(Hetero)arylboration of Alkynes: A Strategy for the Synthesis of α,α-Bis(hetero)arylketones

Yuan Huang, Allison M. Bergmann, and M. Kevin Brown

General. ^{1}H NMR spectra were recorded at room temperature on a Varian I400 (400 MHz), a Varian VXR400 (400 MHz), a Varian I500 (500 MHz), or a Varian I600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CHCl_3$: δ7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a Varian I400 (100 MHz), a Varian VXR400 (100 MHz), or a Varian I500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ77.16 ppm) or (C_6D_6: δ128.06 ppm). High-resolution mass spectrometry was performed on either a Waters/Micromass LCT Classic (ESI-TOF) or a Thermo Electron Corporation MAT 95XP-Trap (GC/MS). Melting points were obtained on a Thomas Hoover capillary melting point apparatus without correction.

Unless otherwise noted, all reactions have been carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven-(135 °C) and flame-dried glassware with standard vacuum-line techniques. Diethyl ether and tetrahydrofuran was purified under a positive pressure of dry argon by passage through two columns of activated alumina. Toluene was purified under a positive pressure of dry argon by passage through columns of activated alumina and Q5 (Grubbs apparatus). All work-up and purification procedures were carried out with reagent grade solvents (purchased from Sigma-Aldrich) in air. Standard column chromatography techniques using ZEOprep 60/40-63 μm silica gel and a Teledyne ISCO CombiFlash NextGen Chromatography System were used for purification.

Reagents and Catalysts:

Alkynes were prepared in accordance with literature procedures.[1]

Aphos ((4-(N,N-Dimethylamino)phenyl)di-tert-butyl phosphine) was purchased from Sigma-Aldrich and used as received.

Barium hydroxide was purchased from Alfa Aesar and used as received.

Bis(pinacolato)diboron was purchased from Oakwood Chemicals and recrystallized from pentane prior to use.

3-Bromofuran was purchased from Combi-Blocks and used as received.

5-Bromo-2-methoxypyridine was purchased from Combi-Blocks and used as received.

Copper chloride (99.995% metals basis) was purchased from Strem and purified by wash with 1M HCl (3 × 3mL), ethanol (3 × 3mL), and diethyl ether (3 × 3mL) and dried *in vacuo* before use.

1-Chloro-2,4-dinitrobenzene was purchased from Alfa Aesar and used as received.

Diphenylacetylene was purchased from Sigma Aldrich and used as received.

3,5-Dibromopyridine was purchased from Chem Impex and used as received.

Hex-3-yne was purchased from Ark Pharm and used as received.

Mesitylamine was purchased from Sigma-Aldrich and used as received.

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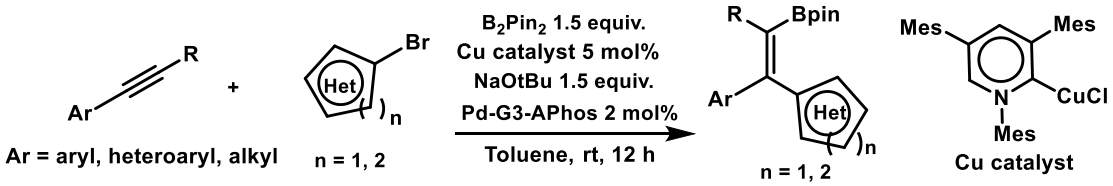
[1] K. L. Wilson, A. R. Kennedy, J. Murray, B. Greatrex, C. Jamieson and A. J. B. Watson, *Beilstein J. Org. Chem.*, 2016, **12**, 2005.

Mesityl boronic acid was purchased from Combi-Blocks and used as received.
$Pd(OAc)_2$ was purchased from Strem and used as received.
Pd-G3-Aphos was prepared in accordance with literature procedures.[2]
$Pd(PPh3)_4$ was purchased from Strem and used as received.
Prop-1-yn-1-ylbenzene was purchased from Sigma-Aldrich and used as received.
Pent-1-yne was purchased from Oakwood and used as received.
Sodium tert-Butoxide was purchased from Strem and used as received.
Sodium perborate tetrahydrate was purchased from EMD Millipore and used as received.
SIMes-CuCl was prepared in accordance with literature procedures.[3]
Silver triflate was purchased from Strem and used as received.
p-Toluenesulfonyl chloride was purchased from Alfa Aesar and used as received.
(1,3,5-trimesityl-1λ 1-pyridin-2-yl)copper chloride was prepared in accordance with literature procedures.[4]
Trimethyl(prop-1-yn-1-yl)silane was purchased from Alfa Aesar and used as received.

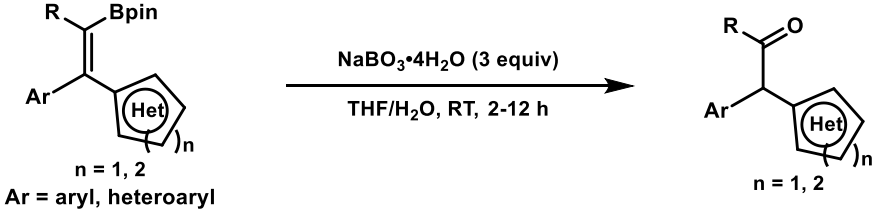
General Procedures:

General procedure A: Heteroarylboration of internal alkynes and heteroaryl bromides



In an N_2-filled glovebox, to a 13 x 100 mm screw-capped vial was added Cu catalyst (7.96 mg, 15.0 μ mmol, 5.00 mol %), APhos-Pd-G3 (3.81 mg, .006 mmol, 2.00 mol %), bis(pinacolato)diboron (114.0 mg, 0.45 mmol, 1.50 equiv), and NaO*t*-Bu (43.0 mg, 0.45 mmol, 1.50 equiv). The vial was sealed with a septum and removed from the glovebox. In the N_2 atmosphere, toluene (3.00 mL) was added, followed by addition of alkynes (0.30 mmol, 1.00 equiv) and the heteroaryl bromide (1.50 equiv.). The septum was quickly exchanged for a Teflon-lined screw cap and the reaction was stirred at room temperature for 12 h. At this time, the reaction was quenched upon the addition of 1 M KOH (2.00 mL) and the mixture was extracted with EtOAc (3 x 2.00 mL). The combined organic layers were concentrated *in vacuo* and the crude material was purified by silica gel column chromatography using hexanes/EtOAc or dichloromethane/EtOAc as the eluent to obtain the desired product.

General procedure B: Oxidation of the vinylboronic esters to ketones

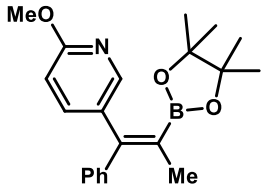


[2] J. H. Clotet, L. O. Viturro, S. R. Popero and P. D. Barjoan, WO2018115362, June 28, 2018.
[3] S. Diez-Gonzalez, E. C. Escudero-Adan, J. Benet-Buchholz, E. D. Stevens, A. M. Z. Slawinc and S. P. Nolan, *Dalton Trans*., 2010, **39**, 7595.
[4] Y. Huang and M. K. Brown, *Angew. Chem. Int. Ed.*, 2019, **58**, 6048.

The purified tetrasubstituted alkene (0.20 mmol) was dissolved in THF (1.00 mL) and $NaBO_3 \bullet 4H_2O$ (96.00 mg, 0.60 mmol, 3.0 equiv) was added, followed by addition of H_2O (1.00 mL). The reaction was allowed to stir at room temperature for 2-12 h until complete conversion was observed by TLC analysis then was quenched upon the addition of aqueous saturated $Na_2S_2O_3$ (3 mL) and extracted with Et_2O (3 x 2 mL). The combined organic layers were washed with 2 M HCl (3 x 3 mL), dried over Na_2SO_4, gravity filtered, and concentrated *in vacuo*. The residue was purified via silica gel chromatography (hexanes/EtOAc) to afford the desired ketone.

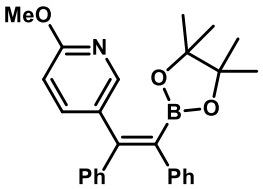
Characterization Data:

(E)-2-methoxy-5-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)pyridine



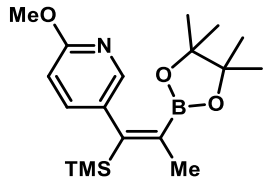
The title compound was prepared according to general procedure **A** to give a white solid in 95% average isolated yield. **M. P.**: 114-116 ^oC. **IR (neat)**: 2974 (w), 2941 (w), 2852 (w), 1599 (m), 1493 (m), 1286 (m), 1109 (m), 843 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 2.4, 0.7 Hz, 1H), 7.34 – 7.19 (m, 4H), 7.10 (s, 2H), 6.57 (dd, *J* = 8.5, 0.7 Hz, 1H), 3.89 (s, 3H), 1.85 (s, 3H), 1.16 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 148.1, 146.5, 141.4, 139.4, 133.6, 129.5, 127.9, 126.9, 109.5, 83.4, 53.3, 24.6, 19.2. **HRMS (EI+):** Calcd for $C_{21}H_{26}O_3NB$ (M^+): 351.2006, Found 351.2005.

(E)-5-(1,2-diphenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)-2-methoxypyridine



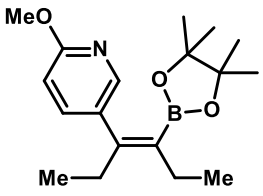
The title compound was prepared according to general procedure **A** to give a white solid in 79% average isolated yield. **M. P.**:158-160 ^oC. **IR (neat)**: 2975 (w), 2923 (w), 2849 (w), 1596 (m), 1491 (m), 1109 (m), 825 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 2.5, 0.7 Hz, 1H), 7.37 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.15 – 6.98 (m, 8H), 6.98 – 6.83 (m, 2H), 6.64 (dd, *J* = 8.5, 0.7 Hz, 1H), 3.93 (s, 3H), 1.14 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.7, 148.1, 146.8, 141.4, 141.3, 139.8, 133.8, 130.8, 129.5, 127.9, 127.6, 127.0, 125.9, 109.9, 83.8, 53.4, 24.5. **HRMS (EI+):** Calcd for $C_{26}H_{28}O_3NB$ (M^+): 413.2162, Found 413.2162.

(Z)-2-methoxy-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(trimethylsilyl)prop-1-en-1-yl)pyridine



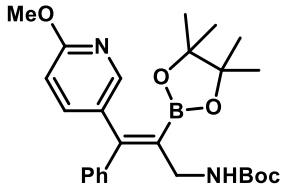
The title compound was prepared according to general procedure **A** to give a colourless liquid in 86% average isolated yield. **IR (neat)**: 2976 (w), 2949 (w), 2898 (w), 1597(m), 1486 (m), 1300 (m), 1117 (m), 837 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 – 7.47 (m, 1H), 7.13 (dd, *J* = 8.4, 2.5 Hz, 1H), 6.53 (dd, *J* = 8.4, 0.7 Hz, 1H), 3.81 (s, 3H), 1.93 (s, 3H), 0.93 (s, 12H), 0.00 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2, 150.5, 144.5, 138.4, 135.5, 109.0, 83.1, 53.1, 24.4, 20.5, 0.21. **HRMS (EI+):** Calcd for $C_{18}H_{30}O_3NBSi$ (M^+): 347.2088, Found 347.2083.

(E)-2-methoxy-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-en-3-yl)pyridine



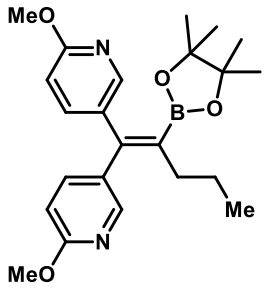
The title compound was prepared according to general procedure **A** to give a colorless liquid in 79% average isolated yield. **IR (neat)**: 2979 (w), 2932 (w), 2871 (w), 1598 (m), 1488 (m), 1359 (m), 1280 (m), 1028 (m), 829 (m), 731 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.4 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.63 (dd, *J* = 8.4, 0.7 Hz, 1H), 3.89 (s, 3H), 2.38 (q, *J* = 7.5 Hz, 2H), 2.27 (q, *J* = 7.5 Hz, 2H), 1.04 (s, 12H), 1.02 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0, 148.7, 146.0, 138.5, 133.5, 109.3, 83.0, 53.3, 26.2, 24.5, 24.2, 14.5, 12.7. **HRMS (EI+):** Calcd for $C_{18}H_{28}O_3NB$ (M^+): 317.2162, Found 317.2163

tert-butyl-(E)-(3-(6-methoxypyridin-3-yl)-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)carbamate



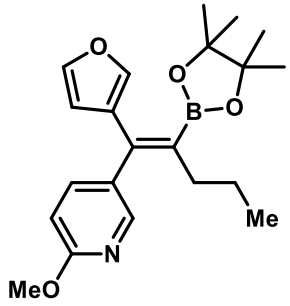
The title compound was prepared according to general procedure **A** (the reaction was run at 45 °C) to give a pale yellow solid in 56% average isolated yield. **M. P.**: 125-127 °C. **IR (neat)**: 3429 (w), 2976 (w), 2930 (w), 2879(w), 1705 (s), 1602 (m), 1487 (m), 1357 (m), 1116 (s), 1028 (m), 841 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.0 Hz, 1H), 7.36 – 7.12 (m, 4H), 7.10 – 6.91 (m, 2H), 6.53 (dd, *J* = 8.6, 1.6 Hz, 1H), 4.74 (s, 1H), 3.87 (s, 2H), 3.83 (s, 3H), 1.34 (s, 9H), 1.21 – 1.06 (m, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.4, 154.2, 148.6, 145.4, 138.3, 131.6, 127.9, 127.2, 126.5, 108.6, 82.7, 77.8, 52.3, 41.9, 27.2, 23.5, 23.4. **HRMS (EI+):** Calcd for $C_{26}H_{36}O_5N_2B$ ($M+H^+$): 467.2717, Found 467.2710.

5,5'-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-ene-1,1-diyl)bis(2-methoxypyridine)



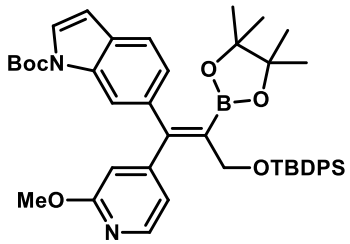
The title compound was prepared according to general procedure **A** to give a pale yellow liquid in 45% average isolated yield. **IR (neat)**: 2976 (w), 2932 (w), 2852 (w), 1599 (w), 1488 (s), 1279 (s), 1126 (s), 1020 (s), 870 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (m, 2H), 7.34 – 7.07 (m, 2H), 6.77 – 6.63 (m, 1H), 6.61 – 6.48 (m, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 2.44 – 2.10 (m, 2H), 1.66 – 1.37 (m, 2H), 1.13 (s, 12H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.9, 146.5, 142.5, 140.9, 139.6, 136.0, 130.0, 128.9, 111.1, 110.1, 83.5, 53.3, 35.1, 24.7, 24.7, 23.3, 14.3. **HRMS (EI+):** Calcd for $C_{23}H_{31}O_4N_2B$ (M^+): 410.2377, Found 410.2378.

(E)-5-(1-(furan-3-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)-2-methoxypyridine



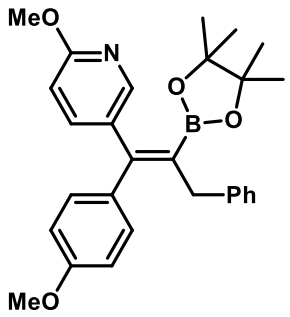
The title compound was prepared according to general procedure **A** to give a white solid in 64% average isolated yield. **M. P.**: 108-111 °C. **IR (neat)**: 2971 (w), 2932 (w), 2852 (w), 1598 (w), 1489 (s), 1282 (s), 1124 (s), 1015 (s), 836 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 2.4, 0.8 Hz, 1H), 7.36 – 7.09 (m, 3H), 6.67 (dd, *J* = 8.5, 0.8 Hz, 1H), 6.23 (dd, *J* = 1.9, 0.8 Hz, 1H), 3.92 (s, 3H), 2.18 – 2.05 (m, 2H), 1.50 – 1.38 (m, 2H), 1.22 (s, 12H), 0.84 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.3, 163.0, 146.7, 146.5, 143.4, 139.7, 139.3, 133.3, 130.3, 110.3, 109.7, 83.5, 53.4, 53.3, 35.7, 24.6, 23.5, 14.3. **HRMS (EI+):** Calcd for $C_{21}H_{28}O_4NB$ (M^+): 369.2111, Found 369.2114.

tert-butyl-(Z)-6-(3-((tert-butyldiphenylsilyl)oxy)-1-(2-methoxypyridin-4-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-1H-indole-1-carboxylate



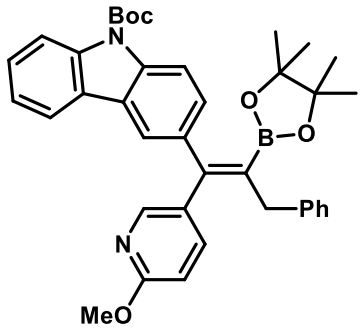
The title compound was prepared according to general procedure **A** to give a colorless oil containing product and 5% impurity (small peaks in 0.8-1.5 ppm region). **IR (neat)**: 2975 (w), 2918 (w), 2856 (w), 1732 (s), 1599 (m), 1305 (s), 1120 (s), 1042(s), 820 (m), 725 (s) cm^{-1}**. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (m, 2H), 7.72 – 7.61 (m, 4H), 7.56 (d, *J* = 3.7 Hz, 1H), 7.49 –7.27 (m, 7H), 7.10 (m, 1H), 6.58 – 6.35 (m, 3H), 4.30 (s, 2H), 3.86 (s, 3H), 1.56 (s, 9H), 1.10 (s, 12H), 1.03 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 152.4, 149.6, 146.3, 138.5, 135.6, 134.7, 133.5, 130.1, 129.4, 127.4, 126.4, 124.0, 120.1, 117.5, 116.3, 110.9, 107.0, 83.5, 65.4, 53.2, 28.0, 26.9, 24.8, 19.2. HRMS (ESI+): Calcd for $C_{44}H_{53}O_6N_2BSi$ (M+H+): 745.3839, Found: 745.3847.

(E)-2-methoxy-5-(1-(4-methoxyphenyl)-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)pyridine



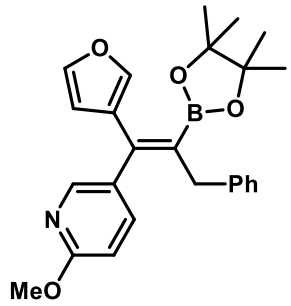
The title compound was prepared according to general procedure **A** to give a white solid in 73% average isolated yield. **M. P.**: 111-116 °C. **IR (neat)**: 3059 (w), 3026 (w), 2977 (m), 1600 (s), 1352 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 – 8.00 (m, 1H), 7.35 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.26 (m, 4H), 7.16 (m, 1H), 7.11 – 7.05 (m, 2H), 6.85 – 6.74 (m, 2H), 6.64 – 6.57 (m, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 3.65 (s, 2H), 0.91 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.4, 158.8, 148.6, 146.5, 141.3, 139.7, 133.8, 133.7, 130.3, 128.8, 128.2, 125.8, 113.5, 109.7, 83.4, 55.2, 53.4, 43.8, 39.5, 27.1, 24.4. **HRMS (EI+):** Calcd for $C_{28}H_{32}BNO_4$ (M^+): 457.2424, Found: 457.2425.

tert-butyl-(Z)-3-(1-(6-methoxypyridin-3-yl)-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-9H-carbazole-9-carboxylate



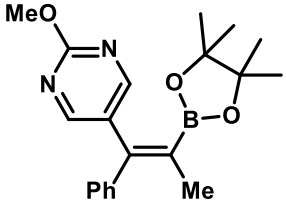
The title compound was prepared according to general procedure **A** to give a white solid in 54% average isolated yield. **M. P.**: 28.4-30.6 °C. **IR (neat)**: 3026 (w), 2976 (M), 1727 (s), 1600 (m), 1489 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.5 Hz, 1H), 8.20 – 8.07 (m, 2H), 7.96 – 7.81 (m, 2H), 7.44 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1H), 7.38 – 7.22 (m, 7H), 7.21 – 7.12 (m, 1H), 6.65 (dd, *J* = 8.5, 0.8 Hz, 1H), 3.91 (s, 3H), 3.71 (s, 2H), 1.73 (s, 9H), 0.83 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 151.0, 148.5, 146.6, 140.8, 139.9, 139.2, 138.9, 137.9, 130.9, 128.9, 128.8, 128.3, 127.1, 126.0, 125.7, 125.4, 123.0, 120.6, 119.7, 116.2, 115.8, 110.5, 83.9, 83.4, 53.4, 39.8, 28.4, 24.4. **HRMS (ESI+):** Calcd for $C_{38}H_{42}BN_2O_5$ ($M+H^+$): 617.3181, Found: 617.3182.

(E)-5-(1-(furan-3-yl)-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-2-methoxypyridine



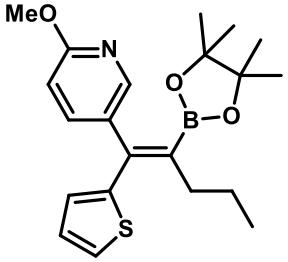
The title compound was prepared according to general procedure **A** to give a colorless oil in 51% average isolated yield. **IR (neat)**: 3004 (w), 2977 (w), 2943 (w), (w), 1732 (s), 1599 (m), 1488 (s) cm^{-1}. ^{1}H **NMR** (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.39 (d, J = 8.5 Hz, 1H), 7.32 (m, 2H), 7.29 – 7.18 (m, 4H), 7.17 – 7.11 (m, 1H), 6.67 (d, J = 8.5 Hz, 1H), 6.39 – 6.19 (m, 1H), 3.91 (s, 3H), 3.56 (s, 2H), 0.98 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.2, 146.4, 142.6, 141.4, 140.4, 139.5, 137.9, 129.8, 128.9, 128.7, 128.2, 126.0, 111.1, 110.4, 83.5, 53.4, 39.1, 24.4. **HRMS (ESI+):** Calcd for $C_{25}H_{29}BNO_4$ ($M+H^+$): 418.2184, Found: 418.2187.

(E)-2-methoxy-5-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)pyrimidine



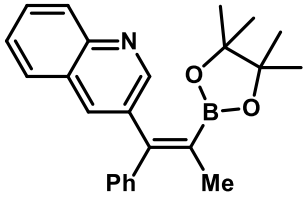
The title compound was prepared according to general procedure **A** to give a colorless oil in 66% average isolated yield. **IR (neat)**: 3053 (w), 2959 (m), 2853 (w), 1657 (s), 1474 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (s, 2H), 7.34 – 7.21 (m, 3H), 7.12 – 6.98 (m, 2H), 3.93 (s, 3H), 1.82 (s, 3H), 1.13 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 164.5, 159.0, 145.9, 140.9, 131.6, 129.4, 128.3, 127.4, 83.7, 54.9, 29.7, 24.7, 19.5. **HRMS (ESI):** Calcd for $C_{20}H_{26}BN_2O_3$ ($M+H^+$): 353.2035, Found 353.2033.

(Z)-2-methoxy-5-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(thiophen-2-yl)pent-1-en-1-yl)pyridine



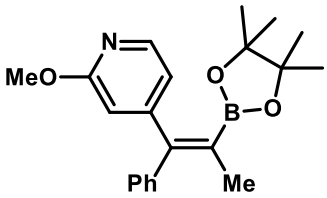
The title compound was prepared according to general procedure **A** to give a colorless oil in 63% average isolated yield. **IR (neat)**: 3066 (w), 2969 (m), 2936 (m), 1582 (s), 1461 (m) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 2.5, 0.8 Hz, 1H), 7.44 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.31 (dt, *J* = 5.1, 1.0 Hz, 1H), 7.08 – 6.94 (m, 1H), 6.84 (dd, *J* = 3.6, 1.3 Hz, 1H), 6.66 (dd, *J* = 8.5, 0.8 Hz, 1H), 3.95 (d, *J* = 1.3 Hz, 3H), 2.58 – 2.41 (m, 2H), 1.64 – 1.54 (m, 2H), 1.13 (s, 12H), 1.00 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 163.4, 146.4, 143.6, 134.0, 139.3, 134.0, 127.7, 126.6, 126.0, 109.7, 83.5, 53.5, 35.8, 24.7, 23.4, 14.4. **HRMS (ESI):** Calcd for $C_{21}H_{29}BNO_3S$ ($M+H^+$): 386.2037, Found 386.1963.

(E)-3-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)quinoline



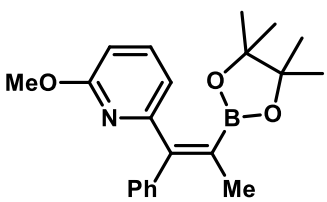
The title compound was prepared according to general procedure **A** to give a colorless oil in 50% average isolated yield. **IR (neat)**: 3043 (w), 2979 (m), 2853 (w), 1617 (m), 1331 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.83 – 8.63 (m, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.90 (t, *J* = 1.5 Hz, 1H), 7.77 – 7.58 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.21 (m, 3H), 7.21 – 7.08 (m, 2H), 1.94 (s, 3H), 1.08 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.6, 148.7, 141.2, 137.5, 135.5, 129.7, 129.1, 128.9, 128.6, 128.2, 127.8, 127.5, 127.2, 126.6, 83.6, 24.6, 19.6. **HRMS (APCI):** Calcd for $C_{24}H_{27}BNO_2$ ($M+H^+$): 372.2129, Found 372.2135.

(E)-2-methoxy-4-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)pyridine



The title compound was prepared according to general procedure **A** to give a colorless oil in 78% average isolated yield. **IR (neat)**: 3016 (w), 2975 (m), 2905 (w), 2341 (w), 1538 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 – 7.88 (m, 1H), 7.34 – 7.26 (m, 2H), 7.26 – 7.18 (m, 1H), 7.15 – 7.04 (m, 2H), 6.64 (dd, *J* = 5.3, 1.3 Hz, 1H), 6.60 (t, *J* = 1.3 Hz, 1H), 3.89 (s, 3H), 1.83 (s, 3H), 1.17 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 154.7, 148.8, 145.9, 140.4, 129.4, 128.1, 127.1, 117.7, 111.0, 83.6, 53.3, 24.5, 19.2. **HRMS (EI+):** Calcd for $C_{21}H_{27}BNO_3$ ($M+H^+$): 352.2079, Found 352.2079.

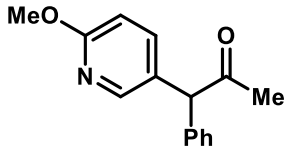
(E)-2-methoxy-6-(1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)pyridine



The title compound was prepared according to general procedure **A** to give a colorless oil containing the desired product and an inseparable impurity (observed at 1.20 ppm). **IR (neat)**: 3054 (w), 2975 (m), 2947 (w), 2341 (m), 1597 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.3, 7.6 Hz, 1H), 7.42 – 7.32 (m, 2H), 7.32 – 7.24 (m, 1H), 7.21 – 7.14 (m, 2H), 6.60 – 6.41 (m, 2H), 3.95 (s, 3H), 1.83 (s, 3H), 1.35 (s, 12H). ^{13}**C NMR** (100 MHz, $CDCl_3$) δ 162.5, 158.4, 143.1, 136.7, 129.7, 128.3, 126.9,

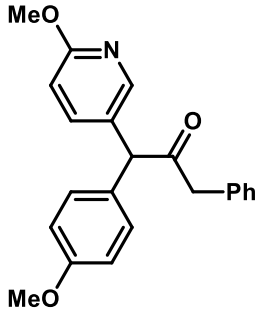
111.6, 103.5, 81.1, 55.0, 27.2, 24.8, 15.9. **HRMS (ESI):** Calcd for $C_{21}H_{27}BNO_3$ ($M+H^+$): 352.2079, Found 352.2080.

1-(6-methoxypyridin-3-yl)-1-phenylpropan-2-one



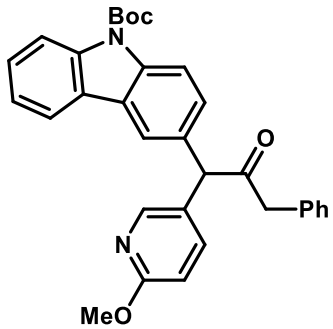
The title compound was prepared according to general procedure B to give a colorless oil in 92% isolated yield. **IR (neat)**: 2945 (w), 2941 (w), 2846 (w), 1713 (s) 1604 (m), 1489 (m), 1281 (m), 1125 (m), 825 (m) $cm^{-1.}$ **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.6 Hz, 1H), 7.44 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.37 – 7.30 (m, 2H), 7.27 – 7.25 (m, 1H), 7.24 – 7.16 (m, 2H), 6.68 (d, *J* = 8.6 Hz, 1H), 5.00 (s, 1H), 3.88 (s, 3H), 2.21 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 205.9, 163.3, 146.6, 139.1, 137.7, 129.0, 128.6, 127.5, 126.9, 110.8, 61.5, 53.3, 29.8. **HRMS (EI+):** Calcd for $C_{15}H_{15}O_2N$ (M+): 241.1103, Found: 241.1099.

1-(4-methoxyphenyl)-1-(6-methoxypyridin-3-yl)-3-phenylpropan-2-one



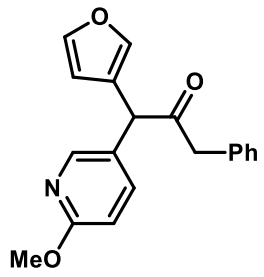
The title compound was prepared according to general procedure **B** to give a colorless oil in 94% average isolated yield. **IR (neat)**: 3008 (m), 2954 (m), 2926 (w), 1717 (s), 1605 (m) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.5 Hz, 1H), 7.42 – 7.32 (m, 1H), 7.32 – 7.20 (m, 3H), 7.16 – 7.00 (m, 4H), 6.93 – 6.82 (m, 2H), 6.65 (d, *J* = 8.6 Hz, 1H), 5.06 (s, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 3.77 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.7, 163.3, 159.1, 146.6, 139.3, 133.9, 130.0, 129.5, 129.4, 128.8, 127.2, 127.1, 114.5, 110.8, 58.5, 55.3, 53.5, 49.4. **HRMS (EI+):** Calcd for $C_{22}H_{21}NO_3$ (M+): 347.1521, Found: 347.1525.

***tert*-butyl-3-(1-(6-methoxypyridin-3-yl)-2-oxo-3-phenylpropyl)-9H-carbazole-9-carboxylate**



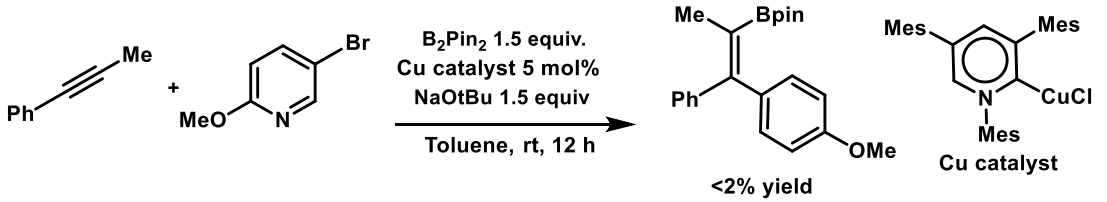
The title compound was prepared according to general procedure **B** to give a colorless oil in 92% isolated yield. **IR (neat)**: 3061 (w), 3004 (w), 2944 (w), 1717 (s), 1604 (s) cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (m, 2H), 7.98 – 7.86 (m, 2H), 7.75 (d, *J* = 1.9 Hz, 1H), 7.53 – 7.37 (m, 2H), 7.37 – 7.22 (m, 5H), 7.14 (m, 2H), 6.67 (d, *J* = 8.6 Hz, 1H), 5.29 (s, 1H), 3.89 (d, *J* = 1.2 Hz, 3H), 3.83 (s, 2H), 1.74 (d, *J* = 1.3 Hz, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 205.7, 163.3, 151.0, 146.6, 139.4, 138.9, 137.9, 133.8, 132.1, 129.6, 128.9, 127.8, 127.5, 127.3, 127.2, 126.5, 125.3, 123.2, 119.8, 119.7, 116.9, 116.3, 110.8, 84.2, 59.1, 53.5, 49.6, 28.4. **HRMS (ESI+):** Calcd for $C_{32}H_{31}N_2O_4$ ($M+H^+$): 507.2278, Found: 507.2278.

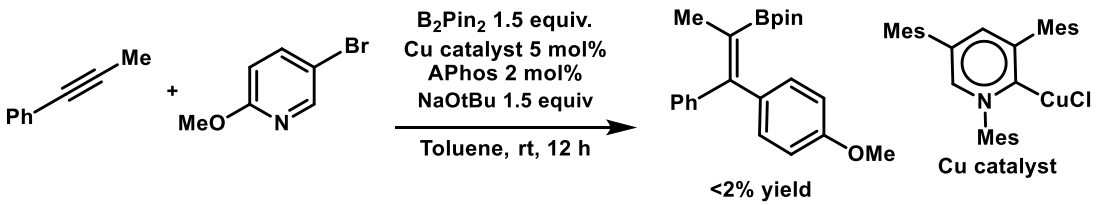
1-(furan-3-yl)-1-(6-methoxypyridin-3-yl)-3-phenylpropan-2-one

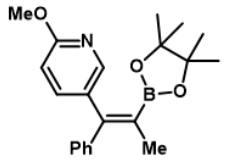


The title compound was prepared according to general procedure **B** to give a white solid in 87% isolated yield. **M. P.** 65-68 °C. **IR (neat)**: 3137 (w), 3014 (w), 2991 (w), 1715 (s), 1604 (m) cm^{-1}. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.5 Hz, 1H), 7.43 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.40 (t, *J* = 1.7 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.32 – 7.26 (m, 1H), 7.19 – 7.12 (m, 2H), 6.72 (d, *J* = 8.6 Hz, 1H), 6.26 – 6.21 (m, 1H), 4.99 (s, 1H), 3.95 (s, 3H), 3.82 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 204.8, 163.6, 146.6, 143.4, 140.6, 138.8, 133.6, 129.5, 128.8, 127.3, 126.3, 122.3, 111.2, 110.6, 53.5, 50.5, 48.9. **HRMS (ESI+):** Calcd for $C_{19}H_{17}NO_3Na$ ($M+Na^+$): 330.1101, Found: 330.1103.

Control Experiments:







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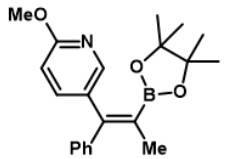
1.00
4.73
2.00
1.03
2.80
2.84
10.95

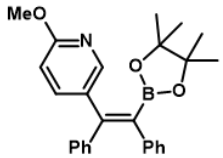
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

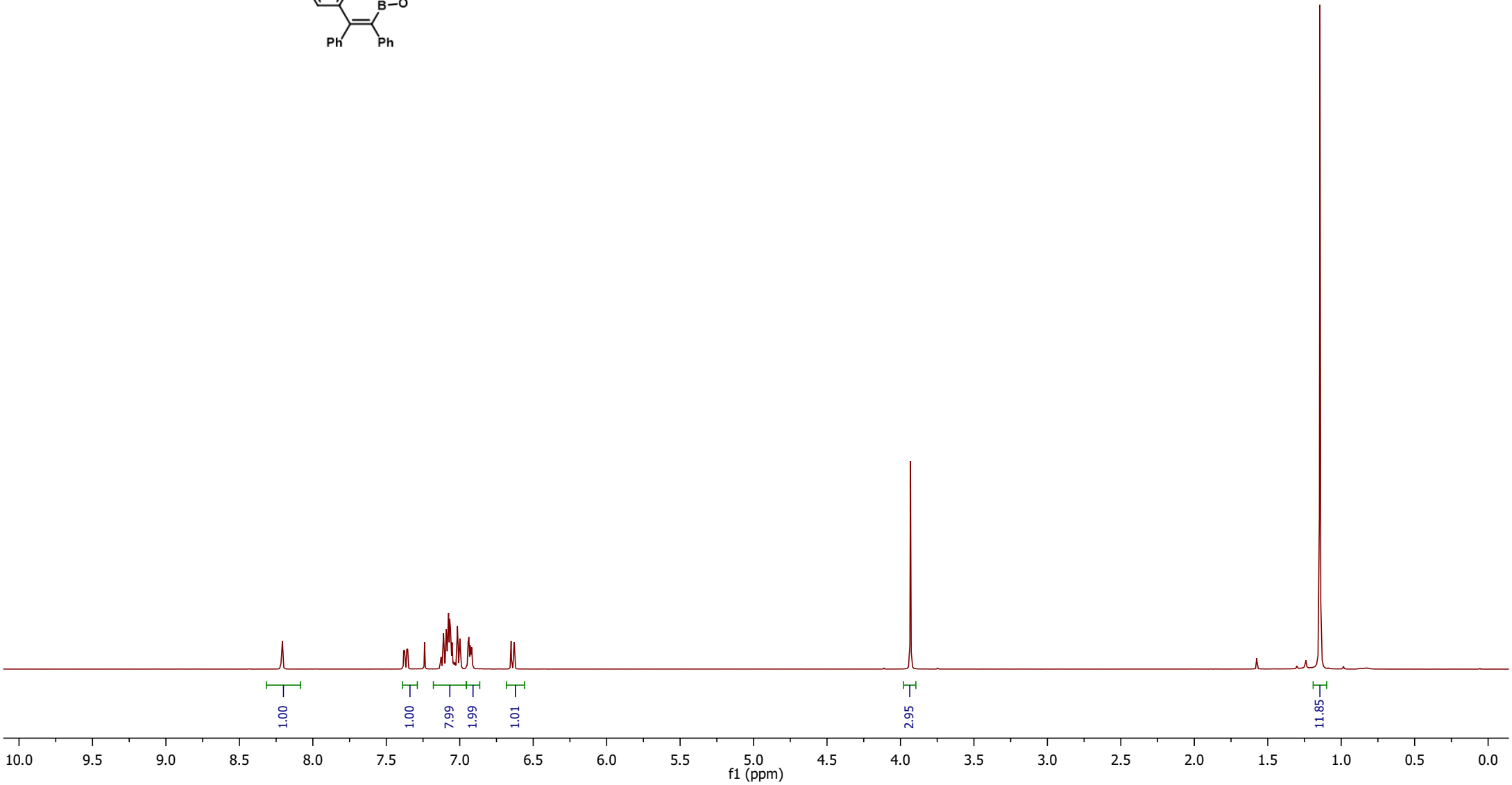
f1 (ppm)



163.21
148.17
146.50
141.49
139.43
133.66
129.55
127.96
126.95
109.54
83.45
53.37
24.61
19.25

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
N
O
B
O
Ph
Ph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7.99
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2.95
11.85
10.0
9.5
9.0
8.5
8.0
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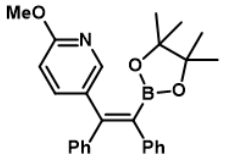
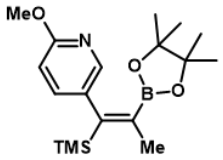
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



163.73
148.13
146.88
141.48
141.31
139.82
133.81
130.89
129.51
127.95
127.63
127.02
125.95
109.97
83.82
53.49
24.56

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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N
O
B
O
TMS
Me

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1.05
1.05
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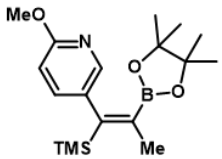
3.19
12.71
9.29
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


MeO
N
O
B
O
TMS
Me

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144.55
138.49
135.52
109.03
83.16
53.19
24.40
20.52
0.21
230
220
210
200
190
180
170
160
150
140
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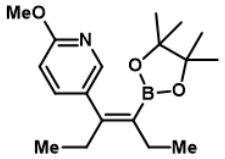
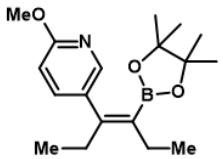
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


MeO
N
O
B
O
Me
Me

1.00
1.02
1.01
2.98
1.84
2.03
11.90
2.56
2.97
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
f1 (ppm)



163.00
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146.07
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109.35
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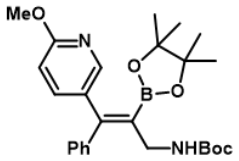
24.54
24.27
14.57
12.72

f1 (ppm)


MeO
N
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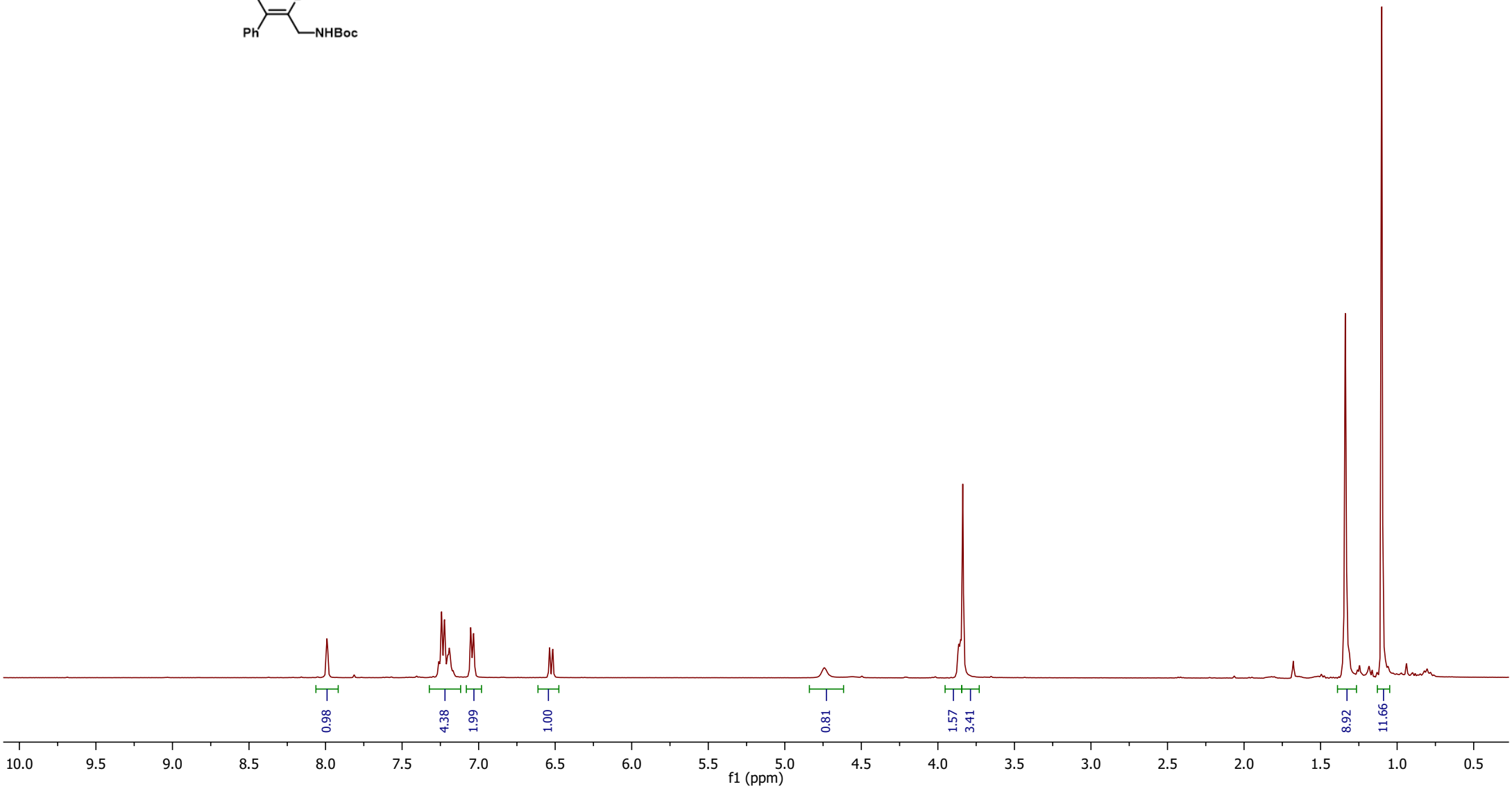
B
O
Ph
NHBoc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8.92
11.66
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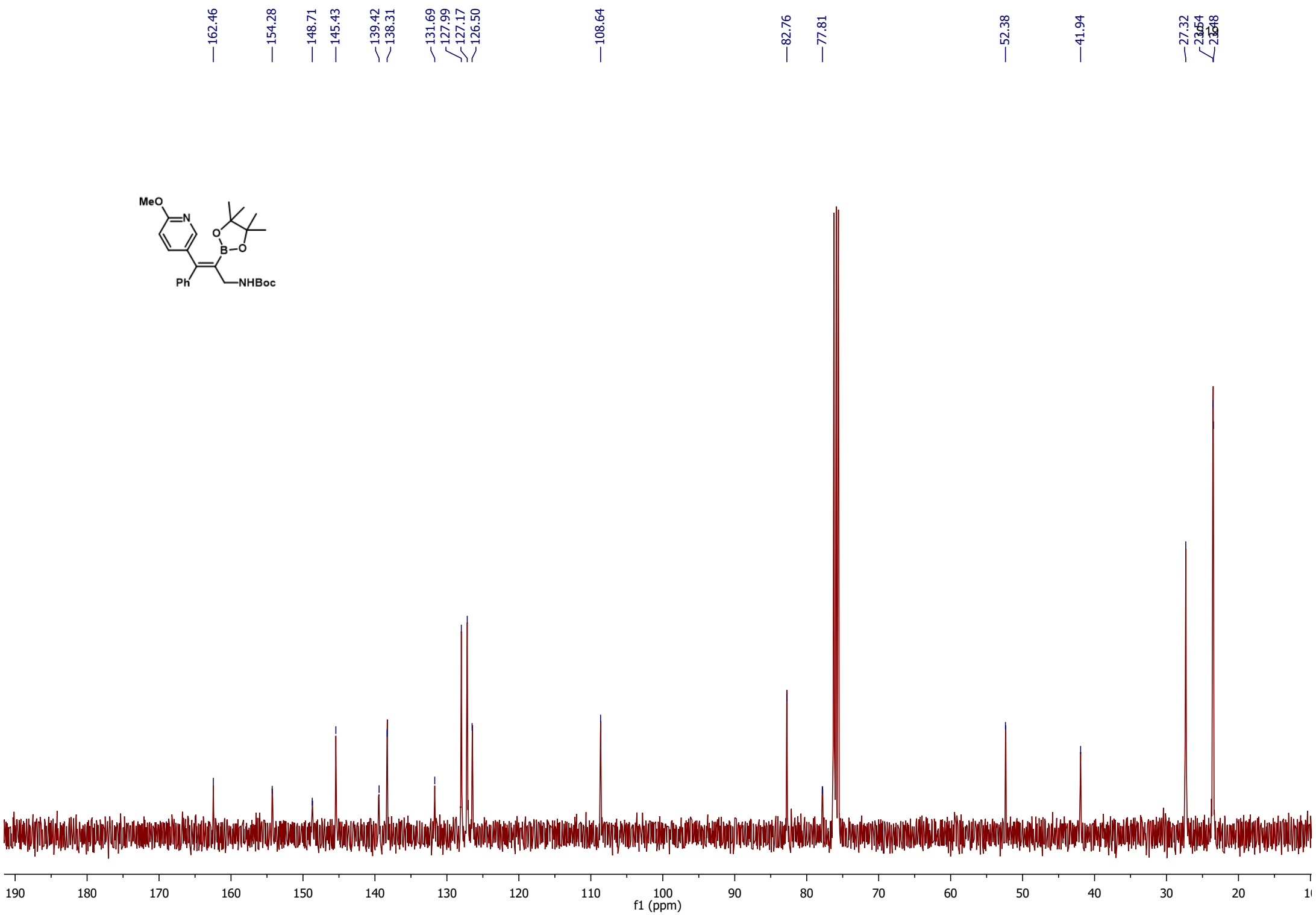
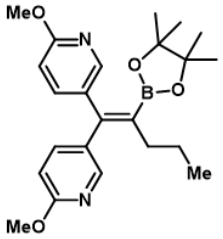
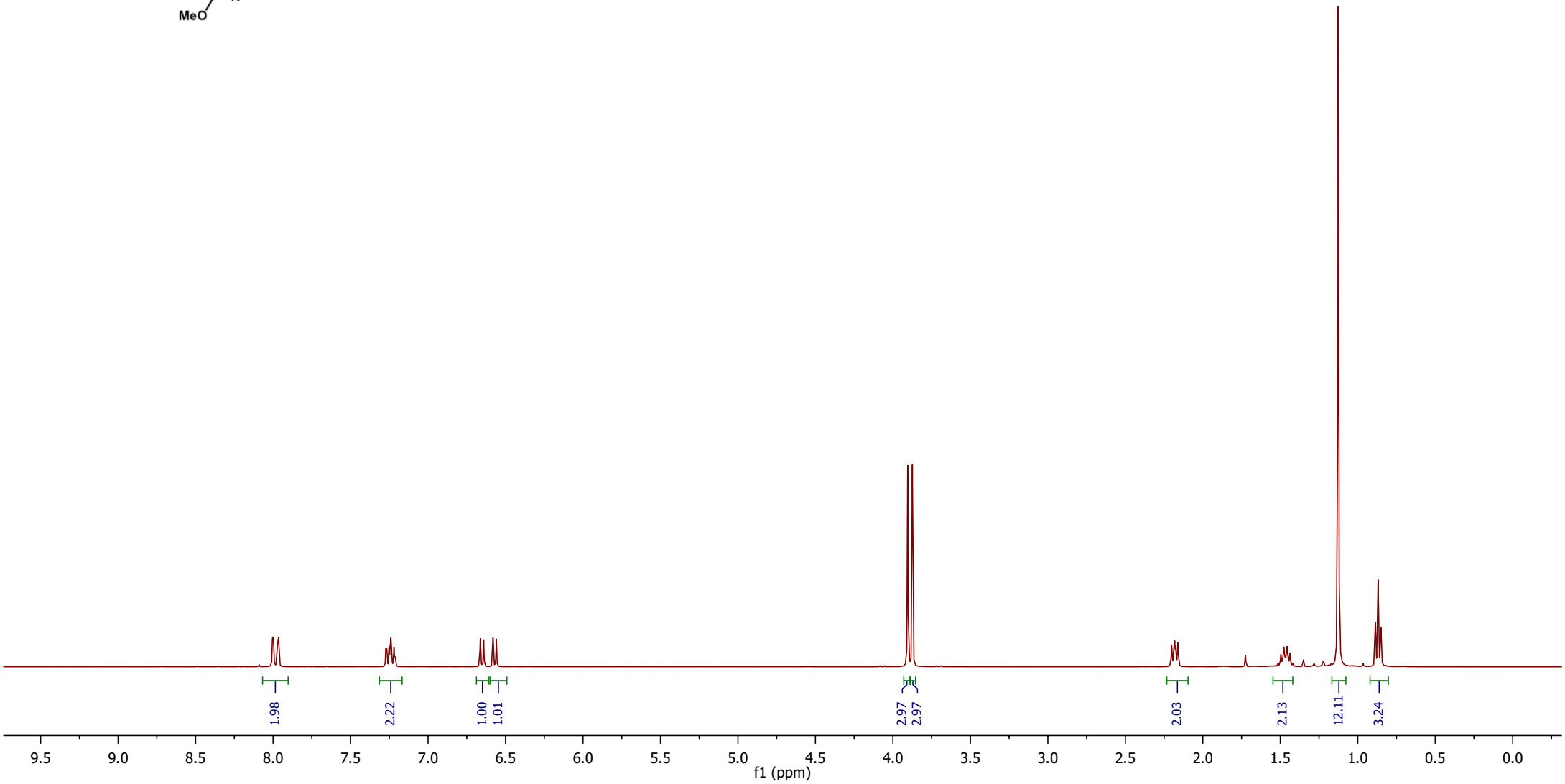
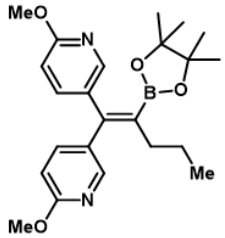
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

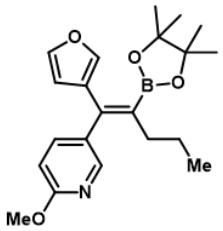

162.46
154.28
148.71
145.43
139.42
138.31
131.69
127.99
127.17
126.50
108.64
82.76
77.81
52.38
41.94
27.32
23.54
23.48
MeO
N
O
B
O
Ph
NHBoc
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


MeO
N
O
B
O
Me
N
MeO

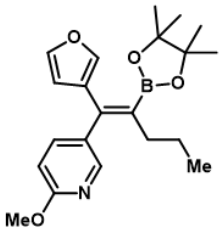

1.98
2.22
1.00
1.01
2.97
2.97
2.03
2.13
12.11
3.24
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



163.34
163.02
146.71
146.50
143.42
139.71
139.39
133.33
130.38
110.33
109.73
83.50
53.40
53.38
35.77
24.66
23.58
14.32

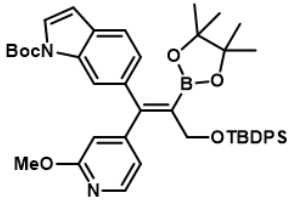

O
O
B
O
Me
N
MeO

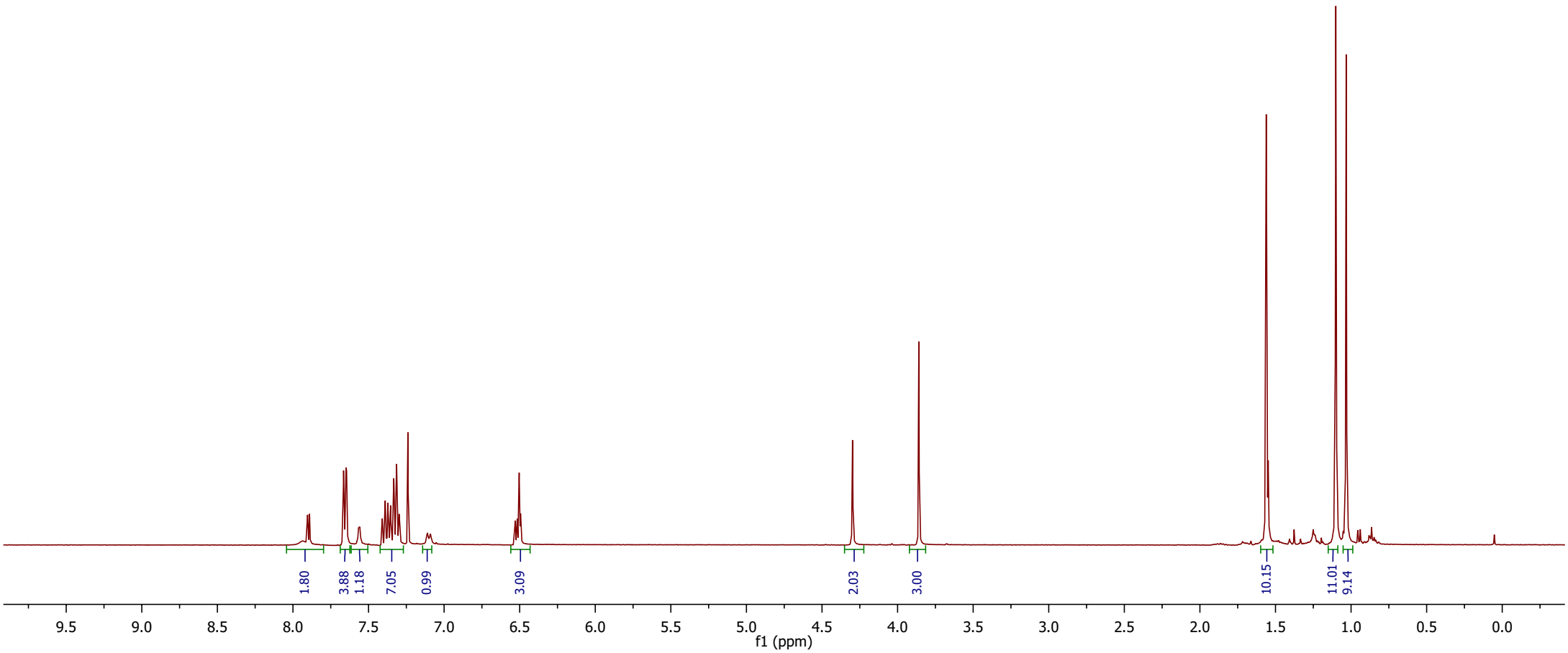
1.00
2.93
0.98
0.87
2.89
1.86
2.09
10.94
2.91
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

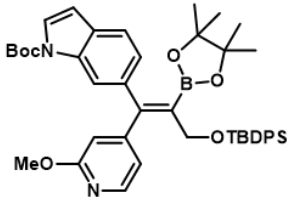


162.95
146.53
142.52
140.90
139.62
136.08
130.01
128.93
111.11
110.16
83.58
53.35
35.19
24.79
24.70
23.33
14.31

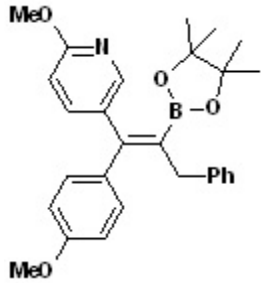
f1 (ppm)


BocN
O
B
O
OTBDPS
MeO
N

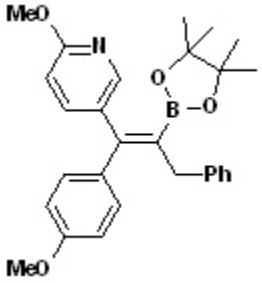

1.80
3.88
1.18
7.05
0.99
3.09
2.03
3.00
10.15
11.01
9.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


BocN
O
B
O
OTBDPS
MeO
N

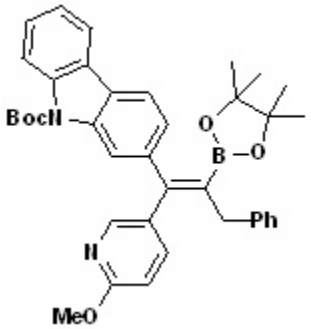
164.08
152.47
149.67
146.37
138.54
135.69
134.73
133.53
130.18
129.43
127.46
126.46
124.04
120.12
117.59
116.31
110.99
107.03
83.59
65.45
53.23
28.00
26.95
24.83
19.23
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

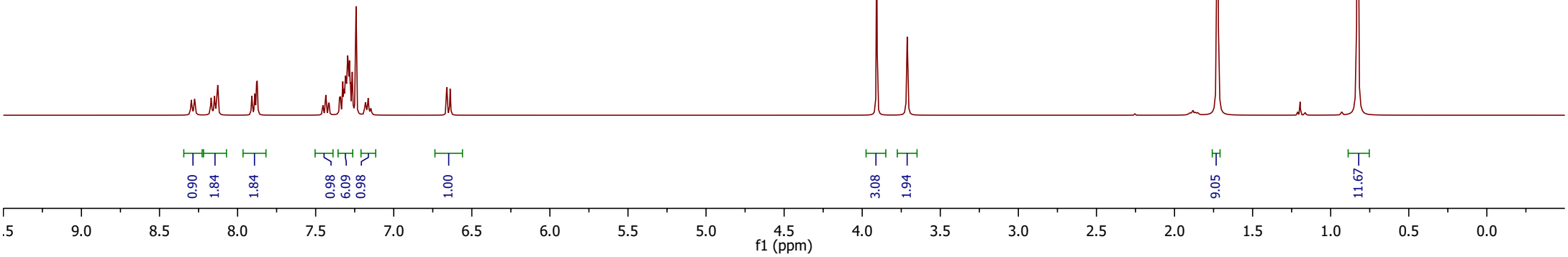

MeO
O
B
O
Ph
MeO

0.91
1.08
4.12
0.97
1.93
2.01
1.00
3.01
3.00
1.93
11.58
.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
f1 (ppm)

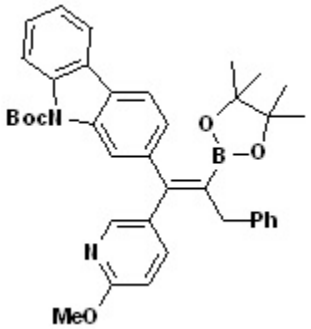


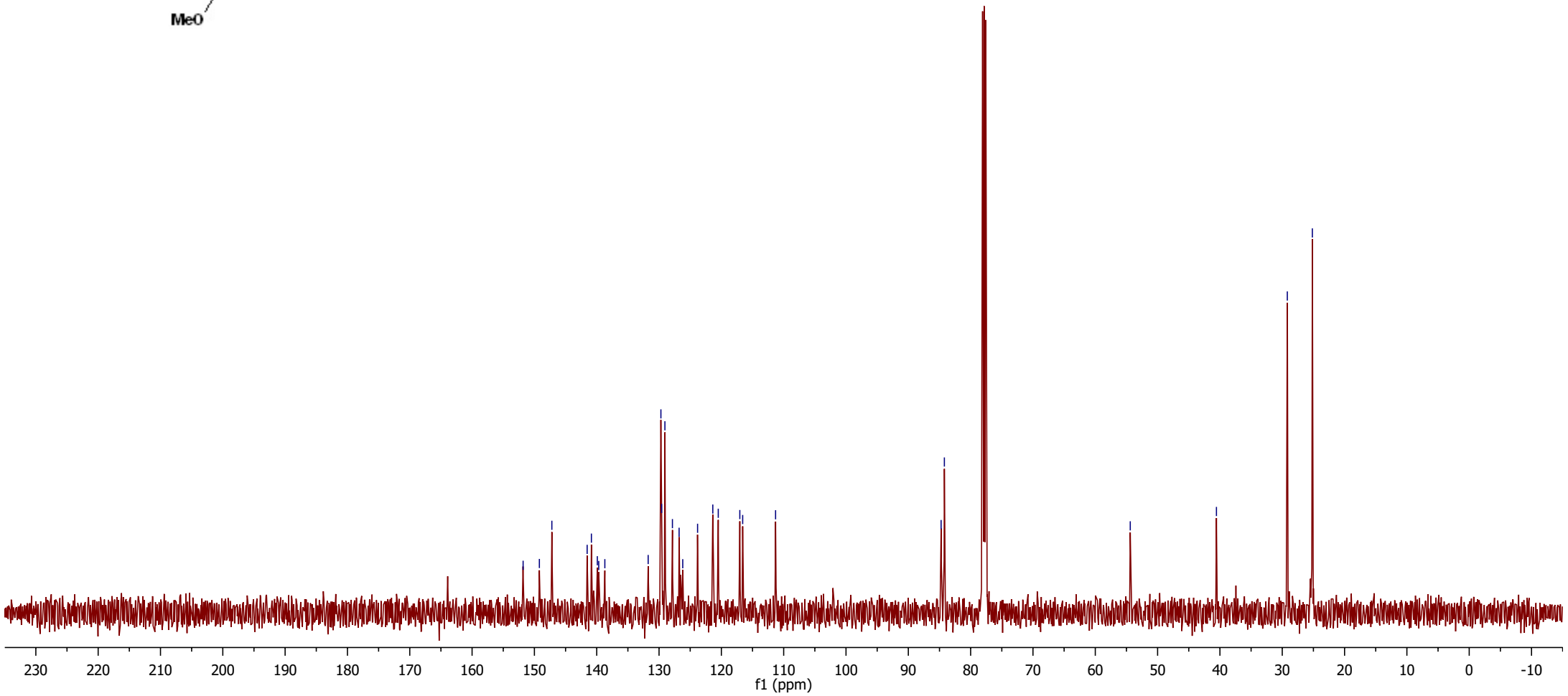
163.41
158.80
148.59
146.54
141.25
139.65
133.84
133.71
130.32
128.76
128.15
125.78
113.53
109.66
83.36
55.17
53.44
43.78
39.53
27.06
24.37

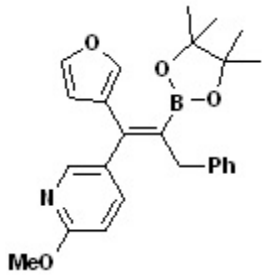

BocN
O
B
O
Ph
N
MeO

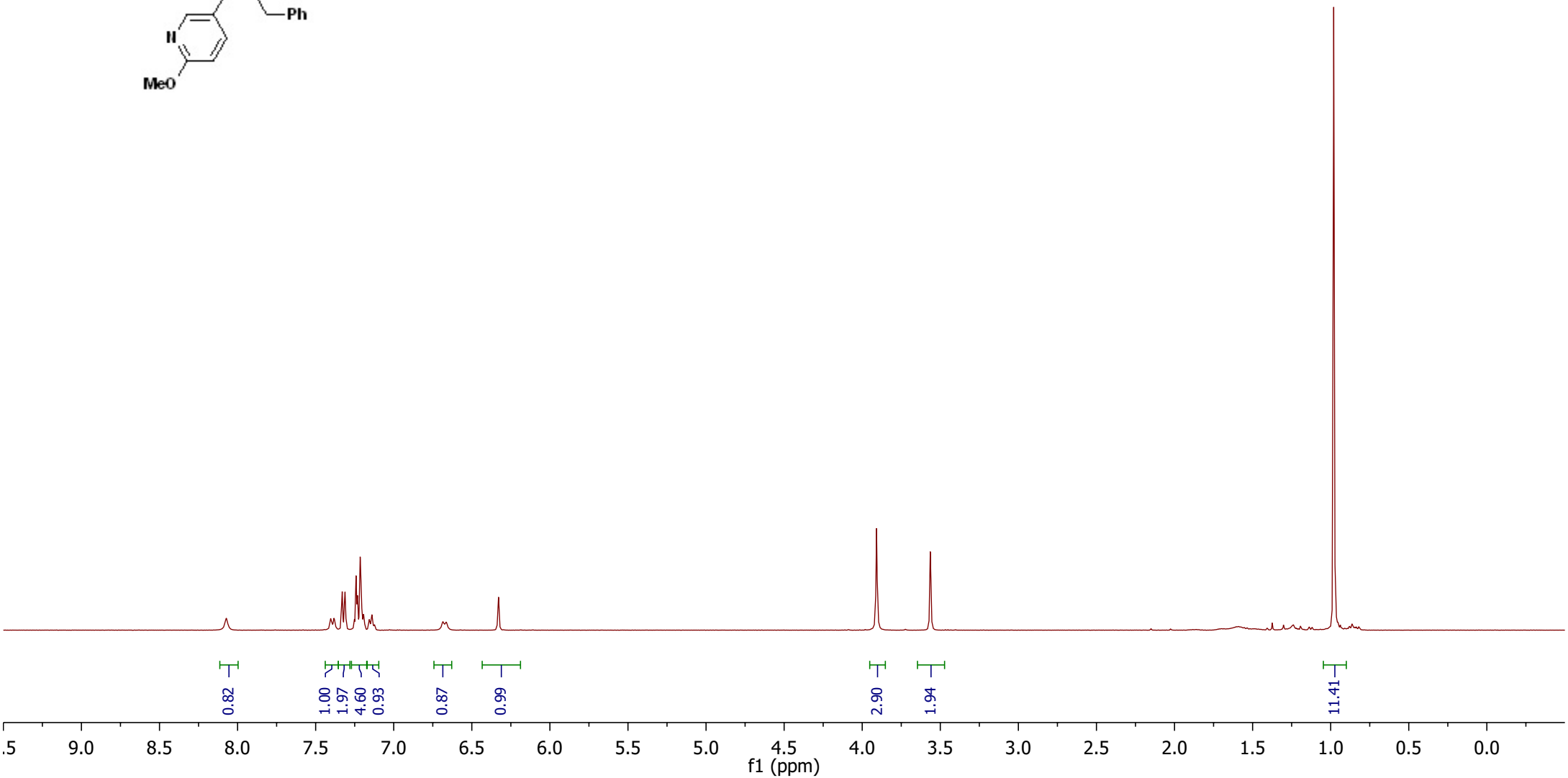

0.90
1.84
1.84
0.98
6.09
0.98
1.00
3.08
1.94
9.05
11.67
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

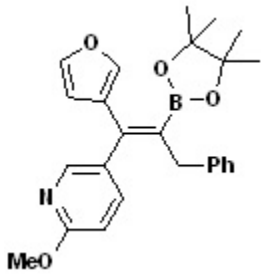
151.81
149.20
147.20
141.54
140.85
139.90
139.68
138.70
131.75
129.70
129.58
129.06
127.85
126.78
126.20
123.82
121.37
120.50
117.04
116.58
111.30
84.74
84.22
54.39
40.56
29.19
25.17



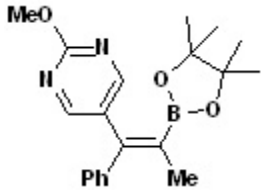



O
O
B
O
Ph
N
MeO

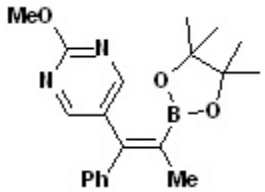

0.82
1.00
1.97
4.60
0.93
0.87
0.99
2.90
1.94
11.41
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


O
O
B
O
Ph
H
MeO

163.18
146.39
142.64
141.38
140.36
139.48
137.92
129.79
128.91
128.74
128.17
125.97
111.12
110.35
83.53
53.38
39.08
24.43
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

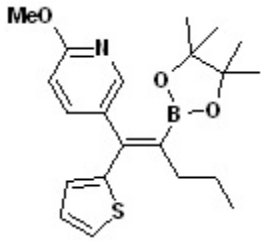

MeO
O
B
O
Ph
Me

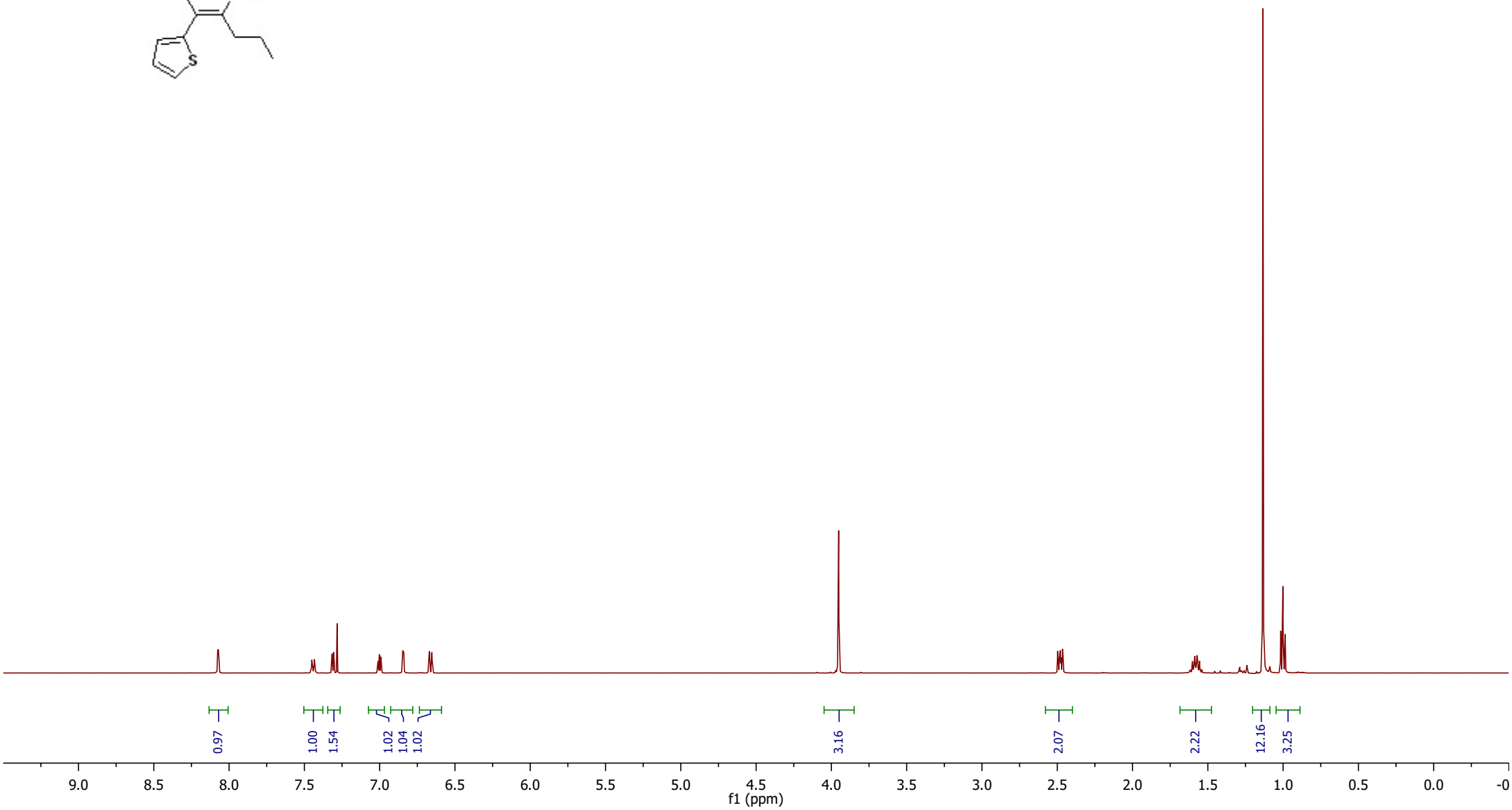
2.00
3.29
2.19
3.20
3.29
11.51
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

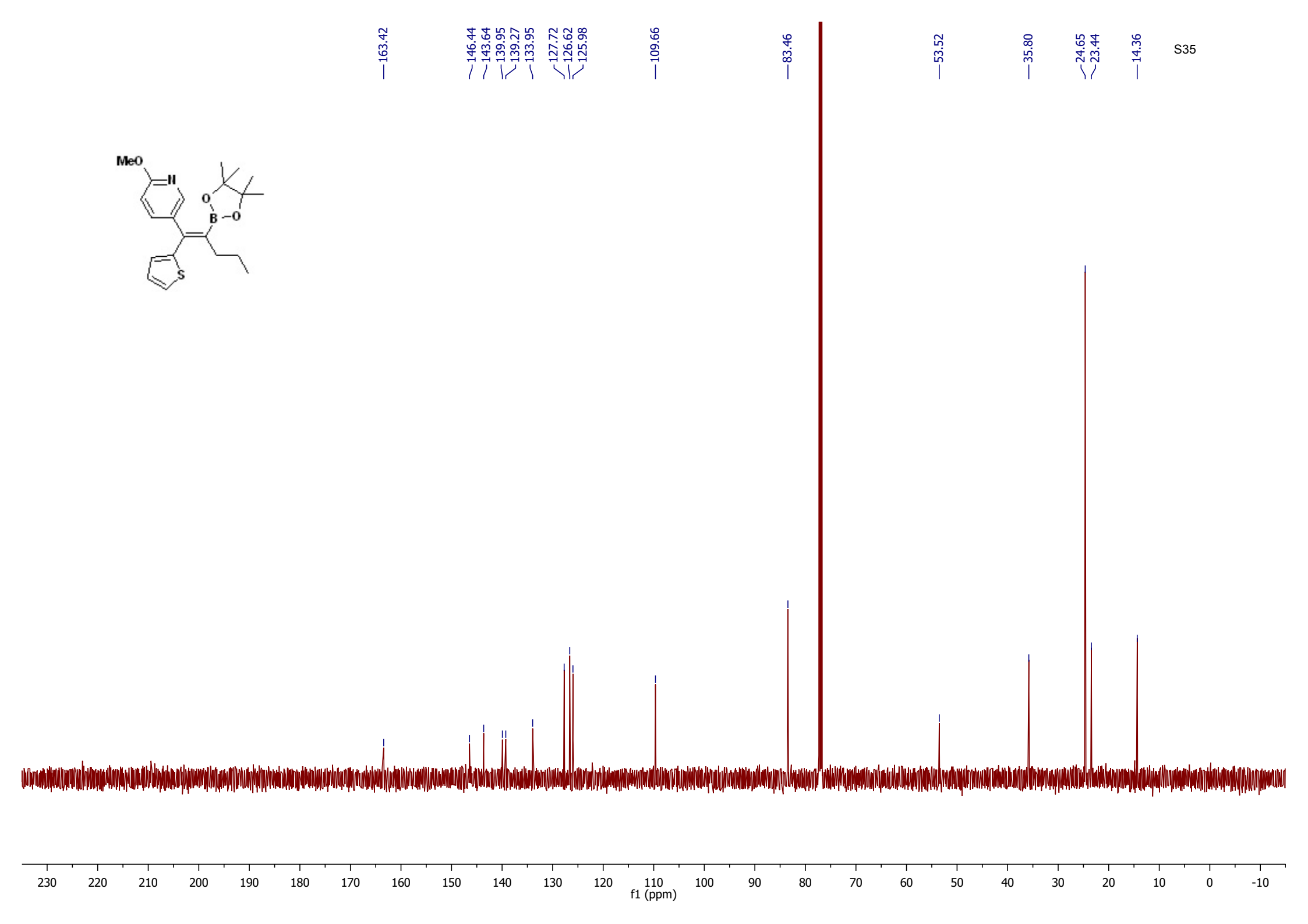


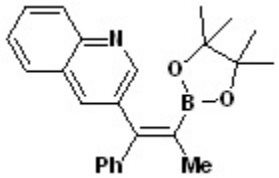
164.53
159.00
145.92
140.91
131.60
129.39
128.28
127.42
83.73
54.89
29.71
24.68
19.51

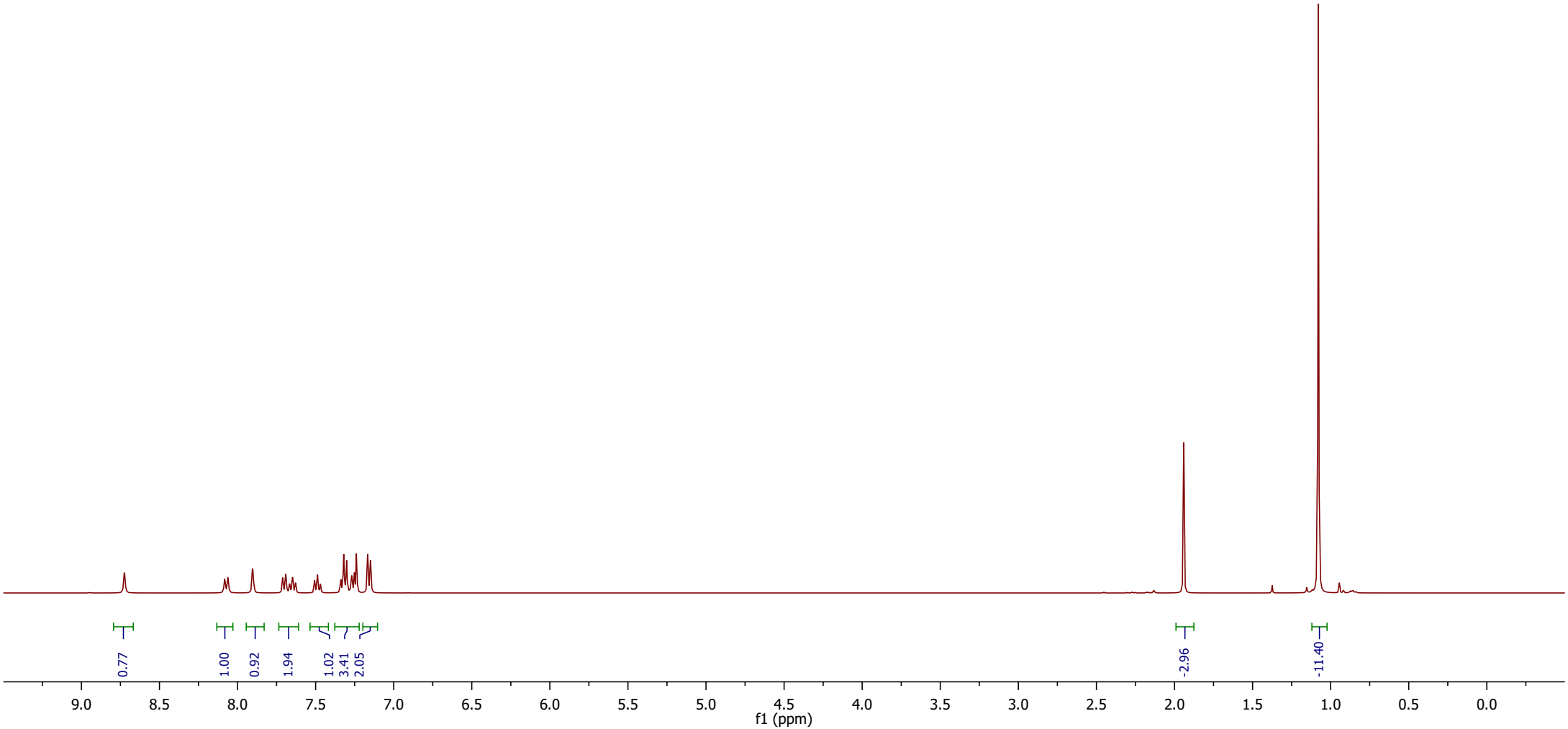
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

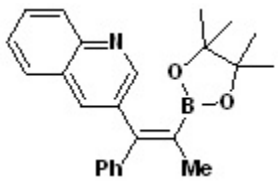

MeO
O
B
O
S


0.97
1.00
1.54
1.02
1.04
1.02
3.16
2.07
2.22
12.16
3.25
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
-0
f1 (ppm)


163.42
146.44
143.64
139.95
139.27
133.95
127.72
126.62
125.98
109.66
83.46
53.52
35.80
24.65
23.44
14.36
S35
MeO
O
B
O
S
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
B
O
Ph
Me

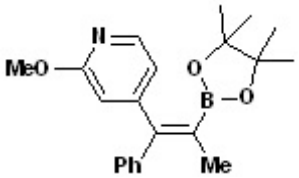

0.77
1.00
0.92
1.94
1.02
3.41
2.05
2.96
11.40
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

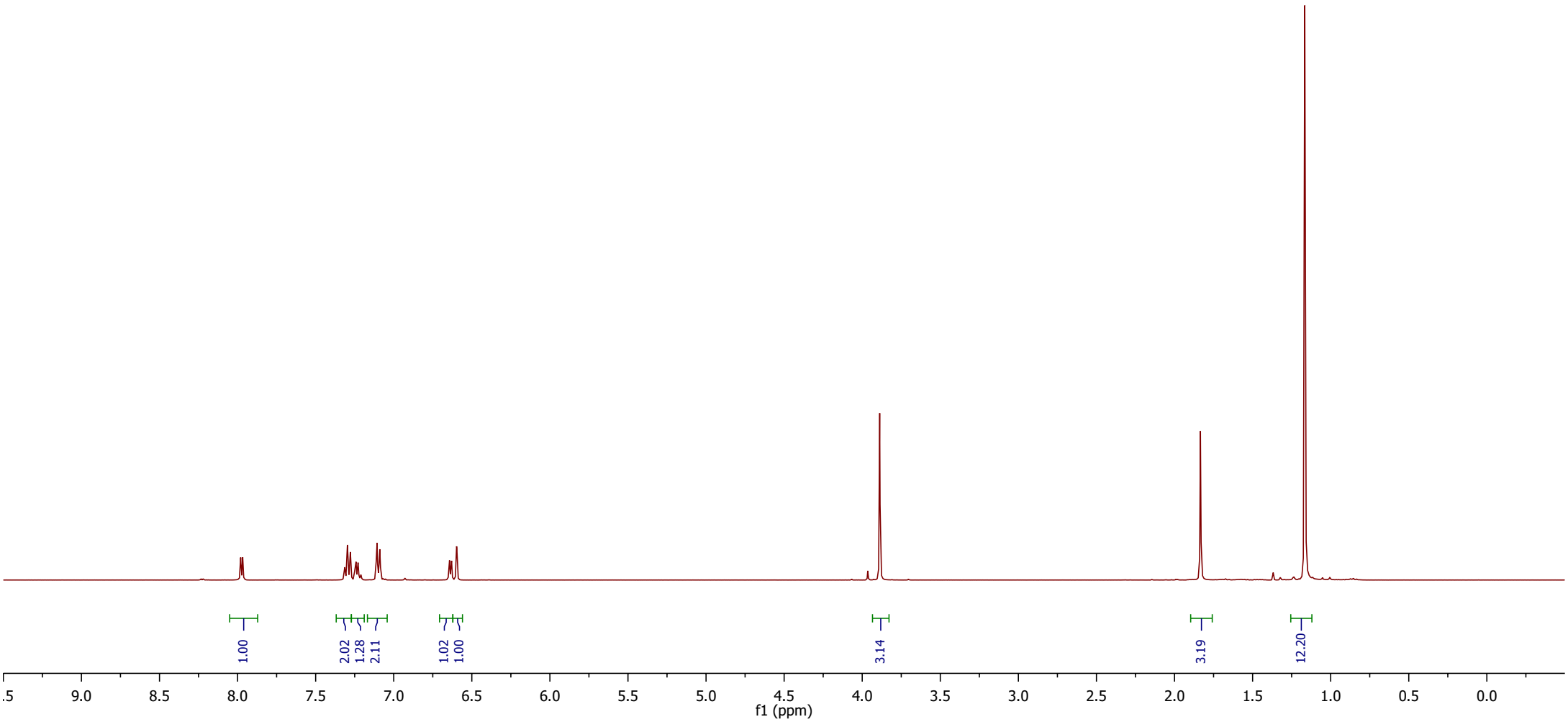


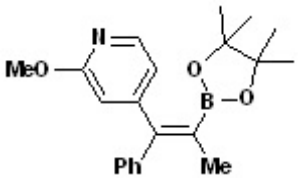
151.58
148.68
141.24
137.45
129.65
129.09
128.85
128.15
127.80
127.47
127.23
126.59
83.59
24.57
19.58

230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

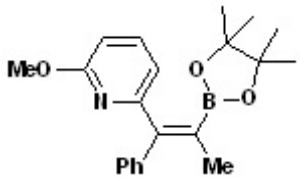
f1 (ppm)

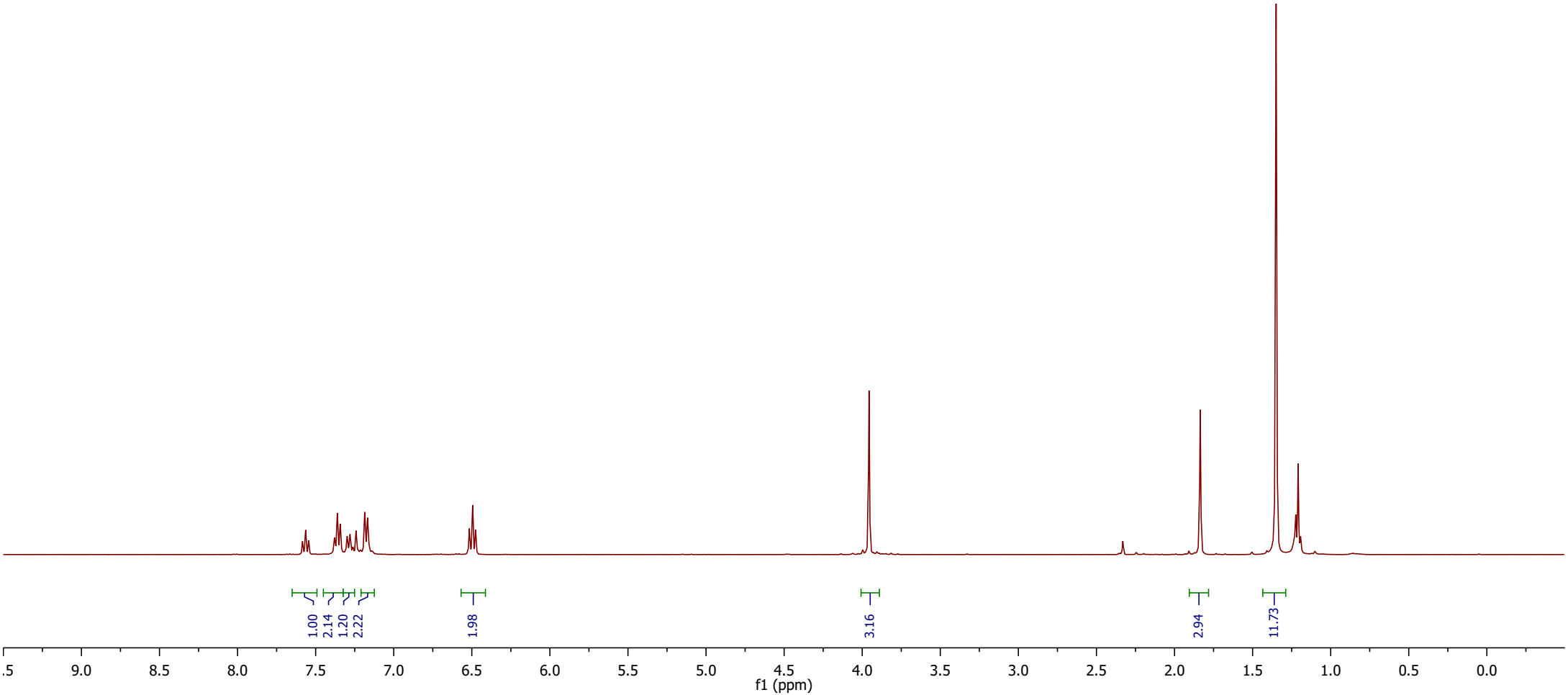

MeO
O
B
O
Ph
Me

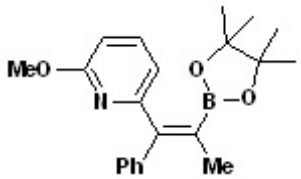

1.00
2.02
1.28
2.11
1.02
1.00
3.14
3.19
12.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


MeO
N
O
B
O
Ph
Me

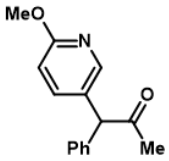
163.98
154.70
148.79
145.93
140.43
129.42
128.07
127.14
117.72
111.02
83.61
53.32
24.50
19.17
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

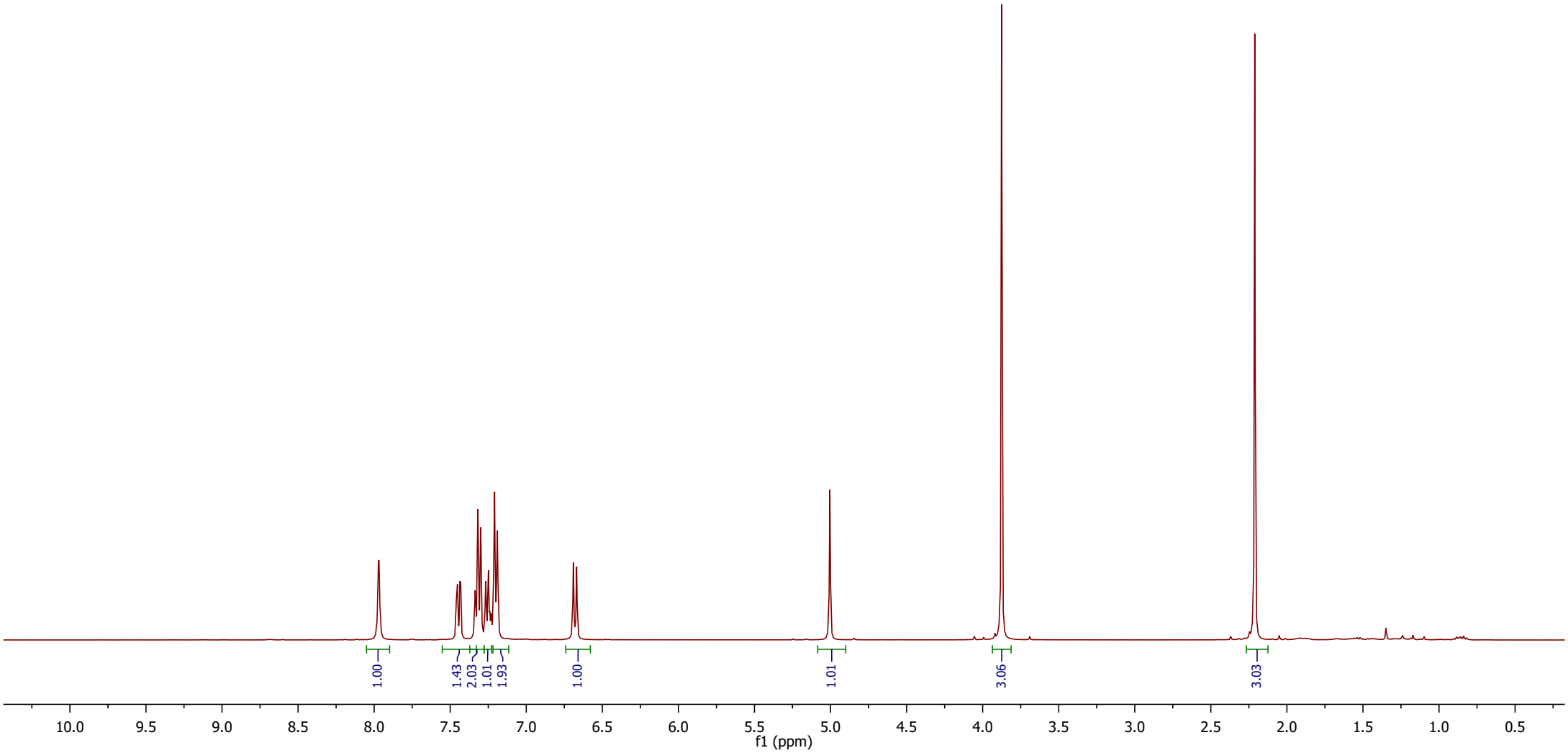

MeO
N
O
B
O
Ph
Me

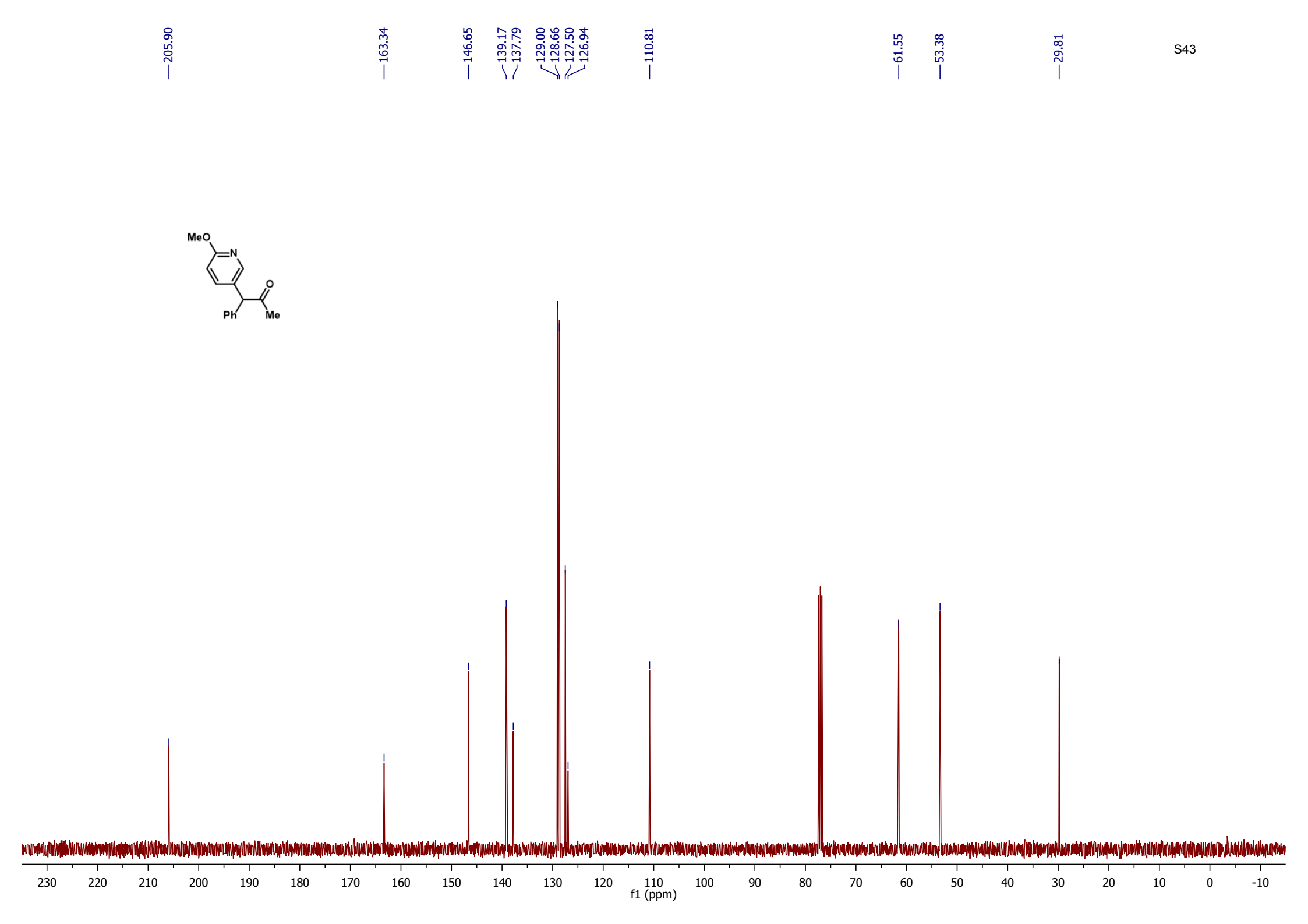

1.00
2.14
1.20
2.22
1.98
3.16
2.94
11.73
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

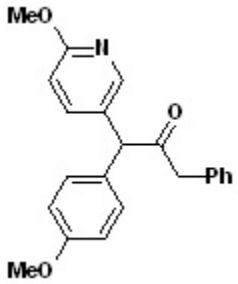

MeO
N
O
B
O
Ph
Me

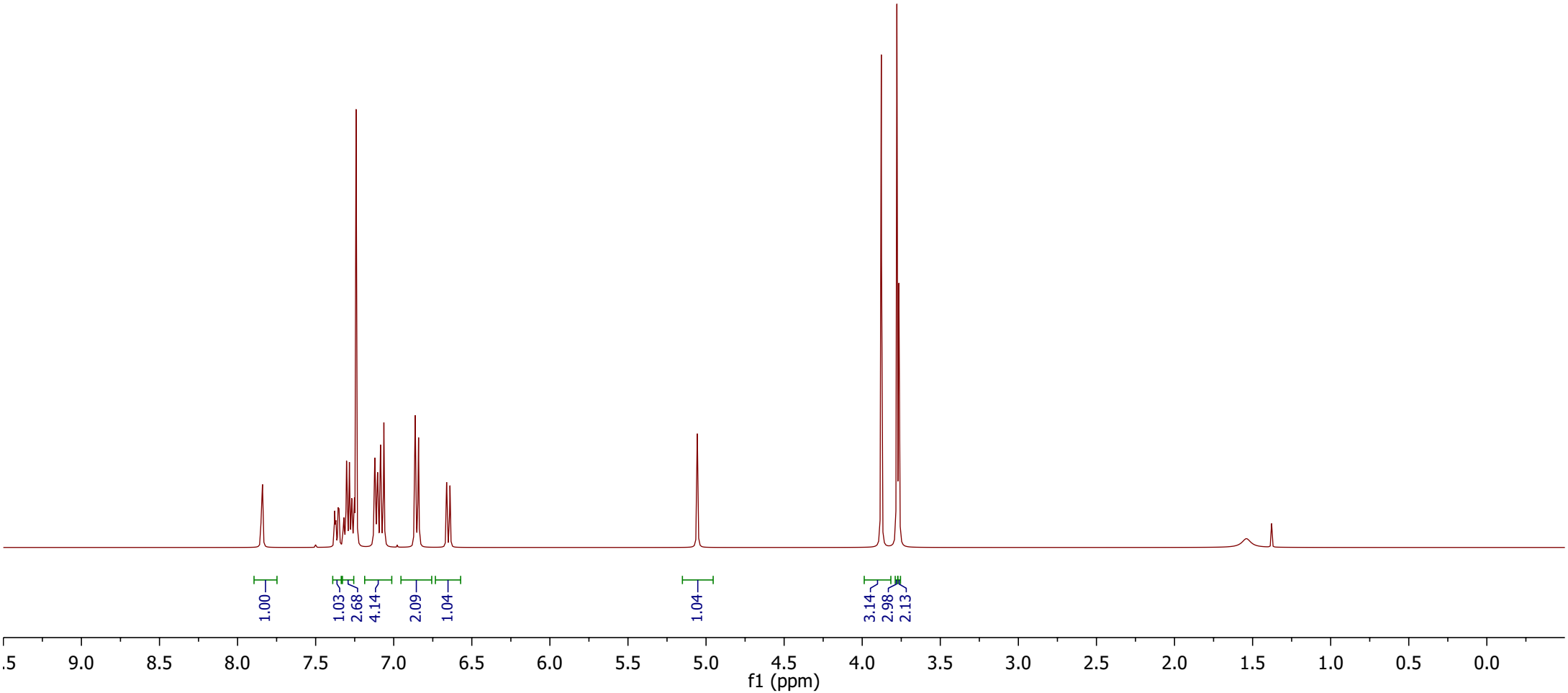
162.50
158.44
143.11
136.73
129.68
128.27
126.94
111.60
103.48
81.11
54.98
27.22
24.82
15.93
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

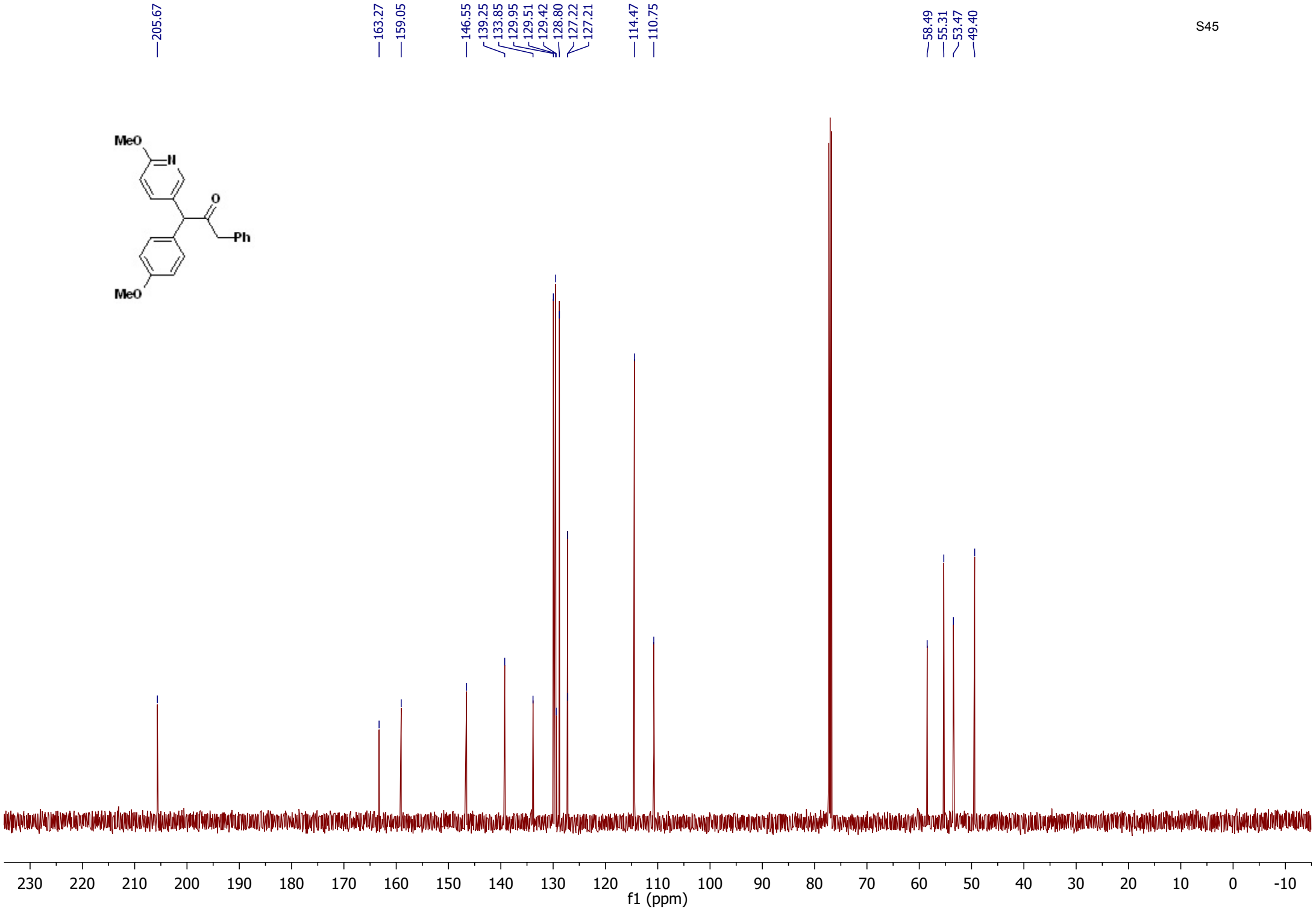

MeO
N
O
Ph
Me

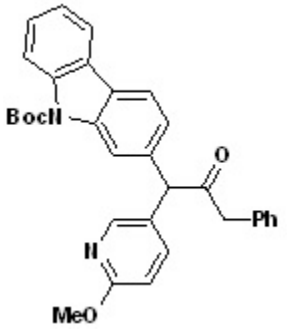

1.00
1.43
2.03
1.01
1.93
1.00
1.01
3.06
3.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


205.90
163.34
146.65
139.17
137.79
129.00
128.66
127.50
126.94
110.81
61.55
53.38
29.81
MeO
N
O
Ph
Me
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

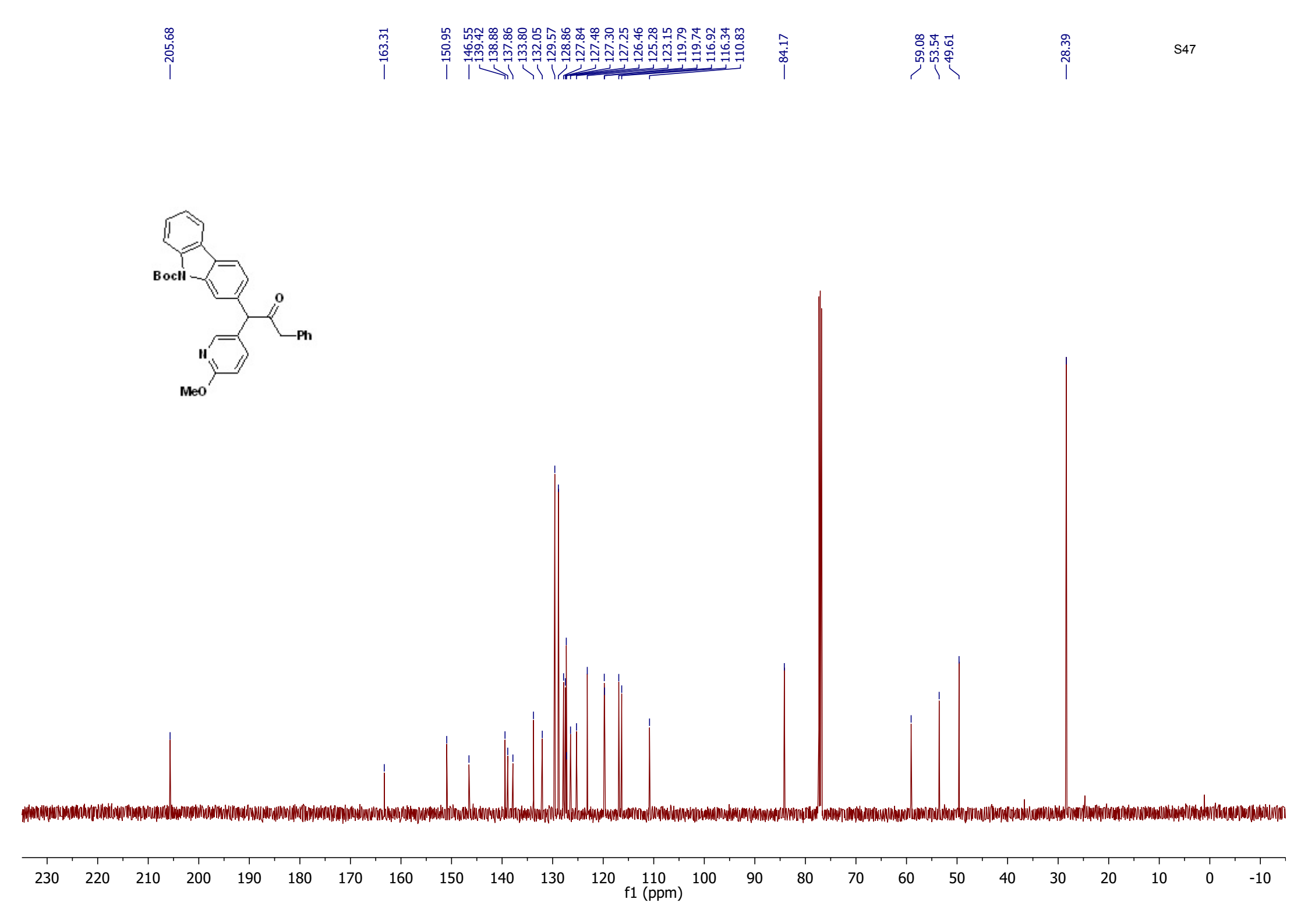

MeO
O
Ph
MeO

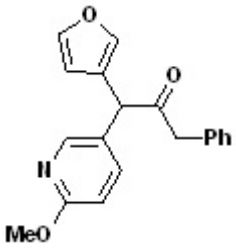

1.00
1.03
2.68
4.14
2.09
1.04
1.04
3.14
2.98
2.13
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

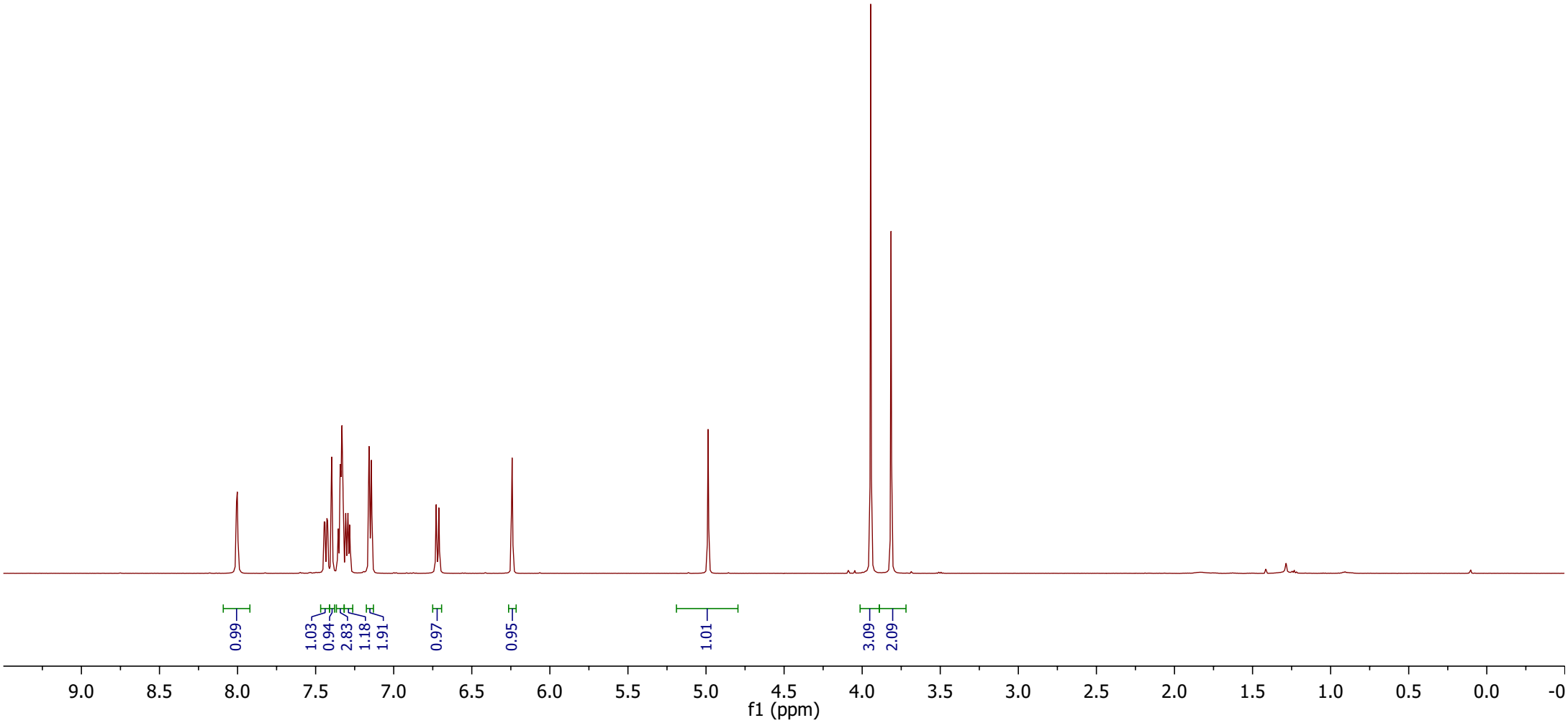

205.67
163.27
159.05
146.55
139.25
133.85
129.95
129.51
129.42
128.80
127.22
127.21
114.47
110.75
58.49
55.31
53.47
49.40
MeO
O
Ph
MeO
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

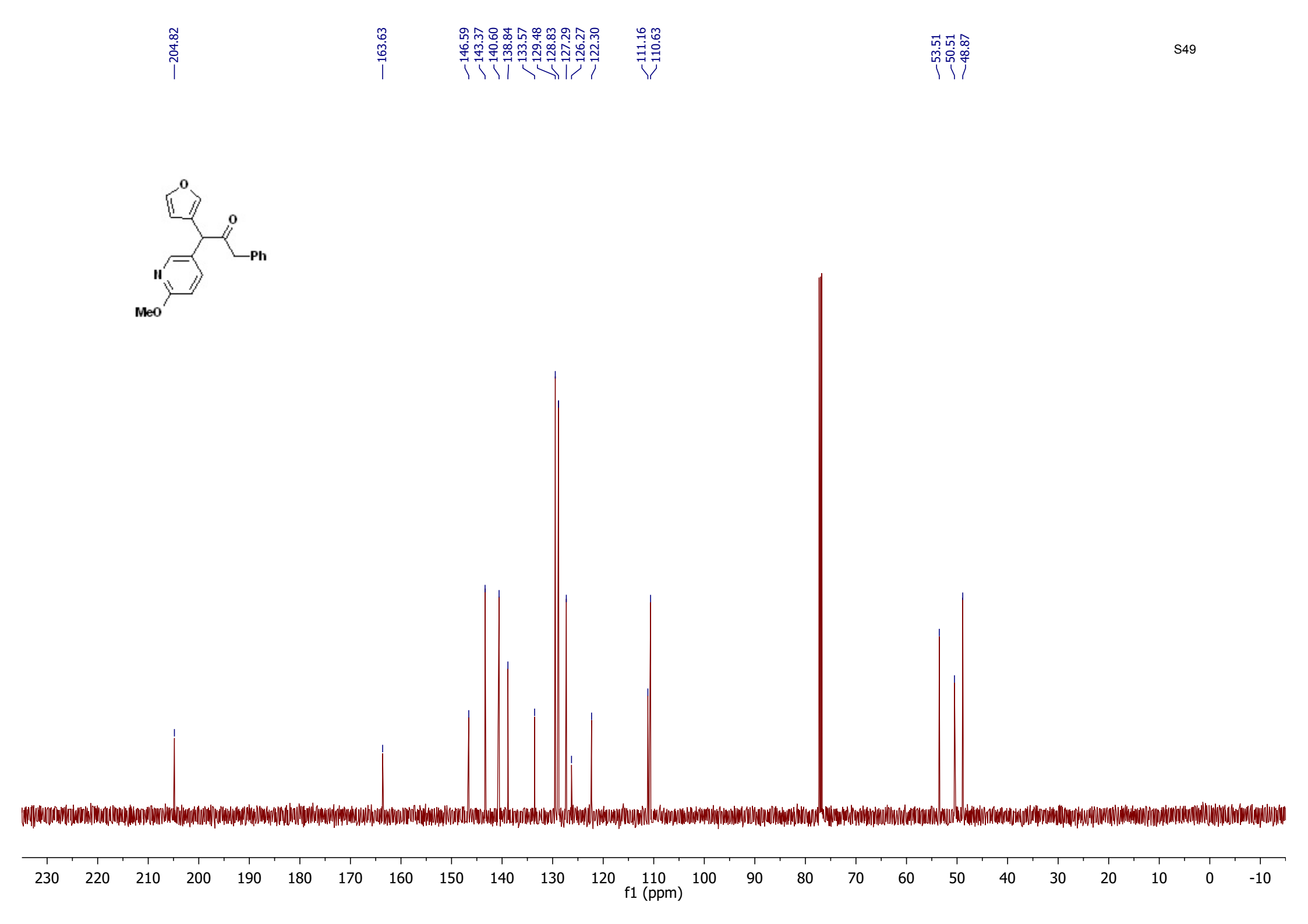

BocN
O
Ph
N
MeO

1.75
1.88
0.95
2.03
4.77
1.96
1.00
1.00
3.09
2.01
9.02
-0.31
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
f1 (ppm)


205.68
163.31
150.95
146.55
139.42
138.88
137.86
133.80
132.05
129.57
128.86
127.84
127.48
127.30
127.25
126.46
125.28
123.15
119.79
119.74
116.92
116.34
110.83
84.17
59.08
53.54
49.61
28.39
BocN
O
Ph
N
MeO
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
O
Ph
N
MeO


0.99
1.03
0.94
2.83
1.18
1.91
0.97
0.95
1.01
3.09
2.09
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
-0
f1 (ppm)


204.82
163.63
146.59
143.37
140.60
138.84
133.57
129.48
128.83
127.29
126.27
122.30
111.16
110.63
53.51
50.51
48.87
O
O
Ph
H
MeO
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)