Direct, Catalytic Hydroaminoalkylation of Unactivated Olefins with *N*-Alkyl Arylamines

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Supporting Information

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1. General Experimental Information

General Procedures. All reactions were conducted in flame- or oven-dried round-bottomed or Kjeldahl-shaped flasks fitted with rubber septa under a positive pressure of argon or 1-dram vials fitted with a Teflon-lined screw cap (13-mm diameter, 425 GPI thread; supplied by Qorpak, Bridgeville, Pennsylvania) under an atmosphere of nitrogen, unless otherwise noted. Air- and moisture-sensitive reagents were transferred via stainless steel cannula or syringe, or were handled in a nitrogen-filled drybox (Innovative Technologies, Newburyport, Massachusetts) equipped with an oxygen sensor (working oxygen level <1.5 ppm) and low-temperature refrigeration unit (–35 °C). Organic solutions were concentrated by rotary evaporation at 23–35 °C. Flash-column chromatography was performed as described by Still et al.[1] employing silica gel (60 Å pore size, 40–64 μm particle size) purchased from Silicycle. Analytical thin-layer chromatography (TLC) was performed using glass plates pre-coated with silica gel (0.25 mm, 60 Å pore size) impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and/or submersion in aqueous ceric ammonium molybdate solution (CAM) or aqueous potassium permanganate solution ($KMnO_4$), followed by brief heating on a hot plate (175 °C, 10–15 s).

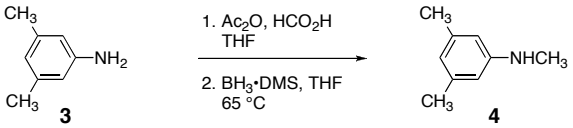
Materials. Commercial solvents and reagents were used as received with the following exceptions. Methylene chloride, toluene, pentane, tetrahydrofuran, and benzene were deoxygenated by sparging with argon and then were purified according to the method of Pangborn et al.[2] *N*-(Methyl-d_3)-aniline was prepared according to the procedure of Sannicolò and Fusco.[3] *N*-Methylaniline, *N*-methyl-4-fluoroaniline, *N*-methyl-3,5-dimethylaniline, *N*-methyl-3,5-difluoroaniline, *N*-(methyl-d_3)-aniline, *N*-(methyl)-*p*-toluidine, and 1,2,3,4-tetrahydroquinoline were stirred over calcium hydride (22 °C, >12 h), degassed by three freeze-pump-thaw-cycles, purified by bulb-to-bulb distillation, and then transferred to a drybox. *N*-Methyl-4-methoxyaniline was dried over phosphorous pentoxide in a vacuum dessicator and was stored in the drybox. 1-Octene, dimethylphenylvinylsilane, allylbenzene, 2-methyl-1-heptene, methylenecyclohexane, and trimethylvinylsilane were degassed by three freeze-pump-thaw cycles, transferred to a drybox, stored over activated 4-Å molecular sieves (>12 h), and filtered through a 0.2-μM PTFE syringe filter before use. Toluene-d_8 and dodecane were vacuum transferred from sodium benzophenone ketyl and degassed by three freeze-pump-thaw cycles. Pentaks(dimethylamino)tantalum was purchased from Strem Chemicals, Newburyport, Massachusetts and was stored at –35 °C in a drybox. ***Caution:*** Attempts to prepare pentakis(dimethylamino)tantalum according to the original reported procedure[4] have occasionally resulted in explosions.[5] The modified procedure of Rothwell and co-workers[6] should be consulted.

Instrumentation. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded at 400 or 500 MHz at 22 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$, δ 7.26; C_6HD_5, δ 7.15; $C_6D_5CHD_2$, δ 2.09). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad, app = apparent), integration, coupling constant in Hertz, and assignment. Proton-decoupled deuterium nuclear magnetic resonance spectra (^{2}H NMR) were recorded at 76.8 MHz at 22 °C. Chemical shifts are expressed in parts per million (ppm, δ scale) and are referenced to added deuterated NMR solvent (ca. 50 μL; $CDCl_3$, δ 7.26). Proton-decoupled carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 or 125 MHz at 22 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$, δ 77.0; C_6D_6, δ 128.0; C_7D_8, δ 20.4). In instances where coupling to fluorine is observed, the multiplicity and coupling constant in Hz are reported. Proton-decoupled fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded at 470 MHz at 22 °C, unless otherwise noted. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from trichlorofluoromethane ($CFCl_3$, δ 0.0). Infrared (IR) spectra were obtained using a Perkin-Elmer Spectrum BX spectrometer referenced to a polystyrene standard. Data are represented as follows: frequency of the absorption (cm^{-1}), intensity of absorption (s = strong, m = medium, w = weak, br = broad). Gas chromatography was performed using an HP 6890 series gas chromatograph equipped with an HP-5 column (25 m, 0.2 mm I.D., 0.33 μm film). Microwave

experiments were conducted in a CEM Discover microwave reactor. Elemental analyses were obtained at the University of Illinois Microanalysis Laboratory or at Robertson Microlit Laboratories, Edison, New Jersey. High resolution mass spectra were obtained at the University of Illinois Mass Spectrometry Facilities.

2. Synthetic Procedures

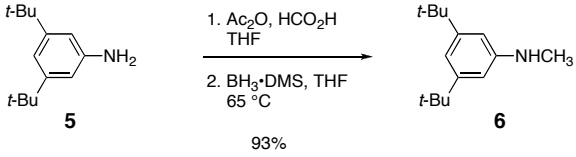
(*For clarity, synthetic compounds that are not numbered in the text are numbered in the Supporting Information starting with* ***3****.)*



Alkylation of 3,5-Dimethylaniline (**3**) [*N*-Methyl-3,5-dimethylaniline (**4**)]:

The following procedure was adapted from that described by Krishnamurthy.[7] 98% Formic acid (4.20 mL, 111 mmol, 3.20 equiv) was added rapidly via syringe to a 100-mL Kjeldahl-shaped flask containing neat acetic anhydride (8.52 mL, 90.2 mmol, 2.60 equiv) at 0 °C. The flask was fitted with a reflux condenser, and the mixture was warmed to 60 °C and stirred at this temperature for 2 h. The reaction mixture was then cooled to 22 °C and the cooled solution was diluted with tetrahydrofuran (10 mL). A solution of 3,5-dimethylaniline (**3**, 4.32 mL, 34.7 mmol, 1 equiv) in tetrahydrofuran (20 mL) was added via cannula over 15 min. The resulting mixture was stirred for 45 min at 22 °C. The mixture was concentrated to dryness to provide an off-white residue. Excess reagents were removed from this residue by azeotropic distillation with toluene (3 × 30 mL) under reduced pressure. The resulting off-white solid was dissolved in tetrahydrofuran (20 mL) and cooled to 0 °C. Neat borane methyl sulfide complex (8.23 mL, 86.7 mmol, 2.50 equiv) was added slowly via syringe (***CAUTION: EXOTHERMIC, HYDROGEN EVOLUTION)*** and the resulting mixture was stirred for 10 min at 22 °C. The reaction vessel was then fitted with a reflux condenser and immersed in an oil bath that had been preheated to 65 °C. The solution was stirred at 65 °C for 1 h and then was cooled to 0 °C. The reflux condenser was removed, and methanol (15 mL) was added dropwise via pipette over 10 min (***CAUTION: EXOTHERMIC, HYDROGEN EVOLUTION)***. The resulting mixture was stirred for 1 h at 0 °C. The product solution was partitioned between hexanes (150 mL), ether (30 mL), and 1N aqueous sodium hydroxide solution (50 mL). The layers that formed were separated, and the organic layer was washed with water (30 mL) and saturated aqueous sodium chloride solution (30 mL). The washed solution was dried over sodium sulfate, and the dried solution was filtered. The filtrate was concentrated in vacuo, and the residue obtained was purified by flash-column chromatography (eluting with 5% ether-hexanes initially, grading to 7% ether-hexanes) to furnish *N*-methyl-3,5-dimethylaniline (**4**) as a clear, colorless liquid (1.57 g, 33%).

R_f = 0.24 (5% ether-hexanes; UV, $KMnO_4$). ^{1}H NMR (400 MHz, $CDCl_3$), δ 6.49 (s, 1H, Ar**H**), 6.35 (s, 2H, Ar**H**), 3.66 (br, 1H, N**H**), 2.89 (s, 3H, NC**H**$_3$), 2.36 (s, 6H, ArC**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ 149.4, 138.7, 119.1, 110.3, 30.6, 21.4. IR (NaCl, thin film), cm^{-1} 3408 (m), 2915 (m), 1605 (s), 1515 (m). Anal. Calcd for $C_9H_{13}N$: C, 79.95; H, 9.69; N, 10.36. Found: C, 79.80; H, 9.74; N, 10.34.

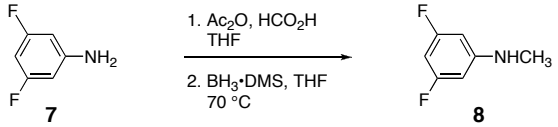


Alkylation of 3,5-Di-*tert*-butylaniline (**5**) [*N*-Methyl-3,5-di-*tert*-butylaniline (**6**)]:

The following procedure was adapted from that described by Krishnamurthy.[7] 98% Formic acid (588 μL, 15.6 mmol, 3.20 equiv) was added rapidly via syringe to a 50-mL round-bottomed flask containing neat acetic anhydride (1.20 mL, 12.7 mmol, 2.60 equiv) at 22 °C. The flask was fitted with a reflux condenser, and the mixture was warmed to 60 °C and stirred at this temperature for 3 h. The warmed mixture was cooled to –20 °C and then diluted with tetrahydrofuran (1.0 mL). A solution of 3,5-

di-*tert*-butylaniline (**5**, 1.00 g, 4.88 mmol, 1 equiv) in tetrahydrofuran (3.0 mL) was then added dropwise via cannula over 5 min. The resulting mixture was stirred for 1 h at –20 °C and then was concentrated to dryness to provide an off-white solid residue. Excess reagents were removed from this solid residue by azeotropic distillation with toluene (3 × 20 mL) under reduced pressure. The residue obtained was dissolved in tetrahydrofuran (2.6 mL) and cooled to ~10 °C. Neat borane methyl sulfide complex (1.16 mL, 12.2 mmol, 2.50 equiv) was added dropwise via syringe over 5 min (***CAUTION: EXOTHERMIC, HYDROGEN EVOLUTION***). The flask was fitted with a reflux condenser and placed in a preheated oil bath (65 °C). The mixture was stirred at 65 °C for 3 h. The product solution was cooled to 0 °C, and was slowly diluted with methanol (2.0 mL) over 5 min (***CAUTION: EXOTHERMIC, HYDROGEN EVOLUTION)***. The resulting mixture was stirred for 1 h at 22 °C, and then was partitioned between ether (15 mL), hexanes (30 mL), and 1N aqueous sodium hydroxide solution (15 mL). The layers that formed were separated, and the organic layer was washed with distilled water (15 mL) and saturated aqueous sodium chloride solution (15 mL). The washed solution was dried over sodium sulfate, and the dried solution was filtered. The filtrate was concentrated, and the residue obtained was purified by flash-column chromatography (eluting with 3.5% ethyl acetate-hexanes) to provide *N*-methyl-3,5-di-*tert*-butylaniline (**6**) as a viscous, colorless oil that solidified upon cooling to –20 °C (989 mg, 93%).

R_f = 0.25 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 6.91 (s, 1H, Ar**H**), 6.58 (s, 2H, Ar**H**), 3.72 (br, 1H, N**H**), 2.93 (s, 3H, NC**H**$_3$), 1.40 (s, 18H, C(C**H**$_3$)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 151.6, 148.7, 112.0, 107.1, 34.8, 31.4, 30.9. IR (NaCl, thin film), cm^{-1} 3410 (m), 2963 (s), 1601 (s), 1477 (m). Anal. Calcd for $C_{15}H_{25}N$: C, 82.13; H, 11.49; N, 6.39. Found: C, 82.07; H, 11.43; N, 6.50.

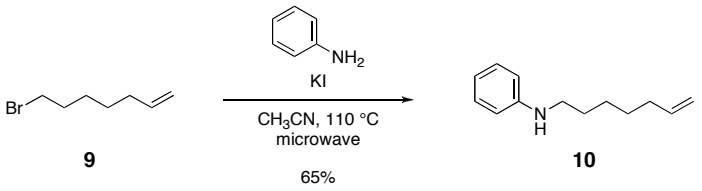


Alkylation of 3,5-Difluoroaniline (**7**) [*N*-Methyl-3,5-difluoroaniline (**8**)]:

The following procedure was adapted from that described by Krishnamurthy.[7] 98% Formic acid (4.67 mL, 124 mmol, 3.20 equiv) was added rapidly via syringe to a 100-mL Kjeldahl-shaped flask containing neat acetic anhydride (9.50 mL, 101 mmol, 2.60 equiv) at 22 °C. The flask was fitted with a reflux condenser and the mixture was warmed to 60 °C and was stirred at this temperature for 3 h. The warmed mixture was cooled to –20 °C and then diluted with tetrahydrofuran (10 mL). A solution of 3,5-difluoroaniline (**7**, 5.00 g, 38.7 mmol, 1 equiv) in tetrahydrofuran (20 mL) was then added dropwise via cannula over 15 min. The resulting mixture was stirred for 1.7 h at –20 °C, and then was concentrated to dryness to provide an off-white solid. Excess reagents were removed from this solid by azeotropic distillation with toluene (3 × 40 mL) under reduced pressure. The solid residue obtained was dissolved in tetrahydrofuran (20 mL) and cooled to 0 °C. Neat borane methyl sulfide complex (9.17 mL, 96.7 mmol, 2.50 equiv) was added dropwise via syringe over 5 min (***CAUTION: EXOTHERMIC, HYDROGEN EVOLUTION)***. After hydrogen evolution ceased (ca. 10 min), the flask was fitted with a reflux condenser and placed in a preheated oil bath (70 °C). The mixture was stirred at 70 °C for 2.2 h then was cooled to 0 °C. The cooled solution was slowly diluted with methanol (15 mL) over 5 min (***CAUTION: EXOTHERMIC, HYDROGEN EVOLUTION)***. The resulting mixture was stirred for 1 h at 22 °C and then was partitioned between ether (40 mL), hexanes (150 mL), and 1N aqueous sodium hydroxide solution (50 mL). The layers that formed were separated, and the organic layer was washed with distilled water (30 mL) and saturated aqueous sodium chloride solution (30 mL). The washed solution was dried over sodium sulfate, and the dried solution was filtered. The filtrate was concentrated, and the residue obtained was purified by flash-column chromatography (eluting with 5% ether-hexanes) to provide *N*-methyl-3,5-difluoroaniline (**8**) as a clear, colorless liquid (2.52 g, 45%).

R_f = 0.12 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 6.15–6.04 (m, 3H, Ar**H**), 3.94 (br, 1H, N**H**), 2.81 (s, 3H, NC**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 164.1 (dd, J = 243, 16.0

Hz), 151.5 (t, J = 13.7 Hz), 94.9 (m), 92.0 (t, J = 25.6 Hz), 30.4. ^{19}F NMR (470 MHz, $CDCl_3$), δ –111.0. IR (NaCl, thin film), cm^{-1} 3452 (m), 2915 (w), 1638 (s), 1521 (m). Anal. Calcd for $C_7H_7F_2N$: C, 58.74; H, 4.93; N, 9.79. Found: C, 58.48; H, 4.72; N, 9.92.

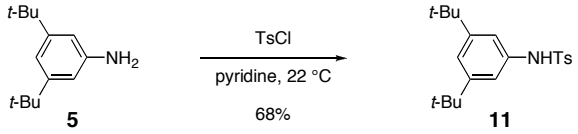


Amination of 7-Bromo-1-heptene (**9**) [*N*-(6-Heptenyl)-aniline (**10**)]:

The following was adapted from the procedure reported by Romera and co-workers for the preparation of related alkylaniline derivatives.[8] A 10-mL pressure tube was charged sequentially with potassium iodide (84.7 mg, 510 μmol, 0.10 equiv), acetonitrile (5.1 mL), aniline (1.39 mL, 15.3 mmol, 3.0 equiv) and 7-bromo-1-heptene (**9**, 777 μL, 5.10 mmol, 1 equiv). The vessel was sealed, and the mixture was heated to 110 °C for 10 min in a microwave reactor (200 W). The product solution was cooled to 22 °C. The cooled solution was partitioned between 50% ether-hexanes (75 mL) and saturated aqueous sodium bicarbonate solution (25 mL). The layers that formed were separated, and the organic layer was washed with distilled water (25 mL) and saturated aqueous sodium chloride solution (25 mL). The washed solution was dried over sodium sulfate, and the dried solution was filtered. The filtrate was concentrated, and the residue obtained was purified by flash-column chromatography (eluting with 4% ether-hexanes) to provide *N*-(6-heptenyl)-aniline (**10**) as a clear, colorless oil (631 mg, 65%).

R_f = 0.30 (5% ether-hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.21 (app t, 2H, J = 8.0 Hz, Ar**H**), 6.72 (t, 1H, J = 7.7 Hz, Ar**H**), 6.63 (d, 2H, J = 8.5 Hz, Ar**H**), 5.89–5.81 (m, 1H, CH_2CH**H**CH_2) 5.05 (dd, 1H, J = 17.0, 2.0 Hz, CH_2CHCH**H**), 4.98 (dd, 1H, J = 10.0, 2.0 Hz, CH_2CHCH**H**), 3.61 (br, 1H, N**H**), 3.13 (t, 2H, J = 7.0 Hz, NHC**H**$_2CH_2$), 2.13–2.09 (m, 2H, C**H**$_2CHCH_2$), 1.69–1.62 (m, 2H, $NHCH_2CH$**H**), 1.51–1.41 (m, 4H, $NHCH_2CH_2CH$**H**$_2CH$**H**). ^{13}C NMR (125 MHz, $CDCl_3$), δ 148.4, 138.8, 129.2, 117.0, 114.4, 112.6, 43.9, 33.7, 29.4, 28.6, 26.6. IR (NaCl, thin film), cm^{-1} 3412 (w), 2929 (s), 1603 (s), 1507 (s). Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.47; H, 10.14; N, 7.45.

Preparation of *N*-(Methyl-d_3)-3,5-di-tert-butylaniline **12**.

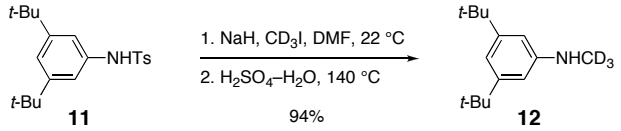


Step 1: Sulfonylation of 3,5-Di-tert-butylaniline (**5**) [*N*-(*para*-Toluenesulfonyl)-3,5-di-*tert*-butylaniline (**11**)]:

para-Toluenesulfonyl chloride (466 mg, 2.44 mmol, 1.0 equiv) was added in one portion to a stirred solution of 3,5-di-*tert*-butylaniline (**5**, 500 mg, 2.44 mmol, 1 equiv) in pyridine (2.6 mL) at 0 °C. The resulting red solution was stirred at 0 °C for 5 min and then was allowed to warm to 22 °C. After 5.5 h, an additional portion of *para*-toluenesulfonyl chloride (46.6 mg, 244 μmol, 0.10 equiv) was added in one portion. The resulting mixture was stirred for 11 h at 22 °C. The product solution was partitioned between 50% ethyl acetate-hexanes (100 mL) and a 1N aqueous sulfuric acid solution (100 mL). The layers that formed were separated, and the organic layer was washed sequentially with saturated aqueous sodium bicarbonate solution (50 mL), distilled water (50 mL), and saturated aqueous sodium chloride solution (50 mL). The washed solution was dried over sodium sulfate, and the dried solution was filtered. The filtrate

was concentrated, and the residue obtained was purified by flash-column chromatography (eluting with 10% acetone-hexanes) to provide *N*-(*para*-toluenesulfonyl)-3,5-di-*tert*-butylaniline (**11**) as an off-white, crystalline solid (599 mg, 68%).

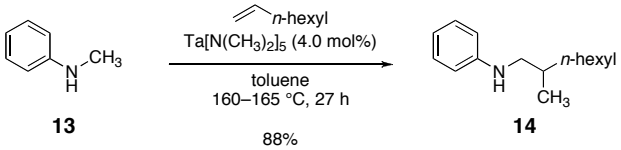
R_f = 0.21 (10% acetone-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.64 (d, 2H, J = 8.5 Hz, $SO_2C_6\mathbf{H}_4CH_3$), 7.21 (d, 2H, J = 8.5 Hz, $SO_2C_6\mathbf{H}_4CH_3$), 7.14 (br s, 1H, NAr**H**), 6.83 (d, 2H, J = 1.5 Hz, NAr**H**), 6.66 (br, 1H, N**H**), 2.37 (s, 3H, $SO_2C_6H_4C\mathbf{H}_3$), 1.22 (s, 18H, $C(C\mathbf{H}_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 151.9, 143.6, 136.1, 135.7, 129.4, 127.5, 119.3, 116.8, 34.8, 31.2, 21.4. IR (NaCl, thin film), cm^{-1} 3259 (m), 2962 (m), 1598 (m), 1162 (s). Anal. Calcd for $C_{21}H_{29}NO_2S$: C, 70.15; H, 8.13; N, 3.90. Found: C, 69.75; H, 8.11; N, 3.95.



Step 2: Alkylation of *N*-(*para*-Toluenesulfonyl)-3,5-di-*tert*-butylaniline (**11**) and Cleavage of the Resulting Tertiary Sulfonamide [*N*-(Methyl-d_3)-3,5-di-tert-butylaniline (**12**)]:

A solution of *N*-(*para*-toluenesulfonyl)-3,5-di-*tert*-butylaniline (**11**, 569 mg, 1.58 mmol, 1 equiv) in *N*,*N*-dimethylformamide (750 μL) was added dropwise via cannula over 5 min to a stirred suspension of sodium hydride (41.8 mg, 1.74 mmol, 1.10 equiv) in *N*,*N*-dimethylformamide (4.75 mL) at 22 °C. The resulting light yellow mixture was stirred for 10 min at 22 °C and then iodomethane-d_3 (103 μL, 1.66 mmol, 1.05 equiv) was added rapidly via syringe. The resulting mixture was stirred for 3 h at 22 °C. The product solution was partitioned between 50% ether-petroleum ether (100 mL) and distilled water (100 mL). The layers that formed were separated, and the organic layer was washed sequentially with distilled water (2 × 50 mL) and saturated aqueous sodium chloride solution (50 mL). The washed solution was dried over sodium sulfate, and the dried solution was filtered. The filtrate was concentrated and the residue obtained was suspended in a mixture of concentrated sulfuric acid (2.10 mL) and distilled water (900 μL). The suspension was placed in a preheated oil bath (140 °C) for 10 min. The reaction mixture gradually became deep brown and homogeneous. The product solution was cooled to 0 °C and the cooled solution was slowly diluted with 35% aqueous sodium hydroxide solution (w/v, 7.8 mL; ***CAUTION: VERY EXOTHERMIC***). The diluted solution was partitioned between distilled water (50 mL) and 50% ether-petroleum ether (40 mL). The layers that formed were separated, and the organic layer was washed sequentially with distilled water (20 mL) and saturated aqueous sodium chloride solution (20 mL). The washed layer was dried over sodium sulfate and the dried solution was filtered. The filtrate was concentrated and the residue obtained was purified by flash-column chromatography (eluting with 3.5% ethyl acetate-hexanes) to provide *N*-(methyl-d_3)-3,5-di-*tert*-butylaniline (**12**) as a colorless, viscous oil (328 mg, 94%).

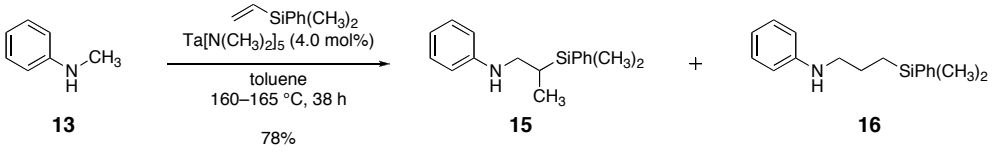
R_f = 0.50 (10% acetone-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 6.82 (t, 1H, J = 1.5 Hz, Ar**H**), 6.50 (d, 2H, J = 2.0 Hz, Ar**H**), 3.64 (br, 1H, N**H**), 1.32 (s, 18H, $C(C\mathbf{H}_3)_3$). ^{2}H NMR ($CHCl_3$, 76.8 MHz), δ 2.86 (s, $NC\mathbf{D}_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 151.7, 148.7, 112.1, 107.1, 34.8, 31.4 ($\mathbf{C}D_3$ not observed). IR (NaCl, thin film), cm^{-1} 3409 (w), 2962 (s), 2187 (w), 2066 (w), 1600 (s), 1446 (w). HRMS–EI (*m*/*z*): $[M]^+$ calcd for $C_{15}H_{22}D_3N$, 222.2175; found, 222.2177.



Alkylation of *N*-Methylaniline (**13**) with 1-Octene (Alkylaniline **14**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (16.0 mg, 40.0 μmol, 0.04 equiv), toluene (400 μL), *N*-methylaniline (**13**, 108 μL, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and 1-octene (235 μL, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 27 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 100% hexanes initially, grading to 2.5% ethyl acetate-hexanes) to provide the alkylaniline **14** as a clear, colorless liquid (193 mg, 88%).

R_f = 0.40 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.18 (app t, 2H, J = 8.2 Hz, Ar**H**), 6.69 (td, 1H, J = 7.2, 1.0 Hz, Ar**H**), 6.61 (dd, 2H, J = 7.5, 0.75 Hz, Ar**H**), 3.72 (br, 1H, N**H**), 3.06 (dd, 1H, J = 12.0, 5.7 Hz, NC**H**$_2$), 2.89 (dd, 1H, J = 12.0, 7.5 Hz, NC**H**$_2$), 1.80–1.70 (m, 1H, $NHCH_2C$**H**), 1.47–1.16 (m, 10H, $NHCH_2CH(CH_3)(C$**H**$_2)_5CH_3$), 0.98 (d, 3H, J = 6.5 Hz, $NHCH_2CH(C$**H**$_3)$), 0.91 (t, 3H, J = 7.5 Hz, $NHCH_2CH(CH_3)(CH_2)_5C$**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 148.6, 129.2, 116.9, 112.6, 50.3, 34.8, 32.9, 31.9, 29.6, 26.9, 22.7, 18.1, 14.1. IR (NaCl, thin film), cm^{-1} 3421 (w), 2926 (s), 2855 (m), 1603 (s), 1506 (s). Anal. Calcd for $C_{15}H_{25}N$: C, 82.13; H, 11.49; N, 6.39. Found: C, 81.93; H, 11.49; N, 6.40.



Alkylation of *N*-Methylaniline (**13**) with Dimethylphenylvinylsilane (Alkylanilines **15** and **16**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (16.0 mg, 40.0 μmol, 0.04 equiv), toluene (400 μL), *N*-methylaniline (**13**, 108 μL, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and dimethylphenylvinylsilane (277 μL, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 38 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 2.5% ether-hexanes) to provide the pure, separated the alkylanilines **15** (134 mg, 50%, clear; colorless oil) and **16** (74.7 mg, 28%; clear, colorless oil).

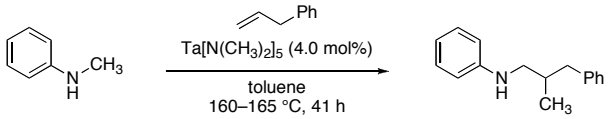
Branched Alkylaniline **15**:

R_f = 0.37 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.56–7.52 (m, 2H, SiAr**H**), 7.42–7.36 (m, 3H, SiAr**H**), 7.14 (app t, 2H, J = 7.7 Hz, NAr**H**), 6.67 (t, 1H, J = 7.5 Hz, NAr**H**), 6.47 (d, 2H, J = 8.5 Hz, NAr**H**), 3.72 (br, 1H, N**H**), 3.25 (dd, 1H, J = 12.2, 5.2 Hz, NC**H**$_2$), 2.96 (dd, 1H, J = 12.0, 9.5 Hz, NC**H**$_2$), 1.32–1.26 (m, 1H, $NHCH_2C$**H**), 1.07 (d, 3H, J = 7.5 Hz, $NHCH_2CHC$**H**$_3$), 0.34 (s, 6H, $Si(C$**H**$_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 148.2, 137.8, 133.9, 129.1 (2C), 127.9, 117.0, 112.8, 46.7, 20.1, 13.1, –4.5, –5.3. IR (NaCl, thin film), cm^{-1} 3414 (w), 2954 (m), 2866 (w), 1602 (s), 1506 (s). Anal. Calcd for $C_{17}H_{23}NSi$: C, 75.78; H, 8.60; N, 5.20. Found: C, 75.73; H, 8.62; N, 4.93.

Linear Alkylaniline **16**:

R_f = 0.31 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.53–7.51 (m, 2H, SiAr**H**), 7.39–7.36 (m, 3H, SiAr**H**), 7.17 (dd, 2H, J = 8.0, 7.5 Hz, NAr**H**), 6.70 (t, 1H, J = 7.0 Hz, NAr**H**), 6.58 (dd, 2H, J = 8.5, 1.0 Hz, NAr**H**), 3.75 (br, 1H, N**H**), 3.09 (t, 2H, J = 7.0 Hz, NC**H**$_2$), 1.67–1.61 (m, 2H, $NHCH_2C$**H**$_2$), 0.85–0.82 (m, 2H, $NHCH_2CH_2C$**H**$_2$Si), 0.30 (s, 6H, $Si(C$**H**$_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 148.2, 139.0, 133.5, 129.2, 128.9, 127.8, 117.2, 112.8, 47.2, 23.9, 13.1, –3.1. IR (NaCl, thin film), cm^{-1}

3411 (w), 2953 (m), 1603 (s), 1506 (s). Anal. Calcd for $C_{17}H_{23}NSi$: C, 75.78; H, 8.60; N, 5.20. Found: C, 75.68; H, 8.79; N, 5.03.

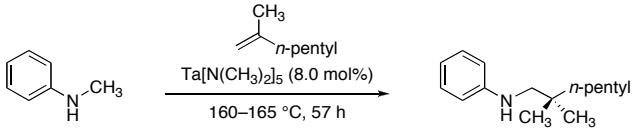


13 **17**

Alkylation of *N*-Methylaniline (**13**) with Allylbenzene (Alkylaniline **17**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (16.0 mg, 40.0 μmol, 0.04 equiv), toluene (400 μL), *N*-methylaniline (**13**, 108 μL, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and allylbenzene (198 μL, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 41 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 2.5% ether-hexanes) to provide the alkylaniline **17** as a clear, colorless oil (173 mg, 77%).

R_f = 0.41 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.31 (app t, 2H, J = 7.0 Hz, CH_2Ar**H**), 7.24–7.15 (m, 5H, 3 × CH_2Ar**H**, 2 × NAr**H**), 6.70 (t, 1H, J = 7.2 Hz, NAr**H**), 6.56 (d, 2H, J = 8.0, NAr**H**), 3.74 (br, 1H, N**H**), 3.11 (dd, 1H, J = 13.0, 6.0 Hz, NC**H**$_2$), 2.97 (dd, 1H, J = 12.5, 7.2 Hz, NC**H**$_2$), 2.78 (dd, 1H, J = 13.5, 6.5 Hz, C**H**$_2$Ph), 2.52 (dd, 1H, J = 13.5, 8.0 Hz, C**H**$_2$Ph), 2.12–2.06 (m, 1H, NCH_2C**H**), 0.99 (d, 3H, J = 6.5 Hz, NCH_2CHCH_3). ^{13}C NMR (125 MHz, $CDCl_3$), δ 148.3, 140.5, 129.2, 129.1, 128.3, 126.0, 117.1, 112.7, 49.8, 41.3, 35.0, 18.0. IR (NaCl, thin film), cm^{-1} 3419 (w), 2955 (w), 2868 (w), 1602 (s), 1507 (s). Anal. Calcd for $C_{16}H_{19}N$: C, 85.28; H, 8.50; N, 6.22. Found: C, 85.11; H, 8.25; N, 6.41.

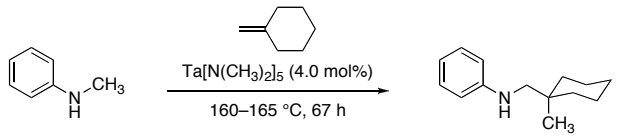


13 **18**

Alkylation of *N*-Methylaniline (**13**) with 2-Methyl-1-heptene (Alkylaniline **18**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (32.0 mg, 80.0 μmol, 0.08 equiv), *N*-methylaniline (**13**, 108 μL, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and 2-methyl-1-heptene (236 μL, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 57 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 1% ethyl acetate-hexanes initially, grading to 2.5% ethyl acetate-hexanes) to provide the alkylaniline **18** as a clear, light yellow oil (167 mg, 76%).

R_f = 0.44 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.18 (dd, 2H, J = 9.0, 7.2 Hz, Ar**H**), 6.68 (t, 1H, J = 7.5 Hz, Ar**H**), 6.64 (d, 2H, J = 8.0 Hz, Ar**H**), 3.62 (br, 1H, N**H**), 2.90 (s, 2H, NC**H**$_2$), 1.35–1.22 (m, 8H, $NHCH_2C(CH_3)_2(C\mathbf{H}_2)_4CH_3$), 0.96 (s, 6H, $NHCH_2C(C\mathbf{H}_3)_2$), 0.90 (t, 3H, J = 7.0 Hz, $NHCH_2C(CH_3)_2(CH_2)_4C\mathbf{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 149.0, 129.2, 116.9, 112.6, 54.1, 40.1, 34.0, 32.7, 25.6, 23.6, 22.7, 14.1. IR (NaCl, thin film), cm^{-1} 3423 (w), 2956 (m), 2929 (m), 1603 (m), 1506 (m). Anal. Calcd for $C_{15}H_{25}N$: C, 82.13; H, 11.49; N, 6.39. Found: C, 82.06; H, 11.12; N, 6.63.

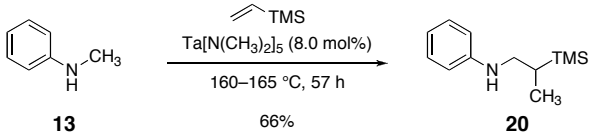


13 **19**

Alkylation of *N*-Methylaniline (**13**) with Methylenecyclohexane (Alkylaniline **19**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (16.0 mg, 40.0 μmol, 0.04 equiv), *N*-methylaniline (**13**, 108 μL, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and methylenecyclohexane (180 μL, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 67 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 2.5% ethyl acetate-hexanes) to provide the alkylaniline **19** as a clear, colorless oil (144 mg, 71%).

R_f = 0.48 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.21 (dd, 2H, J = 8.5, 7.5 Hz, Ar**H**), 6.71 (tt, 1H, J = 7.5, 1.0 Hz, Ar**H**), 6.67 (dd, 2H, J = 8.5, 1.0 Hz, Ar**H**), 3.67 (br, 1H, N**H**), 2.98 (s, 2H, NC**H**$_2$), 1.58–1.47 (m, 5H, NHCH$_2$C(CH$_3$)(C**H**$_2$)$_5$), 1.45–1.34 (m, 5H, NHCH$_2$C(CH$_3$)(C**H**$_2$)$_5$), 1.03 (s, 3H, C**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 149.1, 129.1, 116.7, 112.6, 54.6, 35.8, 34.2, 26.4, 23.3, 21.8. IR (NaCl, thin film), cm $^{-1}$ 3422 (w), 2925 (s), 2850 (m), 1602 (s), 1506 (s). Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.41; H, 10.15; N, 7.15.

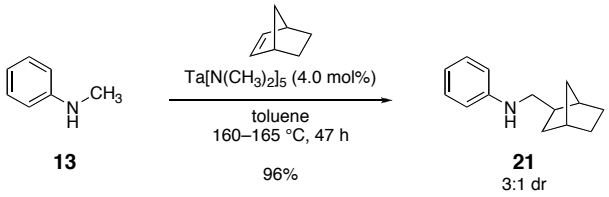


13 **20**

Alkylation of *N*-Methylaniline (**13**) with Trimethylvinylsilane (Alkylaniline **20**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (32.0 mg, 80.0 μmol, 0.08 equiv), *N*-methylaniline (108 μL, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and trimethylvinylsilane (220 μL, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 57 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 2.5% ethyl acetate-hexanes) to provide the alkylaniline **20** as a clear, colorless oil (137 mg, 66%).

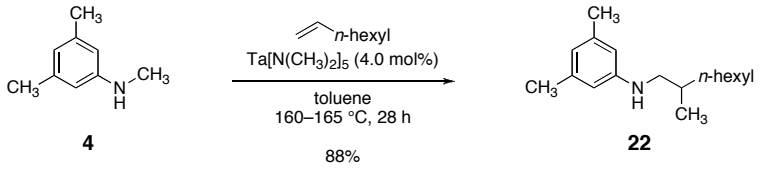
R_f = 0.40 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.20 (dd, 2H, J = 8.5, 7.5 Hz, Ar**H**), 6.71 (tt, 1H, J = 7.5, 0.5 Hz, Ar**H**), 6.62 (dd, 2H, J = 8.5, 1.0 Hz, NAr**H**), 3.72 (br, 1H, N**H**), 3.33–3.29 (m, 1H, NC**H**$_2$), 2.97–2.92 (m, 1H, NC**H**$_2$), 1.07–1.02 (m, 4H, NHCH$_2$C**H**, NHCH$_2$CHC**H**$_3$), 0.65 (s, 9H, Si(C**H**$_3$)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 148.5, 129.2, 117.0, 112.7, 46.6, 20.4, 12.8, –3.1. IR (NaCl, thin film), cm^{-1} 3418 (w), 2953 (m), 2866 (w), 1603 (s), 1506 (s). Anal. Calcd for $C_{12}H_{21}NSi$: C, 69.50; H, 10.21; N, 6.75. Found: C, 69.28; H, 10.24; N, 6.64.



Alkylation of *N*-Methylaniline (**13**) with Norbornene (Alkylaniline **21**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (16.0 mg, 40.0 μmol, 0.04 equiv), toluene (400 μL), *N*-methylaniline (**13**, 108 μL, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and norbornene (141 mg, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 47 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 2.5% ethyl acetate-hexanes) to provide the alkylaniline **21** as a clear, colorless oil (193 mg, 96%, 3:1 mixture of diastereomers).

R_f = 0.42 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$, 3:1 mixture of *exo* and *endo* diastereomers, * denotes minor diastereomer), δ 7.24–7.20 (m, 2H, Ar**H**), 7.40–7.20* (m, 2H, Ar**H**), 6.76–6.72 (m, 1H, Ar**H**), 6.76–6.72* (m, 1H, Ar**H**), 6.67–6.63 (m, 2H, Ar**H**), 6.67–6.63* (m, 2H, Ar**H**), 3.66 (br, 1H, N**H**), 3.66* (br, 1H, N**H**), 3.16* (dd, 1H, J = 11.5, 7.0 Hz, NHC**H**$_2$), 3.03* (dd, 1H, J = 11.5, 8.3 Hz, NHC**H**$_2$), 2.97 (dd, 1H, J = 11.5, 8.5 Hz, NHC**H**$_2$), 2.85 (dd, 1H, J = 12.0, 6.7 Hz, NHC**H**$_2$), 2.33–2.26 (m, 1H, NCH$_2$CHC**H**), 2.33–2.26* (m, 2H, NCH$_2$CHC**H**, NCH$_2$CHCH$_2$C**H**), 2.20–2.12 (m, 1H, NCH$_2$CHCH$_2$C**H**), 2.20–2.12* (m, 1H, NCH$_2$C**H**) 1.85* (tdd, 1H, J = 12.4, 4.7, 3.5 Hz, NCH$_2$CHC**H**$_2$), 1.79–1.73 (m, 1H, NCH$_2$C**H**), 1.63–1.12 (m, 8H, 2 × NCH$_2$CHC**H**$_2$, 2 × NCH$_2$CHCH$_2$CHC**H**$_2$, 2 × NCH$_2$CHCHC**H**$_2$CH$_2$, 2 × NCH$_2$CHCHC**H**$_2$CH), 1.63–1.12* (m, 6H, 2 × NCH$_2$CHCH$_2$CHC**H**$_2$, 2 × NCH$_2$CHCHC**H**$_2$CH$_2$, 2 × NCH$_2$CHCHC**H**$_2$CH), 0.78* (ddd, 1H, J = 12.0, 5.0, 2.0 Hz, NCH$_2$CHC**H**$_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 3:1 mixture of *exo* and *endo* diastereomers, * denotes minor diastereomer), δ 148.5, 148.5*, 129.1, 129.1*, 117.0*, 116.9, 112.6*, 112.5, 49.2, 46.5*, 42.0, 39.7*, 39.5*, 39.2, 38.4*, 36.7*, 36.3, 35.8, 35.3, 35.2*, 29.9*, 29.8, 28.8, 22.5*. IR (NaCl, thin film), cm^{-1} 3416 (w), 2948 (s), 2868 (m), 1603 (s), 1507 (s). Anal. Calcd for $C_{14}H_{19}N$: C, 83.53; H, 9.51; N, 6.96. Found: C, 83.62; H, 9.73; N, 7.03.

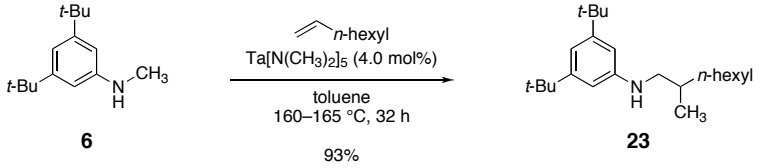


Alkylation of *N*-Methyl-3,5-dimethylaniline (**4**) with 1-Octene (Alkylaniline **22**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (16.0 mg, 40.0 μmol, 0.04 equiv), toluene (400 μL), *N*-methyl-3,5-dimethylaniline (**4**, 135 mg, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and 1-octene (235 μL, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 28 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 1% ethyl acetate-hexanes initially, grading to 2.5% ethyl acetate-hexanes) to provide the alkylaniline **22** as a clear, colorless oil (217 mg, 88%).

R_f = 0.41 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 6.42 (s, 1H, Ar**H**), 6.31

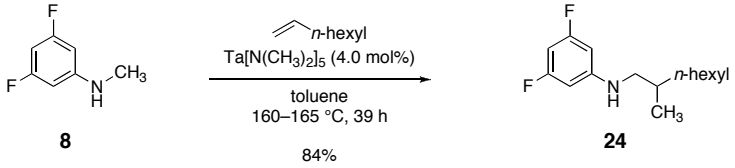
(s, 2H, Ar**H**), 3.64 (br, 1H, N**H**), 3.09 (dd, 1H, J = 12.0, 6.0 Hz, NC**H**$_2$), 2.92 (dd, 1H, J = 12.0, 7.5 Hz, NC**H**$_2$), 2.31 (s, 6H, ArC**H**$_3$), 1.82–1.75 (m, 1H, NHCH$_2$C**H**), 1.54–1.21 (m, 10H, NHCH$_2$CH(CH$_3$)(C**H**$_2$)$_5$CH$_3$), 1.03 (d, 3H, J = 7.0 Hz, NHCH$_2$CHC**H**$_3$), 0.97 (t, 3H, J = 7.0 Hz, NHCH$_2$CH(CH$_3$)(CH$_2$)$_5$C**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 148.7, 138.7, 118.9, 110.5, 50.3, 34.8, 32.9, 31.9, 29.6, 26.9, 22.6, 21.4, 18.0, 14.1. IR (NaCl, thin film), cm^{-1} 3417 (m), 2956 (s), 2855 (s), 1603 (s), 1467 (m). Anal. Calcd for $C_{17}H_{29}N$: C, 82.52; H, 11.81; N, 5.66. Found: C, 82.57; H, 11.98; N, 5.52.



Alkylation of *N*-Methyl-3,5-di-*tert*-butylaniline (**6**) with 1-Octene (Alkylaniline **23**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (16.0 mg, 40.0 μmol, 0.04 equiv), toluene (400 μL), *N*-methyl-3,5-di-*tert*-butylaniline (**6**, 217 mg, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and 1-octene (235 μL, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 32 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 2.5% ethyl acetate-hexanes) to provide the alkylaniline **23** as a clear, colorless oil (305 mg, 93%).

R_f = 0.64 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 6.79 (t, 1H, J = 1.5 Hz, Ar**H**), 6.48 (d, 2H, J = 2.0 Hz, Ar**H**), 3.62 (br, 1H, N**H**), 3.08 (dd, 1H, J = 11.5, 5.5 Hz, NC**H**$_2$), 2.89 (dd, 1H, J = 11.5, 7.2 Hz, NC**H**$_2$), 1.80–1.72 (m, 1H, NHCH$_2$C**H**), 1.50–1.17 (m, 10H, NHCH$_2$CH(CH$_3$)(C**H**$_2$)$_5$CH$_3$), 1.00 (d, 3H, J = 7.0 Hz, NHCH$_2$CHC**H**$_3$), 0.90 (t, 3H, J = 6.7 Hz, NHCH$_2$CH(CH$_3$)(CH$_2$)$_5$C**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 151.6, 147.9, 111.8, 107.3, 50.5, 34.8, 34.8, 33.0, 31.9, 31.4, 29.6, 27.0, 22.7, 18.3, 14.1. IR (NaCl, thin film), cm^{-1} 3419 (w), 2926 (s), 2859 (m), 1600 (s), 1456 (m). Anal. Calcd for $C_{23}H_{41}N$: C, 83.13; H, 12.46; N, 4.22. Found: C, 83.38; H, 12.30; N, 4.42.

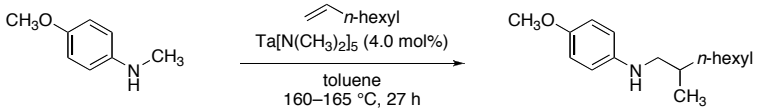


Alkylation of *N*-Methyl-3,5-difluoroaniline (**8**) with 1-Octene (Alkylaniline **24**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (16.0 mg, 40.0 μmol, 0.04 equiv), toluene (400 μL), *N*-methyl-3,5-difluoroaniline (**8**, 143 mg, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and 1-octene (235 μL, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 39 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 1% ethyl acetate-hexanes) to provide the alkylaniline **24** as a clear, colorless oil (215 mg, 84%).

R_f = 0.35 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 6.12–6.03 (m, 3H Ar**H**), 3.92 (br, 1H, N**H**), 3.00 (dt, 1H, J = 12.5, 5.7 Hz, NC**H**$_2$), 2.84 (ddd, 1H, J = 12.2, 7.2, 5.2 Hz, NC**H**$_2$), 1.76–1.68 (m, 1H, NHCH$_2$C**H**), 1.44–1.14 (m, 10H, NHCH$_2$CH(CH$_3$)(C**H**$_2$)$_5$CH$_3$), 0.96 (d, 3H, J = 6.5 Hz, NHCH$_2$CHC**H**$_3$), 0.90 (t, 3H, J = 7.0 Hz, NHCH$_2$CH(CH$_3$)(CH$_2$)$_5$C**H**$_3$). ^{13}C NMR (125 MHz,

$CDCl_3$), δ 164.1 (dd, J = 242, 16.6 Hz), 150.8 (t, J = 13.6 Hz), 95.1 (m), 91.8 (t, J = 26.2 Hz), 50.6, 34.6, 32.8, 31.8, 29.5, 26.9, 22.6, 17.9, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$), δ –111.0. IR (NaCl, thin film), cm^{-1} 3440 (w), 2928 (s), 2856 (m), 1637 (s), 1593 (s). Anal. Calcd for $C_{15}H_{23}F_2N$: C, 70.56; H, 9.08; N, 5.49. Found: C, 70.83; H, 8.77; N, 5.75.

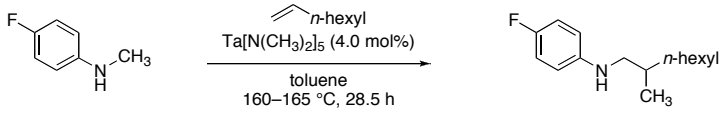


25 **26**

Alkylation of *N*-Methyl-4-methoxyaniline (**25**) with 1-Octene (Alkylaniline **26**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (16.0 mg, 40.0 μmol, 0.04 equiv), toluene (400 μL), *N*-methyl-4-methoxyaniline (**25**, 137 mg, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and 1-octene (235 μL, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 27 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 2.5% ethyl acetate-hexanes initially, grading to 5% ethyl acetate-hexanes) to provide the alkylaniline **26** as a clear, colorless oil (225 mg, 90%).

R_f = 0.33 (5% ethyl acetate-hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$), δ 6.78 (d, 2H, J = 8.5 Hz, Ar**H**), 6.59 (d, 2H, J = 8.5 Hz, Ar**H**), 3.75 (s, 3H, O**CH**$_3$), 3.58 (br, 1H, N**H**), 3.01 (dd, 1H, J = 12.0, 5.5 Hz, NC**H**$_2$), 2.84 (dd, 1H, J = 12.0, 7.5 Hz, NC**H**$_2$), 1.76–1.68 (m, 1H, NHCH$_2$C**H**), 1.46–1.14 (m, 10H, NHCH$_2$CH(CH$_3$)(C**H**$_2$)$_5$CH$_3$), 0.96 (d, 3H, J = 7.0 Hz, NHCH$_2$CHC**H**$_3$), 0.89 (t, 3H, J = 7.0 Hz, NHCH$_2$CH(CH$_3$)(CH$_2$)$_5$C**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 151.9, 142.8, 114.9, 114.0, 55.8, 51.4, 34.8, 32.8, 31.8, 29.6, 26.9, 22.6, 18.0, 14.1. IR (NaCl, thin film), cm^{-1} 3410 (w), 2926 (s), 2870 (m), 1514 (s), 1465 (m). Anal. Calcd for $C_{16}H_{27}NO$: C, 77.06; H, 10.91; N, 5.62. Found: C, 77.41; H, 11.06; N, 5.94.



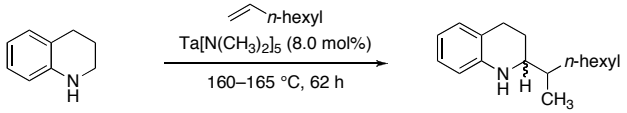
27 **28**

Alkylation of *N*-Methyl-4-fluoroaniline (**27**) with 1-Octene (Alkylaniline **28**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (16.0 mg, 40.0 μmol, 0.04 equiv), toluene (400 μL), *N*-methyl-4-fluoroaniline (**27**, 96.0 μL, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and 1-octene (235 μL, 1.50 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 28.5 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 2.5% ethyl acetate-hexanes initially, grading to 5% ethyl acetate-hexanes) to provide the alkylaniline **28** as a clear, colorless oil (184 mg, 78%).

R_f = 0.44 (5% ethyl acetate-hexanes; UV, CAM). ^{1}H NMR (500 MHz, $CDCl_3$), δ 6.92–6.85 (m, 2H Ar**H**), 6.55–6.51 (m, 2H Ar**H**), 3.55 (br, 1H, N**H**), 3.01 (dd, 1H, J = 12.0, 6.0 Hz, NC**H**$_2$), 2.84 (dd, 1H, J = 12.0, 7.0 Hz, NC**H**$_2$), 1.76–1.68 (m, 1H, NHCH$_2$C**H**), 1.46–1.14 (m, 10H, NHCH$_2$CH(CH$_3$)(C**H**$_2$)$_5$CH$_3$), 0.97 (d,

3H, J = 6.5 Hz, $NHCH_2CHCH_3$), 0.90 (t, 3H, J = 7.0 Hz, $NHCH_2CH(CH_3)(CH_2)_5CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 155.5 (d, J = 232 Hz), 145.0, 115.6 (d, J = 22.4 Hz), 113.3 (d, J = 7.7 Hz), 51.0, 34.8, 32.9, 31.9, 29.6, 26.9, 22.7, 18.0, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$), δ –129.8. IR (NaCl, thin film), cm^{-1} 3427 (w), 2926 (m), 2856 (m), 1511 (s). Anal. Calcd for $C_{15}H_{24}FN$: C, 75.90; H, 10.19; N, 5.90. Found: C, 76.18; H, 10.32; N, 6.22.

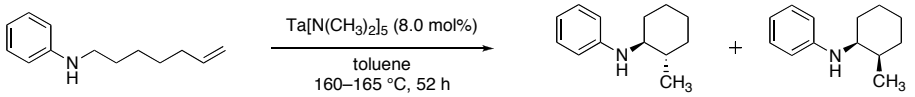


29 **30**

Alkylation of 1,2,3,4-Tetrahydroquinoline (**29**) with 1-Octene (Alkylaniline **30**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (32.0 mg, 80.0 μmol, 0.08 equiv), 1,2,3,4-tetrahydroquinoline (**29**, 125 μL, 1.0 mmol, 1 equiv), a Teflon-coated stir bar, and 1-octene (391 μL, 2.50 mmol, 2.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 62 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 2.5% ethyl acetate-hexanes initially, grading to 5% ethyl acetate-hexanes) to provide the alkylaniline **30** as a clear, colorless oil (177 mg, 72%, relative stereochemistry not assigned).

R_f = 0.43 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$), δ 7.00–6.94 (m, 2H, Ar**H**), 6.60 (t, 1H, J = 7.5 Hz, Ar**H**), 6.50 (d, 1H, J = 8.0 Hz, Ar**H**), 3.75 (br, 1H, N**H**), 3.21–3.17 (m, 1H, NC**H**), 2.86–2.80 (m, 1H, $ArCH_2$), 2.74 (ddd, 1H, J = 16.0, 5.0, 3.5 Hz, $ArCH_2$), 1.89–1.84 (m, 1H, $ArCH_2CH_2$), 1.75–1.67 (m, 1H, $ArCH_2CH_2$), 1.59–1.14 (m, 11H, NHCHC**H**, 10 × $NHCHCH(CH_3)(CH_2)_5CH_3$), 0.97 (d, 3H, J = 7.0 Hz, $NHCHCHCH_3$), 0.90 (t, 3H, J = 7.0 Hz, $NHCHCH(CH_3)(CH_2)_5CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 145.1, 129.1, 126.7, 121.5, 116.7, 114.0, 56.1, 37.6, 32.6, 31.9, 29.6, 27.5, 27.0, 24.9, 22.7, 15.1, 14.1. IR (NaCl, thin film), cm^{-1} 3414 (w), 2926 (s), 2856 (m), 1607 (m), 1484 (m). Anal. Calcd for $C_{17}H_{27}N$: C, 83.20; H, 11.09; N, 5.71. Found: C, 83.18; H, 11.07; N, 5.91.



10 **31** **32**

Cyclization of *N*-(7-Heptenyl)-aniline (**10**) (*trans*-2-Methyl-1-(phenylamino)cyclohexane **31** and *cis*-2-Methyl-1-(phenylamino)cyclohexane **32**):

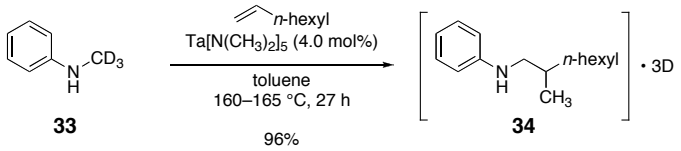
In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (32.0 mg, 80.0 μmol, 0.08 equiv), toluene (400 μL), *N*-(7-heptenyl)-aniline (**10**, 189 μL, 1.0 mmol, 1 equiv) and a Teflon-coated stir bar. The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 52 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 20% methylene chloride-hexanes) to provide separately the *trans*-2-methyl-1-(phenylamino)cyclohexane (**31**, 86.3 mg, 46%, clear, colorless oil) and *cis*-2-methyl-1-(phenylamino)cyclohexane (**32**, 79.3 mg, 42%, clear, colorless oil). The relative stereochemistry of the products **31** and **32** was assigned by comparison of their ^1H NMR spectral data to that reported in the literature.[9]

trans-2-Methyl-1-(phenylamino)cyclohexane **31**:

R_f = 0.32 (30% methylene chloride-hexanes; UV, $KMnO_4$). ^1H NMR (500 MHz, C_6D_6), δ 7.17 (dd, 2H, J = 8.5, 7.5 Hz, Ar**H**), 6.73 (t, 1H, J = 7.5 Hz, Ar**H**), 6.45 (d, 2H, J = 8.5 Hz, Ar**H**), 2.86 (br, 1H, N**H**), 2.72–2.65 (m, 1H, NHC**H**), 2.04–1.96 (m, 1H, NHCHC**H**CH$_3$), 1.62–1.48 (m, 3H, C**H**$_2$), 1.12–0.86 (m, 7H, C**H**$_3$, 4 × C**H**$_2$), 0.80–0.68 (m, 1H, C**H**$_2$). ^{13}C NMR (125 MHz, C_6D_6), δ 148.6, 129.5, 116.9, 113.3, 57.9, 39.2, 34.9, 33.6, 26.2, 25.7, 19.7. IR (NaCl, thin film), cm^{-1} 3399 (w), 2924 (m), 2853 (m), 1601 (m), 1505 (m). Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.39; H, 9.94; N, 7.12.

cis-2-Methyl-1-(phenylamino)cyclohexane **32**:

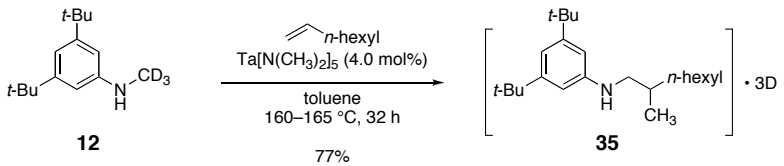
R_f = 0.24 (30% methylene chloride-hexanes; UV, $KMnO_4$). ^1H NMR (500 MHz, C_6D_6), δ 7.17 (dd, 2H, J = 8.5, 7.5 Hz, Ar**H**), 6.73 (t, 1H, J = 7.5 Hz, Ar**H**), 6.48 (d, 2H, J = 9.0 Hz, Ar**H**), 3.32–3.26 (m, 2H, N**H**, NHC**H**), 1.80–1.72 (m, 1H, NHCHC**H**), 1.52–1.20 (m, 8H, C**H**$_2$), 0.76 (d, 3H, J = 7.0 Hz, C**H**$_3$). ^{13}C NMR (125 MHz, C_6D_6), δ 148.2, 129.6, 117.1, 113.6, 53.2, 33.3, 30.3, 28.9, 23.3, 22.9, 15.6. IR (NaCl, thin film), cm^{-1} 3421 (w), 2926 (s), 2853 (m), 1601 (s), 1505 (s). Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.70; H, 10.40; N, 7.63.



Alkylation of *N*-(Methyl-d_3)aniline (**33**)[3] with 1-Octene (Deuterium-labeled Alkylaniline **34**):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (8.0 mg, 20.0 μmol, 0.04 equiv), toluene (200 μL), *N*-(methyl-d_3)-aniline[3] (**33**, 55.6 μL, 500 μmol, 1 equiv), a Teflon-coated stir bar, and 1-octene (117 μL, 750 μmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 27 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 100% hexanes initially, grading to 2.5% ethyl acetate-hexanes) to provide the deuterium-labeled alkylaniline **34** as a clear, colorless liquid (107 mg, 96%).

R_f = 0.40 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^1H NMR (500 MHz, $CDCl_3$), δ 7.20–7.16 (m, 2H, Ar**H**), 6.69 (t, 1H, J = 7.5 Hz, Ar**H**), 6.61 (d, 1.1 H, J = 8.5 Hz, Ar**H**), 3.67 (br, 1H, N**H**), 3.08–3.02 (m, 0.53H, NC**H**$_2$), 2.92–2.86 (m, 0.53H, NC**H**$_2$), 1.78–1.70 (m, 1H, NHCH$_2$C**H**), 1.47–1.16 (m, 10H, NHCH$_2$CH(CH$_3$)(C**H**$_2$)$_5$CH$_3$), 0.99–0.95 (m, 2.64H, J = 6.5 Hz, NHCH$_2$CHC**H**$_3$), 0.91 (t, 3H, J = 7.5 Hz, NHCH$_2$CH(CH$_3$)(CH$_2$)$_5$C**H**$_3$). ^2H NMR (76.8 MHz, $CHCl_3$), δ 6.69 (1D, Ar**D**), 3.08 (0.52D, NCH**D**), 2.91 (0.52D, NCH**D**), 1.02 (0.38D, NHCH$_2$CHCH$_2$**D**).



Alkylation of *N*-(Methyl-d_3)-3,5-di-*tert*-butylaniline (**6**) with 1-Octene (Deuterium-labeled Alkylaniline

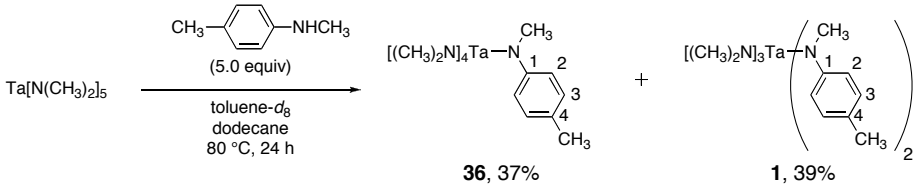
35):

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (8.0 mg, 20.0 μmol, 0.04 equiv), toluene (200 μL), *N*-(methyl-d_3)-3,5-di-*tert*-butylaniline (**12**, 110 mg, 500 μmol, 1 equiv), a Teflon-coated stir bar, and 1-octene (117 μL, 750 μmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 32 h and then was cooled to 22 °C. Without concentration, the product solution was loaded onto a silica gel column and purified by flash-column chromatography (eluting with 2.5% ethyl acetate-hexanes) to provide the deuterium-labeled alkylaniline **35** as a clear, colorless oil (129 mg, 77%).

R_f = 0.64 (5% ethyl acetate-hexanes; UV, $KMnO_4$). ^{1}H NMR (500 MHz, $CDCl_3$), δ 6.78 (s, 1H, Ar**H**), 6.47 (d, 1.68H, J = 2.0 Hz, Ar**H**), 3.60 (br, 1H, N**H**), 3.10–3.04 (m, 0.32H, NC**H**$_2$), 2.91–2.85 (m, 0.32H, NC**H**$_2$), 1.77–1.70 (m, 1H, NHCH$_2$C**H**), 1.48–1.16 (m, 10H, NHCH$_2$CH(CH$_3$)(C**H**$_2$)$_5$CH$_3$), 1.00–0.95 (m, 2.50H, NHCH$_2$CHC**H**$_3$), 0.89 (t, 3H, J = 6.7 Hz, NHCH$_2$CH(CH$_3$)(CH$_2$)$_5$C**H**$_3$). ^{2}H NMR (76.8 MHz, $CHCl_3$), δ 6.55 (0.21D, Ar**D**), 3.09 (0.50D, NCH**D**), 2.90 (0.50D, NCH**D**), 1.03 (0.34D, NHCH$_2$CHCH$_2$**D**).

Preparation of the Bisanilide Complex [(*p*-Tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**) and the Trisanilide Complex [(*p*-Tol)MeN]$_3$Ta(NMe$_2$)$_2$ (**2**):

Studies were conducted to determine the extent of amine exchange in solution. It was found that warming a sealed tube containing Ta(NMe$_2$)$_5$ and *N*-methyl-*para*-toluidine (5.0 equiv) in toluene-d_8 to 80 °C for 24 h resulted in formation of the monoanilide complex [(*p*-Tol)MeN]Ta(NMe$_2$)$_4$ (**36**) and the bisanilide complex [(*p*-Tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**; 37% and 39% yield, respectively, determined against an internal standard).



36, 37% **1**, 39%

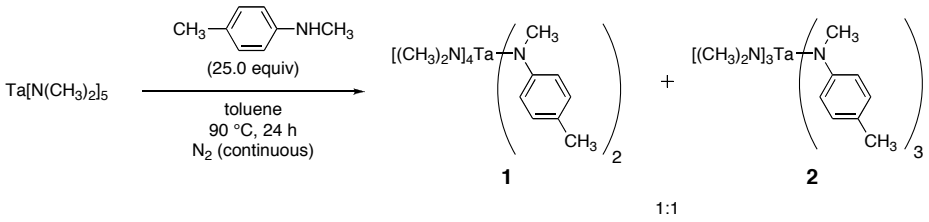
Amine Exchange Under Mild Conditions {Monoanilide Complex [(*p*-Tol)MeN]Ta(NMe$_2$)$_4$ (**36**) and Bisanilide Complex [(*p*-Tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**)}:

In a nitrogen-filled drybox, a 7-inch NMR tube was charged sequentially with pentakis(dimethylamino)tantalum (15.4 mg, 38.4 μmol, 1 equiv), dodecane (10.0 μL, 44.0 μmol, 1.14 equiv), *N*-methyl-*para*-toluidine (24.2 μL, 192 μmol, 5.0 equiv) and toluene-d_8 (384 μL). The tube was fitted with a Cajon adaptor and removed from the drybox. The reaction mixture was frozen in liquid nitrogen, and the headspace above the frozen solution was evacuated (<0.1 Torr). The evacuated tube was flame-sealed, and the sealed tube was placed in a preheated oil bath (80 °C) for 24 h. The product mixture was allowed to cool to 22 °C and was analyzed by ^{1}H NMR spectroscopy. The monoanilide complex [(*p*-Tol)MeN]Ta(NMe$_2$)$_4$ (**36**) and the bisanilide complex [(*p*-Tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**) were identified in solution by ^{1}H, ^{13}C, HMQC and HMBC NMR analysis (37% and 39% yield, respectively, determined by integration against dodecane).

NMR data for Monoanilide Complex [(*p*-Tol)MeN]Ta(NMe$_2$)$_4$ (**36**) and Bisanilide Complex [(*p*-Tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**)}:

	Position	δ H, mult, int., *J* (Hz)	δ C	HMBC (H → C)
[(*p*-tol)MeN]Ta(NMe$_2$)$_4$ (**36**)	N(CH$_3$)$_2$	3.21 (s, 24H)	46.5	—
	ArNCH$_3$	3.23 (s, 3H)	35.3	C$_1$
	1	—	152.7	—
	2	6.55 (d, 2H, J = 9.0)	114.5	C$_3$, C$_4$
	3	7.03 (d, 2H, J = 8.5)	129.4/129.3	C$_1$, C$_2$, ArCH$_3$
	4	—	125.5	—
	ArCH$_3$	2.26 (s, 3H)	20.6/20.7	C$_3$, C$_4$
[(*p*-tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**)	N(CH$_3$)$_2$	3.19 (s, 18H)	47.5	—
	ArNCH$_3$	3.34 (s, 6H)	36.3	C$_1$
	1	—	152.7	—
	2	6.76 (d, 4H, J = 8.5)	116.1	C$_3$, C$_4$
	3	7.04 (d, 4H, J = 8.5)	129.4/129.3	C$_1$, C$_2$, ArCH$_3$
	4	—	125.4	—
	ArCH$_3$	2.26 (s, 6H)	20.6/20.7	C$_3$, C$_4$

Heating a solution of Ta(NMe$_2$)$_5$ and *N*-methyl-*para*-toluidine (25.0 equiv) in toluene to 90 °C for 24 h under a stream of nitrogen generated a ~1:1 mixture of the bisanilide complex [(*p*-Tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**) and the trisanilide complex [(*p*-Tol)MeN]$_3$Ta(NMe$_2$)$_2$ (**2**; ^{1}H NMR analysis).



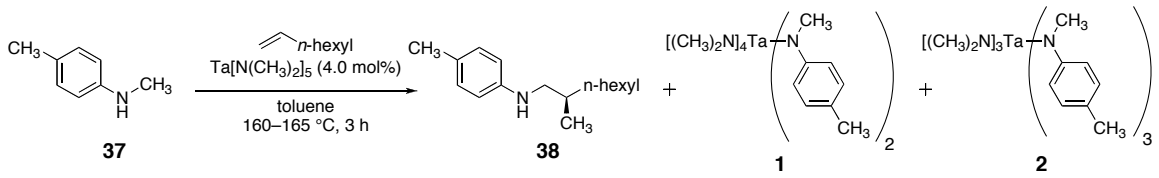
Amine Exchange Driven by Evaporation of Volatile Materials {Bisanilide Complex [(*p*-Tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**) and the Trisanilide Complex [(*p*-Tol)MeN]$_3$Ta(NMe$_2$)$_2$ (**2**)}:

In a nitrogen-filled drybox, a 25-mL round-bottomed flask was charged sequentially with pentakis(dimethylamino)tantalum (101 mg, 253 μmol, 1 equiv), toluene (2.53 mL), and *N*-methyl-*para*-toluidine (800 μL, 6.33 mmol, 25.0 equiv). The flask was fitted with a reflux condenser, and the top of the condenser was sealed with a rubber septum. The assembled apparatus was removed from the drybox, and an inlet for nitrogen gas (21-GA needle) was inserted into the septum. An outlet (21-GA needle) leading to a mineral oil-filled bubbler was then connected. The reaction vessel was warmed to 90 °C under a gentle stream of nitrogen. After heating for 24 h, the product solution was cooled to 22 °C and concentrated to dryness with rigorous exclusion of oxygen and moisture. ^{1}H NMR analysis of the residue obtained indicated the presence of an approximately equimolar mixture of the bisanilide complex [(*p*-Tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**) and the trisanilide complex [(*p*-Tol)MeN]$_3$Ta(NMe$_2$)$_2$ (**2**).

Bisanilide Complex [(*p*-Tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**): See NMR data above.

Trisanilide Complex [(*p*-Tol)MeN]$_3$Ta(NMe$_2$)$_2$ (**2**):

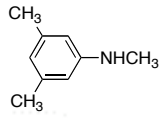
^{1}H NMR (500 MHz, toluene-d_8), δ 7.00–6.96 (m, 2H, NAr**H**), 6.78–6.74 (m, 2H, NAr**H**), 3.29 (s, 9H, ArNC**H**$_3$), 3.20 (s, 12H, N(C**H**$_3$)$_2$), 2.23 (s, 9H, NArC**H**$_3$).



Formation of the Bisanilide Complex [(*p*-Tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**) and the Trisanilide Complex [(*p*-Tol)MeN]$_3$Ta(NMe$_2$)$_2$ (**2**) Under the Conditions of the Catalytic Alkylation:

In a nitrogen-filled drybox, a 1-dram vial was charged sequentially with pentakis(dimethylamino)tantalum (19.7 mg, 49.2 μmol, 0.04 equiv), toluene (492 μL), *N*-(methyl)-*para*-toluidine (**37**, 155 μL, 1.23 mmol, 1 equiv), a Teflon-coated stir bar, and 1-octene (288 μL, 1.84 mmol, 1.50 equiv). The vial was fitted with a Teflon-lined screw-cap and was tightly sealed. The sealed vial was removed from the drybox and placed in a preheated aluminum heating block (160–165 °C). The reaction mixture was heated for 3 h and then was cooled to 22 °C. Volatile materials were evaporated in vacuo, and the residue obtained was dissolved in toluene-d_8. ^{1}H NMR analysis indicated the presence of the bisanilide complex [(*p*-Tol)MeN]$_2$Ta(NMe$_2$)$_3$ (**1**) and the trisanilide complex [(*p*-Tol)MeN]$_3$Ta(NMe$_2$)$_2$ (**2**), as well as the expected alkylaniline **38**. The anilide complexes **1** and **2** were estimated to comprise >70% of the tantalum amido complexes in solution.

3. Catalog of Nuclear Magnetic Resonance and Infrared Spectra



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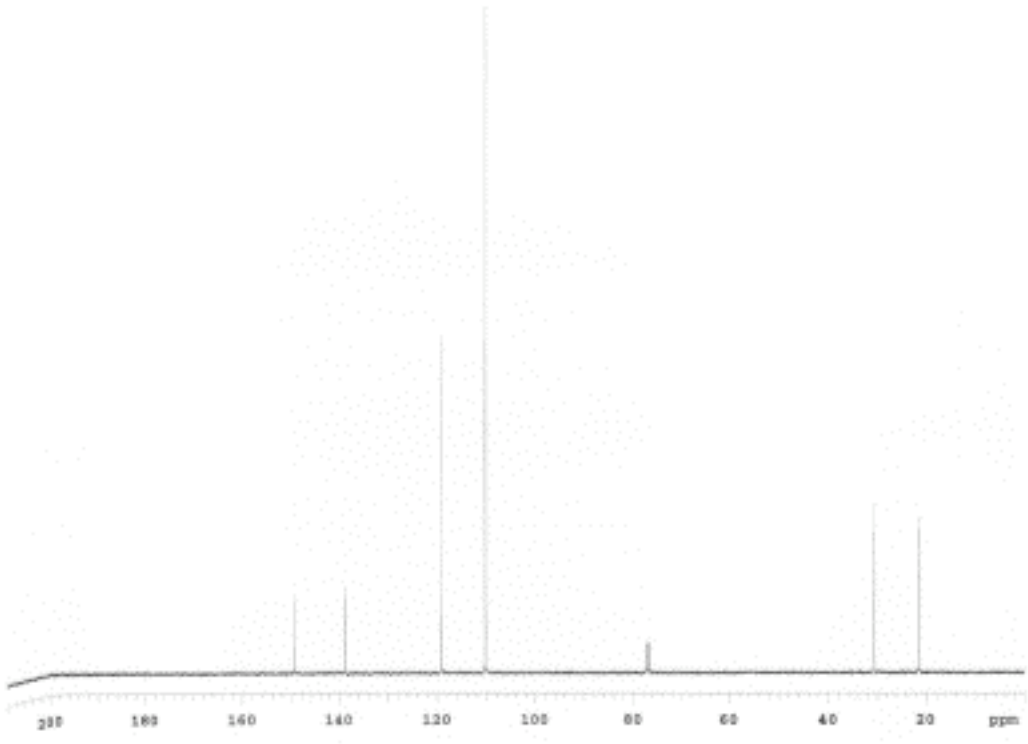

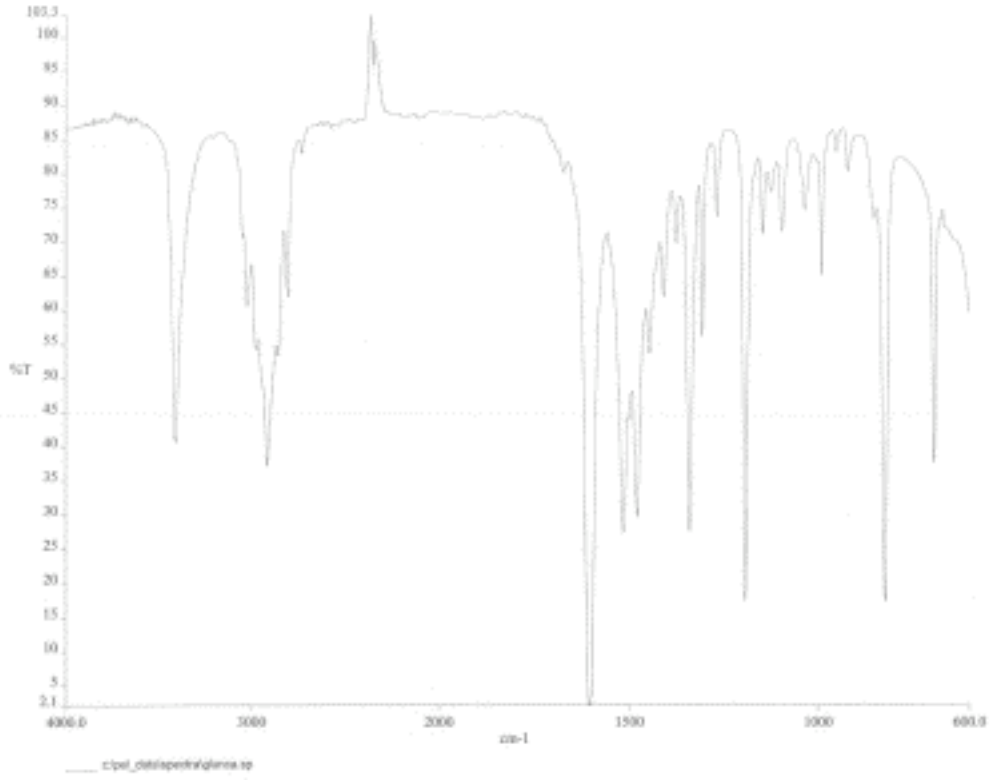
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95
90
85
80
75
70
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60
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%T
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25
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2.1
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3000
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1000
600.0
cm-1
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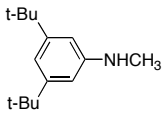
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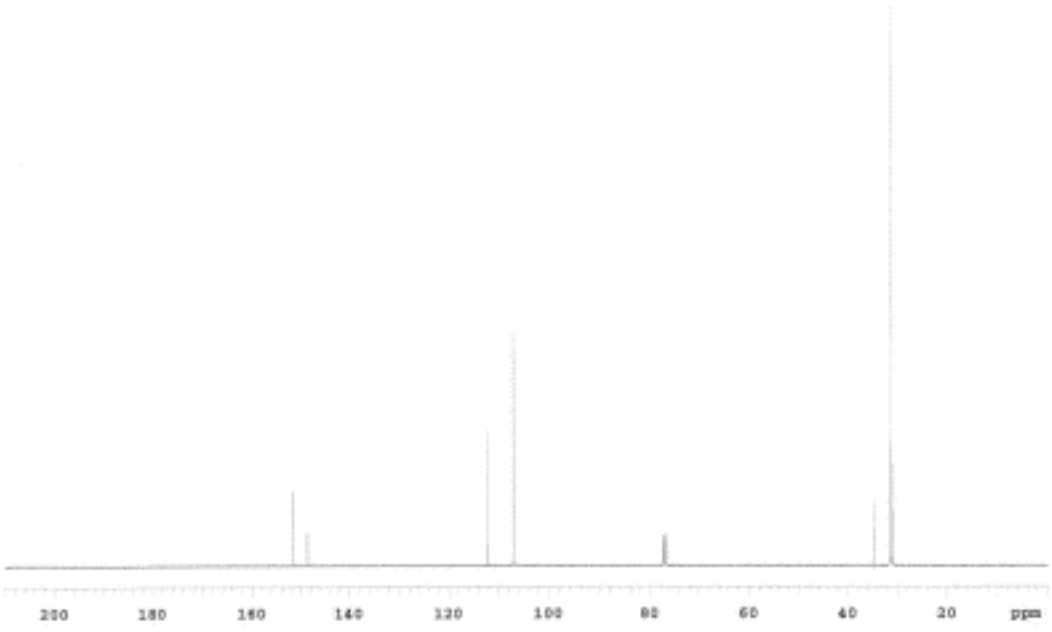
NHCH3
t-Bu

6

9
8
7
6
5
4
3
2
1
ppm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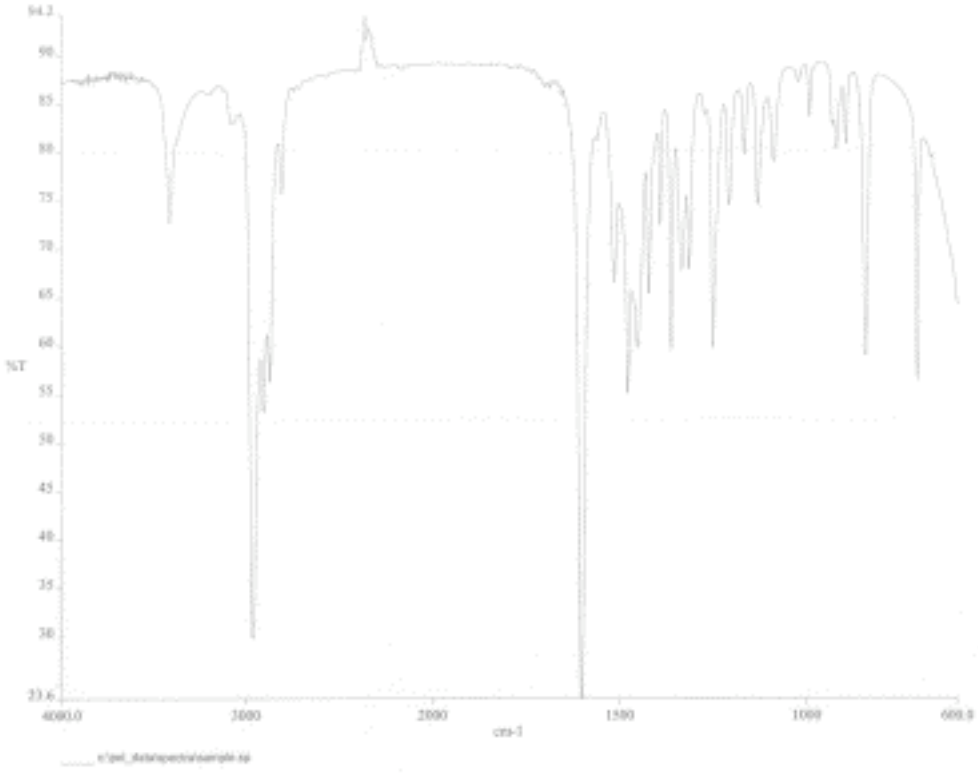
20
ppm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23.6
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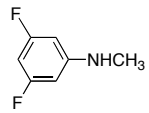
1000
600.0
cm-1



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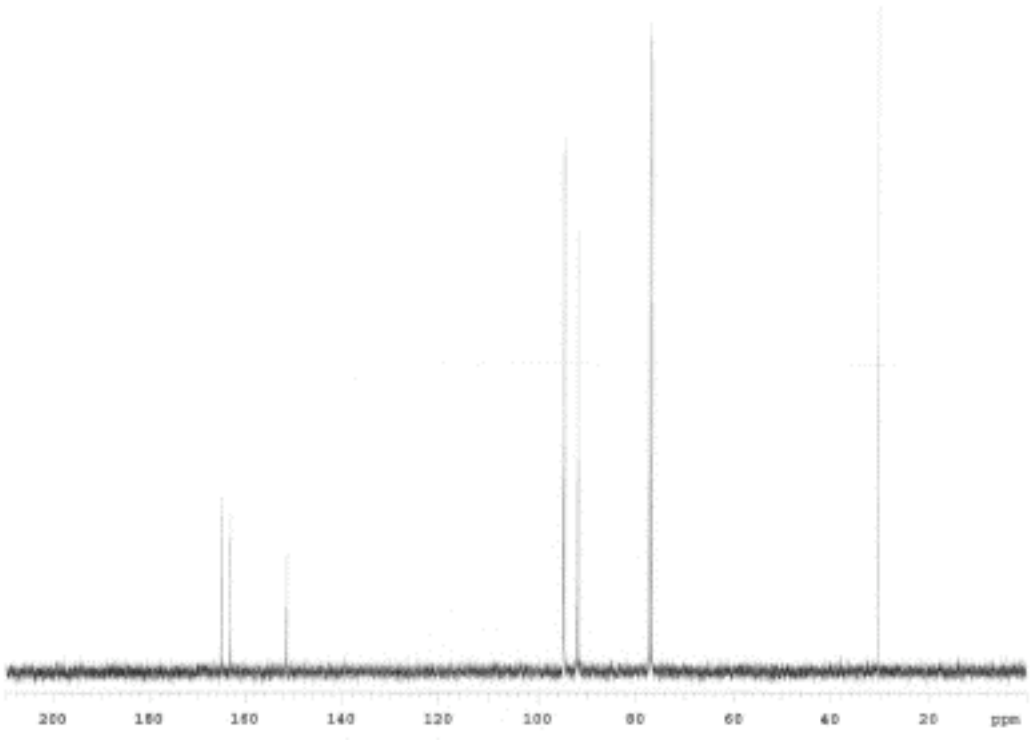

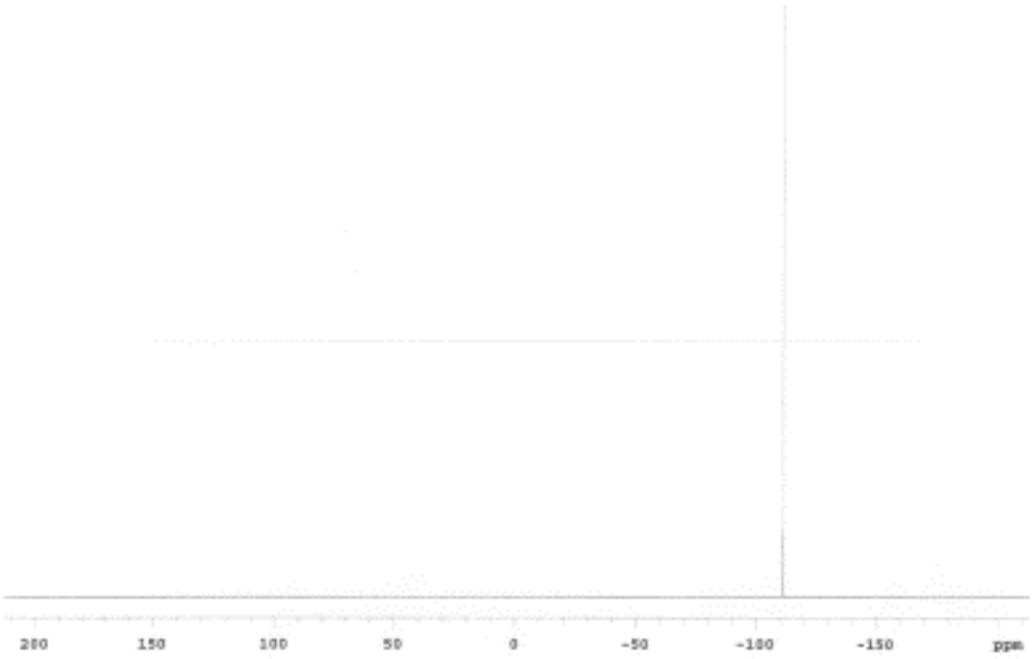
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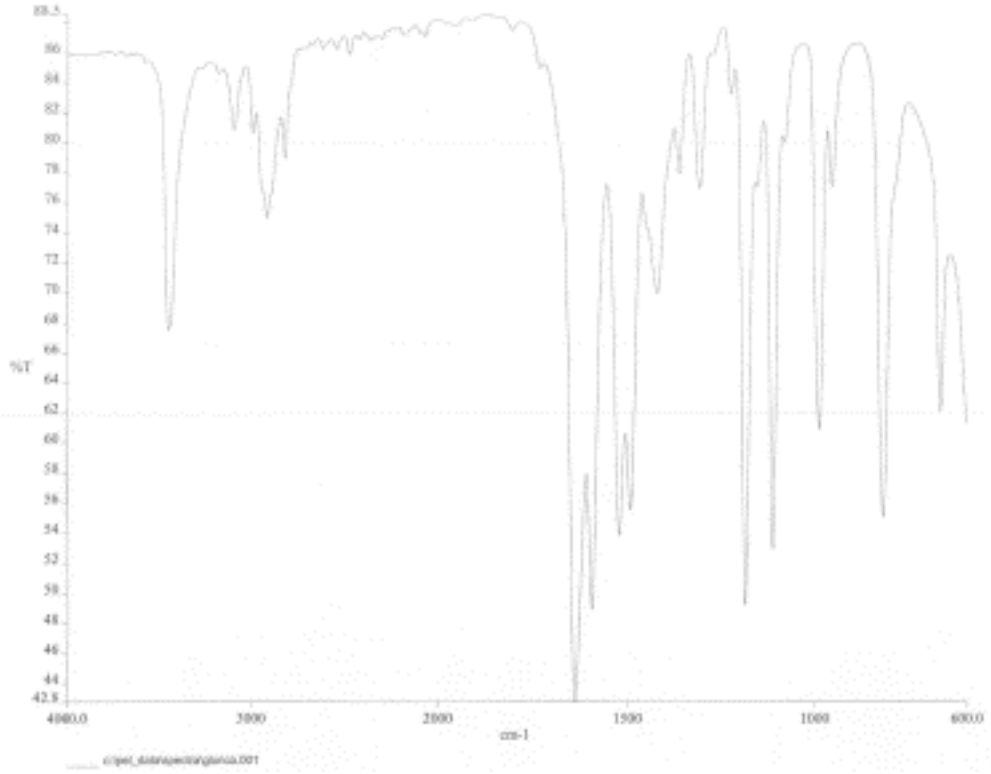
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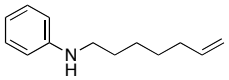
cm-1



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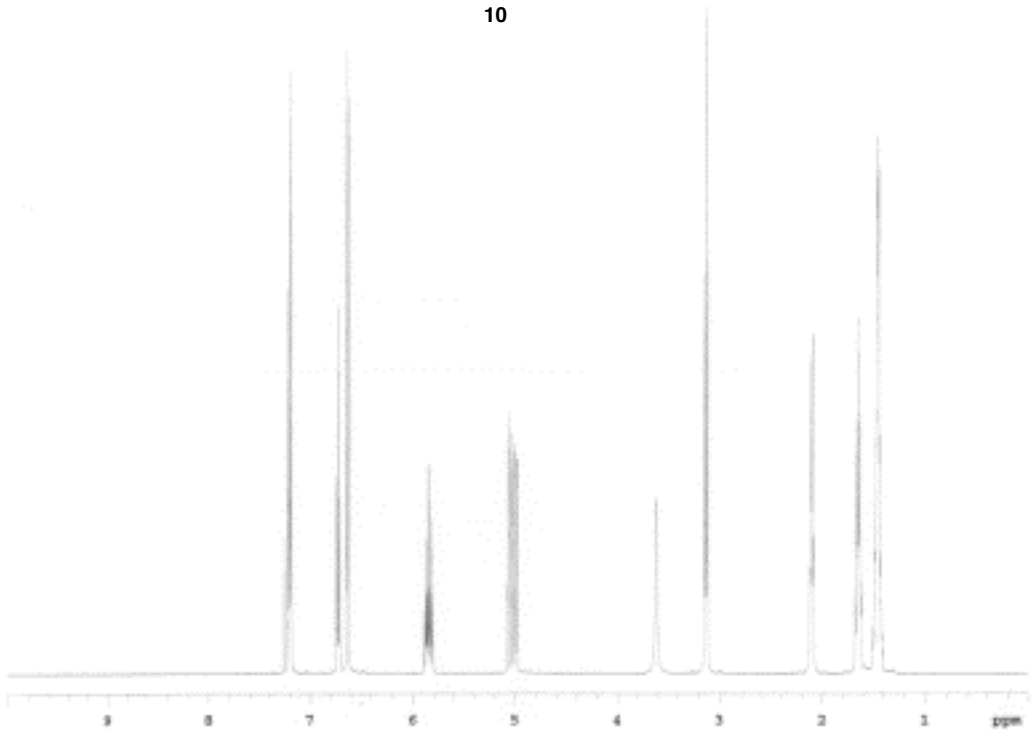

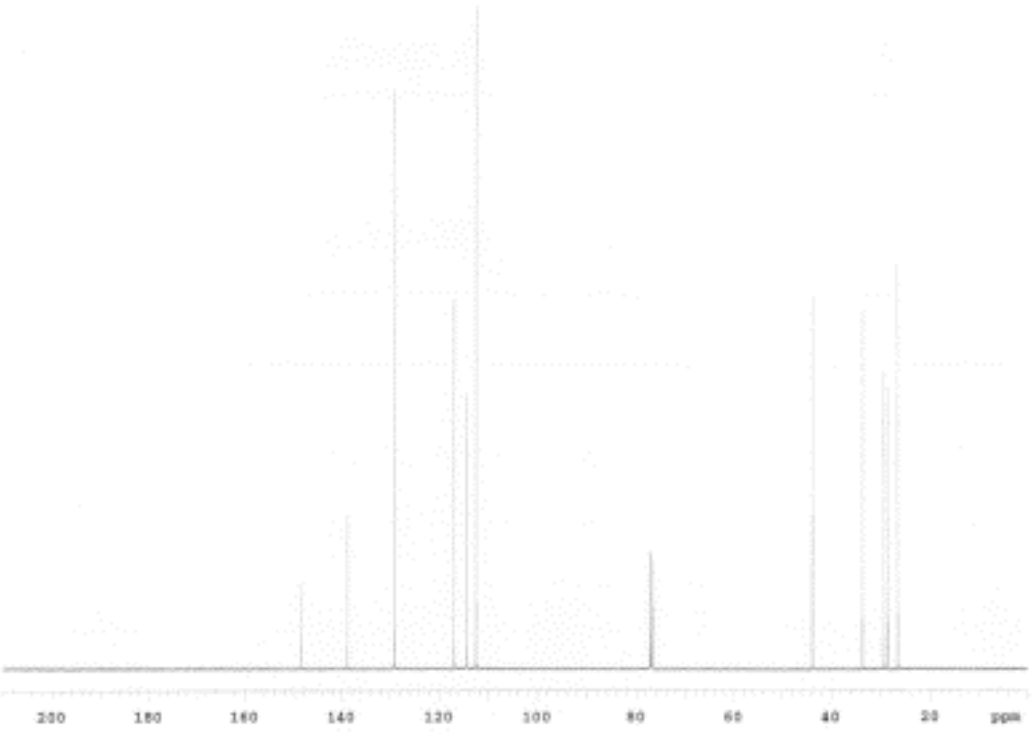

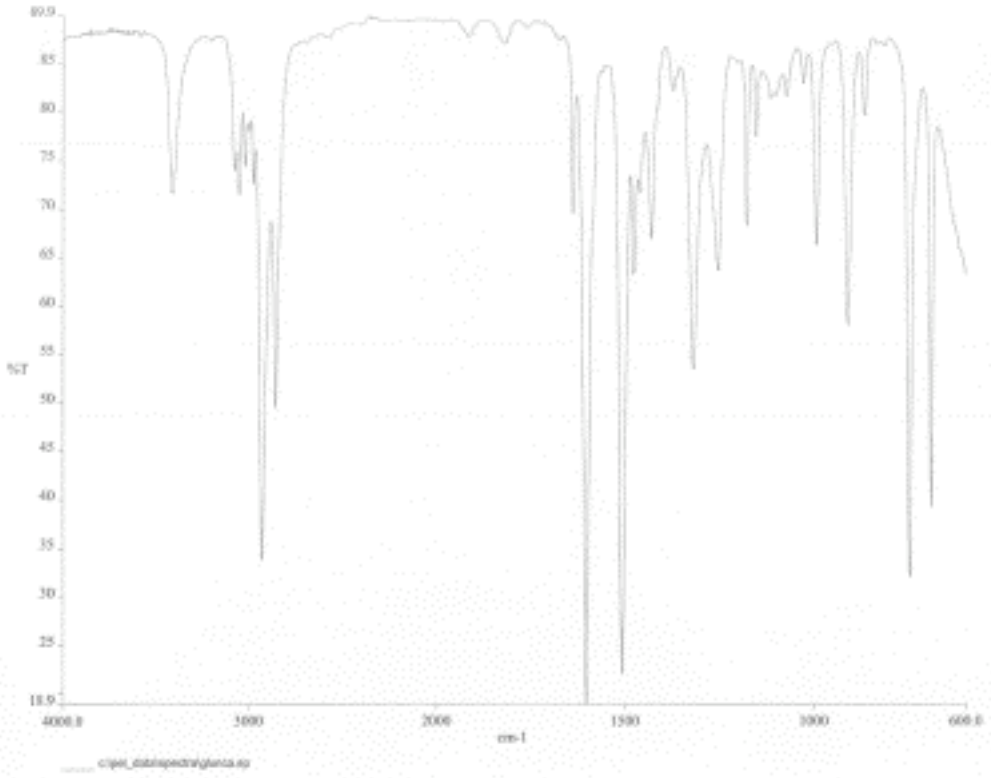
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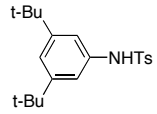
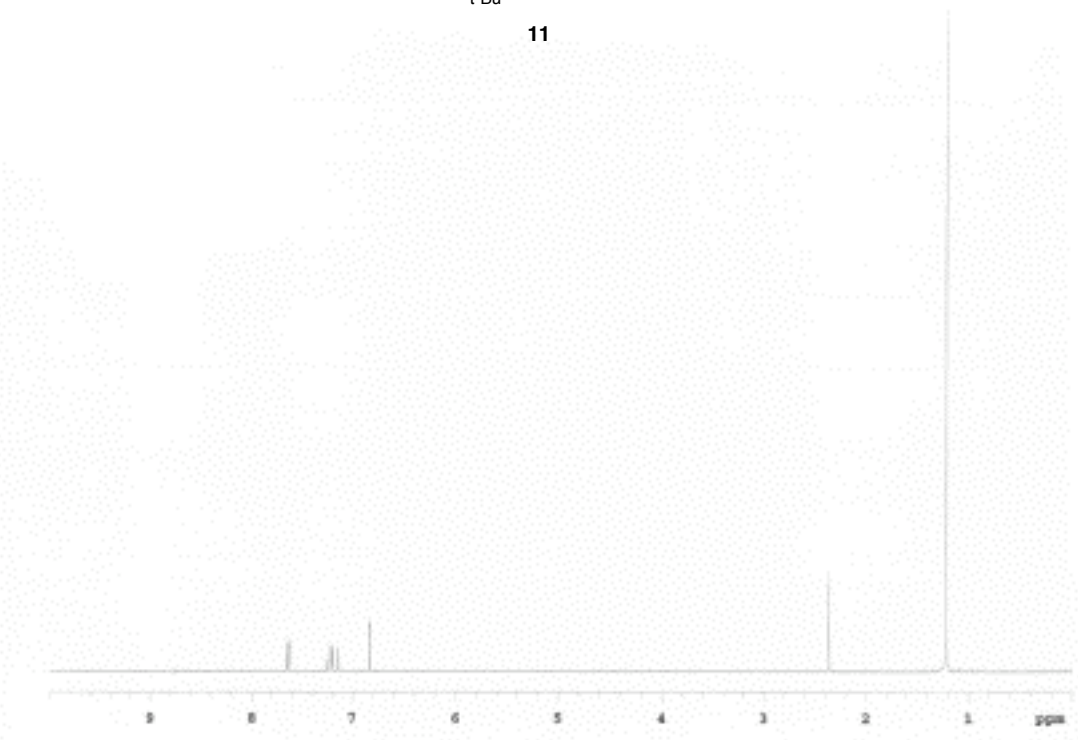

t-Bu
NHTs
t-Bu

11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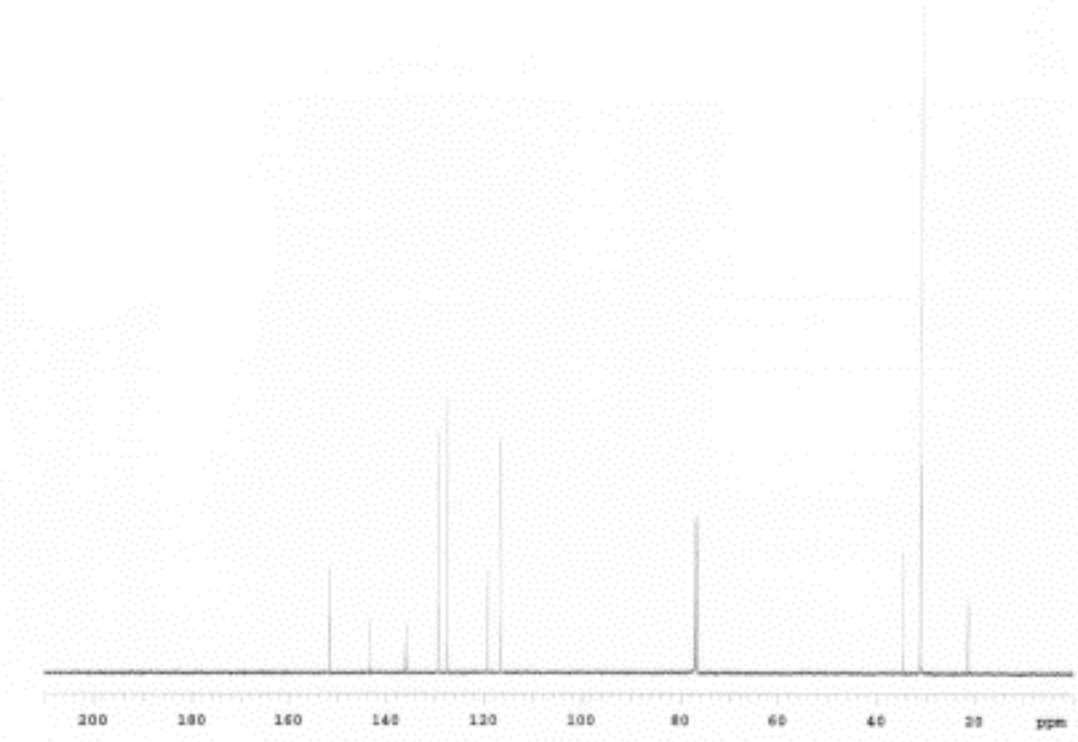
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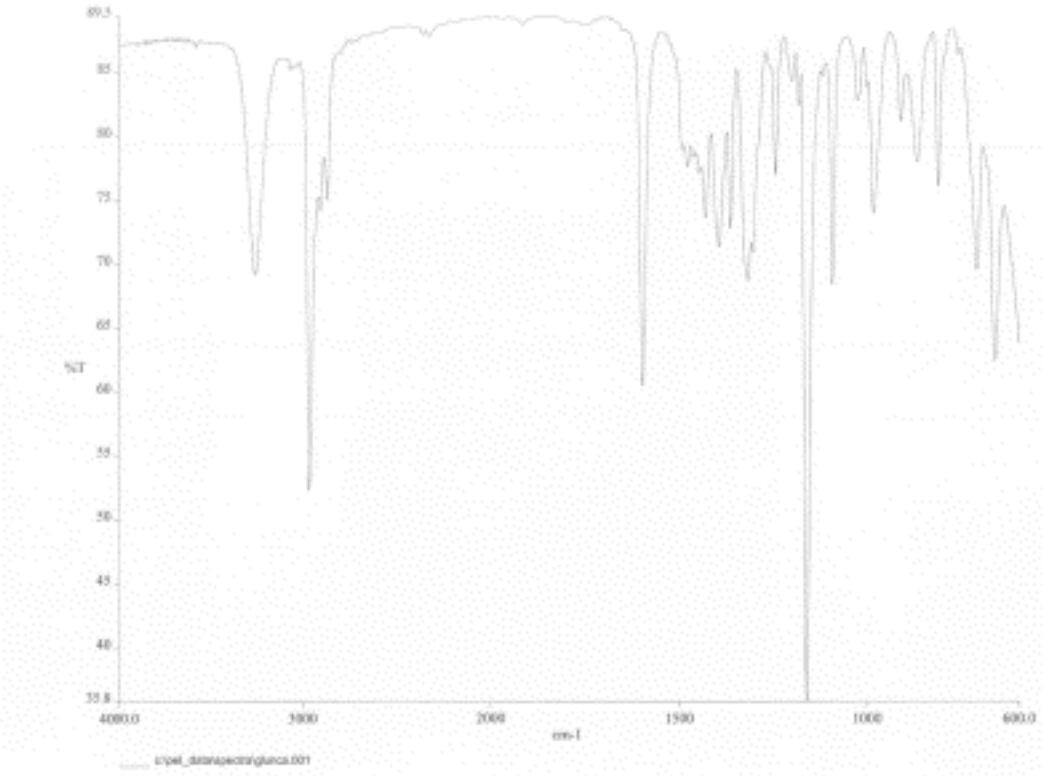
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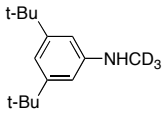
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NHCD3
t-Bu

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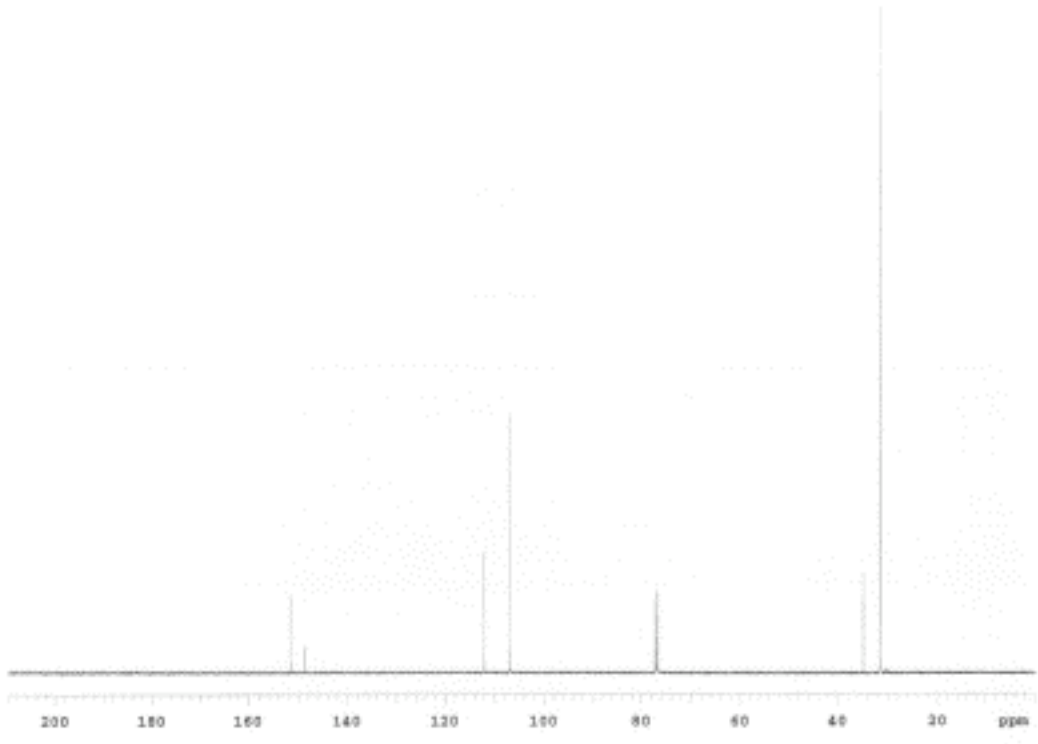
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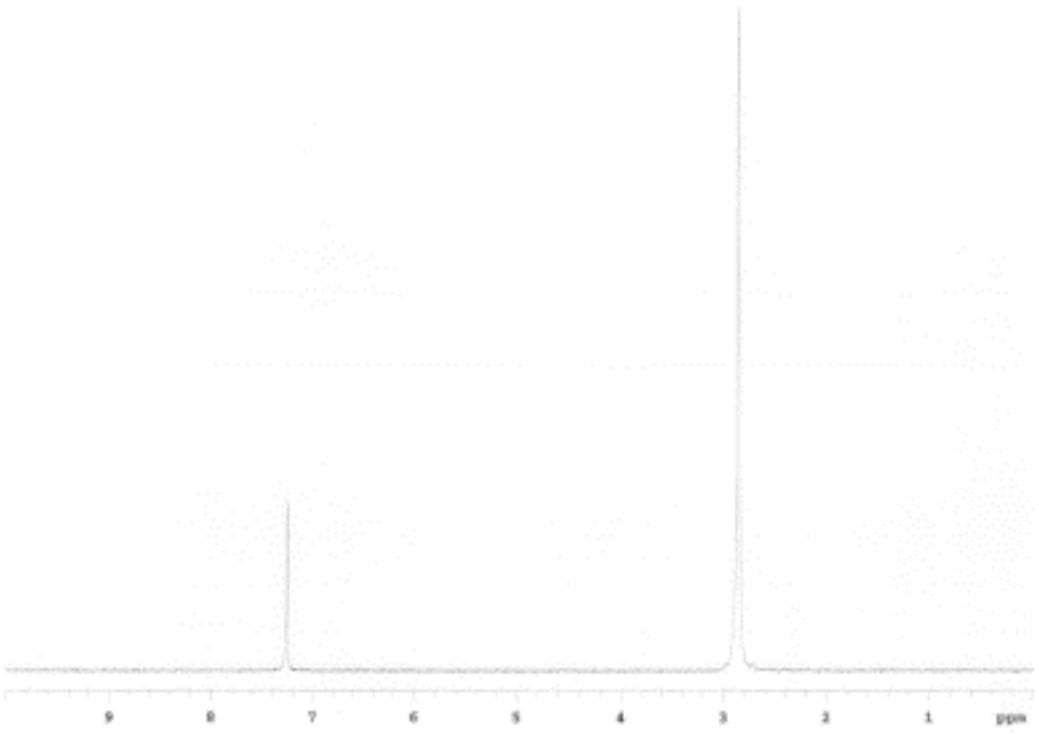
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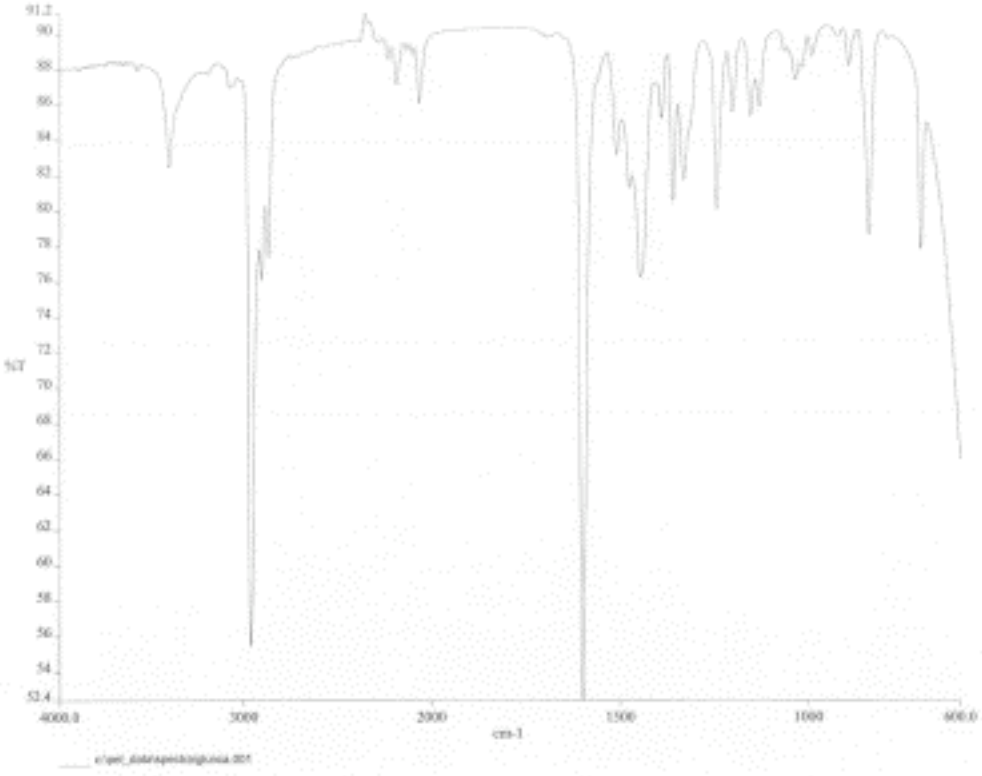
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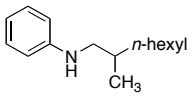
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CH3

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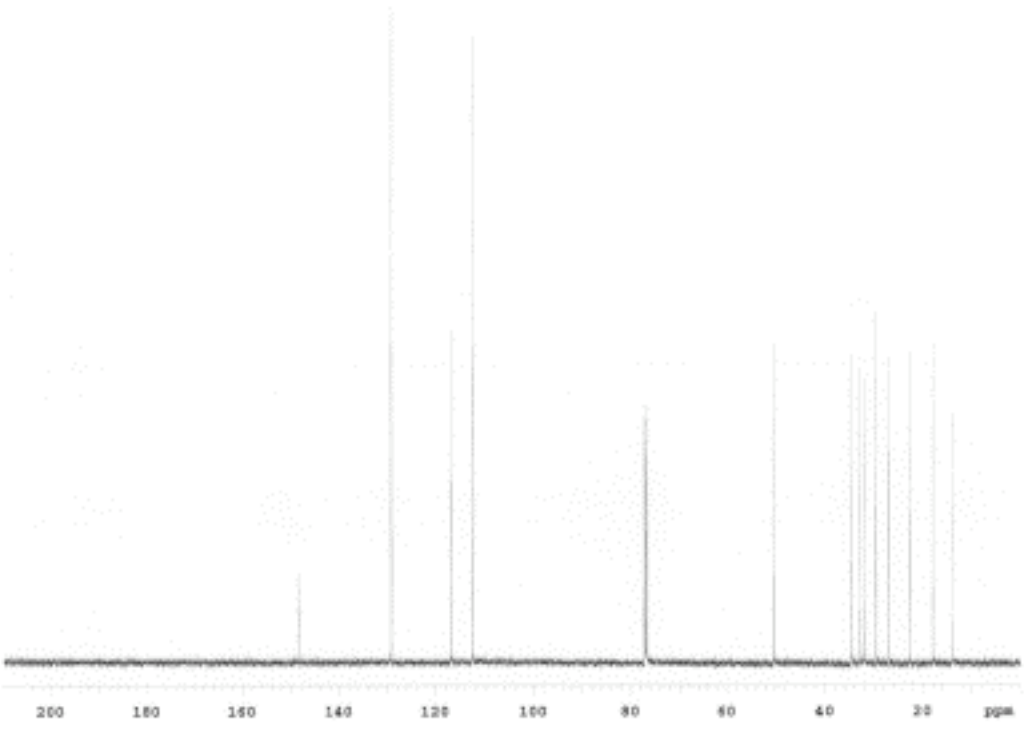
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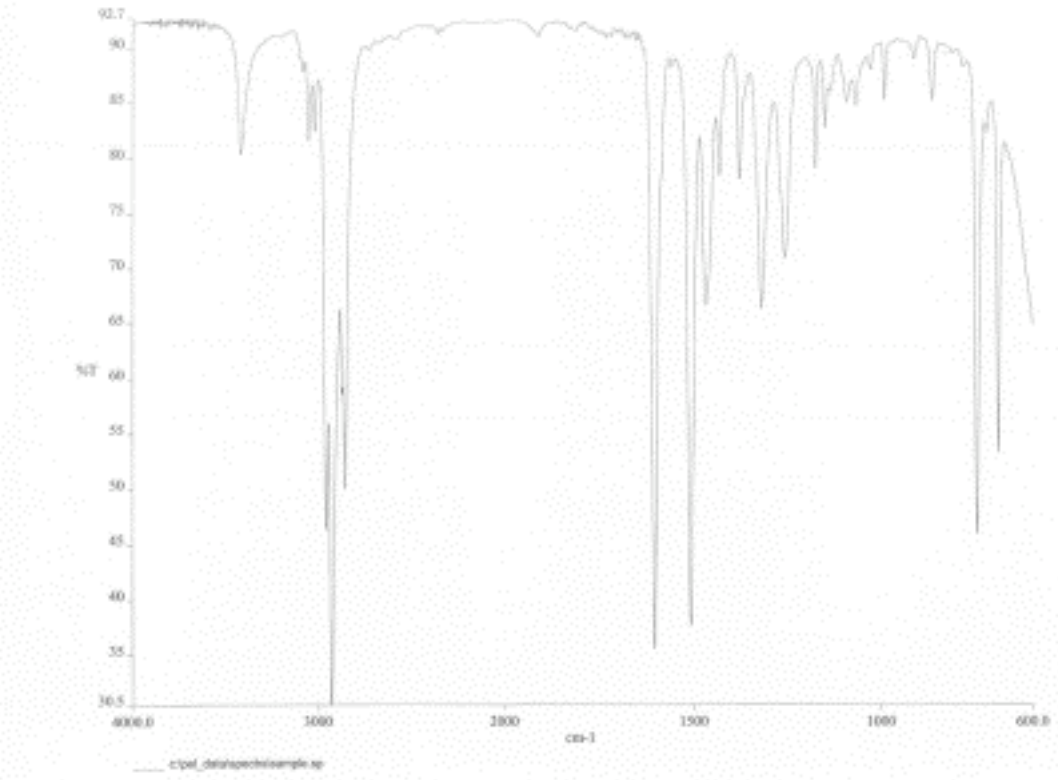
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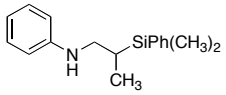
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CH3

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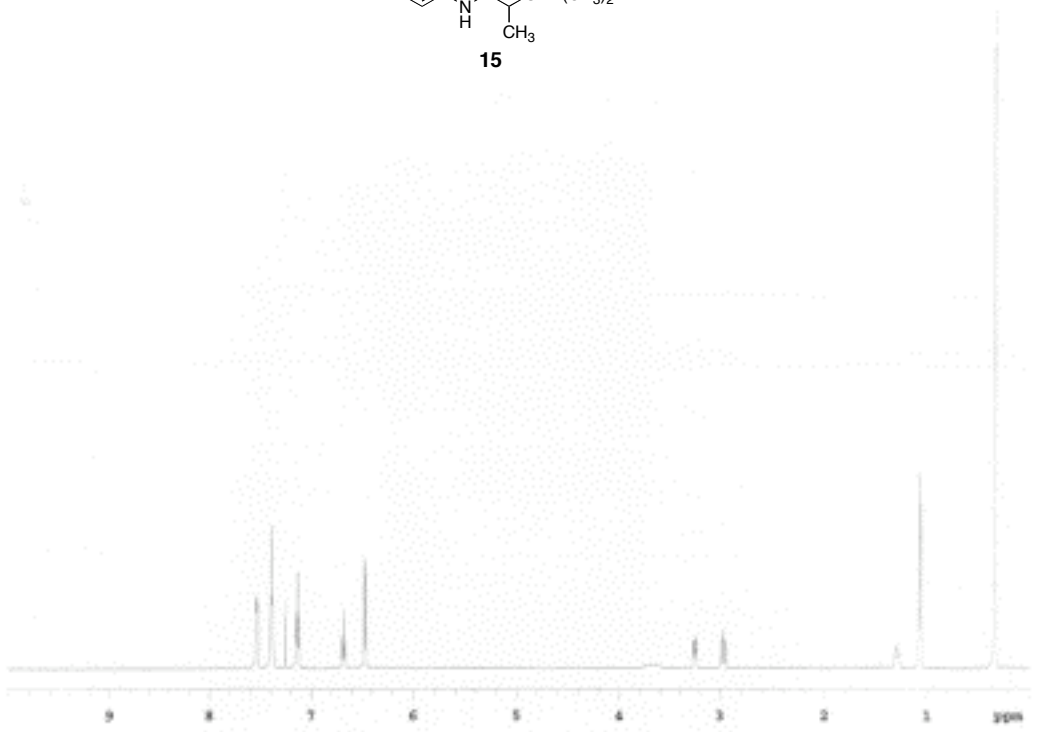
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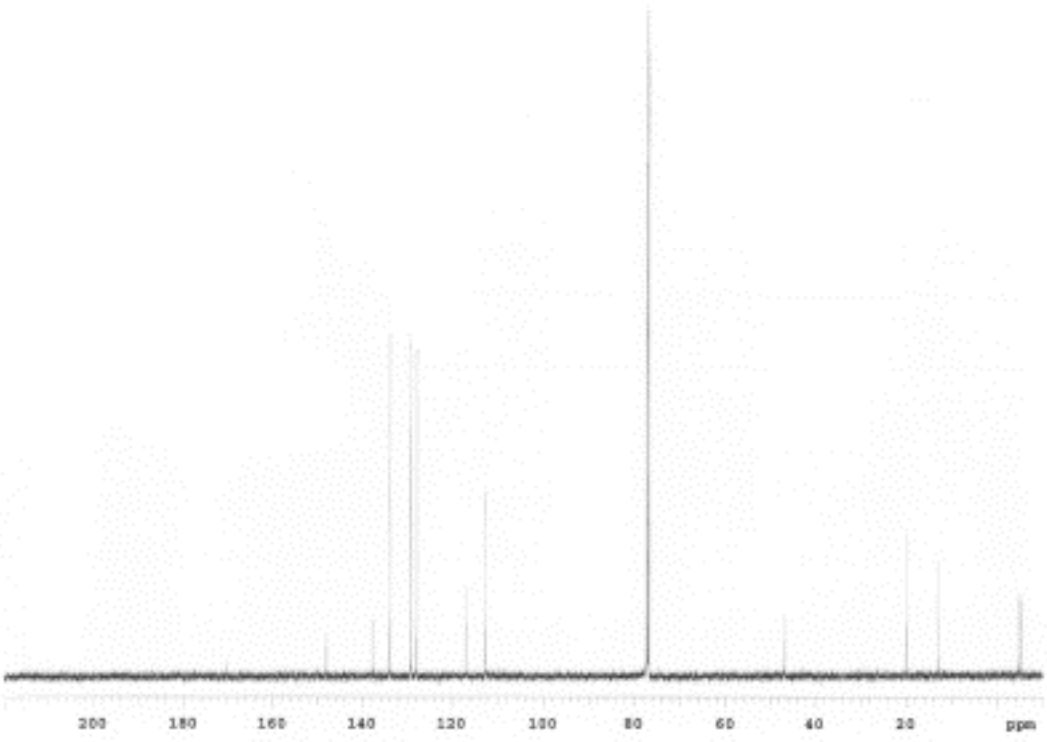
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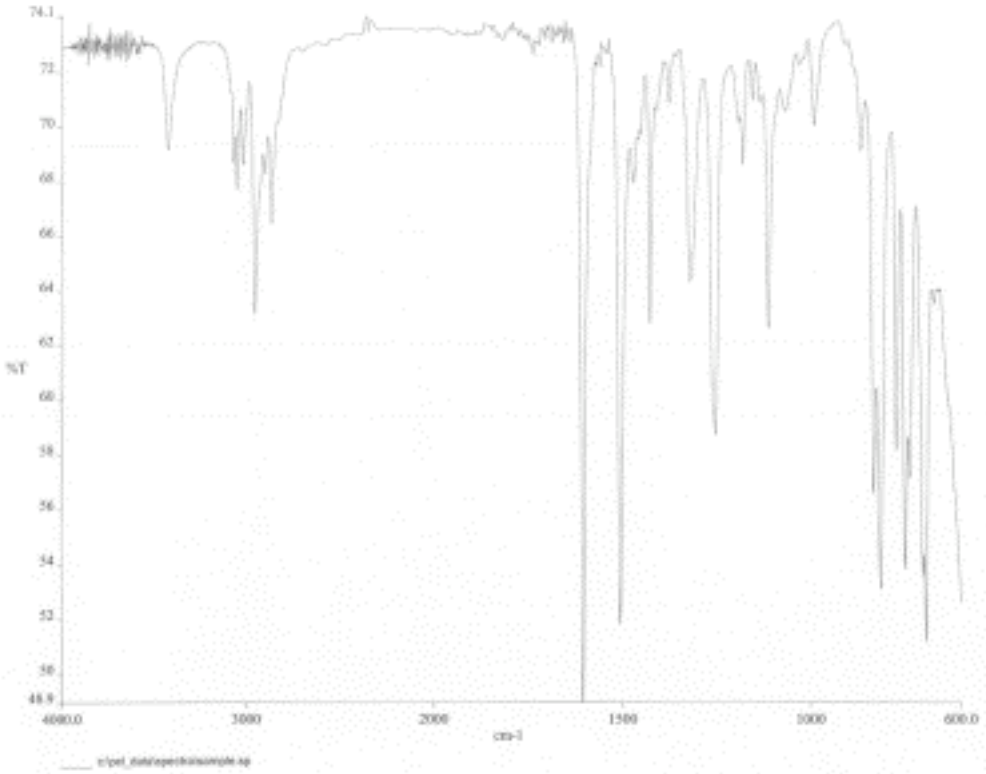
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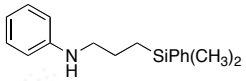
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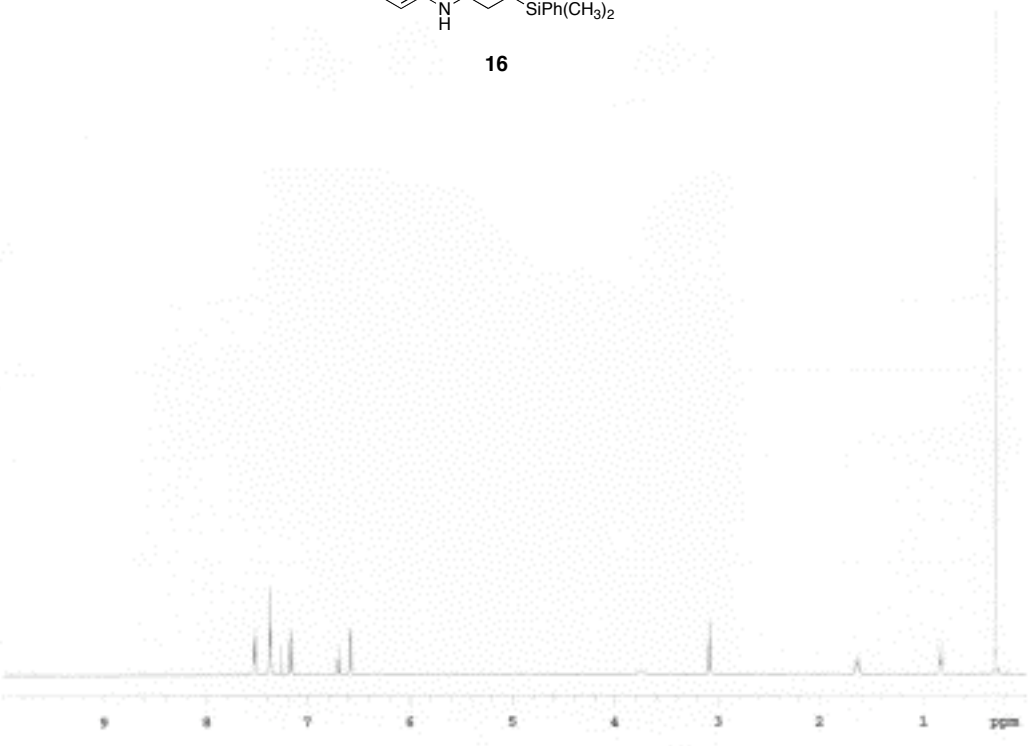
16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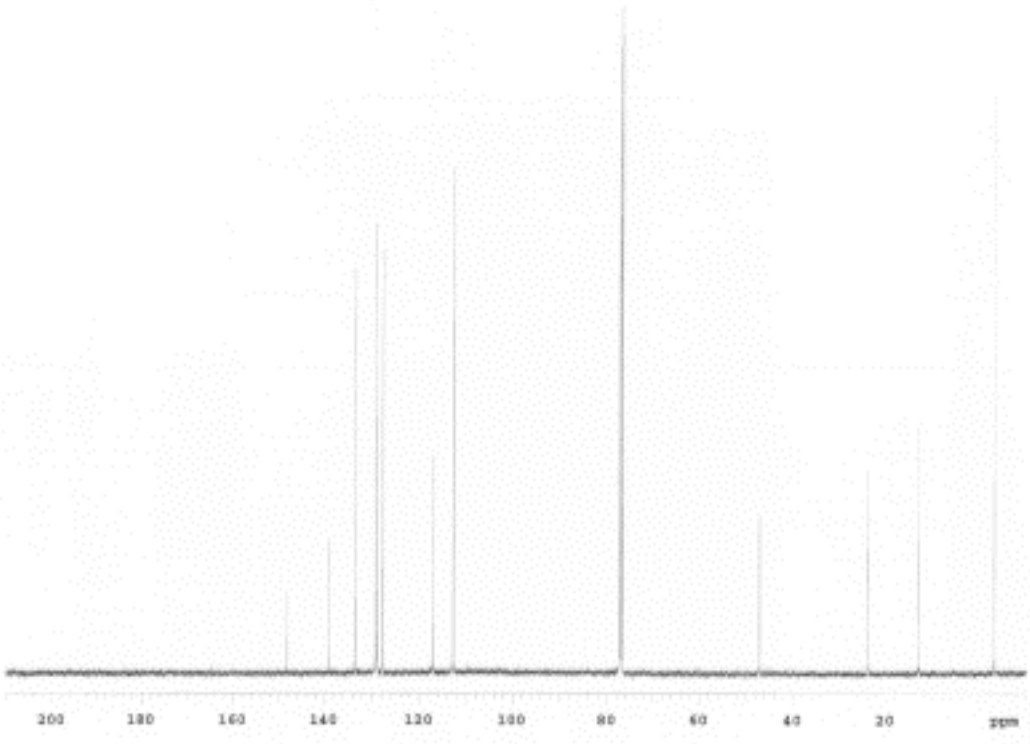
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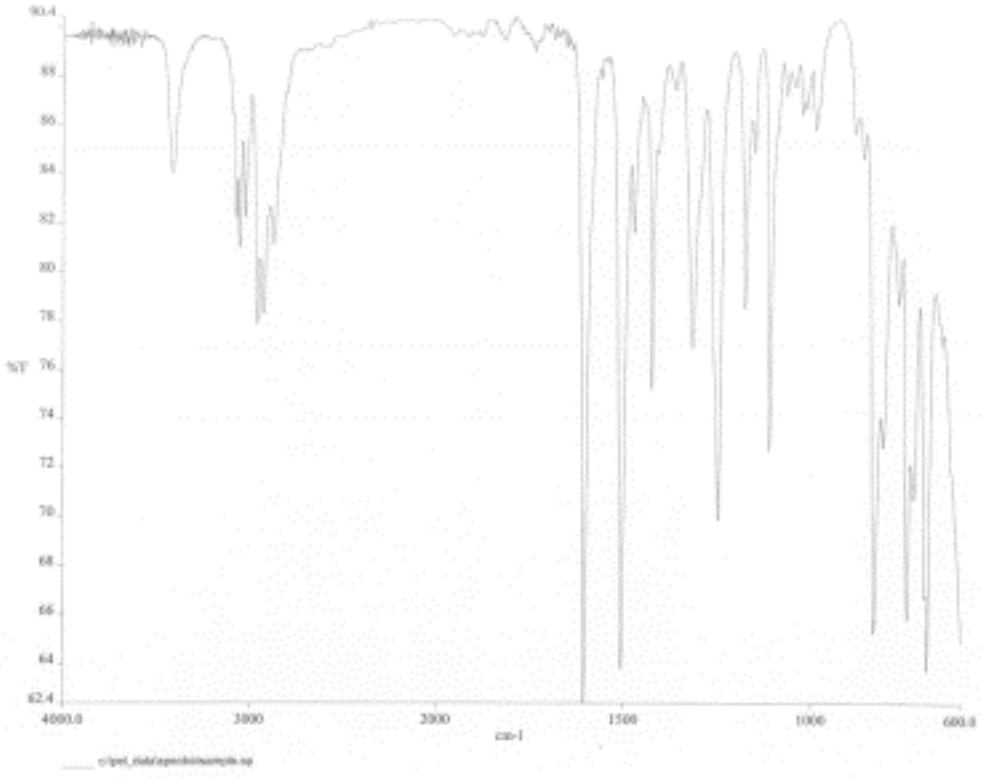
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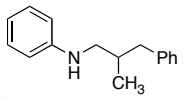

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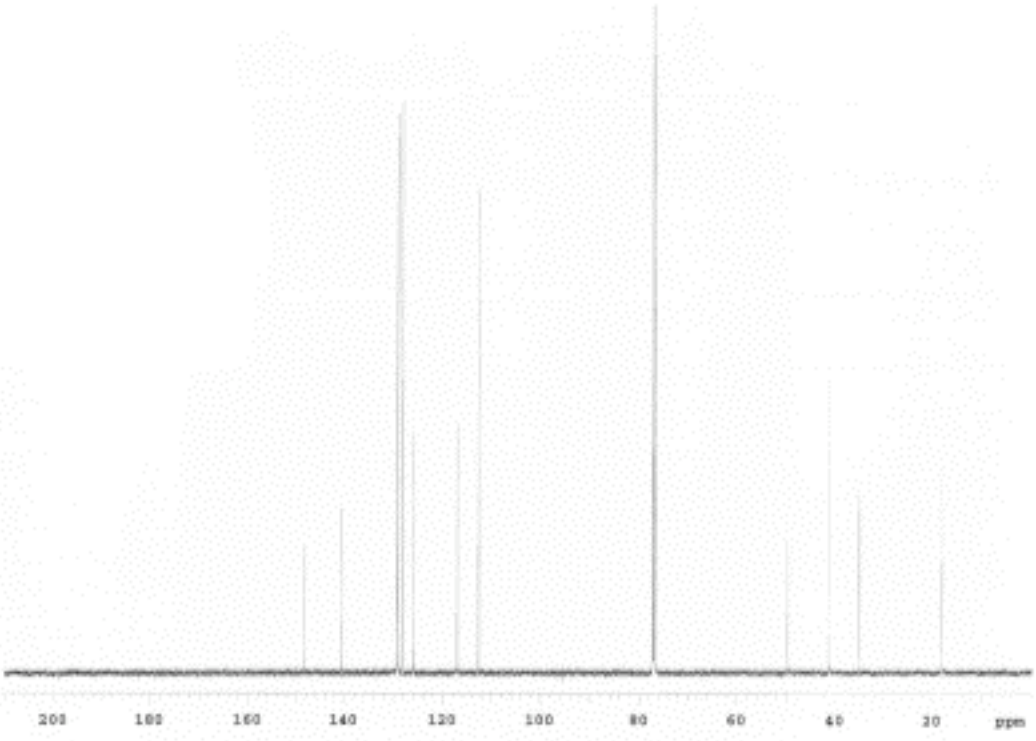

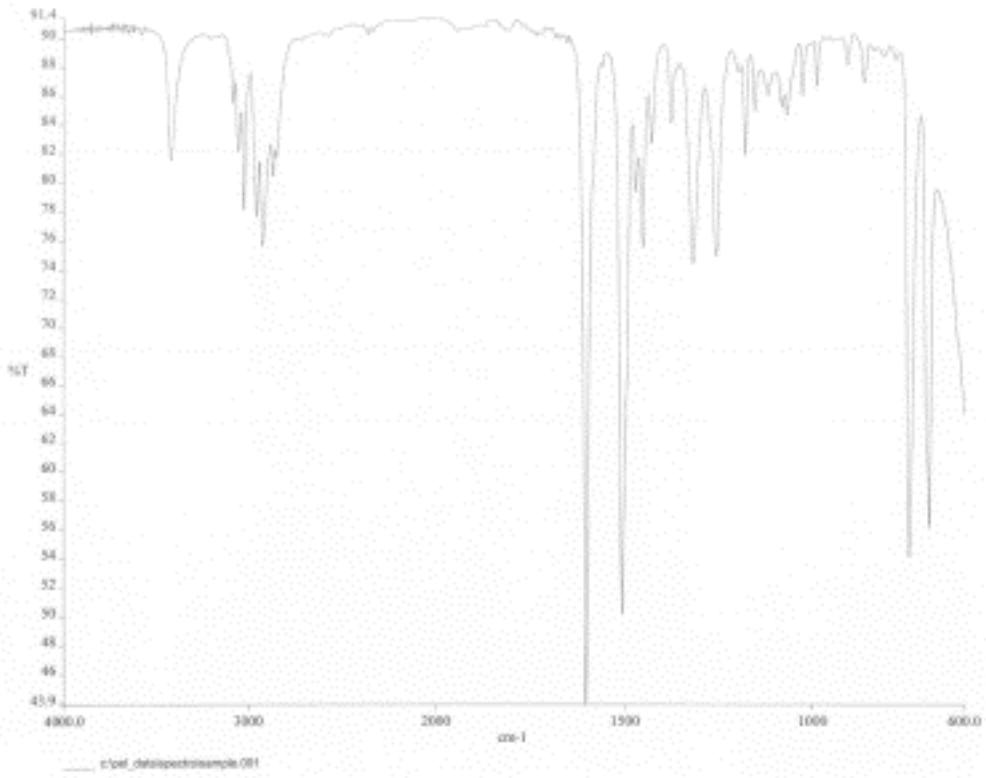
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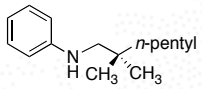
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CH3

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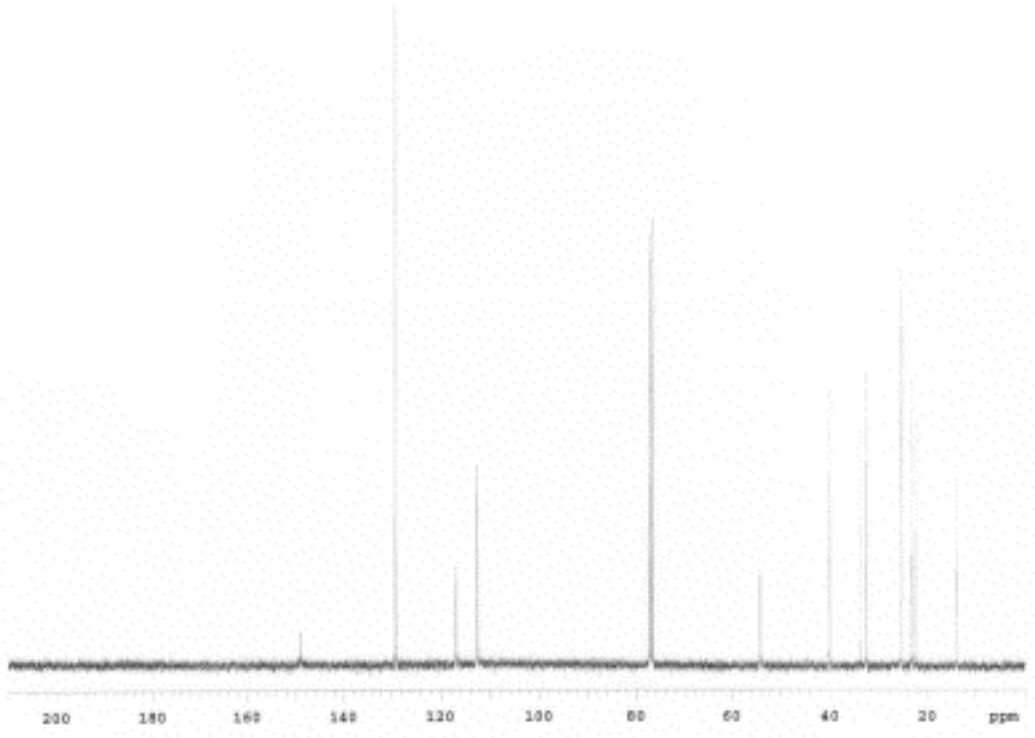
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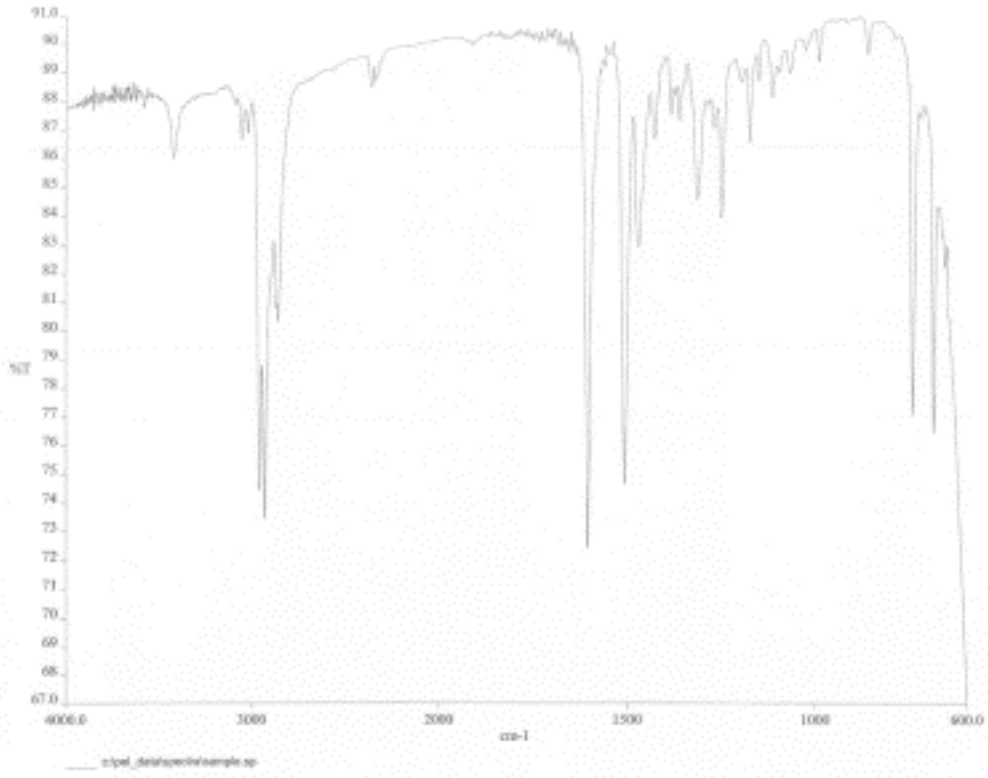
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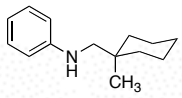
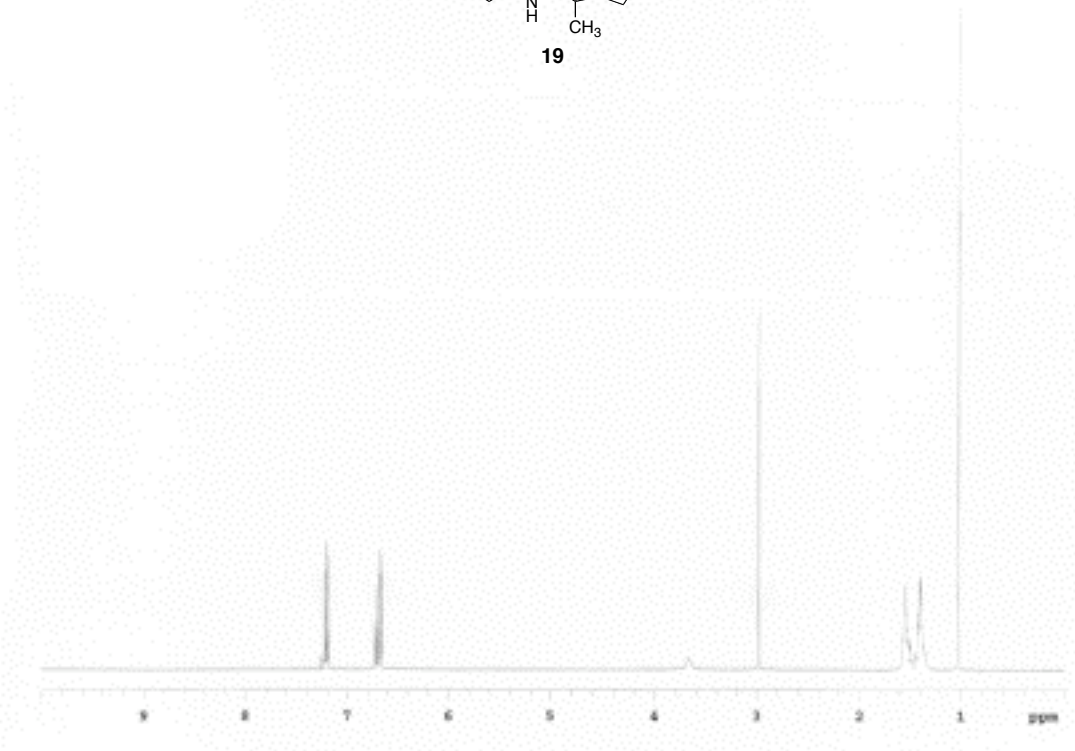
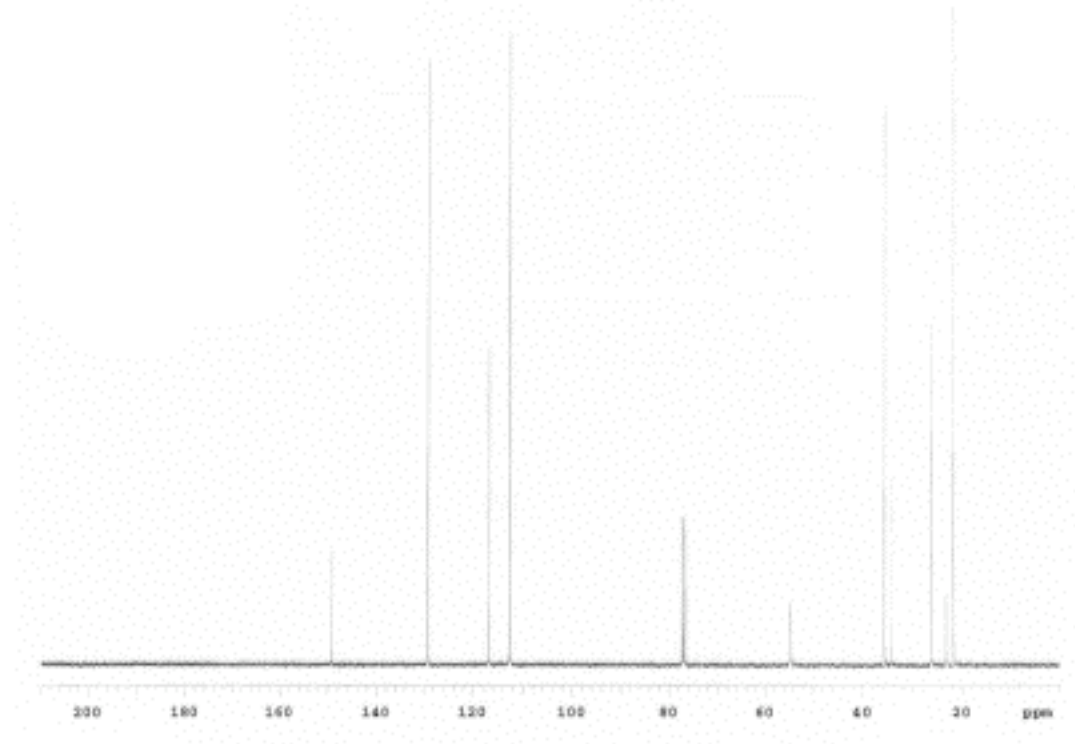
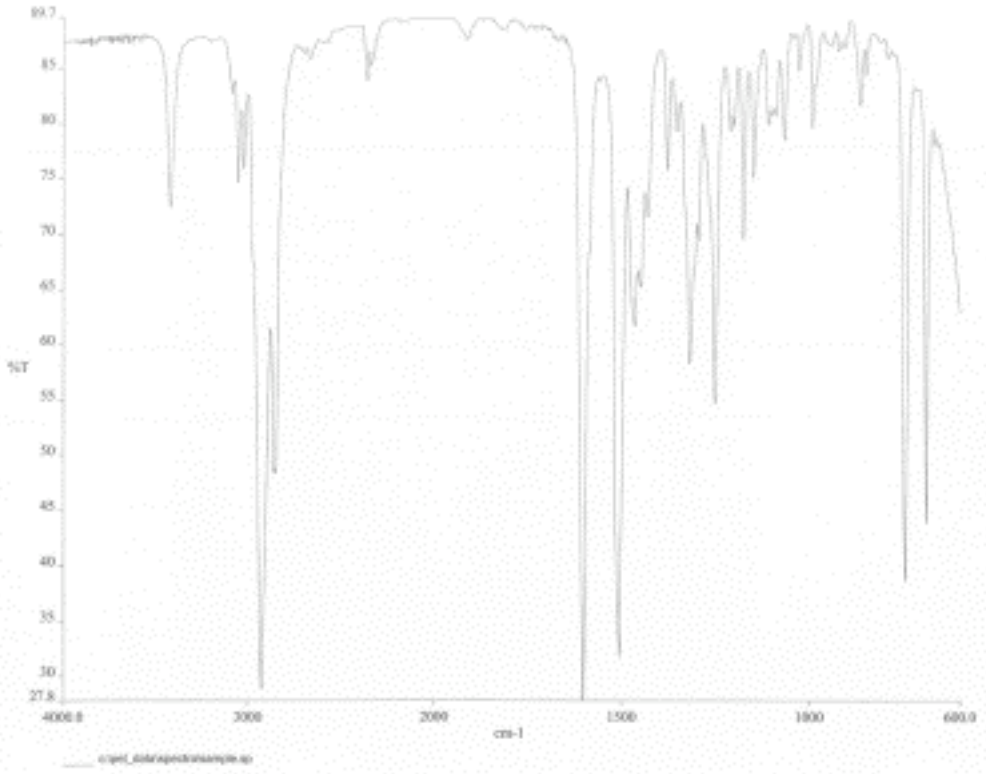
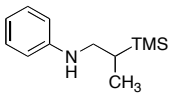


19

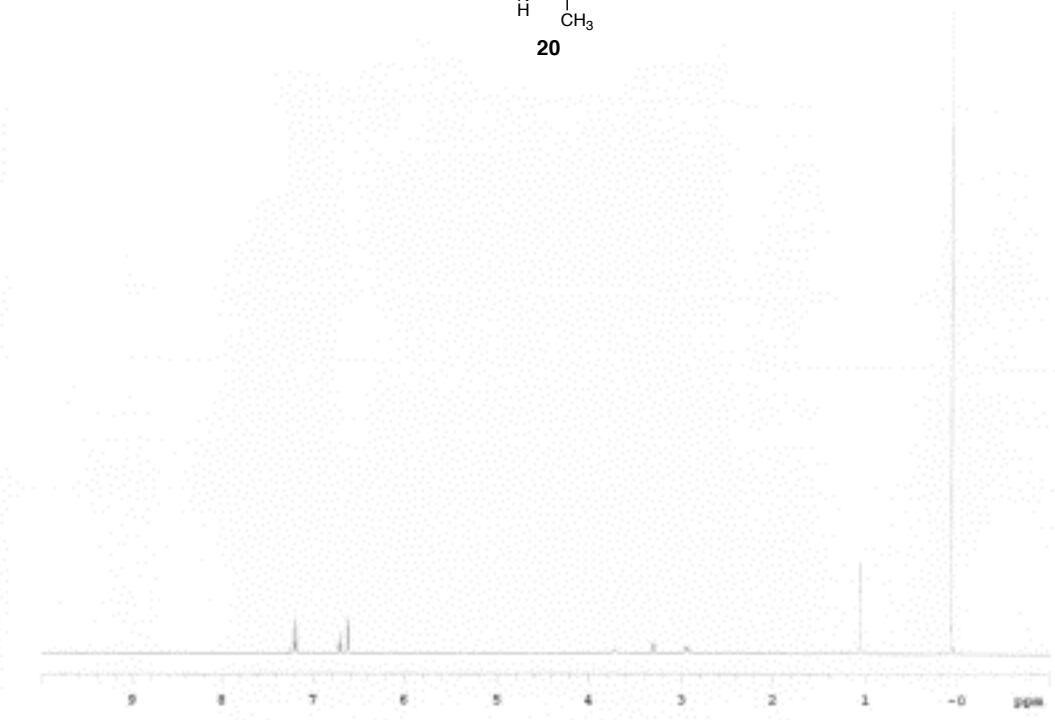


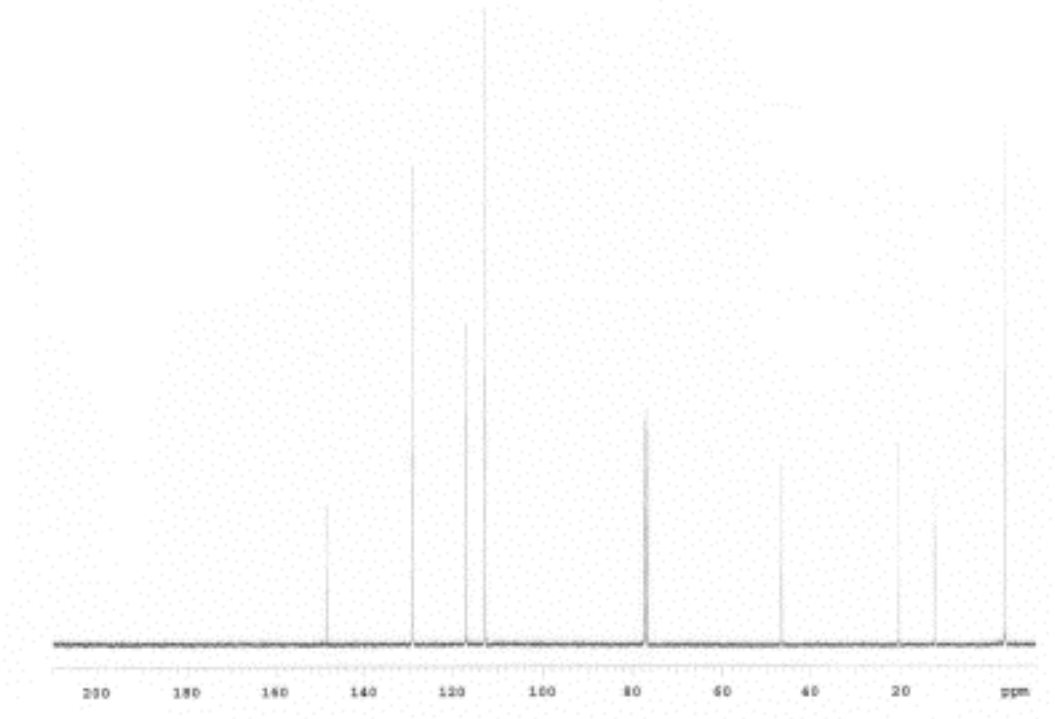


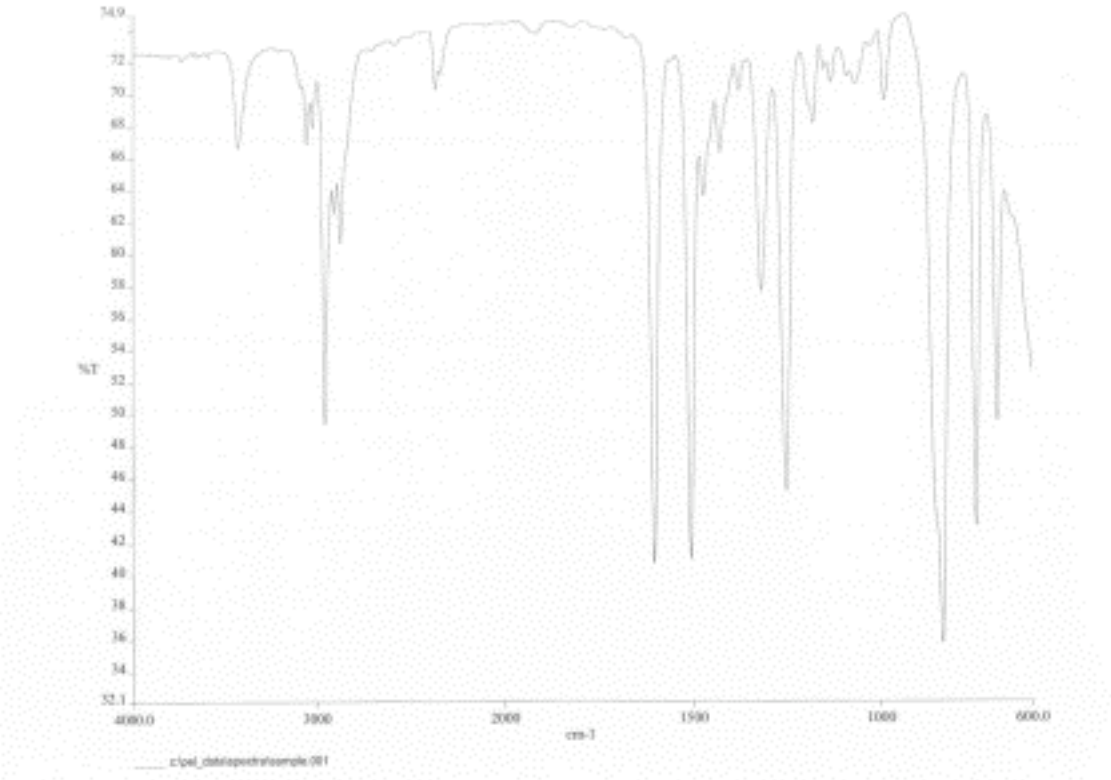

89.7
85
80
75
70
65
60
%T
55
50
45
40
35
30
27.8
4000.0
3000
2000
1500
1000
600.0
cm-1

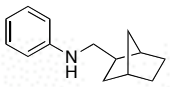

TMS
N
H
CH3

20

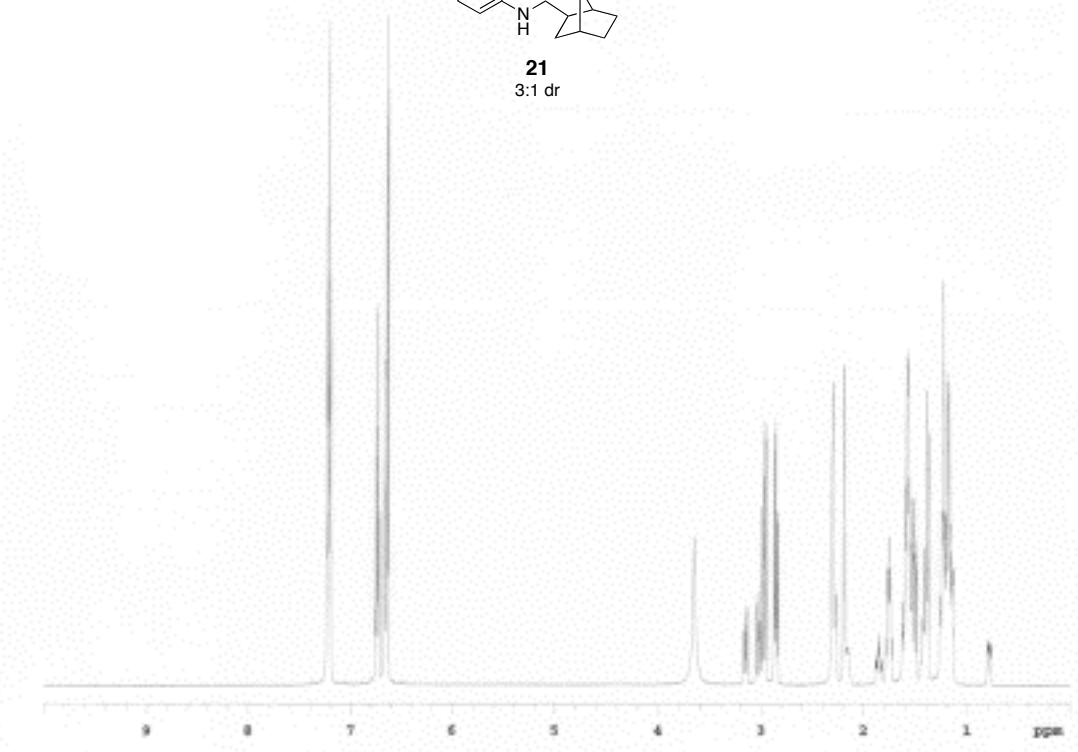

9
8
7
6
5
4
3
2
1
-0
ppm

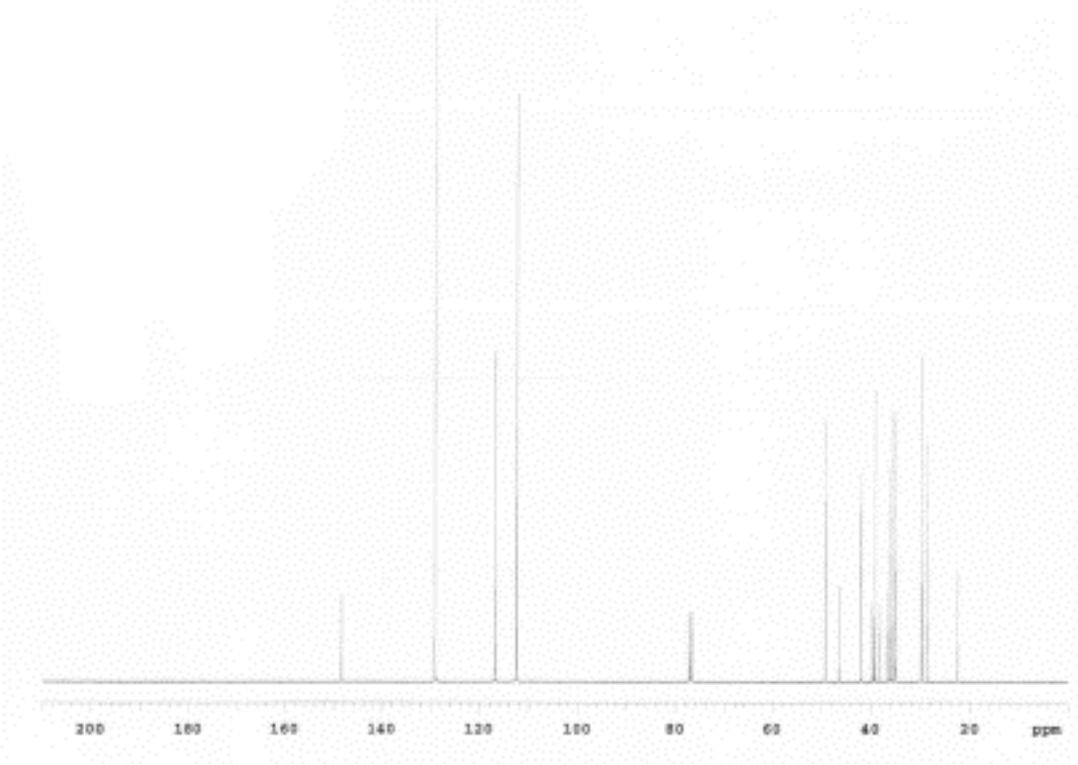

200
180
160
140
120
100
80
60
40
20
ppm

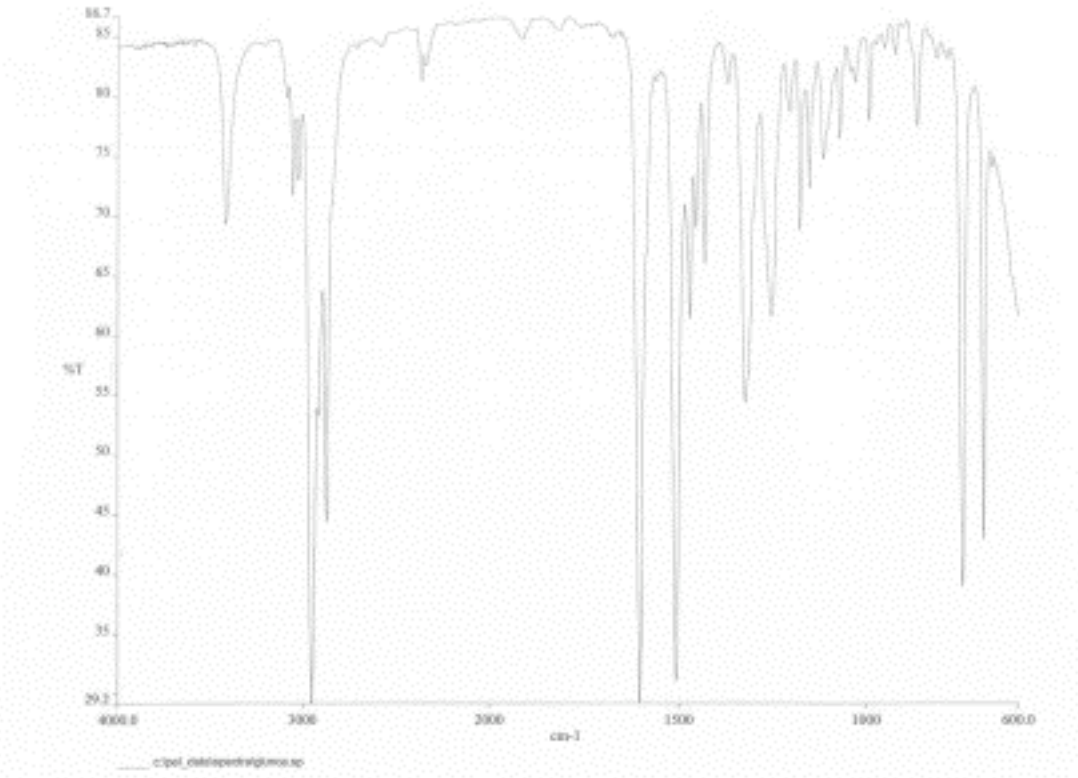

74.9
72
70
68
66
64
62
60
58
56
54
%T
52
50
48
46
44
42
40
38
36
34
32.1
4000.0
3000
2000
1500
1000
600.0
cm-1
c:\pel_data\spectra\sample.001

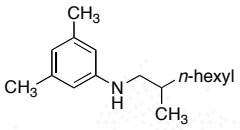


21
3:1 dr



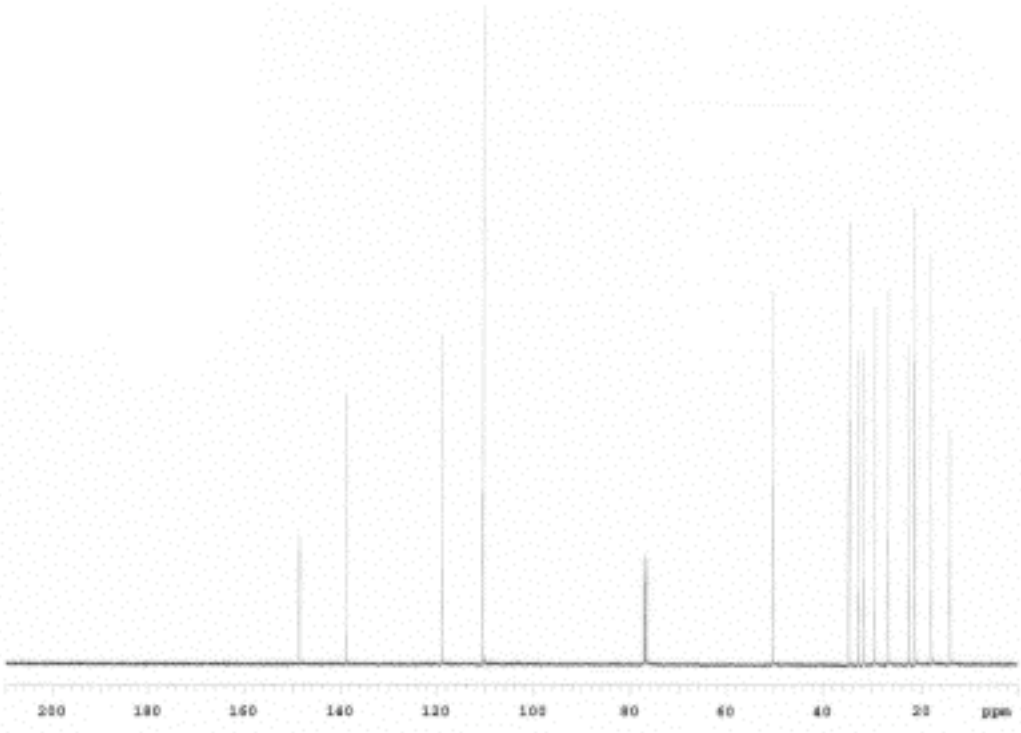


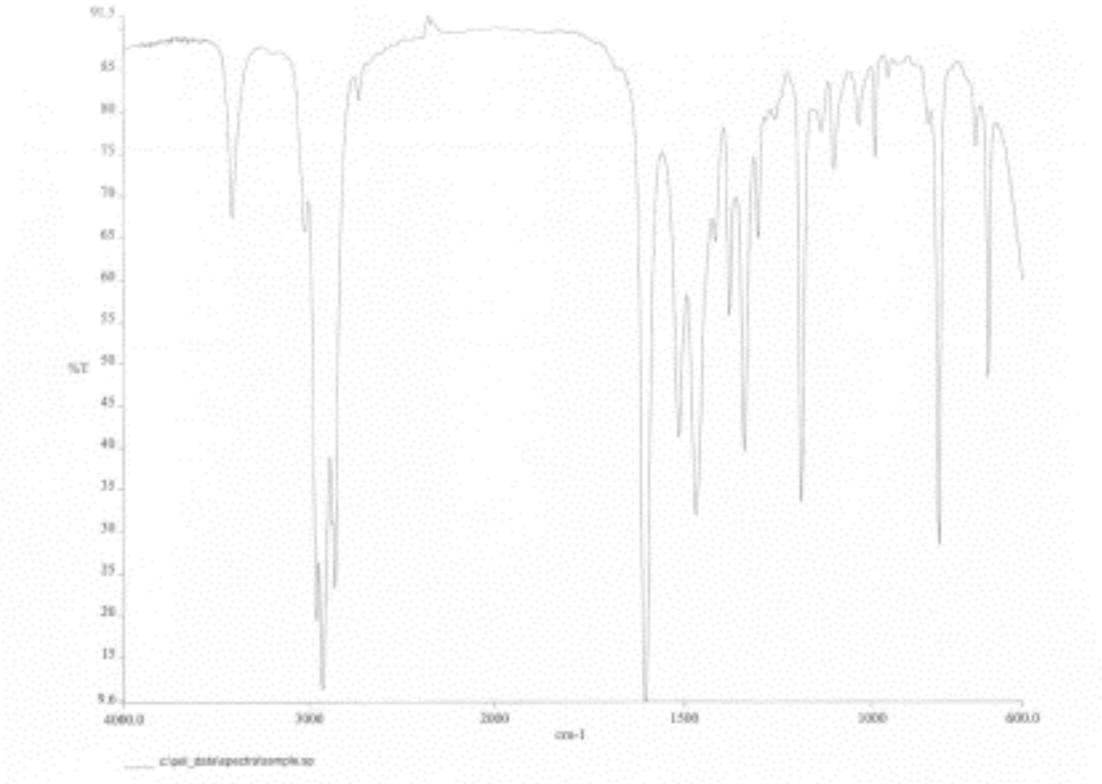

88.7
85
80
75
70
65
60
%T
55
50
45
40
35
29.2
4000.0
3000
2000
1500
1000
600.0
cm-1

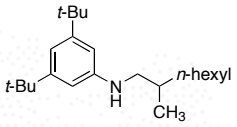

CH3
CH3
N
H
n-hexyl
CH3

22

9
8
7
6
5
4
3
2
1
ppm

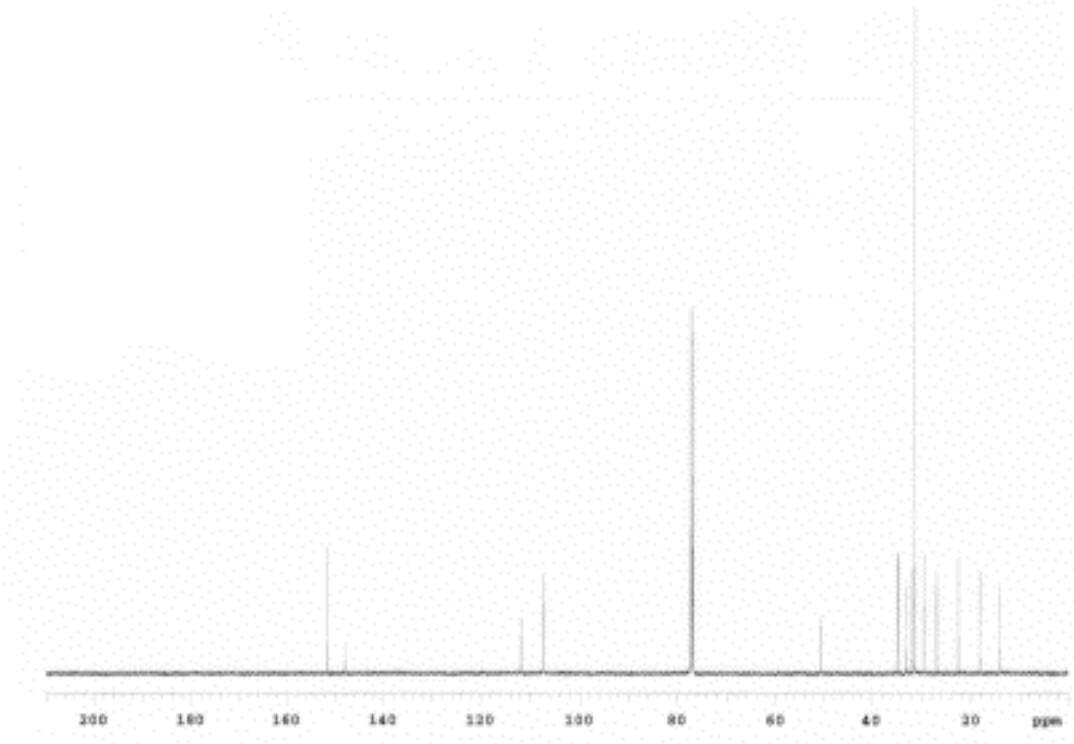

200
180
160
140
120
100
80
60
40
20
ppm

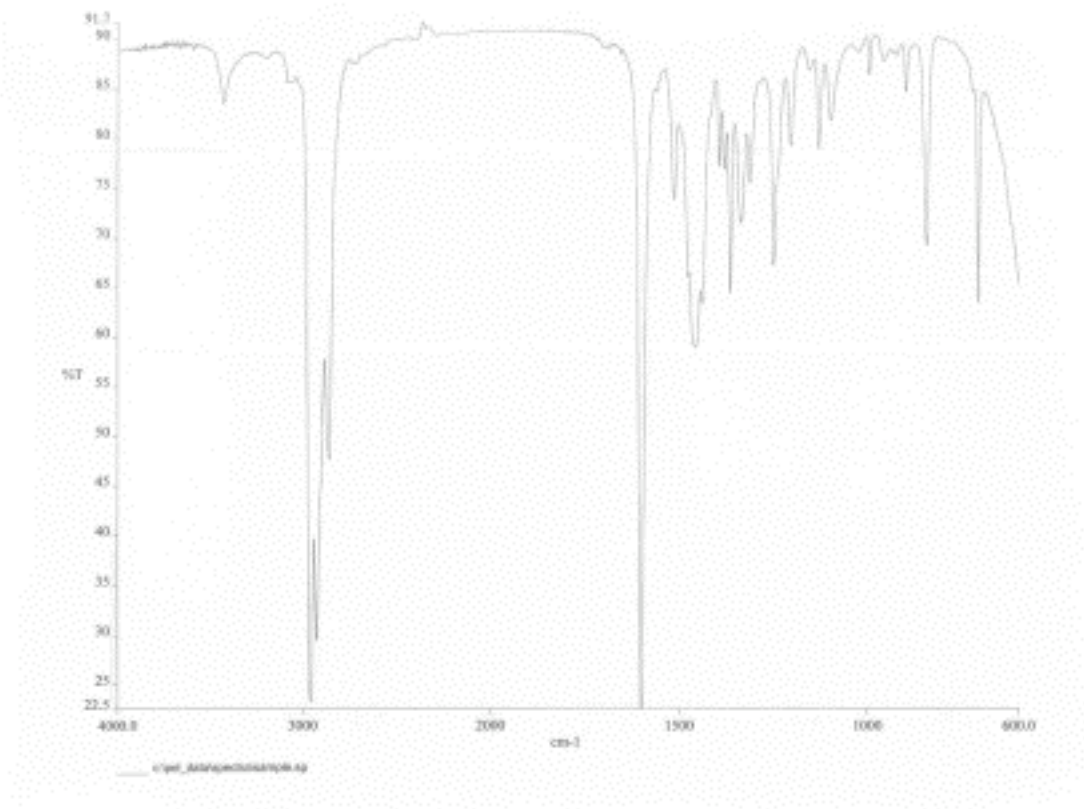

%T
cm-1
4000.0
3000
2000
1500
1000
600.0

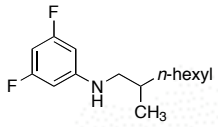

t-Bu
t-Bu
N
H
n-hexyl
CH3

23

9
8
7
6
5
4
3
2
1
ppm

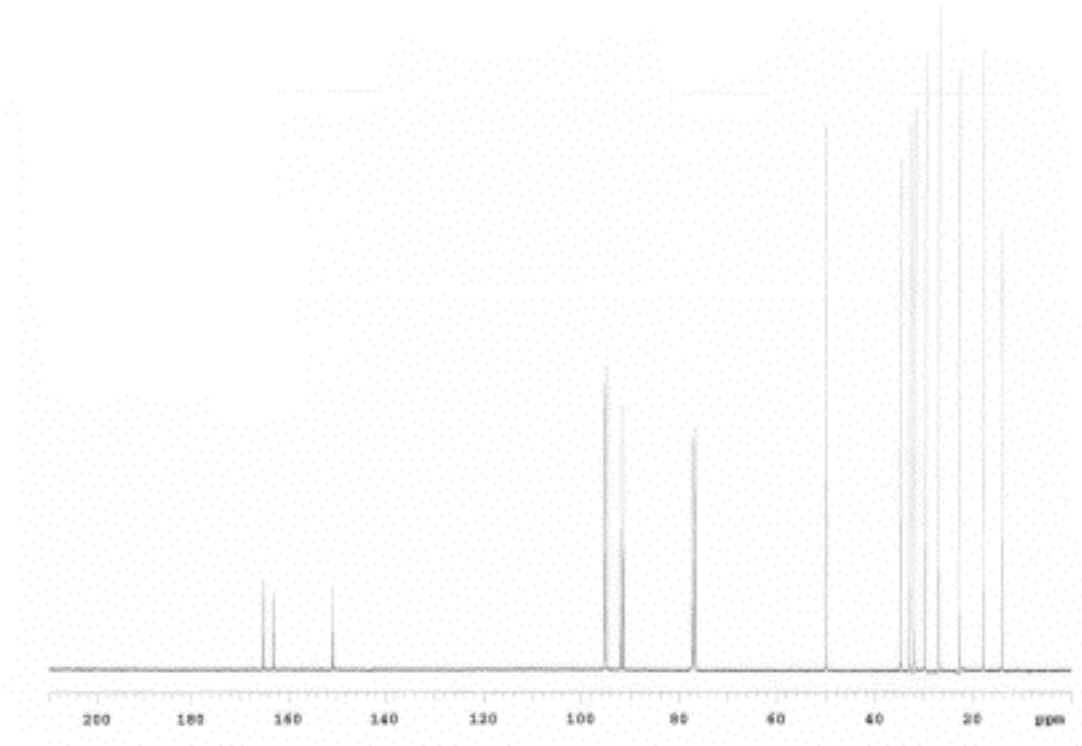

200
180
160
140
120
100
80
60
40
20
ppm

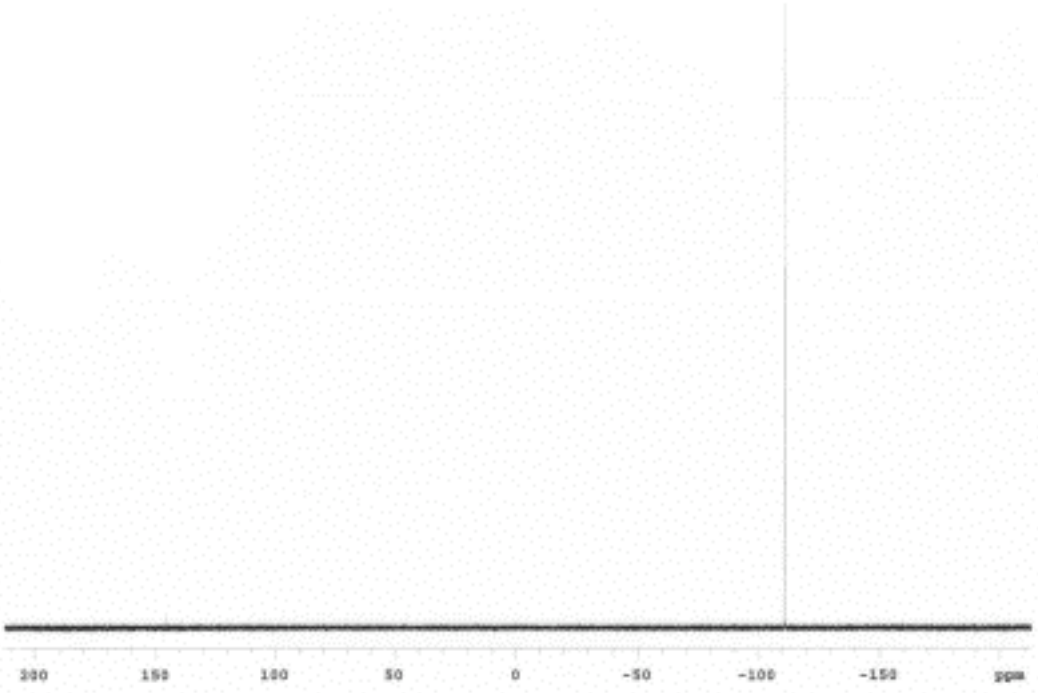

91.3
90
85
80
75
70
65
60
%T
55
50
45
40
35
30
25
22.5
4000.0
3000
2000
1500
1000
600.0
cm-1

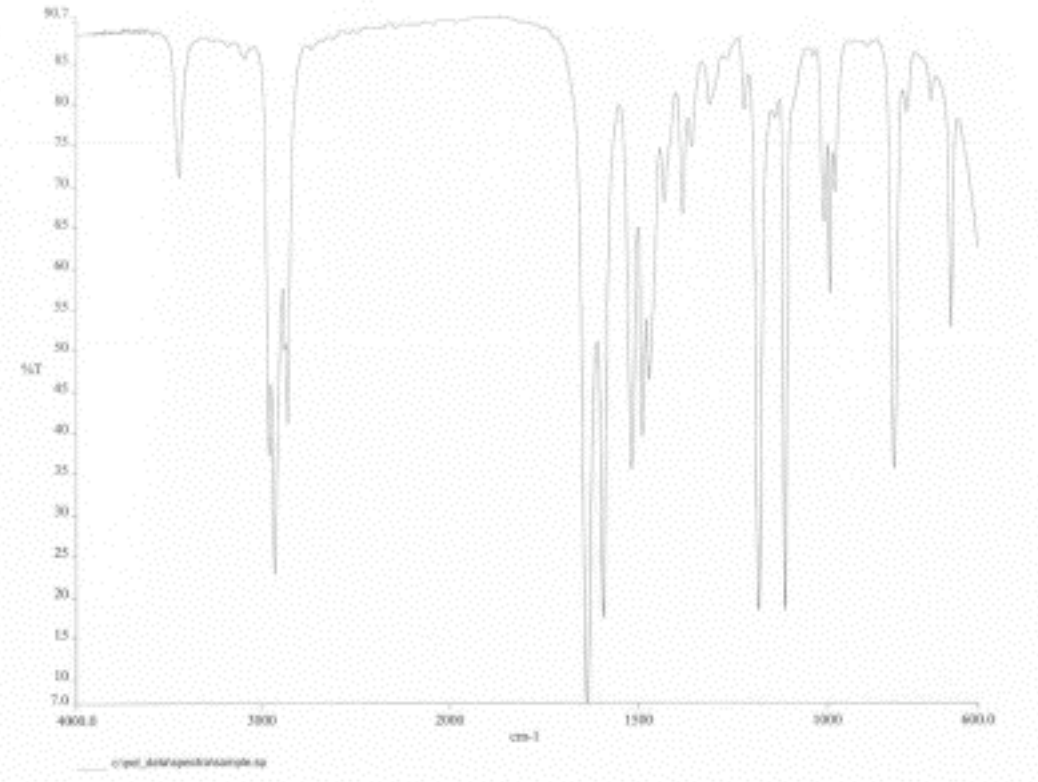

F
F
N
H
n-hexyl
CH3

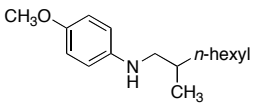
24

9
8
7
6
5
4
3
2
1
ppm

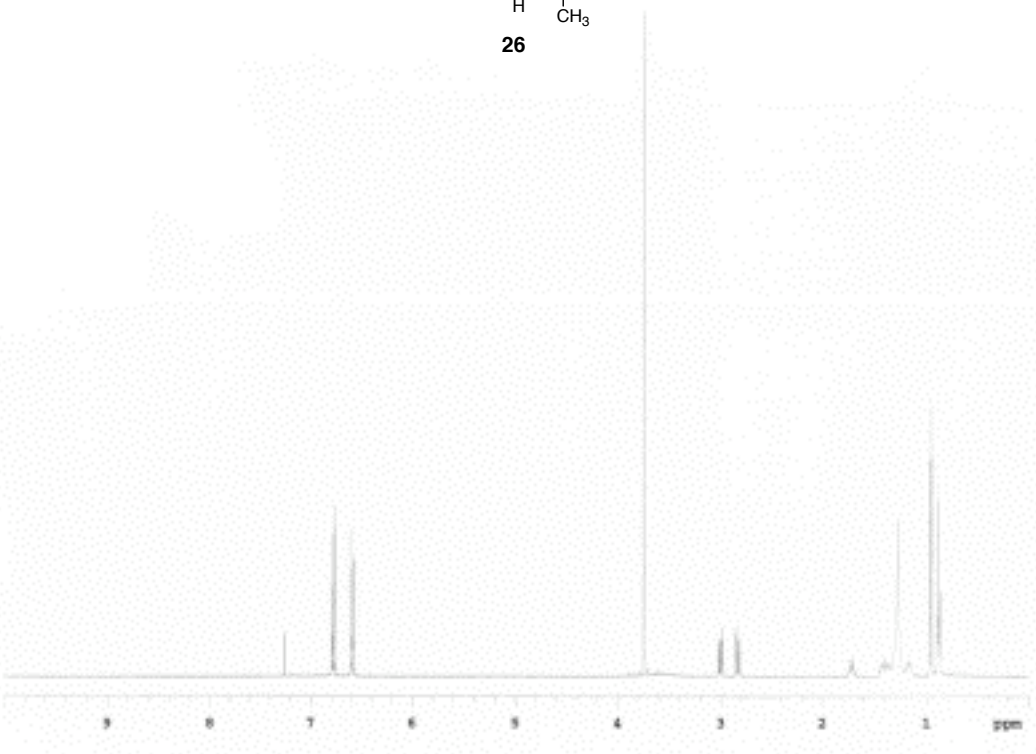

200
180
160
140
120
100
80
60
40
20
ppm

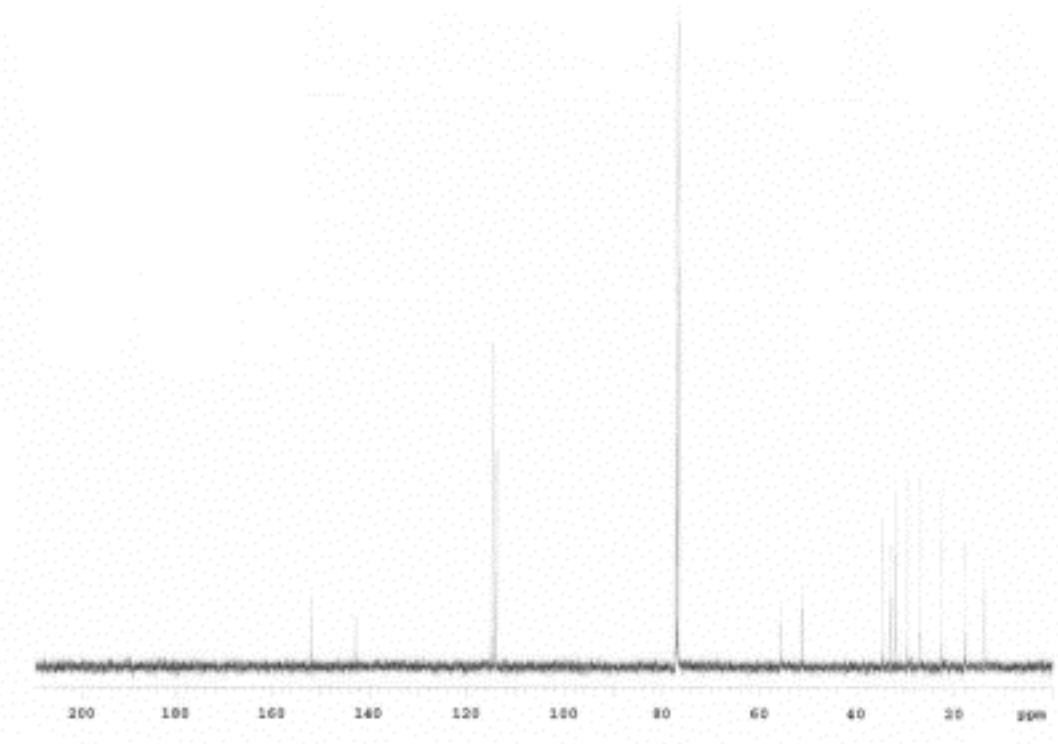

200
150
100
50
0
-50
-100
-150
ppm

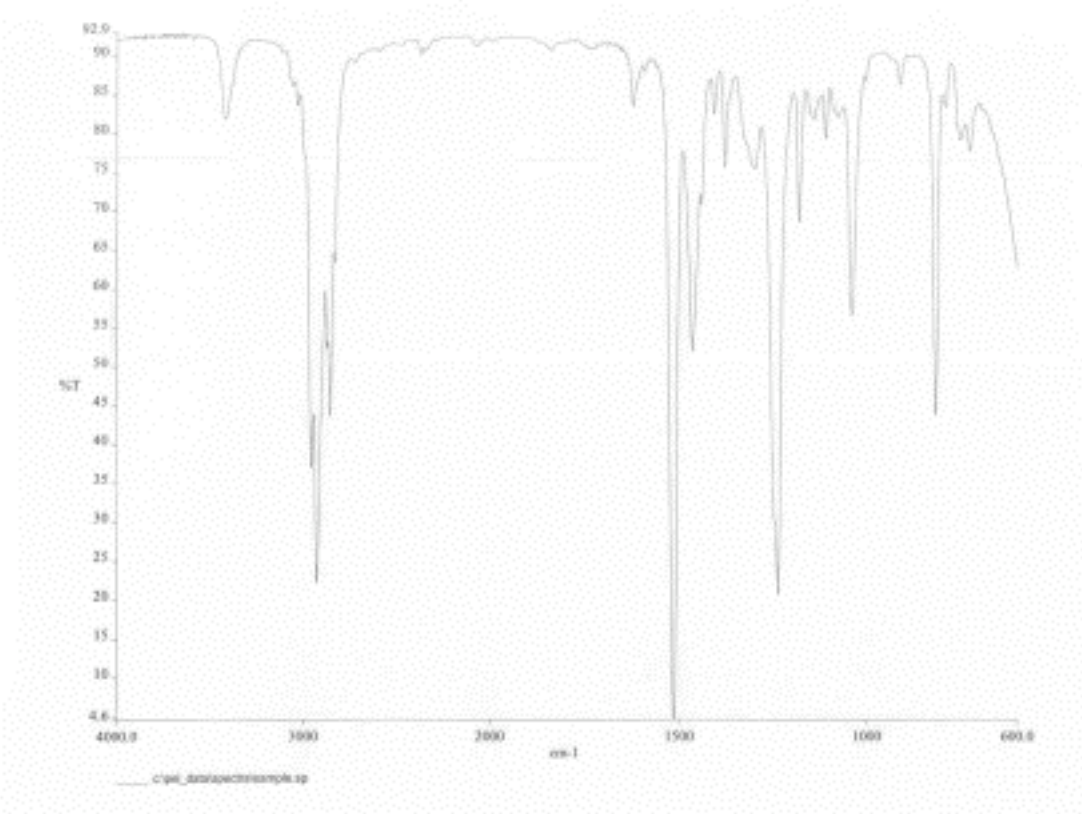

%T
cm-1
4000.0
3000
2000
1500
1000
600.0

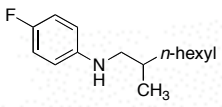

CH3O
N
H
n-hexyl
CH3

26


9
8
7
6
5
4
3
2
1
ppm

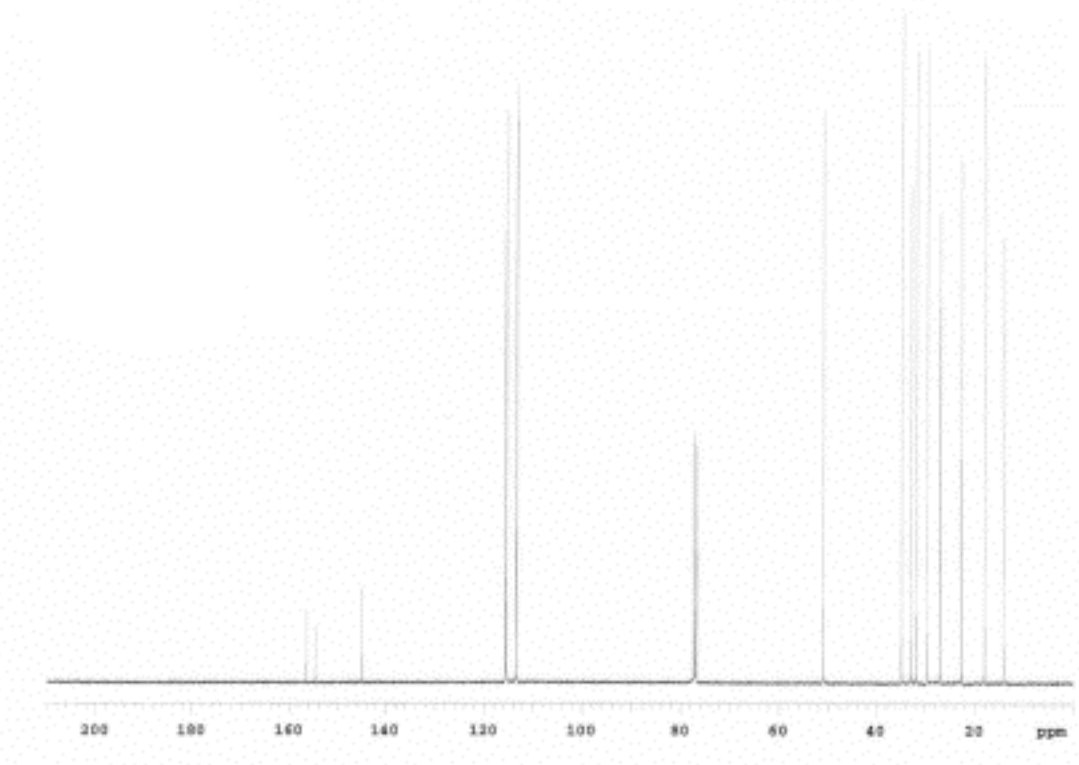

200
180
160
140
120
100
80
60
40
20
ppm

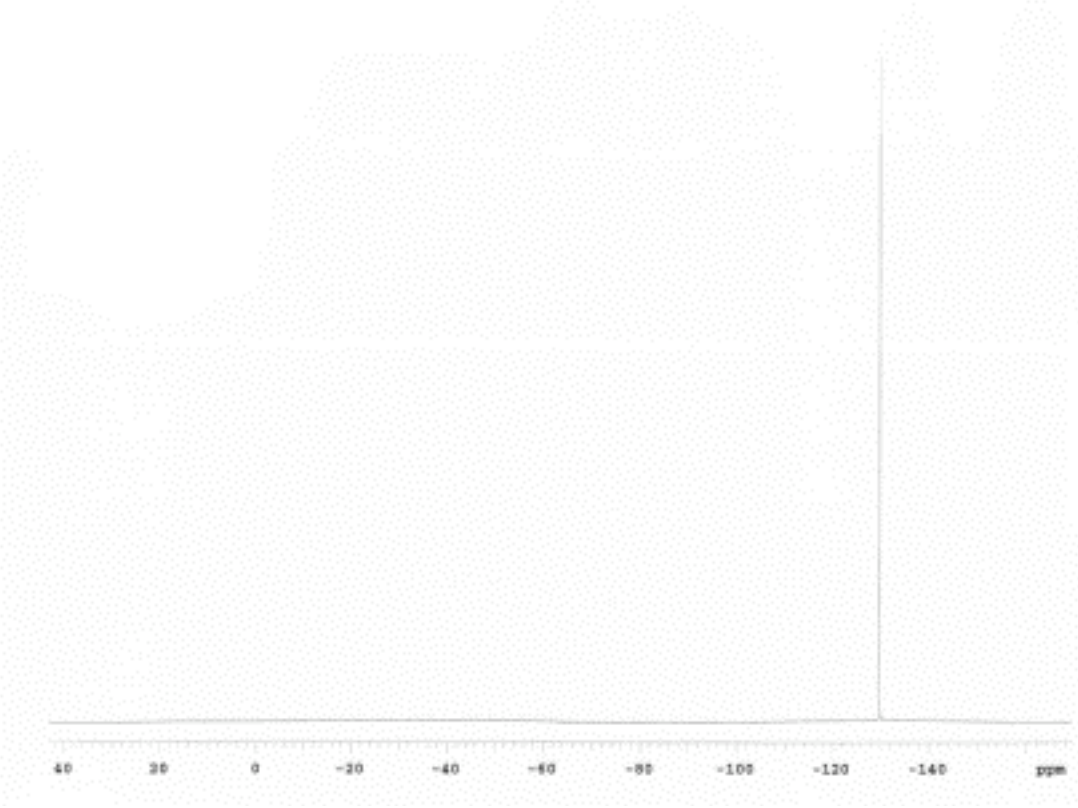

%T
cm-1
4000.0
3000
2000
1500
1000
600.0

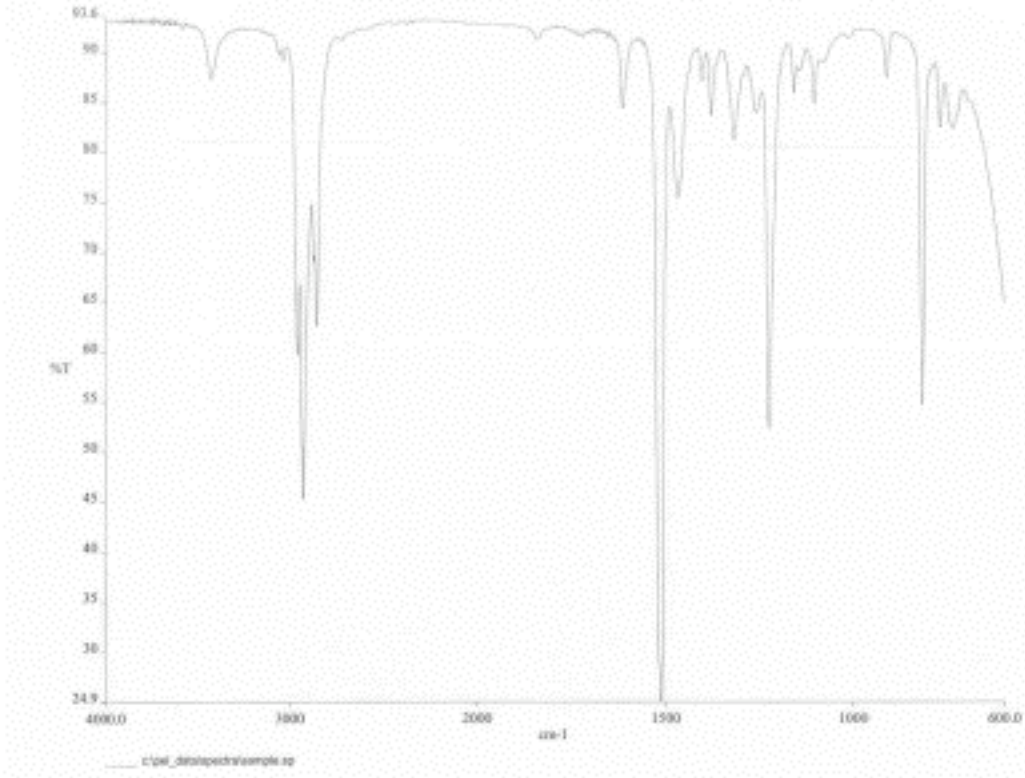

F
N
H
n-hexyl
CH3

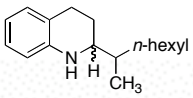
28

9
8
7
6
5
4
3
2
1
ppm

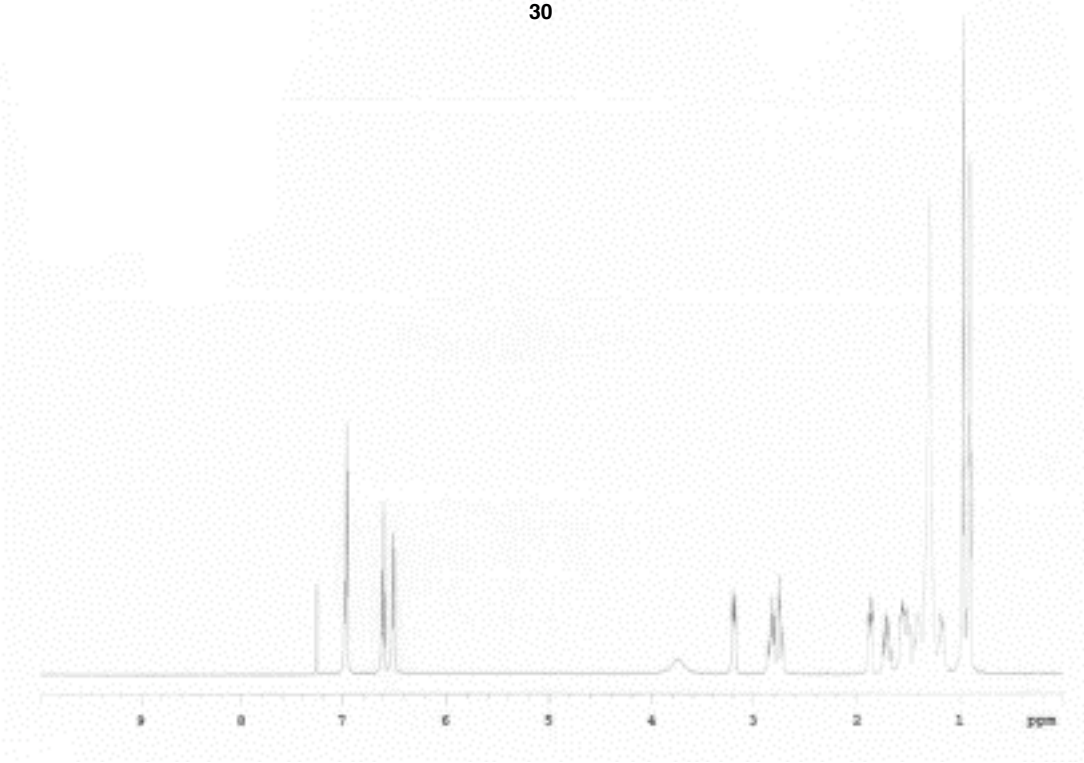

200
180
160
140
120
100
80
60
40
20
ppm

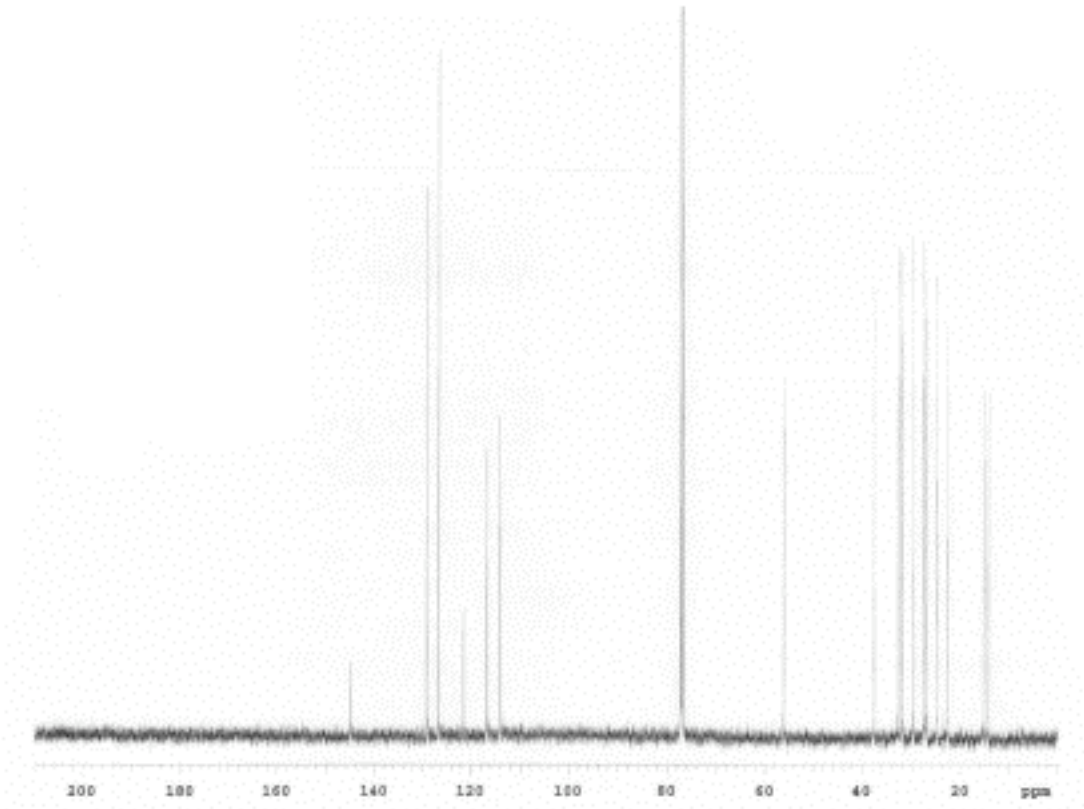

40
20
0
-20
-40
-60
-80
-100
-120
-140
ppm

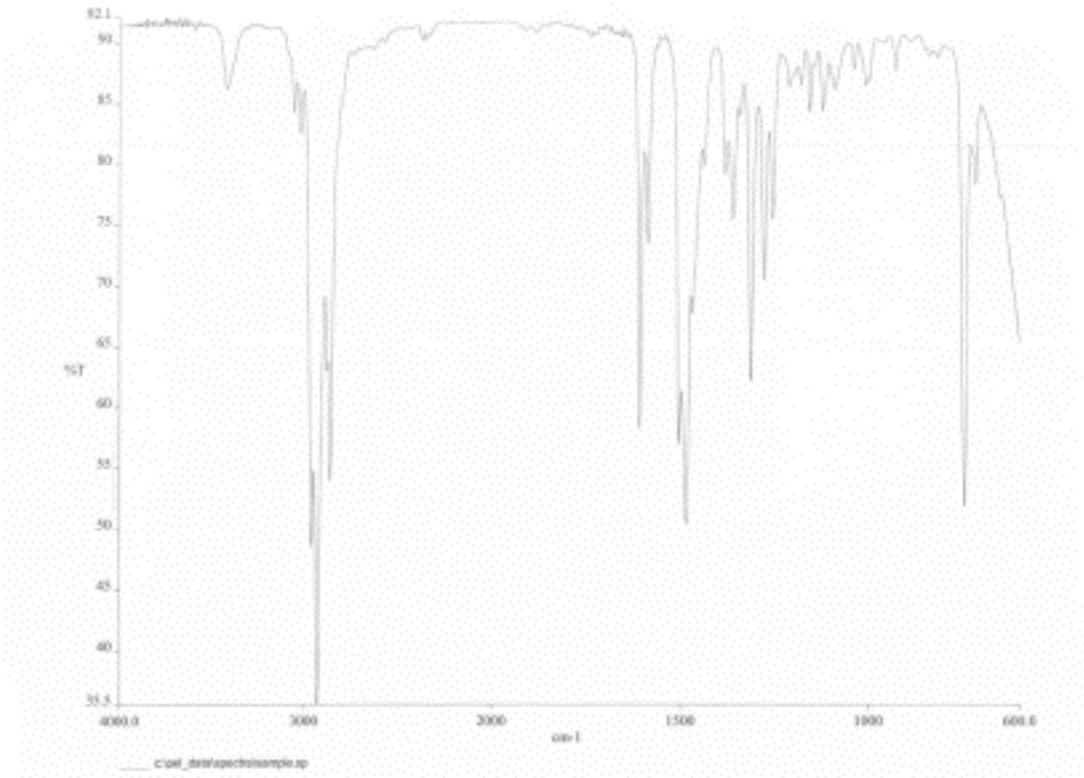

%T
4000.0
3000
2000
1500
1000
600.0
cm-1
c:\pel_data\spectra\sample.sp

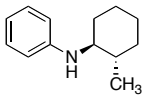

n-hexyl
N
H
H
CH3

30

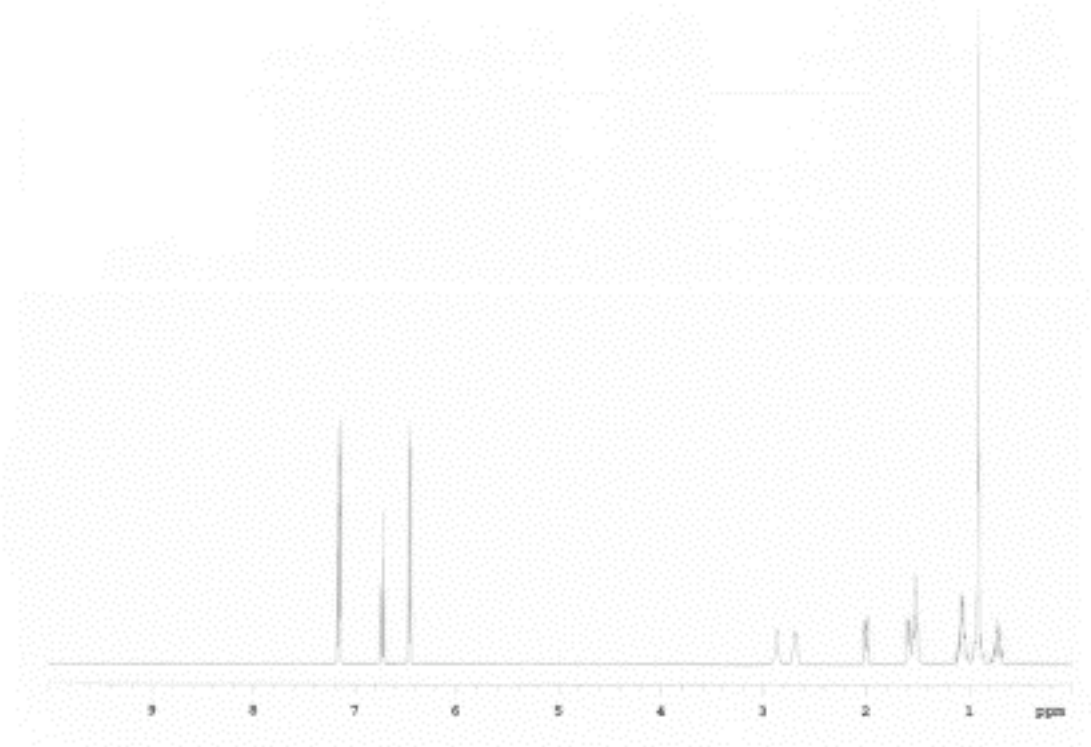

9
8
7
6
5
4
3
2
1
ppm

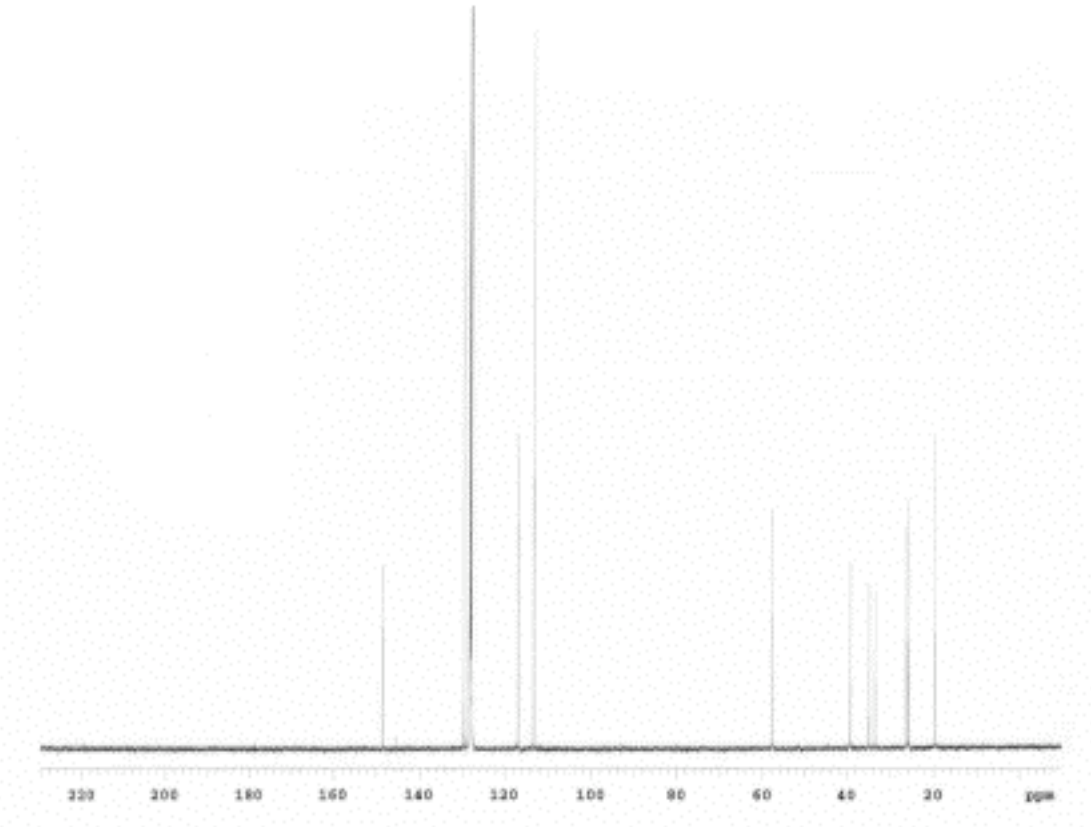

200
180
160
140
120
100
80
60
40
20
ppm

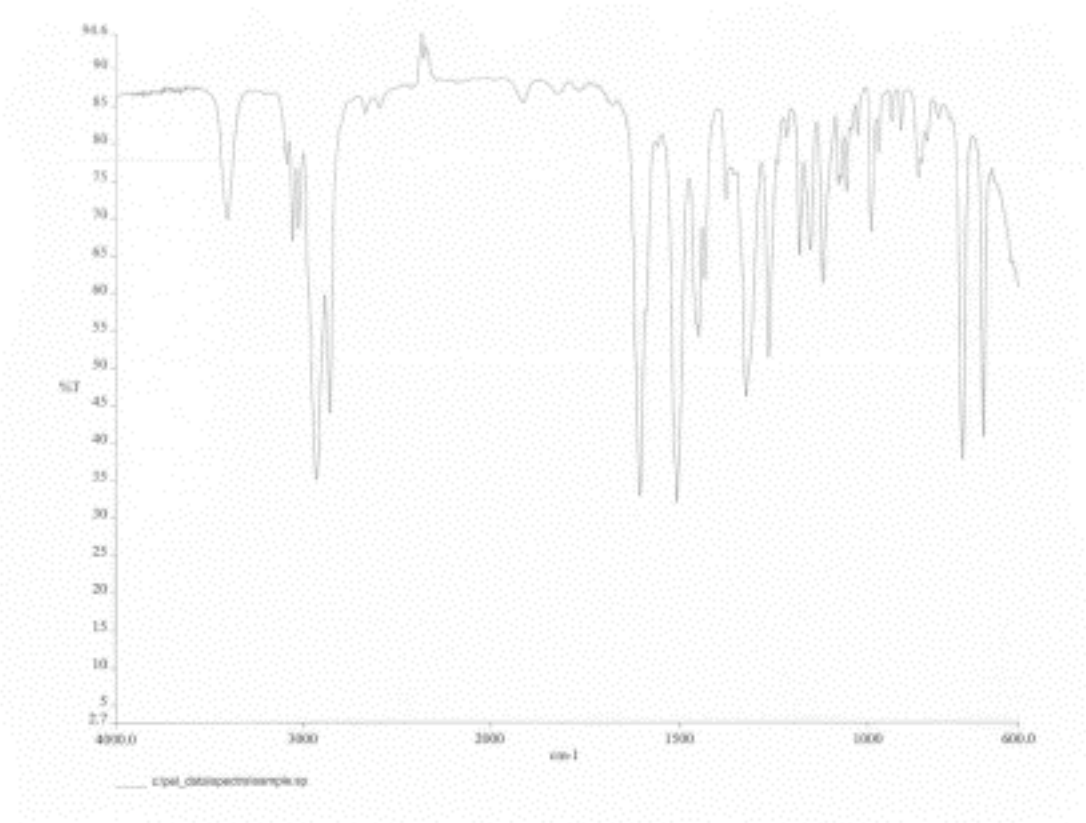

92.1
90
85
80
75
70
65
%T
60
55
50
45
40
35.5
4000.0
3000
2000
1500
1000
600.0
cm-1
c:\oel_data\spectra\sample.sp

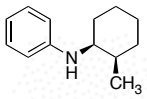


31

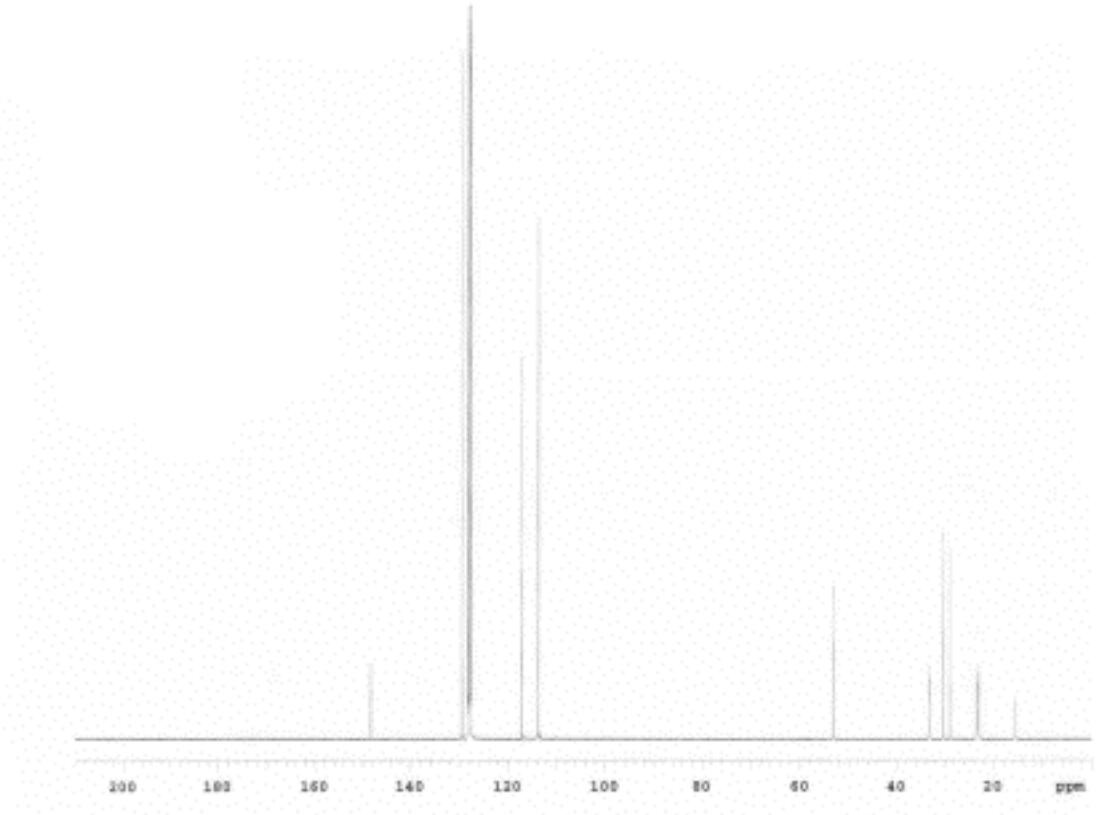


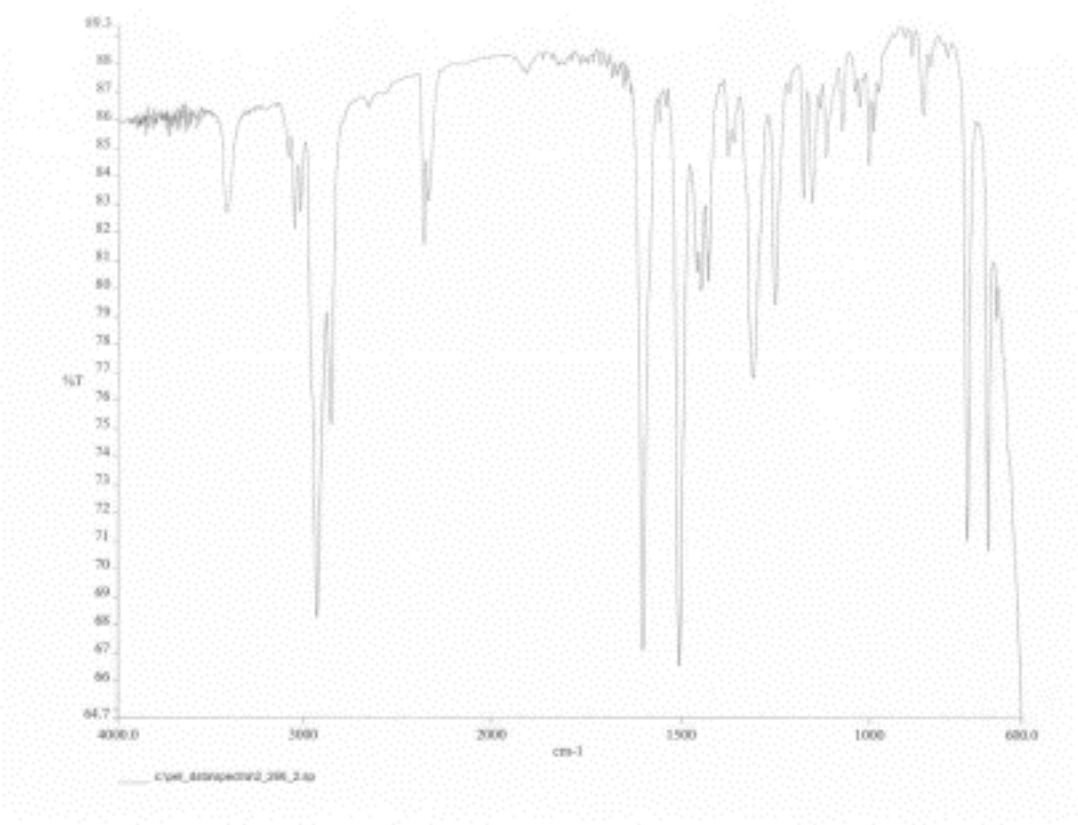


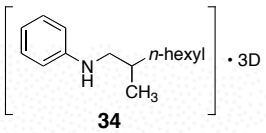

94.6
90
85
80
75
70
65
60
55
50
%T
45
40
35
30
25
20
15
10
5
2.7
4000.0
3000
2000
1500
1000
600.0
cm-1
c:\pal_data\spectra\sample.sp



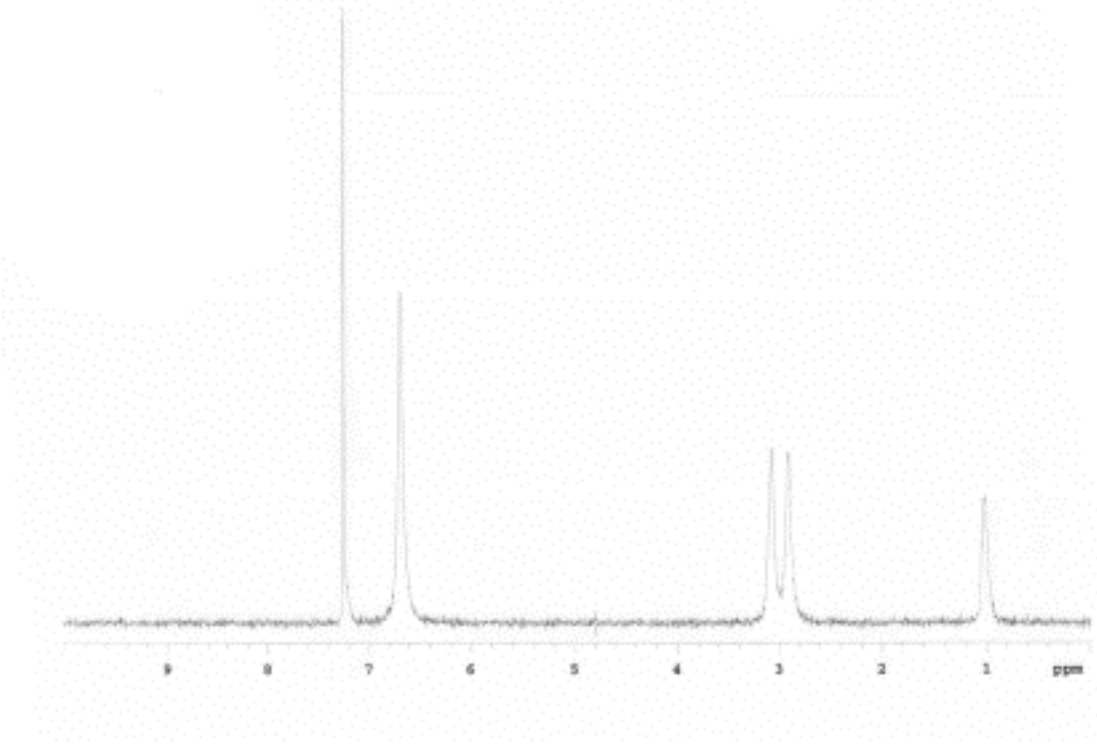
32

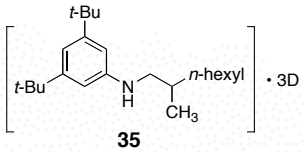



%T
cm-1
4000.0
3000
2000
1500
1000
600.0

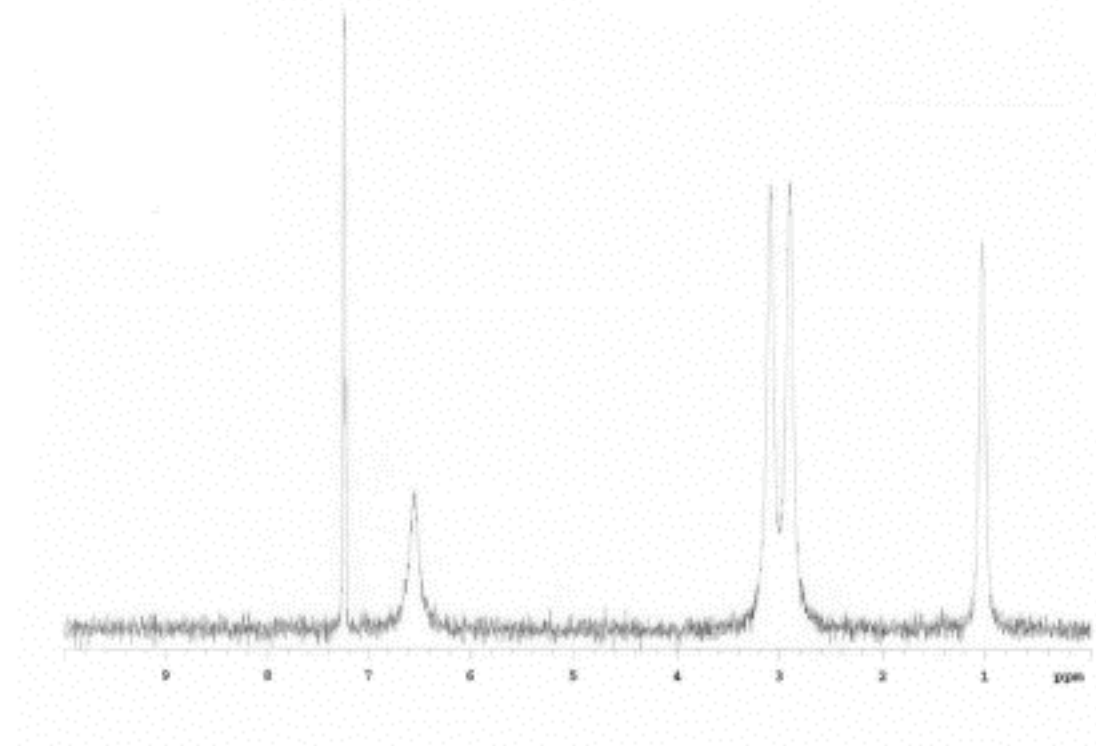


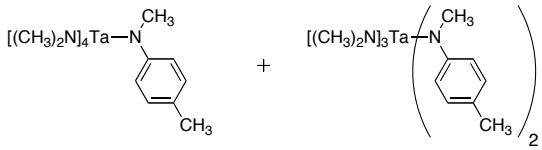
34



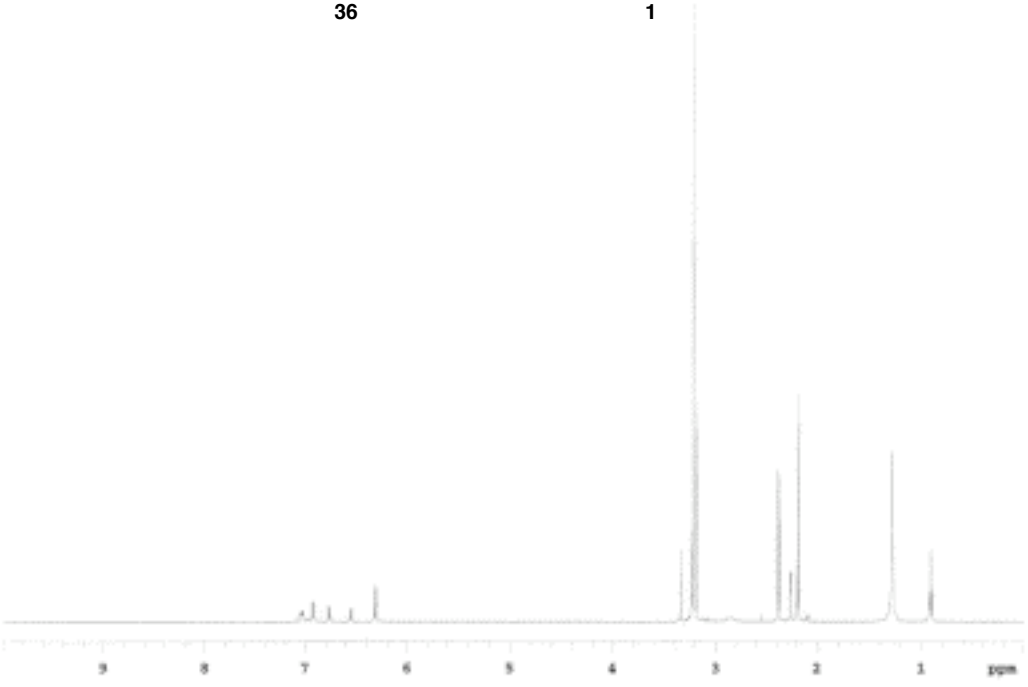


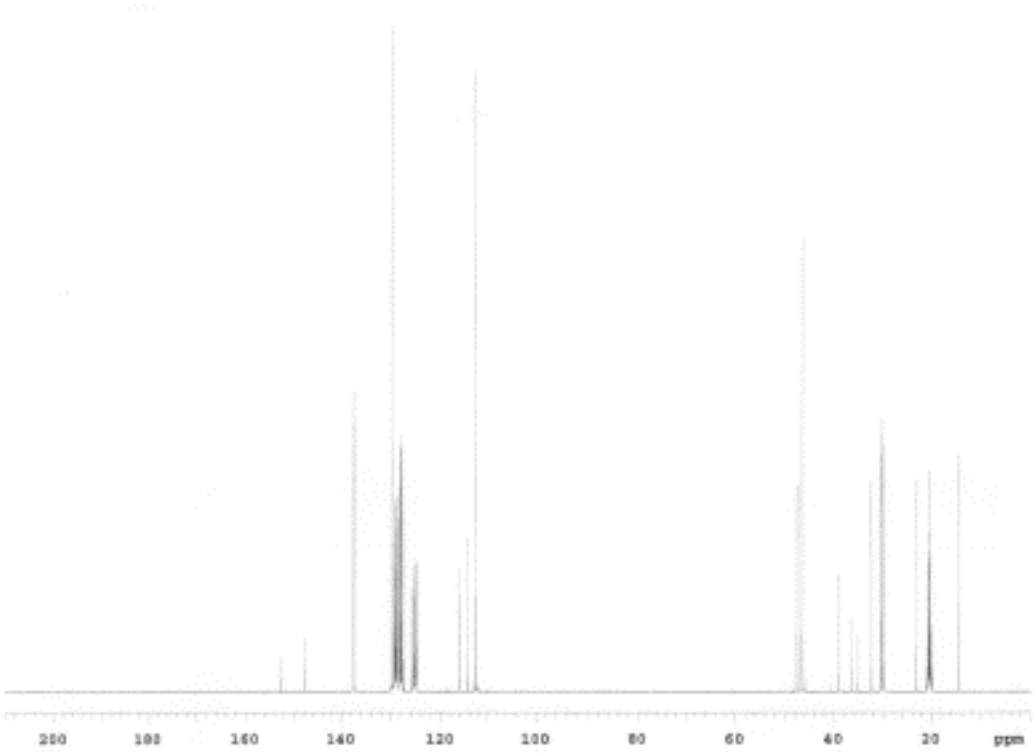
35

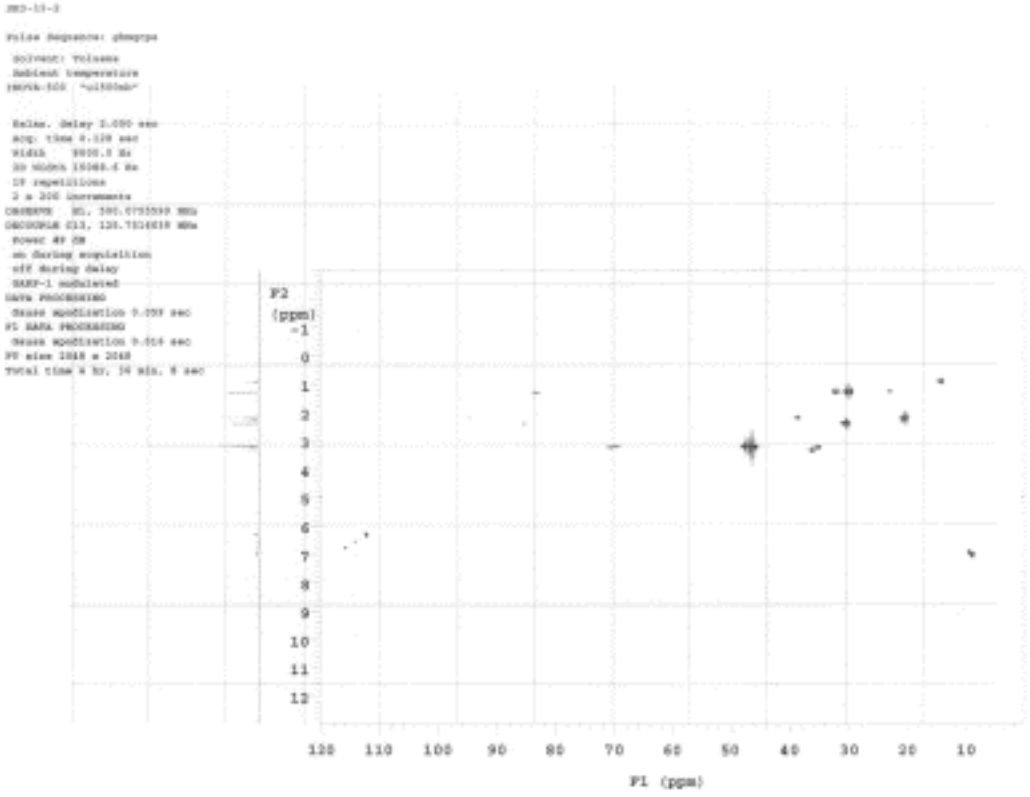


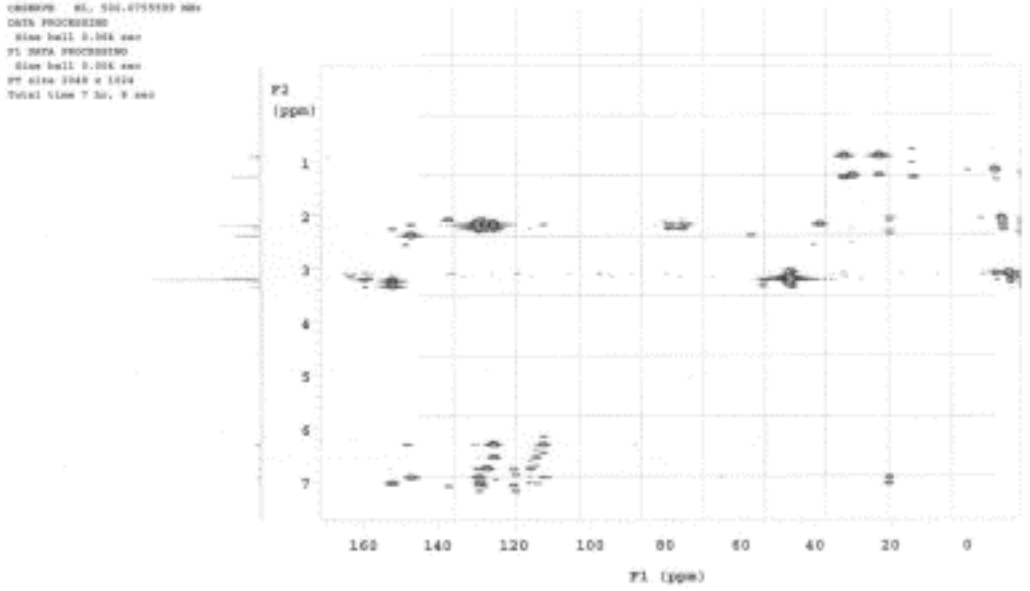

[(CH3)2N]4Ta—N
CH3
CH3
+
[(CH3)2N]3Ta—N
CH3
CH3
2

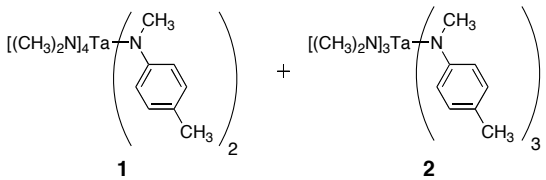
36 **1**


9
8
7
6
5
4
3
2
1
ppm

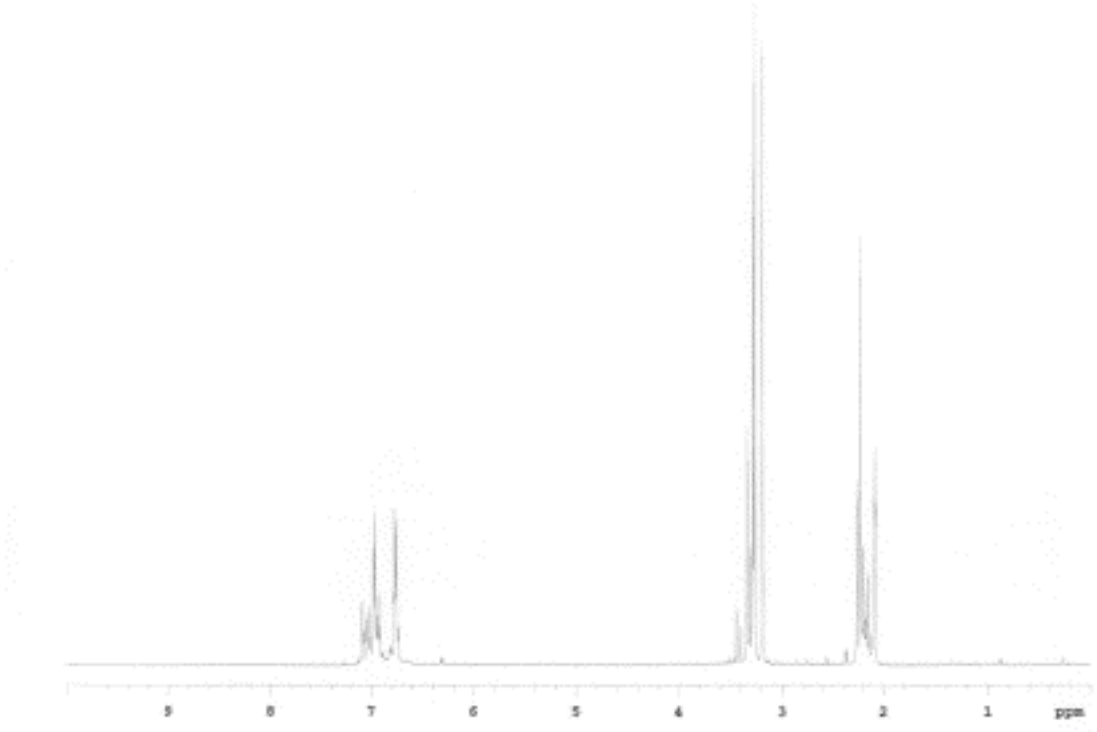

200
180
160
140
120
100
80
60
40
20
ppm

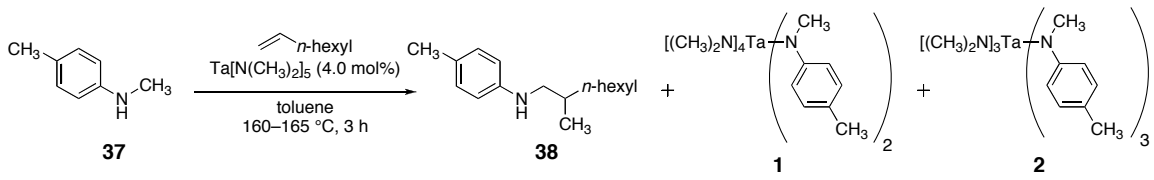

F2
(ppm)
F1 (ppm)

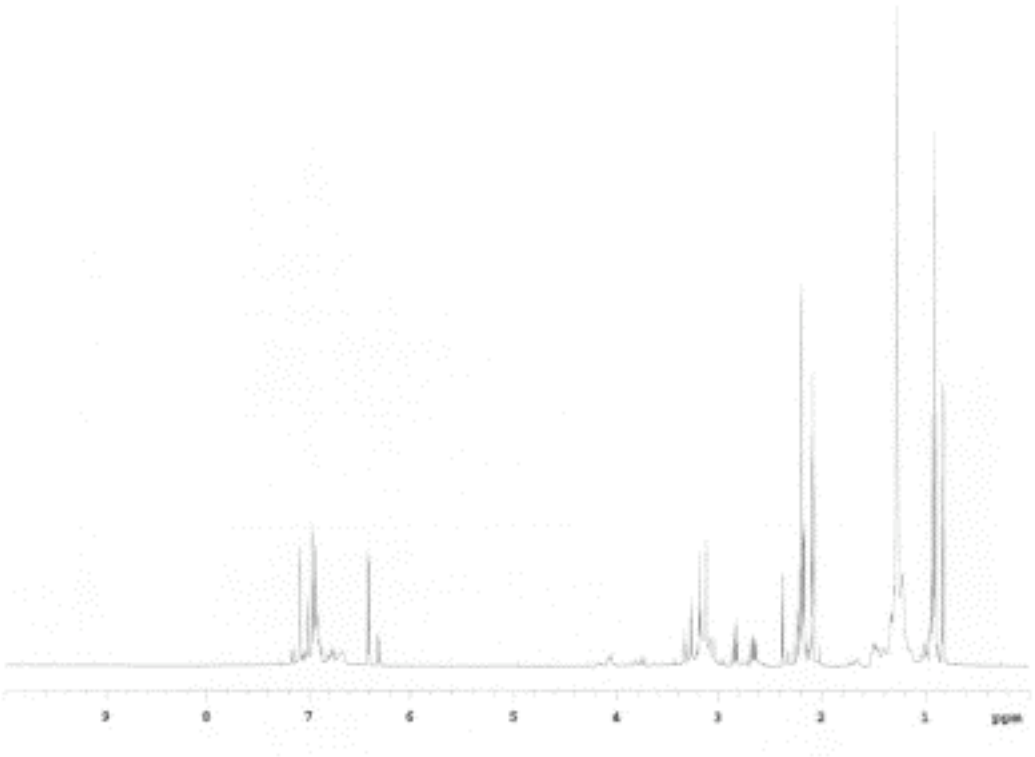

F2
(ppm)
F1 (ppm)



1 **2**




n-hexyl
Ta[N(CH3)2]5 (4.0 mol%)
toluene
160–165 °C, 3 h
37
38
1
2



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