Supporting Information

Enantioselective Hydrophosphonylation of *N*-Boc Imines Using Chiral Guanidine-Thiourea Catalysts.

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General information

^{1}H and ^{13}C NMR spectra were recorded with Bruker 360-WB or JEOL JNM-ECX600 spectrometers in $CDCl_3$ unless otherwise noted. Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane as internal reference (TMS, δ *ppm*= 0.0) or $CDCl_3$ solvent peak (δ *ppm*= 7.26 for ^{1}H and δ *ppm*= 77.0 for ^{13}C). IR spectra were measured with SHIMADZU FT/IR-610 spectrometer. High-performance liquid chromatography was carried out using SHIMADZU LC-20AB (liquid chromatograph), SHIMADZU SPD-MZA (detector). Optical rotation was recorded ANTON-PAAR MCP150 or JASCO P-2100 polarimeters. Column chromatography was conducted on Silica gel Merck (0.04–0.063μm). High-resolution mass spectra were obtained with a MAT95 Thermo-Finnigan spectrometer using electrospray analysis or with a JEOL MS-5414DART ION SENSE using DART analysis. X-ray diffraction analysis of the product was performed using Bruker D8-Venture diffractometer. X-ray diffraction analysis of the catalyst was performed using RIGAKU XtaLAB Synergy-S diffractometer.

All reactions were carried out in Schlenk tubes under an argon atmosphere. All solvents were distilled from appropriate drying agents prior to use, THF and Toluene were purified by Ultimate Solvent System 3S-TSK (Nikko Hansen & co., ltd.) and used directly. Diethyl phosphonate was purchased from Aldrich or Tokyo Chemical Industry Co., Ltd. and used directly. Imines were prepared according to a literature[1]. For continuous-flow experiment Imine was synthesized according to another literature[2], distilled under vacuum and stored in a glove-box.

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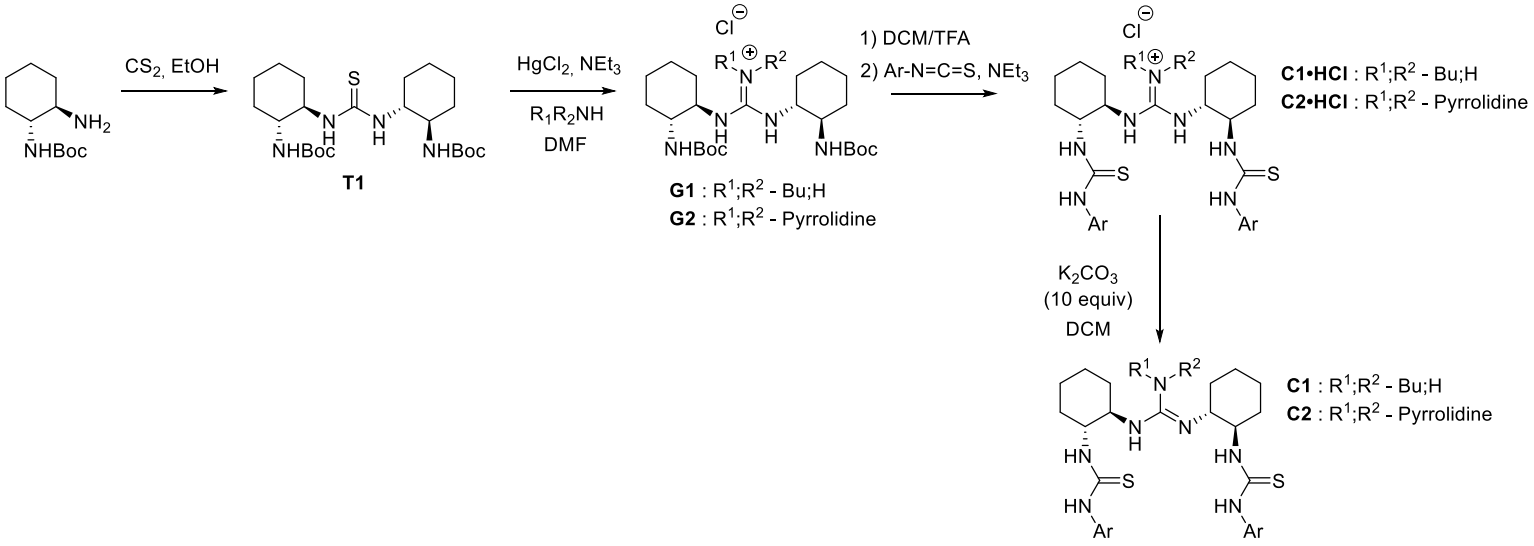
[1] Faming Zhuanli Shenqing, 110845369, 28 Feb 2020

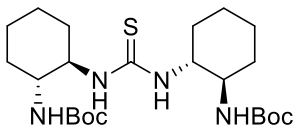
[2] Angew. Chem. Int. Ed. 2021, 60, 13671–13676

Catalyst synthesis

C1 and **C2** synthesis :



di-tert-butyl ((1*R*,1'*R*,2*R*,2'*R*)-(thiocarbonylbis(azanediyl))bis(cyclohexane-2,1-diyl))dicarbamate – T1 :

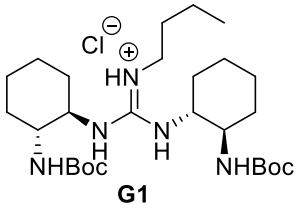


T1

(1*R*,2*R*)-trans-N-Boc-1,2-cyclohexanediamine (2.00 g, 9.33 mmol, 2.0 equiv.) was added to a solution of carbon disulfide (0.28 mL, 4.66 mmol, 1.0 equiv.) in ethanol (4.5 mL) at 0°C. The mixture was heated under reflux for 16h. After completion of the reaction, the mixture was allowed to cool down to r.t and a part of the product crystalized. The mixture was filtered through a fritted glass funnel providing the product as white crystals (440 mg). The filtrate was purified over chromatography column (EtOAc-Pentane 4:6). **T1** was obtained as a white solid (1.23 g). (1.67 g, 76%)

^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.00-1.50 (m, 8H), 1.42 (s, 18H), 1.69 (m, 4H), 1.98 (m, 2H), 2.20 (m, 2H), 3.41 (m, 2H), 4.01 (bs, 2H), 4.86 (bs, 2H), 6.37 (bs, 2H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 24.1, 24.6, 28.4, 31.9, 53.7, 58.6, 79.6, 156.78, 181.53.
IR (cm^{-1}) : 951, 1171, 1232, 1288, 1321, 1367, 1452, 1518, 1554, 1690, 2857, 2937, 2979, 3262, 3373.
MS (ESI) m/z : Calculated for $C_{23}H_{43}N_4O_4S$ – 471.2990[M+H$^+$]. found – 471.3000[M+H$^+$].
[α]$_D$ ($CHCl_3$, C 0.01, 20°C) = + 67.0 °.
Melting point 238-240 °C.

N-(bis(((1*R*,2*R*)-2-((tert-butoxycarbonyl)amino)cyclohexyl)amino)methylene)butan-1-aminium chloride – G1 :

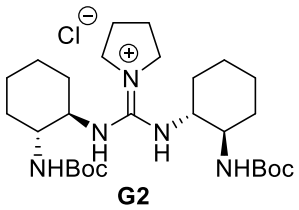


G1

To a solution of **T1** (1.00 g, 2.17 mmol, 1.0 equiv.) in DMF (5 mL) were added triethylamine (0.59 mL, 4.34 mmol, 2.0 equiv.) and N-butylamine (0.64 mL, 6.51 mmol, 3.0 equiv.). Mercury chloride (707 mg, 2.60 mmol, 1.2 equiv.) was added and the mixture was stirred vigorously for 3 days. The reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was washed with a saturated aq. NH_4Cl solution and dried over $MgSO_4$. The crude was then purified by chromatography (EtOAc-pentane 1:1 then DCM-MeOH 9:1) providing **G1** as a white powder (864 mg, 73%)

^{1}H NMR (360 MHz, $CDCl_3$) δ = 0.93 (t, 3H, J = 9.0 Hz),1.18-1.42 (m, 8H), 1.30-1.72 (m, 8H),1.40 (s, 18H), 1.88 (m, 2H), 2.13 (m, 2H), 3.13 (m, 2H), 3.44 (m, 2H), 8.08 (bs, 1H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 13.4, 19.7, 23.3, 24.4, 28.1, 30.5, 31.0, 31.2, 40.8, 53.3, 57.3, 80.3, 152.9, 157.8.
IR (cm^{-1}) : 951, 1023, 1173, 1236, 1256, 1323, 1366, 1391, 1452, 1524, 2862, 2934, 3265, 3337.
MS (ESI) m/z : Calculated for $C_{27}H_{52}N_5O_4$- 510.3993 [M+H$^+$]. found – 510.4014[M+H$^+$].
[α]$_D$ ($CHCl_3$, C 0.01, 20°C) = + 48.0 °.
Melting point 219-223 °C.

1-(bis(((1*R*,2*R*)-2-((tert-butoxycarbonyl)amino)cyclohexyl)amino)methylene)pyrrolidin-1-ium chloride – G2 :

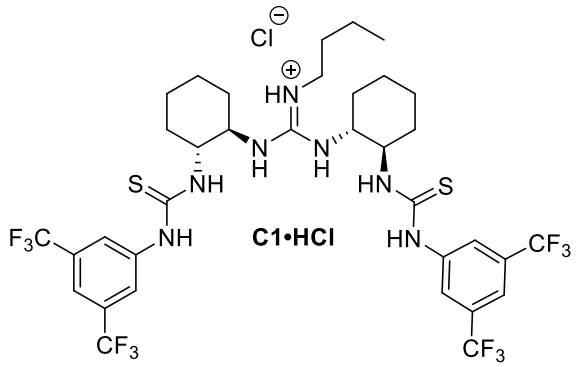


G2

G2 was synthesized using same procedure as **G1**.

^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.20-1.60 (m, 4H), 1.43 (s, 18H), 1.60-2.15 (m, 16H), 3.40-3.68 (m, 6H), 3.97 (m, 2H), 5.58 (bs, 2H), 6.64 (bs, 2H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 23.8, 24.8, 25.3, 28.3, 30.9, 32.73, 49.9, 53.9, 58.29, 80.1, 154.9, 157.4.
IR (cm^{-1}) : 857, 988, 1048, 1161, 1246, 1316, 1363, 1389, 1448, 1517, 1623, 1693, 2959, 2932, 2976, 3243.
MS (ESI) m/z : Calculated for $C_{27}H_{50}N_5O_4$ – 508,3857 [M+H$^+$]. found – 508.3827 [M+H$^+$].
[α]$_D$ ($CHCl_3$, C 0.01, 20°C) = + 85.3 °.
Melting point 134-138 °C.

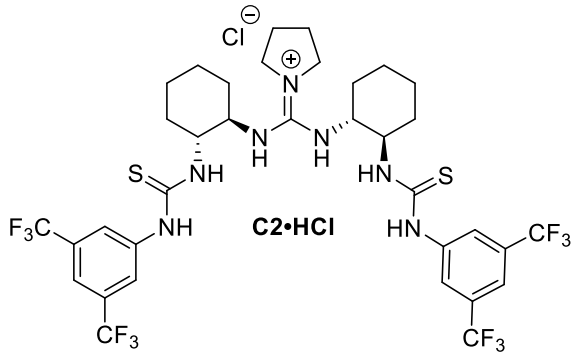
***N*-(bis(((1*R*,2*R*)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)cyclohexyl)amino)methylene)butan-1-aminiumchloride – <u>C1•HCl</u>:**



G1 (700 mg, 1.28 mmol, 1.0 equiv.) was dissolved in a 50/50 V% solution of DCM/TFA (2 mL/2 mL) and the mixture was stirred for 1-2h. The solvent was removed under reduced pressure to provide the diamine salt. The diamine salt was dissolved in DCM (2 mL) and triethylamine (0.71 mL, 5.13 mmol, 4.0 equiv.) and isothiocyanate (0.70 mL, 3.84 mmol, 3.0 equiv.) were added. The mixture was stirred overnight. The product was purified by flash chromatography (Heptane-EtOAc 8:2 then DCM-MeOH 30:1). The product was dissolved in EtOAc and washed with saturated aq. NH_4Cl to perform anion metathesis. **C1•**HCl was obtained as a white powder (375 mg, 33%).

^{1}H NMR (360 MHz, $CDCl_3$) δ = 0.85 (t, 3H, *J*= 7.5 Hz), 1.02-1.64 (m, 12H), 1.64-1.85 (m, 4H), 1.95-2.19 (m, 4H), 3.08-3.37 (m, 2H), 3.51-3.84 (m, 2H), 4.56-4.79 (m, 2H), 6.52-7.00 (bs, 2H), 7.56 (s, 2H), 8.18 (s, 4H), 10.08-10.50 (bs, 2H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 181.7, 140.5, 131.8, 131.4, 127.6; 124.6; 121.6 ; 117.9 (q, *J* = 331 Hz), 122.8, 58.8, 55.6, 42.6, 31.9, 30.8, 23.9, 19.8, 13.3.
IR (cm^{-1}) : 958, 1128, 1174, 1276, 1386, 1474, 1530, 1580, 1611, 2860, 2931, 3248.
MS (ESI) m/z : Calculated for $C_{35}H_{42}F_{12}N_7S_2^+$ - 852.2746 [M+H$^+$]. found – 852.2707 [M+H$^+$].
[α]$_D$ ($CHCl_3$, C 0.01, 25°C) = + 125.6 °.
Melting point 127-139 °C.

1-(bis(((1*S*,2*S*)-2-(3-(3,5) bis(trifluoromethyl)phenyl)thioureido)cyclohexyl)amino)methylene) pyrrolidin-1-iumchloride – <u>C2•HCl</u> :

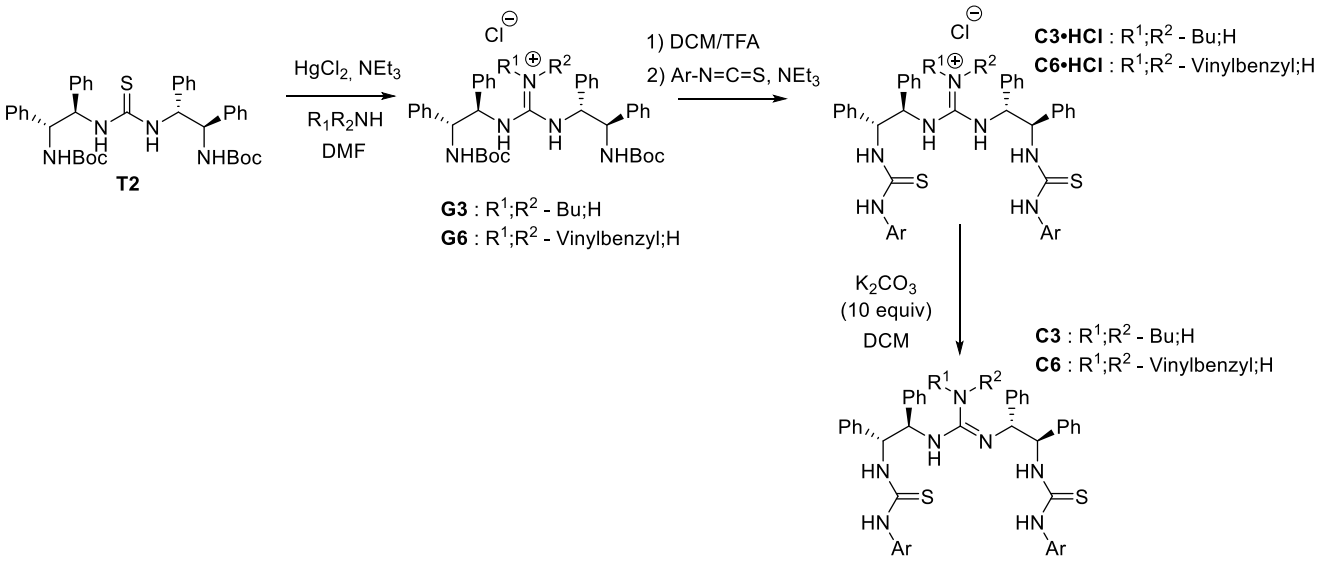


C2 was synthesized using same procedure as **C1**.

^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.04-2.24 (mbr, 20H), 3.46 (m, 6H), 4.69 (bs, 2H), 6.45 (bs, 2H), 7.54 (s, 2H), 8.14 (s, 4H), 8.39 (bs, 2H), 10.40 (s, 2H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 14.2, 21.1, 24.4, 25.3, 32.0, 50.2, 56.6, 60.4, 117.7, 122.3, 122.6, 124.1, 131.2-131.8 (C_{arom}), 140.8, 181.8
IR (cm^{-1}) : 969, 1000, 1128, 1176, 1276, 1332, 1384, 1474, 1535, 1582, 1611, 1678, 1724, 2860, 2931, 3047, 3248.

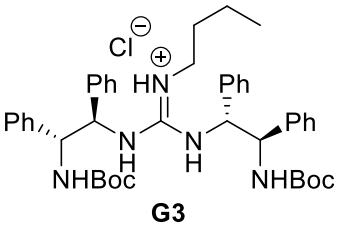
MS (ESI) m/z: Calculated for $C_{35}H_{40}F_{12}N_7S_2^+$ – 850.2590 [M+H$^+$]. found – 850.2560 [M+H$^+$].
[α] $_D$ ($CHCl_3$, C 0.01, 25°C) = + 133.4 °.
Melting point 130-132 °C.

C3 and **C6** synthesis :



For synthesis of **T2**, see : *Organic & Biomolecular Chemistry* (2012), 10(20), 4024-4028.

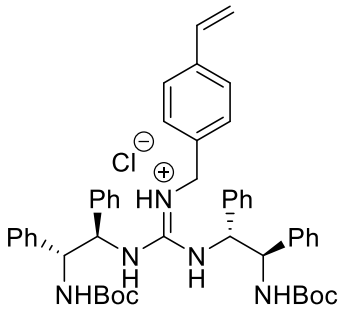
N-((6*R*,7*R*,11*R*,12*R*)-2,2,16,16-tetramethyl-4,14-dioxo-6,7,11,12-tetraphenyl-3,15-dioxa-5,8,10,13-tetraazaheptadecan-9-ylidene)butan-1-aminium chloride - G3 :



To a solution of **T2** (1.00 g, 1.5 mmol, 1.0 equiv.) in DMF (5 mL) were added triethylamine (0.41 mL, 3.0 mmol, 2.0 equiv.) and N-butylamine (0.45 mL, 4.5 mmol, 3.0 equiv.). Mercury chloride (490 mg, 1.8 mmol, 1.2 equiv.) was added and the mixture was stirred vigorously for 3 days. the reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was washed with a saturated aq. NH_4Cl solution and dried over $MgSO_4$. The crude was then purified by chromatography (EtOAc-pentane 1:1 then DCM-MeOH 9:1) providing **G3** as a white powder (800 mg, 72%).

^{1}H NMR (360 MHz, $CDCl_3$) δ = 0.69 (t, 3H), 0.90 (m, 2H), 1.52 (s, 18H), 1.30-1.70 (m, 2H), 3.08 (m, 1H), 3.25 (m, 1H), 4.72 (bs, 4H), 5.49 (bs, 3H), 6.33 (bs, 3H), 6.60-7.60 (m, 20H), 7.94 (bs, 2H), 8.79 (bs, 1H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 13.4, 19.2, 28.4, 30.2, 41.1, 65.1, 62.29, 64.03, 80.9, 82.1, 127.4-128.9 (C_{arom}), 136.8, 137.5, 153.3, 158.4.
IR (cm^{-1}) : 1023, 1048, 1167, 1366, 1498, 1522, 1630, 1692, 2978, 3254.
MS (ESI) m/z : Calculated for $C_{43}H_{56}N_5O_4^+$ – 706.4327 [M+H$^+$]. found – 706.4297 [M+H$^+$].
[α] $_D$ ($CHCl_3$, C 0.01, 20°C) = +85.3 °.
Melting point 138-141 °C.

N-((6R,7R,11R,12R)-2,2,16,16-tetramethyl-4,14-dioxo-6,7,11,12-tetraphenyl-3,15-dioxa-5,8,10,13-tetraazaheptadecan-9-ylidene)-1-(4-vinylphenyl)methanaminium chloride - G6 :

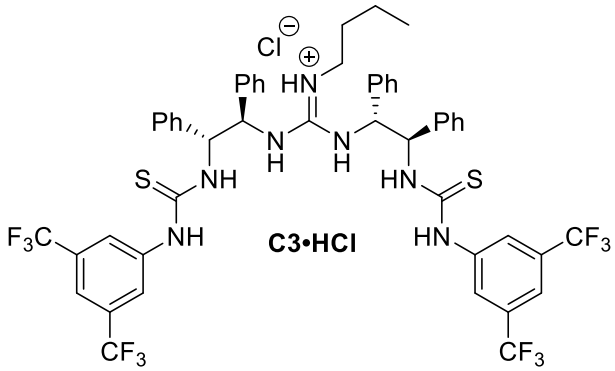


G6

G6 was synthesized using same procedure as **G3**.

^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.47 (s, 9H), 1.56 (s, 9H), 4.10 (m, 1H), 4.38 (m, 2H), 4.58 (m, 2H), 5.08 (bs, 1H), 5.18 (d, 1H, *J* = 11.0 Hz), 5.38 (bs, 1H), 5.66 (d, 1H, *J* = 17.2 Hz), 6.20-6.31 (m, 5H), 6.43 (d, 2H, *J* = 7.6 Hz), 6.62 (dd, 1H, *J* = 11.0, 17.9 Hz), 6.70 (bs, 1H), 6.84-6.93 (m, 5H), 6.84-7.21 (m, 13H), 7.02 (d, 2H, *J* = 8.2 Hz), 7.67 (bs, 1H), 7.78 (bs, 1H), 9.83 (bs, 1H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 14.0, 21.4, 28.4, 41.7, 43.5, 61.0, 62.5, 64.1, 80.9, 82.3, 113.7, 113.8-129.0 (C_{arom}), 136.1, 136.4, 137.8, 153.1, 158.4, 161.2.
IR (cm^{-1}) : 1021, 1048, 1161, 1247, 1365, 1457, 1493, 1515, 1619, 1690, 2929, 2974, 3218.
MS (ESI) m/z : Calculated for $C_{48}H_{56}N_5O_4^+$ – 766.4332 [M+H$^+$]. found – 766.4334[M+H$^+$].
[α]$_D$ ($CHCl_3$, C 0.01, 26°C) = + 161.2 °.
Melting point 156-160 °C.

***N*-((3*R*,4*R*,8*R*,9*R*)-1,11-bis((3,5-bis(trifluoromethyl)phenyl)amino)-3,4,8,9-tetraphenyl-1,11-dithioxo-2,5,7,10-tetraazaundecan-6-ylidene)butan-1-aminium chloride – <u>C3•HCl</u> :**

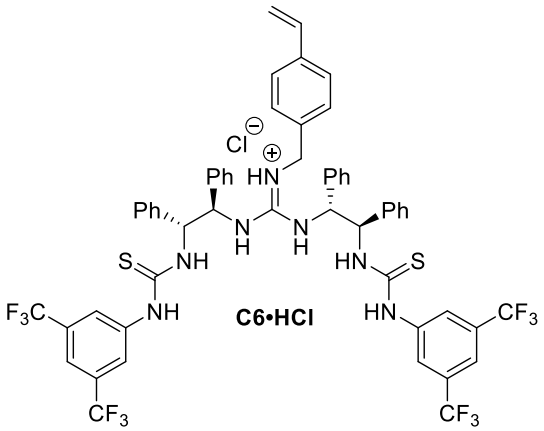


C3•HCl

G3 (770 mg, 1.04 mmol, 1.0 equiv.) was dissolved in a 50/50 V% solution of DCM/TFA (2 mL/2 mL) and the mixture was stirred for 1-2h. The solvent was removed under reduced pressure to provide the diamine salt. The diamine salt was dissolved in DCM (2 mL) and triethylamine (0.42 ml, 4.15 mmol, 4.0 equiv.) and isothiocyanate (0.57 mL, 3.11 mmol, 3.0 equiv.) were added. The mixture was stirred overnight. The product was purified by flash chromatography (Heptane-EtOAc 8:2 then DCM-MeOH 30:1). The TFA guanidinium salt was dissolved in EtOAc and washed with saturated aq. NH_4Cl to perform anion metathesis. **C3•**HCl was obtained as a white powder (536 mg, 48%).

^{1}H NMR (360 MHz, $CDCl_3$) δ = 0.69 (t, 3H), 0.95 (m, 2H), 1.27 (m, 2H), 3.07 (m, 1H), 3.24 (m, 1H), 4.56 (bs, 1H), 4.68 (bs, 1H), 5.25 (bs, 1H), 5.87 (bs, 1H), 6.35 (bs, 1H), 6.59-7.51 (m, 24H), 7.68 (s, 2H), 8.24 (m, 4H), 8.93 (bs, 1H), 9.50 (bs, 1H), 9.89 (bs, 1H), 10.43 (bs, 1H).
^{13}C NMR (91 MHz, $CDCl_3$) δ =13.1, 19.2, 30.2, 42.7, 62.3, 64.2 (bs), 118.3 (bs), 121.6, 122.8 (bs), 124.6, 127.2 (bs), 127.7, 128.5, 128.7, 129.2, 129.4, 131.8 (q, J_{CF} = 34 Hz), 136.1, 140.5 (bs), 154.4, 181.9 (bs).
IR (cm^{-1}) : 957, 1001, 1032, 1076, 1132, 1176, 1218, 1276, 1347, 1383, 1458, 1473, 1496, 1540, 1623, 2965, 3036, 3207.
MS (ESI): m/z: Calculated for $C_{51}H_{46}F_{12}N_7S_2^+$ – 1048.3059 [M+H$^+$]. found – 1048.3000 [M+H$^+$].
[α] $_D$ ($CHCl_3$, C 0.01, 20°C) = + 87.0 °.
Melting point 201-203 °C.

***N*-((3*R*,4*R*,8*R*,9*R*)-1,11-bis((3,5-bis(trifluoromethyl)phenyl)amino)-3,4,8,9-tetraphenyl-1,11-dithioxo-2,5,7,10-tetraazaundecan-6-ylidene)-1-(4-vinylphenyl)methanaminium chloride – <u>C6•HCl</u> :**

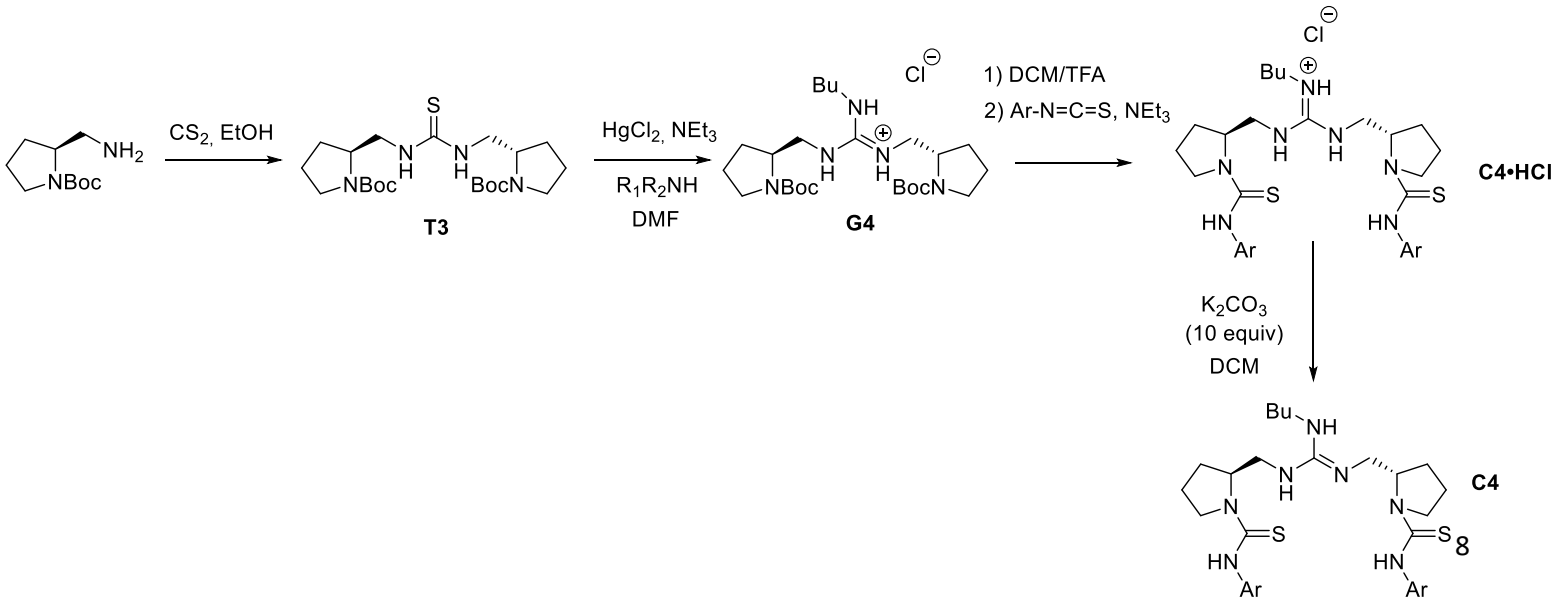


C6•HCl

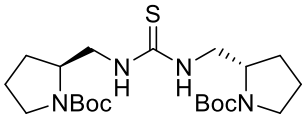
Monomer **C6** was synthesized using same procedure as **C3**.

^{1}H NMR (360 MHz, $CDCl_3$) δ = 4.43 (m, 2H), 5.26 (d, 1H, *J* = 11 Hz), 5.41 (bs, 2H), 5.71 (d, 1H, *J* = 18 Hz), 5.84 (m, 2H), 6.48 (d, 2H, *J* = 7.5 Hz), 6.50 (bs, 2H), 6.64 (dd, 1H, *J* = 11.0, 18.0 Hz), 6.85-7.53 (H_{arom}, 24H), 7.10 (d, 2H, *J* = 7.5 Hz) 7.54 (bs, 2H), 7.82 (NH, 2H), 8.09 (bs, 2H), 8.29 (bs, 2H), 9.52 (NH, 2H), 10,79 (NH, 1H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 63.9, 70.2, 114.5, 117.5, 119.8, 122.7, 126.2-129.1 (C_{arom}), 131.8 (q, J_{CF} = 42 Hz), 136.1,137.3, 138.7, 153.8, 181.6.
IR (cm^{-1}) : 957, 1133, 1171, 1229, 1380, 1472, 1538, 1615, 2962, 3037, 3184.
MS (ESI) m/z: Calculated for $C_{56}H_{46}F_{12}N_7S_2^+$ – 1108.3059 [M+H$^+$]. found – 1108.3016 [M+H$^+$].
[α] $_D$ ($CHCl_3$, C 0.01, 20°C) = + 84.2 °.
Melting point 135-137 °C.

C4 synthesis :



di-tert-butyl 2,2'-((thiocarbonylbis(azanediyl))bis(methylene))(2*S*,2'*S*)-bis(pyrrolidine-1-carboxylate) – T3 :

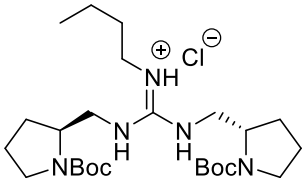


T3

L-N-Boc-amino proline (840 mg, 4.19 mmol, 2.0 equiv.) was added to a solution of carbon disulfide (0.25 mL, 1.42 mmol, 1.0 equiv.) in ethanol (20 mL). The mixture was heated under reflux (80°C) for 16h.The solvent was removed under vacuo and the crude was purified by chromatography (pentane-EtOAc 8:2). The product was obtained as a clear oil (780 mg, 84%).

^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.45 (s, 18H), 1.52-2.10 (m, 12H), 3.20-3.85 (m, 8H), 4.08 (bs, 2H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 22.9, 23.9, 28.5, 29.4, 29.7, 47.06 (t, J = 60.7 Hz), 56.0, 80.4, 156.7, 181.2
IR (cm^{-1}) : 1062, 1166, 1255, 1396, 1550, 1667, 1691, 2812, 1974, 3281.
MS (ESI) m/z : Calculated for $C_{21}H_{39}N_4O_4S$ – 443.2687 [M+H$^+$]. found – 443.2667 [M+H$^+$].
[α]$_D$ ($CHCl_3$, C 0.01, 20°C) = - 35.0 °.

N-(bis((((*S*)-1-(tert-butoxycarbonyl)pyrrolidin-2-yl)methyl)amino)methylene)butan-1-aminium chloride – G4 :

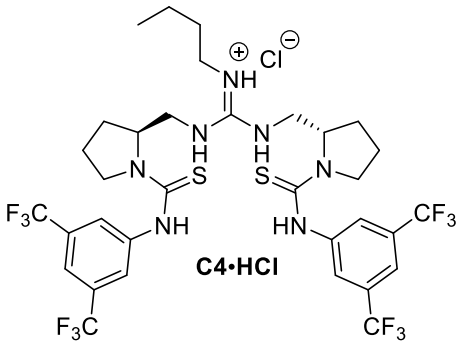


G4

To a solution of **T3** (750 mg, 1.69 mmol, 1.0 equiv.) in DMF (5mL) were added triethylamine (0.46 mL, 3.39 mmol, 2.0 equiv.) and N-butylamine (0.50 mL, 5.08 mmol, 3.0 equiv.). Mercury chloride (552 mg, 2.03 mmol, 1.2 equiv.) was added and the mixture was stirred vigorously for 1 day. the reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was washed with a saturated aq. NH_4Cl solution and dried over $MgSO_4$. The crude was then purified by chromatography (EtOAc-pentane 7:3) providing **G4** as a white powder (642 mg, 88%).

^{1}H NMR (360 MHz, $CDCl_3$) δ = 0.93 (t, 3H), 1.63 (m, 2H), 1.64 (s, 18H), 1.69 (m, 2H), 1.70-2.10 (m, 10H), 3.00-3.96 (m, 8H), 7.85 (bs, 1H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 13.5, 19.9, 23.8, 28.3, 29.7, 30.2, 42.0, 46.9, 57.0, 80.5, 154.6, 156.3.
IR (cm^{-1}) : 1111, 1167, 1259, 1366, 1403, 1621, 1668, 2878, 2972, 3079.
MS (ESI) m/z : Calculated for $C_{25}H_{48}N_5O_4^+$ – 482.3701 [M+H$^+$]. found – 482, 3684 [M+H$^+$].
[α]$_D$ ($CHCl_3$, C 0.01, 20°C) = - 6.1 °.

***N*-(bis((((*S*)-1-((3,5-bis(trifluoromethyl)phenyl)carbamothioyl)pyrrolidin-2-yl)methyl)amino)-methylene)butan-1-aminium chloride – <u>C4•HCl</u> :**

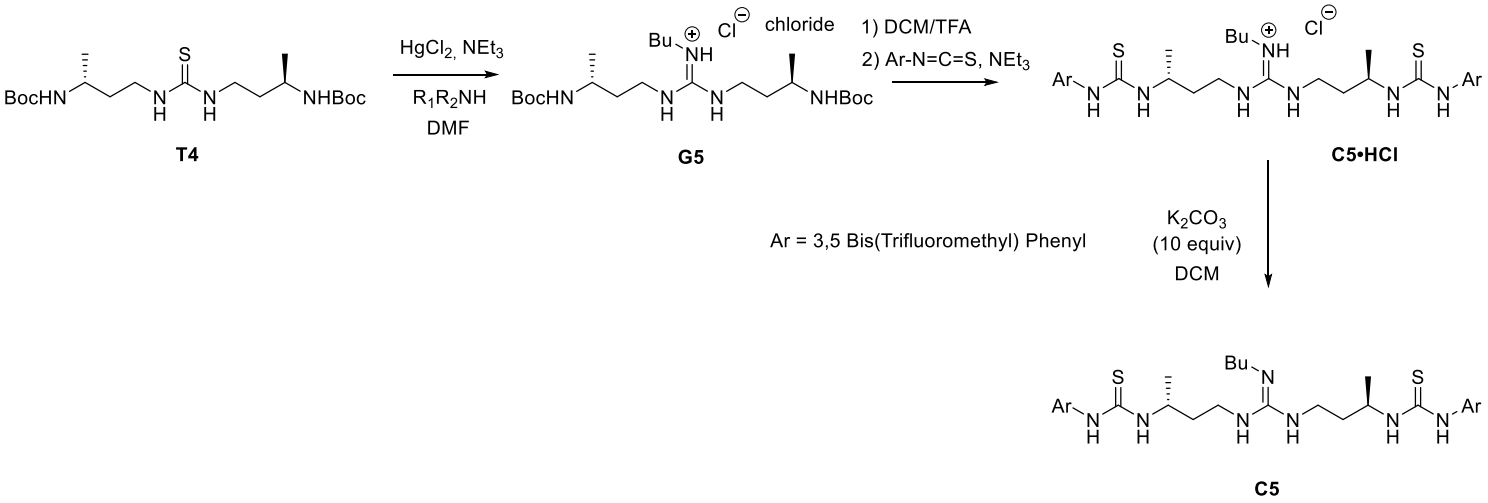


G4 (550 mg, 1.15 mmol, 1.0 equiv.) was dissolved in a 50/50 V% solution of DCM/TFA (2 mL/2 mL) and the mixture was stirred for 1-2h. The solvent was removed under reduced pressure to provide the diamine salt. The diamine salt was dissolved in DCM (2 mL) and triethylamine (0.64 ml, 4.57 mmol, 4.0 equiv.) and isothiocyanate (0.63 mL, 3.43 mmol, 3.0 equiv.) were added. The mixture was stirred overnight. The product was purified by flash chromatography (DCM-MeOH 19:1). The product was dissolved in EtOAc and washed with saturated aq. NH_4Cl to perform anion metathesis. **C4•**HCl was obtained as a white powder (323 mg, 34%).

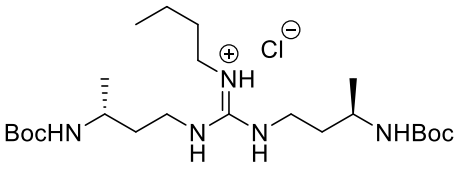
^{1}H NMR (360 MHz, $CDCl_3$) δ = 0.83 (t, 3H, J = 7.3 Hz), 1.30 (m, 2H), 1.54 (m, 2H), 1.70 (bs, 2H), 1.89-2.47 (mbr, 8H), 3.00-3.40 (mbr, 4H), 3.56-4.07 (mbr, 6H), 4.62 (bs, 2H), 7.49 (bs, 1H), 7.66 (s, 2H), 8.02 (s, 4H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 13.4, 20.0, 23.6, 28.0, 30.6, 42.7, 49.7, 60.4, 61.5, 118.6, 119.2, 121.6, 124.6, 126.44, 131.4 (q, J = 33 Hz), 140.7, 154.8, 178.6.
IR (cm^{-1}) : 887, 913, 982, 1013, 1127, 1172, 1226, 1276, 1358, 1374, 1454, 1471, 1535, 1546, 1564, 1628, 2969, 3090, 3190.
MS (ESI): m/z: Calculated for $C_{33}H_{38}F_{12}N_7S_2^+$ – 824.2433 [M+H$^+$]. found – 824.2394 [M+H$^+$].
[α]$_D$ ($CHCl_3$, C 0.01, 20°C) = + 17.0 °.

For synthesis of **C5**, full procedure reported in: *Angew. Chem. Int. Ed.*, 2010, **49**, 7299 –7303

C5 Ssynthesis :



N-((6*R*,14*R*)-2,2,6,14,18,18-hexamethyl-4,16-dioxo-3,17-dioxa-5,9,11,15-tetraazanonadecan-10-ylidene)butan-1-aminium chloride – G5 :

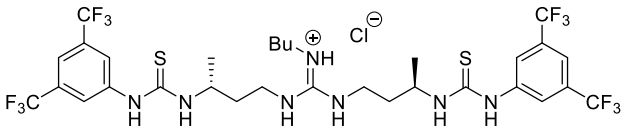


G5

To a solution of **T4** (200 mg, 0.48 mmol, 1.0 equiv.) in DMF (5 mL) were added triethylamine (133 µL, 0.96 mmol, 2.0 equiv.) and N-butylamine (141 µL, 1.44 mmol, 3.0 equiv.). Mercury chloride (195 mg, 0.57 mmol, 1.2 equiv.) was added and the mixture was stirred at 80°C for 16h. the reaction was monitored by TLC. After completion of the reaction, the mixture was diluted with ethyl acetate and filtered through a pad of celite. The filtrate was washed with a saturated aq. NH_4Cl solution and dried over $MgSO_4$. The crude was then purified by chromatography (DCM-MeOH 19:1) providing **G5** as a white powder (150 mg, 70%).

^{1}H NMR (600 MHz, $CDCl_3$) δ = 0.86 (t, 3H, J = 6.2 Hz), 1.13 (m, 6H), 1.36 (s, 18H), 1.59 (m, 4H), 1.84 (bs, 2H), 3.12 (bs, 2H), 3.25 (bs, 2H), 3.58 (bs, 2H), 3.67 (bs, 2H), 4.89 (bs, 2H), 7.41 (bs, 2H), 7.97 (bs, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ = 13.7, 20.0, 21.6, 28.4, 31.1, 37.3, 39.1, 41.7, 44.2, 79.7, 154.2, 156.8.
IR (cm^{-1}) : 1074, 1161, 1210, 1250, 1364, 1457, 1490, 1594, 1617, 1695, 2979, 3300.
MS (ESI) m/z : Calculated for $C_{23}H_{48}N_5O_4^+$ – 458.3701 [M+H$^+$]. found – 458.3705 [M+H$^+$].
[α]$_D$ ($CHCl_3$, C 0.01, 24°C) = + 92.7 °.
Melting point : 67-70 °C.

N-((3*R*,11*R*)-1,13-bis((3,5-bis(trifluoromethyl)phenyl)amino)-3,11-dimethyl-1,13-dithioxo-2,6,8,12-tetraazatridecan-7-ylidene)butan-1-aminium chloride – <u>G5•HCl</u>:



C5.HCl

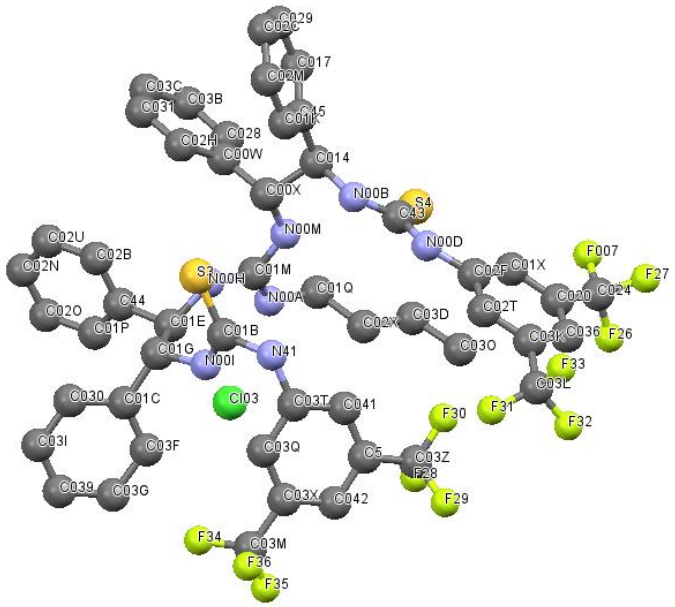
G5 (147 mg, 1.04 mmol, 1.0 equiv.) was dissolved in a 50/50 V% solution of DCM/TFA (1 mL/1 mL) and the mixture was stirred for 1-2h. The solvent was removed under reduced pressure to provide the diamine salt. The diamine salt was dissolved in DCM (2 mL) and triethylamine (0.18 mL, 4.15 mmol, 4.0 equiv.) and isothiocyanate (0.18 mL, 3.11 mmol, 3.0 equiv.) were added. The mixture was stirred overnight. The product was purified by flash chromatography (DCM-MeOH 19:1). The TFA guanidinium salt was dissolved in EtOAc and washed with saturated aq. NH_4Cl to perform anion metathesis. **C3**•HCl was obtained as a white powder (168 mg, 67%).

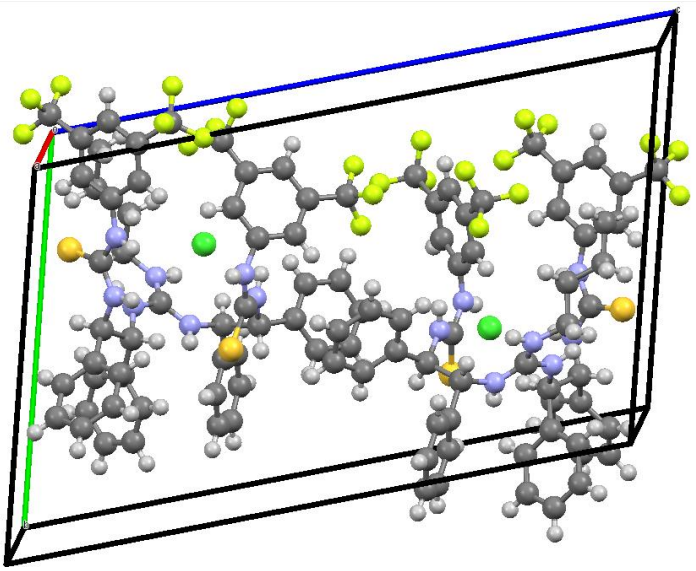
^{1}H NMR (600 MHz, MeOD) δ = 0.81 (t, 3H, J = 7.5 Hz), 1.93 (m, 6H), 1.26 (m, 3H), 1.50 (m, 2H), 1.79 (m, 4H), 3.15 (m, 2H), 4.54 (bs, 2H), 7.50 (s, 2H), 8.15 (s, 4H).
^{13}C NMR (151 MHz, MeOD) δ = 14.0, 20.8 (d, J = 55 Hz), 21.0, 32.1, 36.6, 39.8, 42.8, 117.7, 123.6, 124.7 (q, J = 272 Hz), 132.2-132.9 (C_{arom}), 143.1, 155.7, 182.1.
IR (cm^{-1}) : 883, 945, 1001, 1122, 1169, 1274, 1378, 1428, 1474, 1581, 2362, 12879, 2935, 2968.
MS (ESI) m/z : Calculated for $C_{31}H_{38}F_{12}N_7S_2^+$– 800.2433 [M+H$^+$]. found – 800.2425 [M+H$^+$].
[α]$_D$ (MeOH, C 0.01, 25°C) = + 7.8 °.
Melting point : 109-110 °C.

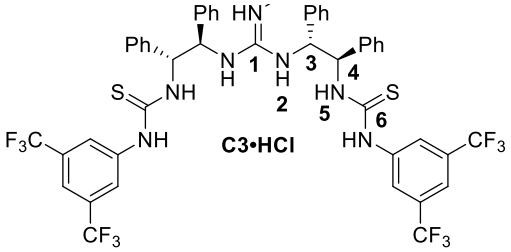
Conversion of Guanidinium chloride to free-base guanidine:

To a solution of guanidinium chloride (**C1**•HCl – **C6**•HCl) in DCM (0.1M) was added K_2CO_3 (10 equiv.) and the mixture was stirred overnight at room temperature. The mixture was filtered and the filtrate was concentrated under reduced pressure to provide the guanidine free-base (**C1** – **C6**).

C3 catalyst X-ray diffraction :

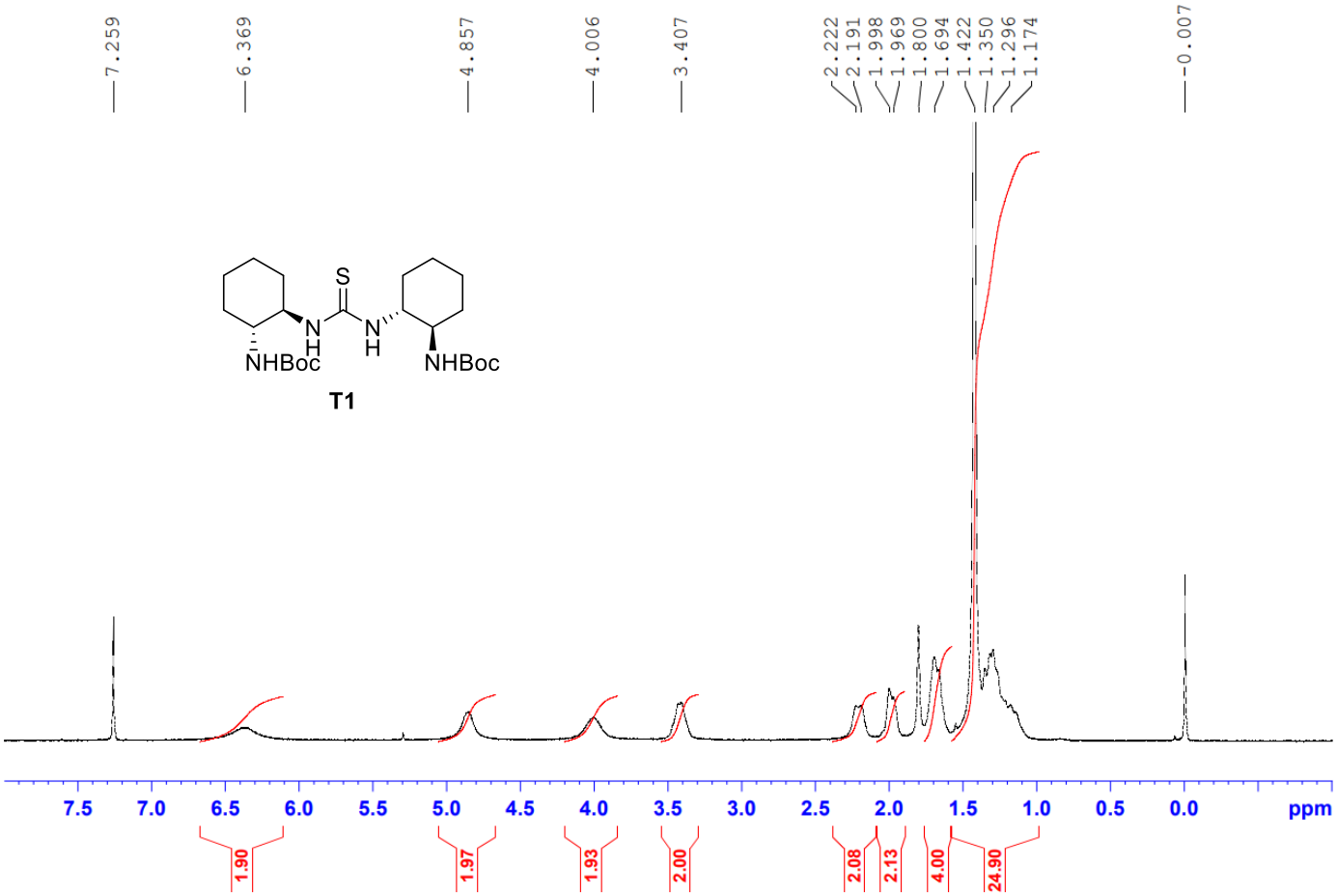






X-ray structure of catalyst **C3**•HCl salt was obtained by mono crystal X-ray diffraction.

Absolute configuration of the catalyst was confirmed to be (3*R*,4*R*,3'*R*,4'*R*)-**C3**.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2.191
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1.800
1.694
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1.350
1.296
1.174
0.007
S
N
H
N
H
NHBoc
NHBoc
T1
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
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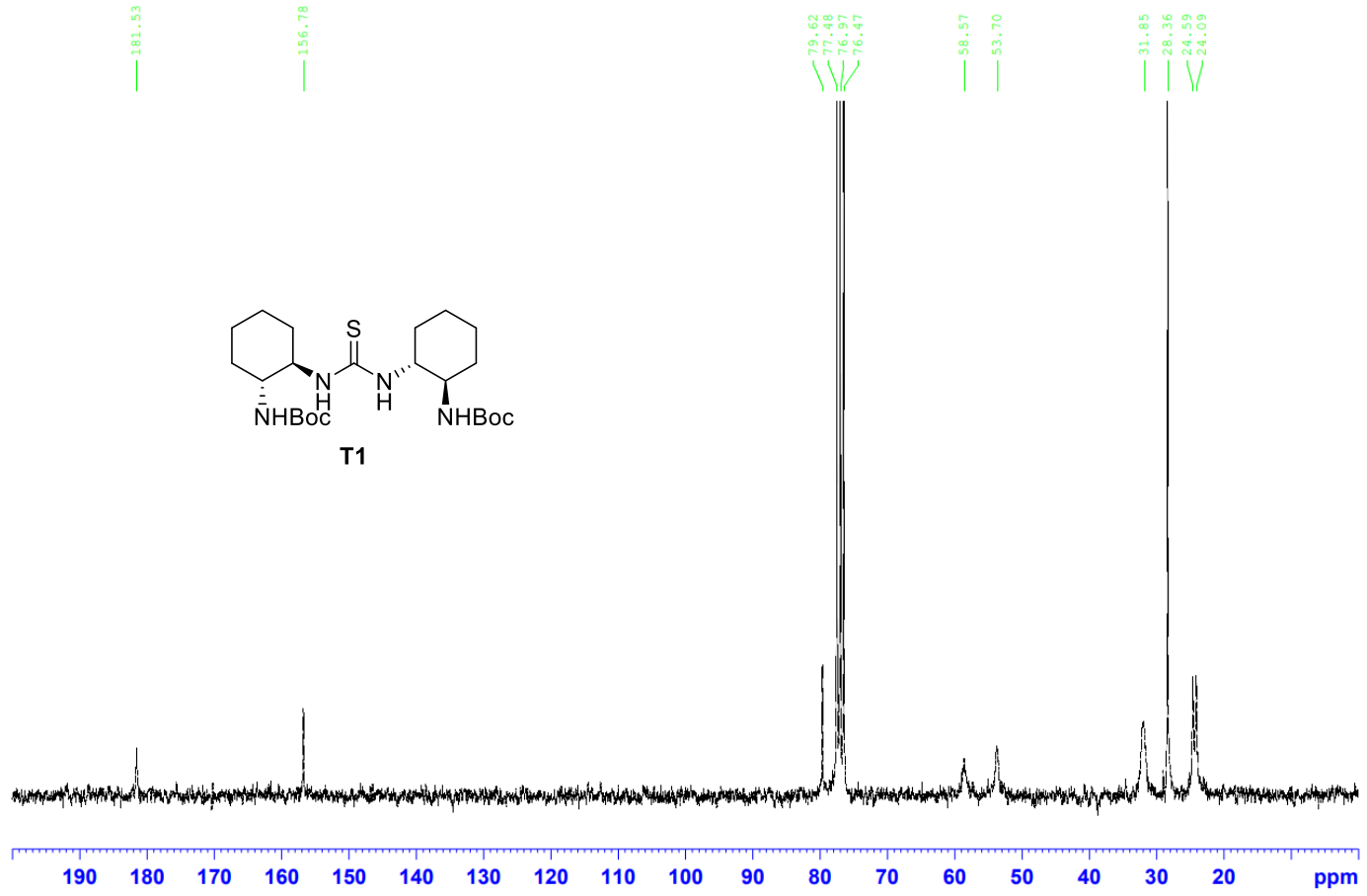
4.00
24.90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H
N
H
NHBoc
NHBoc
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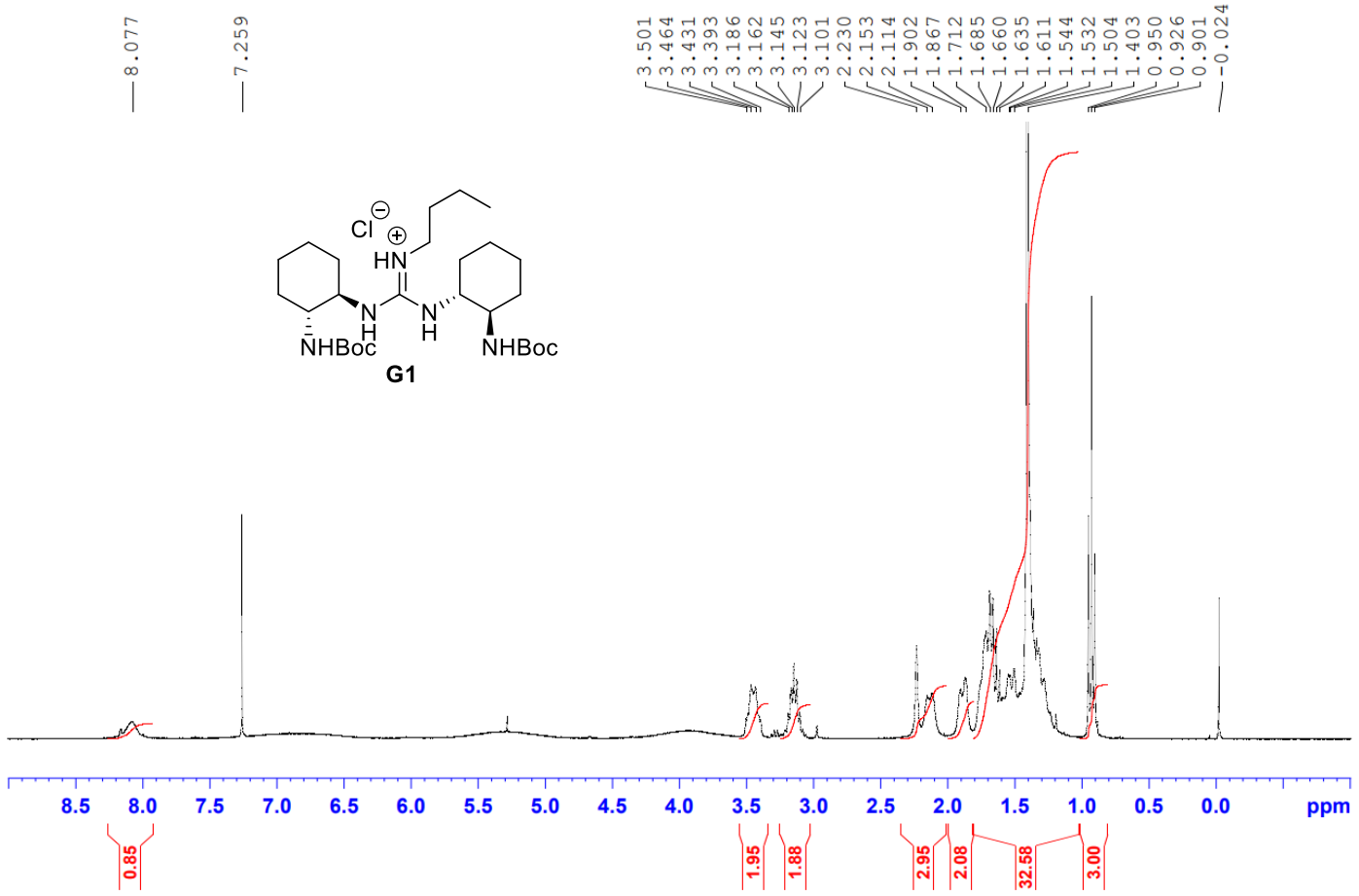
ppm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1.867
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1.660
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1.544
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1.504
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H
N
H
NHBoc
NHBoc
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7.5
7.0
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6.0
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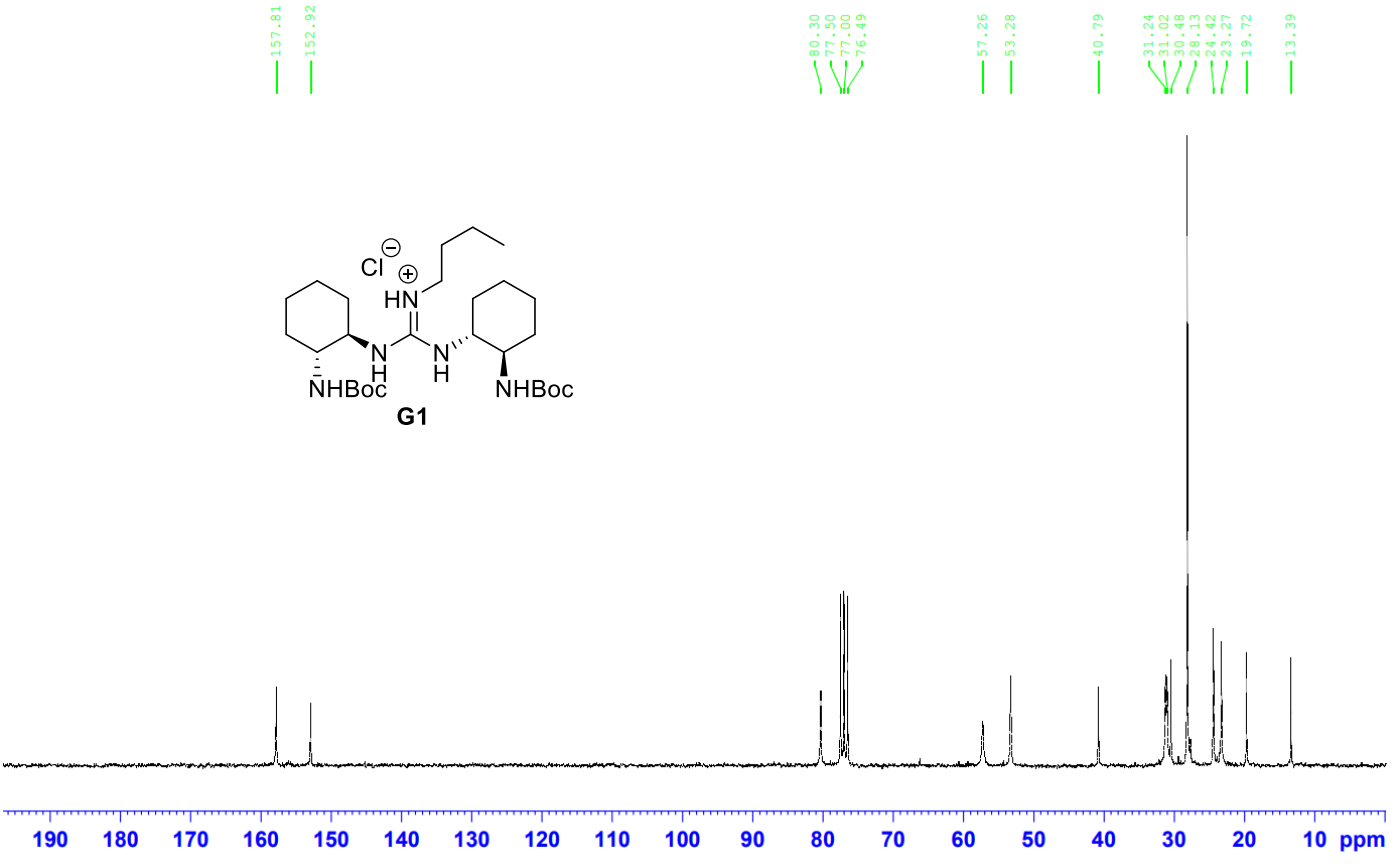
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53.28
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31.02
30.48
28.13
24.42
23.27
19.72
13.39
Cl
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N
H
N
H
NHBoc
NHBoc
G1
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150
140
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20
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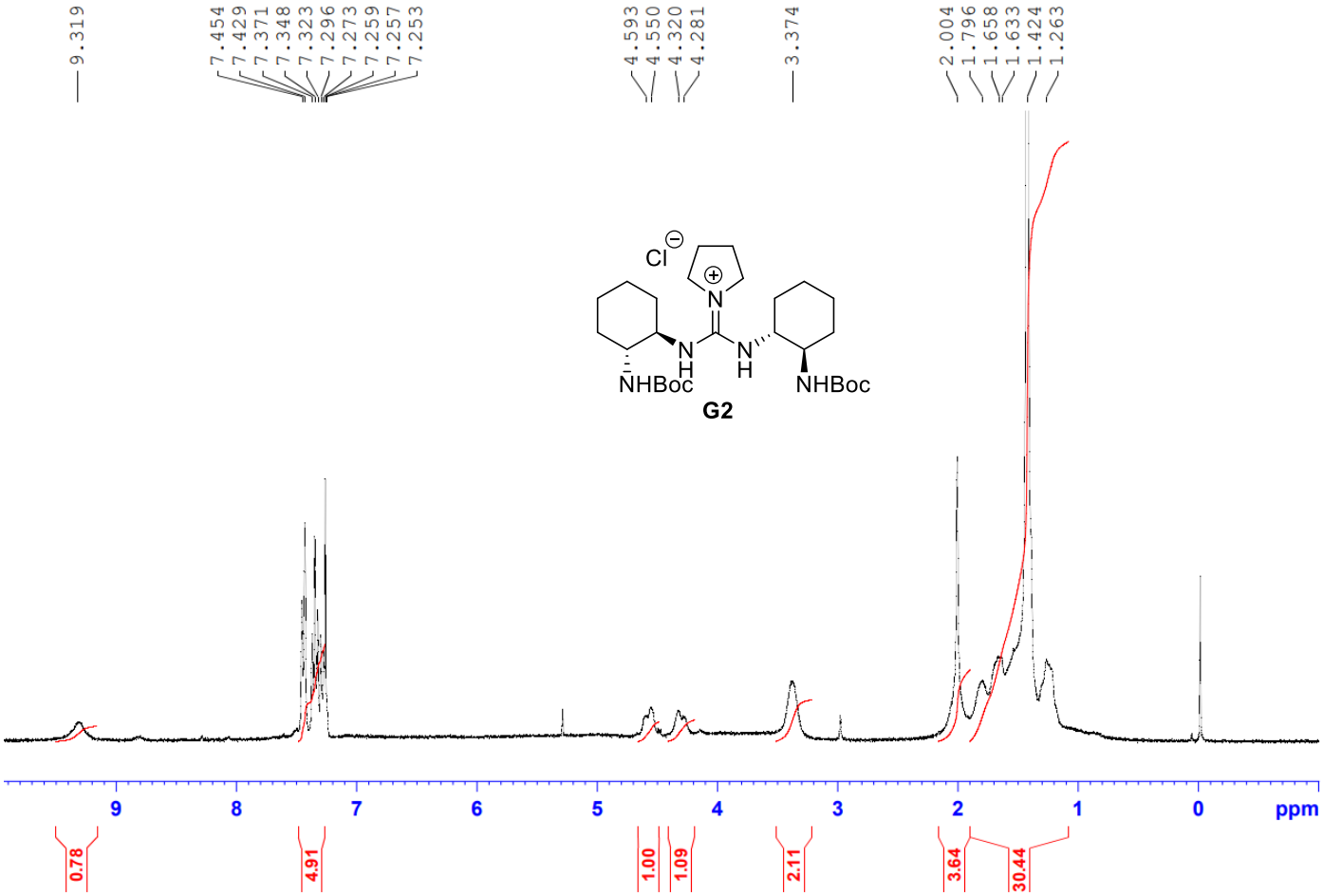
ppm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NHBoc
NHBoc
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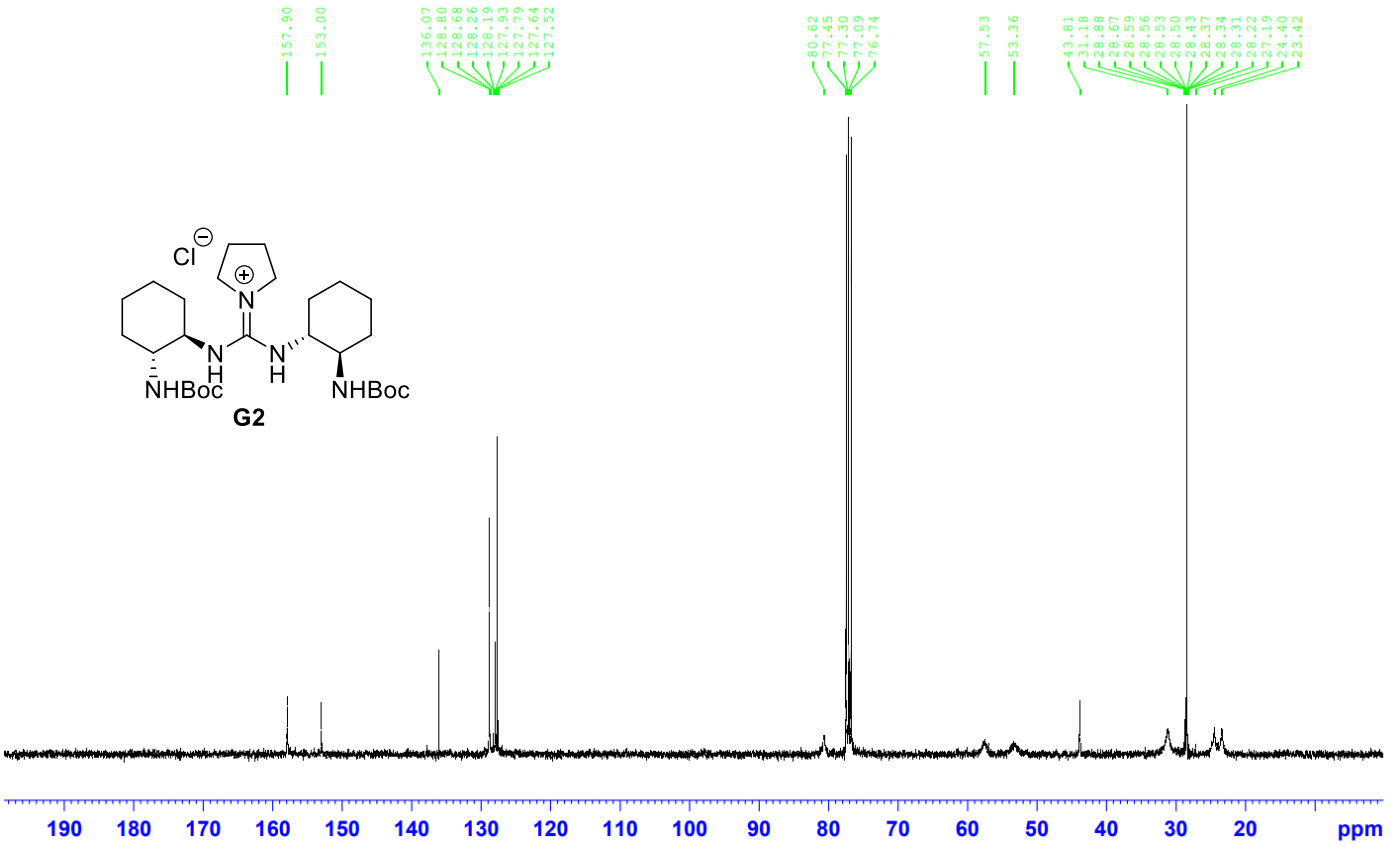
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31.18
28.88
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28.50
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28.34
28.31
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NHBoc
NHBoc
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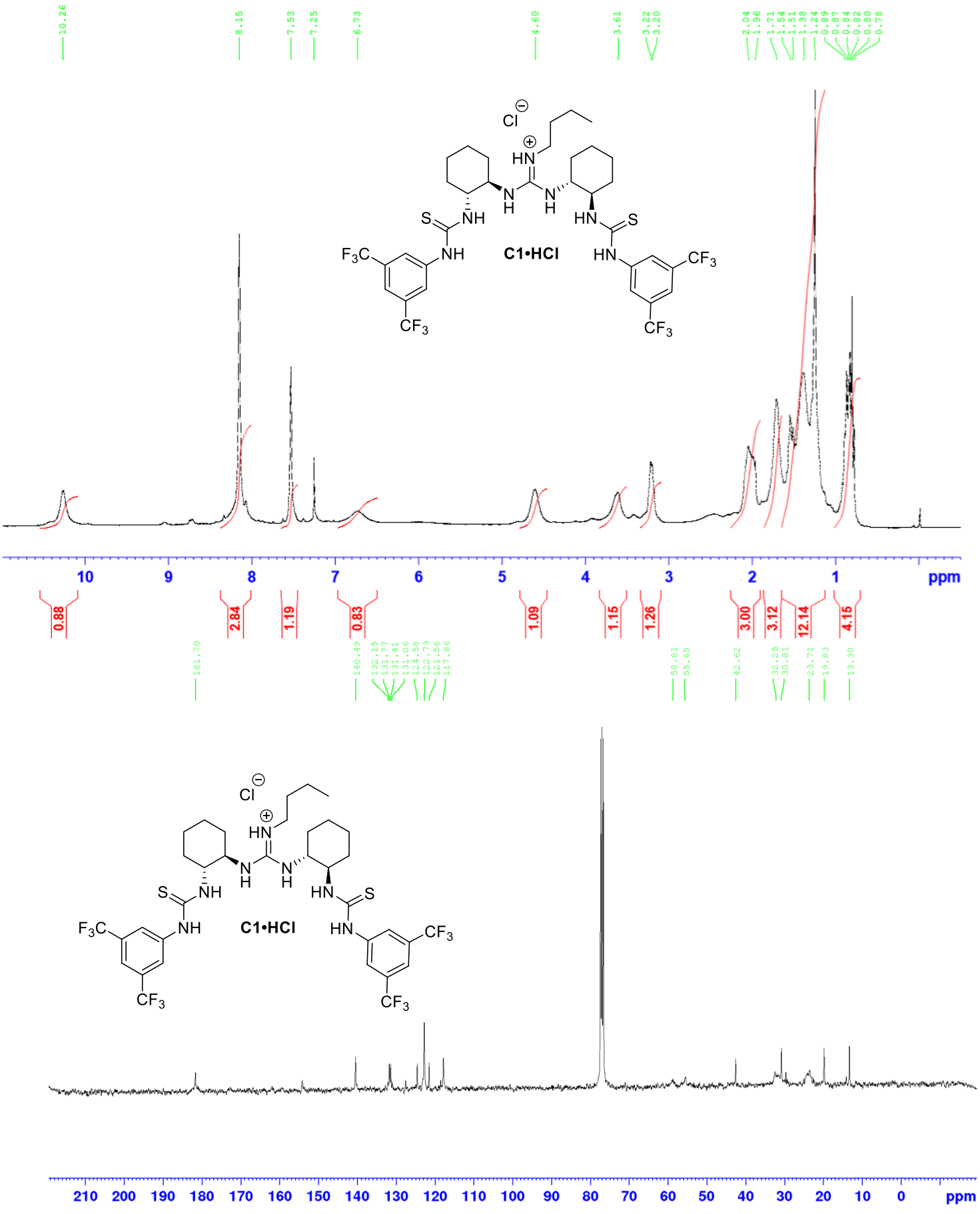
ppm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CF3
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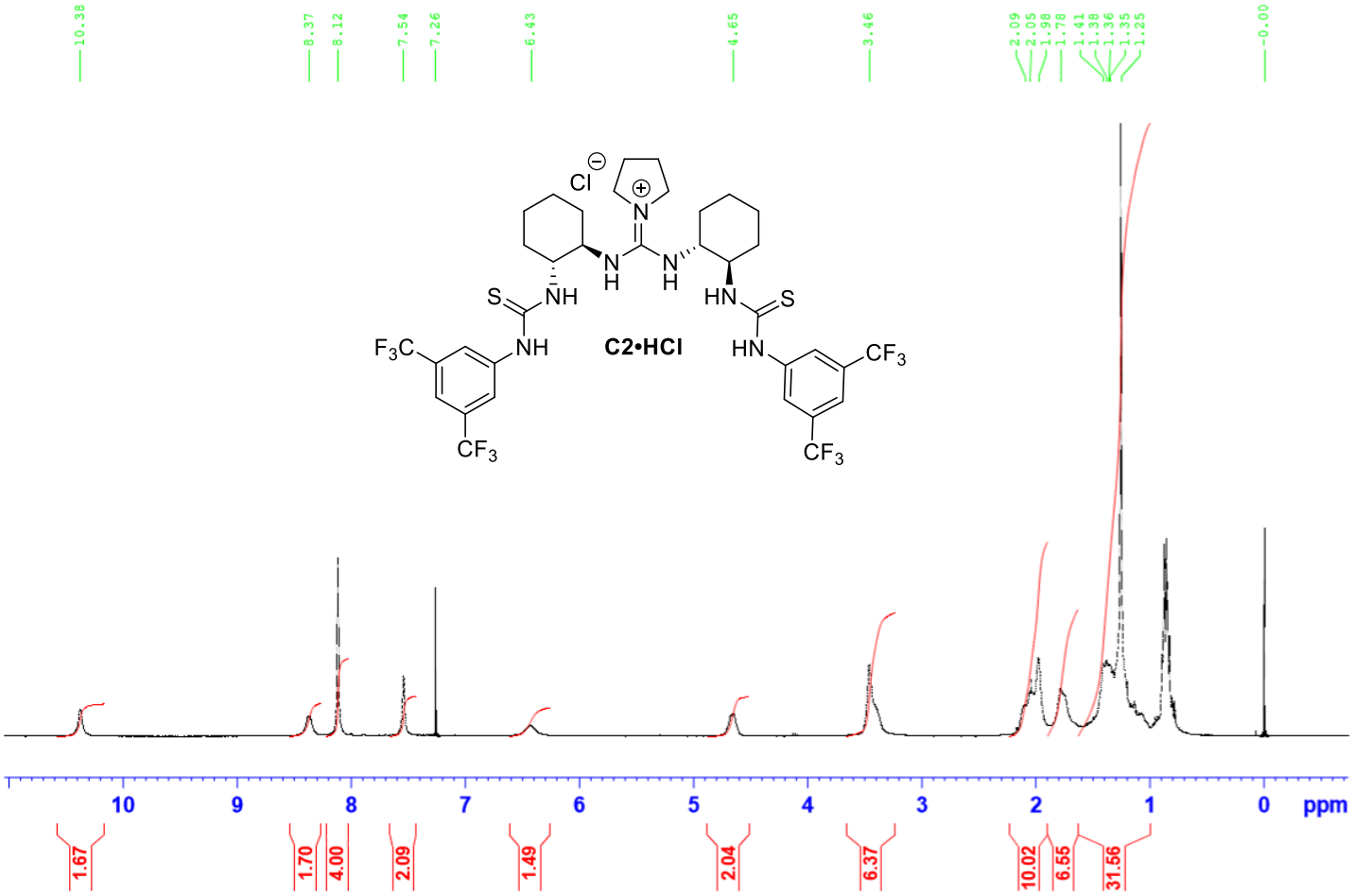
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5
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3
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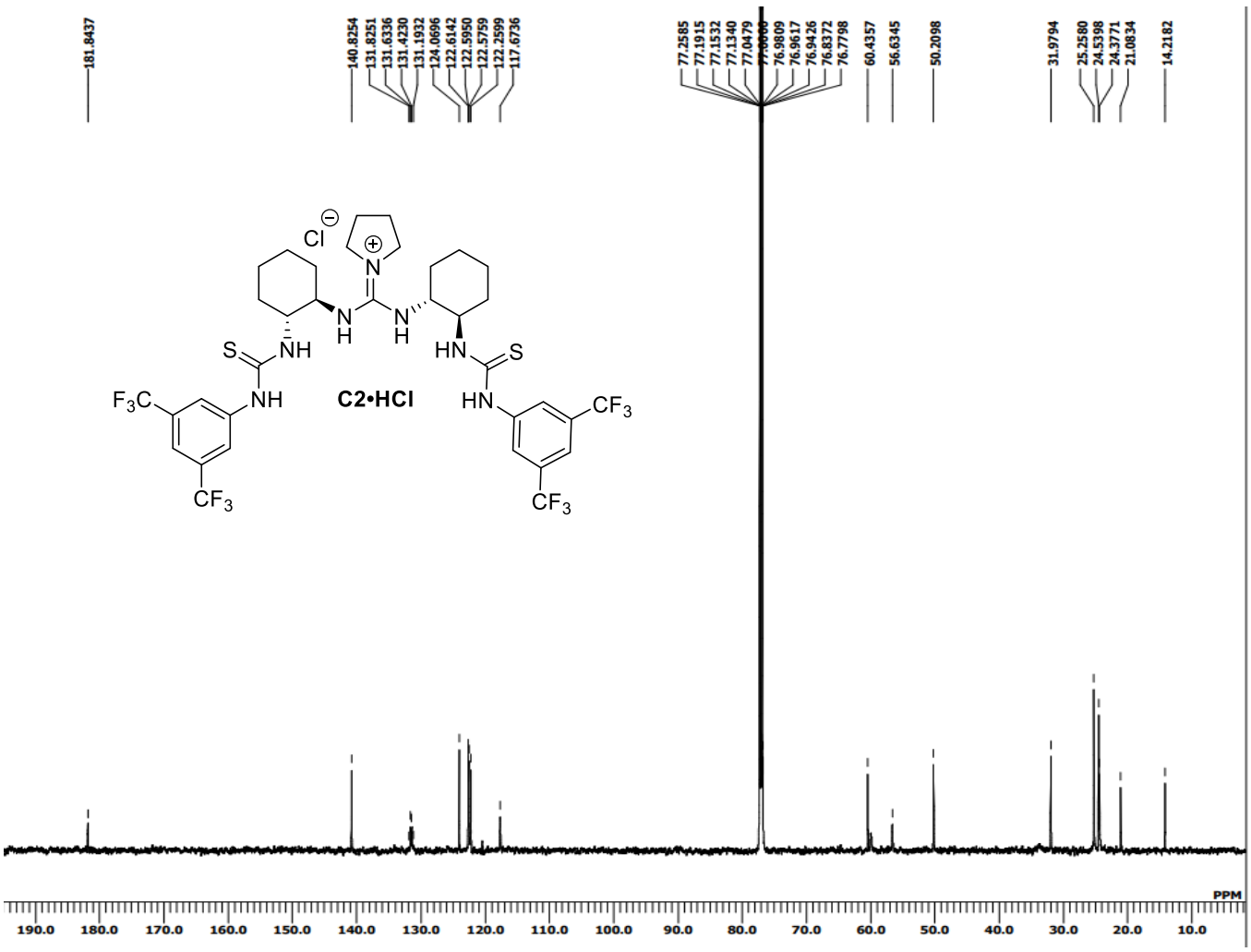
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C2•HCl
PPM
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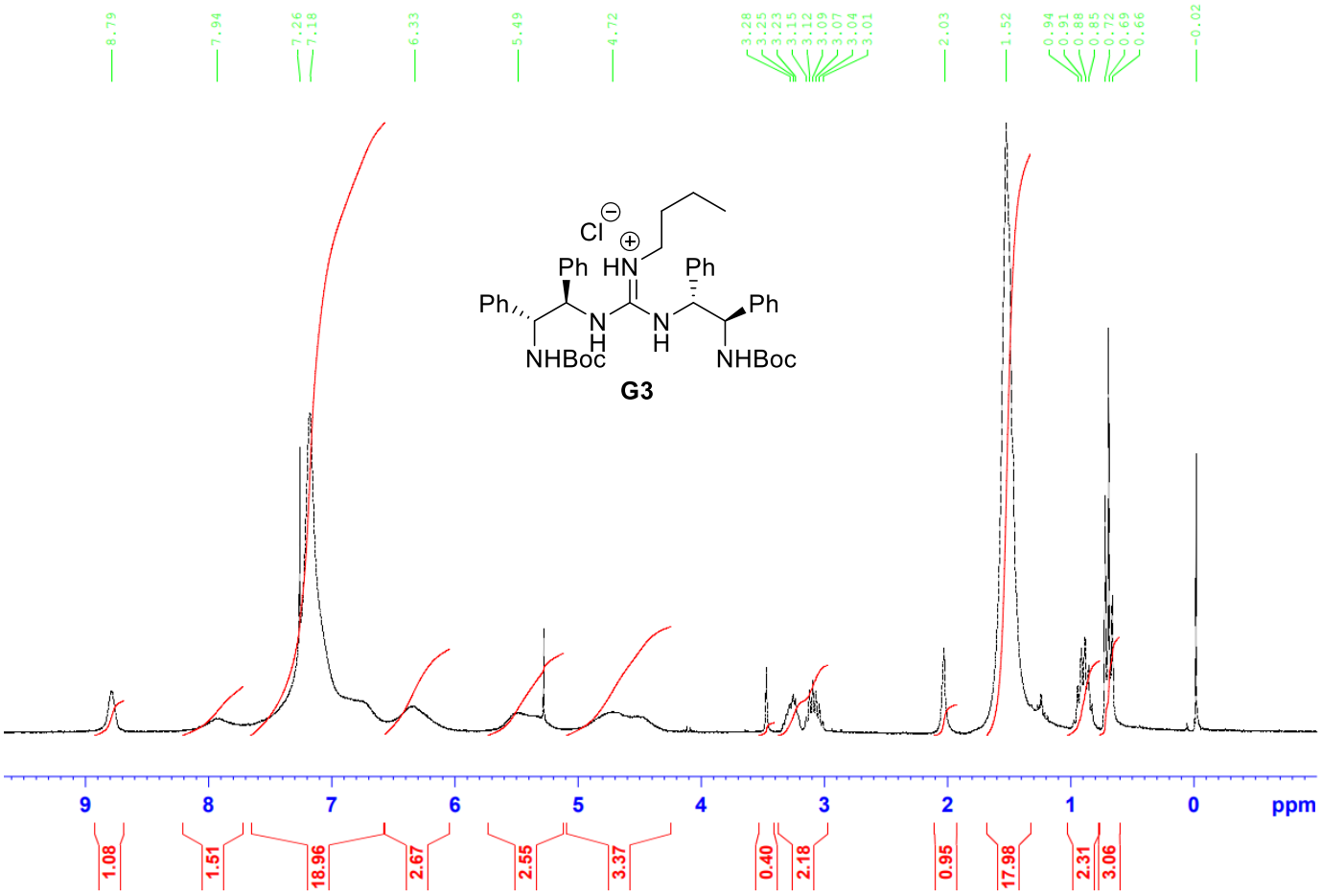
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3.07
3.04
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2.03
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Ph
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Ph
NHBoc
NHBoc
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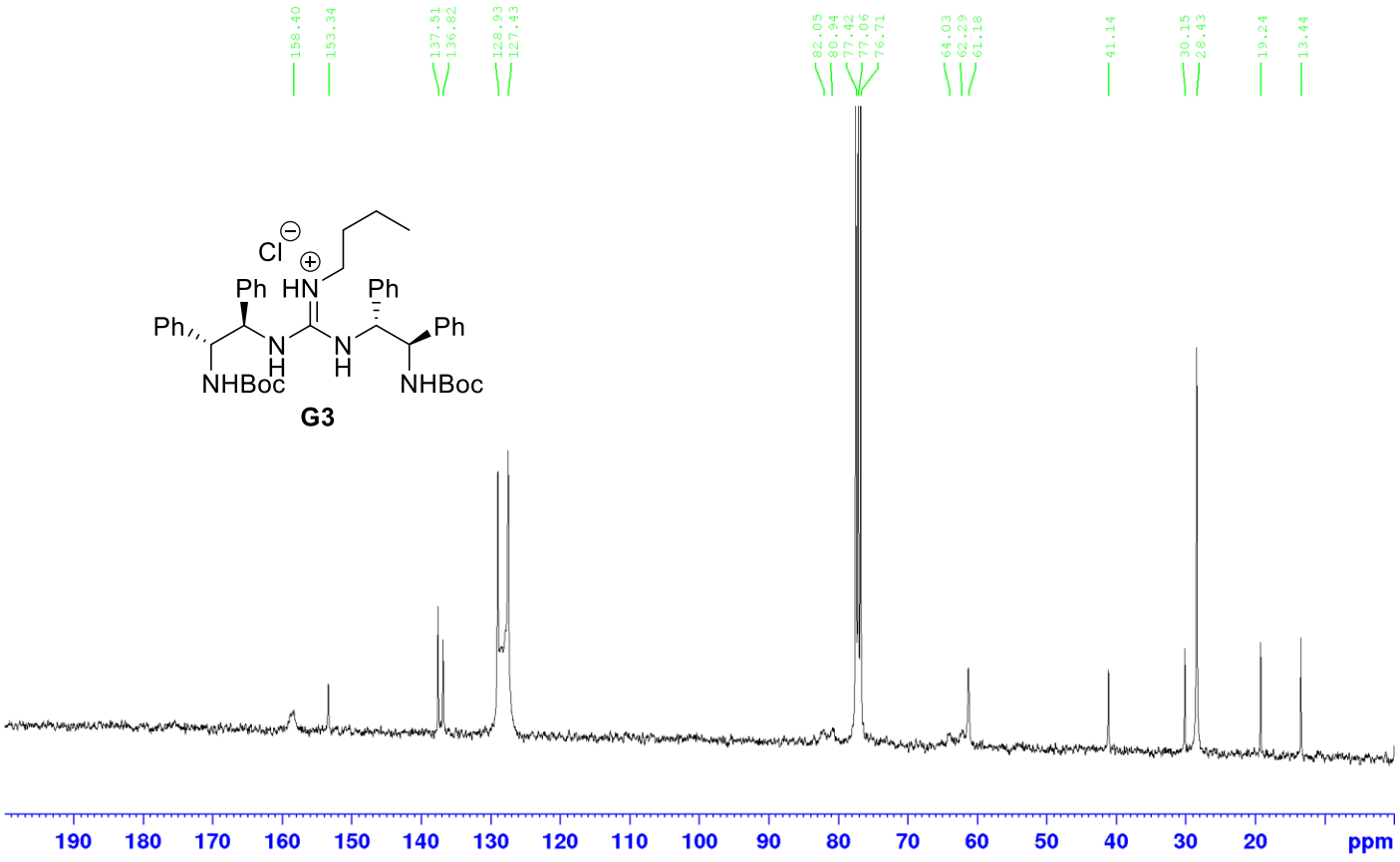
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H
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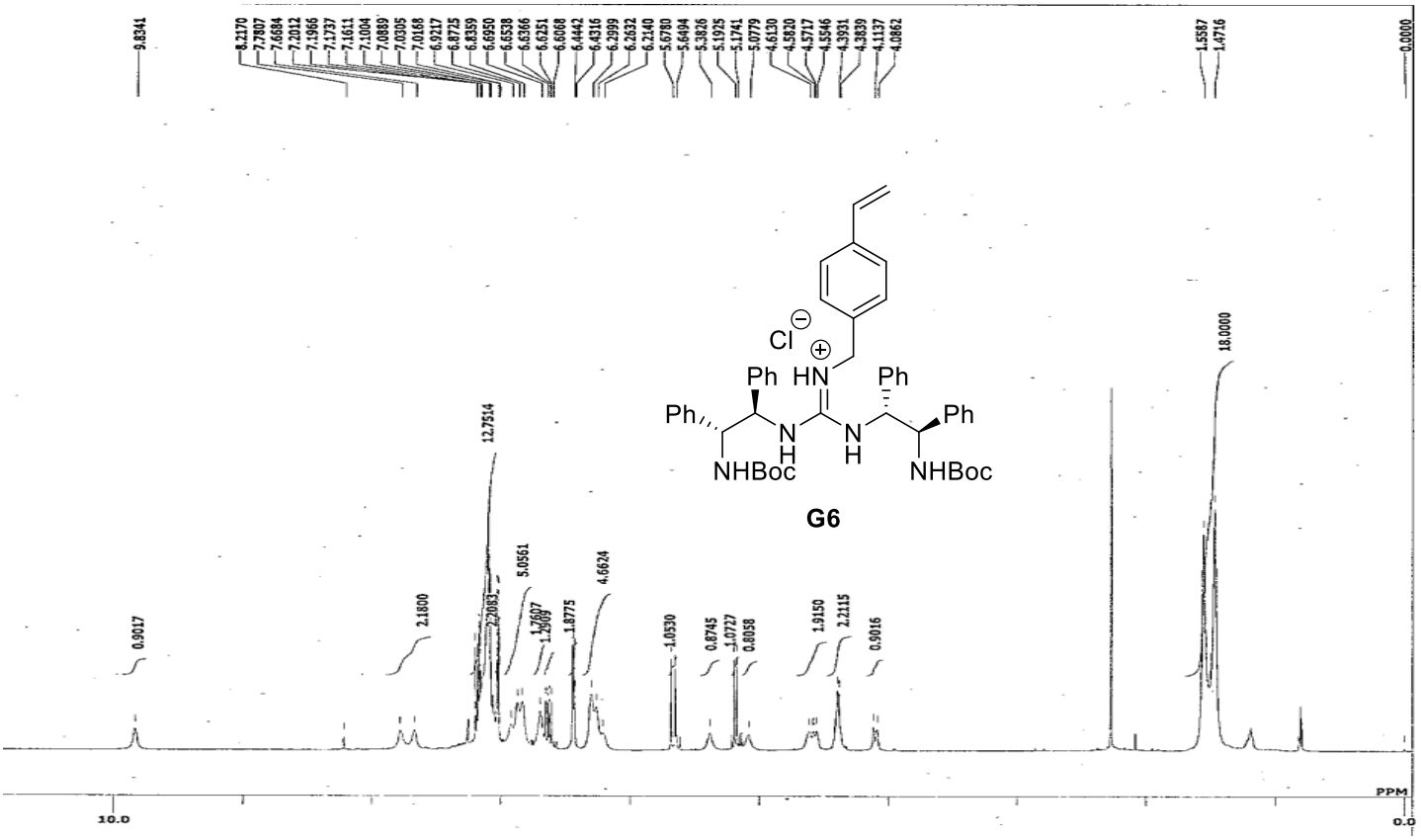
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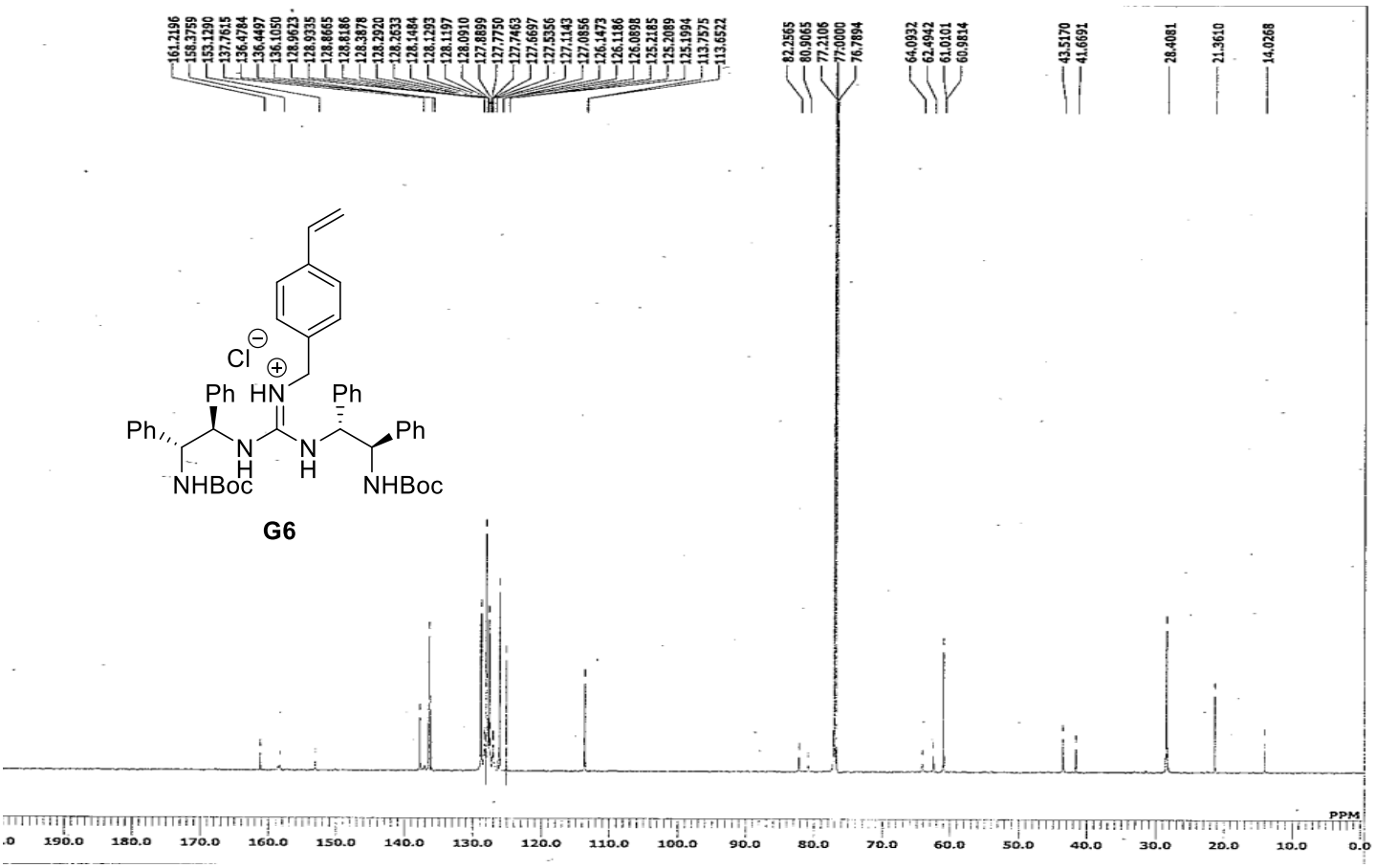
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Ph
Ph
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H
N
H
Ph
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G6
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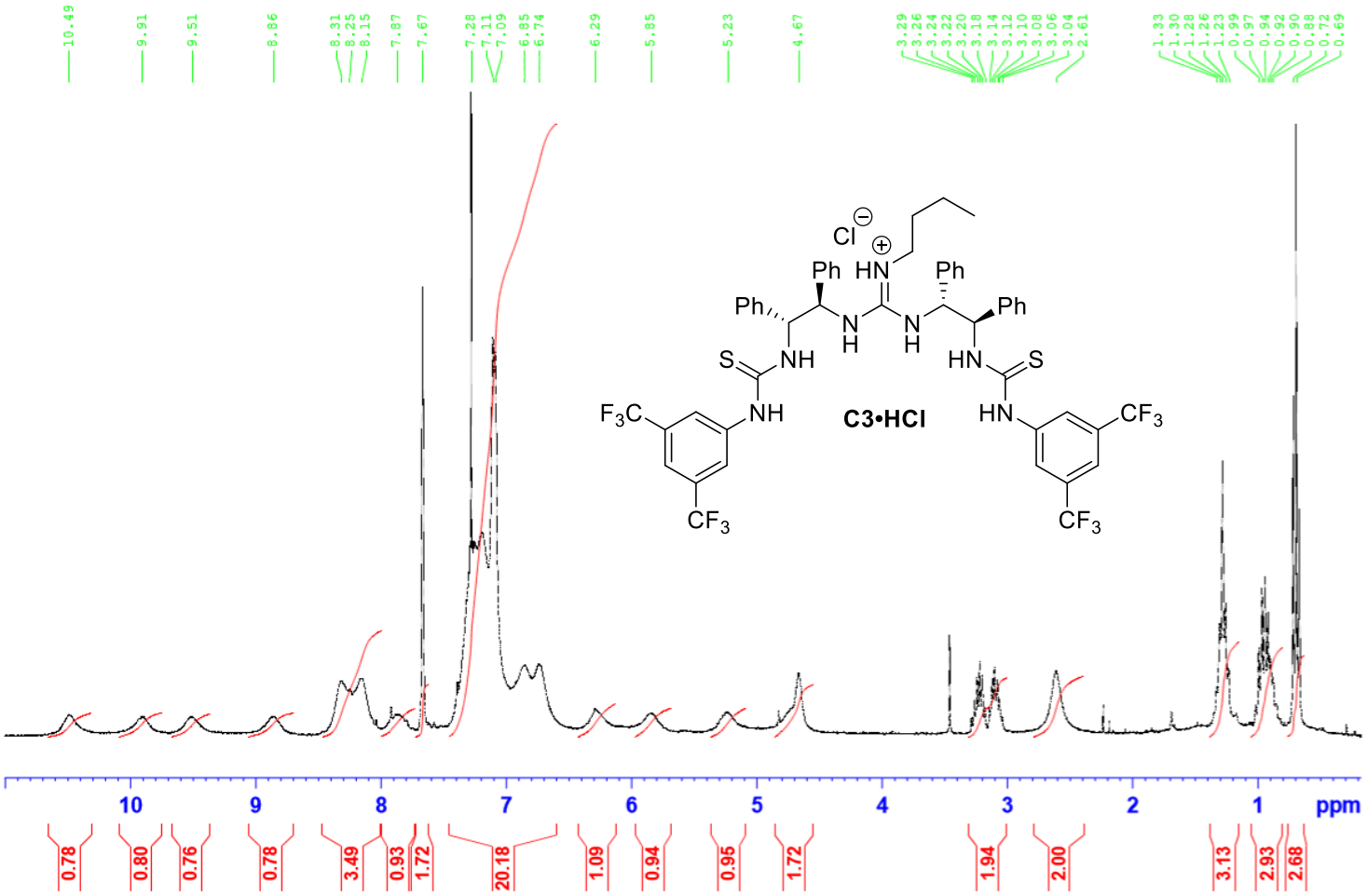
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6.29
5.85
5.23
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3.29
3.26
3.24
3.22
3.20
3.18
3.14
3.12
3.10
3.08
3.06
3.04
2.61
1.33
1.30
1.28
1.26
1.23
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0.94
0.92
0.90
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Ph
Ph
Ph
Ph
N
H
N
H
S
NH
HN
S
F3C
NH
HN
CF3
CF3
CF3
C3•HCl
10
9
8
7
6
5
4
3
2
1
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0.80
0.76
0.78
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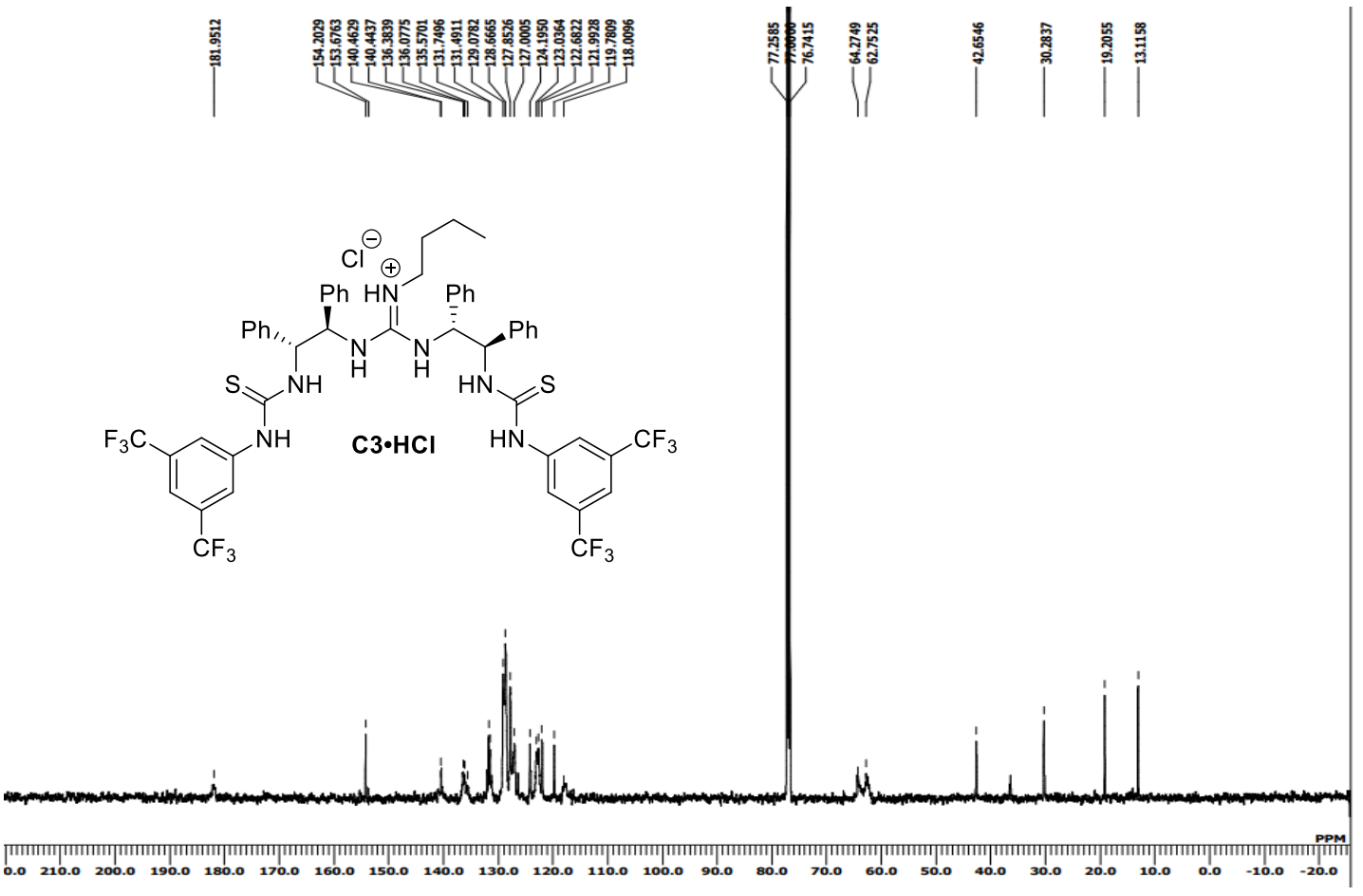
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42.6546
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Ph
Ph
Ph
Ph
N
H
N
H
S
NH
HN
S
F3C
NH
HN
CF3
CF3
CF3
C3•HCl
PPM
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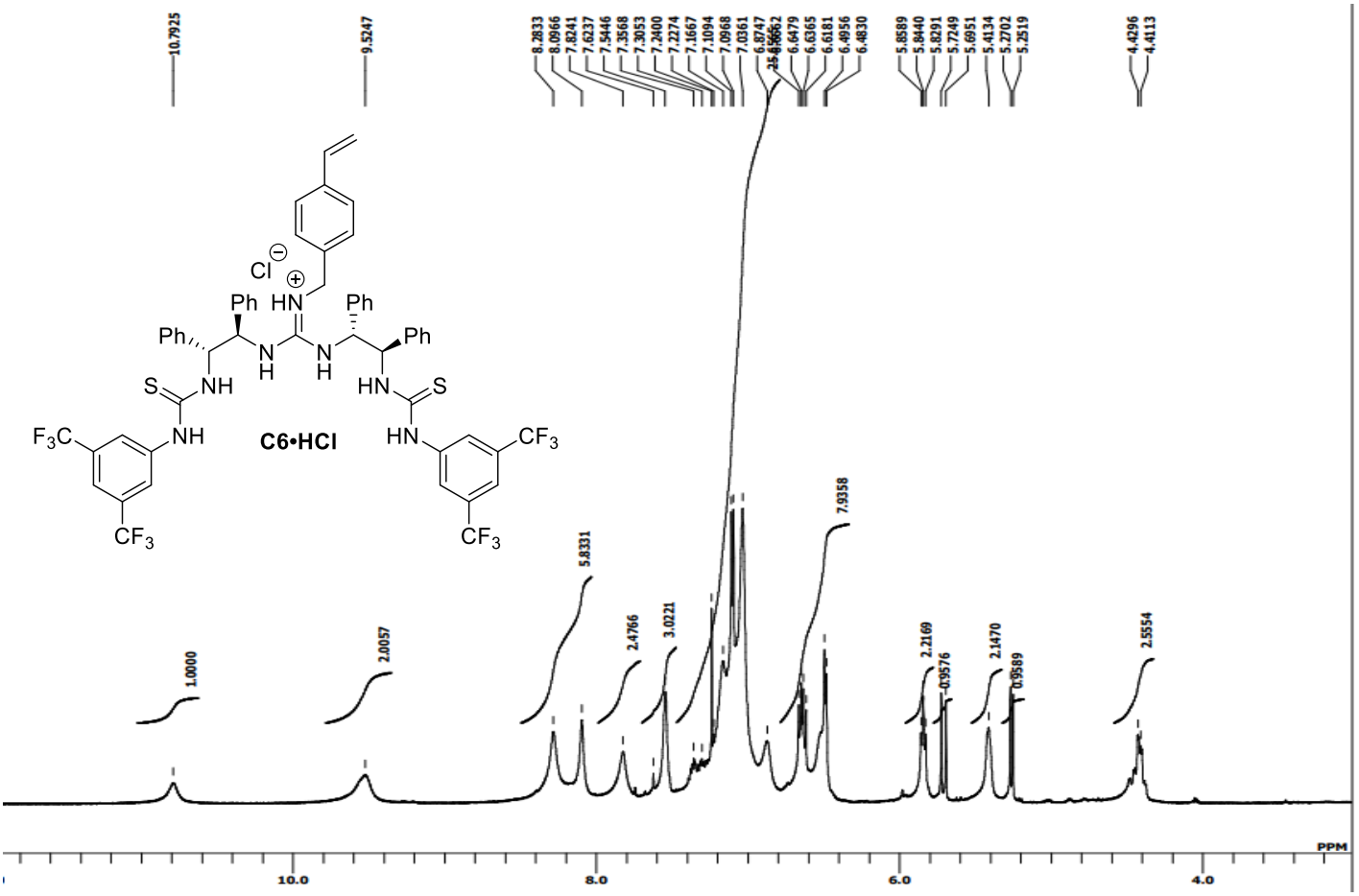
-20.0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6.6365
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5.8440
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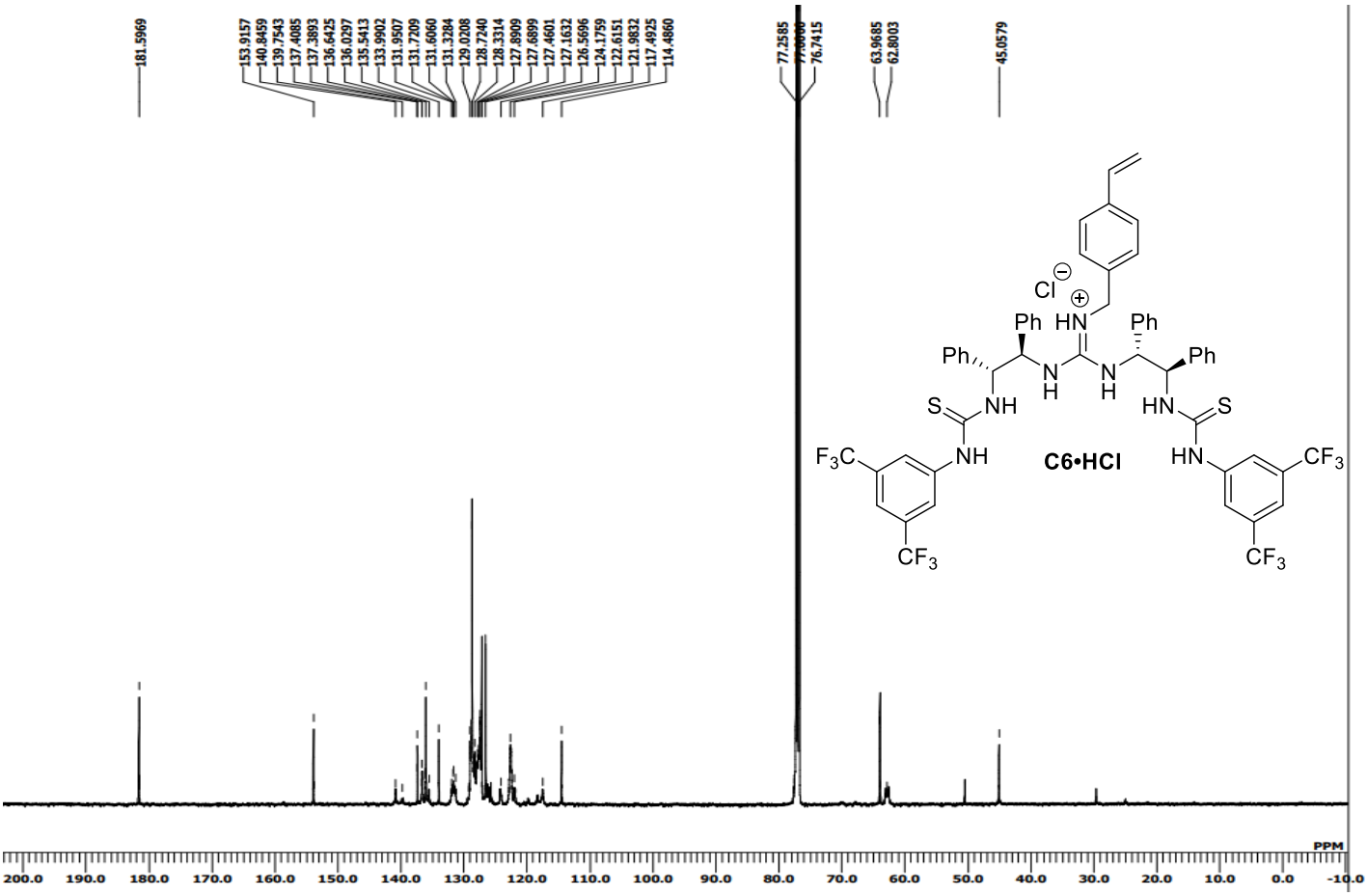
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127.4601
127.1632
126.5696
124.1759
122.6151
121.9832
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77.2585
76.7415
63.9685
62.8003
45.0579
C6•HCl
PPM
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190.0
180.0
170.0
160.0
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130.0
120.0
110.0
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90.0
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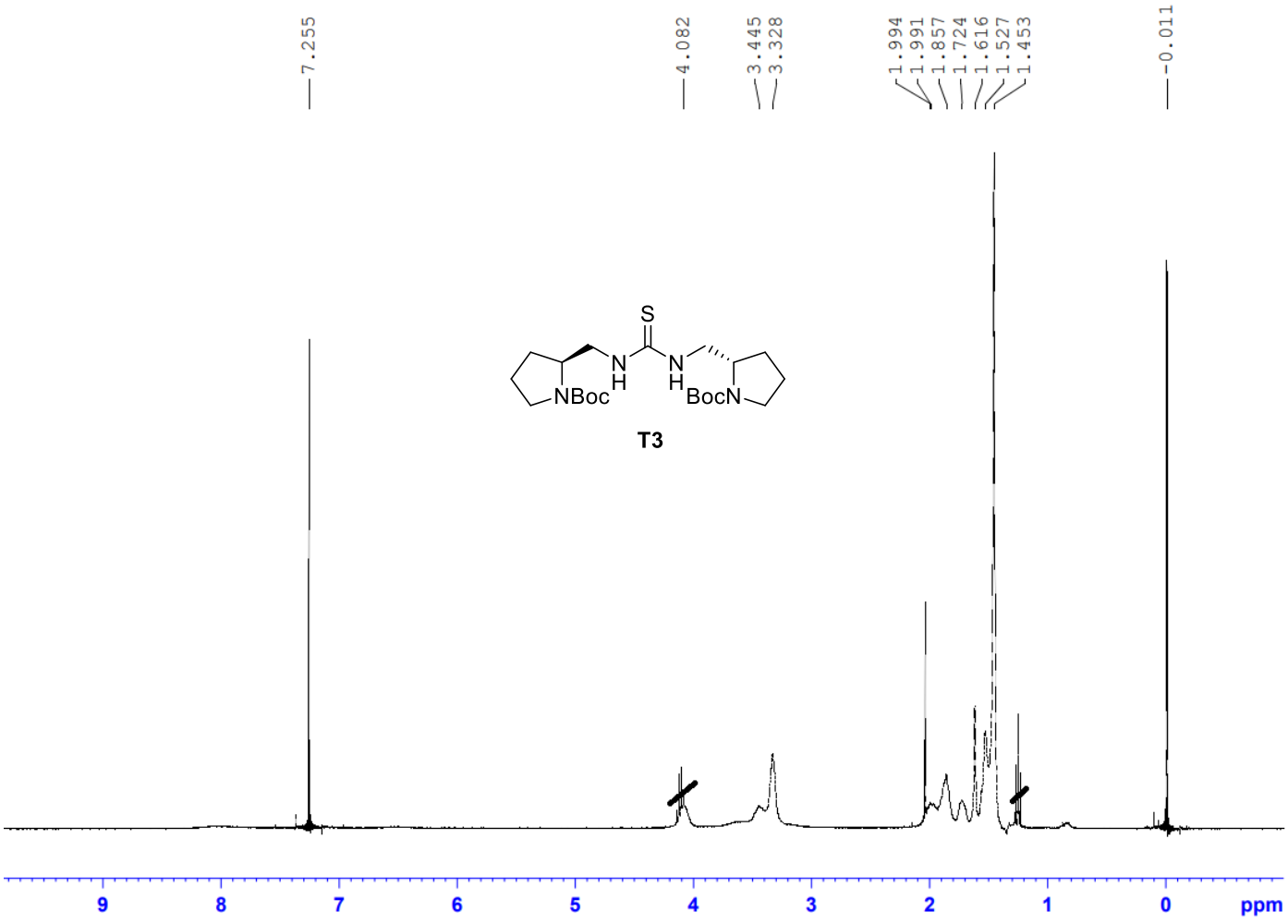
50.0
40.0
30.0
20.0
10.0
0.0
-10.0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BocN
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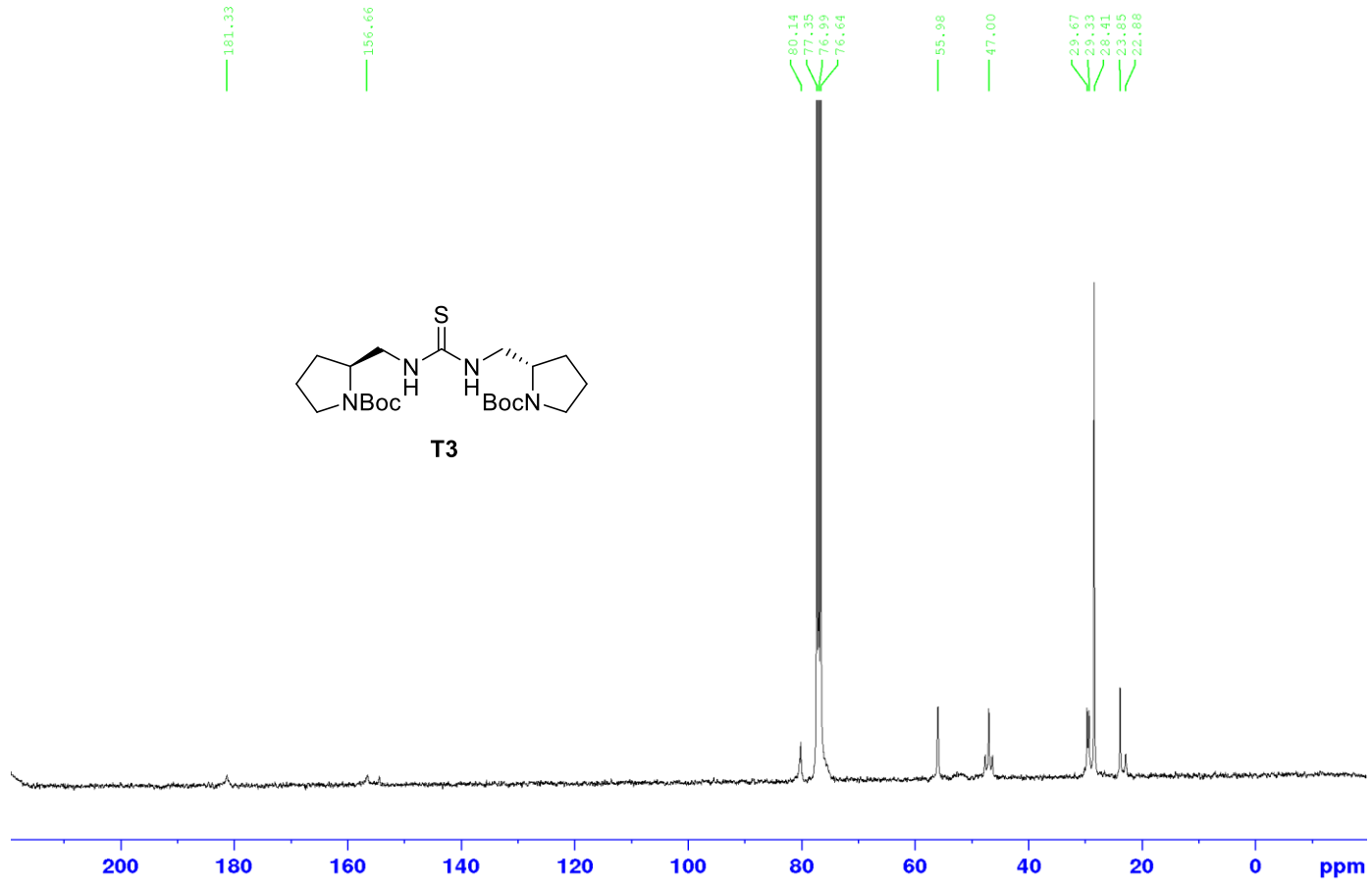
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H
BocN
T3
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120
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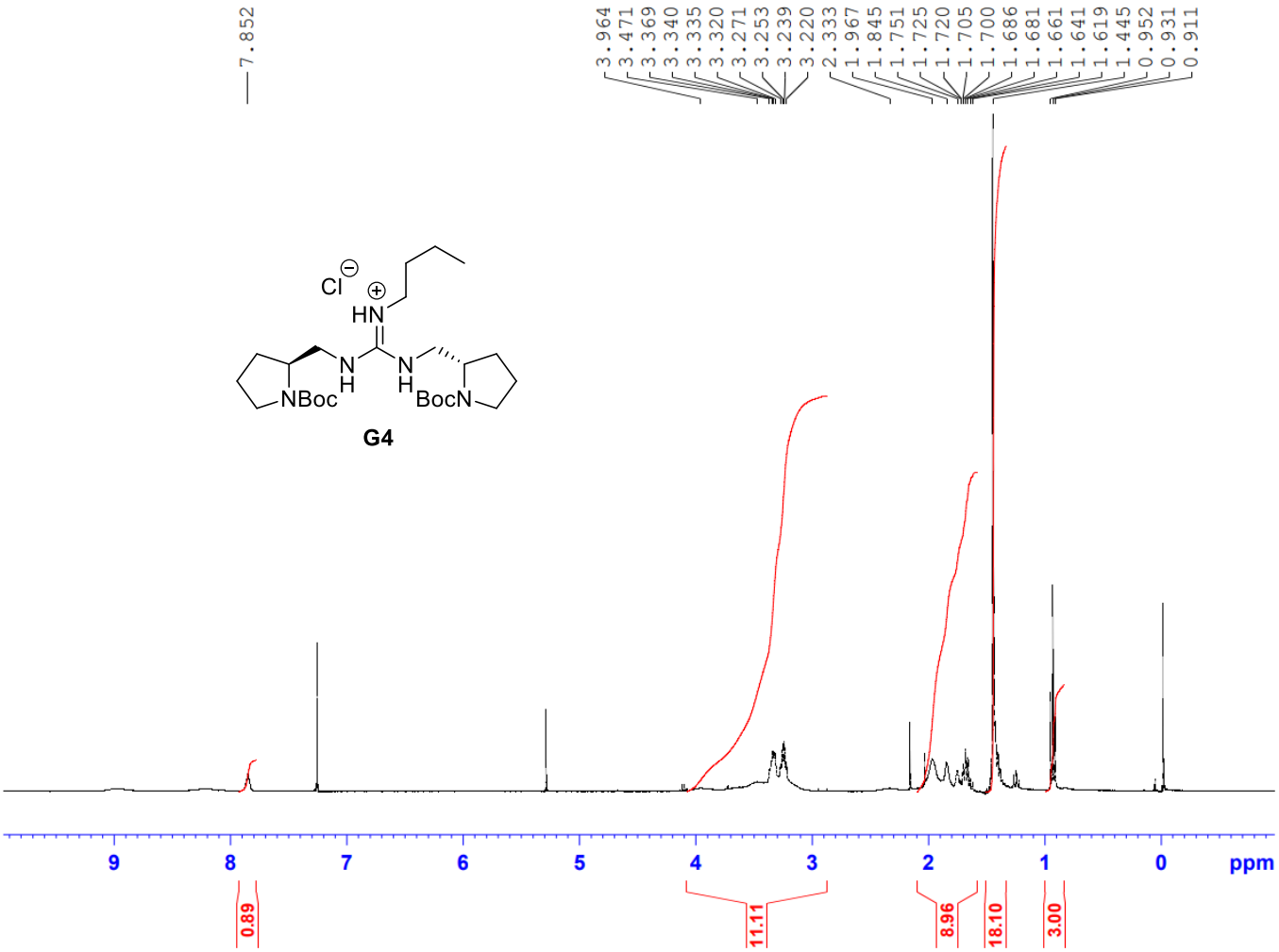
40
20
0
ppm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1.845
1.751
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1.720
1.705
1.700
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1.681
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1.641
1.619
1.445
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H
N
H
NBoc
BocN
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6
5
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2
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0
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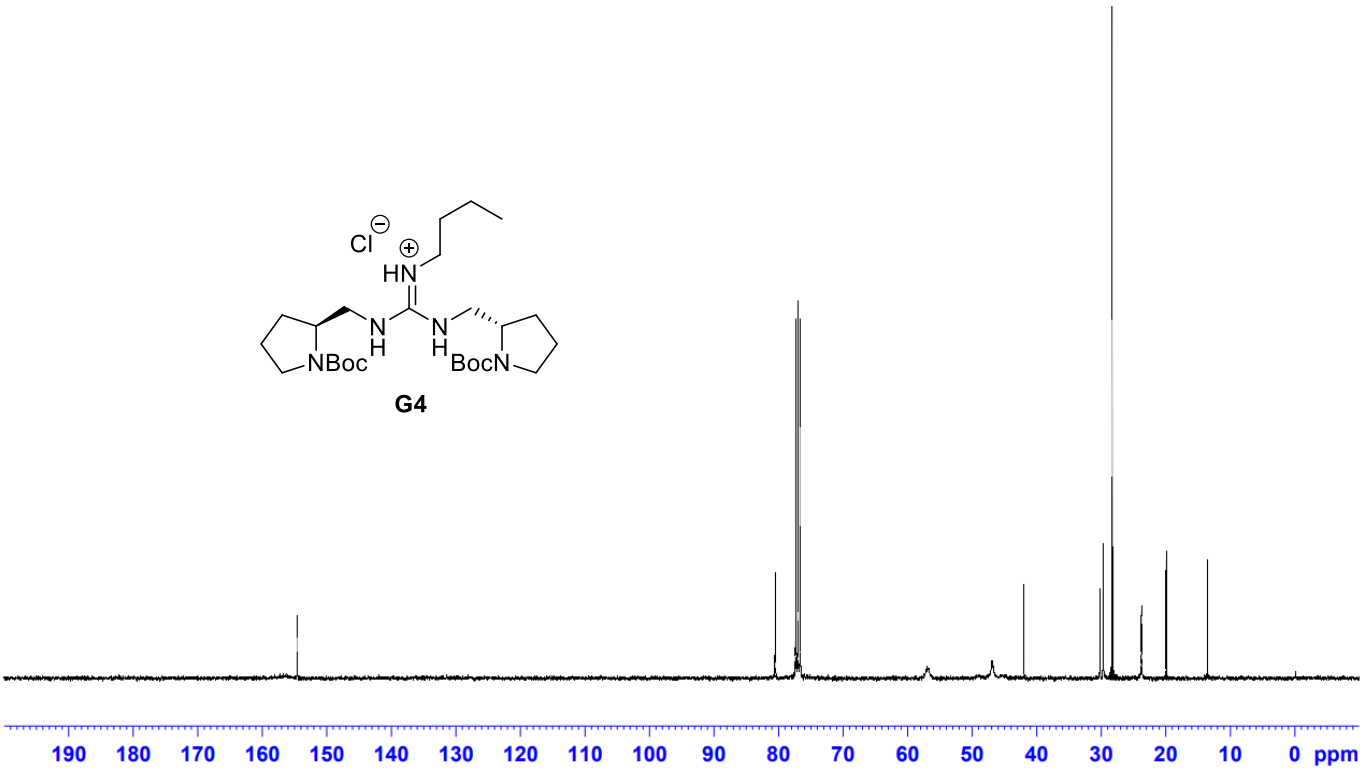
3.00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28.28
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19.93
13.54
Cl
HN
N
H
N
H
NBoc
BocN
G4
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140
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20
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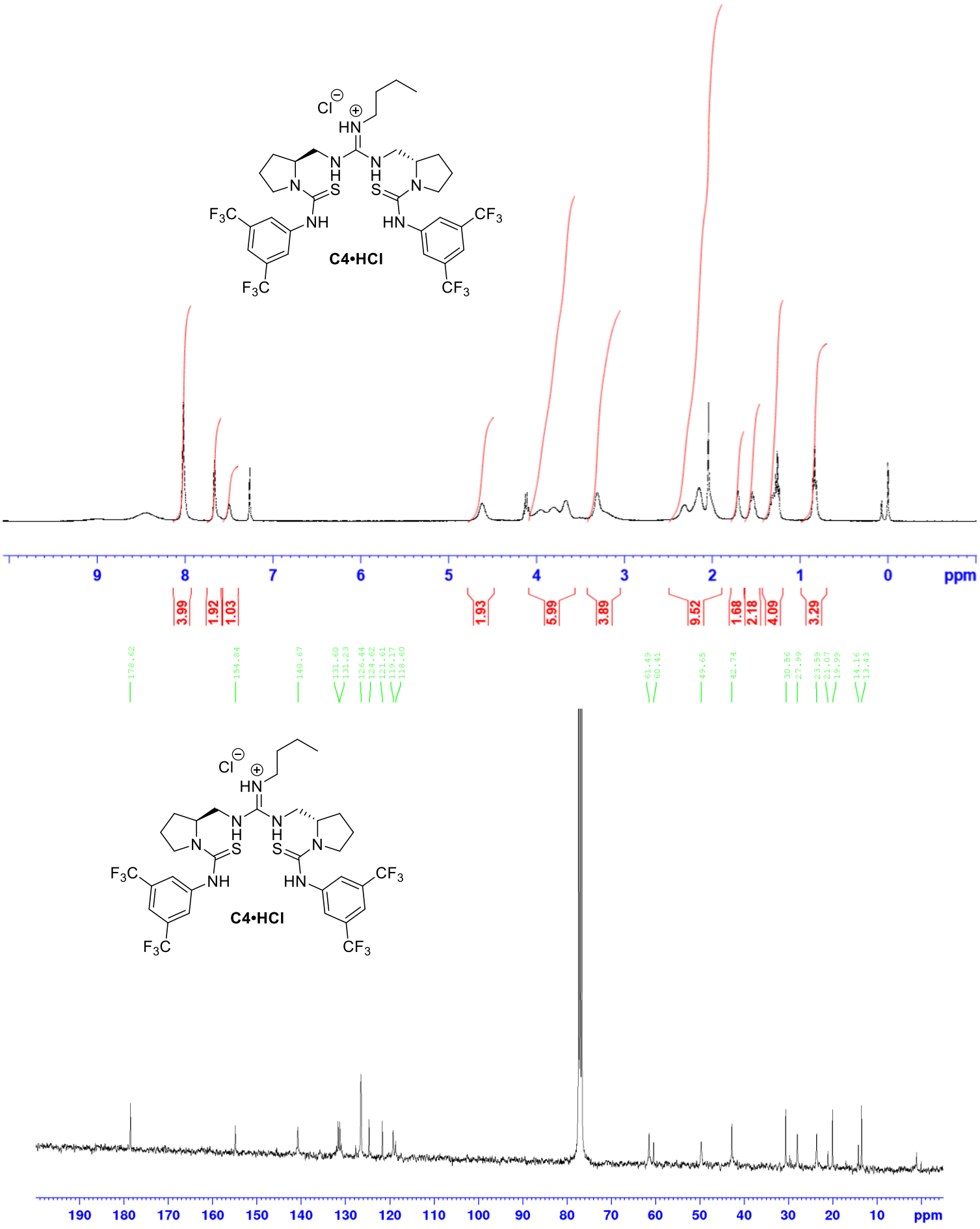
0
ppm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4
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ppm
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3.89
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1.68
2.18
4.09
3.29
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131.23
126.44
124.62
121.61
119.17
118.60
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60.41
49.65
42.74
30.56
27.99
23.59
21.07
19.99
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13.43
C4•HCl
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180
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150
140
130
120
110
100
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70
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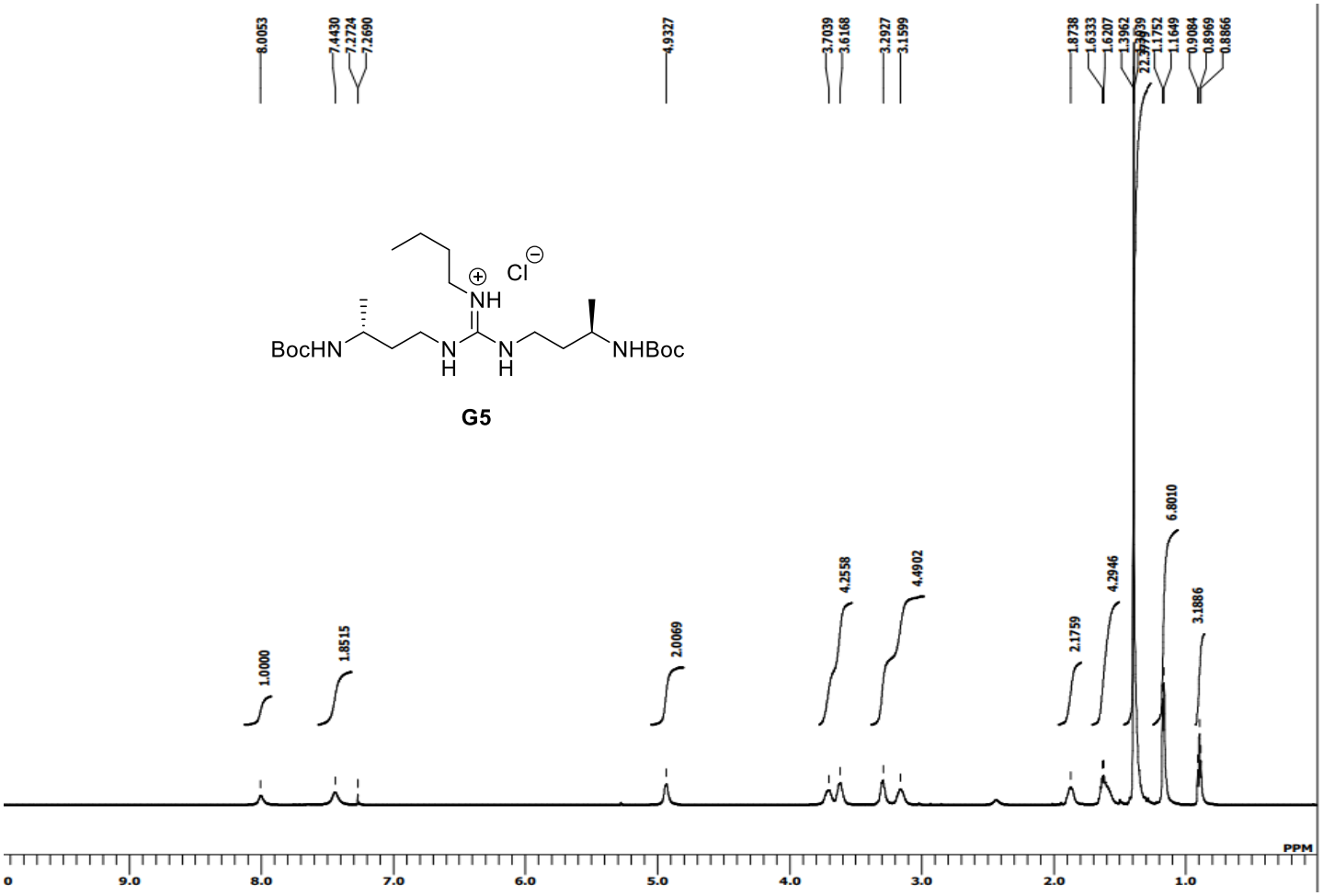
50
40
30
20
10
ppm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1.6207
1.3962
1.1752
1.1649
0.9084
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0.8866
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Cl
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H
N
H
NHBoc
G5
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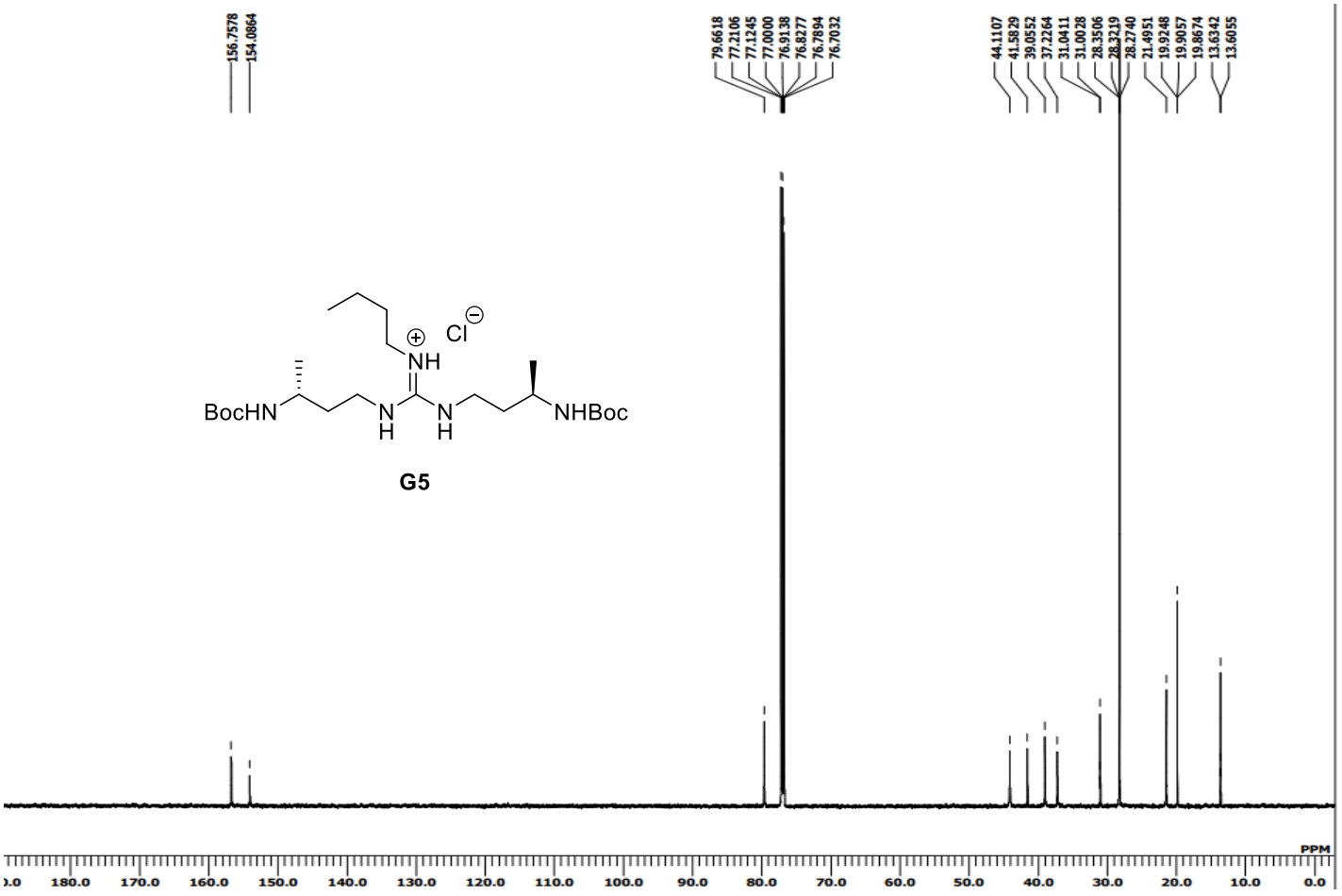
1.0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41.5829
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37.2264
31.0411
31.0028
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28.3219
28.2740
21.4951
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19.9057
19.8674
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13.6055
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Cl
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H
N
H
NHBoc
G5
PPM
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140.0
130.0
120.0
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90.0
80.0
70.0
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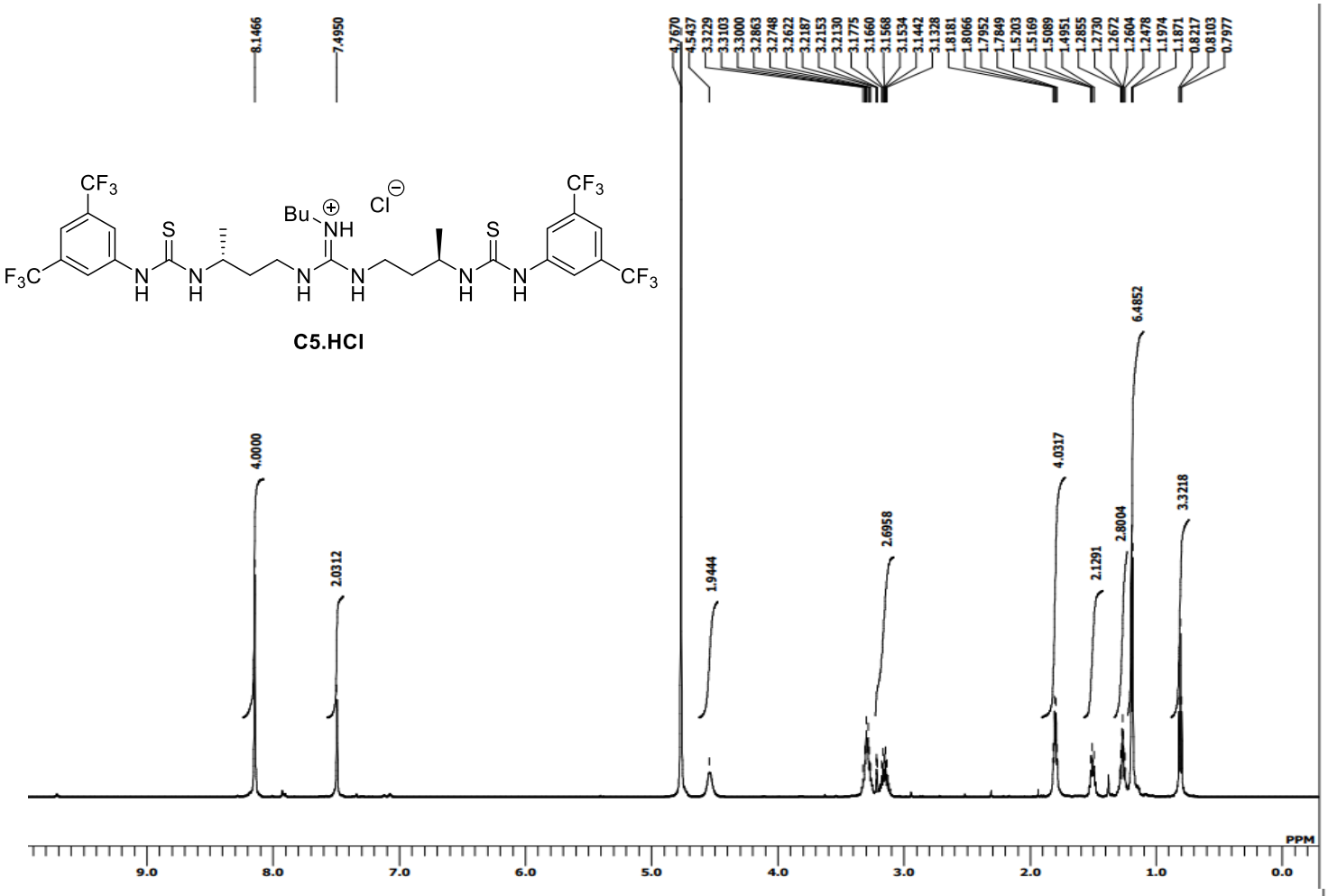
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N
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Cl
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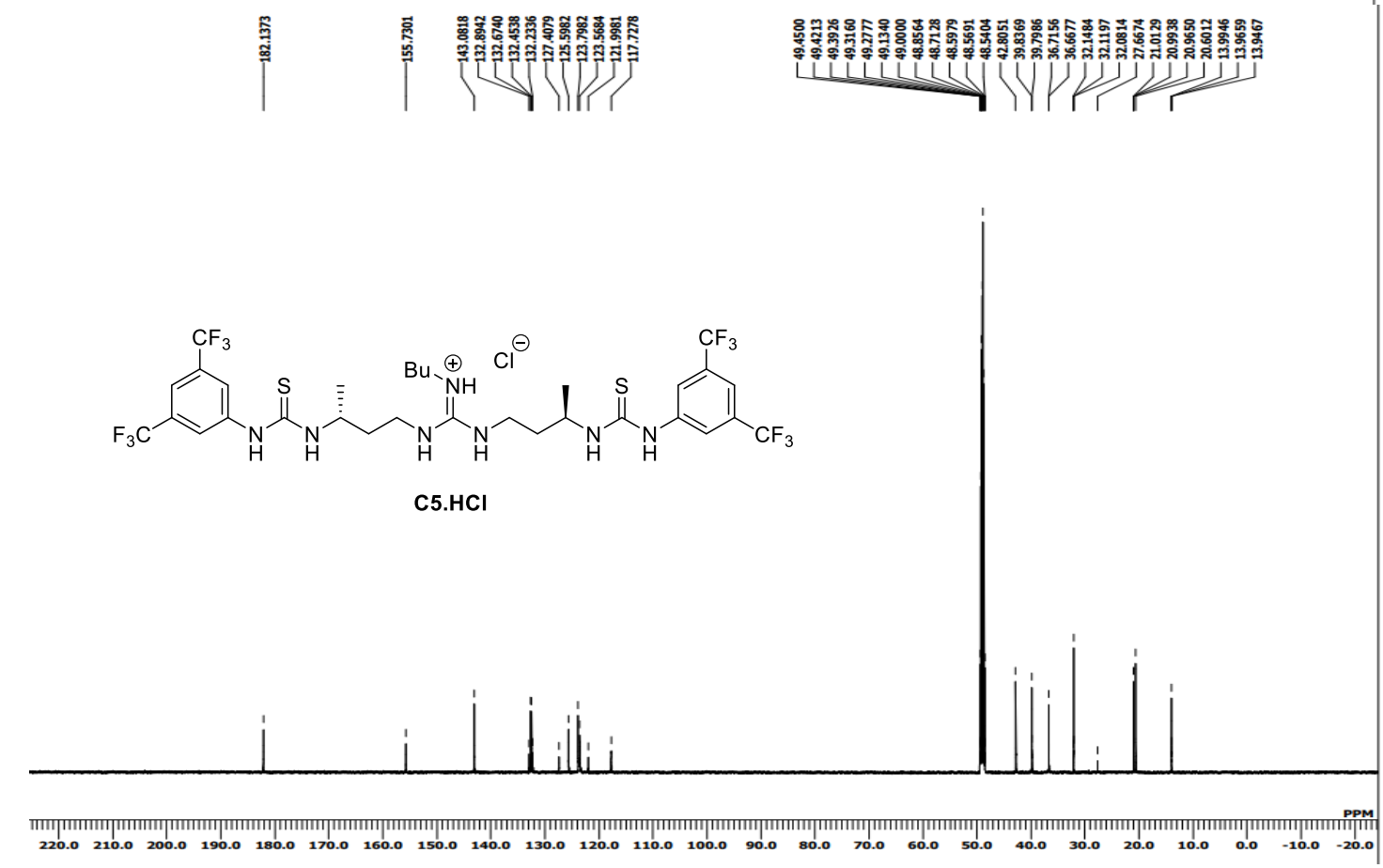
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121.9981
117.7278
49.4500
49.4213
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48.5404
42.8051
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32.1197
32.0814
27.6674
21.0129
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20.9650
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13.9946
13.9659
13.9467
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S
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H
Bu
NH
Cl
C5.HCl
PPM
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140.0
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120.0
110.0
100.0
90.0
80.0
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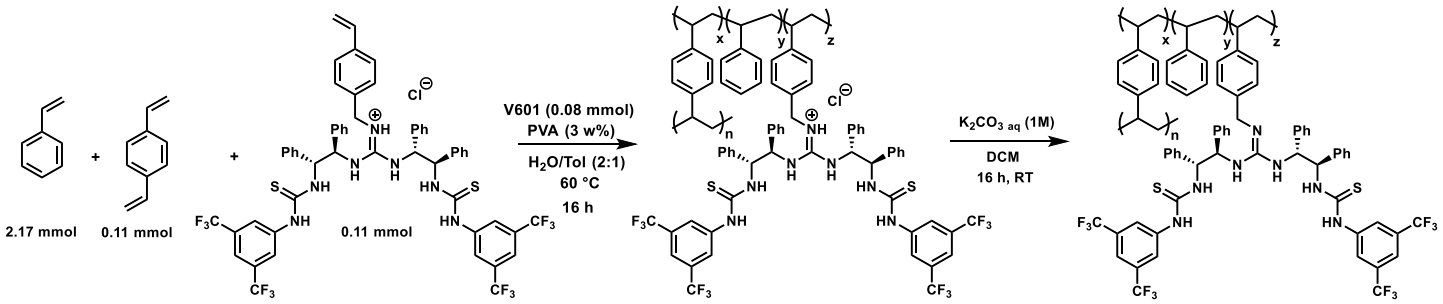
0.0
-10.0
-20.0

Heterogenization :



Polymerization procedure:

In a 10 mL two-neck schlenk tube was prepared a solution of 12 mg PVA (MW = 2000) in 0.8 mL in water at 60°C. After 15 minutes, argon was bubbled in the hot solution for 15 minutes and it was allowed to cool down at room temperature. Styrene (0.239 uL, 2.17 mmol) and DVB (30 uL, 0.11 mmol) were added to the PVA solution. A solution of monomer (120 mg, 0.11 mmol) and V601 (18 mg) in 0.4 mL of toluene was prepared and also added to the schlenk. The resulting biphasic mixture was degassed under sonication and stirred at 60°C for 24h. The reaction mixture was filtered and the polymer beads were successively washed with water, EtOH, Toluene and DCM then dried under vacuum for 1h then crushed using a mortar and the resulting powder was finally dried at 40 °C for 16 h.

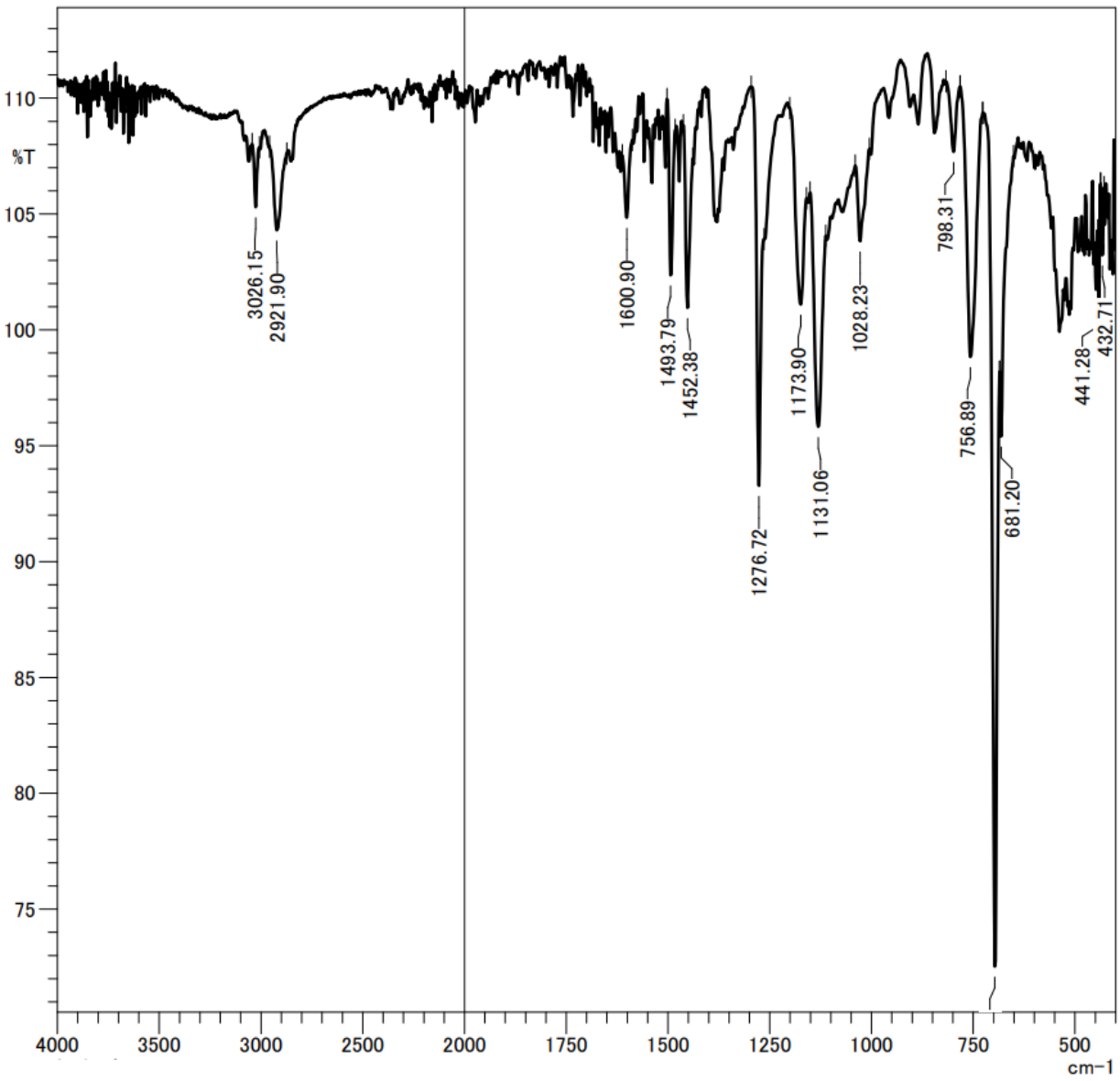
Deprotonation procedure :

The dried polymer (240 mg) was placed in a schlenk tube with a magnetic stirrer under argon. DCM (2 mL) and 1M aqueous K_2CO_3 solution (2 mL) was added. The resulting biphasic mixture was stirred vigourously for 16h. The polymer was washed weveral times with water, EtOH and Toluene then dried under vauum at 40°C for 16h and stored in glove box.

Elemental analysis :

Mass (mg)	C (%)	H (%)	N (%)	S (%)	Cat. Load. (N%)	Cat. Load. (S%)
1.4901	84.17	6.94	1.75	1.17	0.179 mmol/g	0.182 mmol/g

Polymer IR :


110
%T
105
100
95
90
85
80
75
3026.15
2921.90
1600.90
1493.79
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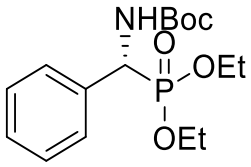
1173.90
1131.06
1028.23
798.31
756.89
681.20
441.28
432.71
4000
3500
3000
2500
2000
1750
1500
1250
1000
750
500
cm-1

Characterization of compounds

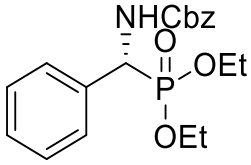
Typical procedure **A**:
The imine (21 mg, 0.10 mmol, 1.0 equiv.) and the catalyst (5.0 mg, 5.0 x 10^{-3} mmol, 5 mol%) were placed in a flame-dried Schlenk-tube. 1 mL of Solvent was added and the phosphonate (15 μL, 0.12 mmol, 1.2 equiv.) was added dropwise. The reaction was stirred at rt for 2 h. The reaction mixture was purified by column chromatography to obtain the desired product.

tert-butyl ((diethoxyphosphoryl)(phenyl)methyl)carbamate - 3aa: [1]



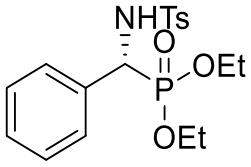
Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (76% yield, 87% ee).
HPLC Chiralpak AD-H – 95/5 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 22.5 min (*S*), tr_2 : 32.2 min (*R*).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.12 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.42 (s, 9H), 3.75 (m, 1H), 3.94 (m, 1H), 4.12 (m, 2H), 5.12 (dd, *J* = 9.3, 22.0 Hz, 1H), 5.51 (bs, 1H), 7.27-7.42 (m, 5H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.1 (d, *J* = 5.6 Hz), 16.4 (d, *J* = 5.6 Hz), 28.3, 51.9 (d, *J* = 157.0 Hz), 63.0 (d, *J* = 6.9 Hz), 63.2 (d, *J* = 6.7 Hz), 80.3, 127.8, 128.0 (d, *J* = 5.7 Hz), 128.5 (d, *J* = 2.5 Hz), 135.5, 154.9.
IR (cm^{-1}**)** 975, 1027, 1064, 1159, 1251, 1531, 1704, 2976, 3265.
MS (IE): *m/z*: 344.16 $[M]^+$, 366.14 $[M\text{-}Na]^+$.
Melting point 122 °C.

Benzyl((diethoxyphosphoryl)(phenyl)methyl)carbamate - 4aa: [2]



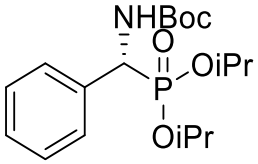
Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (82% yield, 70% ee).
HPLC Chiralcel OD-H – 95/5 Hex-IPA, 20 °C, 254 nm, 1.1 mL/min – tr_1 : 11.9 min (minor), tr_2 : 32.6 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.09 (t, *J* = 6.8 Hz, 3H), 1.26 (t, *J* = 6.8 Hz, 3H), 1.42 (s, 9H), 3.71 (m, 1H), 3.92 (m, 1H), 4.11 (m, 2H), 5.10 (m, 1H), 5.76 (bs, 1H), 7.25-7.41 (m, 12H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.1 (d, *J* = 5.8 Hz), 16.3 (d, *J* = 5.7 Hz), 52.5 (d, *J* = 144.5 Hz), 63.1 (d, *J* = 6.8 Hz), 63.3 (d, *J* = 6.8 Hz), 67.3, 127.8, 127.9, 128.1, 128.5, 128.6, 135.2, 136.1, 155.6.
IR (cm^{-1}**)** 973, 1028, 1057, 1159, 1232, 1252, 1548, 1715, 2929, 3061, 3236.
MS (IE): *m/z*: calc. $C_{19}H_{25}NO_5P$ 378.1465 $[M]^+$, $C_{19}H_{24}NNaO_5PS$ 400.1284 $[M+Na]^+$; found 378.1448 $[M]^+$, 400.1267 $[M\text{-}Na]^+$.
Melting point 117 °C.

Diethyl(4-methylphenylsulfonamido)(phenyl)methylphosphonate - 5aa: [3]



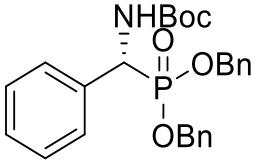
Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (83% yield, 26% ee).
HPLC Chiralpak IA – 50/50 Hex-EtOH, 25 °C, 220 nm, 0.7 mL/min – tr_1 : 9.5 min (minor), tr_2 : 11.6 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.03 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 2.28 (s, 3H), 3.57-3.66 (m, 1H), 3.82-3.91 (m, 1H), 4.19-4.27 (m, 2H), 4.80 (dd, *J* = 10.1, 25.2 Hz, 1H), 6.75 (m, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.09-7.15 (m, 3H), 7.22-7.19 (m, 2H), 7.45 (d, *J* = 7.2 Hz, 2H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.0 (d, *J* = 5.6 Hz), 16.4 (d, *J* = 5.6 Hz), 21.3, 55.2 (d, *J* = 157.0 Hz), 63.5 (d, *J* = 6.9 Hz), 64.0 (d, *J* = 6.7 Hz), 127.0, 127.8, 128.2, 129.0, 129.6, 133.6, 137.8, 142.8.
IR (cm^{-1}**)** 979, 1016, 1044, 1066, 1091, 1236, 1327, 1462, 2883, 2929, 3127.
MS (IE) *m/z*: calc. $C_{18}H_{25}NO_5PS$ 398.1186 $[M]^+$, $C_{18}H_{24}NNaO_5PS$ 420.1005 $[M+Na]^+$; found 398.1176. $[M]^+$, 420.0997 $[M-Na]^+$.
Melting point 124-125 °C.

***tert*-butyl ((diisopropoxyphosphoryl)(phenyl)methyl)carbamate – <u>3ab</u>:** [4]



Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (76% yield, 80% ee).
HPLC Chiralpak AD-H – 95/5 Hex-IPA, 20 °C, 215 nm, 1.0 mL/min – tr_1 : 11.2 min (minor), tr_2 : 18.2 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 0.91 (d, *J* = 6.3 Hz, 3H), 1,24 (t, *J* = 5.9 Hz, 8H), 1.32 (d, *J* = 6.3 Hz, 3H), 1.40 (s, 9H), 4.44 (m, 1H),4.68 (m, 1H), 5.03 (dd, *J* = 9.9, 22.0 Hz, 1H), 5.21 (bs, 1H), 7.22-7.45 (m,5H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 23.2 (d, *J* = 5.5 Hz), 23.8 (d, *J* = 5.5 Hz), 24.1 (d, *J* = 3.2 Hz), 24.2 (d, *J* = 3.2 Hz), 28.3, 52.4 (d, *J* = 155.8 Hz), 71.7 (d, *J* = 7.5 Hz), 72.0 (d, *J* = 7.3 Hz), 80.2, 127.8, 127.9, 128.0, 128.0, 128.4, 136.0, 154.9 (d, *J* = 11.0 Hz).
IR (cm^{-1}**)** 699 761, 879, 991, 1014, 1044, 1164, 1231, 1250, 1285, 1531, 1711, 2928, 2978, 3250.
MS (IE) m/z: 372.19 $[M]^+$, 394.18 $[M-Na]^+$.
Melting point 102-104 °C.

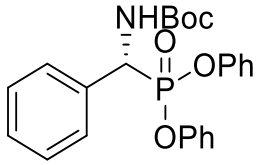
tert-butyl ((dibenzoxyphosphoryl)(phenyl)methyl)carbamate - <u>3ac</u>: [5]



Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (75% yield, 68% ee).
HPLC : Chiralpak AD-H – 80/20 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 25.5 min (minor), tr_2 : 27.4 min (major).

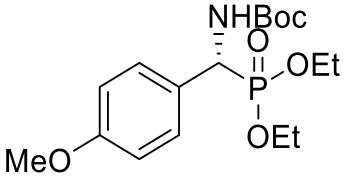
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.39 (s, 9H), 4.63 (dd, *J* = 8.0, 11.80 Hz, 1H), 4.86 (dd, *J* = 7.20, 11.50 Hz, 1H), 5.00 (d, *J* = 8.0 Hz, 2H), 5.23 (d, *J* = 9.8, 21.7 Hz, 1H),5.50 (bs, 1H), 7.05-7.49 (m, 15H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 28.3, 52.0 (d, *J* = 153.8 Hz), 65.1, 68.3 (d, *J* = 7.3 Hz) , 68.5 (d, *J* = 6.9 Hz), 80.4, 126.9, 127.5, 127.8-128.7 (C_{arom}), 135.2, 135.8 (d, *J* = 6.2 Hz)136.0 (d, *J* = 6.1 Hz), 141.2, 154.9 (d, *J* = 9.9 Hz).
IR (cm^{-1}**)** 696, 737, 759, 863, 883, 1021, 1078, 1167, 1250, 1288, 1365, 1533, 1707, 2978, 3033, 3231.
MS (IE) m/z: 468.19 $[M]^+$, 490.18 $[M\text{-}Na]^+$.
Melting point 95-96 °C.

tert-butyl ((diphenoxyphosphoryl)(phenyl)methyl)carbamate - <u>3ae</u>: [6]



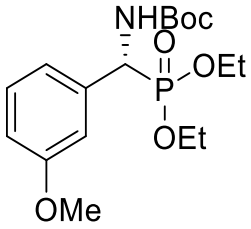
Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (8/2 – pentane/EtOAc). The product was obtained as a white solid (61% yield, 50% ee).
HPLC Chiralpak AD-H – 60/40 Hex-IPA, 20 °C, 215 nm, 1.0 mL/min – tr_1 : 10.7 min (minor), tr_2 : 28.8 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.40 (s, 9H), 5.52 (m, 1H), 5.81 (m, 1H), 6.82 (m, 2H), 7.02–7.32 (m, 11H) 7.45 (m, 2H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 28.2, 52.2 (d, *J* = 157.5 Hz), 80.6, 115.4, 119.7, 120.4 (t, *J* = 4.3 Hz), 125.3, 125.7, 128.2-129.7 (C_{arom}), 134.5, 150.0, 154.7, 156.5.
IR (cm^{-1}**)** : 1006, 1074, 1160, 1210, 1258, 1362, 1455, 1490, 1592, 1695, 2980, 3069, 3297.
MS (DART+) m/z: 440.1518 $[M+H^+]$.
Melting point 154-156 °C.

tert-butyl ((diethoxyphosphoryl)(4-methoxyphenyl)methyl) carbamate - <u>3ba</u> : [1]



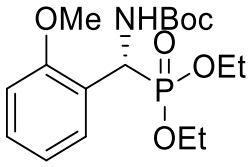
Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (68% yield, 76% ee).
HPLC Chiralpak AD-H – 90/10 Hex-IPA, 20 °C, 215 nm, 1 mL/min – tr_1 : 17.2 min (minor), tr_2 : 35.1 min (major).
^{1}H NMR (360 MHz, CDCl3) δ = 1.12 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.41 (s, 9H), 3.75 (m, 1H), 3.79 (s, 3H), 3.94 (m, 1H), 4.11 (m, 2H), 5.04 (dd, *J* = 10.5, 21.4 Hz, 1H), 5.42 (bs, 1H), 6.83-6.92 (m, 2H), 7.27-7.37 (m, 2H).
^{13}C NMR (91 MHz, CDCl3) δ = 16.2 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 5.4 Hz) 28.3, 51.1 (d, *J* = 156.5) 55.3, 63.1 (d, *J* = 7.0 Hz), 63.2 (d, *J* = 7.2 Hz), 80.4, 114.0, 129.1, 159.5.
IR (cm^{-1}**)** 977, 1026, 1164, 1235, 1284, 1513, 1702, 2980, 3251.
MS (IE) m/z: 374.17 $[M]^+$, 396.15 $[M\text{-}Na]^+$.
Melting point 79-80 °C.

tert-butyl ((diethoxyphosphoryl)(3-methoxyphenyl)methyl) carbamate - <u>3ca</u> :



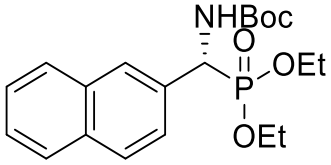
Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (81% yield, 81% ee).
HPLC Chiralpak AD-H – 80/20 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 7.7 min (minor), tr_2 : 9.1 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.13 (t, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.41 (s, 9H), 3.77 (m, 1H), 3.79 (s, 3H), 3.94 (m, 1H), 4.11 (m, 2H), 5.07 (dd, *J* = 9.7, 21.8 Hz, 1H), 5.50 (bs, 1H), 6.80-6.85 (m, 1H), 6.91-7.01 (m, 2H), 7.21-7.27 (m, 2H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.4, 28.2, 51.8 (d, *J* = 154.2 Hz), 55.3, 61.8 (d, *J* = 5.5 Hz), 63,1 (d, *J* = 7.1 Hz), 63.3 (d, *J* = 6.5 Hz), 80.3, 113.3, 113.7, 120.1 (d, *J* = 5.6 Hz), 129.6, 137.0, 154.8 (d, *J* = 9.8 Hz), 159.7,
IR (cm^{-1}) 977, 1032, 1165, 1251, 1537, 1697, 2980, 3252.
MS (IE) m/z: calc. $C_{17}H_{29}NO_6P$ 374.1727 $[M]^+$, $C_{17}H_{28}NNaO_6P$ 396.1546 $[M+Na]^+$; found 374.1710 $[M]^+$, 396.1531 $[M\text{-}Na]^+$.
Melting point 128-129 °C.

tert-butyl ((diethoxyphosphoryl)(2-methoxyphenyl)methyl) carbamate – <u>3da</u>:



Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (70% yield, 74% ee).
HPLC Chiralpak AD-H – 90/10 Hex-IPA, 20 °C, 215 nm, 1 mL/min – tr_1 : 16.5 min (minor), tr_2 : 19.9 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.06 (t, *J* = 6.9 Hz, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.41 (s, 9H), 3.70 (m, 1H), 3.87 (s, 3H), 3.89 (m, 1H), 4.14 (m, 2H), 5.50-5.80 (m, 2H), 6.81-7.02 (m, 2H), 7.18-7.39 (m, 2H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.2 (d, *J* = 5.9 Hz), 28.3, 46.5 (d, *J* = 5.9 Hz), 55.7, 62.9 (t, *J* = 8.1 Hz), 80.0, 111.0, 124.1, 128.8, 129.2, 154.7, 157.0.
IR (cm^{-1}) 977, 1022, 1049, 1164, 1227, 1247, 1289, 1528, 1705, 2982, 3251.
MS (IE) m/z: calc. $C_{17}H_{29}NO_6P$ 374.1727 $[M]^+$, $C_{17}H_{28}NNaO_6P$ 396.1546 $[M+Na]^+$; found 374.1714 $[M]^+$, 396.1531 $[M\text{-}Na]^+$.
Melting point 142-144 °C.

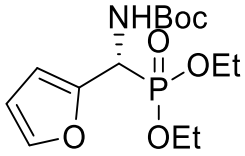
tert-butyl ((diethoxyphosphoryl)(naphthalen-2-yl)methyl) carbamate – <u>3ea</u>: [1]



Synthesized according to typical procedure **A**. The reaction mixture was stirred for 48h instead of 2h. The crude was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (41% yield, 84% ee).

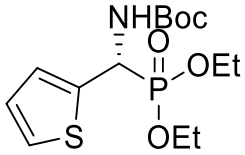
HPLC Chiralpak AD-H – 80/20 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 11.6 min (minor), tr_2 : 15.1 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.08 (t, *J* = 7.0 Hz, 3H), 1.31 (t, *J* = 7.0 Hz, 3H), 1.42 (s, 9H), 3.72 (m, 1H), 3.93 (m, 1H), 4.13 (m, 2H), 5.27 (dd, *J* = 9.9, 22.1 Hz, 1H), 5.62 (bs, 1H), 7.41-7.57 (m, 3H), 7.77-7.91 (m, 4H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.1 (d, *J* = 5.8 Hz), 16.4 (d, *J* = 5.8 Hz), 28.3, 52.00 (d, *J* = 154.0 Hz), 63.1 (d, *J* = 7.1 Hz), 63.3 (d, *J* = 6.7 Hz), 80.4, 125.6, 125.6, 126.2, 126.3, 126.9, 127.7, 128.0, 128.3, 133.0, 133.2, 155.1.
IR (cm^{-1}) 938, 976, 1010, 1027, 1133, 1240, 1356, 1696, 2927, 2977, 3260.
MS (IE) m/z: 394.18 $[M]^+$, 416.16 $[M\text{-}Na]^+$.
Melting point 133-134 °C.

tert-butyl ((diethoxyphosphoryl)(furan-2-yl)methyl)carbamate - 3fa:



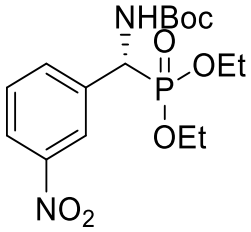
Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained has a white solid (91% yield, 64% ee).
HPLC Chiralpak AD-H – 80/20 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 8.2 min (minor), tr_2 : 9.5min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.23 (t, *J* = 7.4 Hz, 3H), 1.34 (t, *J* = 7.0 Hz, 3H), 1.45 (s, 9H), 3.96 (m, 1H), 4.08 (m, 1H), 4.17 (m, 2H), 5.19-5.43 (m, 2H), 6.34-6.44(m, 2H), 7.41 (s, 1H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.2 (d, *J* = 5.8 Hz), 16.4 (d, *J* = 6.1 Hz), 28.2, 47.4 (d, *J* = 160.5 Hz), 63.3 (d, *J* = 6.5 Hz), 80.5, 108.7, 110.7,142.7, 148.4, 154.7.
IR (cm^{-1}) 976, 1023, 1051, 1163, 1229, 1532, 1710, 2982, 3230.
MS (IE) m/z: calc. $C_{14}H_{25}NO_6P$ 334.1414 $[M]^+$, $C_{14}H_{24}NNaO_6P$ 356.1233 $[M+Na]^+$; found 334.1402 $[M]^+$, 356.1220 $[M\text{-}Na]^+$.
Melting point 89-90°C.

tert-butyl ((diethoxyphosphoryl)(2-thiophene)methyl)carbamate - 3ga:



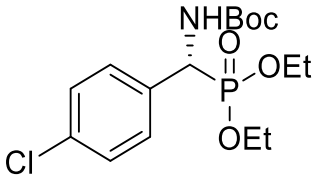
Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (64% yield, 62% ee).
HPLC Chiralpak AD-H – 80/20 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 7.6 min (minor), tr_2 : 10.01 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.23 (t, *J* = 7.4 Hz, 3H), 1.34 (t, *J* = 7.0 Hz, 3H), 1.45 (s, 9H), 3.96 (m, 1H), 4.08 (m, 1H), 4.15 (m, 2H), 5.19-5.50 (m, 2H), 7.00 (dd, *J* = 1.2; 3.7 Hz, 2H), 7.24-7.29 (m, 1H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.2 (d, *J* = 5.8 Hz), 16.4 (d, *J* = 6.1 Hz), 28.2, 47.4 (d, *J* = 160.5 Hz), 63.4 (d, *J* = 6.5 Hz), 80.5, 125.4, 126.6, 126.7, 127.1, 138.1, 154.7 (d, *J* = 7.7 Hz).
IR (cm^{-1}) 976, 1022, 1159, 1218, 1255, 1367, 1391, 1526, 1539, 1699, 2982, 3233.
MS (IE) m/z: calc. $C_{14}H_{25}NO_5PS$ 350.1186 $[M]^+$, $C_{14}H_{24}NNaO_5PS$ 372.1005 $[M+Na]^+$; found 350.1181 $[M]^+$, 372.1000 $[M\text{-}Na]^+$.
Melting point 103-106 °C.

tert-butyl ((diethoxyphosphoryl)(3-nitrophenyl)methyl) carbamate - 3ha:



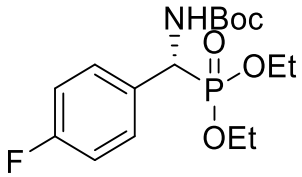
Synthesized according to typical procedure **A**.The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (59% yield, 77% ee).
HPLC Chiralpak AD-H – 90/10 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 13.0 min (minor), tr_2 : 14.4 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.12 (t, *J* = 6.9 Hz, 3H), 1.30 (t, *J* = 6.9 Hz, 3H), 1.43 (s, 9H), 3.95 (m, 1H), 4.03 (m, 1H), 4.14 (m, 2H), 5.21 (dd, *J* = 8.6, 22.5 Hz, 1H), 5.67 (bs, 1H), 7.47-7.60 (m, 1H), 7.72-7.82 (m, 1H), 8.12-8.21 (m, 1H), 8.24-8.31 (m, 1H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.2 (d, *J* = 5.5 Hz), 16.4 (d, *J* =5.5 Hz), 28.2, 51.8 (d, *J* = 152.9 Hz), 63.5 (d, *J* = 7.9 Hz), 81.0, 122.4 (d, *J* = 5.5 Hz), 122.9 (d, *J* = 2.7 Hz), 133.9, 138.2, 148.3, 154.9.
IR (cm^{-1}) 976, 1022, 1047, 1232, 1254, 1350, 1532, 1707, 2980, 3223.
MS (IE) m/z: calc. $C_{16}H_{26}N_2O_7P$ 389.1472 $[M]^+$, $C_{16}H_{25}N_2NaO_7P$ 411.1292 $[M+Na]^+$; found 389.1458 $[M]^+$, 411.1291 $[M-Na]^+$.
Melting point 112-113 °C.

tert-butyl ((diethoxyphosphoryl)(4-chlorophenyl)methyl) carbamate - 3ia: [1]



Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (89% yield, 79% ee).
HPLC Chiralpak AD-H – 80/20 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 9.1 min (minor), tr_2 : 11.5 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.14 (t, *J* = 7.2 Hz, 3H), 1.29 (t, *J* = 6.7 Hz, 3H), 1.41 (s, 9H), 3.81 (m, 1H), 3.97 (m, 1H), 4.11 (m, 2H), 5.09 (dd, *J* = 9.9, 22.1 Hz, 1H), 5.53 (bs, 1H), 7.27-7.38 (m, 4H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.2 (d, *J* = 5.5 Hz), 16.4 (d, *J* = 5.5 Hz), 28.2, 51.3 (d, *J* = 154.2 Hz), 63.3 (t, *J* = 7.0 Hz), 80.6, 128.7, 129.1 (d, *J* = 5.2 Hz), 133.9, 134.2, 154.9.
IR (cm^{-1}) 974, 1029, 1046, 1164, 1234, 1250, 1534, 1706, 2982, 3251.
MS (IE): m/z: 378.12 $[M]^+$, 400.10 $[M-Na]^+$.
Melting point 97-98 °C.

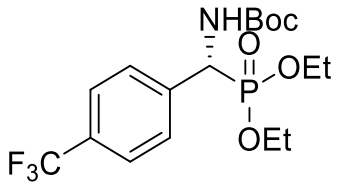
tert-butyl ((diethoxyphosphoryl)(4-Fluorophenyl)methyl) carbamate - 3ja:



Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (97% yield, 73% ee).
HPLC Chiralpak AD-H – 80/20 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 7.6 min (minor), tr_2 : 8.5 min (major).

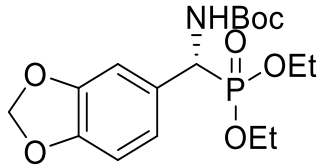
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.07 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.34 (s, 9H), 3.72 (m, 1H), 3.88 (m, 1H), 4.04 (m, 2H), 5.00 (dd, *J* = 9.9, 22.1 Hz, 1H), 5.46 (bs, 1H), 6.96 (t, *J* = 8.5 Hz, 2H), 7.26-7.36 (m, 2H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.2 (d, *J* = 5.8 Hz), 16.4 (d, *J* = 5.5 Hz), 28.2, 51.2 (d, *J* = 154.5 Hz), 63.2 (t, *J* = 7.1 Hz), 80.5, 115.5 (d, *J* = 21.3 Hz), 129.5, 131.5, 154.9 (d, *J* = 10.0 Hz), 160.9, 164.1.
IR (cm^{-1}) 965, 978, 1028, 1160, 1225, 1252, 1534, 1606, 1710, 2981, 3256.
MS (IE) m/z: calc. $C_{16}H_{26}FNO_5P$ 362.1527 $[M]^+$, $C_{16}H_{25}FNNaO_5P$ 384.1347 $[M+Na]^+$; found 362.1512 $[M]^+$, 384.1336 $[M\text{-}Na]^+$.
Melting point 103-104 °C.

tert-butyl ((diethoxyphosphoryl)(4-trifluoromethyl phenyl) carbamate - <u>3ka</u>:



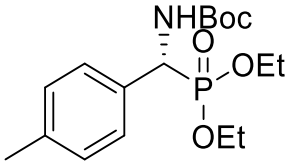
Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (68% yield, 75% ee).
HPLC Lux cellulose 2 – 75/25 Hex-IPA, 20 °C, 215 nm, 1.0 mL/min – tr_1 : 3.4 min (major), tr_2 : 4.0 min (minor).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.09 (t, *J* = 6.9 Hz, 3H), 1.23 (t, *J* = 6.9 Hz, 3H), 1.35 (s, 9H), 3.78 (m, 1H), 3.93 (m, 1H), 4.05 (m, 2H), 5.10 (dd, *J* = 8.8, 22.0 Hz, 1H), 5.56 (bs, 1H), 7.45-7.56 (m, 4H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.2 (d, *J* = 5.7 Hz), 16.3 (d, *J* = 4.5 Hz), 28.2, 51.7 (d, *J* = 154.6 Hz), 63.3 (t, *J* = 7.3 Hz), 80.7, 123.1, 124.9, 125.4, 126.4, 128.1, 130.1, 139.8, 154.9.
IR (cm^{-1}) 974, 1029, 1046, 1164, 1234, 1250, 1534, 1706, 2982, 3251.
MS (DART+) m/z: calc. $C_{17}H_{26}F_3NO_5P$ 412.1495; found 412.1501 $[M\text{-}H^+]$.
Melting point 146-148 °C.

tert-butyl ((diethoxyphosphoryl)(1,3 benzodioxole)methyl)carbamate - <u>3la</u>:



Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained has a white solid (52% yield, 83% ee).
HPLC Chiralpak AD-H – 80/20 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 9.7 min (minor), tr_2 : 14.7 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.14 (t, *J* = 7.0 Hz, 3H), 1.29 (t, *J* = 7.0 Hz, 3H), 1.40 (s, 9H), 3.79 (m, 1H), 3.96 (m, 1H), 4.11 (m, 2H), 4.99 (dd, 1H), 5.49 (bs, 1H),5.92 (s, 2H) 6.71-6.93 (m, 3H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 15.2 (d, *J* = 6.1Hz), 15.4 (d, *J* = 5.9 Hz), 27.2, 50.5 (d, *J* = 155.0 Hz), 62.1 (dd, *J* = 7.3, 16.2 Hz), 79.3, 100.1, 107.3, 120.4 (d, *J* = 6.7Hz), 128.3, 146.4, 146.4, 146.8, 153.8 (d, *J* = 10.6 Hz).
IR (cm^{-1}) 977, 1026, 1047, 1173, 1234, 1302, 1449, 1533, 1707, 2977, 3277.
MS (IE) m/z: $C_{17}H_{27}NO_7P$ 388.1520 $[M]^+$, $C_{17}H_{26}NNaO_7PS$ 410.1339 $[M+Na]^+$; found 388.1503 $[M]^+$, 410.1326 $[M\text{-}Na]^+$.
Melting point 132-134 °C.

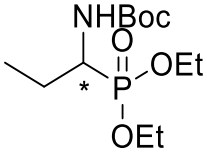
tert-butyl ((diethoxyphosphoryl)(4-methylphenyl)methyl) carbamate – 3ma: [1]



Synthesized according to typical procedure **A**. The reaction mixture was purified by column chromatography (7/3 – pentane/EtOAc). The product was obtained as a white solid (67% yield, 74% ee).
HPLC : Chiralpak AD-H – 80/20 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 8.4 min (minor), tr_2 : 16.5 min (major).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.13 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.4 Hz, 3H), 1.41 (s, 9H), 2.33 (s, 3H), 3.75 (m, 1H), 3.94 (m, 1H), 4.11 (m, 2H), 5.07 (dd, *J* = 9.6, 21.0 Hz, 1H), 5.45 (bs, 1H), 7.14 (d, *J* = 7.7 Hz, 2H) 7.29 (d, *J* = 6.8 Hz, 2H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 16.2 (d, *J* = 5.7 Hz), 16.4 (d, *J* = 5.6 Hz), 21.1, 28.3, 51.5 (d, *J* = 153.8 Hz), 63.0 (d, *J* = 6.9 Hz), 63.2 (d, *J* = 6.9 Hz), 80.3, 127.7, 129.3, 132.4, 137.5, 154.9.
IR (cm^{-1}) 970, 1034, 1166, 1255, 1290, 1539, 1693, 2980, 3247.
MS (IE) m/z**:** 358.17 $[M]^+$, 380.16 $[M\text{-}Na]^+$.
Melting point 87-88 °C.

Procedure for the synthesis of aliphatic α-amino phosphonate **B**:
The α-amino sulfone (90 mg, 0.30 mmol, 1 equiv.), the guanidinium hydrochloride catalyst (65 mg, 0.06 mmol, 20 mol%) and cesium carbonate (117 mg, 0.36 mmol, 1.2 equiv.) were placed in a flame-dried Schlenk-tube. 3 mL of Solvent was added and the phosphonate (46 µL, 0.36 mmol, 1.2 equiv.) was added dropwise. The reaction was stirred at 0°C for 20 h. The reaction mixture was purified by column chromatography to obtain the desired product.

tert-butyl (diethoxyphosphoryl)propylcarbamate – 3na:



Synthesized according to typical procedure **B**. The reaction mixture was purified by column chromatography (1/9 – pentane/EtOAc). The product was obtained has a clear oil (19% yield, 37% ee).
The product was derivatized to determine the ee by HPLC. The Boc was deprotected and replaced by Cbz following already reported procedure.[7]
HPLC (Cbz derivatized product): Chiralpak AD-H – 80/20 Hex-IPA, 20 °C, 215 nm, 0.8 mL/min – tr_1 : 7.4 min (major), tr_2 : 9.2 min (minor).
^{1}H NMR (360 MHz, $CDCl_3$) δ = 1.00 (t, 3H, *J* = 7.5 Hz), 1.30 (t, 3H, *J* = 7.5 Hz), 1.42 (s, 9H), 1.53 (m, 1H), 1.88 (m, 1H), 3.92 (m, 1H), 4.06 (m, 4H), 4.62 (m, 1H).
^{13}C NMR (91 MHz, $CDCl_3$) δ = 10.4, 16.3, 23.3, 28.2, 48.3 (d, *J* = 156.0 Hz), 62.2, 62.4, 79.8, 155.4.
IR (cm^{-1}) 965, 1020, 1097, 1164, 1234, 1284, 1365, 1391, 1457, 1527, 1709, 2933, 2978, 3256.
MS (DART+) m/z: Calculated for $C_{12}H_{27}N_1O_5P_1$ – 296.1621 $[M+H^+]$. found – 296.1618 $[M+H^+]$.

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[2] P.Kaur, W.Wever, T.Rajale, G.Li Chem Biol Drug Des 2010; 76: 314–319

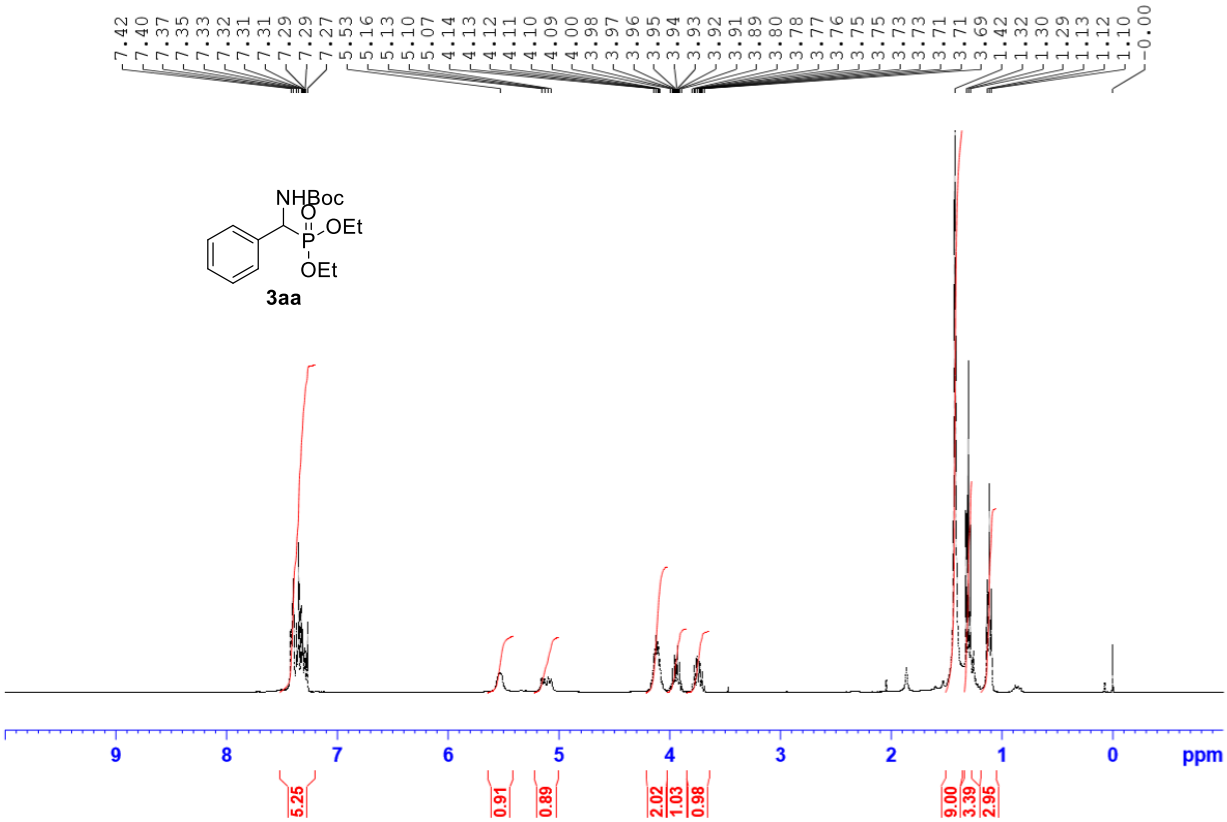
[3] Z. Yan, B. Wu, X. Gao, MW. Chen, and YG. Zhou Org. Lett. 2016, 18, 4, 692–695

[4] B.List, Angew. Chem. Int. Ed. 2015, 45, 355-358.

[5] M. Hoffmann, Journal fur Praktische Chemie, 1988, 5, 820-824

[6] Synthesis 2005, No. 4, 634–638

[7] Chem. Commun., 2008, 4345-4347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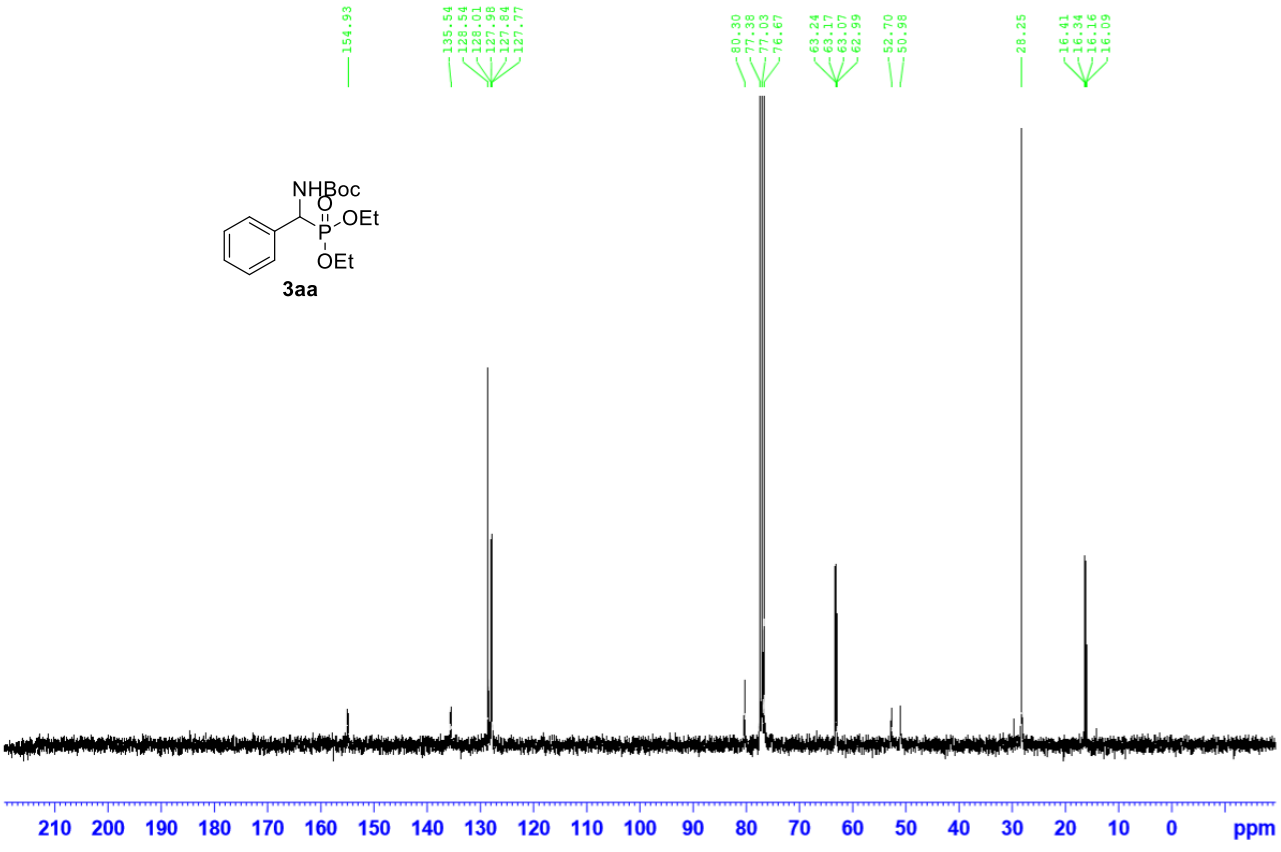
NHBoc
O
P
OEt
OEt
3aa
9 8 7 6 5 4 3 2 1 0 ppm
5.25 0.91 0.89 2.02 1.03 0.98 9.00 3.39 2.95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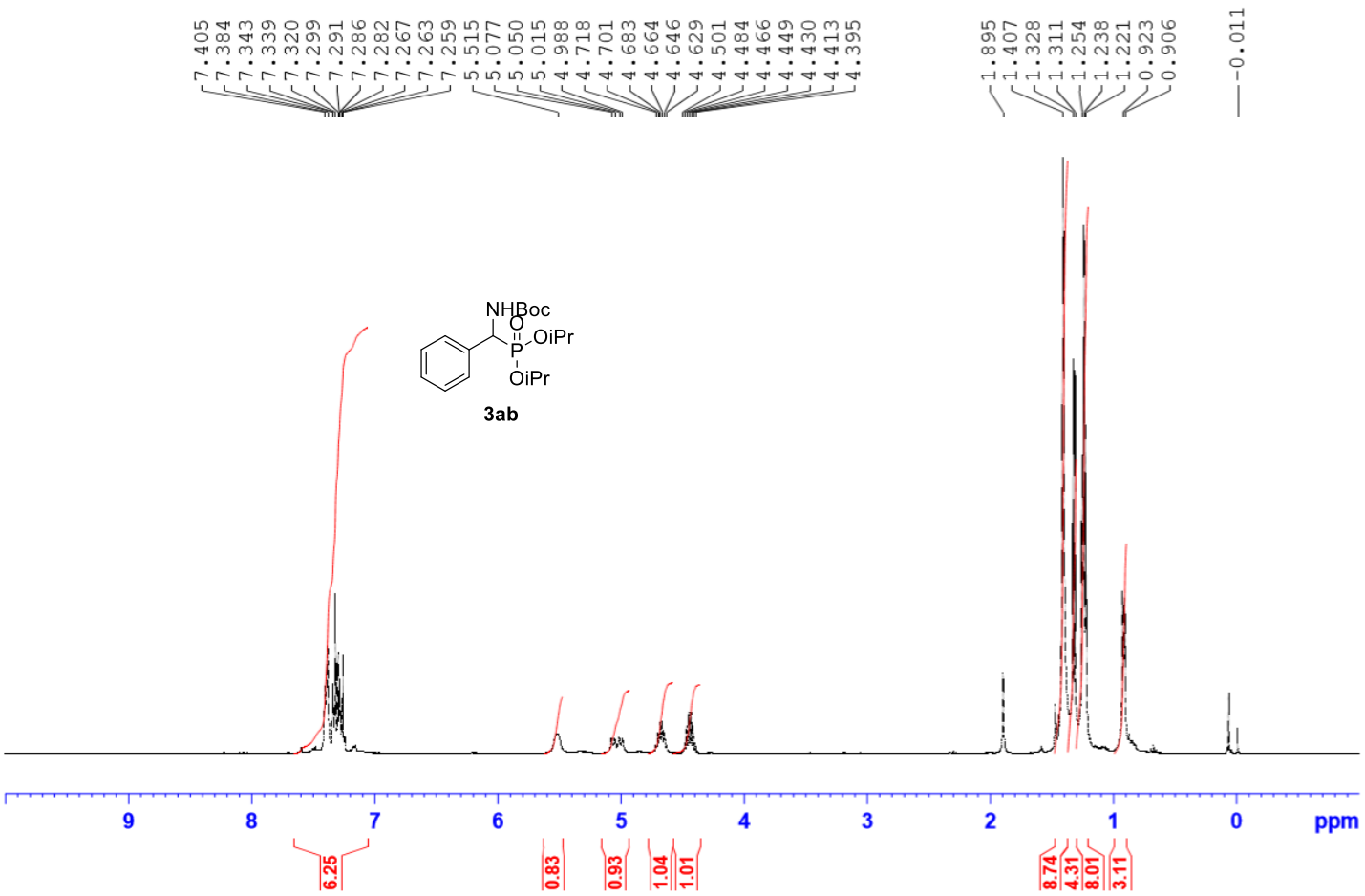
NHBoc
O
P
OEt
OEt
3aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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5.077
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5.015
4.988
4.718
4.701
4.683
4.664
4.646
4.629
4.501
4.484
4.466
4.449
4.430
4.413
4.395
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1.407
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1.311
1.254
1.238
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0.906
-0.011
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O
P
OiPr
OiPr
3ab
9
8
7
6
5
4
3
2
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1.01
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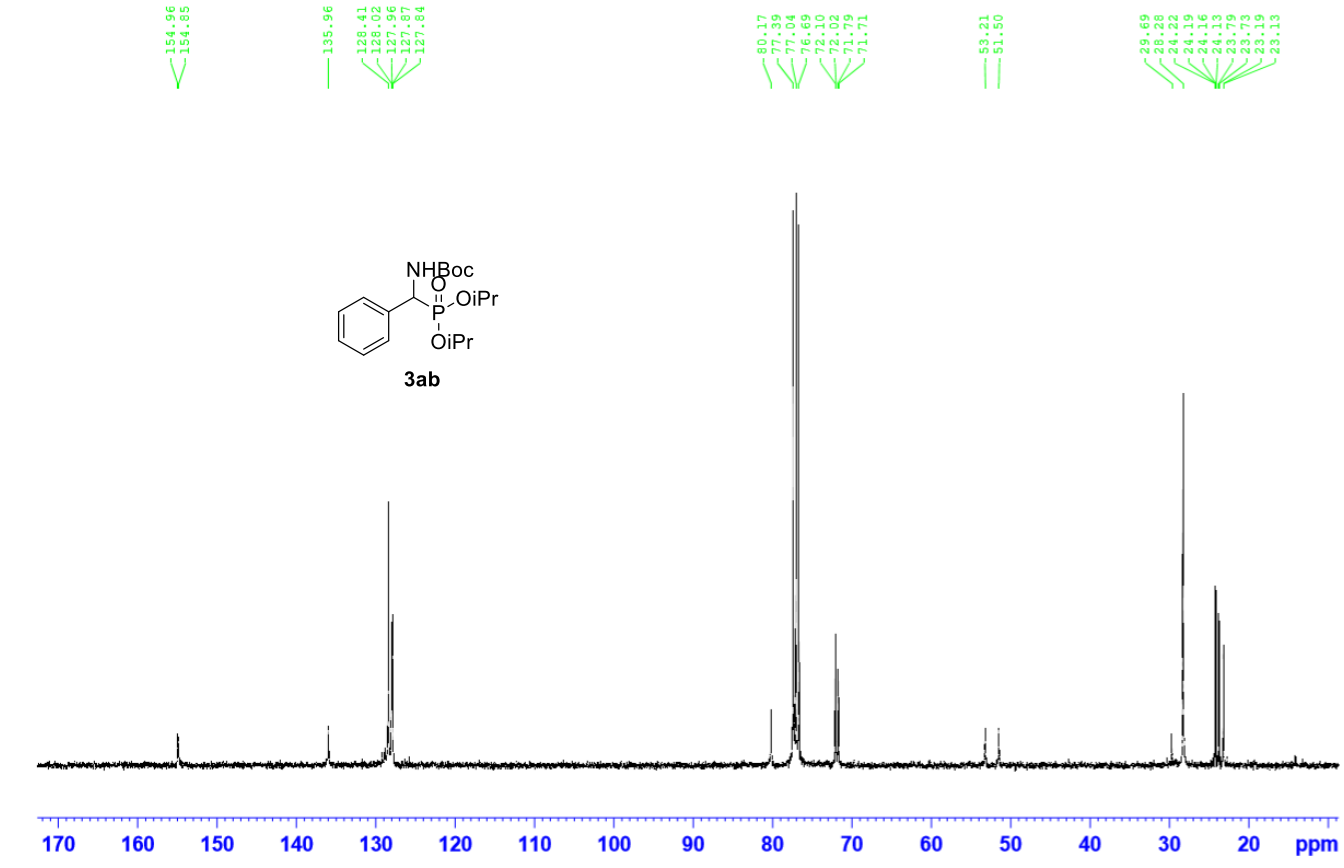
8.01
3.11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128.02
127.96
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80.17
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76.69
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71.71
53.21
51.50
29.69
28.28
24.22
24.19
24.16
24.13
23.79
23.73
23.19
23.13
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O
P
OiPr
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150
140
130
120
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100
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80
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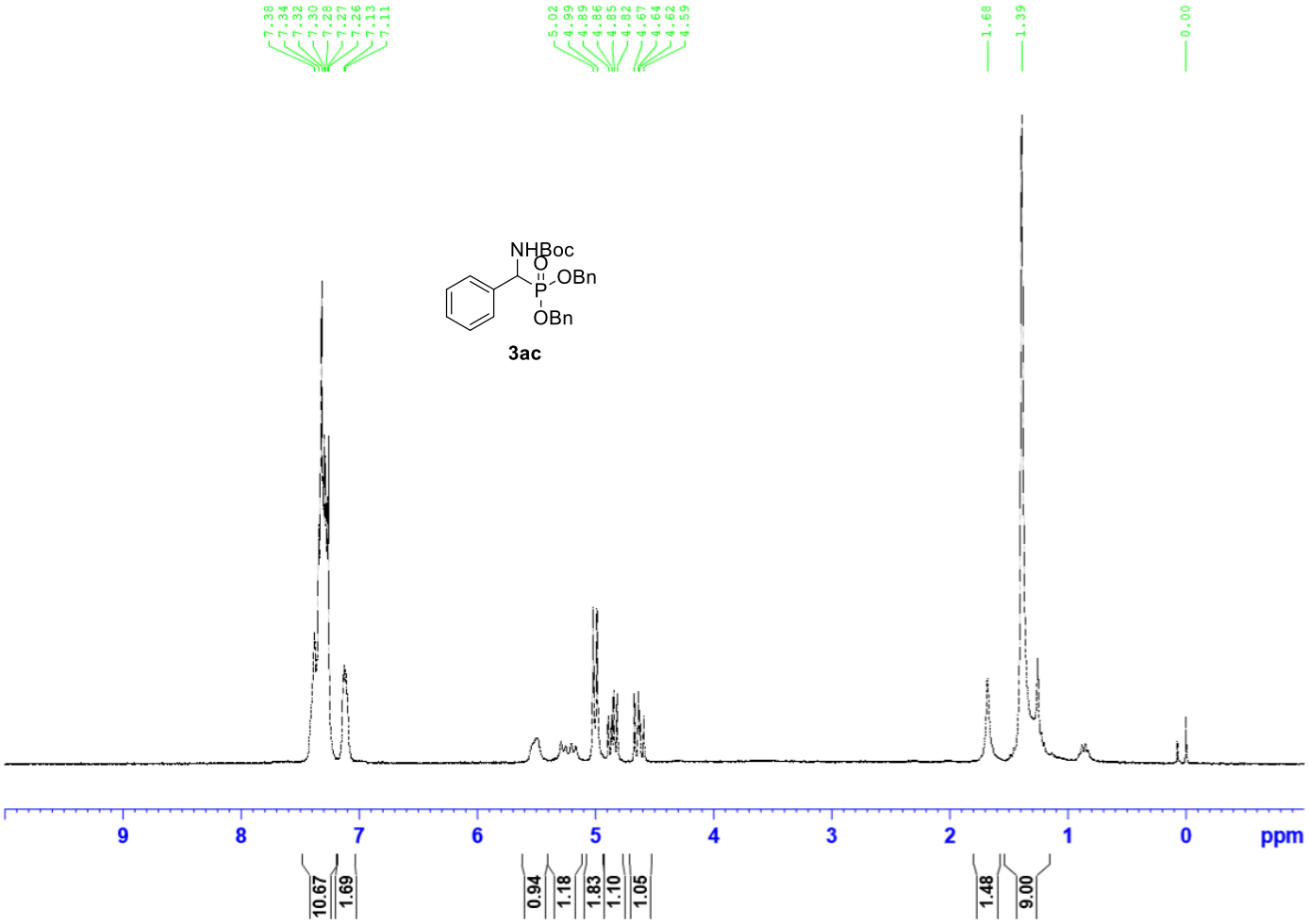
20
ppm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4.85
4.82
4.67
4.64
4.62
4.59
1.68
1.39
0.00
NHBoc
O
P
OBn
OBn
3ac
9
8
7
6
5
4
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ppm
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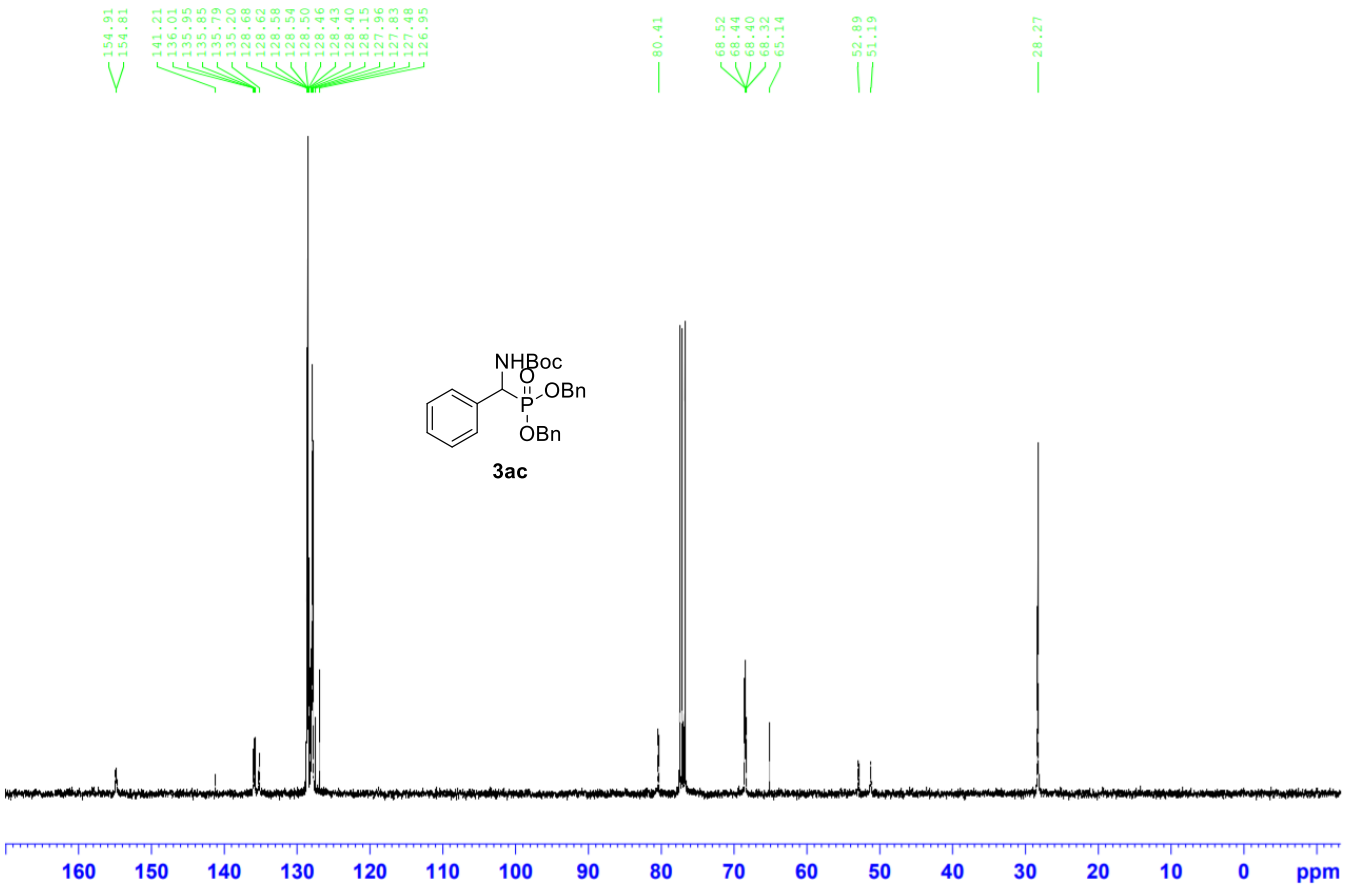
1.05
1.48
9.00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128.40
128.15
127.96
127.83
127.48
126.95
80.41
68.52
68.44
68.40
68.32
65.14
52.89
51.19
28.27
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O
P
OBn
OBn
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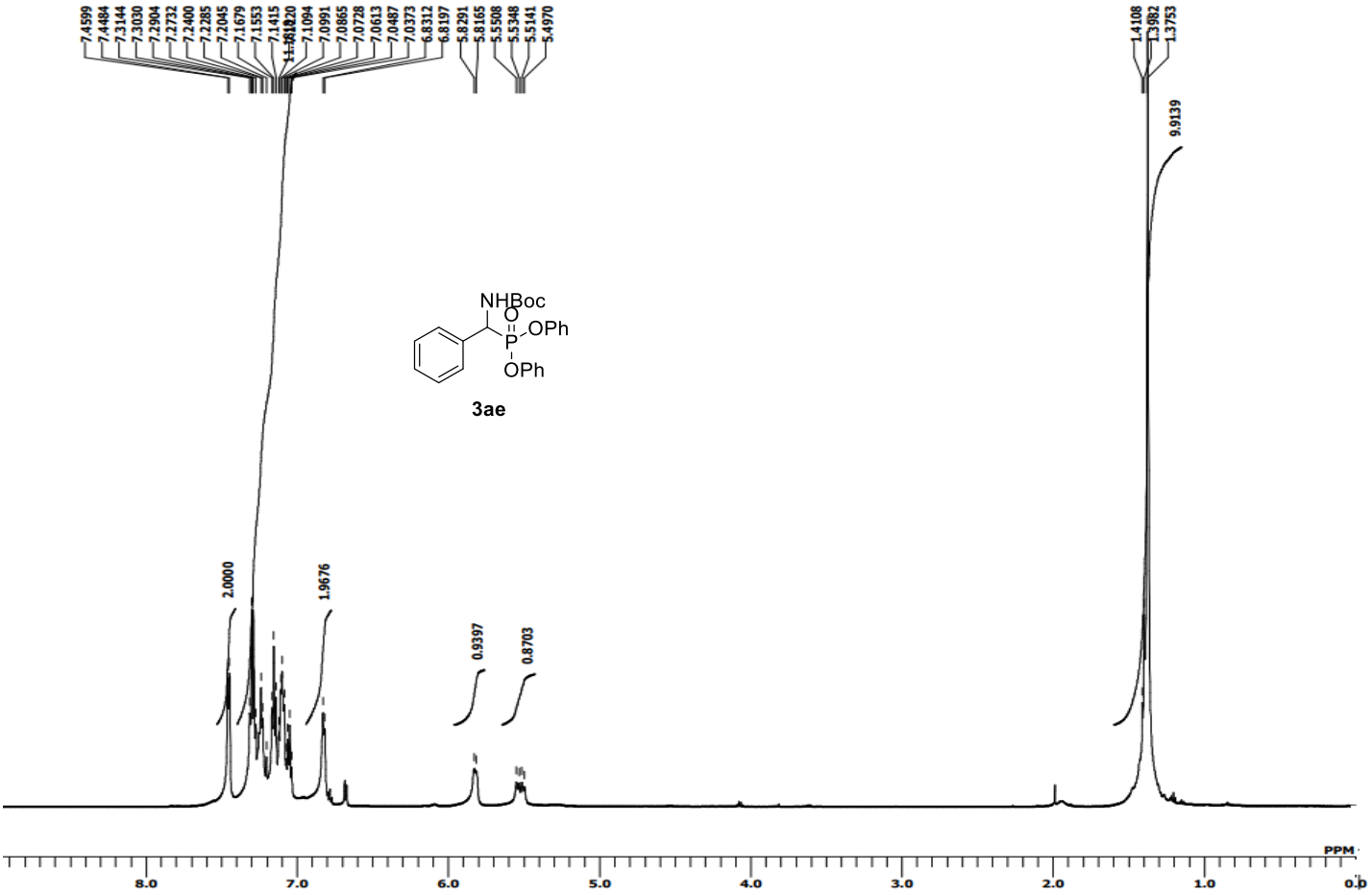
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7.0865
7.0728
7.0613
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0.8703
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5.0
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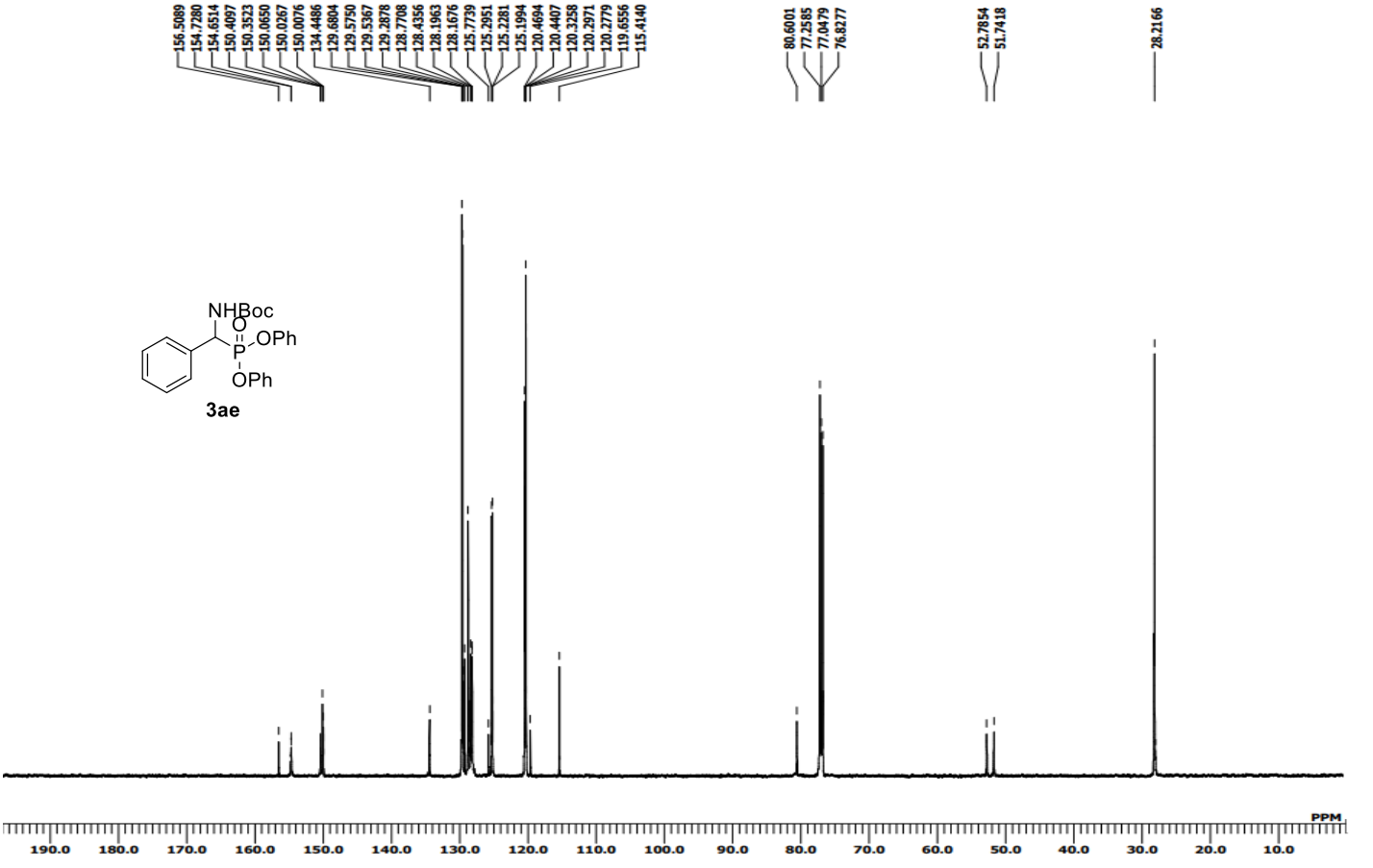
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PPM
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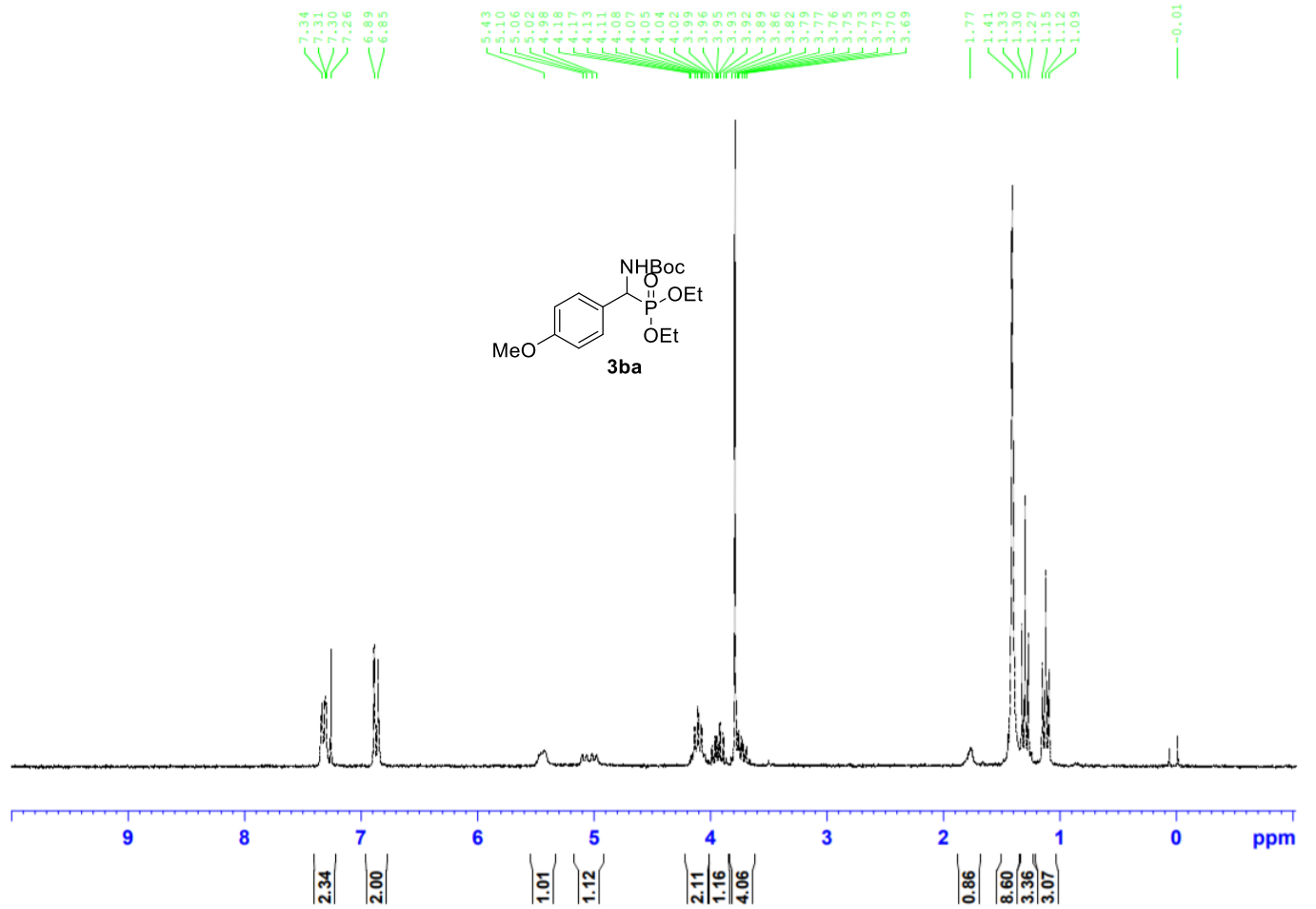
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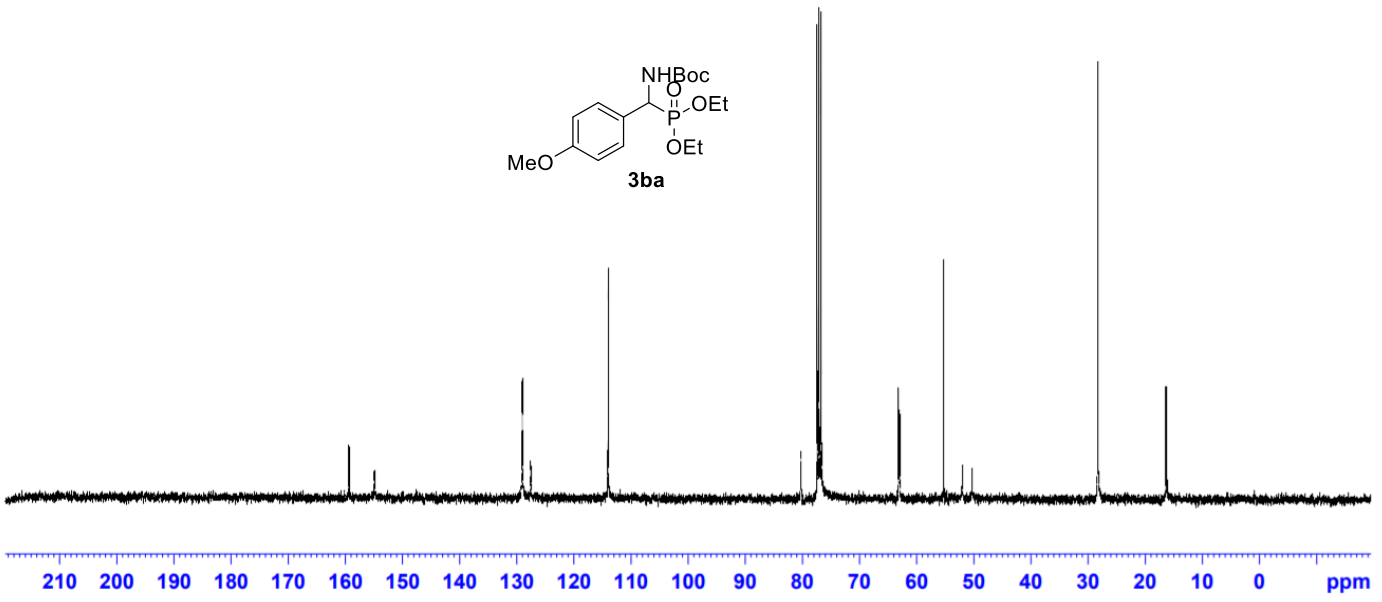
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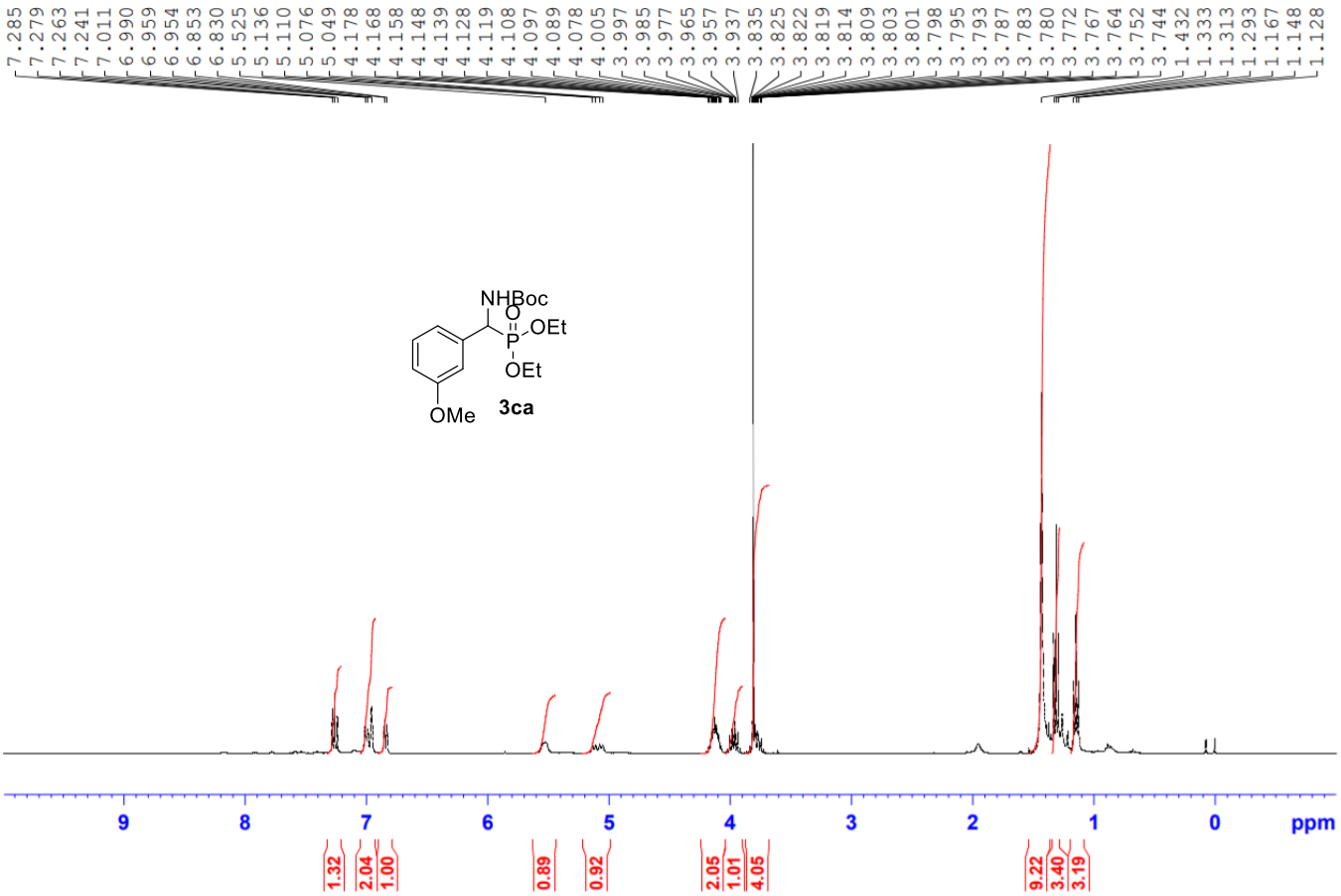
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4.089
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OMe
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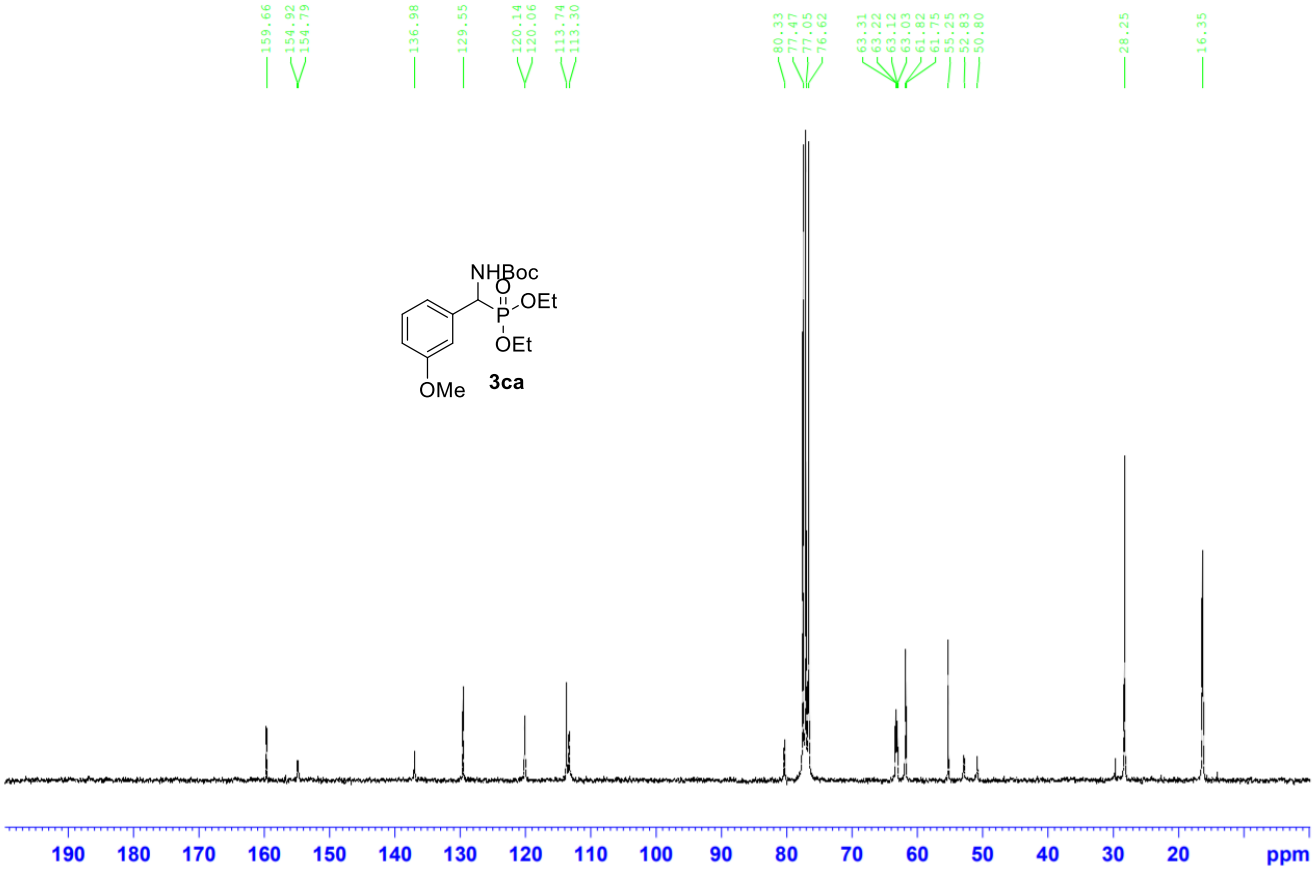
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63.12
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61.82
61.75
55.25
52.83
50.80
28.25
16.35
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OEt
OEt
OMe
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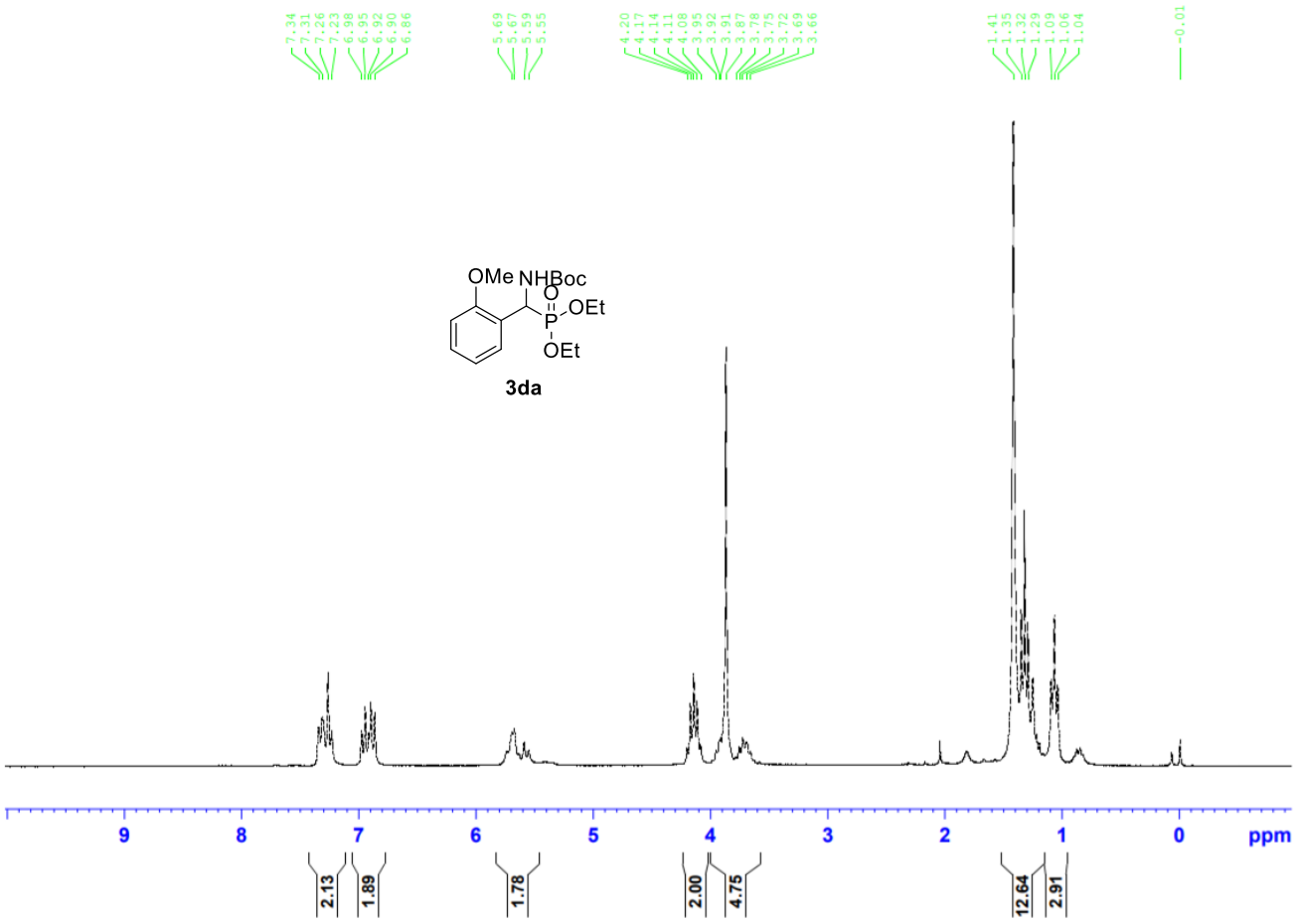
ppm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4.17
4.14
4.11
4.08
3.95
3.92
3.91
3.87
3.78
3.75
3.72
3.69
3.66
1.41
1.35
1.32
1.29
1.09
1.06
1.04
-0.01
OMe
NHBoc
O
P
OEt
OEt
3da
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8
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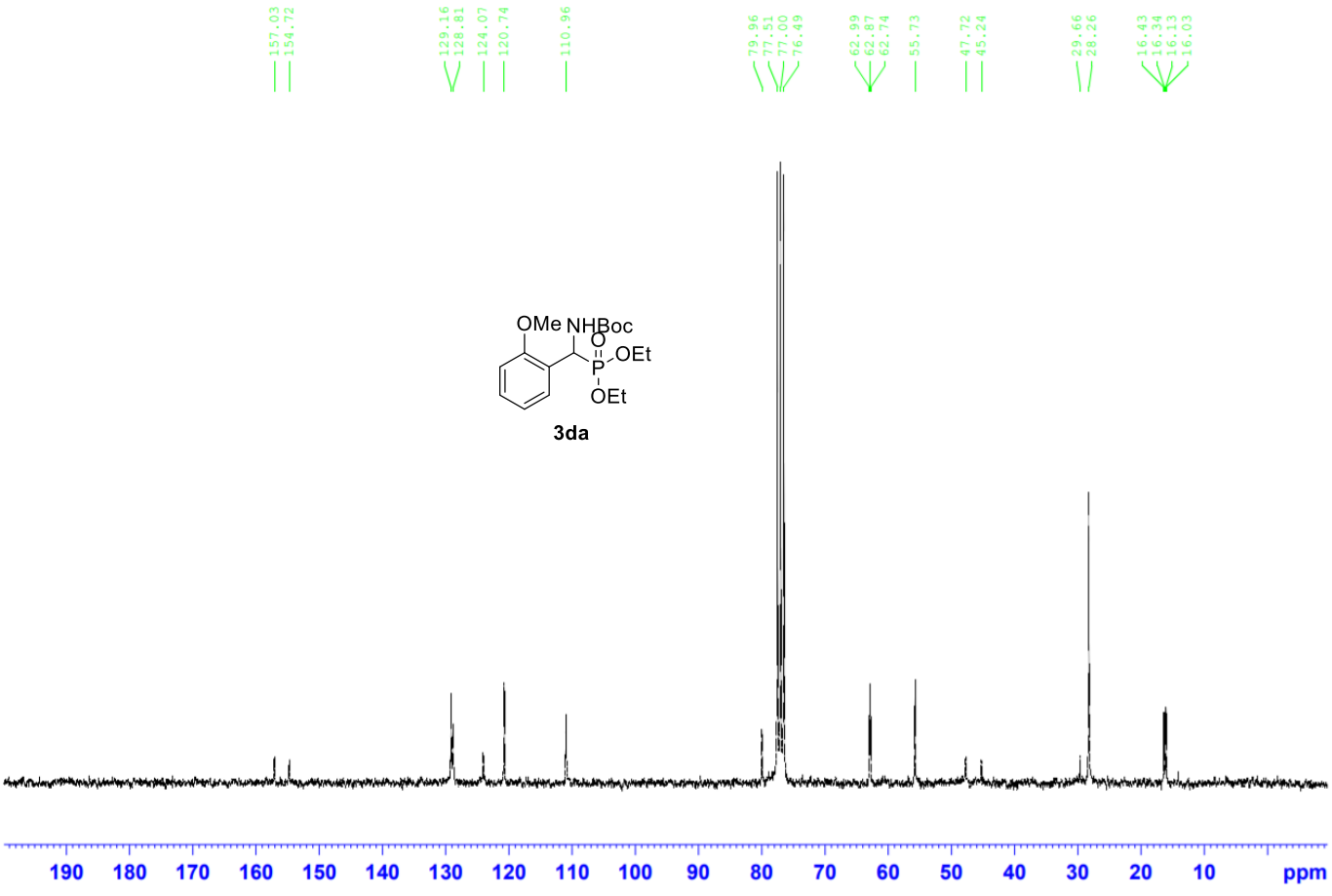
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62.74
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47.72
45.24
29.66
28.26
16.43
16.34
16.13
16.03
OMe
NHBoc
O
P
OEt
OEt
3da
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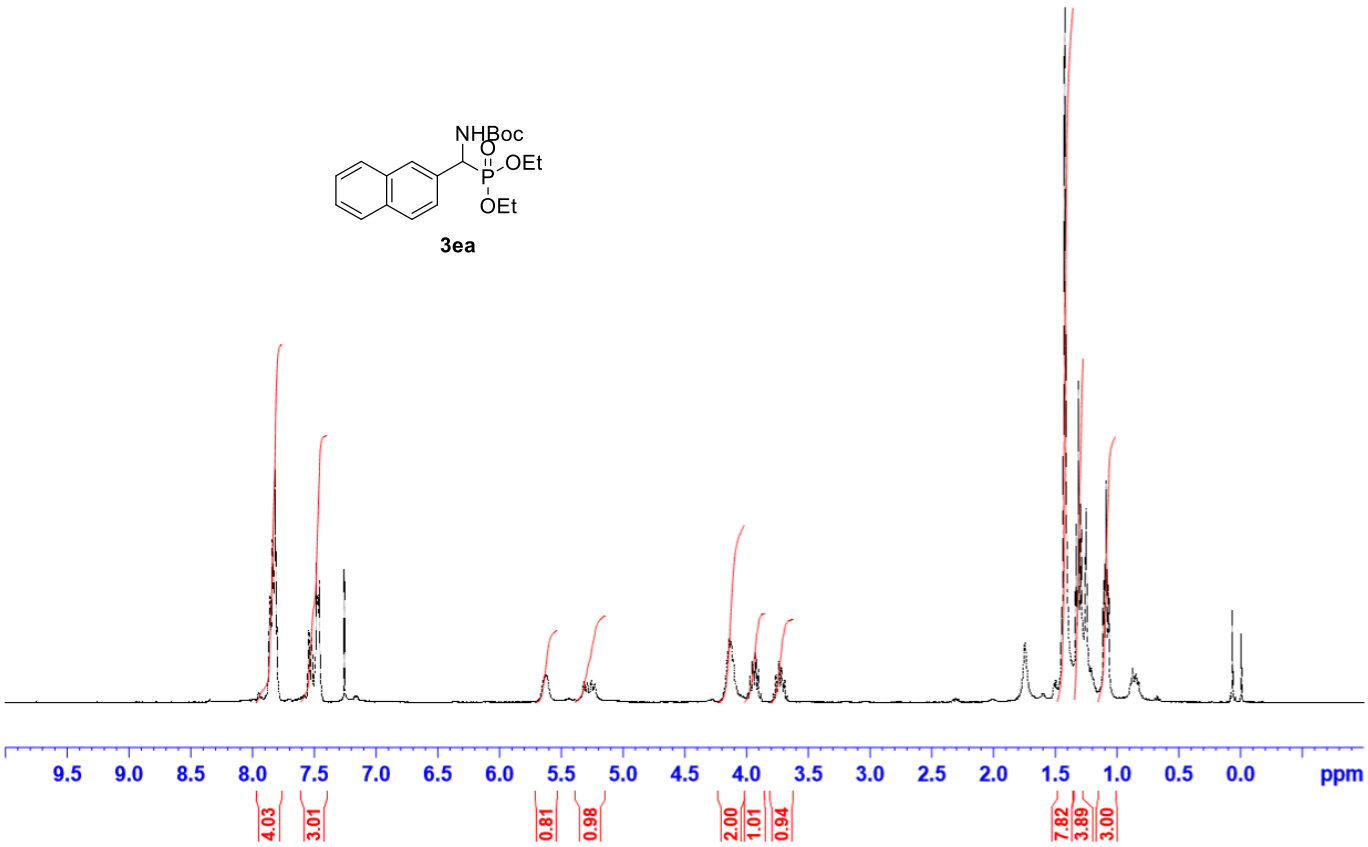
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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O
OEt
P
OEt
3ea
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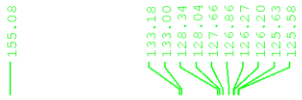
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133.18
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126.27
126.20
125.63
125.58


80.44
77.38
77.03
76.67
63.34
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63.11
52.86
51.16
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28.27
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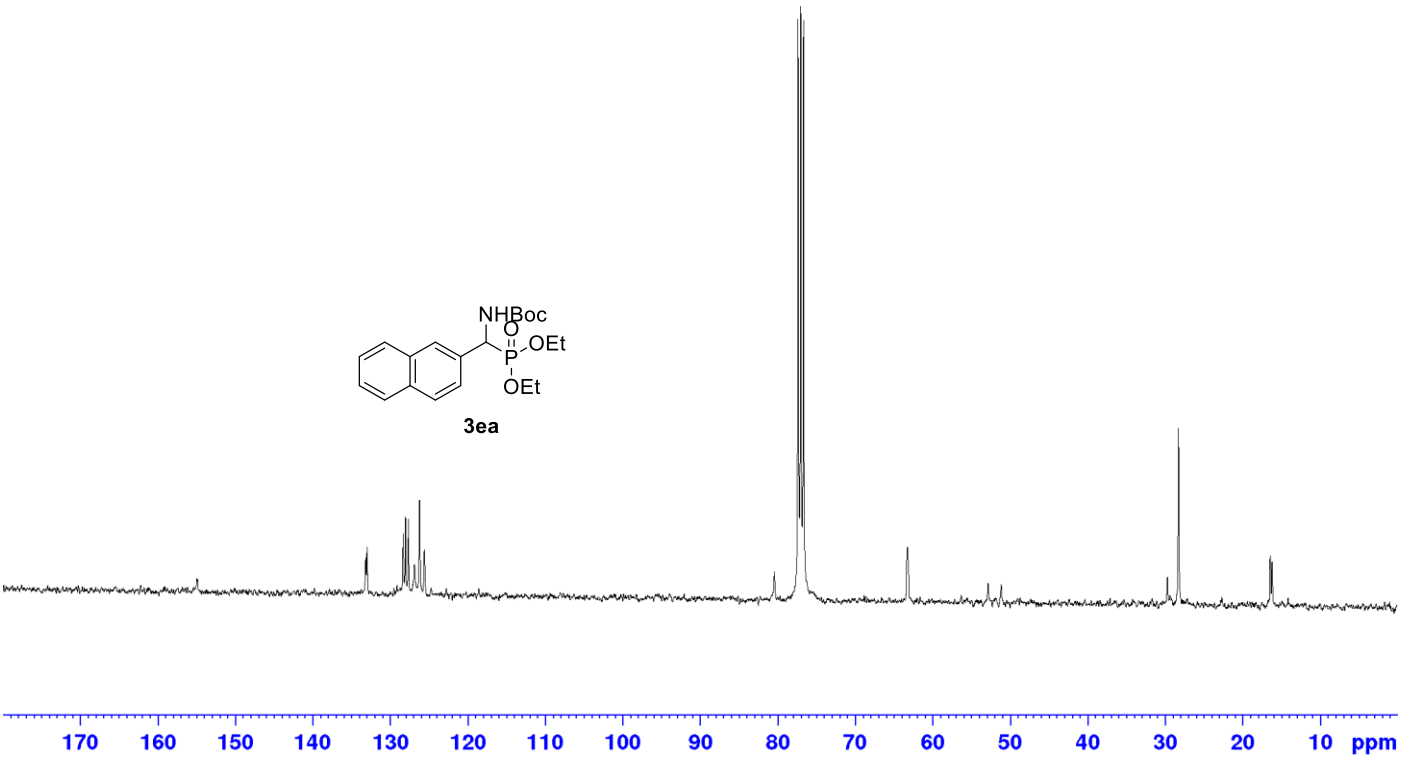
16.40
16.22
16.16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O
OEt
P
OEt
3ea
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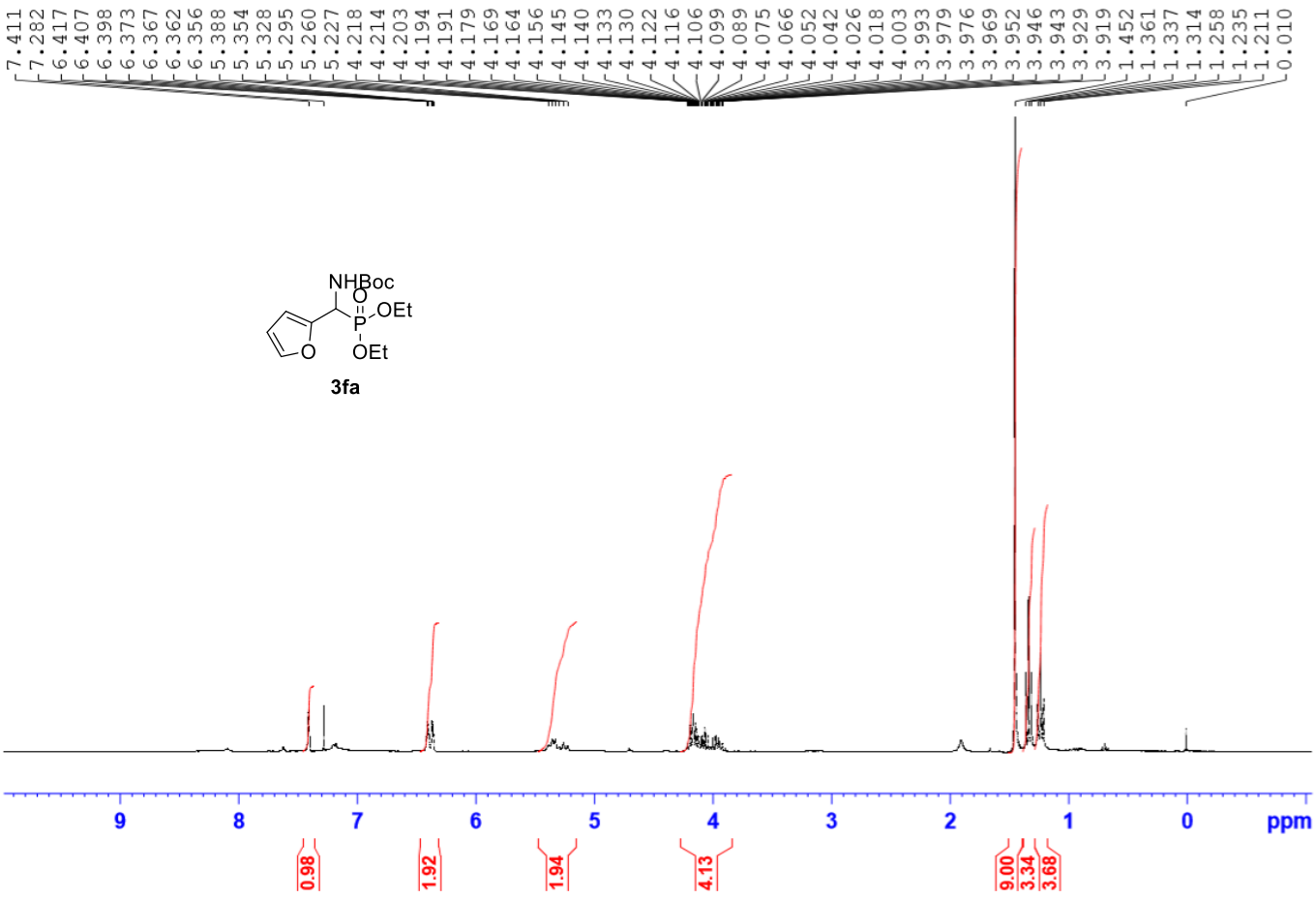
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5.260
5.227
4.218
4.214
4.203
4.194
4.191
4.179
4.169
4.164
4.156
4.145
4.140
4.133
4.130
4.122
4.116
4.106
4.099
4.089
4.075
4.066
4.052
4.042
4.026
4.018
4.003
3.993
3.979
3.976
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3.952
3.946
3.943
3.929
3.919
1.452
1.361
1.337
1.314
1.258
1.235
1.211
0.010
NHBoc
OEt
OEt
3fa
9
8
7
6
5
4
3
2
1
0
ppm
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1.94
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9.00
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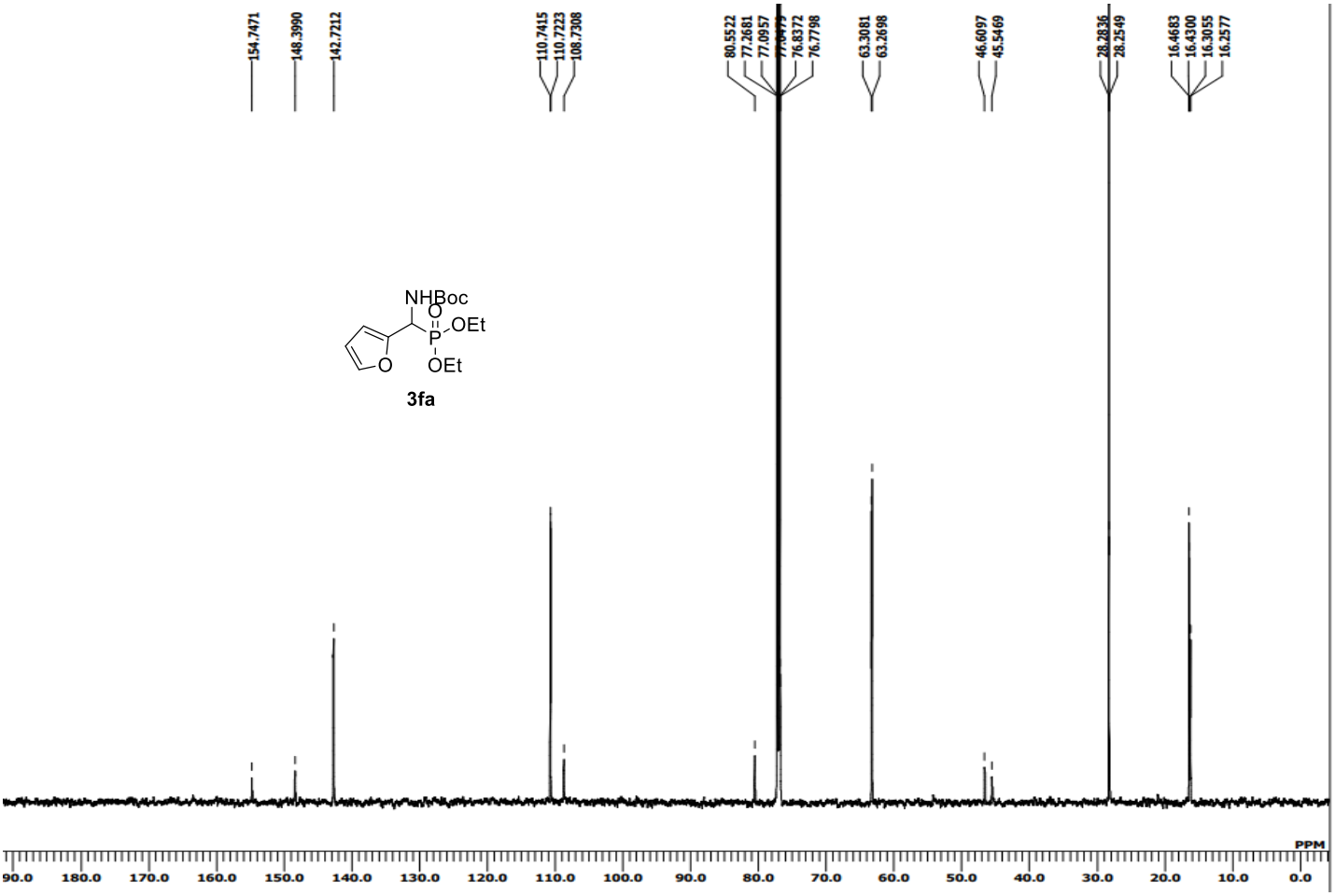
3.68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80.5522
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63.3081
63.2698
46.6097
45.5469
28.2836
28.2549
16.4683
16.4300
16.3055
16.2577
NHBoc
OEt
OEt
3fa
PPM
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180.0
170.0
160.0
150.0
140.0
130.0
120.0
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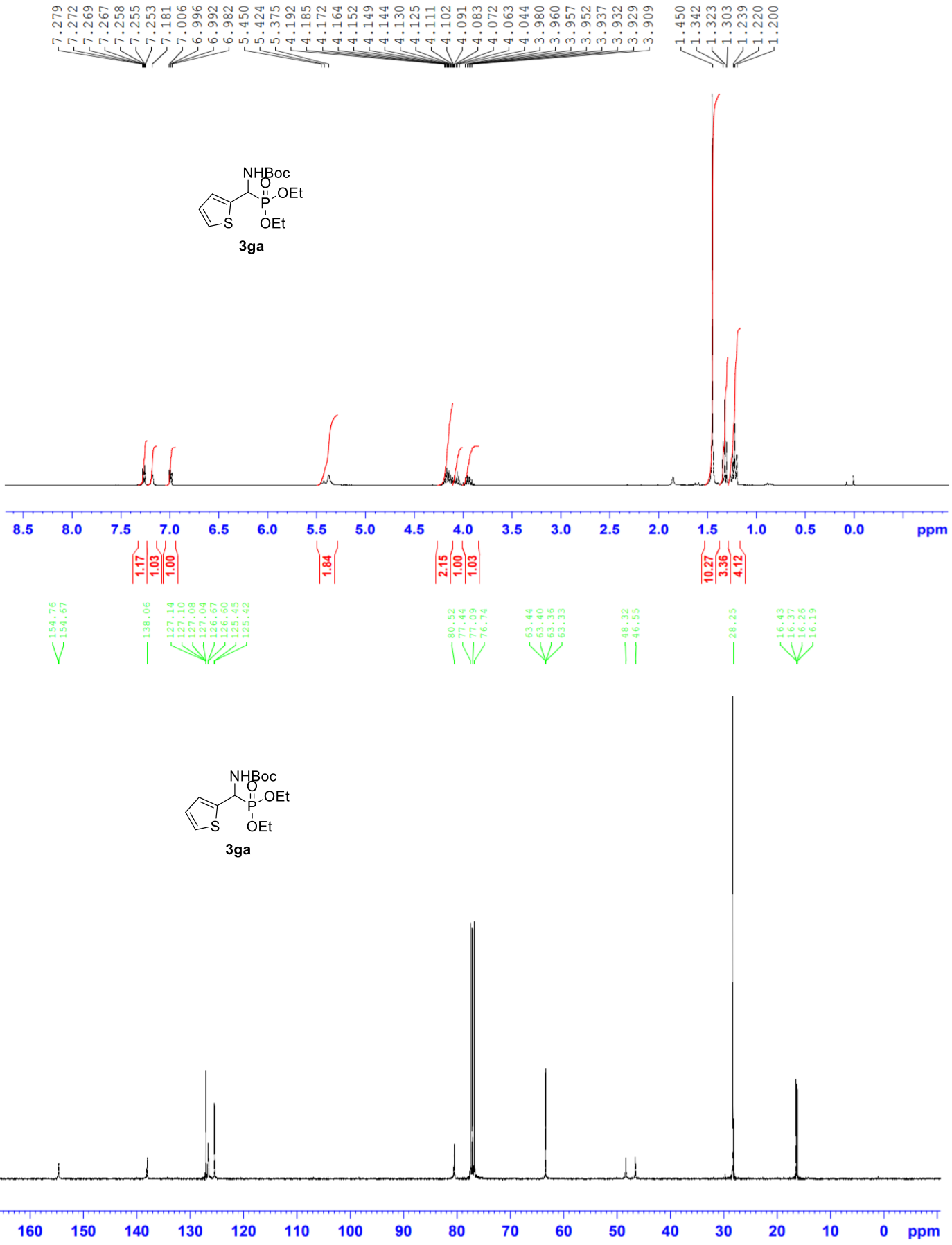
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5.424
5.375
4.192
4.185
4.172
4.164
4.152
4.149
4.144
4.130
4.125
4.111
4.102
4.091
4.083
4.072
4.063
4.044
3.980
3.960
3.957
3.952
3.937
3.932
3.929
3.909
1.450
1.342
1.323
1.303
1.239
1.220
1.200
NHBoc
O
OEt
P
S
OEt
3ga
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.17
1.03
1.00
1.84
2.15
1.00
1.03
10.27
3.36
4.12
154.76
154.67
138.06
127.14
127.10
127.08
127.04
126.67
126.60
125.45
125.42
80.52
77.44
77.09
76.74
63.44
63.40
63.36
63.33
48.32
46.55
28.25
16.43
16.37
16.26
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NHBoc
O
OEt
P
S
OEt
3ga
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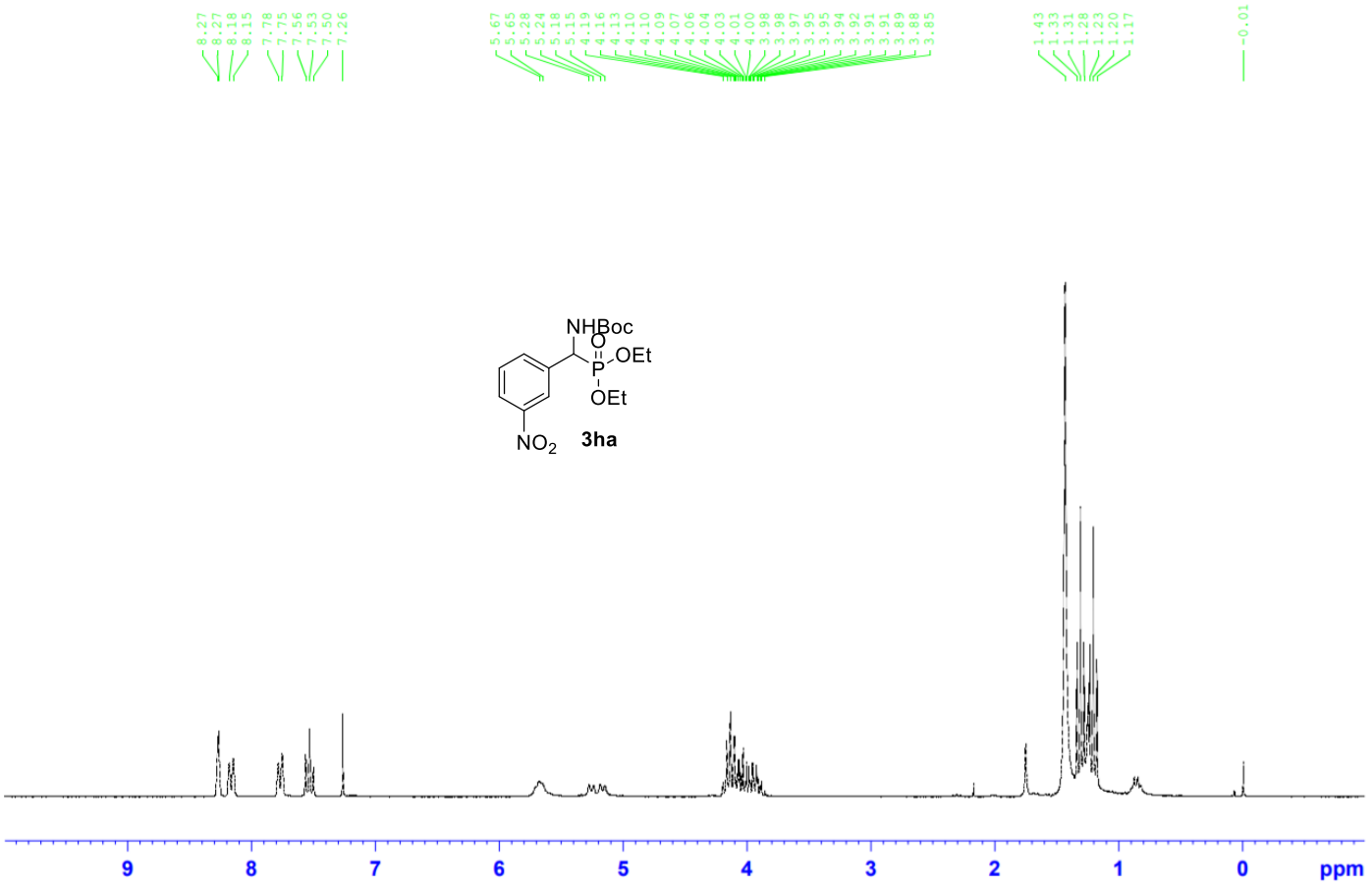
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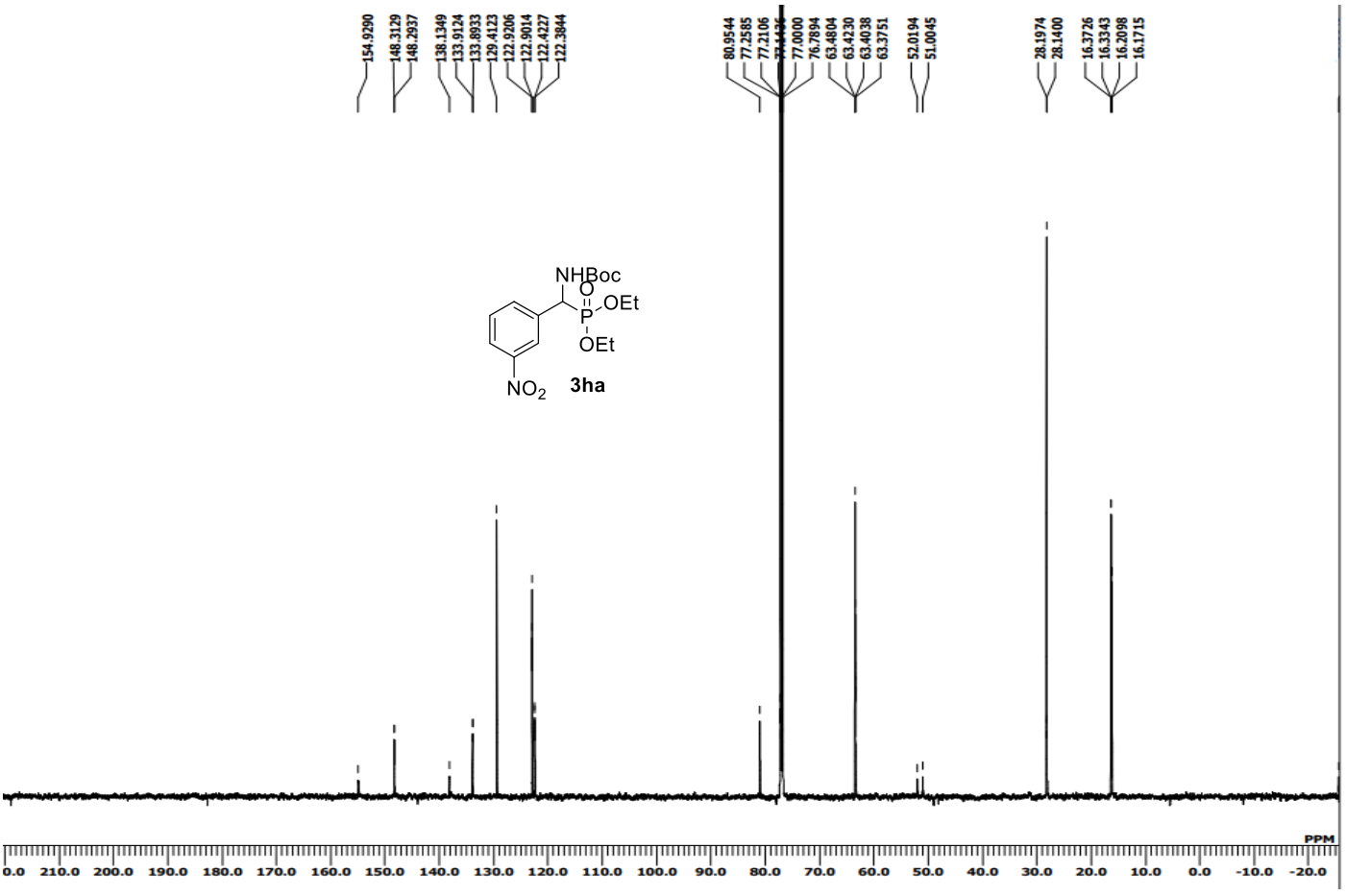
O
OEt
P
OEt
NO2
3ha
9
8
7
6
5
4
3
2
1
0
ppm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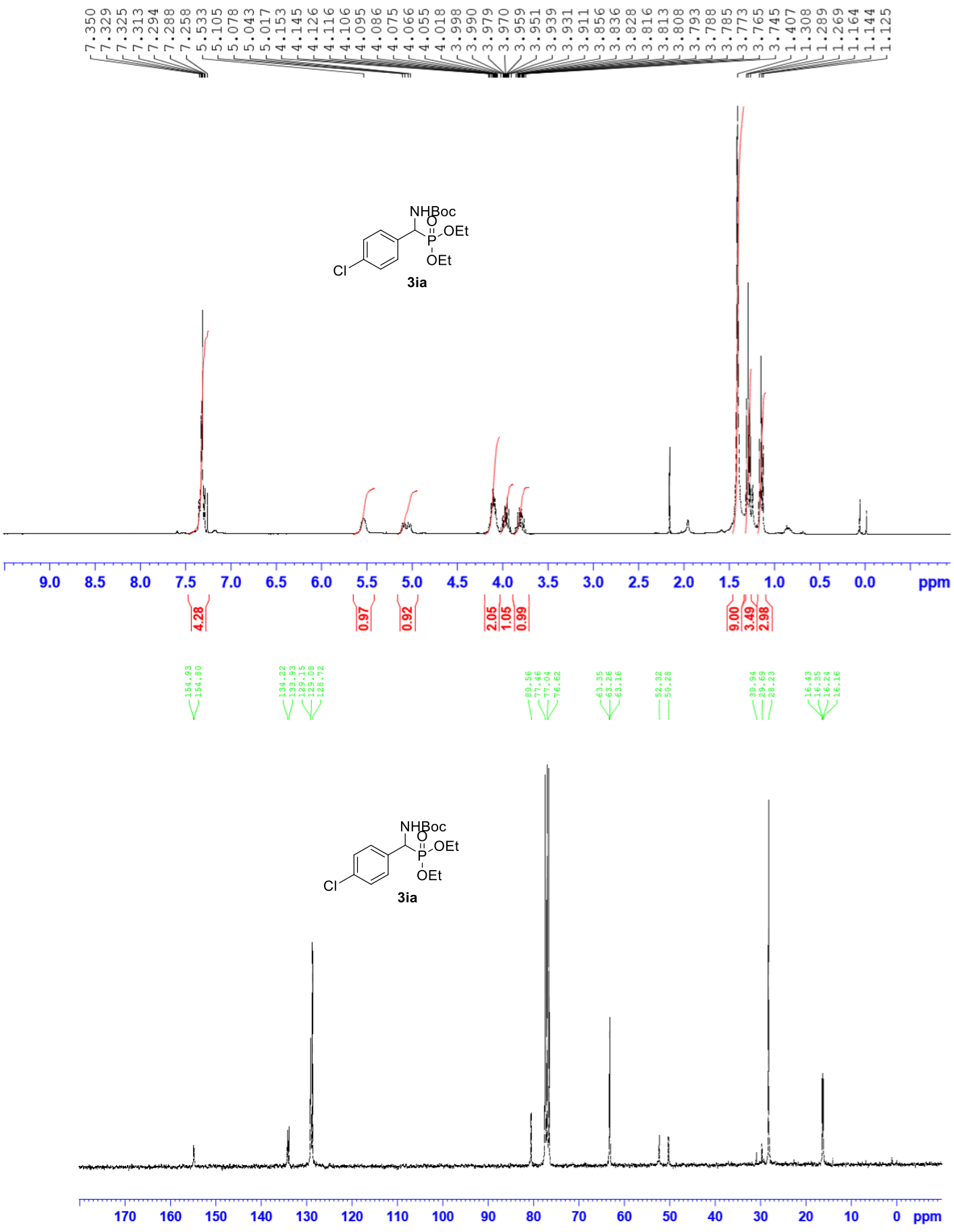
O
OEt
P
OEt
NO2
3ha
PPM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4.145
4.126
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4.106
4.095
4.086
4.075
4.066
4.055
4.018
3.998
3.990
3.979
3.970
3.959
3.951
3.939
3.931
3.911
3.856
3.836
3.828
3.816
3.813
3.808
3.793
3.788
3.785
3.773
3.765
3.745
1.407
1.308
1.289
1.269
1.164
1.144
1.125
NHBoc
O
OEt
P
OEt
Cl
3ia
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
ppm
4.28
0.97
0.92
2.05
1.05
0.99
9.00
3.49
2.98
154.93
154.80
134.22
133.93
129.15
129.08
128.72
80.56
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77.04
76.62
63.35
63.26
63.16
52.32
50.28
30.94
29.69
28.23
16.43
16.35
16.24
16.16
NHBoc
O
OEt
P
OEt
Cl
3ia
170
160
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140
130
120
110
100
90
80
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60
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20
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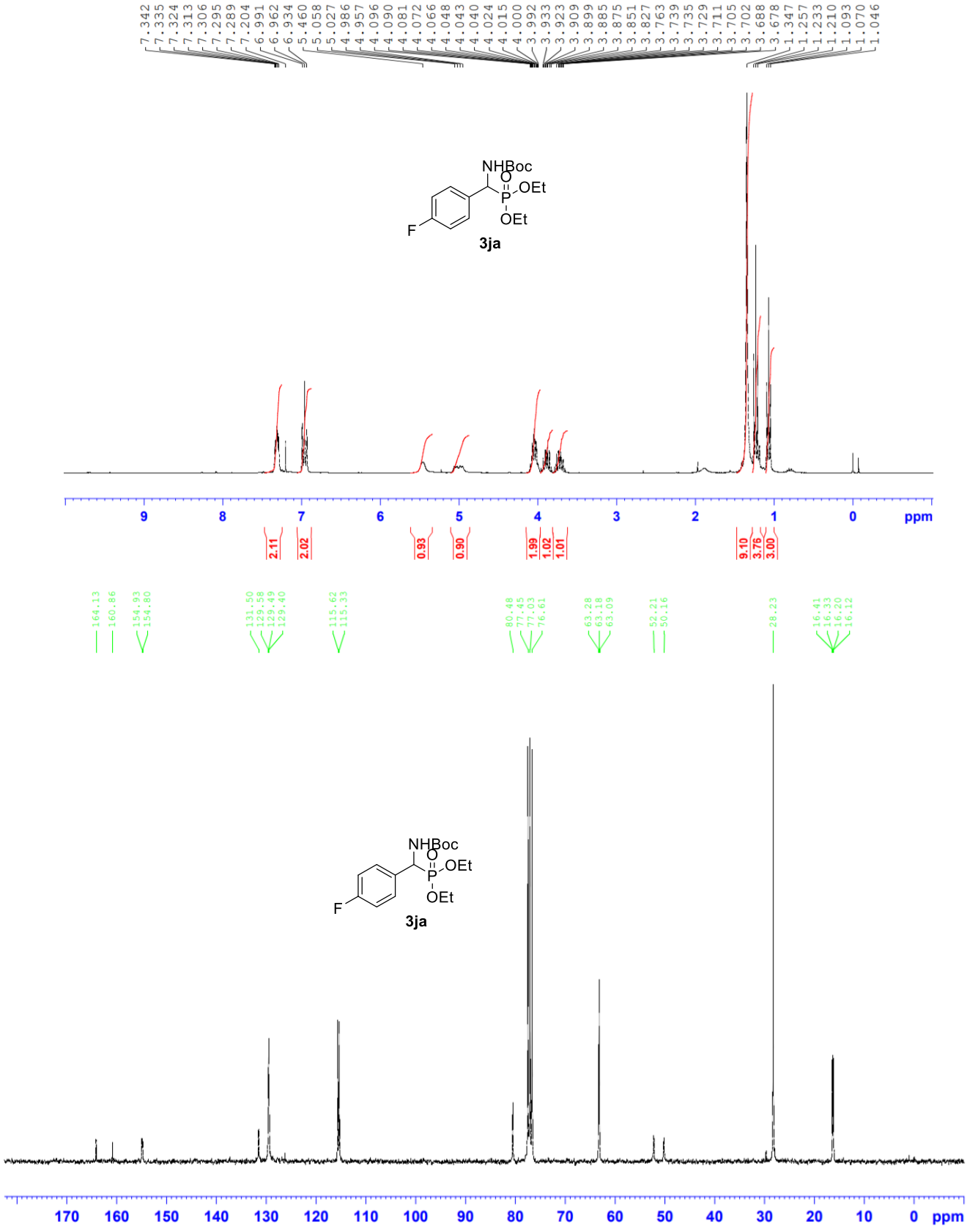
ppm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5.058
5.027
4.986
4.957
4.096
4.090
4.081
4.072
4.066
4.048
4.043
4.040
4.024
4.015
4.000
3.992
3.933
3.923
3.909
3.899
3.885
3.875
3.851
3.827
3.763
3.739
3.735
3.729
3.711
3.705
3.702
3.688
3.678
1.347
1.257
1.233
1.210
1.093
1.070
1.046
NHBoc
O
OEt
P
OEt
F
3ja
9
8
7
6
5
4
3
2
1
0
ppm
2.11
2.02
0.93
0.90
1.99
1.02
1.01
9.10
3.76
3.00
164.13
160.86
154.93
154.80
131.50
129.58
129.49
129.40
115.62
115.33
80.48
77.45
77.03
76.61
63.28
63.18
63.09
52.21
50.16
28.23
16.41
16.33
16.20
16.12
NHBoc
O
OEt
P
OEt
F
3ja
170
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150
140
130
120
110
100
90
80
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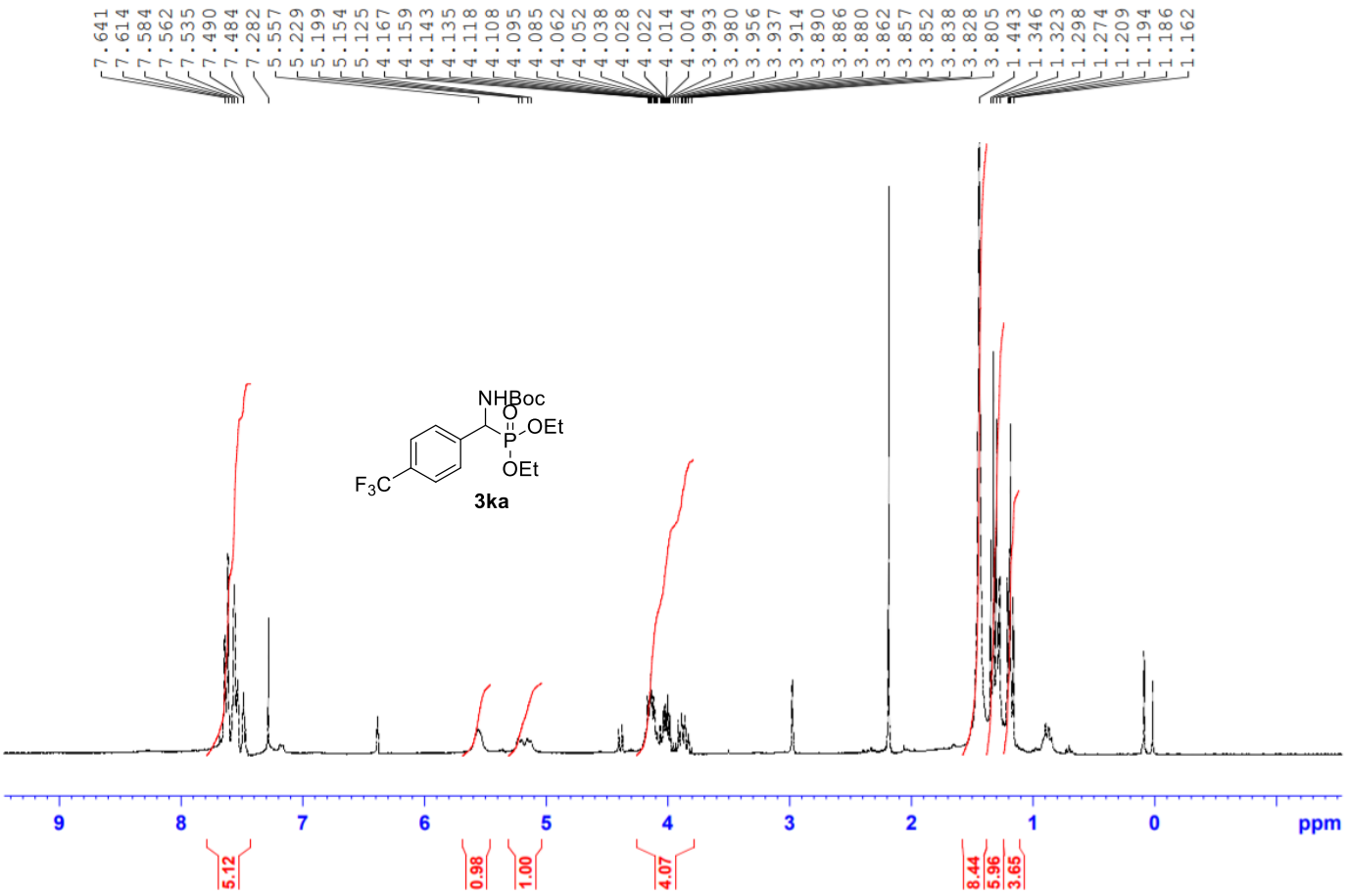
60
50
40
30
20
10
0
ppm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5.125
4.167
4.159
4.143
4.135
4.118
4.108
4.095
4.085
4.062
4.052
4.038
4.028
4.022
4.014
4.004
3.993
3.980
3.956
3.937
3.914
3.890
3.886
3.880
3.862
3.857
3.852
3.838
3.828
3.805
1.443
1.346
1.323
1.298
1.274
1.209
1.194
1.186
1.162
NHBoc
OEt
OEt
F3C
3ka
9
8
7
6
5
4
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1
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ppm
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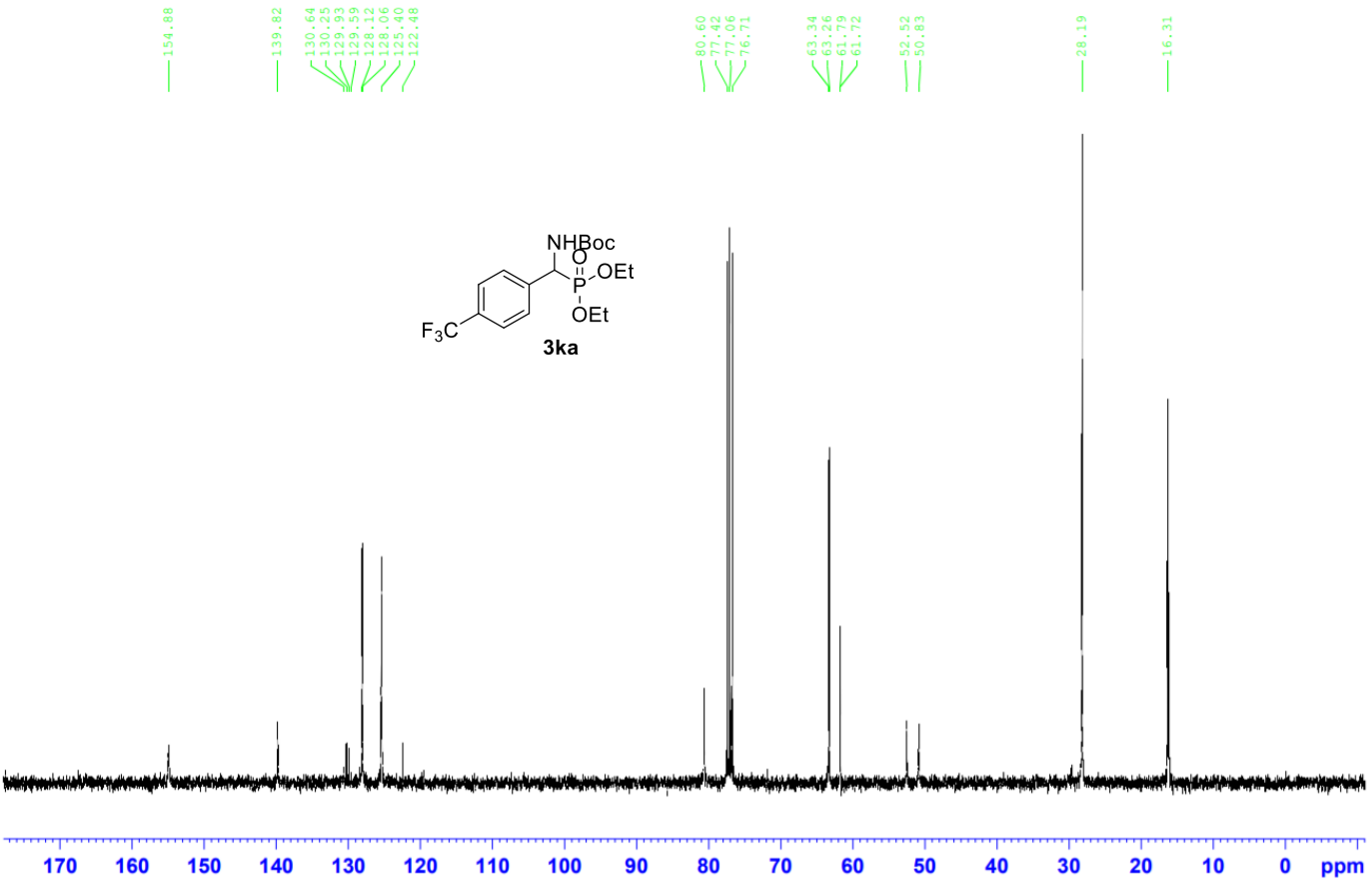
3.65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80.60
77.42
77.06
76.71
63.34
63.26
61.79
61.72
52.52
50.83
28.19
16.31
NHBoc
OEt
OEt
F3C
3ka
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160
150
140
130
120
110
100
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80
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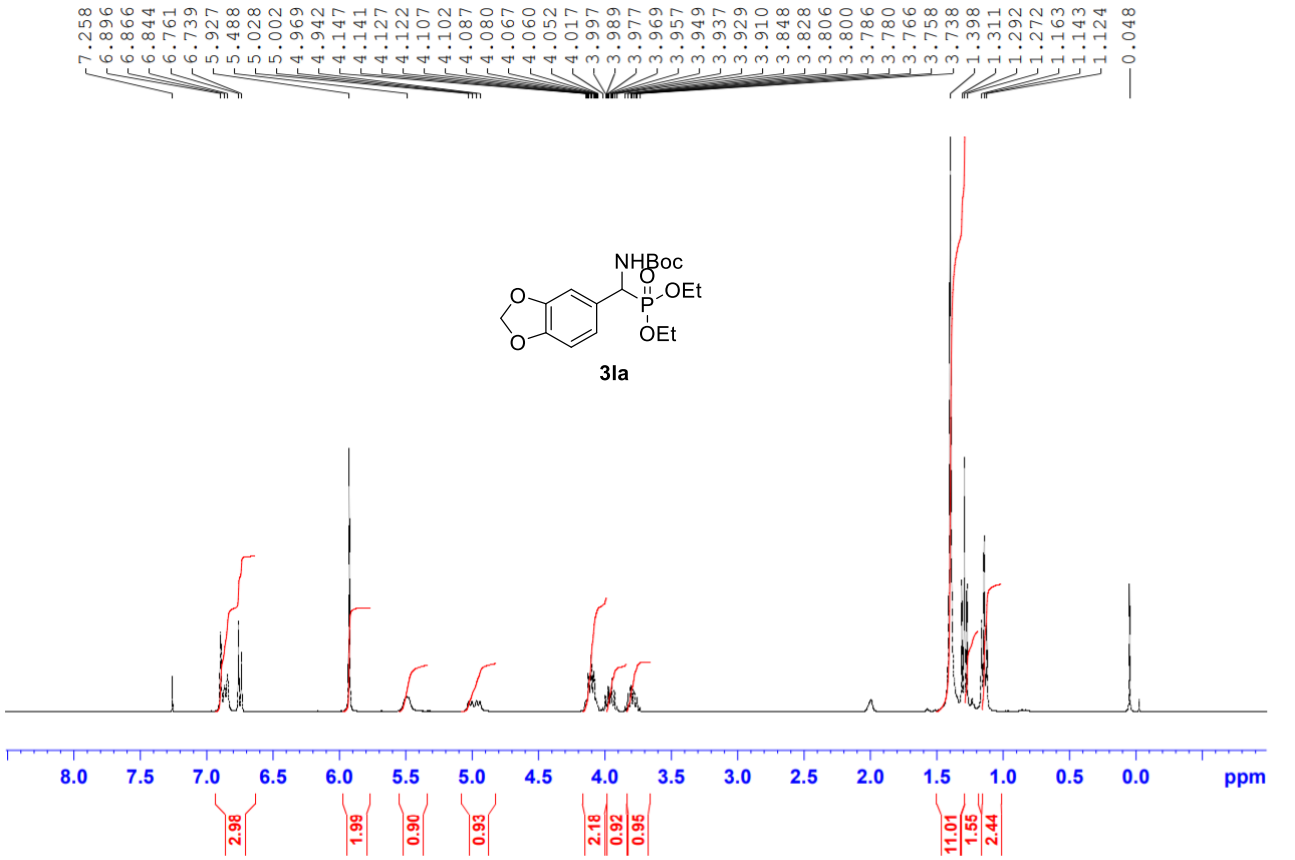
60
50
40
30
20
10
0
ppm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4.127
4.122
4.107
4.102
4.087
4.080
4.067
4.060
4.052
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3.949
3.937
3.929
3.910
3.848
3.828
3.806
3.800
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3.780
3.766
3.758
3.738
1.398
1.311
1.292
1.272
1.163
1.143
1.124
0.048
NHBoc
O
OEt
P
OEt
O
O
3la
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
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0.93
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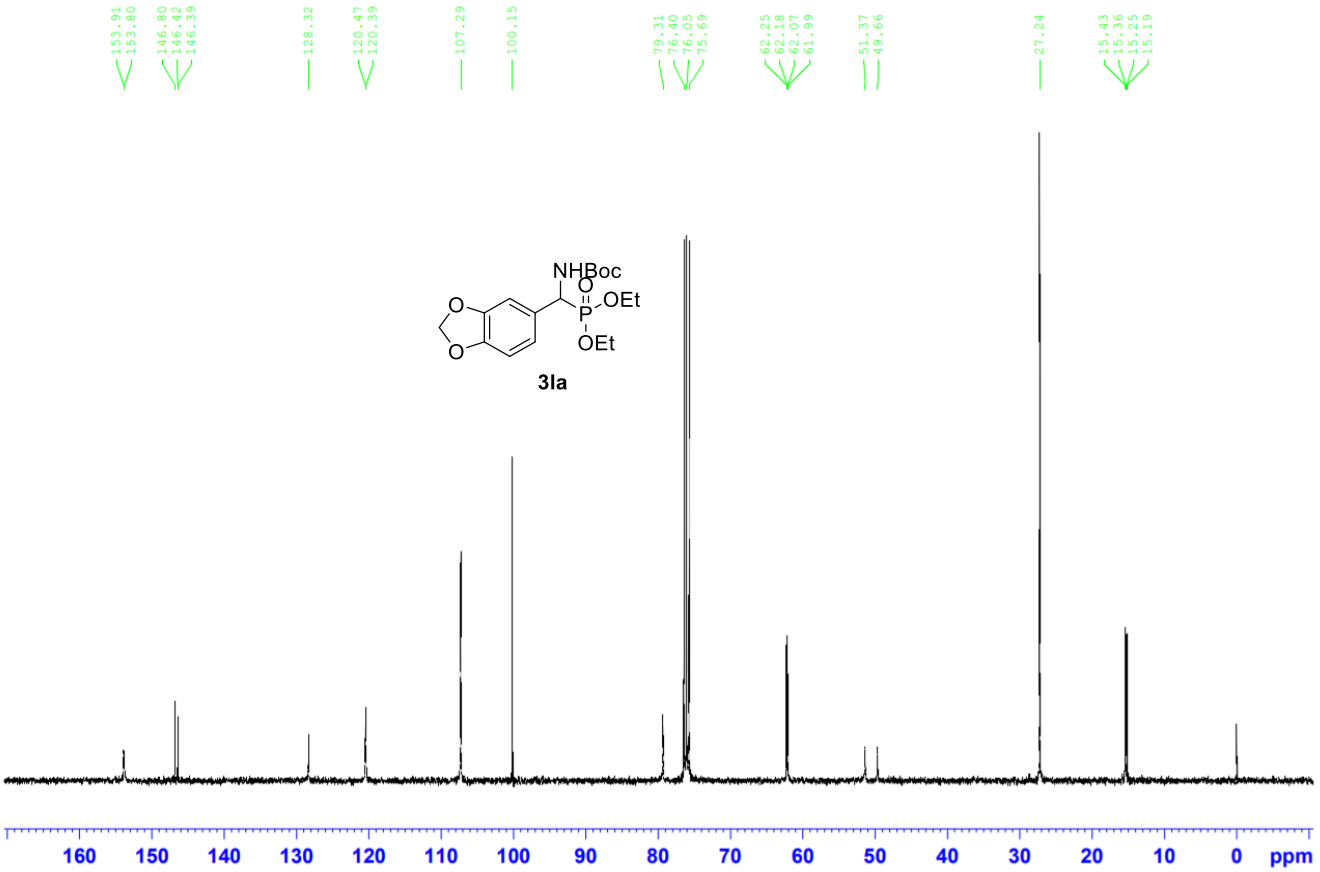
0.92
0.95
11.01
1.55
2.44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120.39
107.29
100.15
79.31
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76.05
75.69
62.25
62.18
62.07
61.99
51.37
49.66
27.24
15.43
15.36
15.25
15.19
NHBoc
O
OEt
P
OEt
O
O
3la
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140
130
120
110
100
90
80
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60
50
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30
20
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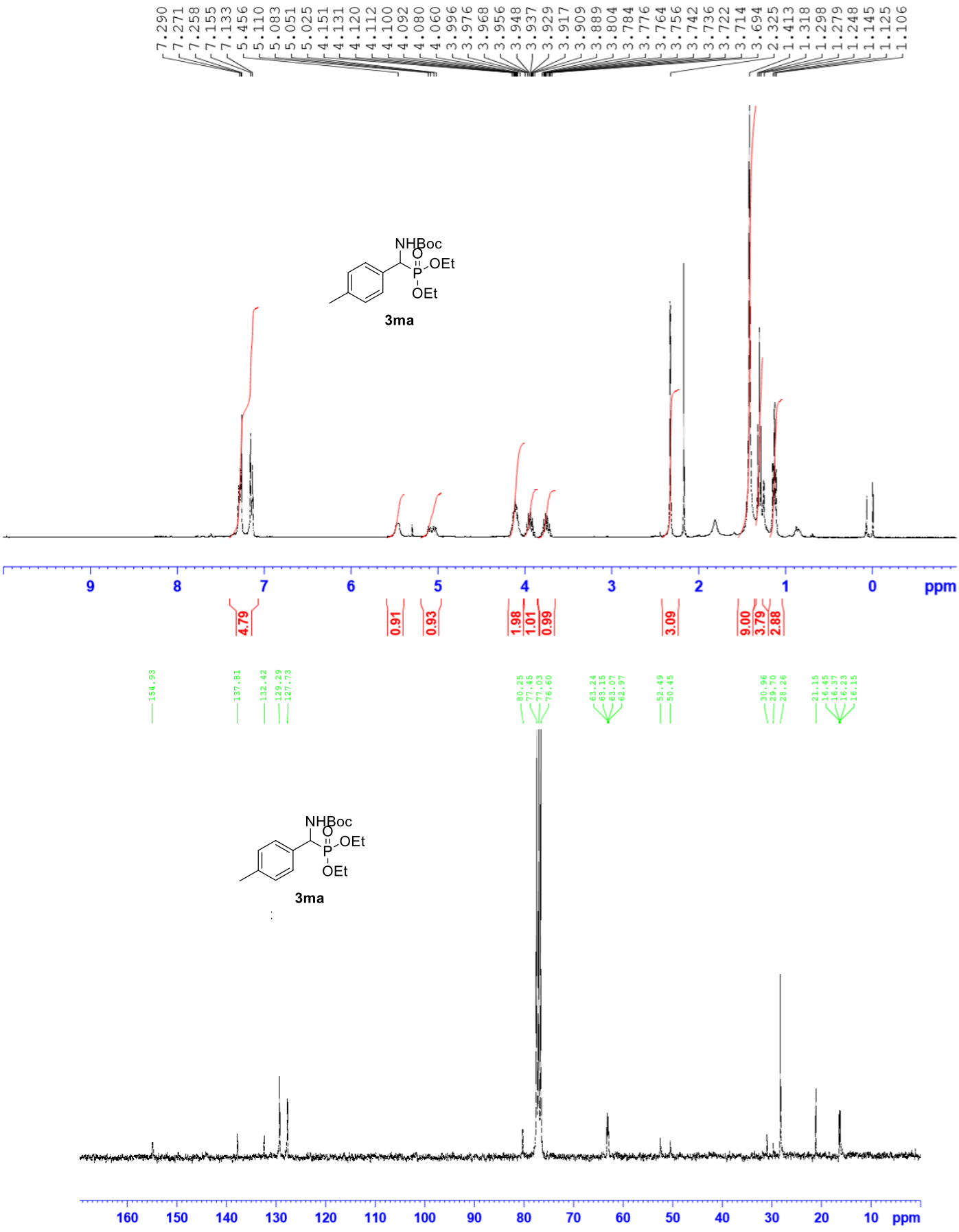
ppm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5.025
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4.112
4.100
4.092
4.080
4.060
3.996
3.976
3.968
3.956
3.948
3.937
3.929
3.917
3.909
3.889
3.804
3.784
3.776
3.764
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3.722
3.714
3.694
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1.413
1.318
1.298
1.279
1.248
1.145
1.125
1.106
NHBoc
O
OEt
P
OEt
3ma
9
8
7
6
5
4
3
2
1
0
ppm
4.79
0.91
0.93
1.98
1.01
0.99
3.09
9.00
3.79
2.88
154.93
137.81
132.42
129.29
127.73
80.25
77.45
77.03
76.60
63.24
63.15
63.07
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52.49
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30.96
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28.26
21.15
16.45
16.37
16.23
16.15
NHBoc
O
OEt
P
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150
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70
60
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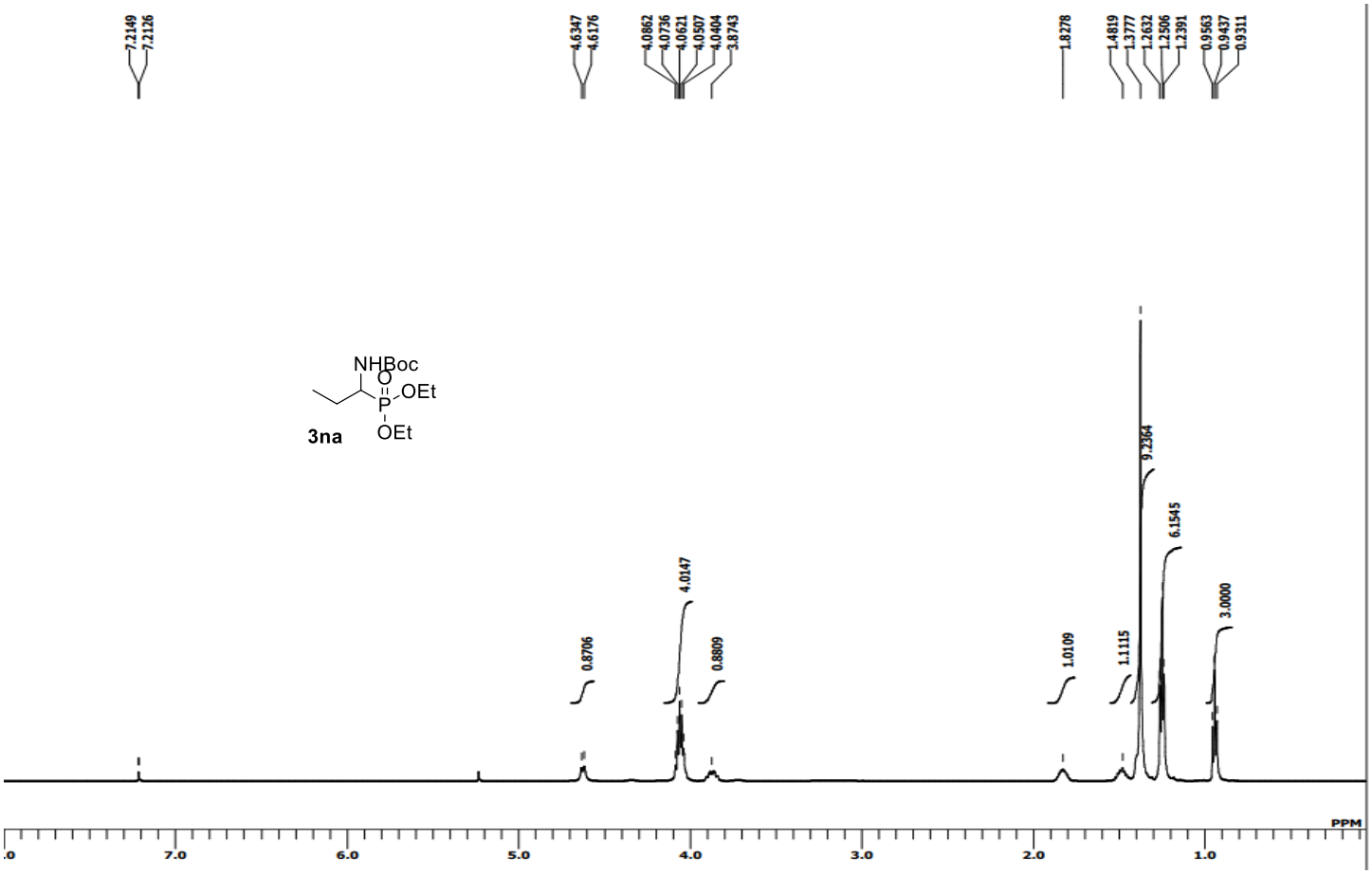
30
20
10
ppm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1.4819
1.3777
1.2632
1.2506
1.2391
0.9563
0.9437
0.9311
NHBoc
OEt
OEt
3na
9.2364
6.1545
4.0147
3.0000
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1.1115
PPM
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5.0
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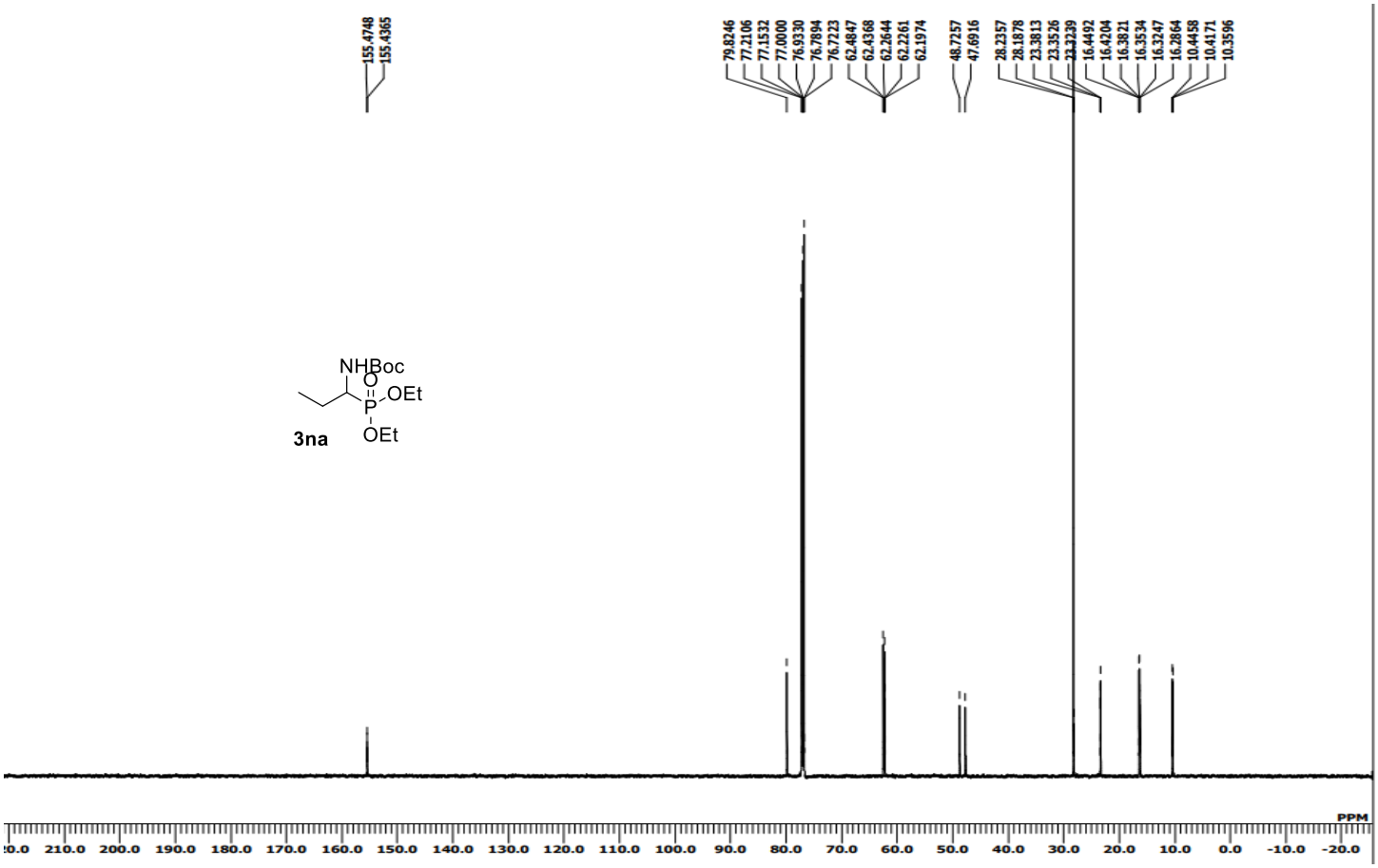
3.0
2.0
1.0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62.1974
48.7257
47.6916
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28.1878
23.3813
23.3526
23.3239
16.4492
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16.3821
16.3534
16.3247
16.2864
10.4458
10.4171
10.3596
NHBoc
OEt
OEt
3na
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
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50.0
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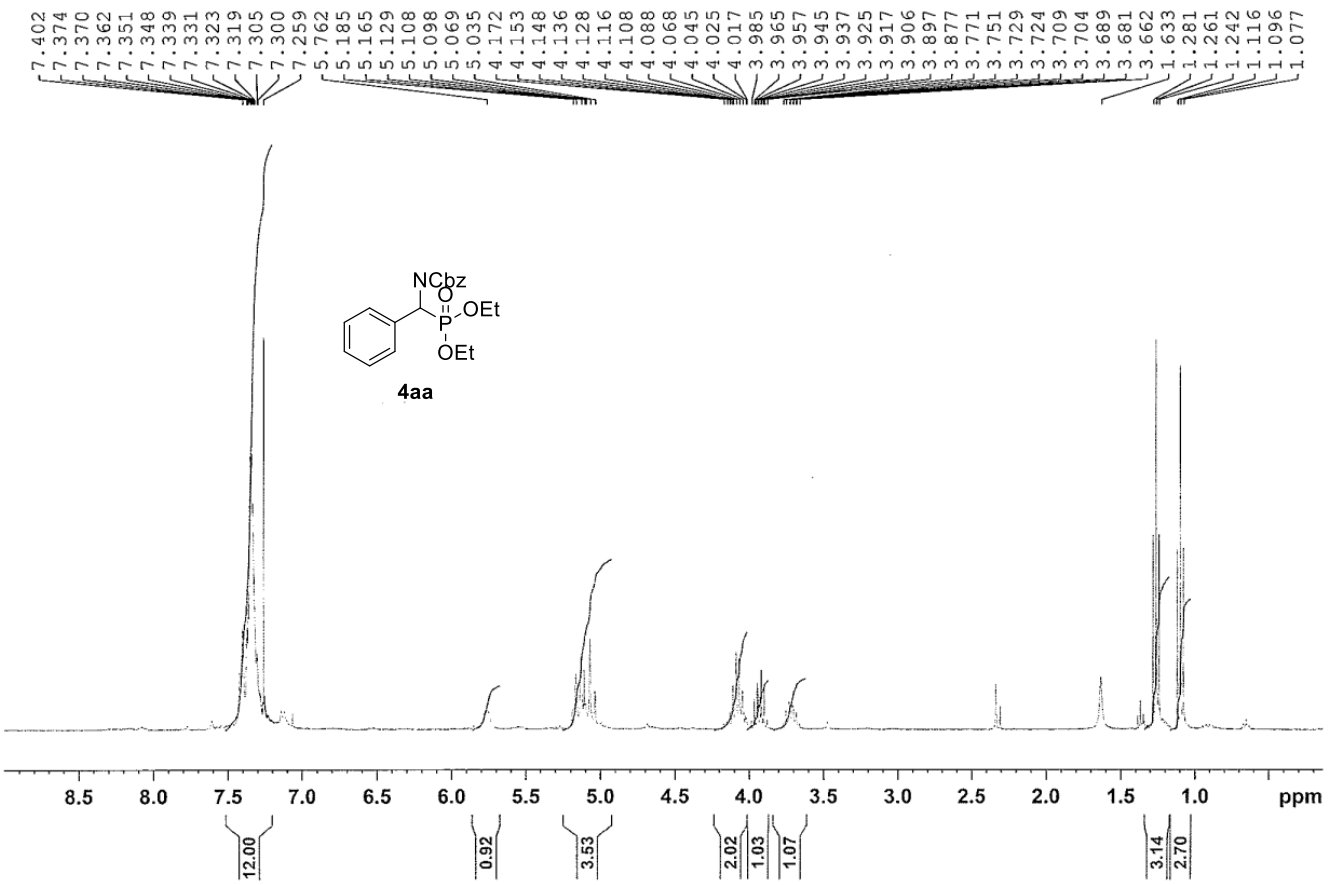
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7.259
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5.069
5.035
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4.136
4.128
4.116
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4.088
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3.957
3.945
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3.662
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1.281
1.261
1.242
1.116
1.096
1.077
NCbz
O
OEt
P
OEt
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7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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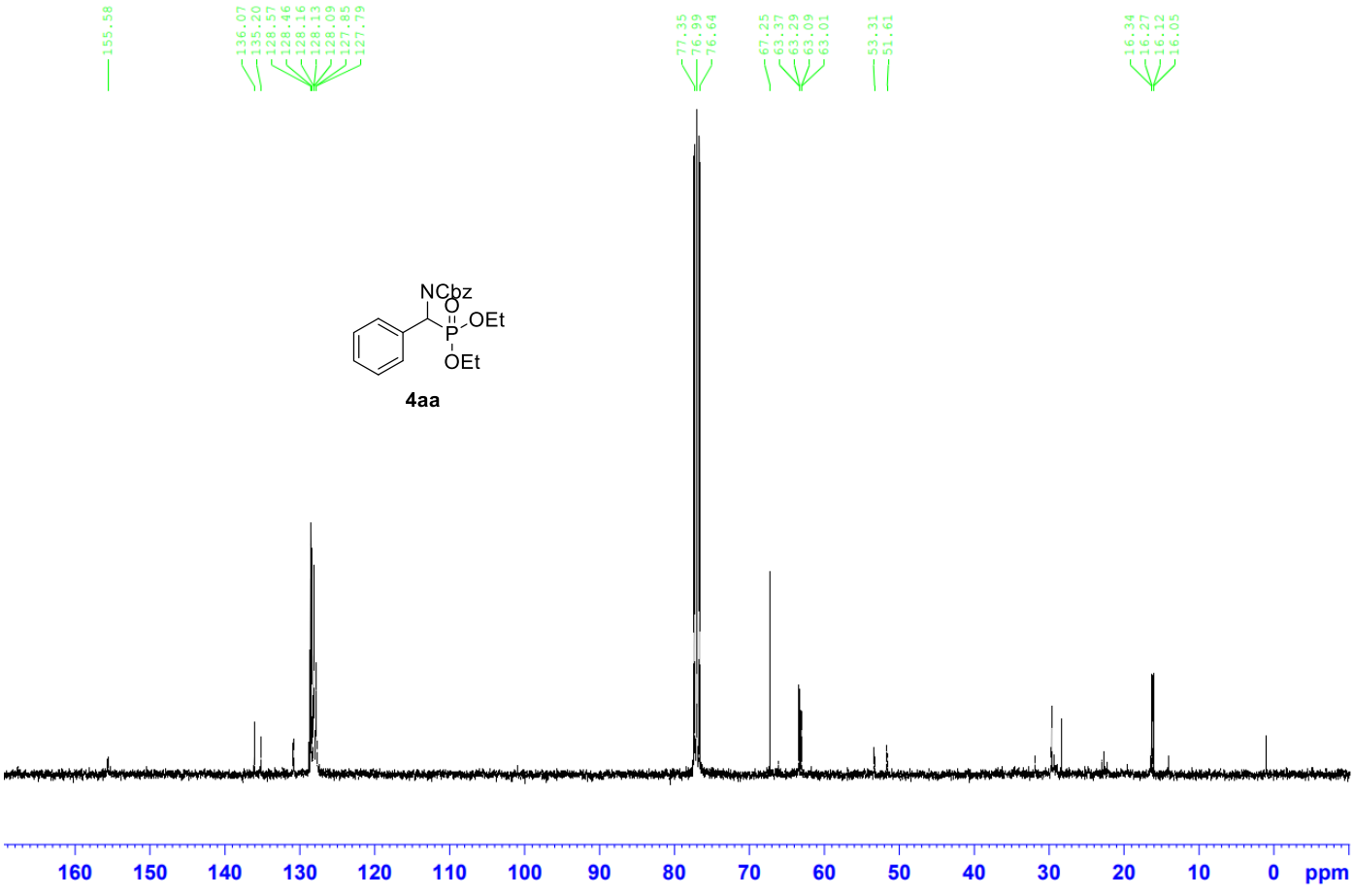
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77.35
76.99
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67.25
63.37
63.29
63.09
63.01
53.31
51.61
16.34
16.27
16.12
16.05
NCbz
O
OEt
P
OEt
4aa
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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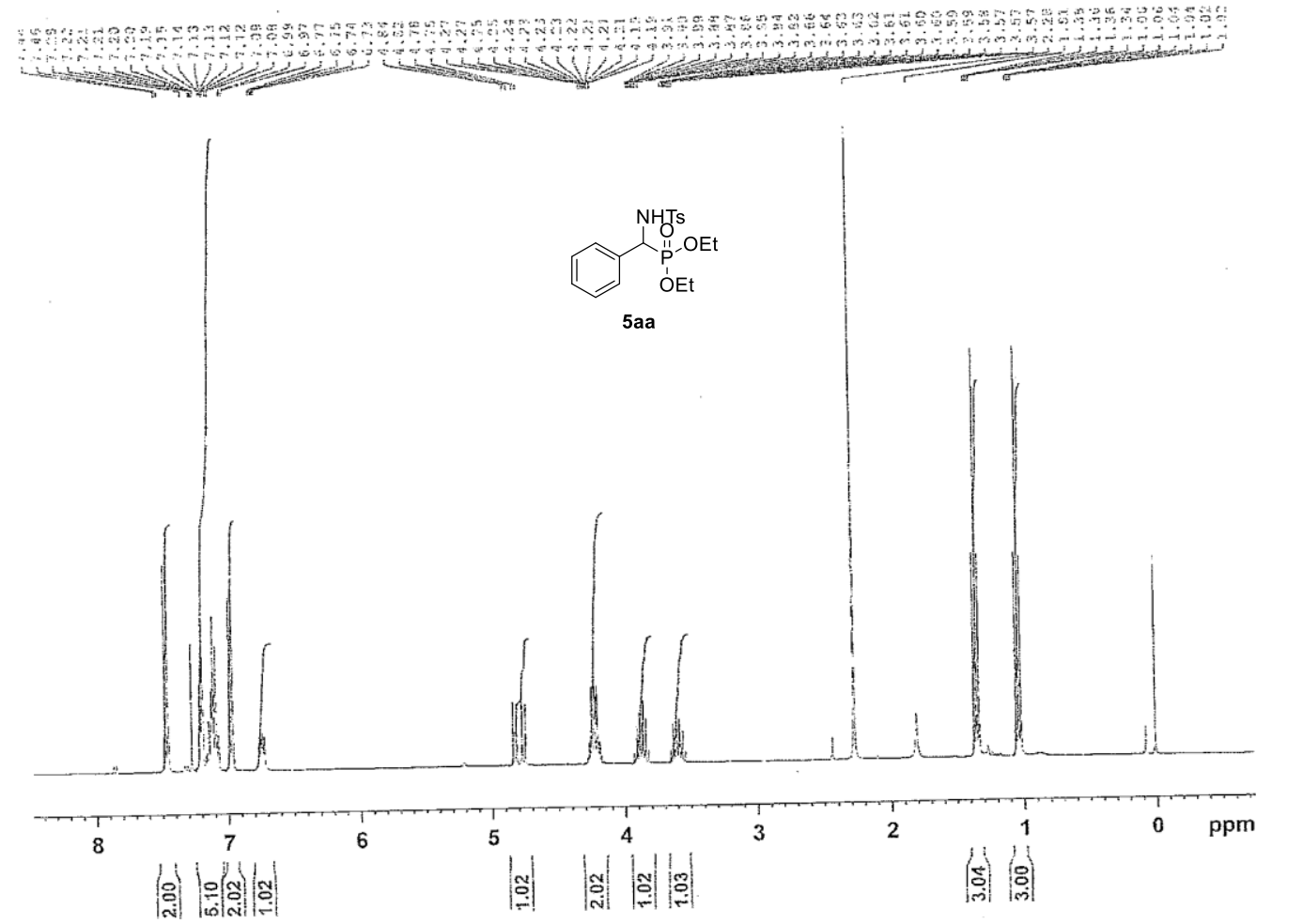
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1.03
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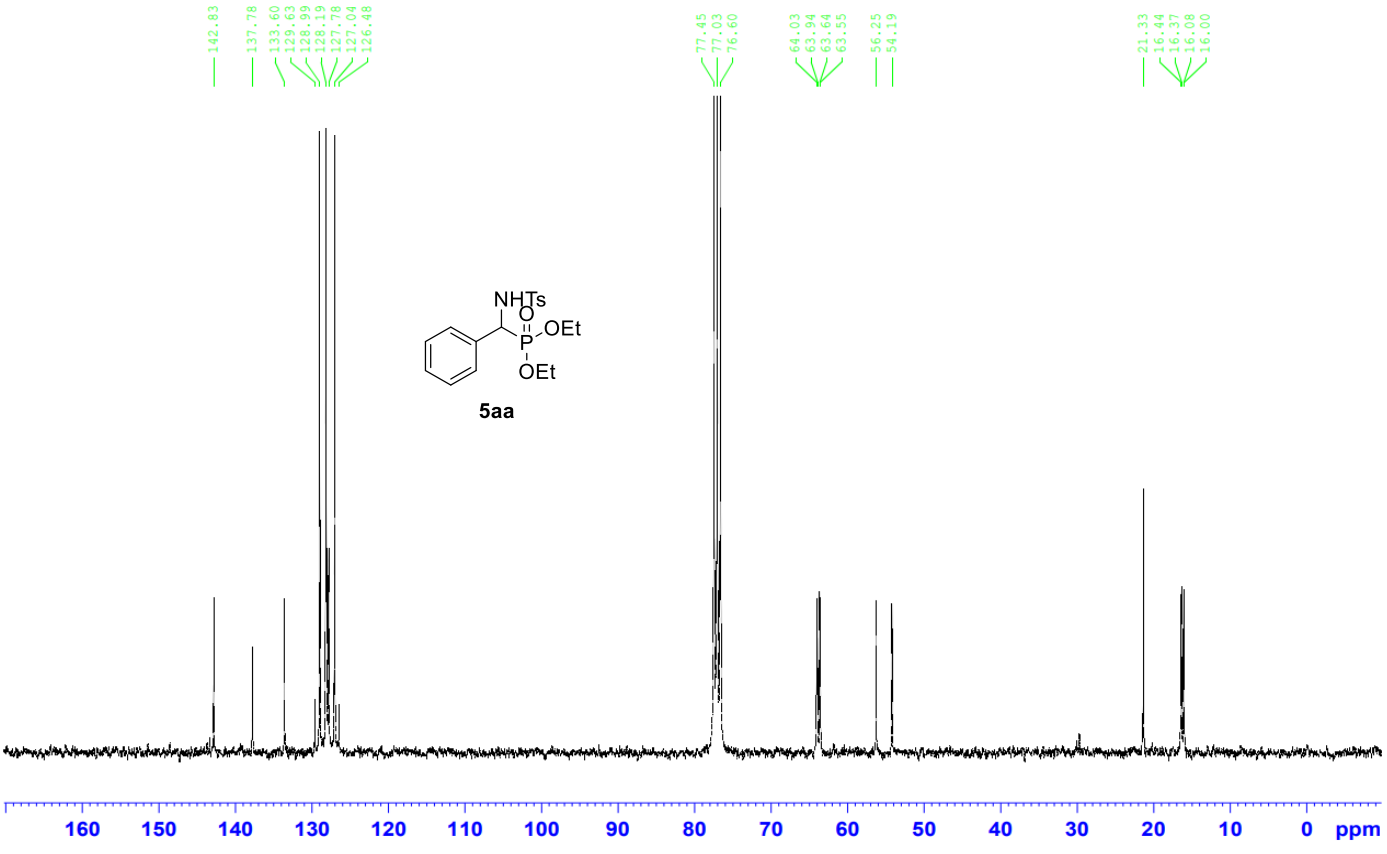
3.00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129.63
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76.60
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63.64
63.55
56.25
54.19
21.33
16.44
16.37
16.08
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NHTs
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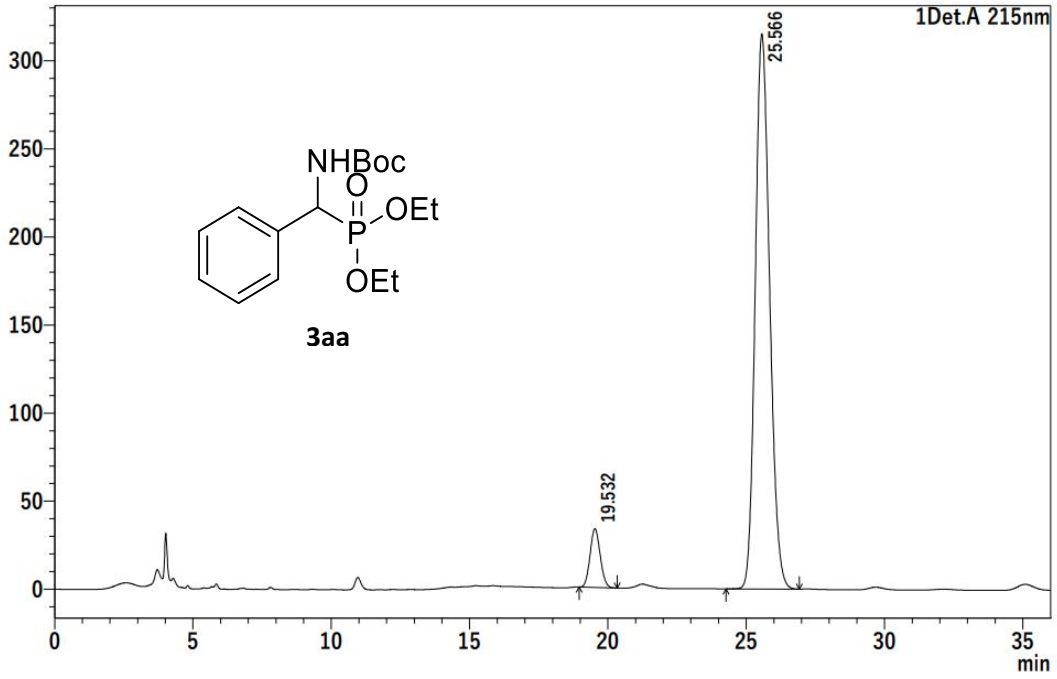
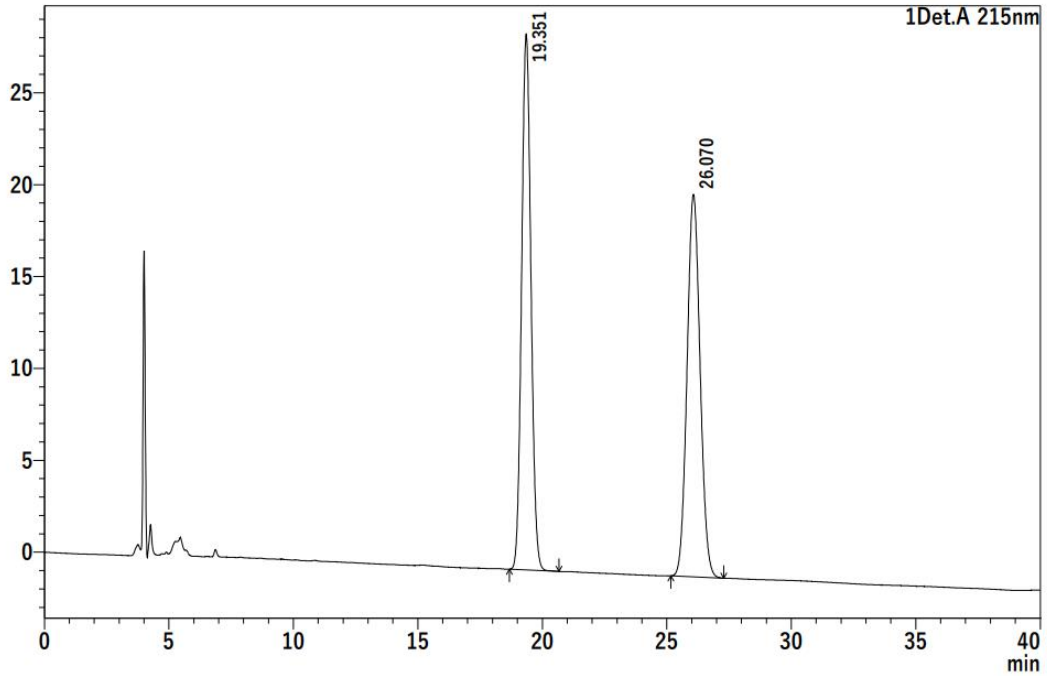
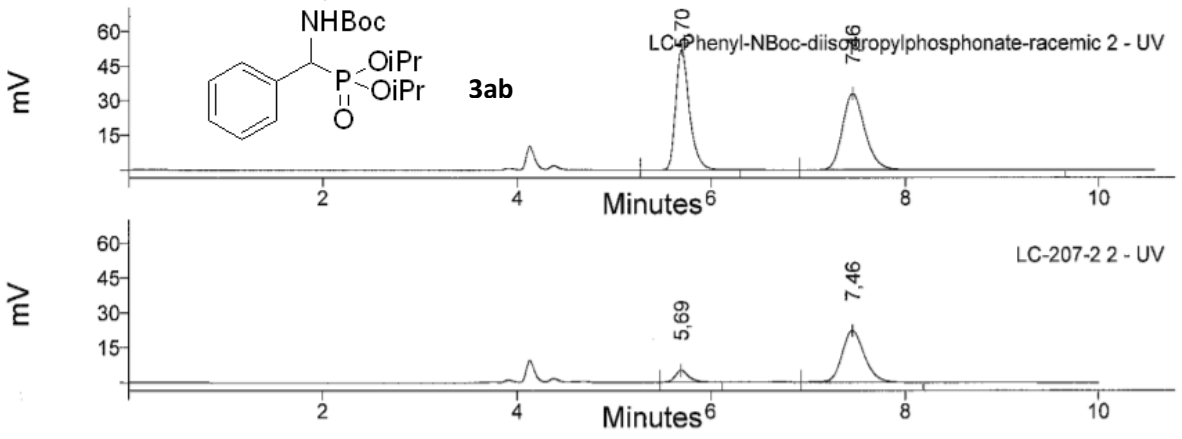


Peak#	Ret. Time	Area	Height	Mark	Conc.
1	19.582	854517	39889		6.970
2	25.566	11406268	315206		93.030
Total		12260785	348595		100.000



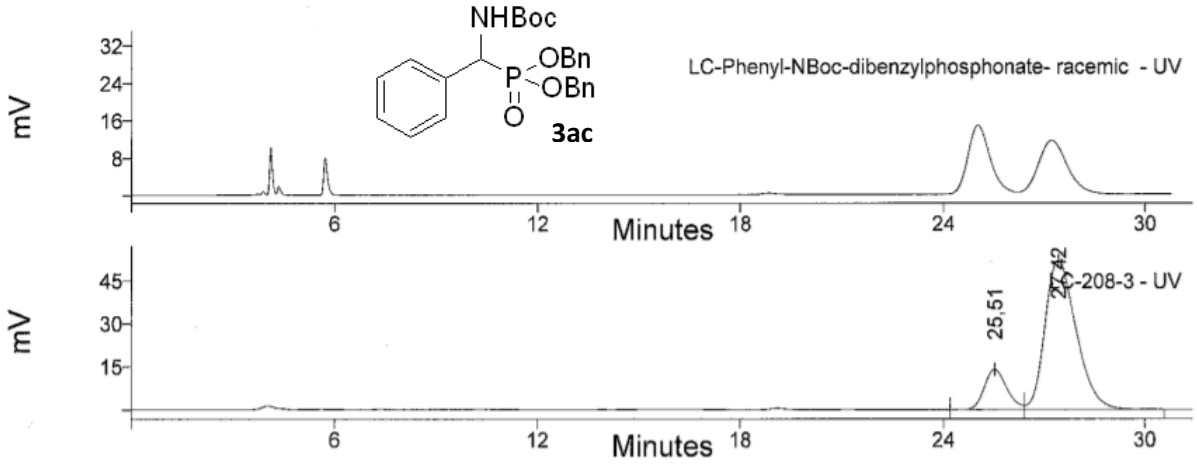
Peak#	Ret. Time	Area	Height	Mark	Conc.
1	19.351	758942	29176		49.981
2	26.070	759506	20804		50.019
Total		1518448	49980		100.000



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		5,70	511,49	**49,25**	1,37	8531,87
2		7,46	527,12	**50,75**	1,22	5183,64
SOMME			**1038,61**	**100,00**		

Résultats d'intégration (LC-207-2 2 - UV)

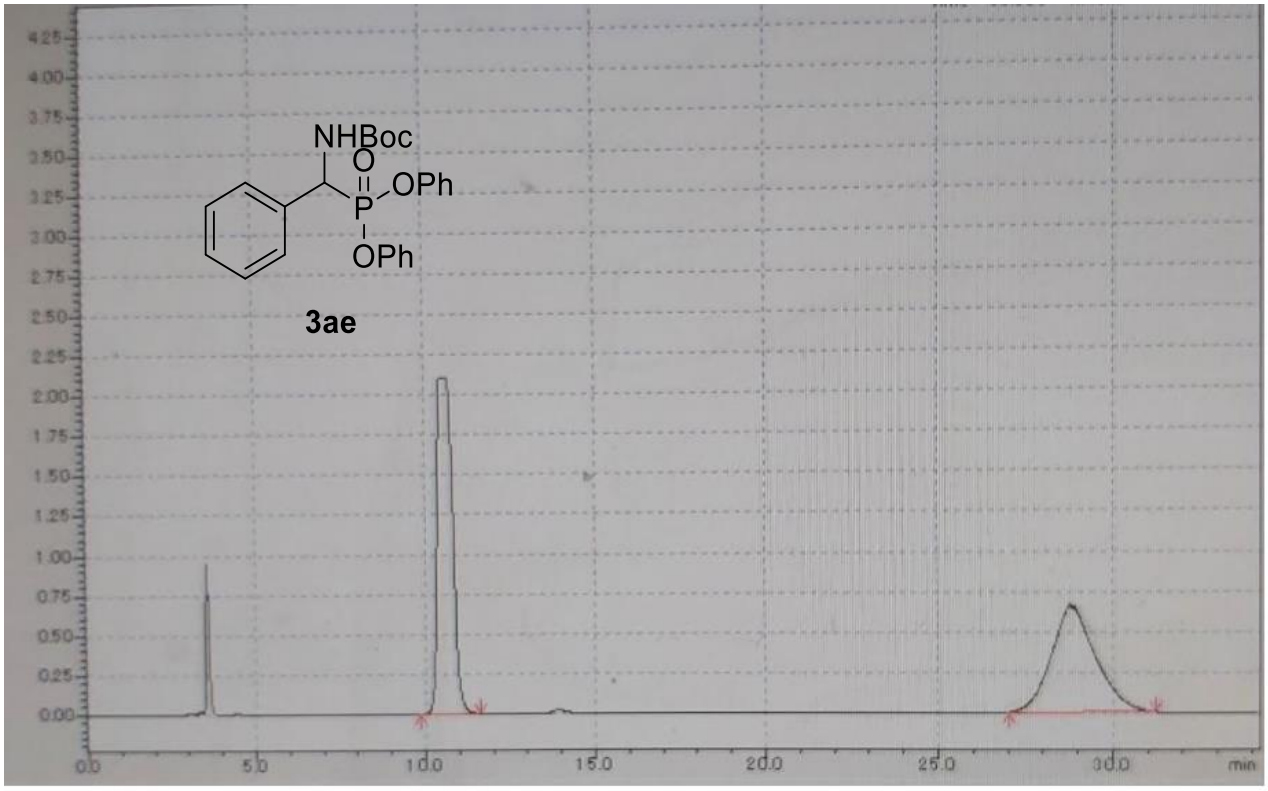
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		5,69	49,21	**12,20**	1,30	9099,22
2		7,46	354,01	**87,80**	1,17	5279,37
SOMME			**403,22**	**100,00**		



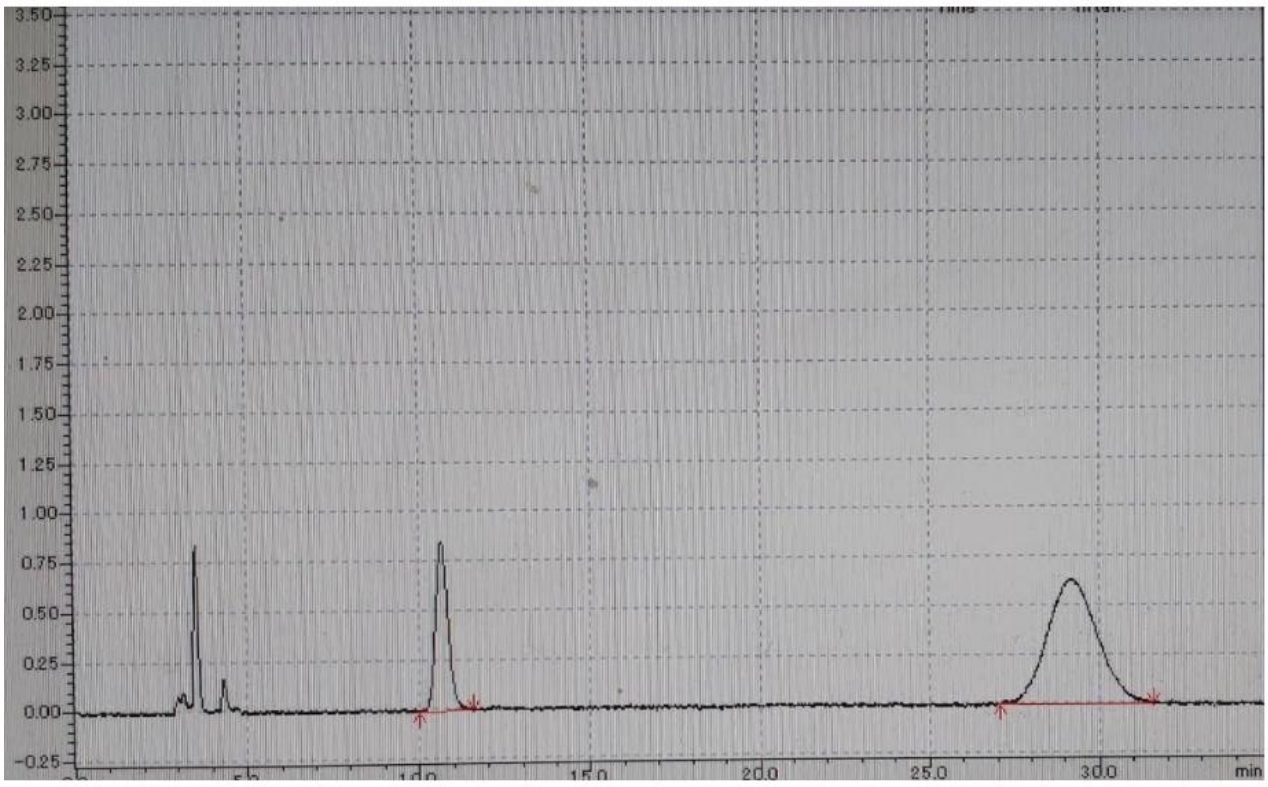
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
SOMME			**0,00**	**0,00**		

Résultats d'intégration (LC-208-3 - UV)

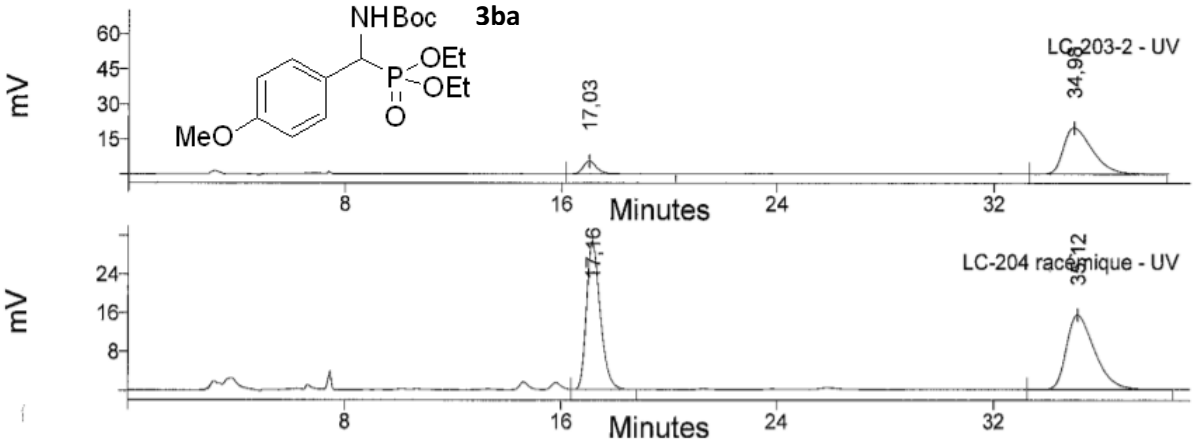
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		25,51	646,43	**16,14**	#	7078,04
2		27,42	3358,02	**83,86**	1,31	4223,45
SOMME			**4004,45**	**100,00**		



Peak#	Ret. Time	Area	Height	Mark	Area%
1	10.694	64655689	2106365	M	52.802
2	28.775	57794211	671012	M	47.198
Total		122449900	2777377		100.000



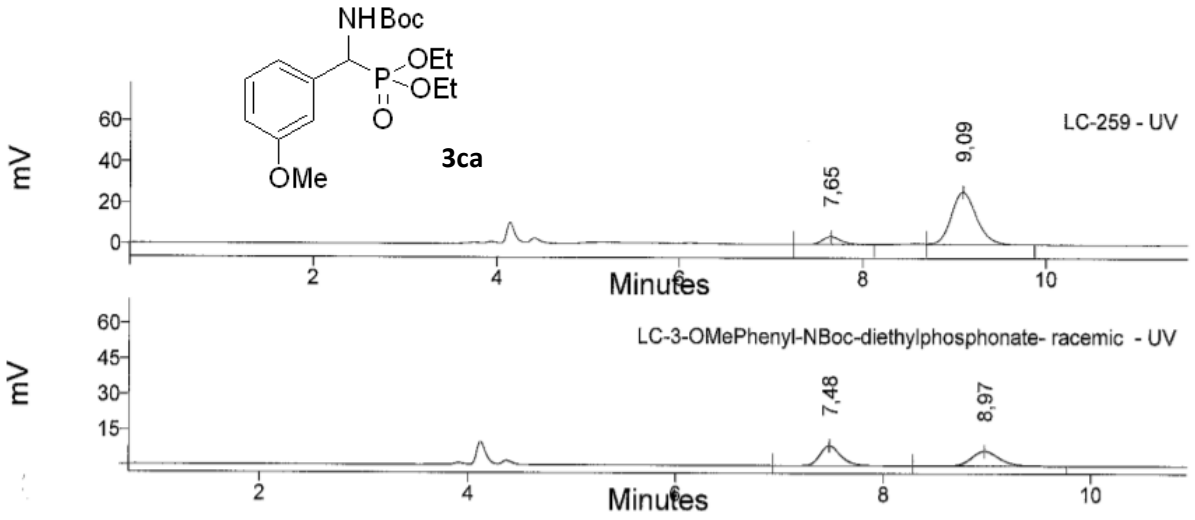
Peak#	Ret. Time	Area	Height	Mark	Area%
1	10.644	2156411	85961	M	25.133
2	29.149	6423580	63597	M	74.867
Total		8579991	149558		100.000



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		17,03	194,54	**11,76**	1,24	5704,63
2		34,98	1459,77	**88,24**	1,57	5285,12
S	ME		**1654,31**	**100,00**		

Résultats d'intégration (LC-204 racémique - UV)

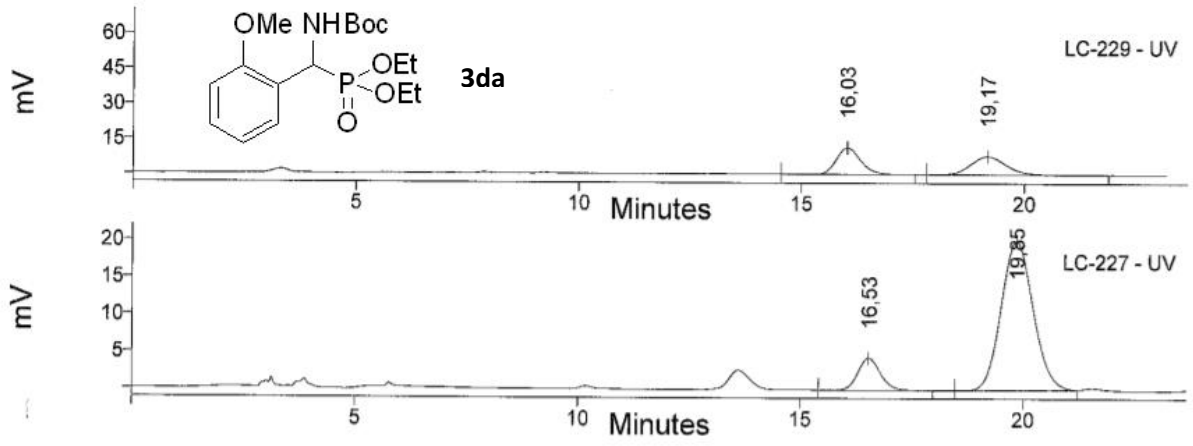
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		17,16	1089,43	**49,63**	1,36	5526,46
2		35,12	1105,67	**50,37**	1,48	5544,68
SOMME			**2195,10**	**100,00**		



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		7,65	52,31	**9,55**	1,26	7328,64
2		9,09	495,43	**90,45**	1,17	5473,25
S	ME		**547,74**	**100,00**		

Résultats d'intégration (LC-3-OMePhenyl-NBoc-diethylphosphonate- racemic - UV)

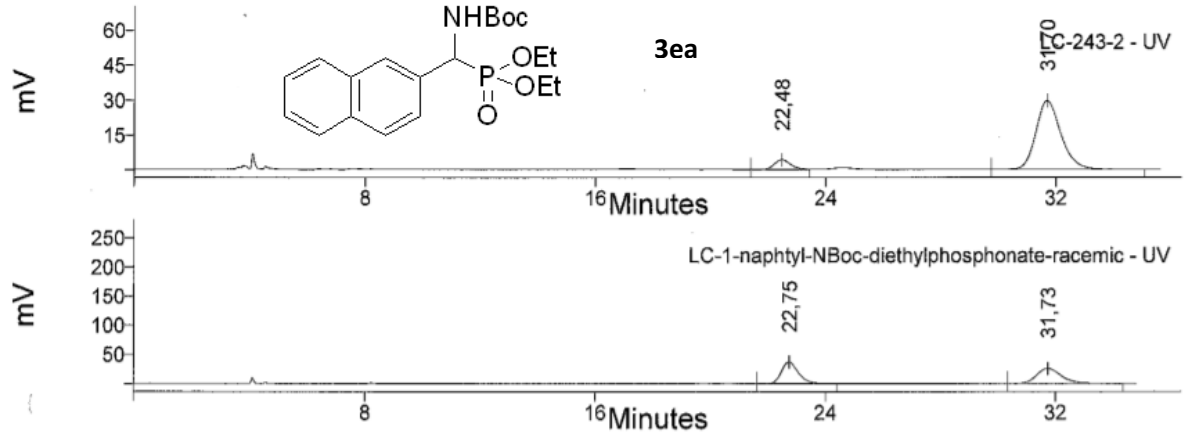
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		7,48	118,79	**50,00**	1,27	7203,30
2		8,97	118,79	**50,00**	1,20	5539,58
SOMME			**237,58**	**100,00**		



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		16,03	432,40	**49,90**	1,20	4227,53
2		19,17	434,07	**50,10**	1,13	2759,21
S	ME		**866,46**	**100,00**		

Résultats d'intégration (LC-227 - UV)

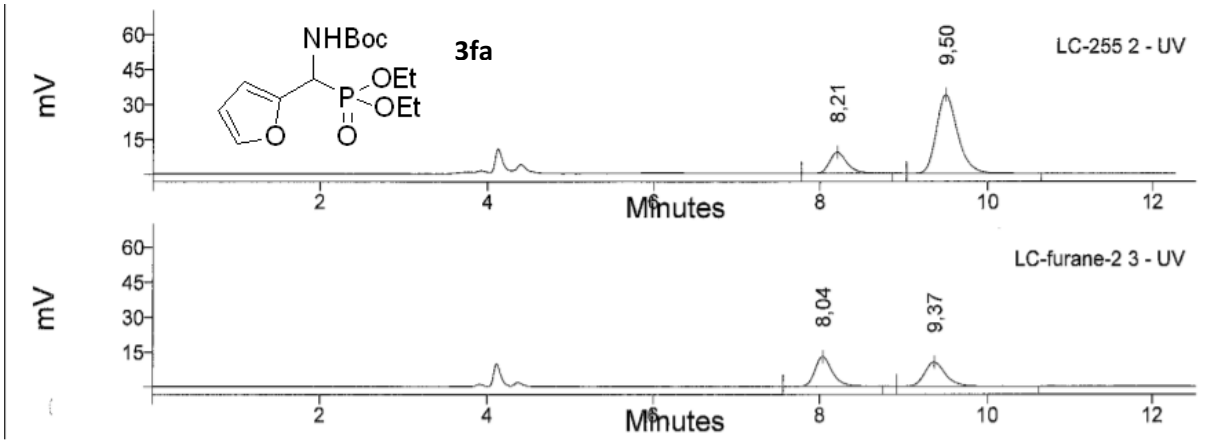
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		16,53	152,36	**13,10**	1,14	5270,17
2		19,85	1011,00	**86,90**	1,11	3567,42
SOMME			**1163,36**	**100,00**		



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		22,48	160,50	**8,16**	1,22	8172,17
2		31,70	1807,34	**91,84**	1,21	6622,01
S	ME		**1967,83**	**100,00**		

Résultats d'intégration (LC-1-naphtyl-NBoc-diethylphosphonate-racemic - UV)

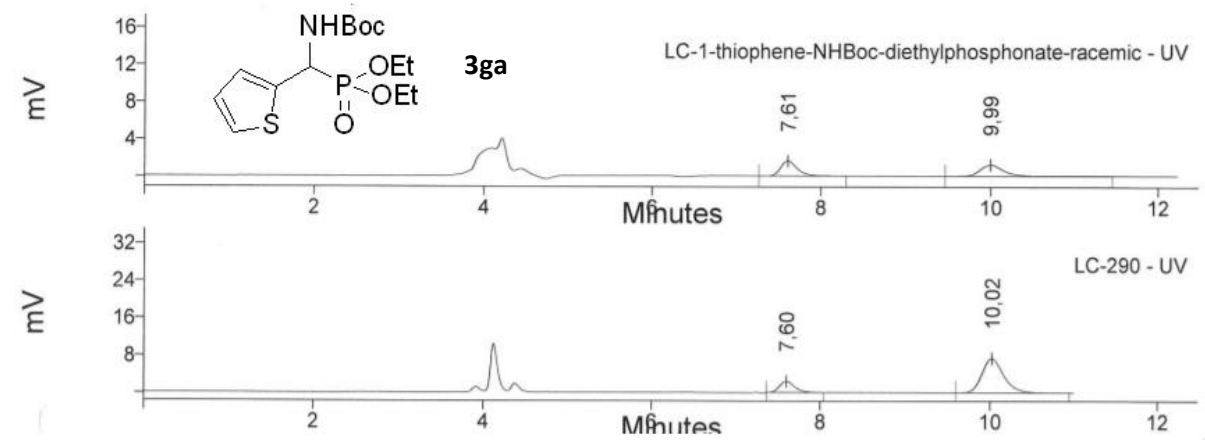
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		22,75	1494,15	**49,40**	1,27	7682,44
2		31,73	1530,52	**50,60**	1,23	6895,47
SOMME			**3024,67**	**100,00**		



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		8,21	130,94	**17,84**	1,26	8062,24
2		9,50	603,17	**82,16**	1,25	7008,95
SOMME			**734,11**	**100,00**		

Résultats d'intégration (LC-furane-2 3 - UV)

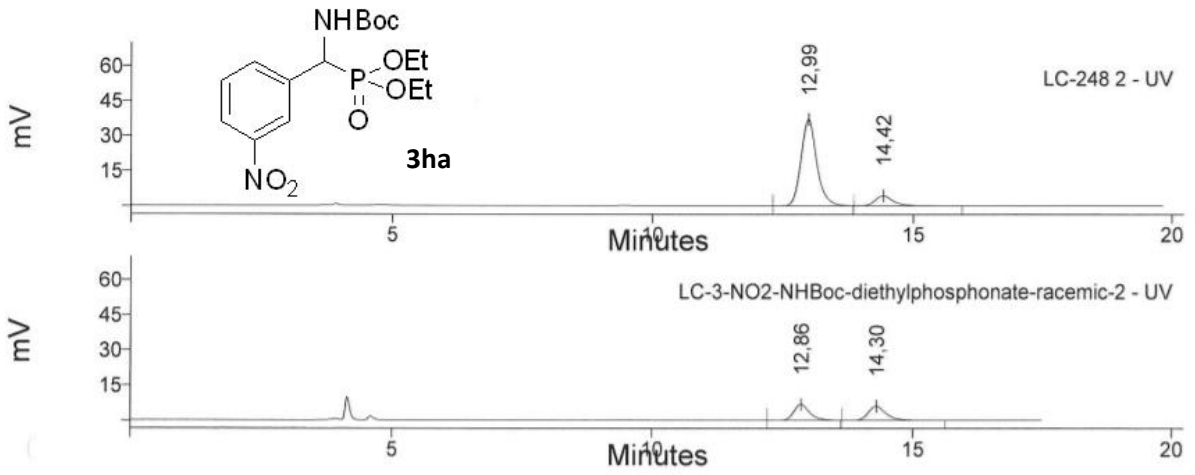
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		8,04	184,32	**50,52**	1,29	7991,12
2		9,37	180,52	**49,48**	1,23	7127,59
SOMME			**364,84**	**100,00**		



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		7,61	22,20	**50,28**	1,35	7751,87
2		9,99	21,95	**49,72**	1,29	7143,34
SOMME			**44,14**	**100,00**		

Résultats d'intégration (LC-290 - UV)

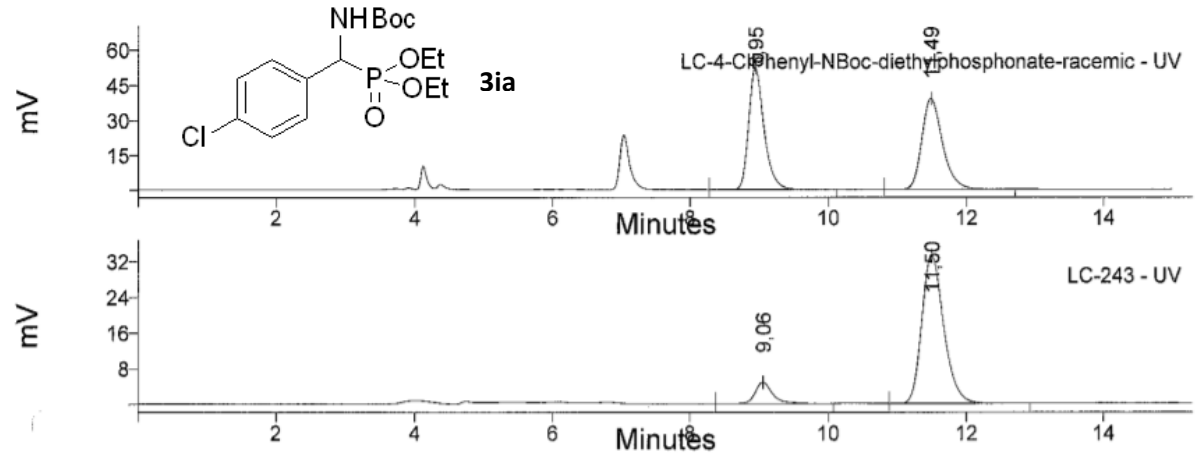
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		7,60	30,43	**19,04**	1,30	8845,83
2		10,02	129,35	**80,96**	1,26	7792,55
SOMME			**159,77**	**100,00**		



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		12,99	770,32	**88,73**	1,19	9737,95
2		14,42	97,84	**11,27**	1,26	9438,23
S ME			**868,16**	**100,00**		

Résultats d'intégration (LC-3-NO2-NHBoc-diethylphosphonate-racemic-2 - UV)

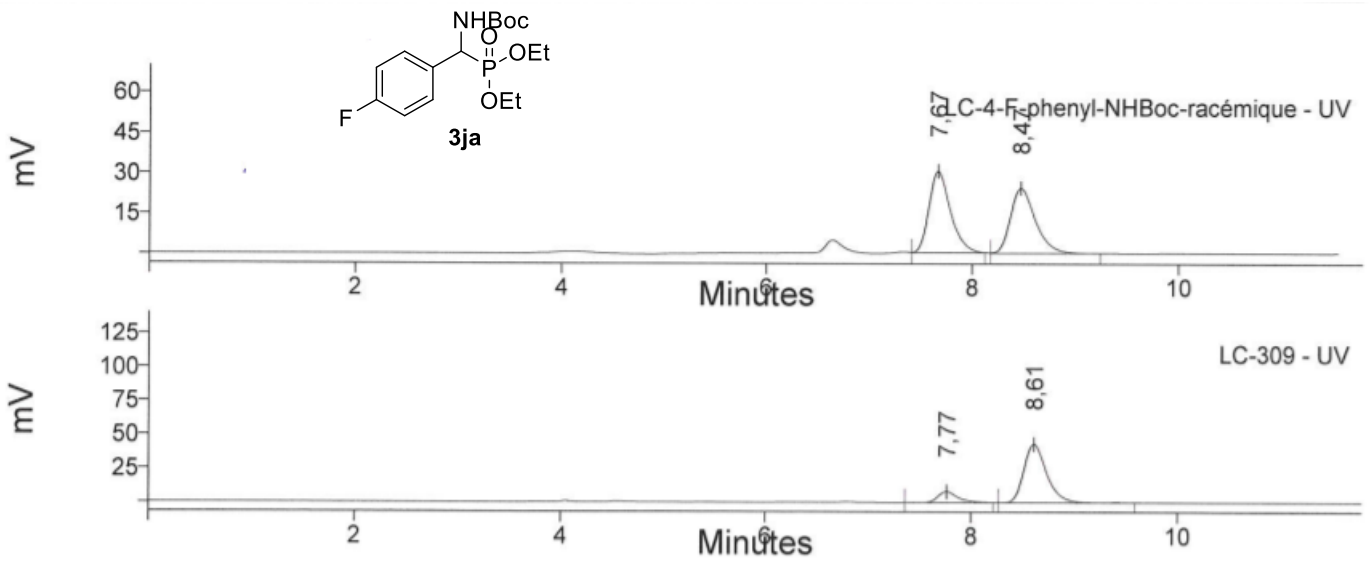
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		12,86	138,94	**49,99**	1,28	9800,65
2		14,30	139,02	**50,01**	1,29	9373,80
SOMME			**277,96**	**100,00**		



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		8,95	813,47	**50,03**	1,31	8243,98
2		11,49	812,50	**49,97**	1,28	7529,93
S ME			**1625,96**	**100,00**		

Résultats d'intégration (LC-243 - UV)

#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		9,06	84,82	**10,36**	1,41	7425,50
2		11,50	734,07	**89,64**	1,25	6558,09
SOMME			**818,88**	**100,00**		

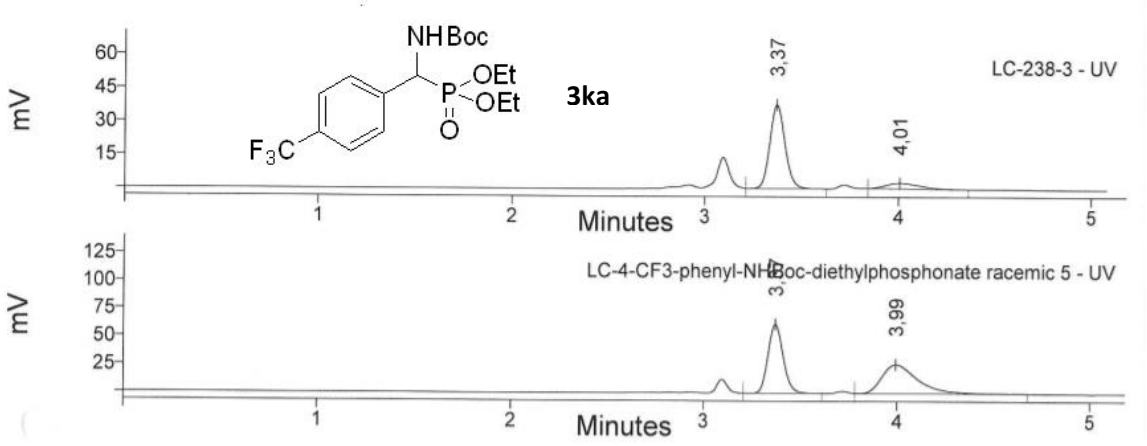


Résultats d'intégration (LC-4-F-phenyl-NHBoc-racémique - UV)

#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		7,67	441,04	**52,16**	1,32	6726,12
2		8,47	404,56	**47,84**	1,34	6274,43
SOMME			**845,60**	**100,00**		

Résultats d'intégration (LC-309 - UV)

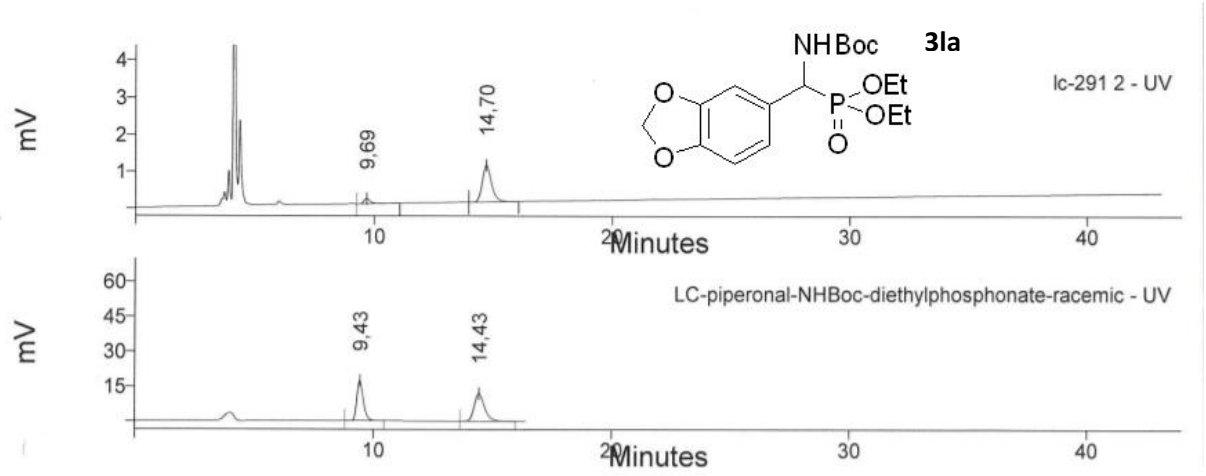
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		7,77	107,61	**13,98**	1,43	8812,54
2		8,61	662,20	**86,02**	1,31	7738,58
SOMME			**769,81**	**100,00**		



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		3,37	202,59	**87,28**	1,15	9334,74
2		4,01	29,54	**12,72**	#	2523,20
SOMME			**232,13**	**100,00**		

Résultats d'intégration (LC-4-CF3-phenyl-NHBoc-diethylphosphonate racemic 5 - UV)

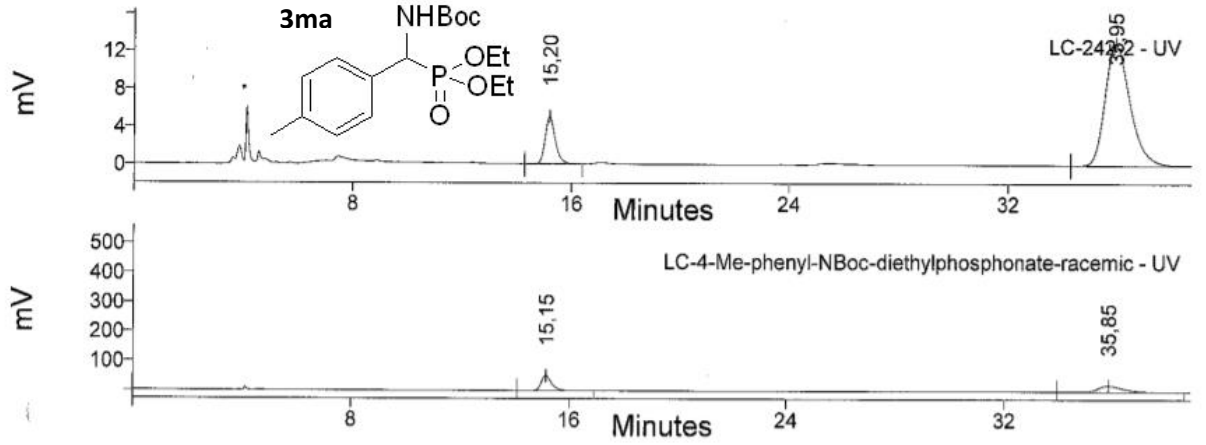
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		3,37	330,77	**50,38**	1,16	9282,17
2		3,99	325,77	**49,62**	1,57	2490,94
SOMME			**656,54**	**100,00**		



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		9,69	2,52	**8,56**	1,64	7740,60
2		14,70	26,95	**91,44**	1,29	7305,01
S ME			**29,47**	**100,00**		

Résultats d'intégration (LC-piperonal-NHBoc-diethylphosphonate-racemic - UV)

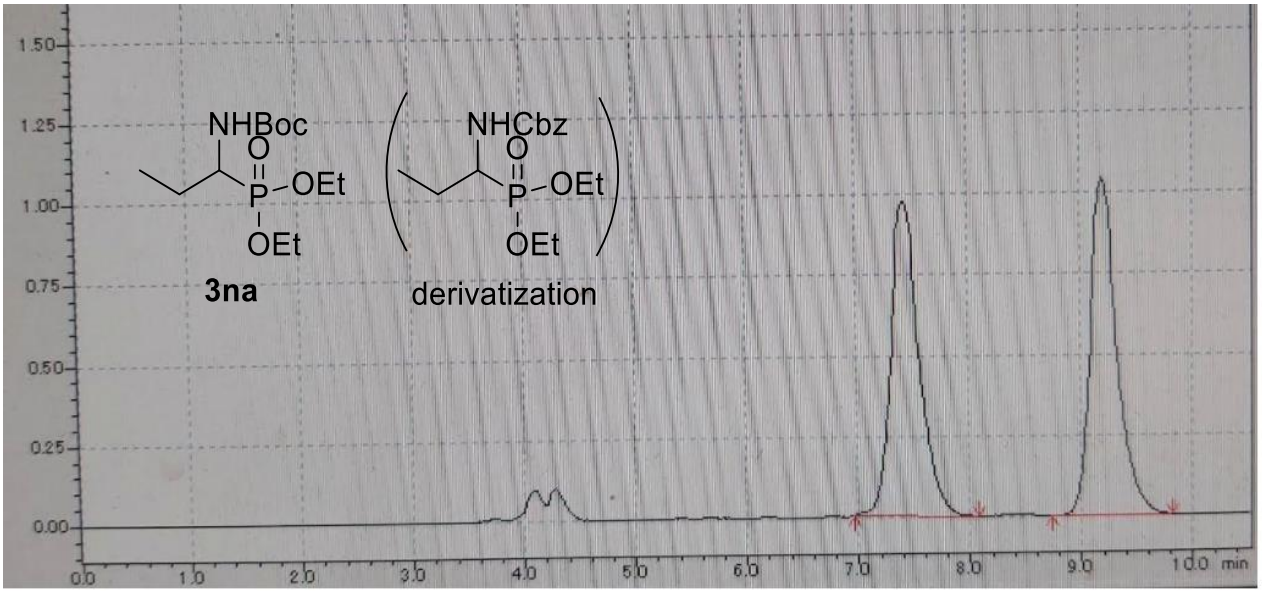
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		9,43	334,66	**48,68**	1,30	5755,00
2		14,43	352,87	**51,32**	1,28	5560,58
SOMME			**687,53**	**100,00**		



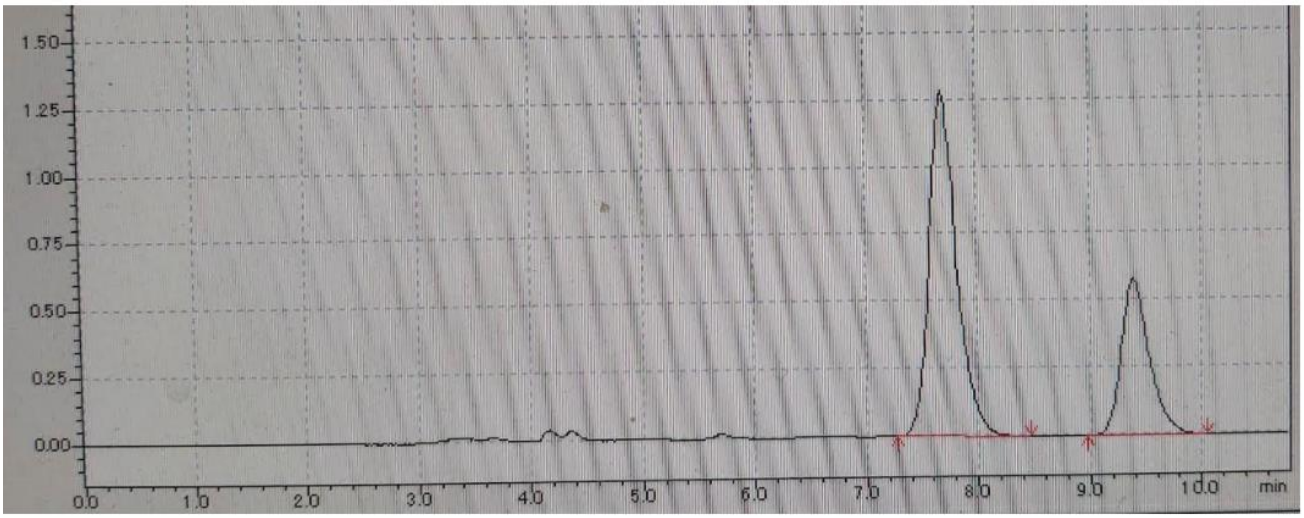
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		15,20	130,53	**13,58**	1,25	8452,39
2		35,95	830,50	**86,42**	1,33	7752,57
S ME			**961,03**	**100,00**		

Résultats d'intégration (LC-4-Me-phenyl-NBoc-diethylphosphonate-racemic - UV)

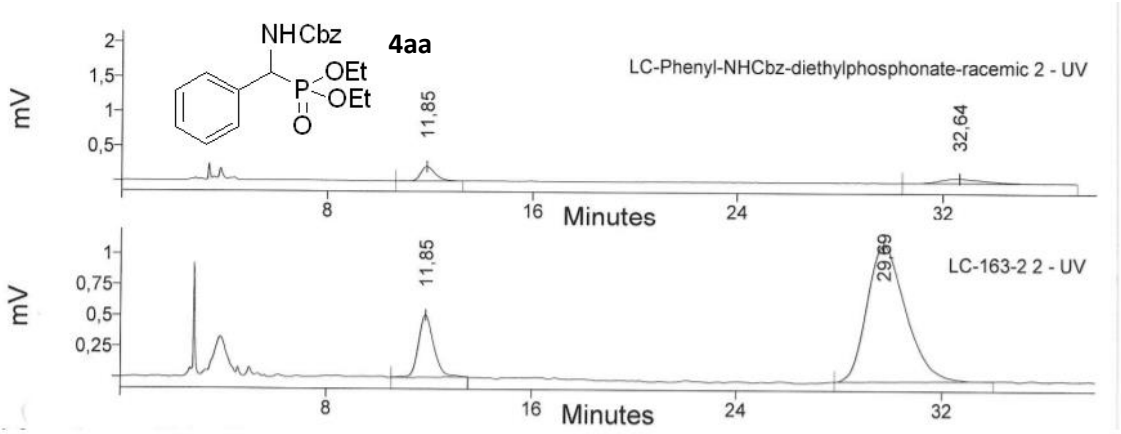
#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		15,15	1351,38	**49,69**	1,36	7964,19
2		35,85	1368,42	**50,31**	1,40	7466,09
SOMME			**2719,80**	**100,00**		



Peak#	Ret. Time	Area	Height	Mark	Area%
1	7.432	16884433	974954	M	49.721
2	9.194	17073618	1043418	M	50.279
Total		33958050	2018372		100.000



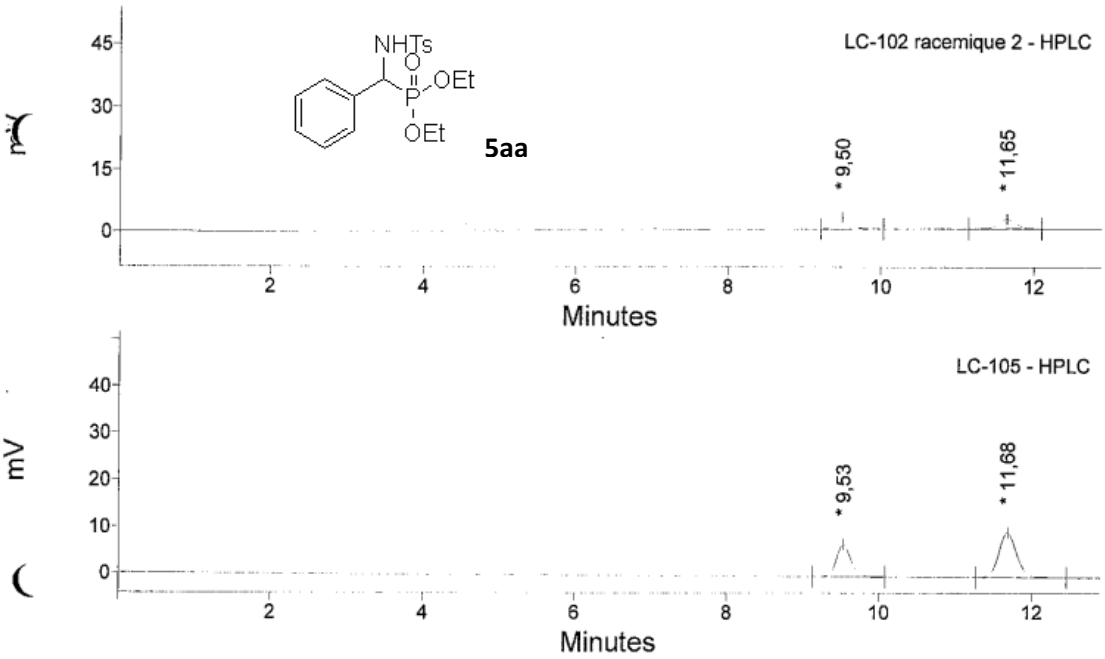
Peak#	Ret. Time	Area	Height	Mark	Area%
1	7.697	21675360	1283398	M	68.300
2	9.391	10060356	583255	M	31.700
Total		31735716	1866653		100.000



#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		11,85	8,06	**49,50**	1,39	2239,40
2		32,64	8,22	**50,50**	1,41	1655,26
SOMME			**16,28**	**100,00**		

Résultats d'intégration (LC-163-2 2 - UV)

#	Nom du pic	Tr.	Aire	% Aire	Asymétrie (USP, EP)	Plateaux (EP)
1		11,85	21,00	**15,30**	1,26	2014,17
2		29,69	116,33	**84,70**	1,35	1869,64
SOMME			**137,33**	**100,00**		



Résultats d'intégration (LC-102 racemique 2 - HPLC)

#	Nom du pic	Tr.	Aire	% Aire	Hauteur	Largeur (50%)	Plateaux (EP)
1		9,50	37,38	**50,45**	2,84	0,20	12356,92
2		11,65	36,71	**49,55**	2,29	0,25	12382,31
SOMME			**74,09**	**100,00**	**5,13**		

Résultats d'intégration (LC-105 - HPLC)

#	Nom du pic	Tr.	Aire	% Aire	Hauteur	Largeur (50%)	Plateaux (EP)
1		9,53	89,63	**36,91**	6,98	0,20	13131,27
2		11,68	153,19	**63,09**	9,63	0,24	12818,25
SOMME			**242,82**	**100,00**	**16,60**		

X-ray analysis

Crystals suitable of **3aa** for X-ray analysis could be successfully grown by slow diffusion of n-hexane in isopropanol solution.

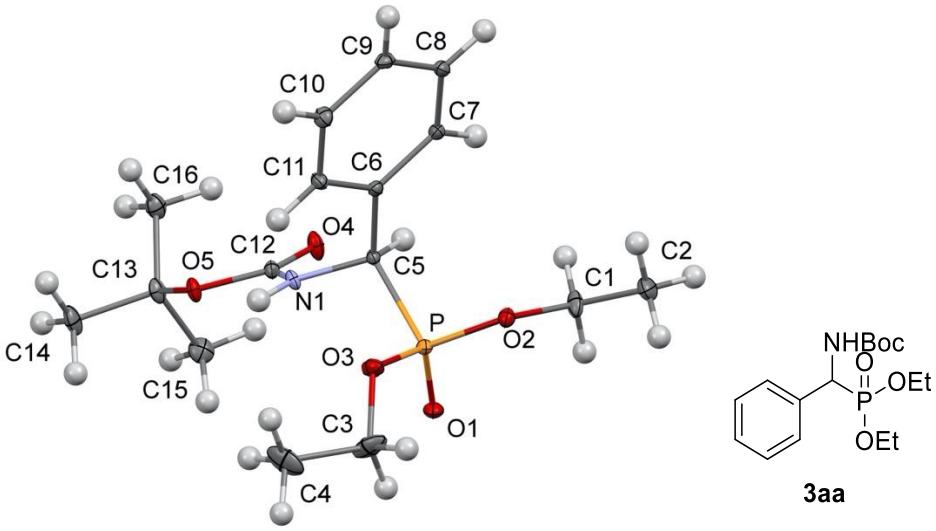


Fig.01. An ORTEP drawing of compound **3aa.** Thermal ellipsoids are shown at the 30% level.

X-ray diffraction data for compound **3aa** were collected by using a VENTURE PHOTON100 CMOS Bruker diffractometer with Micro-focus IμS source CuK_α radiation (λ=1.54178 Å). Crystals were mounted on a CryoLoop (Hampton Research) with Paratone-N (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100K. The temperature of the crystal was maintained at the selected value by means of a 700+ series Cryostream cooling device to within an accuracy of ±1K. The data were corrected for Lorentz polarization, and absorption effects. The structures were solved by direct methods using SHELXS-97[1] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2018[2] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX[3].

The crystal data collection and refinement parameters are given in Table S1.Absolute configuration of compound **3aa** has been established by anomalous-dispersion effects in diffraction measurements on the crystal (using a large number of Friedel's pairs). CCDC 2109370 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/. Absolute configuration of the other products was determined by analogy to **3aa**.

Table S1. *Crystallographic data and structure refinement details* ***3aa****.*

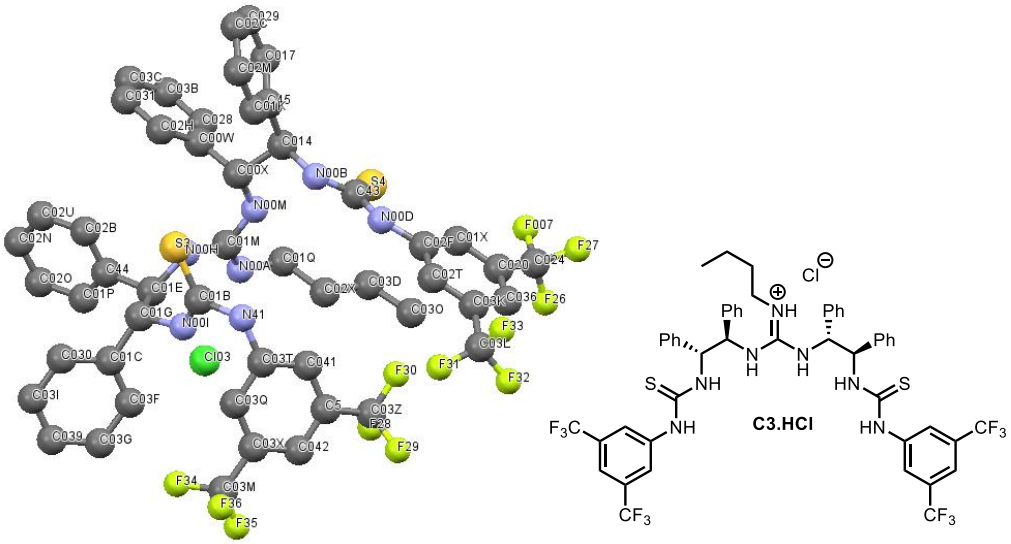
Compound	**3aa**
CCDC	2109370
Empirical Formula	C_{16} H_{26} N O_5 P
M_r	343.35
Crystal size, mm^3	0.18 x 0.16 x 0.10
Crystal system	orthorhombic
Space group	*P* 2_1 2_1 2_1
a, Å	9.3576(3)
b, Å	9.4918(3)
c, Å	20.6459(7)
α, °	90
β, °	90
γ, °	90
Cell volume, $Å^3$	1833.78(10)
Z ; Z’	4 ; 2
T, K	100(1)
Radiation type ; wavelength Å	CuKα ; 1.54178
F_{000}	736
μ, mm^{-1}	1.533
range, °	4.283 - 68.330
Reflection collected	23 674
Reflections unique	3 363
R_{int}	0.0297
GOF	1.091
Refl. obs. (I>2(I))	3 332
Parameters	213
wR_2 (all data)	0.0622
R value (I>2(I))	0.0243
Flack parameter [4]	0.031(4)
Largest diff. peak and hole (e-.$Å^{-3}$)	0.191 ; -0.313

1) Sheldrick, G. M. SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Göttingen, Germany, 1997.

2) G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., 2008, 64, 112-122

3) Farrugia, L. J. J. Appl. Cryst., 1999, 32, 837.

4) G. Bernardinelli and H. D. Flack, Acta Crystallogr., Sect. A: Found. Crystallogr., 1985, 41, 500-511.



X-ray diffraction data for compound **C3**•HCl were collected by using Rigaku XtaLab Synergy-S using a CuKα radiation source. Crystals were flashfrozen in a nitrogen-gas stream at 100K. The structure was solved by using the Crystal Structure crystallographic software package Olex2.

The crystal data collection and refinement parameters are given in Table S2. CCDC 2108751 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/Community/.

Table S2. *Crystallographic data* ***C3***.

Compound	**C3**
CCDC	2108751
Empirical Formula	C_{51} H_{46} F_{12} N_7 S_2 Cl
Crystal system	Triclinic
Space group	*P* 1
a, Å	9.28710(10)
b, Å	14.25610(10)
c, Å	22.5780(2)
α, °	105.5400(10)
β, °	90.7230(10)
γ, °	90.9620(10)
Cell volume, Å^3	2879.14
Z ; Z’	2 ; 0
T, K	100.15