

Chiral Lithium Amide Mediated Desymmetrization of 3-Substituted Cyclobutanone

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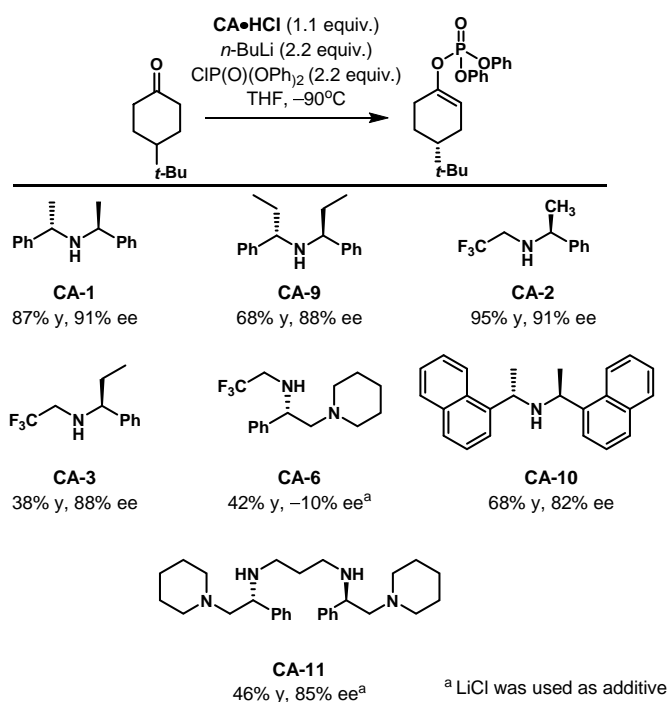
Supporting Information

1. Lithium Chiral amide mediated deprotonation of 4- <i>tert</i> -butylcyclohexanone	S2
2. Experiment procedure and characterization data	S3
3. Copies of ^1H , ^{13}C NMR spectra and HPLC traces	S33

General Information.

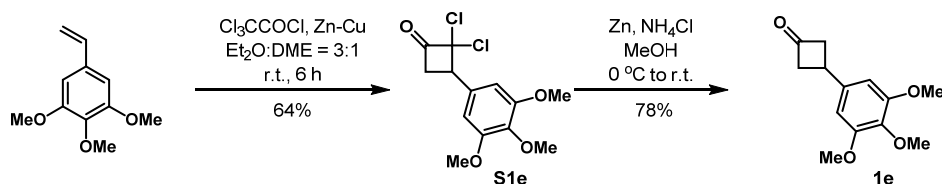
All reactions were carried out under an inert atmosphere of dry argon in oven or flame-dried glassware, unless the reaction procedure states otherwise. Tetrahydrofuran (THF), toluene and ether (diethyl ether) were distilled from sodium-benzophenone in a continuous still under an atmosphere of argon. Dichloromethane and triethylamine were distilled from calcium hydride in a continuous still under an atmosphere of argon. Reaction temperatures were controlled by Heidolph MR Hei-Standard. Analytical thin-layer chromatography (TLC) was performed using pre-coated TLC plates and visualized using combinations of UV, anisaldehyde, ceric ammonium molybdate (CAM), potassium permanganate, and iodine staining. Flash column chromatography was performed using 300-400 mesh silica gel (Huanghai, Shandong) as the stationary phase. Proton nuclear magnetic resonance spectra were recorded at Agilent-400 MHz spectrometer and Bruker-400 MHz spectrometer, in relative to the solvent residual signal (7.26 ppm) in CDCl₃. Carbon nuclear magnetic resonance spectra were recorded at Agilent-100 MHz spectrometer and Bruker-100 MHz spectrometer, in relative to the signal of CDCl₃ (77.0 ppm). Optical Rotations were measured on a Rudolph Autopol III S2 polarimeter. The enantiomeric excess (ee) of the products was determined by chiral stationary phase HPLC (SHIMADZU LC 20AB and Daicel Chiralpak columns). The temperature -90 °C was maintained using liquid nitrogen/methanol cooling bath. EA = ethyl acetate; PE = petroleum ether; DCM = dichloromethane

1. Lithium Chiral amide mediated deprotonation of 4-*tert*-butylcyclohexanone



2. Experiment procedure and characterization data

a) Synthesis of Cyclobutanone 1:



General procedure A:

3-(3,4,5-Trimethoxyphenyl)cyclobutan-1-one (**1e**)

a) A flame-dried 250 mL round-bottom flask was charged with 3,4,5-trimethoxy styrene (7.80 g, 40.2 mmol), Zn-Cu coupling (8.04 g, 0.123 mol), 150 mL of Et_2O and 50 mL of DME. Then Cl_3CCOCl (9.20 mL, 14.9 g, 82.0 mmol) was added dropwise at room temperature. After stirring overnight, the reaction mixture was filtered through a pad of celite, and rinsed with 100 mL of Et_2O . The filtrate was treated with a cold aqueous solution of HCl (1 M, 100 mL) and extracted with EA twice. The combined organic phase was washed sequentially with a saturated solution of NaHCO_3 , brine, dried over Na_2SO_4 , concentrated, and purified by column chromatography on silica gel (PE:EA = 95:5) to afford the product **S1e** (7.80 g, 25.6 mmol, 64% yield) as a yellow solid, which was directly submitted to next step without further characterization. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 6.49 (s, 2H), 4.17 (t, $J = 10.3$ Hz, 1H), 3.90 (s, 6H), 3.88 (s, 3H), 3.72-3.61 (m, 1H), 3.60-3.49 (m, 1H).

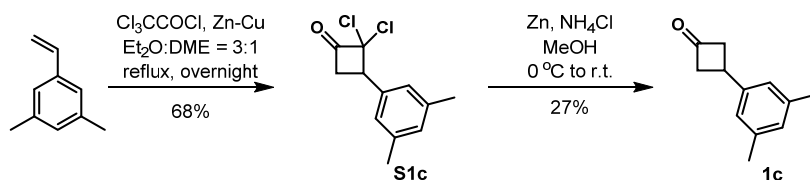
b) To a solution of **S1e** (7.80 g, 25.6 mmol) in MeOH (180 mL) was added NH_4Cl (13.8 g, 0.257 mol), zinc dust (10.1 g, 0.154 mol) sequentially at 0°C. After stirring for 6 h at room temperature, the reaction mixture was filtered through a pad of celite, and rinsed with EA. The filtrate was concentrated under vacuum. Then water was added, the aqueous phase was extracted with EA three times. The combined organic phase was washed with brine, dried over Na_2SO_4 , concentrated, and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the product **1e** (4.73 g, 20.0 mmol, 78% yield) as a white solid.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 6.49 (s, 2H), 3.87 (s, 6H), 3.83 (s, 3H), 3.71-3.57 (m, 1H), 3.55-3.42 (m, 2H), 3.31-3.16 (m, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 206.59, 153.38, 139.29, 136.73, 103.47, 60.86, 56.15, 54.69, 28.81.

IR (neat, cm^{-1}): 3013, 2990, 2978, 2970, 2946, 2920, 2835, 1788, 1771, 1586, 1511, 1469, 1457, 1422, 1370, 1345, 1317, 1237, 1188, 1153, 1126, 1103, 1107.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{13}\text{H}_{16}\text{O}_4$, 236.1043; found, 236.1041.



3-(3,5-Dimethylphenyl)cyclobutan-1-one (**1c**)

a) The substrate **S1c** was prepared according to **General Procedure A**; using 3,5-dimethylstyrene (1.29 g, 9.77 mmol), Zn-Cu (1.28 g, 19.6 mmol), CCl_3COCl (2.66 g, 14.7 mmol), Et_2O (30 mL) and DME (10 mL); flash chromatography on silica gel (PE:EA = 98:2) provided **S1c** (1.60 g, 8.37 mmol, 67% yield) as a yellow oil. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.01 (s, 1H), 6.91 (s, 2H), 4.17 (t, $J = 10.3$ Hz, 1H), 3.70 (dd, $J = 17.6, 10.4$ Hz, 1H), 3.51 (dd, $J = 17.6, 10.2$ Hz, 1H), 2.36 (s, 6H).

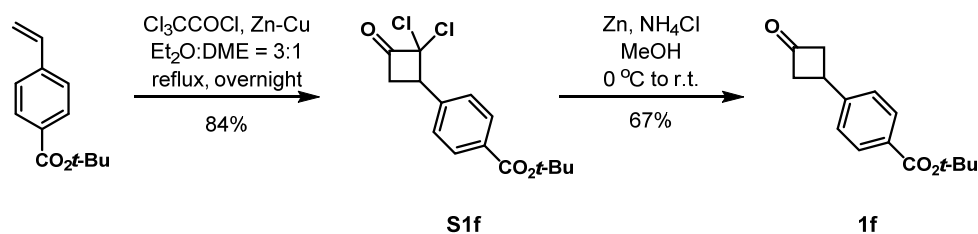
b) The substrate **1c** was prepared according to **General Procedure A**; using **S1c** (1.60 g, 6.58 mmol), NH_4Cl (3.52 g, 65.8 mmol), Zn (2.58 g, 39.5 mmol) and MeOH (15 mL); flash chromatography on silica gel (PE:EA = 95:5) provided **1c** (0.304 g, 1.74 mmol, 27% yield) as a colorless oil.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 6.93 (s, 2H), 6.91 (s, 1H), 3.71-3.53 (m, 1H), 3.53-3.38 (m, 2H), 3.29-3.19 (m, 2H), 2.33 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 207.21, 143.54, 138.28, 128.24, 124.28, 54.63, 28.22, 21.29.

IR (neat, cm^{-1}): 3020, 2949, 2919, 1784, 1604, 1473, 1458, 1380, 1341, 1261, 1199, 1172, 1154, 1109.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{12}\text{H}_{14}\text{O}$, 174.1039; found, 174.1040.



tert-Butyl 4-(3-oxocyclobutyl)benzoate (**1f**)

a) The substrate **S1f** was prepared according to **General Procedure A**; using 4-*t*-butyloxycarbonylstyrene (2.04 g, 10.0 mmol), Zn-Cu (1.95 g, 30.0 mmol), CCl_3COCl (5.45 g, 30.0 mmol), Et_2O (30 mL) and DME (10 mL); flash chromatography on silica gel (PE:EA = 98:2) provided **S1f** (2.64 g, 8.37 mmol, 84% yield) as a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.03 (dd, $J = 10.5, 8.9$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 4.29 (t, $J = 10.3$ Hz, 1H), 3.74 (dd, $J = 17.6, 10.4$ Hz, 1H), 3.58 (dd, $J = 17.6, 10.2$ Hz, 1H), 1.60 (s, 9H).

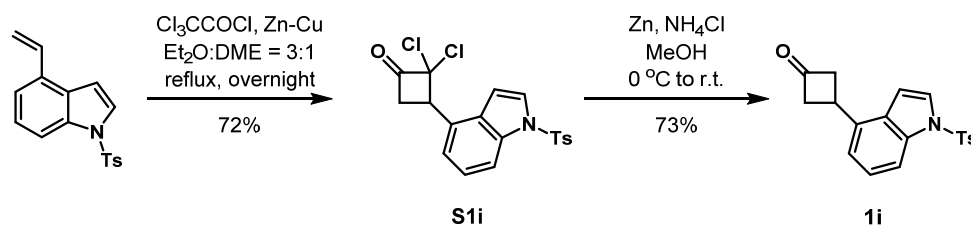
b) The substrate **1f** was prepared according to **General Procedure A**; using **S1f** (2.64 g, 8.37 mmol), NH₄Cl (10.1 g, 87.0 mmol), Zn (3.28 g, 50.4 mmol) and MeOH (20 mL); flash chromatography on silica gel (PE:EA = 95:5) provided **1f** (1.39 g, 5.65 mmol, 67% yield) as a colorless oil.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.97 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 3.80-3.67 (m, 1H), 3.62-3.45 (m, 2H), 3.33-3.18 (m, 2H), 1.59 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 205.83, 165.41, 148.18, 130.52, 129.85, 126.34, 81.01, 54.66, 28.48, 28.16.

IR (neat, cm⁻¹): 3003, 2981, 2970, 2932, 2908, 2869, 1783, 1703, 1607, 1479, 1458, 1422, 1391, 1367, 1312, 1295, 1252, 1203, 1159, 1115, 1099, 1018, 1003.

HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₁₅H₁₉O₃, 247.1329; found, 247.1328.



3-(1-Tosyl-1*H*-indol-4-yl)cyclobutan-1-one (**1i**)

a) The substrate **S1i** was prepared according to **General Procedure A**; using 1-tosyl-4-vinyl-1*H*-indole (1.77 g, 5.92 mmol), Zn-Cu (1.15 g, 17.7 mmol), CCl₃COCl (3.22 g, 17.7 mmol), Et₂O (20 mL) and DME (7 mL); flash chromatography on silica gel (PE:EA = 10:1) provided **S1i** (1.76 g, 4.31 mmol, 72% yield) as a yellow solid. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.01 (t, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.66 (dd, *J* = 7.1, 2.7 Hz, 1H), 7.35 (dt, *J* = 16.4, 8.1 Hz, 1H), 7.28-7.23 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.94 (dd, *J* = 3.8, 0.7 Hz, 1H), 4.58-4.47 (m, 1H), 3.89 (dd, *J* = 17.9, 10.3 Hz, 1H), 3.64-3.43 (m, 1H), 2.36 (s, 3H).

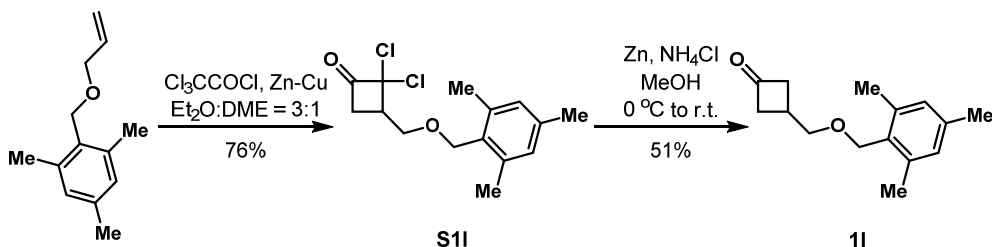
b) The substrate **1i** was prepared according to **General Procedure A**; using **S1i** (1.76 g, 4.31 mmol), NH₄Cl (2.30 g, 43.0 mmol), Zn (1.68 g, 25.8 mmol) and MeOH (15 mL); flash chromatography on silica gel (PE:EA = 3:1) provided **1i** (1.07 g, 3.15 mmol, 73% yield) as a colorless foam.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.91 (d, *J* = 8.3 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.62 (t, *J* = 6.2 Hz, 1H), 7.31 (t, *J* = 7.9 Hz, 1H), 7.27-7.20 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 3.7 Hz, 1H), 3.98-3.86 (m, 1H), 3.60-3.47 (m, 2H), 3.43-3.25 (m, 2H), 2.34 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 206.37, 145.06, 135.82, 135.20, 134.80, 129.92, 129.24, 126.87, 126.23, 124.69, 119.73, 112.11, 106.82, 53.68, 26.29, 21.56.

IR (neat, cm^{-1}): 3143, 3118, 3063, 3033, 2979, 2923, 1780, 1733, 1596, 1527, 1484, 1422, 1371, 1361, 1283, 1179, 1163, 1129, 1089, 1038, 1017.

HRMS-EI (m/z): $[M]^+$ calcd. for $\text{C}_{19}\text{H}_{17}\text{NO}_3\text{S}$, 339.0924; found, 339.0922.



3-(((2,4,6-Trimethylbenzyl)oxy)methyl)cyclobutan-1-one (**11**)

a) The substrate **S11** was prepared according to **General Procedure A**; using 3-(((2,4,6-trimethylbenzyl)oxy)methyl)cyclobutan-1-ol (7.40 g, 39.0 mmol), Zn-Cu (7.60 g, 65.4 mmol), CCl_3COCl (14.2 g, 0.078 mmol), Et_2O (100 mL) and DME (30 mL); flash chromatography on silica gel (PE:EA = 15:1) provided **S11** (8.96 g, 29.7 mmol, 76% yield) as a yellow solid. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 6.86 (s, 2H), 4.57 (s, 2H), 3.87 (dd, $J = 9.9, 6.4$ Hz, 1H), 3.74-3.60 (m, 1H), 3.46-3.37 (m, 1H), 3.22-3.04 (m, 2H), 2.36 (s, 6H), 2.26 (s, 3H).

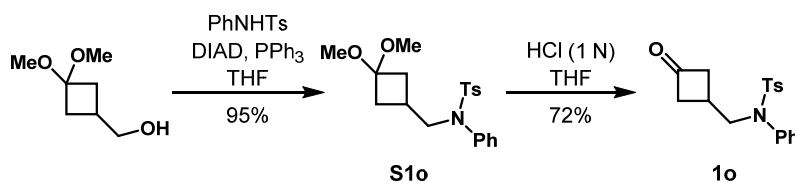
b) The substrate **11** was prepared according to **General Procedure A**; using **S11** (8.96 g, 29.7 mmol), NH_4Cl (16.0 g, 0.300 mol), Zn (11.8 g, 0.182 mol) and MeOH (100 mL); flash chromatography on silica gel (PE:EA = 10:1) provided **11** (3.55 g, 15.3 mmol, 51% yield) as a white solid.

^1H NMR (400 MHz, CDCl_3) δ (ppm): 6.86 (s, 2H), 4.56 (d, $J = 8.5$ Hz, 2H), 3.86 (dt, $J = 18.4, 9.2$ Hz, 2H), 3.75-3.65 (m, 2H), 3.51-3.33 (m, 2H), 3.23-3.02 (m, 1H), 2.35 (s, 6H), 2.26 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 207.61, 137.72, 137.68, 130.92, 128.98, 72.91, 67.10, 50.06, 23.65, 20.94, 19.53.

IR (neat, cm^{-1}): 3055, 2970, 2915, 2872, 1778, 1611, 1582, 1434, 1379, 1358, 1317, 1266, 1214, 1146, 1108, 1083, 1031, 1016.

HRMS-ESI (m/z): $[\text{M}+\text{NH}_4]^+$ calcd. for $\text{C}_{15}\text{H}_{24}\text{NO}_2$, 250.1802; found, 250.1798.



4-Methyl-N-((3-oxocyclobutyl)methyl)-N-phenylbenzenesulfonamide (**1o**)

A flame-dried 250 mL round-bottom flask was charged with (3,3-dimethoxycyclobutyl)methanol (1.32 g, 8.90 mol), phenyl toluenesulfonamide (2.65 g, 10.7 mmol), PPh₃ (2.83 g, 10.7 mmol) and 50 mL of THF. DIAD (2.10 mL, 2.16 g, 10.7 mmol) was added dropwise at 0 °C. After stirring for 17 h, the reaction mixture was concentrated, diluted with PE and Et₂O (1:1, 50 mL) and stirred for 10 min. The resultant mixture was filtered through a pad of celite, and rinsed with PE and Et₂O. The filtrate was then concentrated under vacuum, and purified by column chromatography on silica gel (PE:EA = 5:1) to afford **S1o** (3.18 g, 8.47 mmol, 95% yield) as a colorless oil, which was directly submitted to next step without further characterization. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.50-7.42 (m, 2H), 7.31-7.26 (m, 3H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.03-6.94 (m, 2H), 3.59 (d, *J* = 7.3 Hz, 2H), 3.09 (s, 3H), 3.07 (s, 3H), 2.41 (s, 3H), 2.18-2.00 (m, 3H), 1.84-1.74 (m, 2H).

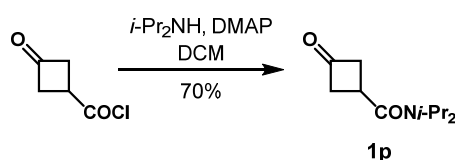
b) To a solution of **S1o** (3.18 g, 8.47 mmol) in 40 mL THF was added 2 M aqueous solution of HCl (85 mL, 85.0 mmol). After stirring for 6 h at room temperature, the solvent was removed under vacuum. A saturated aqueous solution of NaHCO₃ was added until pH=7, the aqueous phase was extracted with EA three times. The combined organic phase was washed with brine, dried over Na₂SO₄, concentrated, and purified by column chromatography on silica gel (PE:EA = 5:1) to afford the product **1o** (2.01 g, 6.10 mmol, 72% yield) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.47 (d, *J* = 8.3 Hz, 1H), 7.37-7.30 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 3H), 7.07-6.99 (m, 2H), 3.73 (d, *J* = 7.7 Hz, 2H), 3.09-2.95 (m, 2H), 2.89-2.75 (m, 2H), 2.52-2.45 (m, 2H), 2.43 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 206.05, 143.63, 138.98, 135.00, 129.46, 129.20, 128.78, 128.27, 127.63, 55.07, 50.64, 22.89, 21.51.

IR (neat, cm⁻¹): 2967, 2901, 1786, 1593, 1488, 1475, 1451, 1394, 1377, 1339, 1309, 1230, 1161, 1100, 1089, 1049, 1026, 1011.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₁₈H₁₉NO₃S, 329.1080; found, 329.1078.



***N,N*-Diisopropyl-3-oxocyclobutane-1-carboxamide (1p)**

A flame-dried 250 mL round-bottom flask was charged with 3-oxocyclobutane-1-carbonyl chloride (10.0 g, 75.5 mmol), DMAP (0.922 g, 7.55 mmol) and DCM (80 mL). *i*-Pr₂NH (60.0 mL, 38.8 g, 0.383 mol) was added dropwise under 0 °C. The resultant mixture was allowed to stir at room temperature for 20 h. Then the

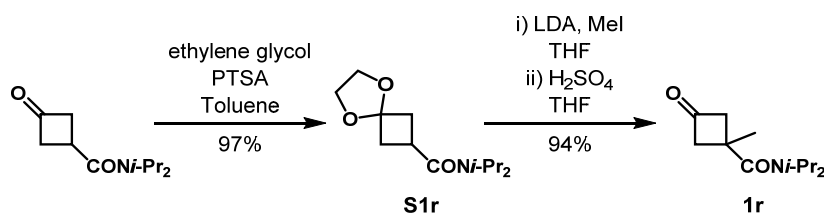
mixture was quenched with water (100 mL), the resultant was extracted with DCM. The combined organic phase was washed with brine, dried over Na₂SO₄, to afford **1p** (11.4 g, 57.8 mmol, 77% yield) as a faint yellow solid.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 4.02-3.88 (m, 1H), 3.57-3.39 (m, 3H), 3.31-3.18 (m, 1H), 3.15-3.03 (m, 2H), 1.36 (d, *J* = 6.8 Hz, 6H), 1.19 (d, *J* = 6.7 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 204.87, 170.72, 50.65, 48.35, 45.86, 27.28, 20.97, 20.45.

IR (neat, cm⁻¹): 2976, 2941, 2922, 2915, 2888, 1779, 1619, 1504, 1472, 1445, 1370, 1352, 1324, 1293, 1265, 1209, 1202, 1141, 1121, 1103, 1049, 1030.

HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₁₁H₂₀NO₂, 198.1489; found, 198.1487.



N,N-Diisopropyl-1-methyl-3-oxocyclobutane-1-carboxamide (**1r**)

a) To a round-bottom flask was charged with *N,N*-diisopropyl-3-oxocyclobutane-1-carboxamide (2.00 g, 10.1 mmol), ethylene glycol (0.9 mL, 0.943 g, 15.2 mmol), *p*-toluenesulfonic acid monohydrate (9.63 mg, 5.07 mmol) and toluene (50 mL). The flask was fitted with a Dean Stark trap and the reaction was heated to reflux for 10 h. The resultant mixture was cooled down to room temperature, diluted with water, and the aqueous phase was extracted with DCM. The combined organic phase was dried over Na₂SO₄, concentrated, and purified by column chromatography on silica gel (PE:EA = 4:1) to afford the product **S1r** (2.52 g, 9.87 mmol, 97% yield) as a yellow oil, which was directly submitted to next step without further characterization. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 3.97-3.80 (m, 5H), 2.93 (p, *J* = 8.8 Hz, 1H), 2.71-2.61 (m, 2H), 2.44-2.33 (m, 2H), 1.37 (d, *J* = 6.8 Hz, 6H), 1.28-1.19 (m, 1H), 1.15 (d, *J* = 6.7 Hz, 6H).

b) A flame-dried 500 mL round-bottom flask was charged with *i*-Pr₂NH (7.4 mL, 5.34 g, 52.8 mmol) and THF (140 mL), and *n*-BuLi (2.28 M, 21.9 mL, 49.9 mmol) was added dropwise under -78 °C. The reaction mixture was stirred for 1 h before **S1r** (6.00 g, 24.9 mmol) in THF (60 mL) was added dropwise. The reaction was stirred at the same temperature for 1 h before warmed to 0 °C. After additional 1 h, the mixture was then again cooled down to -78 °C. MeI (7.8 mL, 17.8 g, 0.125 mol) was then added dropwise. After stirring for 0.5 h at -78 °C and 1 h at 0 °C, the reaction was quenched with a saturated aqueous solution of NH₄Cl, and extracted

with DCM. The combined organic phase was concentrated, and directly submitted to next step without purification.

c) The resultant crude product above was dissolved in THF (100 mL) in a 100 mL round-bottom flask, an aqueous solution of H₂SO₄ (1.0 M, 100 mL, 0.100 mol) was added at 0 °C. The resultant mixture was stirred for 0.5 h before warmed to room temperature. After 20 h, the reaction mixture was extracted with DCM, the combined organic phase was washed with a saturated aqueous solution of NaHCO₃ and brine sequentially, dried over Na₂SO₄, concentrated, and purified by column chromatography on silica gel (PE:EA = 10:1) to afford the product **2r** (4.98 g, 23.4 mmol, 94% yield) as a faint yellow solid.

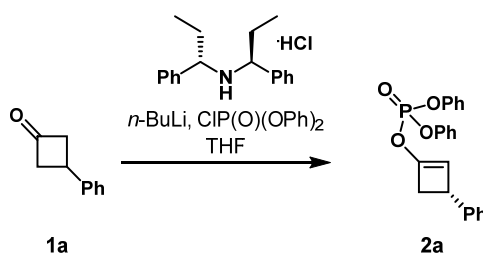
¹H NMR (400 MHz, CDCl₃) δ (ppm): 3.77-3.65 (m, 1H), 3.62-3.53 (m, 2H), 3.36-3.22 (m, 1H), 2.81-2.68 (m, 2H), 1.48 (s, 3H), 1.37 (d, *J* = 6.8 Hz, 6H), 1.17 (d, *J* = 6.6 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 206.27, 173.23, 57.10, 49.12, 46.33, 35.79, 24.58, 20.57, 20.40.

IR (neat, cm⁻¹): 3022, 2999, 2966, 2935, 2877, 1782, 1619, 1470, 1460, 1438, 1373, 1333, 1238, 1213, 1189, 1168, 1135, 1116, 1039.

HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₁₂H₂₂NO₂, 212.1645; found, 212.1643.

b) Synthesis of Cyclobutene 2:



General Procedure B :

(R)-Diphenyl (3-phenylcyclobut-1-en-1-yl) phosphate (2a)

A flame-dried 25 mL Schlenk tube was charged with hydrochloride salt of chiral amine CA-9·HCl (0.127 g, 0.440 mmol) and THF (1.2 mL). The resultant was cooled down to -78 °C, and *n*-BuLi (2.28 M in hexane, 0.39 mL, 0.880 mmol) was added dropwise. The mixture was stirred for 5 min before warmed to room temperature. The mixture was then stirred for additional 15 min until the solution became clear. Then the reaction was cooled down to -90 °C, and a solution of 3-phenylcyclobutan-1-one (58.5 mg, 0.400 mmol) in THF (0.5 mL + 0.3 mL + 0.2 mL) was added over 0.5 h. After stirring for additional 30 min, CIP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol) was added dropwise over 10 min. The reaction mixture was then stirred for

0.5 h at $-90\text{ }^{\circ}\text{C}$ before warmed to $-78\text{ }^{\circ}\text{C}$. After further 3.5 h, the reaction was quenched with THF-MeOH (3:1, 0.4 mL), and followed by 2 M aqueous solution of HCl. The resultant was extracted with ethyl acetate, and the combined organic phase was washed with a saturated aqueous solution of NaHCO_3 and brine sequentially, dried over Na_2SO_4 , concentrated, and purified by column chromatography on silica gel (PE:EA = 10:1) to afford the product **2a** (0.115 g, 0.308 mmol, 76% yield) as a colorless oil.

Ee: 94% (Chiralcel® OJ-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; $t_1=14.2\text{ min}$ (major); $t_2=16.2\text{ min}$ (minor).

$[\alpha]_{\text{D}}^{18}$ 7.58 (c 0.81, CHCl_3).

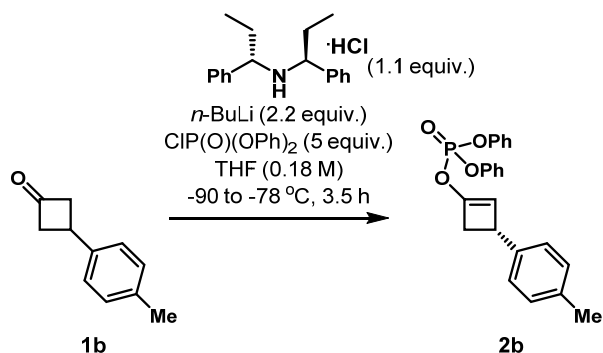
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.46–7.36 (m, 4H), 7.36–7.22 (m, 11H), 5.47 (s, 1H), 3.75–3.67 (m, 1H), 3.33 (dd, $J = 13.3, 4.5\text{ Hz}$, 1H), 2.64 (d, $J = 13.3\text{ Hz}$, 1H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ (ppm): 150.25 (d, $J = 7.3\text{ Hz}$), 142.06 (d, $J = 9.8\text{ Hz}$), 142.06, 129.88, 128.36, 126.60, 126.54, 125.68, 120.02 (d, $J = 4.8\text{ Hz}$), 120.01 (d, $J = 5.0\text{ Hz}$), 113.81 (d, $J = 7.8\text{ Hz}$), 42.90 (d, $J = 5.6\text{ Hz}$), 37.76.

$^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ (ppm): -18.16 .

IR (neat, cm^{-1}): 3062, 3028, 2970, 2931, 1645, 1630, 1589, 1300, 1180, 1161.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{22}\text{H}_{19}\text{O}_4\text{P}$, 378.1015; found, 378.1009.



(*R*)-Diphenyl (3-(*p*-tolyl)cyclobut-1-en-1-yl) phosphate (**2b**)

According to **General Procedure B**, using **1b** (64.0 mg, 0.400 mmol), CA-9·HCl (0.127 g, 0.440 mmol), *n*-BuLi (2.25 M in hexane, 0.39 mL, 0.880 mmol) and CIP(O)(OPh)_2 (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 5:1) afforded **2b** (0.155 g, 0.332 mmol, 85% yield) as a colorless oil. Ee: 93% (Chiralcel® OD-H; 5% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; $t_1=10.5\text{ min}$ (major); $t_2=11.8\text{ min}$ (minor).

$[\alpha]_{\text{D}}^{25}$ 11.44 (c 0.50, CHCl_3).

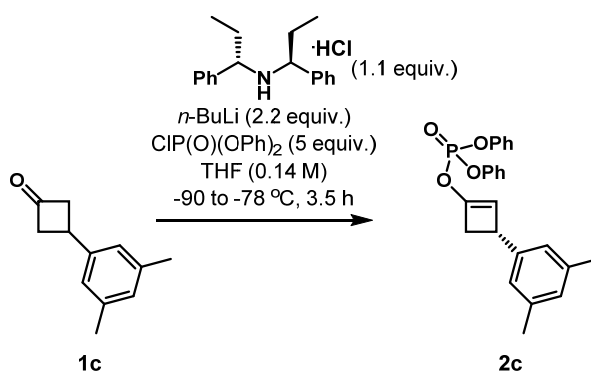
^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.41-7.32 (m, 4H), 7.30-7.19 (m, 7H), 7.15-7.02 (m, 3H), 5.40 (s, 1H), 3.64 (d, $J = 3.4$ Hz, 1H), 3.27 (ddd, $J = 13.2, 4.5, 1.5$ Hz, 1H), 2.57 (d, $J = 13.2$ Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 150.29 (d, $J = 7.3$ Hz), 141.98 (d, $J = 9.9$ Hz), 139.04, 136.19, 129.89, 129.06, 126.46, 125.68, 120.05 (d, $J = 4.9$ Hz), 120.04 (d, $J = 5.0$ Hz), 113.97 (d, $J = 7.8$ Hz), 42.99 (d, $J = 5.6$ Hz), 37.47, 21.02.

^{31}P NMR (162 MHz, CDCl_3) δ (ppm): -18.19.

IR (neat, cm^{-1}): 3070, 3044, 3014, 2973, 2941, 2990, 2837, 1786, 1716, 1645, 1631, 1590, 1488, 1310, 1219, 1812, 1611, 1025, 1009.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{23}\text{H}_{21}\text{O}_4\text{P}$, 392.1172; found, 392.1167.



(R)-3-(3,5-Dimethylphenyl)cyclobut-1-en-1-yl diphenyl phosphate (**2c**)

According to **General Procedure B**, using **1c** (47.4 mg, 0.272 mmol), CA-9-HCl (96.0 mg, 0.33 mmol), $n\text{-BuLi}$ (2.25 M in hexane, 0.29 mL, 0.66 mmol) and ClP(O)(OPh)_2 (0.31 mL, 0.40 g, 1.50 mmol); flash chromatography on silica gel (PE:EA = 95:5) afforded **2c** (97.4 mg, 0.240 mmol, 88% yield) as a colorless oil. Ee: 93% (Chiralcel® OJ-H; 10% $i\text{-PrOH}$ in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; $t_1=7.0$ min (major); $t_2=8.2$ min (minor).

$[\alpha]_D^{24}$ 8.70 (c 1.0, CHCl_3).

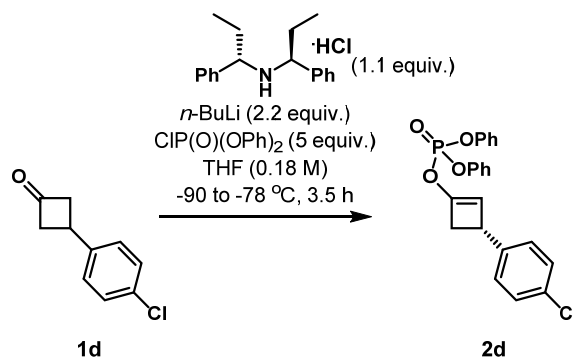
^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.45-7.30 (m, 4H), 7.30-7.17 (m, 6H), 6.85 (s, 3H), 5.41 (s, 1H), 3.63-3.59 (m, 1H), 3.26 (ddd, $J = 13.2, 4.5, 1.5$ Hz, 1H), 2.59 (d, $J = 13.2$ Hz, 1H), 2.28 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 150.27 (d, $J = 7.3$ Hz), 142.00, 141.87 (d, $J = 9.9$ Hz), 137.91, 129.87, 128.27, 125.67, 124.34, 120.02 (d, $J = 4.9$ Hz), 120.01 (d, $J = 4.9$ Hz), 113.89 (d, $J = 7.8$ Hz), 42.82 (d, $J = 5.6$ Hz), 37.64, 21.22.

^{31}P NMR (162 MHz, CDCl_3) δ (ppm): -18.20.

IR (neat, cm^{-1}): 3072, 3043, 3013, 2973, 2943, 2910, 2835, 1786, 1716, 1646, 1631, 1590, 1489, 1313, 1302, 1219, 1184, 1161, 1051, 1026, 1010.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{24}\text{H}_{23}\text{O}_4\text{P}$, 407.1407; found, 407.1406.



(R)-3-(4-Chlorophenyl)cyclobut-1-en-1-yl diphenyl phosphate (2d)

According to **General Procedure B**, using **1d** (76.0 mg, 0.421 mmol), CA-9·HCl (0.127 g, 0.440 mmol), $n\text{-BuLi}$ (2.25 M in hexane, 0.39 mL, 0.880 mmol) and CIP(O)(OPh)_2 (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 95:5) afforded **2d** (0.132 g, 0.320 mmol, 80% yield) as a colorless oil. Ee: 93% (Chiralcel® OJ-H; 10% $i\text{-PrOH}$ in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; $t_1=18.0$ min (major); $t_2=26.4$ min (minor).

$[\alpha]_D^{25}$ 12.74 (c 1.0, CHCl_3).

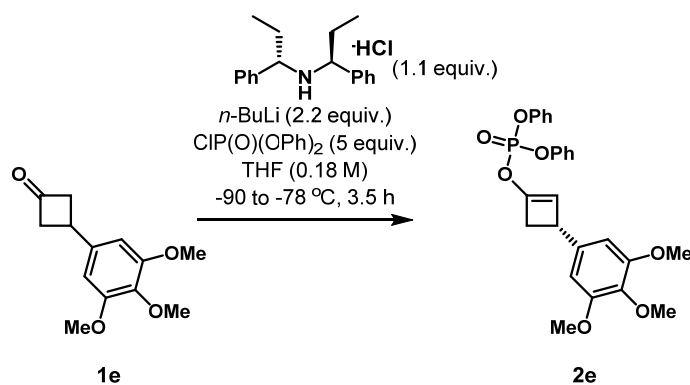
^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.37 (t, $J = 7.9$ Hz, 4H), 7.32-7.19 (m, 8H), 7.17-7.11 (d, $J = 8.4$ Hz, 2H), 5.38 (s, 1H), 3.64 (d, $J = 3.7$ Hz, 1H), 3.28 (ddd, $J = 13.3, 4.5, 1.4$ Hz, 1H), 2.54 (d, $J = 13.3$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 150.23 (d, $J = 7.2$ Hz), 142.35 (d, $J = 9.7$ Hz), 140.61, 132.27, 129.92, 128.49, 127.93, 125.75, 120.02 (d, $J = 5.0$ Hz), 120.01 (d, $J = 5.1$ Hz), 113.48 (d, $J = 7.9$ Hz), 42.95 (d, $J = 5.7$ Hz), 37.20.

^{31}P NMR (162 MHz, CDCl_3) δ (ppm): -18.21 .

IR (neat, cm^{-1}): 3070, 2974, 2941, 2899, 2839, 1786, 1716, 1646, 1631, 1590, 1489, 1409, 1312, 1300, 1181, 1161, 1090, 1026, 1010.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{22}\text{H}_{18}\text{ClO}_4\text{P}$, 413.0704; found, 413.0700.



(R)-Diphenyl (3-(3,4,5-trimethoxyphenyl)cyclobut-1-en-1-yl) phosphate (2e)

According to **General Procedure B**, using **1e** (95.0 mg, 0.400 mmol), CA-9·HCl (0.127 g, 0.440 mmol), *n*-BuLi (2.28 M in hexane, 0.39 mL, 0.880 mmol) and CIP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 5:1) afforded **2e** (0.136 g, 0.290 mmol, 73% yield) as a colorless oil. Ee: 88% (Chiralcel® OZ-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t₁=43.8 min (major); t₂=51.6 min (minor)).

[α]_D²² 1.54 (c 1.0, CHCl₃).

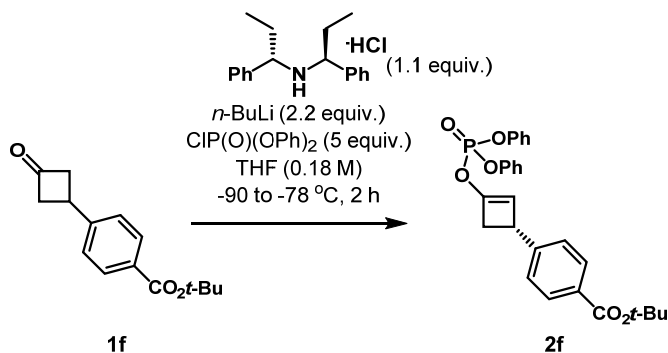
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.37 (t, *J* = 7.8 Hz, 4H), 7.29-7.20 (m, 6H), 6.47 (s, 2H), 5.42 (s, 1H), 3.82 (s, 3H), 3.81 (s, 6H), 3.63 (s, 1H), 3.32-3.23 (m, 1H), 2.61 (d, *J* = 13.2 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 153.26, 150.26 (d, *J* = 7.2 Hz), 142.35 (d, *J* = 9.8 Hz), 137.94, 136.70, 129.91, 125.74, 119.99 (d, *J* = 4.9 Hz), 119.98 (d, *J* = 5.0 Hz), 113.69 (d, *J* = 7.7 Hz), 103.37, 60.82, 56.04, 43.09 (d, *J* = 5.5 Hz), 38.13.

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -18.16.

IR (neat, cm⁻¹): 3077, 2972, 2940, 2911, 2840, 1783, 1645, 1631, 1588, 1506, 1488, 1457, 1418, 1342, 1313, 1301, 1234, 1183, 1162, 1123, 1025, 1009.

HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₂₅H₂₆O₇P, 469.1411; found, 469.1403.



***tert*-Butyl (R)-4-(3-((diphenoxyphosphoryl)oxy)cyclobut-2-en-1-yl)benzoate (2f)**

According to **General Procedure B**, using **1f** (98.5 mg, 0.400 mmol), CA-9·HCl (0.127 g, 0.440 mmol), *n*-

BuLi (2.25 M in hexane, 0.39 mL, 0.880 mmol) and ClP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 5:1) afforded **2f** (0.159 g, 0.332 mmol, 83% yield) as a colorless oil. Ee: 90% (Chiralcel® OD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t₁=20.5 min (major); t₂=23.9 min (minor).

[α]_D²² 12.57 (c 0.81, CHCl₃).

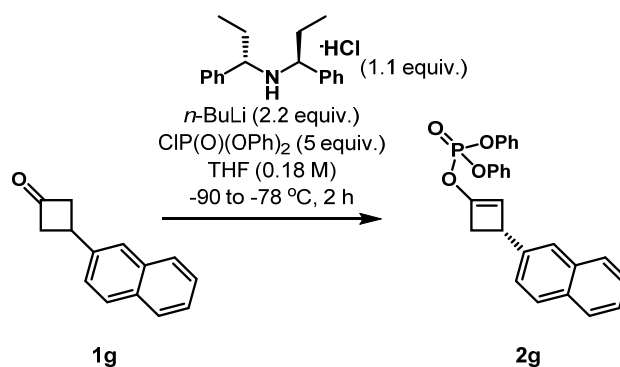
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.90 (d, *J* = 8.3 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 4H), 7.30-7.20 (m, 8H), 5.42 (s, 1H), 3.76-3.67 (m, 1H), 3.31 (ddd, *J* = 13.3, 4.5, 1.5 Hz, 1H), 2.57 (d, *J* = 13.3 Hz, 1H), 1.59 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 165.62, 150.22 (d, *J* = 7.1 Hz), 150.18, 146.96, 142.35 (d, *J* = 9.7 Hz), 130.47, 129.91, 129.57, 126.39, 125.75, 120.01 (d, *J* = 5.0 Hz), 120.00 (d, *J* = 4.9 Hz), 113.40 (d, *J* = 7.8 Hz), 80.83, , 42.82 (d, *J* = 5.8 Hz), 37.69, 28.17.

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -18.21.

IR (neat, cm⁻¹): 3070, 3005, 2976, 2932, 1708, 1645, 1631, 1590, 1488, 1456, 1415, 1392, 1368, 1309, 1291, 1220, 1182, 1161, 1115, 1102, 1082, 1025, 1009.

HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₂₇H₂₇O₆P, 479.1618; found, 479.1613.



(*R*)-3-(Naphthalen-2-yl)cyclobut-1-en-1-yl diphenyl phosphate (**2g**)

According to **General Procedure B**, using **1g** (78.5 mg, 0.400 mmol), CA-9·HCl (0.127 g, 0.440 mmol), *n*-BuLi (2.25 M in hexane, 0.39 mL, 0.880 mmol) and ClP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 10:1) afforded **2g** (0.134 g, 0.313 mmol, 78% yield) as a colorless oil. Ee: 92% (Chiralcel® OJ-H; 40% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t₁=20.8 min (major); t₂=26.3 min (minor).

[α]_D²⁶ 19.54 (c 1.0, CHCl₃).

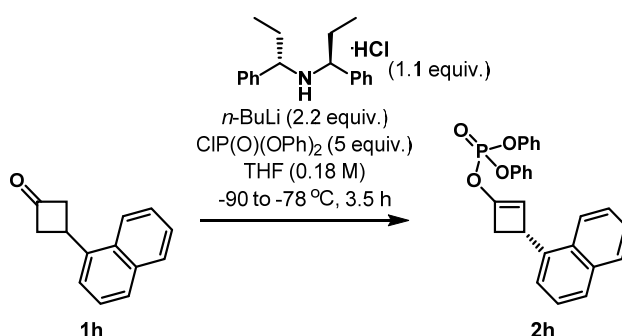
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.82-7.73 (m, 3H), 7.66 (s, 1H), 7.48-7.19 (m, 13H), 5.51 (s, 1H), 3.87-3.81 (m, 1H), 3.35 (ddd, *J* = 13.3, 4.5, 1.5 Hz, 1H), 2.67 (d, *J* = 13.3 Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 150.28 (d, $J = 7.2$ Hz), 142.22 (d, $J = 9.8$ Hz), 139.59, 133.39, 132.46, 129.91, 128.11, 127.59, 127.51, 126.05, 125.72, 125.44, 124.99, 124.92, 120.05 (d, $J = 5.0$ Hz), 113.81 (d, $J = 7.8$ Hz), 42.82 (d, $J = 5.7$ Hz), 37.95.

^{31}P NMR (162 MHz, CDCl_3) δ (ppm): -18.15.

IR (neat, cm^{-1}): 3094, 3054, 3015, 2978, 2928, 1652, 1625, 1587, 1485, 1456, 1308, 1292, 1220, 1184, 1163, 1124, 1071, 1024, 1009.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{26}\text{H}_{22}\text{O}_4\text{P}$, 429.1250; found, 429.1246.



(*R*)-3-(Naphthalen-1-yl)cyclobut-1-en-1-yl diphenyl phosphate (**2h**)

According to **General Procedure B**, using **1h** (81.0 mg, 0.413 mmol), CA-9-HCl (0.127 g, 0.440 mmol), $n\text{-BuLi}$ (2.25 M in hexane, 0.39 mL, 0.880 mmol) and $\text{ClP}(\text{O})(\text{OPh})_2$ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 10:1) afforded **2h** (0.153 g, 0.313 mmol, 86% yield) as a colorless oil. Ee: 93% (Chiralcel® OD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; $t_1=12.1$ min (major); $t_2=14.1$ min (minor).

$[\alpha]_D^{24}$ -171.82 (c 1.0, CHCl_3).

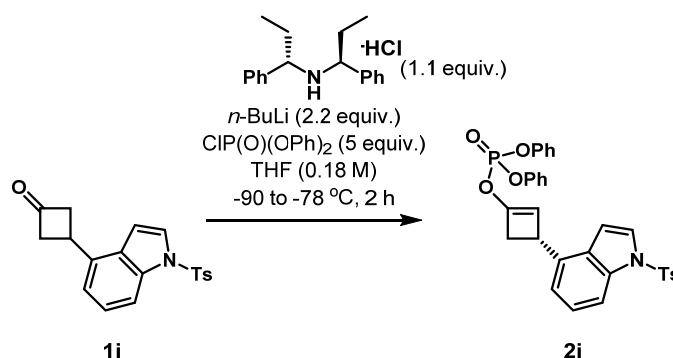
^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.00-7.93 (m, 1H), 7.89-7.85 (m, 1H), 7.74 (d, $J = 8.1$ Hz, 1H), 7.55-7.46 (m, 2H), 7.44-7.17 (m, 12H), 5.67 (s, 1H), 4.34 (d, $J = 3.6$ Hz, 1H), 3.53 (ddd, $J = 13.0, 4.6, 1.5$ Hz, 1H), 2.62 (d, $J = 13.0$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 150.27 (d, $J = 7.4$ Hz), 150.25 (d, $J = 7.2$ Hz), 141.92 (d, $J = 9.8$ Hz), 138.11, 133.52, 131.59, 129.89, 128.77, 127.17, 126.01, 125.70, 125.65, 125.37, 123.31, 123.10, 120.07 (d, $J = 4.9$ Hz), 120.05 (d, $J = 5.0$ Hz), 111.80 (d, $J = 7.8$ Hz), 42.08 (d, $J = 5.8$ Hz), 34.93.

^{31}P NMR (162 MHz, CDCl_3) δ (ppm): -18.13.

IR (neat, cm^{-1}): 3062, 3064, 2974, 2942, 2900, 2834, 1786, 1716, 1647, 1634, 1590, 1488, 1457, 1396, 1301, 1219, 1184, 1161, 1072, 1025, 1009.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{26}H_{22}O_4P$, 429.1250; found, 429.1247.



(R)-Diphenyl (3-(1-tosyl-1H-indol-4-yl)cyclobut-1-en-1-yl) phosphate (2i)

According to **General Procedure B**, using **1i** (0.136 g, 0.400 mmol), CA-9·HCl (0.127 g, 0.440 mmol), *n*-BuLi (2.28 M in hexane, 0.39 mL, 0.880 mmol) and ClP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 95:5) afforded **2i** (91.0 mg, 0.159 mmol, 40% yield) as a colorless oil. Ee: 93% (Chiralcel® AD-H; 40% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t_1 =34.8 min (major); t_2 =38.3 min (minor).

$[\alpha]_D^{23}$ -19.78 (c 1.0, CHCl₃).

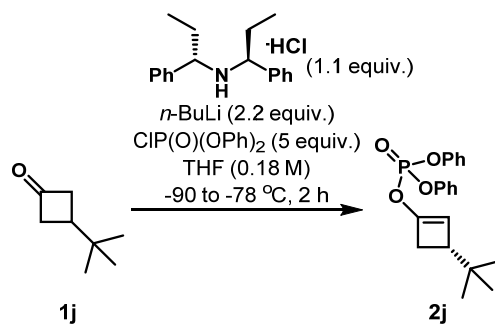
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.86 (d, J = 8.3 Hz, 1H), 7.78-7.73 (m, 2H), 7.55 (d, J = 3.7 Hz, 1H), 7.39-7.31 (m, 4H), 7.28-7.18 (m, 9H), 7.07 (d, J = 7.4 Hz, 1H), 6.72 (dd, J = 3.7, 0.6 Hz, 1H), 5.49 (s, 1H), 3.97-3.93 (m, 1H), 3.34 (ddd, J = 13.2, 4.5, 1.5 Hz, 1H), 2.66 (d, J = 13.2 Hz, 1H), 2.33 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 150.21 (d, J = 7.3 Hz), 144.91, 142.01 (d, J = 9.8 Hz), 135.25, 134.83, 134.68, 129.89, 129.86, 129.16, 126.82, 125.99, 125.72, 124.53, 120.53, 120.01 (d, J = 4.9 Hz), 120.00 (d, J = 4.9 Hz), 112.95 (d, J = 7.8 Hz), 111.95, 106.79, 41.89 (d, J = 5.7 Hz), 35.57, 21.53.

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -18.15.

IR (neat, cm⁻¹): 3061, 2043, 2977, 2938, 1786, 1730, 1646, 1631, 1590, 1527, 1487, 1421, 1372, 1301, 1282, 1179, 1161, 1130, 1089, 1025, 1009.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for $C_{31}H_{27}NO_6PS$, 572.1291; found, 572.1290.



(R)-3-(tert-Butyl)cyclobut-1-en-1-yl diphenyl phosphate (2j)

According to **General Procedure B**, using **1j** (50.5 mg, 0.400 mmol), CA-9·HCl (0.127 g, 0.440 mmol), *n*-BuLi (2.25 M in hexane, 0.39 mL, 0.880 mmol) and ClP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 98:2) afforded **2j** (0.103 g, 0.288 mmol, 72% yield) as a colorless oil. Ee: 87% (Chiralcel® AD-H; 5% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t₁=20.0 min (minor); t₂=23.5 min (major)).

[α]_D²¹ 11.24 (c 1.0, CHCl₃).

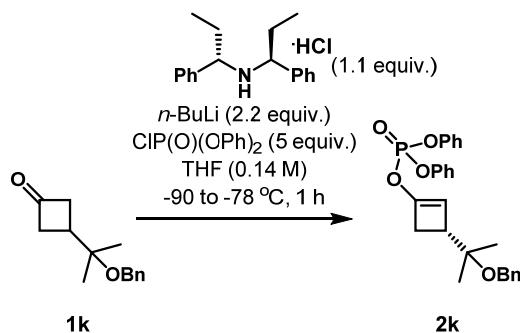
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.39-7.32 (m, 4H), 7.27-7.18 (m, 6H), 5.18 (s, 1H), 2.68 (ddd, *J* = 13.4, 4.4, 1.6 Hz, 1H), 2.45 (d, *J* = 13.4 Hz, 1H), 2.34 (s, 1H), 0.87 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 150.32 (d, *J* = 7.3 Hz), 141.50 (d, *J* = 10.2 Hz), 129.83, 125.57, 120.02 (d, *J* = 5.0 Hz), 112.82 (d, *J* = 7.7 Hz), 44.76, 34.31 (d, *J* = 5.6 Hz), 31.21, 26.43.

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -18.12.

IR (neat, cm⁻¹): 3072, 2957, 2867, 1642, 1627, 1590, 1489, 1365, 1313, 1301, 1285, 1221, 1180, 1161, 1071, 1025, 1009.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₂₀H₂₃O₄P, 358.1328; found, 358.1328.



(R)-3-(2-(Benzyloxy)propan-2-yl)cyclobut-1-en-1-yl diphenyl phosphate (2k)

According to **General Procedure B**, using **1k** (89.6 mg, 0.410 mmol), CA-9·HCl (0.127 g, 0.440 mmol), *n*-BuLi (2.25 M in hexane, 0.39 mL, 0.880 mmol) and ClP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash

chromatography on silica gel (PE:EA = 10:1) afforded **2k** (0.133 g, 0.295 mmol, 74% yield) as a colorless oil. Ee: 90% (Chiralcel® OD-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t_1 =14.0 min (major); t_2 =24.0 min (minor).

$[\alpha]_D^{24}$ 7.76 (c 1.0, CHCl₃).

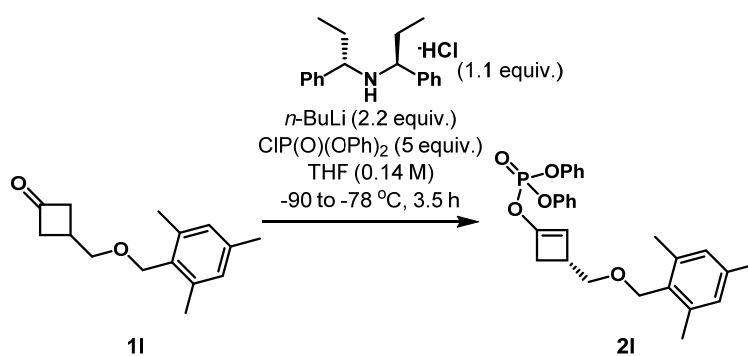
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.31-7.20 (m, 8H), 7.20-7.08 (m, 7H), 5.15 (s, 1H), 4.40 (s, 1H), 2.79-2.67 (m, 2H), 2.62-2.56 (m, 1H), 1.16 (d, J = 2.0 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 150.26 (d, J = 7.3 Hz), 142.06 (d, J = 9.9 Hz), 139.80, 129.85, 128.24, 127.09, 125.62, 120.03 (d, J = 5.0 Hz), 112.02 (d, J = 7.8 Hz), 75.47, 64.11, 42.93, 34.88 (d, J = 5.7 Hz), 22.75, 22.11.

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -18.17.

IR (neat, cm⁻¹): 3062, 2973, 2901, 2833, 1786, 1711, 1631, 1590, 1489, 1313, 1220, 1185, 1160, 1054, 1026, 1009.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for C₂₆H₂₈O₅P, 451.1671; found, 451.1671.



(R)-Diphenyl (3-(((2,4,6-trimethylbenzyl)oxy)methyl)cyclobut-1-en-1-yl) phosphate (2I)

According to **General Procedure B**, using **1I** (93.0 mg, 0.400 mmol), CA-9·HCl (0.127 g, 0.440 mmol), *n*-BuLi (2.25 M in hexane, 0.39 mL, 0.880 mmol) and CIP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 10:1) afforded **2I** (0.153 g, 0.329 mmol, 83% yield) as a colorless oil. Ee: 81% (Chiralcel® OJ-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t_1 =14.5 min (major); t_2 =16.8 min (minor).

$[\alpha]_D^{24}$ 15.80 (c 1.0, CHCl₃).

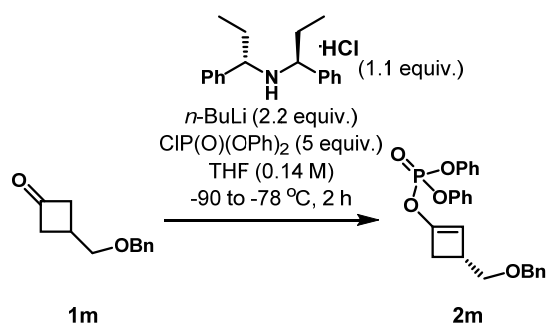
^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.38-7.29 (m, 4H), 7.25-7.17 (m, 6H), 6.83 (s, 2H), 5.22 (s, 1H), 4.49 (s, 2H), 3.47 (ddd, $J = 16.6, 9.3, 6.9$ Hz, 2H), 2.90 (ddd, $J = 13.5, 4.2, 1.4$ Hz, 1H), 2.79-2.69 (m, 1H), 2.40 (d, $J = 13.5$ Hz, 1H), 2.33 (s, 6H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 150.22 (d, $J = 7.3$ Hz), 141.99 (d, $J = 9.9$ Hz), 137.69, 137.54, 131.11, 129.83, 128.92, 125.63, 125.62, 120.02 (d, $J = 4.9$ Hz), 112.38 (d, $J = 7.9$ Hz), 73.42, 67.13, 36.96 (d, $J = 5.8$ Hz), 33.57, 20.92, 19.50.

^{31}P NMR (162 MHz, CDCl_3) δ (ppm): -18.25.

IR (neat, cm^{-1}): 3069, 2974, 2940, 2901, 2483, 1791, 1716, 1642, 1629, 1590, 1489, 1313, 1302, 1220, 1185, 1161, 1083, 1053, 1026, 1009.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{27}\text{H}_{29}\text{O}_5\text{P}$, 465.1825; found, 465.1825.



(*R*)-3-((Benzyloxy)methyl)cyclobut-1-en-1-yl diphenyl phosphate (**2m**)

According to **General Procedure B**, using **1m** (76.1 mg, 0.400 mmol), CA-9-HCl (0.127 g, 0.440 mmol), $n\text{-BuLi}$ (2.44 M in hexane, 0.36 mL, 0.880 mmol) and CIP(O)(OPh)_2 (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 10:1) afforded **2m** (0.136 g, 0.322 mmol, 81% yield) as a colorless oil.

Ee: 83% (Chiralcel® OJ-H; 5% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; $t_1=27.4$ min (minor); $t_2=29.2$ min (major)).

$[\alpha]_D^{24}$ 20.02 (c 1.0, CHCl_3).

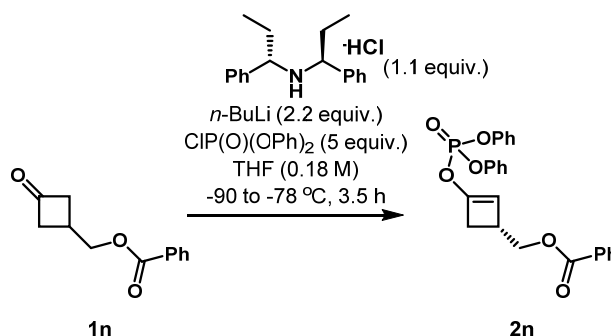
^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.38-7.26 (m, 9H), 7.27-7.17 (m, 6H), 5.24 (s, 1H), 4.52 (s, 2H), 3.47 (ddd, $J = 26.0, 9.4, 7.0$ Hz, 2H), 2.95-2.87 (m, 1H), 2.82-2.73 (m, 1H), 2.43 (d, $J = 13.5$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 150.24 (d, $J = 7.3$ Hz), 142.02 (d, $J = 9.7$ Hz), 138.29, 129.85, 128.38, 127.65, 127.62, 125.65, 120.04 (d, $J = 5.0$ Hz), 112.30 (d, $J = 7.9$ Hz), 73.40, 73.18, 36.86 (d, $J = 5.8$ Hz), 33.54.

^{31}P NMR (162 MHz, CDCl_3) δ (ppm): -18.17.

IR (neat, cm^{-1}): 3062, 3029, 2978, 2936, 2865, 2848, 1783, 1723, 1702, 1641, 1626, 1589, 1488, 1455, 1311, 1301, 1219, 1184, 1160, 1093, 1025, 1009.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{24}\text{H}_{24}\text{O}_5\text{P}$, 423.1356; found, 423.1350.



(R)-3-((Diphenoxyphosphoryl)oxy)cyclobut-2-en-1-yl)methyl benzoate (2n)

According to **General Procedure B**, using **1n** (81.8 mg, 0.400 mmol), CA-9-HCl (0.127 g, 0.440 mmol), $n\text{-BuLi}$ (2.49 M in hexane, 0.35 mL, 0.880 mmol) and ClP(O)(OPh)_2 (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 6:1) afforded **2n** (0.110 g, 0.252 mmol, 63% yield) as a colorless oil. Ee: 81% (Chiralcel® OJ-H; 10% $i\text{-PrOH}$ in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; $t_1=39.2$ min (major); $t_2=43.9$ min (minor)).

$[\alpha]_D^{20}$ 16.69 (c 0.58, CHCl_3).

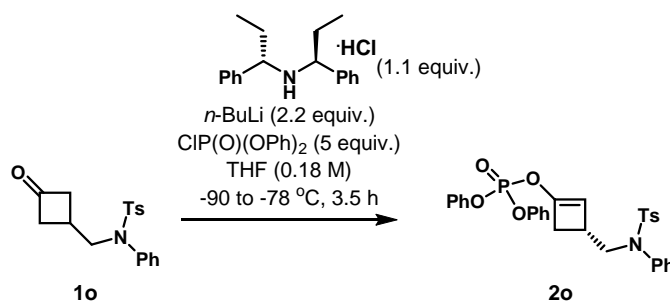
^1H NMR (400 MHz, CDCl_3) δ (ppm): 8.03 (d, $J = 7.6$ Hz, 1H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.41 (t, $J = 7.7$ Hz, 1H), 7.35 (t, $J = 7.8$ Hz, 2H), 7.27-7.17 (m, 3H), 5.27 (s, 1H), 4.42-4.27 (m, 1H), 3.05-2.86 (m, 1H), 2.59 (d, $J = 13.4$ Hz, 1H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 166.44, 150.19 (d, $J = 7.2$ Hz), 142.26 (d, $J = 9.8$ Hz), 132.96, 130.10, 129.88, 129.57, 128.34, 125.72, 120.01 (d, $J = 4.9$ Hz), 111.47 (d, $J = 7.9$ Hz), 67.18, 36.54 (d, $J = 5.9$ Hz), 32.61.

^{31}P NMR (162 MHz, CDCl_3) δ (ppm): -18.25.

IR (neat, cm^{-1}): 3060, 2982, 2949, 2882, 2829, 1716, 1629, 1588, 1488, 1452, 1313, 1269, 1183, 1160, 1110, 1070, 1025, 1009.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{24}\text{H}_{22}\text{O}_6\text{P}$, 437.1149; found, 437.1141.



(R)-3-(((4-Methyl-N-phenylphenyl)sulfonamido)methyl)cyclobut-1-en-1-yl diphenyl phosphate (2o)

According to **General Procedure B**, using **1o** (0.264 g, 0.800 mmol), CA-9·HCl (0.255 g, 0.880 mmol), *n*-BuLi (2.49 M in hexane, 0.71 mL, 1.76 mmol) and ClP(O)(OPh)₂ (0.84 mL, 1.08 g, 4.00 mmol); flash chromatography on silica gel (PE:Acetone = 6:1) afforded **2o** (0.369g, 0.657 mmol, 82% yield) as a white solid.

Ee: 90% (Chiralcel® IA; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; $t_1=87.9$ min (major); $t_2=94.9$ min (minor).

$[\alpha]_D^{23}$ 17.12 (c 0.5, CHCl₃).

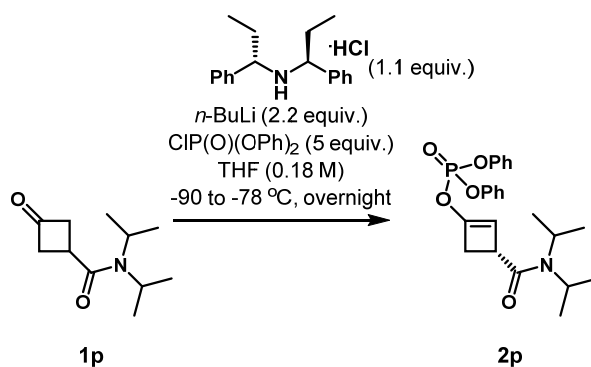
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.46 (d, J = 8.1 Hz, 2H), 7.35 (t, J = 7.2 Hz, 4H), 7.31-7.27 (m, 3H), 7.25 (d, J = 4.0 Hz, 2H), 7.21 (t, J = 8.7 Hz, 6H), 7.05-6.99 (m, 2H), 4.99 (s, 1H), 3.59 (d, J = 7.1 Hz, 2H), 2.79 (dd, J = 13.6, 3.7 Hz, 1H), 2.59 (d, J = 4.5 Hz, 1H), 2.42 (s, 3H), 2.38 (d, J = 13.7 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 150.15 (d, J = 7.3 Hz), 143.41, 141.85 (d, J = 9.9 Hz), 139.44, 135.23, 129.86, 129.39, 129.06, 128.97, 128.07, 127.66, 125.67, 119.99 (d, J = 4.9 Hz), 112.21 (d, J = 7.9 Hz), 54.58, 37.13 (d, J = 5.9 Hz), 33.12, 21.52.

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -18.32.

IR (neat, cm⁻¹): 3060, 2839, 2796, 1794, 1639, 1626, 1588, 1489, 1349, 1337, 1302, 1278, 1222, 1187, 1181, 1163, 1027, 1009.

HRMS-ESI (m/z): $[M+H]^+$ calcd. for C₃₀H₂₈NO₆PS, 562.1448; found, 562.1445.



(R)-3-(Diisopropylcarbamoyl)cyclobut-1-en-1-yl diphenyl phosphate (2p)

According to **General Procedure B**, using **1p** (79.0 mg, 0.400 mmol), CA-9·HCl (0.127 g, 0.440 mmol), *n*-BuLi (2.25 M in hexane, 0.39 mL, 0.880 mmol) and CIP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:Acetone = 7:1) afforded **2p** (86.8 mg, 0.202 mmol, 51% yield) as a colorless oil.

Ee: 70% (Chiralcel® IA; 3% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t₁=53.7 min (minor); t₂=57.7 min (major).

[α]_D¹⁹ 14.40 (c 1.0, CHCl₃).

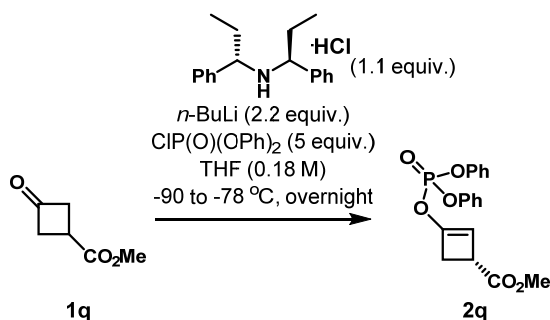
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.44-7.30 (m, 4H), 7.30-7.16 (m, 6H), 5.47 (s, 1H), 3.83-3.70 (m, 1H), 3.34-3.21 (m, 1H), 3.17 (d, *J* = 12.8 Hz, 1H), 2.64 (d, *J* = 12.8 Hz, 1H), 1.45 (s, 3H), 1.40 (t, *J* = 6.1 Hz, 6H), 1.22-1.14 (dd, *J* = 6.3, 2.7 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 170.19, 150.14 (d, *J* = 7.5 Hz), 150.10 (d, *J* = 7.5 Hz), 142.18 (d, *J* = 9.5 Hz), 129.82, 125.67, 125.66, 120.06 (d, *J* = 4.9 Hz), 120.05 (d, *J* = 4.9 Hz), 110.63 (d, *J* = 8.3 Hz), 48.11, 45.68, 37.29, 36.83 (d, *J* = 5.7 Hz), 20.81 (d, *J* = 5.5 Hz), 20.46 (d, *J* = 5.8 Hz).

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -18.31.

IR (neat, cm⁻¹): 3096, 3068, 2999, 2966, 2932, 2873, 1632, 1589, 1488, 1440, 1371, 1342, 1313, 1301, 1269, 1216, 1282, 1160, 1315, 1072, 1025, 1009.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₂₃H₂₈NO₅P, 429.1700; found, 429.1700.



Methyl (*R*)-3-((diphenoxyphosphoryl)oxy)cyclobut-2-ene-1-carboxylate (**2q**)

According to **General Procedure B**, using **1q** (51.3 mg, 0.400 mmol), CA-9·HCl (0.127 g, 0.440 mmol), *n*-BuLi (2.25 M in hexane, 0.39 mL, 0.880 mmol) and ClP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:Acetone = 5:1) afforded **2q** (0.118 g, 0.327 mmol, 82% yield) as a colorless oil.

Ee: 47% (Chiralcel® IC; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t₁=33.0 min (major); t₂=37.2 min (minor).

[α]_D²² 22.84 (c 1.0, CHCl₃).

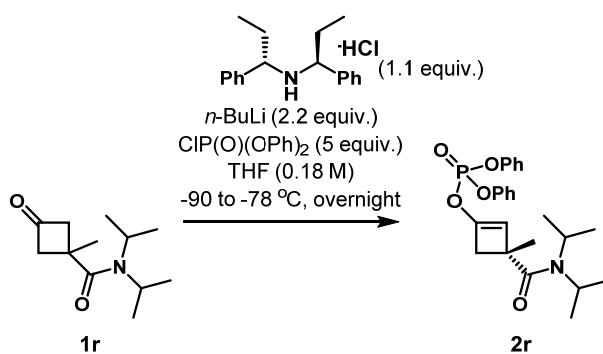
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.40 (7.40-7.33, 4H), 7.29-7.19 (m, 6H), 5.25 (s, 1H), 3.70 (s, 3H), 3.34-3.29 (m, 1H), 3.11-2.92 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 173.17, 150.14 (d, *J* = 7.4 Hz), 150.12 (d, *J* = 7.4 Hz), 150.11, 150.08, 143.58 (d, *J* = 9.5 Hz), 129.91, 125.80, 120.05 (d, *J* = 4.9 Hz), 109.98 (d, *J* = 8.1 Hz), 51.99, 37.13 (d, *J* = 6.2 Hz), 36.33.

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -18.46.

IR (neat, cm⁻¹): 3075, 2952, 2844, 1735, 1648, 1634, 1590, 1488, 1457, 1436, 1340, 1302, 1222, 1183, 1161, 1072, 1026, 1010.

HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₁₈H₁₈O₆P, 361.0836; found, 361.0831.



(*R*)-3-(Diisopropylcarbamoyl)-3-methylcyclobut-1-en-1-yl diphenyl phosphate (**2r**)

According to **General Procedure B**, using **1r** (84.7 mg, 0.400 mmol), CA-9·HCl (0.127 g, 0.440 mmol), *n*-BuLi (2.49 M in hexane, 0.35 mL, 0.880 mmol) and ClP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:Acetone = 7:1) afforded **2r** (0.160 g, 0.361 mmol, 90% yield) as a colorless oil.

Ee: 17% (Chiralcel® OZ-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t_1 =14.9 min (major); t_2 =32.2 min (minor).

$[\alpha]_D^{17}$ -4.42 (c 1.0, CHCl₃).

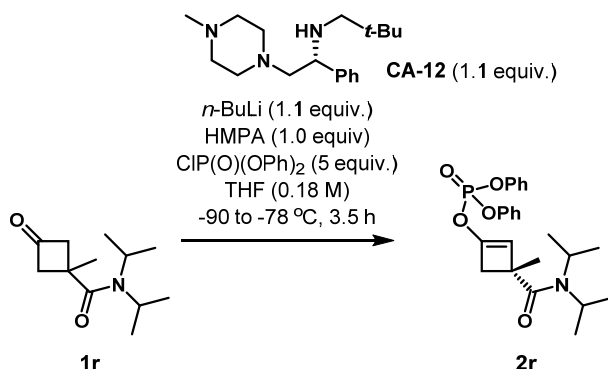
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.40-7.30 (m, 4H), 7.30-7.15 (m, 6H), 5.47 (s, 1H), 3.85-3.68 (m, 1H), 3.33-3.21 (m, 1H), 3.17 (d, J = 12.8 Hz, 1H), 2.64 (dd, J = 12.8, 1.1 Hz, 1H), 1.44 (d, J = 8.1 Hz, 3H), 1.40 (t, J = 6.2 Hz, 6H), 1.21-1.13 (m, 6H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 172.64, 150.11 (d, J = 7.4 Hz), 150.06 (d, J = 7.3 Hz), 141.24 (d, J = 9.0 Hz), 129.79, 125.64, 125.63, 120.02 (d, J = 4.9 Hz), 119.99 (d, J = 4.8 Hz), 116.63 (d, J = 8.2 Hz), 48.50, 45.89, 44.44, 44.23 (d, J = 5.3 Hz), 22.82, 20.46, 20.43, 20.27, 20.23.

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -18.24.

IR (neat, cm⁻¹): 3064, 2979, 2921, 1659, 1628, 1587, 1488, 1345, 1329, 1290, 1266, 1215, 1185, 1166, 1085, 1070, 1037, 1027, 1009.

HRMS-EI (m/z): [M]⁺ calcd. for C₂₄H₃₀NO₅P, 443.1856; found, 443.1858.

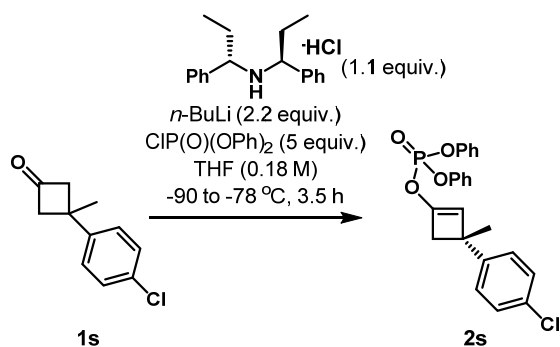


(*R*)-3-(Diisopropylcarbamoyl)-3-methylcyclobut-1-en-1-yl diphenyl phosphate (**2r**)

According to **General Procedure B**, using **1r** (84.5 mg, 0.400 mmol), CA-12 (0.127 g, 0.440 mmol), HMPA (70.0 μ L, 0.400 mmol) as co-solvent, *n*-BuLi (2.50 M in hexane, 0.18 mL, 0.440 mmol) and CIP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:Acetone = 7:1) afforded **2r** (0.118 g, 0.265 mmol, 66% yield) as a colorless oil.

Ee: 62% (Chiralcel® OZ-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t_1 =14.9 min (major); t_2 =32.2 min (minor).

$[\alpha]_D^{18}$ -12.54 (c 1.0, CHCl₃).



(R)-3-(4-Chlorophenyl)-3-methylcyclobut-1-en-1-yl diphenyl phosphate (2s)

According to **General Procedure B**, using **1s** (135.8 mg, 0.400 mmol), CA-9·HCl (77.9 mg, 0.440 mmol), *n*-BuLi (2.25 M in hexane, 0.39 mL, 0.880 mmol) and CIP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 10:1) afforded **2s** (0.133 g, 0.312 mmol, 78% yield) as a colorless oil. Ee: 10% (Chiralcel® OJ-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t₁=11.6 min (minor); t₂=21.5 min (major)).

[α]_D²² 1.56 (c 0.5, CHCl₃).

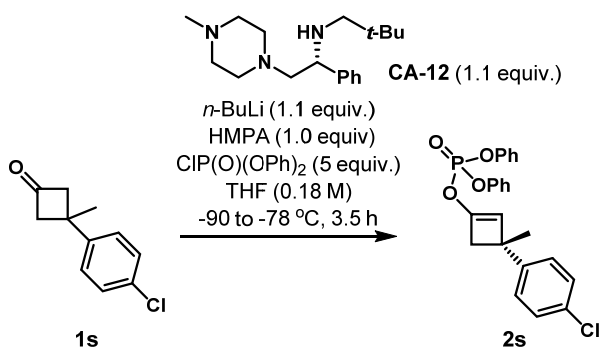
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.35 (t, *J* = 7.9 Hz, 4H), 7.30-7.18 (m, 10H), 5.55 (s, 1H), 2.95-2.76 (m, 2H), 1.53 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 150.23 (d, *J* = 7.4 Hz), 150.21 (d, *J* = 7.2 Hz), 144.66, 141.86 (d, *J* = 9.8 Hz), 131.85, 129.88, 128.23, 127.33, 125.72, 125.71, 120.03 (d, *J* = 4.9 Hz), 117.38 (d, *J* = 7.6 Hz), 48.60 (d, *J* = 5.6 Hz), 41.60, 26.87.

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -18.12.

IR (neat, cm⁻¹): 3062, 2973, 2892, 2834, 1781, 1722, 1648, 1633, 1590, 1488, 1312, 1301, 1286, 1206, 1184, 1161, 1088, 1073, 1026, 1010.

HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₂₃H₂₀ClO₄P, 427.0860; found, 427.0858.

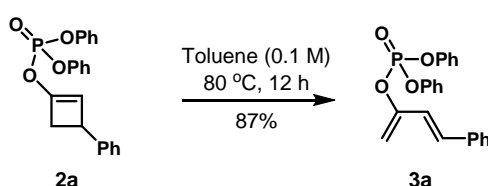


(*R*)-3-(4-Chlorophenyl)-3-methylcyclobut-1-en-1-yl diphenyl phosphate (**2s**)

According to **General Procedure B**, using **1s** (77.9 mg, 0.400 mmol), CA-12 (0.127 g, 0.440 mmol), HMPA (70.0 μ L, 0.400 mmol) as co-solvent, *n*-BuLi (2.50 M in hexane, 0.18 mL, 0.440 mmol) and ClP(O)(OPh)₂ (0.42 mL, 0.540 g, 2.00 mmol); flash chromatography on silica gel (PE:EA = 10:1) afforded **2s** (0.123 g, 0.287 mmol, 72% yield) as a colorless oil.

Ee: 63% (Chiralcel® OJ-H; 10% *i*-PrOH in hexanes; flow rate = 1.0 mL/min; detection at 210 nm; t_1 =11.6 min (minor); t_2 =21.5 min (major).

$[\alpha]_D^{21}$ 15.18 (c 1.0, CHCl₃).



(*E*)-Diphenyl (4-phenylbuta-1,3-dien-2-yl) phosphate (**3a**)

A solution of **2a** (37.8 mg, 0.100 mmol) in toluene (1.0 mL) was stirred at 80 °C for 12 h. After cooling, the mixture was concentrated, and purified by column chromatography on silica gel (PE:EA = 5:1) to afford the product **3a** (32.7 mg, 86.4 μ mol, 87% yield) as a faint yellow oil.

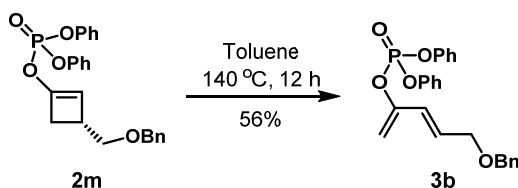
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.41-7.19 (m, 15H), 6.66 (d, J = 15.8 Hz, 1H), 6.54 (dd, J = 15.8, 2.6 Hz, 1H), 5.25 (t, J = 2.2 Hz, 1H), 4.95 (t, J = 2.5 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 151.34 (d, J = 8.1 Hz), 150.51 (d, J = 7.5 Hz), 135.74, 131.13, 129.85, 128.63, 128.37, 126.90, 125.62 (d, J = 1.1 Hz), 121.84 (d, J = 6.9 Hz), 120.20 (d, J = 4.9 Hz), 102.18 (d, J = 3.5 Hz).

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -17.93.

IR (neat, cm⁻¹): 3062, 3026, 2246, 1948, 1817, 1750, 1639, 1589, 1488, 1449, 1298, 1274, 1214, 1184, 1161, 1072, 1009.

HRMS-ESI (m/z): [M+H]⁺ calcd. for C₂₂H₂₀O₄P, 379.1094; found, 379.1091.



(*E*)-5-(Benzyloxy)penta-1,3-dien-2-yl diphenyl phosphate (**3b**)

A solution of **2m** (42.2 mg, 0.100 mmol) in toluene (1.0 mL) was stirred at 140 °C for 20 h. After cooling, the mixture was concentrated, and purified by column chromatography on silica gel (PE:EA = 10:1) to afford the product **3b** (23.8 mg, 56.3 μmol, 56% yield) as a colorless oil.

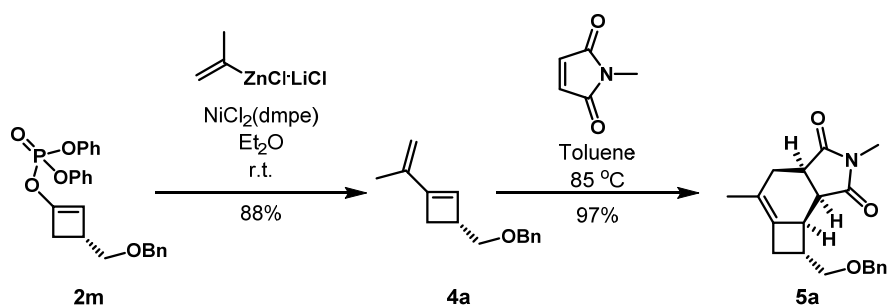
¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.42-7.15 (m, 15H), 6.22-6.12 (m, 1H), 5.99 (dt, *J* = 15.5, 5.1 Hz, 1H), 5.17 (s, 1H), 4.84 (t, *J* = 2.2 Hz, 1H), 4.50 (s, 2H), 4.09-3.99 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 150.71 (d, *J* = 8.1 Hz), 150.46 (d, *J* = 7.4 Hz), 137.99, 129.82, 129.35, 128.41, 127.70, 127.66, 125.56 (d, *J* = 1.1 Hz), 124.89 (d, *J* = 6.8 Hz), 120.15 (d, *J* = 4.9 Hz), 101.79, 72.38, 69.22.

³¹P NMR (162 MHz, CDCl₃) δ (ppm): -17.88.

IR (neat, cm⁻¹): 3063, 3030, 2850, 2790, 1955, 1809, 1725, 1662, 1610, 1589, 1488, 1455, 1360, 1300, 1271, 1211, 1185, 1162, 1115, 1071, 1009.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₂₄H₂₄O₅P, 423.1356; found, 423.1354.



(3aR,7R,7aR,7bS)-7-((Benzyloxy)methyl)-2,5-dimethyl-3a,4,6,7,7a,7b-hexahydro-1H-cyclobuta[e]isoindole-1,3(2H)-dione (5a)

A flame-dried 10 mL screw tube was charged with NiCl₂(dmpe) (9.9 mg, 35.5 μmol), and a solution of **2m** (0.300 g, 0.710 mmol) in Et₂O (4 mL+3 mL) and prop-1-en-2-ylzinc (0.51 M in THF, 2.00 mL, 1.07 mmol) were added sequentially at 0 °C. After stirring for 3 h at room temperature, the reaction mixture was quenched with a saturated aqueous solution of NH₄Cl, diluted with H₂O, extracted with Et₂O. The combined organic phase was washed with brine, dried over Na₂SO₄, concentrated, and purified by column chromatography on silica gel (PE:EA = 98:2) to afford **4a** (0.134 g, 0.624 mmol, 88% yield) as a colorless oil.

[α]_D²³ 117.26 (c 0.71, CHCl₃).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.35 (d, $J = 4.4$ Hz, 4H), 7.31-7.27 (m, 1H), 6.00 (s, 1H), 4.89 (d, $J = 12.4$ Hz, 2H), 4.54 (s, 2H), 3.65-3.36 (m, 2H), 2.97 (dd, $J = 11.9, 6.3$ Hz, 1H), 2.73 (dd, $J = 13.0, 4.5$ Hz, 1H), 2.23 (dd, $J = 13.0, 1.6$ Hz, 1H), 1.82 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 148.69, 138.95, 138.57, 129.35, 128.35, 127.66, 127.51, 112.19, 74.08, 73.12, 37.77, 31.98, 17.59.

IR (neat, cm^{-1}): 3086, 3064, 3031, 2943, 2917, 2851, 1583, 1496, 1453, 1435, 1375, 1361, 1141, 1094, 1028.

HRMS-EI (m/z): $[\text{M}]^+$ calcd. for $\text{C}_{15}\text{H}_{18}\text{O}$, 214.1352; found, 214.1357.

A solution of **4a** (0.134 g, 0.624 mmol) and *N*-methylmaleimide (0.138 g, 1.240 mmol) in toluene (7 ml) was stirred at 85 °C for 48 h. The mixture was then concentrated, and purified by column chromatography on silica gel (DCM to PE:EA = 3:1) to afford the product **5a** (0.195 g, 0.600 mmol, 97% yield) as a colorless oil.

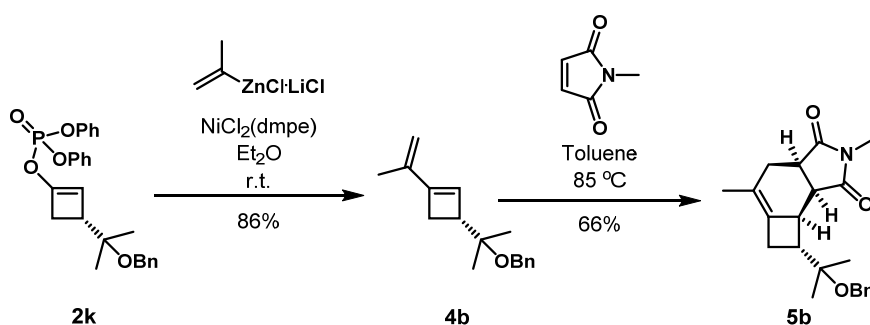
$[\alpha]_D^{23}$ 23.76 (c 0.50, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.39-7.27 (m, 5H), 4.56 (q, $J = 12.0$ Hz, 2H), 3.59 (ddd, $J = 15.2, 9.7, 4.9$ Hz, 2H), 3.18 (dd, $J = 11.1, 8.6$ Hz, 1H), 3.10-2.98 (m, 1H), 2.97 (s, 3H), 2.96-2.91 (m, 1H), 2.64-2.38 (m, 4H), 2.17-2.05 (m, 1H), 1.58 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 180.04, 178.04, 138.63, 131.29, 128.30, 127.57, 127.45, 122.17, 72.84, 72.54, 41.93, 40.66, 39.75, 37.93, 29.82, 27.03, 24.86, 17.76.

IR (neat, cm^{-1}): 2972, 2942, 2901, 2846, 1773, 1694, 1592, 1492, 1432, 1382, 1314, 1282, 1189, 1163, 1063, 1075, 1052, 1027.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{20}\text{H}_{24}\text{O}_3\text{P}$, 326.1751; found, 326.1751.



(3a*R*,7*R*,7a*R*,7b*S*)-7-(2-(Benzyloxy)propan-2-yl)-2,5-dimethyl-3a,4,6,7,7a,7b-hexahydro-1*H*-cyclobuta[*e*]isoindole-1,3(2*H*)-dione (5b)

A flame-dried 10 mL screw tube was charged with $\text{NiCl}_2(\text{dmpe})$ (2.8 mg, 10.0 μmol), and a solution of **2k** (0.103 g, 0.229 mmol) in Et_2O (1 mL+1 mL) and prop-1-en-2-ylzinc (0.51 M in THF, 0.67 mL, 0.334 mmol) were added sequentially at 0 °C. After stirring for 3 h at room temperature, the reaction mixture was quenched

with a saturated aqueous solution of NH_4Cl , diluted with H_2O , extracted with Et_2O . The combined organic phase was washed with brine, dried over Na_2SO_4 , concentrated, and purified by column chromatography on silica gel (PE:EA = 98:2) to afford **4b** (47.5 mg, 0.196 mmol, 86% yield) as a colorless oil.

$[\alpha]_{\text{D}}^{18}$ 37.28 (c 0.50, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.38-7.29 (m, 4H), 7.26-7.21 (m, 6H), 5.98 (s, 1H), 4.90 (d, $J = 13.4$ Hz, 2H), 4.55-4.47 (m, 2H), 2.99 (d, $J = 4.2$ Hz, 1H), 2.60 (dd, $J = 12.9, 4.7$ Hz, 1H), 2.44 (dd, $J = 12.9, 2.0$ Hz, 1H), 1.84 (s, 3H), 1.25 (d, $J = 2.7$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 148.47, 140.08, 138.84, 129.32, 128.22, 127.19, 127.02, 111.98, 76.21, 64.20, 46.91, 30.19, 22.97, 22.32, 17.69.

IR (neat, cm^{-1}): 3081, 3055, 3034, 2972, 2919, 2887, 1582, 1453, 1382, 1363, 1266, 1235, 1145, 1085, 1061, 1028.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{17}\text{H}_{23}\text{O}_3$, 243.1743; found, 243.1740.

A solution of **4b** (47.5 mg, 0.196 mmol) and *N*-methylmaleimide (48.0 mg, 0.430 mmol) in toluene (2 ml) was stirred at 85 °C for 20 h. The mixture was then concentrated, and purified by column chromatography on silica gel (DCM to PE:EA = 5:1) to afford the product **5b** (46.5 mg, 0.132 mmol, 66% yield) as a colorless oil.

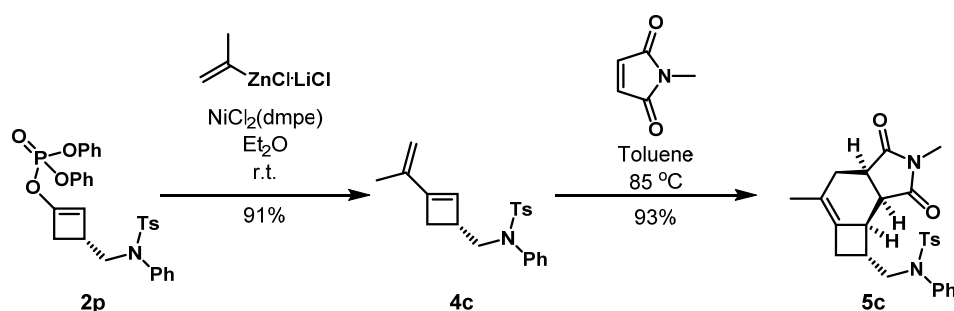
$[\alpha]_{\text{D}}^{18}$ -6.21 (c 1.04, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.38-7.30 (m, 4H), 7.28-7.22 (m, 1H), 4.50 (dd, $J = 16.0, 12.0$ Hz, 2H), 3.23-3.14 (m, 1H), 3.11 (t, $J = 9.5$ Hz, 1H), 3.07-3.02 (m, 1H), 2.97 (s, 3H), 2.79-2.70 (m, 1H), 2.59-2.37 (m, 3H), 2.17-2.07 (m, 1H), 1.57 (s, 3H), 1.35 (s, 3H), 1.21 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 180.21, 178.19, 140.30, 131.32, 128.16, 126.96, 126.91, 122.13, 74.66, 63.49, 47.28, 42.18, 41.33, 37.82, 27.70, 26.60, 24.94, 23.03, 22.53, 17.69.

IR (neat, cm^{-1}): 3088, 3062, 3030, 2968, 2929, 2908, 2868, 2852, 2728, 1772, 1696, 1497, 1434, 1383, 1364, 1319, 1283, 1243, 1212, 1163, 1132, 1089, 1059, 1027.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{22}\text{H}_{28}\text{NO}_3$, 354.2064; found, 354.2064.



***N*-(((3*aR*,7*R*,7*aR*,7*bS*)-2,5-Dimethyl-1,3-dioxo-2,3,3*a*,4,6,7,7*a*,7*b*-octahydro-1*H*-cyclobuta[*e*]isoindol-7-yl)methyl)-4-methyl-*N*-phenylbenzenesulfonamide (**5c**)**

A flame-dried 10 mL screw tube was charged with NiCl₂(dmpe) (3.5 mg, 12.5 μmol), and a solution of **2p** (0.125 g, 0.250 mmol) in Et₂O (2 mL+1 mL) and prop-1-en-2-ylzinc (0.51 M in THF, 0.73 mL, 0.325 mmol) were added at 0 °C. After stirring for 3 h at room temperature, the reaction mixture was quenched with a saturated aqueous solution of NH₄Cl, diluted with H₂O, extracted with Et₂O. The combined organic phase was washed with brine, dried over Na₂SO₄, concentrated, and purified by column chromatography on silica gel (PE:EA =5:1) to afford **4c** (72.0 mg, 0.204 mmol, 91% yield) as a white solid.

[α]_D²³ 79.39 (c 0.82, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.50-7.46 (m, 2H), 7.32-7.28 (m, 3H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.07-7.02 (m, 2H), 5.70 (s, 1H), 4.84 (s, 2H), 3.63 (dd, *J* = 7.3, 1.4 Hz, 2H), 2.80-2.68 (m, 1H), 2.57 (dd, *J* = 13.0, 4.5 Hz, 1H), 2.42 (s, 3H), 2.17 (dd, *J* = 13.1, 1.7 Hz, 1H), 1.74 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 148.30, 143.23, 139.60, 138.67, 135.48, 129.34, 129.07, 129.00, 128.93, 127.92, 127.70, 112.55, 54.76, 36.98, 32.25, 21.53, 17.52.

IR (neat, cm⁻¹): 3064, 3034, 2981, 2943, 2900, 2822, 1581, 1487, 1347, 1163, 1090, 1061, 1043.

HRMS-EI (*m/z*): [M]⁺ calcd. for C₂₁H₂₃NO₂S, 353.1444; found, 353.1440.

A solution of **4c** (72.0 mg, 0.204 mmol) and *N*-methylmaleimide (44.0 mg, 0.396 mmol) in toluene (5 ml) was stirred at 85 °C for 25 h. The mixture was then concentrated, and purified by column chromatography on silica gel (DCM to PE:EA = 2:1) to afford the product **5c** (86.6 mg, 0.186 mmol, 93% yield) as a white solid.

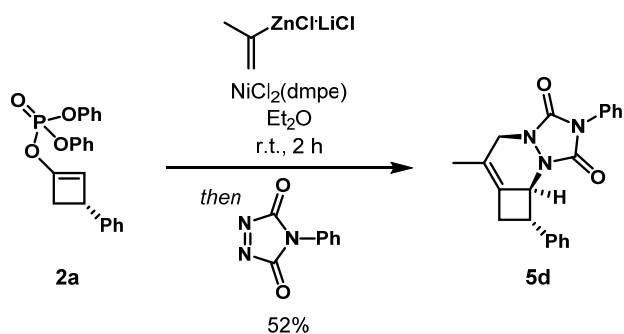
[α]_D²⁵ -48.86 (c 1.0, CHCl₃).

¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.40-7.35 (m, 2H), 7.26-7.16 (m, 6H), 7.03-6.98 (m, 2H), 3.63 (ddd, *J* = 18.3, 12.9, 7.3 Hz, 2H), 3.05-2.95 (m, 1H), 2.94-2.87 (m, 1H), 2.79-2.71 (m, 1H), 2.69 (s, 3H), 2.42-2.33 (m, 5H), 2.31-2.20 (m, 1H), 2.09-1.88 (m, 2H), 1.46 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm): 179.73, 177.76, 143.35, 138.94, 134.82, 130.13, 129.35, 128.76, 128.63, 127.75, 127.71, 122.12, 54.00, 41.70, 41.64, 40.36, 37.02, 31.37, 26.71, 24.62, 21.51, 17.82.

IR (neat, cm⁻¹): 3061, 3045, 2974, 2943, 2900, 2840, 1774, 1696, 1594, 1492, 1432, 1381, 1345, 1305, 1188, 1161, 1091, 1050, 1026.

HRMS-ESI (*m/z*): [M+H]⁺ calcd. for C₂₆H₂₉N₂O₄, 465.1843; found, 465.1842.



(8*S*,8*aS*)-6-Methyl-2,8-diphenyl-5,7,8,8*a*-tetrahydro-1*H*-cyclobuta[*c*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3(2*H*)-dione (5d**)**

A flame-dried 10 mL screw tube was charged with $\text{NiCl}_2(\text{dmpe})$ (1.3 mg, 4.5 μmol), and a solution of **2a** (34.2 mg, 90.0 μmol) in Et_2O (0.3 mL+0.2 mL) and prop-1-en-2-ylzinc (0.52 M in THF, 0.26 mL, 0.135 mmol) were added sequentially at room temperature. After stirring for 2 h, 4-phenyl-1,2,4-triazolidine-3,5-dione (47.3 mg, 0.270 mmol) in DCM (0.5 mL+0.5 mL) was added. After stirring overnight, the mixture was quenched with a saturated aqueous solution of NH_4Cl , diluted with H_2O , and extracted with EA. The combined organic phase was washed with brine, dried over Na_2SO_4 , concentrated, and purified by column chromatography on silica gel (PE:EA =3:1) to afford **5d** (16.2 mg, 46.9 μmol , 52% yield) as a white solid.

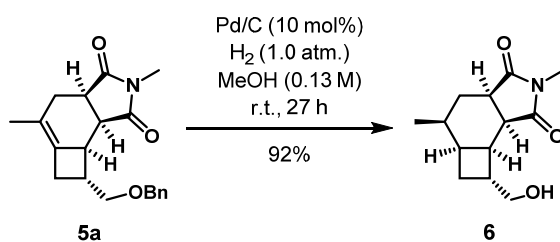
$[\alpha]_D^{13}$ -262.29 (c 0.59, CHCl_3).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.56 (d, $J = 7.6$ Hz, 2H), 7.53-7.48 (m, 2H), 7.48-7.42 (m, 2H), 7.38-7.32 (m, 3H), 7.26-7.22 (m, 1H), 4.70-4.61 (m, 1H), 4.37 (d, $J = 15.8$ Hz, 1H), 3.95 (d, $J = 15.8$ Hz, 1H), 3.71 (dd, $J = 15.9, 8.7$ Hz, 1H), 3.32-3.21 (m, 1H), 3.06-2.95 (m, 1H), 1.82 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 152.99, 151.03, 140.58, 131.10, 129.09, 128.41, 128.05, 127.06, 126.87, 125.50, 124.07, 118.12, 62.51, 46.56, 44.72, 34.92, 14.66.

IR (neat, cm^{-1}): 3077, 3061, 3031, 2970, 2935, 2893, 2868, 2839, 1801, 1772, 1706, 1600, 1502, 1456, 1412, 1381, 1361, 1330, 1278, 1245, 1177, 1133, 1067, 1031.

HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{21}\text{H}_{20}\text{N}_3\text{O}_2$, 346.1550; found, 346.1547.



(3*aR*,5*S*,5*aS*,7*R*,7*aR*,7*bS*)-7-(Hydroxymethyl)-2,5-dimethyloctahydro-1*H*-cyclobuta[*e*]isoindole-1,3(2*H*)-dione (6**)**

A flame-dried 10 mL Schlenk tube was charged with Pd/C (10%, 27.0 mg, 25.4 μmol), then evacuated and backfilled with H_2 from a balloon for three times. A solution of **5a** (82.8 mg, 0.254 mmol) in MeOH (1 mL+1 mL) was added, and the mixture was stirred at room temperature for 27 h. The mixture was filtered through celite, washed with EA, concentrated, and purified by column chromatography on silica gel (PE:EA =2:1) to afford **6** (54.5 mg, 0.230 mmol, 92% yield) as a white solid.

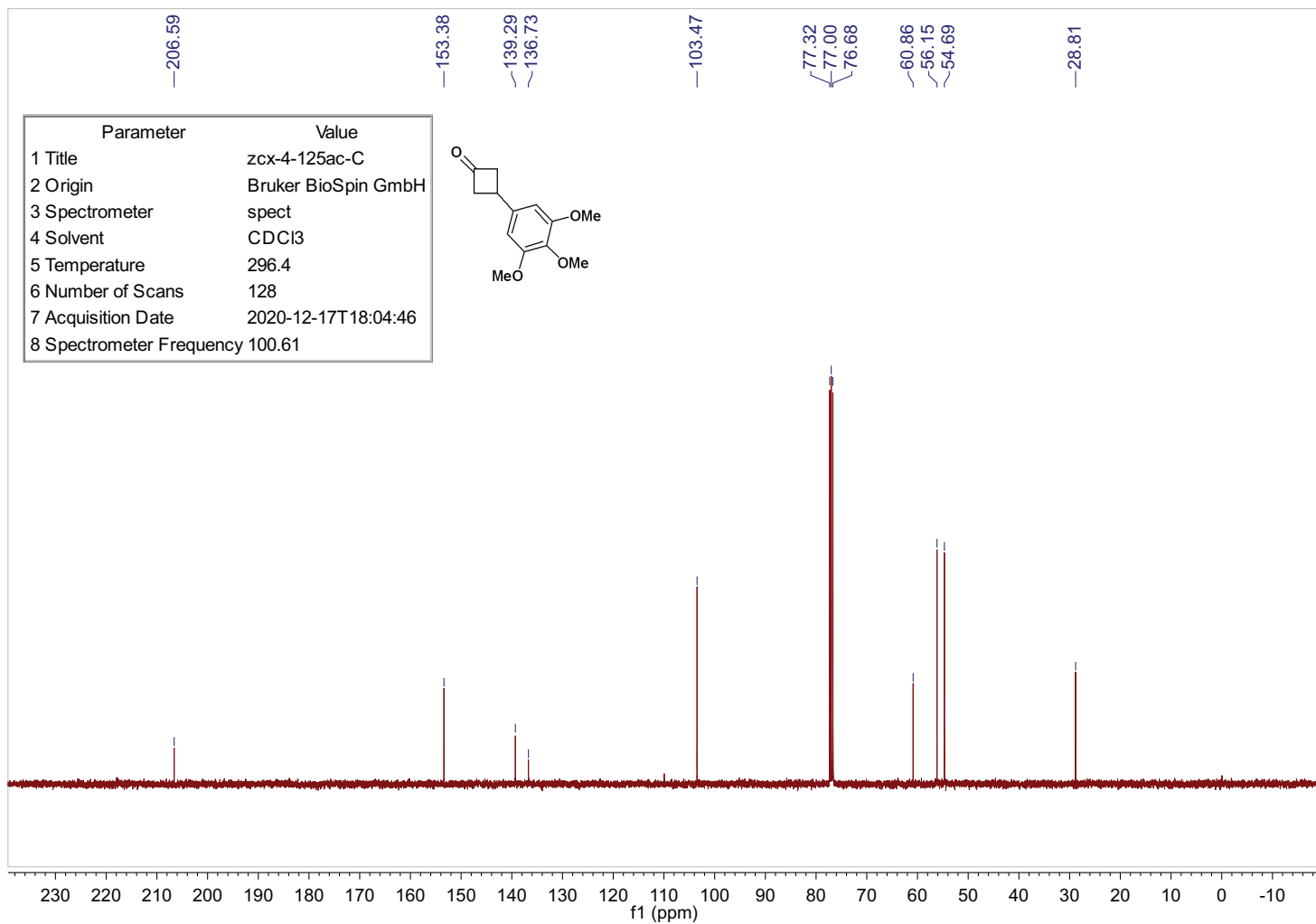
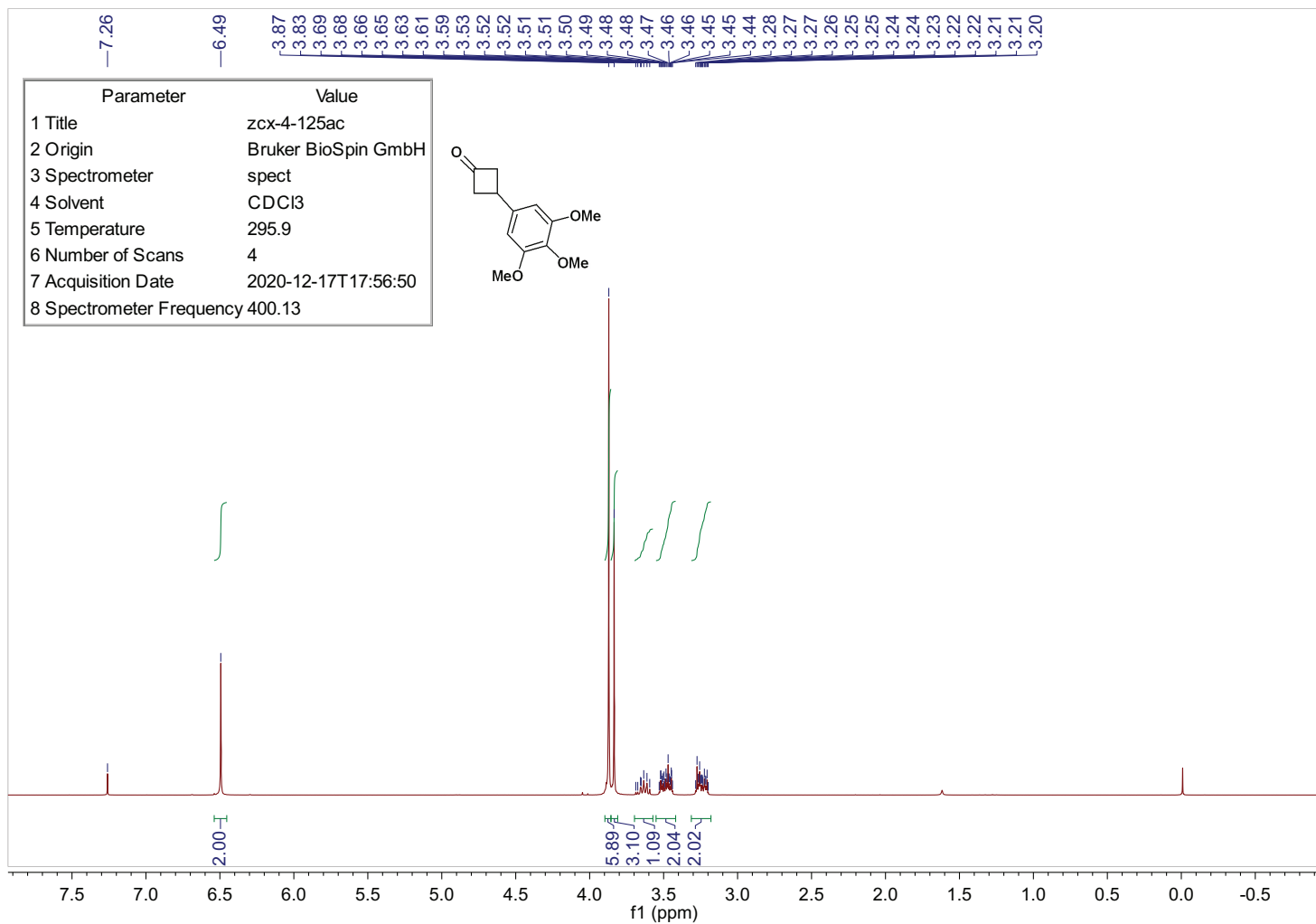
$[\alpha]_{\text{D}}^{24}$ 52.76 (c 0.50, CHCl_3).

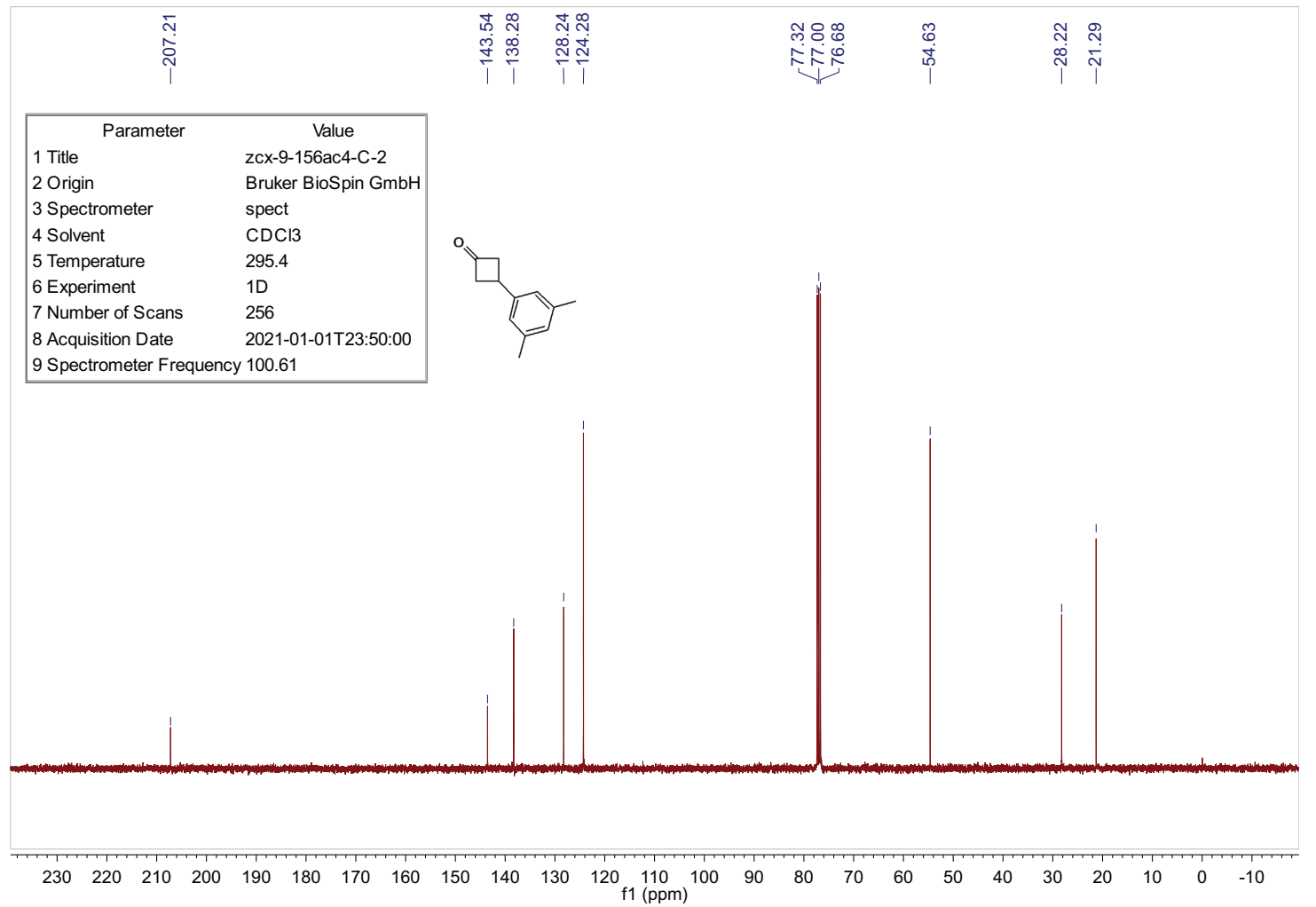
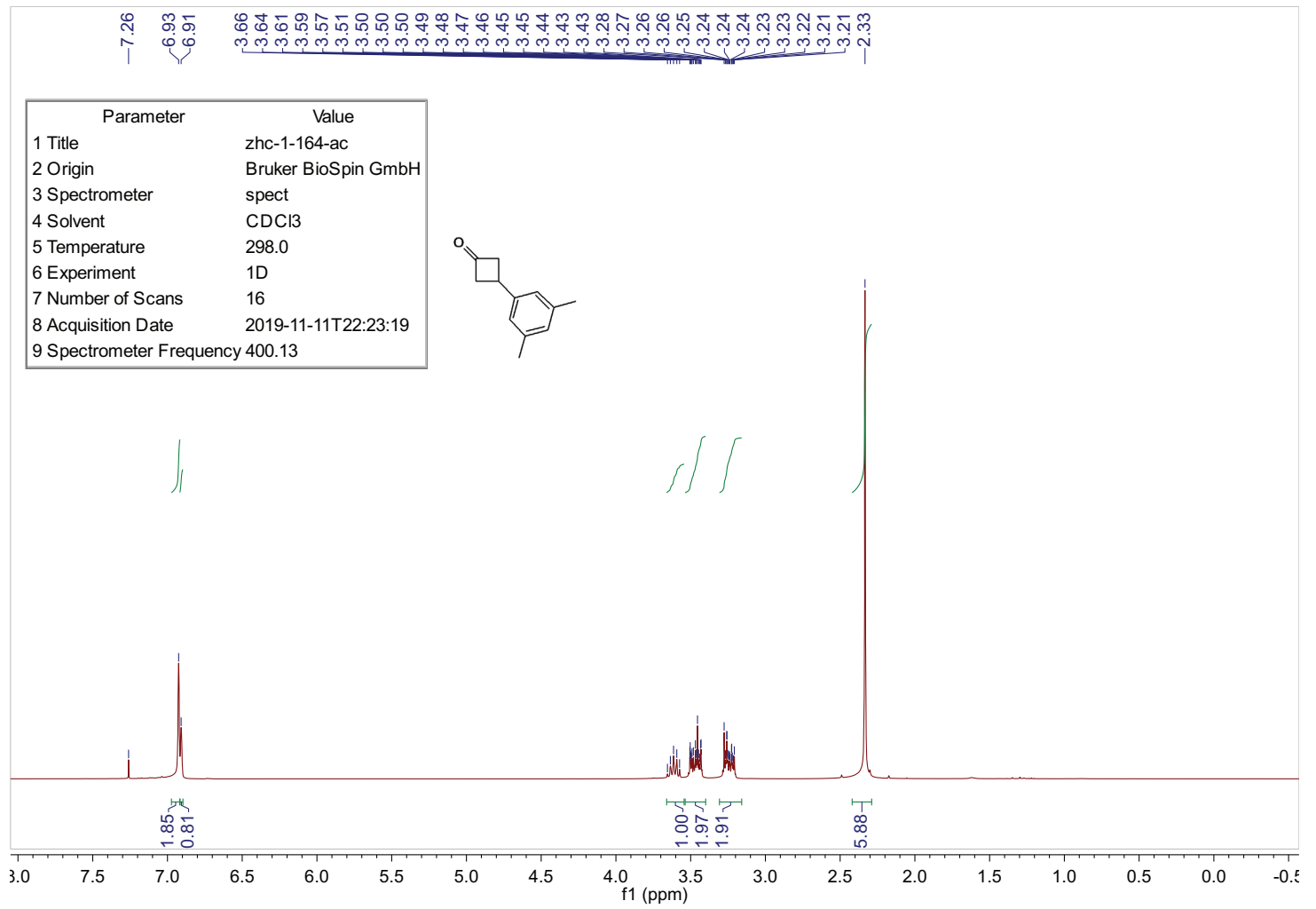
^1H NMR (400 MHz, CDCl_3) δ (ppm): 3.49 (qd, $J = 11.2, 6.2$ Hz, 2H), 3.05-2.96 (m, 1H), 2.99 (s, 3H), 2.94-2.87 (m, 1H), 2.54-2.43 (m, 1H), 2.08-1.99 (m, 1H), 1.90-1.78 (m, 2H), 1.77-1.55 (m, 5H), 0.90 (d, $J = 6.7$ Hz, 3H).

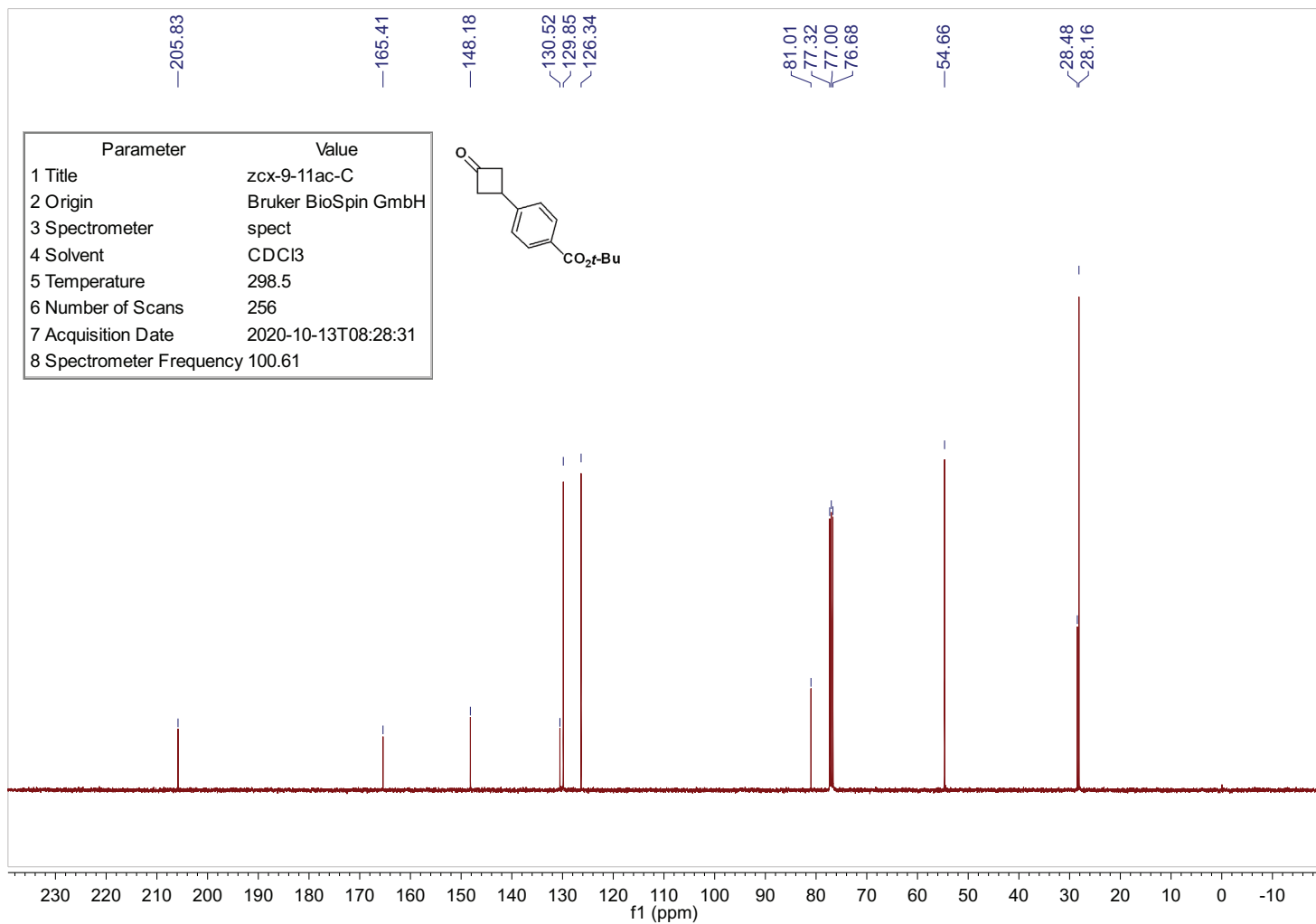
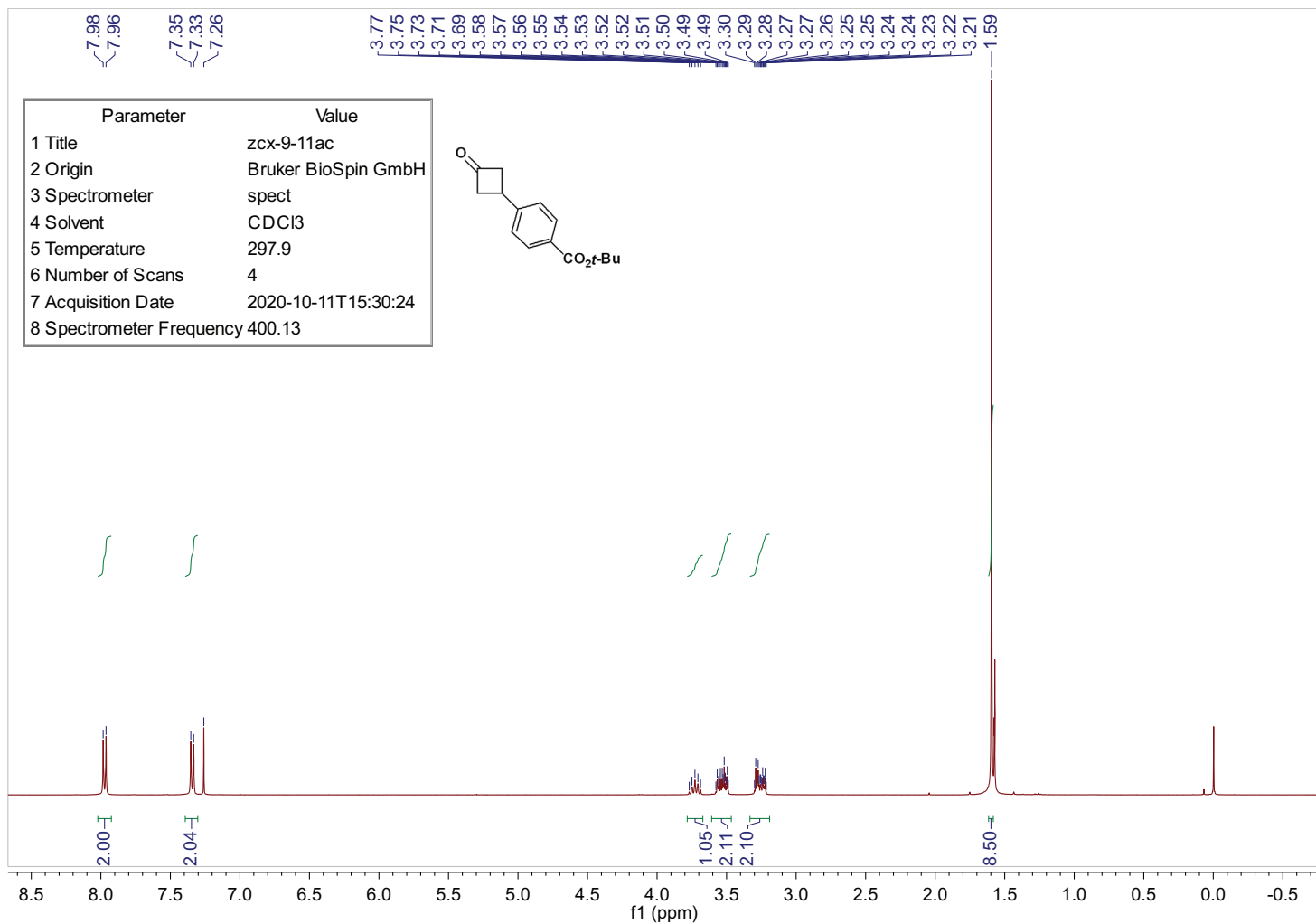
^{13}C NMR (101 MHz, CDCl_3) δ (ppm): 181.21, 180.29, 67.59, 39.69, 39.66, 38.72, 37.24, 32.59, 29.49, 26.56, 24.67, 19.46, 17.06.

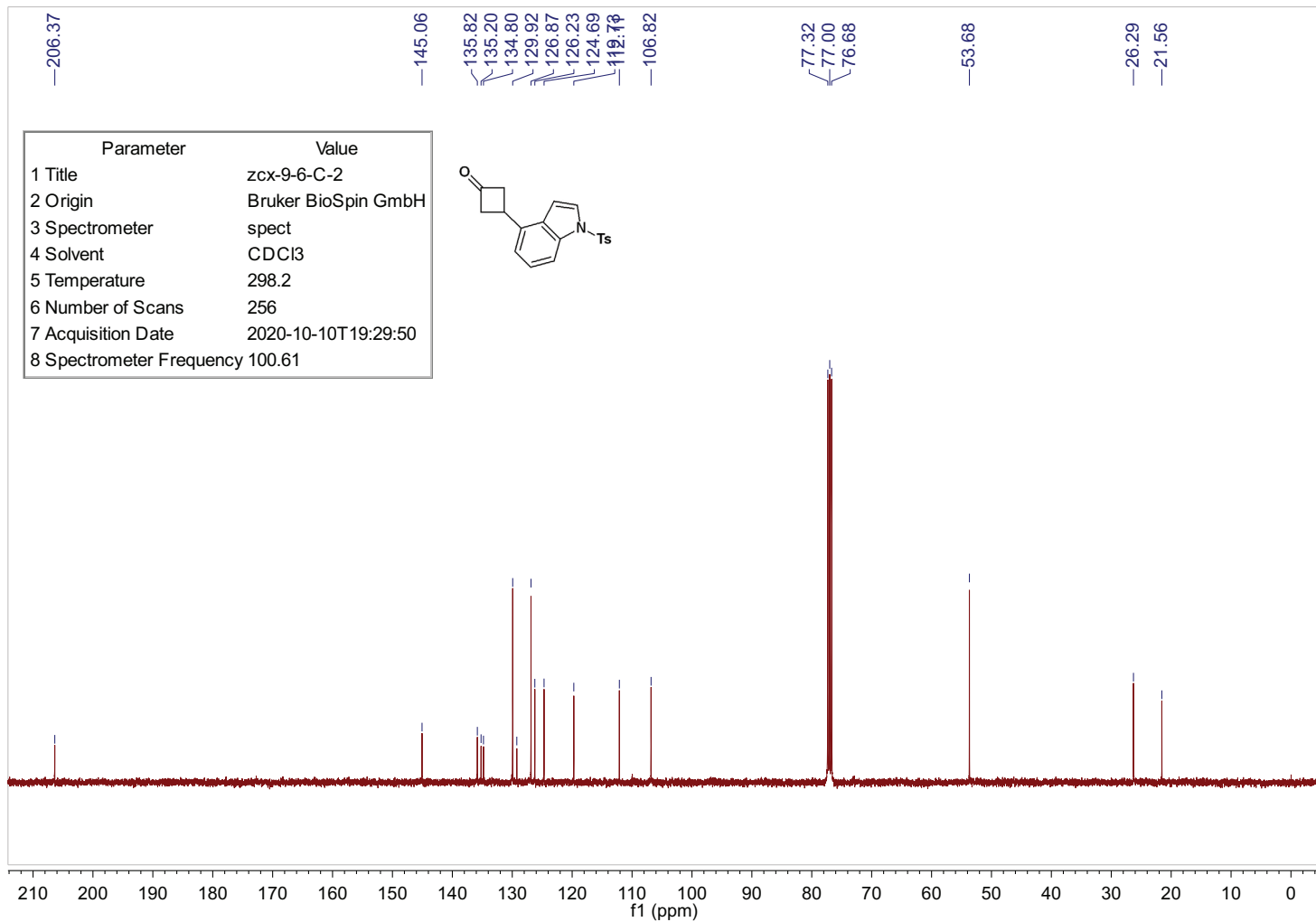
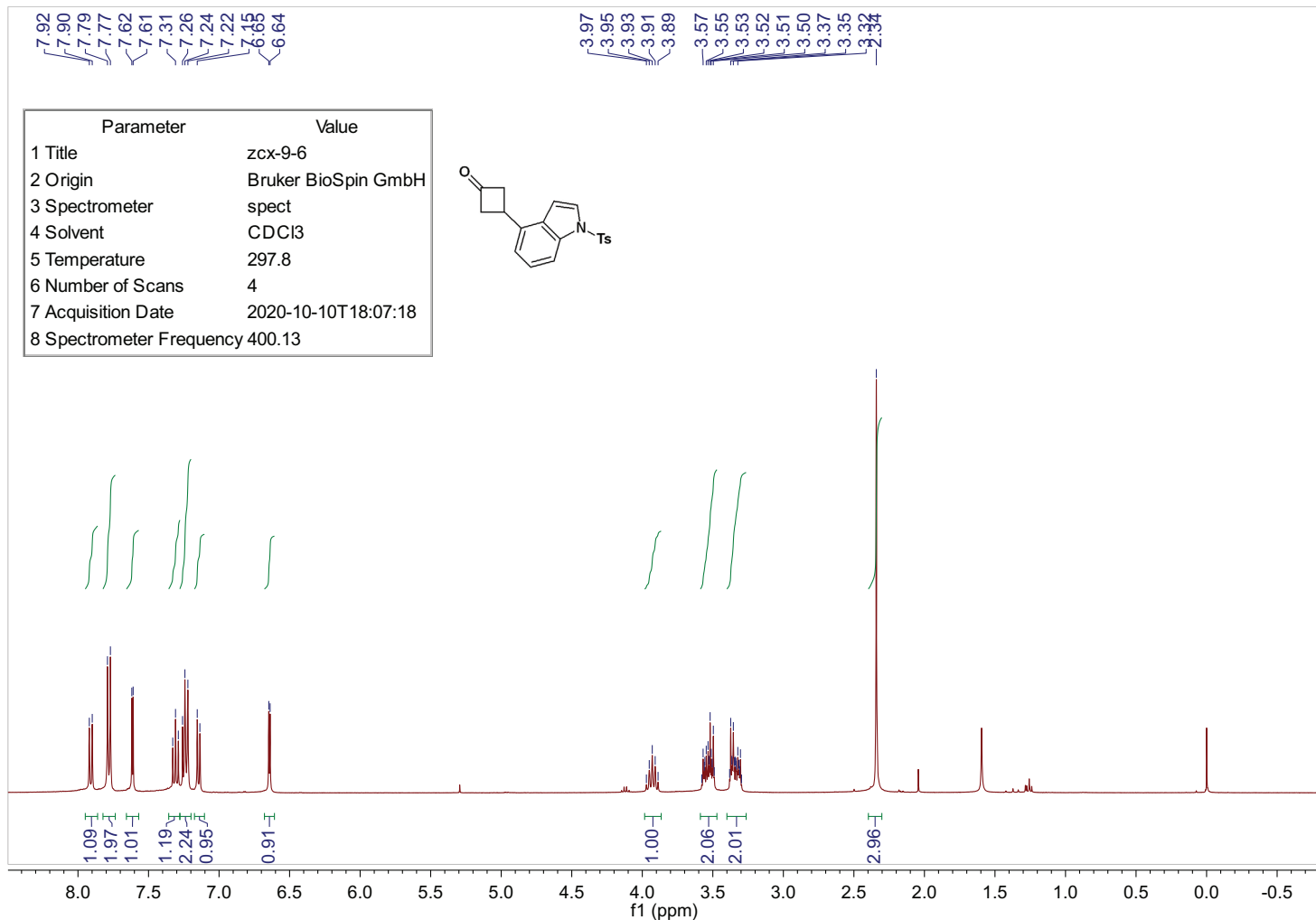
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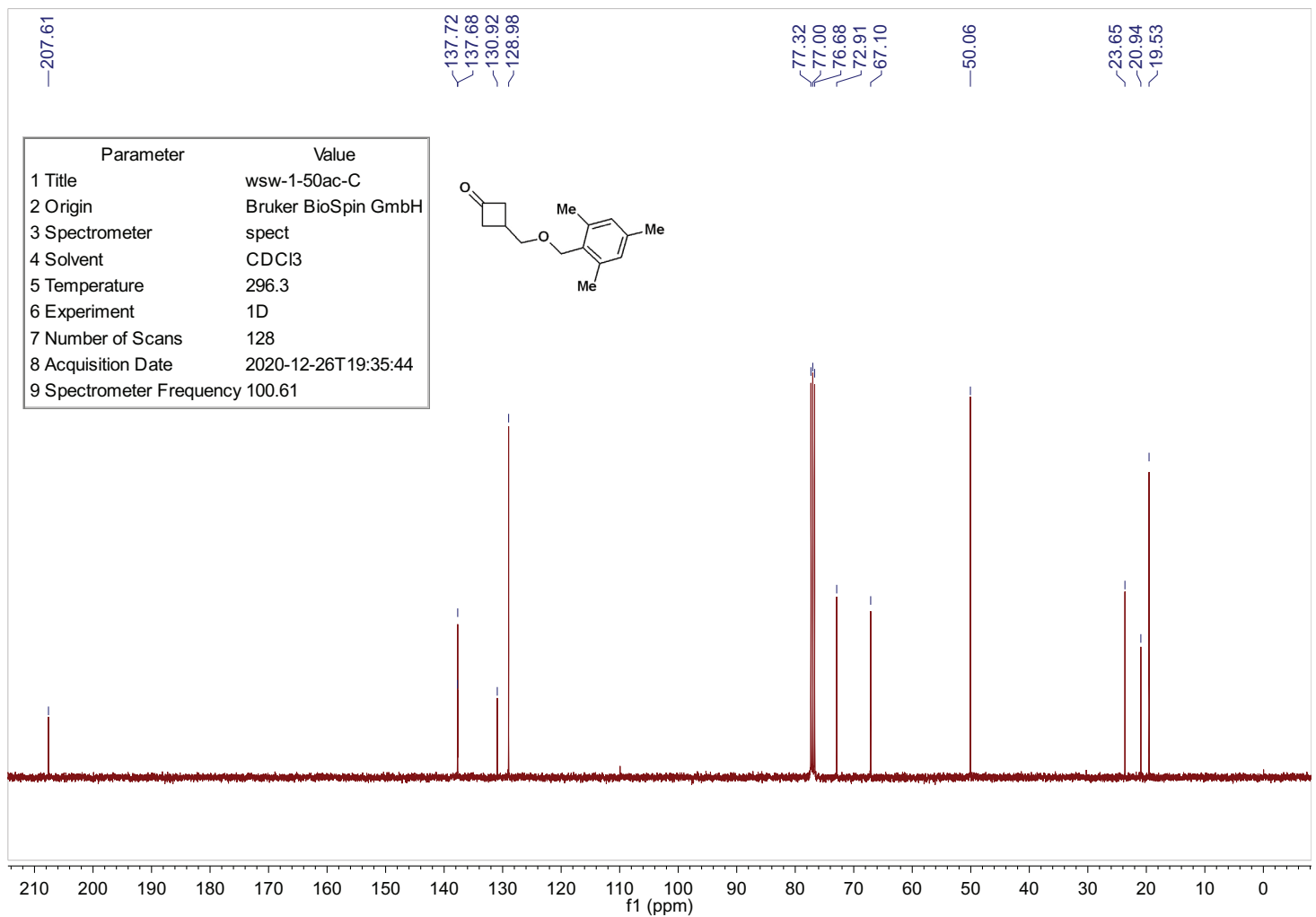
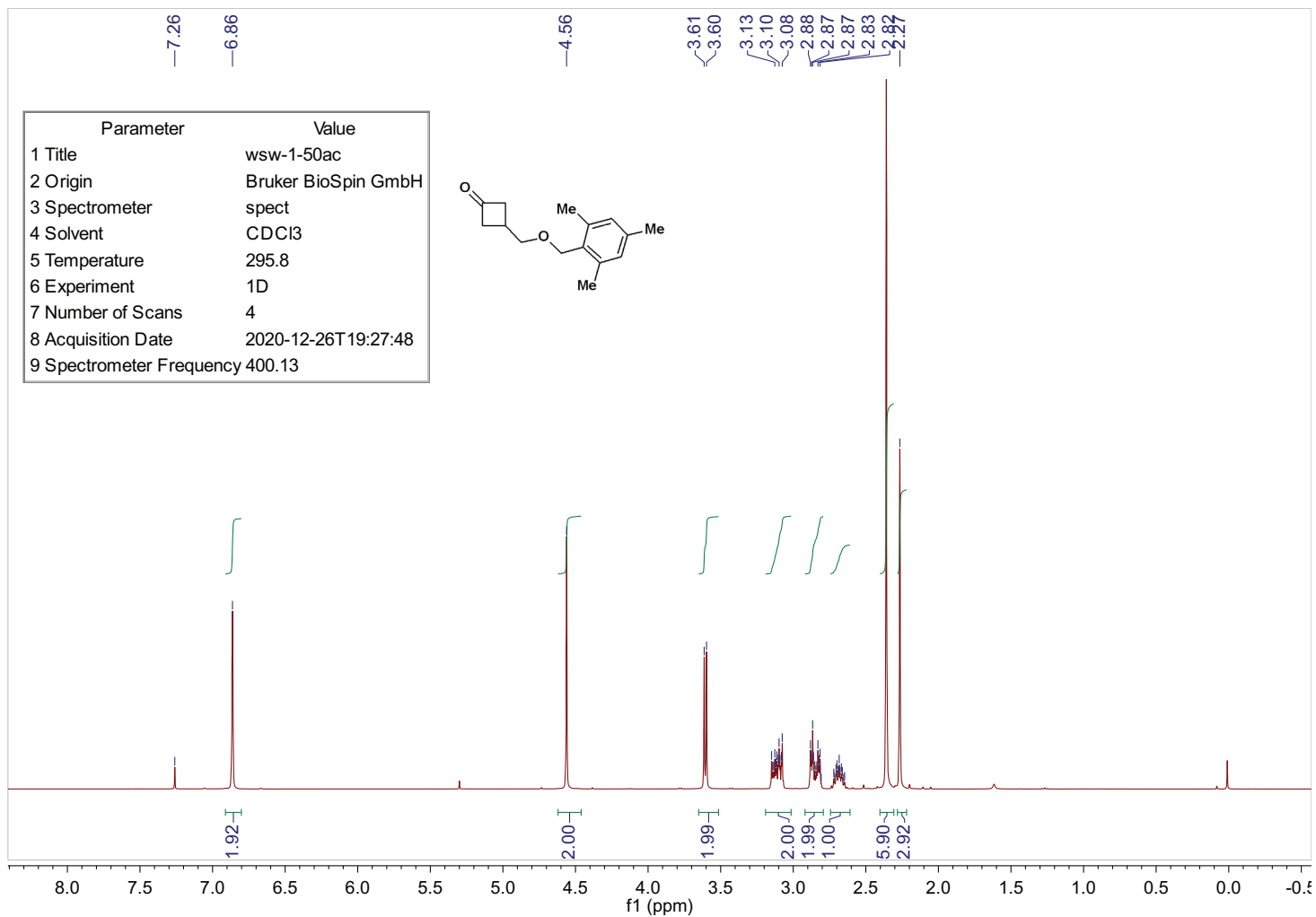
HRMS-ESI (m/z): $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{13}\text{H}_{20}\text{NO}_3$, 238.1438; found, 238.1438.

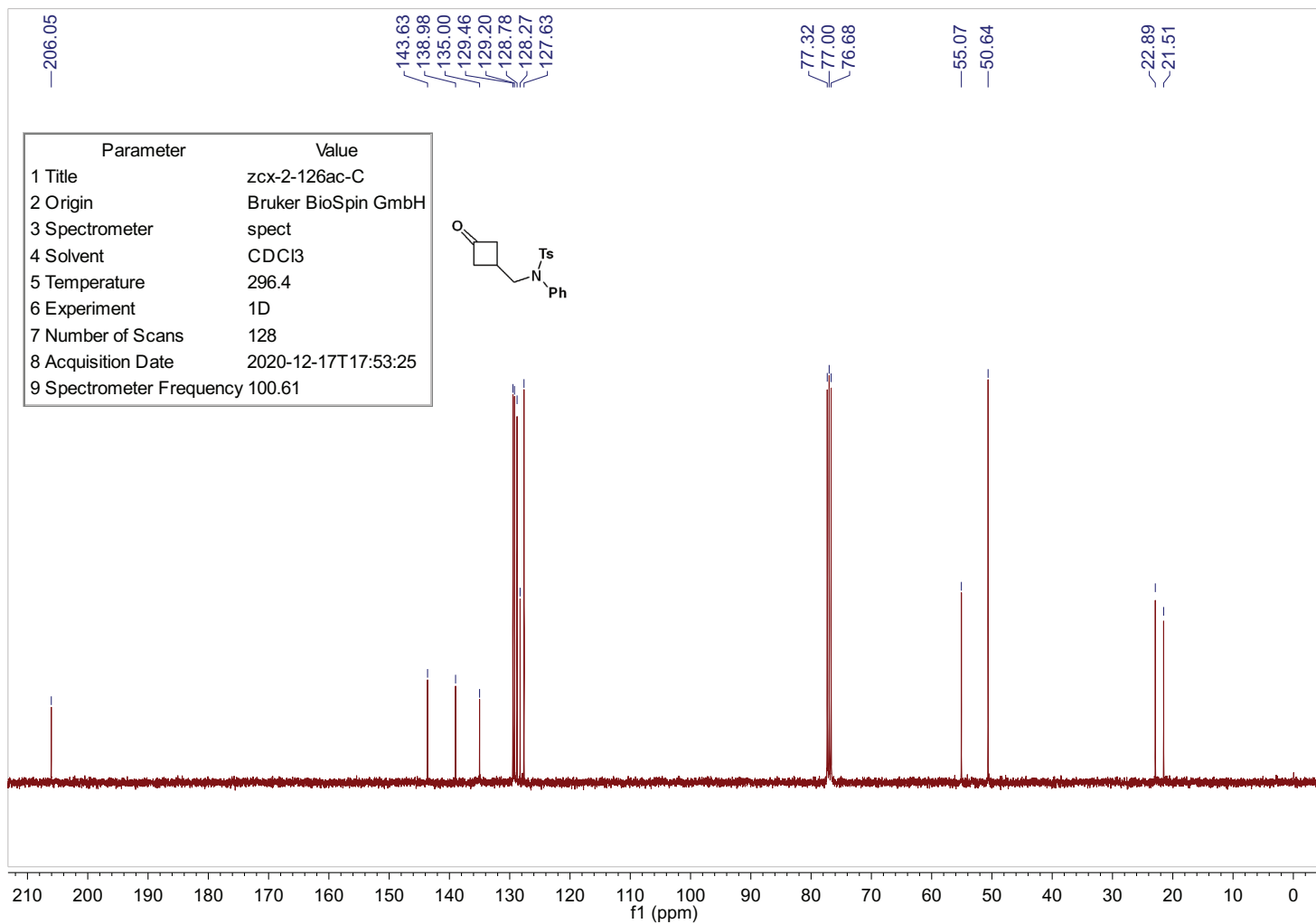
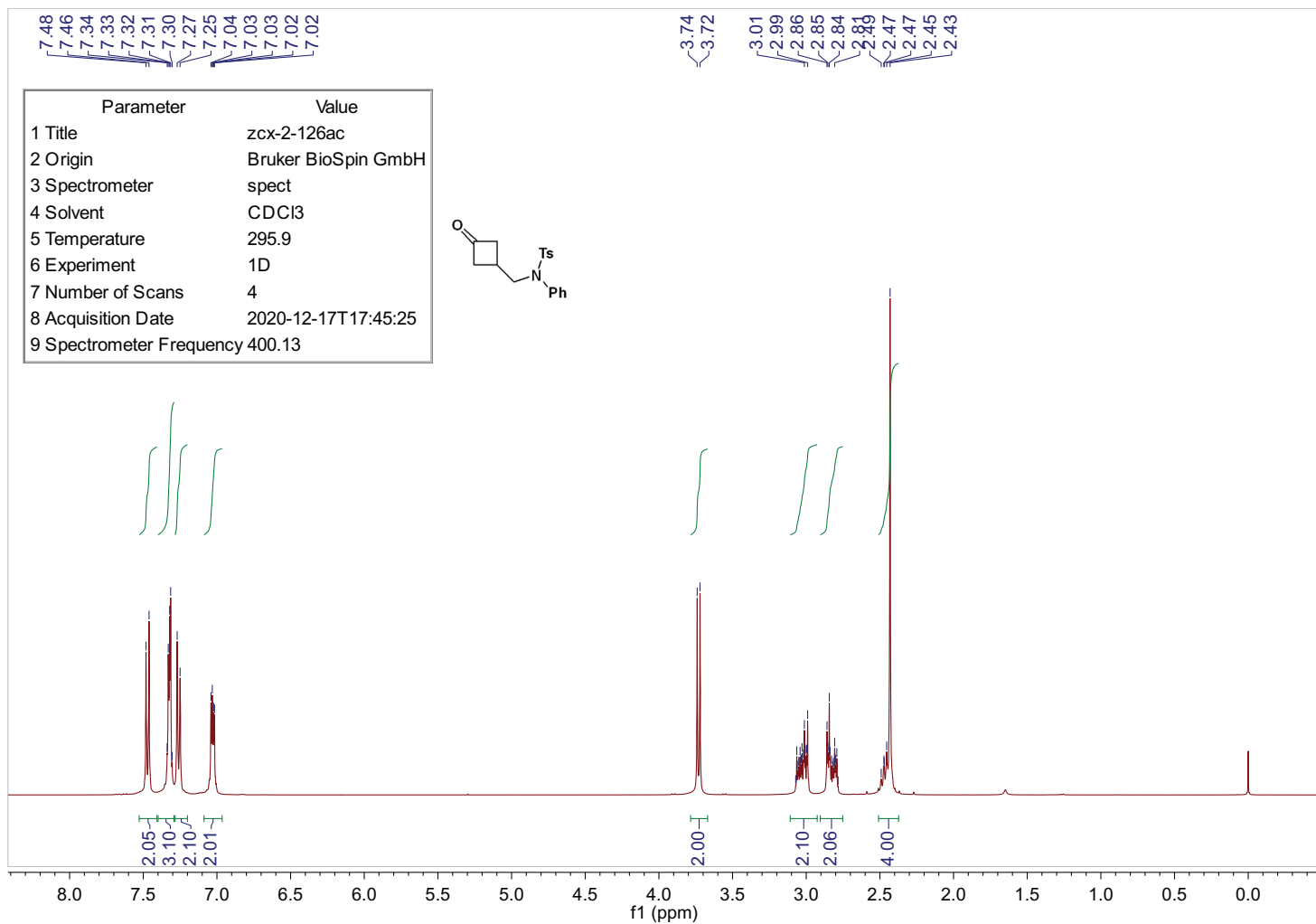


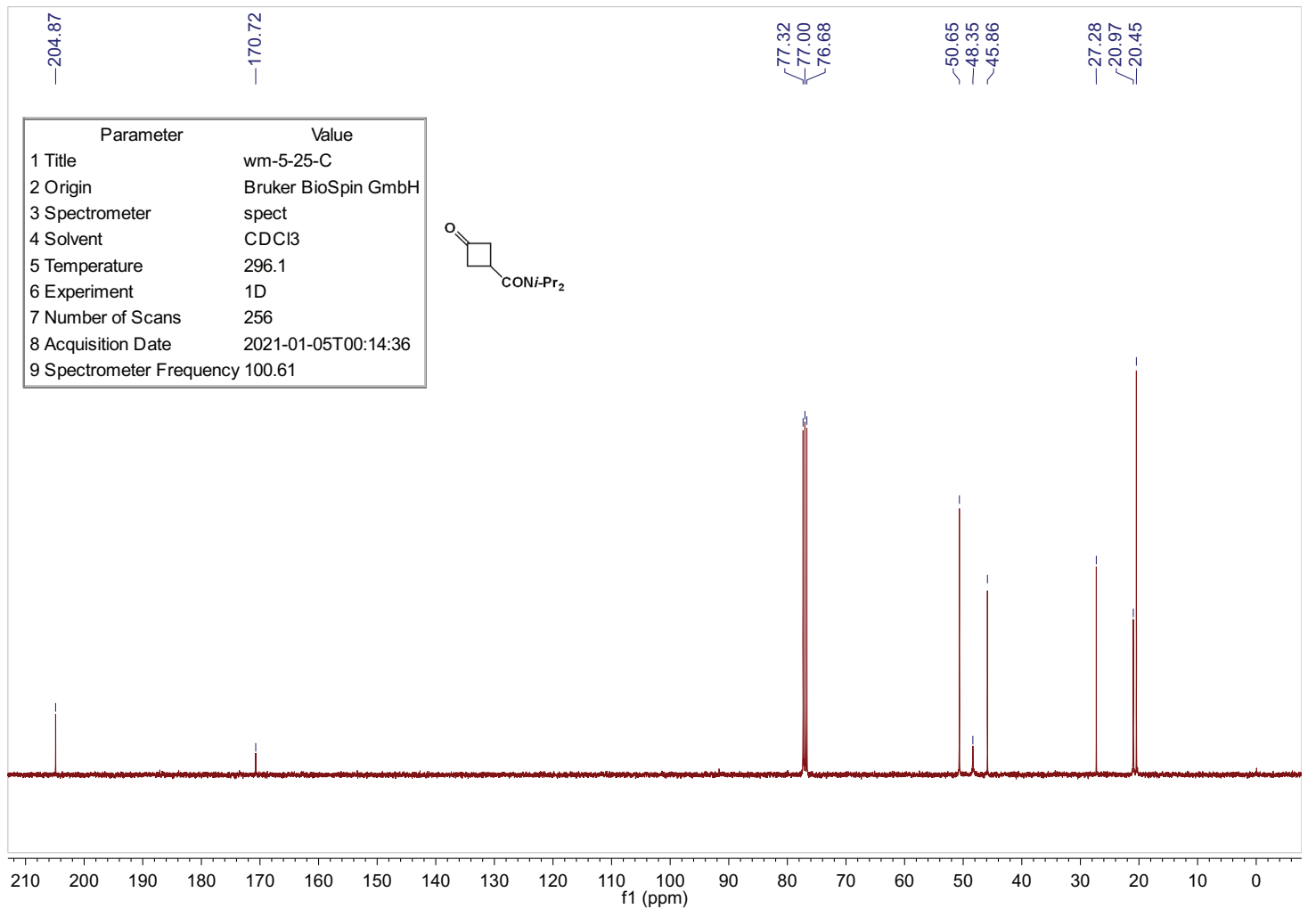
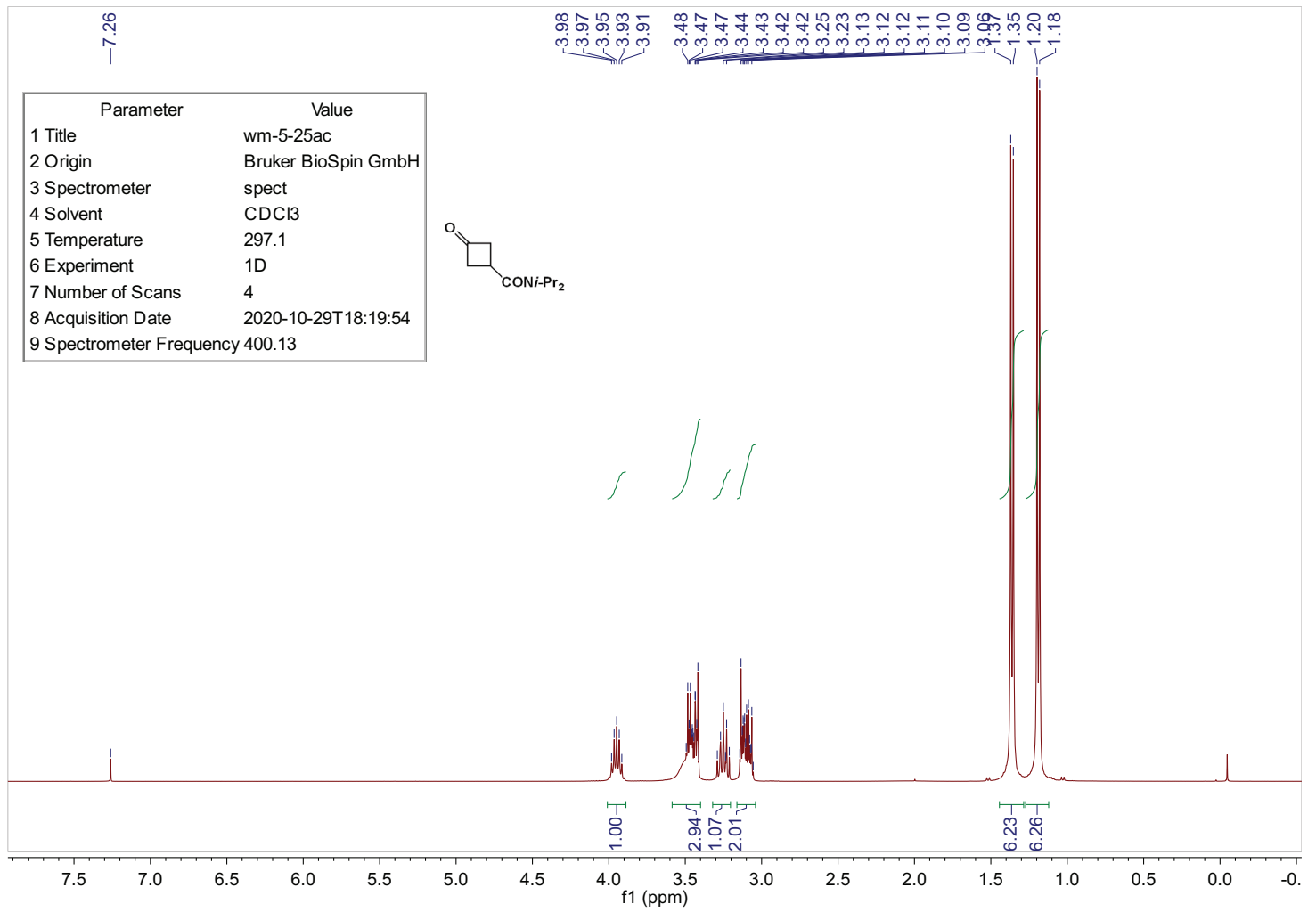










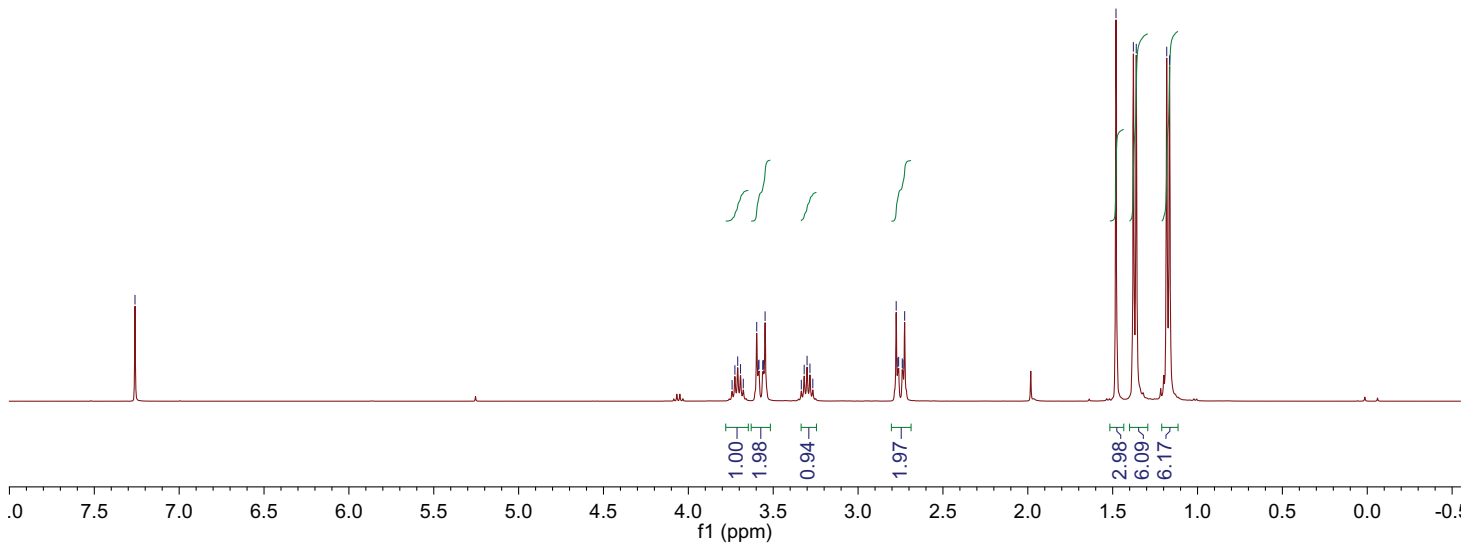
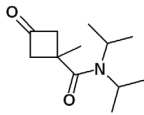


-7.26

3.74
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2.73

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1.18
1.16

Parameter	Value
1 Title	wm-5-33ac-1
2 Origin	Bruker BioSpin GmbH
3 Solvent	CDCl3
4 Temperature	298.2
5 Number of Scans	4
6 Relaxation Delay	5.0000
7 Acquisition Date	2018-10-11T17:19:02
8 Spectrometer Frequency	400.13



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-57.10

-49.12

-46.33

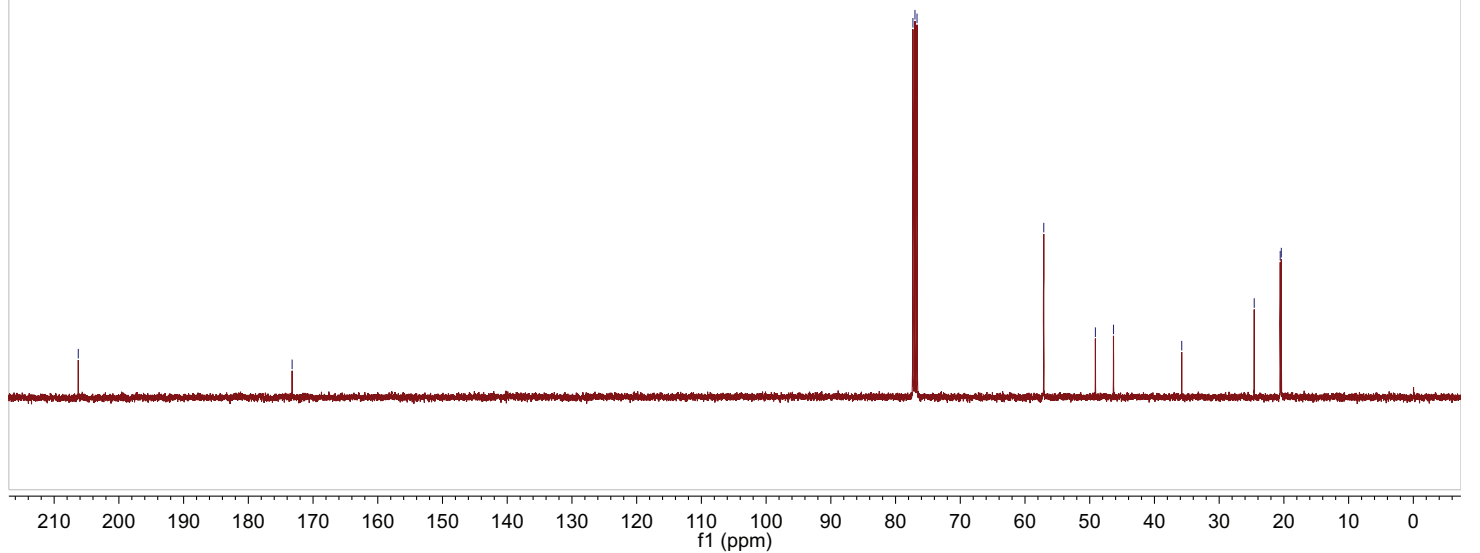
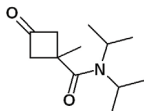
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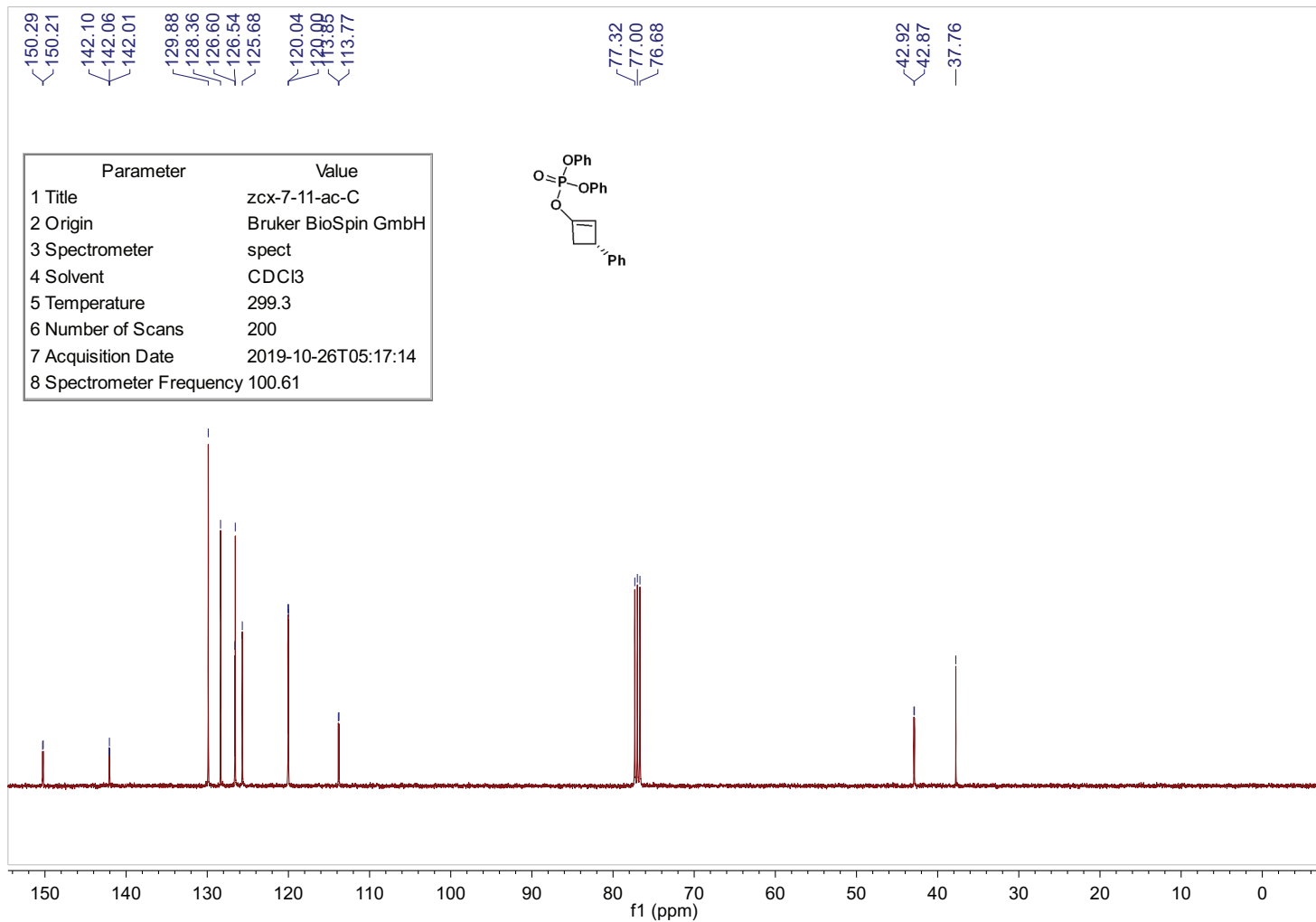
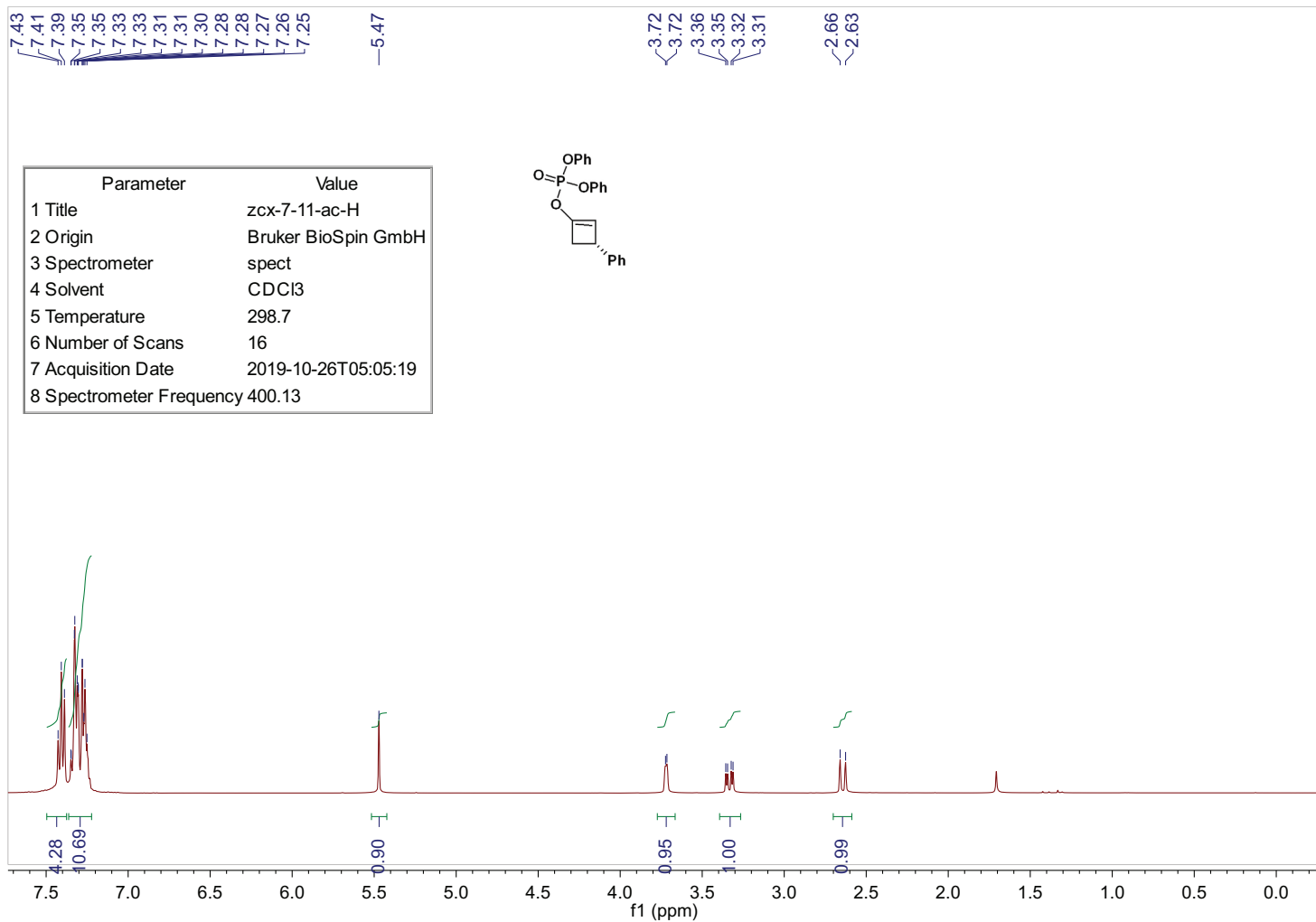
-24.58

-20.57

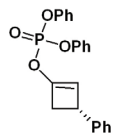
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Parameter	Value
1 Title	wm-5-33
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
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6 Experiment	1D
7 Number of Scans	128
8 Acquisition Date	2020-12-27T02:28:46
9 Spectrometer Frequency	100.61

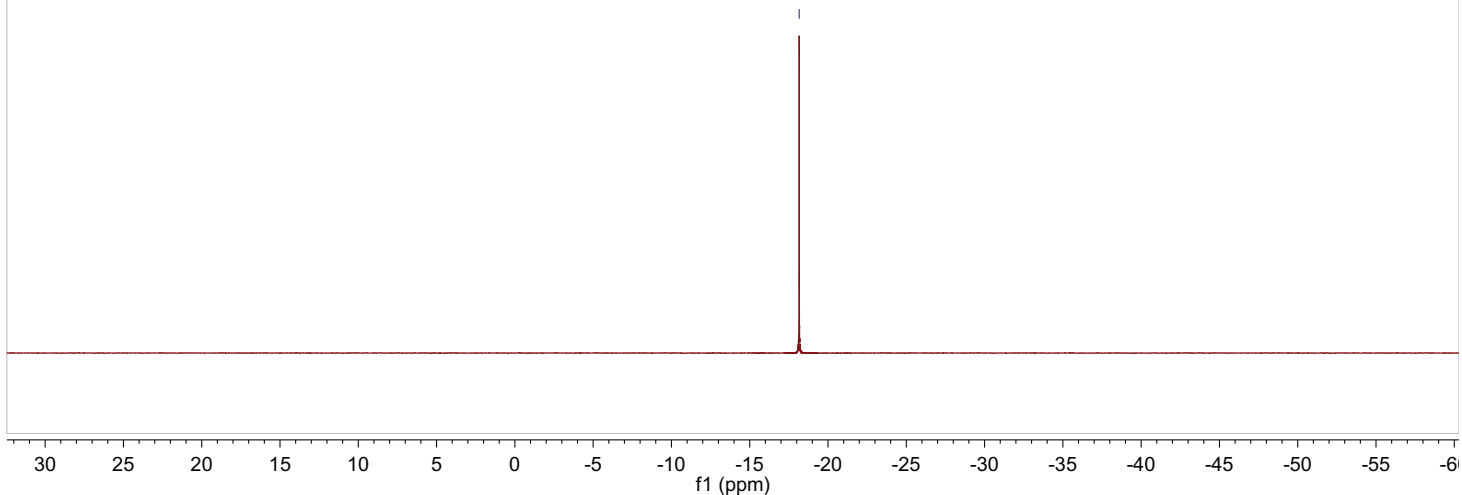




Parameter	Value
1 Title	zcx-7-11-ac-P
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	299.2
6 Number of Scans	16
7 Acquisition Date	2019-10-26T05:19:07
8 Spectrometer Frequency	161.98



---18.16

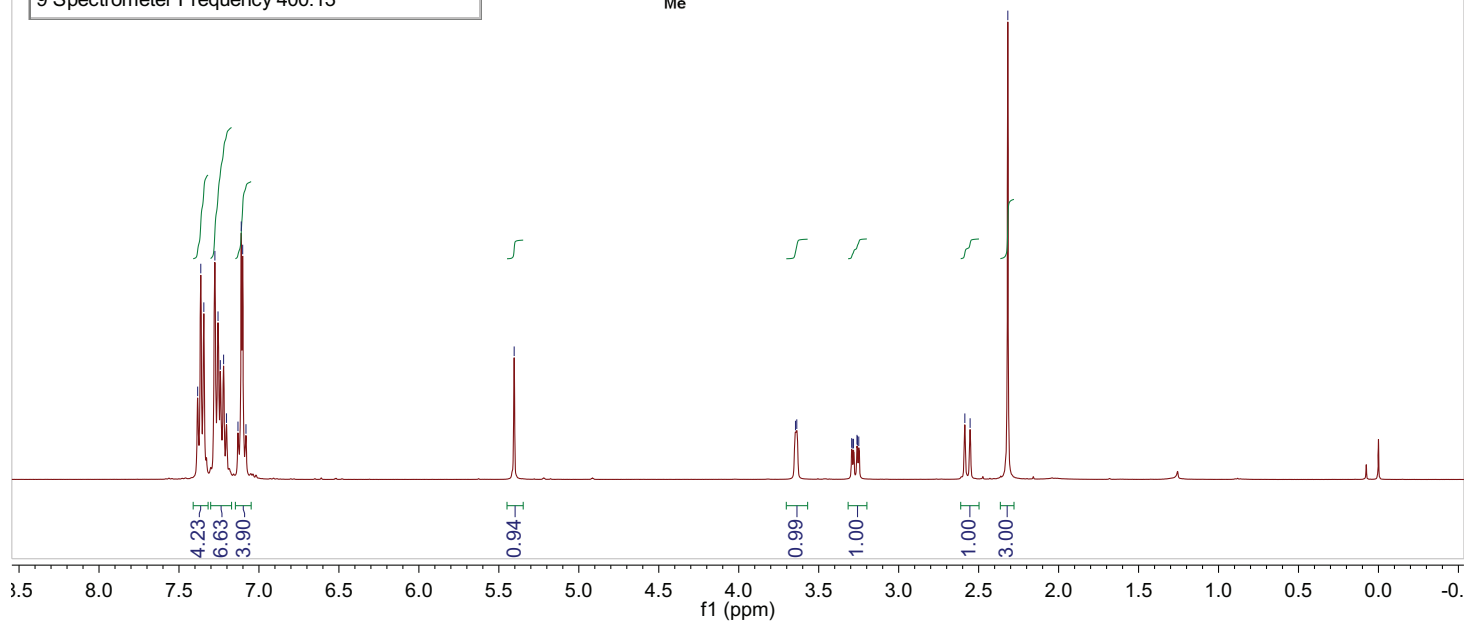
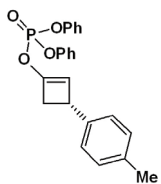


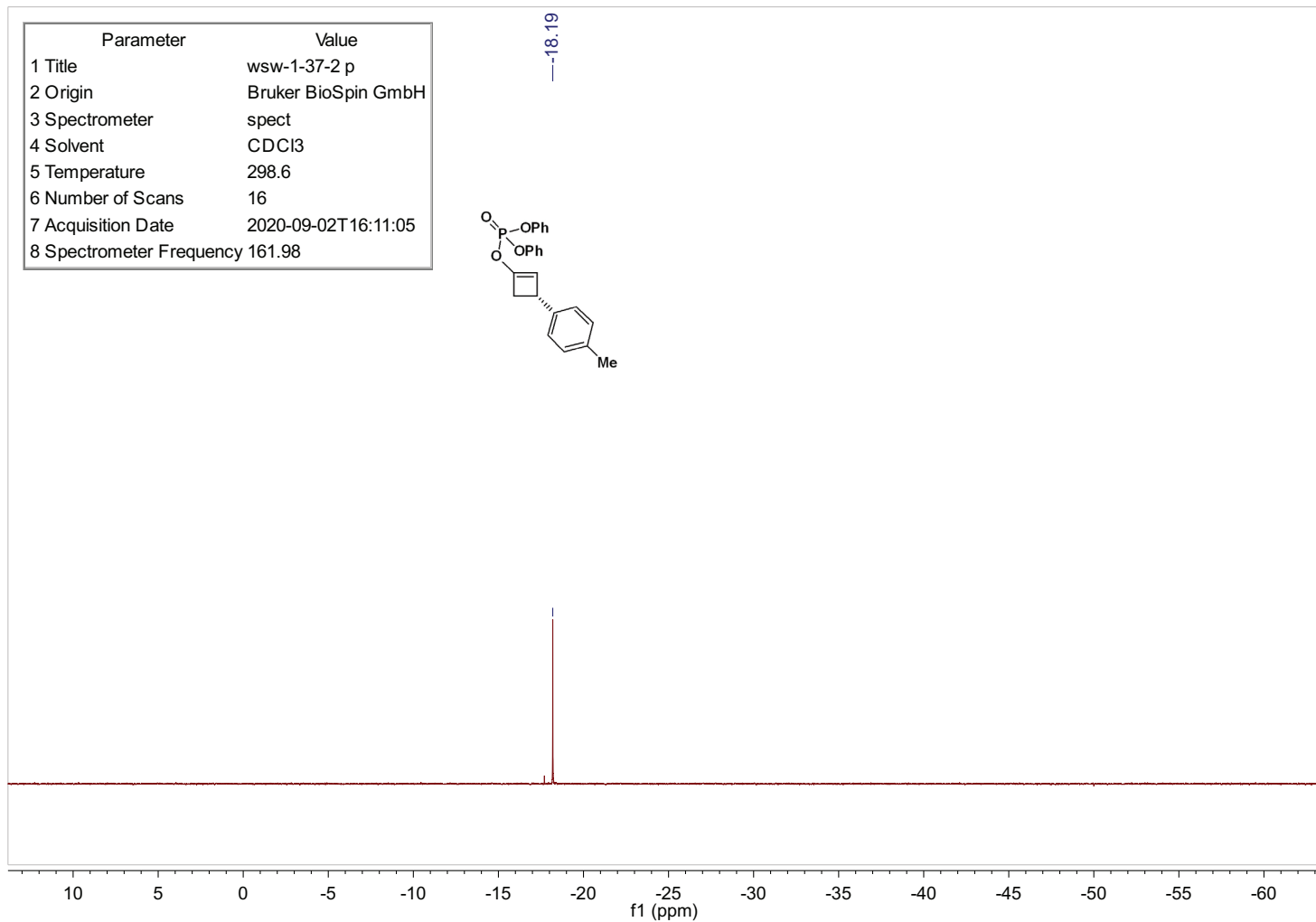
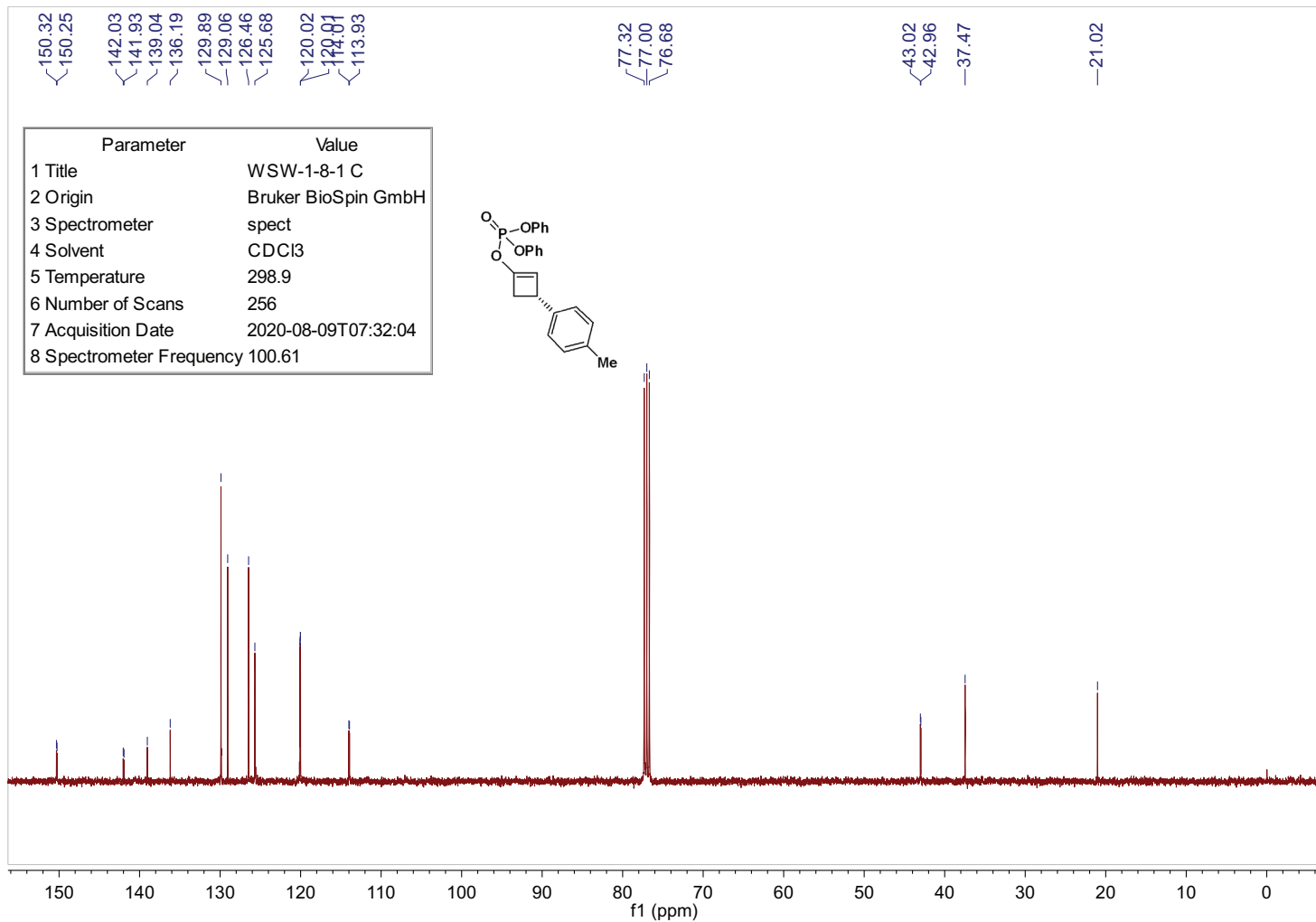
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7.36
7.34
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7.24
7.22
7.20
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7.11
7.10
7.08

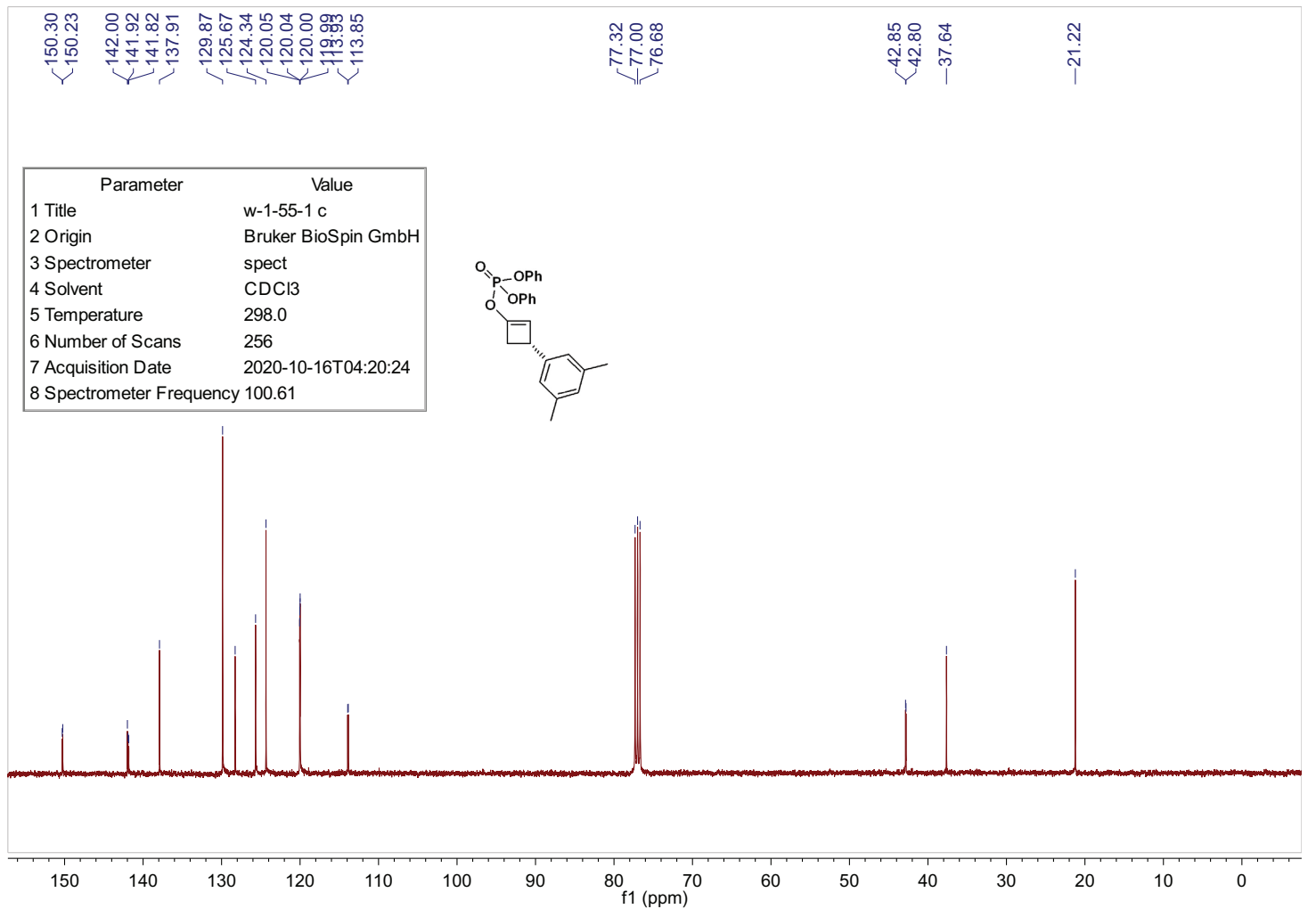
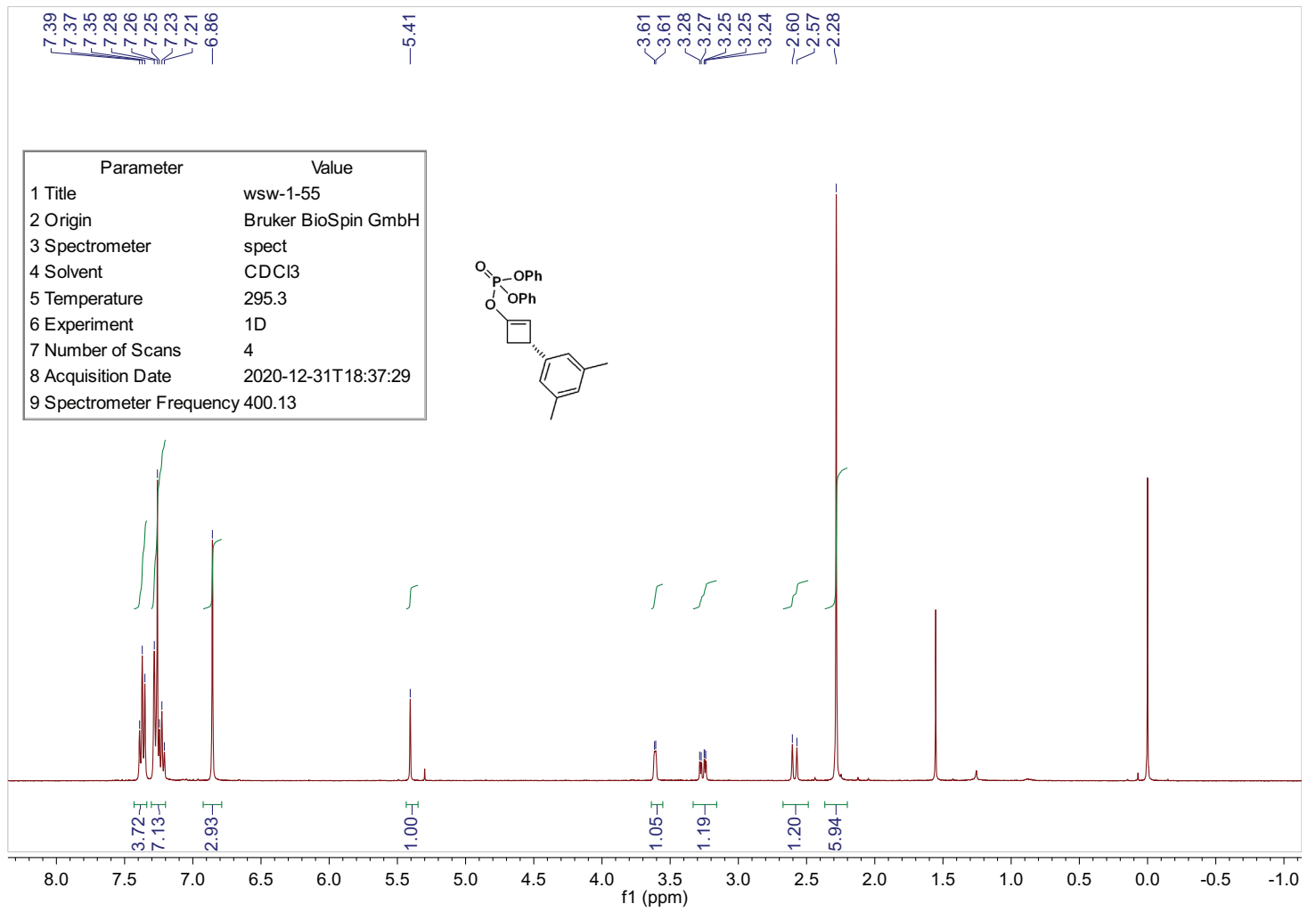
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3.65
3.64
3.29
3.28
3.26
3.26
3.25
2.55
2.32

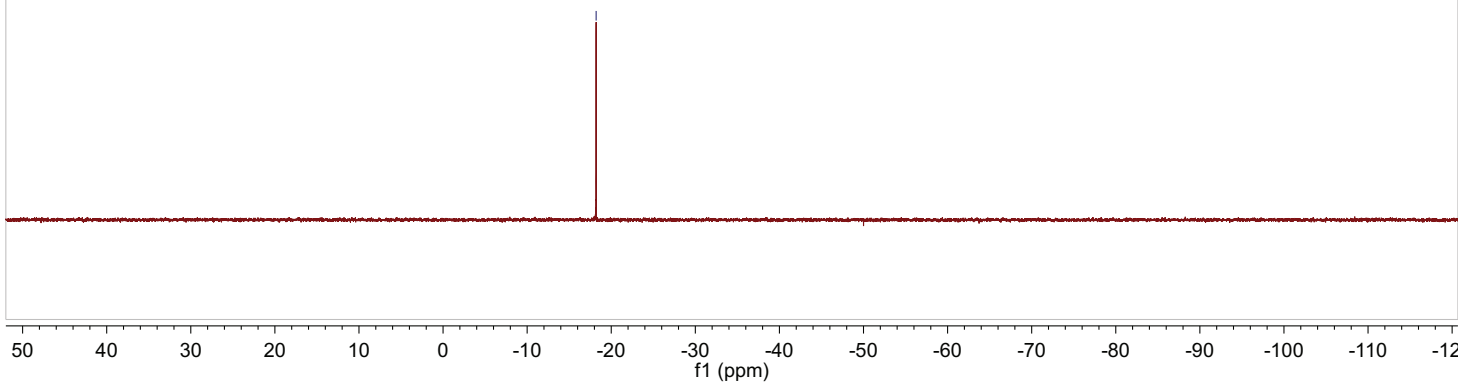
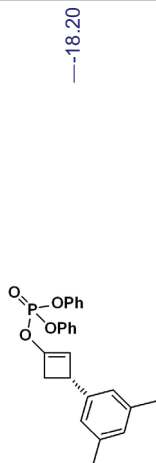
Parameter	Value
1 Title	wsw-1-8
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	294.2
6 Experiment	1D
7 Number of Scans	4
8 Acquisition Date	2020-12-31T07:51:01
9 Spectrometer Frequency	400.13



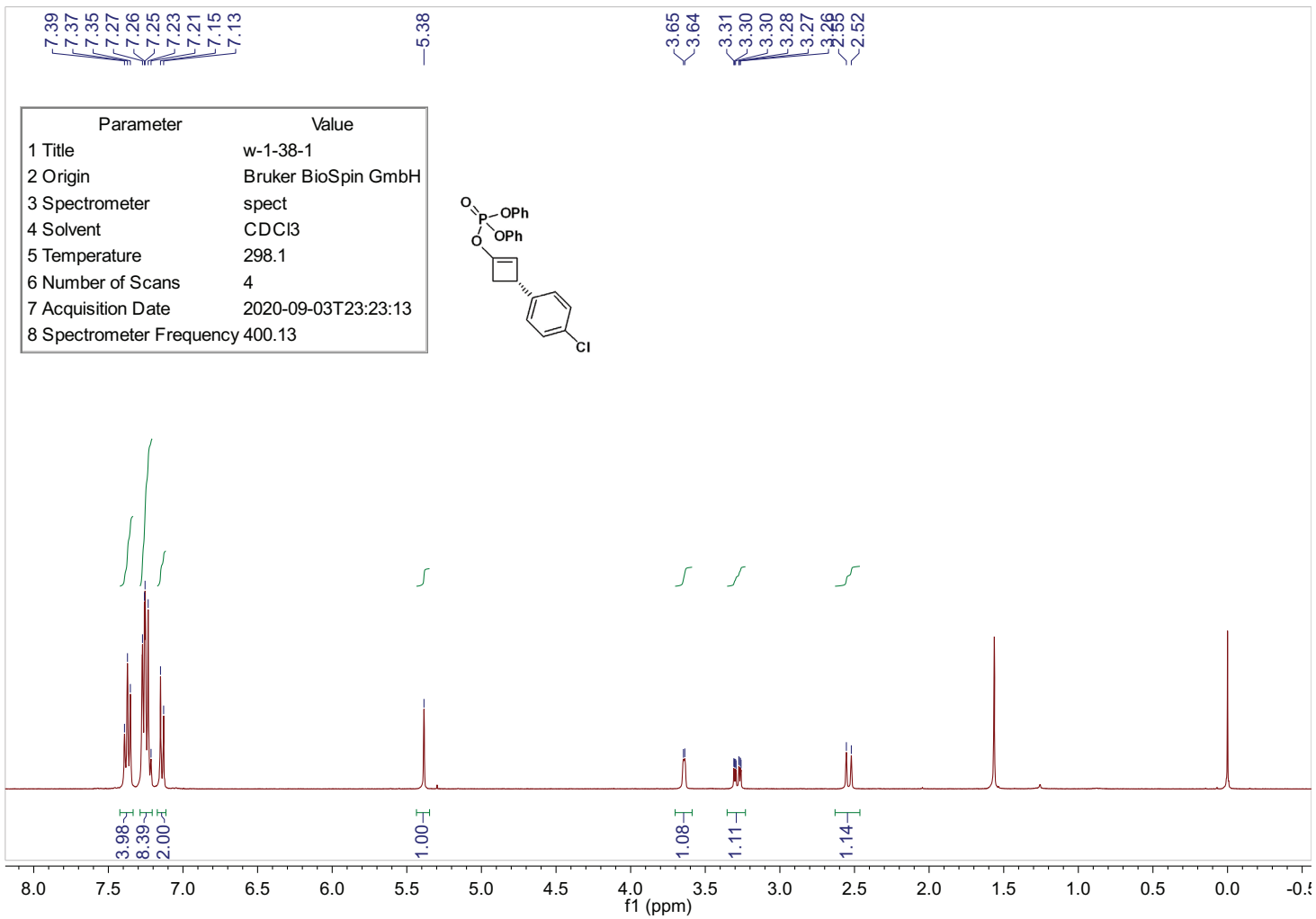
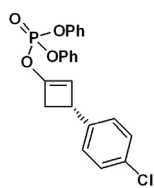


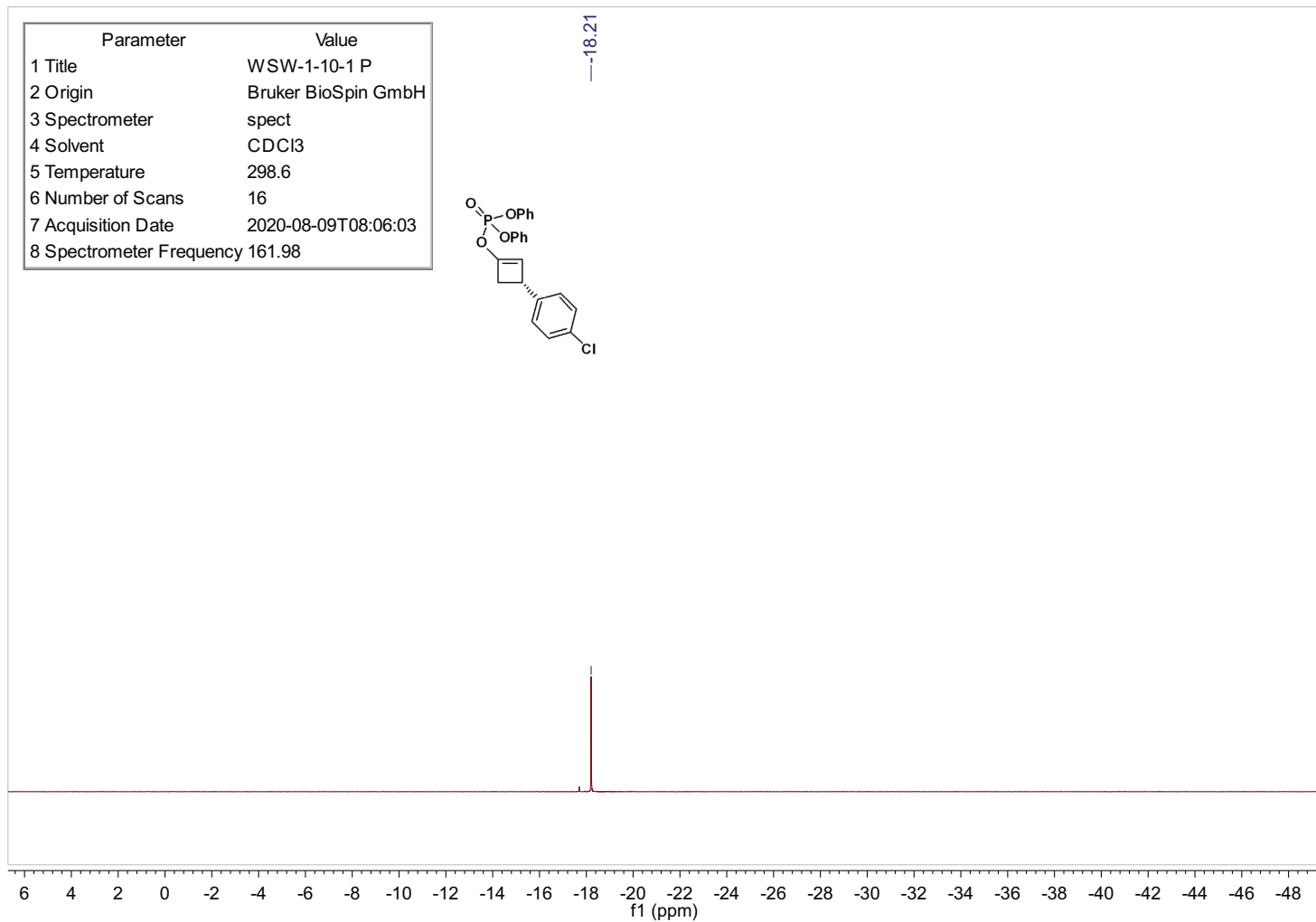
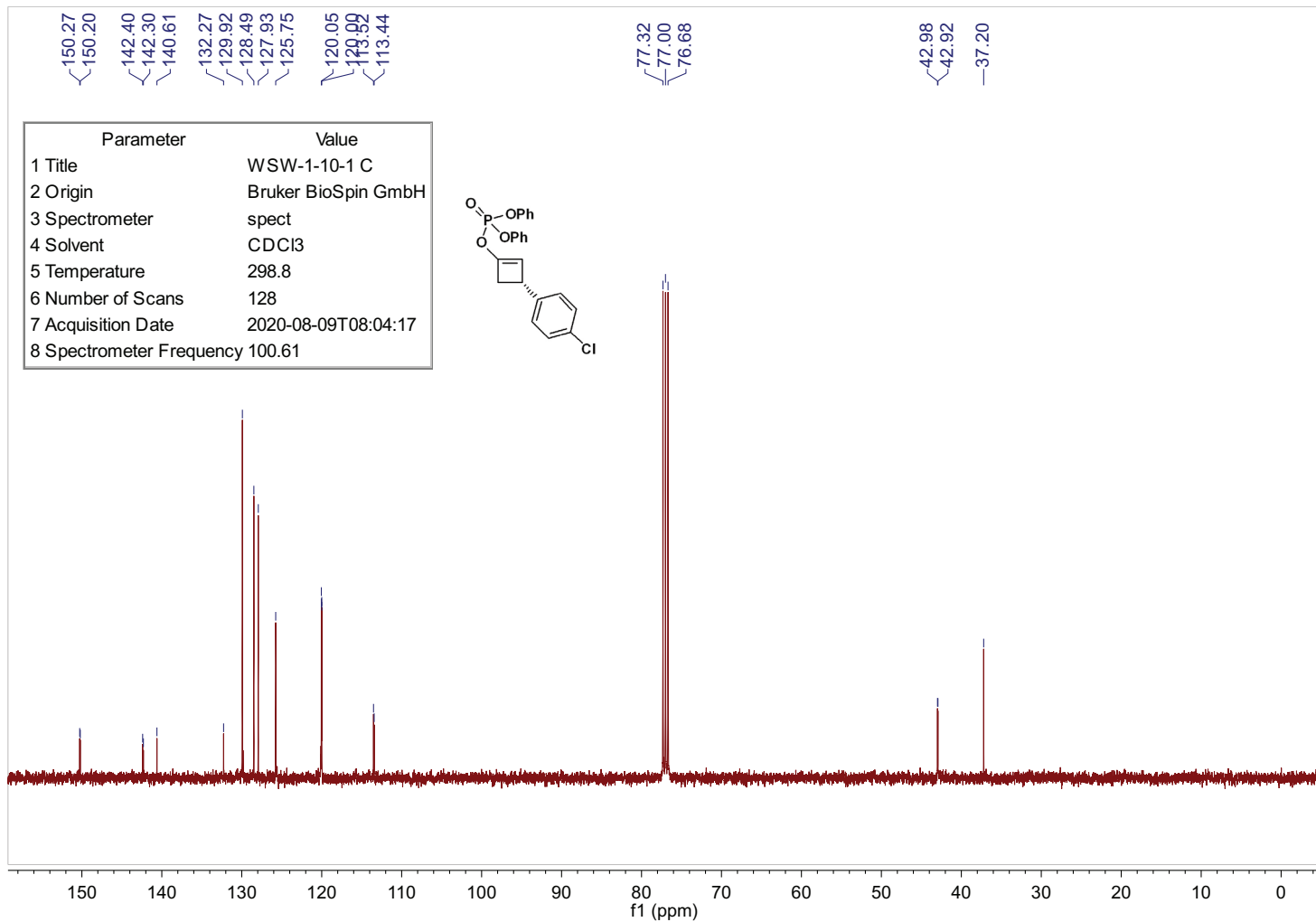


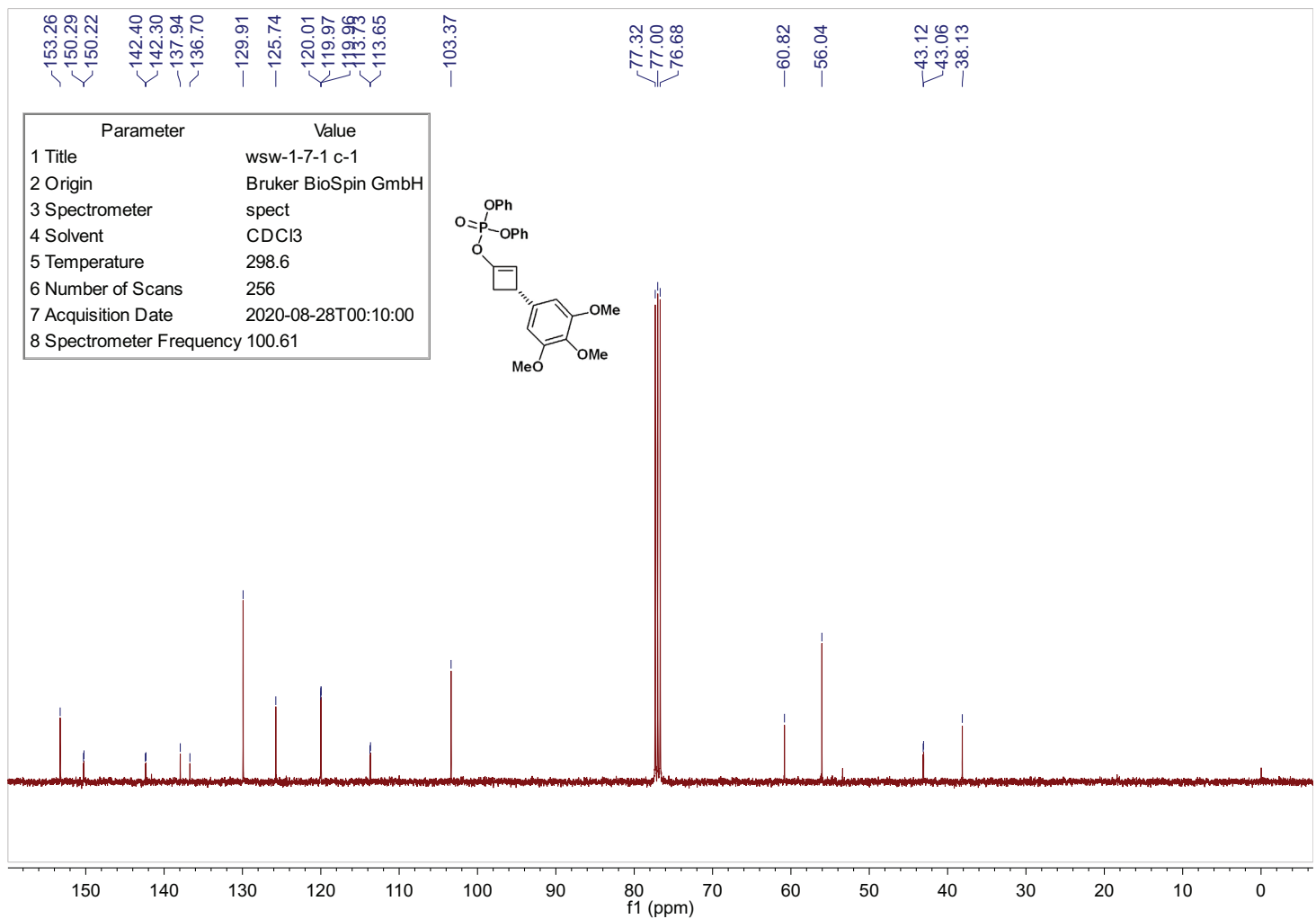
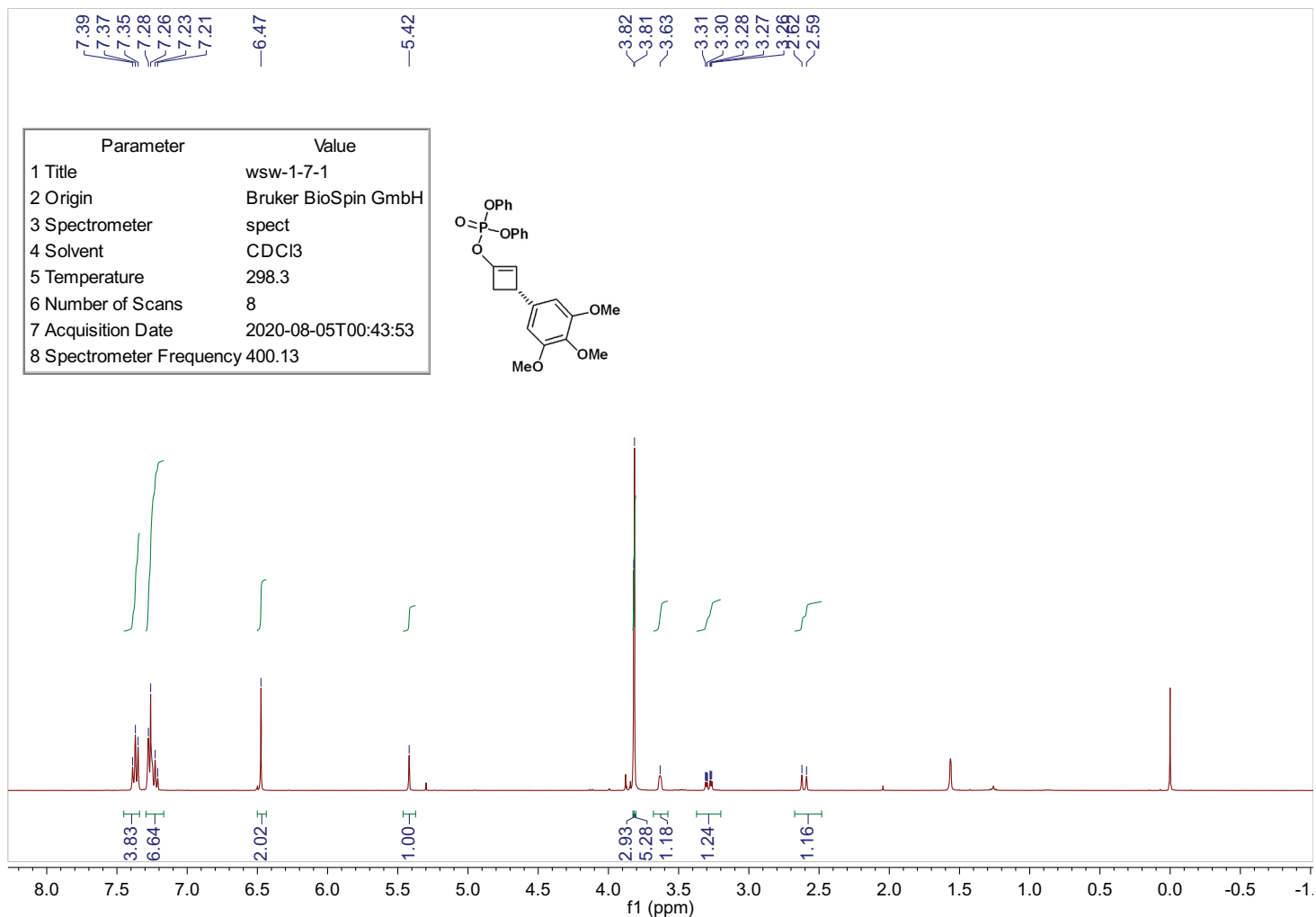
Parameter	Value
1 Title	w-1-55-1 p
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	297.7
6 Number of Scans	16
7 Acquisition Date	2020-10-16T03:41:52
8 Spectrometer Frequency	161.98



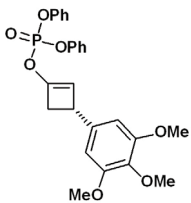
Parameter	Value
1 Title	w-1-38-1
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	298.1
6 Number of Scans	4
7 Acquisition Date	2020-09-03T23:23:13
8 Spectrometer Frequency	400.13



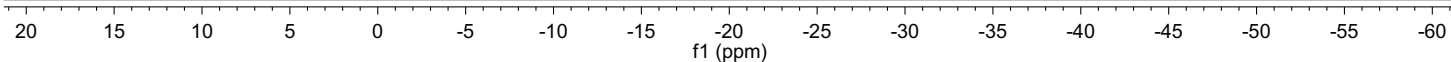




Parameter	Value
1 Title	WSW-1-7-1 P
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	298.8
6 Number of Scans	16
7 Acquisition Date	2020-08-09T07:14:27
8 Spectrometer Frequency	161.98



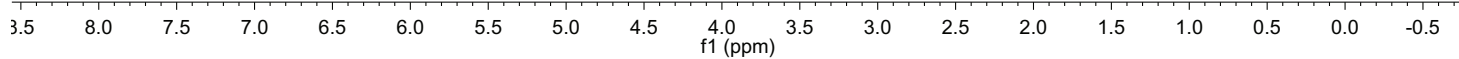
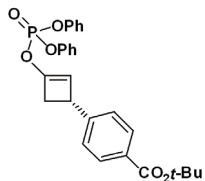
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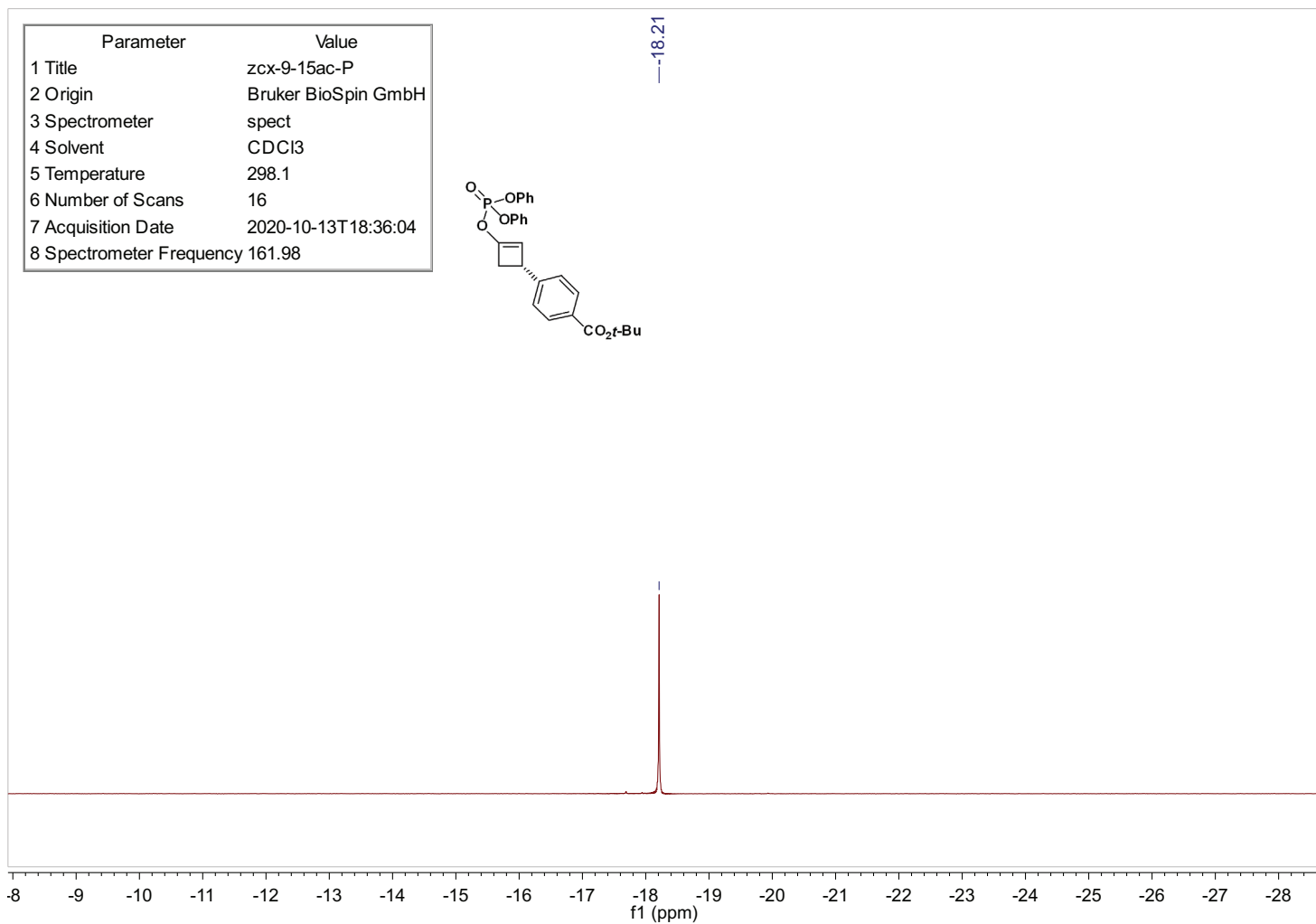
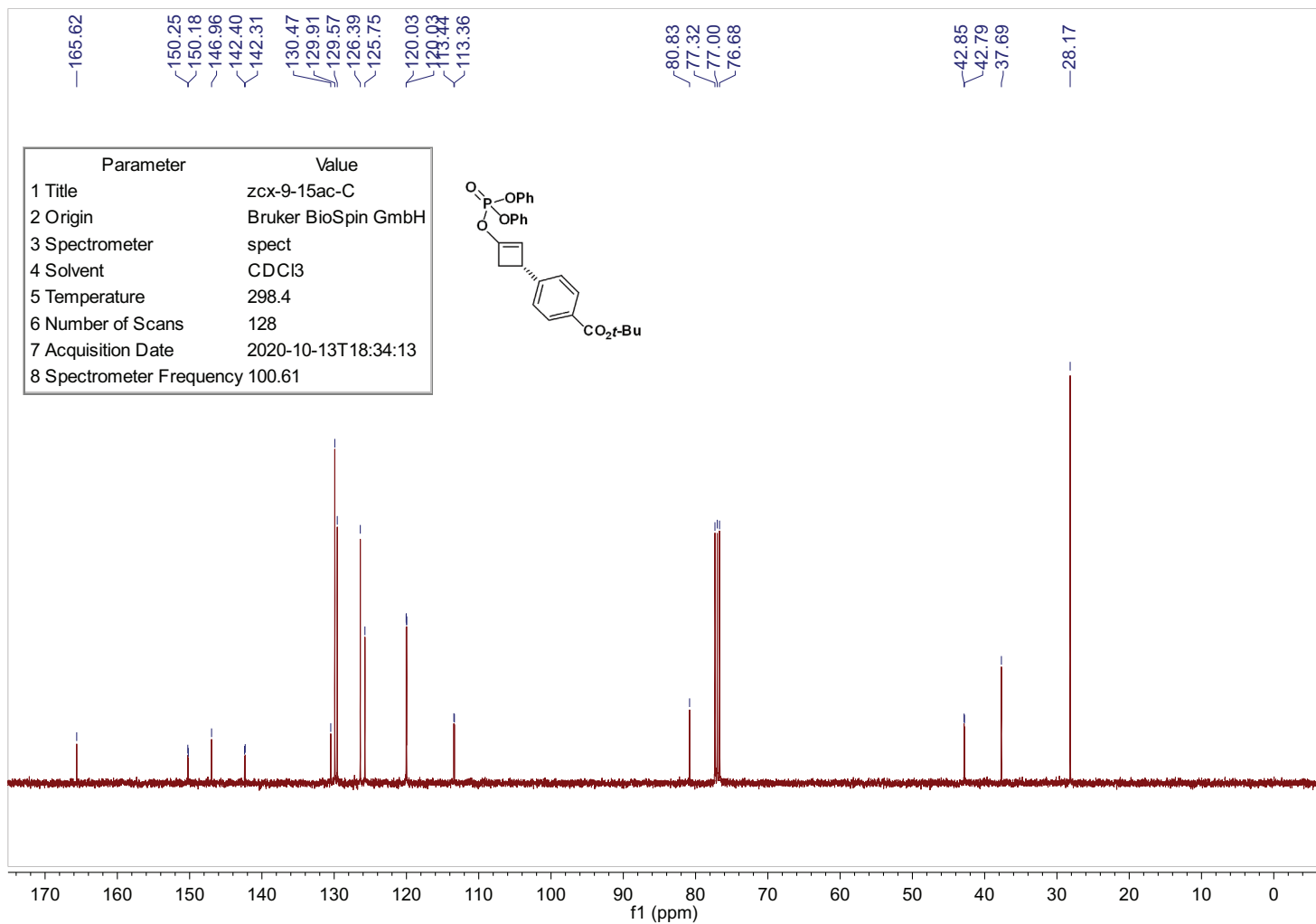


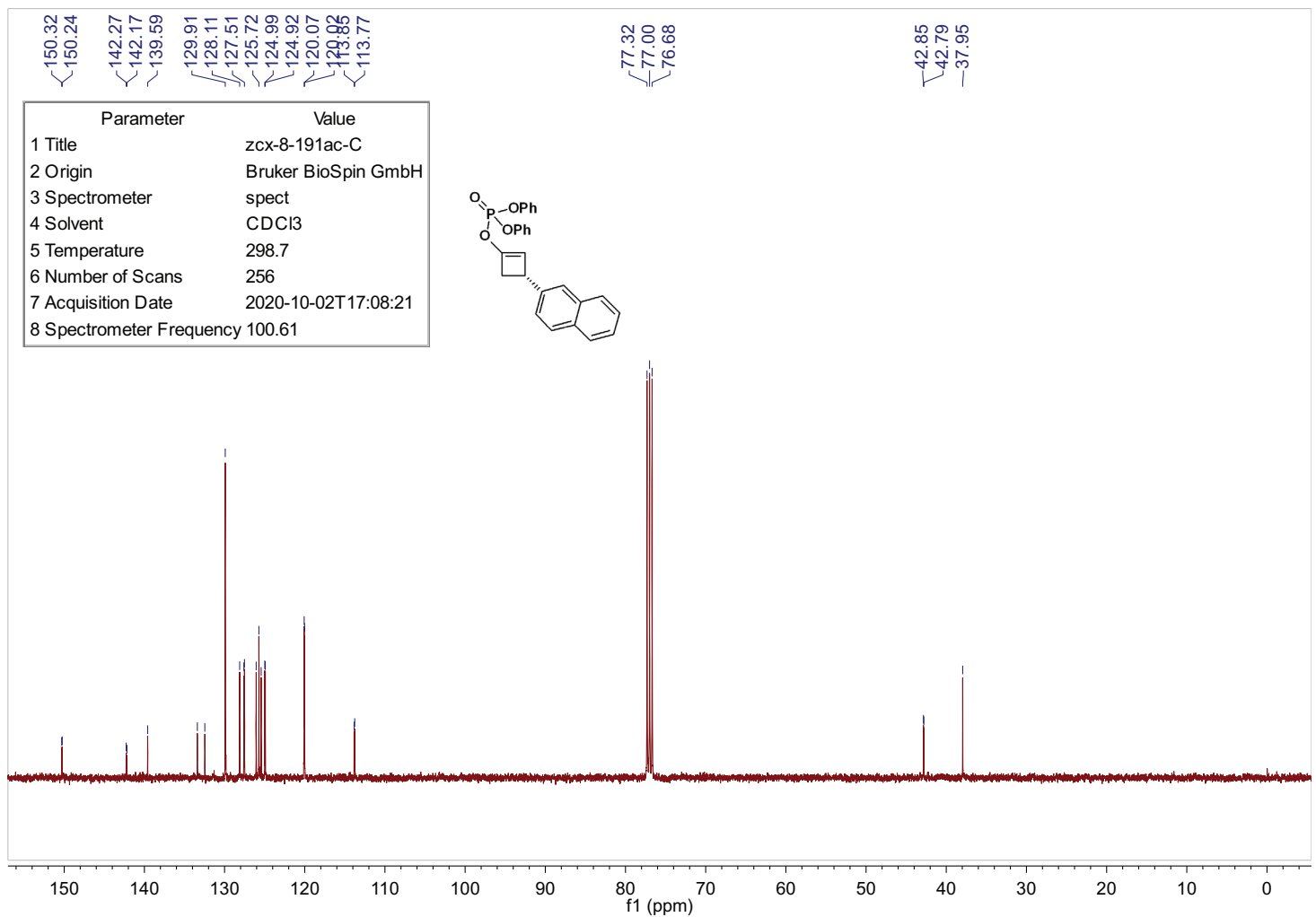
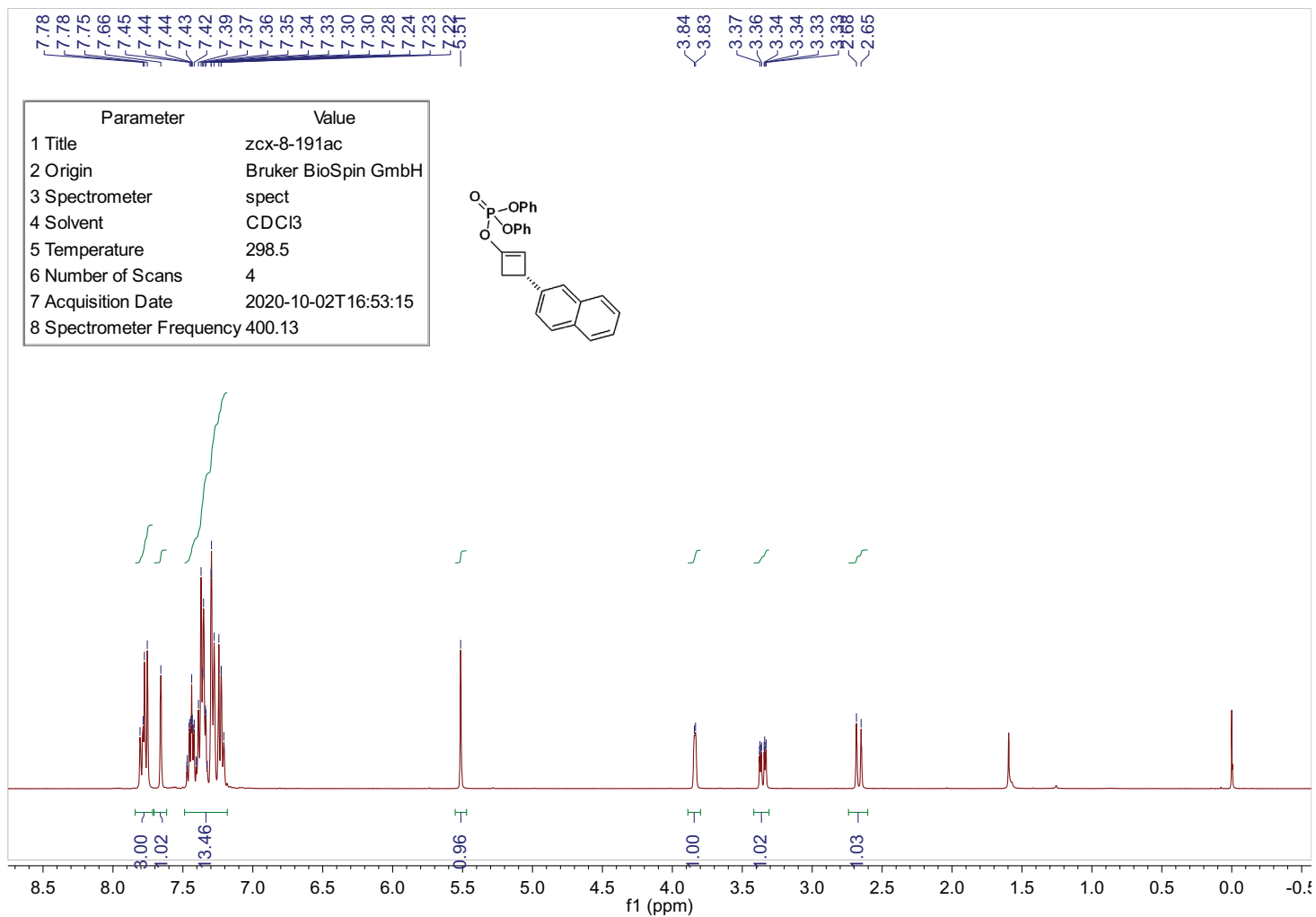
7.91
7.89
7.39
7.37
7.35
7.28
7.28
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.23
7.21
7.21
-5.42

3.72
3.71
3.71
3.33
3.30
3.30
3.29
3.29
2.56
-1.59

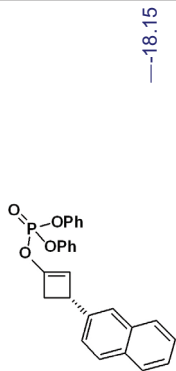
Parameter	Value
1 Title	zcx-9-15ac
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	297.8
6 Number of Scans	4
7 Acquisition Date	2020-10-13T18:28:14
8 Spectrometer Frequency	400.13



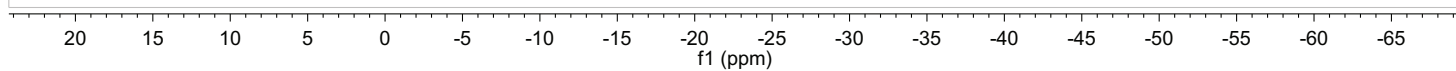




Parameter	Value
1 Title	zcx-8-191ac-P
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	299.5
6 Number of Scans	16
7 Acquisition Date	2020-10-01T16:47:18
8 Spectrometer Frequency	161.98



-18.15



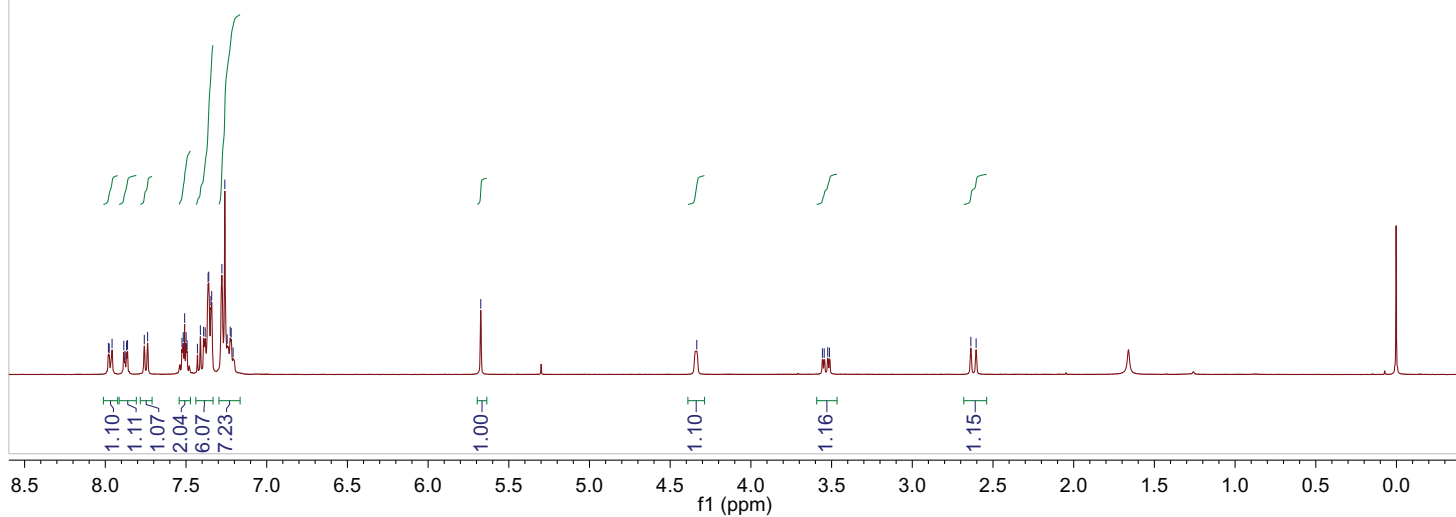
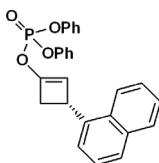
7.96
7.86
7.76
7.74
7.52
7.52
7.51
7.50
7.41
7.39
7.38
7.36
7.36
7.35
7.34
7.28
7.26
7.24
7.23
5.67

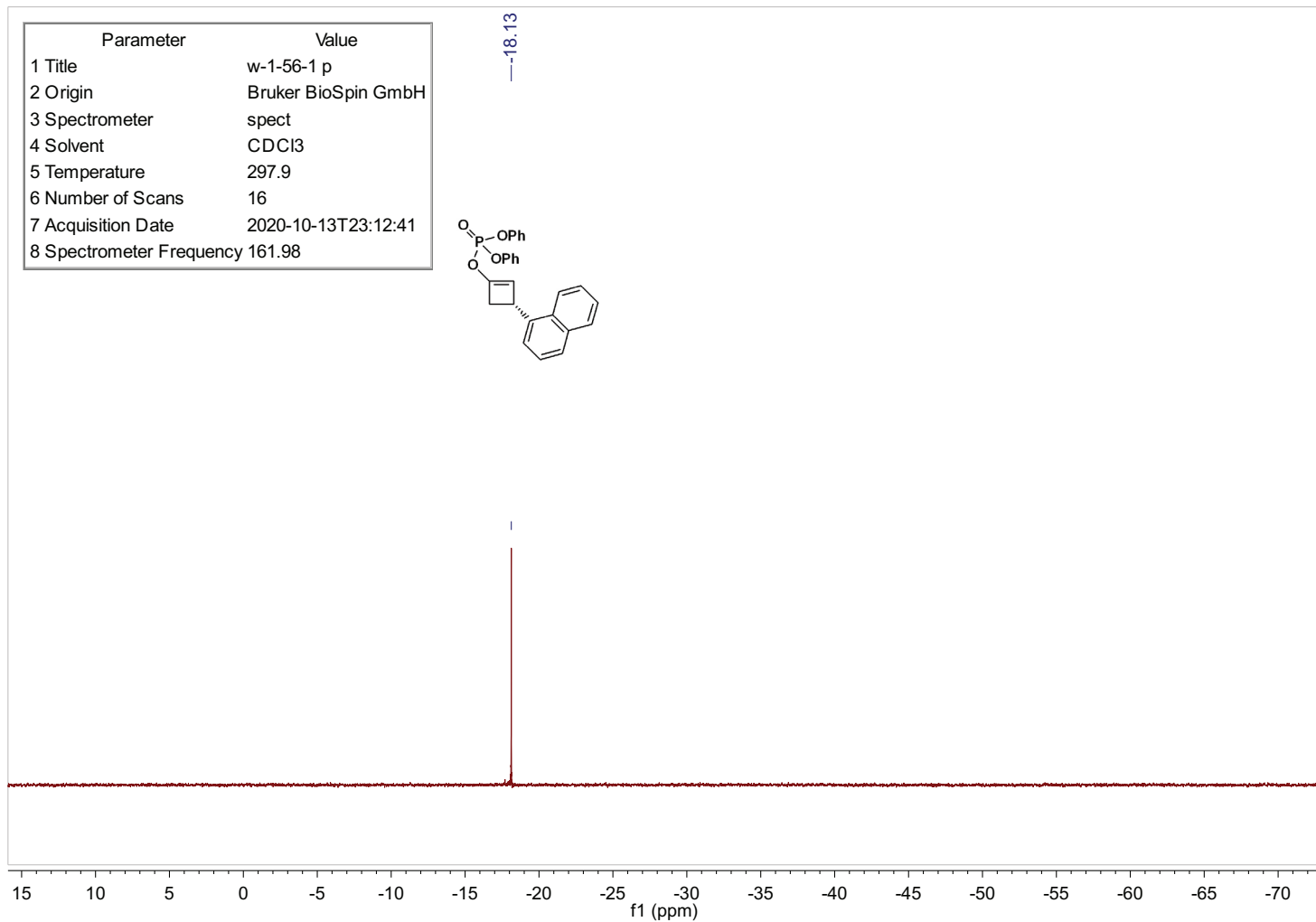
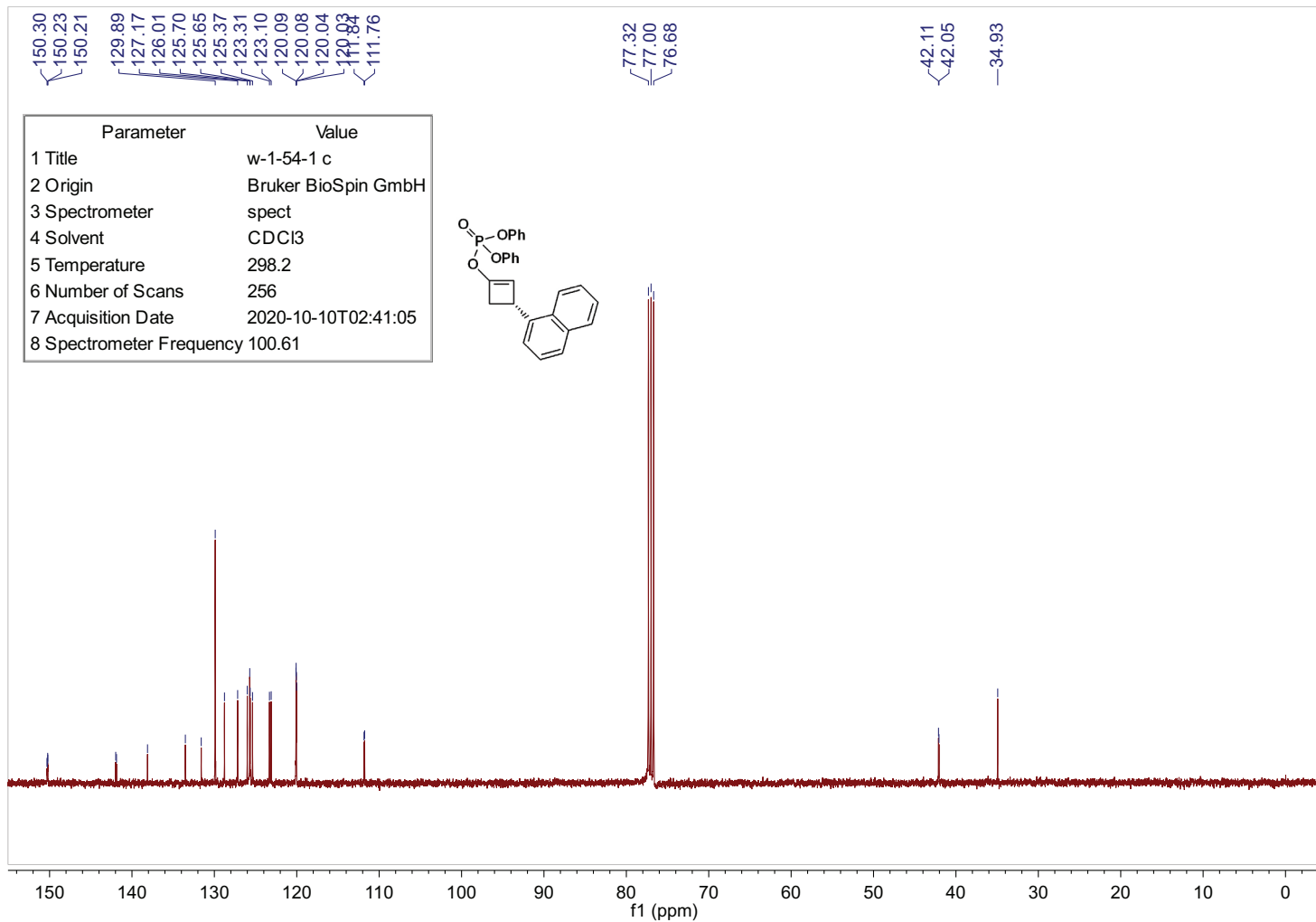
-4.34

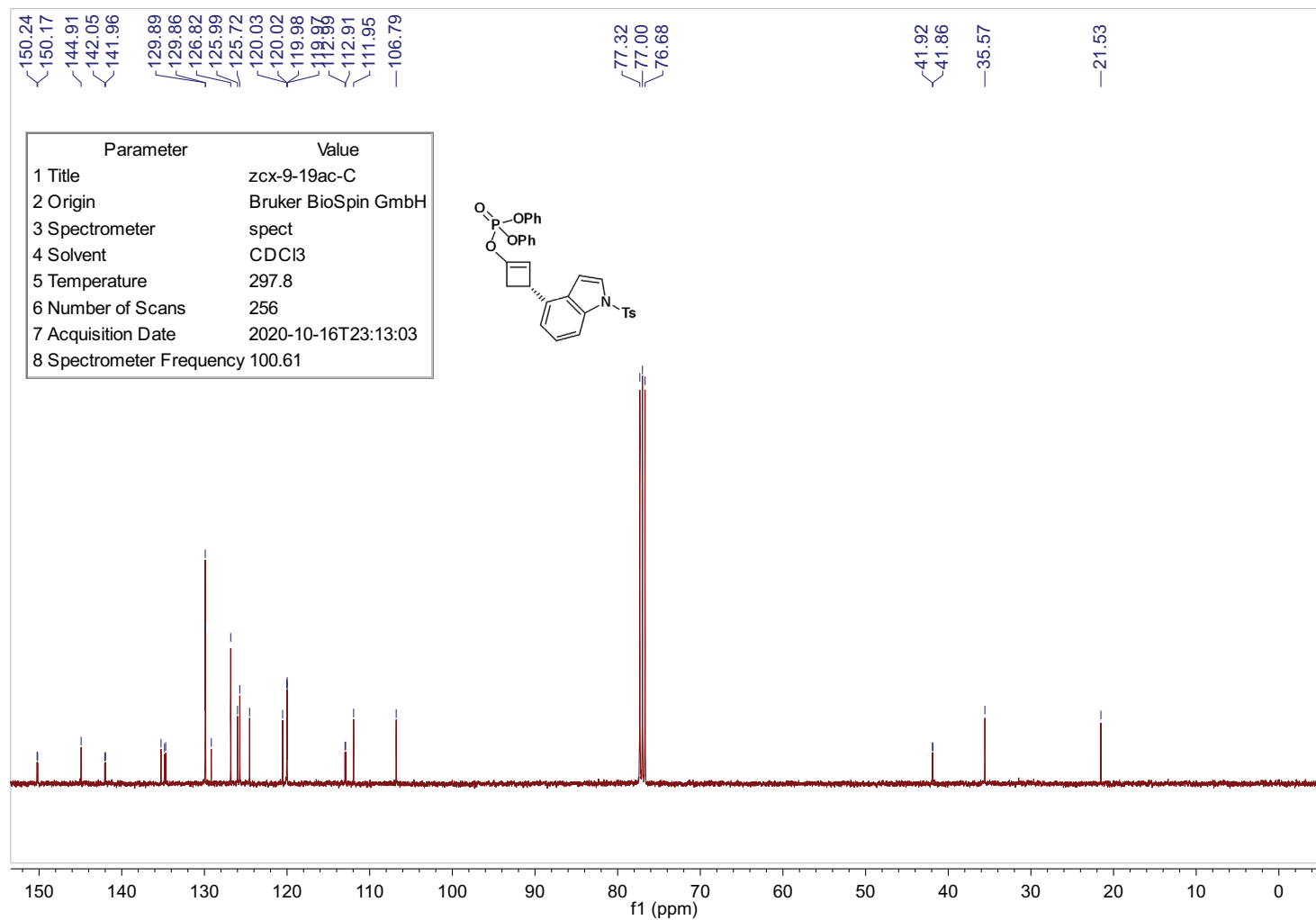
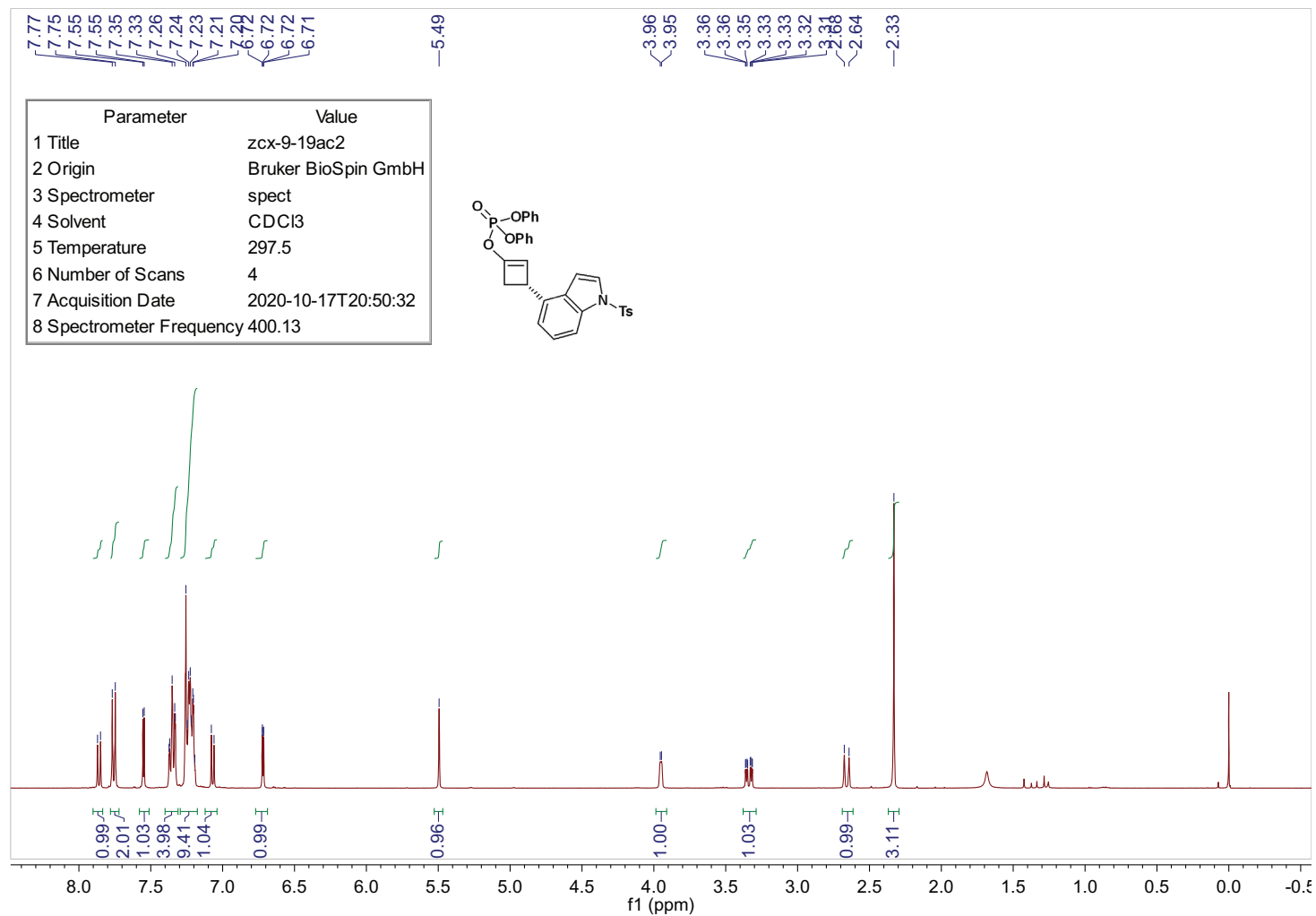
3.56
3.55
3.52
3.51

2.64
2.60

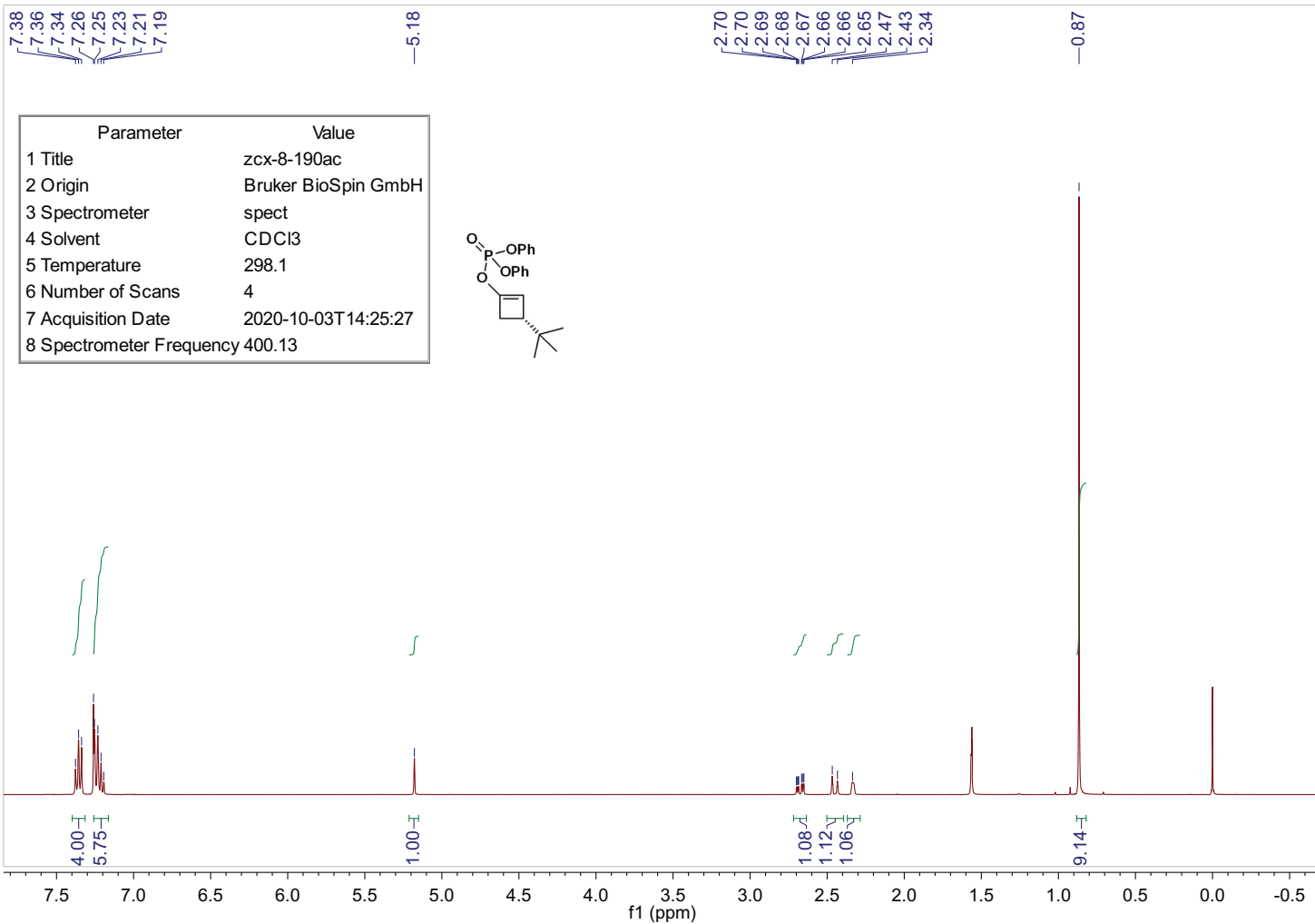
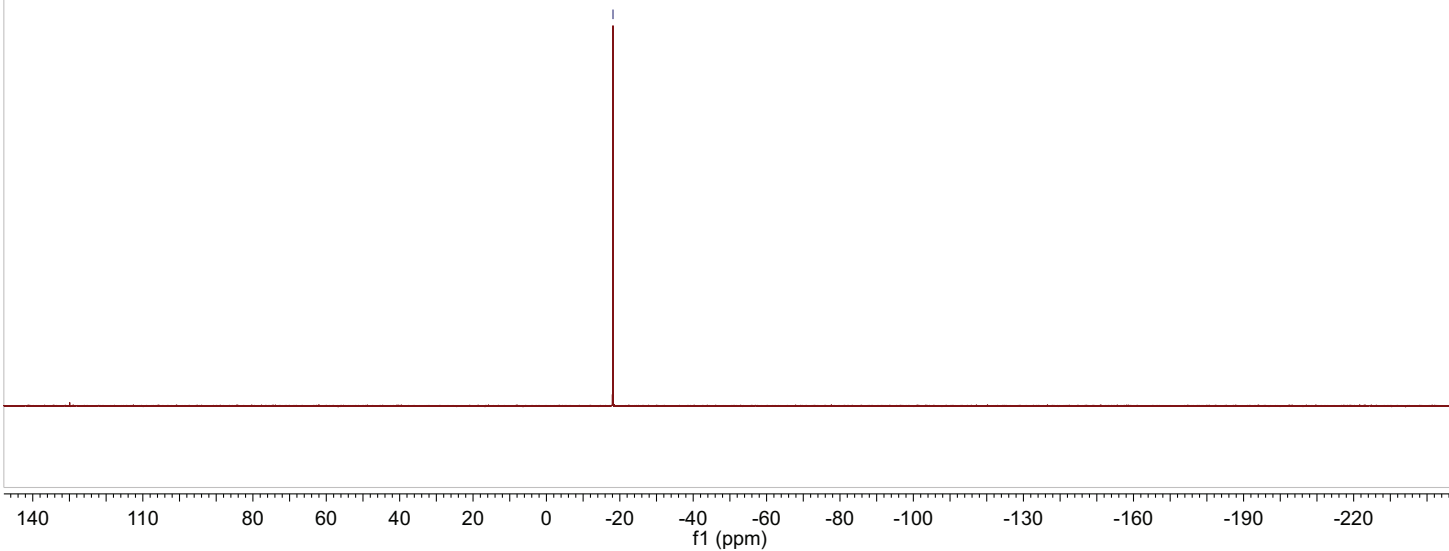
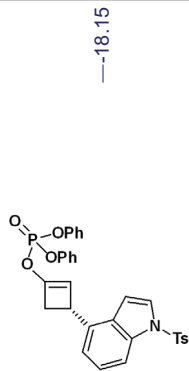
Parameter	Value
1 Title	wsw-1-56
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	295.0
6 Experiment	1D
7 Number of Scans	4
8 Acquisition Date	2021-01-03T02:45:57
9 Spectrometer Frequency	400.13



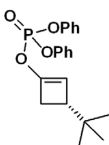


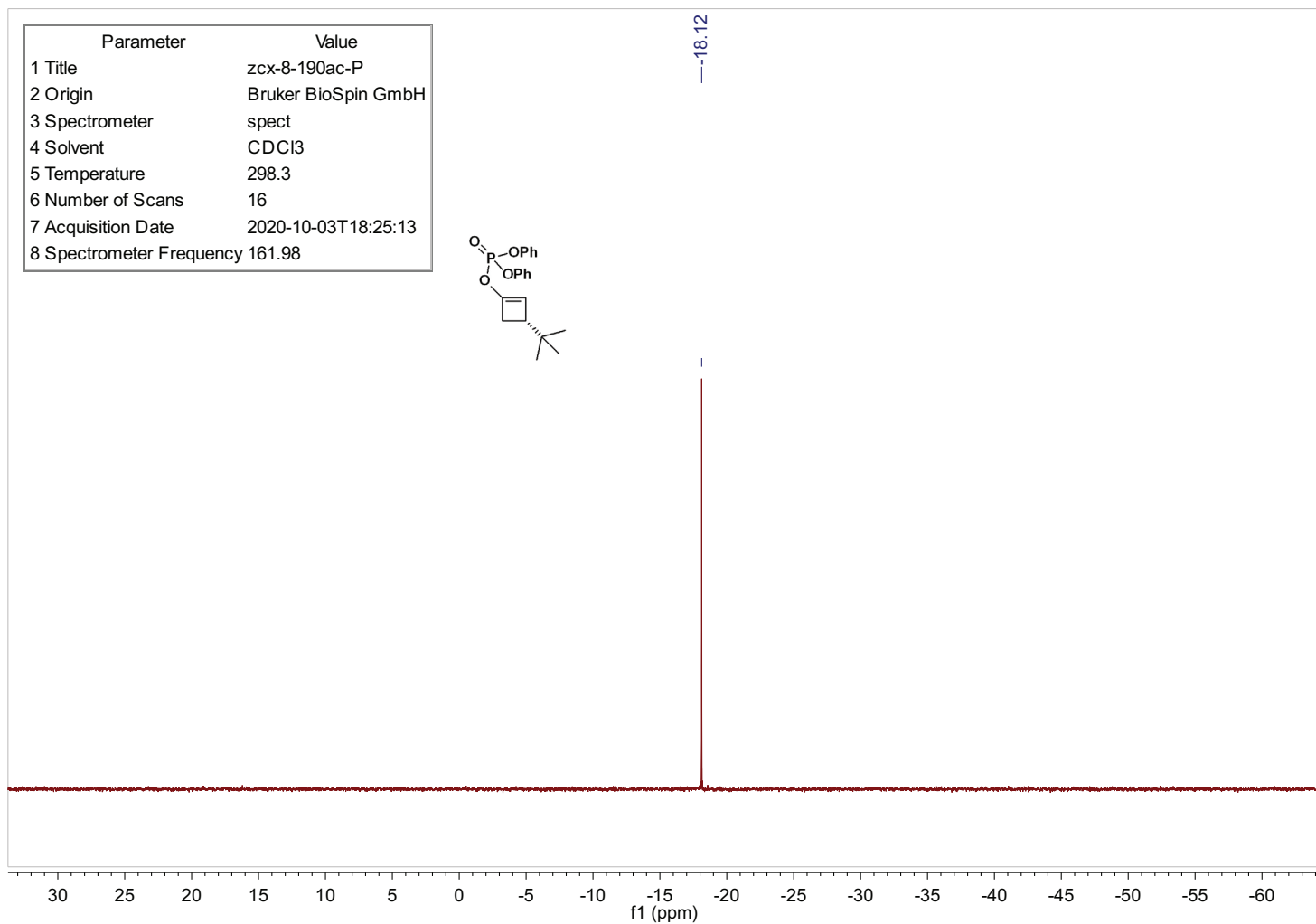
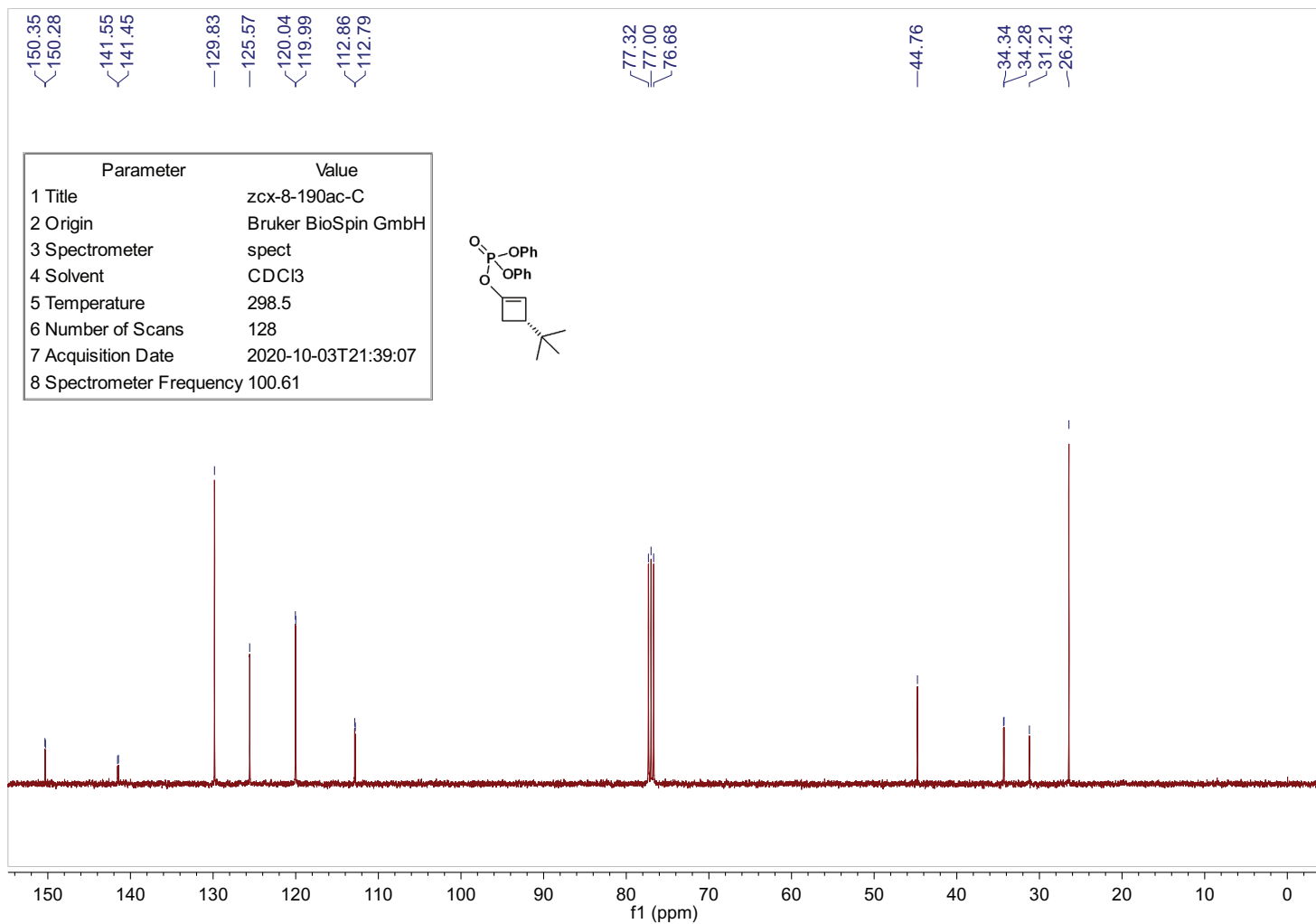


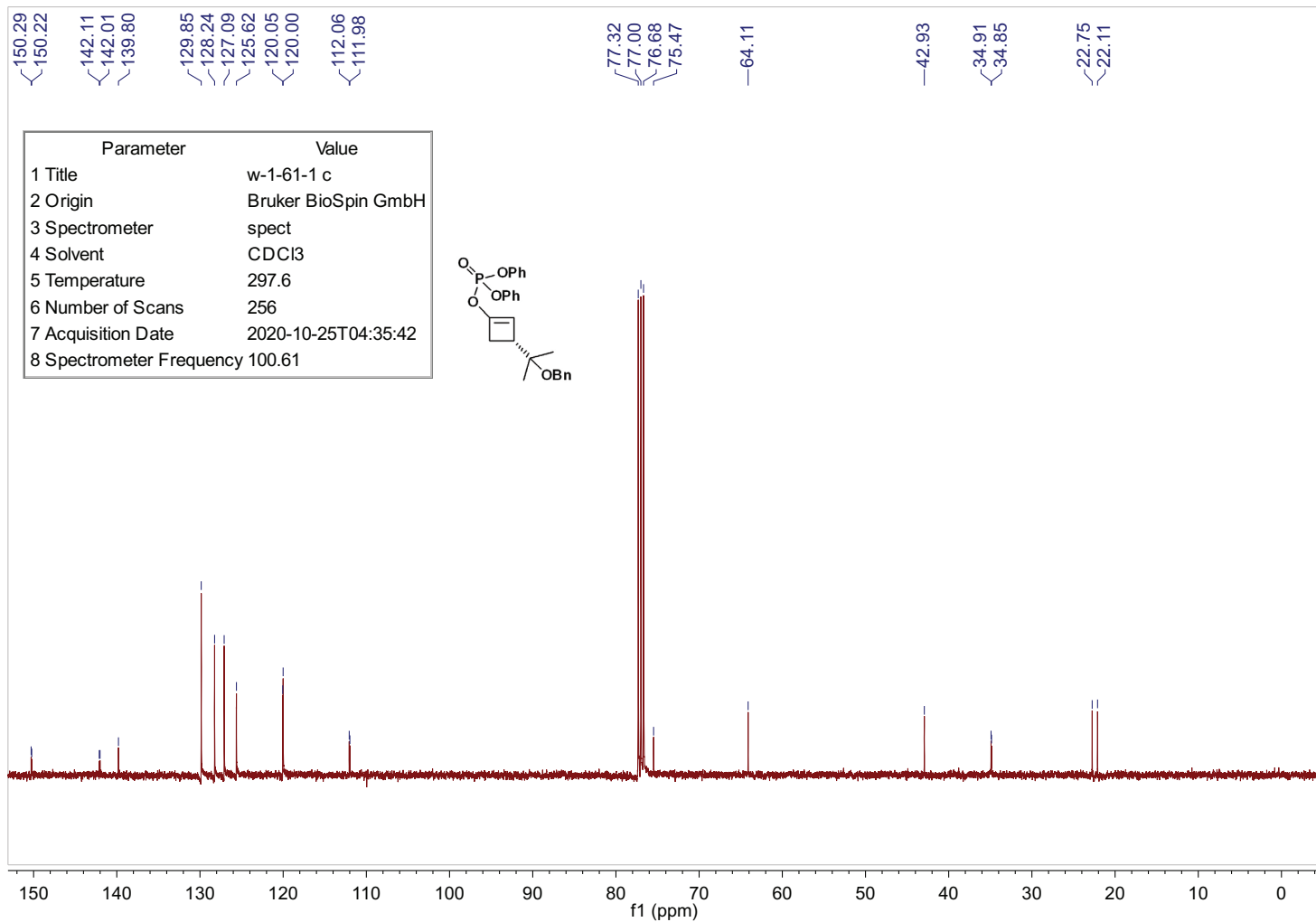
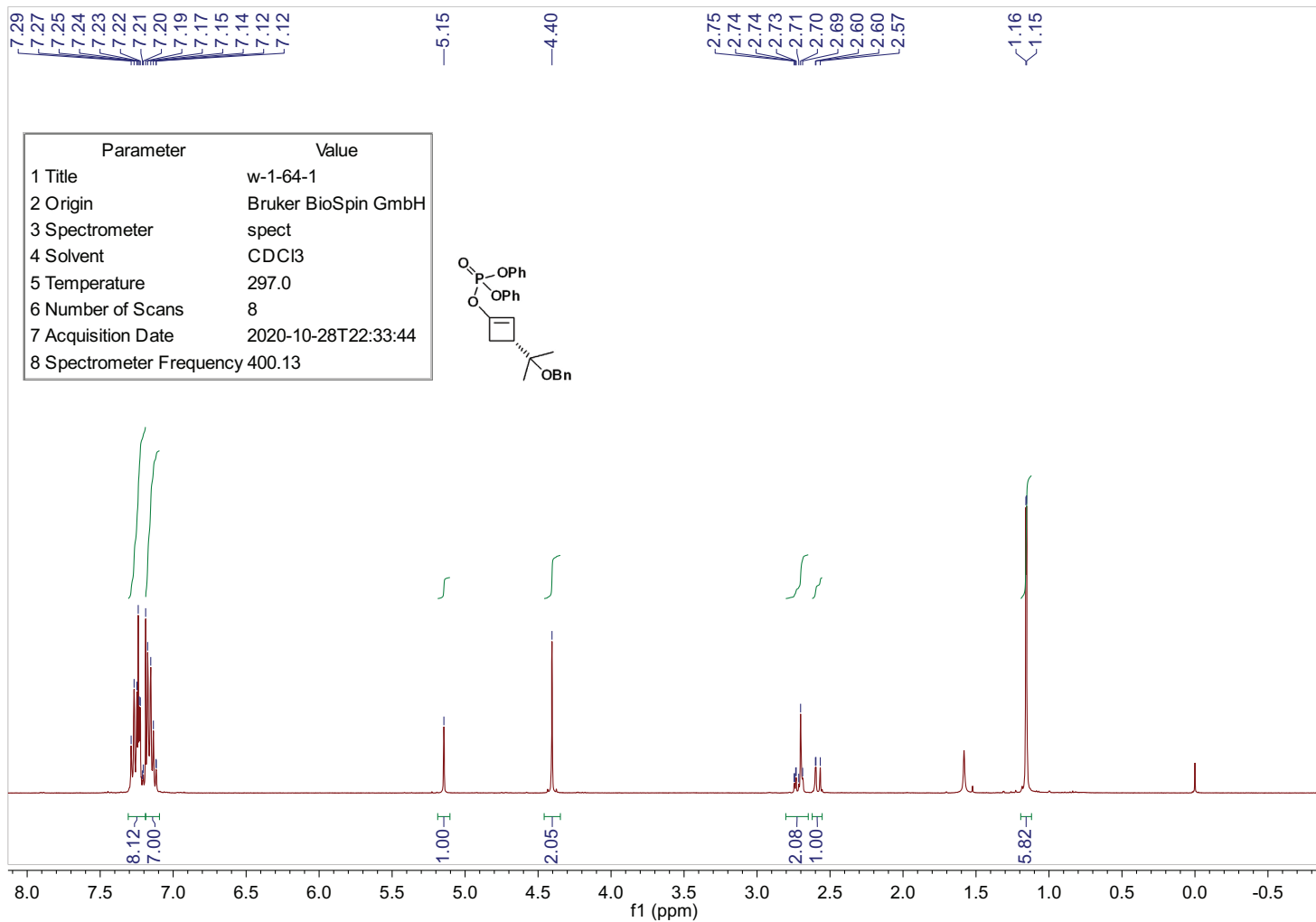
Parameter	Value
1 Title	zcx-9-19ac-P
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	297.6
6 Number of Scans	16
7 Acquisition Date	2020-10-16T23:14:54
8 Spectrometer Frequency	161.98



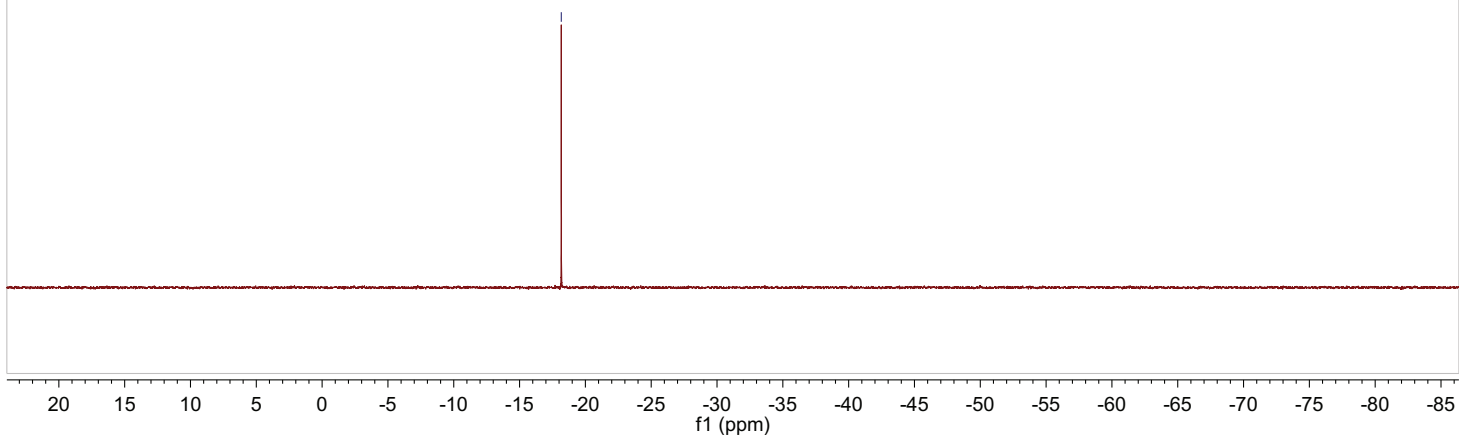
Parameter	Value
1 Title	zcx-8-190ac
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	298.1
6 Number of Scans	4
7 Acquisition Date	2020-10-03T14:25:27
8 Spectrometer Frequency	400.13







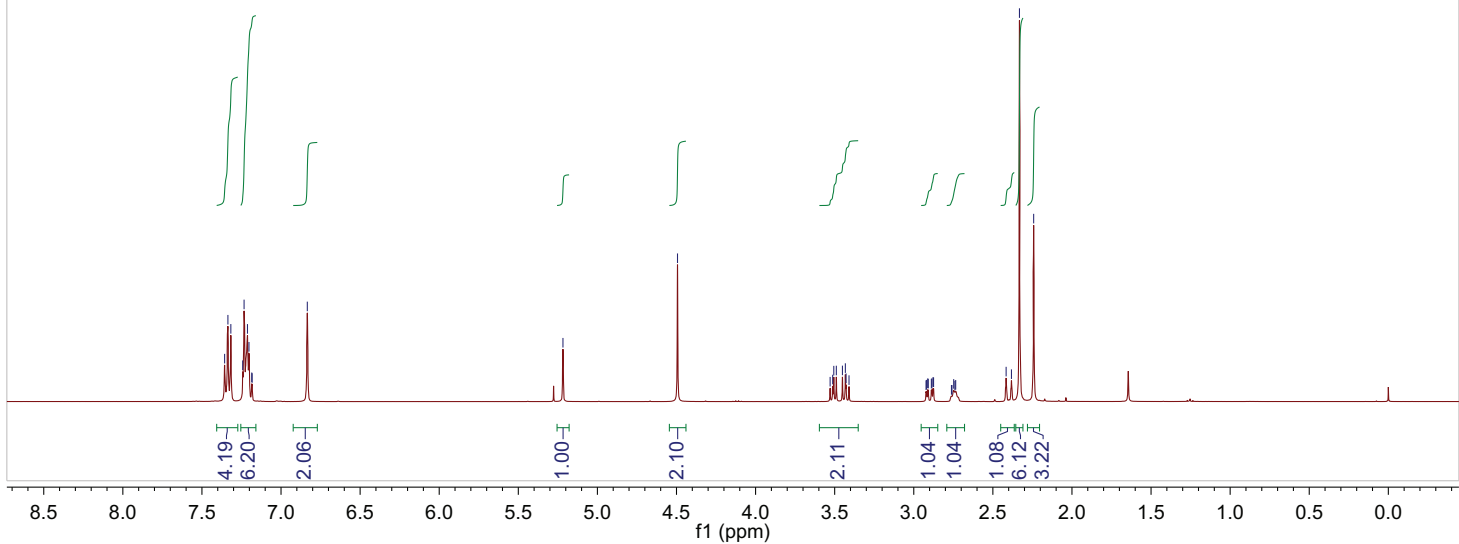
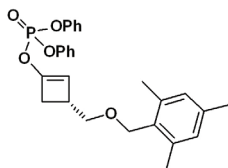
Parameter	Value
1 Title	w-1-61-1 p
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	297.3
6 Number of Scans	16
7 Acquisition Date	2020-10-24T03:24:06
8 Spectrometer Frequency	161.98



7.36
7.34
7.32
7.24
7.23
7.21
7.20
7.18
7.18
6.83

5.22
4.49
3.53
3.51
3.51
3.49
3.45
3.43
3.43
3.41
2.91
2.89
2.88
2.87
2.38
2.33
2.24

Parameter	Value
1 Title	W-1-53-1 H
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	297.6
6 Number of Scans	4
7 Acquisition Date	2020-10-08T08:49:10
8 Spectrometer Frequency	400.13



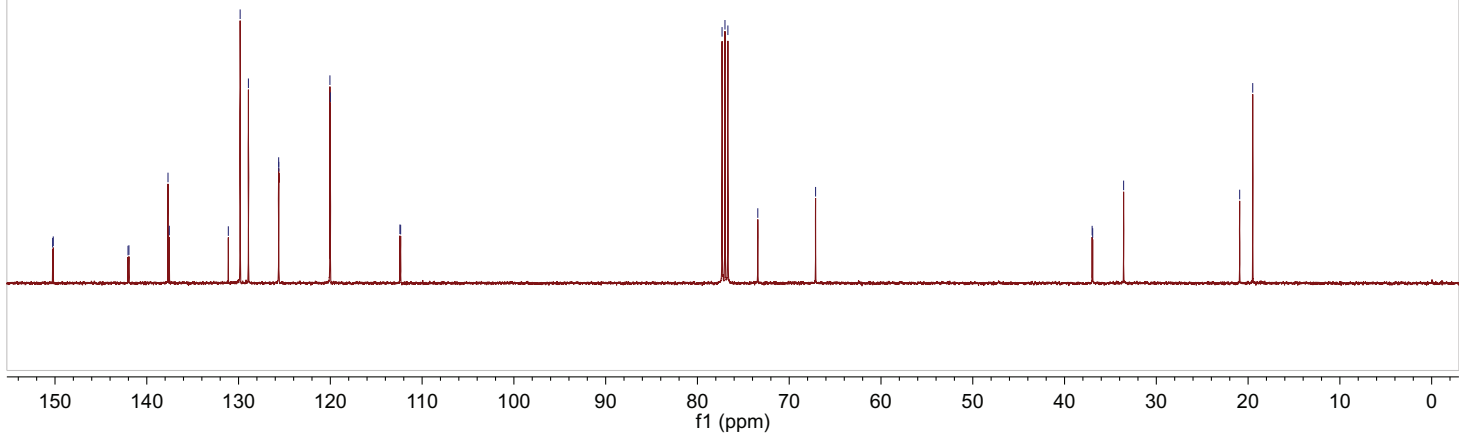
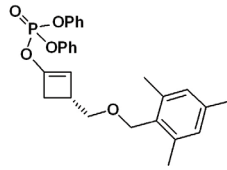
150.26
150.19
142.04
141.95
137.69
137.54
131.11
129.83
128.92
125.63
125.62
120.05
120.00
112.42
112.34

77.32
77.00
76.68
73.42
—67.13

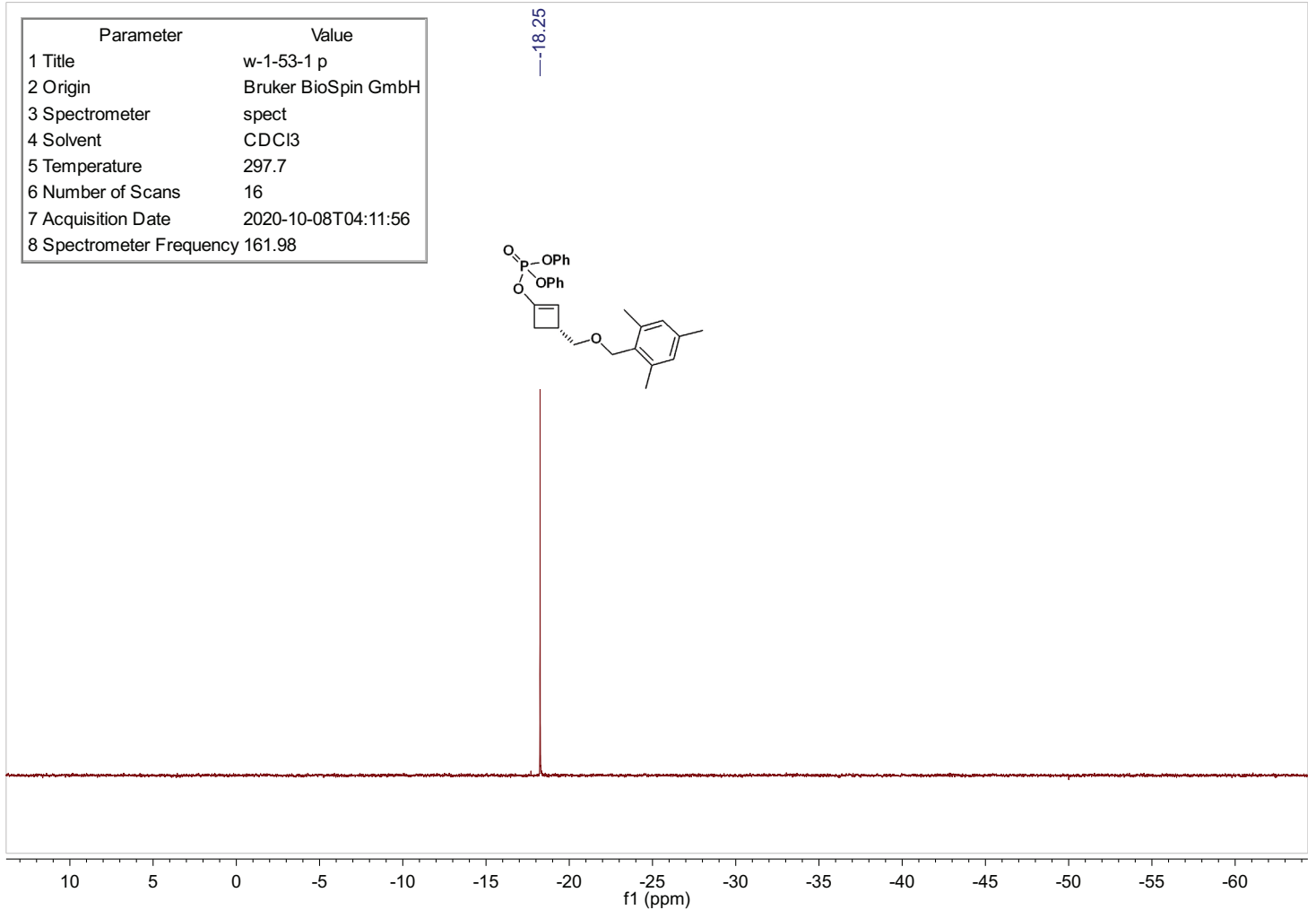
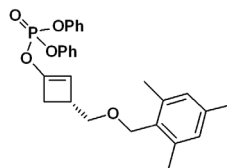
36.99
36.94
33.57

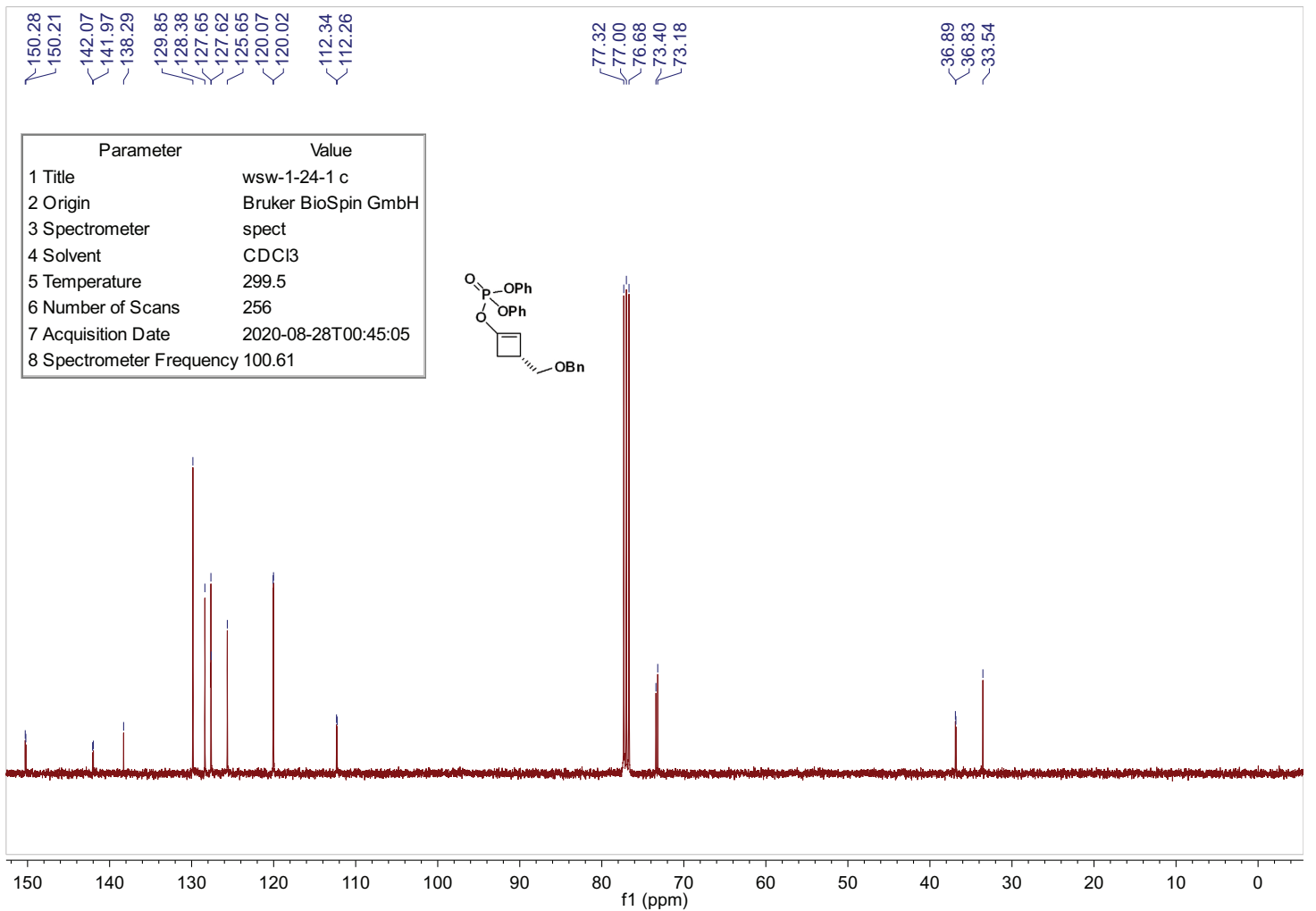
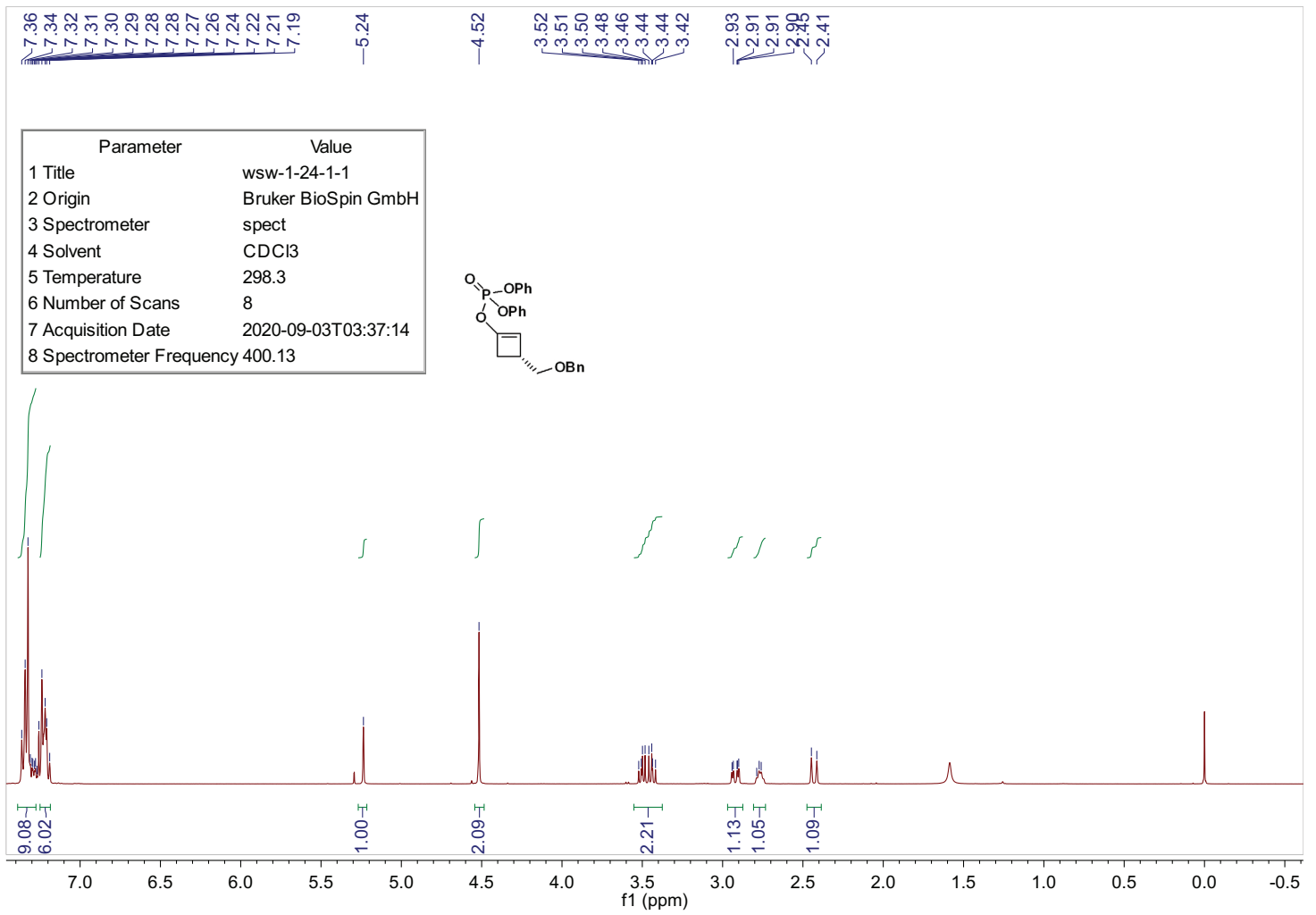
20.92
19.50

Parameter	Value
1 Title	W-1-53-1 C
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	298.1
6 Number of Scans	384
7 Acquisition Date	2020-10-08T09:11:16
8 Spectrometer Frequency	100.61

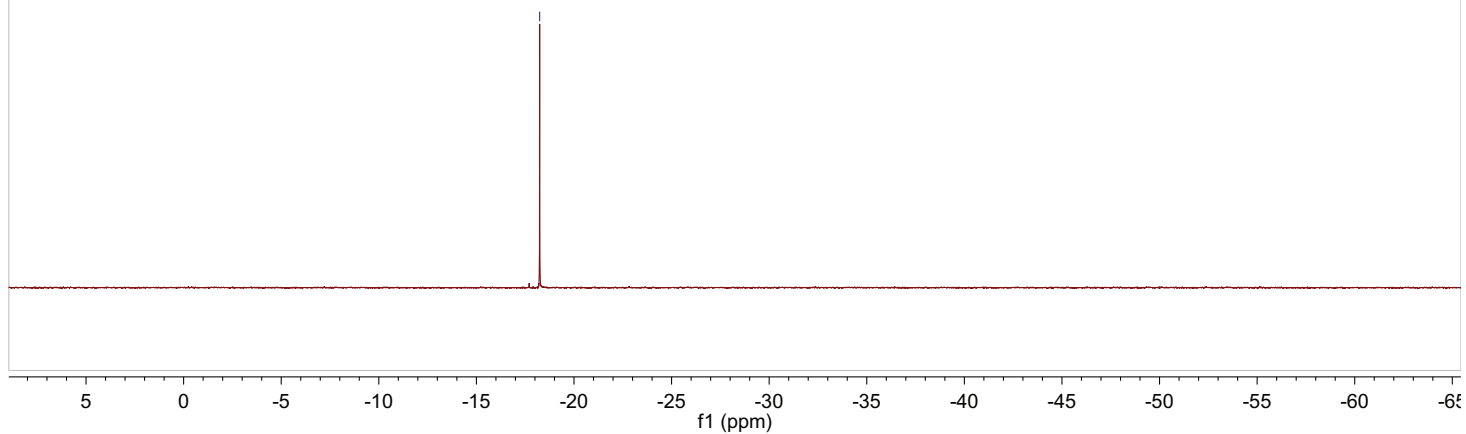


Parameter	Value
1 Title	w-1-53-1 p
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	297.7
6 Number of Scans	16
7 Acquisition Date	2020-10-08T04:11:56
8 Spectrometer Frequency	161.98





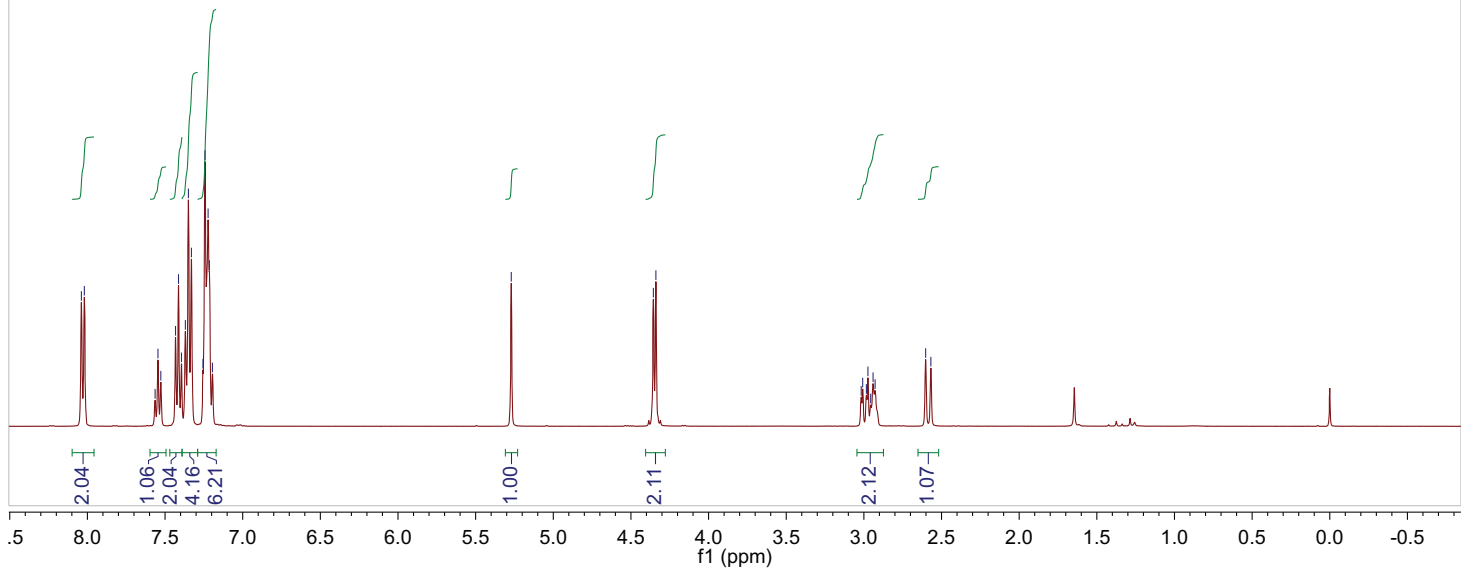
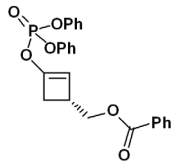
Parameter	Value
1 Title	wsw-1-24-1-1 p
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	298.6
6 Number of Scans	16
7 Acquisition Date	2020-09-03T03:38:50
8 Spectrometer Frequency	161.98

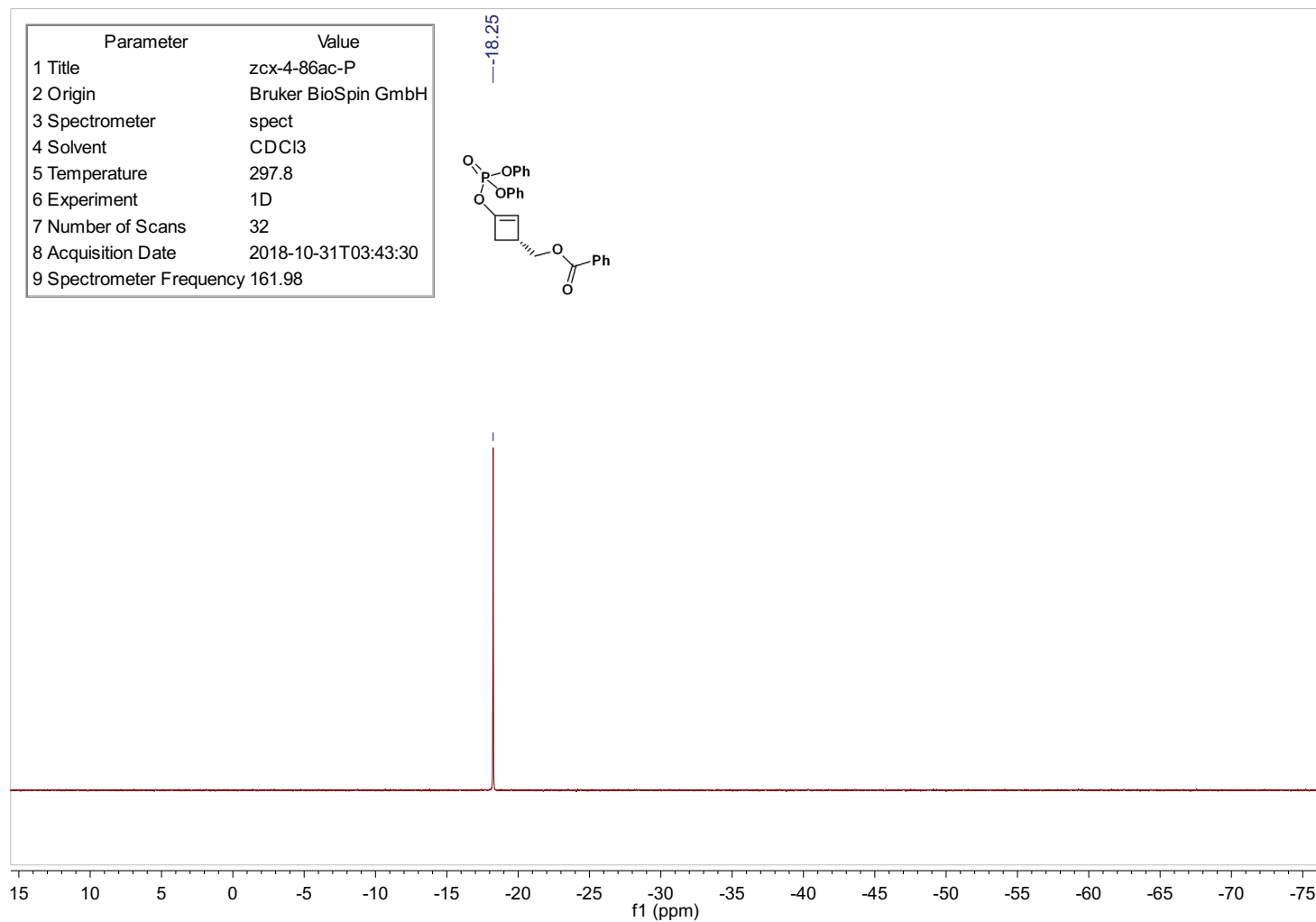
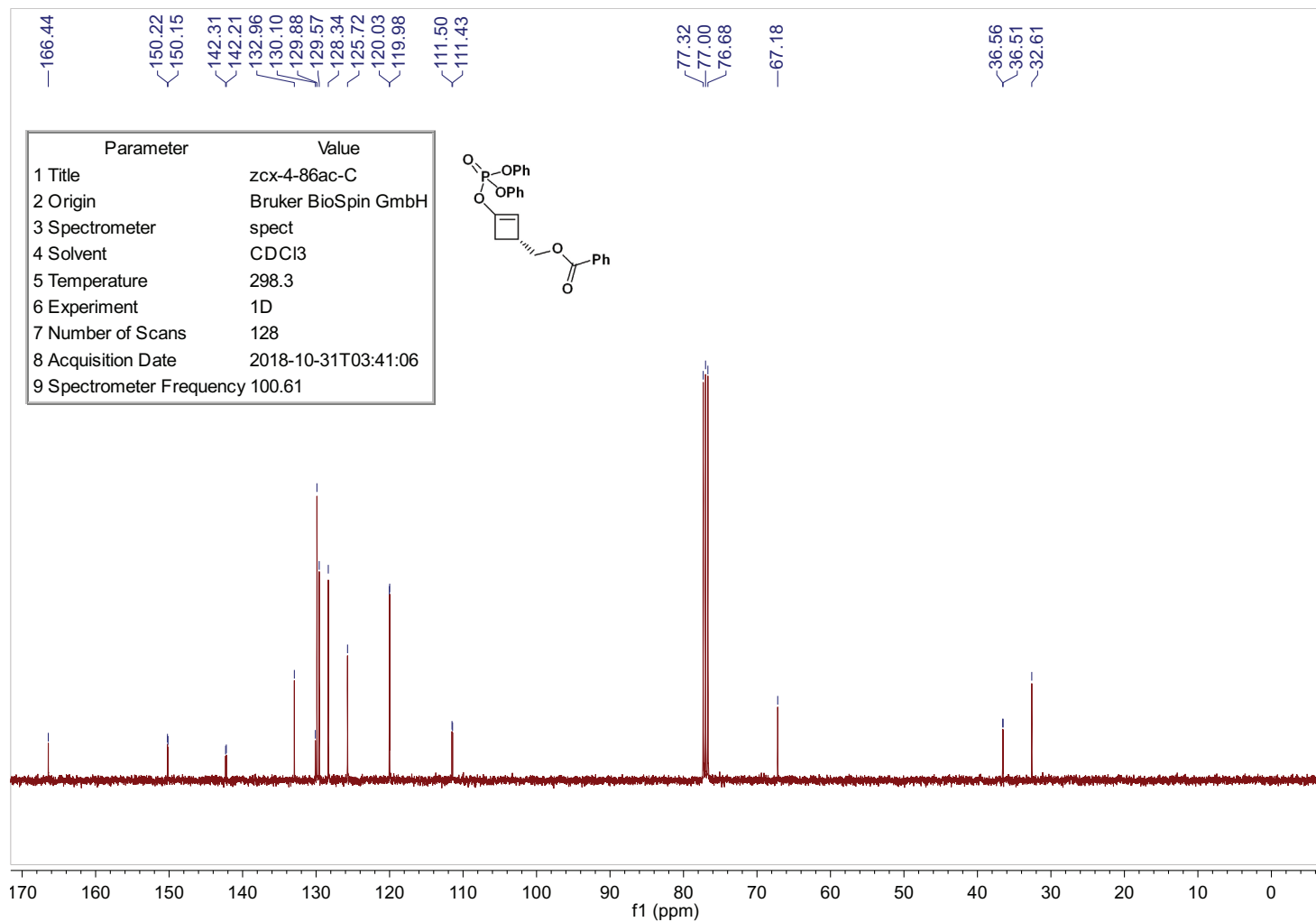


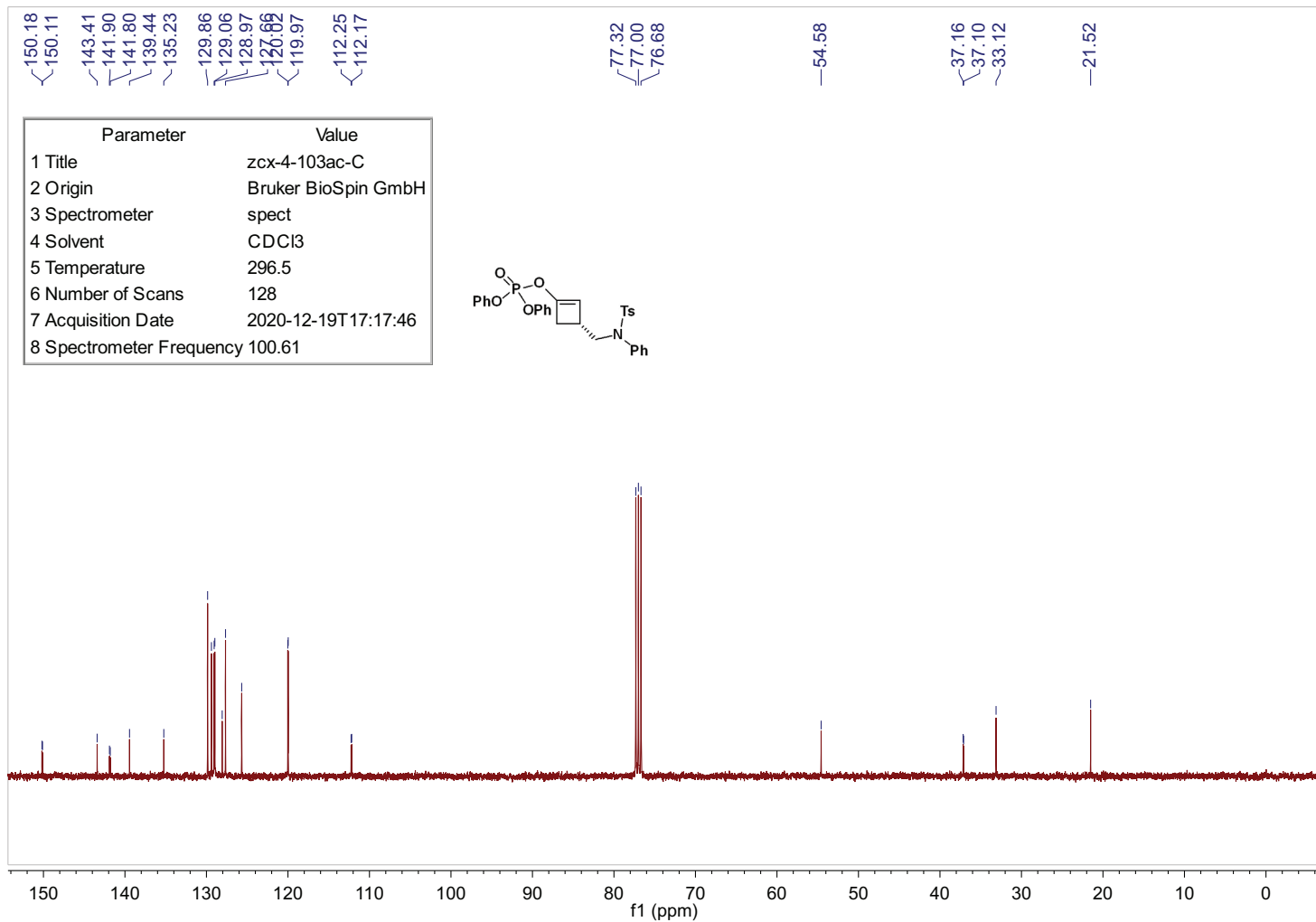
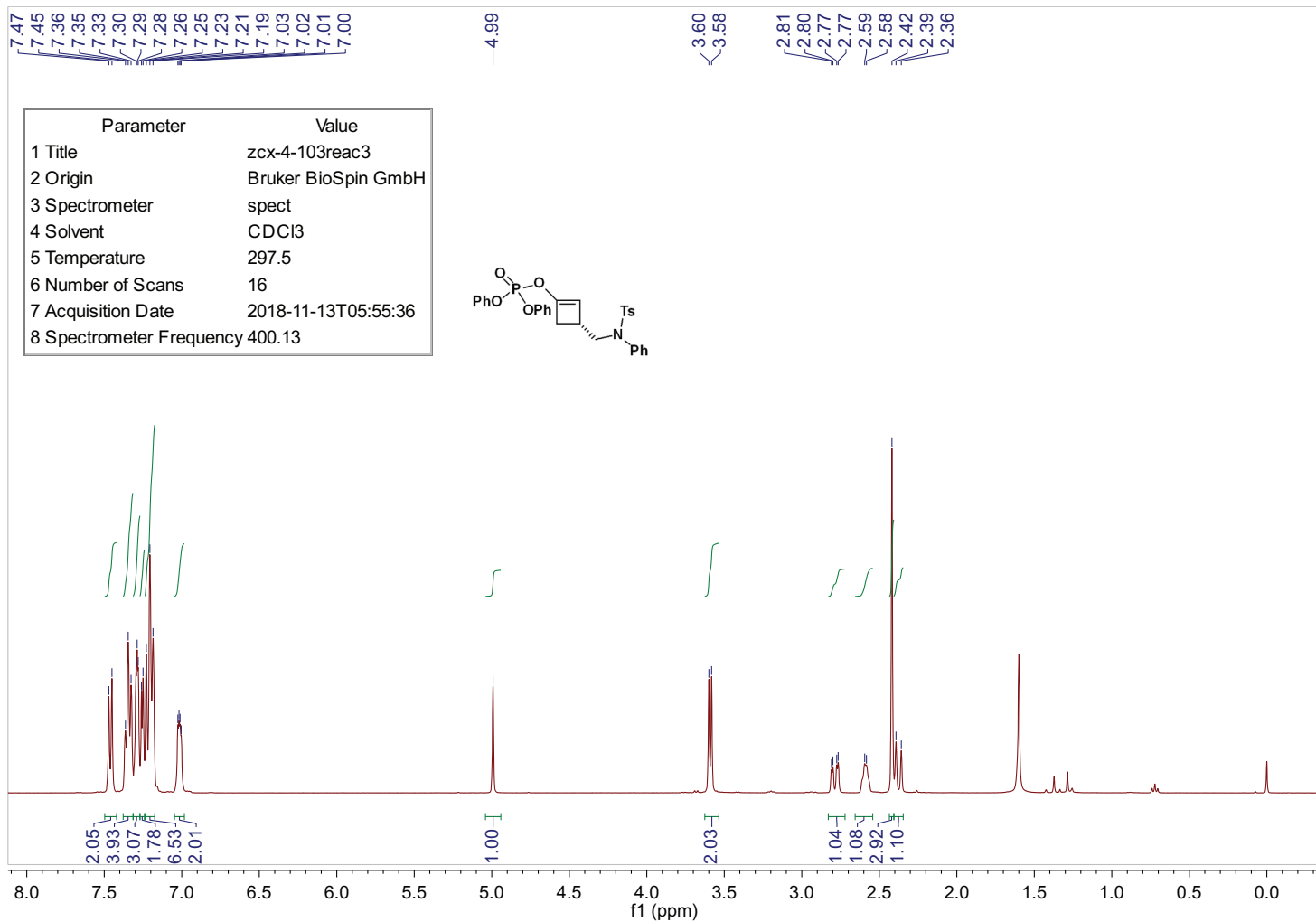
8.04
8.02
7.56
7.55
7.53
7.43
7.41
7.39
7.37
7.35
7.33
7.26
7.24
7.22
7.21
7.19

5.27
4.36
4.34
3.02
3.01
2.98
2.97
2.96
2.94
2.93
2.60
2.57

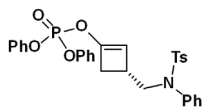
Parameter	Value
1 Title	zcx-4-86ac2
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	297.7
6 Experiment	1D
7 Number of Scans	4
8 Acquisition Date	2018-10-30T21:07:28
9 Spectrometer Frequency	400.13



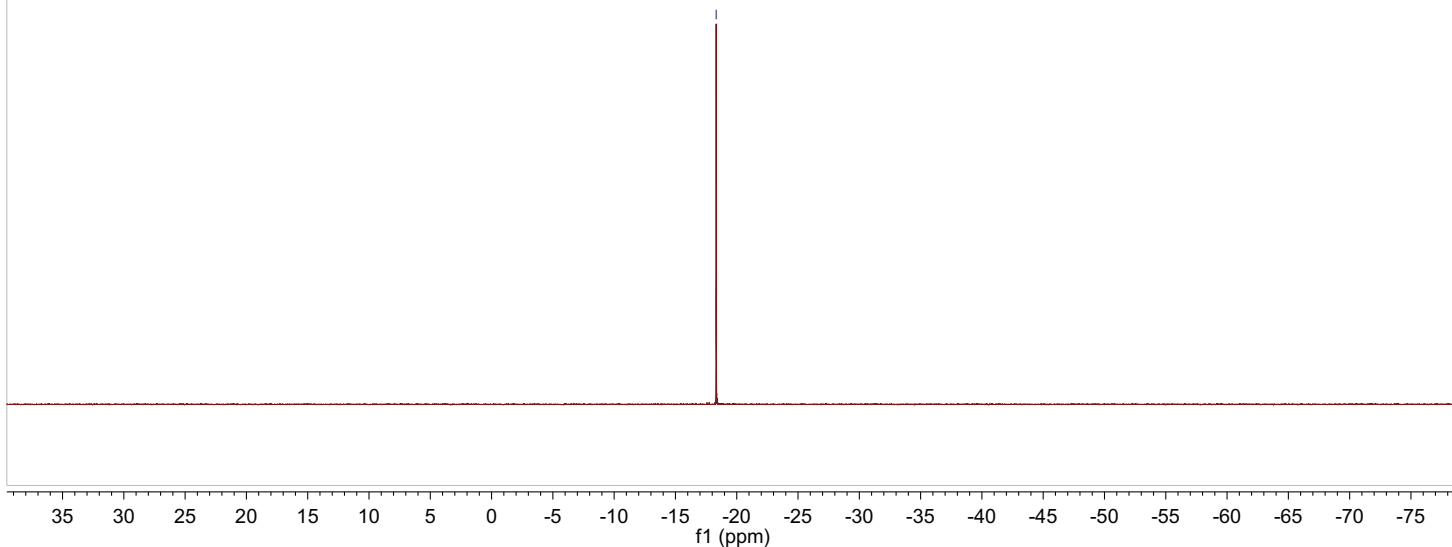




Parameter	Value
1 Title	zcx-4-103ac-P
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	296.2
6 Number of Scans	16
7 Acquisition Date	2020-12-19T17:19:37
8 Spectrometer Frequency	161.98



-18.32



7.37
7.35
7.34
7.27
7.25
7.23
7.21
7.19

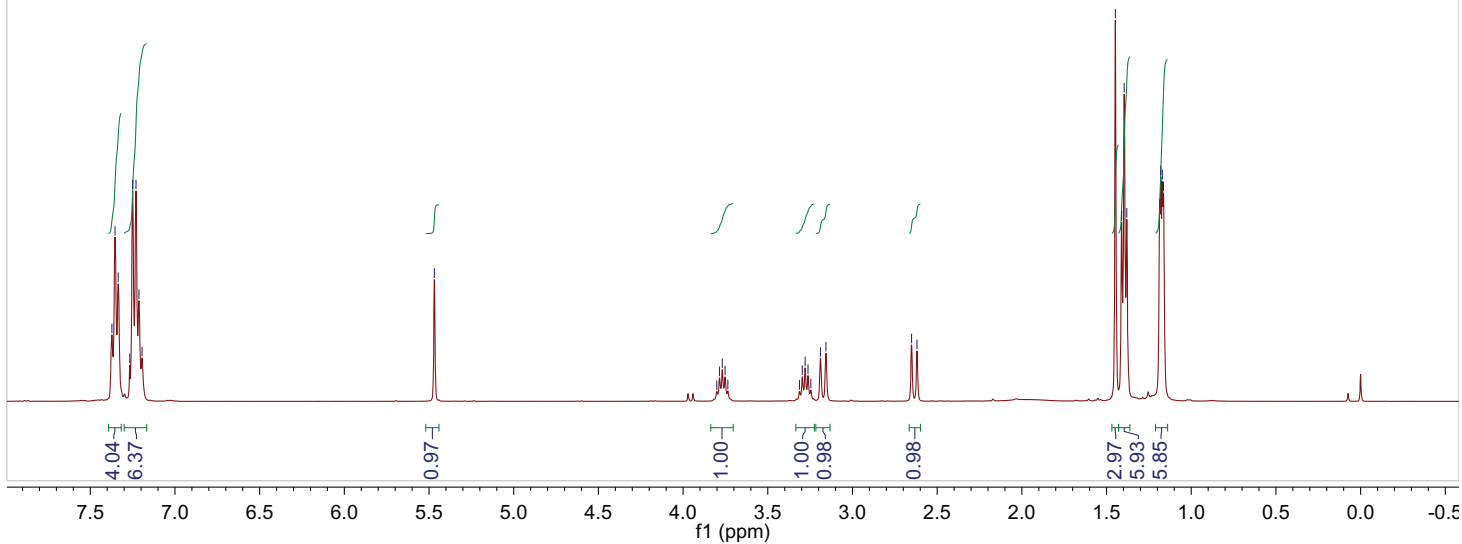
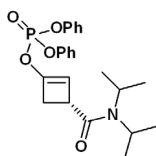
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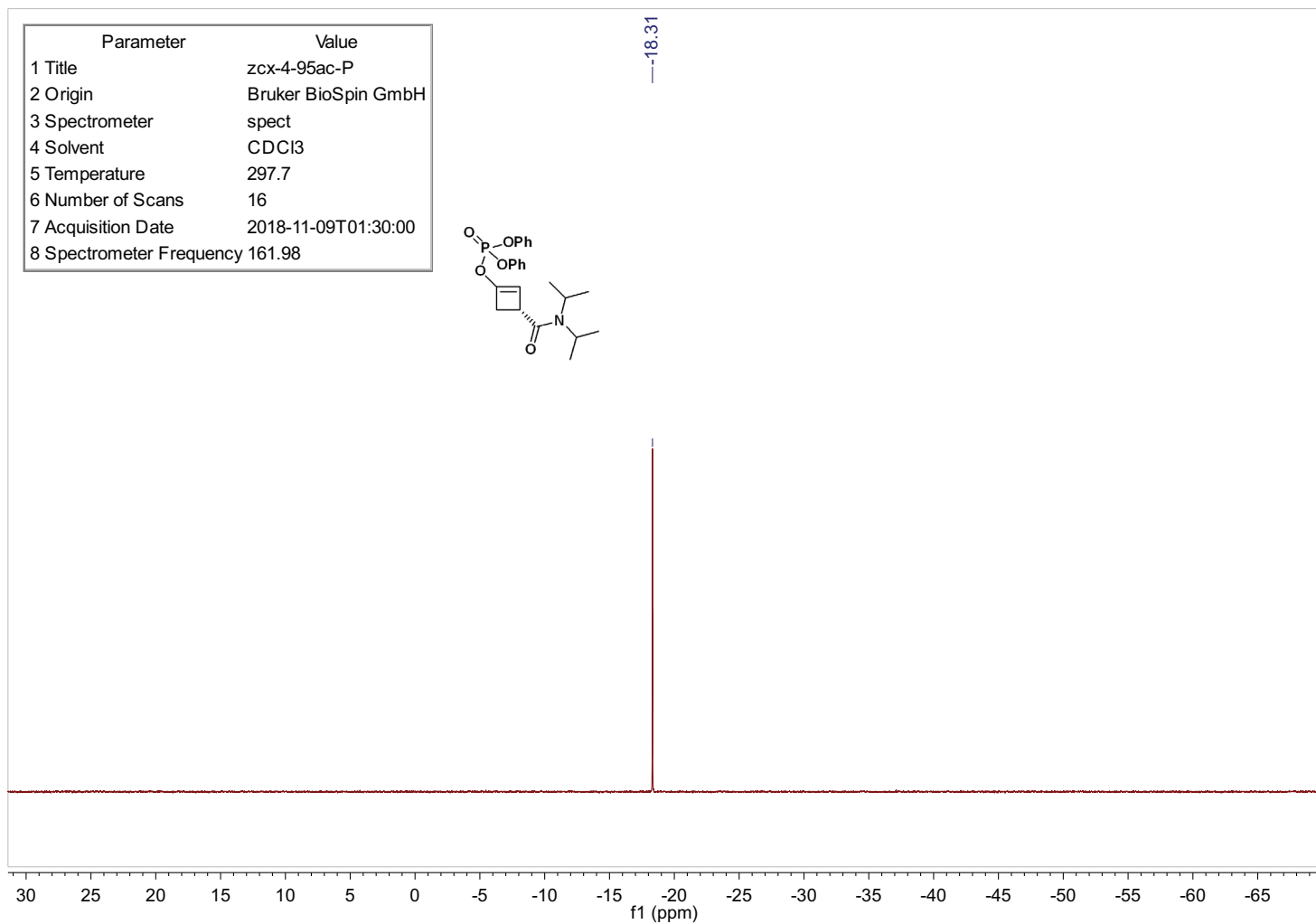
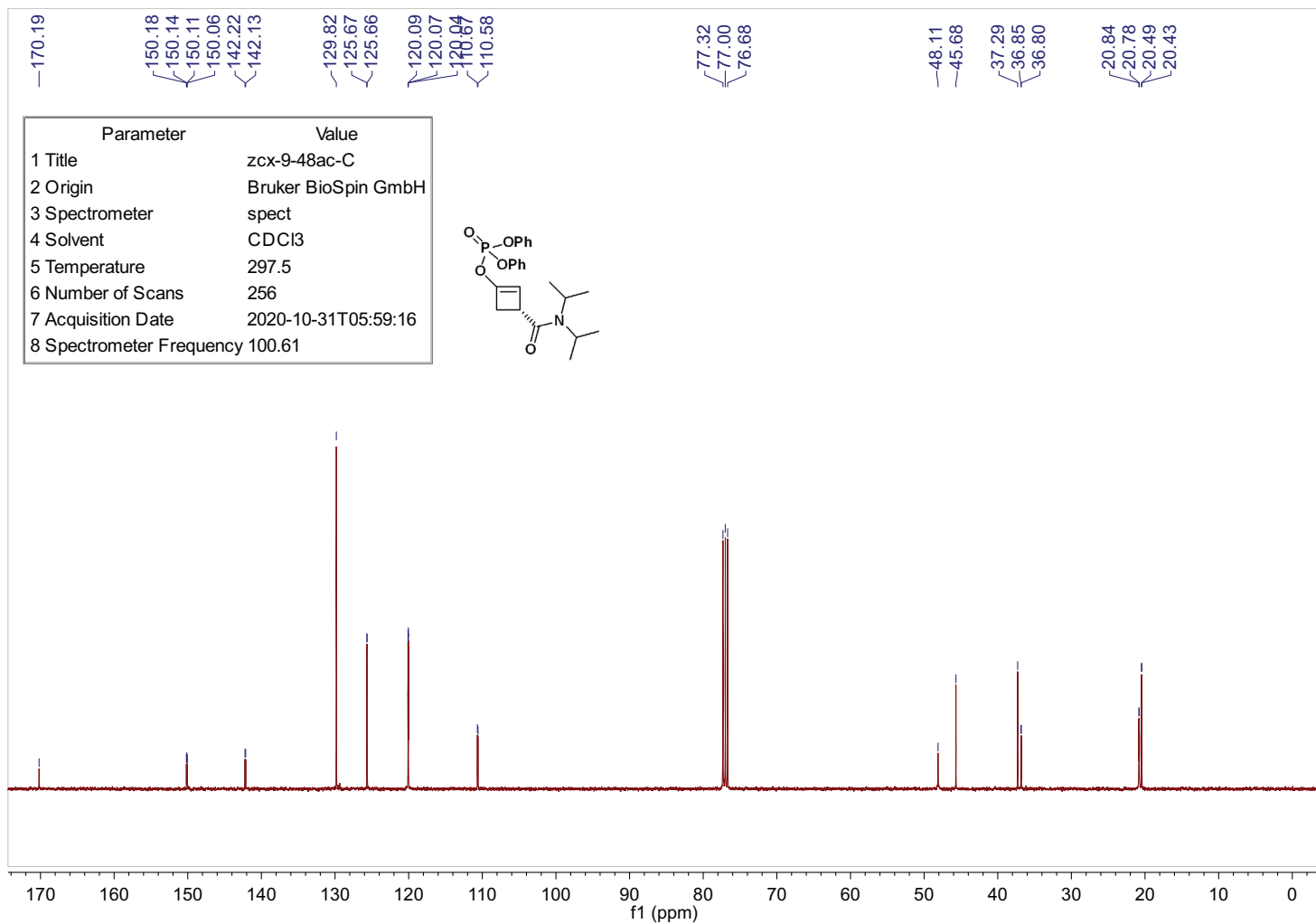
3.80
3.79
3.77
3.75
3.74

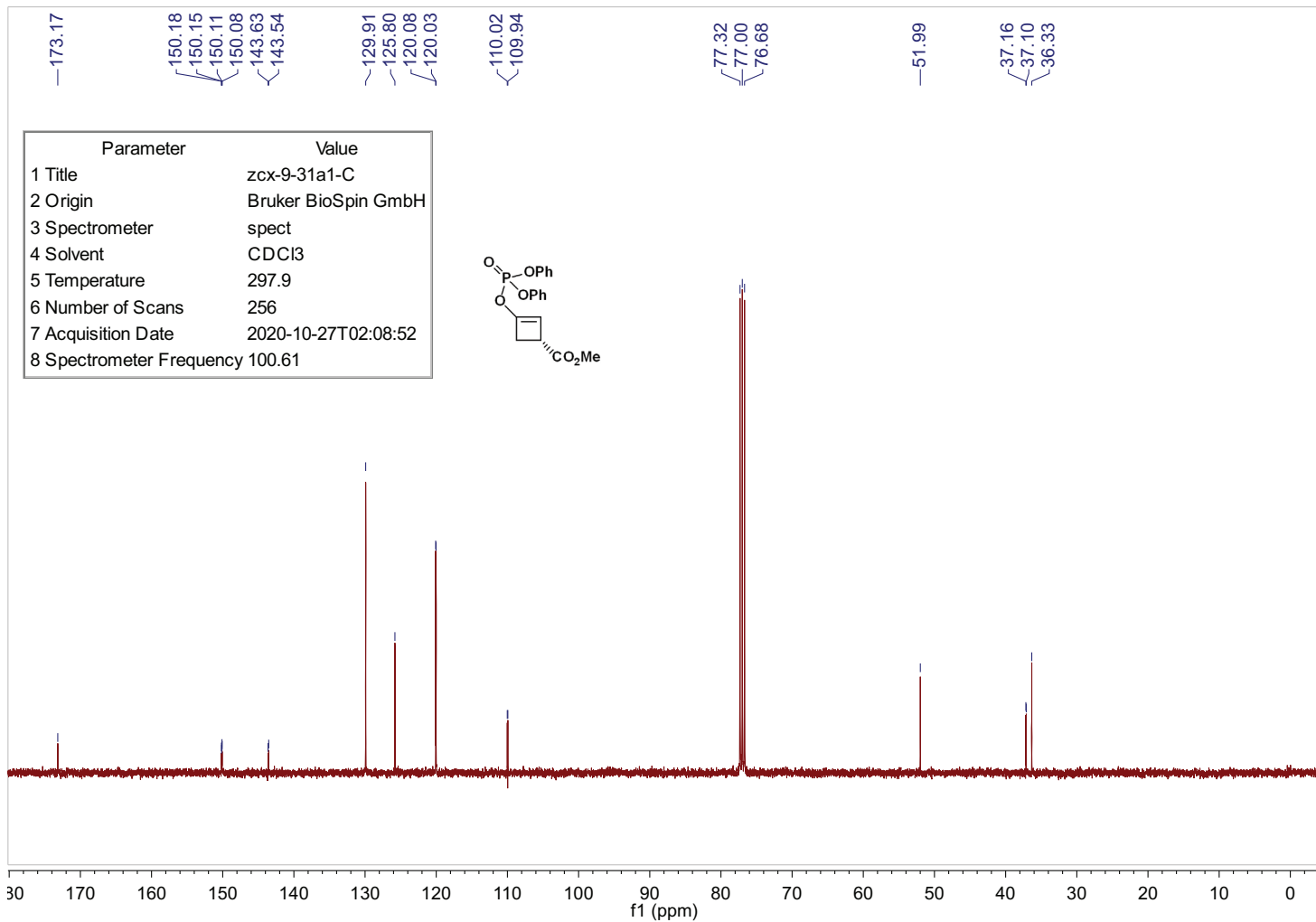
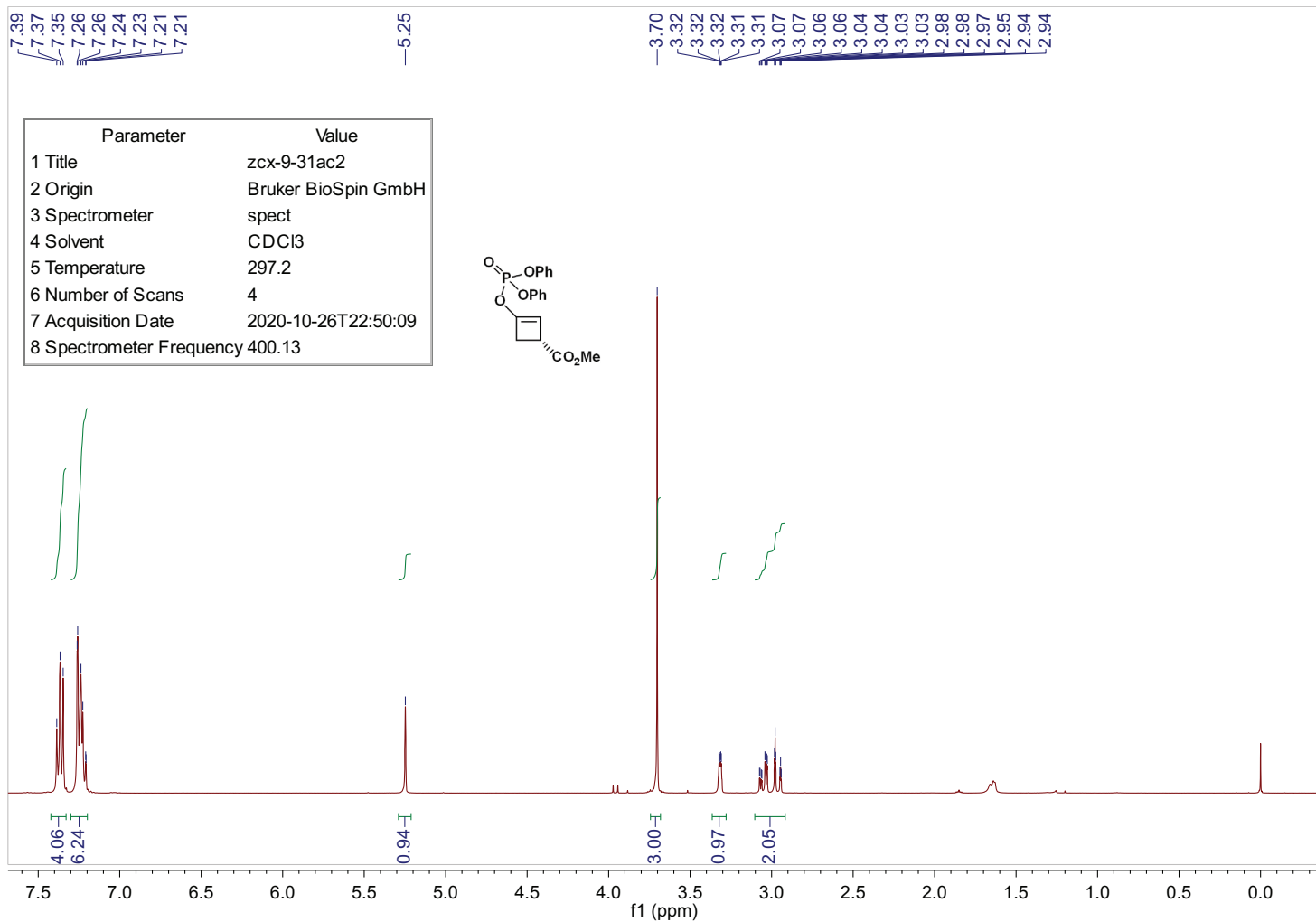
3.30
3.28
3.26
3.19
2.65
2.62

1.45
1.41
1.40
1.38
1.19
1.18
1.17
1.16

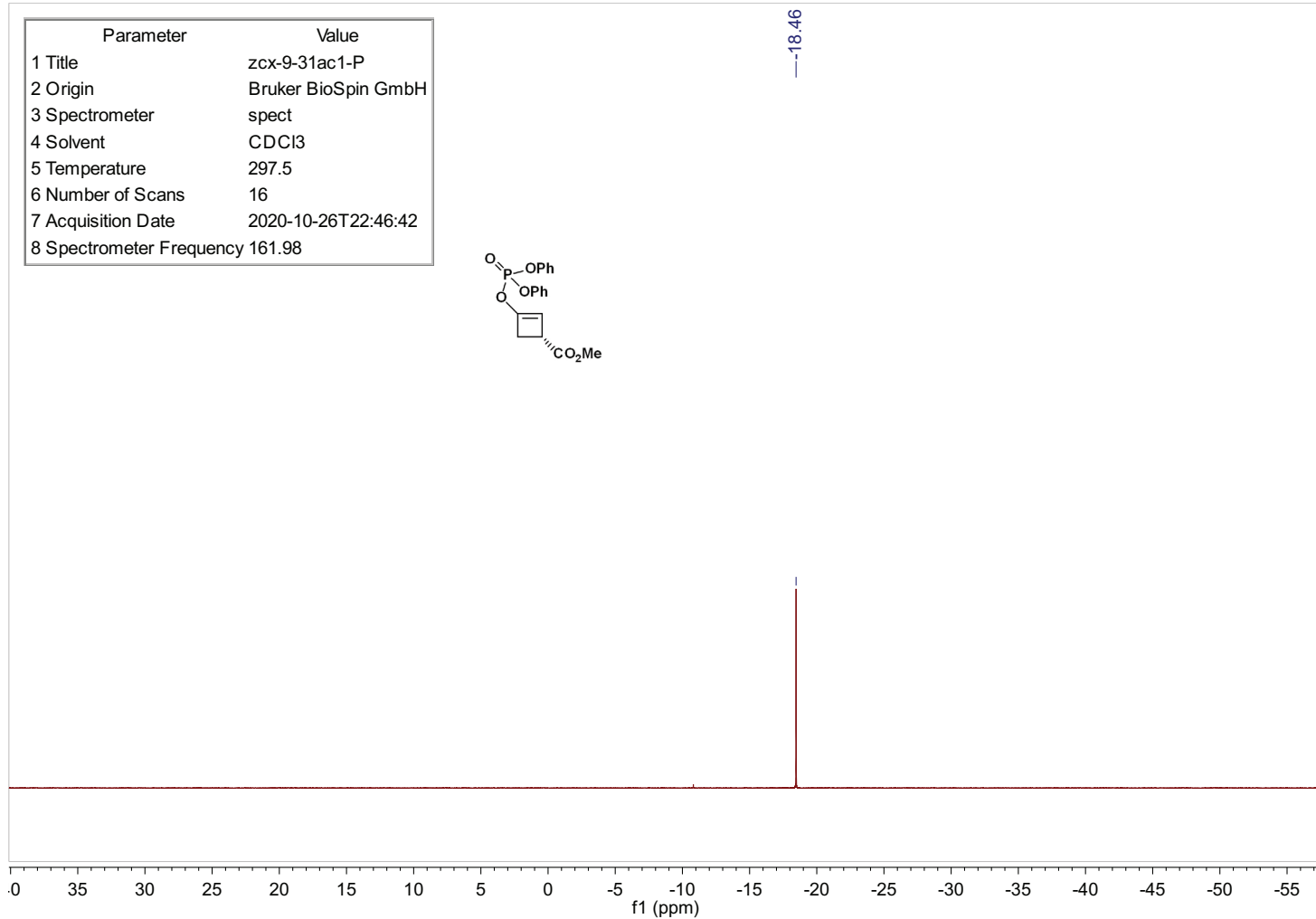
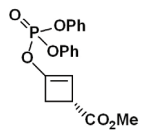
Parameter	Value
1 Title	zcx-4-97ac
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	297.7
6 Number of Scans	4
7 Acquisition Date	2018-11-09T05:22:02
8 Spectrometer Frequency	400.13







Parameter	Value
1 Title	zcx-9-31ac1-P
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	297.5
6 Number of Scans	16
7 Acquisition Date	2020-10-26T22:46:42
8 Spectrometer Frequency	161.98



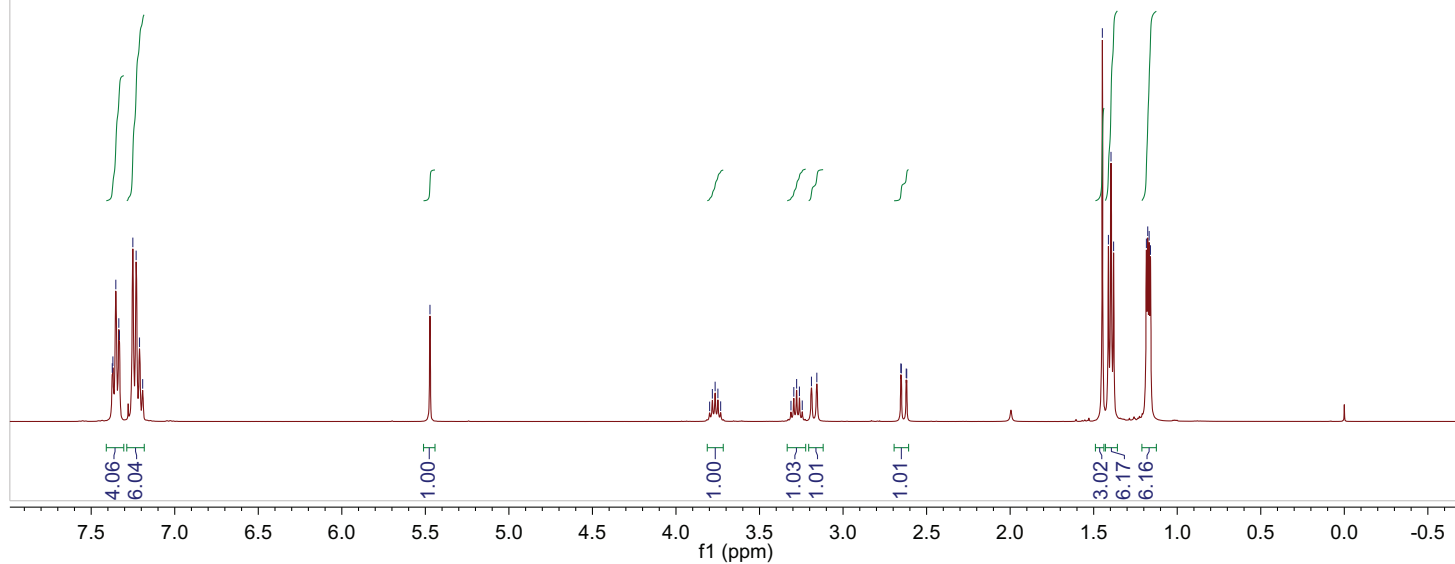
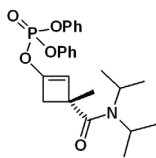
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7.33
7.33
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7.23
7.21
7.19

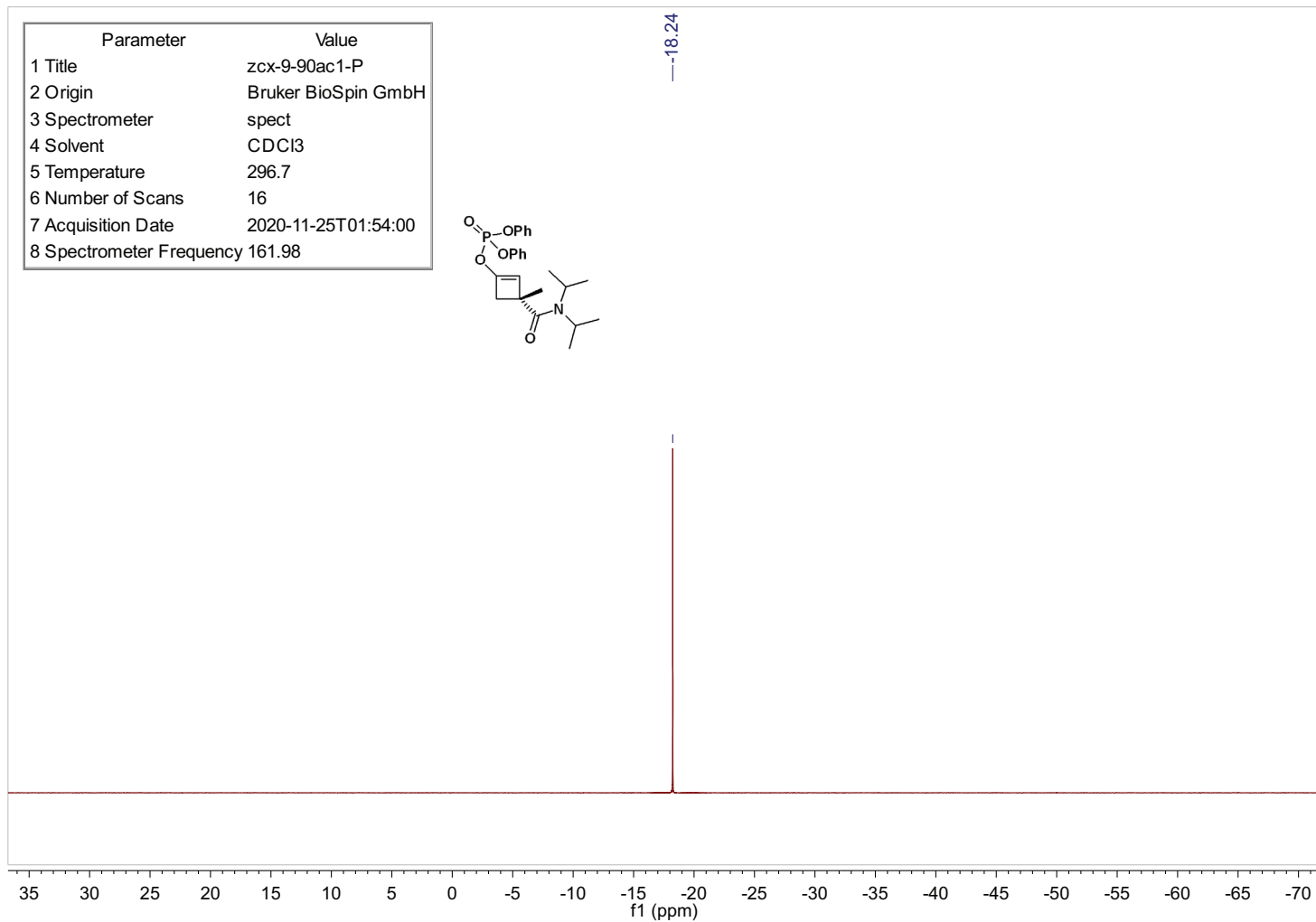
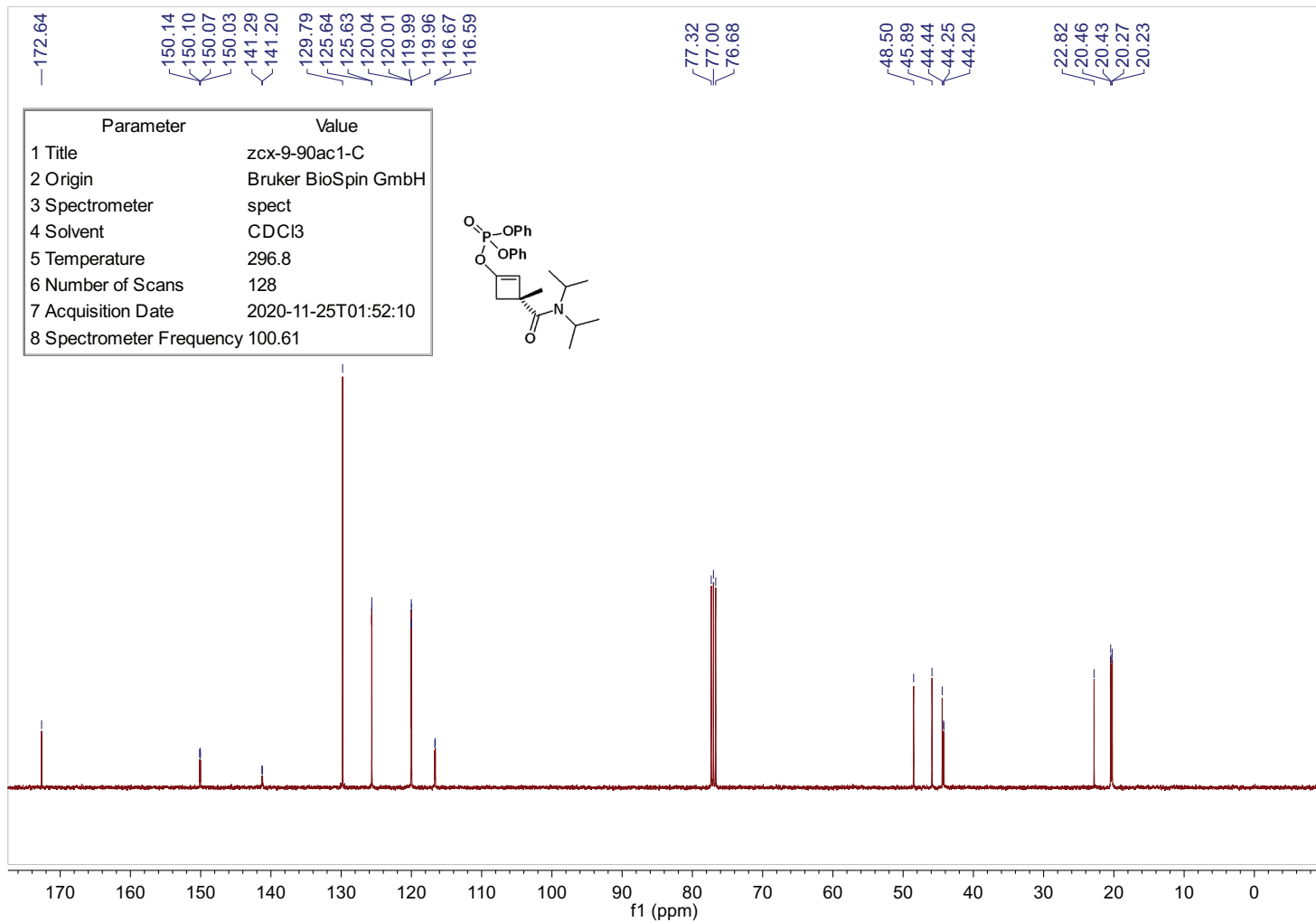
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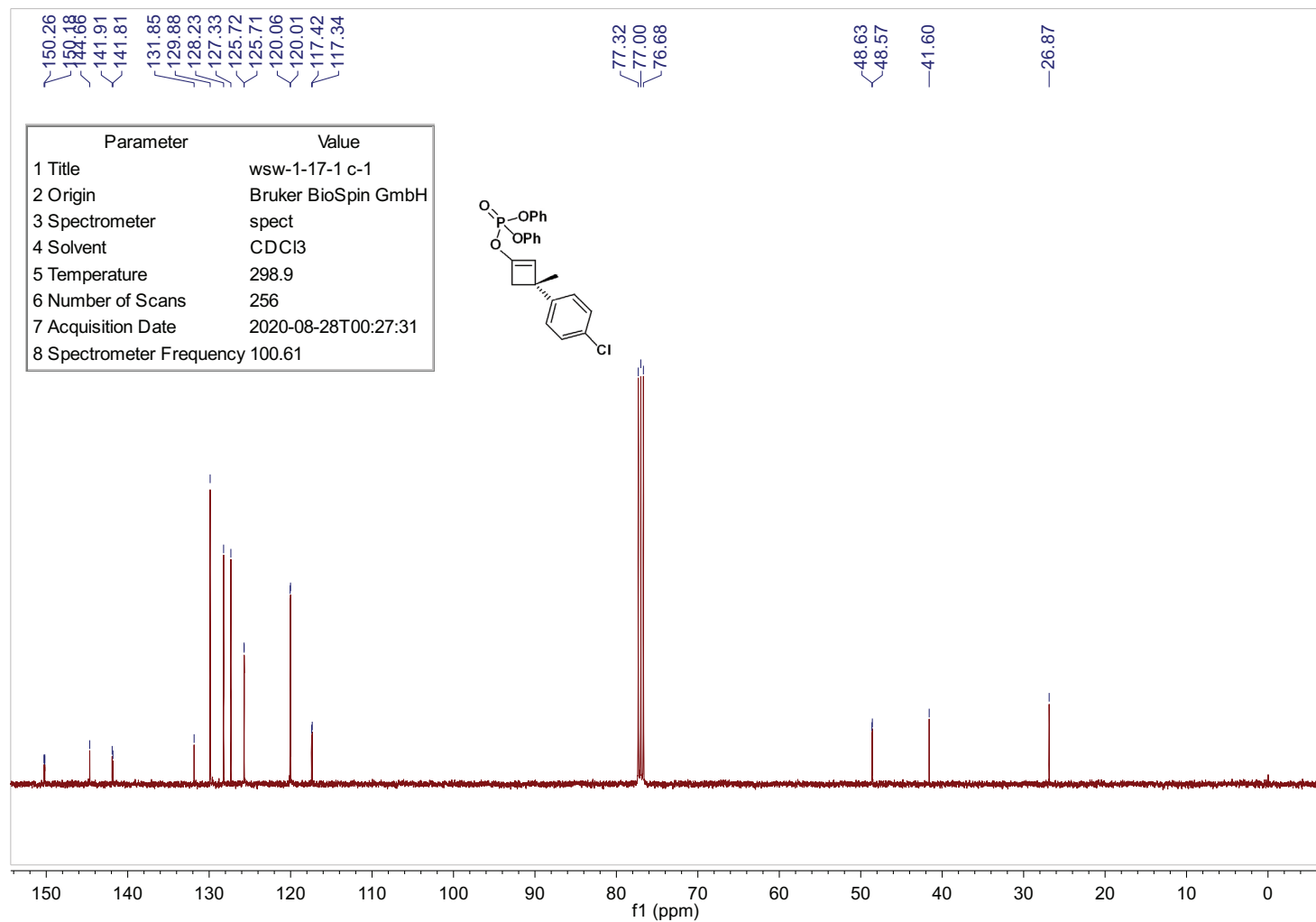
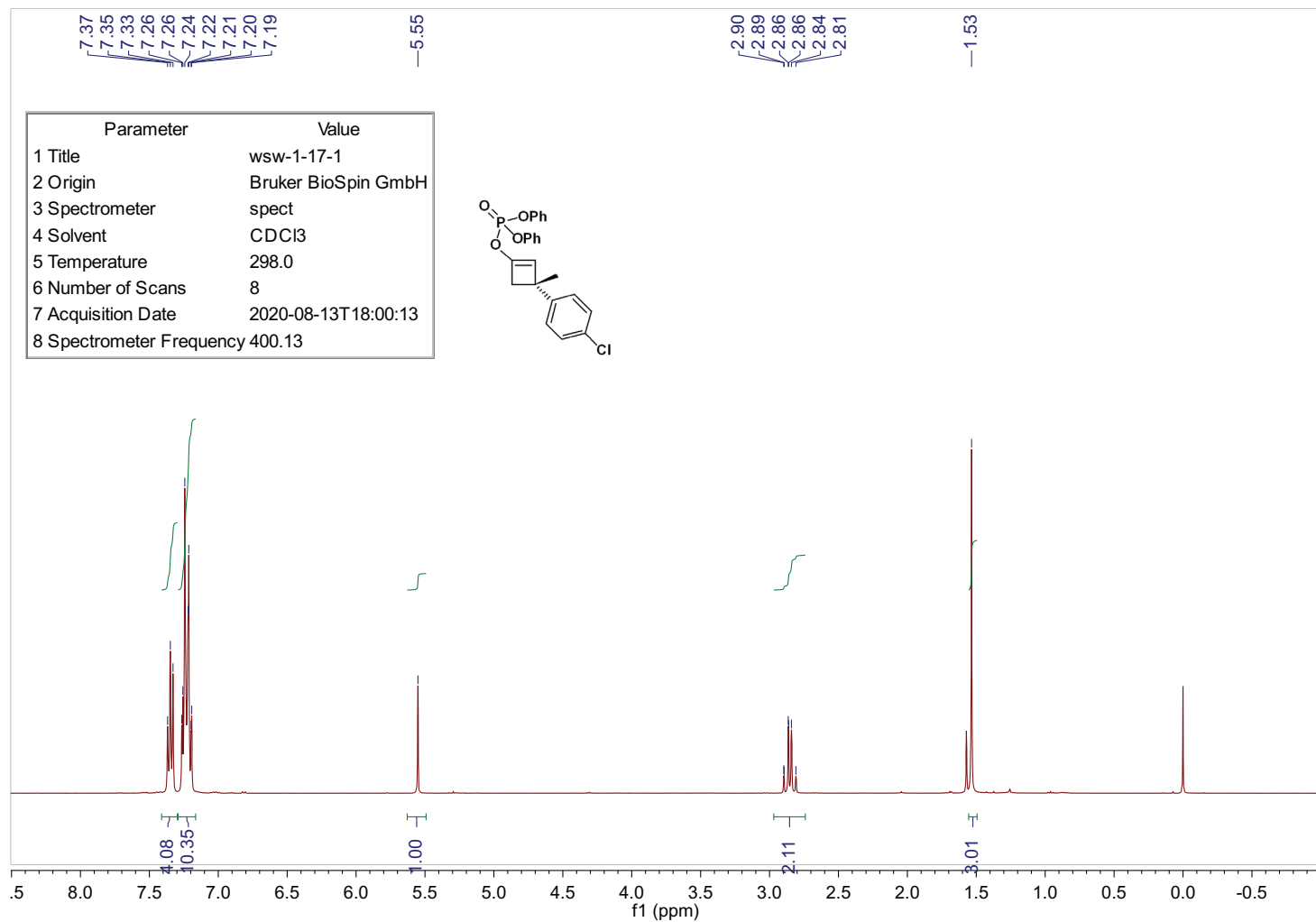
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3.77
3.75
3.73
3.28
3.26
3.19
2.65
2.62
2.62

1.45
1.41
1.40
1.38
1.18
1.18
1.17
1.16

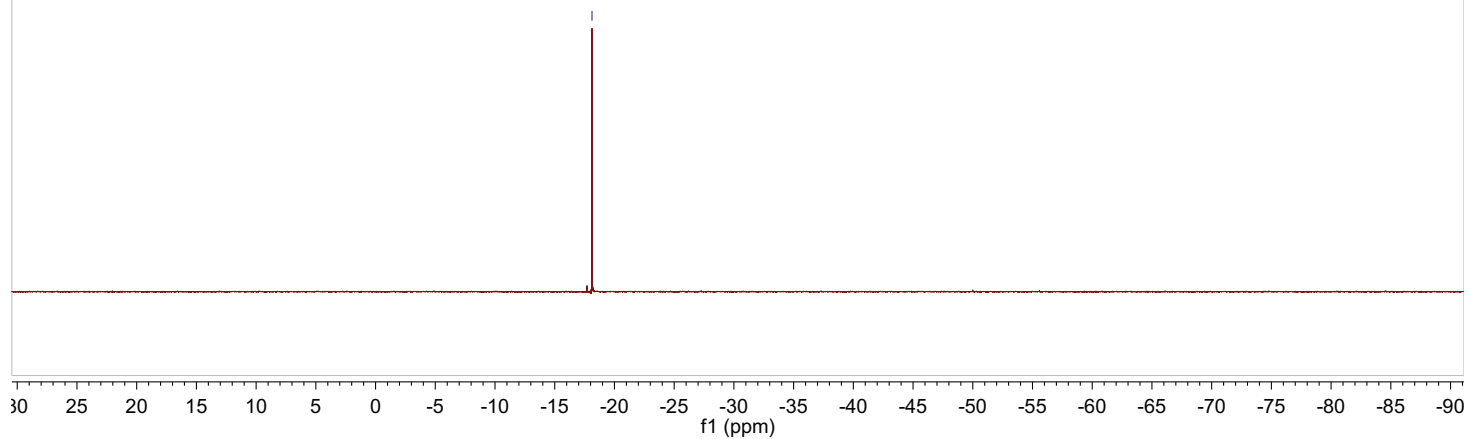
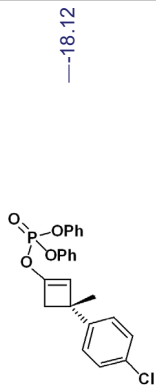
Parameter	Value
1 Title	zcx-9-90ac1
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	296.2
6 Number of Scans	4
7 Acquisition Date	2020-11-25T01:44:12
8 Spectrometer Frequency	400.13







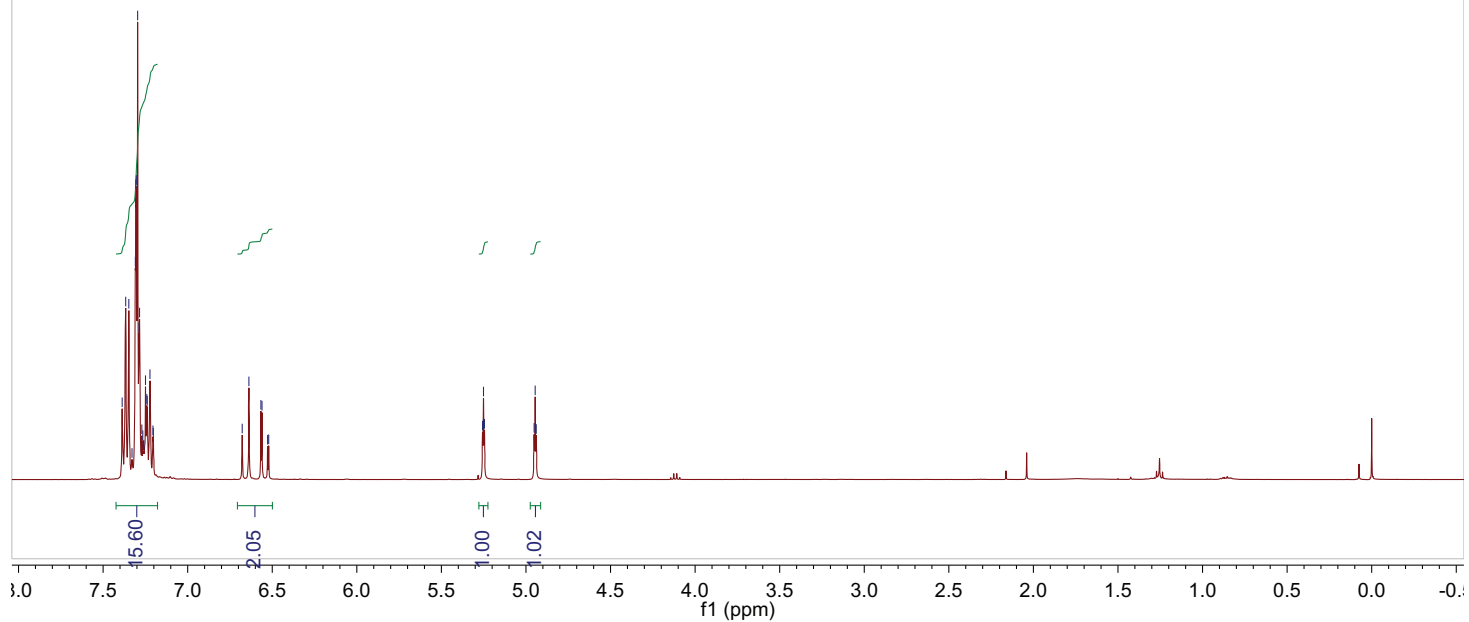
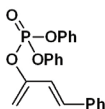
Parameter	Value
1 Title	wsw-1-17-1 p
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	298.3
6 Number of Scans	16
7 Acquisition Date	2020-08-13T18:10:01
8 Spectrometer Frequency	161.98

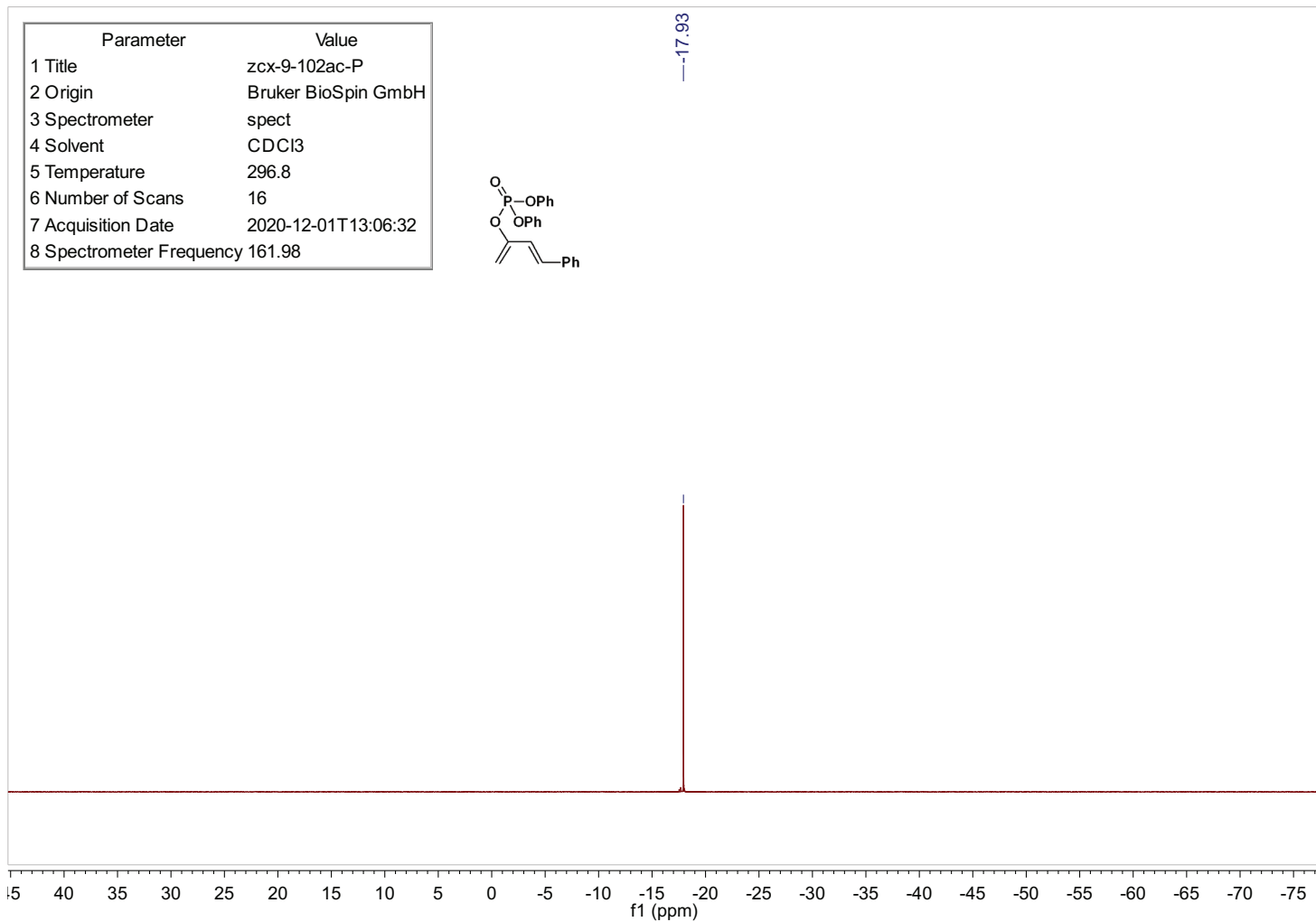
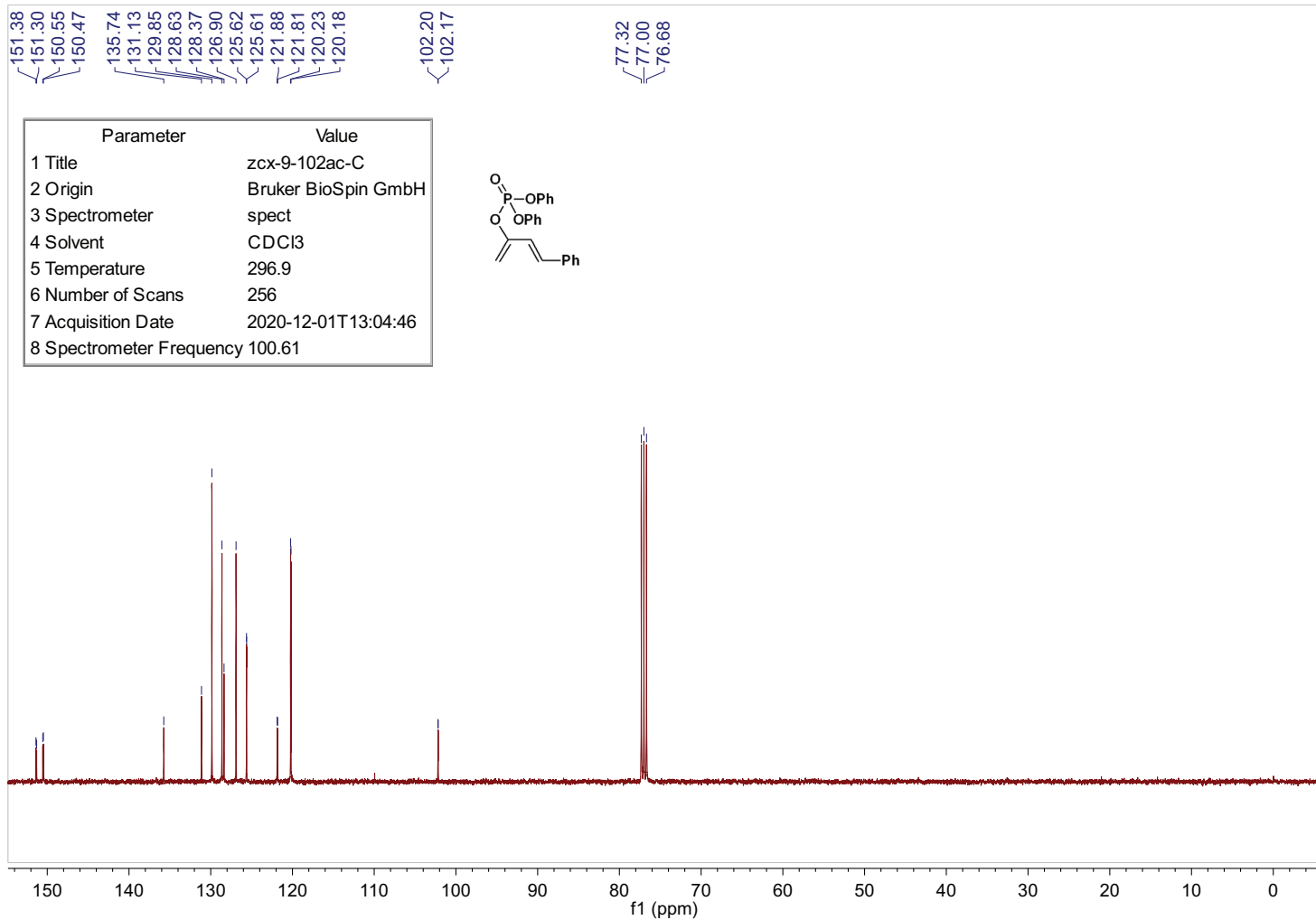


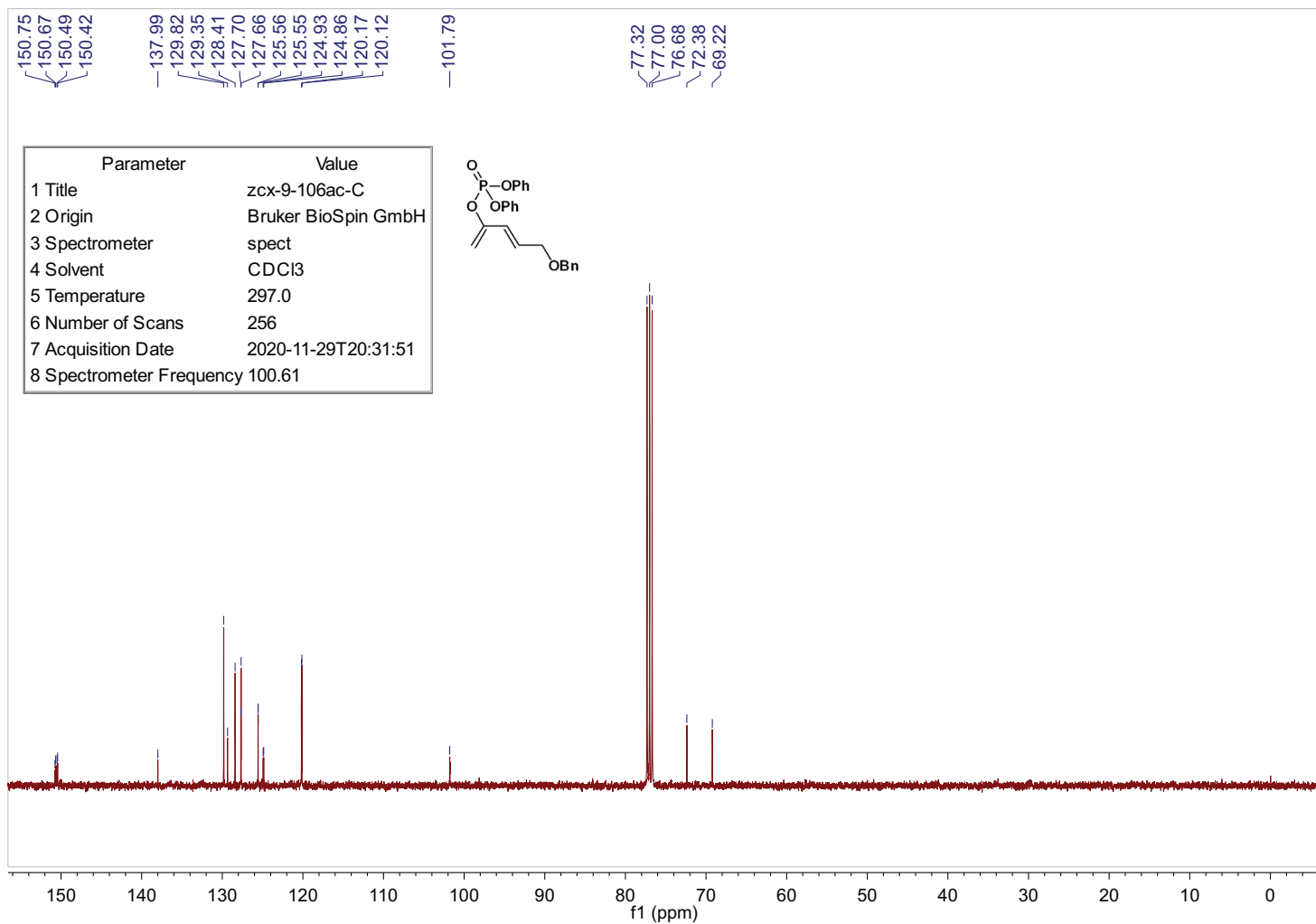
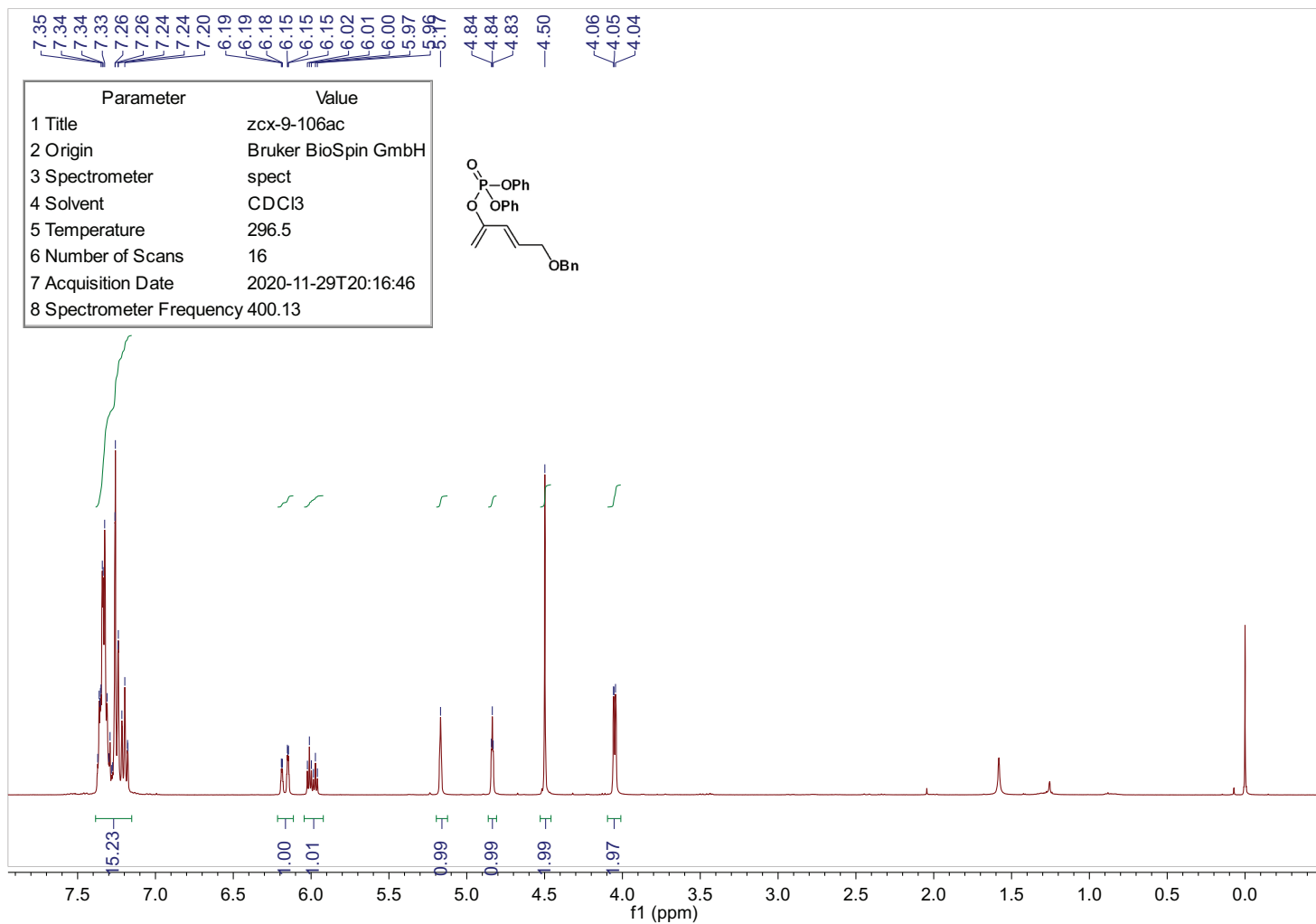
7.37
7.35
7.31
7.31
7.30
7.30
7.29
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6.64
6.57
6.56
6.53
6.52

5.26
5.25
5.25
4.95
4.94

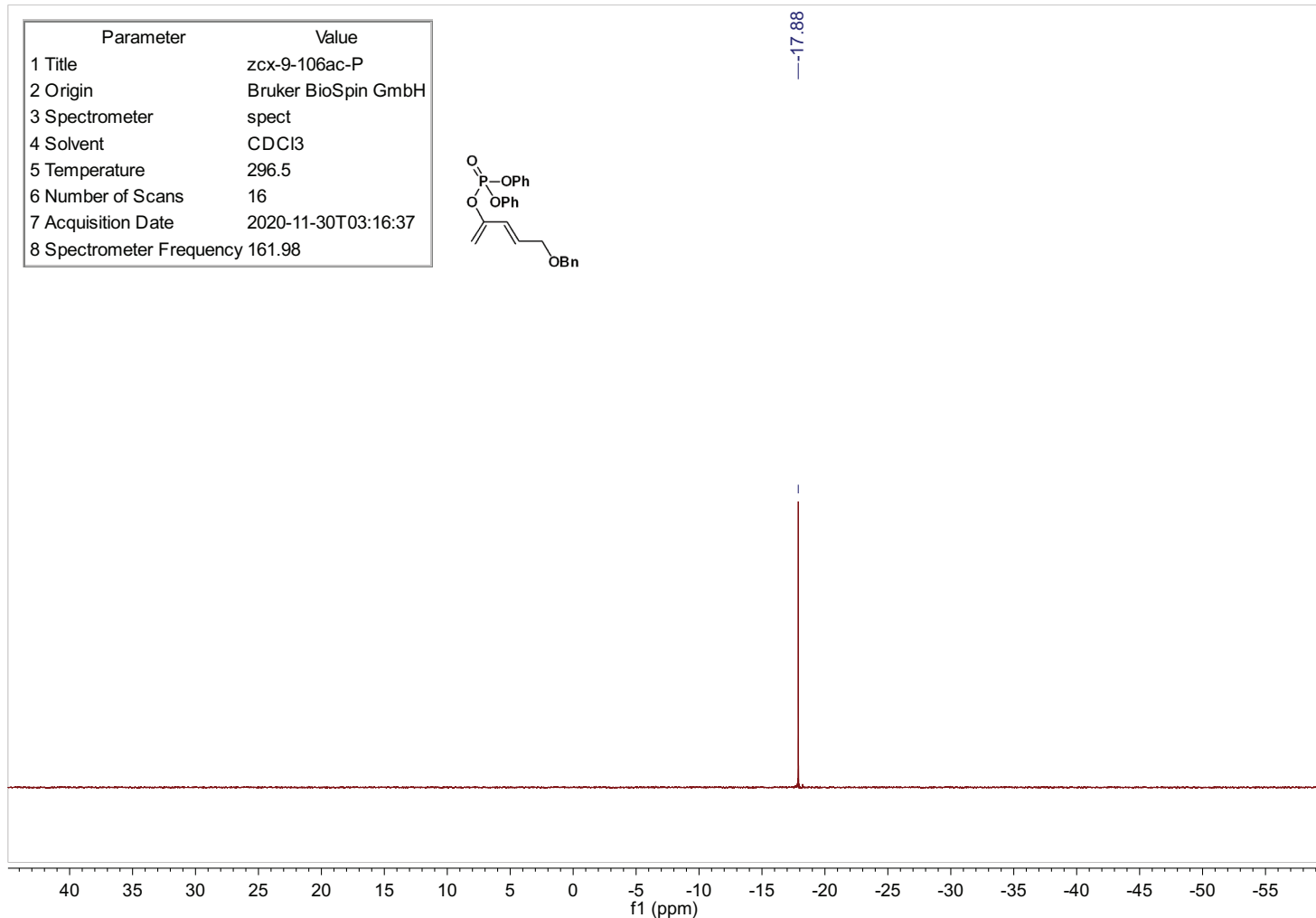
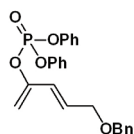
Parameter	Value
1 Title	zcx-9-102ac
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	296.3
6 Number of Scans	4
7 Acquisition Date	2020-12-01T12:49:45
8 Spectrometer Frequency	400.13



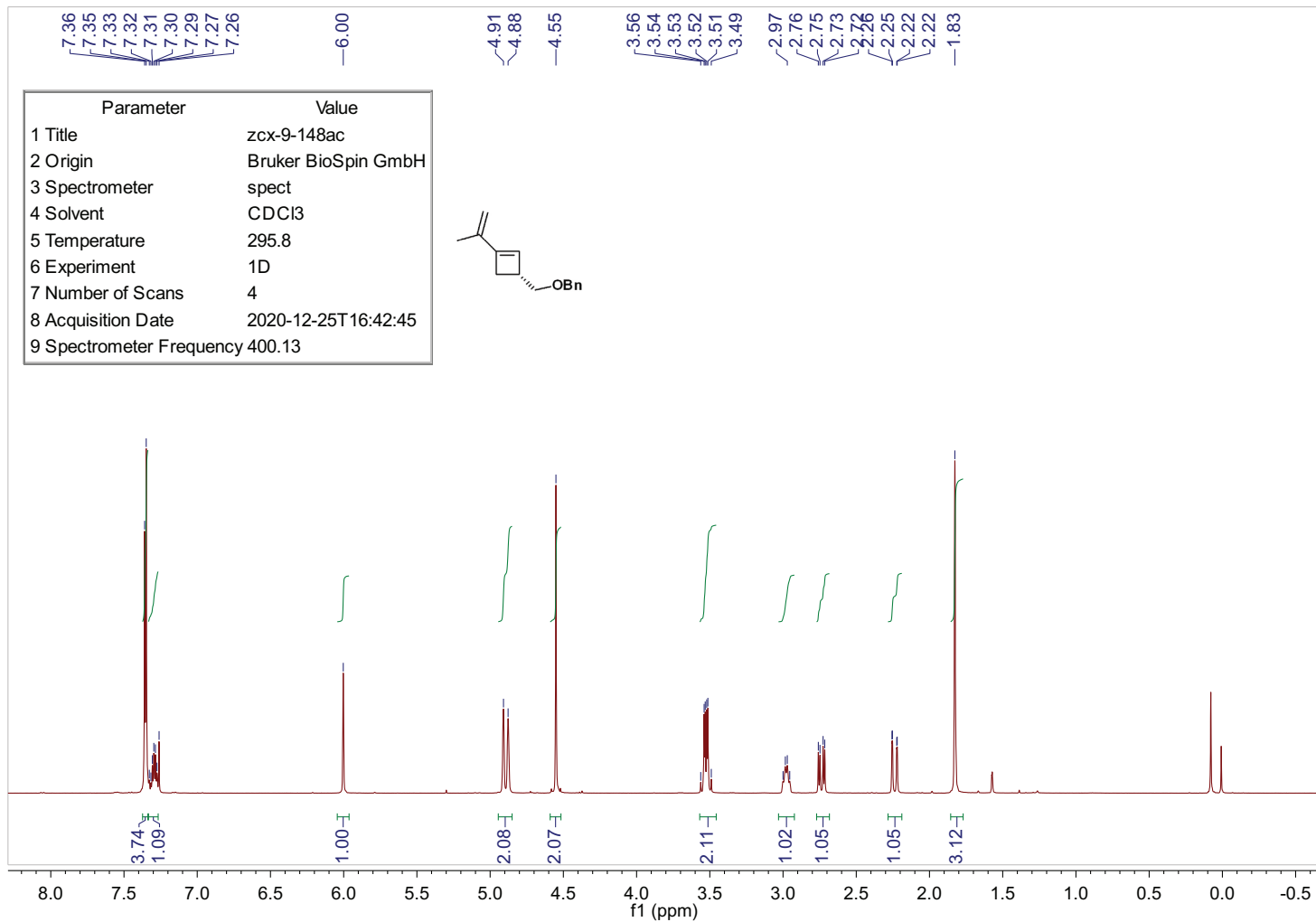
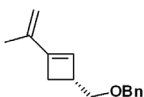


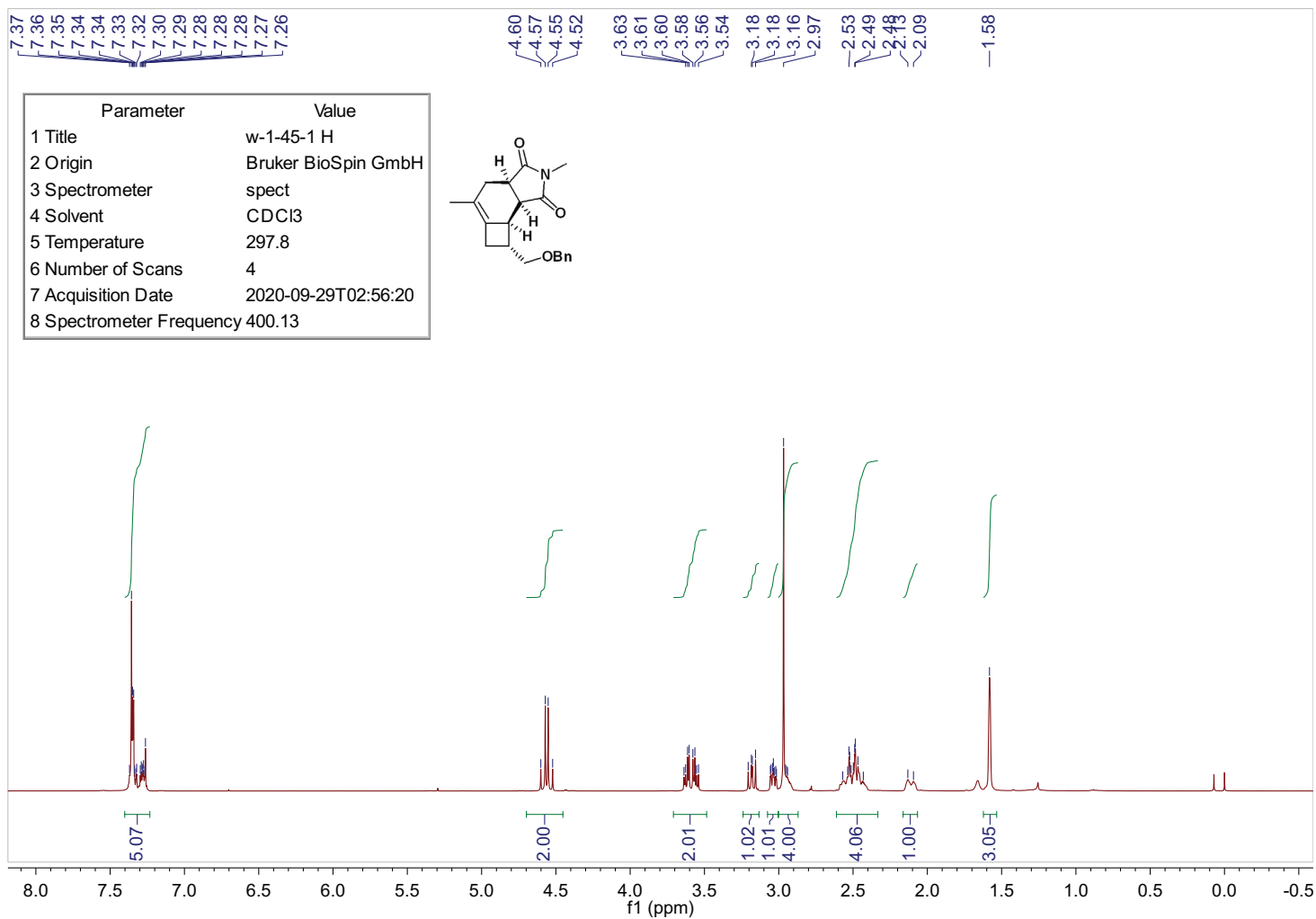
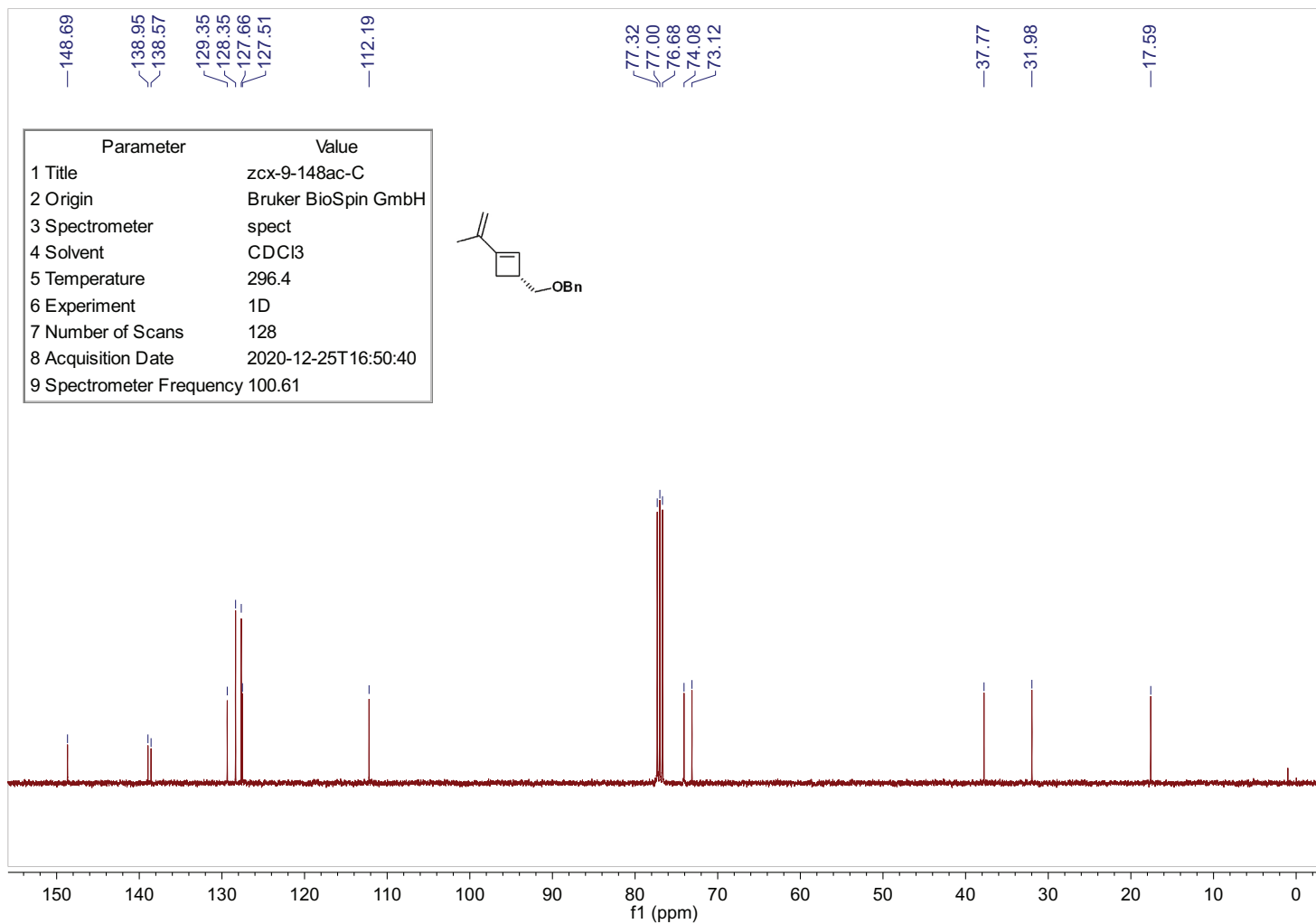


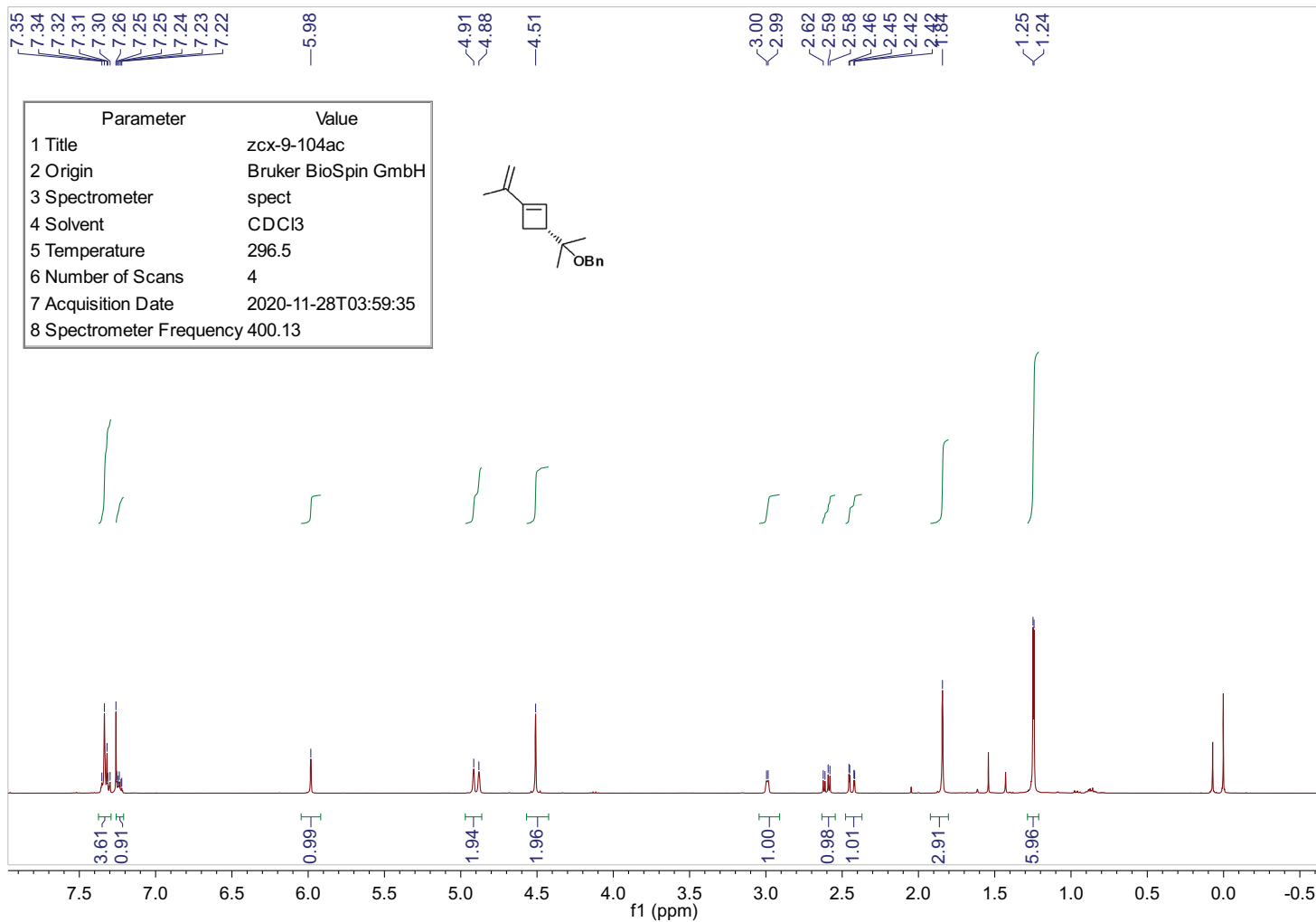
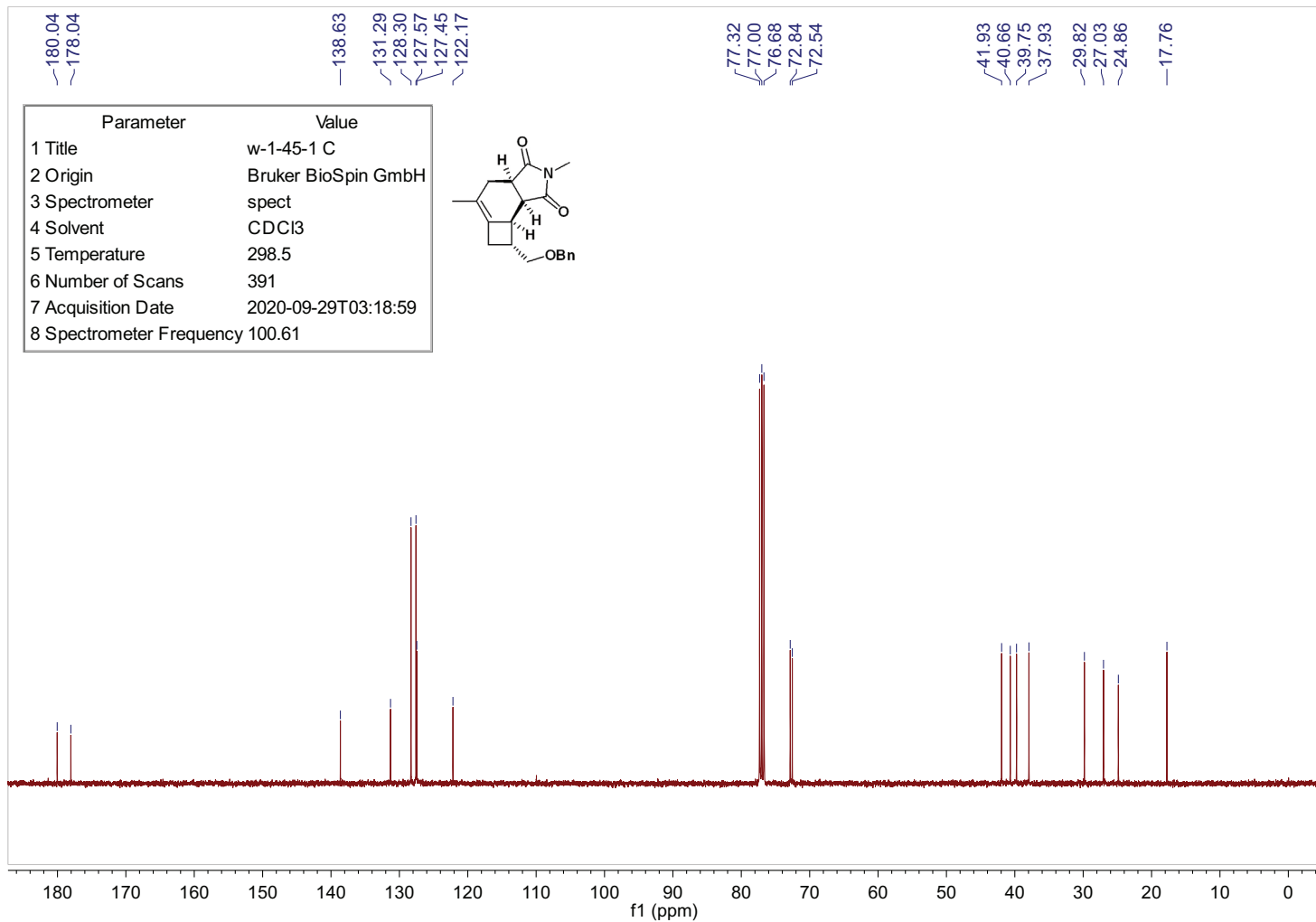
Parameter	Value
1 Title	zcx-9-106ac-P
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	296.5
6 Number of Scans	16
7 Acquisition Date	2020-11-30T03:16:37
8 Spectrometer Frequency	161.98

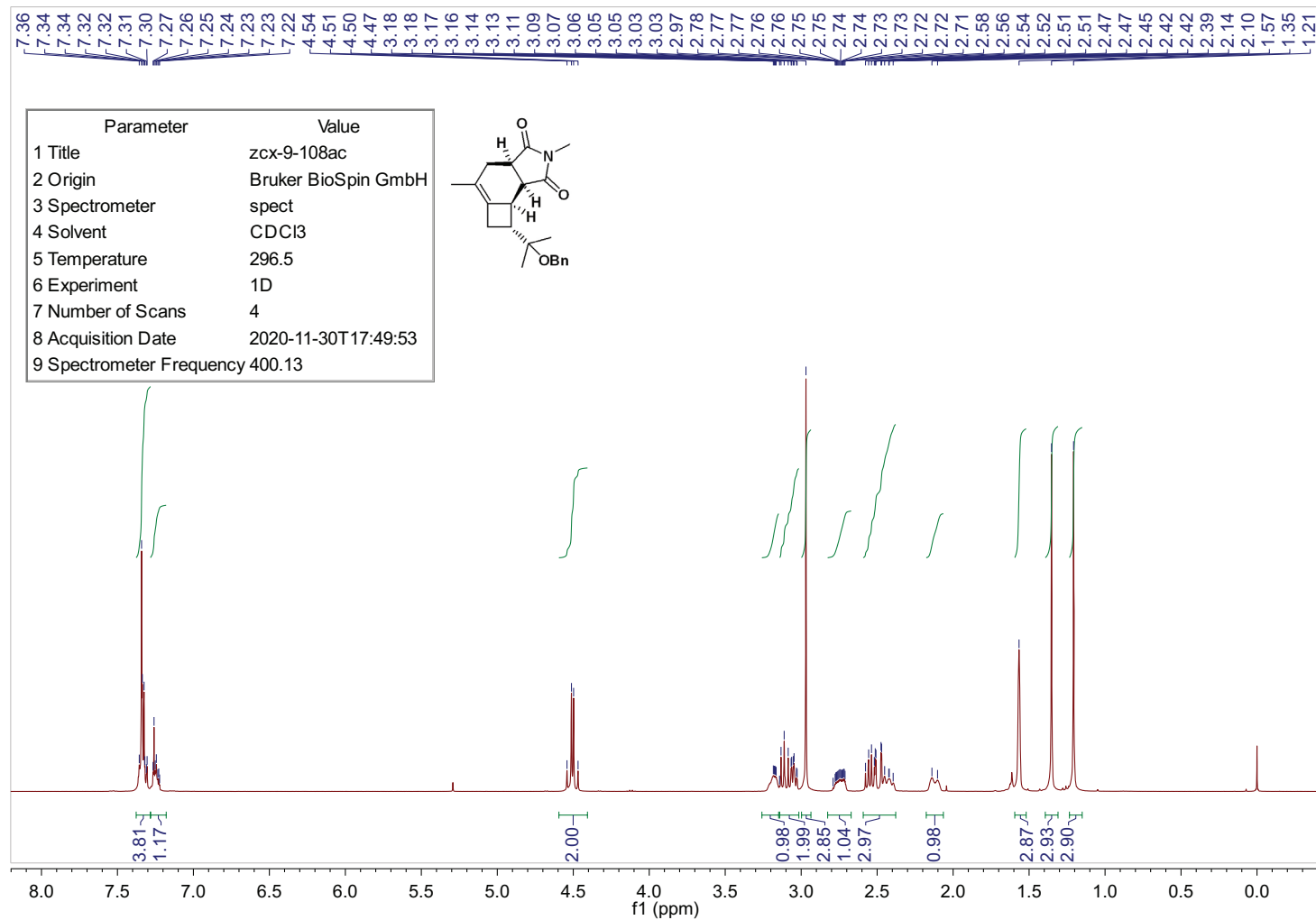
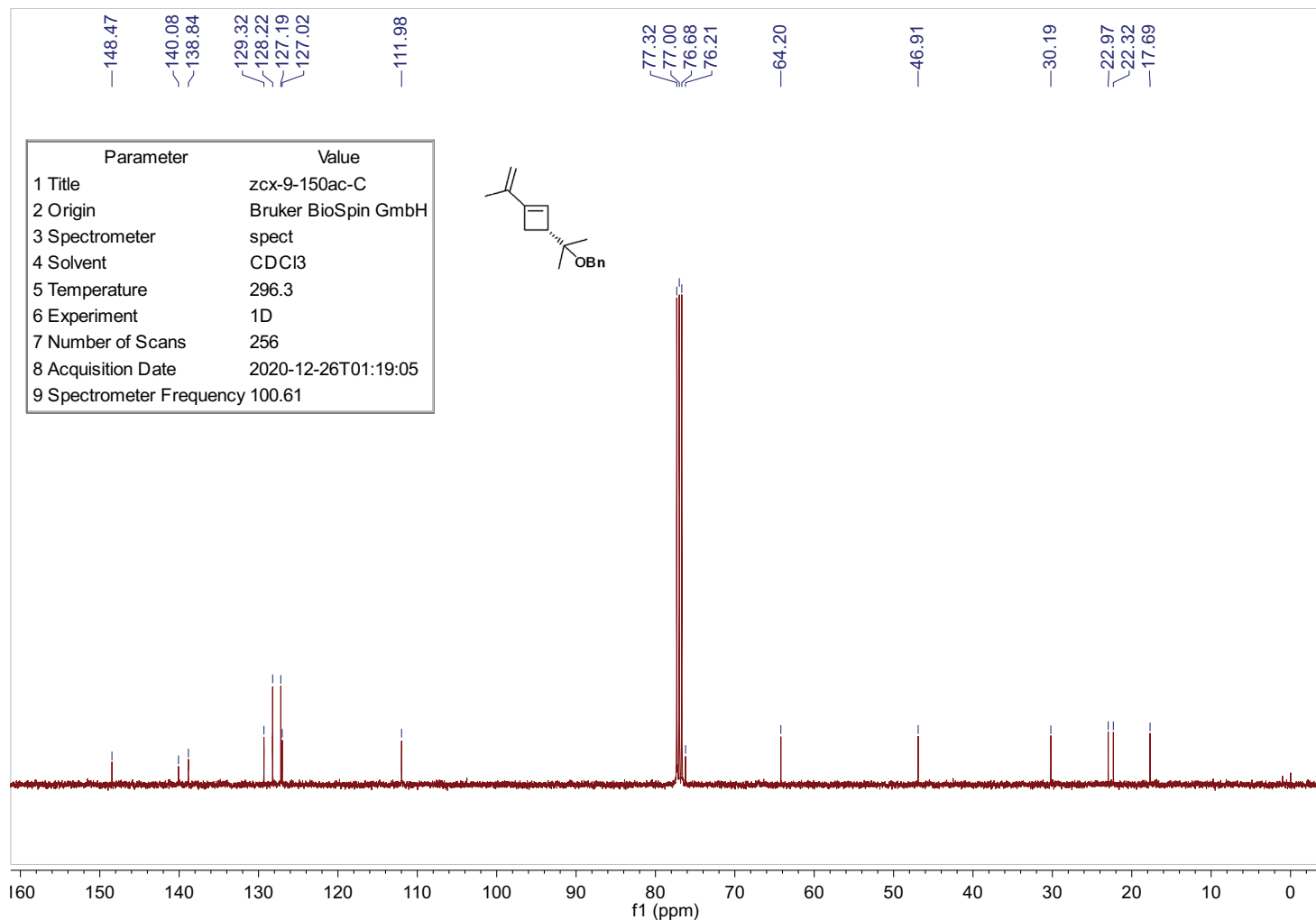


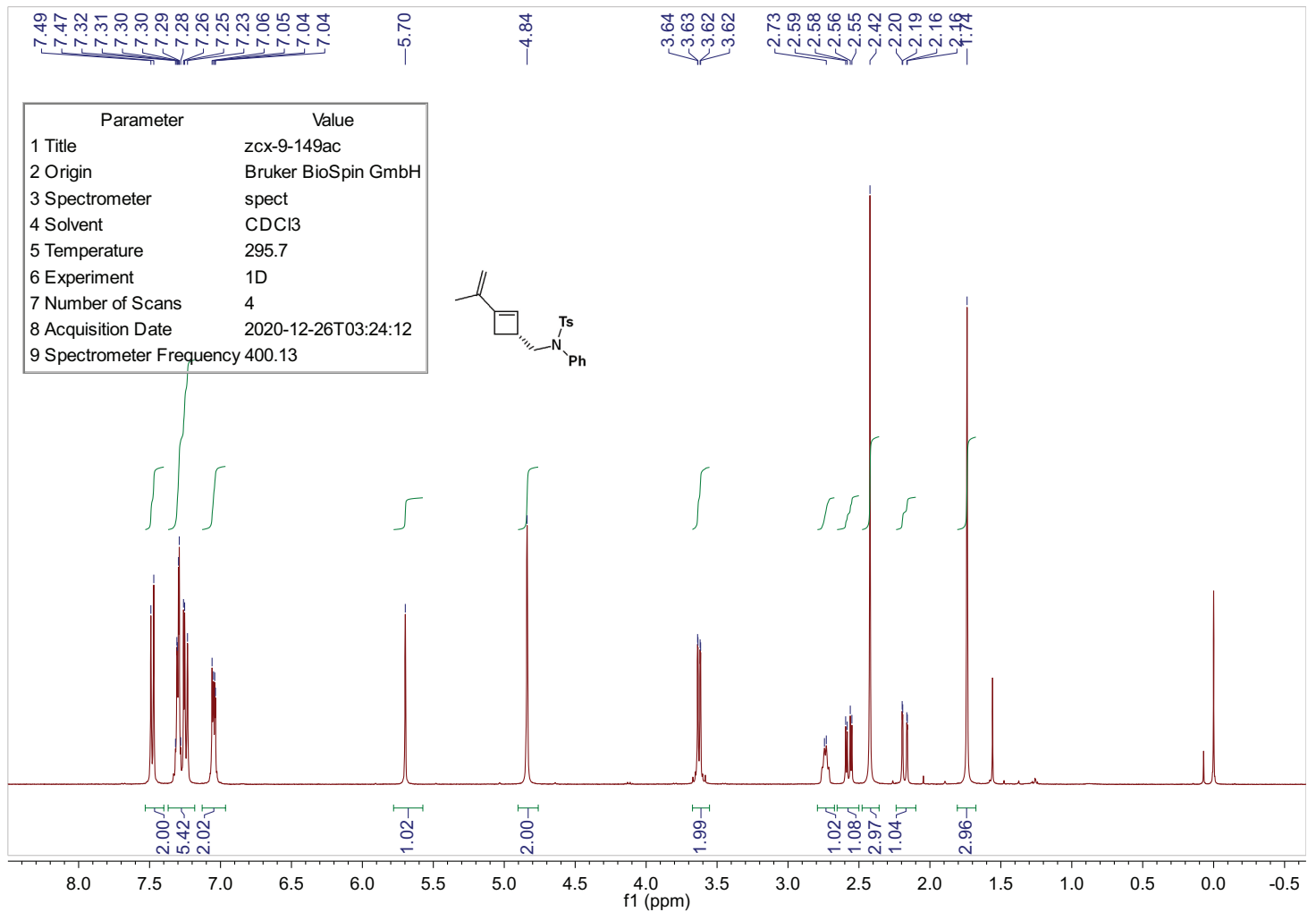
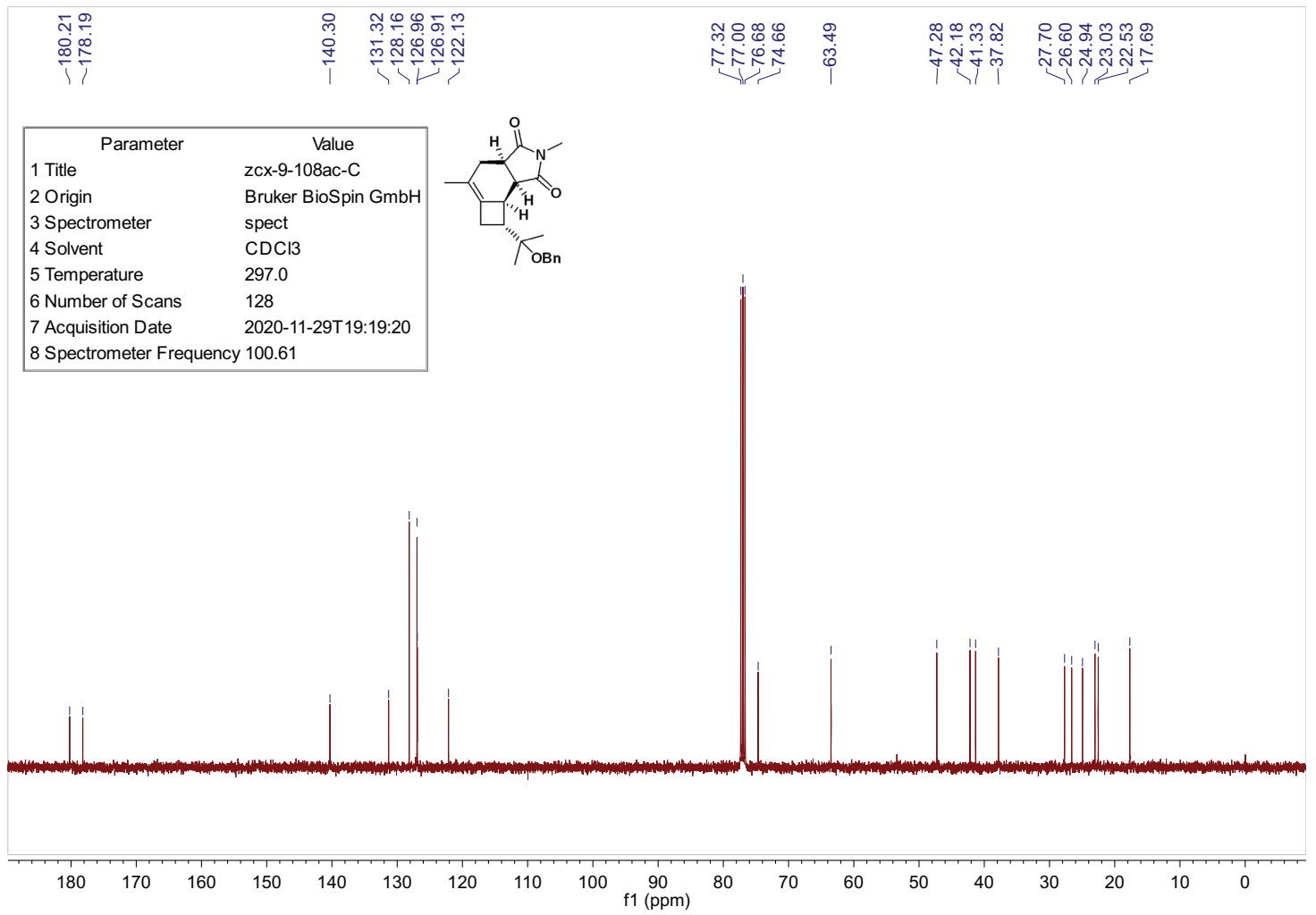
Parameter	Value
1 Title	zcx-9-148ac
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	295.8
6 Experiment	1D
7 Number of Scans	4
8 Acquisition Date	2020-12-25T16:42:45
9 Spectrometer Frequency	400.13

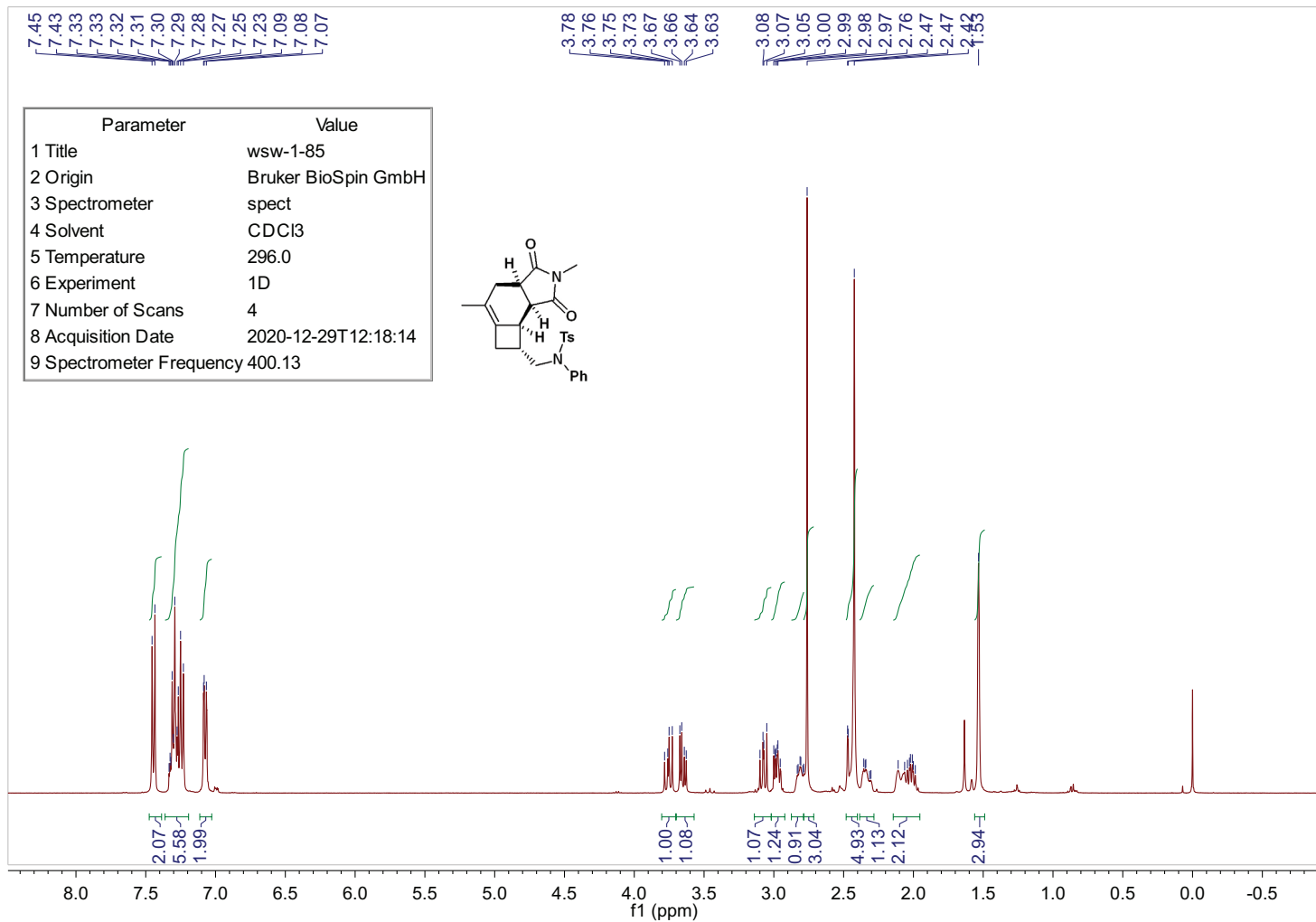
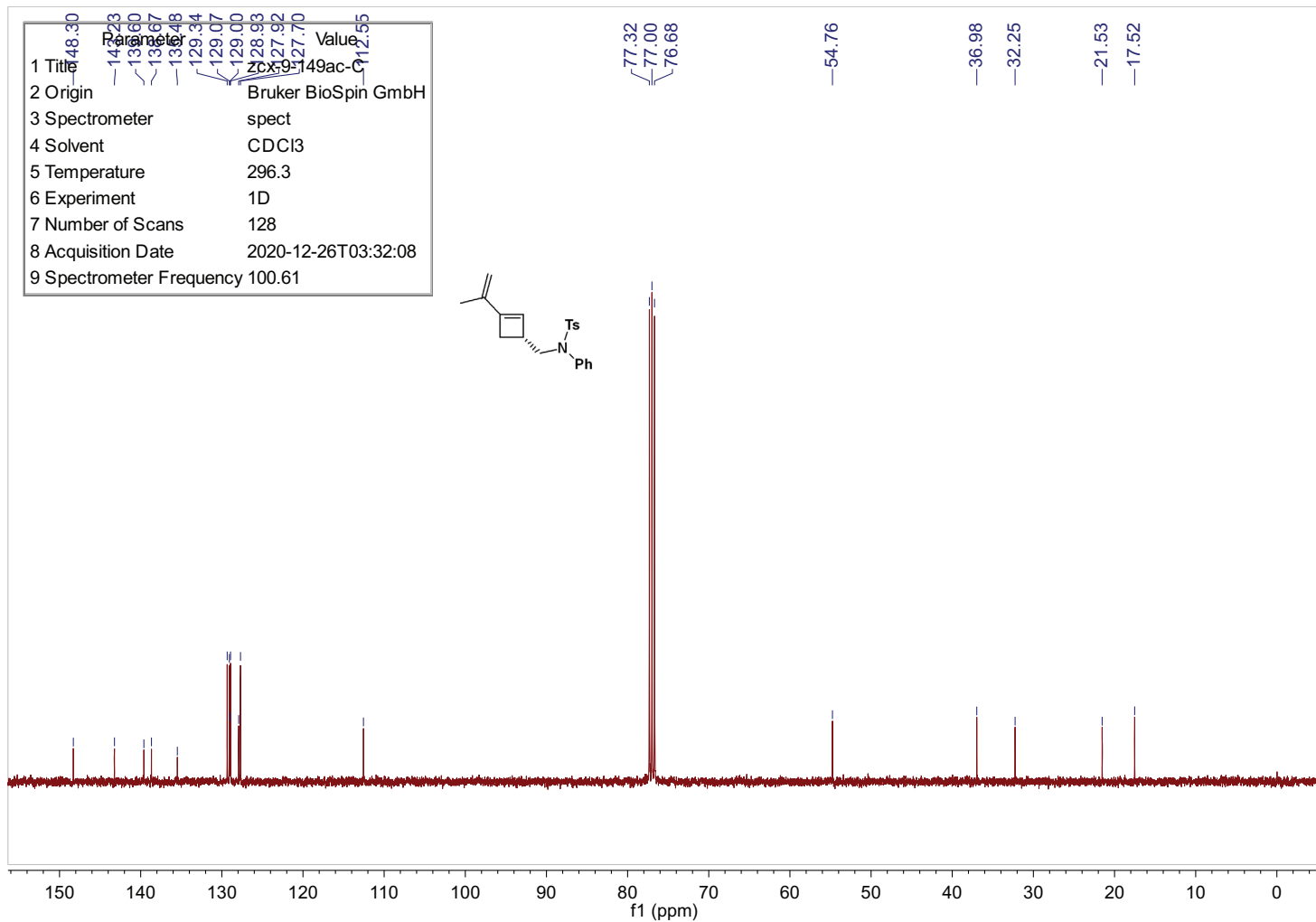


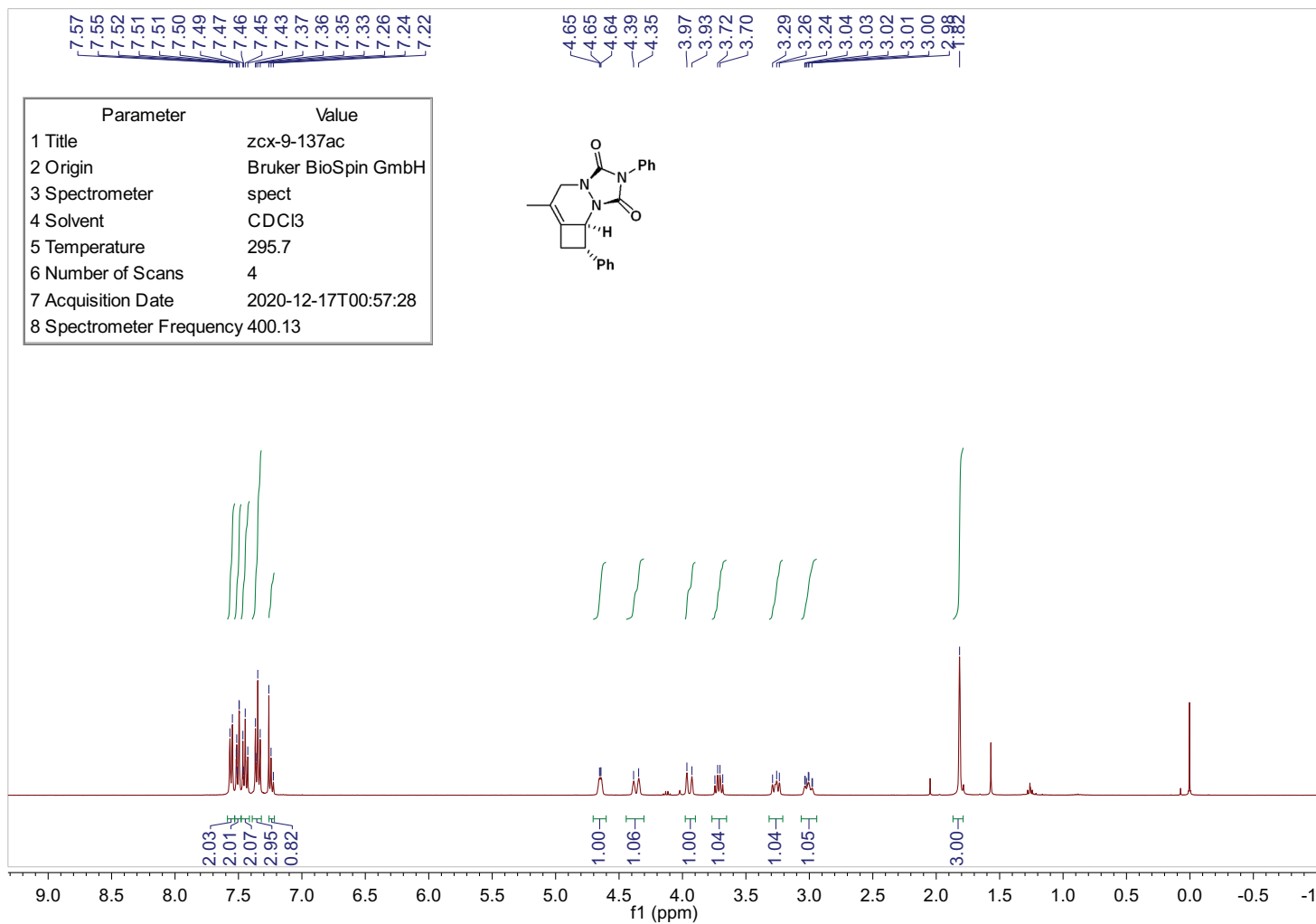
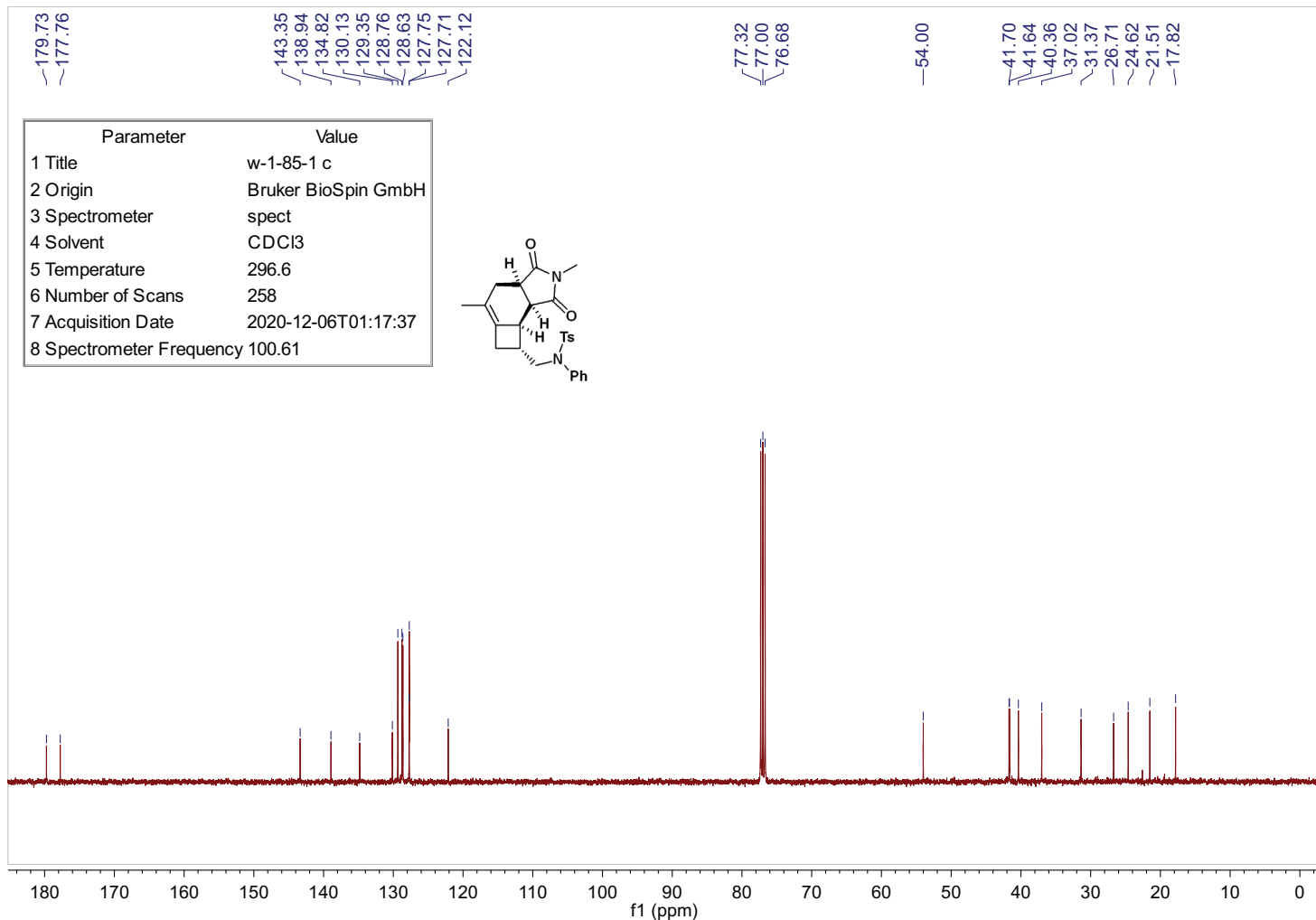


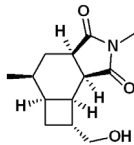
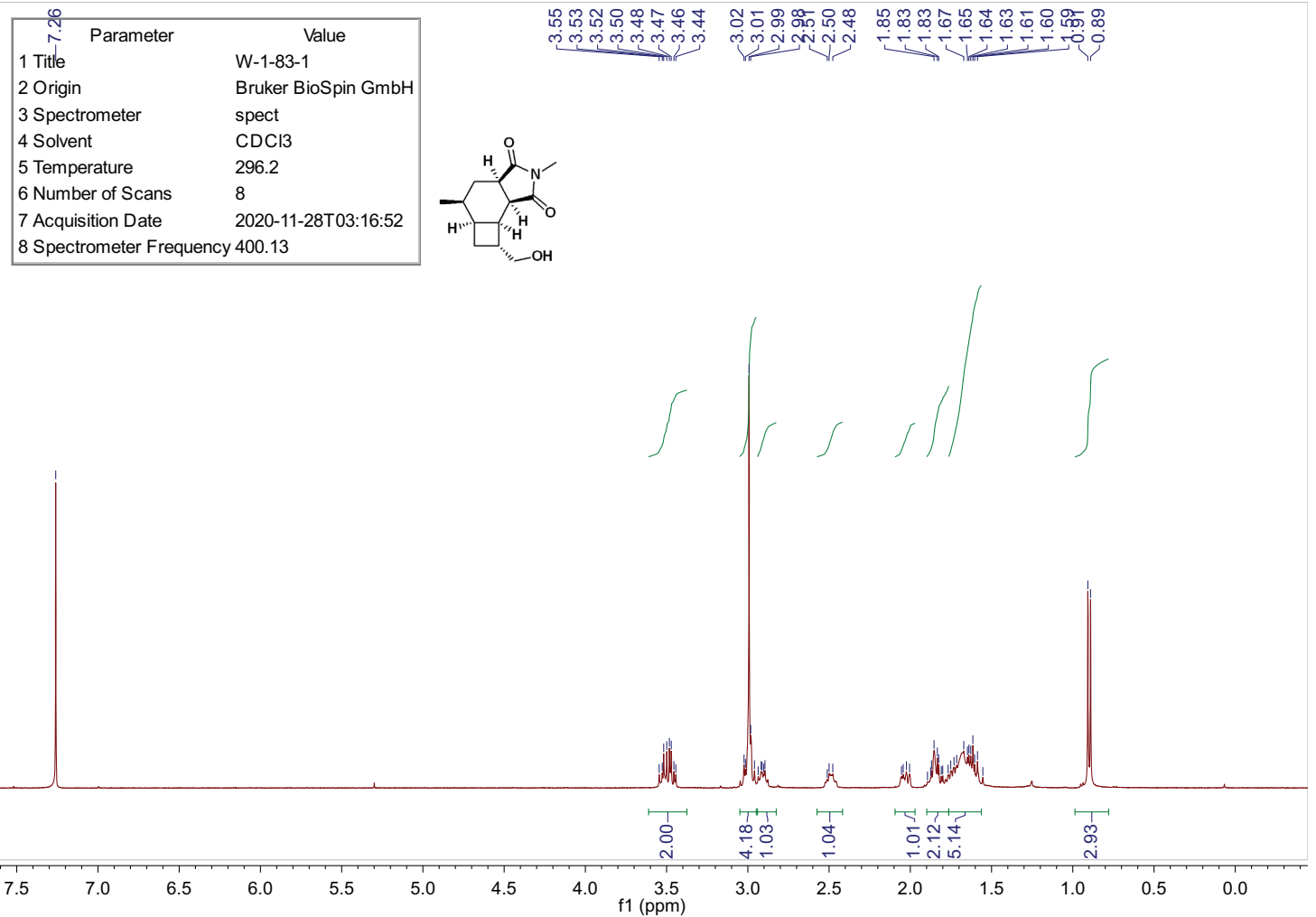
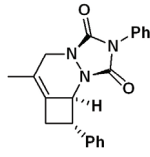
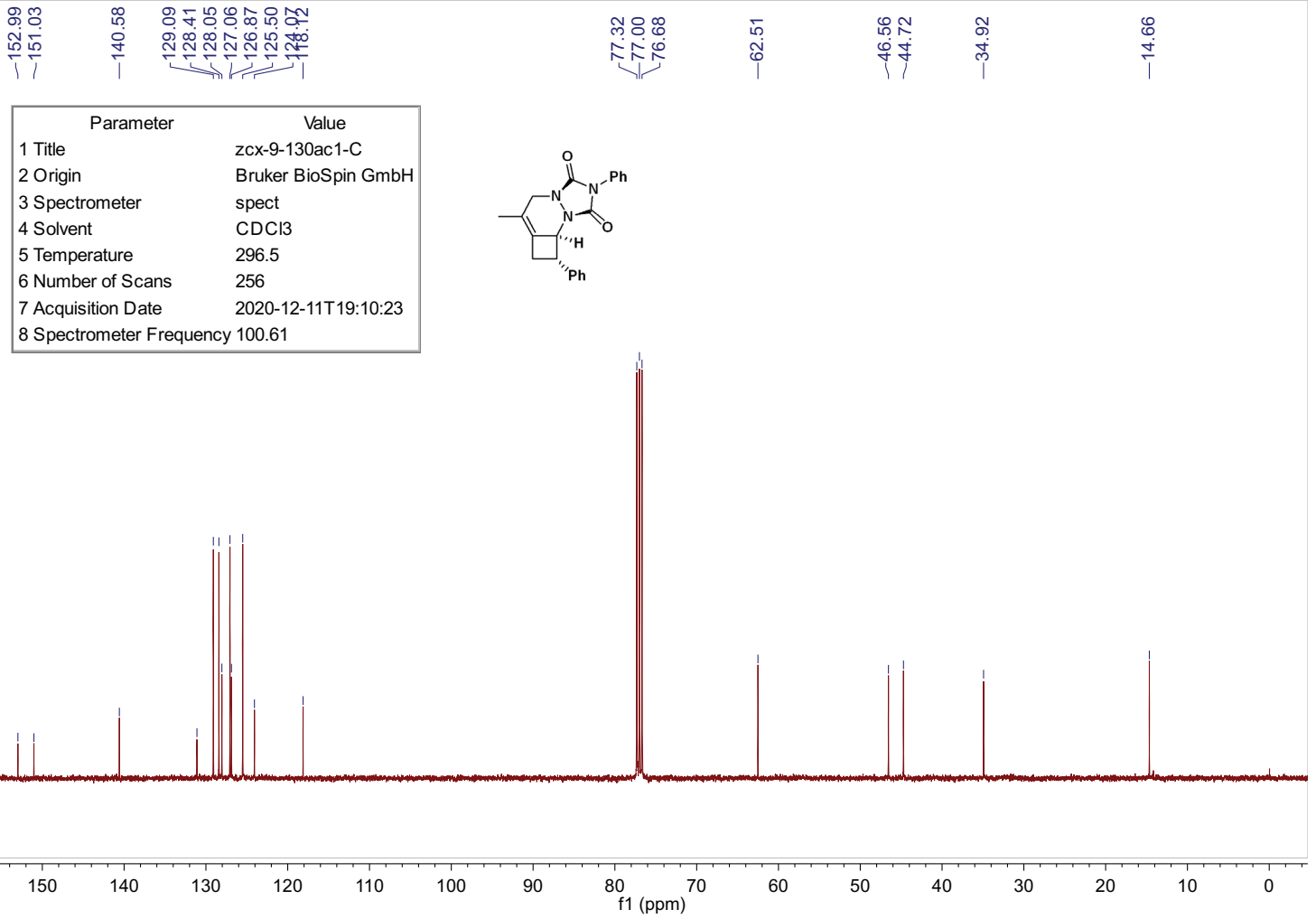










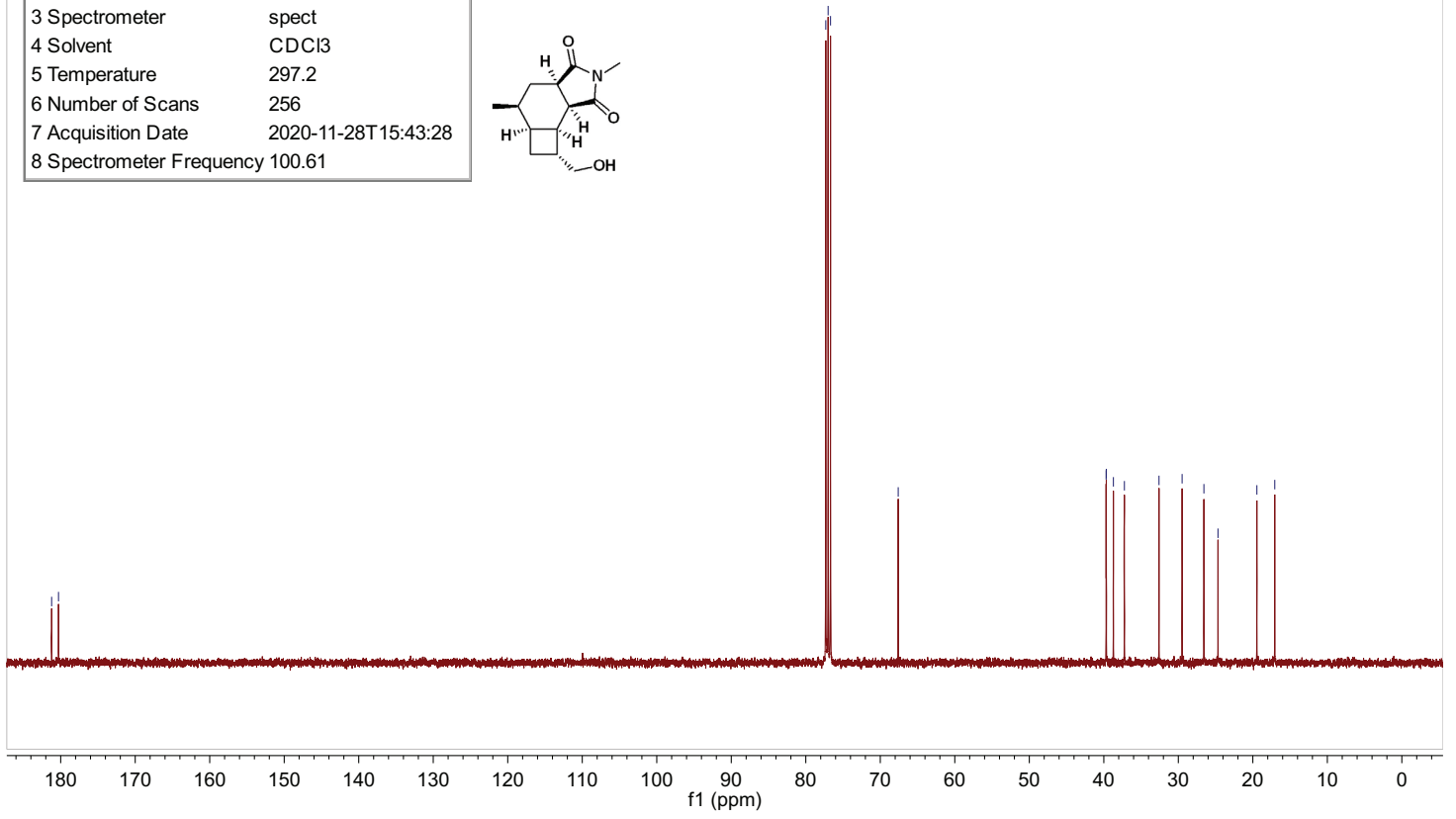
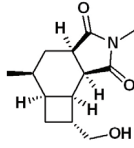


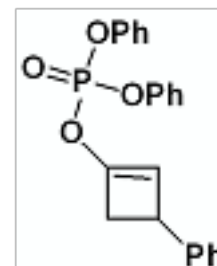
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77.32
77.00
76.68
67.59

39.69
39.66
38.72
37.24
32.59
29.49
26.56
24.67
19.46
17.06

Parameter	Value
1 Title	w-1-83-1 c
2 Origin	Bruker BioSpin GmbH
3 Spectrometer	spect
4 Solvent	CDCl3
5 Temperature	297.2
6 Number of Scans	256
7 Acquisition Date	2020-11-28T15:43:28
8 Spectrometer Frequency	100.61





<Sample Information>

Sample Name : zcx-7-11ac
 Sample ID :
 Data Filename : zcx-7-11ac.lcd

Method Filename : OJ-H;1 ml; 10% IPA in Hex;40 min.lcm

Batch Filename : zcx-7-11ac zcx-5-95 96ac.lcb

Vial # : 1-46

Sample Type : Unknown

Injection Volume : 10 uL

Date Acquired : 10/26/2019 11:13:36 AM

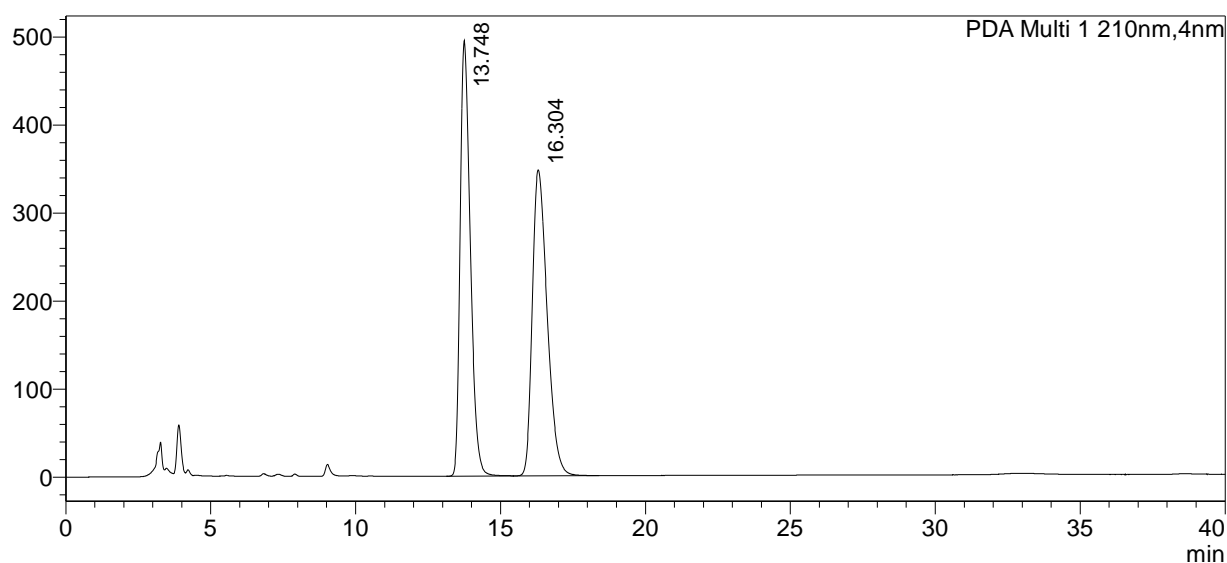
Acquired by : System Administrator

Date Processed : 10/26/2019 11:53:38 AM

Processed by : System Administrator

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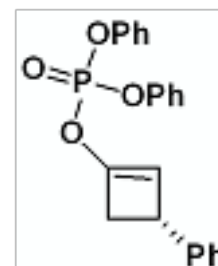
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.748	12107636	495033	49.358			
2	16.304	12422395	347484	50.642		V	
Total		24530031	842517				



<Sample Information>

Sample Name : wsw-1-30-1
 Sample ID :
 Data Filename : wsw-1-30-1.lcd

Method Filename : OJ-H;1 ml; 10% IPA in Hex;40 min.lcm

Batch Filename : zcx-8-81ac.lcb

Vial # : 1-31

Sample Type : Unknown

Injection Volume : 10 uL

Date Acquired : 8/28/2020 12:04:23 AM

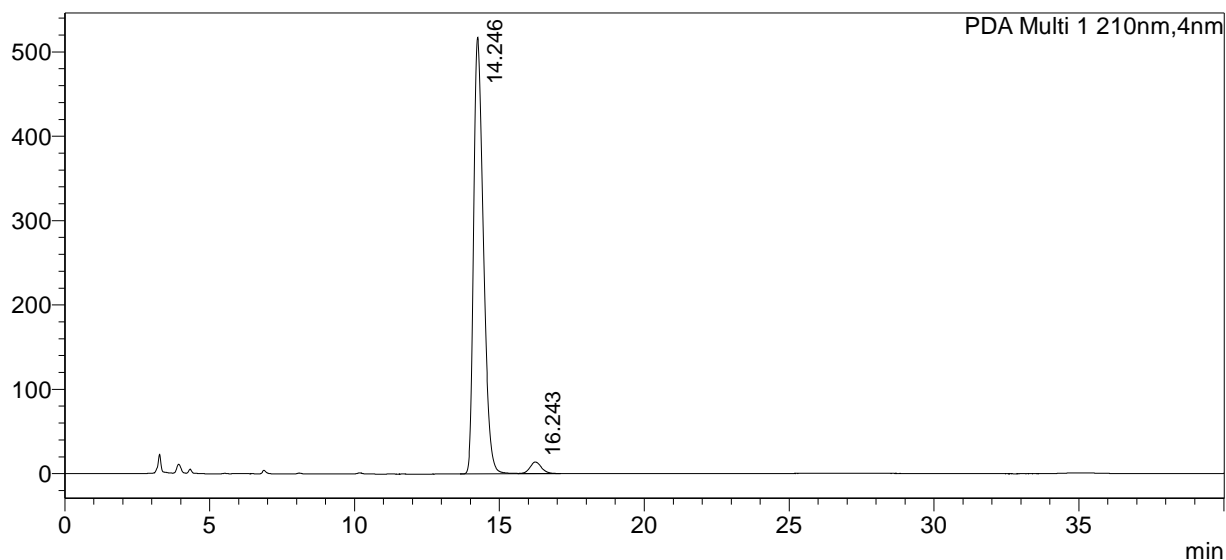
Acquired by : System Administrator

Date Processed : 8/28/2020 12:44:26 AM

Processed by : System Administrator

<Chromatogram>

mAU



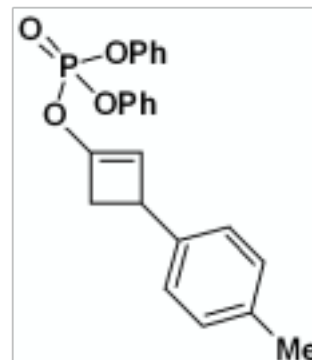
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.246	12194364	517584	97.061		S	
2	16.243	369253	13558	2.939		T	
Total		12563617	531141				

SHIMADZU
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Analysis Report



<Sample Information>

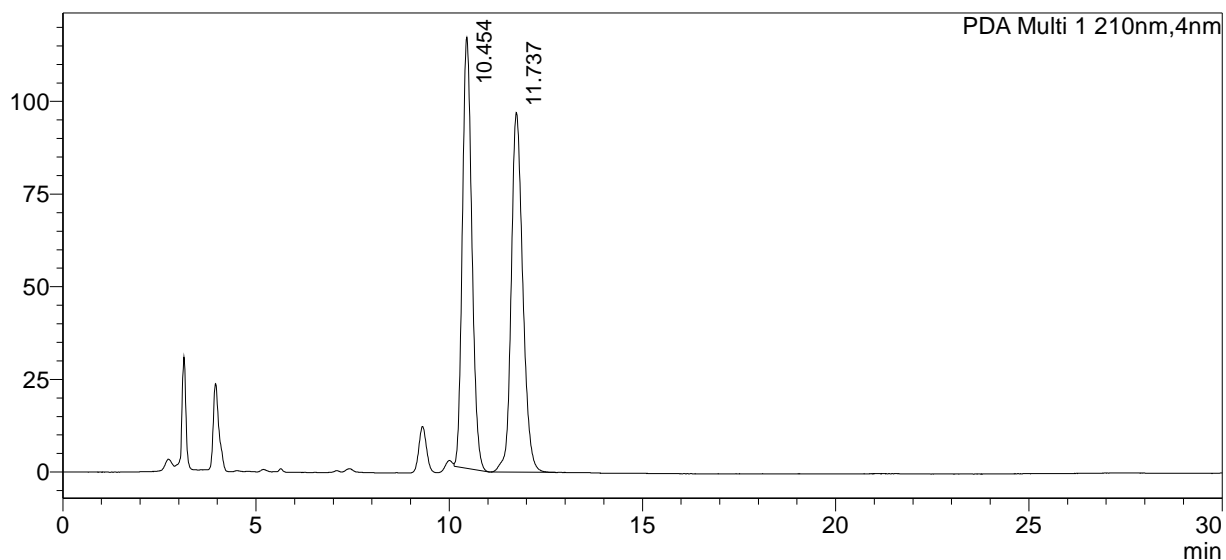
Sample Name : w-1-8-1-1 ODH 5%
 Sample ID :
 Data Filename : w-1-8-1-1 ODH 5%.lcd

 Method Filename : OD-H,1ml 5%IPA in Hex;40min.lcm
 Batch Filename : ZJ-1-89.lcb
 Vial # : 1-16
 Injection Volume : 10 uL
 Date Acquired : 9/4/2020 11:31:31 PM
 Date Processed : 9/5/2020 12:11:34 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

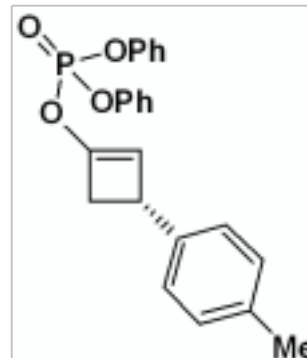
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.454	1997289	116284	49.741			
2	11.737	2018088	97032	50.259			
Total		4015376	213316				



<Sample Information>

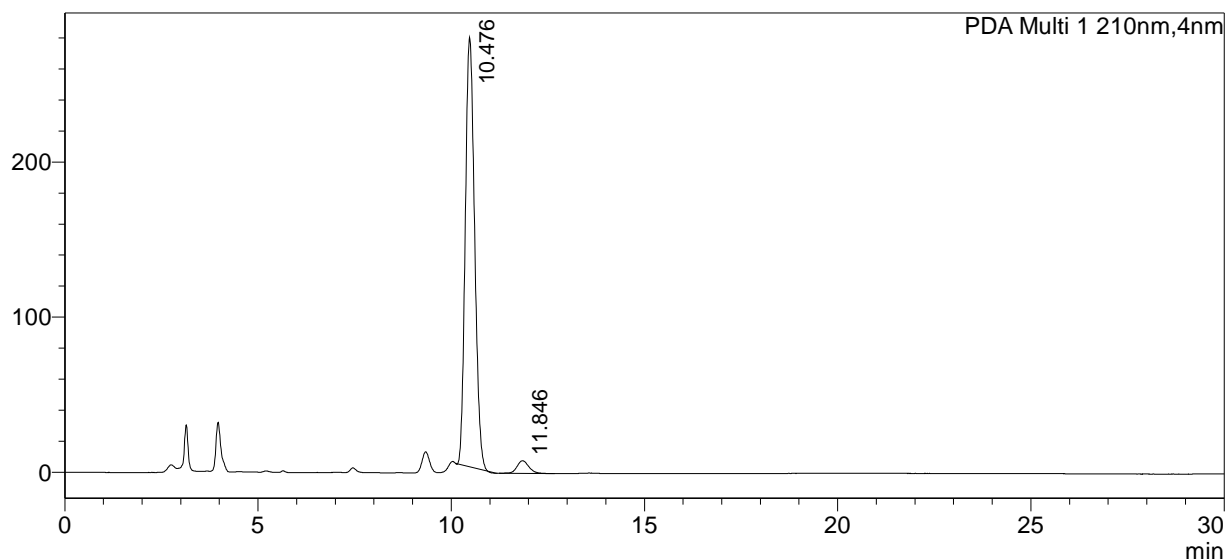
Sample Name : w-1-37-2-1 ODH 5%
 Sample ID :
 Data Filename : w-1-37-2-1 ODH 5%.lcd

Method Filename : OD-H,1ml 5%IPA in Hex;40min.lcm
 Batch Filename : ZJ-1-89.lcb
 Vial # : 1-17
 Injection Volume : 10 uL
 Date Acquired : 9/5/2020 12:12:04 AM
 Date Processed : 9/5/2020 12:52:08 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU



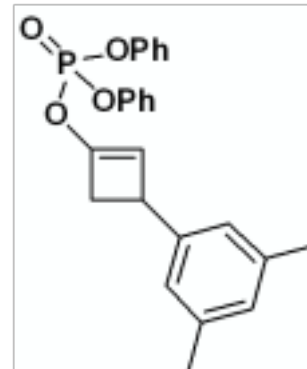
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.476	4645956	276892	96.405			
2	11.846	173227	8152	3.595			
Total		4819183	285044				



Analysis Report



<Sample Information>

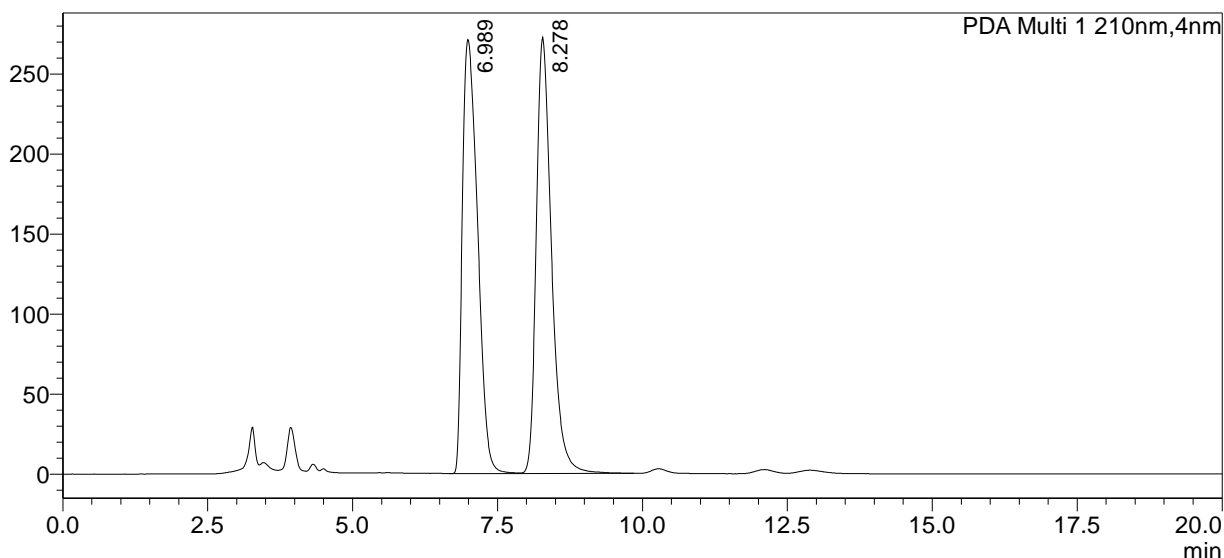
Sample Name : w-1-55-1 ojh 10%
 Sample ID :
 Data Filename : w-1-55-1 ojh 10%.lcd

 Method Filename : OJ-H;1 ml; 10% IPA in Hex; 40 min.lcm
 Batch Filename : w-1-55-1
 Vial # : 1-4
 Injection Volume : 10 uL
 Date Acquired : 10/16/2020 1:45:39 AM
 Date Processed : 10/16/2020 2:25:41 AM

 Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

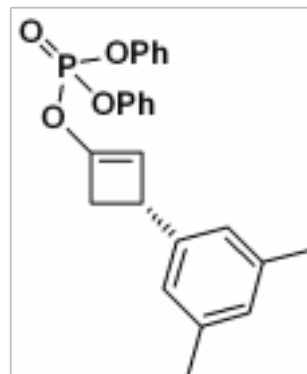
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.989	4957619	271180	49.880			
2	8.278	4981525	272479	50.120		V	
Total		9939144	543658				



<Sample Information>

Sample Name : w-1-58-2 ojh 10%
 Sample ID :
 Data Filename : w-1-58-2 ojh 10%.lcd

Method Filename : OJ-H;1 ml; 10% IPA in Hex; 20 min.lcm

Batch Filename : zcx-9-15ac.lcb

Vial # : 1-5

Sample Type : Unknown

Injection Volume : 10 uL

Date Acquired : 10/16/2020 6:17:41 PM

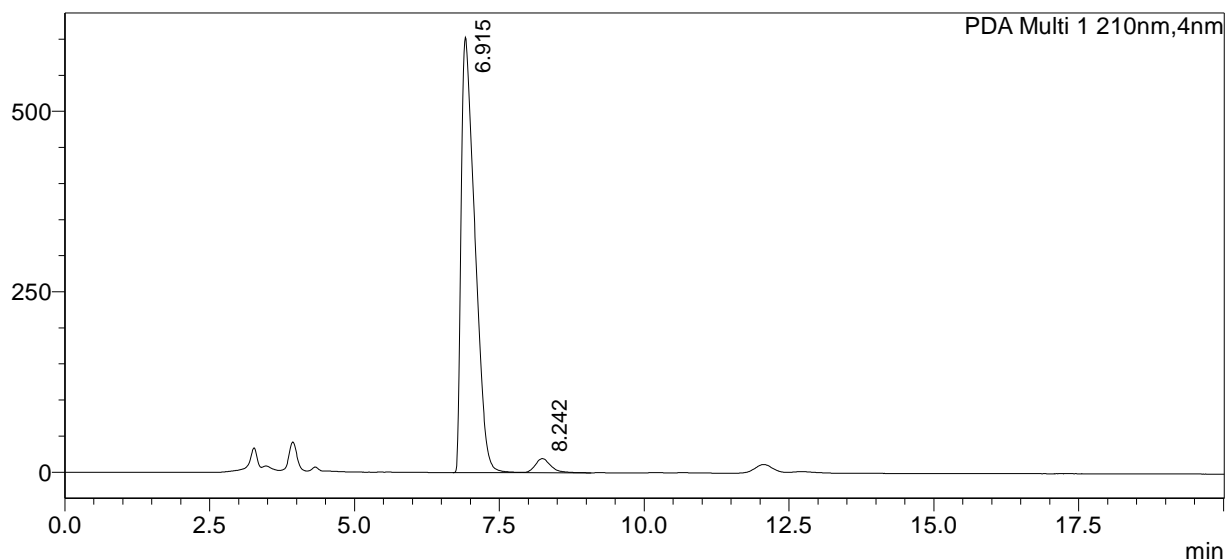
Acquired by : System Administrator

Date Processed : 10/16/2020 6:37:45 PM

Processed by : System Administrator

<Chromatogram>

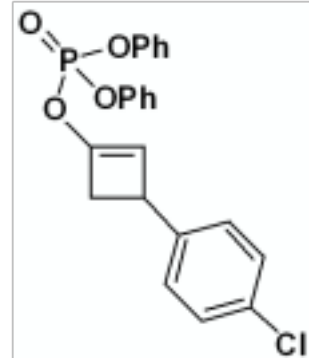
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.915	9962642	603076	96.422		V	
2	8.242	369708	19590	3.578		V	
Total		10332350	622666				



<Sample Information>

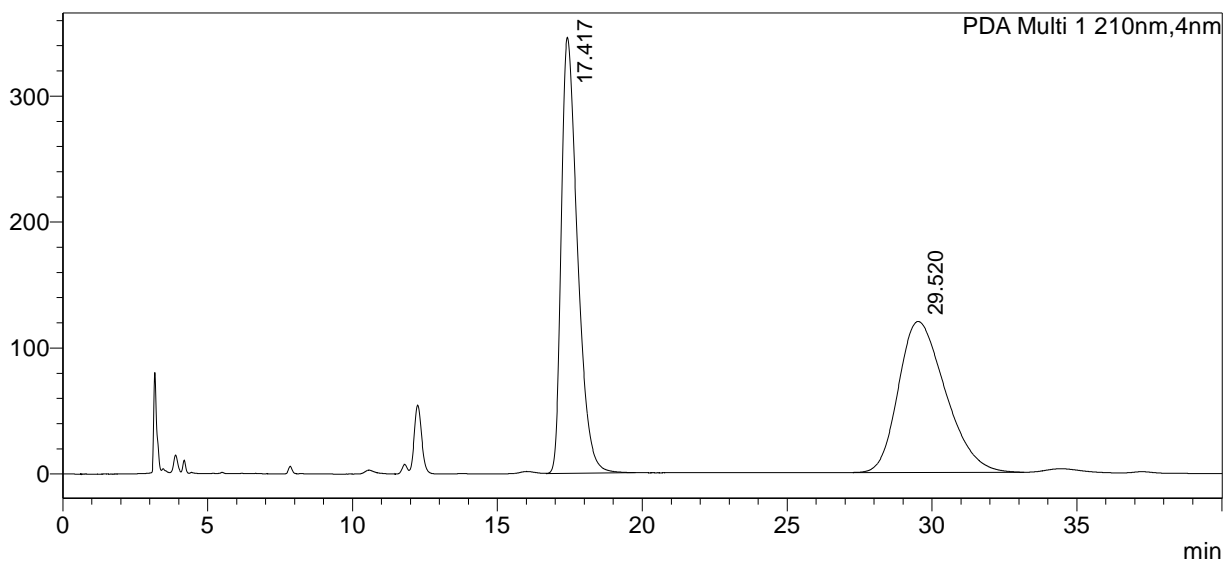
Sample Name : wsw-1-10-1
 Sample ID :
 Data Filename : wsw-1-10-1.lcd

Method Filename : OJ-H;1 ml; 10% IPA in Hex;40 min.lcm
 Batch Filename : zcx-8-81ac.lcb
 Vial # : 1-32
 Injection Volume : 10 uL
 Date Acquired : 8/9/2020 6:34:39 AM
 Date Processed : 8/9/2020 7:14:42 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

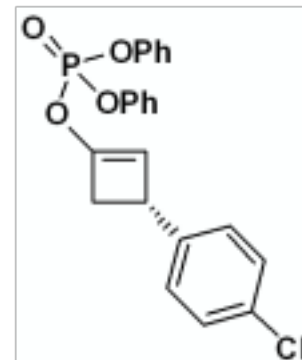
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.417	13476708	346008	49.946			
2	29.520	13505743	119847	50.054			
Total		26982451	465855				



<Sample Information>

Sample Name : w-1-38-2
 Sample ID :
 Data Filename : w-1-38-2.lcd

Method Filename : OJ-H;1 ml; 10% IPA in Hex; 40 min.lcm

Batch Filename : ZJ-1-89.lcb

Vial # : 1-3

Sample Type : Unknown

Injection Volume : 10 uL

Date Acquired : 9/4/2020 12:17:41 AM

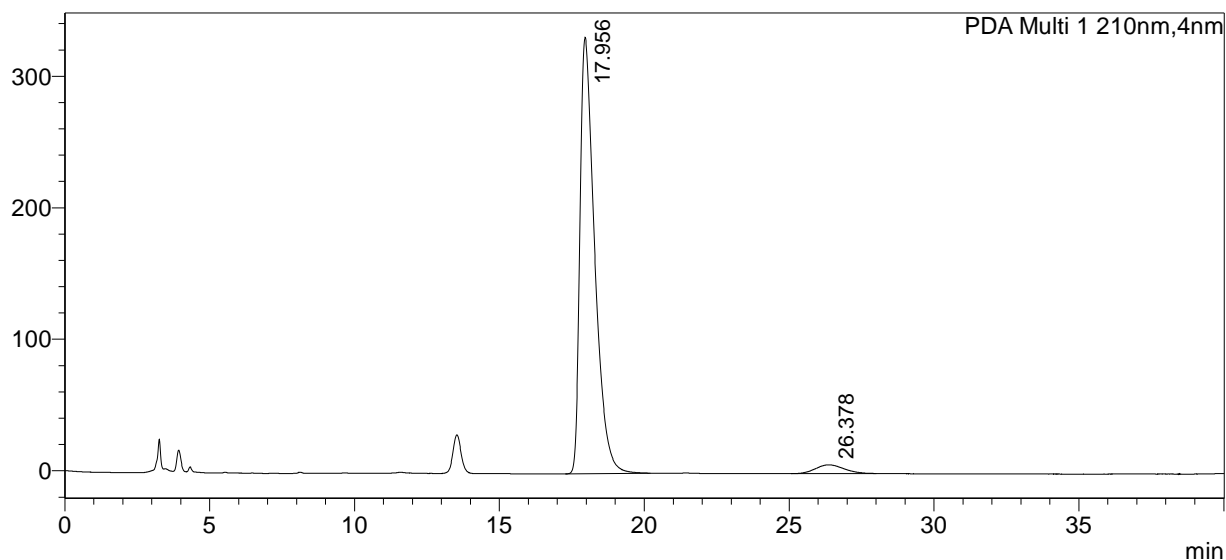
Acquired by : System Administrator

Date Processed : 9/4/2020 12:57:43 AM

Processed by : System Administrator

<Chromatogram>

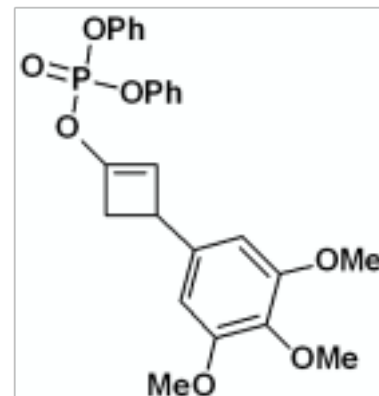
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.956	11710884	331764	96.261			
2	26.378	454938	6661	3.739			
Total		12165822	338426				



<Sample Information>

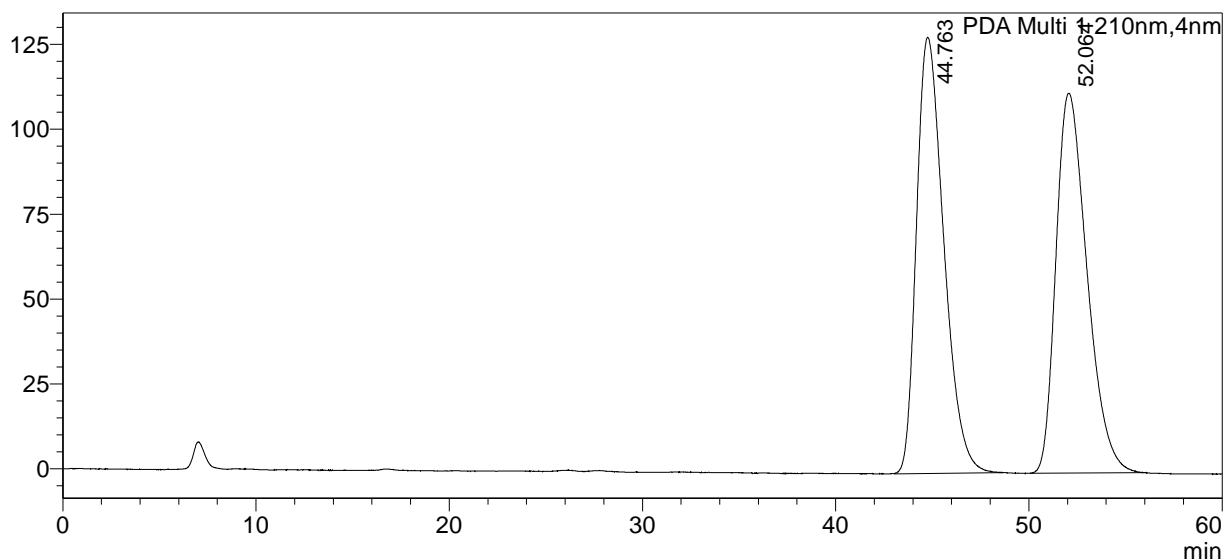
Sample Name : wsw-1-7-1-1-1
 Sample ID :
 Data Filename : wsw-1-7-1-1-1.lcd

Method Filename : OZ-H;1 ml; 10% IPA in Hex; 80 min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-92
 Injection Volume : 10 uL
 Date Acquired : 9/2/2020 8:26:32 AM
 Date Processed : 9/2/2020 9:46:36 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

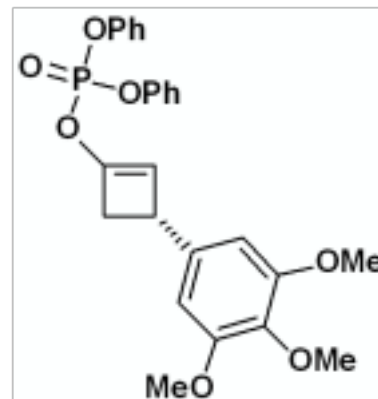
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	44.763	12629993	128426	50.236		S	
2	52.064	12511376	111871	49.764		S	
Total		25141369	240296				



<Sample Information>

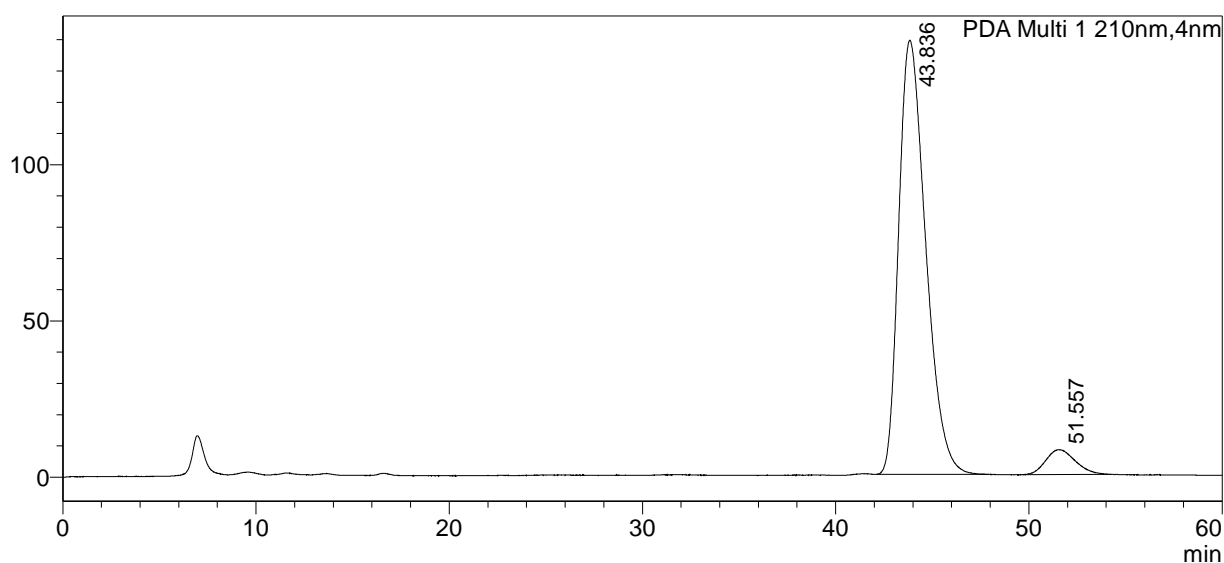
Sample Name : zcx-4-93ac
 Sample ID :
 Data Filename : zcx-4-93ac001.lcd

Method Filename : OZ-H;1 ml; 10% IPA in Hex; 80 min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-93
 Injection Volume : 10 uL
 Date Acquired : 9/1/2020 7:33:16 PM
 Date Processed : 9/1/2020 8:53:20 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

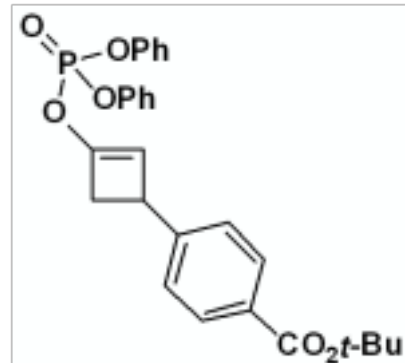
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	43.836	13479704	138931	94.037		SV	
2	51.557	854720	7985	5.963		S	
Total		14334425	146915				



<Sample Information>

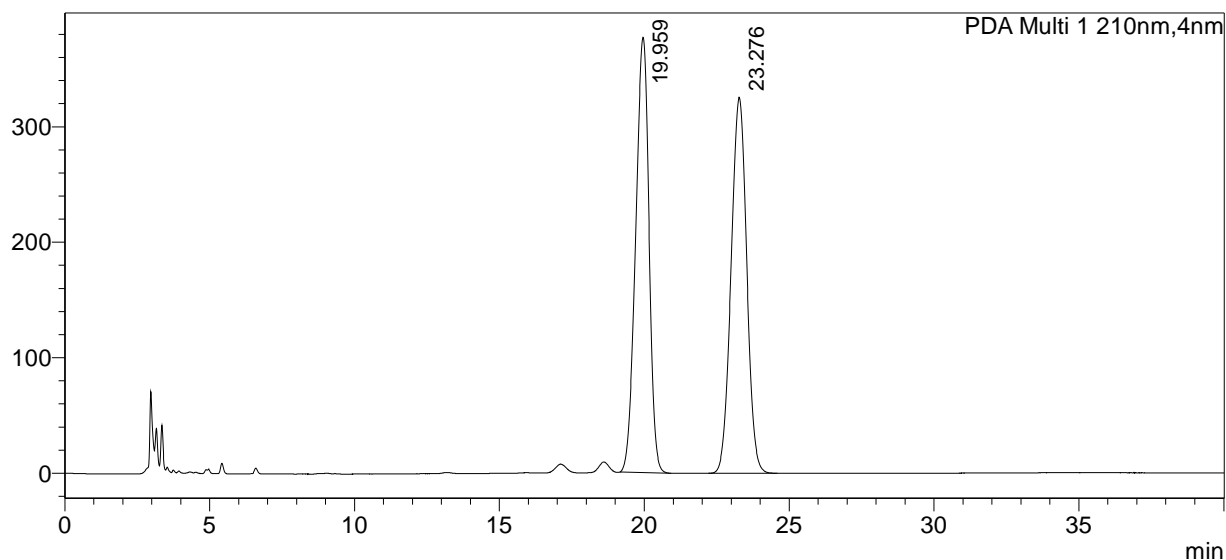
Sample Name : zcx-9-15ac AD
 Sample ID :
 Data Filename : zcx-9-15ac AD.lcd

Method Filename : AD-H;1 ml; 20% IPA in Hex;40 min.lcm
 Batch Filename : zcx-9-15ac.lcb
 Vial # : 1-68
 Injection Volume : 10 uL
 Date Acquired : 10/13/2020 7:37:51 PM
 Date Processed : 10/13/2020 8:17:54 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

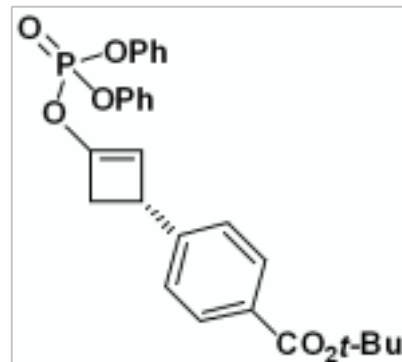
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.959	12041382	376739	49.649			
2	23.276	12211554	325618	50.351			
Total		24252936	702356				



<Sample Information>

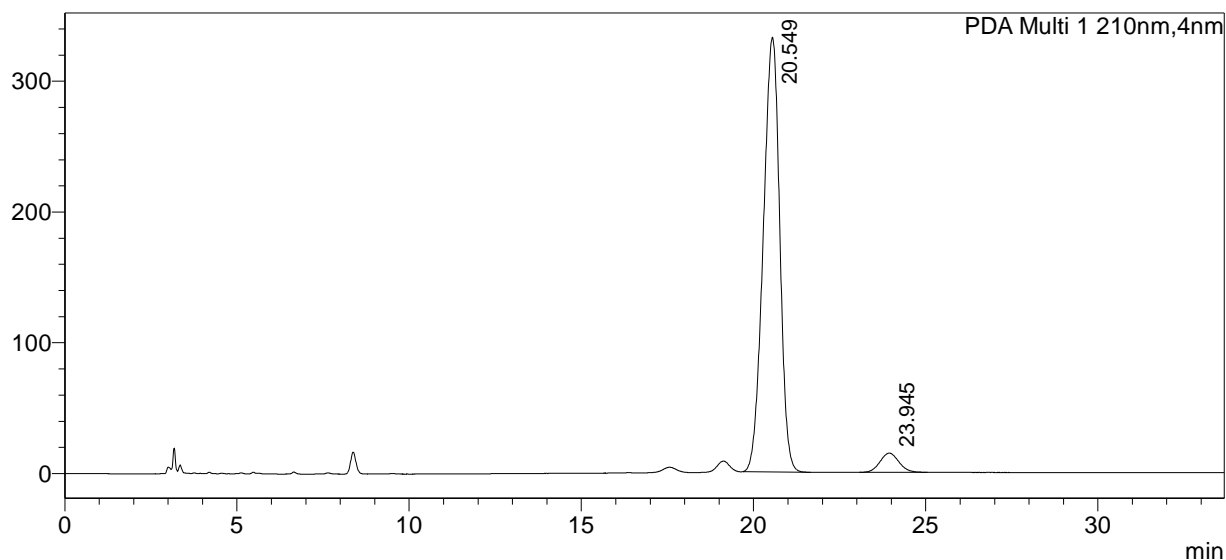
Sample Name : zcx-9-23ac
 Sample ID :
 Data Filename : zcx-9-23ac001.lcd

Method Filename : AD-H;1 ml; 20% IPA in Hex;40 min.lcm
 Batch Filename : zcx-9-15ac.lcb
 Vial # : 1-18
 Injection Volume : 10 uL
 Date Acquired : 10/18/2020 9:41:15 AM
 Date Processed : 10/18/2020 10:14:57 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

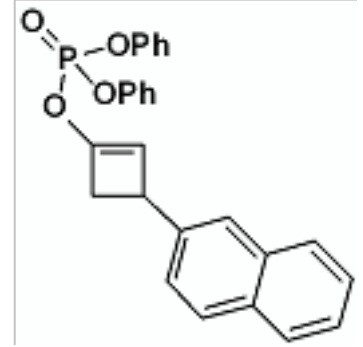
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.549	11044940	332257	95.178			
2	23.945	559557	14701	4.822			
Total		11604496	346958				



<Sample Information>

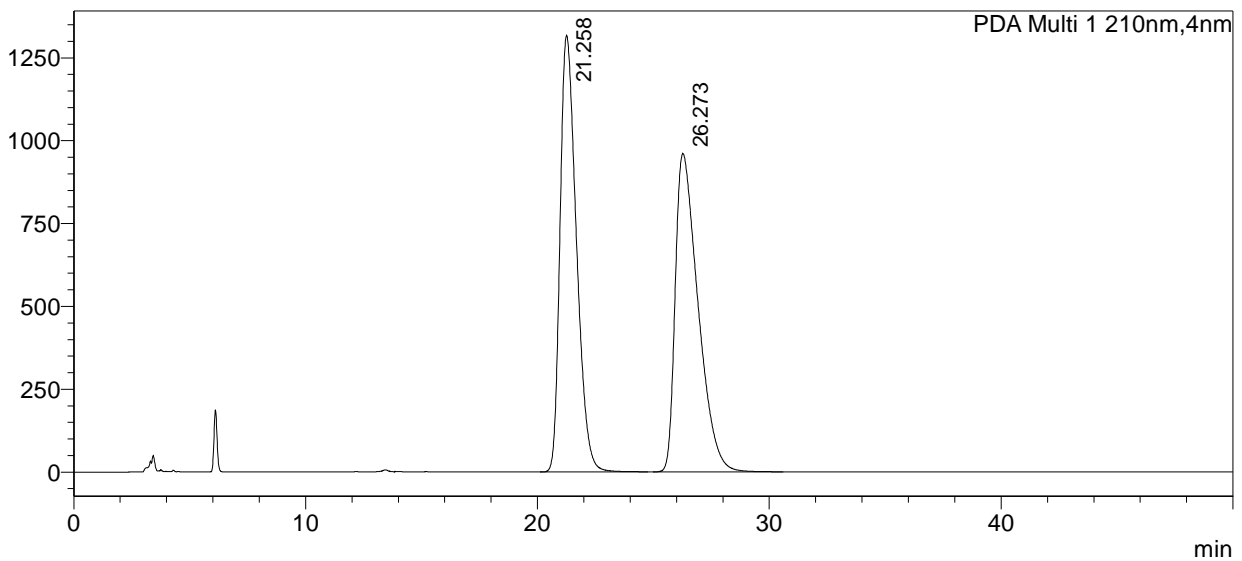
Sample Name : zcx-8-191ac
 Sample ID :
 Data Filename : zcx-8-191ac002.lcd

Method Filename : OJ-H;1 ml; 40% IPA in Hex;50 min.lcm
 Batch Filename : zcx-8-188ac.lcb
 Vial # : 1-5
 Injection Volume : 10 uL
 Date Acquired : 10/4/2020 6:51:14 PM
 Date Processed : 10/4/2020 7:41:17 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

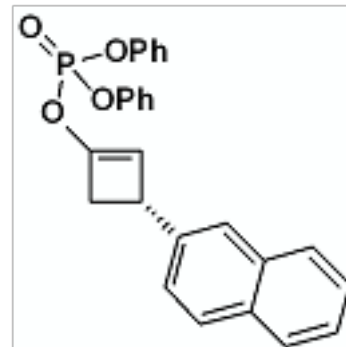
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.258	64609006	1317358	49.626			
2	26.273	65582178	960549	50.374		S	
Total		130191184	2277907				



<Sample Information>

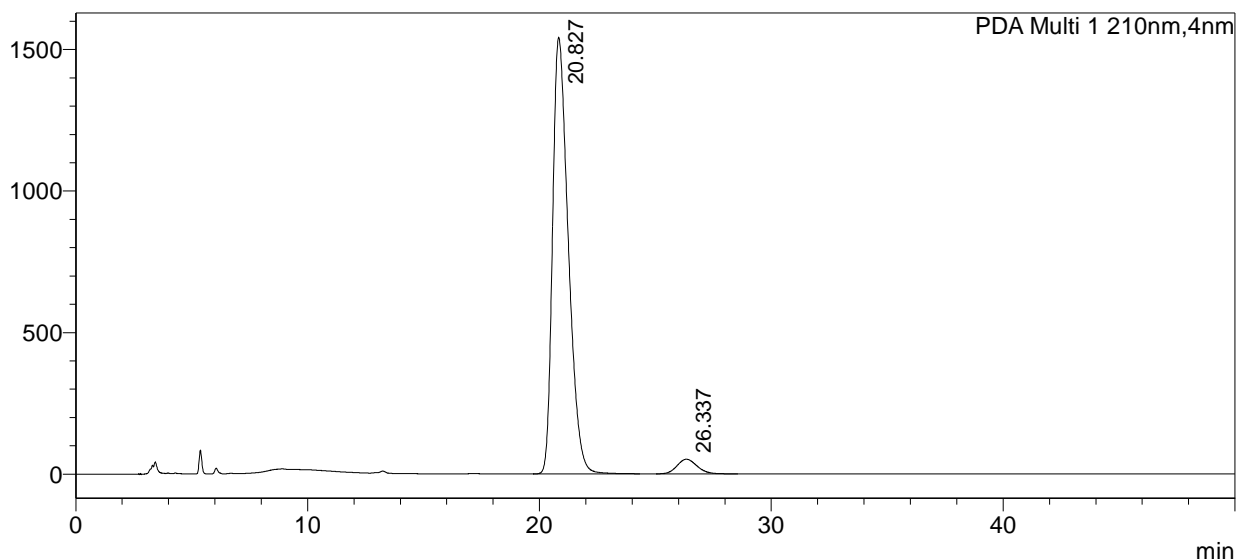
Sample Name : zcx-8-193ac
 Sample ID :
 Data Filename : zcx-8-193ac002.lcd

Method Filename : OJ-H;1 ml; 40% IPA in Hex;50 min.lcm
 Batch Filename : zcx-8-188ac.lcb
 Vial # : 1-6
 Injection Volume : 10 uL
 Date Acquired : 10/4/2020 7:41:46 PM
 Date Processed : 10/4/2020 8:31:49 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

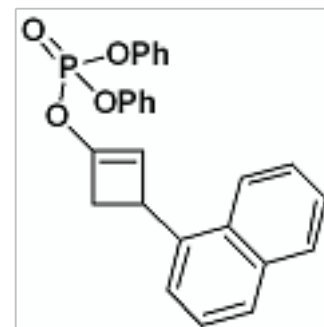
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.827	72777069	1541987	95.925		S	
2	26.337	3091792	51635	4.075		S	
Total		75868862	1593622				



<Sample Information>

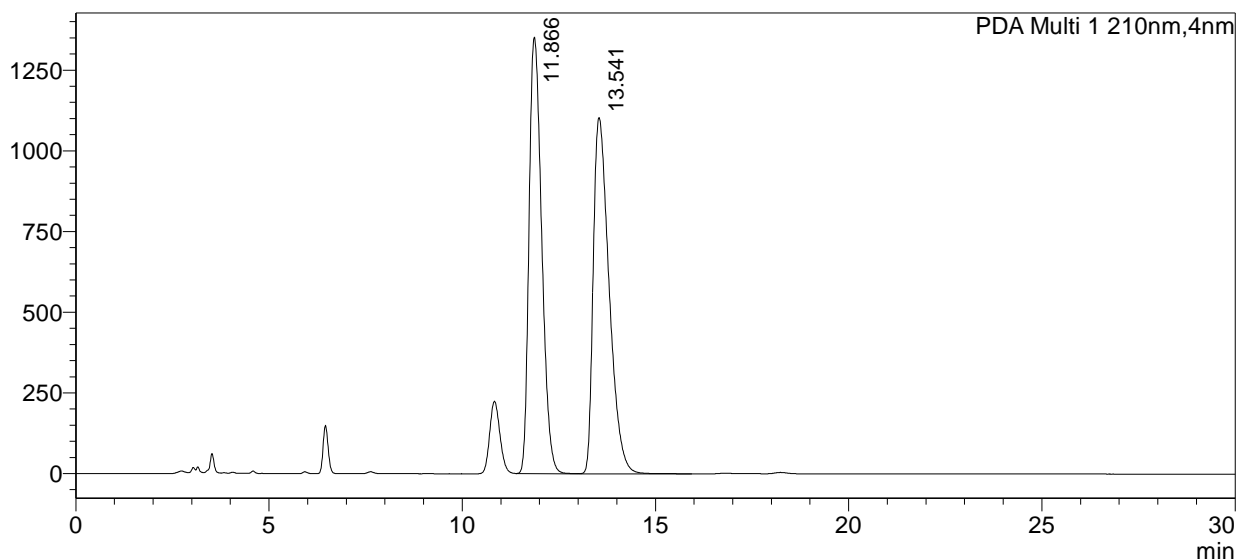
Sample Name : w-1-54-1 odh 10%
 Sample ID :
 Data Filename : w-1-54-1 odh 10%.lcd

Method Filename : OD-H;1 ml; 10% IPA in Hex; 40 min.lcm
 Batch Filename : w-1-54-1 odh
 Vial # : 1-4
 Injection Volume : 10 uL
 Date Acquired : 10/11/2020 3:21:17 PM
 Date Processed : 10/11/2020 4:01:20 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

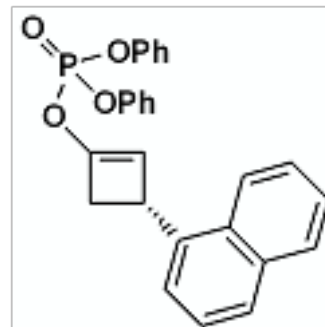
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.866	30859421	1351950	49.507			
2	13.541	31473851	1103407	50.493		V	
Total		62333272	2455357				



<Sample Information>

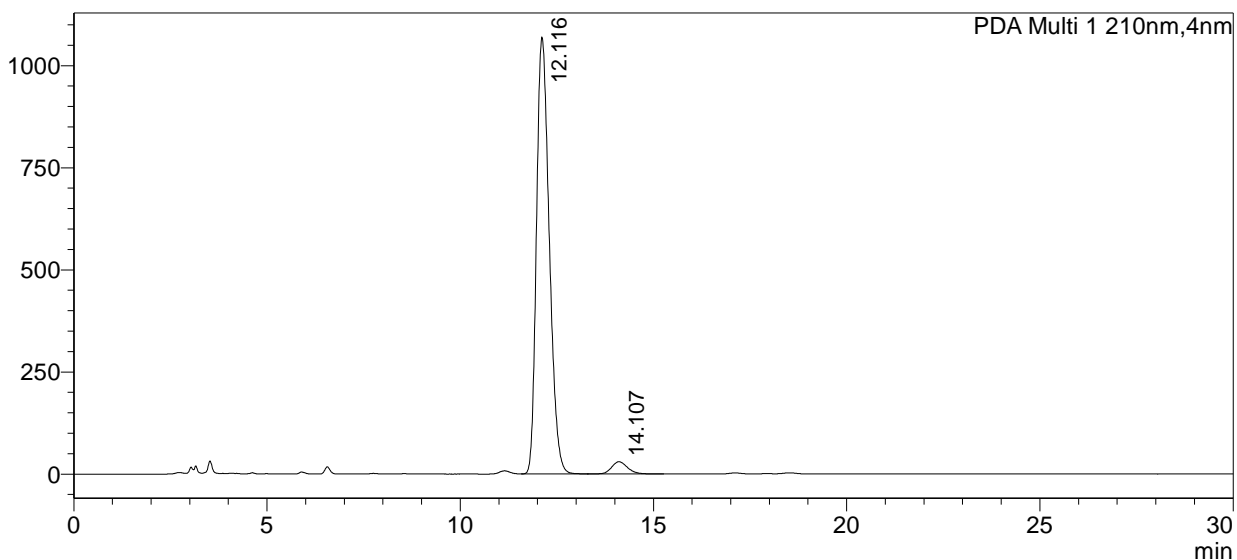
Sample Name : w-1-56-1 odh
 Sample ID :
 Data Filename : w-1-56-1 odh.lcd

Method Filename : OD-H;1 ml; 10% IPA in Hex; 40 min.lcm
 Batch Filename : w-1-56-1 odh
 Vial # : 1-3
 Injection Volume : 10 uL
 Date Acquired : 10/16/2020 12:44:51 AM
 Date Processed : 10/16/2020 1:24:53 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

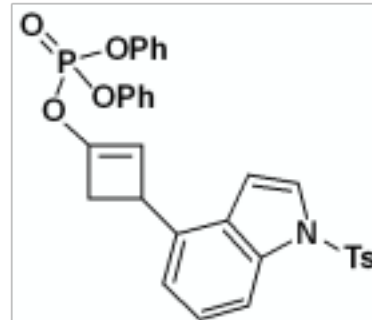
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.116	24623294	1069048	96.584			
2	14.107	870853	29984	3.416		V	
Total		25494147	1099031				



<Sample Information>

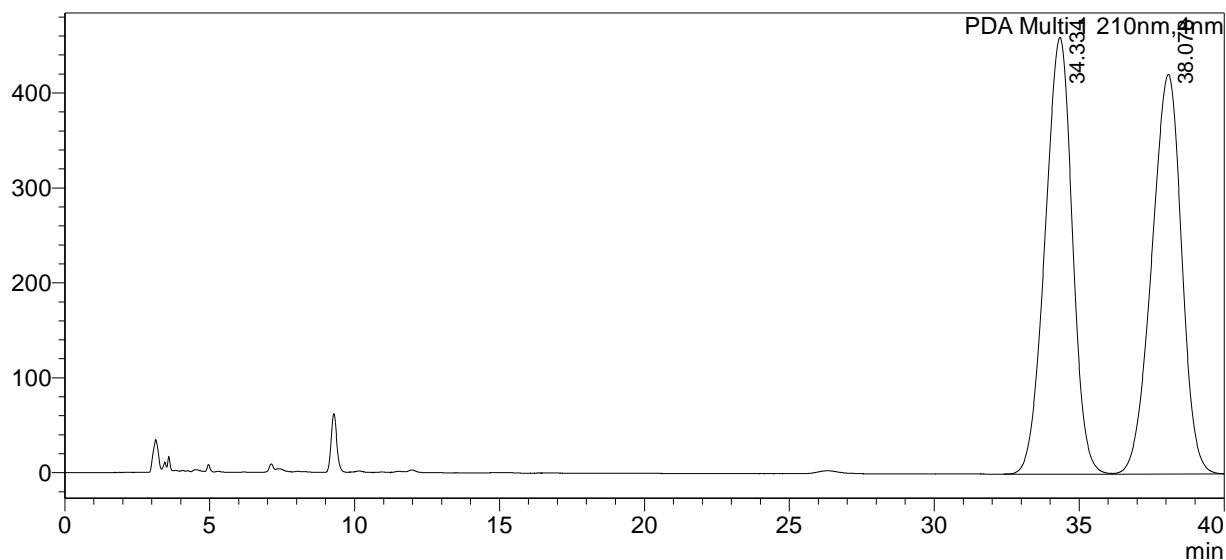
Sample Name : zcx-9-19ac
 Sample ID :
 Data Filename : zcx-9-19ac.lcd

Method Filename : AD-H;1 ml; 40% IPA in Hex;60 min.lcm
 Batch Filename : zcx-9-15ac.lcb
 Vial # : 1-16
 Injection Volume : 10 uL
 Date Acquired : 10/19/2020 4:55:54 PM
 Date Processed : 10/19/2020 5:55:53 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU



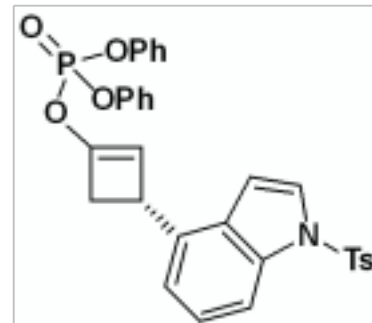
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.334	30126377	460054	49.971		V	
2	38.078	30161860	421062	50.029		SV	
Total		60288236	881117				



Analysis Report



<Sample Information>

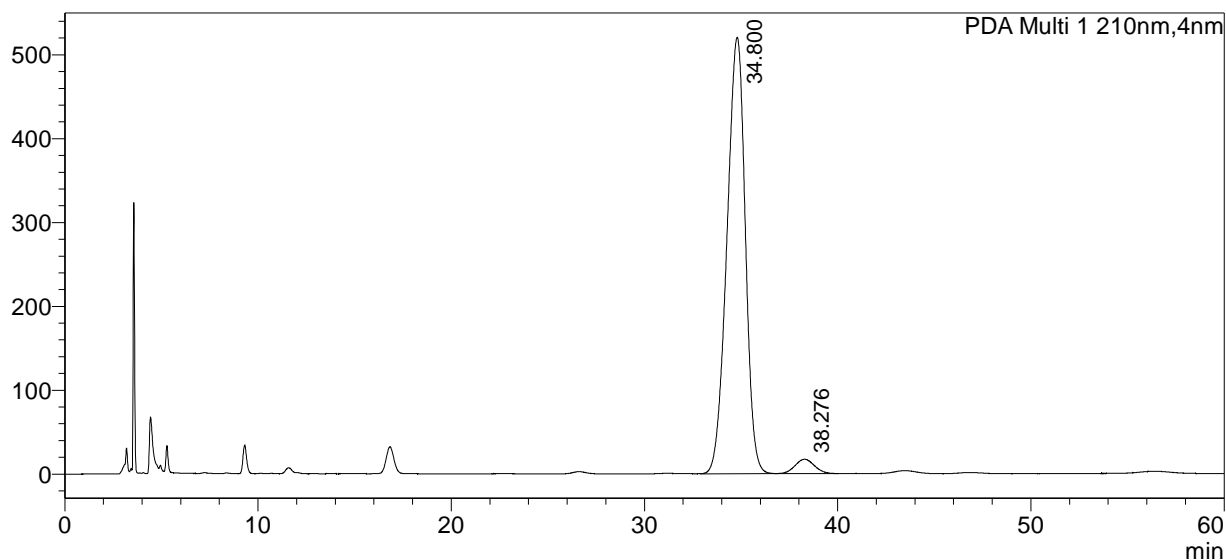
Sample Name : zcx-9-24ac
 Sample ID :
 Data Filename : zcx-9-24ac001.lcd

Method Filename : AD-H;1 ml; 40% IPA in Hex;60 min.lcm
 Batch Filename : zcx-9-15ac.lcb
 Vial # : 1-20
 Injection Volume : 10 uL
 Date Acquired : 10/20/2020 12:31:00 AM
 Date Processed : 10/20/2020 1:31:02 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

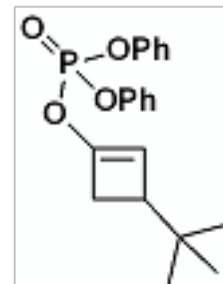
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.800	34400277	520415	96.607		V	
2	38.276	1208091	17151	3.393		V	
Total		35608368	537565				



<Sample Information>

Sample Name : zcx-8-190ac AD
 Sample ID :
 Data Filename : zcx-8-190ac AD.lcd

Method Filename : AD-H; 1 ml; 5%IPA in Hex; 40min.lcm

Batch Filename : zcx-8-188ac.lcb

Vial # : 1-65

Sample Type : Unknown

Injection Volume : 10 uL

Date Acquired : 10/5/2020 10:58:09 AM

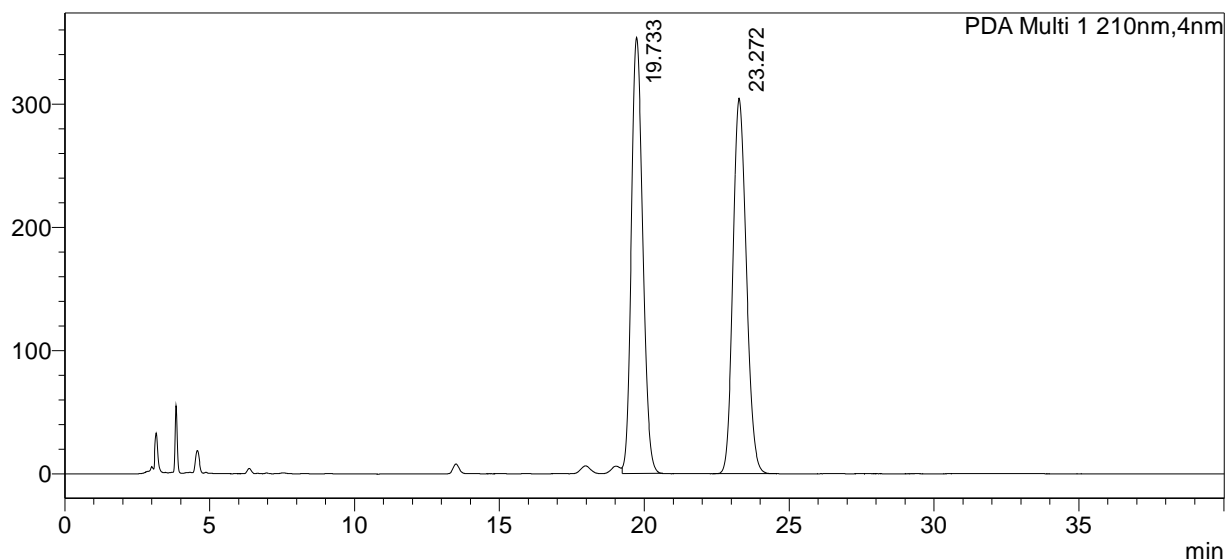
Acquired by : System Administrator

Date Processed : 10/5/2020 11:38:12 AM

Processed by : System Administrator

<Chromatogram>

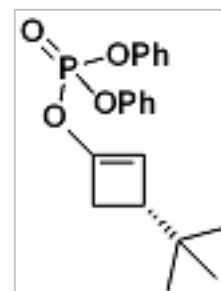
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.733	9647918	353667	49.578			
2	23.272	9812280	304598	50.422			
Total		19460198	658265				



<Sample Information>

Sample Name : zcx-8-194ac AD
 Sample ID :
 Data Filename : zcx-8-194ac AD.lcd

Method Filename : AD-H; 1 ml; 5%IPA in Hex; 40min.lcm

Batch Filename : zcx-8-188ac.lcb

Vial # : 1-66

Sample Type : Unknown

Injection Volume : 10 uL

Date Acquired : 10/5/2020 3:01:11 PM

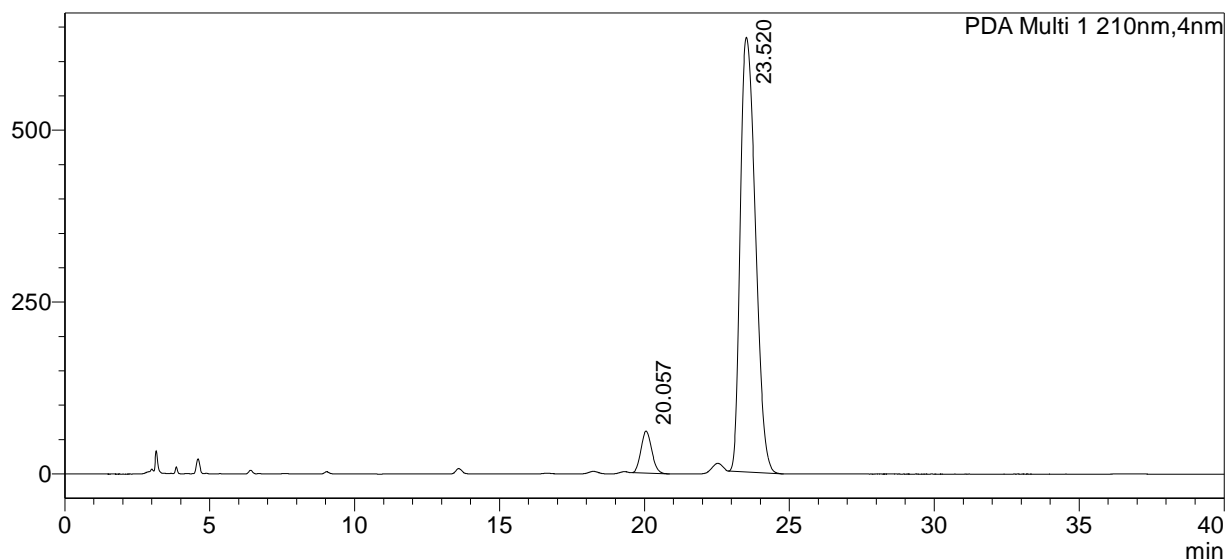
Acquired by : System Administrator

Date Processed : 10/5/2020 3:41:13 PM

Processed by : System Administrator

<Chromatogram>

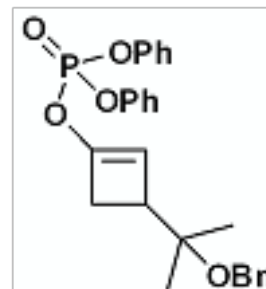
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.057	1572259	60971	6.395			
2	23.520	23013204	632321	93.605			
Total		24585463	693291				



<Sample Information>

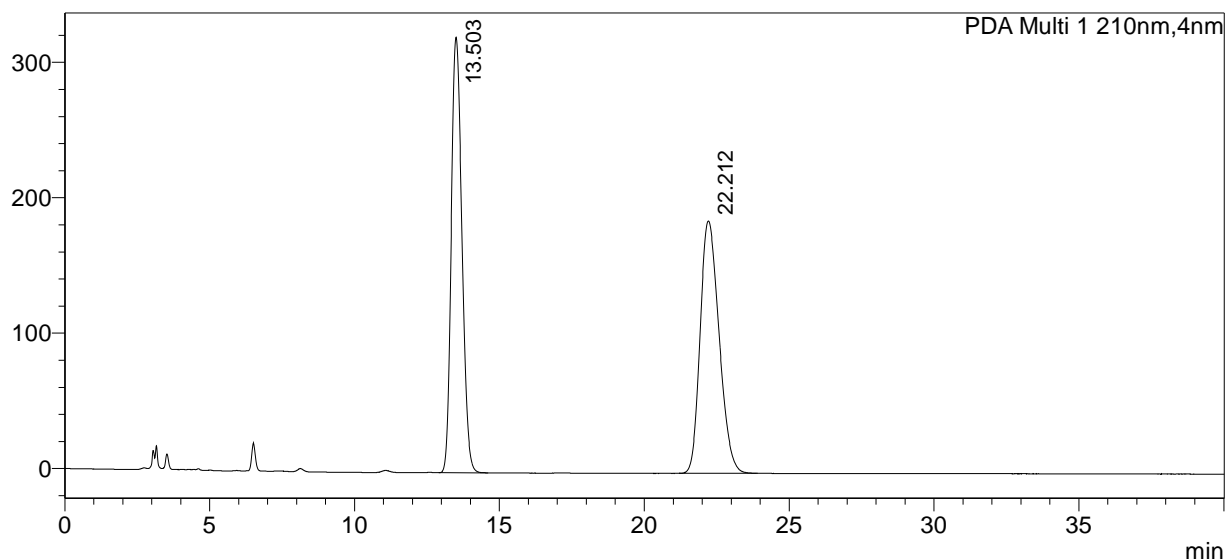
Sample Name : w-1-61-1 odh 10%
 Sample ID :
 Data Filename : w-1-61-1 odh 10%.lcd

Method Filename : OD-H;1 ml; 10% IPA in Hex; 40 min.lcm
 Batch Filename : zcx-9-15ac.lcb
 Vial # : 1-1
 Injection Volume : 10 uL
 Date Acquired : 11/2/2020 6:00:05 PM
 Date Processed : 11/2/2020 6:40:07 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

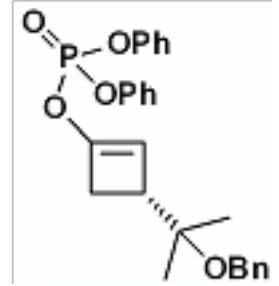
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.503	8217860	321558	49.271			
2	22.212	8461186	186389	50.729			
Total		16679046	507947				



<Sample Information>

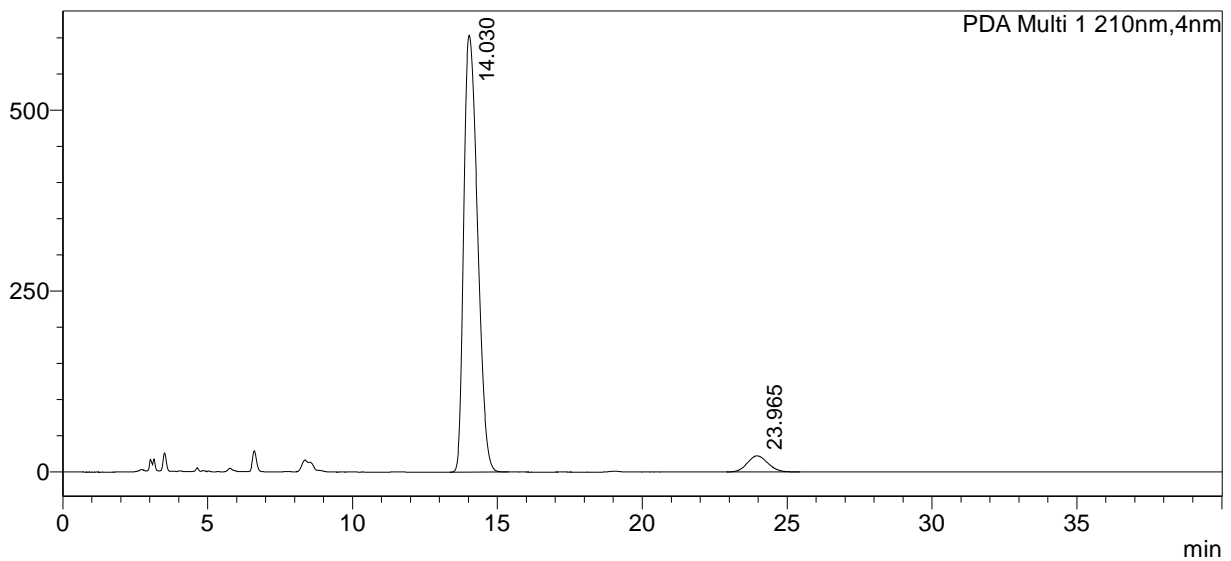
Sample Name : w-1-64-1
 Sample ID :
 Data Filename : w-1-64-1.lcd

Method Filename : OD-H;1 ml; 10% IPA in Hex; 40 min.lcm
 Batch Filename : zcx-9-15ac.lcb
 Vial # : 1-2
 Injection Volume : 10 uL
 Date Acquired : 11/3/2020 3:02:41 PM
 Date Processed : 11/3/2020 3:42:44 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU



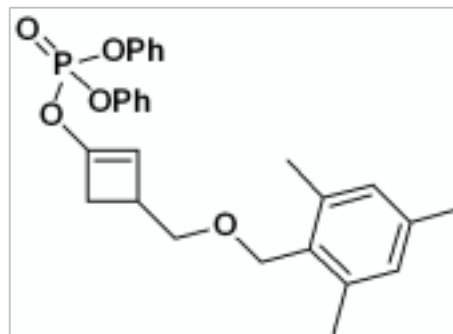
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.030	20003424	603559	94.807			
2	23.965	1095602	22214	5.193		SV	
Total		21099026	625773				



Analysis Report



<Sample Information>

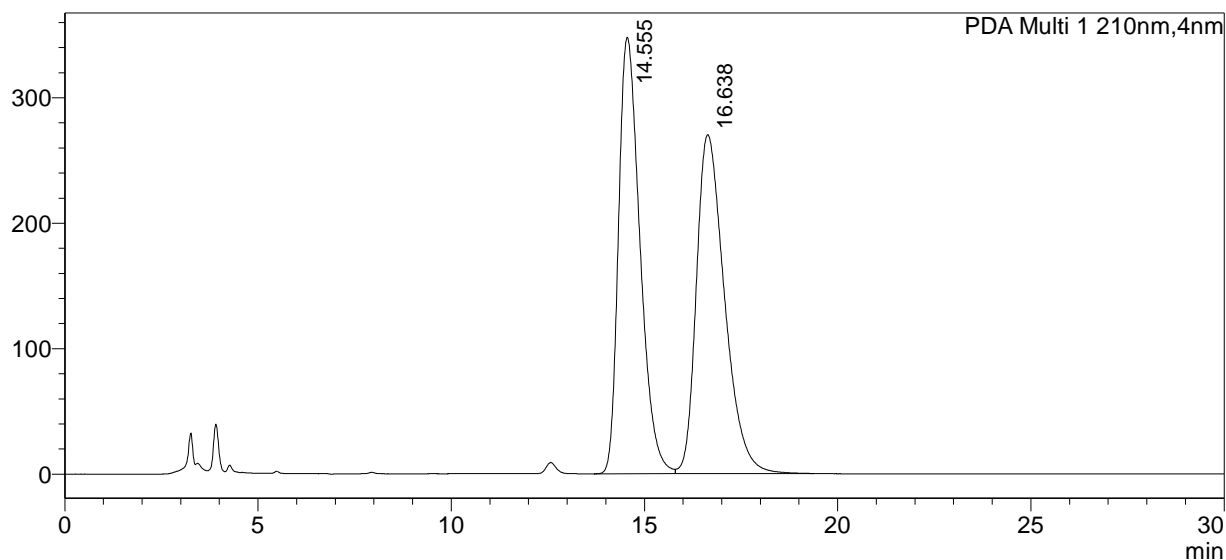
Sample Name : w-1-53-1 ojh 10%
 Sample ID :
 Data Filename : w-1-53-1.lcd

Method Filename : OJ-H;1 ml; 10% IPA in Hex;40 min.lcm
 Batch Filename : zcx-8-188ac.lcb
 Vial # : 1-3
 Injection Volume : 10 uL
 Date Acquired : 10/10/2020 2:10:55 AM
 Date Processed : 10/10/2020 2:50:58 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU



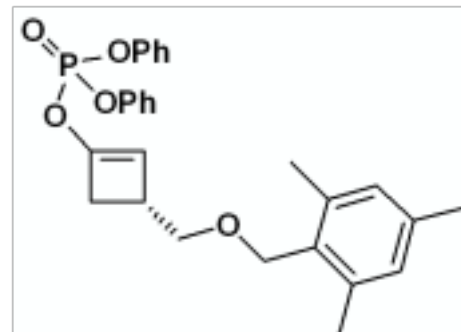
<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.555	13424563	347891	49.516			
2	16.638	13686807	270219	50.484		V	
Total		27111370	618110				



Analysis Report



<Sample Information>

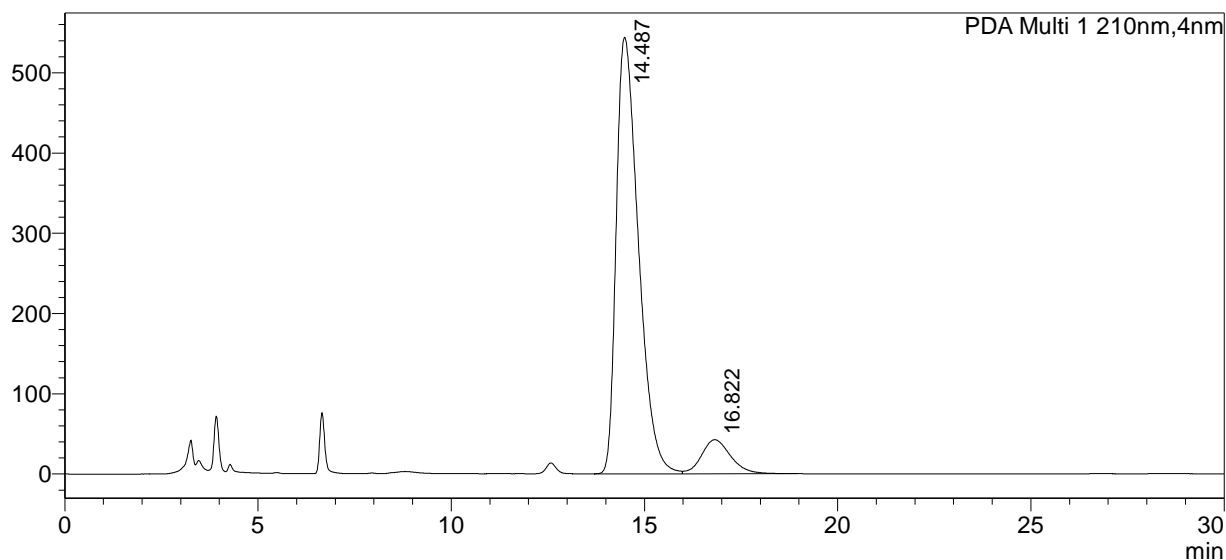
Sample Name : w-1-52-1-1 ojh 10%
 Sample ID :
 Data Filename : w-1-52-1-1.lcd

Method Filename : OJ-H;1 ml; 10% IPA in Hex;40 min.lcm
 Batch Filename : zcx-8-188ac.lcb
 Vial # : 1-2
 Injection Volume : 10 uL
 Date Acquired : 10/10/2020 1:10:07 AM
 Date Processed : 10/10/2020 1:50:10 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

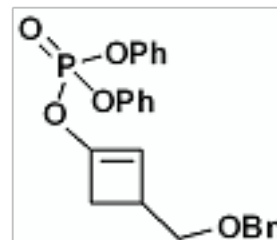
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.487	21703620	543789	90.682			
2	16.822	2230231	42434	9.318		SV	
Total		23933851	586223				



<Sample Information>

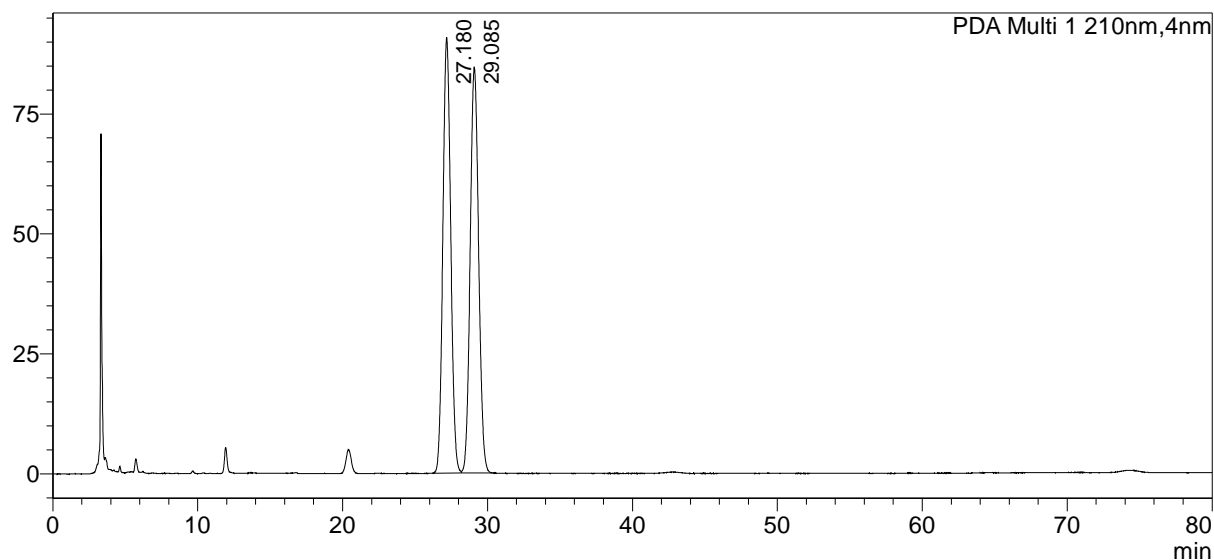
Sample Name : wsw-1-24-1
 Sample ID :
 Data Filename : wsw-1-24-1-1.lcd

Method Filename : OJ-H;1 ml; 5% IPA in Hex;80 min.lcm
 Batch Filename : zcx-8-81ac.lcb
 Vial # : 1-1
 Injection Volume : 10 uL
 Date Acquired : 8/23/2020 10:56:41 AM
 Date Processed : 8/23/2020 12:16:43 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

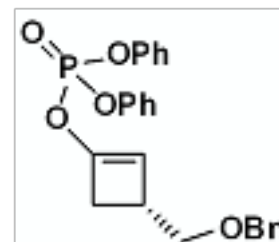
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.180	3421314	90803	49.947			
2	29.085	3428570	84642	50.053		V	
Total		6849884	175445				



<Sample Information>

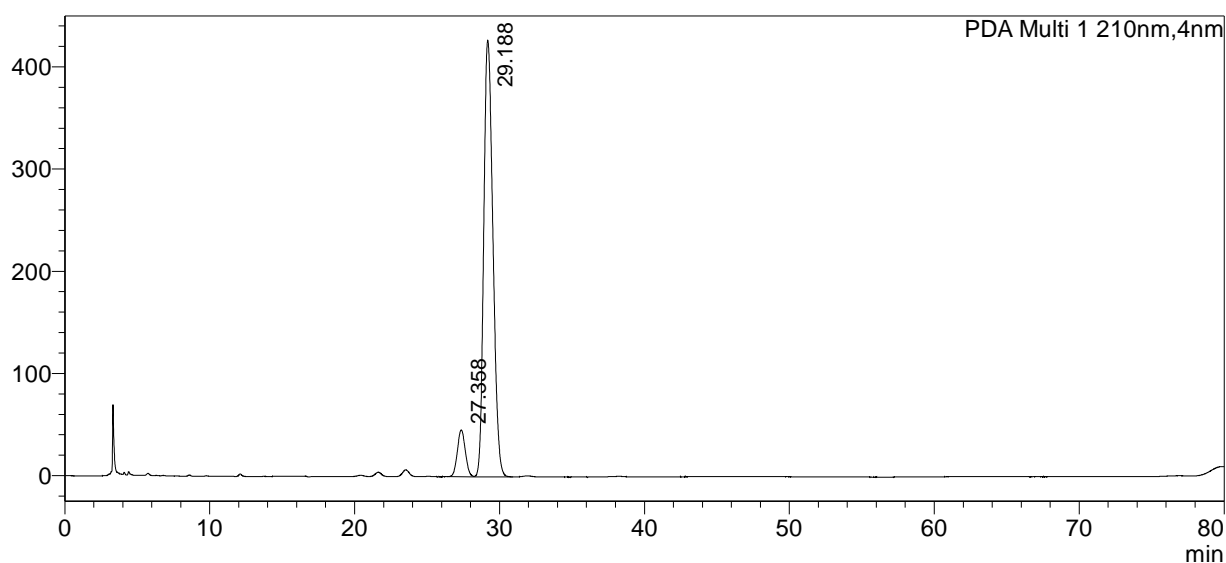
Sample Name : w-1-31-2
 Sample ID :
 Data Filename : w-1-31-2.lcd

Method Filename : OJ-H;1 ml; 5% IPA in Hex;80 min.lcm
 Batch Filename : zcx-8-81ac.lcb
 Vial # : 1-63
 Injection Volume : 10 uL
 Date Acquired : 8/29/2020 7:30:09 PM
 Date Processed : 8/29/2020 8:50:12 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

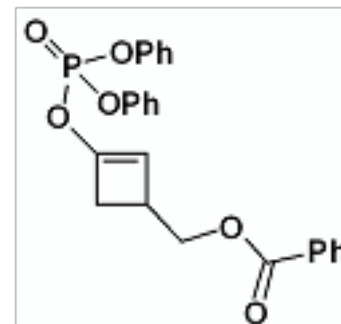
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.358	1748461	45780	8.506			
2	29.188	18807982	426953	91.494		V	
Total		20556443	472733				



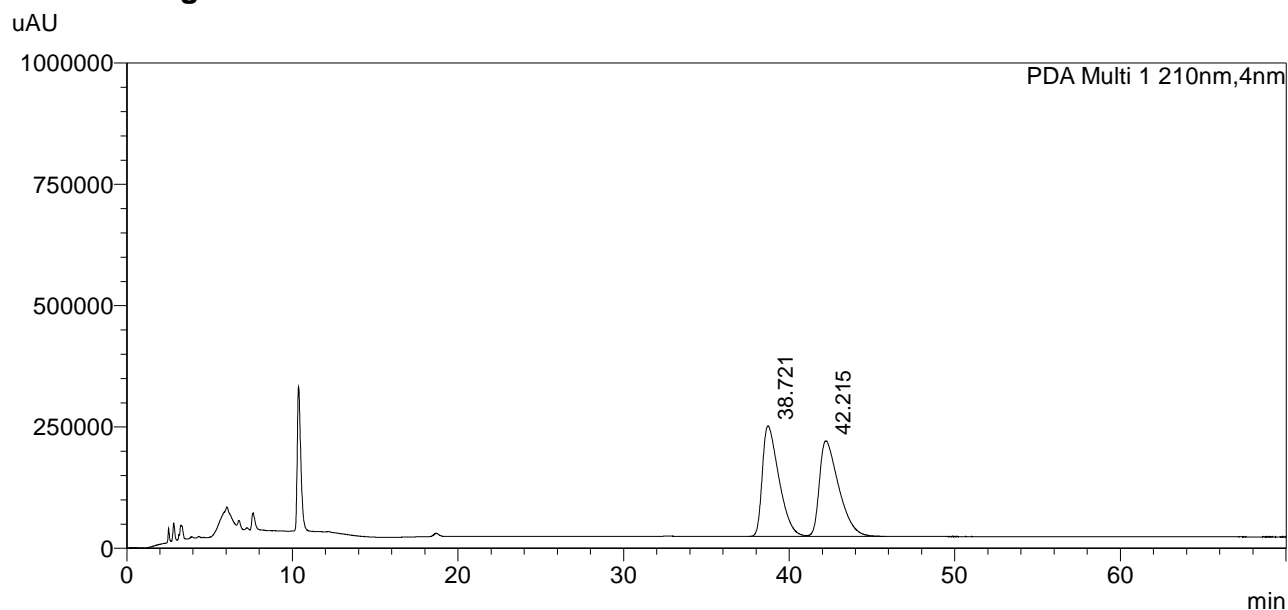
<Sample Information>

Sample Name : zcx-4-86ac
 Sample ID :
 Data Filename : zcx-4-86ac002.lcd

Method Filename : OJ-H;1 ml; 10% IPA in Hex;70 min.lcm
 Batch Filename : zcx-9-109.lcb
 Vial # : 1-46
 Injection Volume : 10 uL
 Date Acquired : 12/28/2020 9:06:55 AM
 Date Processed : 12/29/2020 8:45:28 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

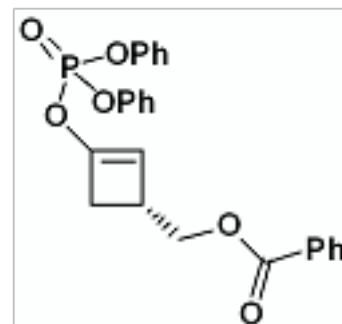
<Chromatogram>



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	38.721	15876765	227712	49.887			
2	42.215	15948650	196861	50.113		V	
Total		31825415	424573				



<Sample Information>

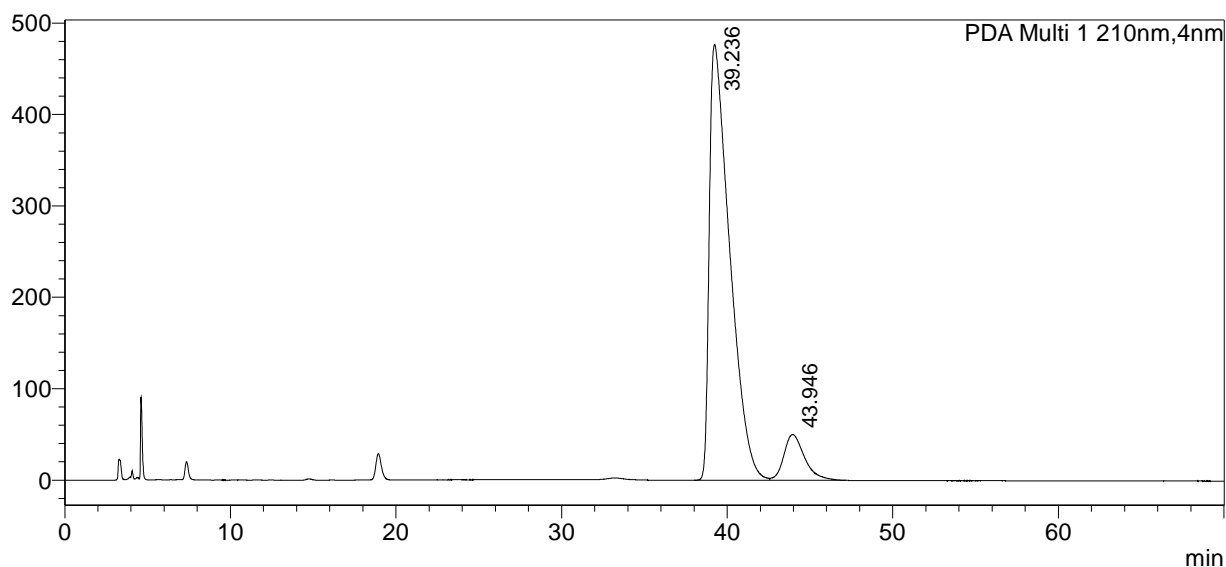
Sample Name : zcx-9-152ac
 Sample ID :
 Data Filename : zcx-9-152ac.lcd

Method Filename : OJ-H;1 ml; 10% IPA in Hex;70 min.lcm
 Batch Filename : zcx-9-109.lcb
 Vial # : 1-47
 Injection Volume : 10 uL
 Date Acquired : 12/27/2020 3:44:23 PM
 Date Processed : 12/27/2020 4:54:26 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

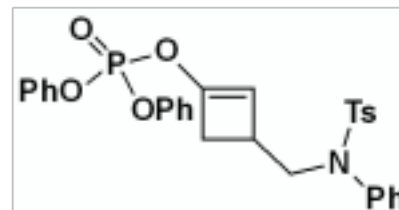
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	39.236	40832720	476910	90.341			
2	43.946	4365691	50065	9.659		V	
Total		45198411	526975				



<Sample Information>

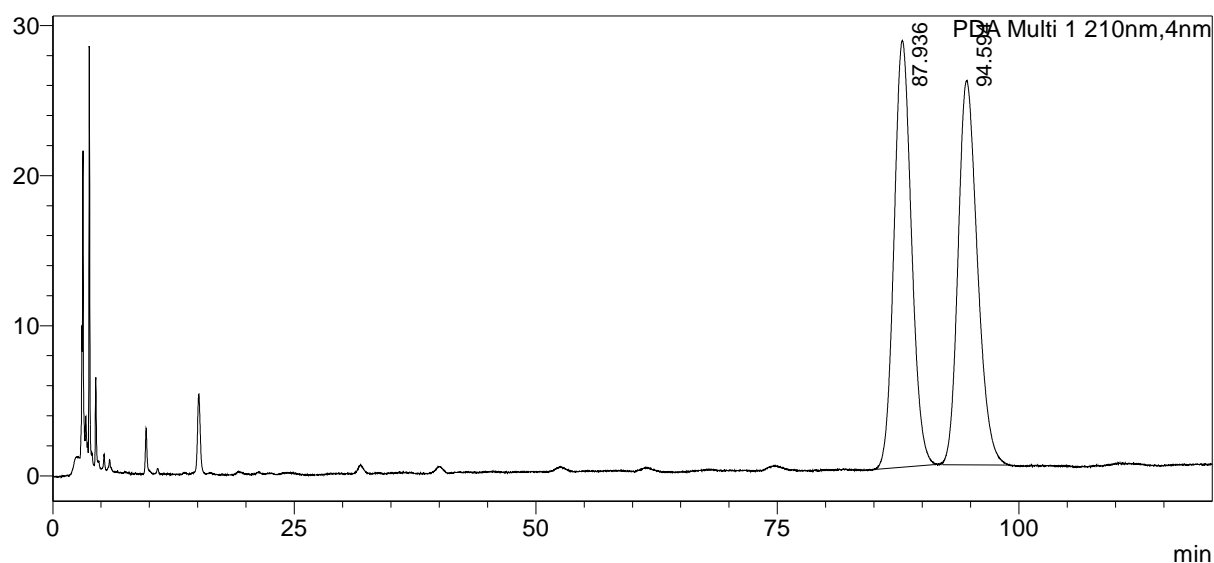
Sample Name : zcx-2-140-1
 Sample ID :
 Data Filename : zcx-2-140-1-1.lcd

Method Filename : 6; IA;1ml;10% IPA in Hex;120 min.lcm
 Batch Filename : 2.lcb
 Vial # : 1-1
 Injection Volume : 10 uL
 Date Acquired : 12/5/2020 1:17:40 PM
 Date Processed : 12/5/2020 3:17:42 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

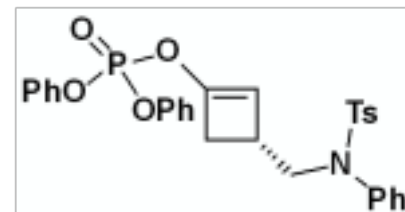
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	87.936	3558876	28431	49.966			
2	94.594	3563762	25600	50.034		S	
Total		7122637	54031				



<Sample Information>

Sample Name : w-1-87-1-1
 Sample ID :
 Data Filename : wsw-1-87-1-1.lcd

Method Filename : 6; IA;1ml;10% IPA in Hex;120 min.lcm

Batch Filename : 1.lcb

Vial # : 1-9

Injection Volume : 10 uL

Date Acquired : 12/4/2020 11:20:49 PM

Date Processed : 12/5/2020 1:20:52 AM

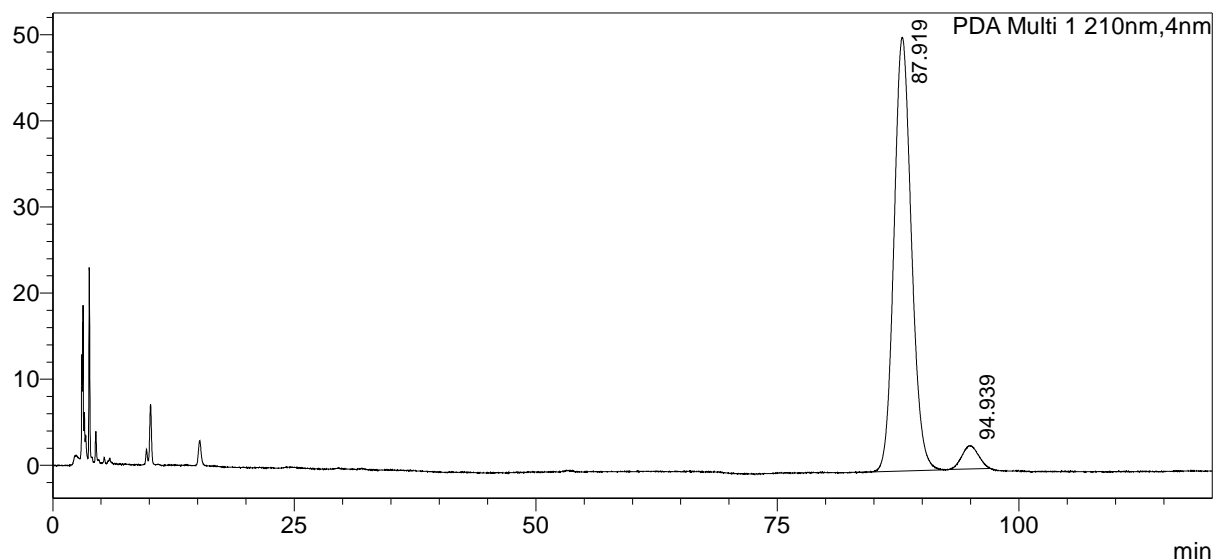
Sample Type : Unknown

Acquired by : System Administrator

Processed by : System Administrator

<Chromatogram>

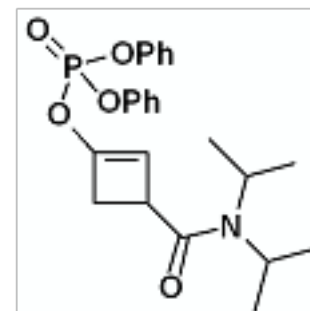
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	87.919	6310280	50347	95.083			
2	94.939	326354	2718	4.917			
Total		6636633	53065				



<Sample Information>

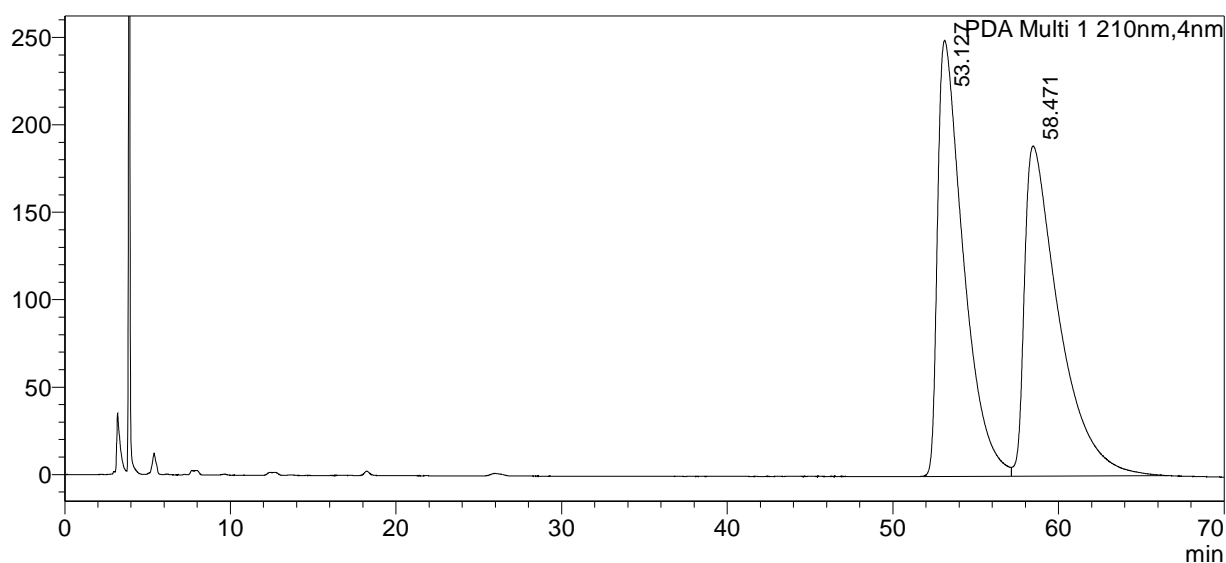
Sample Name : wsw-1-69
 Sample ID :
 Data Filename : wsw-1-69.lcd

Method Filename : 6; IA;1ml;3% IPA in Hex;80 min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-50
 Injection Volume : 10 uL
 Date Acquired : 11/9/2020 9:19:43 PM
 Date Processed : 11/9/2020 10:39:46 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

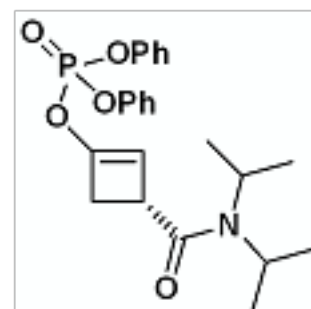
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	53.127	27040812	249382	49.738		V	
2	58.471	27325658	188801	50.262		SV	
Total		54366470	438183				



<Sample Information>

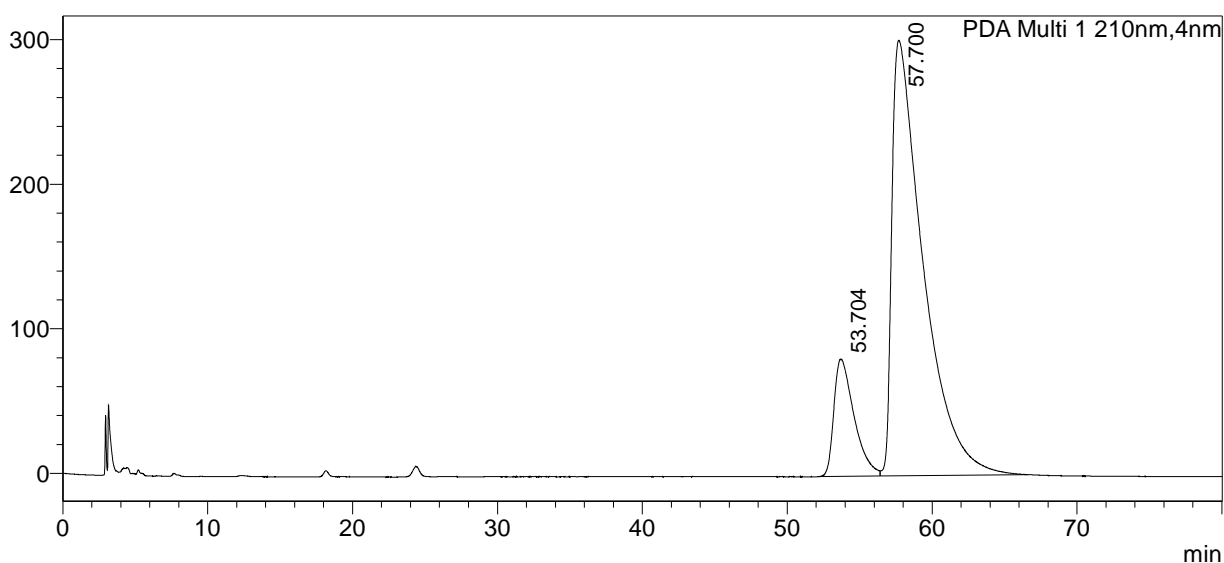
Sample Name : zcx-9-50ac
 Sample ID :
 Data Filename : zcx-9-50ac.lcd

Method Filename : 6; IA;1ml;3% IPA in Hex;80 min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-51
 Injection Volume : 10 uL
 Date Acquired : 11/9/2020 10:40:17 PM
 Date Processed : 11/10/2020 12:00:19 AM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

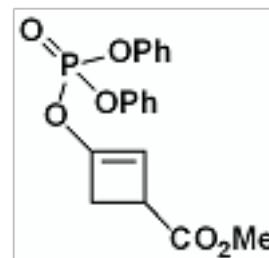
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	53.704	7900795	81239	14.882			
2	57.700	45190295	301192	85.118		V	
Total		53091091	382431				



<Sample Information>

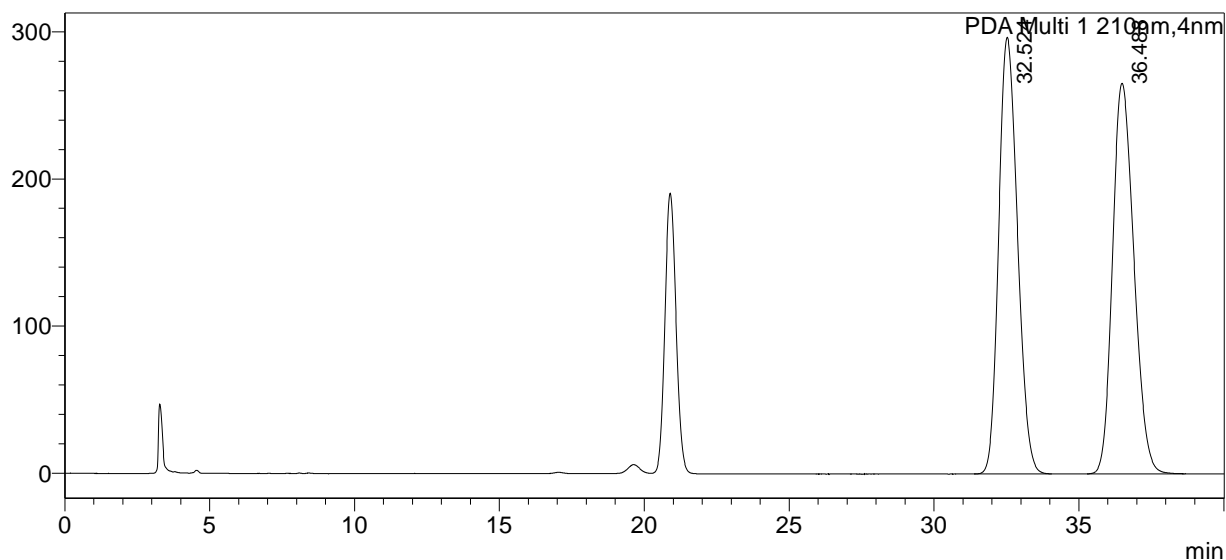
Sample Name : zcx-9-35ac IC
 Sample ID :
 Data Filename : zcx-9-35ac IC.lcd

Method Filename : IC,1ml 10%IPA in Hex;40min.lcm
 Batch Filename : zcx-9-15ac.lcb
 Vial # : 1-46
 Injection Volume : 10 uL
 Date Acquired : 10/28/2020 5:00:19 PM
 Date Processed : 10/28/2020 5:40:22 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

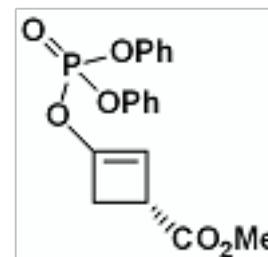
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	32.524	13385551	296796	49.575			
2	36.488	13614875	265569	50.425			
Total		27000426	562366				



<Sample Information>

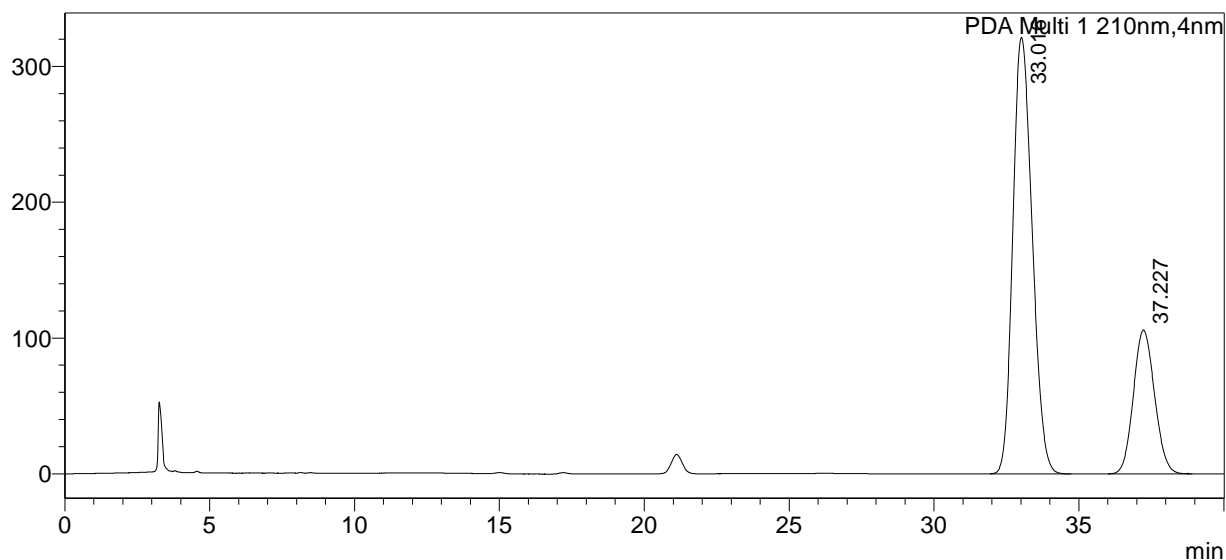
Sample Name : zcx-9-31ac IC
 Sample ID :
 Data Filename : zcx-9-31ac IC.lcd

Method Filename : IC,1ml 10%IPA in Hex;40min.lcm
 Batch Filename : zcx-9-15ac.lcb
 Vial # : 1-46
 Injection Volume : 10 uL
 Date Acquired : 11/6/2015 1:19:00 PM
 Date Processed : 11/6/2015 1:59:03 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

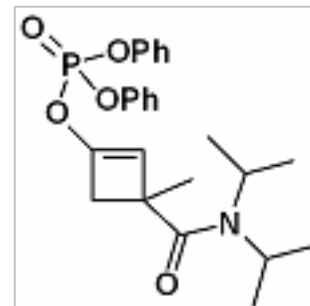
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	33.016	14946416	321483	73.489		SV	
2	37.227	5391822	106070	26.511		V	
Total		20338238	427553				



<Sample Information>

Sample Name : zcx-4-96ac2-1 OZ
 Sample ID :
 Data Filename : zcx-4-96ac2-1 OZ.lcd

Method Filename : OZ-H;1 ml; 10% IPA in Hex;40 min.lcm

Batch Filename : zcx-4-96ac2.lcb

Vial # : 1-5

Injection Volume : 10 uL

Date Acquired : 11/7/2018 2:35:17 AM

Date Processed : 11/7/2018 3:15:20 AM

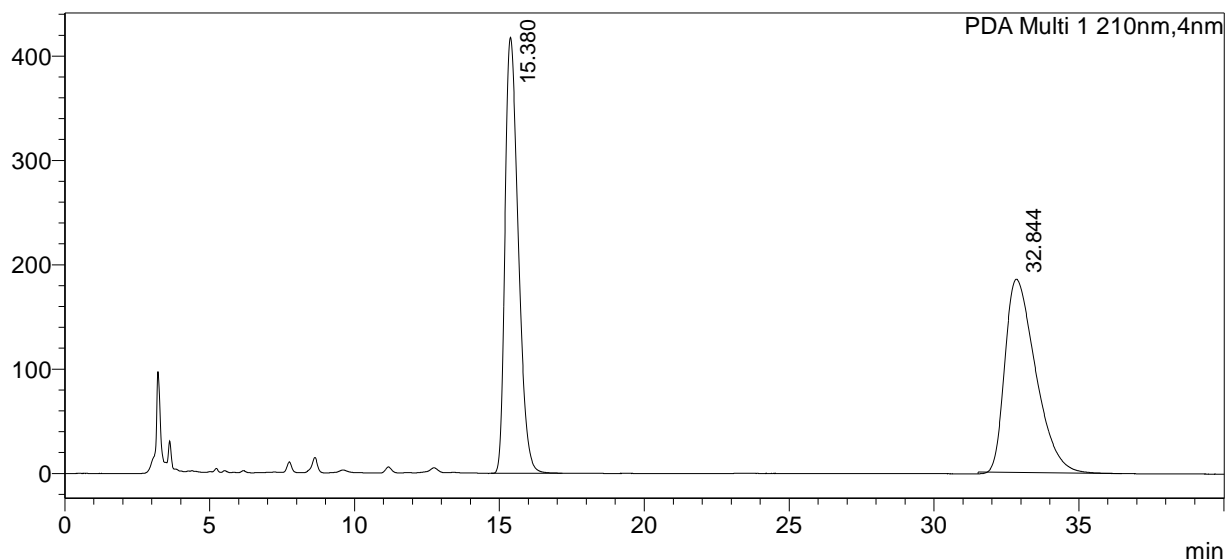
Sample Type : Unknown

Acquired by : System Administrator

Processed by : System Administrator

<Chromatogram>

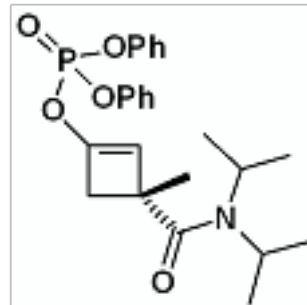
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.380	13277289	417839	49.419			
2	32.844	13589645	185204	50.581			
Total		26866934	603043				



<Sample Information>

Sample Name : zcx-9-90ac
 Sample ID :
 Data Filename : zcx-9-90ac.lcd

Method Filename : OZ-H;1 ml; 10% IPA in Hex;60 min.lcm

Batch Filename : 1.lcb

Vial # : 1-79

Injection Volume : 10 uL

Date Acquired : 11/22/2020 12:34:55 AM

Date Processed : 11/22/2020 1:34:58 AM

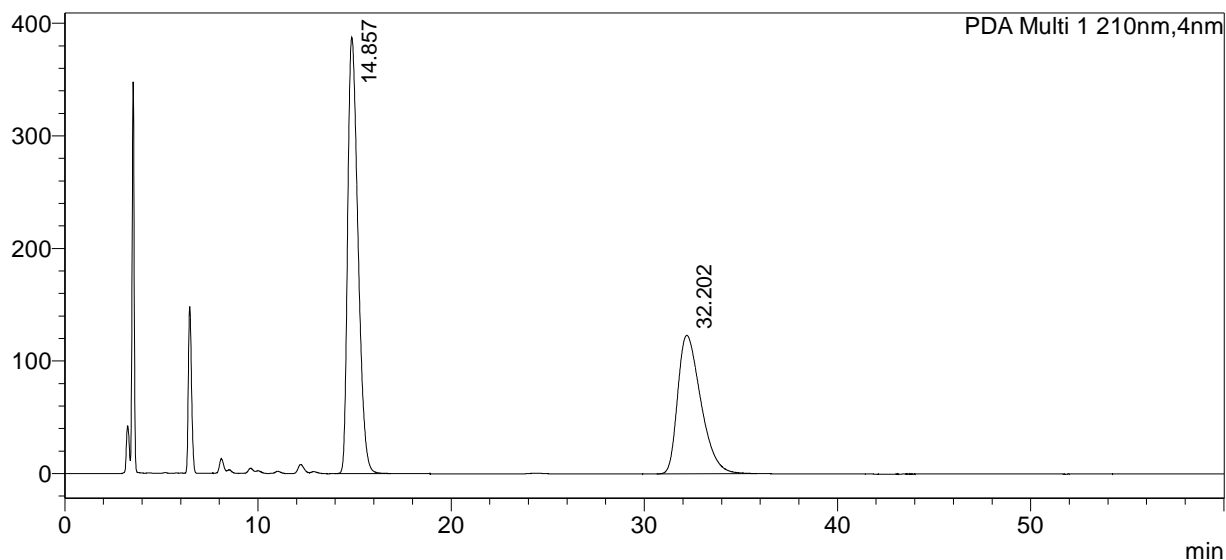
Sample Type : Unknown

Acquired by : System Administrator

Processed by : System Administrator

<Chromatogram>

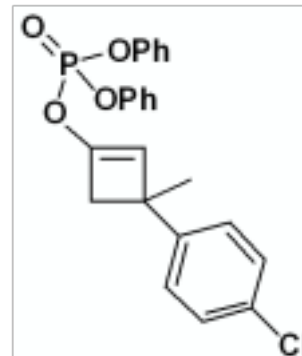
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.857	14412414	387497	58.483		S	
2	32.202	10231360	123076	41.517		S	
Total		24643774	510573				



<Sample Information>

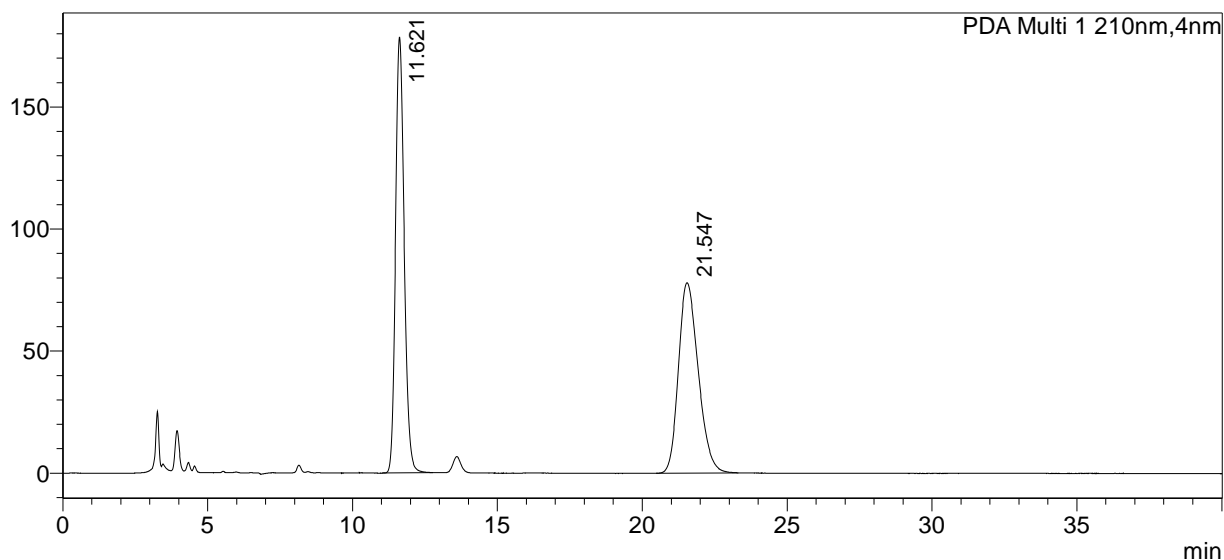
Sample Name : w-1-17-1
 Sample ID :
 Data Filename : w-1-17-1.lcd

Method Filename : OJ-H;1 ml; 10% IPA in Hex;40 min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-78
 Injection Volume : 10 uL
 Date Acquired : 9/2/2020 2:47:45 PM
 Date Processed : 9/2/2020 3:27:47 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

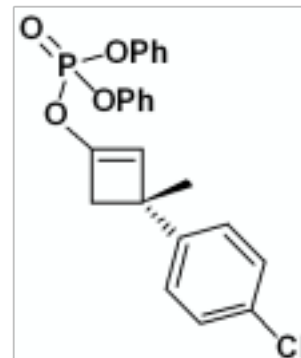
mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.621	3698064	178444	49.978			
2	21.547	3701264	77985	50.022		S	
Total		7399328	256429				



<Sample Information>

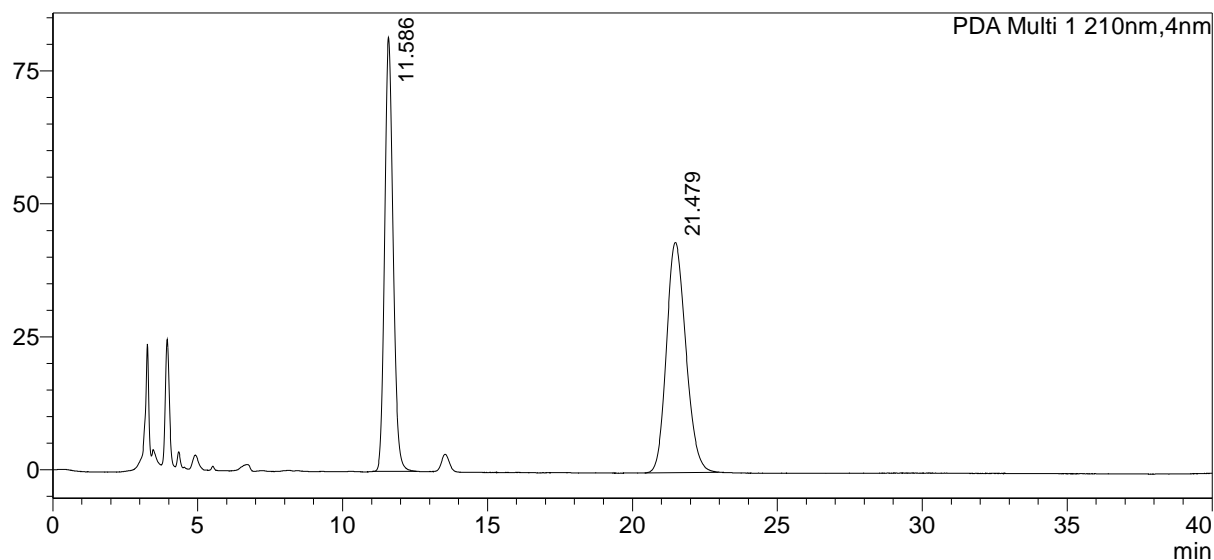
Sample Name : zcx-4-70ac
 Sample ID :
 Data Filename : zcx-4-70ac.lcd

Method Filename : OJ-H;1 ml; 10% IPA in Hex;40 min.lcm
 Batch Filename : 1.lcb
 Vial # : 1-79
 Injection Volume : 10 uL
 Date Acquired : 9/2/2020 3:28:16 PM
 Date Processed : 9/2/2020 4:08:18 PM

Sample Type : Unknown
 Acquired by : System Administrator
 Processed by : System Administrator

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.586	1658899	81600	45.182			
2	21.479	2012705	43303	54.818			
Total		3671604	124903				