Supporting Information

Mechanism-Inspired Design of Bifunctional Catalysts for the Alternating Ring-Opening Copolymerization of Epoxides and Cyclic Anhydrides

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1. General Considerations

All manipulations of air and water sensitive compounds were carried out under nitrogen in an MBraun Labmaster glove box or by using standard Schlenk line technique. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV III HD (^{1}H, 500 MHz) spectrometer with a broad band Prodigy cryoprobe or Varian INOVA 400 (^{1}H, 400 MHz) spectrometer. Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra were referenced to protons on the residual solvent (for ^{1}H) and deuterated solvent itself (for ^{13}C). High-resolution mass spectrometry (HRMS) analyses were performed on a Thermo Scientific Exactive Orbitrap MS system equipped with an Ion Sense DART ion source.

Gel permeation chromatography (GPC) analyses were carried out using an Agilent 1260 Infinity GPC System equipped with an Agilent 1260 Infinity autosampler and a refractive index detector. The Agilent GPC system was equipped with two Agilent PolyPore columns (5 micron, 4.6 mm ID) which were eluted with THF at 30 °C at 0.3 mL/min and calibrated using monodisperse polystyrene standards. Flash column chromatography was performed using silica gel (particle size 40–64 μm, 230–400 mesh).

2. Materials

2.1. General Materials

Solvents for air sensitive reactions were purchased from Fisher and sparged with ultrahigh purity (UHP) grade nitrogen and either passed through two columns containing reduced copper (Q-5) and alumina (hexanes, PhMe, and THF) or passed through two columns of alumina (DCM) and dispensed into an oven-dried Straus flask, followed by three freeze-pump-thaw cycles, and vacuum transferred before use. Otherwise, solvents (EtOAc, Et_2O, hexanes, MeOH, EtOH, $CHCl_3$, DMF, pentane, heptane) were used as received. Triethylamine was dried over calcium hydride for

three days, vacuum transferred to an oven-dried Schlenk flask, degassed by three freeze-pump-thaw cycles, and stored under nitrogen. All other chemicals and reagents, except for polymerization materials (*vide infra*), were purchased from commercial sources (Aldrich, Oakwood Chemical, Strem, Advanced ChemBlocks Inc., TCI, Alfa Aesar, Acros, and Fisher) and used without further purification.

2.2. Polymerization Materials

Carbic anhydride (CPMA; Acros >99%) was recrystallized from a saturated solution of EtOAc and dried in vacuo 18 h before subliming at 65 °C under dynamic vacuum and storing under nitrogen. Phthalic anhydride (PA; Aldrich ≥99%) was purified by heating a 10 wt.% solution of PA in $CHCl_3$ to reflux for 30 min, followed by hot filtration through Celite. The filtrate was concentrated to 50% the original volume and PA recrystallized at –10 °C, followed by sublimation at 70 °C under dynamic vacuum. 3,6-Dimethylphthalic anhydride (DMA)[1] and rac-*cis*-endo-1-isopropyl-4-methyl-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (TMA)[2] were synthesized according to literature procedures and sublimed under dynamic vacuum. All anhydrides were stored at 22 °C in a glove box under nitrogen atmosphere.

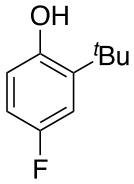
Epoxides were stirred over calcium hydride for at least three days, vacuum transferred to an oven-dried Straus flask, degassed by three freeze-pump-thaw cycles, and stored in a glove box under nitrogen atmosphere.

Bis(triphenylphosphine)iminium chloride ([PPN]Cl, 97%, Aldrich) was recrystallized by layering a saturated DCM solution with dry, degassed Et_2O. The resulting crystals were ground into a fine powder and then dried at 60 °C under vacuum prior to use. Tetrabutyl ammonium bromide (>98% Aldrich) was dried in vacuo at 60 °C for 18 h prior to use.

3. Synthesis

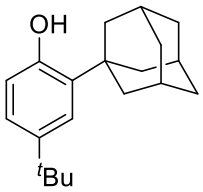
3.1. Salicylaldehyde Syntheses

2-*tert*-Butyl-4-fluorophenol (S1)



Concentrated sulfuric acid (4 mL) was added dropwise to a solution of 4-fluorophenol (5.0 g, 44.6 mmol, 1.0 equiv) in *tert*-butanol (8.50 mL, 88.9 mmol, 2.0 equiv), resulting in a color change from pale yellow to orange. The reaction mixture was stirred at 22 °C for 18 h before diluting with Et_2O (70 mL). The lower acid layer was removed, and the resulting organic phase neutralized with saturated aq. $NaHCO_3$ (12 mL) then washed with brine (100 mL) and dried over $MgSO_4$. The concentrated product was purified by silica column chromatography (95:5, hexanes:EtOAc R_f = 0.30) to afford a pale yellow oil (2.83 g, 38% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.99 (dd, *J* = 10.9, 2.9 Hz, 1H), 6.76 (m, 1H), 6.59 (dd, *J* = 8.7, 4.9 Hz, 1H), 4.67 (s, 1H), 1.40 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 157.1, 150.0, 138.0, 116.9, 114.0, 112.6, 34.7, 29.3. **HRMS** (DART-MS): *m/z* calculated for $C_{10}H_{13}FO$ $[M]^{\bullet+}$ 168.0950, found 168.0949. Characterization data were consistent with literature reports.[3]

2-(Adamantan-1-yl)-4-*tert*-butylphenol (S2)

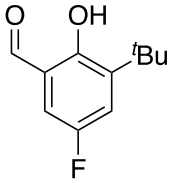


Tert-butyl phenol (4.0 g, 26.6 mmol, 1.0 equiv) and 1-adamantanol (4.05 g, 26.6 mmol, 1.0 equiv) were dissolved in DCM (45 mL) and the solution cooled to 0 °C. Concentrated sulfuric acid (1.6 mL, 30.0 mmol, 1.13 equiv) was added dropwise, and the reaction mixture warmed to 22 °C and stirred for 18 h. The acid layer was removed, and the organic phase neutralized with 1 M NaOH before washing with saturated aq. $NaHCO_3$ and brine before drying over $MgSO_4$. Concentrating in vacuo afforded a white solid that was purified by silica column chromatography (95:5 hexanes:EtOAc, R_f = 0.33) to yield a white solid (5.58 g, 74% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.27 (s, 1H), 7.08 (d, *J* = 8.2 Hz, 1H),

6.59 (d, J = 8.2 Hz, 1H), 4.59 (br s, 1H), 2.19–2.13 (m, 6H), 2.13–2.08 (m, 3H), 1.85–1.75 (m, 6H), 1.31 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.96, 143.06, 135.50, 123.28, 123.28, 116.12, 40.59, 37.08, 36.86, 34.33, 31.63, 29.08. **HRMS** (DART-MS): *m/z* calculated for $C_{20}H_{28}O$ $[M]^{\bullet+}$ 284.2140, found 284.2137. Characterization data were consistent with literature reports.[4]

General Formylation Procedure. To an oven dried Schlenk flask equipped with stir bar was added the appropriately substituted phenol. The flask was placed under nitrogen, dry THF added via cannula, and the resulting solution cooled to 0 °C. MeMgBr (3.0 M in Et_2O) was added dropwise via syringe over 5 min. The reaction mixture was warmed to 22 °C and stirred for 30 min. Dry triethylamine was added via syringe, followed by paraformaldehyde against positive nitrogen pressure. The reaction mixture was then heated to reflux (70 °C) for 18 h. After cooling to 0 °C, an equal volume of 1 M HCl was added and the resulting biphasic mixture transferred to a separatory funnel. The mixture was extracted three times with Et_2O. The combined organic extracts were washed with brine before drying over magnesium sulfate. Filtering and concentrating in vacuo afforded the crude product that was further purified by recrystallization or column chromatography as indicated below.

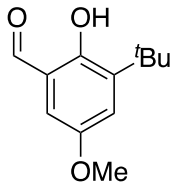
3-*tert*-Butyl-5-fluorosalicylaldehyde (S3)



According to the general formylation procedure, a solution of 2-*tert*-butyl-4-fluoro phenol (**S1**) (4.32 g, 25.7 mmol, 1.00 equiv) in dry THF (30 ML) was treated with 3.0 M in Et_2O MeMgBr (8.70 mL, 28.9 mmol, 1.12 equiv), triethylamine (5.74 mL, 41.1 mmol, 1.60 equiv), and paraformaldehyde (2.32 g, 77.1 mmol, 3.00 equiv). The product was recrystallized by cooling a saturated hexanes solution to –10 °C and was isolated as a yellow crystalline solid (4.74 g, 94% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 11.58 (s, 1H), 9.82 (s, 1H),

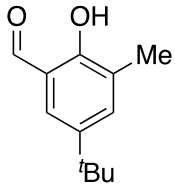
7.29 (dd, *J* = 10.5, 3.1 Hz, 1H), 7.07 (dd, *J* = 7.0, 3.1, 1H), 1.41 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 196.24, 157.71, 156.32, 154.43, 141.23, 122.54, 122.35, 120.00, 119.94, 115.67, 115.50, 35.25, 29.10. **HRMS** (DART-MS): *m/z* calculated for $C_{11}H_{14}FO_2$ $[M+H]^+$ 197.09723, found 197.09792. Characterization data were consistent with literature reports.[5]

3-*tert*-Butyl-5-methoxysalicylaldehyde (S4)



According to the general formylation procedure, a solution of 2-*tert*-butyl-4-methoxyphenol (**S2**) (5.00 g, 27.7 mmol, 1.00 equiv) in dry THF (50 mL) was treated with 3.0 M in Et_2O MeMgBr (11.6 mL, 34.7 mmol, 1.25 equiv), triethylamine (6.19 mL, 44.3 mmol, 1.60 equiv), and paraformaldehyde (2.50 g, 83.2 mmol, 3.00 equiv). The crude product was purified by column chromatography (95:5 hexanes:EtOAc, R_f = 0.31) to give a yellow oil (5.20 g, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 11.51 (s, 1H), 9.84 (s, 1H), 7.17 (d, *J* = 3.0 Hz, 1H), 6.81 (d, *J* = 3.1 Hz, 1H), 3.81 (s, 3H), 1.41 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 196.76, 156.33, 152.15, 140.29, 124.00, 119.94, 111.83, 55.90, 35.12, 29.24. **HRMS** (DART-MS): *m/z* calculated for $C_{12}H_{16}O_3$ $[M]^{\bullet+}$ 208.1099, found 208.1097. Characterization data were consistent with literature reports.[6]

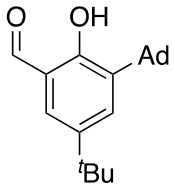
3-Methyl-5-*tert*-butylsalicylaldehyde (S5)



According to the general formylation procedure, a solution of 2-methyl-4-*tert*-butylphenol (7.00 g, 42.6 mmol, 1.0 equiv) in dry THF (50 mL) was treated with 3.0 M in Et_2O MeMgBr (15.6 mL, 46.9 mmol, 1.1 equiv), triethylamine (9.51 mL, 68.2 mmol, 1.6 equiv), and paraformaldehyde (3.84 g, 128 mmol, 3.0 equiv). The crude product was purified by column chromatography (95:5 hexanes:EtOAc, R_f = 0.26) to give a pale yellow oil that solidified upon drying 18 h in vacuo (5.80 g, 71% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ

11.11 (s, 1H), 9.87 (s, 1h), 7.44 (s, 1H), 7.35 (s, 1H), 2.28 (s, 3H), 1.32 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 196.93, 157.88, 142.15, 135.72, 127.31, 126.23, 119.39, 33.98, 31.27, 15.28. **HRMS** (DART-MS): *m/z* calculated for $C_{12}H_{16}O_2$ $[M]^{\bullet+}$ 192.1150, found 192.1147. Characterization data were consistent with literature reports.[7]

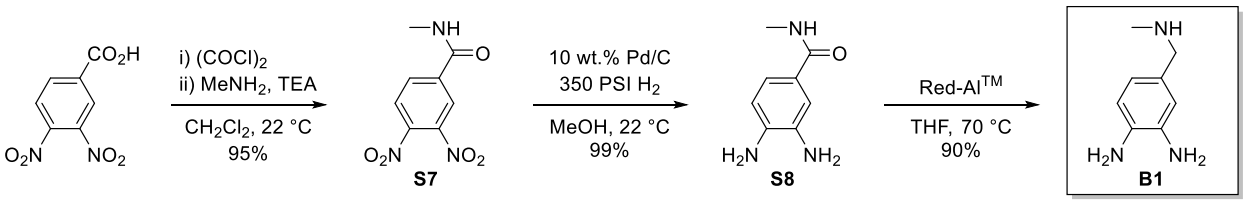
3-(Adamantan-1-yl)-5-*tert*-butylsalicylaldehyde (S6)



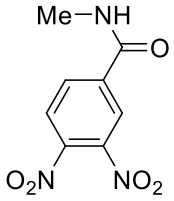
According to the general formylation procedure, 2-(adamantan-1-yl)-4-*tert*-butylphenol (**S2**) (5.0 g, 17.6 mmol, 1.0 equiv) was treated with 3.0 M in Et_2O MeMgBr (6.45 mL, 19.4 mmol, 1.1 equiv), triethylamine (3.90 mL, 28.2 mmol, 1.6 equiv), and paraformaldehyde (1.58 g, 52.8 mmol, 3 equiv). No additional purification following work up was required. The product was isolated as a white solid (4.59, 48% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 11.70 (s, 1H), 9.87 (s, 1H), 7.54 (s, 1H), 7.34 (s, 1H), 2.18–2.13 (m, 6H), 2.13–2.07 (m, 3H), 1.81–1.78 (m, 6H), 1.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 197.42, 159.34, 141.69, 137.78, 131.95, 127.68, 119.96, 40.18, 37.21, 37.00, 34.28, 31.31, 28.96. **HRMS** (DART-MS): *m/z* calculated for $C_{21}H_{28}O_2$ $[M]^{\bullet+}$ 312.2089, found 312.2089. Characterization data were consistent with literature reports.[4]

3.2. Diamine Backbone Syntheses

Scheme S1. Synthesis of 4-*N*-methyl-methanamine-1,2-diaminobenzene (**B1**).

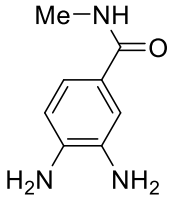


3,4-Dinitro-*N*-methyl-benzamide (S7)



A round bottom flask equipped with stir bar was charged with 3,4-dinitrobenzoic acid (6.37 g, 30.0 mmol, 1.0 equiv) and placed under nitrogen. Dry, degassed DCM (100 mL) was then added via syringe. The solution was cooled to 0 °C, and oxalyl chloride (3.09 mL, 36.0 mmol, 1.2 equiv) was added via syringe, followed by 12 drops of dry DMF. The mixture was stirred at 0 °C for 10 min before warming to 22 °C and stirring for 2 h. The reaction mixture was then concentrated in vacuo. The crude acid chloride was redissolved in dry DCM (100 mL), and the resultant solution cooled to 0 °C. Dry triethylamine (6.28 mL, 45.0 mmol, 1.5 equiv) and a 2.0 M solution of methylamine in THF (16.5 mL, 33.0 mmol, 1.1 equiv) were added sequentially via syringe. The reaction mixture was stirred at 0 °C for 30 min and then at 22 °C for 4 h. The reaction mixture was then concentrated by rotary evaporation and the resulting solid suspended in 0.1 M HCl (100 mL). After stirring for 30 min at 22 °C, the solids were isolated by vacuum filtration. The resulting pale-yellow powder **S7** was dried for 18 h in vacuo at 22 °C (6.44 g, 95% yield). **^{1}H NMR** (500 MHz, DMSO-d_6): δ 8.97 (s, 1H), 8.58 (s, 1H), 8.34 (s, 2H), 2.83 (d, J = 4.6 Hz, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 162.93, 143.21, 141.64, 139.23, 133.07, 126.00, 124.35, 26.50. **HRMS** (DART-MS): *m/z* calculated for $C_8H_8N_3O_5$ $[M+H]^+$ 226.04585, found 226.04585.

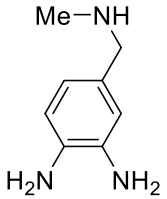
3,4-Diamino-*N*-methyl-benzamide (S8)



A 100 mL beaker containing stir bar was charged with 3,4-dinitro-*N*-methyl-benzamide (**S7**) (6.15 g, 27.3 mmol, 1.0 equiv), 10 wt.% Pd/C (0.35 g), and methanol (80 mL), and the beaker placed in a Parr pressure reactor. The reactor was pressurized with H_2 to 350 PSI and vented three times before pressurizing with H_2 to a final pressure of 350 PSI and sealing. The reaction mixture was stirred at 22 °C for 18 h before slowly

venting into a fume hood. The solution was filtered through a plug of Celite, and the filtrand washed with methanol (3 x 20 mL). The filtrate was collected, diluted with PhMe (50 mL), and the solvent removed by rotary evaporation. The resulting dark oil was azeotroped with PhMe (3 x 50 mL) until a reddish-brown powder was obtained (4.50 g, 99% yield). The isolated solid **S8** was stored at –10 °C under nitrogen. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 7.82 (d, J = 4.3 Hz, 1H), 7.04 (d, J = 1.8 Hz, 1H), 6.93 (dd, J = 8.1, 1.9 Hz, 1H), 6.46 (d, J = 8.1 Hz, 1H), 4.91 (s, 1H), 4.53 (s, 1H), 2.69 (d, J = 4.5 Hz, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 167.34, 138.15, 133.85, 123.09, 116.83, 113.75, 112.75, 26.13. **HRMS** (DART-MS): *m/z* calculated for $C_8H_{12}N_3O$ $[M+H]^+$ 166.09749, found 166.09806.

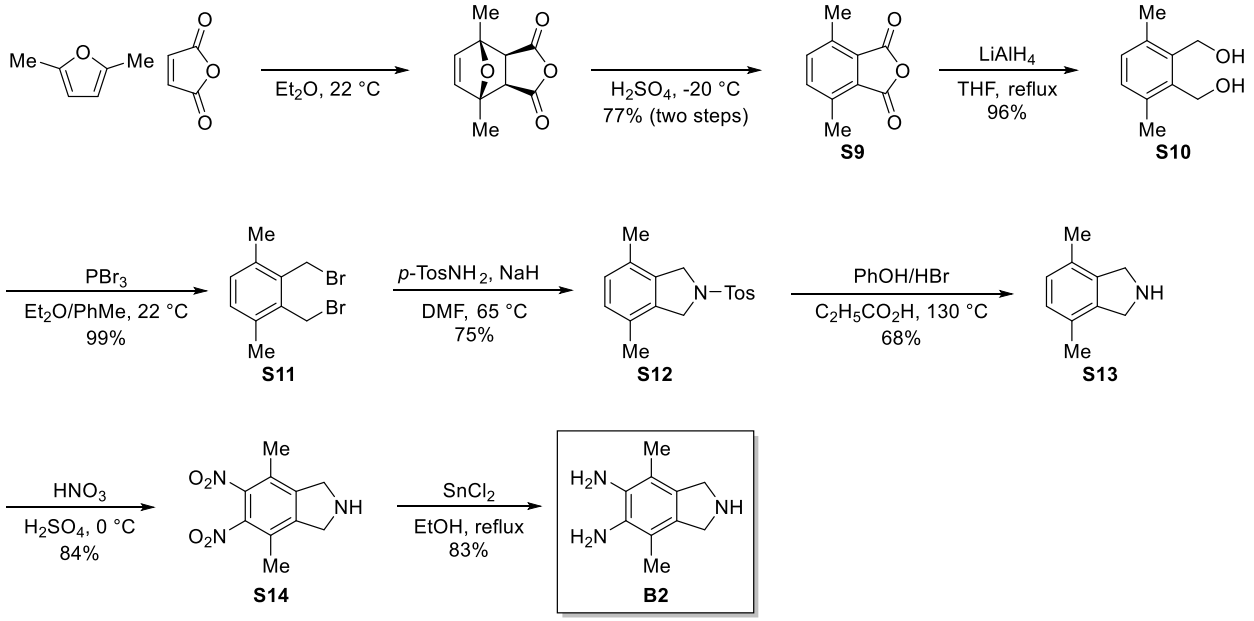
4-*N*-Methyl-methanamine-1,2-diaminobenzene (B1)



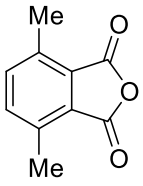
A 250 mL round-bottom flask containing a stir bar was charged with 3,4-diamino-*N*-methyl-benzamide (**S8**) (4.30 g, 26.0 mmol, 1.0 equiv), fitted with a reflux condenser, and placed under nitrogen by evacuating/backfilling the reaction setup with nitrogen three times. The condenser was then fitted with a nitrogen inlet/outlet, and dry THF (125 mL) was added via cannula before cooling the resulting solution to 0 °C. RedAl® (65 wt% in PhMe) (42 mL, 142 mmol, 5.4 equiv) was added via syringe over 10 min and the reaction mixture heated to 75 °C for 18 h under nitrogen. The reaction mixture was then quenched by cooling to 0 °C, slowly adding H_2O (4.0 mL) then 2 M NaOH (4.0 mL), and subsequently stirring the mixture at 22 °C for 15 min. $MgSO_4$ (8 g) was added and the mixture stirred a further 15 min at 22 °C before filtering through Celite and washing the filtrand with EtOAc (50 mL). The filtrate was concentrated in vacuo to give a dark brown oil that was dried in vacuo for 18 h to provide the product **B1** as a sticky brown solid that was stored under nitrogen at –10 °C (3.55 g, 90% yield). **^{1}H NMR** (500 MHz, DMSO-d_6): δ 6.46 (s, 1H), 6.42 (d, 1H, J = 7.63), 6.31 (d, 1H, J = 7.60),

3.55–3.50 (m, 1H), 3.36 (s, 2H), 3.33–3.27 (m, 2H), 3.23 (s, 2H), 2.20 (s, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 134.64, 133.39, 129.48, 117.03, 114.59, 114.19, 55.35, 35.49. **HRMS** (DART-MS): *m/z* calculated for $C_8H_{13}N_3$ $[M]^{\bullet+}$ 151.11095, found 151.11040.

Scheme S2. Synthesis of 4,7-dimethyl-5,6-diaminoisoindoline (**B2**).



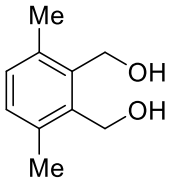
3,6-Dimethylphthalic anhydride (S9)



Using a modified procedure,[1] a mixture of mortar-ground maleic anhydride (13.6 g, 139 mmol, 1.00 equiv) and 2,5-dimethylfuran (15.0 mL, 146 mmol, 1.05 equiv) in Et_2O (15 mL) was prepared in a 250 mL round-bottom flask containing a stir bar and stirred for 3 h at 22 °C. The heterogenous mixture was then diluted with hexanes (15 mL), cooled to 0 °C using an ice bath, and the resulting solids isolated by vacuum filtration. The isolated product was washed once with a 1:1 (v:v) mixture of hexanes:Et_2O (75 mL) before drying in vacuo for 1 h, affording the product as a white crystalline solid (19.0 g, 71% yield). The product was used immediately in the next step due to rapid decomposition of the Diels-Alder adduct intermediate under ambient temperature. A 500 mL round-bottom flask was first charged with

concentrated sulfuric acid (190 mL) and subsequently cooled to –20 °C using an ice-methanol bath. The Diels-Alder adduct intermediate (17.1 g, 88.1 mmol, 1 equiv) was then added portionwise as a solid over 30 min to vigorously stirred concentrated sulfuric acid (175 mL) while maintaining the reaction temperature below –10 °C. The pale orange reaction mixture was stirred for 30 min at –20 °C and then 3 h at 0 °C before pouring onto ice (1000 g). The resulting solids were isolated by vacuum filtration, rinsed with deionized H_2O (2 x 100 mL), and dried for 18 h in vacuo to give the product as a white solid (13.2 g, 77% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.50 (s, 2H), 2.67 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 163.39, 137.92, 137.89, 128.61, 17.50. **HRMS** (DART-MS): *m/z* calculated for $C_{10}H_9O_3$ $[M+H]^+$ 177.0546, found 177.05539. Characterization data were consistent with literature reports.[1]

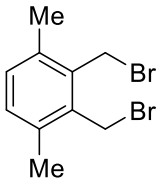
3,6-Dimethyl-1,2-bis(hydroxymethyl)benzene (S10)



Using a modified procedure,[1] a suspension of $LiAlH_4$ (8.82 g, 233 mmol, 4.0 equiv) in dry THF (90 mL) was first prepared under nitrogen in a 500 mL 3-neck round-bottom flask equipped with reflux condenser and nitrogen inlet and outlet. A solution of 3,6-dimethylphthalic anhydride (**S9**) (10.2 g, 58.0 mmol, 1.0 equiv) in dry THF (90 mL) was then added via cannula over 45 min at 22 °C to the stirred suspension of $LiAlH_4$ in THF while venting the reaction to an oil bubbler. The reaction mixture was then stirred at reflux (70 °C) for 18 h and subsequently cooled to 0 °C using an ice bath. The reaction mixture was diluted with Et_2O (200 mL) and slowly quenched via sequential addition of H_2O (8.8 mL), 15 wt.% aq. NaOH (8.8 mL), and H_2O (24 mL). The mixture was stirred at 22 °C for 15 min, $MgSO_4$ (10 g) added, and stirring continued for an additional 15 min. The mixture was then filtered through a Celite pad and the filtrand washed with a 90:10 (v:v) mixture of EtOAc:EtOH (300 mL). The combined filtrates were dried over Na_2SO_4 and the solvent removed by rotary evaporation to give an oil that

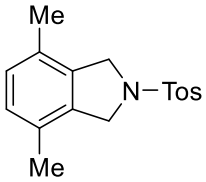
solidified into a pale-yellow solid upon drying in vacuo (9.23 g, 96% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.04 (s, 2H), 4.71 (d, *J* = 3.9 Hz, 4H), 3.26 (s, 2H), 2.37 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 138.13, 135.01, 130.44, 59.38, 19.63. **HRMS** (DART-MS): *m/z* calculated for $C_{10}H_{14}O_2$ $[M]^{\bullet+}$ 166.0994, found 166.0990. Characterization data were consistent with literature reports.[1]

3,6-Dimethyl-1,2-bis(bromomethyl)benzene (S11)



According to a literature procedure,[1] a solution of PBr_3 (11.0 mL, 116 mmol, 2.1 equiv) in dry Et_2O (21 mL) was added over 5 min at 22 °C to a stirred solution of 3,6-dimethyl-1,2-bis(hydroxymethyl)benzene (**S10**) (9.20 g, 55.3 mmol, 1.0 equiv) in dry PhMe (21 mL) and Et_2O (21 mL). The mixture was then stirred for 18 h at 22 °C, followed by pouring onto ice (220 g) and neutralizing with saturated aq. $NaHCO_3$ solution (65 mL). The solution was then transferred to a separatory funnel and extracted with Et_2O (3 x 150 mL). The organic extracts were combined, washed with brine (1 x 300 mL), and dried over Na_2SO_4. The solvent was removed in vacuo to give **S11** as a white solid (16.2 g, 99% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.07 (s, 2H), 4.68 (s, 4H), 2.39 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 136.10, 135.05, 131.28, 27.82, 19.28. Characterization data were consistent with literature reports.[1]

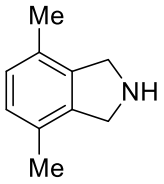
4,7-Dimethyl-2-tosylisoindoline (S12)



Using an adapted procedure,[8] a suspension of 95% NaH (0.82 g, 34.2 mmol, 2.5 equiv) in dry DMF (30 mL) was first prepared under nitrogen in a 250 mL round-bottomed flask fitted with a nitrogen inlet and outlet. A solution of *p*-toluenesulfonamide (5.86 g, 34.2 mmol, 2.5 equiv) in dry DMF (20 mL) was next added dropwise by syringe over 30 min at 22 °C to the stirred suspension of NaH, accompanied by the vigorous evolution of H_2 gas. The reaction mixture was stirred for 1 h at 22 °C and then heated to 65 °C for

1 h. A solution of 3,6-dimethyl-1,2-bis(bromomethyl)benzene (**S11**) (4.00 g, 13.7 mmol, 1.0 equiv) in dry DMF (45 mL) was next added to the *p*-toluenesulfonamide sodium salt solution at 110 °C and the reaction stirred for 3 h at 110 °C. The reaction mixture was cooled to 22 °C and poured onto ice (600 g), followed by stirring for 30 min. The resulting solids were isolated by vacuum filtration, rinsed with H_2O (150 mL), and dried in vacuo to give an off-white solid that was further purified by column chromatography to afford the product as a white solid (3.51 g, 75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 2H), 4.57 (s, 4H), 2.41 (s, 6H), 2.16 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 143.74, 134.93, 134.02, 129.96, 129.84, 128.89, 127.70, 53.58, 21.65, 18.41. **HRMS** (DART-MS): *m/z* calculated for $C_{17}H_{20}NO_2S$ $[M+H]^+$ 302.1209, found 302.1215.

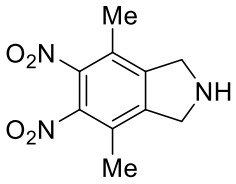
4,7-Dimethylisoindoline (S13)



Using an adapted procedure,[8] a 50 mL round-bottom flask containing a stir bar was charged with 4,7-dimethyl-2-tosylisoindoline (**S12**) (1.50 g, 4.98, 1.0 equiv), phenol (1.50 g), 48 wt.% HBr (12.0 mL), and propionic acid (2.0 mL). The reaction mixture was stirred vigorously while heating at 135 °C for 6 h. Upon cooling to 22 °C, the dark colored mixture was transferred to a separatory funnel and washed with Et_2O (2 x 50 mL), discarding the organic extracts. The remaining aqueous layer was then added dropwise over 10 min to a stirred solution of NaOH (10 g) in H_2O (25 mL). The basified aqueous layer was extracted with a 9:1 (v:v) mixture of Et_2O:EtOAC (5 x 45 mL), the organic extracts dried over anhydrous Na_2SO_4/K_2CO_3, and the solvent removed in vacuo to give the product as a dark colored oil that was stored under nitrogen in the dark at –10 °C (0.50 g, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.94 (s, 2H), 4.22 (s, 4H), 2.23 (s, 6H), 2.20 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 140.21,

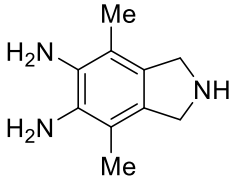
129.38, 127.80, 52.56, 18.61. **HRMS** (DART-MS): *m/z* calculated for $C_{10}H_{14}N$ $[M+H]^+$ 148.1121, found 148.1126.

4,7-Dimethyl-5,6-dinitroisoindoline (S14)



A mixture of concentrated sulfuric acid (12 mL) and 16 M nitric acid (3 mL) was first prepared at 0 °C and then added to a flask containing 4,7-dimethylisoindoline (**S13**) (0.50 g, 3.4 mmol, 1.0 eq). The mixture was stirred at 0 °C for 6 h, followed by stirring at 22 °C for 1 h. The reaction mixture was then added dropwise over 20 min to a stirred solution of NaOH (25 g) in H_2O (110 mL) at 0 °C. The basified solution was transferred to a separatory funnel and extracted with DCM (5 x 40 mL), followed by washing the combined organic extracts with saturated aq. $NaHCO_3$ (1 x 200 mL) and drying over Na_2SO_4. Solvent removal in vacuo afforded the product as a yellow solid (0.68 g, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.33 (s, 4H), 2.28 (s, 6H), 2.10 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 145.33, 143.57, 124.83, 53.35, 15.10. **HRMS** (DART-MS): *m/z* calculated for $C_{10}H_{12}N_3O_4$ $[M+H]^+$ 238.0822, found 238.0830.

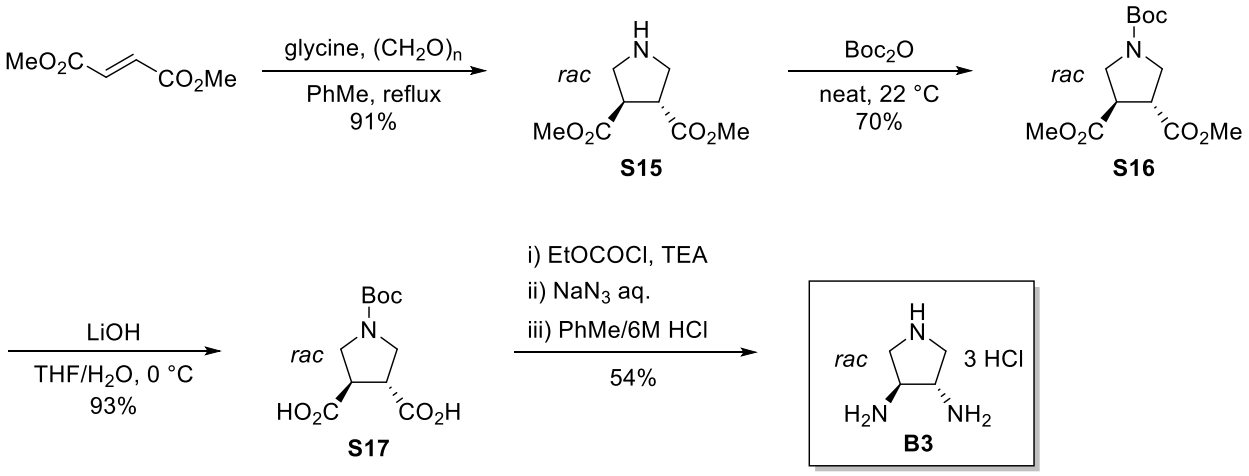
4,7-Dimethyl-5,6-diaminoisoindoline (B2)



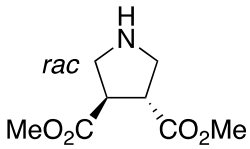
A solution of 4,7-dimethyl-5,6-dinitroisoindoline (**S14**) (1.36 g, 5.7 mmol, 1.0 equiv) and $SnCl_2$ (10.9 g, 57.3 mmol, 10 equiv) in absolute EtOH (50 mL) and H_2O (1 mL) was prepared under nitrogen and heated to reflux for 18 h. The reaction mixture was then cooled to 0 °C and the resulting yellow solids isolated by vacuum filtration. The solids were then dissolved in 2 M NaOH (50 mL) at 0 °C and the aqueous mixture extracted with $CHCl_3$ (3 x 75 mL), followed by drying the combined organic extracts over Na_2SO_4. The solvent was removed in vacuo to give the product as an orange solid that was stored under

nitrogen (0.85 g, 83% yield). **^{1}H NMR** (500 MHz, DMSO-d_6): δ 3.96 (s, 4H), 3.93 (b, 5H), 1.92 (s, 6H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 131.43, 128.54, 112.97, 52.28, 14.05. **HRMS** (DART-MS): *m/z* calculated for $C_{10}H_{16}N_3$ $[M+H]^+$ 178.1339, found 178.1346.

Scheme S3. *trans*-3,4-Pyrrolidine diamine trihydrochloride (**B3**).



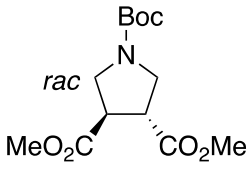
***trans*-3,4-Pyrrolidinedicarboxylic acid dimethyl ester (S15)**



According to a modified procedure,[9] a solution of dimethyl fumarate (6.00 g, 41.6 mmol, 1.0 equiv) in dry PhMe (200 mL) was prepared in a 500 mL 3-necked round-bottom flask equipped with Dean-Stark trap and reflux condenser. The solution was vigorously refluxed by heating in an oil bath heated to 150 °C, while a mortar-ground mixture of glycine (5.62 g, 74.9 mmol, 1.8 equiv) and paraformaldehyde (4.38 g, 146 mmol, 3.5 equiv) was added portion wise in 15 min intervals over 2 h. Stirring was continued for an additional 2 h at 150 °C, followed by cooling to 22 °C and filtering the mixture by vacuum filtration. The filtrate was collected and washed with saturated aq. $NaHCO_3$ (2 x 200 mL), brine (1 x 200 mL), and then dried over Na_2SO_4. Removal of the solvent in vacuo afforded the product as a pale-yellow oil that was used without further purification (7.06 g, 91% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.66 (s, 6H), 3.36 (p, *J* = 6.1 Hz, 2H), 3.13 (d, *J* = 5.3 Hz, 1H), 2.96–2.88 (m,

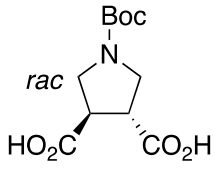
2H), 2.78 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 173.90, 74.59, 74.31, 55.10, 55.04, 52.27, 45.22. **HRMS** (DART-MS): *m/z* calculated for $C_8H_{14}NO_4$ $[M+H]^+$ 188.09173, found 188.09240. Characterization data were consistent with literature reports.[10]

***N*-Boc *trans*-3,4-Pyrrolidinedicarboxylic acid, dimethyl ester (S16)**



S15 (6.64 g, 35.5 mmol, 1.0 equiv) and di-*tert*-butyl dicarbonate (9.29 g, 42.6 mmol, 1.2 equiv) were combined in a 250 mL round-bottom flask under nitrogen and the mixture stirred for 24 h at 45 °C. The reaction mixture was then cooled to 22 °C and diluted with Et_2O (125 mL), followed by washing with 0.1 M HCl (1 x 100 mL), H_2O (1 x 100 mL), saturated aq. $NaHCO_3$ (1 x 100 mL), and brine (1 x 100 mL). The organic layer was isolated and dried over anhydrous $MgSO_4$, followed by concentration in vacuo to give an oil that was further purified by column chromatography (70:30 hexanes:EtOAc, R_f = 0.35), affording the product as a waxy solid (5.60 g, 70% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.72 (s, 8H), 3.49 (s, 2H), 3.39 (s, 2H), 1.43 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.24, 153.95, 80.07, 52.55, 47.96, 45.89, 45.12, 28.53. **HRMS** (DART-MS): *m/z* calculated for $C_8H_{14}NO_4$ $[M–Boc+H]^+$ 188.09173, found 188.09241.

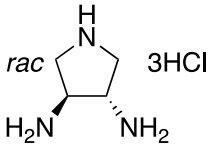
***N*-Boc *trans*-3,4-Pyrrolidinedicarboxylic acid (S17)**



A solution of **S16** (5.40 g, 19.2 mmol, 1.0 equiv) in a 1:1 (v:v) mixture of THF and H_2O (100 mL) was initially prepared at 22 °C and then cooled to 0 °C using an ice bath. LiOH•H_2O (4.03 g, 96.0 mmol, 5.0 equiv) was added as a solid and the mixture vigorously stirred at 0 °C for 3 h. The reaction mixture was warmed to 22 °C and concentrated to approximately half the original volume. The solution was then cooled to 0 °C and acidified to pH ~2 by slow addition of 1 M HCl. The acidified mixture was saturated with NaCl

(35 g) and extracted with $CHCl_3$ (5 x 75 mL), adding small amounts (~5 mL) of 1 M HCl to the aqueous phase after isolation of each organic extract. The organic extracts were combined, diluted with EtOH (100 mL) and dried over anhydrous Na_2SO_4. Note: the addition of EtOH improves the solubility of the diacid product to prevent precipitation while drying over Na_2SO_4. The solvent was removed in vacuo and the product obtained as a white solid (4.56 g, 93% yield). **^{1}H NMR** (500 MHz, DMSO-d_6): δ 3.51 (t, J = 8.1 Hz, 2H), 3.34 (q, J = 10.3 Hz, 2H), 3.21–3.03 (m, 2H), 1.39 (s, 9H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 173.45, 153.23, 78.51, 48.07, 45.46, 44.65, 28.14. **HRMS** (DART-MS): *m/z* calculated for $C_6H_{10}NO_4$ $[M–Boc+H]^+$ 160.06043, found 160.06118. Characterization data were consistent with literature reports.[11]

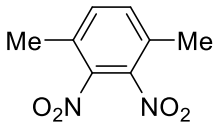
***trans*-3,4-Pyrrolidine diamine trihydrochloride (B3)**



CAUTION: *Sodium azide is toxic and must be kept away from acids, halogenated solvents, and heavy metals due to the risk of forming energetically unstable compounds. Organic azides can decompose energetically in response to thermal or mechanical shock. Such compounds must be handled carefully and only by skilled persons in accordance with Environmental Health & Safety guidelines.*[12] A solution of **S17** (4.60 g, 17.7 mmol, 1.0 equiv) and dry triethylamine (12.4 mL, 88.7 mmol, 5.0 equiv) in dry THF (200 mL) was prepared under nitrogen in a 500 mL round-bottom flask equipped with a stir bar and the solution cooled to 0 °C using an ice bath. Ethyl chloroformate (6.76 mL, 70.9 mmol, 4.0 equiv) was added dropwise by syringe over 5 min and the reaction mixture stirred for 30 min at 0 °C. A solution of NaN_3 (9.23 g, 142 mmol, 8.0 equiv) in H_2O (40 mL) was then added via syringe and the reaction mixture stirred vigorously for 3 h at 0 °C. Upon warming to 22 °C, the reaction mixture was transferred to a separatory funnel and extracted with Et_2O (3 x 120 mL). The organic extracts were combined, washed with brine (1 x 250 mL), and dried over $MgSO_4$. The solution of bisacyl

azide was transferred to an oven-dried 500 mL round-bottom flask containing dry PhMe (125 mL) and a stir bar. The flask was fitted with a reflux condenser and concentrated at 22 °C in vacuo to a final volume of ~80 mL, followed by backfilling with nitrogen. Note: do not fully concentrate or isolate the bisacyl azide due to the potential instability of this compound in its pure form. The solution of bisacyl azide in PhMe was then heated at reflux for 1 h, accompanied by slow evolution of nitrogen gas during the Curtius rearrangement. The reaction mixture was cooled to 22 °C and diluted with 6 M HCl (100 mL) and the mixture stirred vigorously for 18 h at 22 °C. The aqueous layer was isolated, washed with PhMe (1 x 50 mL), and vacuum distilled to dryness. The resulting pink-colored solid was triturated with methanol (3 x 15 mL) and dried in vacuo to give a hygroscopic off-white solid (2.01 g, 54% yield). **^{1}H NMR** (500 MHz, D_2O): δ 4.42 (p, *J* = 6.0 Hz, 2H), 4.12 (dd, *J* = 13.2, 7.7 Hz, 2H), 3.70 (dd, *J* = 13.2, 6.8 Hz, 2H). **^{13}C NMR** (125 MHz, D_2O): δ 52.31, 47.67. **HRMS** (DART-MS): *m/z* calculated for $C_4H_{12}N_3$ $[M+H]^+$ 102.10312, found 102.10348.

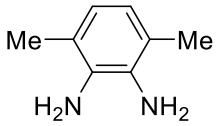
1,4-Dimethyl-2,3-dinitrobenzene (S18)



According to a literature procedure,[13] *p*-xylene (11.5 mL, 93.3 mmol, 1.0 equiv) was added to concentrated sulfuric acid (10 mL) at 0 °C, followed by the dropwise addition of a 1:1 (v:v) mixture of concentrated sulfuric acid and concentrated nitric acid (24 mL) over 5 min. The reaction was then heated at 80 °C for 30 min, cooled to 22 °C, and the mixture poured onto ice (100 g). The aqueous mixture was extracted with DCM (3 x 60 mL) and the combined organic extracts washed with H_2O (3 x 60 mL), saturated aq. $NaHCO_3$ (1 x 60 mL), and dried over $MgSO_4$, followed by solvent removal in vacuo to give a pale-yellow solid. The crude product was further purified by column chromatography (75:25 hexanes:EtOAc, R_f = 0.38) to afford the product as a yellow solid (5.80 g, 32% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.39

(s, 2H), 2.42 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 134.08, 130.78, 18.00. **HRMS** (DART-MS): *m/z* calculated for $C_8H_7N_2O_4$ $[M–H]^-$ 195.0400, found 195.0407.

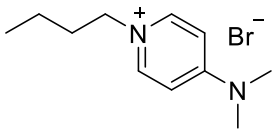
3,6-Dimethyl-1,2-diaminobenzene (S19)



A 20 mL vial containing a stir bar was charged with 1,4-dimethyl-2,3-dinitrobenzene (**S18**) (1.00 g, 5.1 mmol, 1.0 equiv), 10 wt.% Pd/C (100 mg), and MeOH (3 mL), followed by placing the uncapped vial in a Parr pressure reactor. The reactor was filled and vented four times with H_2 to 350 PSI, sealing the reactor after the fourth pressurization. The reaction was stirred for 18 h at 22 °C, vented, and the solution filtered through Celite while rinsing the Celite pad with MeOH (5 mL). The filtrate was collected and concentrated in vacuo to give the product as a brown solid that was stored under nitrogen at –10 °C (0.69 g, 99% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.59 (s, 2H), 3.37 (s, 4H), 2.21 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 132.67, 121.43, 120.94, 17.51. **HRMS** (DART-MS): *m/z* calculated for $C_8H_{13}N_2$ $[M+H]^+$ 137.1073, found 137.1077.

3.3. Cocatalyst Syntheses

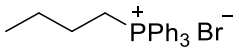
1-Butyl-4-dimethylaminopyridinium bromide ([DMAP]Br)



A solution of 4-dimethylaminopyridine (1.32 g, 10 mmol, 1.0 equiv) and 1-bromobutane (1.51 g, 11.0 mmol, 1.1 equiv) in PhMe (10 mL) was prepared in a 20 mL scintillation vial containing stir bar and the mixture heated at 90 °C for 18 h. The heterogeneous reaction mixture was then cooled to 22 °C and the solids isolated by vacuum filtration, followed by rinsing with PhMe (10 mL) and hexanes (20 mL). The resulting solids were dried in vacuo to afford the product as a white powder (2.40 g, 92% yield). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53–8.46 (m, 2H), 7.03–6.95 (m, 2H), 4.29 (t, *J* = 7.3 Hz, 2H), 3.21 (s, 6H), 1.80 (p, *J*

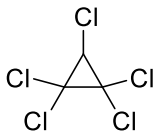
= 7.5 Hz, 2H), 1.29 (sx, *J* = 7.4 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 156.19, 142.54, 108.40, 57.90, 40.53, 33.05, 19.30, 13.56. **HRMS**-ESI: *m/z* calculated for $C_{11}H_{19}N_2$ $[M]^{\bullet+}$ 179.15428, found 179.15503. Characterization data were consistent with literature reports.[14]

Butyltriphenylphosphonium bromide ([PPh$_3$]Br)



A solution of triphenylphosphine (2.62 g, 10.0 mmol, 1.0 equiv) and 1-bromobutane (1.51 g, 11.0 mmol, 1.1 equiv) in PhMe (10 mL) was prepared in a 20 mL scintillation vial containing stir bar and the mixture heated at 90 °C for 18 h. The heterogeneous reaction mixture was cooled to 22 °C and the solids isolated by vacuum filtration, followed by rinsing with PhMe (10 mL) and hexanes (20 mL). The resulting solids were dried in vacuo to afford the product as a white powder (2.40 g, 92% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86–7.72 (m, 9H), 7.70–7.64 (m, 6H), 3.78–3.65 (m, 2H), 1.70–1.46 (m, 4H), 0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 135.09, 135.06, 133.73, 133.65, 130.61, 130.51, 118.71, 118.03, 24.69, 24.65, 23.85, 23.72, 22.90, 22.50, 13.83. **HRMS**-ESI: *m/z* calculated for $C_{22}H_{24}P$ $[M]^{\bullet+}$ 319.16101, found 319.16230. Characterization data were consistent with previous literature reports.[15]

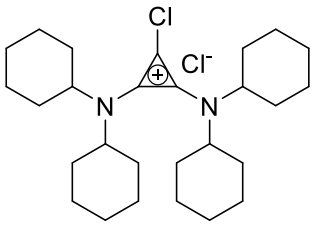
Pentachlorocyclopropane (S20)



Based on the method of West,[16] a 2 L 3-neck round-bottom flask fitted with reflux condenser was charged with sodium trichloroacetate (300 g, 1.00 eq, 1.62 mol), trichloroethylene (500 mL, 3.44 eq, 5.56 mol), and dimethoxyethane (145 mL) and the reaction mixture heated to reflux at 90 °C for three days. The dark brown heterogeneous mixture was cooled to 0 °C and then filtered. The isolated precipitate was dissolved in H_2O (1 L) and extracted with

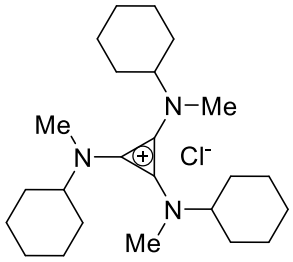
DCM (3 x 150 mL). The organic extracts were combined with the filtrate, dried over magnesium sulfate, filtered, and concentrated in vacuo to give a crude oil. The product was isolated by vacuum distillation (60 g, 17% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.91 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 66.42, 51.67. Characterization data were consistent with literature reports.[17]

2,3-Bis(dicyclohexylamino)-1-chlorocyclopropenium chloride (S21)



According to a literature procedure,[18] dicyclohexylamine (64.0 mL, 322 mmol, 6.0 equiv) was added dropwise over 30 min via addition funnel to a stirred solution of pentachlorocyclopropane (**S20**) (11.50 g, 53.7 mmol, 1.0 equiv) in DCM (500 mL) at 0 °C. The reaction mixture was stirred at 22 °C for 48 h, followed by addition of 12 M HCl (2.0 mL). The amine salts were removed by vacuum filtration, rinsed with DCM (100 mL), and the combined filtrates transferred to a separatory funnel and washed with 1.0 M HCl (5 x 400 mL) and brine (1 x 400 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo to give a tan-colored solid. The crude solid was then suspended in EtOAc (150 mL) and stirred at 50 °C for 30 min, followed by filtering the hot solution by vacuum filtration. The isolated solids were rinsed with EtOAc (50 mL) and dried in vacuo to give the product as a white solid (18.98 g, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.63 (tt, *J* = 12.1, 3.5 Hz, 2H), 3.38 (tt, *J* = 12.4, 3.8 Hz, 2H), 2.05 (d, *J* = 11.3 Hz, 4H), 1.96–1.80 (m, 12H), 1.69 (d, *J* = 13.1 Hz, 4H), 1.63–1.44 (m, 8H), 1.31 (ddt, *J* = 26.3, 13.1, 8.2 Hz, 8H), 1.15 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 132.68, 93.72, 66.08, 57.15, 33.04, 31.14, 25.80, 25.62, 24.92, 24.80. **HRMS** (DART-MS): *m/z* calculated for $C_{27}H_{44}ClN_2$ $[M]^{\bullet+}$ 431.31875, found 431.31973. Characterization data were consistent with literature reports.[18]

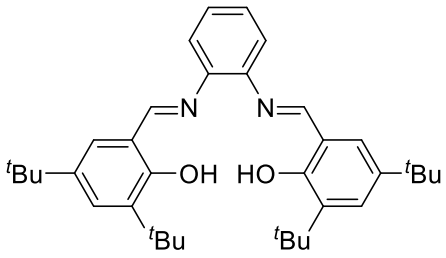
Tris(cyclohexylmethyl)cyclopropenium chloride ([CyPr]Cl)



N-Methylcyclohexylamine (23.5 mL, 180 mmol, 9.0 equiv) was added dropwise over 10 min via syringe to a stirred solution of pentachlorocyclopropane (**S20**) (4.29 g, 20.0 mmol, 1.0 equiv) in DCM (150 mL) at 0 °C. The reaction mixture was then stirred at 22 °C for 18 h, followed by removal of the solvent in vacuo to give a light orange solid that was taken up in 1.0 M HCl (100 mL). The aqueous mixture was extracted with DCM (3 x 75 mL) and the combined organic extracts washed vigorously with 1.0 M HCl (2 x 100 mL), brine (1 x 100 mL), and dried over Na_2SO_4. The solvent was removed in vacuo, and the crude solid was suspended in EtOAc (85 mL) and stirred at 50 °C for 30 min, followed by vacuum filtering the hot solution. The isolated solids were rinsed with EtOAc (15 mL) and dried in vacuo to give the product as a white solid (5.06 g, 62% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 3.24 (tt, *J* = 11.8, 3.2 Hz, 3H), 2.99 (s, 9H), 1.91–1.71 (m, 12H), 1.69–1.56 (m, 3H), 1.49 (qd, *J* = 12.6, 3.5 Hz, 6H), 1.21 (qt, *J* = 13.2, 3.4 Hz, 6H), 1.07 (qt, *J* = 13.1, 3.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 117.01, 63.16, 34.19, 30.92, 30.29, 25.57, 24.83. **HRMS** (DART-MS): *m/z* calculated for $C_{24}H_{42}N_3$ $[M]^{\bullet+}$ 372.33732, found 372.33869.

3.4. Ligand Synthesis and Tethering Reactions

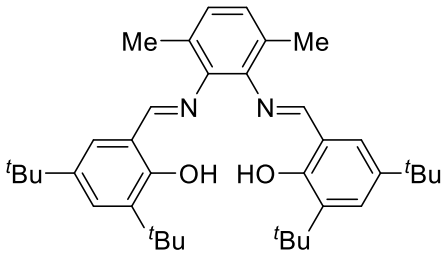
***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminobenzene (1-H_2)**



Phenylenediamine (0.100 g, 0.92 mmol, 1 equiv) and 3,5-di-*tert*-butylsalicylaldehyde (0.455 g, 1.94 mmol, 2.1 equiv) were stirred in MeOH (8 mL) at reflux for 18 h. Upon cooling to 22 °C, **1-H_2** precipitated as a bright yellow powder which was isolated by filtration (0.342 g, 68% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 13.54 (s, 2H), 8.67

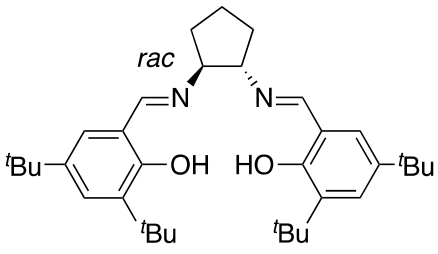
(s, 2H), 7.45 (d, *J* = 2.4 Hz, 2H), 7.32 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.24 (dd, *J* = 5.9, 3.4 Hz, 2H), 7.22 (d, *J* = 2.4 Hz, 2H), 1.45 (s, 18H), 1.33 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.85, 158.71, 142.90, 140.44, 137.33, 128.31, 127.44, 126.91, 119.94, 118.49, 35.27, 34.31, 31.62, 29.58. **HRMS** (DART-MS): *m/z* calculated for $C_{36}H_{48}N_2O_2$ $[M]^{\bullet+}$ 540.3716, found 540.371559. Characterization data were consistent with literature reports.[19]

***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-3,6-dimethyl-1,2-diaminobenzene (3-H$_2$)**



A solution of **S19** (0.70g, 5.1 mmol, 1.0 equiv) and 3,5-di-*tert*-butyl salicylaldehyde (2.47 g, 10.5 mmol, 2.05 equiv) in methanol (30 mL) was heated at 60 °C for 18 h under a nitrogen atmosphere. The reaction mixture was subsequently cooled to 0 °C using an ice bath and the bright orange solids isolated by vacuum filtration, rinsed with cold methanol (5 mL), and dried in vacuo to give the product as an orange solid (2.20 g, 75% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 13.38 (s, 2H), 8.45 (s, 2H), 7.39 (d, *J* = 2.2 Hz, 2H), 7.06 (d, *J* = 2.3 Hz, 2H), 7.02 (s, 2H), 2.28 (s, 6H), 1.41 (s, 18H), 1.27 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 169.02, 158.49, 140.39, 136.99, 128.17, 127.17, 126.85, 117.98, 35.18, 34.23, 31.54, 29.57, 18.77. **HRMS** (DART-MS): *m/z* calculated for $C_{38}H_{52}N_2O_2$ $[M]^{\bullet+}$ 568.4029, found 568.4032.

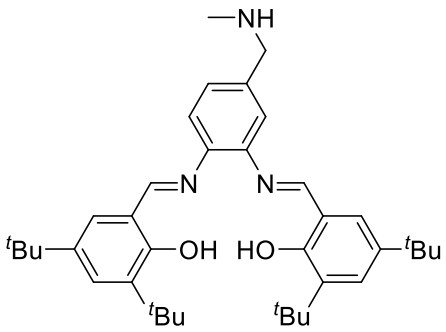
***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-*trans*-1,2-diaminocyclopentane (5-H$_2$)**



A solution of *trans*-cyclopentane-1,2-diamine dihydrochloride (75.0 mg, 0.433 mmol, 1 equiv) and K_2CO_3 (225 mg, 1.62 mmol, 3.75 equiv) in MeOH (5 mL) was stirred at 22 °C for 5 min. 3,5-Di-*tert*-butyl salicylaldehyde (213 mg,

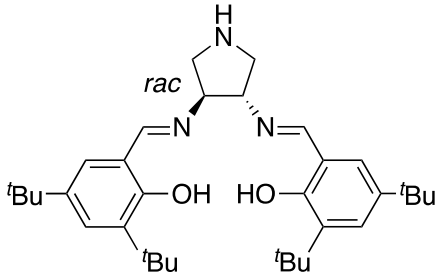
0.909 mmol, 2.1 equiv) was added, and the resulting mixture stirred at 60 °C for 18 h. Upon cooling to 22 °C, the product was isolated as an off-white powder by filtration (176 mg, 76% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 13.77 (s, 2H), 8.41 (s, 2H), 7.45 (d, *J* = 2.4 Hz, 2H), 7.13 (d, *J* = 2.4 Hz, 2H), 3.83 (m, 2H), 2.28 (m, 2H), 2.13–1.95 (m, 4H), 1.55 (s, 18H), 1.36 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.84, 158.09, 140.19, 136.62, 127.00, 126.24, 117.94, 76.67, 35.16, 34.24, 33.33, 31.63, 29.63, 22.28. **HRMS** (DART-MS): *m/z* calculated for $C_{35}H_{52}N_2O_2$ $[M]^{\bullet+}$ 532.4029, found 532.404738. Characterization data were consistent with literature reports.[20]

***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-4-*N*-methyl-methanamine-1,2-diaminobenzene (S22)**



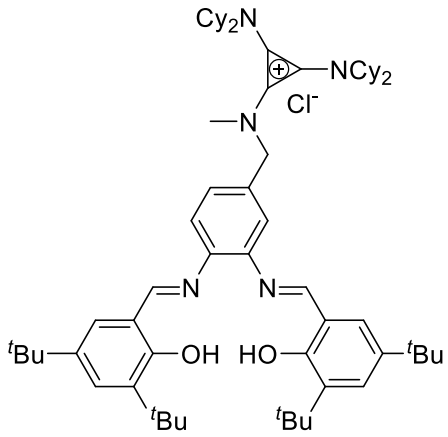
To a solution of 4-*N*-methyl-methanamine-1,2-diaminobenzene (**B1**) (3.50 g, 23.1 mmol, 1.0 equiv) in MeOH (150 mL) was added 3,5-di-*tert*-butylsalicylaldehyde (10.9 g, 46.3 mmol, 2.0 equiv). The red-brown reaction mixture was heated at 40 °C for 18 h, resulting in precipitation of an orange-colored solid. Upon cooling to 22 °C, the resulting solids were isolated by filtration, washed with cold MeOH (5 mL), and dried for 18 h in vacuo at 22 °C to give the product as a dark yellow powder (12.10 g, 90% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 13.57 (s, 1H), 13.55 (s, 1H), 8.70 (s, 1H), 8.67 (s, 1H), 7.46–7.42 (m, 2H), 7.28–7.19 (m, 5H), 3.83 (s, 2H), 2.52 (s, 3H), 1.44 (s, 18H), 1.32 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.79, 164.50, 158.72, 158.69, 142.82, 141.71, 140.41, 139.77, 137.30, 137.28, 128.28, 128.23, 127.13, 126.97, 126.86, 119.81, 119.54, 118.52, 118.51, 55.80, 36.32, 35.26, 34.31, 31.62, 29.58. **HRMS** (DART-MS): *m/z* calculated for $C_{38}H_{53}N_3O_2$ 583.4138, found 583.4089.

***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-3,4-diaminopyrrolidine (S23)**



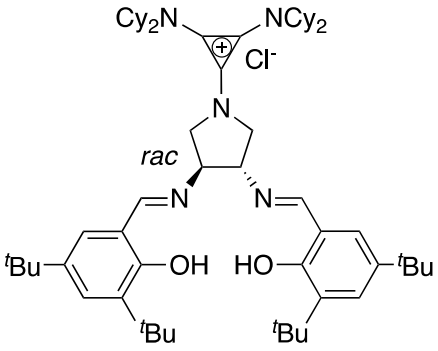
A solution of *trans*-3,4-pyrrolidine diamine trihydrochloride (**B3**) (0.60 g, 2.85 mmol, 1.00 equiv) and K_2CO_3 (1.18 g, 8.55 mmol, 3.00 equiv) in H_2O (2.5 mL) and EtOH (25 mL) was first prepared in a 100 mL round-bottom flask and stirred for 5 min at 22 °C. 3,5-Di-*tert*-butylsalicyladlehyde (1.37 g, 5.84 mmol, 2.05 equiv) was added and the mixture heated at reflux (90 °C) for 4 h. The reaction was then cooled to 22 °C, concentrated in vacuo, diluted with brine (60 mL), and extracted with DCM (3 x 60 mL). The organic extracts were combined, dried over Na_2SO_4, and concentrated in vacuo to give an orange solid that was further purified by column chromatography using a gradient of 90:10 (v:v) hexanes:EtOAc to 90:10 (v:v) DCM:MeOH, affording the product as a microcrystalline orange solid (1.01 g, 66% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 13.37 (s, 2H), 8.34 (s, 2H), 7.39 (s, 2H), 7.06 (s, 2H), 3.90 (p, *J* = 4.2 Hz, 2H), 3.52 (dd, *J* = 11.8, 6.2 Hz, 2H), 3.18 (dd, *J* = 12.0, 5.1 Hz, 2H), 2.33 (s, 1H), 1.45 (s, 19H), 1.28 (s, 19H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.49, 157.91, 140.52, 136.78, 127.41, 126.37, 117.78, 78.00, 54.89, 35.18, 34.28, 31.60, 29.58. **HRMS** (DART-MS): *m/z* calculated for $C_{34}H_{51}N_3O_2$ $[M]^{\bullet+}$ 533.3981, found 533.3917. Characterization data were consistent with literature reports.[21]

Aminocyclopropenium Ligand (2a-H$_2$)



2,3-Bis(dicyclohexylamino)-1-chlorocyclopropenium chloride (**S21**) (0.90 g, 1.92 mmol, 1.05 equiv) and dry triethylamine (0.51 mL, 3.67 mmol, 2.0 equiv) were added sequentially to a solution of ligand **S22** (1.07 g, 1.83 mmol, 1.0 equiv) in $CHCl_3$ (8.0 mL) in a 20 mL vial containing a stir bar. The vial was capped and stirred for 18 h at 22 °C before concentrating in vacuo. The residue was taken up in a 4:1 (v:v) mixture of Et_2O and DCM (50 mL) and stirred for 3 h at 22 °C before removal of the precipitated amine salts by syringe filtration through a 0.45 µm syringe filter. The filtered solution was concentrated in vacuo and the residue triturated with hexanes (4 x 15 mL). The resulting orange solids were dried in vacuo (1.80 g, 97% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 13.42 (s, 1H), 13.42 (s, 1H), 8.69 (s, 1H), 8.66 (s, 1H), 7.43 (t, *J* = 2.6 Hz, 3H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.22 (dd, *J* = 3.9, 2.5 Hz, 2H), 7.17 (s, 1H), 5.03 (s, 2H), 3.39 (tt, *J* = 12.4, 3.5 Hz, 4H), 3.36 (s, 3H), 1.94–1.80 (m, 16H), 1.70–1.58 (m, 12H), 1.42 (s, 9H), 1.40 (s, 9H), 1.34–1.20 (m, 26H), 1.09 (q, *J* = 13.2 Hz, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.80, 165.10, 158.64, 143.33, 142.24, 140.69, 140.64, 137.25, 137.22, 134.57, 128.60, 128.53, 127.12, 127.04, 125.96, 120.65, 120.07, 119.23, 118.39, 118.33, 118.30, 60.88, 57.77, 40.26, 35.21, 34.29, 33.17, 32.31, 31.56, 29.53, 26.39, 25.81, 24.76. **HRMS**-ESI: *m/z* calculated for $C_{65}H_{96}N_5O_2$ $[M]^{\bullet+}$ 978.75585, found 978.75585.

Aminocyclopropenium Ligand (6-H_2)



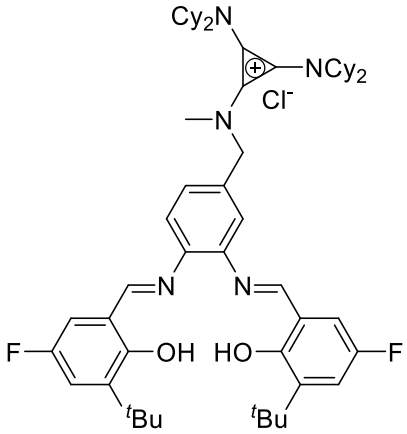
2,3-Bis(dicyclohexylamino)-1-chlorocyclopropenium chloride (**S21**) (1.62 g, 3.5 mmol, 1.05 equiv) and dry triethylamine (0.92 mL, 6.6 mmol, 2.0 equiv) were added sequentially to a solution of ligand **S23** (1.07 g, 1.83 mmol, 1.0 equiv) in $CHCl_3$ (8.0 mL) in a 20 mL vial containing a stir bar. The vial was capped and the reaction mixture stirred for 18 h at 22 °C, after which the solvent was removed in vacuo. The crude product was taken up into 9:1 (v:v) mixture of Et_2O:EtOAc (50 mL) and stirred at 22 °C for 1 h before removal of the precipitated amine salts by syringe filtration through a 0.45 µm syringe filter. The filtrate was collected, washed with 0.1 M HCl (1 x 15 mL), H_2O (1 x 15 mL), and brine (1 x 15 mL), and the organic layer dried over Na_2SO_4. The solvent was removed in vacuo, affording the product as a microcrystalline orange solid (3.09 g, 97% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 12.85 (s, 2H), 8.64 (s, 2H), 7.39 (d, *J* = 2.2 Hz, 2H), 7.15 (d, *J* = 2.3 Hz, 2H), 4.47 (dd, *J* = 8.8, 4.5 Hz, 2H), 4.25 (s, 2H), 3.96–3.86 (m, 2H), 3.42–3.28 (m, 4H), 2.00–1.80 (m, 16H), 1.74–1.57 (m, 12H), 1.40 (s, 18H), 1.37–1.29 (b, 8H), 1.28–1.22 (s, 18H), 1.20–1.11 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 169.27, 157.88, 140.90, 136.67, 128.17, 127.17, 118.16, 117.54, 115.76, 72.96, 60.47, 57.18, 35.09, 34.25, 33.13, 31.88, 31.51, 29.46, 26.36, 25.71, 24.77, 22.76, 14.19. **HRMS**-ESI: *m/z* calculated for $C_{61}H_{94}N_5O_2$ $[M]^{\bullet+}$ 928.74020, found 928.74026.

One-Pot Condensation and Tethering Procedure

In a 20 mL vial containing 3 Å molecular sieves and a stir bar, a solution of 4-*N*-methyl-methanamine-1,2-diaminobenzene and the appropriate salicylaldehyde in $CHCl_3$ was stirred at 22 °C for 24 h. 2,3-Bis(dicyclohexylamino)-1-chlorocyclopropenium chloride and triethylamine were

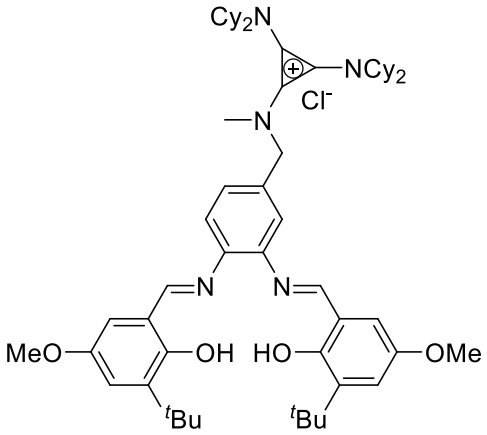
added and the reaction mixture stirred for an additional 24 h at 22 °C. The reaction mixture was concentrated in vacuo and a 2:1 mixture of PhMe:hex was added. The resulting suspension was stirred at 22 °C for 1 h and then centrifuged to remove solids, followed by filtering through a 0.45 μm syringe filter and concentrating. Dry hexanes was added to the resulting solid, and the mixture sonicated to afford an orange powder that was isolated by filtration, washed with hexanes, and dried in vacuo at 22 °C for 18 h.

Aminocyclopropenium Ligand (2b-H_2)



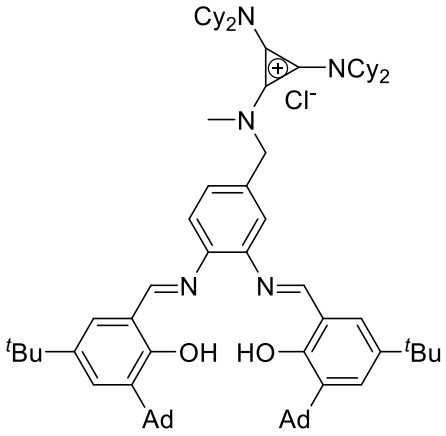
Synthesized from **B1** and **S3** according to the general procedure detailed above. (220 mg, 24% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 13.50 (s, 1H), 13.42 (s, 1H), 8.90 (s, 1H), 8.61 (s, 1H), 7.55 (s, 1H), 7.31 (s, 2H), 7.08 (qd, *J* = 10.3, 8.8, 3.0 Hz, 4H), 6.95 (dd, *J* = 7.7, 3.0 Hz, 1H), 4.98 (s, 2H), 3.41–3.33 (m, 4H), 3.31 (s, 3H), 1.92–1.78 (m, 16H), 1.66–1.56 (m, 12H), 1.38 (s, 9H), 1.37 (s, 9H), 1.30–1.17 (m, 8H), 1.05 (q, *J* = 13.0 Hz, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.83, 163.88, 157.10, 157.02, 155.99, 154.13, 142.51, 141.90, 140.17, 140.13, 139.92, 139.87, 134.99, 126.13, 120.64, 119.57, 118.74, 118.68, 118.57, 118.52, 118.37, 118.32, 115.51, 115.33, 115.04, 114.86, 77.37, 60.83, 40.07, 35.18, 35.14, 33.11, 32.24, 29.16, 26.34, 25.76, 24.70. **HRMS**-ESI: *m/z* calculated for $C_{57}H_{78}F_2N_5O_2$ $[M]^{\bullet+}$ 902.61181, found 902.61199.

Aminocyclopropenium Ligand (2c-H_2)



Synthesized from **B1** and **S4** according to the general procedure detailed above (590 mg, 82% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 13.29 (s, 1H), 13.26 (s, 1H), 8.79 (s, 1H), 8.65 (s, 1H), 7.34 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.27 (s, 1H), 6.99 (s, 2H), 6.81 (d, *J* = 2.8 Hz, 1H), 6.73 (d, *J* = 2.9 Hz, 1H), 4.96 (s, 2H), 3.75 (s, 6H), 3.35 (t, *J* = 12.1 Hz, 4H), 3.30 (s, 3H), 1.89–1.78 (m, 16H), 1.66–1.56 (m, 12H), 1.37 (s, 18H), 1.28–1.18 (m, 8H), 1.05 (q, *J* = 11.6, 10.2 Hz, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.36, 164.53, 155.59, 155.56, 151.49, 142.86, 142.02, 139.48, 139.35, 134.38, 125.67, 120.72, 120.14, 120.05, 119.77, 119.54, 118.42, 118.38, 118.25, 112.12, 111.91, 65.87, 60.81, 55.92, 55.88, 40.08, 35.07, 33.08, 32.20, 29.28, 26.31, 25.72, 24.65, 15.31. **HRMS**-ESI: *m/z* calculated for $C_{59}H_{84}N_5O_4$ $[M]^{\bullet+}$ 926.65178, found 926.65192.

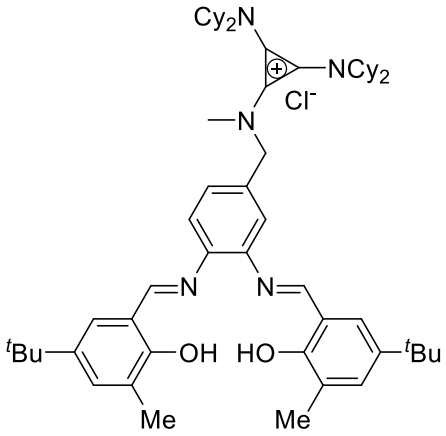
Aminocyclopropenium Ligand (2d-H_2)



Synthesized from **B1** and **S5** according to the general procedure detailed above (398 mg, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 13.26 (s, 1H), 13.26 (s, 1H), 8.60 (s, 1H), 8.60 (s, 1H), 7.36–7.34 (dd, *J* = 2.46, 2.49, 2H), 7.27 (d, *J* = 2.1, 8.1 Hz, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.18 (dd, *J* = 2.44, 2.45, 2H), 7.04 (d, *J* = 2.1, 1H), 4.93 (s, 2H), 3.39–3.32 (m, 4H), 3.30 (s, 3H), 2.15–2.08 (m, 12H), 2.02–1.96 (m, 6H), 1.89–1.79 (m, 16H), 1.76–1.68 (m, 12H), 1.65–1.57 (m, 12H), 1.27 (s, 9H), 1.26 (s, 9H), 1.25–1.20 (m, 8H), 1.09–1.04 (q, *J* = 9.78, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.21, 165.51, 158.66, 143.43, 142.26, 140.72,

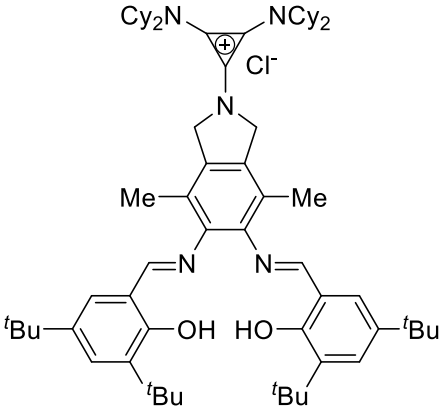
140.65, 137.30, 134.42, 128.50, 128.46, 126.94, 126.87, 126.81, 120.81, 120.05, 119.18, 118.31, 118.25, 118.13, 117.51, 60.74, 40.18, 37.26, 37.11, 34.21, 33.03, 32.18, 31.43, 29.07, 26.26, 25.69, 24.64. **HRMS**-ESI: *m/z* calculated for $C_{77}H_{108}N_5O_2$ $[M]^{\bullet+}$ 1134.84975, found 1134.85052.

Aminocyclopropenium Ligand (2e-H$_2$)



Synthesized from **B1** and **S6** according to the general procedure detailed above (277 mg, 30% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 12.92 (s, 1H), 12.87 (s, 1H), 8.69 (s, 1H), 8.66 (s, 1H), 7.39–7.34 (m, 1H), 7.28 (d, *J* = 3.7 Hz, 3H), 7.24 (d, *J* = 2.3 Hz, 1H), 7.22 (d, *J* = 2.3 Hz, 1H), 7.17 (d, 1H), 5.05 (s, 2H), 3.44–3.37 (m, 4H), 3.37 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 1.88 (t, *J* = 27.3 Hz, 16H), 1.70–1.58 (m, 12H), 1.34–1.24 (m, 26H), 1.09 (q, *J* = 11.8, 10.3 Hz, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.90, 165.00, 157.53, 143.20, 142.02, 141.41, 141.36, 134.71, 132.39, 132.37, 126.83, 126.66, 126.12, 125.86, 125.79, 121.18, 119.89, 118.30, 117.86, 117.82, 60.90, 40.27, 34.07, 32.35, 31.57, 25.84, 24.79, 15.93. **HRMS**-ESI: *m/z* calculated for $C_{59}H_{84}N_5O_2$ $[M]^{\bullet+}$ 895.66531, found 895.66502.

Aminocyclopropenium Ligand (4-H$_2$)



In a glove box, an oven dried 10 mL round bottomed flask containing a stir bar was charged with 4,7-dimethyl-5,6-diaminoisoindoline (**B2**) (0.125 g, 0.71 mmol, 1.0 equiv), 3,5-di-*tert*-butylsalicylaldehyde (0.331 g, 1.4 mmol, 2.0 equiv), 3Å molecular sieves (0.4 g), and dry $CHCl_3$ (3.5 mL). The flask was fitted with a rubber septum and stirred for 24

h at 22 °C upon which a solution of 2,3-bis(dicyclohexylamino)-1-chlorocyclopropenium chloride (0.346 g, 0.74 mmol, 1.05 equiv) and dry triethylamine (0.20 mL, 1.4 mmol, 2.0 equiv) in dry $CHCl_3$ (3.5 mL) was added to the reaction mixture via syringe. The dark orange mixture was stirred for 18 h at 22 °C to give a mixture of atropisomers that were isomerized into one species by heating the reaction mixture at 60 °C for 30 min, followed by cooling to 22 °C. The mixture was then filtered through a 0.45 μm syringe filter and concentrated in vacuo. The resulting solid was taken up into a 1:1 (v:v) mixture of PhMe:Et_2O (15 mL), followed by stirring the suspension at 22 °C for 1 h to promote precipitation of residual salts. The solution was filtered through a 0.45 μm syringe filter and the solvent removed before azeotroping the resulting solid with PhMe (2 x 10 mL) to remove residual triethylamine. After drying for 18 h in vacuo at 22 °C the product was obtained as an orange powder (0.70 g, 96% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 13.11 (s, 2H), 8.40 (s, 2H), 7.38 (d, *J* = 2.2 Hz, 2H), 7.05 (d, *J* = 2.2 Hz, 2H), 5.24 (s, 4H), 3.50 (tt, *J* = 12.2, 3.5 Hz, 4H), 2.18 (s, 6H), 1.96 (d, *J* = 11.3 Hz, 16H), 1.83 (d, *J* = 12.1 Hz, 2H), 1.78–1.68 (m, 16H), 1.66–1.59 (m, 4H), 1.44–1.38 (m, 2H), 1.36 (s, 18H), 1.24 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 169.81, 158.41, 141.02, 140.60, 136.98, 131.20, 128.50, 127.04, 121.88, 117.80, 117.63, 117.18, 116.03, 60.72, 58.45, 58.34, 35.13, 34.21, 33.17, 31.89, 31.48, 29.50, 26.40, 25.93, 25.32, 24.88, 15.49. **HRMS**-ESI: *m/z* calculated for $C_{67}H_{98}N_5O_2$ $[M]^{\bullet+}$ 1004.77150, found 1004.77166.

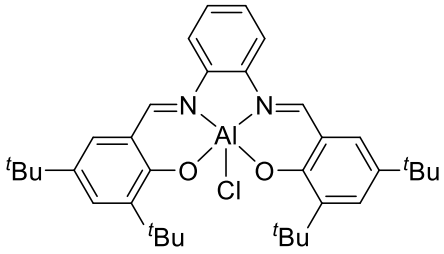
3.5. Metalations

General Aluminum Metalation

In a glove box, salen ligand was dissolved in dry, degassed PhMe in an oven-dried Schlenk flask equipped with stir bar. A 1 M solution of Et_2AlCl was added while stirring for 5 min. The flask was then sealed, removed from the glove box, and heated at 90 °C for 18 h. After cooling to 22 °C, the resulting solids were filtered and washed with dry, degassed hexanes. If no precipitate

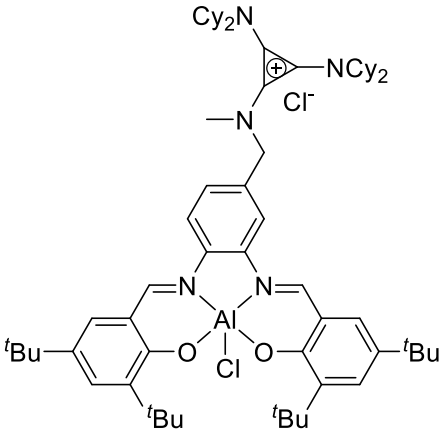
formed, the reaction mixture was concentrated in vacuo and dry, degassed hexanes added via cannula. The resulting suspension was sonicated and then filtered to afford the desired complex as a powder. The isolated complexes were dried in vacuo for 18 h at 22 °C before storing in a nitrogen-filled glove box.

Complex 1-AlCl



1-AlCl was prepared according to the general aluminum metalation procedure. The product precipitated as a yellow powder which was isolated by filtration and washed with dry, degassed hexanes before drying at 22 °C in vacuo (1.40 g, 45% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.96 (s, 2H), 7.75 (dd, *J* = 6.2, 3.4 Hz, 2H), 7.68 (d, *J* = 2.5. 2H), 7.39 (dd, *J* = 6.2, 3.3 Hz, 2H), 7.24 (d, *J* = 2.5, 2H), 1.61 (s, 18H), 1.36 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.33, 162.45, 141.56, 139.67, 137.74, 133.04, 128.21, 128.13, 118.45, 115.40, 35.67, 34.11, 31.25, 29.82. **HRMS**-ESI: *m/z* calculated for $C_{36}H_{46}AlN_2O_2$ $[M]^{\bullet+}$ 565.33747, found 565.33671. Characterization data were consistent with literature reports.[22]

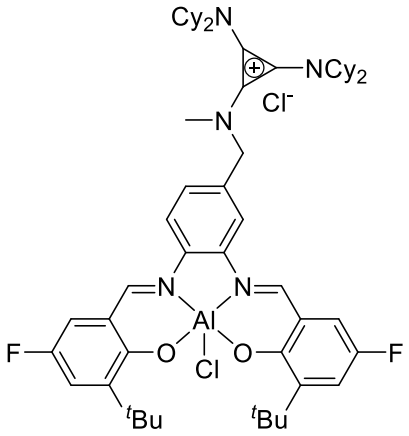
Complex 2a-AlCl



2a-AlCl was prepared according to the general aluminum metalation procedure. As no precipitate formed, solvent was removed in vacuo to afford a glassy solid which was triturated with 20 mL dry, degassed hexanes and the solids briefly isolated by vacuum filtration. The resulting orange-yellow powder was dried in vacuo for 18 h at 22 °C (2.10 g, 91% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 9.42 (s, 1H), 9.07 (s, 1H), 8.33 (s, 1H), 7.89 (d, *J* =

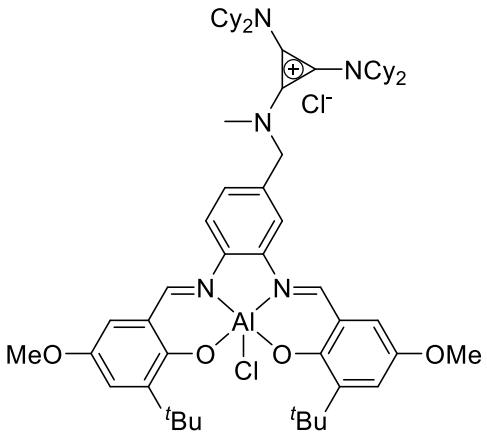
8.5 Hz, 1H), 7.64 (d, *J* = 2.1 Hz, 2H), 7.56 (s, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.33 (d, *J* = 1.9 Hz, 1H), 5.07 (s, 2H), 3.42–3.34 (m, 4H), 3.34 (s, 3H), 1.93–1.79 (m, 16H) 1.67–1.59 (m, 12H), 1.58 (s, 18H), 1.34 (s, 9H), 1.33 (s, 9H), 1.24 1.30–1.18(m, 8H), 1.06 (q, *J* = 12.4, 12.0 Hz, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 164.50, 164.42, 164.40, 162.81, 141.56, 141.14, 139.81, 139.73, 138.73, 137.60, 135.78, 133.21, 133.09, 129.40, 128.51, 126.09, 119.97, 119.05, 118.71, 118.60, 116.58, 116.27, 60.89, 57.86, 40.28, 35.78, 35.75, 34.31, 34.26, 32.30, 31.46, 31.40, 29.99, 29.96, 25.82, 24.76. **HRMS**-ESI: *m/z* calculated for $C_{65}H_{94}AlClN_5O_2$ $[M]^{\bullet+}$ 1038.69059, found 1038.69174.

Complex 2b-AlCl



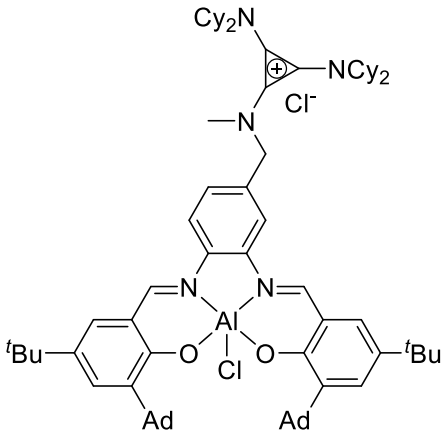
2b-AlCl was prepared according to the general aluminum metalation procedure. As no precipitate formed, solvent was removed in vacuo to afford a glassy solid which was triturated with 20 mL dry, degassed hexanes and isolated by filtration. The resulting orange solids were dried in vacuo at 22 °C for 18 h (151 mg, 64% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 10.02 (s, 1H), 9.26 (s, 1H), 8.85 (s, 1H), 8.15–8.04 (m, 1H), 7.68 (d, *J* = 5.9 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 7.24 (s, 1H), 4.83 (s, 2H), 3.37–3.30 (m, 4H), 3.30 (s, 3H), 1.84 (dd, *J* = 40.9, 11.6 Hz, 16H), 1.62–1.55 (m, 12H), 1.54 (s, 9H), 1.54 (s, 9H), 1.25–1.13 (m, 8H), 1.02 (q, *J* = 12.7, 12.0 Hz, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 165.20, 162.61, 162.45, 162.39, 155.04, 154.99, 153.17, 153.12, 144.44, 144.39, 143.61, 143.56, 138.81, 137.18, 136.23, 129.14, 128.33, 126.55, 125.40, 123.20, 123.07, 123.00, 122.87, 120.06, 119.48, 119.40, 118.85, 118.73, 118.66, 117.61, 117.17, 116.98, 115.83, 115.65, 60.90, 40.26, 35.81, 35.72, 32.33, 29.68, 25.84, 24.80. **HRMS**-ESI: *m/z* calculated for $C_{57}H_{76}AlClF_2N_5O_2$ $[M]^{\bullet+}$ 962.54655, found 962.54734.

Complex 2c-AlCl



2c-AlCl was prepared according to the general aluminum metalation procedure. As no precipitate formed, solvent was removed in vacuo to afford a glassy solid which was triturated with 20 mL dry, degassed hexanes and isolated by filtration. The resulting orange solids were dried in vacuo at 22 °C for 18 h (317 mg, 99% yield. **^{1}H NMR** (500 MHz, DMSO-d_6): δ 9.33 (d, J = 3.7 Hz, 1H), 8.20 (d, J = 8.7 Hz, 1H), 8.16 (s, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.15–7.08 (m, 4H), 4.77 (s, 2H), 3.76 (s, 6H), 3.49–3.42 (m, 4H), 3.17 (s, 3H), 1.85–1.74 (m, 16H), 1.73–1.63 (m, 12H), 1.54 (s, 18H), 1.31–1.22 (m, 8H), 1.14–1.06 (m, 4H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 161.50, 161.27, 160.50, 160.40, 148.96, 141.58, 141.53, 137.74, 136.93, 136.07, 126.44, 123.85, 119.27, 118.54, 118.25, 117.21, 115.63, 113.87, 113.51, 113.38, 59.54, 58.45, 57.10, 55.34, 35.12, 31.29, 31.20, 29.44, 25.14, 24.16, 24.00. **HRMS-**ESI: *m/z* calculated for $C_{59}H_{82}AlClN_5O_4$ $[M]^{\bullet+}$ 986.58652, found 986.58755.

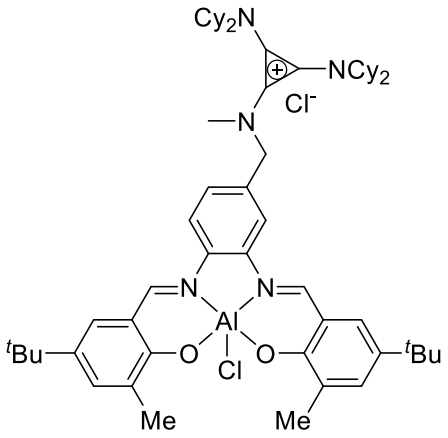
Complex 2d-AlCl



2d-AlCl was prepared according to the general aluminum metalation procedure. As no precipitate formed, solvent was removed in vacuo to afford a glassy solid which was triturated with 20 mL dry, degassed hexanes and isolated by filtration. The resulting orange solids were dried in vacuo at 22 °C for 18 h (330 mg, 79% yield). **^{1}H NMR** (500 MHz, DMSO-d_6): δ 9.06 (s, 1H), 8.95 (s, 1H), 7.99–7.97 (d, J = 8.5 Hz, 1H), 7.90 (s, 1H), 7.51–7.50 (d, J = 2.4 Hz, 2H), 7.47–7.46 (m, 2H), 7.38–7.36 (d, J = 2.4 Hz, 1H), 4.77 (s, 2H), 3.51–3.42 (m,

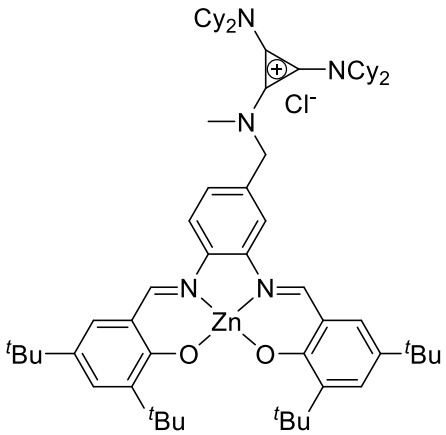
4H), 3.14 (s, 3H), 2.27–2.17 (m, 12H), 2.10–2.04 (m, 6H), 1.84–1.63 (m, 44H), 1.60–1.54 (m, 4H), 1.29 (s, 18H), 1.12–1.07 (m, 4H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 164.52, 164.25, 164.11, 139.72, 139.57, 138.87, 138.11, 137.57, 137.52, 135.85, 131.41, 131.37, 129.60, 129.27, 126.57, 119.78, 119.58, 119.04, 118.07, 117.48, 115.87, 59.54, 57.07, 40.88, 40.85, 37.38, 36.56, 34.19, 33.73, 33.69, 31.16, 31.12, 28.41, 25.14, 24.16. **HRMS**-ESI: *m/z* calculated for $C_{77}H_{106}AlClN_5O_2$ $[M]^{\bullet+}$ 1194.78450, found 1194.78608.

Complex 2e-AlCl



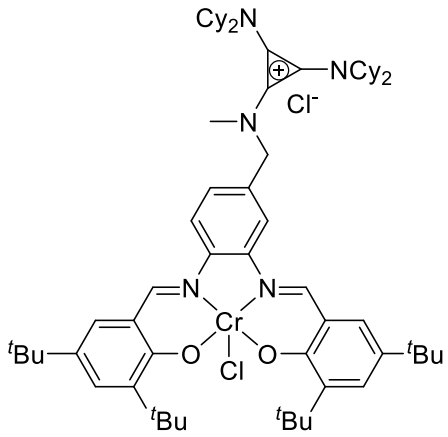
2e-AlCl was prepared according to the general aluminum metalation procedure. As no precipitate formed, solvent was removed in vacuo to afford a glassy solid which was triturated with 20 mL dry, degassed hexanes and isolated by filtration. The resulting yellow solids were dried in vacuo at 22 °C for 18 h (282 mg, 96% yield). **^{1}H NMR** (500 MHz, DMSO-d_6): δ 9.32 (s, 1H), 9.27 (s, 1H), 8.19 (d, J = 8.7 Hz, 1H), 8.12 (s, 1H), 7.57–7.56 (m, 1H), 7.57 (d, J = 2.8 Hz, 1H), 7.55 (d, J = 2.6 Hz, 1H), 7.52 (s, 1H), 7.48–7.45 (m, 2H), 4.75 (s, 2H), 3.45 (t, J = 9.1 Hz, 4H), 3.18 (s, 3H), 2.33 (s, 6H), 1.86–1.73 (m, 16H), 1.71–1.62 (m, 12H), 1.31 (s, 18H), 1.29–1.22 (m, 8H), 1.10 (q, J = 12.1, 10.4 Hz, 4H). **^{13}C NMR** (125 MHz, DMSO-d_6): δ 162.09, 161.90, 161.70, 137.93, 137.84, 137.12, 136.07, 135.02, 134.92, 129.17, 129.02, 128.58, 128.42, 126.49, 119.13, 118.38, 117.73, 117.59, 117.37, 115.64, 59.56, 57.07, 33.62, 31.20, 25.13, 24.16, 16.27. **HRMS**-ESI: *m/z* calculated for $C_{59}H_{82}AlClN_5O_2$ $[M]^{\bullet+}$ 954.59669, found 954.59763.

Complex 2a-Zn



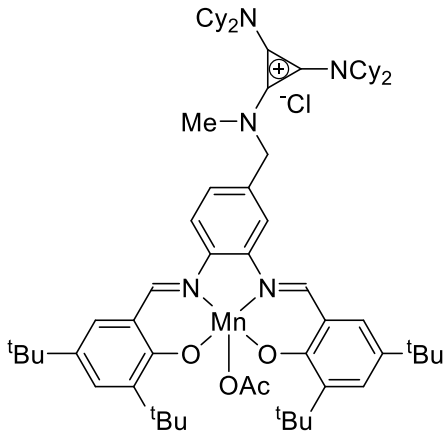
In a glove box, a solution of **2a-H$_2$** (0.500 g, 0.49 mmol, 1.0 equiv) in dry PhMe (10 mL) was prepared in an oven-dried Schlenk tube containing a stir bar, followed by the dropwise addition of 2 M Me_2Zn in PhMe (0.26 mL, 0.52 mmol, 1.05 equiv) over 1 min. The mixture was stirred open in the glove box for 10 min, the flask stoppered and removed from the glove box, and the reaction mixture heated at 60 °C for 4 h. Upon cooling to 22 °C, dry hexanes (20 mL) was added to the reaction mixture, followed by isolating the resulting solids by vacuum filtration in air. The solids were rinsed with dry hexanes (10 mL) and dried for 18 h in vacuo at 22 °C to give the product as a bright orange solid (0.441 g, 83% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.58 (s, 1H), 8.33 (s, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.30 (dd, *J* = 8.1, 2.5 Hz, 3H), 7.03 (s, 1H), 6.90 (d, *J* = 2.4 Hz, 1H), 6.83 (d, *J* = 2.4 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 4.62–4.25 (m, 3H), 3.24 (t, *J* = 12.1 Hz, 6H), 2.97 (s, 3H), 1.74 (t, *J* = 14.3 Hz, 16H), 1.57 (s, 9H), 1.56 (s, 9H), 1.54–1.42 (m, 12H), 1.31 (s, 9H), 1.30 (s, 9H), 1.23–1.10 (m, 8H), 0.99 (q, *J* = 13.0 Hz, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 172.29, 172.23, 160.66, 160.52, 142.58, 142.43, 141.66, 140.81, 132.39, 132.33, 132.31, 128.48, 128.39, 128.30, 123.08, 119.95, 118.42, 118.30, 118.13, 115.42, 112.60, 60.61, 57.77, 41.13, 35.75, 35.72, 33.79, 33.78, 32.10, 31.57, 31.54, 29.84, 25.63, 24.62. **HRMS**-ESI: *m/z* calculated for $C_{65}H_{94}N_5O_2Zn$ $[M]^{\bullet+}$ 1040.66935, found 1040.66965.

Complex 2a-CrCl



2a-H₂ (0.400 g, 0.39 mmol, 1.0 equiv) was added to an oven-dried Schlenk flask equipped with stir bar against a positive pressure of nitrogen. Dry, degassed THF (5 mL) was added via cannula. In the glove box, a separate Schlenk flask was charged with $CrCl_2$ (51 mg, 0.41 mmol, 1.05 equiv). The sealed flask was brought out of the box, and dry, degassed THF (5 mL) was added via cannula, followed by the ligand solution. The resulting reaction mixture stirred at 40 °C for 3 h and then opened to dry air and stirred for 18 h at 22 °C. The resulting bright red solids were isolated by filtration and washed with Et_2O. The isolated product was sonicated in pentane, filtered, and dried in vacuo at 55 °C for 6 h (0.258 g, 60% yield). **HRMS**-ESI: *m/z* calculated for $C_{65}H_{94}ClCrN_5O_2$ $[M]^{\bullet+}$ 1063.64957, found 1063.65118. Due to the paramagnetic nature of the catalyst, the ^1H NMR spectrum exhibited significant broadening resulting in peak overlap. Further NMR characterization was not performed.

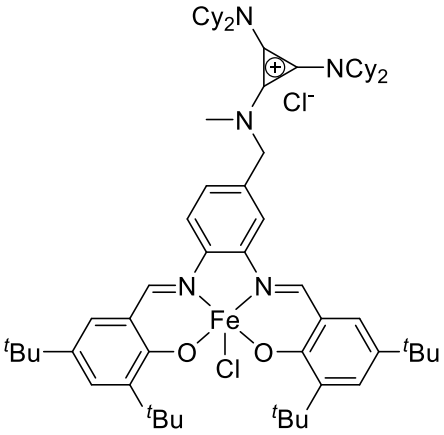
Complex 2a-MnOAc



A solution of **2a-H₂** (0.400 g, 0.39 mmol, 1.0 equiv) and manganese(III) acetate dihydrate (116 mg, 0.43 mmol, 1.1 equiv) was stirred at reflux in EtOH (10 mL) for 2 h before concentrating in vacuo. The resulting brown glassy solids were sonicated in pentane, filtered, and dried in vacuo at 55 °C for 6 h (0.425 g, 94% yield). **HRMS**-ESI: *m/z* calculated for $C_{65}H_{94}ClMnN_5O_2$ $[M]^{\bullet+}$ 1066.64711, found 1066.64800. The ^1H NMR spectrum exhibited

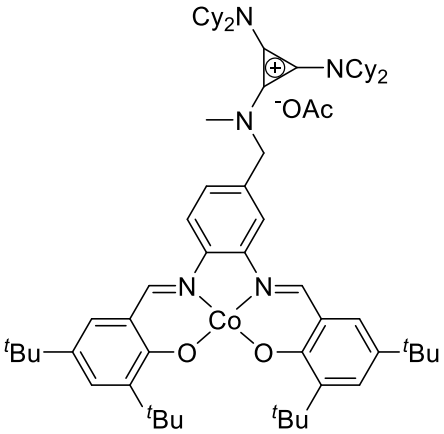
significant broadening and was paramagnetically shifted. Further NMR characterization was not performed due to the paramagnetic nature of the catalyst.

Complex 2a-FeCl



A solution of **2a-H$_2$** (0.400 g, 0.39 mmol, 1.0 equiv) and iron(III) chloride hexahydrate (116 mg, 0.43 mmol, 1.1 equiv) was stirred in MeOH (5 mL) at reflux for 2 h. The resulting brown solids were isolated by filtration through Celite while washing with methanol. The green filtrate was concentrated, triturated with pentane, and filtered to afford a brown powder that was dried in vacuo at 55 °C for 6 h (0.117 g, 27% yield). **HRMS**-ESI: *m/z* calculated for $C_{65}H_{94}ClFeN_5O_2$ $[M]^{\bullet+}$ 1067.64400, found 1067.64516. The ^{1}H NMR spectrum exhibited significant broadening and was paramagnetically shifted. Further NMR characterization was not performed due to the paramagnetic nature of the catalyst.

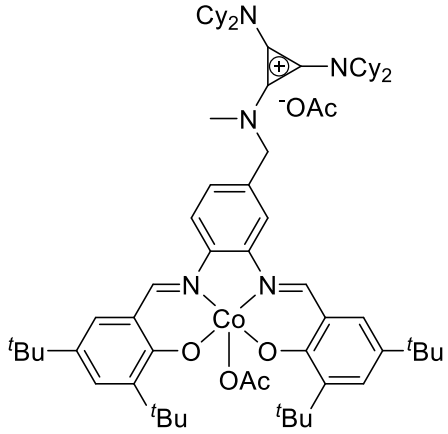
Complex 2a-Co



2a-H$_2$ (0.700 g, 0.69 mmol, 1.0 equiv) was placed in a Schlenk flask under nitrogen to which was added dry, degassed DCM via cannula. In a separate Schlenk flask, cobalt(II) acetate tetrahydrate (0.172 g, 0.69 mmol, 1 equiv) was dehydrated by heating in vacuo, resulting in a color change from pink to dark purple. Dry, degassed MeOH was added to the cobalt(II) acetate, followed by the solution of **2a-H$_2$** via cannula. The reaction mixture was stirred at 22 °C for 12 h before concentrating in vacuo. The residue was suspended in dry,

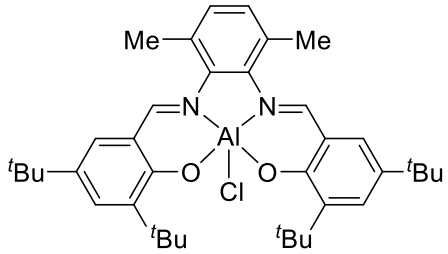
degassed hexanes, sonicated, and isolated by filtration. The resulting red powder was dried in vacuo at 22 °C for 18 h (0.401 g, 54% yield). **HRMS**-ESI: *m/z* calculated for $C_{65}H_{94}CoN_5O_2$ $[M]^{\bullet+}$ 1035.67340, found 1035.67823. The ^{1}H NMR spectrum exhibited significant broadening and was paramagnetically shifted. Further NMR characterization was not performed due to the paramagnetic nature of the catalyst.

Complex 2a-CoOAc



Acetic acid (213 μL) was added to a solution of **2a-Co** in DCM (10 mL). The reaction was stirred open to air at 22 °C for 18 h, resulting in evaporation of the solvent. Dry PhMe (8 mL) was added and evaporated 4 times to remove residual acetic acid. The residue was suspended in heptane, filtered, washed with heptane, and dried in vacuo at 60 °C for 18 h to afford the product as dark red microcrystals (0.390 g, 91% yield). **HRMS**-ESI: *m/z* calculated for $C_{67}H_{97}CoN_5O_4$ $[M–OAc]^+$ 1094.68671, found 1094.68762. The ^{1}H NMR spectrum in $CDCl_3$ exhibited significant broadening and was paramagnetically shifted. Further NMR characterization was not performed due to the paramagnetic nature of the catalyst.

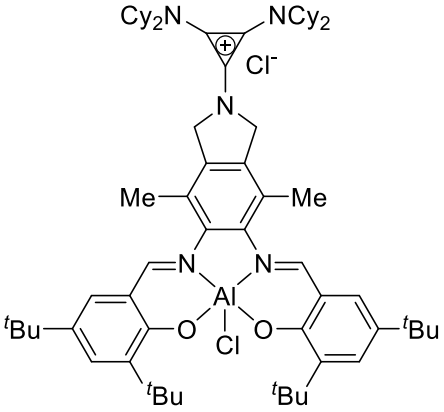
Complex 3-AlCl



3-AlCl was prepared according to the general aluminum metalation procedure (1.07 g, 84% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.65 (s, 2H), 7.63 (d, *J* = 2.2 Hz, 2H), 7.14 (s, 2H), 7.09 (d, *J* = 2.2 Hz, 2H), 2.59 (s, 6H), 1.56 (s, 18H), 1.33 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.94, 163.64, 141.35, 139.36, 138.77, 132.58,

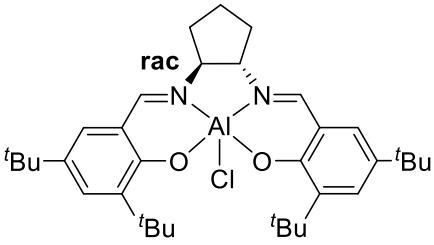
131.40, 127.35, 126.75, 118.20, 35.65, 34.21, 31.44, 30.13, 20.47. **HRMS**-ESI: *m/z* calculated for $C_{38}H_{50}AlN_2O_2$ $[M]^{\bullet+}$ 593.36877, found 593.36849.

Complex 4-AlCl



4-AlCl was prepared according to the general aluminum metalation procedure (0.41 g, 67% yield). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.63 (s, 2H), 7.62 (d, *J* = 2.3 Hz, 2H), 7.12 (d, *J* = 2.2 Hz, 2H), 5.38 (s, 4H), 3.51 (t, *J* = 12.1 Hz, 4H), 2.50 (s, 6H), 1.97 (d, *J* = 11.0 Hz, 16H), 1.81–1.67 (m, 12H), 1.53 (s, 18H), 1.47–1.36 (m, 8H), 1.32 (s, 18H), 1.28–1.17 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 167.25, 163.62, 139.38, 138.88, 135.02, 132.65, 127.51, 121.12, 118.05, 117.23, 116.02, 60.59, 58.61, 35.48, 34.10, 31.84, 31.29, 30.02, 25.83, 24.86, 17.10. **HRMS**-ESI: *m/z* calculated for $C_{67}H_{96}AlClN_5O_2$ $[M]^{\bullet+}$ 1064.70624, found 1064.70694.

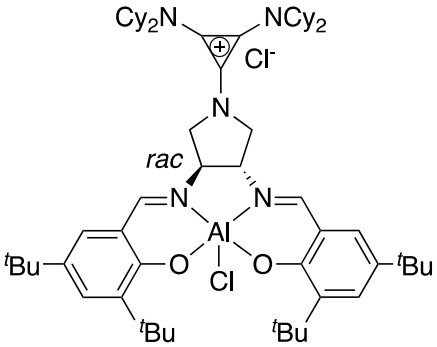
Complex 5-AlCl



5-AlCl was prepared according to the general aluminum metalation procedure. As no precipitate formed, the reaction mixture was syringe filtered, and solvent was removed in vacuo to afford a pale green powder. The residue was resuspended in PhMe, centrifuged, and filtered to remove a dark oil. The resulting yellow solution was concentrated in vacuo to afford a pale yellow solid (308 mg, 79% yield). **^{1}H NMR** (500 MHz, PhMe-d_8): δ 7.78 (d, *J* = 2.2 Hz, 1H), 7.76 (d, *J* = 2.7 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.03 (d, *J* = 2.2 Hz, 1H), 3.83 (td, *J* = 11.2, 5.5 Hz, 1H), 2.31 (td, *J* = 12.1, 10.2, 6.5 Hz, 1H), 1.85 (s, 9H), 1.83 (s, 9H), 1.50–1.40 (m, 2H), 1.37 (s, 9H), 1.35 (s, 9H), 1.32–1.26 (m, 2H), 0.88 (ddd, *J* = 23.7, 11.9, 8.6 Hz, 2H). **^{13}C NMR** (125 MHz, PhMe-d_8): δ 168.27, 164.03, 162.92, 162.07, 141.84,

141.56, 138.64, 137.99, 131.08, 130.09, 118.59, 118.43, 69.68, 65.83, 35.86, 35.76, 33.87, 33.83, 31.28, 31.21, 30.01, 29.84, 22.33, 21.31. **HRMS**-ESI: *m/z* calculated for $C_{35}H_{50}AlN_2O_2$ $[M]^{\bullet+}$ 557.36877, found 557.36830.

Complex 6-AlCl



6-AlCl was prepared according to the general aluminum metalation procedure. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.04 (s, 2H), 7.52 (d, *J* = 2.0 Hz, 2H), 6.91 (d, *J* = 2.0 Hz, 2H), 4.93 (s, 0H), 4.46 (s, 2H), 4.28 (s, 2H), 3.46 (t, *J* = 11.8 Hz, 4H), 2.02–1.86 (m, 16H), 1.81–1.62 (m, 12H), 1.51 (s, 18H), 1.44–1.35 (m, 8H), 1.29 (s, 18H), 1.22–1.14 (m, 4H). **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.86, 162.84, 141.09, 138.21, 137.86, 131.26, 129.03, 128.22, 127.65, 125.29, 117.92, 117.45, 117.21, 63.99, 60.52, 50.82, 35.57, 33.88, 32.00, 31.69, 31.45, 31.28, 29.68, 25.82, 25.77, 24.80, 22.66, 21.46, 14.13. **HRMS**-ESI: *m/z* calculated for $C_{61}H_{92}AlClN_5O_2$ $[M]^{\bullet+}$ 988.67494, found 988.67543.

4. Copolymerizations and Polymer Characterization Data

4.1. General Polymerization Procedure and Living Behavior Using 2a-AlCl

In a glove box, the appropriate amount of metal complex (1 equiv) and cocatalyst (if required, 1 equiv) were weighed into an oven-dried 4 mL vial. Cyclic anhydride (X equiv) was then weighed into the vial, and epoxide (5X equiv) added by volume. The vial was sealed with a Teflon-lined cap, removed from the glove box, and placed in an oil bath preheated to 60 °C. At desired time points, small aliquots were removed for ^{1}H NMR spectroscopic analysis and GPC to determine conversion of the anhydride and molecular weight and dispersity of the polymer, respectively. At low catalyst loadings, GPC traces of the polymers revealed a bimodal molecular

weight distribution. This bimodality is common for anionic ring-opening copolymerizations and indicates the presence of adventitious water or diacid (Figure S1).

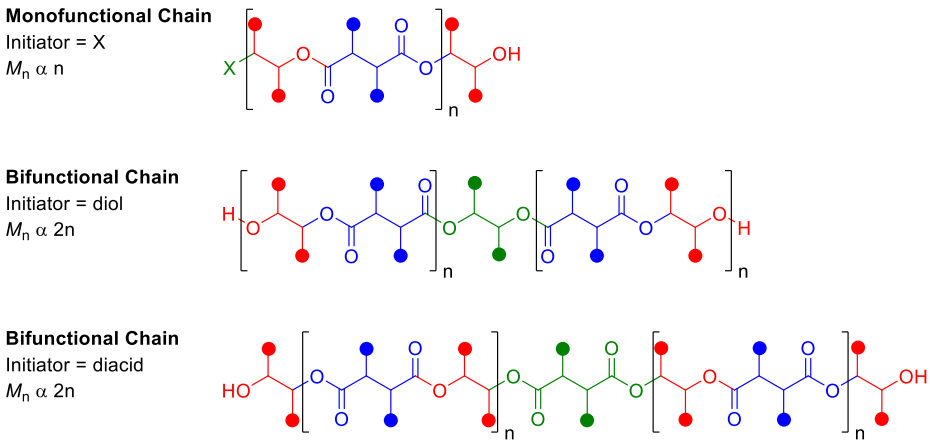


Figure S1. Mono- and bifunctional chains initiated from catalyst/cocatalyst X-type ligand, ring-opened PO, and diacid.

In copolymerizations catalyzed by **2a-AlCl**, molecular weights increase linearly with conversion and dispersities remain low, consistent with living polymerization behavior. M_n and $Đ$ are plotted as a function of conversion for a representative copolymerization of PO and CPMA with **2a-AlCl** ([**2a-AlCl**]$_0$:[CPMA]$_0$:[PO]$_0$ = 1:400:2000, Figure S2).

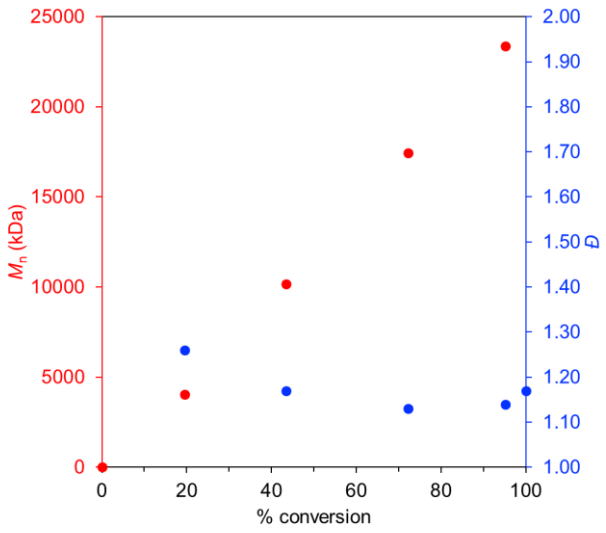
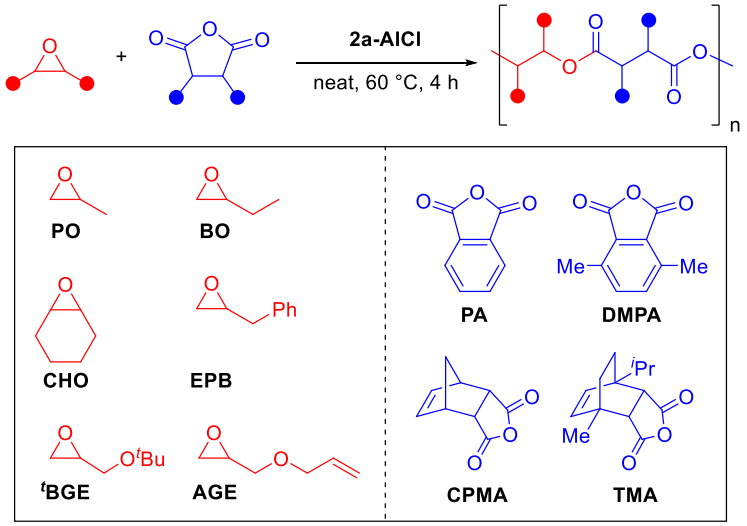


Figure S2. M_n and $Đ$ as a function of conversion for the copolymerization of PO and CPMA by **2a-AlCl** ([**2a-AlCl**]$_0$:[CPMA]$_0$:[PO]$_0$ = 1:400:2000).

4.2. Copolymerization of Epoxides and Cyclic Anhydrides at Low Catalyst Concentration

Table S1. Monomer Variants Polymerized by **2a-AlCl** at Low Catalyst Loading [a]



entry	comonomers	conv. (%) [b]	TOF (h^{-1}) [c]	M_n (kDa) [d]	$Đ$ [d]
1	**PO/PA**	90	108	45.4	1.19
2	**PO/DMPA**	63	75	31.4	1.14
3	**PO/TMA**	20	24	13.7	1.15
4	**PO/CPMA**	69	83	43.5	1.16
5	**BO/CPMA**	45	54	24.1	1.16
6 [e]	**CHO/CPMA**	56	38	12.4	1.18
7	**EPB/CPMA**	38	46	5.9	1.29
8	**AGE/CPMA**	48	58	22.2	1.17
9	**^{t}BGE/CPMA**	27	32	9.4	1.32

[a] [**2a-AlCl**]$_0$:[anhydride]$_0$:[epoxide]$_0$=1:1200:6000. [b] Determined by ^{1}H NMR analysis of crude reaction mixture. [c] TOF = Turnover frequency, mol anhydride consumed × mol **2a-AlCl**$^{-1}$ × h^{-1}. [d] Determined by GPC in THF, calibrated with polystyrene standards. [e] Reaction time of 18 h.

4.3. Representative GPC Traces of Polyester Copolymers

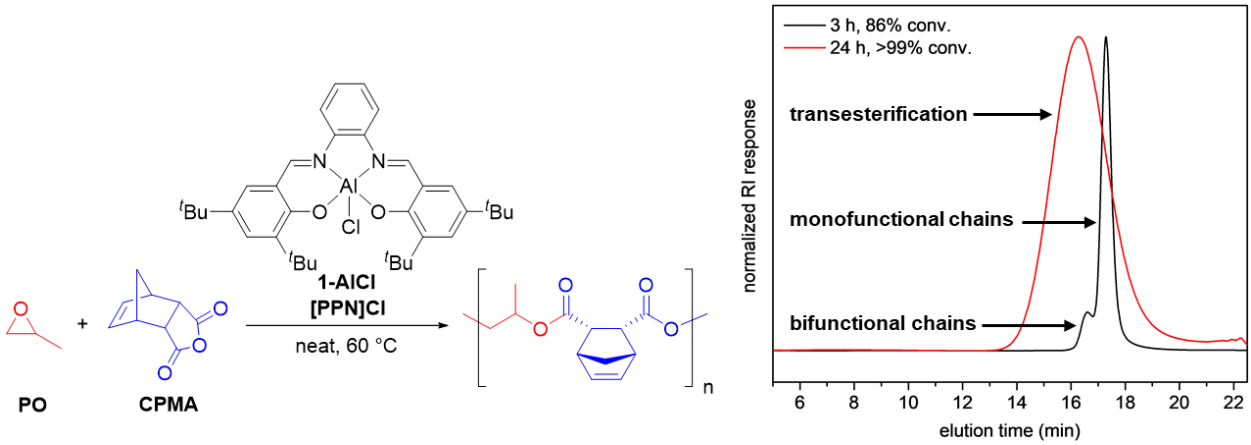


Figure S3. GPC traces of PO/CPMA copolymerizations catalyzed by **1-AlCl**/[PPN]Cl before (black) and after (red) full conversion of cyclic anhydride.

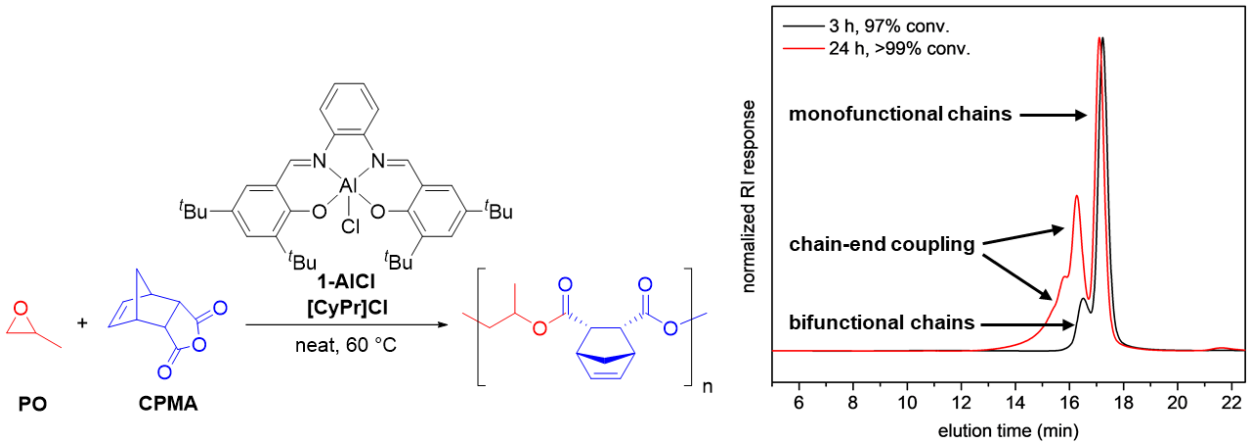


Figure S4. GPC traces of PO/CPMA copolymerizations catalyzed by **1-AlCl**/[CyPr]Cl before (black) and after (red) full conversion of cyclic anhydride.

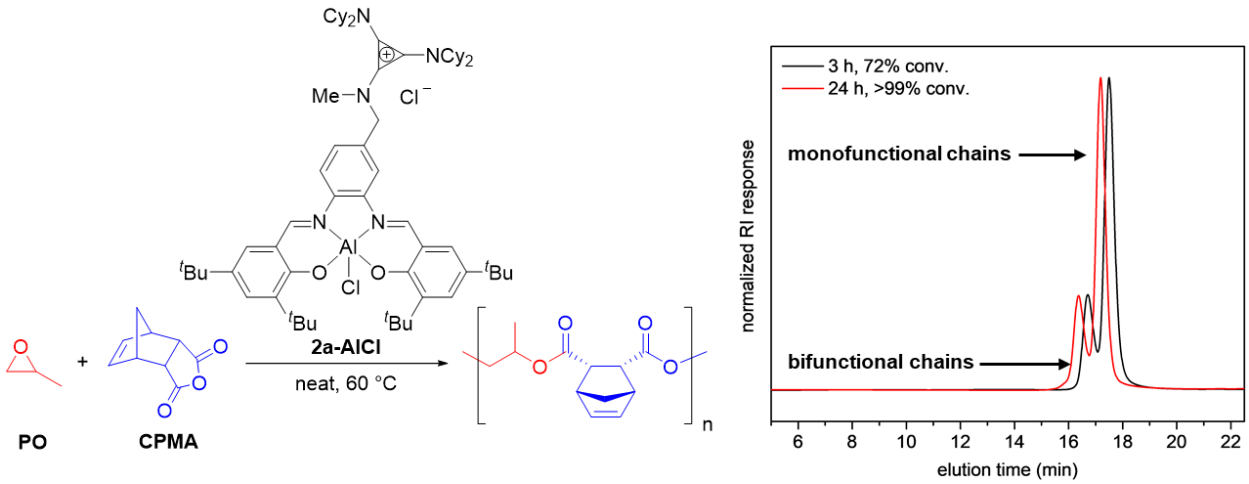
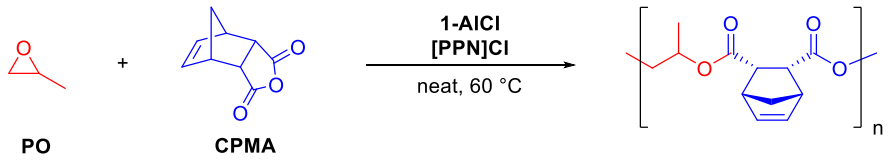


Figure S5. GPC traces of PO/CPMA copolymerizations catalyzed by **2a-AlCl** before (black) and after (red) full conversion of cyclic anhydride.

4.4. Stereochemistry of Polyester Diester Units

The carbonyl region of the ^{13}C NMR spectrum is diagnostic for diester stereochemistry of the CPMA/PO copolyester. For highly regioregular copolymers, the two expected carbonyl signals (171.50 and 172.04 ppm) are observed. When the copolymerization using the binary **1-AlCl**/[PPN]Cl system is run beyond full conversion, the ^{13}C NMR of the resulting polyester exhibits four new carbonyl signals (173.90, 173.47, 172.75, and 172.28 ppm) with similar integration values associated with the two possible *trans*-diester structures. Previous work has corroborated that the *cis*-diester content determined by ^{13}C NMR integrations is consistent with the ratio of *cis*- and *trans*-diols obtained by degrading the copolymer with lithium aluminum hydride.[23]

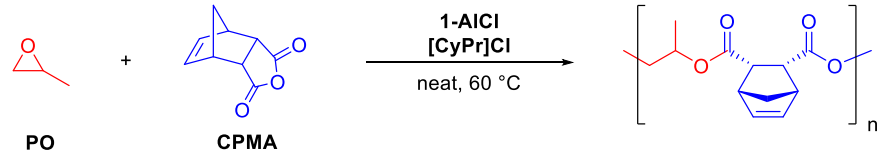
Table S2. Transesterification and Epimerization in the Binary System **1-AlCl**/[PPN]Cl [a]



entry	time (h)	% conv.[b]	$M_{n,th}$ (kDa)	$M_{n,exp}$[c] (kDa)	$Đ$[c]	% *cis*[d]
1	1	24	10.7	6.8	1.11	>99
2	2	52	23.1	15.3	1.10	>99
3	3	86	38.3	24.5	1.09	>99
4	4	>99	44.5	28.9	1.24	>99
5	5	>99	44.5	29.0	1.66	86
6	6	>99	44.5	28.9	1.91	71
7	8	>99	44.5	29.0	2.24	64
8	12	>99	44.5	28.7	2.20	55
9	24	>99	44.5	29.4	2.23	47

[a] [**1-AlCl**]$_0$:[PPNCl]$_0$:[CPMA]$_0$:[PO]$_0$ = 1:1:400:2000. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Determined by GPC in THF, calibrated with polystyrene standards. [d] Determined by quantitative ^{13}C NMR analysis of the crude reaction mixture.

Table S3. Transesterification and Epimerization in the Binary System **1-AlCl**/[CyPr]Cl [a]



entry	time (h)	% conv.[b]	$M_{n,th}$ (kDa)	$M_{n,exp}$[c] (kda)	$Đ$[c]	% *cis*[d]
1	1	24	10.8	6.8	1.11	>99
2	2	61	27.2	17.2	1.09	>99
3	3	97	43.2	27.4	1.09	>99
4	4	>99	44.5	31.3	1.31	>99
5	5	>99	44.5	35.9	1.33	>99
6	6	>99	44.5	37.4	1.34	>99
7	8	>99	44.5	37.7	1.38	>99
8	12	>99	44.5	37.4	1.31	>99
9	24	>99	44.5	40.1	1.49	>99

[a] [**1-AlCl**]$_0$:[CyPrCl]$_0$:[CPMA]$_0$:[PO]$_0$ = 1:1:400:2000. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Determined by GPC in THF, calibrated with polystyrene standards. [d] Determined by quantitative ^{13}C NMR analysis of the crude reaction mixture.

Table S4. Transesterification and Epimerization in the Bifunctional System **2a-AlCl** [a]

entry	time (h)	% conv.[b]	$M_{n,th}$ (kDa)	$M_{n,exp}$[c] (kDa)	$Đ$[c]	% *cis*[d]
1	1	20	9.0	4.0	1.26	>99
2	2	44	19.7	10.2	1.17	>99
3	3	72	31.1	18.3	1.13	>99
4	4	95	42.3	23.4	1.14	>99
5	5	>99	44.5	22.7	1.17	>99
6	6	>99	44.5	25.2	1.17	>99
7	8	>99	44.5	23.4	1.18	>99
8	12	>99	44.5	26.0	1.17	>99
9	24	>99	44.5	26.9	1.17	>99

[a] [**2a-AlCl**]$_0$:[CPMA]$_0$:[PO]$_0$ = 1:400:2000. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Determined by GPC in THF, calibrated with polystyrene standards. [d] Determined by quantitative ^{13}C NMR analysis of the crude reaction mixture.

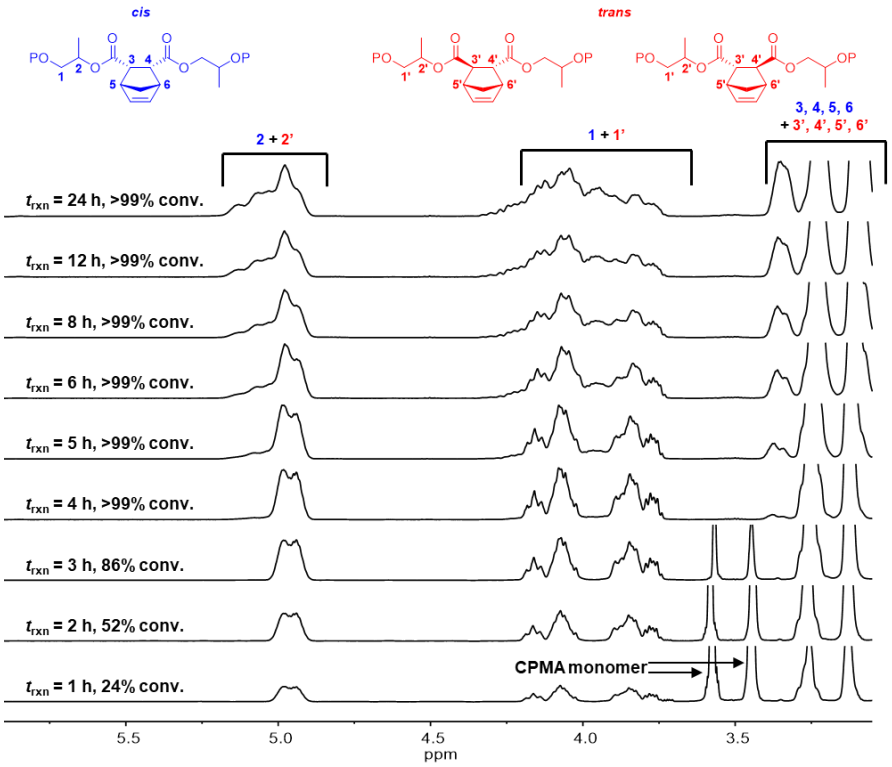


Figure S6. ^{1}H NMR spectra of CPMA/PO copolyester synthesized using **1-AlCl/[PPN]Cl** showing transesterification and epimerization at extended reaction times.

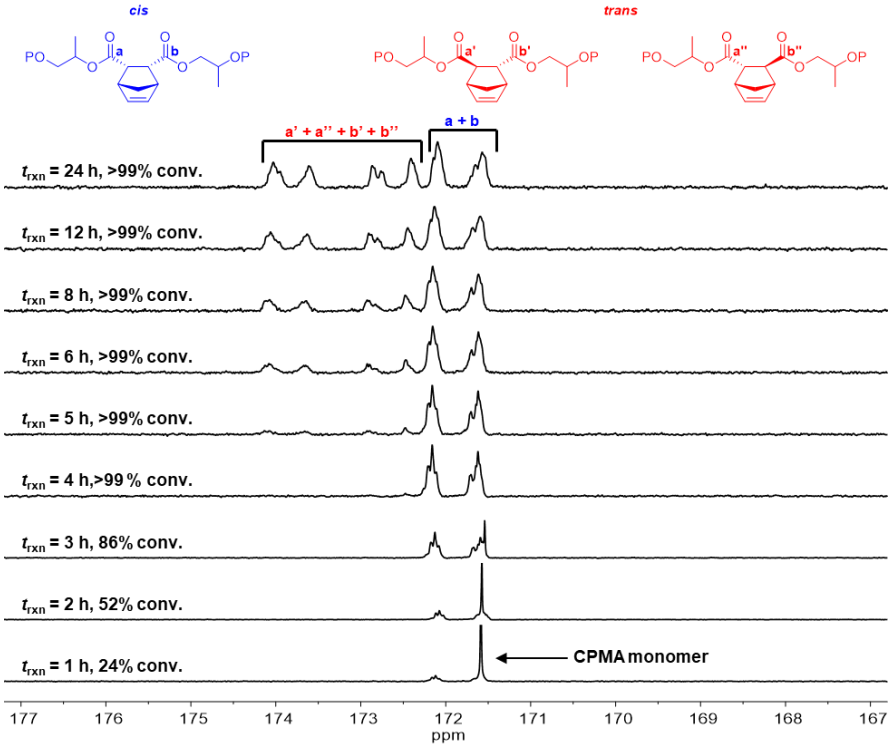


Figure S7. ^{13}C NMR spectra of CPMA/PO copolyester synthesized using **1-AlCl/[PPN]Cl** showing transesterification and epimerization at extended reaction times.

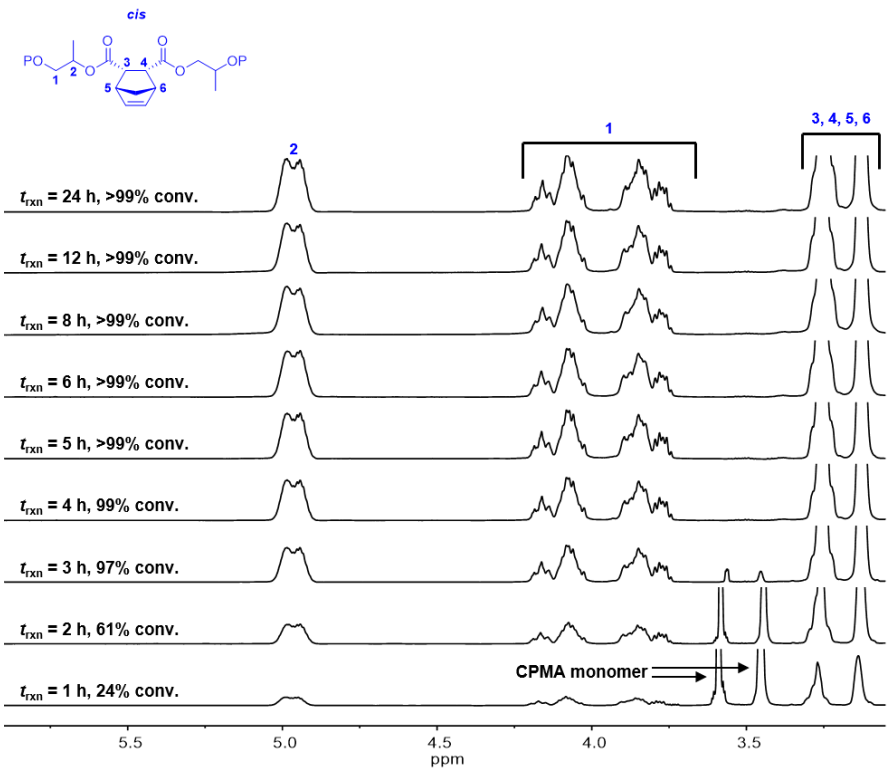


Figure S8. ^{1}H NMR spectra of CPMA/PO copolyester synthesized using **1-AlCl/[CyPr]Cl** showing conserved diester stereochemistry at extended reaction times.

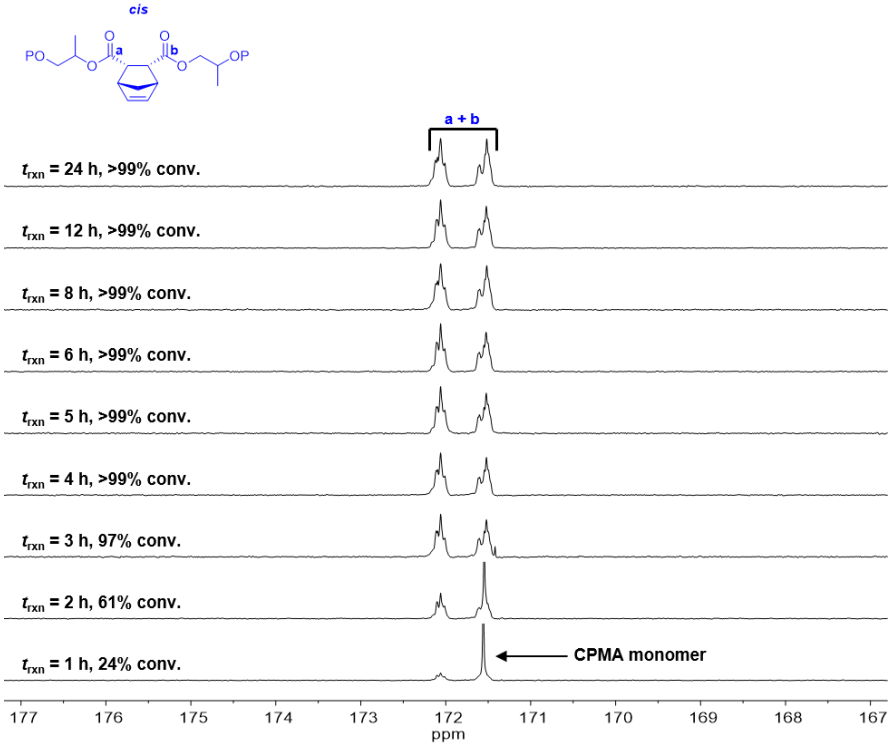


Figure S9. ^{13}C NMR spectra of CPMA/PO copolyester synthesized using **1-AlCl/[CyPr]Cl** showing conserved diester stereochemistry at extended reaction times.

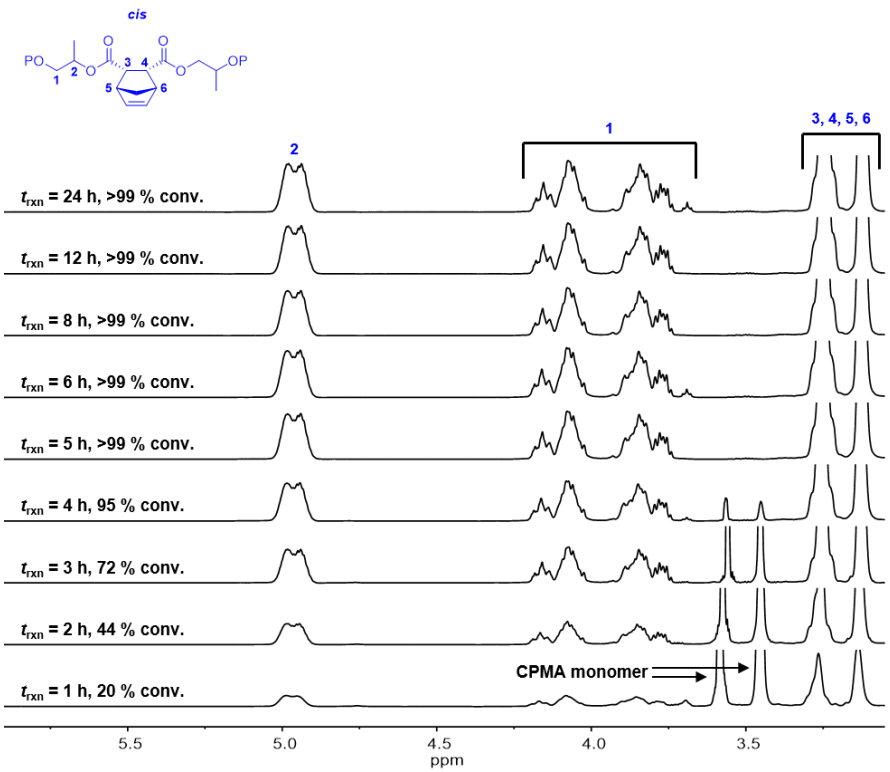


Figure S10. ^{1}H NMR spectra of CPMA/PO copolyester synthesized using **2a-AlCl** showing conserved diester stereochemistry at extended reaction times.

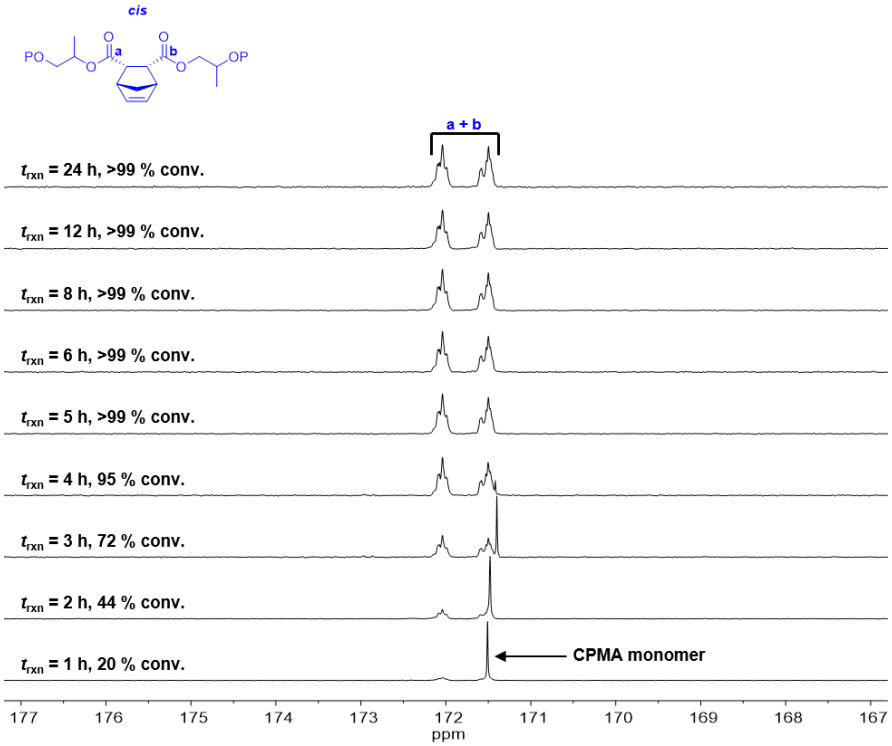
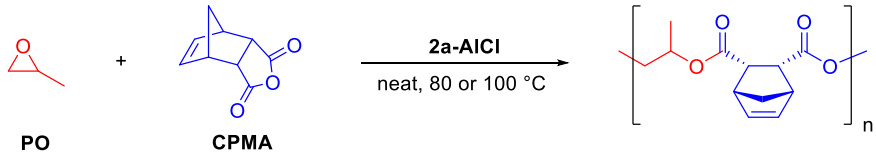


Figure S11. ^{13}C NMR spectra of CPMA/PO copolyester synthesized using **2a-AlCl** showing conserved diester stereochemistry at extended reaction times.

4.5. Effect of Elevated Temperature on 2a-AlCl-Mediated Copolymerization of PO/CPMA

Table S5. Transesterification and Epimerization in the Bifunctional System **2a-AlCl** at 80 and 100 °C [a]



entry	temp (°C)	time (h)	% conv.[b]	TOF[c] (h^{-1})	$M_{n,th}$ (kDa)	$M_{n,exp}$[d] (kDa)	$Đ$[c]	% *cis*[e]
1	80	1.7	77	186	34.3	20.8	1.10	>99
2	80	24	>99	-	44.5	27.9	1.13	>99
3	100	0.67	78	466	34.8	18.8	1.14	>99
4	100	24	>99	-	44.5	24.5	1.16	>99

[a] [**2a-AlCl**]:[CPMA]$_0$:[PO]$_0$ = 1:400:2000. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. TOF = Turnover frequency, mol anhydride consumed × mol **2a-AlCl**$^{-1}$ × h^{-1}. [d] Determined by GPC in THF, calibrated with polystyrene standards. [e] Determined by quantitative ^{13}C NMR analysis of the crude reaction mixture.

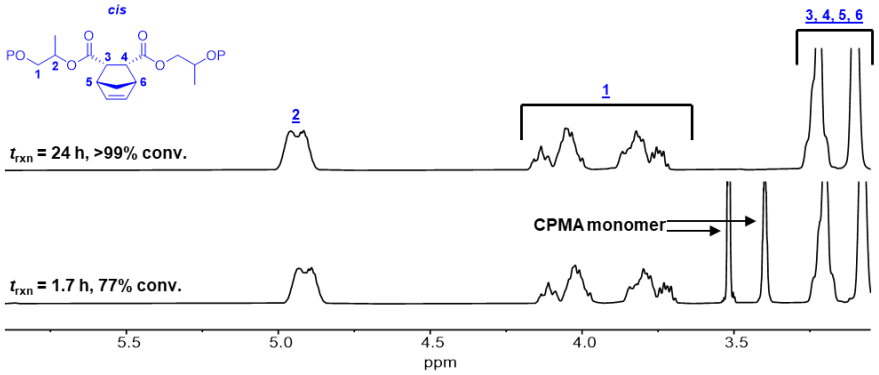


Figure S12. ^{1}H NMR spectra of CPMA/PO copolyester synthesized at 80 °C using **2a-AlCl** showing conserved diester stereochemistry at extended reaction times.

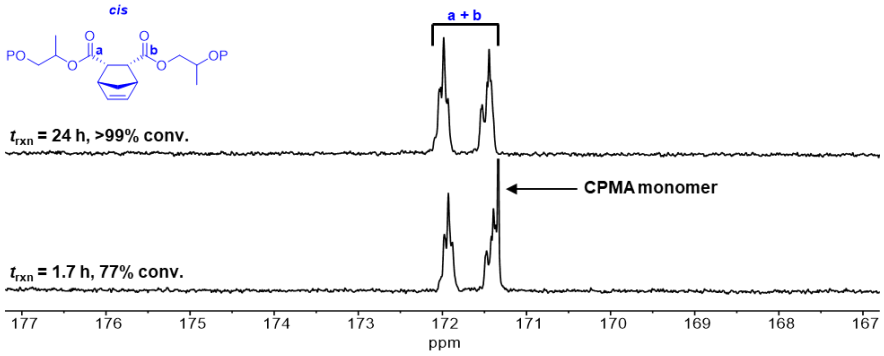


Figure S13. ^{13}C NMR spectra of CPMA/PO copolyester synthesized at 80 °C using **2a-AlCl** showing conserved diester stereochemistry at extended reaction times.

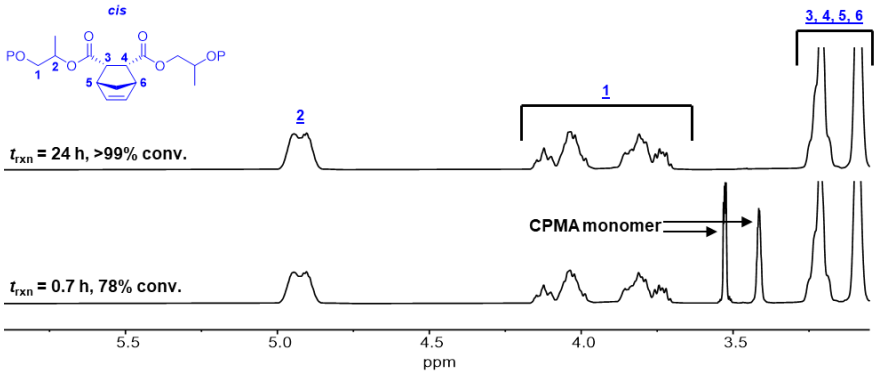


Figure S14. ^{1}H NMR spectra of CPMA/PO copolyester synthesized at 100 °C using **2a-AlCl** showing conserved diester stereochemistry at extended reaction times.

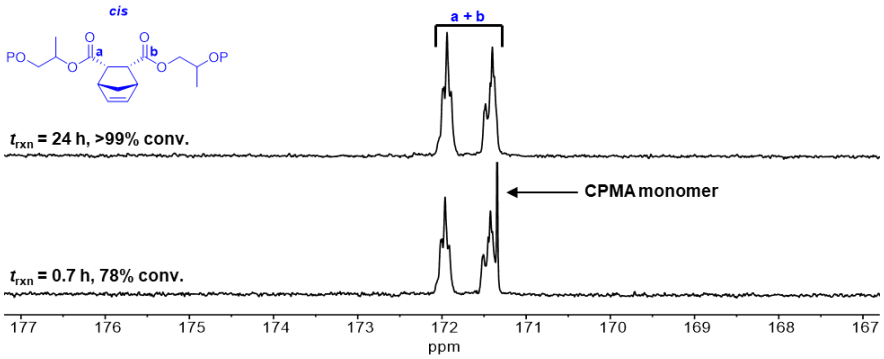


Figure S15. ^{13}C NMR spectra of CPMA/PO copolyester synthesized at 100 °C using **2a-AlCl** showing conserved diester stereochemistry at extended reaction times.

5. Procedures for Kinetic Measurements

Polymerizations for Figures 1, 2, and 3 were performed according to the general polymerization procedure, unless the amount of catalyst required was less than 1.5 mg. In that case, a stock solution of catalyst in PhMe (~0.1 mg/mL) was prepared. The appropriate amount of stock solution was added to an oven-dried 4 mL vial, and solvent removed in vacuo at 22 °C for 18 h. In the glove box, CPMA (0.250 g, 1.52 mmol, X equiv) was weighed into the vial containing catalyst and cocatalyst (if required), and PO was added by volume (0.53 mL, 7.61 mmol, 5X equiv). The vial was sealed with a Teflon-lined cap, removed from the glove box, and placed in an oil bath preheated to 60 °C. At desired time points, small aliquots were removed for ^{1}H NMR spectroscopic analysis to determine conversion of the cyclic anhydride.

5.1. Polymerization Kinetics Using Binary Systems 1-AlCl/[PPN]Cl and 1-AlCl/[CyPr]Cl

Polymerization Kinetics at Various Loadings of 1-AlCl/[PPN]Cl

According to the general kinetics procedure, the catalyst, **1-AlCl**, and cocatalyst, [PPN]Cl, concentrations were varied as a pair in a 1:1 ratio while the initial amounts of CPMA and PO were maintained. ^{1}H NMR analysis of aliquots removed throughout the course of the reactions revealed linear conversion of anhydride CPMA with time (Figure S16). The reaction rates depended non-linearly on the catalyst loading, and time normalization was used to determine the reaction order in catalyst (*vide infra*).

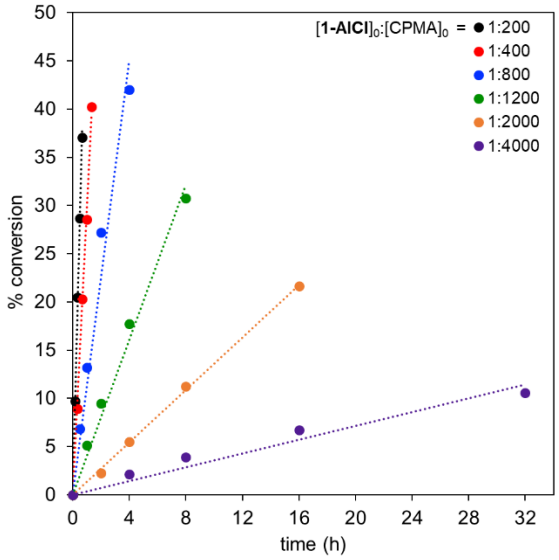


Figure S16. PO/CPMA copolymerization kinetics with **1-AlCl**/[PPN]Cl.

Determination of the Reaction Order in 1-AlCl/[PPN]Cl Using the Time Normalized Method

The normalized time scale method relies on the invariance of catalyst concentration during the course of a reaction.[24] In the binary **1-AlCl**/[PPN]Cl system, both the concentration of the aluminum catalyst and the concentration of the [PPN] cocatalyst are constant throughout the reaction. Accordingly, the normalized time scale method can be used to identify the reaction order in both species. Using the normalized time scale method, the consumption of CPMA was plotted

against the normalized time scale t×[**1-AlCl**]^n, where t is time in hours, [**1-AlCl**] is the initial concentration of the aluminum catalyst, and *n* is the order in catalyst. CPMA consumption at six different catalyst loadings was plotted against normalizations using possible reaction orders *n*. At high catalyst loadings ([**1-AlCl**]:[CPMA] ≥1:800), excellent overlay was obtained for first-order behavior in catalyst (Figure 1, left). However, the normalized traces for low catalyst loadings ([**1-AlCl**]:[CPMA] <1:800) did not overlap with *n* = 1 (Figure S17, left). Accounting for [PPN] at low catalyst loadings with a time normalization of t×[**1-AlCl**]^1×[PPN]^1 afforded excellent overlay (Figure 1, right), but applying the same t×[**1-AlCl**]^1×[PPN]^1 normalization at high catalyst loadings yield poor agreement (Figure S17, right). The polymerization therefore appears to exhibit a change in reaction order at reduced loadings of the catalytic pair.

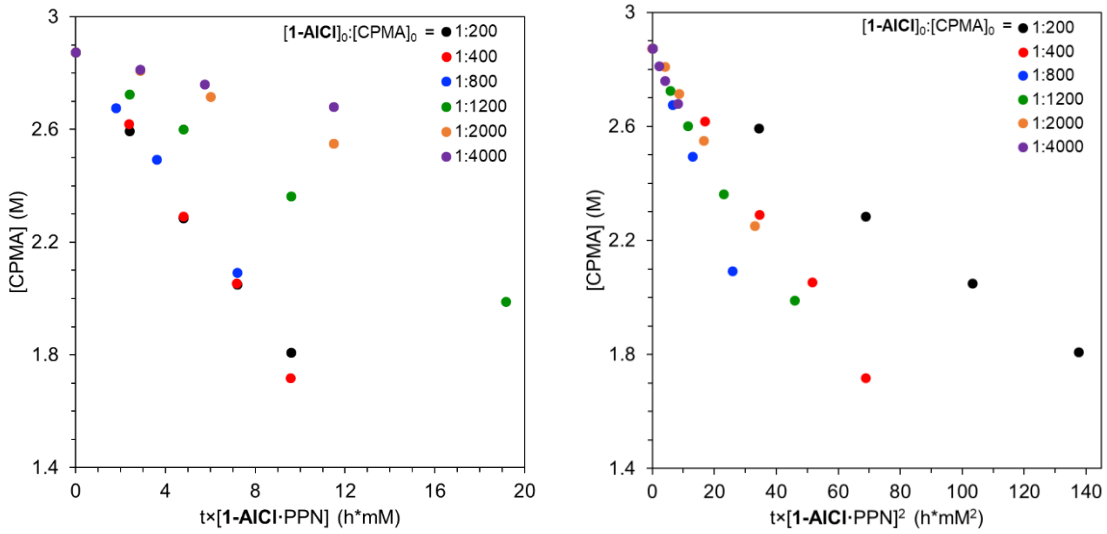


Figure S17. Anhydride decay versus normalized time scale for first-order (left) and second-order (right) behavior in the binary catalyst system **1-AlCl**/PPN.

Due to the equivalent concentrations of **1-AlCl** and PPN, good overlay is also obtained with time normalizations of t×[PPN]^2 or t×[**1-AlCl**]^2 at low catalyst loadings. From the existing experimental and computation studies, however, there is no evidence implicating a mechanistic step in which two equivalents of the cocatalyst or two equivalents of the Lewis acid come together.

Yet previous mechanistic investigations do suggest that PPN delivers a carboxylate chain-end to ring-open the Lewis-activated epoxide, consistent with the proposed orders [**1-AlCl**]^{1}[PPN]^{1}.[25]

Initial Rate Determination of the Reaction Order in Epoxide in the Binary System 1-AlCl/PPN

The order in epoxide in the binary catalyst system **1-AlCl**/PPN was determined by varying the PO concentration while catalyst and CPMA concentrations were held constant ([**1-AlCl**]:[PPNCl]:[CPMA] = 1:1:1200). As the polymerizations are typically performed in neat epoxide, THF was added at lower epoxide concentrations to maintain a consistent total volume. A representative procedure follows: catalyst and cyclic anhydride were weighed into an oven-dried 4 mL glass vial in a nitrogen-filled glove box. Appropriate volumes of THF and PO were added sequentially via gastight syringe, and the vial was sealed with a Teflon coated cap. The vial was then transferred to an oil bath at 60 °C. At desired time points, small aliquots were removed for ^{1}H NMR spectroscopic analysis to determine conversion of anhydride. Initial rates were determined before 20% conversion of anhydride was reached. A linear correlation between polymerization rate and [PO] is consistent with first-order behavior in epoxide (Figure S18).

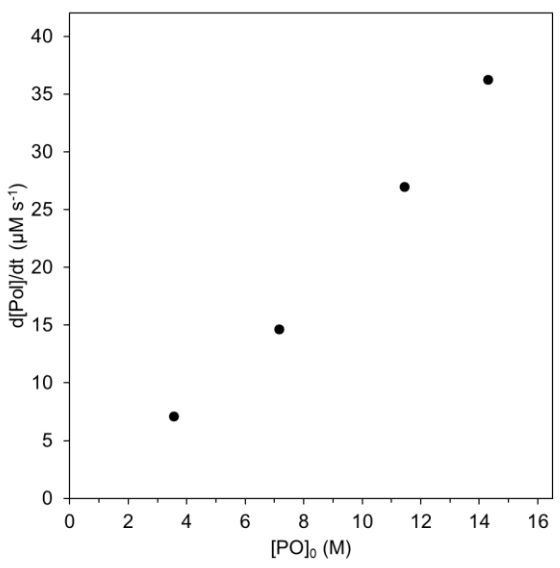


Figure S18. Initial rates of PO/CPMA copolymerization (<20% conversion) versus initial PO concentration using the binary catalyst system **1-AlCl**/[PPN]Cl.

Polymerization Kinetics Controls with Various Loadings of 1-AlCl/[CyPr]Cl

According to the general kinetics procedure, the catalyst, **1-AlCl**, and cocatalyst, [CyPr]Cl, concentrations were varied as a pair in a 1:1 ratio while the initial amounts of CPMA and PO were maintained. Analysis of aliquots removed throughout the course of the reactions revealed linear conversion of anhydride CPMA with time (Figure S19). The observed reaction profiles using [CyPr]Cl as a cocatalyst were in excellent agreement with those obtained using [PPN]Cl (Figure S20), suggesting that the two cocatalysts in the binary systems perform similarly.

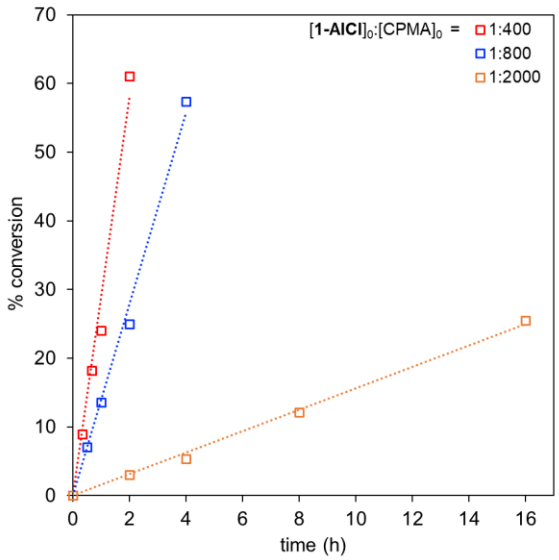


Figure S19. PO/CPMA copolymerization kinetics with **1-AlCl**/[CyPr]Cl.

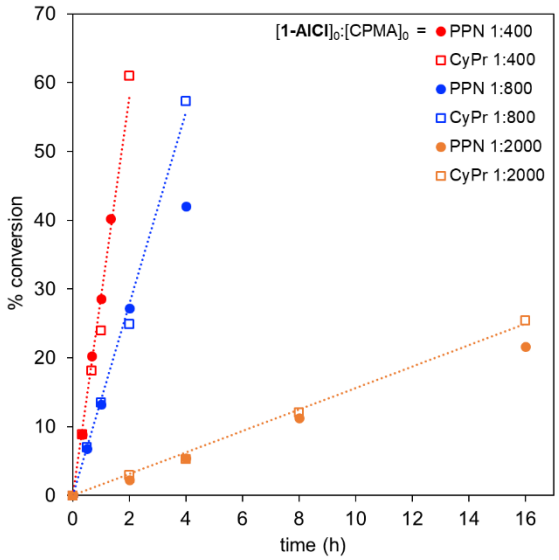


Figure S20. Comparison of PO/CPMA copolymerization kinetics using **1-AlCl**/[PPN]Cl (closed circles) and **1-AlCl**/[CyPr]Cl (open squares) demonstrating comparable rates.

5.2. Cobalt Catalyst Deactivation Kinetics in the Bifunctional System 2a-CoOAc

Despite first-order behavior in the bifunctional catalyst systems, PO/CPMA copolymerizations catalyzed by **2a-CoOAc** exhibited non-linear conversion with time at low catalyst loadings (Figure S21). Further evidence of catalyst deactivation was observed by formation of a paramagnetic species in the ^{1}H NMR, consistent with reduction to inactive **2a-Co(II)**.

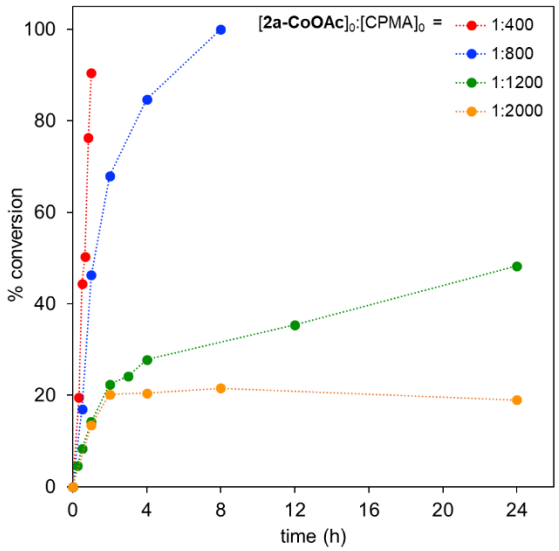


Figure S21. PO/CPMA copolymerization kinetics with **2a-CoOAc** demonstrating catalyst deactivation at low loadings.

5.3. Polymerization Kinetics Using Bifunctional System 2a-AlCl

Initial Rate Determination of the Reaction Order in Epoxide

The order in epoxide in the bifunctional catalyst system was determined by varying the PO concentration while catalyst and CPMA concentrations were held constant ([**2a-AlCl**]:[CPMA] = 1:1200). As the polymerizations are typically performed in neat epoxide, THF was added at lower epoxide concentrations to maintain a consistent total volume. A representative procedure follows: catalyst and cyclic anhydride were weighed into an oven-dried 4 mL glass vial in a nitrogen-filled

glove box. Appropriate volumes of THF and PO were added sequentially via gastight syringe, and the vial was sealed with a Teflon coated cap. The vial was then transferred to an oil bath at 60 °C. At desired time points, small aliquots were removed for ^{1}H NMR spectroscopic analysis to determine conversion of anhydride. Initial rates were determined before 20% conversion of anhydride was reached.

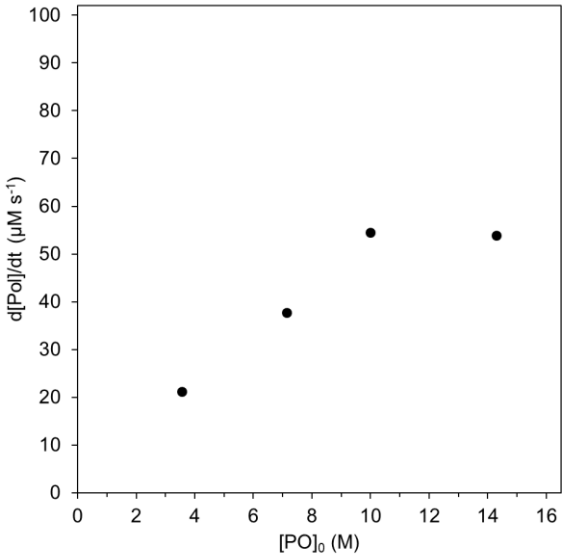


Figure S22. Initial rates of PO/CPMA copolymerization (<20% conversion) versus initial PO concentration using the bifunctional catalyst **2a-AlCl**.

A linear relationship between the initial rates of polymerization at various concentrations of PO (3.5–14 M, [**2a-AlCl**]$_0$:[CPMA]$_0$ = 1:1200) indicates a first-order dependence on epoxide (Figure S22). Upon increasing the initial concentration of PO above 10 M ([PO]$_0$:[CPMA]$_0$ = 3.5:1), no additional rate enhancement was observed, suggesting the onset of pseudo-zero-order kinetics.

Initial Rate Determination of the Reaction Order in Cyclic Anhydride

The order in cyclic anhydride in the bifunctional catalyst system was determined by varying the CPMA concentration while catalyst and PO concentrations were held constant ([**2a-**

AlCl]:[PO] = 1:6000). A representative procedure follows: catalyst and cyclic anhydride were weighed into an oven-dried 4 mL glass vial in a nitrogen-filled glove box. PO was added via syringe, and the vial was sealed with a Teflon coated cap. The vial was then transferred to an oil bath at 60 °C. At desired time points, small aliquots were removed for ^{1}H NMR spectroscopic analysis to determine conversion of anhydride. Initial rates were determined before 20% conversion of anhydride was reached. Polymerization rates were invariant with different initial concentrations of CPMA, indicating a zero-order dependence on cyclic anhydride (Figure S23).

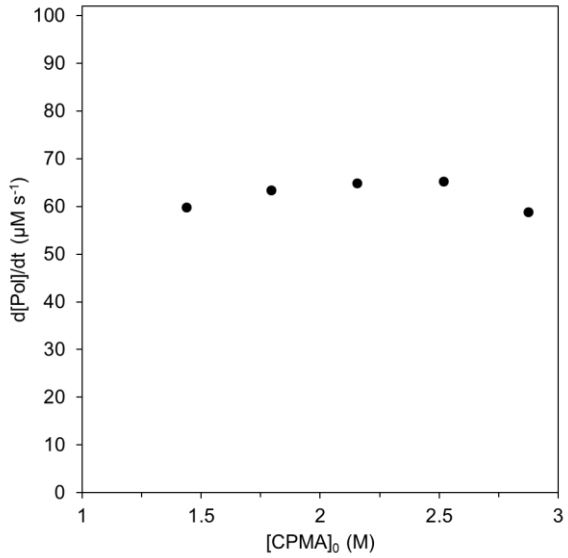


Figure S23. Initial rates of PO/CPMA copolymerization (<20% conversion) versus initial CPMA concentration using the bifunctional catalyst **2a-AlCl**.

Polymerization Kinetics at Various Loadings of Bifunctional Catalysts 2a-AlCl, 4-AlCl, and 6-AlCl

According to the general kinetics procedure, the catalyst loading was varied while the initial amounts of CPMA and PO were maintained. Analysis of aliquots removed throughout the course of the reactions revealed linear conversion of cyclic anhydride with time for catalysts **2a-AlCl** (Figure S24) and **6-AlCl** (Figure S26). Catalyst **4-AlCl** exhibited linear conversion of CPMA

at high catalyst loadings, but extremely low catalyst loadings (<0.05 mol%) resulted in catalyst deactivation slowing conversion at extended reaction times (Figure S25).

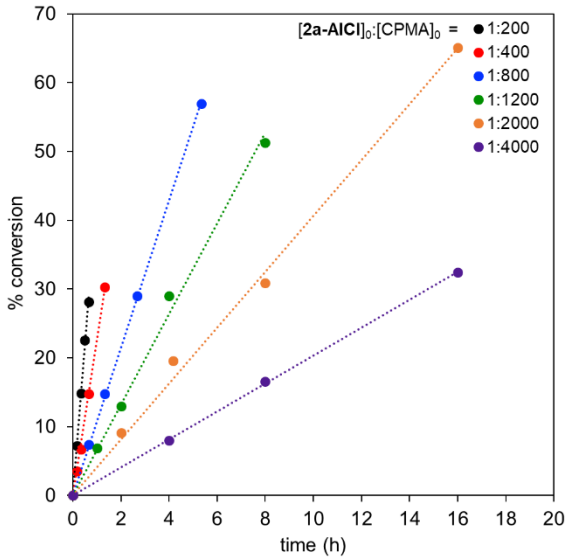


Figure S24. PO/CPMA copolymerization kinetics using bifunctional catalyst **2a-AlCl**.

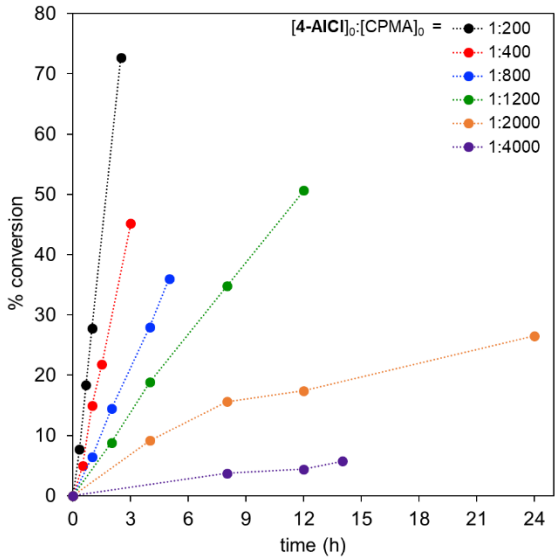


Figure S25. PO/CPMA copolymerization kinetics using bifunctional catalyst **4-AlCl**.

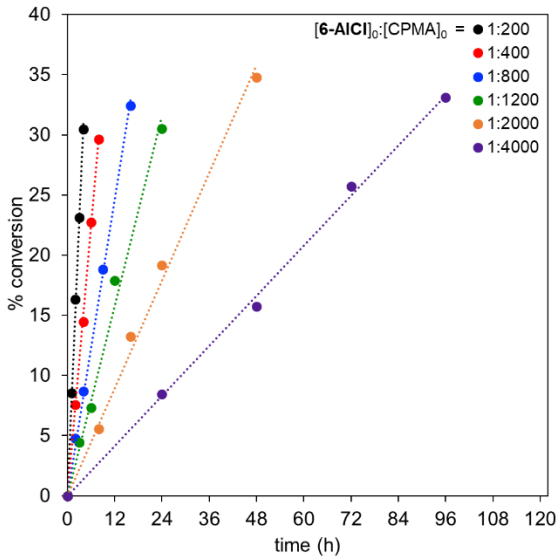


Figure S26. PO/CPMA copolymerization kinetics using bifunctional catalyst **6-AlCl**.

Determination of the Reaction Order in 2a-AlCl Using the Time Normalized Method

Time normalization analysis[24] was used to determine the reaction order in bifunctional catalyst **2a-AlCl**. The consumption of [CPMA] was plotted against the normalized time scale t×[**2a-AlCl**]^n, where t is time in hours, [**2a-AlCl**] is the initial catalyst concentration, and *n* is the order in catalyst. The reaction progress for the six different catalyst loadings was plotted against normalizations using possible reaction orders *n*. At all catalyst loadings studied ([**2a-AlCl**]:[CPMA] = 1:200–1:4000), excellent overlay was obtained for first-order behavior in catalyst (Figure 2). Zero-order and second-order fits did not provide good overlay (Figure S27).

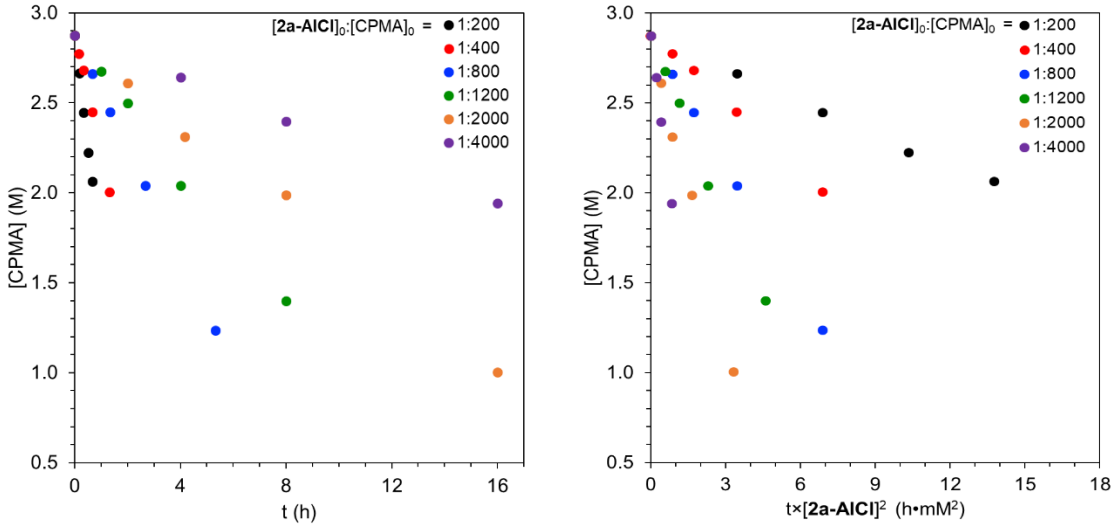


Figure S27. Anhydride decay versus normalized time scale for zero-order (left) and second-order (right) behavior in the tethered catalyst system **2a-AlCl**.

5.4. TOF as a Function of Catalyst Loading in Binary and Bifunctional Catalyst Systems

Average turnover frequencies from kinetics experiments (Figure S16, Figure S19, Figure S24–S26) and time points taken between 30–64% conversion (Table S6) were used to plot turnover frequency as a function of catalyst loading in the binary and bifunctional systems (Figure S28).

Table S6. Conversion as a function of catalyst loading in the binary **1-AlCl** and bifunctional **2a-AlCl** systems for PO/CPMA copolymerization.

entry	catalyst	cocatalyst [a]	$[catalyst]_0$:$[CPMA]_0$	time (h)	% conv. [b]	TOF (h^{-1})[c]
1	**1-AlCl**	[PPN]Cl	1:1000	6	45	75
2	**1-AlCl**	[PPN]Cl	1:1600	24	64	42
3	**1-AlCl**	[PPN]Cl	1:2400	48	51	25
4	**1-AlCl**	[PPN]Cl	1:3200	72	34	15
5	**1-AlCl**	[CyPr]Cl	1:1000	6	44	73
6	**1-AlCl**	[CyPr]Cl	1:1600	24	50	34
7	**1-AlCl**	[CyPr]Cl	1:2400	48	56	27
8	**1-AlCl**	[CyPr]Cl	1:3200	72	43	19
9	**2a-AlCl**	- [d]	1:1000	6	52	87
10	**2a-AlCl**	- [d]	1:1600	9	50	90
11	**2a-AlCl**	- [d]	1:2400	14	52	89
12	**2a-AlCl**	- [d]	1:3200	18	52	89

[a] $[catalyst]_0$:$[cocatalyst]_0$ = 1:1. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] TOF = Turnover frequency, mol anhydride consumed × mol catalyst^{-1} × h^{-1}. [d] No exogenous cocatalyst was used.

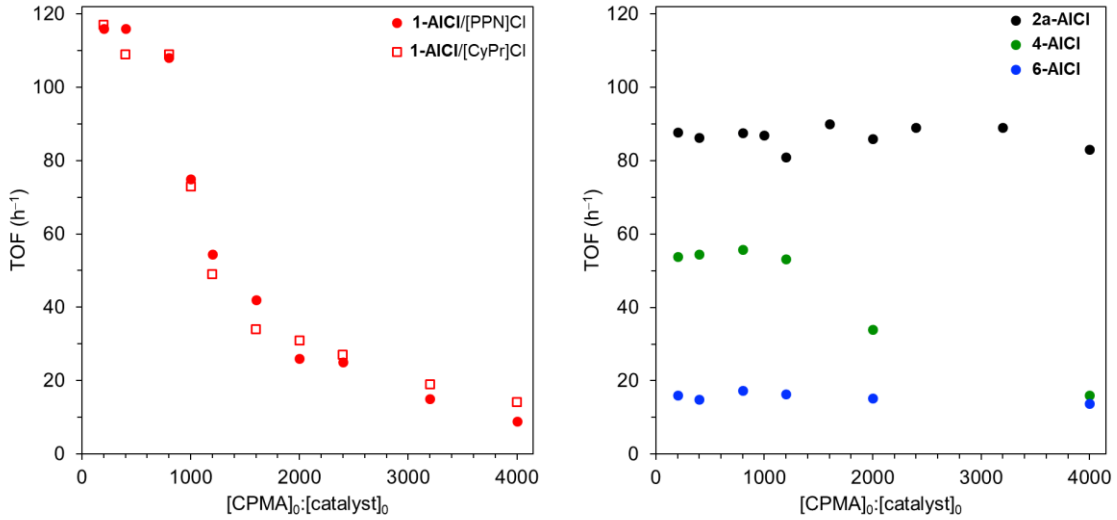
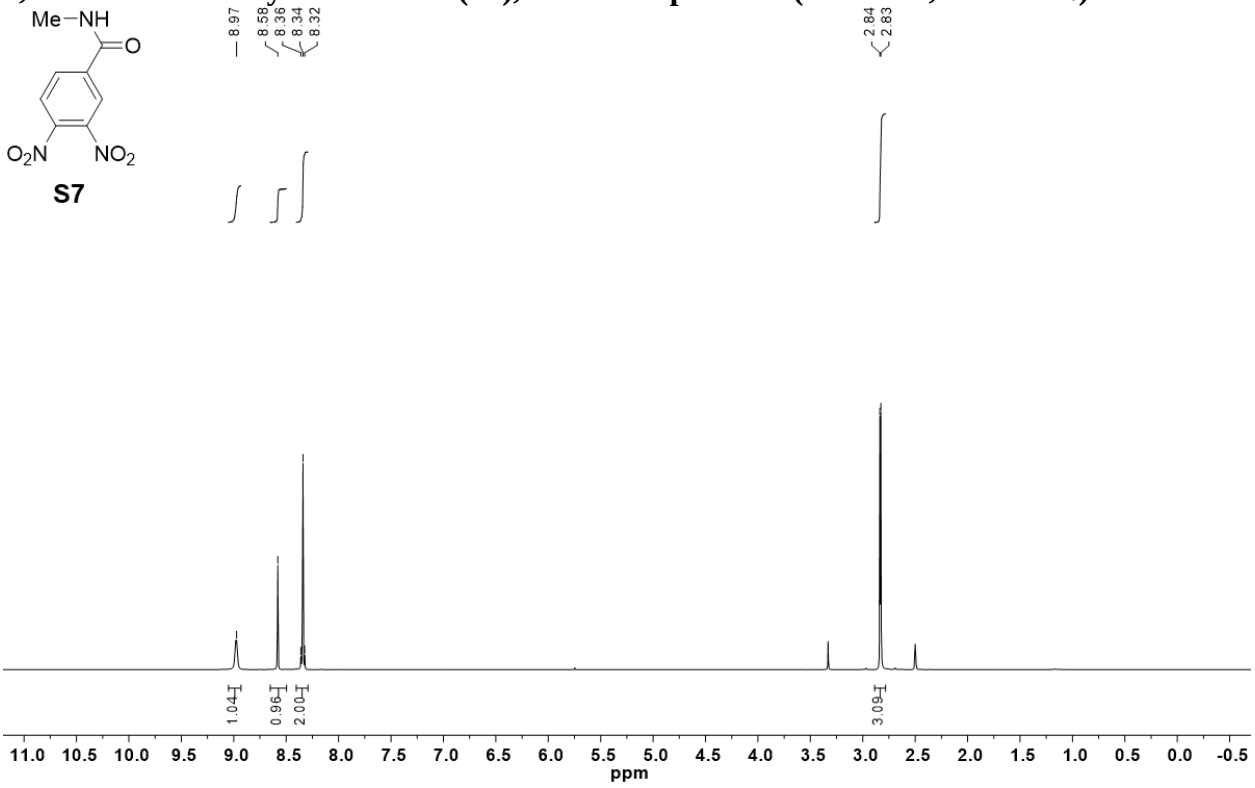


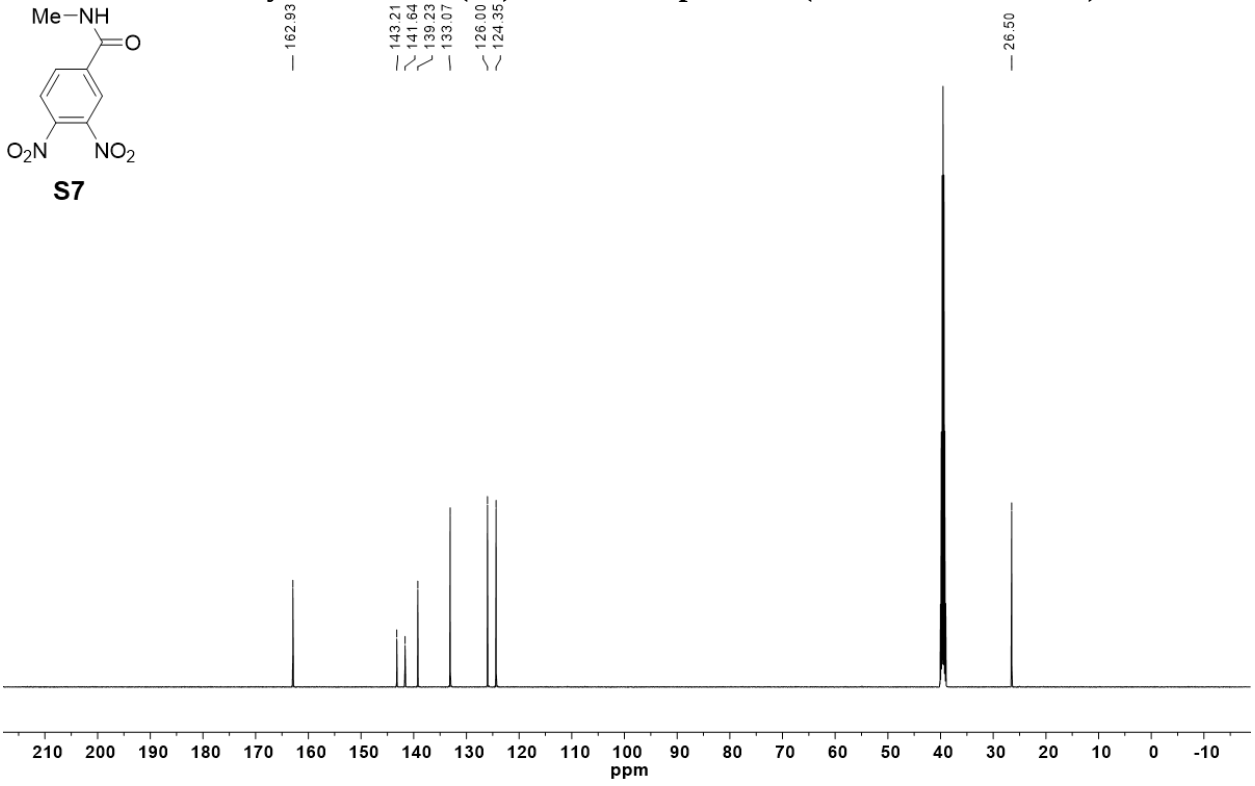
Figure S28. Comparison of TOF in binary systems **1-AlCl**/[PPN]Cl and **1-AlCl**/[CyPr]Cl (left) and bifunctional systems **2a-AlCl**, **4-AlCl**, and **6-AlCl** (right) as a function of catalyst loading for PO/CPMA copolymerization. $[catalyst]_0$:$[CPMA]_0$:$[PO]_0$ = 1:200:1000–1:4000:20000. For polymerizations performed using **1-AlCl**, $[catalyst]_0$:$[cocatalyst]_0$ = 1:1. TOF = Turnover frequency, mol anhydride consumed × mol catalyst^{-1} × h^{-1}.

6. ^{1}H and ^{13}C NMR Spectra of Synthesized Compounds

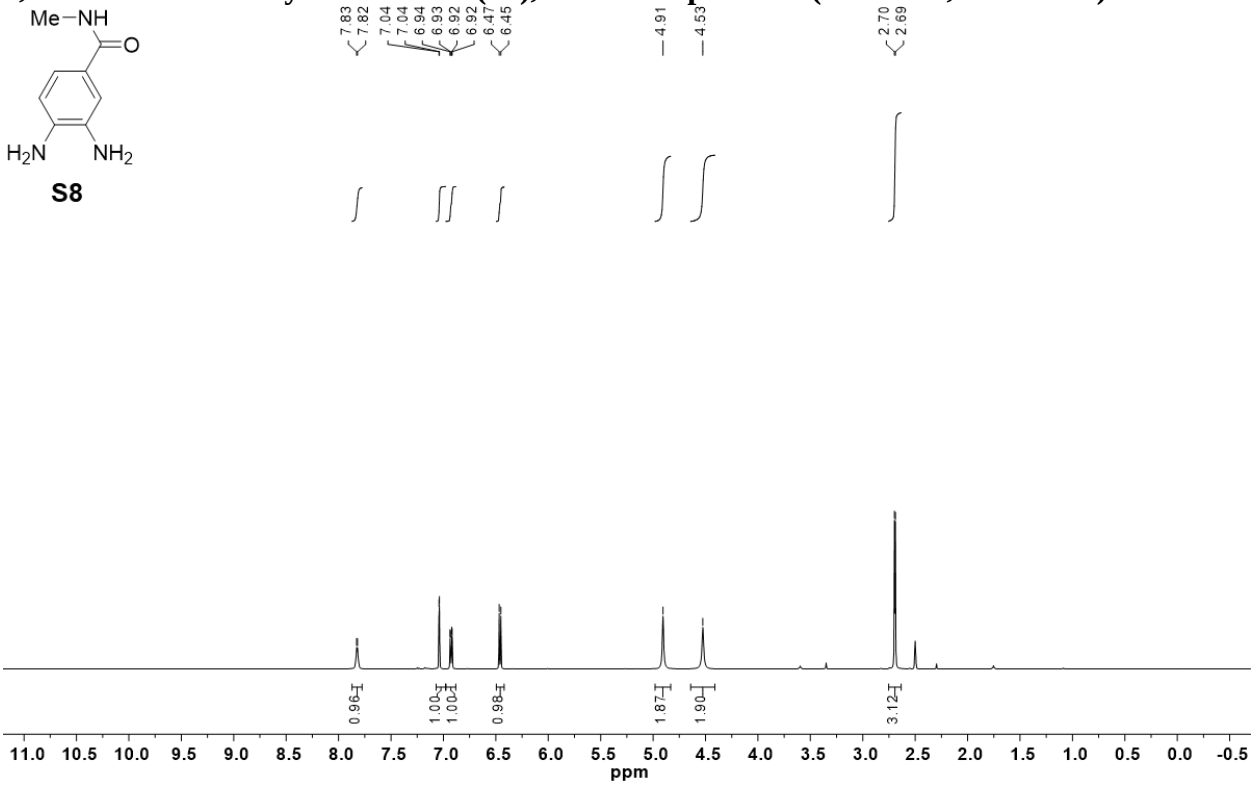
3,4-Dinitro-*N*-methyl-benzamide (S7), ^{1}H NMR spectrum (500 MHz, DMSO-d_6)



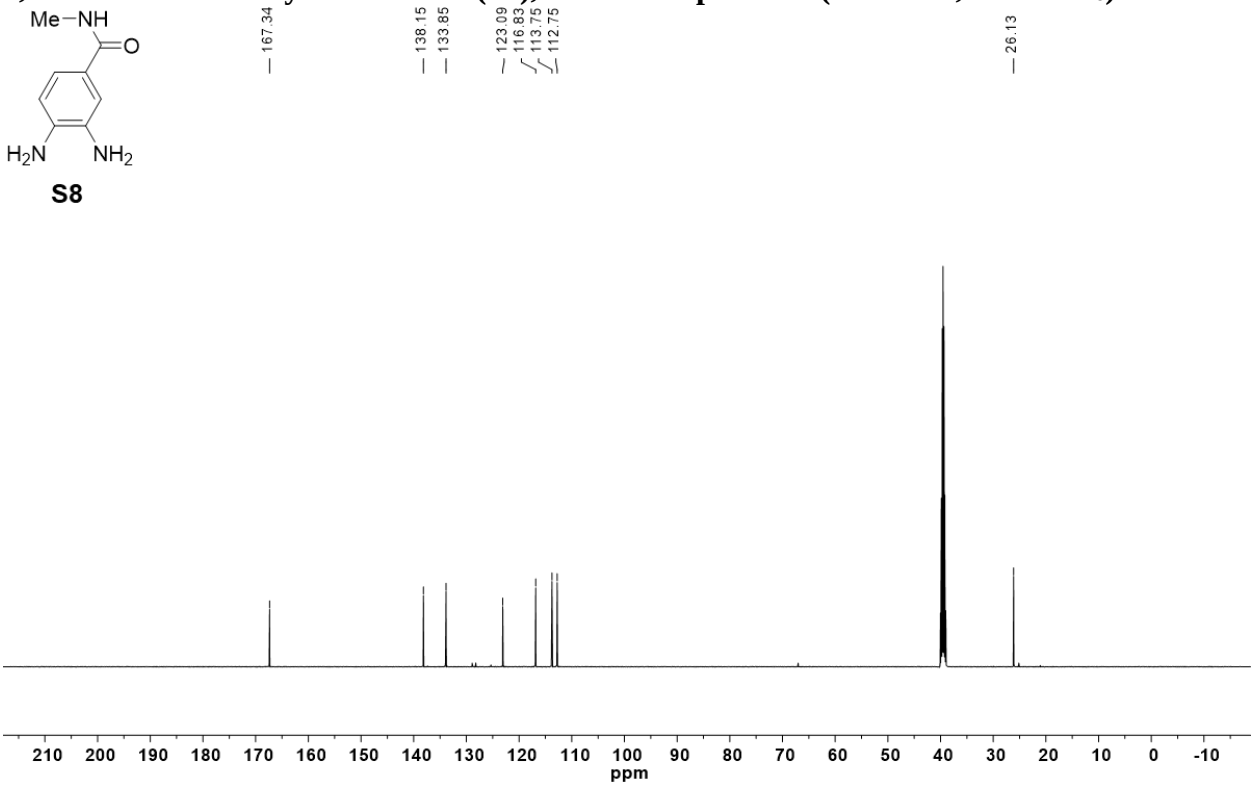
3,4-Dinitro-*N*-methyl-benzamide (S7), ^{13}C NMR spectrum (125 MHz, DMSO-d_6)



3,4-Diamino-*N*-methyl-benzamide (S8), ^{1}H NMR spectrum (500 MHz, DMSO-d_6)

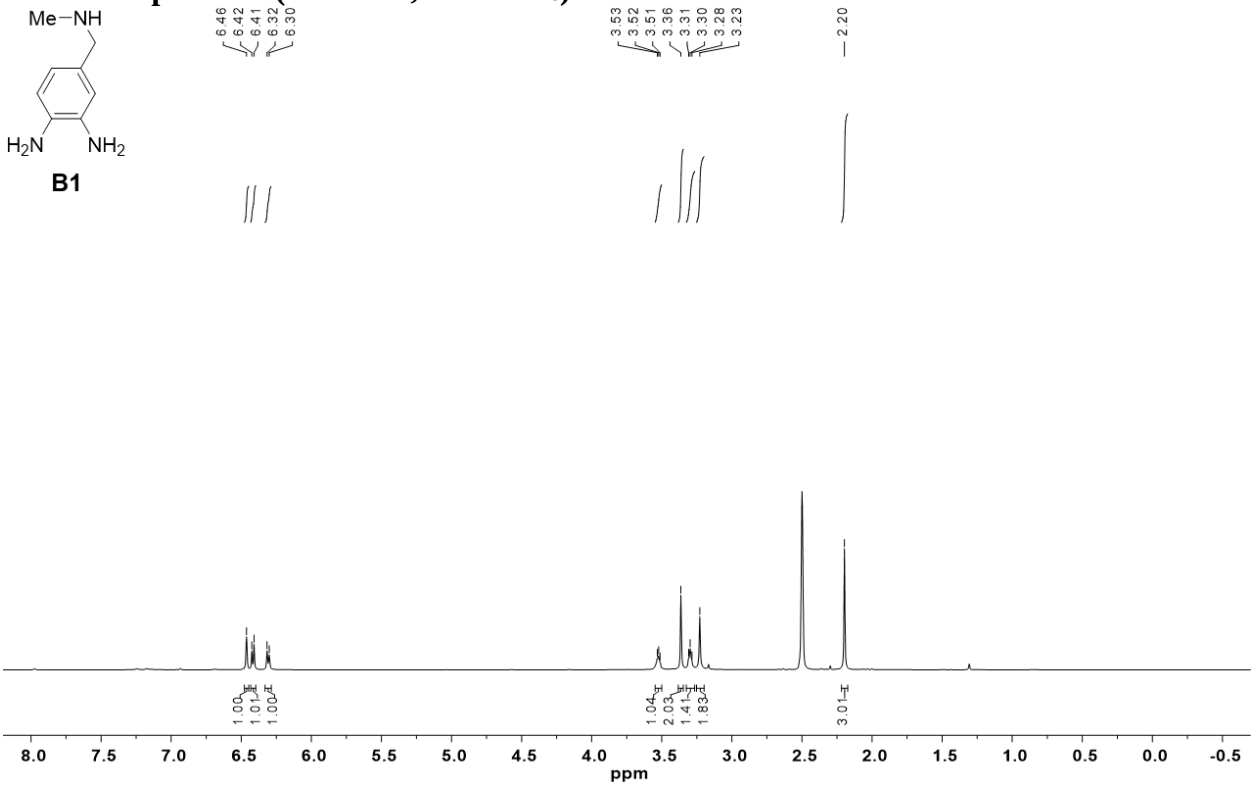


3,4-Diamino-*N*-methyl-benzamide (S8), ^{13}C NMR spectrum (125 MHz, DMSO-d_6)



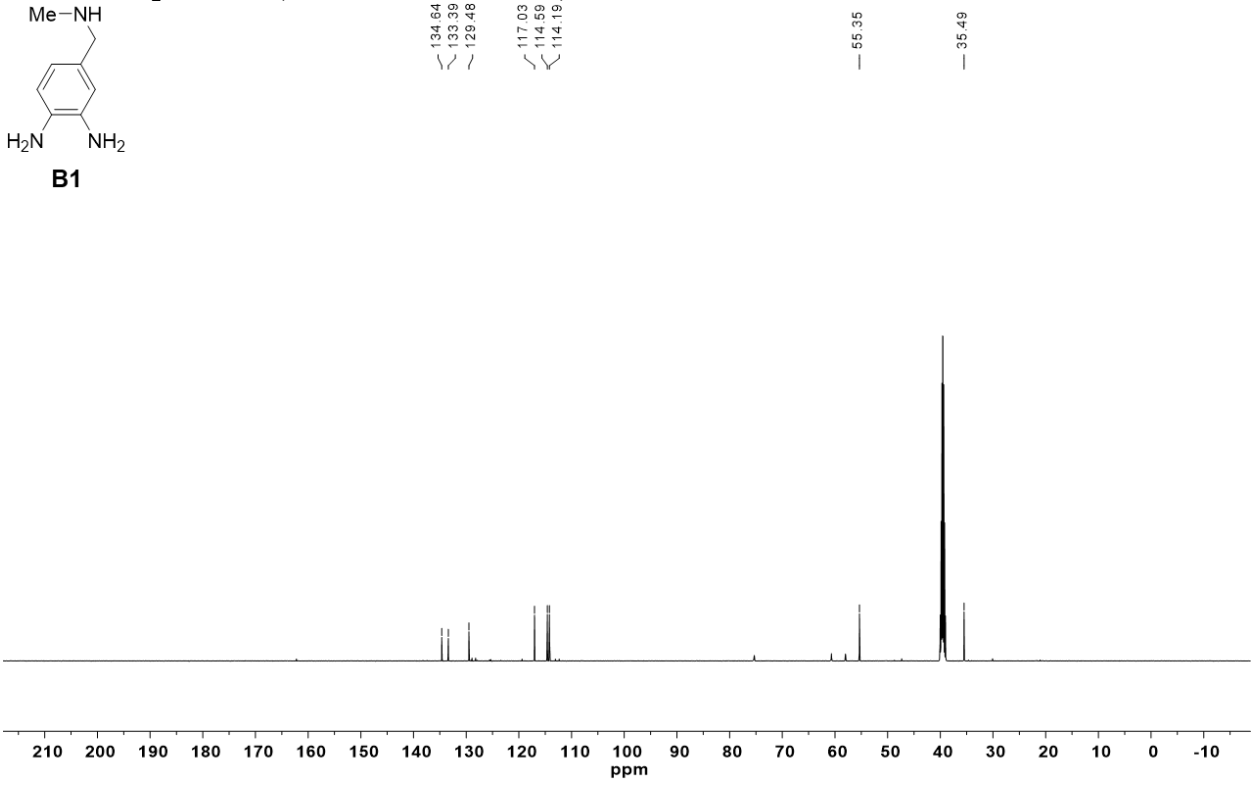
4-*N*-Methyl-methanamine-1,2-diaminobenzene (B1)

^{1}H NMR spectrum (500 MHz, DMSO-d_6)

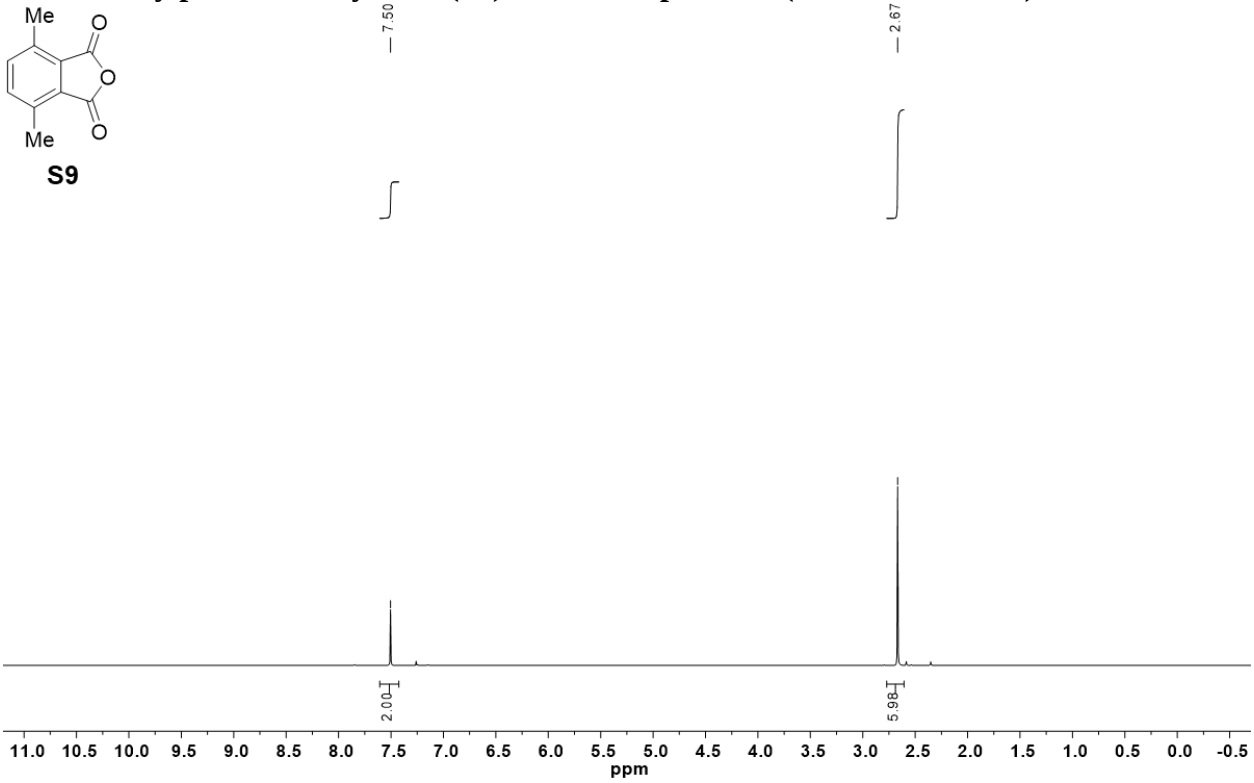


4-*N*-Methyl-methanamine-1,2-diaminobenzene (B1)

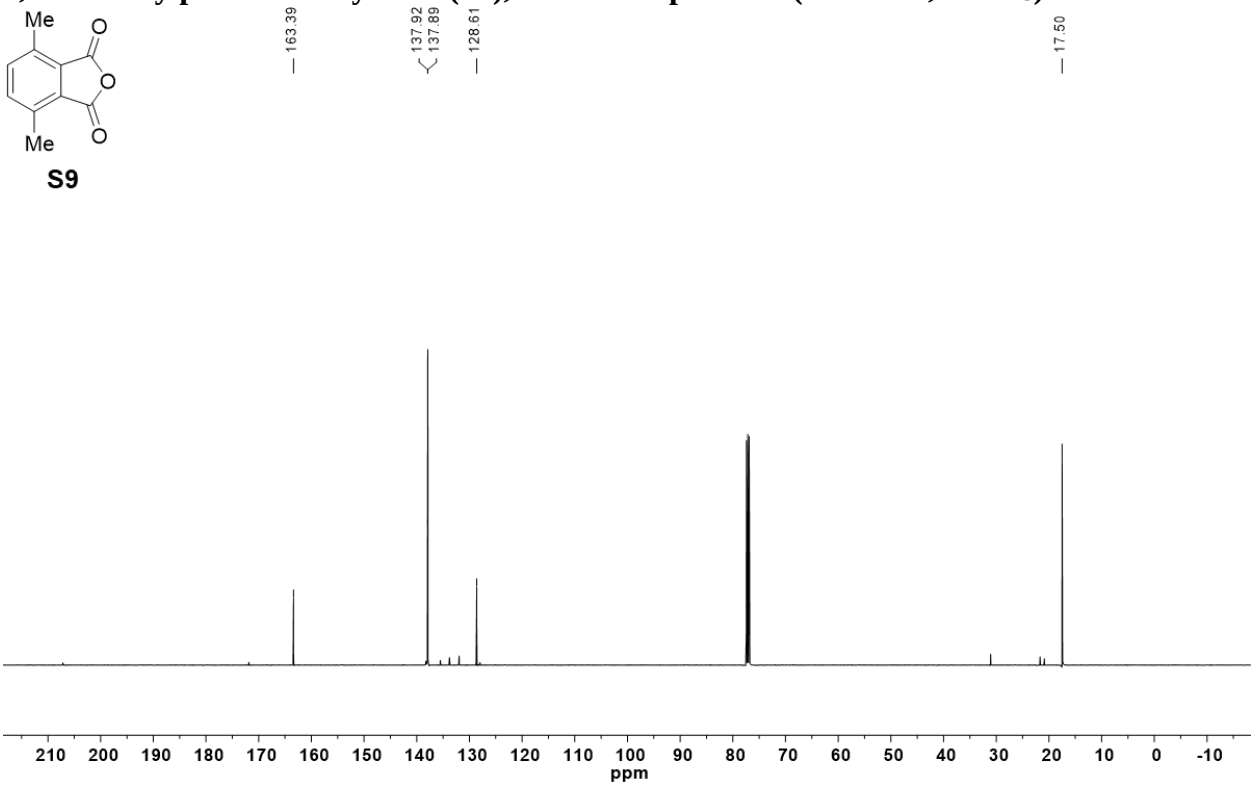
^{13}C NMR spectrum (125 MHz, DMSO-d_6)



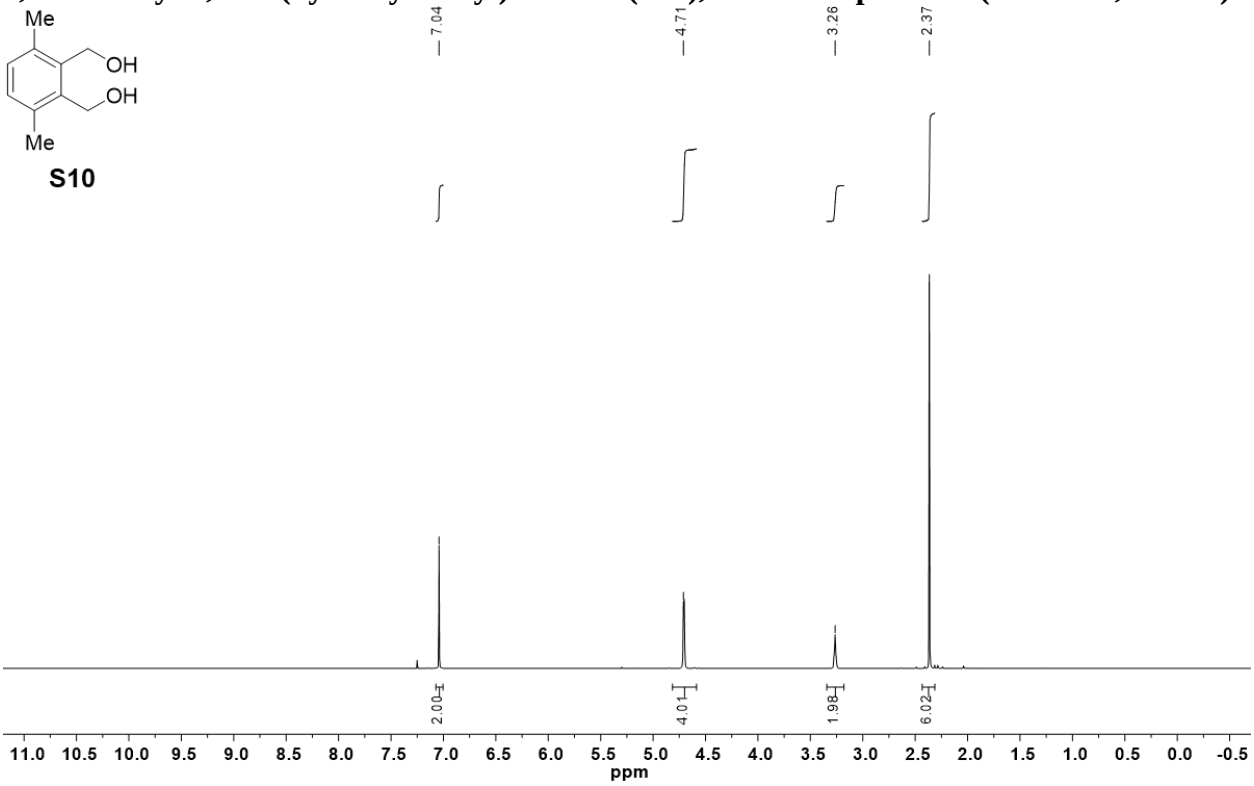
3,6-Dimethylphthalic anhydride (S9), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



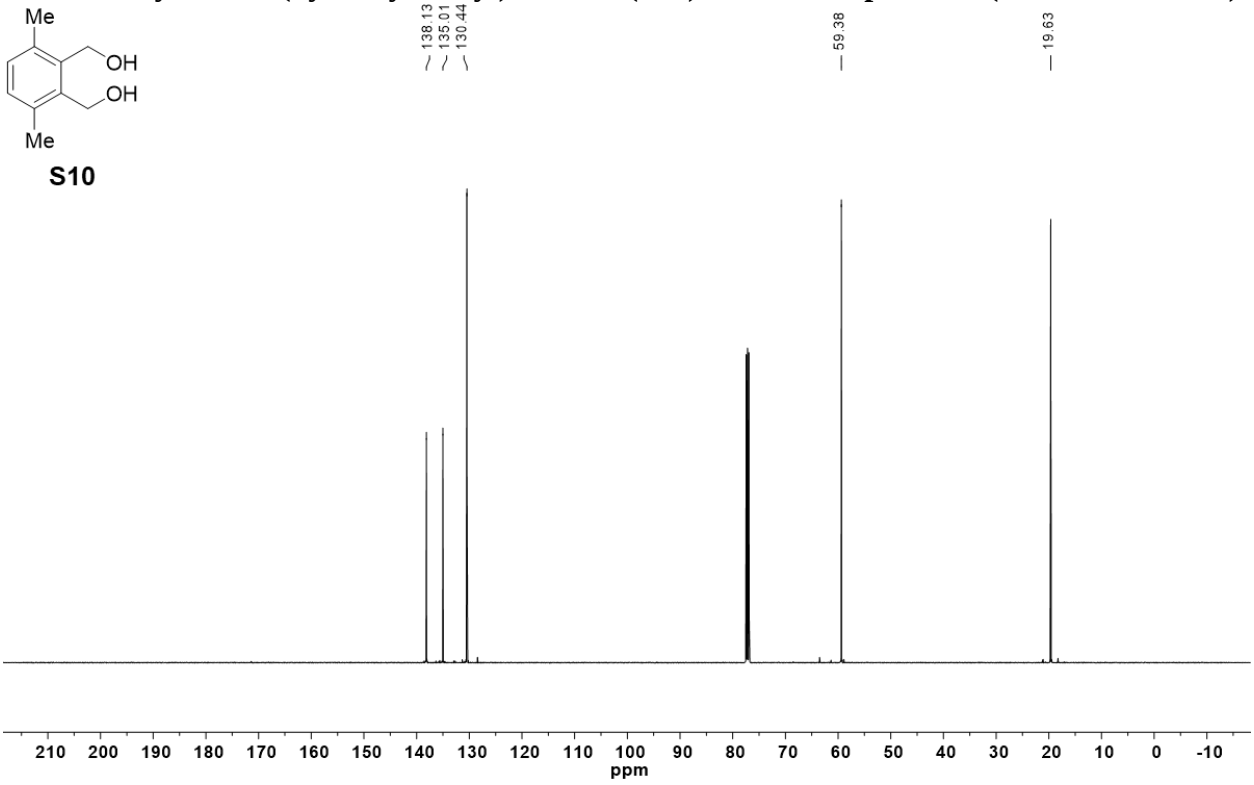
3,6-Dimethylphthalic anhydride (S9), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



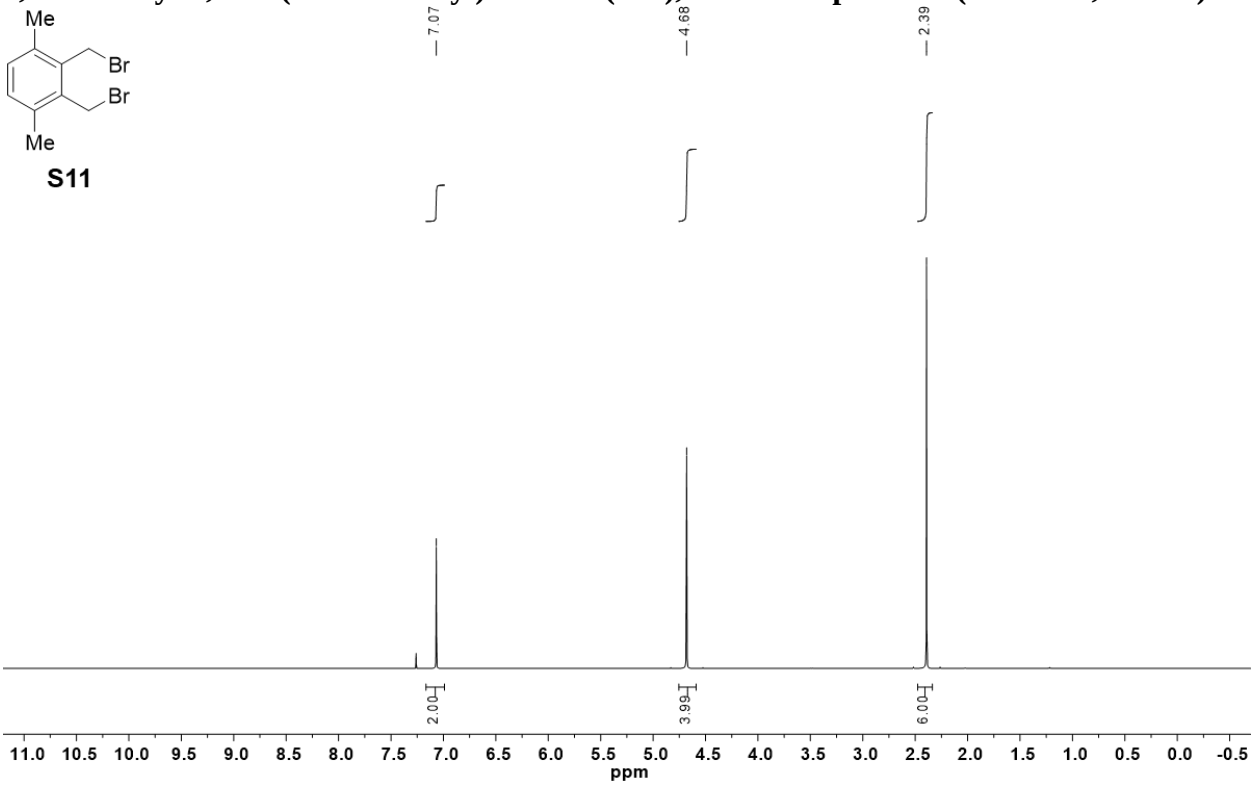
3,6-Dimethyl-1,2-bis(hydroxymethyl)benzene (S10), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



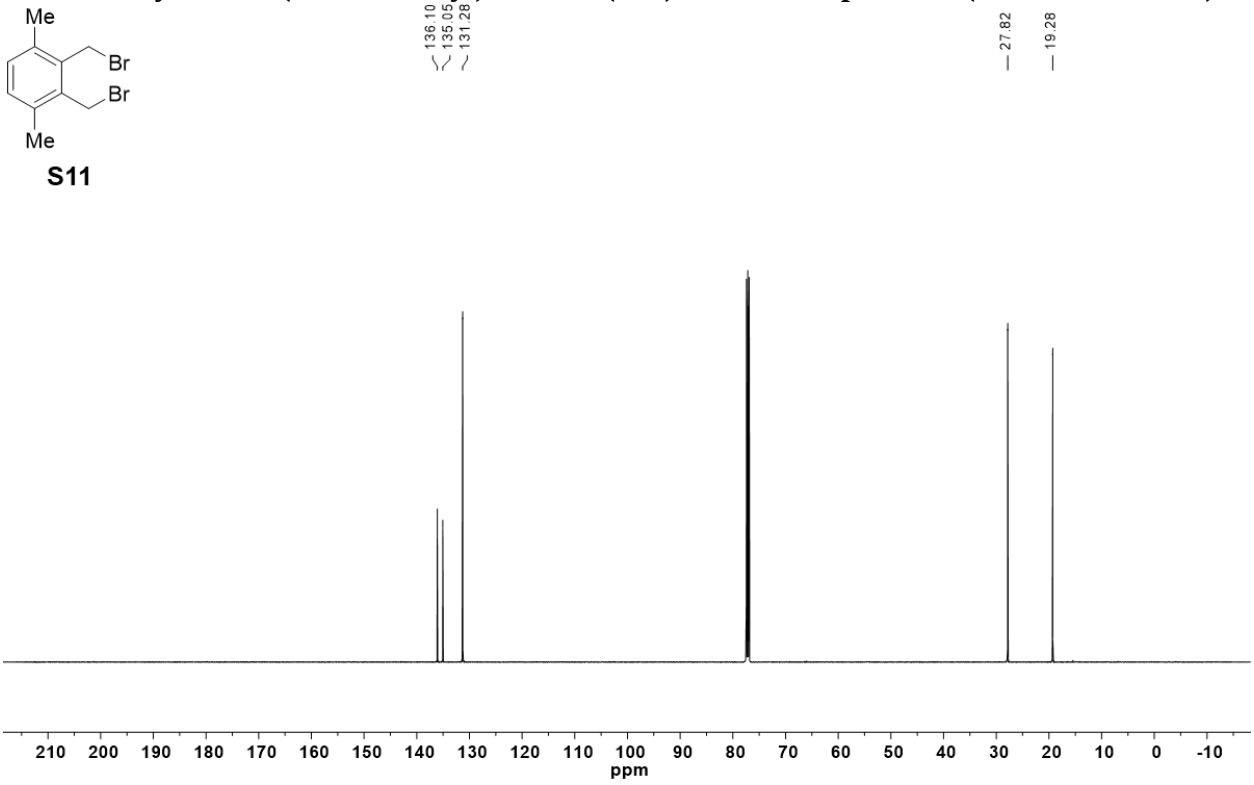
3,6-Dimethyl-1,2-bis(hydroxymethyl)benzene (S10), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



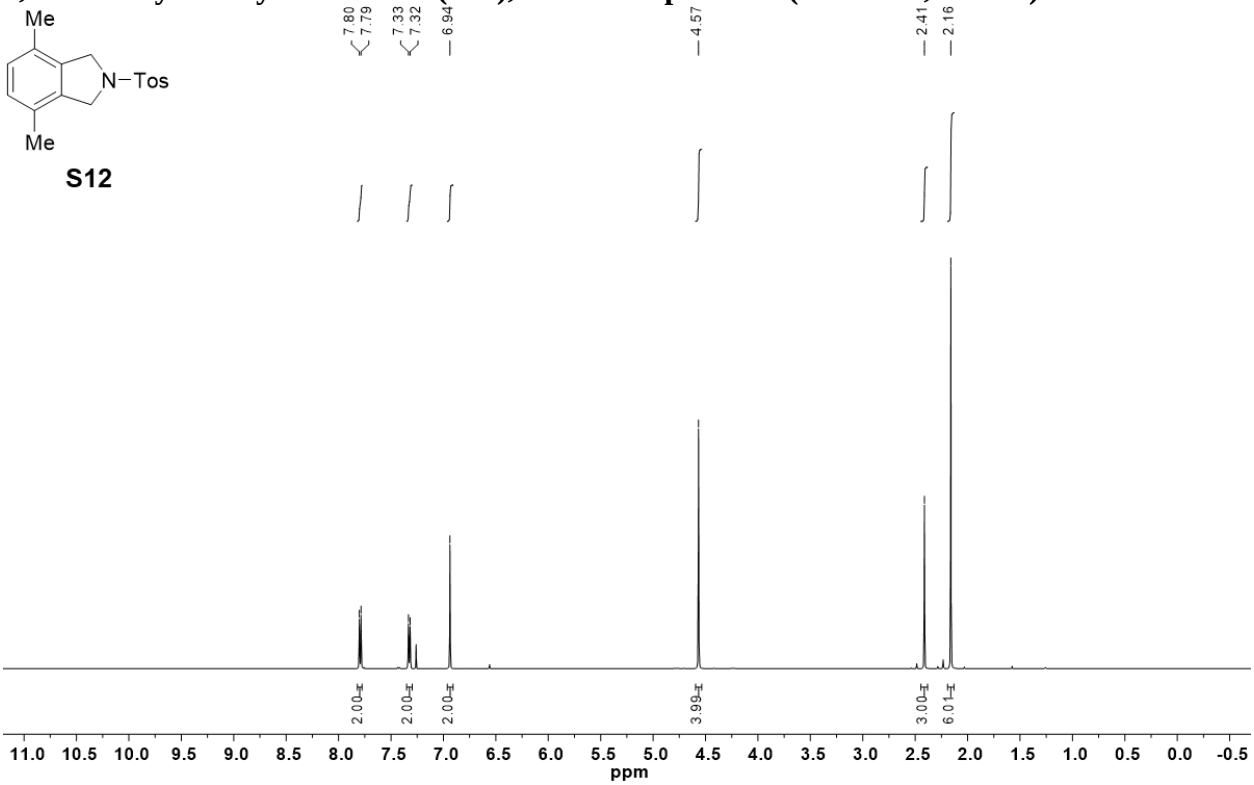
3,6-Dimethyl-1,2-bis(bromomethyl)benzene (S11), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



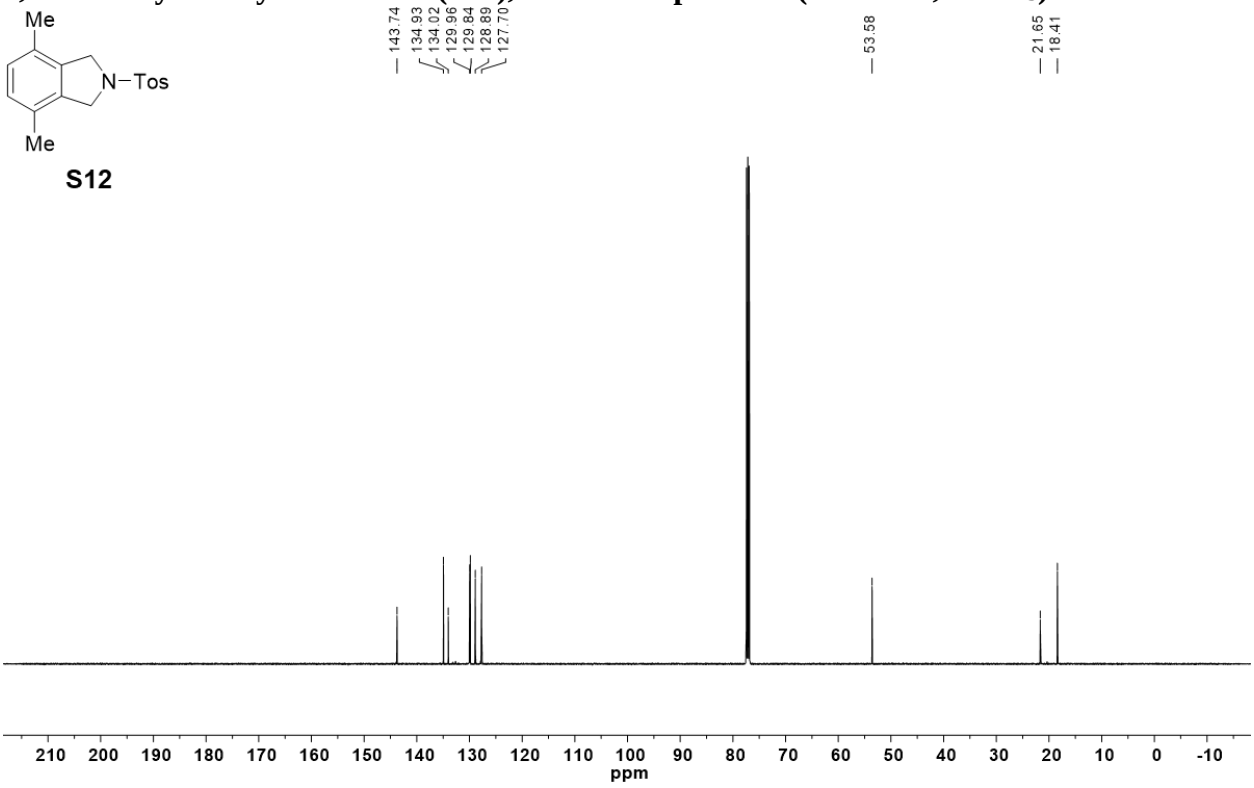
3,6-Dimethyl-1,2-bis(bromomethyl)benzene (S11), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



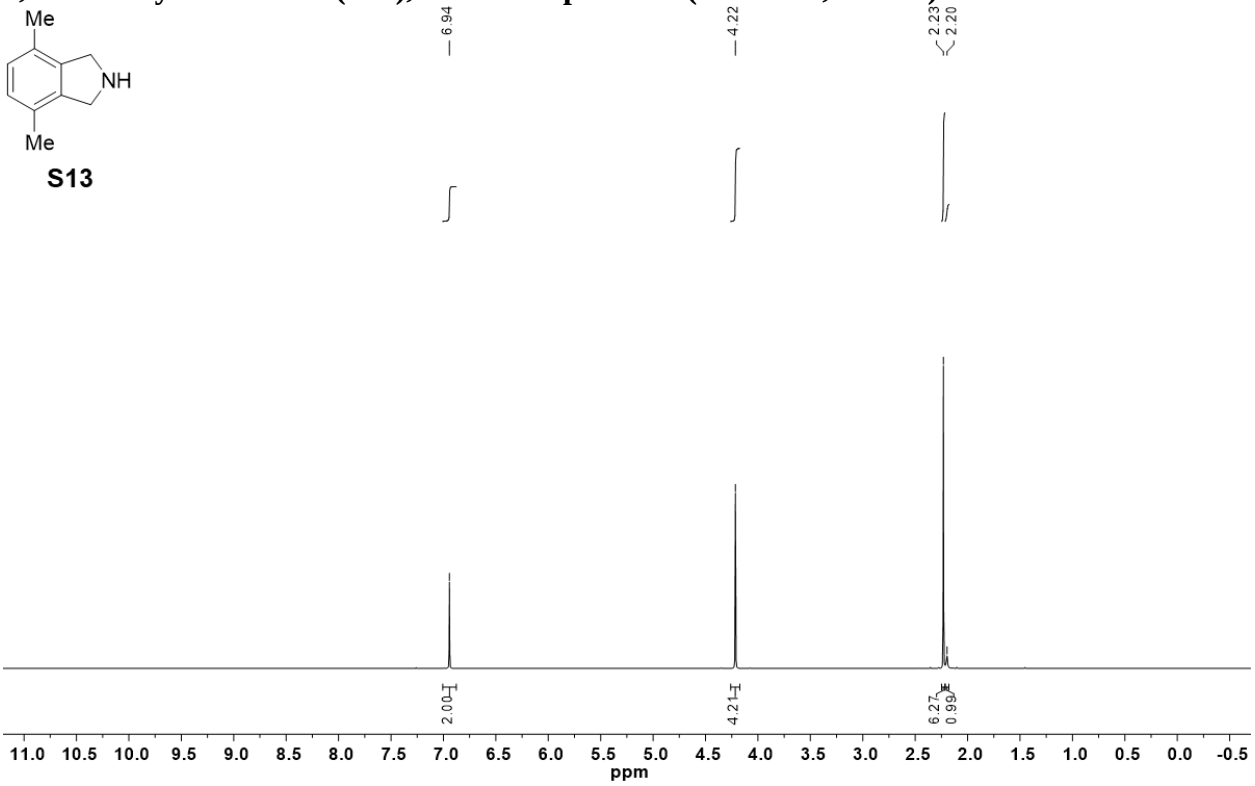
4,7-Dimethyl-2-tosylisoindoline (S12), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



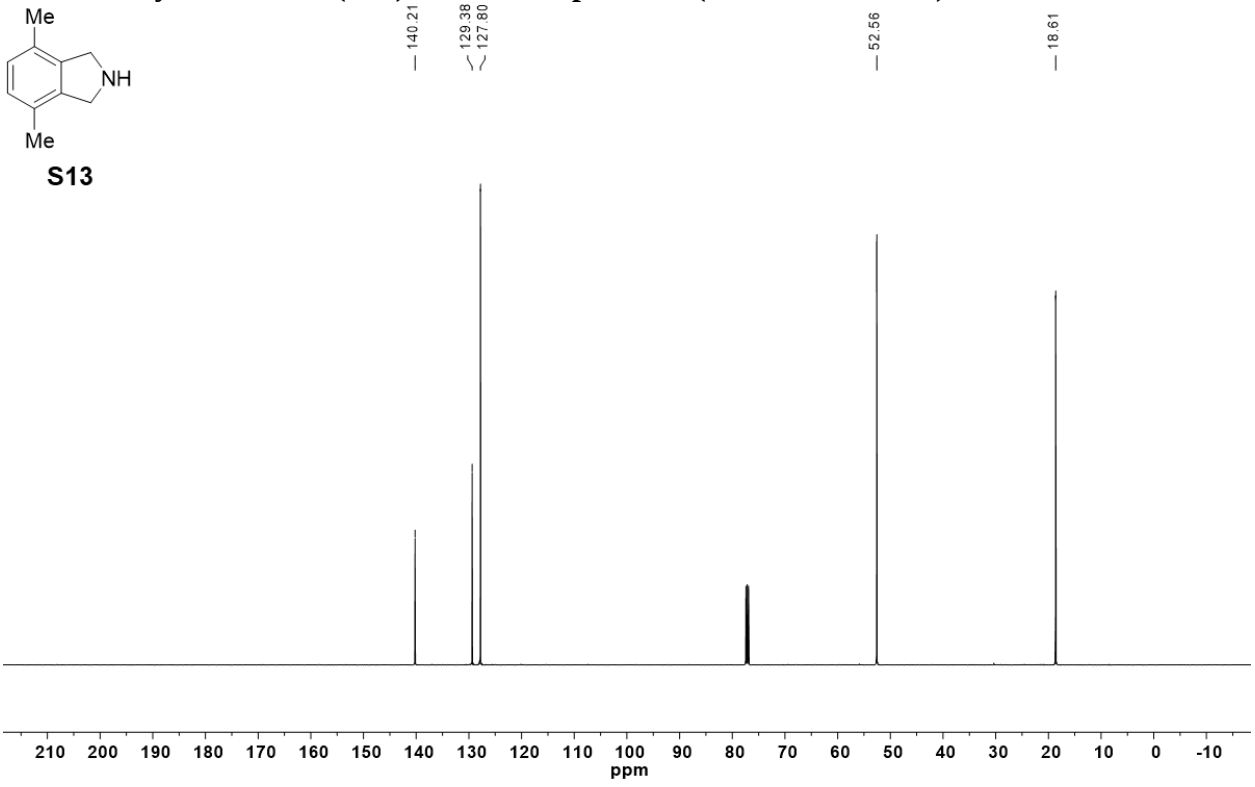
4,7-Dimethyl-2-tosylisoindoline (S12), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



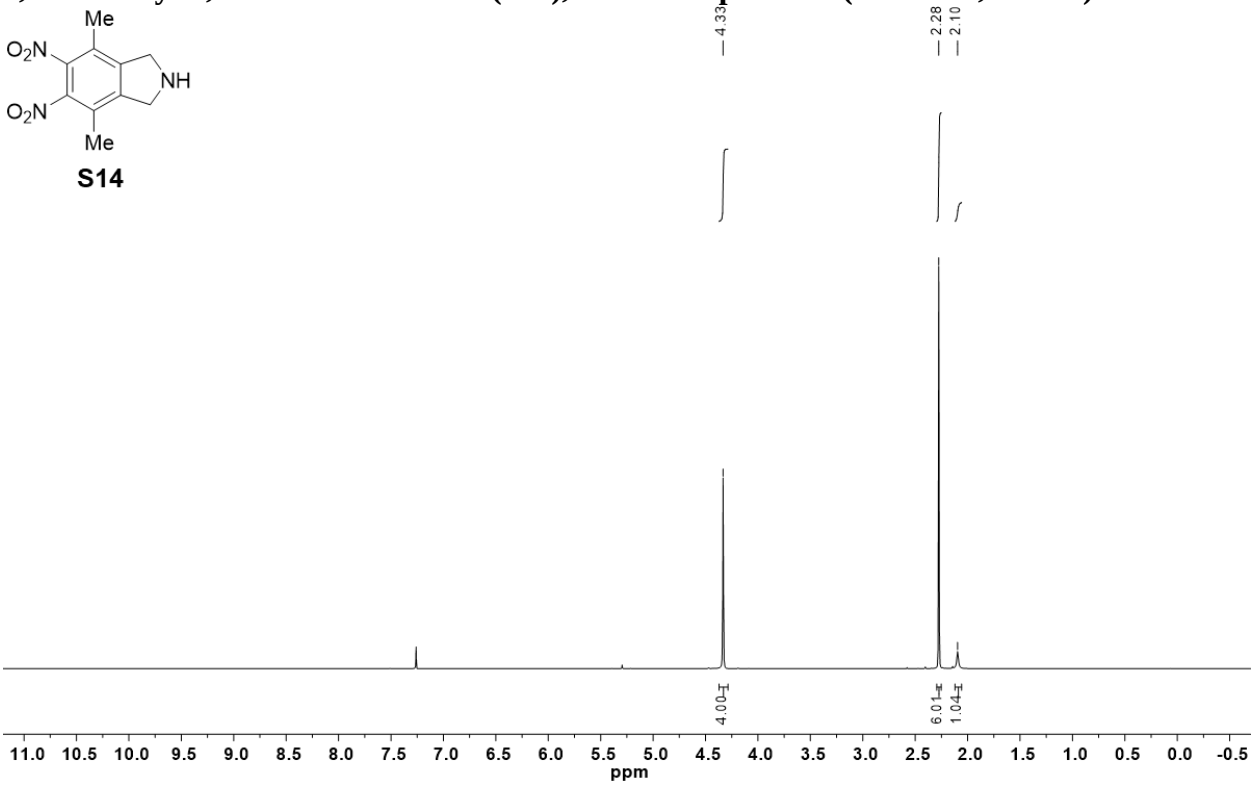
4,7-Dimethylisoindoline (S13), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



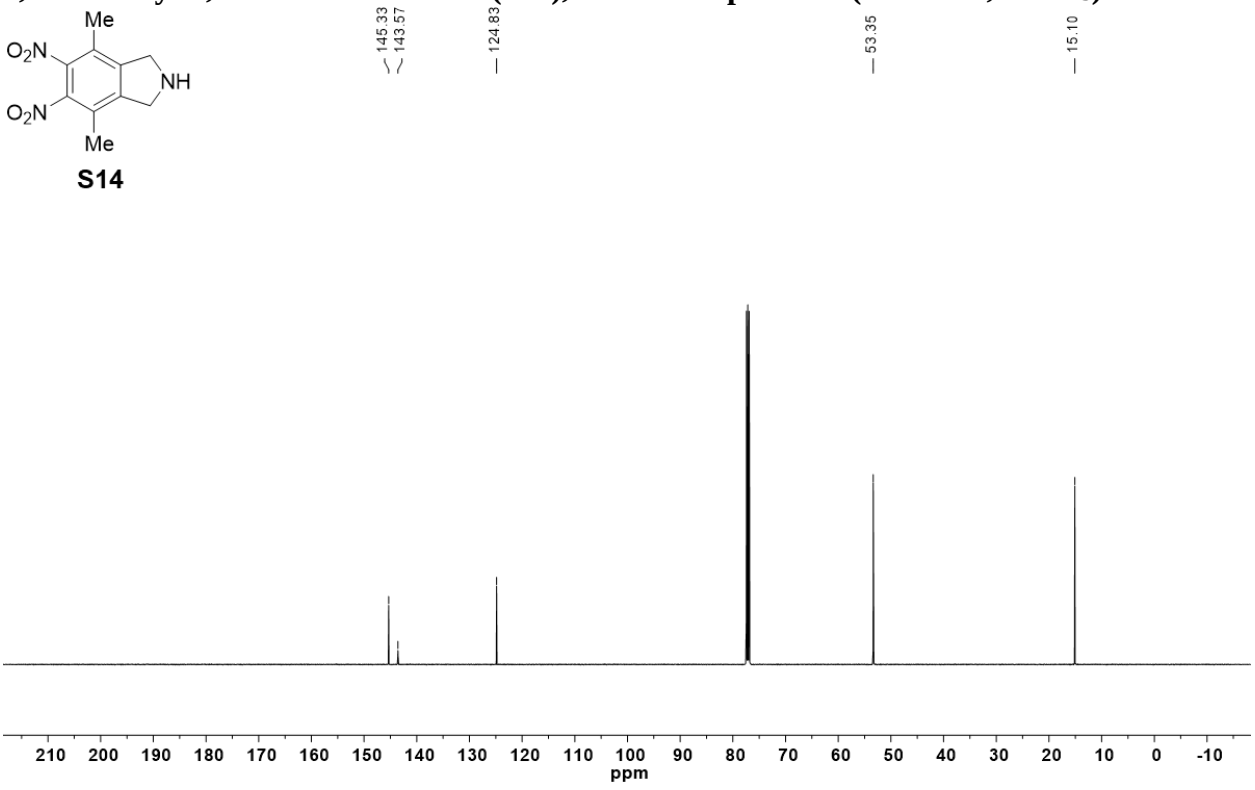
4,7-Dimethylisoindoline (S13), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



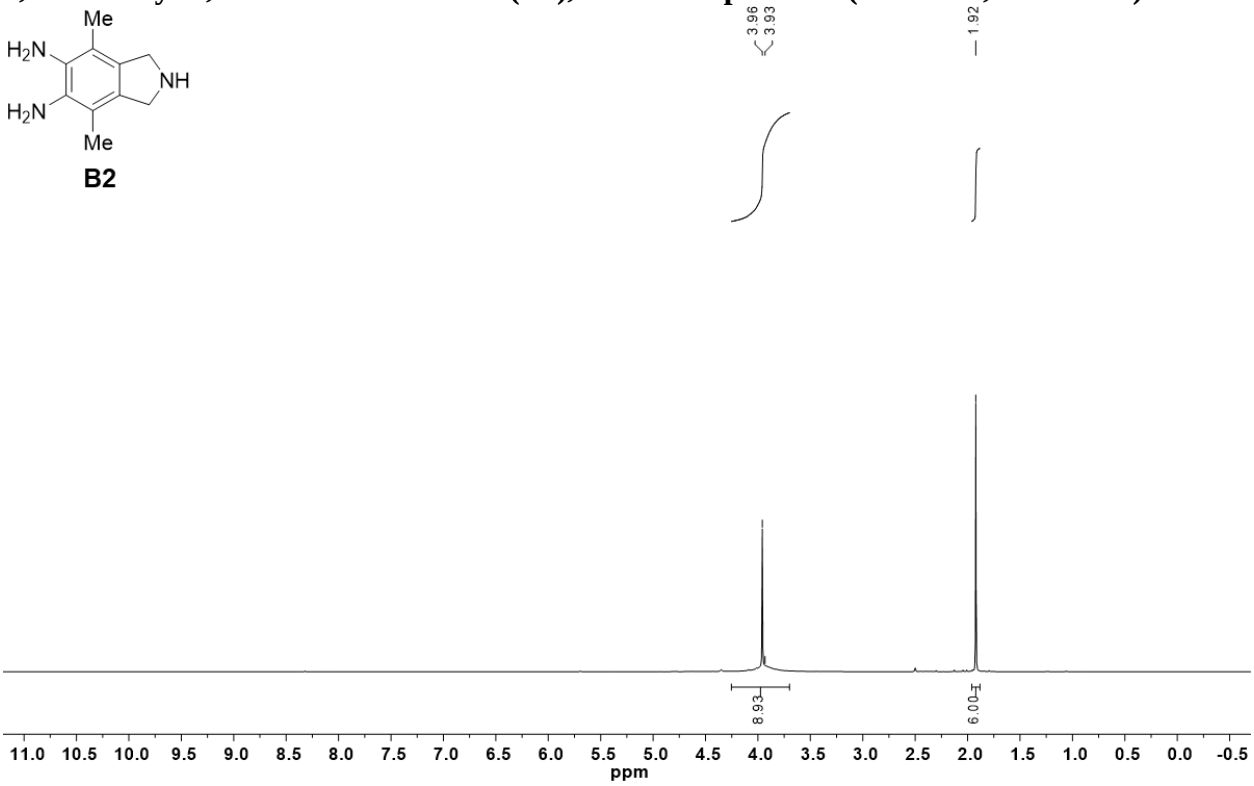
4,7-Dimethyl-5,6-dinitroisoindoline (S14), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



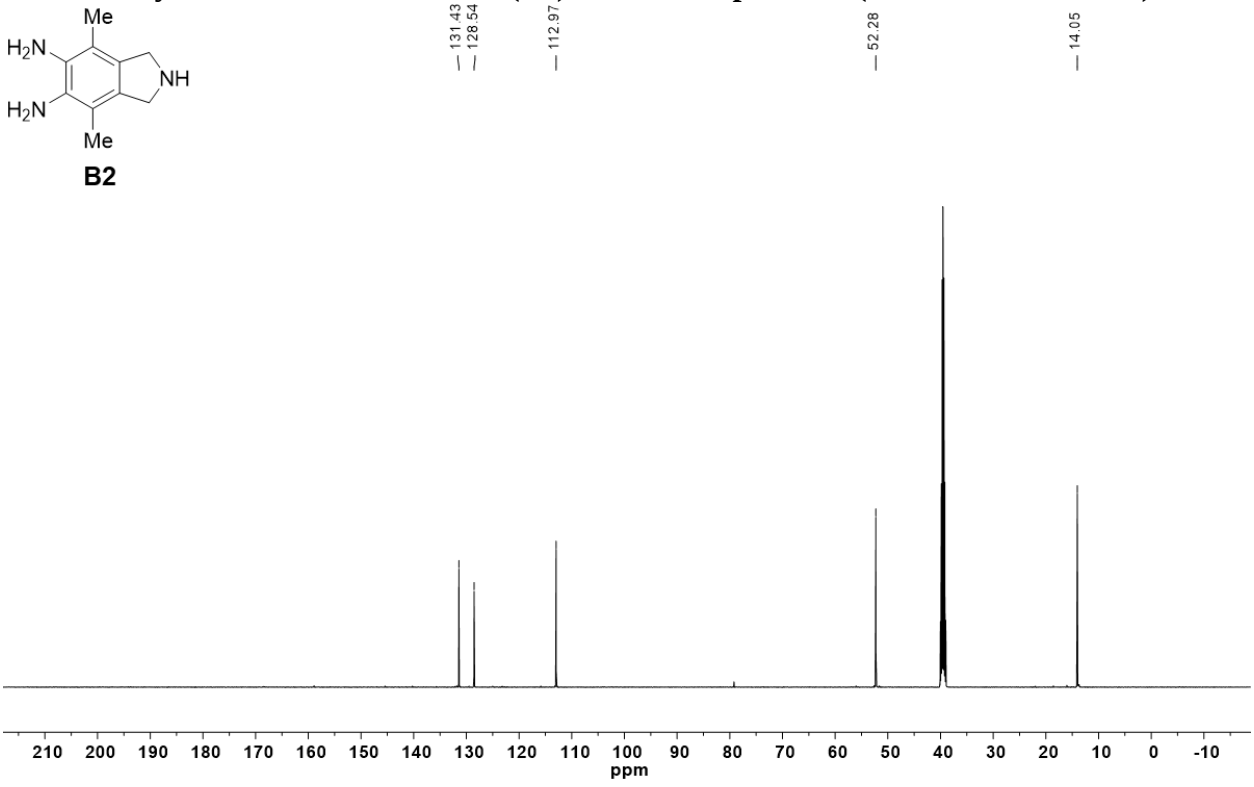
4,7-Dimethyl-5,6-dinitroisoindoline (S14), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



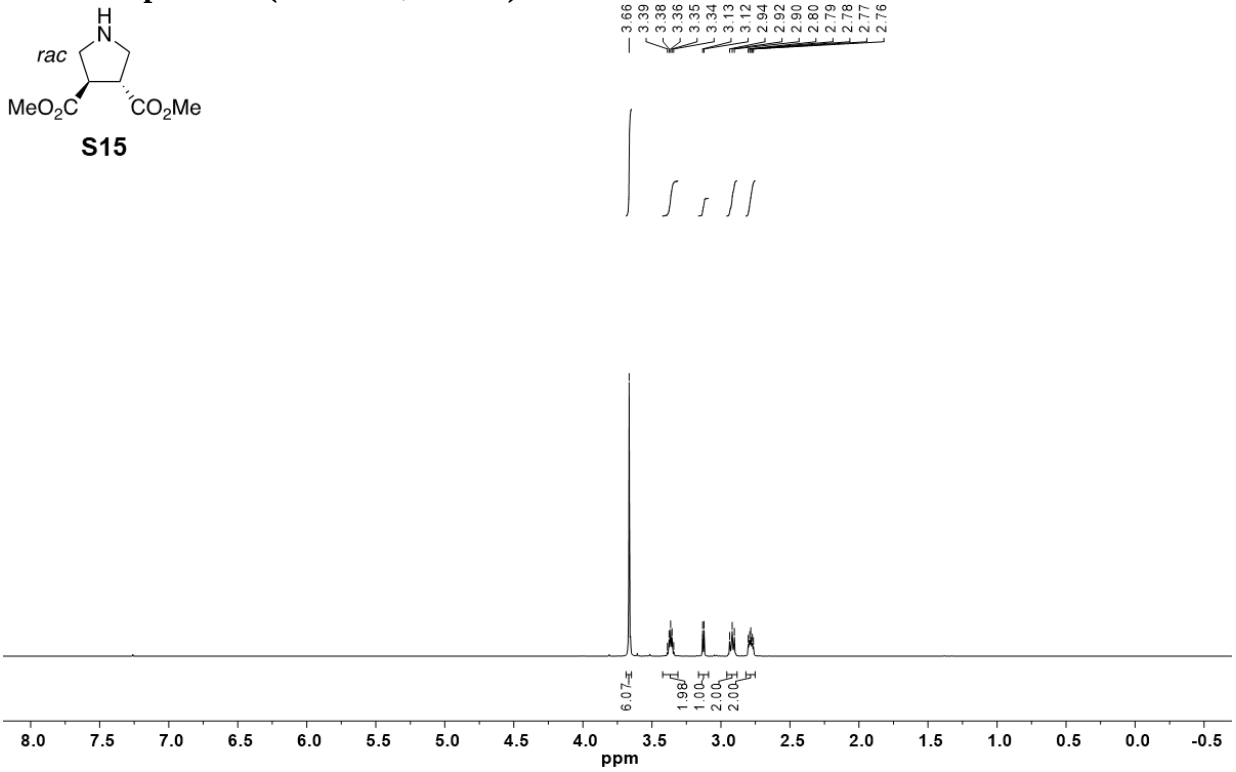
4,7-Dimethyl-5,6-diaminoisoindoline (B2), ^{1}H NMR spectrum (500 MHz, DMSO-d_6)



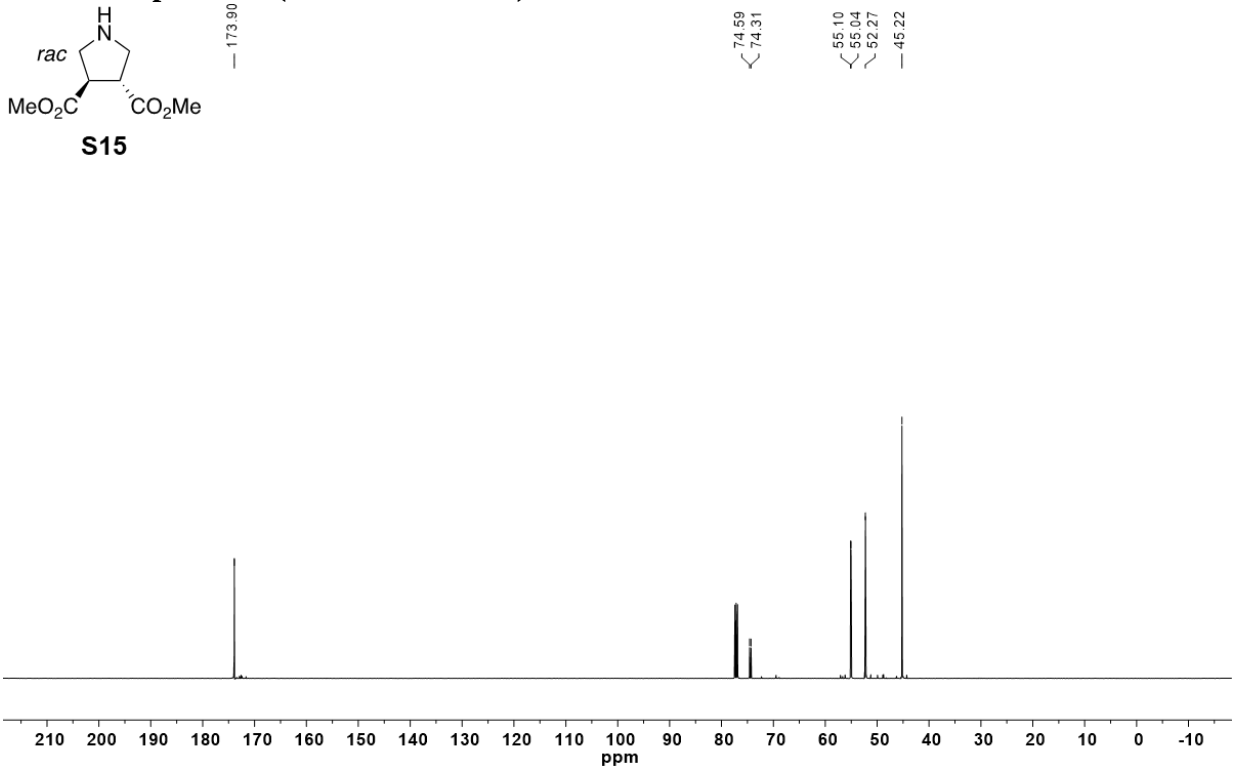
4,7-Dimethyl-5,6-diaminoisoindoline (B2), ^{13}C NMR spectrum (125 MHz, DMSO-d_6)



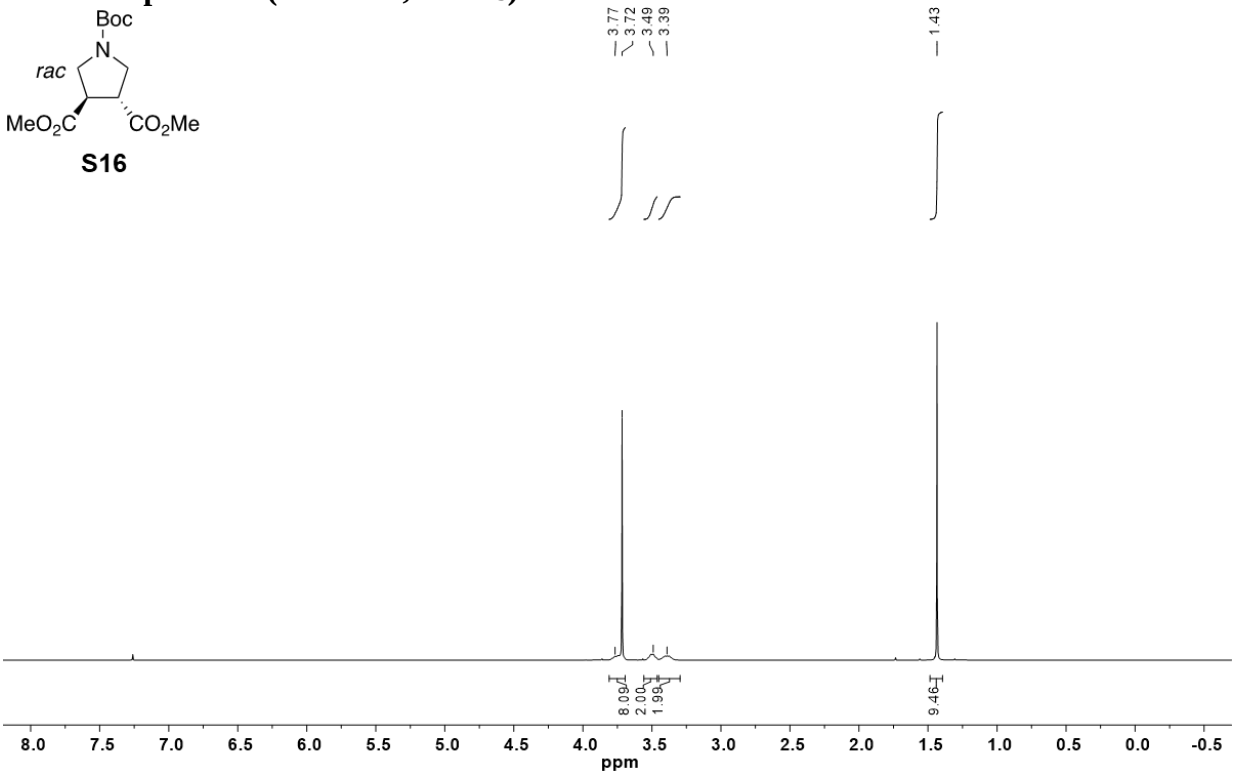
***trans*-3,4-Pyrrolidinedicarboxylic acid dimethyl ester (S15)**
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



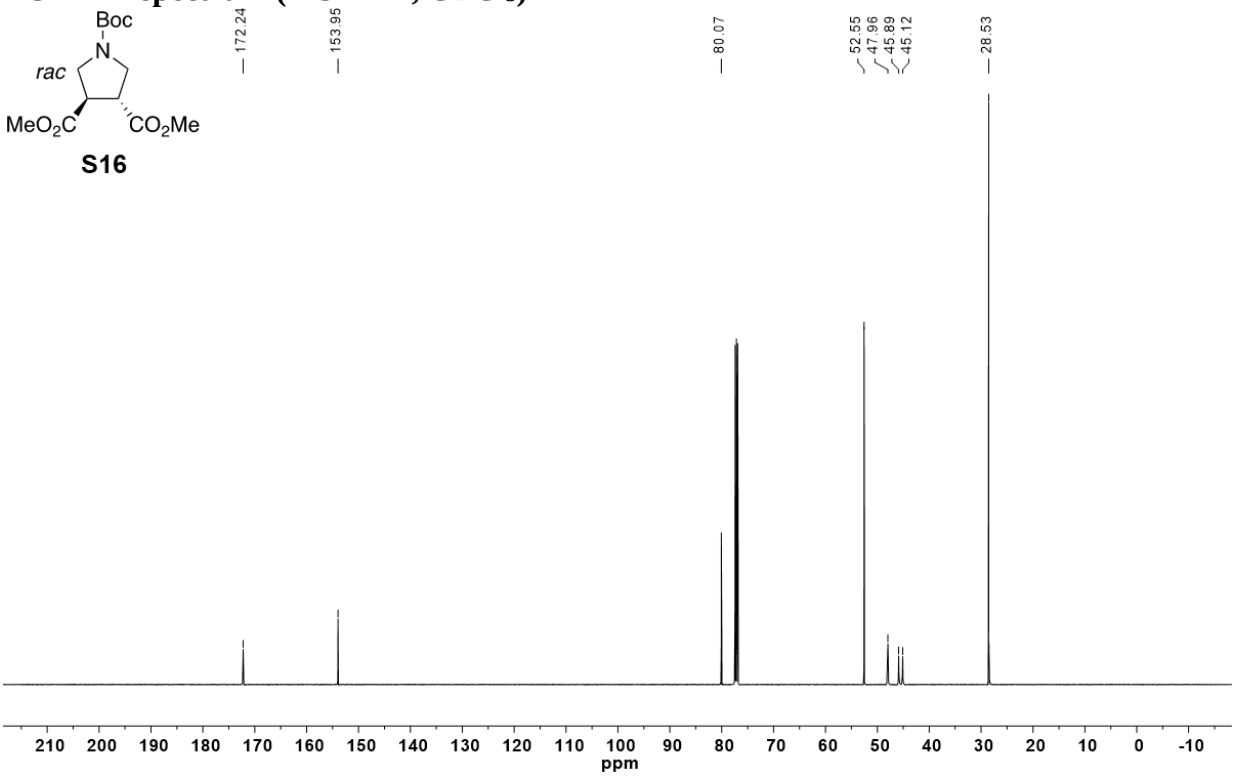
***trans*-3,4-Pyrrolidinedicarboxylic acid dimethyl ester (S15)**
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



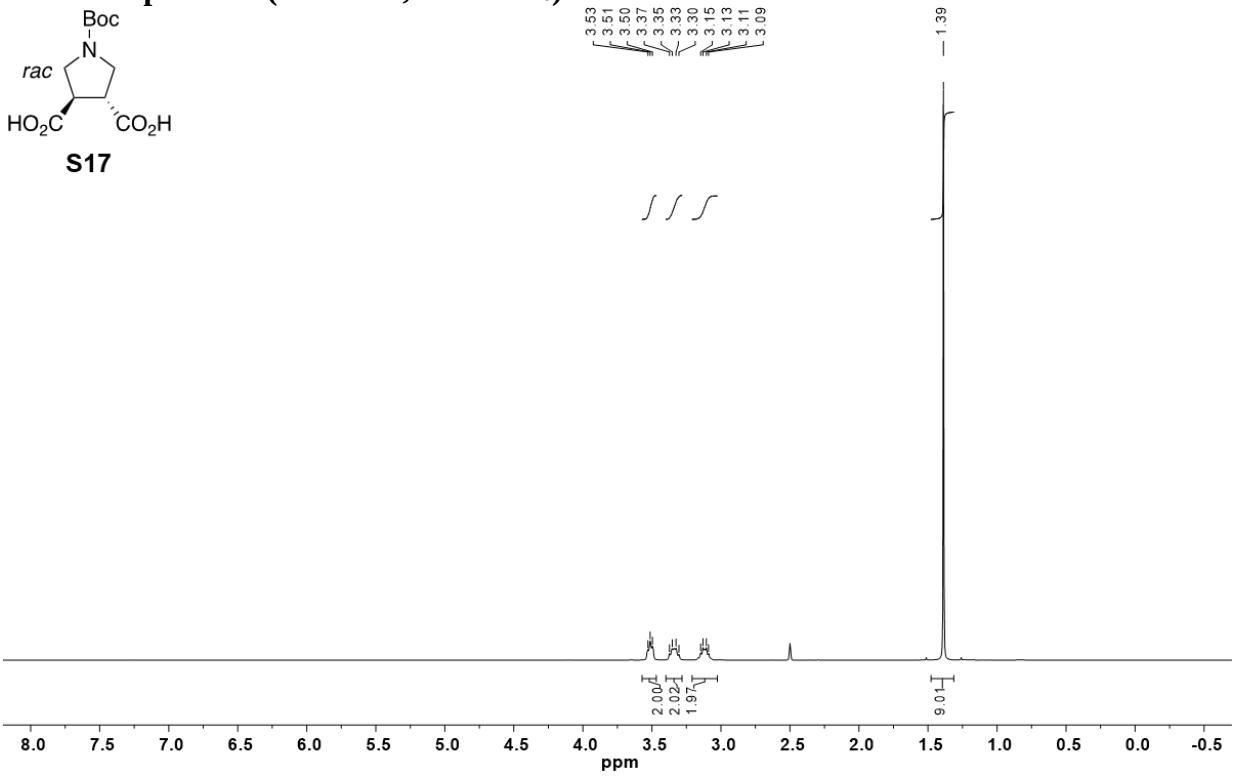
***N*-Boc *trans*-3,4-Pyrrolidinedicarboxylic acid, dimethyl ester (S16)**
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



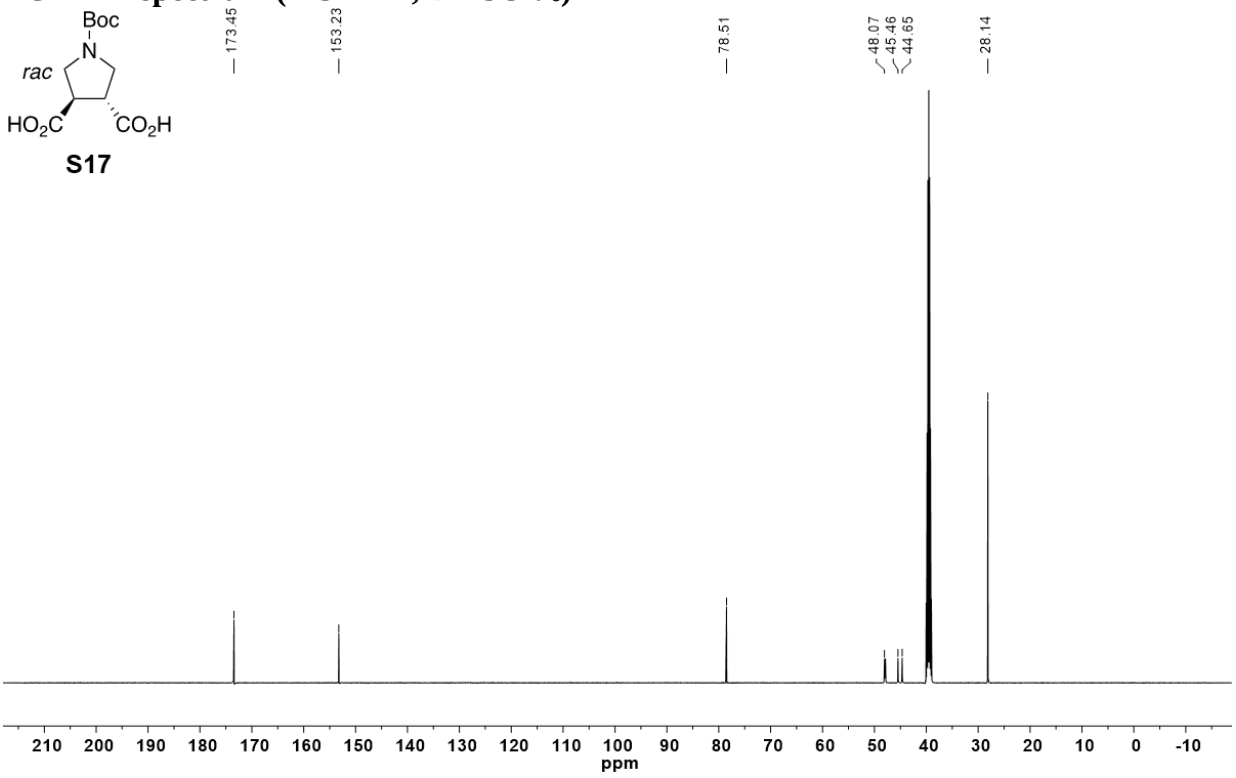
***N*-Boc *trans*-3,4-Pyrrolidinedicarboxylic acid, dimethyl ester (S16)**
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



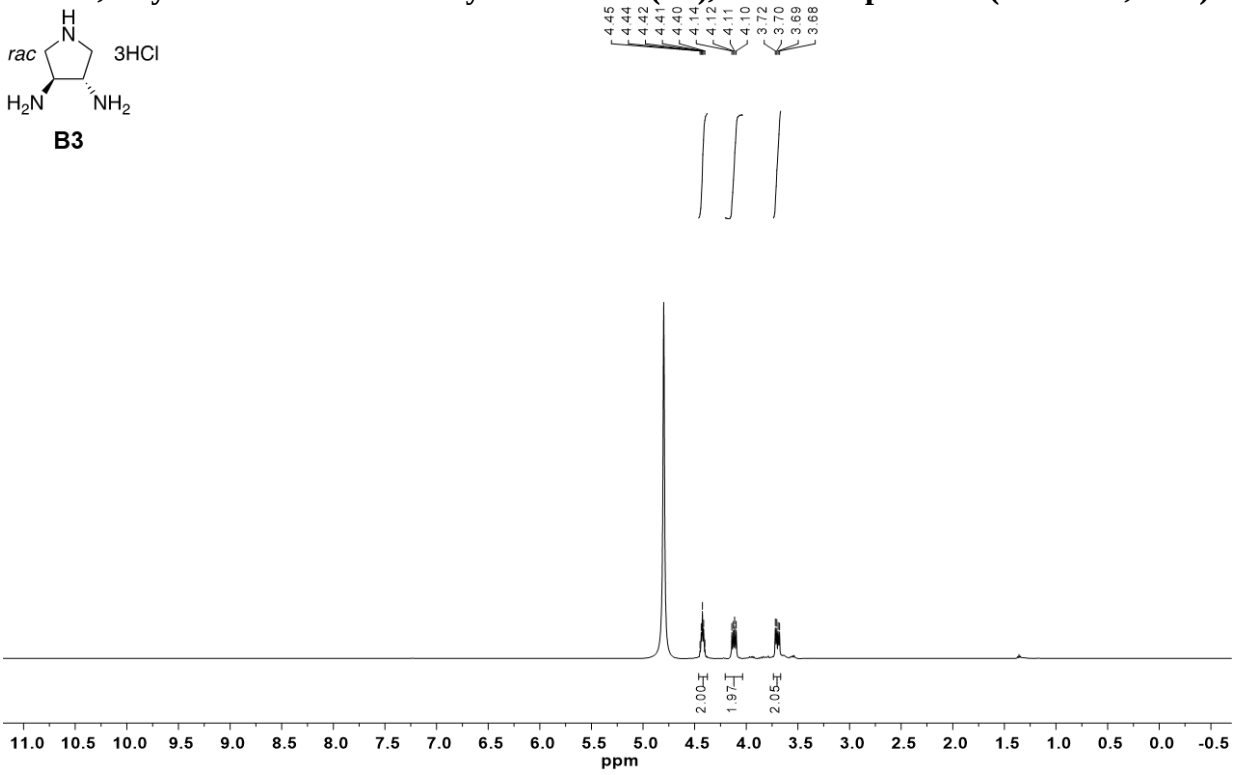
***N*-Boc *trans*-3,4-Pyrrolidinedicarboxylic acid (S17)**
^{1}H NMR spectrum (500 MHz, DMSO-d_6)



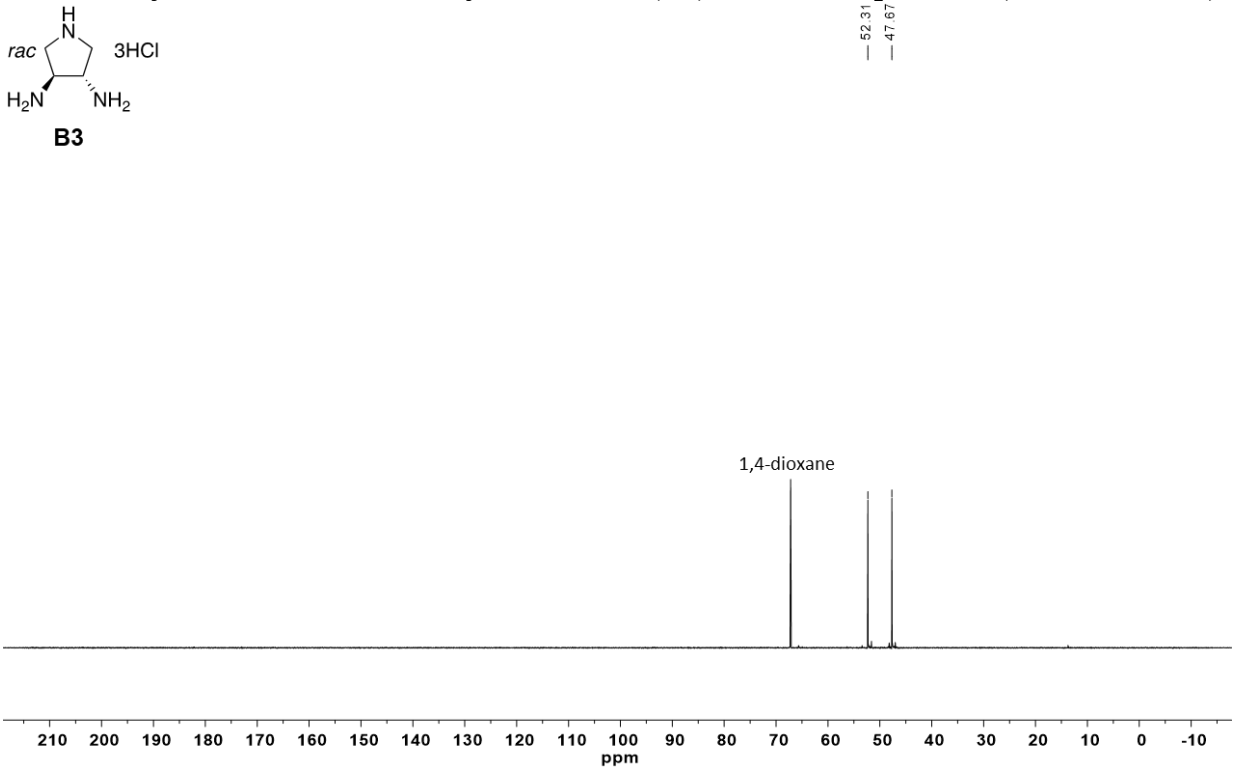
***N*-Boc *trans*-3,4-Pyrrolidinedicarboxylic acid (S17)**
^{13}C NMR spectrum (125 MHz, DMSO-d_6)



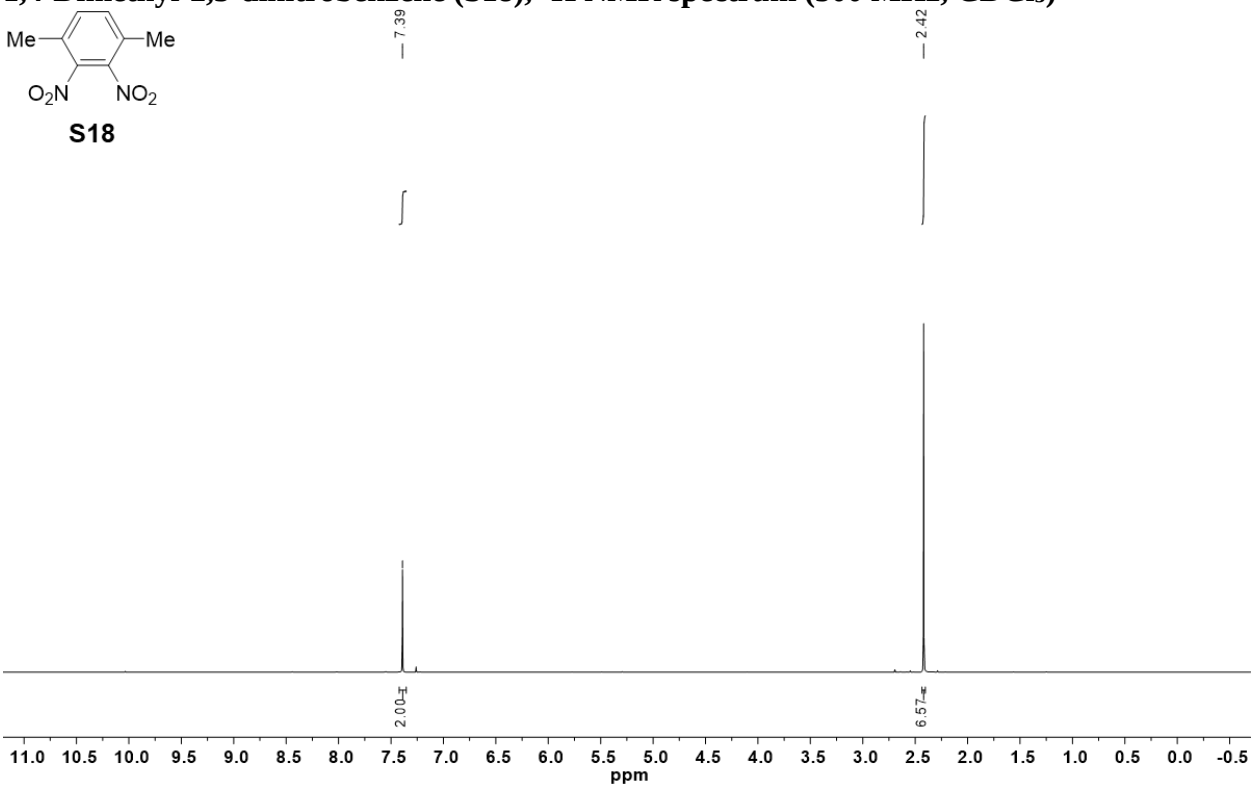
trans-3,4-Pyrrolidine diamine trihydrochloride (B3), ^{1}H NMR spectrum (500 MHz, D_2O)



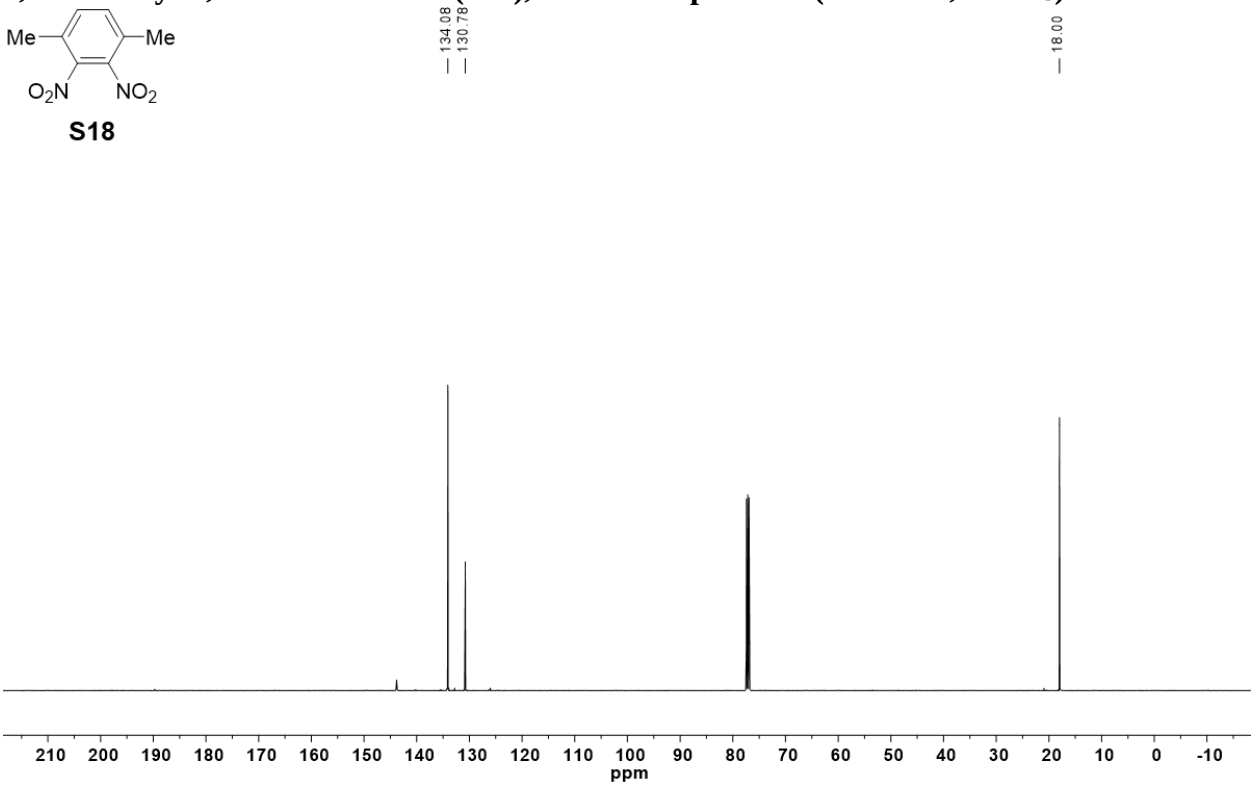
trans-3,4-Pyrrolidine diamine trihydrochloride (B3), ^{13}C NMR spectrum (125 MHz, D_2O)



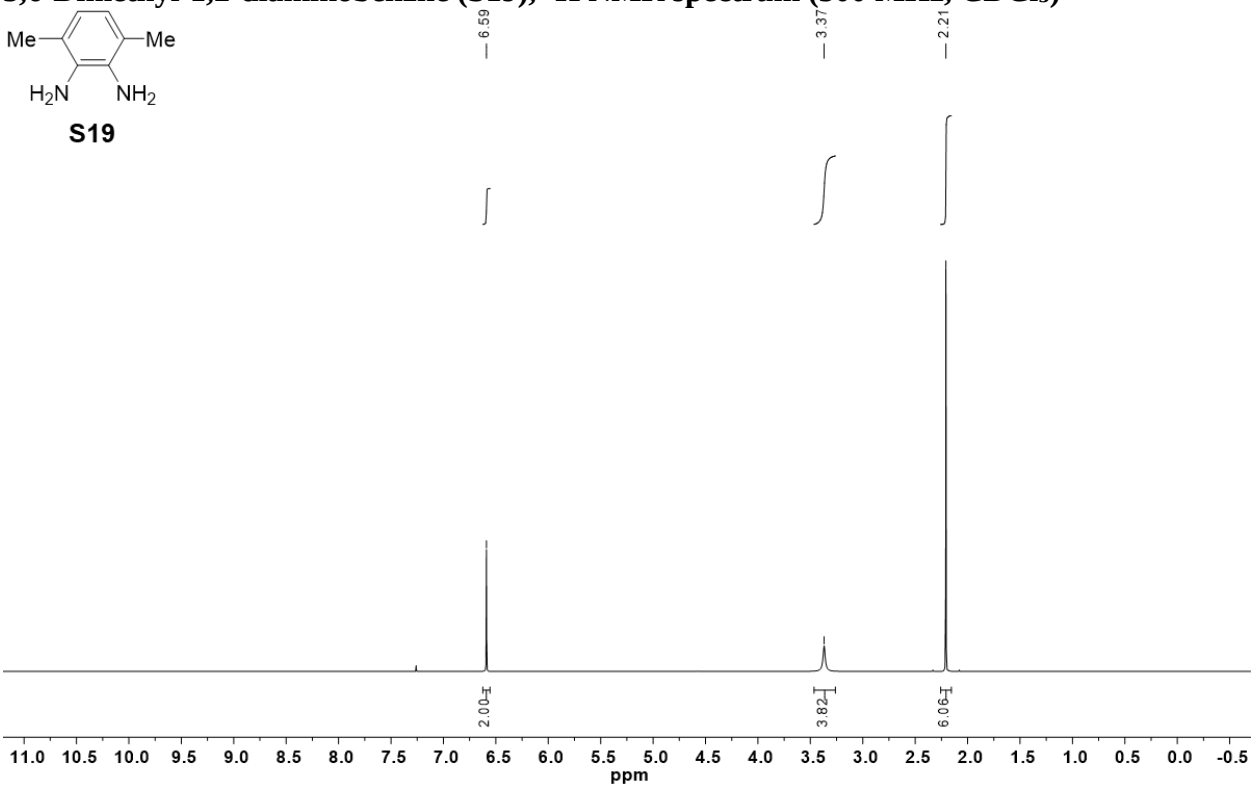
1,4-Dimethyl-2,3-dinitrobenzene (S18), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



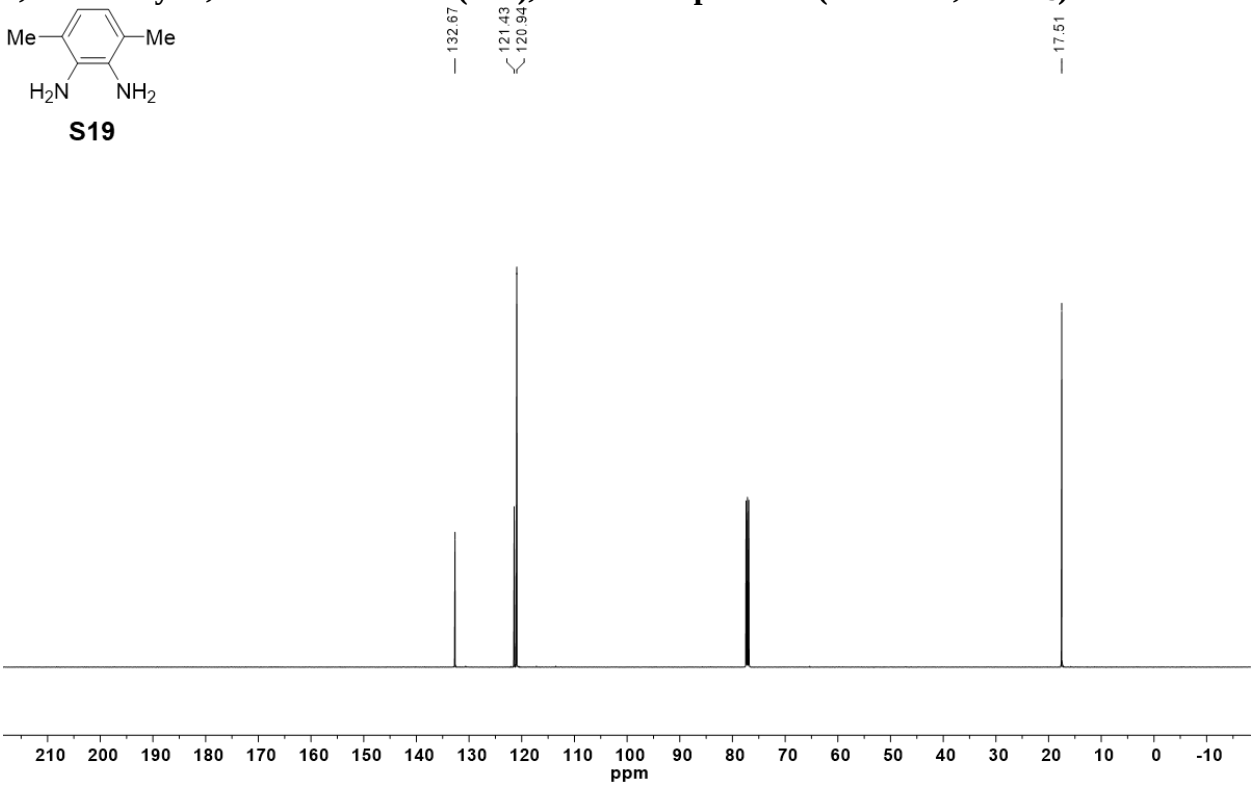
1,4-Dimethyl-2,3-dinitrobenzene (S18), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



3,6-Dimethyl-1,2-diaminobenzne (S19), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)

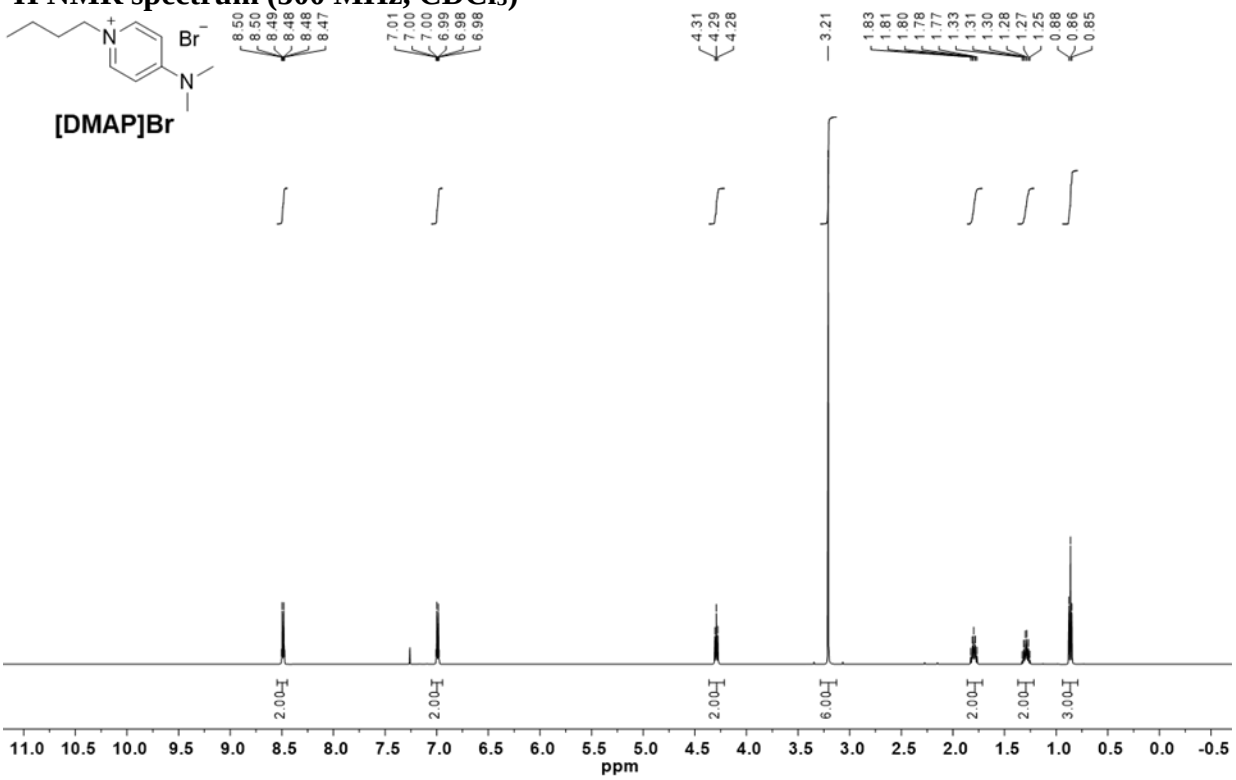


3,6-Dimethyl-1,2-diaminobenzne (S19), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



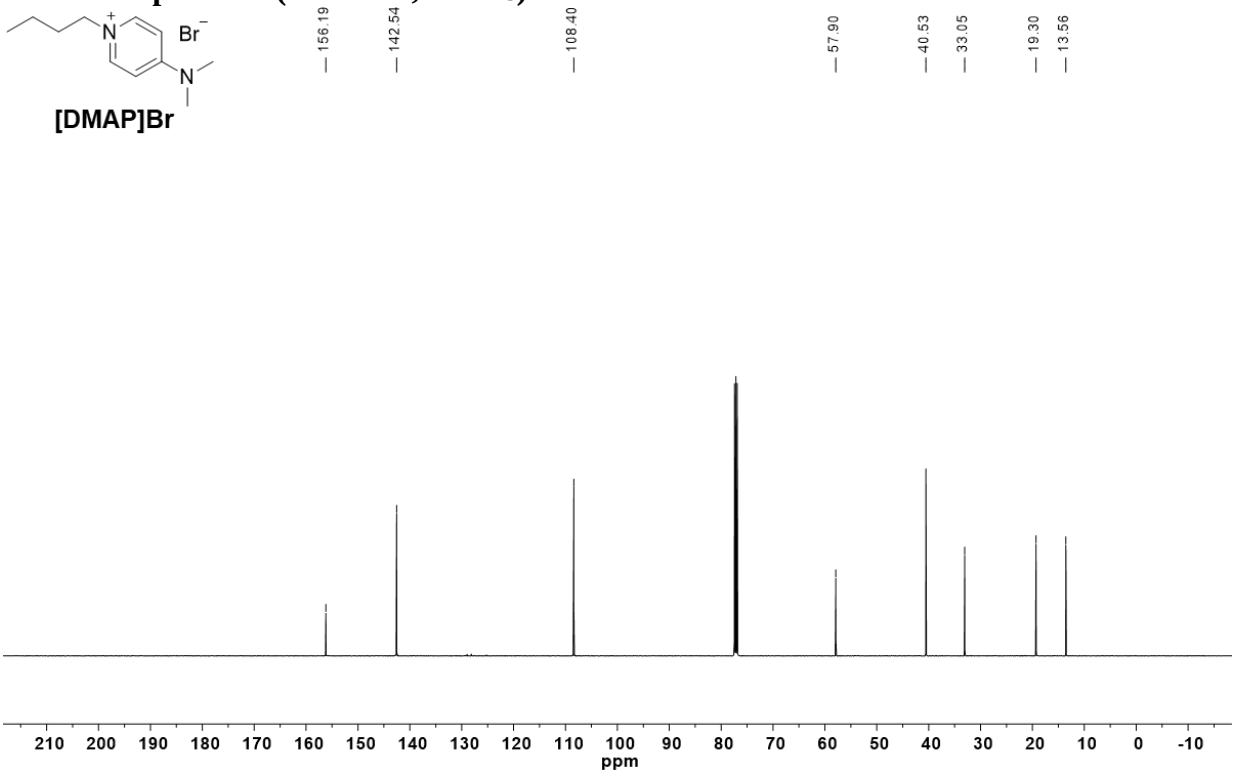
1-Butyl-4-dimethylaminopyridinium bromide ([DMAP]Br)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

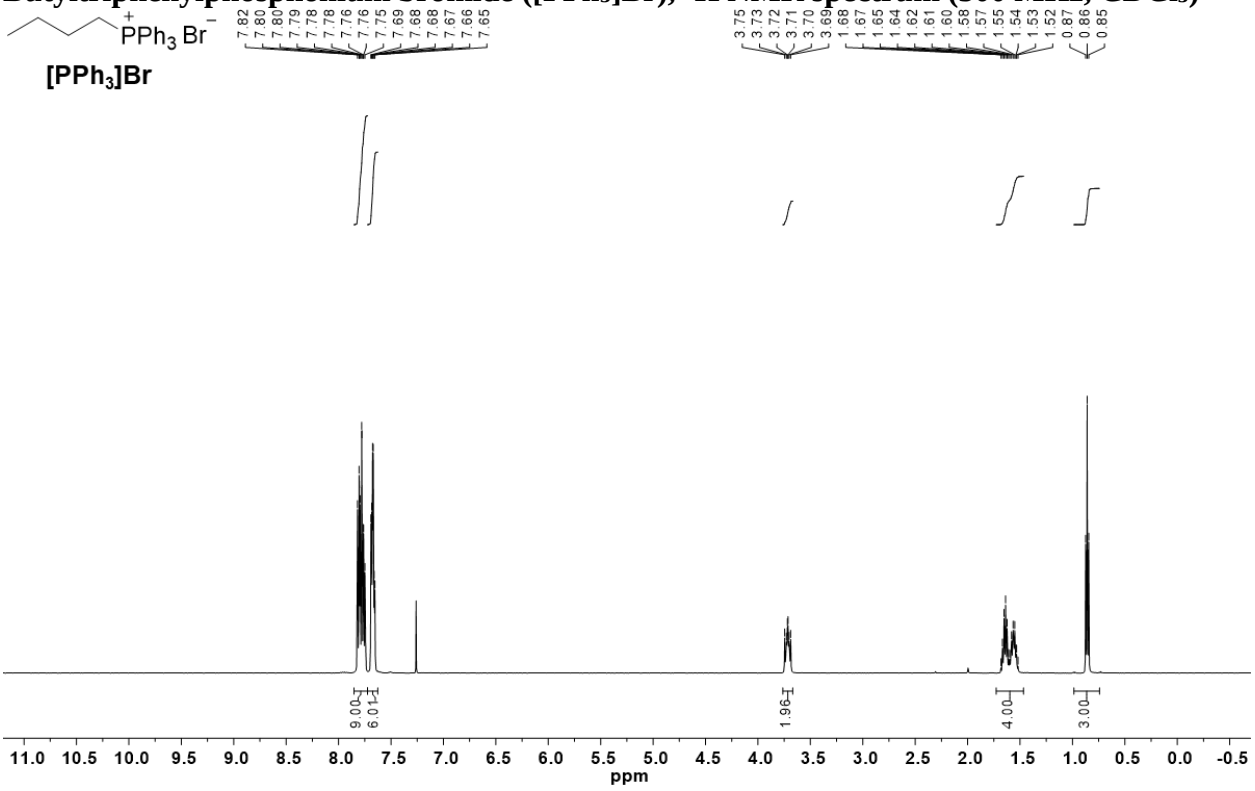


1-Butyl-4-dimethylaminopyridinium bromide ([DMAP]Br)

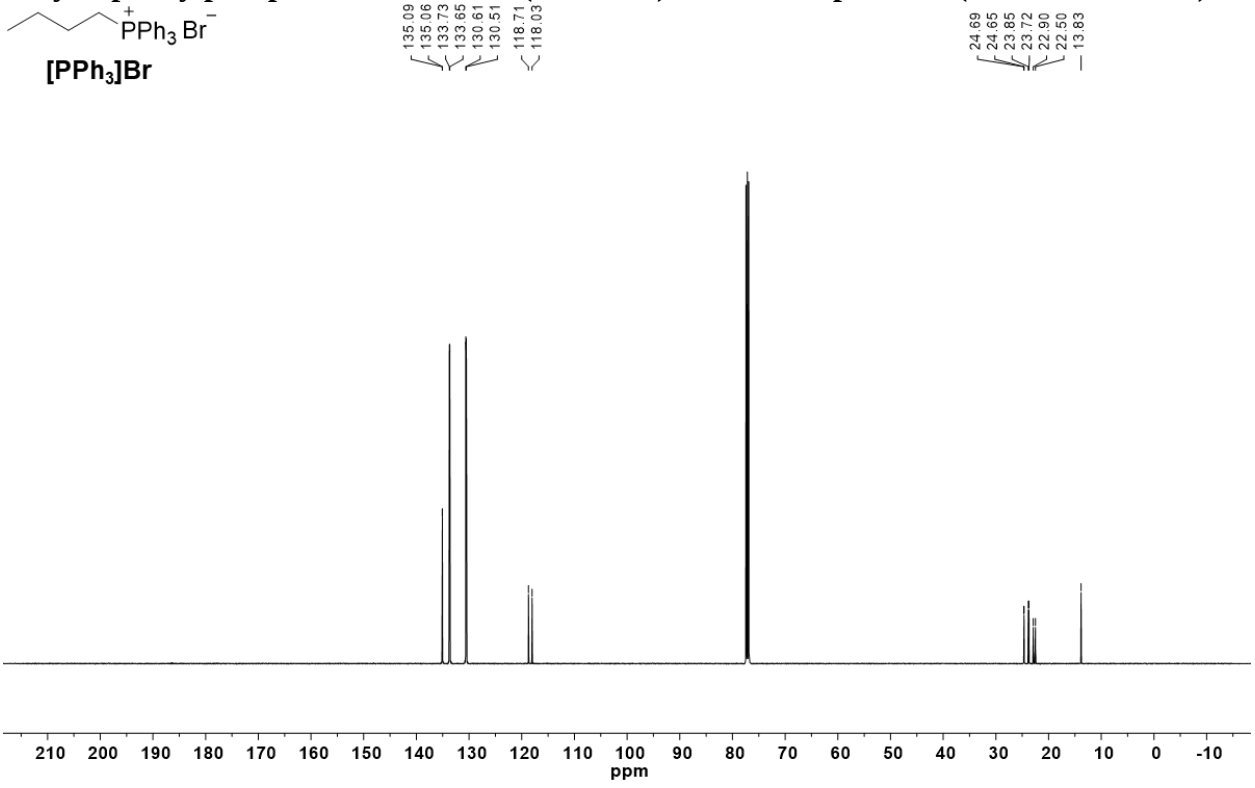
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



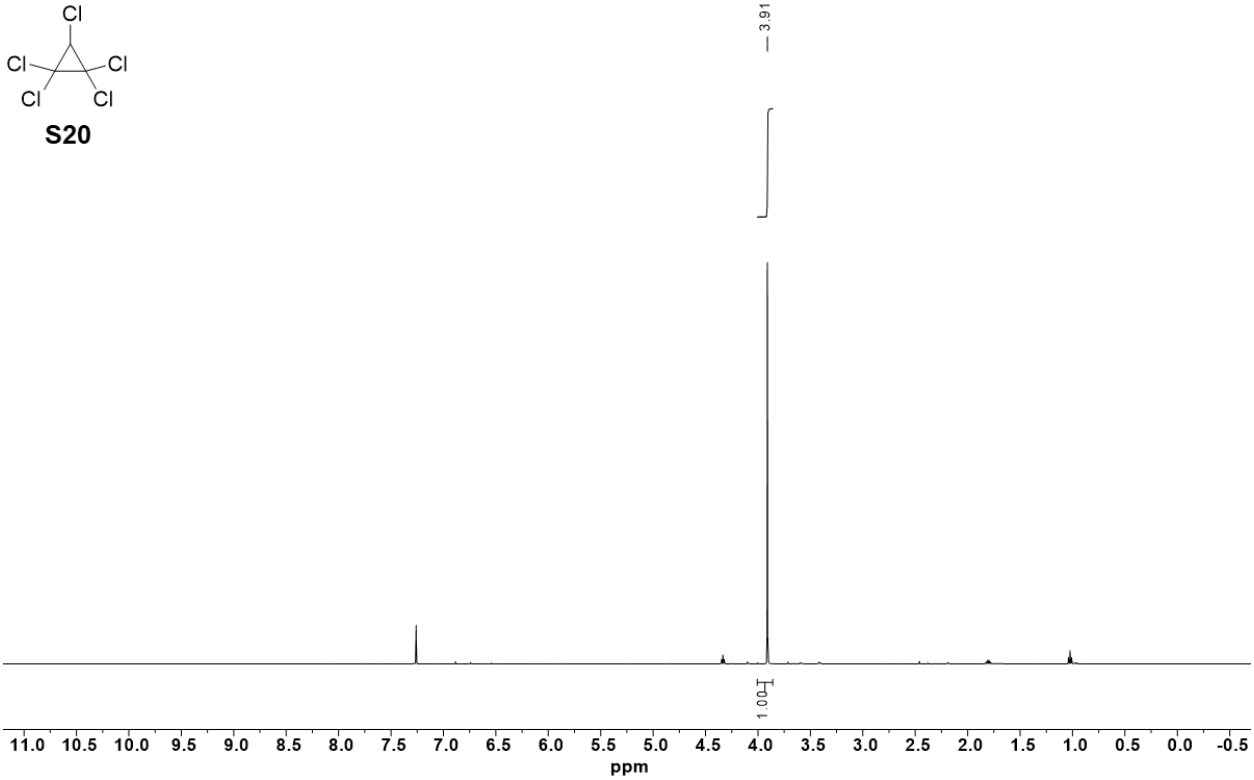
Butyltriphenylphosphonium bromide ([PPh$_3$]Br), ^{1}H NMR spectrum (500 MHz, CDCl$_3$)



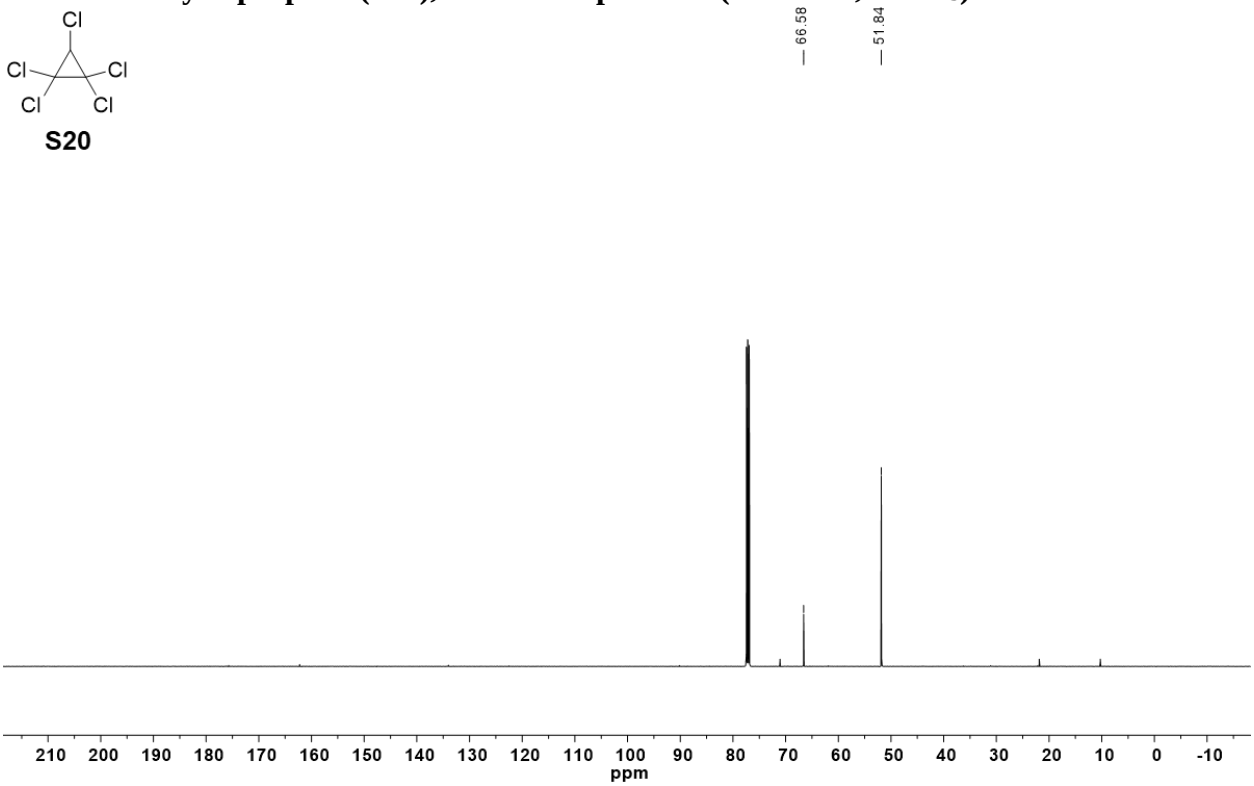
Butyltriphenylphosphonium bromide ([PPh$_3$]Br), ^{13}C NMR spectrum (125 MHz, CDCl$_3$)



Pentachlorocyclopropane (S20), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)

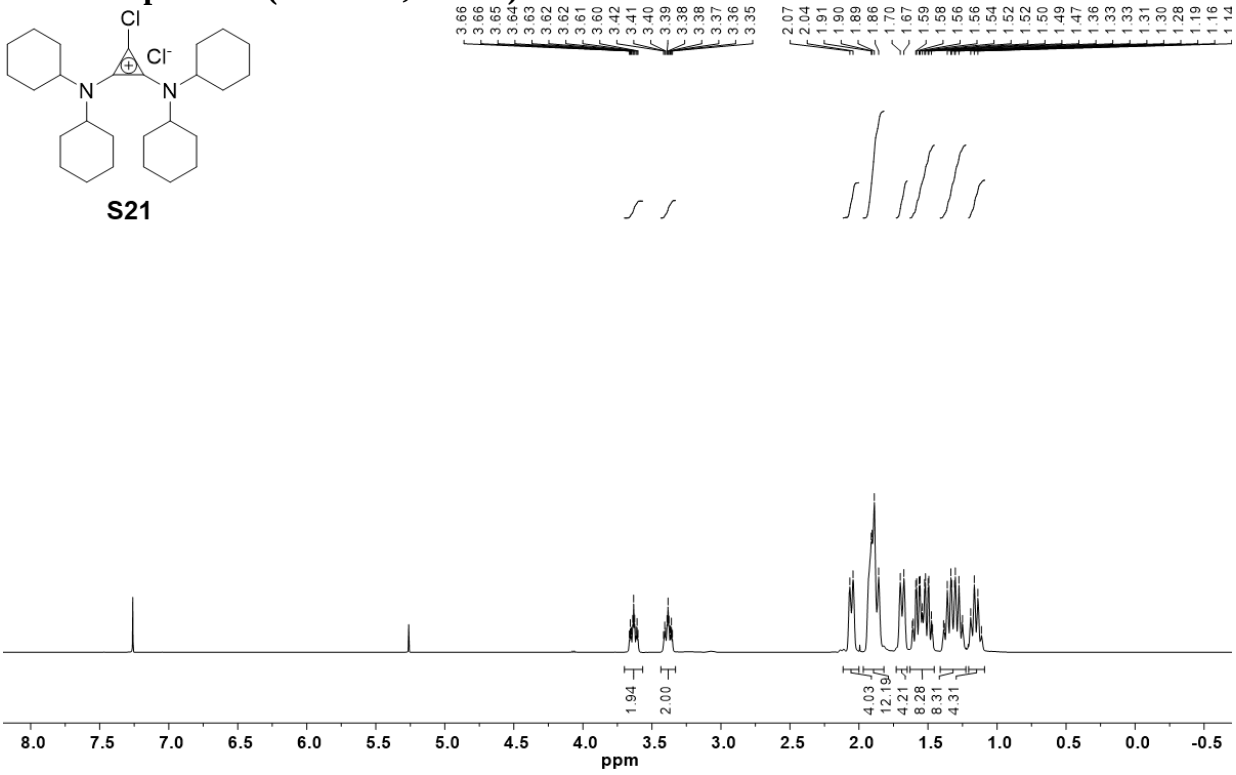


Pentachlorocyclopropane (S20), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



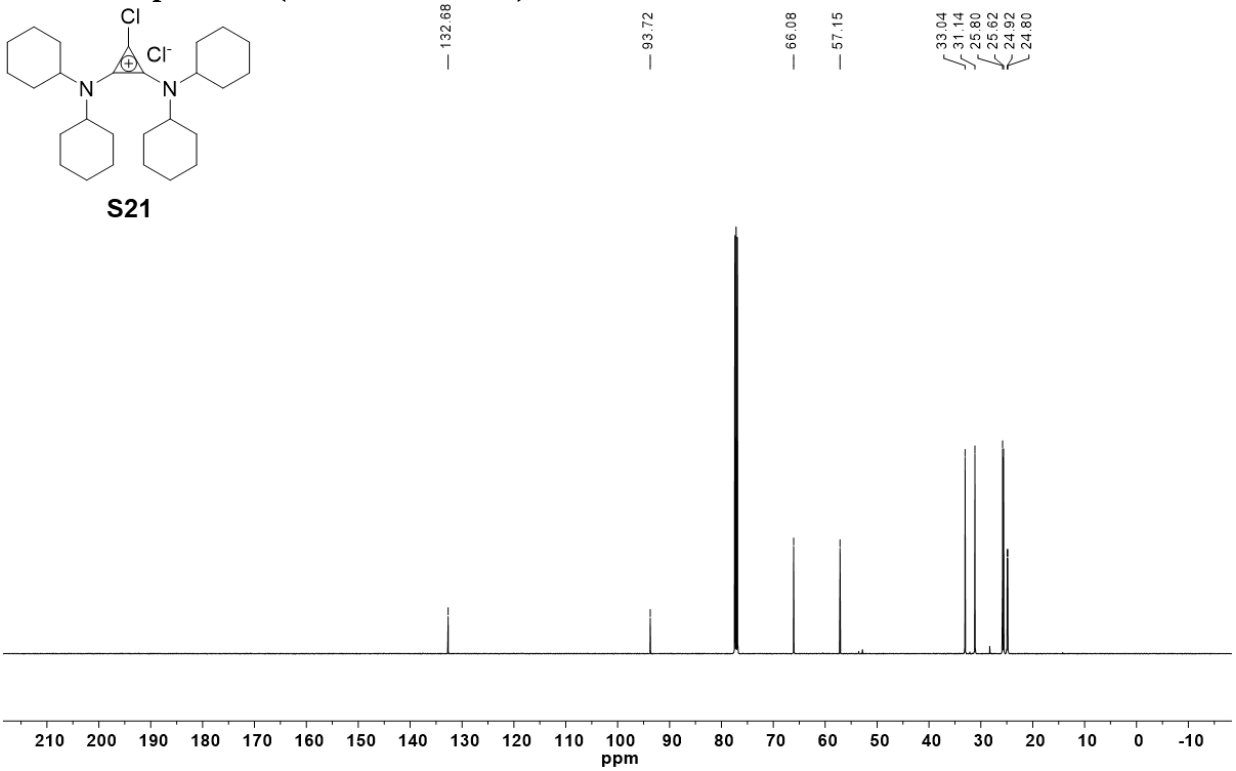
2,3-Bis(dicyclohexylamino)-1-chlorocyclopropenium chloride (S21)

^{1}H NMR spectrum (500 MHz, $CDCl_3$)

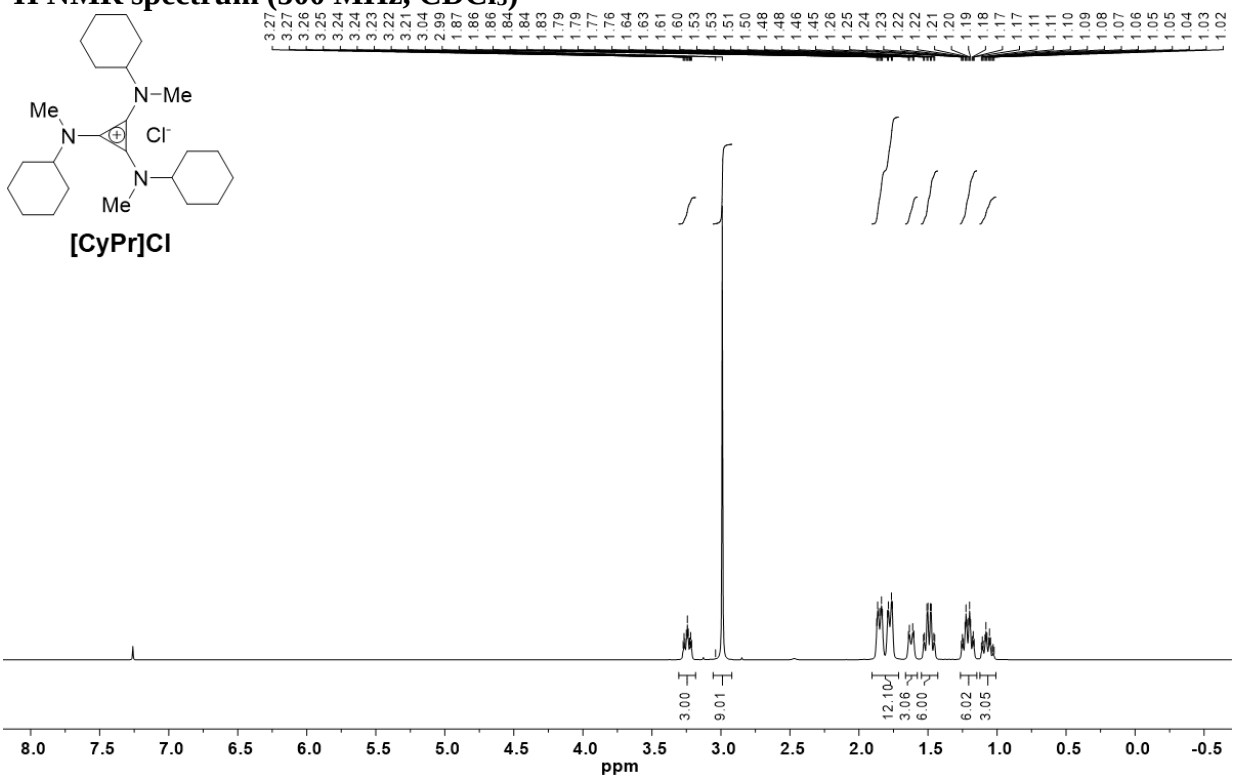


2,3-Bis(dicyclohexylamino)-1-chlorocyclopropenium chloride (S21)

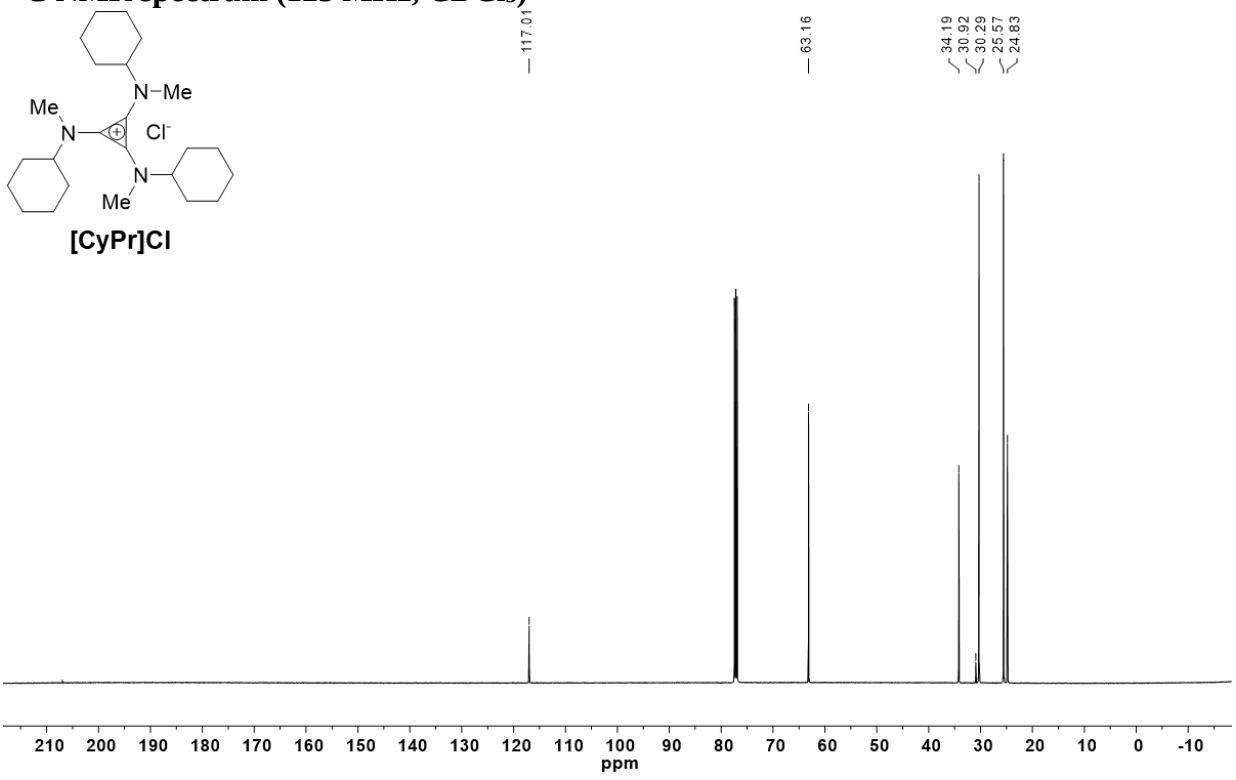
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



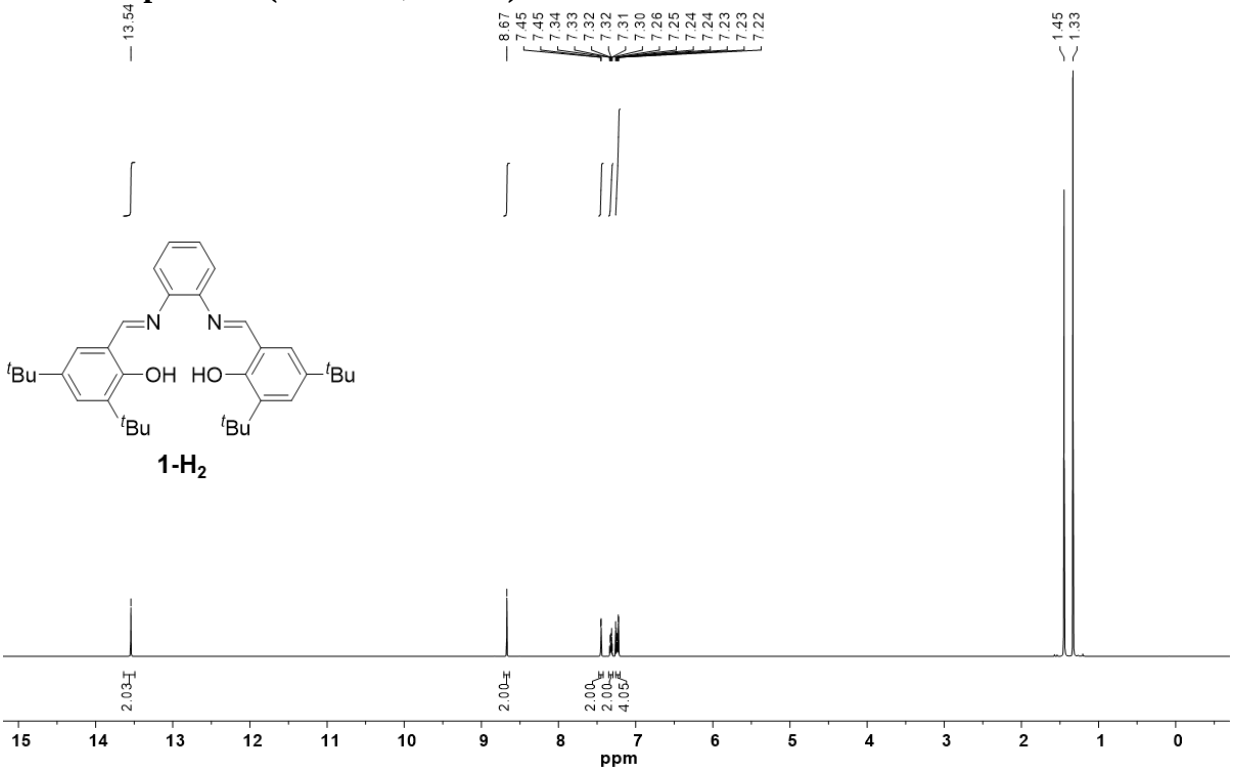
Tris(cyclohexylmethyl)cyclopropenium chloride ([CyPr]Cl)
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



Tris(cyclohexylmethyl)cyclopropenium chloride ([CyPr]Cl)
^{13}C NMR spectrum (125 MHz, $CDCl_3$)

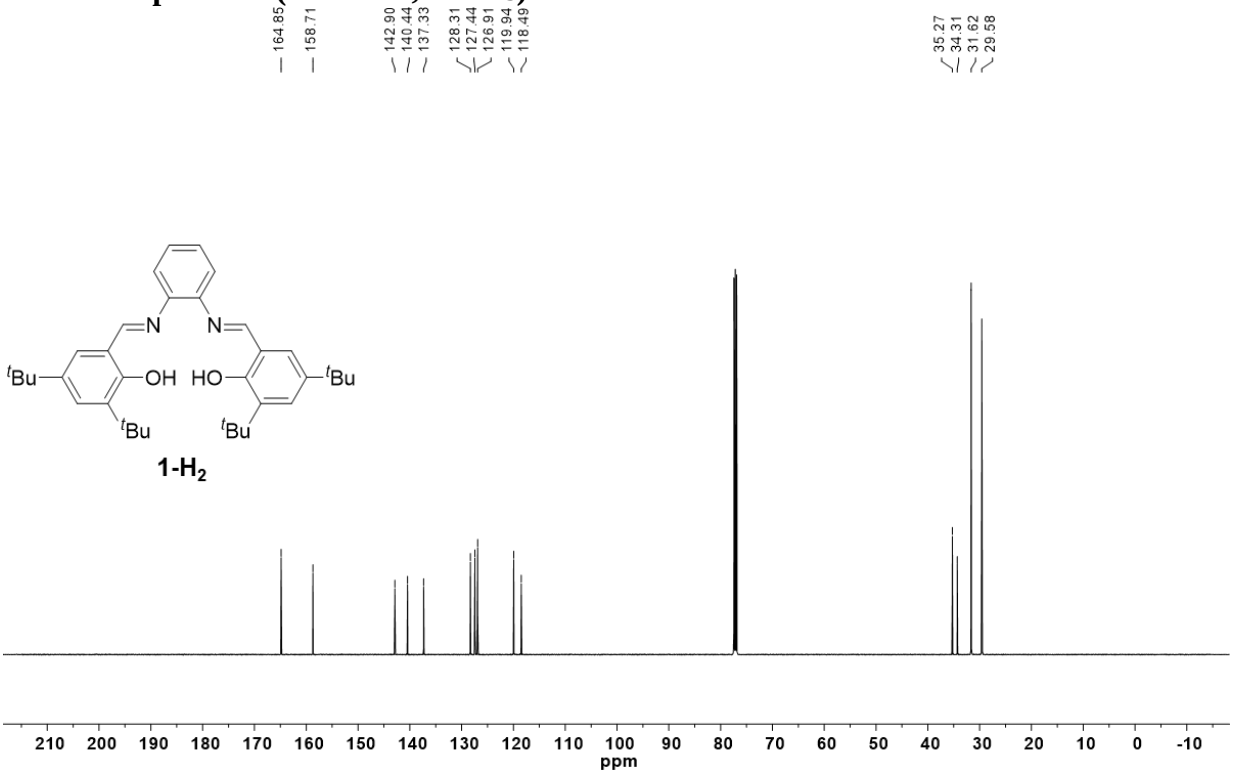


***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminobenzene (1-H_2)**
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



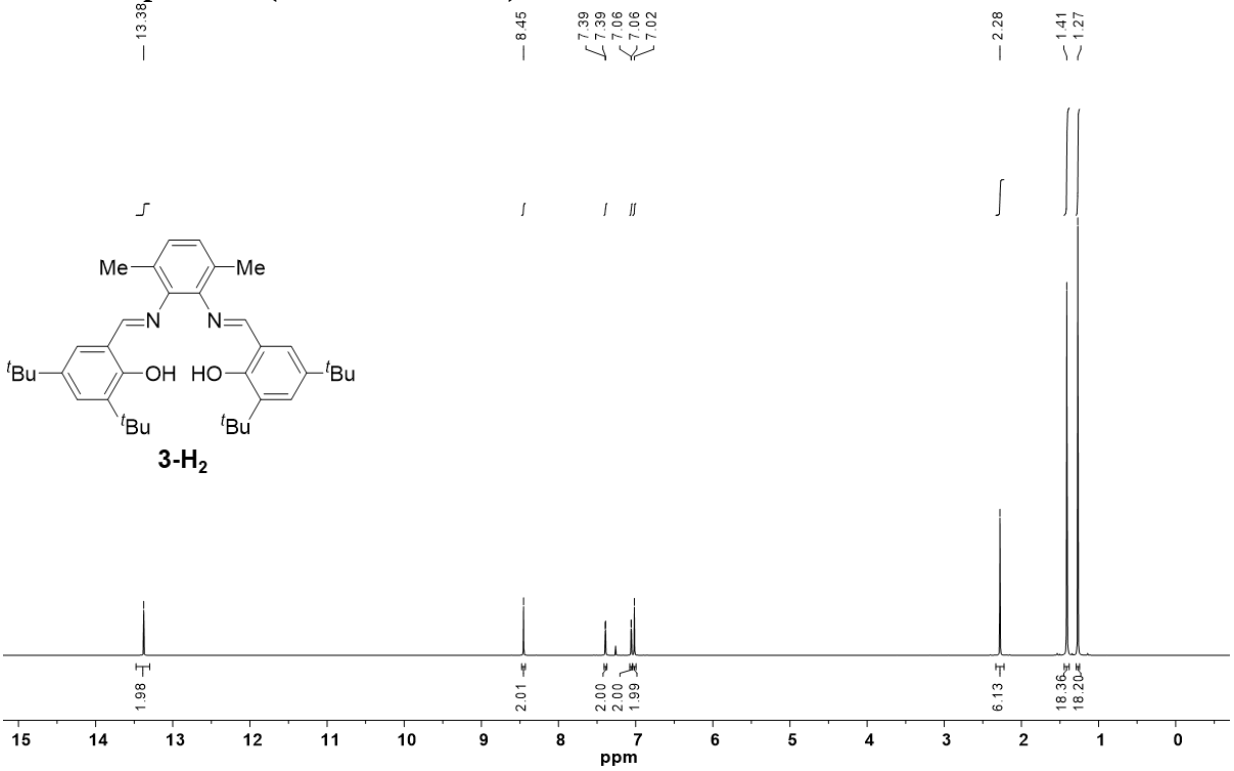
1-H_2

***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminobenzene (1-H_2)**
^{13}C NMR spectrum (125 MHz, $CDCl_3$)

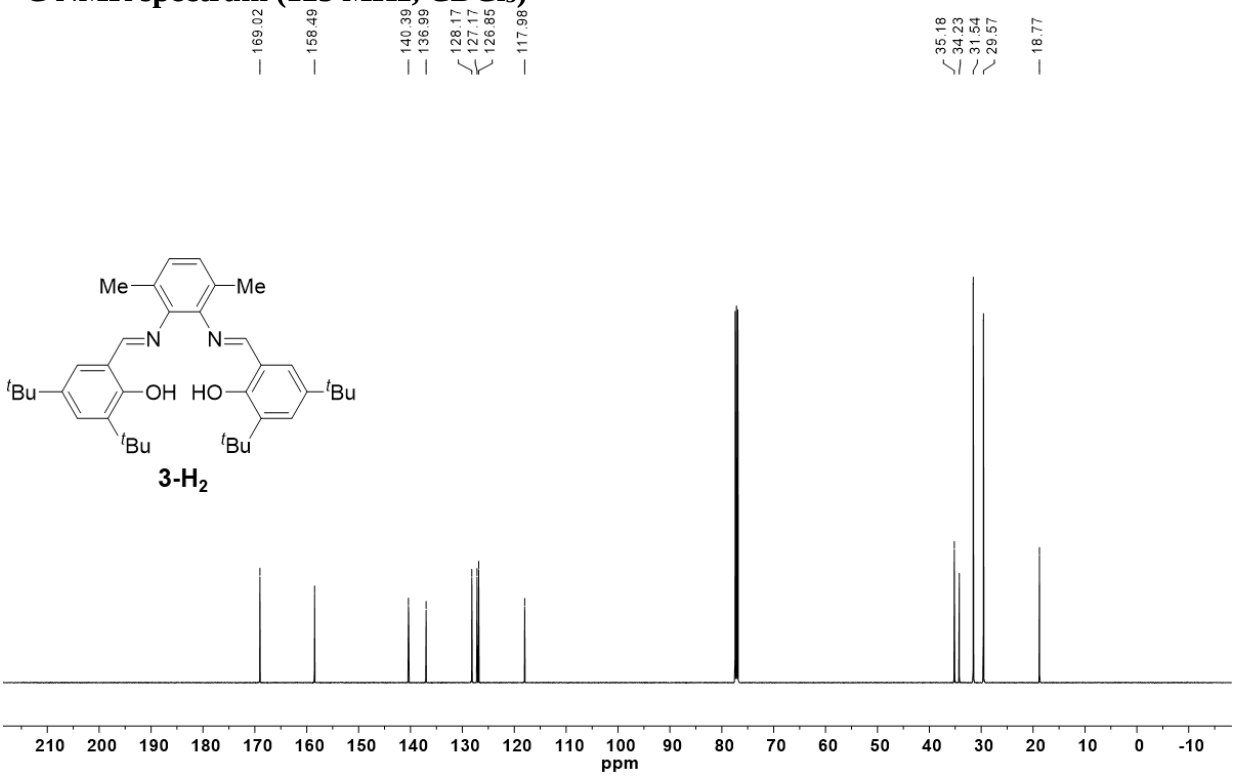


1-H_2

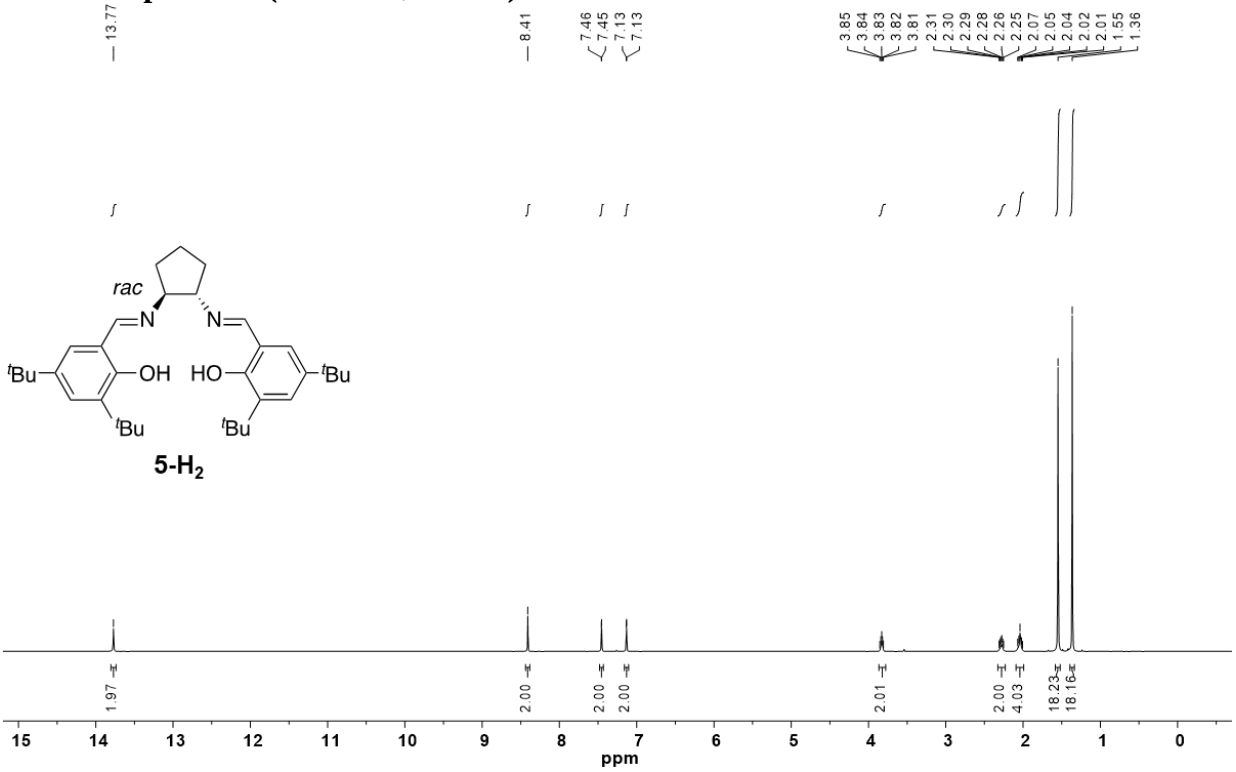
***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-3,6-dimethyl-1,2-diaminobenzene (3-H_2)**
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



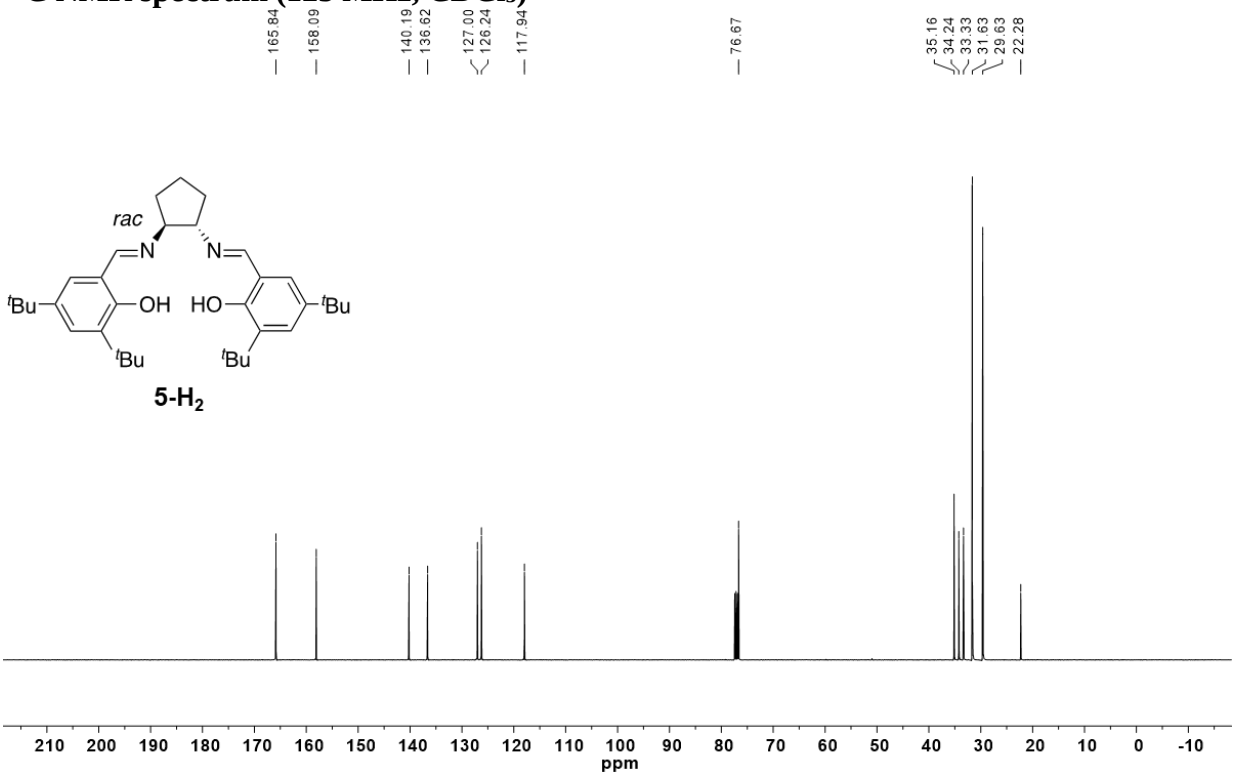
***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-3,6-dimethyl-1,2-diaminobenzene (3-H_2)**
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



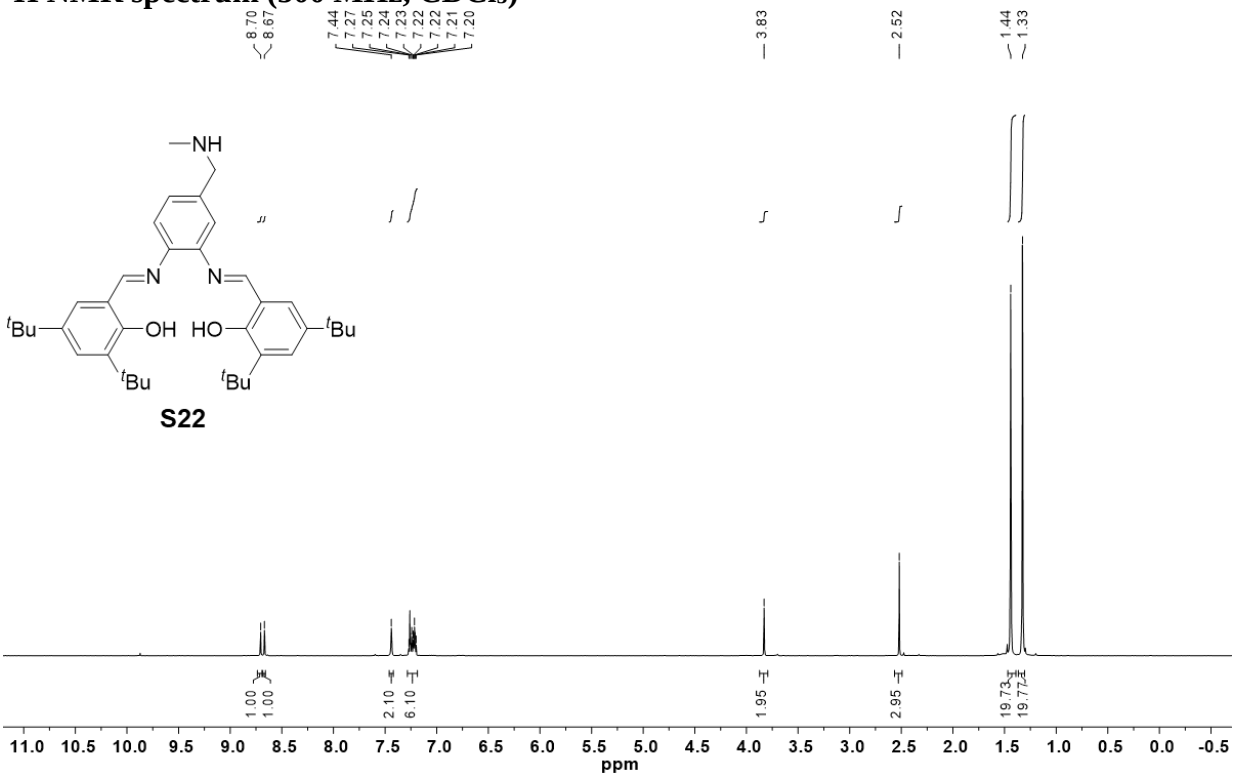
***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-*trans*-1,2-diaminocyclopentane (5-H_2)**
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



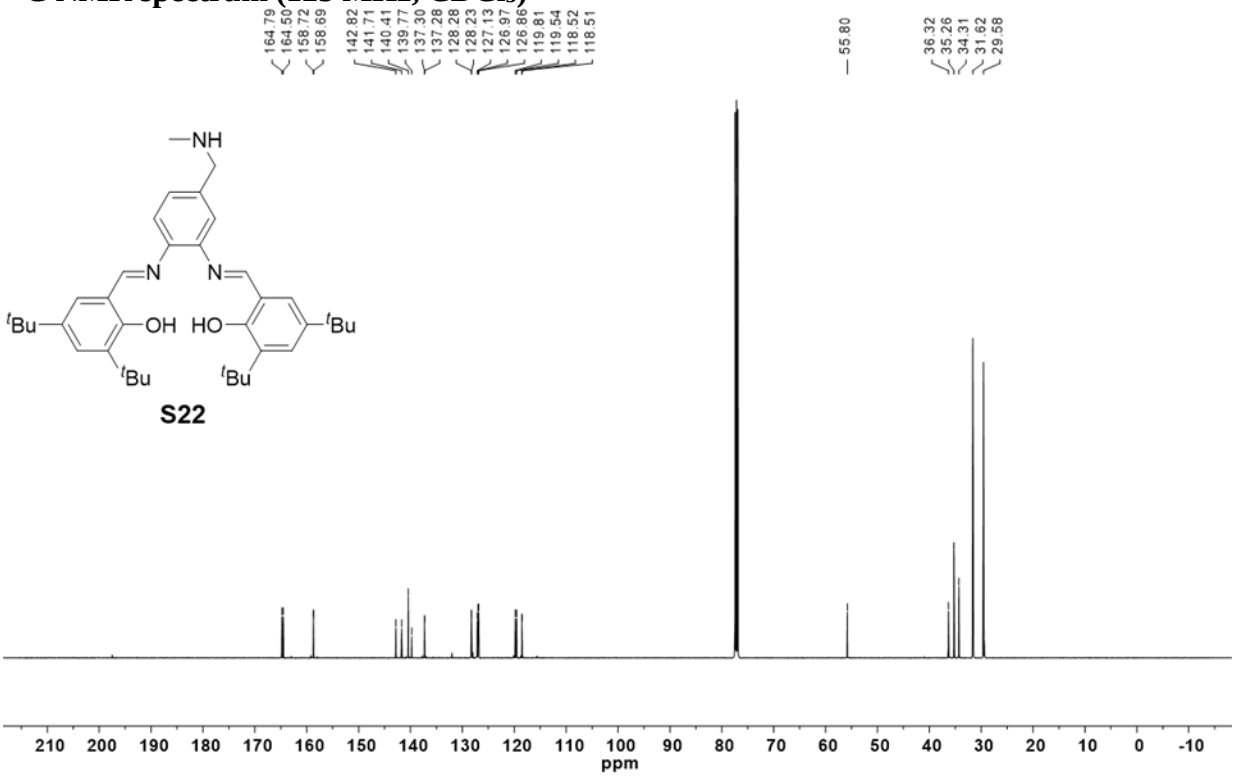
***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-*trans*-1,2-diaminocyclopentane (5-H_2)**
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



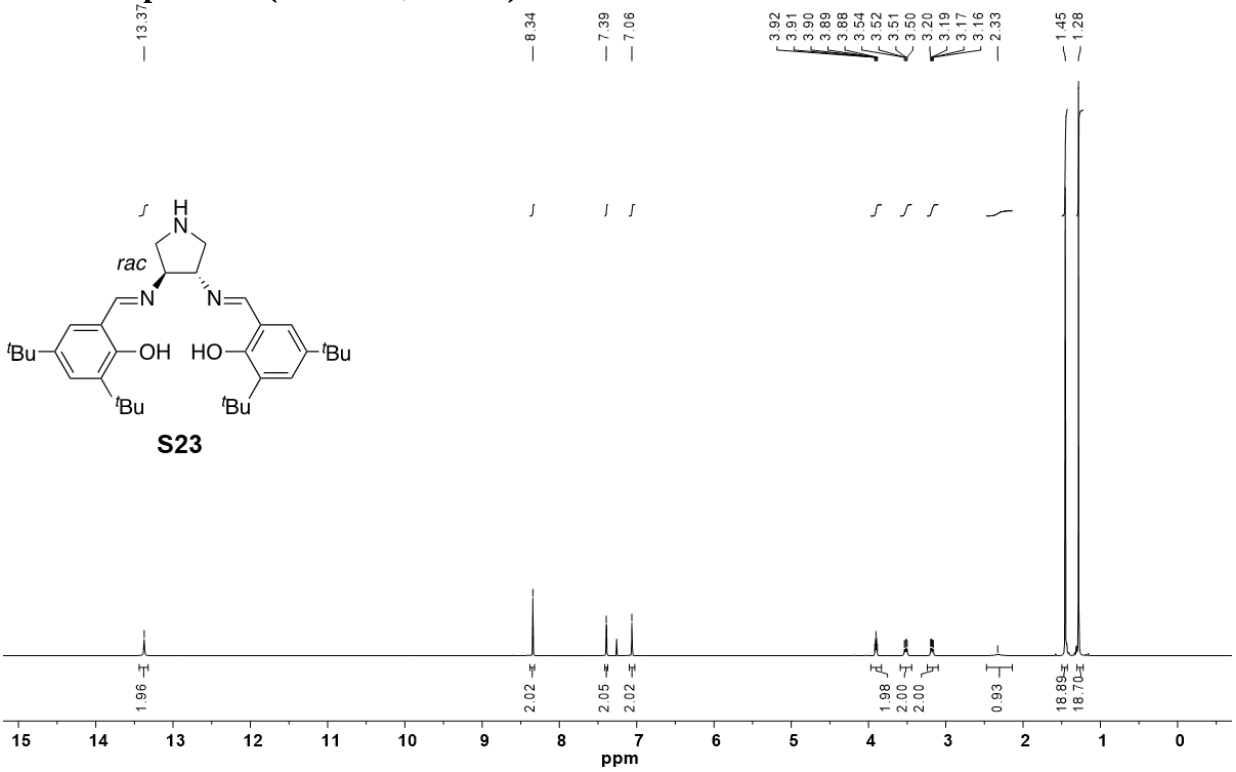
***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-4-*N*-methyl-methanamine-1,2-diaminobenzene (S22)**
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



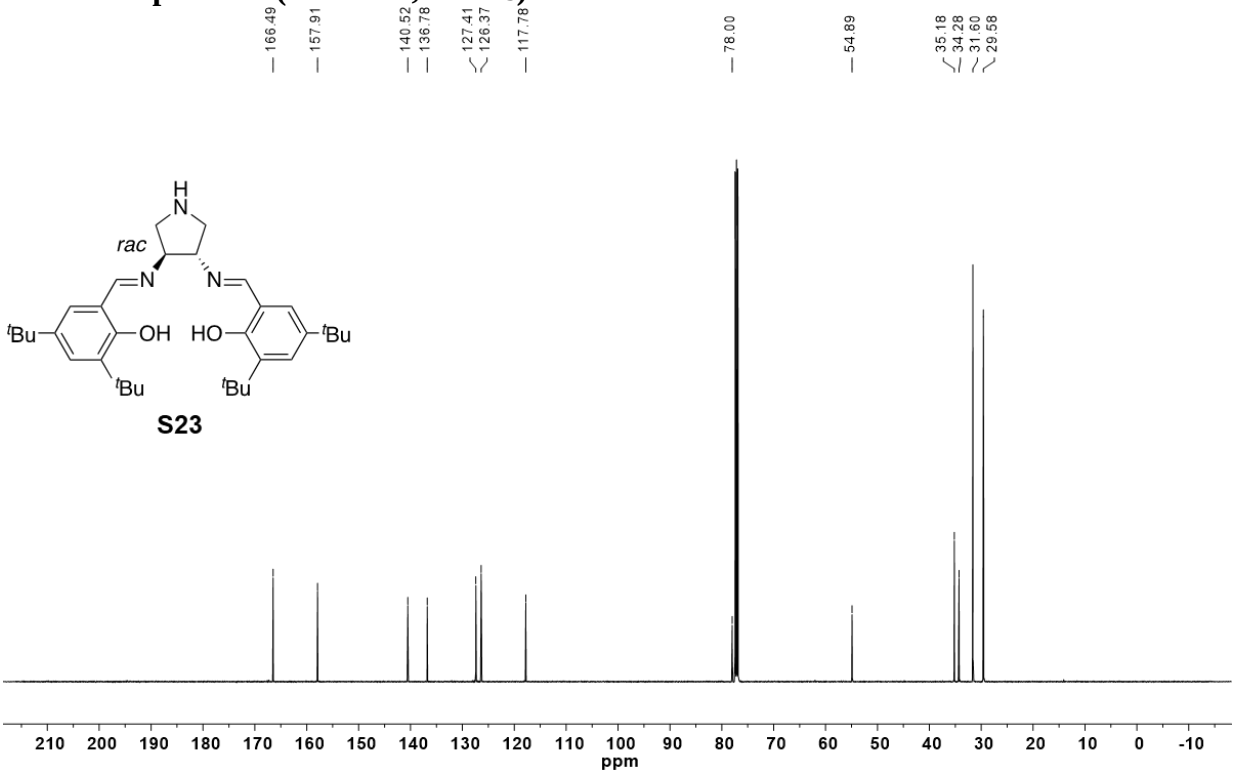
***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-4-*N*-methyl-methanamine-1,2-diaminobenzene (S22)**
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



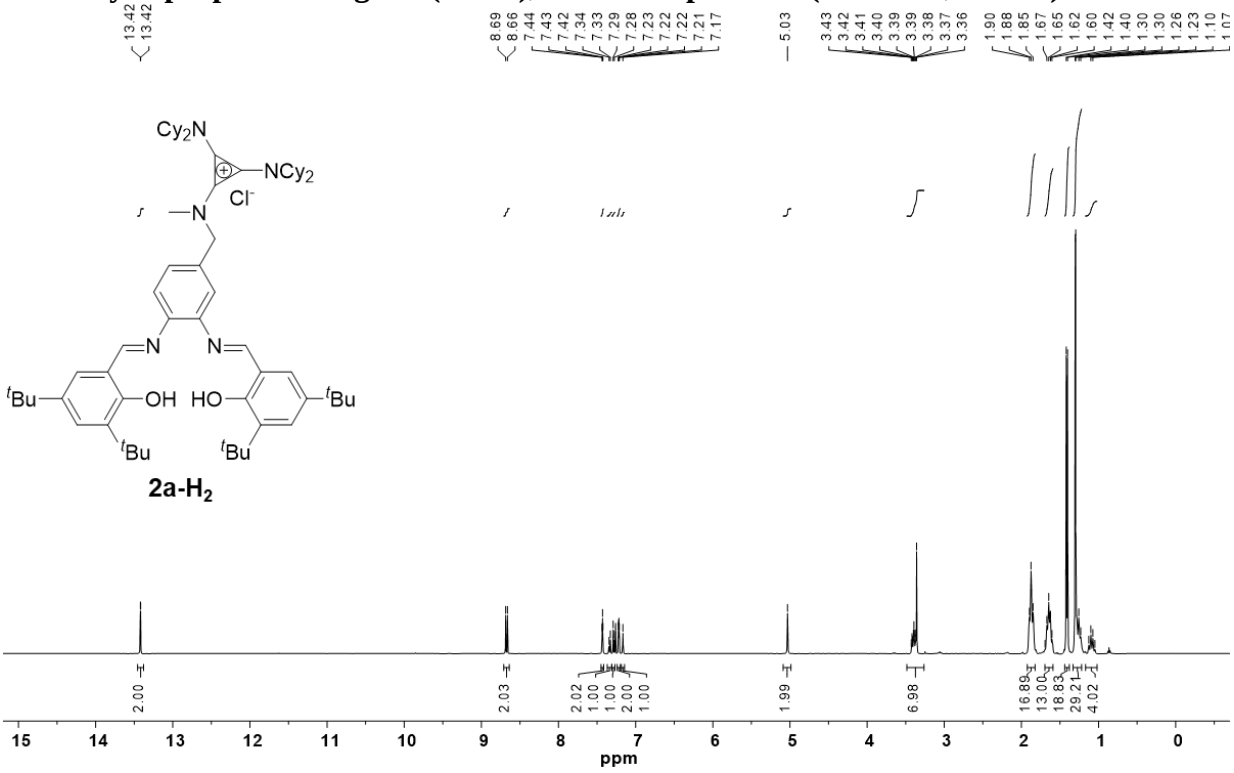
***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-3,4-diaminopyrrolidine (S23)**
^{1}H NMR spectrum (500 MHz, $CDCl_3$)



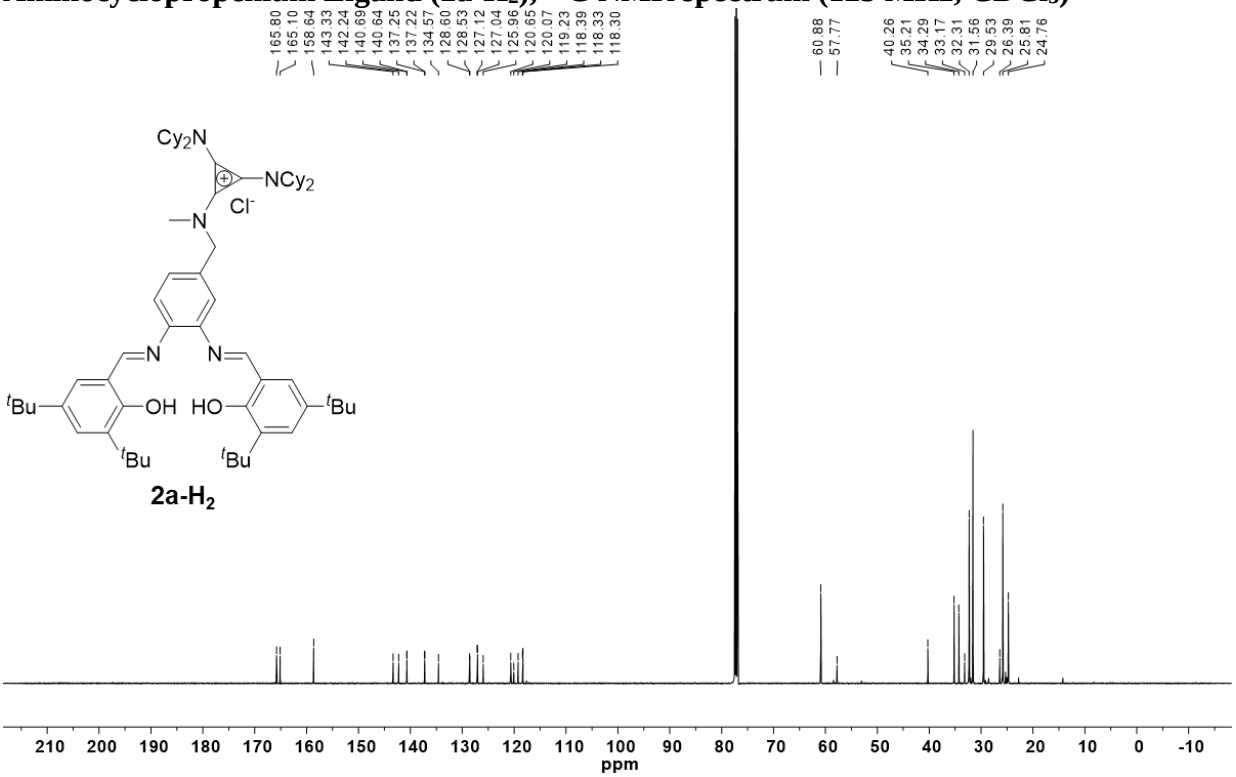
***N, N'*-Bis(3,5-di-*tert*-butylsalicylidene)-3,4-diaminopyrrolidine (S23)**
^{13}C NMR spectrum (125 MHz, $CDCl_3$)



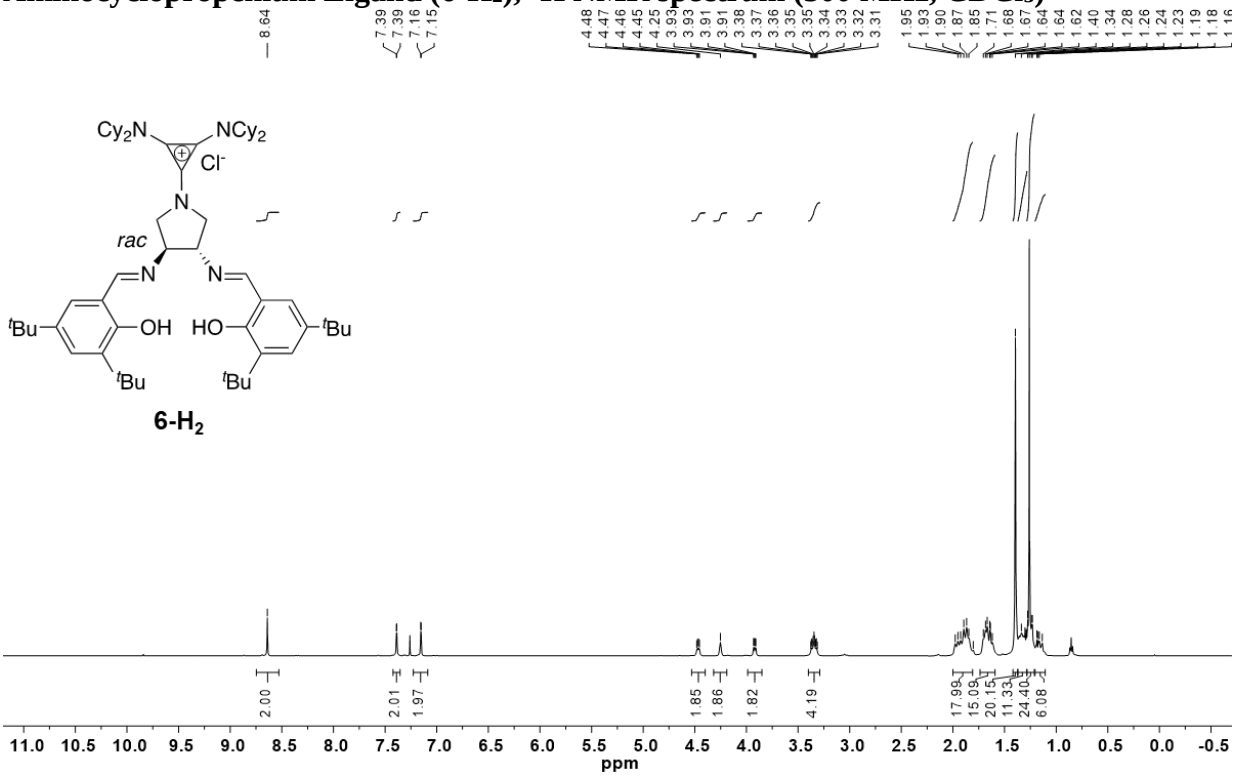
Aminocyclopropenium Ligand (2a-H_2), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



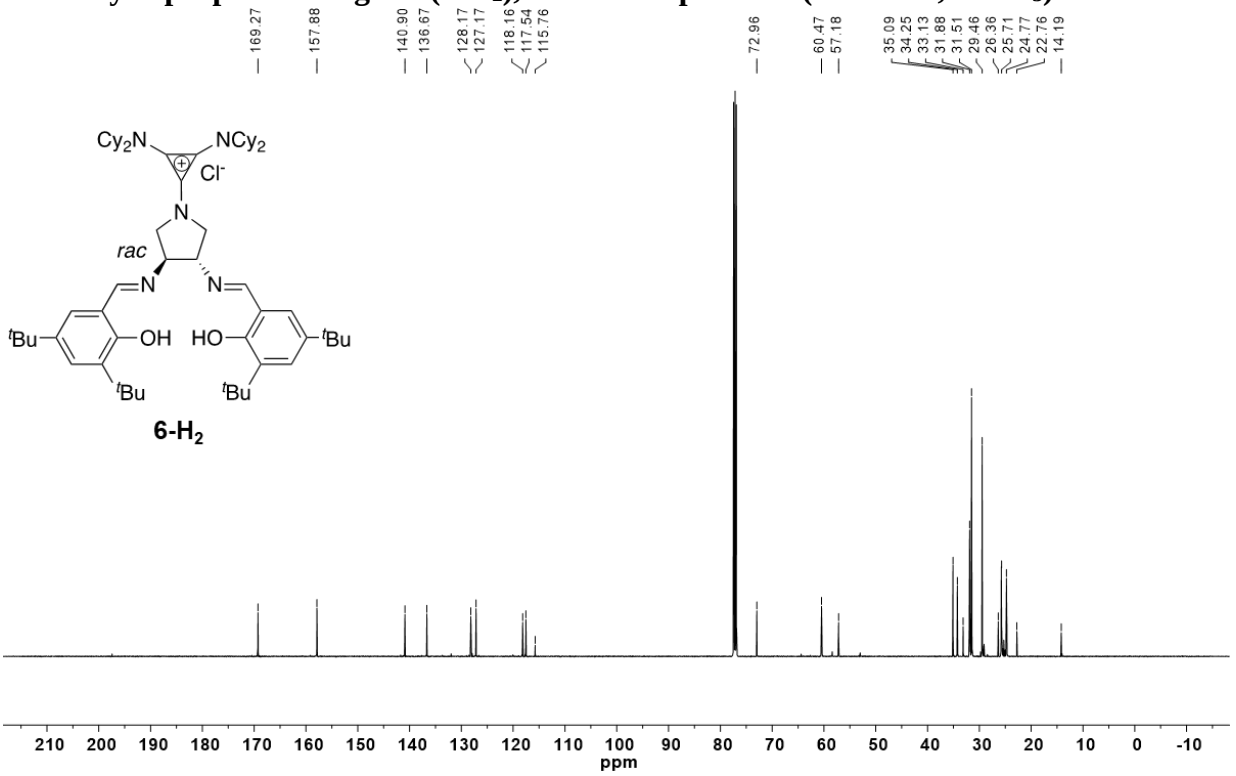
Aminocyclopropenium Ligand (2a-H_2), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



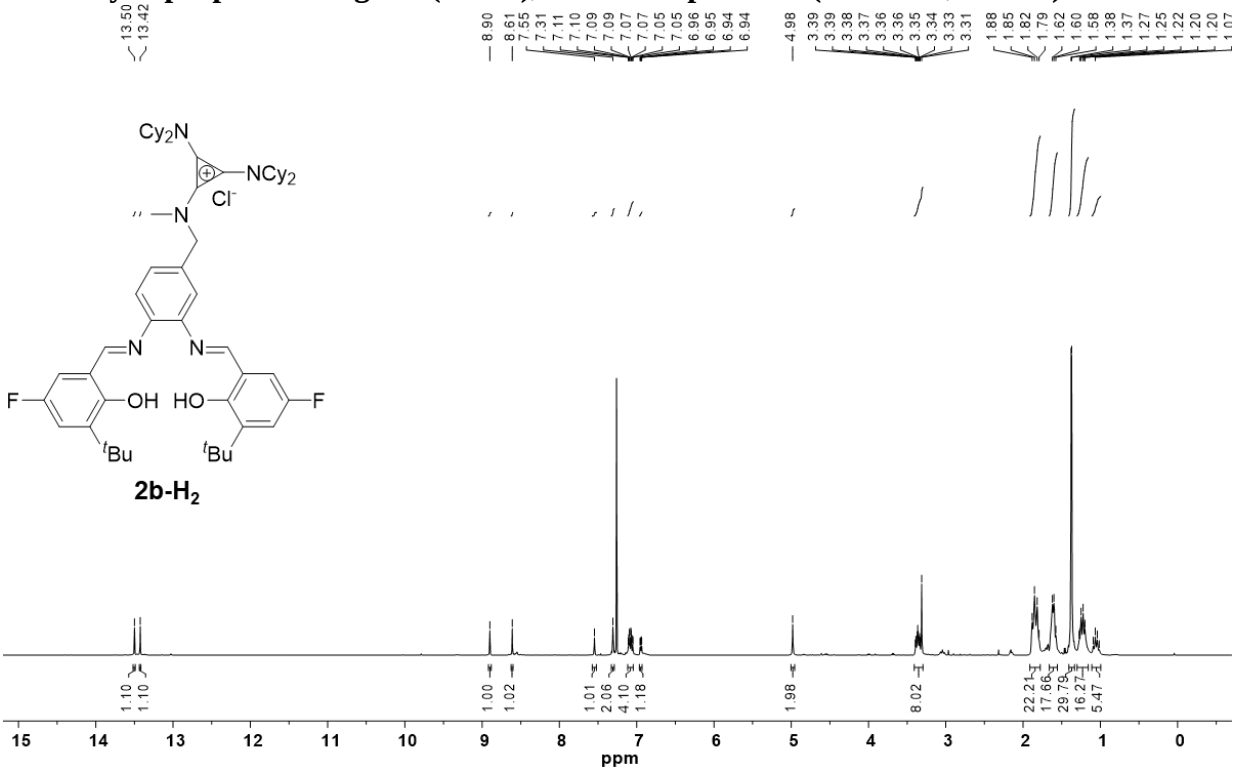
Aminocyclopropenium Ligand (6-H_2), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



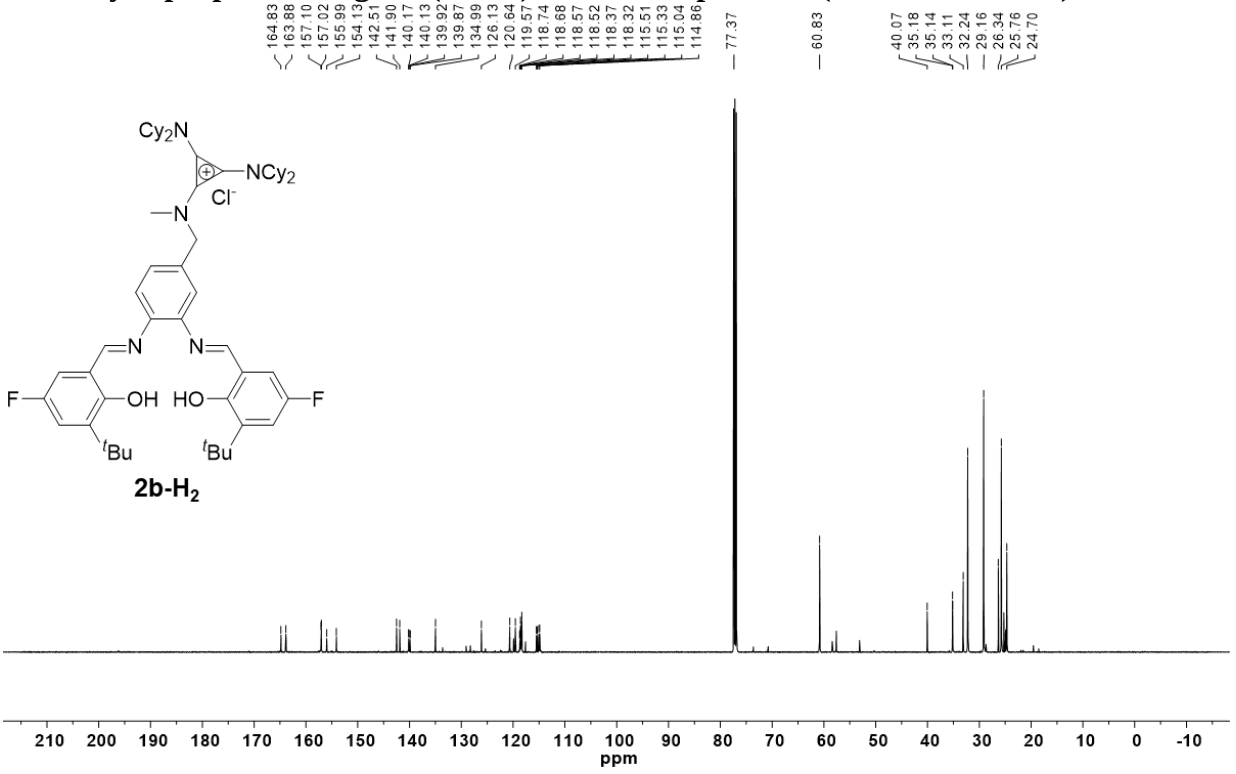
Aminocyclopropenium Ligand (6-H_2), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



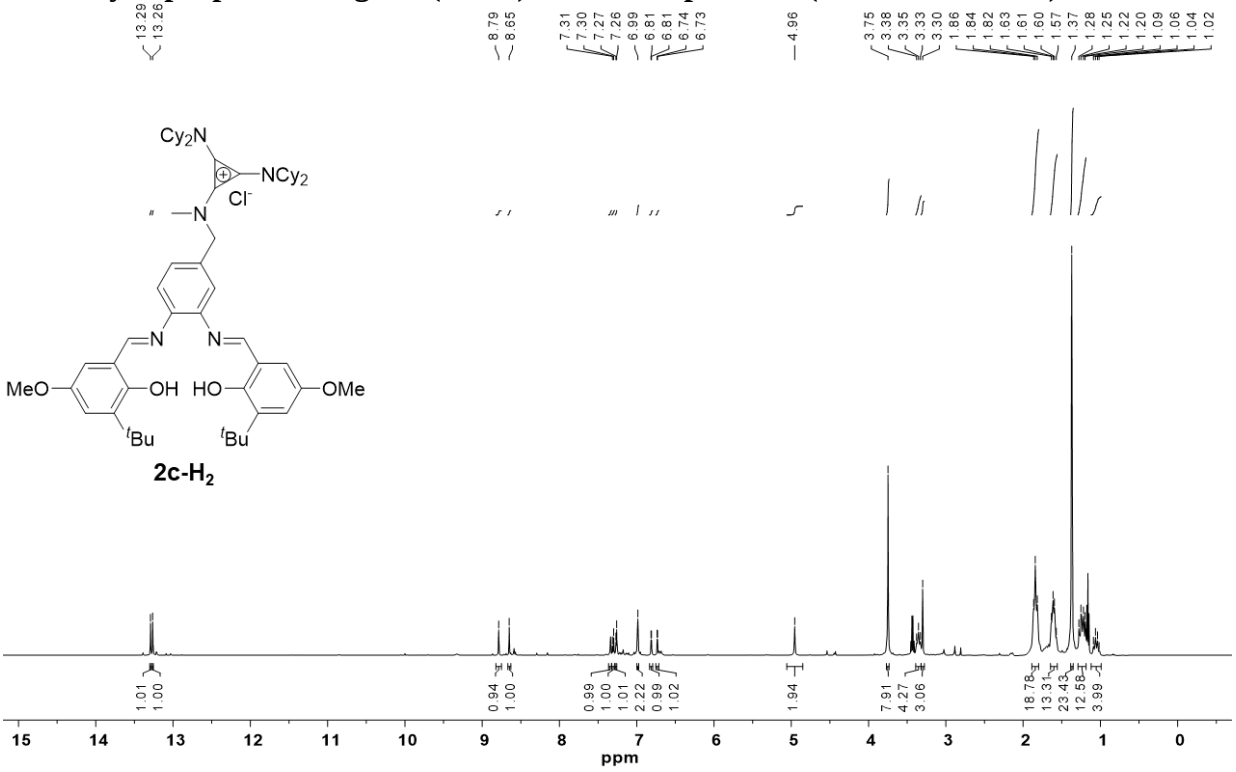
Aminocyclopropenium Ligand (2b-H_2), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



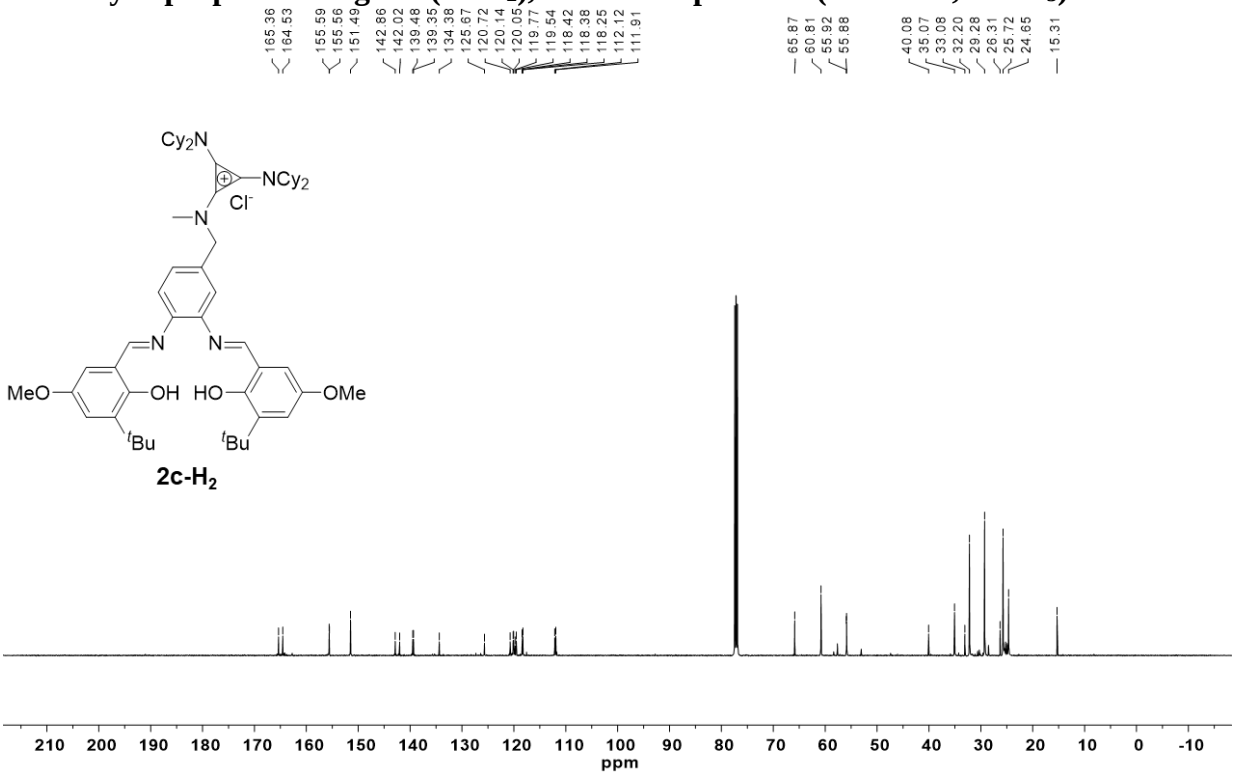
Aminocyclopropenium Ligand (2b-H_2), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



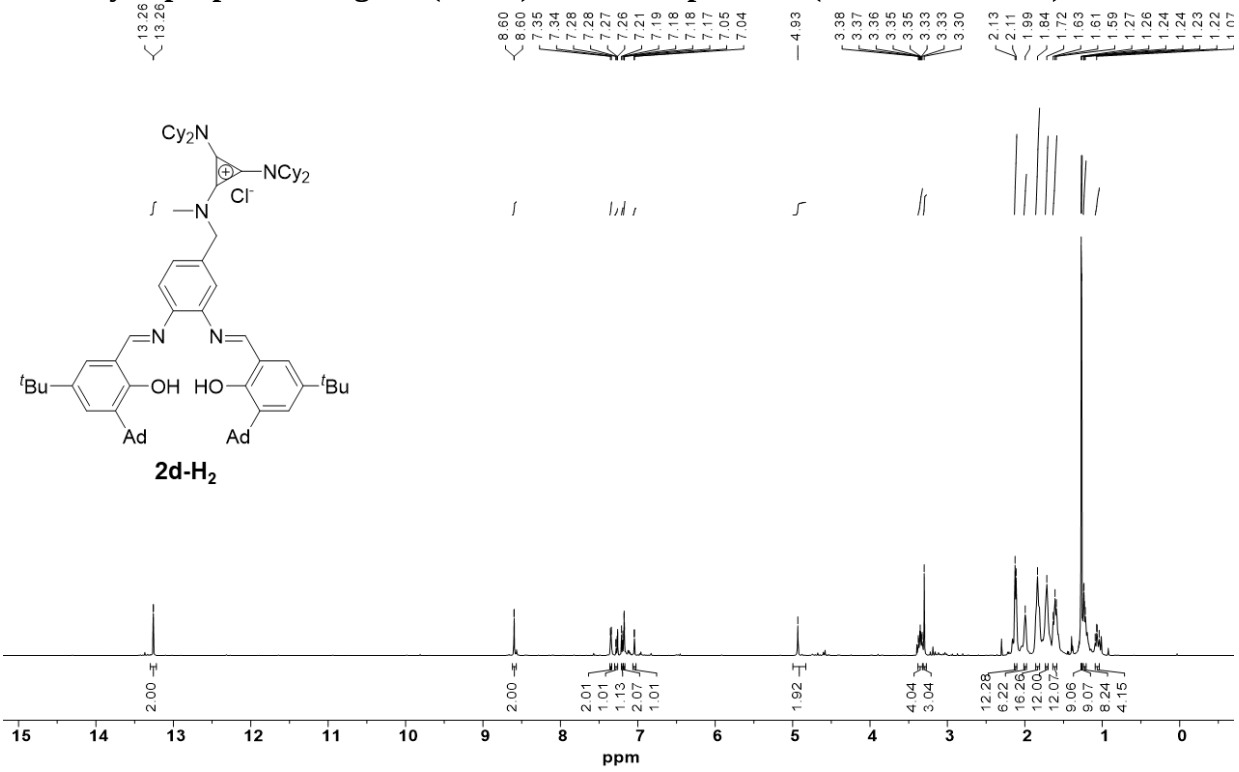
Aminocyclopropenium Ligand (2c-H_2), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



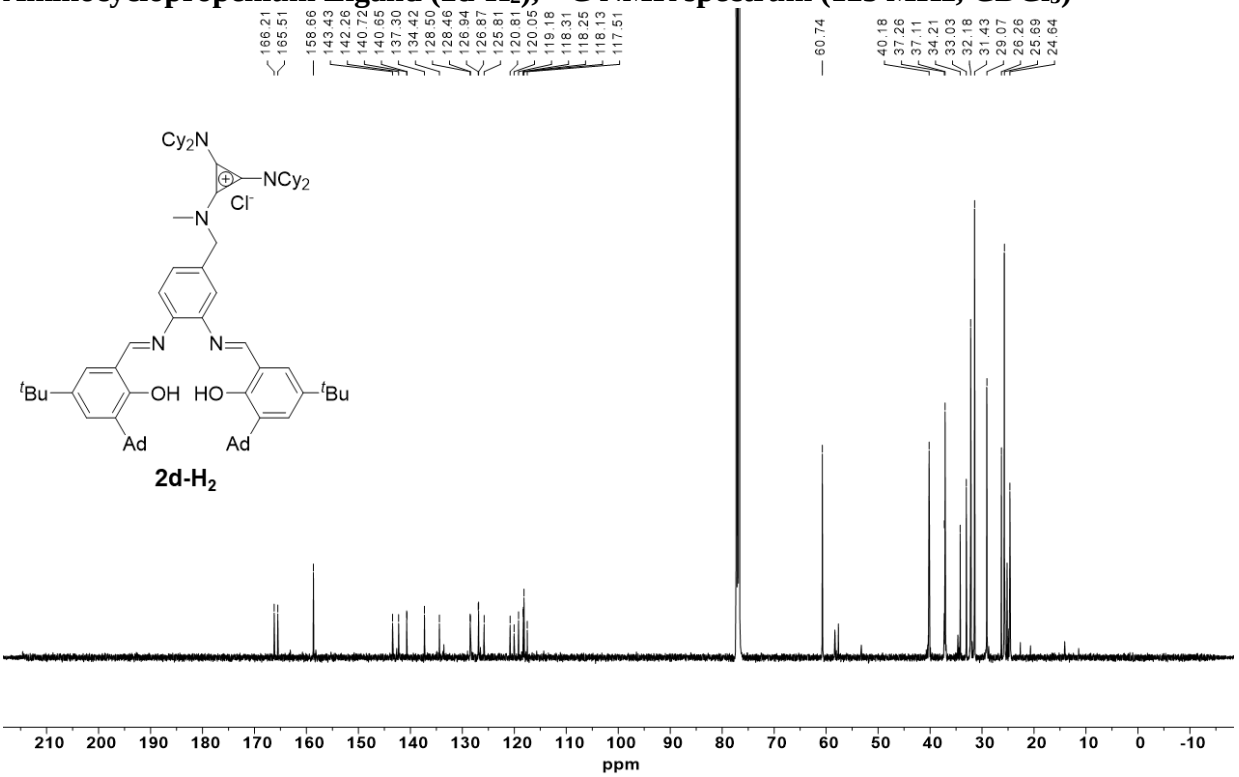
Aminocyclopropenium Ligand (2c-H_2), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



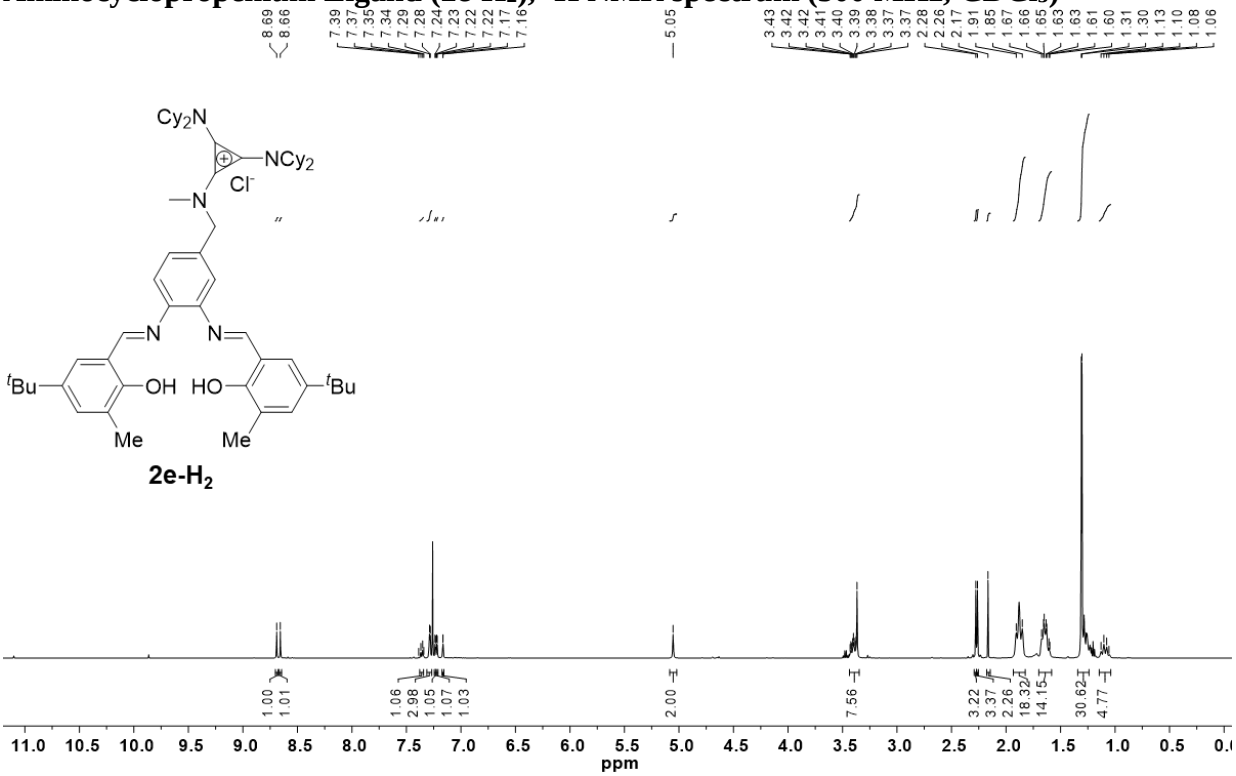
Aminocyclopropenium Ligand (2d-H_2), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



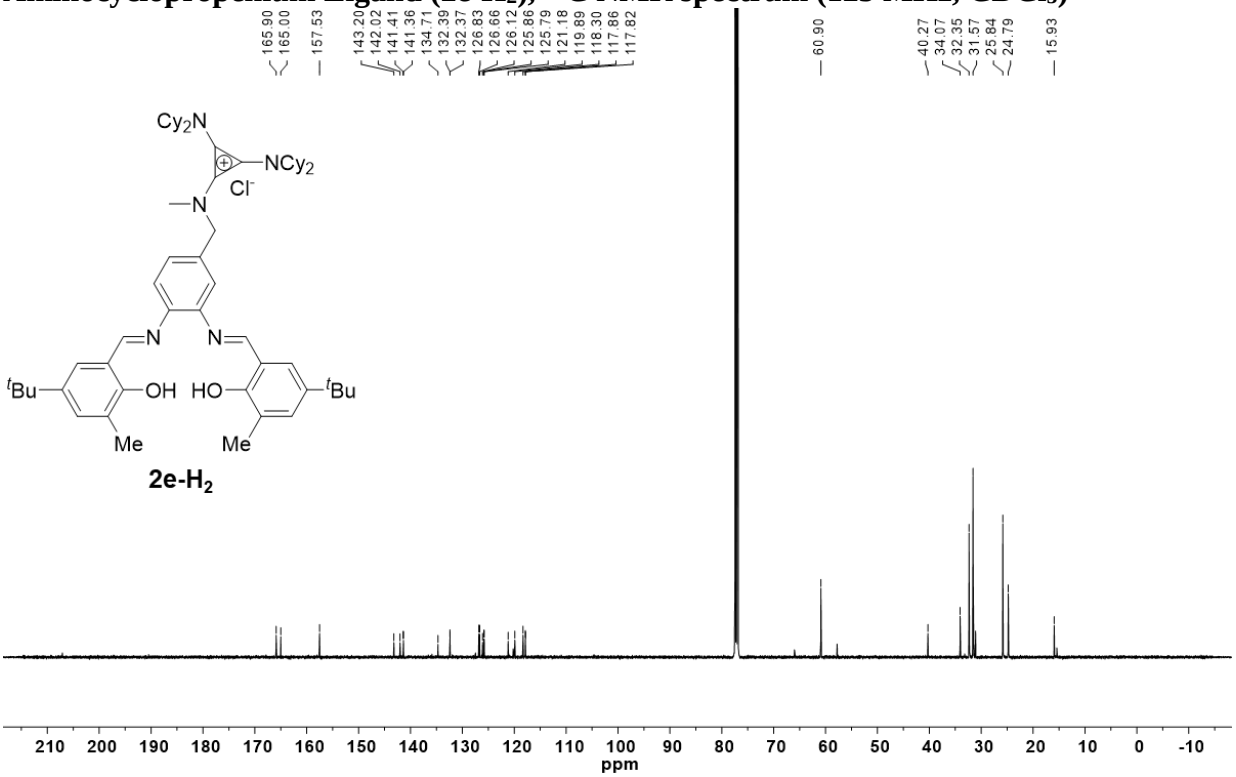
Aminocyclopropenium Ligand (2d-H_2), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



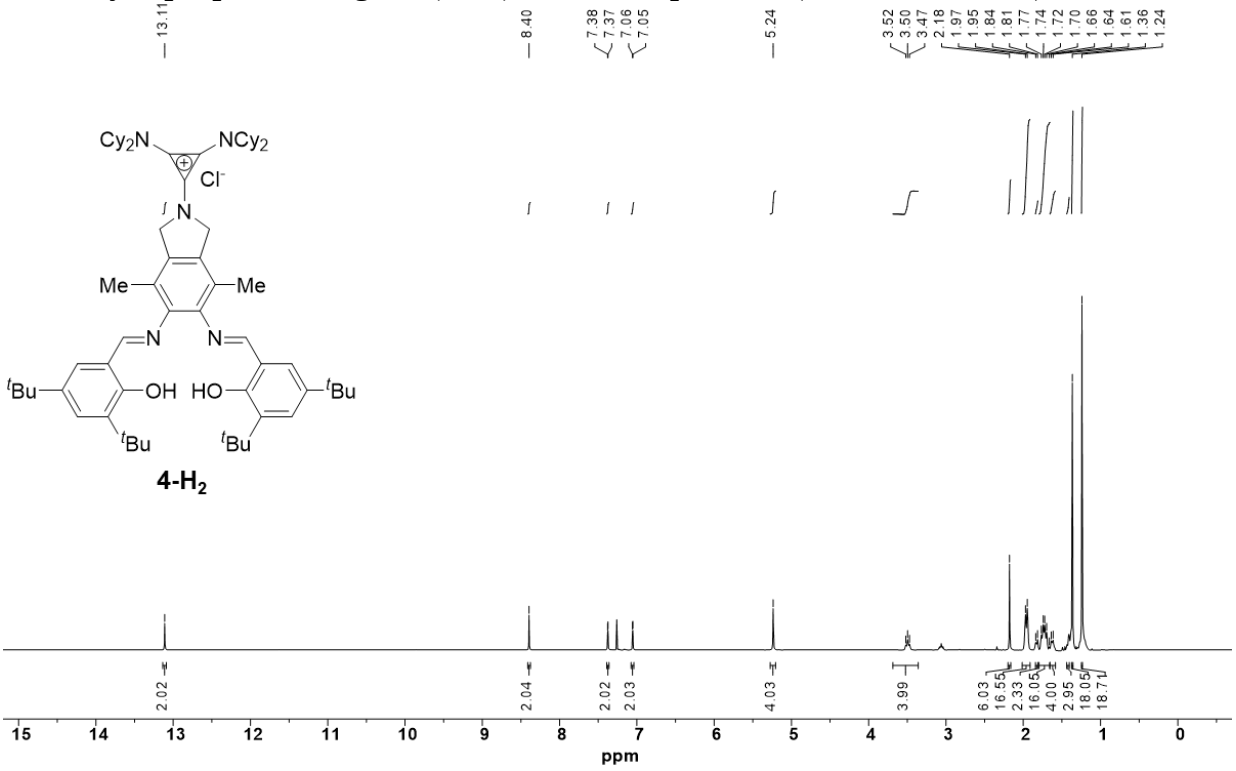
Aminocyclopropenium Ligand (2e-H_2), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



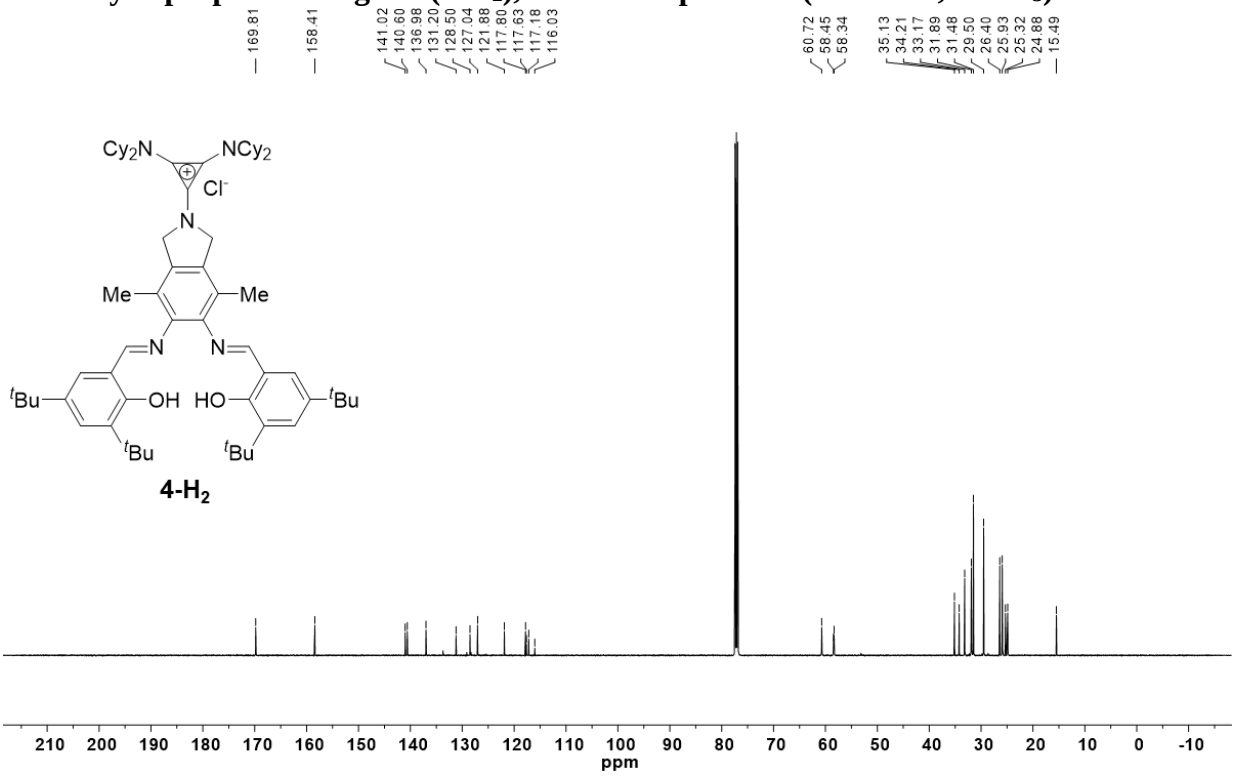
Aminocyclopropenium Ligand (2e-H_2), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



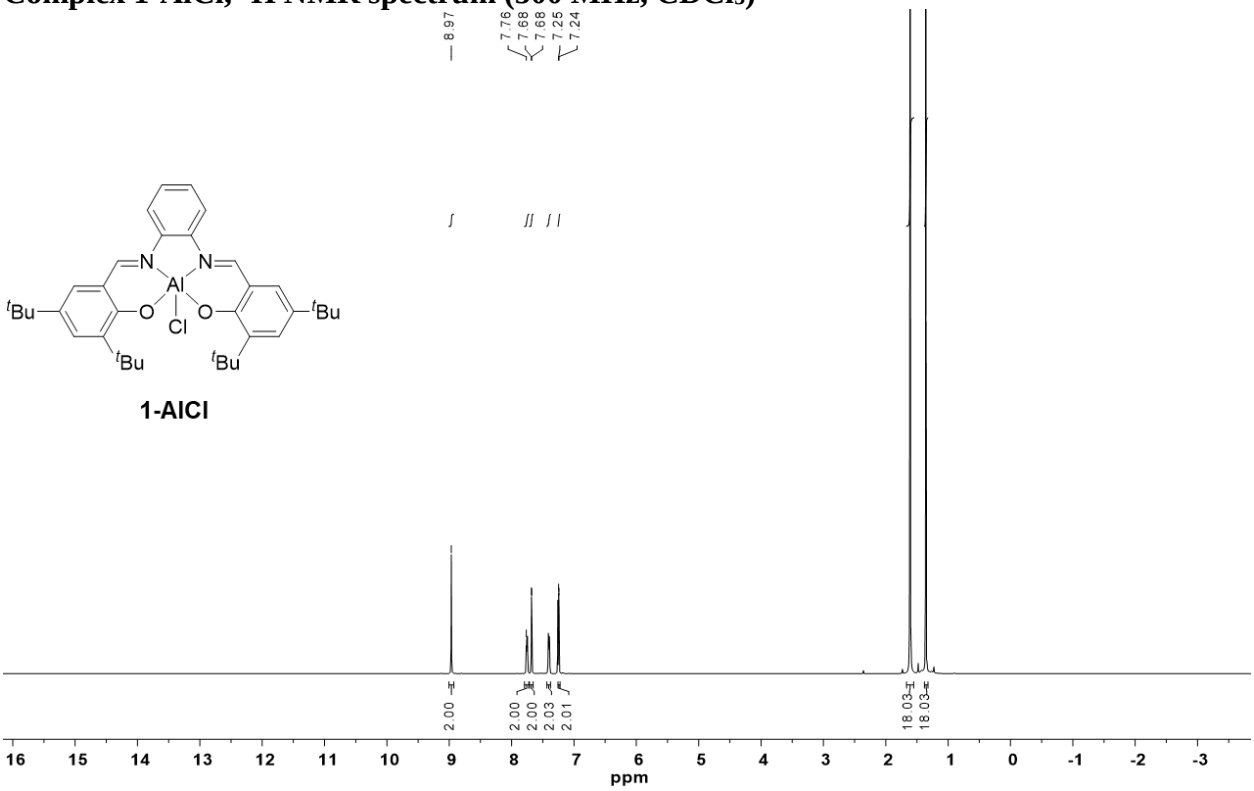
Aminocyclopropenium Ligand (4-H_2), ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



Aminocyclopropenium Ligand (4-H_2), ^{13}C NMR spectrum (125 MHz, $CDCl_3$)

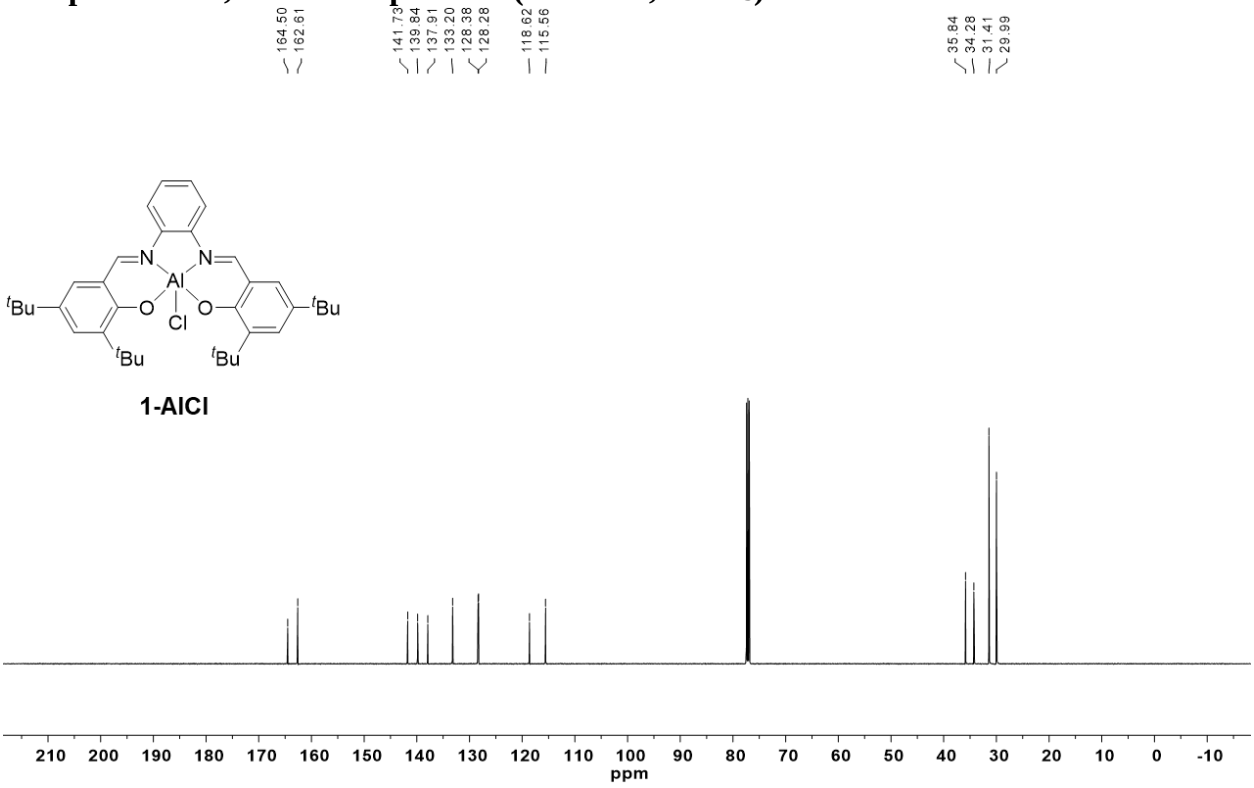


Complex 1-AlCl, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



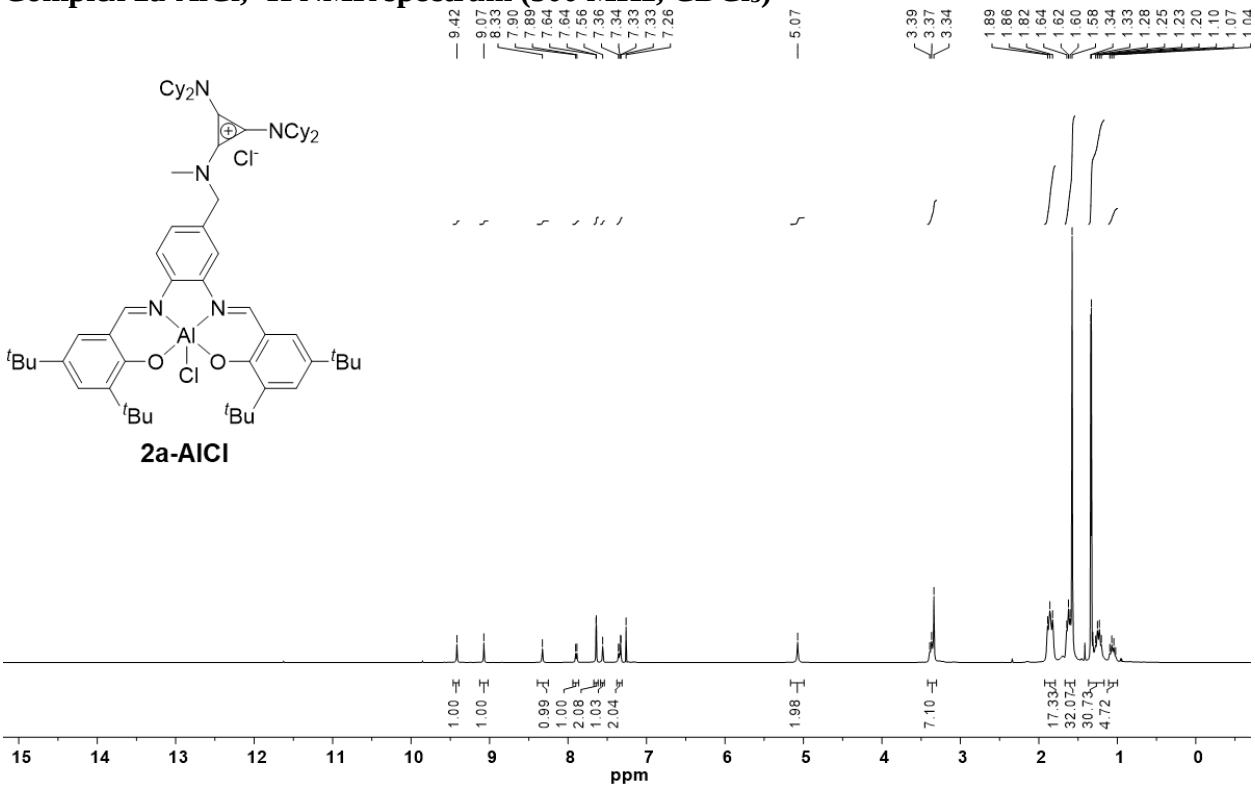
1-AlCl

Complex 1-AlCl, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)

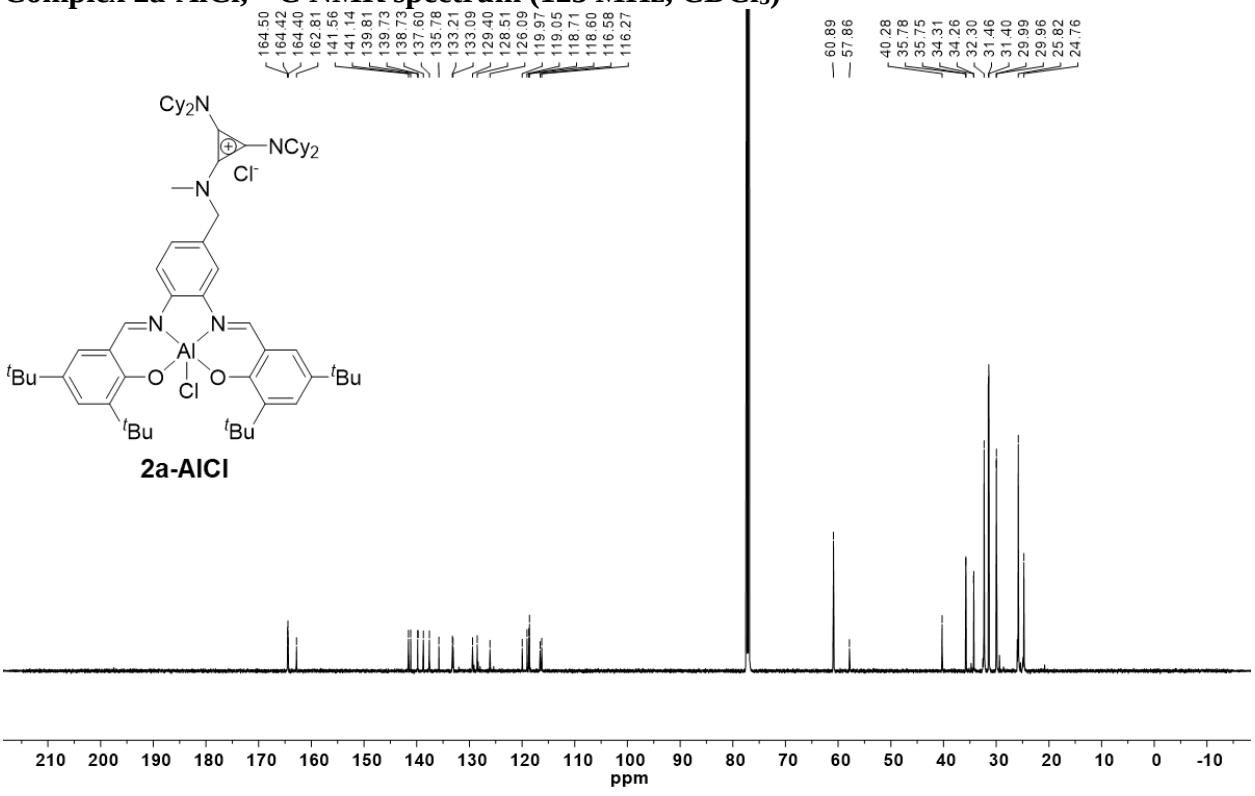


1-AlCl

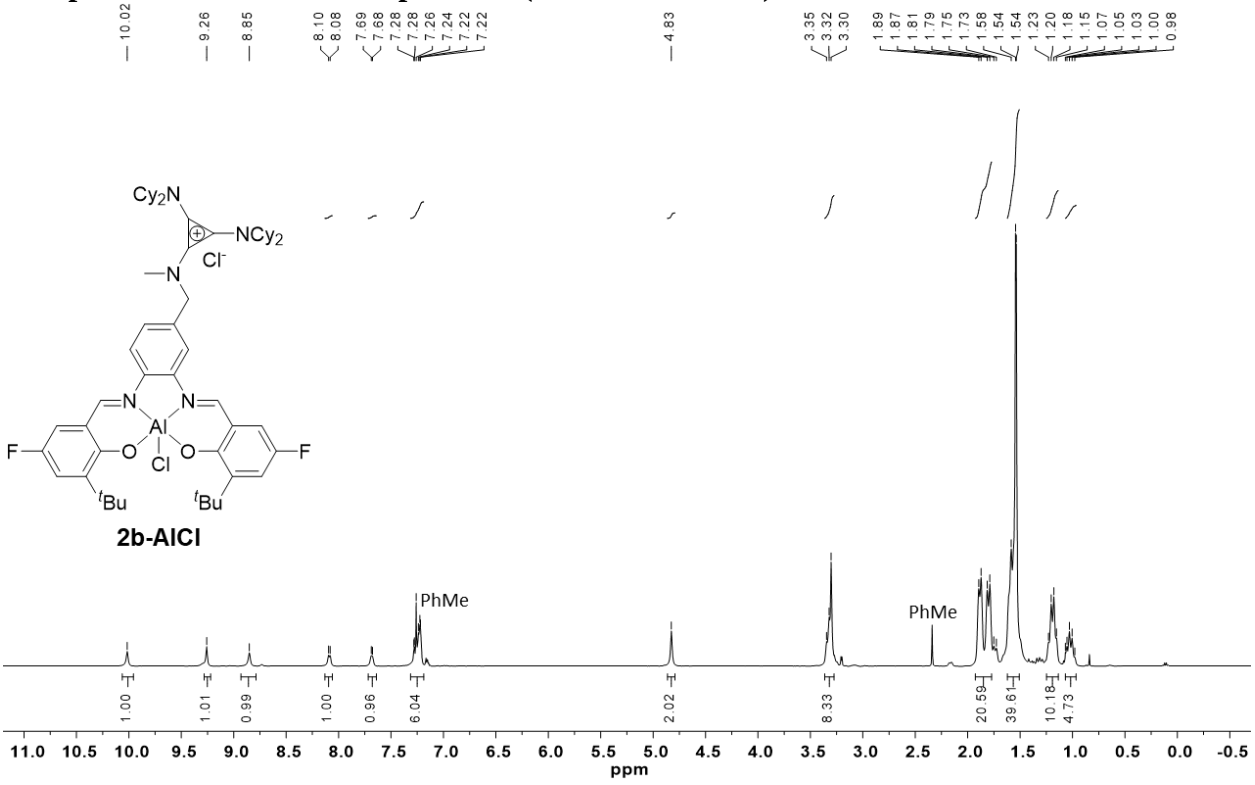
Complex 2a-AlCl, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



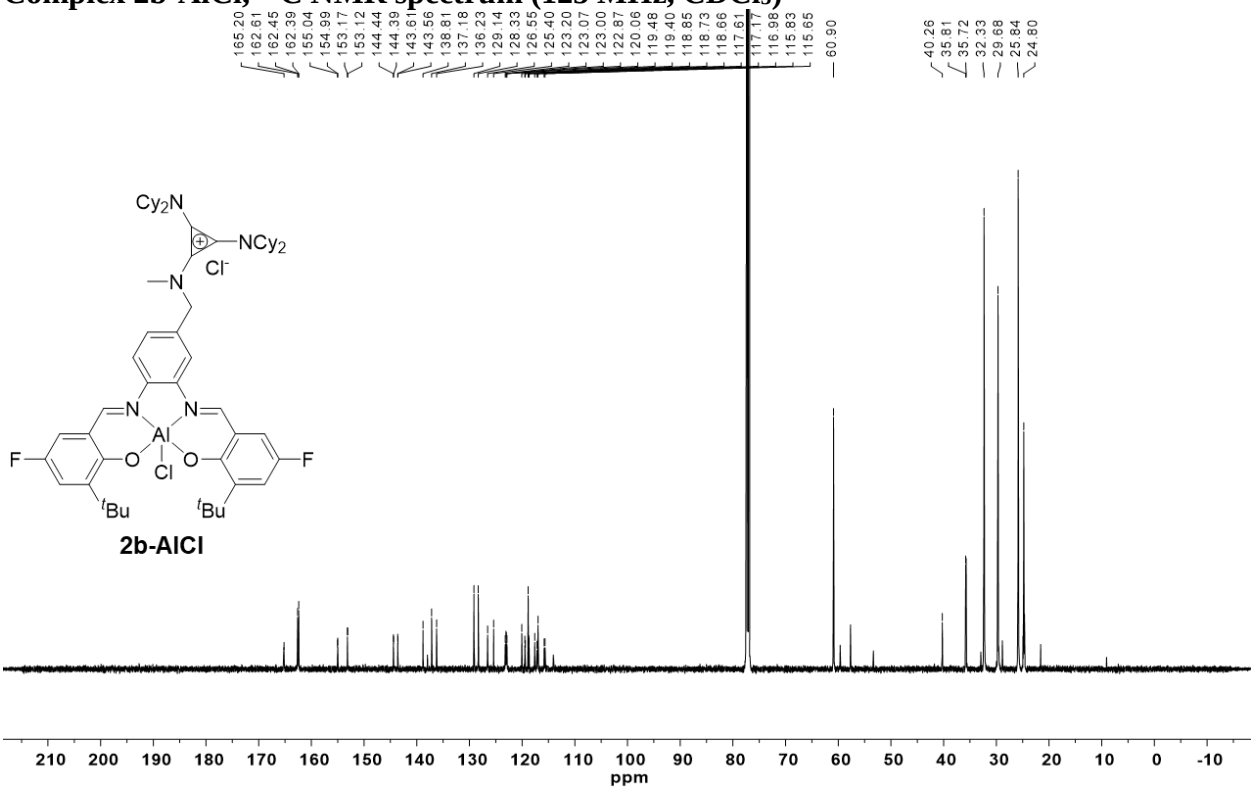
Complex 2a-AlCl, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



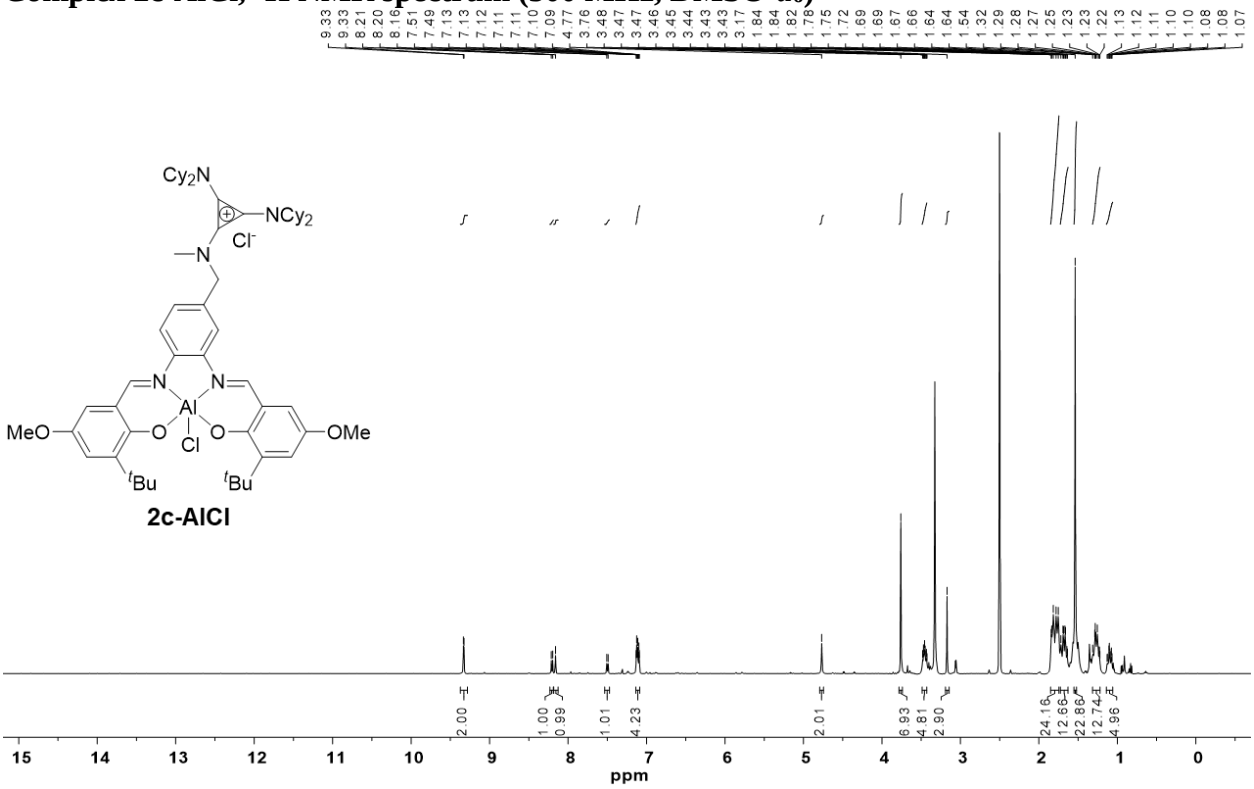
Complex 2b-AlCl, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



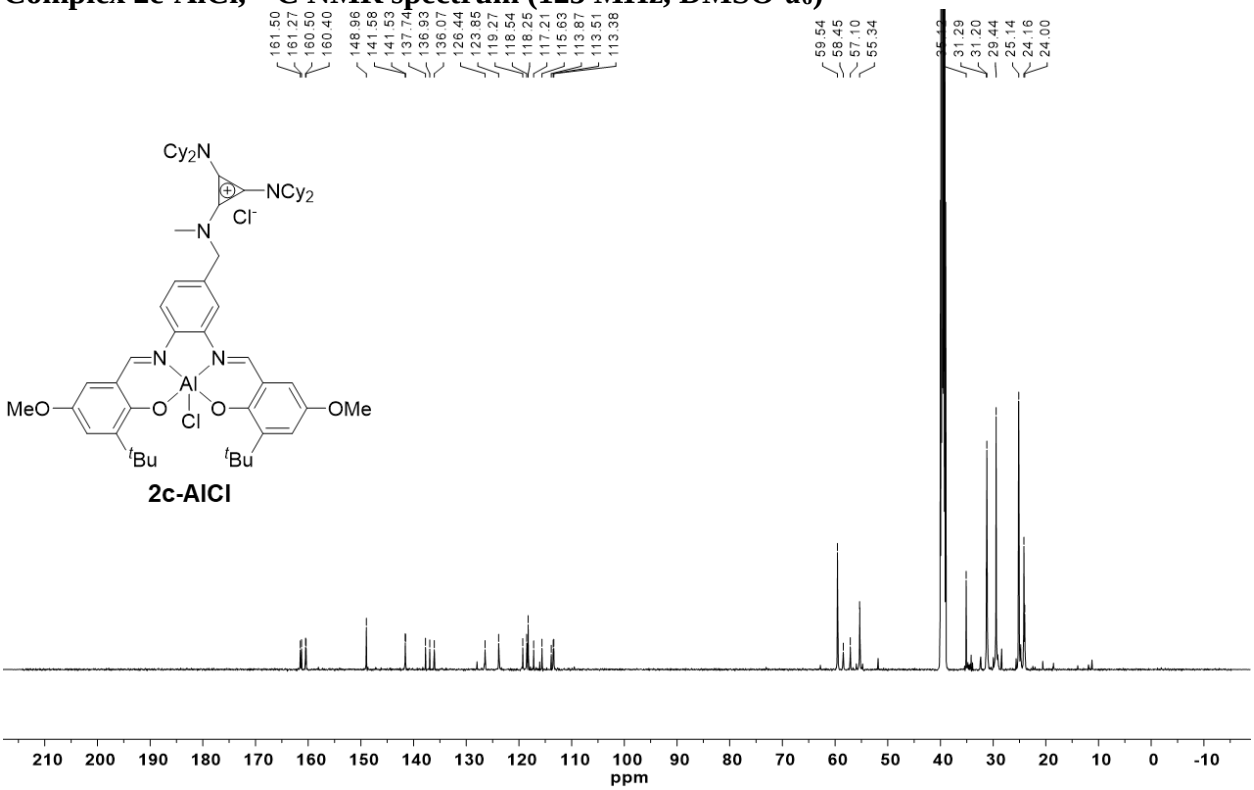
Complex 2b-AlCl, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



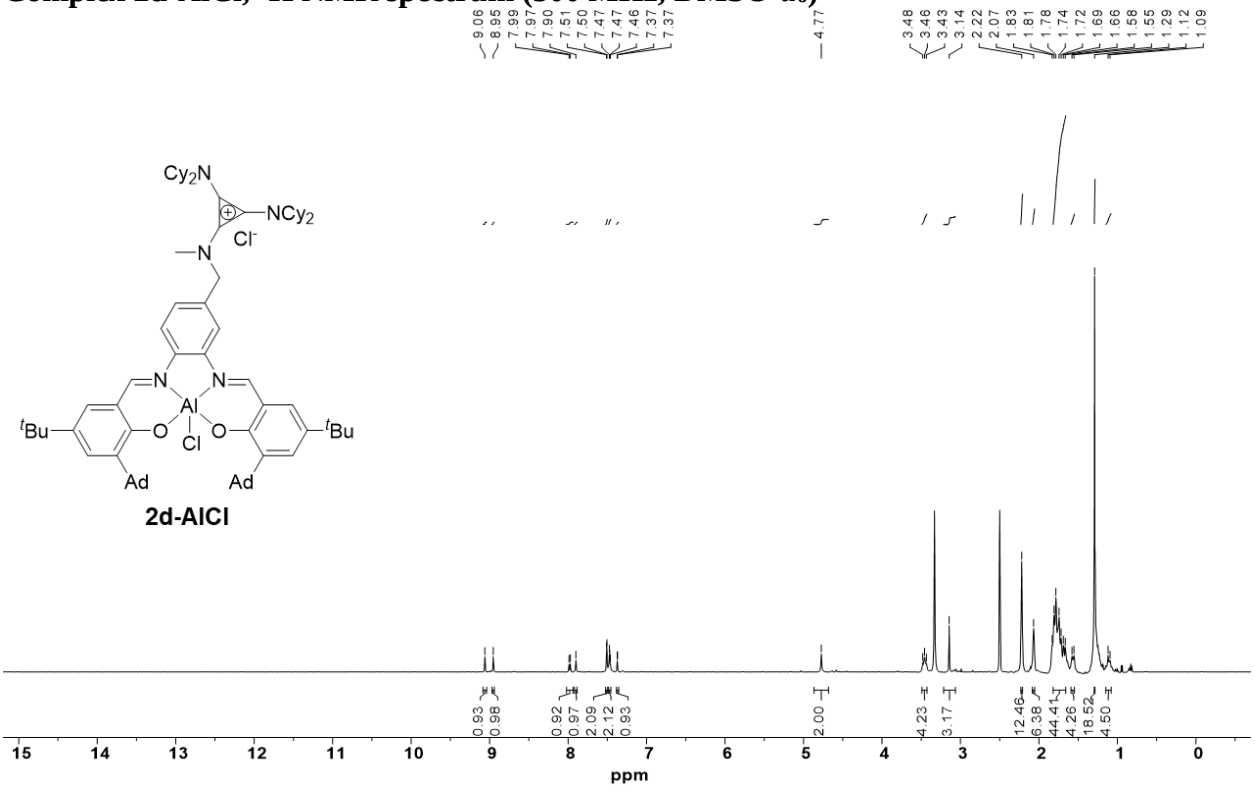
Complex 2c-AlCl, ^{1}H NMR spectrum (500 MHz, DMSO-*d*$_6$)



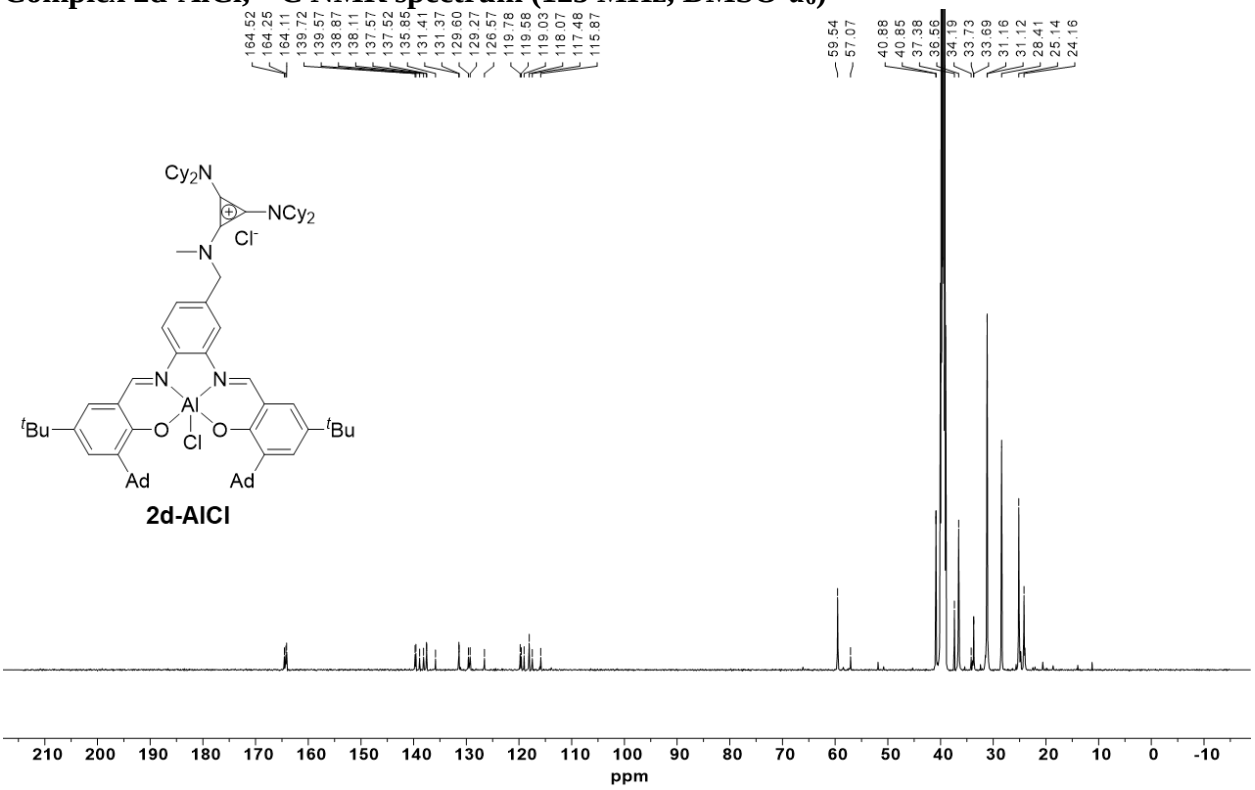
Complex 2c-AlCl, ^{13}C NMR spectrum (125 MHz, DMSO-*d*$_6$)



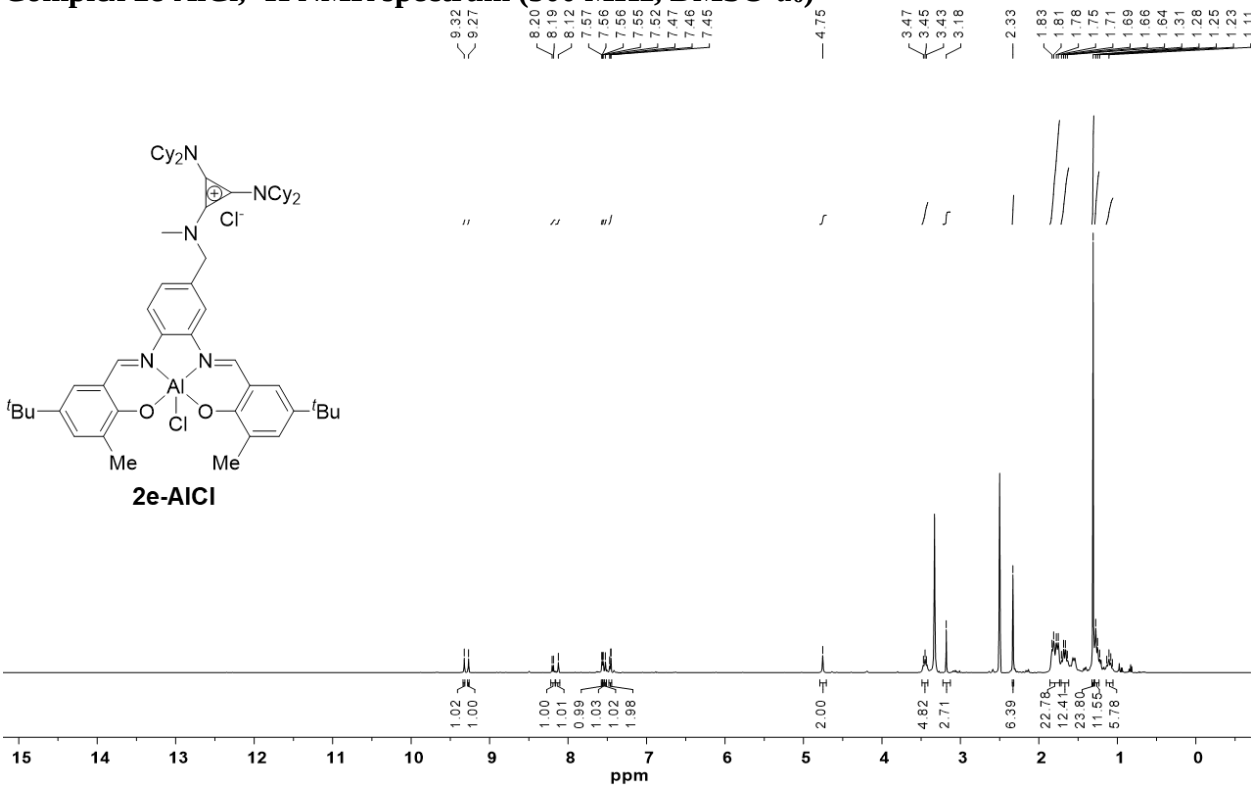
Complex 2d-AlCl, ^{1}H NMR spectrum (500 MHz, DMSO-d_6)



Complex 2d-AlCl, ^{13}C NMR spectrum (125 MHz, DMSO-d_6)

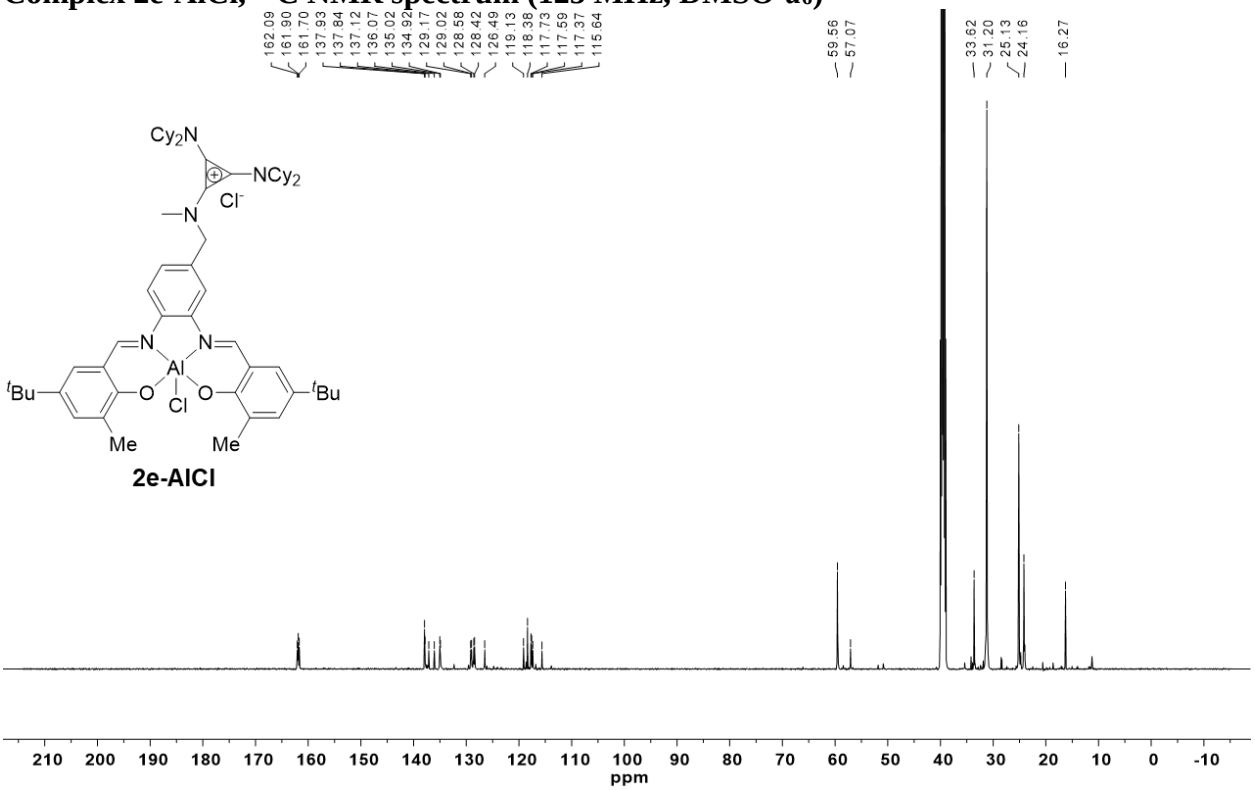


Complex 2e-AlCl, ^{1}H NMR spectrum (500 MHz, DMSO-*d*$_6$)



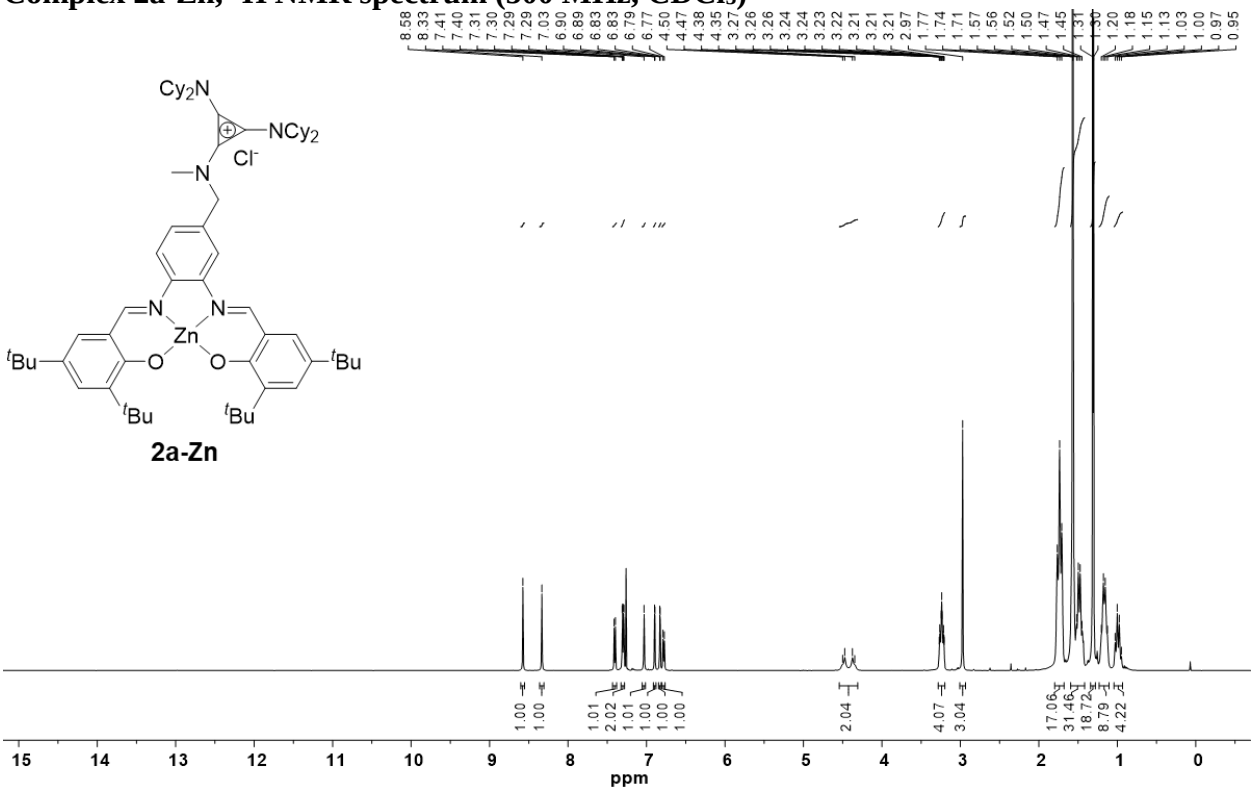
2e-AlCl

Complex 2e-AlCl, ^{13}C NMR spectrum (125 MHz, DMSO-*d*$_6$)

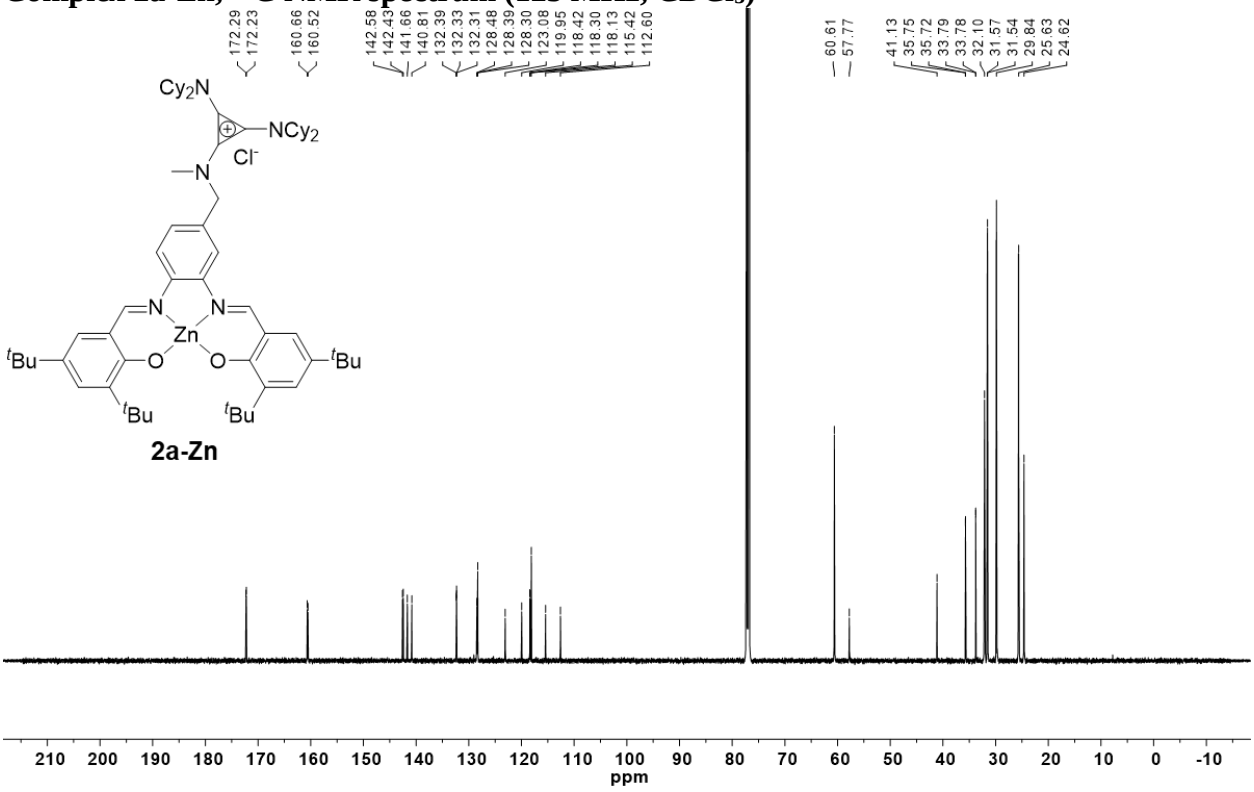


2e-AlCl

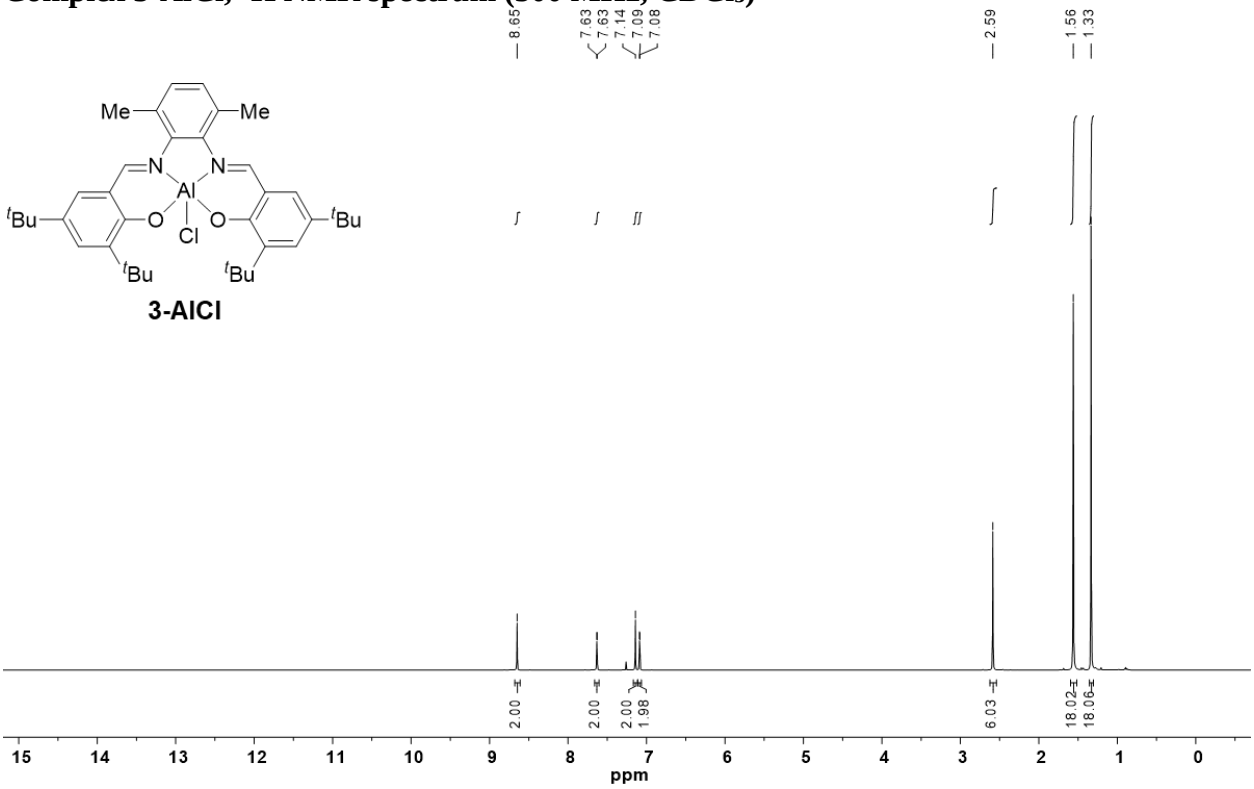
Complex 2a-Zn, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



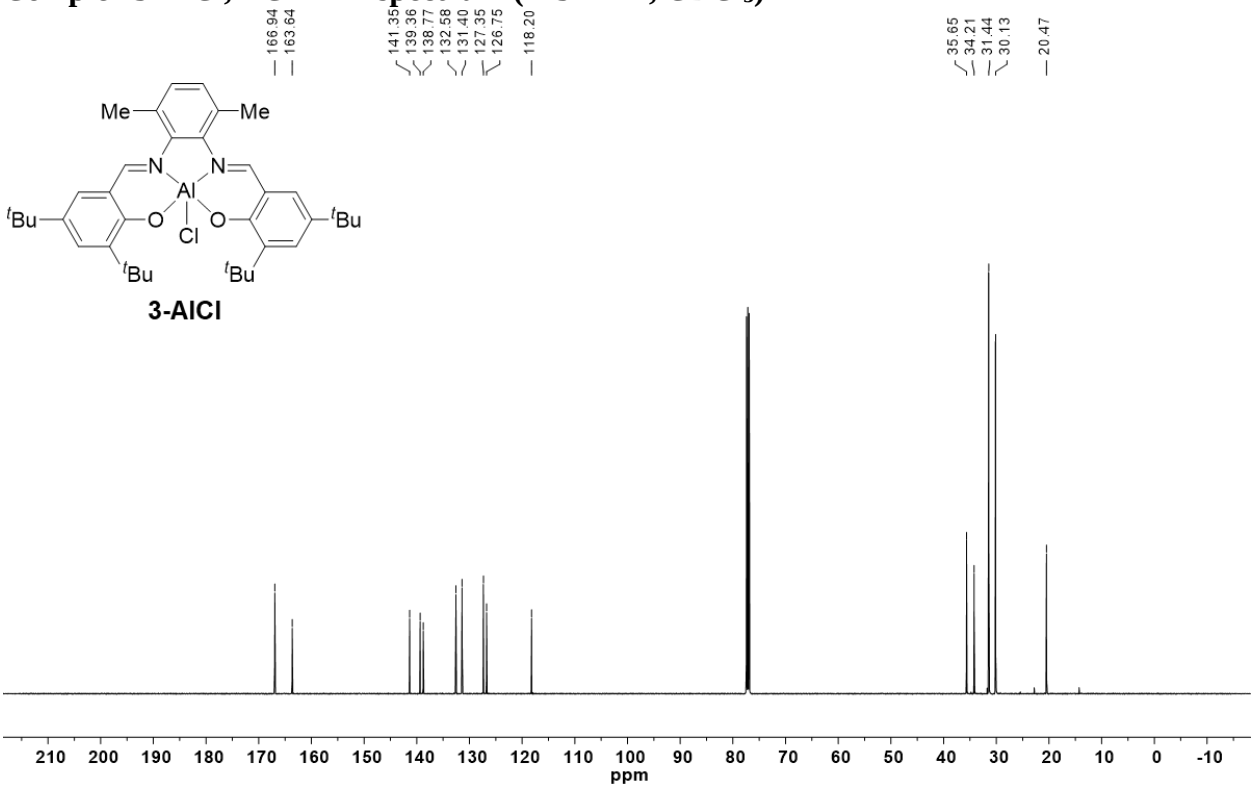
Complex 2a-Zn, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



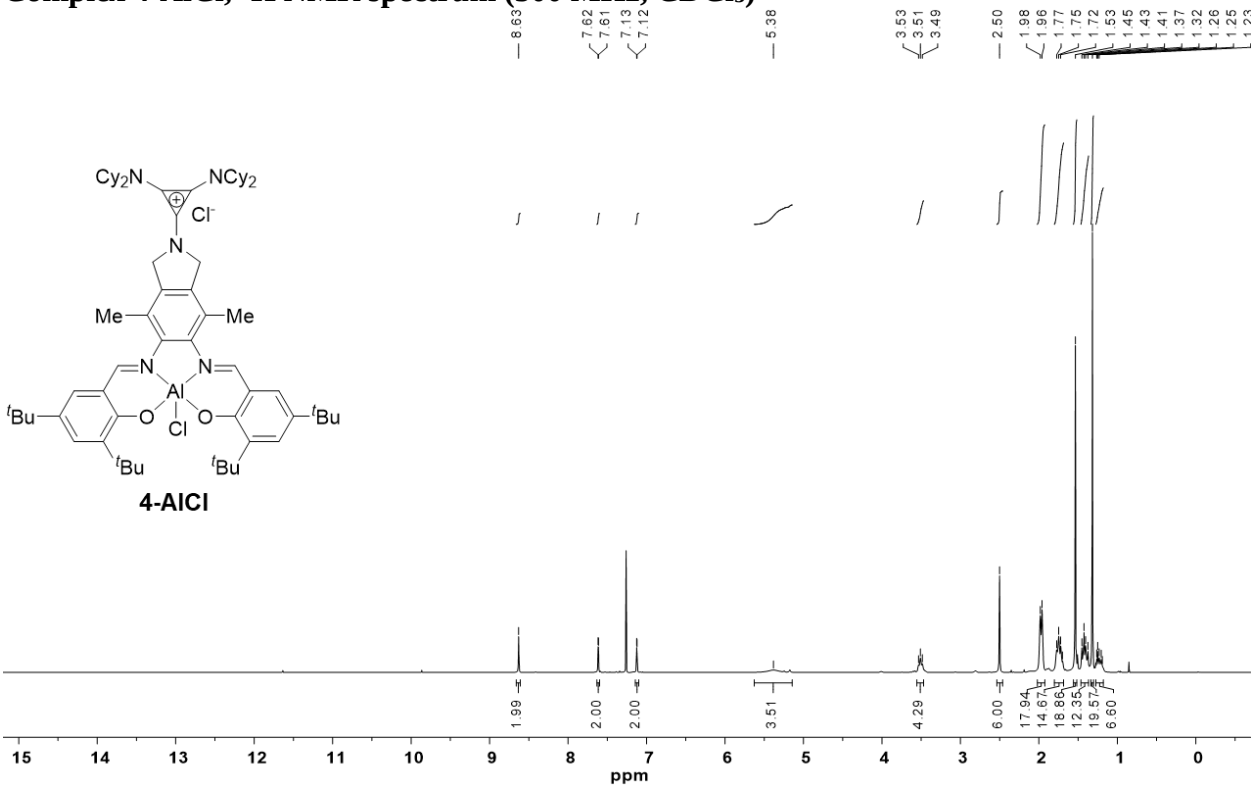
Complex 3-AlCl, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



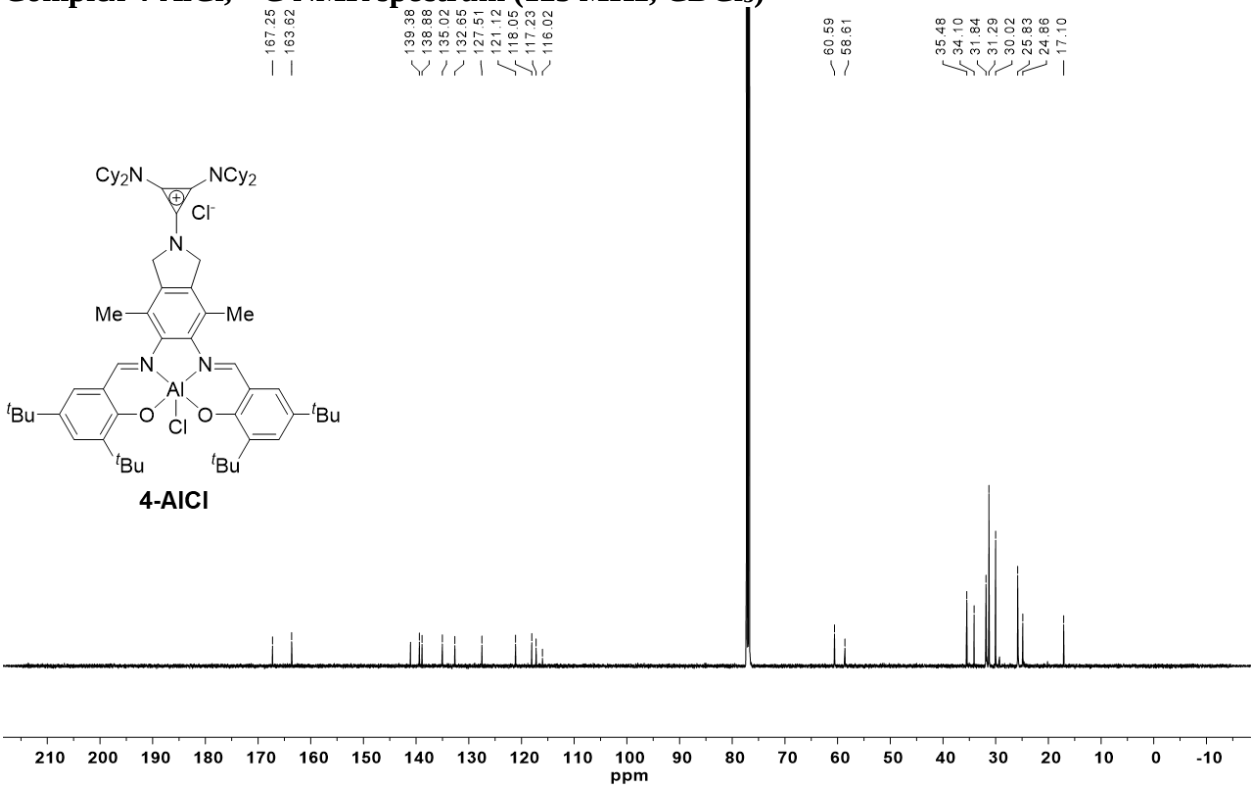
Complex 3-AlCl, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



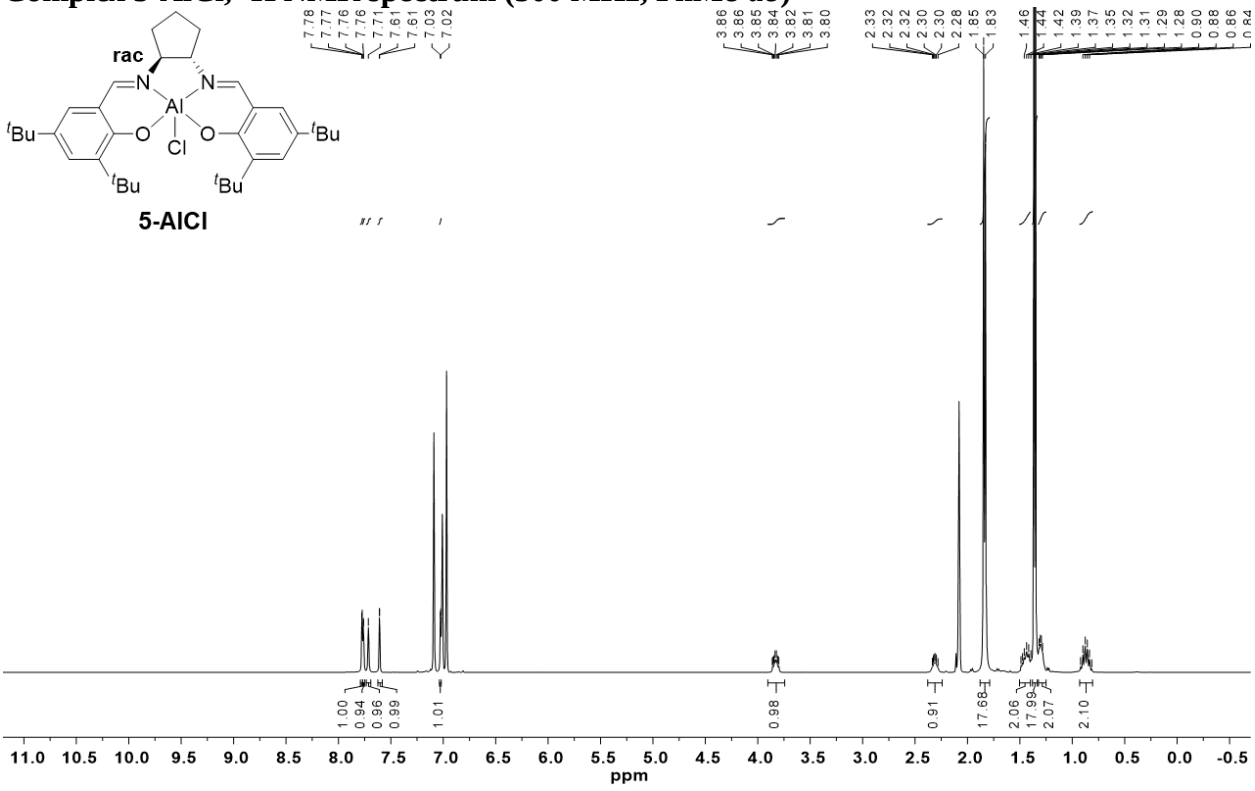
Complex 4-AlCl, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



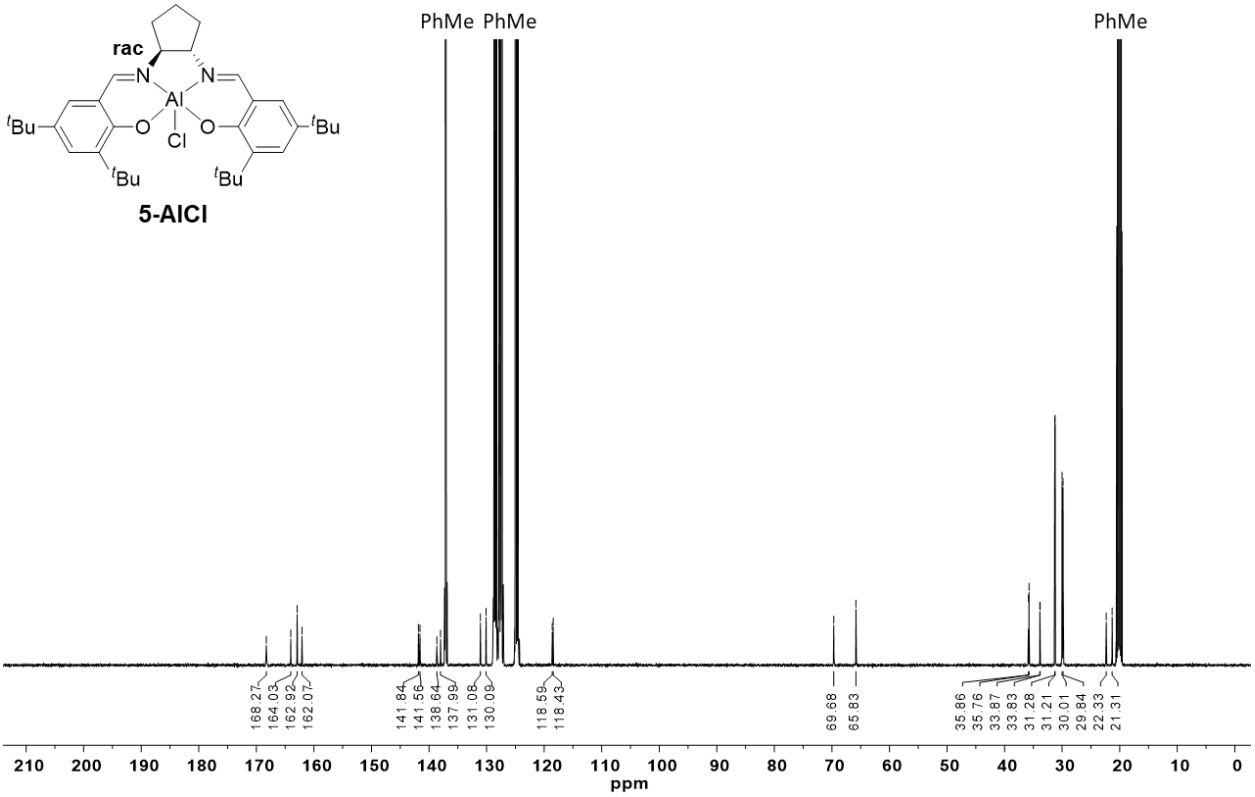
Complex 4-AlCl, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



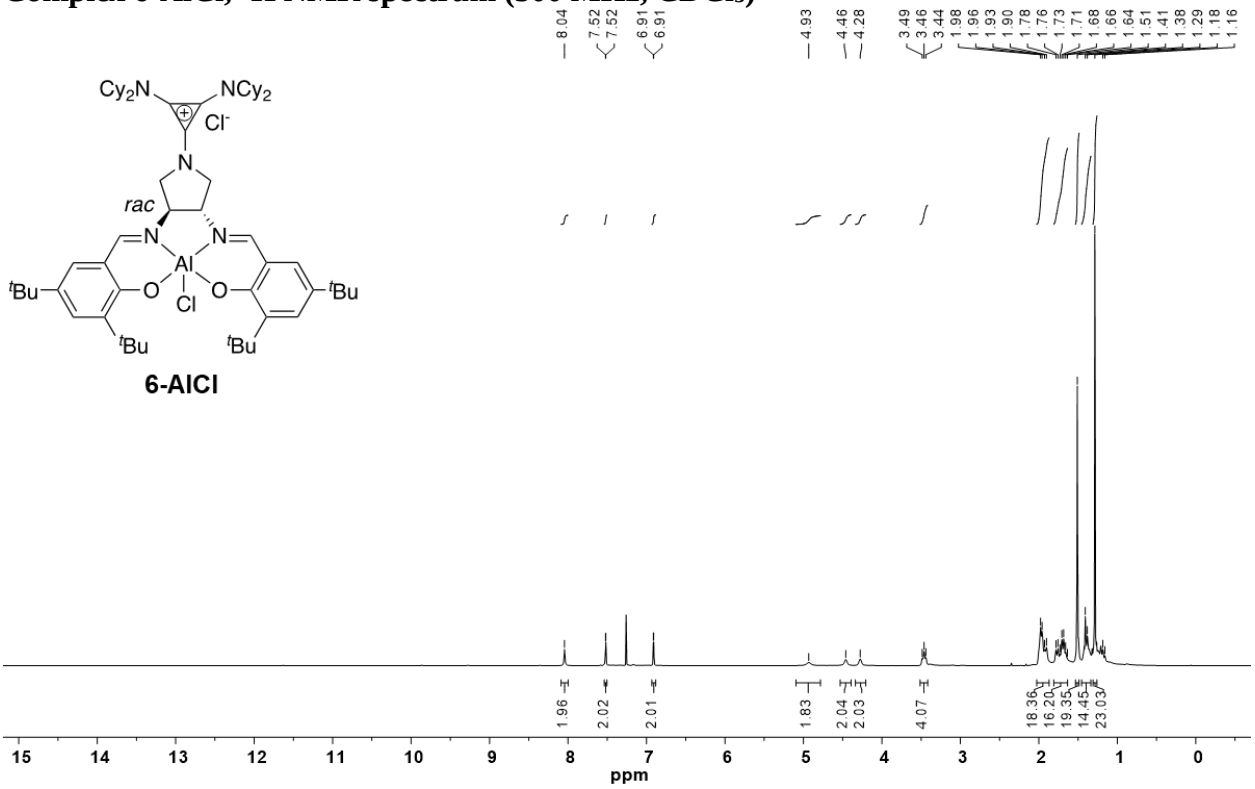
Complex 5-AlCl, ^{1}H NMR spectrum (500 MHz, PhMe-*d8*)



Complex 5-AlCl, ^{13}C NMR spectrum (125 MHz, PhMe-*d8*)

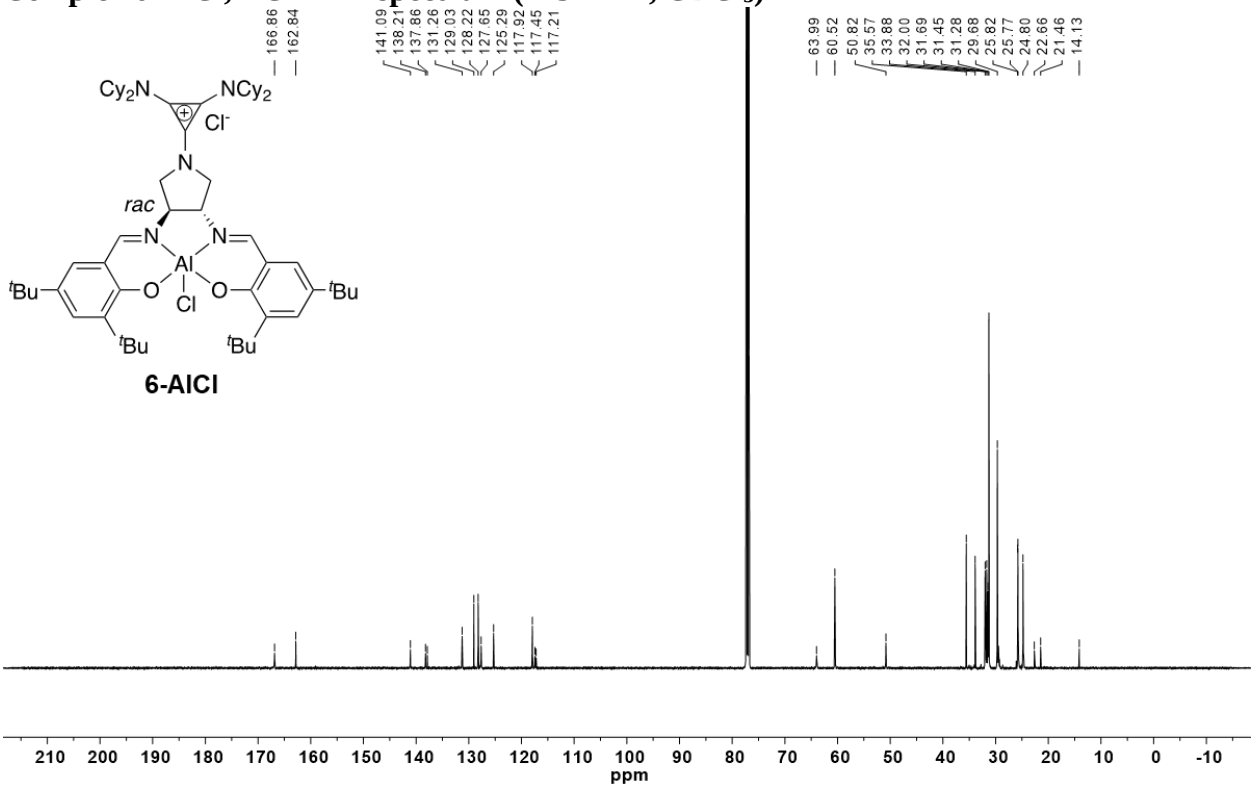


Complex 6-AlCl, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



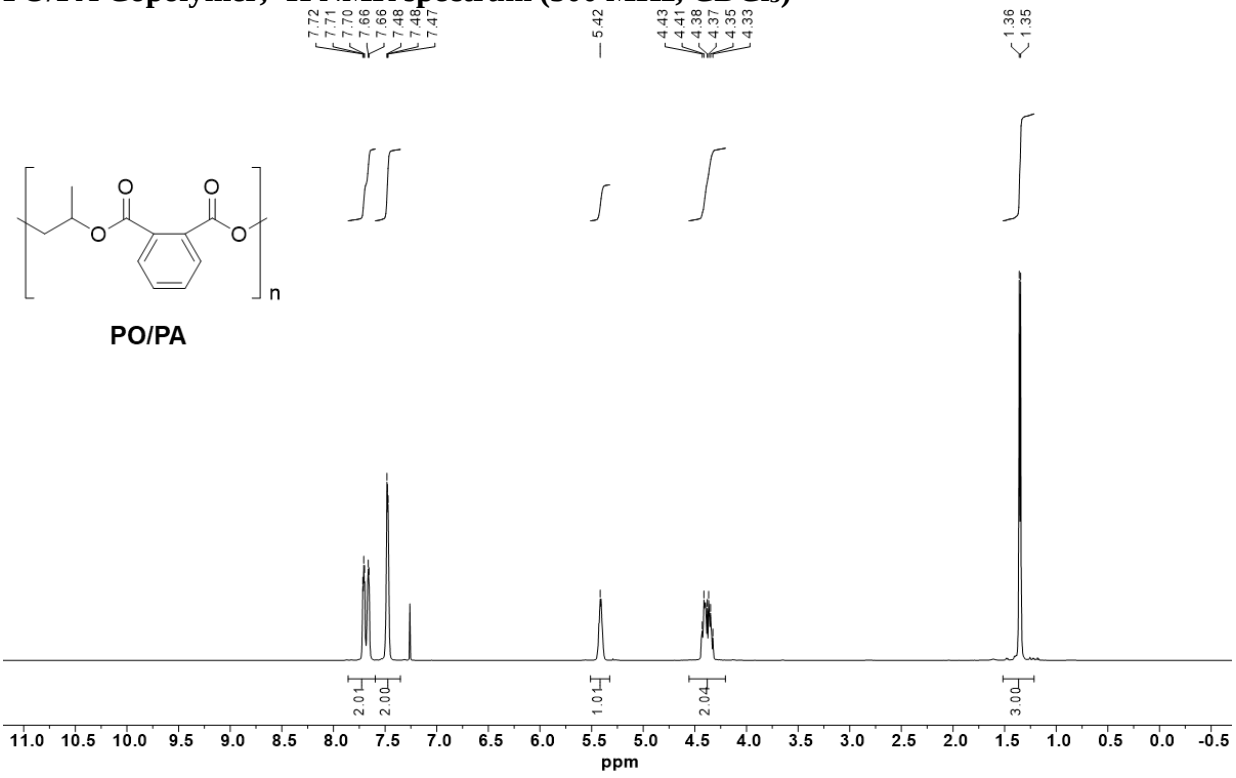
6-AlCl

Complex 6-AlCl, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)

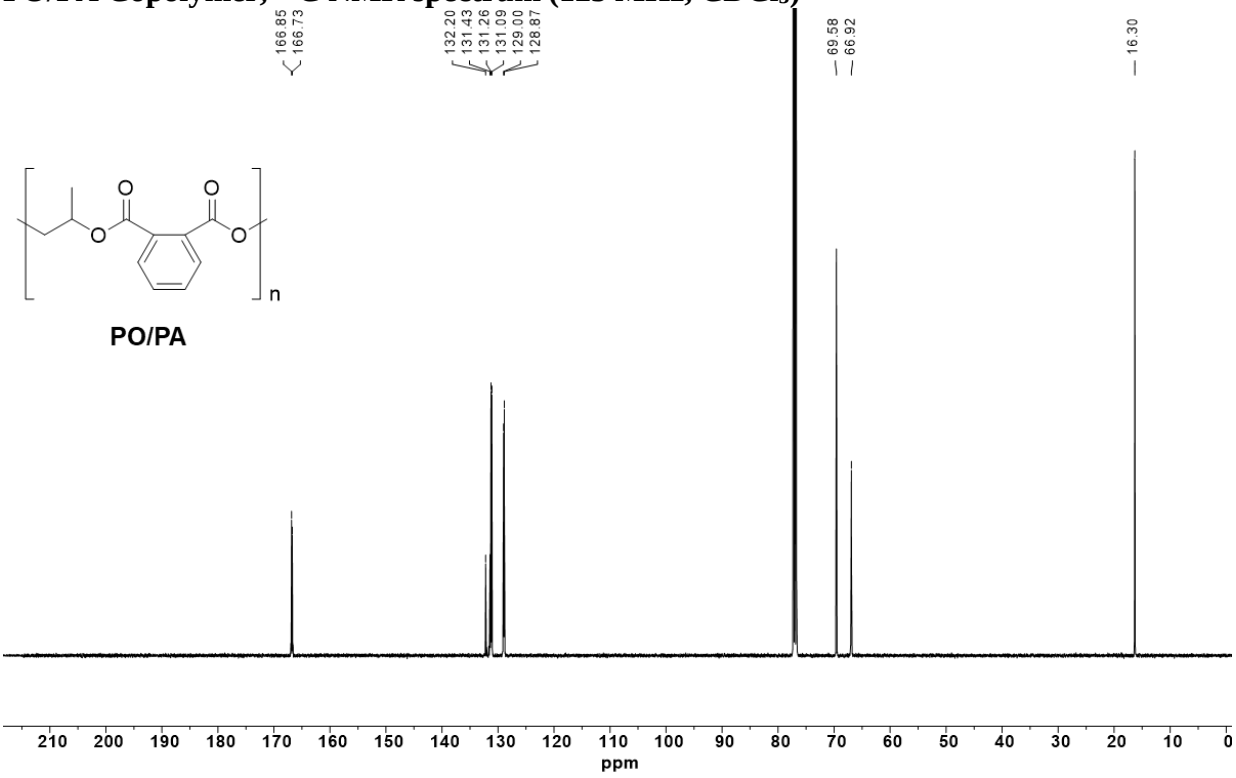


6-AlCl

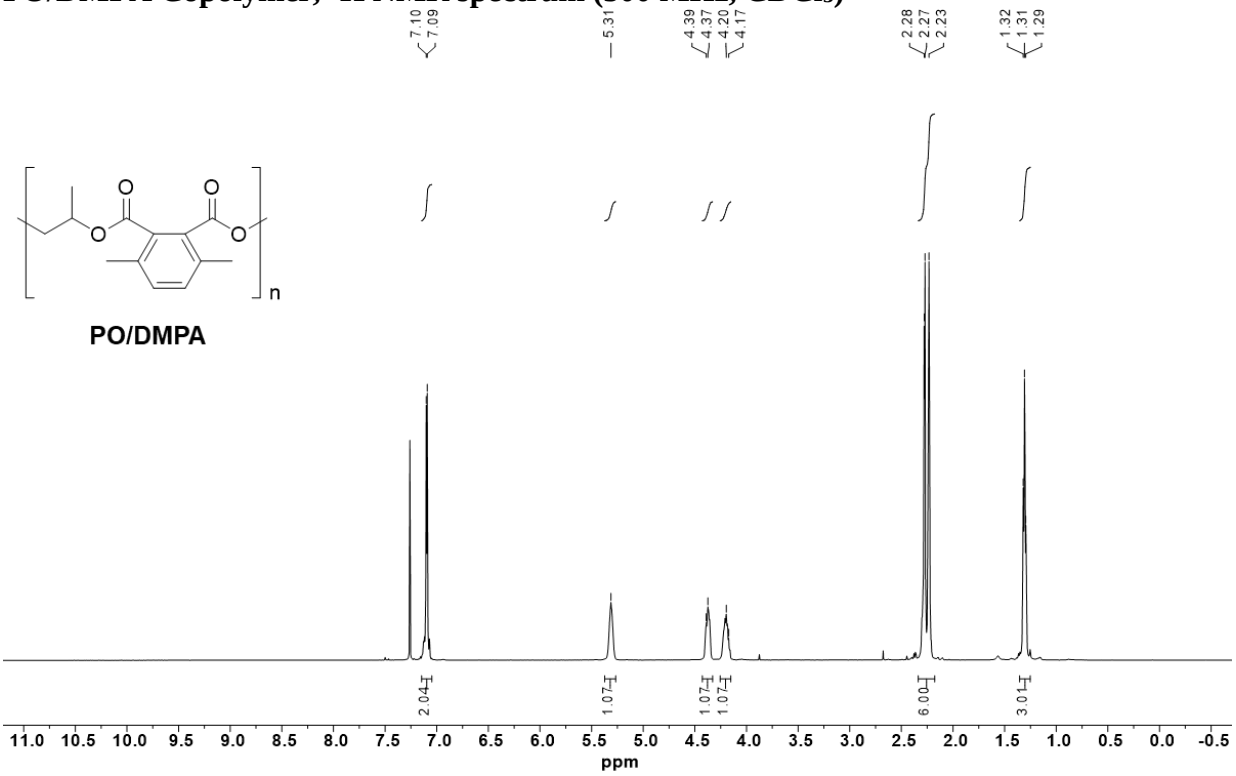
PO/PA Copolymer, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



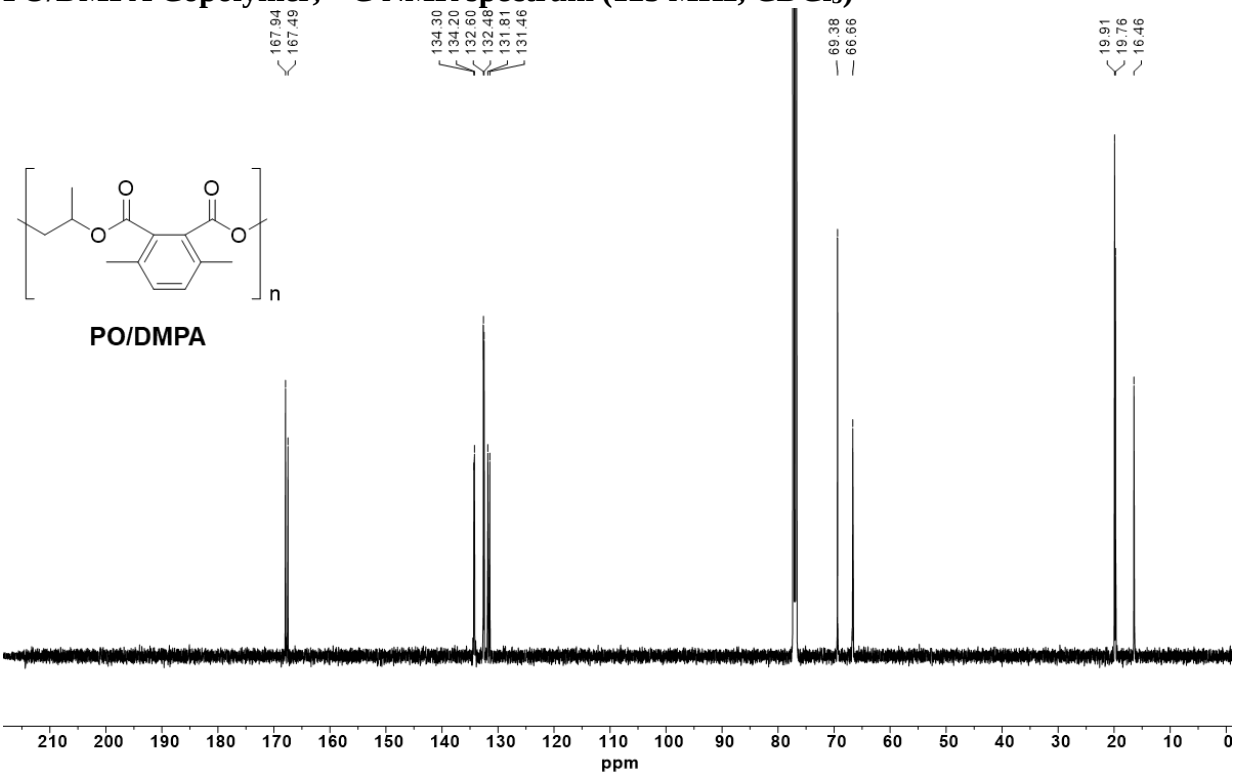
PO/PA Copolymer, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



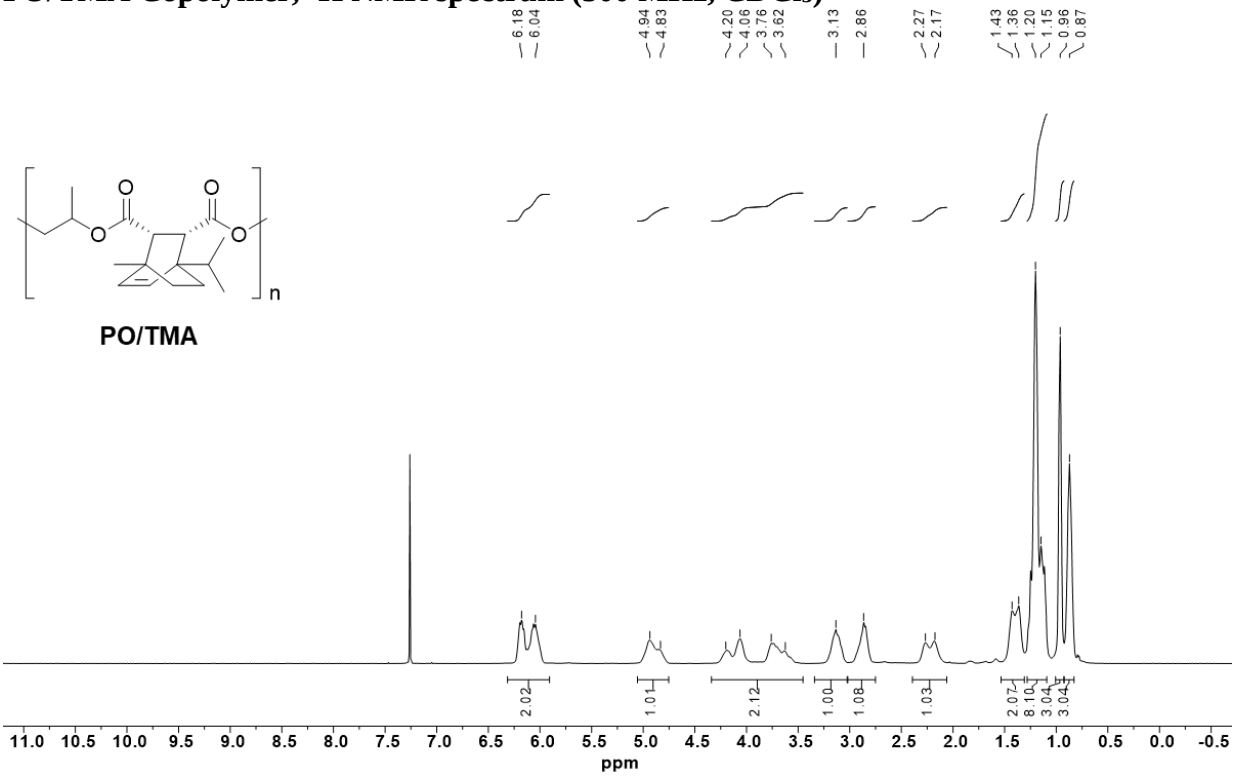
PO/DMPA Copolymer, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



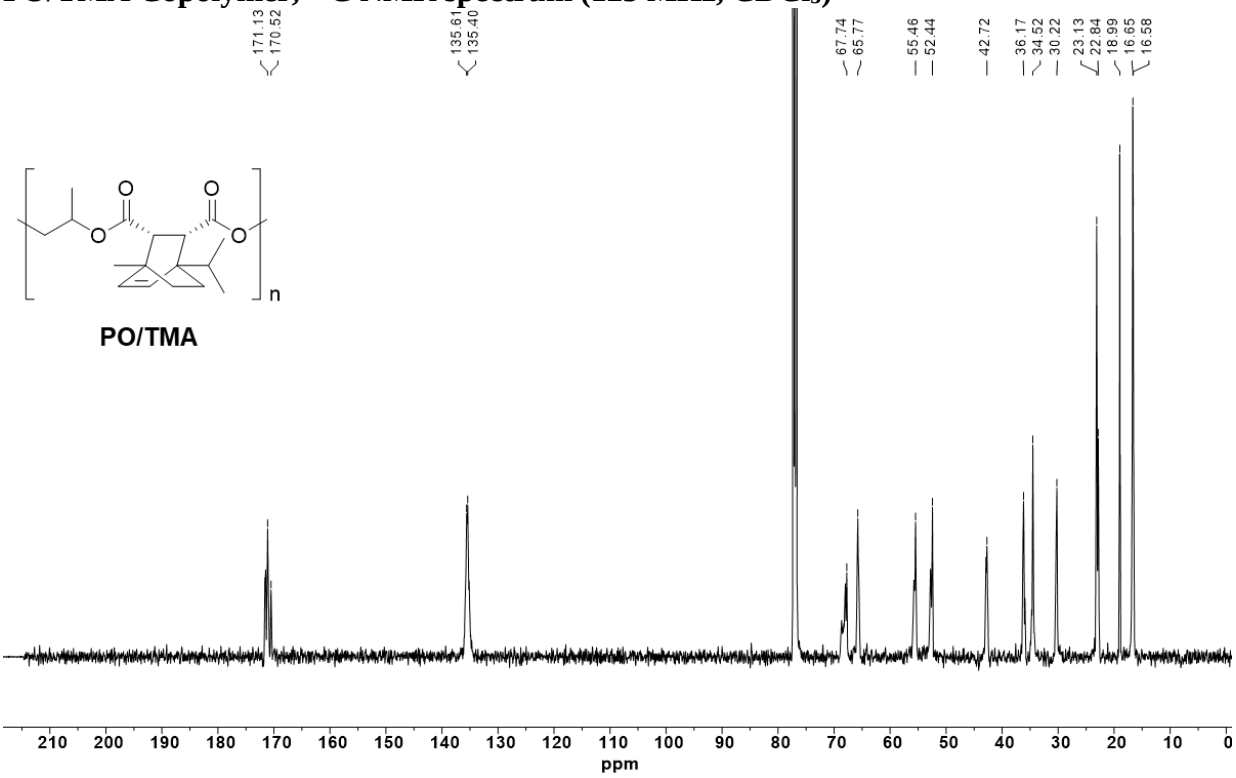
PO/DMPA Copolymer, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



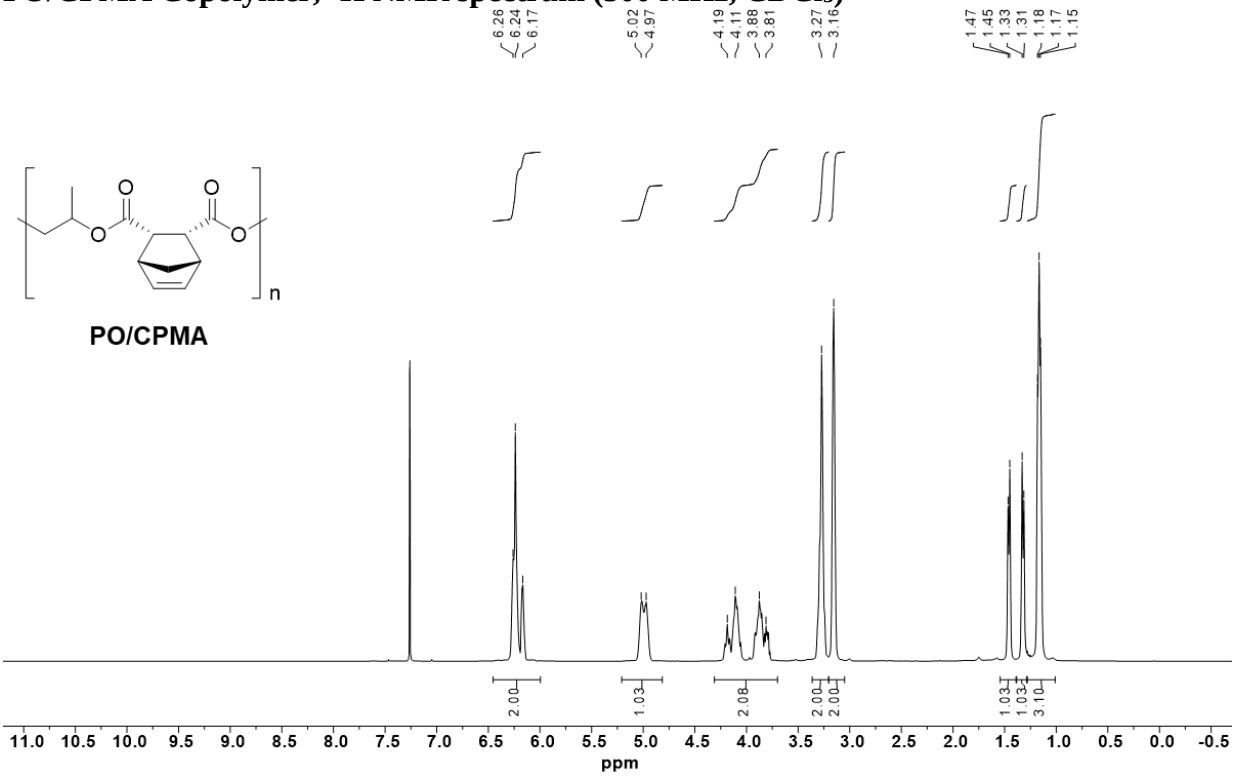
PO/TMA Copolymer, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



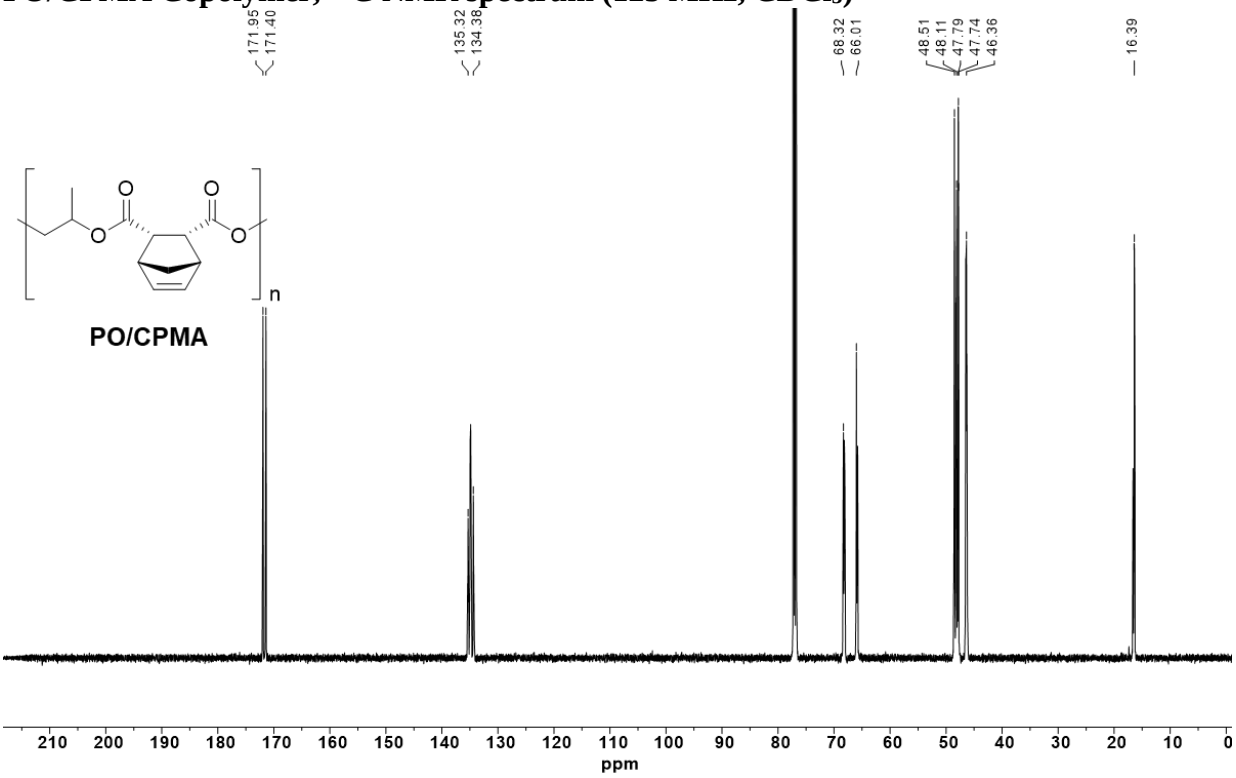
PO/TMA Copolymer, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



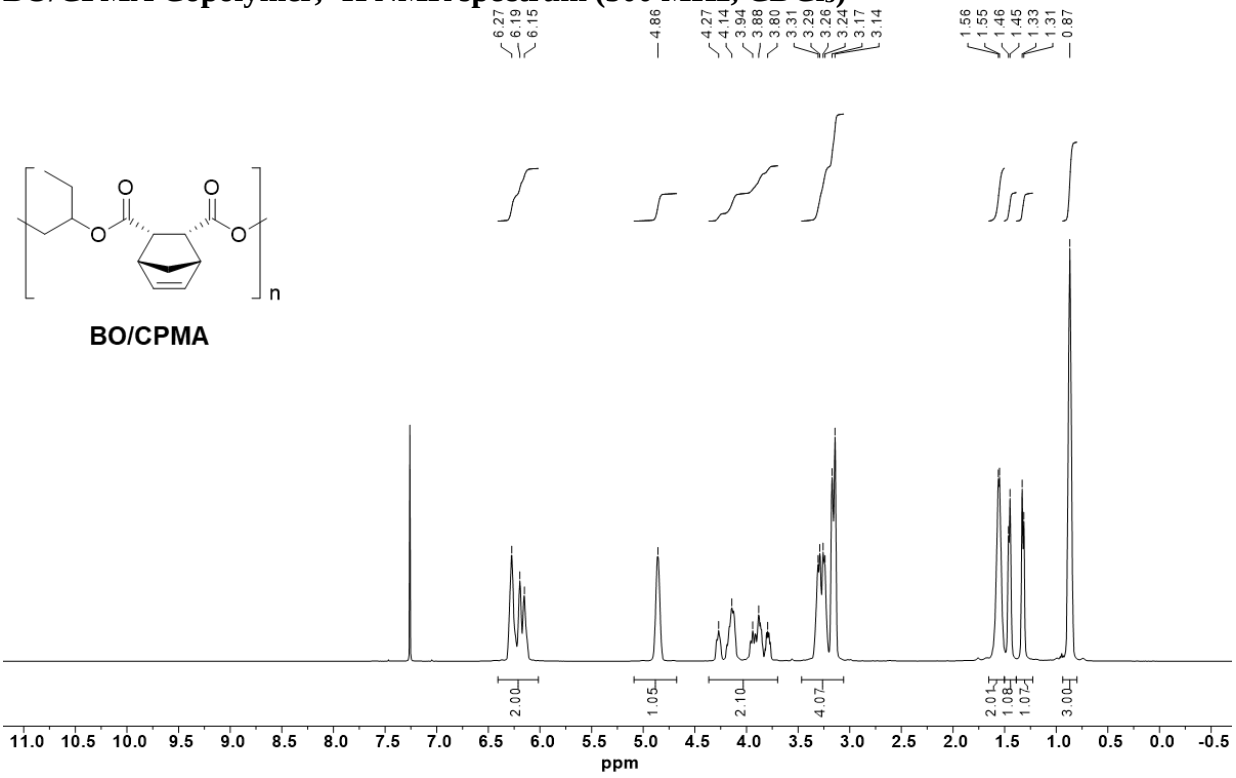
PO/CPMA Copolymer, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



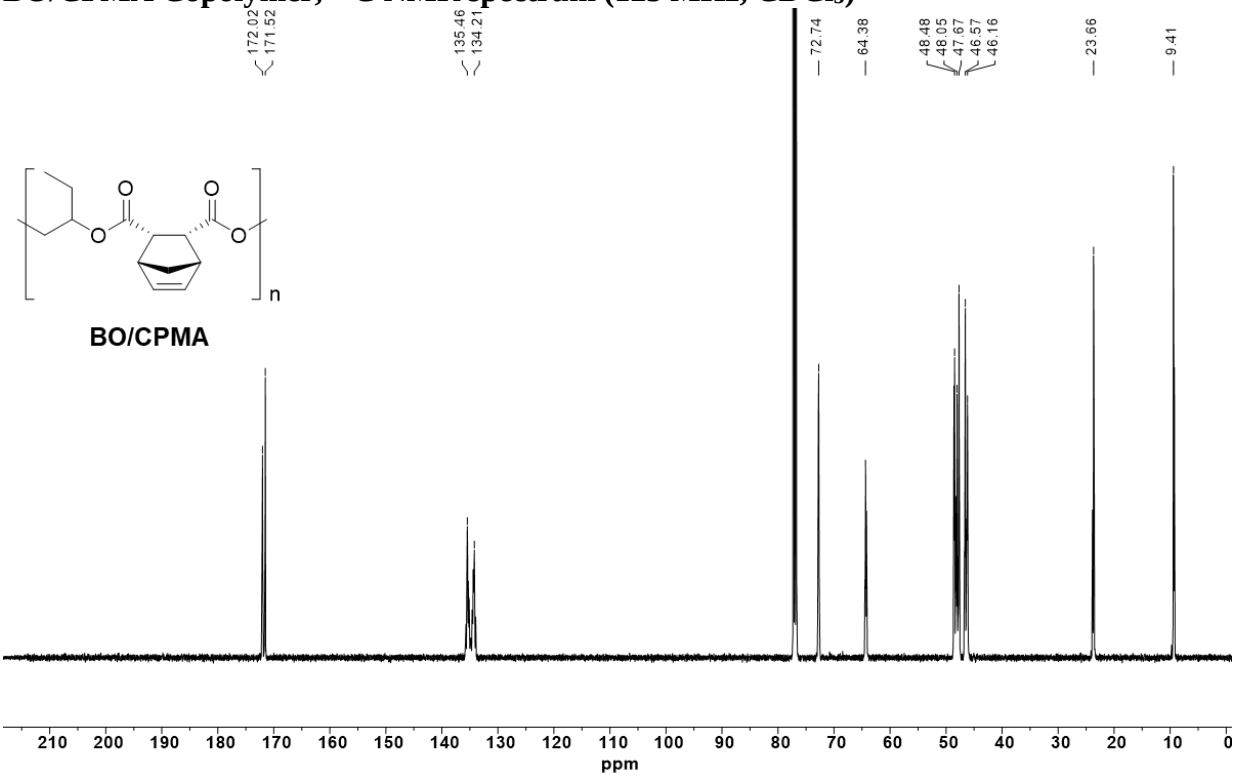
PO/CPMA Copolymer, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



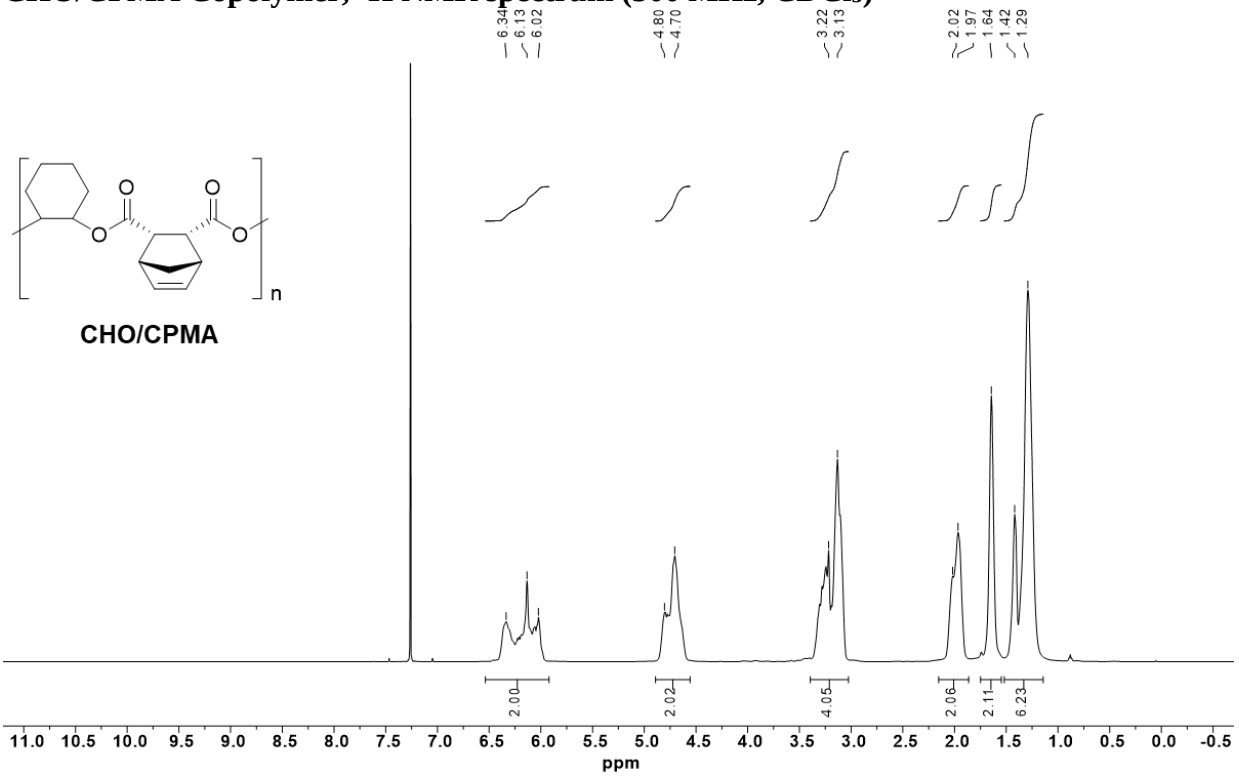
BO/CPMA Copolymer, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



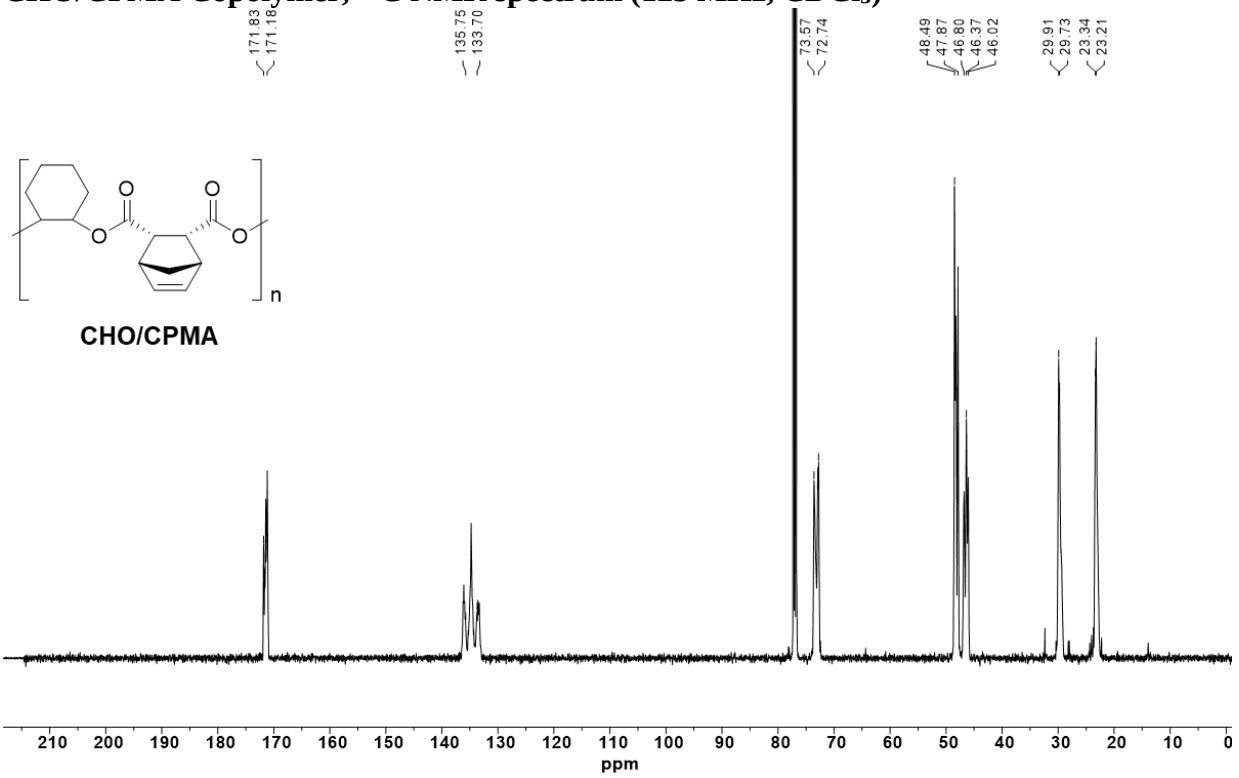
BO/CPMA Copolymer, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



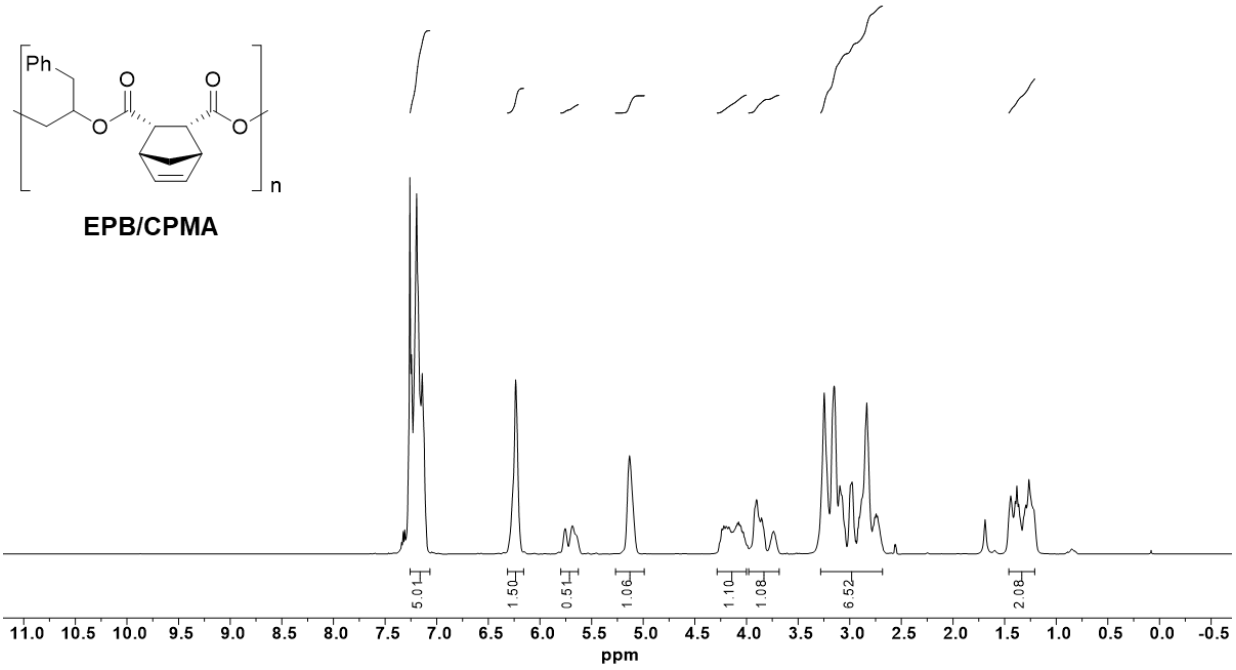
CHO/CPMA Copolymer, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



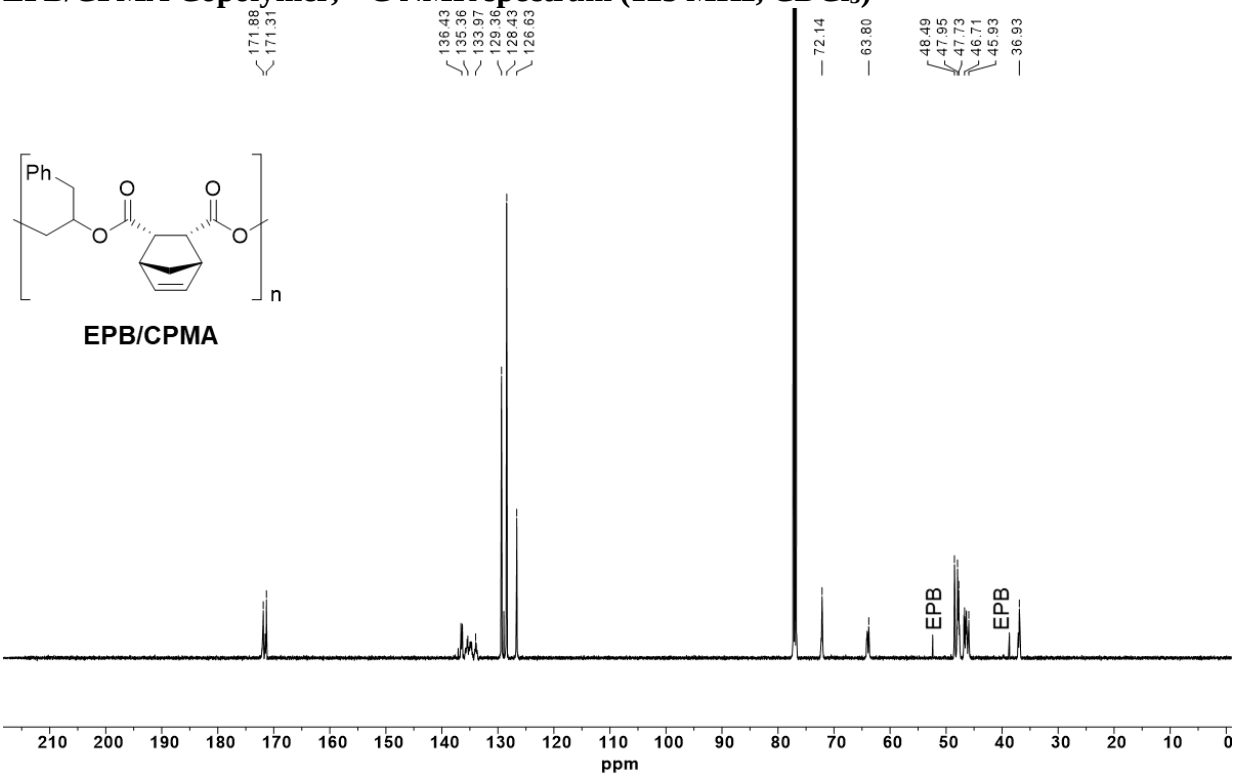
CHO/CPMA Copolymer, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



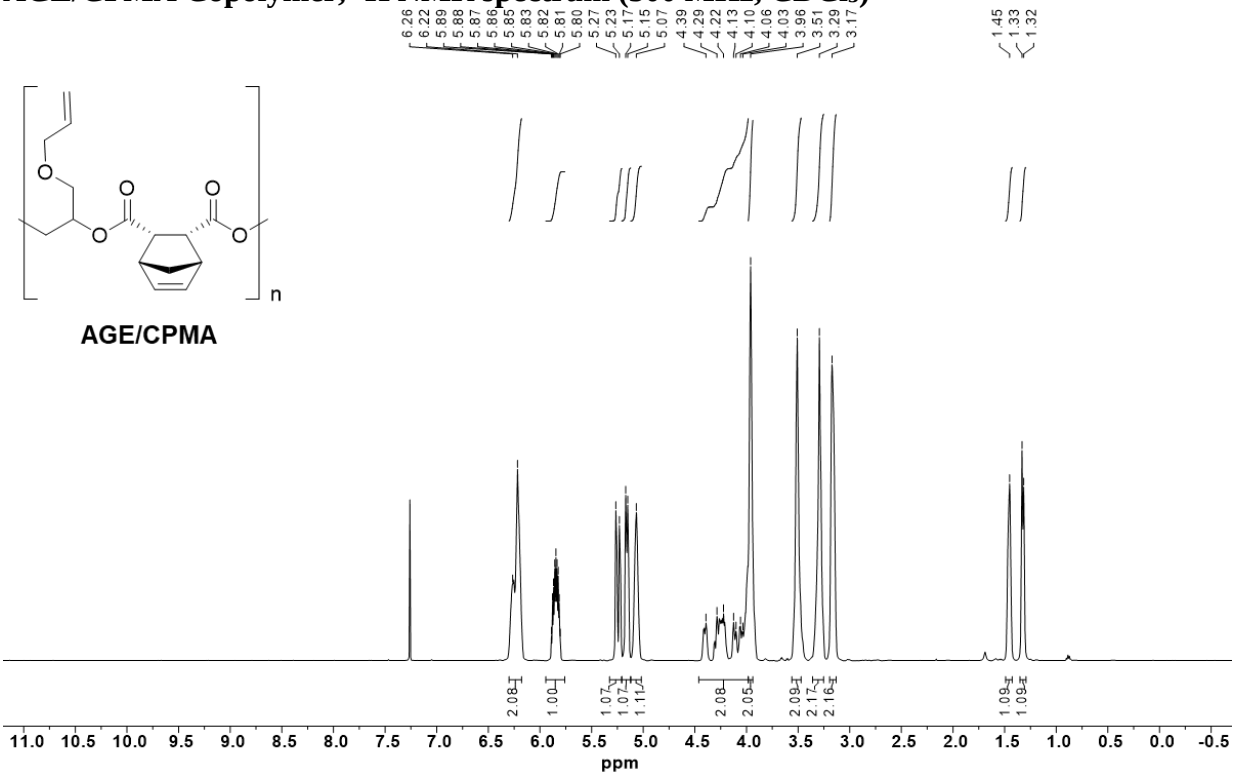
EPB/CPMA Copolymer, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



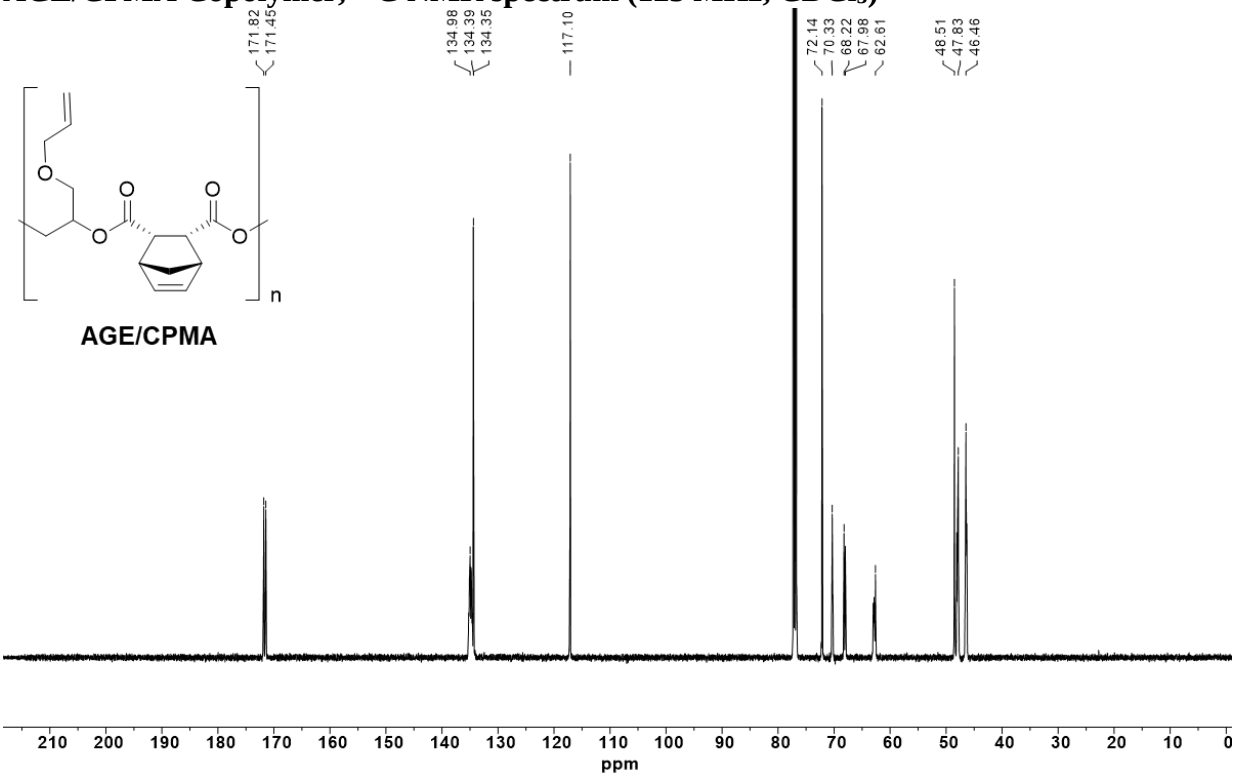
EPB/CPMA Copolymer, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



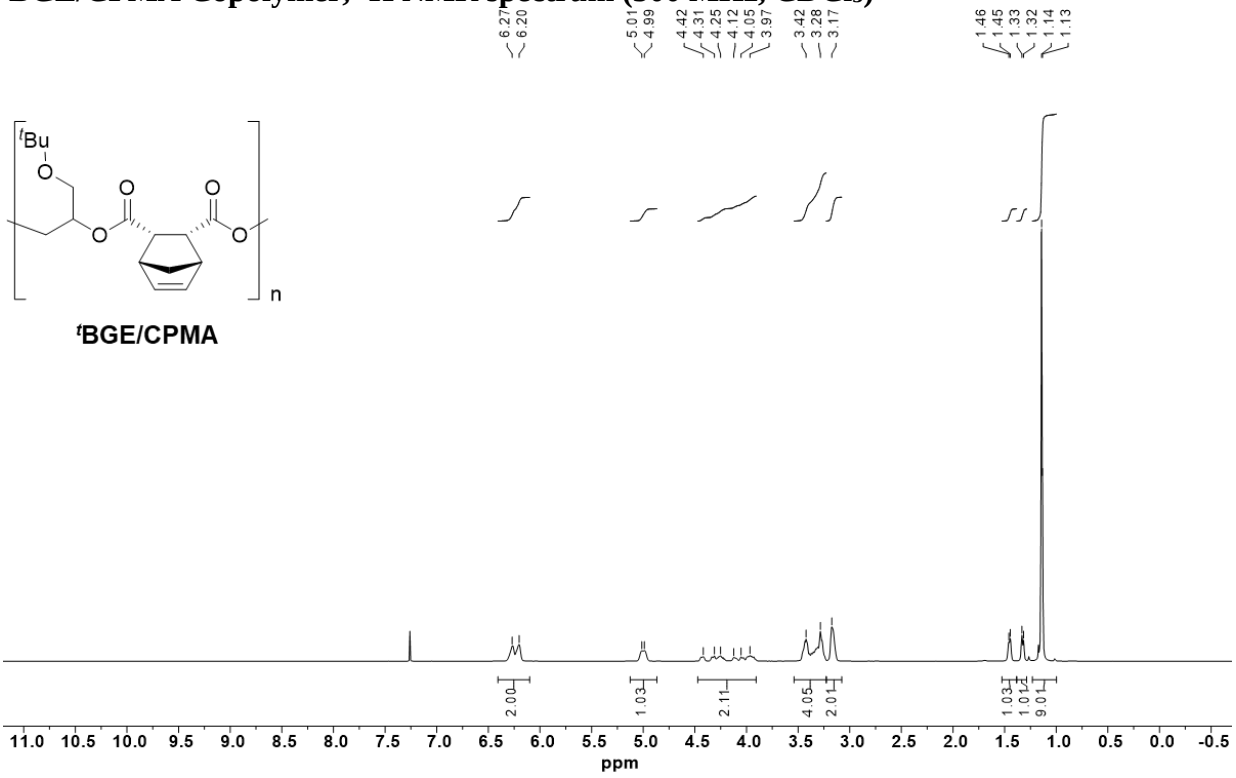
AGE/CPMA Copolymer, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



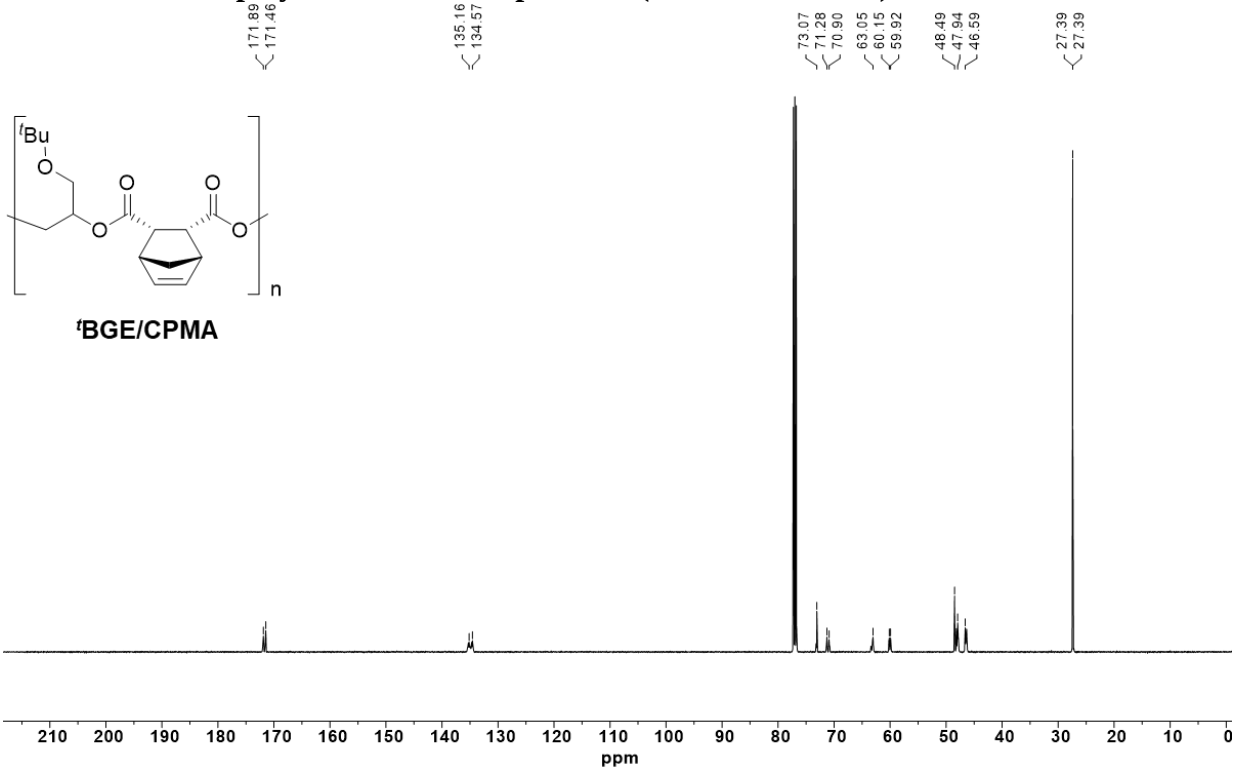
AGE/CPMA Copolymer, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



^{t}BGE/CPMA Copolymer, ^{1}H NMR spectrum (500 MHz, $CDCl_3$)



^{t}BGE /CPMA Copolymer, ^{13}C NMR spectrum (125 MHz, $CDCl_3$)



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