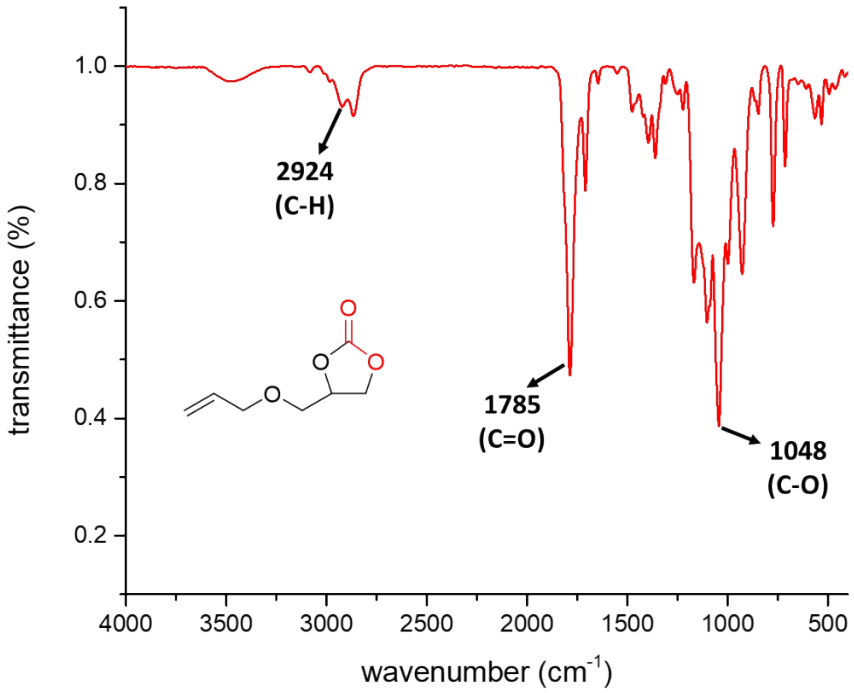


Figure S41. ATR-FTIR spectrum of the isolated 4-((allyloxy)methyl)-1,3-dioxolan-2-one.

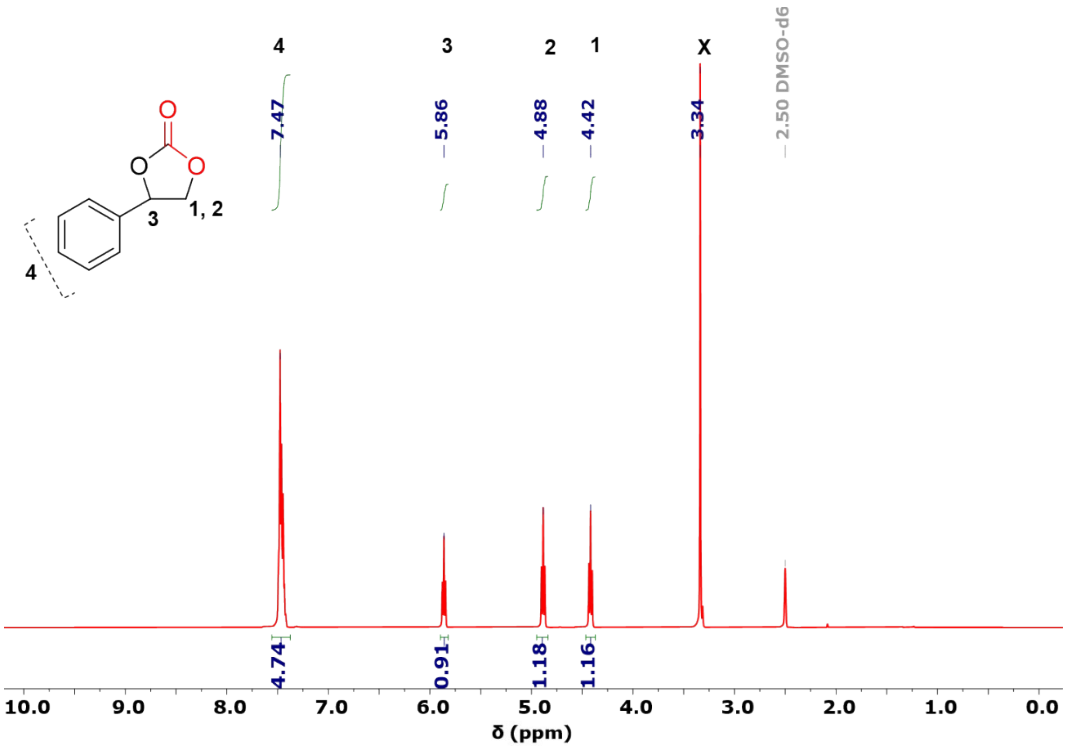


Figure S42. [1]H NMR spectrum of the isolated 4-phenyl-1,3-dioxolan-2-one in DMSO-d_6. **s**: water.

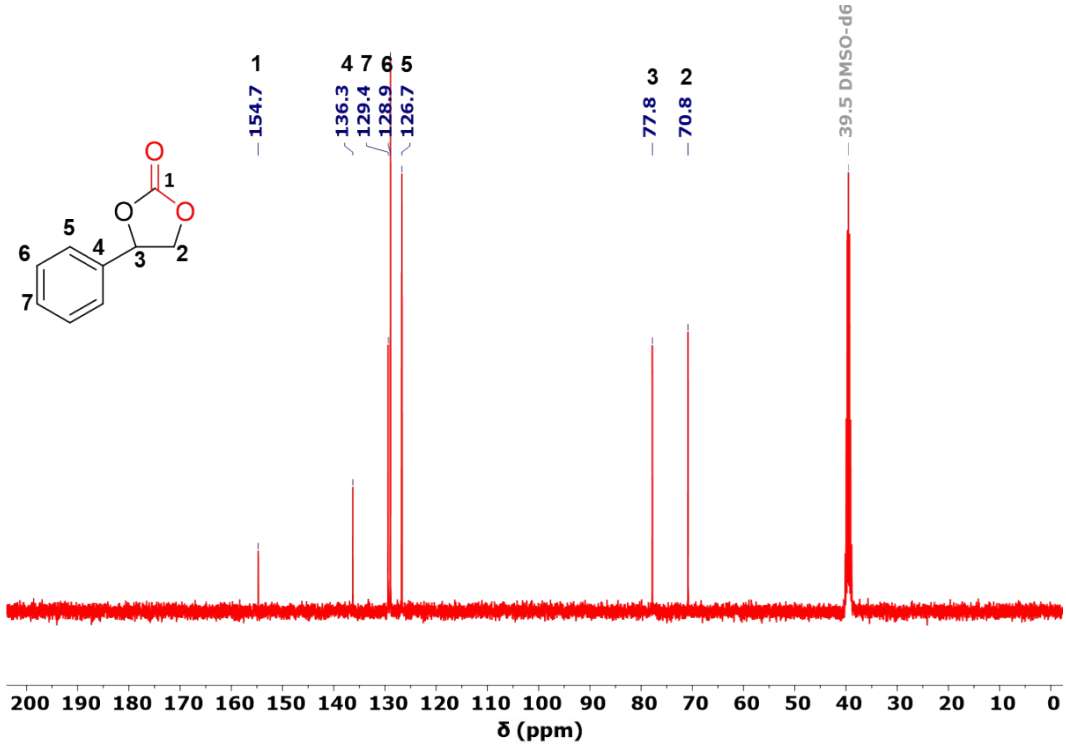


Figure S43.[13]C NMR spectrum of the isolated 4-phenyl-1,3-dioxolan-2-one in DMSO-d_6.

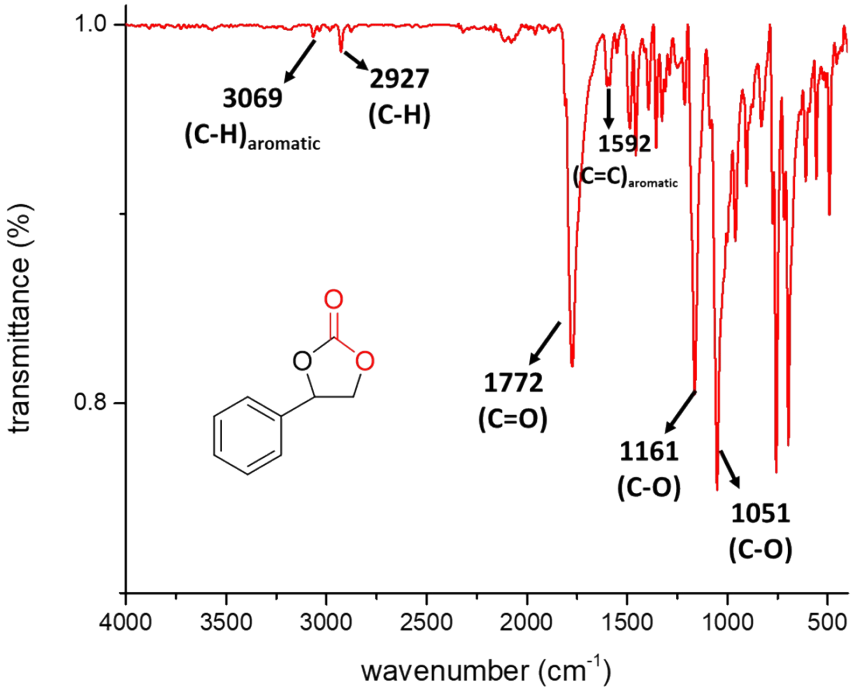


Figure S44. ATR-FTIR spectrum of the isolated 4-phenyl-1,3-dioxolan-2-one.

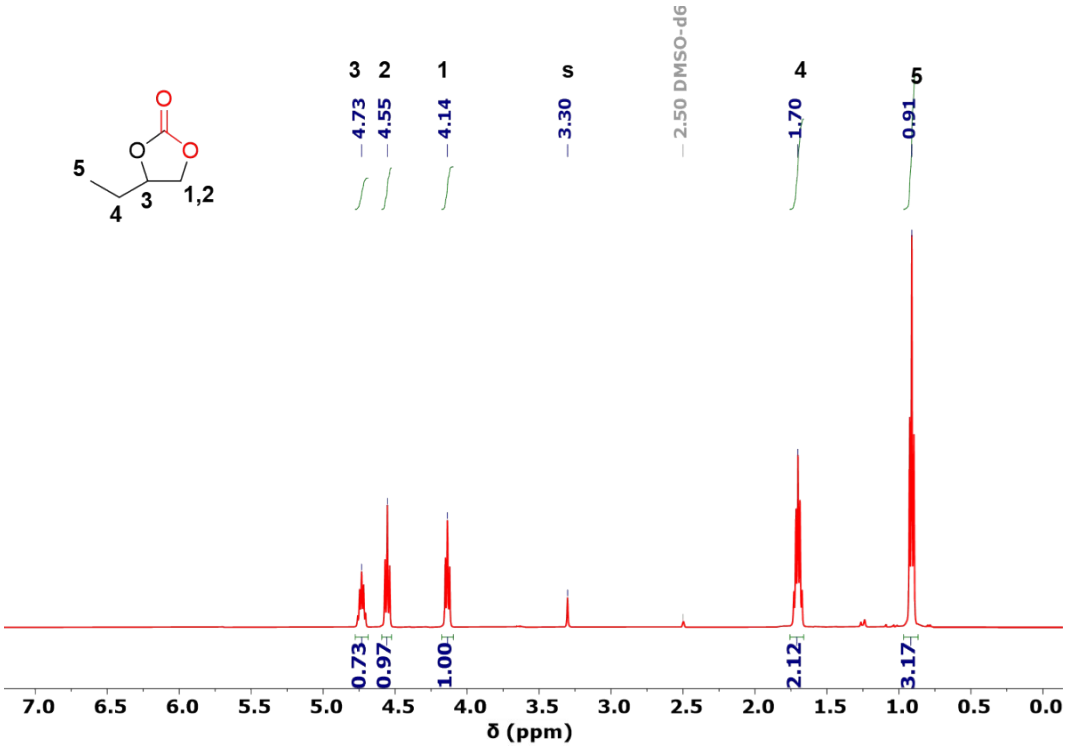


Figure S45. ^{1}H NMR spectrum of the isolated 4-ethyl-1,3-dioxolan-2-one in DMSO-d_6. **s**: water.

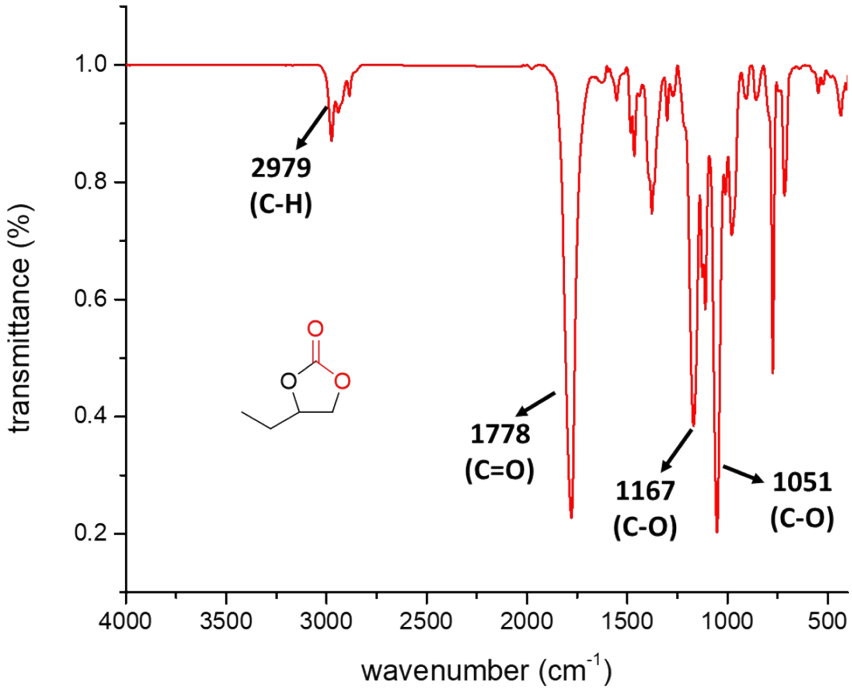


Figure S46. ATR-FTIR spectrum of the isolated 4-ethyl-1,3-dioxolan-2-one.

7 ^{1}H NMR spectra of the cycloaddition reaction using different catalysts (1, 3, 3'', 3''', 3 a-b, 4, 5, 5a, 6, 7)

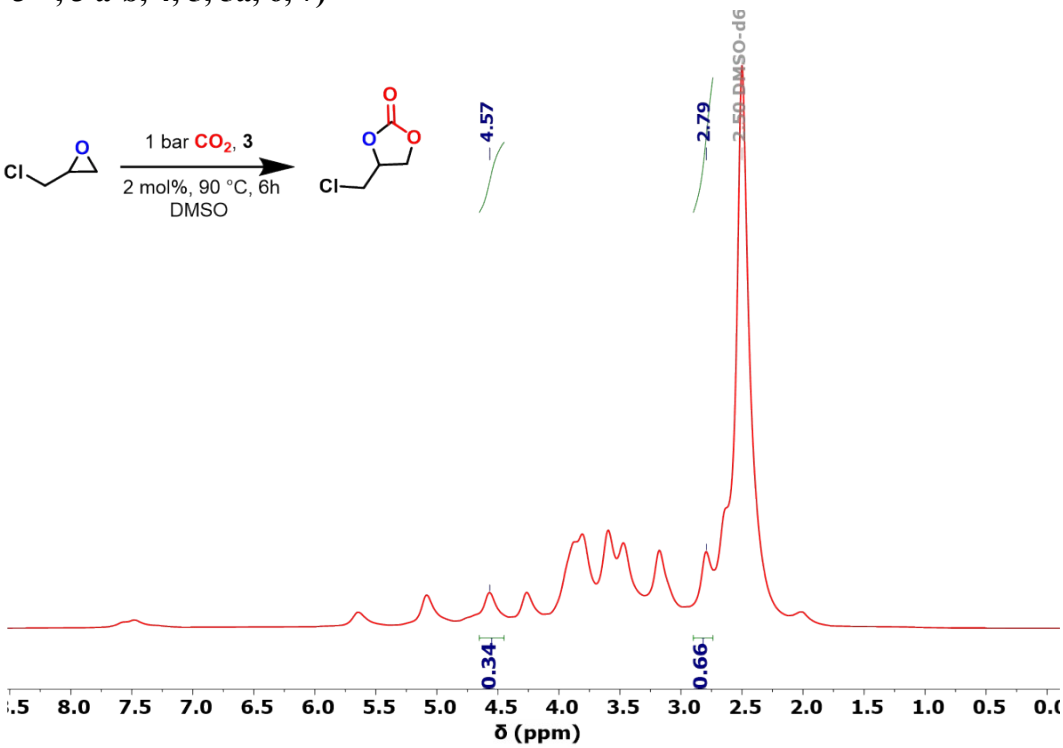


Figure S47. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **3** (**Table 2**, entry 1).

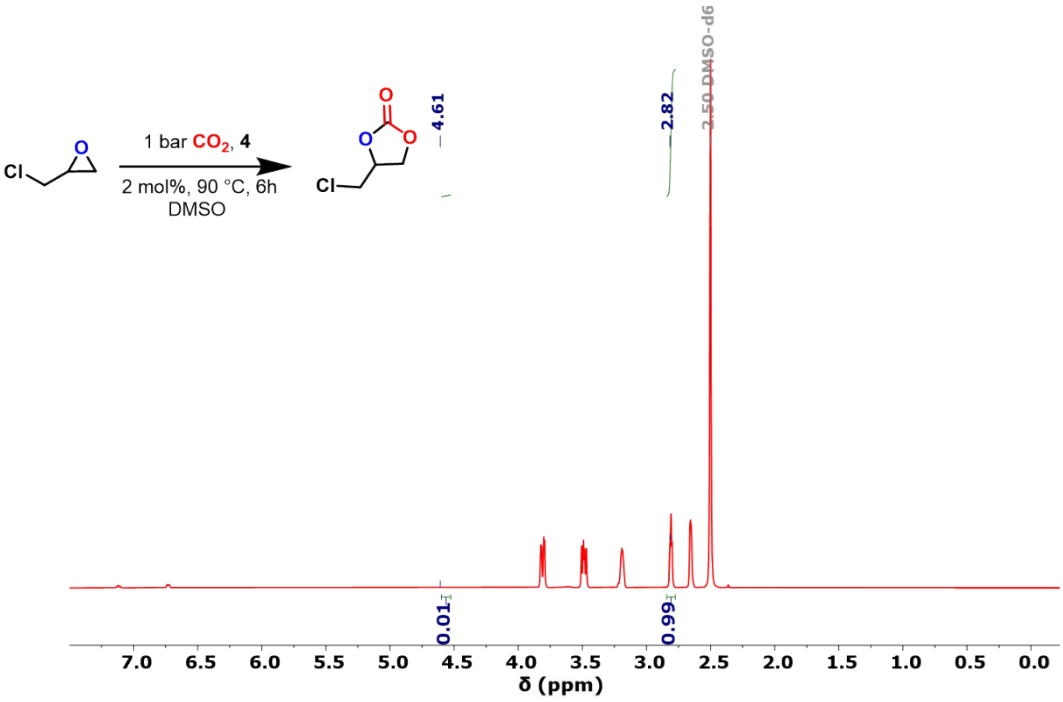


Figure S48. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **4** (**Table 2**, entry 2).

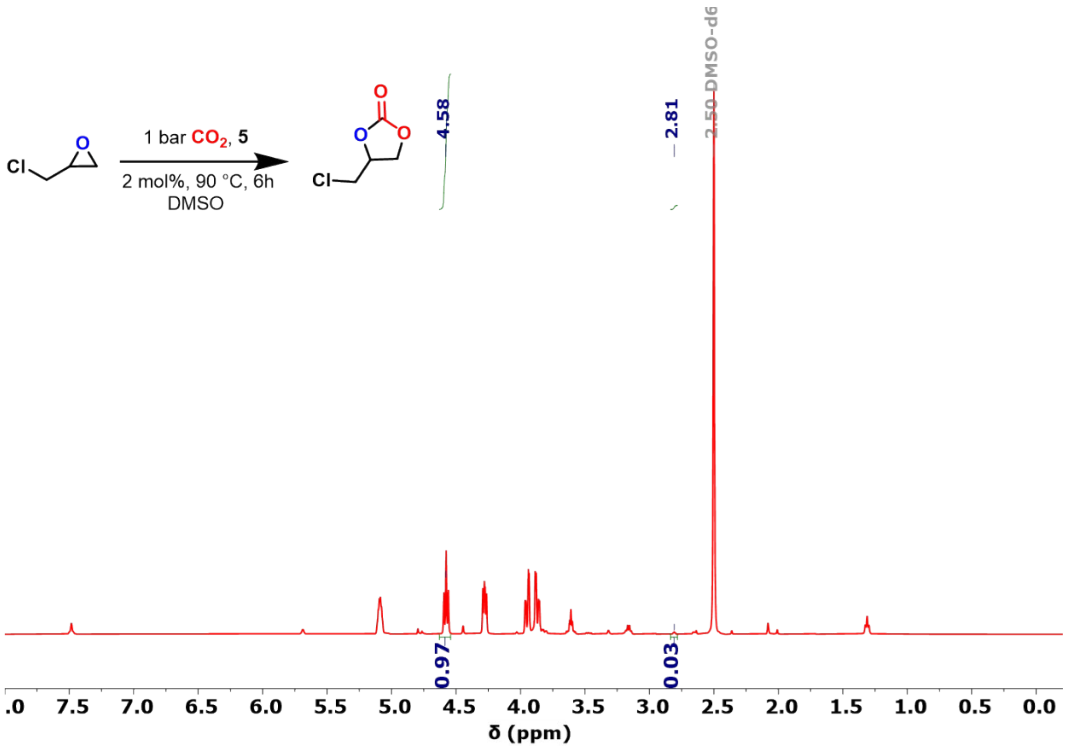


Figure S49. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **5** (**Table 2**, entry 3).

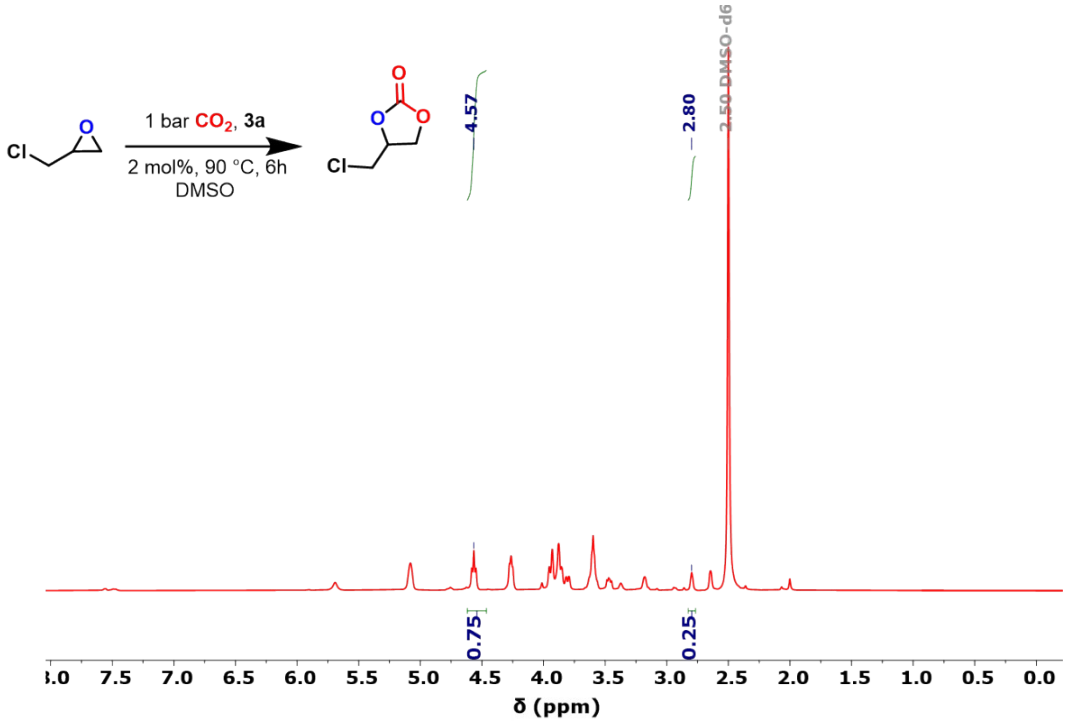


Figure S50. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **3a** (**Table 2**, entry 4).

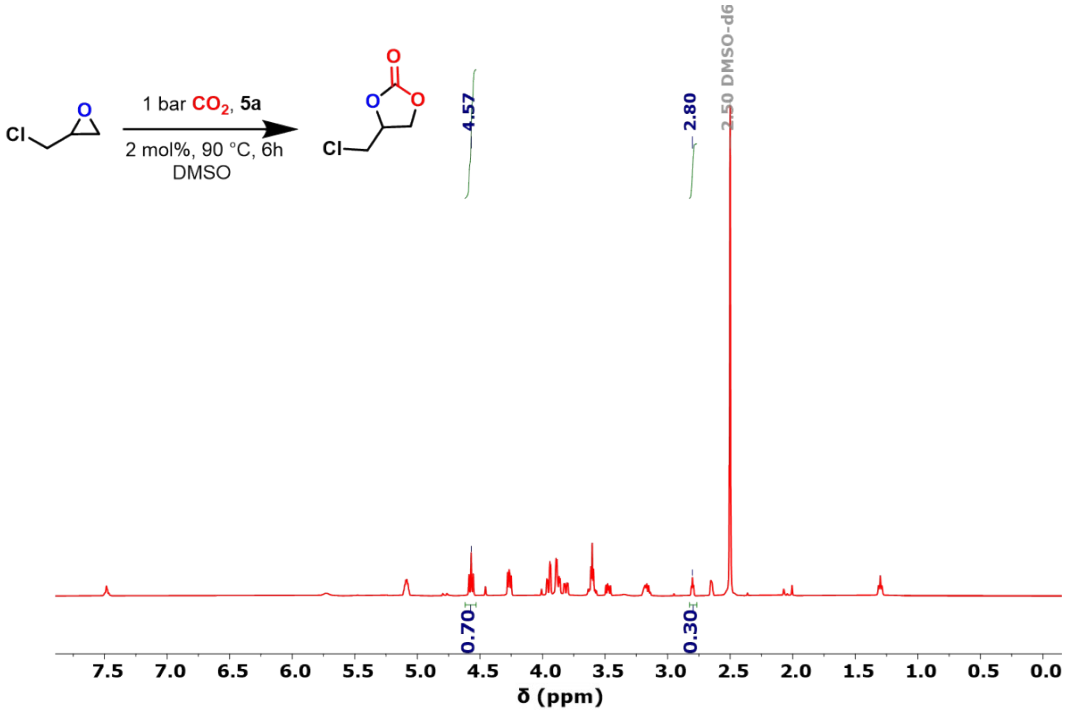


Figure S51. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **5a** (**Table 2**, entry 5).

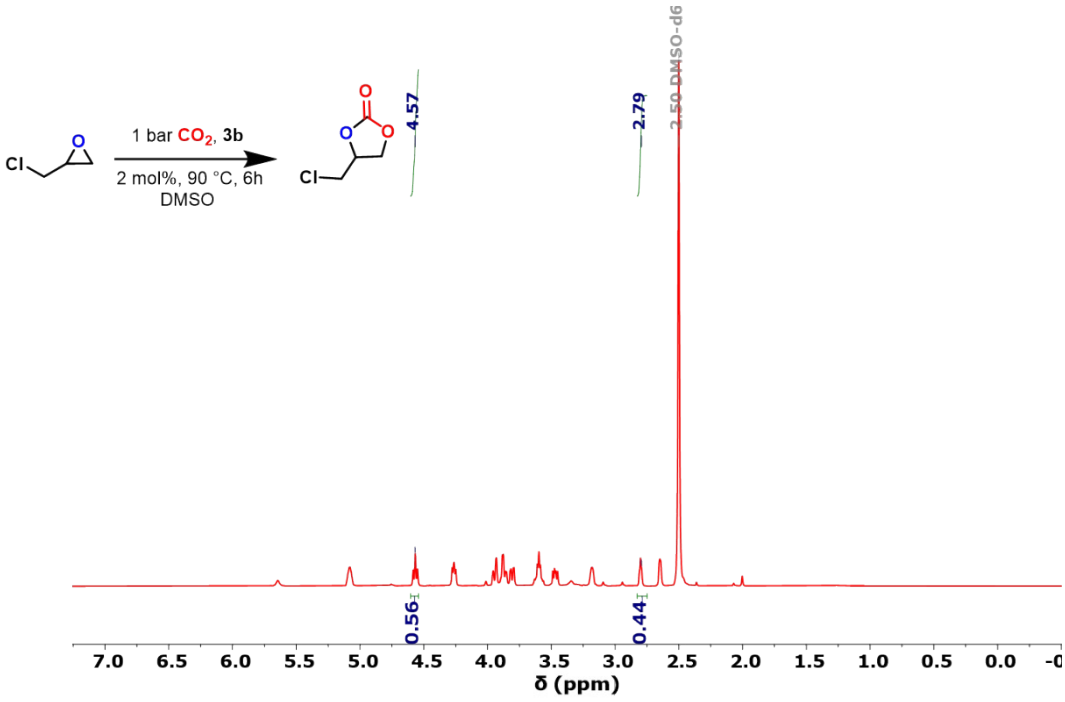


Figure S52. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **3b** (**Table 2**, entry 6).

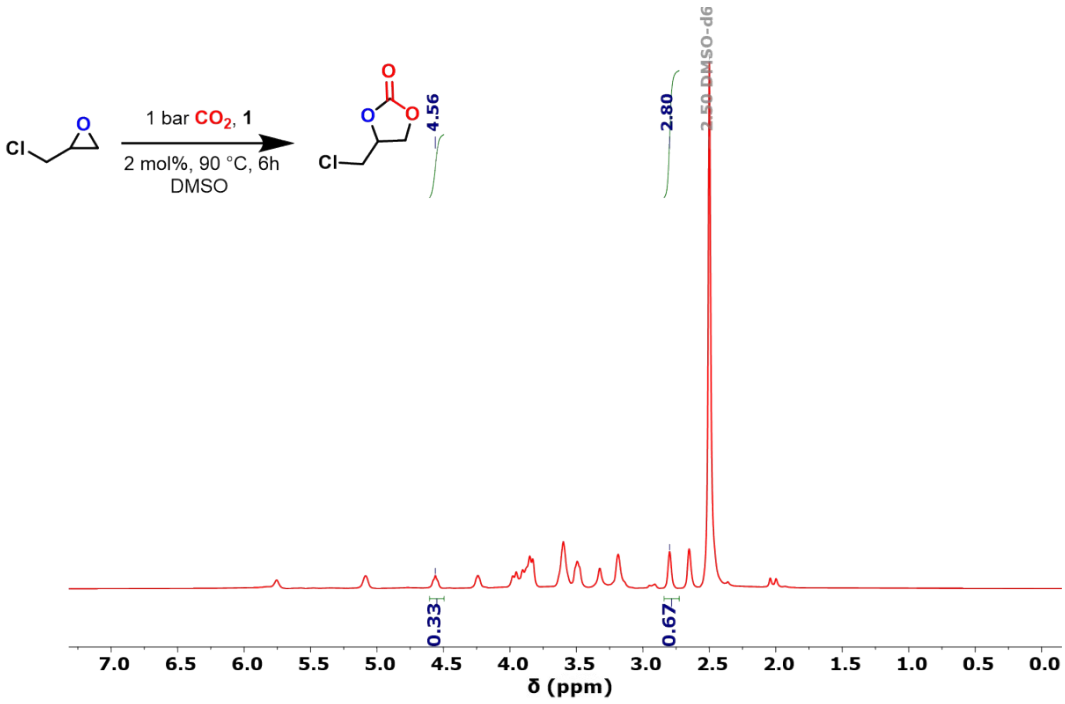


Figure S53. [1]H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **1** (**Table 2**, entry 7).

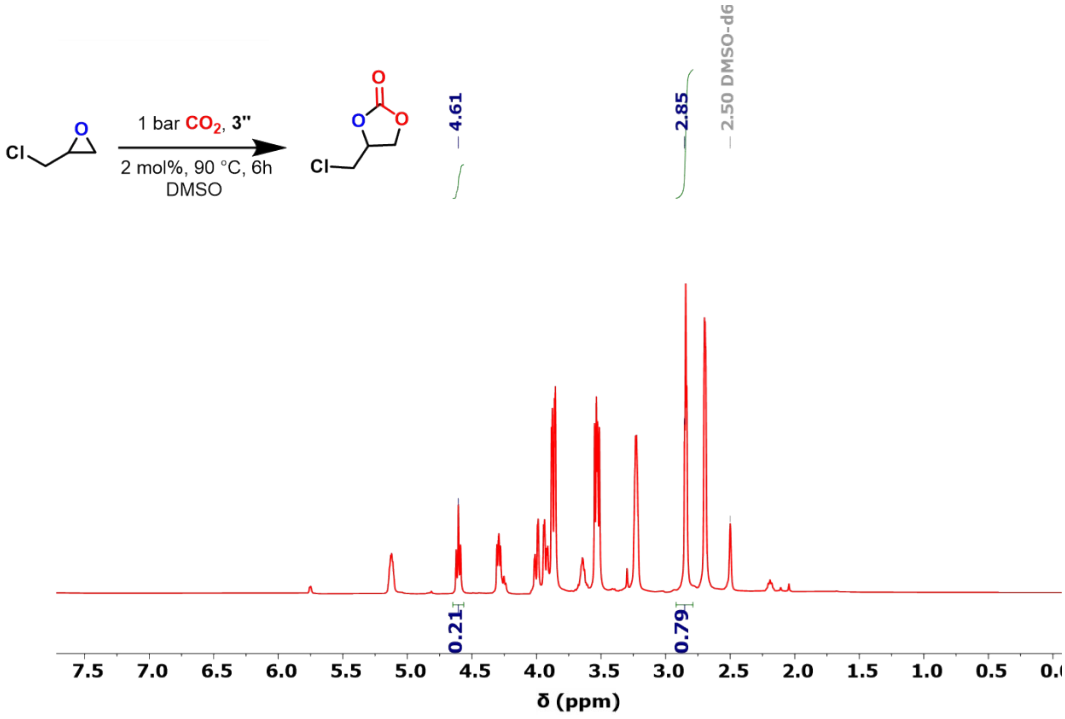


Figure S54. [1]H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **3"** (**Table 2**, entry 8).

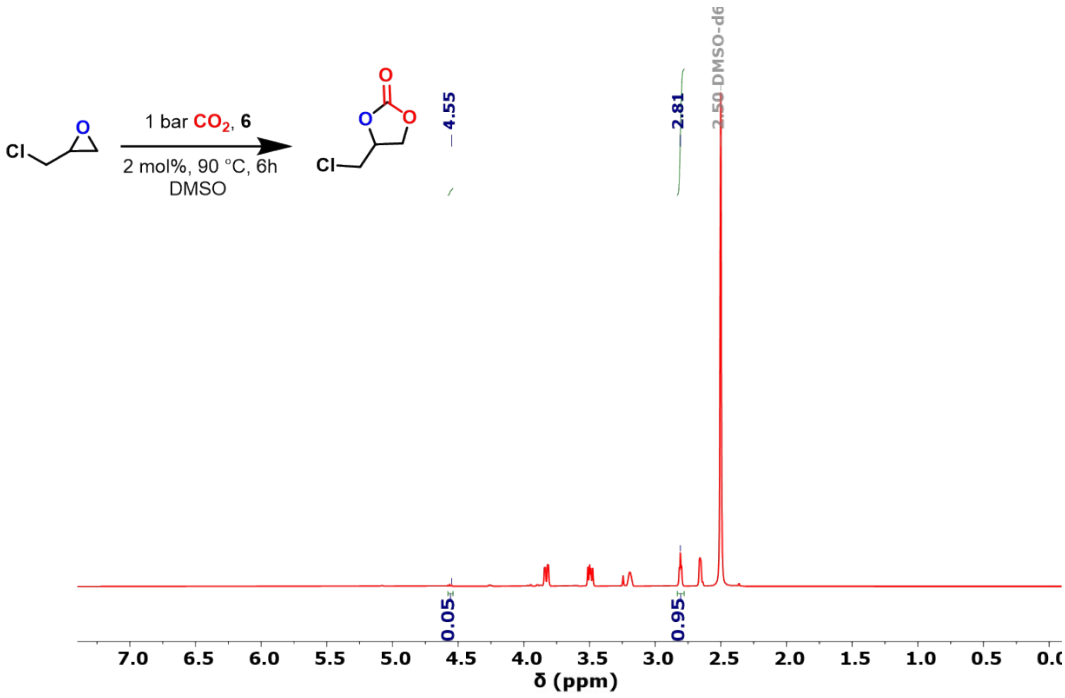


Figure S55. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **6** (**Table 2**, entry 9).

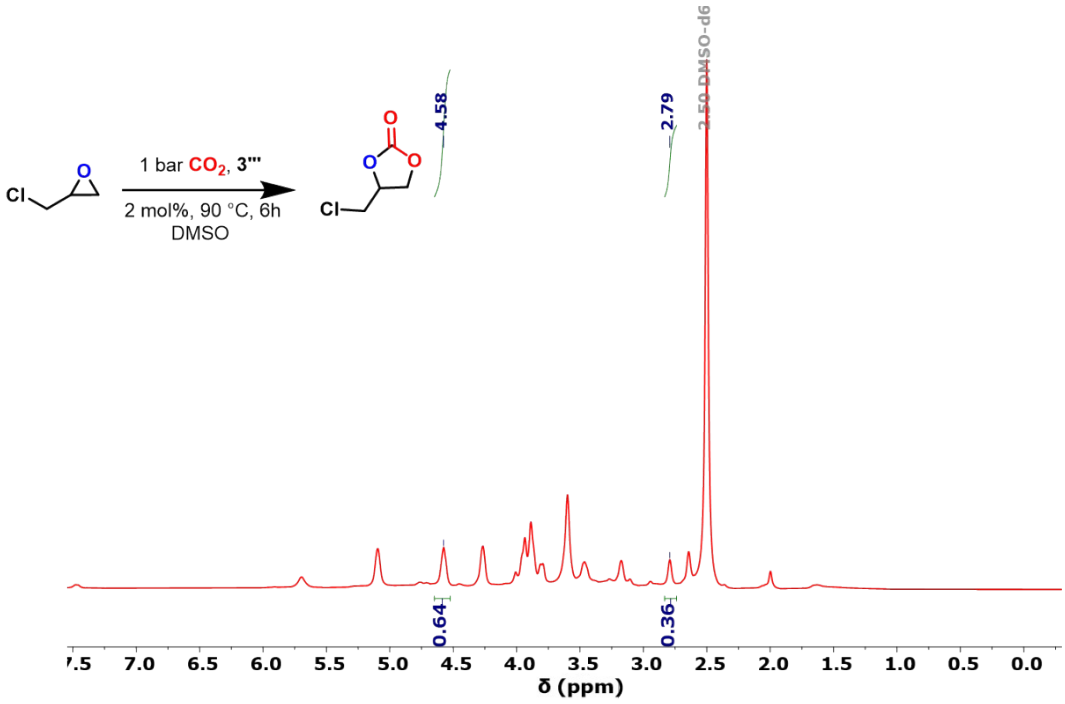


Figure S56. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **3'''** (**Table 2**, entry 10).

8 [1]H NMR spectra of the cycloaddition reaction catalyzed by the organocatalysts (3, 9, 11, 13, 16)

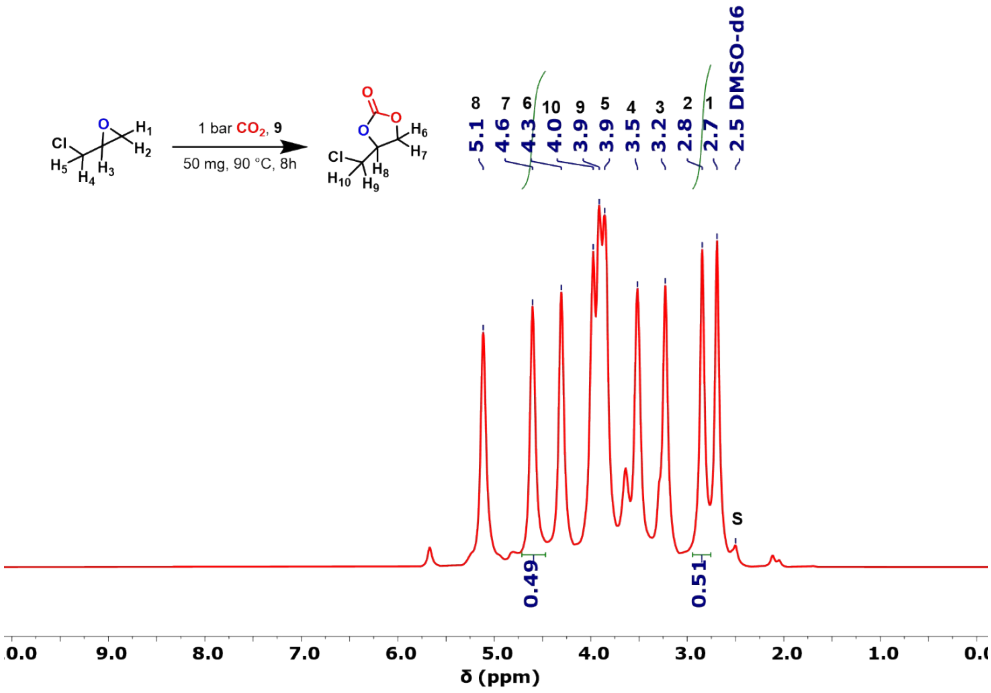


Figure S57. [1]H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **9**, (**Table 3**, entry 1).

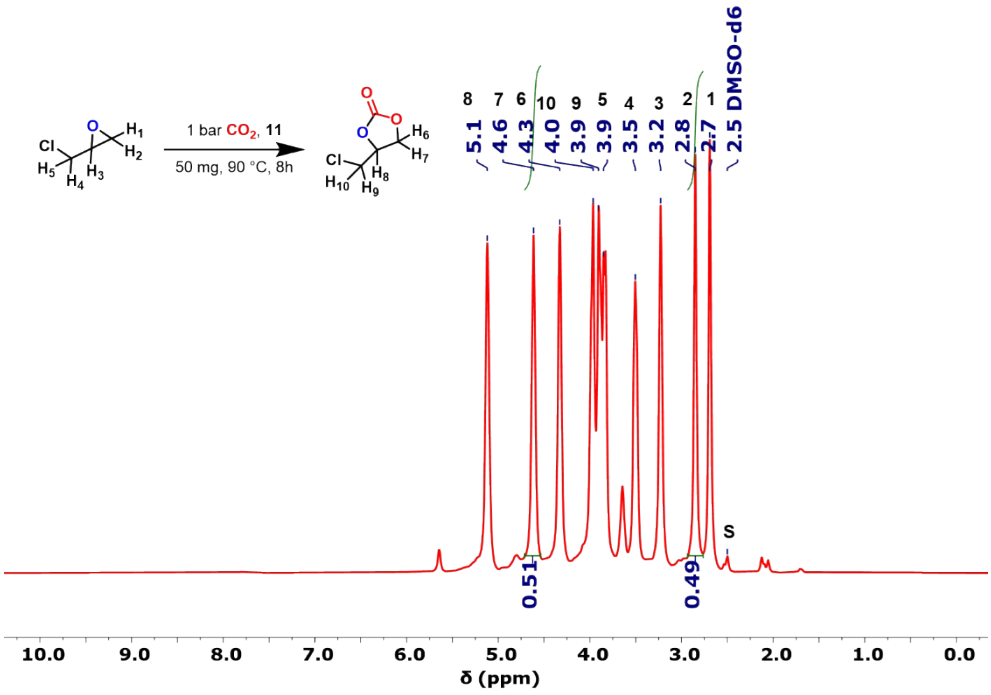


Figure S58. [1]H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **11**, (**Table 3**, entry 2).

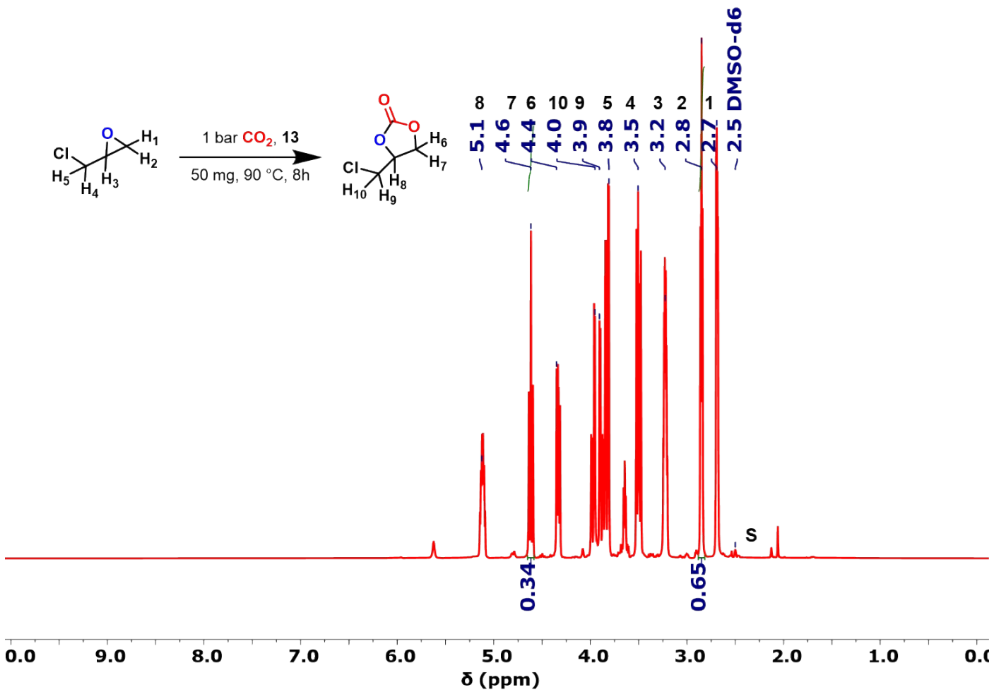


Figure S59. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **13**, (**Table 3**, entry 3).

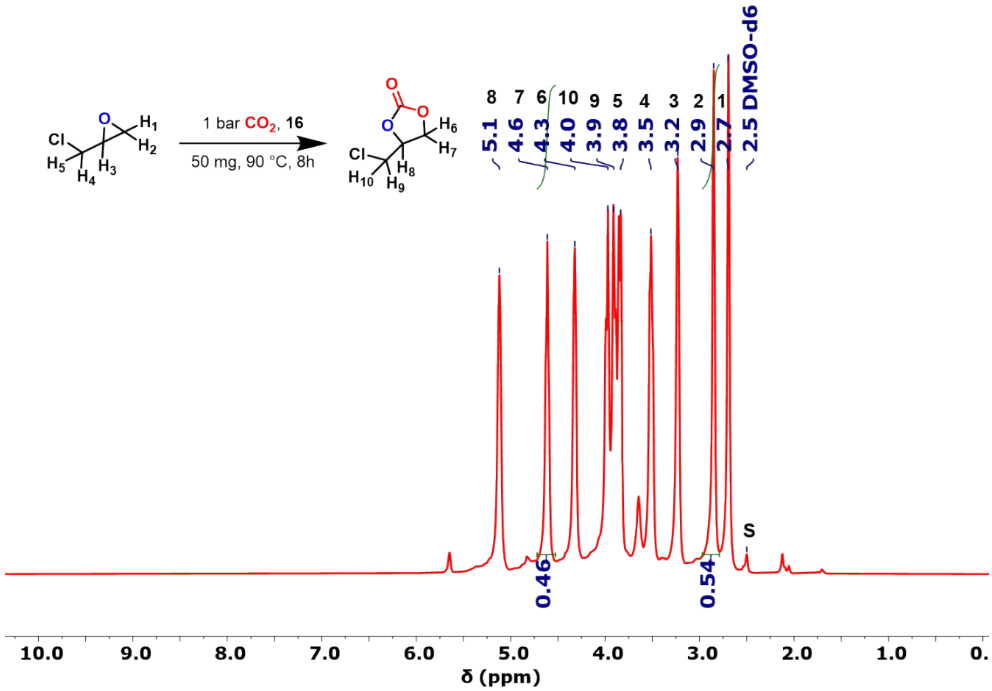


Figure S60. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **16**, (**Table 3**, entry 4).

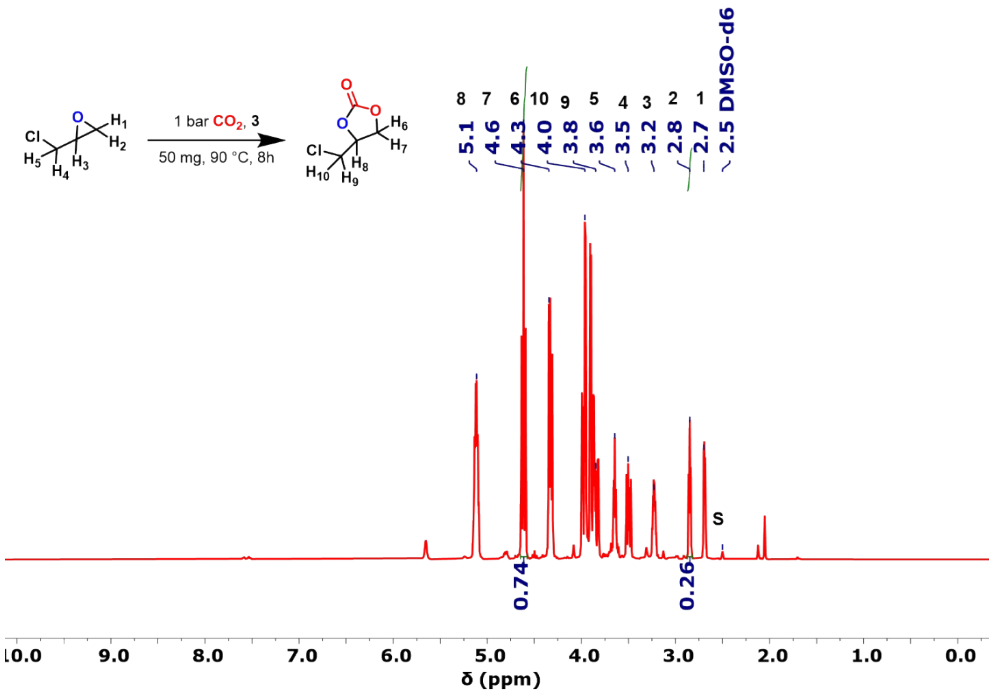


Figure S61. ^{1}H NMR spectrum of ECH conversion to its corresponding CC in DMSO-d_6 using **3**, (**Table 3**, entry 5).

9 References:

(1) Lugemwa, F.; Shaikh, K.; Hochstedt, E. Facile and Efficient Acetylation of Primary Alcohols and Phenols with Acetic Anhydride Catalyzed by Dried Sodium Bicarbonate. Catalysts 2013, 3 (4), 954–965.

(2) Ponmuthu, K. V.; Kumaraguru, D.; Arockiam, J. B.; Velu, S.; Sepperumal, M.; Ayyanar, S. New Quaternary Phosphonium Salt as Multi-Site Phase-Transfer Catalyst for Various Alkylation Reactions. Res Chem Intermed 2016, 42 (12), 8345–8358.

(3) Xu, X.-Q.; Wang, Z.; Li, R.; He, Y.; Wang, Y. A Degradable and Recyclable Photothermal Conversion Polymer. Chem. Eur. J. 2018, 24 (39), 9769–9772.

(4) Lauer, J. C.; Zhang, W.-S.; Rominger, F.; Schröder, R. R.; Mastalerz, M. Shape-Persistent [4+4] Imine Cages with a Truncated Tetrahedral Geometry. Chem. Eur. J. 2018, 24 (8), 1816–1820.