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Supplementary Electronic Materials

A Phase Separable Polycarbonate Polymerization Catalyst

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Reagents and Starting Materials. Acetonitrile, heptane, dimethylformamide, ethanol, dichloromethane, and toluene were purchased from EMD and used as received. All other chemicals were purchased from Sigma-Aldrich and used as received. Polyisobutylene (Glissopal) was a gift from BASF.

Instrumentation. ^{1}H NMR spectra were recorded on an Inova 500MHz spectrometer operating at 499.95 MHz or a Inova 300 MHz spectrometer operating at 299.91 MHz. ^{13}C NMR spectra were recorded on an Inova 500 MHz spectrometer operating at 125.719 MHz or a Inova 300 MHz spectrometer operating at 75.41 MHz. Chemical shifts were reported in parts per million (δ) relative to residual proton resonances in the deuterated chloroform ($CDCl_3$). Coupling constants (J values) were reported in hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). UV-Vis spectra were obtained using a Varian Cary 100 spectrometer. IR spectra were obtained using a Bruker Tensor 27 FT-IR. ICP-MS were obtained using a Perkin Elmer DRC II instrument. The polycarbonate polymerization carried out in a Parr autoclave modified with a SiComp attenuated total reflectance window to allow for *in situ* infrared measurements with an ASI®

ReactIR 1000 instrument**.** ICP-MS analyses were carried out using a Perkin Elmer DRC II instrument.

General Experimental Procedures. All reactions were carried out under an inert atmosphere unless otherwise noted. Products were isolated simply by evaporation of solvent without chromatography. The product spectra contain traces of alkane solvents, residual polyisobutylene, or water.

Synthesis of Polyisobutylene Supported Salen Cr(III) Complex

2-*tert*-Butyl-4-(polyisobutyl)phenol (5): A mixture of 15 g (1008 mmol) of 2-*tert*-butyl phenol, 8.9 g (8.9 mmol) of polyisobutylene (Glissopal® 1000), and 1.05 g (10.7 mmol) of concentrated sulfuric acid in 200 mL of dichloromethane was stirred for 3 d at room temperature. The solvent was removed under reduced pressure and then 250 mL of hexanes was added to the viscous residue. The hexanes solution was washed with 150 mL of dimethyl formamide three times, then 150 mL of 90% ethanol/water three times. The hexane phase was dried over sodium sulfate. The solvent was removed under reduced pressure resulted in light yellow viscous residue. The yield was 85%. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.8-1.8 (m, 140H), 1.8 (s, 2H), 6.6 (d, J = 7.75, 1H), 7.05 (dd, J = 5.69, 1H), and 7.3 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$), δ: 151.83, 142.07, 135.04, 125.42, 124.53, 115.91, multiple peaks were present between 58 – 60 and 22-39.

2-Hydroxy-5-(polyisobutyl)benzaldehyde (6). A mixture of 3.42 g (2.97 mmol) of **5** and 0.58 mL (5 mmol) of 2,6-lutidine in 40 mL of toluene was stirred under room temperature for 30 min. A solution of $SnCl_4$ (0.15 mL, 1.25 mmol) in 10 mL of toluene was added slowly to the reaction. The reaction was then stirred under room temperature for 1 h at which point 0.56 g (18.78 mmol) of paraformaldehyde was added to reaction. The reaction was heated for 12 h at 100 °C. After the reaction mixture cooled to room temperature, it was acidified to pH 2.0 with

2M HCl. The organic layer was separated, the solvent was removed under reduced pressure, and then 250 mL of hexanes was added to the viscous residue. The hexanes solution was washed first with 150 mL of dimethyl formamide three times and then with 150 mL of 90% ethanol/water three times. The hexane phase was dried over sodium sulfate. The solvent was removed under reduced pressure to yield a light yellow viscous residue. The yield was 76%. ^{1}H NMR (500 MHz, $CDCl_3$), δ: 0.8-1.8 (m, 140H), 1.8 (s, 2H), 6.94 (d, *J* = 8.54 Hz, 1H), 7.48 (m, 1H), 7.57 (dd, *J* = 2.44, 8.54 Hz, 1H), 9.9 (s, 1H), and 10.88 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$), δ:197.55, 159.30, 140.89, 137.40, 133.20, 128.74, 120.19, multiple peaks were present between 58 – 60 and 22-39.

PIB supported salen(ethylene diamine) (7). A mixture of 3.0 g (2.6 mmol) of **6**, 0.08 g (1.3 mmol) of ethylenediamine, and catalytic amount of PTSA in 30 mL of toluene was refluxed overnight with a Dean-Stark trap. The solvent was removed under reduced pressure and then 150 mL of hexanes was added to the viscous residue. The hexane solution was washed with 100 mL of dimethyl formamide three times, then 100 mL of 90% ethanol/water three times. The hexane phase was dried over sodium sulfate. The solvent was removed under reduced pressure resulted in yellow viscous residue. The yield was 99%. ^{1}H NMR (300 MHz, $CDCl_3$), δ: 0.8-1.8 (m, 280H), 3.95 (s, 4H), 7.05 (d, *J* = 2.20, 1H), 7.40 (d, *J* = 2.20, 1H), and 8.43 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$), δ: 168.10, 158.20, 139.80, 136.50, 128.40, 127.70, 118.20, multiple peaks were present between 58 – 60 and 22-39.

PIB supported salen Cr(III) complex (8). A mixture of 6.62 g (2.78 mmol) of **7** and 0.378 g (3.07 mmol) of $CrCl_2$ in 30 mL of THF was put under N_2 atmosphere. The reaction was stirred under room temperature for 24 h and then 24 h in air. The solvent was removed under reduced pressure and then 150 mL of hexane was added to the viscous residue. The hexane solution was washed with a solution of NH_4Cl three times, and then washed with 100 mL of brine. The hexane phase was dried over sodium sulfate. The solvent was removed under reduced pressure resulted in dark brown viscous residue. The yield was 65%. IR (neat): cm^{-1} 1625 (m), 1535 (s), 1467 (s), 1394 (s), 1364 (s), and 1235 (m). UV-visible spectroscopy (λ_{max} = 350 nm, ε = 4514 $M^{-1}cm^{-1}$). Elemental analysis showed the product polymer had 82.39% C, 13.51% H, and 1.06% N. A separate experiment where the catalyst was digested and the residue analyzed by ICP-MS for Cr showed 1.45% Cr. If the polyisobutylene has a degree of polymerization of 20 and were monodisperse, the product would have 81.61% C, 12.94% H, 1.03% N and 1.92% Cr.

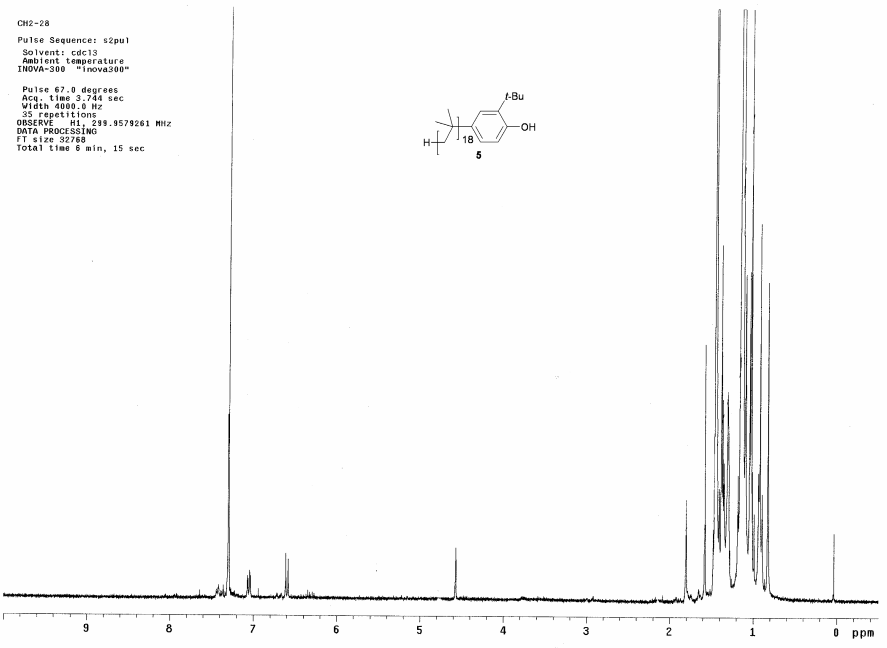
Polymerization of cyclohexene oxide and carbon dioxide using salen Cr(III) complexes 8 or 2. A typical procedure using catalyst **8** began by placing 210 mg (approx. 0.085 mmol) of catalyst **8** and 37 mg (0.064 mmol) of PPNCl (PPNCl = bis(triphenylphosphoranylidene)ammonium chloride) into a glass vial in a controlled atmosphere glove box and sealing the vial with a septum. The catalyst/cocatalyst mixture was then dissolved in 20 mL of CH_2Cl_2 and stirred for 30 minutes. After removal of the solvent via vacuum, the activated catalyst was dissolved in 10 mL of cyclohexene oxide. The catalyst solution was then loaded via cannula into a 300-mL Parr reactor that had been previously dried via heating overnight at 80 °C. The vial was rinsed with an additional 10 mL of cyclohexene oxide which was added to the reactor. The reaction vessel was pressurized to 35 bar CO_2 and heated to 80 °C for 4 h. Upon completion of the reaction, the vessel was cooled to room temperature and the CO_2 vented. The resulting polymer solution was dissolved in CH_3CN (for biphasic separation with **8**) or CH_2Cl_2 (for acidified methanol workup with **2**) depending on the chosen method of isolation of the polymer product and the catalyst used. In the case of **8**, approximately 1 mL of concentrated HCl was added to the CH_3CN solution of the product and the resulting mixture was stirred for 3 h. The solution was then concentrated at reduced pressure and the residue was added slowly to excess heptane to yield the white powdery polymer product shown in Figure 4. To compare the efficiency of PIB at separation, a separate polymerization reaction using both **2** and **8** was worked up to yield a crude yellowish solid that was dissolved in acetonitrile. Addition of HCl and heptane led to a biphasic mixture of heptane and acetonitrile. The biphasic mixture so formed separated with polycarbonate-containing acetonitrile phase being visibly more colored in the case of **2** and with the heptane phase being visibly more colored for the product prepared using **8** (Figure 4a versus 4b).

In kinetic experiments, the reaction was carried out in a Parr autoclave modified with a SiComp attenuated total reflectance window to allow for *in situ* infrared measurements using an ASI® ReactIR 1000 instrument. In these experiments, the catalyst and PPNCl were dissolved in 10 mL of cyclohexene oxide and loaded into the reaction vessel at 80 °C at which time a single 128 scan background spectrum was collected. The vial was then rinsed with and additional 10 mL of cyclohexene oxide and loaded into the autoclave. After pressurization with 35 bar CO_2, a single 128 scan spectrum was collected every 3 min for 4 to 6 h. The reaction progress was can be followed by monitoring the absorbance of the polycarbonate the absorbance for formation of the polycarbonate (1750 cm^{-1}) versus time. Similarly, the slow production of cyclic carbonate (~ 1825 cm^{-1}) byproduct can be observed for both catalysts 2 and 8 over the course of the reaction. There is a marked increase in the rate of cyclic carbonate production as the polymerization process subsides. Upon completion of the reaction, the reaction vessel was cooled and the CO_2 vented followed by isolation of the product polymer as discussed above.

The products of polymerization using **2** were characterized by GPC which showed the polycarbonate had an M_n of 33,269, an M_w of 50,896 and a PDI of 1.53. A similar analysis of the products of polymerization of cyclohexene oxide and carbon dioxide using **8** showed that polycarbonate had an M_n of 28,829, an M_w of 47,975 and a PDI of 1.66.

ICP-MS Analysis of Polycarbonate Products for Cr. A sample of the polycarbonate product that was to be analyzed (151.5 mg) was added to a vial along with concentrated nitric acid were added. The mixture was heated to 120 °C until everything dissolved. At this point of concentrated sulfuric acid was added to the solution to yield 22.74 g of solution. The solution was then allowed to stand at room temperature for 24 h. At this point, the concentrated acidic aqueous solution was transferred to a 50 mL plastic bottle and 0.563 g of this solution was diluted with 1% nitric acid solution to produce 11.93 g of a diluted sample solution that was analyzed by ICP-MS for Cr. This analysis showed the solution had 12.4 ppb Cr. Considering the dilutions, this result means that in the case of polycarbonate prepared using catalyst **8**, the product polymer after one precipitation in heptane had 39 ppm Cr (ca. 3.6% of the starting Cr) based on the fact that 151.5 mg of the polymer, dissolved in 22.7395 g of . Polycarbonate prepared using catalyst **2** had ca. 4 time higher Cr content after one precipitation in methanol (samples of polycarbonate precipitated multiple times from methanol had visibly less color and presumably lower Cr contamination but were not analyzed by ICP-MS).

Copies of spectra



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CH2-28

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 Solvent: cdcl3
 Ambient temperature
INOVA-300  "inova300"

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Total time 6 min, 15 sec
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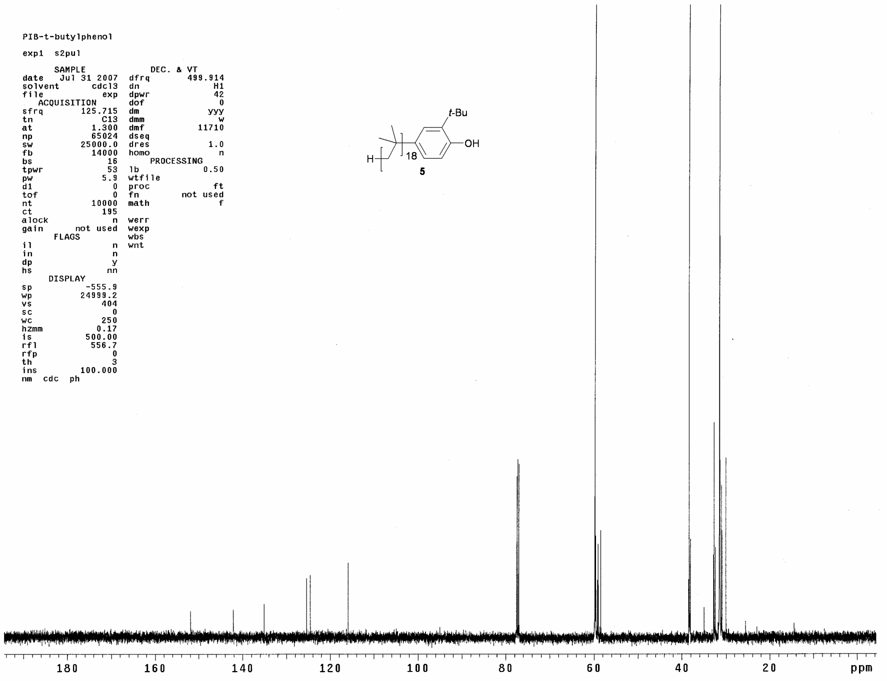

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PIB-t-butylphenol

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solvent      cdcl3  dn               H1
file           exp  dpwr             42
   ACQUISITION      dof               0
sfrq       125.715  dm              yyy
tn             C13  dmm               w
at           1.300  dmf           11710
np           65024  dseq
sw         25000.0  dres            1.0
fb           14000  homo              n
bs              16      PROCESSING
tpwr            53  lb             0.50
pw             5.9  wtfile
d1               0  proc             ft
tof              0  fn         not used
nt           10000  math              f
ct             195
alock            n  werr
gain      not used  wexp
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il               n  wnt
in               n
dp               y
hs              nn
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wp         24999.2
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rfp              0
th               3
ins        100.000
nm  cdc  ph
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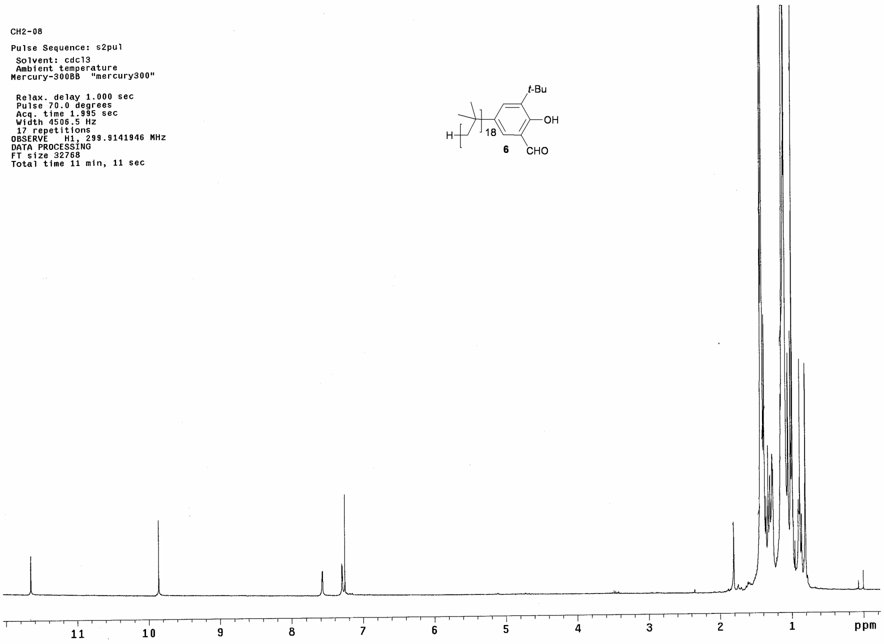

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CH2-08

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 Solvent: cdcl3
 Ambient temperature
Mercury-300BB  "mercury300"

 Relax. delay 1.000 sec
 Pulse 70.0 degrees
 Acq. time 1.995 sec
 Width 4506.5 Hz
 17 repetitions
OBSERVE   H1, 299.9141946 MHz
DATA PROCESSING
FT size 32768
Total time 11 min, 11 sec
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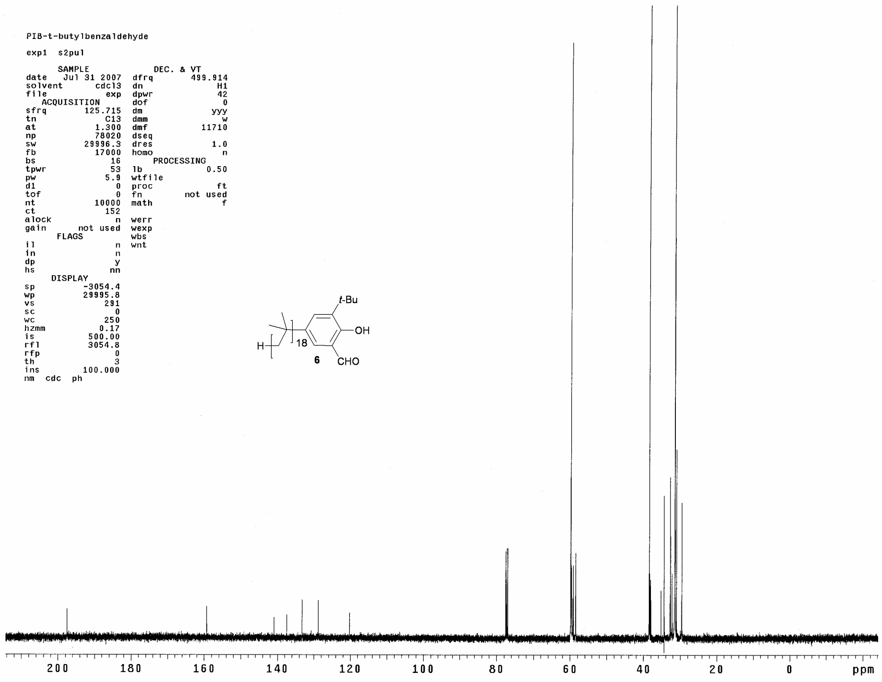

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PIB-t-butylbenzaldehyde

exp1  s2pul

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solvent      cdcl3  dn               H1
file           exp  dpwr             42
   ACQUISITION      dof               0
sfrq       125.715  dm              yyy
tn             C13  dmm               w
at           1.300  dmf           11710
np           78020  dseq
sw         29996.3  dres            1.0
fb           17000  homo              n
bs              16       PROCESSING
tpwr            53  lb             0.50
pw             5.9  wtfile
d1               0  proc             ft
tof              0  fn         not used
nt           10000  math              f
ct             152
alock            n  werr
gain      not used  wexp
      FLAGS         wbs
il               n  wnt
in               n
dp               y
hs              nn
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wp         29995.8
vs             291
sc               0
wc             250
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th               3
ins        100.000
nm  cdc  ph
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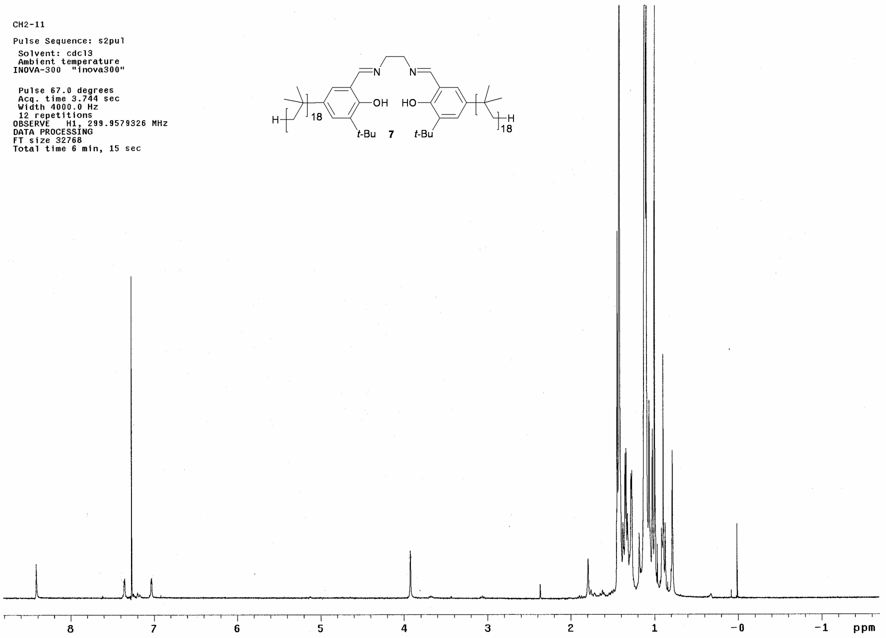
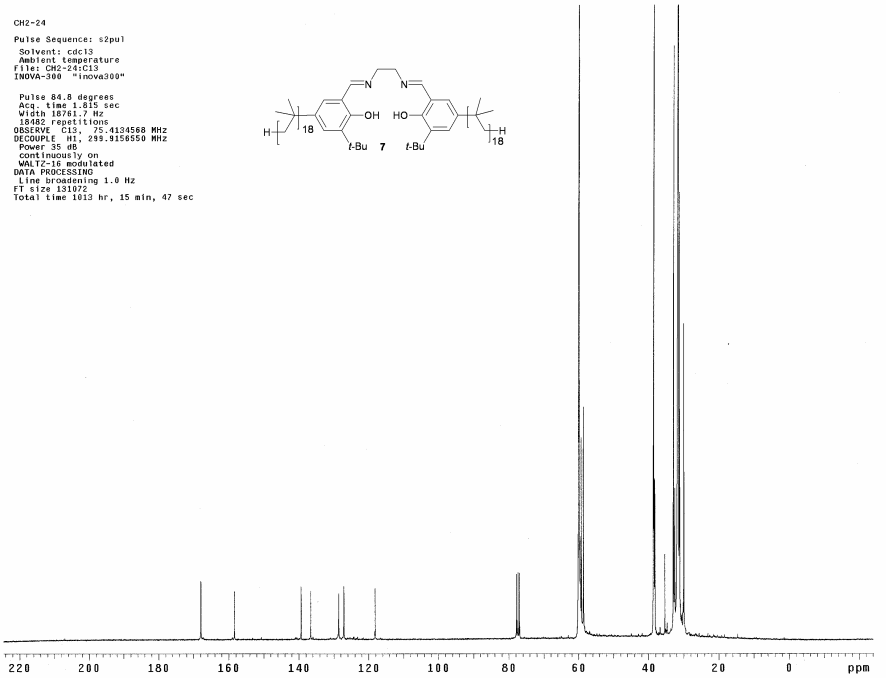


```
CH2-11

Pulse Sequence: s2pul
 Solvent: cdcl3
 Ambient temperature
INOVA-300  "inova300"

 Pulse 67.0 degrees
 Acq. time 3.744 sec
 Width 4000.0 Hz
 12 repetitions
OBSERVE   H1, 299.9579326 MHz
DATA PROCESSING
FT size 32768
Total time 6 min, 15 sec
```



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CH2-24

Pulse Sequence: s2pul
 Solvent: cdcl3
 Ambient temperature
File: CH2-24:C13
INOVA-300  "inova300"

 Pulse 84.8 degrees
 Acq. time 1.815 sec
 Width 18761.7 Hz
 18482 repetitions
OBSERVE  C13,  75.4134568 MHz
DECOUPLE  H1, 299.9156550 MHz
 Power 35 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 1013 hr, 15 min, 47 sec
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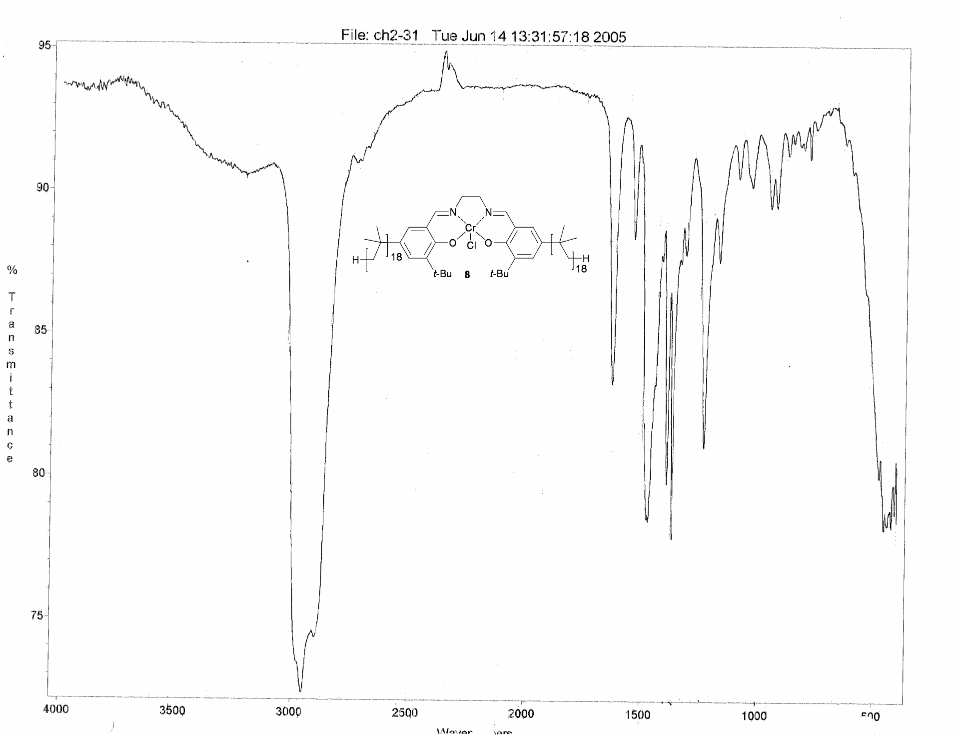
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95
90
85
80
75
% Transmittance
4000
3500
3000
2500
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Waven ers
H
18
N
Cr
Cl
O
t-Bu
8
t-Bu
H
18