

Supporting Information for:

**New cobalt, iron and chromium catalysts based on easy-to-handle N<sub>4</sub>-chelating ligands for the coupling reaction of epoxides with CO<sub>2</sub>**

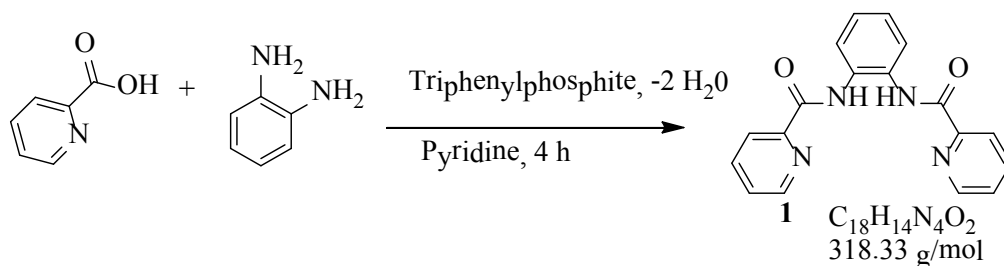
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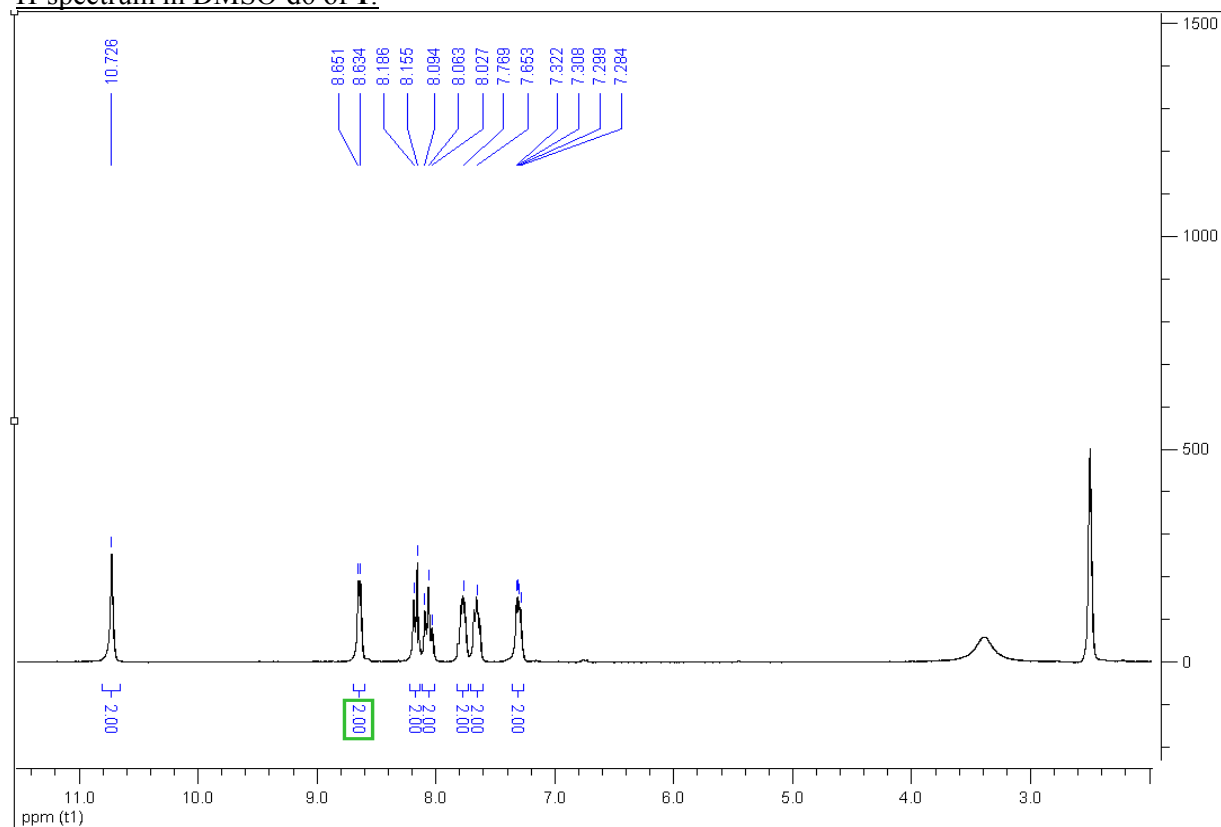
### Experimental data for 1:



The bpb-ligand was prepared according to the procedure described by Vagg *et al.* [1]. 0.12 mol picolinic acid in 48 ml abs. pyridine was mixed with 0.06 mol o-phenylenediamine in 12 ml abs. pyridine. After adding 31.5 ml (0.12 mol) triphenylphosphite the reaction solution was heated for 4 h at 120 °C and subsequently stirred at room temperature overnight. The solvent was removed under vacuum and the raw product was obtained as a brown solid. Through washing with 50 ml of ethanol and following drying under vacuum the pure product was obtained as a white powder. Yield: 9.39 g (50 %).

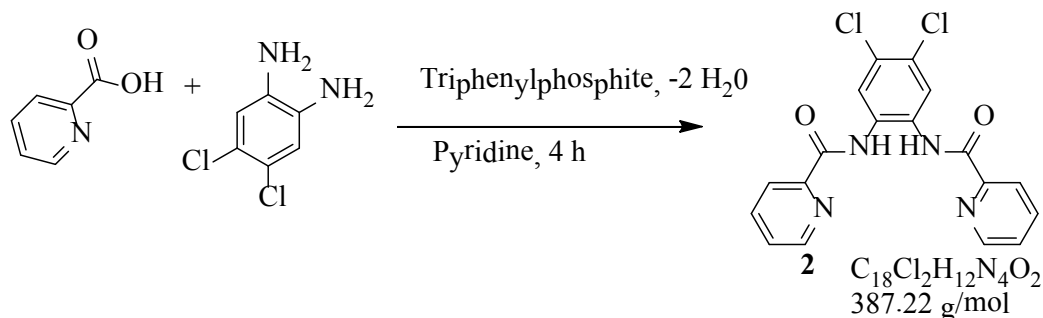
IR (cm<sup>-1</sup>): 3061 (m), 1942 (w), 1673 (s), 1592 (s), 1521 (s), 1451 (s), 1430 (s), 1300 (m), 1238 (m), 1127 (m), 1100 (m), 996 (m), 748 (m), 687 (m). <sup>1</sup>H-NMR: δ (ppm, DMSO-d<sub>6</sub>) = 7.30 (dd, *J* = 5.9 Hz, *J* = 3.6 Hz, 2 H), 7.60 - 7.70 (m, 2 H), 7.73 - 7.82 (m, 2 H), 8.10 (dt, *J* = 7.8 Hz, *J* = 1.4 Hz, 2 H), 8.14 - 8.22 (m, 2H) 8.64 (d, *J* = 4.2 Hz, 2 H), 10.72 (s, 2 H). <sup>13</sup>C{<sup>1</sup>H}NMR / DEPT135 (prim. =primary carbon ; sec.=secondary carbon ; tert.=tertiary carbon ; quat.= quaternary carbon): δ (ppm, CDCl<sub>3</sub>) = 123.2 (tert., 2 C), 126.6 (tert., 2 C), 127.0 (tert., 2 C), 127.9 (tert, 2 C), 132.4 (quat., 2 C), 139.2 (tert., 2 C), 149.9 (tert., 2 C), 150.3 (quat., 2 C), 163.4 (quat., 2 C). MS: (EI<sup>+</sup>) *m/z* = 319 [M+H]<sup>+</sup>. Anal. Calcd for C<sub>18</sub>H<sub>14</sub>N<sub>4</sub>O<sub>2</sub>: C, 67.91; H, 4.43; N, 17.60 Found: C, 67.75; H, 4.36; N, 17.82.

### <sup>1</sup>H-spectrum in DMSO-d<sub>6</sub> of 1:



[1] R.S. Vagg, D.J. Barnes, R.L. Chapman, E.C. Watton, *J. Chem. Eng. Data*, 1978, **23**, 349.

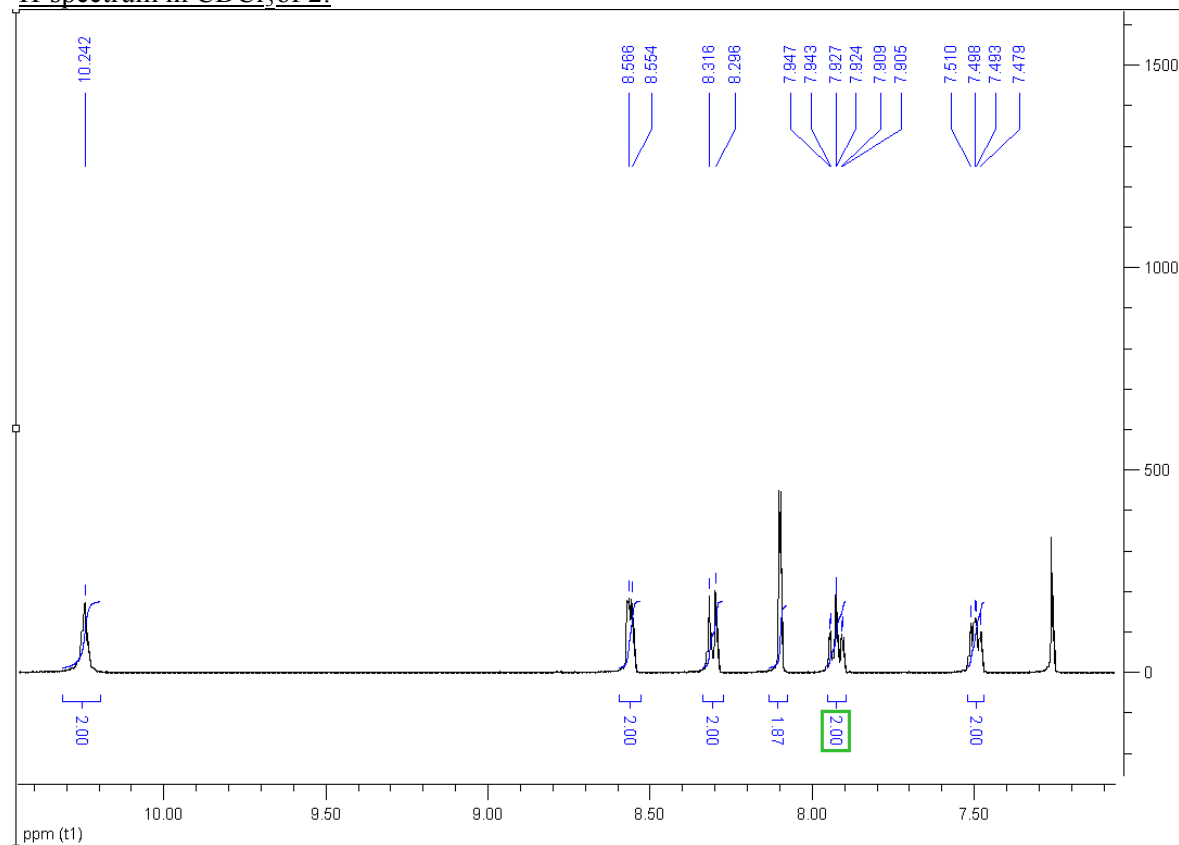
Experimental data for 2:



The bpbc<sub>l</sub><sub>2</sub>-ligand was prepared according to the procedure described by Vagg *et al.* [1]. 0.06 mol picolinic acid in 24 ml abs. pyridine was mixed with 0.03 mol 4,5-dichloro-o-phenylenediamine in 6 ml abs. pyridine. After adding 15.72 ml (0.06 mol) triphenylphosphite the reaction solution was heated for 4 h at 120 °C and subsequently stirred at room temperature overnight. The solvent was removed under vacuum and the raw product was obtained as a brown solid. Through washing with 50 ml of ethanol and following drying under vacuum the pure product was obtained as a white powder. Yield: 7.18 g (62 %).

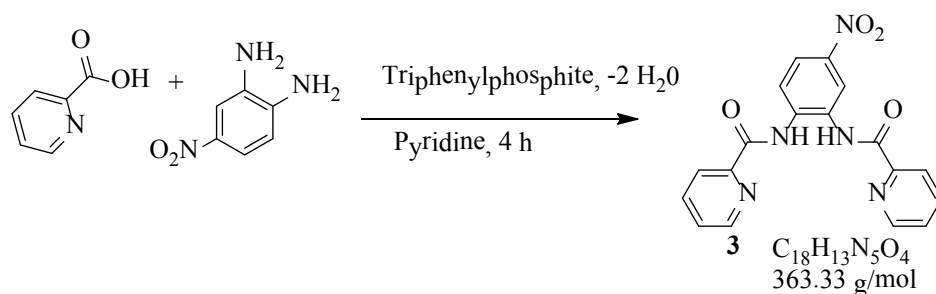
IR (cm<sup>-1</sup>): 3290 (m), 3053 (w), 1700 (s), 1582 (m), 1497 (vs), 1462 (m), 1429 (m), 1384 (m), 1278 (m), 1227 (m), 1127(w), 1040 (w), 998 (m), 879 (w), 815 (m), 743 (s), 691 (s), 569 (m). <sup>1</sup>H-NMR: δ (ppm, CDCl<sub>3</sub>) = 7.50 (dd, J = 6.9 Hz, J = 5.3 Hz, 2 H), 7.93 (dt, J = 7.8 Hz, J = 1.5 Hz, 2 H), 8.10 (s, 2 H), 8.31 (d, J = 7.9 Hz, 2 H), 8.56 (d, J = 4.7 Hz, 2 H), 10.24 (s, 2 H). <sup>13</sup>C{<sup>1</sup>H}-NMR / DEPT135: δ (ppm, CDCl<sub>3</sub>) = 122.9 (tert., 2 C), 125.8 (tert., 2 C; quat., 2 C), 127.07 (tert., 2 C), 129.6 (quat., 2 C), 137.9 (tert., 2 C), 148.5 (tert., 2 C), 149.3 (quat., 2 C), 163.1 (quat., 2 C). MS: (EI<sup>+</sup>) m/z = 387 [M+H]<sup>+</sup>. Anal. Calcd for C<sub>18</sub>Cl<sub>2</sub>H<sub>12</sub>N<sub>4</sub>O<sub>2</sub>: C 55.83; H 3.12; N 14.47 Found: C 54.91; H 3.08; N 14.32.

<sup>1</sup>H-spectrum in CDCl<sub>3</sub> of 2:



[1] R.S. Vagg, D.J. Barnes, R.L. Chapman, E.C. Watton, *J. Chem. Eng. Data*, 1978, **23**, 349.

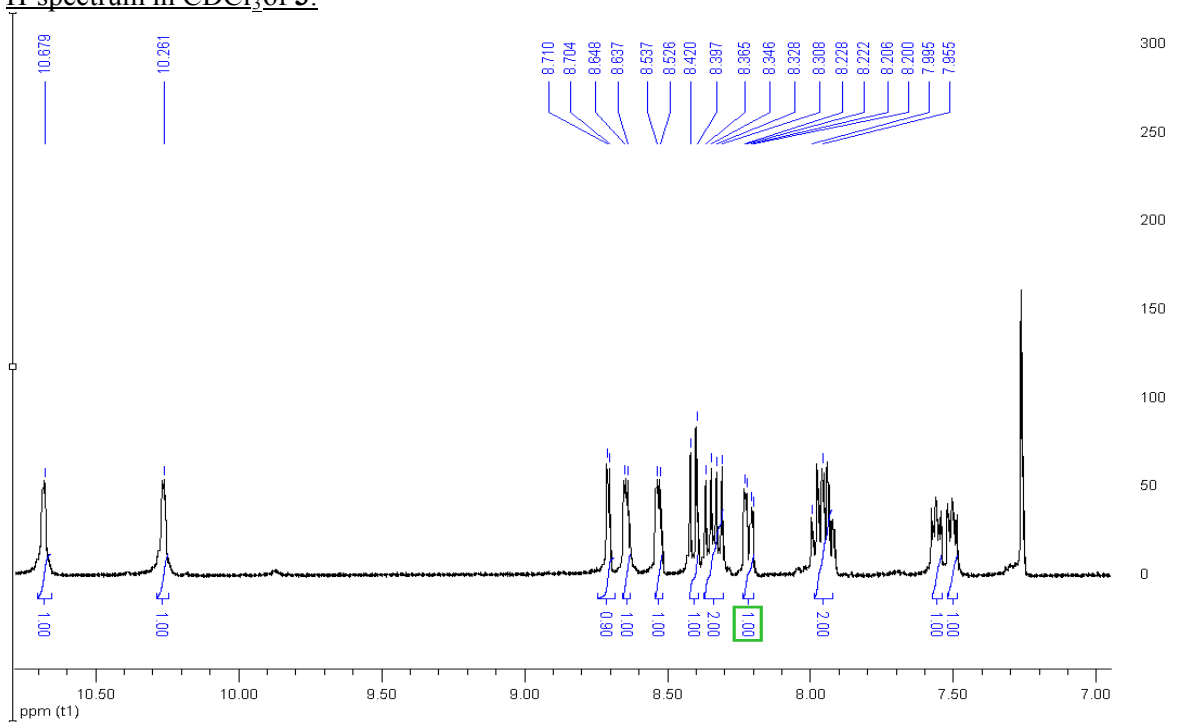
Experimental data for 3:



The bpbNO<sub>2</sub>-ligand was prepared according to the procedure described by Vagg *et al.* [1]. 0.06 mol picolinic acid in 24 ml abs. pyridine was mixed with 0.03 mol 4-nitro-o-phenylenediamine in 6 ml abs. pyridine. After adding 15.72 ml (0.06 mol) triphenylphosphite the reaction solution was heated for 4 h at 120 °C and subsequently stirred at room temperature overnight. The solvent was removed under vacuum and the raw product was obtained as a brown solid. Through washing with 50 ml of ethanol and following drying under vacuum the pure product was obtained as a light yellow powder. Yield: 3.90 g (36 %).

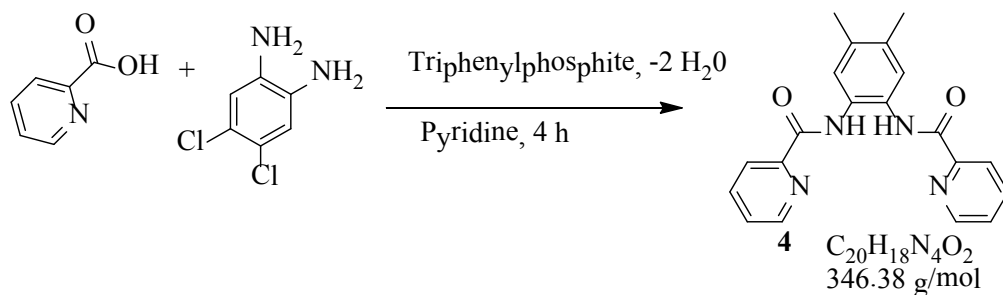
IR (cm<sup>-1</sup>): 3336 (m), 3269 (m), 3126 (w), 3052(m), 3005 (w), 2925 (m), 1701 (s), 1667 (vs), 1611 (m), 1592 (s), 1536 (s), 1503 (vs), 1475 (s), 1432 (m), 1344 (s), 1284 (s), 1235 (m), 1136 (w), 1109 (m), 1042 (w), 998 (m), 883 (m), 828 (w), 750 (m), 694 (m), 621 (m). <sup>1</sup>H-NMR: δ (ppm, CDCl<sub>3</sub>) = 7.50 (dd, J = 7.5 Hz, J = 4.8 Hz, 1 H), 7.60 (dd, J = 7.4 Hz, J = 4.7 Hz, 1 H), 7.91 – 8.00 (m, 2 H), 8.21 (dd, J = 9.0 Hz, J = 2.3 Hz, 1 H), 8.34 (dd, J = 15.2 Hz, J = 8.0 Hz, 2 H), 8.40 (d, J = 9.0 Hz, 1 H), 8.53 (d, J = 4.6 Hz, 1 H), 8.64 (d, J = 4.8 Hz, 1 H), 8.71 (d, J = 2.4 Hz, 1 H), 10.26 (s, 1 H), 10.68 (s, 1 H). <sup>13</sup>C{<sup>1</sup>H}-NMR / DEPT135: δ (ppm, DMSO-d<sub>6</sub>) = 121.0 (tert., 1 C), 121.2 (tert., 1 C), 122.7 (tert., 1 C), 124.4 (tert., 1 C), 127.5 (tert., 1 C), 127.6 (tert., 1 C), 130.5 (tert., 1 C), 137.5 (quat., 1 C), 138.3 (tert., 1 C), 138.5 (tert., 1 C), 143.7 (quat., 1 C), 148.7 (tert., 1 C), 148.7 (tert., 1 C), 148.9 (quat., 1 C), 149.6 (quat., 1 C), 150.3 (quat., 1 C), 162.8 (quat., 1 C), 163.5 (quat., 1 C). MS: (EI<sup>+</sup>) m/z = 364 [M+H]<sup>+</sup>. Anal. Calcd for C<sub>18</sub>H<sub>13</sub>N<sub>5</sub>O<sub>4</sub>: C 59.50; H 3.61; N 19.28 Found: C 59.46; H 3.72; N 19.63.

<sup>1</sup>H-spectrum in CDCl<sub>3</sub> of 3:



[1] R.S. Vagg, D.J. Barnes, R.L. Chapman, E.C. Watton, *J. Chem. Eng. Data*, 1978, **23**, 349.

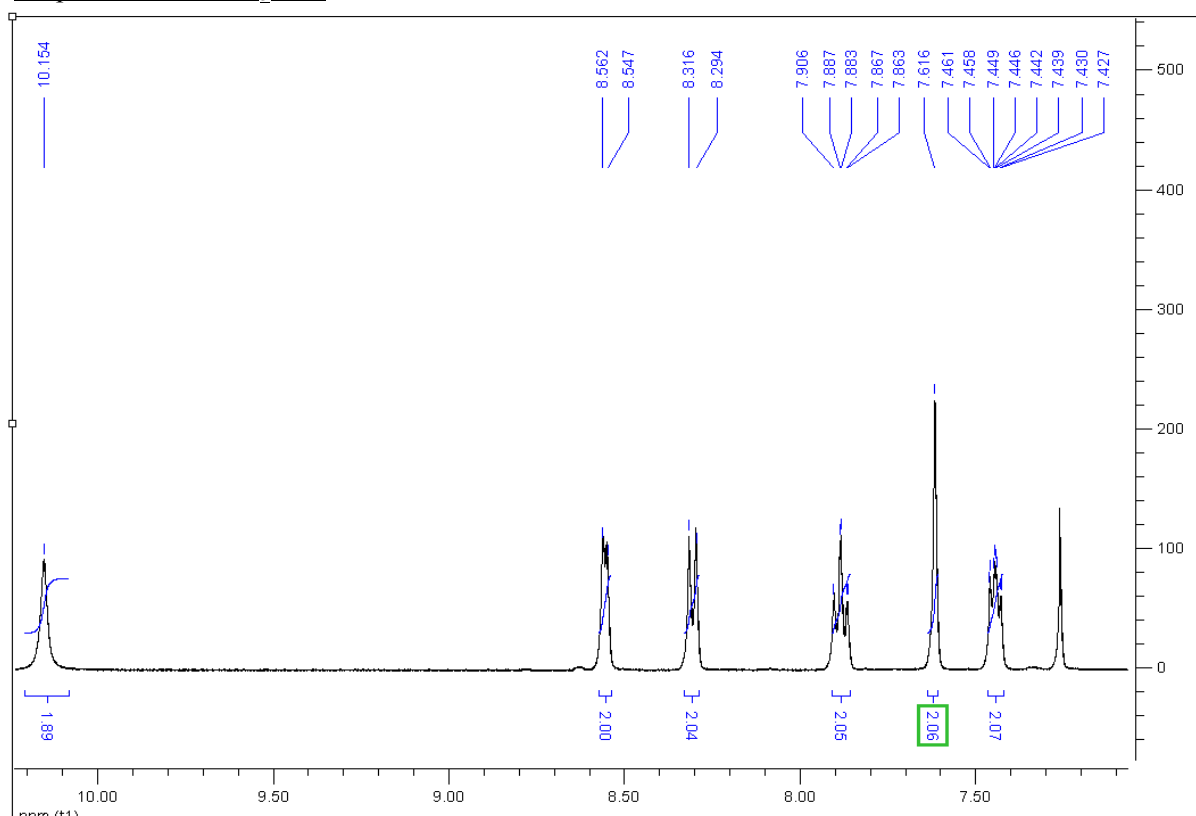
Experimental data for 4:



The bpbMe<sub>2</sub>-ligand was prepared according to the procedure described by Vagg *et al.* [1]. 0.06 mol picolinic acid in 24 ml abs. pyridine was mixed with 0.03 mol 4,5-dimethyl-o-phenylenediamine in 6 ml abs. pyridine. After adding 15.72 ml (0.06 mol) triphenylphosphite the reaction solution was heated for 4 h at 120 °C and subsequently stirred at room temperature overnight. The solvent was removed under vacuum and the raw product was obtained as a brown solid. Through washing with 50 ml of ethanol and following drying under vacuum the pure product was obtained as a white powder. Yield: 8.09 g (78 %).

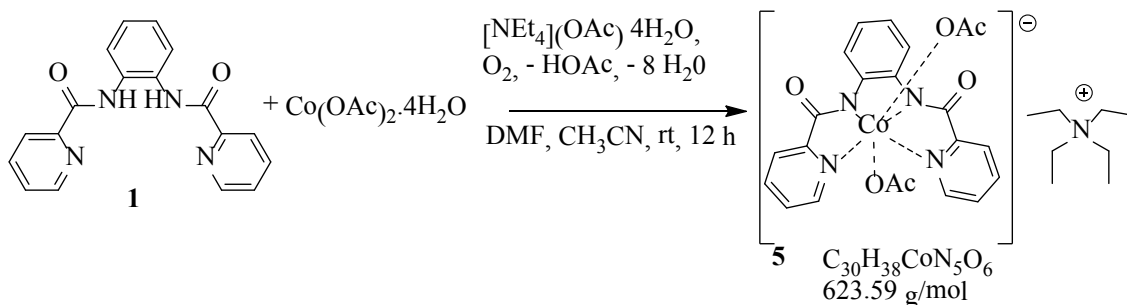
IR (cm<sup>-1</sup>): 3055 (w), 2923 (m), 2856 (w), 1669 (vs), 1592 (m), 1512 (s), 1457 (m), 1433 (m), 1316 (m), 1282 (w), 1238 (m), 1126(m), 1041 (w), 997 (m), 875 (w), 820 (m), 748 (s), 690 (s), 553 (m). <sup>1</sup>H-NMR: δ (ppm, CDCl<sub>3</sub>) = 2.30 (s, 6 H), 7.44 (ddd, J = 7.6 Hz, J = 4.8 Hz, J = 1.2 Hz, 1 H), 7.62 (s, 2 H), 7.89 (dt, J = 7.7 Hz, J = 1.7 Hz, 2 H), 8.29 – 8.32 (m, 2 H), 8.54 – 8.57 (m, 2 H), 10.15 (s, 2 H). <sup>13</sup>C{<sup>1</sup>H}-NMR / DEPT135: δ (ppm, CDCl<sub>3</sub>) = 19.5 (prim., 2 C), 122.5 (tert., 2 C), 125.6 (tert., 2 C), 126.3 (tert., 2 C), 127.7 (quat., 2 C), 134.8 (quat., 2 C), 137.4 (tert., 2 C), 148.1 (tert., 2 C), 149.8 (quat., 2 C), 162.8 (quat., 2 C). MS: (EI<sup>+</sup>) m/z = 347 [M+H]<sup>+</sup>. Anal. Calcd for C<sub>20</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>: C 69.35; H 5.24; N 16.17 Found: C 69.69; H 5.41; N 16.42.

<sup>1</sup>H-spectrum in CDCl<sub>3</sub> of 4:



[1] R.S. Vagg, D.J. Barnes, R.L. Chapman, E.C. Watton, *J. Chem. Eng. Data*, 1978, **23**, 349.

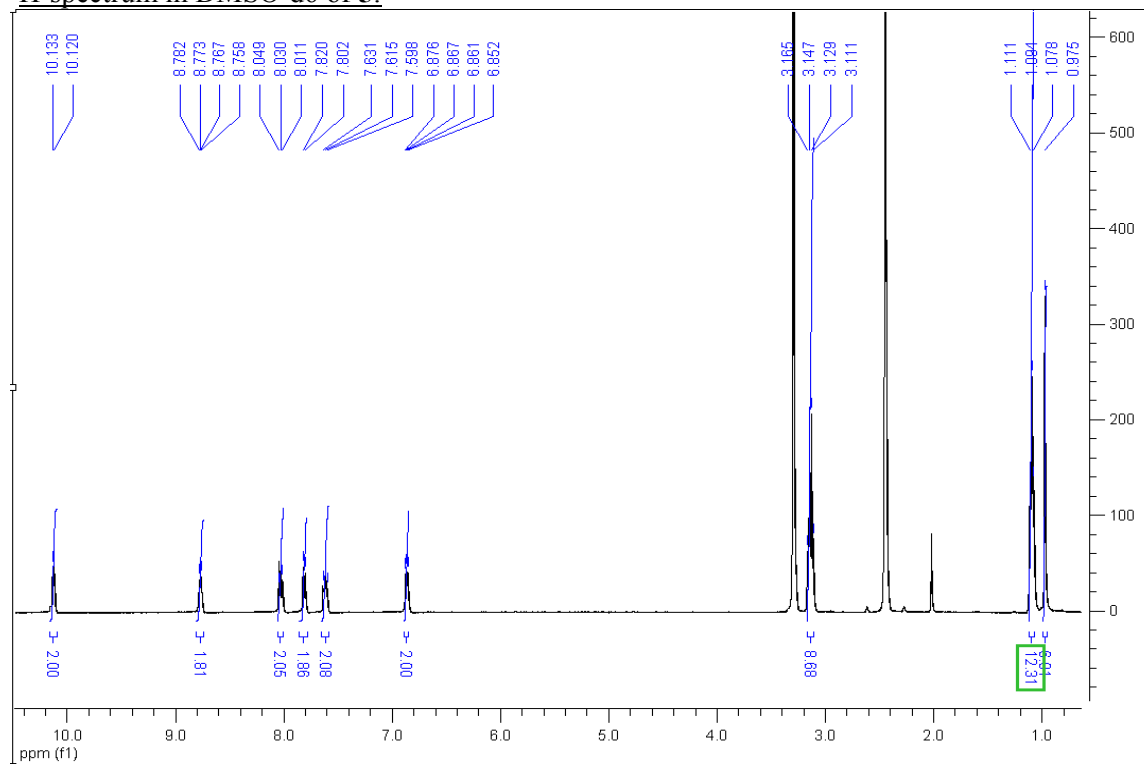
Experimental data for 5:



According to literature procedure [2] 2.0 mmol of  $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$  and 2.0 mmol of ligand **1** were dissolved in 20 ml of DMF and stirred at RT under normal atmosphere for 20 min. Then 2.88 mmol of  $\text{NEt}_4\text{Cl} \cdot \text{H}_2\text{O}$  was added and the solution was stirred at RT for additional 12 hours. DMF was removed in vacuo and the residue was dissolved in 20 ml of acetonitrile and filtered. Through adding 20 ml of diethyl ether to the solution and cooling down to 2 °C a green precipitate was formed. After filtering, washing with 20 ml of 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as green crystals. Yield 885 mg (71 %).

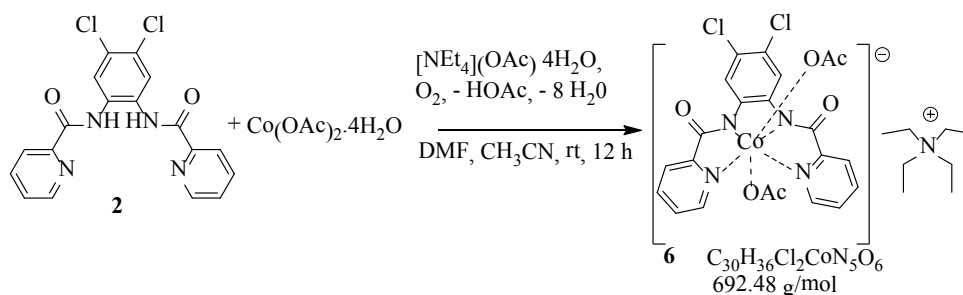
IR ( $\text{cm}^{-1}$ ): 3058 (w), 2978 (m), 2940 (m), 2655 (w), 1621 (s), 1595 (s), 1567 (s), 1478 (s), 1399 (s), 1371 (m), 1173 (w), 1096 (w), 1032 (w), 961 (w), 784 (m), 681 (m).  $^1\text{H-NMR}$ :  $\delta$  (ppm,  $\text{dmsO-d}_6$ ) = 0.98 (s, 6 H), 1.09 (tr,  $J = 7.2 \text{ Hz}$ , 12 H), 3.14 (q,  $J = 7.2 \text{ Hz}$ , 8 H), 6.87 (dd,  $J = 5.9 \text{ Hz}$ ,  $J = 3.5 \text{ Hz}$ , 2 H), 7.61 (tr,  $J = 7.1 \text{ Hz}$ , 2 H), 7.81 (d,  $J = 7.7 \text{ Hz}$ , 2 H), 8.03 (tr,  $J = 7.6 \text{ Hz}$ , 2 H), 8.77 (dd,  $J = 6.0 \text{ Hz}$ ,  $J = 3.5 \text{ Hz}$ , 2 H), 10.13 (d,  $J = 5.5 \text{ Hz}$ , 2 H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR / DEPT135:  $\delta$  (ppm,  $\text{dmsO-d}_6$ ) = 7.7 (prim., 4 C), 24.7 (prim., 2 C), 52.0 (sec., 4 C), 122.0 (tert., 2 C), 122.7 (tert., 2 C), 122.9 (tert., 2 C), 124.2 (tert., 2 C), 139.7 (tert., 2 C), 144.5 (quat., 2 C), 157.5 (tert., 2 C), 160.5 (quat., 2 C), 166.5 (quat., 2 C), 176.4 (quat., 2 C). MS: (ESI $^-$ )  $m/z = 375$   $[\text{M}-2 \cdot (\text{OAc})-\text{NEt}_4]^+$ . Anal. Calcd for  $\text{C}_{30}\text{H}_{38}\text{CoN}_5\text{O}_6$ : C, 57.78; H, 6.14; N, 11.23. Found: C, 57.26; H, 6.35; N, 10.82.

$^1\text{H}$ -spectrum in DMSO- $d_6$  of 5:



[2] R.N. Mukherjee, M. Ray, *Polyhedron*, 1992, **11**, 2929.

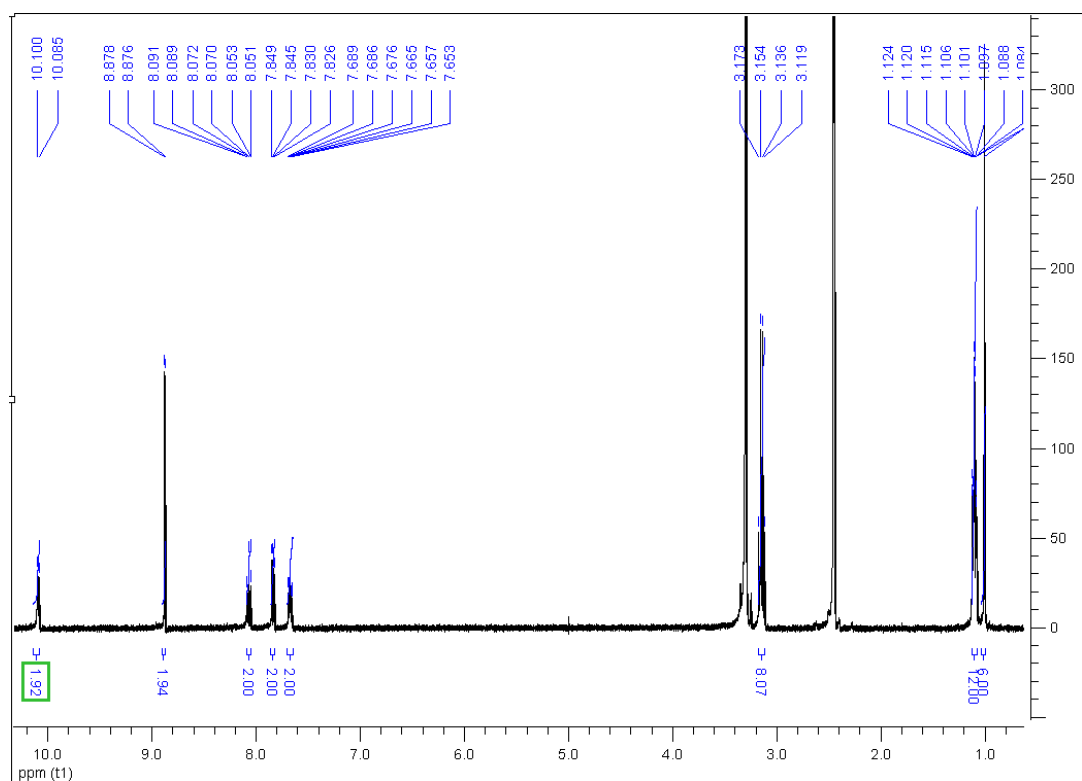
Experimental data for 6:



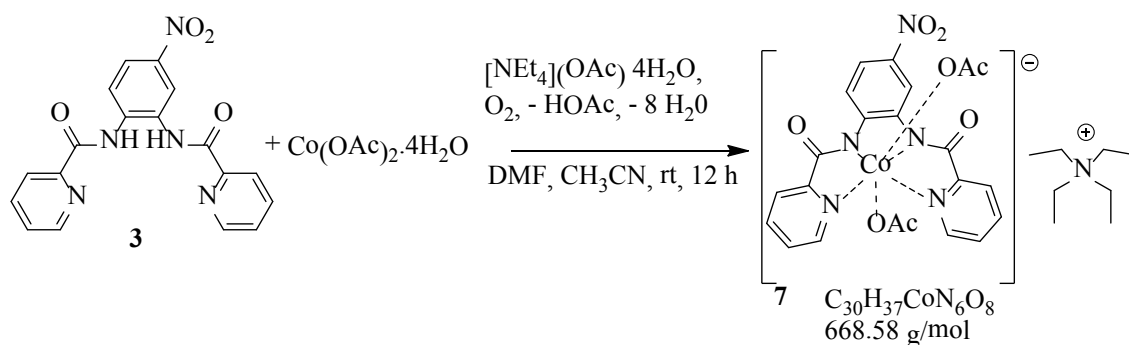
2.0 mmol of  $CoOAc_2 \cdot 4 H_2O$ , 2.0 mmol of ligand **2** were dissolved in 15 ml of DMF and stirred at RT under air for 10 min. Then 2.88 mmol of  $NEt_4OAc \cdot 4 H_2O$  were added and the solution stirred at 70 °C for 12 h. After cooling, the solution was stirred for additional 6 hours. DMF was removed in vacuo and the residue was dissolved in 20 ml of acetonitrile. A precipitate was formed on adding 20 ml of diethyl ether to the solution and cooling down to 2 °C. The product was isolated after filtering, washing two times with 20 ml of a 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as green powder/crystals. For complex **6** green crystals were obtained by slowly adding a small excess of diethyl ether into an acetonitrile solution of **6** and subsequently cooling down to 2 °C. After 2 days small green crystals were formed Yield 885 mg (71 %).

IR ( $cm^{-1}$ ): 2985 (w), 2924 (w), 2853 (w), 1625 (s), 1598 (s), 1557 (m), 1470 (s), 1400 (m), 1314 (m), 1229 (w), 1102 (w), 1002 (w), 977 (w), 926 (w), 764 (w), 683 (m), 670 (m), 548 (w).  $^1H$ -NMR  $\delta$  (ppm,  $dms\text{-}d_6$ ) = 1.01 (s, 6 H), 1.10 (t,  $J = 7.3$  Hz, 12 H), 3.15 (q,  $J = 7.3$  Hz, 8 H), 7.65 – 7.69 (m, 2H), 7.84 (dd,  $J = 7.6$  Hz,  $J = 1.5$  Hz, 2 H), 8.07 (t,  $J = 7.3$  Hz, 2 H), 8.88 (d,  $J = 0.6$  Hz, 2 H), 10.09 (d,  $J = 5.8$  Hz, 2 H).  $^{13}C\{^1H\}$ NMR / DEPT135:  $\delta$  (ppm,  $dms\text{-}d_6$ ) = 7.1 (prim., 4 C), 24.1 (prim., 2 C), 51.4 (sec., 4 C), 121.0 (tert., 2 C), 122.5 (tert., 2 C; quat., 2 C), 124.3 (tert., 2 C), 139.5 (tert., 2 C), 143.7 (quat., 2 C), 156.8 (tert., 2 C), 158.8 (quat., 2 C), 166.5 (quat., 2 C), 175.9 (quat., 2 C). MS: (ESI $^-$ )  $m/z = 561$  [M- $NEt_4$ ] $^-$ . Anal. Calcd for  $C_{30}H_{36}Cl_2CoN_5O_6$ : C, 52.03; H, 5.24; N, 10.11. Found: C, 51.27; H, 5.49; N, 10.05.

$^1H$ -spectrum in DMSO- $d_6$  of 6:



**Experimental data for 7:**



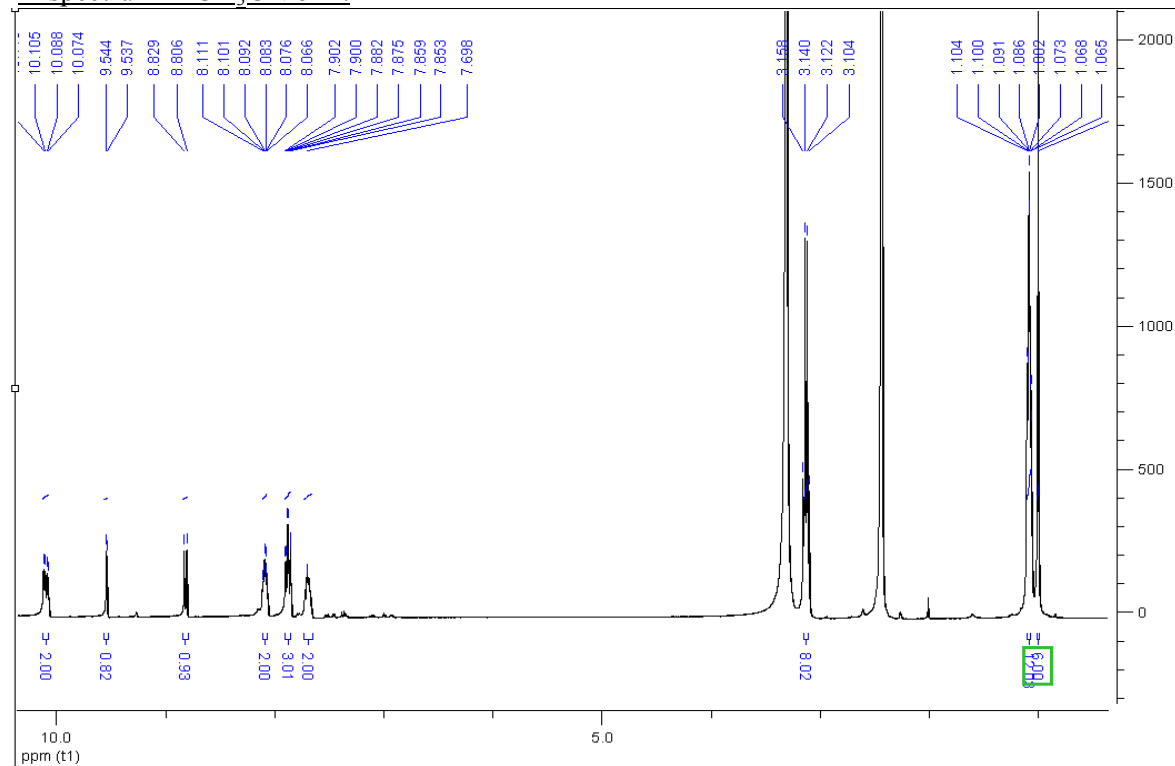
A

2.0 mmol of  $\text{Co(OAc)}_2 \cdot 4\text{H}_2\text{O}$ , 2.0 mmol of ligand **3** were dissolved in 15 ml of DMF and stirred at RT under air for 10 min. Then 2.88 mmol of  $\text{NEt}_4\text{OAc} \cdot 4\text{H}_2\text{O}$  were added and the solution stirred at  $70\text{ }^\circ\text{C}$  for 12 h. After cooling, the solution was stirred for additional 6 hours. DMF was removed in vacuo and the residue was dissolved in 20 ml of acetonitrile. A precipitate was formed on adding 20 ml of diethyl ether to the solution and cooling down to  $2\text{ }^\circ\text{C}$ . The product was isolated after filtering, washing two times with 20 ml of a 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as brown powder. Yield 839 mg (63 %).

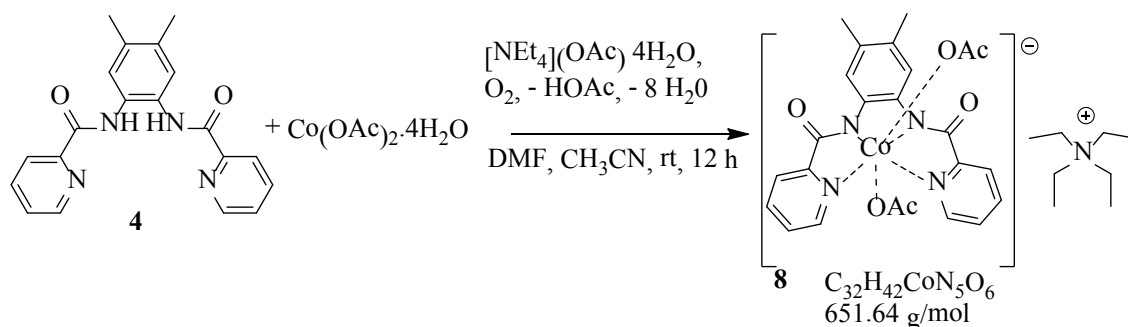
IR ( $\text{cm}^{-1}$ ): 3081 (w), 2985 (w), 2926 (w), 1629 (vs), 1601 (s), 1557 (m), 1482 (s), 1427 (m), 1386 (s), 1315 (vs), 1297 (s), 1146 (m), 1062 (w), 1002 (w), 957 (w), 898 (w), 756 (w), 683 (m), 616 (m), 505 (w), 464 (w).  $^1\text{H-NMR}$   $\delta$  (ppm,  $\text{CD}_3\text{CN}$ ) = 1.01 (s, 6 H), 1.09 (tt,  $J = 7.3\text{ Hz}$ ,  $J = 1.7\text{ Hz}$ , 12 H), 3.13 (q,  $J = 7.2\text{ Hz}$ , 8 H), 7.65 – 7.73 (m, 2H), 7.88 (dt,  $J = 8.6\text{ Hz}$ ,  $J = 1.6\text{ Hz}$ , 3 H), 8.06 – 8.12 (m, 2 H), 8.82 (d,  $J = 9.0\text{ Hz}$ , 1 H), 9.54 (d,  $J = 2.6\text{ Hz}$ , 2 H), 10.10 (dd,  $J = 12.2\text{ Hz}$ ,  $J = 5.3\text{ Hz}$ , 2 H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR / DEPT135:  $\delta$  (ppm,  $\text{CD}_3\text{CN}$ ) = 7.5 (prim., 4 C), 24.5 (prim., 2 C), 51.8 (sec., 4 C), 116.0 (tert., 1 C), 119.5 (tert., 1 C), 120.1 (tert., 1 C), 123.0 (tert., 1 C), 123.3 (tert., 1 C), 124.8 (tert., 1 C), 125.1 (tert., 1 C), 140.0 (tert., 2 C), 141.8 (quat., 1 C), 144.2 (quat., 1 C), 151.3 (quat., 1 C), 157.1 (tert., 1 C), 157.2 (tert., 1 C), 158.7 (quat., 1 C), 159.2 (quat., 1 C), 167.2 (quat., 1 C), 167.7 (quat., 1 C), 176.4 (quat., 2 C). MS: (ESI<sup>-</sup>)  $m/z = 538$  [M- $\text{NEt}_4$ ]. Anal. Calcd for  $\text{C}_{30}\text{H}_{37}\text{CoN}_6\text{O}_8 \cdot \text{H}_2\text{O}$ : C, 53.89; H, 5.73; N, 12.24. Found: C, 52.48; H, 5.72; N, 12.49.



<sup>1</sup>H-spectrum in CD<sub>3</sub>CN of **7**:



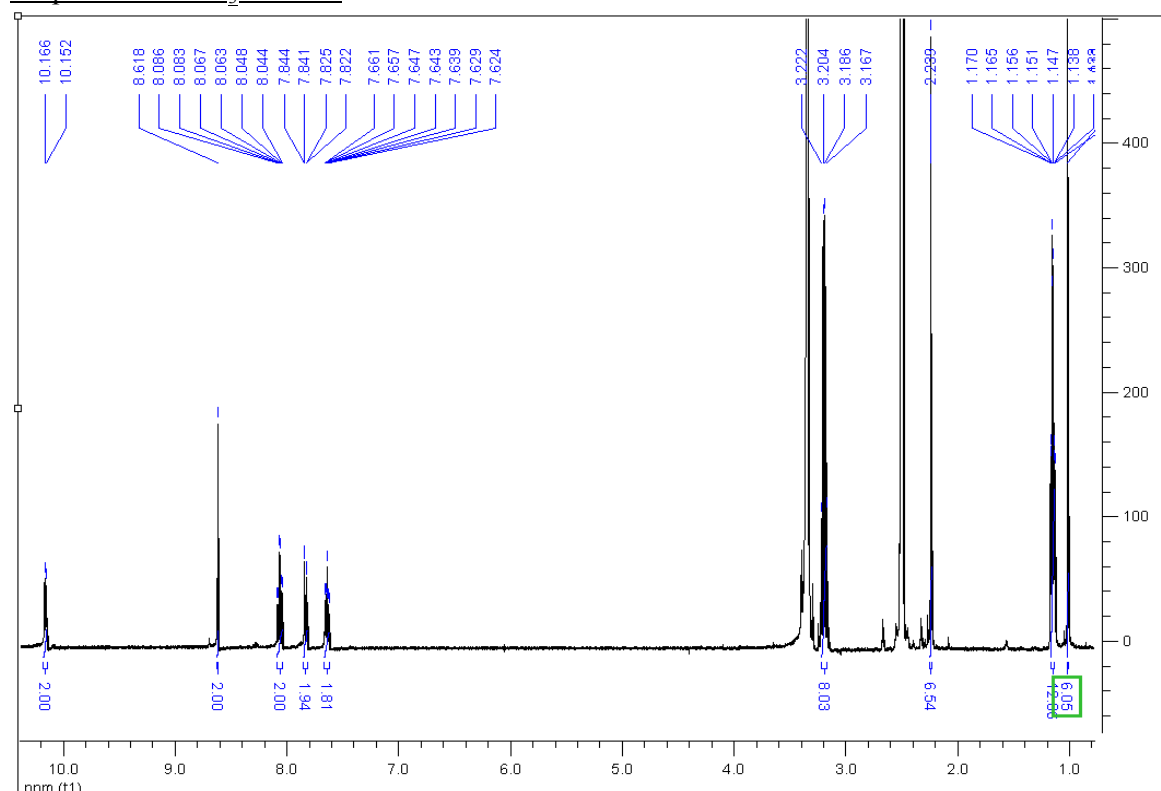
Experimental data for **8**:



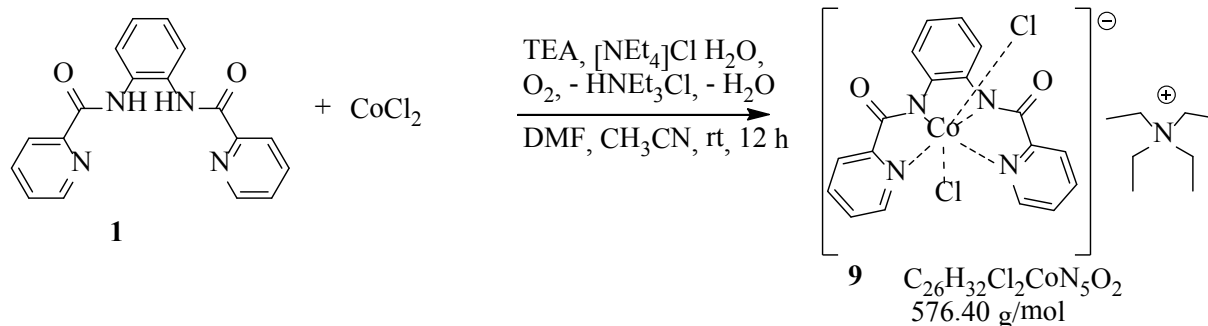
2.0 mmol of CoOAc<sub>2</sub>·4 H<sub>2</sub>O, 2.0 mmol of ligand **4** were dissolved in 15 ml of DMF and stirred at RT under air for 10 min. Then 2.88 mmol of NEt<sub>4</sub>OAc·4 H<sub>2</sub>O were added and the solution stirred at 70 °C for 12 h. After cooling, the solution was stirred for additional 6 hours. DMF was removed in vacuo and the residue was dissolved in 20 ml of acetonitrile. A precipitate was formed on adding 20 ml of diethyl ether to the solution and cooling down to 2 °C. The product was isolated after filtering, washing two times with 20 ml of a 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as green powder. Yield 660 mg (51 %).

IR (cm<sup>-1</sup>): 3087 (w), 2978 (w), 2921 (w), 2857 (w), 1621 (s), 1596 (vs), 1485 (s), 1456 (m), 1405 (s), 1371 (s), 1316 (m), 1172 (w), 1095 (w), 1001 (m), 886 (w), 759 (m), 681 (m), 619 (w), 509 (w). <sup>1</sup>H-NMR δ (ppm, dms<sub>o</sub>-d<sub>6</sub>) = 1.02 (s, 6 H), 1.15 (t, J = 7.3 Hz, 12 H), 2.24 (s, 6 H), 3.20 (q, J = 7.2 Hz, 8 H), 7.64 (ddd, J = 7.4 Hz, J = 5.6 Hz, J = 1.6 Hz, 2H), 7.83 (dd, J = 7.7 Hz, J = 1.2 Hz, 2 H), 8.07 (dt, J = 7.6 Hz, J = 1.3 Hz, 2 H), 8.62 (s, 2 H), 10.16 (d, J = 5.5 Hz, 2 H). <sup>13</sup>C{<sup>1</sup>H}-NMR / DEPT135: δ (ppm, dms<sub>o</sub>-d<sub>6</sub>) = 7.1 (prim., 4 C), 19.8 (prim., 2 C), 24.2 (prim., 2 C), 51.4 (sec., 4 C), 122.1 (tert., 2 C), 122.4 (tert., 2 C), 123.5 (tert., 2 C), 129.5 (quat., 2 C), 139.1 (quat., 2 C), 141.7 (tert., 2 C), 156.8 (quat., 2 C), 160.2 (tert., 2 C), 165.3 (quat., 2 C), 175.8 (quat., 2 C). MS: (ESI<sup>-</sup>) m/z = 521 [M-NEt<sub>4</sub>]<sup>-</sup>. Anal. Calcd for C<sub>32</sub>H<sub>42</sub>CoN<sub>5</sub>O<sub>6</sub>·H<sub>2</sub>O: C, 57.39; H, 6.62; N, 10.46. Found: C, 56.22; H, 6.89; N, 10.34.

<sup>1</sup>H-spectrum in CD<sub>3</sub>CN of 8:



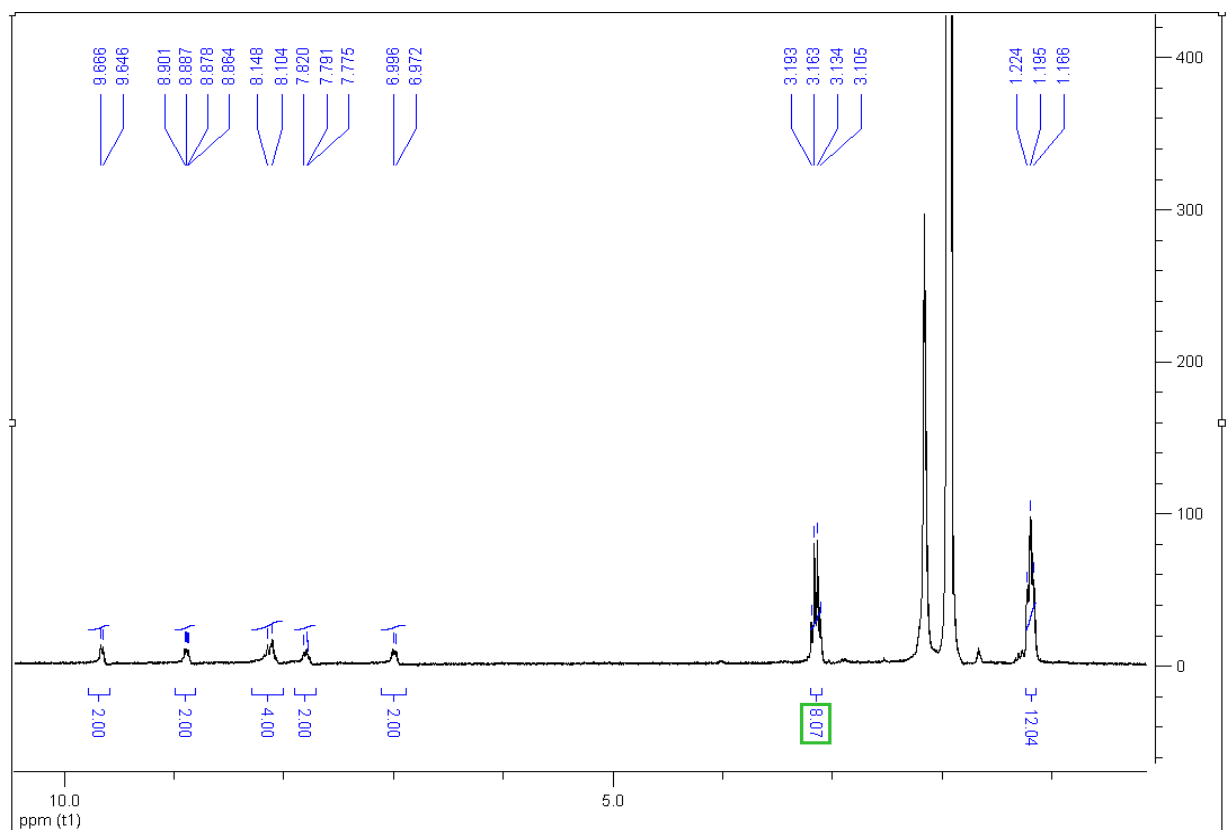
Experimental data for 9:



According to literature procedure [2] 2.0 mmol of CoCl<sub>2</sub>, 2.0 mmol of ligand **1** and 4.0 mmol triethylamine were dissolved in 20 ml of DMF and stirred at RT under normal atmosphere for 20 min. Then 4.42 mmol of NEt<sub>4</sub>Cl·H<sub>2</sub>O was added and the solution was stirred at RT an additional 12 hours. DMF was removed in vacuo and the residue was dissolved in 30 ml of acetonitrile and filtered. Through adding 30 ml of diethyl ether to the solution and cooling down to 2 °C a brown precipitate was formed. After filtering, washing with 20 ml of 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as an orange-brown powder. Yield 991 mg (86 %).

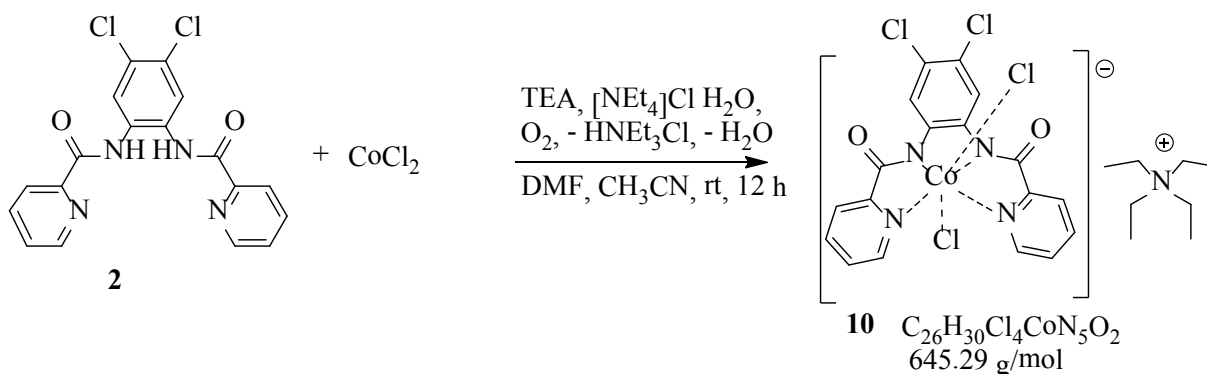
IR (cm<sup>-1</sup>): 3058 (w), 2979 (m), 2940 (m), 2677 (m), 2494 (w), 1621 (s), 1595 (s), 1563 (s), 1474 (s), 1393 (s), 1291 (m), 1183 (w), 1091 (w), 1032 (m), 949 (w), 762 (m), 680 (m). <sup>1</sup>H-NMR: δ (ppm, CD<sub>3</sub>CN) = 1.19 (tr, *J* = 7.5 Hz, 12 H), 3.15 (q, *J* = 7.3 Hz, 8 H), 6.94 - 7.04 (m, 2 H), 7.76 - 7.86 (m, 2 H), 8.06- 8.20 (m, 4 H), 8.89 (dd, *J* = 5.9 Hz *J* = 3.6 Hz, 2 H), 9.65 (d, *J* = 5.6 Hz, 2 H). <sup>13</sup>C{<sup>1</sup>H}-NMR / DEPT135: δ (ppm, dms<sub>o</sub>-d<sub>6</sub>) = 7.8 (prim., 4 C), 52.0 (sec., 4 C), 122.5 (tert., 2 C), 123.2 (tert., 2 C), 124.0 (tert., 2 C), 127.7 (tert., 2 C), 139.8 (tert., 2 C), 143.8 (quat., 2 C), 152.0 (tert., 2 C), 152.4 (quat., 2 C), 161.3 (quat., 2 C).

<sup>1</sup>H-spectrum in CD<sub>3</sub>CN of 9:



[2] R.N. Mukherjee, M. Ray, *Polyhedron*, 1992, **11**, 2929.

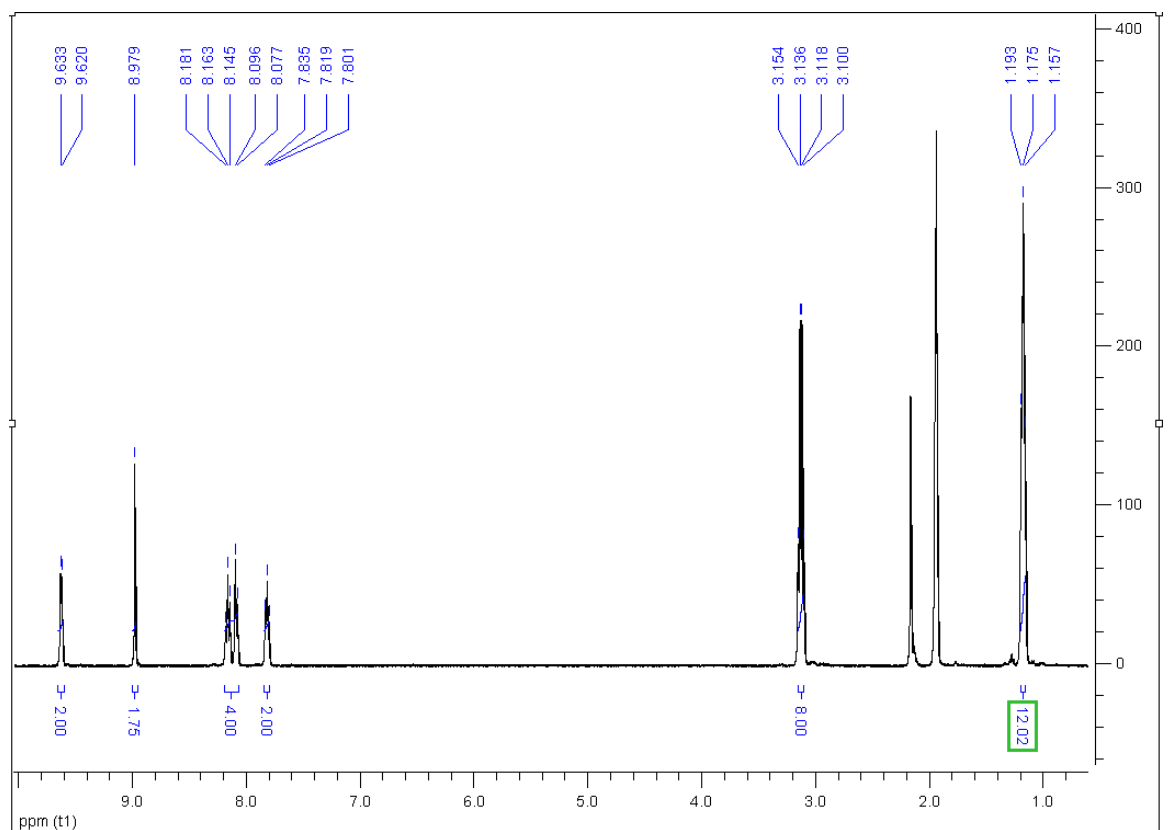
Experimental data for 10:



According to literature procedure [2] 2.0 mmol of  $\text{CoCl}_2$ , 2.0 mmol of ligand **2** and 4.0 mmol triethylamine were dissolved in 20 ml of DMF and stirred at RT under normal atmosphere for 20 min. Then 4.42 mmol of  $\text{NEt}_4\text{Cl} \cdot \text{H}_2\text{O}$  was added and the solution was stirred at RT an additional 12 hours. DMF was removed in vacuo and the residue was dissolved in 20 ml of acetonitrile and filtered. Through adding 20 ml of diethyl ether to the solution and cooling down to 2 °C a brown precipitate was formed. After filtering, washing with 40 ml of 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as a red-brown powder. Yield 857 mg (66 %).

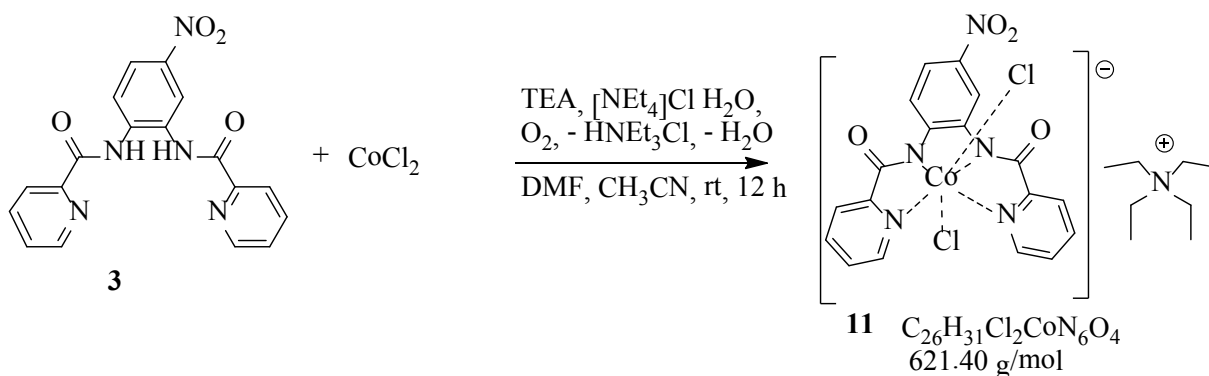
IR ( $\text{cm}^{-1}$ ): 3070 (w), 2980 (w), 2948 (w), 1631 (s), 1598 (s), 1553 (m), 1471 (vs), 1388 (vs), 1286 (m), 1174 (w), 1095 (m), 997 (w), 976 (w), 880 (w), 760 (m), 683 (m), 544 (w), 479 (w).  $^1\text{H-NMR}$ :  $\delta$  (ppm,  $\text{CD}_3\text{CN}$ ) = 1.17 (tr,  $J = 7.1$  Hz, 12 H), 3.12 (q,  $J = 7.2$  Hz, 8 H), 7.81 (tr,  $J = 5.6$  Hz, 2 H), 8.05-8.20 (m, 4 H), 8.96 (s, 2 H), 9.61 (d,  $J = 5.1$  Hz, 2 H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR / DEPT135:  $\delta$  (ppm,  $\text{dmsO-d}_6$ ) = 7.6 (prim., 4 C), 53.0 (sec., 4 C), 122.9 (tert., 2 C), 124.9 (tert., 2 C; quat., 2 C), 128.2 (tert., 2 C), 140.4 (tert., 2 C), 144.1 (quat., 2 C), 152.0 (tert., 2 C), 161.0 (quat., 2 C), 167.6 (quat., 2C).

$^1\text{H}$ -spectrum in  $\text{CD}_3\text{CN}$  of 10:



[2] R.N. Mukherjee, M. Ray, *Polyhedron*, 1992, **11**, 2929.

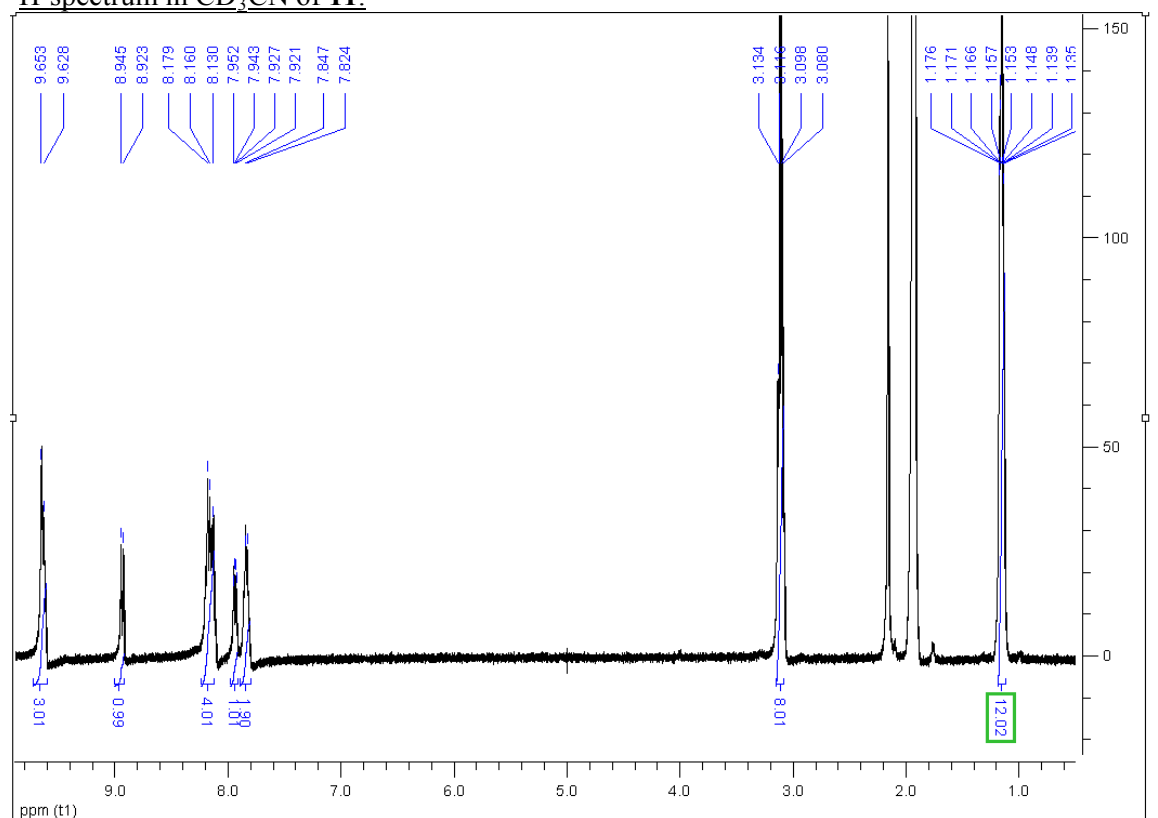
**Experimental data for 11:**



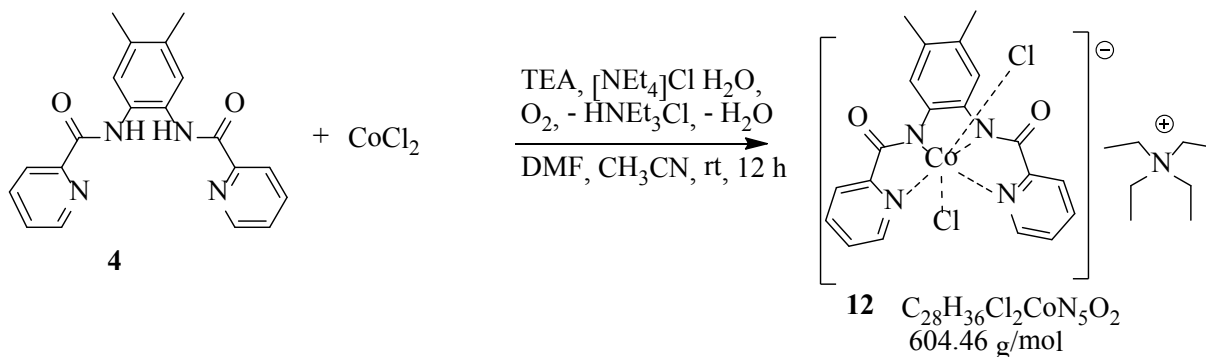
2.0 mmol of  $\text{CoCl}_2$ , 2.0 mmol of ligand **3**, 4.0 mmol triethylamine and 4.42 mmol of  $\text{NEt}_4\text{Cl}\cdot\text{H}_2\text{O}$  were dissolved in 15 ml of DMF and stirred at RT under normal atmosphere for 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. A precipitate was formed, which was filtered and washed with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a red-brown powder. Yield 1134 mg (91 %).

IR ( $\text{cm}^{-1}$ ): 3070 (w), 2986 (w), 2949 (w), 1632 (vs), 1600 (s), 1558 (s), 1481 (vs), 1426 (m), 1390 (s), 1319 (vs), 1296 (s), 1142 (m), 1062 (m), 999 (w), 958 (w), 895 (w), 758 (m), 684 (m), 615 (w), 508 (w), 465 (w), 352 (w).  $^1\text{H-NMR}$   $\delta$  (ppm,  $\text{CD}_3\text{CN}$ ) = 1.12 – 1.19 (m, 12 H), 3.11 (q,  $J = 7.3$  Hz, 8 H), 7.80 – 7.86 (m, 2H), 7.94 (dd,  $J = 9.0$  Hz,  $J = 2.6$  Hz, 1 H), 8.10 – 8.21 (m, 4 H), 8.93 (d,  $J = 8.8$  Hz, 1 H), 9.60 – 9.67 (m, 3 H).  $^{13}\text{C}\{^1\text{H}\}$ -NMR / DEPT135:  $\delta$  (ppm,  $\text{CD}_3\text{CN}$ ) = 7.5 (prim., 4 C), 52.9 (sec., 4 C), 117.5 (tert., 1 C), 120.4 (tert., 1 C), 121.4 (tert., 1 C), 125.0 (tert., 1 C), 125.3 (tert., 1 C), 128.4 (tert., 1 C), 128.7 (tert., 1 C), 140.5 (tert., 2 C), 143.5 (quat., 1 C), 144.3 (quat., 1 C), 151.0 (quat., 1 C), 152.0 (tert., 1 C), 152.1 (tert., 1 C), 160.5 (quat., 1 C), 161.0 (quat., 1 C), 168.0 (quat., 1 C), 168.4 (quat., 1 C). MS: (ESI $^-$ )  $m/z = 490$   $[\text{M-NEt}_4]^+$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{31}\text{Cl}_2\text{CoN}_6\text{O}_4$ : C, 50.25; H, 5.03; N, 13.52. Found: C, 50.05; H, 4.96; N, 13.67.

<sup>1</sup>H-spectrum in CD<sub>3</sub>CN of 11:



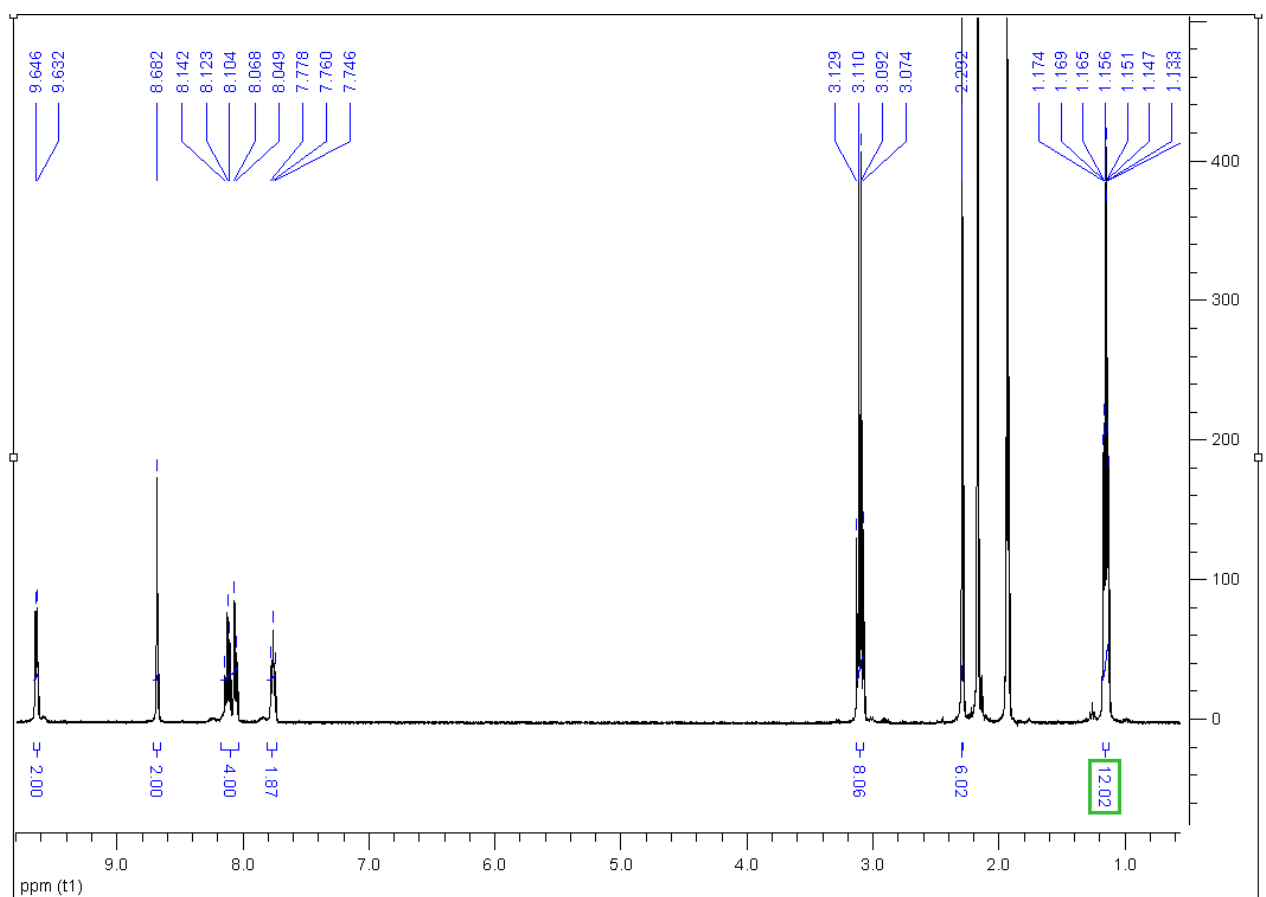
Experimental data for 12:



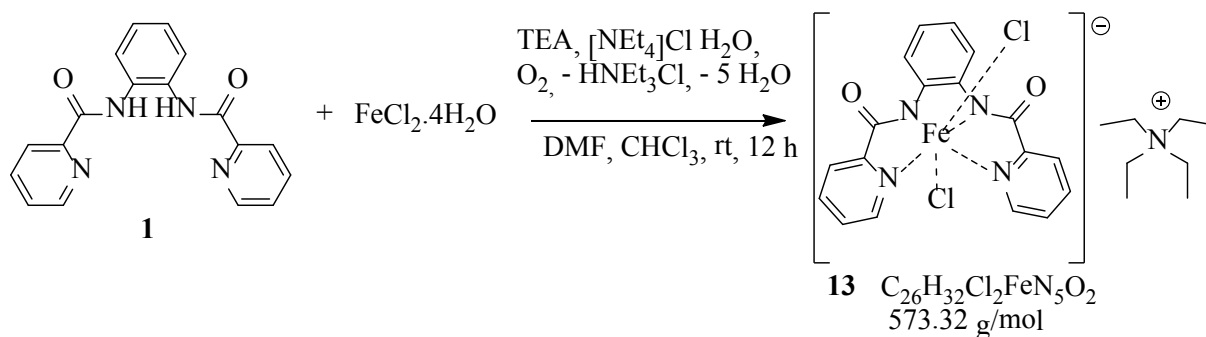
2.0 mmol of CoCl<sub>2</sub>, 2.0 mmol of ligand **4**, 4.0 mmol triethylamine and 4.42 mmol of NEt<sub>4</sub>Cl·H<sub>2</sub>O were dissolved in 15 ml of DMF and stirred at RT under normal atmosphere for 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. A precipitate was formed, which was filtered and washed with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a red powder. Yield 1060 mg (88 %).

IR (cm<sup>-1</sup>): 3077 (w), 2984 (w), 2924 (w), 2856 (w), 1625 (vs), 1595 (s), 1577 (s), 1486 (m), 1456 (m), 1404 (s), 1290 (m), 1251 (m), 1178 (m), 1092 (w), 1003 (w), 943 (w), 889 (w), 765 (m), 681 (m), 651 (w), 509 (w), 406 (w). <sup>1</sup>H-NMR δ (ppm, CD<sub>3</sub>CN) = 1.16 (t, J = 7.3 Hz, 12 H), 2.29 (s, 6 H), 3.10 (q, J = 7.3 Hz, 8 H), 7.76 (t, J = 6.4 Hz, 2 H), 8.05-8.16 (m, 4 H), 8.68 (s, 2 H), 9.64 (d, J = 5.5 Hz, 2 H). <sup>13</sup>C{<sup>1</sup>H}-NMR / DEPT135: δ (ppm, CD<sub>3</sub>CN) = 7.6 (prim., 4 C), 20.0 (prim., 2 C), 52.9 (sec., 4 C), 123.9 (tert., 2 C), 124.4 (tert., 2 C), 127.5 (tert., 2 C), 131.9 (quat., 2 C), 140.0 (tert., 2 C), 142.1 (quat., 2 C), 151.7 (tert., 2 C), 162.4 (quat., 2 C). MS: (ESI-) m/z = 473 [M-NEt<sub>4</sub>]. Anal. Calcd for C<sub>28</sub>H<sub>36</sub>Cl<sub>2</sub>CoN<sub>5</sub>O<sub>2</sub>·H<sub>2</sub>O: C, 54.03; H, 6.15; N, 11.25. Found: C, 54.26; H, 6.39; N, 11.38.

<sup>1</sup>H-spectrum in CD<sub>3</sub>CN of 12:



**Experimental data for 13:**

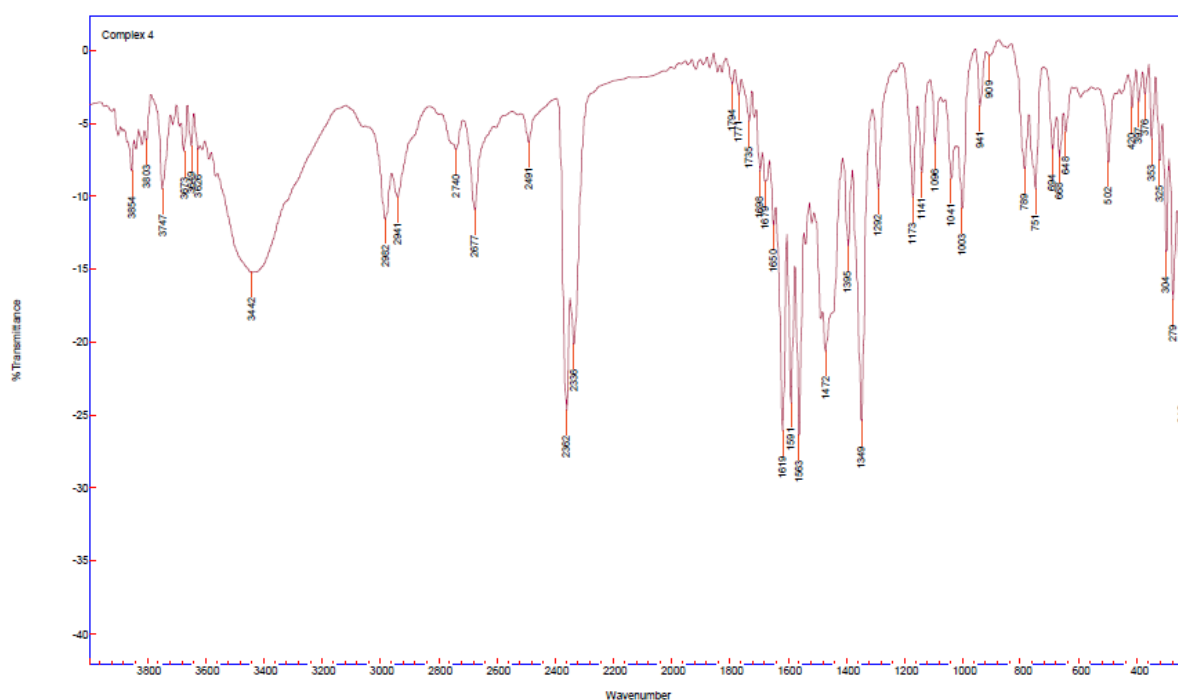


According to literature procedure [3] 2.0 mmol of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , 2.0 mmol of  $\text{H}_2\text{bpb}$  (**1**) and 4.0 mmol triethylamine were dissolved in 20 ml of DMF and stirred at RT under normal atmosphere for 20 min. Then 4.42 mmol of  $\text{NET}_4\text{Cl} \cdot \text{H}_2\text{O}$  was added and the solution was stirred at RT for additional 12 hours. DMF was removed in vacuo and the residue was dissolved in 30 ml of acetonitrile and filtered. Adding 30 ml of diethyl ether to the solution and cooling down to 2 °C yielded a green precipitate. After filtering, washing with 20 ml of 1:1 acetonitrile/diethyl ether mixture and drying under vacuo the product was isolated as a green powder. Yield 957 mg (83 %).

IR ( $\text{cm}^{-1}$ ): 2982 (m), 2942 (m), 2739 (w), 2677 (m), 2491 (w), 1619 (s), 1591 (s), 1563 (s), 1472 (m), 1349 (s), 1292 (m), 1173 (m), 1096 (w), 1003 (m), 942 (w), 750 (m), 668 (m). MS: (EI+)  $m/z = 372$   $[\text{M}-2\text{Cl}-\text{NET}_4]^+$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{32}\text{Cl}_2\text{FeN}_5\text{O}_2$ : C, 54.47; H, 5.63; N, 12.22. Found: C, 53.55; H, 5.78; N, 11.69.

**IR-spectrum of 13:**

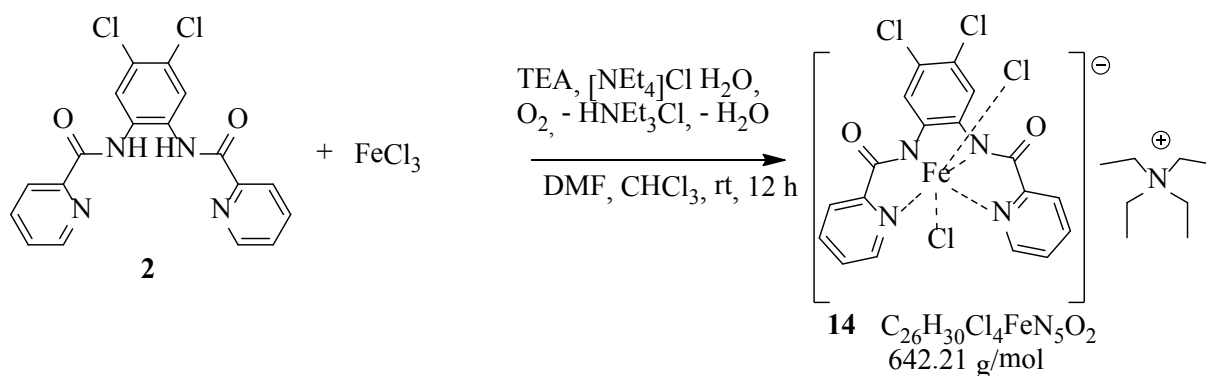
IKFT / KIT CN / IR-Labor



Name
Complex 4

[3] X.-G. Zhou, J.-L. Zuo, L. Yang, R.-N. Wei, R. Li, *J. Molecular Catalysis A: Chem.*, 2007, **266**, 284.

Experimental data for **14**:

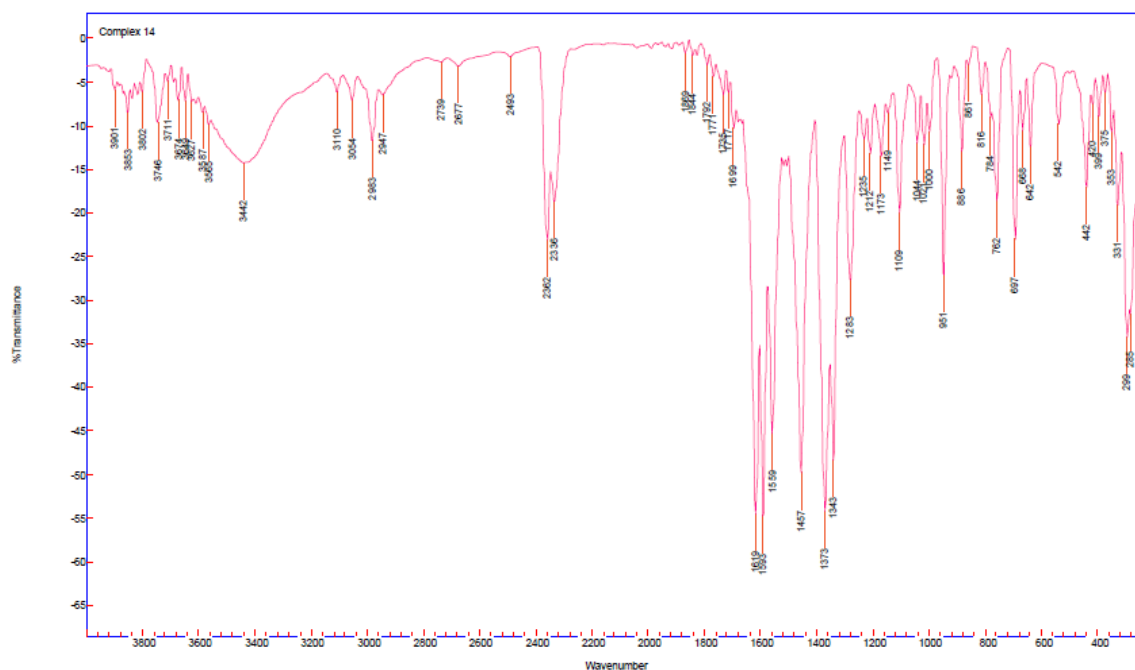


According to literature procedure [4] 2.0 mmol of  $FeCl_3$ , 2.0 mmol of ligand **2** and 4.0 mmol triethylamine were dissolved in 20 ml of DMF and stirred at RT under normal atmosphere for 20 min. Then 4.42 mmol of  $NEt_4Cl \cdot H_2O$  was added and the solution was stirred at RT for additional 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. A precipitate was formed, which was filtered and washed with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a green powder. Yield 957 mg (83 %).

IR ( $cm^{-1}$ ): 3110 (w), 3054 (w), 2983 (m), 2947 (w), 1619 (s), 1593 (vs), 1559 (s), 1457 (s), 1373 (vs), 1343 (s), 1283 (m), 1235 (w), 1173 (w), 1109 (m), 1044 (w), 1021 (w), 951 (m), 886 (w), 816 (w), 762 (m), 697 (m), 642 (w), 542 (w), 442 (w). MS: (EI)  $m/z$  = 512 (100 %), 510 (81 %) [ $M-NEt_4$ ]. Anal. Calcd for  $C_{26}H_{30}Cl_4FeN_5O_2$ : C, 48.63; H, 4.71; N, 10.91. Found: C, 48.51; H, 4.53; N, 10.89.

IR-spectrum of 14:

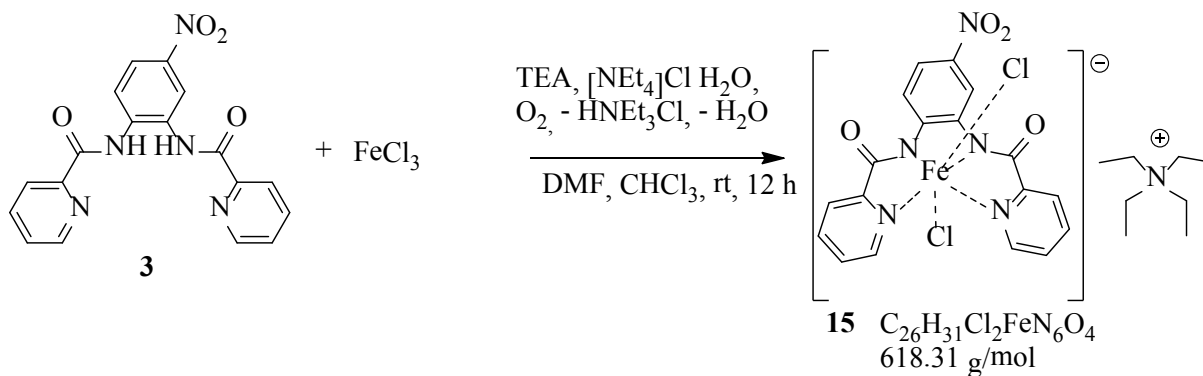
Agilent Resolutions Pro



Name
Complex 14

[4] R.N. Mukherjee, M. Ray, J.F. Richardson, R.M. Buchanan, *J. Chem. Soc. Dalton Trans.*, 1993, **1**, 2451.

Experimental data for 15:

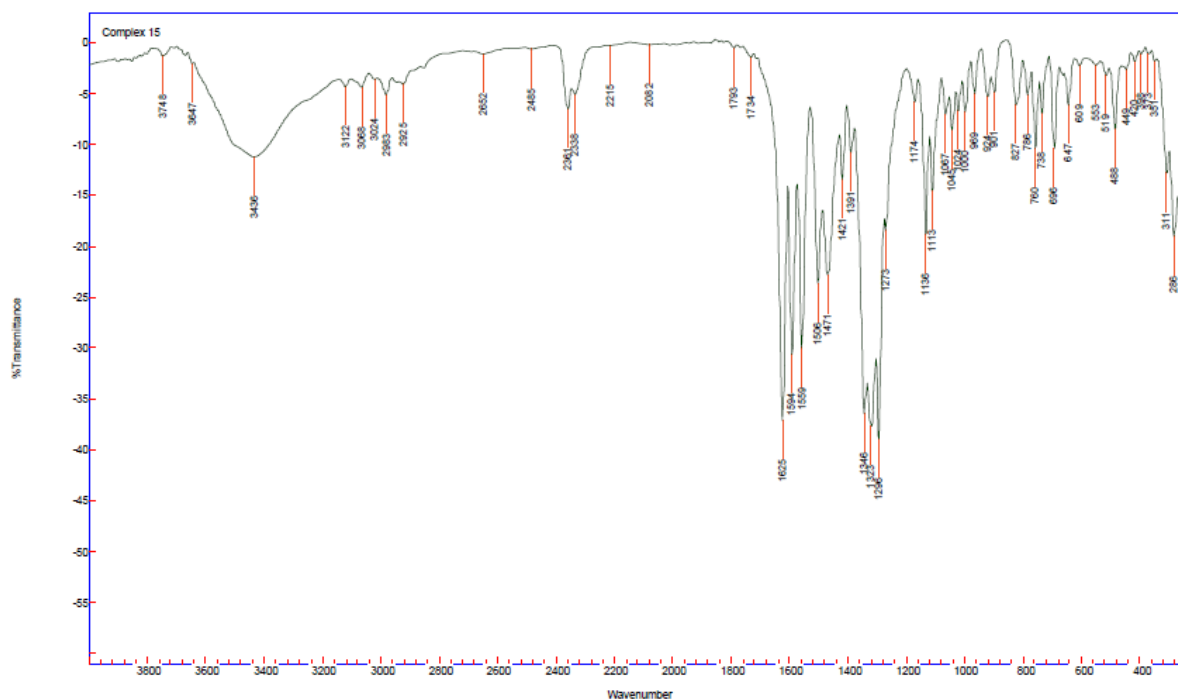


2.0 mmol of  $FeCl_3$ , 2.0 mmol of ligand **3**, 4.0 mmol triethylamine and 4.42 mmol of  $NEt_4Cl \cdot H_2O$  were dissolved in 15 ml of DMF and stirred at RT and air for 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. The resulting precipitate was filtered and washed twice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a green powder. Yield 992 mg (80 %).

IR ( $cm^{-1}$ ): (cm-1): 3122 (w), 3068 (w), 2983 (w), 2925 (w), 1625 (vs), 1594 (s), 1559 (s), 1506 (m), 1471 (m), 1421 (w), 1346 (s), 1323 (vs), 1296 (s), 1136 (m), 1113 (m), 1045 (w), 1000 (w), 969 (w), 924 (w), 827 (w), 760 (m), 696 (m), 647 (w), 488 (m). MS: (ESI-)  $m/z = 487$  (100 %), 489 (65 %)  $[M-NEt_4]^+$ . Anal. Calcd for  $C_{26}H_{31}Cl_2FeN_6O_4 \cdot H_2O$ : C, 49.08; H, 5.23; N, 13.21. Found: C, 49.18; H, 4.95; N, 13.40.

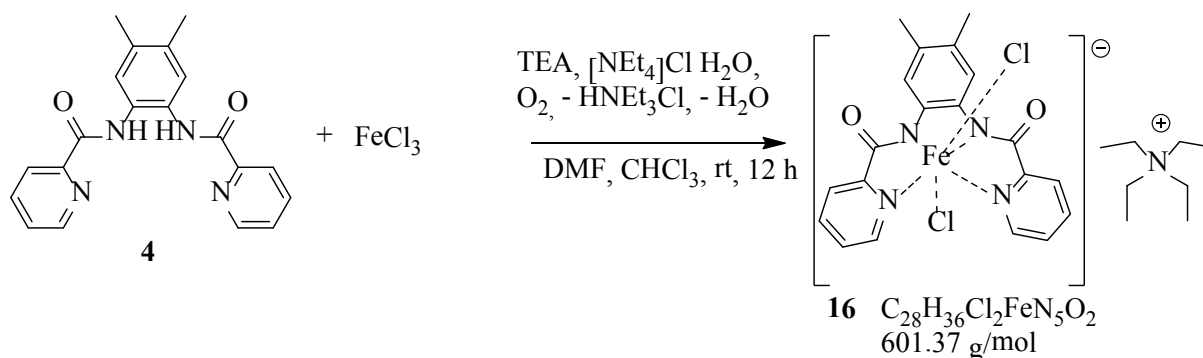


**IR-spectrum of 15:**  
*Agilent Resolutions Pro*



Name
Complex 15

**Experimental data for 16:**

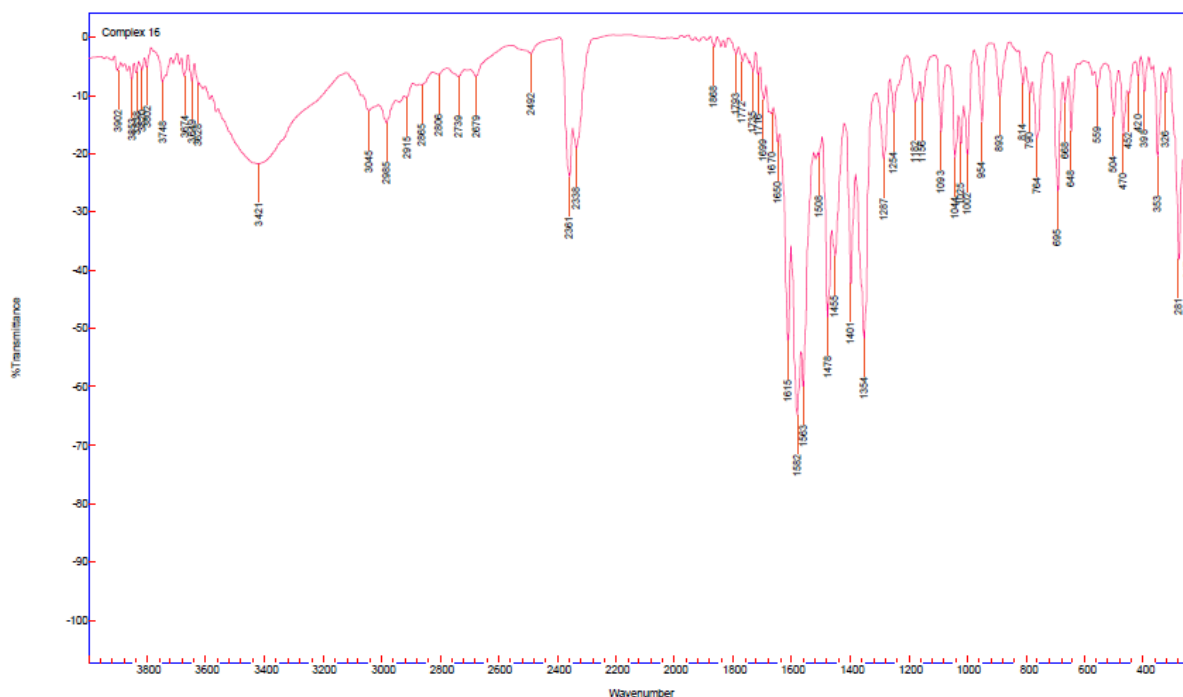


2.0 mmol of  $\text{FeCl}_3$ , 2.0 mmol of ligand **4**, 4.0 mmol triethylamine and 4.42 mmol of  $\text{NEt}_4\text{Cl} \cdot \text{H}_2\text{O}$  were dissolved in 15 ml of DMF and stirred at RT and air for 12 hours. DMF was removed in vacuo and 20 ml of a 1:1 acetonitrile/diethyl ether mixture was added to the residue. The resulting precipitate was filtered and washed thrice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a green powder. Yield 818 mg (68 %).

IR ( $\text{cm}^{-1}$ ): 3045 (w), 2985 (w), 2915 (w), 2865 (w), 1615 (s), 1582 (vs), 1563 (s), 1478 (s), 1455 (m), 1401 (m), 1354 (s), 1287 (m), 1254 (w), 1182 (w), 1093 (w), 1044 (m), 1002 (w), 954 (w), 893 (w), 764 (m), 695 (m), 648 (w), 504 (w), 470 (w). MS: (ESI<sup>-</sup>)  $m/z = 470$  [ $\text{M-NEt}_4$ ]<sup>-</sup>. Anal. Calcd for  $\text{C}_{28}\text{H}_{36}\text{Cl}_2\text{FeN}_5\text{O}_2 \cdot 2\text{H}_2\text{O}$ : C, 52.76; H, 6.33; N, 10.99. Found: C, 53.03; H, 6.62; N, 11.19.

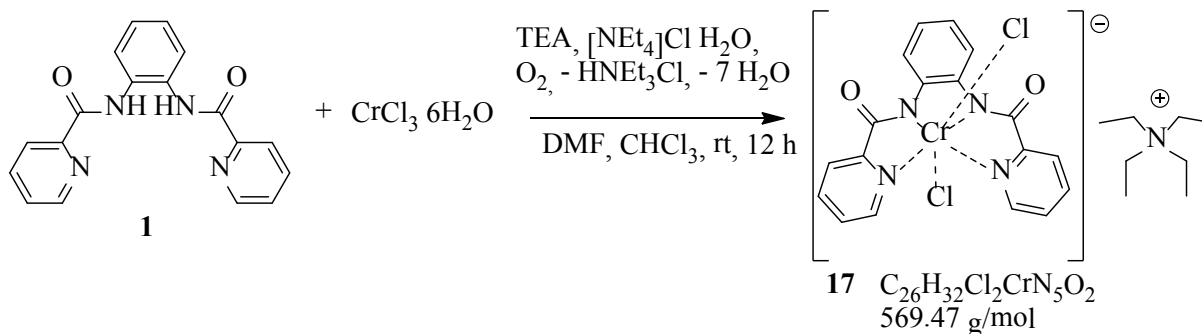
**IR-spectrum of 16:**

Agilent Resolutions Pro



Name	Complex 16
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Experimental data for 17:

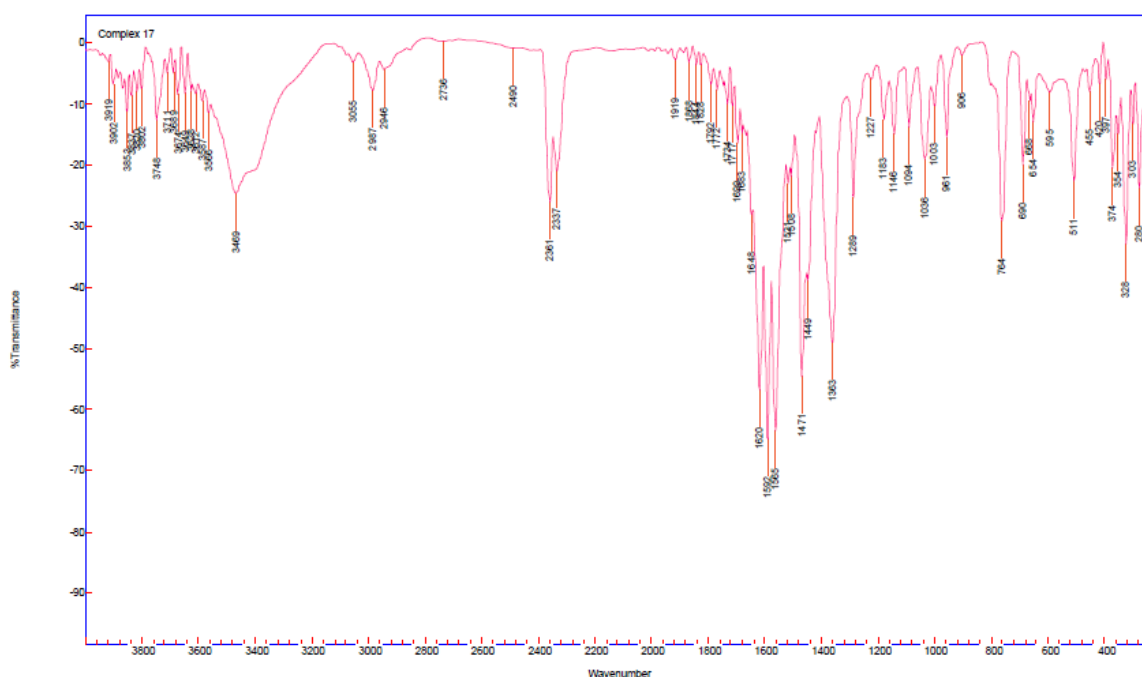


2.0 mmol of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , 2.0 mmol of ligand **1**, 4.0 mmol triethylamine and 4.42 mmol of  $\text{NEt}_4\text{Cl} \cdot \text{H}_2\text{O}$  were dissolved in 15 ml of DMF and stirred at  $120^\circ\text{C}$  for 12 hours. After cooling the solution was stirred at RT and under air for additional 6 hours. DMF was removed in vacuo and 20 ml of a 1:1 acetonitrile/diethyl ether mixture was added to the residue yielding a precipitate, which was filtered, washed twice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a red powder. Yield 1005 mg (88 %).

IR ( $\text{cm}^{-1}$ ): 3055 (w), 2987 (w), 2946 (w), 1620 (s), 1592 (vs), 1565 (vs), 1471 (s), 1363 (s), 1289 (m), 1183 (w), 1146 (w), 1094 (w), 1036 (m), 961 (w), 906 (w), 764 (m), 690 (m), 654 (w), 595 (w), 511 (m), 328 (m). MS: (ESI<sup>-</sup>)  $m/z = 438$  [ $\text{M}-\text{NEt}_4$ ]. Anal. Calcd for  $\text{C}_{26}\text{H}_{32}\text{Cl}_2\text{CrN}_5\text{O}_2 \cdot \text{H}_2\text{O}$ : C, 53.16; H, 5.83; N, 11.92. Found: C, 52.48; H, 5.57; N, 11.86.

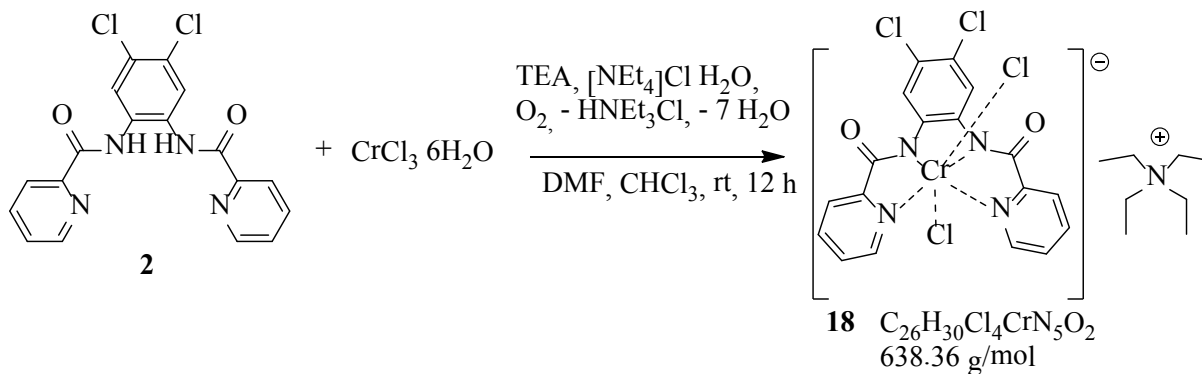
IR-spectrum of 17:

Agilent Resolutions Pro



Name	
Complex 17	—

Experimental data for 18:

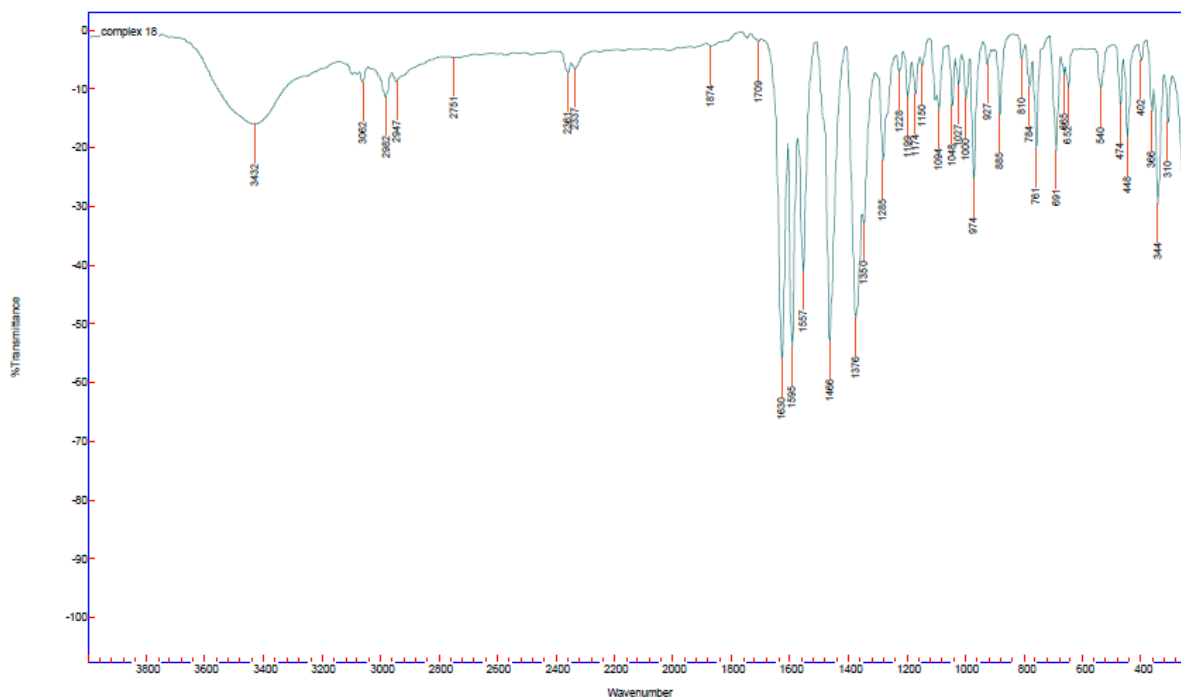


According to literature procedure [5] 2.0 mmol of  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , 2.0 mmol of ligand **2**, 4.0 mmol triethylamine and 4.42 mmol of  $\text{NEt}_4\text{Cl} \cdot \text{H}_2\text{O}$  were dissolved in 15 ml of DMF and stirred at  $120^\circ\text{C}$  for 12 hours. After cooling the solution was stirred at RT and under air for additional 6 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. The resulting precipitate was filtered and washed with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a red-brown powder. Yield 906 mg (71 %).

IR ( $\text{cm}^{-1}$ ): 3062 (w), 2982 (m), 2947 (w), 1630 (vs), 1595 (s), 1557 (s), 1466 (s), 1376 (s), 1285 (m), 1228 (w), 1199 (w), 1174 (w), 1094 (m), 1048 (w), 1027 (w), 974 (m), 885 (w), 810 (w), 761 (m), 691 (m), 652 (w), 540 (w), 448 (m). MS: (ESI<sup>-</sup>)  $m/z = 506$   $[\text{M-NEt}_4]^-$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{32}\text{Cl}_2\text{CrN}_5\text{O}_2 \cdot \text{H}_2\text{O}$ : C, 53.16; H, 5.83; N, 11.92. Found: C, 52.48; H, 5.57; N, 11.86.

**IR-spectrum of 18:**

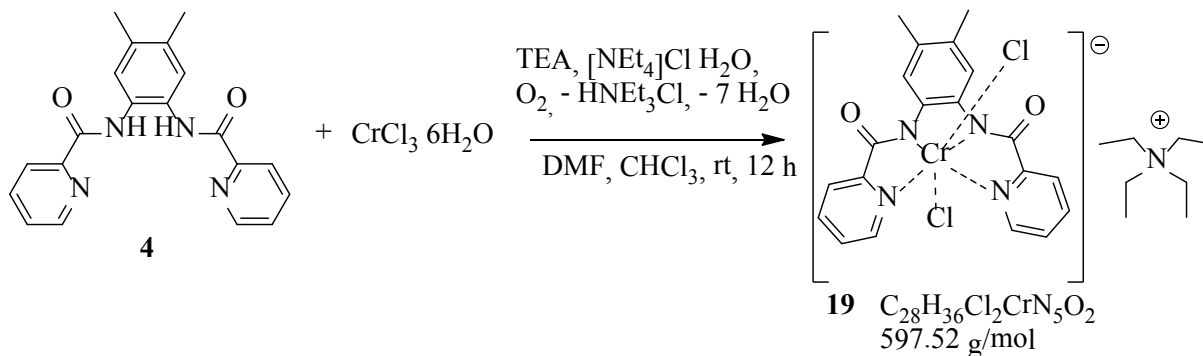
*Agilent Resolutions Pro*



Name
complex 18

[5] Y. Kim, Y.W. Choi, S.H. Kim, D.N. Lee, C. Kim, *Acta. Cryst. E62*, 2006, m2715.

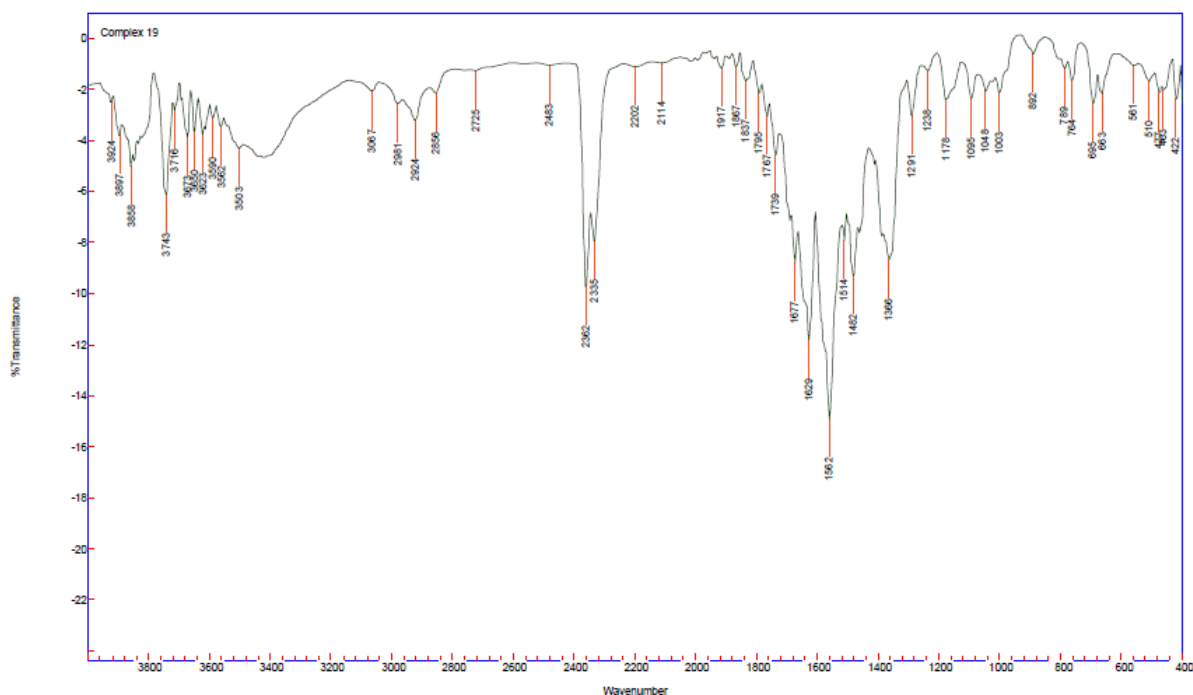
**Experimental data for 19:**



2.0 mmol of  $CrCl_3 \cdot 6H_2O$ , 2.0 mmol of ligand **4**, 4.0 mmol triethylamine and 4.42 mmol of  $NEt_4Cl \cdot H_2O$  were dissolved in 15 ml of DMF and stirred at  $120^\circ C$  for 12 hours. After cooling the solution was stirred at RT and under air for additional 6 hours. DMF was removed in vacuo and 20 ml of a 1:1 acetonitrile/diethyl ether mixture was added to the residue yielding a precipitate, which was filtered, washed twice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was isolated as a red-brown powder. Yield 1035 mg (87 %).

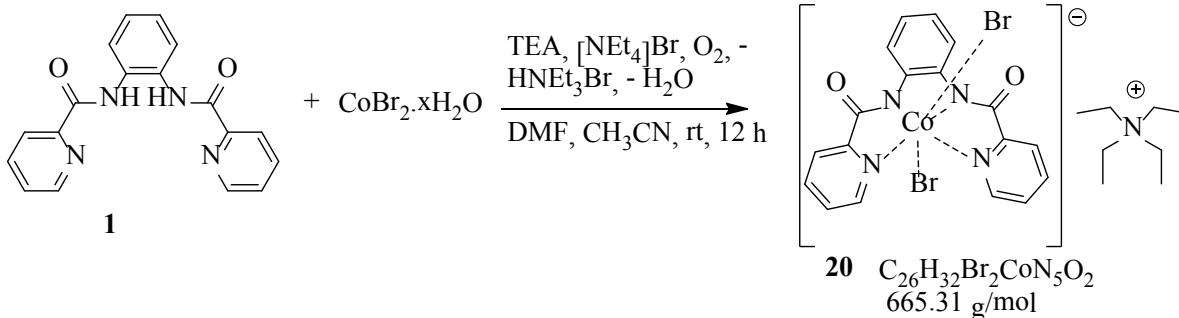
IR ( $cm^{-1}$ ): 3067 (w), 2981 (w), 2924 (w), 1629 (s), 1562 (vs), 1514 (m), 1482 (s), 1366 (s), 1291 (m), 1238 (w), 1178 (m), 1095 (w), 1048 (w), 1003 (w), 892 (w), 764 (w), 695 (m), 663 (w), 510 (w), 422 (w). MS: (ESI<sup>-</sup>)  $m/z = 466 [M-NEt_4]^+$ . Anal. Calcd for  $C_{28}H_{36}Cl_2CrN_5O_2 \cdot 2 H_2O$ : C, 53.08; H, 6.36; N, 11.05. Found: C, 52.76; H, 6.33; N, 11.42.

**IR-spectrum of 19:**  
**Agilent Resolutions Pro**



Name	
Complex 19	

**Experimental data for 20:**



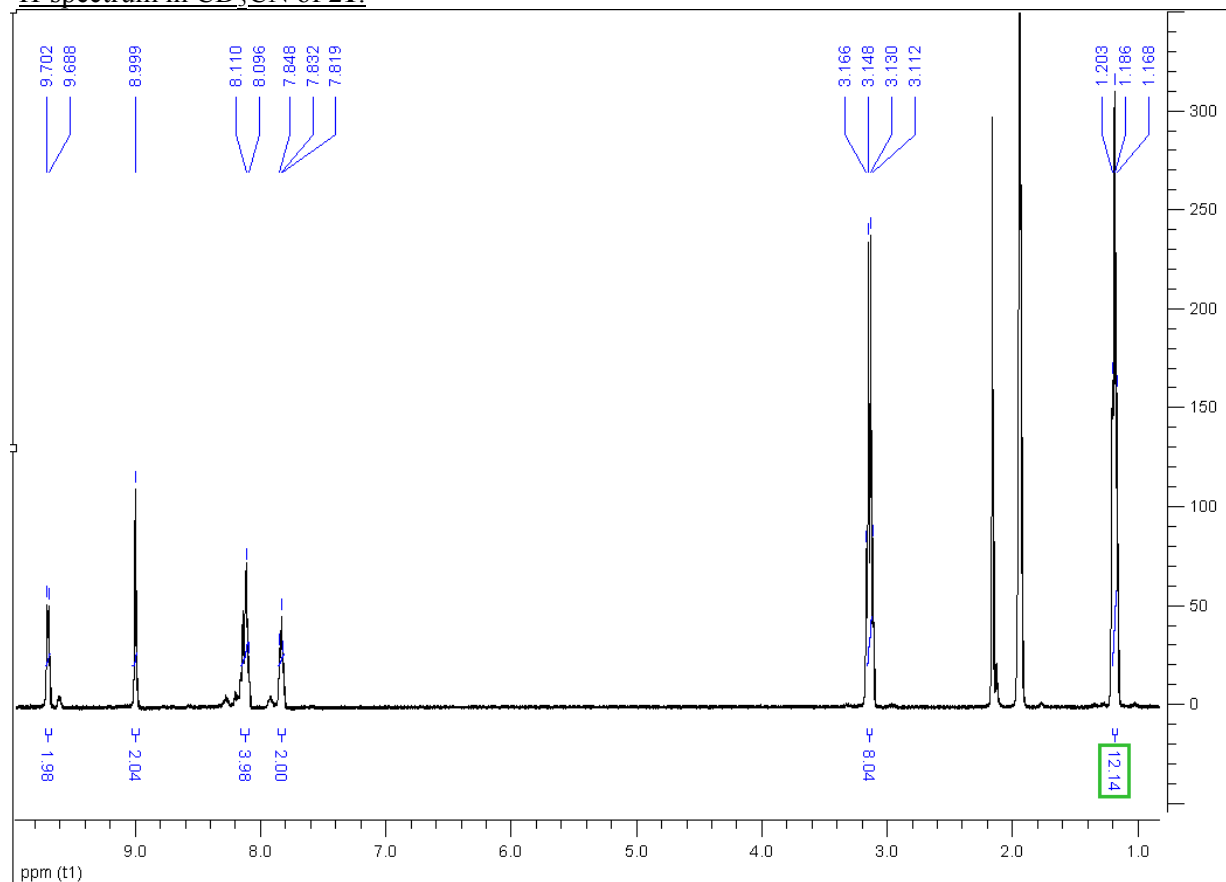
According to literature procedure [6] 2.0 mmol of  $\text{CoBr}_2 \cdot x\text{H}_2\text{O}$ , 2.0 mmol of ligand **1** and 4.0 mmol triethylamine were dissolved in 20 ml of DMF and stirred at RT and air for 20 min. Then 4.42 mmol of  $\text{NEt}_4\text{Br}$  was added and the solution was stirred at RT under normal atmosphere for additional 12 hours. DMF was removed in vacuo and the residue was dissolved in 30 ml of acetonitrile and filtered. Through adding 30 ml of diethyl ether to the solution and cooling down to 2 °C a brown precipitate was formed. After filtering, washing with diethyl ether and drying under vacuo the product was separated as a brown powder. Yield 745 mg (56 %).

IR ( $\text{cm}^{-1}$ ): 3058 (w), 2984 (w), 2924 (m), 2853(w), 1620 (s), 1595 (vs), 1564 (s), 1475 (s), 1393 (s), 1291 (m), 1183 (w), 1092 (w), 1031 (m), 950 (w), 760 (s), 678 (m), 516 (m).  $^1\text{H-NMR}$ :  $\delta$  (ppm,  $\text{dmsO-d}_6$ ) = 1.16 (tr,  $J = 5.5$  Hz, 12 H), 3.20 (q,  $J = 7.0$  Hz, 8 H), 7.00-7.07 (m, 2 H), 7.94-8.04 (m, 2 H), 8.16 (d,  $J = 7.7$  Hz, 2 H), 8.34 (tr,  $J = 7.4$  Hz, 2 H), 8.85-8.95 (m, 2 H), 9.85-9.95 (m, 2 H).  $^{13}\text{C}\{^1\text{H}\}$ NMR / DEPT135:  $\delta$  (ppm,  $\text{dmsO-d}_6$ ) = 7.8 (prim., 4 C), 52.0 (sec., 4 C), 122.7 (tert., 2 C),

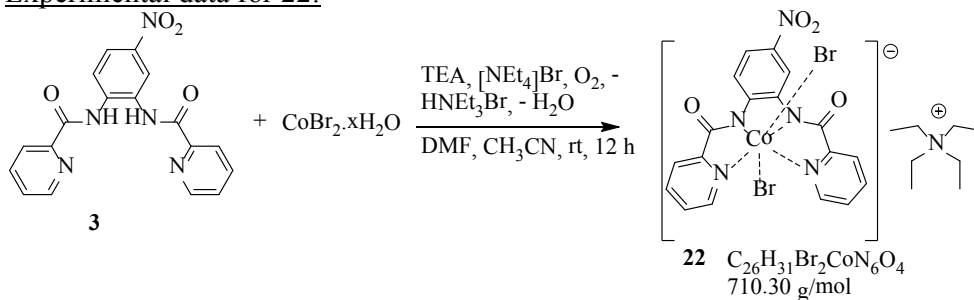


(quat., 2 C), 167.9 (quat., 2C). MS: (ESI-)  $m/z = 602$  [M-NEt<sub>4</sub>]. Anal. Calcd for C<sub>26</sub>H<sub>30</sub>Br<sub>2</sub>Cl<sub>2</sub>CoN<sub>5</sub>O<sub>2</sub>: C, 42.53; H, 4.12; N, 9.54. Found: C, 42.08; H, 4.52; N, 10.12.

<sup>1</sup>H-spectrum in CD<sub>3</sub>CN of **21**:



Experimental data for **22**:

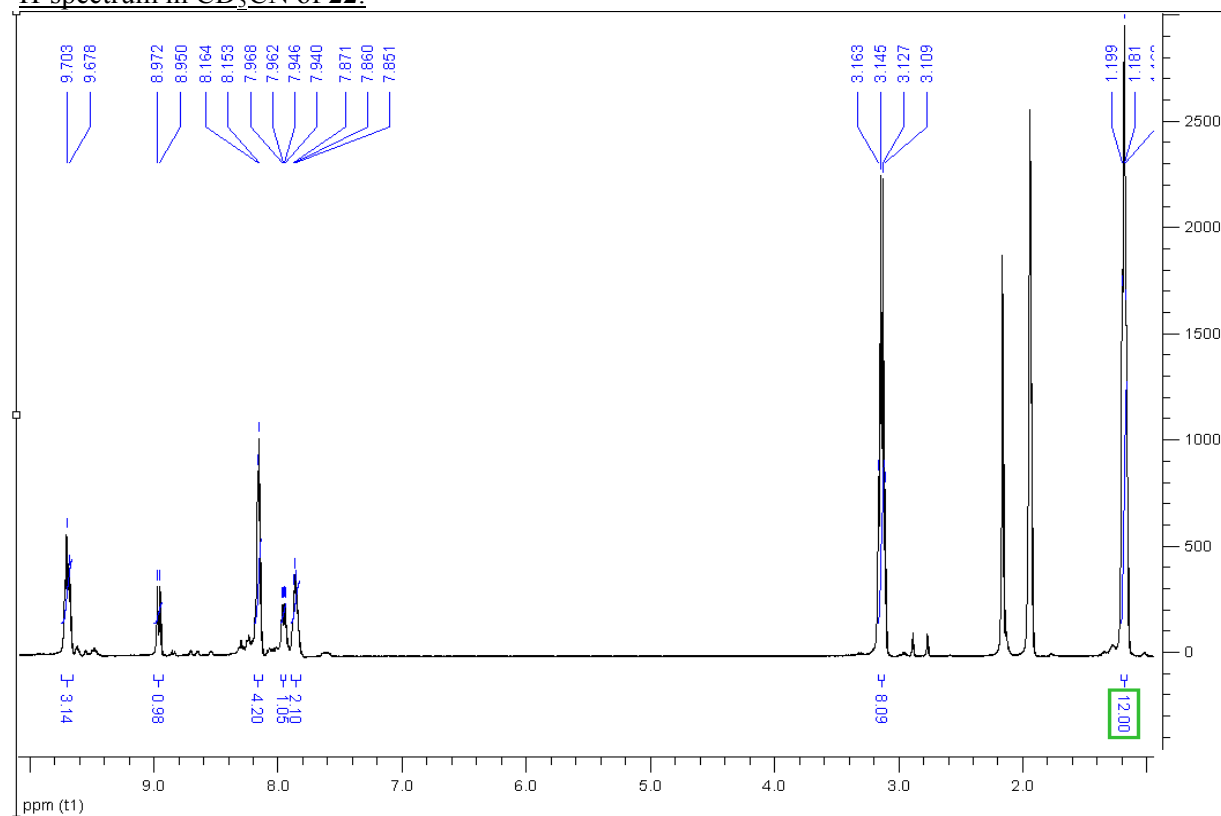


2.0 mmol of CoBr<sub>2</sub>·xH<sub>2</sub>O, 2.0 mmol of ligand **3**, 4.0 mmol triethylamine and 4.42 mmol of NEt<sub>4</sub>Br were dissolved in 15 ml of DMF and stirred under air at RT for 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. A precipitate was formed, which was filtered and washed twice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was obtained as a red-brown powder/crystal. For complex **22** red-brown crystals were obtained by slowly adding a small excess of diethyl ether into an acetonitrile solution of **22** and subsequently cooling down to 2 °C. After 2 days small red-brown crystals were formed. Yield 887 mg (62 %).

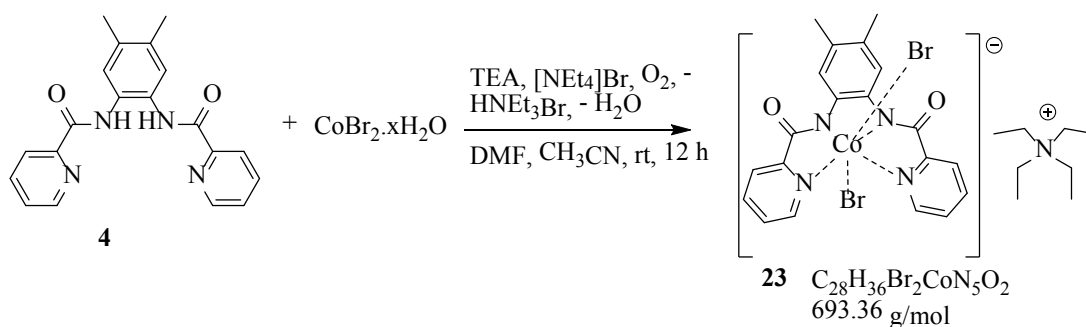
IR (cm<sup>-1</sup>): 3124 (w), 3054 (w), 2987 (w), 2925 (w), 1631 (vs), 1598 (s), 1558 (vs), 1493 (s), 1478 (s), 1422 (m), 1389 (s), 1318 (s), 1293 (s), 1140 (m), 1094 (w), 1058 (m), 998 (w), 985 (w), 897 (w), 759 (m), 682 (m), 616 (w), 506 (w), 459 (w). <sup>1</sup>H-NMR δ (ppm, CD<sub>3</sub>CN) = 1.15 – 1.21 (m, 12 H), 3.14 (q, J = 7.2 Hz, 8 H), 7.83 – 7.90 (m, 2H), 7.95 (dd, J = 8.9 Hz, J = 2.5 Hz, 1 H), 8.14 – 8.20 (m, 4 H), 8,96 (d, J = 9.0 Hz, 1 H), 9.65 – 9.74 (m, 3 H). <sup>13</sup>C{<sup>1</sup>H}-NMR / DEPT135: δ (ppm, CD<sub>3</sub>CN) = 7.6 (prim., 4 C), 52.9 (sec., 4 C), 117.9 (tert., 1 C), 120.5 (tert., 1 C), 121.8 (tert., 1 C), 125.0 (tert., 1 C),

125.3 (tert., 1 C), 128.5 (tert., 1 C), 128.8 (tert., 1 C), 140.4 (tert., 1 C), 140.5 (tert., 1 C), 143.6 (quat., 1 C), 143.7 (quat., 1 C), 151.1 (quat., 1 C), 153.0 (tert., 1 C), 153.1 (tert., 1 C), 161.2 (quat., 1 C), 161.7 (quat., 1 C), 167.5 (quat., 1 C), 167.7 (quat., 1 C). MS: (ESI-)  $m/z = 580 [M-NEt_4]$ . Anal. Calcd for  $C_{26}H_{31}Br_2CoN_6O_4$ : C, 43.96; H, 4.40; N, 11.83. Found: C, 43.68; H, 4.41; N, 12.25.

$^1H$ -spectrum in  $CD_3CN$  of **22**:



Experimental data for **23**:



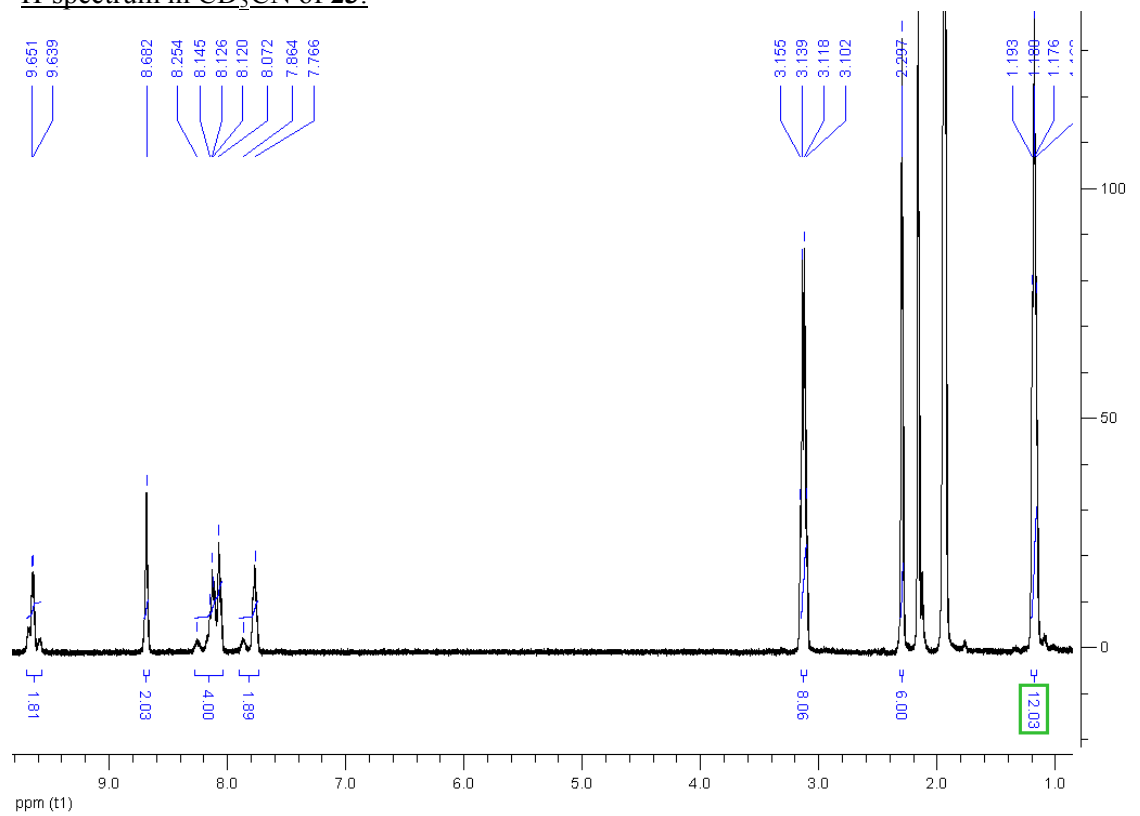
2.0 mmol of  $CoBr_2 \cdot xH_2O$ , 2.0 mmol of ligand **4**, 4.0 mmol triethylamine and 4.42 mmol of  $NEt_4Br$  were dissolved in 15 ml of DMF and stirred under air at RT for 12 hours. DMF was removed in vacuo and 50 ml of acetonitrile was added to the residue. A precipitate was formed, which was filtered and washed twice with 20 ml of a 1:1 acetonitrile/diethyl ether mixture. After drying under vacuo the product was obtained as a brown powder/crystal. For complex **23** brown crystals were obtained by slowly adding a small excess of diethyl ether into an acetonitrile solution of **23** and subsequently cooling down to 2 °C. After 2 days small brown crystals were formed. Yield 1025 mg (74 %).

IR (cm<sup>-1</sup>): 3077 (w), 2984 (w), 2923 (w), 2858 (w), 1625 (s), 1594 (vs), 1485 (s), 1456 (m), 1404 (s), 1290 (w), 1251 (w), 1178 (w), 1093 (w), 1003 (m), 889 (w), 764 (m), 680 (m), 588 (w), 509 (w), 406 (w).  $^1H$ -NMR  $\delta$  (ppm,  $CD_3CN$ ) = 1.15 – 1.20 (m, 12 H), 2.29 (s, 6 H), 3.13 (q,  $J = 7.3$  Hz, 8 H), 7.72 – 7.90 (m, 2H), 8.02 – 8.28 (m, 4 H), 8.68 (s, 2 H), 9.56 – 9.70 (m, 2 H).  $^{13}C\{^1H\}$ -NMR /

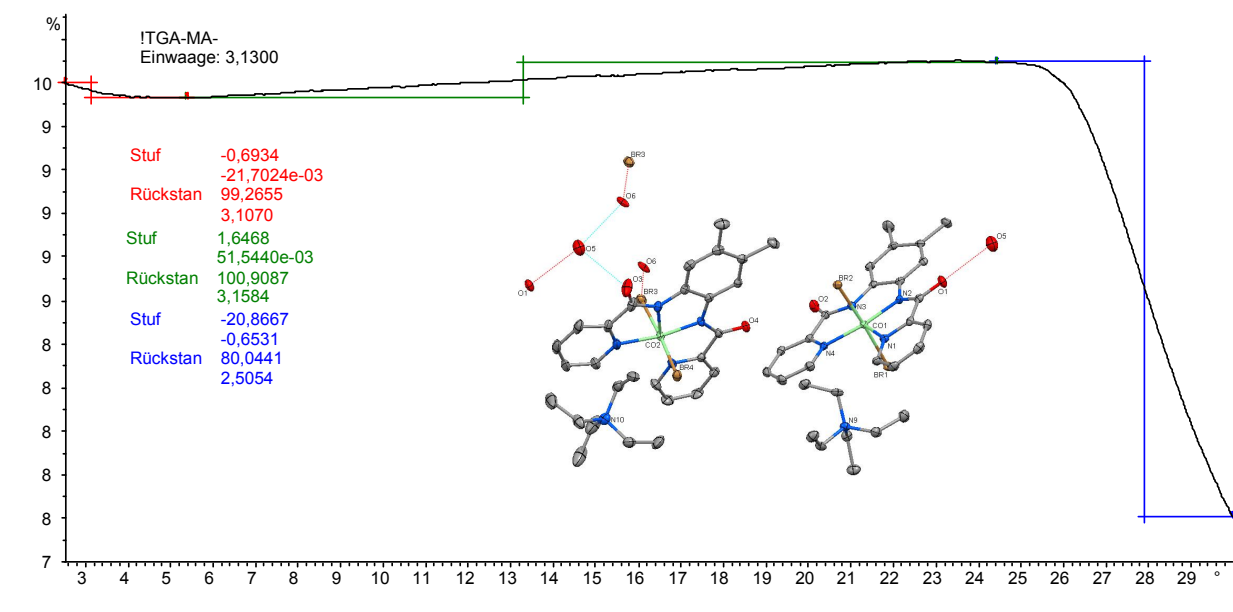


DEPT135:  $\delta$  (ppm, CD<sub>3</sub>CN) = 7.6 (prim., 4 C), 20,0 (prim., 2 C), 53,0 (sec., 4 C), 124.3 (tert., 2 C), 124.4 (tert., 2 C), 127.7 (tert., 2 C), 127.7 (quat., 2 C), 132.2 (quat., 2 C), 140,0 (tert., 2 C), 142.0 (quat., 2 C), 152.7 (tert., 2 C), 163.1 (quat., 2 C). MS: (ESI<sup>-</sup>)  $m/z$  = 561 [M-NEt<sub>4</sub>]. Anal. Calcd for C<sub>28</sub>H<sub>36</sub>CoN<sub>5</sub>O<sub>2</sub>.H<sub>2</sub>O: C, 47.27; H, 5.38; N, 9.84. Found: C, 46.28; H, 5.34; N, 9.71.

<sup>1</sup>H-spectrum in CD<sub>3</sub>CN of **23**:

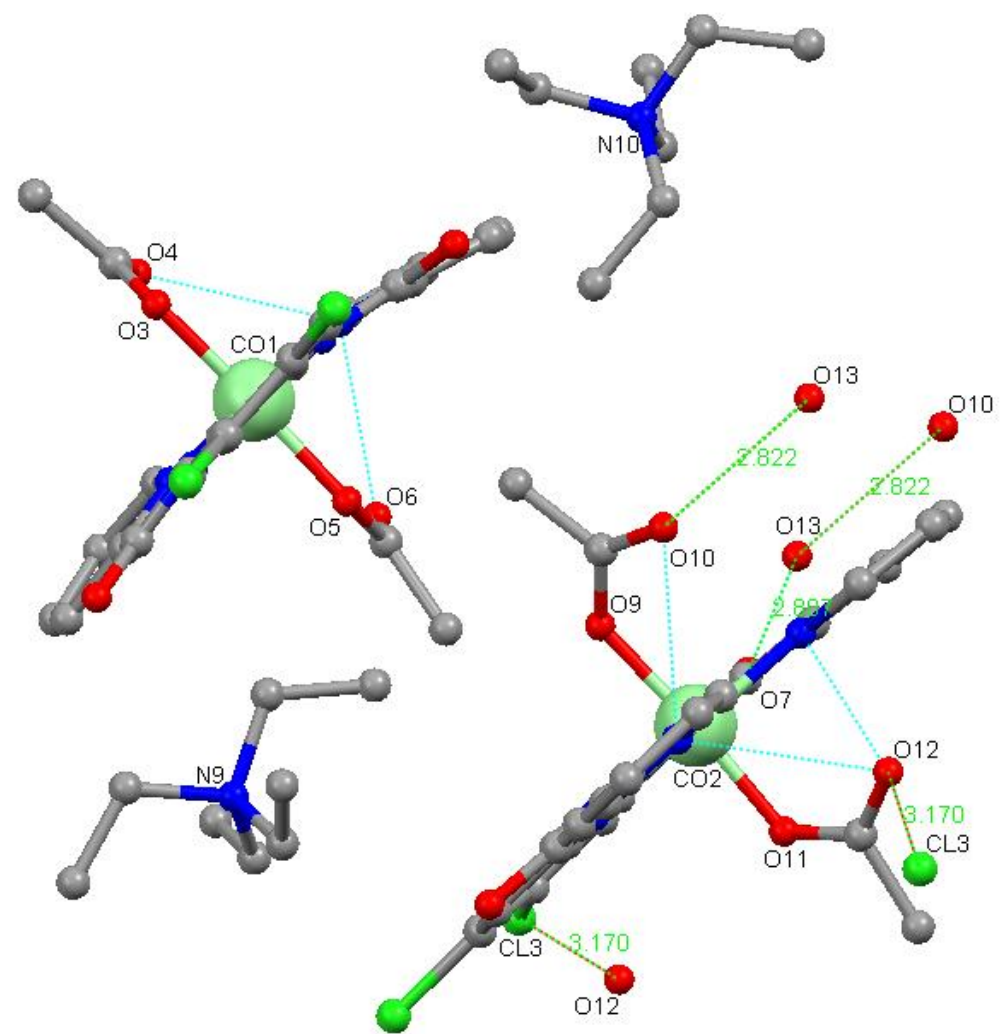


TGA of complex **23** : [(LMe<sub>2</sub>)CoBr<sub>2</sub>]NEt<sub>4</sub> (TGA recorded for the purpose of the recycling study)

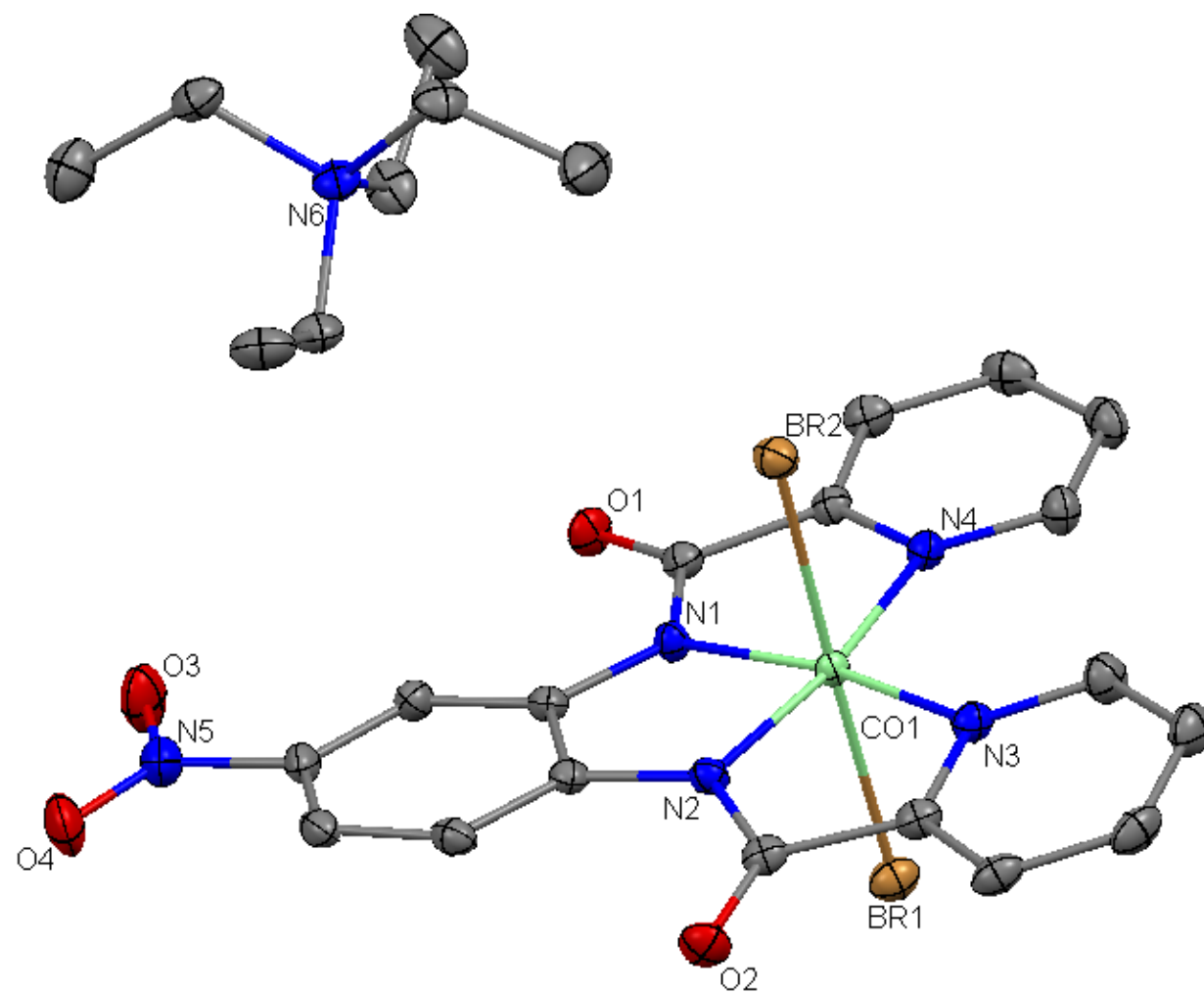


X-ray structure determination of 6, 22 and 23:

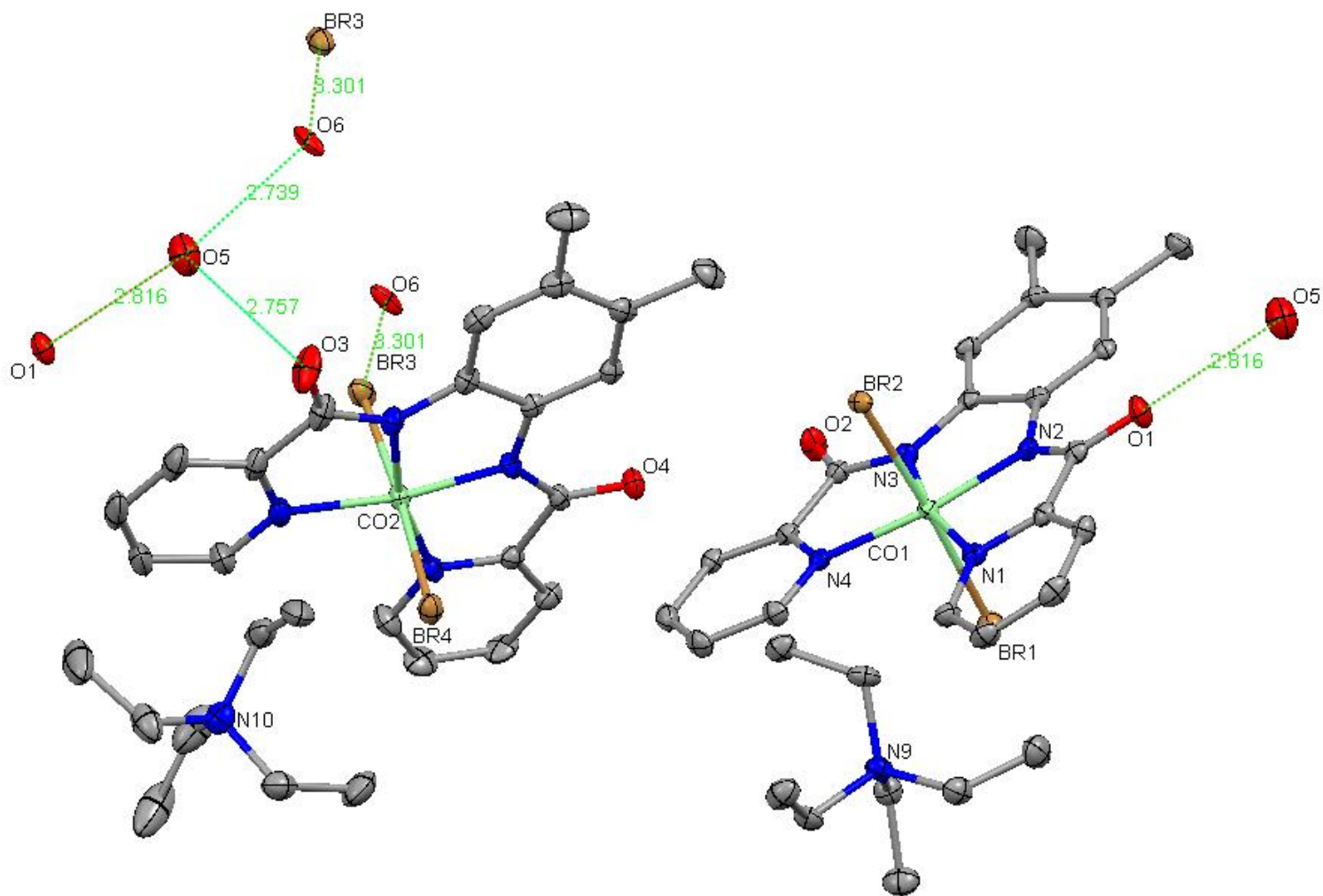
Molecular structure of 6:



Molecular structure structure of **22**



Molecular structure structure of **23**:



Quick evaluation of the operating conditions for the screening tests (propylene oxide with catalyst **10**)

**Table 1** Setting tests for propylene oxide with catalyst **10** (Co/LCl<sub>2</sub>/Cl<sub>2</sub>)<sup>a</sup>

Entry	Mol % catalyst	p (bar)	T (°C)	Conversion (%) <sup>b</sup>	Selectivity of the coupling <sup>c</sup>
1	0.2	35	60	0	0
2	0.2	35	80	78	0 / 100
3	0.2	35	100	94	0 / 100
4	0.2	50	80	3	0 / 100
5	0.5	35	80	86	0 / 100
6	0.1	35	80	71	0 / 100

<sup>a</sup> Standard reaction conditions: 10 ml of Epoxide, 20 h, 80 °C

<sup>b</sup> Conversion = n(Monomer units in isolated product)/n(epoxide)\*100

<sup>c</sup> Mass of isolated long chain polymers / mass of isolated cyclic monomer

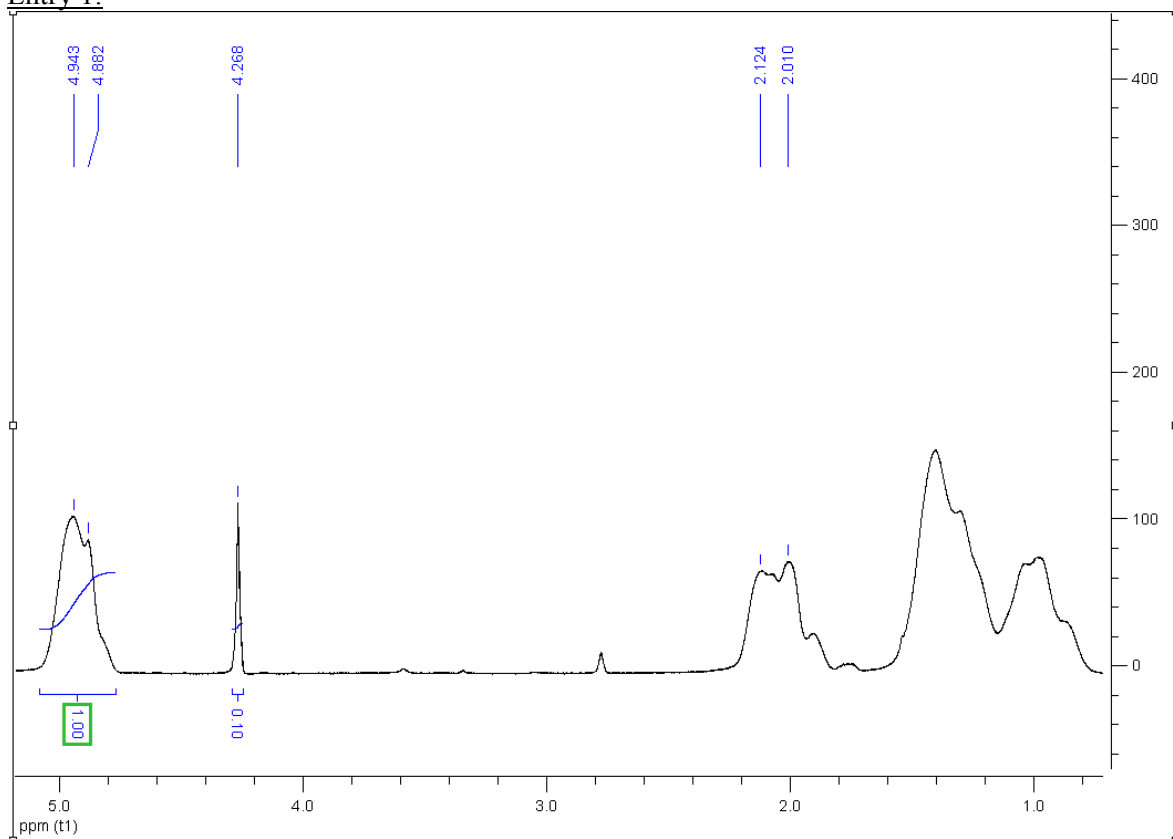
Considering the different reaction parameters for complex **10** (Table 1), three parameters were firstly investigated. Studying the influence of temperature (Entry 1-3, from 60°C to 100 °C in 20 °C steps) revealed that higher temperatures increased the overall conversion up to 94 %. 80 °C seems to be the lowest temperature necessary to achieve an acceptable conversion.

The second parameter was the amount of carbon dioxide i.e. the epoxide: CO<sub>2</sub> molar ratio. Two ratio were tested 1:1 (entry 2: 35 bar, 7 g CO<sub>2</sub>) and 1:2 (entry 4: 50, 10 g CO<sub>2</sub>), showing that higher CO<sub>2</sub> concentration induces a markedly decreased conversion. This suggests that an excess of CO<sub>2</sub> inhibits the coupling reaction via either a dilution effect of the reaction medium or a decrease of the catalyst solubility in this CO<sub>2</sub>-expanded mixture.

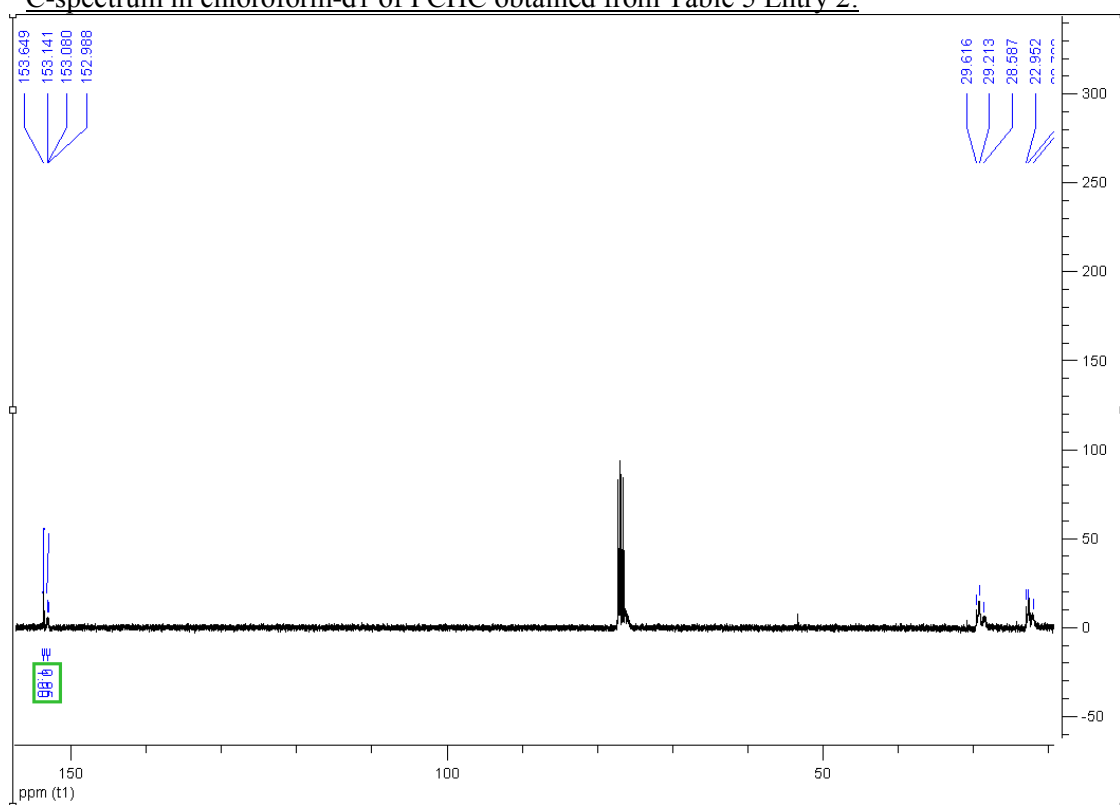
The last parameter studied was the influence of the substrate-to-catalyst molar ratio (Entry 5: 0.5 Mol% catalyst; Entry 2: 0.2 Mol% catalyst and Entry 6: 0.1 Mol% catalyst) which showed that a lower substrate-to-catalyst molar ratio leads only two a slightly decreased conversion.

PCHC characterization:

$^1\text{H}$ -spectrum in benzene- $d_6$  of PCHC (with traces of dichloromethane: 4.26 ppm) obtained from Table 8 Entry 1:

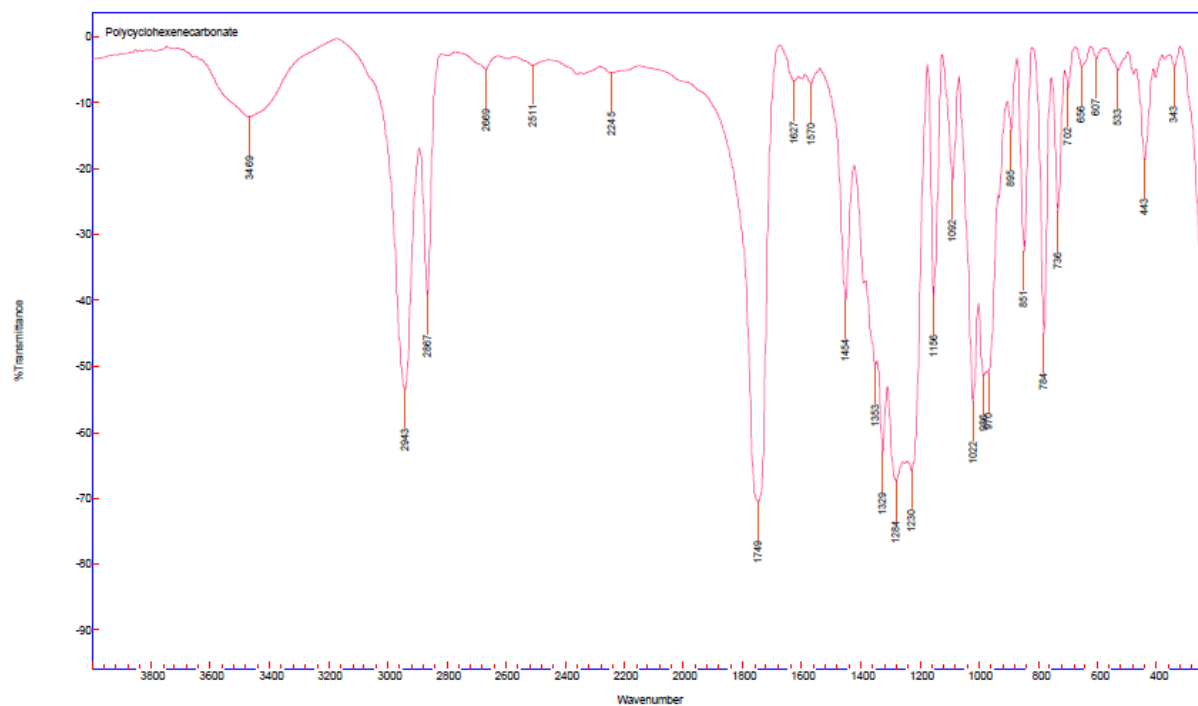


$^{13}\text{C}$ -spectrum in chloroform- $d_1$  of PCHC obtained from Table 5 Entry 2:



IR-spectrum of PCHC obtained from Table 5 Entry 2:

*Agilent Resolutions Pro*

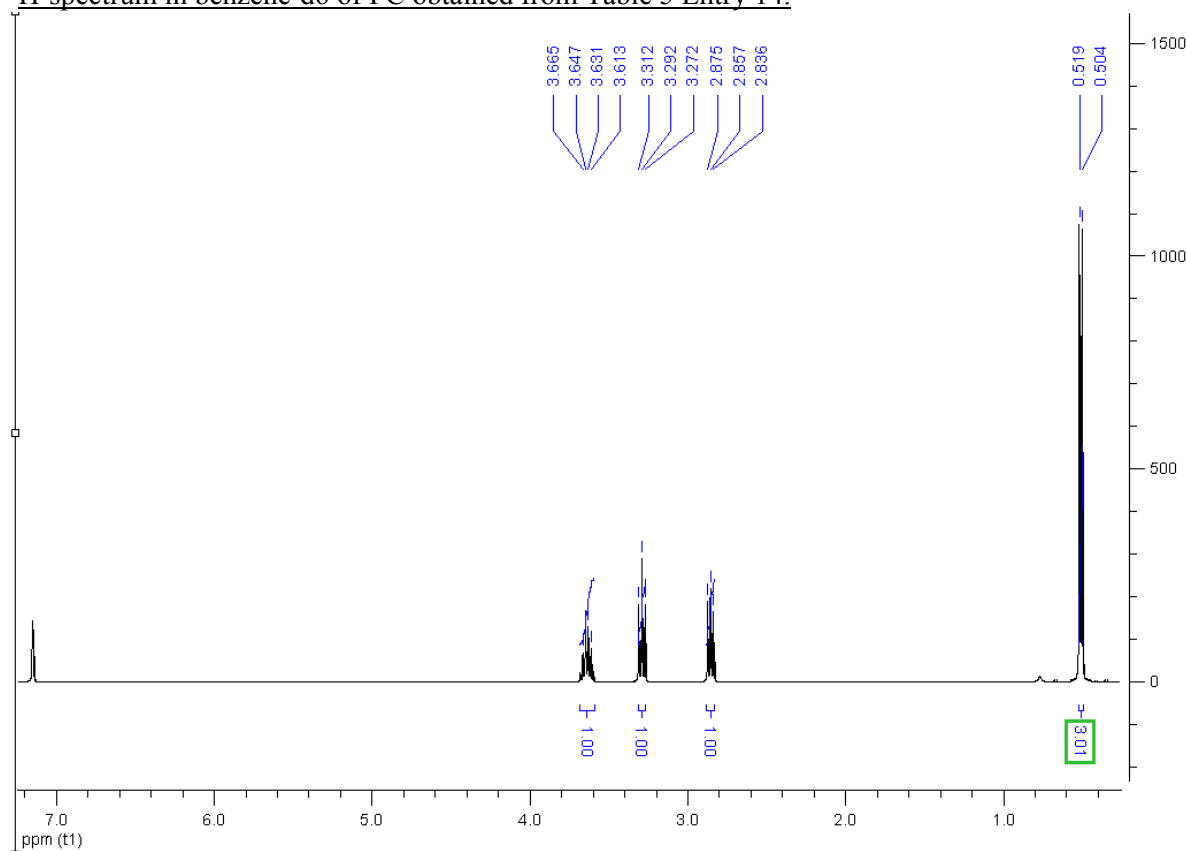


Name
Polycyclohexenecarbonate



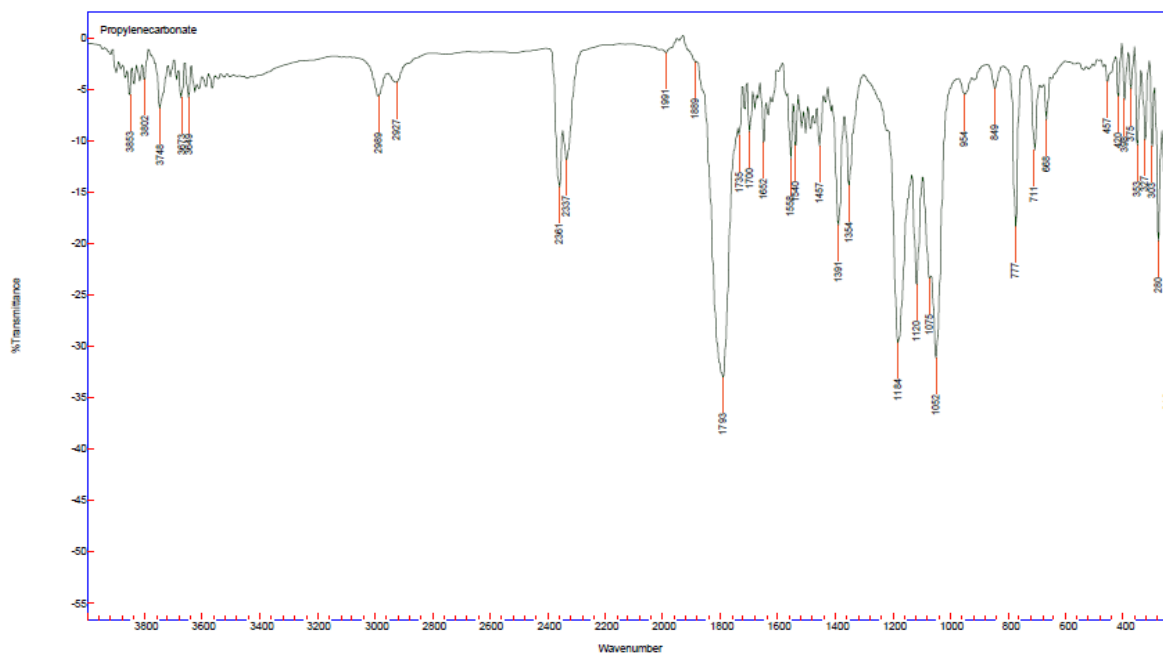
PC characterization:

$^1\text{H}$ -spectrum in benzene- $d_6$  of PC obtained from Table 5 Entry 14:



IR-spectrum of PC obtained from Table 4 Entry 8:

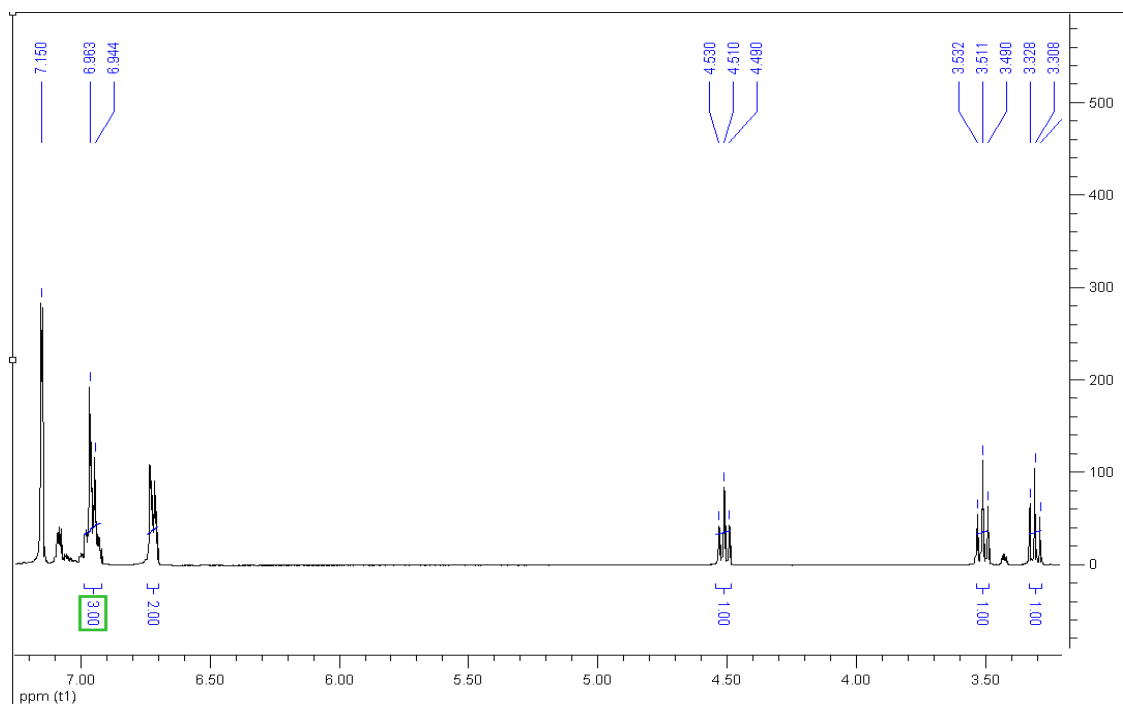
*Agilent Resolutions Pro*



Name
Propylenecarbonate

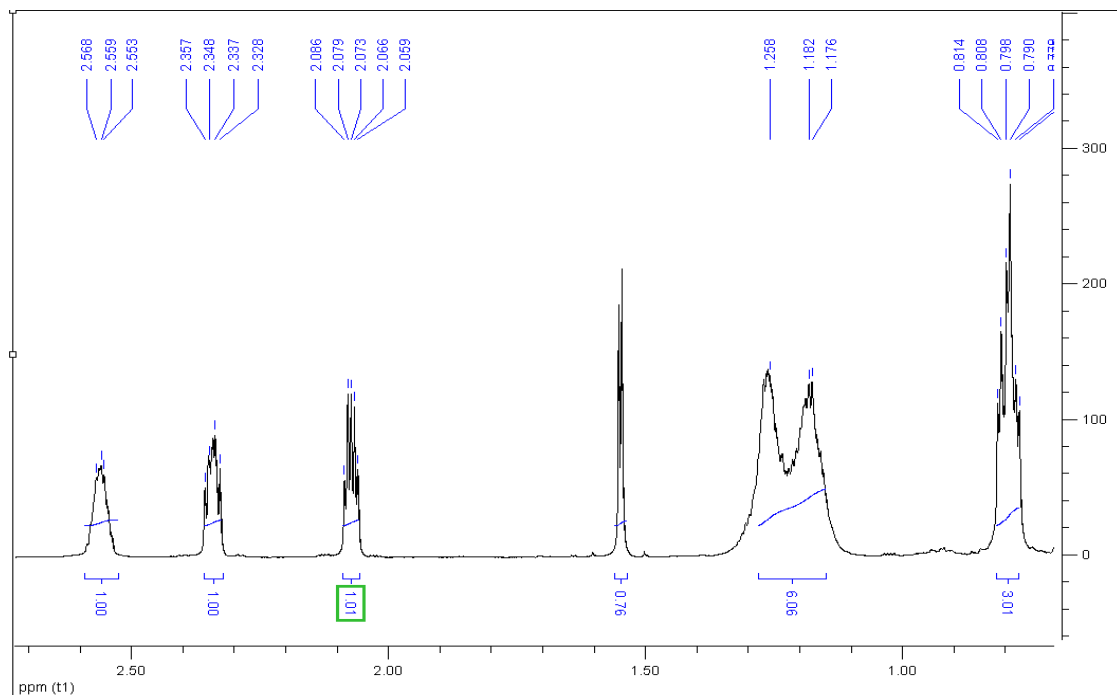
Characterization of products summarized in table 7:

Characterization of 4-phenyl-1,3-dioxolan-2-one (Entry 3):



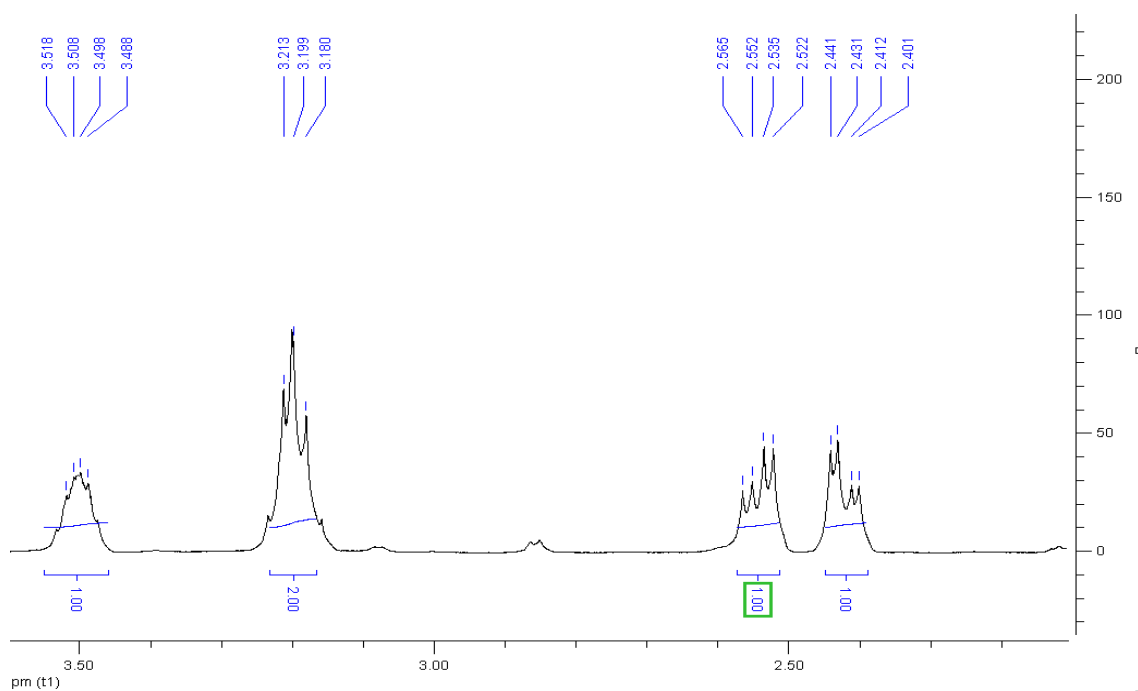
$^1\text{H-NMR } \delta$  (ppm,  $\text{C}_6\text{D}_6$ ) = 3.33 (t,  $J$  = 8.2 Hz, 1H), 3.50 (t,  $J$  = 8.3 Hz, 1H), 4.50 (t,  $J$  = 8.9 Hz, 1H), 6.73 (dd,  $J$  = 7.6 Hz,  $J$  = 1.4 Hz, 2H), 6.92 – 7.00 (m, 3H).

Characterization of 4-butyl-dioxolan-2-one (Entry 4):



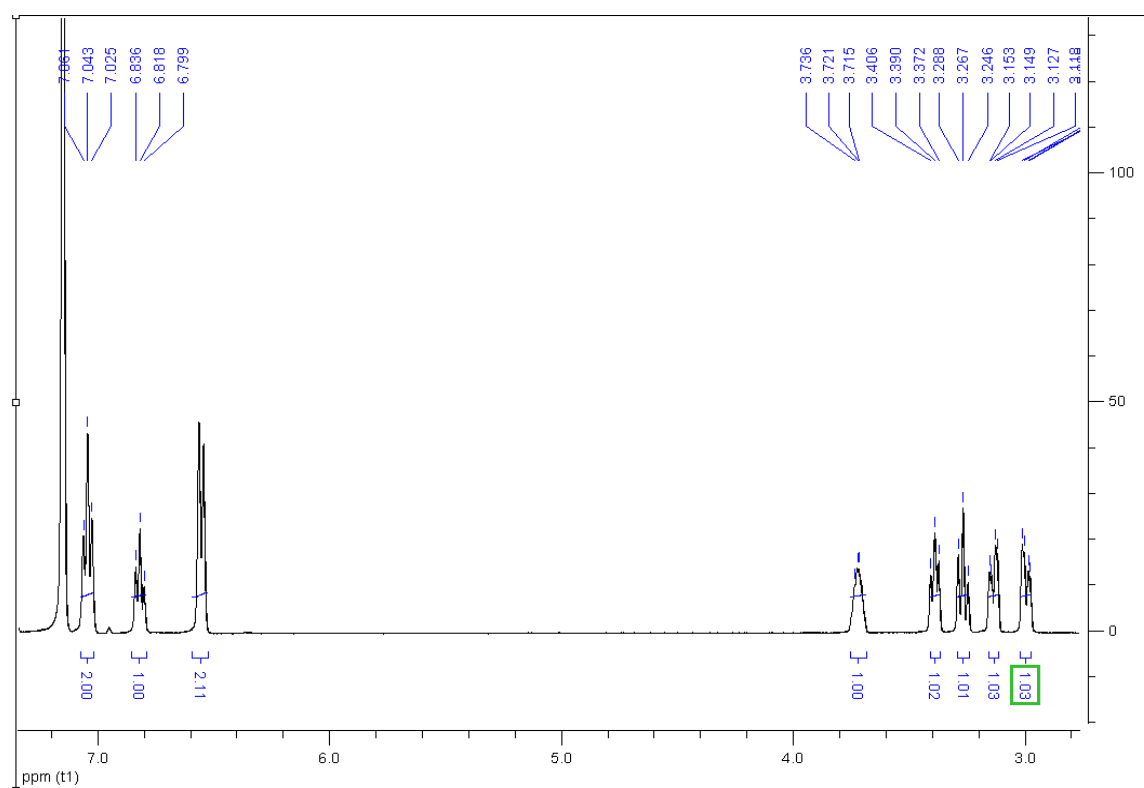
$^1\text{H-NMR } \delta$  (ppm,  $\text{C}_6\text{D}_6$ ) = 0.77 – 0.82 (m, 3H), 1.15 - 1.30 (m, 6H), 2.07 (td,  $J$  = 5.3 Hz,  $J$  = 2.6 Hz, 1H), 2.32 – 2.34 (m, 1H), 2.53 – 2.59 (m, 1H).

**Characterization of 4-chloromethyl-1,3-dioxolan-2-one (Entry 5):**



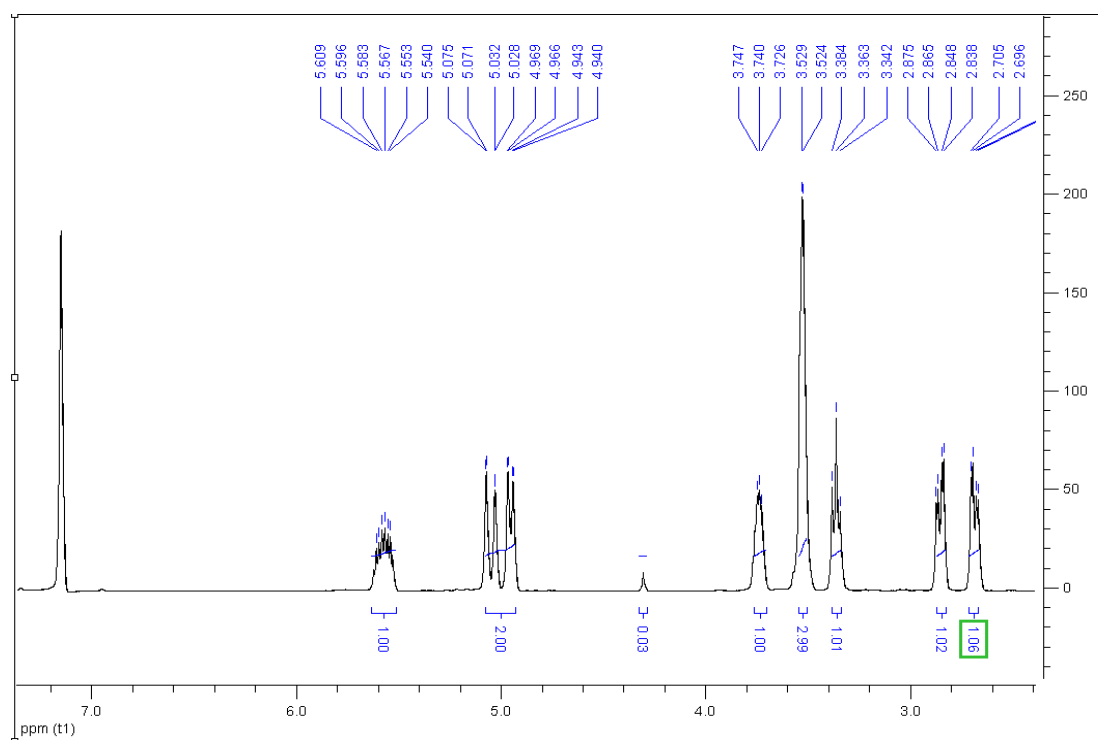
$^1\text{H-NMR } \delta$  (ppm,  $\text{C}_6\text{D}_6$ ) = 2.42 (dd,  $J = 11.9$  Hz,  $J = 4.1$  Hz, 1H), 2.54 (dd,  $J = 12.0$  Hz,  $J = 5.4$  Hz, 1H), 3.16 – 3.23 (m, 2H), 3.46 – 3.54 (m, 1H).

**Characterization of 4-phenyloxymethyl-1,3-dioxolan-2-one (Entry 6):**



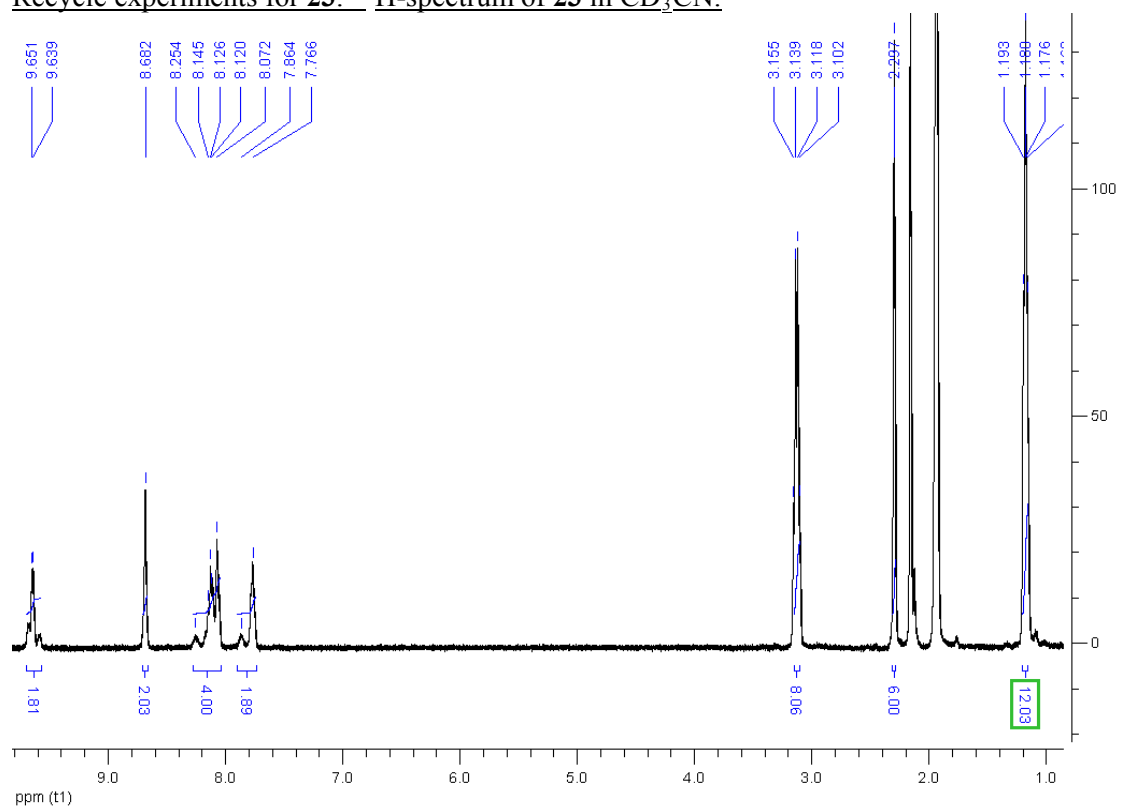
$^1\text{H-NMR } \delta$  (ppm,  $\text{C}_6\text{D}_6$ ) = 2.99 (dd,  $J = 10.4$  Hz,  $J = 3.2$  Hz, 1H), 3.14 (dd,  $J = 10.4$  Hz,  $J = 3.5$  Hz, 1H), 3.27 (t,  $J = 8.4$  Hz, 1H), 3.38 (t,  $J = 6.9$  Hz, 1H), 3.69 – 3.75 (m, 1H), 6.55 (d,  $J = 7.8$  Hz, 2H), 6.82 (t,  $J = 7.3$  Hz, 1H), 7.04 (t,  $J = 7.3$  Hz, 2H).

**Characterization of 4-Allyloxymethyl-1,3-dioxolan-2-one (Entry 7):**



$^1\text{H-NMR } \delta$  (ppm,  $\text{C}_6\text{D}_6$ ) = 2.69 (dd,  $J = 10.8$  Hz,  $J = 3.8$  Hz, 1H), 2.86 (dd,  $J = 10.9$  Hz,  $J = 3.7$  Hz, 1H), 3.36 (t,  $J = 8.3$  Hz, 1H), 3.50-3.55 (m, 3H), 3.71 – 3.77 (m, 1H), 4.95 (dd,  $J = 10.4$  Hz,  $J = 1.3$  Hz, 1H), 5.05 (dd,  $J = 17.3$  Hz,  $J = 1.5$  Hz, 1H), 5.55 – 5.65 (m, 1H).

Recycle experiments for 23:  $^1\text{H}$ -spectrum of 23 in  $\text{CD}_3\text{CN}$ :



Typical  $^1\text{H}$ -spectrum of 23 in  $\text{CD}_3\text{CN}$  (end of recycling, with traces of propylene carbonate):

