Supplementary information

Salophen chromium(III) complexes functionalized with pyridinium salts as catalysts of carbon dioxide cycloaddition to epoxides

1. General information

All works with air- and/or water-sensitive compounds were performed under dry argon atmosphere in a glovebox or using the standard Schlenk techniques.

1.1. Materials

4-*tert*-butylphenol, 2,4-di-*tert*-butylphenol, propylene oxide, 1,2-epoxybutane, 1,2-epoxyhexane, 1,2-epoxyoctane, epichlorohydrin, glycidol, phenyl glycidyl ether, *tert*-butyl glycidyl ether, glycidyl methacrylate, styrene oxide, pyridine, 4-(dimethylamine)pyridine, 2,6-lutydine, anhydrous chromium(II) chloride and other basic reagents and solvents used in this work were purchased from Sigma-Aldrich, Alfa Aesar, Acros and applied as received, unless otherwise stated. Carbon dioxide, 99,9995%, was purchased from Air products and used as received.

Tetrahydrofuran was refluxed with sodium/benzophenone under argon until the deep blue colour of benzophenone ketyl was formed. The dry solvent was collected directly prior to use. Methanol and acetonitrile were stirred overnight with calcium hydride and refluxed for 6 hours under argon atmosphere. The dry solvents were collected and stored over freshly activated molecular sieves 3A. Diethyl ether, toluene and hexane were dried and stored with activated molecular sieves 4A.

1.2. Methods

NMR experiments. ^{1}H and ^{13}C NMR spectra of the synthesized compounds/post-reaction mixtures were recorded at 298 K temperature in $CDCl_3$ or dmso-d6 using a Bruker Avance 500 MHz spectrometer (^{1}H, 500 MHz and ^{13}C, 125 MHz). TMS was used as a standard. The samples for analysis were prepared by dissolving 15-30 mg of an isolated compound/post-reaction mixture in *ca.* 0.6 ml of a solvent.

Infrared experiments. FT-IR spectra were recorded using a Thermo Scientific Nicolet 8700 spectrometer in the range of 4000-650 cm^{-1}. All measurements were performed by the ATR method.

Mass spectroscopy. Laser desorption/ionization (LDI) time-of-flight (ToF) mass spectrometry experiments were performed using a Bruker Autoflex Speed reflectron time-of-flight mass spectrometer equipped with a SmartBeam II laser (352 nm) in the range of 80-2000 m/z. The laser impulse energy and laser repetition were approximately 60−120 µJ and 1000 Hz, respectively. The first accelerating voltage was held at 19 kV and the second ion source voltage at 16.7 kV. The applied reflector voltages were 21 kV (first) and 9.55 kV (second). Analytical data was collected and studied using the software provided with the Autoflex instrument (FlexAnalysis version 3.3). Mass calibration (typically cubic calibration based on five to seven points) was performed using internal standards (gold ions and clusters from Au^+ to $Au10^+$ depending on the m/z range). The sum of *ca.* 7000 scans was collected for each sample. Analytical samples were prepared by dissolution/suspending *ca.* 0.5 mg substances in 1 mL toluene. A drop of the resulting solution/suspension was placed in AuNPET.[S1]

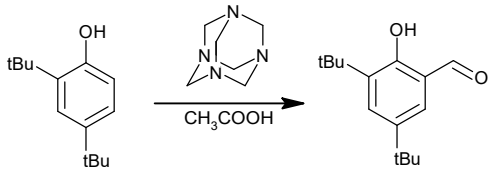
ICP-OES analysis. Chromium content in the synthesized metal complexes was determined using an ICP-OES ULTIMA 2 HORIBA JOBIN YVON spectrometer (λ = 283.563 nm, photomultiplier voltage 950 V and generator power 1400 W). The samples of the complexes (about 20 mg) were mineralized in conc. nitric acid (5.0 ml) using a *Plazmatronika Uni Claver II* microwave mineralizer and diluted with demineralized water prior to analysis.

Thermogravimetric analysis (TG) was performed using a Mettler-Toledo TGA/DSC1 analyzer. TG experiments were carried out in nitrogen in the temperature range of 25 to 600°C with a heating rate of 10 °C min^{-1}. Sample weight ca. 2 mg, 50 ml min^{-1} gas flow, and 150 µl open alumina pan were used.

Melting point measurements. The melting points of the obtained ligands were determined using an SRS OptiMelt MPA100 instrument with a heating rate of 5°C/min.

2. Syntheses

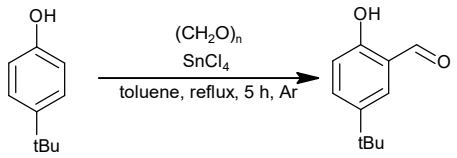
2.1. 3,5-Di-tert-butyl-2-hydroxybenzaldehyde (A1)



A1 46 %

Aldehyde **A1** was prepared according to the procedure described by Jacobsen et al.[S2] The synthesis was performed in a four-neck 750 ml flask equipped with a reflux condenser, a thermometer, a dropping funnel, a mechanical stirrer, and a heating coat. 2,4-di-*tert*-butylophenol (41.67 g, 200 mmol) and urotropine (56.63 g, 400 mmol) were dissolved in 100 ml acetic acid and the obtained solution was heated at 130°C for 2 hours, vigorously stirring. The reaction mixture was then, cooled to 80°C and 100 ml 33% sulphuric acid solution was added dropwise keeping the temperature below 100°C. After that, the reaction mixture was refluxed for an additional hour and cooled again to 80°C to separate an organic phase in a coated separatory funnel. The separated organic phase was diluted with 33 ml methanol after its previous cooling to room temperature, and the obtained solution was cooled to about 5°C in a water-ice bath, vigorously stirring with a magnetic stirrer. The precipitated crude product was filtered and recrystallized from methanol to yield 21.8 g **A1** as pale-yellow powder (46%; m.p. 56-58°C). **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 11.64 (s, 1H); 9.87 (s, 1H), 7.59 (d, *J=2.5 Hz,* 1H), 7.34 (d, *J=2.5 Hz,* 1H), 1.43 (s, 9H), 1.33 (s, 9H). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 197.5, 159.1, 141.6, 137.6, 131.9, 127.8, 120.0, 35.0, 34.2, 31.3, 29.3. **FTIR** (KBr, cm^{-1}) 2958, 1651, 1612, 1440, 1381, 1362, 1323, 1270, 1249, 1228, 1170, 1024, 965, 894, 829, 800, 769, 737, 713, 644, 534. The analytical data are in agreement with the literature.[S2]

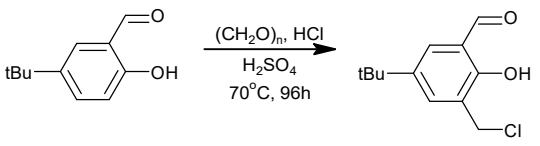
2.2. 5-tert-butyl-2-hydroxybenzaldehyde (A2)



A2 56%

Aldehyde **A2** was prepared according to the procedure described by Casiraghi et al.[S3] The synthesis was performed in a four-neck 750 ml flask equipped with a reflux condenser, a thermometer, a dropping funnel, a mechanical stirrer, and a heating-coat. 19.62 g (130 mmol) 2-*tert*-Butylofenol (19.62 g; 130 mmol) and paraformaldehyde (15.64 g) were dissolved in 200 ml dry toluene and then tin(IV) chloride (4.56 ml, 39 mmol) was added. The obtained heterogeneous reaction mixture was stirred vigorously at 110°C for 5 hour and then overnight at ambient temperature. After that, water (200 ml) and ethyl acetate (300 ml) were added to the post-reaction mixture, and pH=2 was adjusted by adding the concentrated hydrochloric acid dropwise. The mixture was then filtered through a pad of celite 545 and separated to water and organic phases. The organic phase was washed with brine and dried under anhydrous $MgSO_4$. After removing solvents, crude product (brown oil) was purified by vacuum distillation at p=1 bar. Aldehyde **A2** was obtained with the yield of 79% (18.26 g) as yellow oil. **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 10.86 (s, 1H); 9.89 (s, 1H), 7.58 (dd, *J=8.9 Hz, J=2.5 Hz*, 1H), 7.51 (d, *J=2.5 Hz,* 1H), 6.94 (d, *J=8.9 Hz,* 1H), 1.33 (s, 9H). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 197.0, 159.7, 143.0, 134.9, 129.9, 120.2, 117.4, 34.3, 31.5. **FTIR** (ATR, diamond, cm^{-1}) 2961, 1651, 1591, 1483, 1374, 1362, 1288, 1263, 1228, 1179, 1105, 923, 888, 832, 774, 731, 653. The analytical data are in agreement with the literature.[S3]

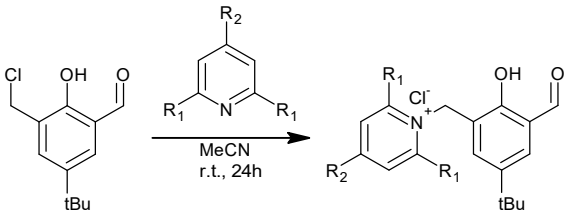
2.3. 3-chloromethyl-5-tert-butyl-2-hydroxybenzaldehyde (A3)



A3 99 %

Aldehyde **A3** was prepared according to the procedure described in Ref. [S4]. Aldehyde **A2** (9.56 g, 53.6 mmol), paraformaldehyde (2.41 g, 80.3 mmol) and 33.5 ml conc. The HCl solution was placed in a 100 ml round-bottom flask and 25 drops of conc. H_2SO_4 was added. The obtained reaction mixture was stirred using a magnetic stirrer at 70°C for 4 days. After that, the post-reaction mixture was cooled to ambient temperature and water (100 ml) and methylene chloride (100 ml) were added. The resulting liquid layers were separated. The water phase was extracted with 3x50 ml CH_2Cl_2 and the combined organic phases were dried under anhydrous Na_2SO_4. The solvent was removed under vacuum in a rotary evaporator. The final product was obtained with satisfactory purity as brown oil (>99% yield, 12.10 g). **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 11.27 (s, 1H), 9.90 (s, 1H), 7.67 (d, *J=2.5Hz*, 1H), 7.52 (d, *J=2.5Hz*, 1H), 4.70 (s, 2H), 1.34 (s, 9H). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 196.7, 157.3, 142.9, 135.3, 130.5, 125.4, 120.1, 40.2, 34.2, 31.2. **FTIR** (ATR, diamond, cm^{-1}): 2962, 2867, 1652, 1616, 1462, 1440 1382, 1364, 1273, 1217, 1003, 887, 827, 771, 740, 718, 668. The analytical data are in agreement with the literature.[S4]

2.4. Synthesis of salicylaldehydes A4-A6



A4 R_1, R_2 = H 88%
A5 $R_1 = CH_3, R_2$ = H 80%
A6 R_1 = H, $R_2 = N(CH_3)_2$ 99%

***General procedure (GP1)*:** Salicylaldehydes with units of pyridinium chloride (**A4**-**A6**) were synthesized based on the procedure described by Peters et al. [S5] Aldehyde **A3** (1.36 g; 6 mmol) was placed in a 50 ml round-bottom flask equipped with a magnetic stirrer and dissolved in 10 ml acetonitrile. Separately, an appropriate pyridine derivative (6.6 mmol) was dissolved in acetonitrile (8 ml) in a 10 ml vial. The solution of a pyridine derivative was added dropwise to the solution of **A3**. The resulting reaction mixture was stirred at ambient temperature for 24 hours. Next, diethyl ether (5 ml) was added to the post-reaction mixture to precipitate a

product. The product was filtered and rinsed additionally with diethyl ether and dried under reduced pressure.

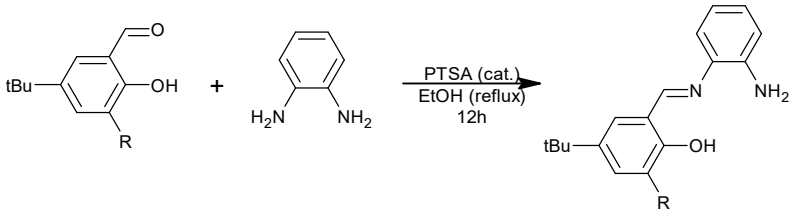
1-(5-tert-Butyl-3-formyl-2-hydroxybenzyl)pyridinium chloride (**A4**) was prepared in the reaction of 1.36 g (6 mmol) aldehyde **A3** with 0.52g (6.6 mmol) pyridine according to GP1. The product was formed as a white solid (1.61g, 88%), m.p. 245-247°C.**^{1}H-NMR** (DMSO-d^{6}, 500 MHz), δ ppm: 11.22 (s, 1H); 10.10 (s, 1H); 9.17 (d, *J=5.5 Hz*, 2H); 8.63-8.56 (m, 1H); 8.14 (t, *J=7.2Hz*, 2H); 8.09 (d, *J=2.5Hz*, 1H); 7.85 (d, *J=2.5Hz*, 1H); 5.91 (s, 2H); 1.30 (s, 9H). **^{13}C-NMR** (DMSO-d^{6}, 125 MHz), δ ppm: 196.1, 157.3, 146.4, 145.5, 143.3, 136.6, 130.5, 128.6, 122.7, 122.3, 59.6, 34.6, 31.4. **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* $C_{17}H_{20}NO_2^+$ $[M\text{-}Cl]^+$ = 270.1483 *found* 270.1476. **FTIR** (KBr, cm^{-1}): 3415, 3024, 2960, 1651, 1632, 1486, 1425, 1384, 1272, 1226, 1149, 1025, 1013, 831, 820, 786, 760, 718, 684, 622, 569, 464.

1-(5-tert-Butyl-3-formyl-2-hydroxybenzyl)-2,6-dimethylpyridinium chloride (**A5**) was prepared in the reaction of 1.36 g (6 mmol) aldehyde **A3** with 0.71g (6.6 mmol) 2,6-lutydine according to GP1. The product was formed as a white solid (1.20 g, 80%), m.p. 123-130°C . **^{1}H-NMR** (dmso-d^{6}, 500 MHz), δ ppm: 11.13 (s, 1H); 10.10 (s, 1H); 8.42 (t, *J=8.0Hz*, 1H); 7.94 (d, *J=8.0Hz*, 2H); 7.77 (d, *J=2.5Hz*, 1H); 7.11 (d, *J=2.5Hz*, 1H); 5.84 (s, 2H); 3.30 (s, 6H); 1.17 (s, 9H). **^{13}C-NMR** (dmso-d^{6}, 125 MHz), δ ppm: 196,6; 157,1; 156,3; 145,7; 143,2; 131,9; 129,3; 128,3; 122,2; 121,2; 52,9; 34,4; 31,3; 21,7. **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* $C_{19}H_{24}NO_2^+$ $[M\text{-}Cl]^+$ = 298.1796 *found* 298.1830 *calculated for* $C_{38}H_{48}ClN_2O_4^+$ $[2M\text{-}Cl]^+$ = 631.3291 *found* 631.3268. **FTIR** (KBr, cm^{-1}): 3442, 2964, 1655, 1624, 1588, 1497, 1390, 1364, 1278, 1219, 1192, 1038, 1005, 819, 720, 509.

1-(5-tert-Butyl-3-formyl-2-hydroxybenzyl)-4-(dimethylamino)pyridinium chloride (**A6**) was prepared in the reaction of 1.36 g (6 mmol) aldehyde **A3** with 0.81g (6.6 mmol) 4-(dimetyloamino)pyrydine according to GP1. The product was formed as a white solid (2.09 g, 80%), m.p. 170-173°C. **^{1}H-NMR** (dmso-d^{6}, 500 MHz), δ ppm: 11.21 (s, 1H); 10.10 (s, 1H); 8.36 (d, *J=7.6 Hz* 2H); 7.97 (d, *J=8.0Hz*, 1H); 7.79 (d, *J=2.5Hz*, 1H); 7.01 (d, *J=7.6 Hz* 2H); 5.43 (s, 2H); 3.15 (s, 6H); 1.28 (s, 9H). **^{13}C-NMR** (dmso-d^{6}, 125 MHz), δ ppm: 196.5; 157.2; 156.3; 143.1; 142.6; 136.0; 129.9; 124.1; 122.0; 108.1; 55.5; 34.5; 31.4. **HRMS** (AuNPET LDI-ToF) m/z:

calculated for $C_{19}H_{25}N2O_2^+$ $[M\text{-}Cl]^+$ = 313.1905 *found* 313.1920 *calculated for* $C_{39}H_{52}ClN_4O_4^+$ $[2M\text{-}Cl]^+$ = 661.3510 *found* 661.3496. **FTIR** (KBr, cm^{-1}): 3456, 3384, 3065, 2956, 1647, 1621, 1568, 1473,1447, 1405, 1382, 1365, 1280, 1226, 1213, 1167, 1008, 845, 829, 816, 775, 720, 614, 507.

2.5. Synthesis of monoimines M1-M2



M1 R = tBu, 79%
M2 R = H, 34%

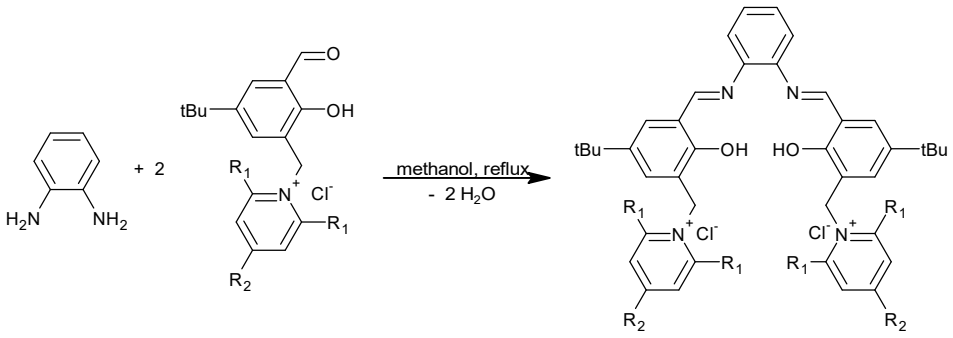
***General procedure (GP2)*:** Monoimines **M1** and **M2** were synthesized in the reaction between 1,2-phenylenodiamine, an appropriate derivative of salicylaldehyde, similarly to what was previously described in the literature.[S6] 1,2-Phenylenodiamine (30 mmol) and 20 mg *p*-toluenesulphonic acid (as a catalyst) were placed in a 250 ml flask and dissolved in 75 ml ethanol. Separately, the solution of a salicylaldehyde (15 mmol) in ethanol (80 ml) was prepared in a conical flask. The solution was then added dropwise to the solution of amine and the catalyst. The resulting reaction mixture was refluxed for 4 hours, vigorously stirring with magnetic stirrer and then the mixing was continued overnight at 50°C. After that, the post-reaction mixture was concentrated to about 20% of the volume and cooled to 0°C. The precipitated solid was filtered, rinsed with cooled ethanol (3x) and dried under reduced pressure.

2-{E)-[(2-aminophenylo)imino]methyl}-4,6-di-tert-butylophenol (**M1**) was obtained in the reaction of 1,2-phenylenediamine (3.24 g, 30 mmol) with aldehyde **A1** (3.51 g, 15 mmol) according to GP2. The product was formed as a yellow solid (3.84 g, 79%), m.p. 134-136.5°C. **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 13.40 (s, 1H); 8.63 (s, 1H); 7.45 (d, *J=2.5 Hz*, 1H); 7.23 (d, *J=2.5 Hz*, 1H); 7.13-7.06 (m, 1H); 7.06-7.01 (m, 1H); 6.83-6.75 (m, 2H); 4.01 (s, 2H); 1.47 (s, 9H); 1.33 (s, 9H). **^{13}C-NMR** (CDCl, 125 MHz), δ ppm: 163.4; 157.9; 140.77; 140.75; 136.9; 135.6; 128.0; 127.8; 126.8; 118.8; 118.6; 118.4; 115.7; 35.1; 34.2; 31.5; 29.4. **FTIR** (KBr, cm^{-1}): 3487,

3390, 2955, 2950, 1617, 1570, 1495, 1475, 1440, 1362, 1312, 1268, 1250, 1193, 1170, 1157, 1134, 886, 814, 753. The analytical data are in agreement with the literature.[S6]

2-{E)-[(2-aminophenyl)imino]methyl}-4-tert-butylophenol (**M2**) was prepared in the reaction of 1,2-phenylenediamine (3.24 g, 30 mmol) with aldehyde **A2** (2.67 g, 15 mmol) according to GP2. The product was formed as a yellow solid (1.37 g, 34%), m.p: 130-132°C. **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 12.80 (s, 1H); 8.62 (s, 1H); 7.43 (dd, *J=8.9 Hz, J=2.5 Hz,* 1H); 7.38 (d, *J=2.1 Hz,* 1H); 7.12-7.07 (m, 1H); 6.97 (d, *J=8.6 Hz* 1H); 6.78 (d, *J=7.6* Hz 2H); 3.96 (s, 2H); 1.33 (s, 9H). **^{13}C-NMR** (CDCl, 125 MHz), δ ppm: 162.7, 158.5, 142.0, 140.7, 135.6, 130.6, 128.6, 128.0, 118.85, 118.79, 118.4, 116.7, 115.8, 34.1, 31.4. **FTIR** (KBr, cm^{-1}): 3483, 3381, 2951, 2904, 1609, 1585, 1572, 1458, 1392, 1364, 1353, 1321, 1309, 1287, 1265, 1245, 1174, 1155, 1133, 978, 820, 793, 758, 754, 744, 618. The analytical data are in agreement with the literature.[S7]

2.6. Synthesis of ligands L1-L3



L1 R_1, R_2 = H, 98%
L2 R_1 = CH3, R2 = H, 95%
L3 R_1 = H, R2 = N(CH3)2 88%

***General procedure (GP3)*:** In a 50 ml two-necked round bottom flask equipped with a magnetic stirrer, a dropping funnel, and a condenser, the appropriate salicylaldehyde derivative with pyridine chloride units (3 mmol) was dissolved in methanol (20 ml). The resulting solution was heated to reflux and a solution of 1,2-phenylenediamine (162 mg; 1.5 mmol) in MeOH (10 ml) was added dropwise. The reaction mixture was vigorously mixed and refluxed first for 4 hours, and then overnight at ambient temperature. The post-reaction mixture was concentrated using a rotary evaporator to about 1/10 volume and diethyl ether (10 ml) was added. The

precipitated yellow solid was powdered using a magnetic stirrer for approximately 1 hour, filtered, rinsed with ethyl ether, and dried under reduced pressure (~1 mbar).

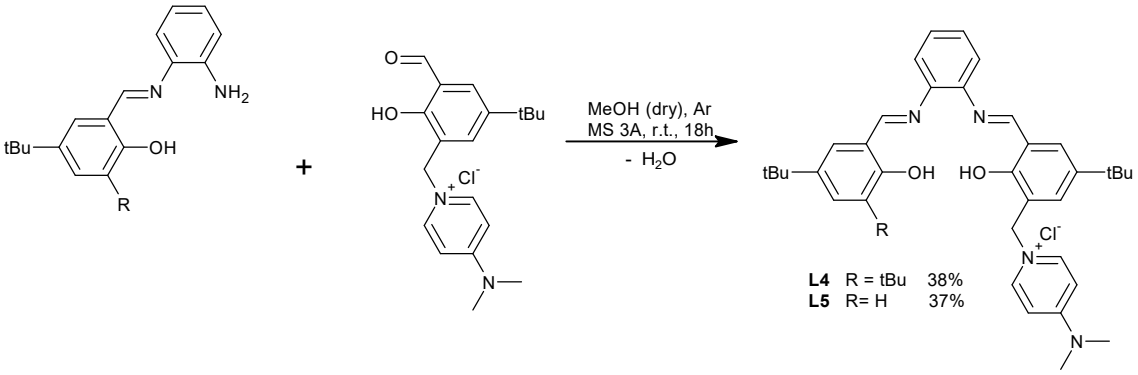
N,N'-Bis-{5-tert-butyl-3-[pyridinium-1-methyl)]salicylidene}-1,2-phenylenediamine dichloride (**L1**) was synthesized in the reaction of 1,2-phenylenediamine (162 mg, 1.5 mmol) with aldehyde **A4** (917 mg; 3 mmol) according to GP3. The product was formed as a yellow solid (1005 mg, 98%), 216°C (decomposition). **^{1}H-NMR** (dmso-d^{6}, 500 MHz), δ ppm: 13.80 (s, 2H), 9.21 (d, *J=5.5Hz*, 4H); 9.03 (s, 2H); 8.62-8.55 (m, 2H); 8.14-8.07 (m, 4H); 7.92 (d, *J=2.5Hz*, 2H); 7.82 (d, *J=2.5Hz*, 2H); 7.52-7.39 (m, 4H); 5.94 (s, 4H); 1.33 (s, 18H). **^{13}C-NMR** (dmso-d^{6}, 125 MHz), δ ppm: 165.2; 158.2; 146.3; 145.4; 142.1; 141.7; 133.4; 131.5; 128.7; 128.5; 128.6; 121.6; 120.4; 119.4; 59.8; 34.5; 31,6. **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* $C_{40}H_{44}N_4O_2^{2+}$ $[M\text{-}2Cl]^{2+}$ = 306.1724 *found* 306.1693. **FTIR** (KBr, cm^{-1}): 3407, 3045, 2956, 2865, 1618, 1580, 1483, 1364, 1278, 1210, 1155, 1040, 818, 762, 753, 689.

N,N'-Bis-{5-tert-butyl-3-[4-[(2,6-dimethyl)pyridinium-1-methyl)]salicylidene}-1,2-phenylenediamine dichloride **(L2)** was prepared in the reaction of 1,2-phenylenediamine (162 mg, 1.5 mmol) with aldehyde **A5** (1054 mg; 3 mmol) according to GP3. The product was formed as bright orange solid (1054 mg, 95%), m.p. 129-131°C. **^{1}H-NMR** (dmso-d^{6}, 500 MHz), δ ppm: 13.78 (s, 2H), 9.05 (s, 2H); 8.47 (t, *J=7.9Hz* 2H); 8.47 (d, *J=7.9Hz*, 4H); 7.77 (d, *J=1.5Hz*, 2H); 7.55-7.40 (m, 4H); 6.91 (d, *J=1.5Hz*, 2H); 5.85 (s, 4H); 2.84 (s, 12H); 1.21 (s, 18H). **^{13}C-NMR** (dmso-d^{6}, 125 MHz), δ ppm: 165.5; 157.1; 157.0; 145.7; 142.0; 141.8; 130.1; 128.7; 128.42; 128.38; 120.5; 119.8; 119.4; 52.8; 34.4; 31.4; 21.7. **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* $C_{44}H_{52}ClN_4O_2^{+}$ $[M\text{-}Cl]^{+}$ = 703.3768 *found* 703.3724 *calculated for* $C_{44}H_{52}N_4O_2^{2+}$ $[M\text{-}2Cl]^{2+}$ = 334.2040 *found* 334.2004. **FTIR** (KBr, cm^{-1}): 3415, 2954, 1620, 1574, 1492, 1364, 1273, 1234, 1206, 1183, 1109, 1042, 1018, 878, 802, 767, 496.

N,N'-Bis-{5-tert-butyl-3-[(4-dimethylamino)pyridinium-1-methyl]salicylidene}-1,2-phenylenediamine dichloride (**L3**) was prepared in the reaction of 1,2-phenylenediamine (162 mg, 1.5 mmol) with aldehyde **A6** (1017 mg; 3 mmol) according to GP3. The product was formed as a yellow solid (1017 mg, 88%), m.p: 243-246°C. **^{1}H-NMR** (dmso-d^{6}, 500 MHz), δ ppm: 13.84 (s, 2H); 9.01 (s, 2H); 8.38 (d, *J=7.7Hz,* 4H); 7.80 (d, *J=2.5Hz*, 2H); 7.75 (d, *J=2.5Hz*, 2H); 7.55-7.39 (m, 4H); 6.91 (d, *J=7.7Hz,* 4H); 5.43 (s, 4H); 3.10 (s, 12H); 1.29 (s, 18H). **^{13}C-NMR**

(dmso-d^6, 125 MHz), δ ppm: 165.3; 157.9; 156.2; 142.6; 142.0; 141.8; 132.7; 130.9, 128.7; 122.9; 120.3; 119.2; 108.0; 55.7; 34.5; 31.6. **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* $C_{44}H_{54}ClN_6O_2^+$ $[M\text{-}Cl]^+$ = 733.3986 *found* 733.3953 *calculated for* $C_{44}H_{54}N_6O_2^{2+}$ $[M\text{-}2Cl]^{2+}$ = 349.2149 *found* 349.2115. **FTIR** (KBr, cm^{-1}): 3403, 2951, 1648, 1617, 1570, 1480, 1402, 1276, 1263, 1230, 1206, 1161, 1040, 856, 821, 757, 514.

2.7. Syntheses of ligands L4-L5



(5-tert-butyl-3-{[(2-{[(3,5-di-tert-butyl-2-hydroxyphenyl)methylidene]amino}phenyl)imino]methyl}-2-hydroxyphenyl)methanepyridinium chloride **(L4)**

To synthesize ligand **L4**, molecular sieves 3A (1,5 g) were first placed in a 100 ml Schlenk flask. The flask was next equipped with a magnetic bar, sealed with a rubber septum, heated with a heating gun, and finally cooled to ambient temperature under argon atmosphere before adding reagents. Aldehyde **A6** (1047 mg, 3 mmol) and monosalicylaldimine **M1** (973, 3 mmol) were used for the synthesis. then placed in the flask after short opening of the flask in an argon atmosphere and dry methanol (30 ml) was next added through the septum using a glass syringe. The mixture was stirred vigorously under argon atmosphere at 25°C for 18 hours. The heterogeneous post-reaction mixture was filtered on a fritted glass funnel to remove molecular sieves. Methanol from the post-reaction mixture was removed at 40°C under decreased pressure using a vacuum rotary evaporator. The residual was dissolved in 20 ml dry methylene chloride and the crude product was purified chromatographically in a column with SiO_2 neutralized with triethylamine (2 ml TEA/10 g SiO_2). The mixture of methylene chloride-methanol (9/1 v/v) with 1% TEA was applied as an eluent. The product isolated after removal of the eluent was pre-dried under vacuum (1 mbar, at 50°C) for 2 hours, then redissolved in 50 ml of methylene chloride and washed with 25 ml of a saturated aqueous solution of NH_4Cl.

After removal of the drying agent and solvent, the residue was further dried under vacuum (1 mbar, 50°C) for 2 hours, The product was obtained as orange powder (740 mg, 38% yield); m.p. 193-198°C. **^{1}H-NMR** (dmso-d^{6}, 500 MHz), δ ppm: 13.84 (s, 1H); 13.82 (s, 1H); 9.03 (s, 1H); 8.98 (s, 1H); 8.32 (d, *J = 8.0 Hz*, 2H); 7.77 (d, *J = 2.5 Hz*, 1H); 7.73 (d, *J = 2.5 Hz*, 1H); 7.56-7.46 (m, 3H); 7.45-7.36 (m, 3H); 6.98 (d, *J = 8 Hz*, 2H); 5.35 (s, 2H); 3.14 (s, 6H); 1.38 (s, 9H); 1.30 (s, 18H). **^{13}C-NMR** (dmso-d^{6}, 125 MHz), δ ppm: 166.4; 165.9; 158.3; 157.7; 156.3; 142.3; 142.0; 141.9; 140.6; 136.3; 132.7; 130.9; 128.5; 128.2; 128.1; 128.0; 122.5; 120.8; 120.4; 119.1; 118.9; 108.1; 79.7; 55.6; 35.1; 34.43; 34.40; 31.7; 31.6; 29.7. **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* $C_{40}H_{51}N_4O_2^+$ [M-Cl]$^+$ = 619,4001 *found* 619,3938. **FTIR** (KBr, cm^{-1}): 509, 753, 818, 1035, 1168, 1200, 1232, 1275, 1362, 1393, 1439, 1479, 1570, 1616, 1651, 2954, 3405.

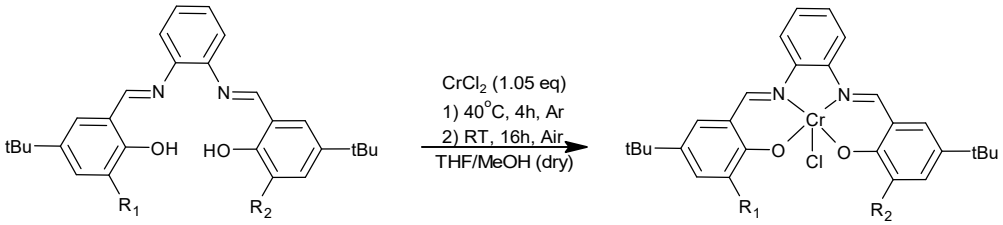
(5-tert-butyl-3-{[(2-{[(5-tert-butyl-2-hydroxyphenyl)methylidene]amino}phenyl)imino]methyl}-2-hydroxyphenyl)methanepyridin-1-ium chloride (**L5**) was synthesized analogously as ligand **L4**. Aldehyde **A6** (1047 mg, 3 mmol) and monosalicylaldimine **M2** (805 mg, 3 mmol) were used for the reaction. The product was obtained as a fine crystalline orange solid (664 mg, 37%); m.p. 159-163°C. **^{1}H-NMR** (dmso-d^{6}, 500 MHz), δ ppm: 14.26 (s, 1H), 12.46 (s, 1H), 9.02 (s, 1H), 8.95 (s, 1H), 8.40 (d, *J = 8 Hz*, 2H); 7.82 (d, *J = 2.5 Hz*, 1H); 7.74 (d, *J = 2.5 Hz*, 1H); 7.71 (d, *J = 2.5 Hz*, 1H); 7.55-7.45 (m, 3H); 7.43-7.37 (m, 2H); 6.96 (d, *J = 8 Hz*, 1H); 6.93 (d, *J = 7 Hz*, 2H); 5.39 (s, 2H); 3.13 (s, 6H); 1.31 (s, 9H); 1.29 (s, 9H). **^{13}C-NMR** (dmso-d^{6}, 125 MHz), δ ppm: 164.8; 164.7; 158.54; 158.51; 156.2; 143.2; 142.6; 141.8; 141.7; 141.4; 132.7; 131.3; 130.7; 129.2; 128.7; 128.2; 123.0; 120.2; 120.0; 119.4; 119.0; 116.7; 107.9; 56.0; 55.4; 34.4; 34.3; 31.7; 31.6. **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* $C_{36}H_{43}N_4O_2^+$ [M-Cl]$^+$ = 563.3375 *found* 563.3311. **FTIR** (KBr, cm^{-1}): 511, 622, 648, 668, 757, 819, 884, 945, 975, 1020, 1036, 1106, 1164, 1194, 1231, 1261, 1279, 1362, 1395, 1447, 1488, 1568, 1618, 1651, 2865, 2953, 3389.

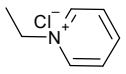
2.8. Synthesis of ligand L6

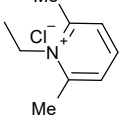
To obtain ***N,N´-bis(5-tert-butylsalicylidene)-1,2-phenylenediamine*** *(**L6**)* the solution of 1,2-phenylenediamine (0.54 g, 5 mmol) in 10 ml methanol was added to the refluxing solution of salicylaldehyde **A2** (1.87 g, 10.5 mmol) in 10 ml methanol. The resulting mixture was refluxed

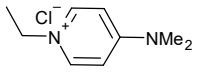
for several hours (TLC controlled, hexane:ethyl acetate = 90:10). The product of reaction was isolated by filtration and purified by recrystallization from CH_2Cl_2/MeOH. The product was obtained as a fine crystalline orange solid (1.28 g, 61%); m.p. 177-180°C. **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 12.82 (s, 2H), 8.63 (s, 2H), 7.41 (dd, *J* = 8.7, *J* = 2.4 Hz, 2H), 7.35 (d, *J* = 2.3 Hz, 2H), 7.34-7.29 (m, 2H), 7.25-7.20 (m, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 1.32 (s, 18H). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 164.0, 159.2, 142.8, 141.6, 130.9, 128.6, 127.5, 119.6, 118.5, 117.1, 34.0, 31.4. **FTIR** (KBr, cm^{-1}): 504, 622, 653, 740, 750, 758, 782, 792, 807, 822, 837, 894, 939, 963, 1104, 135, 1159, 1183, 1204, 1241, 1266, 1288, 1365, 1393, 1462, 1488, 1569, 1588, 1622, 2865, 2902, 2950.

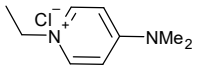
2.9. Synthesis of salophen chromium(III) complexes 1-6

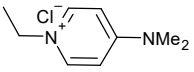


1 R_1, R_2 =  96%

2 R_1, R_2 =  97%

3 R_1, R_2 =  98%

4 R_1 = tBu, R_2 =  88%

5 R_1 = H, R_2 =  86%

6 R_1, R_2 = H 75%

General procedure (GP4): Anhydrous $CrCl_2$ (65 mg of 0.525 mmol) was dissolved in 8 ml THF that was dried over sodium benzophenone and freshly distilled. A 25 ml Schlenk flask equipped with a magnetic stirrer and a rubber septum, previously heated with a heat gun and cooled under argon, was used. In the second 5 ml Schlenk flask, equipped and treated similarly, salophen ligand (0.5 mmol) was dissolved in the mixture of THF (3 ml) and methanol (2 ml, dried under molecular sieves 3A). The

ligand solution was transferred to the $CrCl_2$ solution using a steal canula. The canula and the empty flask were additionally rinsed with 2 ml methanol. The flask with the reaction mixture was placed in the heating block on a magnetic stirrer and mixed under an argon atmosphere at 40°C for 4 hours. After that time, the heating block was removed, the flask opened and filled with air. The mixing under air atmosphere was continued at ambient temperature for 16 hours. The reaction mixture was concentrated to about 1/5 volume and 5 ml of dried diethyl ether was added. The precipitate was ground with a magnetic stirrer for 1 hour. The crushed precipitate was filtered on a fritted glass funnel and washed with an additional portion of diethyl ether. The resulting solid was dried under vacuum (1 mbar) at 50°C for 4 hours.

The structures of the chromium(III) complexes were concluded based on the results of FT-IR, HRMS, and ICP-OES analyses. The results of elementary analysis showed that the resulting salophen chromium(III) complexes **1-6** contain a molecule of THF coordinated additionally to the metal center. The HRMS spectra provided the peaks with values corresponding to (*salophen*)Cr^+ ions, without THF and Cl^- which are lost during analysis.

[N,N'-bis-{5-tert-butyl-3-[pyridinium-1-methyl]salicylidene}-1,2-phenylenediamine] chromium(III) trichloride (**1**)

To obtain complex **1**, was obtained according to GP4. ligand **L1 (**342 mg 0.5 mmol) and $CrCl_2$ (65 mg of 0.525 mmol) were used for the reaction. The product was obtained as brown solid (403 mg, 96%, calculated for the complex including a molecule of THF coordinated to Cr(III) ion). **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* $C_{40}H_{42}CrN_4O_2^{3+}$ $[M\text{-}3Cl]^{3+}$ = 220.7565 *found* 220.7547. ***Elemental analysis*** *calculated (%) for* $C_{44}H_{50}Cl_3CrN_4O_3$ (**1**·**THF**) Cr 6.18 *found* Cr 6.28. **FTIR** (KBr, cm^{-1}): 3365, 3054, 2959, 1631, 1613, 1582, 1542, 1485, 1391, 1365, 1258, 1206, 1153, 1042, 836, 761, 685, 534.

***[N,N'-bis-{5-tert-butyl-3-[(2,6-dimethyl)pyridinium-1-methyl]salicylidene}-1,2-phenylenediamine]chromium(III) trichloride* (2)**

To obtain complex **2**, was obtained according to GP4. ligand **L2 (**370 mg 0.5 mmol) and $CrCl_2$ (65 mg of 0.525 mmol) were taken to the reaction. The product was obtained as brown powder (436 mg, 97%, calculated for the complex including a molecule of THF coordinated to

Cr(III) ion). **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* $C_{44}H_{50}CrN_4O_2^{3+}$ $[M\text{-}3Cl]^{3+}$ = 239.4441 *found* 239.4409. ***Elemental analysis*** *calculated (%) for* $C_{48}H_{58}Cl_3CrN_4O_3$ (**2** ·**THF**) Cr 5.79 *found* Cr 5.82. **FTIR** (KBr, cm^{-1}): 3376, 2958, 1614, 1584, 1546, 1492, 1442, 1392, 1256, 1198, 760, 534.

[N,N'-bis-{5-tert-butyl-3-[(4-dimethylamino)pyridinium-1-methyl]salicylidene}-1,2-phenylenediamine]chromium(III) trichloride (3)

To obtain complex **3**, was obtained according to GP4. ligand **L3** (385 mg 0.5 mmol) and $CrCl_2$ (65 mg of 0.525 mmol) were taken to the reaction. The product was obtained as brown powder (451.5 mg, 98%, calculated for the complex including a molecule of THF coordinated to Cr(III) ion). **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* $C_{44}H_{52}CrN_6O_2^{+}$ $[M\text{-}3Cl]^{3+}$ = 249.4513 *found* 249.4498. ***Elemental analysis*** *calculated (%) for* $C_{48}H_{60}Cl_3CrN_6O_3$ (**3** ·**THF**) Cr 5.61 *found* Cr 5.68. **FTIR** (KBr, cm^{-1}): 3359, 3070, 2958, 1652, 1612, 1568, 1540, 1439, 1390, 1229, 1201, 1162, 833, 816, 762.

[N-{5-tert-butyl-3-[(4-dimethylamino)pyridinium-1-methyl}-N'-{(3,5-di-tert-butyl)salicylidene}-1,2-phenylenediamine]chromium(III) dichloride (4)

To obtain complex **4**, was obtained according to GP4. ligand **L4** (328 mg 0.5 mmol) and $CrCl_2$ (65 mg of 0.525 mmol) were taken to the reaction. The product was obtained as dark red powder (352 mg, 88%, calculated for the complex including a molecule of THF coordinated to Cr(III) ion). **HRMS** (AuNPET LDI-ToF) m/z: *calculated for* $C_{44}H_{57}CrN_4O_3^{2+}$ $[M\text{-}2Cl]^{2+}$ = 334.6625 *found* 334.6585. ***Elemental analysis*** *calculated (%) for* $C_{44}H_{57}Cl_2CrN_4O_3$ (**4** ·**THF**) Cr 6.40 *found* Cr 6.40. **FTIR** (KBr, cm^{-1}): 3369, 3072, 2959, 2867, 1652, 1614, 1580, 1540, 1462, 1385, 1230, 1190, 1164, 834, 759.

***[N-{3-tert-butyl-5-[(4-dimethylamino)pyridinium-1-methyl]}-N'-{(5-tert-butyl)salicylidene}-1,2-phenylenediamine]chromium(III) dichloride* (5)**

To obtain complex **5**, was obtained according to GP4. ligand **L5** (300 mg 0.5 mmol) and $CrCl_2$ (65 mg of 0.525 mmol) were taken to the reaction. The product was obtained as brown powder (326 mg, 86%, calculated for the complex including a molecule of THF coordinated to Cr(III) ion). **HRMS** (AuNPET LDI-ToF) *calculated for* $C_{40}H_{49}CrN_4O_3^{2+}$ $[M\text{-}2Cl]^{2+}$ = 306.6312 *found*

306.6299. ***Elemental analysis*** *calculated (%) for* $C_{33}H_{51}ClCrNO_3$ (**5** ·**THF**) Cr 6.87 *found* Cr 6.70. **FTIR** (KBr, cm^{-1}): 3378, 3066, 2904, 2867, 1650, 1608, 1580, 1567, 1532, 1460, 1441, 1420, 1384, 1362, 1271, 1256, 1195, 1163, 836, 816, 785, 748, 536.

[N,N´-Bis(5-tert-butylsalicylidene)-1,2-phenylenediamine]chromium(III) chloride (6)

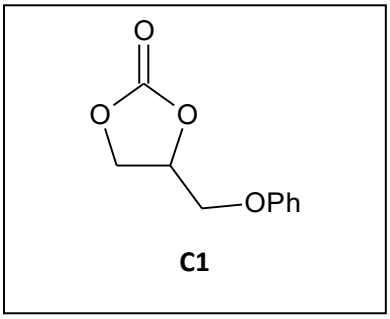
To obtain complex, ligand **L6** (429 mg, 0.5 mmol) and $CrCl_2$ (65 mg, 0.525 mmol) were used. transferred to the Schlenk tube under argon and 12 ml of anhydrous THF was added. The resulting mixture, which was deep red in color, was stirred under an argon atmosphere at 40°C for 4 hours. After that time, the heating block was removed, the flask was opened, and air could fill the flask. The mixing under air atmosphere was continued at ambient temperature for 16 hours. After the addition of 50 ml of diethyl ether, the organic layer was washed with saturated aqueous solutions of NH_4Cl (3 x 50 ml) and NaCl (1 x 50 ml) and dried over Na_2SO_4. The organic solvent was evaporated under reduced pressure to yield a dark red-brown solid. It was then resuspended in pentane and the resulting mixture was cooled to -20°C. The final product was filtered off and dried under vacuum. The product was obtained as brown powder (222 mg, 75%, calculated for the complex including a molecule of THF coordinated to Cr(III) ion). **HRMS** (AuNPET LDI-ToF) *calculated for* $C_{28}H_{30}CrN_2O_2^+$ $[M\text{-}Cl]^+$ = 478.1707 *found* 478.1702. ***Elemental analysis*** *calculated (%) for* $C_{32}H_{38}ClCrN_2O_3$ (**6** ·**THF**) Cr 8.87 *found* Cr 8.79. **FTIR** (KBr, cm^{-1}): 448, 502, 537, 566, 612, 674, 722, 748, 813, 835, 878, 1106, 1144, 1180, 1261, 1319, 1363, 1383, 1409, 1464, 1528, 1550, 1580, 1649, 2866, 2958, 3295.

2.10. Synthesis of cyclic carbonates

General procedure (GP5)**:** A glass pressure vessel (10 ml) was equipped with a magnetic bar, charged with chromium(III) complex (0.05 %-mol), biphenyl (100 mg) and epoxide (1,5 ml), sealed, placed in the preheated to 120°C oil bath, and finally pressurized to 6 bar with carbon dioxide. The reaction mixture was stirred vigorous for 2 hours. After that time, the oil bath was removed, the CO_2 flow was cut off, and the reactor was gently cooled first to room temperature in a water bath and then in an ice bath, before the CO_2 pressure was released

and the pressure vessel opened. The reaction mixture was solubilized with approx. 5-10 ml of acetone. All cyclic carbonates were isolated by column chromatography.

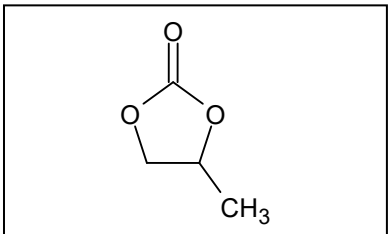
3-Phenoxypropylene carbonate **(CC1)**



C1

Carbonate **CC1** synthesis was carried out using 1.5 ml (1521 mg, 10.13 mmol) of phenyl glycidyl ether, 4.12 mg of **4** (5.07 mmol), 82 mg of biphenyl (0.53 mmol). The product was isolated by column chromatography (SiO_2, hexane : ethyl acetate = 2:1) obtained as white solid (1820 mg, 92%) m.p: 100-103°C. **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 7.35-7.27 (m, 2H); 7.02 (d, *^3J=7.4 Hz,* 1H); 6.91 (d, *^3J=8.2 Hz,* 2H); 5.06-4.98 (m, 1H); 4.61 (t, *^3J=8.4 Hz,* 1H); 4.53 (dd, *^2J=8.5 Hz, ^3J=5.9 Hz,* 1H); 4.23 (dd, *^2J=10.6 Hz, ^3J=4.2 Hz,* 1H); 4.14 (dd, *^2J=10.6 Hz, ^3J=3.6 Hz,* 1H); **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 157.8; 154.7; 129.7; 122.0; 114.6; 74.2; 66.9; 66.2. The analytical data are in agreement with the literature.[S8]

Propylene carbonate **(CC2)**

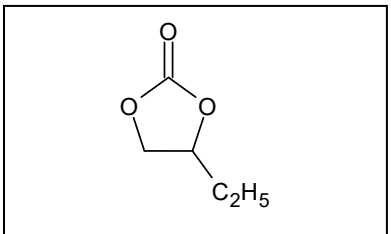


C2

Carbonate **CC2** synthesis was carried out using 1.5 ml (1104 mg, 19.01 mmol) of propylene oxide, 7.73 mg of **4** (9.50 mmol), 165 mg of biphenyl (1.07 mmol). The product was isolated by column chromatography (SiO_2, hexane : ethyl acetate = 3:1) obtained as light yellow oil (1378 mg, 71%). %). **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 4.89-4.80 (m, 1H); 4.54 (t, *^3J=8.3Hz,* 1H); 4.01 (dd, *^2J=8.2 Hz, ^3J=7.4 Hz,* 1H); 1.48 (d, *^3J=6.3Hz,* 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 155.0; 73.5; 70.7; 19.4 The analytical data are in agreement with the literature.[S8]

1,2-Butylene carbonate **(CC3)**

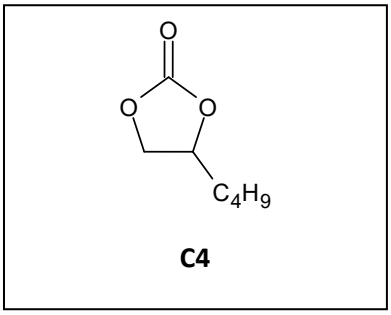
(4-ethyl-1,3-dioxolan-2-one)



C3

Carbonate **CC3** synthesis was carried out using 1.5 ml (1135 mg, 15.74 mmol) 1-butylene oxide, 6.38 mg of **4** (7.85 mmol), 133 mg of biphenyl (0.86 mmol). The product was isolated by column chromatography (SiO_2, hexane : ethyl acetate = 3:1) obtained as light yellow oil (1088 mg, 60%). **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 4.69-4.61 (m, 1H); 4.51 (t, *^3J=8.0Hz,* 1H); 4.07 (dd, *^2J=8.5 Hz, ^3J=7.0 Hz,* 1H); 1.86-1.70 (m, 2H); 1.01 (t, *^3J=7.4Hz,* 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 155.1; 78.0; 69.0; 26.9; 8.5. The analytical data are in agreement with the literature.[S8]

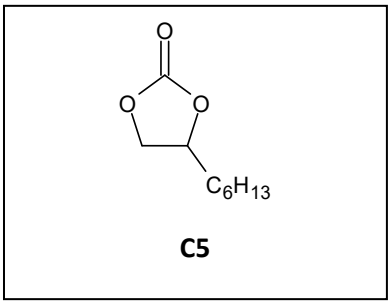
***1,2-hexylene carbonate* (CC4)**
(4-butyl-1,3-dioxolan-2-one)



C4

Carbonate **CC4** was carried out using 1.5 ml (1217 mg, 12.16 mmol) of 1-hexene oxide, 4.94 mg of **4** (6.08 mmol), 92 mg of biphenyl (0.60 mmol). The product was isolated by column chromatography (SiO_2, hexane : ethyl acetate = 5:1) obtained as light yellow oil (723 mg, 41%). **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 4.78-4.62 (m, 1H); 4.51 (t, *^3J=8.1Hz,* 1H); 4.06 (dd, *^2J=8.4 Hz, ^3J=7.3 Hz,* 1H); 1.87-1.73 (m, 1H); 1.73-1.60 (m, 1H); 1.51-1.41 (m, 1H); 1.41-1.29 (m, 3H); 0.91 (t, *^3J=7.0Hz,* 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 155.1; 77.1; 69.4; 33.6; 26.4; 22.2; 13.8. The analytical data are in agreement with the literature.[S8]

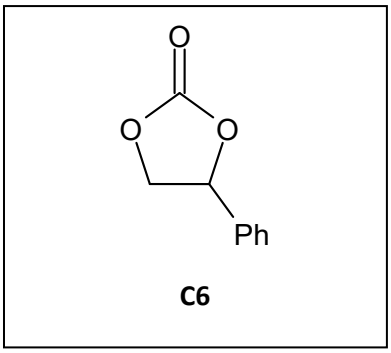
***1,2-Octylene carbonate* (CC5)**
(4-hexyl-1,3-dioxolan-2-one)



C5

Carbonate **CC5** was carried out using 1.5 ml (1261 mg, 9.44 mmol) of 1-octene oxide, 3.84 mg of **4** (4.72 mmol), 94 mg of biphenyl (0.61 mmol). The product was isolated by column chromatography (SiO_2, hexane : ethyl acetate = 5:1) obtained as light yellow oil (304 mg, 19%). **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 4.75-4.63 (m, 1H); 4.51 (t, *^3J=8.1Hz,* 1H); 4.05 (dd, *^2J=8.3 Hz, ^3J=7.3 Hz,* 1H); 1.86-1.75 (m, 1H); 1.72-1.63 (m, 1H); 1.52-1.41 (m, 1H); 1.40-1.22 (m, 7H); 0.88 (t, *^3J=6.9Hz,* 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 155.3; 77.2; 69.6; 34.1; 31.7; 29.0; 24.5; 22.6; 14.2.

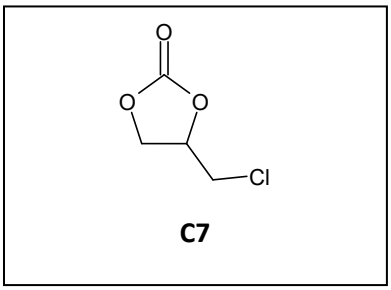
***Styrene carbonate* (CC6)**
(4-phenyl-1,3-dioxolan-2-one)



C6

Carbonate **CC6** was carried out using 1.5 ml (1468 mg, 12.21 mmol) of styrene oxide, 4.96 mg of **4** (6.10 mmol), 101 mg of biphenyl (0.65 mmol). The product was isolated by column chromatography (SiO_2, hexane : ethyl acetate = 5:1) obtained as white solid (697 mg, 35%) m.p: 56-59°C (5°/min). **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 7.48-7.40; (m, 3H); 7.39-7.33 (m, 2H); 5.67 (t, *^2J=8.0 Hz,* 1H); 4.80 (t, *^2J=8.4 Hz,* 1H); 4.39-4.30 (m, 1H). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 154.8; 135.8; 129.8; 129.3, 125.9; 78.0, 71.2. The analytical data are in agreement with the literature.[S8]

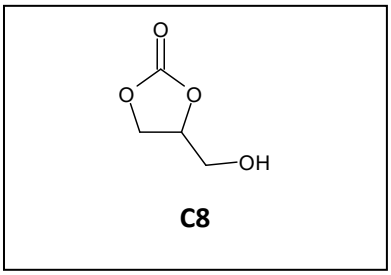
3-Chloropropylene carbonate (**CC7**)
(4-(chloromethyl)-1,3-dioxolan-2-one)



C7

Carbonate **CC7** was carried out using 1.5 ml (1606 mg, 17.35 mmol) of epichlorohydrin, 7.05 mg of **4** (8.67 mmol), 150 mg of biphenyl (0.97 mmol). The product was isolated by column chromatography (SiO_2, hexane : ethyl acetate = 3:1) obtained as light yellow oil (2130 mg, 91%). **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 5.01-4.93 (m, 1H); 4.58 (t, *^3J=8.4, Hz* 1H) 4.39 (dd, *^2J=8.9 Hz, ^3J=5.8 Hz,* 1H); 3.78 (dd, *^2J=12.2 Hz, ^3J=5.4 Hz,* 1H); 3.71 (dd, *^2J=12.2 Hz, ^3J=3.7 Hz,* 1H);. **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 154.3; 74.3; 67.0; 43.8. The analytical data are in agreement with the literature.[S8]

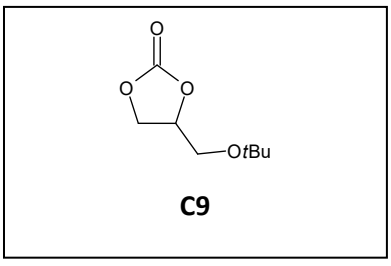
3-Hydroxypropylene carbonate (**CC8**)
(4-(Hydroxymethyl)-1,3-dioxolan-2-one)



C8

Carbonate **CC8** was carried out using 1.5 ml (1690 mg, 21.90 mmol) glycidol, 8.90 mg of **4** (10.95 mmol), 155 mg of biphenyl (1,00 mmol). The product was isolated by column chromatography (SiO_2, DCM : MeOH = 9:1) obtained as light yellow oil (2385 mg, 92%). **^{1}H-NMR** (dmso-d^6, 500 MHz), δ ppm: 5.23 (t, *^3J=5.6 Hz*, 1H); 4.81-4.73 (m, 1H); 4.47 (t, *^3J=8.3 Hz*, 1H); 4.26 (dd, *^2J=8.2 Hz, ^3J=5.9 Hz,* 1H); 3.68-3.61 (m, 1H); 3.53-3.45 (m, 1H). **^{13}C-NMR** (dmso-d6, 125 MHz), δ ppm: 155.6; 77.5; 66.3; 61.0. The analytical data are in agreement with the literature.[S8]

3-tert-Butyloxypropylene carbonate (**CC9**)
(4-(tert-butoxymethyl)-1,3-dioxolan-2-one)

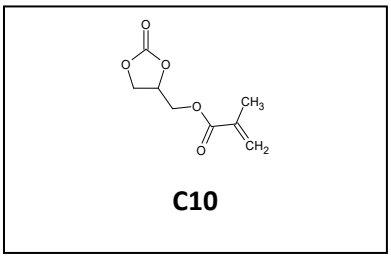


C9

Carbonate **CC9** was carried out using 1.5 ml (1263 mg, 9.71 mmol) *tert*-butyl glycidyl ether, 3.95 mg of **4** (4.86 mmol), 81 mg of biphenyl (0.52 mmol). The product was isolated by column chromatography (SiO_2, hexane : ethyl acetate = 3:1) obtained as light yellow oil (776 mg, 46%). **^{1}H-NMR** ($CDCl_3$, 500 MHz), δ ppm: 4.79-4.72 (m, 1H); 4.46 (t, *^3J=8.3, Hz* 1H); 4.37 (dd, *^2J=8.3 Hz, ^3J=5.8 Hz,* 1H); 3.60 (dd, *^2J=10.3 Hz, ^3J=4.6 Hz,* 1H); 3.59 (dd, *^2J=10.3 Hz, ^3J=3.6 Hz,* 1H). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 154.3; 74.3; 67.0; 43.8.

Glycerol carbonate methacrylate **(CC11)**

(4-(methacryloxymethyl)-1,3-dioxolan-2-one)



C10

Carbonate **CC11** was carried out using 1.5 ml (1614 mg, 11.35 mmol) glycidyl methacrylate, 4.48 mg of **4** (5.51 mmol), 89 mg of biphenyl (0.58 mmol). The product was isolated by column chromatography (SiO_2, hexane : ethyl acetate = 5:1) and obtained as light yellow oil (1653 mg, 78%). **^{1}H-NMR** ($CDCl_3$, 500 MHz) δ ppm: 6.13 (s, 1H); 5.64 (t, *^3J=1.2, Hz* 1H); 5.00-4.93 (m, 1H); 4.57 (t, *^3J=8.6, Hz* 1H); 4.41 (dd, *^2J=12.6 Hz, ^3J=3.1 Hz,* 1H), 4.36-4.28 (m, 2H); 1.93 (s, 3H). **^{13}C-NMR** ($CDCl_3$, 125 MHz), δ ppm: 166.8; 154.7; 135.3; 127.4; 74.0; 66.3; 63.6; 18.3.

3. Copies of NMR spectra

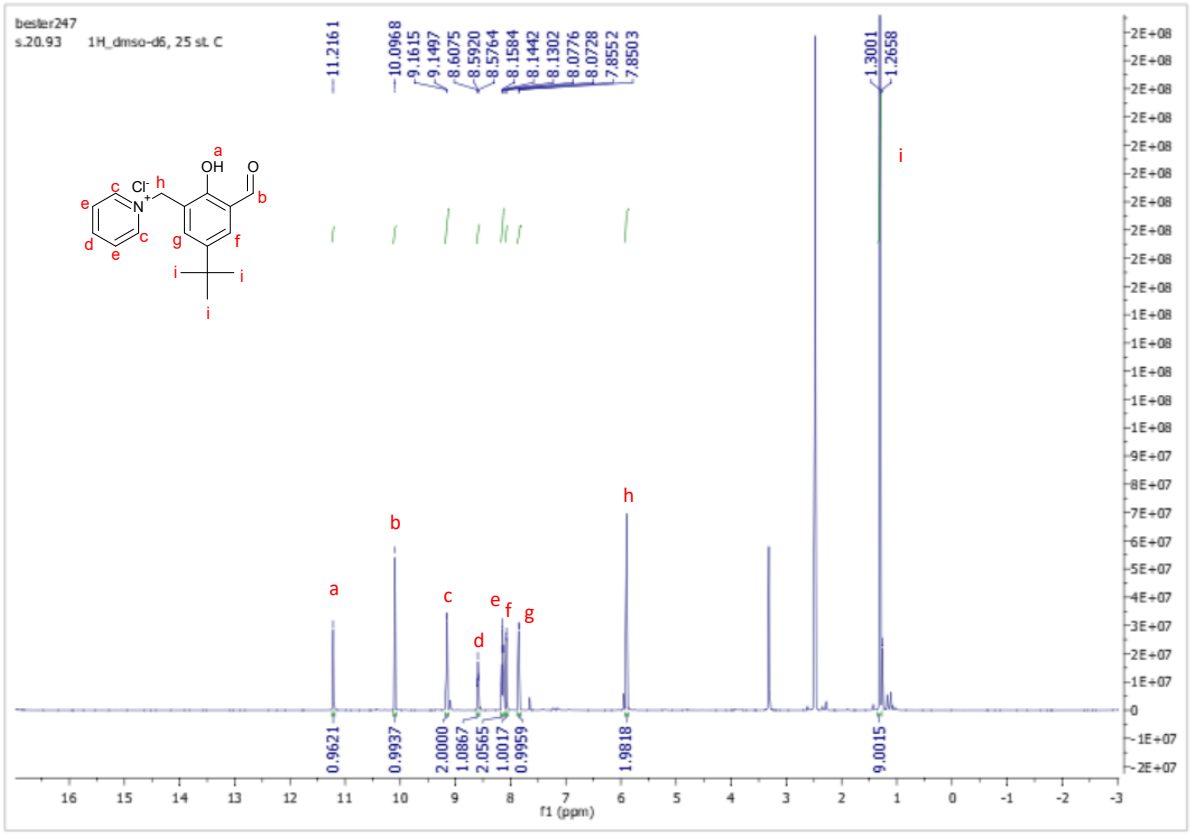


Figure 1 *^{1}H-NMR spectrum (dmso-d^6, 500 MHz) of* ***A4****.*

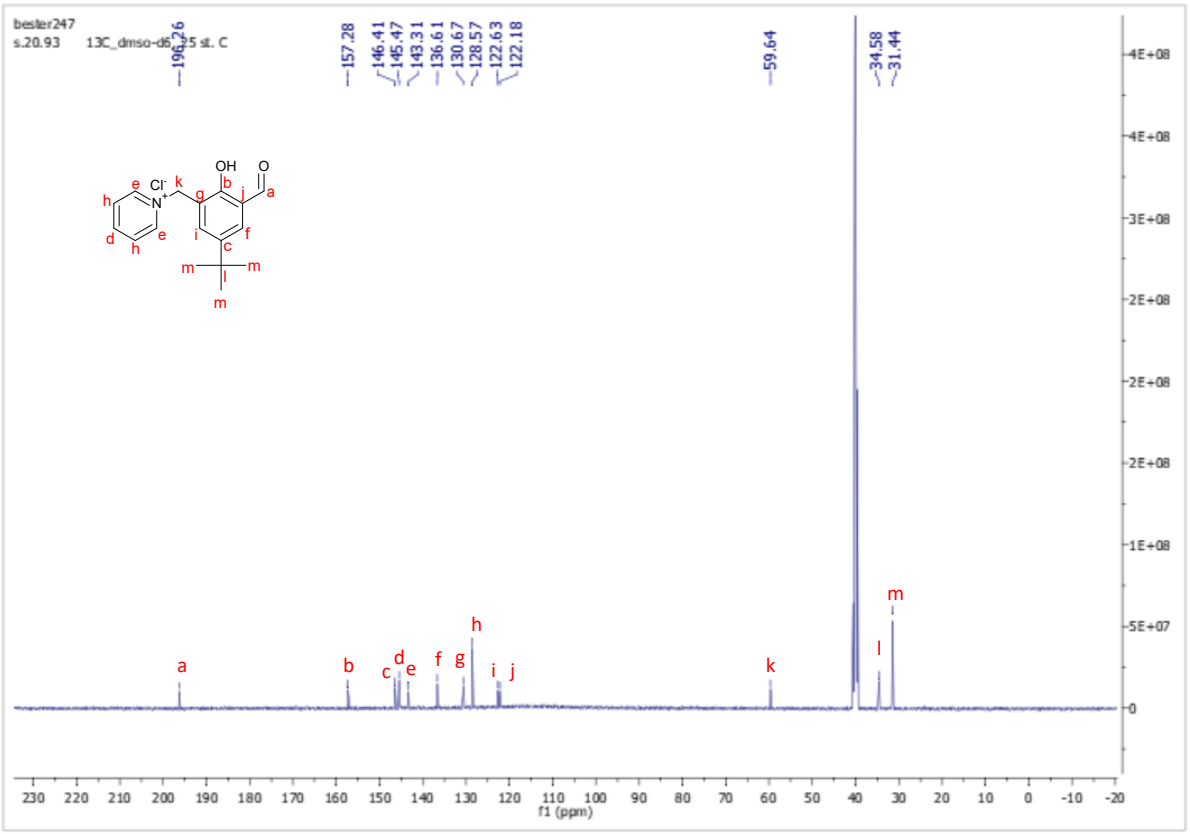


Figure 2 *^{13}C-NMR spectrum (dmso-d^6, 125 MHz) of* ***A4****.*

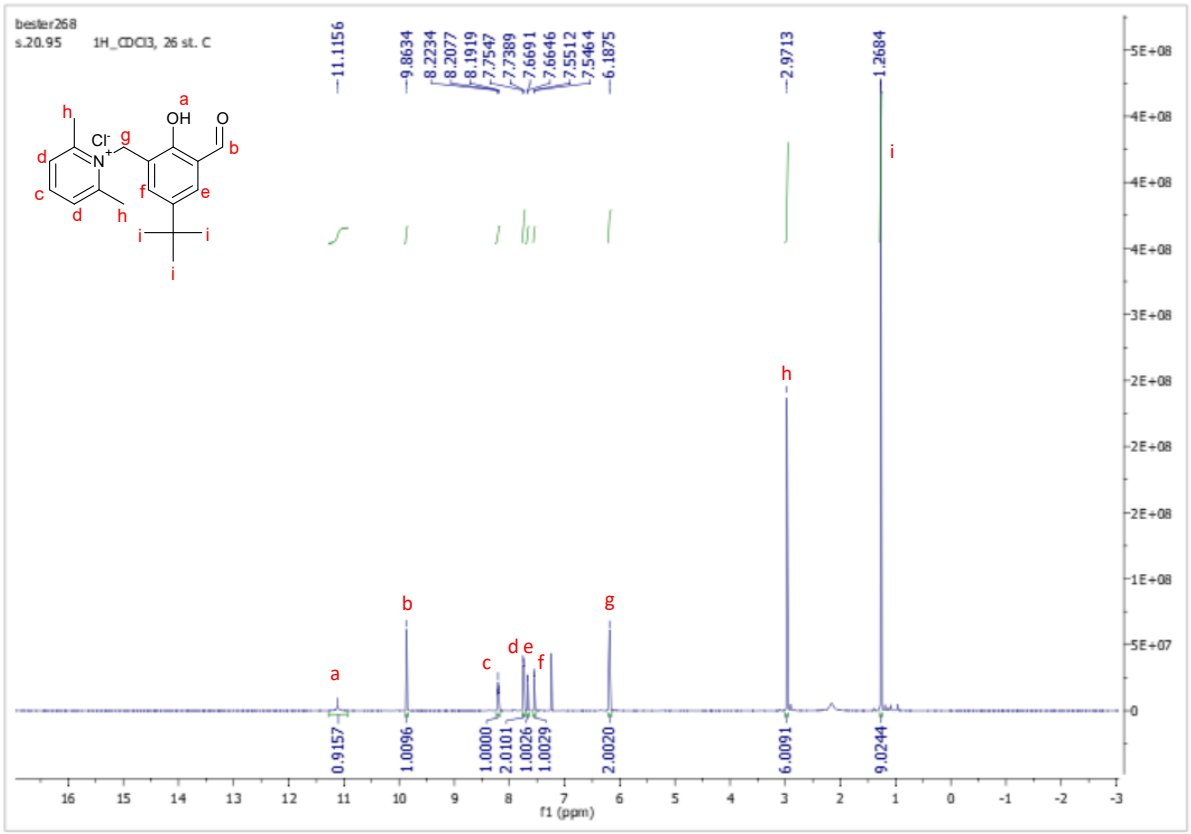


Figure 3 *^{1}H-NMR spectrum (dmso-d^6, 500 MHz) of* ***A5****.*

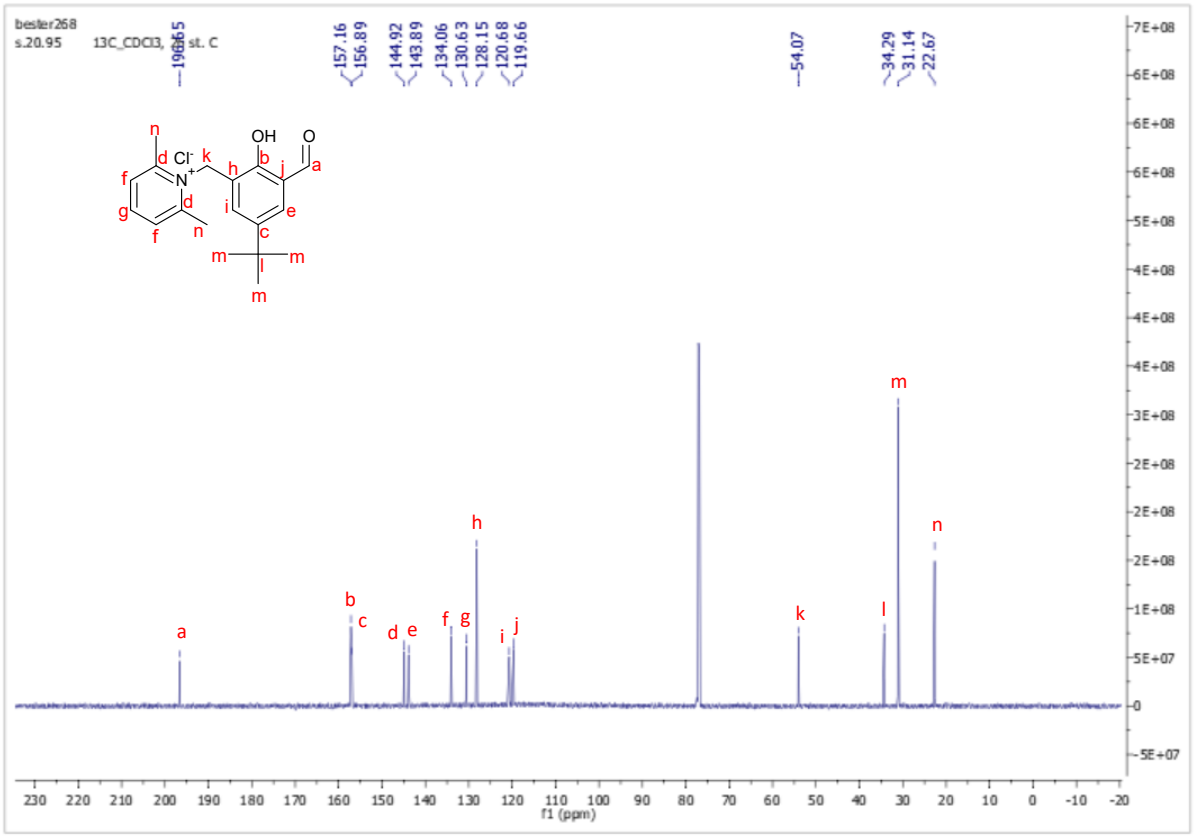


Figure 4 *^{13}C-NMR spectrum (dmso-d^6, 125 MHz) of* ***A5****.*

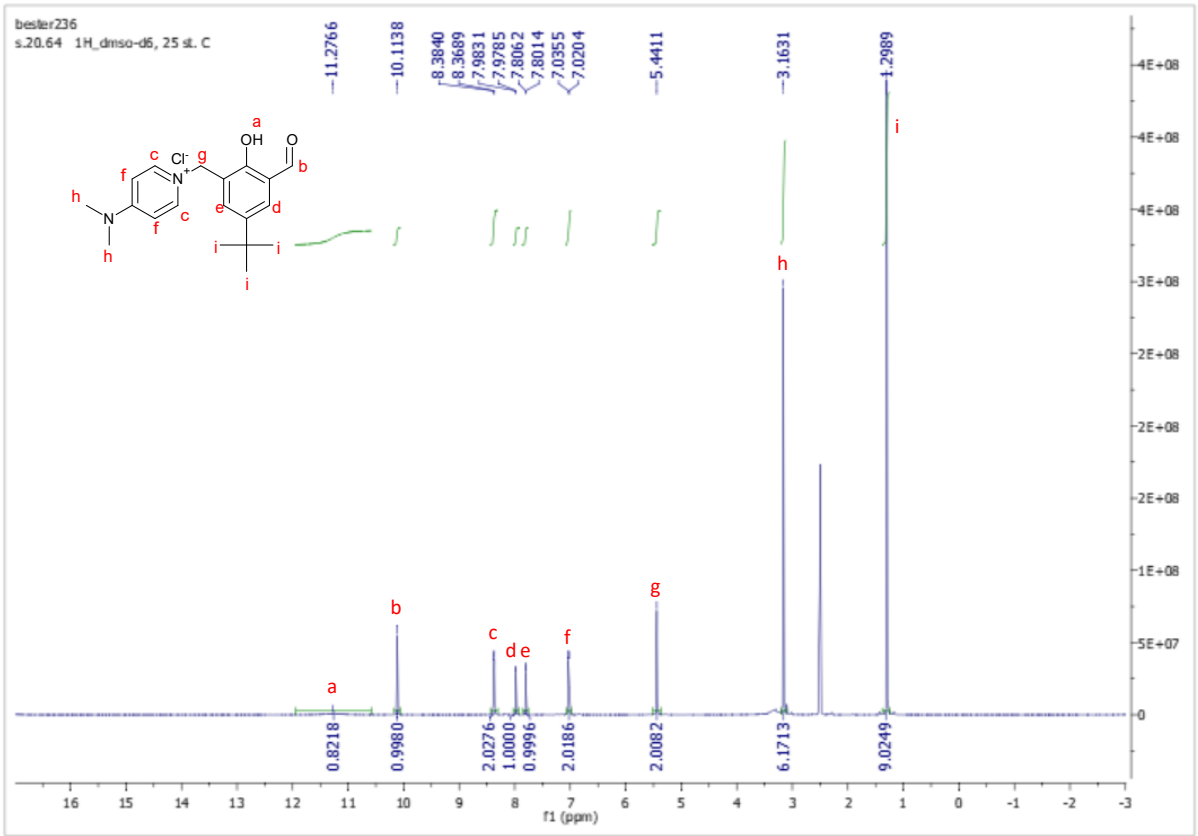


Figure 5 *^{1}H-NMR spectrum (dmso-d^6, 500 MHz) of* ***A6****.*

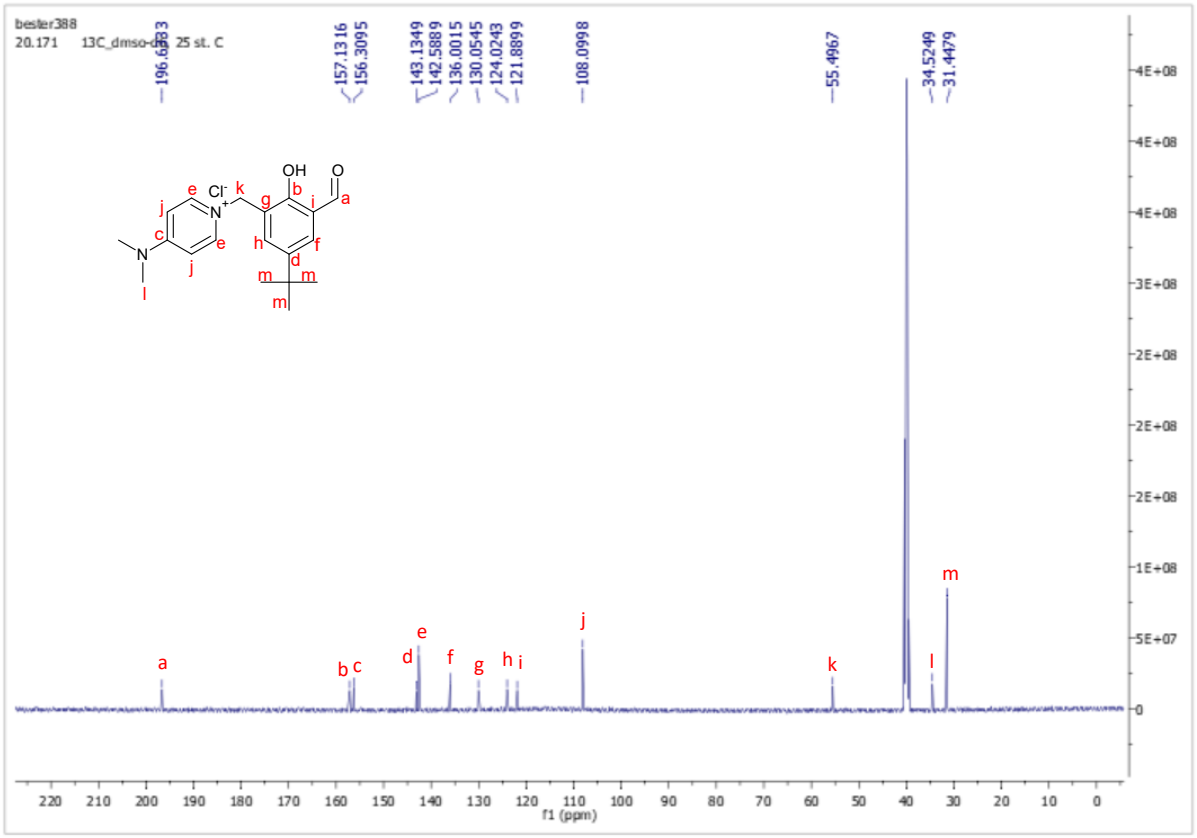


Figure 6 *^{13}C-NMR spectrum (dmso-d^6, 125 MHz) of* ***A6****.*

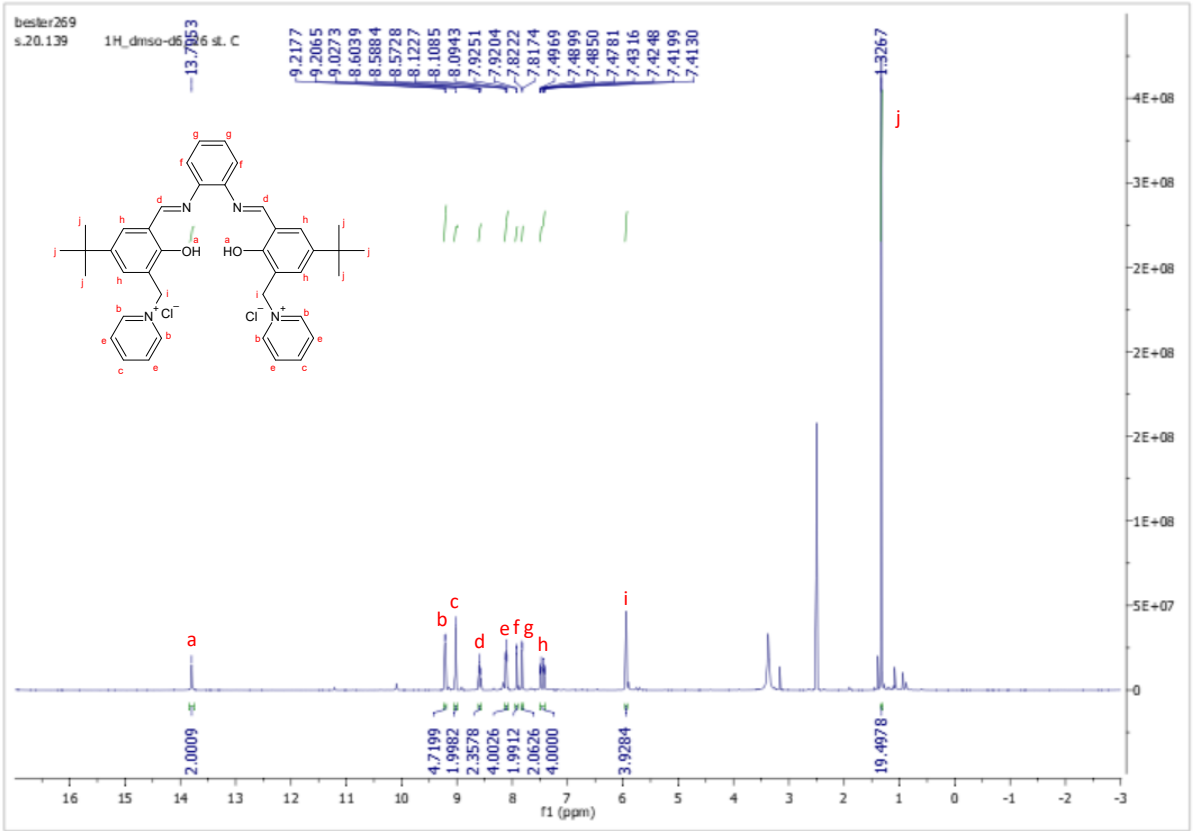


Figure 7 *^{1}H-NMR spectrum (dmso-d^6, 500 MHz) of* ***L1****.*

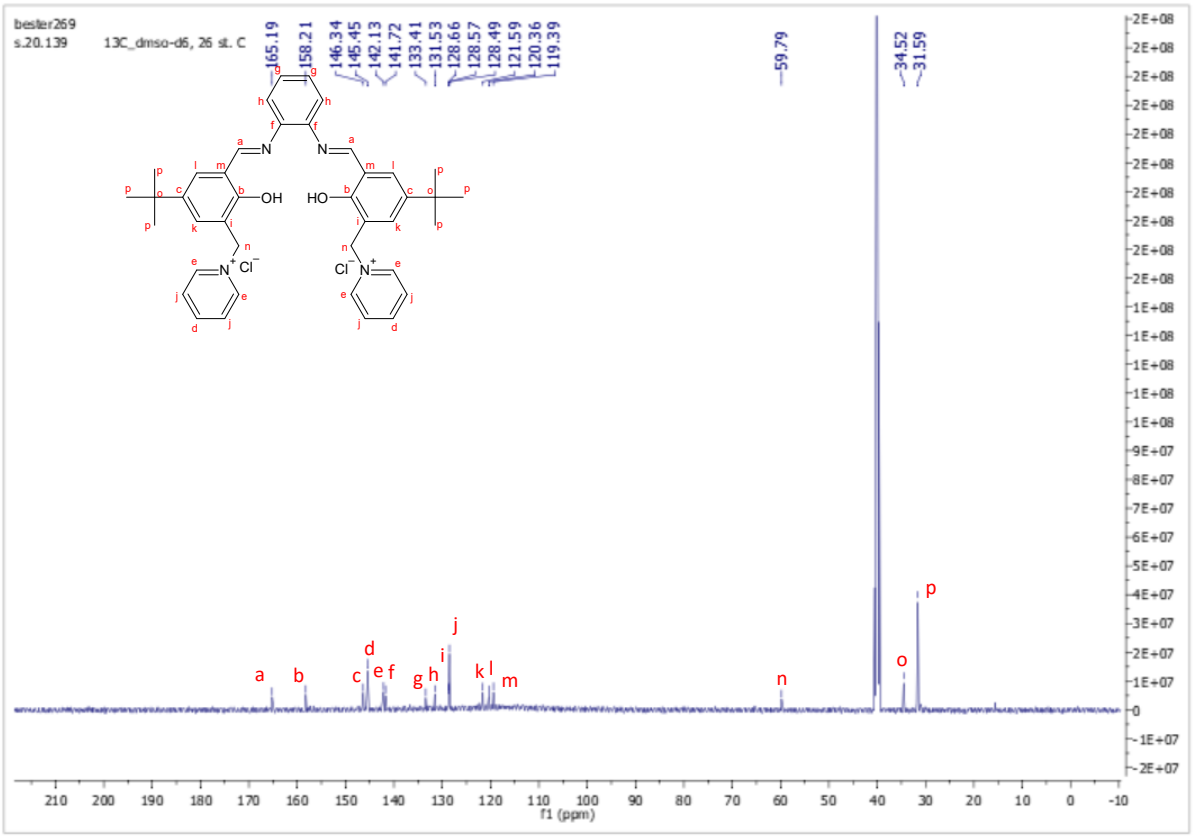


Figure 8 *^{13}C-NMR spectrum (dmso-d^6, 125 MHz) of* ***L1****.*

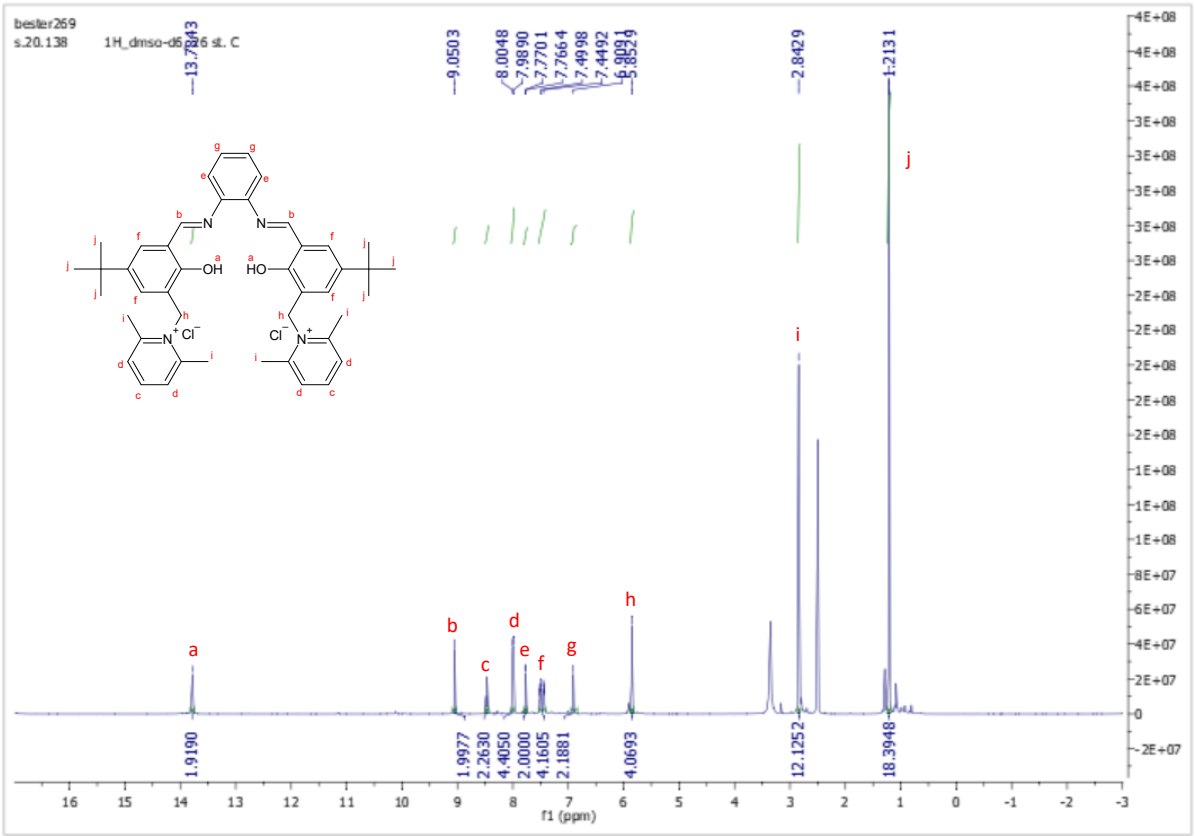


Figure 9 *^{1}H-NMR spectrum (dmso-d^6, 500 MHz) of* ***L2****.*

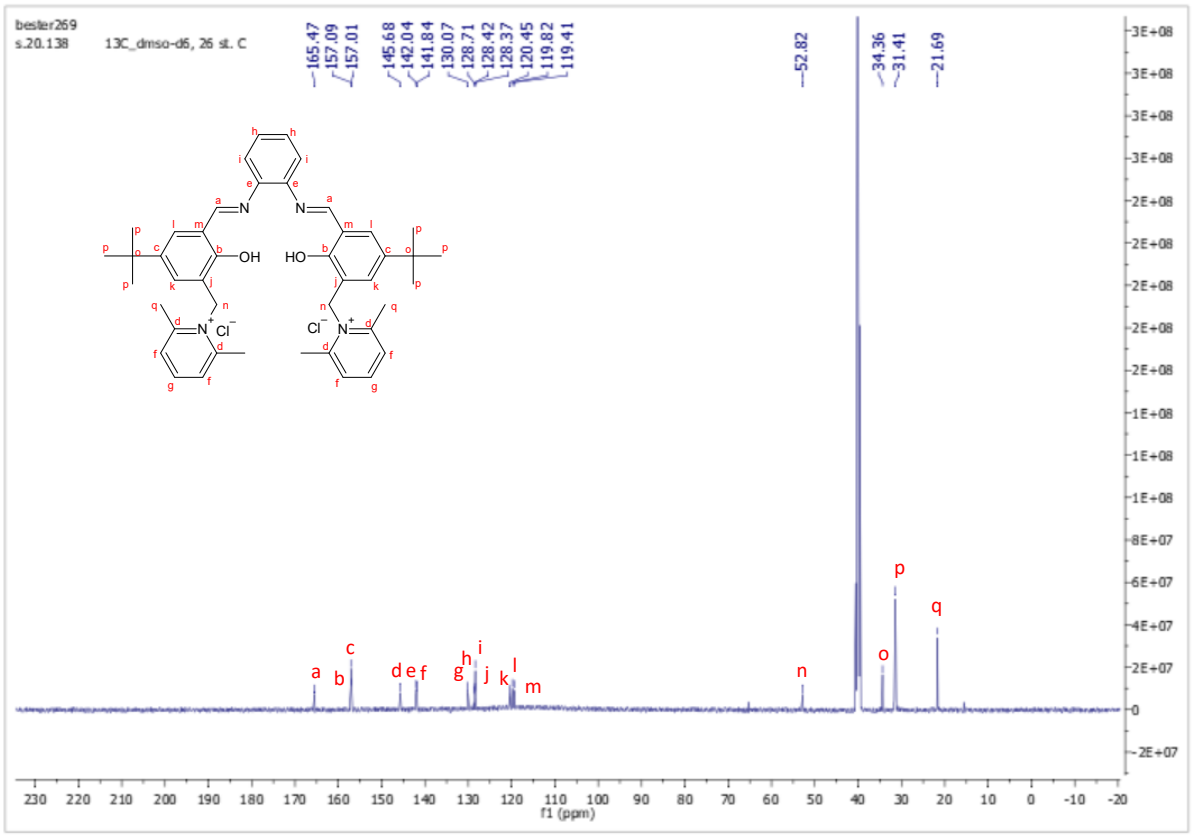


Figure 10 *^{13}C-NMR spectrum (dmso-d^6, 125 MHz) of* ***L2****.*

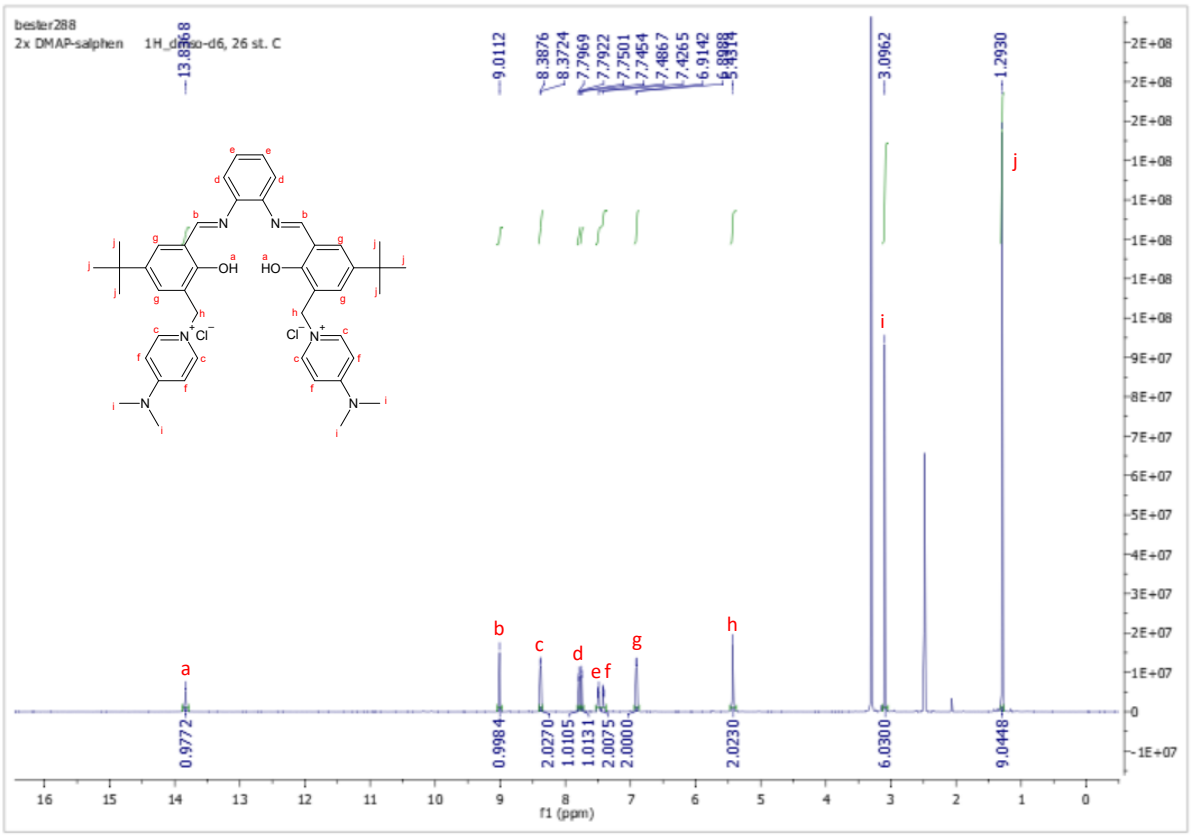


Figure 11 *^{1}H-NMR spectrum (dmso-d^6, 500 MHz) of* ***L3****.*

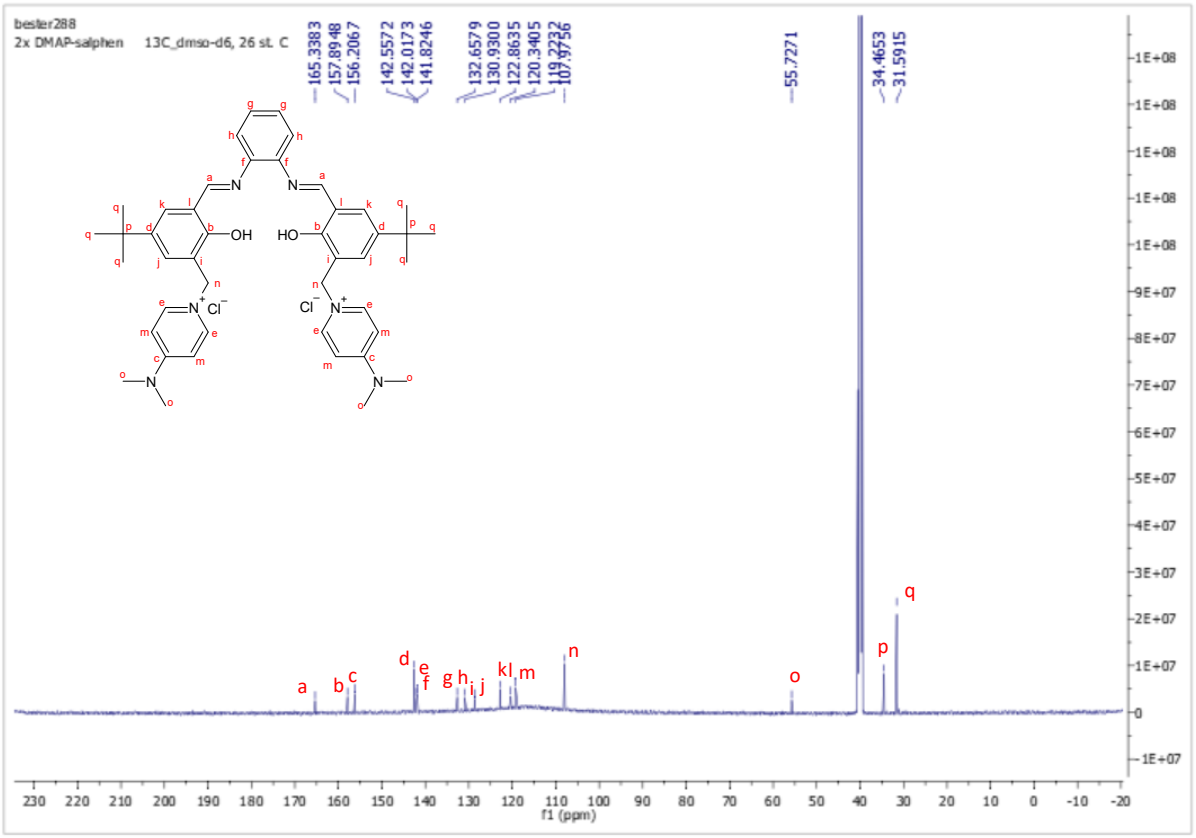


Figure 12 *^{13}C-NMR spectrum (dmso-d^6, 125 MHz) of* ***L3****.*

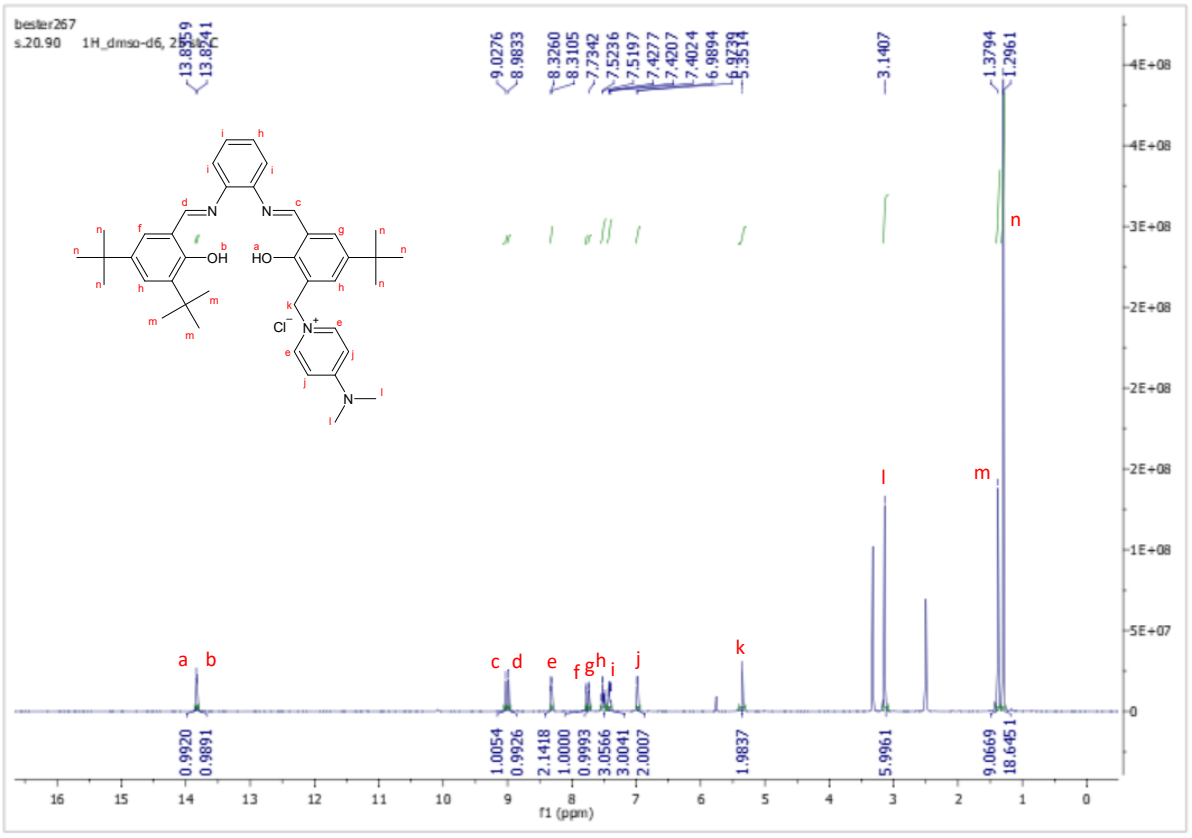


Figure 13 *^{1}H-NMR spectrum (dmso-d^6, 500 MHz) of* ***L4****.*

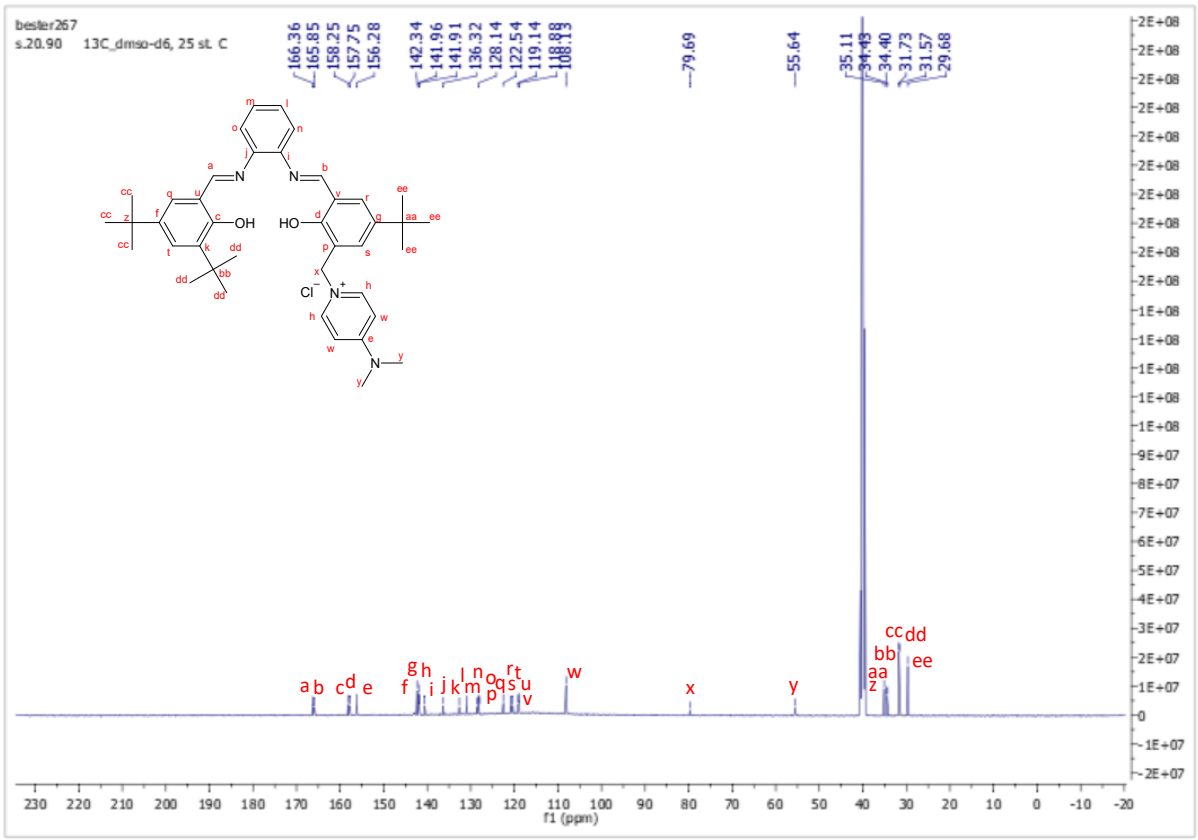


Figure 14 *^{13}C-NMR spectrum (dmso-d^6, 125 MHz) of **L4**.*

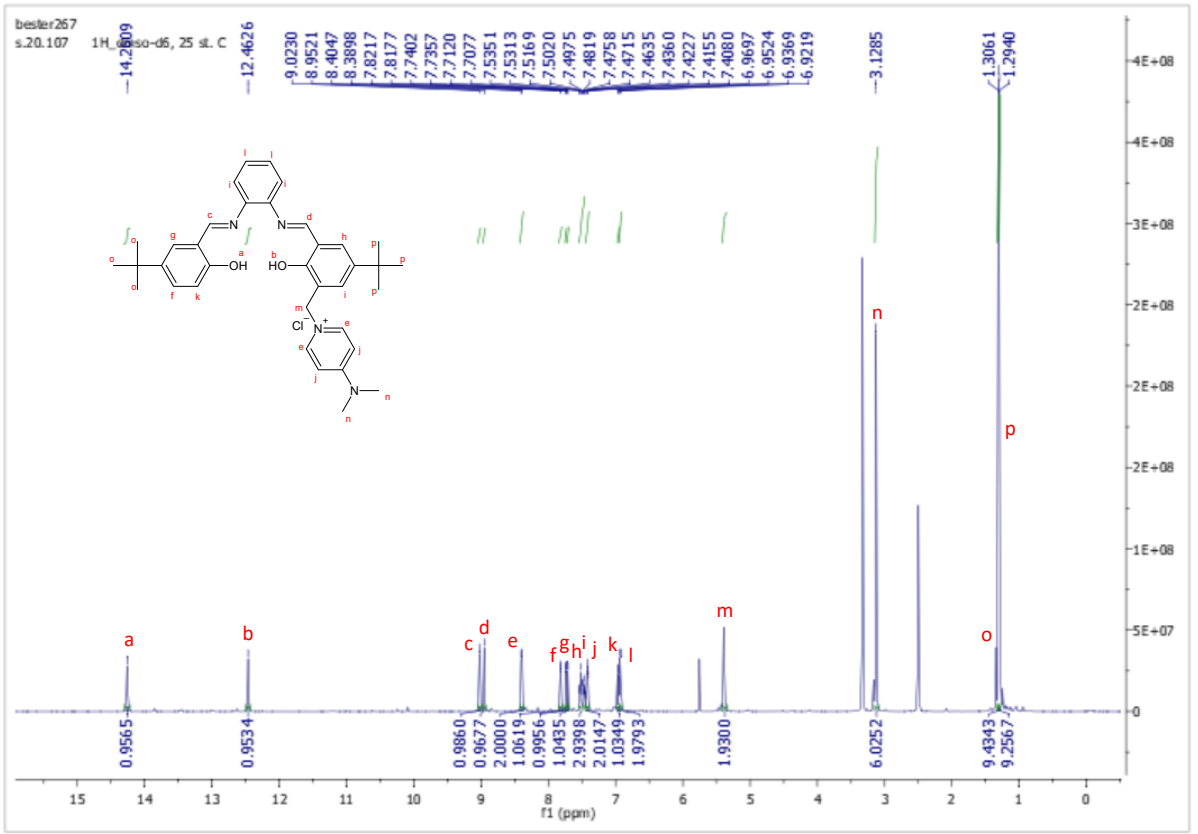


Figure 15 *^{1}H-NMR spectrum (dmso-d^6, 500 MHz) of **L5**.*

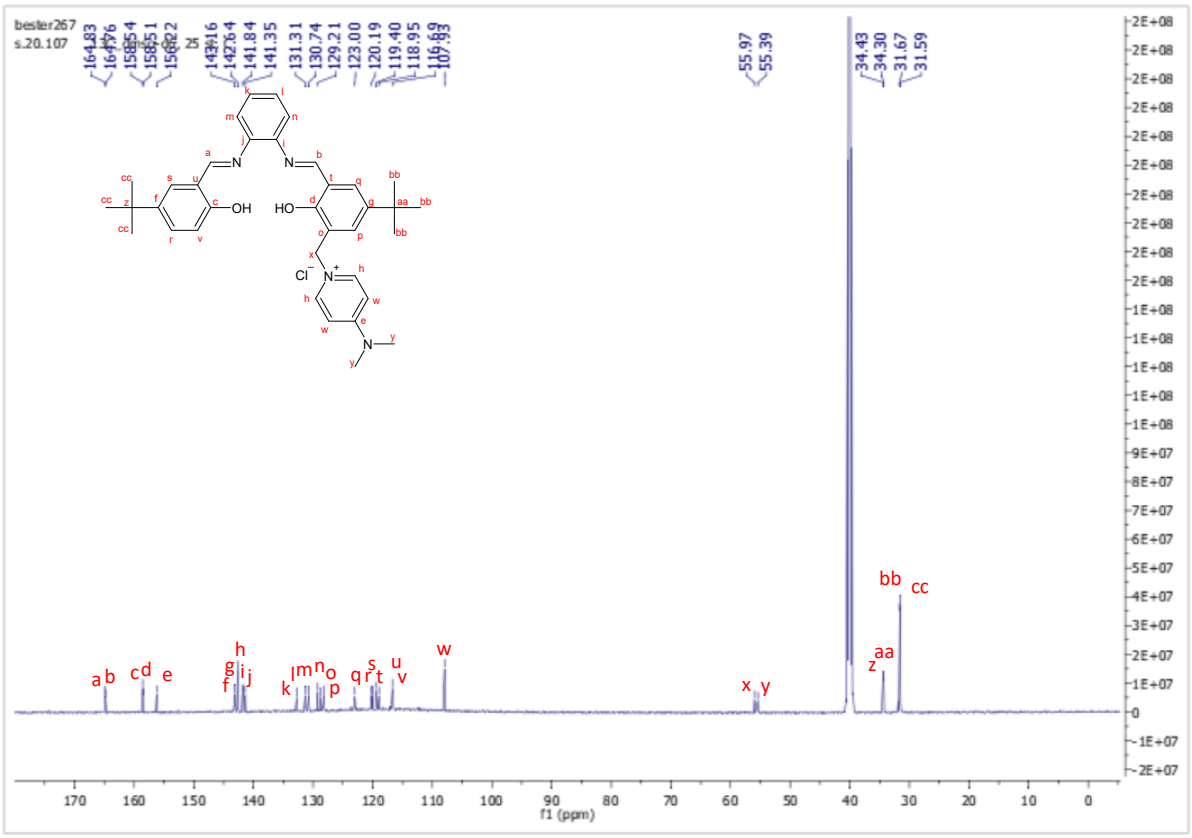


Figure 16 *^{13}C-NMR spectrum (dmso-d^{6}, 125 MHz) of* ***L5****.*

References

[1] J. Sekuła, J. Nizioł, W. Rode and Ruman T., *Anal. Chim. Acta,* 2015, **875**, 61.

[2] J. F. Larrow, E. N. Jacobsen, Y. Gao, Y. Hong, X. Nie, and C. M. Zepp., *J. Org. Chem*., 1994, **59**, 1939.

[3] G. Casiraghi, G. Casnati, G. Puglia, G. Sartori and G. Terenghi *J. Chem. Soc., Perkin Trans., 1980, **1**, 1862.*

[4] M. Mechler, K. Latendorf, W. Frey, R. Peters, *Organometallics,* 2013, **32**, 112.

[5] P. Meier, F. Broghammer, K. Latendorf, G. Rauhut, and R. Peters, *Molecules,* 2012, **17**, 7121.

[6] W. Luo, T. Shi, S. Liu, W. Zuo, Z. Li, *Organometallics,* 2017, **36**, 1736.

[7] Q.-H. You, L. Fan, W.-H. Chan, A. W. M. Lee, S. Shuang, *RSC Adv*., 2013, **3**, 15762.

[8] Á. Mesías-Salazar, Y. R. Yepes, J. Martínez, R. S. Rojas, *Catalysts,* **2021**, **11**(1), 2.