Stereoretentive Pd-Catalyzed Cross-Coupling Reactions of Secondary Alkyl Azastannatranes and Aryl Halides

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Supporting Information

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General Reagent Information

BDH brand ethyl ether was purchased from VWR. EMD brand Omnisolv THF (unstabilized) was also purchased from VWR. These solvents were transferred to separate 20 L solvent-delivery kegs and vigorously purged with argon for 2 h. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina. *s*-BuLi (1.4 M in cyclohexane), isopropylmagnesium chloride (2.0 M in ether), and 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane were purchased from SigmaAldrich. $Pd(dba)_2$ and JackiePhos were purchased from Strem. Acetonitrile (Sigma-Aldrich) was purged with argon prior to use. Grignard reagents were prepared from their corresponding alkyl chlorides or bromides using a literature procedure.[1] Molarities of Grignard reagents and zinc reagents were determined using iodine titration.[2] Optically active organostannatranes were prepared via preparatory chiral HPLC. Reagents and solvents were used as received unless otherwise noted. Flash chromatography was performed using Silicylcle silica gel (ultra pure grade).

General Analytical Information

All compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. Copies of the ^{1}H and ^{13}C spectra for all new compounds can be found at the end of the Supporting Information. All previously unreported compounds were additionally characterized by high resolution MS. Nuclear Magnetic Resonance spectra were recorded on a Varian 300 or 500 MHz instrument. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm). All ^{13}C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm), and were obtained with ^{1}H decoupling. High resolution MS analyses were performed on an Agilent 6520 Q-TOF instrument. All GC analyses were performed on a Shimadzu GC-2010 gas chromatograph with an FID detector using a 25 m x 0.20 mm capillary column with cross-linked methyl siloxane as the stationary phase, or using a 30 m x 0.32 mm chiral column (Rt®-βDEXsm from RESTEK). All GC yields were calibrated using dodecane as an internal standard. Chiral HPLC analyses were performed by Chiral Technologies Inc using an OZ-H or OJ-H chiral column. ICP-MS analysis was performed by Exova Inc.

Procedural Information

General procedure for the preparation of secondary alkyl azastannatranes

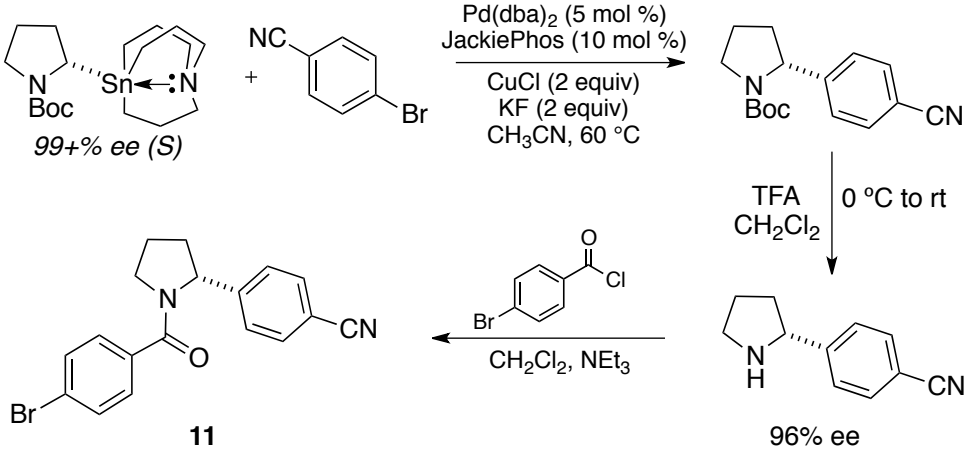
All reactions were performed in oven-dried glassware under an atmosphere of Ar. *sec*-Butyllithium or sec-alkyl Grignard reagents (1.5–2.0 equiv.) were added to the suspension of 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (**4b**) (1 equiv.) in anhydrous solvent at -78 °C. The resulting mixture was stirred at -78 °C for 3 h, allowed to warm to room temperature, and stirred overnight. The reaction mixture was poured into a separatory funnel containing a mixture of water and ether. The organic layer was

separated, washed with brine, dried over Na_2SO_4, and filtered. Solvent was removed under reduced pressure and dried *in vacuo* to provide the crude product. The crude secondary alkyl tin reagents were used without further purification. Homocoupling from Grignard formation constituted the major residual byproduct in the crude product.

General procedure for cross-coupling reactions

$Pd(dba)_2$ (5 mol %, 14.4 mg for 0.5 mmol scale and 28.8 mg for 1.0 mmol scale), JackiePhos (6-10 mol %), CuCl (2 equiv, 100 mg for 0.5 mmol scale and 200 mg for 1.0 mmol scale) and KF (2 equiv, 58 mg for 0.5 mmol scale and 116 mg for 1.0 mmol scale) were weighed out on the benchtop, and transferred to an oven-dried Schlenk tube with stir bar. With stirring begun, the Schlenk tube was evacuated (50 mTorr) and backfilled three times with argon using a needle attached to a vacuum manifold. The tin reagent (1.1-2.0 equiv) and aryl halide/triflate (1 equiv) was then added to the Schlenk tube via microsyringe, followed by degassed CH_3CN (3 mL for 0.5-1.0 mmol scale). If the aryl halide/triflate or the tin reagent was a solid, it was weighed out on the benchtop alongside the other solids. The Schlenk tube was sealed with a Teflon stopper and heated to 60 °C for 18 h (unoptimized reaction time). The reaction mixture was cooled to rt, diluted with ether, washed sequentially with saturated aqueous KF and brine, and dried over Na_2SO_4. The reaction solution was filtered and concentrated to provide the crude product. The crude product was purified by column chromatography.

*Synthesis of **11** for absolute configuration determination via x-ray crystallography*

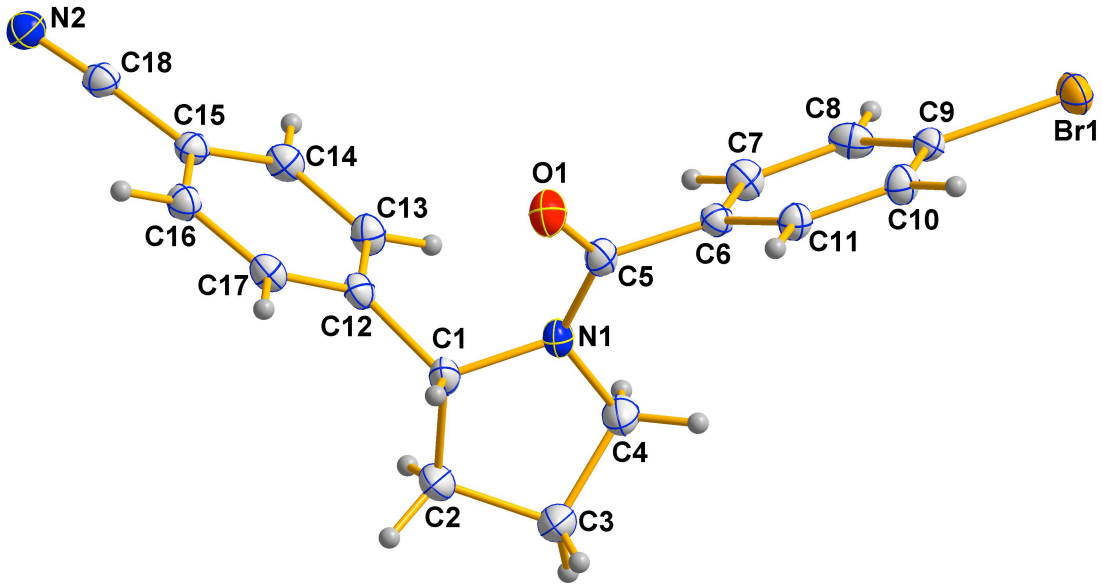


Single Crystal Structure Determination

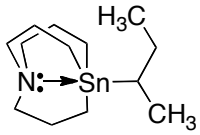
Experimental Description

A colorless slab-like crystal (grown by slow evaporation from ether at -20 ºC) with the size of 0.05 × 0.20 × 0.54 mm^3 was selected for geometry and intensity data collection with a Bruker SMART APEXII CCD area detector on a D8 goniometer at 100 K. The temperature during the data collection was controlled with an Oxford Cryosystems Series 700+ instrument. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. Data were collected using graphite-monochromated and 0.5 mm-MonoCap-collimated Mo-K_α radiation (λ = 0.71073 Å) with the ω scan method.[3] Data were processed with the INTEGRATE program of the APEX2 software[3] for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SCALE program for the area detector. The structure was solved by the direct method and refined on F^2 (SHELXTL).[4] Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions (C-H = 0.95-1.00 Å) and included as riding with $U_{iso}(H) = 1.2\ U_{eq}$(non-H), and the hydrogen atoms on the oxygen atoms were refined with a restrained O-H distance of 0.83 Å.

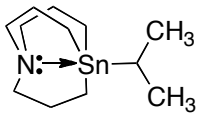
*Crystal Structure of **11***



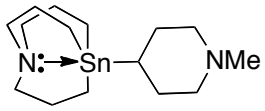
Compound Characterization



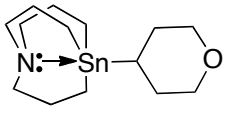
5-(*sec*-Butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (6).[5] The general procedure was employed using 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (2.94 g, 10.2 mmol) in ether (40 mL), and *s*-BuLi (1.4 M in cyclohexane, 15 mL, 21.0 mmol). A yellow oil (3.18 g, 99%) was isolated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.35 (t, *J* = 6.0 Hz, 6H), 1.64 (quint, *J* = 6.0 Hz, 6H), 1.41-1.51 (m, 2H), 1.05 (d, *J* = 7.5 Hz, 3H), 0.86 (t, *J* = 7.5 Hz, 3H), 0.66 (m, 1H), 0.63 (t, *J* = 6.5 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.0, 29.4, 26.7, 23.7, 18.5, 14.8, 5.7 ppm.



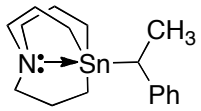
5-(*iso*-Propyl)-1-aza-5-stannabicyclo[3.3.3]undecane. The general procedure was employed using 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (1.47 g, 5.0 mmol) in ether (20 mL), and isopropylmagnesium chloride (2.0 M in ether, 5.0 mL, 10.0 mmol). A yellow oil (1.41 g, 95%) was isolated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.35 (t, *J* = 6.0 Hz, 6H), 1.64 (quint, *J* = 6.0 Hz, 6H), 1.06 (d, *J* = 7.5 Hz, 6H), 0.70 (m, 1H), 0.62 (t, *J* = 6.5 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 54.9, 23.6, 21.6, 17.7, 4.6 ppm. HRMS (FAB^+): Calcd (^{116}Sn) $(M-H)^+$ 298.0926; Found (^{116}Sn) 298.0929.



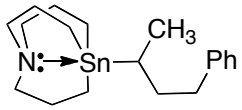
5-(1-Methylpiperidin-4-yl)-1-aza-5-stannabicyclo[3.3.3]undecane. The general procedure was employed using 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (1.06 g, 3.6 mmol) in THF (36 mL), and (1-methylpiperidin-4-yl)magnesium chloride (0.78 M in THF, 7 mL, 5.5 mmol). A pale yellow solid (1.25 g, 97%) was isolated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.76 (d, *J* = 9.0 Hz, 2H), 2.34 (t, *J* = 6.0 Hz, 6H), 2.19 (s, 3H), 1.55-1.79 (m, 13H), 0.63 (t, *J* = 6.5 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 59.0, 54.8, 47.3, 30.8, 26.2, 23.5, 4.7 ppm. HRMS (FAB^+): Calcd (^{116}Sn) $(M-H)^+$ 353.1348; Found (^{116}Sn) 353.1356.



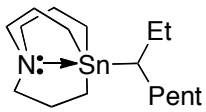
5-(Tetrahydro-2H-pyran-4-yl)-1-aza-5-stannabicyclo[3.3.3]undecane. The general procedure was employed using 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (883 mg, 3.0 mmol) in THF (30 mL), and (tetrahydro-2*H*-pyran-4-yl)magnesium chloride (0.62 M in THF, 7 mL, 4.3 mmol). A pale yellow solid (983 mg, 95%) was isolated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.87 (m, 2H), 3.33 (dt, *J* = 11.0, 2.0 Hz, 2H), 2.36 (t, *J* = 6 Hz, 6H), 1.64 (quint, *J* = 6.0 Hz, 6H), 1.50-1.65 (m, 4H), 0.90 (tt, *J* = 12.5, 4.0 Hz, 1H), 0.64 (t, *J* = 6.5 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 71.0, 54.8, 31.3, 26.0, 23.4, 4.6 ppm. HRMS (FAB$^+$): Calcd (^{116}Sn) (M-H)$^+$ 340.1031; Found (^{116}Sn) 340.1025.



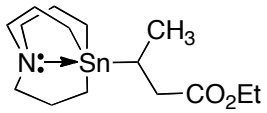
5-(1-Phenylethyl)-1-aza-5-stannabicyclo[3.3.3]undecane. The general procedure was employed using 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (882 mg, 3.0 mmol) in THF (15 mL), and (1-phenylethyl)magnesium chloride (0.56 M in THF, 8 mL, 4.5 mmol). A yellow liquid (995 mg, 91%) was isolated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (t, *J* = 7.5 Hz, 2H), 6.90-7.00 (m, 3H), 2.30 (t, *J* = 6.0 Hz, 6H), 2.21 (quart, *J* = 7.5 Hz, 1H), 1.61 (quint, *J* = 6.0 Hz, 6H), 1.44 (d, *J* = 7.5 Hz, 3H), 0.61 (dt, *J* = 6.5, 3 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.5, 128.0, 124.9, 121.7, 54.7, 32.7, 23.5, 16.7, 5.3 ppm. HRMS (FAB$^+$): Calcd (^{116}Sn) (M-H)$^+$ 360.1082; Found (^{116}Sn) 360.1072.



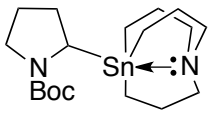
5-(4-Phenylbutan-2-yl)-1-aza-5-stannabicyclo[3.3.3]undecane (12). The general procedure was employed using 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (1.65 g, 5.6 mmol) in THF (50 mL), and (4-phenylbutan-2-yl)magnesium chloride (0.28 M in THF, 23 mL, 6.4 mmol). A yellow liquid (1.74 g, 79%) was isolated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25-7.28 (m, 2H), 7.16-7.19 (m, 3H), 2.50-2.65 (m, 2H), 2.36 (t, *J* = 6.0 Hz, 6H), 1.68-1.81 (m, 2H), 1.65 (quint, *J* = 6.0 Hz, 6H), 1.13 (d, *J* = 7.5 Hz, 3H), 0.79 (quart, *J* = 7.5 Hz, 1H), 0.67 (t, *J* = 6.5 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 128.6, 128.3, 125.5, 55.0, 39.0, 36.5, 24.2, 23.6, 18.6, 5.6 ppm. HRMS (FAB$^+$): Calcd (^{116}Sn) (M-H)$^+$ 388.1396; Found (^{116}Sn) 388.1409. Enantiomeric separation was achieved using a Chiralcel OJ-H chiral column with 95:5 MeOH:H_2O as eluent (see chiral HPLC data below).



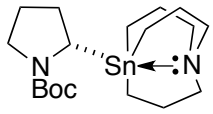
5-(Octan-3-yl)-1-aza-5-stannabicyclo[3.3.3]undecane. The general procedure was employed using 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (736 mg, 2.5 mmol) in THF (25 mL), and octan-3-ylmagnesium chloride (0.35 M in THF, 11 mL, 3.8 mmol). A colorless liquid (1.074 g, > 100%) was isolated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.36 (t, *J* = 6.0 Hz, 6H), 1.64 (quint, *J* = 6.0 Hz, 6H), 1.20-1.52 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.84 (t, *J* = 7.5 Hz, 3H), 0.74 (m, 1H), 0.64 (t, *J* = 6.5 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.1, 34.0, 33.3, 32.6, 29.9, 26.3, 23.8, 23.0, 14.7, 14.4, 6.9 ppm. HRMS (FAB^+): Calcd (^{116}Sn) $(M-H)^+$ 368.1708; Found (^{116}Sn) 368.1698.



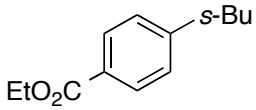
Ethyl 3-(1-aza-5-stannabicyclo[3.3.3]undecan-5-yl)butanoate. The general procedure was employed using 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (882 mg, 3.0 mmol) in DMF (8 mL), and (4-ethoxy-4-oxobutan-2-yl)zinc iodide (0.61 M in DMF, 10 mL, 6.1 mmol). An orange oil (509 mg, 45%) was isolated. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.09 (quart, *J* = 7.0 Hz, 2H), 2.40 (m, 1H), 2.35 (t, *J* = 6.0 Hz, 6H), 2.25 (m, 1H), 1.64 (quint, *J* = 6 Hz, 6H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.02-1.13 (m, 4H), 0.65 (t, *J* = 6.5 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.5, 60.0, 54.9, 40.7, 23.5, 19.8, 18.4, 14.6, 5.2 ppm. HRMS (FAB^+): Calcd (^{116}Sn) $(M-H)^+$ 370.1138; Found (^{116}Sn) 370.1136.



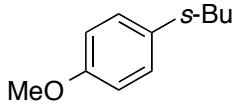
***tert*-Butyl 2-(1-aza-5-stannabicyclo[3.3.3]undecan-5-yl)pyrrolidine-1-carboxylate.** TMEDA (0.8 mL, 5.5 mmol) in ether (1 mL) was precooled to -78 ºC for 15 min. *s*-BuLi (1.4 M in cyclohexane, 3.6 mL, 5.0 mmol) was added dropwise to this solution. The resulting solution was allowed to stir for 15 min. A solution of *N*-Boc-pyrrolidine (855 mg, 5.0 mmol) in ether (10 mL) was then added dropwise. This reaction mixture was stirred at -78 ºC for 3h. The resulting solution (1-*tert*-butoxycarbonyl)pyrrolidin-2-yl)lithium (0.22 M in ether, 17 mL, 3.7 mmol)[6] was employed in the general procedure with 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (736 mg, 2.5 mmol) in ether (25 mL). A yellow oil (854 mg, 80%) was isolated. ^{1}H NMR for two rotomers with a ratio of 3:2 (500 MHz, $CDCl_3$): δ 3.01-3.34 (m, 2H), 2.32-2.38 (m, 6H), 2.01-2.21 (m, 1H), 1.63-1.70 (m, 10H), 1.43-1.47 (two singlet, 9H), 0.70-0.73 (m, 6H) ppm. ^{13}C NMR for the major rotomer (125 MHz, $CDCl_3$): δ 154.0, 77.9, 55.2, 51.4, 46.7, 30.3, 28.9, 27.2, 23.7, 7.0 ppm. HRMS (FAB^+): Calcd (^{116}Sn) $(M-H)^+$ 425.1559; Found (^{116}Sn) 425.1560.



***(S)-tert*-Butyl 2-(1-aza-5-stannabicyclo[3.3.3]undecan-5-yl)pyrrolidine-1-carboxylate (10)**. (-)-Sparteine (258 mg, 1.1 mmol) in ether (1 mL) was precooled to -78 ºC for 15 min. *s*-BuLi (1.4 M in cyclohexane, 0.8 mL, 1.1 mmol) was added dropwise to the solution. The resulting solution was allowed to stir for 15 min. A solution of *N*-Boc-pyrrolidine (171 mg, 1.0 mmol) in ether (2 mL) was then added dropwise. This mixture was stirred at -78 ºC for 3 h. The resulting (1-*tert*-butoxycarbonyl)pyrrolidin-2-yl)lithium solution (0.23 M in ether, 4 mL, 0.9 mmol)[6] was employed in the general procedure with 5-chloro-1-aza-5-stannabicyclo[3.3.3]undecane (176 mg, 0.6 mmol) in ether (6 mL), and (1-*tert*-butoxycarbonyl)pyrrolidin-2-yl)lithium. A yellow oil (160 mg, 62%, 93% ee) was isolated. ^{1}H NMR for two rotomers with a ratio of 3:2 (500 MHz, $CDCl_3$): δ 3.01-3.34 (m, 2H), 2.32-2.38 (m, 6H), 2.01-2.21 (m, 1H), 1.63-1.70 (m, 10H), 1.43-1.47 (two singlet, 9H), 0.70-0.73 (m, 6H) ppm. ^{13}C NMR for the major rotomer (125 MHz, $CDCl_3$): δ 154.0, 77.9, 55.2, 51.4, 46.7, 30.3, 28.9, 27.2, 23.7, 7.0 ppm. Preparative enantiomeric separation could also be achieved using a Chiralcel OZ-H chiral column with CH_3CN as eluent (see chiral HPLC data below).

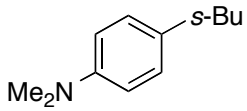


Ethyl 4-(*sec*-butyl)benzoate[7] (7b) (Table 1, row 1, column 1). The general procedure was employed using ethyl 4-bromobenzoate (229 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (348 mg, 1.1 mmol), and JackiePhos (48 mg, 0.06 mmol). A colorless liquid (180 mg, 87%) was isolated by column chromatography (98:2 Hex/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.36 (quartet, J = 7.0 Hz, 2H), 2.65 (m, 1H), 1.61 (m, 2H), 1.38 (t, J = 7.0 Hz, 3H), 1.24 (d, J = 6.5 Hz, 3H), 0.81 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.8, 153.2, 129.8, 128.3, 127.2, 60.8, 41.9, 31.0, 21.7, 14.5, 12.3 ppm.

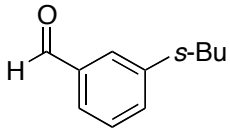


1-(*sec*-Butyl)-4-methoxybenzene[8] (7c) (Table 1, row 2, column 1). The general procedure was employed using 1-bromo-4-methoxybenzene (187 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (475 mg, 1.5 mmol), and JackiePhos (80 mg, 0.1 mmol). A colorless liquid (124.7 mg, 77%) was isolated by column chromatography (97:3 Hex/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.11 (d, J = 8.5, 2H), 6.86 (d, J = 8.5 Hz, 2H), 3.80 (s, 3H), 2.56 (m, 1H), 1.58 (m, 2H), 1.23 (d, J = 7 Hz, 3H),

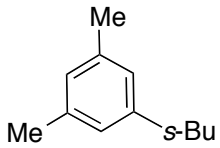
0.83 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 140.0, 128.0, 113.8, 55.4, 41.0, 31.5, 22.2, 12.4 ppm.



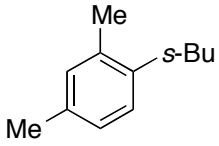
4-(*sec*-Butyl)-*N*,*N*-dimethylaniline[9] (7d) (Table 1, row 3, column 1). The general procedure was employed using 4-bromo-*N*,*N*-dimethylaniline (200 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (475 mg, 1.5 mmol), and JackiePhos (80 mg, 0.1 mmol). An oily, brown solid (110 mg, 62%) was isolated by column chromatography (99:1 Hex/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (d, J = 8.5 Hz, 2H), 6.73 (d, J = 8.5 Hz, 2H), 2.93 (s, 6H), 2.52 (m, 1H), 1.57 (m, 2H), 1.22 (d, J = 7.0 Hz, 3H), 0.84 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.2, 136.2, 127.8, 113.1, 41.1, 40.8, 31.6, 22.2, 12.5 ppm.



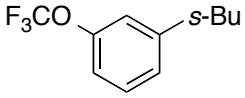
3-(*sec*-Butyl)benzaldehyde (7e) (Table 1, row 4, column 1). The general procedure was employed using 3-bromobenzaldehyde (185 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (348 mg, 1.1 mmol), and JackiePhos (48 mg, 0.06 mmol). A oily, yellow liquid (120.1 mg, 74%) was isolated by column chromatography (98.5:1.5 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.00 (s, 1H), 7.70 (m, 2H), 7.46 (m, 2H), 7.04 (s, 1H), 2.69 (m, 1H), 1.63 (m, 2H), 1.27(d, J = 7 Hz, 3H), 0.83 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 192.8, 149.0, 136.8, 133.7, 129.1, 128.2, 128.0, 41.7, 31.2, 21.9, 12.3 ppm. HRMS (EI^+): Calcd (M^+) 162.1045; Found 162.1047.



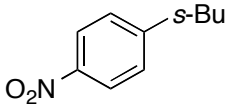
1-(*sec*-Butyl)-3,5-dimethylbenzene[8] (7f) (Table 1, row 5, column 1). The general procedure was employed using 1-bromo-3,5-dimethylbenzene (185 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (475 mg, 1.5 mmol), and JackiePhos (80 mg, 0.1 mmol). A colorless liquid (128 mg, 77%) was isolated by column chromatography (97.5:2.5 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.84 (s, 1H), 6.82 (s, 2H), 2.52 (m, 1H), 2.31 (s, 6H), 1.59 (m, 2H), 1.22 (d, J = 6.5 Hz, 3H), 0.84 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5, 148, 137.8, 125.1, 41.8, 31.4, 22.1, 21.6, 12.6 ppm.



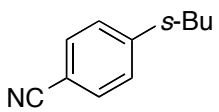
1-(*sec*-Butyl)-2,4-dimethylbenzene[10] (7g) (Table 1, row 1, column 2). The general procedure was employed using 1-bromo-2,4-dimethylbenzene (185 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (475 mg, 1.5 mmol), and JackiePhos (80 mg, 0.1 mmol). A colorless liquid (125 mg, 74%) was isolated by column chromatography (97.5:2.5 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.08 (d, J = 8 Hz, 1H), 6.98 (m, 2H), 2.84 (m, 1H), 2.29 (s, 6H), 1.58 (m, 2H), 1.18 (d, J = 6.5 Hz, 3H), 0.86 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.1, 135.5, 134.9, 131.2, 127.0, 125.4, 36.1, 30.8, 21.5, 21.1, 19.7, 12.5 ppm.



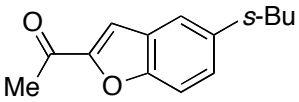
1-(*sec*-Butyl)-3-(trifluoromethoxy)benzene (7h) (Table 1, row 2, column 2). The general procedure was employed using bromo-3-(trifluoromethoxy)benzene (241 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (348 mg, 1.1 mmol), JackiePhos (48 mg, 0.06 mmol). A colorless liquid (152.4, 73%) was isolated by column chromatography (98.5:1.5 Hex/Ether). ^{1}H NMR (500 MHz $CDCl_3$): δ 7.30 (t, J = 7.5 Hz, 1H), 7.18 (d, J = 7.5 Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 7.02 (s, 1H), 2.62 (m,1H), 1.59 (m, 2H), 1.24 (d, J = 6.5 Hz, 3H), 0.83 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.3, 142.0, 129.7, 125.7, 120.5, 119.8, 118.3, 41.7, 31.2, 21.8, 12.3 ppm. HRMS (EI^+): Calcd (M^+) 218.0918; Found 218.0919.



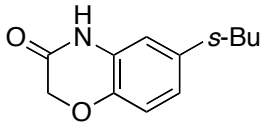
1-(*sec*-Butyl)-4-nitrobenzene[11] (7i) (Table 1, row 3, column 2). The general procedure was employed using 1-chloro-4-nitrobenzene (158 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (475 mg, 1.5 mmol), and JackiePhos (80 mg, 0.1 mmol). An oily, yellow liquid (168 mg, 93%) was isolated by column chromatography (99:1 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, J = 9 Hz, 2H), 7.33 (d, J = 8.5 Hz, 2H), 2.73 (M, 1H), 1.63 (m, 2H), 1.27 (d, J = 7 Hz, 3H), 0.83 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7, 146.5, 128.1, 123.8, 42.0, 31.1, 21.7, 12.3 ppm.



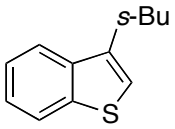
4-(*sec*-Butyl)benzonitrile[9] (7j) (Table 1, row 4, column 2). The general procedure was employed using 4-chlorobenzonitrile (138 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (475 mg, 1.5 mmol), and JackiePhos (80 mg, 0.1 mmol). An oily, yellow solid (125.8 mg, 79%) was isolated by column chromatography (99:1 Hex/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 2.67 (M, 1H), 1.61 (m, 2H), 1.25 (d, *J* = 7 Hz, 3H), 0.83 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 132.4, 128.1, 119.4, 109.8, 42.1, 31.0, 21.6, 12.2 ppm.



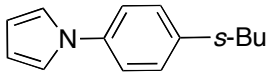
2-Acetyl-(5-(*sec*-butyl)benzofuran (7k) (Table 1, row 5, column 2). The general procedure was employed using 2-Acetyl-5-bromobenzofuran (239 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (348 mg, 1.1 mmol), and JackiePhos (48 mg, 0.06 mmol). A pale yellow solid (175 mg, 82%) was isolated by column chromatography (97:3 Hex/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46-7.50 (m, 3H), 7.31 (dd, *J* = 8.5, 2.0 Hz, 1H), 2.71 (m, 1H), 2.60 (s, 3H), 1.63 (m, 2H), 1.28 (d, *J* = 7 Hz, 3H), 0.83 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.9, 165.3, 154.7, 143.8, 128.2, 127.3, 121.1, 113.3, 112.3, 41.8, 31.7, 26.6, 22.5, 12.4 ppm. HRMS (EI^+): Calcd (M^+) 216.1150; Found 216.1141.



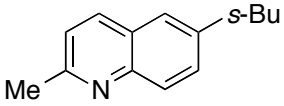
6-(*sec*-Butyl)-2*H*-benzo[*b*][1,4]oxazin-3(4*H*)-one[12] (7l) (Table 1, row 1, column 3). The general procedure was employed using 6-bromo-2*H*-benzo[*b*][1,4]oxarin-3(4*H*)-one (228 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (475 mg, 1.5 mmol), and JackiePhos (80 mg, 0.1 mmol). A pale yellow solid (133 mg, 67%) was isolated by column chromatography (80:20 Hex/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.43 (br s, 1H) 6.89 (d, *J* = 8 Hz, 1H), 6.79 (dd, *J* = 8, 2 Hz, 1H), 6.65 (s, 1H), 4.61(s, 2H), 2.53 (m, 1H), 1.55 (m, 2H), 1.20 (d, *J* = 7 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.3, 142.8, 141.8, 126.0, 122.7, 116.5, 115.0, 67.3, 41.2, 31.3, 22.1, 12.4 ppm.



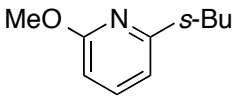
3-(*sec*-Butyl)thionaphthene[13] (7m) (Table 1, row 2, column 3). The general procedure was employed using 3-bromothionaphthene (213 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (475 mg, 1.5 mmol), and JackiePhos (80 mg, 0.1 mmol). A colorless liquid (85.5 mg, 45%) was isolated by column chromatography (99:1 Hex/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.87 (d, J = 7.5 Hz, 1H), 7.80 (d, J = 8 Hz, 1H), 7.37 (m, 2H), 7.09 (s, 1H), 3.12 (m, 1H), 1.86 (m, 1H), 1.68 (m, 1H), 1.37 (d, J = 7 Hz, 3H), 0.95 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.7, 140.9, 139.0, 124.2, 123.8, 123.1, 122.1, 119.7, 34.8, 30.0, 20.5, 12.2 ppm.



1-(4-(*sec*-Butyl)phenyl)-1*H*-pyrrole[8] (7n) (Table 1, row 3, column 3). The general procedure was employed using 1-(4-bromophenyl)-1*H*-pyrrole (222 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (348 mg, 1.1 mmol), and JackiePhos (48 mg, 0.06 mmol). A brown liquid (131 mg, 77%) was isolated by column chromatography (99:1 Hex/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 8.5 Hz, 2H), 7.08 (t, J = 2 Hz, 2H), 6.35 (t, J = 2 Hz, 2H), 2.64 (m, 1H), 1.62 (m, 2H), 1.27 (d, J = 7 Hz, 3H), 0.86 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.4, 138.9, 128.2, 120.8, 119.6, 110.2, 41.3, 31.4, 22.1, 12.4 ppm.

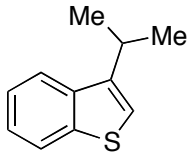


6-(*sec*-Butyl)-2-methylquinoline (7o) (Table 1, row 4, column 3). The general procedure was employed using 6-bromo-2-methylquinoline (222 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (348 mg, 1.1 mmol), and JackiePhos (48 mg, 0.06 mmol). A yellow liquid (172 mg, 86%) was isolated by column chromatography (95:5 Hex/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 8.5 Hz, 1H), 7.51-7.56 (m, 2H), 7.24 (d, J = 8.5 Hz, 1H), 2.77 (m, 1H), 2.72 (s, 3H), 1.68 (m, 2H), 1.32 (d, J = 7.0 Hz, 3H), 0.84 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.2, 147.1, 145.2, 136.0, 129.6, 128.7, 126.7, 124.9, 122.0, 41.8, 31.3, 25.5, 22.0, 12.4 ppm. HRMS (EI^+): Calcd (M^+) 199.1361; Found 199.1359.

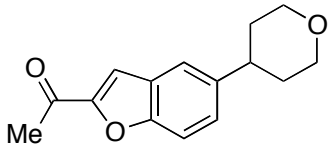


2-(*sec*-Butyl)-6-methoxypyridine (7p) (Table 1, row 5, column 3). The general procedure was employed using 2-bromo-6-methoxypyridine (188 mg, 1 mmol), 5-(*sec*-butyl)-1-aza-5-stannabicyclo[3.3.3]undecane (475 mg, 1.5 mmol), and JackiePhos (80 mg, 0.1 mmol). A colorless liquid (92.5 mg, 56%) was isolated by column chromatography (99:1 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (t, J = 7.5 Hz,

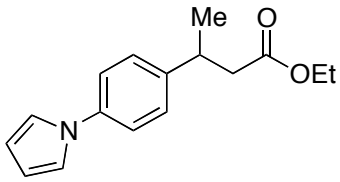
1H), 6.67 (d, J = 7.5 Hz, 1H), 6.52 (d, J = 8 Hz, 1H), 3.92 (s, 3H), 2.66 (m, 1H), 1.76 (m, 1H), 1.57 (m, 1H), 1.25 (d, J = 6.5 Hz, 3H), 0.83 (t, J = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.6, 163.8, 138.7, 114.3, 107.3, 53.3, 43.4, 29.8, 20.4, 12.3 ppm. HRMS (EI^+): Calcd (M^+) 165.1154; Found 165.1154.



3-Isopropylthionaphthene[14] (9b) (Table 2, row 1, column 1). The general procedure was employed using 3-bromothionaphthene (107 mg, 0.5 mmol), 5-(*iso*-Propyl)-1-aza-5-stannabicyclo[3.3.3]undecane (166 mg, 0.55 mmol), and JackiePhos (24 mg, 0.03 mmol). A colorless liquid (125 mg, 71%) was isolated by column chromatography (99.5:0.5 Hex/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.86 (dd, J = 8, 0.5 Hz, 1H), 7.80 (dd, J = 8, 0.5 Hz, 1H), 7.36 (m, 2H), 7.10 (s, 1H), 3.32 (septet, J = 7 Hz, 1H), 1.39 (d, J = 7 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.9, 141.0, 138.8, 124.3, 123.9, 123.1, 122.1, 119.1, 28.1, 23.0 ppm.

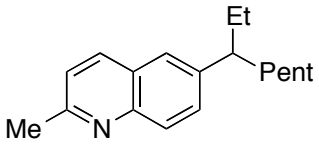


2-Acetyl-(5-(tetrahydro-2H-pyran-4-yl)benzofuran (9c) (Table 2, row 2, column 1). The general procedure was employed using 2-Acetyl-5-bromobenzofuran (120 mg, 0.5 mmol), 5-(tetrahydro-2H-pyran-4-yl)-1-aza-5-stannabicyclo[3.3.3]undecane (189 mg, 0.55 mmol), and JackiePhos (24 mg, 0.03 mmol). A brown solid (103 mg, 85%) was isolated by column chromatography (70:30 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51-7.53 (m, 2H), 7.47 (s, 1H), 7.36 (dd, J = 8.5, 1.5 Hz, 1H), 4.12 (dd, J = 11.0, 3.5 Hz, 2H), 3.55 (td, J = 11.5, 2.0 Hz, 2H), 2.86 (m, 1H), 2.60 (s, 3H), 1.79-1.90 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.5, 154.6, 153.0, 141.9, 127.8, 127.3, 120.6, 113.1, 112.4, 68.4, 41.5, 34.4, 26.5 ppm. HRMS (FAB^+): Calcd $(M+H)^+$ 245.1178; Found 245.1187.

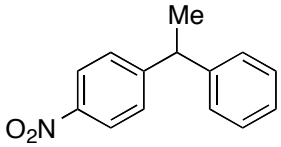


Ethyl 3-(4-(1H-pyrrol-1-yl)phenyl)butanoate (9d) (Table 2, row 3, column 1). The general procedure was employed using 1-(4-bromophenyl)-1*H*-pyrrole (111 mg, 0.5

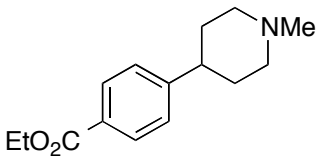
mmol), and ethyl 3-(1-aza-5-stannabicyclo[3.3.3]undecan-5-yl)butanoate (206 mg, 0.55 mmol), and JackiePhos (24 mg, 0.03 mmol). A reddish brown oil (104 mg, 81%) was isolated by column chromatography (92:8 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 7.06 (t, *J* = 2.0 Hz, 2H), 6.33 (t, *J* = 2.0 Hz, 2H), 4.09 (quartet, *J* = 7.0 Hz, 2H), 3.31 (m, 1H), 2.54-2.64 (m, 2H), 1.32 (d, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.4, 143.4, 139.4, 128.1, 120.9, 119.5, 110.4, 60.5, 43.2, 36.2, 22.1, 14.4 ppm. HRMS (FAB^+): Calcd (M^+) 257.1416; Found 257.1424.



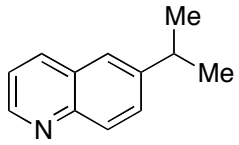
2-Methyl-6-(octan-3-yl)quinoline (9e) (Table 2, row 4, column 1). The general procedure was employed using 6-bromo-2-methylquinoline (111 mg, 0.5 mmol), 5-(octan-3-yl)-1-aza-5-stannabicyclo[3.3.3]undecane (279 mg, 0.75 mmol), and JackiePhos (40 mg, 0.05 mmol). An oily, yellow solid (128 mg, 100%) was isolated by column chromatography (80:20 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (t, *J* = 9.0 Hz, 2H), 7.50 (dd, *J* = 8.5, 2 Hz, 1H), 7.47 (d, *J* = 2.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 2.72 (s, 3H), 2.56 (m, 1H), 1.57-1.83 (m, 4H), 1.15-1.27 (m, 6H), 0.80 (t, *J* = 6.5 Hz, 3H), 0.76 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.2, 147.1, 143.7, 136.0, 129.7, 128.6, 126.6, 126.0, 122.0, 48.0, 36.7, 32.2, 29.8, 27.5, 25.5, 22.7, 14.3, 12.4 ppm. HRMS (FAB^+): Calcd $(M+H)^+$ 256.2065; Found 256.2063.



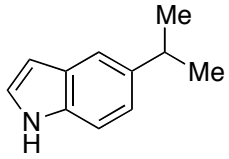
1-Nitro-4-(1-phenylethyl)benzene[15] (9f) (Table 2, row 1, column 2). The general procedure was employed 1-bromo-4-nitrobenzene (101 mg, 0.5 mmol), 5-(1-phenylethyl)-1-aza-5-stannabicyclo[3.3.3]undecane (273 mg, 0.75 mmol), and JackiePhos (40 mg, 0.05 mmol). A brownish liquid (104.5 mg, 92%) was isolated by column chromatography (99:1 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.18 (dd, *J* = 8.5, 2.0 Hz, 2H), 7.41-7.22 (m, 7H), 4.29 (quartet, *J* = 7.5 Hz, 1H), 1.72 (d, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.2, 146.6, 144.7, 128.9, 128.6, 127.7, 126.9, 123.9, 44.9, 21.7 ppm. HRMS (EI^+): Calcd (M^+) 227.0946; Found 227.0947.



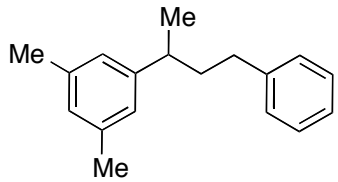
Ethyl 4-(1-methylpiperidin-4-yl)benzoate (9g) (Table 2, row 2, column 2). The general procedure was employed using ethyl 4-bromobenzoate (115 mg, 0.5 mmol), 5-(1-methylpiperidin-4-yl)-1-aza-5-stannabicyclo[3.3.3]undecane (268 mg, 0.75 mmol), and JackiePhos (40 mg, 0.05 mmol). A brown solid (94 mg, 76%) was isolated by column chromatography (91:9 CH_2Cl_2/MeOH). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 8 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 4.33 (quartet, J = 7.0 Hz, 2H), 3.27 (d, J = 6.0 Hz, 2H), 2.65 (m, 1H), 2.56 (s, 3H), 2.48 (t, J = 11.0 Hz, 2H), 2.15 (m, 2H), 1.91 (d, J = 13.0 Hz, 2H), 1.35 (t, J = 7.0 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.5, 149.7, 130.1, 129.2, 127.0, 61.0, 55.6, 45.1, 41.1, 31.6, 14.5 ppm. HRMS (FAB^+): Calcd $(M+H)^+$ 248.1651; Found 248.1655.



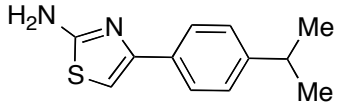
6-Isopropylquinoline (9h) (Table 2, row 3, column 2). The general procedure was employed using quinolin-6-yl trifluoromethanesulfonate (139 mg, 0.5 mmol), 5-(*iso*-propyl)-1-aza-5-stannabicyclo[3.3.3]undecane (166 mg, 0.55 mmol), and JackiePhos (24 mg, 0.03 mmol). A yellow liquid (74.2 mg, 88%) was isolated by column chromatography (90:10 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.84 (dd, J = 4.0, 2.0 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 8.5 Hz, 1H), 7.62 (dd, J = 8.5, 2.0 Hz, 1H), 7.60 (s, 1H), 7.35 (dd, J = 8.5, 4.0 Hz, 1H), 3.10 (septet, J = 7.0 Hz, 1H), 1.34 (d, J = 7.0 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.8, 147.4, 147.3, 135.9, 129.6, 129.5, 128.5, 124.0, 121.2, 34.3, 24.0 ppm.



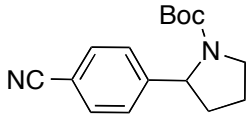
5-Isopropyl-1H-indole[8] (9i) (Table 2, row 4, column 2). The general procedure was employed using 3-iodo-1*H*-indole (122 mg, 0.5 mmol), 5-(*iso*-propyl)-1-aza-5-stannabicyclo[3.3.3]undecane (166 mg, 0.55 mmol), and JackiePhos (24 mg, 0.03 mmol). A reddish brown solid (48 mg, 60%) was isolated by column chromatography (92:8 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (br s, 1H), 7.53 (s, 1H), 7.33 (d, J = 8.5 Hz, 1H), 7.18 (t, J = 3.0 Hz, 1H), 7.10 (dd, J = 7.0, 1.5 Hz, 1H), 6.54 (s, 1H), 3.05 (m, 1H), 1.35 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.7, 134.5, 128.2, 124.5, 121.5, 117.8, 111.0, 102.6, 34.4, 24.9 ppm.



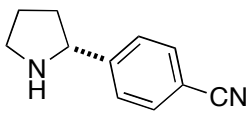
1,3-Dimethyl-5-(4-phenylbutan-2-yl)benzene[8] (9j) (Table 2, row 1, column 3). The general procedure was employed using 1-bromo-3,5-dimethylbenzene (93 mg, 0.5 mmol), 5-(4-phenylbutan-2-yl)-1-aza-5-stannabicyclo[3.3.3]undecane (294 mg, 0.75 mmol), and JackiePhos (40 mg, 0.05 mmol). A colorless liquid (104 mg, 87%) was isolated by column chromatography (99.7:0.3 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (t, *J* = 7 Hz, 2H), 7.18-7.22 (m, 3H), 6.88 (s, 1H), 6.86 (s, 2H), 2.69 (m, 1H), 2.60 (m, 2H), 2.35 (s, 6H), 1.95 (m, 2H), 1.30 (d, *J* = 7 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.6, 142.9, 138.0, 128.6, 128.4, 127.8, 125.8, 125.1, 40.2, 39.6, 34.3, 22.7, 21.6 ppm.



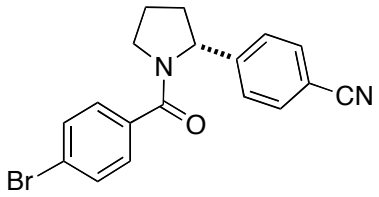
2-Amino-4-(4-isopropylphenyl)thiazole[16] (9k) (Table 2, row 2, column 3). The general procedure was employed using 2-amino-4-(4-bromophenyl)thiazole (128 mg, 0.5 mmol), 5-(*iso*-propyl)-1-aza-5-stannabicyclo[3.3.3]undecane (302 mg, 1 mmol), and JackiePhos (40 mg, 0.05 mmol). A brown oil (30.5 mg, 28%) was isolated by column chromatography (75:25 Hex/EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.67 (s, 1H), 5.06 (br s, 2H), 2.92 (septet, *J* = 7.0 Hz, 1H), 1.26 (d, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.5, 151.6, 148.8, 132.5, 126.9, 126.2, 102.3, 34.1, 24.1 ppm.



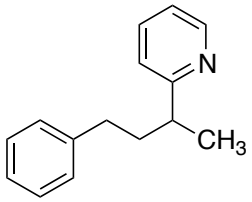
***tert*-Butyl 2-(4-cyanophenyl)pyrrolidine-1-carboxylate[6] (9l)** (Table 2, row 3, column 3). The general procedure was employed using 4-bromobenzonitrile (91 mg, 0.5 mmol) *tert*-butyl 2-(1-aza-5-stannabicyclo[3.3.3]undecan-5-yl)pyrrolidine-1-carboxylate (429 mg, 1 mmol), and JackiePhos (40 mg, 0.05 mmol). A white solid (85 mg, 63%) was isolated by column chromatography (70:30 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$) (two rotamers in a ratio of 3:2 were observed – major rotomer given): δ 7.60 (d, *J* = 8 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 4.80 (m, 1H), 3.50-3.64 (m, 2H), 2.37 (m, 1H), 1.78-1.89 (m, 3H), 1.18 (s, 9H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) (two rotamers were observed – minor rotomer in parentheses): δ 154.3 (154.3), 151.0 (149.0), 132.3 (132.4), 126.4 (126.4), 119.1 (119.1), 110.6 (110.6), 79.9 (83.0), 61.3 (60.3), 47.3 (48.3), 36.1 (34.1), 28.3 (28.3), 23.4 (23.7) ppm.



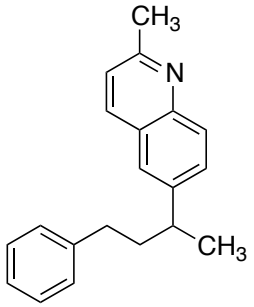
(*R*)-4-(Pyrrolidin-2-yl)benzonitrile.[17] To a solution of *t*-butyl 2-(4-cyanophenyl)pyrrolidine-1-carboxylate (54.5 mg, 0.2 mmol) in CH_2Cl_2 (1 mL) at 0 ºC, trifluoroacetic acid (114 mg, 1.0 mmol) in CH_2Cl_2 (1 mL) was added dropwise. After having stirred for 3h, the reaction was quenched with saturated aqueous $NaHCO_3$ solution. The resulting mixture was extracted CH_2Cl_2 (3x). The combined CH_2Cl_2 layers were washed with brine and dried over Na_2SO_4. A pale yellow oil was obtained (26.9 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 4.20 (t, *J* = 6.0 Hz, 1H), 3.17 (m, 1H), 3.06 (m, 1H), 2.87 (br, 1H), 2.22 (m, 1H), 1.89 (m, 2H), 1,62 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.9, 132.2, 127.6, 119.3, 110.6, 61.9, 53.8, 29.9, 25.7 ppm.



(*R*)-4-(1-(4-Bromobenzoyl)pyrrolidin-2-yl)benzonitrile (11). 4-(Pyrrolidin-2-yl)benzonitrile (8.5 mg, 0.05 mmol) and triethylamine (5 mg, 0.05 mmol) were dissolved into CH_2Cl_2 (2.0 mL) and cooled to 0 ºC. 4-Bromobenzoyl chloride (8.8 mg, 0.04 mmol) was added, and the reaction mixture was stirred for 3h. The mixture was concentrated and a white solid was isolated by column chromatography (60:40 Hex/Ether) quantitatively determined by calibrated GC analysis. ^{1}H NMR for the major rotomer ($CDCl_3$): δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 5.27 (t, *J* = 7.5 Hz, 1H), 3.67-3.79 (m, 2H), 2.50 (m, 1H), 1.85-2.04 (m, 3H). ^{13}C NMR for the major rotomer: δ 169.3, 148.7, 135.2, 132.7, 131.8, 129.4, 126.6, 125.2, 119.1, 111.0, 61.5, 51.5, 34.9, 25.7 ppm.



2-(4-Phenylbutan-2-yl)pyridine (13b). The general procedure was employed using 2-bromopyridine (79 mg, 0.5 mmol), 5-(4-phenylbutan-2-yl)-1-aza-5 stannabicyclo[3.3.3]undecane (294 mg, 0.75 mmol), and JackiePhos (40 mg, 0.05 mmol). A colorless liquid (68.3 mg, 64.6%) was isolated by column chromatography (10:90 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.60 (m, 1H), 7.63 (m, 1H), 7.12-7.29 (m, 7H), 2.96 (q, J = 7 Hz, 1H), 2.58 (m, 2H), 2.15 (m, 1H), 1.95 (m, 1H), 1.36 (d, J = 7 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.3, 149.5, 142.6, 136.5, 128.6, 128.4, 125.8, 121.9, 121.3, 41.8, 38.9, 34.1, 21.1 ppm. HRMS (FAB^+): Calcd $(M+H)^+$ 212.1429; Found 212.1439. E.e. (91.2%) was determined using a ChiralCel OJ-3 column with 95:5 hexanes:isopropanol as eluent.



2-Methyl-6-(4-phenylbutan-2-yl)quinolone (13c). The general procedure was employed using 6-bromo-2-methylquinoline (111 mg, 0.5 mmol), 5-(4-phenylbutan-2-yl)-1-aza-5-stannabicyclo[3.3.3]undecane (294 mg, 0.75 mmol), and JackiePhos (40 mg, 0.05 mmol). A colorless liquid (89.2 mg, 64.8%) was isolated by column chromatography (10:90 Hex/Ether). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (m, 2H), 7.59 (m, 2H), 7.14-7.30 (m, 6H), 2.93 (q, J = 7 Hz, 1H), 2.77 (s, 3H), 2.56 (m, 2H), 2.05 (m, 2H), 1.39 (d, J = 7 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.4, 147.1, 144.8, 142.5, 136.0, 129.5, 128.9, 128.5, 128.5, 126.7, 125.9, 125, 122.1, 40.1, 39.6, 34.1, 25.5, 22.6 ppm. HRMS (FAB^+): Calcd $(M+H)^+$ 276.1754; Found 276.1752. E.e. (91.7%) was determined using a ChiralCel OJ-3 column with 95:5 hexanes:isopropanol as eluent.

References

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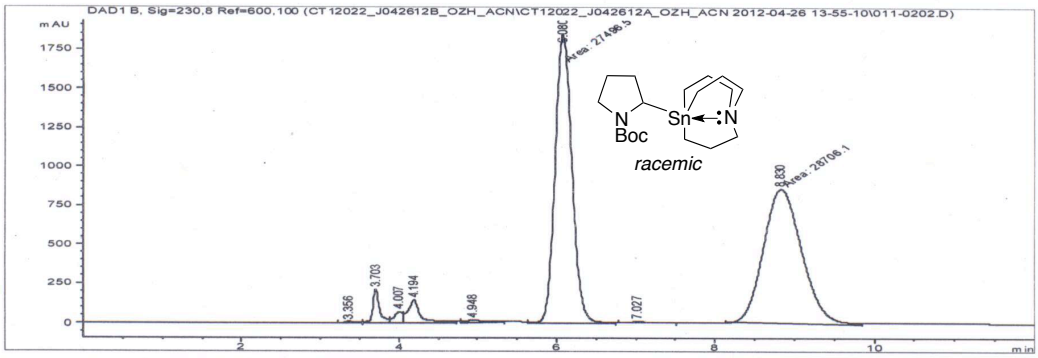
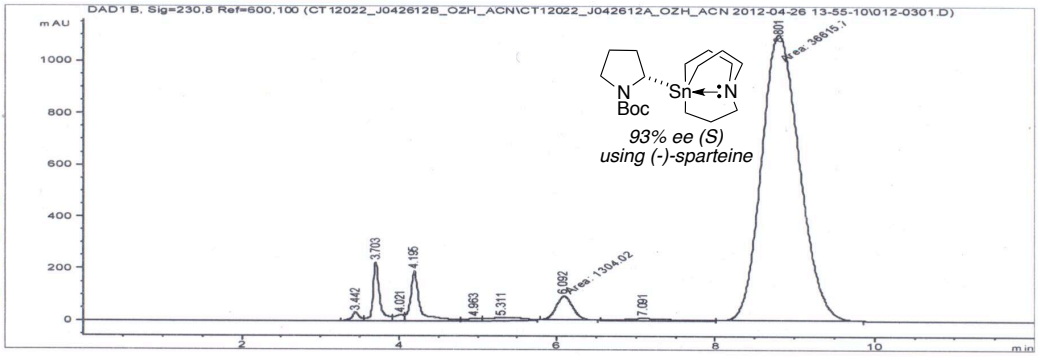
*Optically active stannatrane (**8**) prepared using Beak's enantioselective deprotonation method:*

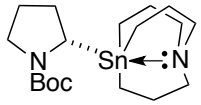


CT12022 (CCNY), racemate. OZH, acetonitrile, 1 ml./min., 25 deg. C. (5.0 mg./ ml. solution, 20 uL injection).



CT12022B (CCNY), optically active sample: E.e.: 93.2 %. (5.0 mg./ml. solution, 20 uL injection).

*Separation of enantiomers of **8** via preparatory chiral HPLC:*



99+% ee (S)

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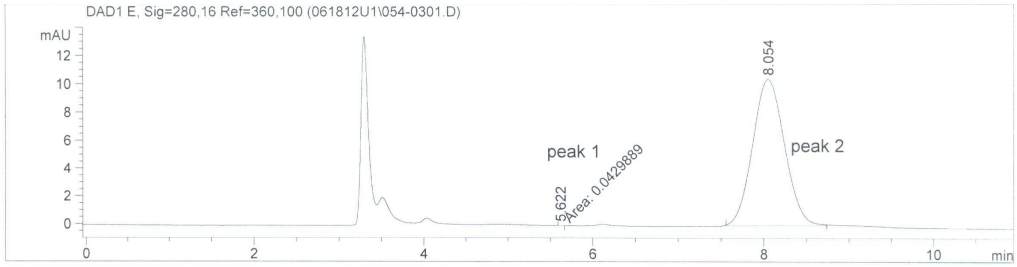
100% ACN

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Use Multiplier & Dilution Factor with ISTDs


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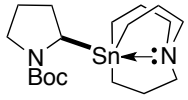

99+% ee (R)

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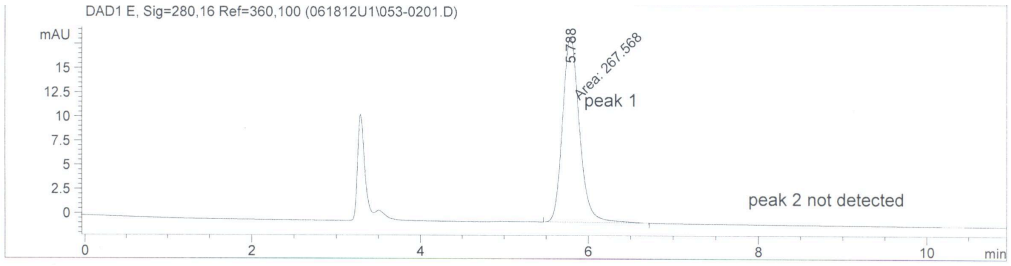


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================================================================================
                            Area Percent Report
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Use Multiplier & Dilution Factor with ISTDs


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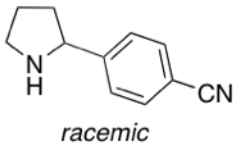
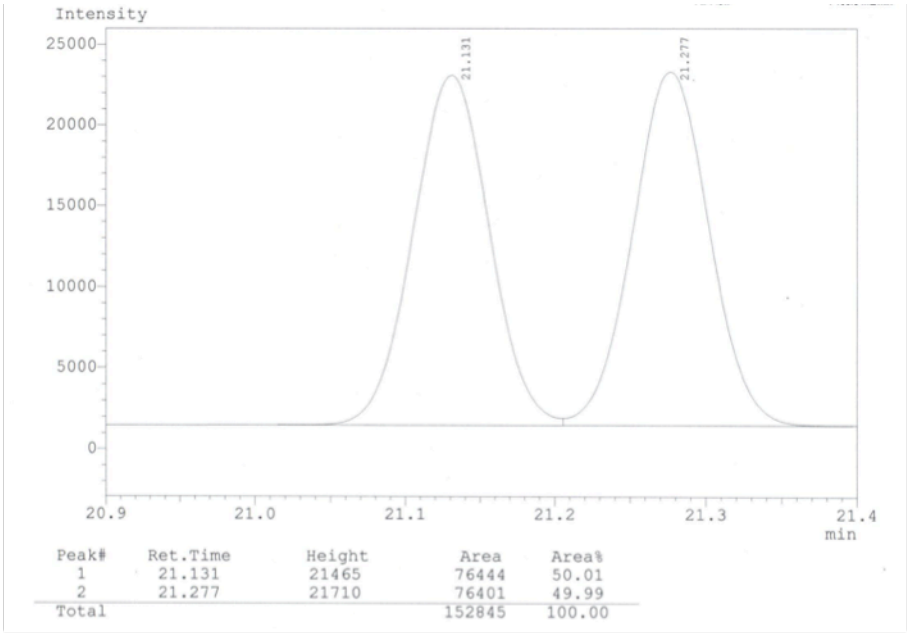
*Chiral GC of cross-coupling reaction using 99% ee pyrrolidine stannatrane (**8**) (after Boc deprotection)*



racemic



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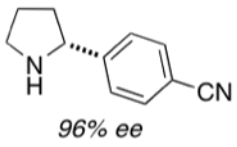
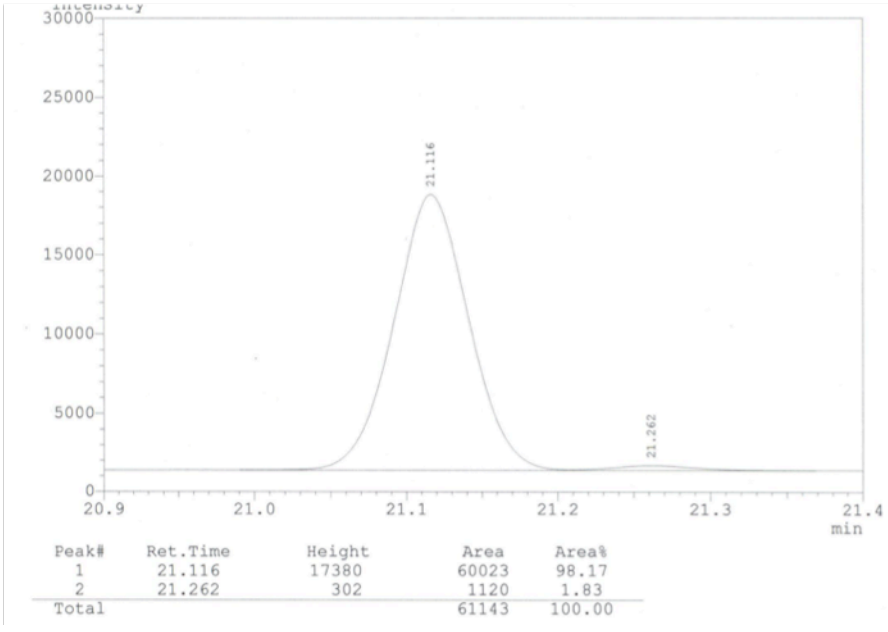
1	21.131	21465	76444	50.01
2	21.277	21710	76401	49.99
Total			152845	100.00



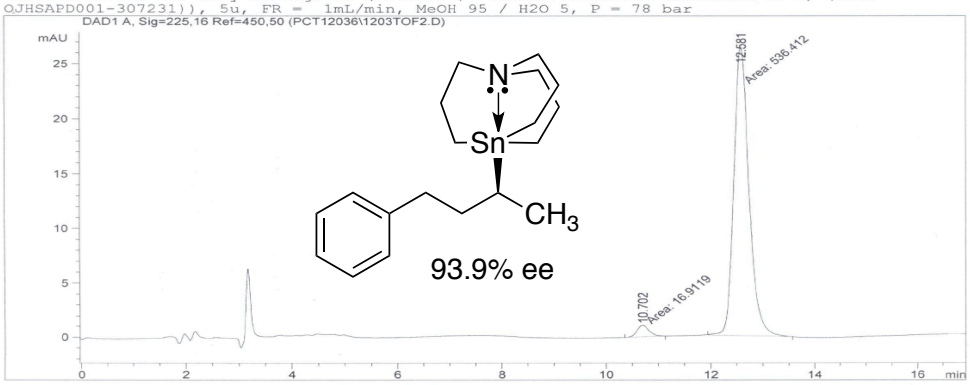
96% ee



Peak#	Ret.Time	Height	Area	Area%
1	21.116	17380	60023	98.17
2	21.262	302	1120	1.83
Total			61143	100.00

*Separation of enantiomers of **11** via preparatory chiral HPLC:*

Check fraction for City College NY (PCT12036). Column:0.46x25cm CHIRALCEL OJ-H, (Lot# OJHSAPD001-307231)), 5u, FR = 1mL/min, MeOH 95 / H2O 5, P = 78 bar



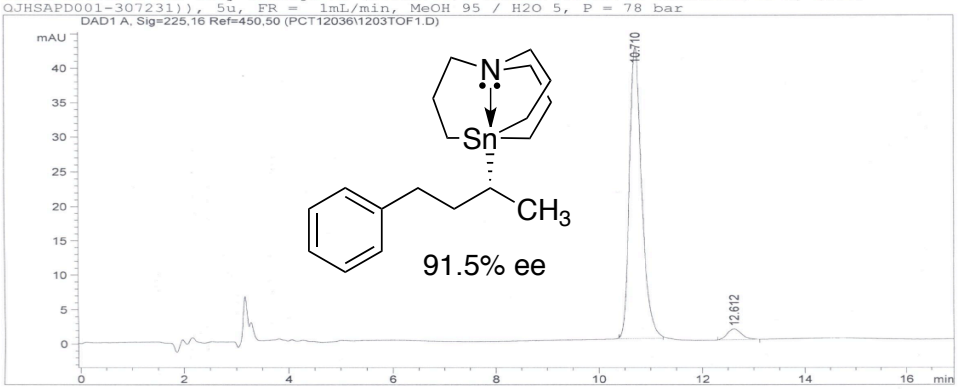
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=225,16 Ref=450,50

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.702	MM	0.2647	16.91189	1.06481	3.0564
2	12.581	MM	0.3386	536.41187	26.40066	96.9436

Check fraction for City College NY (PCT12036). Column:0.46x25cm CHIRALCEL OJ-H, (Lot# OJHSAPD001-307231)), 5u, FR = 1mL/min, MeOH 95 / H2O 5, P = 78 bar



Area Percent Report

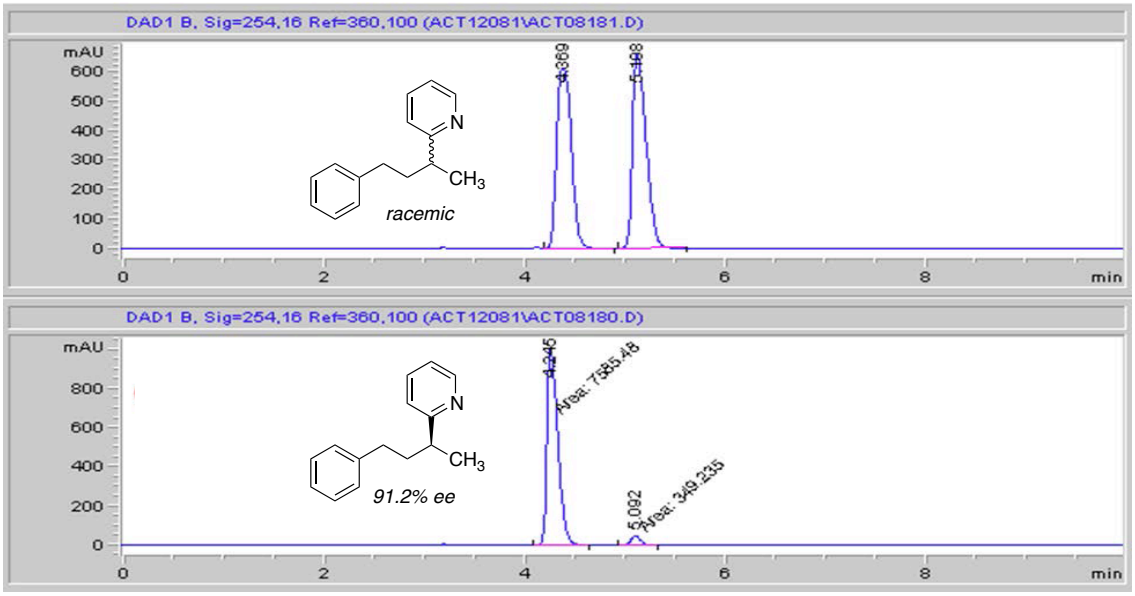
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=225,16 Ref=450,50

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.710	BB	0.2537	702.60809	42.31002	95.7986
2	12.612	BB	0.2966	30.81401	1.61521	4.2014

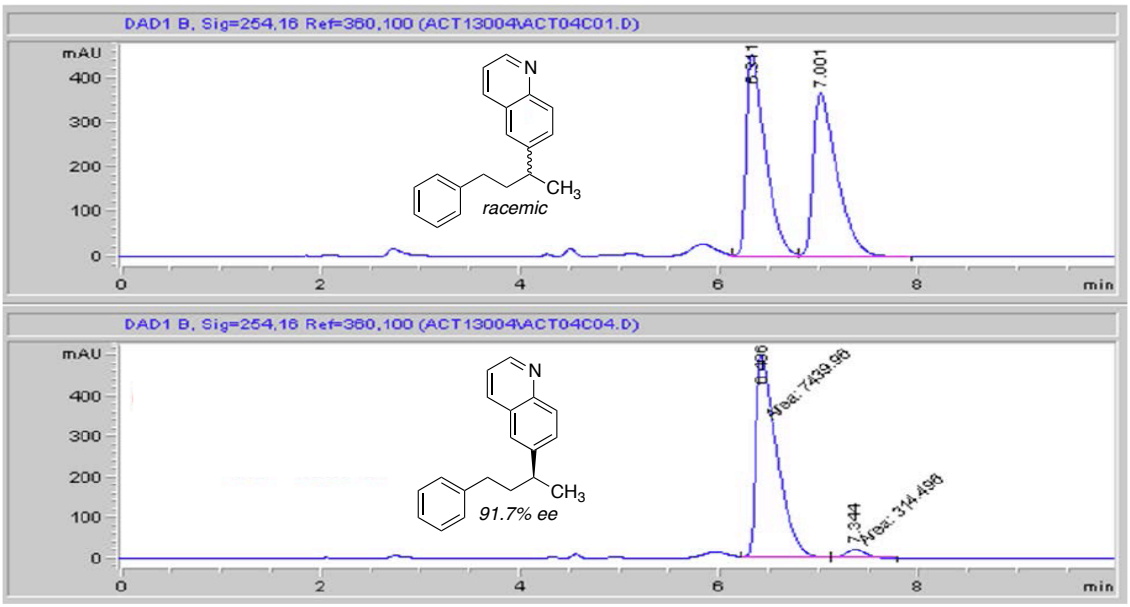
Note: Absolute configuration not determined for enantiomers of 11

*HPLC of product **13b** from reaction of 2-(4-Phenylbutan-2-yl)pyridine and optically-active **12** (93.9% ee)*

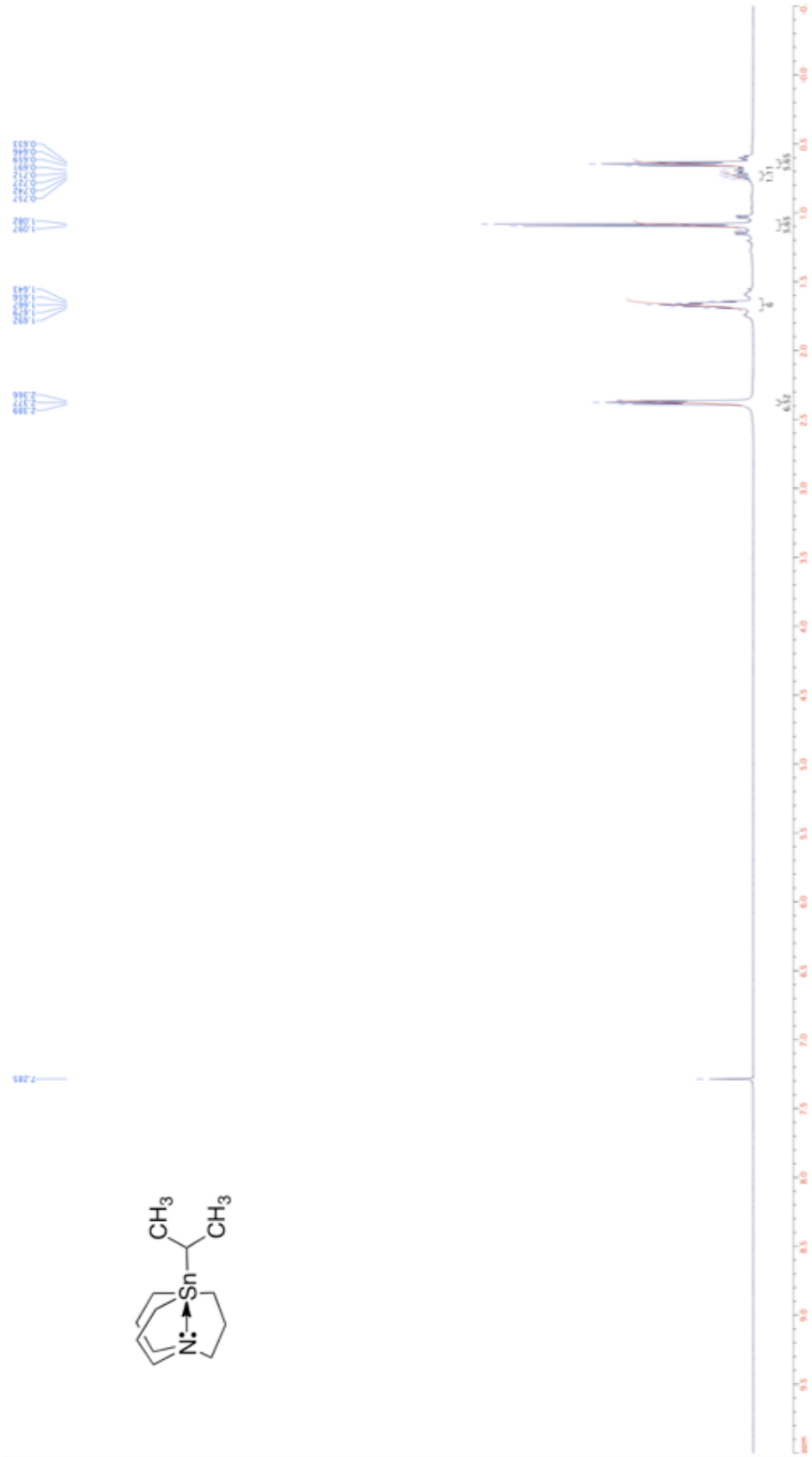


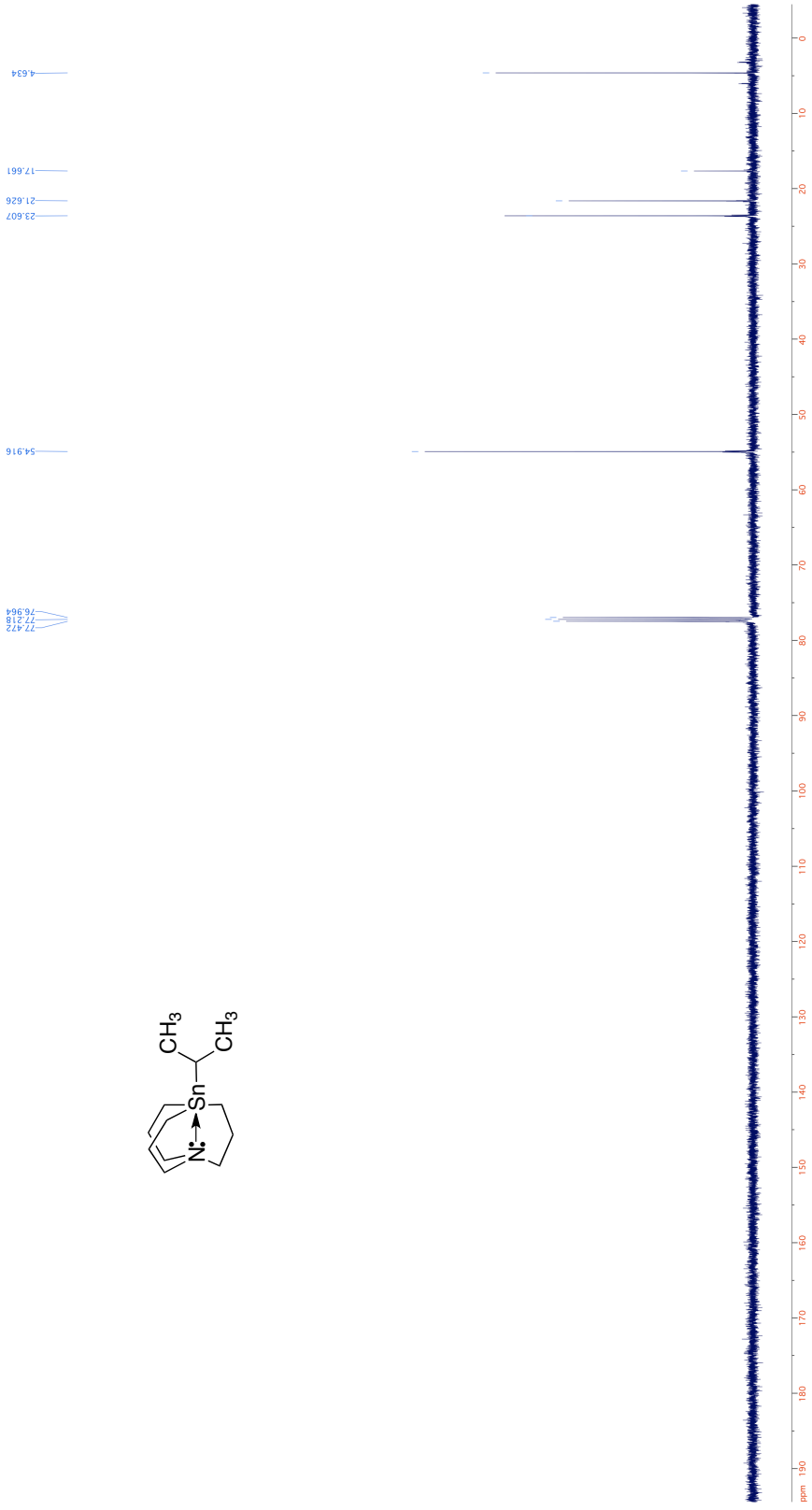
Chromatographic Conditions for the Separation of the Enantiomers of MRB-2-Pyridine on CHIRACEL OJ-3	
Column	CHIRALCEL OJ-3 (150 x 4.6 mm i.d., 3 micron) Part # 17524
Mobile Phase	Hexane/ Isopropanol 95:5
Flow Rate	1.0 mL/min
Detection	UV, 254 nm; ref 360 nm
Temperature	25°C
Sample	ca. 2.0 mg /mL in mobile phase
Inject. Volume	5.0 microL

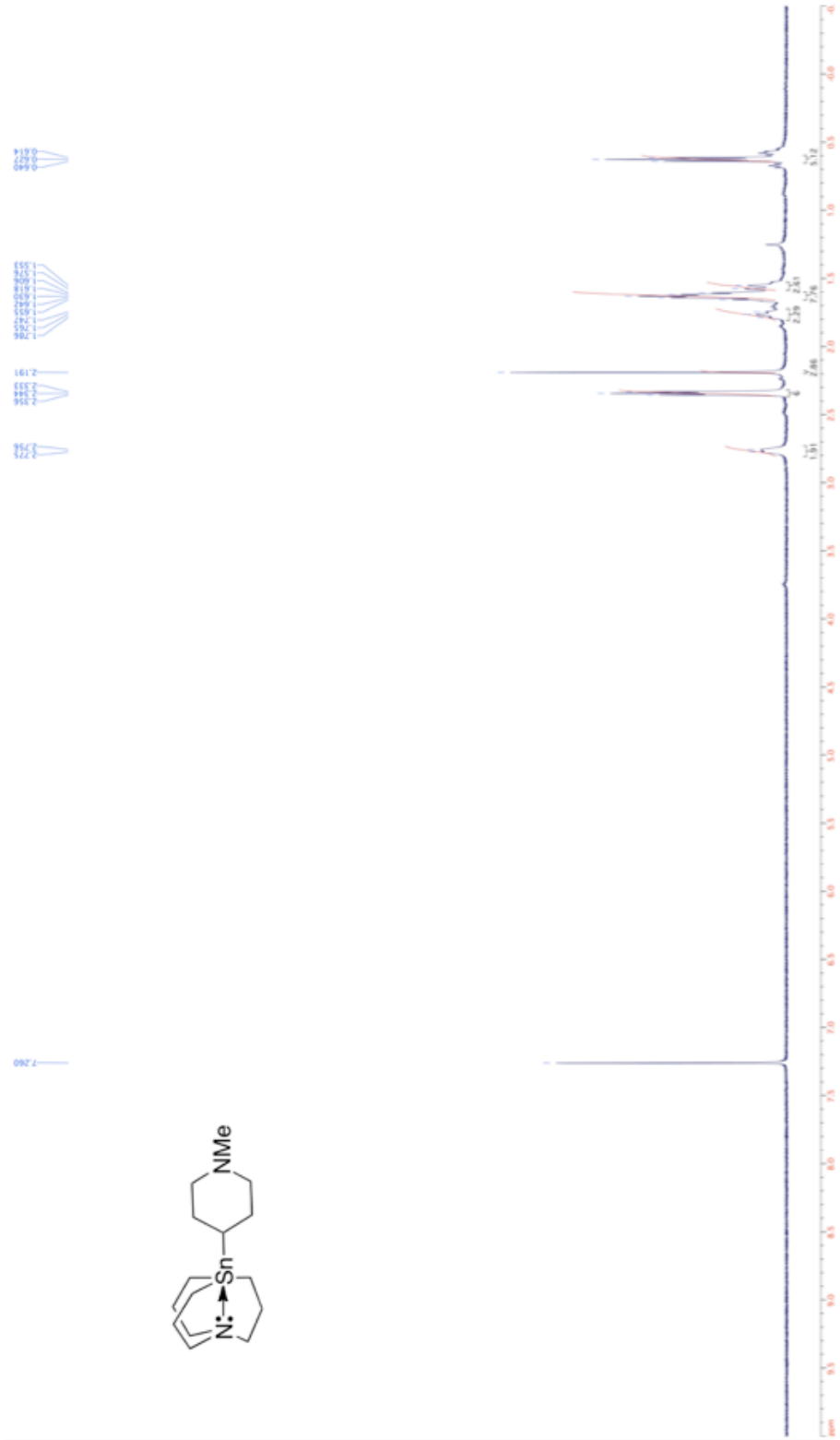
*HPLC of product **13c** from reaction of 2-Methyl-6-(4-phenylbutan-2-yl)quinolone and optically-active **12** (93.9% ee)*

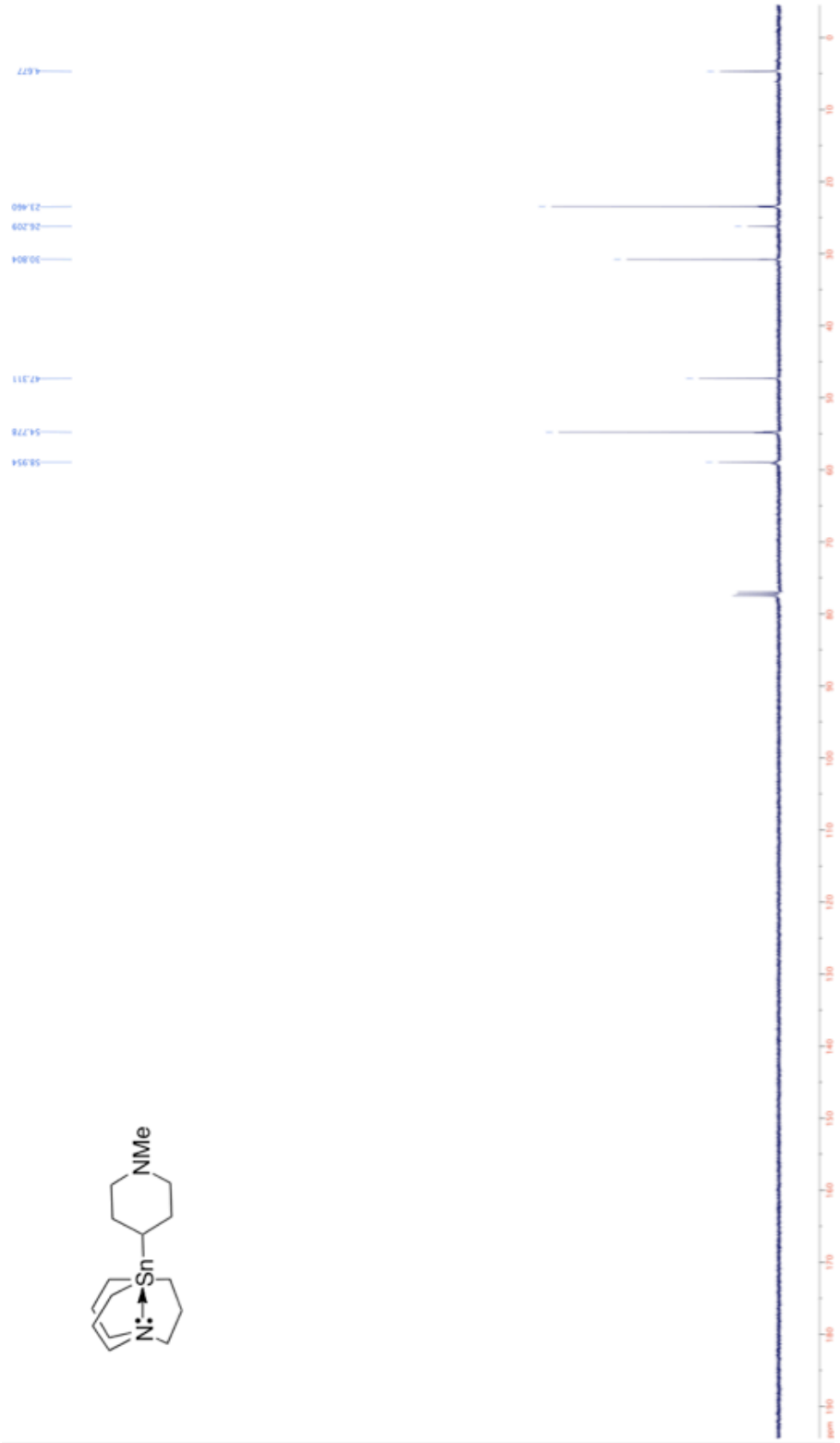


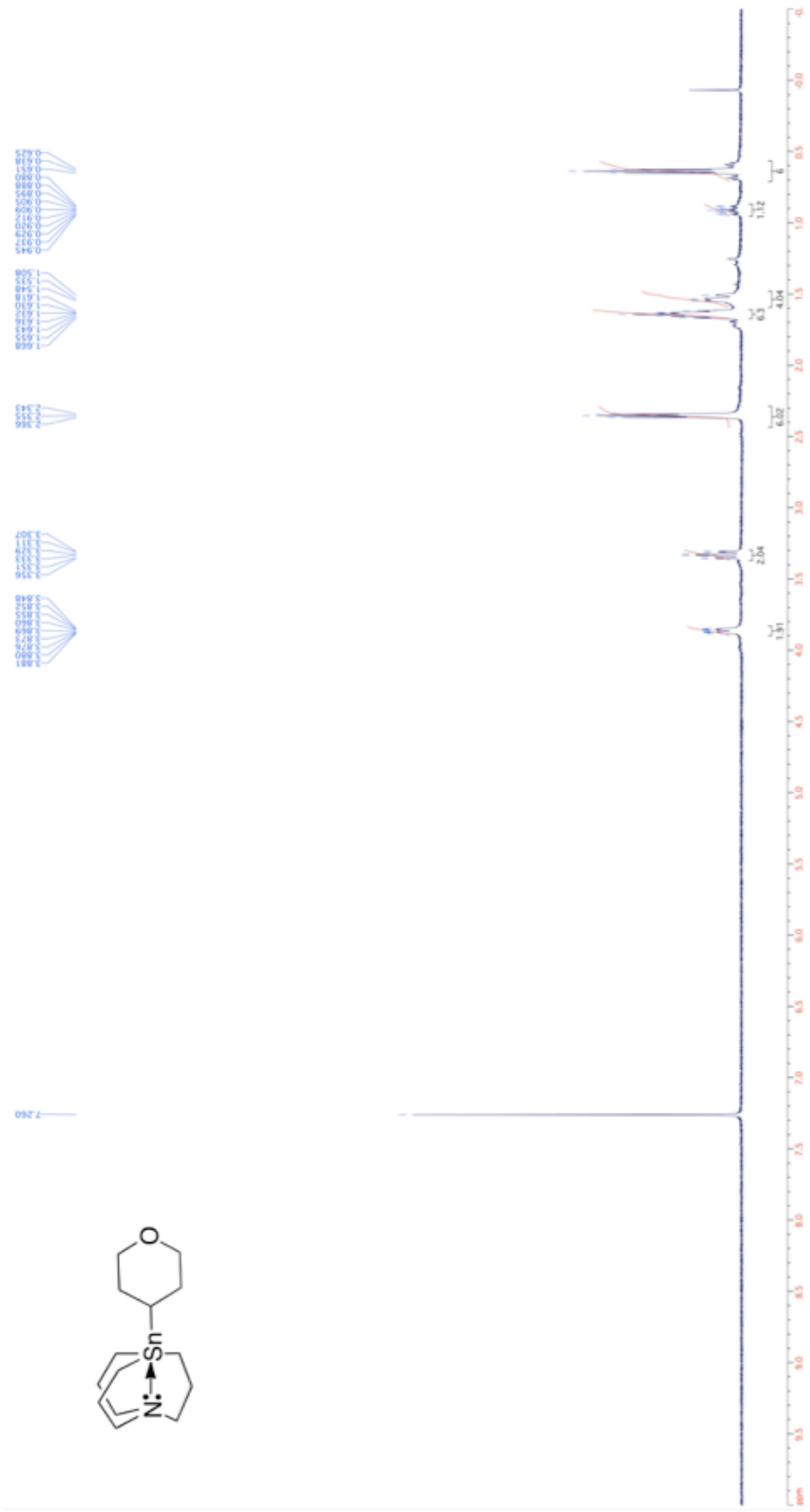
Chromatographic Conditions for the Separation of the Enantiomers of MRB-Quinoline on CHIRACEL OJ-3	
Column	CHIRALCEL OJ-3 (150 x 4.6 mm i.d., 3 micron) Part # 17524
Mobile Phase	Hexane/ Isopropanol 95:5
Flow Rate	1.0 mL/min
Detection	UV, 254 nm; ref 360 nm
Temperature	25°C
Sample	ca. 2.0 mg /mL in mobile phase
Inject. Volume	5.0 microL

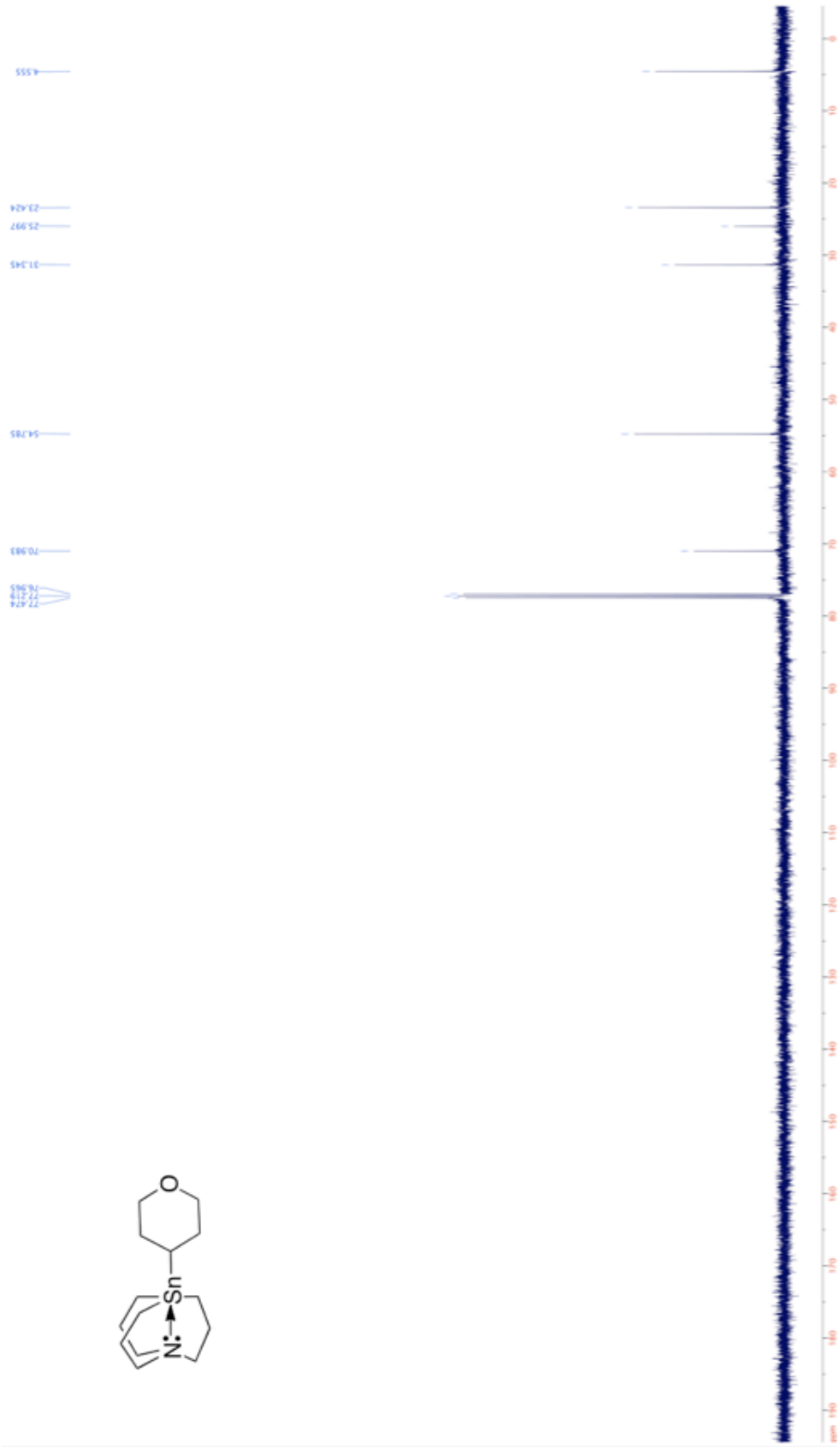

CH3
CH3
Sn
N:

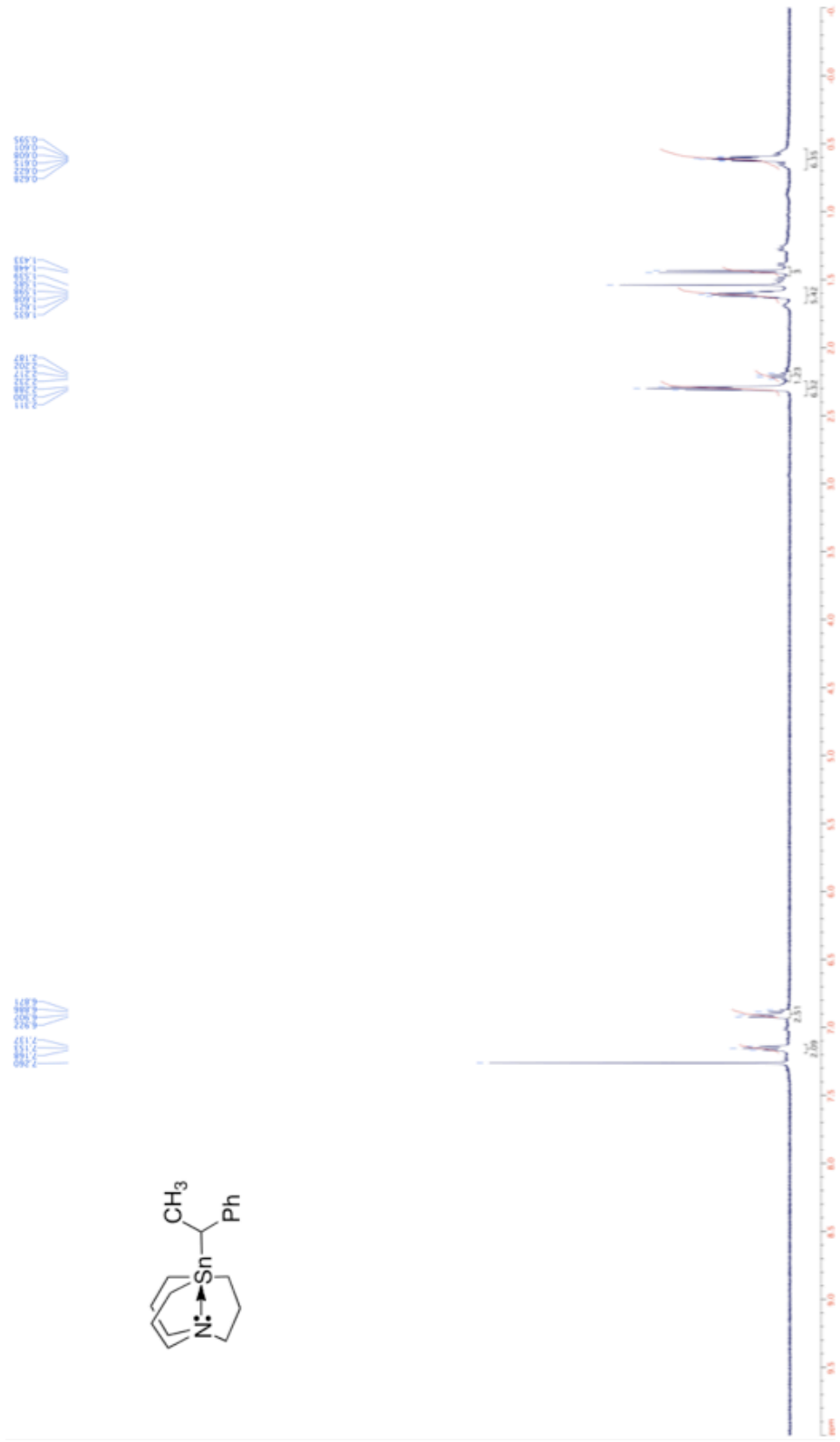

4.634
17.661
21.626
23.607
54.916
76.964
77.218
77.472
CH3
CH3
Sn
N
ppm

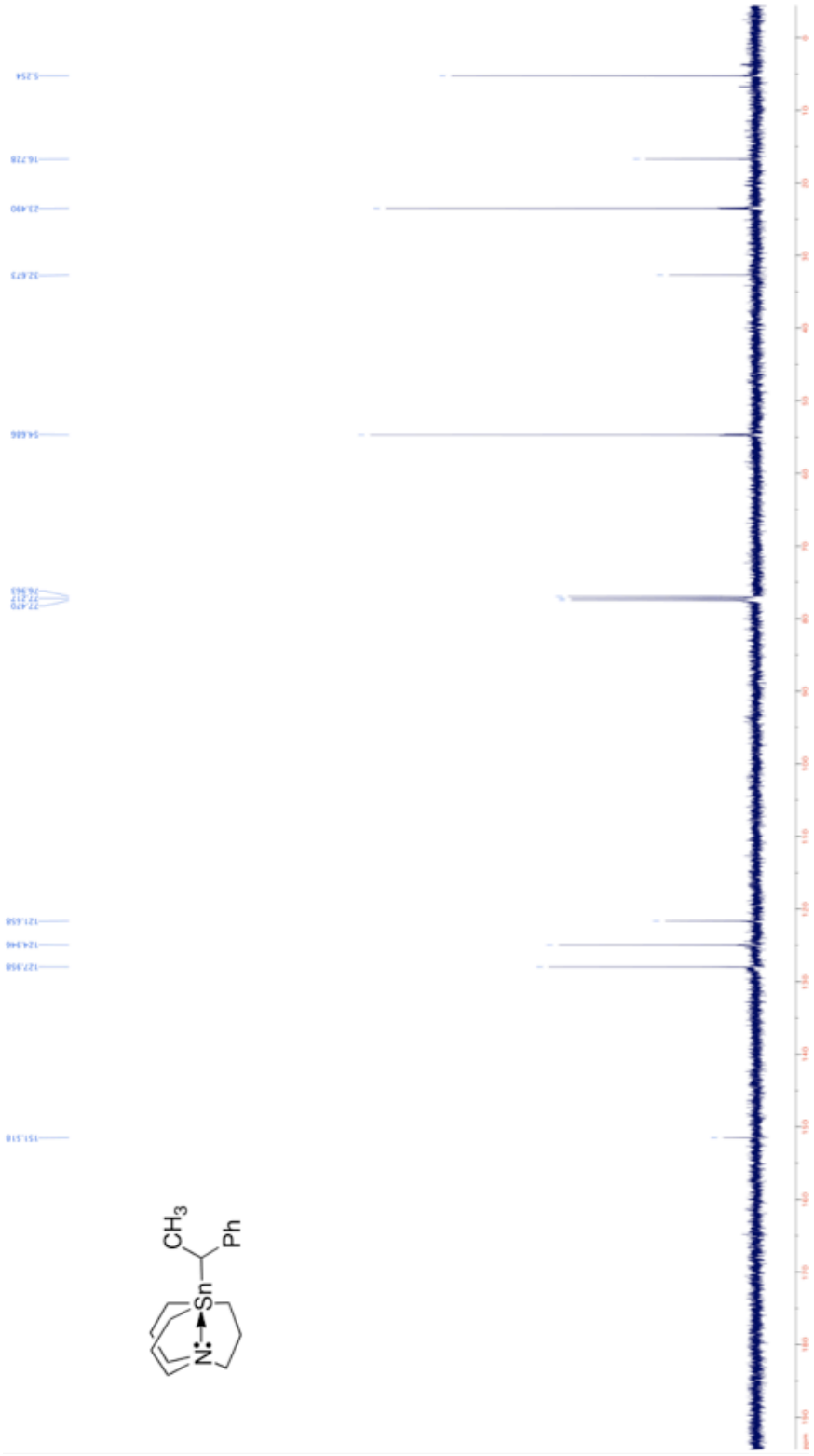

NMe
Sn
N:


NMe
Sn
N:
4.677
23.460
26.209
30.804
47.311
54.728
58.954


O
Sn
N


4.555
23.424
25.997
31.345
54.785
70.983
76.965
77.219
77.474
O
Sn
N


CH3
Ph
Sn
N


CH3
Ph
Sn
N
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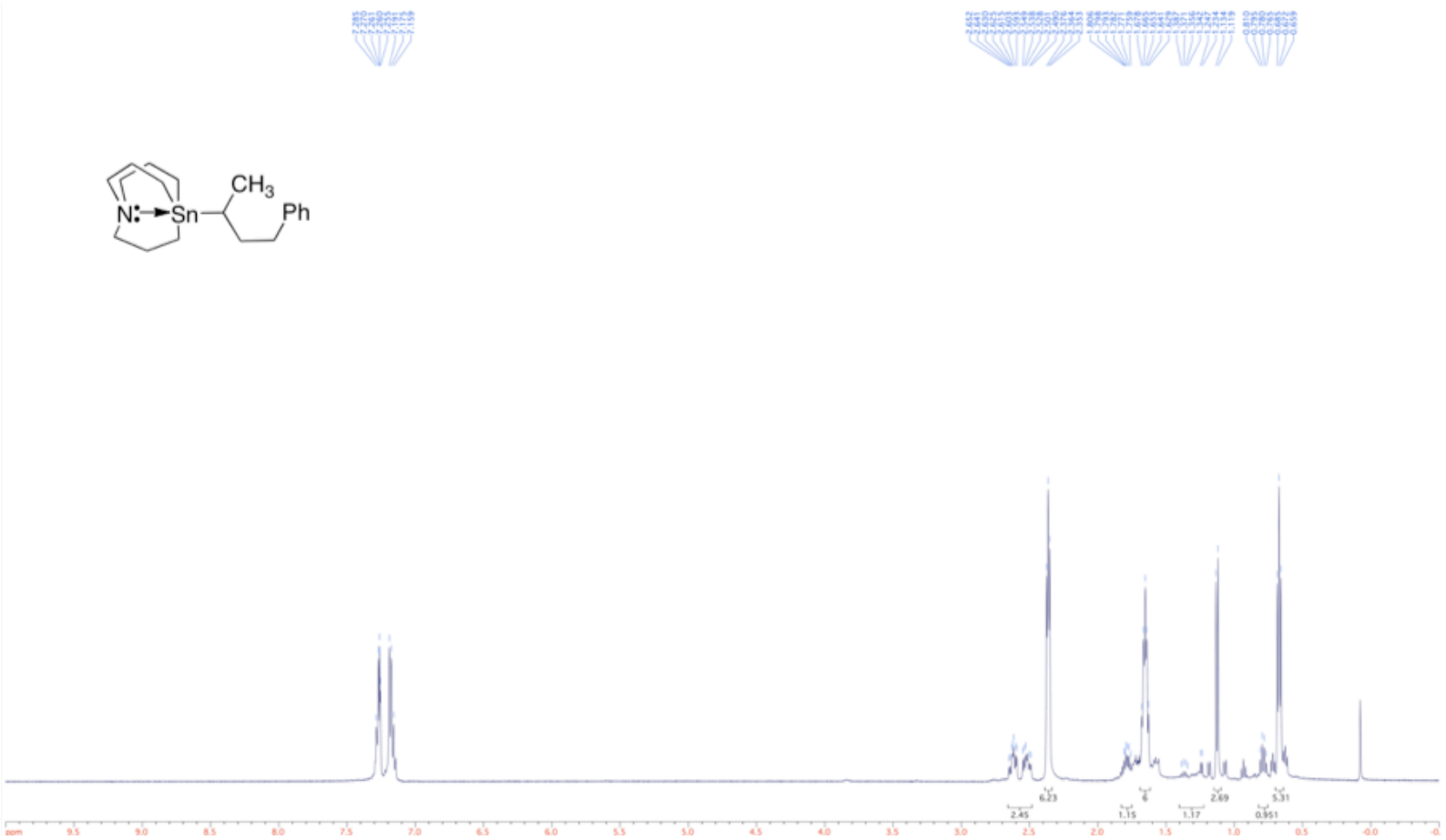
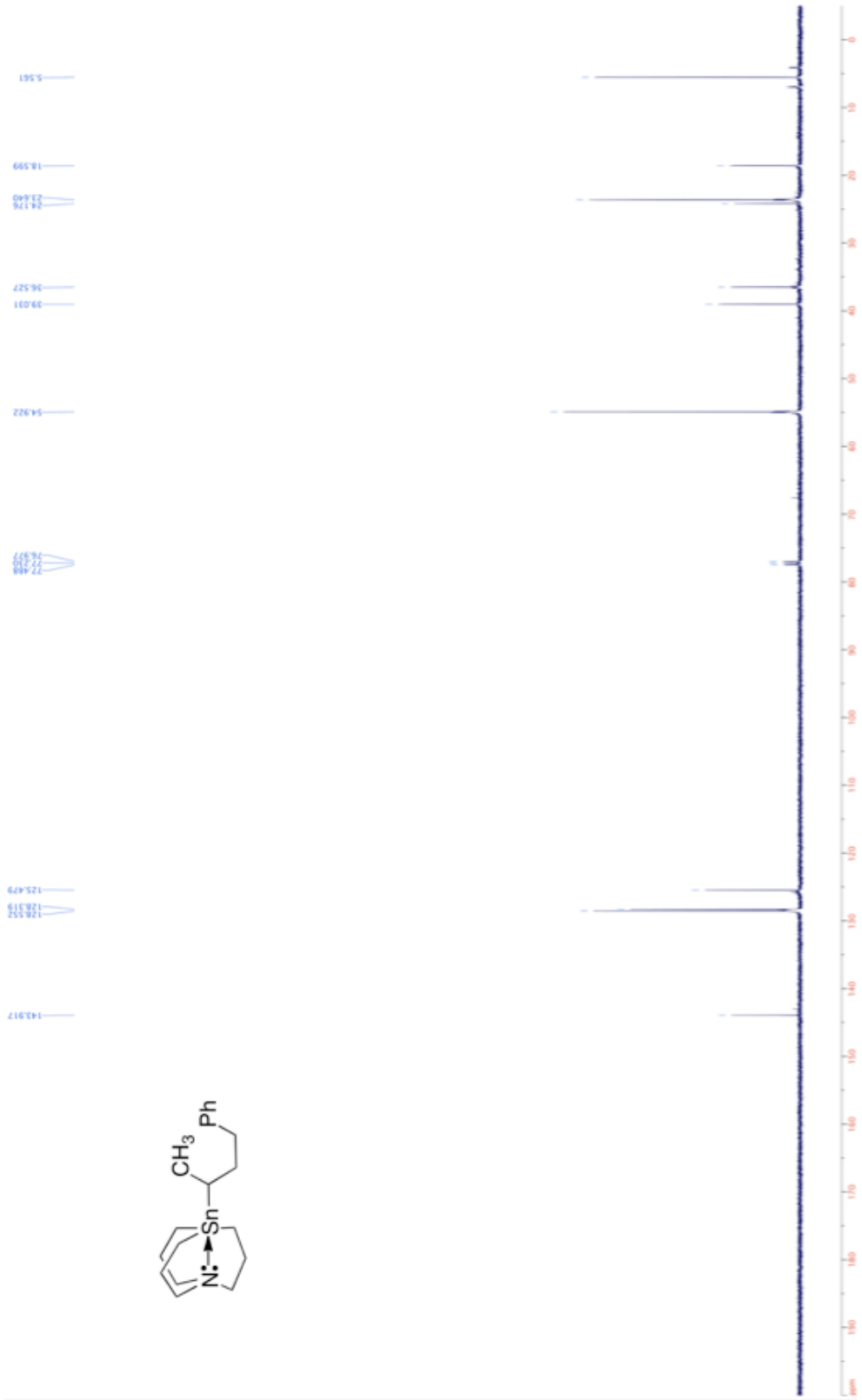
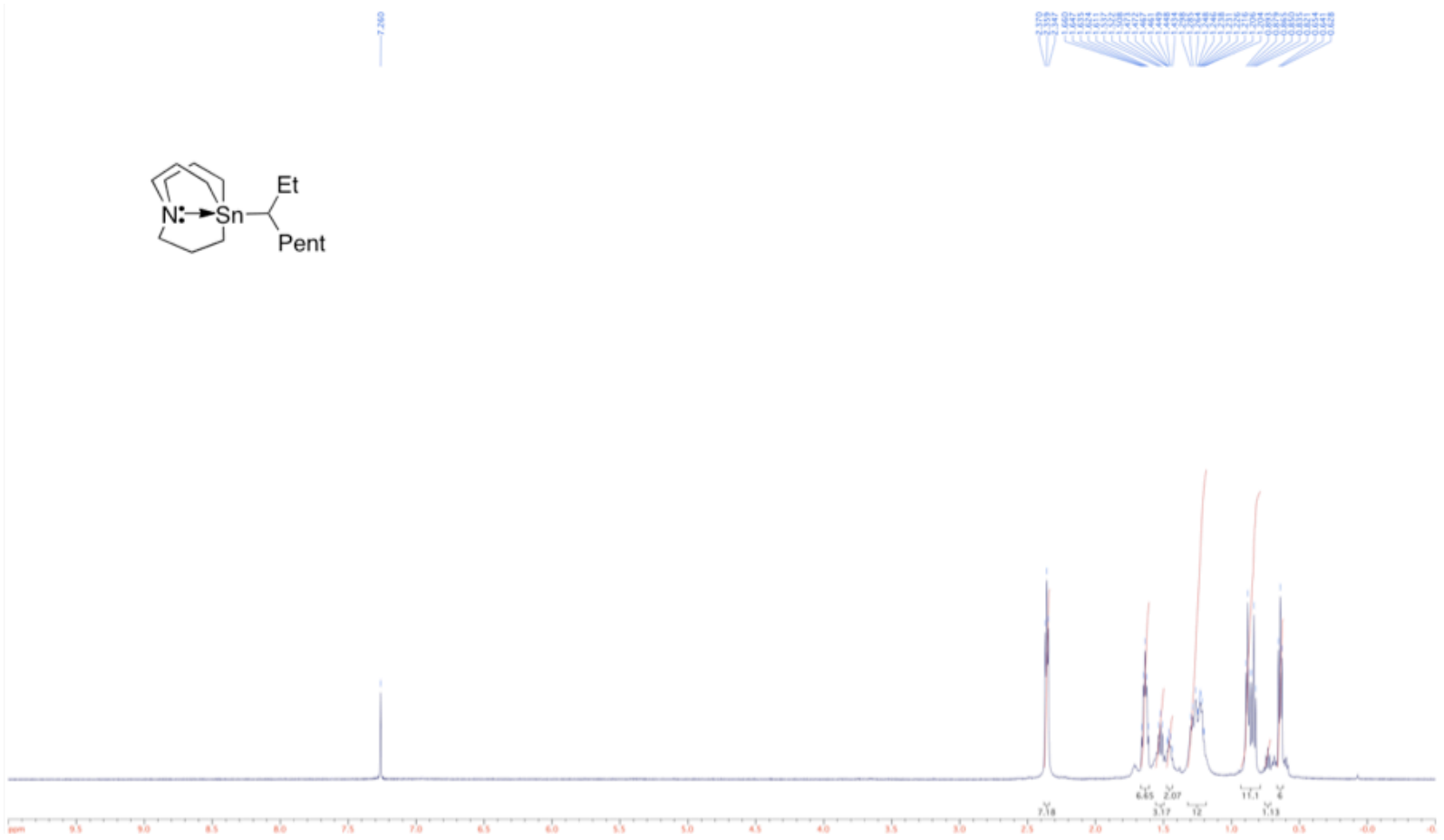
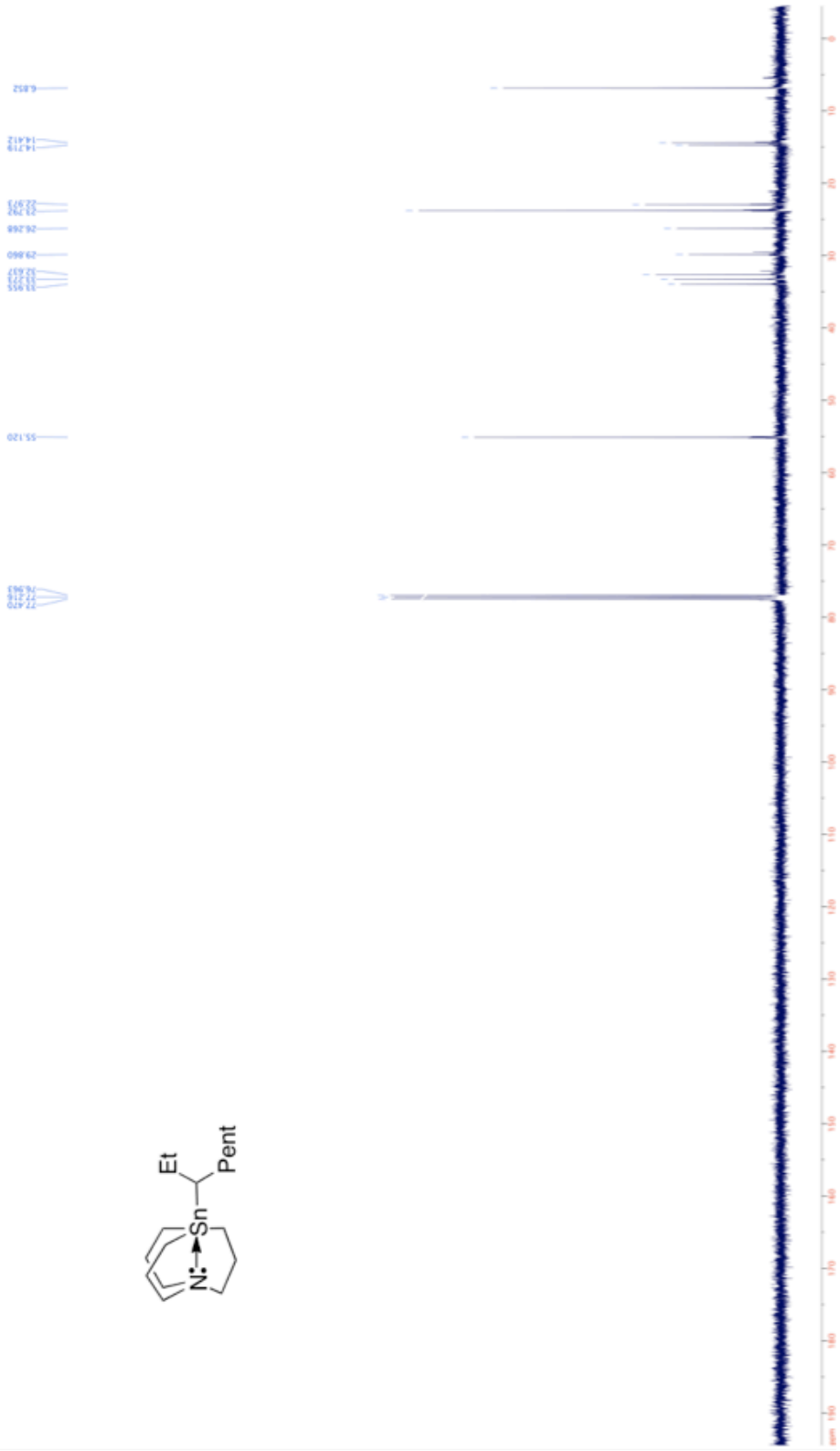
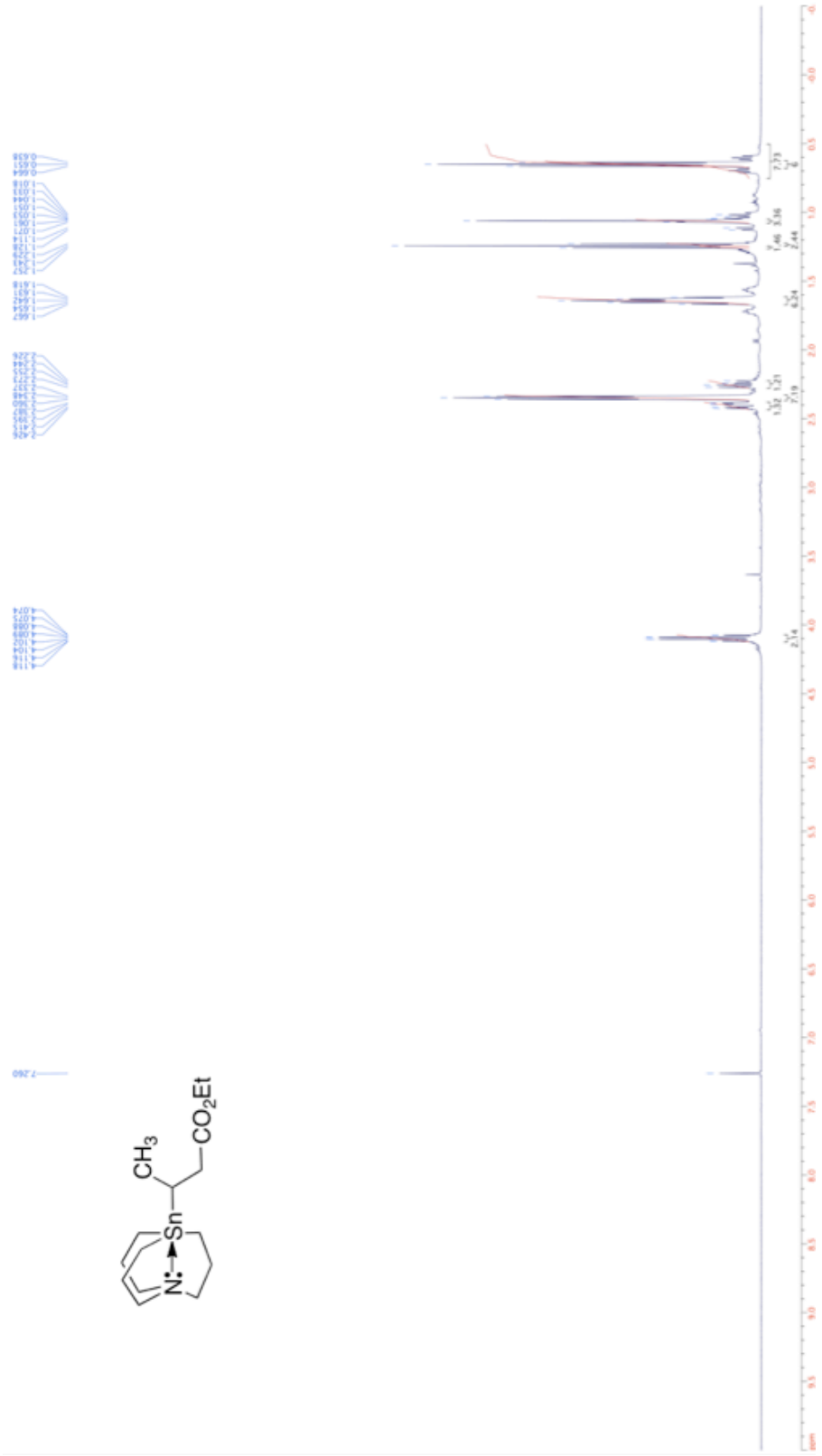
16.228
23.490
32.673
54.686
77.420
77.211
76.963
121.658
124.946
127.950
151.518

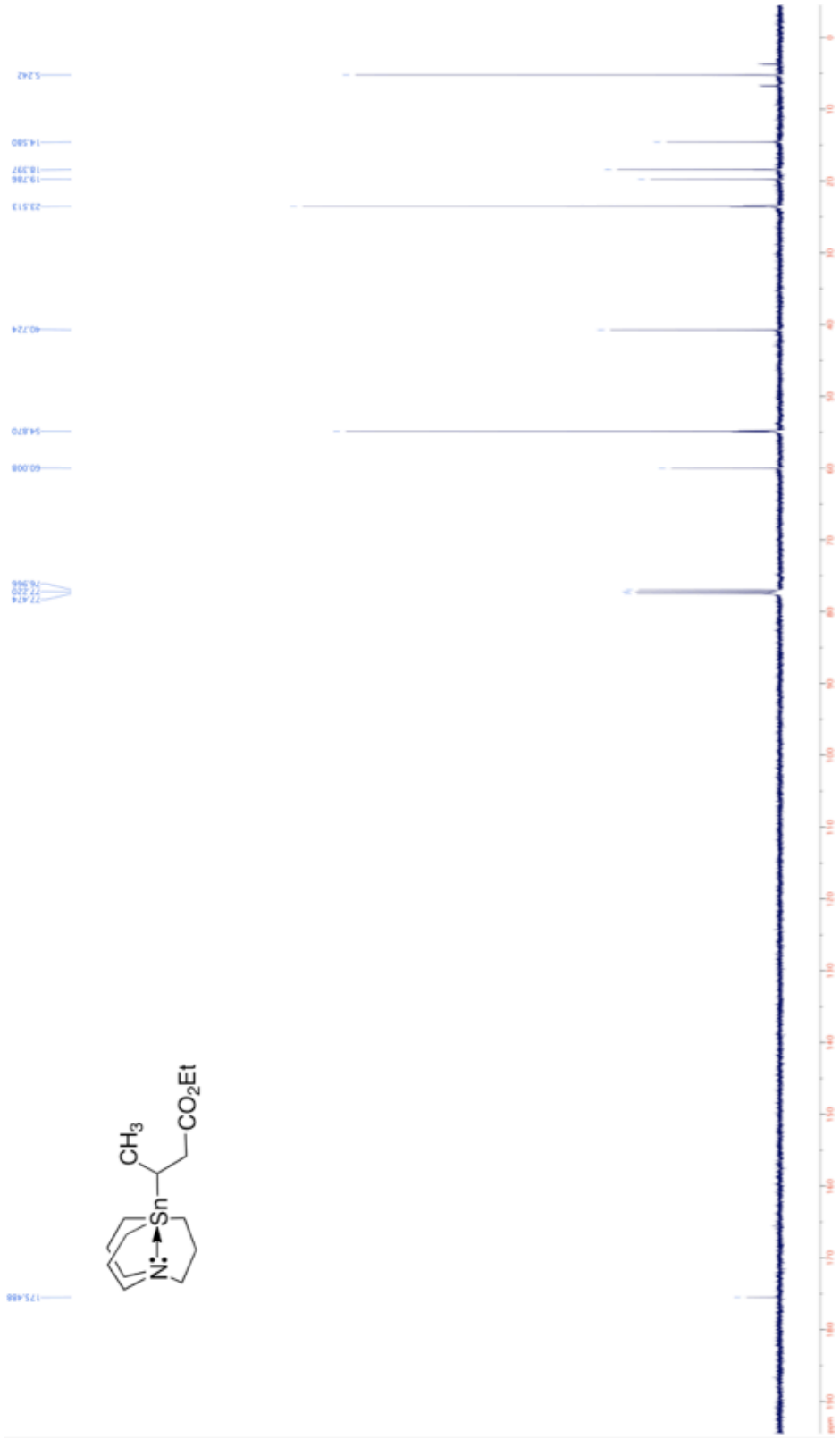

CH3
N
Sn
Ph
6.23
4
2.69
5.31
2.45
1.15
1.17
0.951

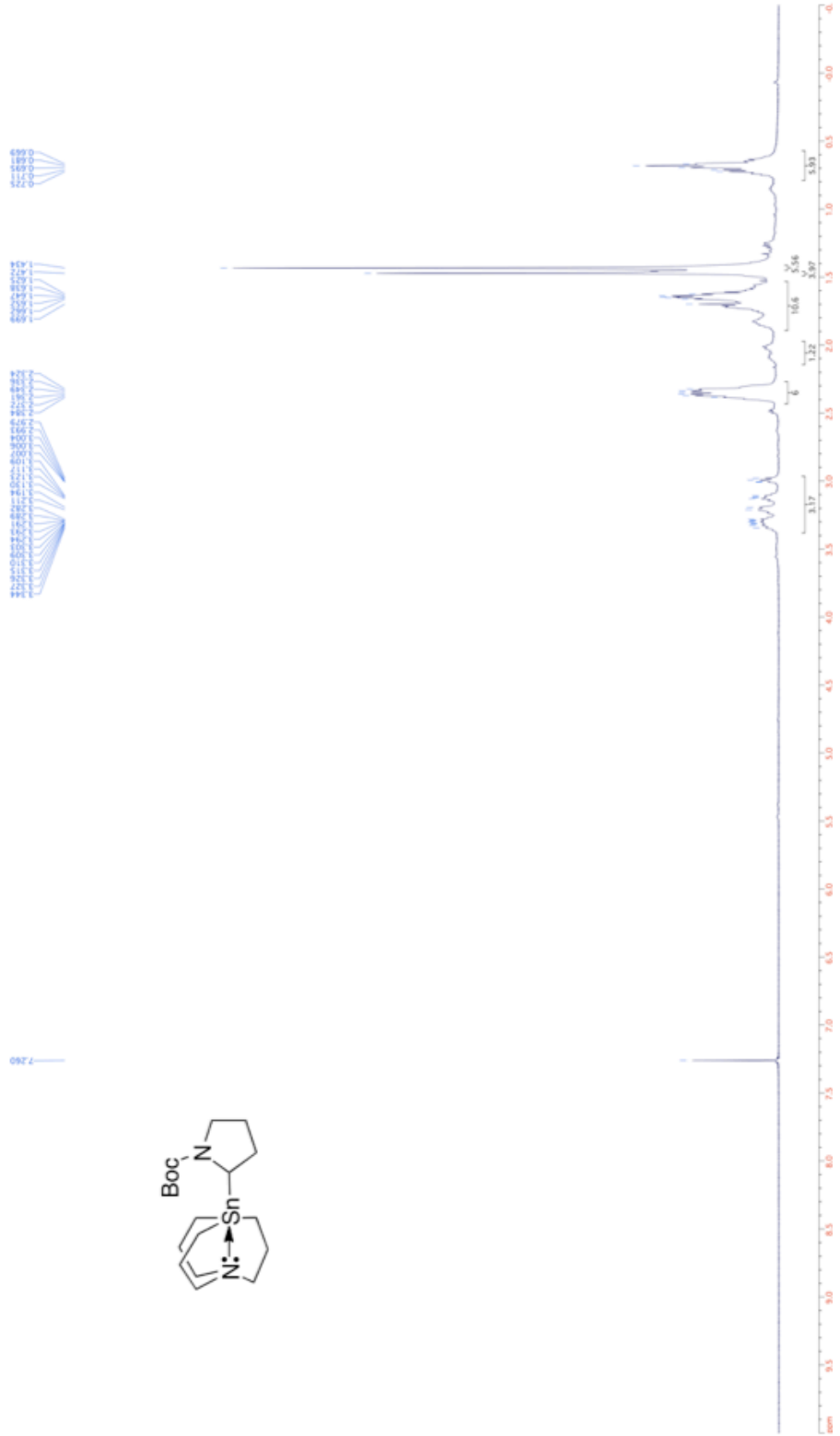

Ph
CH3
Sn
N


Et
N
Sn
Pent

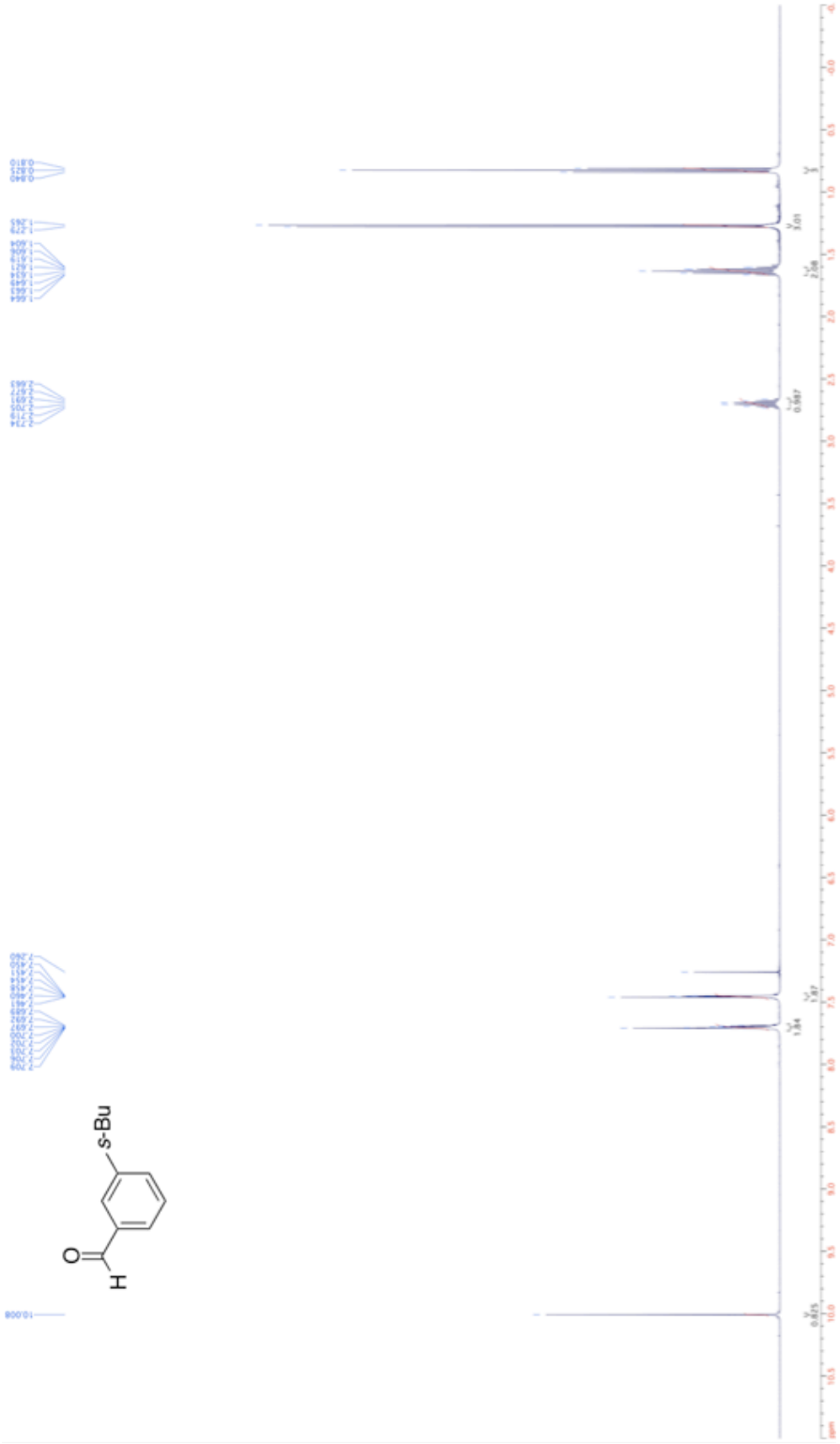

Et
Pent
Sn
N

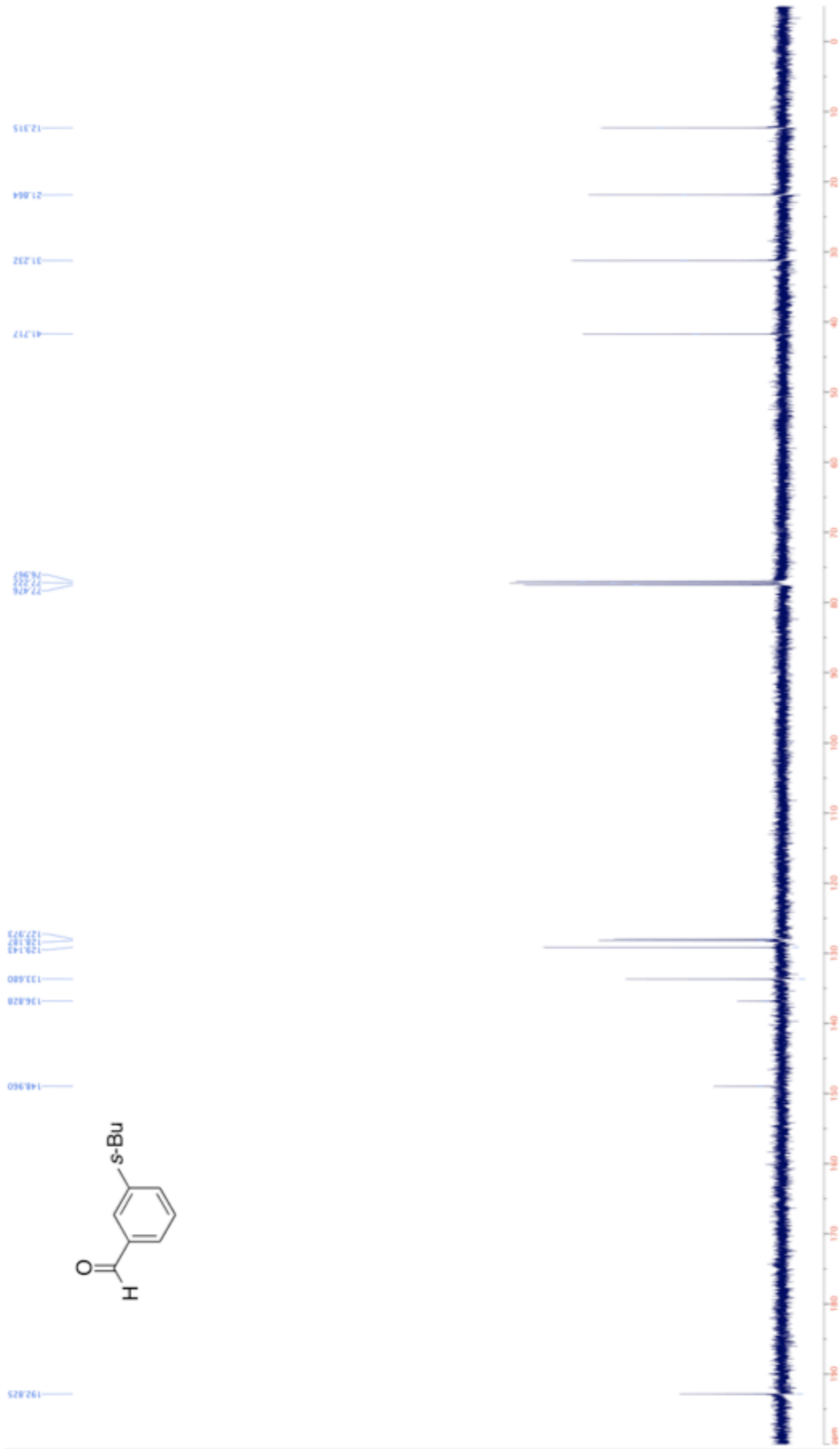

CH3
CO2Et
Sn
N:

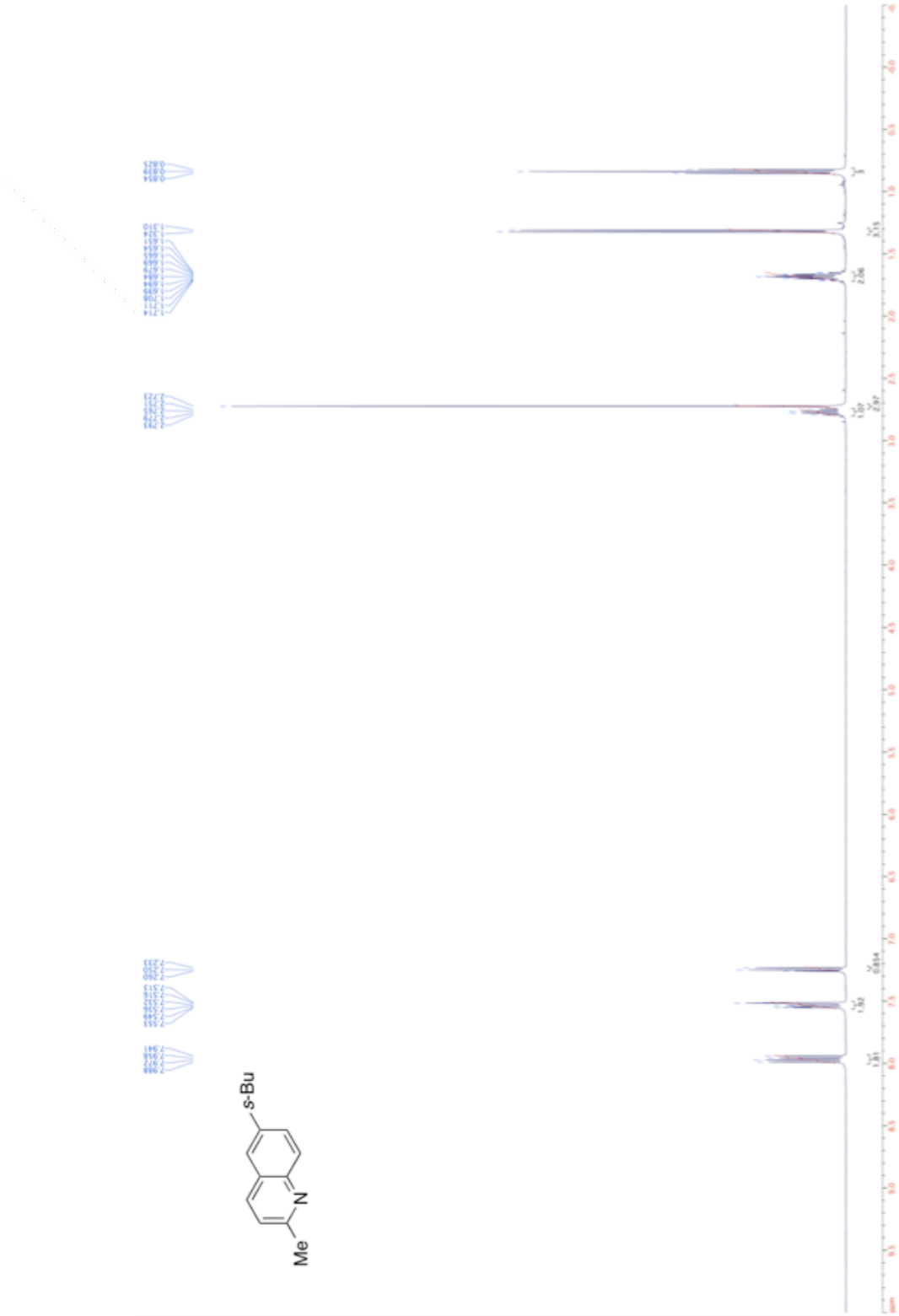

5.242
14.580
18.397
19.786
23.513
40.724
54.870
60.008
77.474
77.220
76.966
175.488
CH3
CO2Et
Sn
N:

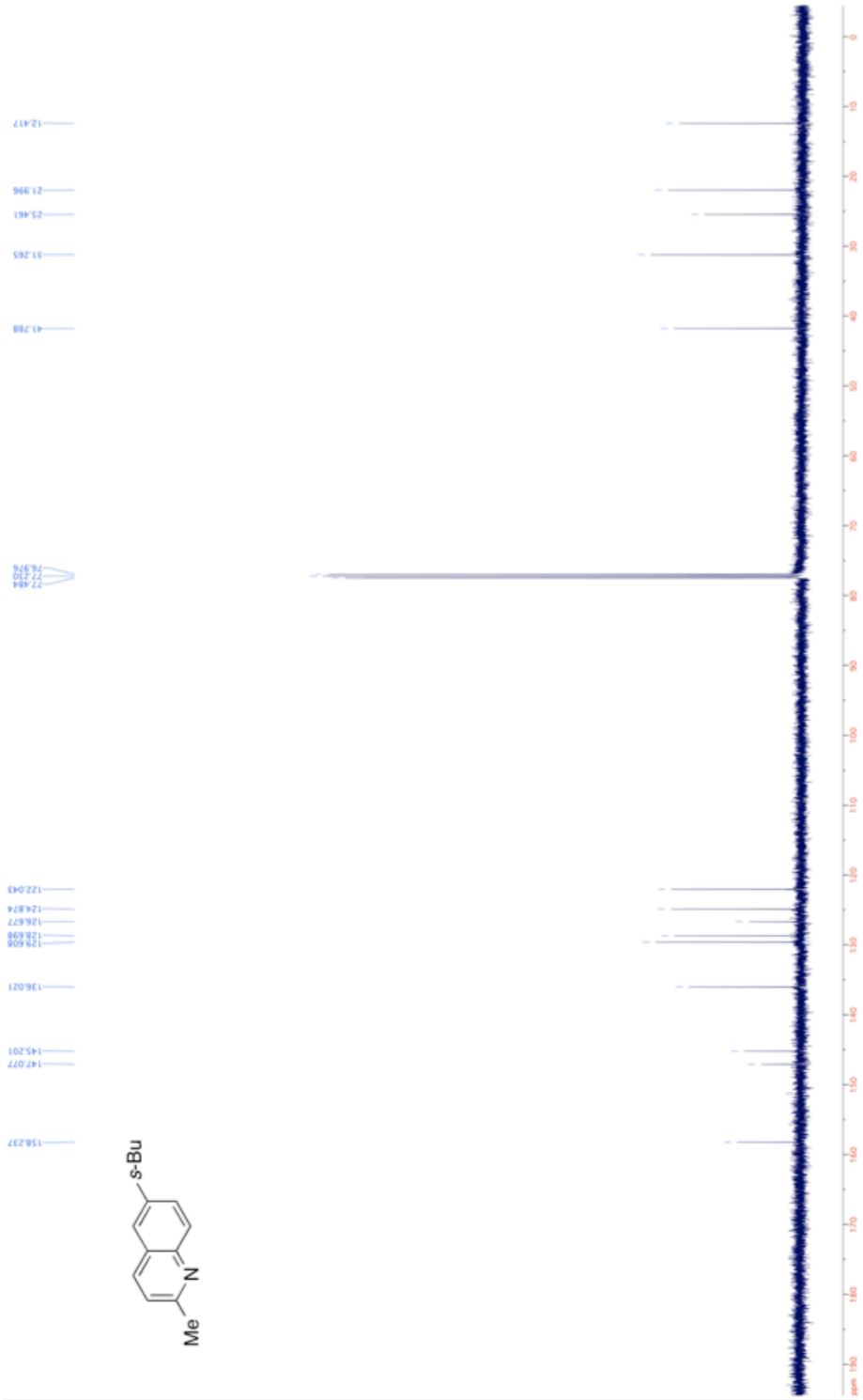

Boc
N
Sn
N:

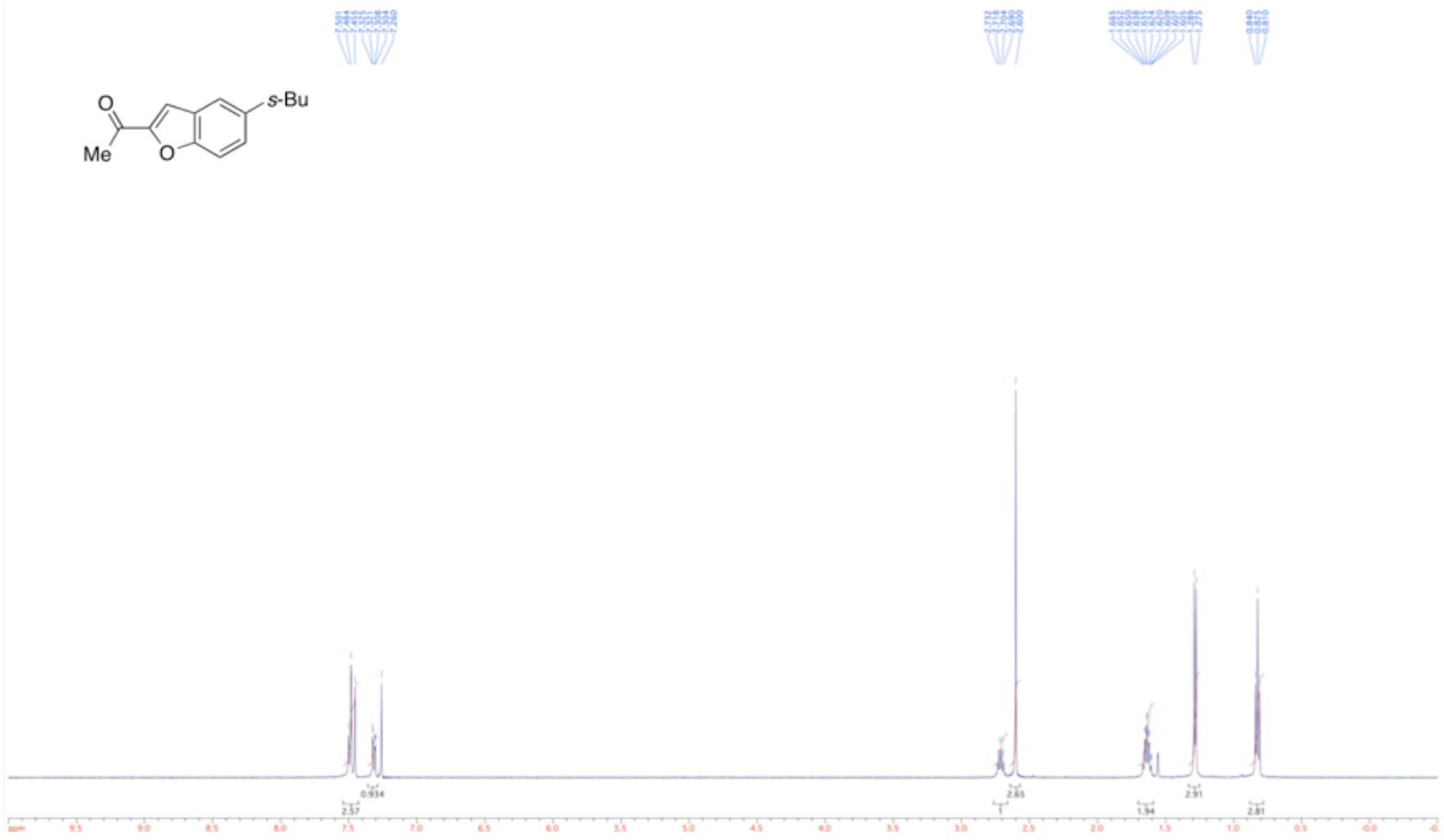

Boc
N
Sn
N

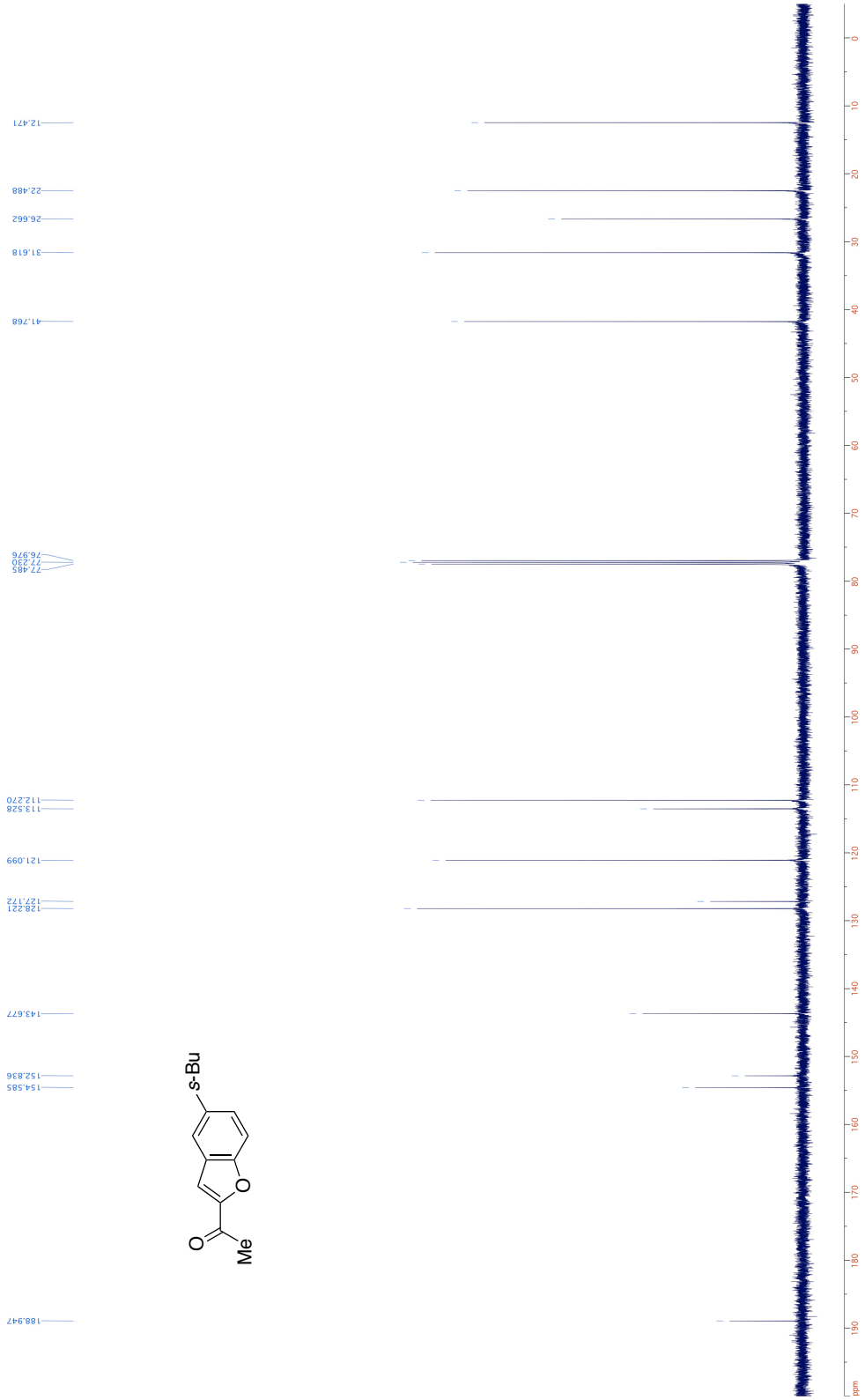

s-Bu
O
H


12.315
21.864
31.232
41.217
76.967
77.222
77.476
127.973
128.187
129.143
133.680
136.828
148.960
192.825
s-Bu
O
H

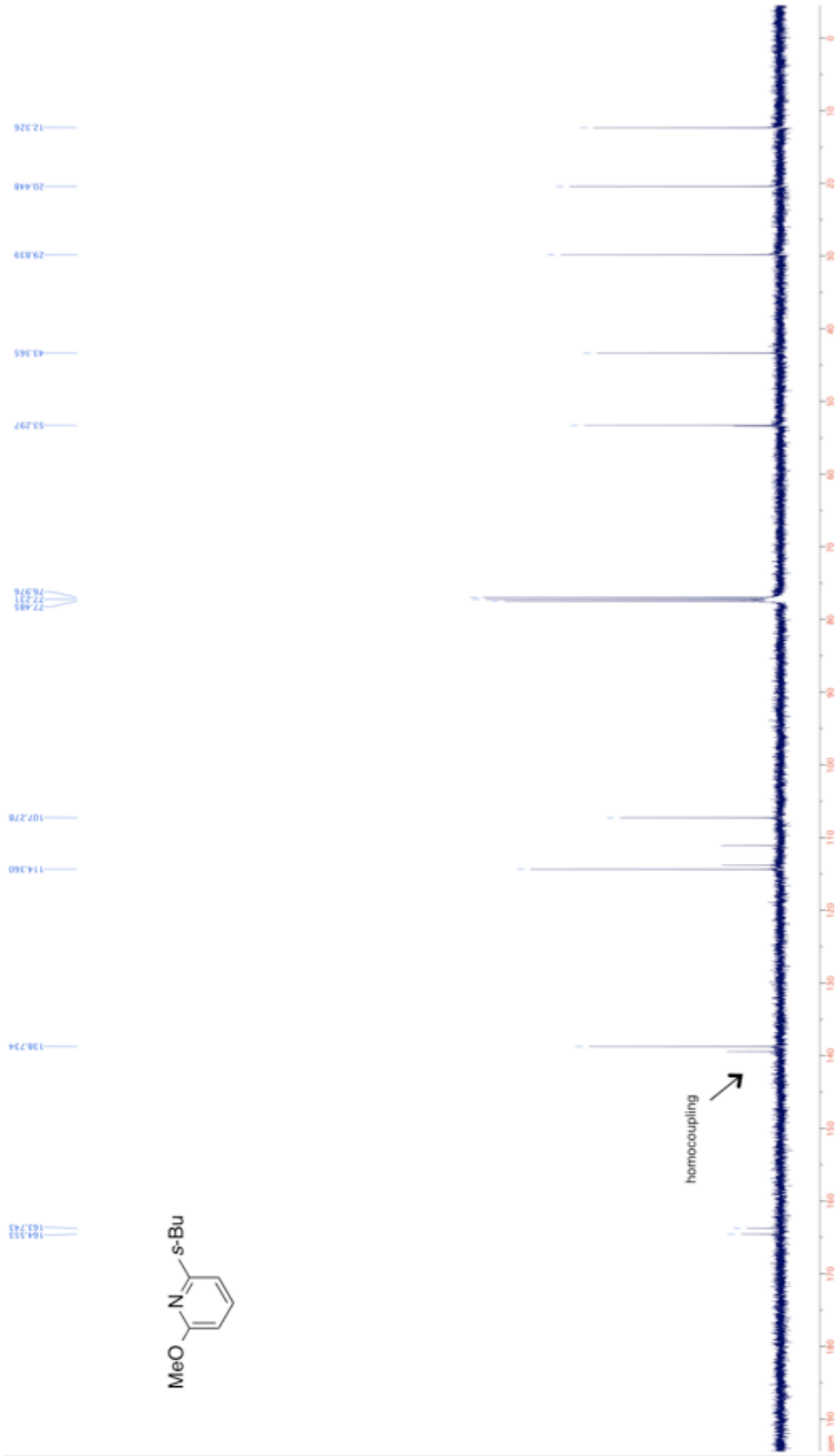

s-Bu
N
Me

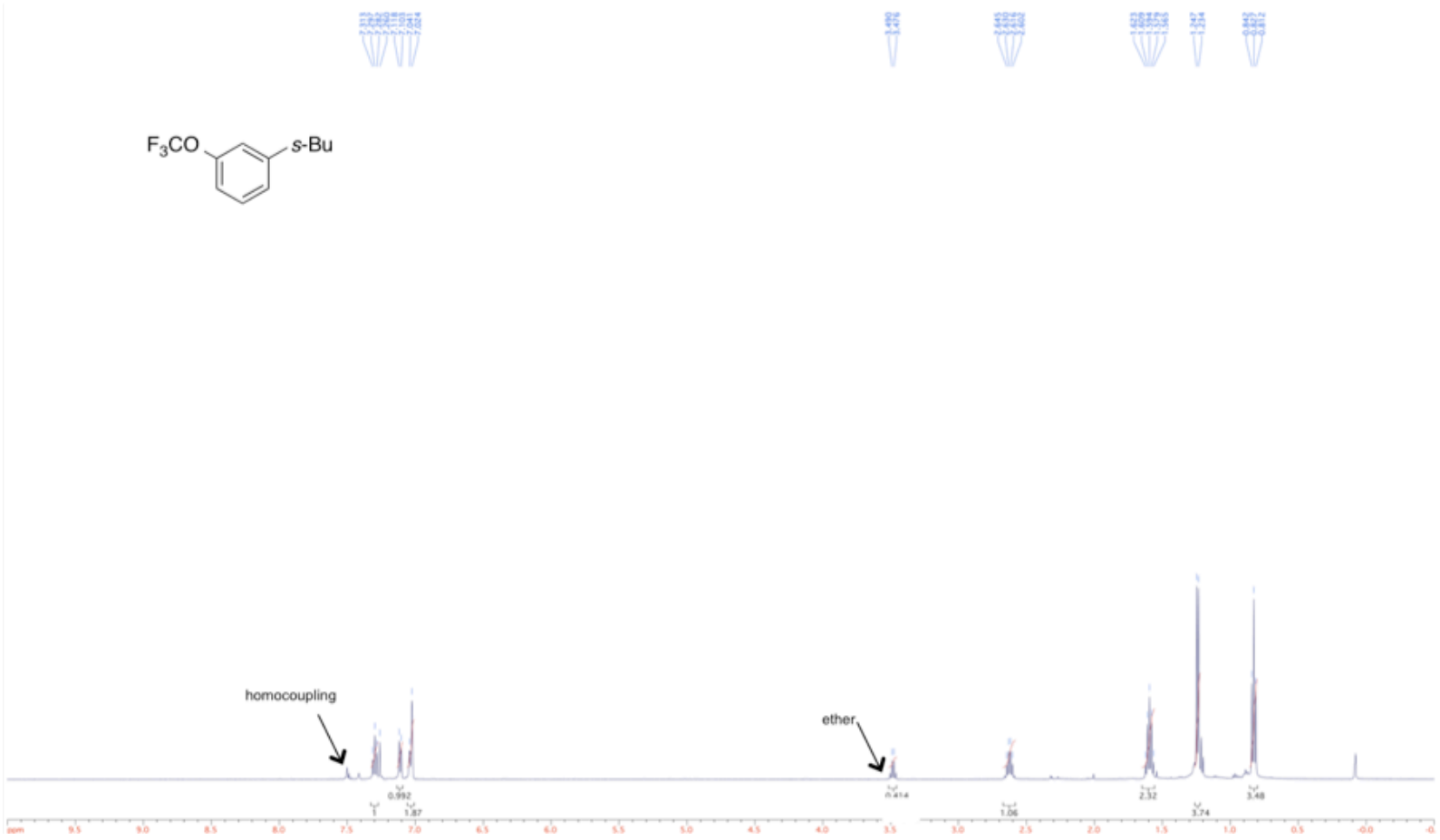

12.417
21.996
25.461
31.265
41.788
76.976
77.484
77.210
122.043
124.874
126.677
128.636
129.606
136.021
145.201
147.077
158.237
s-Bu
N
Me

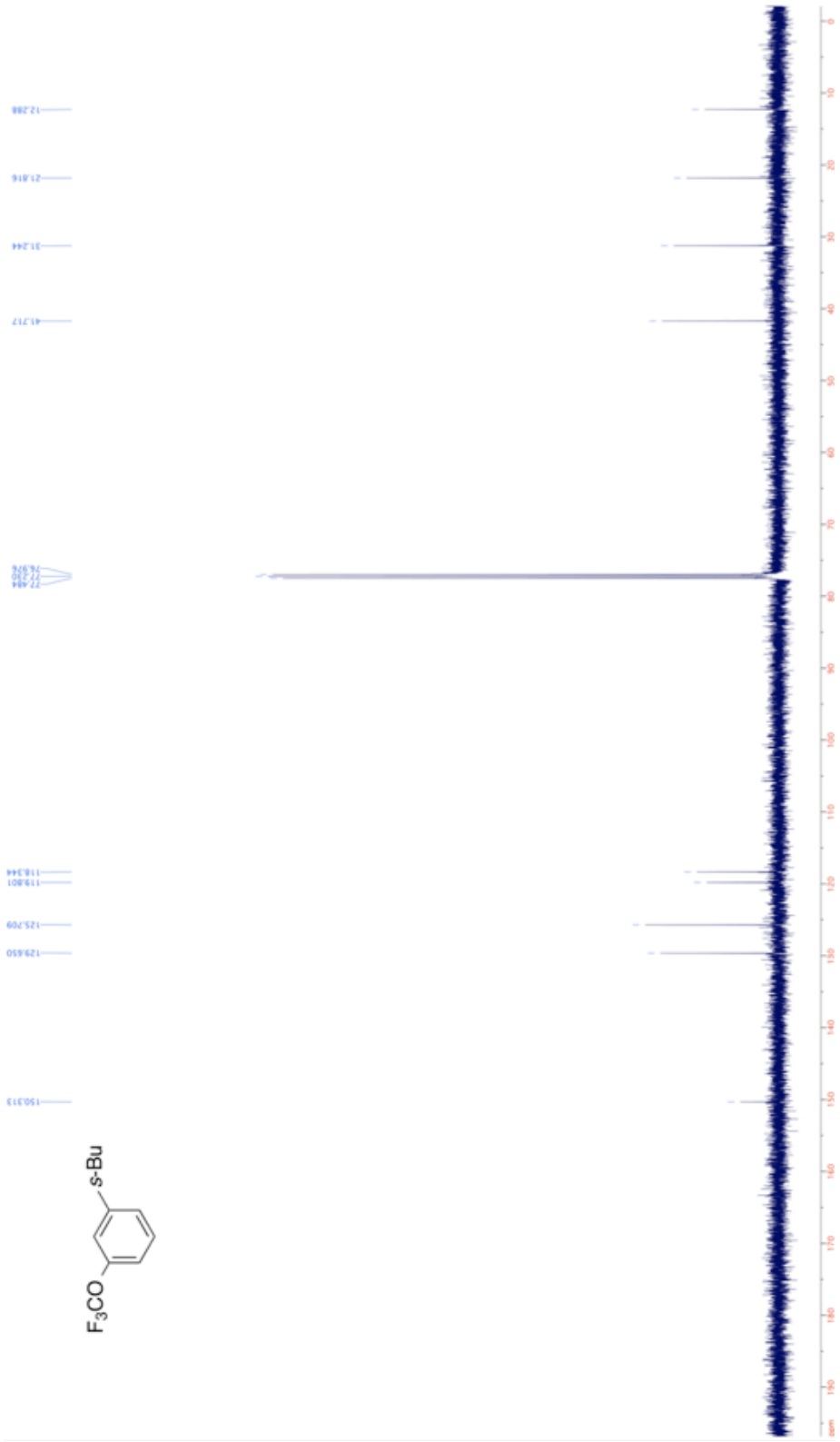

O
Me
O
s-Bu
2.57
0.934
1
2.65
1.94
2.91
2.81
ppm

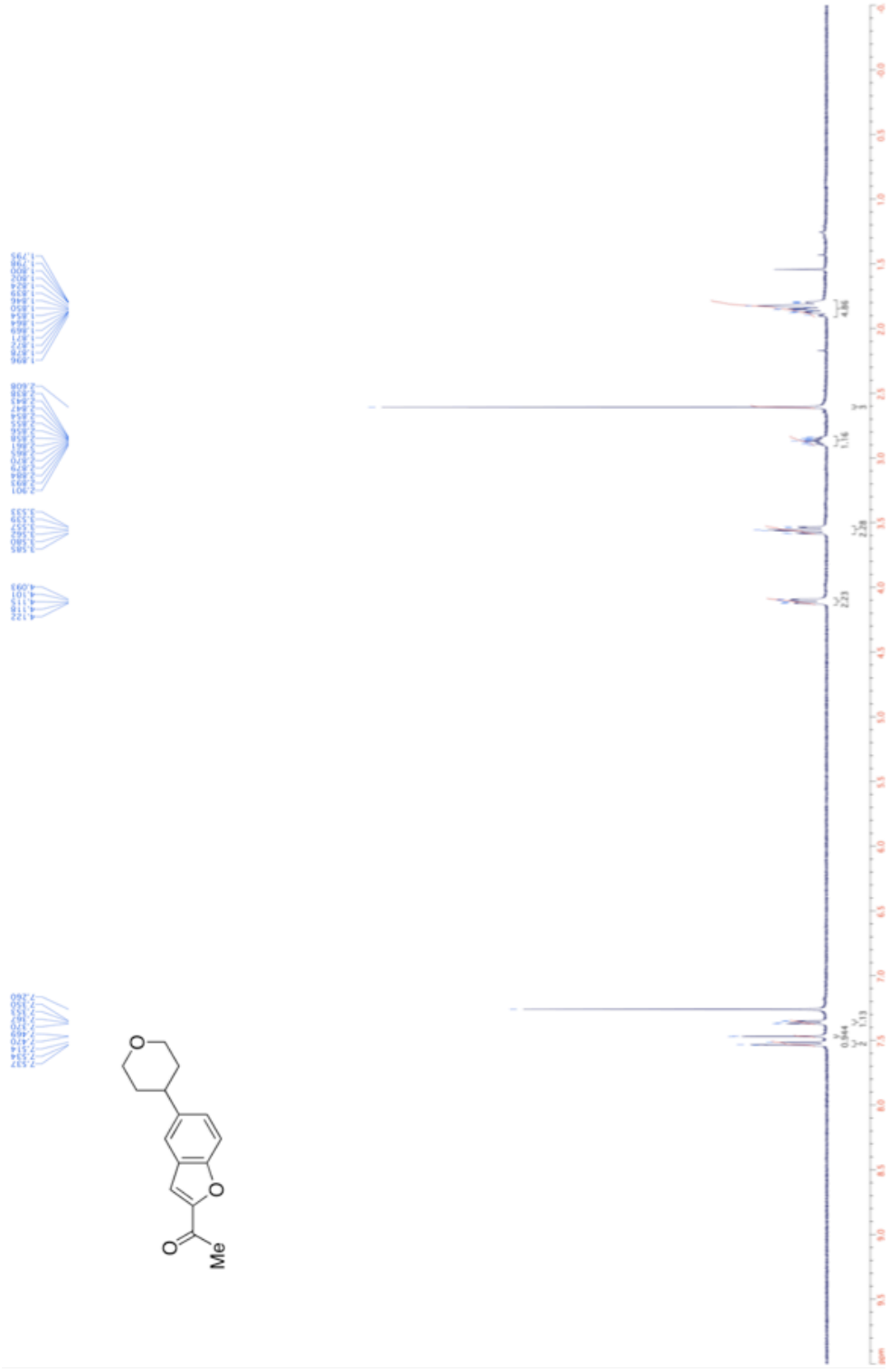

12.471
22.488
26.662
31.618
41.768
76.976
77.230
77.485
112.270
113.528
121.099
127.172
128.221
143.677
152.836
154.585
188.947
s-Bu
O
O
Me
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
ppm

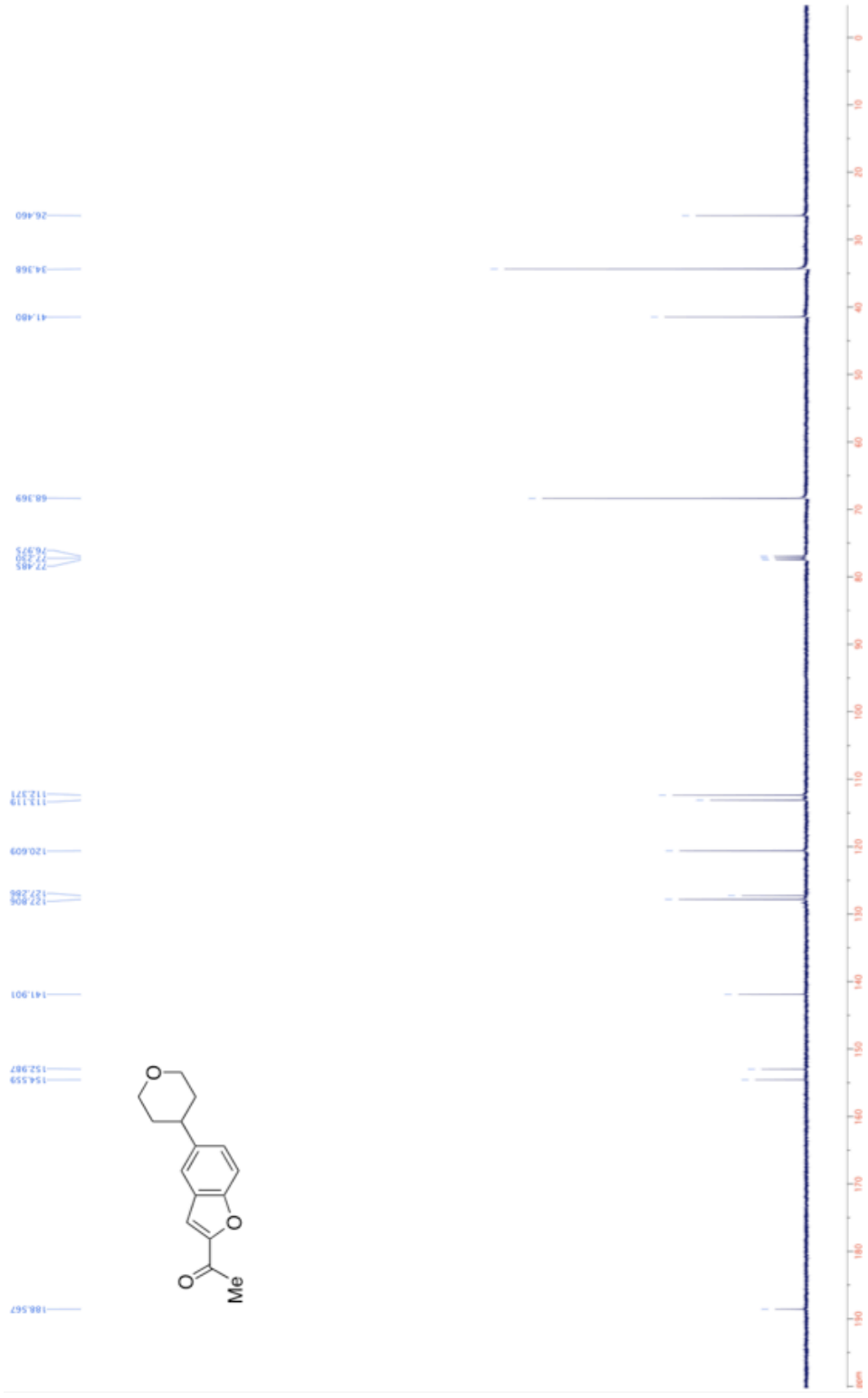
MeO
N
s-Bu
homocoupling

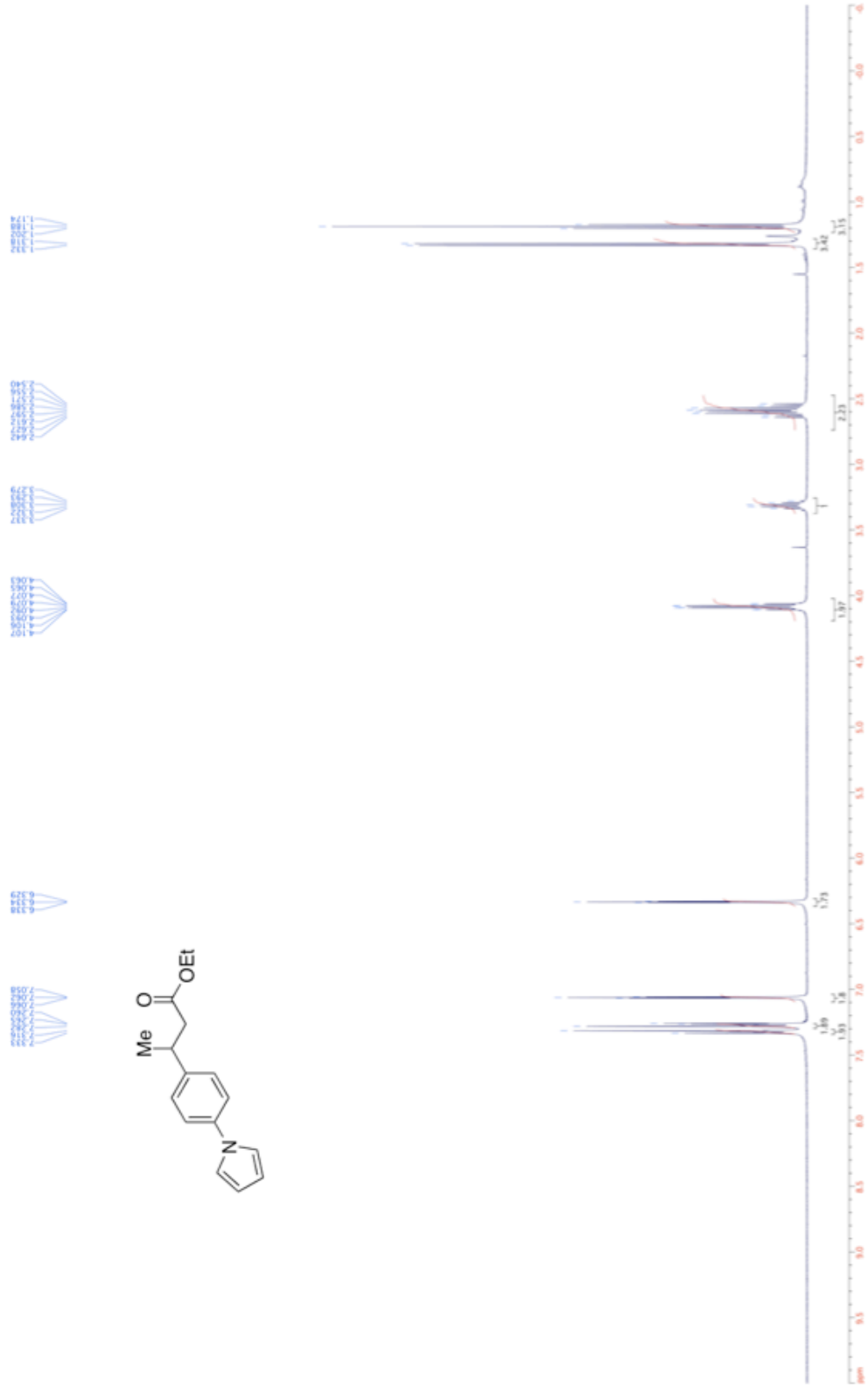

MeO
N
s-Bu
homocoupling

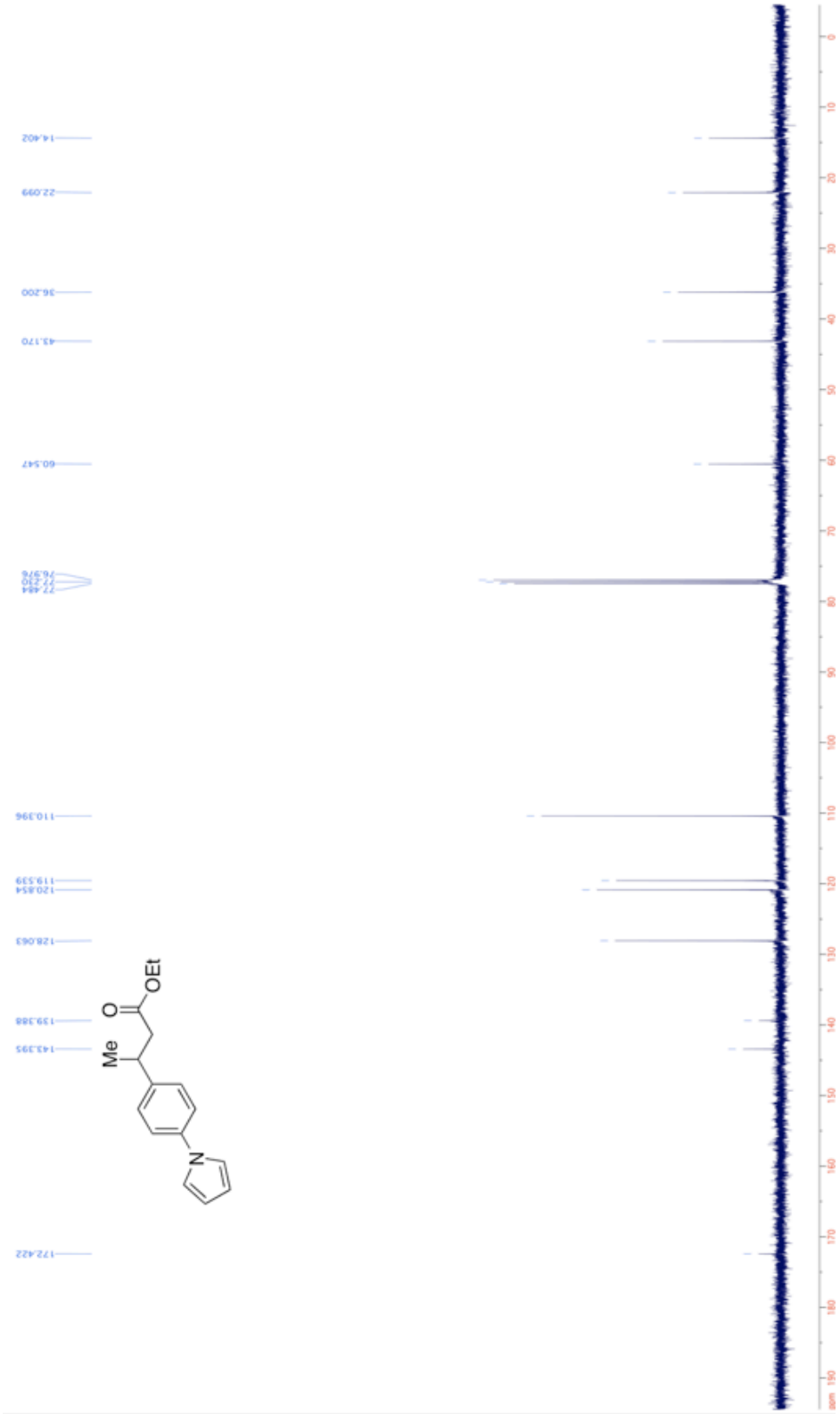

F3CO
s-Bu
homocoupling
ether

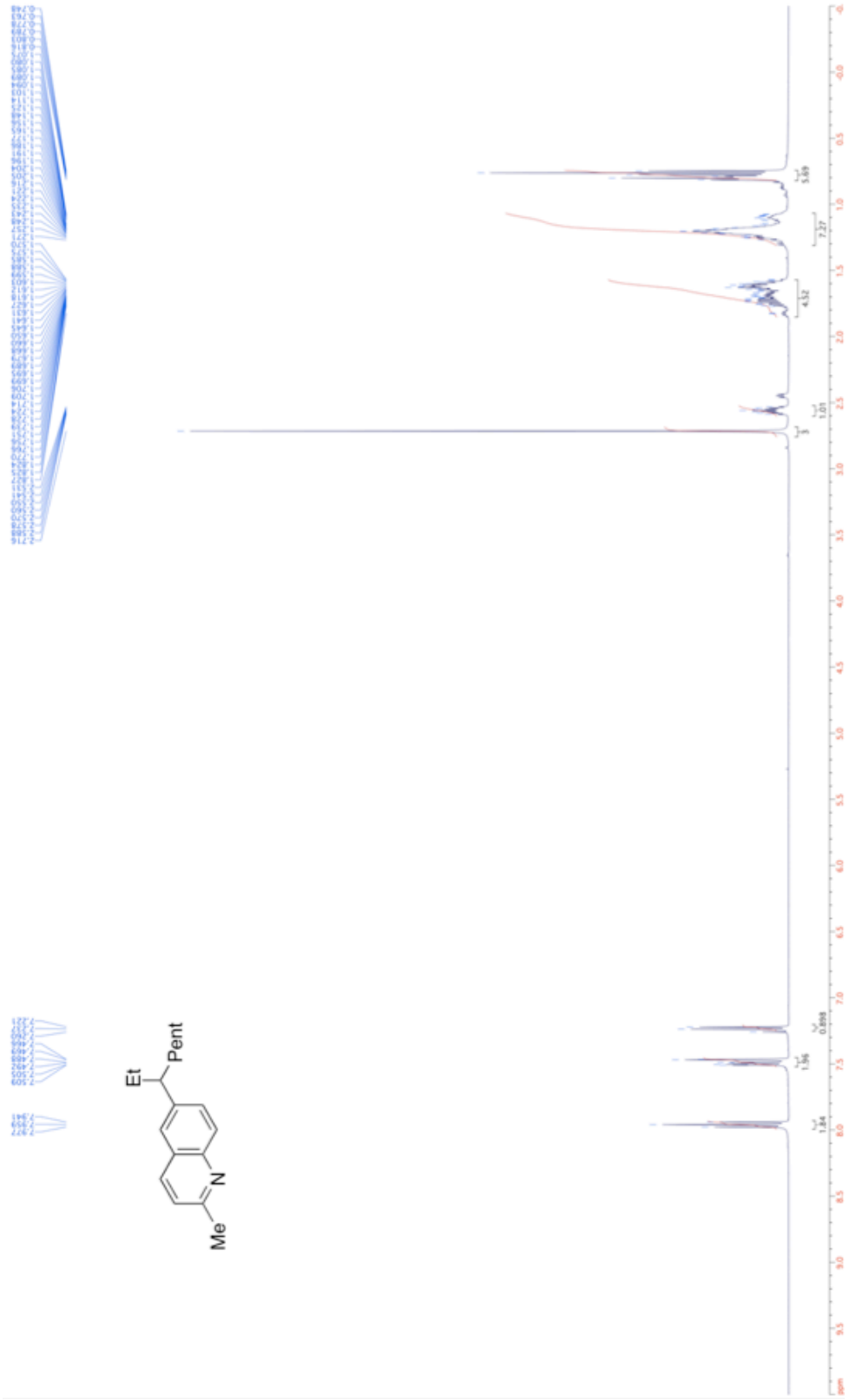

12.288
21.816
31.244
41.717
77.484
77.200
76.916
118.344
119.801
125.709
129.650
150.313
s-Bu
F3CO

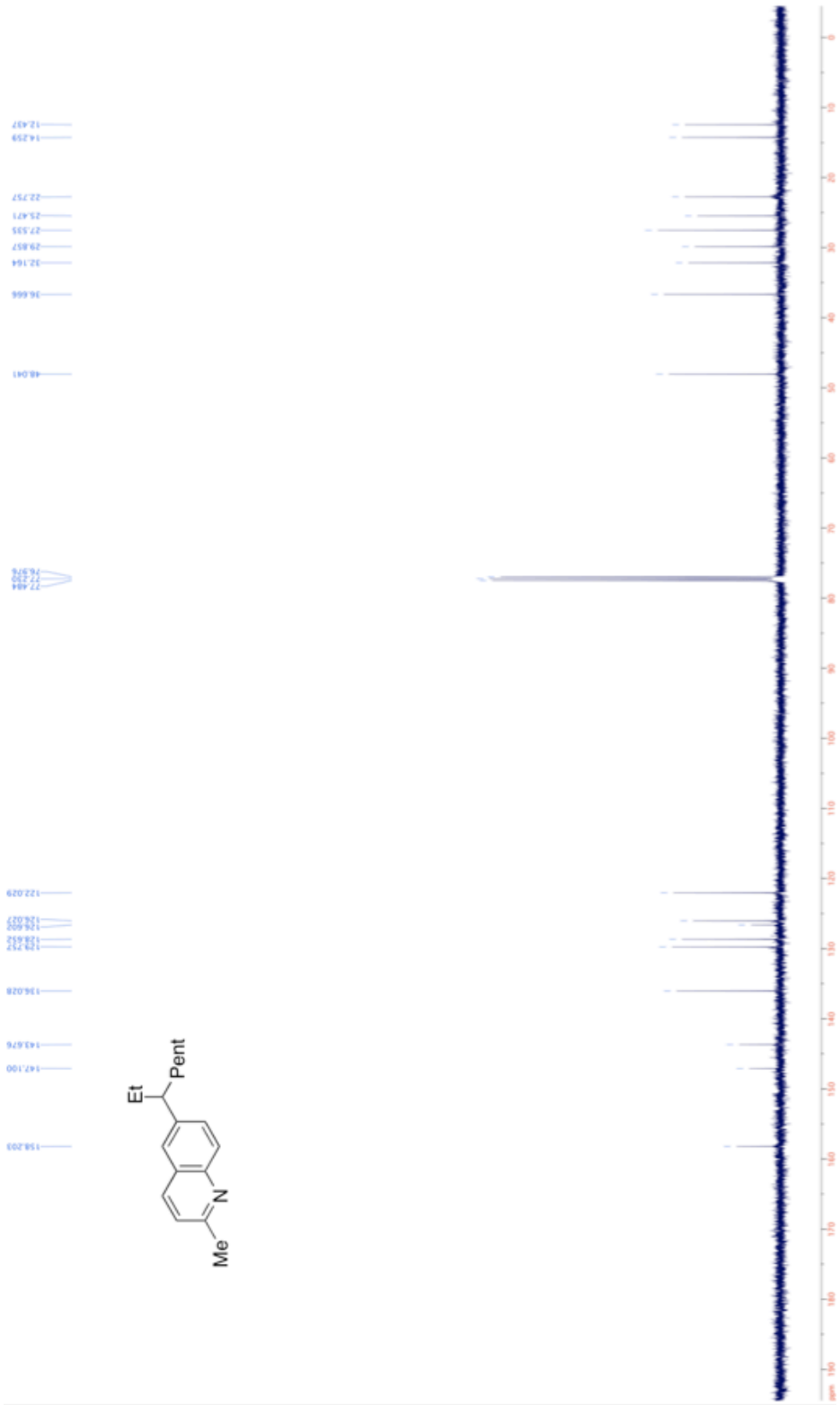

O
O
O
Me


26.460
34.368
41.480
68.369
77.485
76.975
112.371
113.119
120.609
122.826
127.266
141.901
152.987
154.559
188.567
Me

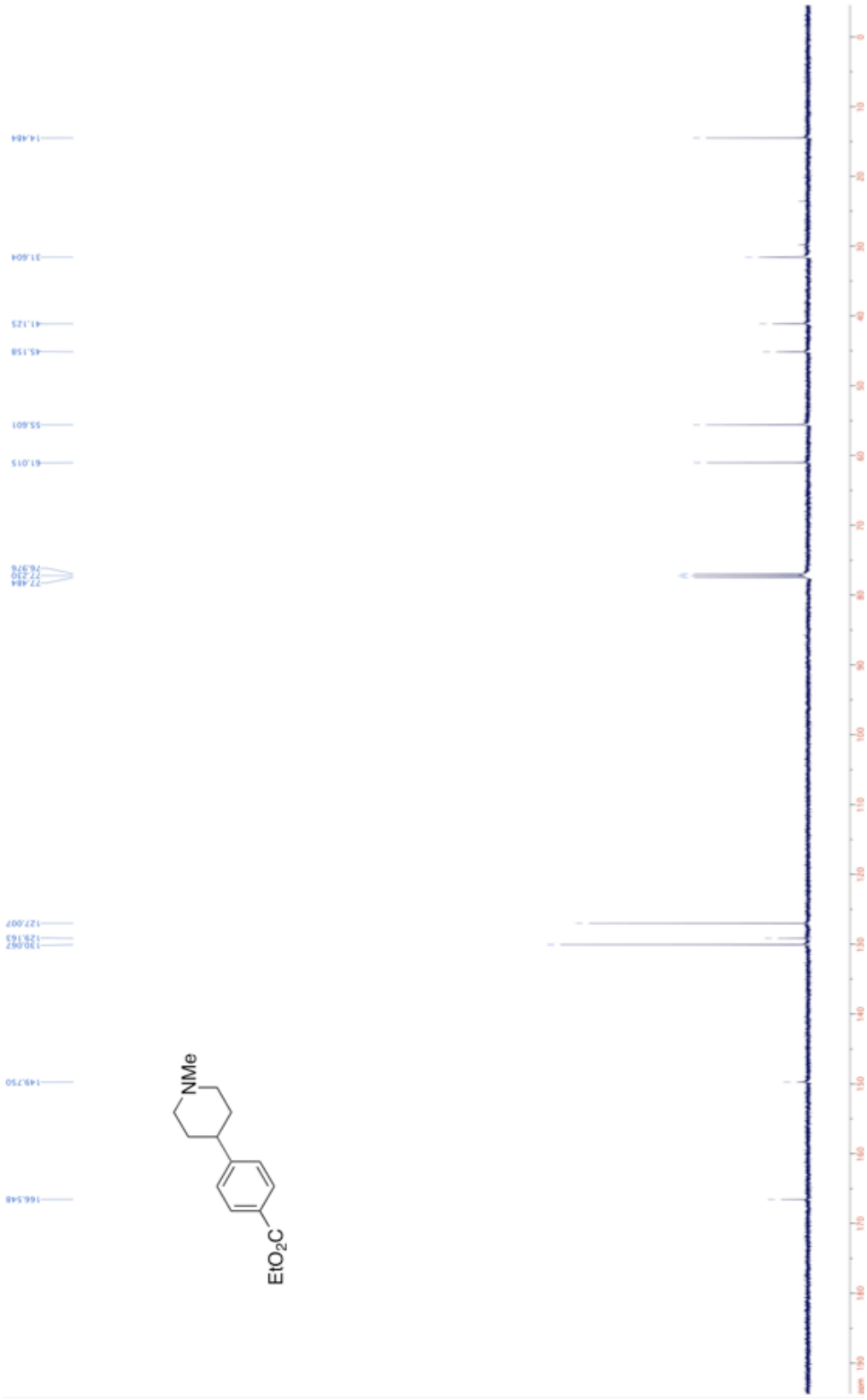

Me
O
OEt
N

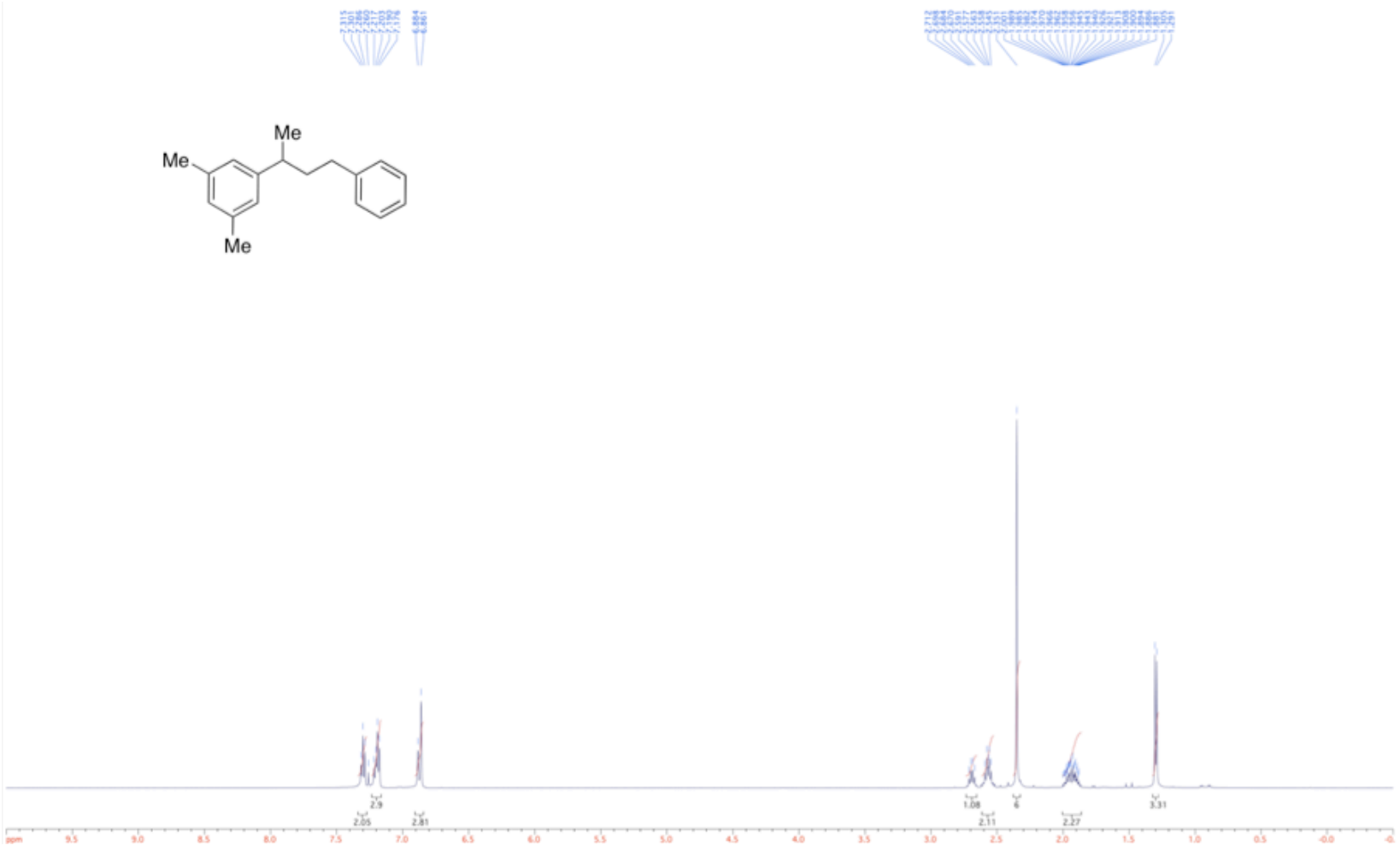

14.402
22.099
36.200
43.170
60.547
76.976
110.396
119.539
120.854
128.063
139.388
143.395
172.422
Me
O
OEt
N

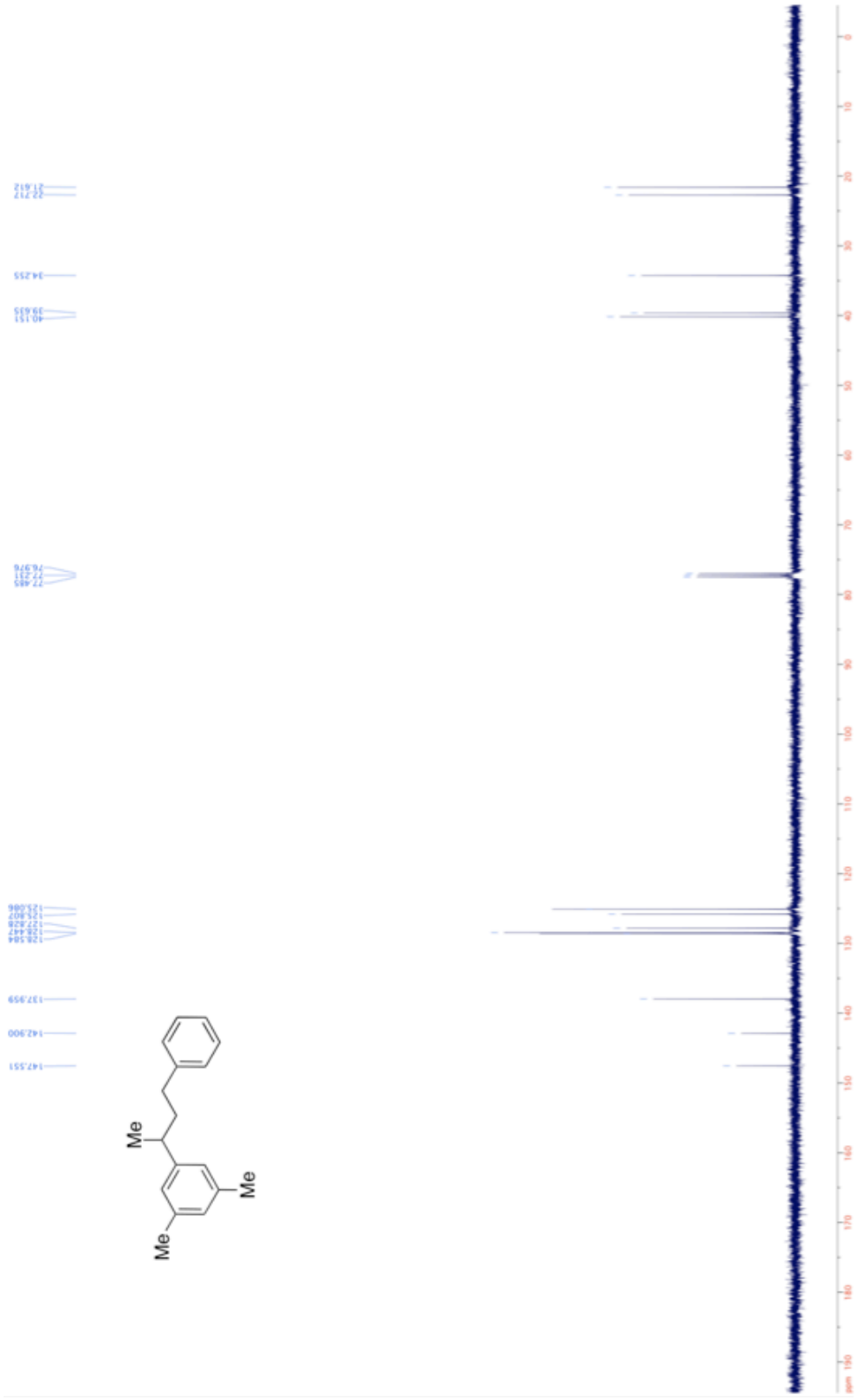

Et
Pent
N
Me


Et
Pent
N
Me

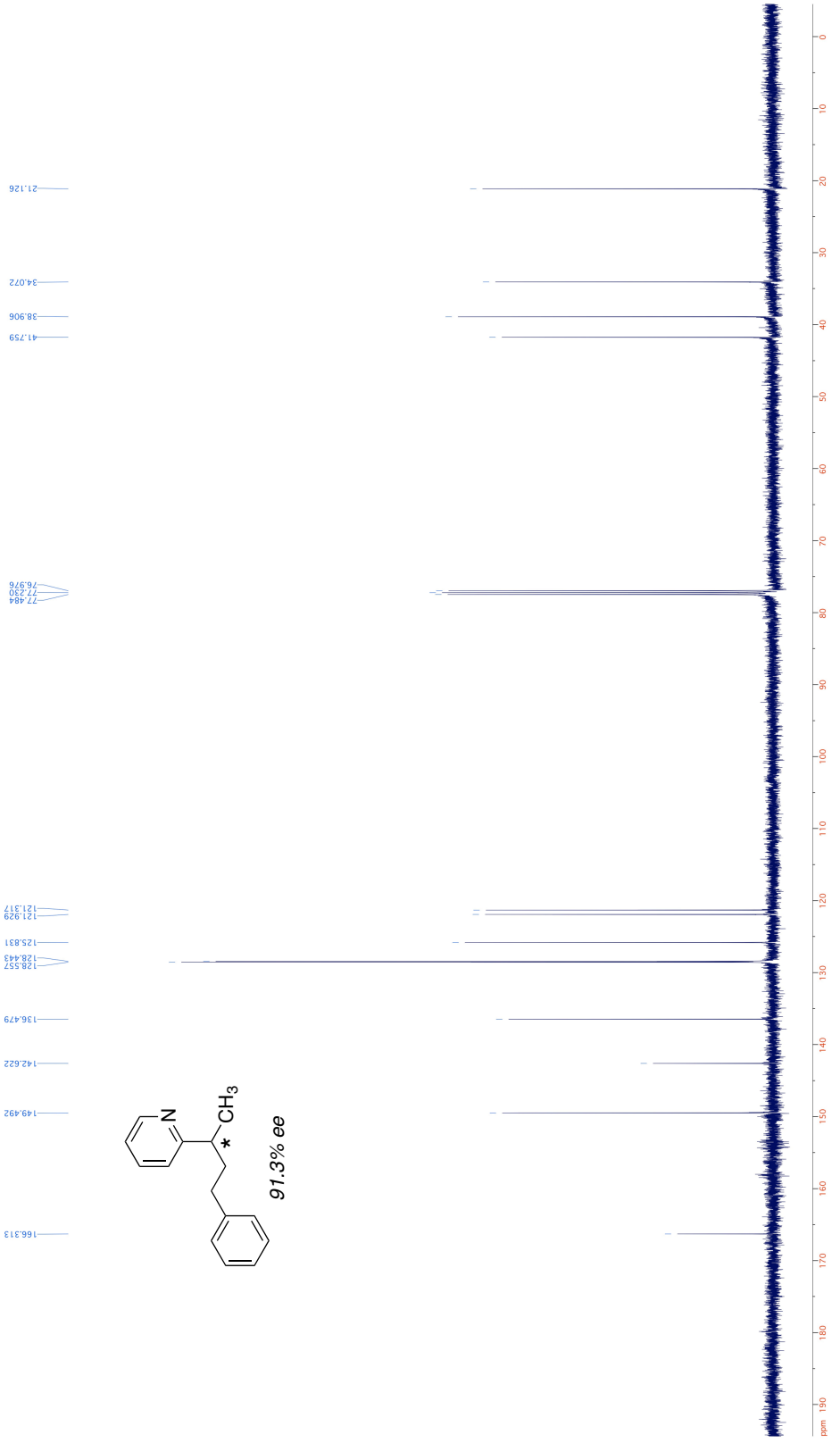
NMe
EtO2C

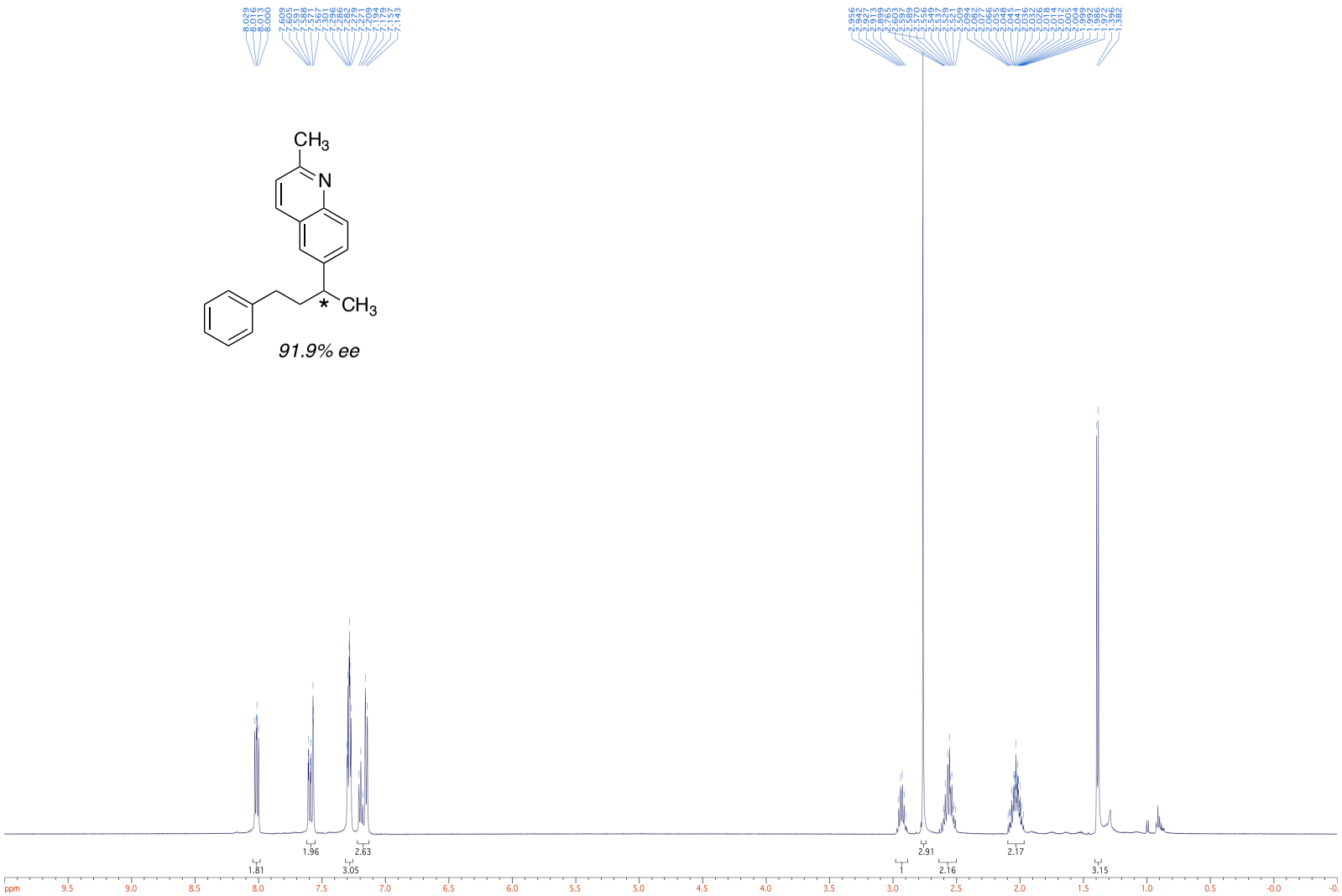

14.484
31.504
41.125
45.158
55.601
61.015
77.484
77.230
76.976
127.007
130.067
126.163
149.750
166.546
NMe
EtO2C

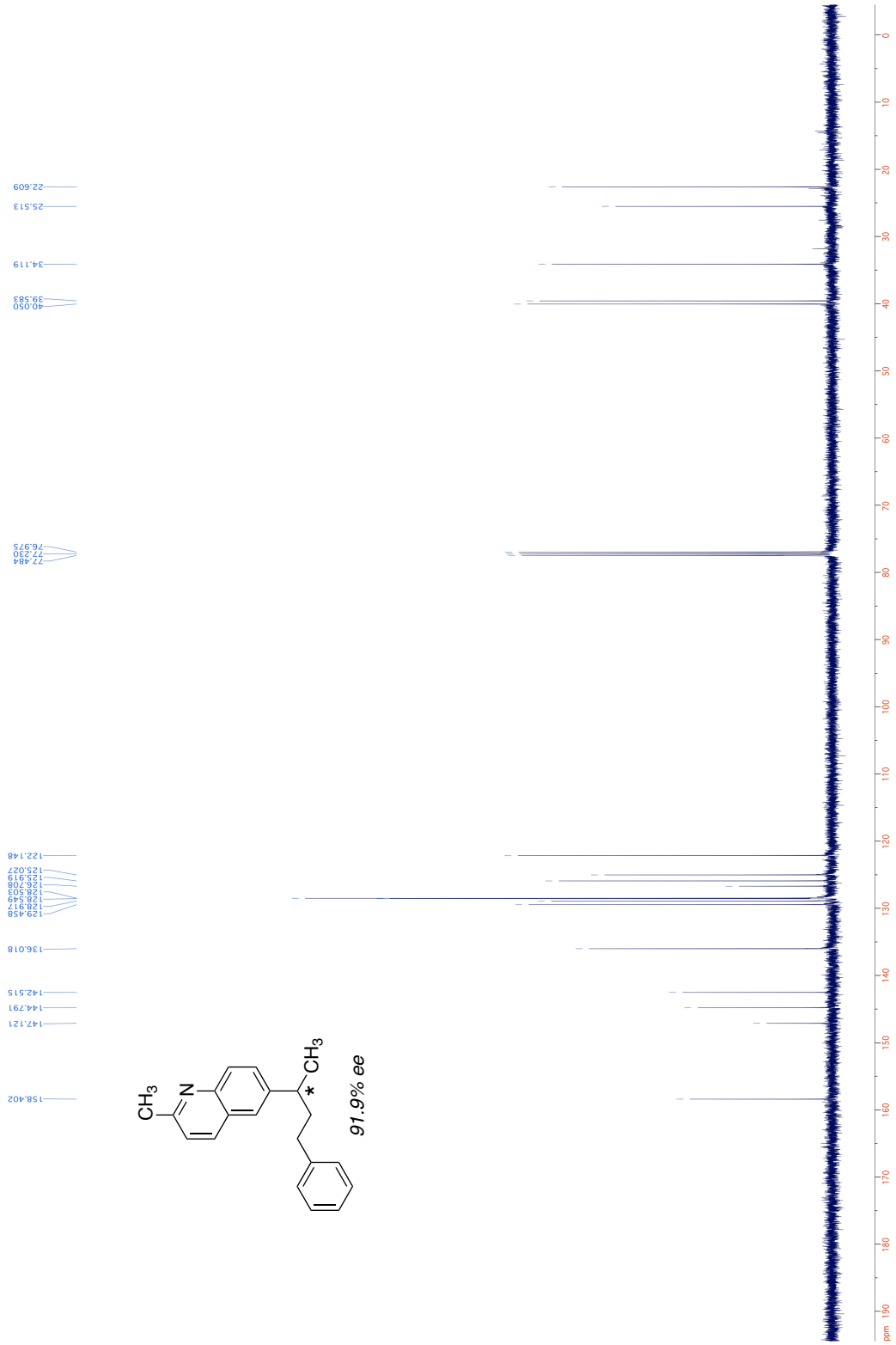

Me
Me
Me
2.05
2.9
2.81
1.08
2.11
6
2.27
3.31
ppm


Me
Me
Me


8.603
8.602
8.597
8.596
7.639
7.638
7.625
7.610
7.294
7.293
7.264
7.197
7.178
7.164
7.149
7.131
7.119
2.986
2.977
2.956
2.944
2.930
2.627
2.613
2.599
2.586
2.565
2.550
2.542
2.531
2.515
2.503
2.167
2.153
2.145
2.140
2.137
2.125
2.117
2.109
1.998
1.966
1.959
1.952
1.946
1.939
1.933
1.927
1.918
1.906
1.893
1.349
N
CH3
91.3% ee
0.835
0.906
4.66
2.02
0.953
2.02
1
1.02
3.07
ppm
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
-0.0


21.126
34.072
38.906
41.759
77.484
77.230
76.976
121.317
121.929
125.831
128.443
128.557
136.479
142.622
149.492
166.313
N
CH3
*
91.3% ee
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
ppm


CH3
N
CH3
*
91.9% ee
1.81
1.96
2.63
3.05
1
2.91
2.16
2.17
3.15
ppm


158.402
147.121
144.791
142.515
136.018
129.458
128.917
128.708
128.503
128.349
126.708
125.979
125.027
122.148
77.484
77.230
76.975
40.050
39.583
34.119
25.513
22.609
ppm
91.9% ee