

Elucidation of the Structure of A Highly Active Catalytic System for CO₂/Epoxide Copolymerization: A Salen-Cobaltate Complex of An Unusual Binding Mode

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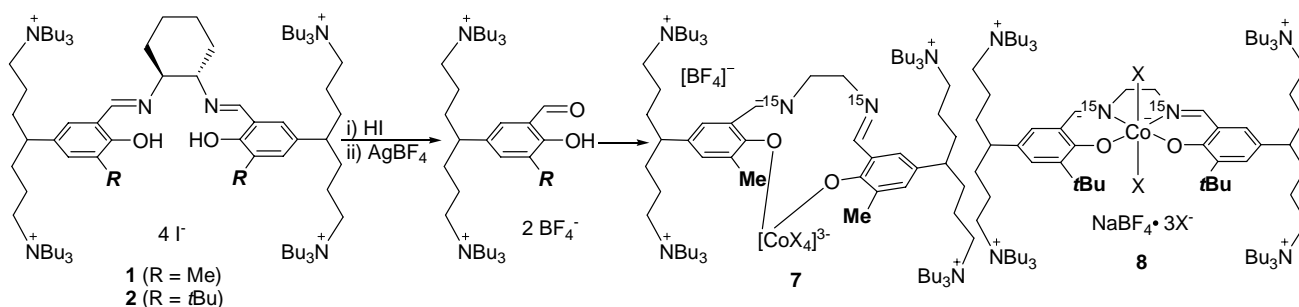
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Supporting Information

General Remarks. All manipulations were performed in an inert atmosphere using a standard glove box and Schlenk techniques. THF was distilled from benzophenone ketyl. Ethanol was dried by a method in the literature, using sodium and diethyl phthalate.¹ CH₃CN, CH₂Cl₂, and CDCl₃ were dried by stirring over CaH₂, followed by vacuum-transfer to reservoirs. DMSO-d₆ was stored in molecular sieves inside a glove box. The CO₂ gas (99.999%) was dried by storage in a column of molecular sieves 3A at a pressure of 30 bar. Propylene oxide (PO) was dried by stirring over CaH₂ for several days,

followed by vacuum-transfer to a reservoir. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Mercury Plus 400. Elemental analyses were performed at the Analytical Center of Kyunghee University. Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high-resolution mass spectrometer. Gel permeation chromatograms (GPC) were obtained at room temperature in THF using Waters Millennium with polystyrene standards. Complexes **3**,² **4**,² **10**³ and **12**² were prepared according to the previous reports.



[3-Methyl-5-[(Bu₃N⁺(CH₂)₃)₂CH]]-salicylaldehyde)(BF₄⁻)₂. This compound was prepared through the hydrolysis of **1** (X = I⁻). Thus, **1** (X = I⁻, 0.500 g, 0.279 mmol) was dissolved in CH₂Cl₂ (4.0 mL). After addition of aqueous HI solution (2.5 mL, 2.0 N), the two-phased mixture was heated reflux for 3 hours and then the CH₂Cl₂-phase was collected and washed with water. The solution was dried over anhydrous MgSO₄, followed by removal of solvent by a rotary evaporator. The pure iodide salt of the hydrolyzed product was purified by column chromatography on silica gel, eluting with CH₂Cl₂/ethanol (v/v, 10:1). A 95% yield of the product was obtained, which was then dissolved in ethanol (6.0 mL) containing AgBF₄ (0.225 g, 1.16 mmol). After stirring at room temperature for 1.5 hours, filtration was performed over Celite to remove generated AgI. The solvent was then removed and the product was purified by column chromatography on silica gel, eluting with CH₂Cl₂/ethanol (v/v, 10:1). A white solid was obtained with a quantitative yield (0.410 g). IR (KBr): 3422 (OH), 1644 (C=O) cm⁻¹. ^1H NMR (CDCl₃): δ 11.19 (s, 1H, OH), 9.89 (s, 1H, CHO), 7.48 (s, 1H, *m*-H), 7.29 (s, 1H, *m*-H), 3.32-3.26 (m, 4H, NCH₂), 3.10-3.06 (m, 12H, NCH₂), 2.77 (septet, *J* = 6.8 Hz, 1H, CH), 2.24 (s, 3H, CH₃), 1.76-1.64 (m, 8H, CH₂), 1.58-1.44 (m, 16H, CH₂), 1.34-1.29 (m, 8H, CH₂), 0.90 (t, *J* = 7.6 Hz, 18H, CH₃) ppm.

^{13}C $\{^1\text{H}\}$ NMR (CDCl_3): δ 197.29, 158.40, 136.63, 133.48, 130.51, 127.12, 119.74, 58.23, 40.91, 32.51, 23.58, 19.48, 18.82, 15.10, 13.45 ppm. HRMS (FAB): m/z calcd ($[\text{M-BF}_4]^+ \text{C}_{39}\text{H}_{74}\text{BF}_4\text{N}_2\text{O}_2$) 689.5779, found 689.5775.

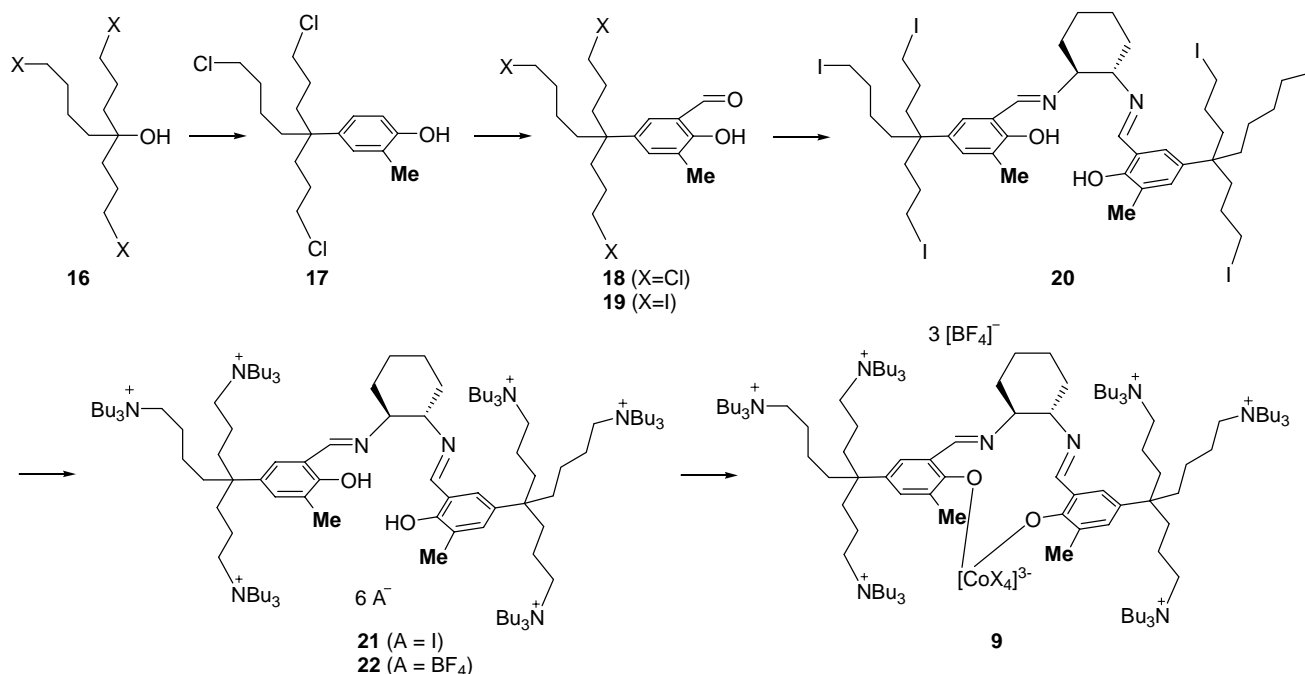
[3-*tert*-Butyl-5- $\{[\text{Bu}_3\text{N}^+(\text{CH}_2)_3\}_2\text{CH}\}$]-salicylaldehyde](BF_4^-) $_2$. This compound was synthesized using the same conditions and procedures as those used to synthesize [3-Methyl-5- $\{[\text{Bu}_3\text{N}^+(\text{CH}_2)_3\}_2\text{CH}\}$]-salicylaldehyde(BF_4^-) $_2$, starting with **2** ($\text{X} = \text{I}^-$). A white solid was obtained with a quantitative yield. IR (KBr): 3506 (OH), 1661 (C=O) cm^{-1} . ^1H NMR (CDCl_3): δ 11.76 (s, 1H, OH), 9.92 (s, 1H, CHO), 7.53 (s, 1H, *m*-H), 7.35 (s, 1H, *m*-H), 3.36-3.22 (m, 16H, NCH_2), 2.82 (br, 1H, CH), 1.78-1.70 (m, 4H, CH_2), 1.66-1.46 (m, 16H, CH_2), 1.42 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.38-1.32 (m, 12H, CH_2), 0.93 (t, $J = 7.6$ Hz, 18H, CH_3) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 197.76, 159.67, 138.70, 133.50, 132.63, 131.10, 120.40, 58.55, 41.45, 34.99, 32.28, 29.31, 23.72, 19.59, 19.00, 13.54 ppm. HRMS (FAB): m/z calcd ($[\text{M-BF}_4]^+ \text{C}_{42}\text{H}_{80}\text{BF}_4\text{N}_2\text{O}_2$) 731.6249, found 731.6254.

Complex 7. Ethylenediamine- $^{15}\text{N}_2$ -dihydrochloride (0.010 g, 0.074 mmol), sodium *tert*-butoxide (0.014 g, 0.15 mmol) and [3-Methyl-5- $\{[\text{Bu}_3\text{N}^+(\text{CH}_2)_3\}_2\text{CH}\}$]-salicylaldehyde(BF_4^-) $_2$ (0.115 g, 0.150 mmol) were added to a flask, followed by the addition of anhydrous ethanol (2.0 mL). The solution was stirred overnight and ethanol was removed after filtration over Celite. Filtration was performed again after the residue was dissolved in CH_2Cl_2 . Removal of solvent produced the white solid **3**, which was used without any further purification in the metallation reaction. $\text{Co}(\text{OAc})_2$ (0.013 g, 0.074 mmol) and ethanol (2.0 mL) was added to a flask containing **3**. After stirring for 3 hours at room temperature, the solvent was removed under a vacuum to give a residue which was washed with diethyl ether (2.0 mL \times 2). The solid, after being evacuated overnight, was dissolved in CH_2Cl_2 (2.0 mL) containing 2,4-dinitrophenol (0.014 g, 0.074 mmol). The resulting solution was stirred under O_2 atmosphere for 3 hours, after which sodium-2,4-dinitrophenolate (0.092 g, 0.440 mmol) was added. After stirring overnight at room temperature, the solution was filtered over Celite. The solvent was then removed by vacuum to give a dark brown powder pure enough for use in NMR characterization and polymerization. Yields were quantitative (0.149 g, 100%). ^1H NMR (dmsO-d_6 , 40°C): δ 8.84 (br, 2H, $(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}$), 8.09 (br,

2H, (NO₂)₂C₆H₃O), 8.04 (s, 1H, CH=N), 7.12 (br, 2H, *m*-H), 6.66 (br, 2H, (NO₂)₂C₆H₃O), 4.21 (br, 2H, ethylene-CH₂), 3.35-2.90 (br, 16H, NCH₂), 2.62 (s, 3H, CH₃), 1.91 (s, 1H, CH), 1.68-1.42 (br, 20H, CH₂), 1.19 (br, 12H, CH₂), 0.83 (br, 18H, CH₃) ppm. ¹H NMR (THF-d₈, 20°C): δ 8.59 (br, 1H, (NO₂)₂C₆H₃O), 8.10 (br, 1H, (NO₂)₂C₆H₃O), 7.93 (s, 1H, CH=N), 7.88 (br, 1H, (NO₂)₂C₆H₃O), 7.05 (s, 1H, *m*-H), 6.90 (s, 1H, *m*-H), 4.51 (s, 2H, ethylene-CH₂), 3.20-2.90 (br, 16H, NCH₂), 2.69 (s, 3H, CH₃), 1.73 (s, 1H, CH), 1.68-1.38 (br, 20H, CH₂), 1.21 (m, 12H, CH₂), 0.84 (t, *J* = 6.8 Hz, 18H, CH₃) ppm. ¹H NMR (CD₂Cl₂, 20°C): δ 8.43 (br, 1H, (NO₂)₂C₆H₃O), 8.15 (br, 1H, (NO₂)₂C₆H₃O), 7.92 (br, 1H, (NO₂)₂C₆H₃O), 7.79 (s, 1H, CH=N), 6.87 (s, 1H, *m*-H), 6.86 (s, 1H, *m*-H), 4.45 (s, 2H, ethylene-CH₂), 3.26 (br, 2H, NCH₂), 3.0-2.86 (br, 14H, NCH₂), 2.65 (s, 3H, CH₃), 2.49 (br, 1H, CH), 1.61-1.32 (br, 20H, CH₂), 1.31-1.18 (m, 12H, CH₂), 0.86 (t, *J* = 6.8 Hz, 18H, CH₃) ppm. ¹³C{¹H} NMR(dmsO-d₆, 20°C): δ 170.33, 165.12, 160.61, 132.12 (br), 129.70, 128.97, 127.68 (br), 124.51 (br), 116.18 (br), 57.32, 56.46, 40.85, 31.76, 24.12, 21.92, 20.03, 18.04, 16.16, 12.22 ppm. ¹⁵N{¹H} NMR (dmsO-d₆, 20°C): δ -156.32, -159.21 ppm. ¹⁵N{¹H} NMR (THF-d₈, 20°C): δ -154.19 ppm. ¹⁹F{¹H} NMR (dmsO-d₆, 20°C): δ -50.63, -50.69 ppm.

Complex 8. This compound was synthesized using the same conditions and procedures as those used for synthesis of **7**, starting with [3-*tert*-butyl-5-[{Bu₃N⁺(CH₂)₃}₂CH}]-salicylaldehyde](BF₄⁻)₂. A brown powder was obtained in a quantitative yield. ¹H NMR (dmsO-d₆, 40°C): δ 8.82 (br, 2.5H, (NO₂)₂C₆H₃O), 7.89 (br, 3.5H, (NO₂)₂C₆H₃O, CH=N), 7.21 (s, 1H, *m*-H), 7.19 (s, 1H, *m*-H), 6.46 (br, 2.5H, (NO₂)₂C₆H₃O), 4.12 (s, 2H, ethylene-CH₂), 3.25-2.96 (br, 16H, NCH₂), 1.90 (s, 1H, CH), 1.71 (s, 9H, C(CH₃)₃), 1.67-1.32 (br, 20H, CH₂), 1.32-1.15 (m, 12H, CH₂), 0.88 (t, *J* = 7.2 Hz, 18H, CH₃) ppm. ¹H NMR (THF-d₈, 20°C): δ 7.78 (s, 1H, CH=N), 7.31 (s, 1H, *m*-H), 7.12 (s, 1H, *m*-H), 4.19 (br, 2H, ethylene-CH₂), 3.43-2.95 (br, 16H, NCH₂), 2.48 (br, 1H, CH), 1.81-1.52 (br, 20H, CH₂), 1.50 (s, 9H, C(CH₃)₃), 1.42-1.15 (br, 12H, CH₂), 0.89 (t, *J* = 6.8 Hz, 18H, CH₃) ppm. ¹H NMR (CD₂Cl₂, 20°C): δ 7.47 (s, 1H, CH=N), 7.10 (s, 1H, *m*-H), 7.07 (s, 1H, *m*-H), 4.24 (s, 2H, ethylene-CH₂), 3.31 (br, 2H, NCH₂), 3.09-2.95 (br, 14H, NCH₂), 2.64 (br, 1H, CH), 1.68-1.50 (br, 20H, CH₂), 1.49 (s, 9H, C(CH₃)₃), 1.39-1.26 (m, 12H, CH₂), 0.93 (t, *J* = 6.8 Hz, 18H, CH₃) ppm. ¹³C{¹H} NMR(dmsO-d₆, 20°C): δ 166.57,

166.46, 161.55, 142.16, 129.99, 129.26, 128.39, 128.13, 127.63, 124.18, 118.34, 57.59, 56.93, 41.64, 34.88, 32.27, 29.63, 22.37, 18.64, 18.51, 12.70 ppm. $^{15}\text{N}\{^1\text{H}\}$ NMR (dmso- d_6 , 20°C): -163.43 ppm. $^{15}\text{N}\{^1\text{H}\}$ NMR (THF- d_8 , 20°C): δ -166.80 ppm. $^{19}\text{F}\{^1\text{H}\}$ NMR (dmso- d_6 , 20°C): δ -50.65, -50.70 ppm.



Compound 16. A 0.1 M solution of 1-chloro-4-iodobutane (1.00 g, 4.57 mmol) in ether-pentane (v/v, 2:3) was cooled to -78°C, followed by the addition of *tert*-BuLi (3.69 g, 9.61 mmol, 1.7 M in pentane) by syringe under N₂ atmosphere.⁴ After stirring the reaction mixture for 2 hours at -78°C, a solution of 1,5-dichloropentane-3-one (838 mg, 4.58 mmol) in diethyl ether (8.0 mL) was added. The solution was stirred for 4 hours at -78°C, and then ice water (50 mL) was added to quench the reaction. The product was extracted with diethyl ether (3 × 100 mL). After the combined organic phase was dried over anhydrous MgSO₄, the solvent was removed using a rotary evaporator to give an oily residue. It was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 5:1) to give pale yellow oil (0.820 g, 65% yield). The product is very susceptible to dehydration reaction. Therefore it was not stored but used immediately upon preparation. ^1H NMR (CDCl₃): δ 3.52 (t, J = 6.4 Hz, 6H, CH₂Cl), 1.80-1.73 (m, 6H, CH₂), 1.56-1.52 (m, 4H, CH₂), 1.42 (s, 4H, CH₂) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl₃): δ 73.58, 45.69, 44.95, 38.29, 36.48, 32.94, 26.96, 20.88 ppm.

Compound 17. *o*-Cresol (26.6 g, 246 mmol), **16** (6.73 g, 30.8 mmol) and AlCl₃ (4.52 g, 33.9 mmol)

were dissolved in 20 mL methylene chloride and the mixture was stirred overnight under an N₂ atmosphere. The reaction was quenched by the addition of methylene chloride (100 mL) and water (100 mL). The organic phase was collected and the water phase was further extracted using additional methylene chloride (3 × 50 mL). The combined diethyl ether was dried over anhydrous MgSO₄ and the solvent was removed using a rotary evaporator. Excess *o*-cresol was recovered by vacuum distillation (45°C/2 mmHg). The residue was purified by column chromatography on silica gel eluting with hexane and ethyl acetate (v/v, 10:1). Yield was 10.1 g (90%). IR (KBr): 3535 (OH) cm⁻¹. ¹H NMR (CDCl₃): δ 7.02 (s, 1H, *m*-H), 6.99 (d, *J* = 8.8 Hz, 1H, *m*-H), 6.73 (d, *J* = 8.0 Hz, 1H, *o*-H), 4.67 (s, 1H, OH), 3.53-3.46 (m, 6H, CH₂Cl), 2.27 (s, 3H, CH₃), 1.79-1.44 (m, 6H, CH₂), 1.67-1.62 (m, 2H, CH₂), 1.58-1.53 (m, 4H, CH₂), 1.28-1.20 (br, 2H, CH₂) ppm. ¹³C{¹H} NMR (CDCl₃): δ 151.81, 137.96, 128.89, 124.87, 123.39, 114.70, 60.83, 46.05, 45.04, 42.09, 36.69, 35.07, 33.36, 27.26, 21.40, 21.02, 16.54, 14.49 ppm. HRMS (FAB): *m/z* calcd ([M+H]⁺ C₁₈H₂₇Cl₃O) 365.1206, found 365.1206

Compound 18. Compound **17** (4.54 g, 12.4 mmol) was dissolved in anhydrous THF (250 mL). Paraformaldehyde (1.49 g, 49.7 mmol), triethylamine (5.28 g, 25.1 mmol) and magnesium chloride (4.73 g, 52.16 mmol) were added under a N₂ atmosphere. The reaction mixture was heated to reflux for 5 hours and then cooled to room temperature. The solvent was removed using a rotary evaporator, after which water (100 mL) and CH₂Cl₂ (200 mL) were added to the residue and the mixture was filtered over Celite. The organic phase was collected and the aqueous phase was further extracted using CH₂Cl₂ (2 × 50 mL). The combined organic phase was dried over anhydrous MgSO₄. The solvent was removed using a rotary evaporator to give an oily residue that was further evacuated to remove some residual triethylamine. The product was purified by column chromatography on silica gel, eluting with hexane and ethyl acetate (v/v, 20:1). Yellow oil was obtained in 80% yield (3.91 g). IR (KBr): 3258 (OH), 1650 (C=O) cm⁻¹. ¹H NMR (CDCl₃): δ 11.05 (s, 1H, OH), 9.78 (s, 1H, CHO), 7.25 (s, 1H, *m*-H), 7.19 (s, 1H, *m*-H), 3.44-3.39 (m, 6H, CH₂Cl), 2.19 (s, 3H, CH₃), 1.74-1.43 (m, 12H, CH₂), 1.20-1.11 (br, 2H, CH₂) ppm. ¹³C{¹H} NMR (CDCl₃): δ 196.79, 158.07, 136.98, 135.85, 128.95, 126.85, 119.52, 45.77, 44.88, 42.12, 36.50, 34.64, 33.09, 27.07, 20.85, 15.71 ppm. HRMS (FAB): *m/z* calcd ([M+H]⁺ C₁₉H₂₇Cl₃O) 379.1206, found 379.1206

393.1155, found 393.1155.

Compound 19. Compound **18** (2.97 g, 7.54 mmol) was dissolved in CH₃CN (12 mL), followed by the addition of NaI (16.9 g, 113 mmol). The resulting mixture was refluxed for 20 hours and then cooled to room temperature. Water (100 mL) was added and then the product was extracted using methylene chloride (3 × 100 mL). After the collected organic phase was dried over anhydrous MgSO₄, all volatiles were removed using a rotary evaporator to give a yellow oil. The yield was 89% (4.49 g). IR (KBr): 3299 (OH), 1648 (C=O) cm⁻¹. ¹H NMR (CDCl₃): δ 11.06 (s, 1H, OH), 9.80 (s, 1H, CHO), 7.25 (s, 1H, *m*-H), 7.17 (s, 1H, *m*-H), 3.21-3.14 (m, 6H, CH₂Cl), 2.27 (s, 3H, CH₃), 1.79-1.53 (m, 12H, CH₂), 1.28-1.19 (br, 2H, CH₂) ppm. ¹³C{¹H} NMR (CDCl₃): δ 196.81, 158.20, 137.00, 135.90, 128.90, 126.98, 119.54, 42.17, 38.45, 36.11, 33.93, 27.83, 24.50, 15.84, 7.96, 7.14 ppm. Anal. Calcd. (C₁₉H₂₇I₃O₂): C, 34.16; H, 4.07 %. Found: C, 34.44; H, 4.08%. HRMS (FAB): *m/z* calcd ([M+H]⁺ C₁₉H₂₇I₃O) 668.9223, found 668.9228.

Compound 20. Compound **19** (0.680 g, 1.02 mmol) and (±)-*trans*-1,2-diaminocyclohexane (0.058 g, 0.509 mmol) were weighed into a vial, followed by the addition of CH₂Cl₂ (5.0 mL). The solution was stirred overnight under a N₂ atmosphere and the solvent was removed under vacuum to give a pure compound (0.706 g, 98%). Yellow solid was obtained in quantitative yield. IR (KBr): 3419 (OH), 1629 (C=N) cm⁻¹. ¹H NMR (CDCl₃): δ 13.45 (s, 1H, OH), 8.34 (s, 1H, CH=N), 7.05 (s, 1H, *m*-H), 6.94 (s, 1H, *m*-H), 3.39-3.36 (m, 1H, cyclohexyl-CH), 3.17-3.09 (m, 6H, CH₂I), 2.26 (s, 3H, CH₃), 1.96-1.89 (m, 2H, cyclohexyl-CH₂), 1.89-1.43 (m, 14H, cyclohexyl-CH₂ and CH₂), 1.18-1.20 (br, 2H, CH₂) ppm. ¹³C{¹H} NMR (CDCl₃): δ 164.97, 157.2, 135.58, 131.25, 127.12, 125.50, 117.65, 72.89, 42.00, 38.71, 36.14, 34.18, 33.73, 27.91, 24.57, 24.50, 16.32, 8.26, 7.18 ppm. Anal. Calcd. (C₄₄H₆₄I₆N₂O₂): C, 37.36; H, 4.56; N, 1.98 %. Found: C, 37.29; H, 4.52; N, 1.88 %.

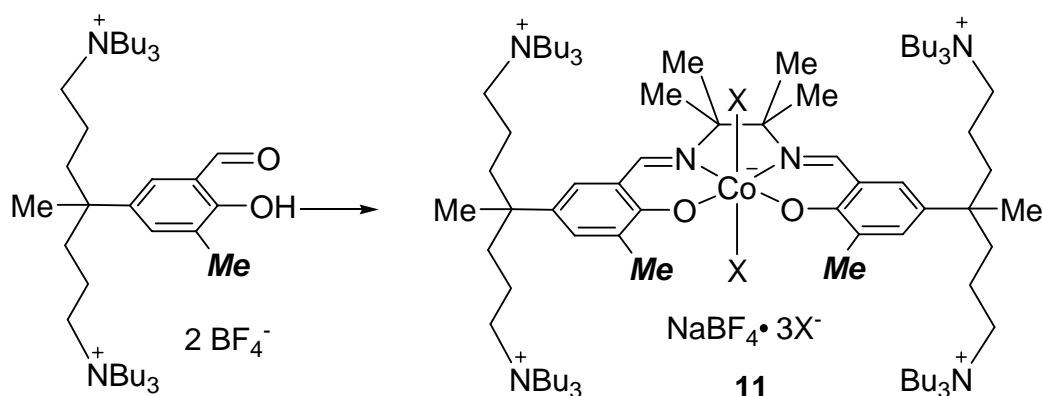
Compound 21. Compound **20** (0.364 g, 0.257 mmol) and tributylamine (0.291 g, 1.57 mmol) were weighed into a one-neck flask, followed by the addition of CH₃CN (5.0 mL). The solution was refluxed for 2 days under a N₂ atmosphere. After cooling to room temperature, the solvent was removed under vacuum to give a residue that was subsequently triturated three times in diethyl ether (2.5 mL) to give a

light yellow powder in 88% yield (0.579 g). IR (KBr): 3442 (OH), 1627 (C=N) cm^{-1} . ^1H NMR (CDCl_3): δ 13.46 (s, 1H, OH), 8.58 (s, 1H, CH=N), 7.18(s, 1H, *m*-H), 7.07 (s, 1H, *m*-H), 3.42 (br, 1H, cyclohexyl-CH), 3.32 (br, 8H, NCH₂), 3.16 (br, 16H, NCH₂), 2.10 (s, 3H, CH₃), 1.74-1.20 (br, 54H, cyclohexyl-CH₂, CH₂), 0.86 (br, 9H, CH₃), 0.75 (br, 18H, CH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 164.78, 157.27, 134.04, 130.82, 127.22, 125.15, 117.46, 71.01, 59.96, 59.63, 59.00, 58.86, 53.52, 43.03, 34.89, 33.90, 33.68, 24.16, 24.05, 23.07, 22.78, 20.69, 19.68, 19.53, 17.64, 15.79, 13.58 ppm. Anal. Calcd. ($\text{C}_{116}\text{H}_{226}\text{I}_6\text{N}_8\text{O}_2$): C, 55.14; H, 9.02; N, 4.44 %. Found: C, 54.44; H, 8.87; N, 4.34 %.

Compound 22. CH_2Cl_2 (12 mL) was added rapidly with stirring to a flask containing **21** (0.455 g, 0.180 mmol) and AgBF_4 (0.211 g, 1.08 mmol). Black precipitates observed upon the addition of methylene chloride prompted stirring to be ceased due to the formation of light yellow lump. The lump was broken down with a spatula to facilitate further stirring for a day in the dark. Newly formed AgI was filtered off over Celite inside a glove box, followed by immediate removal of solvent by vacuum to give a yellow residue. The residue was subsequently purified by column chromatography on a short pad of silica gel, eluting with ethanol and CH_2Cl_2 (v/v, 1:5). The yield was 0.322 g (78%). IR (KBr): 3422 (OH), 1628 (C=N) cm^{-1} . ^1H NMR (CDCl_3): δ 13.64 (s, 1H, OH), 8.52 (s, 1H, CH=N), 7.27 (s, 1H, *m*-H), 7.16 (s, 1H, *m*-H), 3.44 (br, 1H, cyclohexyl-CH), 3.30-3.10 (br, 24H, NCH₂), 2.24 (s, 3H, CH₃), 1.95-1.29 (br, 54H, cyclohexyl-CH₂, CH₂), 0.99 (br, 9H, CH₃), 0.90 (br, 18H, CH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 165.61, 157.84, 134.63, 131.42, 127.59, 125.75, 118.15, 72.10, 59.84, 58.97, 58.83, 50.12, 43.15, 34.32, 33.95, 33.84, 24.13, 23.65, 22.51, 20.65, 20.05, 19.90, 19.42, 16.73, 16.11, 13.98, 13.89 ppm. Anal. Calcd. ($\text{C}_{116}\text{H}_{226}\text{B}_6\text{F}_{24}\text{N}_8\text{O}_2$): C, 60.95; H, 9.97; N, 4.90 %. Found: C, 61.20; H, 10.22; N, 4.92 %.

Complex 9. Cobalt(II) acetate (5.30 mg, 0.030mmol) and **22** (68.2 mg, 0.030 mmol) were dissolved in ethanol (2.0 mL) inside a glove box. The solid was precipitated in approximately 5 minutes and the resulting slurry was stirred overnight at room temperature. The solvent was removed under vacuum to give a red solid subsequently triturated two times with diethyl ether (2.0 mL) to remove acetic acid that had been generated. The solid was evacuated by vacuum overnight and dissolved in CH_2Cl_2 (2.0 mL)

containing 2,4-dinitrophenol (5.40 mg, 0.030 mmol) followed by stirring under an O₂ atmosphere for 3 hours. Sodium-2,4-dinitrophenolate (61.4 mg, 0.300 mmol) was added and the solution was stirred overnight at room temperature. The solution was filtered over Celite, after which the solvent was removed by vacuum to give a dark brown powder pure enough for use in NMR characterization. Yields were quantitative (68.5 mg). ¹H NMR (dmsO-d₆, 40°C): δ 8.68 (br, 2H, (NO₂)₂C₆H₃O), 8.05 (br, 2H, (NO₂)₂C₆H₃O), 7.85 (br, 1H, CH=N), 7.30 (br, 2H, *m*-H), 6.76 (br, 2H, (NO₂)₂C₆H₃O), 3.58 (br, 1H, cyclohexyl-CH), 3.09 (br, 24H, NCH₂), 2.63 (s, 3H, CH₃), 1.53-1.06 (br, 54H, CH₂), 0.93-0.85 (m, 27H, CH₃) ppm. ¹³C{¹H} NMR (dmsO-d₆): δ 170.93, 160.72, 131.45 (br), 129.71 (br), 129.30 (br), 127.58 (br), 124.40 (br), 115.82 (br), 68.91, 57.58, 57.08, 41.04, 35.80, 32.41, 29.03, 23.92, 22.49, 20.50, 19.76, 18.62, 16.84, 15.71, 12.81, 12.78 ppm. ¹⁹F{¹H} NMR (dmsO-d₆, 20°C): δ -50.72, -50.77 ppm.



Complex 11. 2,3-Diamino-2,3-dimethylbutane (0.027 g, 0.232 mmol)⁵ and [3-methyl-5-[(Bu₃N⁺(CH₂)₃)₂CMe]-salicylaldehyde](BF₄⁻)₂ (0.367 g, 0.464 mmol) were refluxed overnight in ethanol (3.0 mL) with molecular sieves (0.180 g) under N₂ atmosphere. After filtration, the solvent was removed to obtain a yellow solid in quantitative yield (0.385 g). IR (KBr): 3432 (OH), 1620 (C=N) cm⁻¹. ¹H NMR (CD₂Cl₂): δ 14.19 (s, 1H, OH), 8.54 (s, 1H, CH=N), 7.24 (s, 1H, *m*-H), 7.18 (s, 1H, *m*-H), 3.05-3.02 (m, 16H, NCH₂), 2.24 (s, 3H, CH₃), 1.79-1.32 (m, 41H, CH₂), 0.91 (t, *J* = 7.6 Hz, 18H, CH₃) ppm. ¹³C{¹H} NMR (CD₂Cl₂): δ 163.04, 158.59, 134.68, 131.27, 127.94, 126.25, 118.32, 65.66, 59.61, 59.01, 40.54, 38.45, 24.82, 24.20, 23.39, 20.18, 17.59, 16.08, 13.85 ppm. Anal. Calc. (C₈₆H₁₆₄B₄F₁₆N₆O₂): C, 62.17; H, 9.95; N, 5.06 %. Found: C, 62.23; H, 10.16; N, 5.24 %. Cobalt(II) acetate (0.016 g, 0.090 mmol) and ligand prepared as above (0.150 g, 0.090 mmol) were dissolved in

ethanol (5.0 mL) inside a glove box and stirred for 5 hours at room temperature. The solvent was removed by vacuum to give a red solid subsequently triturated two times in diethyl ether (5.0 mL). The solid was evacuated overnight to remove acetic acid that had been generated. The solid was dissolved in CH₂Cl₂ (5.0 mL) containing 2,4-dinitrophenol (0.017 g, 0.090 mmol), and then the solution was stirred under an O₂ atmosphere for 12 hours. Sodium-2,4-dinitrophenolate (0.093 g, 0.451 mmol) was added, after which the solution was stirred overnight at room temperature and filtered over Celite. The solvent was removed by vacuum to give a dark brown powder pure enough for use in NMR characterization and polymerization. Yields were quantitative (0.214 g). ¹H NMR (dmso-d₆, 40°C): δ 8.62 (br, 1.5H, (NO₂)₂C₆H₃O), 7.87 (br, 1.5H, (NO₂)₂C₆H₃O), 7.72 (br, 1H, CH=N), 7.50 (br, 1H, *m*-H), 7.35 (br, 1H, *m*-H), 6.47 (br, 1.5H, (NO₂)₂C₆H₃O), 3.11 (br, 16H, NCH₂), 2.70 (s, 3H, CH₃), 1.66-1.22 (br, 41H, CH₂), 0.88 (br, 18H, CH₃) ppm. ¹³C{¹H} NMR (dmso-d₆): δ 164.67, 159.42, 132.30, 129.71, 128.86 (br), 128.46 (br), 127.42 (br), 124.05 (br), 118.84, 73.92, 57.74, 57.19, 25.94, 23.33, 22.61, 21.05, 18.73, 16.68, 16.43, 12.93 ppm.

Complex 13. The compound was prepared following the same method and conditions applied for the preparation of **12** and using the corresponding Salen-type ligand of which synthesis was reported.² ¹H NMR (dmso-d₆, 40°C): δ 7.68 (s, 1H, CH=N), 7.36 (s, 1H, *m*-H), 7.23 (s, 1H, *m*-H), 3.61 (br, 1H, NCH), 3.31-2.91 (br, 16H, NCH₂), 2.04 (br, 1H, cyclohexyl-CH₂), 1.89 (br, 1H, cyclohexyl-CH₂), 1.74 (s, 9H, C(CH₃)₃), 1.68-1.35 (br, 20H, CH₂), 1.32-1.18 (br, 15H, CH₂), 0.91 (t, *J* = 7.2 Hz, 18H, CH₃) ppm. ¹³C{¹H} NMR (dmso-d₆): δ 161.66, 160.42, 140.90, 129.71, 128.38, 127.31, 117.38, 67.40, 55.85, 33.89, 31.11, 28.70, 27.70 (br), 22.58, 21.29, 19.47, 17.45, 15.21, 11.69 ppm.

Complex 14. Complex **10** (0.100 g, 0.0460 mmol) was dissolved in propylene oxide (5.0 mL) inside a glove box, follow by stirring for 1 h. Propylene oxide was removed by vacuum vacuum to give a red powder used for NMR characterization and polymerization. ¹H NMR (dmso-d₆): δ 8.57 (s, 1H, (NO₂)₂C₆H₃O), 8.45, 8.43 (d, ⁴*J* = 2.8 Hz, 1H, *m*-H spiro-Meisenheimer anion), 7.75 (dd, *J* = 9.6 Hz, 2.8 Hz, 1H, (NO₂)₂C₆H₃O), 7.39-6.98 (m, 3H, *m*-H, CH=N), 6.84, 6.81 (dd, *J* = 9.6 Hz, 2.8 Hz, 1H, *m*-H spiro-Meisenheimer anion), 6.28 (d, *J* = 9.6 Hz, (NO₂)₂C₆H₃O), 5.36, 5.30 (d, *J* = 9.6 Hz, 1H, *o*-H spiro-

Meisenheimer anion), 4.46-4.29 (m, 1H, spiro-Meisenheimer anion), 4.21-3.99 (m, 1H, spiro-Meisenheimer anion), 3.65-3.48 (m, 1H, spiro-Meisenheimer anion), 3.20 (br, 1H, NCH), 3.07 (br, 16H, NCH₂), 2.47 (m, 3H, CH₃), 1.98 (br, 1H, cyclohexyl-CH₂), 1.62-1.39 (br, 20H), 1.39-1.15 (br, 18H), 0.91 (br, 18H, CH₃) ppm.

Preparation of 60mol% sodium 2,4-dinitrophenolate. Commercially available 2,4-dinitrophenol is wetted one which was dried through dissolving in CH₂Cl₂ and then treatment of anhydrous MgSO₄. After removing MgSO₄ by filtration, methylene chloride was removed by vacuum to give anhydrous 2,4-dinitrophenol, which was stored in a glove box. Anhydrous 2,4-dinitrophenol (10.0 g, 54.3 mmol) was dissolved in THF (300 mL), followed by step-wise addition of NaH (0.782 g, 32.6 mmol). After stirring for three hours, THF was removed by vacuum to give an orange-colored solid. The color of the solid was slowly changed from orange to yellow during storage. The yellow-colored solid was used in the anion exchange reaction. ¹H NMR (dmso-d₆, 20°C): δ 12.42 (br, 0.4H, OH), 8.64 (d, ⁴J = 2.8 Hz, 1H, *m*-H), 8.05 (dd, J = 9.2 Hz, 2.8 Hz, 1H, *m*-H), 6.79 (d, J = 9.2 Hz, 1H, *o*-H) ppm.

Complex 15. Cobalt(II) acetate (0.107 g, 0.602 mmol) and the corresponding ligand (1.00 g, 0.602 mmol) were dissolved in ethanol (20 mL) inside a glove box. The solid was precipitated in approximately 5 minutes and the resulting slurry was stirred for 3 hours at room temperature. The solvent was removed by vacuum to give a red solid subsequently triturated two times with diethyl ether (10 mL) to remove newly generated acetic acid. The solid was evacuated by vacuum overnight, after which it was dissolved in CH₂Cl₂ (20 mL) containing 2,4-dinitrophenol (0.111 g, 0.602 mmol). The resulting solution was stirred under an O₂ atmosphere for 3 hours. 60mol% sodium-2,4-dinitrophenolate (0.594 g, 3.01 mmol) was added and the solution was stirred overnight at room temperature, followed by filtration over Celite. The solvent was removed by vacuum to give a dark brown powder pure enough for use in NMR characterization and polymerization. Yields were quantitative (1.45 g). ¹H NMR (dmso-d₆, 40°C): δ 8.61 (br, 3H, (NO₂)₂C₆H₃O), 8.02 (br, 3H, (NO₂)₂C₆H₃O), 7.91 (br, 1H, CH=N), 7.41-7.19 (br, 2H, *m*-H), 6.71 (br, 3H, (NO₂)₂C₆H₃O), 3.61 (br, 1H, NCH), 3.29-2.84 (br, 16H, CH₂), 2.62 (s, 3H, CH₃), 2.08 (br, 1H, cyclohexyl-CH₂), 1.82 (br, 1H, cyclohexyl-CH₂), 1.65-1.40 (br, 20H), 1.40-1.06 (br,

15H), 0.85 (br, 18H, CH₃) ppm. ¹³C{¹H} NMR (dmso-d₆): δ 165.64 (br), 163.62, 160.82, 135.86 (br), 132.25, 131.66, 130.80, 130.07, 129.68, 127.91, 123.67, 117.05 (br), 69.23 (br), 57.81, 57.29, 38.28, 29.35 (br), 24.15 (br), 23.47, 22.84, 19.02, 17.31, 16.61, 13.29 ppm.

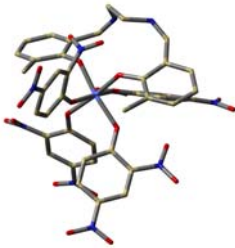
DFT Calculations. Computational calculations were performed using the Gaussian 03 program package.⁶ In the computational model, butyl groups located in the peripheral ammonium moieties were replaced with methyl groups. The geometry optimizations were performed at the DFT level of theory using the B3LYP hybrid functional without any symmetry restriction.⁷ The cobalt atom was described using the LANL2DZ basis set, which includes the relativistic effective core potential (ECP) of Hay and Wadt⁸ for the inner electrons and a double- ζ basis set for the outer electrons. The standard 6-31G(d) basis set was used for the remaining atoms. Table S1 shows the results of the calculation. Table S2 shows the atomic coordinates for model compounds **7-A** and **7-B**.

Table S1. Selected bond distances and relative energies of **7-A** and **7-B**

	Bond distances (Å)								<i>E</i> ^a (kcal/mol)
	Co-O1	Co-O2	Co-O3	Co-O4	Co-O5	Co-O6	Co-N1	Co-N2	
7-A	1.9606	1.9056	1.9388	1.9890	2.0362	2.0321			0
7-B	1.8863	1.8987	1.9376	1.9558			1.9329	1.9191	34 ^b

^aRelative energy $\Delta E = E_{7-B} + 2 \times E_{DNP} + 2 \times E_{Coul.} - E_{7-A}$. E_{7-A} , E_{7-B} , and E_{DNP} are SCF energies separately obtained from DFT calculations in gas phase. $E_{Coul.}$ is Coulombic interaction between DNP anion and peripheral $-NBu_3^+$ cationic moiety calculated by the equation $E_{Coul.} = \frac{q_1 q_2}{4\pi\epsilon_0 R}$, where $R = R_1 + R_2$. R_1 and R_2 denote radii of DNP⁻ and $-NBu_3^+$ ions for the former and the latter, respectively. These values were estimated from calculated volumes assuming both entities are spheres.

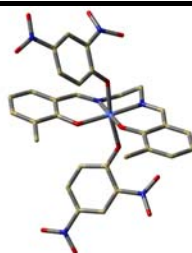
Table S2. Atomic coordinates for model compounds **7-A** and **7-B**.

7-A				
	Atomic	Coordinates (Å)	Atomic	Coordinates (Å)

Number	X	Y	Z	Numb	X	Y	Z
6	4.4477890	0.7102650	-2.1489540	6	0.8514000	0.1000190	5.0466230
6	3.0919500	1.0813490	-2.0789580	6	2.0613350	-0.4802780	5.4941910
6	2.5558700	1.4914510	-0.8030710	6	2.7013910	-0.9308600	3.2209830
6	3.5010200	1.7337060	0.2534470	6	2.9726630	-0.9874210	4.5953180
6	4.8328340	1.3621780	0.1084800	7	3.6718270	-1.5424670	2.3695490
6	5.3277080	0.7996670	-1.0739140	8	3.4044800	-1.7163110	1.1690090
6	2.4239590	0.9701820	-3.4177380	8	4.7609180	-1.9217860	2.8572140
7	1.4199000	1.4755560	-4.0153250	7	2.3453100	-0.5645630	6.9162650
6	0.4410710	2.3479370	-3.3942950	8	3.4089140	-1.0853130	7.2695940
6	-0.9509880	2.0816870	-3.9927570	8	1.5034800	-0.1098330	7.6964250
7	-1.2457810	0.6561430	-4.0094030	6	-3.2032040	2.9400730	0.8864290
6	-2.1079140	0.1242070	-3.2417050	6	3.0911920	2.4648280	1.5028240
6	-3.0280750	0.7085220	-2.2205620	1	-0.3260750	0.6401230	3.3444020
6	-4.3928230	0.4669970	-2.4215090	1	0.1487100	0.4748850	5.7817880
6	-5.3656260	0.9419930	-1.5420920	1	3.8875530	-1.4440720	4.9446240
6	-4.9356430	1.7260360	-0.4591220	8	-0.4309420	-0.8520170	-0.7503320
6	-3.5939680	2.0071140	-0.2245690	6	0.2549780	-1.7814760	-1.2668120
6	-2.5919780	1.4345180	-1.0734390	6	1.6910810	-1.7297870	-1.3326630
6	6.7839210	0.3857130	-1.1975710	6	2.4441210	-2.6964430	-1.9284950
6	-6.8346440	0.6010810	-1.7373770	6	1.8260720	-3.8460250	-2.4804290
6	-7.2671700	-0.5679360	-0.8114720	6	-0.3340930	-2.9952440	-1.8293830
6	-6.5701690	-1.8907040	-1.1848640	6	0.4453550	-3.9843870	-2.4282540
6	-6.8157420	-2.9483460	-0.1100700	7	-1.7491060	-3.2708040	-1.7467330
7	-6.3282100	-4.3624720	-0.4516990	8	-2.5056610	-2.4305530	-1.2481900
6	-7.7147680	1.8567210	-1.5243390	8	-2.1655650	-4.3681230	-2.1715620
6	-9.1360360	1.7729210	-2.1186130	7	2.6258830	-4.8971790	-3.0300060
6	-9.8241160	3.1141850	-1.8818750	8	2.0838880	-5.8379310	-3.6142660
7	-11.2373810	3.2909490	-2.4671660	8	3.8738400	-4.8319710	-2.8735570
6	6.9442650	-1.1150650	-1.5450300	1	2.1621770	-0.8774490	-0.8760980
6	6.4031670	-2.0386910	-0.4344600	1	3.5183060	-2.5843180	-1.9917260
6	6.4611010	-3.4947010	-0.8978080	1	-0.0320550	-4.8692510	-2.8254000
7	6.0026500	-4.5557380	0.1126730	8	-1.7194480	0.0199300	1.4133420
6	7.4897870	1.3110380	-2.2224420	6	-2.0134090	-1.1604120	1.7791780
6	9.0330240	1.3125840	-2.1665420	6	-1.0820060	-2.2669490	1.7805380
6	9.5411410	2.4017850	-3.1071560	6	-1.4282980	-3.5400530	2.1488200
7	11.0608560	2.6530920	-3.1322780	6	-2.7560870	-3.8309260	2.5368870
8	1.2715770	1.6996600	-0.6259880	6	-3.3481010	-1.5173530	2.2375990
8	-1.3118160	1.6640280	-0.8681990	6	-3.7002240	-2.8123490	2.5881570
27	-0.1523260	0.7769620	0.3564710	7	-4.4043980	-0.5325510	2.3642780
8	1.2481420	-0.2118840	1.4475350	8	-4.1238820	0.6105610	2.6968230
6	1.4906160	-0.3098660	2.6966410	8	-5.5791050	-0.9167330	2.1573050
6	0.5833290	0.1803580	3.7054890	7	-3.1391560	-5.1684160	2.8796680
8	-4.3482580	-5.4049680	3.0944440	1	9.0988070	3.3672700	-2.8453730
8	-2.2666210	-6.0409780	2.9302100	1	-2.6421380	2.4125630	1.6583790
1	-0.0721640	-2.0477530	1.4682160	1	-2.5564400	3.7322580	0.4972920
1	-0.6990580	-4.3419030	2.1405640	1	-4.0913770	3.3898030	1.3443530
1	-4.7021680	-3.0155020	2.9403360	1	2.8856360	3.5139030	1.2612880
8	-0.2592390	2.2165370	1.6507810	1	2.1862980	2.0603280	1.9493920
6	-0.0297870	3.4542040	1.9345700	1	3.8934080	2.4419430	2.2491240
6	-0.1630260	3.8152700	3.3208710	6	-11.7195760	4.6743010	-2.1093630
6	0.1316200	5.0623460	3.8204510	6	-12.1875260	2.2782810	-1.8864110
6	0.5956520	6.0591720	2.9477710	6	-7.1354700	-4.9471260	-1.5721960
6	0.3813930	4.5392340	1.0880060	6	-4.8686130	-4.3494300	-0.8457280
6	0.7245480	5.7873050	1.5900530	6	6.3615670	-5.9015640	-0.4559290
7	0.4498710	4.4732340	-0.3798920	6	4.5033010	-4.5157500	0.3022610
8	-0.6036600	4.3154770	-0.9863860	6	6.6668780	-4.3627830	1.4482050
8	1.5411550	4.7007730	-0.9076820	6	11.8015000	1.4115660	-3.5505180
7	0.9367830	7.3696860	3.4495920	6	11.5499590	3.1002100	-1.7793980
8	1.3552550	8.2152620	2.6475380	6	11.3350570	3.7469240	-4.1334100
8	0.7946820	7.5824100	4.6604290	1	-11.7425050	4.7715080	-1.0229030
1	-0.4989710	3.0275600	3.9858790	1	-12.7206560	4.8200390	-2.5189910
1	0.0247760	5.2865300	4.8751170	1	-11.0323870	5.4084010	-2.5326570
1	1.0761550	6.5618670	0.9201680	1	-12.1745340	2.3659220	-0.7987530
1	4.8093970	0.3431920	-3.1097200	1	-11.8736880	1.2785800	-2.1833440

1	5.5085240	1.5175620	0.9499350	1	-13.1909750	2.4807430	-2.2648960
1	3.0399800	0.3405050	-4.0777100	1	-8.1846280	-4.9873680	-1.2721430
1	0.7160850	3.3886810	-3.6188420	1	-6.7693560	-5.9544910	-1.7769880
1	0.3946990	2.2428060	-2.3146100	1	-7.0209580	-4.3309410	-2.4627620
1	-0.9591380	2.4027110	-5.0437990	1	-4.7417760	-3.8209270	-1.7855240
1	-1.6828640	2.6839350	-3.4351410	1	-4.5292810	-5.3797500	-0.9541740
1	-2.2658130	-0.9508940	-3.3922630	1	-4.2959550	-3.8389280	-0.0736920
1	-4.6931930	-0.1117500	-3.2960900	1	7.4461750	-5.9704100	-0.5612950
1	-5.6622120	2.1372250	0.2393960	1	5.8714310	-6.0076420	-1.4258710
1	7.2613810	0.5566630	-0.2202880	1	6.0051790	-6.6753990	0.2261340
1	-6.9690100	0.2757300	-2.7816310	1	4.0441860	-4.7253160	-0.6630200
1	-7.0112260	-0.3048580	-0.2218720	1	4.2095870	-3.5305130	0.6657070
1	-8.3588790	-0.7167160	-0.8532190	1	4.2412020	-5.2848550	1.0320600
1	-6.9374130	-2.2198110	-2.1666170	1	6.2468290	-3.4752280	1.9256980
1	-5.4968790	-1.7028360	-1.2817850	1	7.7445560	-4.2643810	1.2998450
1	-6.3009120	-2.6548220	0.8087570	1	6.4573020	-5.2408060	2.0621260
1	-7.8831770	-3.0617680	0.1093330	1	11.4202110	1.0824250	-4.5186860
1	-7.7875540	2.0760150	-0.4515400	1	11.6474000	0.6326310	-2.8049960
1	-7.1958100	2.7086160	-1.9796740	1	12.8645260	1.6461280	-3.6285700
1	-9.0597700	1.5532750	-3.1903740	1	10.9902580	3.9869300	-1.4775690
1	-9.6960660	0.9566790	-1.6484410	1	12.6130320	3.3360230	-1.8516870
1	-9.9306840	3.3086680	-0.8108210	1	11.3959550	2.2996260	-1.0577150
1	-9.2338420	3.9266800	-2.3152070	1	10.7974910	4.6463610	-3.8298270
1	6.4136420	-1.3161690	-2.4852300	1	10.9896080	3.4223580	-5.1160860
1	8.0040680	-1.3567710	-1.7271880	1	12.4080810	3.9444100	-4.1605560
1	7.0091190	-1.8961280	0.4679000	6	-6.4993200	-5.2309470	0.7685860
1	5.3821620	-1.7458920	-0.1746020	1	-6.2593830	-6.2608010	0.4979210
1	5.8344190	-3.6557110	-1.7794620	1	-7.5366940	-5.1652740	1.1031250
1	7.4901880	-3.7739820	-1.1502130	1	-5.8182460	-4.9056350	1.5571790
1	7.1584290	1.0562210	-3.2376940	6	-11.2144850	3.1586860	-3.9675100
1	7.1350970	2.3307620	-2.0310590	1	-10.5013430	3.8779420	-4.3735730
1	9.3455650	1.5099230	-1.1338260	1	-12.2143840	3.3663190	-4.3524640
1	9.4278470	0.3313000	-2.4531890	1	-10.9155010	2.1467270	-4.2364750
1	9.2697090	2.1761700	-4.1425870				

7-B



Atomic Number	Coordinates (Å)			Atomic Number	Coordinates (Å)		
	X	Y	Z		X	Y	Z
6	-0.9230840	-2.7683720	0.5578710	7	7.3837360	4.2850840	0.9356300
6	-1.0807830	-2.6611040	-0.8658950	6	-7.0454390	1.7891170	-0.5318230
6	-2.0438980	-3.3702640	-1.5396190	6	-8.5141710	2.1819700	-0.2552050
6	-2.8603690	-4.2871530	-0.8386140	6	-8.7354250	3.6122140	-0.7542440
6	-1.6917600	-3.8093910	1.1977030	1	-8.0565910	4.3018770	-0.2446310
6	-2.6507800	-4.5341100	0.5187130	6	-7.2513220	-0.7709800	-0.7636830
7	-1.5694900	-4.0602960	2.6324270	6	-7.1782830	-2.1173420	-0.0121060
8	-2.5762000	-4.4689130	3.2216300	6	-7.4472750	-3.2869640	-0.9699800
8	-0.4816360	-3.8658090	3.1719260	7	-7.9192930	-4.5962520	-0.3216480
7	-3.9848150	-4.8840140	-1.4777410	8	-0.9192320	0.2619210	-0.3141560
8	-4.6168890	-5.7771120	-0.8673260	8	1.5599580	-0.5858150	-0.3642520

8	-4.3452180	-4.4624220	-2.5873300	27	0.3628640	-0.1458470	1.0255570
1	-0.4477240	-1.9447920	-1.3734590	6	2.8939210	-0.5595870	-2.7688660
1	-2.1969540	-3.2359890	-2.6043210	6	-2.3018380	0.4979270	-2.6868410
1	-3.2542880	-5.2549990	1.0529230	8	1.1707040	1.6349400	1.0592920
6	-4.3068710	0.2836990	1.1345500	6	0.8524660	2.7397720	0.4911660
6	-2.8883190	0.2708630	1.0937870	6	-0.5017740	3.1687260	0.2920140
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6	-3.0042650	0.3889460	-1.3602890	6	0.1986250	5.1728230	-0.8459800
6	-4.3801840	0.3900970	-1.2566750	6	1.8585430	3.6661130	0.0119990
6	-5.0715800	0.3261320	-0.0180890	6	1.5259030	4.8436380	-0.6684910
6	-2.1597670	0.3056530	2.3369720	7	3.2597990	3.4364530	0.2272410
7	-0.8749280	0.2664640	2.4517110	8	4.0761130	4.0481810	-0.5001180
6	-0.1892290	0.3492550	3.7418040	8	3.6316380	2.6828010	1.1348020
6	0.9420180	-0.6863350	3.7198810	7	-0.1484110	6.4091760	-1.5344260
7	1.6086930	-0.5641870	2.4241290	8	0.7706240	7.1285990	-1.9273850
6	2.8705440	-0.7552230	2.2590380	8	-1.3482330	6.6570030	-1.6827240
6	3.5583020	-0.7336740	0.9972250	1	-1.2852970	2.5346090	0.6797070
6	4.9707380	-0.8088440	1.0061560	1	-1.8536820	4.6473690	-0.4757660
6	5.7154880	-0.7660510	-0.1591990	1	2.3031460	5.4986230	-1.0366560
6	5.0032820	-0.6825840	-1.3826570	1	-4.7930860	0.2696170	2.1096550
6	3.6243470	-0.6364390	-1.4549550	1	-4.9512250	0.4551560	-2.1818260
6	2.8510560	-0.6441290	-0.2439640	1	-2.7538210	0.3957800	3.2528020
6	-6.5956050	0.4028930	0.0113520	1	-0.8784930	0.1713720	4.5757500
6	7.2383770	-0.7462480	-0.1408380	1	0.2328440	1.3568500	3.8373070
6	7.8237470	-1.8664020	-1.0406700	1	0.5213360	-1.6948020	3.7935640
6	9.3100840	-2.2004480	-0.7833450	1	1.6441610	-0.5250030	4.5466040
6	9.7187070	-3.3694540	-1.6821510	1	3.4770260	-0.9550000	3.1486630
1	9.0772810	-4.2355870	-1.4956640	1	5.4750060	-0.8874810	1.9690880
6	7.7578600	0.6643730	-0.5355690	1	5.5567850	-0.6481220	-2.3203120
6	7.4737950	1.7218430	0.5555780	1	-6.9154200	0.3422920	1.0625610
6	7.3379340	3.1165030	-0.0597650	1	7.5622890	-0.9512250	0.8907650
<hr/>							
85	7.2276550	-2.7719460	-0.8748530	6	-7.0760100	-4.9656010	0.8746450
86	7.6906680	-1.5988870	-2.0973960	6	-9.3567580	-4.4779790	0.1034170
87	9.9343450	-1.3226360	-0.9841550	1	12.3514730	-5.4185790	-2.4276090
88	9.4358590	-2.4610400	0.2742510	1	10.6155460	-5.8174260	-2.2846470
89	9.6173510	-3.0970040	-2.7366790	1	11.1671200	-4.6575260	-3.5283290
90	11.1553950	-3.8950390	-1.5369320	1	13.1614030	-3.2519560	-1.8196370
91	8.8368570	0.6486590	-0.7431650	1	11.9599730	-2.4323060	-2.8565730
92	7.2665760	0.9534980	-1.4736920	1	12.0794720	-2.0194520	-1.1199790
93	6.5341080	1.4709120	1.0567580	1	12.4010710	-4.8553510	-0.1074340
94	8.2732880	1.6817700	1.3061940	1	11.3351780	-3.5967260	0.5688570
95	8.1333580	3.3248320	-0.7822360	1	10.6547160	-5.1782600	0.0860740
96	6.3692550	3.2020980	-0.5581620	1	7.0141640	6.3805330	0.8854900
97	-6.3923100	2.5438560	-0.0773440	1	7.5205800	5.6713680	-0.6745630
98	-6.8565010	1.8332810	-1.6127340	1	5.8618740	5.3777970	-0.0598760
99	-9.1949980	1.4874680	-0.7594940	1	6.3920310	4.9497080	2.6887830
100	-8.7069170	2.1123220	0.8219410	1	5.4959770	3.7119630	1.7368160
101	-8.5365800	3.6780500	-1.8278950	1	6.9056170	3.2431880	2.7306930
102	-10.1359620	4.2148100	-0.5665720	1	8.7768630	5.3349010	2.1453760
103	-8.3076810	-0.5535690	-0.9752200	1	9.1561940	3.6099570	1.9049730
104	-6.7580440	-0.8642770	-1.7393610	1	9.4198890	4.7768500	0.5755720
105	-6.1870830	-2.2301930	0.4397140	1	-11.1026750	6.0652110	-1.0000020
106	-7.9054260	-2.0954170	0.8096950	1	-9.3722010	6.2061910	-0.5774520
107	-8.2327210	-3.0343030	-1.6889390	1	-9.8527330	5.5790250	-2.1810300
108	-6.5454190	-3.5363690	-1.5360680	1	-12.1380160	3.9180540	-1.2156850
109	2.2475870	-1.4340660	-2.9118110	1	-10.8890760	3.3657340	-2.3667030
110	2.2362790	0.3164310	-2.8013160	1	-11.2346000	2.4158310	-0.8903930
111	3.5925050	-0.5068660	-3.6098460	1	-11.4676750	4.7891160	0.9875570
112	-1.6672630	-0.3749590	-2.8746660	1	-10.5872360	3.2696570	1.2939820
113	-3.0185280	0.5893000	-3.5087910	1	-9.7378670	4.8379710	1.4295350
114	-1.6355300	1.3680260	-2.7042040	1	-8.2177810	-6.6120750	-0.9384410
115	11.3353720	-5.0313140	-2.5172480	1	-8.3696920	-5.3988050	-2.2425770
116	12.1607480	-2.8183780	-1.8557480	1	-6.7447760	-5.8310090	-1.5970180
117	11.4023750	-4.4174250	-0.1439670	1	-7.4334100	-5.9229050	1.2578090
118	6.9064680	5.5254060	0.2158890	1	-6.0397450	-5.0666800	0.5521310

119	6.4717290	4.0274530	2.1105490	1	-7.1833840	-4.1984330	1.6406080
120	8.7858940	4.5155310	1.4246160	1	-9.6646720	-5.4173270	0.5649920
121	-10.1138880	5.6205460	-1.1225680	1	-9.4584700	-3.6666830	0.8245790
122	-11.1736110	3.4172620	-1.3143820	1	-9.9719780	-4.2811670	-0.7761170
123	-10.5073260	4.2796570	0.8937960	8	-0.1944960	-1.9866000	1.2603620
124	-7.8017600	-5.6947620	-1.3587650				

Cyclic voltammetry (CV) measurement. Except for the experiments using a Pt microdisk electrode (dia. 100 μm), all the electrochemical measurements were performed using a BAS 100B electrochemical analyzer at room temperature in an Ar atmosphere glove box. CVs performed in DMSO and CH_2Cl_2 solution contained 0.5 mM cobalt complex and 0.1 M tetrabutylammonium tetrafluoroborate (TBABF_4), respectively, with scan rates of 0.1 V/s for Pt disk or 5 mV/s for Pt microdisk, also respectively. A Pt disk (dia. 1.6 mm or 100 μm) and Pt wire were used as working and counter electrodes. The reference electrode used was $\text{Ag}|\text{AgNO}_3$ (0.1 M), and all potential values were calibrated vs. the ferrocene/ferrocenium ($\text{Fc}|\text{Fc}^+$) redox couple. The potential values shown in this text were calibrated again to the saturated calomel electrode (SCE) using $\text{Fc}|\text{Fc}^+$ redox potential, unless otherwise specified.

CO_2 /(propylene oxide) copolymerization (small scale). The bomb reactor (50 mL) containing the catalyst [4.5 mg for $[\text{PO}]/[\text{Cat}] = 100000$ and **15** (entry 10 in Table 1)] was assembled inside a glove box. After bringing out the bomb reactor from the box, propylene oxide (10 g, 170 mmol) was transferred through the schlenk line into the bomb reactor. The CO_2 gas was pressurized to 15 bar, then it was immersed in an 80°C oil bath. The pressure increased according to the increase of the solution temperature, reaching ~23 bar around ~50 minutes. After reaching its maximum, the pressure remained steady for a time. However, as polymerization started, a pressure drop was observed. Polymerization was performed for 1 hour after initiation, during which 3-4 bar pressure drop was observed. The reactor was cooled to room temperature by immersion in an ice bath. After the release of CO_2 gas, the reactor was opened and an aliquot was taken and dissolved in CDCl_3 . ^1H NMR analysis of the solution allowed the selectivity and carbonate linkage to be calculated. The viscous solution was diluted with 20 mL of methylene chloride and the viscous solution was filtered over a short pad of silica gel to give a colorless

solution. Volatiles were removed using a rotary evaporator to give a white residue. The polymer lump removed from the flask and then broken manually into pieces. After being placed in a hood overnight to evaporate any residual PO, the polymer pieces were completely dried in an oven at approximately 150°C for 30 minutes. The yield was 2.70 g for entry 9 in Table 1, which correspond to PO conversion of 15%. PO conversion of ~15% is almost maximum attainable in this copolymerization. Due to the high molecular weight of the formed polymer, polymerization solution of ~15% conversion is very viscous and stirring with magnetic bar is ceased at this point.⁹

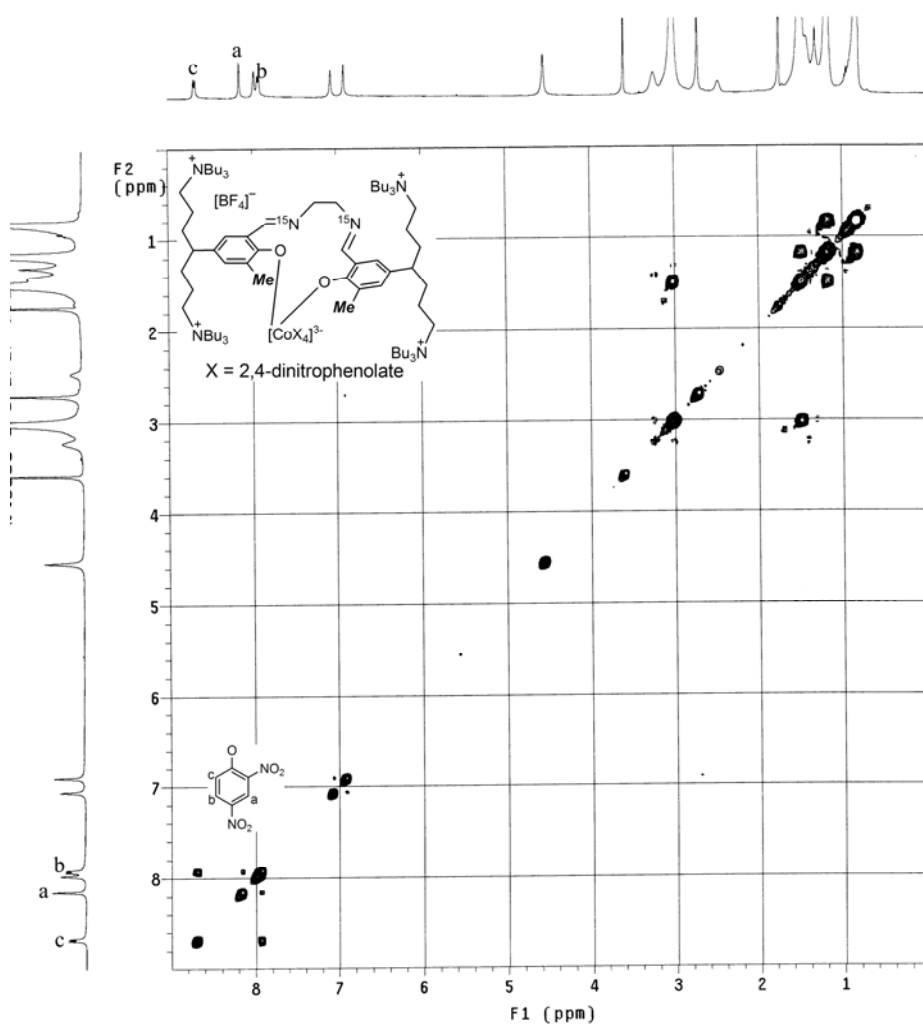
The temperature inside the bomb reactor was measured using a thermocouple. It took ~50 minutes for the solution temperature to reach ~70°C. Therefore, 50 minutes was subtracted from the measured induction time since polymerization did not start under 70°C.

CO₂/(propylene oxide) copolymerization (70 g scale). A bomb reactor (500 mL scale) equipped with a mechanical stirrer was evacuated at 150°C for 12 hours. After the reactor was cooled to room temperature, PO (220 g) was charged using a cannula. A solution of **15** (0.090 g, 0.035 mmol) in PO (~10 g, making total PO = 230 g) was added using a syringe. CO₂ gas was charged to 15 bar, and the solution was heated to 75°C. After heating the solution to ~70°C for 1 hour, a pressure drop was observed. The initial stirring rate was ~420 rpm, but when the stirring power was not changed during polymerization, it decreased gradually. We terminated the polymerization when the stirring rate had dropped to ~270 rpm (1 h); running the polymerization beyond that point slightly increased TON, but it detrimentally sacrificed the selectivity and TOF. When the stirring rate reached ~270 rpm, the reactor was immersed in an ice bath to cool it to below 35 °C. After the CO₂ pressure was released, the reactor was opened. A very thick viscous polymerization solution was obtained (See a picture below). An aliquot was taken for NMR analysis. The thick viscous solution was diluted with PO (200 g). The light yellow solution was filtered through a short pad of silica gel (12 g) previously wetted with PO (40 mL). PO was removed from the colorless filtrate by vacuum-transfer to a reservoir containing CaH₂. After several days of drying over CaH₂, the recovered PO was used for polymerization. The polymer strongly adhered to glass surfaces, making detachment difficult. However, it was easily detachable by wetting

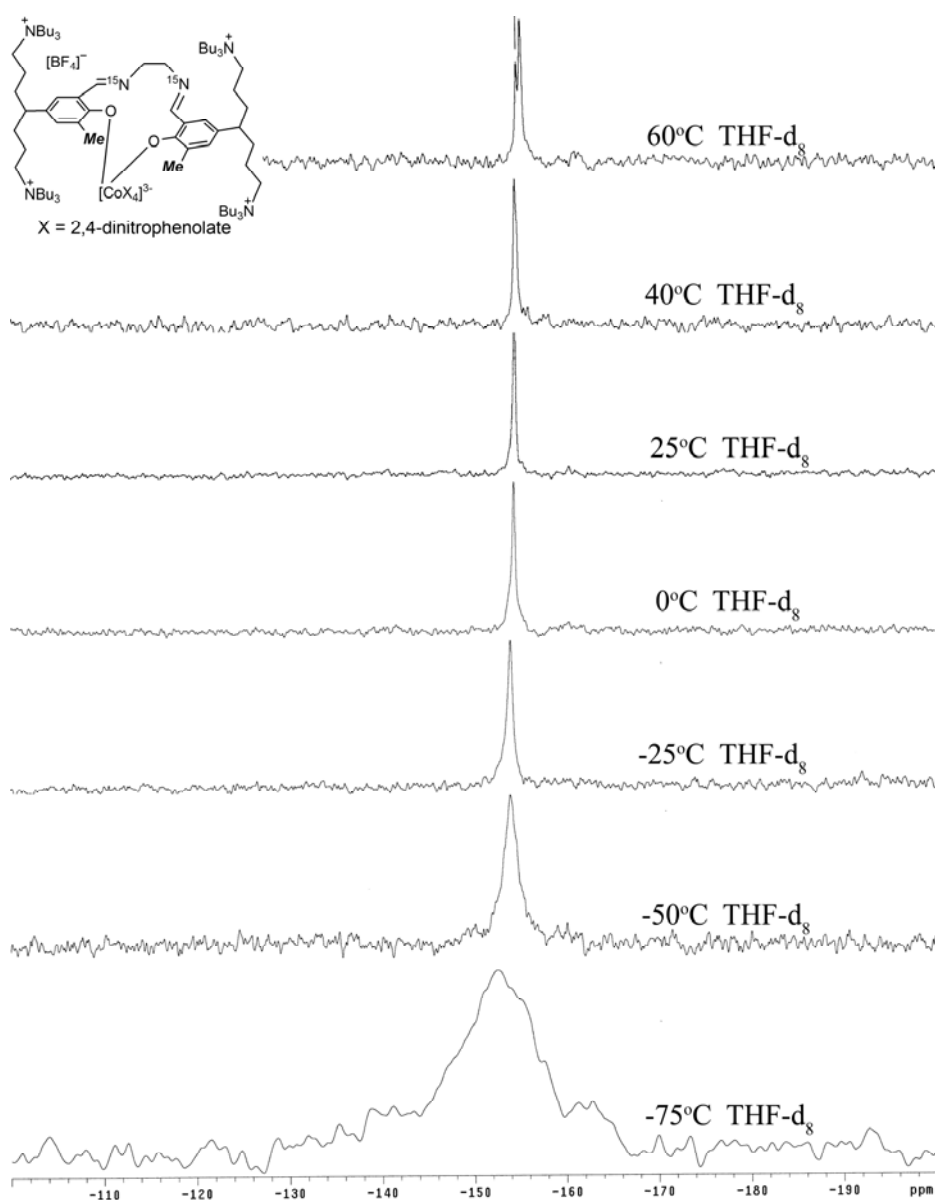
with diethyl ether, in which the copolymer is insoluble. The polymer lump was removed from the flask and then broken manually into pieces. The polymer pieces were placed in a hood overnight to evaporate residual PO and then they were completely dried in an oven ($\sim 150^{\circ}\text{C}$) for 30 minutes. 70 g of polymer was isolated for entry 10 in Table 1.



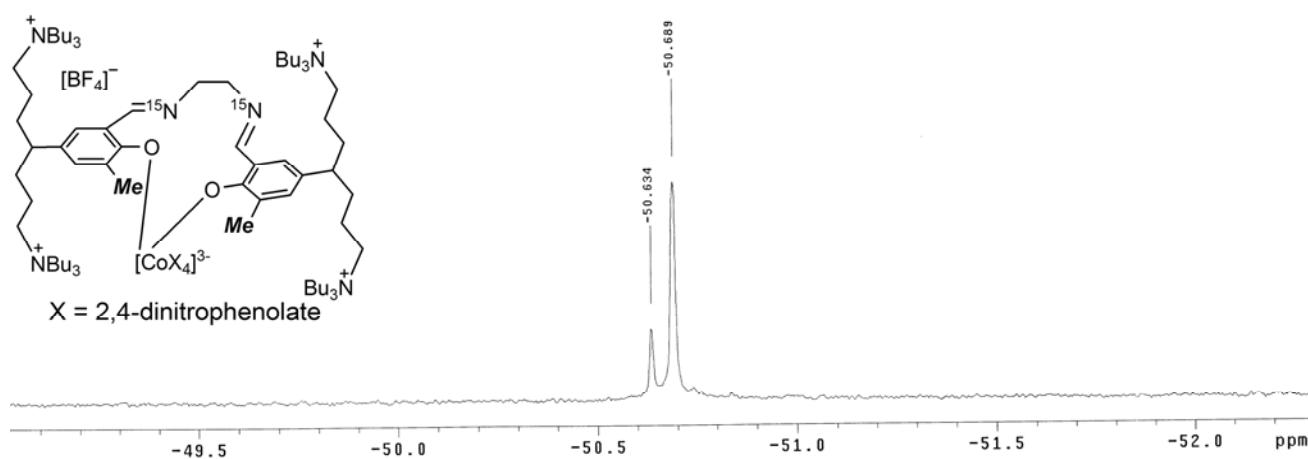
<The ^1H - ^1H COSY NMR spectrum of **7** in THF-d_6 at 0°C >



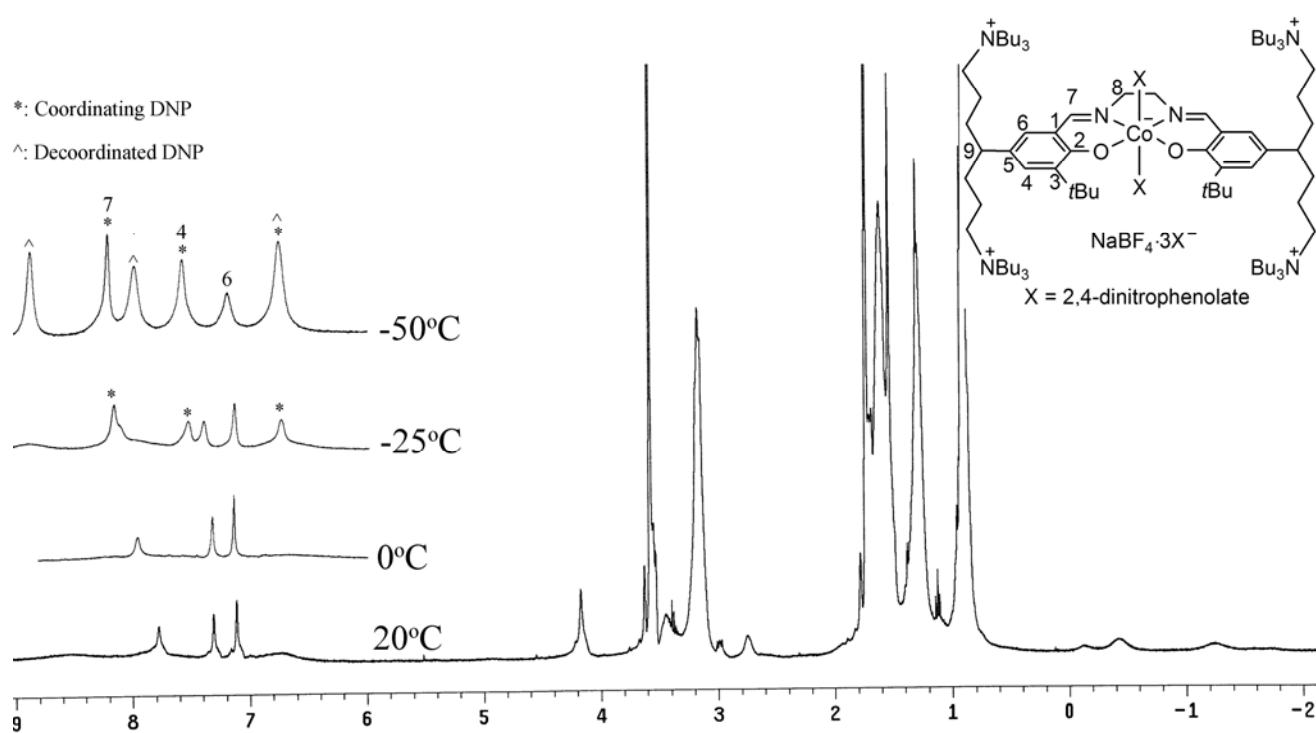
<The variable temperature ^{15}N NMR spectra of **7** in THF- d_6 >



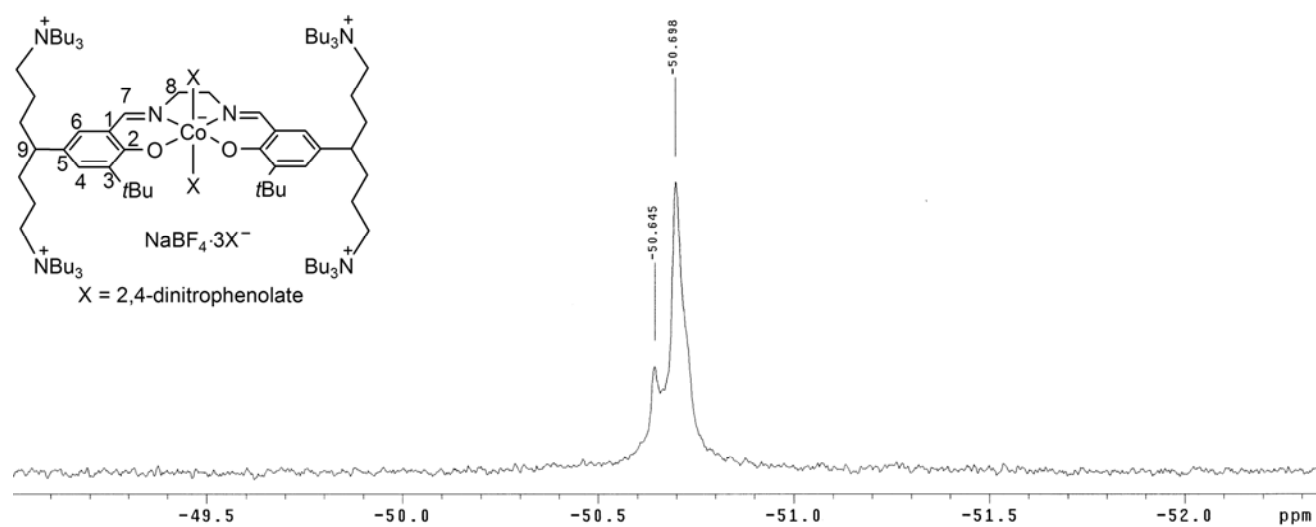
<The ^{19}F NMR spectrum of **7** in $\text{dms}\text{-d}_6$ at room temperature>



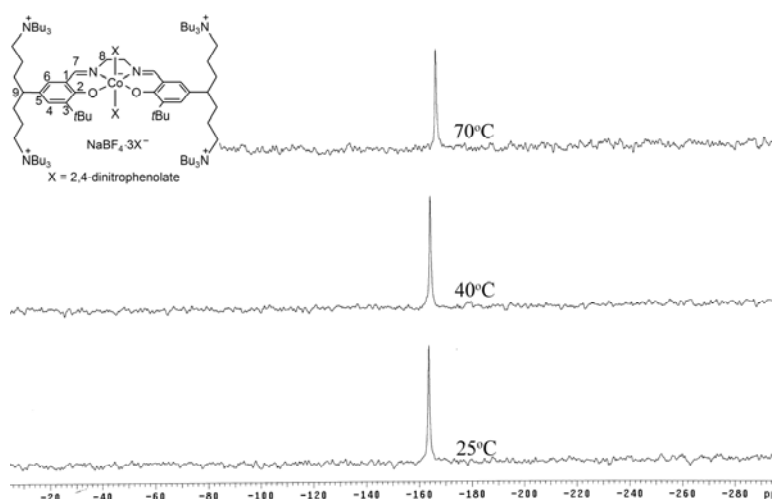
<The variable temperature ^1H NMR spectra of **8** in THF- d_8 >



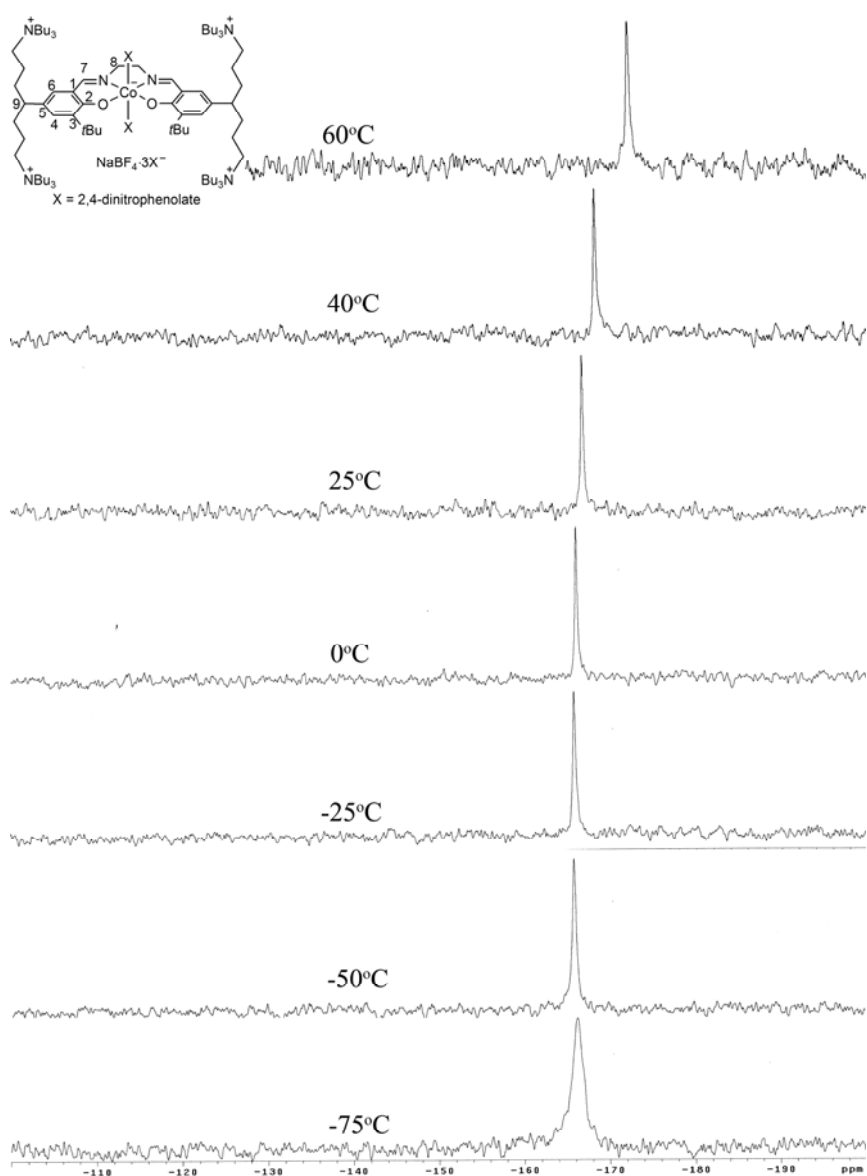
<The ^{19}F NMR spectrum of **8** in $\text{dms}\text{-}d_6$ at room temperature>



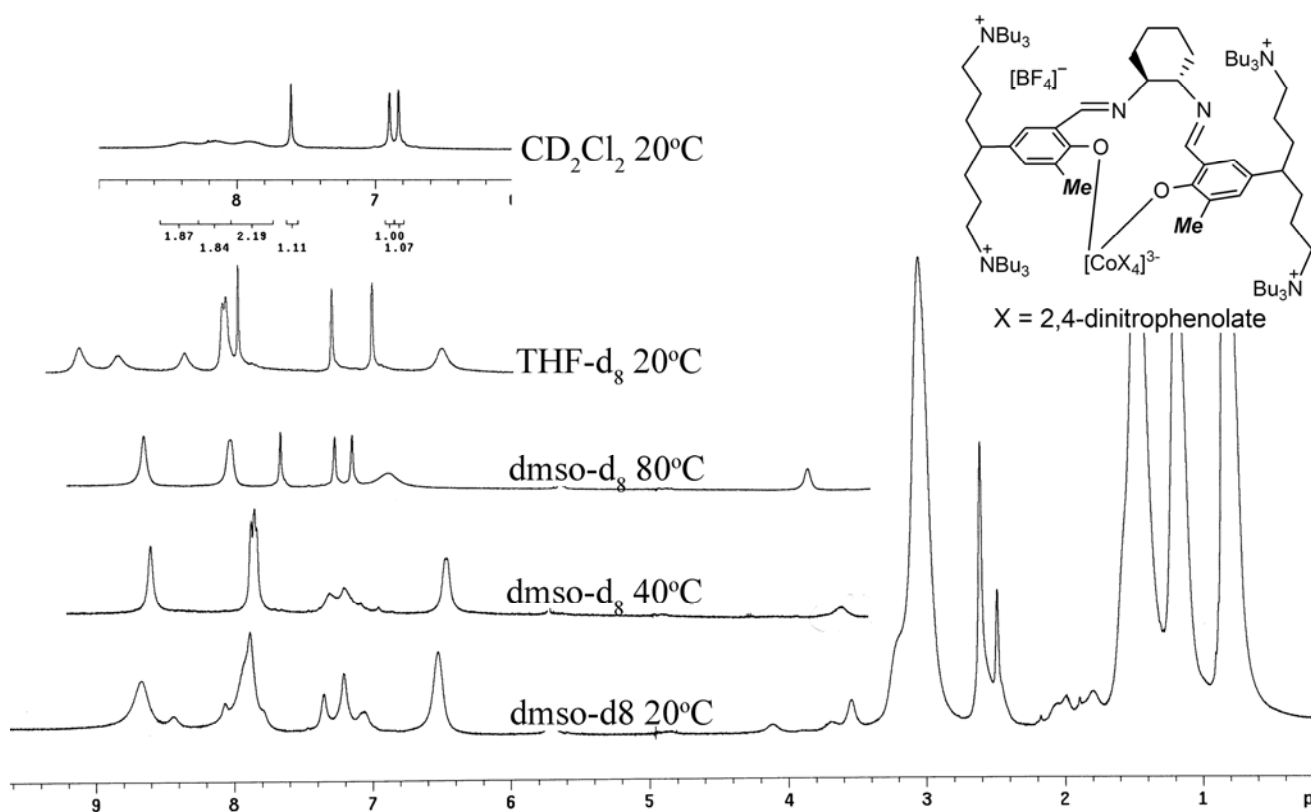
<The variable temperature ^{15}N NMR spectra of **8** in $\text{dms}\text{-d}_6$ >



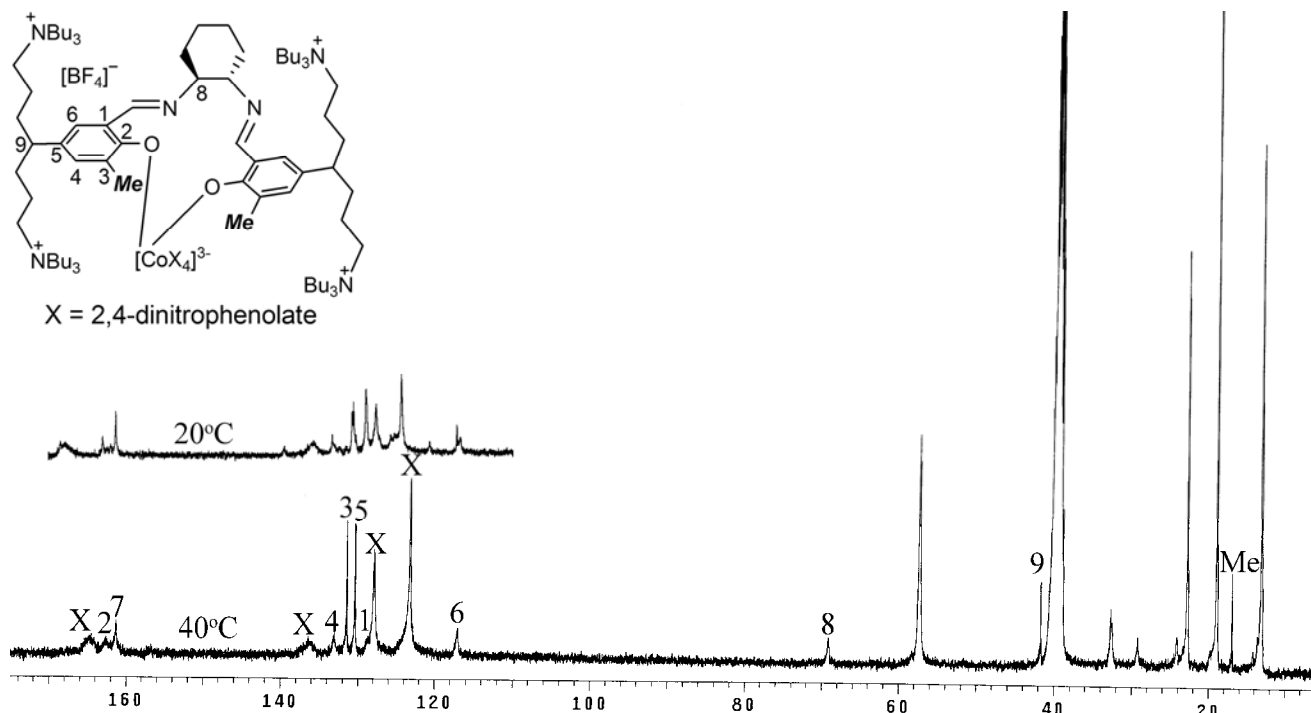
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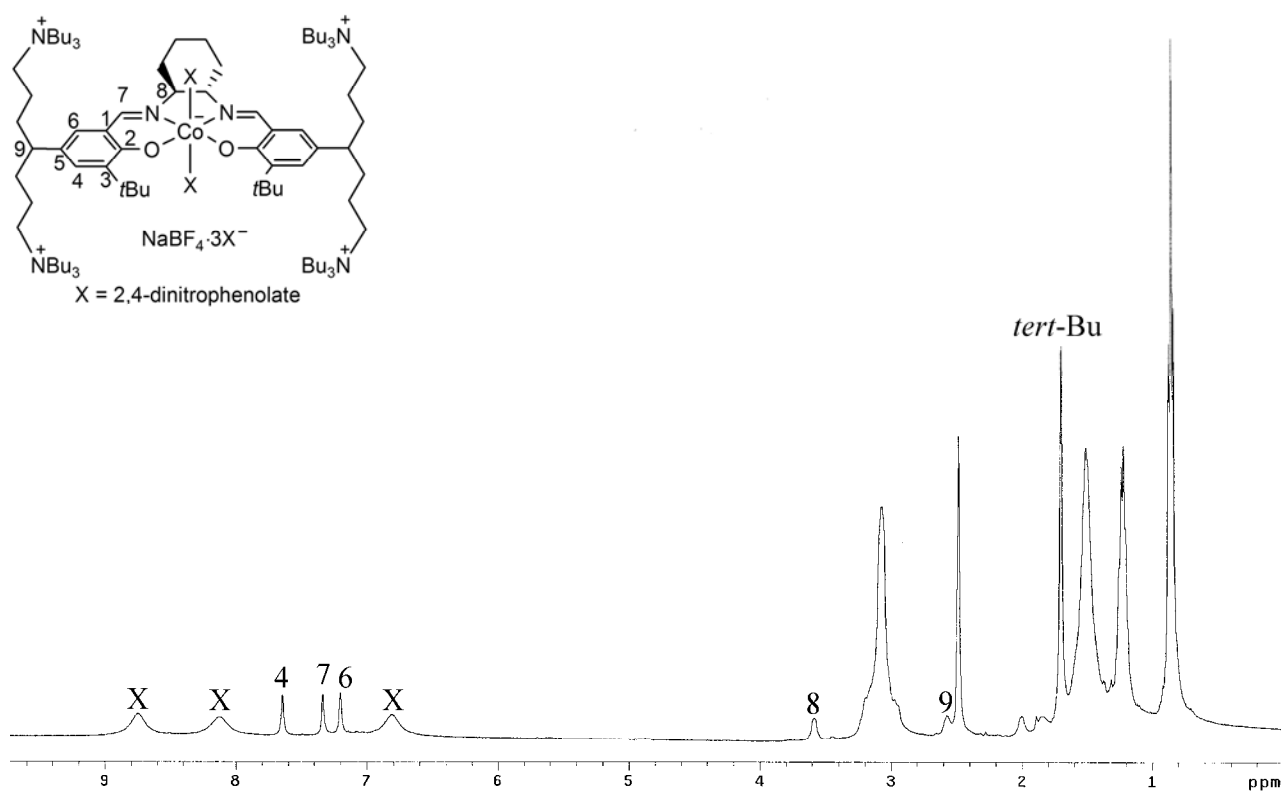
<The ^1H NMR spectra of **3**>



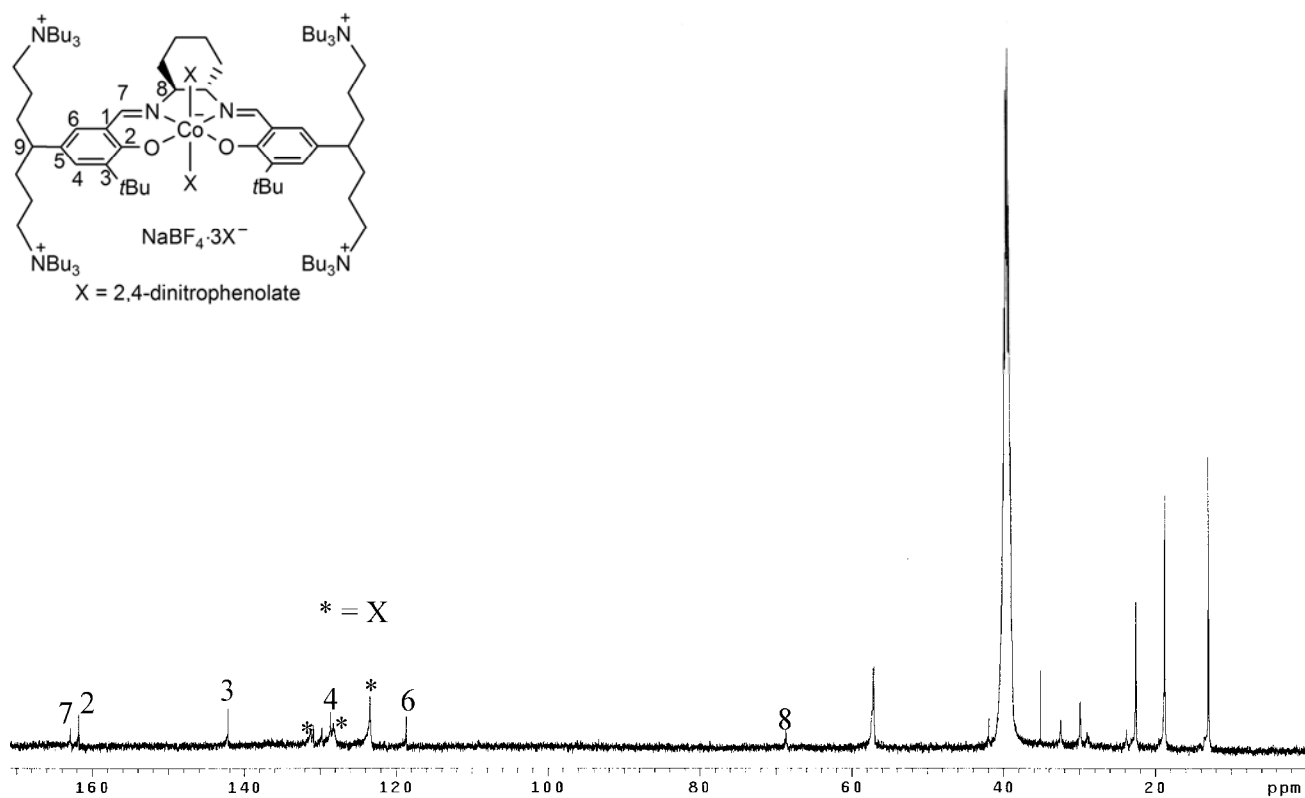
<The ^{13}C NMR spectra of **3** in $\text{dmsO}-\text{d}_6$ and its signal assignment>



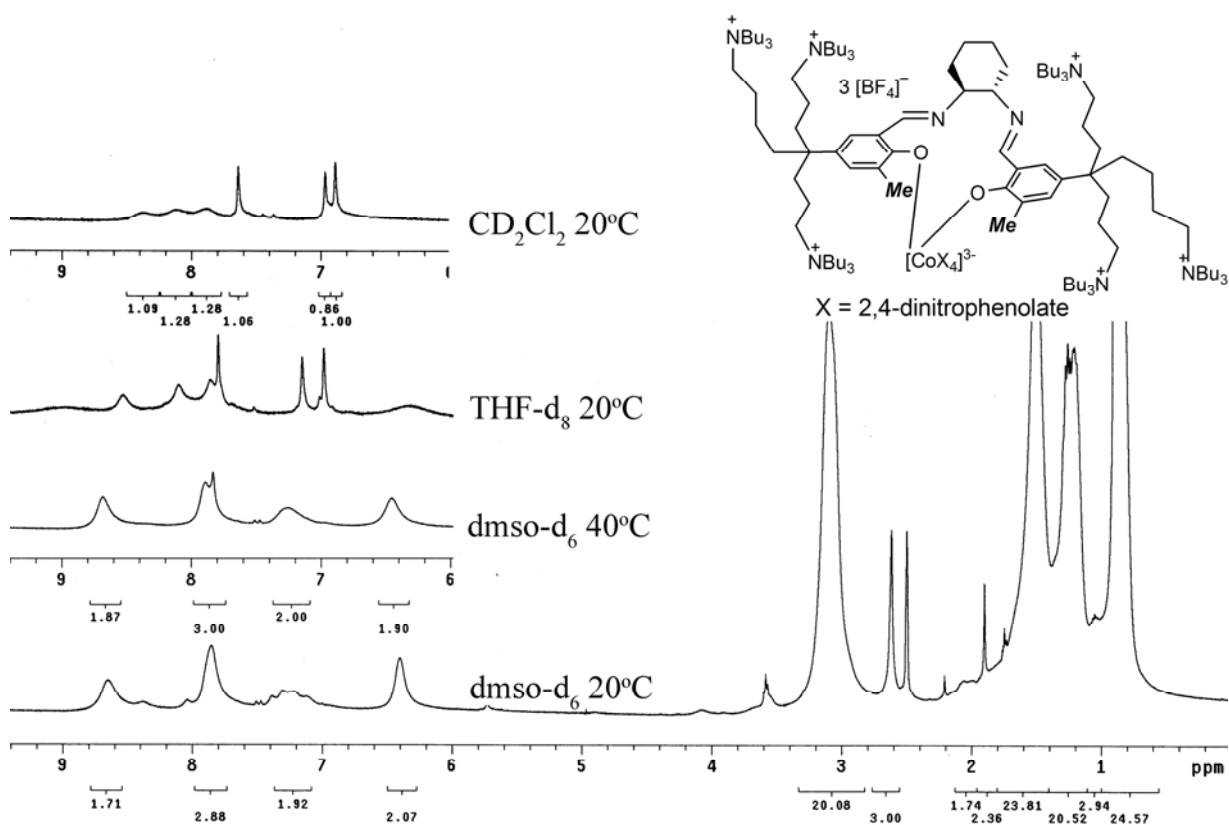
<The ^1H NMR spectrum of **4** in $\text{dms}\text{-d}_6$ at 20°C and its signal assignment>



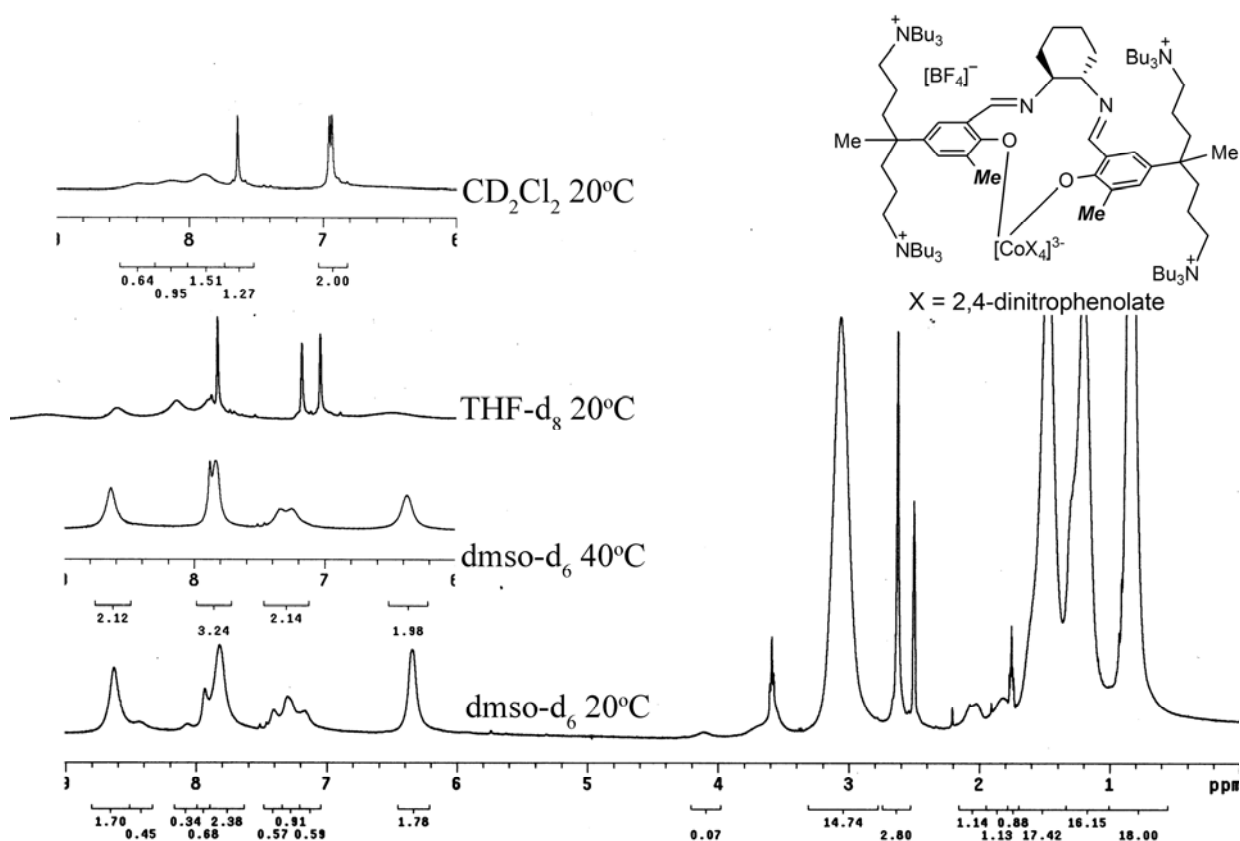
<The ^{13}C NMR spectrum of **4** in $\text{dms}\text{-d}_6$ at 20°C and its signal assignment>



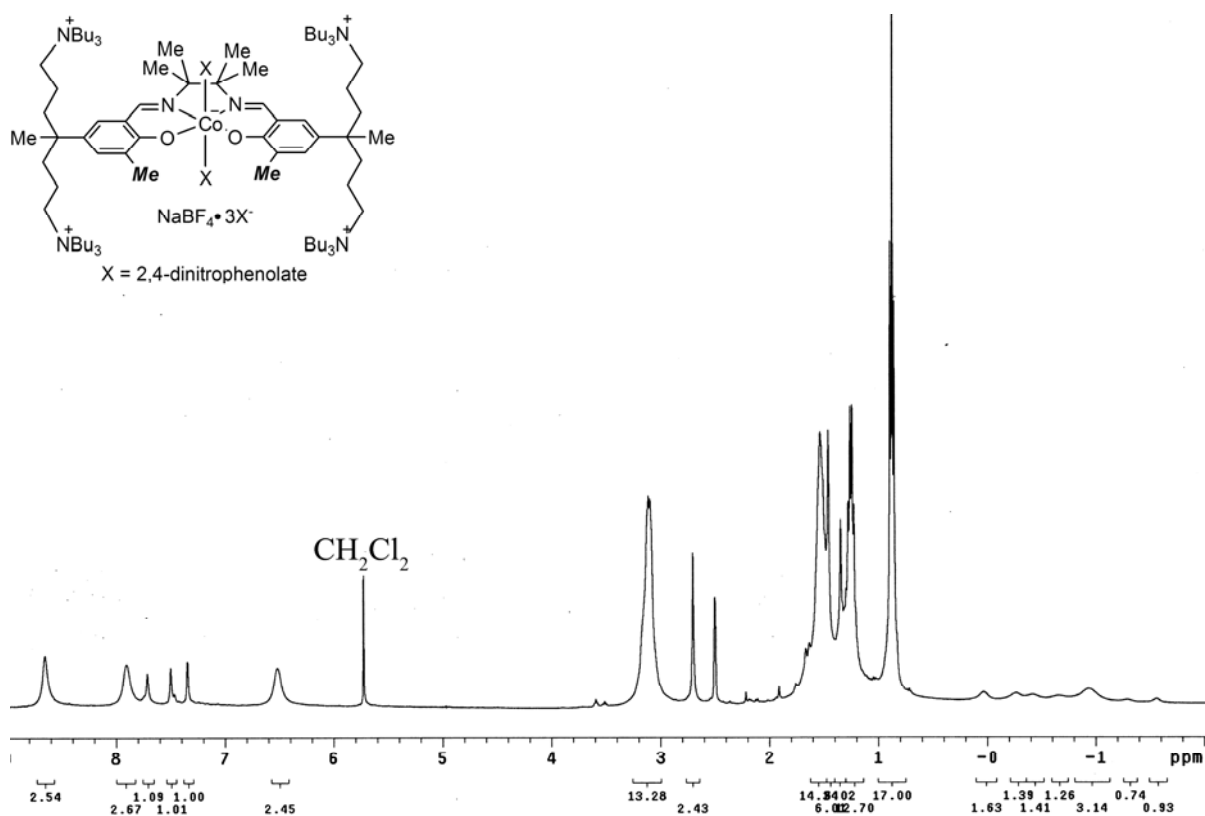
<The ^1H NMR spectra of **9**>



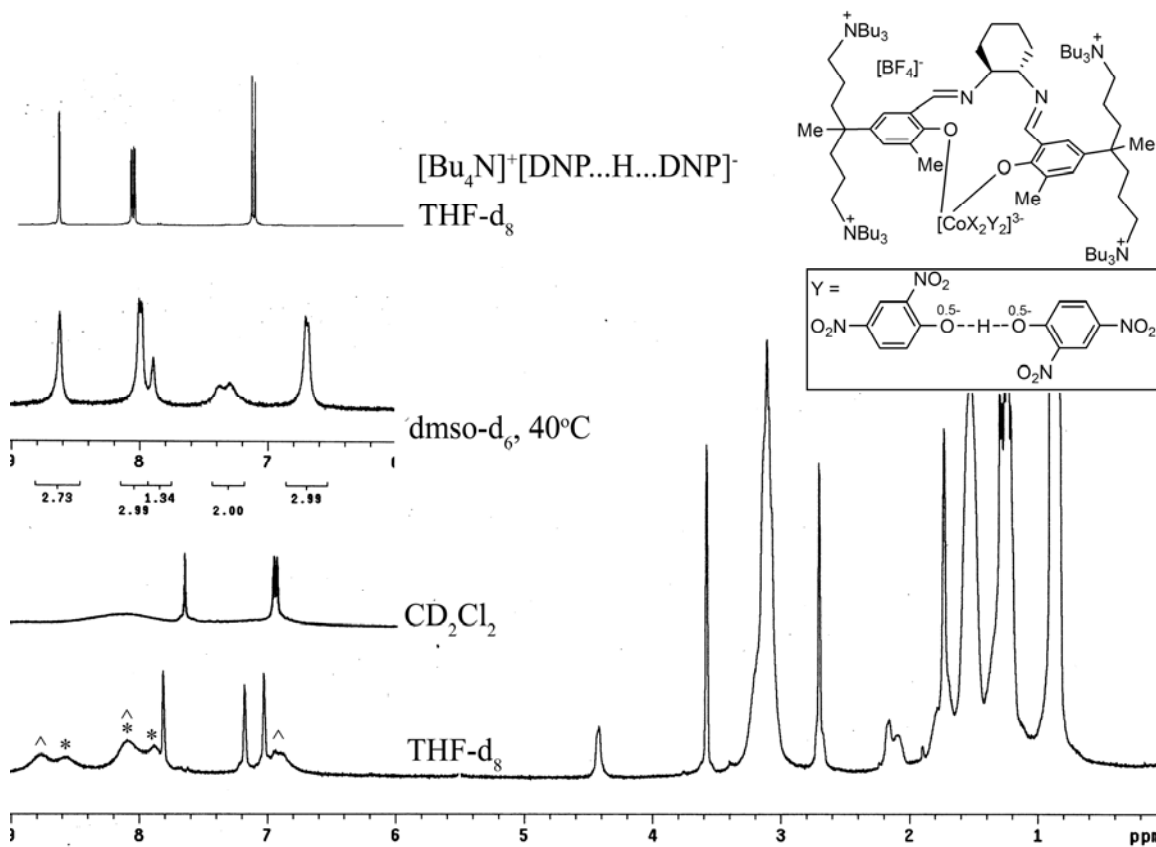
<The ^1H NMR spectra of **10**>



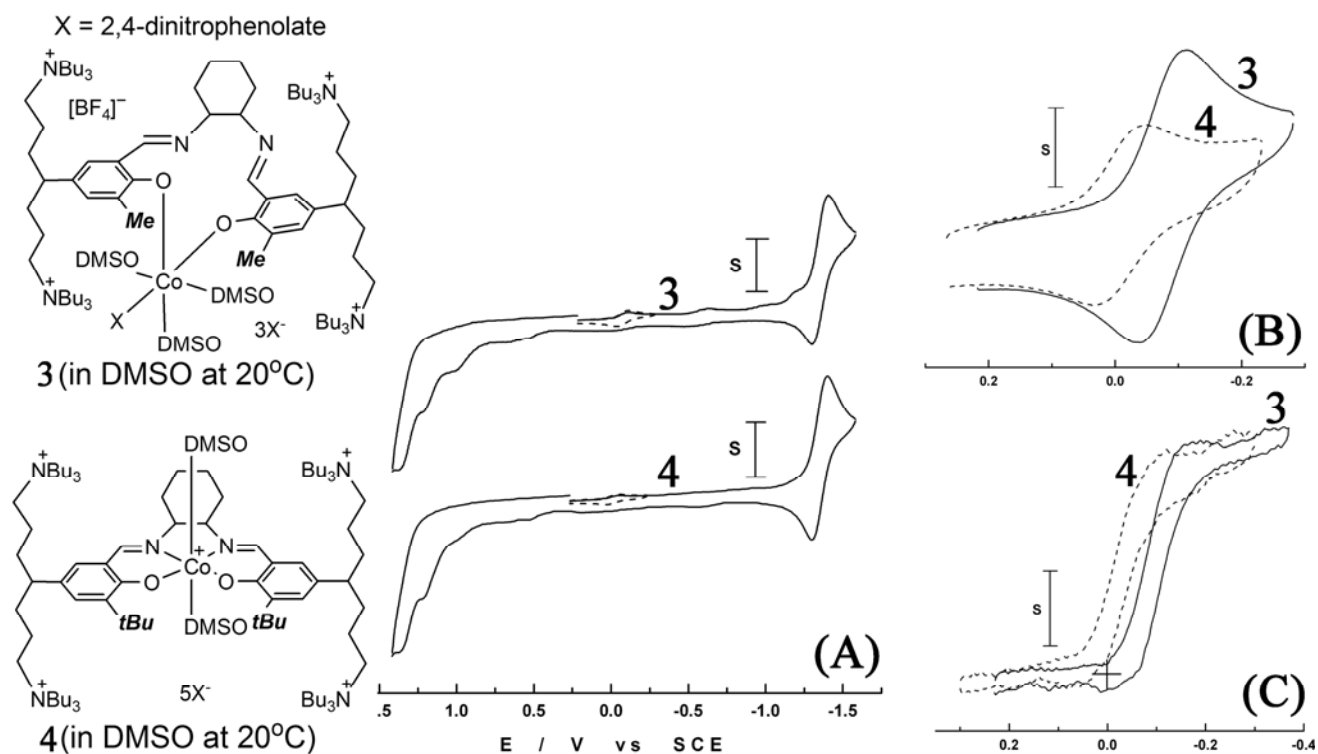
<The ^1H NMR spectrum of **11** in dmso-d_6 at 20°C >



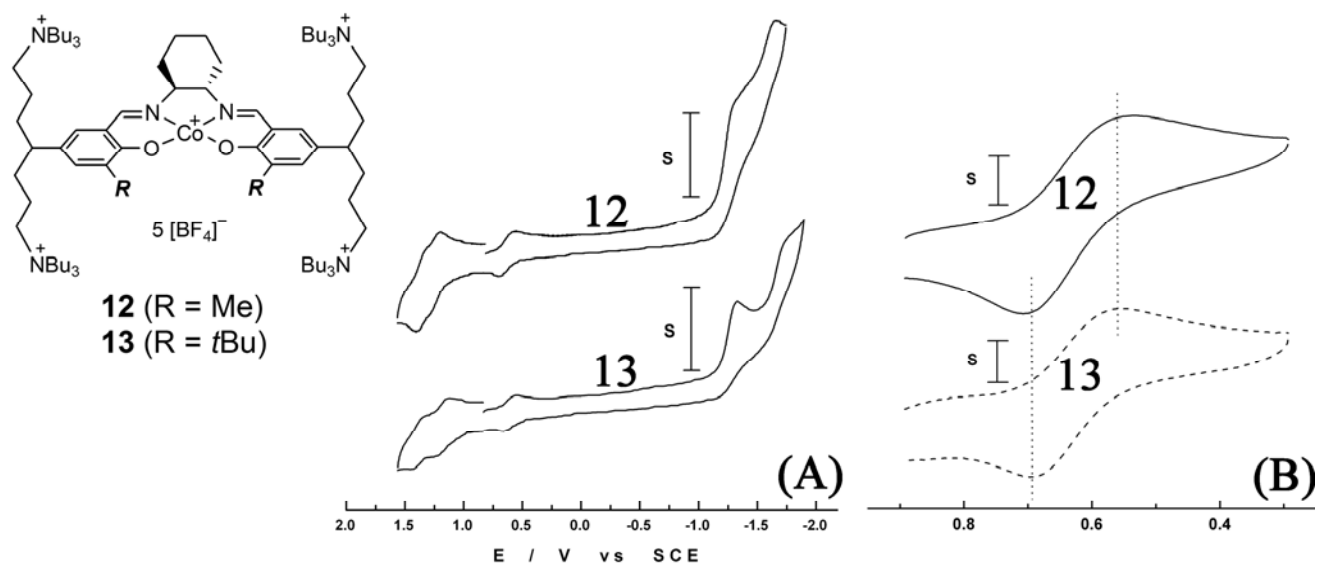
<The ^1H NMR spectra of **15**>



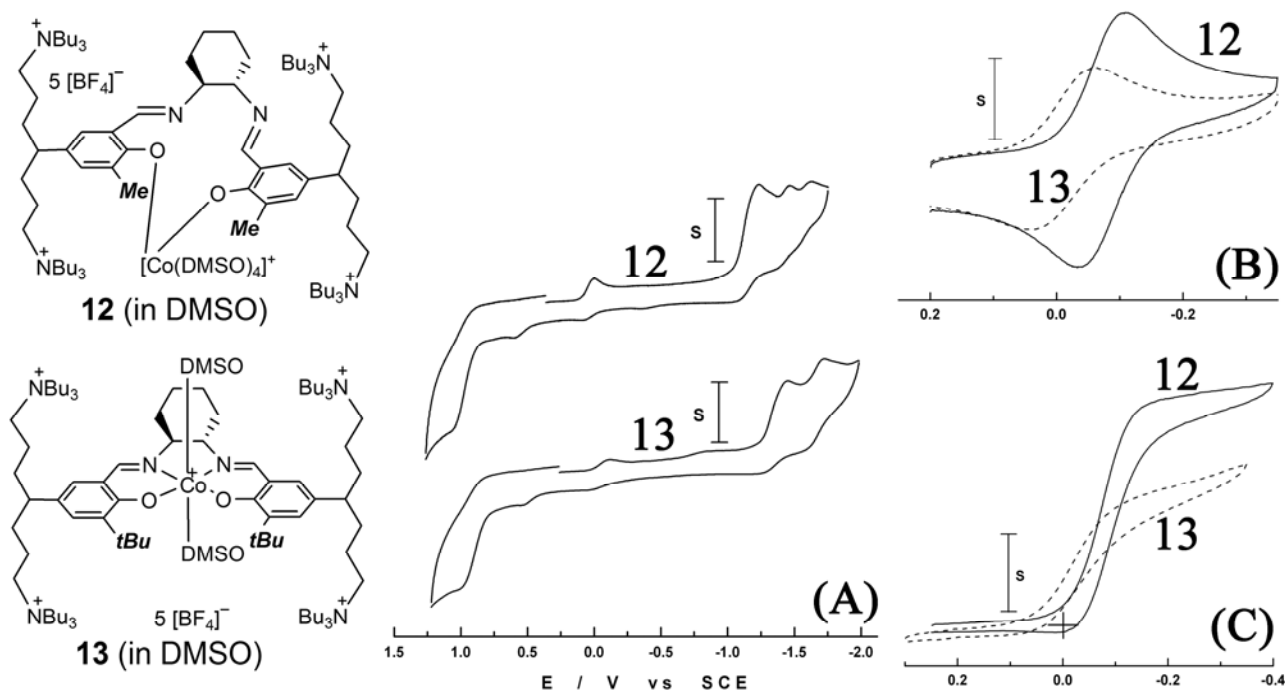
<Cyclic voltammograms of **3** and **4** in DMSO ((A): At a platinum disk electrode with negative direction; $\nu = 0.1$ V/s; the scale bar, 5 μ A. (B): Magnified CVs, the scale bar 0.4 μ A. (C) Steady-state voltammograms at a platinum micro-disk electrode (dia. 100 μ m); $\nu = 5$ mV/s; the scale bar, 0.4 nA)>



<Cyclic voltammograms of **12** and **13** in CH₂Cl₂ ((A): At a platinum disk electrode with negative direction; $\nu = 0.1$ V/s; the scale bar, 5 μ A. (B): Magnified CVs, the scale bar 0.4 μ A)>



<Cyclic voltammograms of **12** and **13** in DMSO ((A): At a platinum disk electrode with negative direction; $\nu = 0.1$ V/s; the scale bar, 5 μ A. (B): Magnified CVs, the scale bar 0.4 μ A. (C) Steady-state voltammograms at a platinum micro-disk electrode (dia. 100 μ m); $\nu = 5$ mV/s; the scale bar, 0.4 nA)>



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³ Min, J.; Seong, J. E.; Na, S. J.; Cyriac, A.; Lee, B. Y. *Bull. Kor. Chem. Soc.* **2009**, 30, 745.

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