**Supporting Information for:**

# Silyl-Protected Dioxaborinanes: Application in the Suzuki Cross-Coupling Reaction

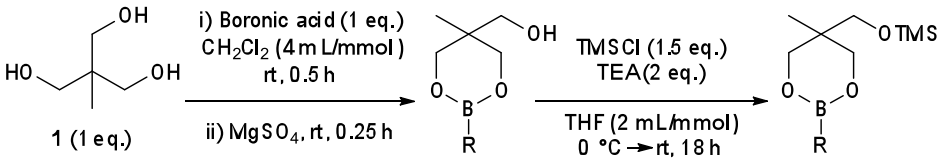
Sean Goggins, Eleanor Rosevere, Clément Bellini, Joseph C. Allen, Barrie J. Marsh, Mary F. Mahon and Christopher G. Frost*

***Department of Chemistry, University of Bath, Bath, BA2 7AY, UK***

***c.g.frost@bath.ac.uk***

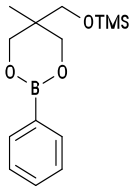
**General information:** IR spectra were recorded on a Perkin-Elmer 1600 FT IR spectrophotometer, with absorbencies quoted as ν in $cm^{-1}$. $^{1}H$ NMR data were obtained on a Bruker Avance 300 spectrometer operating at 300 MHz, unless otherwise noted, with tetramethylsilane as an internal standard. *J* values are given in Hz. $^{11}B$ NMR data were obtained on a Bruker Avance 300 spectrometer operating at 96 MHz, unless otherwise noted, with boron trifluoride diethyl etherate as an internal standard. $^{13}C$ NMR data were obtained on a Bruker Avance 300 spectrometer operating at 75.5 MHz, unless otherwise noted, with tetramethylsilane as an internal standard. High resolution mass spectrometry was performed on a microTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik). Melting points were obtained on a Bibby-Sterilin SMP10 melting point machine. All reactions were carried out under an atmosphere of nitrogen unless otherwise stated. Tetrahydrofuran and dichloromethane were dried and degassed by passing through anhydrous alumina columns using an Innovative Technology Inc. PS-400-7 solvent purification system and stored under an atmosphere of argon prior to use. TLCs were performed using aluminium-backed plates coated with Alugram® SIL G/UV purchased from Macherey-Nagel and visualised by UV light (254 nm) and/or $KMnO_4$ staining. Flash column chromatography was carried out using 60 Å, 200-400 mesh particle size silica gel purchased from Sigma-Aldrich. Boronic acids were purchased from Frontier Scientific and used as received. All other chemicals were purchased from Sigma-Aldrich and used as received. $^{1}H$ and $^{13}C$ spectra for compounds **2c** – **2e**, **2h** – **2j**, **2l** – **2r**, **4e**, **4f**, **4h** and **4q** are included.

# General Procedure for the Synthesis of trimethyl((5-methyl-2-substituted-1,3,2-dioxaborinan-5-yl)methoxy)silanes:




Boronic acid (8 mmol) was suspended in anhydrous dichloromethane (32 mL) under nitrogen. 2-(hydroxymethyl)-2-methylpropane-1,3-diol (1 eq., 8 mmol) was then added and the reaction mixture was stirred until homogenous (~0.5 h.). $MgSO_4$ (~3.0 g) was then added and the reaction stirred for an additional 0.25 h. The solids were then filtered off and the filtrate concentrated. The residue was then dissolved in anhydrous tetrahydrofuran (16 mL) under nitrogen and cooled to 0 °C. Triethylamine (2 eq., 16 mmol) was then added, followed by chlorotrimethylsilane (1.5 eq., 12 mmol) and the reaction mixture was allowed to warm to room temperature and left to stir for 18 hours. The reaction was then quenched with water (20 mL) and extracted with ethyl acetate (3 × 25 mL), dried over $MgSO_4$, filtered and concentrated to obtain the crude product, which was purified by silica gel column chromatography (Hexane 9:1 EtOAc).

## Trimethyl((5-methyl-2-phenyl-1,3,2-dioxaborinan-5-yl)methoxy)silane (2a)




Phenylboronic acid (0.98 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (2.14 g, 96% yield).

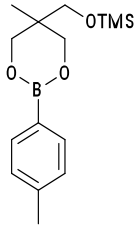
**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 7.70 (2H, d, $J$ = 8.0 Hz), 7.36-7.23 (3H, m), 3.92 (2H, d, $J$ = 11.0 Hz), 3.68 (2H, 11.0 Hz), 3.41 (2H, s), 0.85 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.9.

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 134.5, 131.3, 128.3, 68.8, 65.3, 37.6, 18.4, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

NMR data in accordance with literature precedent.[S1]

## Trimethyl((5-methyl-2-(*p*-tolyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2b)




*p*-tolylboronic acid (1.09 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (2.22 g, 95% yield).

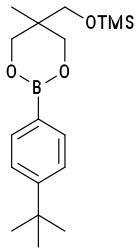
**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 7.60 (2H, d, *J* = 7.7 Hz), 7.08 (2H, d, *J* = 7.7 Hz), 3.91 (2H, d, *J* = 11.0 Hz), 3.67 (2H, d, *J* = 11.0 Hz), 3.41 (2H, s), 2.27 (3H, s), 0.84 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 30.0.

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 141.4, 134.6, 129.1, 68.7, 65.2, 37.6, 22.4, 18.4, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

NMR data in accordance with literature precedent.[S1]

## Trimethyl((5-methyl-2-(4-(*tert*-butyl)phenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2c)




(4-(*tert*-butyl)phenyl)boronic acid (1.42 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (1.31 g, 49% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 7.64 (2H, d, *J* = 8.2 Hz), 7.29 (2H, d, 8.2 Hz), 3.91 (2H, d, *J* = 11.0 Hz), 3.66 (2H, d, *J* = 11.0 Hz), 3.40 (2H, s), 1.23 (9H, s), 0.84 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.8.

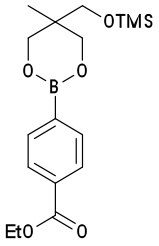
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 154.4, 134.4, 125.2, 68.7, 65.1, 37.6, 35.5, 31.9, 18.3, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

**IR** (solid, $cm^{-1}$); ν 2959, 2903, 2875, 1606, 1554, 1478, 1422, 1404, 1390, 1366, 1348, 1318, 1297, 1286, 1266, 1245, 1204, 1192, 1177, 1132, 1091, 1018, 986, 961, 937, 918, 876, 833, 777, 749, 697, 669, 644, 624,

**HRMS** (ESI); calc'd for $C_{18}H_{31}BO_3Si$ $[M+Na]^+$ : *m/z* 357.2031, found 357.2034.

**Melting Point**; 106 – 108 °C.

## Trimethyl((5-methyl-2-(4-(ethoxycarbonyl)phenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2d)




(4-(ethoxycarbonyl)phenyl)boronic acid (1.55 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (1.57 g, 56% yield).

**$^1$H-NMR** (300 MHz, $CDCl_3$); δ 7.92 (2H, d, *J* = 8.3 Hz), 7.76 (2H, d, *J* = 8.3 Hz), 4.29 (2H, q, 7.1 Hz), 3.95 (2H, d, 11.0 Hz), 3.70 (2H, d, 11.0 Hz), 3.41 (2H, s), 1.31 (3H, t, 7.1 Hz), 0.86 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.7.

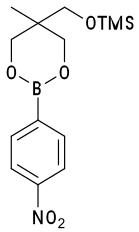
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 167.6, 134.4, 132.9, 129.2, 68.9, 65.3, 61.6, 37.6, 18.4, 15.0, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

**IR** (solid, $cm^{-1}$); ν 2989, 2957, 2907, 2877, 1712, 1591, 1561, 1506, 1480, 1448, 1423, 1395, 1368, 1344, 1326, 1309, 1271, 1249, 1203, 1180, 1130, 1109, 1087, 1017, 983, 935, 917, 873, 841, 816, 777, 744, 724, 707, 689, 656, 640, 621.

**HRMS** (ESI); calc'd for $C_{17}H_{27}BO_5Si$ $[M+Na]^+$ : *m/z* 373.1616, found 373.1594.

**Melting Point**; 89 – 93 °C.

## Trimethyl((5-methyl-2-(4-nitrophenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2e)




(4-nitrophenyl)boronic acid (1.34 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as a yellow powder; (1.81 g, 70% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.09 (2H, d, *J* = 8.7 Hz), 7.85 (2H, d, *J* = 8.7 Hz), 3.97 (2H, d, *J* = 11.1 Hz), 3.71 (2H, d, 11.1 Hz), 3.41 (2H, s), 0.87 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.3.

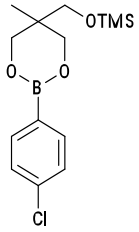
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 150.3, 135.5, 123.0, 69.0, 65.3, 37.6, 18.4, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

**IR** (solid, $cm^{-1}$); ν 2957, 2907, 2872, 1596, 1548, 1517, 1479, 1425, 1406, 1390, 1367, 1349, 1334, 1310, 1297, 1263, 1250, 1205, 1178, 1127, 1086, 1031, 1015, 984, 968, 957, 936, 874, 837, 818, 782, 755, 746, 730, 699, 658, 632.

**HRMS** (ESI); calc'd for $C_{14}H_{22}BNO_5Si$ $[M+Na]^+$ : *m/z* 346.1255, found 346.1231.

**Melting Point**; 84 – 86 °C.

## Trimethyl((5-methyl-2-(4-chlorophenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2f)




(4-chlorophenyl)boronic acid (1.25 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (2.45 g, 98% yield).

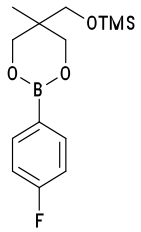
**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 7.62 (2H, d, *J* = 8.4 Hz), 7.23 (2H, d, *J* = 8.4 Hz), 3.92 (2H, d, 11.0 Hz), 3.67 (2H, d, 11.0 Hz), 3.40 (2H, s), 0.85 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.7.

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 137.6, 136.0, 128.5, 68.8, 65.3, 37.6, 18.4, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

NMR data in accordance with literature precedent.[S1]

**Trimethyl((5-methyl-2-(4-fluorophenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2g)**




(4-fluorophenyl)boronic acid (1.12 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (2.30 g, 97% yield).

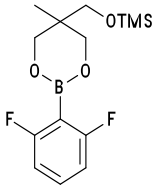
**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 7.68 (2H, m), 6.94 (2H, m), 3.92 (2H, d, $J$ = 11.0 Hz), 3.67 (2H, d, $J$ = 11.0 Hz), 3.41 (2H, s), 0.85 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.6

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 165.5 (d, $^{1}J_{C\text{-}F}$ = 249 Hz), 136.7 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 115.3 (d, $^{2}J_{C\text{-}F}$ = 20 Hz), 68.8, 65.3, 37.6, 18.4, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

NMR data in accordance with literature precedent.[S1]

**Trimethyl((5-methyl-2-(2,6-difluorophenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2h)**




(2,6-difluorophenyl)boronic acid (1.26 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as a white solid; (0.38 g, 15% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 7.17 (2H, m), 6.75 (1H, tt, $^{3}J_{H\text{-}H}$ = 9.1 Hz, $^{4}J_{H\text{-}F}$ = 2.5 Hz), 3.92 (2H, d, 11.1 Hz), 3.67 (2H, d, 11.1 Hz), 3.39 (2H, s), 0.85 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.1.

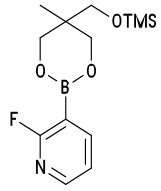
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 163.5 (dd, $^1J_{C\text{-}F}$ = 249 Hz, $^3J_{C\text{-}F}$ = 11 Hz), 116.6 (dd, $^2J_{C\text{-}F}$ = 23 Hz, $^4J_{C\text{-}F}$ = 7 Hz), 106.6 (t, $^3J_{C\text{-}F}$ = 25 Hz), 68.9, 65.3, 37.6, 18.4, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

**IR** (solid, $cm^{-1}$); ν 2967, 2896, 1586, 1495, 1482, 1430, 1405, 1391, 1372, 1352, 1330, 1311, 1282, 1242, 1220, 1200, 1177, 1114, 1083, 1045, 1018, 1000, 986, 972, 934, 920, 874, 837, 814, 780, 747, 715, 695, 655, 603.

**HRMS** (ESI); calc'd for $C_{14}H_{21}BF_2O_3Si$ $[M+Na]^+$ : *m/z* 337.1216, found 337.1205.

**Melting Point**; 63 – 65 °C.

## Trimethyl((5-methyl-2-(2-fluoropyridin-3-yl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2i)




(2-fluoropyridin-3-yl)boronic acid (1.13 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as a colourless oil; (0.88 g, 37% yield).

**$^1$H-NMR** (300 MHz, $CDCl_3$); δ 8.15 (1H, m), 8.05 (1H, m), 7.06 (1H, m), 3.96 (2H, d, 11.1 Hz), 3.70 (2H, d, 11.1 Hz), 3.42 (2H, s), 0.86 (3H, s), 0.00 (9H, s).

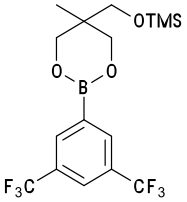
**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.1.

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 167.6 (d, $^1J_{C\text{-}F}$ = 244 Hz), 150.6 (d, $^3J_{C\text{-}F}$ = 15 Hz), 148.5 (d, $^3J_{C\text{-}F}$ = 7 Hz), 121.6 (d, $^4J_{C\text{-}F}$ = 4 Hz), 114.6, 69.1, 65.4, 37.5, 18.4, 0.0.

**IR** (film, $cm^{-1}$); ν 2957, 2899, 1787, 1600, 1567, 1482, 1432, 1374, 1343, 1315, 1265, 1251, 1218, 1177, 1136, 1089, 1061, 1036, 998, 971, 949, 910, 871, 840, 813, 774, 714, 680, 656, 620.

**HRMS** (ESI); calc'd for $C_{13}H_{21}BFNO_3Si$ $[M+Na]^+$ : *m/z* 320.1263, found 320.1268.

## Trimethyl((5-methyl-2-(3,5-bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2j)




(2-fluoropyridin-3-yl)boronic acid (2.06 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as a colourless oil; (2.09 g, 63% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.14 (2H, s), 7.81 (1H, s), 3.98 (2H, s, 11.1 Hz), 3.71 (2H, s, 11.1 Hz), 3.42 (2H, s), 0.87 (3H, s), 0.00 (9H, s).

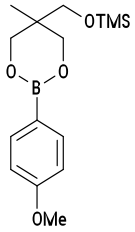
**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.2.

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 134.9, 131.7, (q, $^{2}J_{C\text{-}F}$ = 33 Hz), 125.1 (ap quin, $^{3}J_{C\text{-}F}$ = 4 Hz), 124.7 (q, $^{1}J_{C\text{-}F}$ = 272 Hz), 69.3, 65.6, 37.8, 18.5, 0.00. (*C*-B signal not observed due to quadrupolar relaxation).

**IR** (film, $cm^{-1}$); ν 2962, 2900, 2118, 1618, 1484, 1418, 1274, 1253, 1170, 1127, 1095, 1039, 1021, 987, 906, 871, 839, 799, 748, 708, 681, 621.

Mass ion could not be obtained.

**Trimethyl((5-methyl-2-(4-methoxyphenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2k)**




(4-methoxyphenyl)boronic acid (1.22 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (2.32 g, 94% yield).

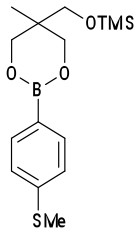
**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 7.64 (2H, d, *J* = 8.7 Hz), 6.79 (2H, d, *J* = 8.7 Hz), 3.90 (2H, d, *J* = 11.0 Hz), 3.73 (3H, s), 3.66 (2H, d, *J* = 11.0 Hz), 0.84 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.8

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 162.4, 136.2, 113.8, 68.7, 65.2, 55.7, 37.6, 18.4, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

NMR data in accordance with literature precedent.[S1]

**Trimethyl((5-methyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2l)**




(4-(methylthio)phenyl)boronic acid (1.34 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (0.96 g, 37% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 7.60 (2H, d, *J* = 8.3 Hz), 7.13 (2H, d, *J* = 8.3 Hz), 3.91 (2H, d, *J* = 11.0 Hz), 3.67 (2H, d, *J* = 11.0), 3.41 (2H, s), 2.40 (3H, s), 0.84 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.8.

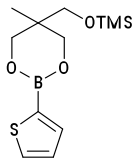
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 142.3, 134.9, 125.7, 68.7, 65.2, 37.6, 18.4, 15.8, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

**IR** (solid, $cm^{-1}$); ν 3056, 2951, 2896, 2869, 1590, 1548, 1479, 1419, 1405, 1389, 1368, 1345, 1325, 1310, 1294, 1283, 1275, 1262, 1251, 1243, 1205, 1179, 1129, 1110, 1087, 1015, 1032, 1015, 984, 968, 956, 936, 875, 838, 818, 774, 755, 744, 726, 693, 658, 640, 623.

**HRMS** (ESI); calc'd for $C_{15}H_{25}BO_3SSi$ $[M+Na]^+$ : *m/z* 347.1282, found 347.1282.

**Melting Point**; 80 – 83 °C.

**Trimethyl((5-methyl-2-(thiophen-2-yl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2m)**




Thiophen-2-ylboronic acid (1.02 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (0.39 g, 17% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 7.49-7.46 (2H, m), 7.06 (1H, dd, *J* = 4.7, 3.5 Hz), 3.91 (2H, d, *J* = 11.0 Hz), 3.66 (2H, d, *J* = 11.0 Hz), 3.41 (2H, s), 0.84 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 28.4.

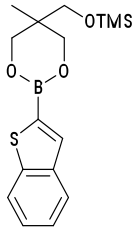
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 136.3, 132.0, 128.7, 68.9, 65.3, 37.7, 18.4, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

**IR** (solid, $cm^{-1}$); ν 3273, 3108, 3096, 2966, 2894, 1513, 1486, 1476, 1414, 1398, 1357, 1311, 1288, 1279, 1266, 1244, 1205, 1176, 1119, 1077, 1014, 988, 979, 934, 917, 901, 874, 849, 813, 780, 749, 728, 699, 677, 624.

**HRMS** (ESI); calc'd for $C_{12}H_{21}BO_3SSi$ $[M+Na]^+$ : *m/z* 307.0969, found 307.0965.

**Melting Point**; 63 – 64 °C.

## Trimethyl((5-methyl-2-(benzo[*b*]thiophen-2-yl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2n)




Thiophen-2-ylboronic acid (1.42 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (1.52 g, 57% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 7.82–7.71 (2H, m), 7.70 (1H, m), 7.28–7.21 (2H, m), 3.96 (2H, d, *J* = 11.0 Hz), 3.71 (2H, d, *J* = 11.0 Hz), 3.43 (2H, s), 0.86 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 28.7.

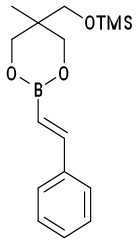
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 144.1, 141.4, 133.5, 125.6, 124.9, 124.6, 123.2, 69.0, 65.3, 37.8, 18.4, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

**IR** (solid, $cm^{-1}$); ν 2960, 2903, 2876, 1594, 1508, 1479, 1420, 1404, 1389, 1374, 1346, 1308, 1295, 1264, 1246, 1216, 1180, 1124, 1084, 1030, 1016, 984, 963, 933, 916, 874, 837, 780, 759, 746, 727, 709, 624, 611.

**HRMS** (ESI); calc'd for $C_{16}H_{23}BNO_3SSi$ $[M+Na]^+$ : *m/z* 357.1126, found 357.1135.

**Melting Point**; 114 – 117 °C.

**(*E*)-Trimethyl((5-methyl-2-styryl-1,3,2-dioxaborinan-5-yl)methoxy)silane (2o)**




(*E*)-styrylboronic acid (1.18 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an white solid; (0.92 g, 38% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 7.39-7.37 (2H, m), 7.26-7.16 (4H, m), 6.00 (1H, d, *J* = 18.3 Hz), 3.83 (2H, d, *J* = 10.9 Hz), 3.58 (2H, d, *J* = 10.9 Hz), 3.37 (2H, s), 0.80 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 29.5.

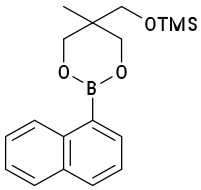
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 147.8, 138.5, 129.2, 127.7, 121.6, 68.6, 65.2, 37.5, 18.3, 0.0.

**IR** (solid, $cm^{-1}$); ν 2957, 2911, 1928, 1734, 1625, 1587, 1576, 1508, 1488, 1478, 1459, 1433, 1414, 1394, 1369, 1344, 1311, 1273, 1248, 1209, 1195, 1152, 1102, 1067, 1018, 991, 962, 931, 872, 838, 817, 801, 770, 744, 698, 683, 655.

**HRMS** (ESI); calc'd for $C_{16}H_{25}BO_3Si$ $[M+Na]^+$ : *m/z* 327.1561, found 327.1562.

**Melting Point**; 65 – 67 °C.

**Trimethyl((5-methyl-2-(naphthalene-1-yl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2p)**




Naphthalen-1-ylboronic acid (1.38 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (1.55 g, 59% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.67-8.64 (1H, m), 7.93 (1H, dd, *J* = 6.9, 1.3 Hz), 7.78 (1H, d, *J* = 8.2 Hz), 7.73-7.70 (1H, m), 7.42-7.31 (3H, m), 4.02 (2H, d, *J* = 11.0 Hz), 3.77 (2H, d, *J* = 11.0 Hz), 3.47 (2H, s), 0.89 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 30.9

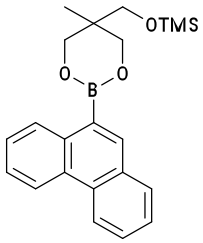
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 137.4, 135.1, 134.0, 131.6, 129.1, 129.0, 126.6, 125.9, 125.6, 68.9, 65.3, 37.4, 18.4, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

**IR** (solid, $cm^{-1}$); ν 3042, 2955, 2888, 2857, 1948, 1571, 1507, 1477, 1435, 1414, 1368, 1325, 1301, 1265, 1250, 1240, 1212, 1143, 1089, 1020, 1007, 981, 927, 871, 839, 802, 782, 758, 744, 697, 683, 654, 611.

**HRMS** (ESI); calc'd for $C_{18}H_{25}BO_3Si$ $[M+Na]^+$ : *m/z* 351.1562, found 351.1568.

**Melting Point**; 66 – 67 °C.

**Trimethyl((5-methyl-2-(phenanthren-9-yl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2q)**




Phenanthren-9-ylboronic acid (1.78 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (0.85 g, 28% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.71-8.68 (1H, m), 8.60-8.54 (2H, m), 8.21 (1H, s), 7.81-7.78 (1H, m), 7.58-7.43 (4H, m), 4.06 (2H, d, *J* = 11.0 Hz), 3.81 (2H, d, *J* = 11.0 Hz), 3.49 (2H, s), 0.92 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 30.7.

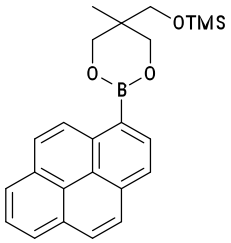
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 137.3, 135.2, 132.3, 131.8, 130.7, 129.9, 129.7, 128.0, 127.1, 127.0, 126.5, 123.3, 123.1, 69.0, 65.3, 37.4, 18.4, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

**IR** (solid, $cm^{-1}$); ν 3054, 2959, 2894, 2859, 1611, 1586, 1574, 1528, 1491, 1476, 1442, 1416, 1387, 1350, 1330, 1311, 1245, 1206, 1196, 1167, 1158, 1145, 1093, 1104, 983, 957, 937, 924, 875, 838, 792, 769, 750, 725, 701, 692, 677, 616, 610.

**HRMS** (ESI); calc'd for $C_{22}H_{27}BO_3Si$ $[M+H]^+$ : *m/z* 379.1900, found 379.1928.

**Melting Point**; 138 – 141 °C.

**Trimethyl((5-methyl-2-(pyren-1-yl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (2r)**




Pyren-1-ylboronic acid (1.97 g, 8 mmol), 2-(hydroxymethyl)-2-methylpropane-1,3-diol (0.96 g, 8 mmol), chlorotrimethylsilane (1.52 mL, 12 mmol) and triethylamine (2.23 mL, 16 mmol) were reacted together under standard protocol to give the desired product as an off-white solid; (0.87 g, 27% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.96 (1H, d, *J* = 9.3 Hz), 8.40 (1H, d, *J* = 7.7 Hz), 8.09-7.85 (7H, m), 4.11 (2H, d, *J* = 11.0 Hz), 3.86 (2H, d, *J* = 11.0 Hz), 3.52 (2H, s), 0.94 (3H, s), 0.00 (9H, s).

**$^{11}$B-NMR** (96 MHz, $CDCl_3$); δ 31.3.

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 136.5, 133.6, 133.6, 131.8, 131.4, 128.8, 128.7, 128.2, 128.0, 126.2, 125.7, 125.6, 125.4, 125.2, 124.7, 69.1, 65.3, 37.5, 18.5, 0.0. (*C*-B signal not observed due to quadrupolar relaxation).

**IR** (solid, $cm^{-1}$); ν 3057, 1586, 1563, 1527, 1495, 1470, 1450, 1429, 1382, 1279, 1254, 1142, 1092, 1047, 992, 947, 892, 862, 795, 770, 746, 725, 683, 645, 617.

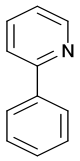
**HRMS** (ESI); calc'd for $C_{24}H_{27}BO_3Si$ $[M+Na]^+$ : *m/z* 425.1719, found 425.1716.

**Melting Point**; 96 – 98 °C

## General Procedure for the Synthesis of 2-Substituted Pyridines:

To an oven-dried carousel tube charged with a cross-head magnetic stirrer bar and screw-cap was added tetrakis(triphenylphosphine)palladium (0.01 mmol, 1 mol%) and potassium carbonate (2 mmol, 2 eq.) under argon and dissolved in 2 mL of ethanol. A solution of trimethyl((5-methyl-2-substituted-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 1.5 eq.) dissolved in 2 mL of ethanol was then added followed by the addition of 2-bromopyridine. The reaction mixture was then heated to 100 °C and stirred for 18 hours. After cooling to room temperature, 20 mL of water was added and the product was extracted with ethyl acetate (3 × 20 mL). The combined organics were then washed with brine, dried over magnesium sulphate and the solvent removed under reduced pressure. The crude product was then purified by silica gel column chromatography (Hexane 9:1 EtOAc).

**2-phenylpyridine (4a)**



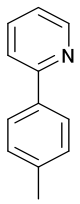

Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-phenyl-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 417 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a colourless oil; (152 mg, 98% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.62-8.60 (1H, m), 7.92-7.89 (2H, m), 7.70-7.62 (2H, m), 7.42-7.30 (3H, m), 7.17-7.12 (1H, m).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 157.5, 149.6, 139.3, 136.9, 129.0, 128.8, 127.0, 122.1, 120.6.

NMR data in accordance with literature precedent.[S2]

**2-(*p*-tolyl)pyridine (4b)**



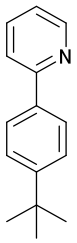
Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(*p*-tolyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 438 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a colourless oil; (162 mg, 96% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.55-8.52 (1H, m), 7.77-7.73 (2H, m), 7.63-7.54 (2H, m), 7.16-7.13 (2H, m), 7.09-7.08 (1H, m), 2.26 (3H, s).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 157.4, 149.4, 139.1, 136.9, 136.5, 129.5, 126.8, 121.9, 120.4, 21.3.

NMR data in accordance with literature precedent.[S3]

**2-(4-(*tert*-butyl)phenyl)pyridine (4c)**




Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(4-(*tert*-butyl)phenyl)-1,3,2-dioxaborinan-5-yl)methoxy) silane (1.5 mmol, 502 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a colourless liquid; (169 mg, 80% yield).

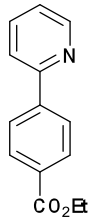
**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.58 (1H, dt, $J$ = 4.8, 1.3 Hz), 7.86-7.82 (2H, m), 7.63-7.60 (2H, m), 7.43-7.39 (2H, m), 7.11-7.07 (1H, m), 1.27 (9H, s).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 157.4, 149.6, 136.8, 136.6, 126.7, 125.8, 121.9, 120.4, 34.7, 31.3.

**IR** (film, $cm^{-1}$); ν 2962, 2904, 2865, 1610, 1587, 1576, 1560, 1514, 1465, 1433, 1396, 1363, 1288, 1269, 1251, 1196, 1153, 1113, 1094, 1060, 1013, 988, 875, 844, 781, 734, 683, 619.

NMR data in accordance with literature precedent.[S4]

**2-(4-(ethoxycarbonyl)phenyl)pyridine (4d)**




Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(4-(*tert*-butyl)phenyl)-1,3,2-dioxaborinan-5-yl)methoxy) silane (1.5 mmol, 525 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a white solid; (109 mg, 48% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.73 (1H, dt, *J* = 4.8, 1.3 Hz), 8.15 (2H, d, *J* = 8.6 Hz), 8.07 (2H, d, *J* = 8.6 Hz), 7.81-7.79 (2H, m), 7.32-7.28 (1H, m), 4.41 (2H, q, *J* = 7.1 Hz), 1.42 (3H, t, *J* = 7.1 Hz).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 166.4, 156.2, 149.8, 143.2, 137.1, 130.8, 130.1, 126.8, 122.9, 121.1, 61.1, 14.4.

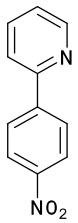
**IR** (solid, $cm^{-1}$); ν 3055, 2985, 2904, 1706, 1608, 1586, 1565, 1509, 1468, 1436, 1404, 1364, 1320, 1310, 1278, 1261, 1183, 1156, 1123, 1103, 1061, 1013, 988, 900, 866, 854, 797, 753, 695, 666, 638, 616.

**HRMS** (ESI); calc'd for $C_{14}H_{13}NO_2$ $[M+Na]^+$ : *m/z* 250.0844, found 250.0828.

**Melting Point**; 56 – 61 °C

Data in accordance with literature precendent.[S5]

## 2-(4-nitrophenyl)pyridine (4e)




Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(4-nitrophenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 485 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a yellow solid; (134 mg, 67% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.66-8.63 (1H, m), 8.22 (2H, d, *J* = 9.0 Hz), 8.07 (2H, d, *J* = 9.0 Hz), 7.77-7.66 (2H, m), 7.25 (1H, ddd, *J* = 6.7, 4.8, 2.0 Hz).

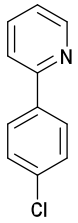
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 154.9, 150.1, 148.2, 145.2, 137.3, 127.7, 124.1, 123.6, 121.4.

**IR** (solid, $cm^{-1}$); ν 3108, 3054, 3011, 2446, 1924, 1598, 1586, 1569, 1510, 1466, 1436, 1405, 1383, 1341, 1324, 1239, 1183, 1154, 1106, 1060, 1033, 1009, 990, 962, 856, 842, 786, 759, 737, 688, 669, 634, 616.

**HRMS** (ESI); calc'd for $C_{11}H_9N_2O_2$ $[M+H]^+$ : *m/z* 201.0664, found 201.0662.

**Melting Point**; 125 – 127 °C

## 2-(4-chlorophenyl)pyridine (4f)




Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(4-chlorophenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 469 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a colourless oil; (165 mg, 67% yield).

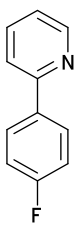
**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.60-8.58 (1H, m), 7.84 (2H, d, $J$ = 8.6 Hz), 7.69-7.59 (2H, m), 7.34 (2H, d, $J$ = 8.6 Hz), 7.17-7.13 (1H, m).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 156.2, 149.7, 137.8, 136.9, 135.1, 128.9, 128.2, 122.4, 120.3.

**IR** (film, $cm^{-1}$); ν 3048, 3005, 1587, 1562, 1495, 1462, 1433, 1399, 1349, 1312, 1294, 1234, 1184, 1154, 1119, 1104, 1096, 1087, 1059, 1011, 989, 886, 848, 831, 797, 767, 748, 736, 703, 678, 634, 616.

**HRMS** (ESI); calc'd for $C_{11}H_9NCl$ $[M+H]^+$ : *m/z* 190.0424, found 190.0428.

## 2-(4-fluorophenyl)pyridine (4g)



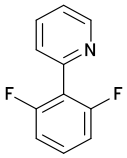
Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(4-fluorophenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 444 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a white solid; (170 mg, 98% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.66-8.64 (1H, m), 7.99-7.93 (2H, m), 7.71-7.66 (2H, m), 7.19-7.09 (3H, m).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 163.5 (d, $^{1}J_{C\text{-}F}$ = 248 Hz), 156.4, 149.7, 136.8, 135.6 (d, $^{4}J_{C\text{-}F}$ = 3 Hz), 128.7 (d, $^{3}J_{C\text{-}F}$ = 8 Hz), 122.0, 120.2, 115.6 (d, $^{2}J_{C\text{-}F}$ = 22 Hz).

NMR data in accordance with literature precedent.[S6]

## 2-(2,6-difluorophenyl)pyridine (4h)




Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(2,6-difluorophenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 471 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a white solid; (80 mg, 42% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.61-8.59 (1H, m), 7.68 (1H, td, $J$ = 7.8, 1.8 Hz), 7.58 (1H, ap d, $J$ = 8.0 Hz), 7.49-7.41 (2H, m), 7.19 (1H, ddd, $J$ = 7.3, 4.8, 1.1 Hz), 6.76 (1H, tt, $J$ = 8.7, 2.3 Hz).

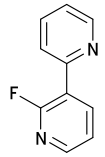
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 163.4 (dd, $^{1}J_{C\text{-}F}$ = 248 Hz, $^{3}J_{C\text{-}F}$ = 13 Hz), 154.8 (t, $^{3}J_{C\text{-}F}$ = 3 Hz), 149.8, 142.7 (t, $^{3}J_{C\text{-}F}$ = 9 Hz), 137.1, 123.2, 120.5, 109.7 (dd, $^{2}J_{C\text{-}F}$ = 26 Hz, $^{4}J_{C\text{-}F}$ = 8 Hz), 104.2 (t, $^{2}J_{C\text{-}F}$ = 26 Hz).

**IR** (solid, $cm^{-1}$); ν 3057, 3009, 2963, 2896, 2118, 1621, 1609, 1583, 1569, 1485, 1469, 1443, 1418, 1332, 1313, 1288, 1246, 1225, 1125, 1092, 1065, 1052, 1005, 986, 924, 889, 879, 849, 837, 770, 752, 734, 701, 676, 668, 620.

**HRMS** (ESI); calc'd for $C_{11}H_8F_2N$ $[M+H]^+$ : *m/z* 192.0625, found 192.0614.

**Melting Point**; 63 – 65 °C

## 2-(2-fluoropyridin-3-yl)pyridine (4i)



Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(2-fluoropyridin-3-yl)-1,3,2-dioxaborinan-5-yl)methoxy) silane (1.5 mmol, 446 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as pale yellow needles; (16 mg, 9% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.70-8.61 (1H, m), 8.46 (1H, ddd, $J$ = 9.7, 7.6, 2.0 Hz), 8.22-8.15 (1H, m), 7.82 (1H, dd, $J$ = 8.0, 1.0 Hz), 7.72 (1H, td, $J$ = 7.8, 1.7 Hz), 7.31-7.18 (2H, m).

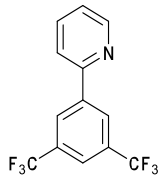
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 158.9 (d, $^{1}J_{C\text{-}F}$ = 241 Hz), 149.5 (d, $^{3}J_{C\text{-}F}$ = 7 Hz), 148.1, 145.7 (d, $^{2}J_{C\text{-}F}$ = 15 Hz), 139.6 (d, $^{4}J_{C\text{-}F}$ = 4 Hz), 134.9, 122.4 (d, $^{3}J_{C\text{-}F}$ = 10 Hz), 121.3, 120.2 (d, $^{4}J_{C\text{-}F}$ = 4 Hz).

**IR** (solid, $cm^{-1}$); ν 3061, 1602, 1586, 1575, 1475, 1432, 1416, 1309, 1291, 1247, 1205, 1155, 1120, 1099, 1071, 1056, 1024, 989, 852, 817, 779, 744, 732, 613.

**HRMS** (ESI); calc'd for $C_{10}H_8N_2F$ $[M+H]^+$ : *m/z* 175.0672, found 175.0673.

NMR data in accordance with literature precedent.[S7]

## 2-(3,5-bis(trifluoromethyl)phenyl)pyridine (4j)



Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(3,5-bis(trifluoromethyl)phenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 621 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as an off-white solid; (256 mg, 88% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.66 (1H, dt, $J$ = 4.8, 1.3 Hz), 8.39 (2H, s), 7.83 (1H, s), 7.78-7.71 (2H, m), 7.26 (1H, ddd, $J$ = 6.7, 4.8, 2.1 Hz).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 154.1, 150.2, 141.3, 137.3, 132.1 (q, $^{2}J_{C\text{-}F}$ = 33 Hz), 126.9 (m), 123.6, 123.4 (q, $^{1}J_{C\text{-}F}$ = 273 Hz), 122.4 (ap quin, $^{3}J_{C\text{-}F}$ = 4 Hz), 120.6.

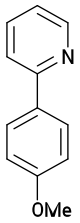
**IR** (solid, $cm^{-1}$); ν 2877, 1618, 1590, 1573, 1486, 1468, 1454, 1426, 1380, 1273, 1263, 1236, 1166, 1117, 1107, 1073, 1046, 993, 935, 907, 895, 838, 783, 725, 682, 629, 620.

**HRMS** (ESI); calc'd for $C_{13}H_7F_6N$ $[M+H]^+$ : *m/z* 292.0561, found 292.0547.

**Melting Point**; 48 – 49 °C

NMR data in accordance with literature precedent.[S8]

## 2-(4-methoxyphenyl)pyridine (4k)



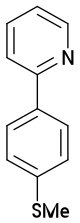

Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(4-methoxyphenyl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 462 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as an off-white solid; (180 mg, 97% yield).

**$^1$H-NMR** (300 MHz, $CDCl_3$); δ 8.65 (1H, dt, *J* = 4.8, 1.3 Hz), 7.96 (2H, d, *J* = 8.9 Hz), 7.74-7.65 (2H, m), 7.17 (1H, ddd, *J* = 6.9, 4.9, 1.6 Hz), 7.00 (2H, d, *J* = 8.9 Hz), 3.86 (3H, s).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 160.5, 157.1, 149.5, 136.8, 131.9, 128.2, 121.4, 119.9, 114.2, 55.4.

NMR data in accordance with literature precedent.[S8]

## 2-(4-(methylthio)phenyl)pyridine (4l)



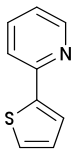

Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(4-(methylthio)phenyl)-1,3,2-dioxaborinan-5-yl)methoxy) silane (1.5 mmol, 486 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as an white solid; (197 mg, 98% yield).

**$^1$H-NMR** (300 MHz, $CDCl_3$); δ 8.68 (1H, dt, *J* = 4.9, 1.3 Hz), 7.94 (2H, d, *J* = 8.6 Hz), 7.79-7.69 (2H, m), 7.35 (2H, d, *J* = 8.6 Hz), 7.23 (1H, ddd, *J* = 6.7, 4.9, 1.6 Hz), 2.53 (3H, s).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 156.8, 149.6, 139.9, 136.8, 136.0, 127.2, 126.3, 122.0, 120.1, 15.5.

$^{1}$H NMR data in accordance with literature precedent.[S9]

## 2-(thiophen-2-yl)pyridine (4m)




Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(thiophen-2-yl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 426 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a brown oil; (127 mg, 79% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.60 (1H, dt, $J$ = 4.8, 1.3 Hz), 7.89 (1H, dd, $J$ = 3.0, 1.3 Hz), 7.68-7.63 (2H, m), 7.58 (1H, dt, $J$ = 7.9, 1.0 Hz), 7.37 (1H, dd, $J$ = 5.1, 3.0 Hz), 7.13 (1H, ddd, $J$ = 7.3, 4.9, 1.3 Hz).

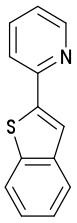
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 153.5, 149.6, 142.2, 136.8, 126.3, 126.2, 123.6, 121.8, 120.3.

**IR** (film, $cm^{-1}$); ν 3101, 3012, 2876, 2342, 2132, 1586, 1567, 1526, 1466, 1434, 1374, 1282, 1265, 1193, 1152, 1093, 1058, 1041, 989, 898, 863, 820, 760, 690, 617, 608.

**HRMS** (ESI); calc'd for $C_9H_7NS$ $[M+H]^+$ : *m/z* 162.0377, found 162.0383.

NMR data in accordance with literature precedent.[S10]

## 2-(benzo[*b*]thiophen-2-yl)pyridine (4n)




Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(benzo[*b*]thiophen-2-yl)-1,3,2-dioxaborinan-5-yl)methoxy) silane (1.5 mmol, 501 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a white solid; (194 mg, 92% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.69-8.60 (1H, m), 7.91-7.78 (4H, m), 7.74 (1H, td, *J* = 7.7, 1.7 Hz), 7.41-7.31 (2H, m), 7.22 (1H, ddd, *J* = 7.2, 4.9, 1.2 Hz).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 152.5, 149.7, 144.8, 140.7, 140.5, 136.7, 125.1, 124.5, 124.1, 122.7, 122.6, 121.1, 119.6.

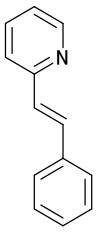
**IR** (solid, $cm^{-1}$); ν 3045, 3001, 1918, 1811, 1674, 1627, 1586, 1559, 1530, 1462, 1428, 1337, 1314, 1268, 1262, 1246, 1190, 1151, 1093, 1072, 1049, 1017, 991, 971, 958, 942, 892, 875, 838, 778, 752, 736, 725, 704, 669, 618.

**HRMS** (ESI); calc'd for $C_{13}H_{10}NS$ $[M+H]^+$ : *m/z* 212.0534, found 212.0543.

**Melting Point**; 129 – 131 °C

NMR data in accordance with literature precedent.[S11]

## (*E*)-2-styrylpyridine (4o)



Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), (*E*)-trimethyl((5-methyl-2-styryl-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 456 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a white solid; (179 mg, 99% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.45 (1H, m), 7.52 (1H, dt, *J* = 7.9, 1.8 Hz), 7.46-7.42 (3H, m), 7.26-7.20 (3H, m), 7.14 (1H, tt, *J* = 7.2, 1.7 Hz), 7.08 (1H, d, *J* = 14.7 Hz), 7.02-6.98 (1H, m).

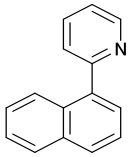
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 155.6, 149.5, 136.7, 136.6, 132.9, 128.8, 128.4, 127.8, 127.2, 122.2, 122.1.

**HRMS** (ESI); calc'd for $C_{13}H_{11}N$ $[M+H]^+$ : *m/z* 182.0964, found 182.1046.

**Melting Point**; 94 – 97 °C

Data in accordance with literature precedent.[S12]

## 2-(naphthalen-1-yl)pyridine (4p)



Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(naphthalen-1-yl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 492 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a yellow oil; (158 mg, 77% yield).

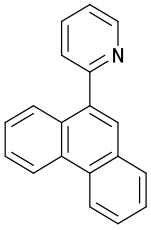
**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.67 (1H, ddd, *J* = 4.8, 1.7, 0.9 Hz), 8.00-7.97 (1H, m), 7.81-7.76 (2H, m), 7.64 (1H, td, *J* = 7.7, 1.8 Hz), 7.50-7.32 (5H, m), 7.16 (1H, ddd, *J* = 7.5, 4.9, 1.1 Hz).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 159.3, 149.5, 138.5, 136.5, 134.0, 131.2, 129.0, 128.4, 127.5, 126.5, 125.9, 125.7, 125.4, 125.1, 122.1.

**IR** (film, $cm^{-1}$); ν 3046, 3008, 1586, 1562, 1508, 1471, 1437, 1425, 1394, 1339, 1277, 1251, 1189, 1150, 1117, 1093, 1062, 1020, 993, 949, 864, 835, 806, 781, 749, 710, 649, 634, 614.

Data in accordance with literature precedent.[S13]

## 2-(phenanthren-9-yl)pyridine (4q)



Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(phenanthren-9-yl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 568 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a white solid; (120 mg, 47% yield).

**$^{1}$H-NMR** (300 MHz, $CDCl_3$); δ 8.86 (1H, ddd, *J* = 4.9, 1.7, 0.9 Hz), 8.80-8.77 (1H, m), 8.74-8.71 (1H, m), 8.18 (1H, dd, *J* = 8.2, 1.2 Hz), 7.94 (1H, dd, *J* = 7.8, 1.4 Hz), 7.90 (1H, s), 7.76-7.57 (6H, m), 7.29 (1H, ddd, *J* = 7.5, 4.9, 1.2 Hz).

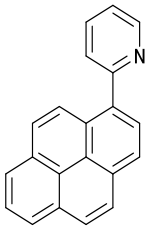
**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 159.4, 149.6, 137.3, 136.6, 131.5, 130.9, 130.6, 130.4, 129.1, 128.6, 127.2, 127.0, 126.9, 126.7, 126.7, 125.2, 123.1, 122.7, 122.2.

**IR** (solid, $cm^{-1}$); ν 3054, 3000, 1952, 1587, 1560, 1526, 1493, 1469, 1448, 1428, 1379, 1290, 1277, 1253, 1150, 1142, 1093, 1042, 992, 945, 897, 856, 796, 774, 763, 744, 722, 682, 639, 617.

**HRMS** (ESI); calc'd for $C_{19}H_{13}N$ $[M+Na]^+$ : *m/z* 278.0946, found 278.0924.

**Melting Point**; 83 – 86 °C

## 2-(pyren-1-yl)pyridine (4r)




Tetrakis(triphenylphoshine)palladium (0.01 mmol, 12 mg), potassium carbonate (2 mmol, 276 mg), trimethyl((5-methyl-2-(pyren-1-yl)-1,3,2-dioxaborinan-5-yl)methoxy)silane (1.5 mmol, 604 mg), and 2-bromopyridine (1 mmol, 0.1 mL) were reacted together under standard protocol to give the desired product as a yellow solid; (56 mg, 20% yield).

**$^1$H-NMR** (300 MHz, $CDCl_3$); δ 8.91-8.89 (1H, m), 8.38 (1H, d, *J* = 9.3 Hz), 8.28 (1H, d, *J* = 7.9 Hz), 8.24-8.15 (3H, m), 8.12-8.09 (2H, m), 8.07 (1H, d, *J* = 6.0 Hz), 8.02 (1H, d, *J* = 7.6 Hz), 7.92 (1H, td, *J* = 7.7, 1.8 Hz), 7.77 (1H, d, *J* = 7.8 Hz), 7.42 (1H, ddd, *J* = 7.5, 4.9, 1.1 Hz).

**$^{13}$C-NMR** (75.5 MHz, $CDCl_3$); δ 159.2, 149.5, 136.8, 135.2, 131.6, 131.4, 130.9, 128.6, 128.2, 128.0, 127.7, 127.4, 126.1, 126.0, 125.5, 125.2, 125.1, 124.9, 124.8, 124.7, 122.1.

**IR** (solid, $cm^{-1}$); ν 3041, 2925, 2185, 2164, 2012, 1585, 1564, 1468, 1427, 847, 784, 748, 720, 617.

**HRMS** (ESI); calc'd for $C_{21}H_{13}N$ $[M+H]^+$ : *m/z* 280.1126, found 280.1099.

**Melting Point**; 80 – 82 °C

NMR data in accordance with literature precedent.[S14]

## References:


S1. J. C. Allen, G. Kociok-Köhn, C. G. Frost, *Org. Biomol. Chem*., 2012, **10**, 32-35.

S2. M. Kagotani, S. Hanessian, *Synthesis*, 1987, **4**, 409-411.

S3. L. Ackermann, A.R. Kapdi, S. Fenner, C. Kornhaaß, C. Schulzke, *Chem. Eur. J.*, 2011, **17**, 2965-2971.

S4. O. Kobayashi, D. Uraguchi, T. Yamakawa, *Org. Lett.*, 2009, **11**, 2679-2682.

S5. J. Norinder, A. Matsumoto, N. Yoshikai, E. Nakamura, *J. Am. Chem. Soc.*, 2008, **130**, 5858-5859.

S6. L. Ackermann, H.K. Potukuchi, A.R. Kapdi, C. Schulzke, *Chem. Eur. J.*, 2010, **16**, 3300-3303.

S7. A. Seggio, A. Jutand, G. Priem, F. Mongin, *Synlett.*, 2008, **12**, 2955-2960.

S8. K. Billingsley, S.L. Buchwald, *Angew. Chem. Int. Ed.*, 2008, **47**, 4695-4698.

S9. Y. Harrak, G. Casula, J. Basset, G. Rosell, S. Plescia, D. Raffa, M.G. Cusimano, R. Pouplana, M.D. Pujol, *J. Med. Chem.*, 2010, **53**, 6560-6571.

S10. M.R. Luzung, J.S. Patel, J. Yin, *J. Org. Chem.*, 2010, **75**, 8330-8332.

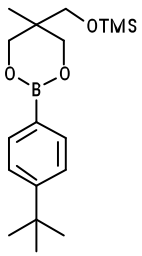
S11. D. Ghosh, H.M. Lee, *Org. Lett.*, 2012, **14**, 5534-5537.

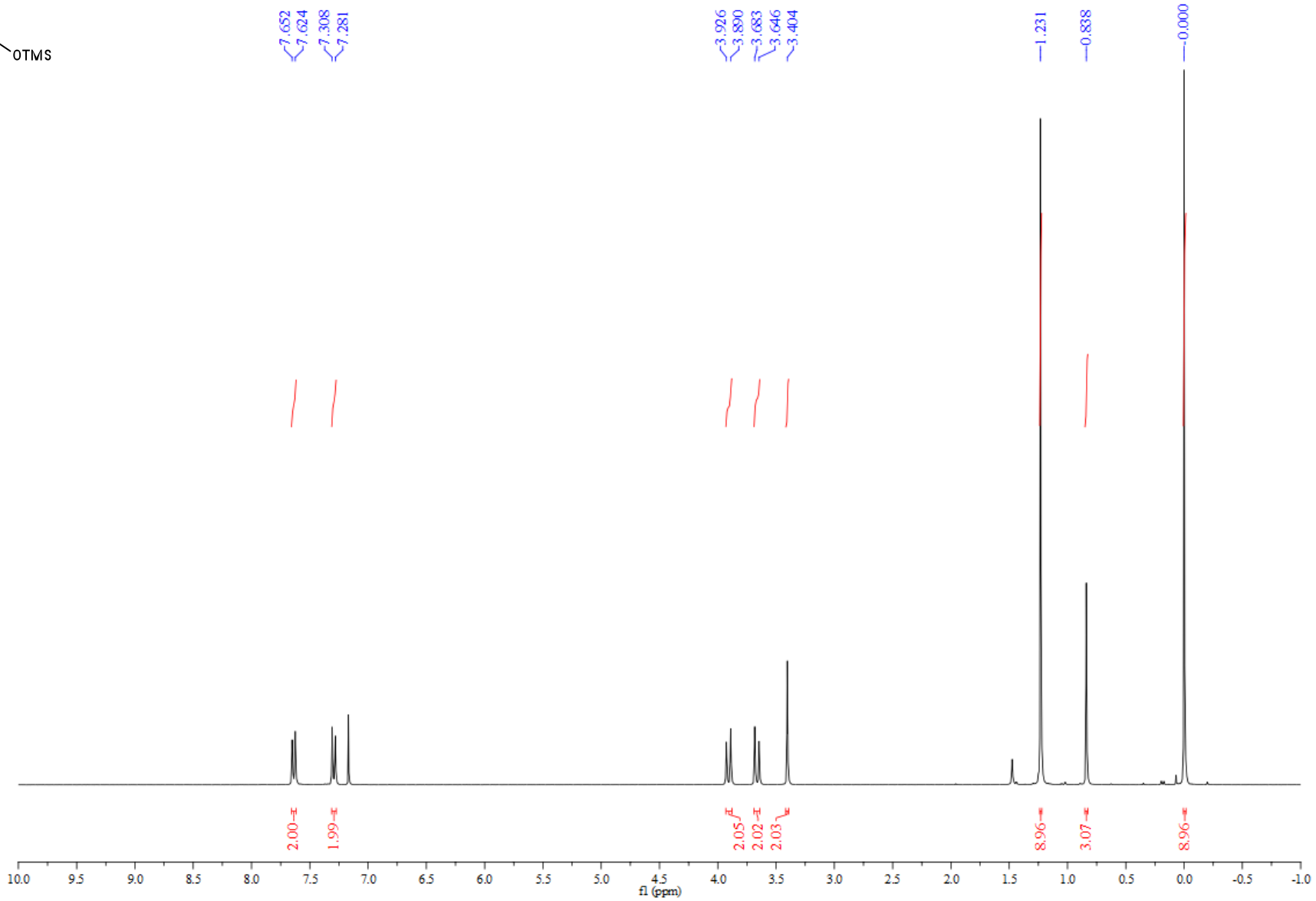
S12. G. Cahiez, O. Gager, F. Lecomte, *Org. Lett.*, 2008, **10**, 5255-5256.

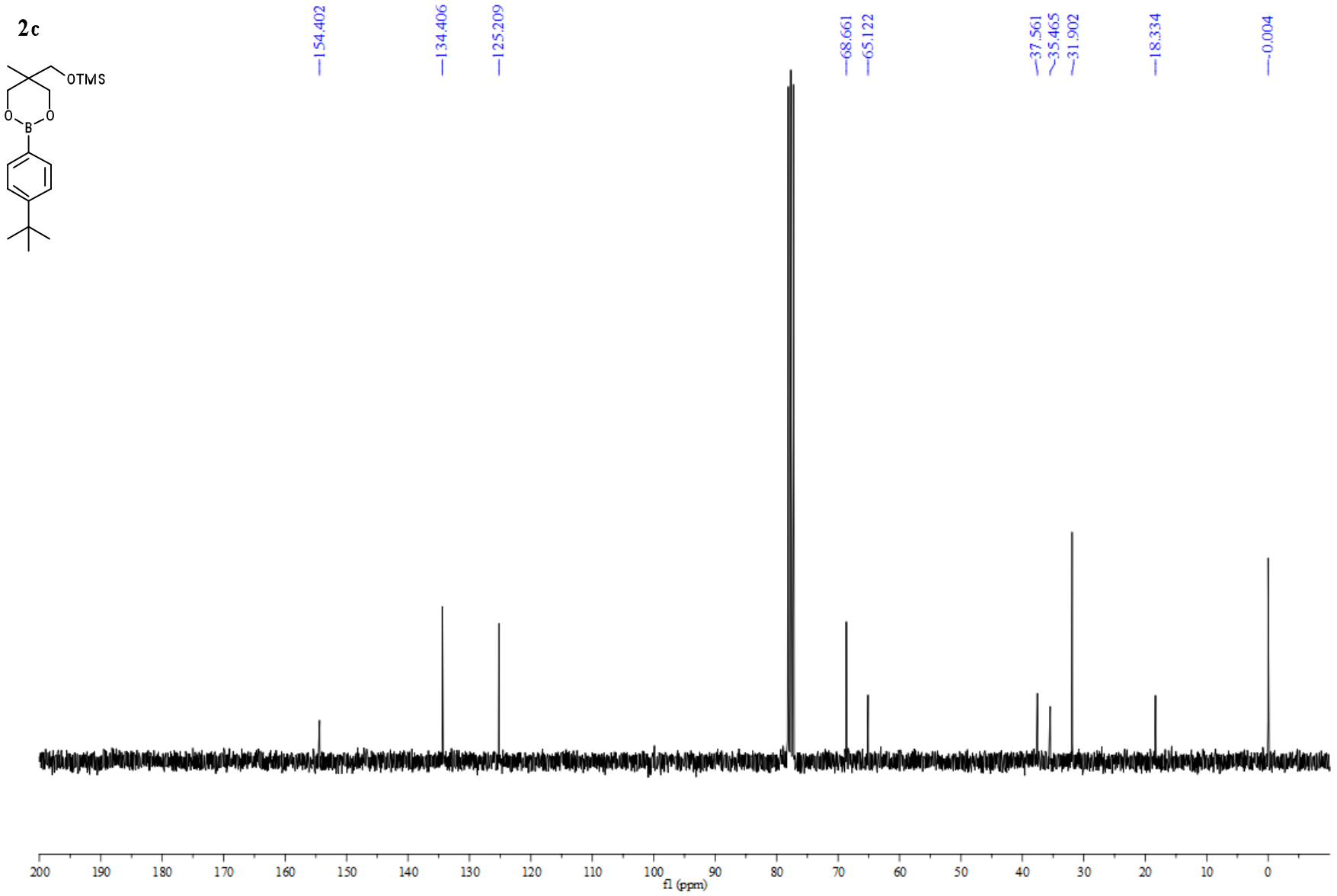
S13. A. Núñez, A. Sánchez, C. Burgos, J. Alvarez-Builla, *Tetrahedron*, 2004, **60**, 6217-6224.

S14. W. Wu, W. Wu, S. Ji, H. Guo, J. Zhao, *Eur. J. Inorg. Chem.*, 2010, **28**, 4470-4482.

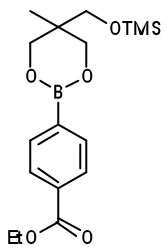
**2c**

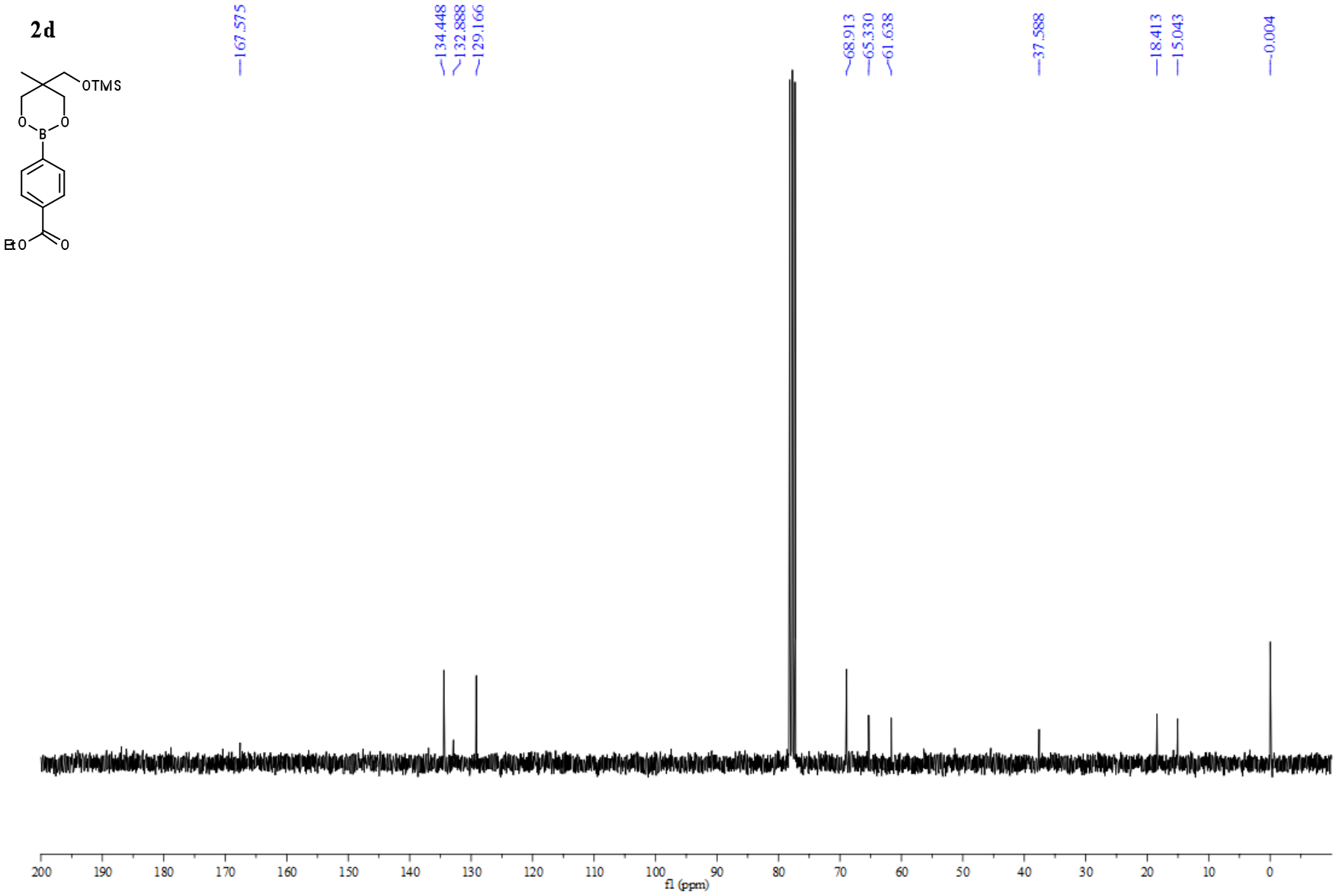


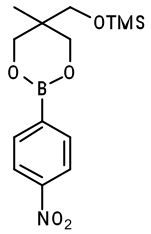


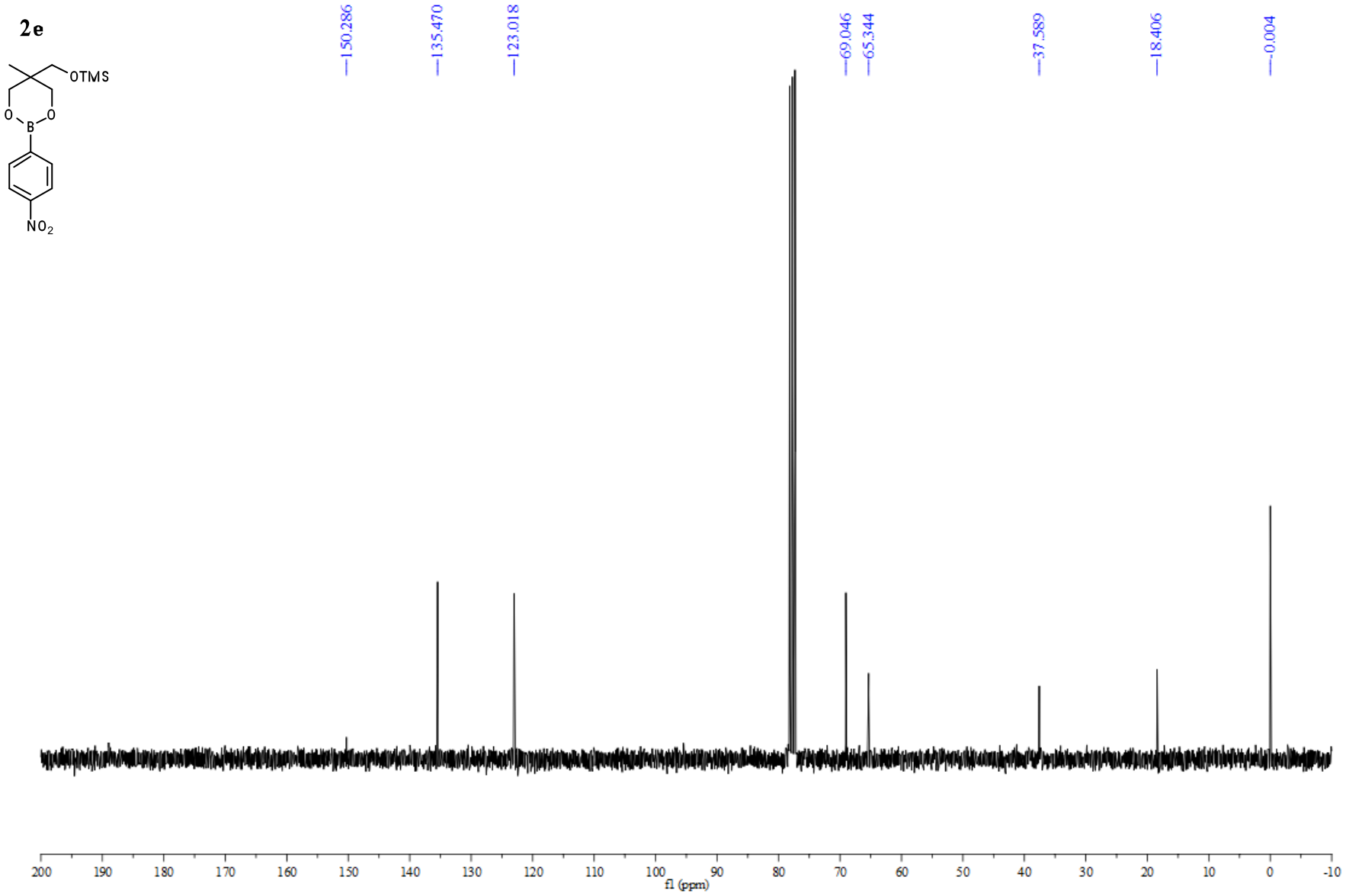
**2d**



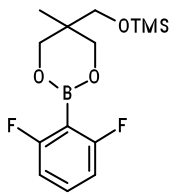


**2e**

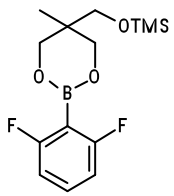




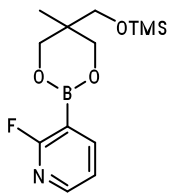
**2h**

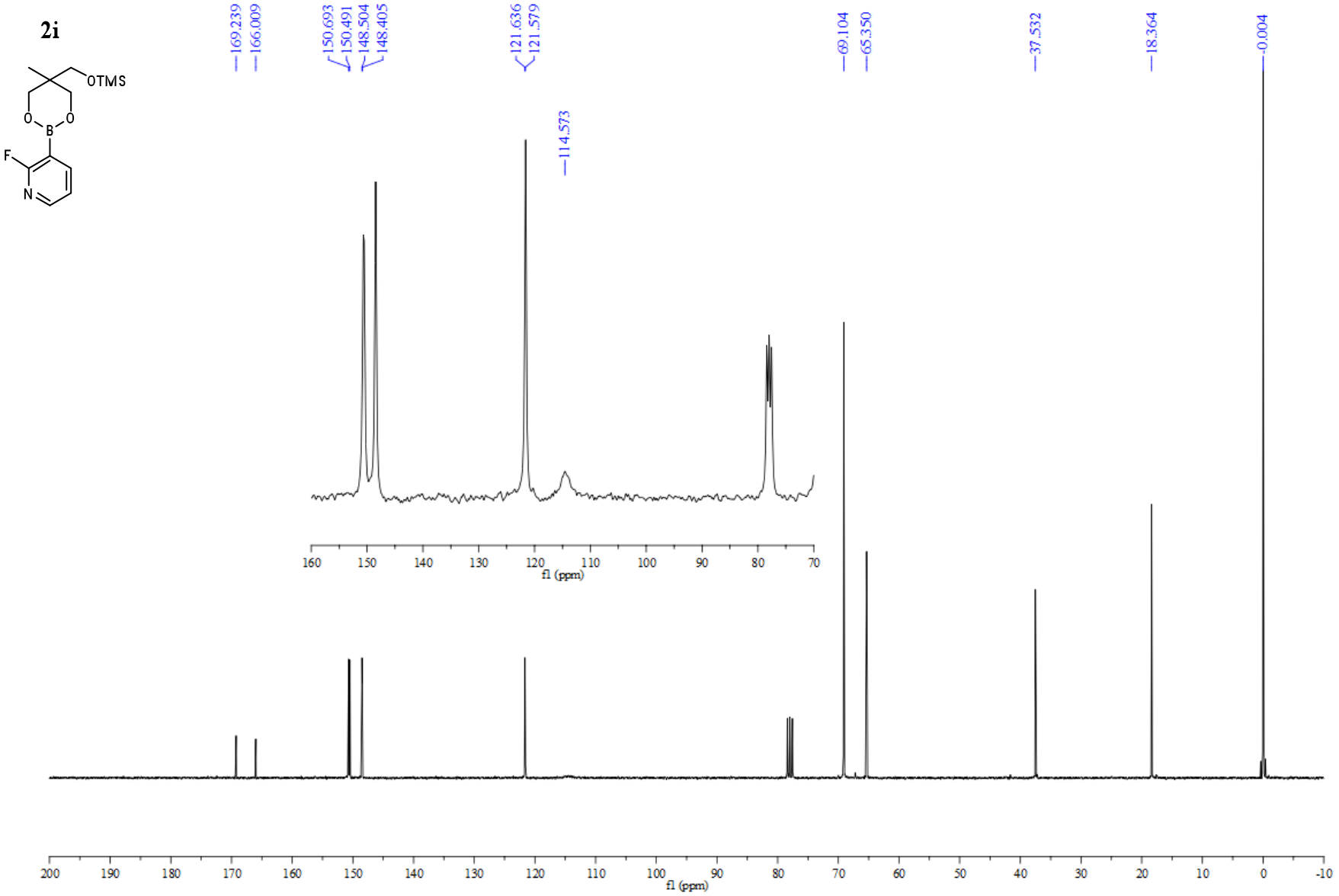


**2h**

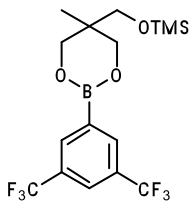


**2i**

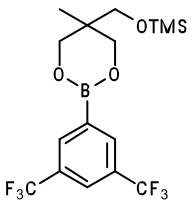




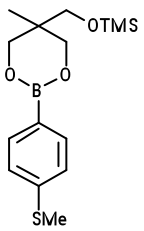
**2j**



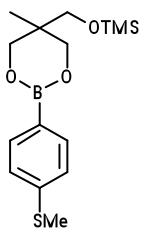
**2j**



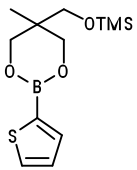
**21**



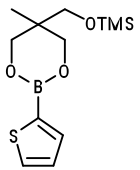
**21**



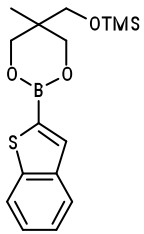
**2m**

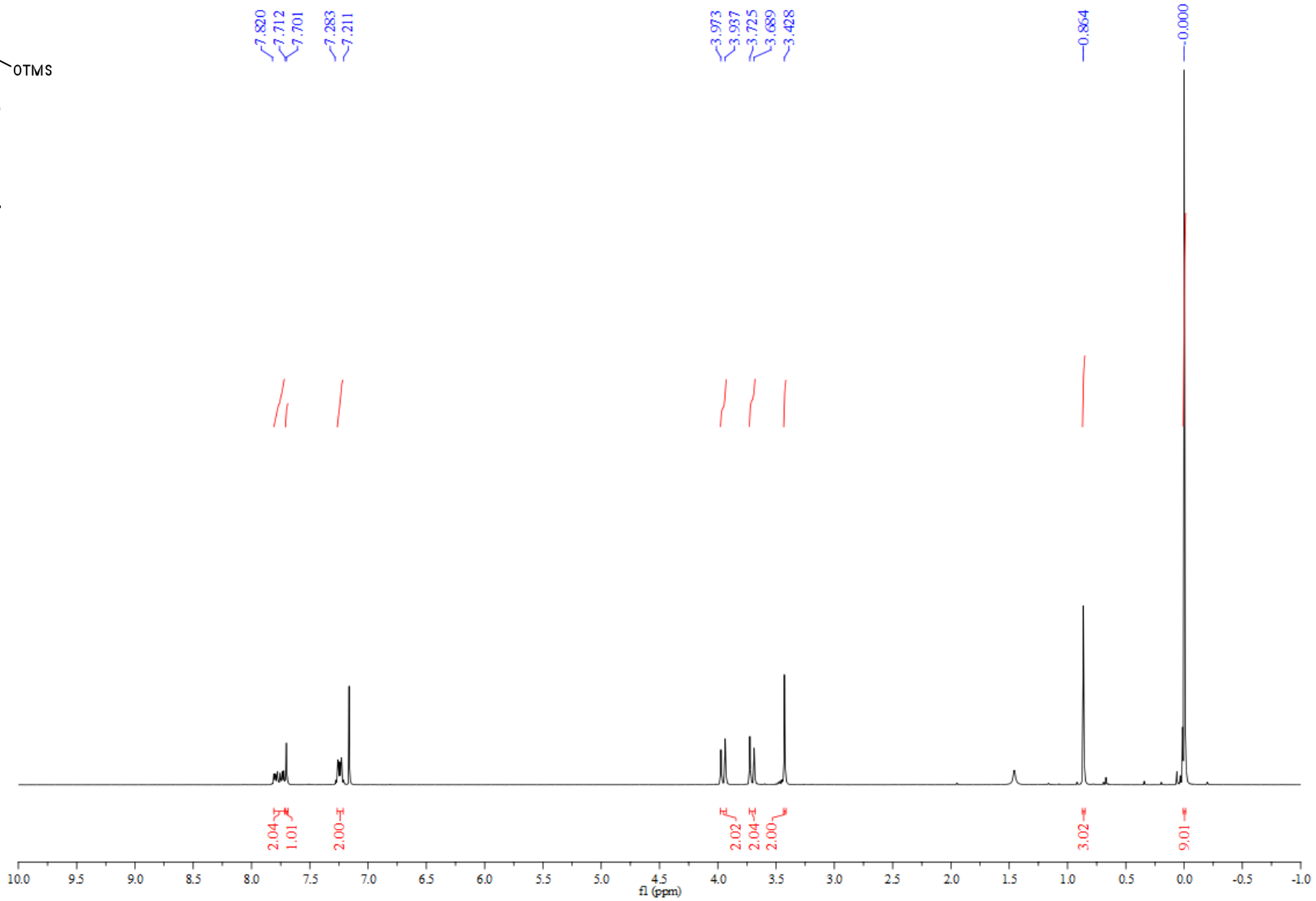


**2m**

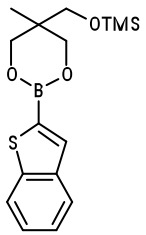


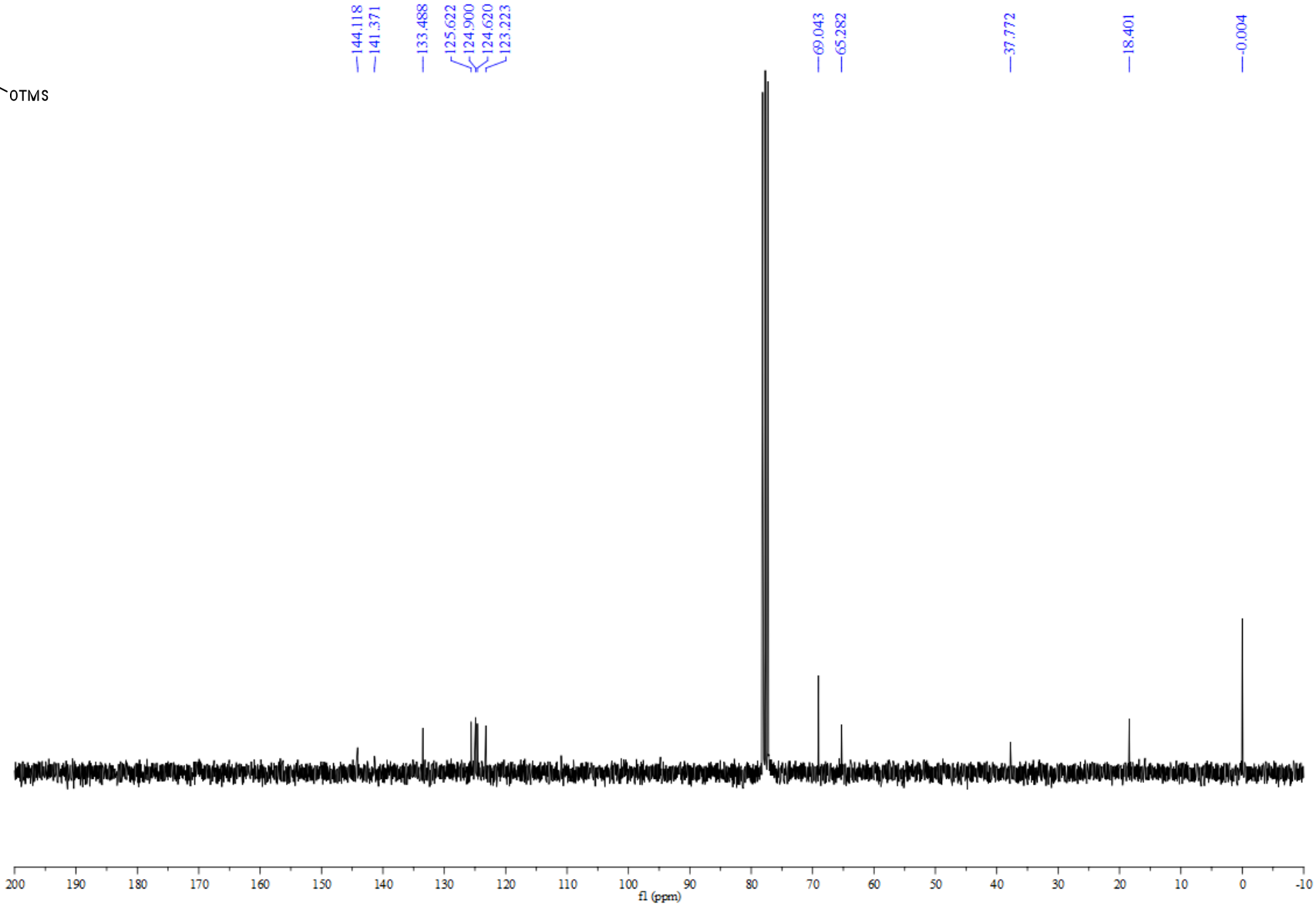
**2n**



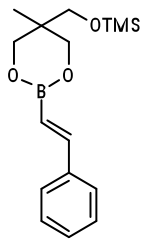



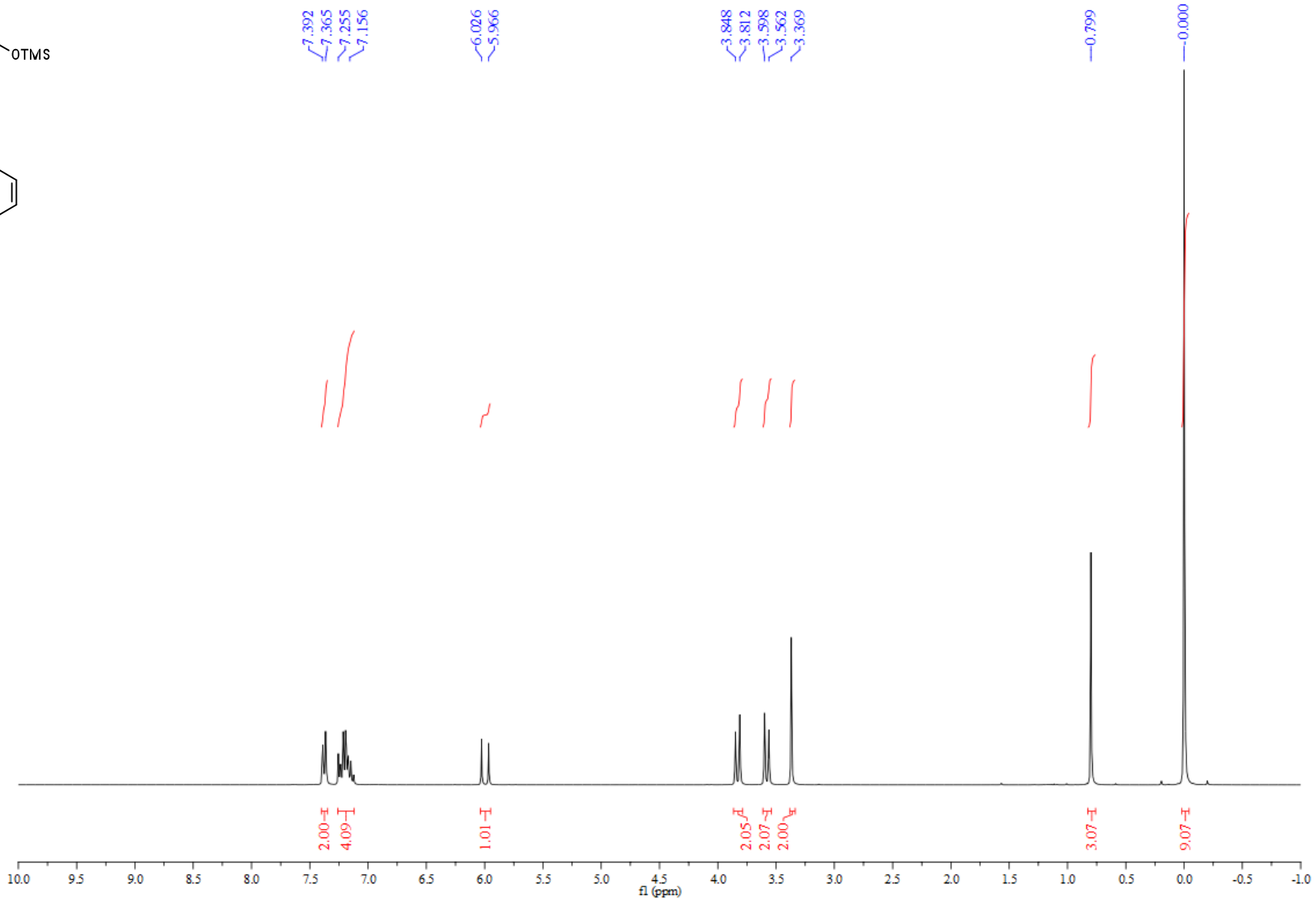
**2n**

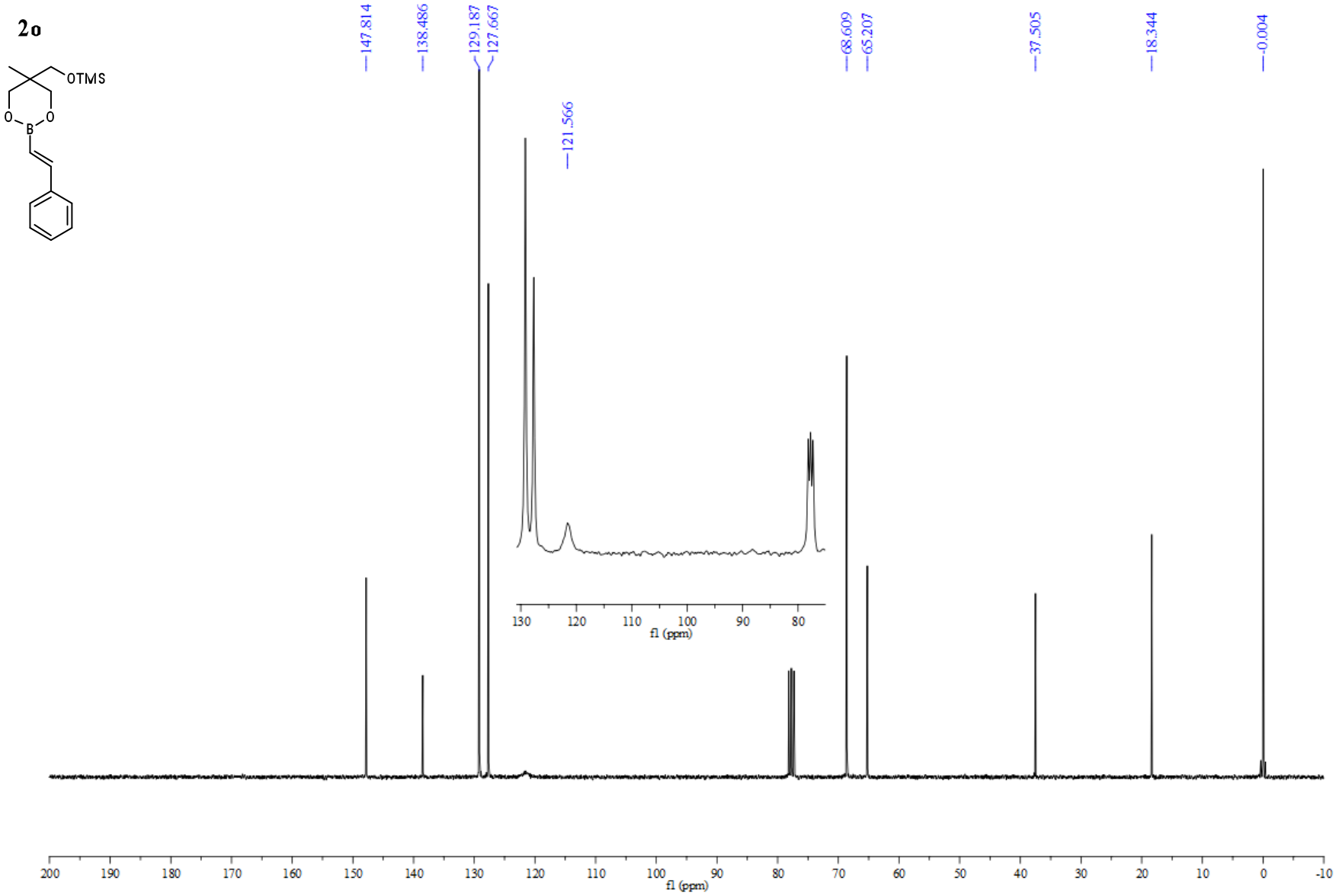


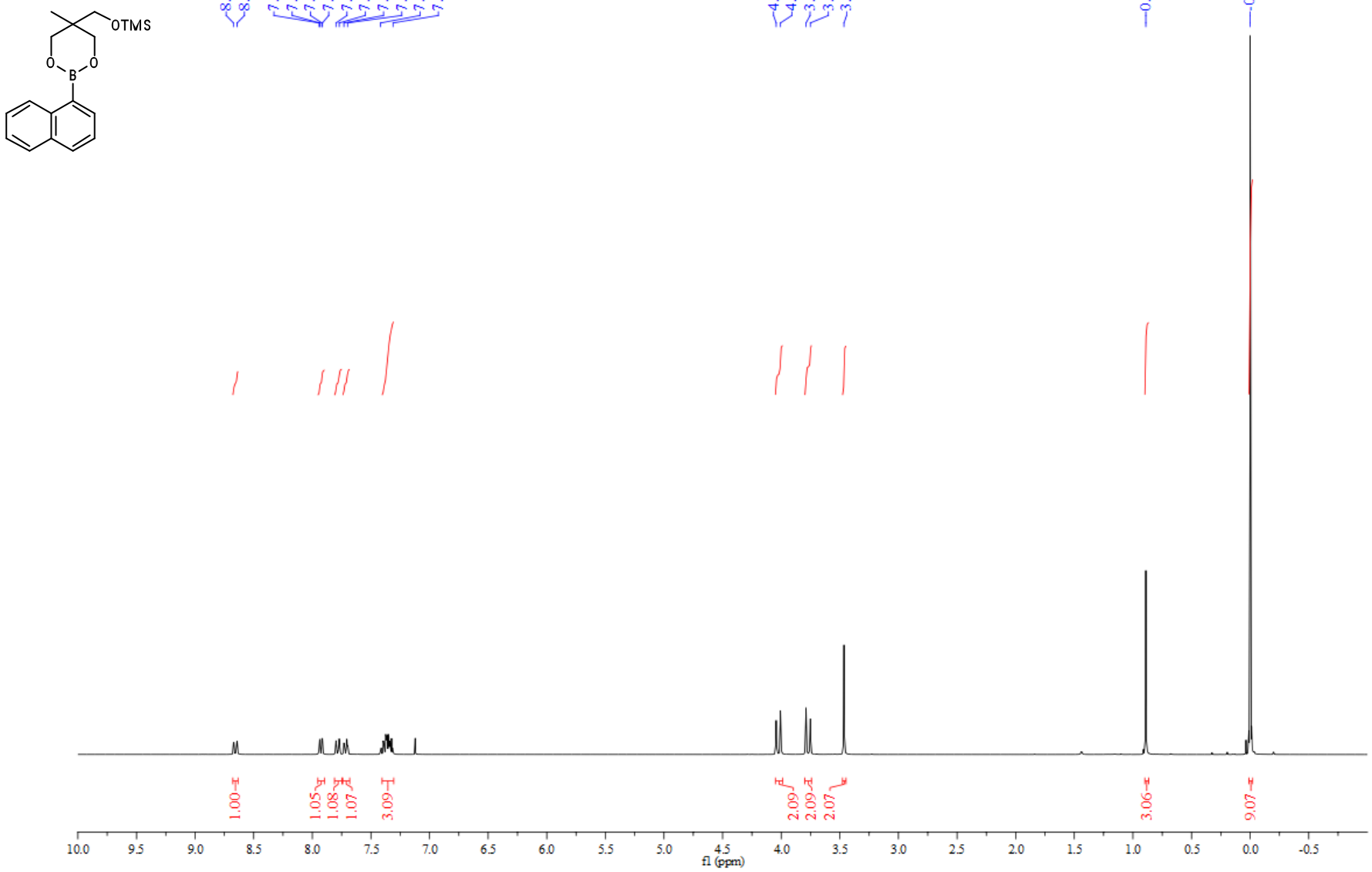
**2o**

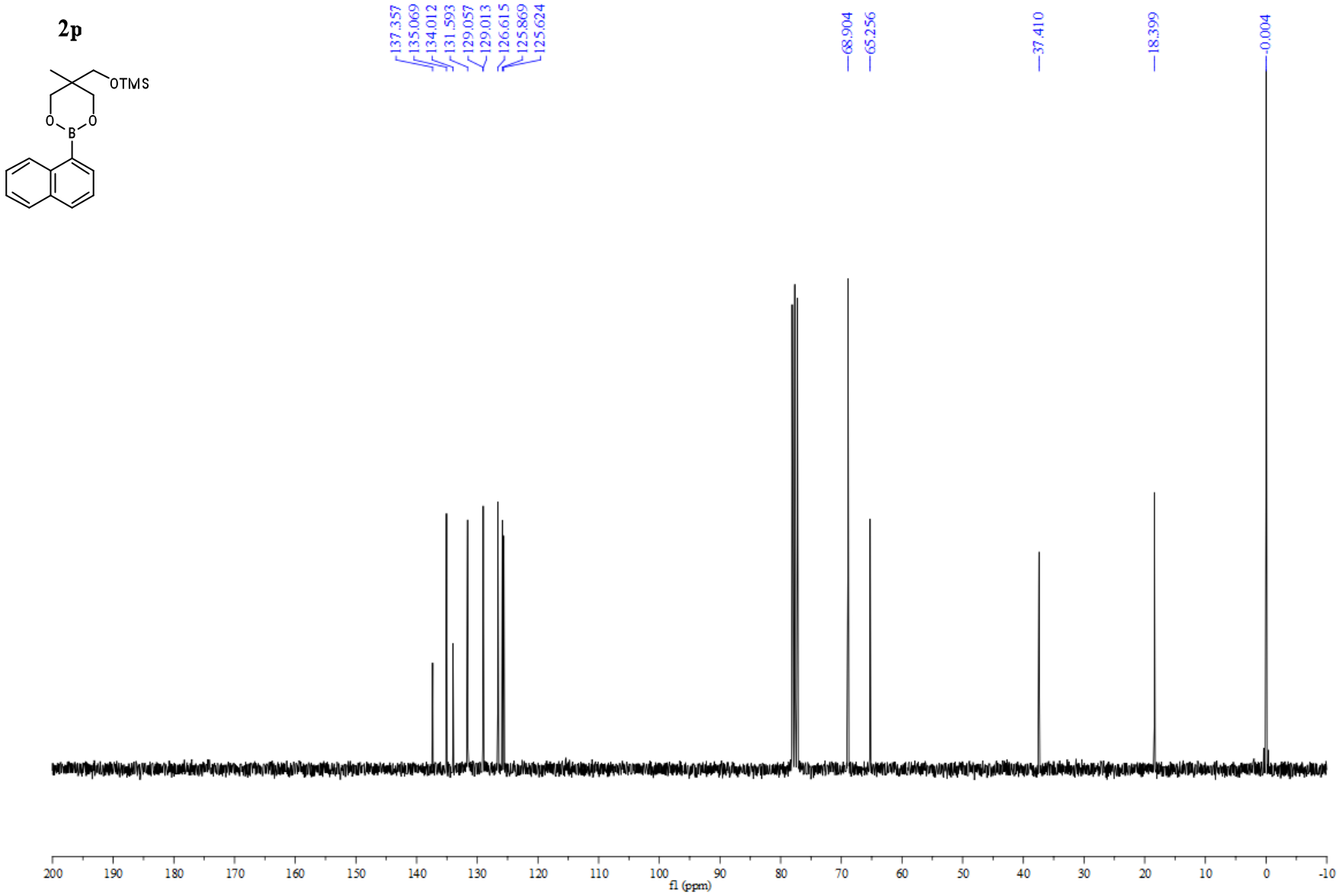


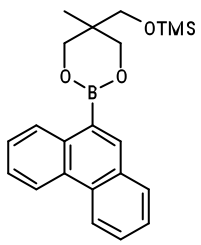


**2p**

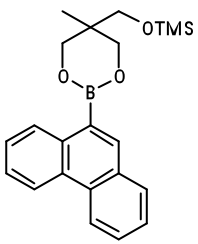


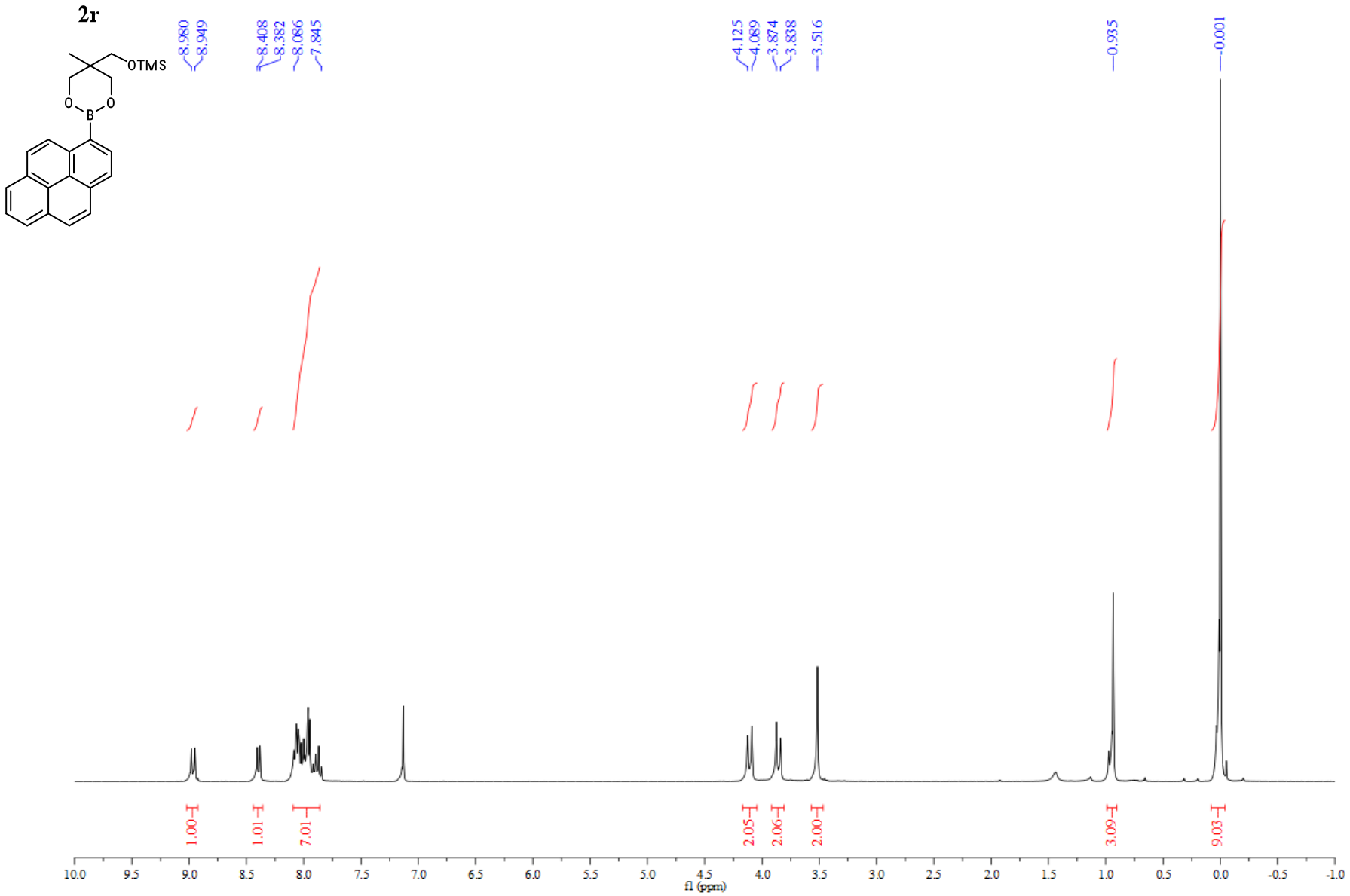


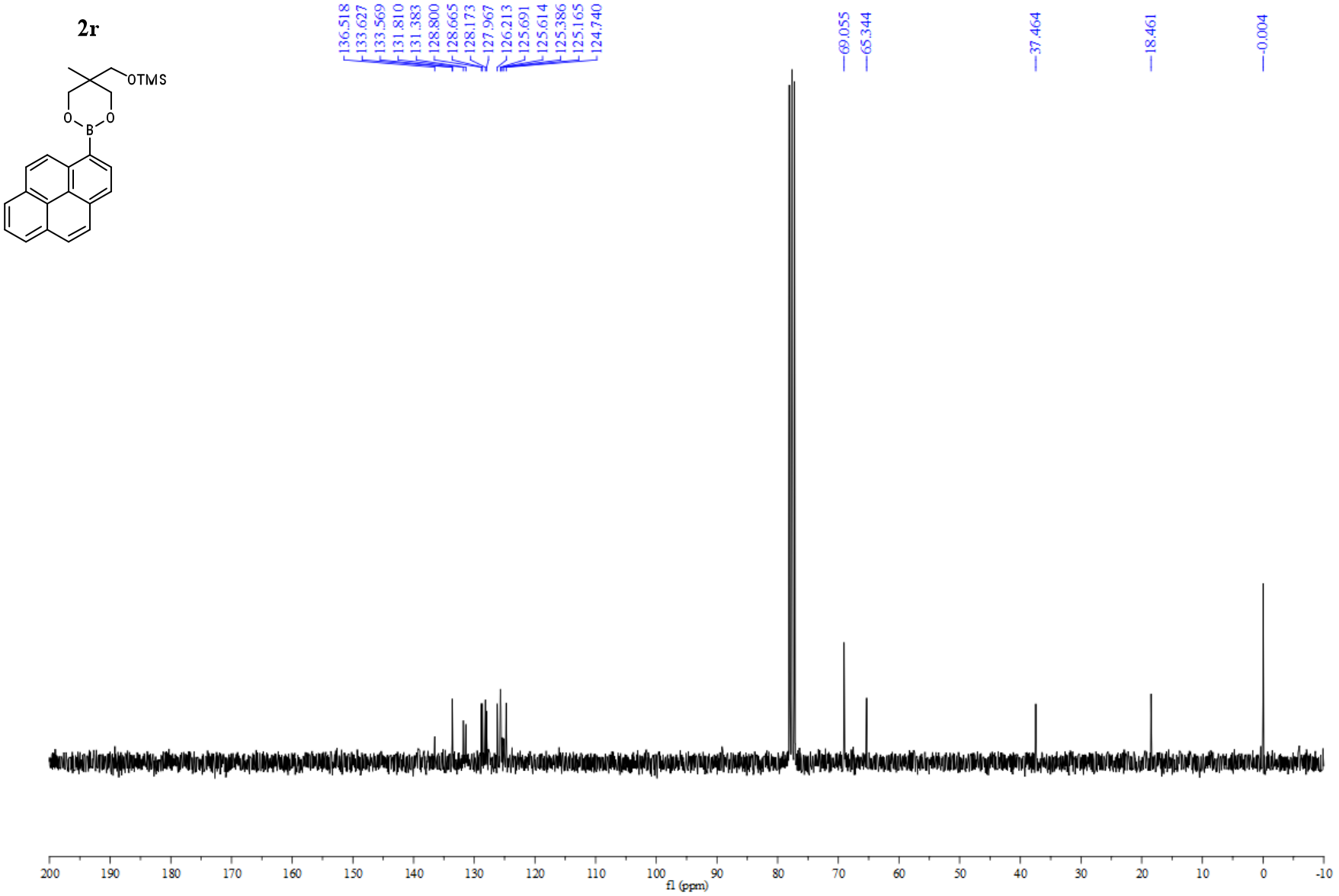
**2q**



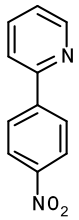
**2q**

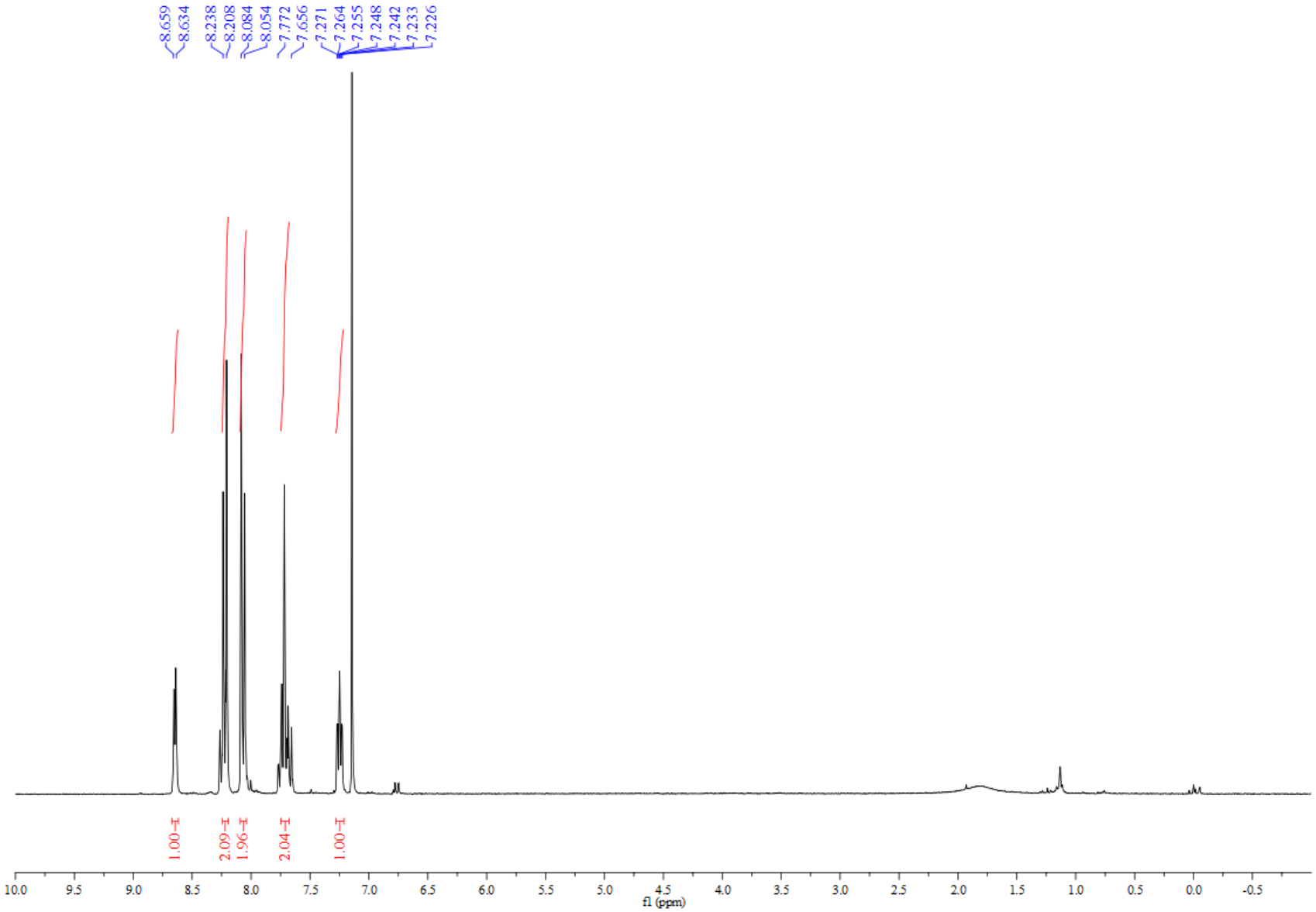


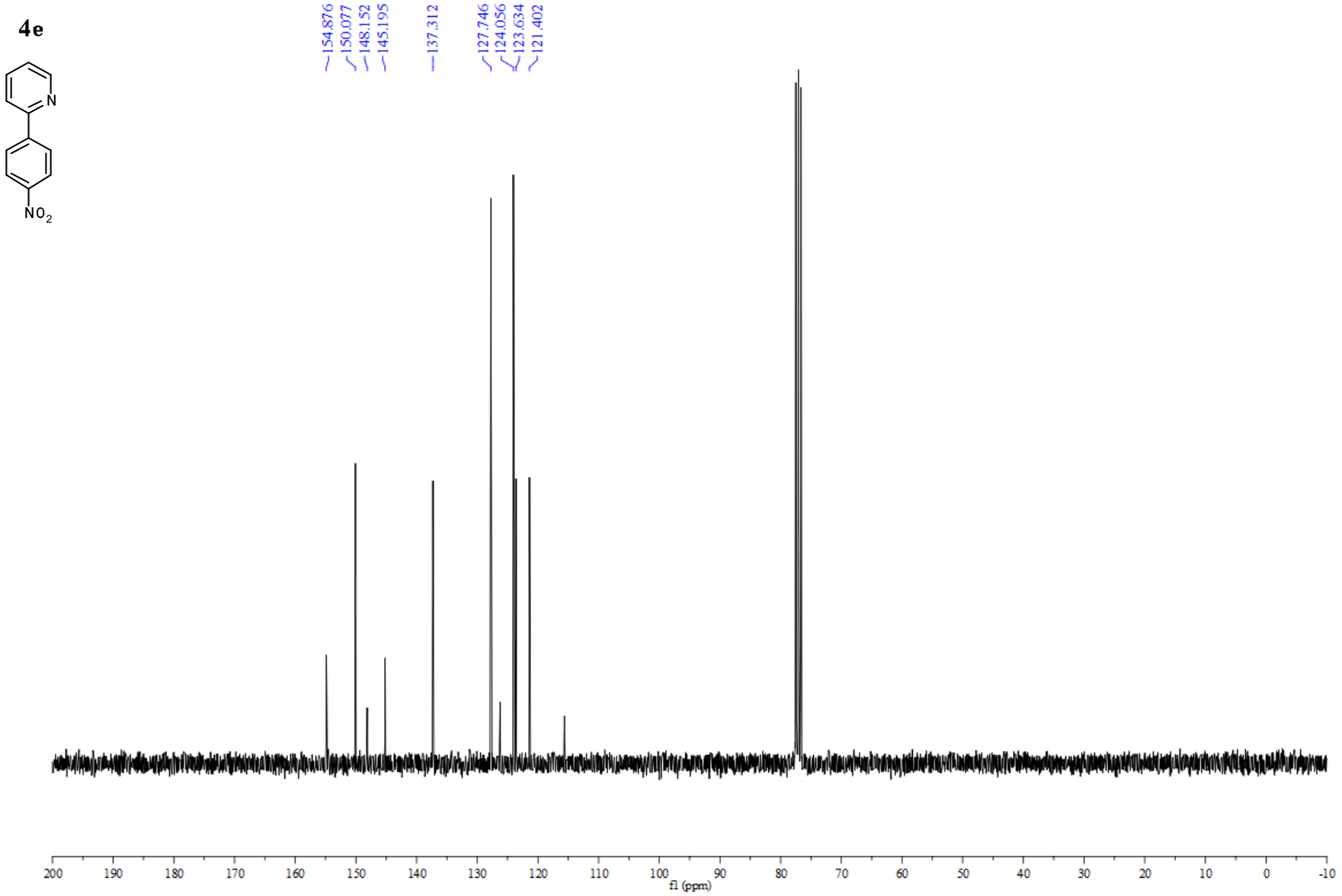




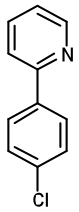
**4e**

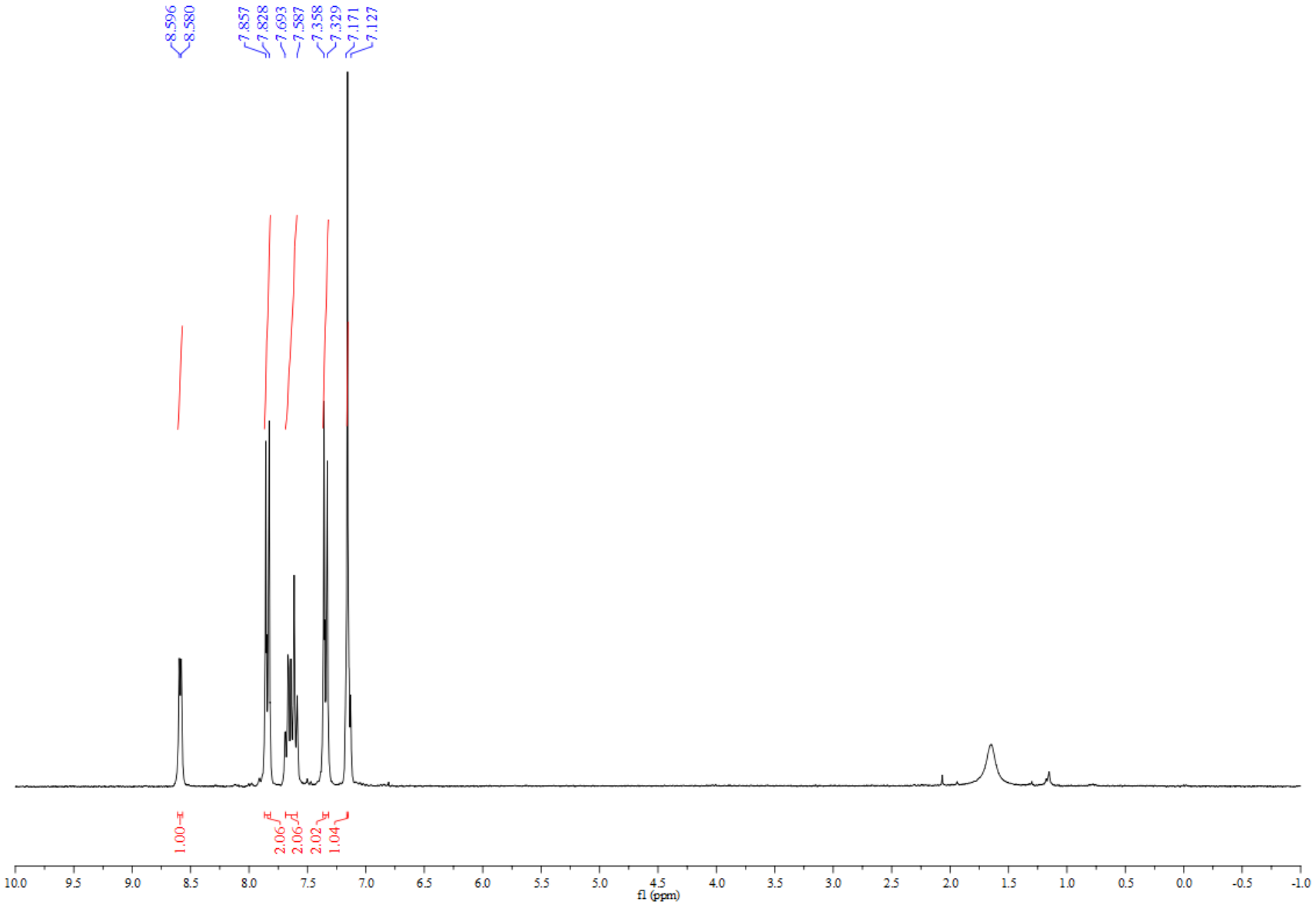


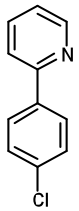


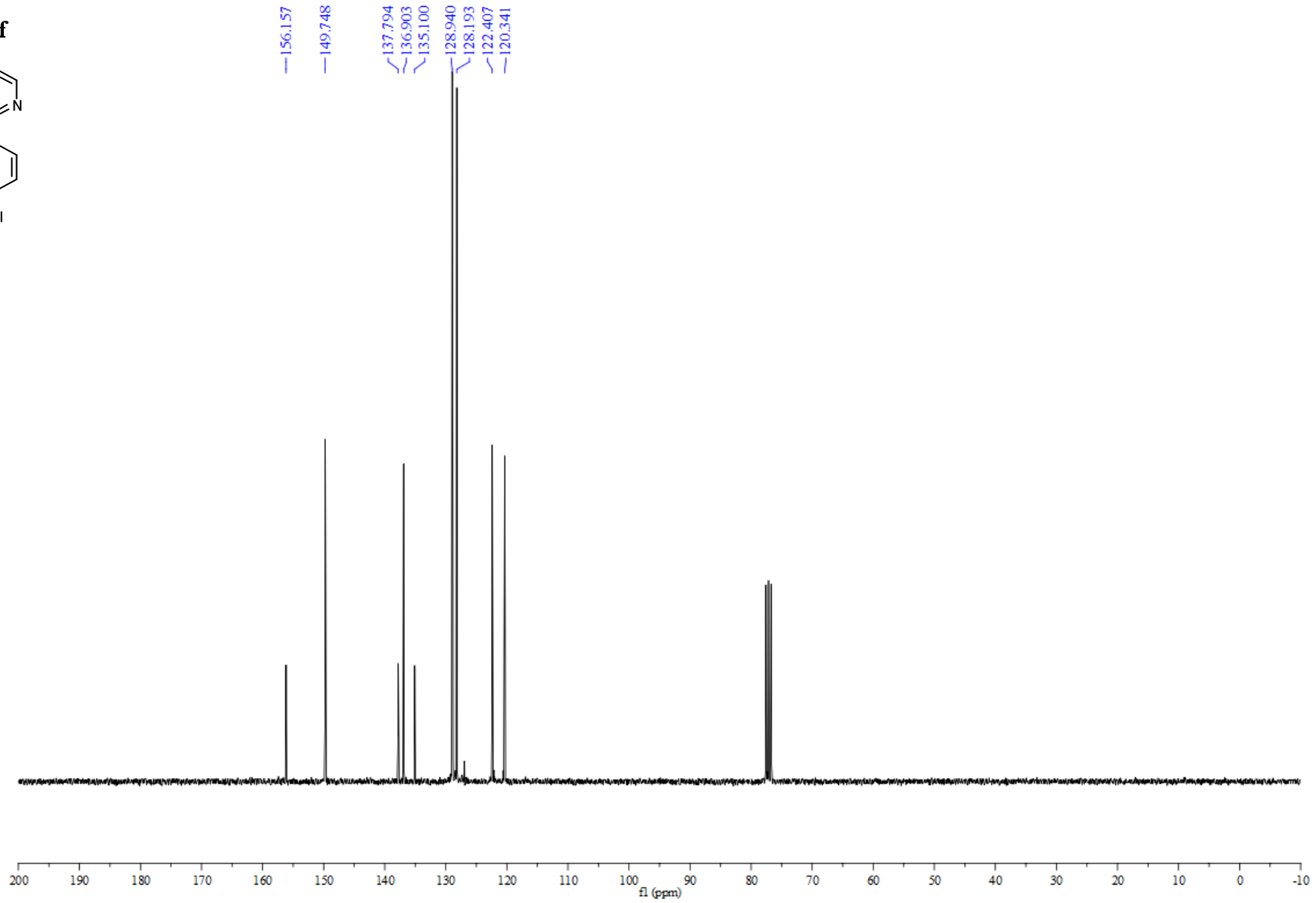
**4f**



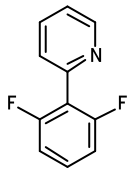



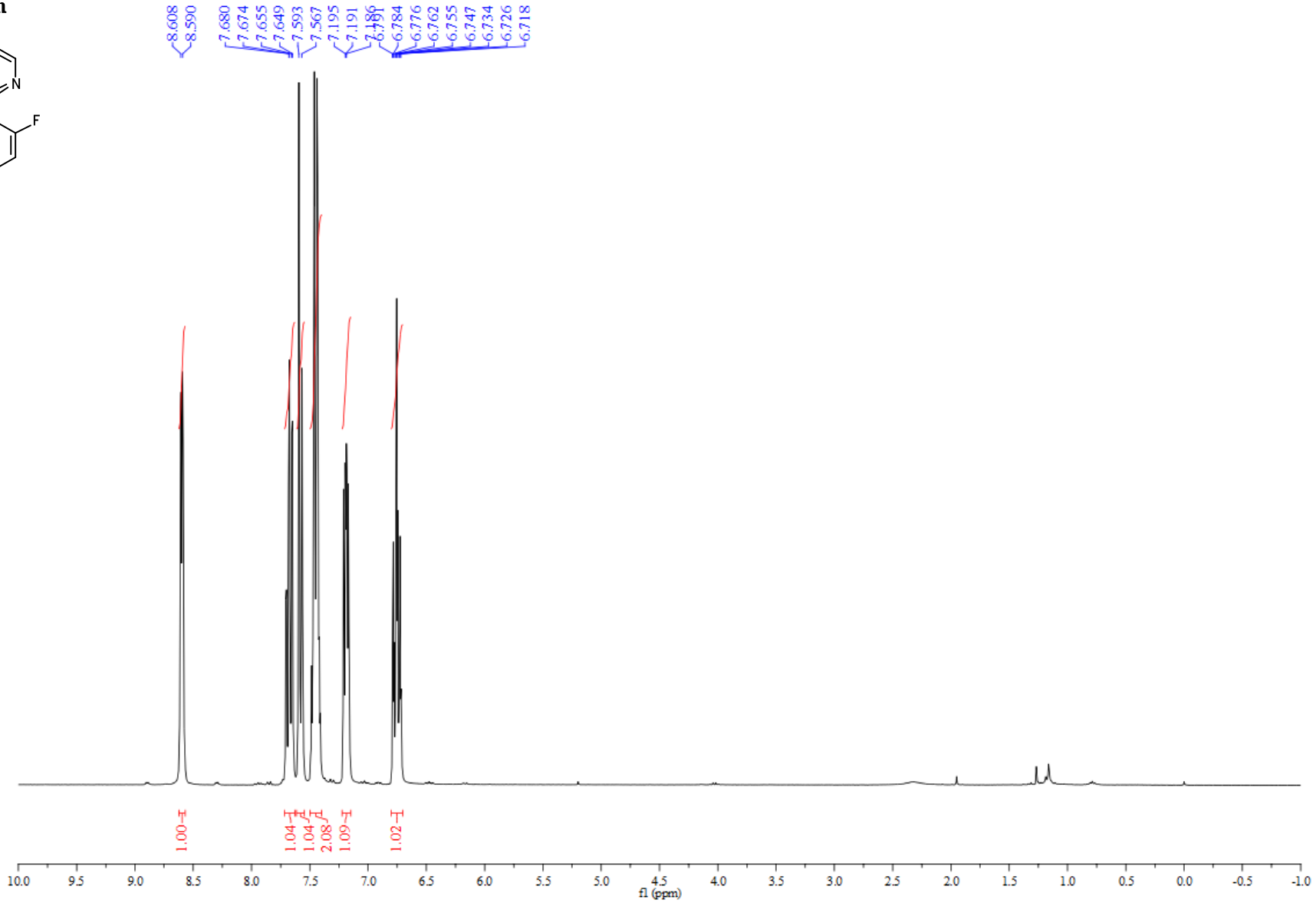
**4f**



**4h**



**4h**