

Supporting Information For: Palladium-Catalyzed Reductive Coupling of Styrenes and Organostannanes under Aerobic Conditions

Keith M. Gligorich, Sarah A. Cummings, and Matthew S. Sigman

Department of Chemistry, University of Utah, 315 S. 1400 E. Salt Lake City, UT 84112, USA

E-mail: sigman@chem.utah.edu

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General Considerations: 2-propanol was dried by refluxing over calcium oxide for 12 h followed by fractional distillation. THF was dried by distilling from sodium benzophenone ketyl. CH₂Cl₂ and triethylamine (TEA) were dried by distilling from calcium hydride. The 3 Å molecular sieves (3 ÅMS) were powdered and activated by heating with a Bunsen burner while under vacuum. Unless noted, all styrenes and MnO₂ were purchased from Aldrich or Acros. Styrenes were purified by passing through a small plug of activated alumina. Bu₃SnCl and PhSnBu₃ were purchased from Gelest Inc. Palladium^{II} chloride was purchased from Pressure Chemicals. Pd[(–)-sparteine]Cl₂ was synthesized according to a previously reported procedure.¹ (–)-sparteine was prepared from (–)-sparteine sulfate pentahydrate (purchased from Acros) according to a previously reported procedure.² ¹H-NMR spectra were obtained at 400 MHz or 300 MHz, chemical shifts are reported in ppm, and referenced to the CHCl₃ singlet at 7.27 ppm. ¹³C-NMR spectra were obtained at 100 MHz or 75 MHz and referenced to the center line of the CDCl₃ triplet at 77.2 ppm. Flash chromatography was performed either using EM reagent silica 60 (230-400 mesh) or GFS Chemicals activated alumina Brockmann 1. All melting points are uncorrected and were recorded on an electrothermal melting point apparatus. IR spectra were recorded using a FTIR instrument and GC/MS were obtained with a HP 5890 (EI) 50:1 split using a DB-5 column. HRMS were obtained with either an ESI or APCI source with an Agilent LCTOF. GC separations were performed with an HP6890 GC with a flame ionization detector equipped with a DB-5 column using a 50:1 split. Optical rotations were obtained (Na D line) using a Perkin Elmer Model 343 Polarimeter fitted with a micro cell with a 1 dm path length. Caution should be taken when heating flammable solvents in the presence of O₂.

Procedure Used for the Initial Identification of the Reductive Coupling (3a) and Oxidative Heck (4)

Products: To a flame dried 100 mL Schlenk flask equipped with a stir bar, was added 10.3 mg Pd[(–)-sparteine]Cl₂ (0.0250 mmol, 0.0250 equiv.), 10.1 mg of CuCl₂ (0.0750 mmol, 0.0750 equiv.), 500 mg of freshly activated 3ÅMS, and 9.20 mL of 2-propanol. A three-way joint fitted with a balloon of O₂ was installed on the flask. The flask was evacuated via water aspiration and refilled with oxygen three times and the mixture was stirred **vigorously** for ca. 20 minutes at room temperature under O₂. To the reaction mixture was added 0.800 mL of a 1.25 M solution of 4-methylstyrene (**1a**) (1.00 mmol, 1.00 equiv.) in 2-propanol dropwise via a syringe over 5 minutes and 425 µL of PhSnBu₃ (1.30 mmol, 1.30 equiv.) was added dropwise over 5 minutes. The reaction mixture was stirred **vigorously** under a balloon of O₂. After 40 h, 10.0 mL of a 1.00 M solution of aqueous NaOH was added to the reaction mixture and was stirred for 1 h.³ The mixture was filtered through Whatman filter paper, rinsed with ca. 10.0 mL of Et₂O, and was transferred to a separatory funnel. The aq. layer was extracted three times with 20.0 mL of Et₂O, all of the organic extracts were combined, washed with 60.0 mL of brine, and dried over MgSO₄. The mixture was filtered and the solvent was removed *in vacuo*. The products were purified via silica-gel column chromatography by eluting with 0 to 4% Et₂O/hexanes. The ¹H-NMR spectra for **3a**⁴ and **4**⁵ were compared to previously reported spectra. Both products were analyzed by GC-MS to obtain their retention times, which were used in the optimization for the reductive coupling product (**3a**).

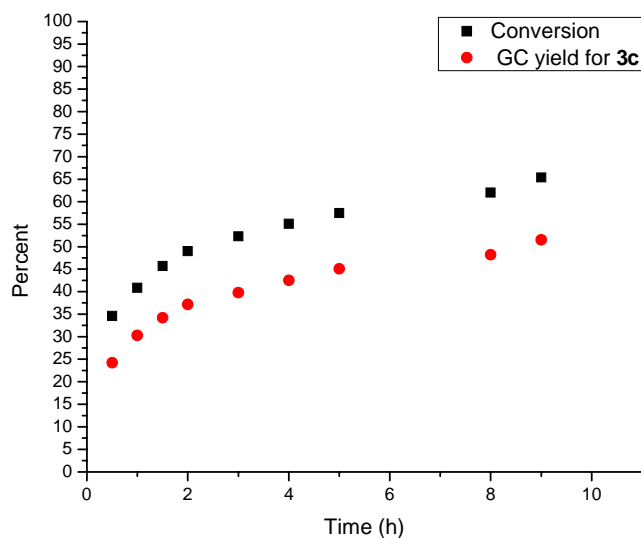
Optimization for the Reductive Coupling Product Procedures (Table 1): (Entry 1) To an oven dried 10 mL Schlenk flask equipped with a stir bar, was added 2.00 mg of CuCl₂ (0.0150 mmol, 0.0750 equiv.), 0.900 mL of 2-propanol, 0.100 mL of a 2.00 M solution of 4-methylstyrene (**1a**) (0.200 mmol, 1.00 equiv.) in 2-propanol, which contained ca. 1% undecane as an internal standard, and 98.0 µL of PhSnBu₃ (0.300 mmol, 1.50 equiv.). The flask was installed on a 4-neck flask equipped with condensers (repeated three more times to perform four reactions at once) and a three-way joint fitted with a balloon of O₂ was installed on the top of the 4-neck flask. The flask was evacuated via water aspiration and refilled with oxygen three times and the mixture was stirred **vigorously** for ca. 20 minutes at room temperature under O₂. The Schlenk flask was removed from the 4-neck flask and to the reaction mixture, was added 2.10 mg of Pd[(–)-sparteine]Cl₂ (0.00500 mmol, 0.0250 equiv.). The flask was reinstalled on the 4-neck flask and was evacuated via water aspiration and refilled with oxygen three times. The reaction mixture was stirred **vigorously** under a balloon of O₂ at ambient temperature for 20 h and was orange in color. A small aliquot of the 2.00 M solution of **1a** with, undecane as the internal standard, was analyzed by GC and used to calculate the conversion of the substrate. After 20 h, a 50 µL aliquot of the reaction mixture was removed and filtered through a small plug of silica eluting with EtOAc. The mixture was analyzed by GC and both the conversion of the substrate was calculated and the GC yields for the products were calculated using a correction factor (¹H-NMR was used to measure the response factor to account for varying detector response).

- **Entry 2:** The same procedure as described above for entry 1 was used except no CuCl₂ was added.
- **Entry 3:** The same procedure as described for entry 1 was used except no CuCl₂ was added and 0.700 mL of 2-propanol and 0.200 mL of a 0.400 M solution of (–)-sparteine (0.080 mmol, 0.400 equiv.) in 2-propanol were added at the same time the solution of **1a** and PhSnBu₃ were added.
- **Entry 4:** The same procedure was used as entry 3 except 5 minutes after the Pd[(–)-sparteine]Cl₂ was added and the flask was filled/purged with O₂, the reaction mixture was heated to 60 °C in an oil bath and **vigorously** stirred for 20 h.
- **Entry 5:** The same procedure was used as entry 4, except 0.100 mL of a 0.400 M solution of (–)-sparteine (0.0400 mmol, 0.200 equiv.) in 2-propanol and 0.100 mL of a 0.400 M solution of (–)-sparteine-*N*-oxide (0.0400 mmol, 0.200 equiv.) in 2-propanol were added at the same time the solution of **1a** and PhSnBu₃ were added. For the synthesis of (–)-sparteine-*N*-oxide see below.
- **Entry 6:** The same procedure was used as entry 4, except 0.600 mL of 2-propanol and 0.100 mL of a 0.400 M solution of (–)-sparteine-*N*-oxide (0.0400 mmol, 0.200 equiv.) in 2-propanol were added at the same time the solution of **1a** and PhSnBu₃ were added.

- **Entry 7:** The same procedure was used as entry 4, except 13.0 mg of MnO₂ (0.150 mmol, 0.750 equiv.) was initially added.
- **Entry 8:** The same procedure was used as entry 6, except 13.0 mg of MnO₂ (0.150 mmol, 0.750 equiv.) was initially added.
- **Entry 9:** To an oven dried 100 mL Schlenk flask equipped with a stir bar, was added 4.30 mL of 2-propanol, 0.200 mL of a 2.00 M solution of (–)-sparteine (0.400 mmol, 0.400 equiv.) in 2-propanol, 0.500 mL of a 2.00 M solution of 4-methylstyrene (**1a**) (1.00 mmol, 1.00 equiv.) in 2-propanol, which contained ca. 1% undecane as an internal standard, and 490 µL of PhSnBu₃ (1.50 mmol, 1.50 equiv.). A condenser was installed on the flask and a three-way joint fitted with a balloon of O₂ was installed on the top of the condenser. The flask was evacuated via water aspiration and refilled with oxygen three times and the mixture was stirred **vigorously** for ca. 20 minutes at room temperature under O₂. The flask was removed from the condenser and to the reaction mixture, was added 10.3 mg of Pd[(–)-sparteine]Cl₂ (0.0250 mmol, 0.0250 equiv.). The condenser was reinstalled on flask and the flask was evacuated via water aspiration and refilled with oxygen three times. The reaction mixture was stirred **vigorously** under a balloon of O₂ at ambient temperature for 5 minutes. The mixture was heated to 60 °C in an oil bath and was stirred **vigorously** for 20 h. The reaction mixture was analyzed by GC in the same manner as described for entry 1.
- **Entry 10:** A three-way joint was fitted to the side arm of an oven dried 100 mL thick-wall glass pressure vessel equipped with a stir bar. An O₂ tank was connected to the three-way joint and O₂ was passed through the vessel. To the vessel, was added 4.30 mL of 2-propanol, 0.200 mL of a 2.00 M solution of (–)-sparteine (0.400 mmol, 0.400 equiv.) in 2-propanol, 0.500 mL of a 2.00 M solution of 4-methylstyrene (**1a**) (1.00 mmol, 1.00 equiv.) in 2-propanol, which contained ca. 1% undecane as an internal standard, and 490 µL of PhSnBu₃ (1.50 mmol, 1.50 equiv.). The vessel was sealed, pressurized to 25 psi, evacuated via water aspiration, and re-pressurized to 25 psi O₂. This procedure was repeated three times. The vessel was sealed and the mixture was stirred **vigorously** for ca. 20 min at room temperature at 25 psi O₂. The vessel was opened and O₂ was passed through the vessel. To the stirred mixture, was added 10.3 mg of Pd[(–)-sparteine]Cl₂ (0.0250 mmol, 0.0250 equiv.). The vessel was immediately pressurized to 25 psi O₂ and was sealed. The three-way joint was removed and the reaction mixture was stirred **vigorously** for 5 min at room temperature. The mixture was then heated to 60 °C in an oil bath and was stirred **vigorously** for 20 h. The vessel was removed from the oil bath and cooled to room temperature. The reaction mixture was analyzed by GC in the same manner as described for entry 1.
- **Entry 11:** The same procedure as entry 10 was used except 65.2 mg of MnO₂ (0.750 mmol, 0.750 equiv.) was initially added.

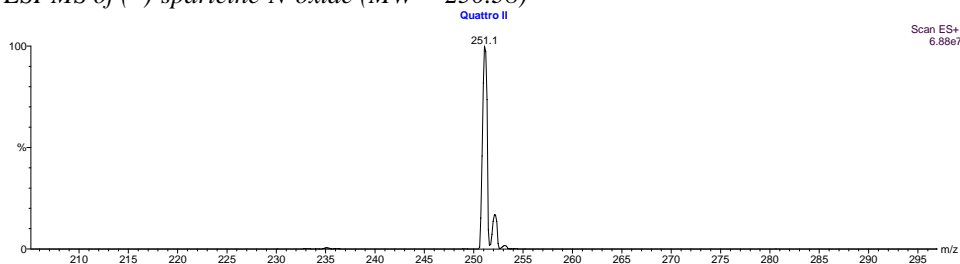
Optimization note: The use of 3Å molecular sieves did not have an appreciable affect upon the reaction.

Time Course of the Reductive Coupling Reaction without MnO₂: To an oven dried 10 mL Schlenk flask equipped with a stir bar, was added 1.25 mL of 2-propanol, 0.150 mL of a 0.800 M solution of (–)-sparteine (0.120 mmol, 0.400 equiv.) in 2-propanol, 0.100 mL of a 3.00 M solution of 4-methylstyrene (**1a**) (0.300 mmol, 1.00 equiv.) in 2-propanol, which contained ca. 1% undecane as an internal standard, and 127 µL of PhSnBu₃ (0.390 mmol, 1.30 equiv.). A condenser was installed on the flask and a three-way joint fitted with a balloon of O₂ was installed on the top of the condenser. The flask was evacuated via water aspiration and refilled with oxygen three times and the mixture was stirred **vigorously** for ca. 20 minutes at room temperature under O₂. The flask was removed from the condenser and to the reaction mixture, was added 3.10 mg of Pd[(–)-sparteine]Cl₂ (0.00750 mmol, 0.0250 equiv.). The condenser was reinstalled on flask and the flask was evacuated via water aspiration and refilled with oxygen three times. The reaction mixture was stirred **vigorously** under a balloon of O₂ at ambient temperature for 5 minutes. The mixture was heated to 60 °C in an oil bath and was stirred **vigorously** for 20 h. The reaction mixture was analyzed by GC at different times in the same manner as described for entry 1 above and the data is plotted below.



Synthesis of (–)-sparteine-*N*-oxide:⁶ To a 50 mL round bottom flask equipped with a stir bar, was added 234 mg of (–)-sparteine (1.00 mmol, 1.00 equiv.), 8.00 mL of MeOH, and 0.943 mL of 30% (v/v) H₂O₂ in water (8.30 mmol, 8.30 equiv.). The flask was sealed and stirred at room temperature for 3 days. To the stirred mixture, was added ca. 20 mg of 10 wt.% palladium on activated carbon. After 2 h, the mixture was filtered through celite and rinsed with ca. 20 mL of Et₂O. The solvent was removed *in vacuo* to produce a yellow oil. To the oil, was added 20 mL of CH₂Cl₂ and the mixture was dried over Na₂SO₄ for 2 h. The mixture was filtered and the solvent was removed *in vacuo* to produce a yellow oil. Trace solvent was removed by high vacuum to yield a white solid. The product was characterized by ESI-MS by dissolving the solid in a 1:1 2-propanol:H₂O solvent mixture containing 1% glacial acetic acid and the solution was injected into the instrument with a syringe pump.

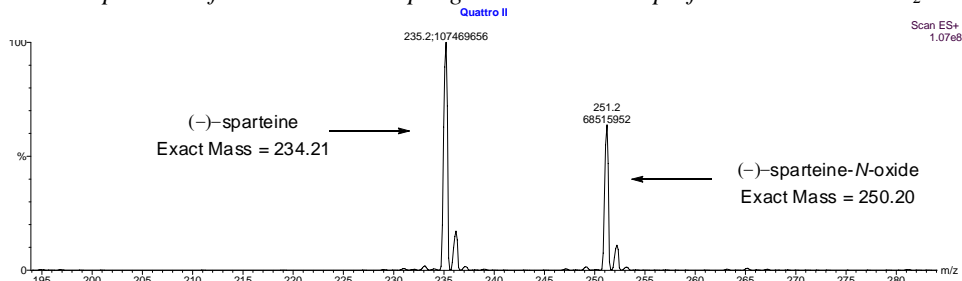
*ESI-MS of (–)-sparteine-*N*-oxide (MW = 250.38)*



ESI-MS Analysis of the Reductive Coupling Reaction Mixtures without and with MnO₂

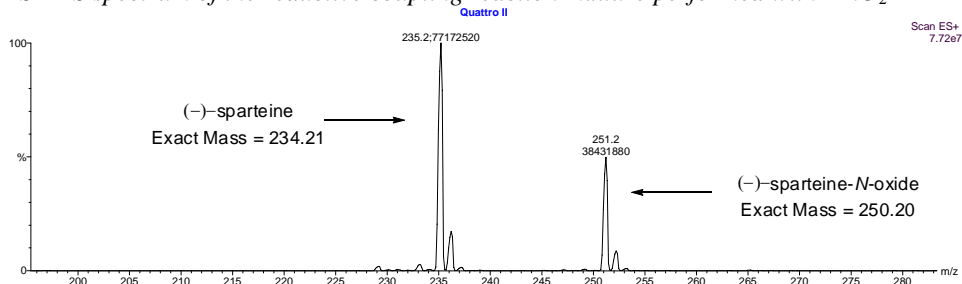
Experiment performed without MnO₂: After cooling to room temperature, a 20 μL aliquot of the reductive coupling reaction mixture, which was performed on 1.0 mmol scale at 25 psi without MnO₂ (Table 1, entry 8) was diluted with 480 μL of 2-propanol, 500 μL H₂O, and 10 μL of glacial acetic acid. The solution was injected into the Micromass Quattro II quadrupole ESI-MS instrument with a syringe pump.

ESI-MS spectrum of the reductive coupling reaction mixture performed without MnO₂



Experiment performed with MnO₂: After cooling the reaction mixture, which was performed on 1.0 mmol scale at 25 psi with MnO₂ (Table 1, entry 9), to room temperature, the mixture was filtered through Whatman filter paper to remove the MnO₂. A 20 μ L aliquot of the reaction mixture was diluted with 480 μ L of 2-propanol, 500 μ L H₂O, and 10 μ L of glacial acetic acid. The solution was injected into the Micromass Quattro II quadrupole ESI-MS instrument with a syringe pump using the same flow rate and settings (ie. voltages, gain, etc.) as the experiment performed without MnO₂.

ESI-MS spectrum of the reductive coupling reaction mixture performed with MnO₂

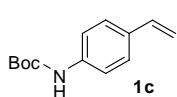


Calculation of the percent difference of (-)-sparteine-N-oxide to (-)-sparteine with and without MnO₂

	Peak heights from ESI-MS experiments	
	No MnO ₂	75 mol% MnO ₂
(-)-sparteine	107469656	77687224
(-)-sparteine-N-oxide	68515952	38769100
(-)-sparteine-N-oxide/ (-)-sparteine	0.63754	0.49904

$$\text{Percent difference} = [(0.63754/0.49904)-1]*100 = 28\%$$

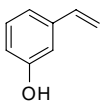
Synthesis of Styrene Derivatives:



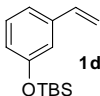
tert-butyl-4-vinylphenylcarbamate (1c): To an oven dried 100 mL round bottom flask equipped with a stir bar, was added 1.15 g Boc₂O (5.27 mmol, 1.15 equiv.) and 20.0 mL THF under a N₂ atmosphere. A solution of 546 mg of 4-vinylaniline (Oakwood Products Inc.) (4.58 mmol, 1.00 equiv.) in 20 mL THF was added to the stirred solution of Boc₂O via syringe, and a dried water condenser was installed on the flask. The mixture was heated to 50 °C in an oil bath, and stirred under N₂ for 12 h. An additional 500 mg Boc₂O (2.29 mmol, 0.500 equiv.) was added, and the reaction was stirred at 50 °C for another 12 h. The mixture was diluted with 20 mL Et₂O, washed twice with 50 mL of sat. aq. NH₄Cl, twice with 50 mL of H₂O, and once with 50 mL of brine. The organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. Column chromatography eluting with 4% Et₂O/hexanes yielded a mixture of *tert*-butyl-4-vinylphenylcarbamate (**1c**) and Boc₂O. The mixture was diluted with 50 mL Et₂O, washed twice with 50 mL of sat. aq. NH₄Cl, once with 50 mL of brine, and

twice with 50 mL of 1:1 aq. $\text{NH}_4\text{OH}/\text{H}_2\text{O}$. The combined aqueous layers were extracted with 50 mL of Et_2O and the organic extracts were washed with 50 mL of brine, dried with MgSO_4 , filtered, and the solvent was removed *in vacuo*. Silica gel flash chromatography, eluting with 4% Et_2O /hexanes to 8% Et_2O /hexanes, yielded the product as a white solid.

1c, Yield: 62% (621.5 mg); R_f : 0.50 w/ 20% EtOAc /hexanes (silica); White solid; mp: 84 °C; IR (KBr) 3376, 2984, 2936, 1754, 1612, 1586, 1523, 1319, 1236, 1160, 1056, 986, 838, 771, 619; ^1H -NMR (300 MHz, CDCl_3) δ 1.52 (s, 9 H), 5.16 (dd, J = 1.0 Hz, 11.0 Hz, 1 H), 5.65 (dd, J = 1.0 Hz, 17.6 Hz, 1 H), 6.49 (br s, 1 H), 6.66 (dd, J = 11.0 Hz, 17.6 Hz, 1 H), 7.34 (m, 4 H); ^{13}C -NMR $\{^1\text{H}\}$ (75 MHz, CDCl_3) δ 28.5, 80.8, 112.5, 118.6, 127.0, 132.7, 136.4, 138.1, 152.8; MS (E.I.) m/z (M) $^+$ calcd. 219.13 obsd. 219.10.



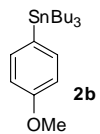
3-vinylphenol:⁷ To a 500 mL flame dried round bottom flask equipped with a stir bar, was added 8.75 g of methyltriphenylphosphonium bromide (24.5 mmol, 2.25 equiv.) and 100 mL of THF under a N_2 atmosphere. To the cloudy white mixture, was added 2.81 g of KO^tBu (25.0 mmol, 2.50 equiv.) in three portions. The reaction mixture turned yellow and was stirred 4 h. The mixture was cooled to -78 °C and 1.22 g of 3-hydroxybenzaldehyde (Acros) (10.0 mmol, 1.00 equiv.) dissolved in 10 mL of THF, was added dropwise via cannulation. The mixture was allowed to slowly warm to ambient temperature and stirred 12 h. To the yellow mixture, was added 100 mL of saturated NH_4Cl solution and the cloudy white solution was stirred for 1 h. The mixture was transferred to a separatory funnel and was extracted three times with 30 mL of Et_2O . The organic extracts were combined, washed once with 100 mL of brine, dried over MgSO_4 , filtered, and the solvent removed *in vacuo* to yield a yellow oil. The product was purified by bulb to bulb distillation and isolated in 87% yield. The ^1H -NMR spectrum was compared to the previously reported spectrum.⁸



tert-butyldimethyl(3-vinylphenoxy)silane (1d): To a flame dried 25 mL round bottom flask equipped with a stir bar, was added 240 mg of 3-vinylphenol (2.00 mmol, 1.00 equiv.) and 5.00 mL of CH_2Cl_2 under a N_2 atmosphere. To the mixture was added 1.86 mL of TEA (4.00 mmol, 2.00 equiv.) and 1.00 g of *tert*-butylchlorodimethylsilane (4.00 mmol, 2.0 equiv.). The reaction mixture turned cloudy white and was stirred overnight. The mixture was filtered through Whatman filter paper and was rinsed with CH_2Cl_2 . The mixture was washed with ca. 10 mL H_2O , ca. 10 mL of sat. NH_4Cl , and was dried over MgSO_4 . The mixture was filtered and the solvent was removed *in vacuo* to produce a clear oil. The product was purified by silica gel flash chromatography eluting with pentane.

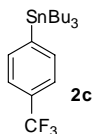
1d, Yield: 82% (386.1 mg); R_f = 0.88 w/ 20% Et_2O /Hexanes (silica); Clear oil; IR (neat) 3089, 2956, 2932, 2859, 1599, 1578, 1484, 1279, 1157, 962, 840, 715 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3): δ 0.22 (s, 6H), 1.0 (s, 9H), 5.25 (dd, J = 0.7 Hz, 10.6 Hz, 1H), 5.72 (dd, J = 0.7 Hz, 17.6 Hz, 1H), 6.67 (dd, J = 10.6 Hz, 17.6 Hz, 1H), 6.75 (ddd, J = 0.7 Hz, 2.6 Hz, 8.1 Hz, 1H), 6.90 (dd, J = 2.0 Hz, 2.0 Hz, 1H), 7.01-7.03 (m, 1H), 7.19 (dd, J = 8.0 Hz, 8.0 Hz, 1H); ^{13}C -NMR $\{^1\text{H}\}$ (100 MHz, CDCl_3): δ -4.2, 18.8, 25.9, 114.1, 118.0, 119.7, 119.8, 129.6, 136.9, 139.3, 156.1; MS (ESI/APCI) m/z (MH) $^+$ calcd.: 235.1518 obsd.: 235.1512.

Synthesis of Organostannane Reagents:

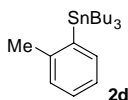


tributyl(4-methoxyphenyl)stannane (2b):⁹ To a flame dried 100 mL Schlenk flask equipped with a stirbar and a dried water condenser under a N_2 atmosphere, was added 25.0 mL of THF and 585 mg of magnesium turnings (24.0 mmol, 1.60 equiv.), which were activated by crushing with a mortar and pestle. To the stirred mixture, was added 4 drops of 1,2-dibromoethane and 1.89 mL of 1-bromo-4-methoxybenzene (Aldrich) (15.0 mmol, 1.00 equiv.), which was added dropwise over 5 minutes. The mixture slowly turned dark brown and the stirred mixture was heated to reflux overnight. The reaction mixture was cooled to room temperature and was cannulated into a dried 100 mL Schlenk flask equipped with a stirbar and condenser under a N_2 atmosphere. To the stirred mixture, was added 4.88 mL of Bu_3SnCl (18.0 mmol, 1.20 equiv.) dropwise over 5 minutes. The stirred mixture was heated to reflux for 4 h and was cooled to room temperature. To the stirred mixture, was added ca. 20 mL of aqueous 1.00 M NaOH .³ After an hour the mixture was transferred to a separatory funnel and the aqueous layer was extracted three times with 20 mL of Et_2O . The organic extracts were collected and washed with 60 mL of brine, dried over MgSO_4 , filtered, and the solvent was removed *in vacuo* to yield a clear oil. The product was purified by silica gel flash chromatography eluting with 2% Et_2O /hexanes. The

product was obtained as a clear oil in 87% yield and the ^1H -NMR spectrum was compared to a previously reported spectrum.¹⁰

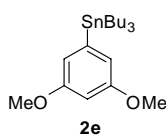


tributyl(4-(trifluoromethyl)phenyl)stannane (2c): The same procedure used for the synthesis of **2b** was used except 2.38 mL of 1-bromo-4-(trifluoromethyl)benzene (Acros) (15.0 mmol, 1.00 equiv.) was used and the product was purified by silica gel flash chromatography eluting with pentane. The product was obtained as a clear oil in 60% yield and the ^1H -NMR spectrum was compared to a previously reported spectrum.¹¹



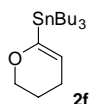
tributyl(o-tolyl)stannane (2d): The same procedure used for the synthesis of **2b** was used except 1.78 mL of 2-bromotoluene (Aldrich) (15.0 mmol, 1.00 equiv.) was used and the product was purified by silica gel flash chromatography eluting with hexanes.

2d, Yield: 97% (5.56 g); R_f = 0.62 w/ Hexanes (silica); Clear oil; IR (neat) 3053, 2958, 2853, 1563, 1421, 1340, 1073, 869, 741, 688, 594 cm^{-1} ; ^1H -NMR (300 MHz, CDCl_3): δ 0.88 (t, J = 7.3 Hz, 9H), 1.04-1.10 (m, 6H), 1.26-1.30 (m, 6H), 1.47-1.57 (m, 6H), 2.39 (s, 3H), 7.10-7.25 (bm, 3H), 7.38 (dd, J = 1.5 Hz, 7.0 Hz, 1H); ^{13}C -NMR { ^1H } (100 MHz, CDCl_3): δ 10.3, 13.9, 25.2, 27.7, 29.4, 125.1, 128.5, 129.1, 136.8, 142.1, 144.8; MS (APCI) m/z (MH^+) calcd.: 383.2 obsd.: 383.8. (the intensity of the (MH^+) peak was very small)

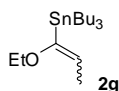


tributyl(3,5-dimethoxyphenyl)stannane (2e): The same procedure used for the synthesis of **2b** was used except 2.59 g of 1-chloro-3,5-dimethoxybenzene (TCI America) (15.0 mmol, 1.00 equiv.) was used and the product was purified by silica gel flash chromatography eluting with 5% Et_2O /hexanes.

2e, Yield: 65% (4.18 g); R_f = 0.65 w/ 10% Et_2O /Hexanes (silica); Clear oil; IR (neat) 2956, 2926, 2851, 1560, 1461, 1378, 1246, 1156, 1063, 860, 734, 597 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3): δ 0.90 (t, J = 7.3 Hz, 9H), 1.03-1.07 (m, 6H), 1.29-1.39 (m, 6H), 1.51-1.59 (m, 6H), 3.81 (s, 6H), 6.41 (dd, J = 2.3 Hz, 2.3 Hz, 1H), 6.62 (d, J = 2.3 Hz, 2H); ^{13}C -NMR { ^1H } (100 MHz, CDCl_3): δ 9.8, 13.8, 27.6, 29.3, 55.1, 99.9, 114.0, 144.1, 160.4; MS (ESI/APCI) m/z (MH^+) calcd.: 429.1816 obsd.: 429.1815.



tributyl(3,4-dihydro-2H-pyran-6-yl)stannane (2f): Stannane **2f** was synthesized according to a previously reported procedure and the ^1H -NMR spectrum was compared to the previously reported spectrum.¹²

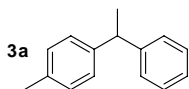


tributyl(1-ethoxyprop-1-enyl)stannane (2g): Stannane **2g** was synthesized according to a previously reported procedure and the ^1H -NMR spectrum was compared to the previously reported spectrum.¹³



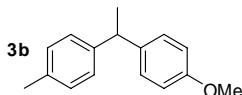
tributyl(2-methylprop-1-enyl)stannane (2h): Stannane **2g** was synthesized according to a previously reported procedure¹⁴ from (2-methylprop-1-enyl)magnesium bromide (Aldrich) and the ^1H -NMR spectrum was compared to the previously reported spectrum.¹⁵

General Reductive Coupling Procedure: IMPORTANT NOTE: A 100 mL thick-wall glass pressure vessel with an approximate 4.5 cm diameter was used. The use of smaller diameter vessels led to catalyst decomposition, which can be attributed to inefficient mass transport of O_2 .¹⁶

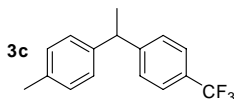


1-methyl-4-(1-phenylethyl)benzene (3a): A three-way joint was fitted to the side arm of an oven dried 100 mL thick-wall glass pressure vessel equipped with a stir bar. An O_2 tank was connected to the three-way joint and O_2 was flowed through the vessel. To the vessel, was added 65.2 mg of MnO_2 (0.750 mmol, 0.750 equiv.), 4.30 mL of 2-propanol, 0.200 mL of a 2.00 M solution of (–)-sparteine (0.400 mmol, 0.400 equiv.) in 2-propanol,

0.132 mL of 4-methylstyrene (**1a**) (1.00 mmol, 1.00 equiv.), and 490 μ L of PhSnBu₃ (1.50 mmol, 1.50 equiv.). The vessel was sealed, pressurized to 25 psi, evacuated via water aspiration, and repressurized to 25 psi O₂. This procedure was repeated three times. The vessel was sealed and the mixture was stirred **vigorously** for ca. 20 min at room temperature at 25 psi O₂. The vessel was opened and O₂ was flowed through the vessel. To the stirred mixture, was added 10.3 mg of Pd[(–)-sparteine]Cl₂ (0.0250 mmol, 0.0250 equiv.). The vessel was immediately pressurized to 25 psi O₂ and was sealed. The three-way joint was removed and the reaction mixture was stirred **vigorously** for 5 min at room temperature. The mixture was then heated to 60 °C in an oil bath and was stirred **vigorously** for 18 h. The vessel was removed from the oil bath and cooled to room temperature. To the reaction mixture, was added 5.0 mL of a 1.00 M solution of aqueous NaOH and was stirred for 1 h.³ The mixture was filtered through Whatman filter paper, rinsed with ca. 10.0 mL of Et₂O, and was transferred to a separatory funnel. The aqueous layer was extracted three times with 20.0 mL of Et₂O, all of the organic extracts were combined, washed with 40.0 mL of brine, and dried over MgSO₄. The mixture was filtered and the solvent was removed *in vacuo*. The product was purified via alumina gel flash chromatography by eluting with pentane. The ¹H-NMR spectrum, see below, was compared to a previously reported spectrum.⁴ For each substrate, this procedure was performed twice and the average isolated yield is reported. **3a**, Yield: 76% (144.6 mg and 155.2 mg); R_f = 0.65 w/ Hexanes (alumina), PMA stain.

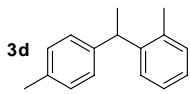


1-methoxy-4-(1-(p-tolylethyl)benzene (3b): The same procedure used to synthesize **3a** was used except 596 mg of tributyl(4-methoxyphenyl)stannane (**2b**) (1.50 mmol, 1.50 equiv.) was added via syringe and the product was purified via alumina gel flash chromatography by eluting with pentane to 3% Et₂O/pentane. The ¹H-NMR spectrum, see below, was compared to a previously reported spectrum.¹⁷ **3b**, Yield: 70% (159.3 mg and 158.2 mg); R_f = 0.23 w/ Hexanes (alumina), PMA stain.



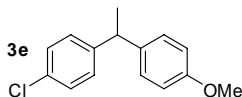
1-methyl-4-(1-(4-(trifluoromethyl)phenyl)ethyl)benzene (3c): The same procedure used to synthesize **3a** was used except 653 mg of tributyl(4-(trifluoromethyl)phenyl)stannane (**2c**) (1.50 mmol, 1.50 equiv.) was added via syringe and the product was purified via alumina gel flash chromatography by eluting with pentane.

3c, Yield: 67% (179.6 mg and 174.4 mg); R_f = 0.61 w/ Hexanes (alumina), PMA stain. IR (neat) 3021, 2972, 2932, 2878, 1918, 1618, 1513, 1415, 1326, 1164, 1122, 1018, 819, 730, 628, 535 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 1.65 (d, *J* = 7.3 Hz, 3H), 2.33 (s, 3H), 4.18 (q, *J* = 7.3 Hz, 1H), 7.09-7.14 (m, 4H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.1 Hz, 2H); ¹³C-NMR {¹H} (100 MHz, CDCl₃): δ 21.2, 21.9, 44.6, 125.6, 127.7, 128.2, 129.6, 136.3, 142.6, 151.0; MS (ESI/APCI) *m/z* (M-H)⁺ calcd.: 263.1048 obsd.: 263.1041.



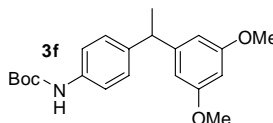
2,4'-(ethane-1,1-diyl)bis(methylbenzene) (3d): The same procedure used to synthesize **3a** was used except 572 mg of tributyl(*o*-tolyl)stannane (**2d**) (1.50 mmol, 1.50 equiv.) was added via syringe, 14.4 mg of Pd[(–)-sparteine]Cl₂ (0.0350 mmol, 0.0350 equiv.) was added, and the product was purified via alumina gel flash chromatography by eluting with pentane.

3d, Yield: 59% (119.5 mg and 126.6 mg); R_f = 0.57 w/ Hexanes (alumina), PMA stain. IR (neat) 3047, 3020, 2967, 2927, 2872, 1901, 1512, 1488, 1375, 1330, 1048, 818, 767, 733, 552 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 1.60 (d, *J* = 7.0 Hz, 3H), 2.25 (s, 3H), 2.31 (s, 3H), 4.29 (q, *J* = 7.3 Hz, 1H), 7.07 (dd, *J* = 8.2 Hz, 11.9 Hz, 4H), 7.13-7.14 (m, 2H), 7.19-7.23 (m, 1H), 7.27-7.29 (m, 1H); ¹³C-NMR {¹H} (100 MHz, CDCl₃): δ 20.0, 21.2, 22.5, 40.8, 126.3, 126.8, 127.8, 129.3, 130.6, 135.5, 136.3, 143.5, 144.4; MS (ESI/APCI) *m/z* (M-H)⁺ calcd.: 209.1330 obsd.: 209.1329.



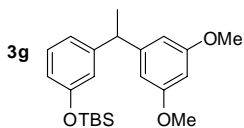
1-chloro-4-(1-(4-methoxyphenyl)ethyl)benzene (3e): The same procedure used to synthesize **3a** was used except 0.120 mL of 4-chlorostyrene (1.00 mmol, 1.00 equiv.), 596 mg of tributyl(4-methoxyphenyl)stannane (**2b**) (1.50 mmol, 1.50 equiv.) was added via syringe and the product was purified via alumina gel

flash chromatography by eluting with pentane to 10% Et₂O/pentane. The ¹H-NMR spectrum, see below, was compared to a previously reported spectrum.¹⁸ **3e**, Yield: 65% (157.4 mg and 161.7 mg); R_f = 0.23 w/ Hexanes (alumina), PMA stain.



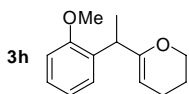
tert-butyl-4-(1-(3,5-dimethoxyphenyl)ethyl)phenylcarbamate (3f): A three-way joint was fitted to the side arm of an oven dried 100 mL thick-wall glass pressure vessel equipped with a stir bar. An O₂ tank was connected to the three-way joint and O₂ was flowed through the vessel. To the vessel, was added 32.6 mg of MnO₂ (0.375 mmol, 0.750 equiv.), 2.30 mL of 2-propanol, 0.200 mL of a 1.00 M solution of (–)-sparteine (0.200 mmol, 0.400 equiv.) in 2-propanol, 110 mg of *tert*-butyl 4-vinylphenylcarbamate (**1c**) (0.500 mmol, 1.00 equiv.), and 320 mL of tributyl(3,5-dimethoxyphenyl)stannane (**2e**) (0.750 mmol, 1.50 equiv.). The vessel was sealed, pressurized to 25 psi, evacuated via water aspiration, and re-pressurized to 25 psi O₂. This procedure was repeated three times. The vessel was sealed and the mixture was stirred **vigorously** for ca. 20 min at room temperature at 25 psi O₂. The vessel was opened and O₂ was flowed through the vessel. To the stirred mixture, was added 5.20 mg of Pd[(–)-sparteine]Cl₂ (0.0125 mmol, 0.0250 equiv.). The vessel was immediately pressurized to 25 psi O₂ and was sealed. The three-way joint was removed and the reaction mixture was stirred **vigorously** for 5 min at room temperature. The mixture was then heated to 60 °C in an oil bath and was stirred **vigorously** for 18 h. The vessel was removed from the oil bath and cooled to room temperature. To the reaction mixture, was added 2.5 mL of a 1.00 M solution of aqueous NaOH and was stirred for 1 h.³ The mixture was filtered through Whatman filter paper, rinsed with ca. 5.0 mL of Et₂O, and was transferred to a separatory funnel. The aqueous layer was extracted three times with 10.0 mL of Et₂O, all of the organic extracts were combined, washed with 20.0 mL of brine, and dried over MgSO₄. The mixture was filtered and the solvent was removed *in vacuo*. The product was purified via silica gel flash chromatography by eluting with 2% EtOAc/hexanes to 10% EtOAc/hexanes.

3f, Yield: 58% (104.4 mg and 98.3 mg); R_f = 0.55 w/ 30% EtOAc/hexanes (silica), PMA stain. IR (neat) 3340, 2970, 2935, 2837, 2284, 1899, 1725, 1598, 1524, 1460, 1427, 1411, 1314, 1158, 1051, 1019, 836, 696 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃): δ 1.50 (s, 9H), 1.57 (d, *J* = 7.3 Hz, 3H), 3.74 (s, 6H), 4.02 (q, *J* = 7.2 Hz, 1H), 6.28 (dd, *J* = 2.4 Hz, 2.4 Hz, 1H), 6.36 (d, *J* = 2.2 Hz, 2H), 6.39–6.41 (bs, 1H), 7.12–7.15 (m, 2H), 7.24–7.29 (m, 2H); ¹³C-NMR {¹H} (75 MHz, CDCl₃): δ 22.0, 28.6, 44.6, 55.4, 80.6, 97.9, 106.2, 118.9, 128.2, 136.6, 141.0, 149.2, 153.2, 160.9; MS (ESI/APCI) *m/z* (MNa)⁺ calcd.: 380.1838 obsd. 380.1840.



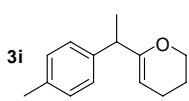
tert-butyl(3-(1-(3,5-dimethoxyphenyl)ethyl)phenoxy)dimethylsilane (3g): The same procedure used to synthesize **3f** was used except 117 mg of *tert*-butyldimethyl(3-vinylphenoxy)silane (**1d**) (0.500 mmol, 1.00 equiv.) was added via syringe, 7.20 mg of Pd[(–)-sparteine]Cl₂ (0.0350 mmol, 0.0350 equiv.) was added, in the workup 2 mL of aqueous 0.5 M NaOH was used (stirred for 20 minutes instead of 1 h), and the product was purified via alumina gel flash chromatography by eluting with 1% Et₂O/pentane to 12% Et₂O/pentane.

3g, Yield: 55% (105.1 mg and 99.8 mg); R_f = 0.43 w/ 5% Et₂O/hexanes (alumina), PMA stain. IR (neat) 2957, 2858, 1740, 1598, 1464, 1278, 1202, 1155, 1048, 957, 836, 784, 698 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃): δ 0.16 (s, 6H), 0.96 (s, 9H), 1.58 (d, *J* = 7.1 Hz, 3H), 3.76 (s, 6H), 4.01 (q, *J* = 7.3 Hz, 1H), 6.29 (dd, *J* = 2.3 Hz, 2.3 Hz, 1H), 6.37 (d, *J* = 2.2 Hz, 2H), 6.66 (ddd, *J* = 1.1 Hz, 2.5 Hz, 8.0 Hz, 1H), 6.70, (dd, *J* = 2.1 Hz, 2.1 Hz, 1H), 6.79–6.82 (m, 1H), 7.12 (dd, *J* = 7.8 Hz, 7.8 Hz, 1H); ¹³C-NMR {¹H} (100 MHz, CDCl₃): δ -4.2, 18.4, 21.8, 25.9, 45.0, 55.4, 98.0, 106.1, 117.9, 119.6, 120.8, 129.3, 147.8, 149.0, 155.8, 160.9; MS (ESI/APCI) *m/z* (MH)⁺ calcd.: 373.2199 obsd. 373.2205.



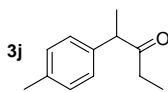
6-(1-(2-methoxyphenyl)ethyl)-3,4-dihydro-2H-pyran (3h): The same procedure used to synthesize **3a** was used except 0.134 μL of 2-vinyanisole (**1e**) (1.00 mmol, 1.00 equiv.) was added via syringe, 560 mg of tributyl(3,4-dihydro-2H-pyran-6-yl)stannane (**2f**) (1.50 mmol, 1.50 equiv.) was added via syringe, 14.4 mg of Pd[(–)-sparteine]Cl₂ (0.0350 mmol, 0.0350 equiv.) was added, and the product was purified via alumina gel flash chromatography by eluting with pentane to 2% Et₂O/pentane.

3h, Yield: 63% (141.0 mg and 135.2 mg); R_f = 0.58 w/ 10% Et₂O/pentane (silica), PMA stain. Clear oil; IR (neat) 3490, 3067, 2935, 2842, 1723, 1669, 1598, 1491, 1461, 1241, 1072, 915, 754 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃): δ 1.26 (d, J = 7.1 Hz, 3H), 1.79 (quint, J = 5.7 Hz, 2H), 2.01-2.10 (m, 2H), 3.83 (s, 3H), 3.86-4.02 (m, 3H), 4.63 (t, J = 3.7 Hz, 1H), 6.82-6.94 (m, 2H), 7.14-7.20 (m, 1H), 7.25-7.29 (m, 1H); ¹³C-NMR {1H} (75 MHz, CDCl₃): δ 18.8, 20.6, 22.7, 36.2, 55.7, 66.5, 95.8, 110.7, 120.7, 127.2, 127.4, 133.4, 157.0, 157.2; MS (ESI/APCI) m/z (MH)⁺ calcd.: 219.1385 obsd.: 219.1390.

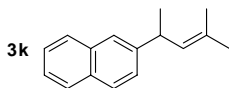


6-(1-*p*-tolylethyl)-3,4-dihydro-2H-pyran (3i): The same procedure used to synthesize **3a** was used except 560 mg of tributyl(3,4-dihydro-2H-pyran-6-yl)stannane (**2f**) (1.50 mmol, 1.50 equiv.) was added via syringe, 14.4 mg of Pd[(-)-sparteine]Cl₂ (0.0350 mmol, 0.0350 equiv.) was added, and the product was purified via alumina gel flash chromatography by eluting with pentane to 2% Et₂O/pentane.

3i, Yield: 69% (144.2 mg and 134.5 mg); R_f = 0.28 w/ Pentane (alumina), PMA stain. Clear oil; IR (neat) 2968, 2929, 2871, 1896, 1659, 1513, 1372, 1231, 1158, 1071, 915, 862, 549 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 1.34 (d, J = 7.1 Hz, 3H), 1.73-1.82 (m, 2H), 2.00-2.06 (m, 2H), 2.32 (s, 3H), 3.35 (q, J = 7.1 Hz, 1H), 3.90-3.95 (m, 2H), 4.60 (t, J = 4.0 Hz, 1H), 7.08-7.20 (m, 4H); ¹³C-NMR {1H} (75 MHz, CDCl₃): δ 19.5, 20.3, 21.0, 22.5, 43.6, 66.4, 95.3, 127.3, 129.2, 135.5, 141.7, 157.6; MS (ESI/APCI) m/z (MH)⁺ calcd.: 203.1436 obsd.: 203.1434.



2-*p*-tolylpentan-3-one (3j): A three-way joint was fitted to the side arm of an oven dried 100 mL thick-wall glass pressure vessel equipped with a stir bar. An O₂ tank was connected to the three-way joint and O₂ was flowed through the vessel. To the vessel, was added 65.2 mg of MnO₂ (0.750 mmol, 0.750 equiv.), 4.30 mL of 2-propanol, 0.200 mL of a 2.00 M solution of (-)-sparteine (0.400 mmol, 0.400 equiv.) in 2-propanol, 0.132 mL of 4-methylstyrene (**1a**) (1.00 mmol, 1.00 equiv.), and 536 mg of tributyl(1-ethoxyprop-1-enyl)stannane (**2g**) (1.50 mmol, 1.50 equiv.). The vessel was sealed, pressurized to 25 psi, evacuated via water aspiration, and repressurized to 25 psi O₂. This procedure was repeated three times. The vessel was sealed and the mixture was stirred **vigorously** for ca. 20 min at room temperature at 25 psi O₂. The vessel was opened and O₂ was flowed through the vessel. To the stirred mixture, was added 14.4 mg of Pd[(-)-sparteine]Cl₂ (0.0350 mmol, 0.0350 equiv.). The vessel was immediately pressurized to 25 psi O₂ and was sealed. The three-way joint was removed and the reaction mixture was stirred **vigorously** for 5 min at room temperature. The mixture was then heated to 60 °C in an oil bath and was stirred **vigorously** for 18 h. The vessel was removed from the oil bath and cooled to room temperature. To the reaction mixture, was added 4.00 mL of a 1:1 solution of glacial acetic acid:H₂O (ca. 35 mmol HOAc) and was stirred for 1 h until the enol ether had been completely hydrolyzed.¹⁹ To the reaction mixture, was added portion wise 10.0 mL of a 4.00 M solution of aqueous NaOH (ca. 40 mmol) and was stirred for 1 h.³ The mixture was filtered through Whatman filter paper, rinsed with ca. 10.0 mL of Et₂O, and was transferred to a separatory funnel. The aqueous layer was extracted three times with 20.0 mL of Et₂O and all organic extracts were combined, washed with 40.0 mL of brine, and dried over MgSO₄. The mixture was filtered and the solvent was removed *in vacuo*. The product was purified via alumina gel flash chromatography by eluting with pentane to 30% Et₂O/pentane. The ¹H-NMR spectrum, see below, was compared to a previously reported spectrum.²⁰ **3j**, Yield: 52% (92.4 mg and 91.6 mg); R_f = 0.51 w/ 5% Et₂O/hexanes (alumina), PMA stain.



2-(4-methylpent-3-en-2-yl)naphthalene (3k): The same procedure used to synthesize **3a** was used except 0.154 mg of 95% 2-vinylnaphthalene (1.00 mmol, 1.00 equiv.), 518 mg of tributyl(2-methylprop-1-enyl)stannane (**2h**) (1.50 mmol, 1.50 equiv.) was added via syringe, 14.4 mg of Pd[(-)-sparteine]Cl₂ (0.0350 mmol, 0.0350 equiv.) was added, and the product was purified via alumina gel flash chromatography by eluting with pentane. The ¹H-NMR spectrum, see below, was compared to a previously reported spectrum.²¹ **3k**, Yield: 50% (based on 95% purity of 2-vinylnaphthalene) (97.0 mg and 101.0 mg); R_f = 0.53 w/ Pentane (silica), PMA stain.

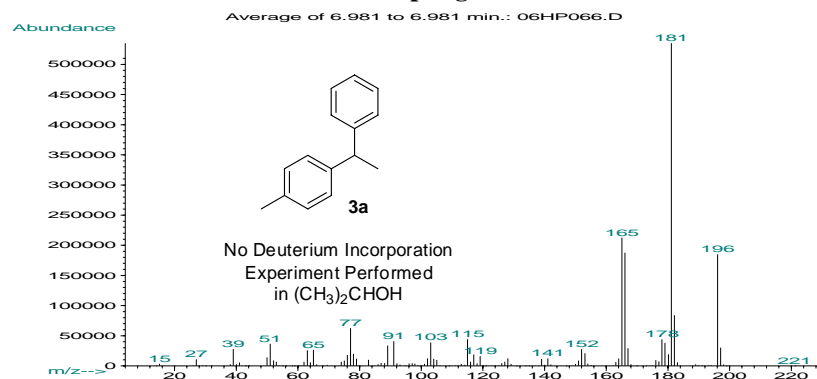
Procedure for the Reductive Coupling Deuterium Labeling Experiment Performed in (CH₃)₂CHOD:

A three-way joint was fitted to the side arm of an oven dried 20 mL thick-wall glass pressure vessel equipped with a stir bar. An O₂ tank was connected to the three-way joint and O₂ was flowed through the vessel. To the vessel, was added 13.0 mg of MnO₂ (0.150 mmol, 0.750 equiv.), 1.00 mL of (CH₃)₂CHOD (98% D incorporation, Acros Organics), 18.0 µL of (–)-sparteine (0.0800 mmol, 0.400 equiv.), 26.0 µL of 4-methylstyrene (**1a**) (0.200 mmol, 1.00 equiv.), and 98.0 µL of PhSnBu₃ (**2a**) (0.300 mmol, 1.50 equiv.). The vessel was sealed, pressurized to 25 psi, evacuated via water aspiration, and re-pressurized to 25 psi O₂. This procedure was repeated three times. The vessel was sealed and the mixture was stirred **vigorously** for ca. 20 min at room temperature at 25 psi O₂. The vessel was opened and O₂ was flowed through the vessel. To the stirred mixture, was added 2.10 mg of Pd[(–)-sparteine]Cl₂ (0.00500 mmol, 0.0250 equiv.). The vessel was immediately pressurized to 25 psi O₂ and was sealed. The three-way joint was removed and the reaction mixture was stirred **vigorously** for 5 min at room temperature. The mixture was then heated to 60 °C in an oil bath and was stirred **vigorously** for 20 h. The vessel was removed from the oil bath and cooled to room temperature. A 50 µL aliquot of the reaction mixture was removed and passed through a small plug of silica with EtOAc as the elutant. The solution was analyzed by GC/MS (see data and calculations below).

Procedure for the Reductive Coupling Deuterium Labeling Experiment Performed in (CH₃)₂CDOH:

A three-way joint was fitted to the side arm of an oven dried 20 mL thick-wall glass pressure vessel equipped with a stir bar. An O₂ tank was connected to the three-way joint and O₂ was flowed through the vessel. To the vessel, was added 19.6 mg of MnO₂ (0.225 mmol, 0.750 equiv.), 1.50 mL of (CH₃)₂CDOH (99.5% D incorporation, Cambridge Isotopes), 28.0 µL of (–)-sparteine (0.120 mmol, 0.400 equiv.), 40.0 µL of 4-methylstyrene (**1a**) (0.300 mmol, 1.00 equiv.), and 148 µL of PhSnBu₃ (**2a**) (0.450 mmol, 1.50 equiv.). The vessel was sealed, pressurized to 25 psi, evacuated via water aspiration, and re-pressurized to 25 psi O₂. This procedure was repeated three times. The vessel was sealed and the mixture was stirred **vigorously** for ca. 20 min at room temperature at 25 psi O₂. The vessel was opened and O₂ was flowed through the vessel. To the stirred mixture, was added 3.10 mg of Pd[(–)-sparteine]Cl₂ (0.00750 mmol, 0.0250 equiv.). The vessel was immediately pressurized to 25 psi O₂ and was sealed. The three-way joint was removed and the reaction mixture was stirred **vigorously** for 5 min at room temperature. The mixture was then heated to 60 °C in an oil bath and was stirred **vigorously** for 20 h. The vessel was removed from the oil bath and cooled to room temperature. A 50 µL aliquot of the reaction mixture was removed and passed through a small plug of silica with EtOAc as the elutant. The solution was analyzed by GC/MS (see data and calculations below). To the remaining reaction mixture, was added 3.0 mL of a 1.00 M solution of aqueous NaOH and was stirred for 1 h. The mixture was filtered through Whatman filter paper, rinsed with ca. 5.0 mL of Et₂O, and was transferred to a separatory funnel. The aqueous layer was extracted three times with 20.0 mL of Et₂O and all organic extracts were combined, washed with 30.0 mL of brine, and dried over MgSO₄. The mixture was filtered and the solvent was removed *in vacuo*. The products were purified via alumina gel flash chromatography by eluting with pentane. The ¹H-NMR spectra in CD₂Cl₂ was compared to the spectra of **3a** prepared in unlabeled 2-propanol (see spectra and calculations below).

GC/MS Data for the Reductive Coupling Product 3a:

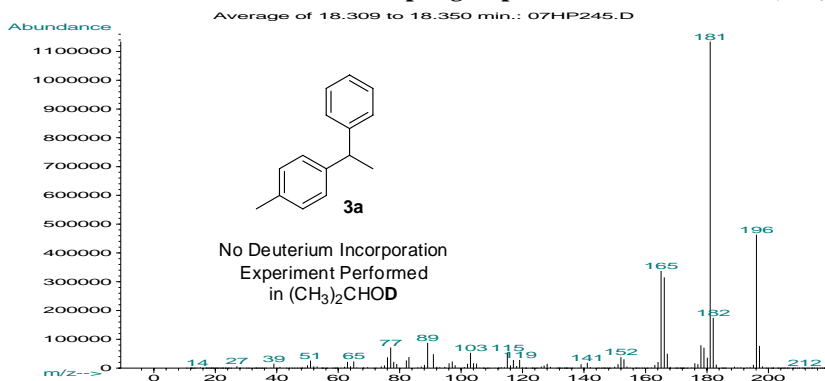


m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
76.05	18128	89.10	33752	101.05	3486	114.10	1918
77.05	62560	91.10	40832	102.05	12426	115.00	44064
78.00	19896	92.10	4177	103.05	38672	116.00	7061
79.00	11892	93.10	2058	104.05	11697	117.00	18992
80.10	901	94.70	663	105.05	9864	118.10	4309
82.90	10223	95.05	719	106.05	1017	119.10	16253
84.10	598	96.05	3959	108.95	119	120.10	1634
85.00	538	97.05	4321	109.95	667	120.90	140
86.00	2680	97.95	3871	111.05	881	122.00	243
87.00	4727	98.95	1419	112.00	288	123.00	213
88.10	4584	100.05	796	113.00	3219	123.80	78

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
125.10	760	139.05	11538	154.00	3763	168.95	434
126.10	4419	140.05	1798	155.10	1454	169.85	79
127.10	7101	141.05	12392	155.90	199	172.85	53
128.10	12426	142.05	2437	161.10	251	174.05	496
129.10	3256	143.15	246	162.10	606	175.05	861
129.95	390	147.00	70	163.10	6372	176.05	9675
130.85	61	148.90	546	164.05	12256	177.05	7610
133.85	69	150.00	3165	165.05	212544	178.05	44064
134.95	96	151.00	8785	166.05	187584	179.05	38360
136.95	817	152.00	27824	167.05	29216	180.15	19200
138.15	966	153.10	21008	168.05	2650	181.10	535296

m/z	abund.	m/z	abund.
182.10	84088	196.10	185088
183.10	5797	197.10	30272
184.10	299	198.05	2306
187.00	336	198.95	130
188.00	315	221.10	67
189.00	2727		
190.00	976		
191.10	1093		
192.00	415		
193.10	850		
194.10	1192		

GC/MS Data for the Reductive Coupling Experiment Performed in (CH₃)₂CHOD:



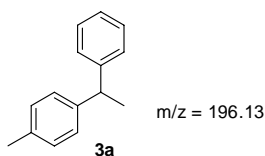
<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>
71.55	50	83.00	38256	95.10	936	106.10	1414
72.15	29	84.75	397	96.10	16466	107.05	29
72.95	457	85.95	2637	97.10	22774	107.40	100
74.00	5984	87.00	5652	98.05	10077	108.45	25
75.05	9641	88.05	10924	98.95	978	108.95	182
76.05	37312	89.10	87686	100.00	881	110.00	727
77.05	71576	91.00	48580	101.05	3867	111.00	1146
78.05	21556	92.05	4383	102.05	14966	111.95	128
79.05	14403	93.05	2471	103.05	53012	112.15	168
80.00	1088	93.70	272	104.05	17182	113.05	3191
82.15	26370	94.65	3754	105.05	15268	114.10	2694

<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>
115.05	53822	123.85	247	132.10	32	139.05	13533
116.05	9178	124.50	92	132.70	60	140.00	2579
117.00	28074	125.05	823	133.50	43	141.05	18121
118.05	7075	126.05	5323	133.95	119	142.05	3152
119.05	28084	127.00	8946	134.15	31	143.05	398
120.05	2841	128.00	14815	134.45	14	144.10	148
120.85	106	129.10	4146	135.00	92	144.70	109
121.15	161	130.05	499	135.55	66	145.60	125
122.00	410	131.05	92	136.05	195	146.05	54
123.00	204	131.60	21	137.00	992	146.55	46
123.20	50	131.80	16	138.00	876	146.85	176

<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>
147.45	125	156.05	571	161.00	1032	169.75	105
148.05	189	156.80	152	161.30	356	170.05	106
148.30	181	157.00	63	161.95	1873	170.55	236
148.90	319	157.75	209	162.20	690	171.25	115
149.10	407	158.20	295	163.05	11370	171.55	85
150.00	4847	158.80	140	164.10	21330	172.00	175
151.05	13248	159.05	300	165.05	337520	172.25	98
152.00	37760	159.50	153	166.10	314928	172.65	79
153.00	30640	160.00	432	167.10	50274	173.20	369
154.00	5439	160.20	315	168.05	4416	173.45	167
155.00	1934	160.50	184	169.00	673	174.00	1261

<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>
175.05	2201	185.15	57	195.10	11571	203.30	20
176.05	16857	185.70	71	196.10	463472	204.00	17
177.05	13937	186.05	109	197.10	77194	204.60	14
178.05	79286	187.00	601	198.10	6081	205.00	13
179.05	71360	188.05	568	199.00	267	205.45	14
180.10	36328	189.00	5143	199.30	55	206.05	14
181.05	1134528	190.00	2236	199.80	19	206.55	21
182.05	174704	191.00	2962	200.80	15	208.00	37
183.05	12306	192.05	1275	201.30	14	208.55	29
184.05	650	193.05	2522	201.50	15	209.35	13
184.80	102	194.10	3244	203.00	21	209.95	17

Calculation of the Deuterium Incorporation for Experiment Performed in (CH₃)₂CHOD:²²



# of Deuterium Atoms	0	1	2	3	4
	M	M+1	M+2	M+3	M+4
Molecular Ions	196	197	198	199	200
Abund. Unlabeled	185088	30272	2306	130	
Abund. Labeled	463472	77194	6081	267	15
Relative Abund. Unlabeled	100	16.36	1.25	0.07	
Relative Abund. Labeled	100.00	16.66	1.31	0.06	
unlabeled: difference:	100.00	16.36 0.30			
D-1 difference		0.30	0.05 1.26		
D-2 difference			1.26	0.21 0.00	
D-3				0.00	
Percent Distribution	98.5	0.3	1.2	0.0	

(M+1)/M not labeled: 0.16

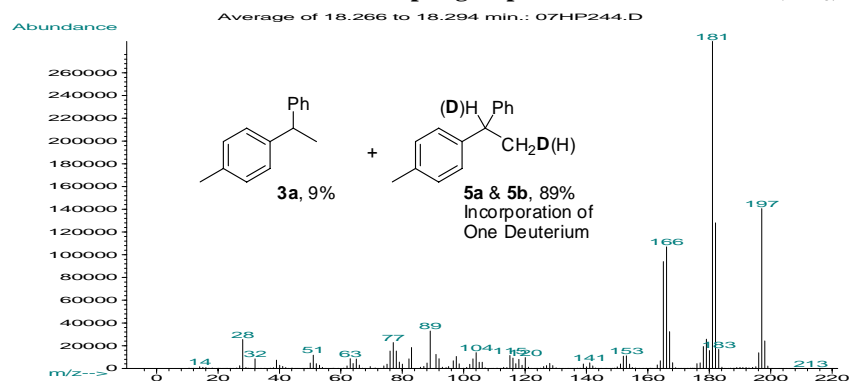
(9.76*0.16) = 1.60

(98.40*0.16) = 16.09

(1.11*0.16) = 0.18

sum relative abund. 110.6

GC/MS Data for the Reductive Coupling Experiment Performed in (CH₃)₂CDOH:



m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
67.05	327	77.05	22720	92.00	8514	102.00	3677
68.05	155	78.05	15348	93.05	1083	103.05	8431
69.55	1610	79.05	5625	94.10	363	104.05	13906
70.75	156	80.05	3825	94.40	441	105.05	5518
71.20	355	82.20	8389	94.60	325	106.05	5439
71.75	101	83.00	18381	95.10	1751	107.00	512
72.20	63	85.95	1057	96.60	6714	108.20	58
72.85	160	87.00	1788	97.60	10518	108.75	27
74.00	2231	88.05	4744	98.55	4121	108.95	43
75.05	3740	89.10	32979	100.00	223	109.35	45
76.05	15292	91.00	12430	101.00	1037	109.80	180

<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>
110.85	312	120.05	9503	129.90	155	135.35	45
111.05	110	121.10	1178	130.10	516	135.55	27
111.85	50	122.00	157	131.10	144	136.15	105
112.15	187	123.00	63	131.95	60	137.00	224
113.05	897	123.60	71	132.30	19	137.85	95
114.05	857	124.05	65	133.10	30	138.00	335
115.05	11439	125.00	273	133.80	54	139.00	3902
116.05	9213	126.05	1683	134.00	83	140.05	1434
117.00	4178	127.00	2525	134.45	37	141.05	4906
118.00	7960	128.05	4497	134.65	45	142.05	2273
119.05	2739	129.05	2465	134.95	51	143.00	453

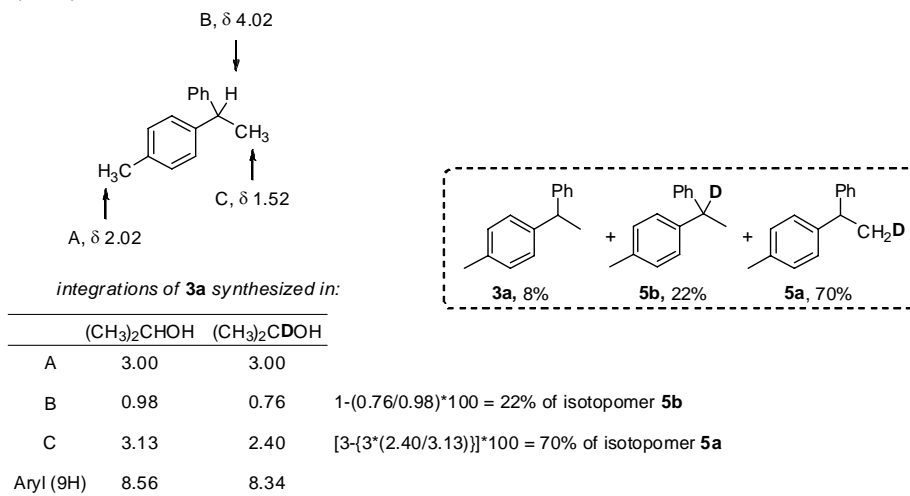
<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>
143.95	81	152.00	10809	160.60	165	170.25	44
144.25	36	153.00	11143	161.00	193	170.55	40
144.95	114	154.05	3761	161.50	162	171.05	75
146.15	61	154.95	809	163.05	3131	171.35	34
146.65	73	156.05	429	164.05	6813	171.75	118
147.65	52	157.00	42	165.05	93936	171.95	57
148.25	29	157.30	108	166.10	106925	172.55	47
148.50	151	158.10	60	167.10	32413	172.85	119
149.15	238	158.55	165	168.05	5016	173.05	86
150.05	1432	159.40	188	169.05	691	173.90	333
151.05	3890	159.60	79	170.00	110	174.15	163

<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>	<i>m/z</i>	<i>abund.</i>
174.65	232	184.90	109	194.05	784	204.00	59
175.05	319	185.15	23	194.30	266	205.00	21
176.00	4257	186.15	148	195.15	1484	206.15	18
177.05	4884	187.00	203	196.10	13718	206.85	24
178.05	19304	188.00	231	197.10	140512	207.35	42
179.05	25685	188.95	873	198.10	24168	208.35	24
180.05	15682	190.00	994	199.05	2093	211.15	48
181.05	287573	190.95	786	200.00	54	213.05	60
182.05	127968	192.00	881	200.30	36	213.75	23
183.05	16728	192.95	361	202.60	51	215.15	24
184.10	1158	193.20	191	203.30	28	218.25	49

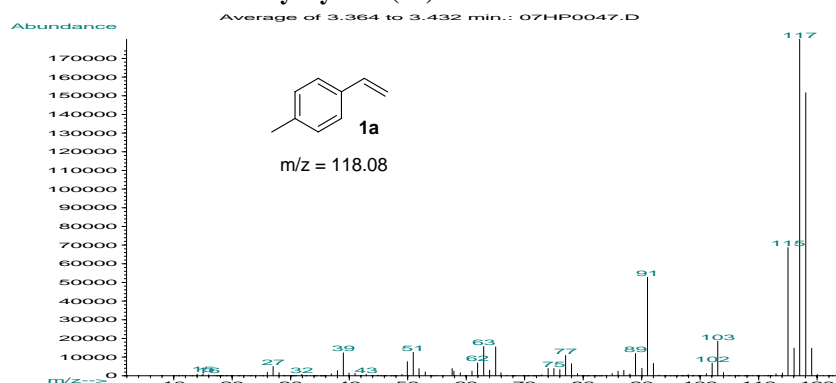
Calculation of the Deuterium Incorporation for Experiment Performed in (CH₃)₂CDOH:²²

# of Deuterium Atoms	0	1	2	3	4	
	M	M+1	M+2	M+3	M+4	
Molecular Ions	196	197	198	199	200	
Abund. Unlabeled	185088	30272	2306	130		(M+1)/M not labeled: 0.16
Abund. Labeled	13718	140512	24168	2093	54	
Relative Abund. Unlabeled	100	16.36	1.25	0.07		
Relative Abund. Labeled	9.76	100	17.20	1.49		
unlabeled: difference:	9.76	1.60 98.40				(9.76*0.16) = 1.60
D-1 difference		98.40	16.09 1.11			(98.40*0.16) = 16.09
D-2 difference			1.11	0.18 1.31		(1.11*0.16) = 0.18
D-3				1.31		
Percent Distribution	8.8	89.0	1.0	1.2		sum relative abund. 110.6

Calculation of the Deuterium Incorporation for the Experiment Performed in (CH₃)₂CDOH by ¹H-NMR:



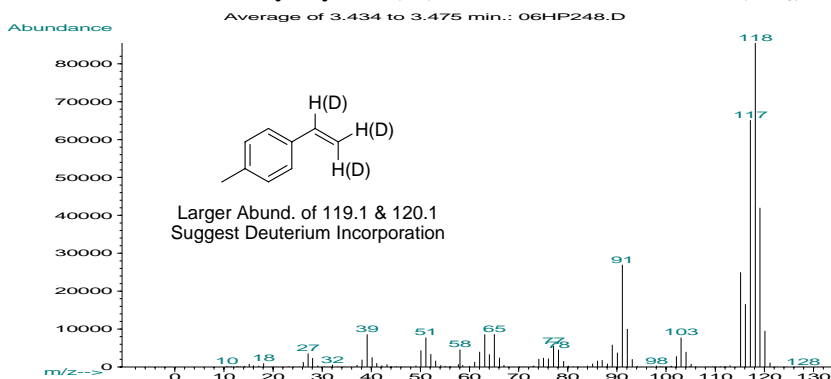
GC/MS Data for 4-methylstyrene (1a):



m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
65.05	15395	71.40	25	79.90	100	86.95	2954
65.95	1601	71.75	46	80.10	20	87.85	322
66.85	89	72.30	15	80.60	11	88.00	900
67.05	72	72.80	179	80.90	14	88.95	11877
67.85	40	72.95	487	81.80	54	90.05	4033
68.30	27	74.00	3887	82.30	16	91.00	52700
68.90	87	75.00	3895	82.75	28	92.00	6589
69.70	12	76.00	3241	83.15	29	93.00	379
69.95	146	77.00	10869	83.95	296	94.10	34
70.40	32	78.00	6434	84.95	1185	94.85	13
70.70	20	79.05	1084	85.95	2353	95.45	13

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
96.00	45	102.05	6674	108.90	194	116.05	14853
96.80	26	103.00	18441	109.70	21	117.00	183332
96.95	156	104.00	1726	110.00	281	118.05	151645
97.15	14	104.90	99	111.05	141	119.05	14735
97.65	34	105.10	63	111.50	31	120.05	695
97.95	582	105.90	15	111.70	142	121.05	51
98.65	9	106.30	25	112.10	46	122.05	14
98.90	259	106.65	26	112.95	1036	122.55	14
99.65	46	107.55	26	113.15	113	123.25	10
100.10	137	107.95	69	114.05	1443	123.65	21
101.05	1096	108.15	29	115.00	68620	124.55	12

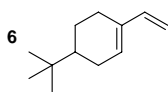
GC/MS Data for 4-methyl styrene (1a) of Reaction Performed in (CH₃)₂CDOH at 2 Hours:



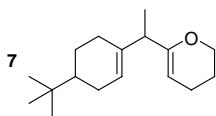
m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
69.45	35	74.10	2136	82.25	122	91.10	26988
70.05	13	75.05	2401	83.00	52	92.10	10030
70.20	122	76.05	2224	83.30	22	93.10	2075
70.60	32	77.10	5508	84.00	318	94.00	50
70.90	57	78.10	4563	85.05	880	94.15	231
71.20	64	79.15	1563	86.05	1626	95.00	20
71.45	35	79.85	73	87.00	1818	95.90	37
71.65	30	80.10	308	87.80	125	96.80	40
72.35	69	81.05	147	88.05	816	97.05	85
72.85	164	81.30	48	89.05	5862	97.40	46
73.10	377	81.85	60	90.10	3768	98.05	326

m/z	abund.	m/z	abund.	m/z	abund.	m/z	abund.
98.85	154	105.10	795	110.65	22	121.15	1128
99.25	114	106.00	113	111.05	144	121.90	13
99.50	27	106.35	29	111.95	142	122.15	62
100.05	88	106.95	27	112.25	72	122.70	28
100.30	31	107.50	55	113.00	417	124.50	25
100.85	133	108.15	26	115.15	24992	126.30	25
101.10	287	108.55	61	116.15	16603	126.90	44
102.10	2830	108.95	35	117.15	65150	127.10	34
103.05	7763	109.15	14	118.15	85484	127.50	26
104.05	3980	109.45	97	119.10	42000	127.90	68
104.85	179	110.10	139	120.10	9523	128.60	18

Reductive Coupling of Diene 6:



4-tert-butyl-1-vinylcyclohex-1-ene (6): Diene **6** was synthesized according to a previously reported procedure and the ¹H-NMR spectrum was compared to the previously reported spectrum.²³

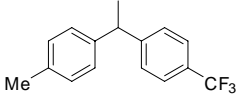
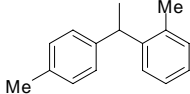
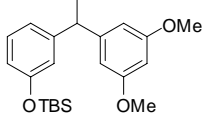
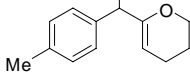
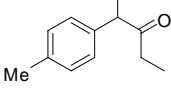
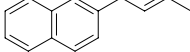
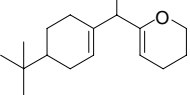


6-(1-(4-tert-butylcyclohex-1-enyl)ethyl)-3,4-dihydro-2H-pyran (7): A three-way joint was fitted to the side arm of an oven dried 100 mL thick-wall glass pressure vessel equipped with a stir bar. An O₂ tank was connected to the three-way joint and O₂ was flowed through the vessel. To the vessel, was added 65.2 mg of MnO₂ (0.750 mmol, 0.750 equiv.), 4.30 mL of 2-propanol, 0.200 mL of a 2.00 M solution of (–)-sparteine (0.400 mmol, 0.400 equiv.) in 2-propanol, 164 mg of 4-tert-butyl-1-vinylcyclohex-1-ene (**6**) (1.00 mmol, 1.00 equiv.), and 560 mg of tributyl(3,4-dihydro-2H-pyran-6-yl)stannane (**2f**) (1.50 mmol, 1.50 equiv.). The vessel was sealed, pressurized to 25 psi, evacuated via water aspiration, and re-pressurized to 25 psi O₂. This procedure was repeated three times. The vessel was sealed and the mixture was stirred **vigorously** for ca. 20 min at room temperature at 25 psi O₂. The vessel was opened and O₂ was flowed through the vessel. To the stirred mixture, was added 14.4 mg of Pd[(–)-sparteine]Cl₂ (0.0350 mmol, 0.0350 equiv.). The vessel was immediately pressurized to 25 psi O₂ and was sealed. The three-way joint was removed and the reaction mixture was stirred **vigorously** for 5 min at room temperature. The mixture was then heated to

60 °C in an oil bath and was stirred **vigorously** for 18 h. The vessel was removed from the oil bath and cooled to room temperature. To the reaction mixture, was added 5.0 mL of a 1.00 M solution of aqueous NaOH and was stirred for 1 h.³ The mixture was filtered through Whatman filter paper, rinsed with ca. 10.0 mL of Et₂O, and was transferred to a separatory funnel. The aqueous layer was extracted three times with 20.0 mL of Et₂O and all organic extracts were combined, washed with 40.0 mL of brine, and dried over MgSO₄. The mixture was filtered and the solvent was removed *in vacuo*. The product was purified via alumina gel flash chromatography by eluting with pentane.

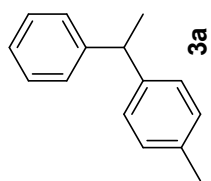
7, Yield: 40% (105.38 mg and 94.6 mg) (1:1 mixture of diastereomers); R_f = 0.38 w/ Pentane (alumina), PMA stain. Clear oil; IR (neat) 2988, 2968, 1713, 1466, 1365, 1230, 1071, 913, 770, 649 cm⁻¹; ¹H-NMR (300 MHz, CDCl₃) δ 0.86 (s, 9H), 1.12 (dd, *J* = 1.6 Hz, 7.1 Hz, 3H), 1.15-1.31 (m, 1H), 1.73-1.88 (m, 5H), 1.97-2.10 (m, 5H), 2.67 (q, *J* = 6.9 Hz, 1H), 3.90-4.04 (m, 2H), 4.52 (t, *J* = 3.7 Hz, 1H), 5.47-5.56 (m, 1H); ¹³C-NMR {1H} (75 MHz, CDCl₃): δ 16.9, 17.3, 20.6, 22.8, 24.5, 24.6, 27.1, 27.5, 27.9, 28.0, 32.5, 44.3, 44.4, 45.0, 45.5, 66.4, 66.5, 95.2, 95.3, 121.4, 121.5, 139.6, 139.8, 157.1; MS (ESI/APCI) *m/z* (MH)⁺ calcd.: 249.2218 obsd. 249.2223.

Optical Rotation Data Measured in CH₂Cl₂:

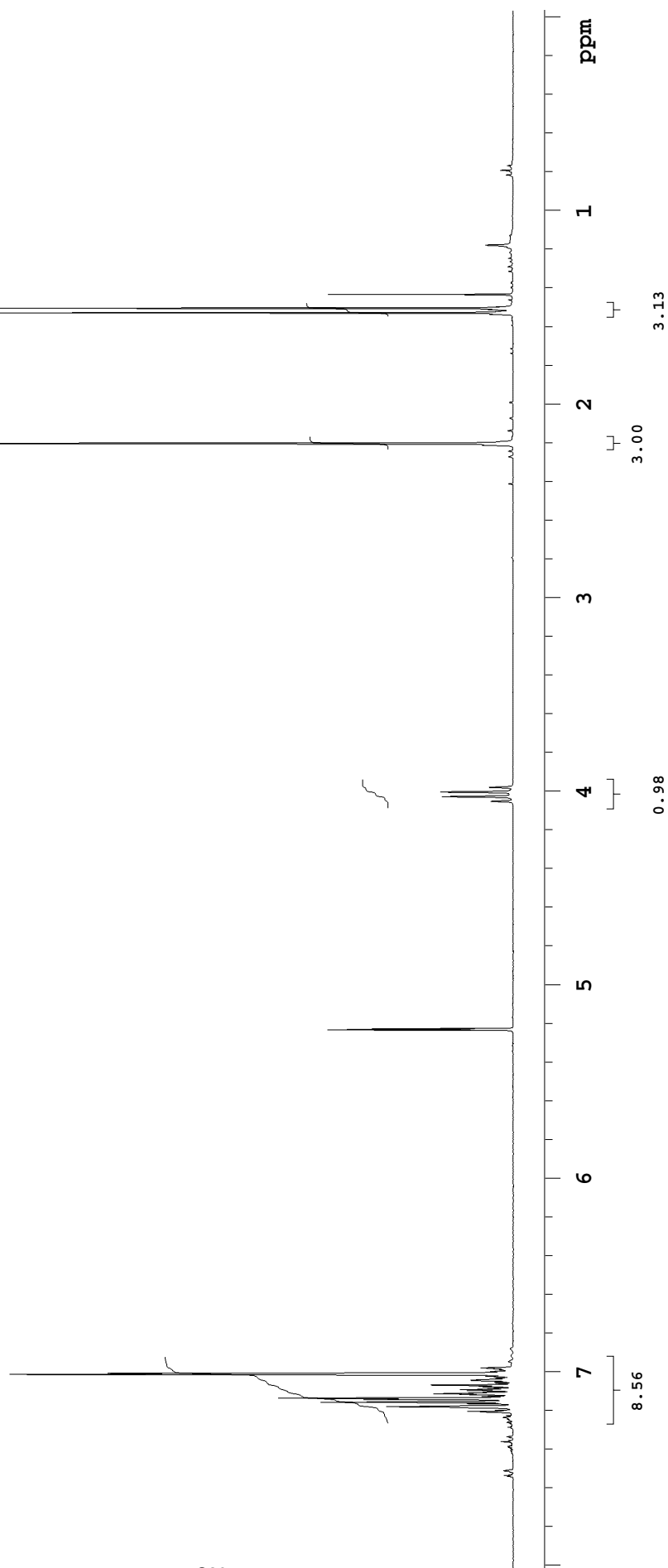
Entry	Product	Concentration (mg/mL)	[α] _D ²²
1	3c 	2.5	+0.009°
2	3d 	3.0	-0.005°
3	3g 	2.7	+0.015°
4	3i 	2.8	-0.005°
5	3j 	3.3	+0.016°
6	3k 	3.4	-0.026°
7	7 	2.5	+0.016°

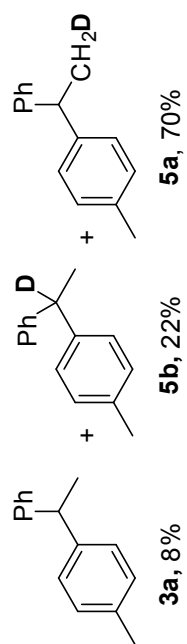
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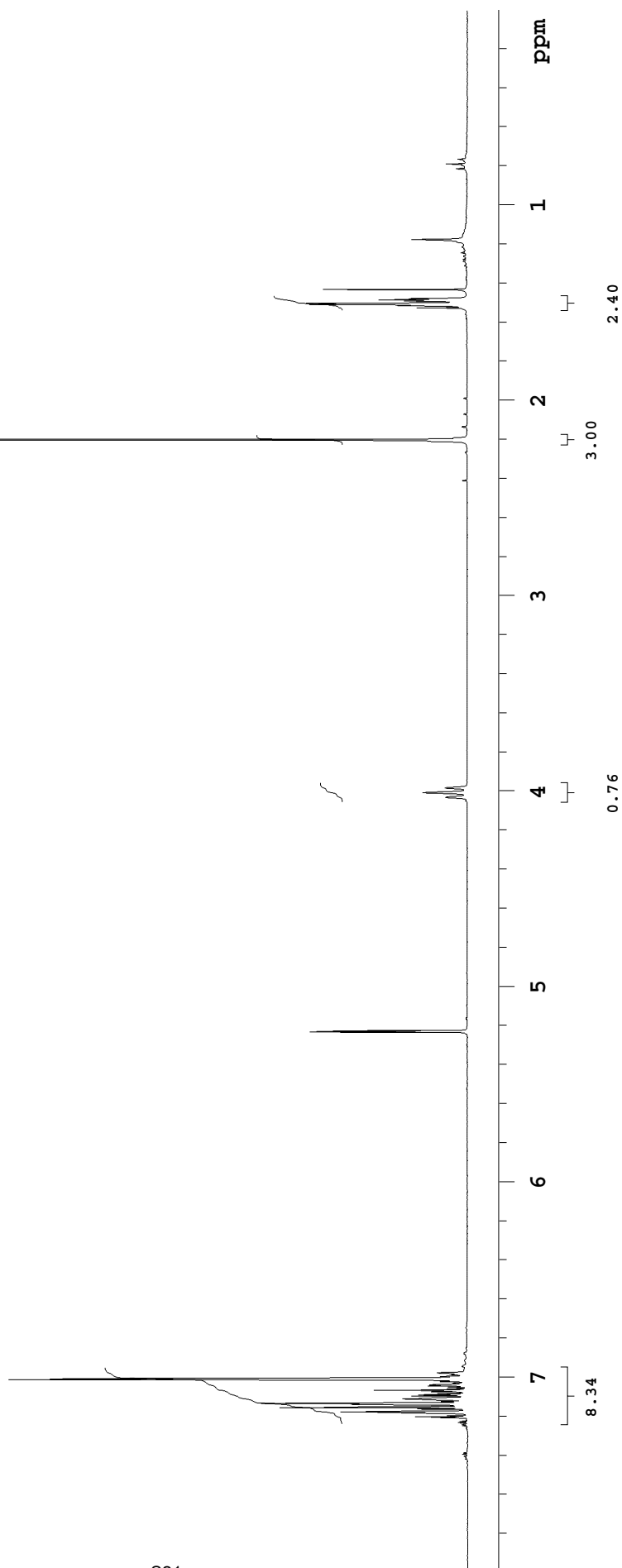


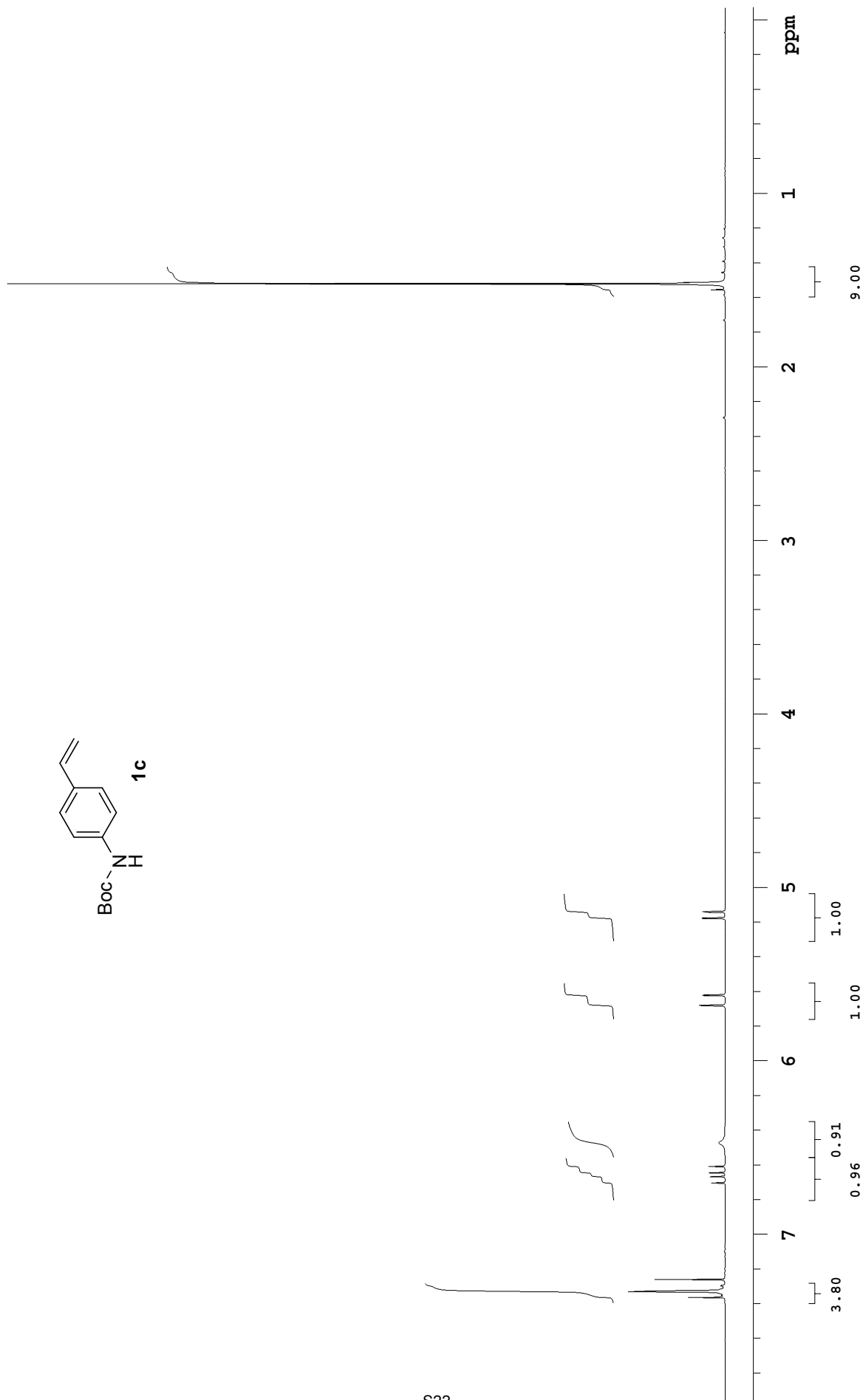
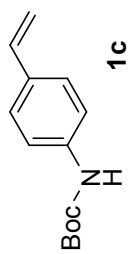
No Deuterium Incorporation
Experiment Performed
in (CH₃)₂CHOD

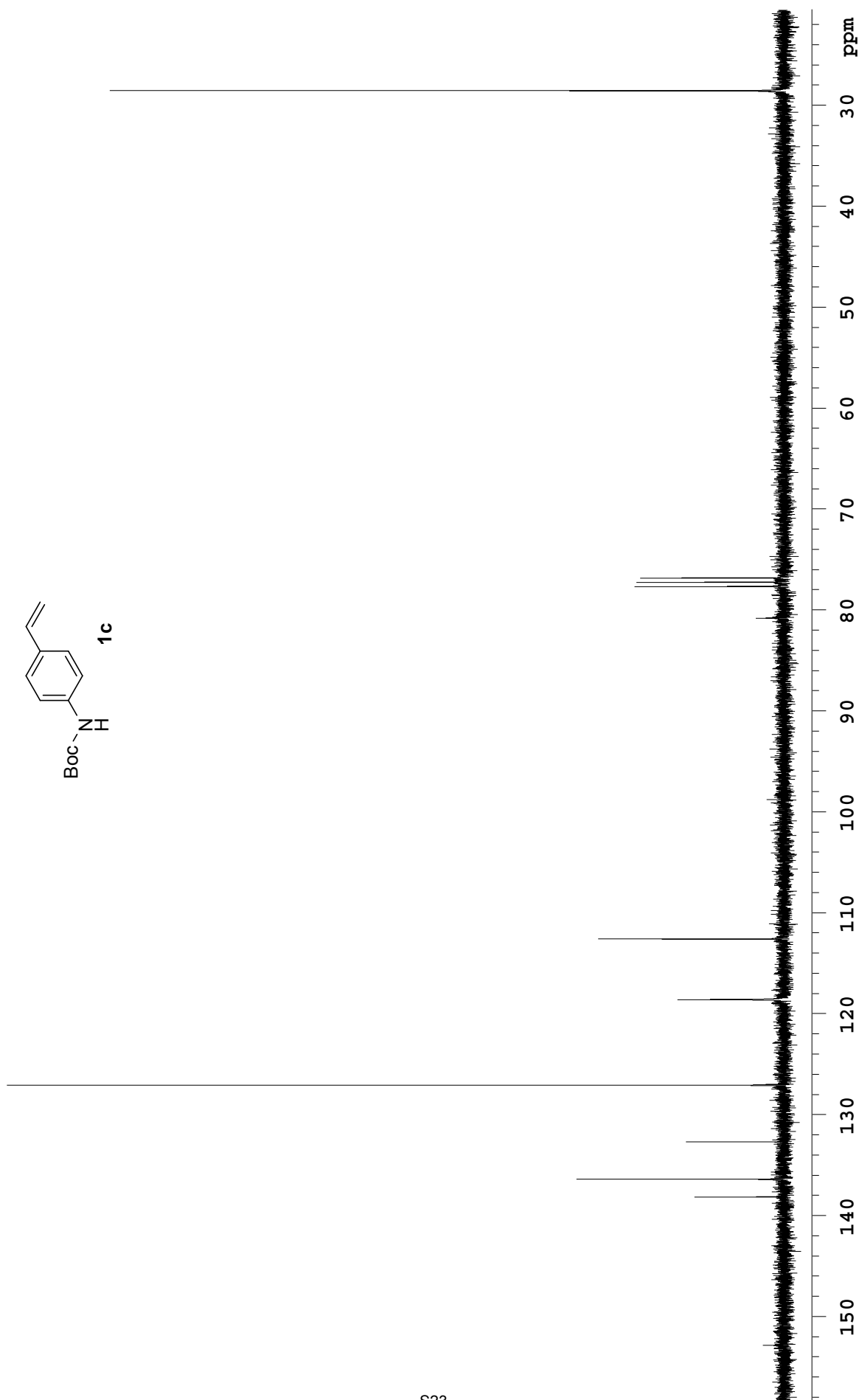
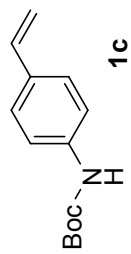


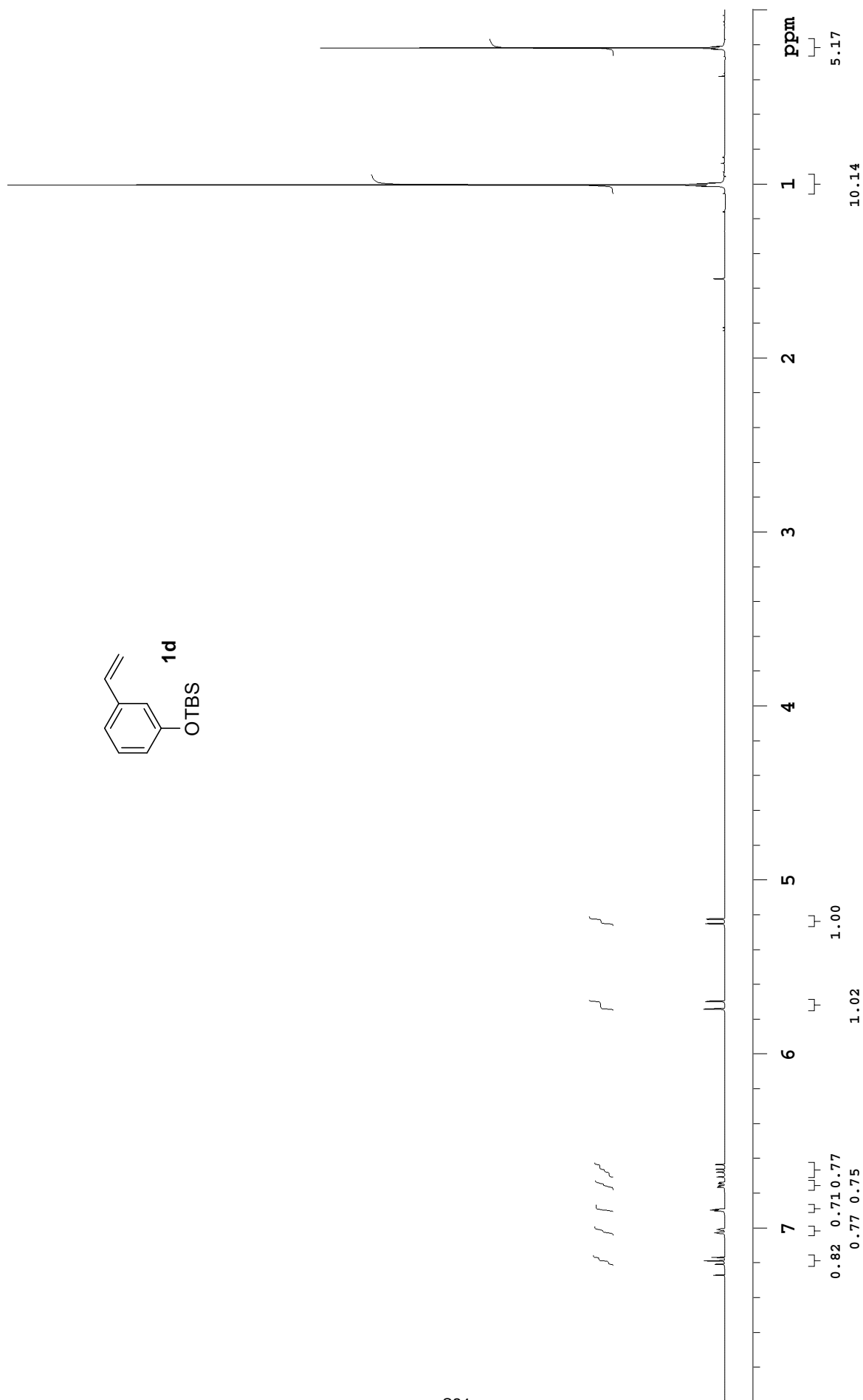
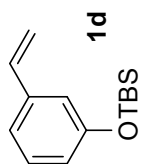


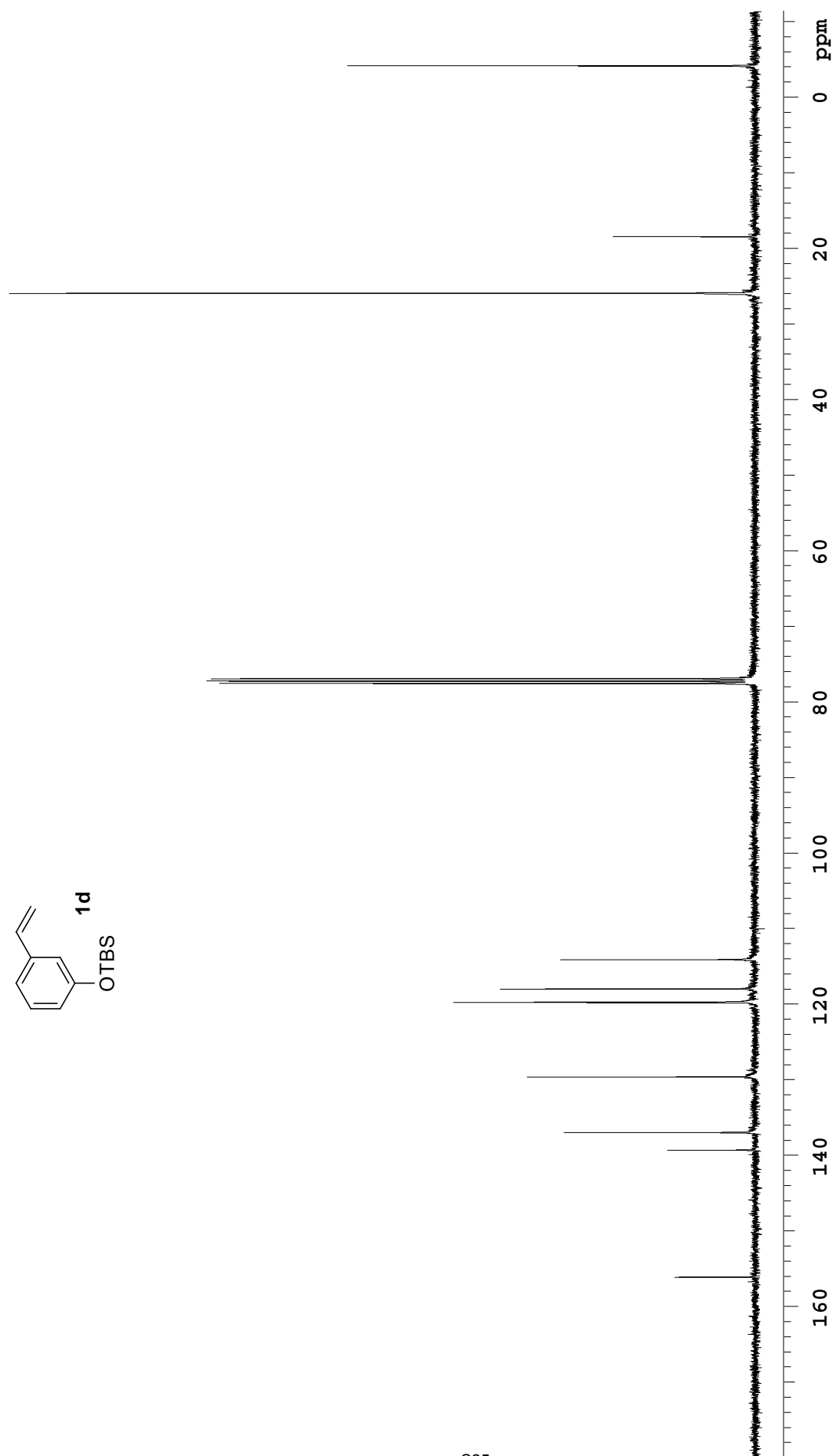
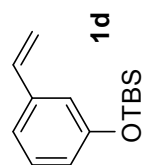
Experiment Performed
in (CH₃)₂CDOH

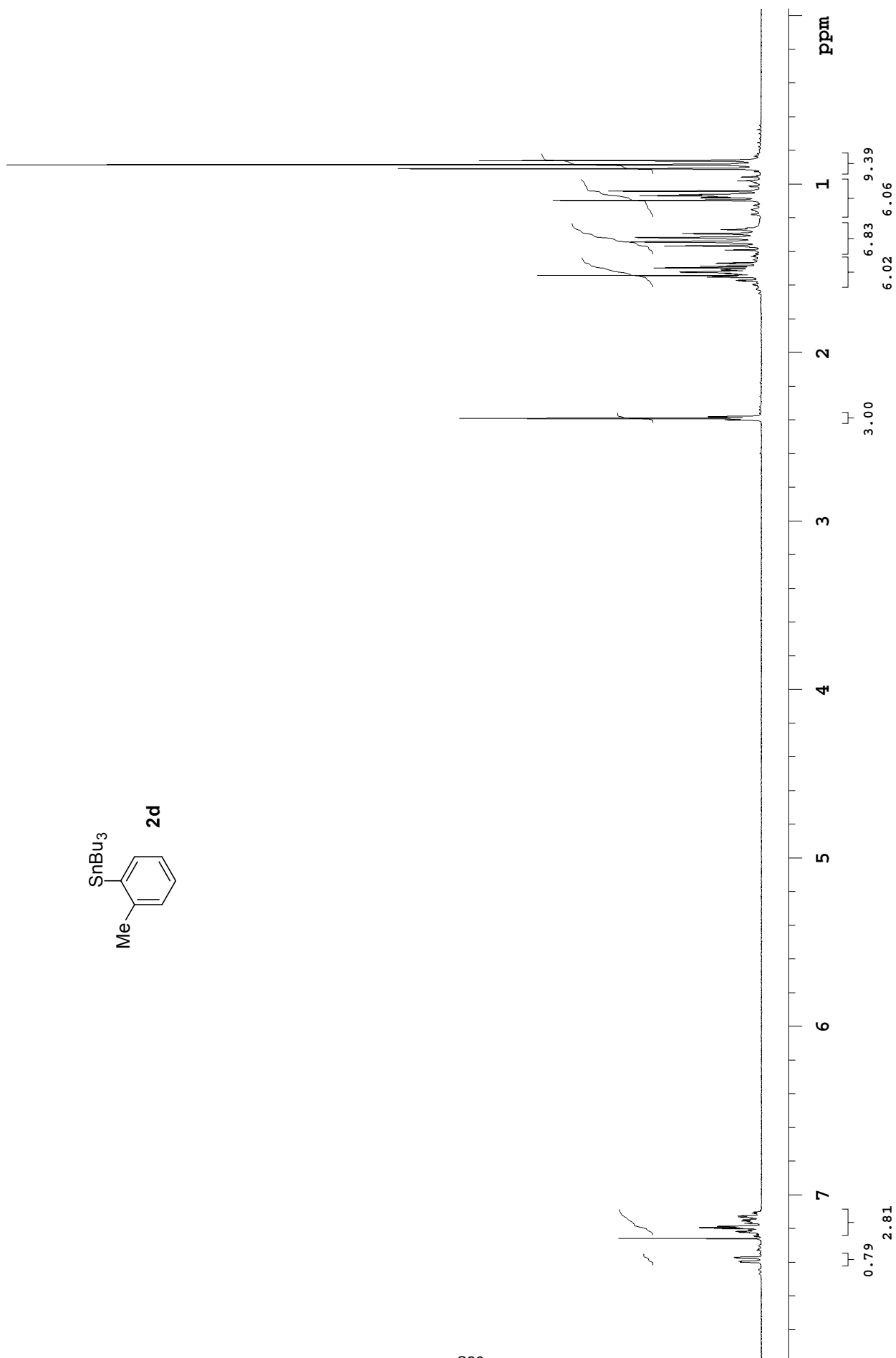
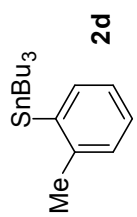


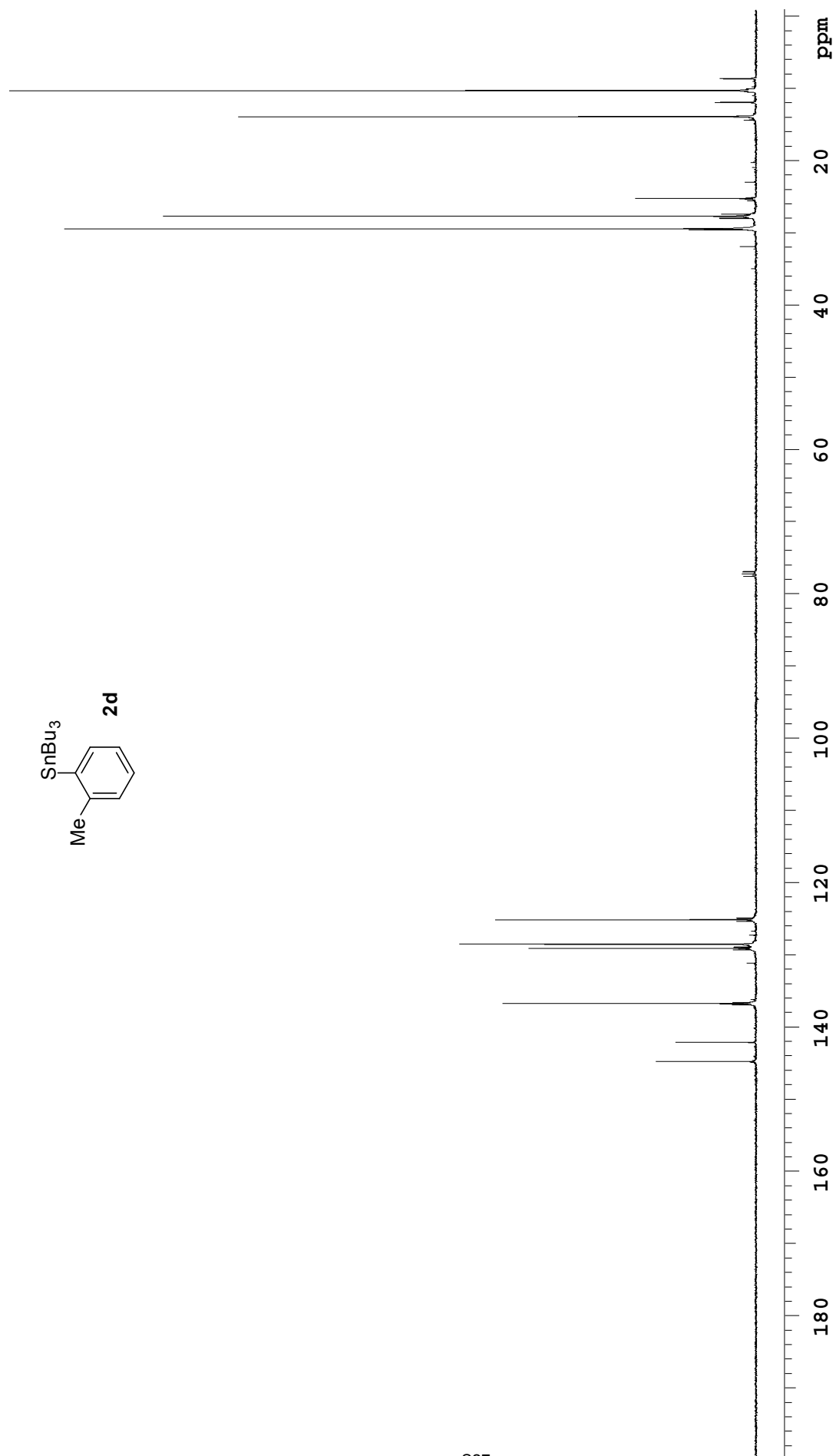
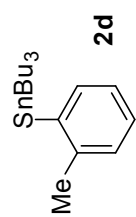


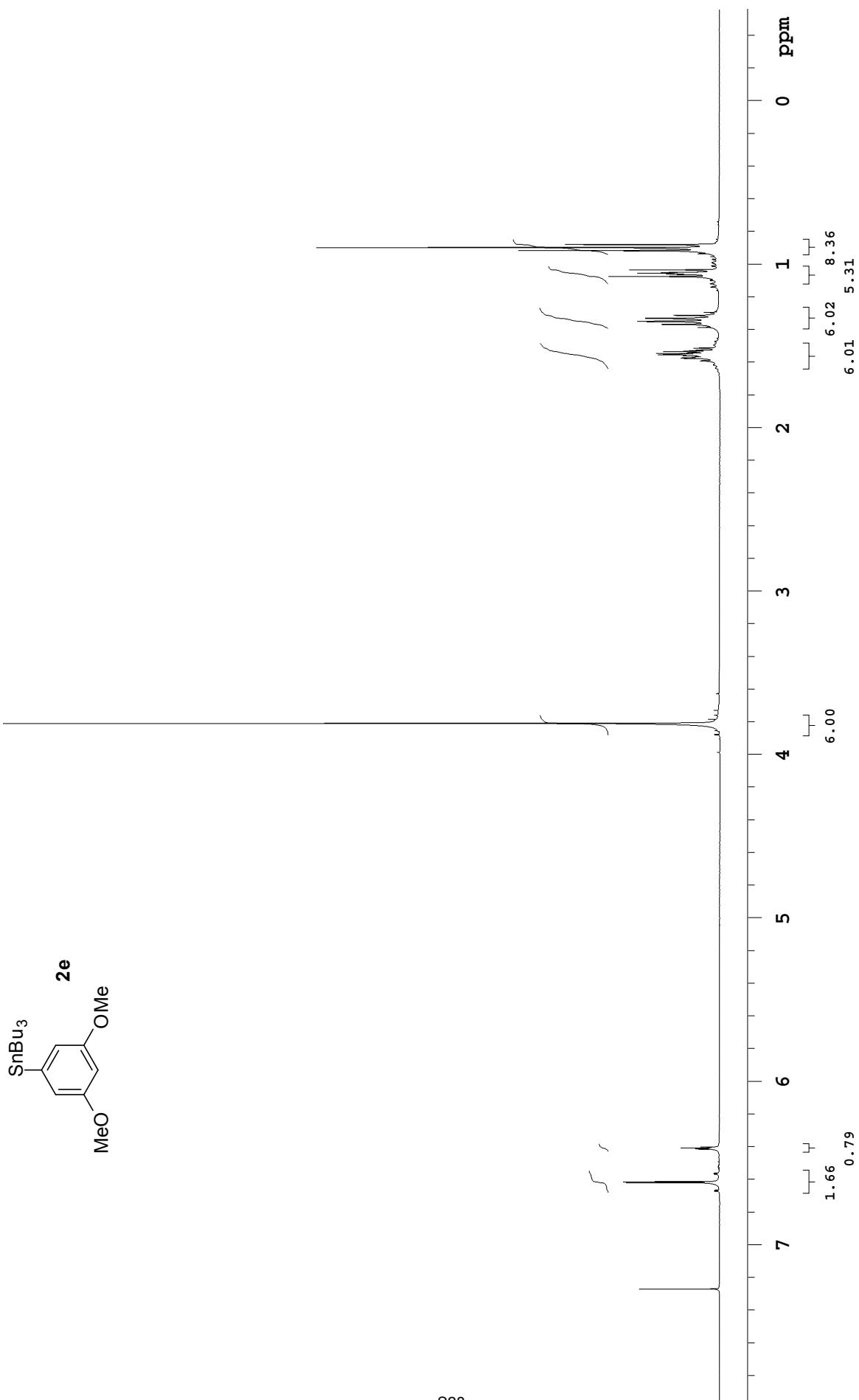
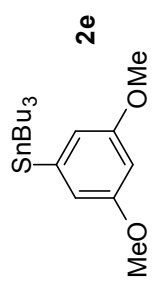


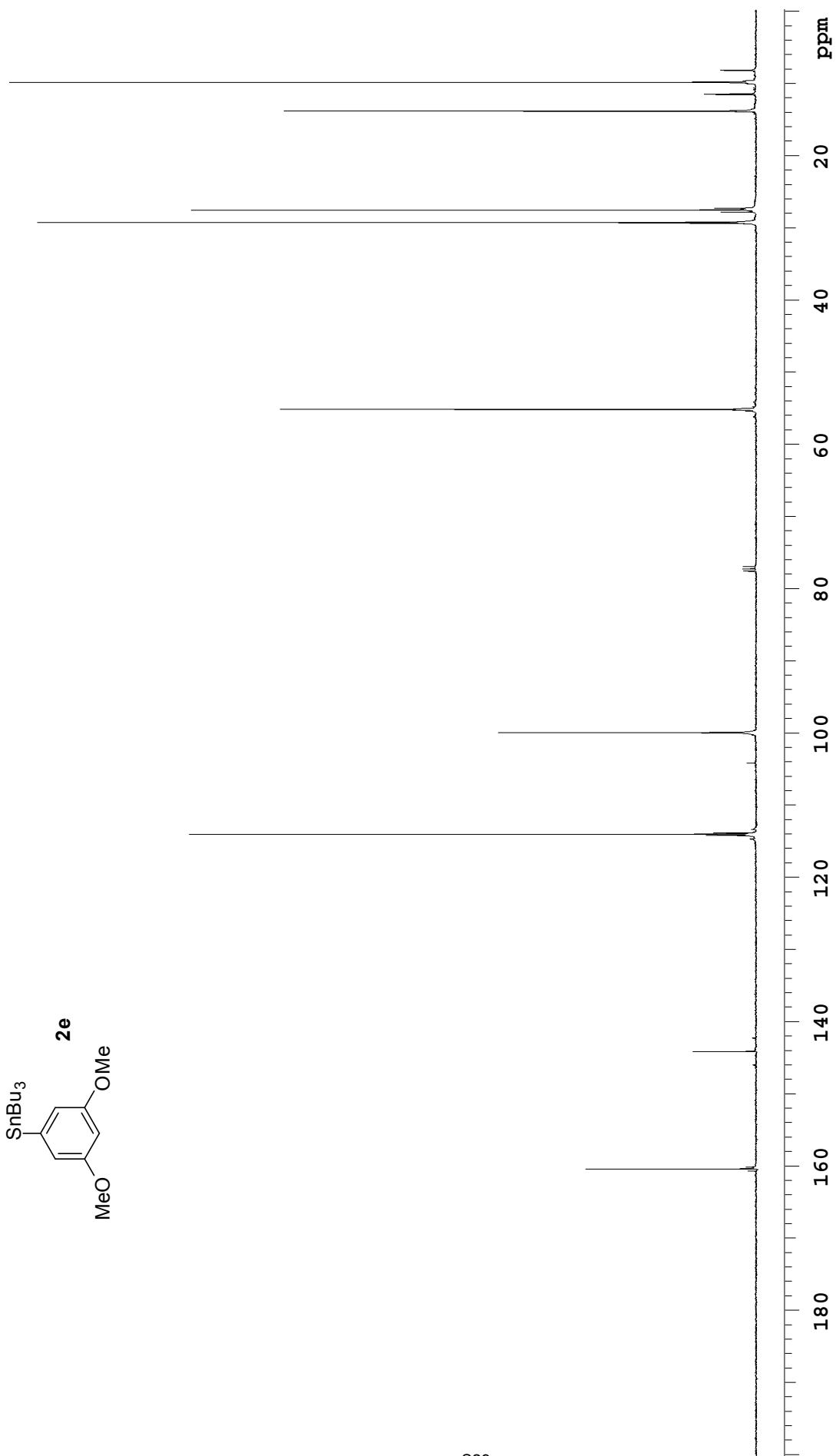
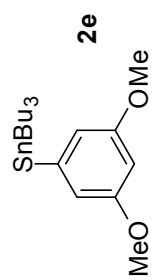


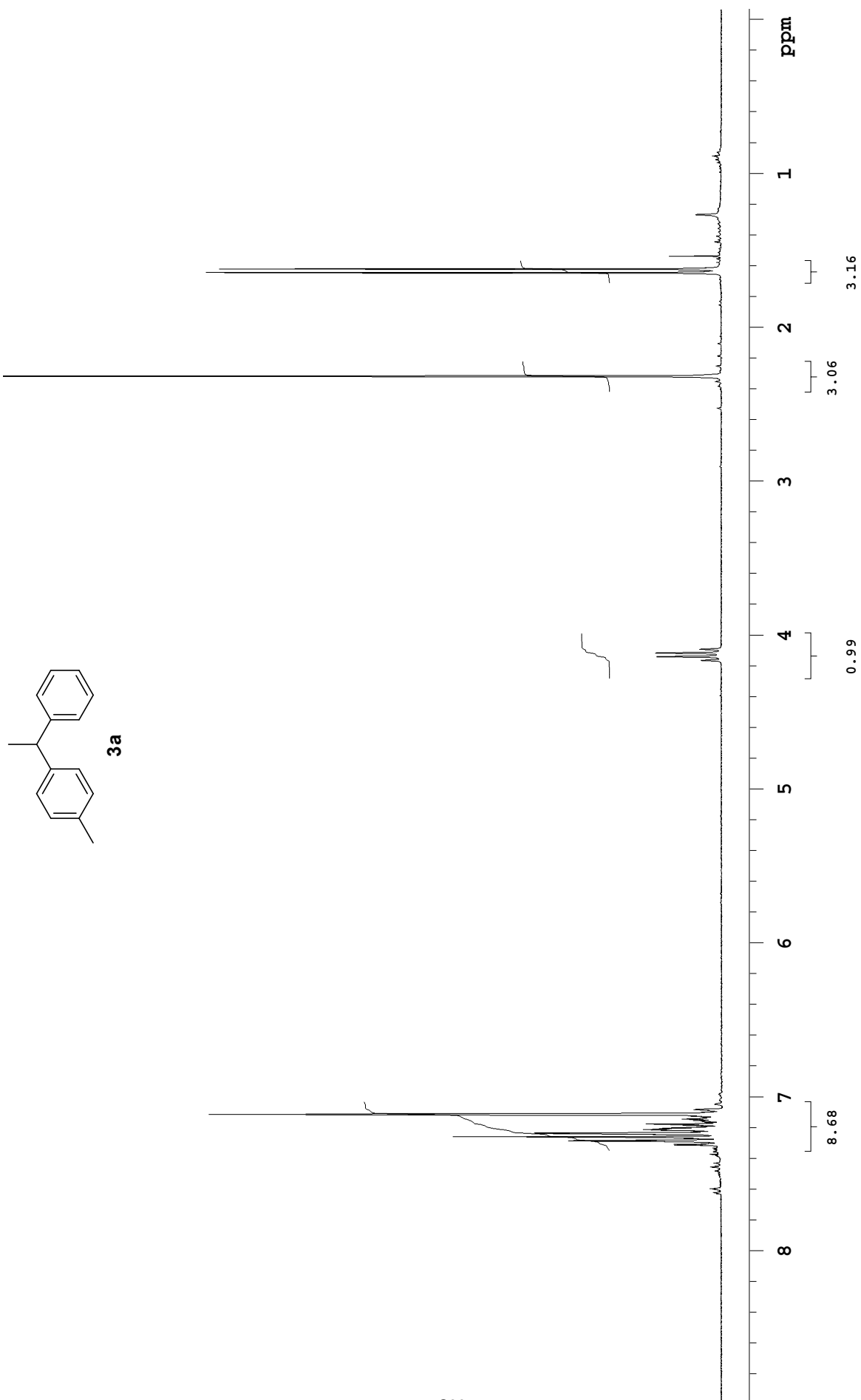
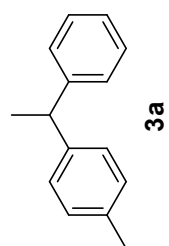


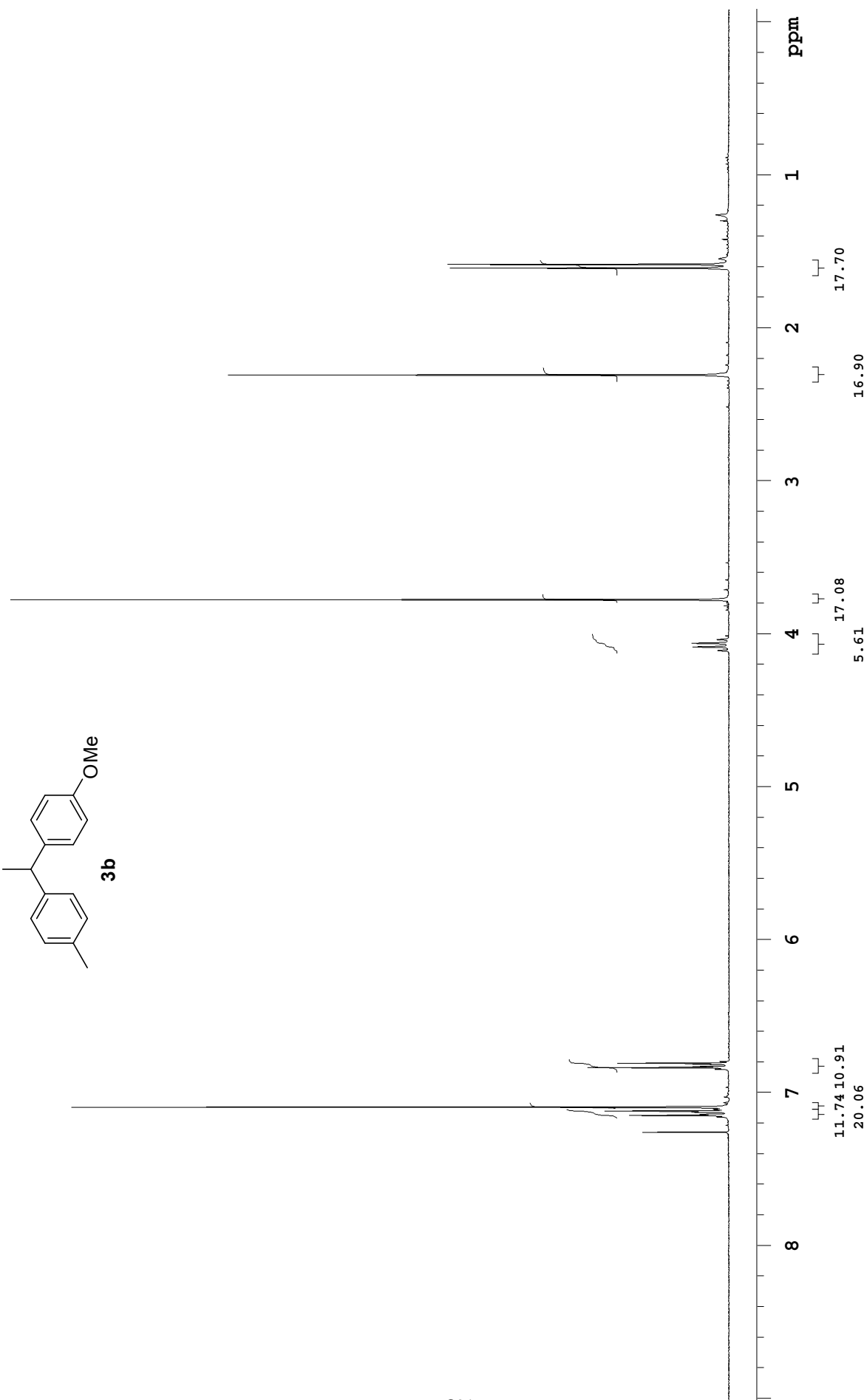
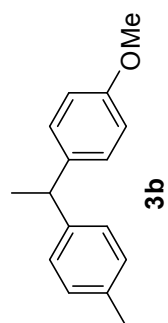


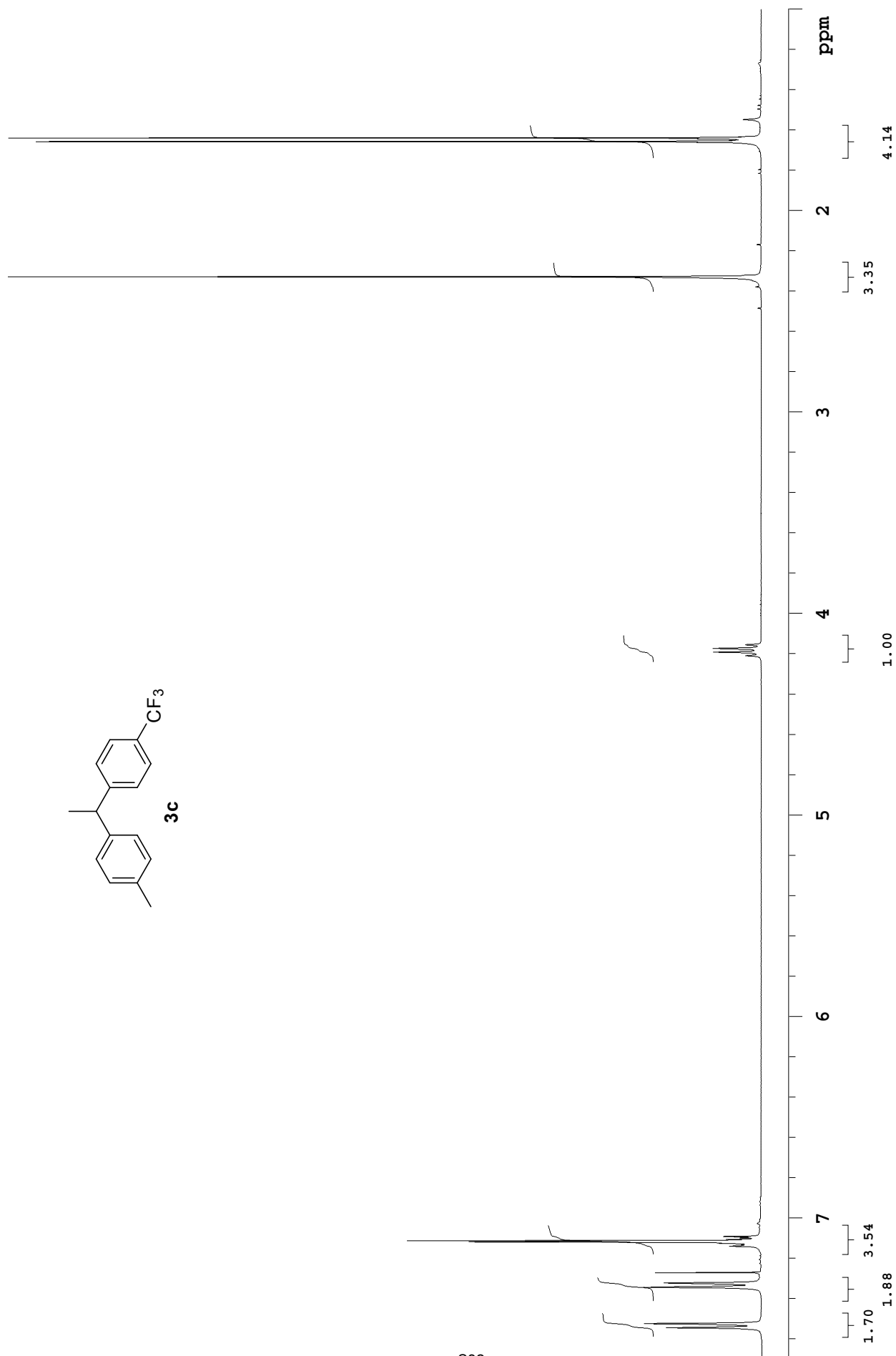
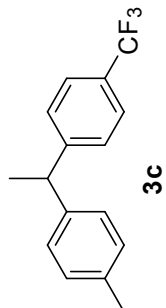


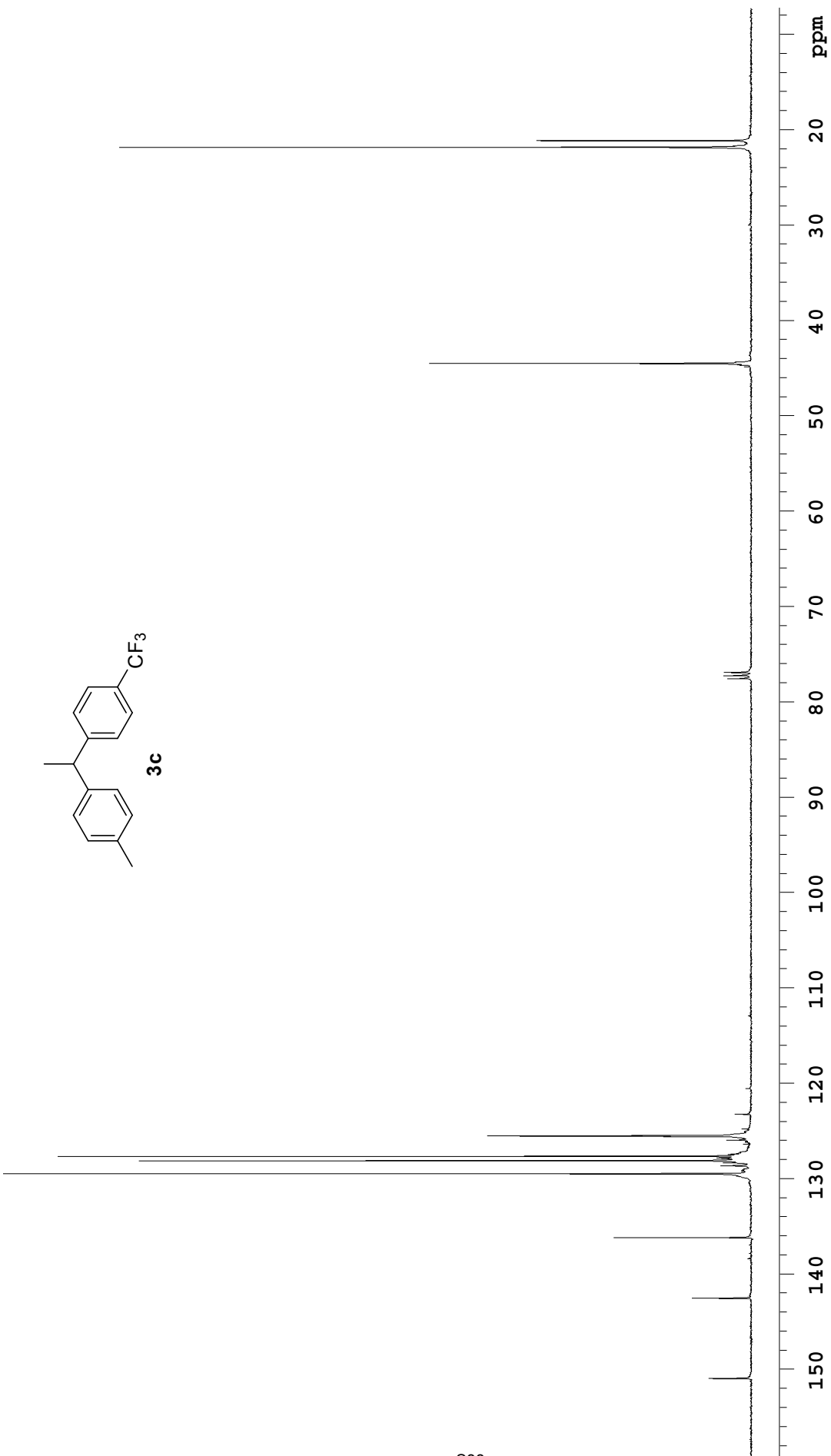


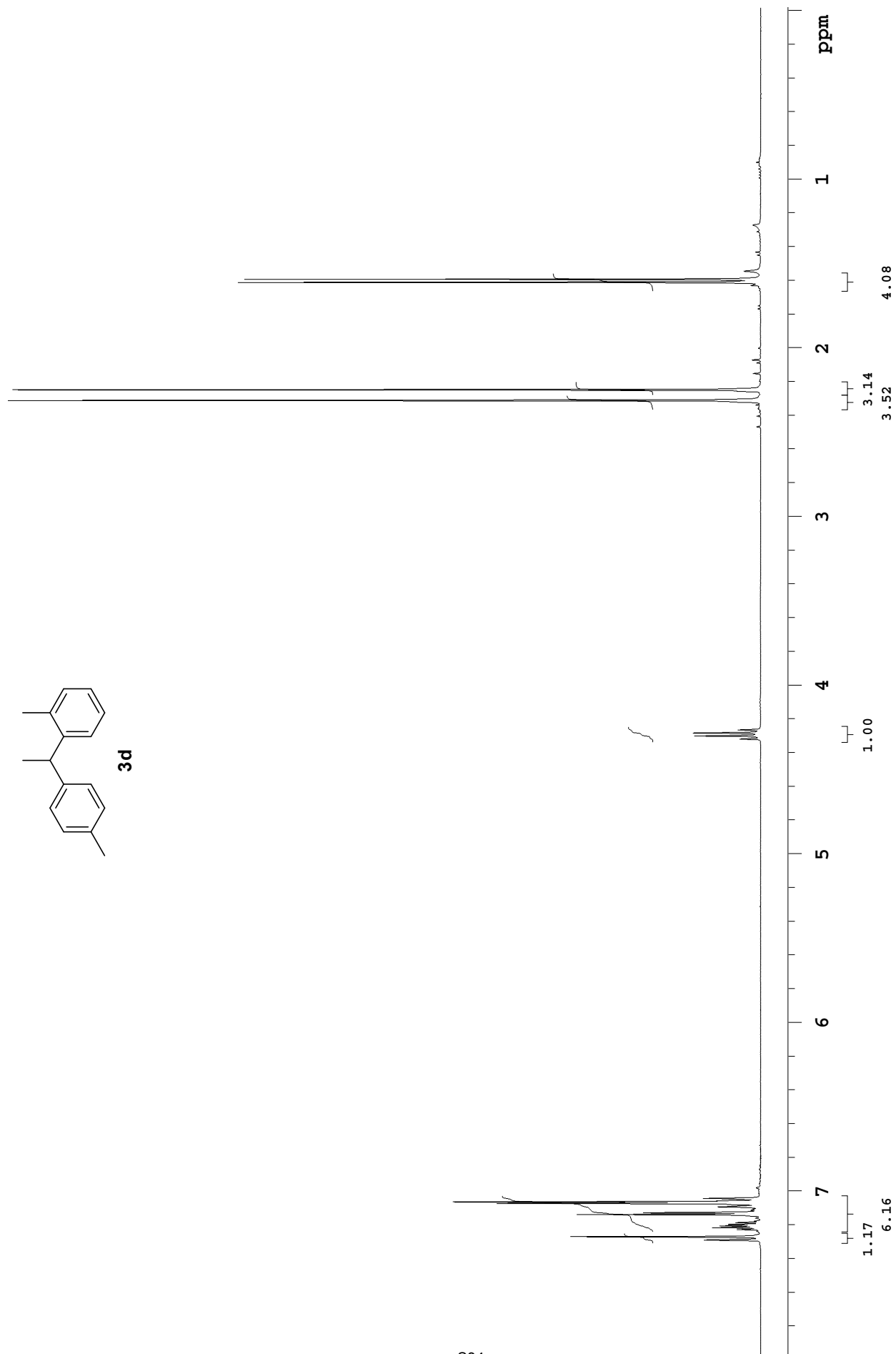
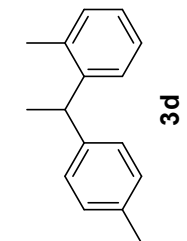


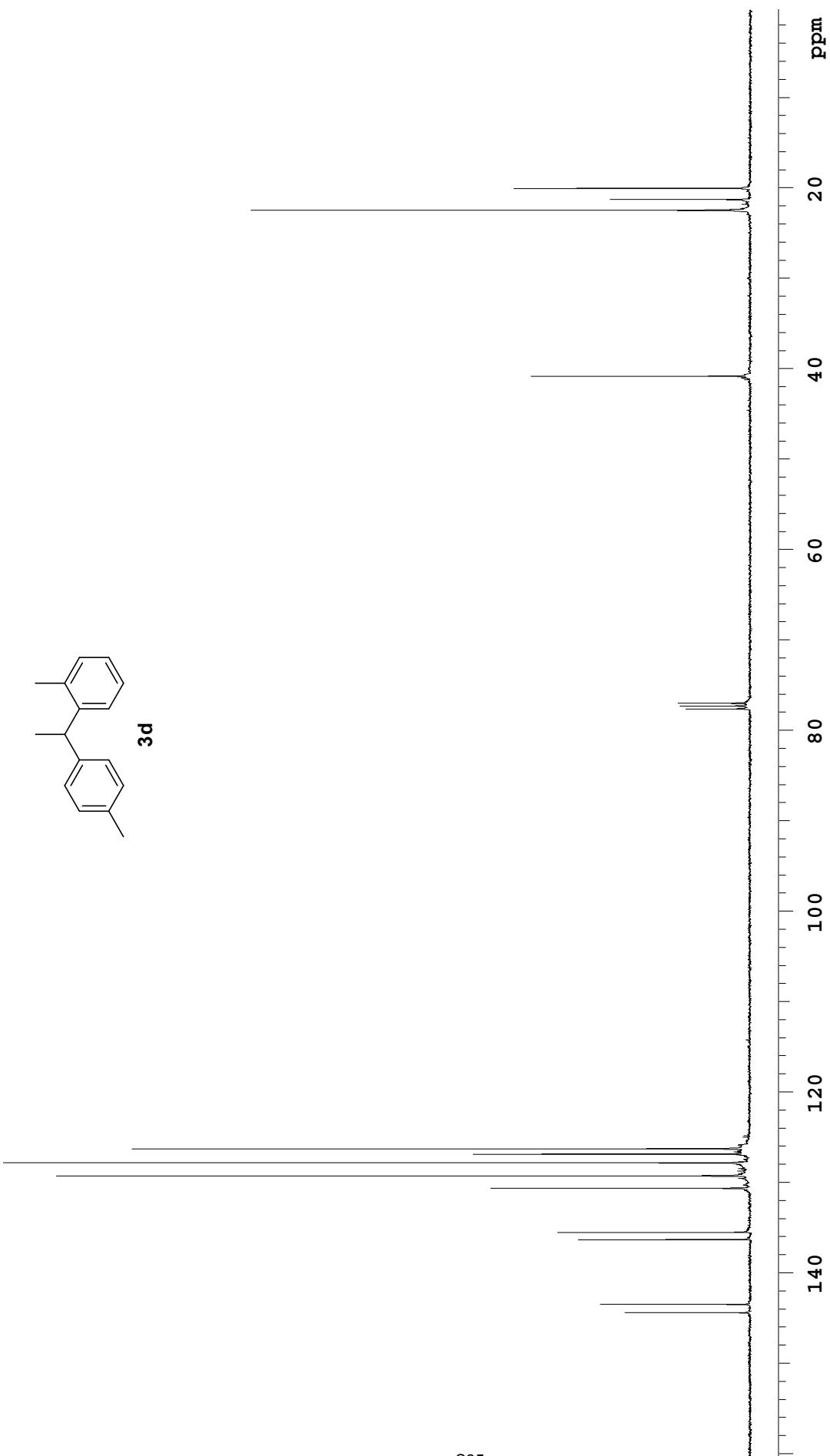
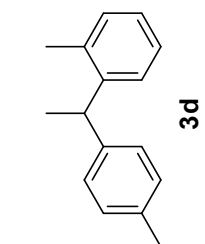


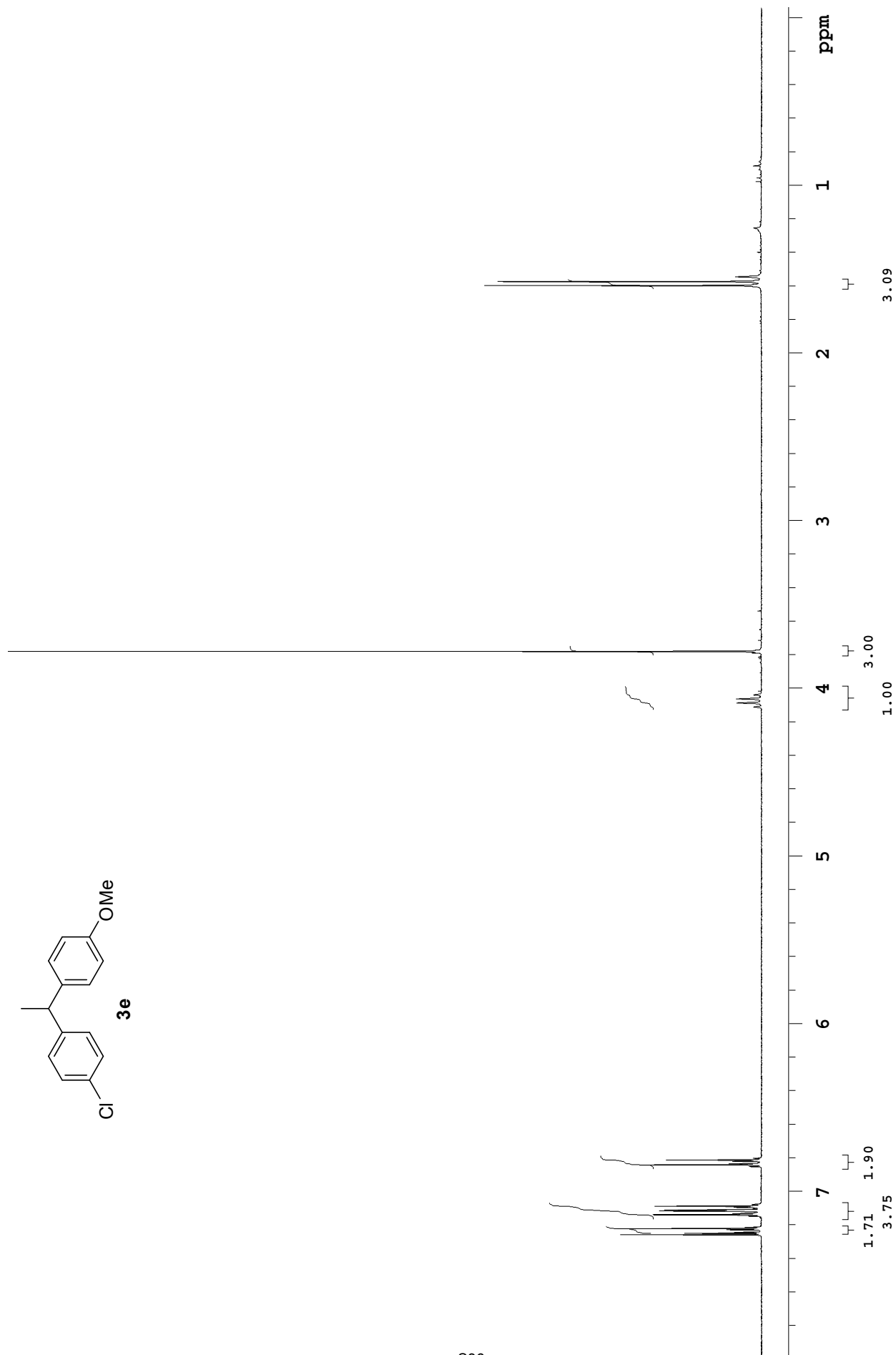
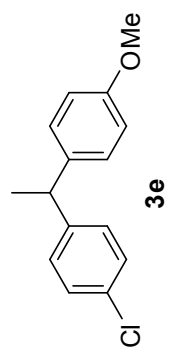


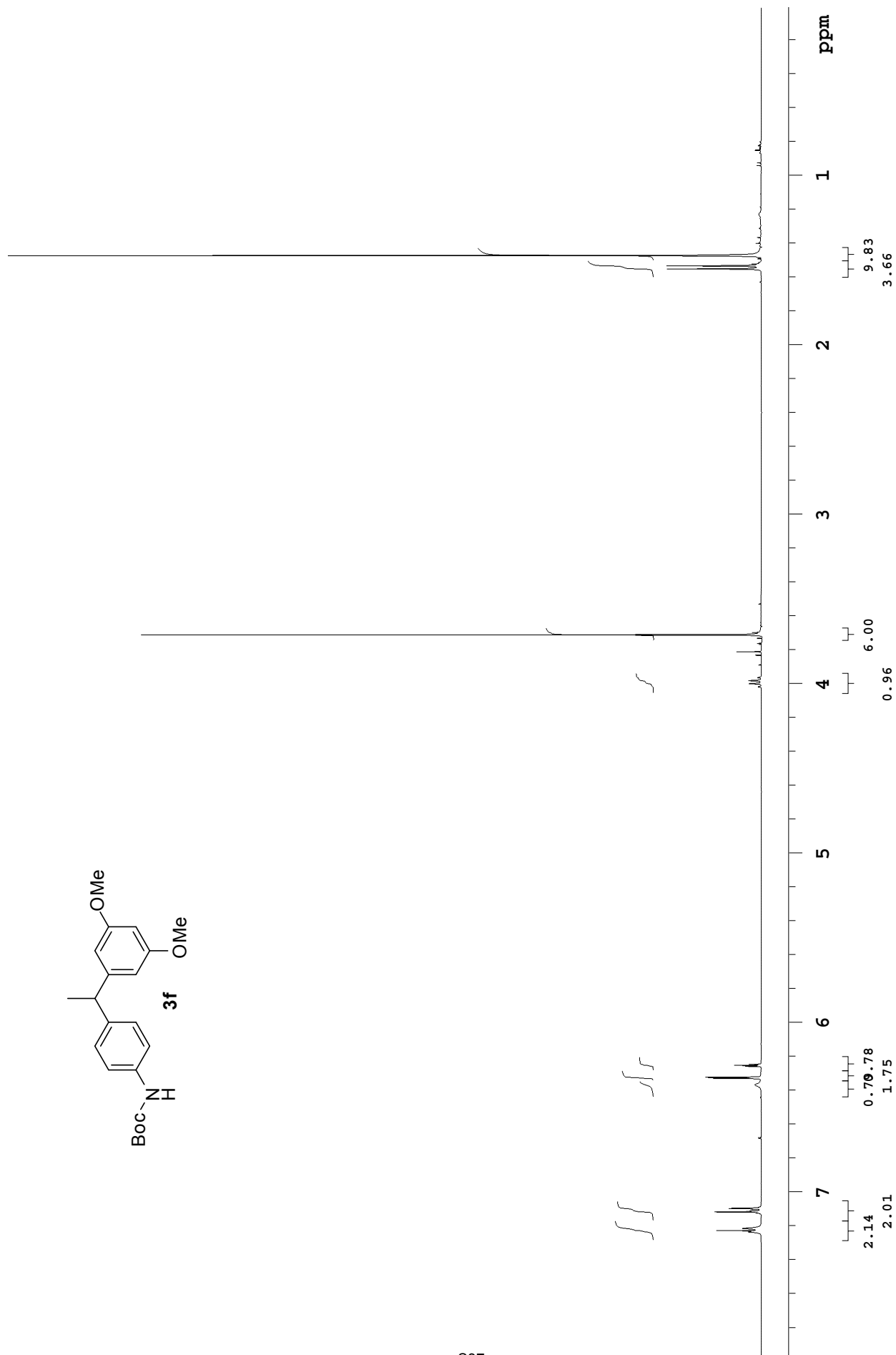
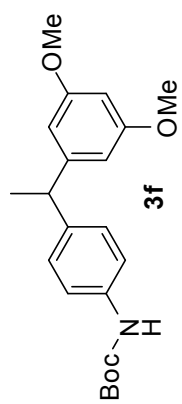


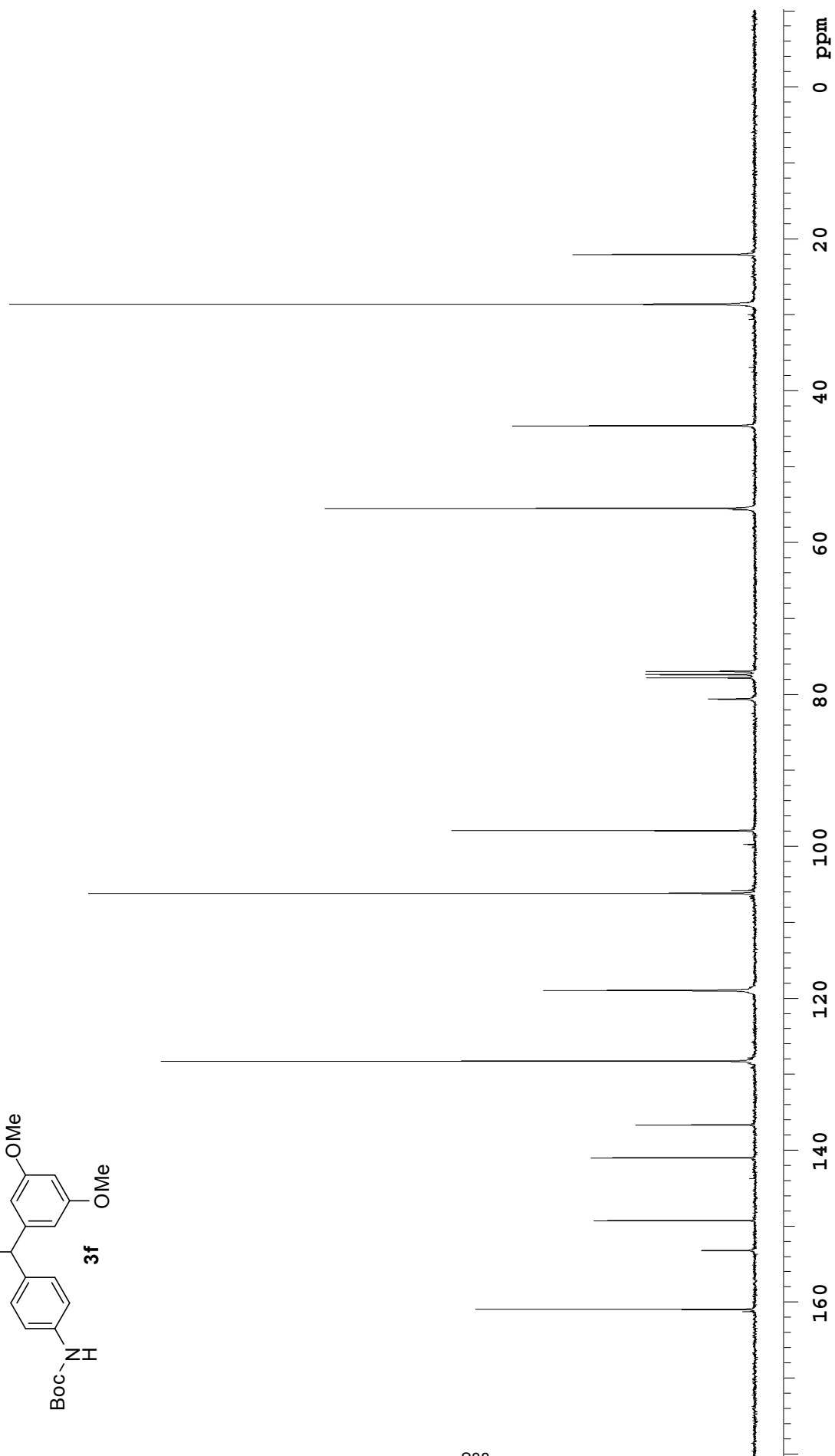
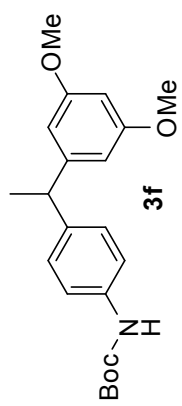


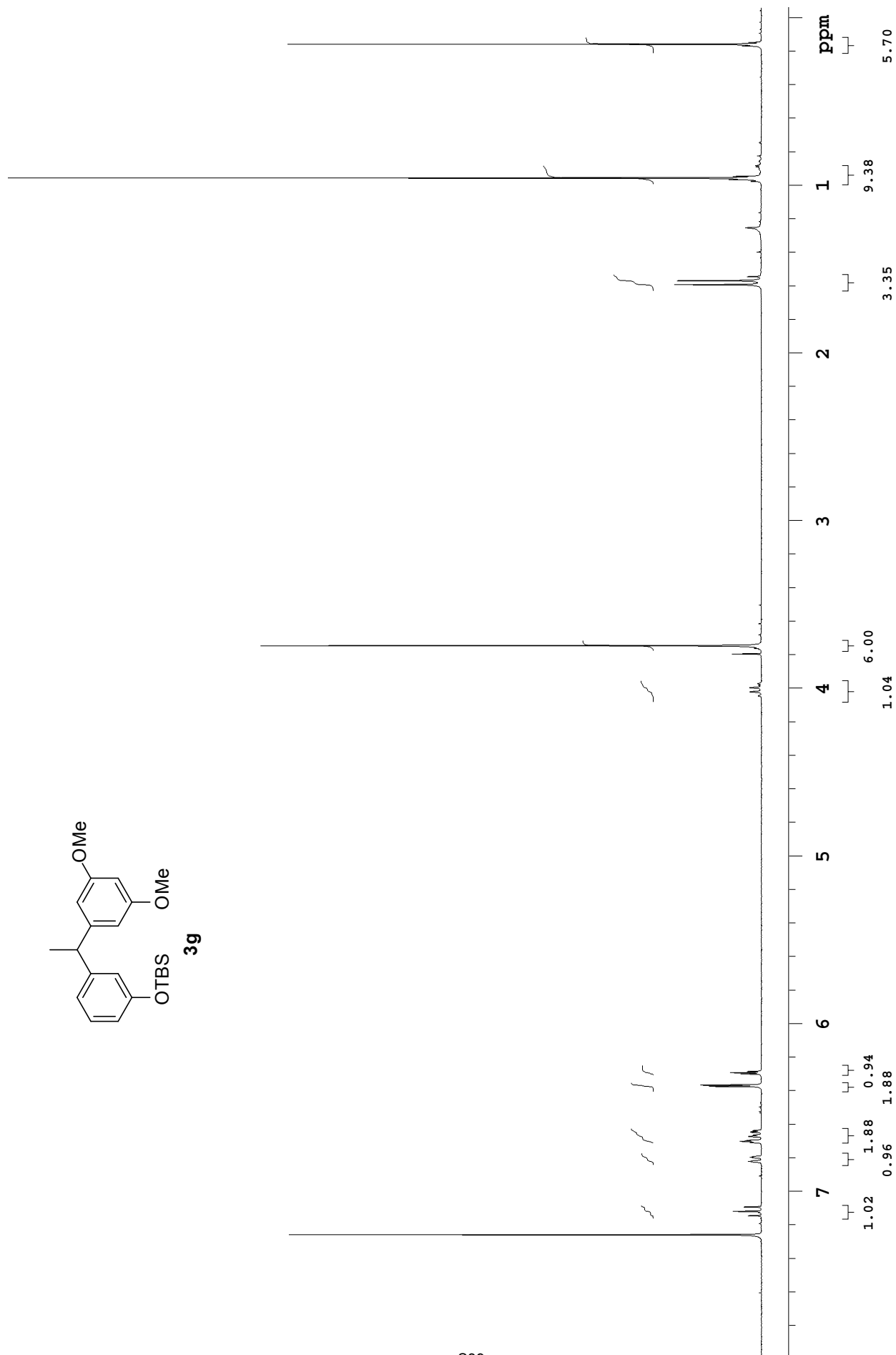
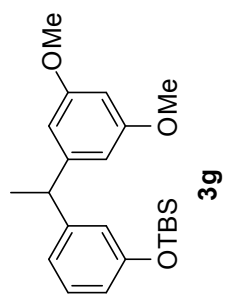


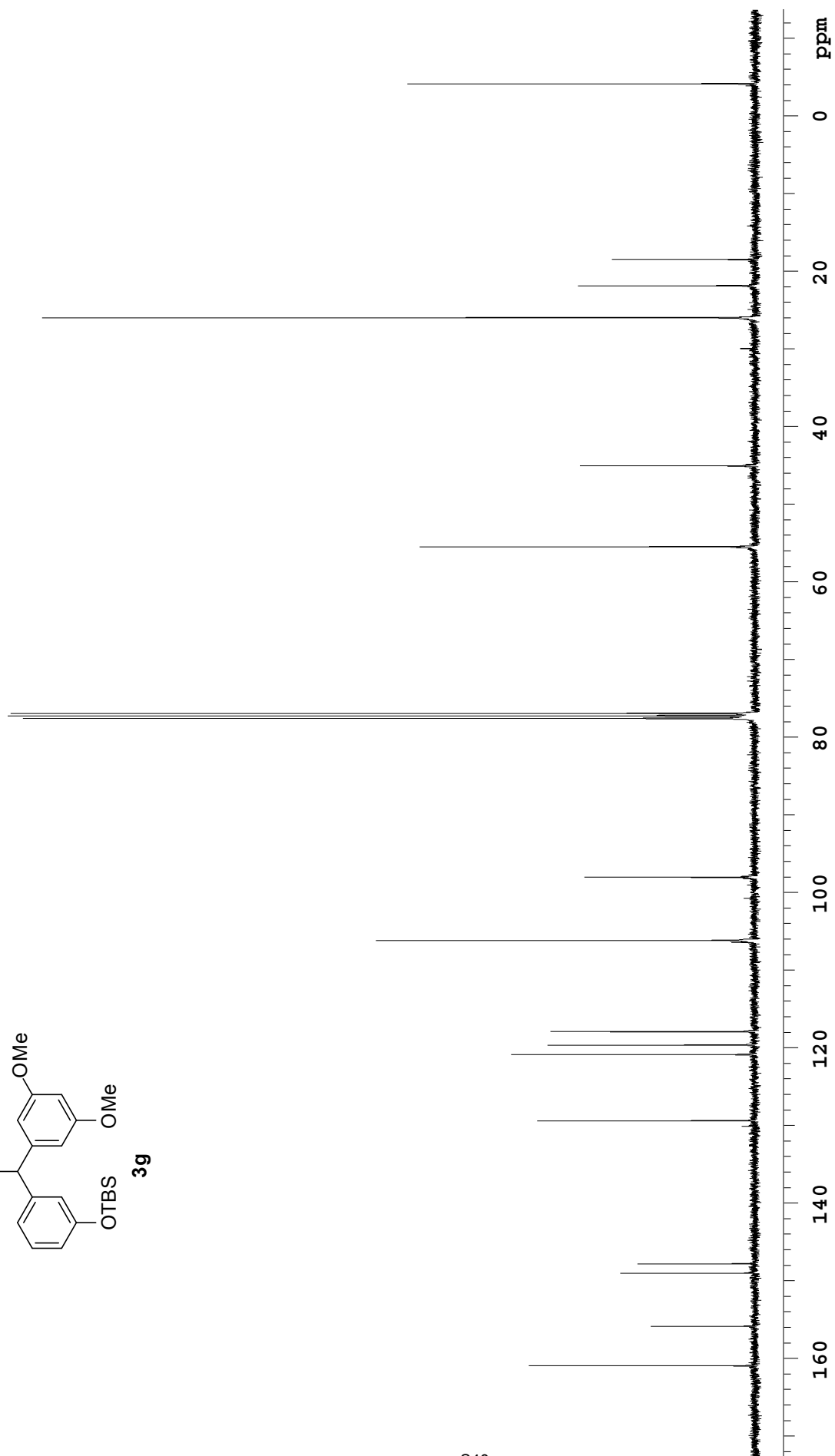
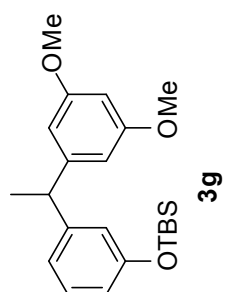


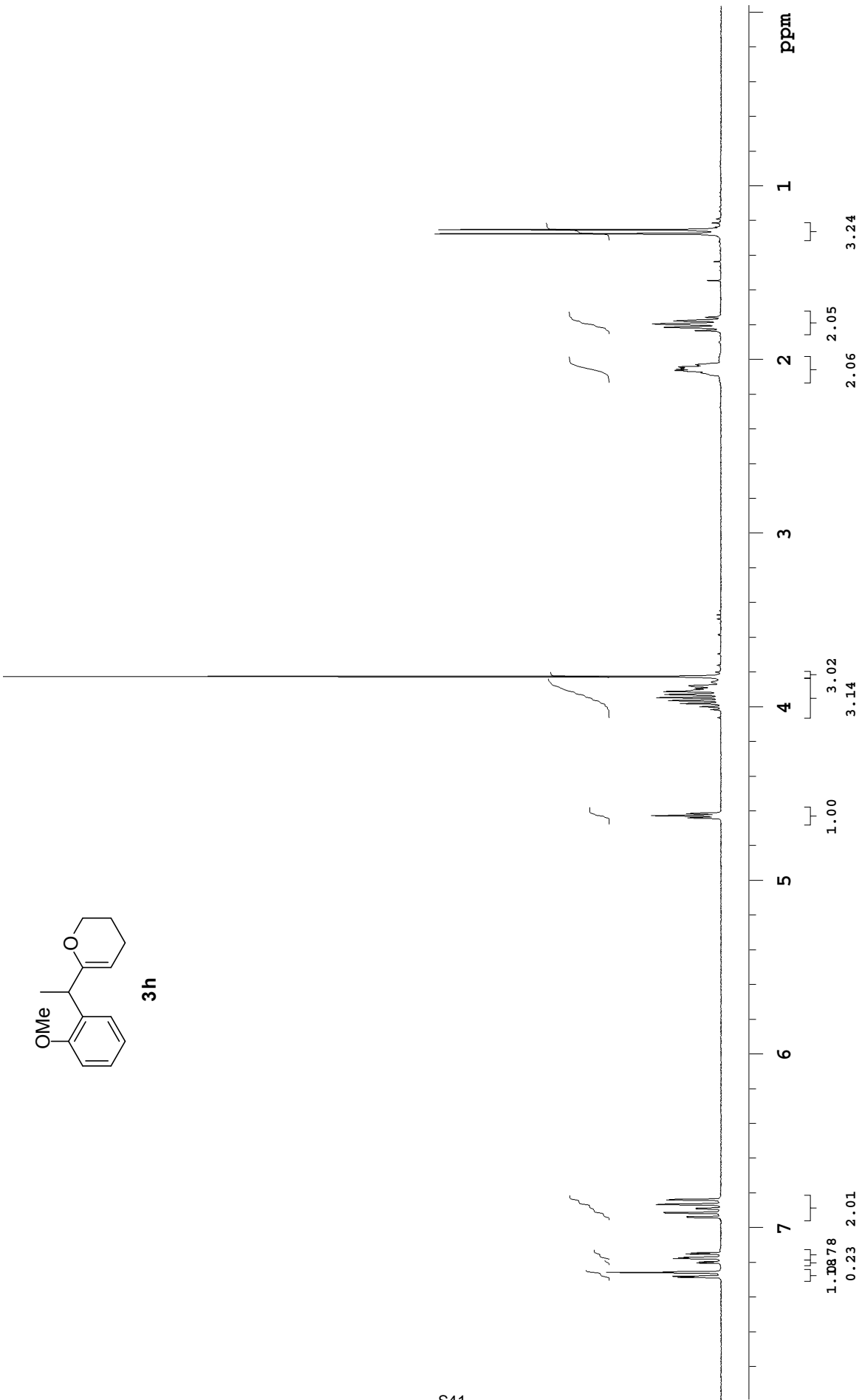


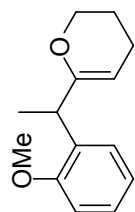




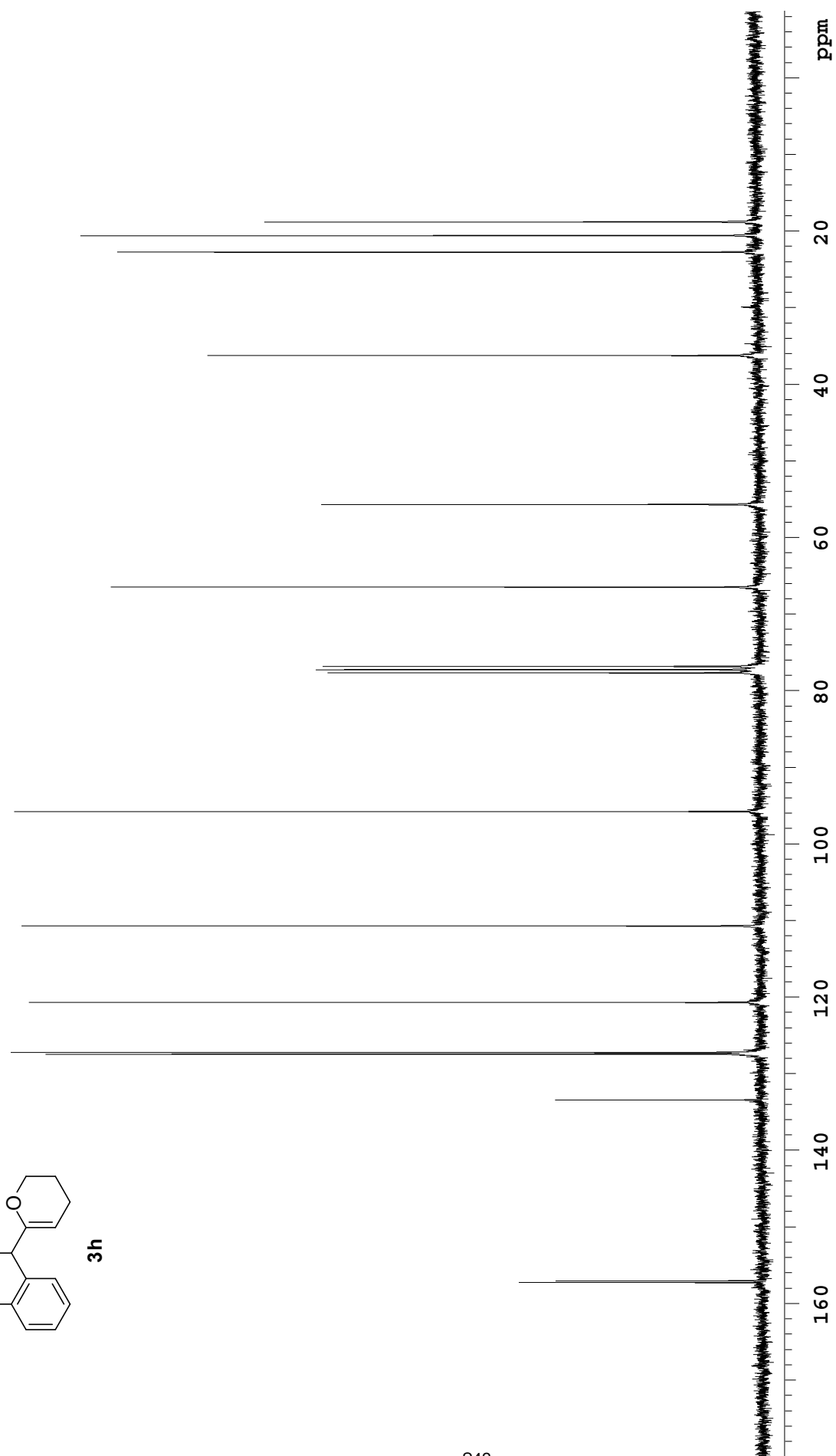


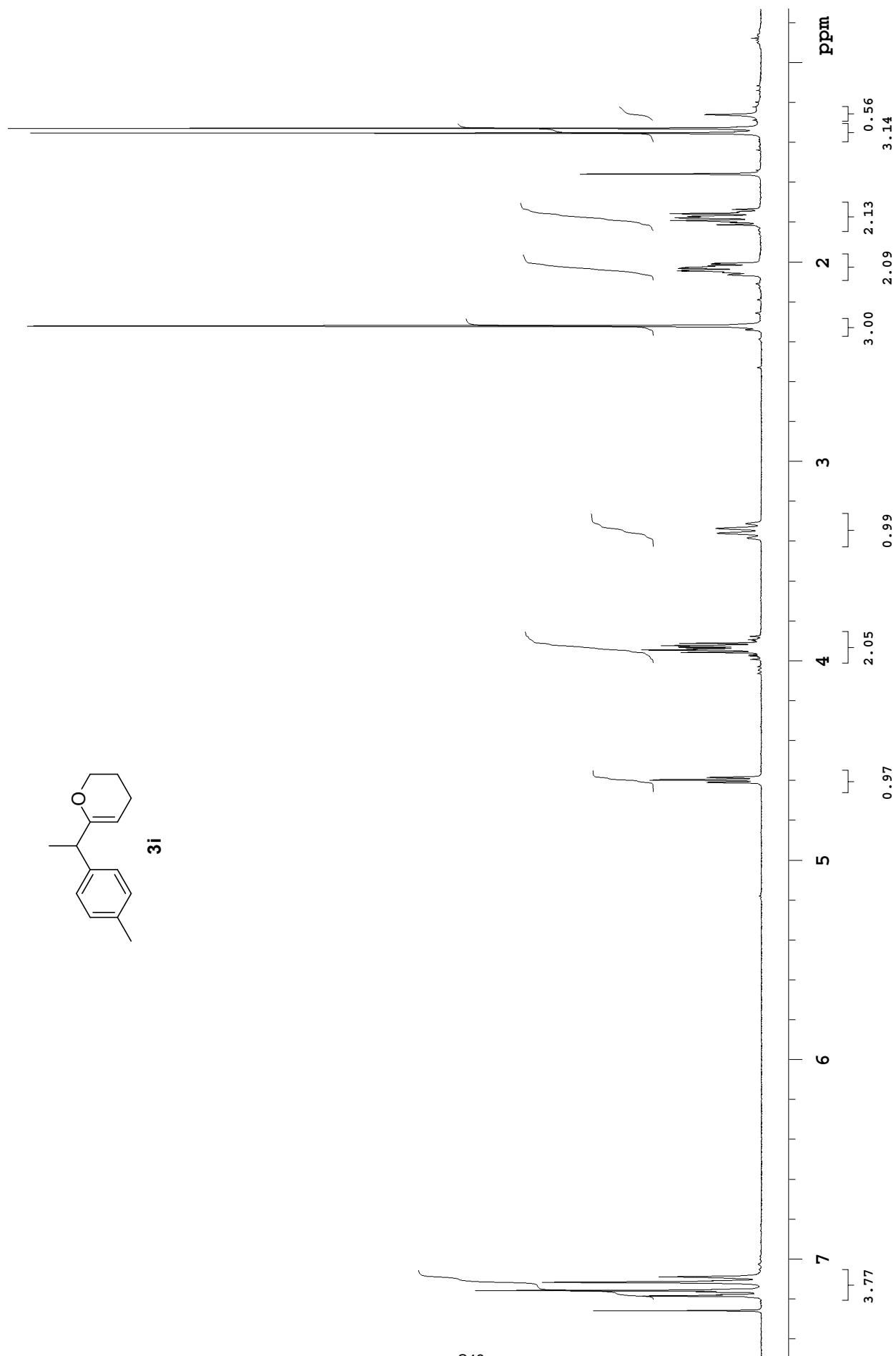
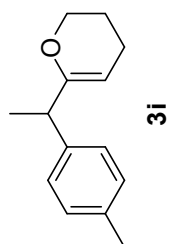


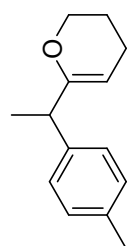




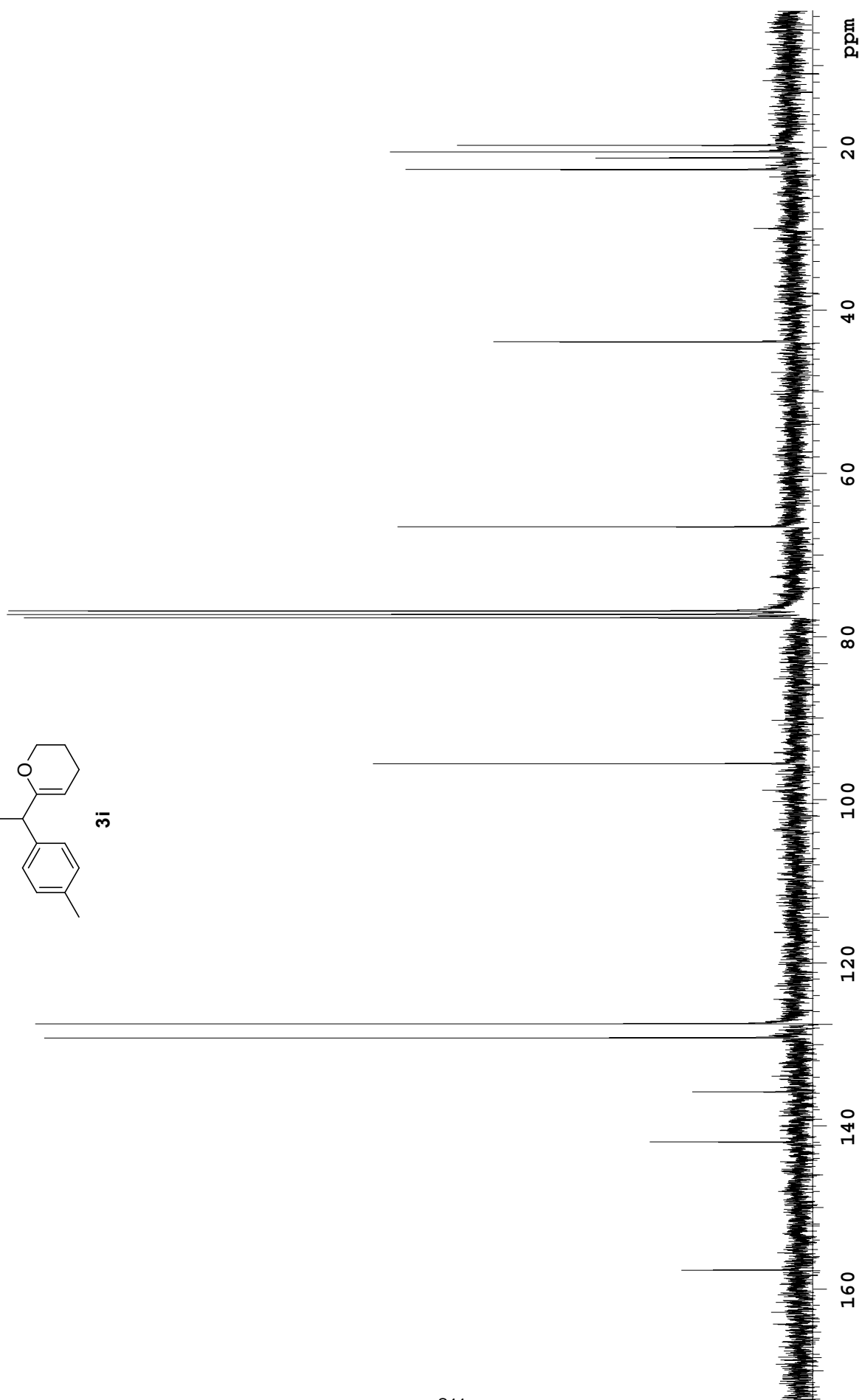
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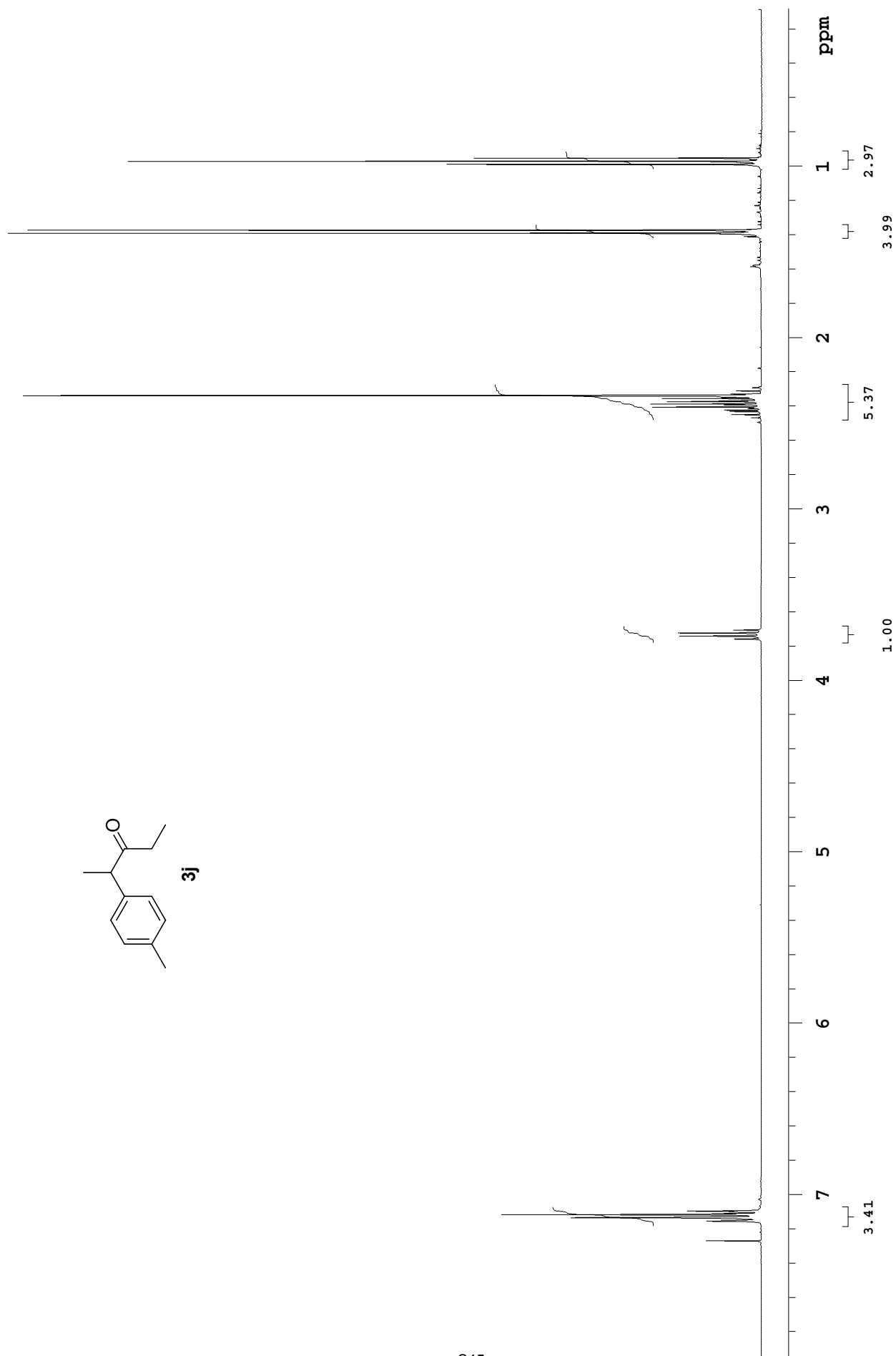
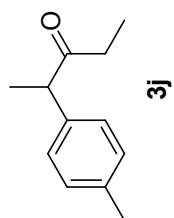


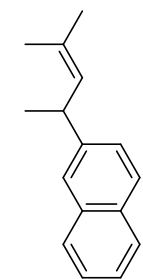




3i







3k

