Supporting Information

Isodesmic C-H Borylation: Perspectives and Proof of Concept of Transfer Borylation Catalysis

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Contents

General experimental

Unless specified otherwise, manipulations were carried out on the bench using no particular precautions. Solvents and reagents were used as bought without drying or further purification.

NMR spectra were recorded on an Agilent Technologies NMR spectrometer at 500 MHz (^{1}H), 125.758 MHz (^{13}C), 160.46 MHz (^{11}B) and on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^{1}H), 100.580 MHz (^{13}C). ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are referenced to residual protons or carbons in deuterated solvent. ^{11}B{^{1}H} was calibrated using an external reference of $BF_3.Et_2O$. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quadruplet (q), multiplet (m). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. GC-MS characterization was carried out using a Thermo Scientific trace GC ultra, coupled with an ITQ 900 mass spectrometer using electronic impact (EI) ionization. Mass Spectrometry analyses were carried out on an Agilent Technologies 6210 LC Time of Flight Mass Spectrometer. Microwave reactions were carried out in an Anton Paar Monowave 300.

Materials

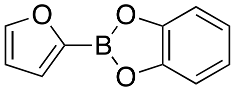
2-Mercaptopyridine, 3-(trifluoromethyl)pyridine-2-thiol, mercaptopyrazine, catecholborane, pyrocatechol, benzylpyrrole, 1-(2-cyanoethyl)pyrrole, 2-methoxythiophene, 2-methylthiophene, 3-methylthiophene, benzofuran, benzothiophene, 2-tert-butylfuran, 1-bromo-2-pentyne, allyl bromide, benzyl bromide, methyl iodide and neopentylglycol were purchased from Sigma Aldrich. 5-(Trifluoromethyl)pyridine-2-thiol, 1-methylindole, 7-methylindole, 5-bromoindole, 6-chloroindole, 6-fluoroindole, 5-cyanoindole, 5-methoxyindole, methyl indole-5-carboxylate, N-methylpyrrole, 3,4-ethylenedioxythiophene, pentafluorobenzene, N,N-dimethylaniline, 2,6-lutidine, tert-butyldimethylsilyl chloride, 4-cyanobenzyl bromide, pinacol, 4-tolylBoronic acid, 4-anisyl boronic acid, and trimethylamine were purchased from Oakwood Chemical. 2-Mercapto-4-(trifluoromethyl)pyrimidine and 2-furanylboronic acid were purchased from Matrix Scientific. Mercaptopyrimidine was purchased from Alfa Aesar. Phenylboronic acid was purchsed from Fluka and Pinacolborane was graciously gifted by BASF. C_6D_6 was purchased from Cambridge Isotope Laboratories and $CDCl_3$ from Fisher Scientific. Quarternary carbon atoms adjacent to boron atoms could not be resolved in ^{13}C NMR spectra as reported previously.

Synthesis of aryl catecholboronic esters

General procedure A

In a typical synthesis, 3 g of the boronic acid was dissolved in *ca.* 150 ml of toluene along with 1 equiv. of pyrocatechol. The reaction flask was then directly placed on the rotary evaporator with the heating bath at 50 °C and the solution evaporated at *ca*. 65 mbar. The grayish solid was then further dried on the rotary evaporator at *ca*. 25 mbar. The resulting solid was then dissolved in *ca*. 150 ml of hexane, filtered and stored at -30 °C overnight, during which the title compound crystallized. The supernatant was removed and the solid dried under vacuum.

2-FurylBCat (1)

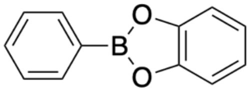


Chemical Formula: $C_{10}H_7BO_3$
Molecular Weight: 185.97

Following the general procedure A starting from 3 g (26.8 mmol) of 2-furanyl boronic acid and using 1 equiv. (2.95 g, 26.8 mmol) of catechol, 3.86 g (77 % yield) of the title compound was obtained as a white fluffy powder. The compound was used without further purification. Slow degradation of the product was observed at room temperature, so the next product batches were kept at -30 °C under a nitrogen as precaution.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 1.6, 0.6 Hz, 1H), 7.41 (dd, *J* = 3.4, 0.5 Hz, 1H), 7.32 (dd, *J* = 5.9, 3.3 Hz, 2H), 7.14 (dd, *J* = 5.9, 3.3 Hz, 2H), 6.58 (dd, *J* = 3.4, 1.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.66 (s), 147.99 (s), 125.37 (s), 123.01 (s), 112.68 (s), 110.98 (s) **^{11}B NMR** (160 MHz, $CDCl_3$) δ 28.3 (s)

PhenylBCat (4)

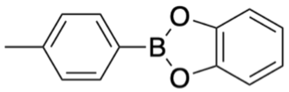


Chemical Formula: $C_{12}H_9BO_2$
Molecular Weight: 196.01

Following the general procedure A starting from 3 g (24.6 mmol) of phenyl boronic acid and using 1 equiv. (2.71 g, 24.6 mmol) of catechol, 3.21 g (67 % yield) of the title compound was obtained as a white fluffy powder. The compound was used without further purification. The compound was stable and was kept on the bench for 2 months without degradation.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, J = 8.1, 1.4 Hz, 2H), 7.67 – 7.50 (m, 3H), 7.35 (dd, J = 5.8, 3.3 Hz, 2H), 7.16 (dd, J = 5.9, 3.3 Hz, 2H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.52 (s), 135.01 (s), 132.40 (s), 128.27 (s), 122.80 (s), 112.59 (s) **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.2 (s)

4-TolylBCat (6)

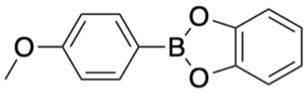


Chemical Formula: $C_{13}H_{11}BO_2$
Molecular Weight: 210.04

Following the general procedure A starting from 3 g (22.7 mmol) of phenyl boronic acid and using 1 equiv. (2.43 g, 22.7 mmol) of catechol, 3.01 g (65 % yield) of the title compound was obtained as a white fluffy crystals. The compound was used without further purification. The compound was stable and was kept on the bench for 2 months without degradation.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 7.9 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.13 (dd, J = 5.9, 3.3 Hz, 2H), 2.44 (s, 3H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.55 (s), 142.81 (s), 135.05 (s), 129.10 (s), 122.69 (s), 112.50 (s), 21.93 (s). **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.2 (s)

4-AnisylBCat (7)



Chemical Formula: $C_{13}H_{11}BO_3$
Molecular Weight: 226.04

Following the general procedure A starting from 3 g (19.7 mmol) of phenyl boronic acid and using 1 equiv. (2.17 g, 19.7 mmol) of catechol, 3.53 g (79 % yield) of the title compound was obtained as a white fluffy crystals. The compound was used without further purification. The compound was stable and was kept on the bench for 2 months without degradation.

^{1}H NMR (500 MHz, $CDCl_3$) 8.04 (d, J = 8.8 Hz, 2H), 7.30 (dd, J = 5.9, 3.3 Hz, 2H), 7.12 (dd, J = 5.9, 3.3 Hz, 2H), 7.02 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H) **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.00 (s), 148.59 (s), 136.85 (s), 122.60 (s), 113.91 (s), 112.40 (s), 55.19 (s) **^{11}B NMR** (160 MHz, $CDCl_3$) δ 32.2 (s)

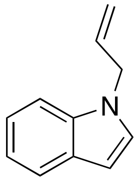
Substrate synthesis and characterization

General procedure B

Indole were protected following a modified procedure from Miranda *et al.*[1] To a DMSO solution of the indole (1 g/20 ml) was added NaOH (2 equiv.) and the protecting reagent: allyl bromide, 1-bromo-2-pentyne, methyl iodide or 4-cyanobenzyl bromide (1-2 equiv.). The reaction was stirred at room temperature until completion as determined by TLC (typically less than 1 h for the reaction with methyl iodide and few hours in the other cases). Water was then added (*ca.* 100ml) followed by EtOAc, and the organic phase was washed twice with ca. 50-100 ml of water. The organic phase was then dried with anhydrous Na_2SO_4, filtered on a short silica pad and the volatiles evaporated under reduced pressure. The products were usually used without further purification, but where the protecting reagents were not volatile, they were further purified using silica gel chromatography with hexanes/EtOAc as eluent.

Details and substrate characterization

1-allyl-1H-indole

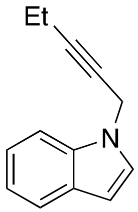


Chemical Formula: $C_{11}H_{11}N$
Molecular Weight: 157.22

Following the general procedure B starting from 1 g (8.5 mmol) of 1H-indole and using 2 equiv. (2.05 g, 17 mmol) of allyl bromide, 1.24 g (92 % yield) of the title compound was obtained as a red-brown oil. The compound was used without further purification. NMR data similar as in literature.[1]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 1H), 7.35 (ddd, *J* = 8.2, 1.6, 0.8 Hz, 1H), 7.24 (ddd, *J* = 8.3, 7.1, 1.2 Hz, 1H), 7.16 – 7.12 (m, 2H), 6.55 (dd, *J* = 3.1, 0.8 Hz, 1H), 6.02 (ddt, *J* = 17.1, 10.3, 5.4 Hz, 1H), 5.22 (ddd, *J* = 10.3, 2.8, 1.5 Hz, 1H), 5.11 (ddd, *J* = 17.1, 3.0, 1.7 Hz, 1H), 4.75 (dt, *J* = 5.4, 1.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.07 (s), 133.48 (s), 128.64 (s), 127.82 (s), 121.50 (s), 120.95 (s), 119.40 (s), 117.23 (s), 109.58 (s), 101.38 (s), 48.83 (s). **HRMS** (ES^+) m/z calculated for $[C_{11}H_{12}N]$: 158.0964, found: 158.0970.

1-(pent-2-yn-1-yl)-1H-indole

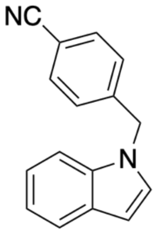


Chemical Formula: $C_{13}H_{13}N$
Molecular Weight: 183.25

Following the general procedure B starting from 500 mg (4.3 mmol) of 1H-indole and 1.5 equiv. (940 mg, 6.4 mmol) of 1-bromo-2-pentyne. After purification by silica gel chromatography, 657 mg (84 % yield) of the title compound was obtained as a red-brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.63 (m, 1H), 7.43 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.15 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.54 (dd, *J* = 3.2, 0.8 Hz, 1H), 4.86 (t, *J* = 2.3 Hz, 2H), 2.23 (qt, *J* = 7.5, 2.3 Hz, 2H), 1.15 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.76 (s), 128.83 (s), 127.29 (s), 121.61 (s), 120.98 (s), 119.61 (s), 109.46 (s), 101.47 (s), 87.25 (s), 73.30 (s), 36.24 (s), 13.71 (s), 12.40 (s). **HRMS** (ES^+) m/z calculated for [$C_{13}H_{14}N$]: 184.1121, found: 184.1131.

4-((1H-indol-1-yl)methyl)benzonitrile

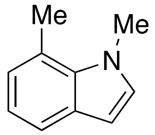


Chemical Formula: $C_{16}H_{12}N_2$
Molecular Weight: 232.29

Following the general procedure B starting from 1 g (8.5 mmol) of 1H-indole and using 0.9 equiv. (1.51 g, 7.7 mmol) of 4-cyanobenzyl bromide, 1.5 g (83 % yield) of the title compound was obtained as a red-brown oil. The compound was used without further purification. NMR data similar as in literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.12 (m, 6H), 6.61 (d, *J* = 3.1 Hz, 1H), 5.38 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.07 (s), 136.05 (s), 132.61 (s), 128.79 (s), 128.14 (s), 127.12 (s), 122.11 (s), 121.23 (s), 119.95 (s), 118.58 (s), 111.50 (s), 109.39 (s), 102.49 (s), 49.63 (s). **HRMS** (ES$^+$) m/z calculated for [$C_{16}H_{13}N_2$]: 233.1073, found: 233.1094.

1,7-dimethyl-1H-indole

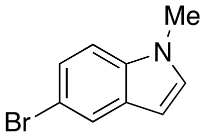


Chemical Formula: $C_{10}H_{11}N$
Molecular Weight: 145.21

Following the general procedure B starting from 1 g (7.6 mmol) of 7-methyl-1H-indole and using 2 equiv. (2.17 g, 15.2 mmol) of methyl iodide, 1.10 g (99 % yield) of the title compound was obtained as a slightly orange solid. The compound was used without further purification. NMR data similar as in literature.[3]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.8, 0.6 Hz, 1H), 7.06 – 7.00 (m, 1H), 7.00 – 6.94 (m, 2H), 6.49 (d, *J* = 3.1 Hz, 1H), 4.09 (s, 3H), 2.82 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.43 (s), 130.42 (s), 129.65 (s), 124.16 (s), 121.22 (s), 119.59 (s), 119.12 (s), 100.92 (s), 36.82 (s), 19.80 (s). **HRMS** (ES$^+$) m/z calculated for [$C_{10}H_{12}N$]: 146.0964, found: 146.0974.

5-bromo-1-methyl-1H-indole

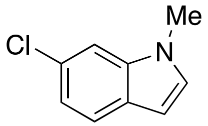


Chemical Formula: C_9H_8BrN
Molecular Weight: 210.07

Following the general procedure B starting from 1 g (5.1 mmol) of 5-bromo-1H-indole and using 2 equiv. (1.45 g, 10.2 mmol) of methyl iodide, 1.04 g (97 % yield) of the title compound was obtained as a yellow oil. The compound was used without further purification. NMR data similar as in literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 1.9 Hz, 1H), 7.32 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.19 (d, *J* = 8.7 Hz, 1H), 7.05 (d, *J* = 3.1 Hz, 1H), 6.44 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.76 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 135.35 (s), 130.11 (s), 130.00 (s), 124.28 (s), 123.26 (s), 112.65 (s), 110.70 (s), 100.52 (s), 33.00 (s). **HRMS** (ES^+) m/z calculated for [C_9H_9BrN]: 209.9913, found: 209.9929.

<u>6-chloro-1-methyl-1H-indole</u>

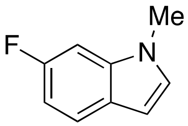


Chemical Formula: C_9H_8ClN
Molecular Weight: 165.62

Following the general procedure B starting from 1 g (6.6 mmol) of 6-chloro-1H-indole and using 2 equiv. (1.87 g, 13.2 mmol) of methyl iodide, 1.03 g (94 % yield) of the title compound was obtained as an orange-brown oil. The compound was used without further purification.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.35 – 7.31 (m, 1H), 7.09 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.04 (d, *J* = 3.1 Hz, 1H), 6.47 (dt, *J* = 3.3, 1.6 Hz, 1H), 3.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.08 (s), 129.52 (s), 127.50 (s), 126.96 (s), 121.67 (s), 119.95 (s), 109.26 (s), 101.14 (s), 32.90 (s). **HRMS** (ES^+) m/z calculated for [C_9H_9ClN]: 166.0418, found: 166.0410.

6-fluoro-1-methyl-1H-indole

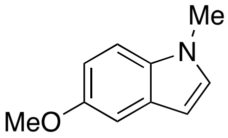


Chemical Formula: C_9H_8FN
Molecular Weight: 149.17

Following the general procedure B starting from 1 g (7.4 mmol) of 6-fluoro-1H-indole and using 2 equiv. (2.1 g, 14.8 mmol) of methyl iodide, 1.10 g (99 % yield) of the title compound was obtained as an orange oil. The compound was used without further purification. NMR data similar as in literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.6, 5.4 Hz, 1H), 7.04 (d, *J* = 3.2 Hz, 1H), 7.01 (dd, *J* = 9.9, 2.3 Hz, 1H), 6.90 (ddd, *J* = 9.6, 8.6, 2.3 Hz, 1H), 6.48 (dd, *J* = 3.2, 0.8 Hz, 1H), 3.75 (s, 3H). **^{19}F NMR** (376 MHz, c) δ -121.25 (td, *J* = 9.7, 5.4 Hz). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.78 (d, *J* = 237.1 Hz), 136.69 (d, *J* = 12.1 Hz), 129.20 (d, *J* = 3.6 Hz), 124.85 (s), 121.52 (d, *J* = 10.2 Hz), 108.00 (d, *J* = 24.7 Hz), 101.09 (s), 95.57 (d, *J* = 26.2 Hz), 32.91 (s). **HRMS** (ES$^+$) m/z calculated for [C_9H_9FN]: 150.0714, found: 150.0647.

5-methoxy-1-methyl-1H-indole

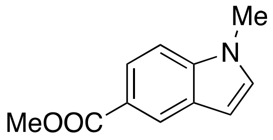


Chemical Formula: $C_{10}H_{11}NO$
Molecular Weight: 161.20

Following the general procedure B starting from 1 g (6.8 mmol) of 5-methoxy-1H-indole and using 2 equiv. (1.9 g, 13.6 mmol) of methyl iodide, 1.03 g (94 % yield) of the title compound was obtained as a golden solid. The compound was used without further purification. NMR data similar as in literature.[5]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.9 Hz, 1H), 7.11 (d, *J* = 2.4 Hz, 1H), 7.03 (t, *J* = 3.6 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.42 (dd, *J* = 3.0, 0.7 Hz, 1H), 3.87 (s, 3H), 3.77 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.95 (s), 132.09 (s), 129.30 (s), 128.74 (s), 111.84 (s), 109.91 (s), 102.45 (s), 100.35 (s), 55.89 (s), 32.99 (s). **HRMS** (ES^+) m/z calculated for [$C_{10}H_{12}NO$]: 162.0913, found: 162.0925.

Methyl 1-methyl-1H-indole-5-carboxylate

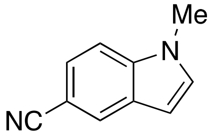


Chemical Formula: $C_{11}H_{11}NO_2$
Molecular Weight: 189.21

Following the general procedure B starting from 1 g (5.7 mmol) of methyl 1H-indole-5-carboxylate and using 2 equiv. (1.6 g, 11.4 mmol) of methyl iodide, 1.04 g (96 % yield) of the title compound was obtained as a slightly orange solid. The compound was used without further purification.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.40 (d, *J* = 1.6 Hz, 1H), 7.93 (dt, *J* = 8.9, 2.6 Hz, 1H), 7.32 (d, *J* = 8.7 Hz, 1H), 7.10 (d, *J* = 3.2 Hz, 1H), 6.59 (dd, *J* = 3.1, 0.8 Hz, 1H), 3.93 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 168.29 (s), 139.07 (s), 130.22 (s), 127.94 (s), 123.91 (s), 122.88 (s), 121.30 (s), 108.84 (s), 102.60 (s), 51.83 (s), 33.01 (s). **HRMS** (ES$^+$) m/z calculated for [$C_{11}H_{12}NO_2$]: 190.0863, found: 190.0875.

1-methyl-1H-indole-5-carbonitrile

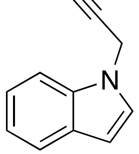


Chemical Formula: $C_{10}H_8N_2$
Molecular Weight: 156.19

Following the general procedure B starting from 1 g (7.0 mmol) of 1H-indole-5-carbonitrile and using 2 equiv. (2.0 g, 14.0 mmol) of methyl iodide, 933 mg (85 % yield) of the title compound was obtained as an orange solid. The compound was used without further purification. NMR data similar as in literature.[6]

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, *J* = 0.8 Hz, 1H), 7.42 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 1H), 7.17 (d, *J* = 3.2 Hz, 1H), 6.56 (d, *J* = 3.4 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 138.11 (s), 131.16 (s), 128.11 (s), 126.43 (s), 124.38 (s), 120.92 (s), 110.07 (s), 102.24 (s), 102.10 (s), 33.08 (s). **HRMS** (ES$^+$) m/z calculated for [$C_{11}H_9N_2$]: 157.0760, found: 157.0776.

1-(prop-2-yn-1-yl)-1*H*-indole



Chemical Formula: $C_{11}H_9N$
Molecular Weight: 155.20

1-(prop-2-yn-1-yl)-1*H*-indole was synthesized according to literature procedures.[15] Sodium hydride (288.0 mg, 12.0 mmol, 1.2 equiv.) was added to a solution of 1*H*-indole (1.17 g,10 mmol,1 equiv.) in DMF (10 ml) at 0° C. The suspension is slowly warmed to room temperature and stirred for an hour. The solution is now cooled to 0° C again and propargyl bromide (1.67 ml,15 mmol,1.5 equiv., 80% in toluene). The mixture allowed to warm to room temperature and stirred over-night. Now water is added to quench the reaction and DCM (3 x 25 ml) is used for extraction. The combined organic layers were dried over $MgSO_4$, all volatiles were removed under vacuum and the residue was purified via column chromatography (SiO_2). NMR data similar as in literature.[15]

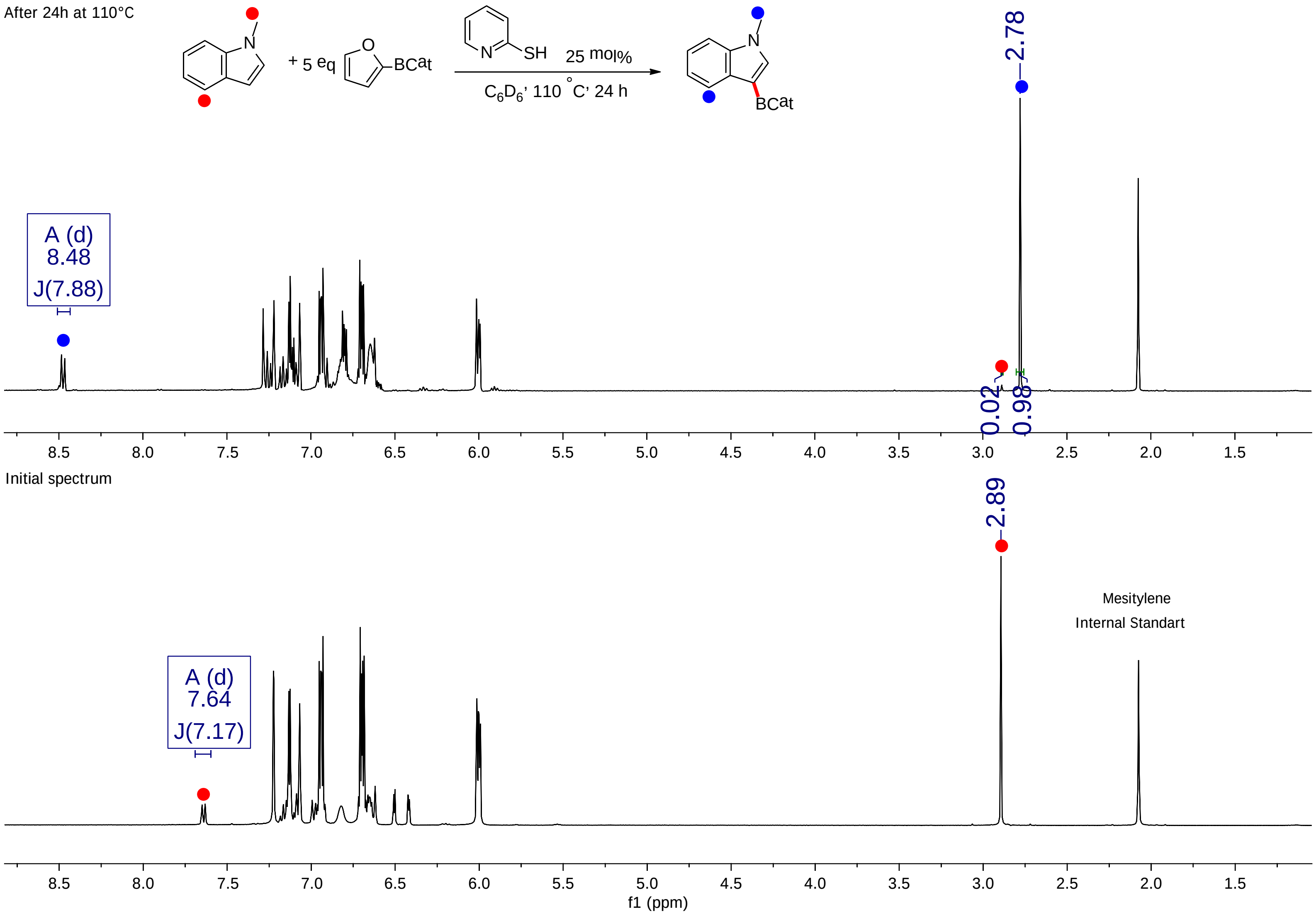
^{1}H NMR (400 MHz, Benzene-*d*$_6$) δ 7.68 – 7.65 (m, 1H), 7.25 – 7.17 (m, 2H), 7.15 – 7.14 (m, 1H), 6.77 (d, *J* = 3.2 Hz, 1H), 6.47 (dd, *J* = 3.2, 0.9 Hz, 1H), 4.03 (d, *J* = 2.5 Hz, 2H), 1.79 (s, 1H). **^{13}C NMR** (101 MHz, Benzene-*d*$_6$) δ 136.35, 129.64, 127.18, 122.15, 121.53, 120.32, 109.76, 102.46, 78.09, 73.48, 35.35.

Substrate scope details

General procedure C

In a standard test run, a solution of 2.5 mg (25 mol%) of 2-mercaptopyridine, 84 mg (5 equiv.) of 2-FurylBCat and 3.2 mg (*ca.* mol 30%) of mesitylene (internal standard) per 0.5 ml of C_6D_6 was prepared. Then, 0.5 ml of the solution was added to 1 equiv. of the substrate, and a small aliquot was taken and analyzed by GC-MS as a reference point. The solution was transferred to a J-Young tube and analyzed by ^{1}H NMR as a reference point. The mixture was then heated at 110 °C for 24 h and analyzed by ^{1}H NMR. In the following section the initial and final spectra are presented. In all cases the conversion was calculated using the most characteristic signals of the substrates and products. Details for each substrate are given directly on each spectrum. After, 10 equiv. of pinacol and 3.3 equiv. of NEt_3 in 1 ml of toluene was added to the reaction, the tube was shaken and left to react for 1 h before it was analyzed by GC-MS. GC-MS data are also presented in the following section. It is to note that during the transesterification to pinacol some protodeborylation may occur. Thus the starting materials signals are observed in all GC-traces. Signals of pinacol converted residual borlyating agent and mesitylene (internal standard) are also present at 5.90 and 4.44 min respectively. All manipulations were performed outside the glovebox in a not air-conditioned laboratory with temperatures between 15-25 °C.

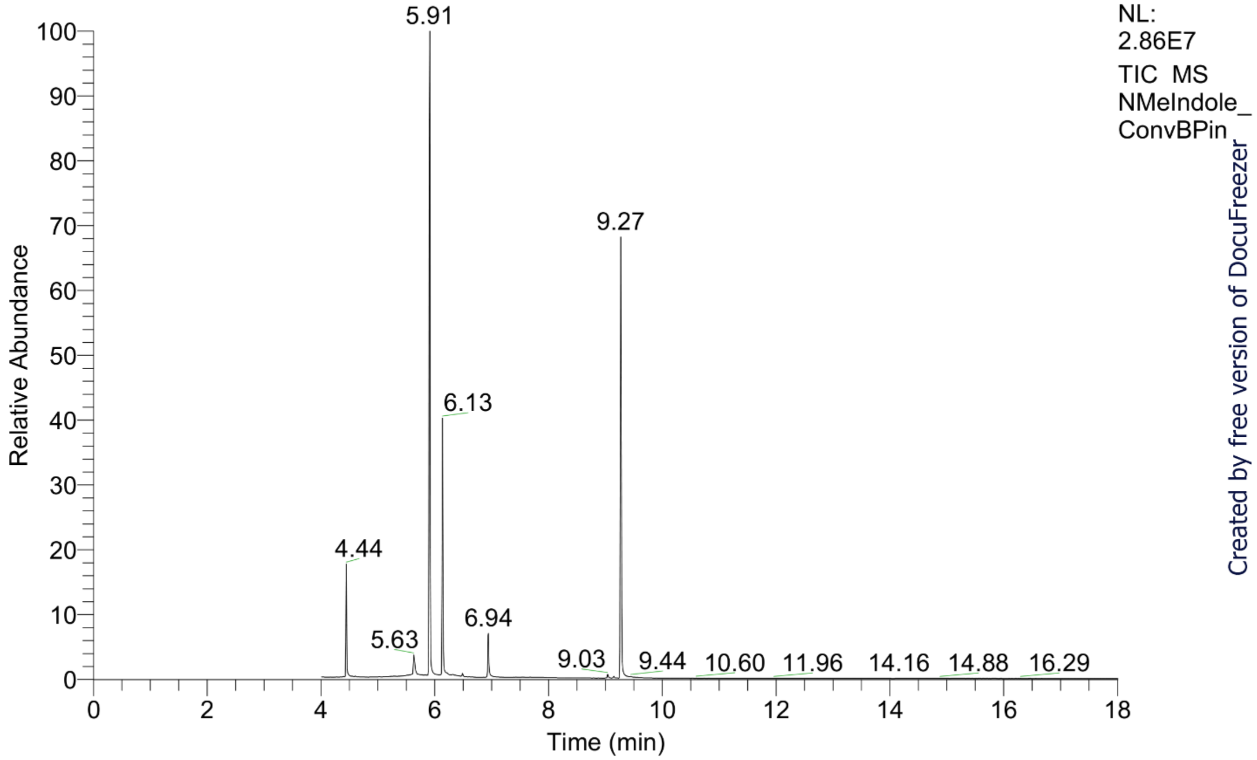
NMR and GC-MS data



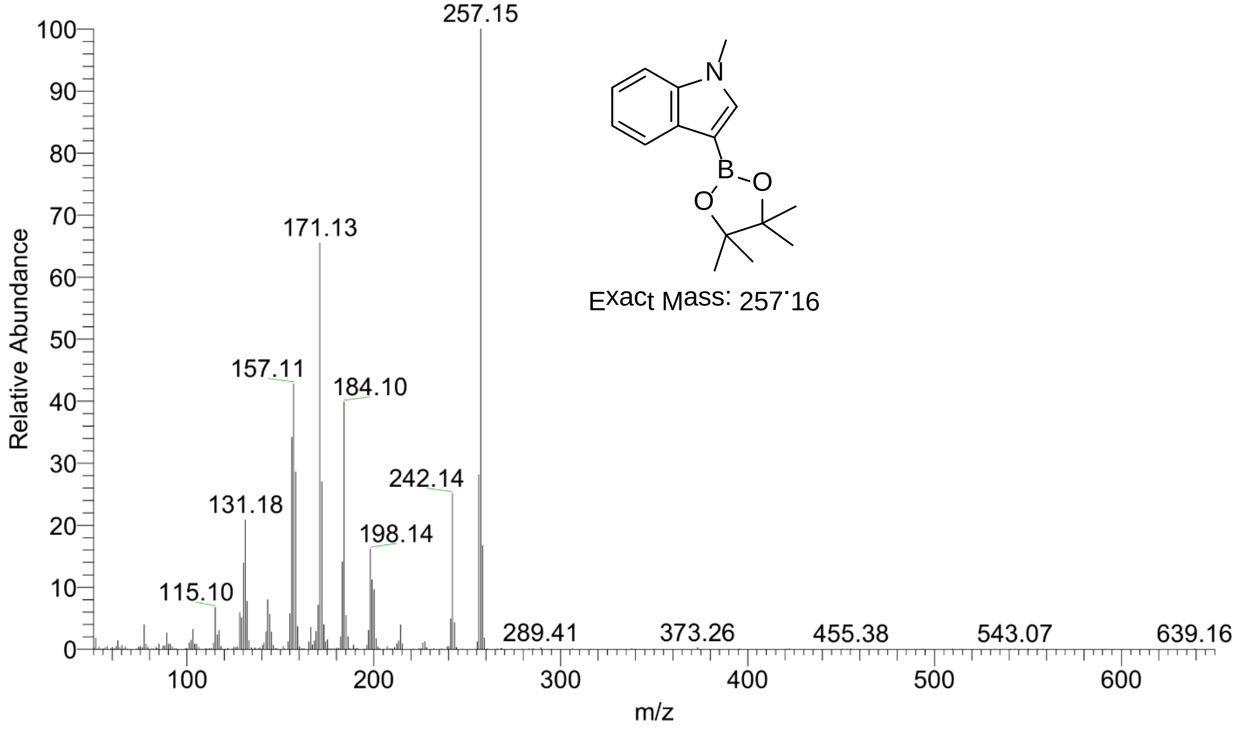
The conversion was determined using the N-methyl signal that shifts from 2.89 in the starting material to 2.78 ppm in the product. A significant shift of the signal associated to the C4 proton from 7.64 to 8.48 ppm was also observed. The product signals are coherent with the literature.[7]

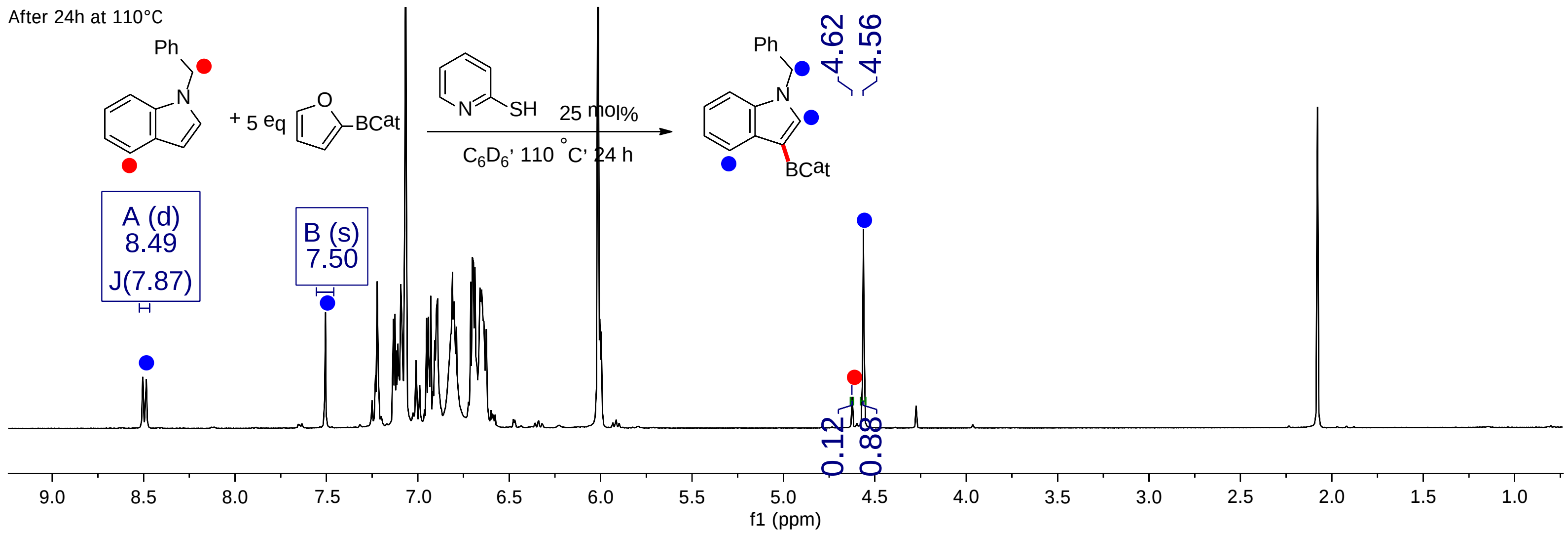
D:\GCMS Data\...\NMeIndole_ConvBPin 08/01/18 11:27:59 1

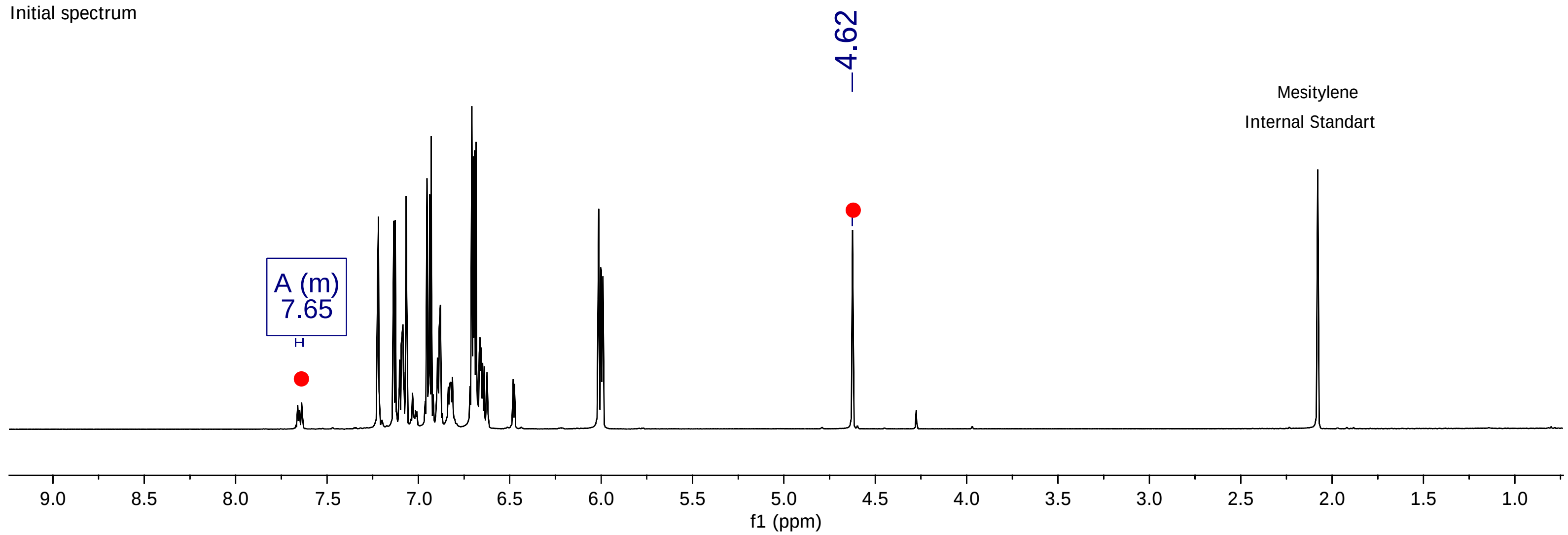
RT: 0.00 - 18.01



NMeIndole_ConvBPin #600 RT: 9.27 AV: 1 NL: 2.96E6
T: + c Full ms [50.00-650.00]

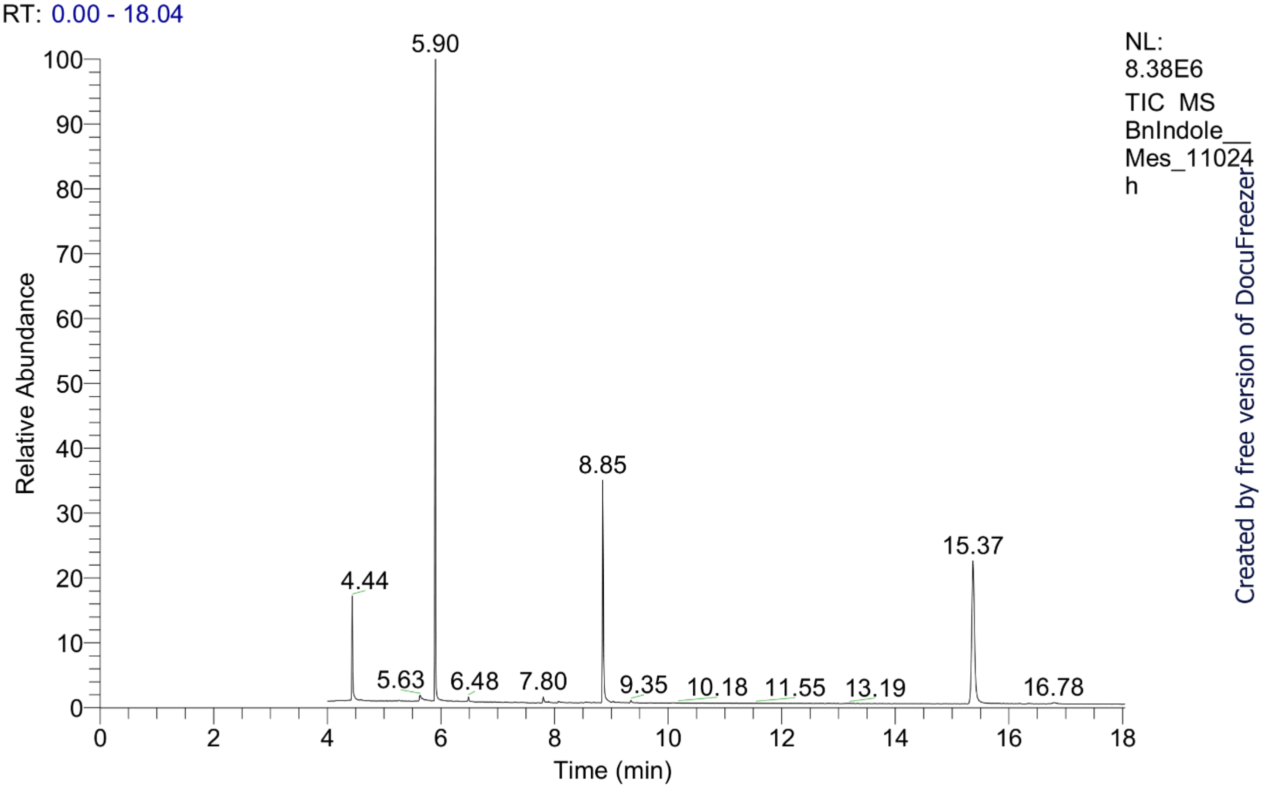


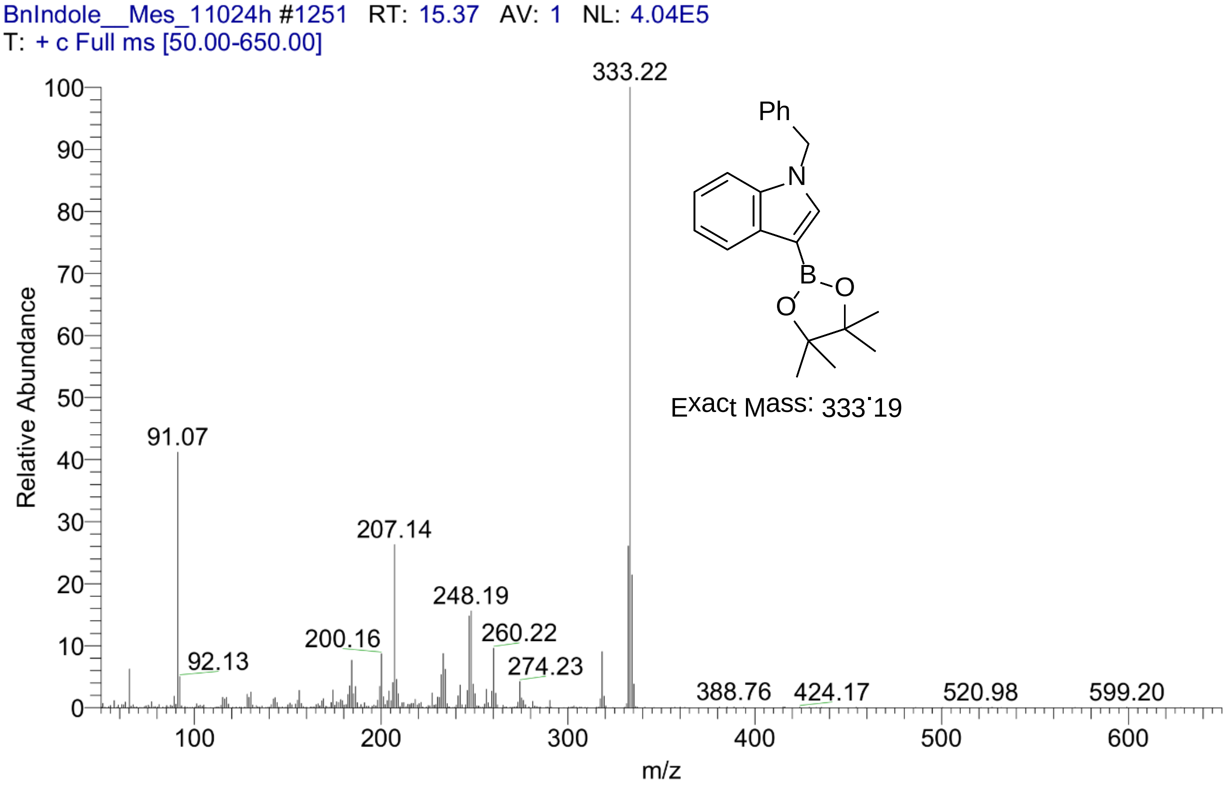


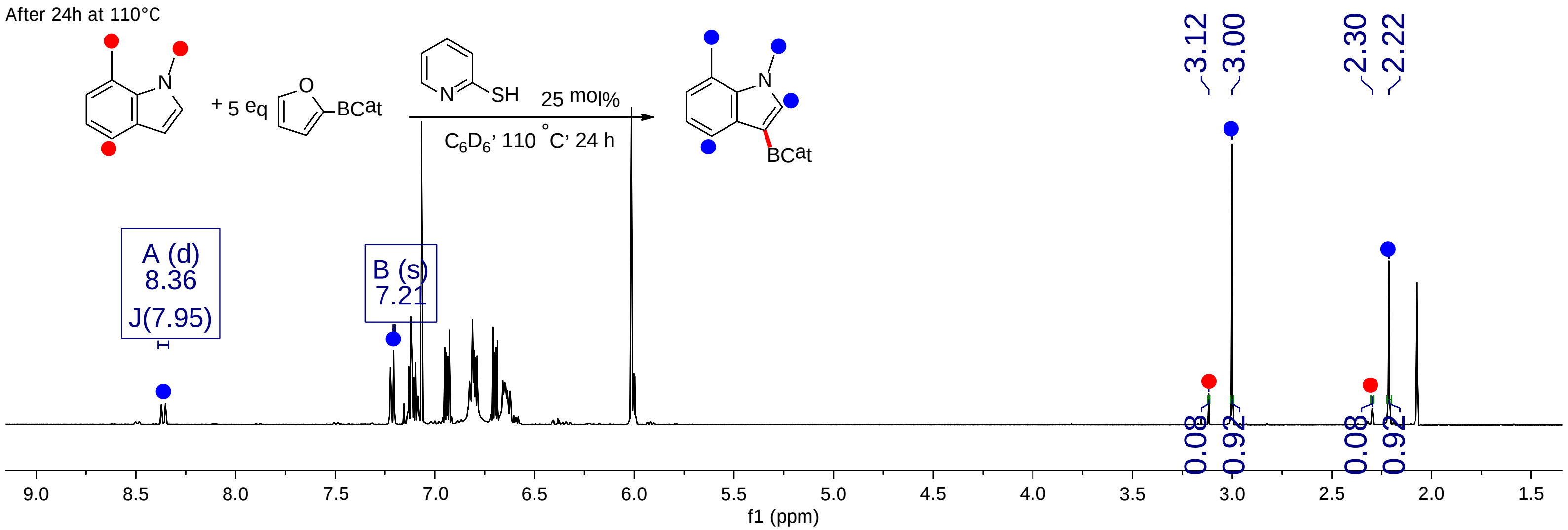


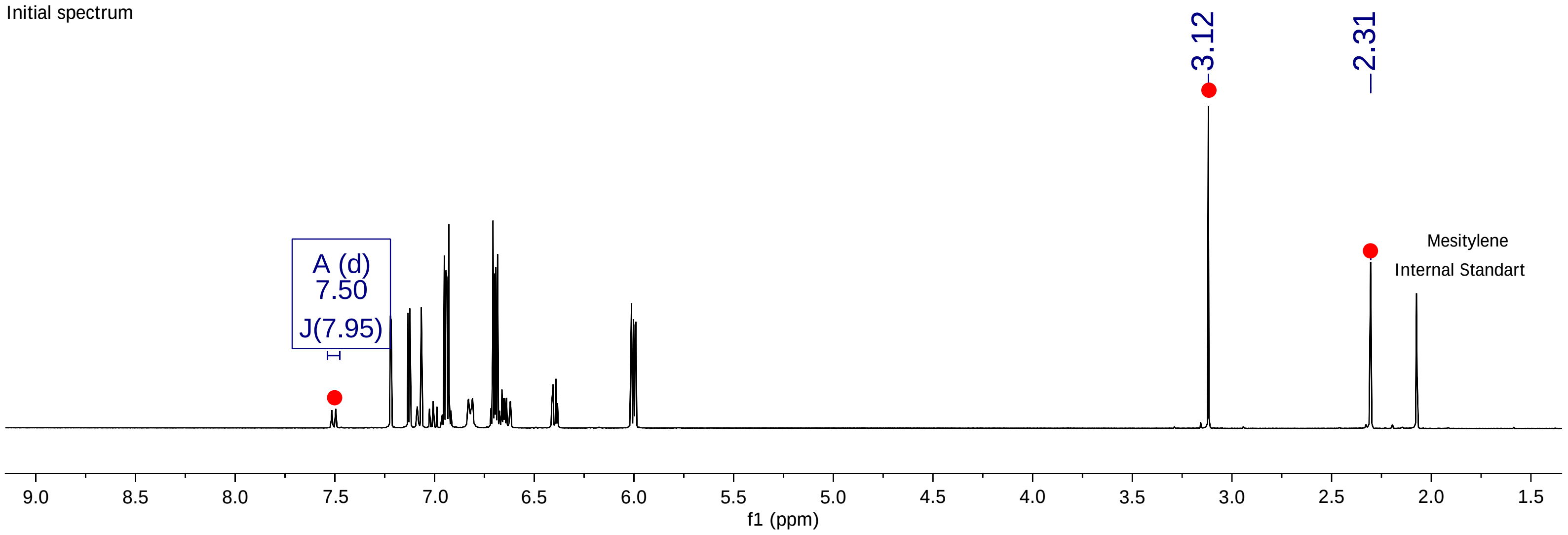
The conversion was determined using the N-CH_2 (benzylic) signal that shifts from 4.62 in the starting material to 4.56 ppm in the product. A significant shift of the signal associated to the C4 proton from 7.65 to 8.49 ppm and the appearance of a characteristic singlet from the C2 proton at 7.50 ppm were also observed.

D:\GCMS Data\...\BnIndole__Mes_11024h 08/09/18 10:21:50

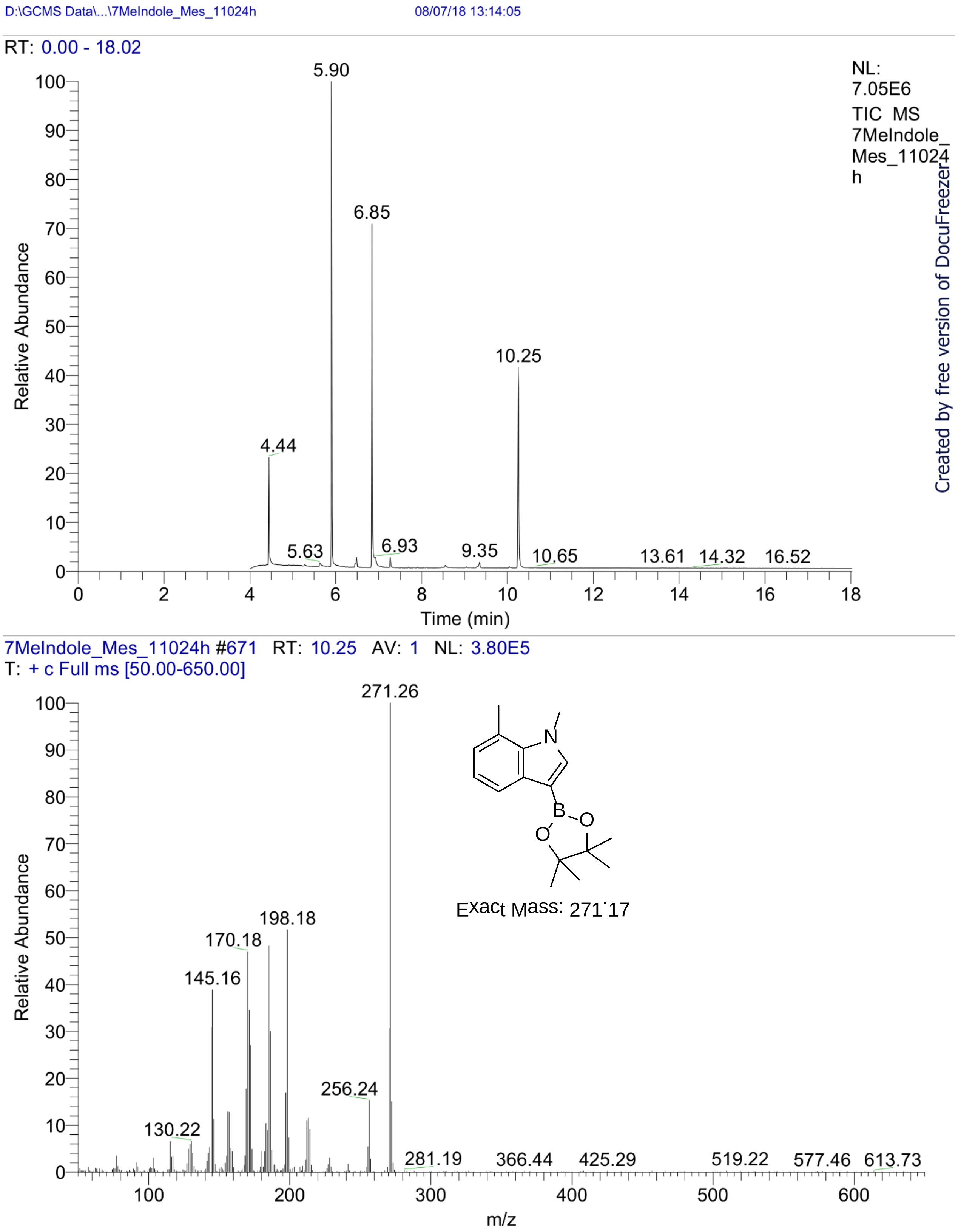


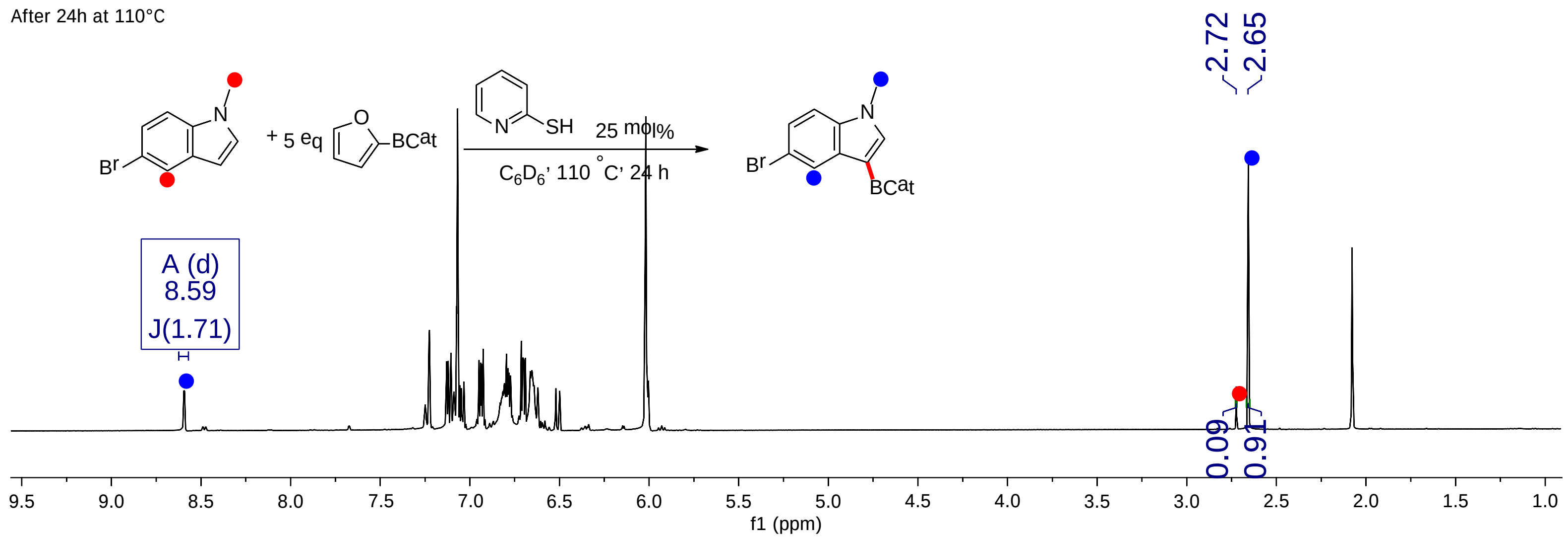


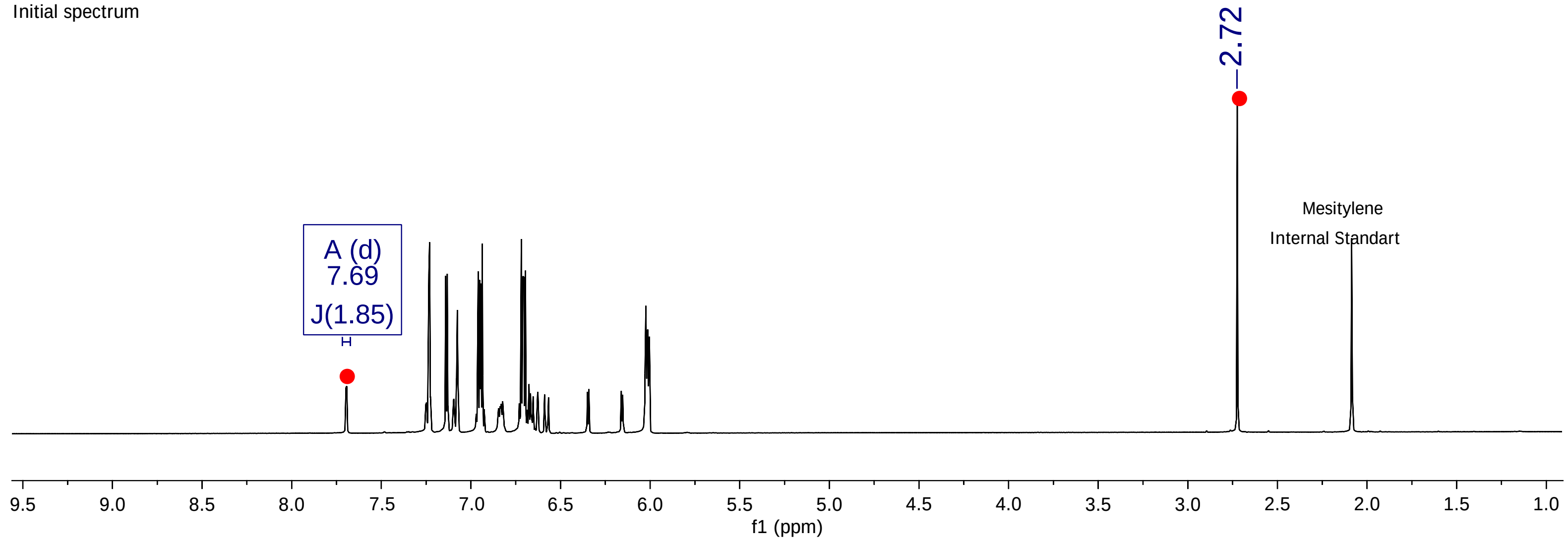

After 24h at 110°C


Initial spectrum

The conversion was determined using the N-Methyl and 7C-Methyl signals that shift respectively from 3.12 and 2.31 ppm in the starting material to 3.00 and 2.22 ppm in the product. A significant shift of the signal associated to the C4 proton from 7.50 to 8.36 ppm and the appearance of a characteristic singlet from the C2 proton at 7.21 ppm were also observed. The product signals are coherent with the literature.[7]

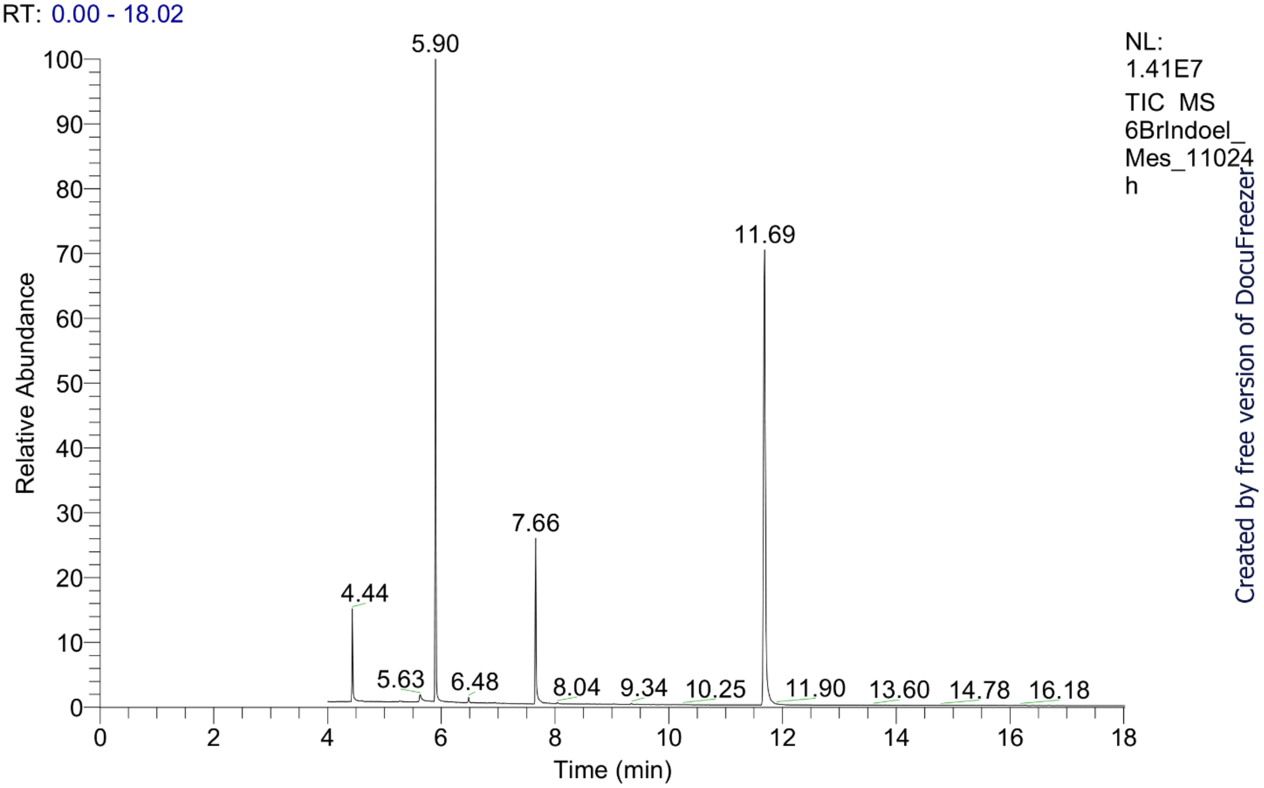

D:\GCMS Data\...\7MeIndole_Mes_11024h
08/07/18 13:14:05
RT: 0.00 - 18.02
NL: 7.05E6
TIC MS 7MeIndole_Mes_11024h
Relative Abundance
Time (min)
0
2
4
6
8
10
12
14
16
18
0
10
20
30
40
50
60
70
80
90
100
5.90
6.85
10.25
4.44
5.63
6.93
9.35
10.65
13.61
14.32
16.52
7MeIndole_Mes_11024h #671 RT: 10.25 AV: 1 NL: 3.80E5
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
100
200
300
400
500
600
271.26
198.18
170.18
145.16
256.24
130.22
281.19
366.44
425.29
519.22
577.46
613.73
N
B
O
O
Exact Mass: 271.17



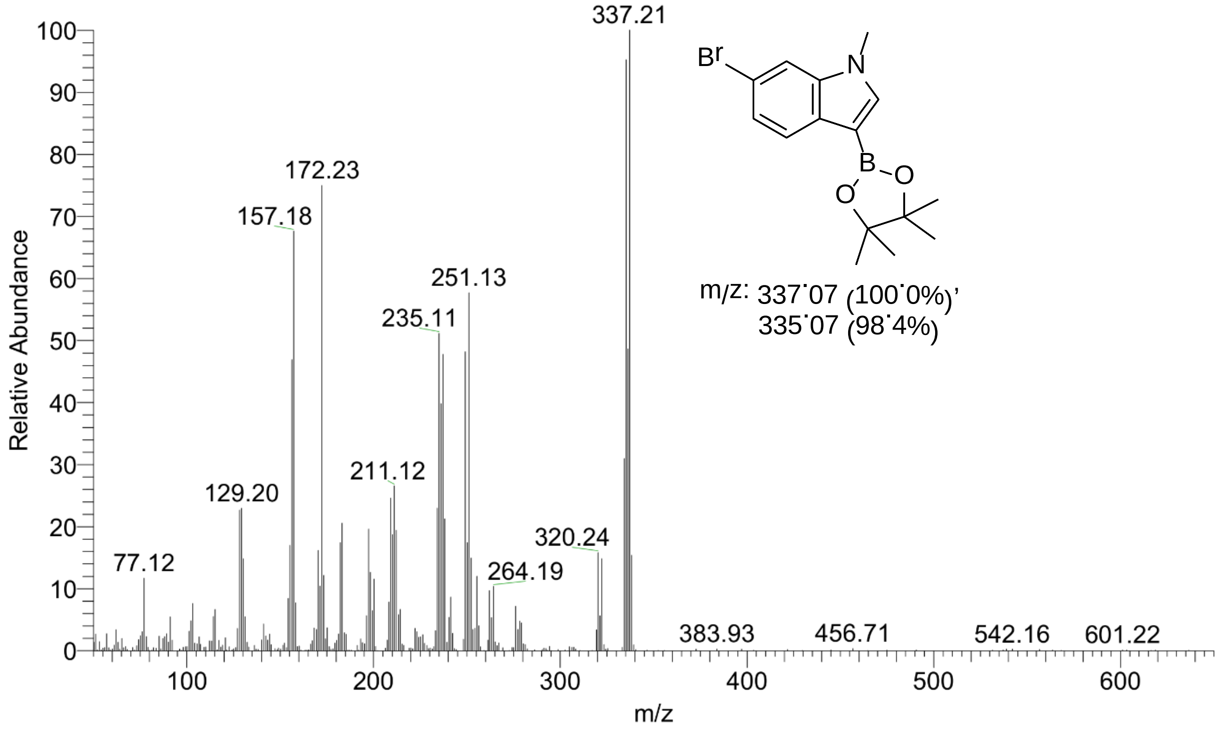


The conversion was determined using the N-Methyl signal that shifts from 2.72 in the starting material to 2.65 ppm in the product. A significant shift of the signal associated to the C4 proton from 7.69 to 8.59 ppm was also observed. The product signals are coherent with the literature.[7]

D:\GCMS Data\...\6BrIndoel_Mes_11024h 08/07/18 13:35:05

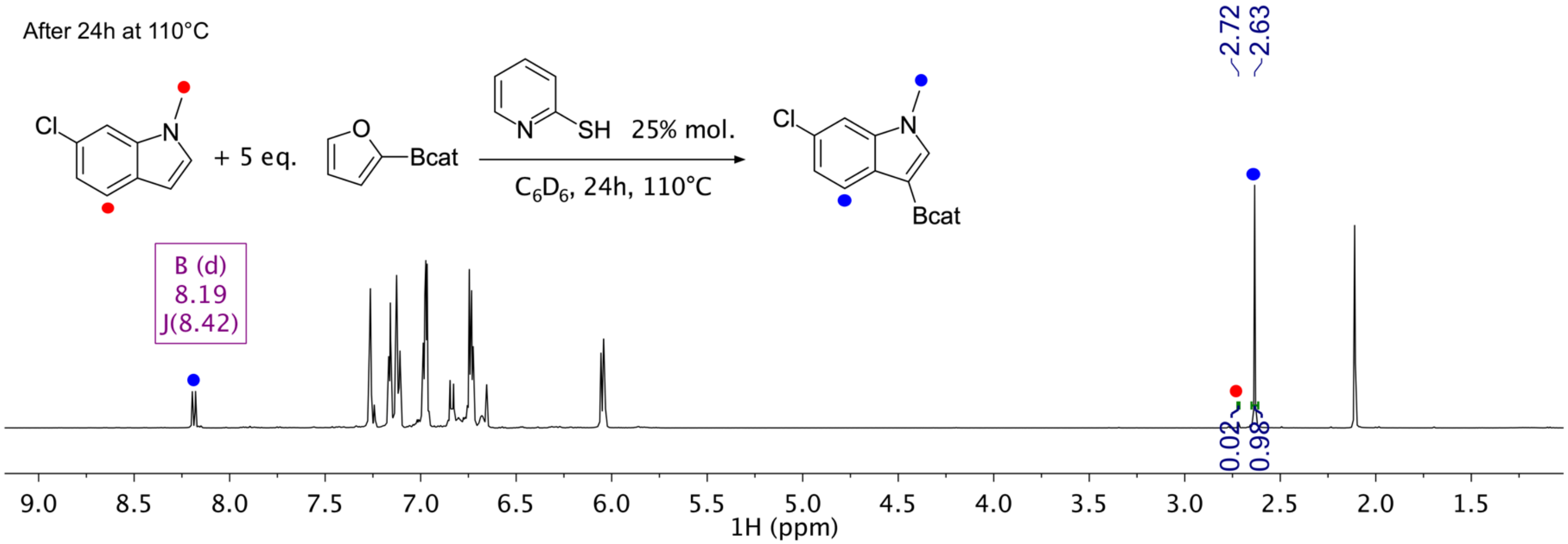


6BrIndoel_Mes_11024h #861 RT: 11.69 AV: 1 NL: 4.65E5
T: + c Full ms [50.00-650.00]

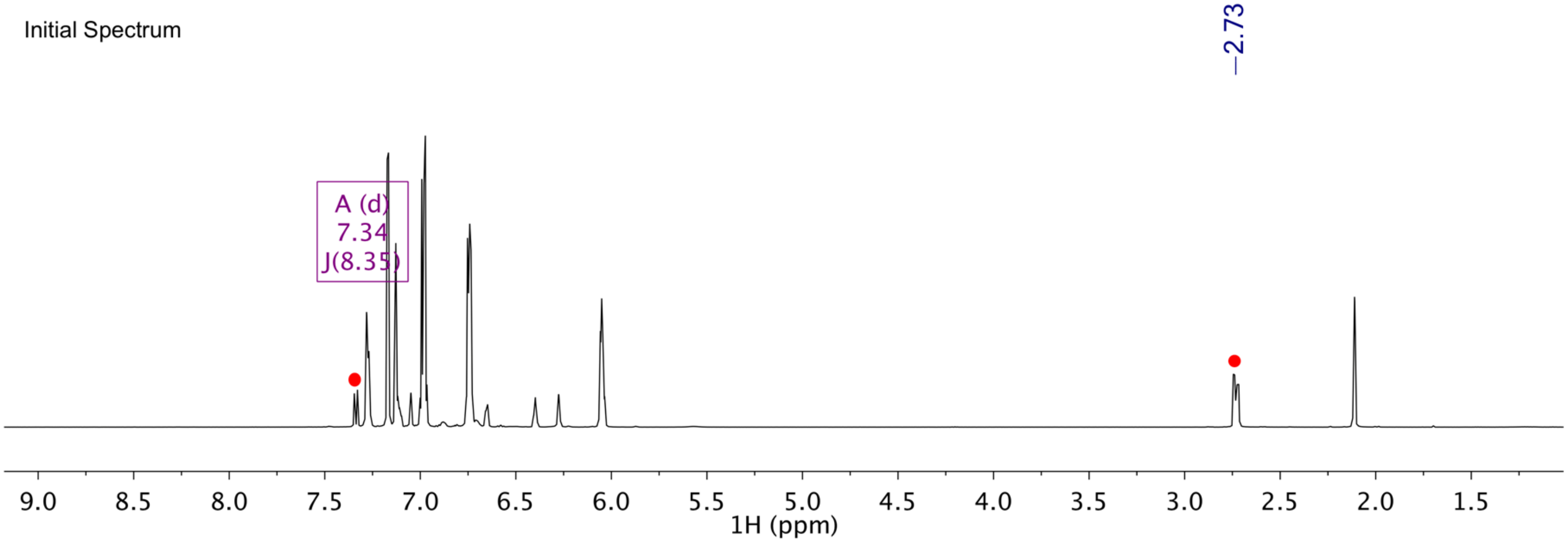


m/z: 337.07 (100.0%),
335.07 (98.4%)

After 24h at 110°C



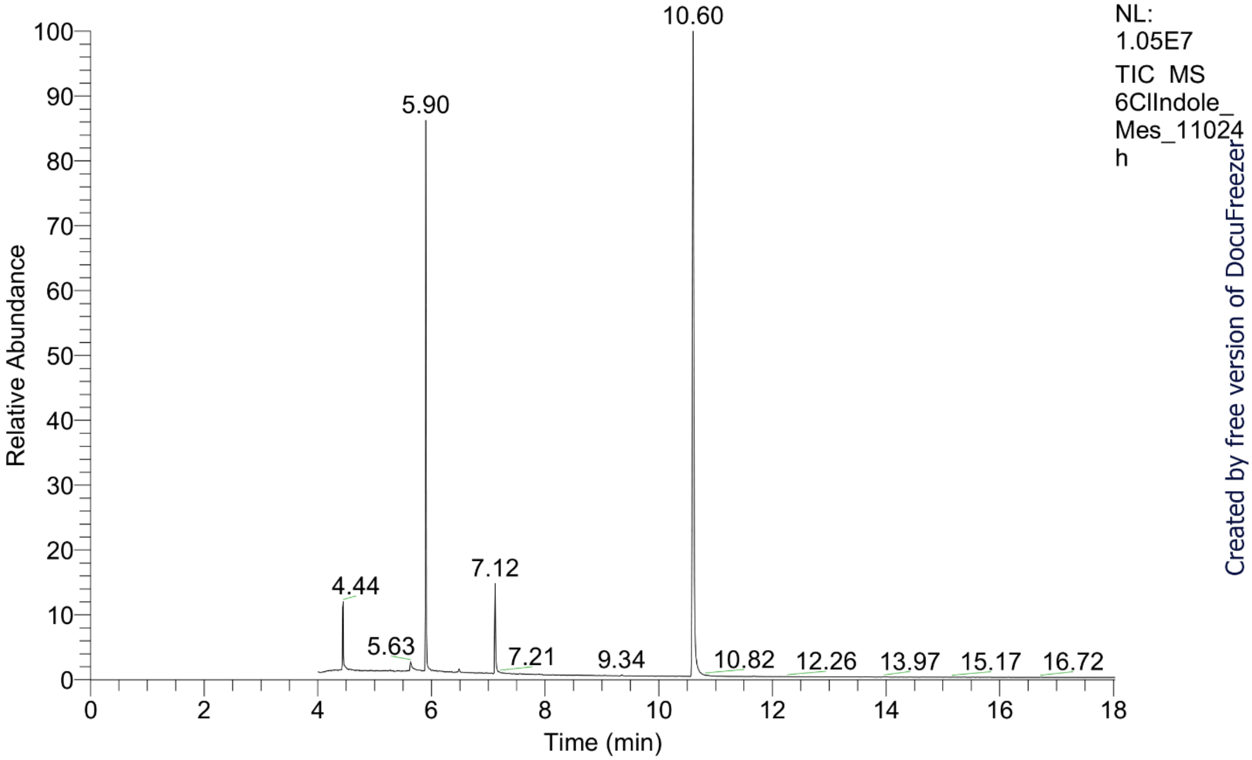
Initial Spectrum



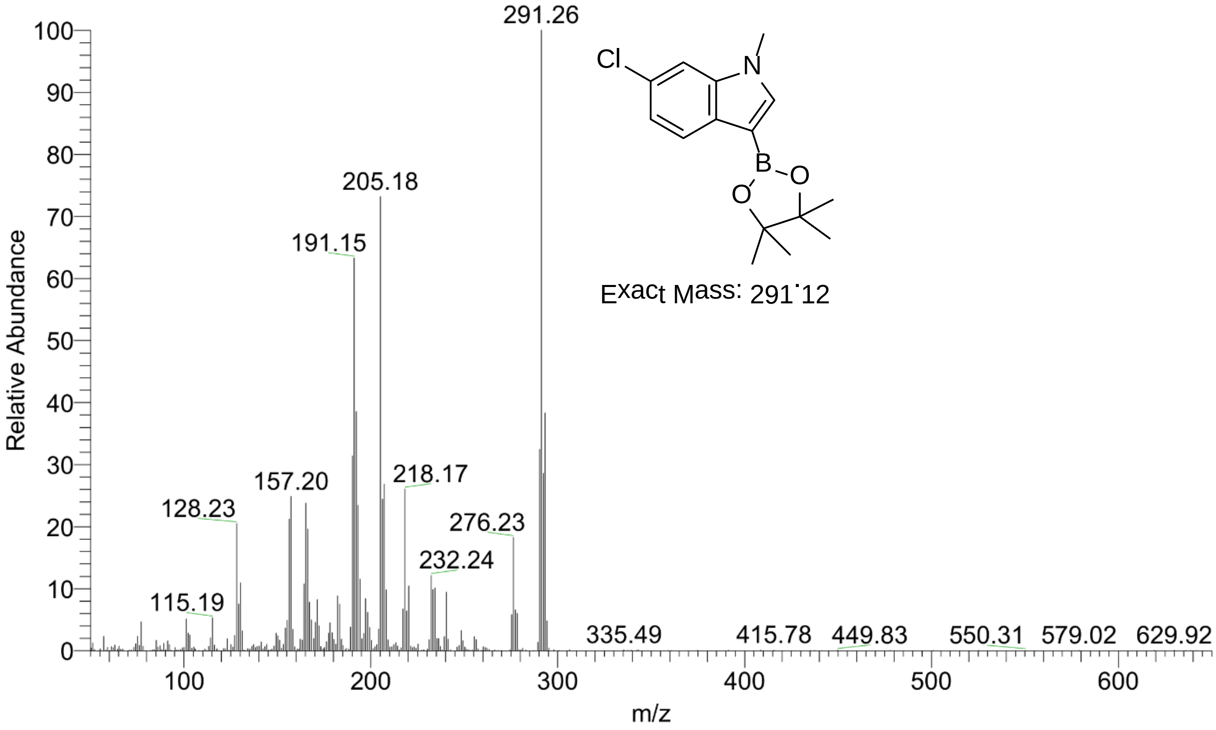
The conversion was determined using the N-Methyl signal that shifts from 2.68 in the starting material to 2.60 ppm in the product. A significant shift of the signal associated to the C4 proton from 7.29 to 8.15 ppm was also observed. The product signals are coherent with the literature.[7]

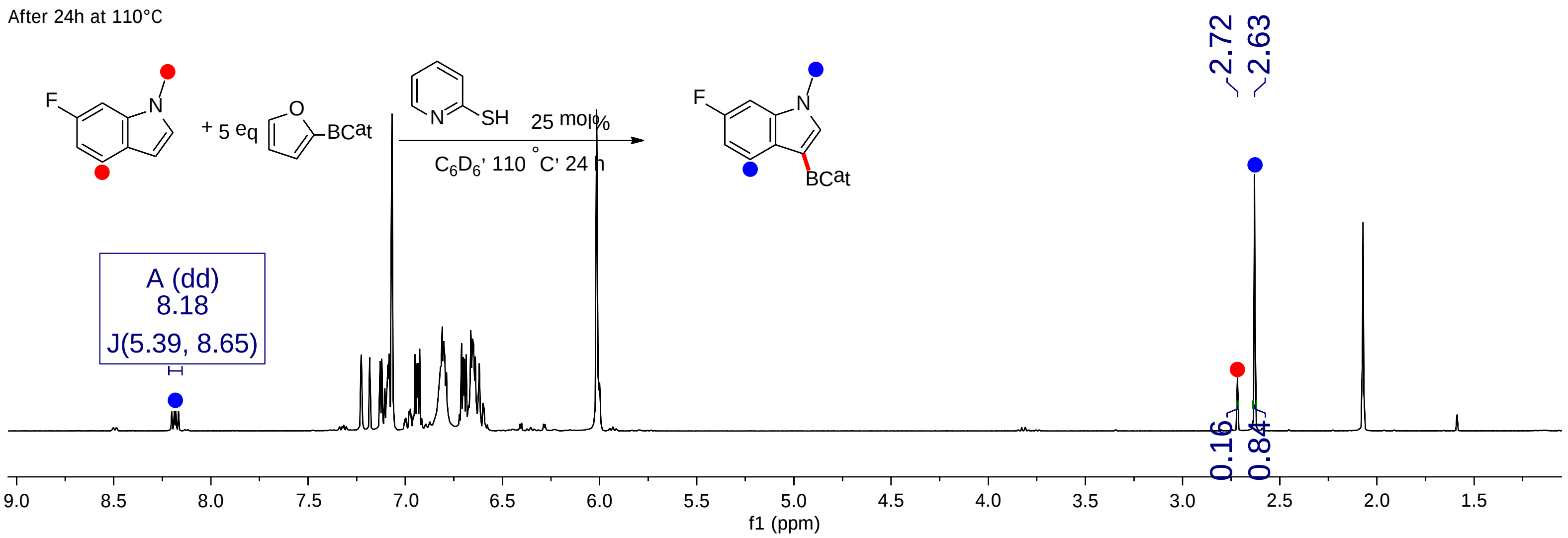
D:\GCMS Data\...\6ClIndole_Mes_11024h 08/07/18 14:02:44

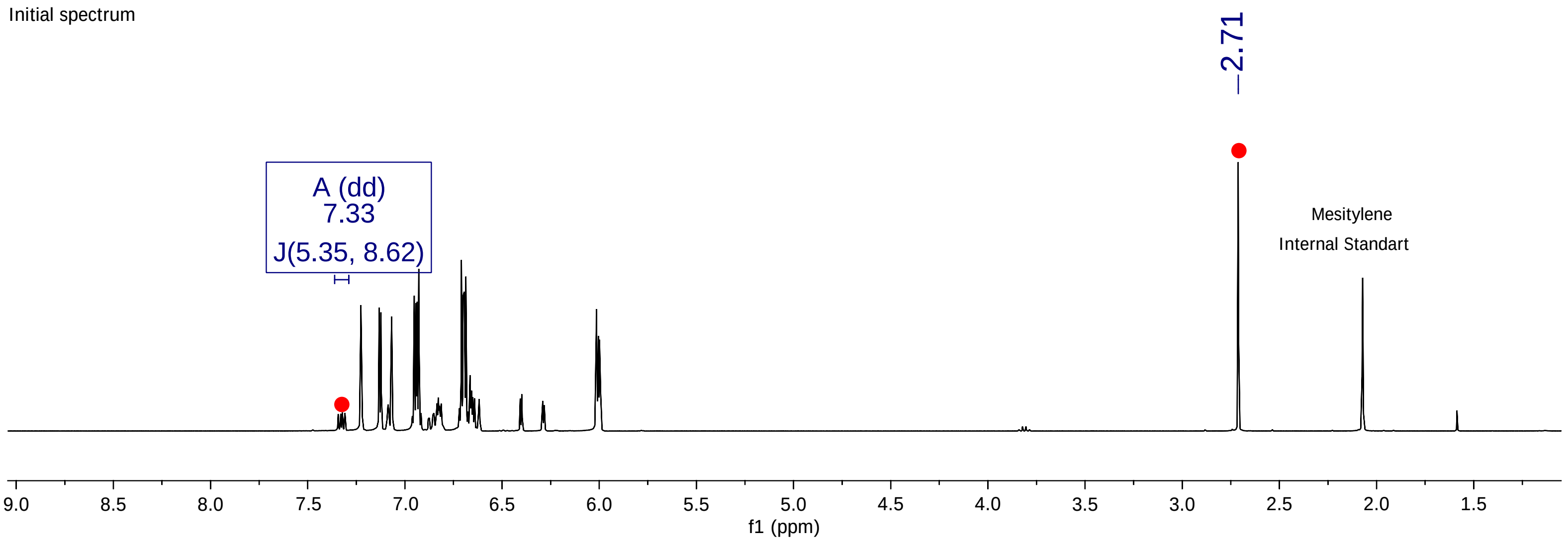
RT: 0.00 - 18.03



6ClIndole_Mes_11024h #747 RT: 10.60 AV: 1 NL: 1.04E6
T: + c Full ms [50.00-650.00]

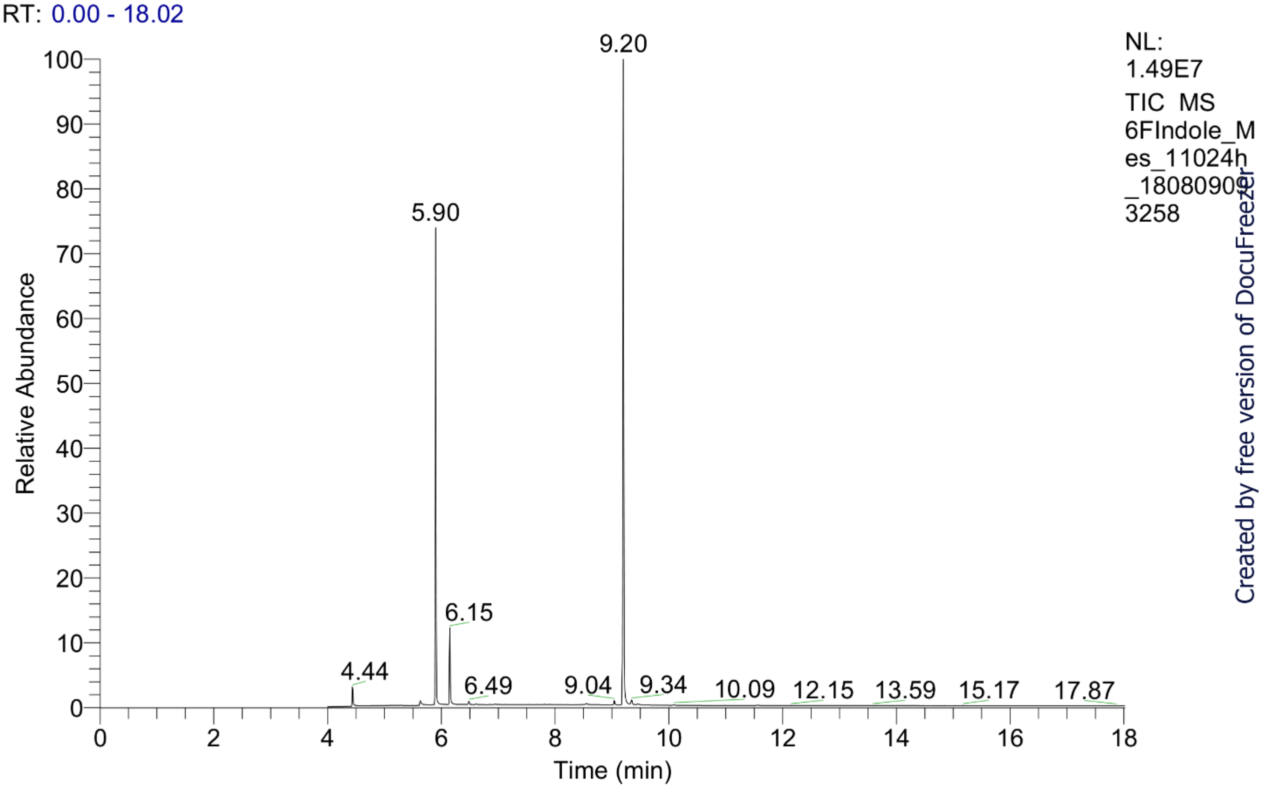



After 24h at 110°C

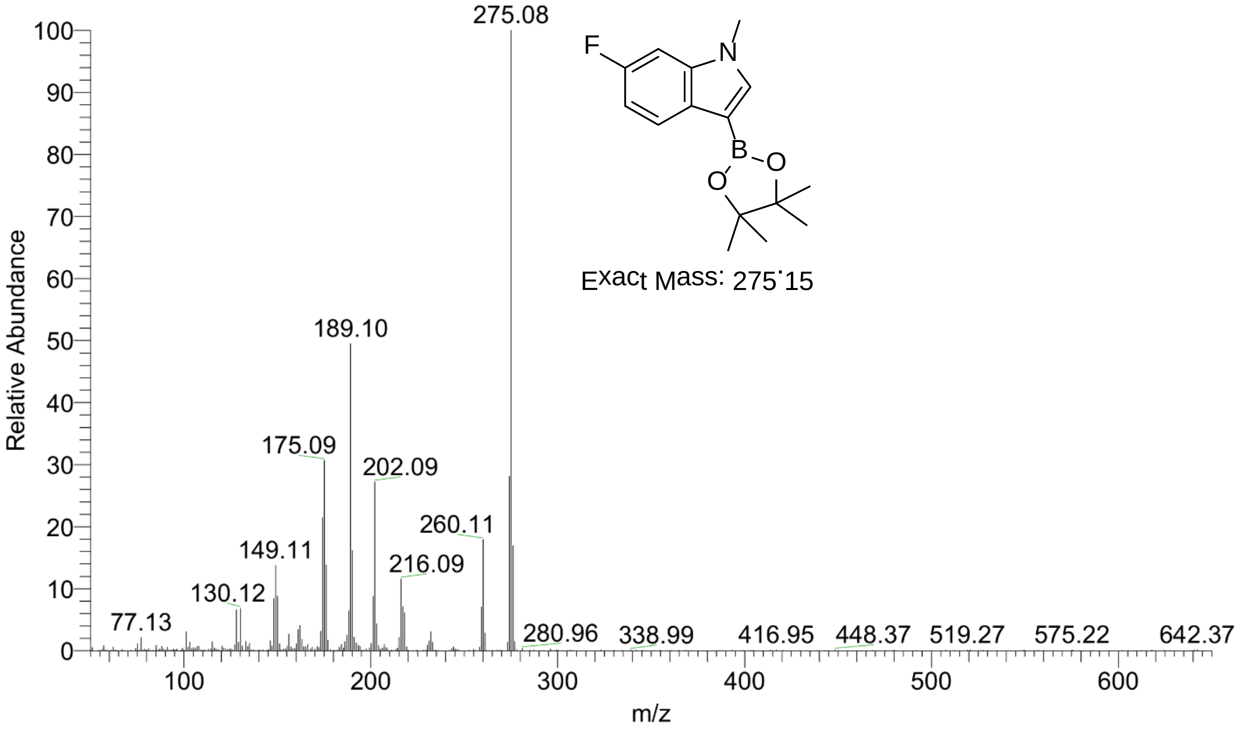

Initial spectrum

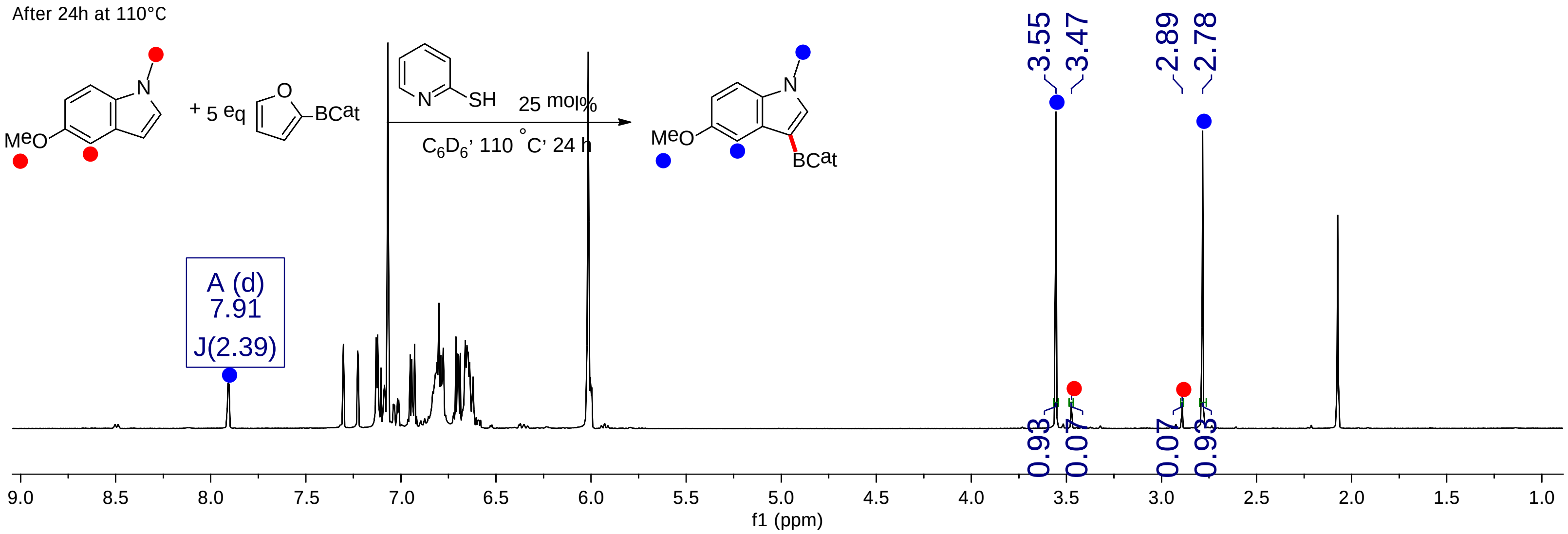
The conversion was determined using the N-Methyl signal that shifts from 2.71 in the starting material to 2.63 ppm in the product. A significant shift of the signal associated to the C4 proton from 7.33 to 8.18 ppm was also observed. The product signals are coherent with the literature.[7]

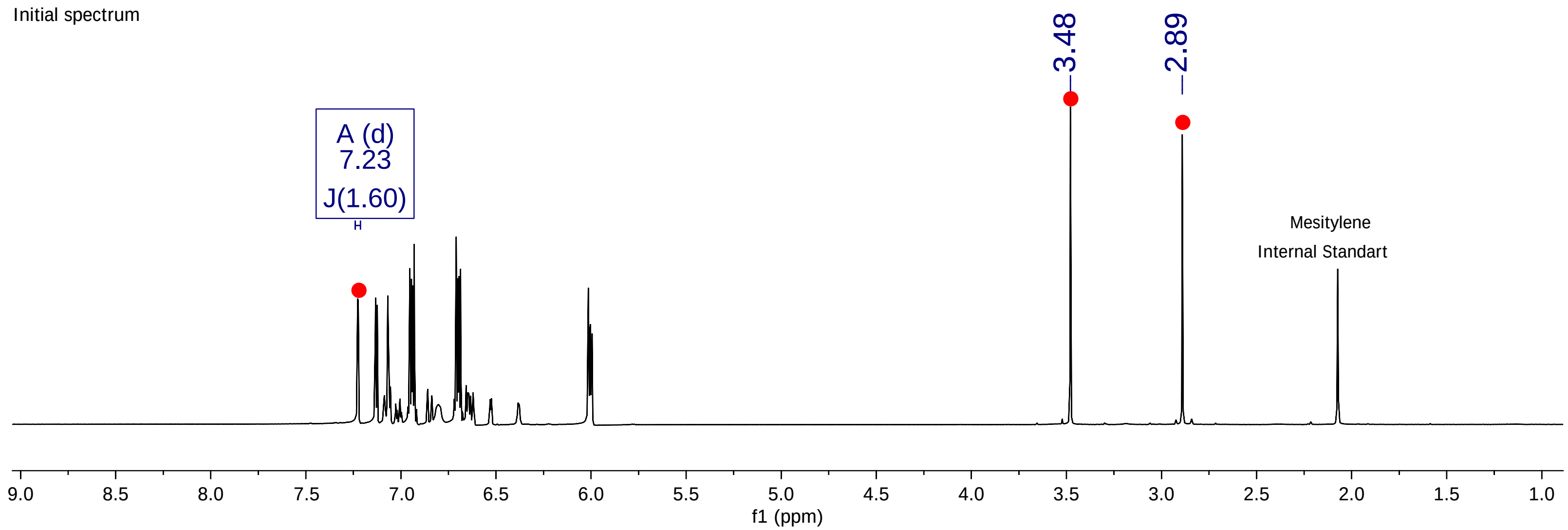
6FIndole_Mes_11024h_180809093258 08/09/18 09:32:58



6FIndole_Mes_11024h_180809093258 #559 RT: 9.20 AV: 1 NL: 2.87E6
T: + c Full ms [50.00-650.00]

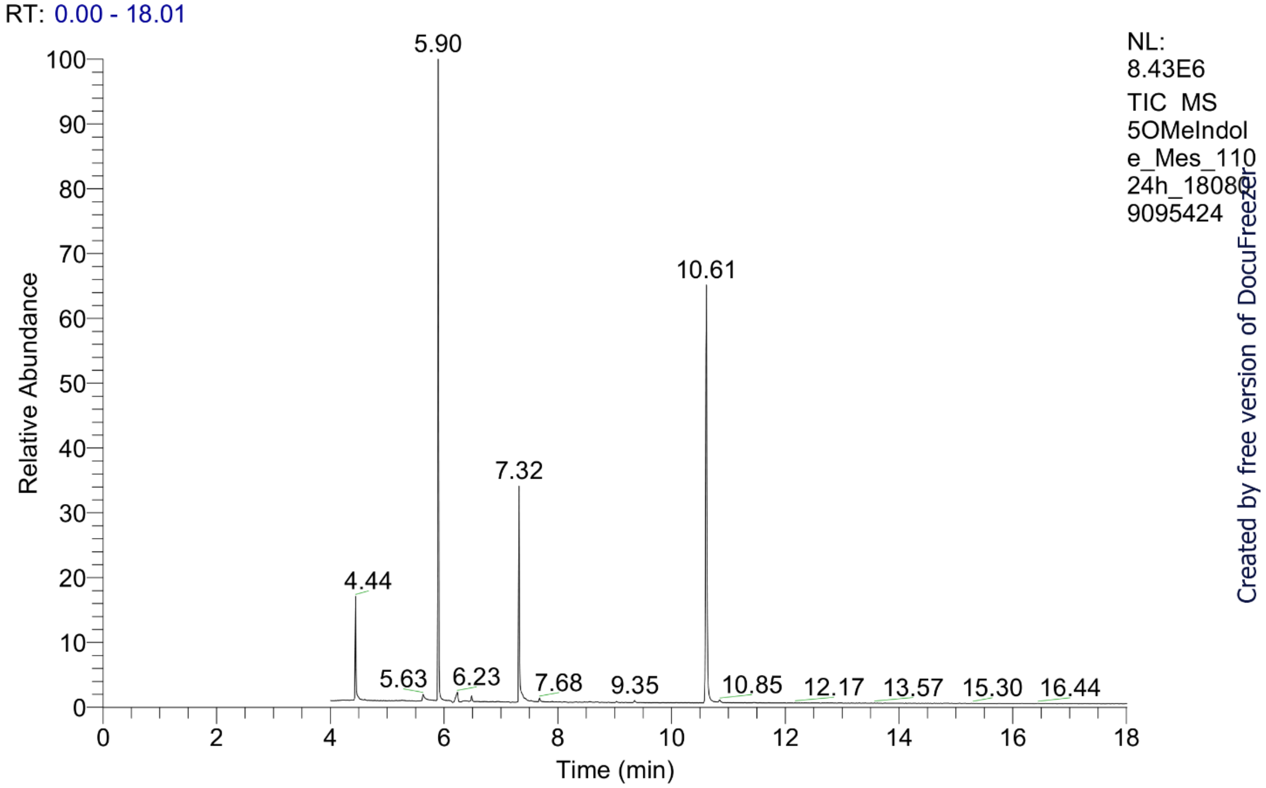


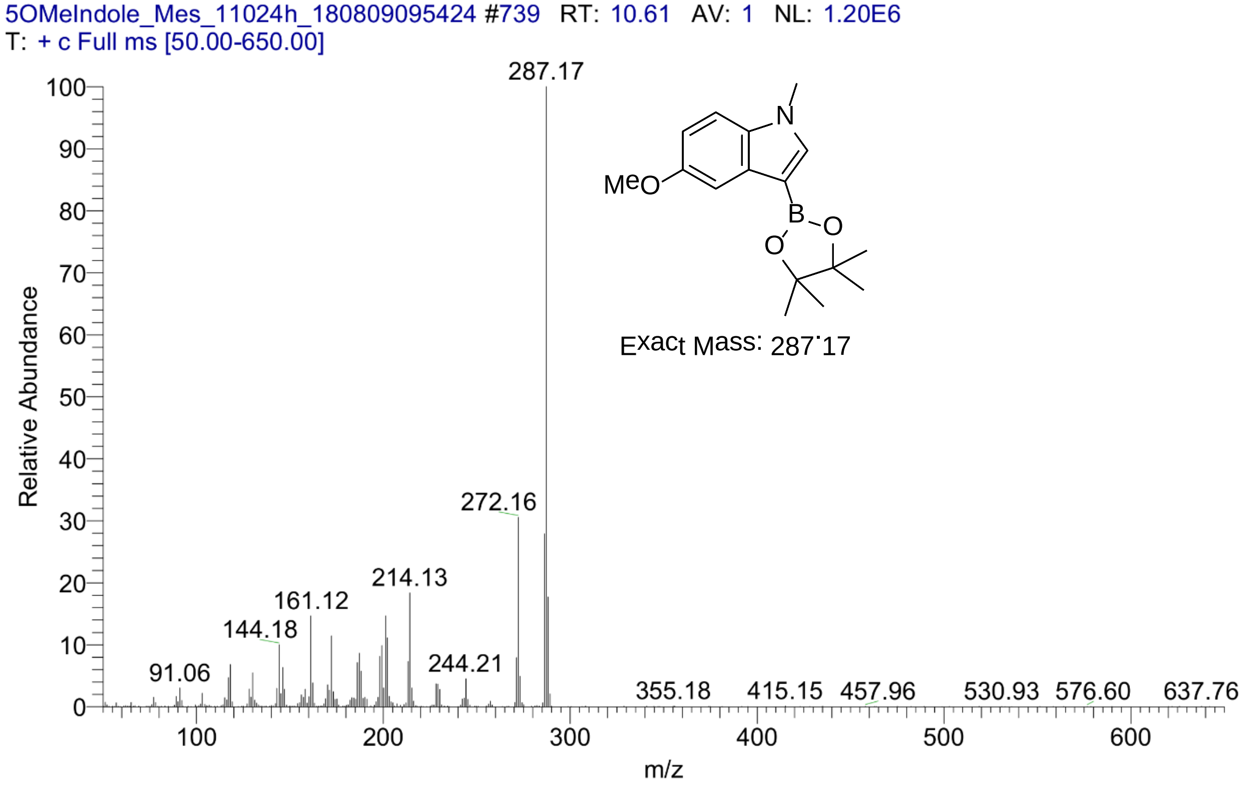




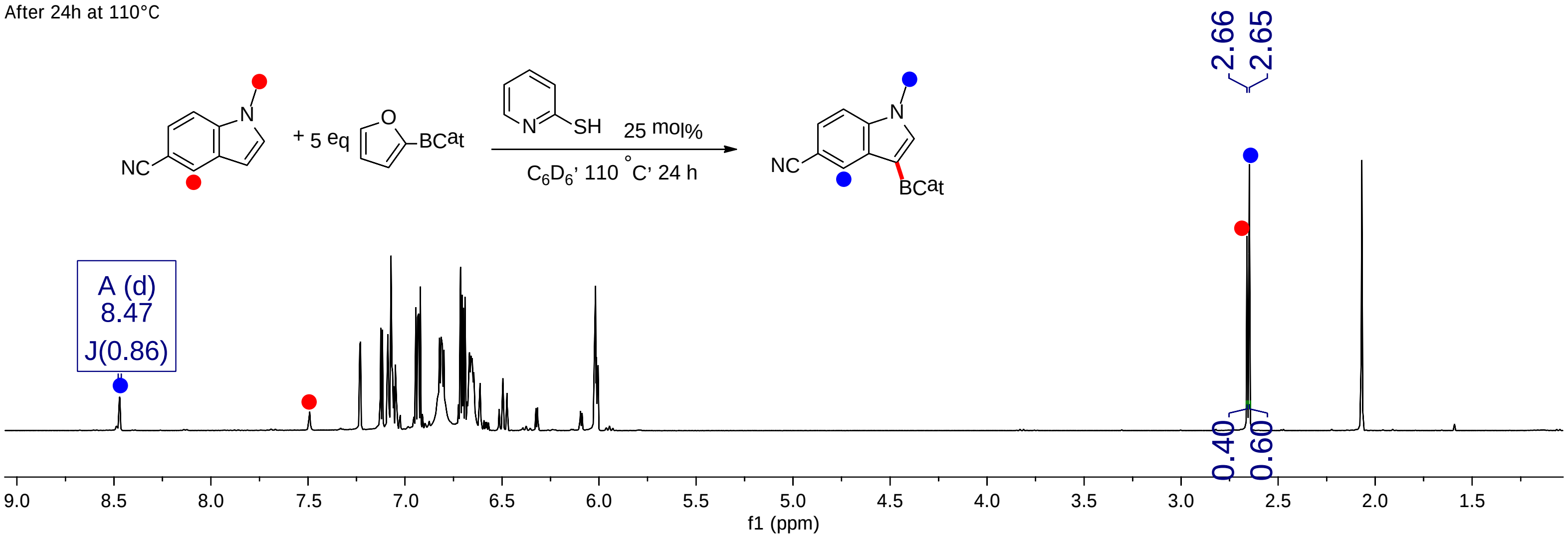
The conversion was determined using the N-Methyl and methoxy signals that shift respectively from 2.89 and 3.48 ppm in the starting material to 2.78 and 3.55 ppm in the product. A significant shift of the signal associated to the C4 proton from 7.23 to 7.91z ppm was also observed.

5OMeIndole_Mes_11024h_180809095424 08/09/18 09:54:24

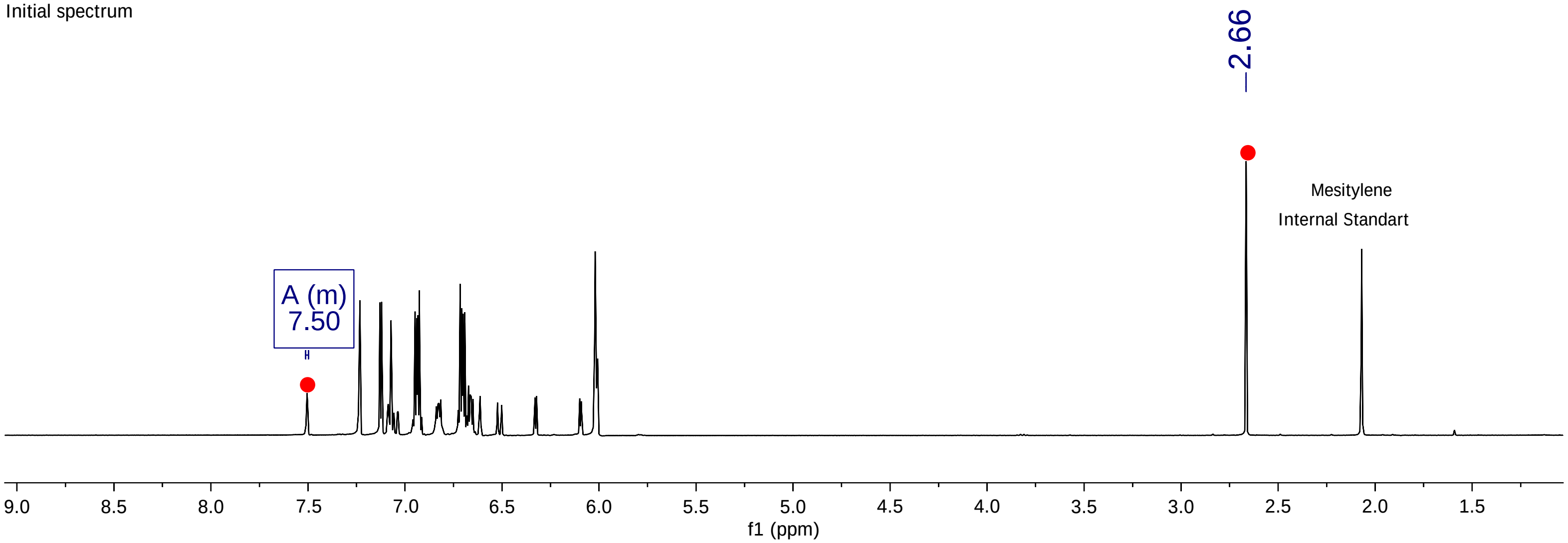




After 24h at 110°C

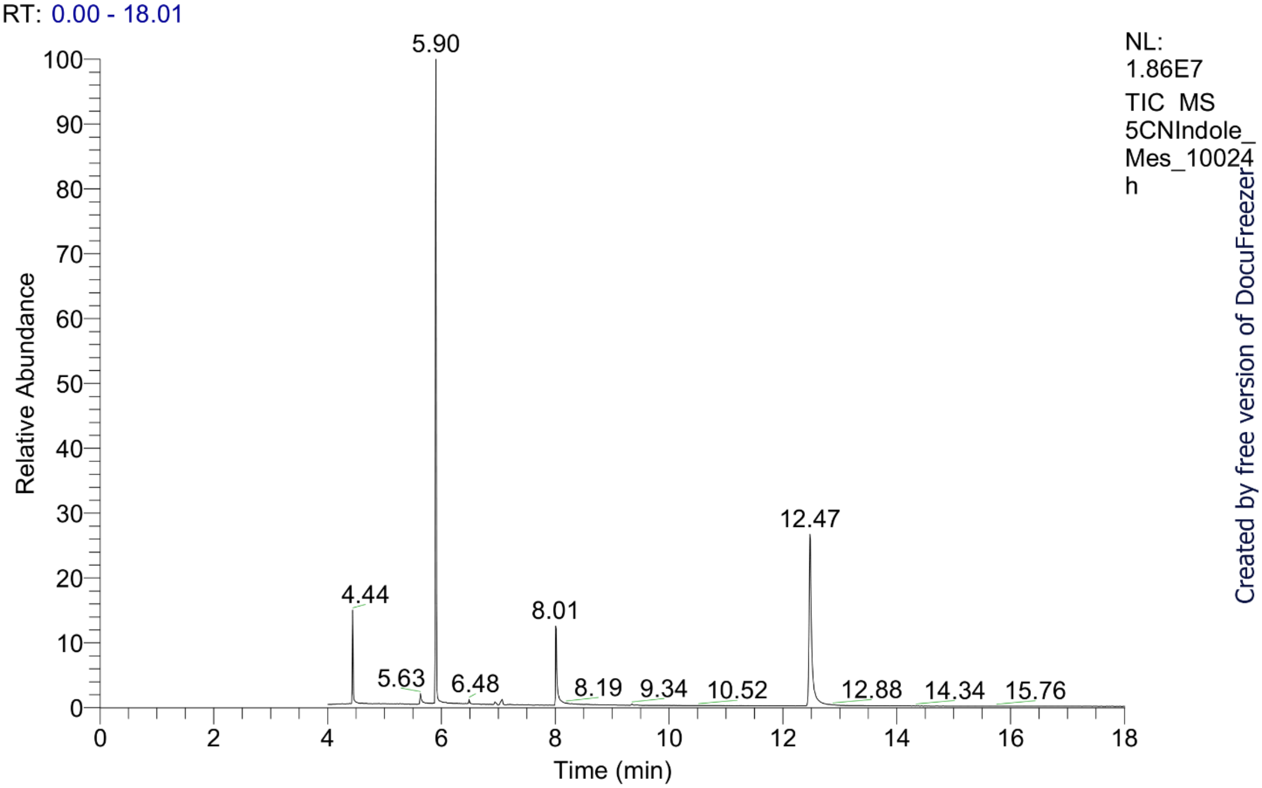


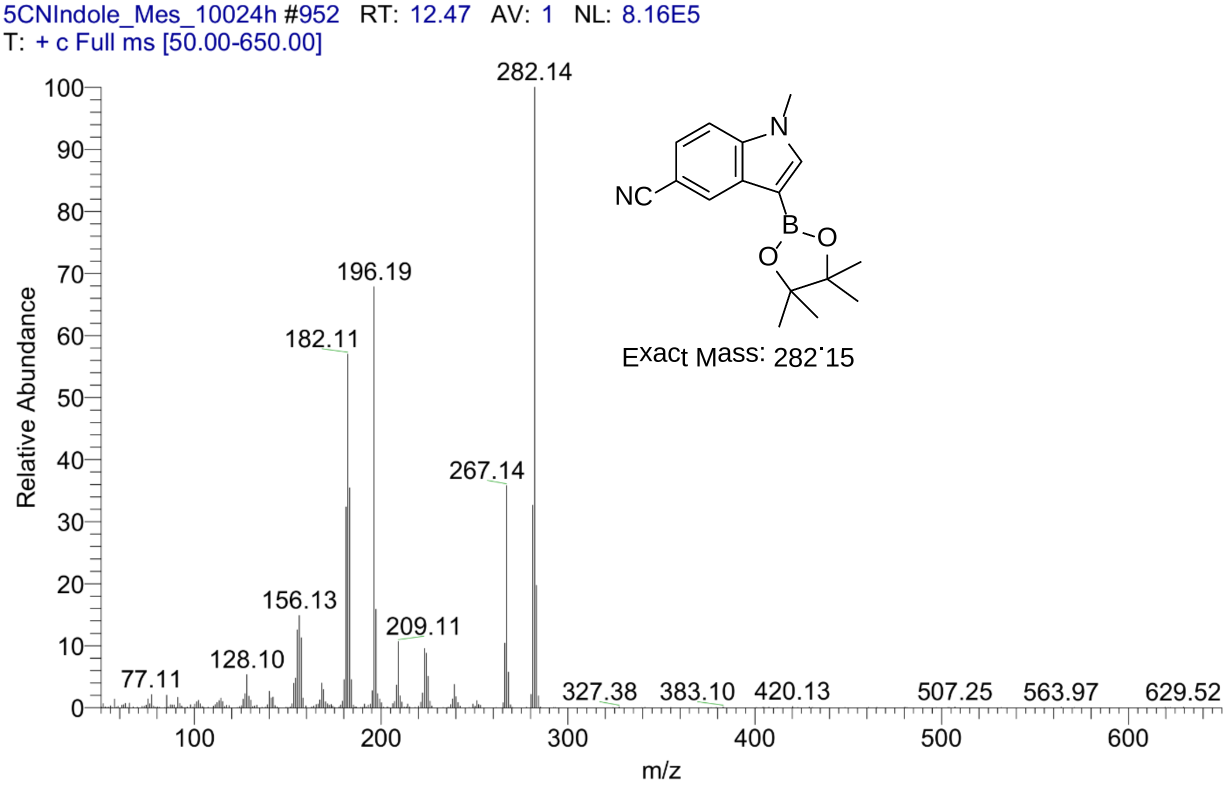
Initial spectrum

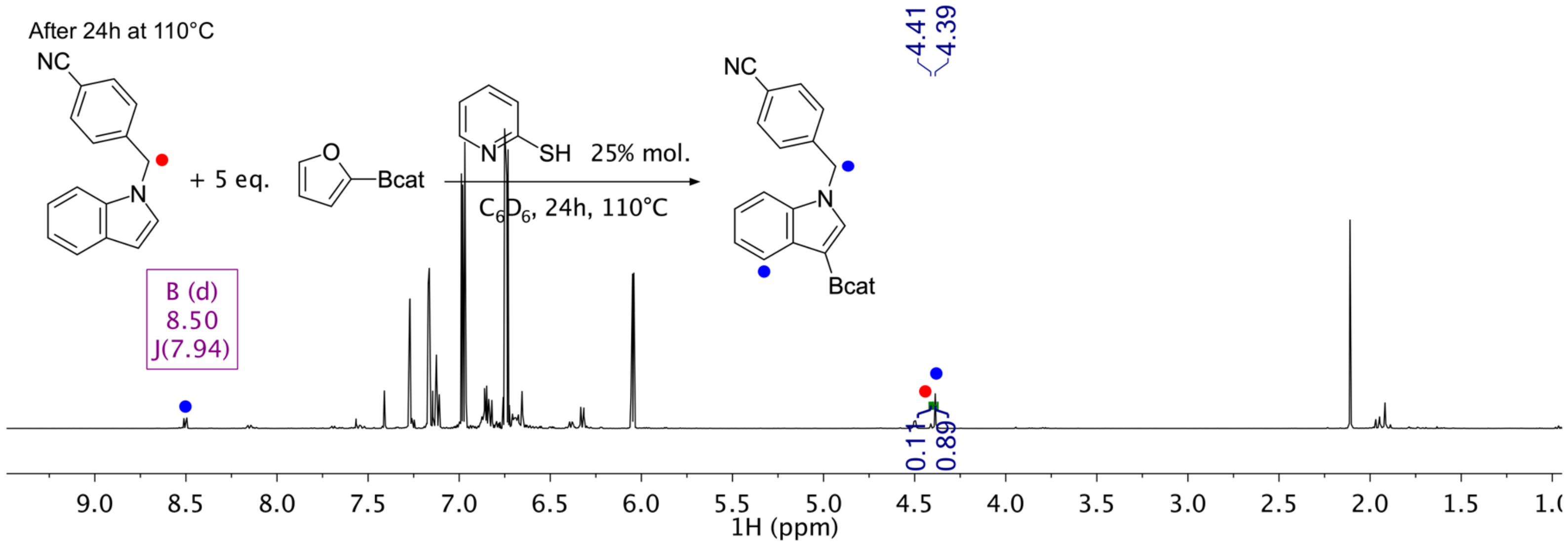


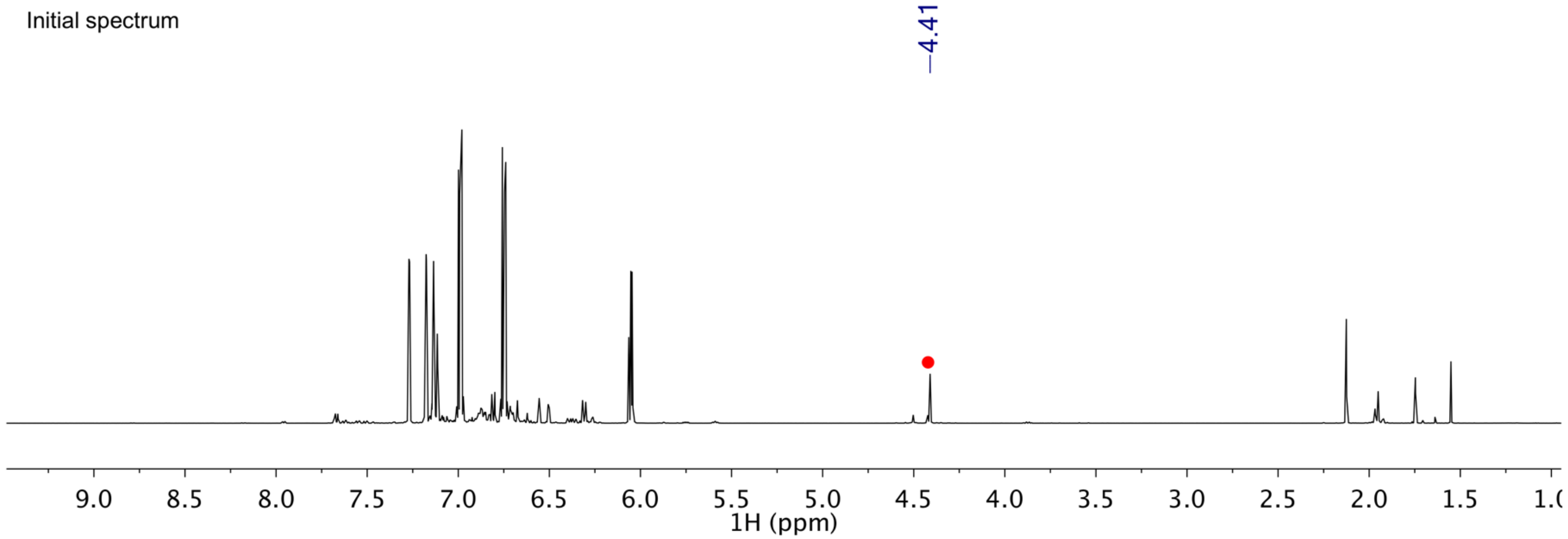
The conversion was determined using the N-Methyl signal that shifts from 2.66 in the starting material to 2.65 ppm in the product. A significant shift of the signal associated to the C4 proton from 7.50 to 8.47 ppm was also observed.

D:\GCMS Data\...\5CNIndole_Mes_10024h 08/09/18 14:04:14



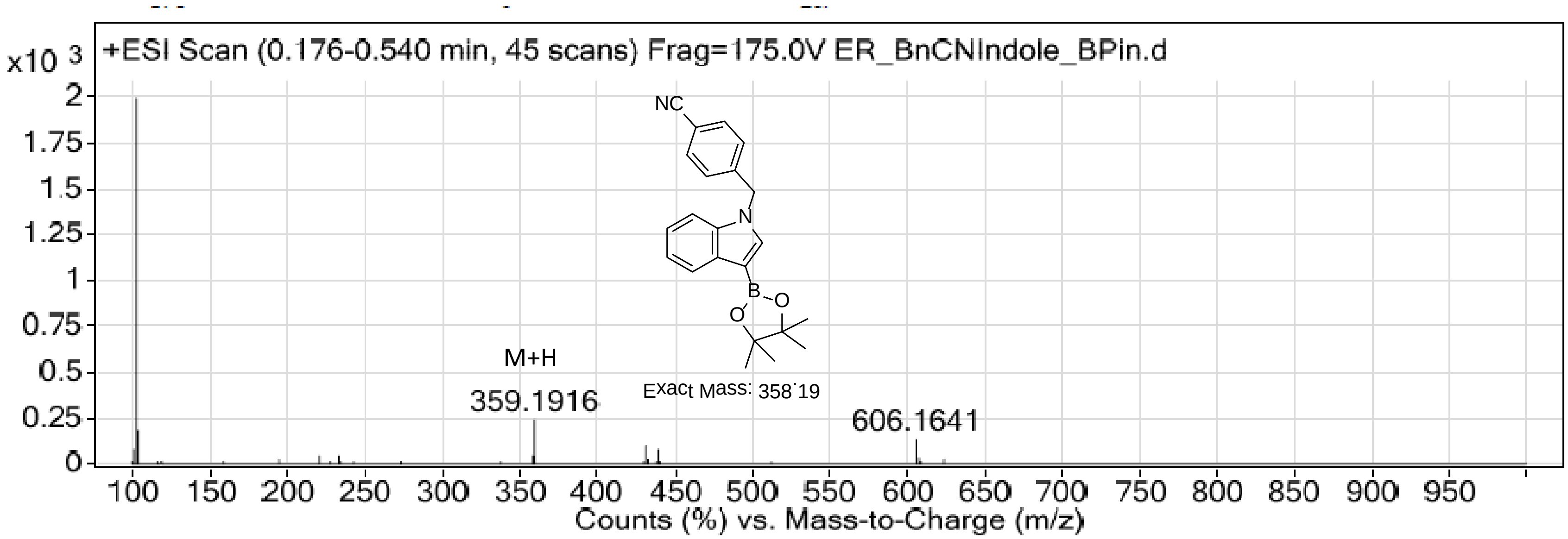






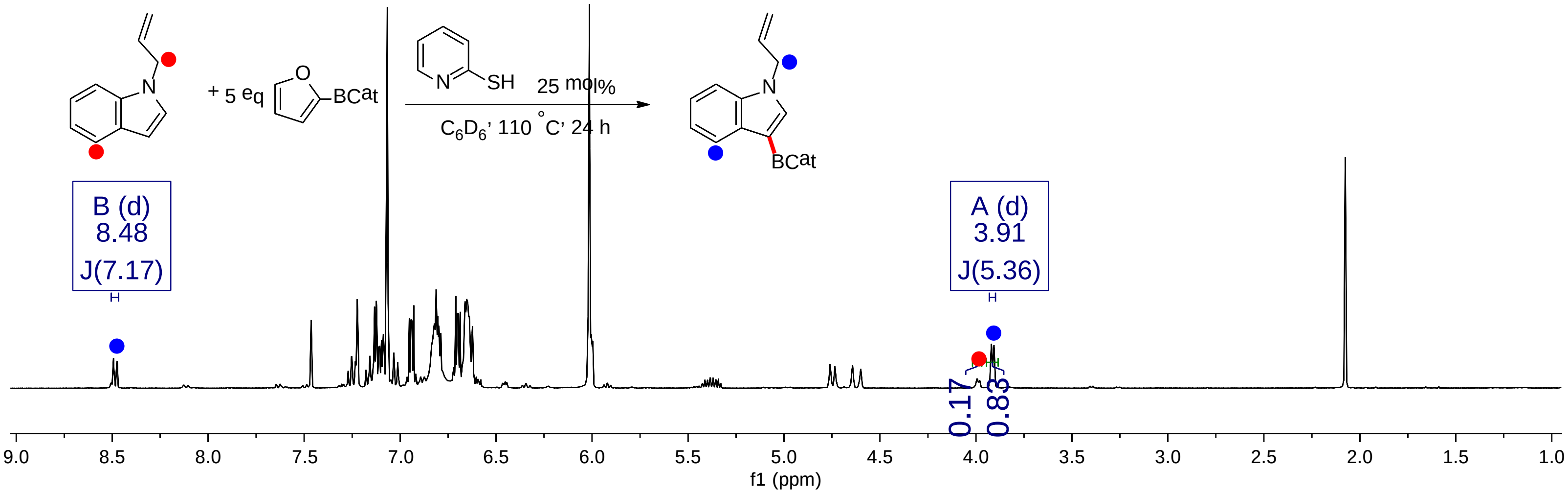
The conversion was determined using the N-CH₂ (benzylic) signal that shifts from 4.41 in the starting material to 4.39 ppm in the product.

A significant shift of the signal associated to the C4 proton from 7.61 to 8.46 ppm was also observed.

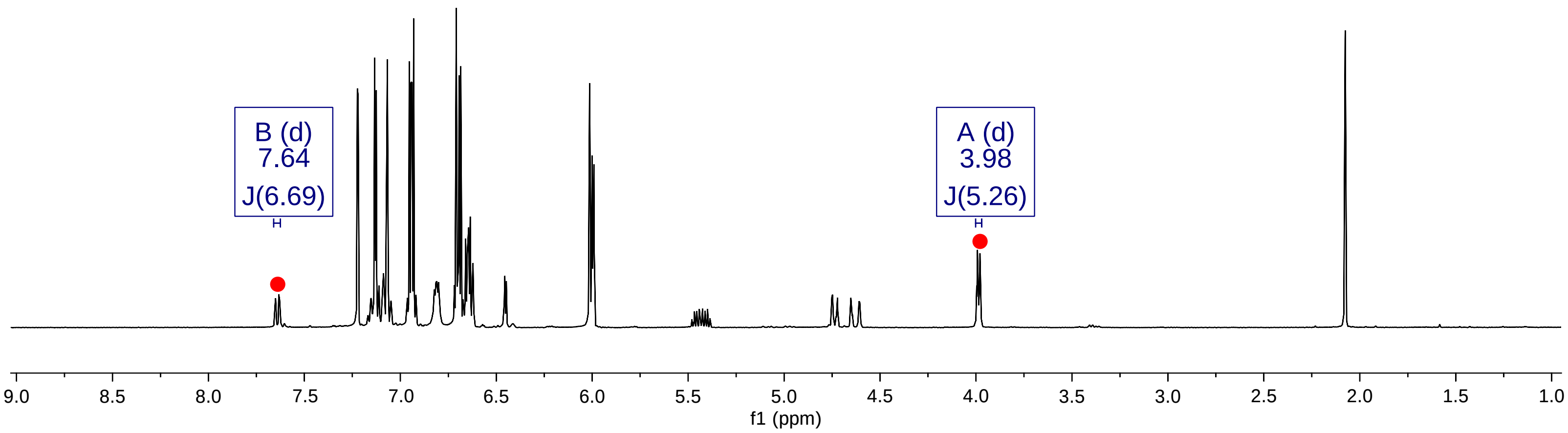


The product was not volatile enough to be analyzed by GC-MS and was thus analyzed using regular mass spectrometry with ESI ionization.

After 24h at 110°C



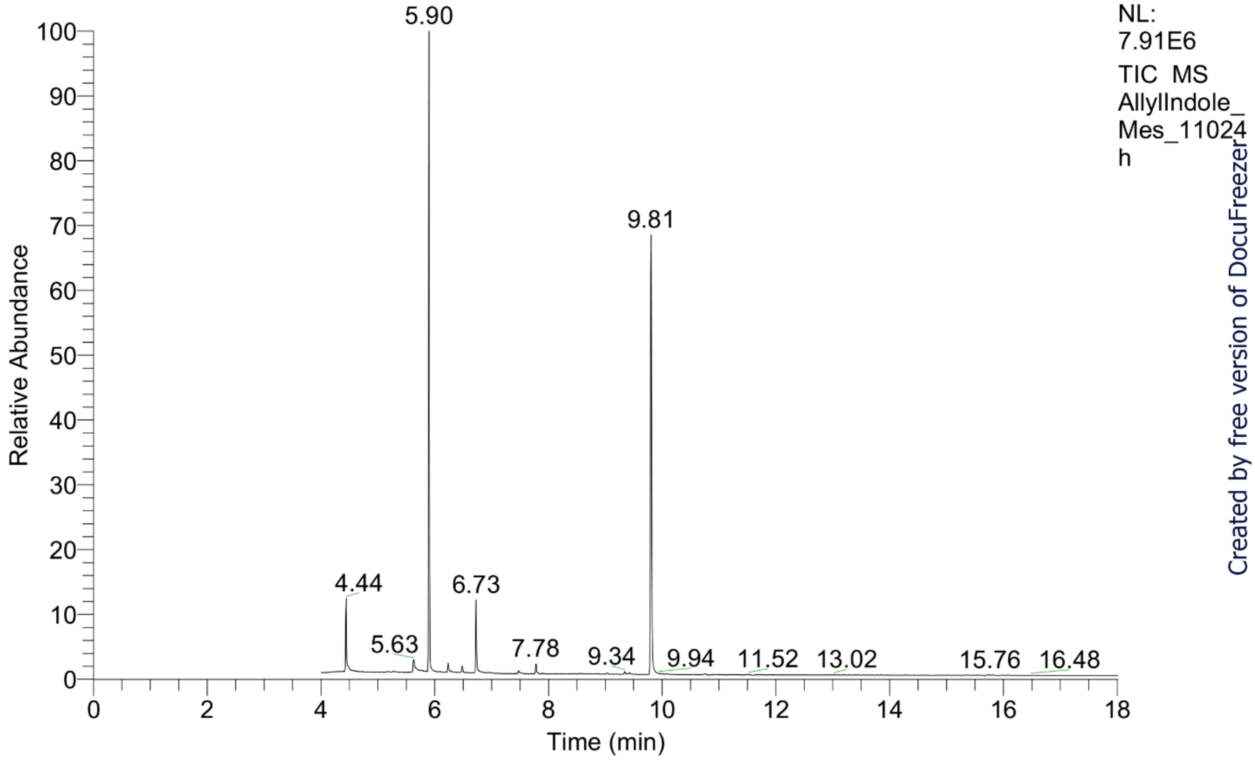
Initial spectrum



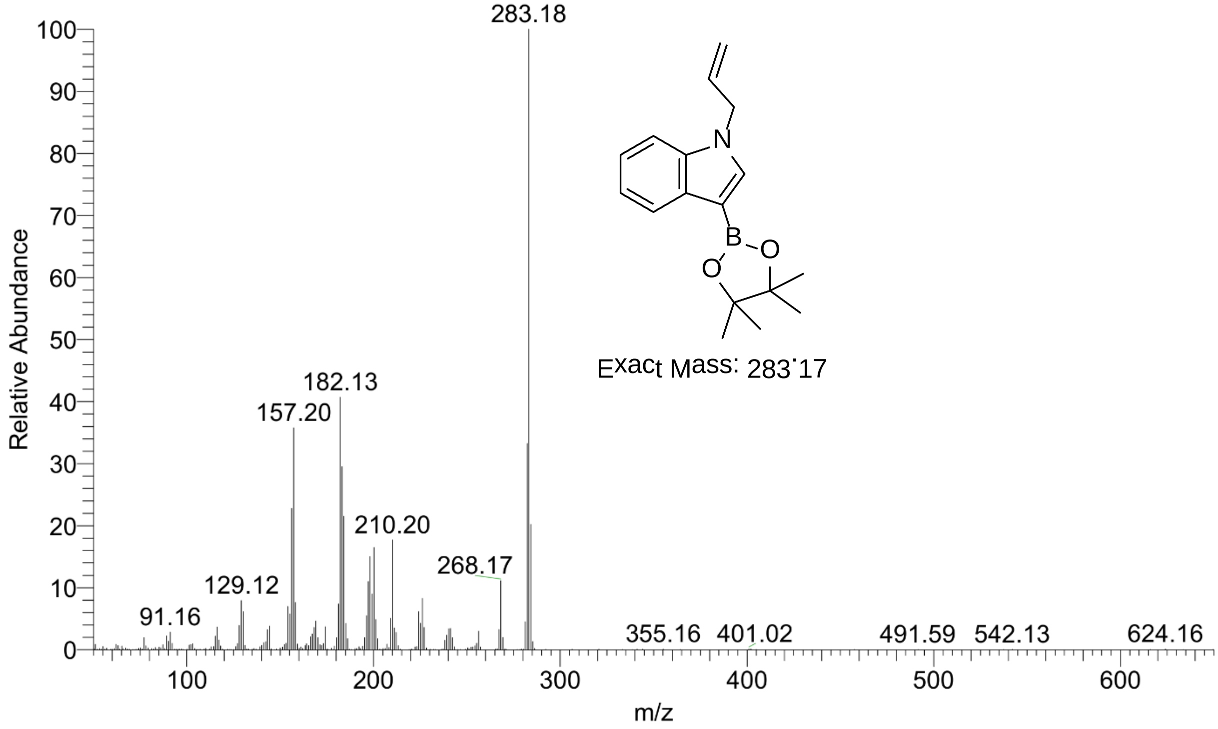
The conversion was determined using the N-CH_2 (allylic) signal that shifts from 3.98 in the starting material to 3.91 ppm in the product. A significant shift of the signal associated to the C4 proton from 7.64 to 8.48 ppm was also observed.

D:\GCMS Data\...\AllylIndole_Mes_11024h 08/09/18 10:49:30

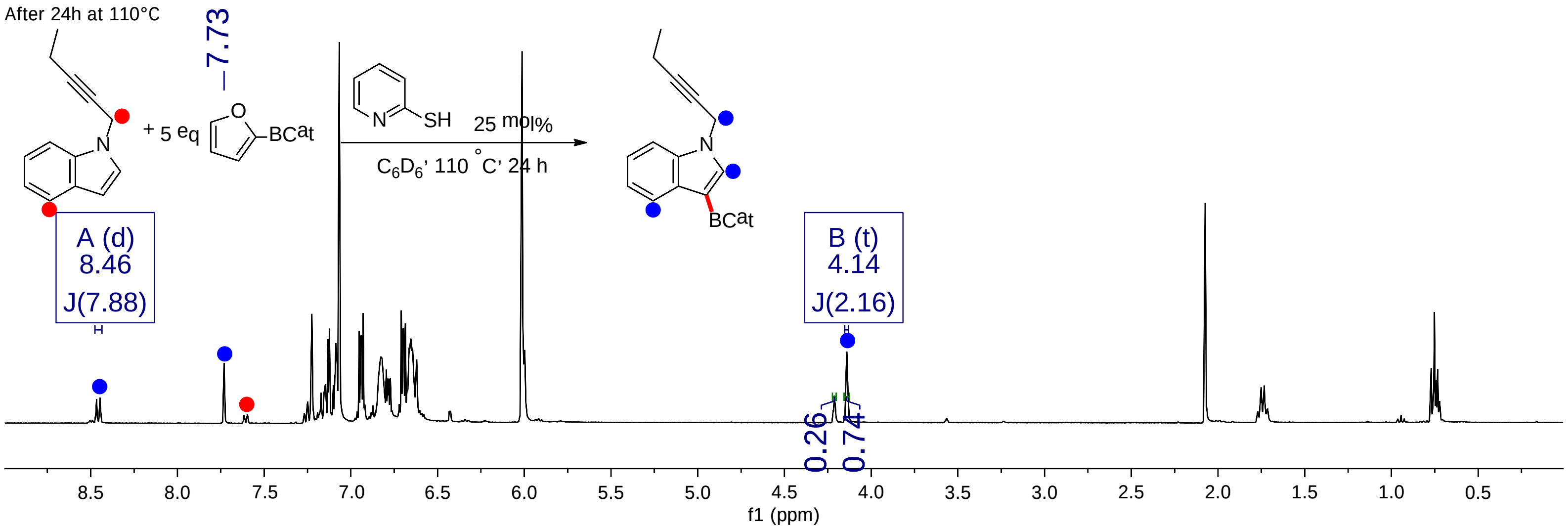
RT: 0.00 - 18.01



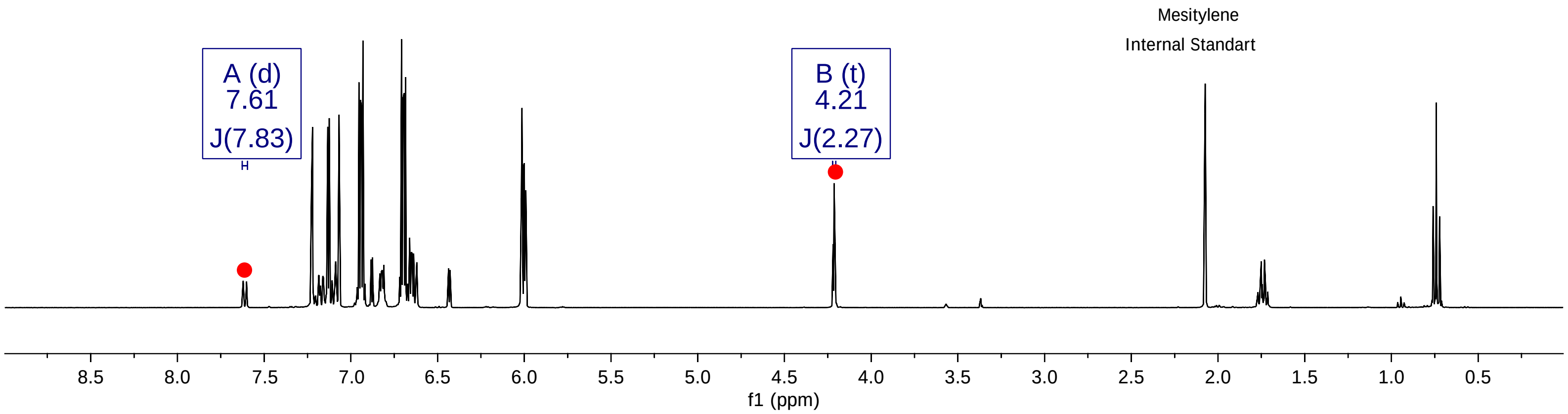
AllylIndole_Mes_11024h #653 RT: 9.81 AV: 1 NL: 9.10E5
T: + c Full ms [50.00-650.00]



After 24h at 110°C

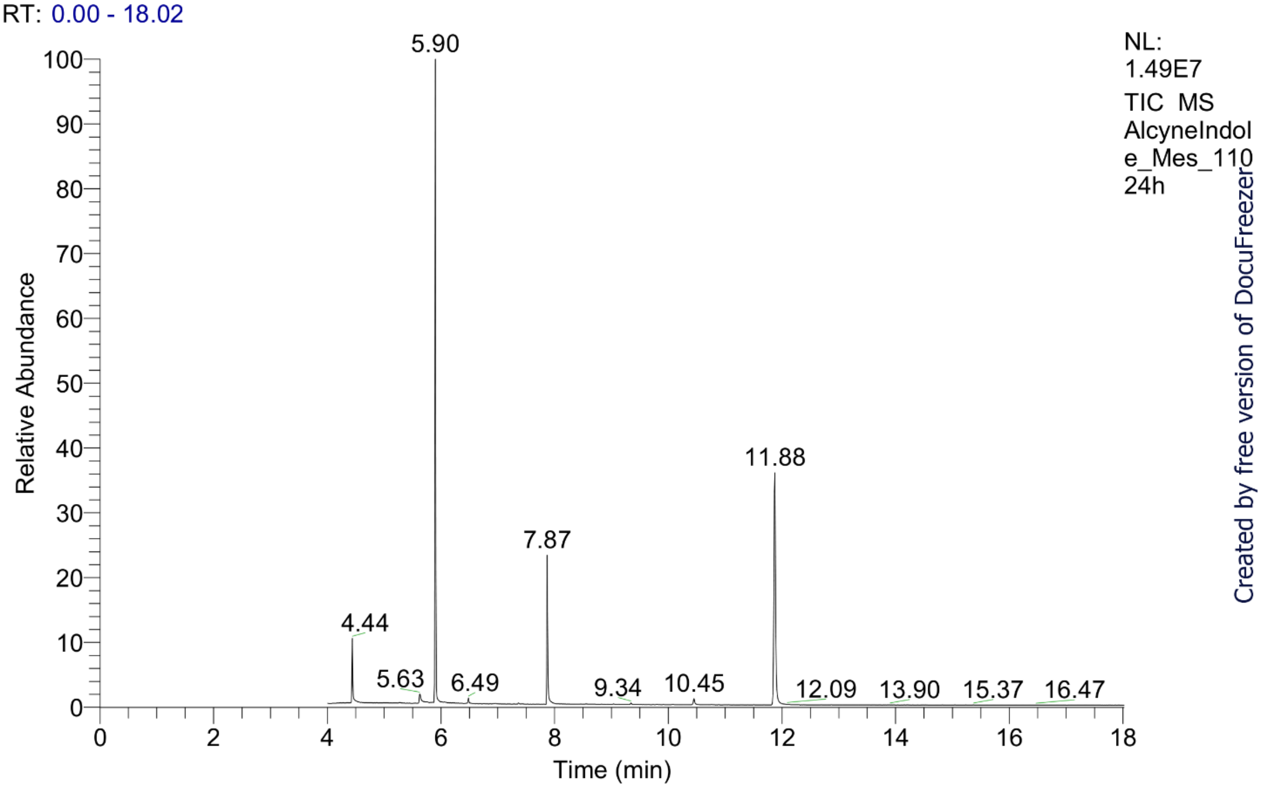


Initial spectrum

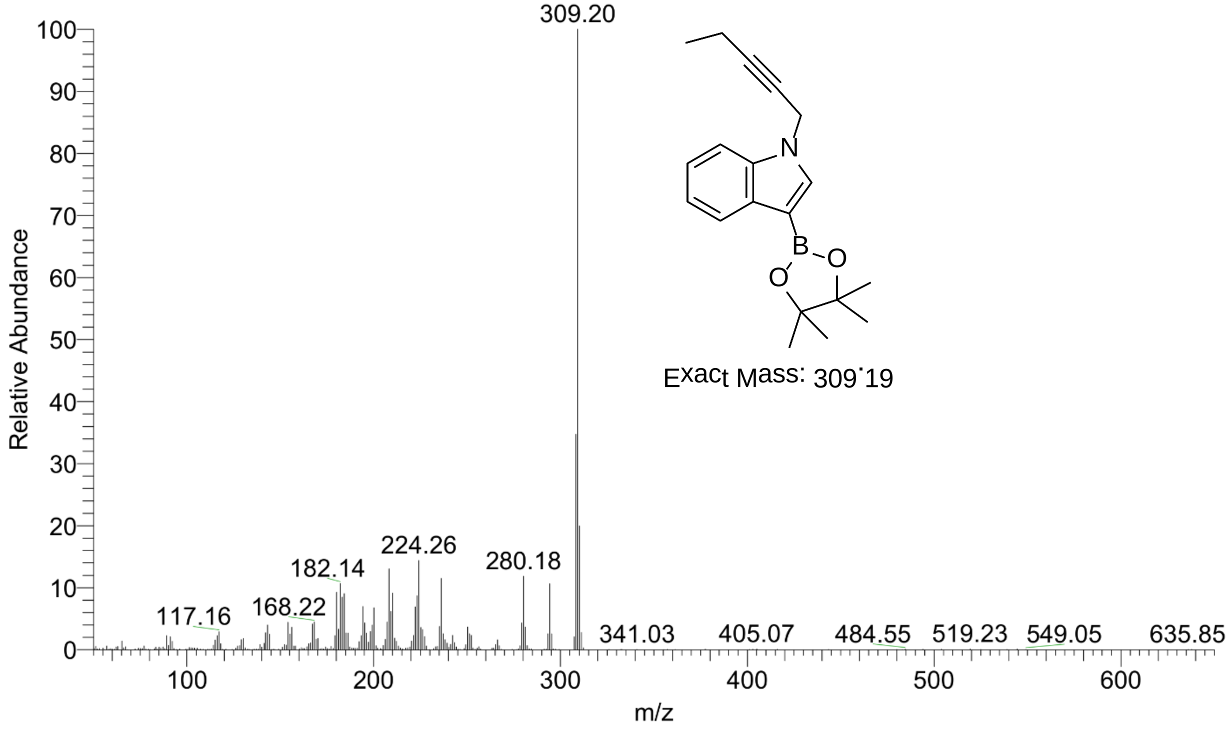


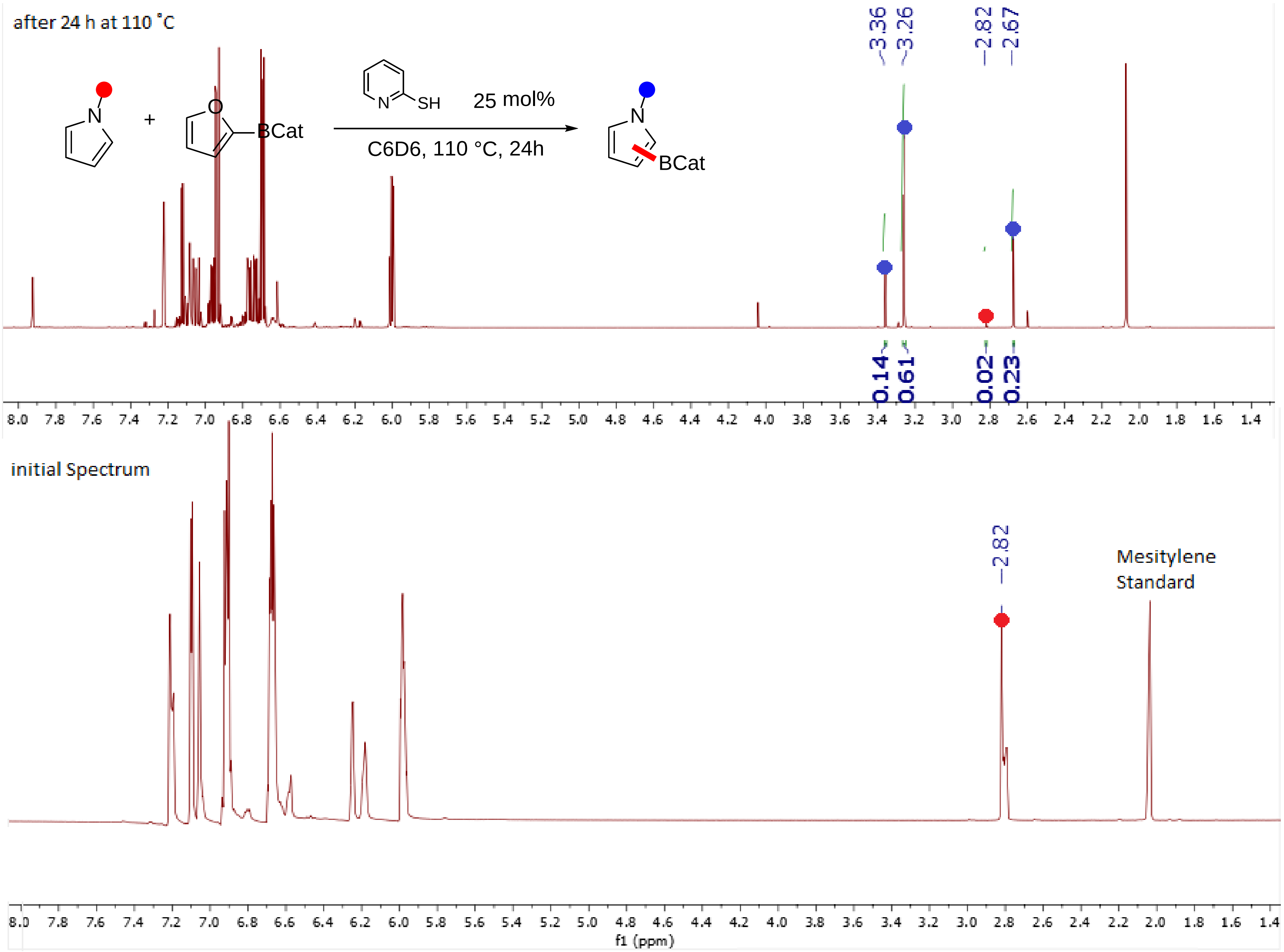
The conversion was determined using the N-CH_2 signal that shifts from 4.21 in the starting material to 4.14 ppm in the product. A significant shift of the signal associated to the C4 proton from 7.61 to 8.46 ppm and the appearance of a characteristic singlet from the C2 proton at 7.61 ppm were also observed.

D:\GCMS Data\...\AlcyneIndole_Mes_11024h   08/09/18 11:17:16



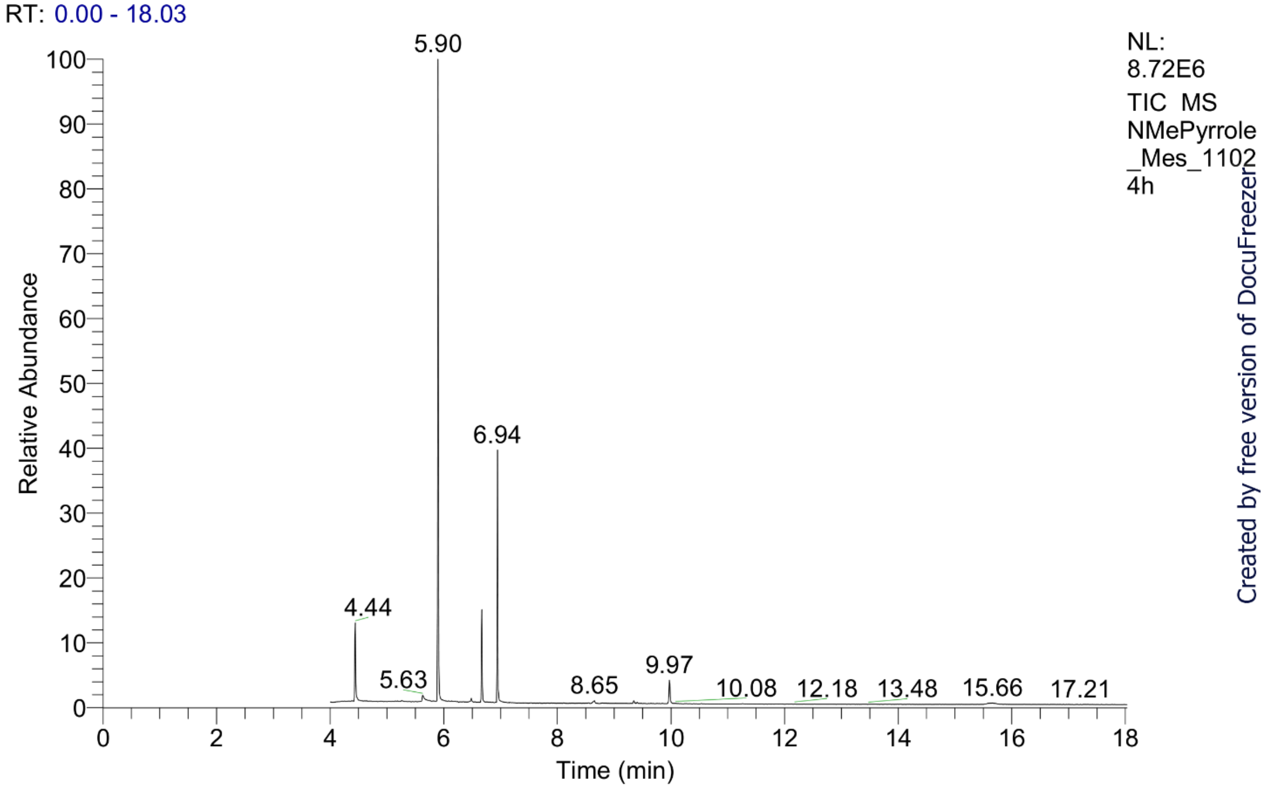
AlcyneIndole_Mes_11024h #881 RT: 11.88 AV: 1 NL: 1.13E6
T: + c Full ms [50.00-650.00]

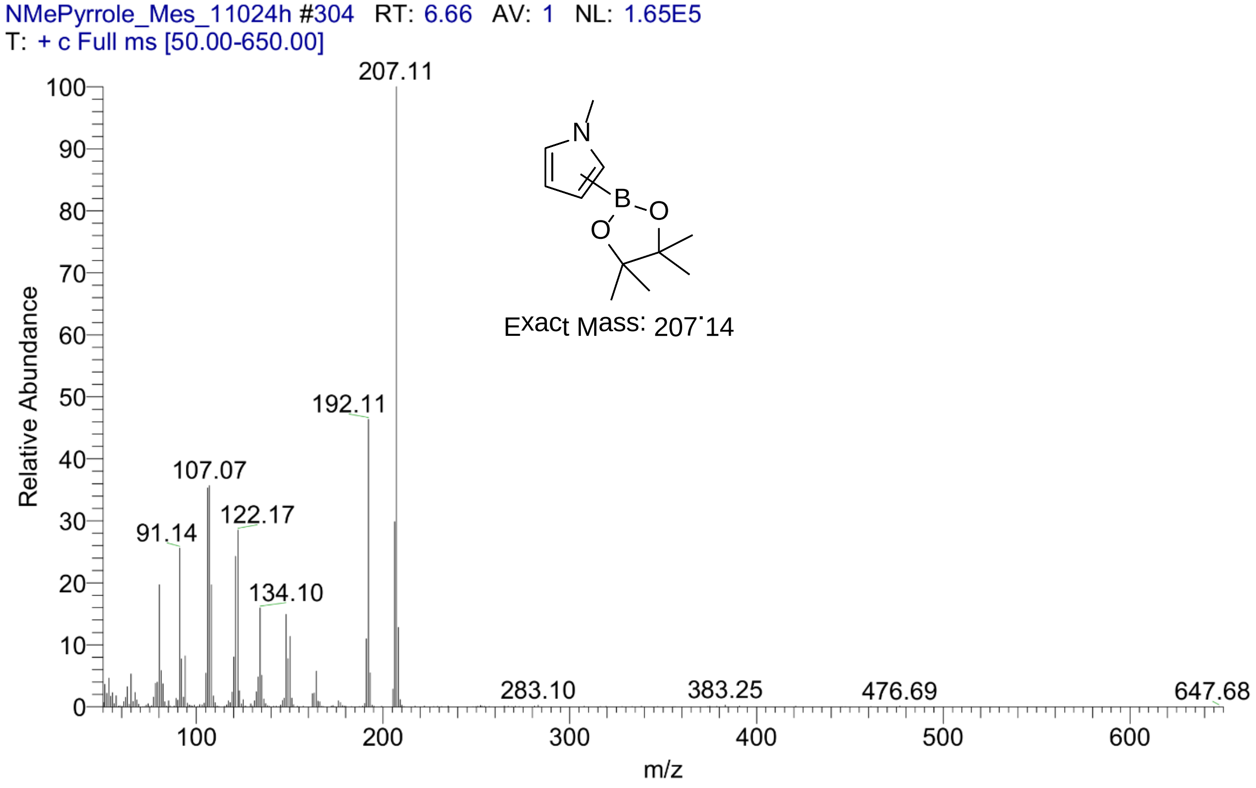




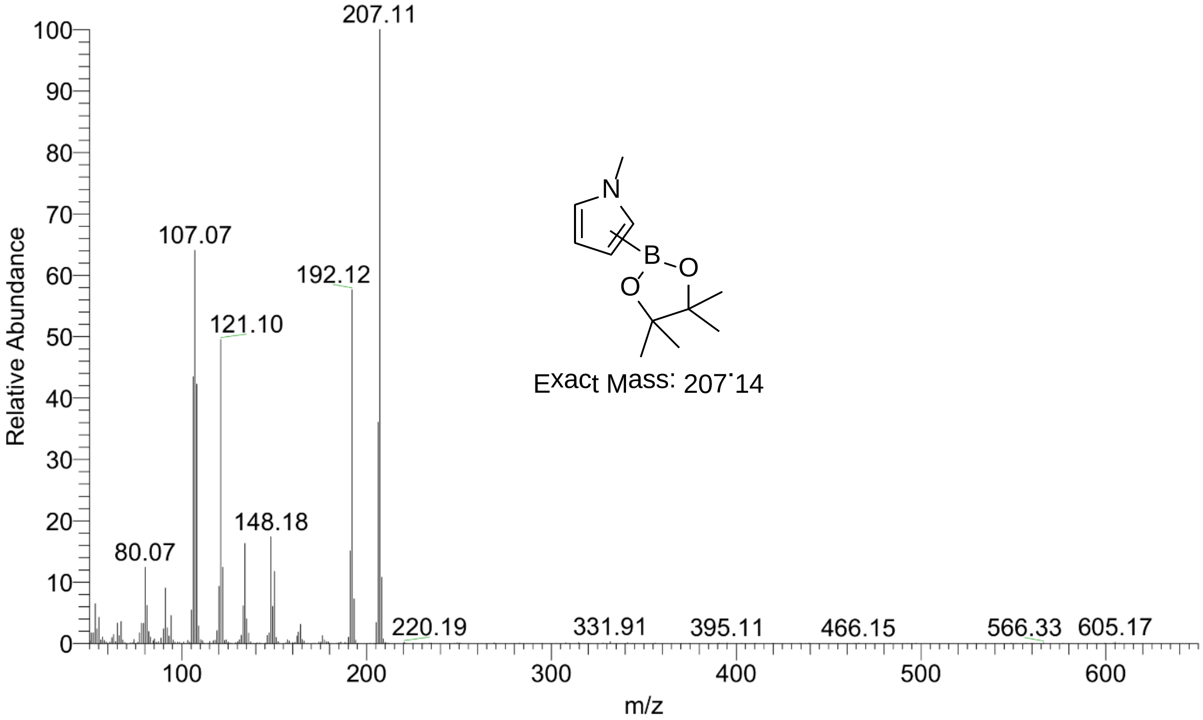
The conversion was determined using the N-Methyl signal that shifts from 2.82 in the starting material to 3.36, 3.26 and 2.68 ppm in the products (C2, C3 and bis borylated compounds).

D:\GCMS Data\...\NMePyrrole_Mes_11024h 08/09/18 12:12:55

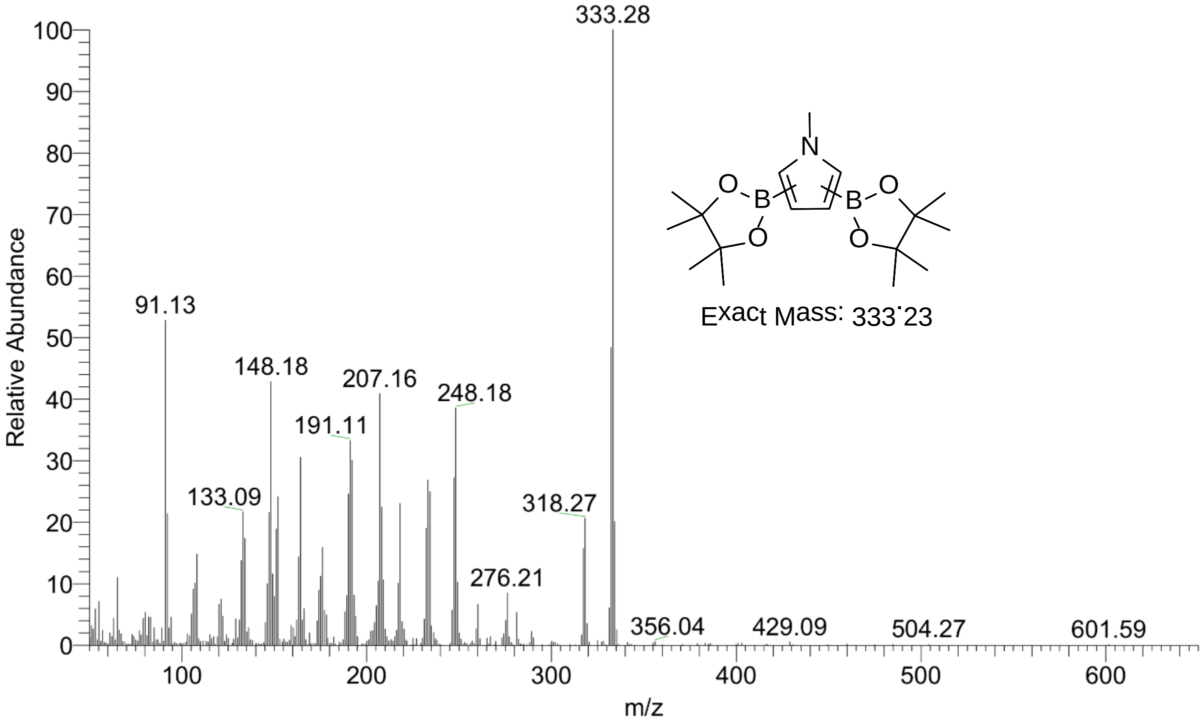


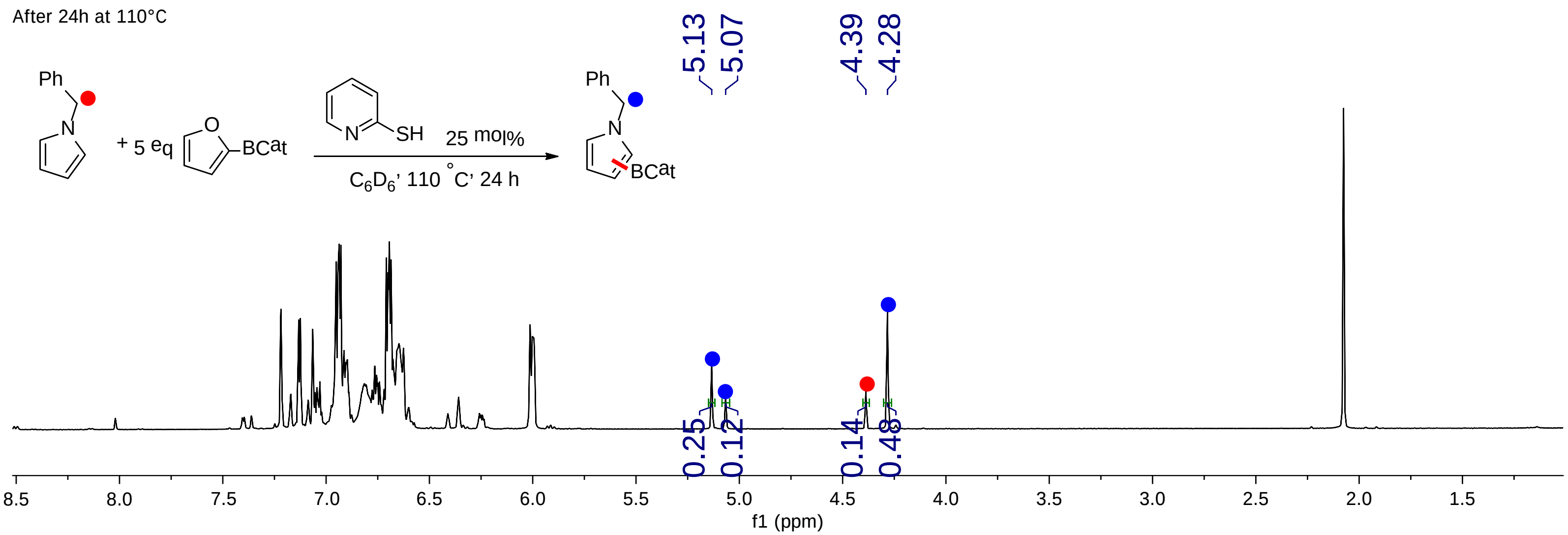


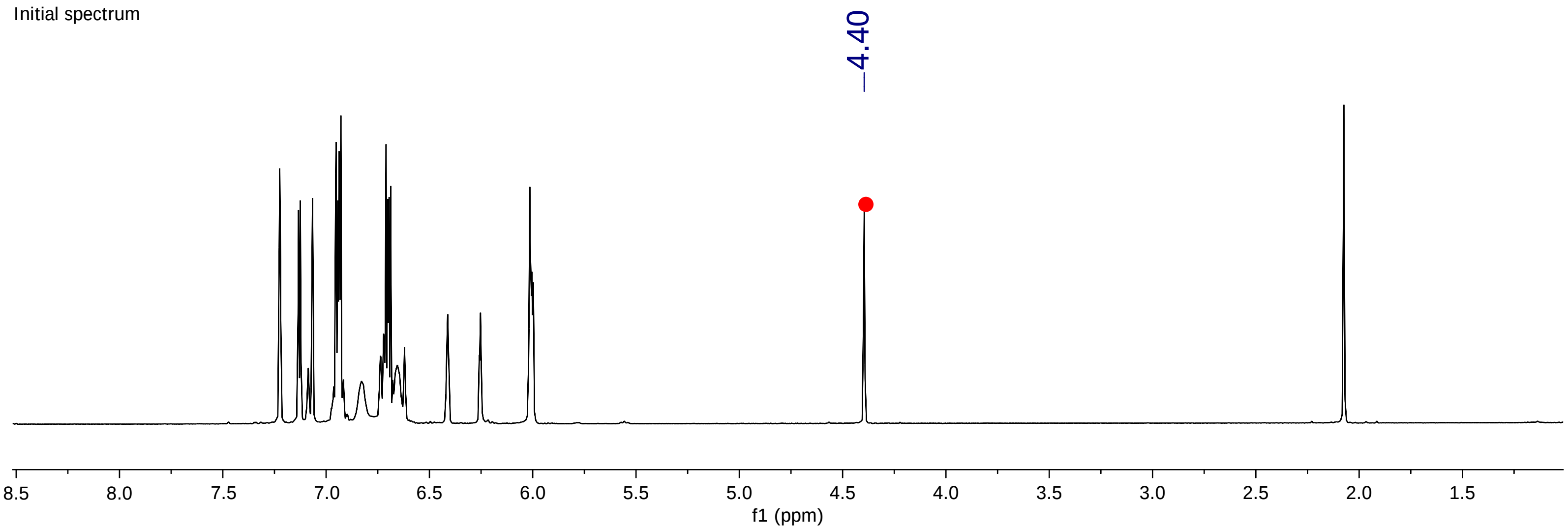
NMePyrrole_Mes_11024h #336 RT: 6.94 AV: 1 NL: 5.42E5
T: + c Full ms [50.00-650.00]



NMePyrrole_Mes_11024h #670 RT: 9.97 AV: 1 NL: 2.85E4
T: + c Full ms [50.00-650.00]

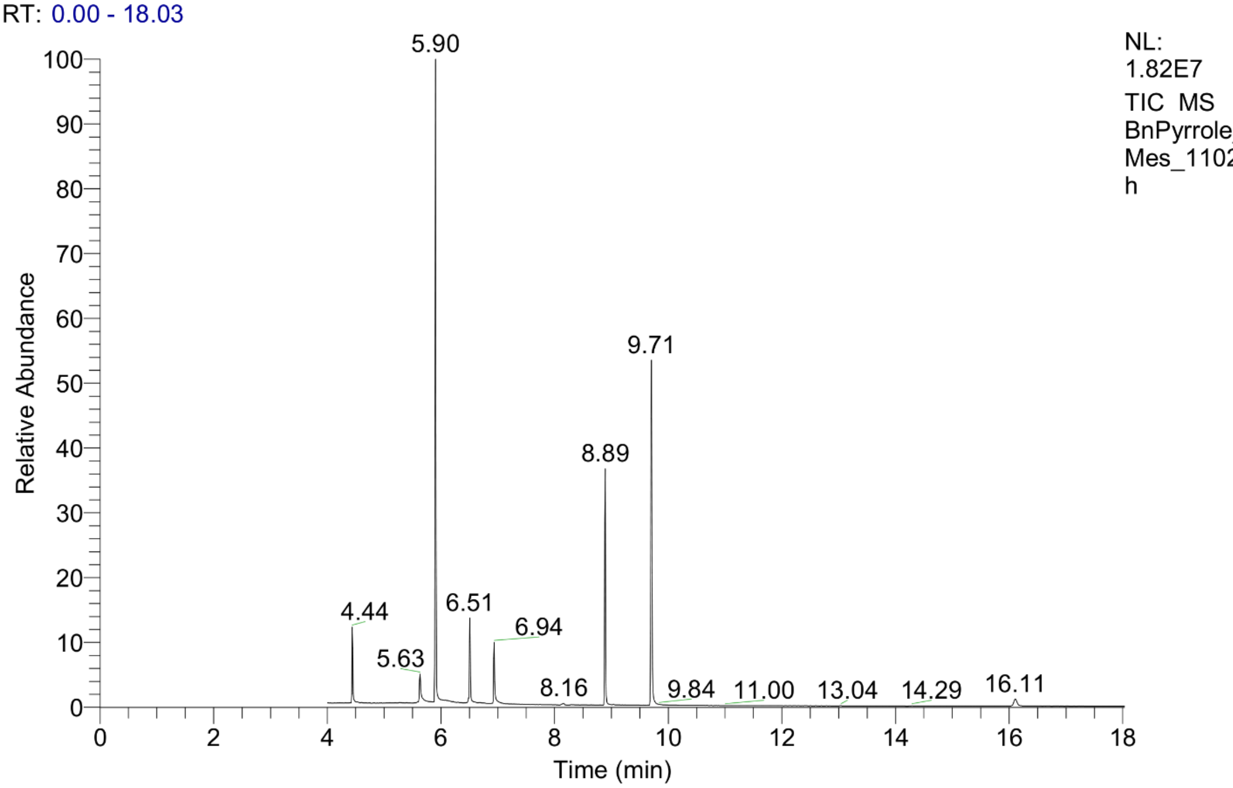




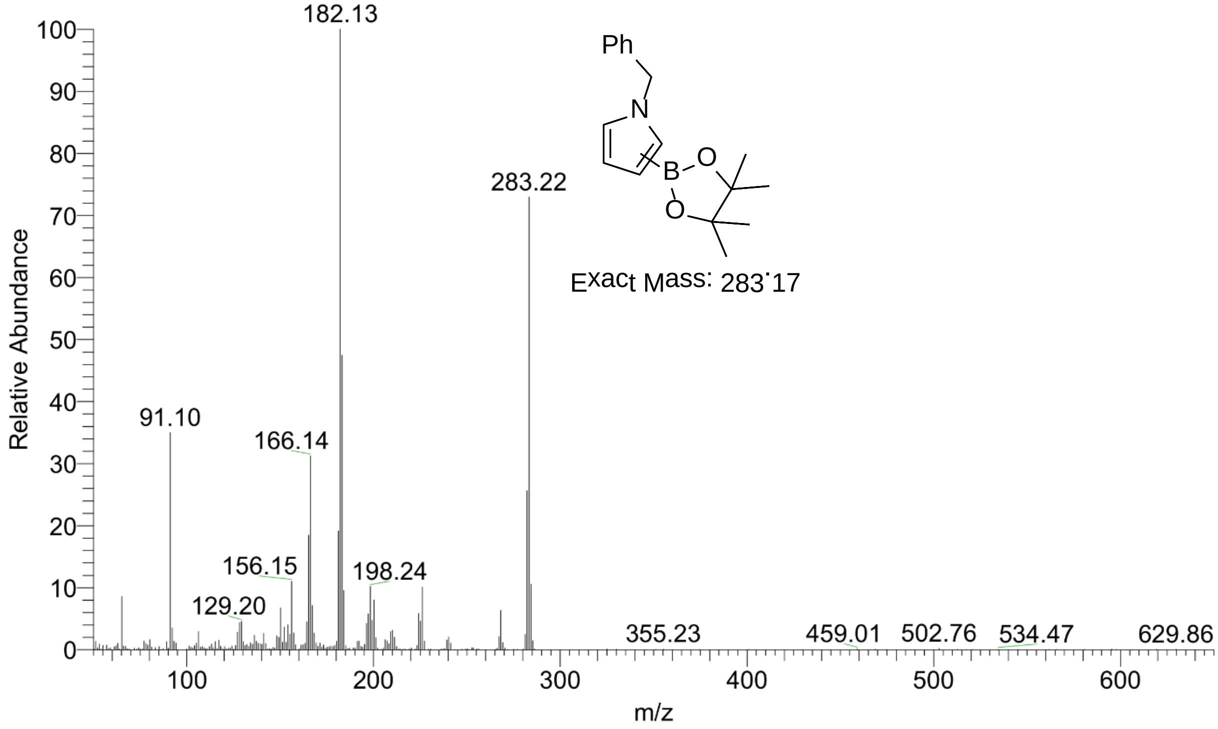


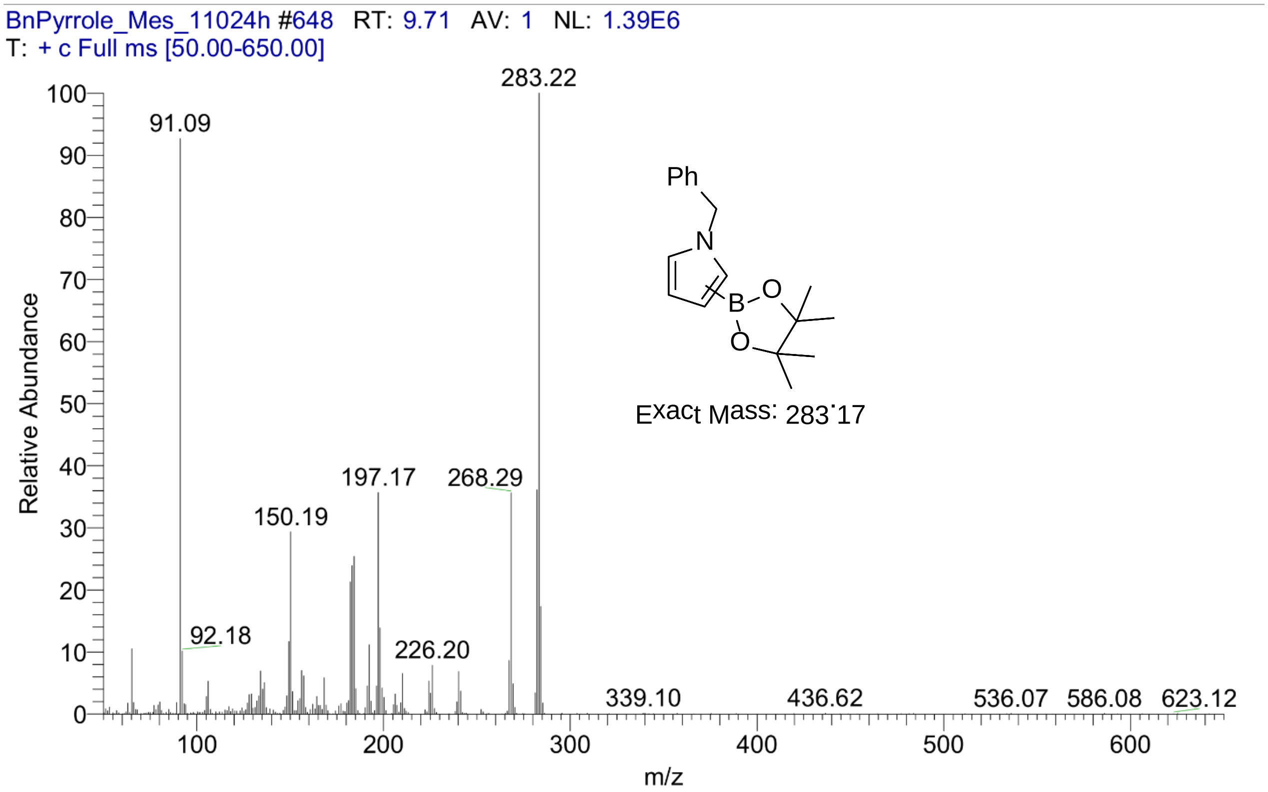
The conversion was determined using the N-CH_2 (benzylic) signal that shifts from 4.40 in the starting material to 5.13, 5.07 and 4.28 ppm in the products (C2, C3 and bis borylated compounds).

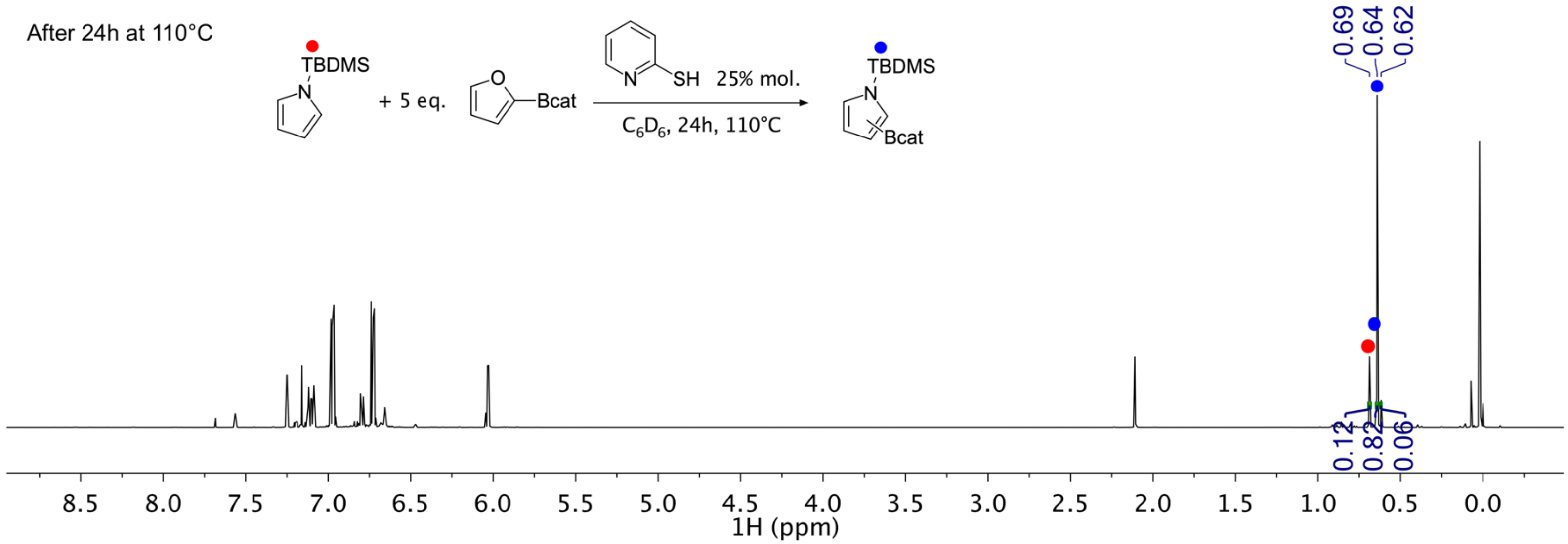
D:\GCMS Data\...\BnPyrrole_Mes_11024h 08/02/18 13:58:08 1

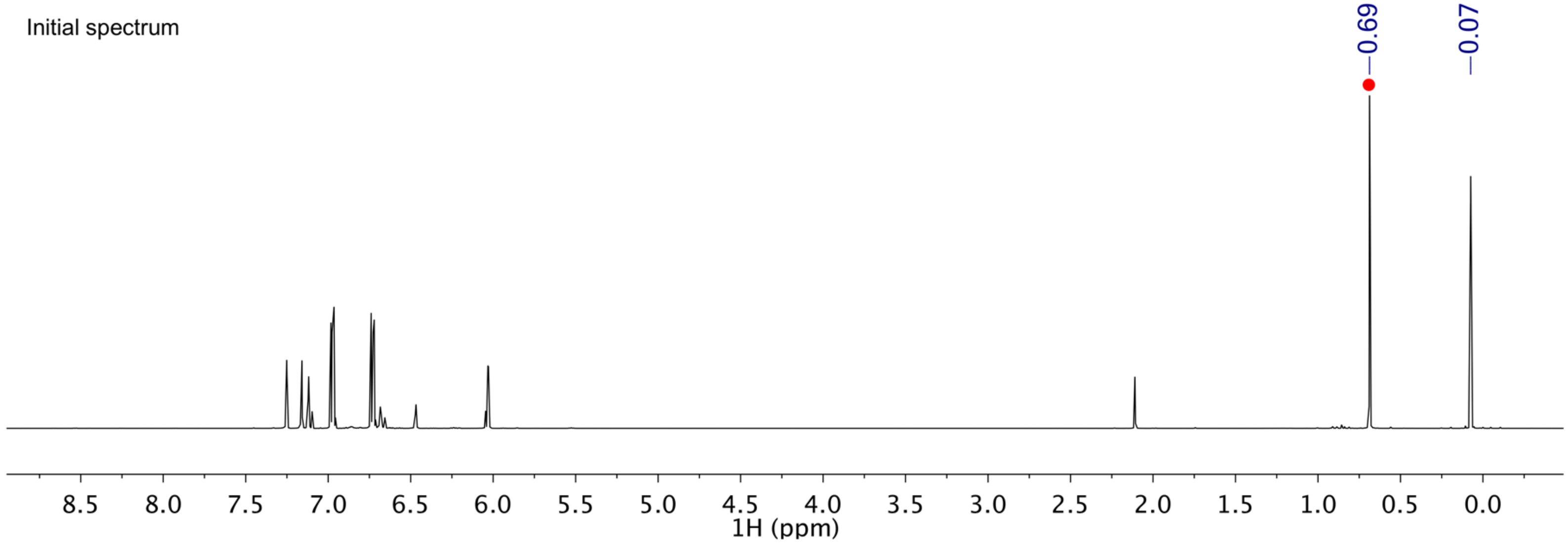


BnPyrrole_Mes_11024h #558 RT: 8.89 AV: 1 NL: 1.11E6
T: + c Full ms [50.00-650.00]




BnPyrrole_Mes_11024h #648 RT: 9.71 AV: 1 NL: 1.39E6
T: + c Full ms [50.00-650.00]
283.22
91.09
92.18
150.19
197.17
268.29
226.20
339.10
436.62
536.07
586.08
623.12
Relative Abundance
m/z
Ph
N
B
O
O
Exact Mass: 283.17

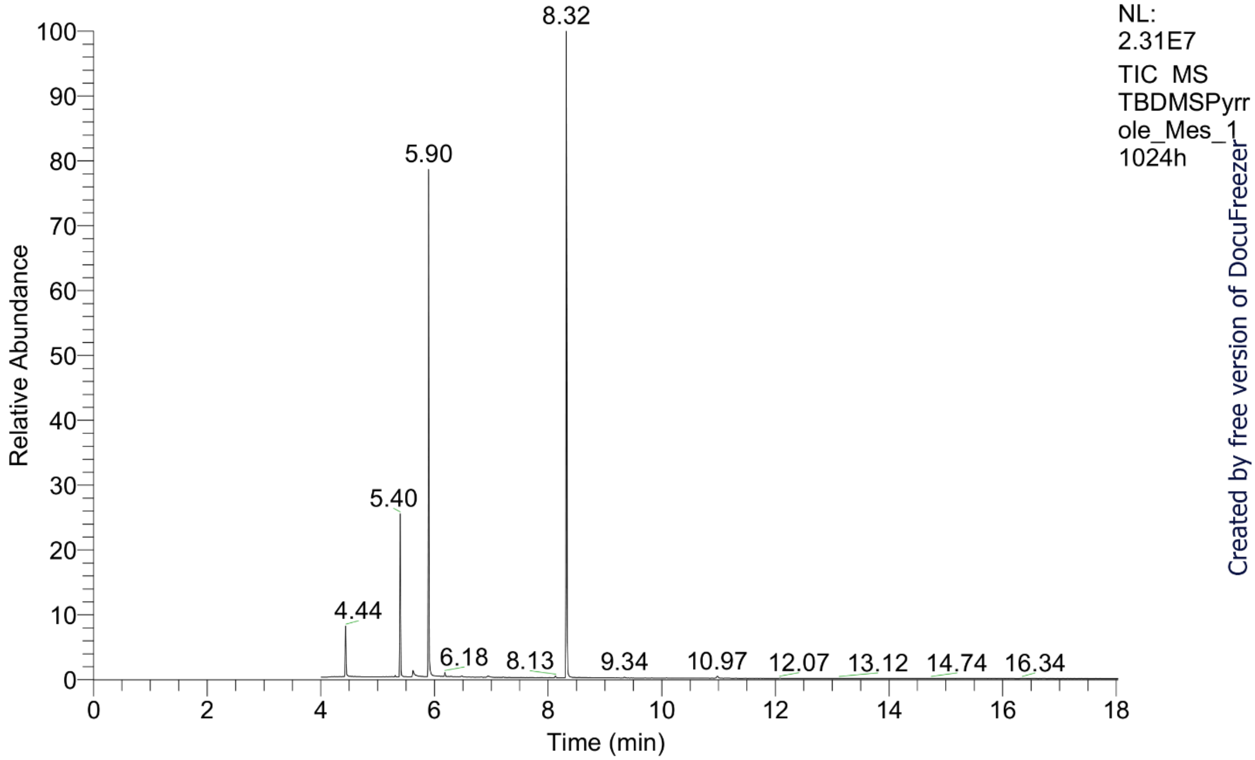

After 24h at 110°C


Initial spectrum

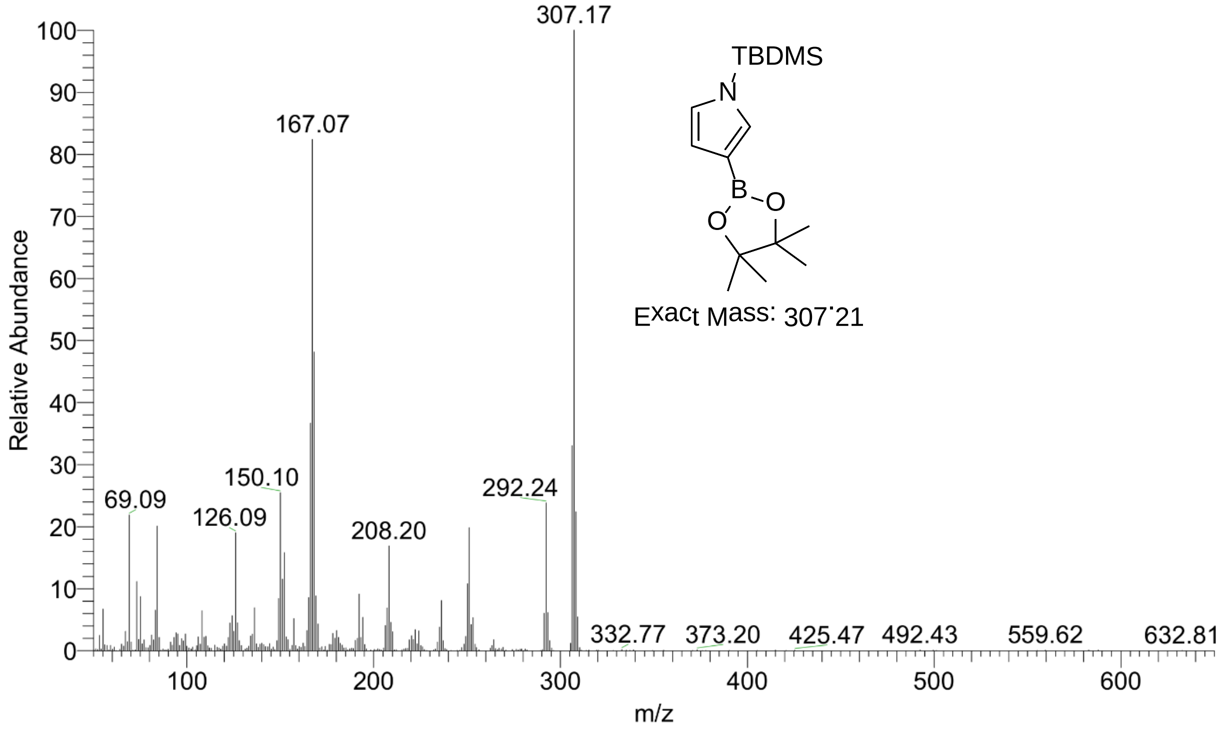
The conversion was determined using the TBDMS *tert*-butyl signal that shifts from 0.69 in the starting material to 0.64 ppm for the mono-borylated product and 0.62 for the bis-borylated product respectively.

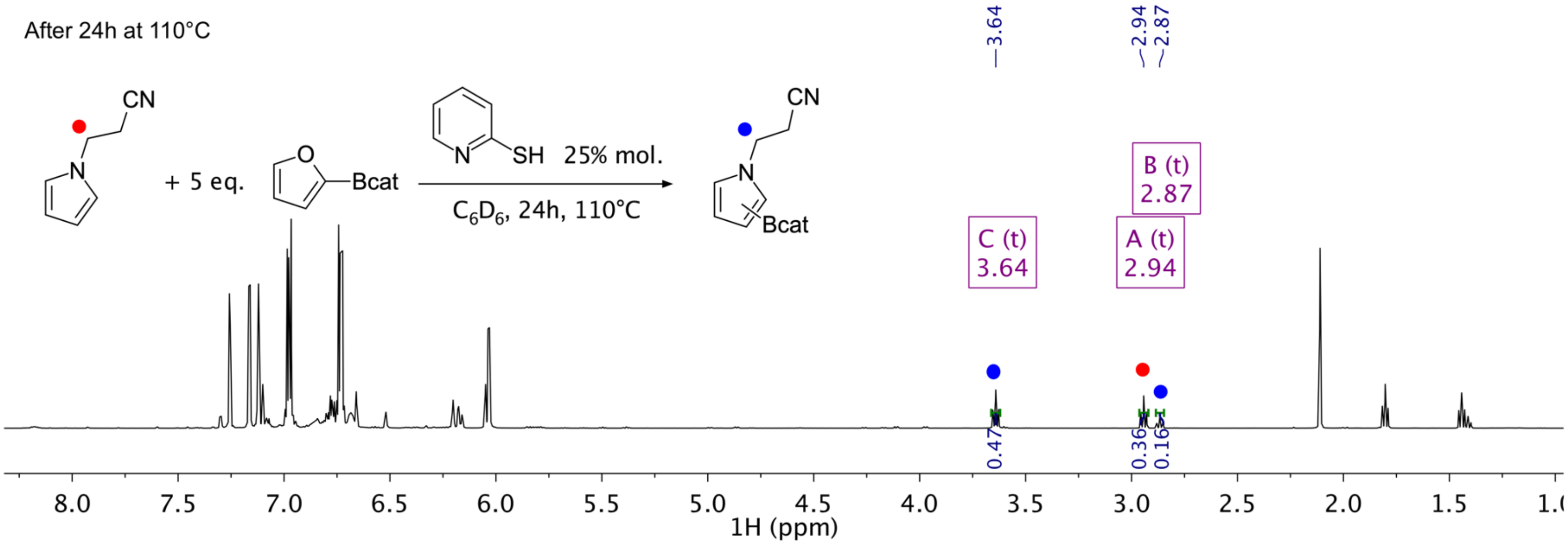
D:\GCMS Data\...\TBDMSPyrrole_Mes_11024h 08/09/18 13:08:34

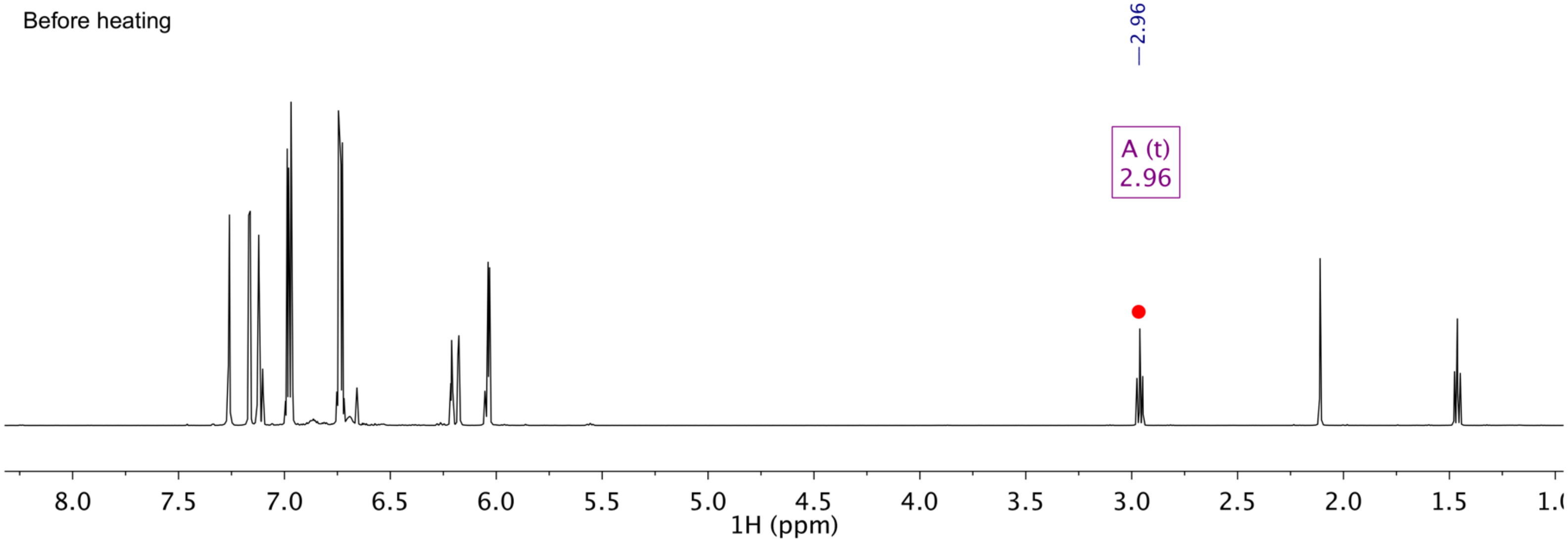
RT: 0.00 - 18.03



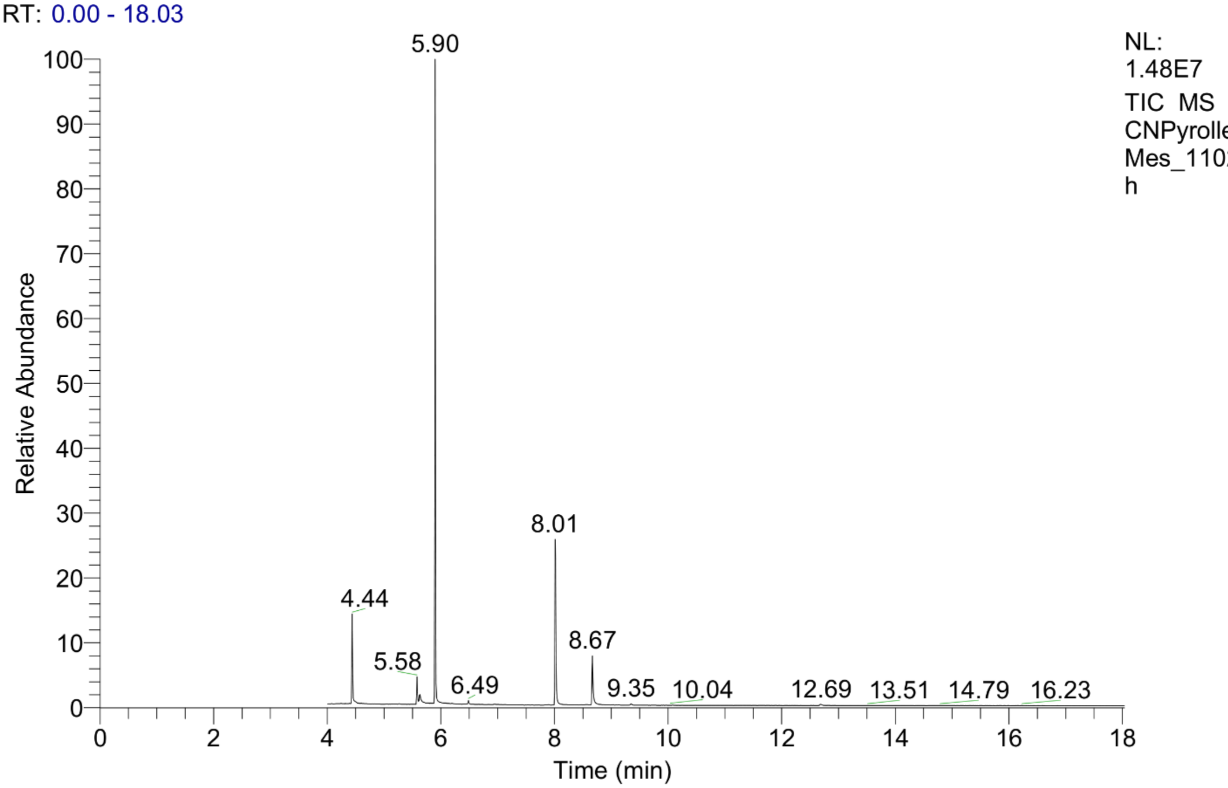
TBDMSPyrrole_Mes_11024h #494 RT: 8.32 AV: 1 NL: 2.75E6
T: + c Full ms [50.00-650.00]

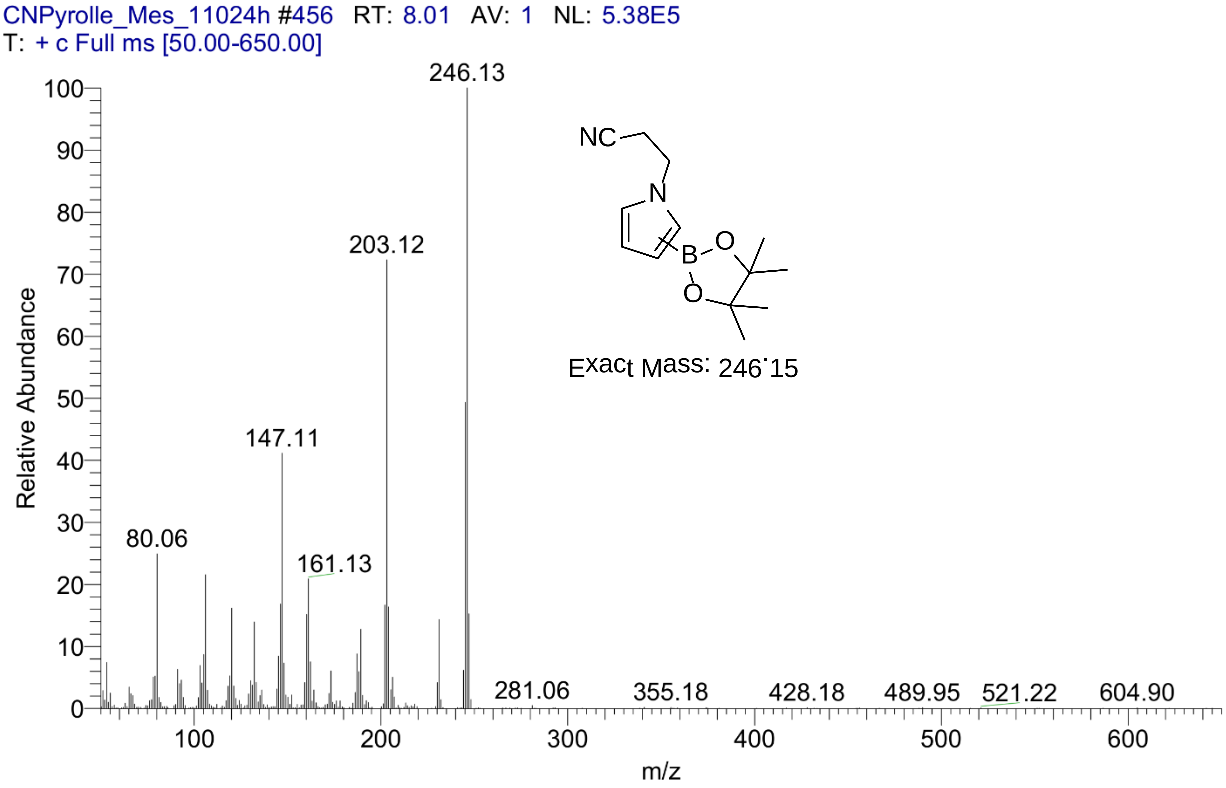


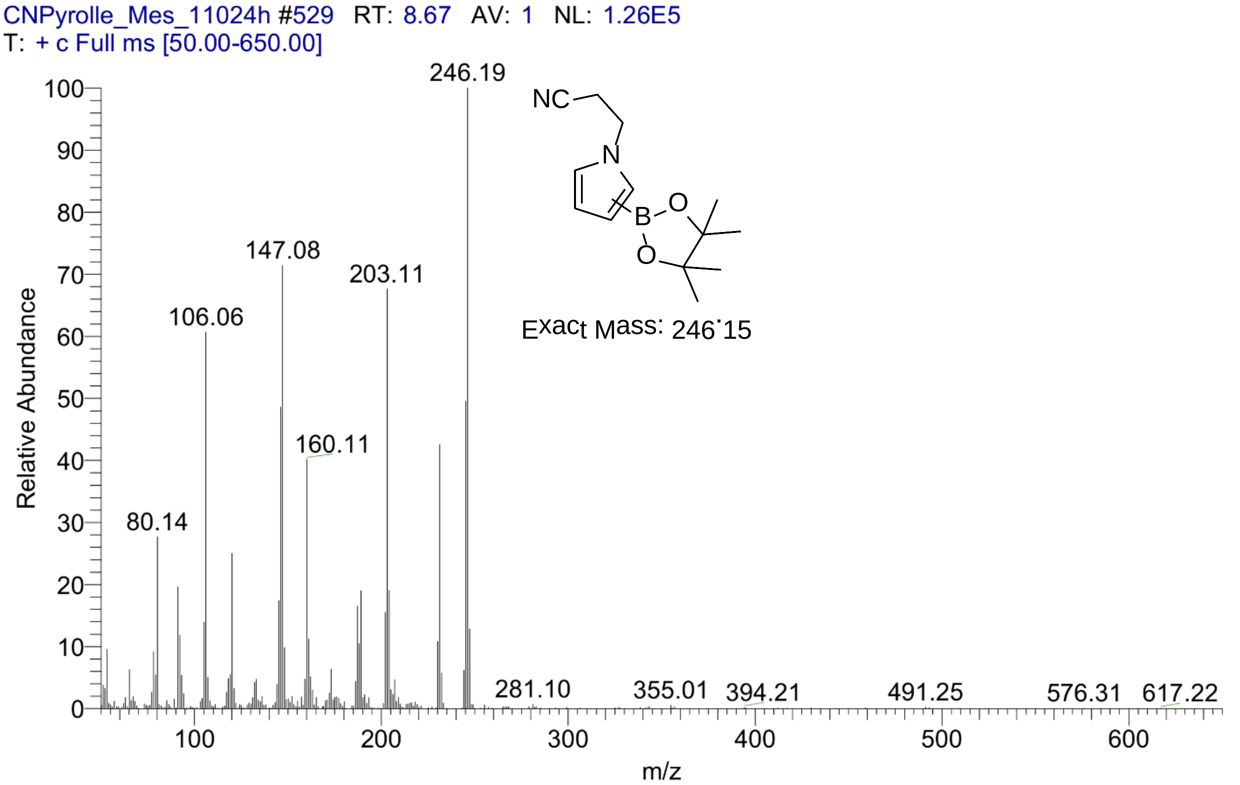

After 24h at 110°C


Before heating

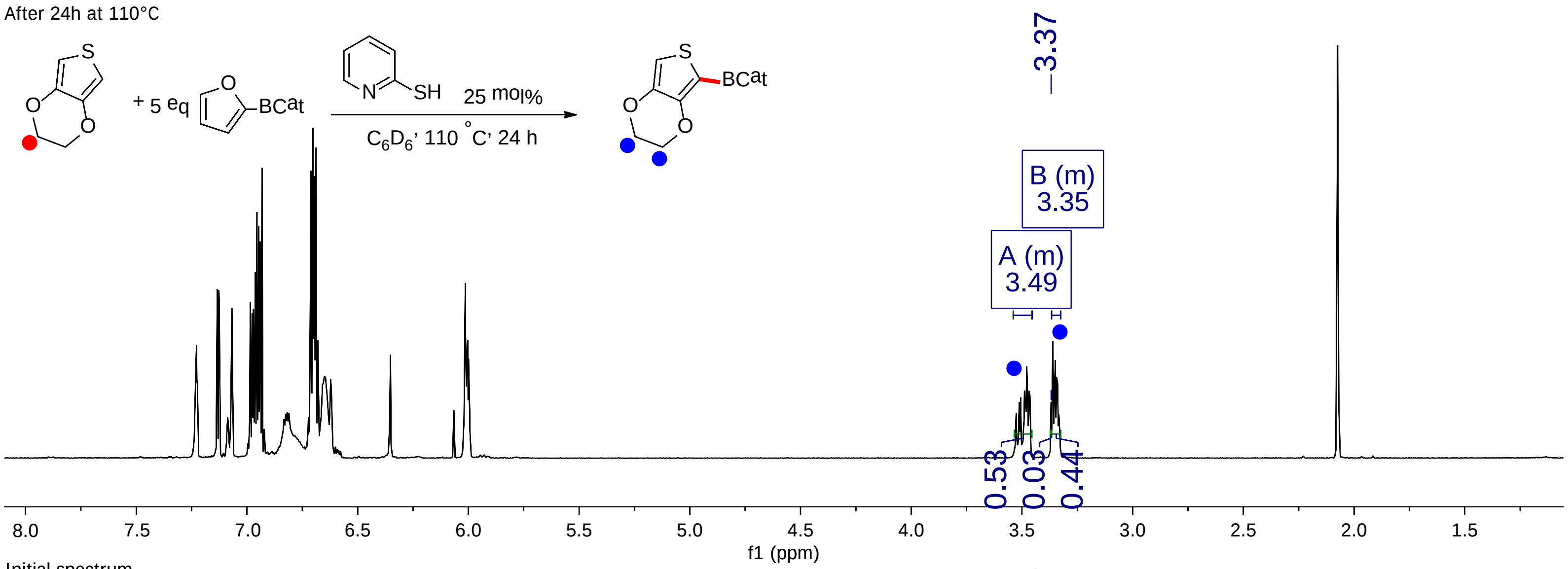
The conversion was determined using the N-CH_2 signal that shifts from 2.95 in the starting material to 3.63 and 2.87 ppm in the products (C2 and C3 borylated compounds). New signals associated with the other CH_2 are also observed, but with some overlap.


RT: 0.00 - 18.03
NL: 1.48E7
TIC MS CNPyrolle_Mes_11024h
Relative Abundance
Time (min)
0
10
20
30
40
50
60
70
80
90
100
0
2
4
6
8
10
12
14
16
18
5.90
8.01
4.44
5.58
6.49
8.67
9.35
10.04
12.69
13.51
14.79
16.23

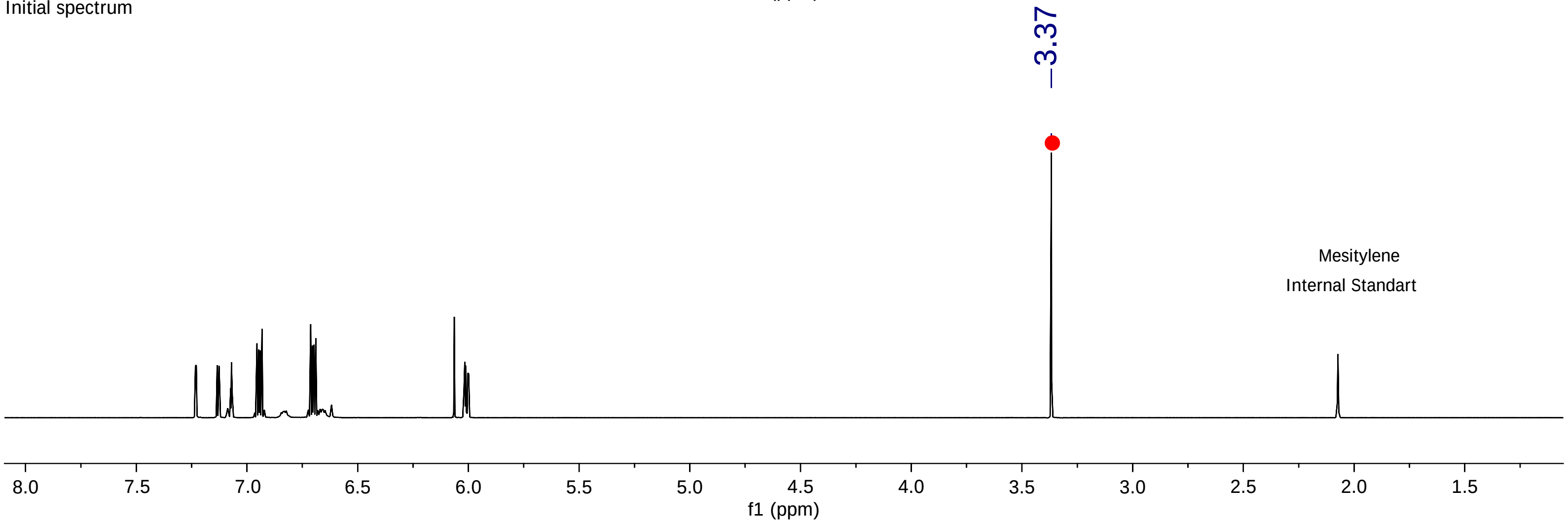

CNPyrolle_Mes_11024h #456 RT: 8.01 AV: 1 NL: 5.38E5
T: + c Full ms [50.00-650.00]
Relative Abundance
m/z
0
10
20
30
40
50
60
70
80
90
100
100
200
300
400
500
600
246.13
203.12
147.11
80.06
161.13
281.06
355.18
428.18
489.95
521.22
604.90
NC
N
B
O
O
Exact Mass: 246.15


CNPyrolle_Mes_11024h #529 RT: 8.67 AV: 1 NL: 1.26E5
T: + c Full ms [50.00-650.00]
246.19
147.08
203.11
106.06
160.11
80.14
281.10
355.01
394.21
491.25
576.31
617.22
Relative Abundance
m/z
0
10
20
30
40
50
60
70
80
90
100
200
300
400
500
600
NC
N
B
O
O
Exact Mass: 246.15

After 24h at 110°C



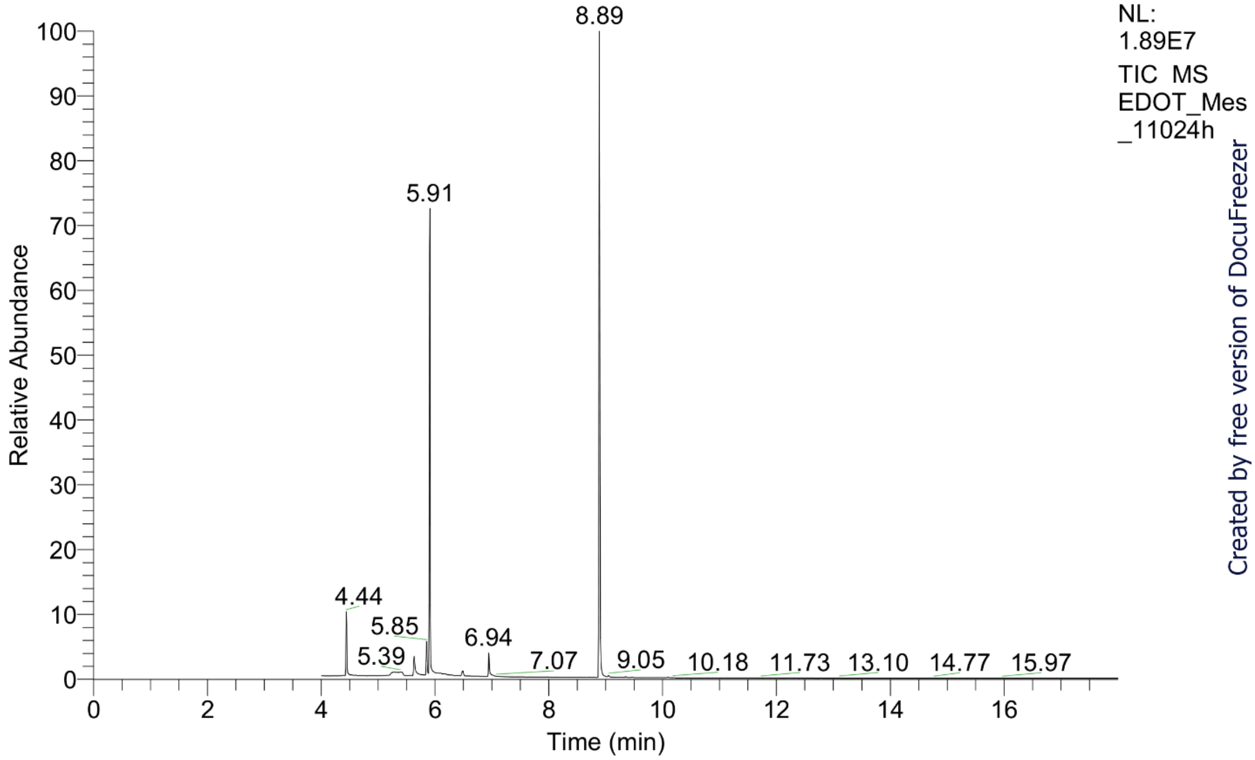
Initial spectrum



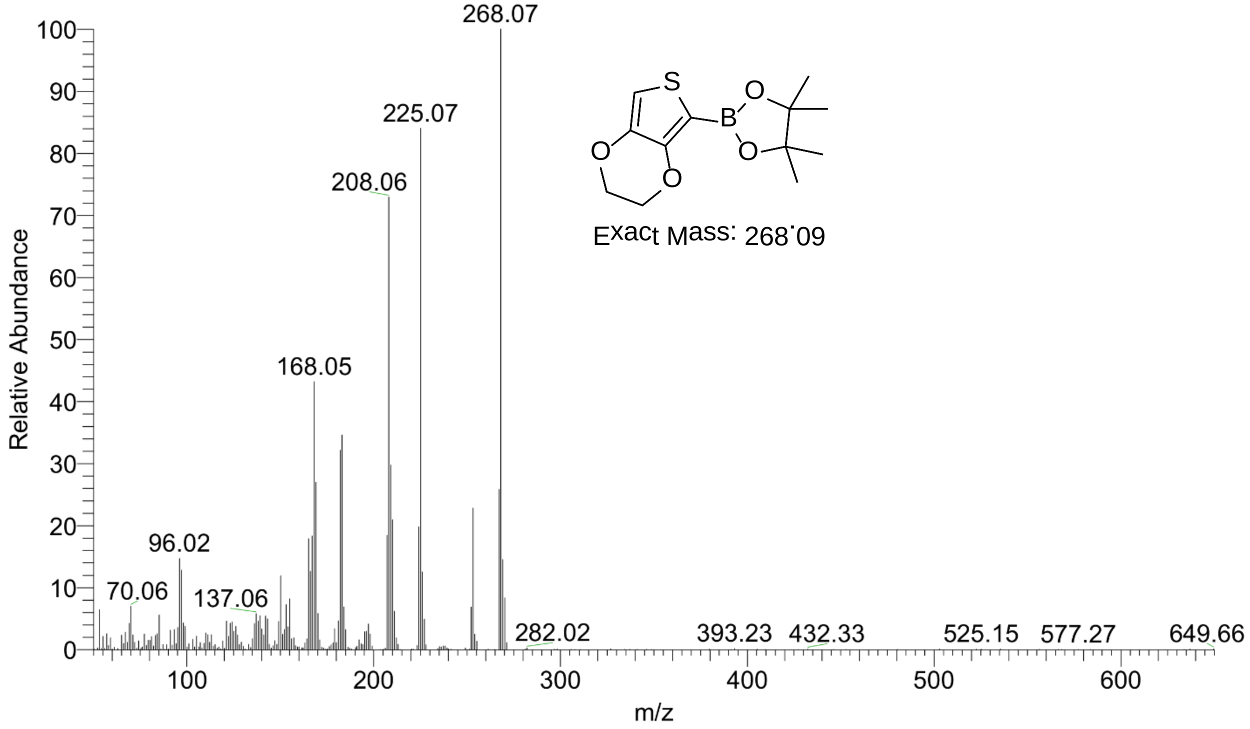
The conversion was determined using the O-CH_2 signals that shift from a singlet at 3.37 ppm in the starting material to multiplets from 3.30 to 3.55 ppm in the product.

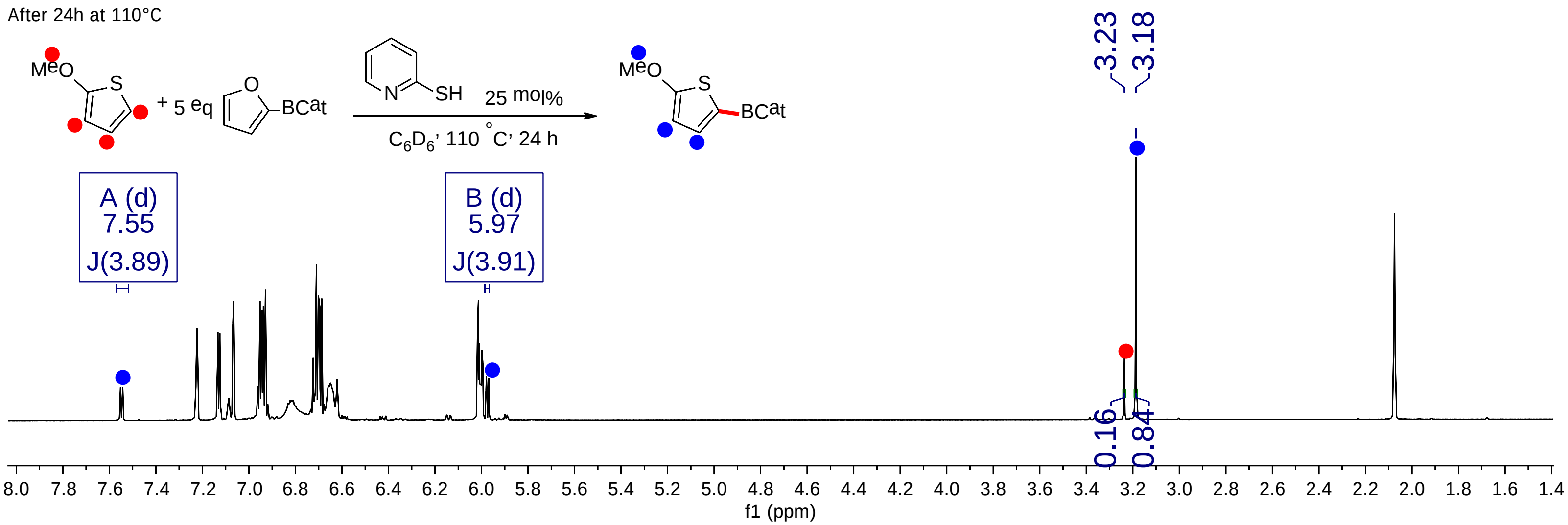
D:\GCMS Data\...\Etienne\EDOT_Mes_11024h 08/02/18 11:42:39 1

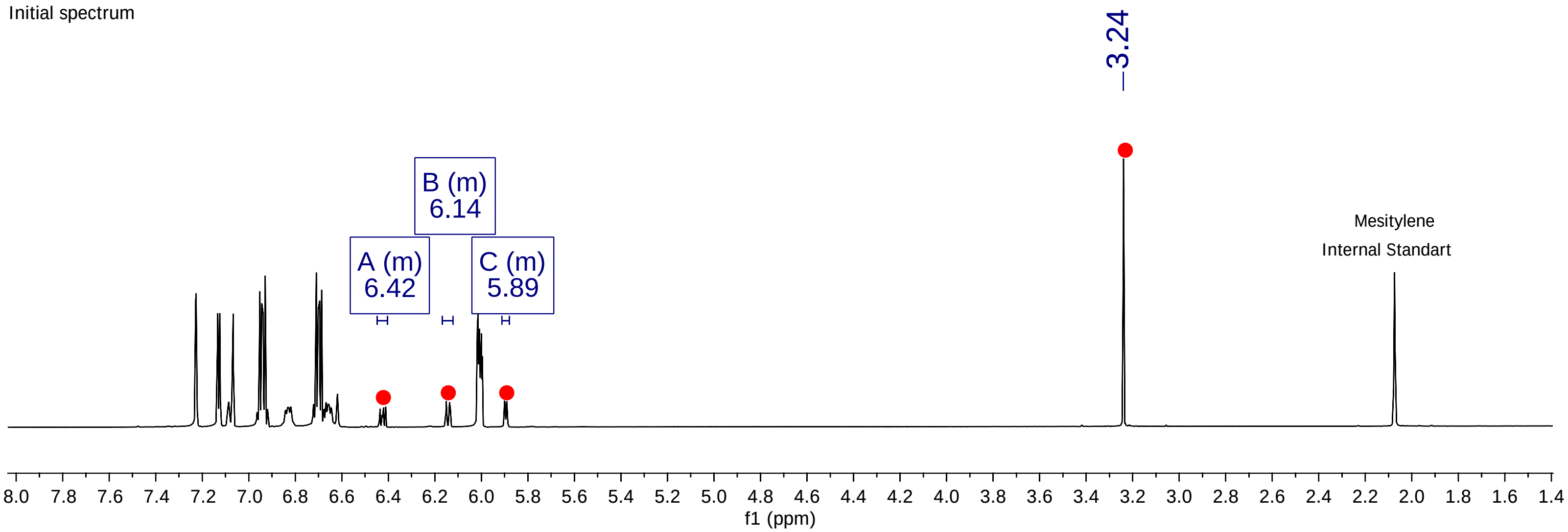
RT: 0.00 - 18.00



EDOT_Mes_11024h #553 RT: 8.89 AV: 1 NL: 2.00E6
T: + c Full ms [50.00-650.00]

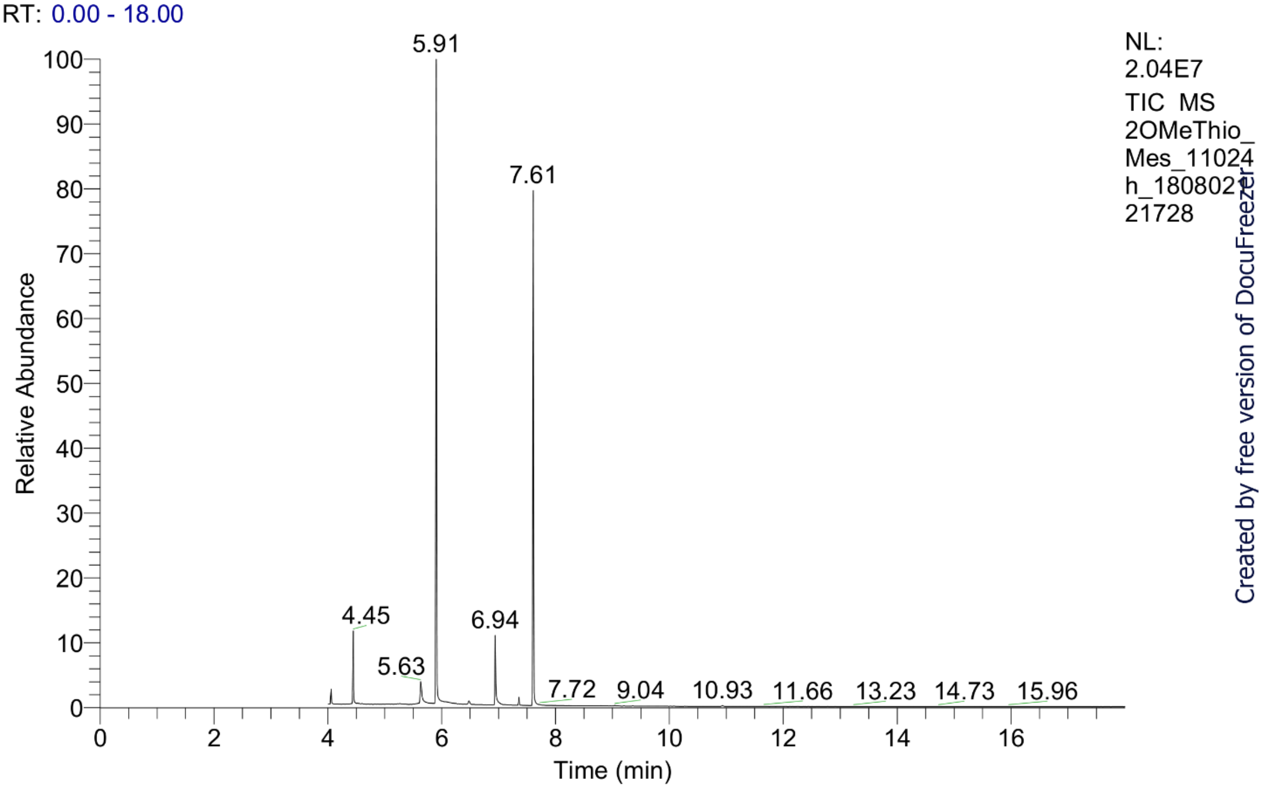




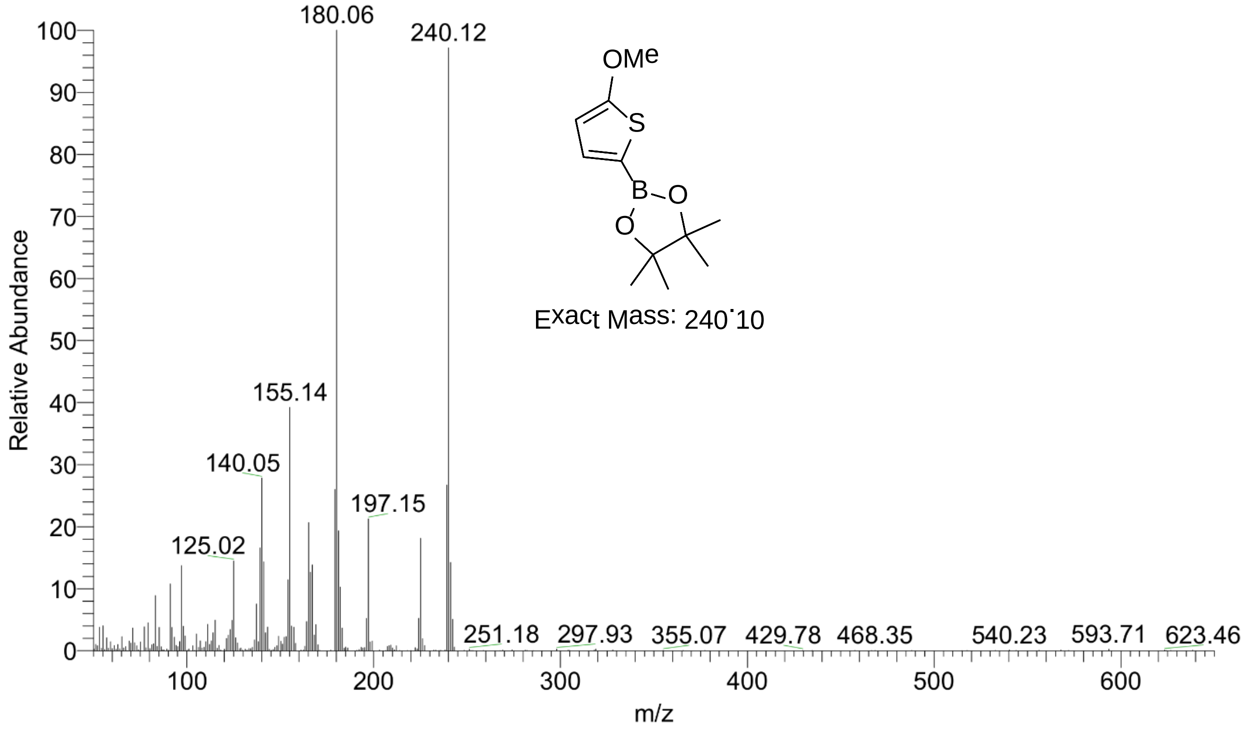


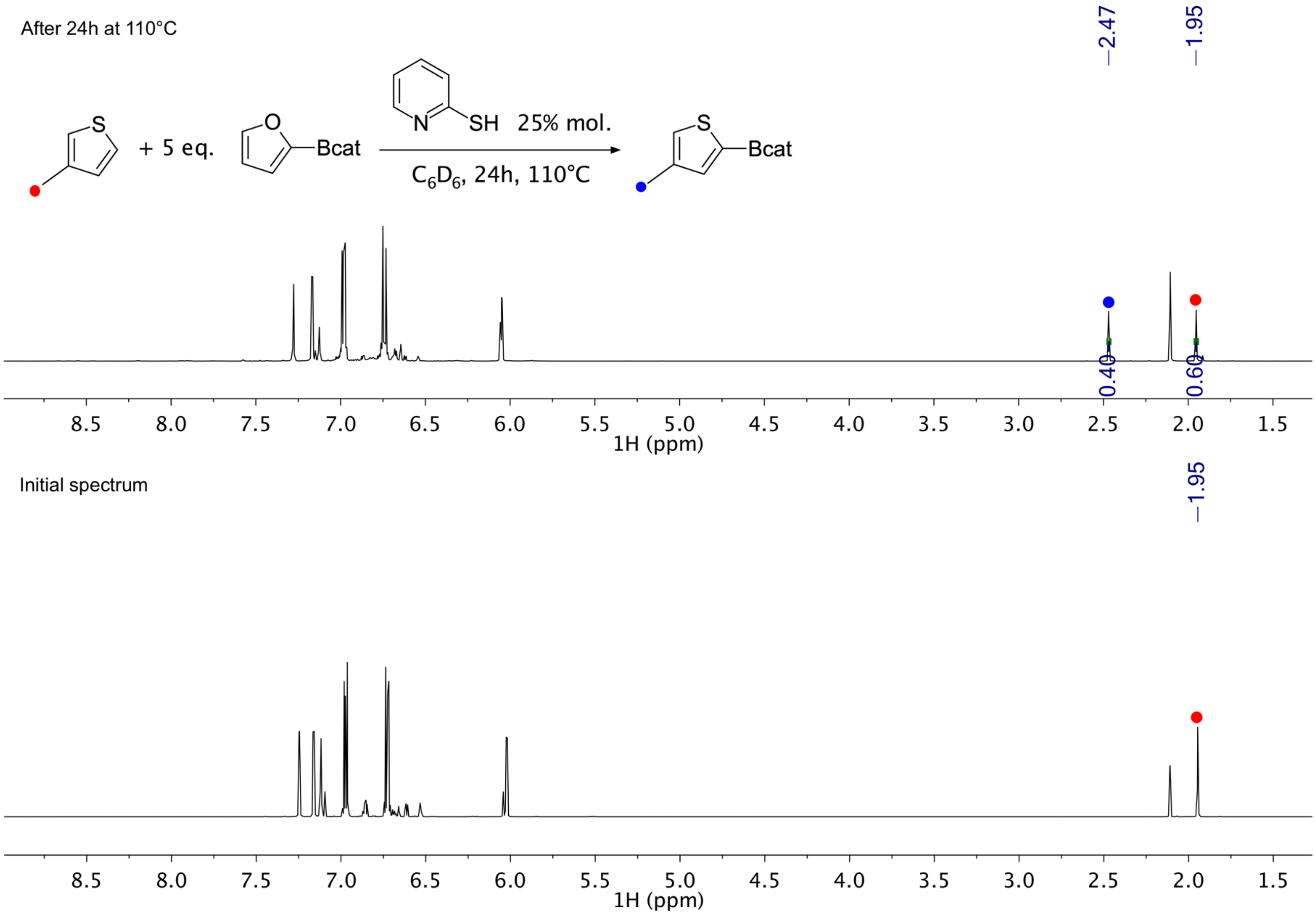
The conversion was determined using the methoxy signals that shifts from a singlet at 3.24 in the starting material to multiplets to 3.18 ppm in the product. Change of the aromatic signals from 6.42, 6.14 and 5.89 ppm to 7.55 and 5.97 ppm was also observed.

2OMeThio_Mes_11024h_180802121728 08/02/18 12:17:28 1



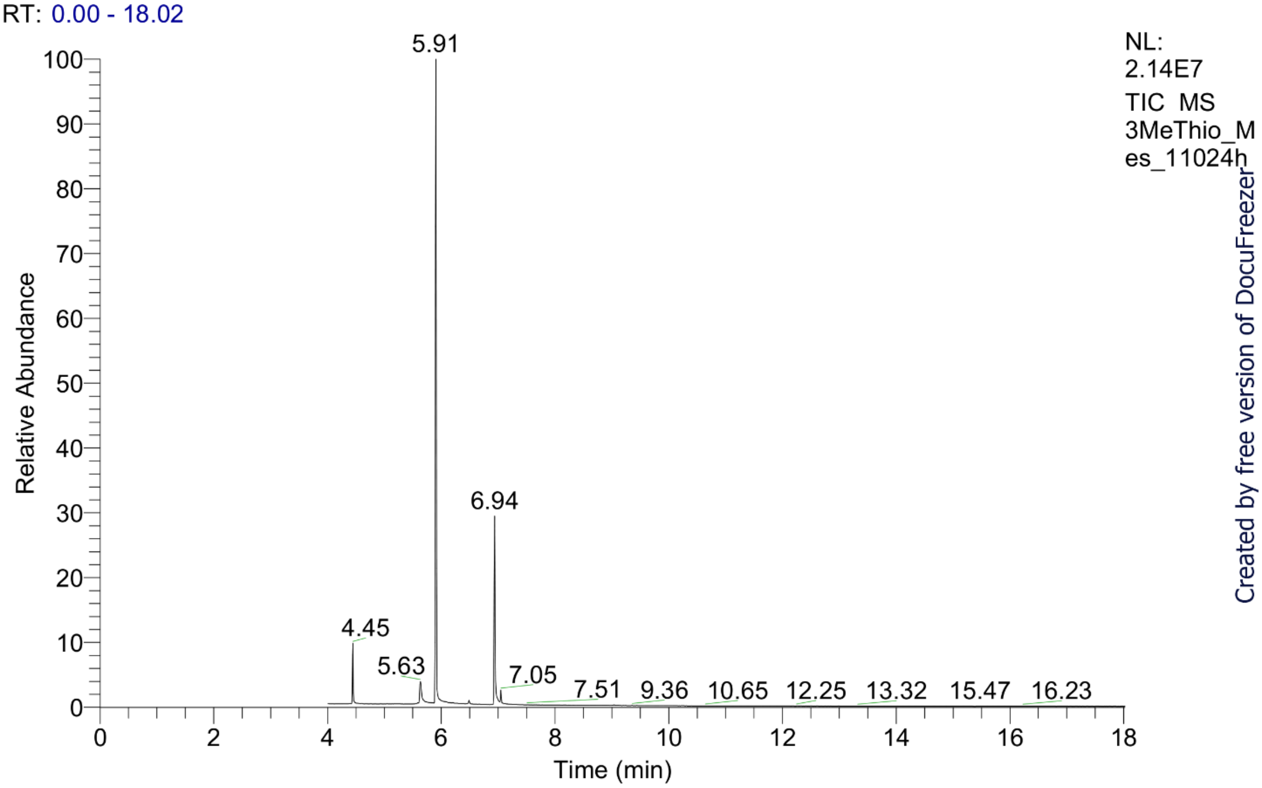
2OMeThio_Mes_11024h_180802121728 #415 RT: 7.62 AV: 1 NL: 5.74E5
T: + c Full ms [50.00-650.00]



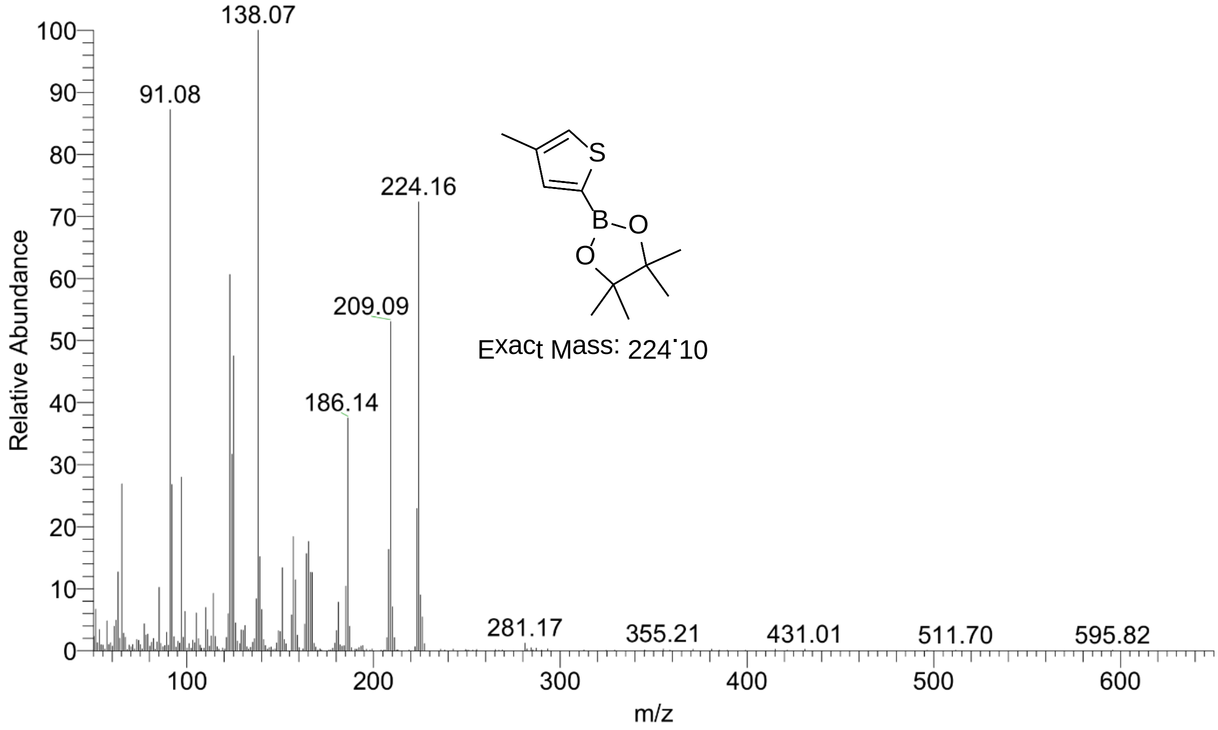


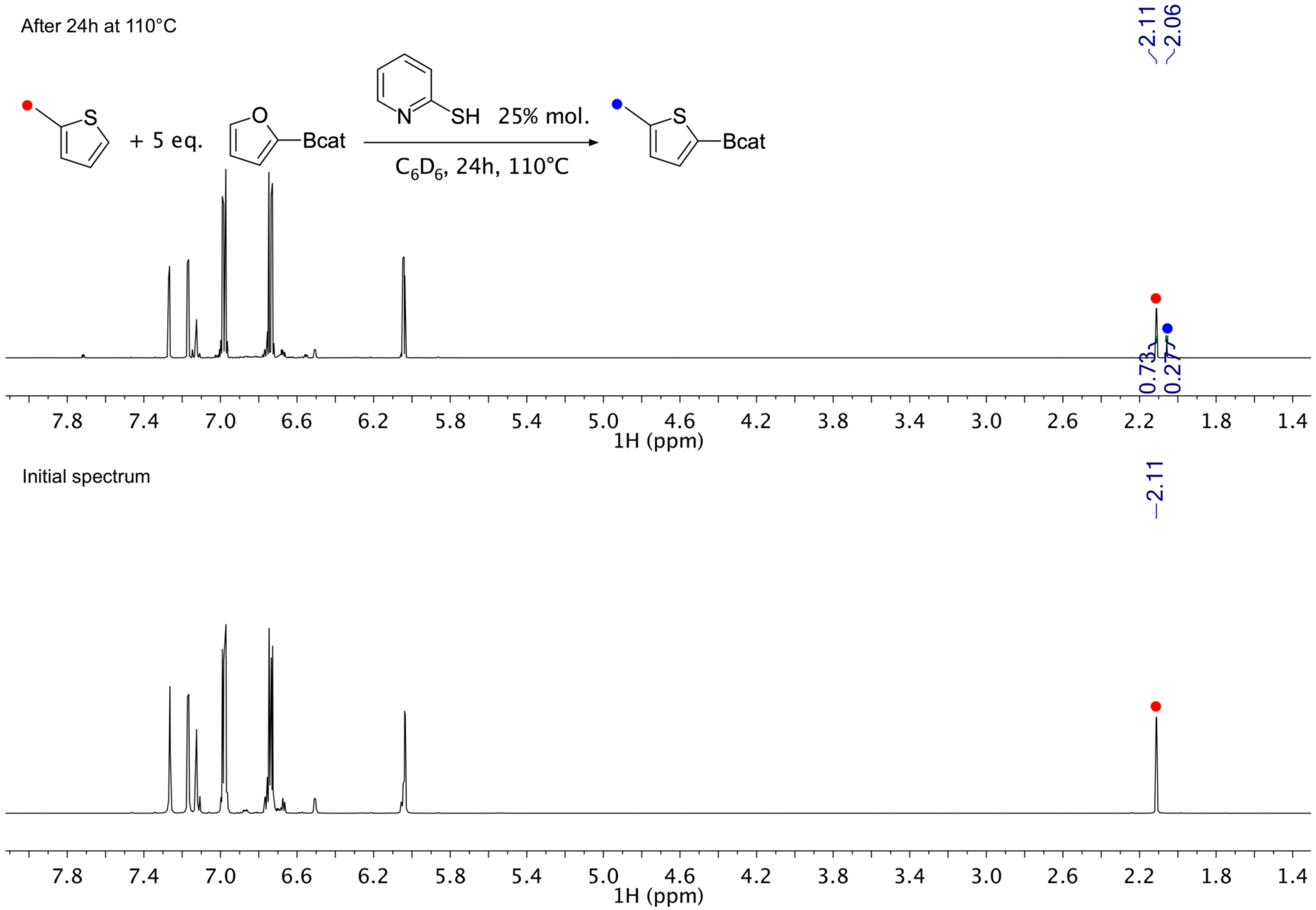
The conversion was determined using the C3-Methyl signal that shifts from 1.95 in the starting material to 2.47 ppm in the product.

D:\GCMS Data\...\3MeThio_Mes_11024h 08/02/18 13:04:40 1



3MeThio_Mes_11024h #351 RT: 7.05 AV: 1 NL: 5.54E4
T: + c Full ms [50.00-650.00]

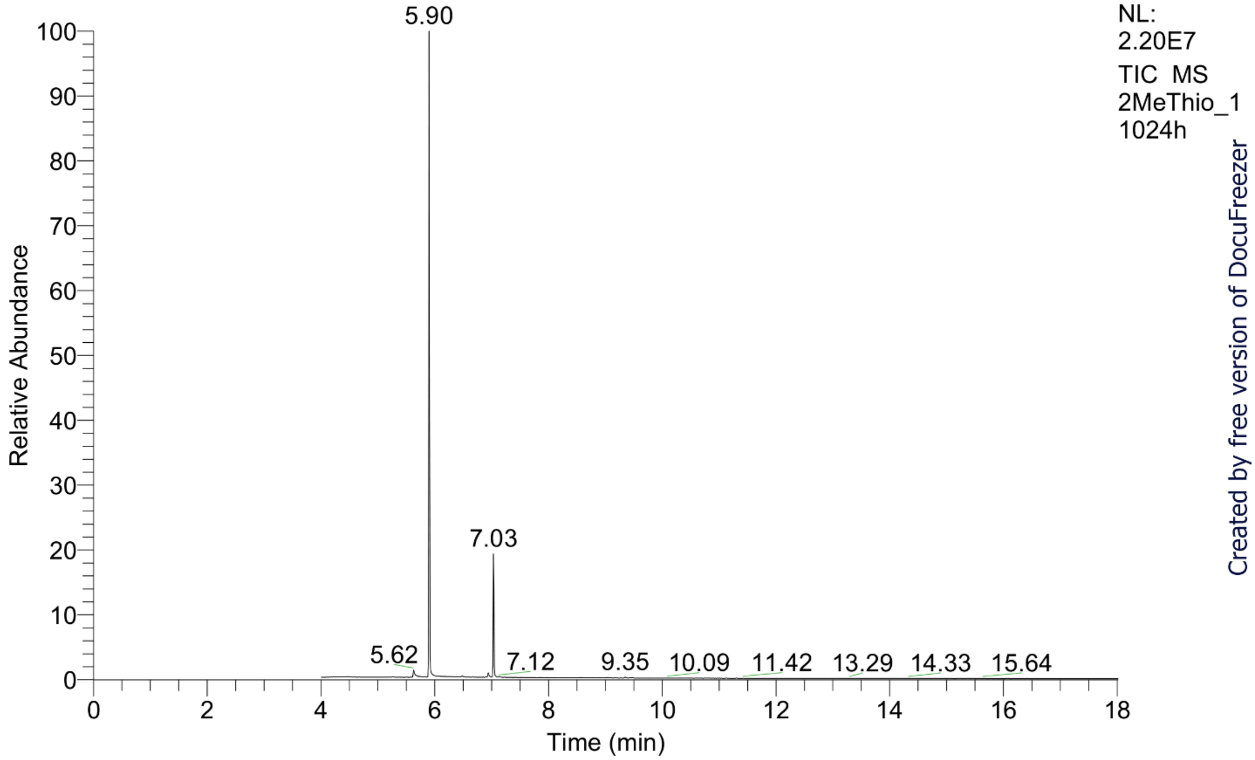




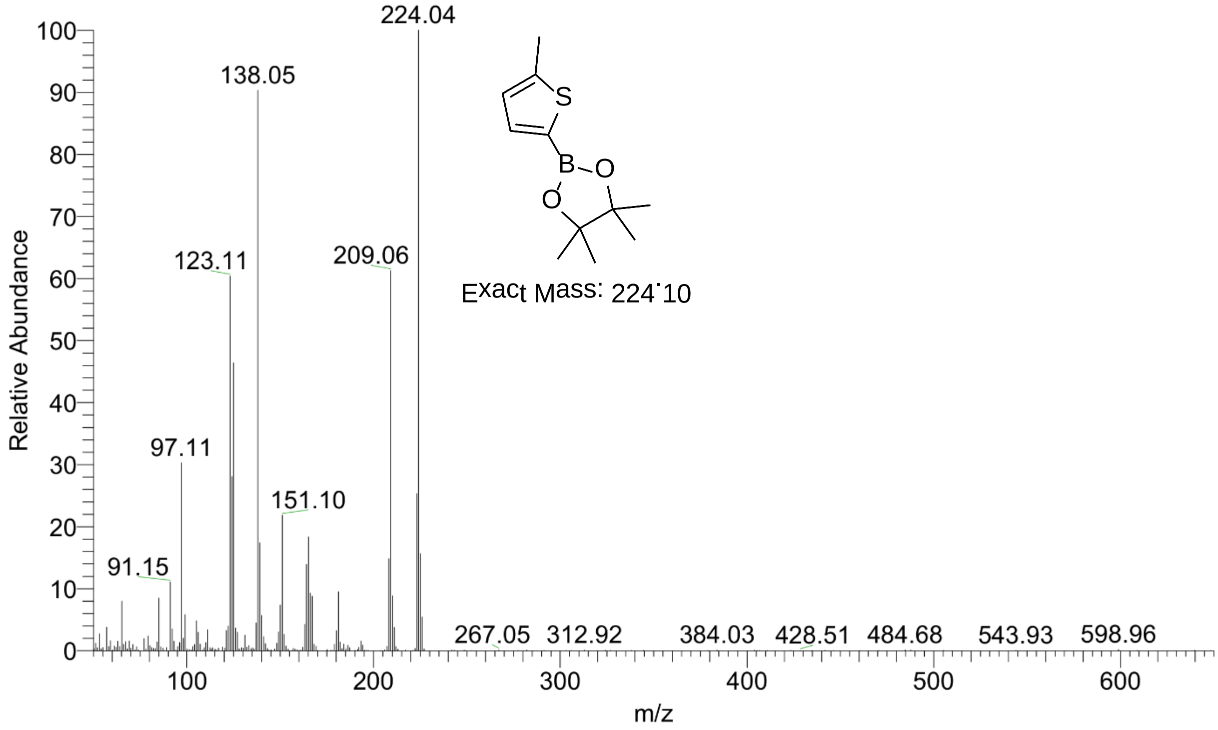
The conversion was determined using the C2-Methyl signal that shifts from 2.11 in the starting material to 2.06 ppm in the product.

D:\GCMS Data\...\Etienne\2MeThio_11024h 08/09/18 14:59:53

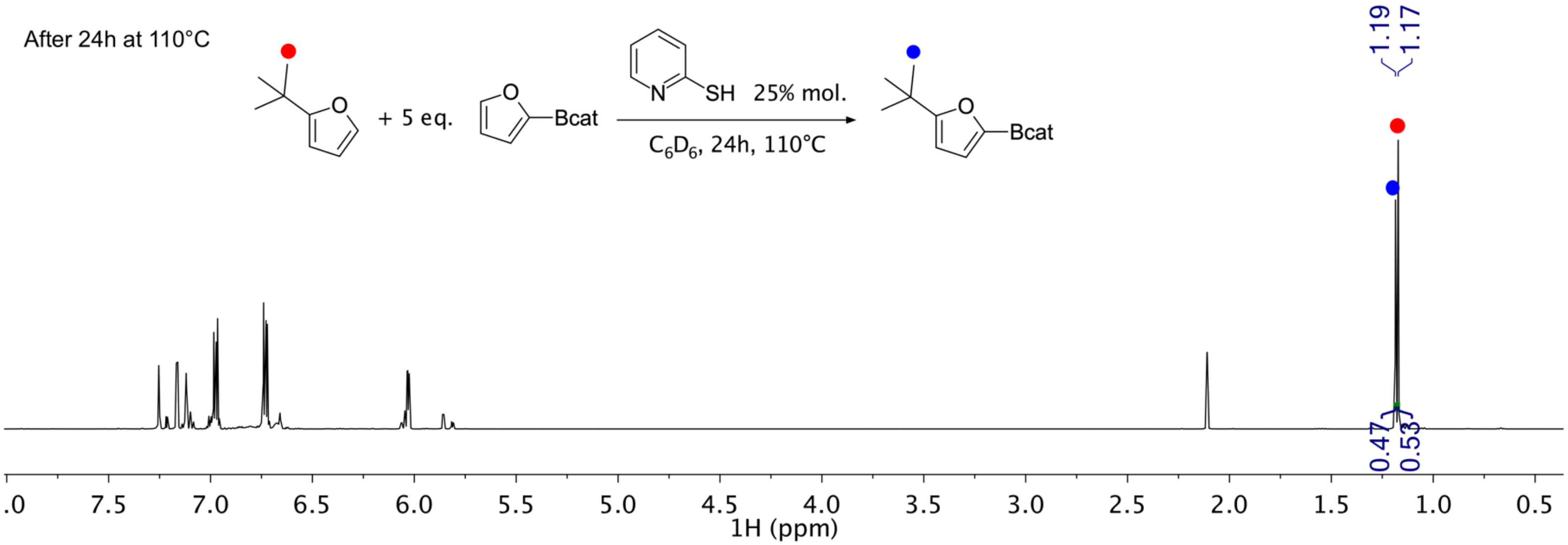
RT: 0.00 - 18.01



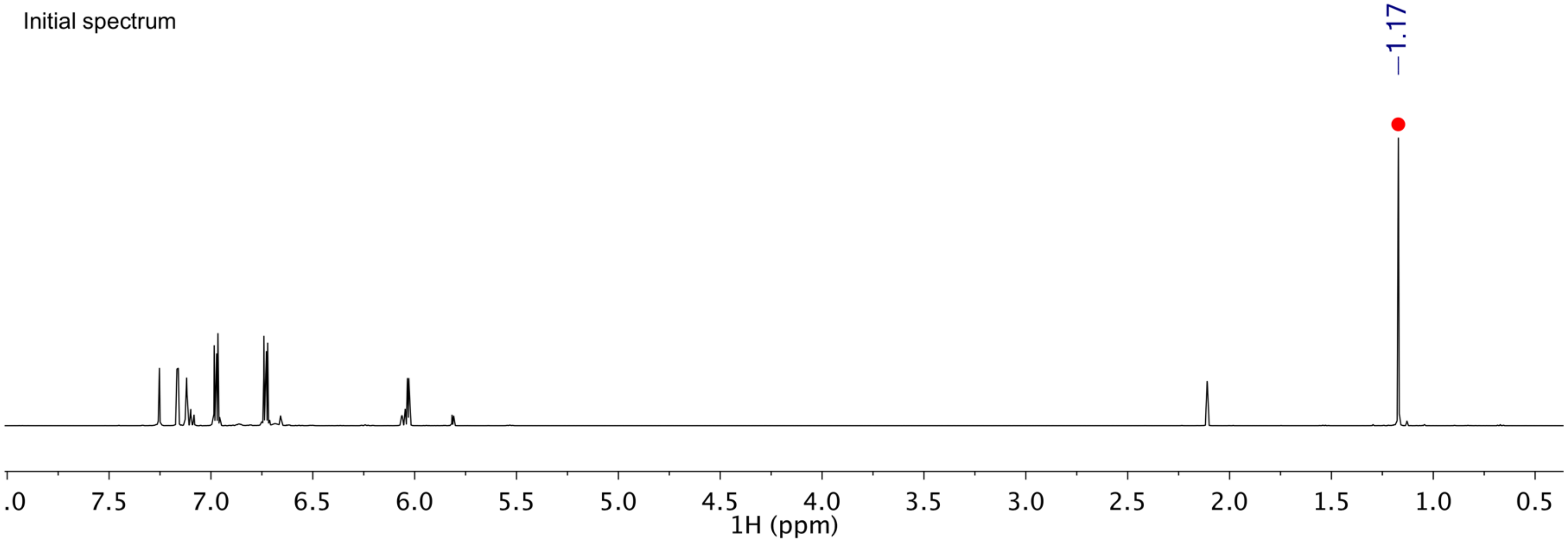
2MeThio_11024h #347 RT: 7.03 AV: 1 NL: 5.66E5
T: + c Full ms [50.00-650.00]



After 24h at 110°C



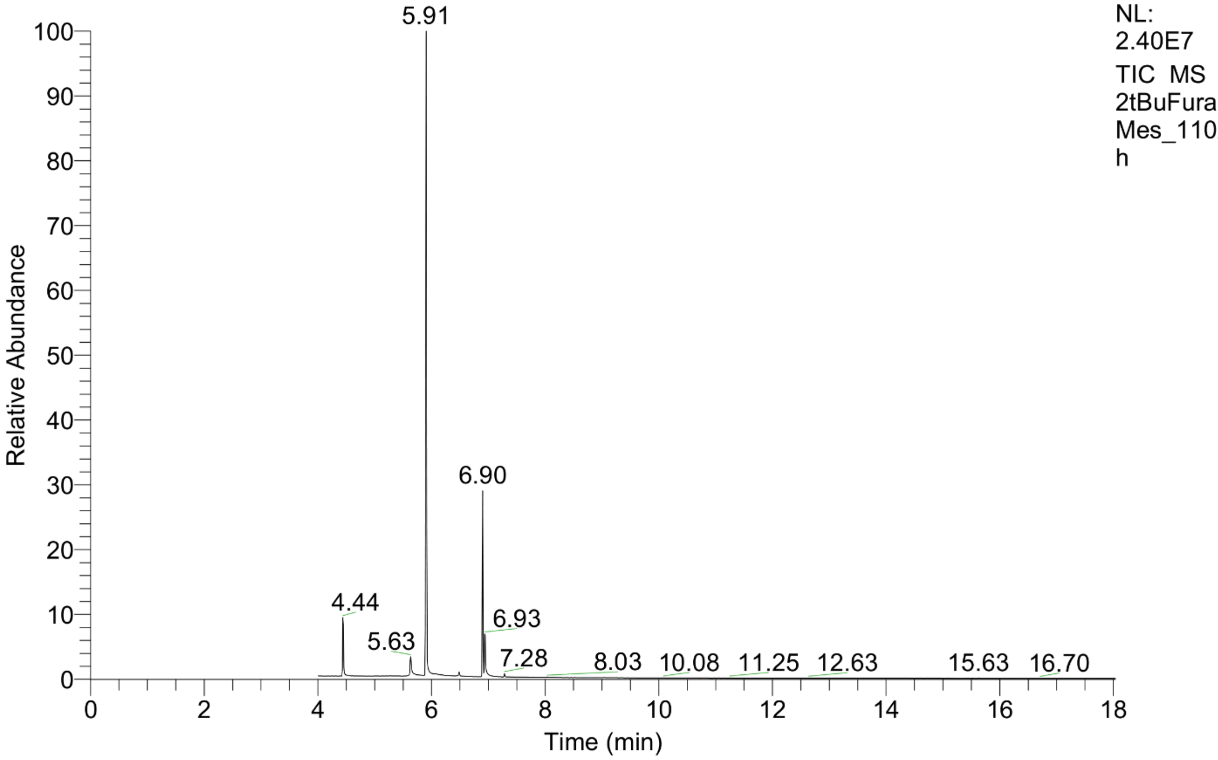
Initial spectrum



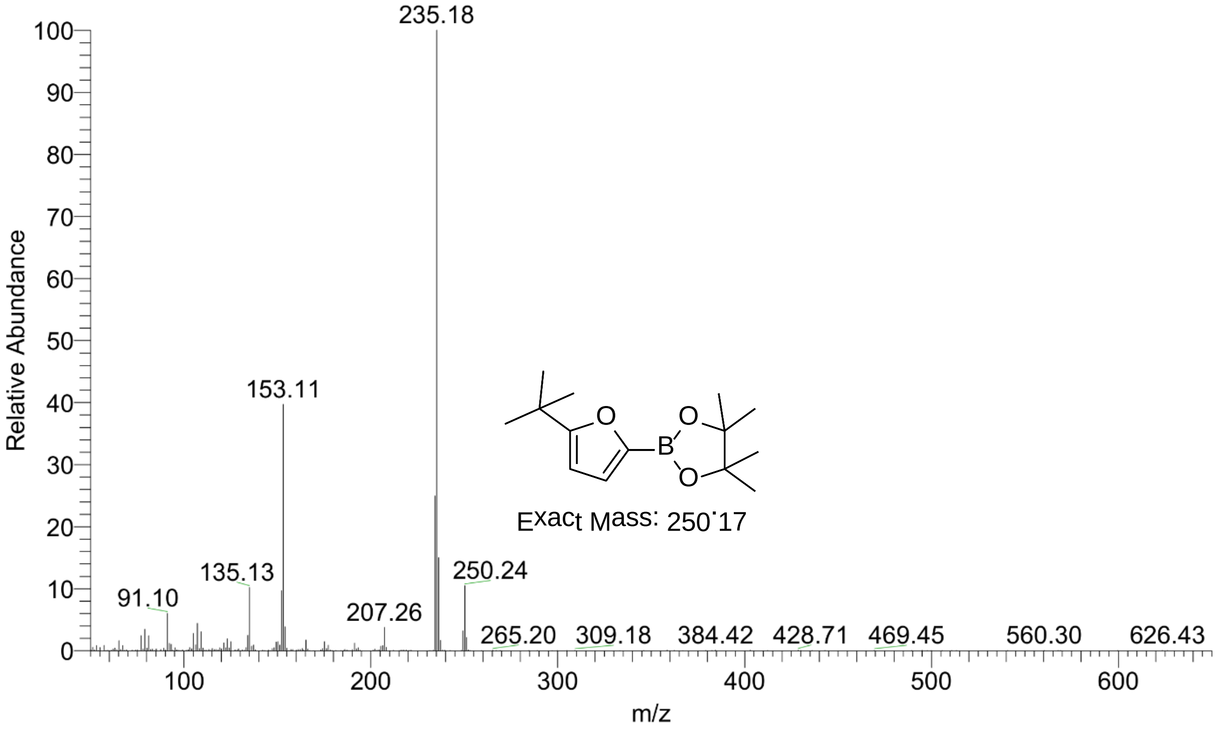
The conversion was determined using the *tert*-butyl signal that shifts from 1.17 in the starting material to 1.19 ppm in the product.

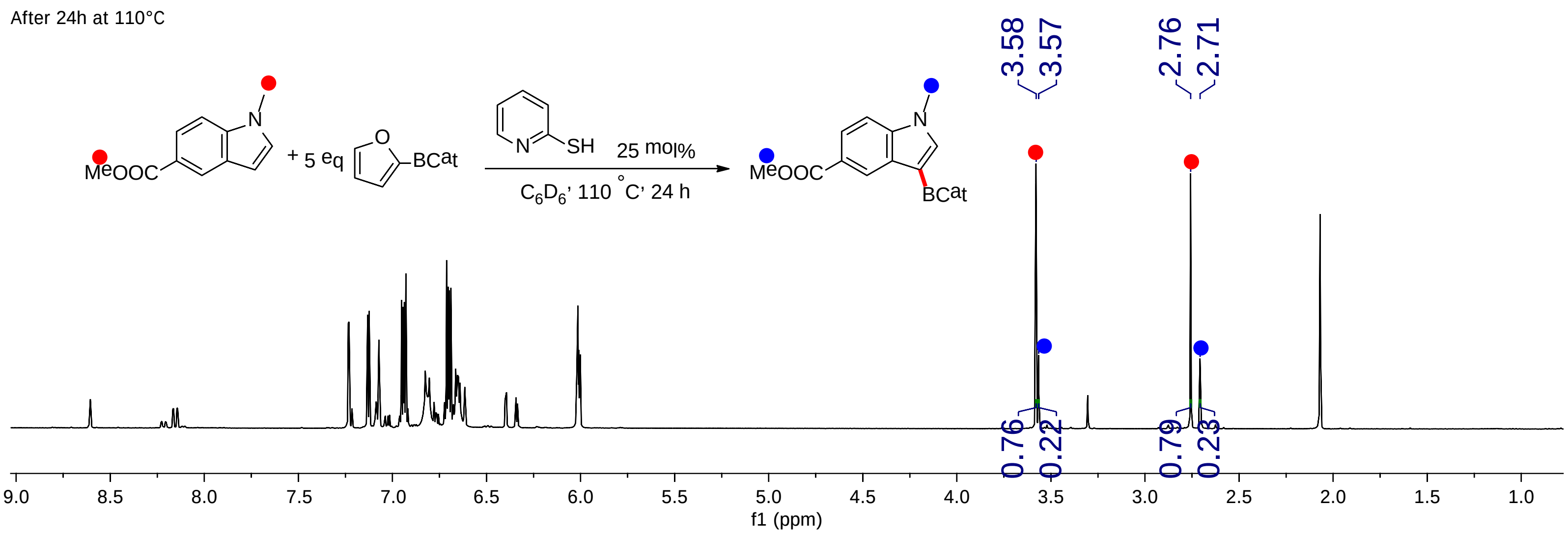
D:\GCMS Data\...\2tBuFuran_Mes_11024h 08/02/18 13:31:22 1

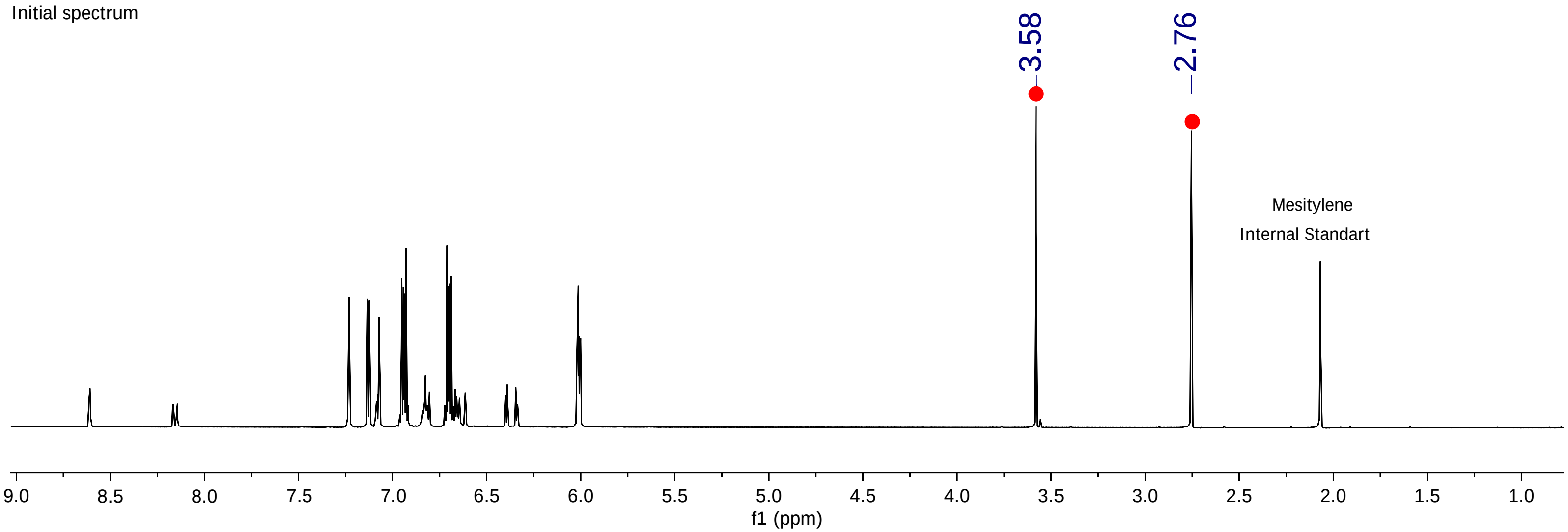
RT: 0.00 - 18.03



2tBuFuran_Mes_11024h #334 RT: 6.90 AV: 1 NL: 2.37E6
T: + c Full ms [50.00-650.00]

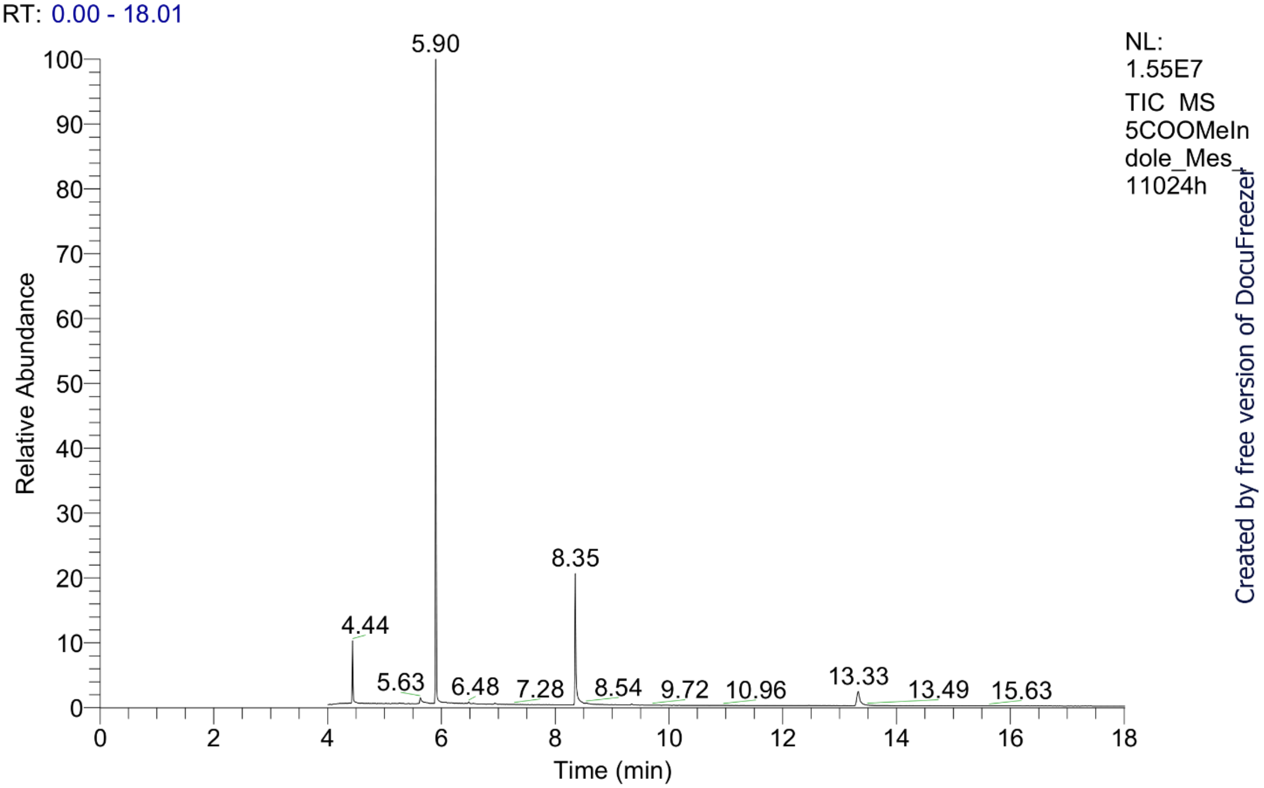


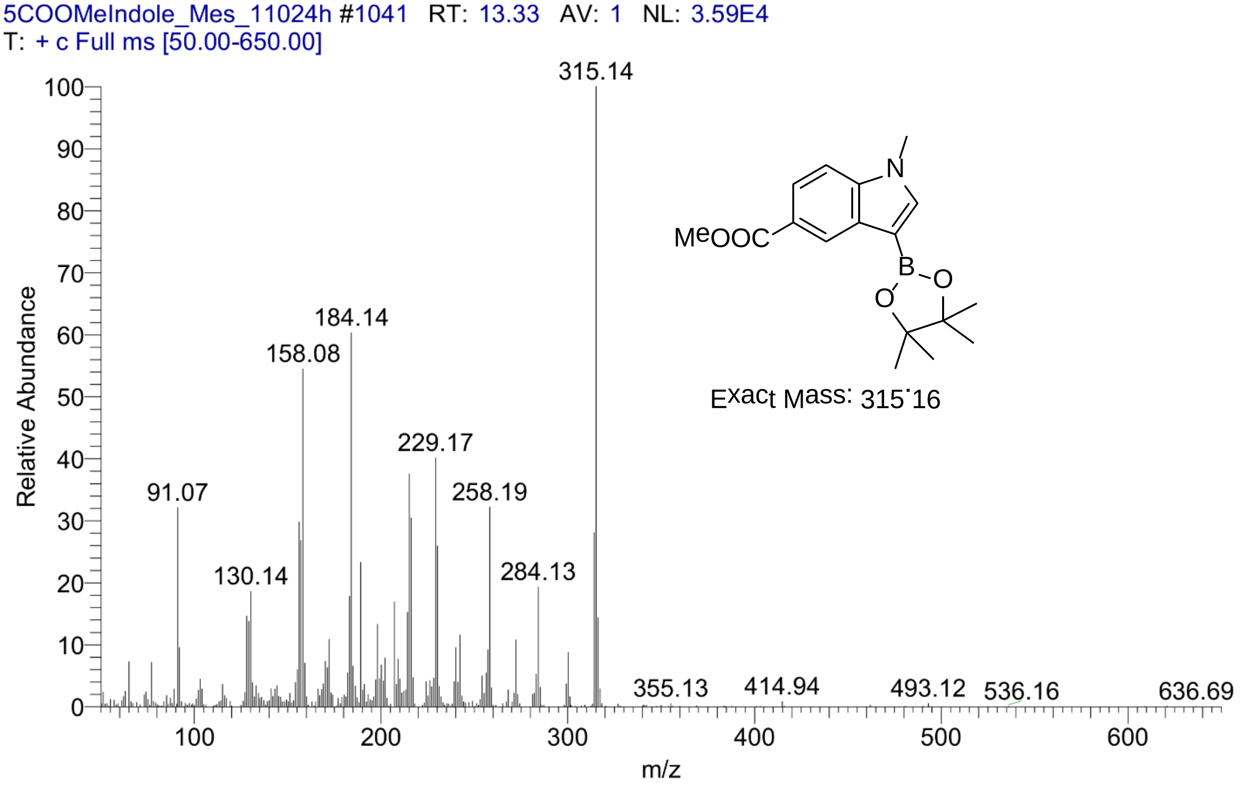

After 24h at 110°C

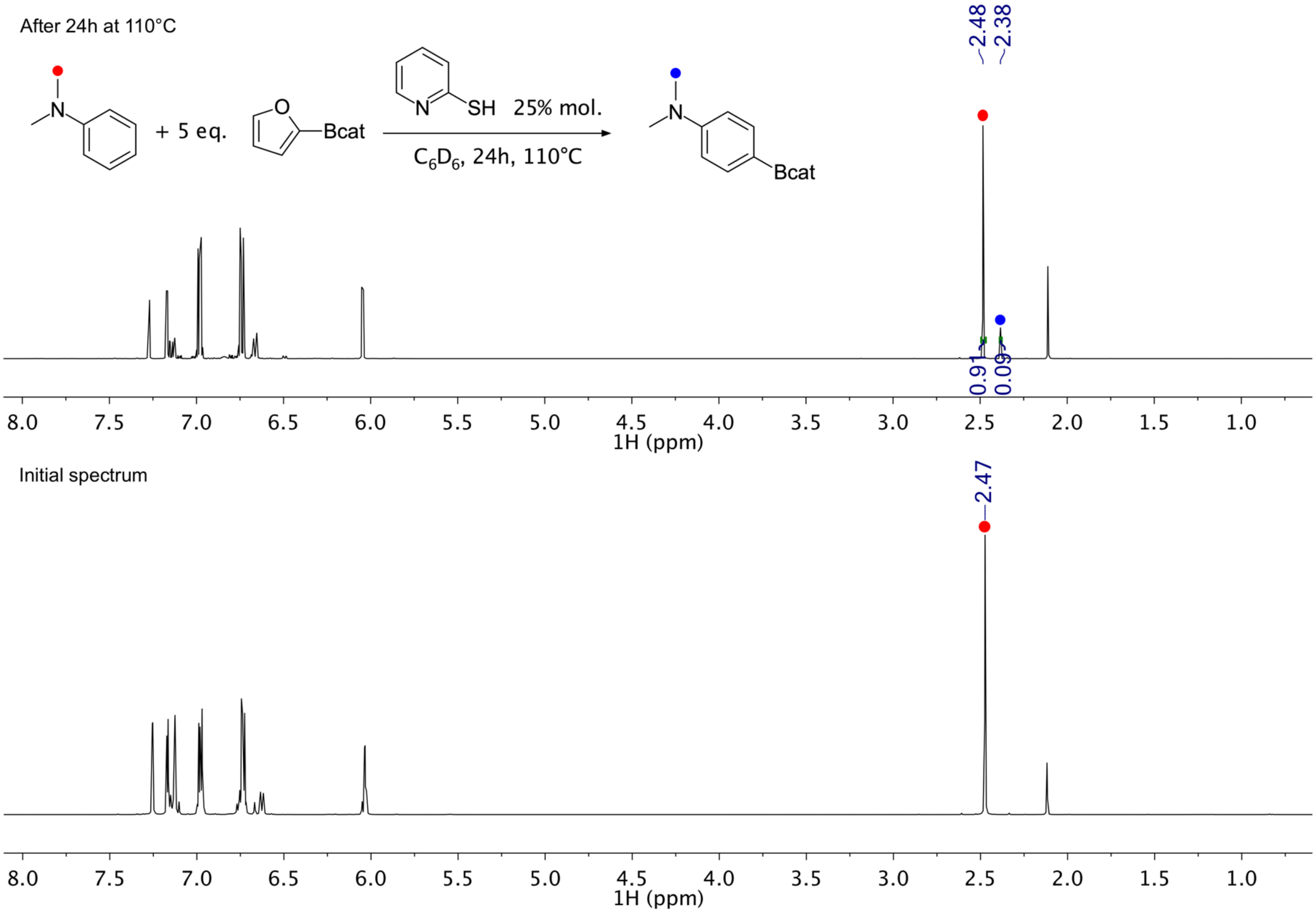

Initial spectrum

The conversion was determined using the N-Methyl and methyl ester signals that shift from 2.76 and 3.58 in the starting material to 2.71 and 3.57 ppm in the product.

D:\GCMS Data\...\5COOMeIndole_Mes_11024h 08/09/18 14:32:04



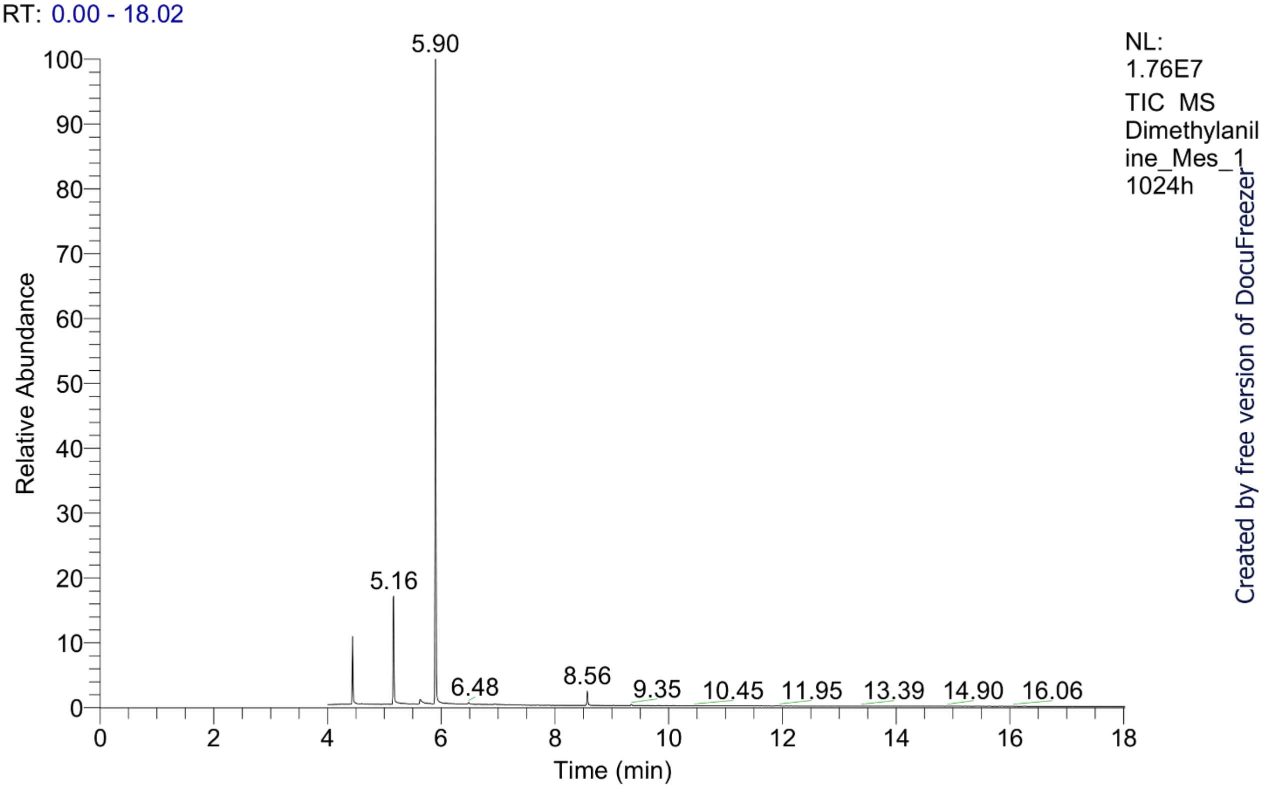


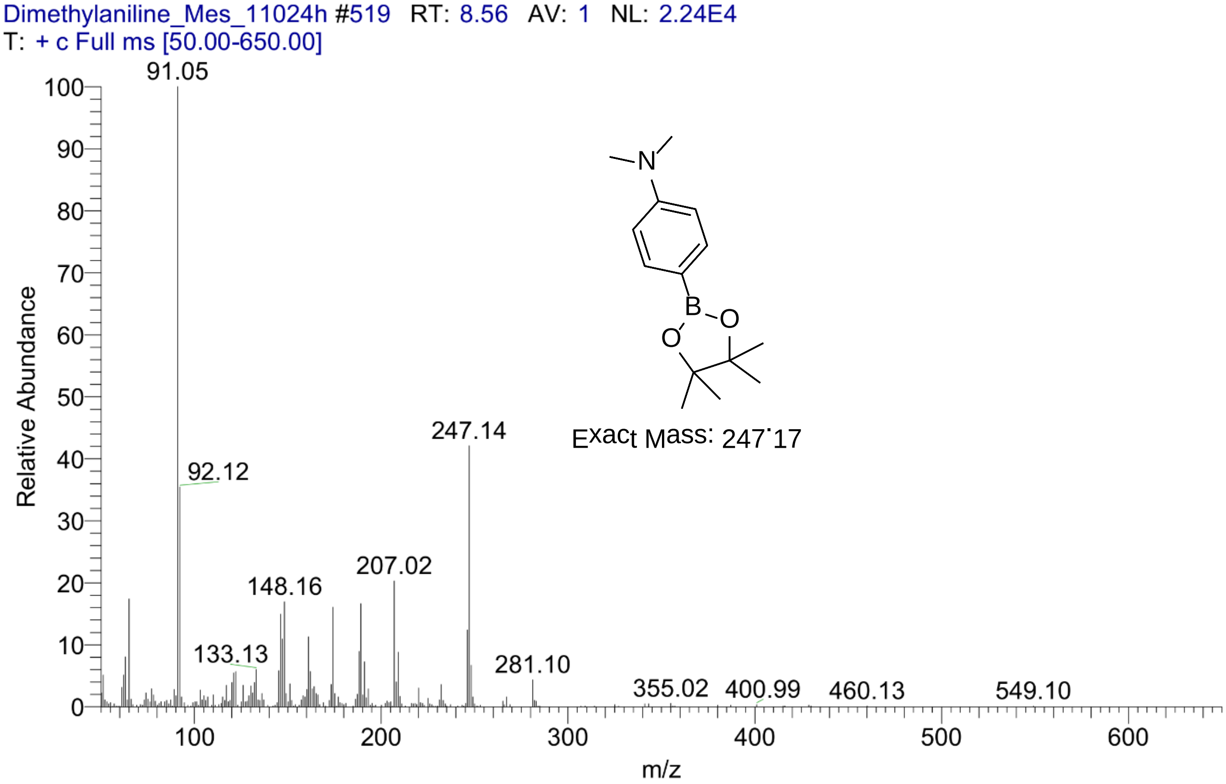

After 24h at 110°C

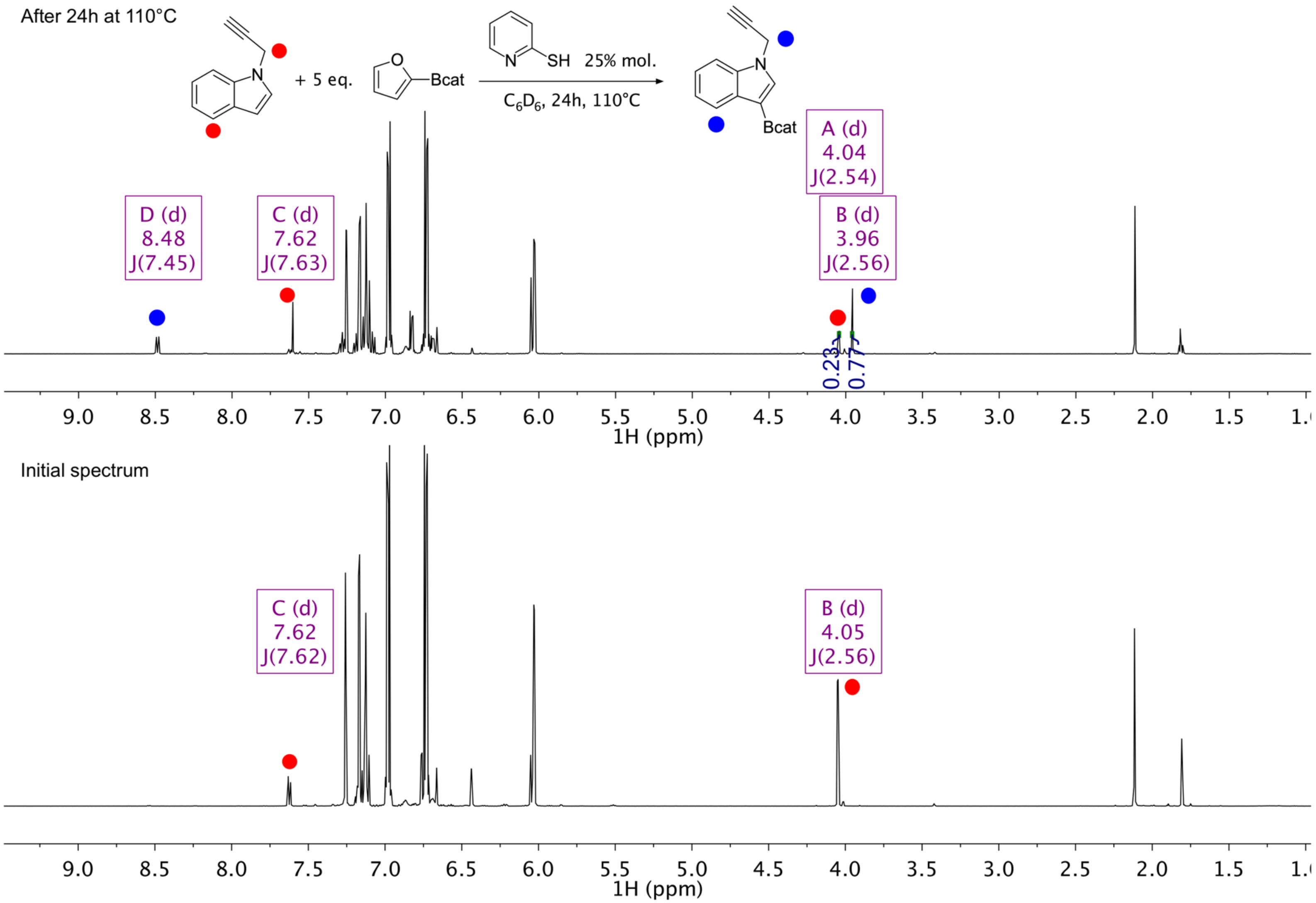
Initial spectrum

The conversion was determined using the N-Methyl signal that shifts from 2.47 in the starting material to 2.38 ppm in the product.

Dimethylaniline_Mes_11024h 08/09/18 15:27:39

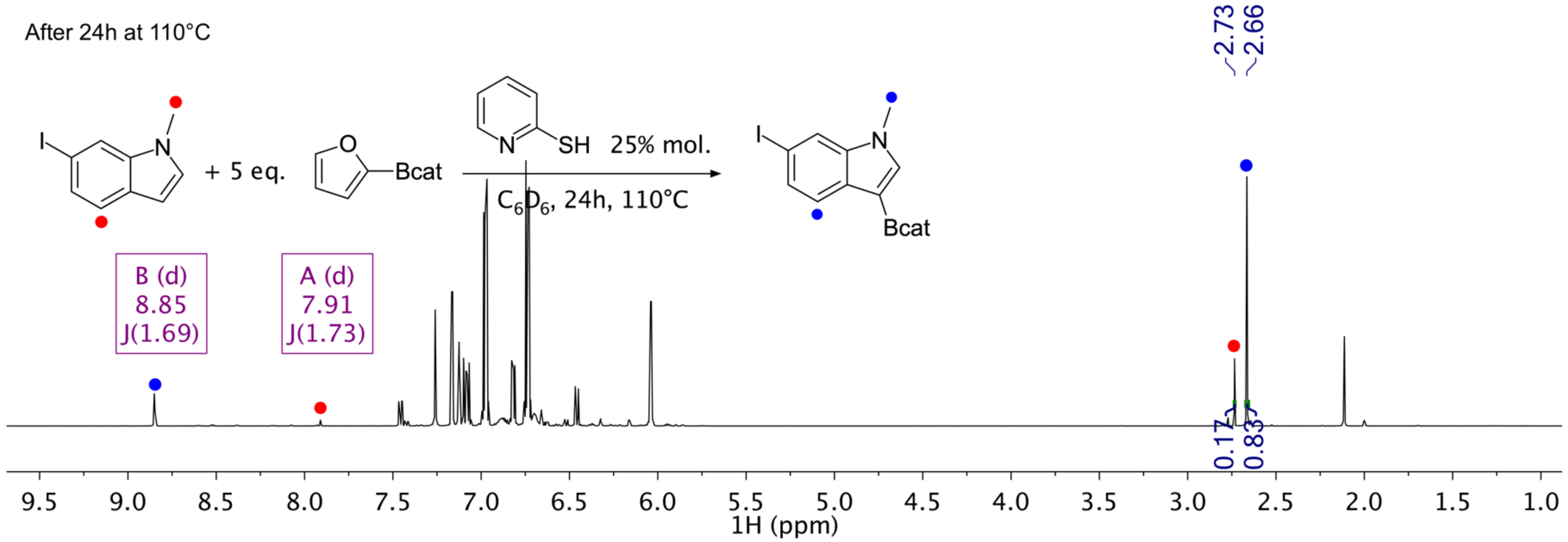




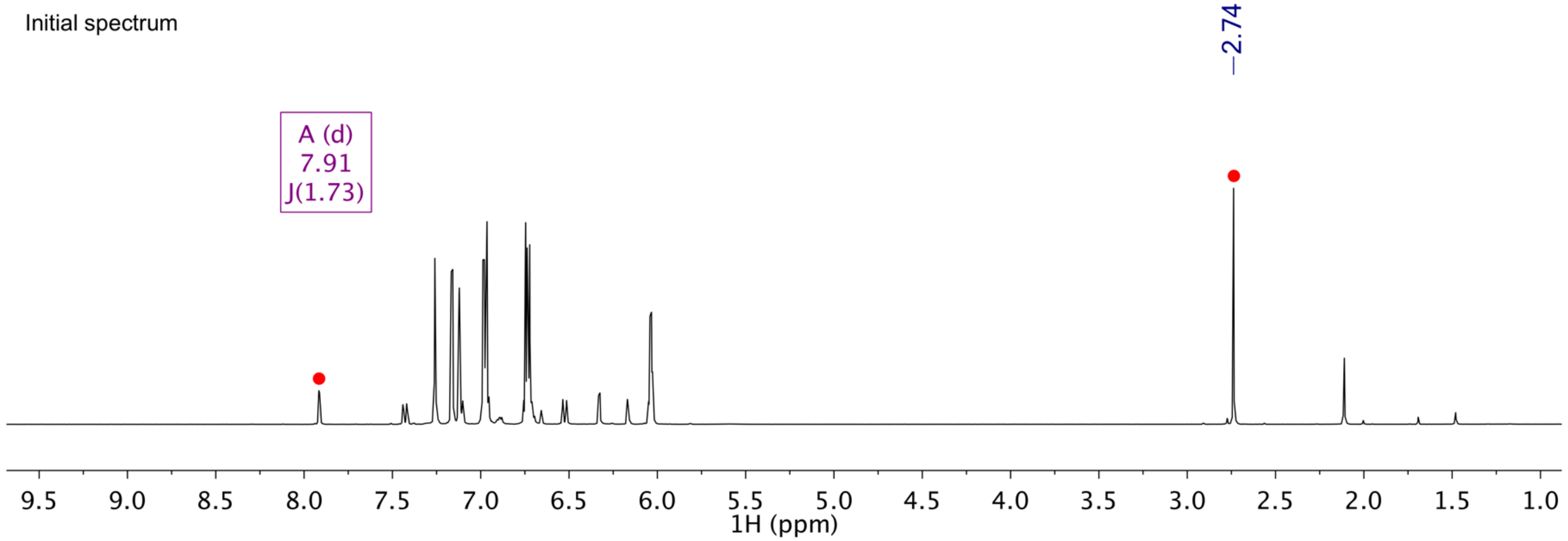


The conversion was determined using the signal of the methylene group adjacent to the nitrogen that shifts from 4.05 in the starting material to 3.96 ppm in the product. HRMS Spectrum was taken of the isolated product. Product crystallised.

After 24h at 110°C

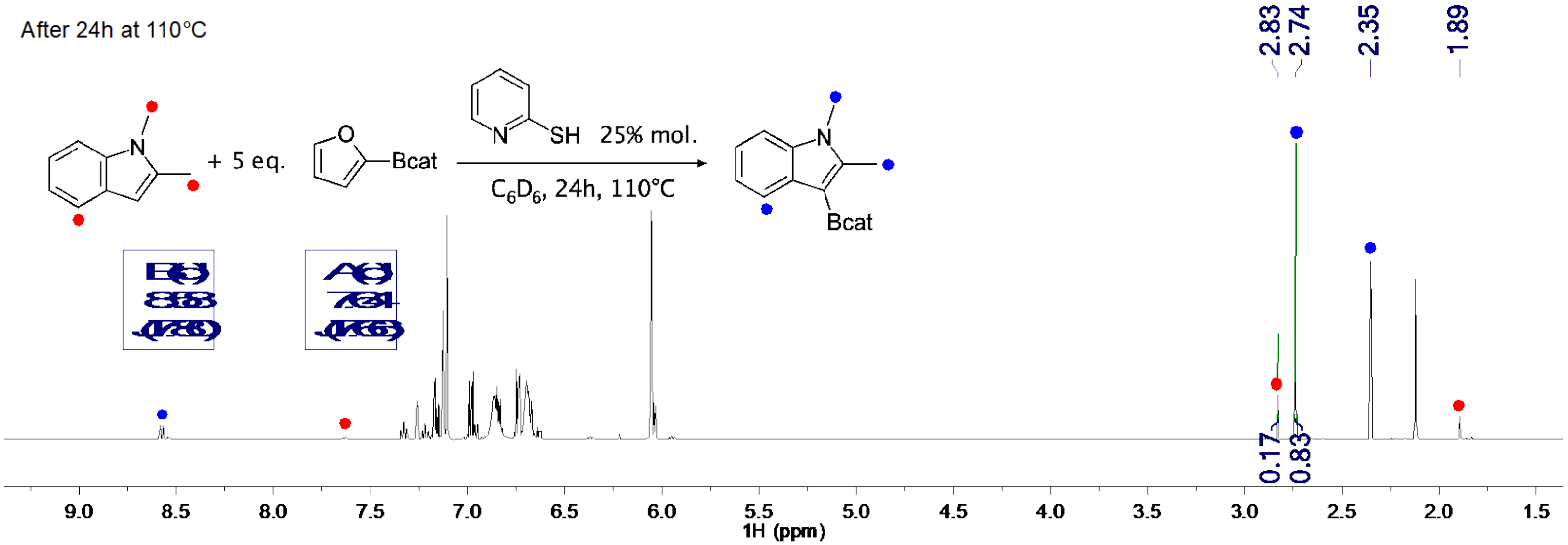


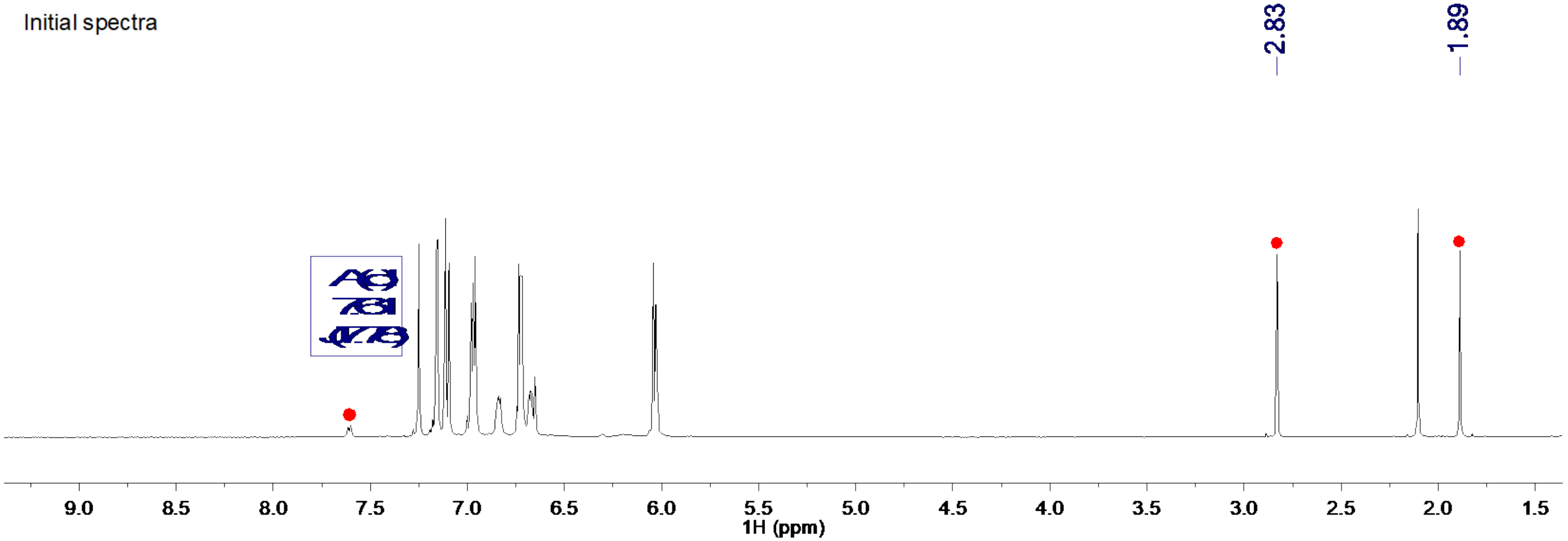
Initial spectrum



The conversion was determined using the N-Methyl signal that shifts from 2.74 in the starting material to 2.66 ppm in the product.

HRMS Spectrum was taken of the isolated product.





The conversion was determined using the N-Methyl signal that shifts from 2.83 in the starting material to 2.74 ppm in the product.

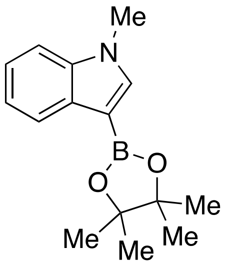
HRMS Spectrum was taken of the isolated product

Isolation of the borylated Products:

General procedure D:

In a microwave vial heterocyclic compound (1 equiv.) was mixed with 2-furyl-Bcat (5 equiv.) and Mercaptopyridine (25 mol%) in toluene (0.17 M). The vial was put in a microwave reactor and was heated to 180 °C for 2 hours. To the resulting mixture pinacol (10 equiv.) was added in a solution of triethylamine (3.33 equiv.) and toluene (1 M). The golden to brown solution was stirred for an hour at room temperature. Subsequently all volatiles were removed, and the resulting residue was purified *via* column chromatography (SiO_2).

1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8a)



8a

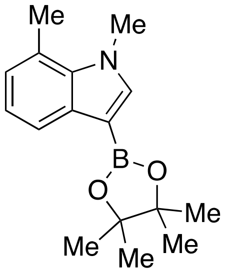
Chemical Formula: $C_{15}H_{20}BNO_2$

Molecular Weight: 257.14

Compound **8a** was synthesized according to general procedure C using 1-methyl-1*H*-indole (52.5 mg, 0.4 mmol). R_f-value: 0.23 (Pet. Ether: Et_2O 10:1). Yield: 70.6 mg, 0.274 mmol, 70%. The spectroscopic data agrees with literature established values.[14]

^{1}**H NMR** (500 MHz, Chloroform-*d*) δ 8.65 – 8.60 (m, 1H), 7.38 (s, 1H), 7.35 – 7.31 (m, 1H), 7.28 – 7.23 (m, 1H), 7.05 – 7.00 (m, 1H), 2.84 (s, 3H), 1.24 (s, 12H). ^{11}**B NMR** (160 MHz, Benzene-d_6) δ 30.72. ^{13}**C NMR** (126 MHz, Chloroform-*d*) δ 138.96, 138.41, 133.58, 123.52, 122.06, 120.71, 109.54, 82.73, 32.08, 25.15.

1,7-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8b)

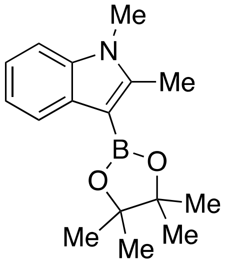


8b
Chemical Formula: $C_{16}H_{22}BNO_2$
Molecular Weight: 271.17

Compound **8b** was synthesized according to general procedure D using 1,7-dimethyl-1*H*-indole (58.1 mg, 0.4 mmol). R_f-value: 0.20 (Pet. Ether: Et_2O 10:1). Yield: 79.0 mg, 0.291 mmol, 72%

^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 8.55 – 8.49 (m, 1H), 7.31 (s, 1H), 7.25 – 7.20 (m, 1H), 6.94 – 6.90 (m, 1H), 3.09 (s, 3H), 2.42 – 2.25 (m, 3H), 1.23 (s, 12H). **^{11}B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.72. **^{13}C NMR** (126 MHz, Benzene-*d*$_6$) δ 140.60, 137.13, 134.76, 124.82, 121.83, 121.17, 121.03, 82.67, 36.21, 25.24, 19.59. **HRMS** (ES$^+$) m/z calculated for $[C_{16}H_{23}BNO_2]$: 272.1816, found: 272.1825

1,2-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8c)



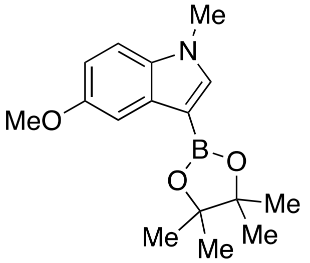
8c

Chemical Formula: $C_{16}H_{22}BNO_2$
Molecular Weight: 271.17

Compound **8c** was synthesized according to general procedure D using 1,2-dimethyl-1*H*-indole (58.1 mg, 0.4 mmol). R_f-value: 0.47 (Pet. Ether: Et_2O 10:1). Yield: 42.4 mg, 0.312 mmol, 39%. The spectroscopic data agrees with literature established values.[13]

^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 8.70 – 8.65 (m, 1H), 7.40 – 7.34 (m, 1H), 7.32 – 7.25 (m, 1H), 7.08 – 7.00 (m, 1H), 2.79 (s, 3H), 2.47 (s, 3H), 1.23 (s, 12H). **^{11}B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.69. **^{13}C NMR** (126 MHz, Benzene-*d*$_6$) δ 138.60, 133.65, 122.92, 121.27, 120.67, 108.84, 82.35, 30.24, 28.69, 25.16, 12.72. **HRMS** (ES$^+$) m/z calculated for $[C_{16}H_{23}BNO_2]$: 273.1851, found: 273.1843

<u>5-methoxy-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8d)</u>



8d

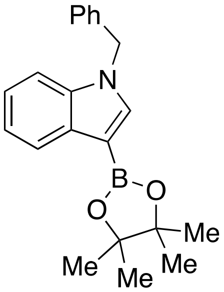
Chemical Formula: $C_{16}H_{22}BNO_3$

Molecular Weight: 287.17

Compound **8d** was synthesized according to general procedure D using 5-methoxy-1-methyl-1*H*-indole (64.5 mg, 0.4 mmol). R_f-value: 0.10 (Pet. Ether: Et_2O 10:1). Yield: 75.5 mg, 0.263 mmol, 67%. The spectroscopic data agrees with literature established values.[13]

^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 8.05 (d, *J* = 2.3 Hz, 1H), 7.39 (s, 1H), 7.12 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.89 (dd, *J* = 8.8, 0.6 Hz, 1H), 3.62 (s, 4H), 2.84 (s, 3H), 1.25 (s, 14H). **^{13}C NMR** (126 MHz, Benzene-*d*$_6$) δ 155.73, 139.50, 133.67, 128.60, 112.63, 110.27, 105.12, 82.71, 55.49, 32.30, 25.15. **^{11}B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.89.

1-benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8f)

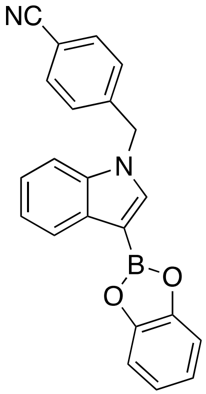


8f
Chemical Formula: $C_{21}H_{24}BNO_2$
Molecular Weight: 333.24

Compound **8f** was synthesized according to general procedure D using 1-benzyl-1*H*-indole (82.9 mg, 0.4 mmol). R_f-value: 0.33 (Pet. Ether: Et_2O 10:1). Yield: 91.6 mg, 0.275 mmol, 78%. The spectroscopic data agrees with literature established values.[14]

^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 8.68 – 8.63 (m, 1H), 7.58 (s, 1H), 7.39 – 7.26 (m, 1H), 7.17 – 7.16 (m, 2H), 7.08 (dt, *J* = 8.2, 1.0 Hz, 1H), 6.96 – 6.86 (m, 2H), 6.74 – 6.69 (m, 2H), 4.60 (s, 2H), 1.23 (s, 12H). **^{11}B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.53. **^{13}C NMR** (126 MHz, Benzene-*d*$_6$) δ 138.53, 137.53, 133.76, 128.82, 128.59, 127.58, 126.94, 123.65, 122.39, 120.96, 110.22, 82.82, 50.02, 25.14.

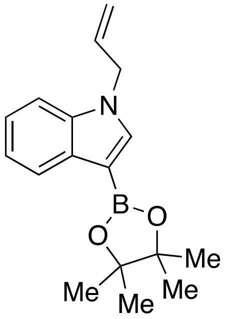
4-((3-(benzo[*d*][1,3,2]dioxaborol-2-yl)-1*H*-indol-1-yl)methyl)benzonitrile (8g)



8g
Chemical Formula: $C_{22}H_{15}BN_2O_2$
Molecular Weight: 350.18

Compound **8g** was synthesized according to general procedure D using 4-((1*H*-indol-1-yl)methyl)benzonitrile (92.9 mg, 0.4 mmol). Conversion was determined before the pinacolation. Yield: 87% (determined via ^{1}H NMR spectroscopy)

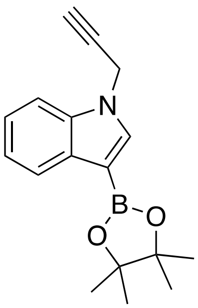
1-allyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8h)



8h
Chemical Formula: $C_{17}H_{22}BNO_2$
Molecular Weight: 283.18

Compound **8h** was synthesized according to general procedure D using 1-allyl-1*H*-indole (62.9 mg, 0.4 mmol). R_f-value: 0.3 (Pet. Ether: Et_2O 10:1). Yield: 91.4 mg, 0.323 mmol, 81%.
^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 8.66 – 8.62 (m, 1H), 7.54 (s, 1H), 7.35 – 7.29 (m, 1H), 7.26 – 7.22 (m, 1H), 7.13 – 7.10 (m, 1H), 5.42 (ddt, *J* = 17.1, 10.3, 5.4 Hz, 1H), 4.81 – 4.56 (m, 2H), 3.96 (dt, *J* = 5.3, 1.7 Hz, 2H), 1.23 (s, 12H). **^{13}C NMR** (126 MHz, Benzene-*d*$_6$) δ 147.15, 137.71, 132.90, 128.21, 123.25, 121.79, 120.47, 116.59, 109.66, 82.40, 48.22, 24.76. **^{11}B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.70. **HRMS** (ES$^+$) m/z calculated for [$C_{15}H_{20}BFNO_2$]: 284.1820, found: 284.1806

1-(prop-2-yn-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8i)



4i

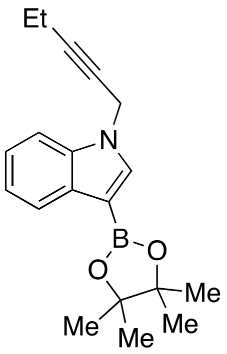
Chemical Formula: $C_{17}H_{20}BNO_2$

Molecular Weight: 281.16

Compound **8i** was synthesized according to general procedure D using 1-(prop-2-yn-1-yl)-1*H*-indole (62.1 mg, 0.4 mmol). R_f-value: 0.37 (Pet. Ether: Et_2O 10:1). Yield: 60.8 mg, 0.216 mmol, 54%

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.07 – 8.04 (m, 1H), 7.69 (s, 1H), 7.40 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.21 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 4.88 (d, *J* = 2.6 Hz, 2H), 2.41 (t, *J* = 2.6 Hz, 1H), 1.37 (s, 12H). **^{11}B NMR** (160 MHz, Chloroform-*d*) δ 30.18. **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 136.90, 136.89, 132.86, 123.03, 122.23, 120.83, 109.42, 82.98, 77.33, 74.13, 36.13, 25.06. **HRMS** (ES^+) m/z calculated for [$C_{17}H_{20}BNO_2$]: 282.1660, found: 282.1663

<u>1-(pent-2-yn-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8j)</u>



8j

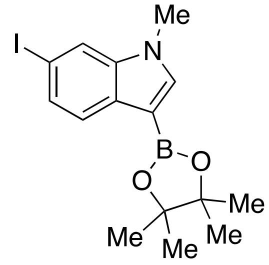
Chemical Formula: $C_{19}H_{24}BNO_2$

Molecular Weight: 309.22

Compound **8j** was synthesized according to general procedure D using 1-(pent-2-yn-1-yl)-1*H*-indole (73.3 mg, 0.4 mmol). R_f-value: 0.21 (Pet. Ether: Et_2O 10:1). Yield: 79.3 mg, 0.312 mmol, 64%

^{1}H NMR (500 MHz, Benzene-d_6) δ 8.62 – 8.59 (m, 1H), 7.80 (s, 1H), 7.31 (ddd, *J* = 8.0, 6.8, 1.3 Hz, 1H), 7.27 – 7.19 (m, 2H), 4.19 (t, *J* = 2.3 Hz, 2H), 1.75 (qt, *J* = 7.5, 2.3 Hz, 2H), 1.21 (s, 12H), 0.78 (t, *J* = 7.5 Hz, 3H). **^{11}B NMR** (160 MHz, Benzene-d_6) δ 30.68. **^{13}C NMR** (126 MHz, Benzene-d_6) δ 137.12, 137.02, 133.47, 123.27, 121.86, 120.64, 109.51, 87.15, 82.40, 73.14, 35.80, 24.73, 13.27, 12.03. **HRMS** (ES^+) m/z calculated for $[C_{19}H_{24}BNO_2]$: 310.1976, found: 310.1993

6-iodo-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8k)



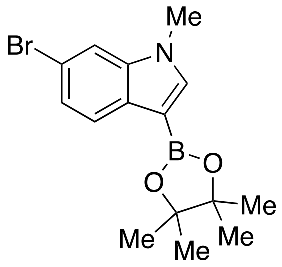
8k

Chemical Formula: $C_{15}H_{19}BINO_2$
Molecular Weight: 383.04

Compound **8k** was synthesized according to general procedure D using 6-iodo-1-methyl-1*H*-indole (102.83 mg, 0.4 mmol). R_f-value: 0.09 (Pet. Ether: Et_2O 10:1). Yield: 121.6 mg, 0.317 mmol, 79%

^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 9.03 – 8.99 (m, 1H), 7.56 – 7.52 (m, 1H), 7.18 (s, 1H), 6.54 – 6.50 (m, 1H), 2.65 (s, 3H), 1.17 (s, 12H). **^{11}B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.36. ^{13}C NMR (126 MHz, Benzene-*d*$_6$) δ 139.44, 137.36, 135.96, 132.14, 130.45, 111.64, 84.96, 82.95, 32.02, 25.00. **HRMS** (ES$^+$) m/z calculated for [$C_{14}{}^{13}C_1H_{20}BINO_2$]: 385.0661, found: 385.0679.

5-bromo-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8l)



8l

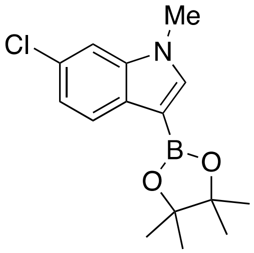
Chemical Formula: $C_{15}H_{19}BBrNO_2$

Molecular Weight: 336.04

Compound **8l** was synthesized according to general procedure D using 5-bromo-1-methyl-1*H*-indole (84.0 mg, 0.4 mmol). R_f-value: 0.09 (Pet. Ether: Et_2O 10:1). Yield: 89.2 mg, 0.266 mmol, 66%

^{1}H NMR (500 MHz, Benzene-d_6) δ 8.85 – 8.80 (m, 1H), 7.44 – 7.34 (m, 1H), 7.23 (s, 1H), 6.63 – 6.58 (m, 1H), 2.66 (d, *J* = 1.2 Hz, 3H), 1.18 (s, 12H). **^{11}B NMR** (160 MHz, Benzene-d_6) δ 30.35. **^{13}C NMR** (126 MHz, Benzene-d_6) δ 139.78, 136.92, 128.59, 125.87, 124.93, 114.57, 111.10, 82.95, 32.09, 25.01. **HRMS** (ES^+) m/z calculated for [$C_{15}H_{20}BBrNO_2$]: 336.0765, found: 336.0753

6-chloro-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8m)

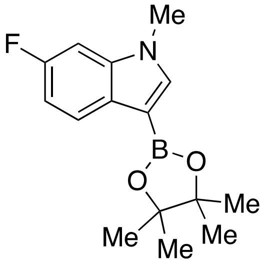


4m
Chemical Formula: $C_{15}H_{19}BClNO_2$
Molecular Weight: 291.58

Compound **8m** was synthesized according to general procedure D using 6-chloro-1-methyl-1*H*-indole (66.3 mg, 0.4 mmol). R_f-value: 0.18 (Pet. Ether: Et_2O 10:1). Yield: 112.6 mg, 0.386 mmol, 97%. The spectroscopic data agrees with literature established values.[13]

^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 8.36 – 8.32 (m, 1H), 7.29 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.15 – 7.12 (m, 1H), 7.06 – 7.03 (m, 1H), 2.59 (s, 3H), 1.17 (s, 12H). **^{11}B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.71. **^{13}C NMR** (126 MHz, Benzene-*d*$_6$) δ 139.61, 138.74, 131.91, 128.16, 124.30, 121.26, 109.95, 82.90, 32.00, 25.09. **HRMS** (ES$^+$) m/z calculated for [$C_{15}H_{20}BClNO_2$]: 292.1270, found: 292.1273

6-fluoro-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (8n)



8n

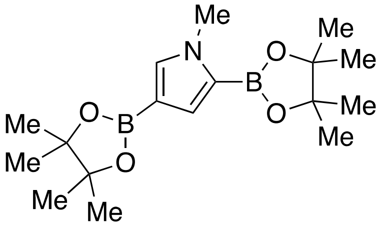
Chemical Formula: $C_{15}H_{19}BFNO_2$

Molecular Weight: 275.13

Compound **8n** was synthesized according to general procedure D using 6-fluoro-1-methyl-1*H*-indole (59.7 mg, 0.4 mmol). R_f-value: 0.15 (Pet. Ether: Et_2O 10:1). Yield: 85.3 mg, 0.312 mmol, 78%. The spectroscopic data agrees with literature established values.[13]

^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 8.39 (dd, *J* = 8.6, 5.5 Hz, 1H), 7.28 (s, 1H), 7.07 (ddd, *J* = 9.7, 8.6, 2.3 Hz, 1H), 6.72 (ddd, *J* = 9.7, 2.4, 0.5 Hz, 1H), 2.65 (s, 3H), 1.21 (s, 12H). **^{11}B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.59. ^{19}F NMR (470 MHz, Benzene-*d*$_6$) δ -120.98 (m). **^{13}C NMR** (126 MHz, Benzene-*d*$_6$) δ 160.14 (d, *J* = 236.9 Hz), 139.00 (d, *J* = 3.2 Hz), 129.36, 127.97, 127.59, 123.84 (d, *J* = 9.9 Hz), 108.72 (d, *J* = 23.9 Hz), 95.81 (d, *J* = 25.9 Hz), 82.47, 31.66, 24.72. **HRMS** (ES$^+$) m/z calculated for [$C_{15}H_{20}BFNO_2$]: 276.1568 , found: 276.1570

1-methyl-2,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole (8o)

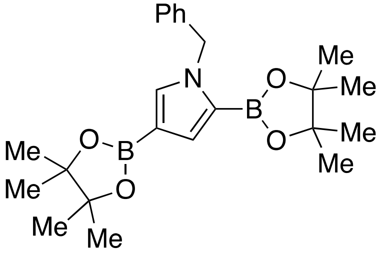


8o
Chemical Formula: $C_{17}H_{29}B_2NO_4$
Molecular Weight: 333.04

Compound **8o** was synthesized according to general procedure D using 1-methyl-1*H*-pyrrole (32.5 mg, 0.4 mmol). R_f-value: 0.17 (Pet. Ether: Et_2O 10:1). Yield: 29.4 mg, 0.140 mmol, 35%. The spectroscopic data agrees with literature established values.[13]

^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.91 (d, *J* = 1.6 Hz, 1H), 7.26 (d, *J* = 1.5 Hz, 1H), 3.44 (s, 3H), 1.16 (s, 12H), 1.06 (s, 12H). **^{11}B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.33, 28.77. **HRMS** (ES$^+$) m/z calculated for [$C_{17}H_{29}B_2NO_4$]: 334.2361, found: 334.2370

1-benzyl-2,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole (8p)

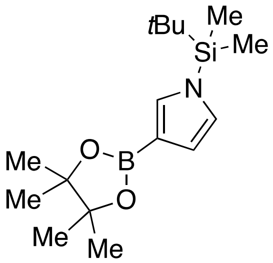


8p
Chemical Formula: $C_{23}H_{33}B_2NO_4$
Molecular Weight: 409.14

Compound **8p** was synthesized according to general procedure D using 1-benzyl-1*H*-pyrrole (62.9 mg, 0.4 mmol). R_f-value: 0.17 (Pet. Ether: Et_2O 10:1). Yield: 30.1 mg, 0.073 mmol, 18%. The spectroscopic data agrees with literature established values. [14]

^{1}H NMR (500 MHz, Benzene-*d*$_6$) δ 7.93 (d, *J* = 1.5 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 1H), 7.01 – 6.89 (m, 5H), 5.13 (s, 2H), 1.11 (s, 12H), 0.94 (s, 12H). **^{11}B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.10, 28.94. **^{13}C NMR** (126 MHz, Benzene-*d*$_6$) δ 139.93, 136.58, 130.88, 128.55, 127.18, 127.13, 83.06, 82.76, 52.90, 25.08, 24.66. **HRMS** (ES$^+$) m/z calculated for [$C_{23}H_{34}B_2NO_4$]: 410.2668 , found: 410.2646

1-(*tert*-butyldimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole (8q)

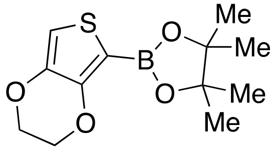


8q
Chemical Formula: $C_{16}H_{30}BNO_2Si$
Molecular Weight: 307.32

Compound **8q** was synthesized according to general procedure D using 1-(*tert*-butyldimethylsilyl)-1*H*-pyrrole (72.5 mg, 0.4 mmol). R_f-value: 0.47 (Pet. Ether: Et_2O 10:1). Yield: 75.6 mg, 0.246 mmol, 62%

^{1}H NMR (400 MHz, Benzene-*d*$_6$) δ 7.54 – 7.51 (m, 1H), 7.11 – 7.07 (m, 1H), 6.76 – 6.63 (m, 1H), 1.20 (s, 12H), 0.68 (s, 9H), 0.05 (s, 6H). **^{11}B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.94. ^{13}C NMR (101 MHz, Benzene-*d*$_6$) δ 134.26, 124.93, 117.11, 82.75, 25.85, 25.15, 18.10, -5.69. ^{29}Si NMR (99 MHz, Benzene-*d*$_6$) δ -110.83. **HRMS** (ES$^+$) m/z calculated for [$C_{16}H_{31}BNO_2Si$]: 308.2215 , found: 308.2203

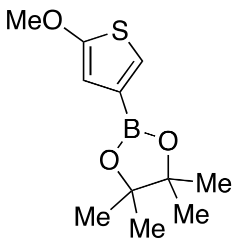
2-(2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8s)



8s
Chemical Formula: $C_{12}H_{17}BO_4S$
Molecular Weight: 268.13

Compound **8s** was synthesized according to general procedure D using 2,3-dihydrothieno[3,4-*b*][1,4]dioxine (56.9 mg, 0.4 mmol). R_f-value: 0.30 (Pet. Ether: Et_2O 2:1). Yield: 48.2 mg, 0.185 mmol, 46%. The spectroscopic data agrees with literature established values.[14]
^{1}H NMR (500 MHz, Benzene-d_6) δ 6.68 – 6.66 (m, 1H), 3.45 – 3.42 (m, 2H), 3.34 – 3.31 (m, 2H), 1.08 (s, 12H). **^{13}C NMR** (126 MHz, Benzene-d_6) δ 150.2, 144.3, 108.4, 83.2, 66.3, 65.5, 23.9 **HRMS** (ES$^+$) m/z calculated for [$C_{12}H_{18}BO_4S$]: 269.1016, found: 269.1017

2-(5-methoxythiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8t)



8t

Chemical Formula: $C_{11}H_{17}BO_3S$

Molecular Weight: 240.12

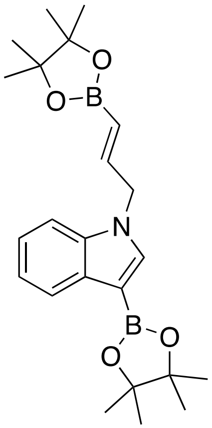
Compound **8t** was synthesized according to general procedure D using 2-methoxythiophene (59.7 mg, 0.4 mmol). R_f-value: 0.39 (Pet. Ether: Et_2O 10:1). Yield: 7.3 mg, 0.030 mmol, 8%. The spectroscopic data agrees with literature established values.[13]

^{1}H NMR (500 MHz, Benzene-d_6) δ 7.38 (d, J = 5.7 Hz, 1H), 6.25 (d, J = 5.7 Hz, 1H), 3.45 (s, 2H), 1.12 (s, 12H). **^{11}B NMR** (160 MHz, Benzene-d_6) δ 29.24. **^{13}C NMR** (126 MHz, Benzene-d_6) δ 131.28, 127.97, 110.93, 82.71, 60.95, 24.61. **HRMS** (ES$^+$) m/z calculated for $[C_{11}H_{18}BO_3S]$: 241.1066, found: 241.1065

Hydroboration of 8i

Compound **8i** (60.8 mg, 2.2 mmol, 1 equiv.), Cp_2ZrHCl (5.6 mg, 0.22 mmol, 10 mol%) and HBpin (33.2 mg, 2.3 mmol, 1.2 equiv.) were dissolved in dry DCM (0.5 ml) and the reaction mixture was stirred under a N_2 atmosphere for 24 h. The resulting yellow solution was filtered through a silica plug and all volatiles were removed to give a mixture of products. Yield 40.8 mg, 50 %

(*E*)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)-1*H*-indole (9a)



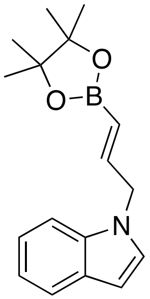
9a

Chemical Formula: $C_{23}H_{33}B_2NO_4$

Molecular Weight: 409.14

Yield (calculated by ^{1}**H NMR**): 29.8 mg, 0.8 mmol, 36 %. ^{1}**H NMR** (500 MHz, Benzene-d_6) δ 8.60 – 8.58 (m, 1H), 7.48 (s, 1H), 7.30 – 7.23 (m, 1H), 7.07 – 7.03 (m, 1H), 6.66 (dt, *J* = 17.9, 4.8 Hz, 1H), 5.46 (dt, *J* = 17.9, 1.8 Hz, 1H), 4.05 (dd, *J* = 4.8, 1.9 Hz, 2H), 1.22 (s, 12H), 0.99 (s, 12H). ^{11}**B NMR** (160 MHz, Benzene-d_6) δ 30.26. **HRMS** (ES$^+$) m/z calculated for [$C_{23}H_{34}B_2NO_4$]: 412.2733, found 412.2734

(*E*)-1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)-1*H*-indole (9b)



9b

Chemical Formula: $C_{17}H_{22}BNO_2$

Molecular Weight: 283.18

Yield (calculated by ^{1}**H NMR**): 11.0 mg, 0.3 mmol, 14 %.

^{1}**H NMR** (500 MHz, Benzene-*d*$_6$) δ 8.58 – 8.54 (m, 1H), 7.68 – 7.64 (m, 1H), 7.44 (s, 1H), 7.27 – 7.20 (m, 1H), 7.04 – 6.99 (m, 1H), 6.69 (dt, *J* = 17.9, 4.8 Hz, 1H), 5.45 (dt, *J* = 17.9, 1.9 Hz, 1H), 4.08 (dd, *J* = 4.8, 1.9 Hz, 2H), 0.96 (s, 12H). ^{11}**B NMR** (160 MHz, Benzene-*d*$_6$) δ 30.26. **HRMS** (ES$^+$) m/z calculated for [$C_{17}H_{23}BNO_2$]: 284.1820, found 284.1806

Computational details

All the calculations were performed on the full structures of the reported compounds. Calculations were performed with the GAUSSIAN 16 suite of programs.[8] The ωB97XD functional[9] was qualified as promising by Grimme[10] and was used to accurately describe the mechanism of FLP mediated hydrogenation of alkynes[11] and was thus used in combination with the Def2TZVP basis set for all atoms[12] The transition states were located and confirmed by frequency calculations (single imaginary frequency). The stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency). All geometry optimizations were carried out without any symmetry constraints. The Cartesian coordinates of all structures are fully detailed in the .xyz file provided as supplementary materials.

Kinetics:

General procedure:

2-FurylBCat (5 equiv., 93.0 mg, 0.5 mmol), 2-mercaptopyridine (25 mol%, 2.78 mg, 0.025 mmol), mesitylene (ca. 0.33 equiv.) and the corresponding heterocycle (1 equiv., 0.1 mmol) were mixed in C_6D_6, transferred into a J Young NMR tube and heated to 110 ˚C. After 30 min the reaction was allowed to cool down to room temperature for approximately 3-5 mins and a ^{1}H NMR spectrum was taken to determine the ratio of products in the reaction mixture. The sample was then heated to 110 ˚C again for an additional 30 mins and again the reaction mixture was monitored *via* ^{1}H NMR spectroscopy. This process was then repeated by 60 min intervals for an additional 7 hours. The measured ratios were plotted against time to give the reaction diagram.

Kinetic of N-methylindole:

Using N-methylindole (13.1 mg, 0.1 mmol) the reaction was monitored over time. The conversion was monitored by comparing the methyl signal of the starting material and of the product. (see P16 ESI)

Kinetic of N-Methylpyrrole:

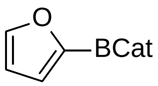
Using N-methylpyrrole (8.1 mg, 0.1 mmol) the reaction was monitored over time. The conversion was monitored by the methyl signal of the starting material and the products. (see P38 ESI)

Kinetic Simulation:

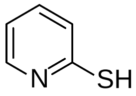
Kinetics simulations were performed using the free simulation software ReactLab Kinsim (http://jplusconsulting.com/products/reactlab-kinsim/). The equilibrium constants for the reaction steps were calculated using equation 1 with the energy values determined *via* DFT calculations (see Scheme 2, Paper). For the activation of 2-furylBCat the transition state energy in Figure 8 (see Paper) was used:

$$K = \frac{k_B}{hT} \cdot e^{-\frac{\Delta G}{RT}} \qquad (1)$$

Table K1: Determining the equilibrium constants for the borylation reactions for T=110 ˚C



A



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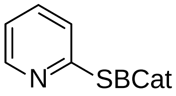

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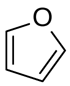

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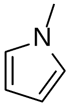

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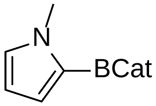

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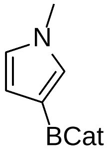

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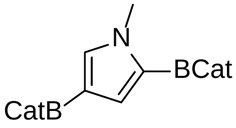
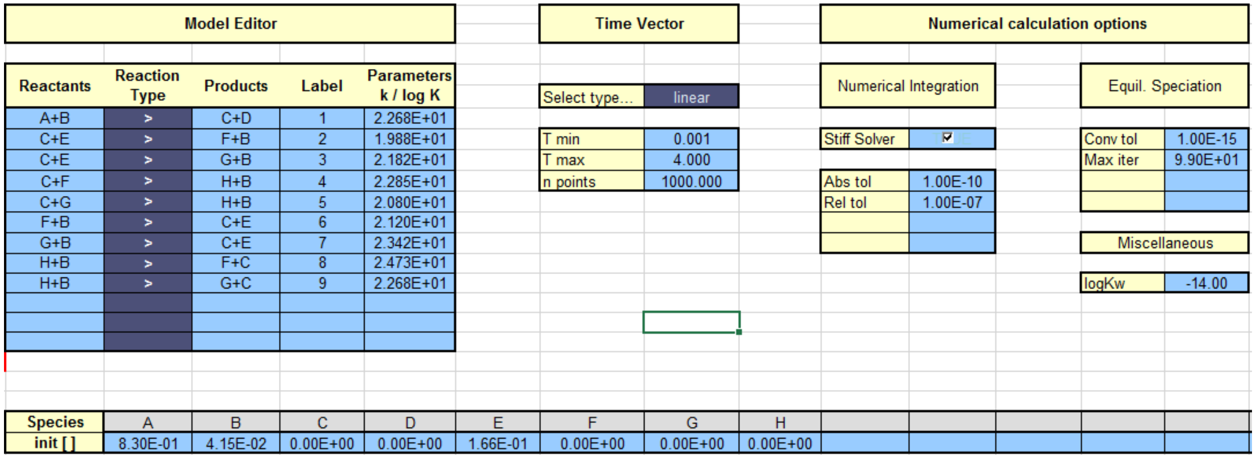


H

(No.) Reaction	ΔG [kcal/mol]	K	$\log_{10}$(K)
(1) A+B->C+D	26.2	$4.78 \cdot 10^{22}$	22.68
(2) C+E->F+B	21.3	$7.67 \cdot 10^{19}$	19.88
(3) C+E->G+B	24.7	$6.67 \cdot 10^{21}$	21.82
(4) C+F->H+B	26.5	$7.09 \cdot 10^{22}$	22.85

(5) C+G->H+B	22.9	$6.27 \cdot 10^{20}$	20.80
(6) F+B->C+E	23.6	$1.57 \cdot 10^{21}$	21.20
(7) G+B->C+E	27.5	$2.63 \cdot 10^{23}$	23.42
(8) H+B->F+C	29.8	$5.40 \cdot 10^{24}$	24.73
(9) H+B->G+C	26.2	$4.78 \cdot 10^{22}$	22.68



Model Editor

Reactants	Reaction Type	Products	Label	Parameters k / log K
A+B	>	C+D	1	2.268E+01
C+E	>	F+B	2	1.988E+01
C+E	>	G+B	3	2.182E+01
C+F	>	H+B	4	2.285E+01
C+G	>	H+B	5	2.080E+01
F+B	>	C+E	6	2.120E+01
G+B	>	C+E	7	2.342E+01
H+B	>	F+C	8	2.473E+01
H+B	>	G+C	9	2.268E+01

Time Vector

Select type...	linear
T min	0.001
T max	4.000
n points	1000.000

Numerical calculation options

Numerical Integration

Stiff Solver	☑
Abs tol	1.00E-10
Rel tol	1.00E-07

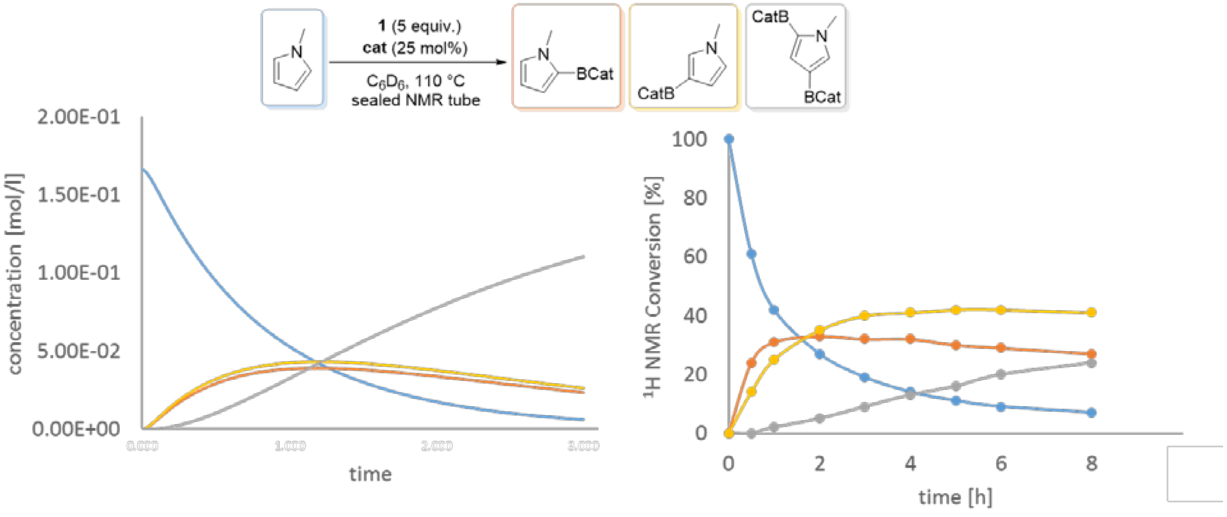
Equil. Speciation

Conv tol	1.00E-15
Max iter	9.90E+01

Miscellaneous

logKw	-14.00

Species	A	B	C	D	E	F	G	H
init [ ]	8.30E-01	4.15E-02	0.00E+00	0.00E+00	1.66E-01	0.00E+00	0.00E+00	0.00E+00



Simulation

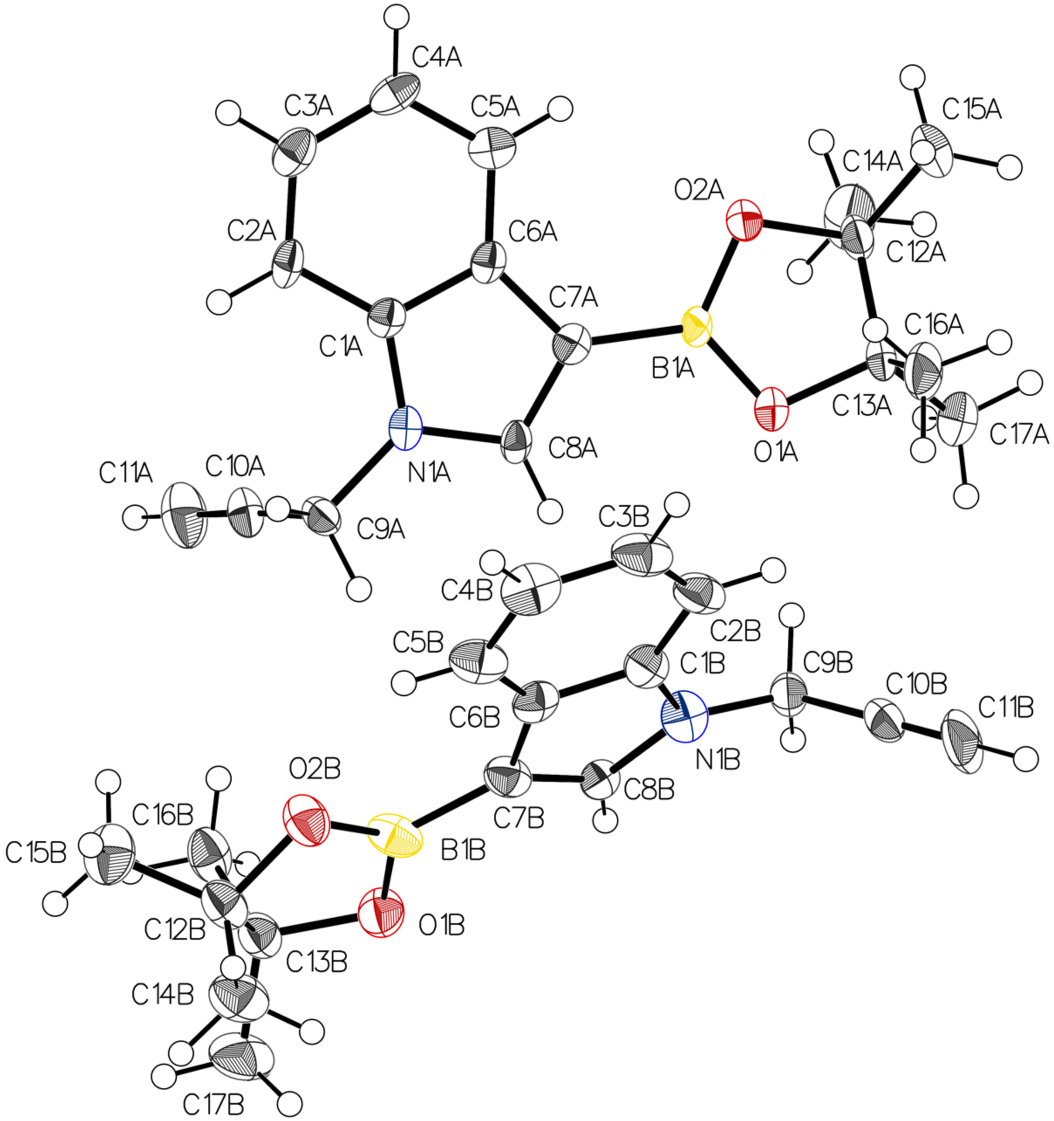
Kinetic experiment

Fig K1: (top) Data in KinSim (bottom) Simulation vs. Kinetic experiment

Crystallographic Data of 8i

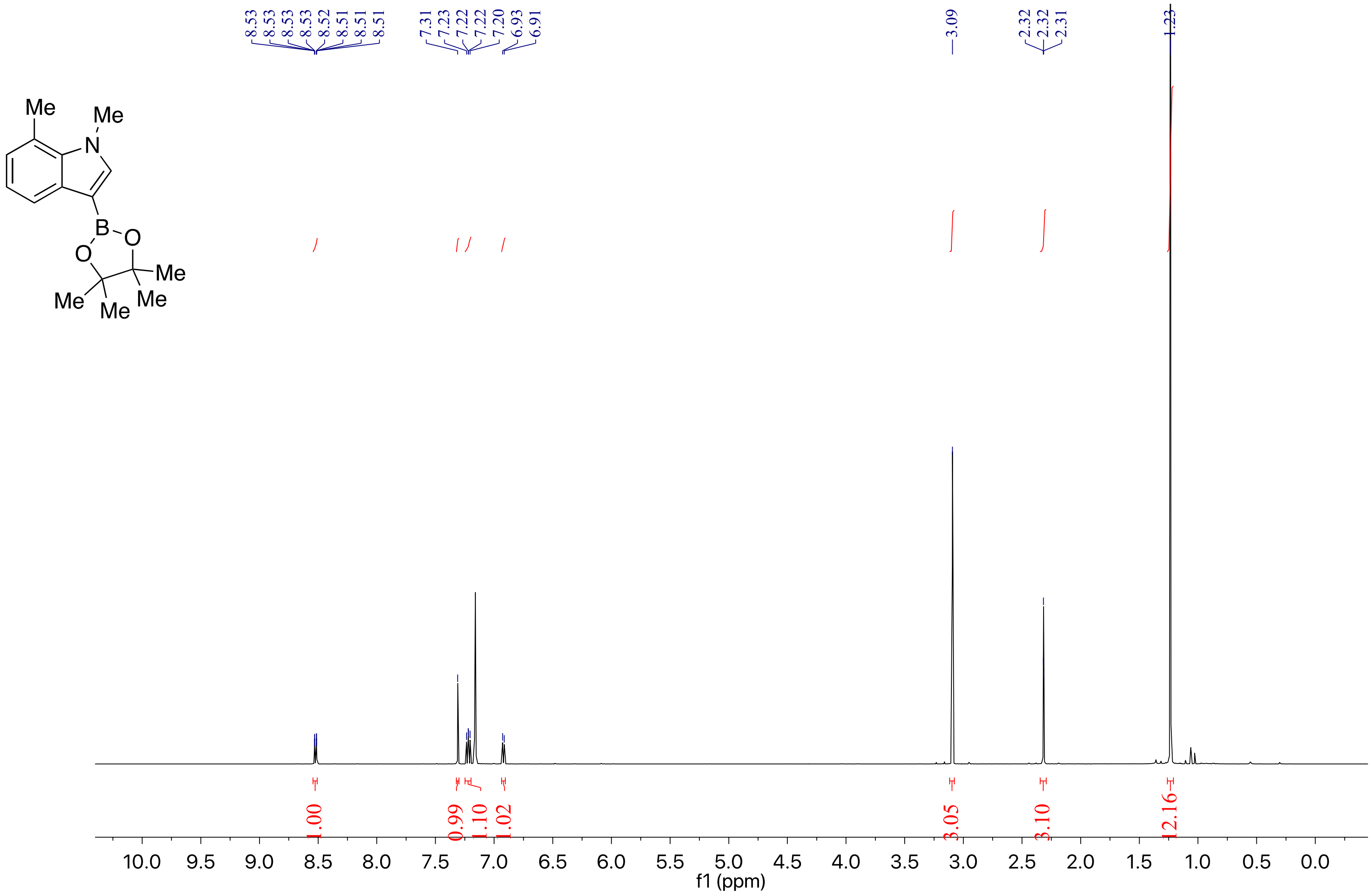
Table 1. Crystal data and structure refinement for compound **8i**.

Empirical formula	$C_{17}H_{20}BNO_2$	
Formula weight	281.15	
Temperature	150(2) K	
Wavelength	1.34139 Å	
Crystal system	cubic	
Space group	Pna**2**$_{/1}$	
Unit cell dimensions	a = 27.4401(11) Å	α = 90°.
	b = 7.2038(3) Å	β = 90°.
	c = 15.7216(6) Å	γ = 90°.
Volume	3107.7(2) Å^3	
Z	8	
Density (calculated)	1.202 Mg/m^3	
F(000)	120012	
Crystal size	1.178 x 0.508 x 0.332 mm^3	
Index ranges	$-12 \le h \le 16$, $-24 \le k \le 25$, $-23 \le l \le 19$	
R indices (all data)	R1 = 0.0964(5623), wR2 = 0.2458(5681)	

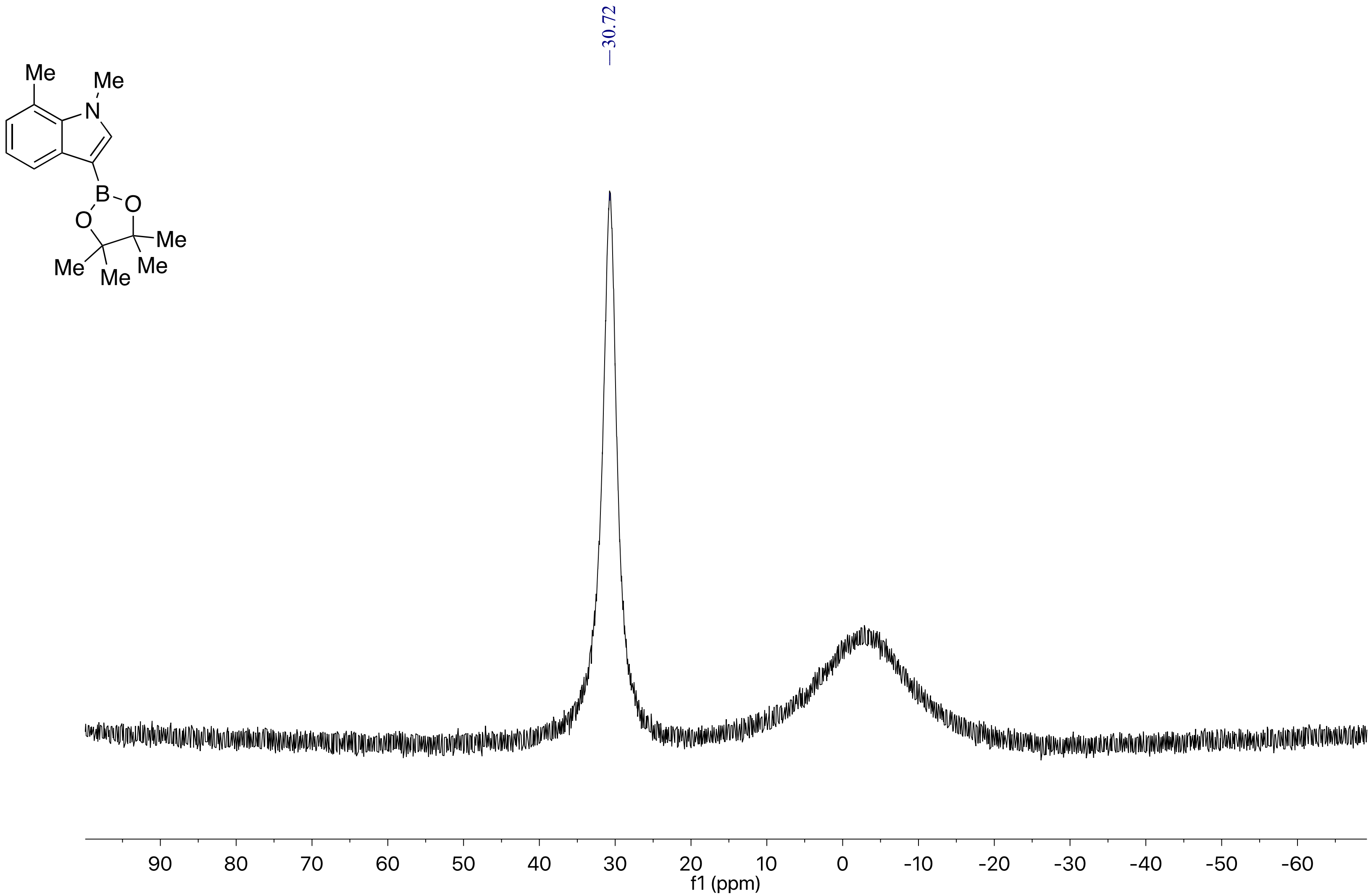

C4A
C3A
C5A
C15A
C14A
O2A
C2A
C6A
C12A
C7A
C16A
C1A
B1A
C13A
C17A
N1A
C8A
O1A
C11A
C10A
C9A
C3B
C4B
C2B
C5B
C9B
C1B
C10B
C11B
C6B
N1B
O2B
C8B
C16B
C7B
B1B
C15B
C12B
O1B
C13B
C14B
C17B

NMR Spectra of the new products:

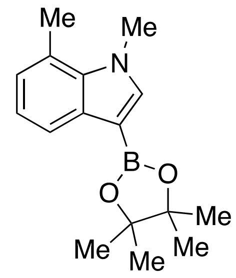
S1 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) Synthesis of 1,7-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8b**)

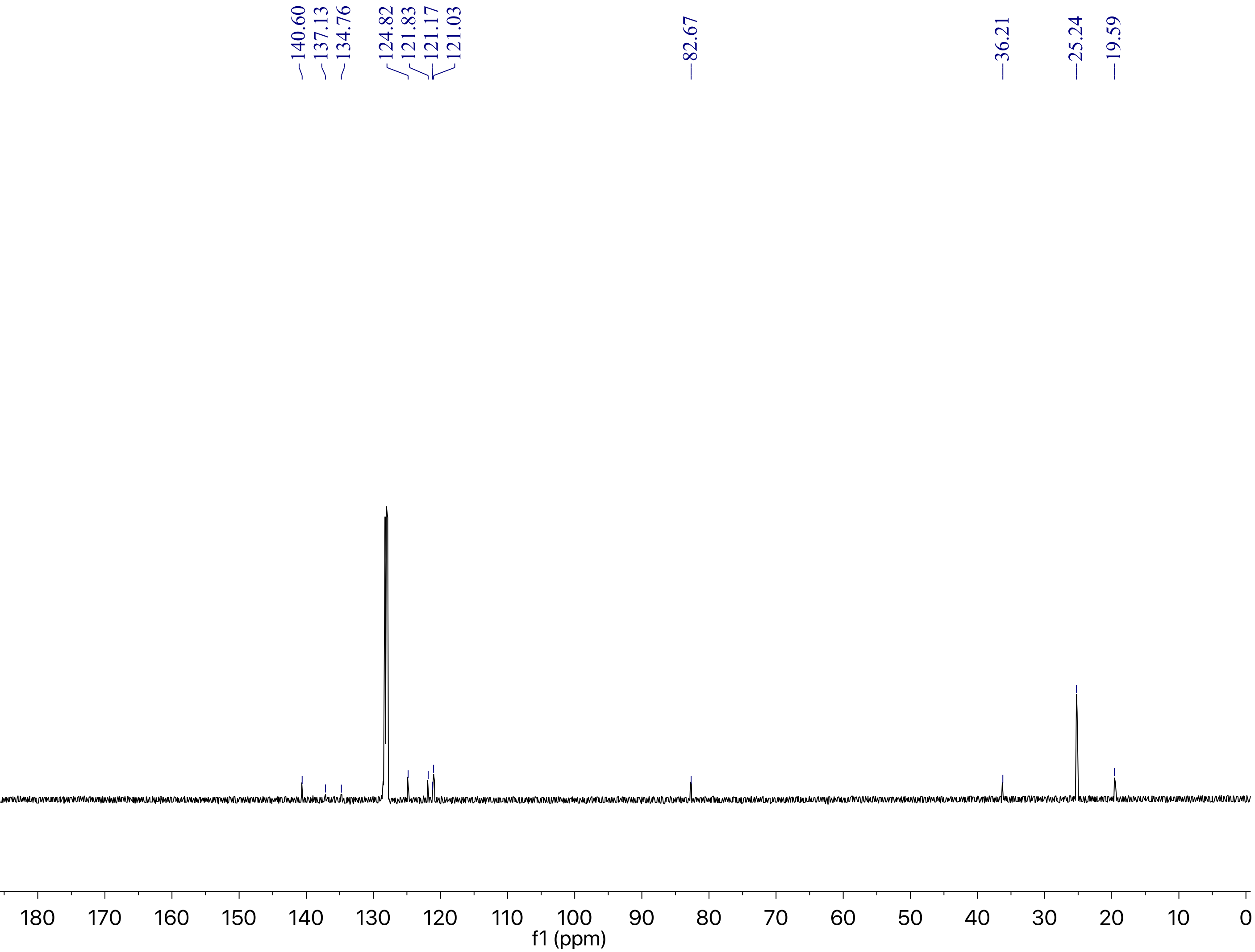


S2 ^{11}B NMR (500 MHz, CDCl$_3$, 298 K) Synthesis of 1,7-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8b**)

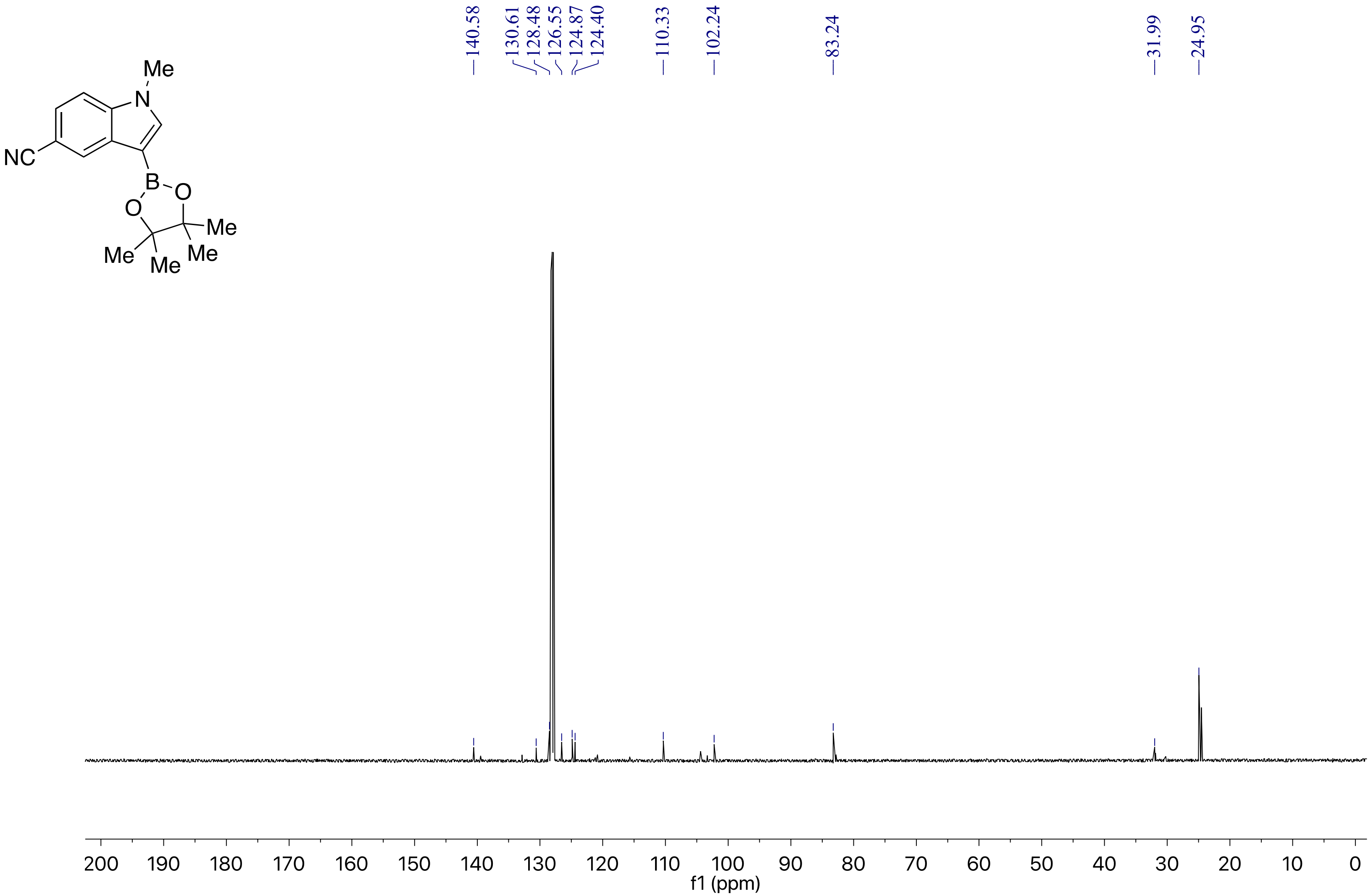


S3 ^{13}C NMR (500 MHz, CDCl$_3$, 298 K) Synthesis of 1,7-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8b**)

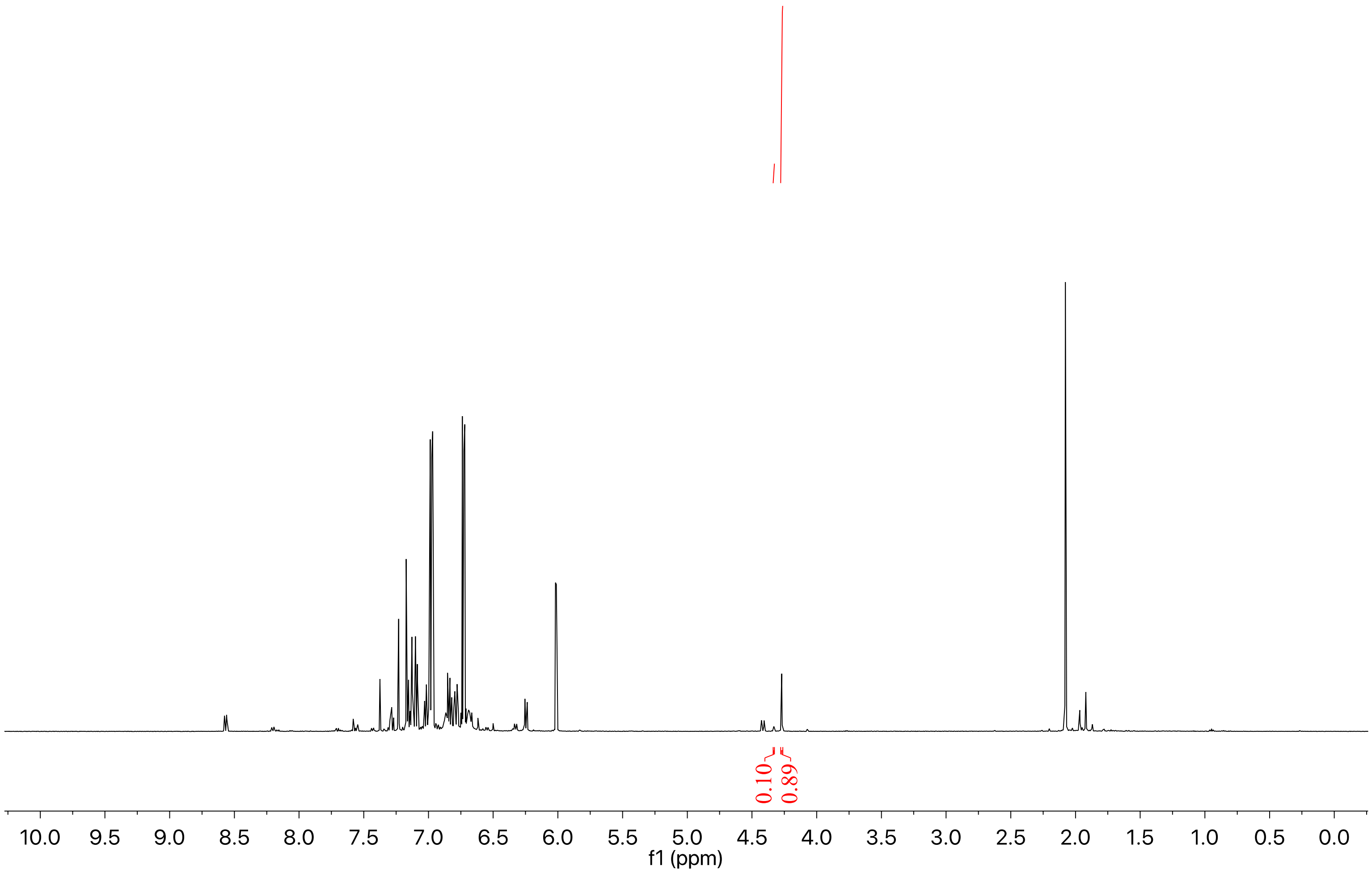




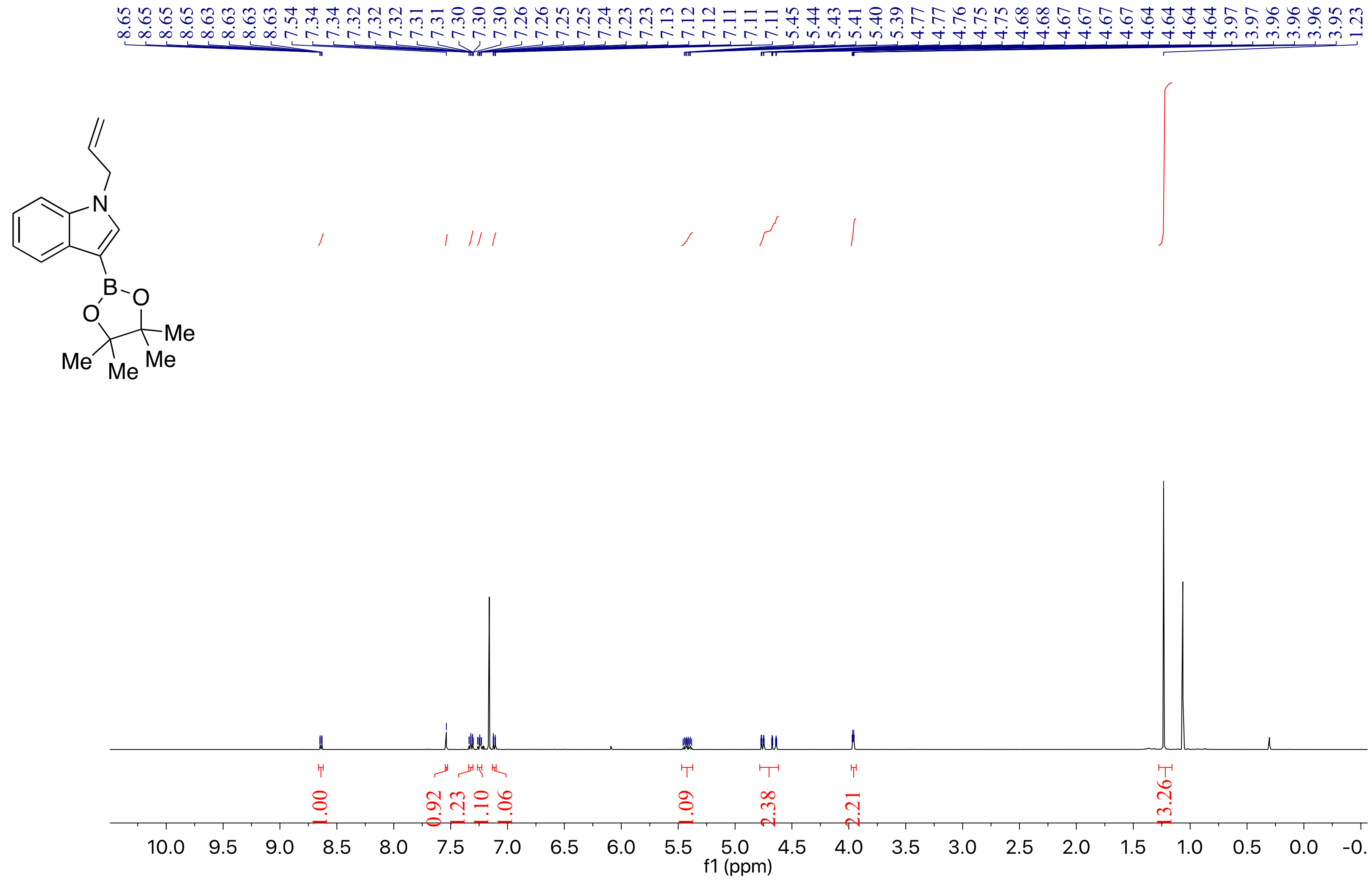
S4 ^{13}C NMR (500 MHz, $CDCl_3$, 298 K) 1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-5-carbonitrile (**8e**)



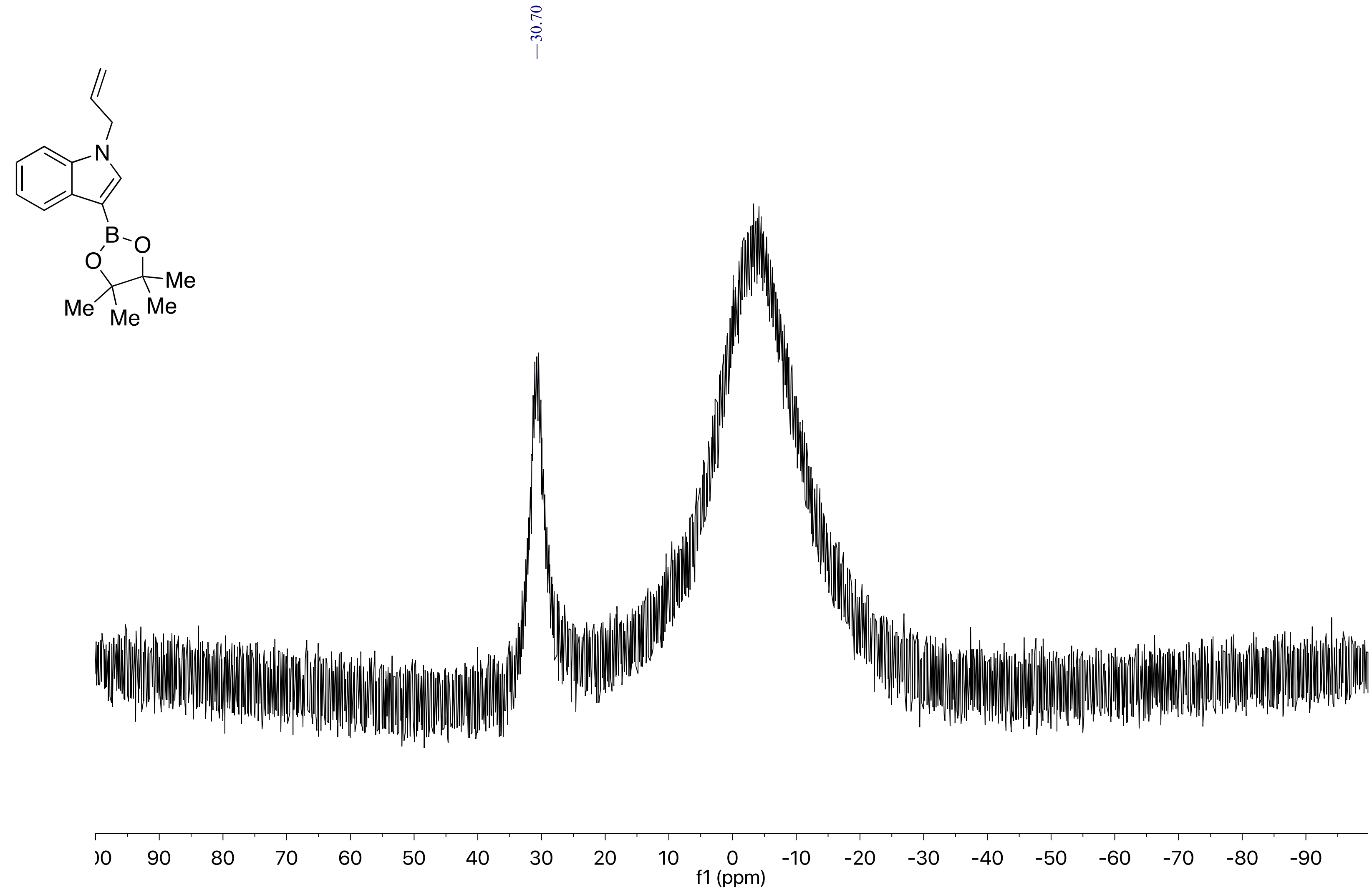
S5 ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) 4-((3-(benzo[*d*][1,3,2]dioxaborol-2-yl)-1*H*-indol-1-yl)methyl)benzonitrile (**8g**)



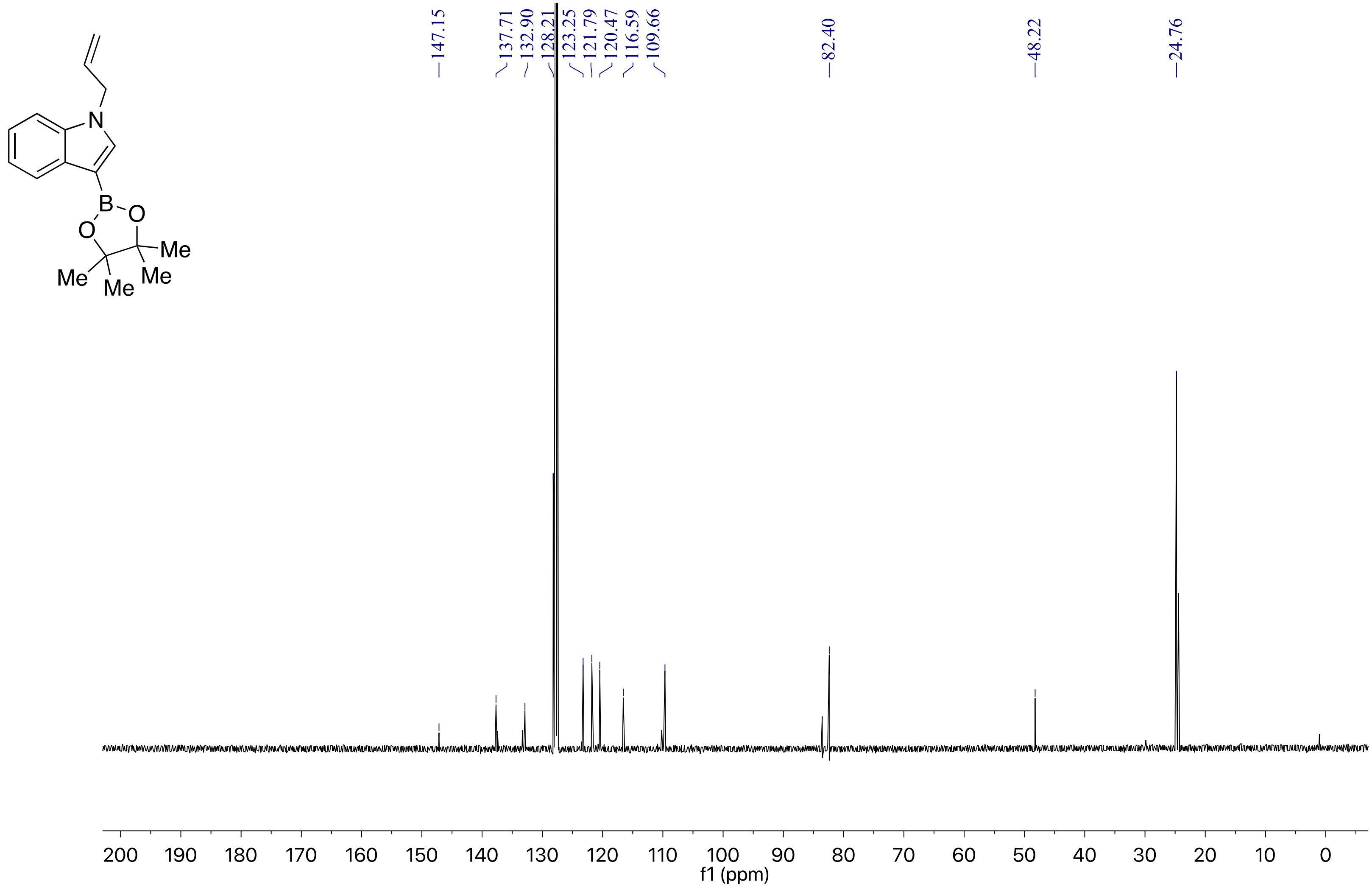
S6 ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) 1-allyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8h**)



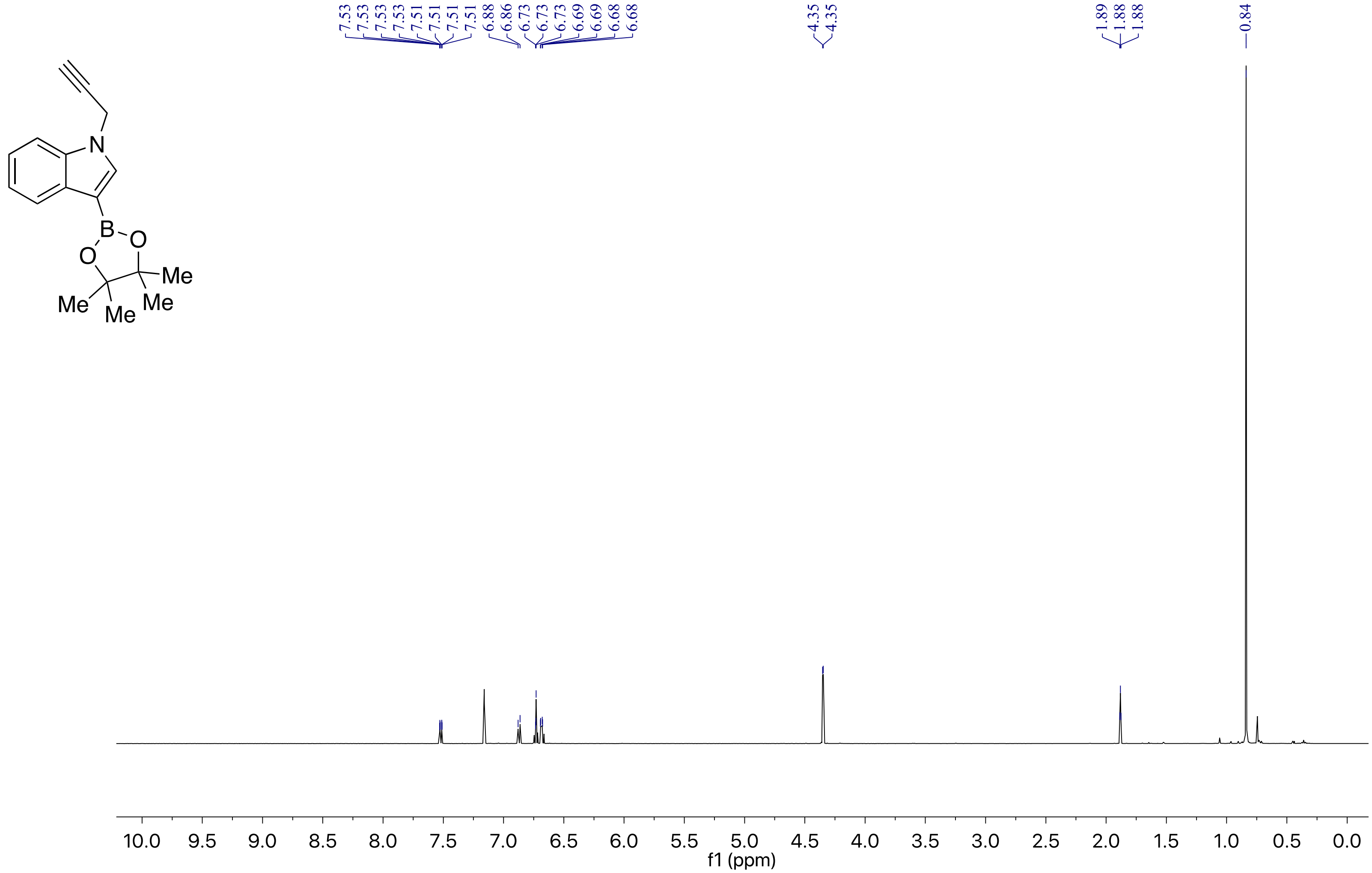
S7 ^{11}B NMR (500 MHz, $CDCl_3$, 298 K) 1-allyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8h**)



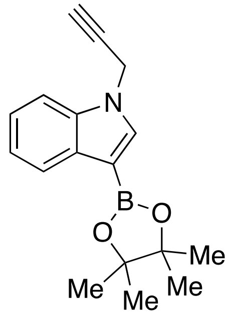
S8 ^{13}C NMR (500 MHz, CDCl$_3$, 298 K) 1-allyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8h**)

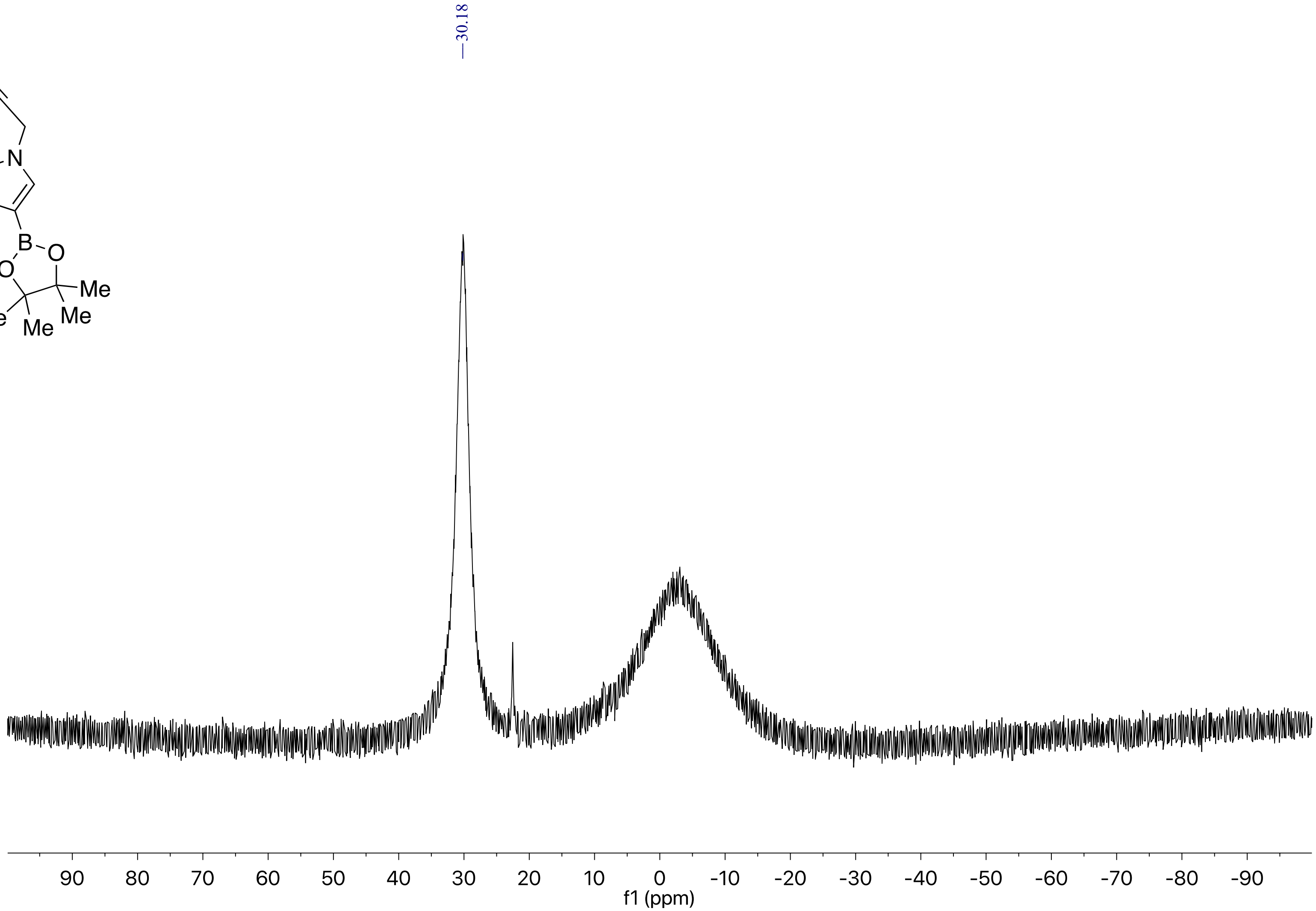


S9 ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) 1-(prop-2-yn-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8i**)

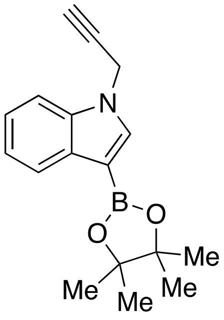


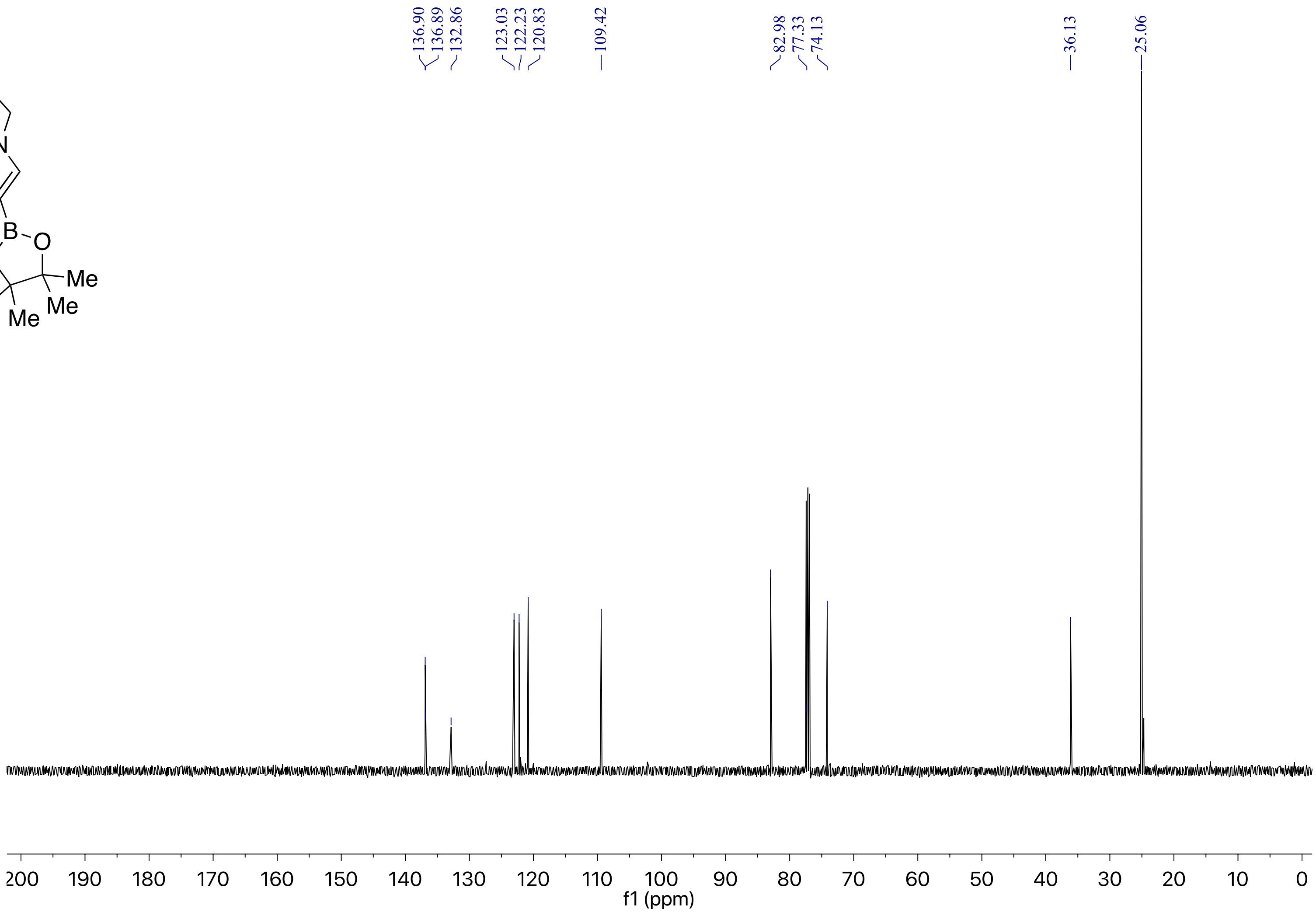
S10 ^{11}B NMR (500 MHz, $CDCl_3$, 298 K) 1-(prop-2-yn-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxabrolan-2-yl)-1*H*-indole (**8i**)



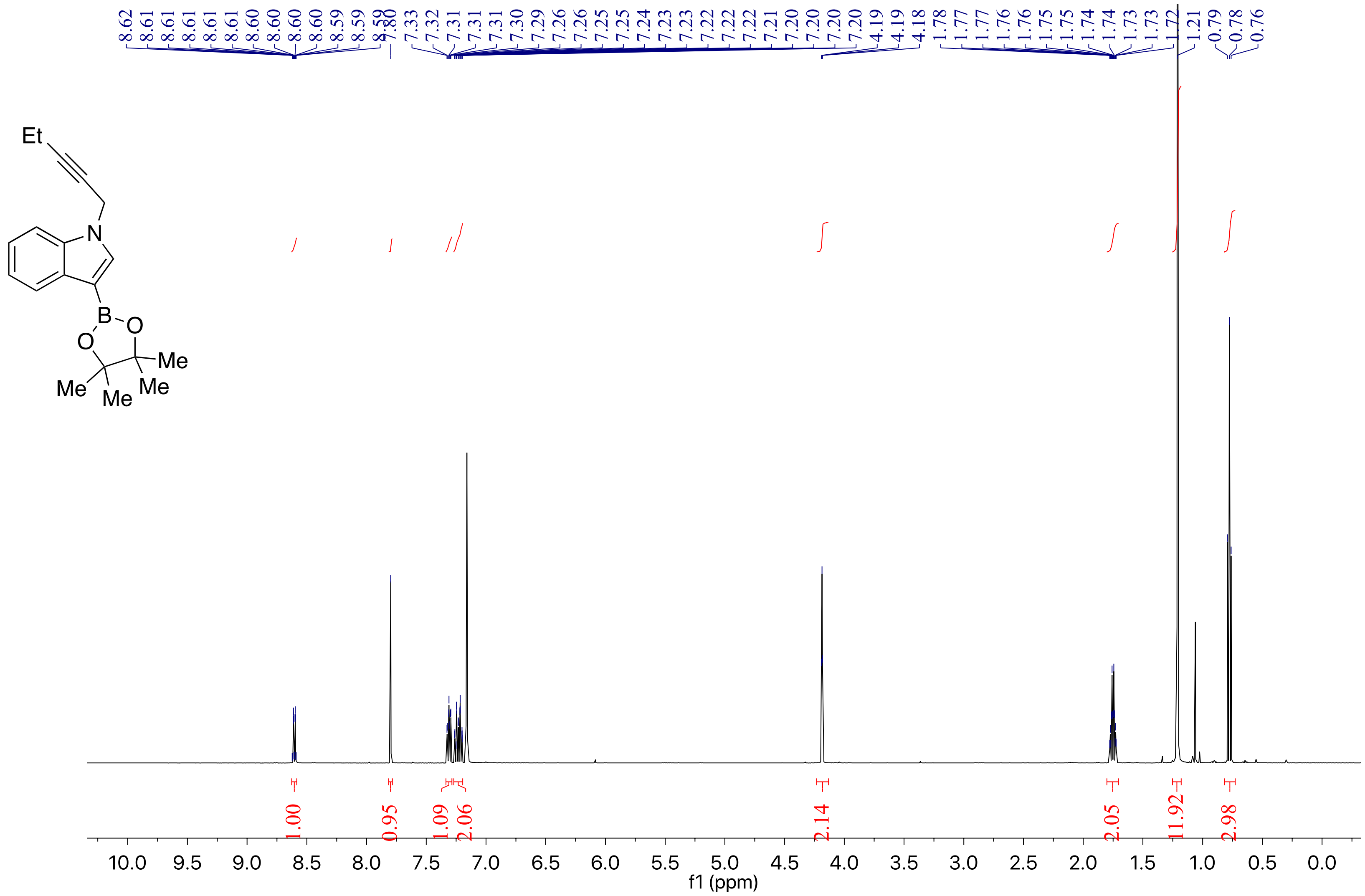


S11 ^{13}C NMR (500 MHz, CDCl$_3$, 298 K) 1-(prop-2-yn-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8i**)

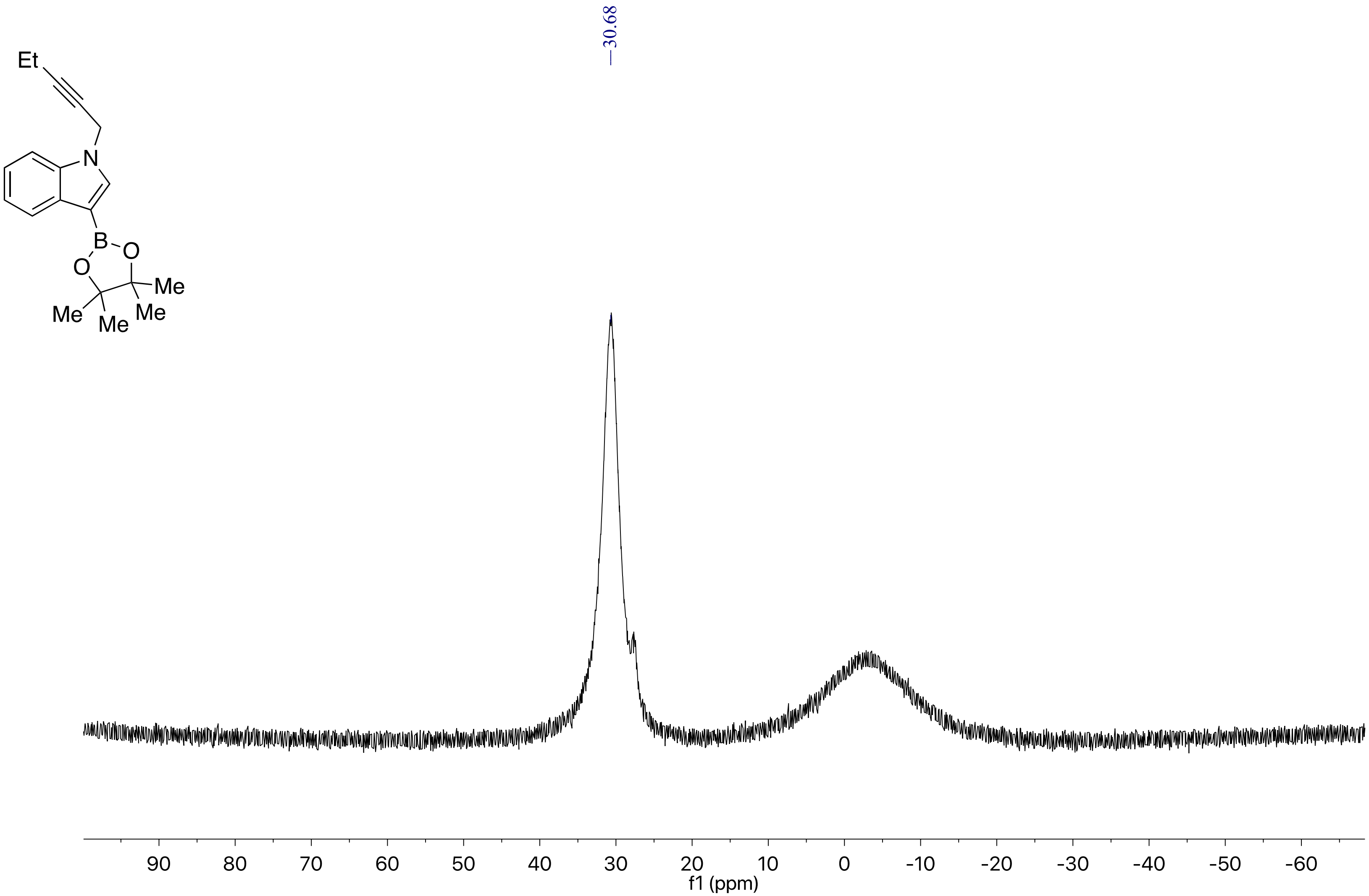




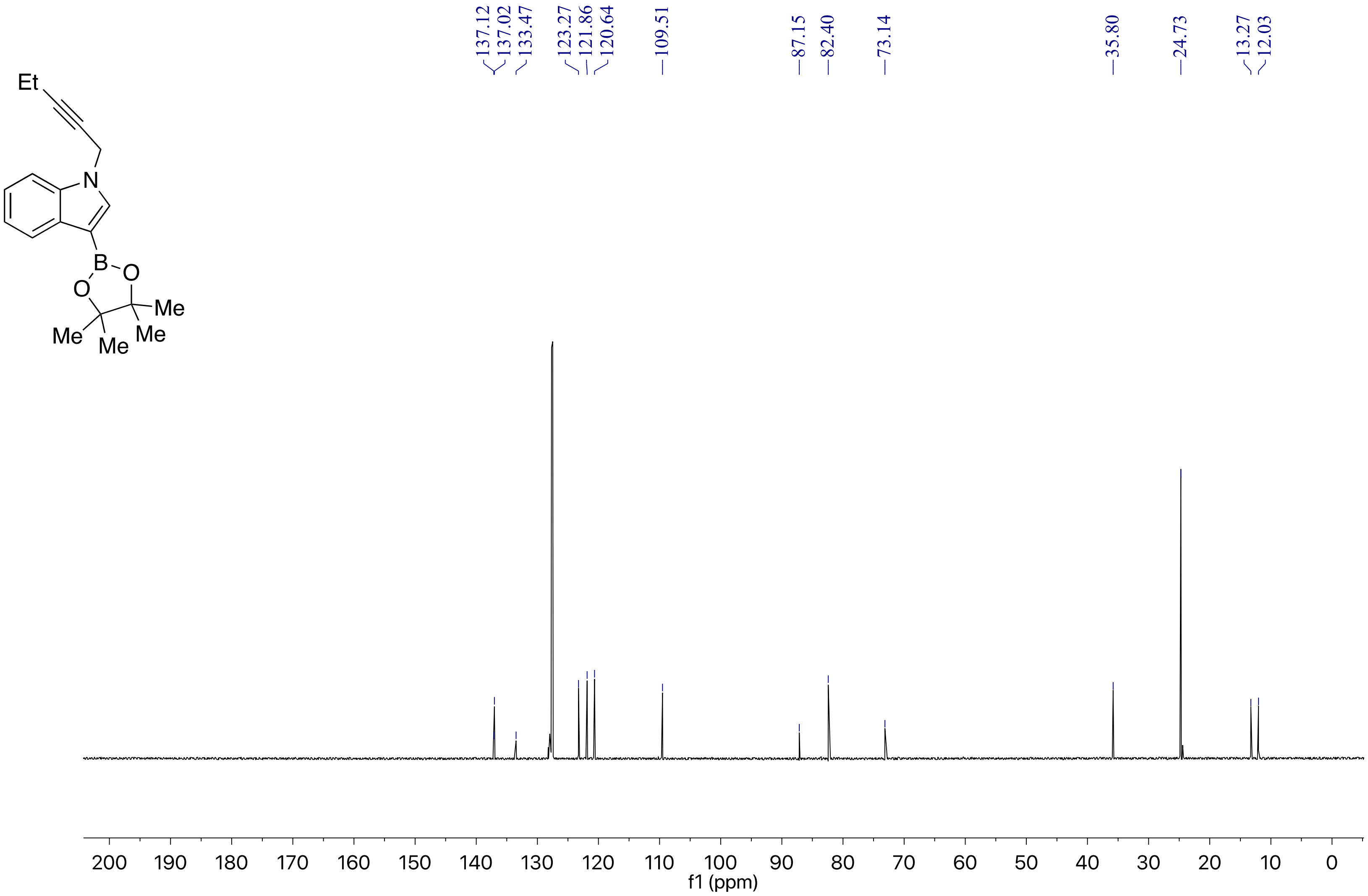
S12 ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) 1-(pent-2-yn-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8j**)



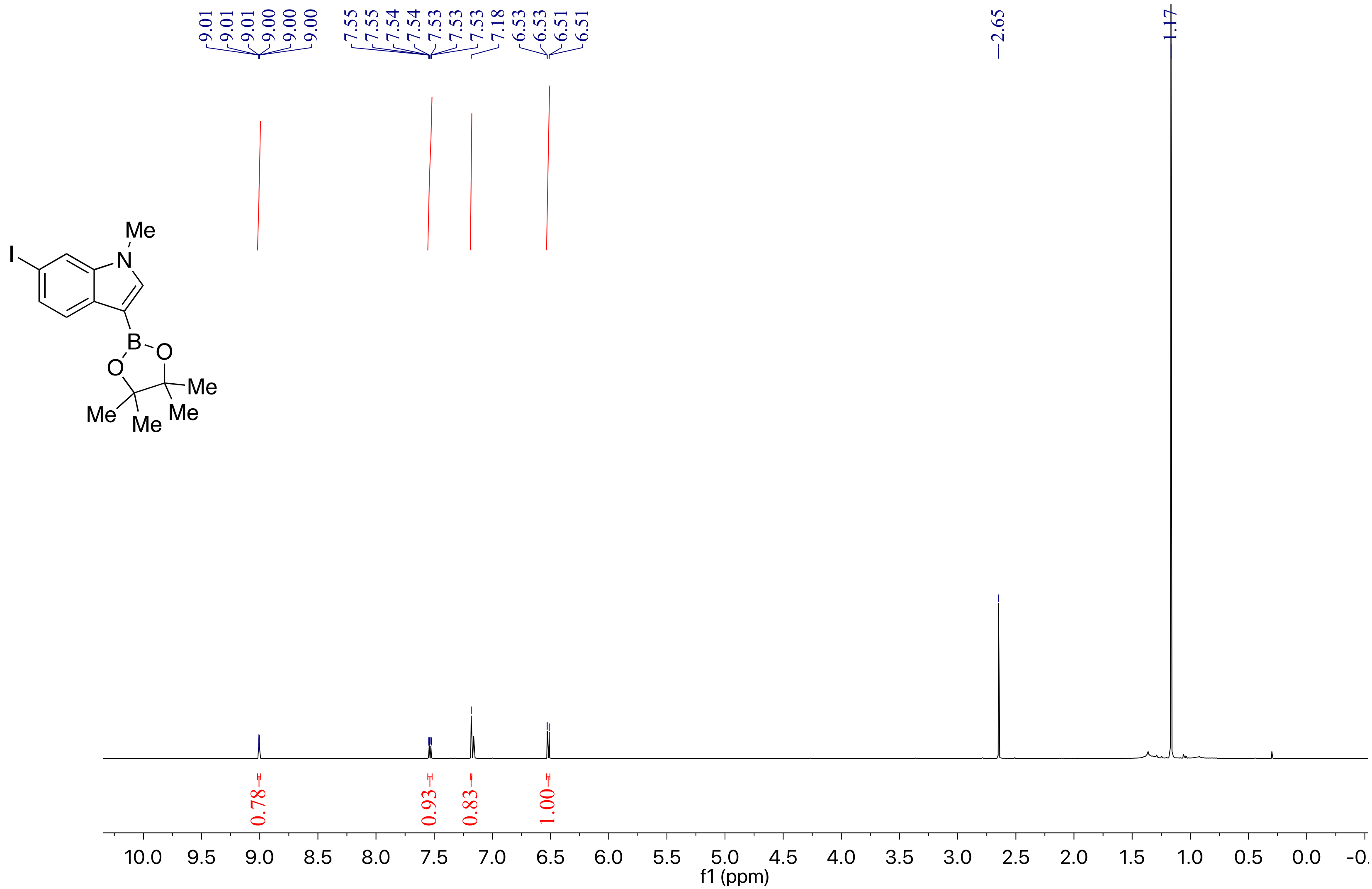
S13 ^{11}B NMR (500 MHz, $CDCl_3$, 298 K) 1-(pent-2-yn-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8j**)



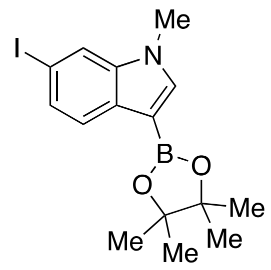
S14 ^{13}C NMR (500 MHz, CDCl$_3$, 298 K) 1-(pent-2-yn-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8j**)

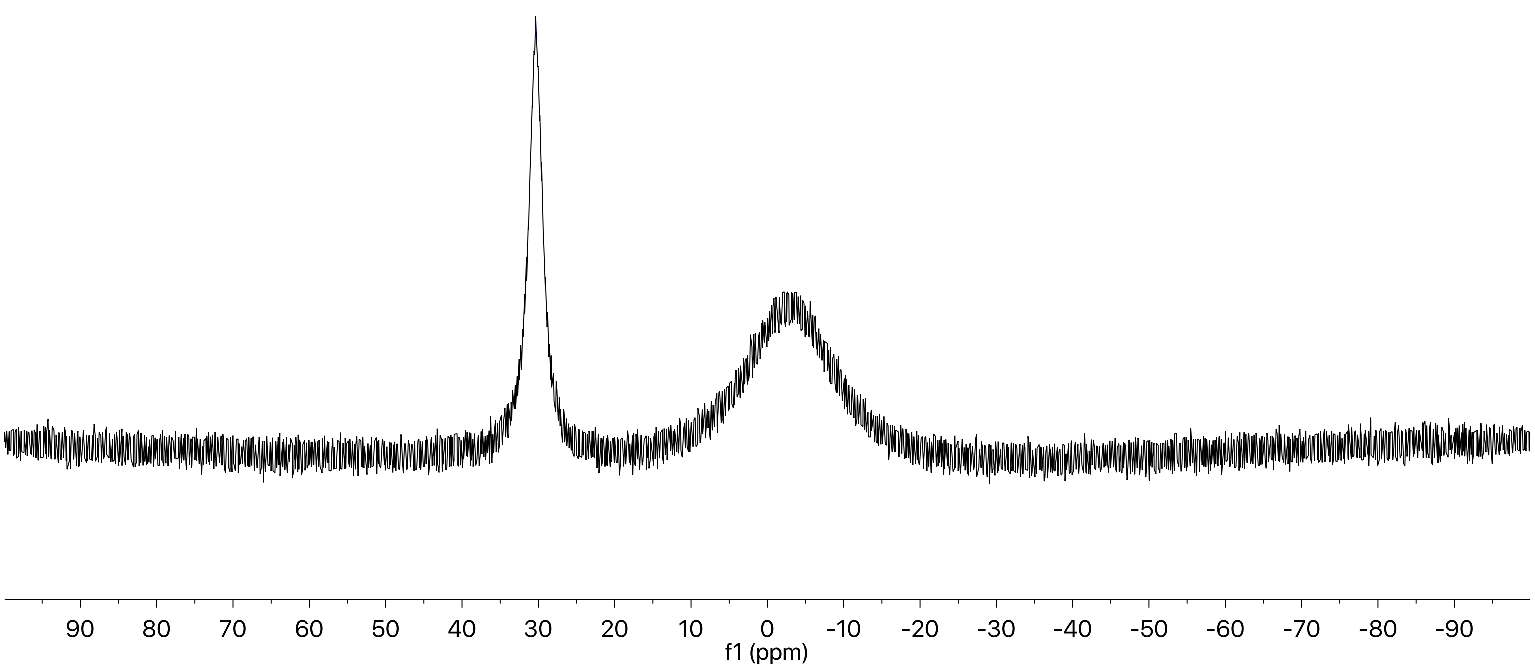


S15 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) 6-iodo-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8k**)

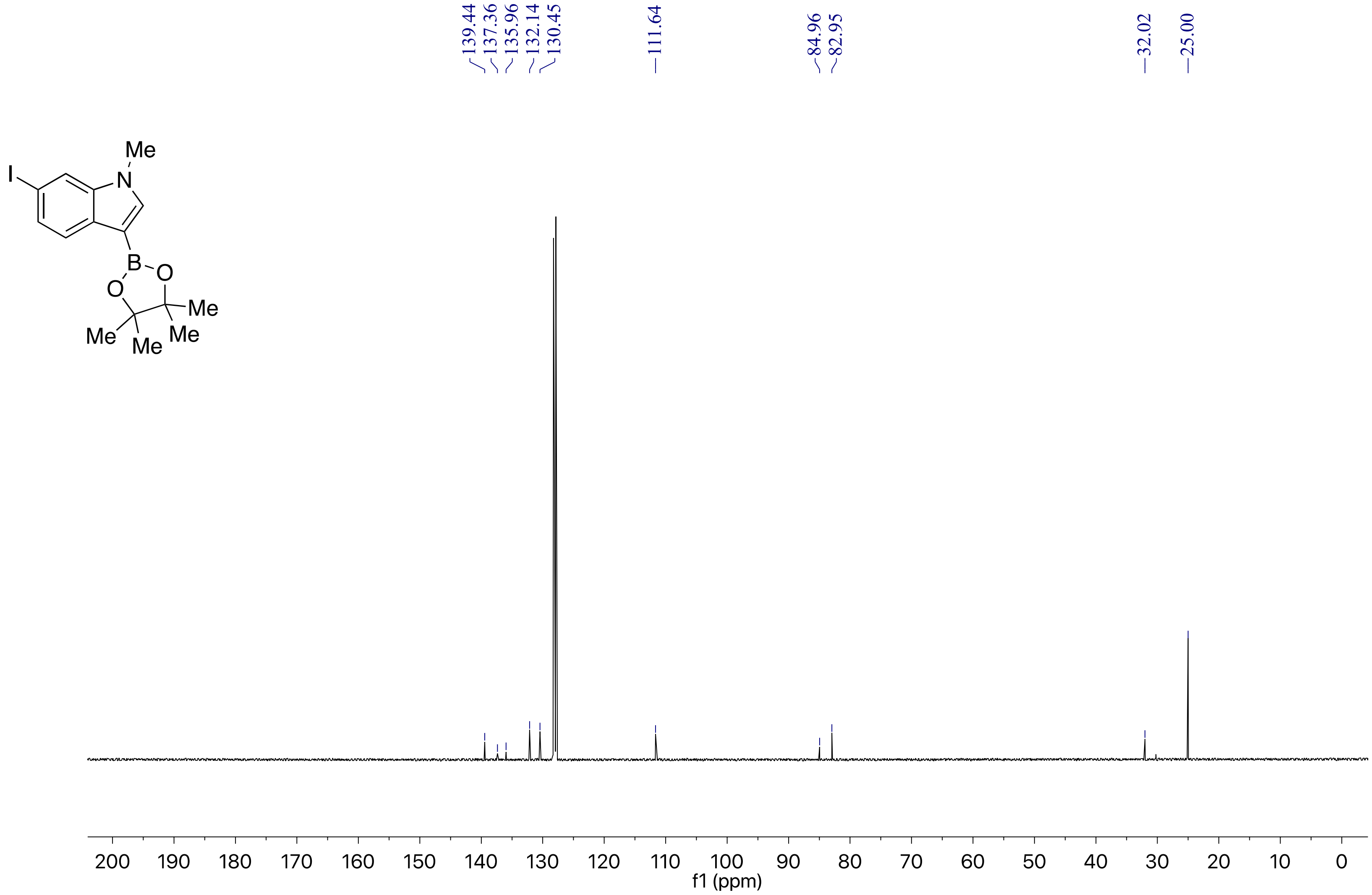


S16 ^{11}B NMR (500 MHz, CDCl$_3$, 298 K) 6-iodo-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8k**)

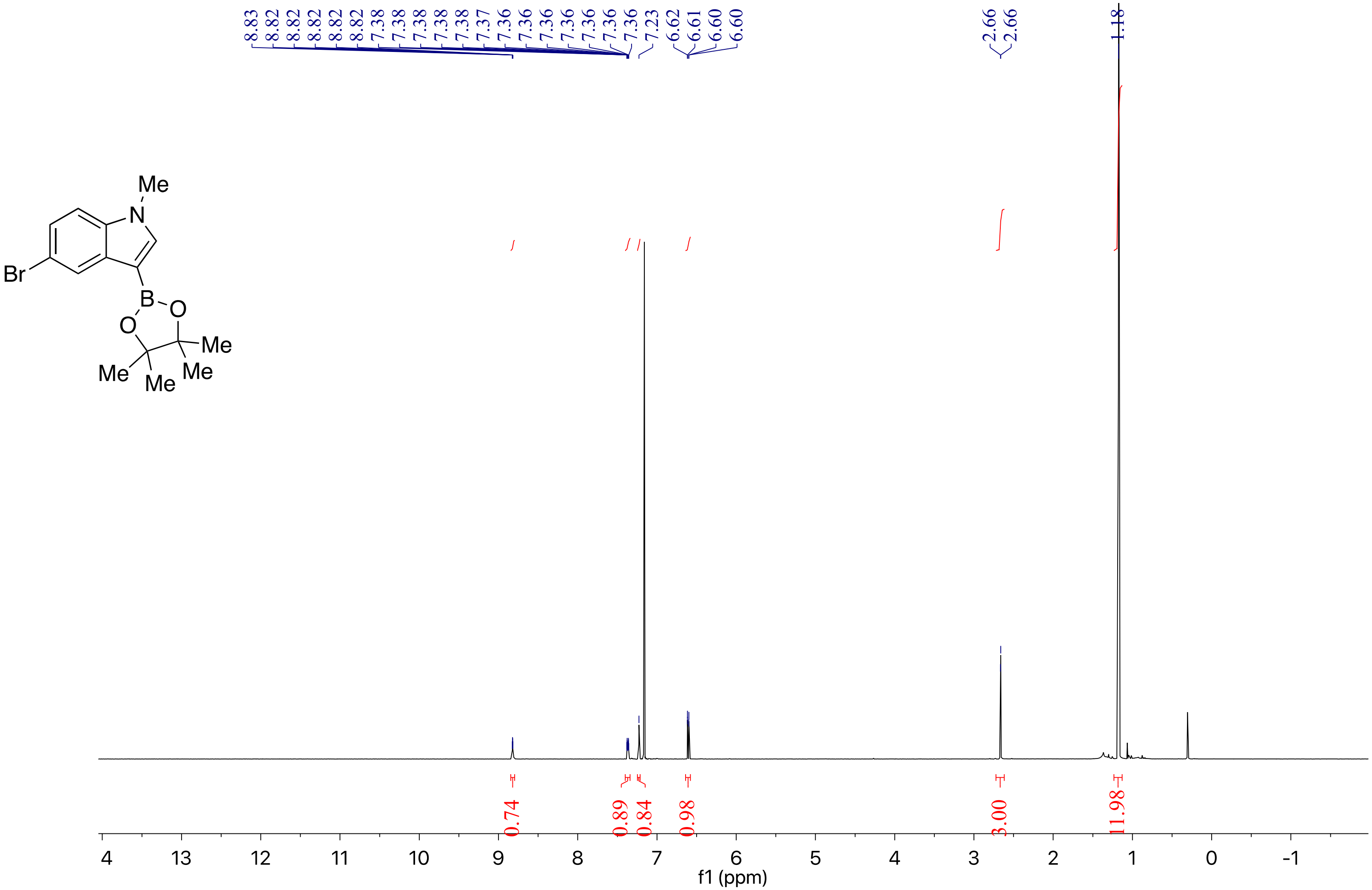




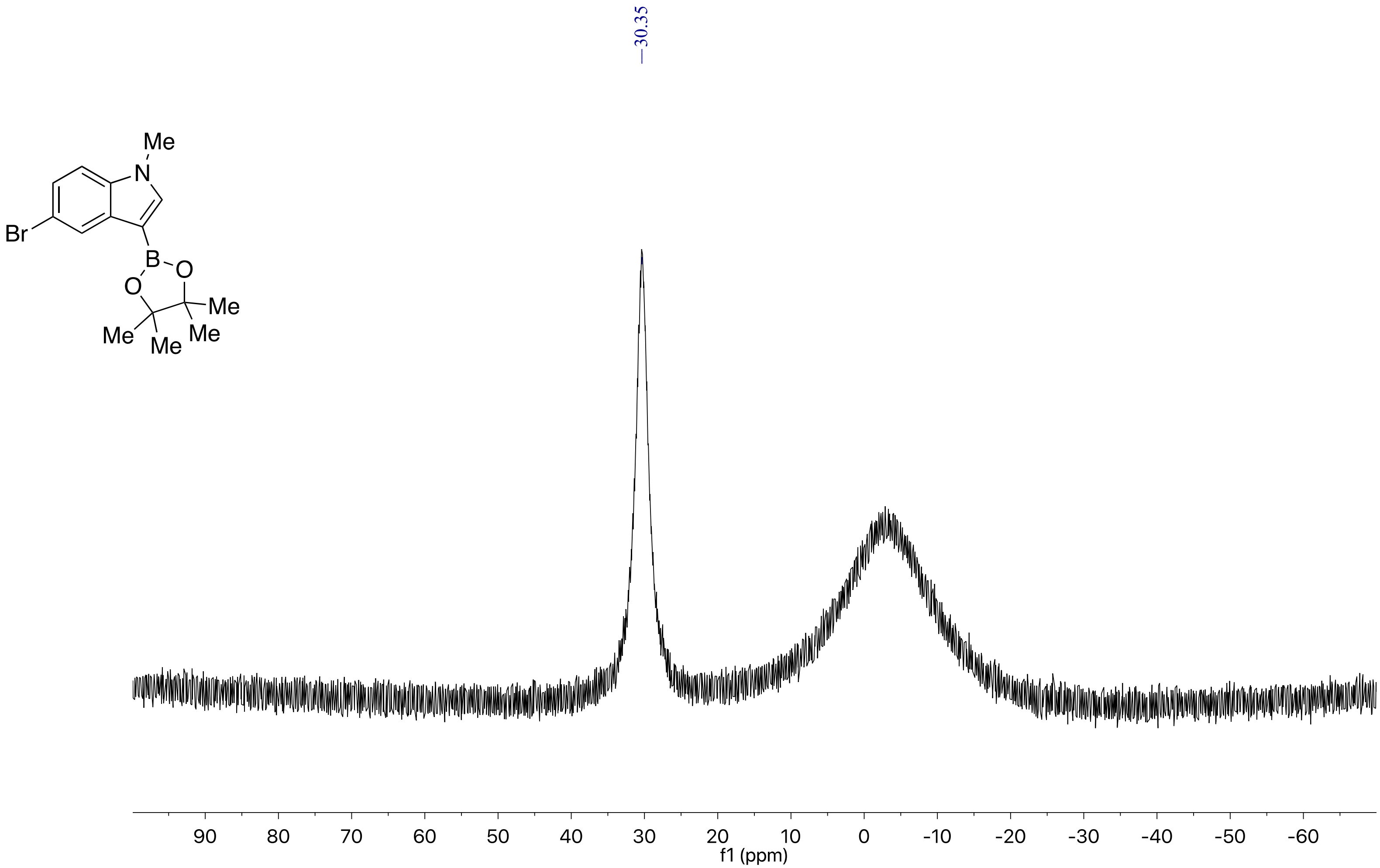
S17 ^{13}C NMR (500 MHz, CDCl$_3$, 298 K) 6-iodo-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8k**)



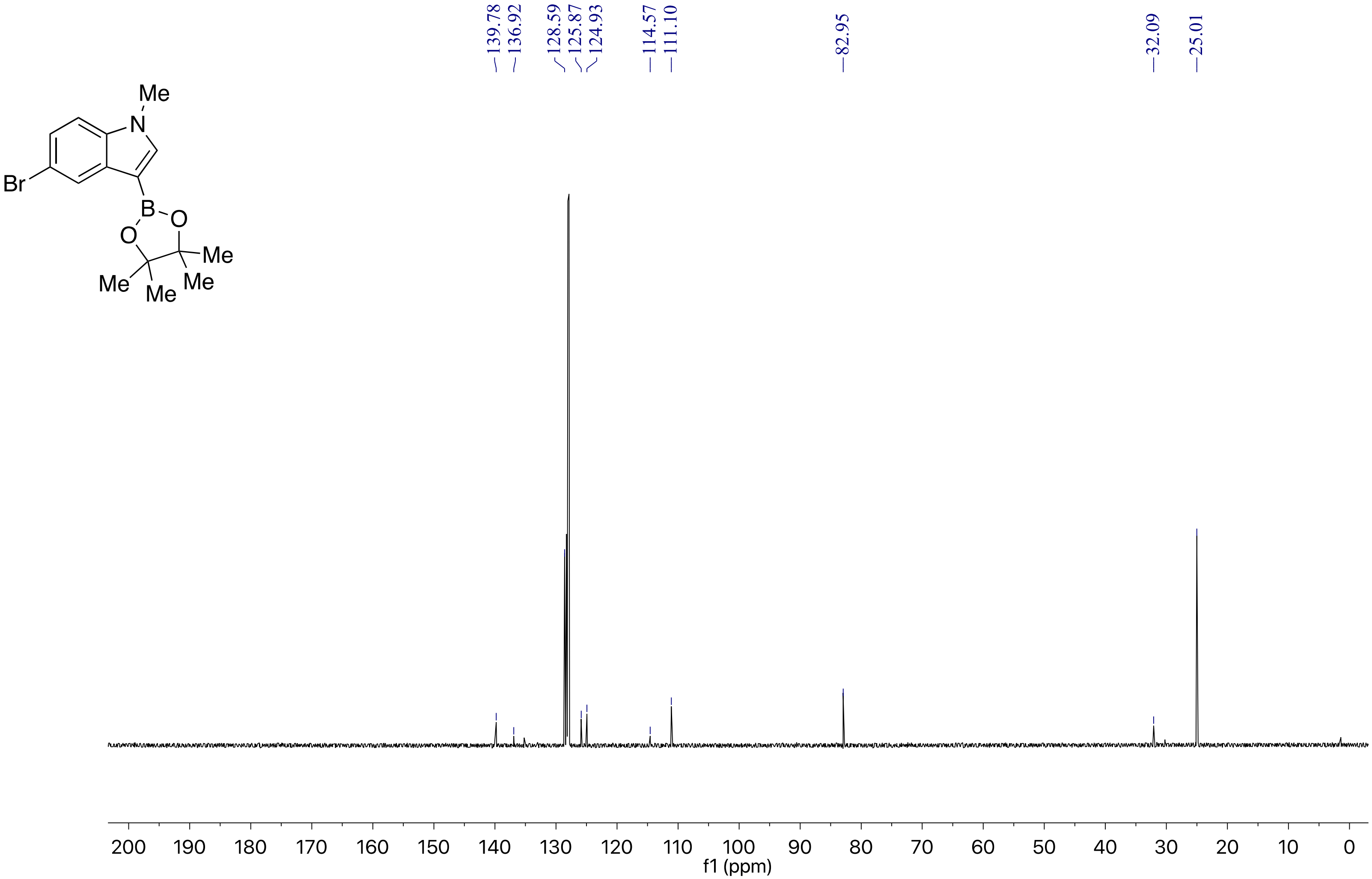
S18 ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) 5-bromo-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8l**)



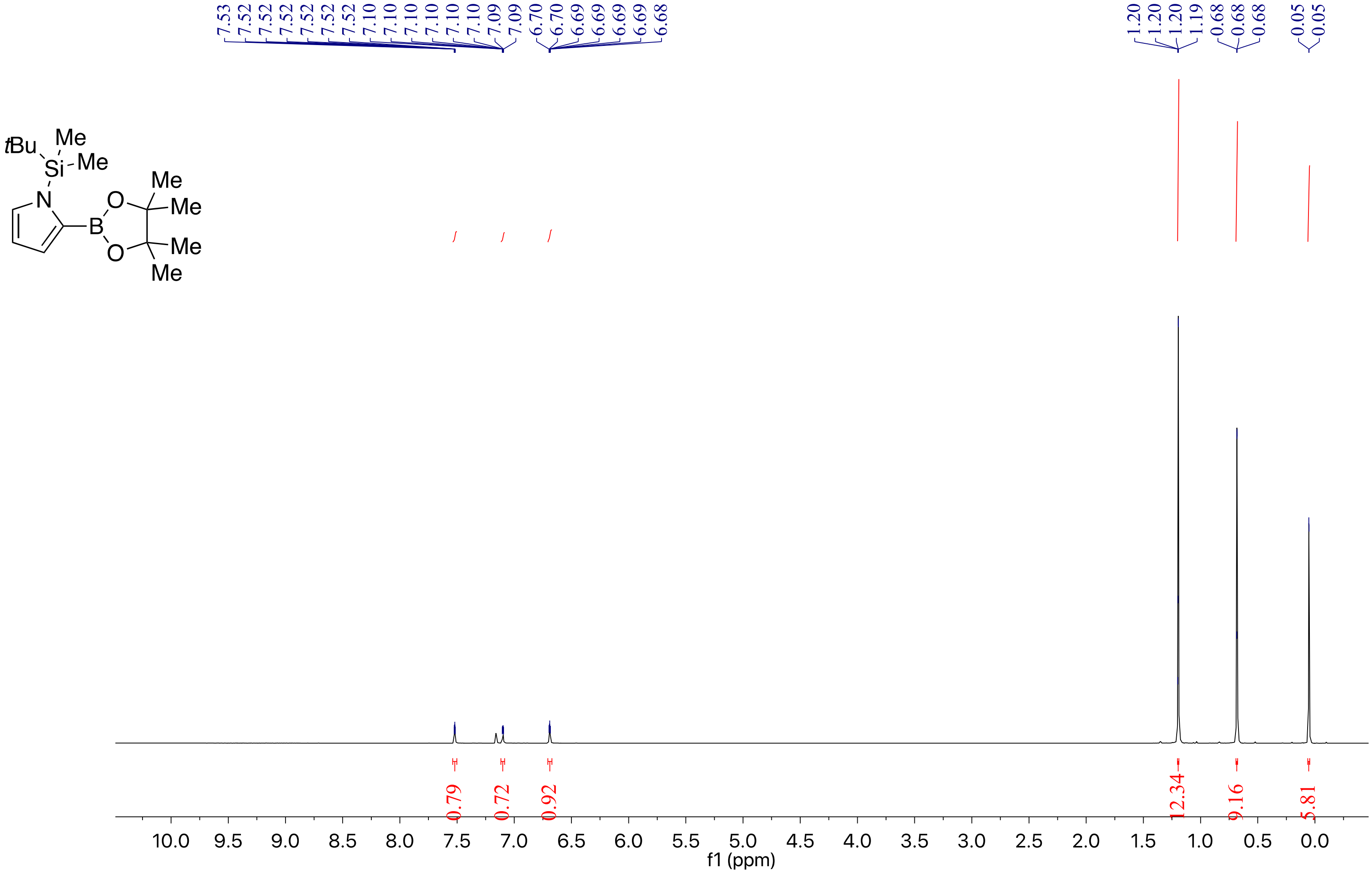
S19 ^{11}B NMR (500 MHz, CDCl$_3$, 298 K) 5-bromo-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8l**)



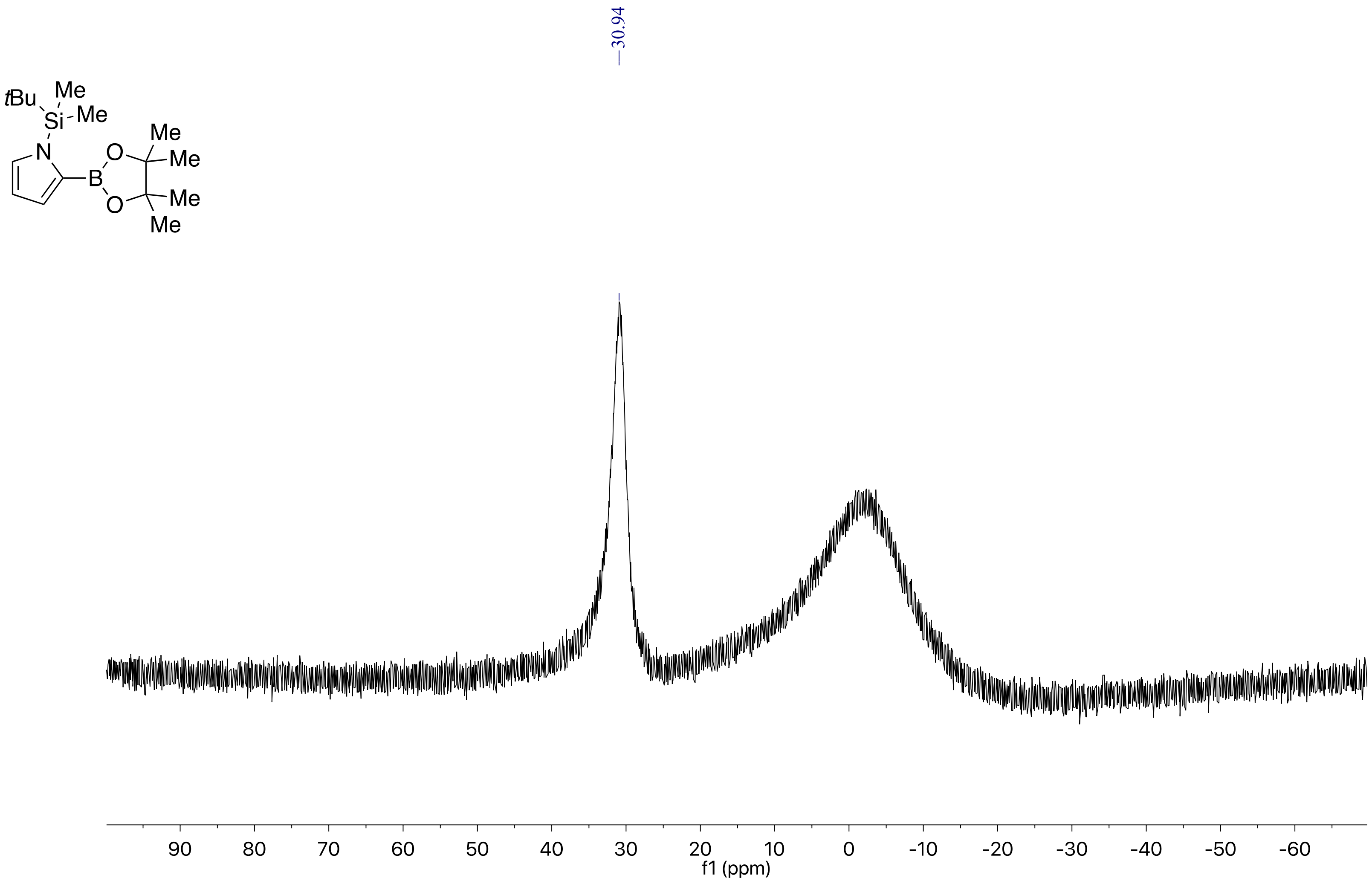
S20 ^{13}C NMR (500 MHz, CDCl$_3$, 298 K) 5-bromo-1-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**8l**)



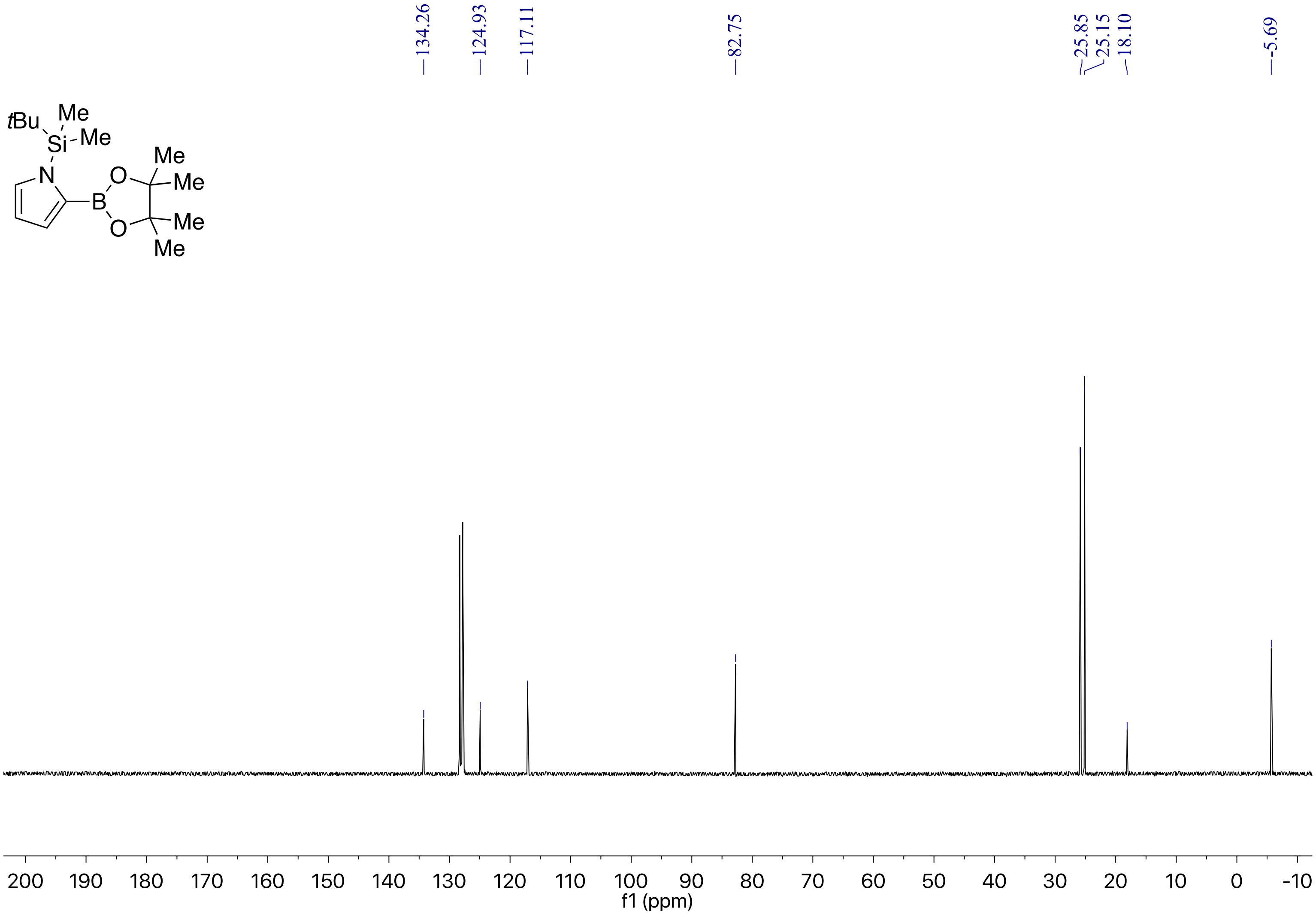
S21 ^{1}H NMR (500 MHz, CDCl$_3$, 298 K) 1-(*tert*-butyldimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole (**8q**)



S22 ^{11}B NMR (500 MHz, $CDCl_3$, 298 K) 1-(*tert*-butyldimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole (**8q**)



S23 ^{13}C NMR (500 MHz, CDCl$_3$, 298 K) 1-(*tert*-butyldimethylsilyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-pyrrole (**8q**)



References

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[1] Olguín-uribe, S.; Mijangos, M. V; Amador-sánchez, Y. A.; Sánchez-carmona, M. A.; Miranda, L. D. *European J. Org. Chem.* **2017**, 2481.

[2] Molander, G. A.; Ryu, D.; Hosseini-sarvari, M.; Devulapally, R.; Seapy, D. G. *J. Org. Chem.* **2013**, *78*, 6648.

[3] Xu, X.; Liu, G.; Azuma, A.; Tokunaga, E.; Shibata, N. *Org. Lett.* **2011**, *13*, 4854.

[4] Klare, H. F. T.; Oestreich, M.; Ito, J.; Nishiyama, H.; Ohki, Y.; Tatsumi, K. *J. Am. Chem. Soc.* **2011**, *133*, 3312.

[5] Taylor, J. E.; Jones, M. D.; Williams, J. M. J.; Bull, S. D. *Org. Lett.* **2010**, *12*, 5740.

[6] Lane, B. S.; Sames, D. *Org. Lett.* **2004**, *6*, 2897.

[7] Zhang, S.; Han, Y.; He, J.; Zhang, Y. *J. Org. Chem.* **2018**, *83*, 1377.

[8] Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[9] J.-D. Chai, M. Head-Gordon, Phys. *Chem. Chem. Phys.,* **2008,** *10*, 6615–6620.

[10] S. Grimme, Goerigk, Lars. *Phys. Chem. Chem. Phys.,* **2011,** *13*, 6670–6688.

[11] K. Chernichenko, Á. Madarász, I. Pápai, M. Nieger, M. Leskelä, T. Repo, *Nat. Chem*. **2013,** 718-723.

[12] a) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, 3297. b) Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, *22*, 1057.

[13] Lavergne, J. L.; Jayaraman, A.; Castro, L. C. M.; Rochette, É.; Fontaine, F.-G. *J. Am. Chem. Soc.* **2017**, *139*, 14714–14723.

[14] Jayaraman, A.; Castro, L. C. M.; Fontaine, F.-G.. *Org. Process Res. Dev.* **2018**, *22*, 1489–1499.

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[15] Li, T.; Yang, P. *J. Org. Chem.* **2018**, *83* (I), 14751–14757.