Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

Supporting Information For: Aerobic Alcohol Oxidation Coupled Palladium-Catalyzed Alkene Hydroarylation with Boronic Esters

Yasumasa Iwai, Keith M. Gligorich and Matthew S. Sigman[*]

Department of Chemistry, University of Utah,
315 S. 1400 East, Salt Lake City, Utah 84112-8500

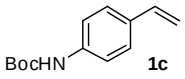
E-mail: sigman@chem.utah.edu

Table of Contents

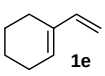
General Information:

2-propanol was dried by distilling from calcium oxide. *sec*-BuOH was initially purified by refluxing over sodium borohydride for 12 hours followed by fractional distillation. Then, it was dried by refluxing over calcium oxide for 12 hours followed by fractional distillation. THF was dried by distilling from sodium benzophenone ketyl. CH_2Cl_2 and 1,2-dichloroethane were dried by distilling from calcium hydride. Toluene was purified by passing through activated alumina. Unless noted, all styrenes were purchased from Aldrich or Acros. Styrenes were purified by passing through a small plug of activated alumina. Unless noted, all boronic acids were purchased from Aldrich, Acros, or Frontier Scientific Inc. Palladium^{II} chloride was purchased from Pressure Chemicals. Pd[(–)-sparteine]Cl_2[1] and [Pd(S*i*Pr)Cl_2]$_2$[2-4] were synthesized according to a previously reported procedure. (–)-Sparteine was prepared from (–)-sparteine sulfate pentahydrate (purchased from Acros) according to a previously reported procedure.[5] ^{1}H-NMR spectra were obtained at 300 MHz, chemical shifts are reported in ppm, and referenced to the $CHCl_3$ singlet at 7.27 ppm. ^{13}C-NMR spectra were obtained at 75 MHz and referenced to the center line of the $CDCl_3$ triplet at 77.2 ppm. Flash chromatography was performed using EM reagent silica 60 (230-400 mesh). All melting points are uncorrected and were recorded on an electrothermal melting point apparatus. IR spectra were recorded using a FTIR instrument. 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 or chiral β-cyclodex column using a 20:1 split. HPLC analysis was performed using a Hewlett Packard Series 1100 instrument fitted with a Chiralcel OJ-H column.

Synthesis of Styrene or Diene Derivatives:

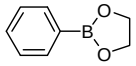


Preparation of *tert*-butyl-4-vinylphenylcarbamate (1c): Styrene **1c** was synthesized according to a previously reported procedure and the ^{1}H-NMR spectrum was compared to the previously reported spectrum.[6]

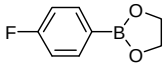


Preparation of 1-vinylcyclohex-1-ene (1e): To a 500 mL flame dried round bottom flask equipped with a stir bar, was added 7.72 g of methyltriphenylphosphonium bromide (21.6 mmol, 1.20 equiv.) and 115 mL of THF under a N_2 atmosphere. To the cloudy white mixture, was added 2.63 g of *tert*-BuOK (23.4 mmol, 1.30 equiv.) in three portions. The reaction mixture turned yellow and was stirred 4 hours. The mixture was cooled to -78 °C and 1.99 mL of 1-cyclohexene-1-carboxaldehyde (Aldrich) (18.0 mmol, 1.00 equiv.) was added dropwise. The mixture was allowed to slowly warm to ambient temperature and was stirred for 12 hours. To the yellow mixture, was added 60.0 mL of saturated NH_4Cl solution and the cloudy white solution was stirred for 1 hour. The mixture was transferred to a separatory funnel and was extracted three times with 20 mL of Et_2O. The organic extracts were combined, washed once with 70.0 mL of brine, dried over magnesium sulfate, filtered, and the solvent removed *in vacuo* to yield a yellow oil. The product was purified by flash chromatography eluting with 5% Et_2O/hexanes and isolated as a clear oil in 31% yield (603 mg). The ^{1}H-NMR spectrum was compared to the previously reported spectrum.[7]

Synthesis of Boron Reagents:

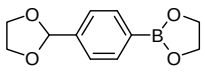

2a

Preparation of 2-phenyl-[1,3,2]-dioxaborolane (2a).
Method A: To an oven dried 100 mL round bottom flask equipped with a stir bar, was added 2.00 g of phenyl boronic acid (16.4 mmol, 1.00 equiv.), 1.12 g of ethylene glycol (18.0 mmol, 1.10 equiv.), 1.97 g of magnesium sulfate (16.4 mmol, 1.00 equiv.) and 20.0 mL of dichloromethane. The mixture was stirred for 20 hours at room temperature under a N_2 atmosphere. The reaction mixture was filtered, washed with dichloromethane, and concentrated under reduced pressure to yield a colorless oil. Purification was accomplished by flash chromatography eluting with hexanes/EtOAc (5:1). The product containing fractions were combined and concentrated under reduced pressure to give the desired compound **2a** (2.22 g, 91% yield) as a colorless oil.
Method B: To an oven dried 100 mL round bottom flask equipped with a stir bar, was added 2.00 g of phenyl boronic acid (16.4 mmol, 1.00 equiv.), 1.07 g of ethylene glycol (17.2 mmol, 1.05 equiv.) and 40.0 mL of toluene. The mixture was azeotoropic-refluxed with a Dean-Stark apparatus for 3 hours under a N_2 atmosphere. Upon cooling, the reaction mixture was concentrated under reduced pressure to yield a colorless oil. Purification was accomplished by flash chromatography eluting with hexanes/EtOAc (5:1). The product containing fractions were combined and concentrated under reduced pressure to give the desired compound **2a** (2.15 g, 89% yield) as a colorless oil:
^{1}H-NMR spectrum was compared to a previously reported spectrum.[8]


2b

Preparation of 2-(4-fluorophenyl)-[1,3,2]-dioxaborolane (2b). To a flame dried 100 mL Schlenck flask equipped with a stirbar and a dried water condenser under a N_2 atmosphere, was added 25.0 mL of THF and 1.00 g of magnesium turnings (41.3 mmol, 1.60 equiv.), which were activated by crushing with a mortar and pestle. To the stirred mixture, was added 2 drops of 1,2-dirbromoethane and 4.50 g of 1-bromo-4-fluorobenzene (25.7 mmol, 1.00 equiv.) in THF (5.00 mL). The stirred mixture was heated to reflux for 3 hours. The reaction mixture was cooled to room temperature and was cannulated into a flame dried 100 mL Schlenck flask equipped with a stir bar. The mixture was cooled to -78 ^{o}C and 5.70 mL of trimethyl borate (51.1 mmol, 2.00 equiv.) in THF (25.0 mL) was added. The mixture was allowed to warm to room temperature and was stirred for 15 hours. The reaction mixture was concentrated under reduced pressure. To the residue, were added 6.80 g of ethylene glycol (110 mmol, 4.30 equiv.) and 90.0 mL of toluene. The mixture was heated to reflux for 3 hours. Upon cooling, the toluene layer was separated and concentrated under reduced pressure. Purification was accomplished by flash chromatography eluting with hexanes/EtOAc (3:1). The product containing fractions were combined and concentrated under reduced pressure to give the desired compound **2b** (2.34 g) as a white solid. ^{1}H NMR analysis of the white solid indicated the presence of starting material. Therefore, to an oven dried 50 mL Schlenk flask equipped with a stir bar, was added 2.34 g of the solid, 153 mg of ethylene glycol (2.47 mmol, 0.096 equiv.), 1.00 g of magnesium sulfate (8.31 mmol, 0.323 equiv.), and 10.0 mL of dichloromethane. The mixture was stirred for 20 hours at room temperature under a N_2 atmosphere. The reaction mixture was filtered,

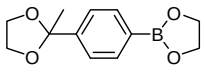
washed with dichloromethane, and concentrated under reduced pressure. Purification was accomplished by mixed solvent recrystallization from 5 mL of hexanes to yield compound **2b** (1.86 g, 44% yield) as white crystals:
mp: 50 - 51 °C; 300 MHz ^{1}H NMR ($CDCl_3$): δ 4.37 (s, 4H), 7.07 (t, *J* = 8.7 Hz, 2H), 7.80 (dd, *J* = 6.4, 8.6 Hz, 2H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ 66.3, 115.2(d, *J* = 20.1 Hz), 137.3(d, *J* = 8.1 Hz), 165.4(d, *J* = 249.8 Hz). ; IR (KBr) 3045, 2991, 2922, 1596, 1405, 1379, 1340, 1215, 1092, 942, 835 cm^{-1}; HRMS (EI) calcd. $C_8H_8BFO_2$ $(M)^+$ 166.0601, obsd. 166.0594.



2c

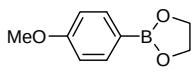
Preparation of 2-[4-(1,3-dioxolan-2-yl)phenyl]-[1,3,2]-dioxaborolane (2c). To a flame dried 100 mL round bottom flask equipped with a stirbar and a dried water condenser under a N_2 atmosphere, was added 1.24 g of 4-formylphenyl boronic acid (8.28 mmol , 1.00 equiv.), 2.06 g of ethylene glycol (33.1 mmol, 4.00 equiv.), 39.4 mg of *p*-toluenesulfonic acid (0.207 mmol, 0.025 equiv.), and 30.0 mL of toluene. The mixture was azeotoropic-refluxed with a Dean-Stark apparatus for 2.5 hours. Upon cooling, the reaction mixture was concentrated under reduced pressure. ^{1}H-NMR analysis indicated the presence of a formyl group. Therefore, to the residue under a N_2 atmosphere, was added 514 mg of ethylene glycol (8.28 mmol, 1.00 equiv.), and 30.0 mL of toluene. The mixture was azeotoropic-refluxed with a Dean-Stark apparatus for 2.5 hours. Upon cooling, the reaction mixture was concentrated under reduced pressure. To the residue under a N_2 atmosphere, was added 1.24 g of magnesium sulfate (10.3 mmol, 1.24 equiv.), and 12.4 mL of dichloromethane. The mixture was stirred for 20 minutes at room temperature under a N_2 atmosphere. The reaction mixture was filtered, washed with dichloromethane, and concentrated under reduced pressure. Purification was accomplished by mixed solvent recrystallization from dichloromethane/hexanes (3:8) to yield compound **2c** (1.29 g) as white crystals. Ethylene glycol was present in the solid by ^{1}H-NMR. Therefore, the solid and the filtrate were combined and concentrated under reduced pressure. To the residue under a N_2 atmosphere, was added 2.00 g of magnesium sulfate (16.6 mmol, 2.00 equiv.), and 10 mL of dichloromethane. The mixture was stirred for 20 hours at room temperature under a N_2 atmosphere. The reaction mixture was filtered, washed with dichloromethane, and concentrated under reduced pressure. Purification was accomplished by mixed solvent recrystallization from dichloromethane/hexanes (3:18) to yield compound **2c** (1.25 g) as white crystals. Ethylene glycol was still present in the solid by ^{1}H-NMR. Therefore, the solid and the filtrate were combined and concentrated under reduced pressure. To a flame dried 100 mL round bottom flask equipped with a stirbar and a dried water condenser under a N_2 atmosphere, was added the residue, 100 mg of ethylene glycol (1.61 mmol, 0.19 equiv.), 15.7 mg of *p*-toluenesulfonic acid (0.083 mmol, 0.01equiv.), and 30.0 mL of toluene. The stirred mixture was heated to reflux for 3 hours. The reaction mixture was cooled to room temperature and 2.00 g of magnesium sulfate (16.6 mmol, 2.00 equiv.) was added. The mixture was stirred 15 hours at room temperature under a N_2 atmosphere. The reaction mixture was filtered, washed with ethyl acetate, and concentrated under reduced pressure. Purification was accomplished by recrystallization from 2-propanol (5.00 mL) to yield the desired compound **2c** (1.23 g, 68% yield) as white crystals:

mp: 104 - 106 °C; 300 MHz ^{1}H NMR ($CDCl_3$): δ 4.02-4.08 (m, 2H), 4.09-4.16 (m, 2H), 4.38 (s, 3H), 5.83 (s, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ 65.6, 66.3, 103.8, 126.1, 135.1, 141.2.; IR (KBr) 2986, 2913, 1612, 1398, 1372, 1336, 1216, 1143, 1095, 978, 945, 641 cm^{-1}; HRMS (EI) calcd. $C_{11}H_{13}BO_4$ $(M-H)^+$ 219.0829, obsd. 219.0836.



2d

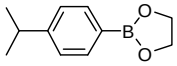
Preparation of 2-[4-(2-methyl-1,3-dioxolan-2-yl)phenyl]-[1,3,2]-dioxaborolane (2d). To a flame dried 100 mL round bottom flask equipped with a stirbar and a dried water condenser under a N_2 atmosphere, was added 1.50 g of 4-acethylphenyl boronic acid (9.15 mmol, 1.00 equiv.), 2.27 g of ethylene glycol (36.6 mmol, 4.00 equiv.), 43.5 mg of *p*-toluenesulfonic acid (0.229 mmol, 0.025 equiv.) and 30.0 mL of toluene. The mixture was azeotoropic-refluxed with a Dean-Stark apparatus for 4 hours. Upon cooling, the reaction mixture was concentrated under reduced pressure. ^{1}H NMR analysis indicated the presence of an acetyl containing compound. Therefore, to the residue under a N_2 atmosphere, was added 2.27 g of ethylene glycol (36.6 mmol, 4.00 equiv.), 43.5 mg of *p*-toluenesulfonic acid (0.229 mmol, 0.025 equiv.) and 30.0 mL of toluene. The mixture was azeotoropic-refluxed with a Dean-Stark apparatus for 3 hours. Upon cooling, the reaction mixture was concentrated under reduced pressure. To the residue under a N_2 atmosphere, was added 90.0 mL of toluene and was concentrated under reduced pressure. To the residue under a N_2 atmosphere, was added 3.00 g of magnesium sulfate (10.3 mmol, 1.20 equiv.) and 15.0 mL of dichloromethane. The mixture was stirred for 30 minutes at room temperature under a N_2 atmosphere. The mixture was filtered, washed with dichloromethane, and concentrated under reduced pressure. Purification was accomplished by recrystallization from 2-propanol (5.00 mL) to yield the desired compound **2d** (1.56 g, 73% yield) as white crystals:
mp: 84 - 85 °C; 300 MHz ^{1}H NMR ($CDCl_3$): δ 1.65 (s, 3H), 3.74-3.78 (m, 2H), 4.02-4.06 (m, 2H), 4.38 (s, 3H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.79 (d, *J* = 7.9 Hz, 2H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ 27.7, 64.7, 66.3, 109.0, 125.0, 135.0, 146.7.; IR (KBr) 2980, 2901, 1403, 1377, 1343, 1222, 1196, 1098, 1025, 873, 842, 639 cm^{-1}; HRMS (ESI/APCI) calcd. $C_{12}H_{16}BO_4$ $(M+H)^+$ 235.1142, obsd. 235.1146.



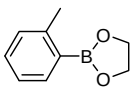
2e

Preparation of 2-(4-methoxyphenyl)-[1,3,2]-dioxaborolane (2e). To a flame dried 250 mL Schlenck flask equipped with a stirbar and a dried water condenser under a N_2 atmosphere, was added 32.0 mL of toluene, 8.00 mL of THF and 3.74 g of 4-bromo anisole (20.0 mmol, 1.00 equiv.). The stirred mixture was cooled to -78 °C and 9.60 mL of 2.50 M *n*-BuLi in hexanes (24.0 mmol, 1.20 equiv.) was added dropwise over 1 hour. Next, 5.50 mL of triispopropyl borate (23.9 mmol, 1.20 equiv.) was added. After stirring the mixture at -78 °C for 30 minutes, the mixture was warmed to -20 °C and 20.0 mL of 2 M HCl was added to the mixture. The mixture was allowed to warm to room temperature and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (40.0 mL x 3 times). The organic layers were combined and washed with saturated NaCl (40.0 mL x 2 times). The combined organic extracts were dried with magnesium sulfate, filtered, washed with

ethyl acetate, and concentrated under reduced pressure. To the residue, was added 5.00 mL of ethyl acetate and 5.00 mL of hexanes. The mixture was heated to 50 ^{o}C and stirred for 10 minutes. Upon cooling to room temperature, 15 mL of hexanes was added and the mixture was stirred at room temperature for 30 minutes. The solid was filtered, washed with hexanes, and dried *in vacuo* to give a mixture of 4-methoxyphenylboroxin and 4-methoxy boronic acid (9.2/1) (2.39 g, 88% yield) as white crystals. Therefore, to an oven dried 100 mL round bottom flask equipped with a stir bar, was added 700 mg of the mixture (5.16 mmol, 1.0 equiv.), 640 mg of ethylene glycol (10.3 mmol, 2.00 equiv.), and 14.0 mL of toluene. The mixture was azeotoropic-refluxed with a Dean-Stark apparatus for 1 hour under a N_2 atmosphere. Upon cooling, the reaction mixture was concentrated under reduced pressure. To the residue, was added 14.0 mL of toluene and the mixture was concentrated under reduced pressure. To the residue, was added 1.00 g of magnesium sulfate and 14.0 mL of hexanes. The mixture was stirred at room temperature for 10 minutes, filtered, rinsed with hexanes, and concentrated under reduced pressure to give the desired compound **2e** (843 mg, 92% yield) as white crystals:
^{1}H-NMR spectrum was compared to a previously reported spectrum.[8]

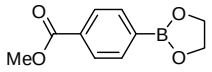

2f

Preparation of 2-(4-isopropylphenyl)-[1,3,2]-dioxaborolane (2f). To an oven dried 100 mL round bottom flask equipped with a stir bar, was added 1.00 g of 4-isopropylphenyl boronic acid (6.10 mmol, 1.00 equiv.), 416 mg of ethylene glycol (6.71 mmol, 1.10 equiv.), and 10.0 mL of dichloromethane. The mixture was stirred for 30 minutes at room temperature under a N_2 atmosphere and 734 mg of magnesium sulfate (2.78 mmol, 1.00 equiv.) was added. The mixture was stirred for 15 hours at room temperature under a N_2 atmosphere. The reaction mixture was filtered, washed with dichloromethane, and concentrated under reduced pressure. Purification was accomplished by flash chromatography eluting with hexanes/ ethyl acetate (8:1). The product containing fractions were combined and concentrated under reduced pressure to give the desired compound **2f** (1.03 g, 89% yield) as a colorless oil:
300 MHz ^{1}H NMR ($CDCl_3$): δ 1.26 (d, J = 6.9 Hz, 6H), 2.79 (sept, J = 6.9 Hz, 1H), 4.37 (s, 4H), 7.26 (d, J = 7.9 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ 24.0, 34.6, 66.2, 126.3, 135.2, 152.7.; IR (neat) 2963, 2908, 1611, 1401, 1374, 1212, 1096, 942, 834, 649 cm^{-1}; HRMS (EI) calcd. $C_{11}H_{15}BO_2$ $(M)^+$ 190.1165, obsd. 190.1158.


2g

2-*o*-tolyl-1,3,2-dioxaborolane (2g). To a flame dried 250 mL Schlenck flask equipped with a stirbar under a N_2 atmosphere, was added 32.0 mL of toluene, 8.00 mL of THF, and 3.40 g of 2-bromotoluene (20.0 mmol, 1.00 equiv.). The stirred mixture was cooled to -78 ^{o}C and 9.60 mL of 2.5 M *n*-BuLi in hexanes (24.0 mmol, 1.20 equiv.) was added drop wise over 1 hour. Next, 5.50 mL of triispopropyl borate (23.9 mmol, 1.20 equiv.) was added. After stirring the mixture at -78 ^{o}C for 30 minutes, the mixture was warmed to -20 ^{o}C and 20 mL of 2 M HCl was added to the mixture. The mixture was allowed to warm to room temperature and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (40 mL x 3 times). The organic extracts were combined and washed with saturated NaCl (40 mL x 2 times). The combined organic extracts were dried with magnesium sulfate,

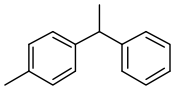
filtered, washed with ethyl acetate, and concentrated under reduced pressure. To the residue, was added 5.00 mL of ethyl acetate. The mixture was heated to 50 °C and stirred for 10 minutes. The mixture was cooled to room temperature and 20.0 mL of hexanes was added. The mixture was stirred at room temperature for 30 minutes. The solid was filtered, washed with hexanes, and dried *in vacuo* to yield 2-methyphenylboroxin (722 mg, 31% yield). The filtrate was concentrated under reduced pressure. To the residue, was added 5.00 mL of hexanes and the mixture was stirred at room temperature for 30 minutes. The solid was filtered, washed with hexanes, and dried *in vacuo* to yield 2-methyphenylboroxin (738 mg, 31% yield) as white crystals.
To an oven dried 50 mL round bottom flask equipped with a stir bar, was added 730 mg of the 2-methyphenylboroxin (2.06 mmol, 1.00 equiv.), 768 mg of ethylene glycol (12.4 mmol, 6.00 equiv.), and 15.0 mL of toluene. The mixture was refluxed for 1 hour, then azeotoropic-refluxed with a Dean-Stark apparatus for 1 hour under a N_2 atmosphere. The reaction mixture was concentrated under reduced pressure. Purification was accomplished by flash chromatography eluting with hexanes/ethyl acetate (10:1). The product containing fractions were combined and concentrated under reduced pressure to yield the desired compound **2g** (843 mg, 84% yield) as white crystals:
^{1}H-NMR spectrum was compared to a previously reported spectrum.[9]



2h

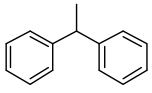
Preparation of methyl 4-(1,3,2-dioxaborolan-2-yl)benzoate (2h). To an oven dried 50 mL round bottom flask equipped with a stir bar, was added 500 mg of 4-(methoxycarbonyl)phenylboronic acid (2.78 mmol, 1.00 equiv.), 181 mg of ethylene glycol (2.92 mmol, 1.05 equiv.) and 10.0 mL of dichloromethane. The mixture was stirred for 20 minutes at room temperature under a N_2 atmosphere and 334 mg of magnesium sulfate (2.78 mmol, 1.00 equiv.) was added. The mixture was stirred for 4 hours at room temperature under a N_2 atmosphere. The reaction mixture was filtered, washed with dichloromethane, and concentrated under reduced pressure to give the desired compound **2h** (564 mg, 99% yield) as a white solid:
mp: 115 - 117 °C; 300 MHz ^{1}H NMR ($CDCl_3$): δ 3.92 (s, 3H), 4.40 (s, 4H), 7.88 (d, J = 7.9 Hz, 2H), 8.04 (d, J = 7.7 Hz, 2H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ 52.4, 66.4, 128.9, 132.7, 135.0, 167.2.; IR (KBr) 2986, 2915, 1720, 1404, 1371, 1338, 1282, 1218, 1115, 1095, 705, 634 cm^{-1}; HRMS (EI) calcd. $C_{10}H_{11}BO_4$ $(M)^+$ 206.0750, obsd. 206.0744.

Reductive Coupling Procedure:

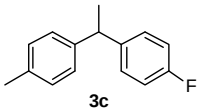

3a

Preparation of 1-methyl-4-(1-phenylethyl)benzene (3a). To an oven dried 100 mL Schlenck flask equipped with a stir bar, was added 4.3 mg of $[Pd(SiPr)Cl_2]_2$ (3.79 μmol, 0.00757 equiv.), 300 μL of a 100 mM solution of (–)-sparteine (30.0 μmol, 0.06 equiv.) in 2-propanol, and 7.40 mL of 2-propanol. A dried water condenser and a three-way joint fitted with a balloon of O_2 were 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 an O_2 atmosphere. To the mixture, was added 1.00 mL of a 500 mM solution of 4-methylstyrene (**1a**) (500 μmol, 1.00 equiv.) in 2-propanol, 1.00 mL of a

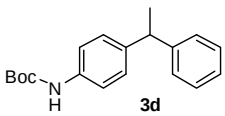
1.50 M solution of 2-phenyl-[1,3,2]-dioxaborolane (**2a**) (1.50 mmol, 3.00 equiv.) in 2-propanol, and 300 μL of a 100 mM solution of potassium *tert*-butoxide (30.0 μmol, 0.06 equiv.) in 2-propanol. The mixture was then heated to 55 °C and was stirred **vigorously** for 24 hours. The reaction mixture was cooled to room temperature. The mixture was concentrated under reduced pressure. To the residue, was added 10 mL of DI-water and was extracted two times with 10 mL of hexanes. To the combined organic extracts, was added 1.00 g of magnesium sulfate, and 1.00 g of silica. The mixture was stirred at room temperature for 10 minutes, filtered, washed with hexanes, and concentrated under reduced pressure to yield a colorless oil. Purification was accomplished by flash chromatography eluting with hexanes. The product containing fractions were combined and concentrated under reduced pressure to give the desired compound **3a** (79.0 mg and 159.6 (1.00 mmol scale), 81% yield) as colorless oil:
The ^{1}H-NMR spectrum, see below, was compared to a previously reported spectrum.[10]


3b

Preparation of ethane-1,1-diyldibenzene (3b). The same procedure used to synthesize **3a** was used except 1.00 mL of a 500 mM solution of styrene (**1b**) (500 μmol, 1.00 equiv.) in 2-propanol was added via syringe.
3b, colorless oil, yield: 91% (85.3 mg and 81.7 mg)
The ^{1}H-NMR spectrum, see below, was compared to a previously reported spectrum.[11]


3c

Preparation of 1-fluoro-4-(1-*p*-tolylethyl)benzene (3c). The same procedure used to synthesize **3a** was used except 1.00 mL of a 1.50 M solution of 2-(4-fluorophenyl)-[1,3,2]-dioxaborolane (**2b**) (1.50 mmol, 3.00 equiv.) in 2-propanol was added via syringe.
3c, colorless oil, yield: 91% (85.3 mg and 81.7 mg); R_f = 0.26 w/ Hexanes (silica), PMA stain.
300 MHz ^{1}H NMR ($CDCl_3$): δ 1.63 (d, *J* = 7.2 Hz, 3H), 2.32 (s, 3H), 4.11 (q, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 8.6 Hz, 2H), 7.10 (s, 4H), 7.17 (dd, *J* = 5.4, 8.9 Hz, 2H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ21.3, 22.4, 43.9, 115.3 (d, *J* = 21.2 Hz), 127.7, 129.1, 129.2, 129.4, 135.9, 143.0 (d, *J* = 72.5 Hz), 161.5 (d, *J* = 243.7 Hz).; IR (neat) 2969, 2875, 1603, 1509, 1454, 1225, 88, 816 cm^{-1}; HRMS (EI) calcd. $C_{15}H_{15}F$ $(M)^+$ 214.1158, obsd. 214.1159.

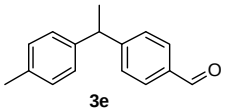

3d

Preparation of *tert*-butyl 4-(1-phenylethyl)phenylcarbamate (3d). The same procedure used to synthesize **3a** was used except 1.00 mL of a 500 mM solution of *tert*-butyl-4-vinylphenylcarbamate (**1c**) (500 μmol, 1.00 equiv.) in 2-propanol was added via syringe. The workup was the same used to synthesize **3a** except the mixture was extracted with hexanes/ethyl acetate (4:1) and the product was purified via flash chromatography by eluting with hexanes/ethyl acetate (20:1).

3d, white solid, yield: 90% (125.6 mg and 139.1 mg); R_f = 0.44 w/ Hexanes/ethyl acetate (10:1) (silica).
mp: 92 - 94 °C; 300 MHz ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 9H), 1.21 (d, *J* = 7.4 Hz, 3H), 4.11 (q, *J* = 7.1 Hz, 1H), 6.43 (br s, 1H), 7.13-7.30(m, 9H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ22.2, 28.6, 44.3, 80.6, 118.9, 126.2, 127.8, 128.3, 128.6, 136.5, 141.3, 146.7, 153.1.; IR (KBr) 3332, 2973, 1703, 1595, 1524, 1236, 1163, 1056, 838, 700 cm^{-1}; HRMS (ESI/APCI) calcd. $C_{19}H_{27}N_2O_2$ $(M+NH_4)^+$ 315.2073, obsd. 315.2071.
The enantiomeric excess was determined to be 4 % by HPLC analysis (Chiralcel OJ-H column, hexanes/*i*-PrOH = 95/5, flow rate = 1.0 mL/min): t_{minor} = 16.1 min, t_{major} = 22.2 min.

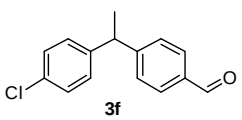
Evaluation of the Pd[(–)-sparteine]Cl_2 catalyst for the synthesis of **3d**

The same procedure (0.25 mmol scale) used to synthesize **3d** was used except 1.50 mg of a Pd[(–)-sparteine]Cl_2 (5.83 mmol, 0.015 equiv.) was added.
3d, white solid, yield: 91% (67.5 mg)
The enantiomeric excess was determined to be 3 % by HPLC analysis (Chiralcel OJ-H column, hexanes/*i*-PrOH = 95/5, flow rate = 1.0 mL/min): t_{minor} = 16.1 min, t_{major} = 22.2 min.



3e

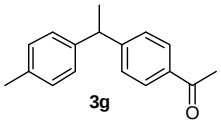
Preparation of 4-(1-*p*-tolylethyl)benzaldehyde (3e). The same procedure used to synthesize **3a** was used except 8.40 mL of 2-propanol and 330 mg of 2-[4-(1,3-dioxolan-2-yl)phenyl][1,3,2] dioxaborolane (**2c**) (1.50 mmol, 3.00 equiv.) was added. The workup was the same used to synthesize **3a** except the mixture was extracted with hexanes/ethyl acetate (4:1). To the concentrated residue after extraction, was added 9.00 mL of acetone, 1.00 mL of water and 20.0 mg of *p*-toluenesulfonic acid. The mixture was heated to reflux for 1 hour under a nitrogen atmosphere. Purification was accomplished by flash chromatography eluting with hexanes/ethyl acetate (20:1). The product containing fractions were combined and concentrated under reduced pressure to yield the desired compound **3e** (92.3 mg and 72.5 mg, 77% yield) as colorless oil:
R_f = 0.24 w/ Hexanes/ethyl acetate (10:1) (silica).
300 MHz ^{1}H NMR ($CDCl_3$): δ 1.66 (d, *J* = 7.2 Hz, 3H), 2.32 (s, 3H), 4.20 (q, *J* = 7.2 Hz, 1H), 7.11 (s, 4H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.80 (d, *J* = 8.2 Hz, 2H), 9.97 (s, 1H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ 21.3, 21.8, 44.9, 127.7, 128.5, 129.5, 130.2, 134.8, 136.3, 142.3, 154.1, 192.2.; IR (neat) 2969, 2734, 1701, 1605, 1513, 1307, 1213, 1169, 843, 818 cm^{-1}; HRMS (ESI/APCI) calcd. $C_{16}H_{17}O$ $(M+H)^+$ 225.1279, obsd. 225.1283.



3f

Preparation of 4-(1-(4-chlorophenyl)ethyl)benzaldehyde (3f). The same procedure used to synthesize **3e** was used except 1.00 mL of a 500 mM solution of 4-chlorostyrene (**1d**) (500 μmol, 1.00 equiv.) in 2-propanol was added via syringe.
3f, white solid, yield: 68% (79.8 mg and 73.0 mg); R_f = 0.27 w/ Hexanes/ethyl acetate (10:1) (silica).

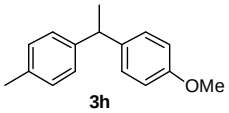
mp: 30 - 32 °C; 300 MHz ^{1}H NMR ($CDCl_3$): δ 1.65 (d, *J* = 7.2 Hz, 3H), 4.20 (q, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ 21.7, 44.6, 128.5, 128.9, 129.2, 130.3, 132.5, 135.0, 143.8, 153.2, 192.1.; IR (KBr) 2971, 2826, 2736, 1701, 1606, 1491, 1213, 1169, 1093, 1046, 1013, 752 cm^{-1}; HRMS (ESI/APCI) calcd. $C_{15}H_{14}ClO$ $(M+H)^+$ 245.0733, obsd. 245.0736.



Preparation of 1-(4-(1-*p*-tolylethyl)phenyl)ethanone (3g). The same procedure used to synthesize **3e** was used except 351 mg of 2-[4-(2-methyl-1,3-dioxolan-2-yl)phenyl]-[1,3,2]-dioxaborolane (**2d**) (1.50 mmol, 3.00 equiv.) was added.

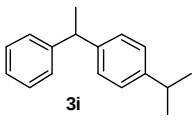
3g, colorless oil, yield: 71% (84.9 mg and 84.8 mg); R_f = 0.23 w/ Hexanes/ethyl acetate (10:1) (silica).

300 MHz ^{1}H NMR ($CDCl_3$): δ 1.65 (d, *J* = 7.2 Hz, 3H), 2.32 (s, 3H), 2.57 (s, 3H), 4.18 (q, *J* = 7.2 Hz, 1H), 7.11 (s, 4H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 2H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ 21.3, 21.8, 26.8, 44.7, 127.7, 128.0, 128.8, 129.5, 135.4, 136.1, 142.6, 152.5, 198.0.; IR (neat) 2969, 2875, 1682, 1605, 1513, 1453, 1358, 1268, 957, 821, 598 cm^{-1}; HRMS (ESI/APCI) calcd. $C_{17}H_{19}O$ $(M+H)^+$ 239.1436, obsd. 239.1439.



Preparation of 1-methoxy-4-(1-*p*-tolylethyl)benzene (3h).
The same procedure used to synthesize **3a** was used except 8.50 mg of $[Pd(SiPr)Cl_2]_2$ (7.48 μmol, 0.015 equiv.) and 1.00 mL of a 1.50 M solution of 2-(4-methoxyphenyl)-[1,3,2]-dioxaborolane (**2e**) (1.50 mmol, 3.00 equiv.) in 2-propanol were added and reaction was heated to 65 °C for 24 hours. The workup used to synthesize **3a** was used except the product was purified via flash chromatography by eluting with hexanes/ethyl acetate (30:1).

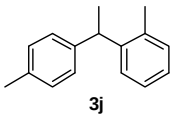
3h, colorless oil, yield: 58% (71.7 mg and 58.9 mg); R_f = 0.23 w/ Hexanes/ethyl acetate (10:1) (silica). The ^{1}H-NMR spectrum, see below, was compared to a previously reported spectrum.[12]



Preparation of 1-isopropyl-4-(1-phenylethyl)benzene (3i). The same procedure used to synthesize **3h** was used except 1.00 mL of a 500 mM solution of styrene (**1b**) (500 μmol, 1.00 equiv.) in 2-propanol and 1.00 mL of a 1.50 M solution of 2-(4-isopropylphenyl)-[1,3,2]-dioxaborolane (**2f**) (1.50 mmol, 3.00 equiv.) in 2-propanol was added via syringe. The same workup used to synthesize **3h** was used except the product was purified via flash chromatography by eluting with hexanes.

3i, colorless oil, yield: 71% (74.6 mg and 72.2 mg); R_f = 0.23 w/ Hexanes (silica) PMA stain.

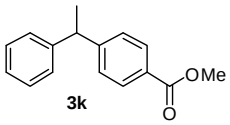
300 MHz ^{1}H NMR ($CDCl_3$): δ 1.25 (d, *J* = 6.9 Hz, 6H), 1.65 (d, *J* = 7.2 Hz, 3H), 2.89 (sept, *J* = 6.9 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 1H), 7.16 (s, 4H), 7.19-7.33 (m, 5H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ 22.3, 24.3, 33.9, 44.7, 126.3, 126.7, 127.8, 127.9, 128.6, 144.0, 146.7, 146.9.; IR (neat) 2963, 2872, 1600, 1511, 1494, 1454, 1417, 1059, 1020, 834, 699 cm^{-1}; HRMS (ESI/APCI) calcd. $C_{17}H_{19}$ $(M-H)^+$ 223.1487, obsd. 223.1486.



Preparation of 1-methyl-2-(1-*p*-tolylethyl)benzene (3j). The same procedure used to synthesize **3h** was used except 1.00 mL of a 1.50 M solution of 2-(2-methyphenyl)-[1,3,2]-dioxaborolane (**2g**) (1.50 mmol, 3.00 equiv.) in 2-propanol was added via syringe. The same workup used to synthesize **3a** was used except the product was purified via flash chromatography by eluting with hexanes.

3j, colorless oil, yield: 68% (68.9 mg and 74.4 mg); R_f = 0.23 w/ Hexanes (silica) PMA stain.

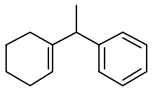
The ^{1}H-NMR spectrum, see below, was compared to a previously reported spectrum.[6]



Preparation of methyl 4-(1-phenylethyl)benzoate (3k). The same procedure used to synthesize **3a** was used except 8.20 mL of 2-propanol, 1.00 mL of a 500 mM solution of styrene (**1b**) (500 μmol, 1.00 equiv.) in 2-propanol, 17.6 mg of (–)-sparteine (75.1 μmol, 0.150 equiv.) in 2-propanol (500 μL), and 309 mg of methyl 4-(1,3,2-dioxaborolan-2-yl)benzoate (**2h**) (1.50 mmol, 3.00 equiv.) were added. The same workup used to synthesize **3a** was used except hexanes/ethyl acetate (4:1) was used in the extraction and the product was purified via flash chromatography by eluting with hexanes/ethyl acetate (20:1).

3k, colorless oil, yield: 63% (73.4 mg and 78.0 mg); R_f = 0.48 w/ Hexanes/ethyl acetate (10:1) (silica).

300 MHz ^{1}H NMR ($CDCl_3$): δ 1.66 (d, *J* = 7.2 Hz, 3H), 3.89 (s, 3H), 4.21 (q, *J* = 7.2 Hz, 1H), 7.17-7.13 (m, 3H), 7.26-7.32 (m, 4H), 7.96 (d, *J* = 8.2 Hz, 2H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ21.8, 45.1, 52.2, 126.6, 127.8, 127.9, 128.7, 130.0, 145.7, 152.9, 167.3.; IR (neat) 3028, 2969, 1722, 1609, 1281, 1184, 1110, 1019, 858, 703 cm^{-1}; HRMS (ESI/APCI) calcd. $C_{16}H_{17}O$ $(M+H)^+$ 241.1229, obsd. 241.1232.



Preparation of (1-cyclohexenylethyl)benzene (3l). The same procedure used to synthesize **3a** was used except 1.00 mL of a 500 mM solution of 1-vinylcyclohex-1-ene (**1e**) (500 μmol, 1.00 equiv.) in 2-propanol was added via syringe.

3l, colorless oil, yield: 41% (40.7 mg and 36.1 mg); R_f = 0.49 w/ Hexanes (silica).

300 MHz ^{1}H NMR ($CDCl_3$): δ 1.34 (d, *J* = 7.0 Hz, 3H), 1.52-1.57 (m, 4H), 1.77-1.80 (m, 2H), 2.04-2.10 (m, 2H), 3.30 (q, *J* = 6.9 Hz, 1H), 5.58-5.62 (m, 1H), 7.15-7.22 (m, 3H), 7.26-7.31 (m, 2H).; 75 MHz ^{13}C NMR ($CDCl_3$) δ20.0, 22.9, 13.3, 25.6, 27.4, 46.7, 120.9, 126.0, 127.7, 128.3, 141.4, 146.2.; IR (neat) 2928, 2837, 1600, 1492, 1451, 1025, 917, 762, 699 cm^{-1}; HRMS (EI) calcd. $C_{14}H_{18}$ $(M)^+$ 186.1409, obsd. 186.1410.

Time Course Experiment Procedure:

To an oven dried 100 mL Schlenck flask equipped with a stir bar, was added 8.50 mg of $[Pd(S\textit{i}Pr)Cl_2]_2$ (7.48 μmol, 0.0075 equiv.), 600 μL of a 100 mM solution of (–)-sparteine (60.0 μmol, 0.06 equiv.) in *sec*-BuOH and 6.80 mL of *sec*-BuOH. A dried water condenser and a three-way joint fitted with a balloon of O_2 were 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 an O_2 atmosphere. To the stirred mixture, was added 2.00 mL of a 500 mM solution of 4-methylstyrene (**1a**) (1.00 mmol, 1.00 equiv.), 1.00 mL of a 1.50 M solution of 2-phenyl-[1,3,2]-dioxaborolane (**2b**) (1.50 mmol, 3.00 equiv.) in *sec*-BuOH with 40.0 μL of bicyclohexyl as an internal standard, and 600 μL of a 100 mM solution of potassium *tert*-butoxide (60.0 μmol, 0.06 equiv.) in *sec*-BuOH. The mixture was heated to 55 °C and was stirred **vigorously** for 24 hours. A small aliquot of the 500 mM solution of **1a** with bicyclohexyl as the internal standard was analyzed by GC and used to calculate the conversion of the substrate. After each time point, a 200 μL aliquot of the reaction mixture was removed by syringe and filtered through a small plug of silica eluting with ether. The mixture was analyzed by GC. The conversion of the substrate was calculated and the GC yields for the products were calculated using a correction factor (^{1}H-NMR was used to measure the response factor to account for varying detector response). Note: All the GC yields are based upon 1.00 equivalent of 4-methylstyrene (**1a**).

Time [h]	**1a** [%]	**2a** [%]	**3a** [%]	PhOH [%]	Ph-Ph [%]	butanone [%]
0.5	96.7	185.4	1.4	8.7	7.6	0.2
1	91.7	156.3	4.8	18.5	7.6	5.9
1.5	87.2	144.3	9.6	28.4	9.1	10.6
2	80.6	135.3	14.7	37.1	9.8	14.4
2.5	77.3	126.9	18.2	44.5	10.3	22.7
3	72.8	136.2	22.2	49.6	10.6	26.6
3.5	68.0	105	26.9	56.4	11.2	28.1
4	62.2	132.3	32.1	63.9	11.6	30.8
4.5	58.2	118.8	35.5	68.9	11.8	32.8
5	52.4	118.2	41.5	75.7	12.2	45.5
5.5	50.3	85.8	42.8	81.7	12.2	45.9
6	46.7	97.5	46.3	86.0	12.4	47.1
7	39.4	69.9	52.7	95.8	12.7	61.4
8	32.2	66.6	58.8	104.1	12.9	71.8
9	25.6	55.2	63.3	112.3	13.3	78.6
10	19.2	42.3	70.4	121.0	13.6	80.2
11	13.6	25.5	73.2	125.3	13.7	95.7
12	8.7	14.4	76.0	132.4	13.8	107.8
13	4.9	4.5	77.8	137.8	13.9	113.7
14	2.5	0	77.7	139.2	14.0	111.6
15	1.4	0	77.7	137.9	13.9	123.1
16	0.6	0	77.4	136.3	14.0	129.8
24	0	0	78.0	128.7	13.9	146.4

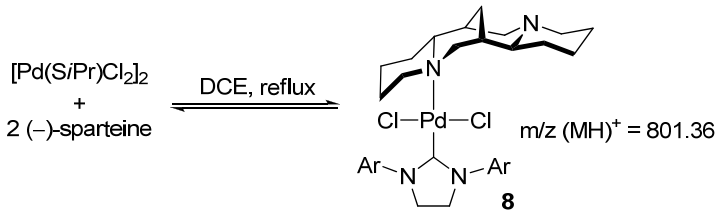
Even after purification, there was butan-2-one present in *sec*-BuOH. In order to calculate the GC yield of butan-2-one, the following equation was used:

Equation

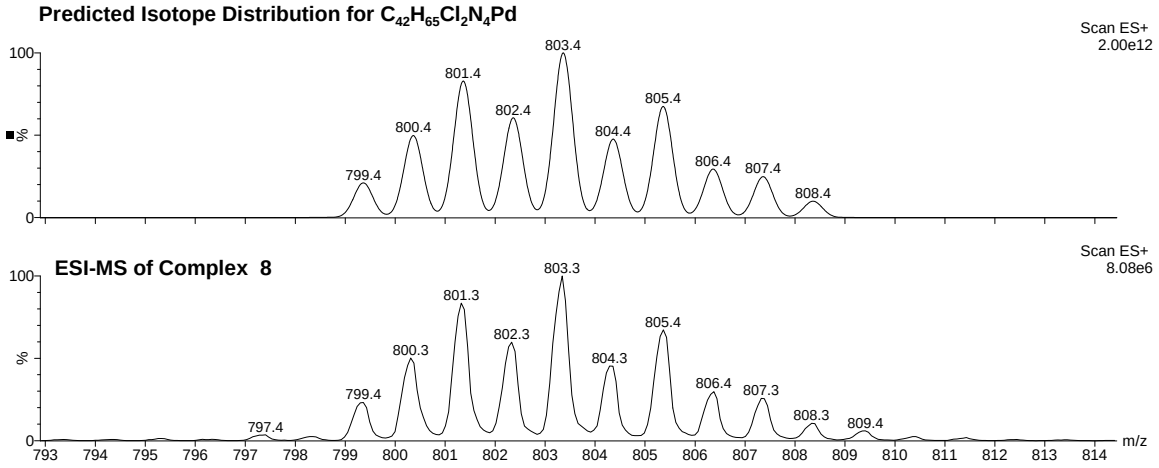
butan-2-one peak area = $A_t - (A_0 * B_t / B_0)$

A_0: peak area of butan-2-one in *sec*-BuOH before reaction
A_t: peak area of butan-2-one for each time point
B_0: peak area of *sec*-BuOH before reaction
B_t: peak area of *sec*-BuOH for each time point

Synthesis of Complex 8 and Characterization by ESI-MS



To an oven dried 5 mL round bottom flask equipped with a stir bar under a N_2 atmosphere, was added 9.60 mg of (–)-sparteine (41.0 μmol, 2.05 equiv.), 1.00 mL of 1,2-dichloroethane, and 22.7 mg of $[Pd(SiPr)Cl_2]_2$ (20.0 μmol, 1.00 equiv.). An oven dried water condenser was installed and the yellow solution was heated to reflux for 2 hours under a N_2 atmosphere. The mixture was cooled to room temperature, a small aliquot was removed, and was diluted with acetone. The solution was infused into a Micromass Quattro II quadrupole ESI-MS instrument with a syringe pump.



Optimization for the Reductive Coupling Product Procedures (Table 1):

Entry 1: To an oven dried 10 mL Schlenck flask equipped with a stir bar, was added 1.00 mg of Pd[(–)-sparteine]Cl_2 (2.43 μmol, 0.024 equiv.), 200 μL of a 200 mM solution of (–)-sparteine (40.0 μmol, 0.400 equiv.) in 2-propanol, and 600 μL of 2-propanol. A dried water condenser and a three-way joint fitted with a balloon of O_2 were installed on the flask. The flask was evacuated via water aspiration and refilled with O_2 three times. The mixture was stirred **vigorously** for ca. 20 minutes at room temperature under an O_2 atmosphere. To the stirred mixture, was added 200 μL of a 500 mM solution of 4-methylstyrene (**1a**) (100 μmol, 1.00 equiv.) in 2-propanol with 2.0 μL of 5-nonanone as an internal standard and 15.9 mg of phenylboronic acid (1.30 mmol, 1.30 equiv.). The mixture was then heated to 50 °C and was stirred **vigorously** for 24 hours. After 24 hr, a 200 μL aliquot of the reaction mixture was removed by syringe and filtered through a small plug of silica eluting with ethyl

acetate. The mixture was analyzed by GC. The conversion of the substrate was calculated and the GC yields for the products were calculated using a correction factor (^{1}H-NMR was used to measure the response factor to account for varying detector response).

Entry 2: To an oven dried 10 mL Schlenck flask equipped with a stir bar, was added 2.80 mg of $[Pd(I\textit{i}Pr)Cl_2]_2$ (24.7 μmol, 0.025 equiv.) and 600 μL of 2-propanol. A dried water condenser and a three-way joint fitted with a balloon of O_2 were installed on the flask. The flask was evacuated via water aspiration and refilled with O_2 three times. The mixture was stirred **vigorously** for ca. 20 minutes at room temperature under an O_2 atmosphere. To the stirred mixture, was added 100 μL of 200 mM solution of (–)-sparteine (20.0 μmol, 0.200 equiv.) in 2-propanol, 100 μL of a 1.00 M solution of 4-methylstyrene (**1a**) (100 μmol, 1.00 equiv.) in 2-propanol with 2.00 μL of undecane as a internal standard, and 200 μL of 650 mM solution of phenylboronic acid (1.30 mmol, 1.30 equiv.) in 2-propanol. The mixture was then heated to 50 °C in an oil bath and was stirred **vigorously** for 24 hours. After 24 hr, a 200 μL aliquot of the reaction mixture was removed by syringe and filtered through a small plug of silica eluting with ethyl acetate. The mixture was analyzed by GC. The conversion of the substrate was calculated and the GC yields for the products were calculated using a correction factor (^{1}H-NMR was used to measure the response factor to account for varying detector response).

Entry 3: The same procedure as described above for entry 2 was used except 550 μL of 2-propanol and 50.0 μL of 100 mM solution of *tert*-BuOK (5.00 μmol, 0.05 equiv.) in 2-propanol were added.

Entry 4: To an oven dried 10 mL Schlenck flask equipped with a stir bar, was added 2.80 mg of $[Pd(I\textit{i}Pr)Cl_2]_2$ (2.47 μmol, 0.025 equiv.) and 700 μL of 2-propanol. A dried water condenser and a three-way joint fitted with a balloon of O_2 were installed on the flask. The flask was evacuated via water aspiration and refilled with O_2 three times. The mixture was stirred **vigorously** for ca. 20 minutes at room temperature under an O_2 atmosphere. To the stirred mixture, was added 50.0 μL of a 100 mM solution of (–)-sparteine (5.00 μmol, 0.05 equiv.) in 2-propanol, 11.8 mg of 4-methylstyrene (**1a**) (100 μmol, 1.00 equiv.) and 26.5 mg of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (130 μmol, 1.30 equiv.) in 2-propanol (200 μL) with 2.00 μL of undecane as a internal standard, and 50.0 μL of a 100 mM solution of *tert*-BuOK (5.00 μmol, 0.05 equiv.) in 2-propanol. The mixture was then heated to 50 °C and was stirred **vigorously** for 24 hours. A 200 μL aliquot of the reaction mixture was removed by syringe and filtered through a small plug of silica eluting with ethyl acetate. The mixture was analyzed by GC. The conversion of the substrate was calculated and the GC yields for the products were calculated using a correction factor (^{1}H-NMR was used to measure the response factor to account for varying detector response).

Entry 5: The same procedure as described above for entry 4 was used except 675 μL of 2-propanol, 75.0 μL of 100 mM solution of (–)-sparteine (7.50 μmol, 0.075 equiv.) in 2-propanol, 11.8 mg of 4-methylstyrene (**1a**) (100 μmol, 1.00 equiv.) and 51.0 mg of 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (250 μmol, 2.50 equiv.) in 2-propanol (200 μL) with 2.0 μL of undecane as a internal standard, and 50.0 μL of a 150 mM solution of *tert*-BuOK (7.50 μmol, 0.075 equiv.) in 2-propanol were added.

Entry 6: To an oven dried 10 mL Schlenck flask equipped with a stir bar, was added 2.80 mg of $[Pd(I\textit{i}Pr)Cl_2]_2$ (2.47 μmol, 0.025 equiv.) and 700 μL of 2-propanol. A dried water condenser and a three-way joint fitted with a balloon of O_2 were installed on the flask. The flask was evacuated via water aspiration and refilled with O_2 three times. The mixture was stirred **vigorously** for ca. 20 minutes at room temperature under an O_2 atmosphere. To the stirred mixture, was added 500 μL of a 150 mM solution of (–)-sparteine (7.50 μmol, 0.075 equiv.) in 2-propanol, 11.8 mg of 4-methylstyrene (**1a**) (100 μmol, 1.00 equiv.) and 37.0 mg of 2-phenyl-1,3,2-dioxaborolane (**2a**) (250 μmol, 2.50 equiv.) in 2-propanol (200 μL) with 2.0 μL of undecane as a internal standard, and 50.0 μL of a 150 mM solution of *tert*-BuOK (7.50 μmol, 0.075 equiv.) in 2-propanol. The mixture was then heated to 50 °C and was stirred **vigorously** for 24 hours. A 200 μL aliquot of the reaction mixture was removed by syringe and filtered through a small plug of silica eluting with ethyl acetate. The mixture was analyzed by GC. The conversion of the substrate was calculated and the GC yields for the products were calculated using a correction factor (^{1}H-NMR was used to measure the response factor to account for varying detector response).

Entry 7: The same procedure as described above for entry 6 was used except 2.80 mg of $[Pd(S\textit{i}Pr)Cl_2]_2$ (2.47 μmol, 0.025 equiv.) was added.

Entry 8: The same procedure as described above for entry 7 was used except 11.8 mg of 4-methylstyrene (**1a**) (100 μmol, 1.00 equiv.) and 40.5 mg of 2-phenyl-1,3,2-dioxaborinane (250 μmol, 2.50 equiv.) in 2-propanol (200 μL) with 2.0 μL of undecane as a internal standard was added.

Entry 9: To an oven dried 10 mL Schlenck flask equipped with a stir bar, was added 1.30 mg of $[Pd(S\textit{i}Pr)Cl_2]_2$ (1.14 μmol, 0.00763 equiv.) and 2.34 mL of 2-propanol. A dried water condenser and a three-way joint fitted with a balloon of O_2 were installed on the flask. The flask was evacuated via water aspiration and refilled with O_2 three times and 180 μL of 50.0 mM solution of (–)-sparteine (9.00 μmol, 0.06 equiv.) in 2-propanol was added. The mixture was stirred **vigorously** for ca. 20 minutes at room temperature under an O_2 atmosphere. To the stirred mixture, was added 17.7 mg of 4-methylstyrene (**1a**) (150 μmol, 1.00 equiv.), 300 μL of a 1.50 M solution of 2-phenyl-1,3,2-dioxaborolane (**2a**) (450 μmol, 3.00 equiv.) in 2-propanol with 6.0 μL of undecane as a internal standard and 180 μL of a 50.0 mM solution of *tert*-BuOK (9.00 mmol, 0.06 equiv.) in 2-propanol. The mixture was then heated to 55 °C in an oil bath and was stirred **vigorously** for 24 hours. A 200 μL aliquot of the reaction

mixture was removed by syringe and filtered through a small plug of silica eluting with ethyl acetate. The mixture was analyzed by GC. The conversion of the substrate was calculated and the GC yields for the products were calculated using a correction factor (^{1}H-NMR was used to measure the response factor to account for varying detector response).

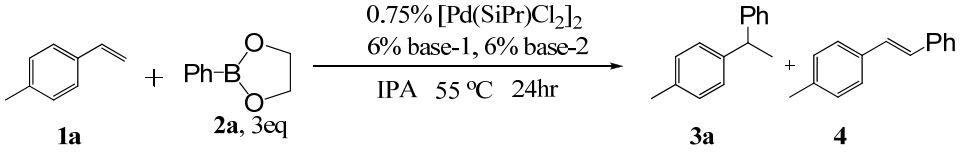
Entry 10: The same procedure as described above for entry 9 was used except 1.30 mg of $[Pd(I\textit{i}Pr)Cl_2]_2$ (1.15 μmol, 0.00766 equiv.) was added.

Entry 11: The same procedure as described above for entry 9 was used except 0.900 mg of Pd[(–)-sparteine]Cl_2 (2.19 μmol, 0.015 equiv.) was added.

Entry 12: The same procedure as described above for entry 9 was used except 2.52 mL of 2-propanol and no (–)-sparteine solution was added.

Entry 13: The same procedure as described above for entry 9 was used except 2.52 mL of 2-propanol and no *tert*-BuOK solution was added.

Table of Other Amines and Bases Evaluated for Reductive Coupling:

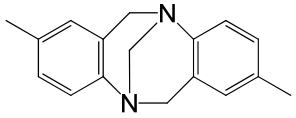


1a **2a**, 3eq **3a** **4**

	Base-1	Base-2	Conv [%][a]	3a [%][b]	3a : 4[c]
(1)	(–)-sparteine	*t*BuOK	>99	91	>30 : 1
(2)	(–)-sparteine	*t*BuOK[d]	86	76	>30 : 1
(3)	(–)-sparteine	*t*BuOK[e]	56	49	>30 : 1
(4)	2, 2'-Bipyridyl	*t*BuOK	---	---	---
(5)	1,10-Phenanthroline	*t*BuOK	---	---	---
(6)	Et_3N	*t*BuOK	5.6	0.5	---
(7)	Et_3N[f]	*t*BuOK	6.0	---	---
(8)	$(iPr)_2NEt$	*t*BuOK	6.2	---	---
(9)	$(iPr)_2NEt$[f]	*t*BuOK	5.8	---	---
(10)	DBU	*t*BuOK	---	---	---
(11)	DBU[f]	*t*BuOK	---	---	---
(12)	2,6-Lutidine	*t*BuOK	2.1	---	---
(13)	2,6-Lutidine[f]	*t*BuOK	6.4	---	---
(14)	Toroger's base	*t*BuOK	5.3	0.5	1 : 4
(15)	(–)-sparteine	Cs_2CO_3	>99	85	>30 : 1
(16)	(–)-sparteine	K_2CO_3	>99	85	>30 : 1
(17)	(–)-sparteine	$KHCO_3$	87	73	17 : 1
(18)	(–)-sparteine	Na_2CO_3	87	75	24 : 1
(19)	(–)-sparteine	CsF	82	74	>30 : 1

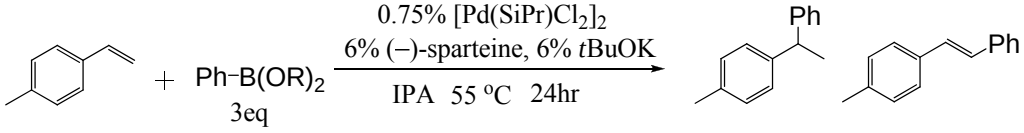
[a] Percent conversion was measured by GC using an internal standard.
[b] Yield was measured by GC using an internal standard.
[c] Ratio of GC yeilds.
[d] 15% of *t*BuOK was used.
[e] 25% of *t*BuOKwas used.
[f] 12% of base was used.

Toroger's base



The same procedure as described above for Table 1 entry 9 was used except amine and inorganic bases were added.

Table of Other Boronic Esters Evaluated Under Optimized Conditions:



1a **3a** **4**

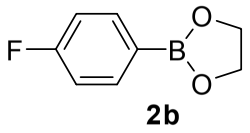
	Boronic ester	Conv [%][a]	3a [%][b]	3a : 4[c]
(1)	EG (**2a**)	>99	91	>30 : 1
(2)	PE	9.3	6.1	>30 : 1
(3)	PD	11	11	>30 : 1
(4)	NE(neopentyl alcohol ester)	7.9	5.4	>30 : 1
(5)	BA	19	11	4.3 : 1

[a] Percent conversion was measured by GC using an internal standard.
[b] Yield was measured by GC using an internal standard.
[c] Ratio of GC yeilds.

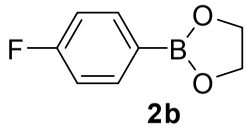
The same procedure as described above for Table 1 entry 9 was used except for the boronic ester or boronic acid (BA).

References:

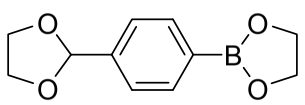
[1] S. K. Mandal, M. S. Sigman, *J. Org. Chem.* **2003**, *68*, 7535-7537.
[2] O. Navarro, H. Kaur, P. Mahjoor, S. P. Nolan, *J. Org. Chem.* **2004**, *69*, 3173-3180.
[3] Y. Ma, C. Song, W. Jiang, G. Xue, J. F. Cannon, X. Wang, M. B. Andrus, *Org. Lett.* **2003**, *5*, 4635-4638.
[4] D. R. Jensen, M. S. Sigman, *Org. Lett.* **2003**, *5*, 63-65.
[5] J. A. Mueller, D. R. Jensen, M. S. Sigman, *J. Am. Chem. Soc.* **2002**, *124*, 8202-8203.
[6] K. M. Gligorich, S. A. Cummings, M. S. Sigman, *J. Am. Chem. Soc.* **2007**, *129*, 14193-14195.
[7] A. Zhang, T. V. RajanBabu, *J. Am. Chem. Soc.* **2006**, *128*, 54-55.
[8] K. T. Wong, Y. Y. Chien, Y. L. Liao, C. C. Lin, M. Y. Chou, M. k. Leung, *J. Org. Chem.* **2002**, *67*, 1041-1044.
[9] P. E. Broutin, F. Colobert, *Eur. J. Org. Chem.* **2005**, 1113-1128.
[10] K. Mertins, I. Iovel, J. Kischel, A. Zapf, M. Beller, *Advanced Synthesis & Catalysis* **2006**, *348*, 691-695.
[11] J.-F. Gal, P.-C. Maria, O. Mo, M. Yanez, D. Kuck, *Chemistry--A European Journal* **2006**, *12*, 7676-7683.
[12] M. Rueping, B. J. Nachtsheim, T. Scheidt, *Org. Lett.* **2006**, *8*, 3717-3719.



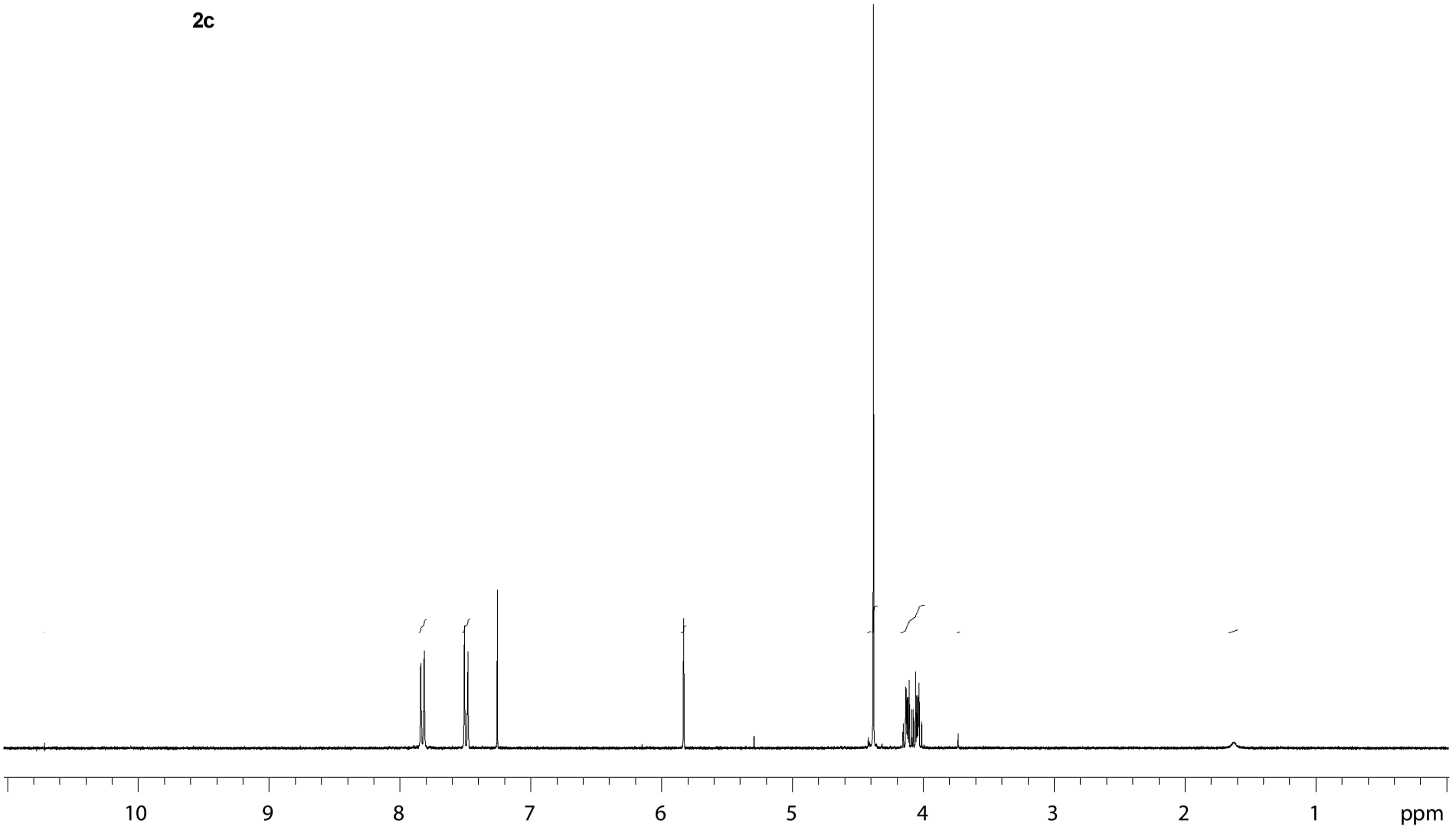
2b

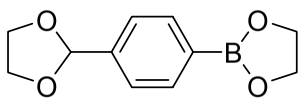


2b

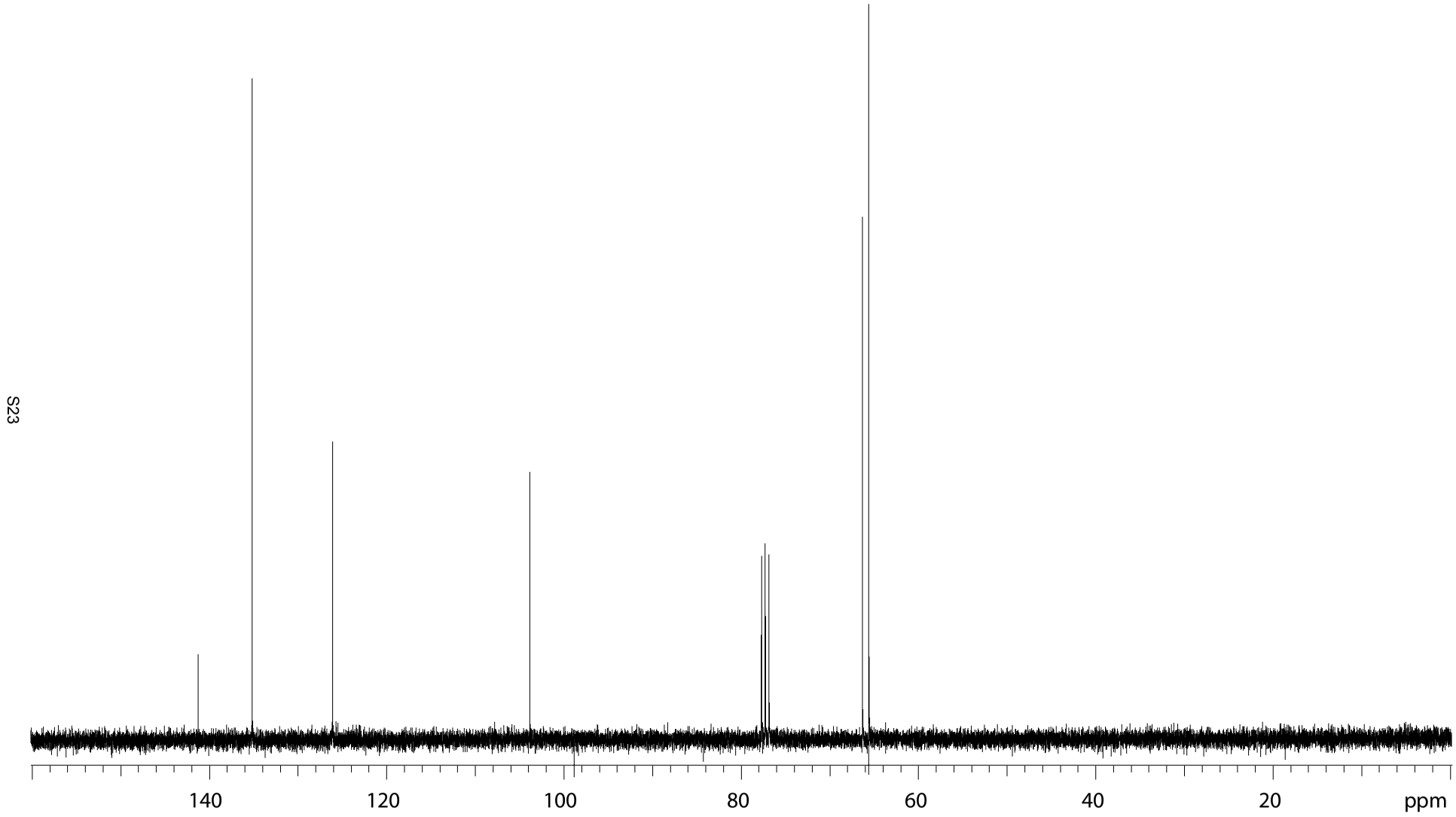


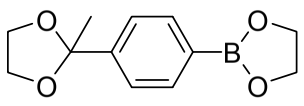
2c



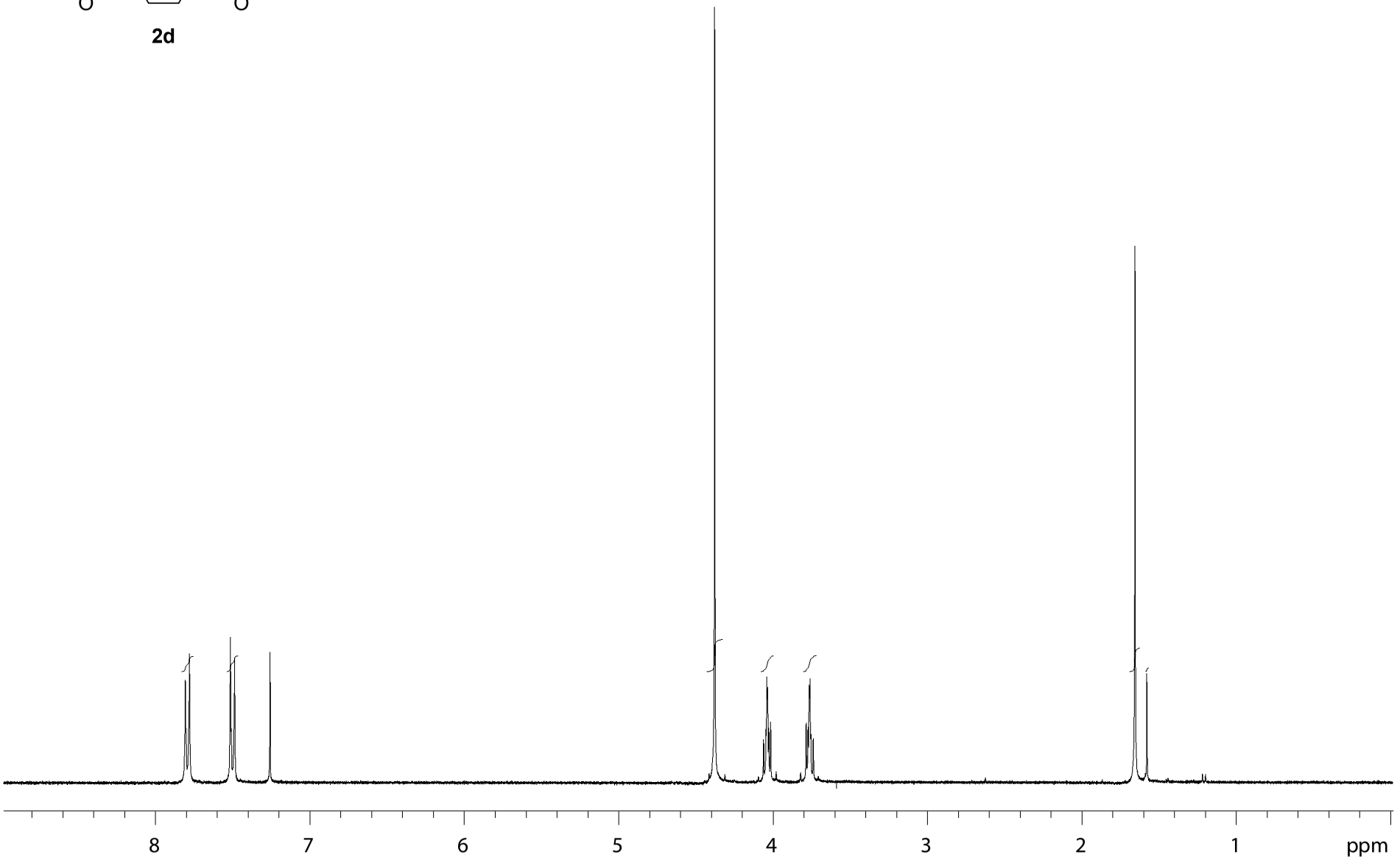


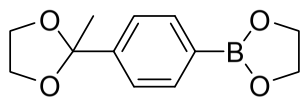
2c



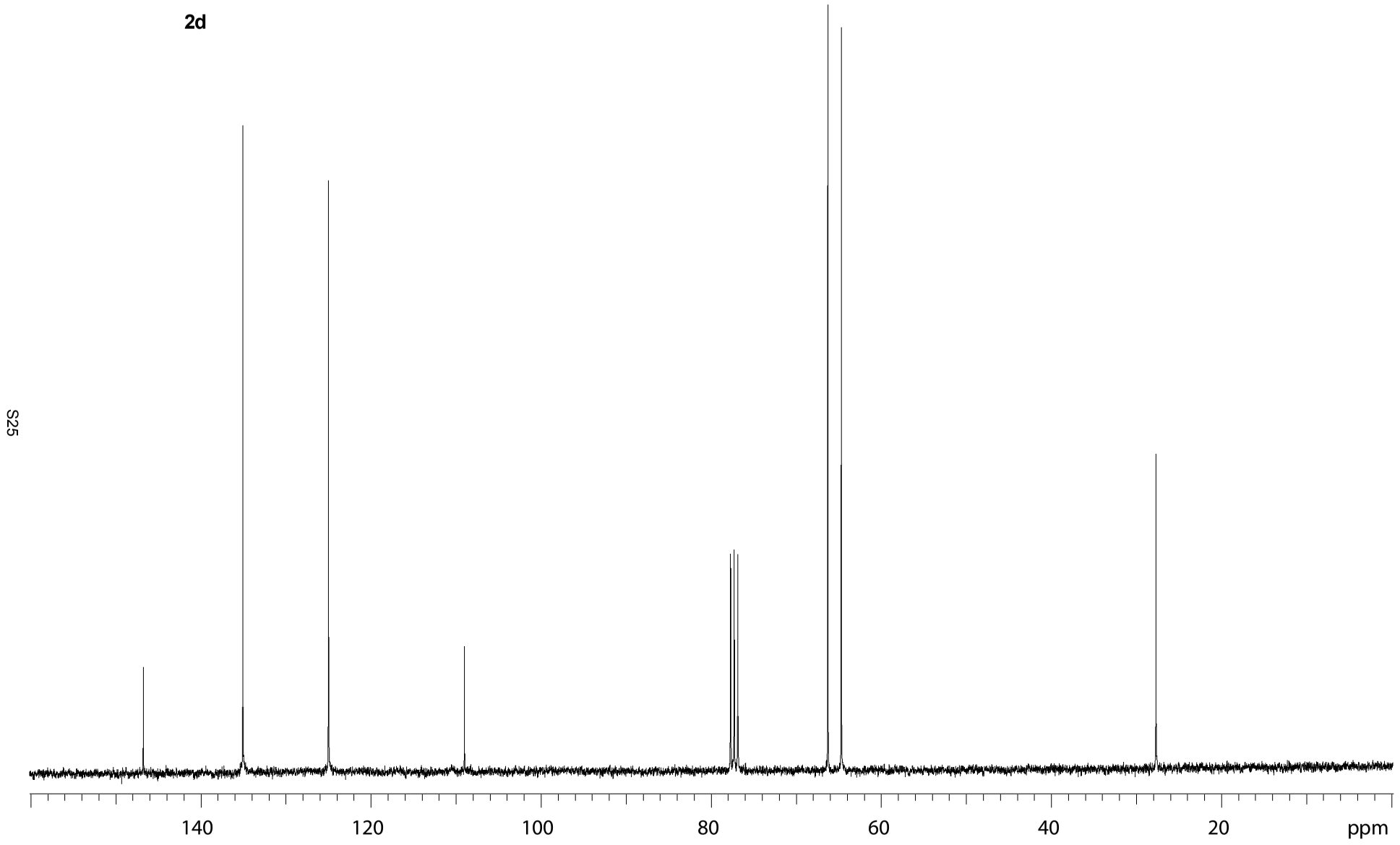


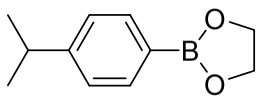
2d



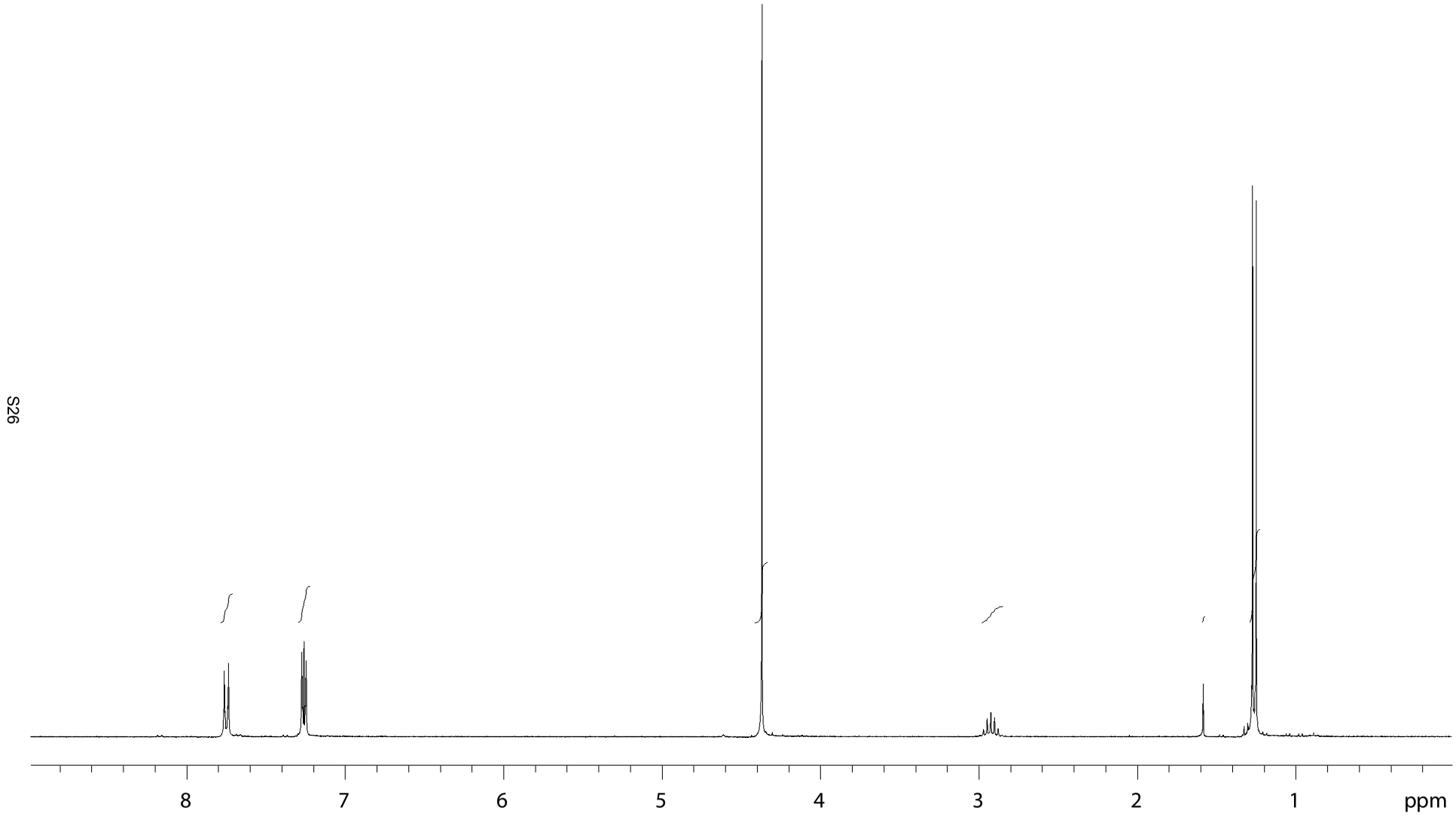


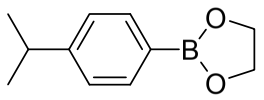
2d



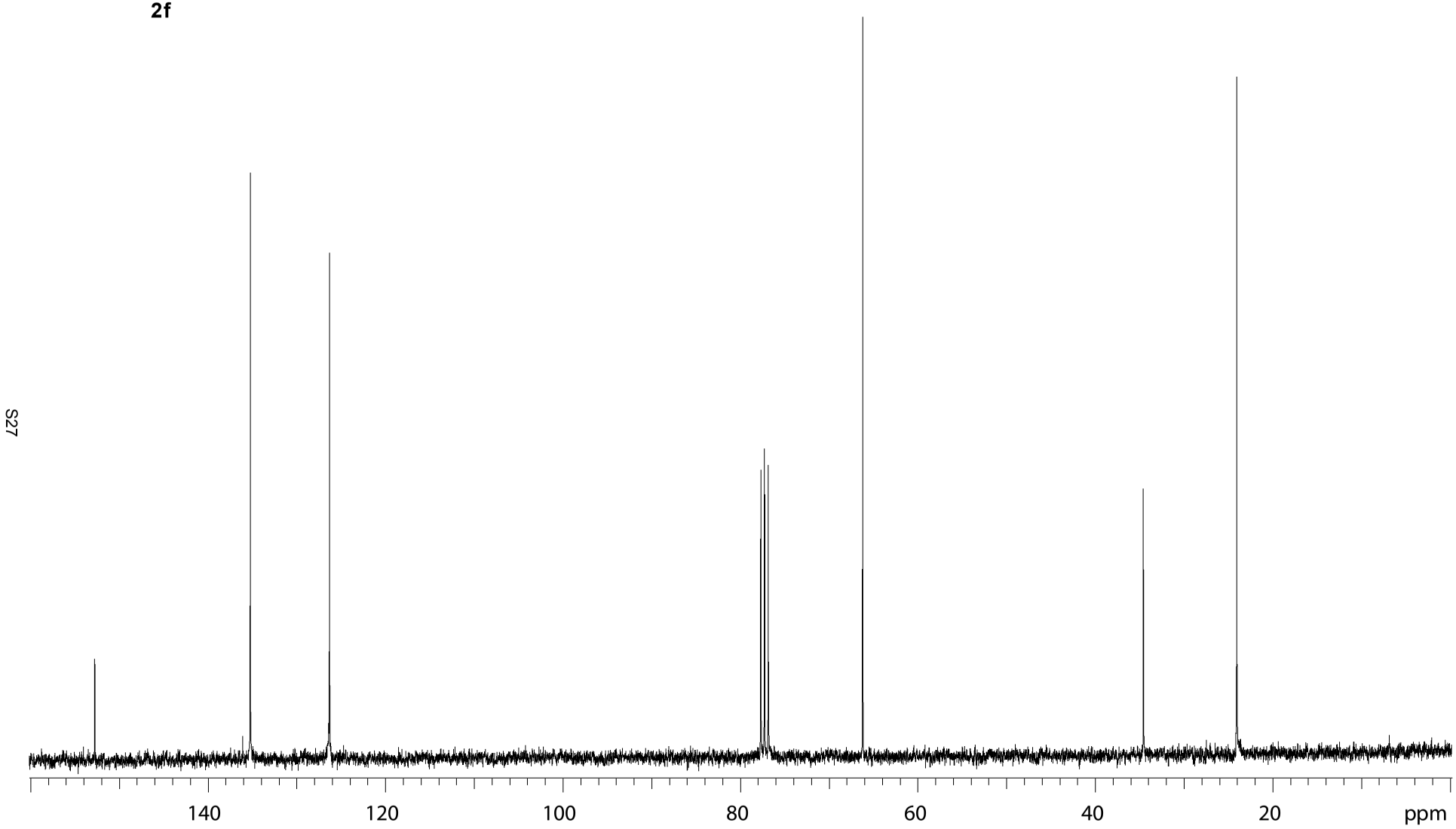


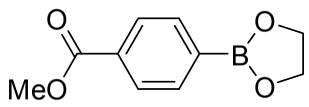
2f



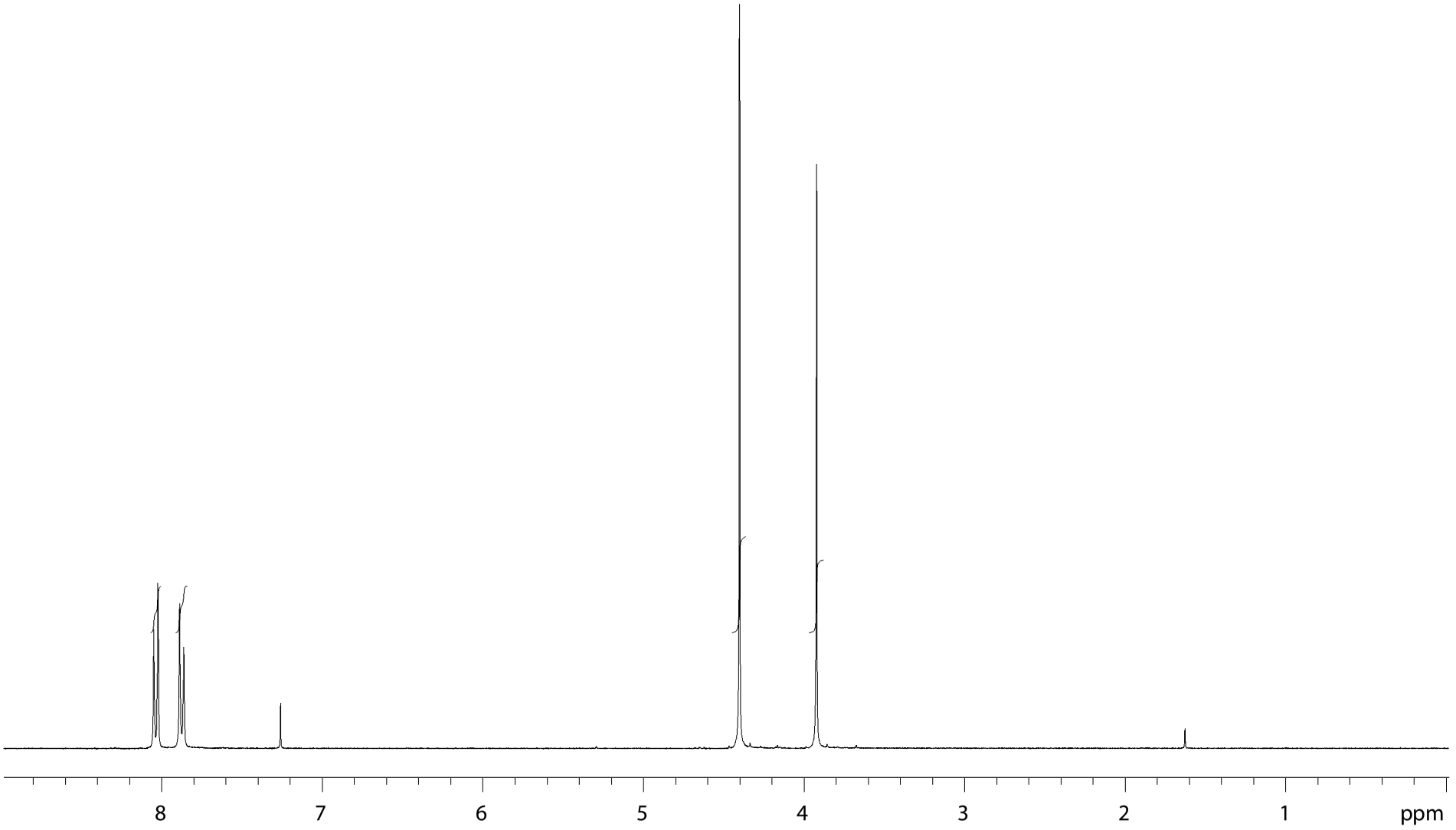


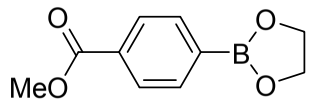
2f



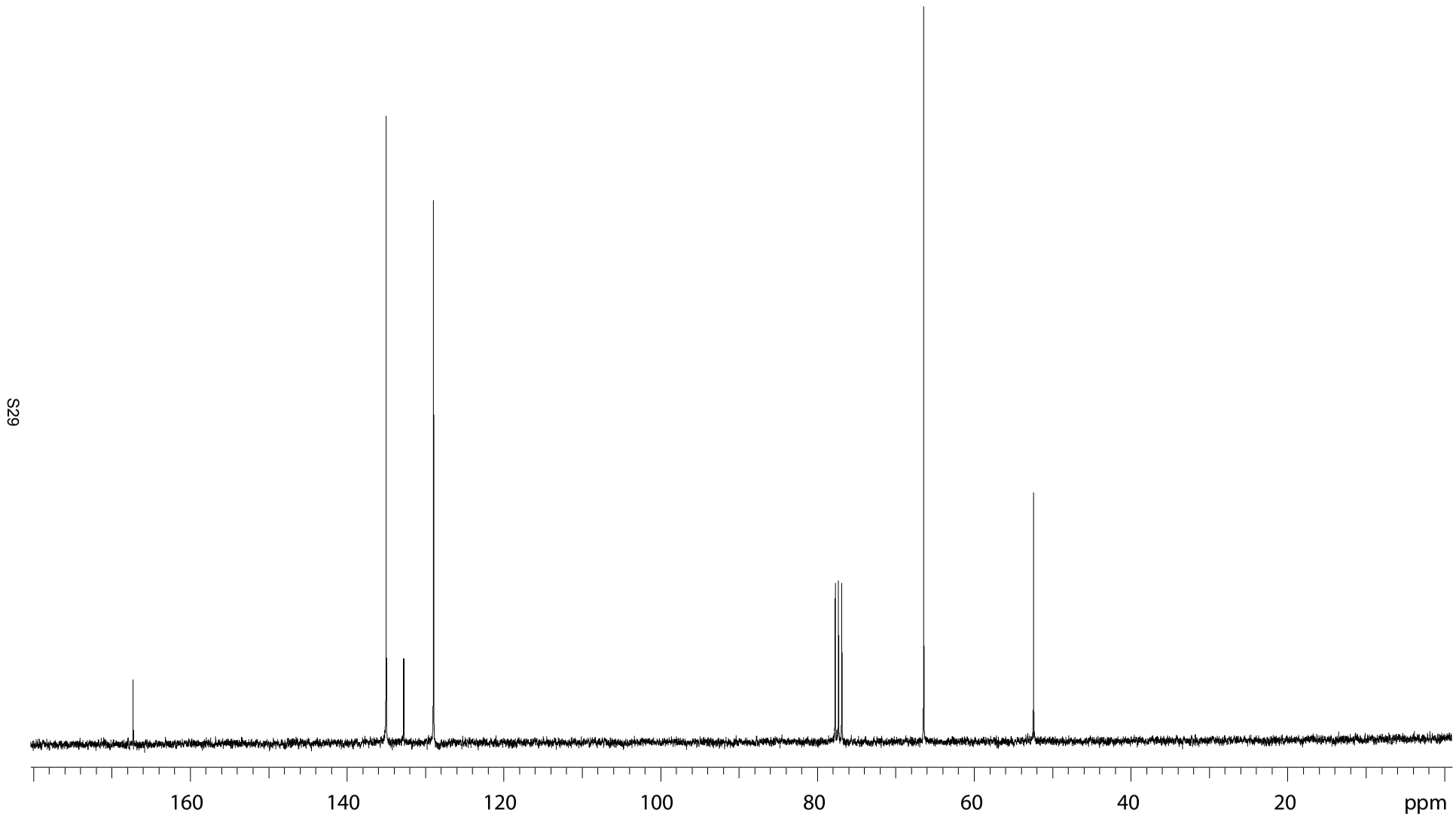


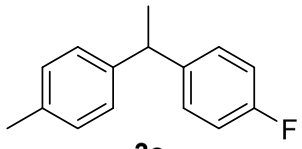
2h



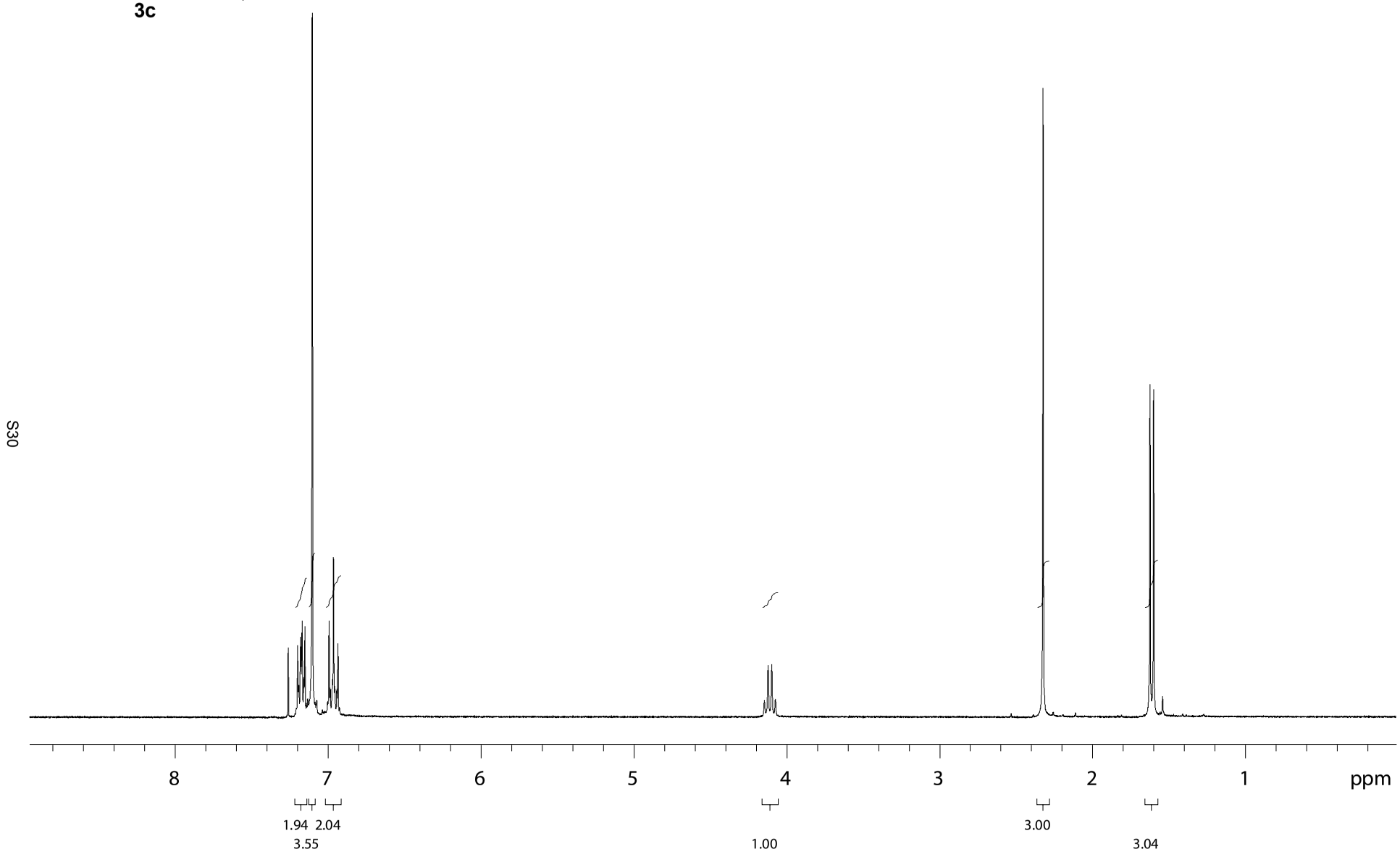


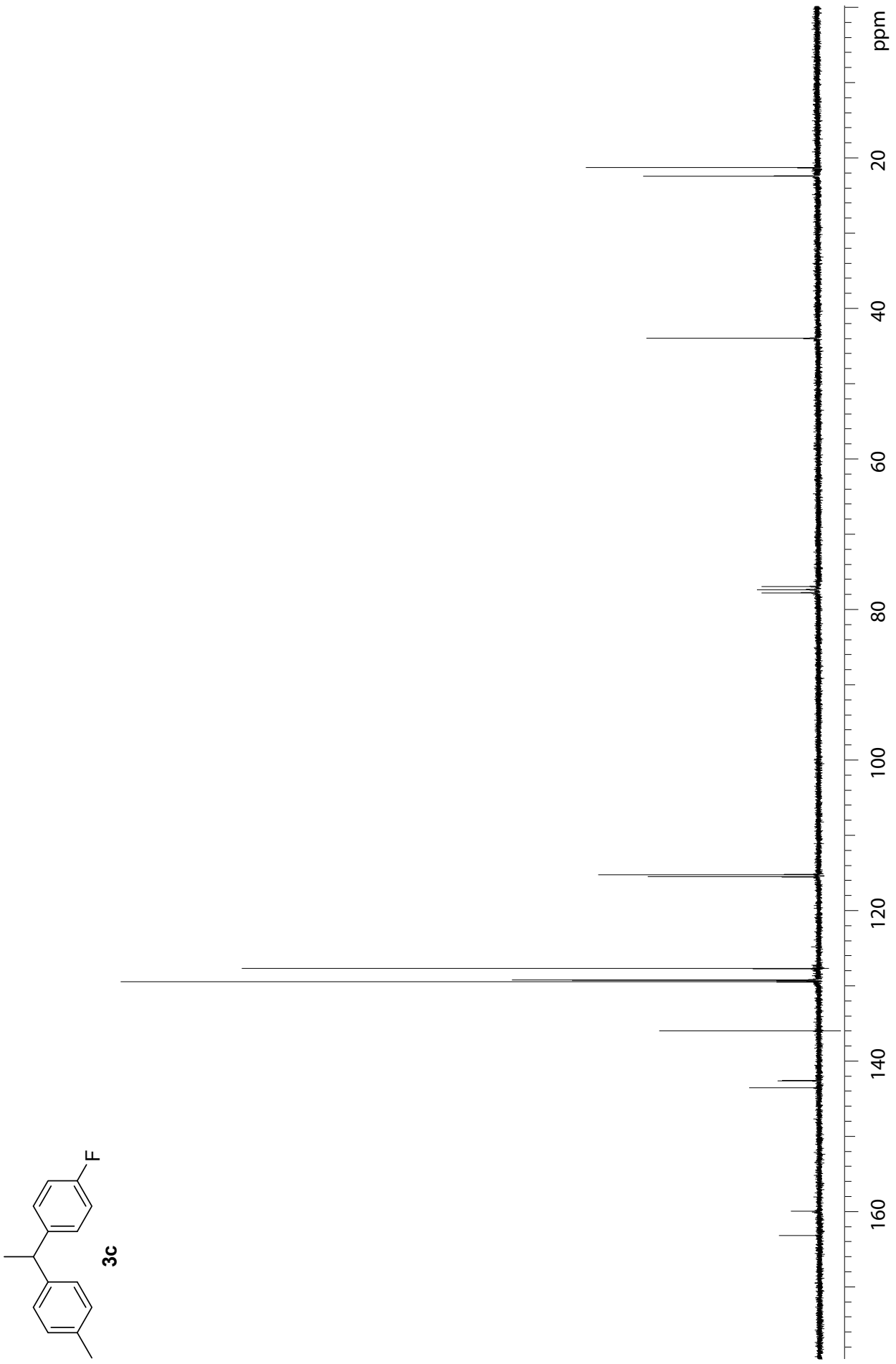
2h

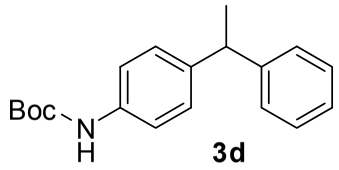




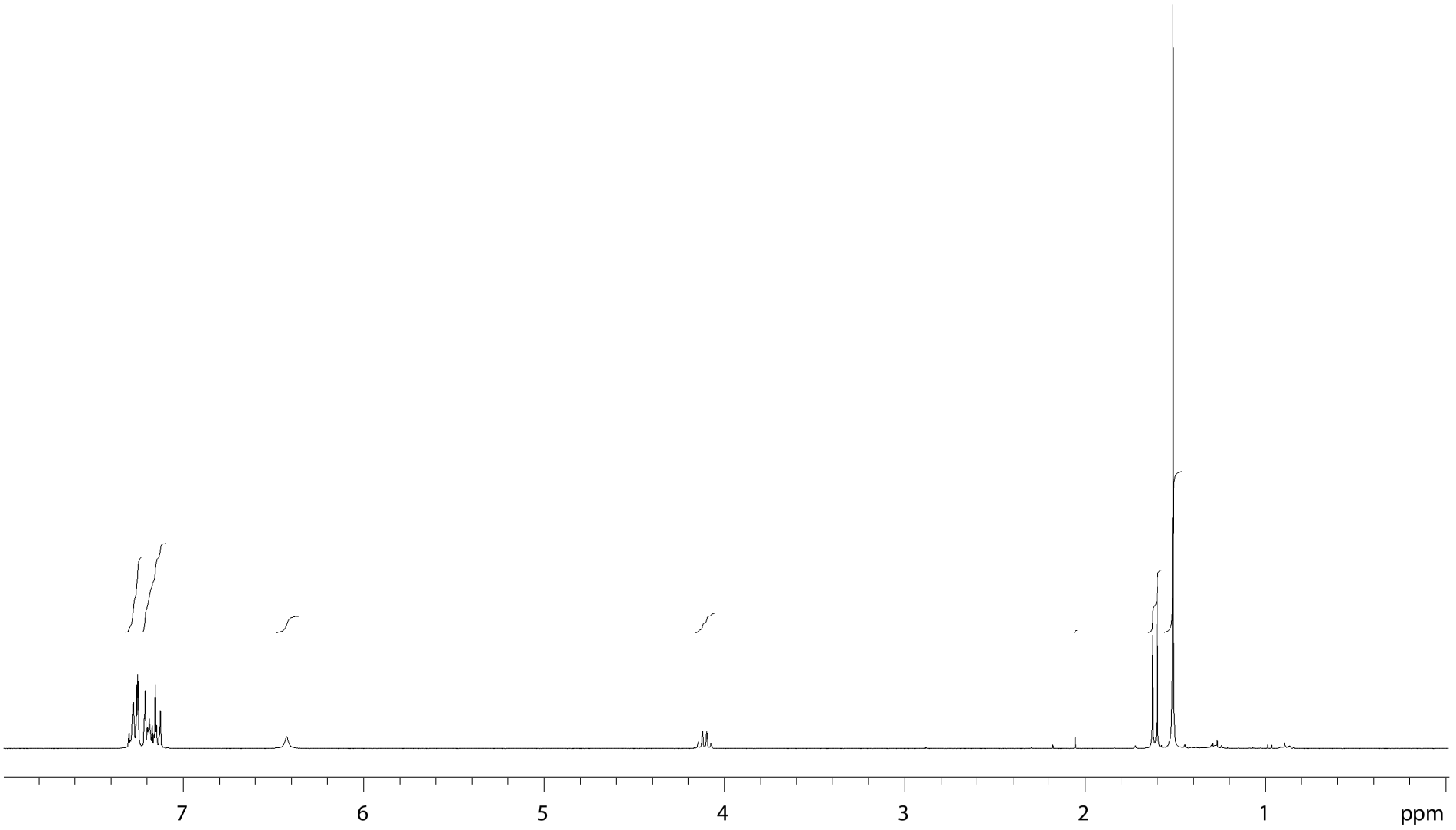
3c

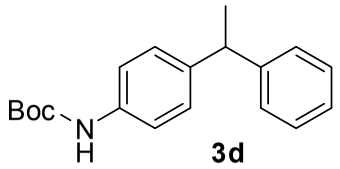



F
3c
ppm
20
40
60
80
100
120
140
160

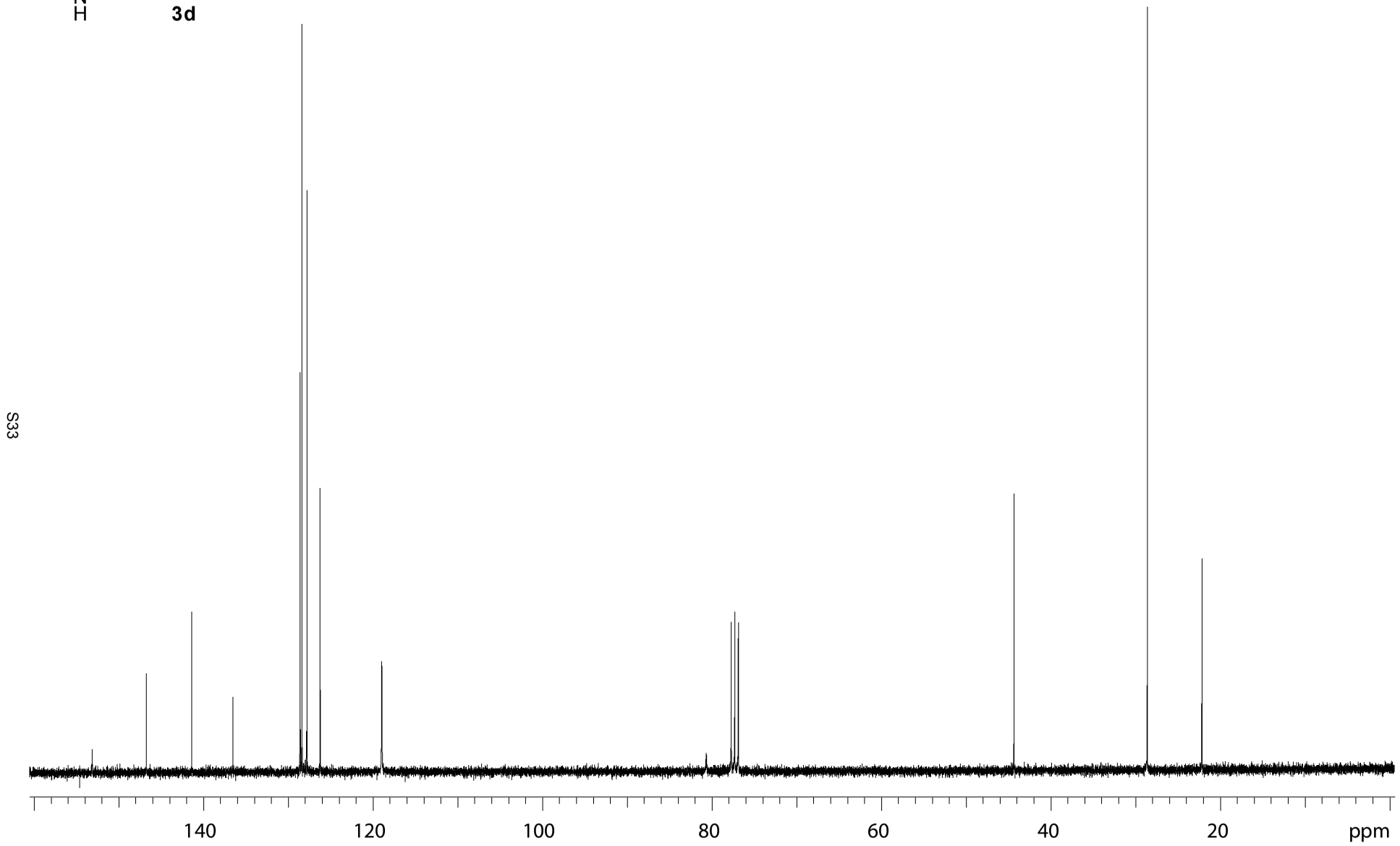


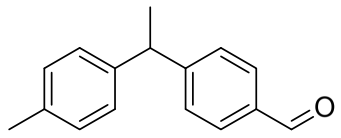
3d



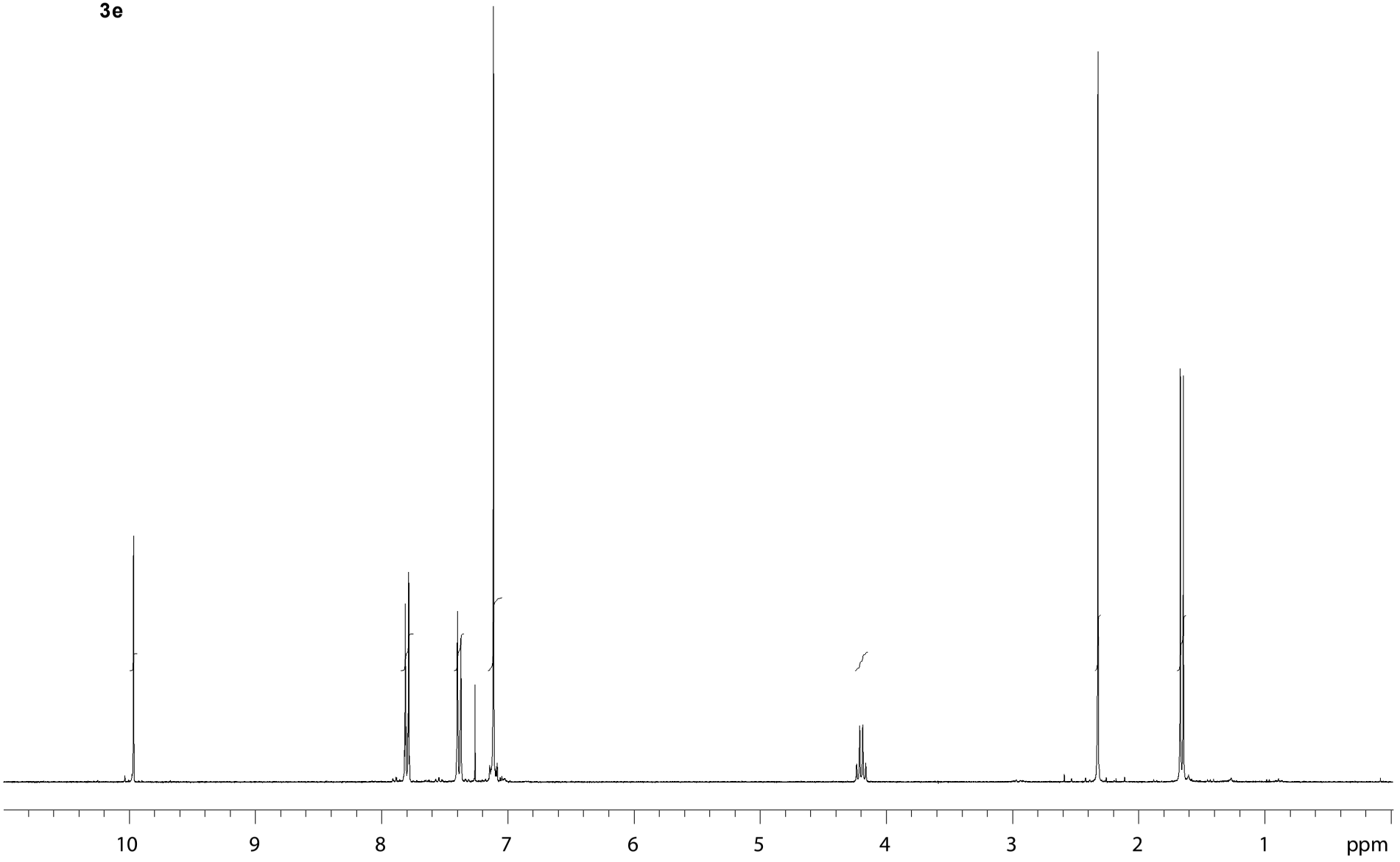


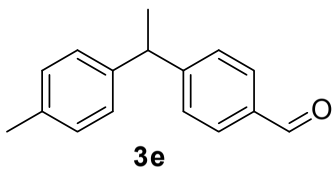
3d



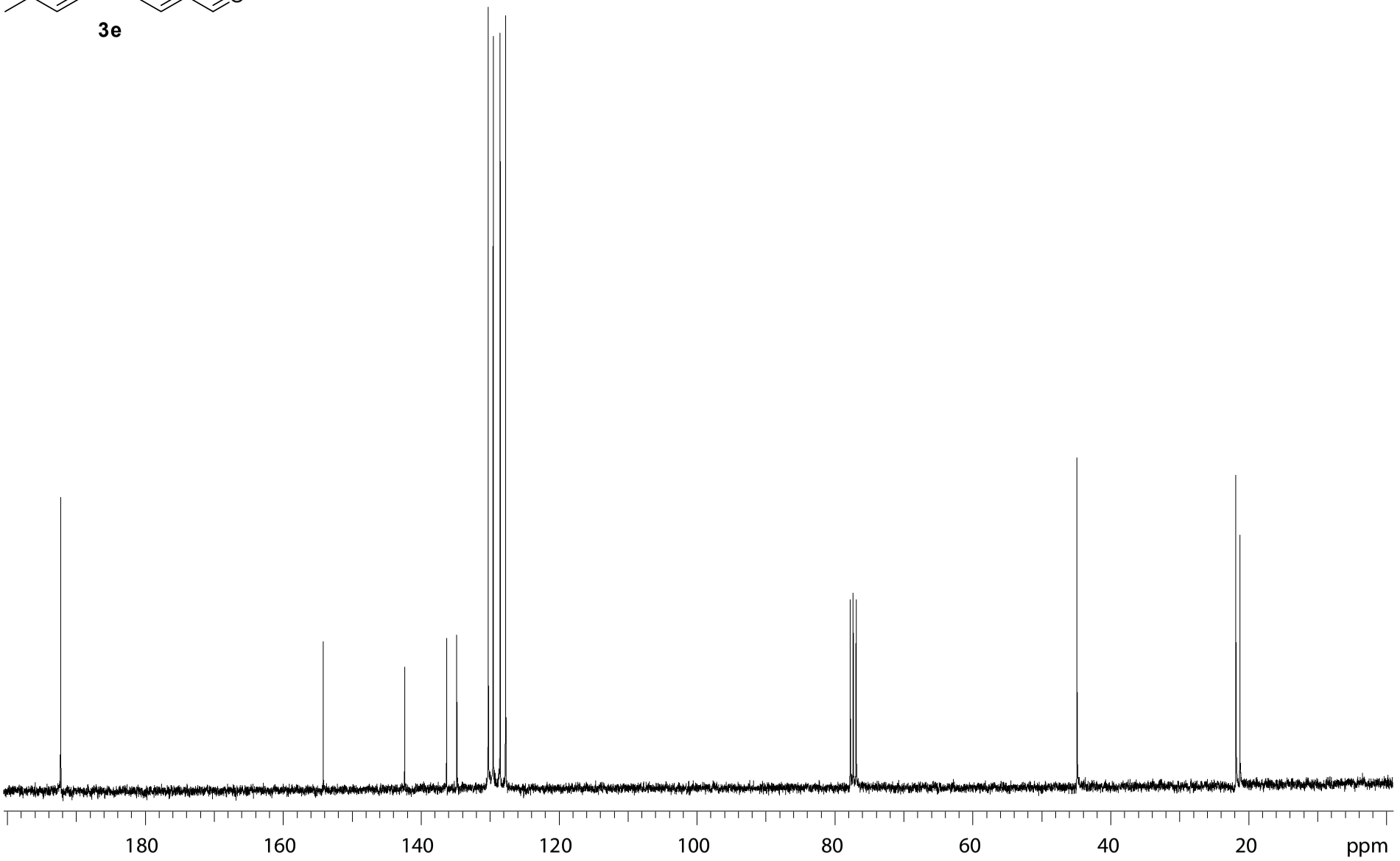


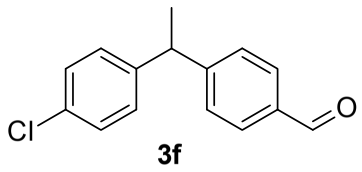
3e



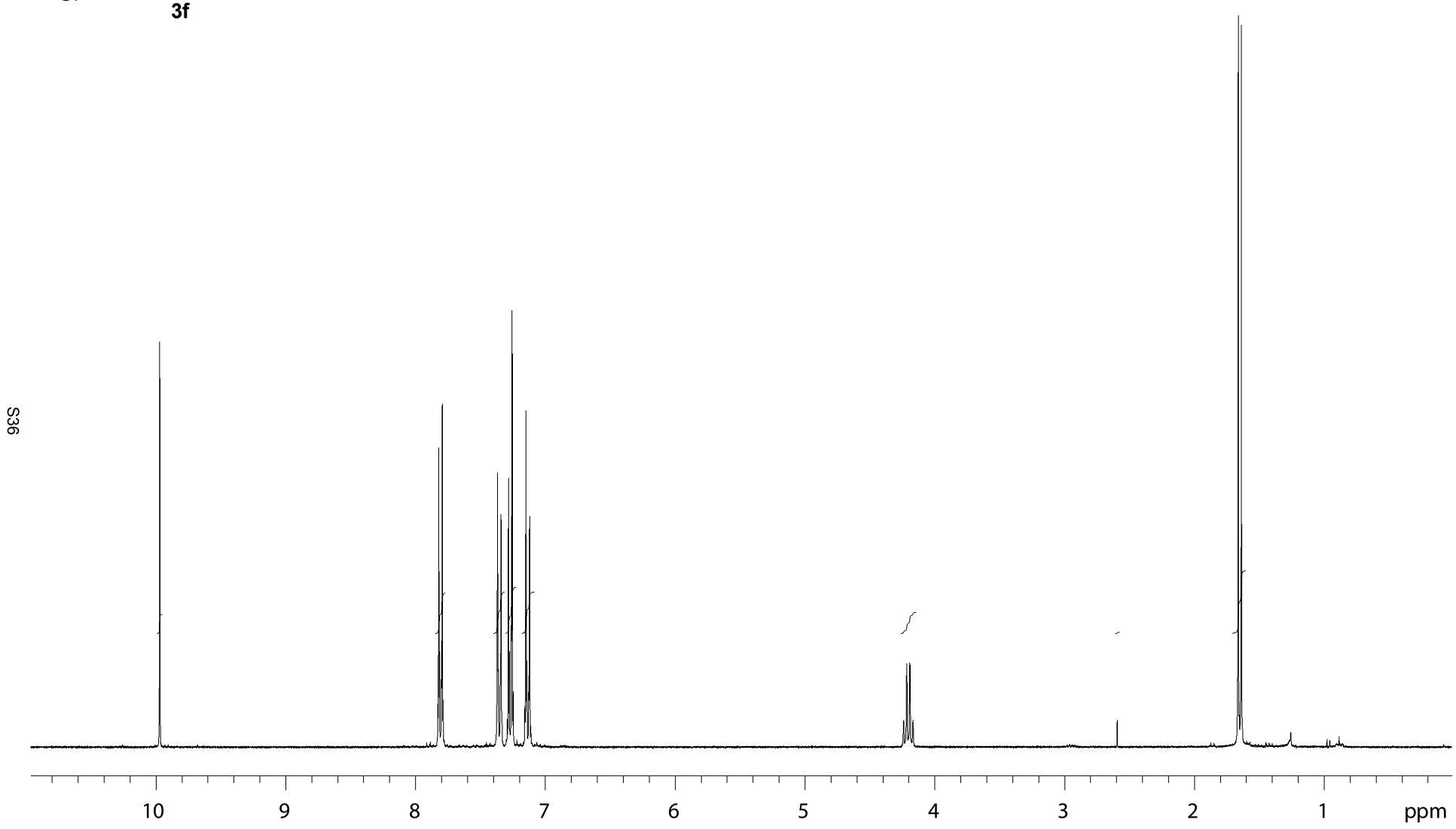


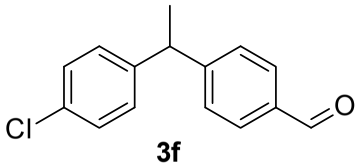
3e



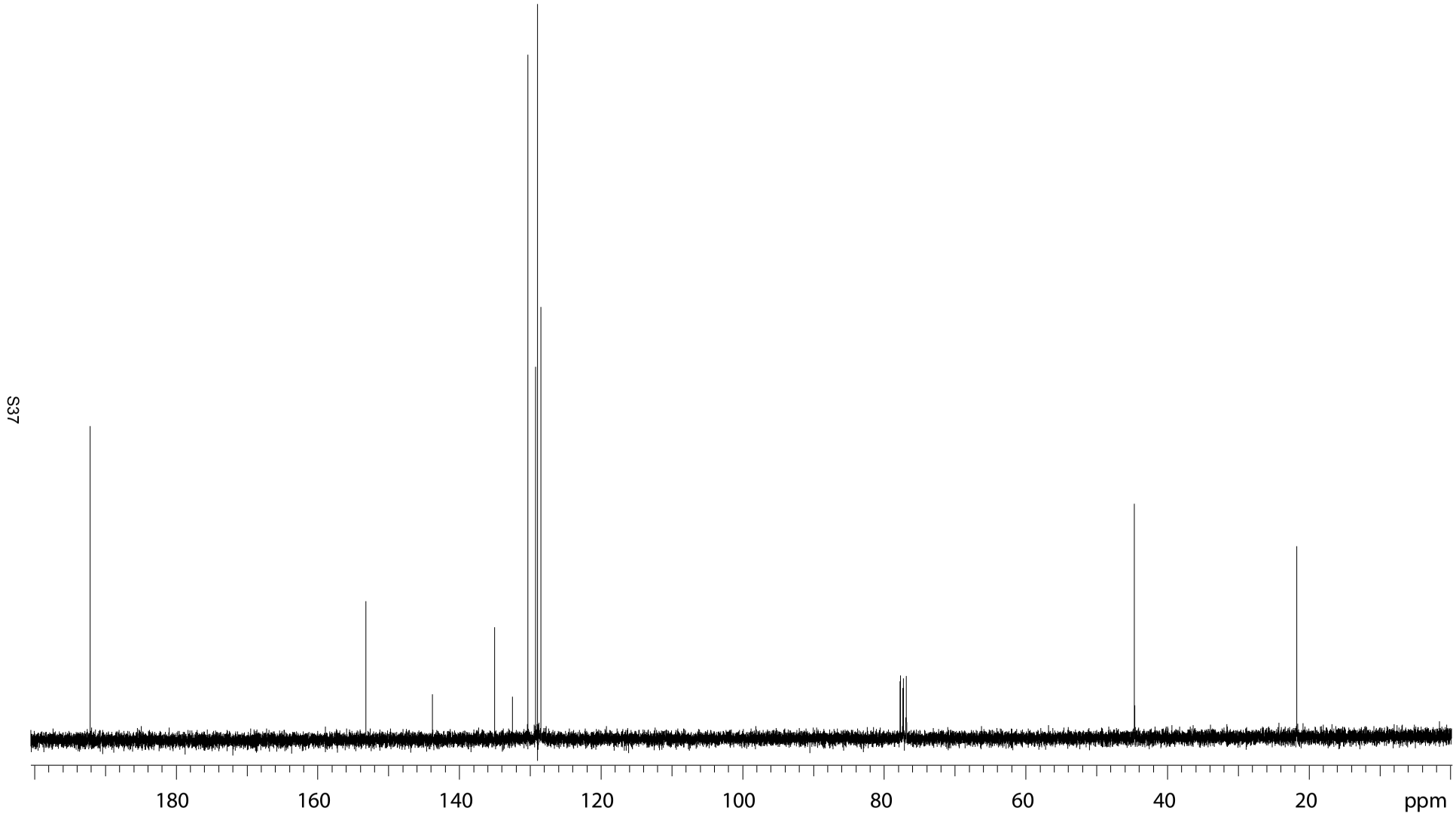


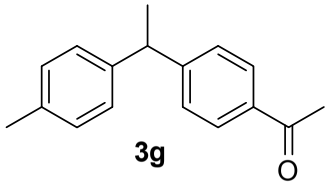
3f



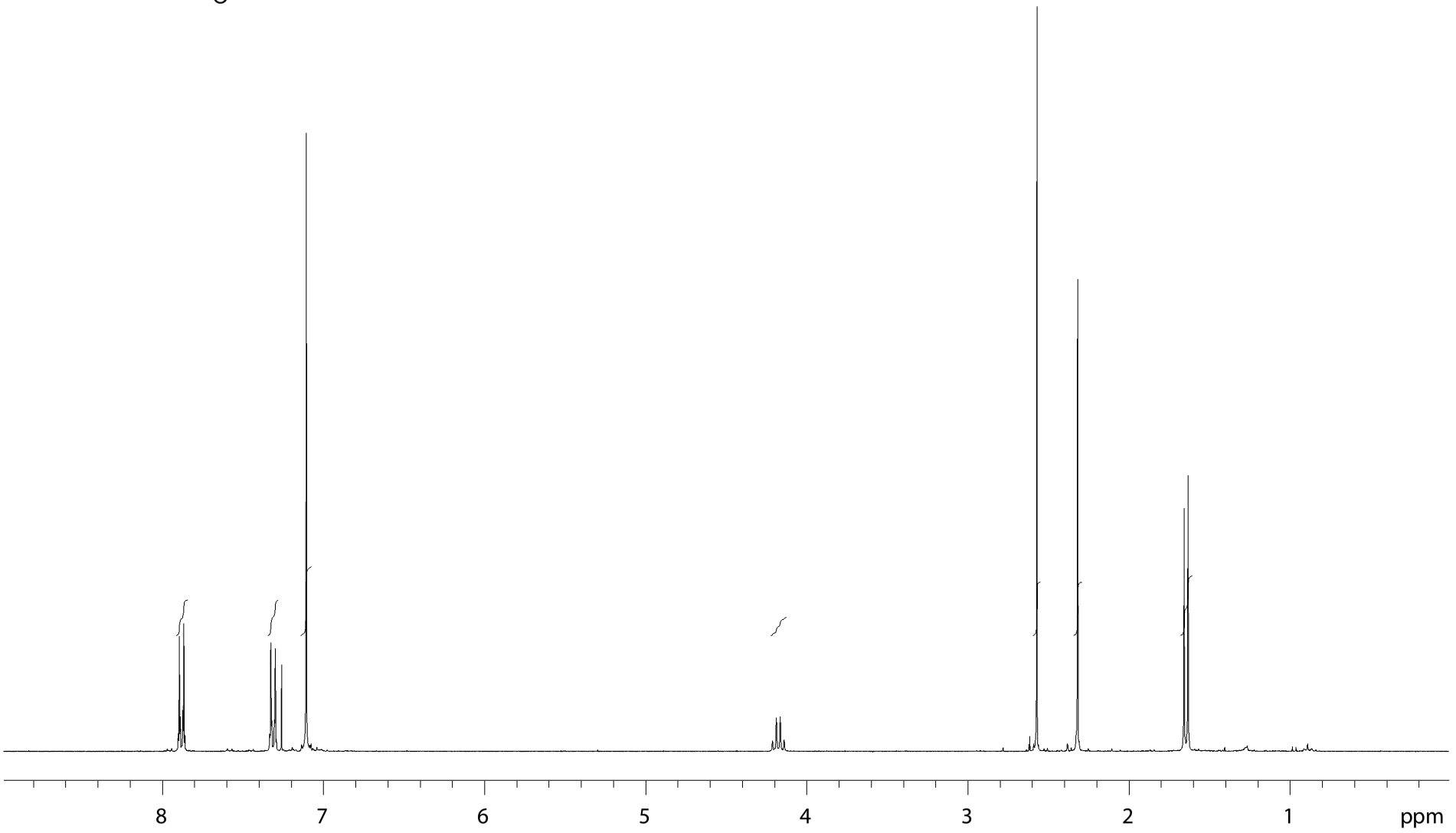


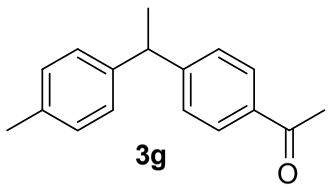
3f



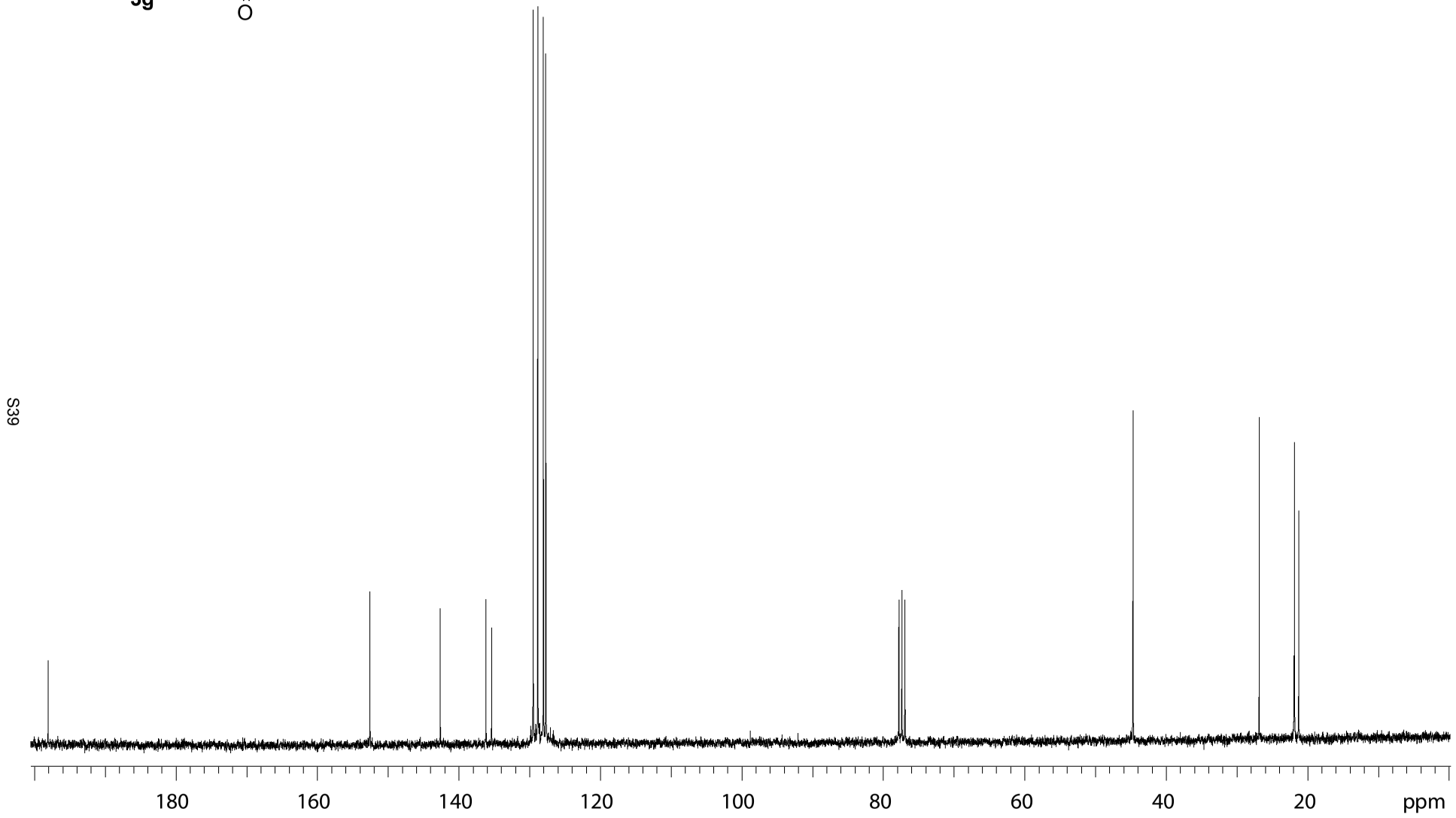


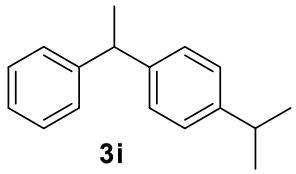
3g



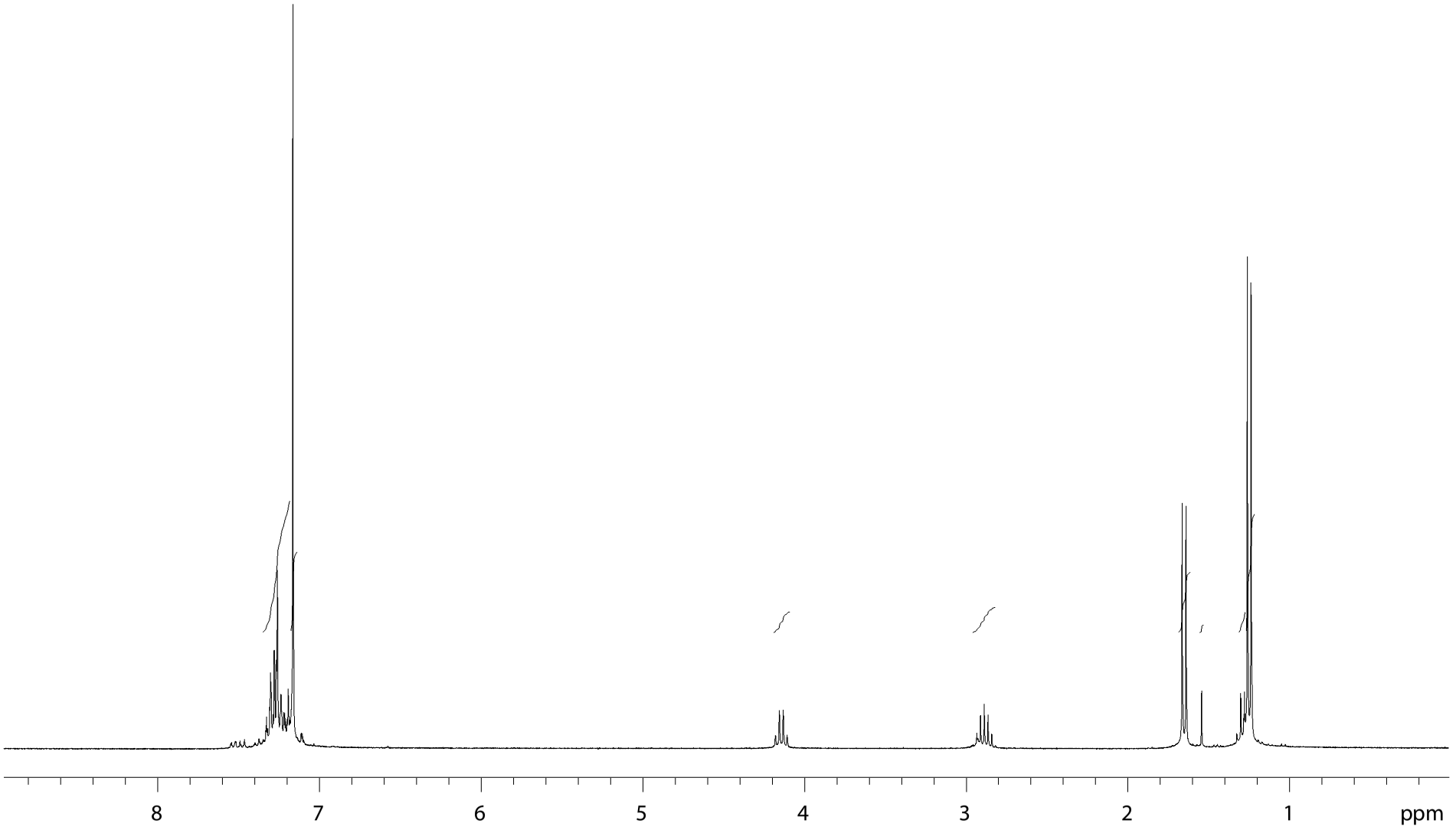


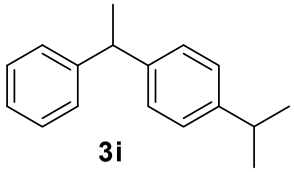
3g



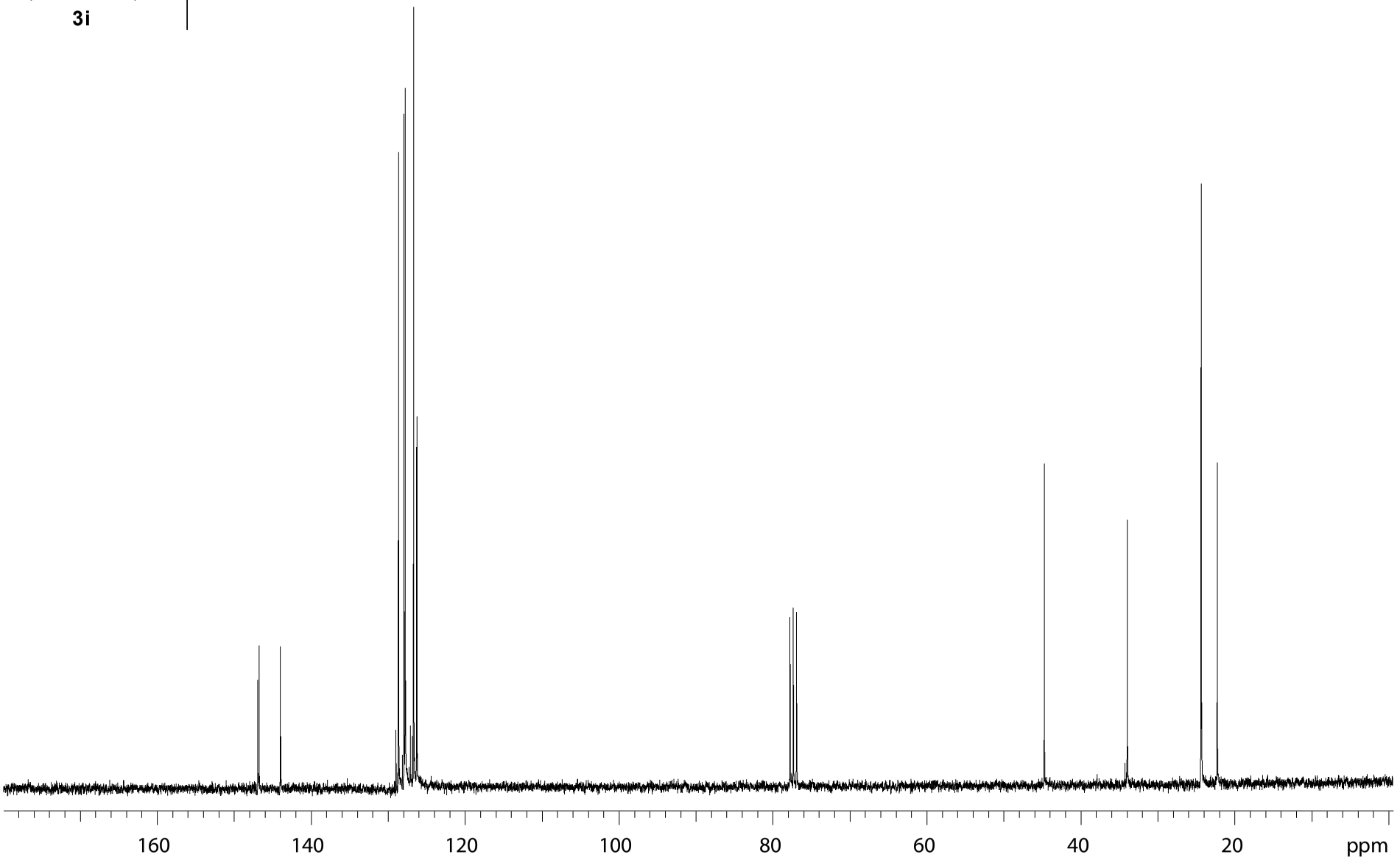


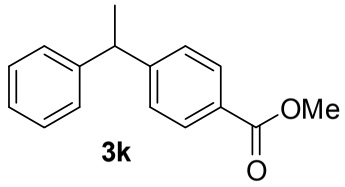
3i



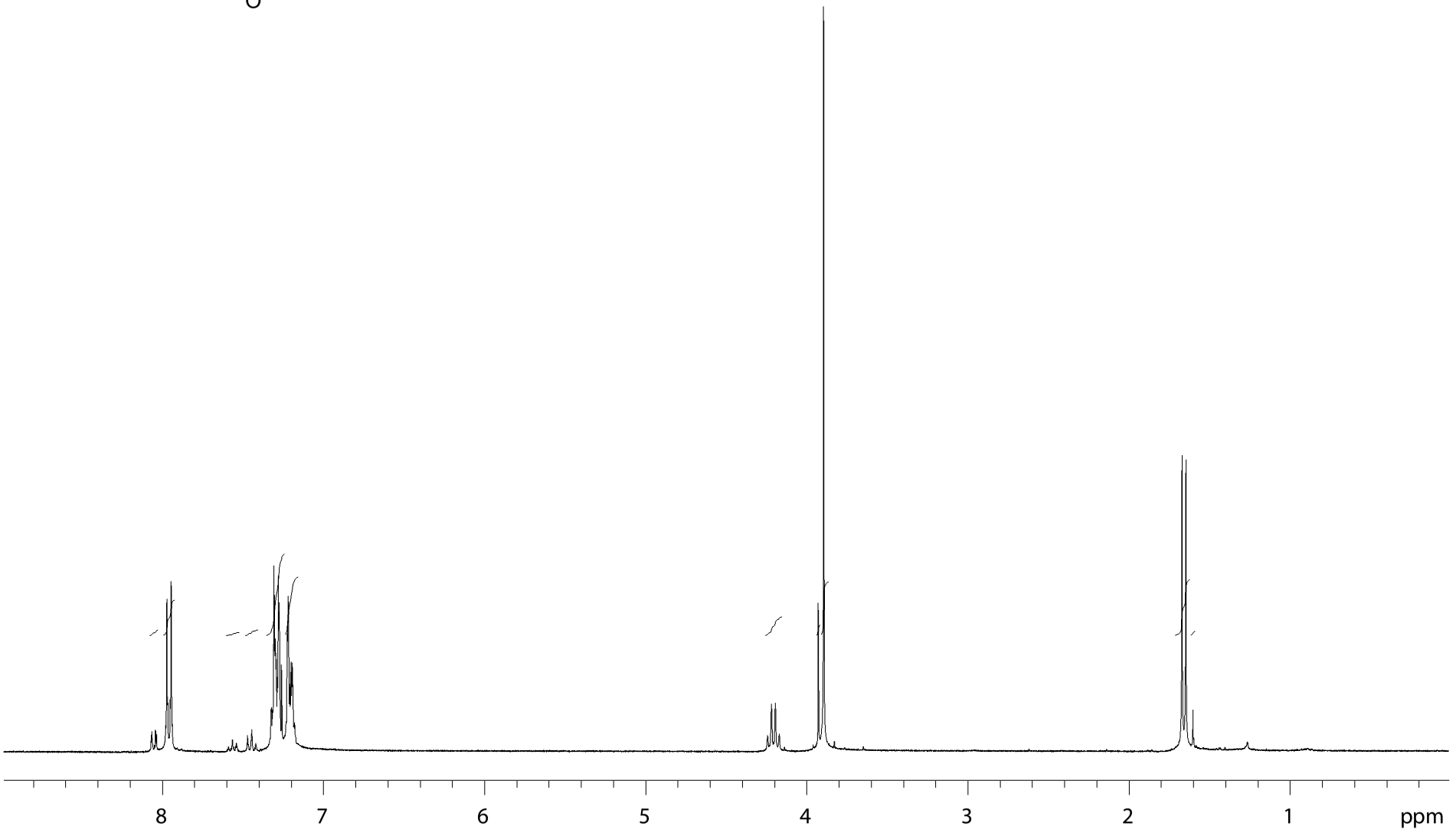


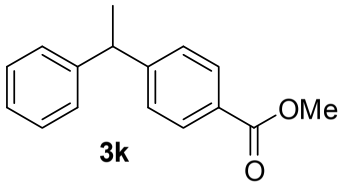
3i



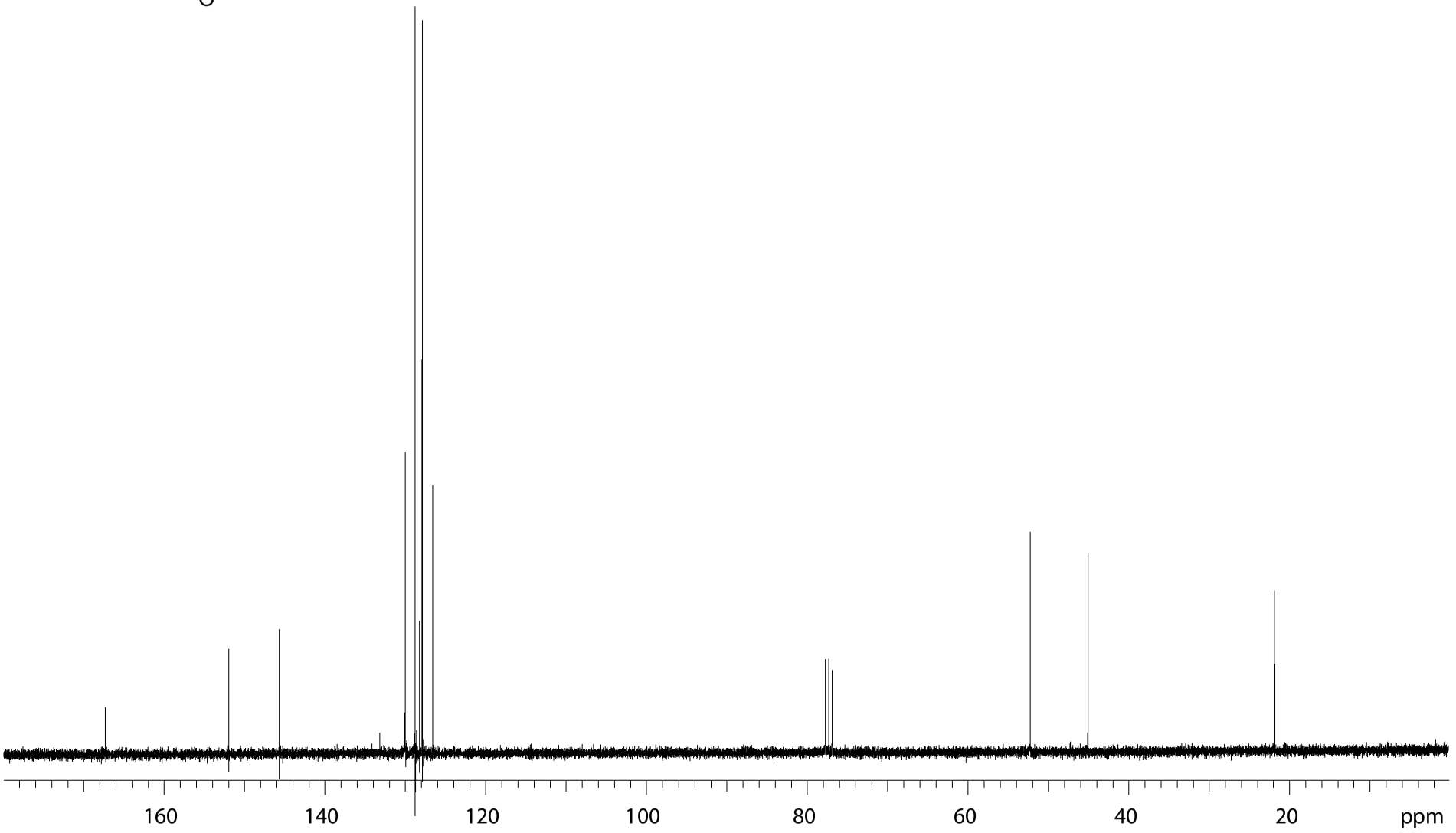


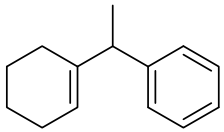
3k



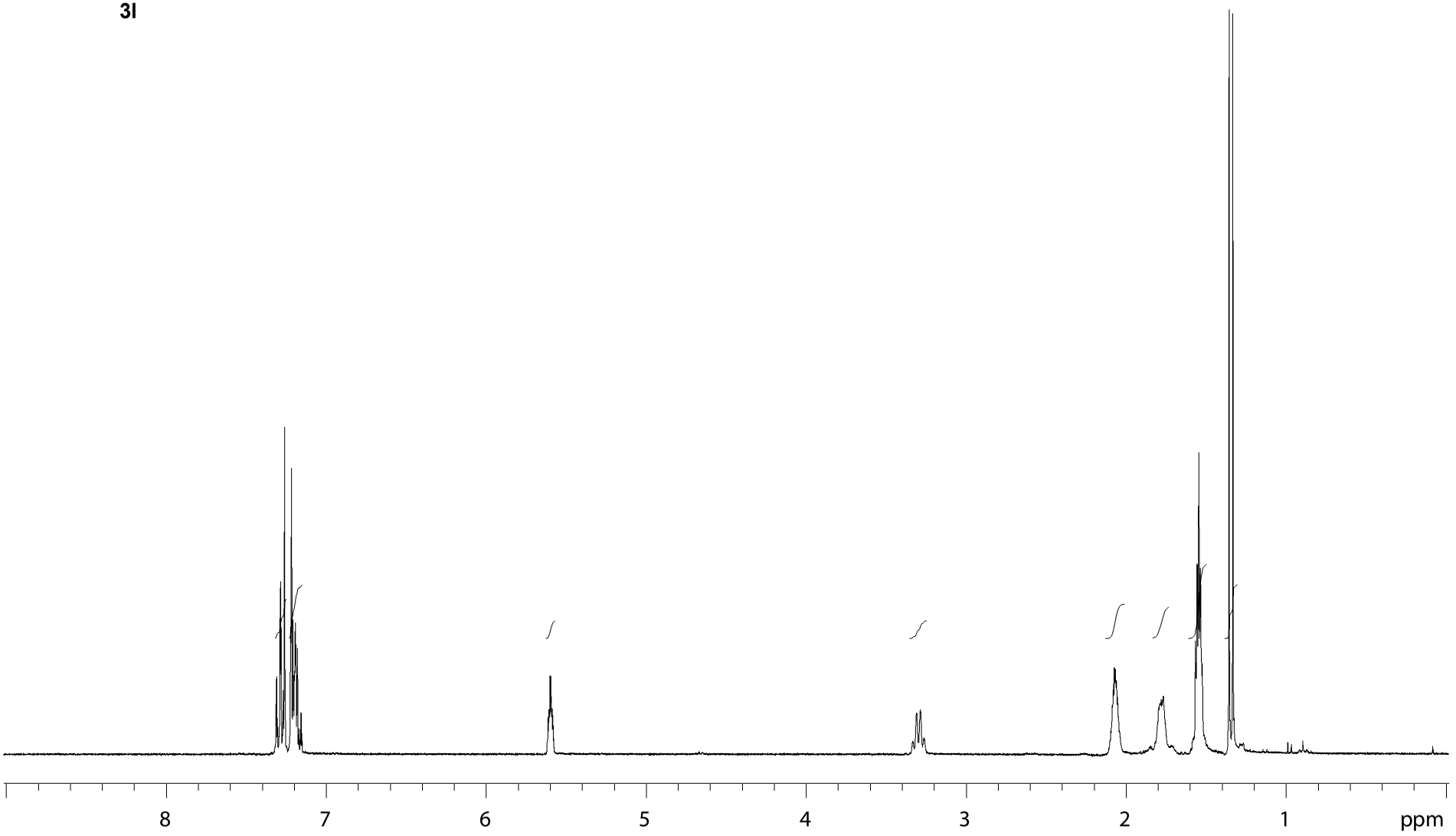


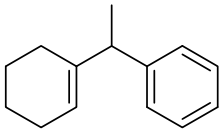
3k





3l





3l