

Steric effects in the design of Co-Schiff base complexes for the catalytic oxidation of lignin models to *para*-benzoquinones

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1. General Information

All reactions were carried out under an atmosphere of nitrogen unless otherwise specified. Anhydrous tetrahydrofuran (THF) was purified by distillation over sodium/benzophenone. All reagents and solvents were purchased from commercial sources and were used as received. Analytical thin layer chromatography (TLC) was performed using 250 μm Silica Gel 60 F254 pre-coated plates. Flash column chromatography was performed using 230-400 Mesh 60Å Silica Gel. The eluents employed are reported as volume:volume percentages. Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Catalytic oxidations were carried out in thick walled glass reactors under the oxygen pressure indicated in the text. ^1H and ^{13}C NMR spectra were measured in CDCl_3 using a Varian Unity 400 MHz instrument. Chemical shifts are reported relative to tetramethylsilane or solvent resonance and reported in ppm. Infrared spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer at 4 cm^{-1} resolution and are reported in cm^{-1} . High resolution mass spectra (HRMS) were obtained by The Center for Mass Spectrometry of the Department of Chemistry at the University of Tennessee, and are reported as m/e (relative ratio). Accurate masses are reported for the molecular ion $(\text{M}+\text{H})^+$ or a suitable fragment ion and are reported with an error $< 5\text{ ppm}$. 1-Octylpiperazine **15b**, 1-methylpiperazine **15c**, 1-phenylpiperazine **15d** and piperidine **15e** were purchased from Sigma-Aldrich and used as received.

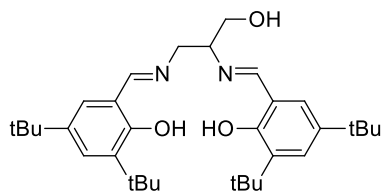
2. General Procedures for the Oxidation of *p*-Phenols to Benzoquinones

In a Fisher-Porter bottle, *p*-phenol substrate (1 mmol) and Co-Schiff base complex **17a-f** (0.05 mmol) were combined in 5 mL of MeOH or 5 mL of MeOH/ CH_2Cl_2 (4/1) for catalyst **22**. The bottle was flushed with oxygen three times and then pressurized with oxygen to 50 psi. After 16 hours under vigorous stirring, the reaction mixture is concentrated under vacuum at room temperature and the crude material purified by flash chromatography (eluent: gradient 0-5-10% EtOAc/ CH_2Cl_2).

- 2,6-dimethoxybenzoquinone **4** (bright yellow):¹ recovered by filtration at the end of the reaction and satisfactorily matched all previously reported data. 2,6-Dimethoxybenzoquinone is only partially soluble in methanol, and between 5 and 10% of residual product remains in solution that can be purified by column chromatography (eluent: gradient 0-5-10% EtOAc/ CH_2Cl_2). When catalyst **22** was used, the reaction mixture was concentrated under vacuum and purified by flash chromatography (eluent: gradient 0-5-10% EtOAc/ CH_2Cl_2).

- 2-methoxybenzoquinone **5** (light green):¹ purified by flash chromatography (eluent: gradient 0-5% EtOAc/ CH_2Cl_2) and satisfactorily matched all previously reported data.

3. Synthesis of Schiff Bases 16a-f



2,3-bis((E)-(3,5-di-tert-butyl-2-hydroxybenzylidene)amino)propan-1-ol (**13**).

To a solution of 2,3-dibromopropanol **8** (2.179 g, 10 mmoles) in **dry DMF** (60 mL) was added NaN_3 (6.500 g, 100 mmoles). The reaction mixture was heated at reflux under N_2 for 24 hours (dark brown), cooled to room temperature and treated with water (100 mL). The crude product was extracted with EtOAc (2 x 100 mL), rinsed with water (2 x 100 mL), dried over Na_2SO_4 and concentrated to afford a mixture of diazide **9** and 2-bromoprop-2-en-1-ol **10**² (10/1) as a light brown oil which was used in the next step without further purification; 2,3-diazidopropan-1-ol **9**: $^1\text{H-NMR}$ (400 MHz, CDCl_3): 3.77-3.62 (m, 3H), 3.47 (dq, $J = 18.1, 4.4\text{ Hz}$, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 62.8, 62.4, 51.7.

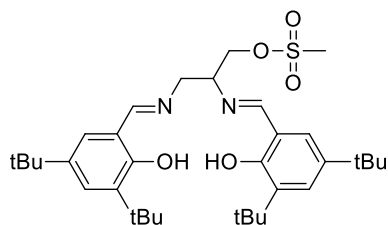
¹ D. Cedenó, J. J. Bozell *Tetrahedron Lett.* **2012**, 53, 2380-2383.

² P. Hayes, C. Maignan *Synthesis* **1999**, 5, 783-786.

When non-dry DMF was used as solvent, 1,3-diazidopropan-2-ol was isolated as the major product: $^1\text{H-NMR}$ (400 MHz, CDCl_3): 3.95-3.91 (m, 1H), 3.42-3.36 (dd, $J = 7.8$ Hz, 4H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 69.8, 54.1.

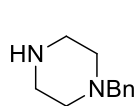
To a solution of diazide **9** obtained above in THF/ H_2O (50 mL, 4/1) was added Ph_3P (5.246 g, 20 mmoles) portionwise at room temperature (N_2 evolution was observed). The reaction mixture was heated at reflux overnight, diluted with water (20 mL) and THF was evaporated under vacuum. The mixture was triturated, the white solid formed was filtered, rinsed with H_2O (10 mL) and the aqueous solution was concentrated under vacuum (60°C) to give 2,3-diaminopropan-1-ol **11** as a yellow oil which was used in the next step without further purification. Presence of residual water or DMF in the crude material does not affect the yield of the next reaction.

To a solution of **11** obtained above in MeOH (50 mL) was added 3,5-di-tert-butyl-2-hydroxybenzaldehyde **12** (2.340 g, 10 mmoles) in one portion. The reaction mixture was heated at reflux for 6 hours, concentrated under vacuum and the crude material purified by flash chromatography (gradient; 0-50-100% CH_2Cl_2 /hexanes) to give **13** as a thick bright yellow oil (2.103 g, 41%) which slowly solidified over time; mp $90\text{-}93^\circ\text{C}$; $R_f = 0.25$ (50% CH_2Cl_2 /hexanes + 1% Et_3N); IR (neat) 3354, 2953, 2911, 2857, 1626, 1439, 1249, 1172, 877, 730 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 13.48 (s, 1H), 13.33 (bs, 1H), 8.45 (s, 1H), 8.36 (s, 1H), 7.38 (d, $J = 2.4$ Hz, 1H), 7.36 (d, $J = 2.4$ Hz, 1H), 7.09 (d, $J = 2.4$ Hz, 1H), 7.05 (d, $J = 2.4$ Hz, 1H), 3.96-3.93 (m, 2H), 3.88-3.83 (m, 1H), 3.76-3.66 (m, 2H), 1.43 (s, 9H), 1.42 (s, 9H), 1.28 (s, 18H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 168.3, 168.0, 140.4, 140.1, 136.6, 127.4, 127.2, 126.4, 126.1, 117.8, 117.7, 71.6, 64.6, 61.1, 35.0, 34.1, 31.5, 29.5, 29.4; HRMS (DART-TOF) Calcd for $\text{C}_{33}\text{H}_{50}\text{N}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 523.38997; found 523.38990.



2,3-bis((E)-(3,5-di-tert-butyl-2-hydroxybenzylidene)amino)propyl methanesulfonate (**14**).

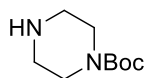
To a solution of alcohol **13** (1.000 g, 1.92 mmoles) and Et_3N (517 μL , 3.84 mmoles) in CH_2Cl_2 (10 mL) was added methanesulfonyl chloride (221 μL , 2.87 mmoles) dropwise at 0°C . The reaction mixture was stirred at the same temperature for 1 hour, quenched by addition of NaHCO_3 (20 mL of a saturated aqueous solution) and diluted with CH_2Cl_2 (20 mL). The organic fraction was separated, dried over Na_2SO_4 and concentrated to give **14** as a thick yellow oil (1.094 g, 95%) which slowly solidified over time; mp $166\text{-}169^\circ\text{C}$; $R_f = 0.25$ (50% CH_2Cl_2 /hexanes + 1% Et_3N); IR (neat) 2959, 2869, 1630, 1439, 1353, 1332, 1180, 996, 979, 826 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 13.26 (s, 1H), 13.06 (bs, 1H), 8.46 (s, 1H), 8.38 (s, 1H), 7.40 (d, $J = 2.4$ Hz, 1H), 7.38 (d, $J = 2.4$ Hz, 1H), 7.09 (d, $J = 2.4$ Hz, 1H), 7.06 (d, $J = 2.4$ Hz, 1H), 4.54 (dd, $J = 10.8, 4.4$ Hz, 1H), 4.43 (dd, $J = 10.0, 7.2$ Hz, 1H), 3.98-3.79 (m, 3H), 3.01 (s, 3H); 1.43 (s, 9H), 1.42 (s, 9H), 1.28 (s, 18H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 169.0, 168.8, 157.9, 157.9, 140.5, 140.3, 136.8, 136.7, 127.9, 127.5, 126.6, 126.3, 117.6, 117.5, 70.4, 68.3, 60.8, 37.5, 35.0, 34.1, 34.1, 31.6, 31.4, 31.4, 29.4; HRMS (DART-TOF) Calcd for $\text{C}_{34}\text{H}_{52}\text{N}_2\text{O}_5\text{S}$ ($\text{M}+\text{H}$) $^+$: 601.36752; found 601.36934.



1-benzylpiperazine (**15a**).³

Benzyl bromide (3.56 mL, 30 mL) was added dropwise at 0°C to a solution of piperazine (12.92 g, 150 mmoles) in dry CH_2Cl_2 (150 mL). The reaction mixture was stirred at the same temperature for 1 h, rinsed with NaHCO_3 (2 x 100 mL of a saturated aqueous solution), dried over Na_2SO_4 and concentrated under vacuum. The crude product was dissolved in 50 mL of absolute EtOH and the white solid formed (1,4-dibenzylpiperazine) was filtered off. The solvent was evaporated under vacuum to give the product as a colorless oil (3.295 g, 63%) which satisfactorily matched all previously reported data.

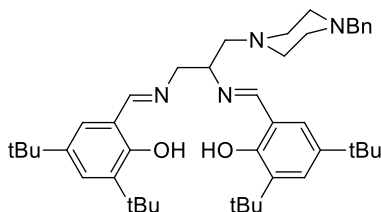
³ D. E. Bergbreiter, P.L. Osburn, C. Li *Org. Lett.* **2002**, *4*, 737-740.



1-Boc-piperazine (15f).⁴

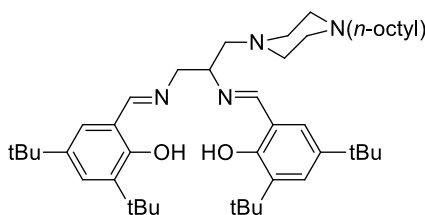
Boc₂O (6.72 g, 30.8 mmole) was added dropwise over 30 minutes to a solution of piperazine (6.685 g, 77.6 mmole) in *t*-BuOH (90 mL) and NaOH (12 mL of a 2.5N aqueous solution). The reaction mixture was stirred at room temperature for 1h. *t*-BuOH was evaporated under vacuum and 1,4-di-Bocpiperazine was filtered off. The aqueous layer was extracted with CH₂Cl₂ (3 x 50 mL), the organic fractions were combined, dried over Na₂SO₄ and condensed under vacuum to give the product as a light yellow oil (4.807 g, 84%) which slowly crystallized over time and satisfactorily matched all previously reported data.

Schiff base 16a.



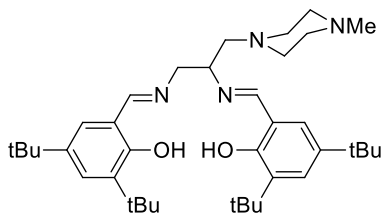
To a solution of mesylate **14** (510.8 mg, 0.85 mmole) in dry MeCN (8 mL) was added successively DIPEA (593 μL, 3.4 mmole), 1-benzylpiperazine **15a** (450.1 mg, 2.55 mmole) and potassium iodide (30.0 mg, 0.18 mmole) at room temperature. The reaction mixture was heated at reflux for 24 hours (dark orange), quenched by addition of water (30 mL) and extracted with CH₂Cl₂ (2 x 50 mL). The organic fractions were combined, dried over Na₂SO₄, concentrated under vacuum and the crude product purified by flash chromatography (gradient; 0-2% MeOH/CH₂Cl₂) to give the product as a thick bright yellow oil (376.3 mg, 65%) which slowly solidified over time; mp 91-93 °C; *R*_f = 0.10 (100% CH₂Cl₂); IR (neat) 2952, 2866, 2807, 1630, 1460, 1443, 1360, 1252, 1176, 830, 736, 698 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 13.68 (bs, 1H), 13.56 (bs, 1H), 8.34 (s, 1H), 8.33 (s, 1H), 7.34-7.04 (m, 7H), 7.04 (d, *J* = 2.4 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 4.09 (dd, *J* = 12.0, 2.4 Hz, 1H), 3.75-3.60 (m, 2H), 3.49 (s, 2H), 2.73 (dd, *J* = 13.2, 6.8 Hz, 1H), 2.60-2.46 (m, 5H), 1.42 (s, 9H), 1.41 (s, 9H), 1.27 (s, 9H), 1.26 (s, 9H); ¹³C-NMR (100 MHz, CDCl₃): δ 167.8, 167.1, 158.3, 158.2, 140.2, 140.2, 138.4, 136.8, 136.7, 129.4, 128.4, 127.2, 127.2, 127.1, 126.4, 126.2, 118.1, 118.0, 67.5, 63.3, 63.0, 62.1, 54.0, 53.4, 35.2, 34.3, 31.7, 29.6, 29.6; HRMS (DART-TOF) Calcd for C₄₄H₆₄N₄O₂ (M+H)⁺: 681.51075; found 681.50843.

Schiff base 16b.



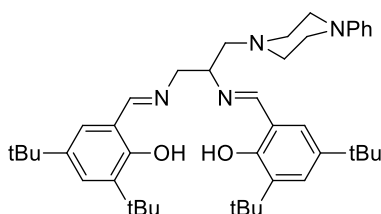
To a solution mesylate **14** (450.6 mg, 0.75 mmole) in dry MeCN (8 mL) was added successively DIPEA (522 μL, 3.0 mmole), 1-*n*-octylpiperazine **15b** (446.4 mg, 2.25 mmole) and potassium iodide (30.0 mg, 0.18 mmole) at room temperature. The reaction mixture was heated at reflux for 24 hours (dark orange), quenched by addition of water (30 mL) and extracted with CH₂Cl₂ (2 x 50 mL). The organic fractions were combined, dried over Na₂SO₄, concentrated under vacuum and the crude product purified by flash chromatography (gradient; 0-1% MeOH/CH₂Cl₂) to give the product as a thick bright yellow gum (376.3 mg, 79%); *R*_f = 0.15 (100% CH₂Cl₂); IR (neat) 2952, 2859, 2803, 1626, 1460, 1443, 1273, 1252, 1176, 830, 729 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 13.70 (bs, 1H), 13.57 (bs, 1H), 8.36 (s, 1H), 8.33 (s, 1H), 7.35 (d, *J* = 2.6 Hz, 1H), 7.33 (d, *J* = 2.6 Hz, 1H), 7.04 (d, *J* = 2.6 Hz, 1H), 7.03 (d, *J* = 2.6 Hz, 1H), 4.09 (dd, *J* = 12.4, 3.2 Hz, 1H), 3.75-3.60 (m, 2H), 2.75 (dd, *J* = 12.8, 6.8 Hz, 1H), 2.61-2.47 (m, 5H), 2.31 (t, *J* = 7.8 Hz, 2H), 1.47-1.41 (m, 20H), 1.32-1.27 (m, 28H), 0.88 (t, *J* = 6.6 Hz, 3H); ¹³C-NMR (100 MHz, CDCl₃): δ 167.8, 167.1, 158.3, 158.2, 140.2, 140.1, 136.8, 136.7, 127.2, 127.1, 126.4, 126.2, 118.0, 67.5, 63.0, 62.1, 59.1, 54.0, 53.5, 35.2, 34.3, 32.0, 31.7, 29.8, 29.6, 29.6, 29.5, 27.9, 27.1, 22.9, 14.3; HRMS (DART-TOF) Calcd for C₄₅H₇₄N₄O₂ (M+H)⁺: 703.58900; found 703.58778.

⁴ H. Naito, T. Hata, H. Urabe *Org. Lett.* **2010**, *12*, 1228–1230.



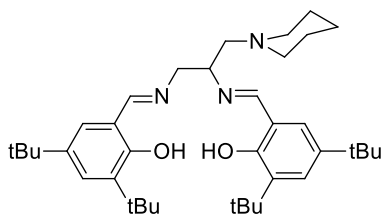
Schiff base 16c.

To a solution of mesylate **14** (231.3 mg, 0.38 mmole) in dry MeCN (3 mL) was added successively DIPEA (258 μ L, 1.5 mmole), 1-methylpiperazine **15c** (171 μ L, 1.5 mmole) and potassium iodide (6.0 mg, 0.036 mmole) at room temperature. The reaction mixture was heated at reflux for 24 hours (dark orange), quenched by addition of water (30 mL) and extracted with CH_2Cl_2 (2 x 50 mL). The organic fractions were combined, dried over Na_2SO_4 , concentrated under vacuum and the crude product purified by flash chromatography (gradient; 0-3% MeOH/ CH_2Cl_2) to give the product as a thick bright yellow oil (179.0 mg, 78%) which slowly solidified over time; mp 90-92 $^\circ\text{C}$; R_f = 0.20 (3% MeOH/ CH_2Cl_2); IR (neat) 2956, 2869, 1630, 1443, 1249, 1173, 830, 774, 733 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 13.69 (bs, 1H), 13.56 (bs, 1H), 8.35 (s, 1H), 8.34 (s, 1H), 7.35 (d, J = 2.8 Hz, 1H), 7.33 (d, J = 2.8, 1H), 7.04 (d, J = 2.8 Hz, 1H), 7.03 (d, J = 2.8 Hz, 1H), 4.10 (dd, J = 12.0, 2.8 Hz, 1H), 3.74-3.60 (m, 2H), 2.75 (dd, J = 13.2, 6.8 Hz, 1H), 2.77-2.57 (m, 9H), 2.28 (s, 3H), 1.42 (s, 9H), 1.41 (s, 9H), 1.27 (s, 9H), 1.26 (s, 9H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 167.6, 166.9, 158.1, 158.0, 140.0, 139.9, 136.5, 136.5, 127.0, 126.9, 126.2, 126.0, 117.8, 67.3, 62.7, 61.8, 55.2, 53.7, 46.0, 35.0, 34.1, 31.4, 29.4, 29.4; HRMS (DART-TOF) Calcd for $\text{C}_{38}\text{H}_{60}\text{N}_4\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 605.47945; found 605.47781.



Schiff base 16d.

To a solution of mesylate **14** (400.3 mg, 0.66 mmole) in dry MeCN (7 mL) was added successively DIPEA (350 μ L, 2.0 mmoles), 1-phenylpiperazine **15d** (325 μ L, 2.0 mmoles) and potassium iodide (11.0 mg, 0.066 mmole) at room temperature. The reaction mixture was heated at reflux for 24 hours (dark orange), quenched by addition of water (30 mL) and extracted with CH_2Cl_2 (2 x 50 mL). The organic fractions were combined, dried over Na_2SO_4 , concentrated under vacuum and the crude product purified by flash chromatography (gradient; 0-30-50% CH_2Cl_2 /hexanes) to give the product as a thick bright yellow oil (381.3 mg, 87%) which slowly solidified over time; mp 87-89 $^\circ\text{C}$; R_f = 0.25 (30% CH_2Cl_2 /hexanes); IR (neat) 2952, 2866, 1630, 1443, 1249, 1173, 774, 729 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 13.68 (bs, 1H), 13.57 (bs, 1H), 8.38 (s, 1H), 8.36 (s, 1H), 7.36 (d, J = 2.4 Hz, 1H), 7.34 (d, J = 2.4 Hz, 1H), 7.27 (m, 2H), 7.05 (d, J = 2.4 Hz, 1H), 7.04 (d, J = 2.4 Hz, 1H), 6.92 (d, J = 8.4 Hz, 2H), 6.85 (t, J = 7.2 Hz, 1H), 4.12 (dd, J = 12.0, 3.2 Hz, 1H), 3.78-3.65 (m, 2H), 3.19 (t, J = 4.8 Hz, 4H), 2.81 (dd, J = 12.8, 6.8 Hz, 1H), 2.78-2.63 (m, 5H), 1.43 (s, 9H), 1.42 (s, 9H), 1.27 (s, 18H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 167.7, 167.0, 158.1, 158.0, 151.3, 140.1, 140.0, 136.6, 136.5, 129.1, 127.1, 127.0, 126.2, 126.0, 119.7, 117.8, 117.8, 116.0, 67.4, 62.8, 61.8, 53.8, 49.2, 35.0, 34.1, 31.4, 29.4, 29.4; HRMS (DART-TOF) Calcd for $\text{C}_{43}\text{H}_{62}\text{N}_4\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 667.49510; found 667.49366.

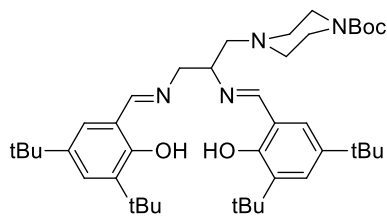


Schiff base 16e.

To a solution of mesylate **14** (400.9 mg, 0.66 mmole) in dry MeCN (7 mL) was added successively DIPEA (350 μ L, 2 mmoles), piperidine **15e** (198 μ L, 2 mmoles) and potassium iodide (11.0 mg, 0.066 mmole) at room temperature. The reaction mixture was heated at reflux for 24 hours (dark orange), quenched by addition of water (30 mL) and extracted with CH_2Cl_2 (2 x 50 mL). The organic fractions were combined, dried over Na_2SO_4 , concentrated under vacuum and the crude product purified by flash chromatography (gradient; 10-30% CH_2Cl_2 /hexanes) to give the product as a thick bright yellow oil (381.3 mg, 87%) which slowly solidified over time; mp 92-95 $^\circ\text{C}$; R_f = 0.20 (30% CH_2Cl_2 /hexanes); IR (neat) 2958, 2865, 1631, 1593, 1472, 1444, 1251, 1175, 829, 771 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ 13.26 (bs, 2H), 8.34 (s, 1H), 8.33 (s, 1H), 7.33 (d, J = 2.4 Hz, 1H), 7.32 (d, J = 2.4, 1H), 7.04 (d, J = 2.4 Hz, 1H), 7.02 (d, J = 2.4 Hz, 1H), 4.11 (dd, J = 11.2, 3.6 Hz, 1H), 3.76-3.70 (m, 1H), 3.61 (dd, J = 12.4, 8.4 Hz, 1H), 2.68 (dd, J = 12.8, 6.4 Hz, 1H), 2.54-2.40 (m, 5H), 1.58-1.53 (m, 4H), 1.44-1.41 (m, 20H), 1.26 (s, 9H), 1.26 (s, 9H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ 167.5, 166.7, 158.1, 158.0, 139.9, 139.9, 136.5,

136.4, 126.9, 126.9, 126.1, 126.0, 117.9, 117.9, 67.4, 62.9, 62.7, 55.3, 35.0, 34.1, 31.4, 29.4, 29.4, 26.1, 24.3; HRMS (DART-TOF) Calcd for C₃₈H₅₉N₃O₂ (M+H)⁺: 590.46855; found 590.46941.

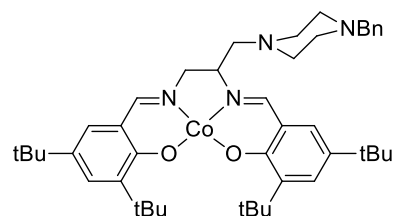
Schiff base 16f.



To a solution of mesylate **14** (450.6 mg, 0.75 mmole) in dry MeCN (8 mL) was added successively DIPEA (524 μ L, 3 mmoles), 1-Boc-piperazine **15f** (419.2 mg, 2.25 mmoles) and potassium iodide (30.0 mg, 0.18 mmole) at room temperature. The reaction mixture was heated at reflux for 24 hours (dark orange), quenched by addition of water (30 mL) and extracted with CH₂Cl₂ (2 x 50 mL). The organic fractions were combined, dried over Na₂SO₄, concentrated under vacuum and the crude product purified by flash chromatography (gradient; 50-100% CH₂Cl₂/hexanes) to give the product as a thick bright yellow oil (367.7 mg, 71%) which slowly solidified over time; mp 90-92 °C; *R*_f = 0.15 (100% CH₂Cl₂); IR (neat) 2952, 2869, 1695, 1626, 1443, 1363, 1245, 1176, 1006, 729 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 13.63 (bs, 1H), 13.53 (bs, 1H), 8.36 (s, 1H), 8.34 (s, 1H), 7.35 (d, J = 2.8 Hz, 1H), 7.34 (d, J = 2.8, 1H), 7.05 (d, J = 2.8 Hz, 1H), 7.04 (d, J = 2.8 Hz, 1H), 4.08 (d, J = 11.6 Hz, 1H), 3.73-3.62 (m, 2H), 3.41 (bs, 4H), 2.76 (dd, J = 13.2, 6.0 Hz, 1H), 2.60 (dd, J = 12.8, 6.0 Hz, 1H), 2.47 (bs, 4H), 1.45 (s, 9H), 1.43 (s, 9H), 1.42 (s, 9H), 1.27 (s, 18H); ¹³C-NMR (100 MHz, CDCl₃): δ 167.9, 167.2, 158.3, 158.2, 155.0, 140.3, 140.2, 127.3, 127.2, 126.4, 126.2, 118.0, 118.0, 79.8, 67.5, 63.0, 62.1, 53.8, 35.2, 34.3, 31.7, 29.6, 29.6, 28.6; HRMS (DART-TOF) Calcd for C₄₂H₆₆N₄O₄ (M+H)⁺: 691.51623; found 691.51329.

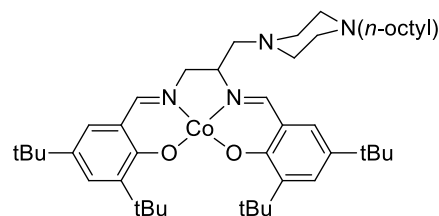
4. Synthesis of Co-complexes 17a-f

Cobalt-Schiff base complex 17a.



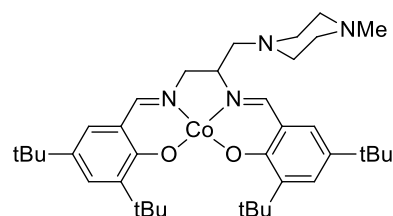
To a solution of Schiff base **16a** (121.3 mg, 0.18 mmol) in *i*-propanol (2 mL) was added a solution of Co(OAc)₂·4H₂O (44.3 mg, 0.18 mmol) in methanol (1 mL). The mixture was heated at reflux for 3 h under argon. The dark brown solution was concentrated and the product was precipitated in 15 mL of hexanes. The green brown solid was recovered by filtration, rinsed with hexanes and then dried under vacuum for 16 h at 80°C to give **17a** (102.1 mg, 78%) as a red/light brown solid. IR (neat) 2952, 2911, 2866, 1595, 1529, 1363, 1315, 1252, 1169, 788, 702 cm⁻¹; HRMS (DART-TOF) Calcd for C₄₄H₆₂CoN₄O₂ (M+H)⁺: 738.42830; found 738.42596.

Cobalt-Schiff base complex 17b.



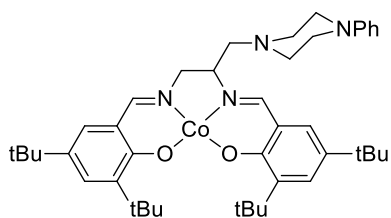
To a solution of Schiff base **16b** (260.3 mg, 0.37 mmol) in *i*-propanol (4 mL) was added a solution of Co(OAc)₂·4H₂O (110.6 mg, 0.44 mmol) in methanol (2 mL). The mixture was heated at reflux for 3 h under argon. The dark brown solution was concentrated and the product was precipitated in 15 mL of hexanes. The green brown solid was recovered by filtration, rinsed with hexanes and then dried under vacuum for 16 h at 80°C to give **17b** (221.2 mg, 78%) as a red/light brown solid. IR (neat) 2949, 2935, 2866, 1588, 1522, 1360, 1318, 1252, 1180, 844, 788 cm⁻¹; HRMS (DART-TOF) Calcd for C₄₅H₇₂CoN₄O₂ (M+H)⁺: 760.50655; found 760.50323.

Cobalt-Schiff base complex 17c.



To a solution of Schiff base **16c** (115.8 mg, 0.19 mmol) in *i*-propanol (2 mL) was added a solution of Co(OAc)₂·4H₂O (71.5 mg, 0.28 mmol) in methanol (1 mL). The mixture was heated at reflux for 3 h under argon. The dark brown solution was concentrated and the product was precipitated in 15 mL of hexanes. The green brown solid was recovered by filtration, rinsed with hexanes and then dried under vacuum for 16 h at 80°C to give **17c** (125.7 mg,

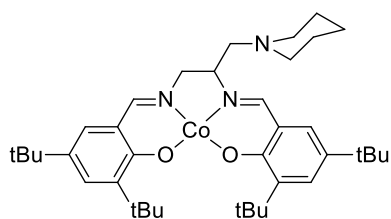
83%) as a red/light brown solid. IR (neat) 2956, 2904, 2862, 1553, 1522, 1408, 1384, 1252, 1180, 788, 671, 615 cm^{-1} ; HRMS (DART-TOF) Calcd for $\text{C}_{38}\text{H}_{58}\text{CoN}_4\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 662.39700; found 662.39375.



Cobalt-Schiff base complex 17d.

To a solution of Schiff base **16d** (264.0 mg, 0.40 mmol) in *i*-propanol (4 mL) was added a solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (112.0 mg, 0.45 mmol) in methanol (2 mL). The mixture was heated at reflux for 3 h under argon. The dark brown solution was concentrated and the product was precipitated in 15 mL of hexanes. The green brown solid was recovered by filtration, rinsed with hexanes and then dried under vacuum for 16 h at 80°C to give **17d** (211.9 mg,

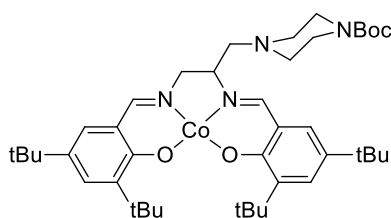
73%) as a red/light brown solid. IR (neat) 2966, 2907, 2862, 1560, 1529, 1412, 1380, 1256, 1180, 677 cm^{-1} ; HRMS (DART-TOF) Calcd for $\text{C}_{43}\text{H}_{60}\text{CoN}_4\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 724.41265; found 724.41061.



Cobalt-Schiff base complex 17e.

To a solution of Schiff base **16e** (241.3 mg, 0.41 mmol) in *i*-propanol (4 mL) was added a solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (112.1 mg, 0.45 mmol) in methanol (2 mL). The mixture was heated at reflux for 3 h under argon. The dark brown solution was concentrated and the product was precipitated in 15 mL of hexanes. The green brown solid was recovered by filtration, rinsed with hexanes and then dried under vacuum for 16 h at 80°C to give **17e** (221.3 mg,

83%) as a red/light brown solid. IR (neat) 2956, 2869, 1585, 1553, 1529, 1439, 1252, 1173 cm^{-1} ; HRMS (DART-TOF) Calcd for $\text{C}_{38}\text{H}_{57}\text{CoN}_3\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 647.38610; found 647.38379.



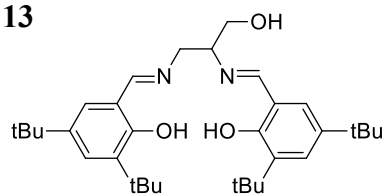
Cobalt-Schiff base complex 17f.

To a solution of Schiff base **16f** (161.3 mg, 0.23 mmol) in *i*-propanol (4 mL) was added a solution of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (62.3 mg, 0.25 mmol) in methanol (2 mL). The mixture was heated at reflux for 3 h under argon. The dark brown solution was concentrated and the product was precipitated in 15 mL of hexanes. The green brown solid was recovered by filtration, rinsed with hexanes and then dried under vacuum for 16 h at 80°C to give **17f** (156.5 mg,

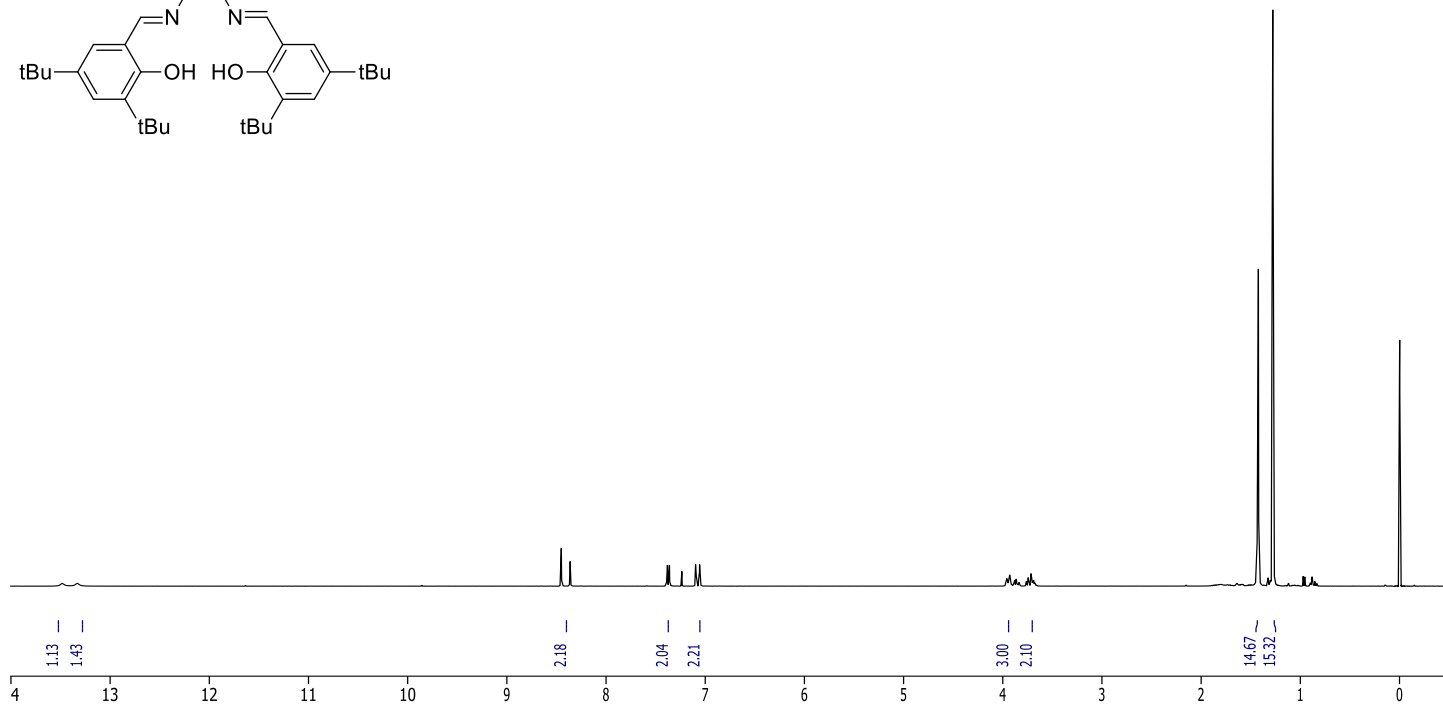
91%) as a red/light brown solid. IR (neat) 2956, 2869, 1585, 1553, 1529, 1439, 1252, 1173, 674 cm^{-1} ; HRMS (DART-TOF) Calcd for $\text{C}_{42}\text{H}_{64}\text{CoN}_4\text{O}_4$ ($\text{M}+\text{H}$) $^+$: 748.43378; found 748.43343.

5. ^1H and ^{13}C -NMR Spectra of New Synthesized Compounds

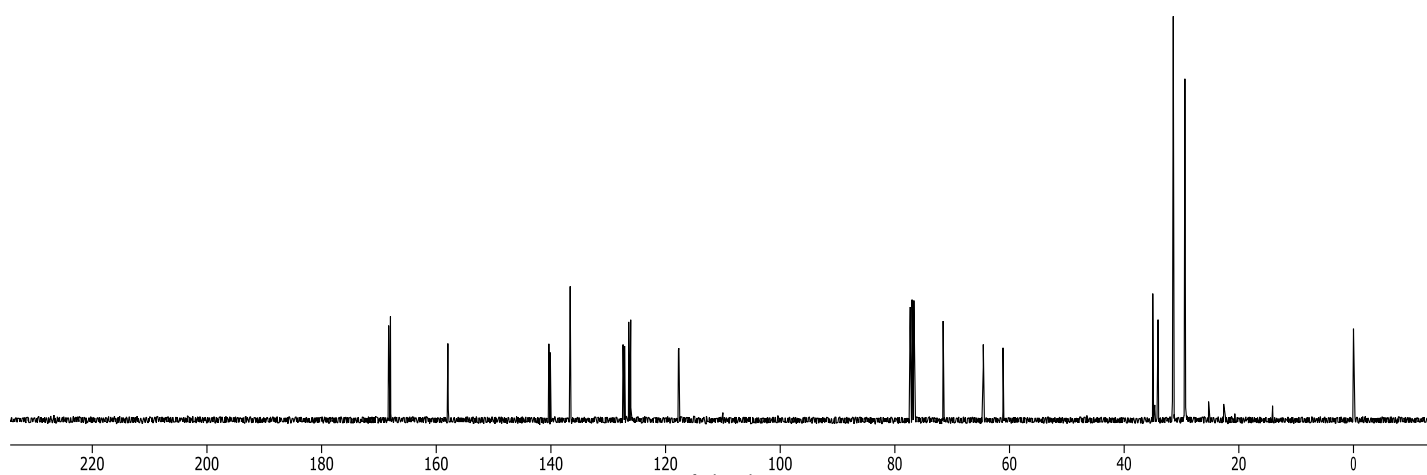
13



CDCl_3 - 400 MHz

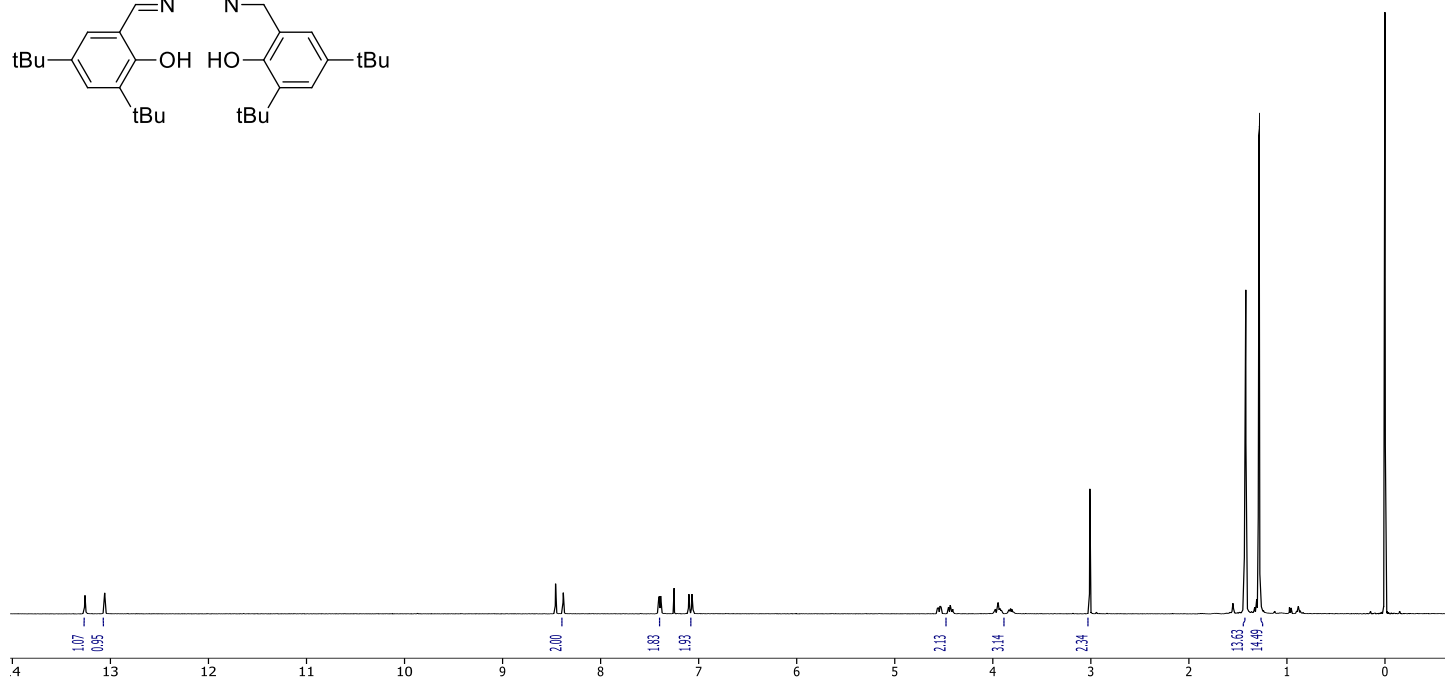
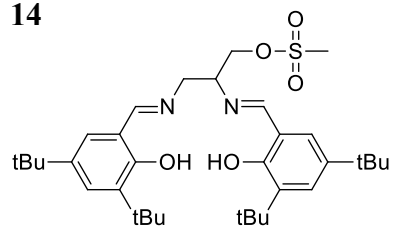


CDCl_3 - 100 MHz

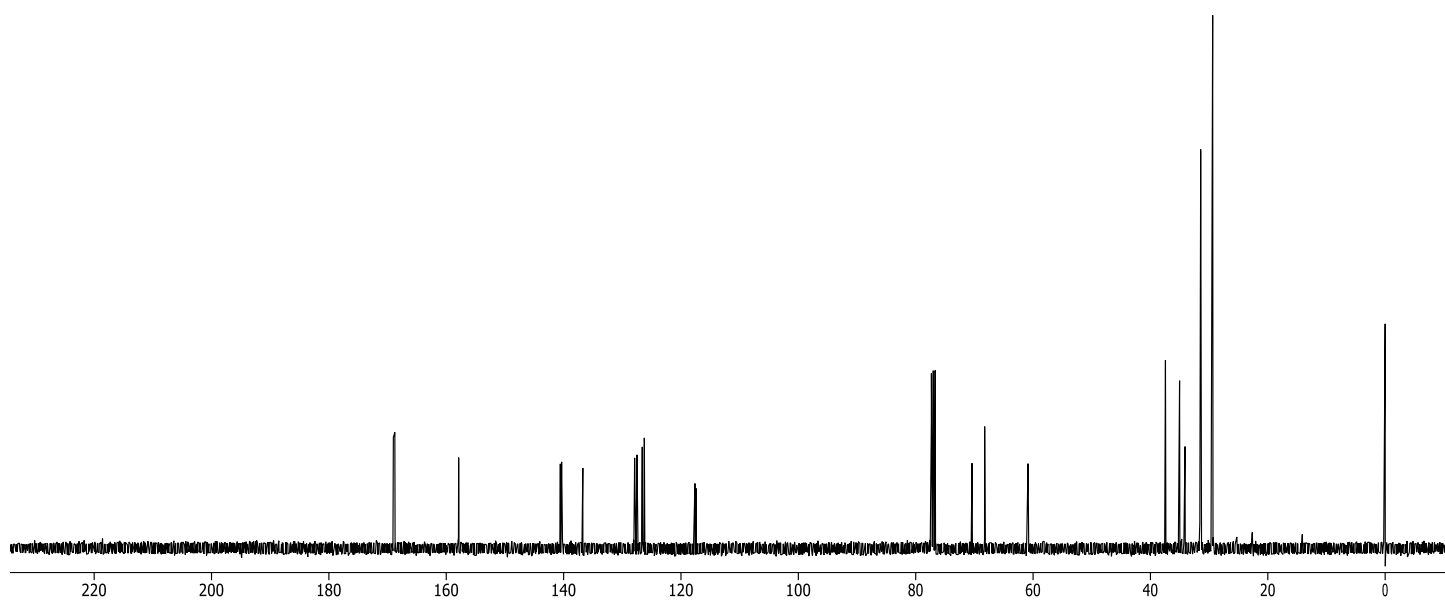


14

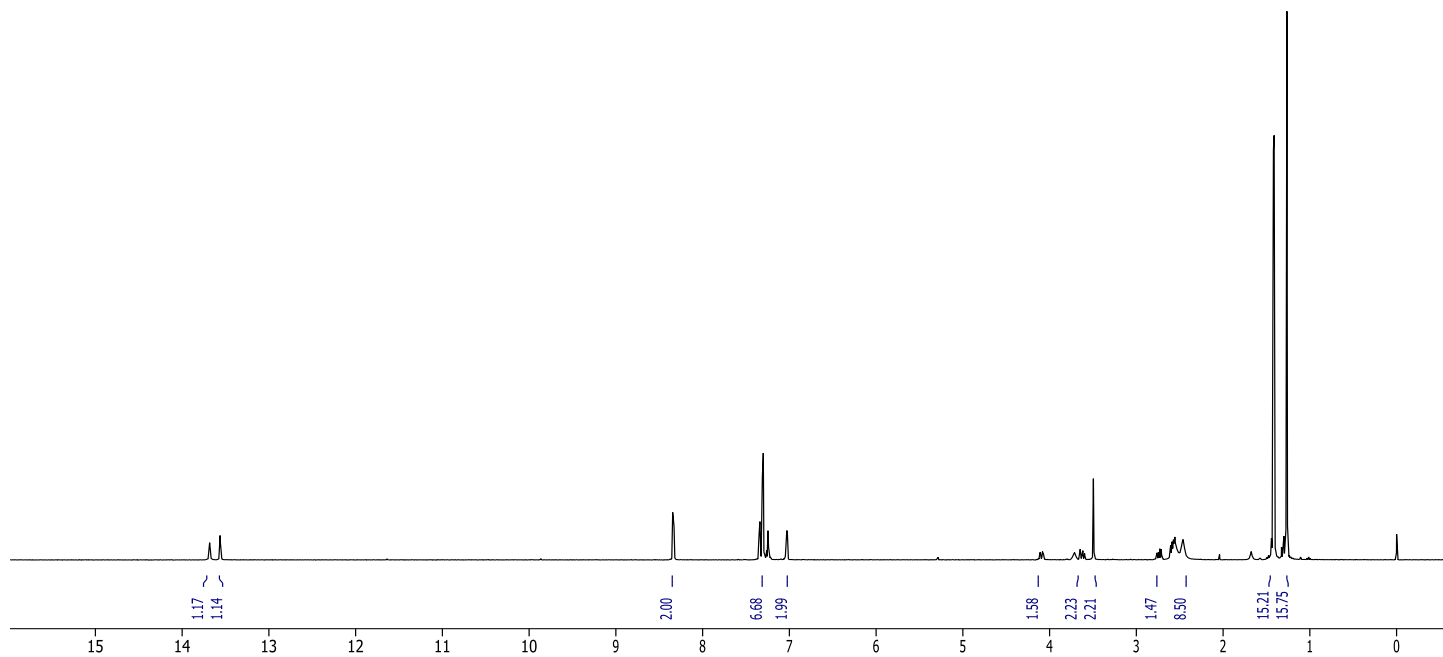
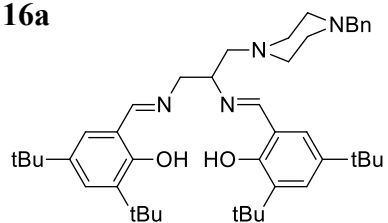
CDCl₃ - 400 MHz



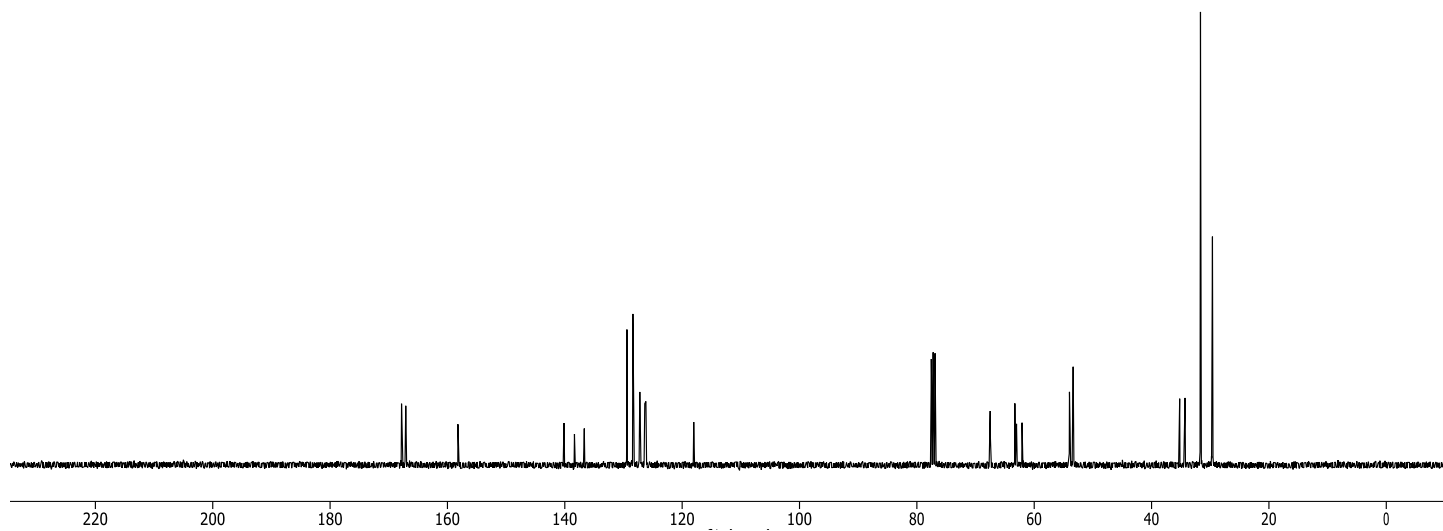
CDCl₃ - 100 MHz



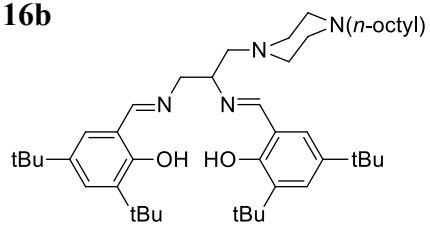
16a



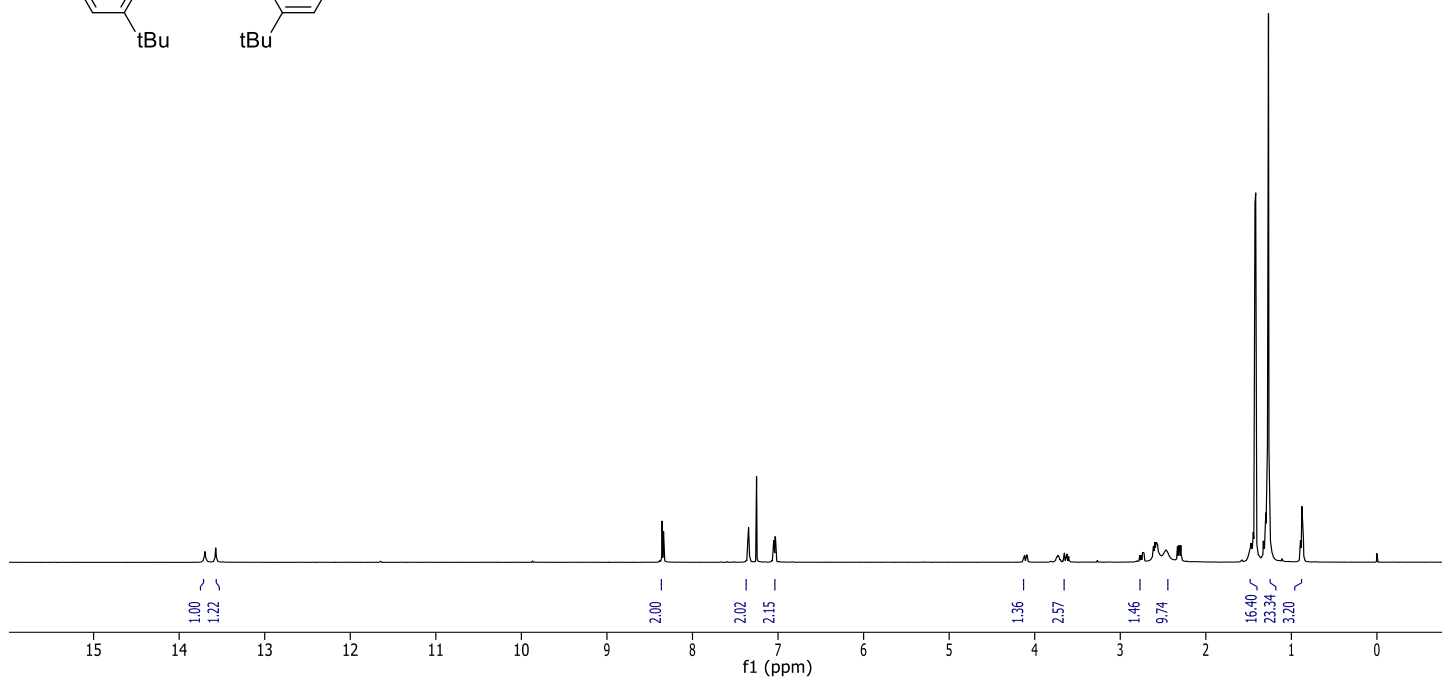
CDCl₃ - 100 MHz



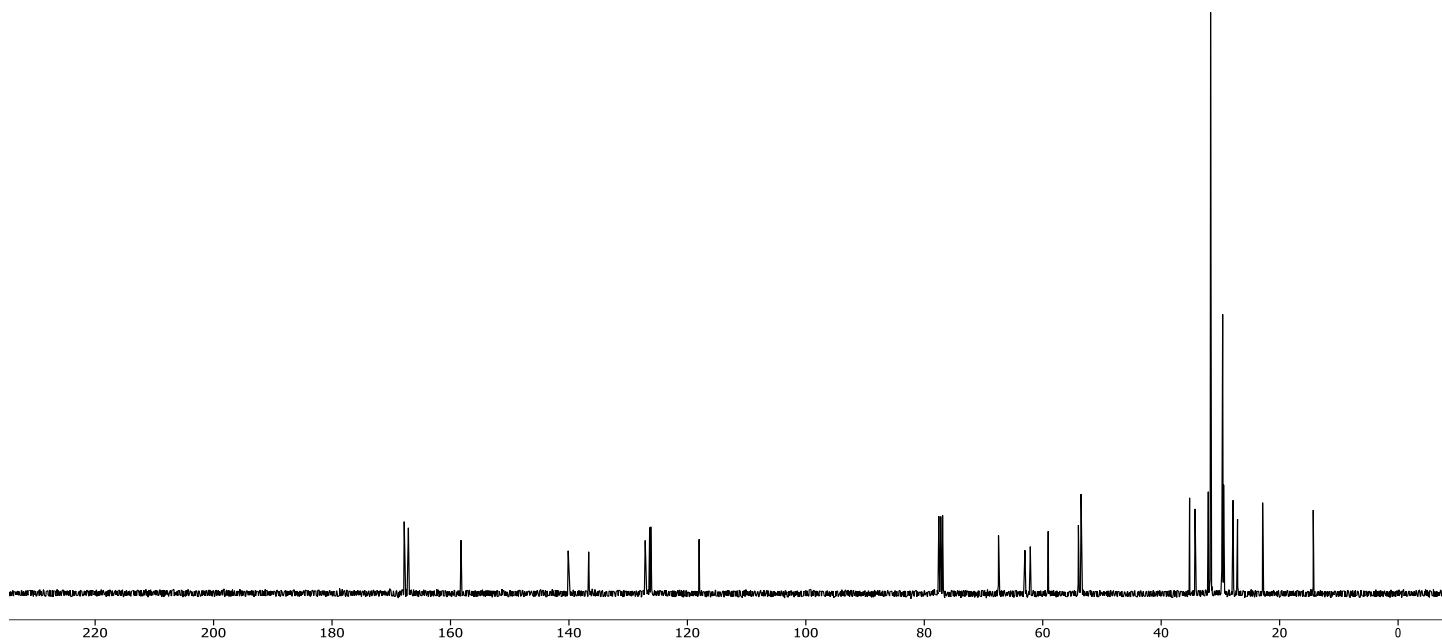
16b



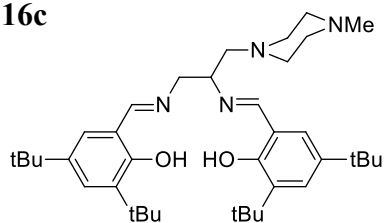
CDCl₃ - 400 MHz



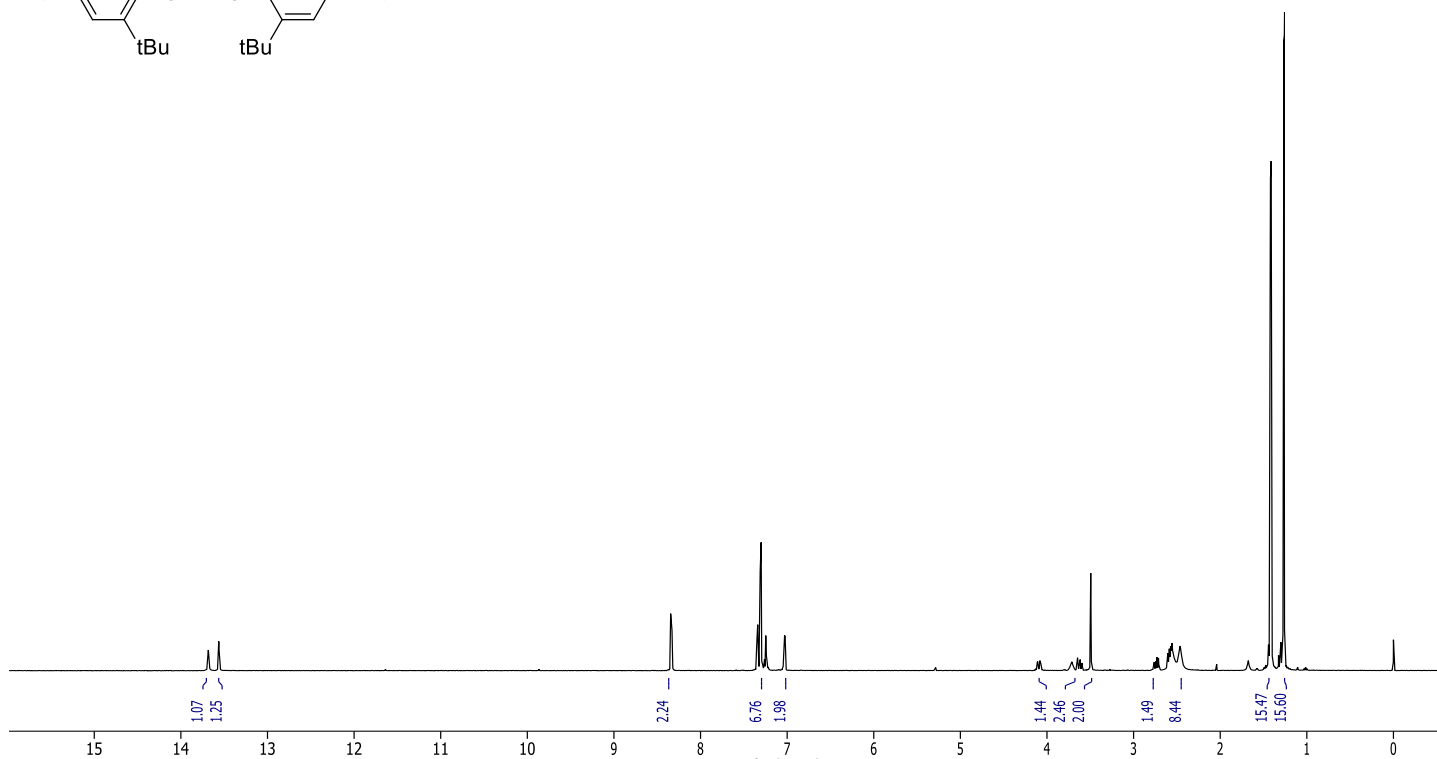
CDCl₃ - 100 MHz



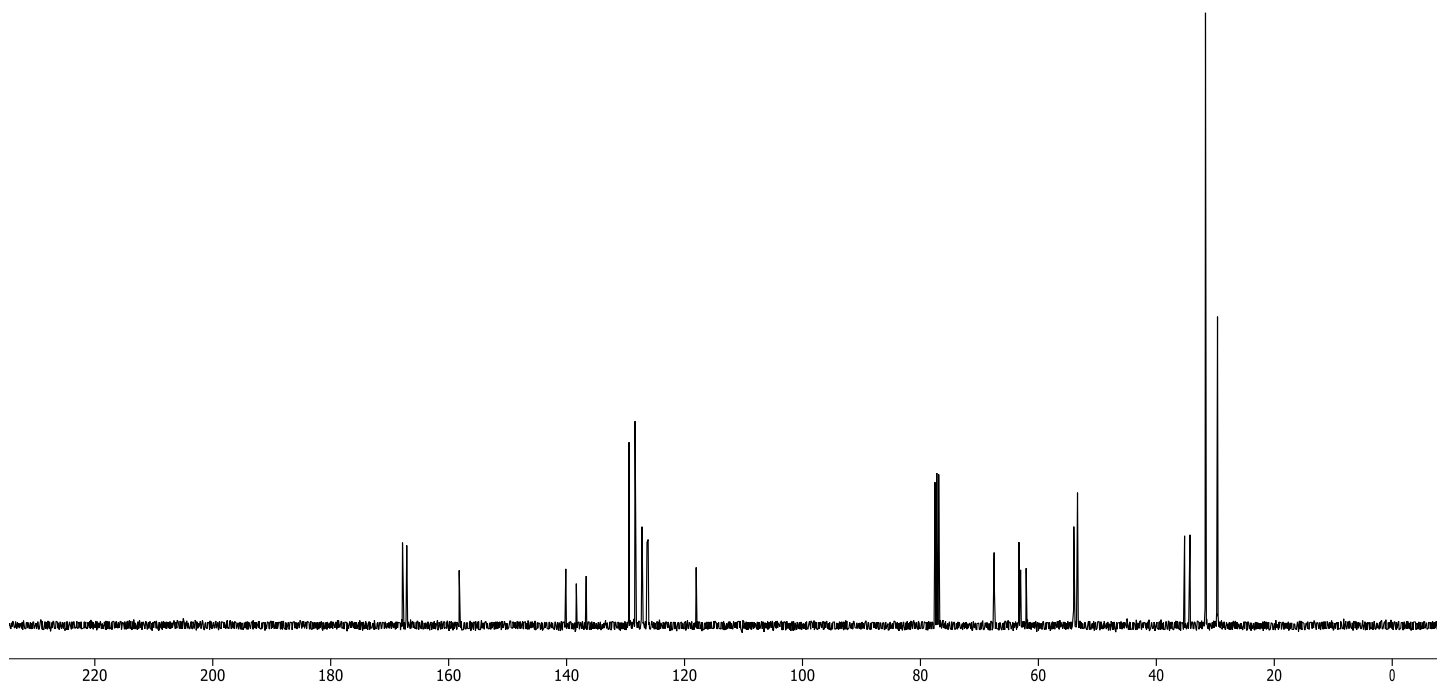
16c



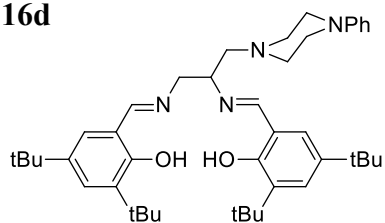
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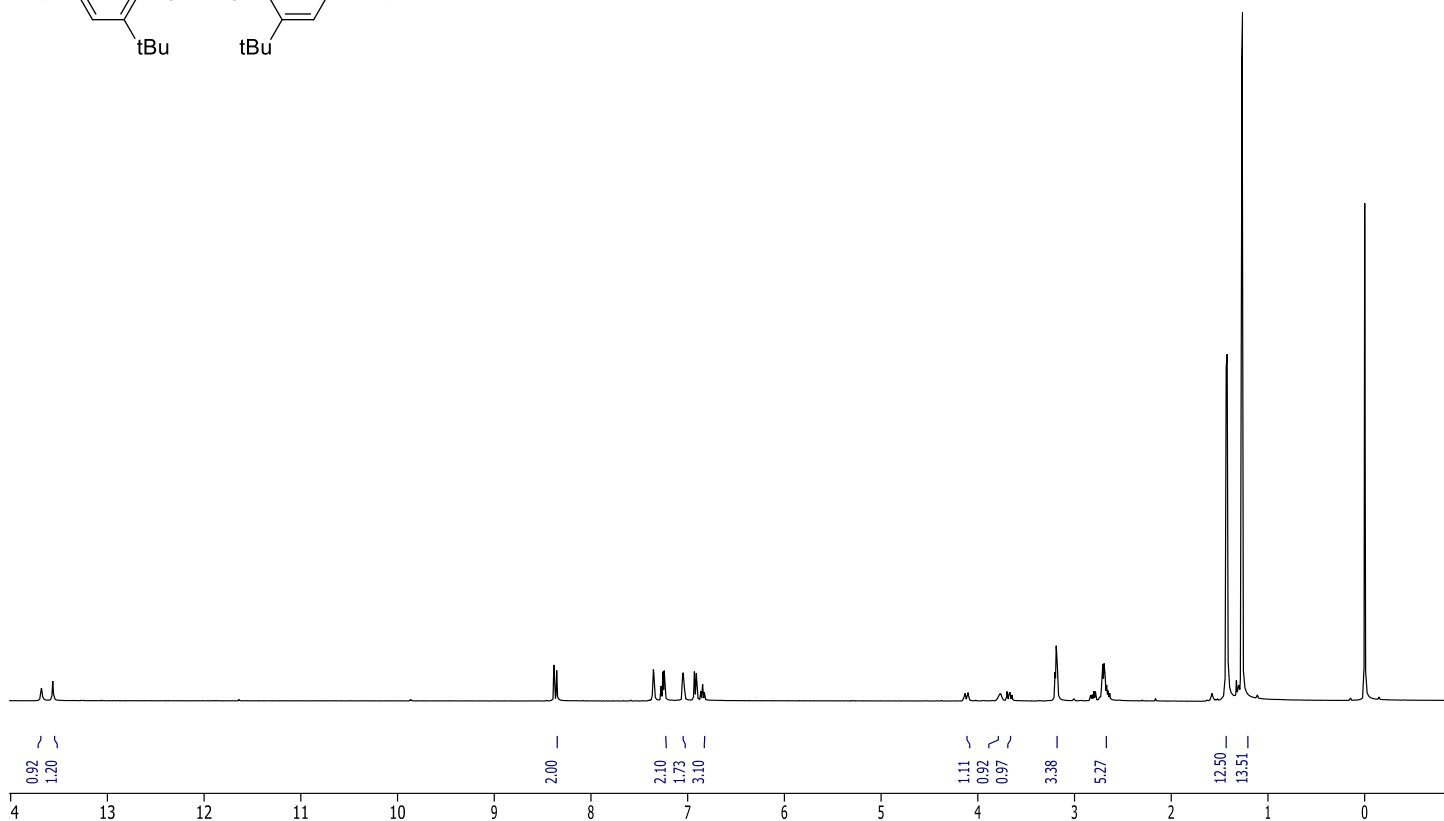
CDCl₃ - 100 MHz



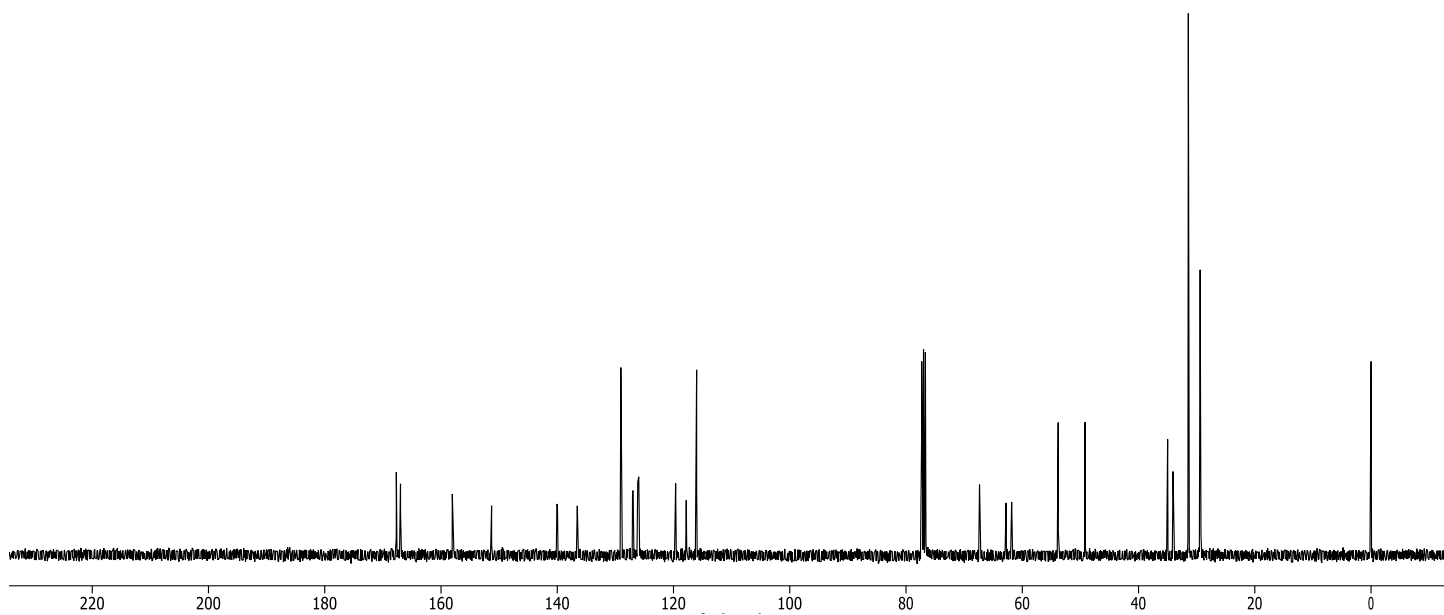
16d



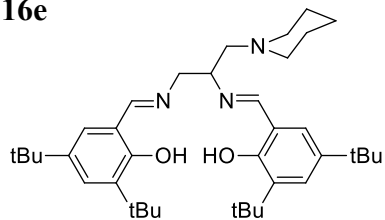
CDCl₃ - 400 MHz



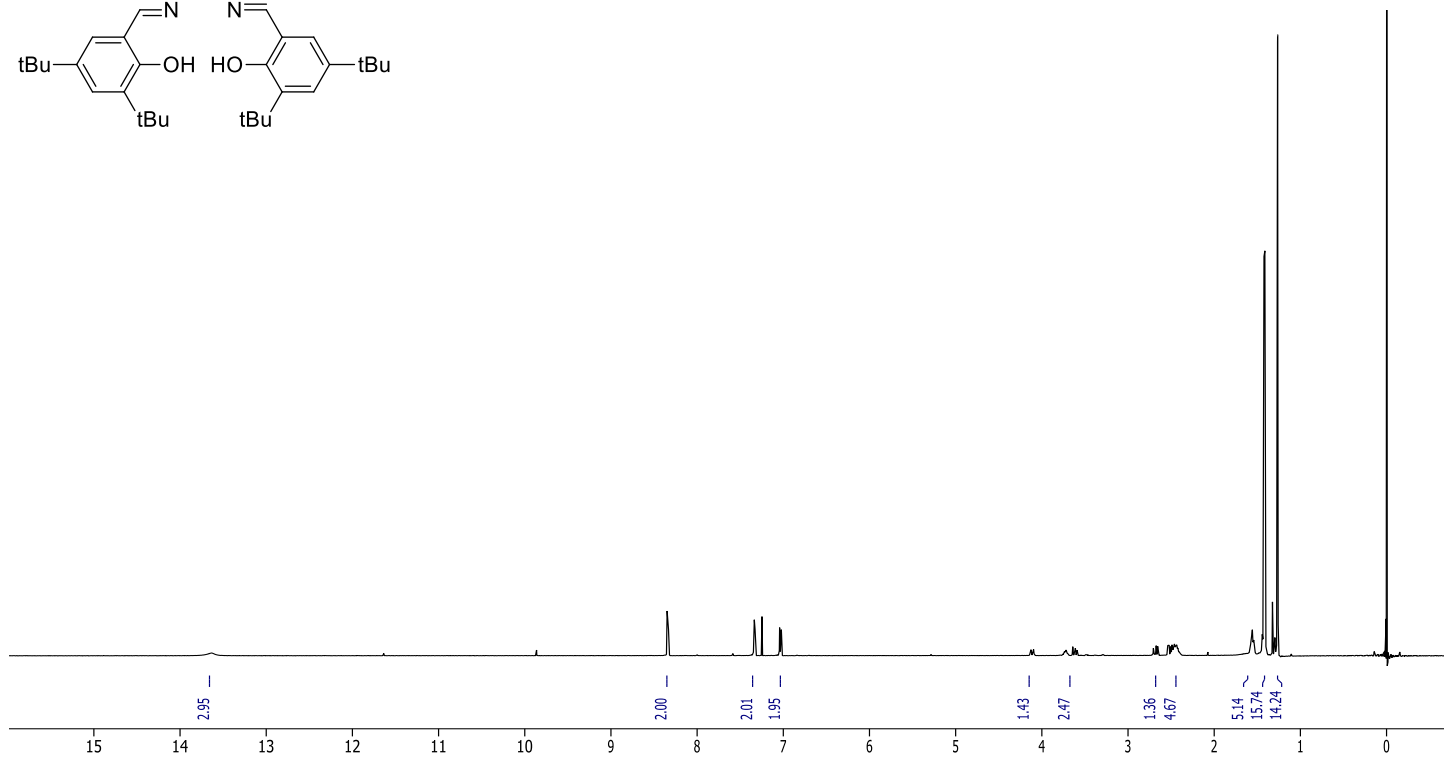
CDCl₃ - 100 MHz



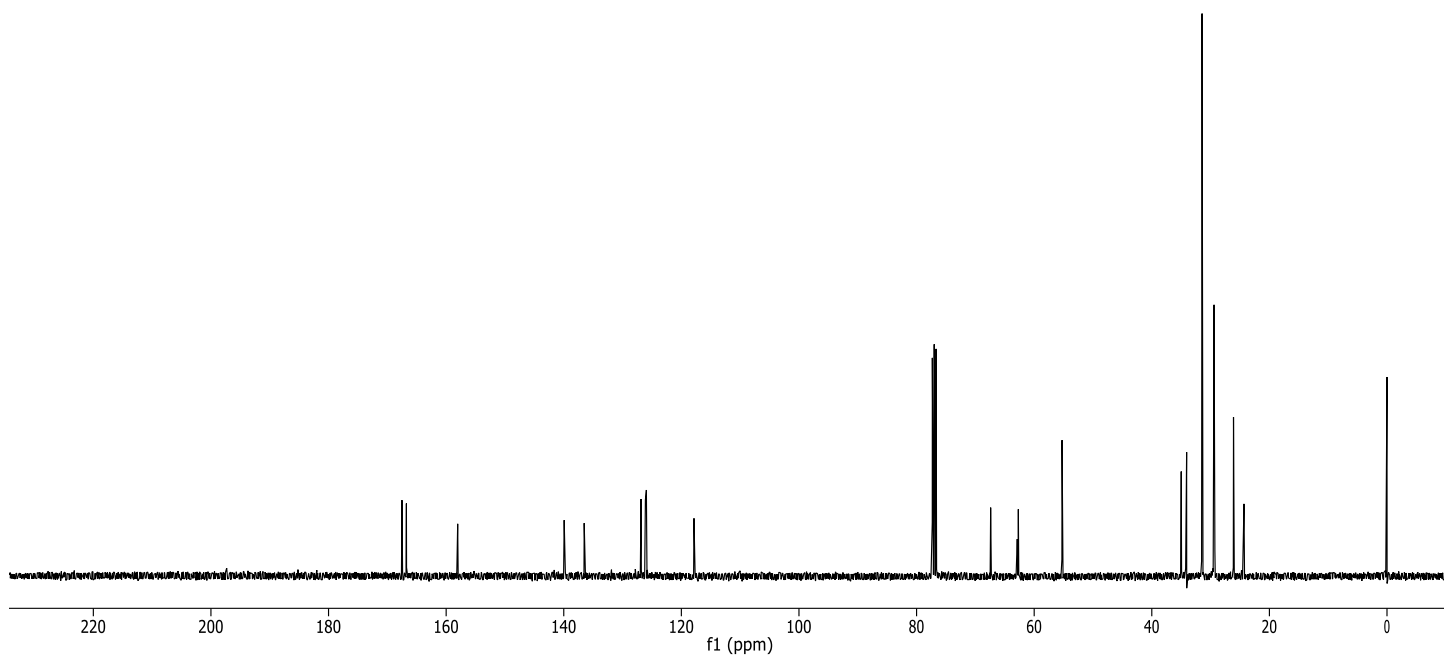
16e



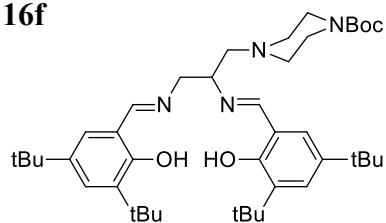
CDCl₃ - 400 MHz



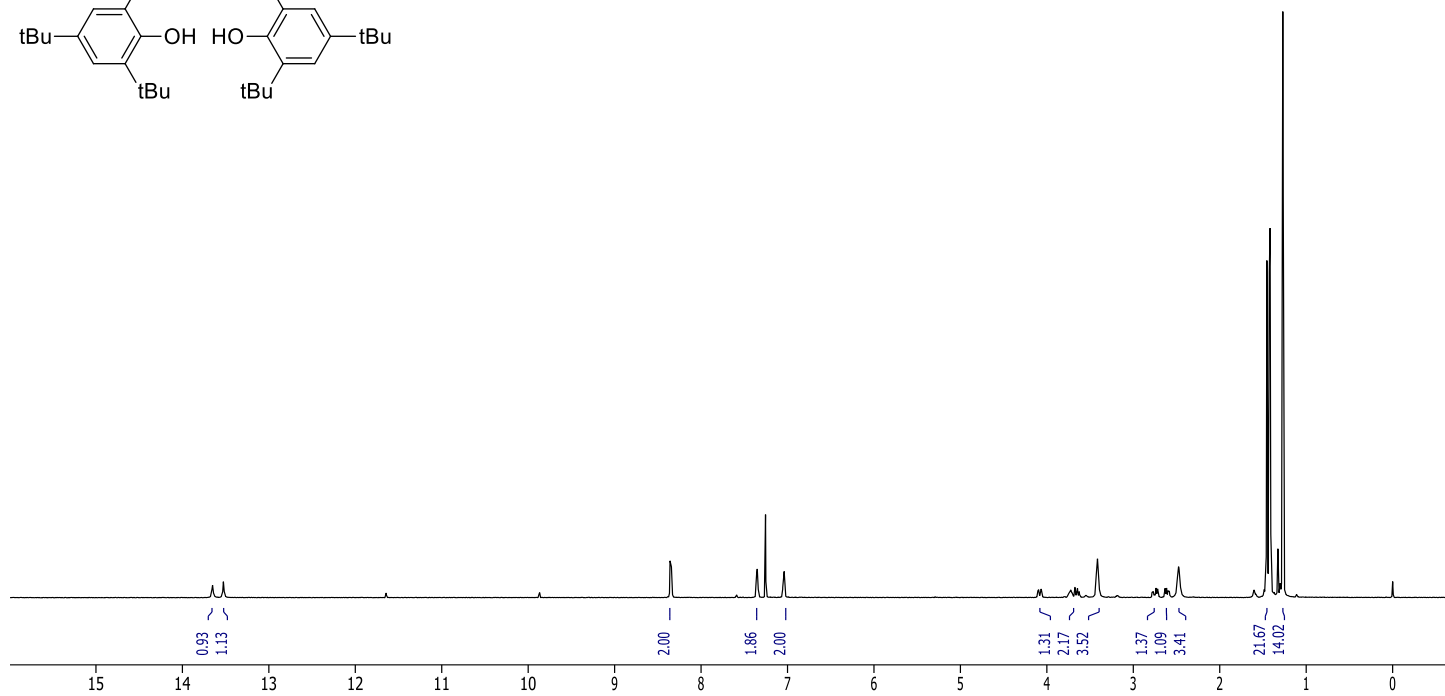
CDCl₃ - 100 MHz



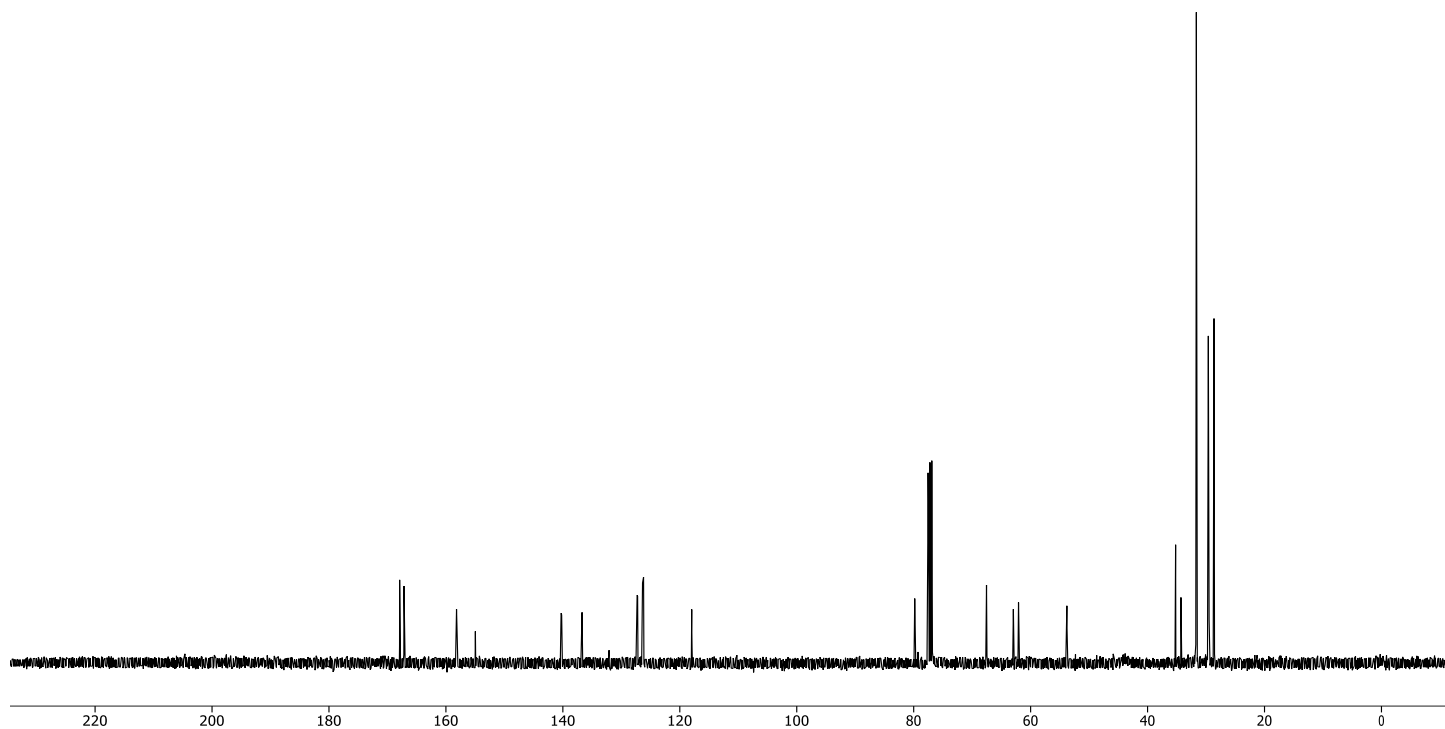
16f



CDCl₃ - 400 MHz



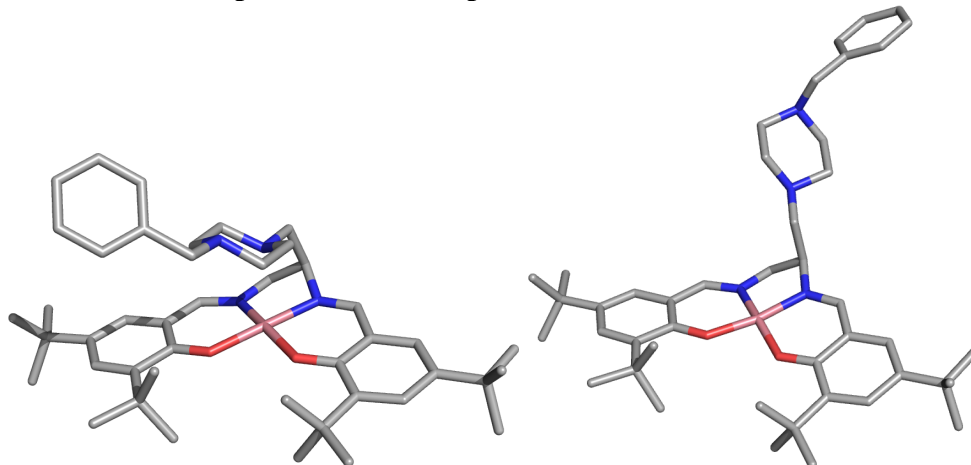
CDCl₃ - 100 MHz



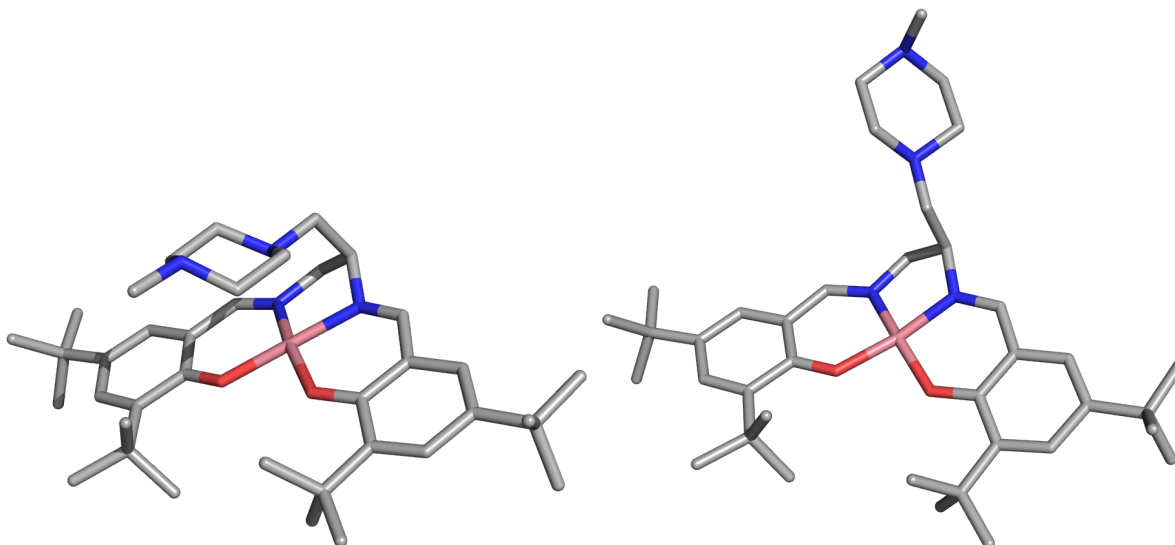
6. Computational methodology

All calculations were performed at the M06-2X level of theory with a mixed basis set using 6-31G(d) for C, H, N, and O and the LANL2DZ basis set for Co. Full geometry optimizations were carried out. The structures were modeled as neutral doublets (i.e. a single unpaired electron) with unrestricted calculations done for each structure. All calculations were done using Gaussian 09, revision B.01.

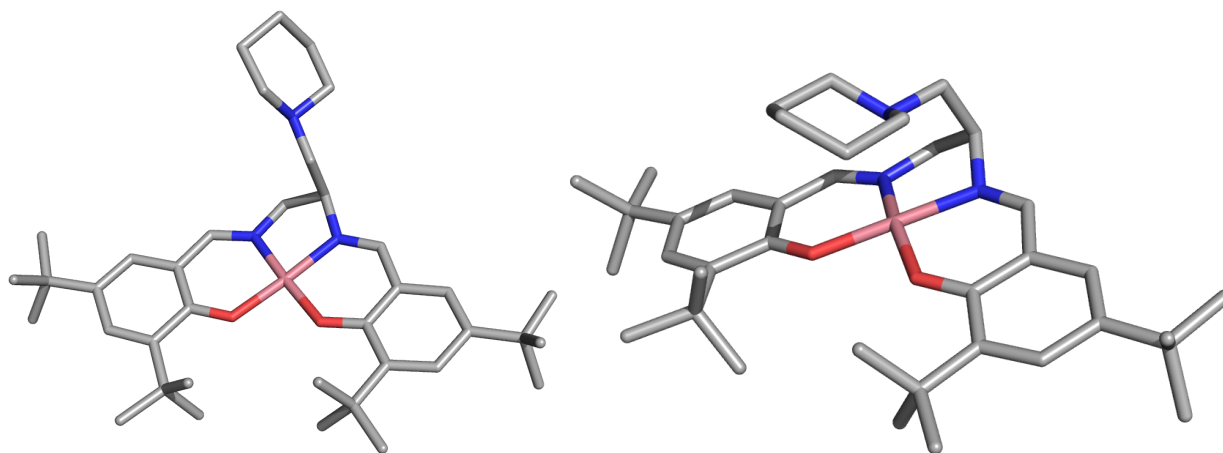
Conformational differences for representative compounds



Endo and *exo* conformations of complex 17a; the *endo* is 11.24 kcal more stable



Exo and *endo* conformations of complex 17c; the *endo* is 10.51 kcal more stable



Exo and *endo* conformations of 17e; the *endo* is 10.05 kcal more stable