Electronic Supporting Information

for

"Chemoselective triazole-phosphonamidate conjugates suitable for photorelease"

1) General information

Analytical HPLC was conducted on a SHIMADZU HPLC system (Shimadzu Corp., Japan) with a SIL-20A autosampler, 2 pumps LC2 AAT, a 2489 UV/Visible detector, a CTO-20A column oven and an RF-10 A X2 fluorescence detector (Em = 495 nm, Ex = 517 nm). The flow rate was 1 mL/min.

Analytical UPLC: UPLC-UV traces were obtained on a Waters H-class instrument equipped with a Quaternary Solvent Manager, a Waters autosampler and a Waters TUV detector connected to a 3100 mass or QDaTM detector with an Acquity UPLC-BEH C18 1.7 µm, 2.1 x 50 mm RP column with a flow rate of 0.6 mL/min (Water Corp., USA). UPLC-UV chromatograms were recorded at 220 nm.

Preparative HPLC was performed on a Gilson PLC 2020 system (Gilson Inc., WI, Middleton, USA) using a Macherey-Nagel Nucleodur C18 HTec Spum column (Macherey-Nagel GmbH & Co. Kg, Germany). The following gradient was used: (A = H2O + 0.1% TFA, B = MeCN + 0.1% TFA) flow rate 30 mL/min, 10% B 0-5 min, 10-100% B 5-55 min, 100 % B 35-40 min.

Column chromatography was performed on silica gel (Acros Silica gel 60 Å, 0.035-0.070 mm).

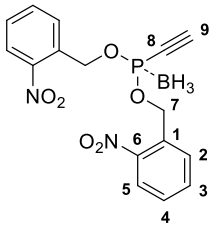
NMR spectra were either recorded with a Bruker Ultrashield 300 MHz spectrometer oder a Bruker Ultrashield 600 MHz (both Bruker Corp., USA) at ambient temperature. The chemical shifts are reported in ppm relative to the residual solvent peak.

Reagents and solvents were, unless stated otherwise, commercially available as reagent grade and did not require further purification. Chemicals were purchased either from Sigma-Aldrich or TCI. Resins and Fmoc-protected amino acids were purchased from IRIS BioTech (Germany) or Novabiochem (Germany).

UV irradiation was carried out with a LOT Hg (Xe) arc lamp (LOT-QuantumDesign GmbH, D-64293 Darmstadt, Germany) using a 297 nm filter from the Andover Incorporation with 15 % transmission. Probes were positioned in 20 cm distance and irradiated while stirring.

Streptavidin beads ("Streptavidin Sepharose High Performance") were purchased from GE Healthcare and have a binding capacity of 300 nmol/mL.

2) Synthesis of central building block **1**



Route **A** via PCl_3:

PCl_3 (0.41 g, 3 mmol) was cooled to -96 °C and triethylamine (0.83 mL, 6 mmol. 2 eq.) was added dropwise. 2-Nitrobenzylalcohol (0.92 g, 6 mmol, 2 eq., dissolved in 1:9 THF:Toluene, 36 mL) was added, stirred for 10 mins at -96 °C and was then warmed to room temperature overnight. The reaction was then cooled to 0 °C and triethylamine (0.11 mL, 0.75 mmol, 0.25 eq.) and 2-nitrobenzylalcohol (0.23 g, 1.5 mmol, 0.5 eq., dissolved in 1:9 THF:Toluene, 9 mL) was slowly added. The reaction was warmed to room temperature and stirred for 2 hrs. After cooling down to -96 °C again, ethynylmagnesium bromide (9 mL, 4.5 mmol, 1.5 eq., 0.5 M in THF) was added dropwise and the reaction was stirred under cooling for 10 mins before it was warmed to room temperature and allowed to react for 2 hrs. BH_3.THF (4.5 mL, 4.5 mmol, 1.5 eq., 1 M in THF) was then added under cooling at 0 °C and stirred for 2 hrs at room temperature. The solvent was removed *in vacuo* and the compound was purified by silica gel column chromatography (Hex 5: EtOAc 1) to yield the desired product **1** as white powder (0.45 g, 1.2 mmol, 40 %).

Route **B** via bis(diisopropylamino)chlorophosphine:

Bis(diisopropylamino)chlorophosphine (0.2 g, 0.79 mmol) was suspended in dry THF (1 mL) and ethynylmagnesium bromide (1.6 mol, 0.8 mmol, 1.01 eq., 0.5 M in THF) was added dropwise at 0 °C, before rhe reaction was stirred for 2 hrs at room temperature. 2-Nitrobenzylalcohol (0.3 g, 1.98 mmol, 2.5 eq., dissolved in 2 mL dry MeCN) and tetrazole (9 mL, 4 mmol, 6.4 eq., 0.45 M in MeCN) was added at 0 °C and stirred for further 2 hrs at room temperature. BH_3.THF (1.1 mL, 1.1 mmol, 1.4 eq., 1 M in THF) was added at 0°C and reacted for 2 hrs at room temperature. The solvent was removed *in vacuo* and the compound was purified by silica gel column chromatography (Hex 5: EtOAc 1) to yield the desired product **1** as white powder (0.190 mmol, 0.51 mmol, 65 %).

Experimental data:

^{1}H-NMR ($CDCl_3$, 300 MHz) δ 8.16 (d, *J* = 8.1 Hz, 2H, C5-H), 7.79-7.70 (m, 2H), 7.56-7.51 (m, 1H, C4-H), 5.66-5.53 (m, 4H, C7-2H), 3.32 (d, *J* = 7.35, 1H, C9-H)

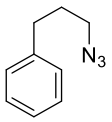
^{13}C-NMR ($CDCl_3$, 75 MHz) δ 146.7 (s, C6), 134.4 (s, C2), 132.0 (d, *J* = 8 Hz, C8), 129.2 (s, C3), 128.6 (s, C4), 125.3 (s, C5), 94.9 (d, *J* = 25 Hz, C9), 66.5 (d, *J* = 5 Hz, C7)

^{31}P-NMR ($CDCl_3$, 121 MHz) δ 108.9 (dd, *J* = 360, 123 Hz)

HRMS (ESI, *m/z*) calcd for $C_{16}H_{16}BN_2O_6PNa$ $[M+Na]^+$: 397.0737, found: 397.0736

3) Synthesis of model azides

3.1 3-Phenylpropyl azide **2a**



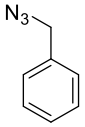
3-Phenylpropyl bromide (2 g, 10 mmol) was diluted in dry DMSO (20 mL) and sodium azide (1.2 g, 18 mmol, 1.8 eq.) was added. The reaction was stirred overnight at room temperature. The reaction mixture was diluted with water (50 mL) and extracted with Et_2O (5 x 50 mL). The organic layer was washed with H_2O (3 x 50 mL) and brine. It was dried with $MgSO_4$, filtered and the solvent was removed *in vacuo*. Product **2a** was isolated as oil (1.66g, 10 mmol, 100 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.31 (m, 2H), 7.23 – 7.16 (m, 3H), 3.30 (t, *J* = 6.8 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.01 – 1.83 (m, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.75, 128.43, 128.37, 126.05, 50.56, 32.68, 30.36.

All values were according to literature[1].

3.2 Benzyl azide **2b**



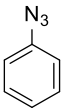
Benzyl bromide (1.71 g, 10 mmol) was dissolved in 4:1 acetone:H_2O (20 mL) and sodium azide (1.9 g, 30 mmol, 3 eq.) was added. The reaction was stirred overnight at room temperature. The reaction mixture was extracted with Et_2O (3 x 50 mL) and the organic phase was washed with H_2O (50 mL) and brine (50 mL). The organic phase was dried with $MgSO_4$, filtered and the solvent was removed *in vacuo* to yield the desired product **2b** as oil (1.3 g, 9.8 mmol, 98 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48 – 7.29 (m, 5H), 4.35 (s, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.29, 128.77, 128.25, 128.16, 54.73.

All values were according to literature[2].

3.3 Phenyl azide **2c**



Aniline (3.1 g, 33 mmol) was dissolved in H_2O (25 mL) and conc. H_2SO_4 (10.5 mL) was added at 0 °C. $NaNO_2$ (2.6 g, 38 mmol, 1,15 eq.) dissolved in H_2O (15 mL), and added dropwise. Hexane (50 mL), followed by sodium azide (2.6 g, 40 mmol, 1.2 eq.) in H_2O (10 mL) was added and the reaction

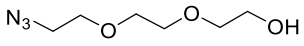
was stirred for 3 hrs at room temperature. The organic phase was separated, washed with H_2O (3 x 50 mL), dried with $MgSO_4$ and filtered. The solvent was removed *in vacuo*, yielding compound **3c** as oil (2.75 g, 23.1 mmol, 70 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.41 – 7.32 (m, 2H), 7.20 – 7.11 (m, 1H), 7.08 – 7.01 (m, 2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.10, 129.88, 124.99, 119.14.

All values were according to literature[3].

3.4 OH-PEG-N_3 **2e**



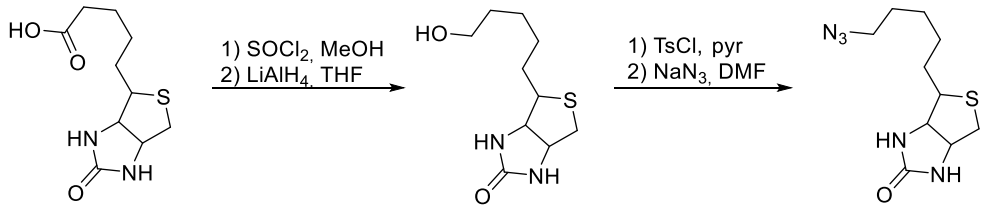
Compound **2e** was synthesized starting from commercially available Cl-TEG-N_3 using a previously published protocol.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.75 – 3.70 (m, 2H), 3.70 – 3.64 (m, 6H), 3.63 – 3.58 (m, 2H), 3.39 (t, *J* = 5.0 Hz, 2H).

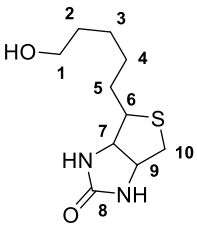
^{13}C NMR ($CDCl_3$, 75 MHz) δ 72.59, 70.74, 70.46, 70.14, 61.84, 50.74.

All values were according to literature[4].

4) Synthesis of biotin azide **2d**



4.1 Synthesis of biotinol **S1**



Biotin (5 g, 20.5 mmol) was suspended in dry MeOH (60 mL) and thionyl chloride (7.4 g, 4.5 mL, 62 mmol (3 eq.) was added dropwise at 0 °C. The reaction was stirred overnight at room temperature and the solvent was removed *in vacuo*. The biotin methyl ester was used without further purification. It was suspended in dry THF (300 mL) and a suspension of $LiAlH_4$ (3.1 g, 82 mmol, 4 eq.) in dry THF

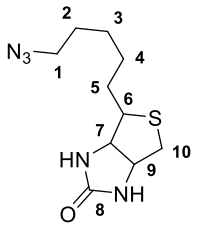
(120 mL) was added dropwise at 0 °C. The reaction was stirred at room temperature overnight, before it was quenched with MeOH (50 mL) and H_2O (50 mL) at 0 °C. Afterwards a solution of conc. Na_2SO_4 (50 mL) was added and the reaction mixture was stirred for another 20 mins. The solvent was removed *in vacuo* and a 1:4 MeOH:DCM (20 mL) mixture was added and stirred for 1 hr. The white solid was filtered off over celite and washed with 1:4 MeOH:DCM and the filtrate was reduced *in vacuo*. Product **S1** was isolated by silica gel column chromatography (DCM: 10% MeOH) as white powder (2.91 g, 12.6 mmol, 62 %, over two steps).

^{1}H NMR (DMSO, 300 MHz) δ 6.44 (s, 1H, NH), 6.36 (s, 1H, NH), 4.35-4.28 (m, 2H, OH, C9-H), 4.17 – 4.06 (m, 1H, C7-1H), 3.37 (m, 2H, C1-2H), 3.10 (m, 1H, C6-H), 2.82 (dd, *J* = 12.4, 5.0 Hz, 1H, C10-1H), 2.57 (d, *J* = 12.4 Hz, 1H, C10-1H), 1.68-1-52 (br s, 1H, OH), 1.52 – 1.20 (m, 8H, C2-5).

^{13}C NMR (DMSO, 75 MHz) δ 162.74, 61.10, 60.67, 59.21, 55.59, 32.36, 28.57, 28.37, 25.58. Carbon C6 is hidden underneath the signal of the deuterated solvent.

HRMS (ESI, *m/z*) calcd for $C_{10}H_{19}N_2O_2S$ $[M+H]^+$: 231.1167, found: 231.1161

Synthesis of biotin azide **2d**



Biotinol (2.91 g, 12.6 mmol) was dissolved in dry pyridine (50 mL) and tosyl chloride (5.76 g, 30.2 mmol, 2.4 eq.) was added in two portions at 0 °C. The reaction was stirred overnight at room temperature. The reaction was diluted with DCM (100 mL) and the organic phase was extracted with 1 M H_2SO_4 (3 x 75 mL), brine (50 mL) and was dried with $MgSO_4$. After filtration, the solvent was removed *in vacuo* and biotin tosylated was used without further purification. The residue was dissolved in dry DMF (50 mL) and biotin azide (3.81 g, 60 mmol, 5 eq.) was added. The reaction was stirred at 80 °C overnight and after removal of the solvent in vacuo, the reaction was purified by silica gel column chromatography (DCM: 5 % MeOH). Compound **3d** was isolated as white powder (1.07 g, 4.19 mmol, 33 % in two steps).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.33 (s, 1H, NH), 5.07 (s, 1H, NH), 4.54 (dd, *J* = 7.7, 5.1 Hz, 1H, C7-H), 4.33 (dd, *J* = 8.1, 4.7 Hz, 1H, C9-H), 3.29 (t, *J* = 6.8 Hz, 2H, C1-2H), 3.21-3.15 (m, 1H, C6-H), 2.95 (dd, *J* = 12.8, 5.0 Hz, 1H, C10-1H), 2.75 (d, *J* = 12.8 Hz, 1H, C10-1H), 1.79 – 1.46 (m, 8H, C2-5).

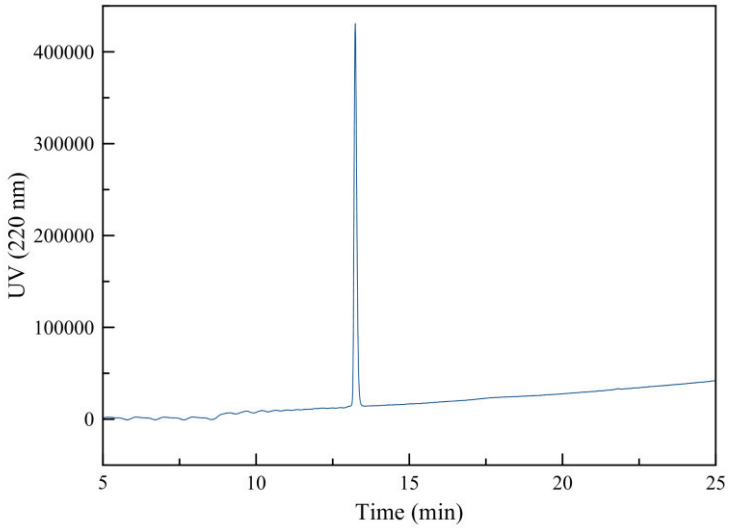
^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.57, 61.97, 60.01, 55.51, 51.29, 40.52, 28.53, 28.44, 26.57. Due to overlapping carbon resonances in the aliphatic chain, one peak is missing.

HRMS (ESI, *m/z*) calcd for $C_{10}H_{19}N_2O_2S$ $[M+H]^+$: 256.1232, found: 256.1223

5) Peptide synthesis

Peptides were either synthesised manually or using the automated PTI Tribute (Gyros Protein Technologies) via standard Fmoc-based conditions (fast-Fmoc protocol with HBTU/HOBt/NMM). Fmoc deprotection was carried out using 20% piperidine in DMF (3 x 3 min). Single couplings were performed for all standard amino acids (aa), using 5. eq. aa, 5 eq. HBTU, 5 eq. HOBt and 5 eq. DIPEA. Unnatural amino acids were incorporated using 2 eq. aa, 2 eq. HATU and 4 eq. DIPEA. Peptides were synthesised on Rink Amide resin and, if not specified otherwise, in 0.1 mmol scale. All peptides were cleaved using 95:2.5:2.5 TFA:TIS:H_2O for 2 hrs. Before purification, all peptides were precipitated in cold diethylether. The crude peptides were all purified by preparative HPLC using a gradient from 10-90% in 50 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA). All peptides were characterized either by analytical HPLC or by UPLC-MS.

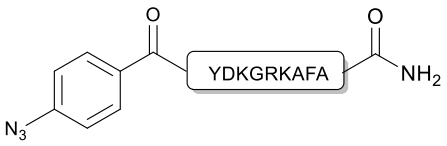
Peptide **2f:**

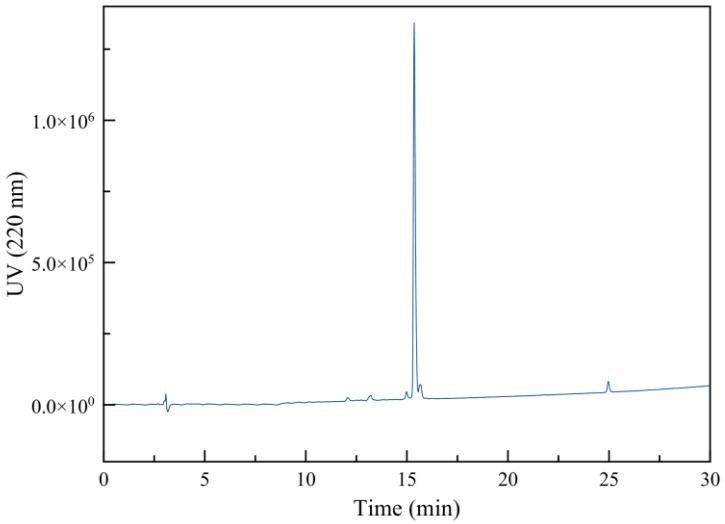


Column: Agilent Eclipse XDB C18, 4.6 x 250 mm (analytical HPLC)
Gradient: 5-95 % B in 30 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA)
Retention time: 13.2 min
Yield: 61.9 mg, 0.0544 mmol, 54.4%

HRMS (ESI, *m/z*) calcd for $C_{55}H_{78}N_{18}O_{13}$ $[M+2H]^{2+}$: 569.2992, found: 569.3021

Peptide **2g**:



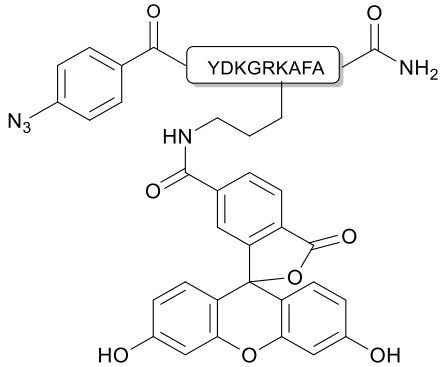


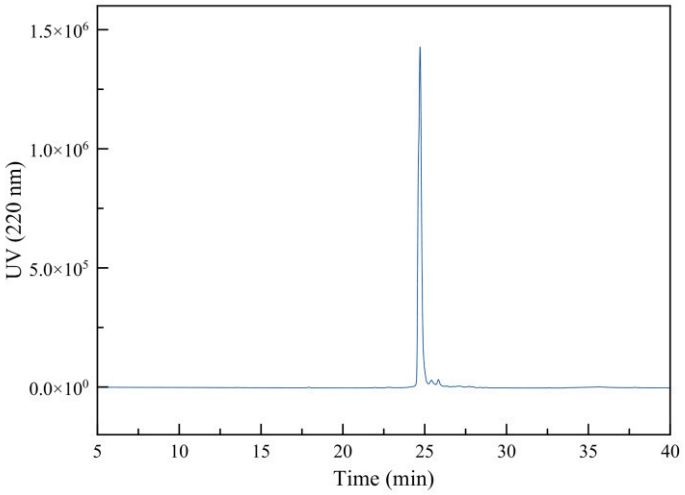
Column: Agilent Eclipse XDB C18, 4.6 x 250 mm (analytical HPLC)
Gradient: 5-95 % B in 30 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA)
Retention time: 15.4 min
Yield: 59.8 mg, 0.0498 mmol, 49.8 %

HRMS (ESI, *m/z*) calcd for $C_{50}H_{76}N_{18}O_{13}$ $[M+2H]^{2+}$: 600.3071, found: 600.3097

Peptide **2h**:

5,6-Carboxyfluorescein was installed via Lys(ivdee), which was selectively deprotected on-resin after capping of the peptide with azidobenzoic acid using hydrazine solution (2 % in DMF, 5 x 2 min). 5,6-Carboxyfluorescein was coupled by using 2 eq. of fluorophore,. 2 eq. of HATU, 2 eq. of HOBt.H_2O and 4 eq. of DIPEA.

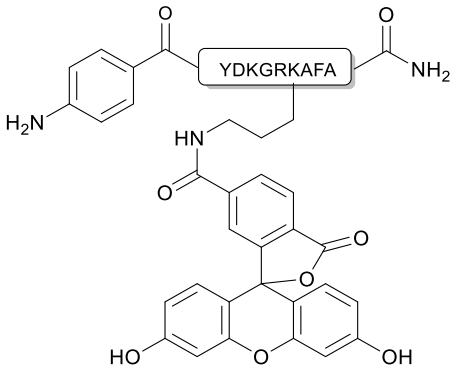


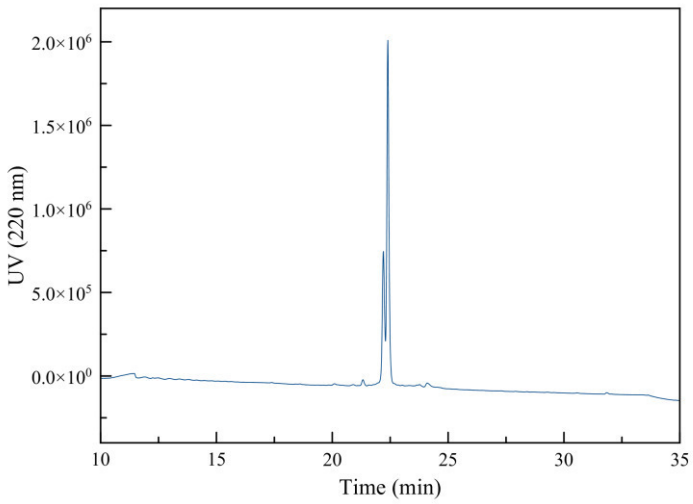


Column: Phenomenex Synergi 4u Hydro-RP, 4.6 x 250 mm (analytical HPLC)
Gradient: 0-60 % B in 25 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA)
Retention time: 24.7 min
Yield: 26 mg, 0.017 mmol, 8.5 % (0.2 mmol scale)

HRMS (ESI, *m/z*) calcd for $C_{55}H_{78}N_{18}O_{13}$ $[M+2H]^{2+}$: 779.3309, found: 779.3339

Peptide **2i**:





Peptide **2i** was synthesized by reduction of peptide **2h** (4 mg, 2.6 µmol) with TCEP (1.5 mg, 5.2 µmol, 2 eq.) for 1 hr in 20 mM NH_4HCO_3 with 10 % MeCN (1 mL, 2.6 mM). The peptide was purified over a SepPak column (1 g) and the product was isolated as a yellow powder in quantitative yield.

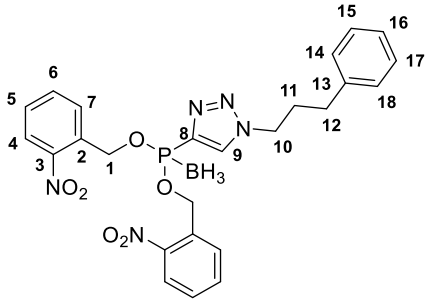
Column: Phenomenex Synergi 4u Hydro-RP, 4.6 x 250 mm (analytical HPLC)
Gradient: 0-60 % B in 25 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA)
Retention time: 22.4 min (Remark: The double peak arises from the two diastereoisomers of the 5,6-carboxyfluorescein. They both have the same mass.)

HRMS (ESI, *m/z*) calcd for $C_{55}H_{78}N_{18}O_{13}$ $[M+2H]^{2+}$: 766.3357, found: 766.3388

6) General procedure for the synthesis of triazole-phosphonites:

To a solution of phosphonite **1** in degassed MeCN (0.03 M), the corresponding azide (1 eq.), 2,6-lutidine (3 eq.), DIPEA (3 eq.) and CuI (30 %) were added. The reaction was stirred overnight at room temperature and purified by silica gel column chromatography (3 Hex: 1 EtOAc), if not otherwise specified.

6.1 Compound **3a**



Isolated yield: 93 %

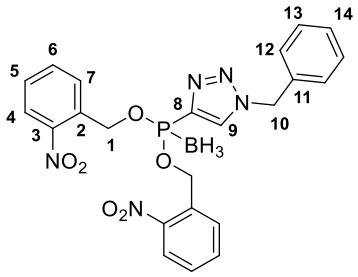
^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.10 (dd, *J* = 8.2, 1.3 Hz, 2H, C4-H), 8.01 (s, 1H, C9-H), 7.80 (dd, *J* = 7.8, 1.4 Hz, 2H, C7-H), 7.66 (td, *J* = 7.6, 1.3 Hz, 2H, C6-H), 7.47 (td, J = 7.8, 1.5, 2H, C5-H), 7.35 – 7.28 (m, 2H, C14-H, C18-H), 7.25 – 7.15 (m, 3H, C15-C17-H), 5.68 – 5.50 (m, 4H, C1-2H), 4.43 (t, *J* = 7.2 Hz, 2H, C10-2H), 2.69 (t, *J* = 7.4 Hz, 2H, C12-2H), 2.39 – 2.25 (m, 2H, C11-2H).

^{13}C NMR ($CDCl_3$, 75 MHz) δ 146.83 (C3), 139.74 (C13), 134.29 (C6), 132.43 (d, *J* = 11 Hz, C9), 130.92 (d, *J* = 34 Hz, C8), 129.09 (C7), 128.89 (C14), 128.87 (C15), 128.56 (C5), 126.70 (C16), 125.13 (C4) , 66.34 (d, *J* = 6 Hz, C1), 49.98 (C12), 32.55 (C11), 31.51 (C10).

^{31}P-NMR ($CDCl_3$, 121 MHz) δ 122.32 (dd, *J* = 153.2, 58.1)

HRMS (ESI, *m/z*) calcd for $C_{25}H_{28}BN_5O_6P$ $[M+H]^+$: 536.1871, found: 536.1858

6.2 Compound **3b**



Isolated yield: 87 %

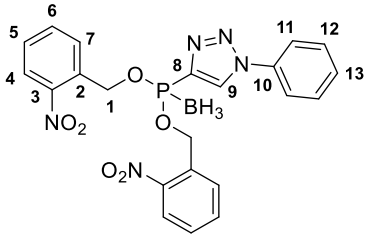
^{1}H-NMR ($CDCl_3$, 300 MHz) δ 8.09 (dd, *J* = 8.2, 1.3 Hz, 2H, C4-H), 7.96 (s, 1H, C9-H), 7.78 (dd, *J* = 7.9, 1.3 Hz, 2H, C7-H), 7.64 (td, *J* = 7.6, 1.3 Hz, 2H, C6-H), 7.51 – 7.46 (m, 2H, C5-H), 7.44 – 7.39 (m, 3H, arom. H), 7.35 – 7.27 (m, 2H, arom. H), 5.66 – 5.48 (m, 6H, C1-2H, C10-2H).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ 146.76 (C3), 139.52 (d, *J* = 103.5, C2), 134.28 (C6), 133.52 (C11), 132.43 (d, *J* = 6.75 Hz, C8), 130.72 (d, *J* = 33.8 Hz, C9), 129.52 (C5), 129.39 (C13), 129.05 (C7), 128.81 (C12), 128.51 (C14), 125.10 (C4), 66.32 (d, *J* = 3.75 Hz, C1), 54.59 (C10).

^{31}P-NMR ($CDCl_3$, 121 MHz) δ 122.5 – 121.4 (m)

HRMS (ESI, *m/z*) calcd for $C_{23}H_{23}BN_5O_6PNa$ $[M+Na]^+$: 530.1377, found: 530.1379

6.3 Compound **3c**



Isolated yield: 71 %

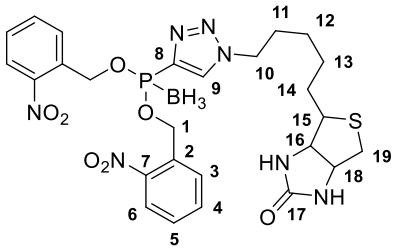
^{1}H-NMR ($CDCl_3$, 300 MHz) δ 8.48 (s, 1H, C9), 8.10 (dd, *J* = 8.2, 1.3 Hz, 2H, C4-H), 7.83 (dd, *J* = 7.8, 1.4 Hz, 2H, C7-H), 7.80 – 7.73 (m, 2H, C11-H), 7.68 (td, *J* = 7.6, 1.3 Hz, 2H, C6-H), 7.61 – 7.45 (m, 5H, C12-2H, C13-H, C5-2H), 5.64 (m, 4H, C1-2H).

^{13}C-NMR ($CDCl_3$, 75 MHz) δ 146.84 (C3), 139.96 (d, *J* = 103.5 Hz, C2), 136.23 (C10), 134.32 (C6), 132.31 (d, *J* = 7.5 Hz, C8), 130.13 (C12), 129.83 (C5), 129.16 (C7), 129.03 (d, *J* = 33.75 Hz, C9), 128.91 (C13), 125.14 (C4), 121.12 (C11), 66.50 (d, *J* = 3.75 Hz, C1).

^{31}P-NMR ($CDCl_3$, 121 MHz) δ 123.43-121.12 (m)

HRMS (ESI, *m/z*) calcd for $C_{22}H_{21}BN_5O_6PNa$ $[M+Na]^+$: 516.1221, found: 516.1216

6.4 Compound **3d**



Compound **3d** was isolated by silica gel column chromatography using 5 % MeOH in DCM as eluent.

Isolated yield: 81 %

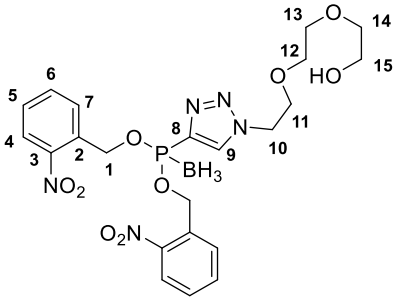
^{1}H NMR (DMSO, 300 MHz) δ 8.84 (s, 1H, C9-H), 8.12 (dd, *J* = 8.2, 1.2 Hz, 2H, C6-H), 7.85 – 7.70 (m, 4H, C4-H, C3-H), 7.62 (dd, *J* = 8.1, 1.7 Hz, 2H, C5-H), 5.60 – 5.42 (m, 4H, C1-2H), 4.47 (t, *J* = 7.1 Hz, 2H,, C10-2H), 4.29 (dd, *J* = 7.7, 4.8 Hz, 1H, C18-1H), 4.12 (dd, *J* = 7.8, 4.4 Hz, 1H, C16-1H), 3.11 – 3.05 (m, 1H, C15-1H), 2.80 (dd, *J* = 12.5, 5.1 Hz, 1H, C19-1H), 2.56 (d, *J* = 12.4 Hz, 1H, C19-1H), 1.87 (quint, *J* = 7.4 Hz, 2H, C11-2H), 1.50 – 1.25 (m, 6H, C12, C13, C14).

^{13}C NMR (DMSO, 75 MHz) δ 162.71 (C17), 146.62 (C7), 137.15 (d, *J* = 109 Hz, C2), 134.38 (C4), 131.75 (d, *J* = 6.8 Hz, C9), 129.41 (C3), 128.52 (C5), 124.90 (C6), 65.45 (d, *J* = 4.1 Hz, C1), 61.00 (C16), 59.19 (C18), 55.42 (C15), 49.74 (C10), 40.34 (C19), 29.38 (C11), 28.09 (C13), 27.91 (C14), 25.81 (C12).

^{31}P-NMR ($CDCl_3$, 121 MHz) δ 122.85 – 120.90 (s br)

HRMS (ESI, *m/z*) calcd for $C_{10}H_{19}N_2O_2SNa$ $[M+Na]^+$: 652.1891, found: 652.1882

6.5 Compound **3e**



Isolated yield: 81 %

^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.31 (s, 1H, C9-H), 8.09 (dd, *J* = 8.2, 1.3 Hz, 2H, C4-H), 7.81 (dd, *J* = 7.8, 1.3 Hz, 2H, C7-H), 7.67 (td, *J* = 7.6, 1.3 Hz, 2H, C6-H), 7.52 – 7.43 (m, 2H, C5-H), 5.58 (qd, *J* = 14.9, 7.5 Hz, 4H, C1-2H), 4.65 (t, *J* = 4.9 Hz, 2H, C10-2H), 3.92 (dd, *J* = 5.5, 4.4 Hz, 2H, C11-2H), 3.78 – 3.60 (m, 9H, C12-2H, C13-H, C14-2H, OH), 3.59 – 3.53 (m, 2H, C15-2H).

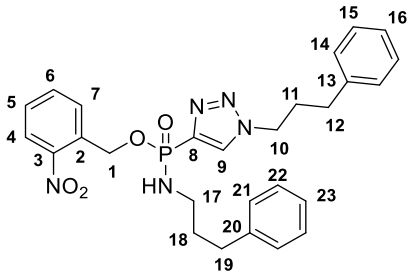
^{13}C NMR ($CDCl_3$, 75z MHz) δ 146.77 (C3), 134.31 (C6), 132.48 (d, *J* = 7.5 Hz, C9), 132.32 (d, *J* = 33.8 Hz, C8), 129.04 (C7), 128.83 (C5), 125.09 (C4), 72.59, 70.78, 70.40, 69.06 (C11), 66.26 (d, *J* = 4.5 Hz, C1) 61.79, 50.64 (C10).

^{31}P-NMR ($CDCl_3$, 121 MHz) δ 123.50 – 121.25 (s br)

HRMS (ESI, *m/z*) calcd for $C_{22}H_{29}BN_5O_9PNa$ [M+Na]$^+$: 572.1694, found: 572.1686

7) Small-molecule phosphoramidates

7.1 Compound **4a**



Triazole-phosphonite **3a** (70 mg, 0.130 mmol) was dissolved in dry, degassed DMF (0.65 mL, 0.2 M) under argon and DABCO (21 mg, 0.195 mmol, 1.5 eq.) was added. The reaction was heated to 80 °C for 4 hrs. The temperature was decreased to 60 °C and azide **2a** (63 mg, 0.39 mmol, 3 eq.) was added for 5 hrs. The solvent was removed by lyophilisation in 50:50 H_2O:MeCN and the crude was purified by silica gel column chromatography (20 % acetone in hexane → EtOAc). Product **4a** was isolated as colourless oil (57 mg, 0.110 mmol, 85 %).

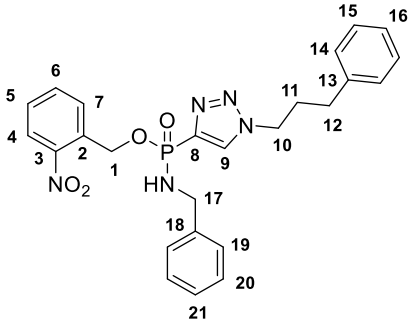
^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.12 (d, *J* = 8.2 Hz, C4-H), 8.03 (s, 1H, C9-1H), 7.88 (d, *J* = 7.8 Hz, 1H, C7-1H), 7.67 (t, *J* = 7.6 Hz, 1H, C6-1H), 7.47 (t, *J* = 7.7 Hz, 1H, C5-1H), 7.36 – 7.10 (m, 10H, C14-C16-5H, C21-C23-5H), 5.62 – 5.42 (m, 2H, C1-2H), 4.42 (t, *J* = 7.1 Hz, 2H, C10-2H), 3.34 (m, 1H, NH), 3.15 (m, 2H, C17-2H), 2.66 (m, C19-2H, C12-2H), 2.29 (m, *J* = 7.3 Hz, 2H, C11-2H), 1.86 (p, *J* = 7.3 Hz, 2H, C18-2H).

^{13}C-NMR ($CDCl_3$, 150 MHz): δ 146.74 (C3), 141.39 (C20), 139.85 (C13), 139.30 (d, *J* = 436 Hz, C2) 134.21 (C6), 133.25 (d, *J* = 8.25 Hz, C9), 129.9 (d, *J* = 32 Hz, C8), 129.68 (C7), 128.81 (C5), 128.64 (C14), 128.62 (C15), 128.52 (C21), 128.43 (C22), 126.60 (C16), 126.04 (C23), 124.99 (C4), 63.40 (d, *J* = 3.8 Hz, C1), 49.75 (C12), 40.55 (C19), 33.58 (C18), 33.50 (C17), 32.51 (C11), 31.60 (C10)

^{31}P-NMR ($CDCl_3$, 121 MHz): 12.5

HRMS (ESI, *m/z*) calcd for $C_{10}H_{19}N_2O_2S$ [M+Na]$^+$: 542.1928, found: 542.1932

7.2 Compound **4b**



Triazole-phosphonite **3a** (22.5 mg, 0.042 mmol) was dissolved in dry, degassed DMF (0.2 mL, 0.2 M) under argon and DABCO (7 mg, 0.062 mmol, 1.5 eq.) was added. The reaction was heated to 80 °C for 4 hrs. The temperature was decreased to 60 °C and azide **2b** (17 mg, 0.13 mmol, 3 eq.) was added for 5 hrs. The solvent was removed by lyophilisation in 50:50 H_2O:MeCN and the crude was purified by silica gel column chromatography (20 % acetone in hexane → EtOAc). Product **4b** was isolated as colourless oil (18 mg, 0.036 mmol, 86 %).

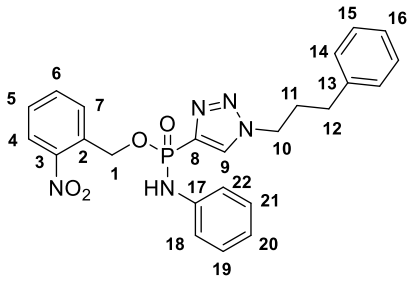
^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.10 (dd, *J* = 8.2, 1.3 Hz, 1H, C4-1H), 7.99 (s, 1H, C9-1H), 7.79 (dd, *J* = 7.9, 1.3 Hz, 1H, C7-1H), 7.63 (dd, *J* = 7.7, 1.3 Hz, 1H, C6-1H), 7.47 – 7.43 (m, 1H, C5-1H), 7.34 – 7.26 (m, 6H, arom. H), 7.25 – 7.21 (m, 2H, arom. H), 7.19 – 7.16 (m, 2H, arom. H), 5.53 – 5.45 (m, 2H, C1-2H), 4.41 (td, *J* = 7.1, 2.8 Hz, 2H, C10-2H), 4.33 – 4.28 (m, 2H, C17-2H), 2.68 (t, *J* = 7.4 Hz, 2H, C12-2H), 2.32 – 2.26 (m, 2H, C11-2H).

^{13}C-NMR ($CDCl_3$, 150 MHz): δ 146.78 (C3), 139.88 (C13), 139.44 (d, *J* = 876 Hz, C2), 139.31 (d, *J* = 24 Hz, C18), 134.21 (C6), 133.21 (d, *J* = 36 Hz, C8), 130.00 (d, *J* = 126 Hz, C9), 128.87 (C5), 128.75 (C6), 128.65 (C14), 128.56 (C15), 127.60 (C19), 127.56 (C21), 126.67 (C16), 125.00 (C4), 63.65 (d, *J* = 18 Hz, C1), 49.81 (C10), 44.84 (C17), 32.56 (C12), 31.60 (C11).

^{31}P-NMR ($CDCl_3$, 242 MHz) δ 12.27

HRMS (ESI, *m/z*) calcd for $C_{25}H_{26}N_5O_4PNa$ $[M+Na]^+$: 514.1620, found: 514.1625

7.3 Compound **4c**



Triazole-phosphonite **3a** (22.5 mg, 0.042 mmol) was dissolved in dry, degassed DMF (0.2 mL, 0.2 M) under argon and DABCO (7 mg, 0.062 mmol, 1.5 eq.) was added. The reaction was heated to 80 °C for 4 hrs. The temperature was decreased to 60 °C and azide **2c** (15 mg, 0.13 mmol, 3 eq.) was added

for 5 hrs. The solvent was removed by lyophilisation in 50:50 H_2O:MeCN and the crude was purified by silica gel column chromatography (20 % acetone in hexane → EtOAc). Product **4c** was isolated as colourless oil (12 mg, 0.021 mmol, 50 %).

^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.11 (dd, *J* = 8.1, 1.1 Hz, 1H, C4-1H), 8.04 (s, 1H, C9-1H), 7.90 (d, *J* = 7.9 Hz, 1H, C7-1H), 7.65 (td, *J* = 7.6, 1.4 Hz, 1H, C6-1H), 7.46 (t, *J* = 7.6 Hz, 1H, C5-1H), 7.29 (m, 2H, C14-2H), 7.24 – 7.18 (m, 3H, C16-H, C15-2H), 7.16 – 7.11 (m, C18-1H, C19-1H, C20-1H, C21-1H), 6.96 (td, *J* = 7.3, 1.1 Hz, 1H, C20-H), 5.93 (d, *J* = 7.8 Hz, 1H, NH), 5.70 – 5.57 (m, 2H, C1-2H), 4.39 (t, *J* = 7.1 Hz, 2H, C10-2H), 2.63 (td, *J* = 7.4, 2.4 Hz, 2H, C12-2H), 2.27 (p, *J* = 7.3 Hz, 2H, C11-2H).

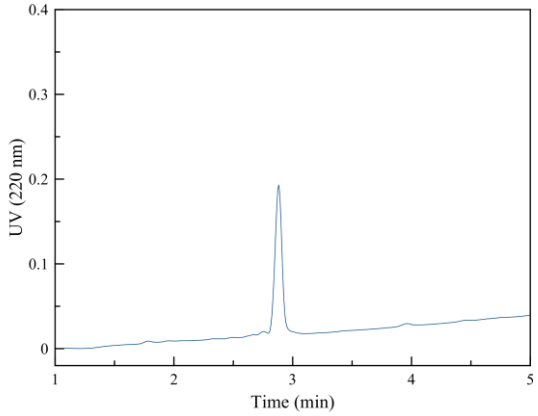
^{13}C-NMR ($CDCl_3$, 150 MHz) δ 146.82 (C3), 139.30 (d, *J* = 147 Hz, C2), 134.30 (C6), 132.75 (d, *J* = 9 Hz, C8), 130.63 (d, *J* = 33 Hz, C9), 129.56 (C7), 128.89 (C5), 128.85 (C19/C21), 128.55 (C15/C14), 126.66 (C16), 125.07 (C4), 122.78 (C20), 118.74 (C18/22), 118.69 (C18/22), 64.13 (d, *J* = 15 Hz, C1), 49.90 (C10), 32.49 (C11), 31.49 (C12).

^{31}P-NMR ($CDCl_3$, 242 MHz) δ 6.68

HRMS (ESI, *m/z*) calcd for $C_{24}H_{24}N_5O_4PNa$ $[M+Na]^+$: 500.1464, found: 500.1470

7.4 Compound **4d**

Triazole-phosphonite **3d** (3 mg, 4.8 µmol) was dissolved in dry, degassed DMF (0.8 mL, 7.5 mM) under argon and DABCO (0.8 mg, 7.2 µmol, 1.5 eq.) was added for 4 hrs at 80 °C, after which 0.4 mL of the solution was added to peptide **2f** (1.1 mg, 0.96 µmol, 0.2 eq.) and the reaction was stirred for 16 hrs at 50 °C, before the remaining deprotected triazole-phosphonite (0.4 mL) was added and stirred for another 24 hrs. The reaction was monitored by UPLC-MS. Afterwards, the reaction was lyophilized with 50:50 H_2O:MeCN and purified by semi-preparative HPLC. Compound **4d** was isolated as white powder (0.84 mg, 0.53 µmol, 55 %).

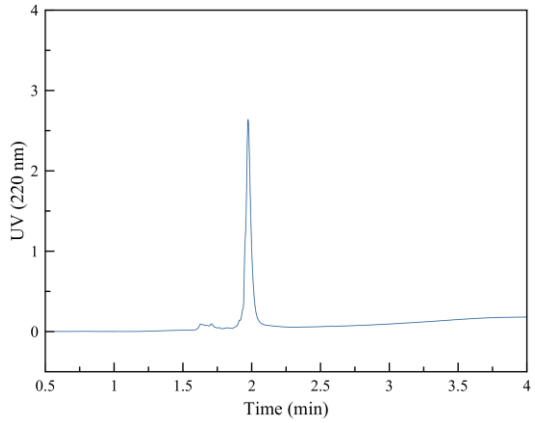


Column: Acquity UPLC-BEH C18 1.7 µm, 2.1x 50 mm RP, (UPLC-MS)
Gradient: 10-95 % B in 8 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA)
Retention time: 2.88 min

LRMS (ESI, *m/z*): calcd for $C_{69}H_{103}N_{22}O_{18}PS$ $[M+2H]^{2+}$: 795.87, found: 795.85

7.5 Compound **4e**

Triazole-phosphonite **3d** (3 mg, 4.8 µmol) was dissolved in dry, degassed DMF (0.8 mL, 6 mM) under argon and DABCO (0.8 mg, 7.2 µmol, 1.5 eq.) was added for 4 hrs at 80 °C. The solution was cooled to room temperature and peptide **2g** (1.2 mg, 0.96 µmol, 0.2 eq.) was added. The reaction was stirred for 24 hrs at room temperature. The reaction was monitored by UPLC-MS. Afterwards, the reaction was lyophilized with 50:50 H_2O:MeCN and purified by semi-preparative HPLC. Compound **4d** was isolated as white powder (1 mg, 0.61 µmol, 63 %).

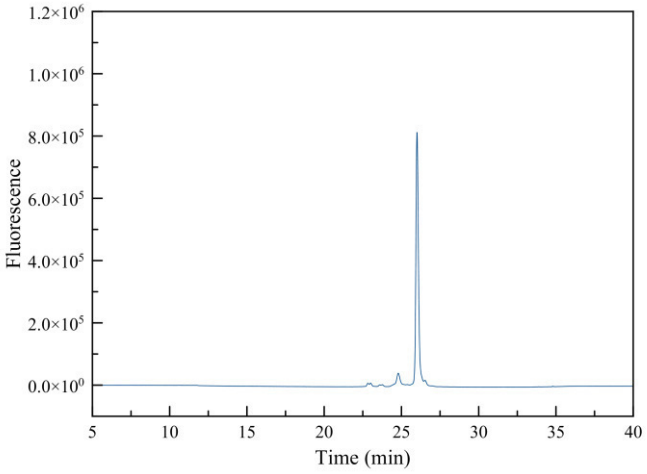


Column: Acquity UPLC-BEH C18 1.7 µm, 2.1x 50 mm RP (UPLC-MS)
Gradient: 5-95 % B in 2.5 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA)
Retention time: 1.97 min

HRMS (ESI, *m/z*): calcd for $C_{74}H_{105}N_{22}O_{18}PS$ $[M+2H]^{2+}$: 826.3712, found: 826.3752

7.6 Compound **4f**

Triazole-phosphonite **3d** (5 mg, 8 µmol) was dissolved in dry, degassed DMF (0.8 mL, 6 mM) under argon and DABCO (1.1 mg, 12 µmol, 1.5 eq.) was added for 4 hrs at 80 °C. Peptide **2g** (2.5 mg, 1.6 µmol, 0.2 eq.) was added at 37 °C and stirred overnight. The reaction was monitored by UPLC-MS. Afterwards, the reaction was lyophilized with 50:50 H_2O:MeCN and purified by semi-preparative HPLC. Compound **5** was isolated as yellow powder (1.2 mg, 0.59 µmol, 37 %).



Column: Phenomenex Synergi 4u Hydro-RP, 4.6 x 250 mm (analytical HPLC)
Gradient: 0-60 % B in 25 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA)
Retention time: 26.0 min

HRMS (ESI, *m/z*): calcd for $C_{95}H_{116}N_{22}O_{24}PS$ $[M+3H]^{3+}$: 670.9336, found: 670.9361

8. Irradiation of phosphonamidate **4f**

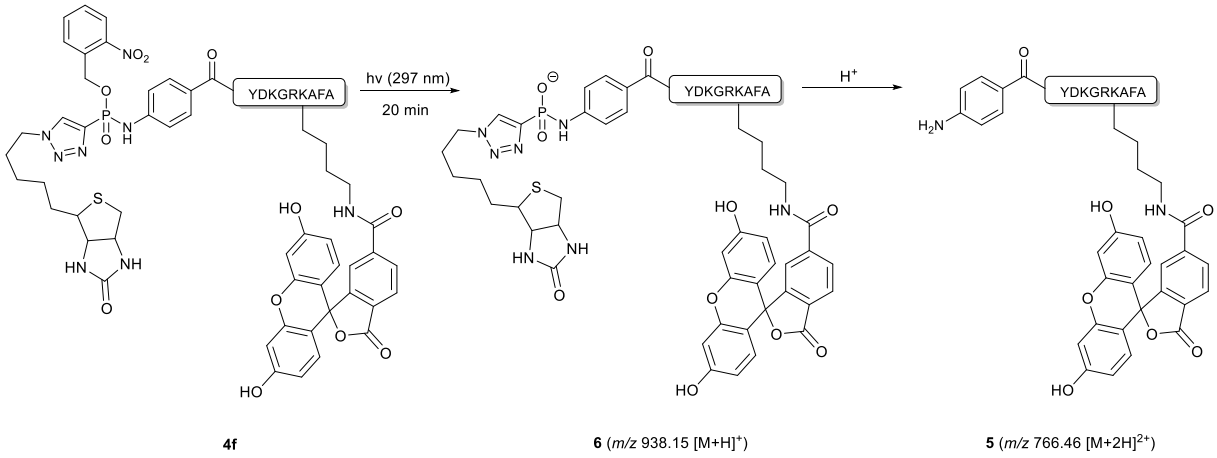


*Figure S1: Photocleavage of phosphonamidate **4f** in two steps. In the first step, 2-nitrosobenzaldehyde is released. In the second step, the reaction solution is acidified and the P-N bond is cleaved to release amine **5**.*

8.1 Release of amine **5** after irradiation of phosphonamidate **4f** via phosphonamidate acid **6**

Phosphonamidate **4f** (0.11 mg, 0.055 µmol) was dissolved in 50:50 NH_4HCO_3:MeCN (pH 7) to a final concentration of 0.038 mM. The probe was irradiated for 20 min at 297 nm and then analyzed by UPLC-MS. The dominant mass (*m/z* 938.15 $[M+H]^+$) corresponded to phosphonamidate acid **6** (see Figure S2) and only little amine **5** was observed. Similarly, the largest peak observed by fluorescence HPLC did not have the same retention time as our reference probe **2i** (see peptide synthesis, page 9). To initiate P-N bond cleavage, the solution was acidified to pH 3 with citric acid, incubated for 16 hrs and analyzed by fluorescence HPLC. Phosphonamidate acid **6** had disappeared and only amine **5** was observed, which had the same retention time as reference peptide **2i**.

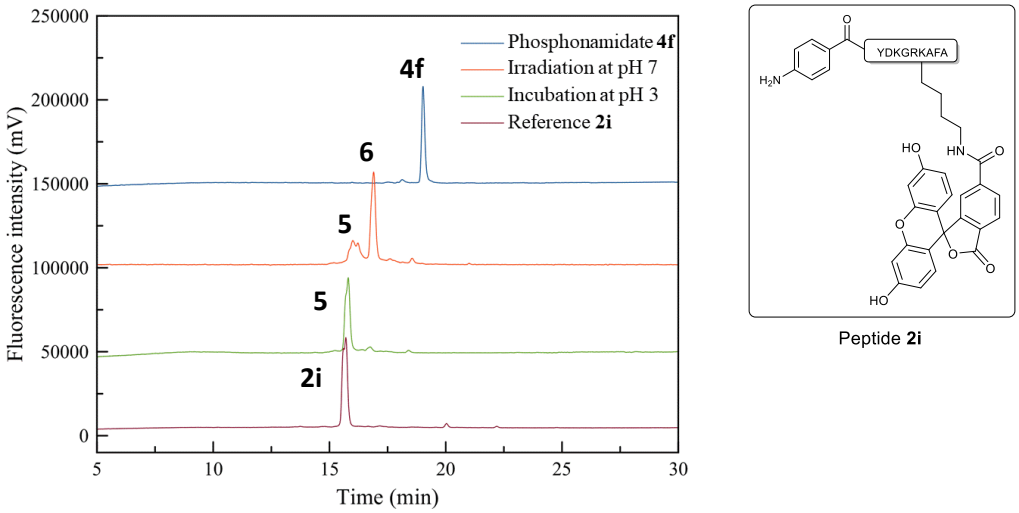


*Figure S2: The irradiation of phosphonamidate **4f** at pH 7 (blue line) led to the formation of phosphonamidate acid **6** and little amine **5** (red line). After incubation at pH 3, only amine **5** was observed (green line). It has the same retention time as reference probe **2i** (purple line).*

Column: Agilent Eclipse XDB C18, 4.6 x 250 mm (analytical HPLC)
Gradient: 5-95 % B in 30 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA)

8.2 Release of amine **5** after irradiation of phosphonamidate **4f** in 0.1% TFA/H_2O

Phosphonamidate **4f** (0.11 mg, 0.055 µmol) was dissolved in 0.1% TFA/H_2O (pH 2) to a final concentration of 0.038 mM. The probe was irradiated for 20 min at 297 nm and then incubated for 16 hrs at room temperature. It was then analyzed by fluorescence HPLC (see Figure 3) and UPLC-MS. Only amine **5** (*m/z* 766.46) was observed.

HPLC conditions for Figure 3:
Column: Phenomenex Synergi 4u Hydro-RP, 4.6 x 250 mm (analytical HPLC)
Gradient: 0-60 % B in 25 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA)

8.3 Stability of peptide **4f** in 0.1% TFA/H_2O

Phosphonamidate peptide **4f** was incubated for 16 hrs in 0.1 % TFA/H_2O (pH 2) and the stability was controlled by fluorescence HPLC. In case of P-N bond cleavage, amine **5** would be formed and have the same retention time as peptide **2i**, which was synthesized as a reference for P-N bond cleavage (see peptide synthesis, page 9).

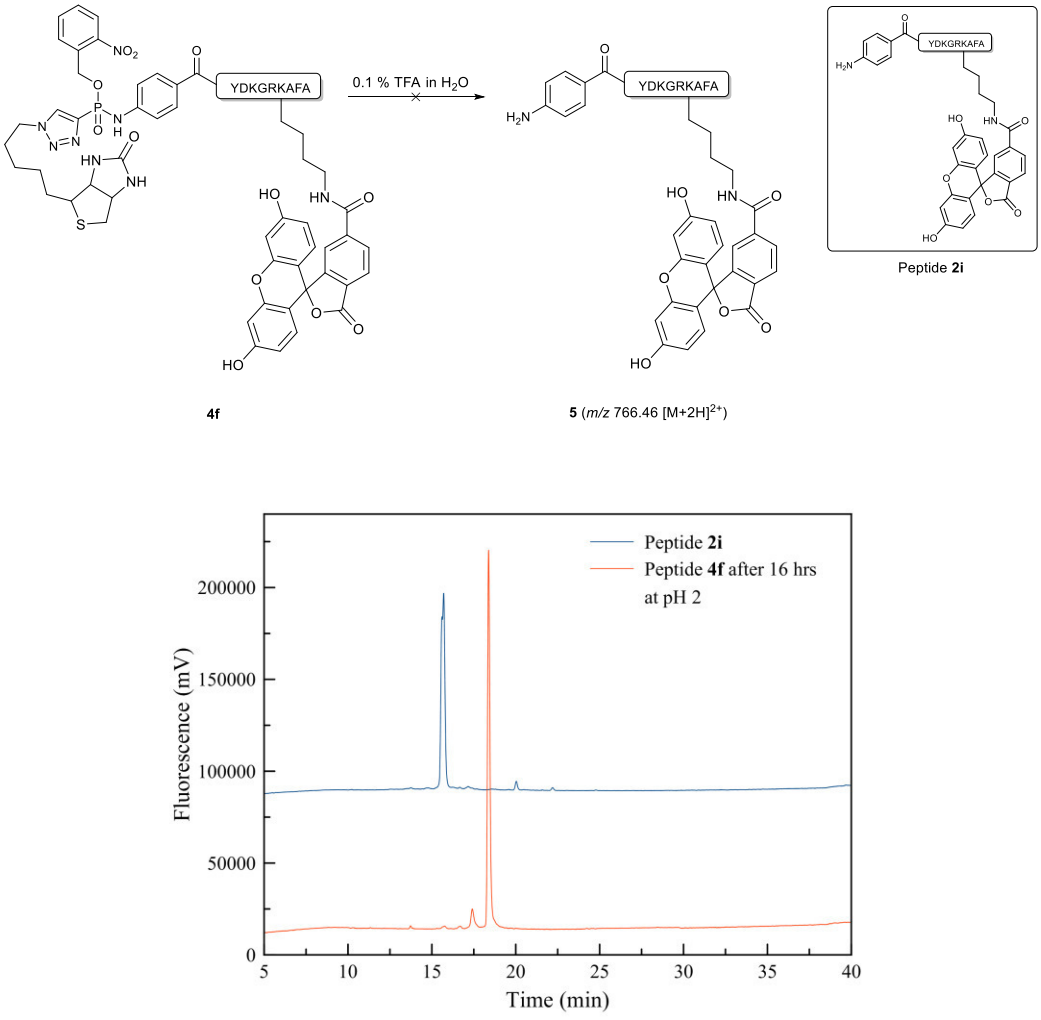


*Figure S3: No formation of amine **5** was observed after incubating phosphonamidate **4f** in 0.1 % TFA/H_2O (pH 2) for 16 hrs.*

No formation of amine **5** was observed after 16 hrs incubation, indicating that the P-N bond of phosphonamidate **4f** is stable at pH 2.

Column: Agilent Eclipse XDB C18, 4.6 x 250 mm (analytical HPLC)
Gradient: 5-95 % B in 30 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA)

8.4 Standard curve for quantification

To quantify the release, we measured the selected ion recording signal of product **5** by integration and compared the obtained area to a standard curve. Completion of irradiation and P-N bond cleavage was verified by UPLC-MS.

The standard curve was generated by measuring the selection ion recording series of a dilution series of peptide **2i** (0.1 mM, 0.05 mM, 0.01 mM, 0.005 mM, 0.001 mM). As ion, the double charged species $[M+2H]^{2+}$ = *m/z* 766.46 was chosen. 10 µL of each dilution was measured and the SIR area was recorded. In total, 3 dilution series were prepared and measured individually. The average of the three measurements was taken for each concentration and the values were plotted and evaluated using GraphPad Prism.

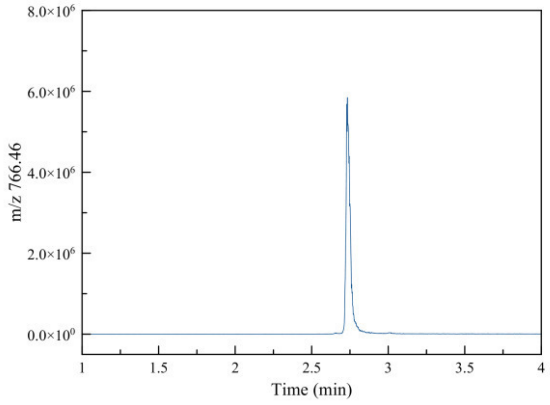


Figure S4: Example of SIR integration (m/z 766.46) for 0.01 mM: 2993497

All area values:

Concentration (mM)	Area *m/z* 766.46		
	1	2	3
0,1	17277860	17051690	21153450
0,05	10683560	10972540	11944450
0,025	3547550	3678688	3957134
0,01	2482786	2993497	3347351
0,005	1660579	1582266	1671098
0,001	337230	364484	512056

*Table T1: All area values from the SIR integration of **2i**.*

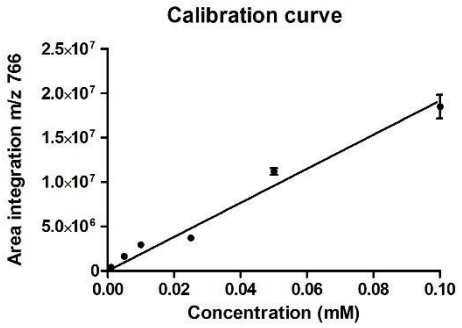


Figure S5: All area values were plotted and fitted

Slope: y = 183807092x

8.5 Quantification

Peptide **4f** (0.25 mg, 0.124 µmol) was dissolved in 150 µL 2:1 H_2O:MeCN (containing 0.1 % TFA). Concentration of peptide **4f**: 0.826 mM.

Three probes were prepared as follows: 15 µL (0.025 mg, 0.0124 µmol) of the stock solution of peptide **4f** were diluted to 200 µL 0.1 % TFA/H_2O (pH 2). Final peptide concentration: 0.062 mM.

Each probe was irradiated for 30 mins at 297 nm, then stirred for 2 hrs at room temperature to ensure P-N bond cleavage. The probes were then analyzed by SIR integration (*m/z* 766.46):

	Area measurement	Concentration (mM)	Release (%)
1	9970971	0.054	87
2	9539093	0.052	84
3	9404347	0.051	82

This results in an overall release of 84 % (± 2.5 %) of amine **5** after irradiation of peptide **4f**.

9. Immobilization and irradiation of beads

9.1 General procedure

For the immobilization of the biotin-phosphonamidates, the beads were first thoroughly washed with 20 mM NH_4HCO_3 (pH 7) buffer to remove the storage buffer. The biotin-phosphonamidates were dissolved in 20 mM NH_4HCO_3 (pH 7) with 5 % MeCN and added to the beads for 2 hrs at room temperature. The beads were then washed 3 times with 20 mM NH_4HCO_3 (pH 7) and 2 times with 0.1 % TFA/H_2O (pH 2). The beads were then transferred to a UV cuvette with a stirrer and were irradiated for 1 hr at 297 nm. Afterwards, the beads were incubated for further 16 hrs at room temperature, before the beads were filtered. The elution was lyophilized and analyzed by UPLC-MS or fluorescence HPLC.

9.2 Phosphonamidate **4f**

Phosphonamidate **4f** (0.19 mg, 0.094 µmol) was dissolved in 400 µL 20 mM NH_4HCO_3 (pH 7) with 5 % MeCN and added to 200 µL beads (dead volume) of GE Healthcare Sepharose Streptavidin beads. The beads were shaken for 2 hrs at room temperature and were then washed three times with 500 µL 20 mM NH_4HCO_3 (pH 7) and two times with 500 µL 0.1 % TFA/H_2O (pH 2). The beads were suspended in 500 µL 0.1 % TFA/H_2O (pH 2), transferred into an UV Quartz cuvette and irradiated for 1 hr at room temperature at 297 nm, followed by 16 hrs incubation. The elute was lyophilized, re-dissolved in 50 µL 50:50 H_2O:MeCN each and analyzed by fluorescence HPLC (see Figure 4).

HPLC conditions for Figure 4:
Column: Agilent Eclipse XDB C18, 4.6 x 250 mm (analytical HPLC)
Gradient: 5-95 % B in 30 mins (Solvent A: H_2O + 0.1% TFA, solvent B: MeCN + 0.1 % TFA)

9.3 Evaluation of different buffers for release of peptide

Streptavidin beads only have a limited stability below pH 3. We therefore wanted to evaluate whether the release of phosphonamidate **4f** from streptavidin beads could be carried out at pH 3 instead of pH 2. To do so, the phosphonamidate-conjugate was immobilized at pH 7 and the irradiation and incubation was carried out in a citric acid-phosphate buffer at pH 3. To check if all the peptide had eluted, the beads were additionally incubated at pH 2 to see whether any more fluorescent peptide was released.

Phosphonamidate **4f** (0.1 mg, 0.049 µmol) was dissolved in 300 µL 20 mM NH_4HCO_3 (pH 7) with 5 % MeCN and added to 150 µL streptavidin beads (dead volume). The beads were shaken for 2 hrs at room temperature and then washed three times with 300 µL NH_4HCO_3 (pH 7) and two times with 300 µL 0.1 % TFA/H_2O (pH 2). The beads were suspended in 300 µL citric acid-phosphate buffer (pH 3), transferred into an UV Quartz cuvette and irradiated for 1 hr at room temperature at 297 nm, followed by 16 hrs incubation. The beads were washed 3 times with 300 µL citric acid-phosphate buffer (pH 3) and once quickly with 300 µL 0.1 % TFA/H_2O (pH 2), before they were suspended in 300 µL 0.1 % TFA/H_2O (pH 2) for 2 hrs. The elutes were lyophilized, re-dissolved in 50 µL 50:50 H_2O:MeCN each and analyzed by fluorescence HPLC (see Figure S6) and UPLC-MS.

As shown in Figure S6, pH 3 could initiate P-N bond cleavage. However, not all of amine **5** was released. Incubation at pH 2 led to additional elution of amine **5**, suggesting that pH 3 is not sufficient to achieve full P-N bond cleavage of phosphonamidate acid **6** on beads.

As control, beads were loaded with phosphonamidate **4f**, but the beads were only incubated at pH 2 without irradiation. The elute was analyzed by UPLC-MS and no release could be observed.

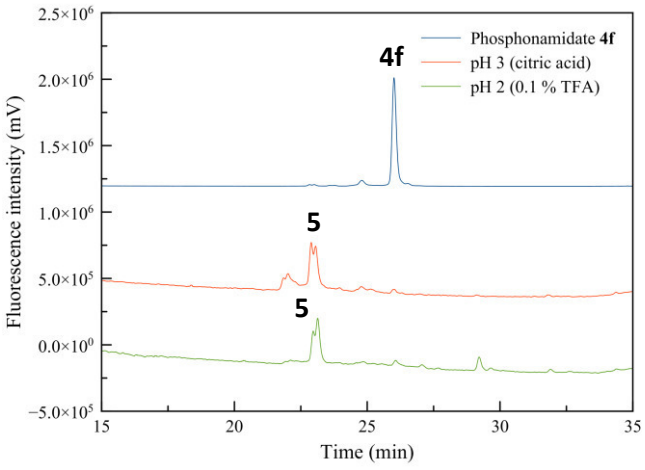


*Figure S6: Phosphonamidate **4f** was immobilised on streptavidin beads (blue), then irradiated and eluted at pH 3 (red) and pH 2 (green) to release amine **5**.*

9.4 Streptavidin beads degradation in 0.1% TFA/H_2O

To probe the stability of streptavidin beads in 0.1% TFA/H_2O, a sample of streptavidin beads was incubated in 0.1% TFA/H_2O overnight and the elute was analyzed by UPLC-MS. The UV trace was measured at 220 nm and 272 nm. A broad elution peak could be seen, suggesting that the beads only have limited stability in 0.1% TFA/H_2O.

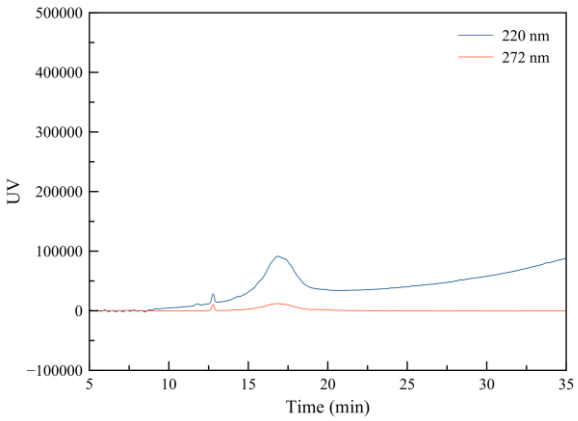


Figure S7: Streptavidin beads were incubated for 16 hrs and the elute was analyzed by UPLC-MS. The UV traces for 220 and 272 nm are shown.

Literature:

1. T. Suzuki, Y. Ota, Y. Kasuya, M. Mutsuga, Y. Kawamura, H. Tsumoto, H. Nakagawa, M. G. Finn and N. Miyata, *Angewandte Chemie International Edition*, 2010, **49**, 6817-6820.
2. S. G. Alvarez and M. T. Alvarez, *Synthesis*, 1997, **1997**, 413-414.
3. A. Cwiklicki and K. Rehse, *Archiv der Pharmazie*, 2004, **337**, 156-163.
4. S. N. Lam, P. Acharya, R. Wyatt, P. D. Kwong and C. A. Bewley, *Bioorganic & Medicinal Chemistry*, 2008, **16**, 10113-10120.

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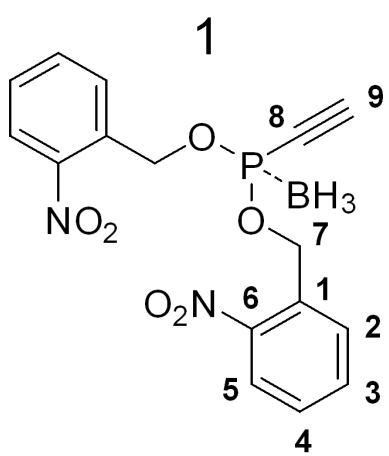

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5.6506 5.6244 5.6009 5.5905 5.5746 5.5640 5.5405 5.5143

3.3222 3.2977

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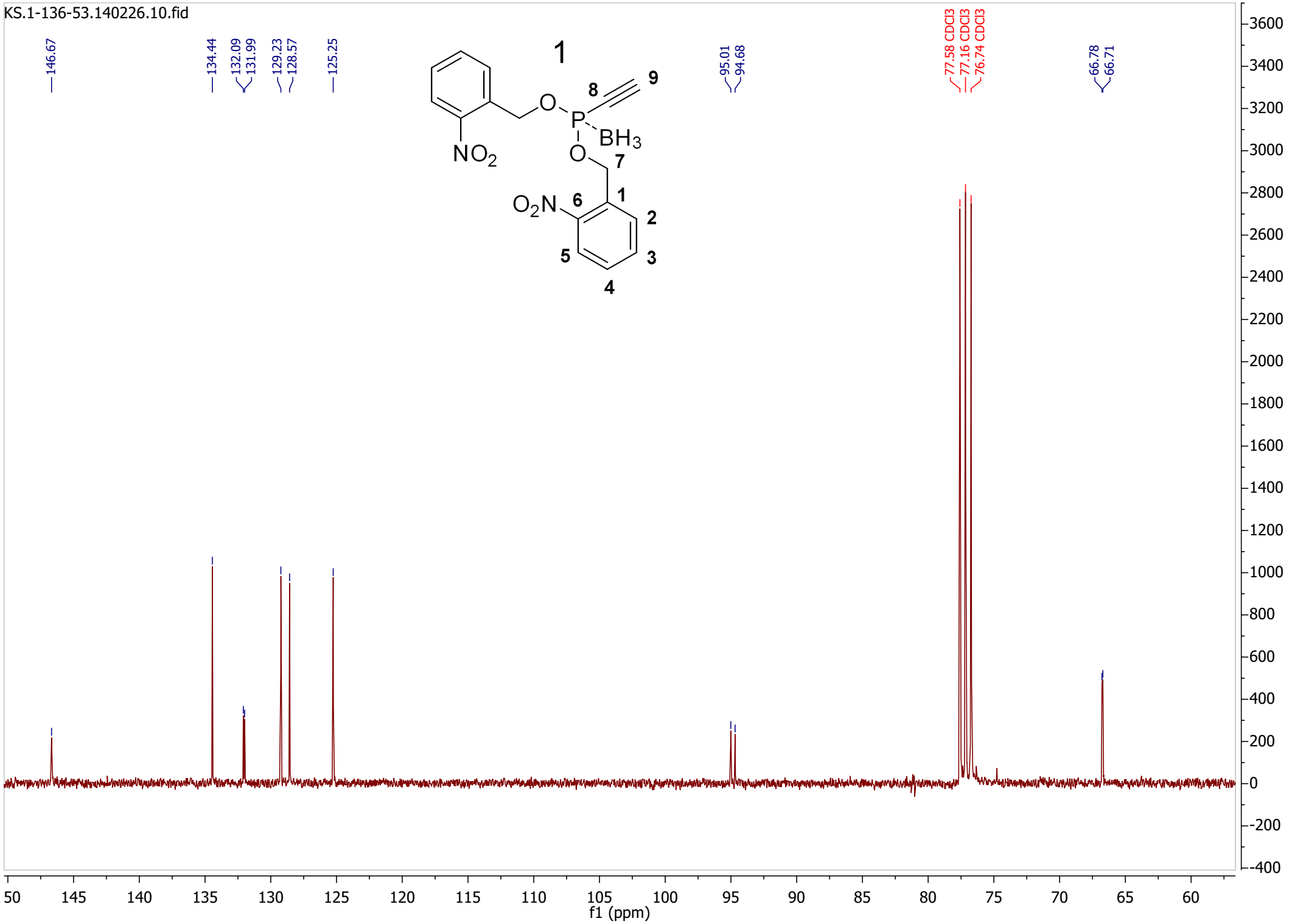

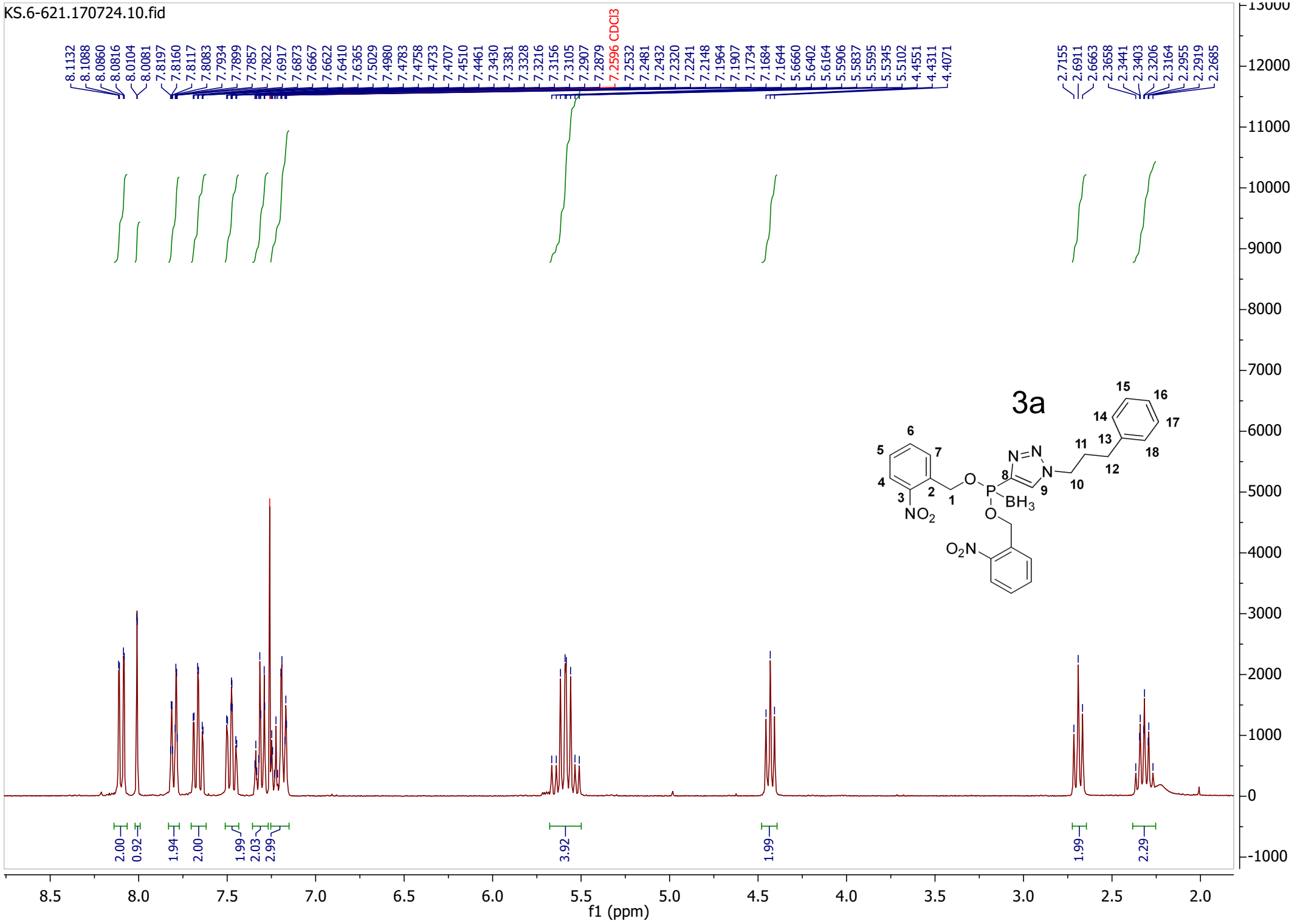
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f1 (ppm)

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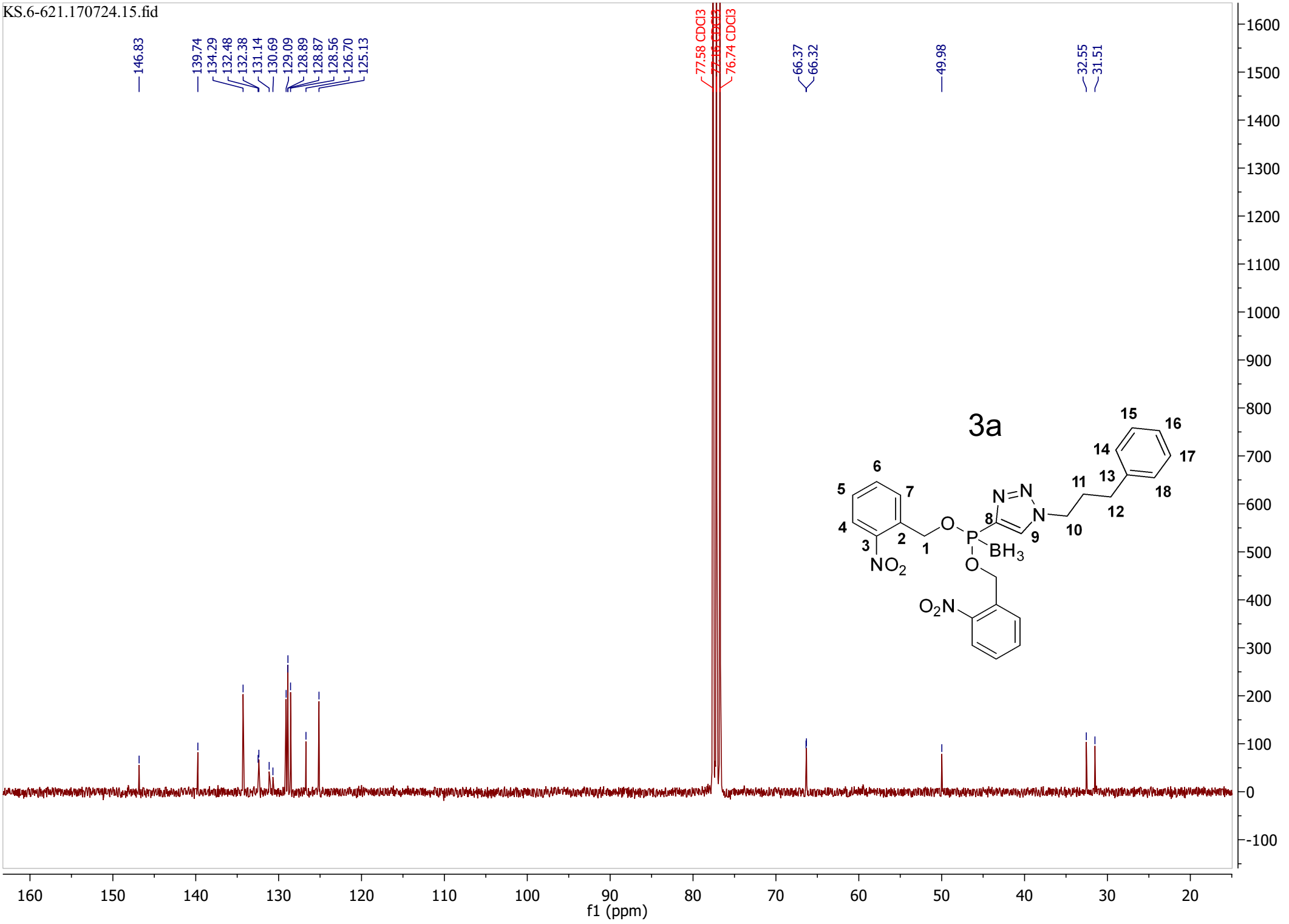

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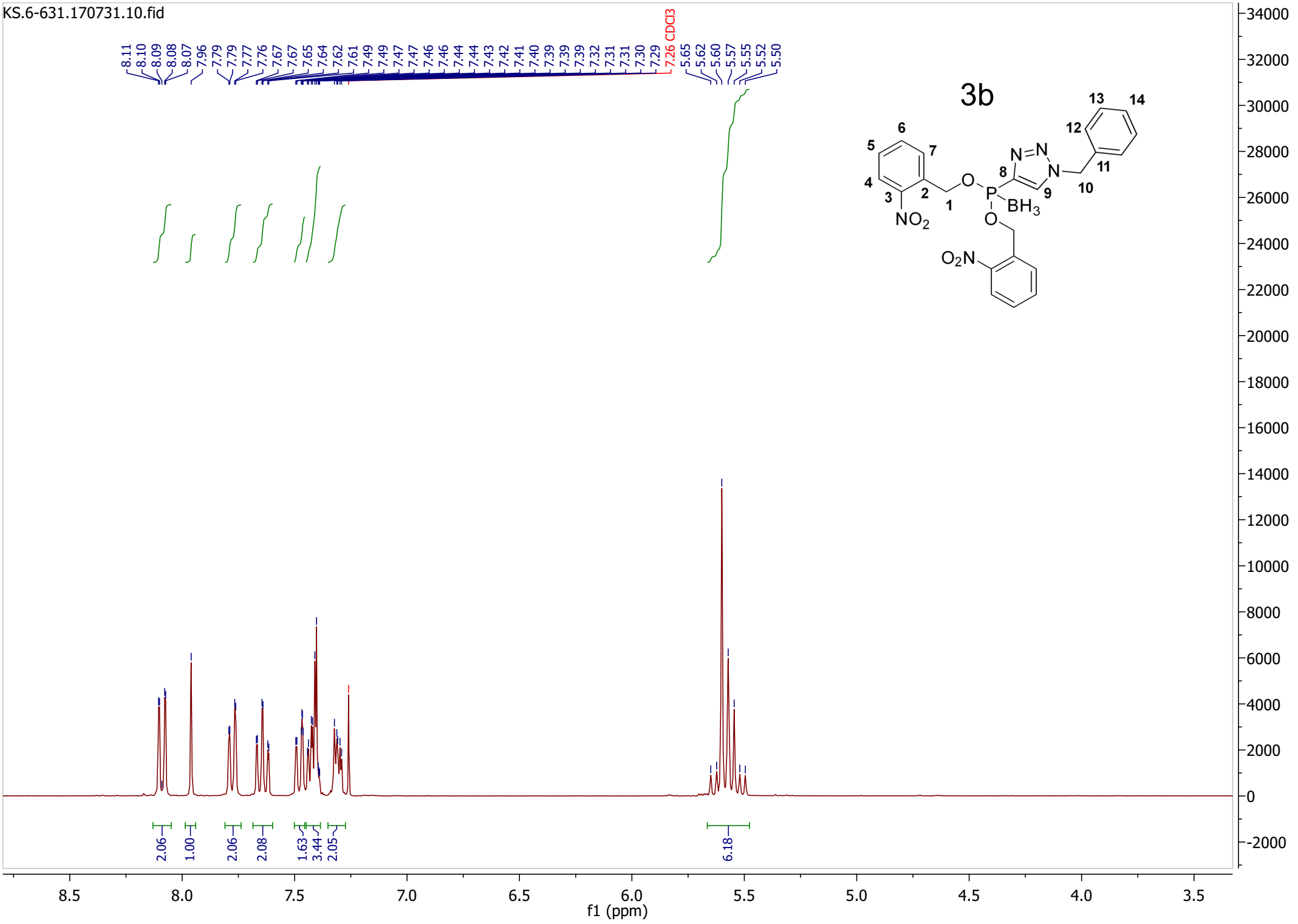

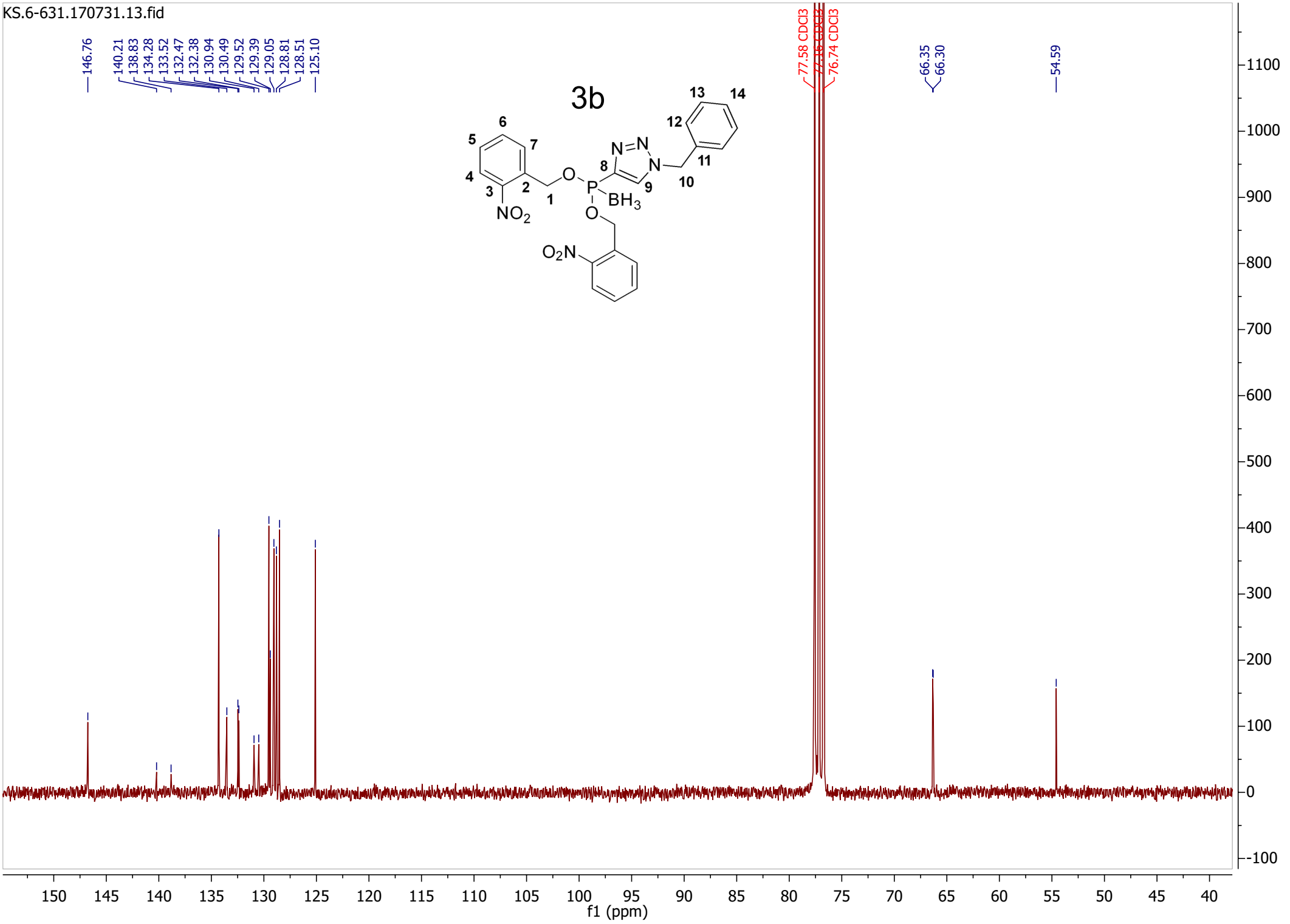
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128.51
125.10
77.58 CDCl3
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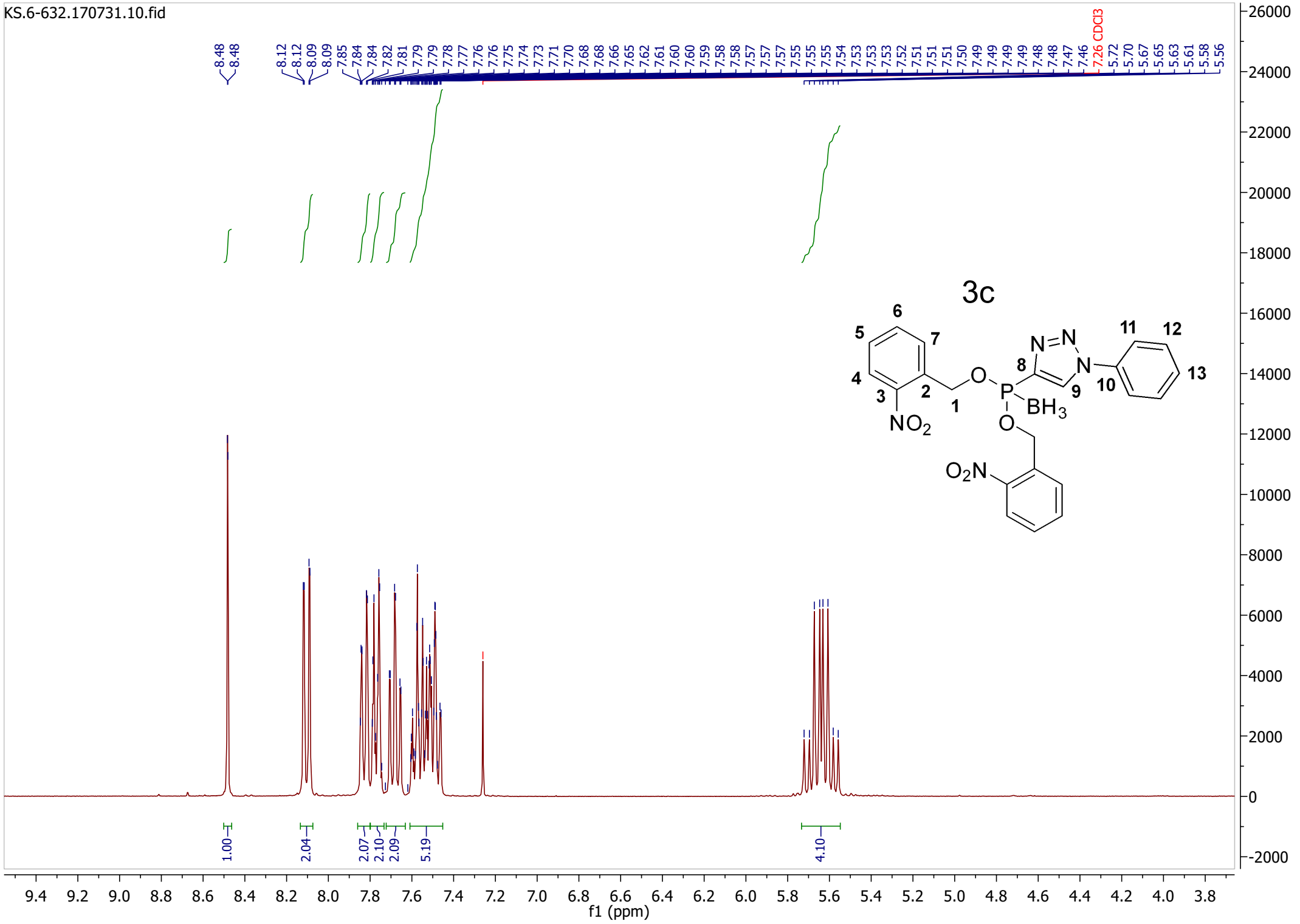
76.74 CDCl3
66.35
66.30
54.59
3b
NO2
O2N
BH3
f1 (ppm)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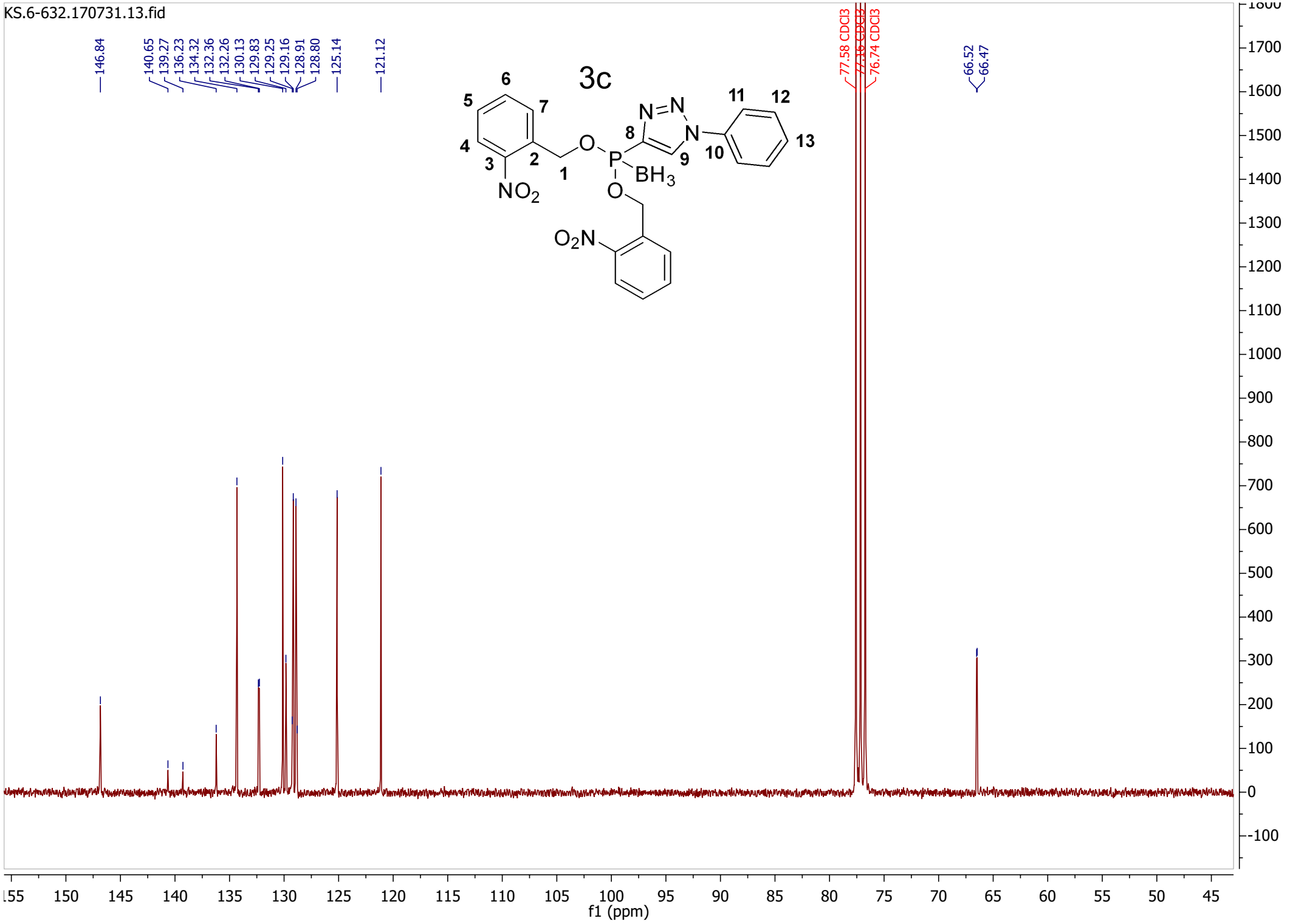
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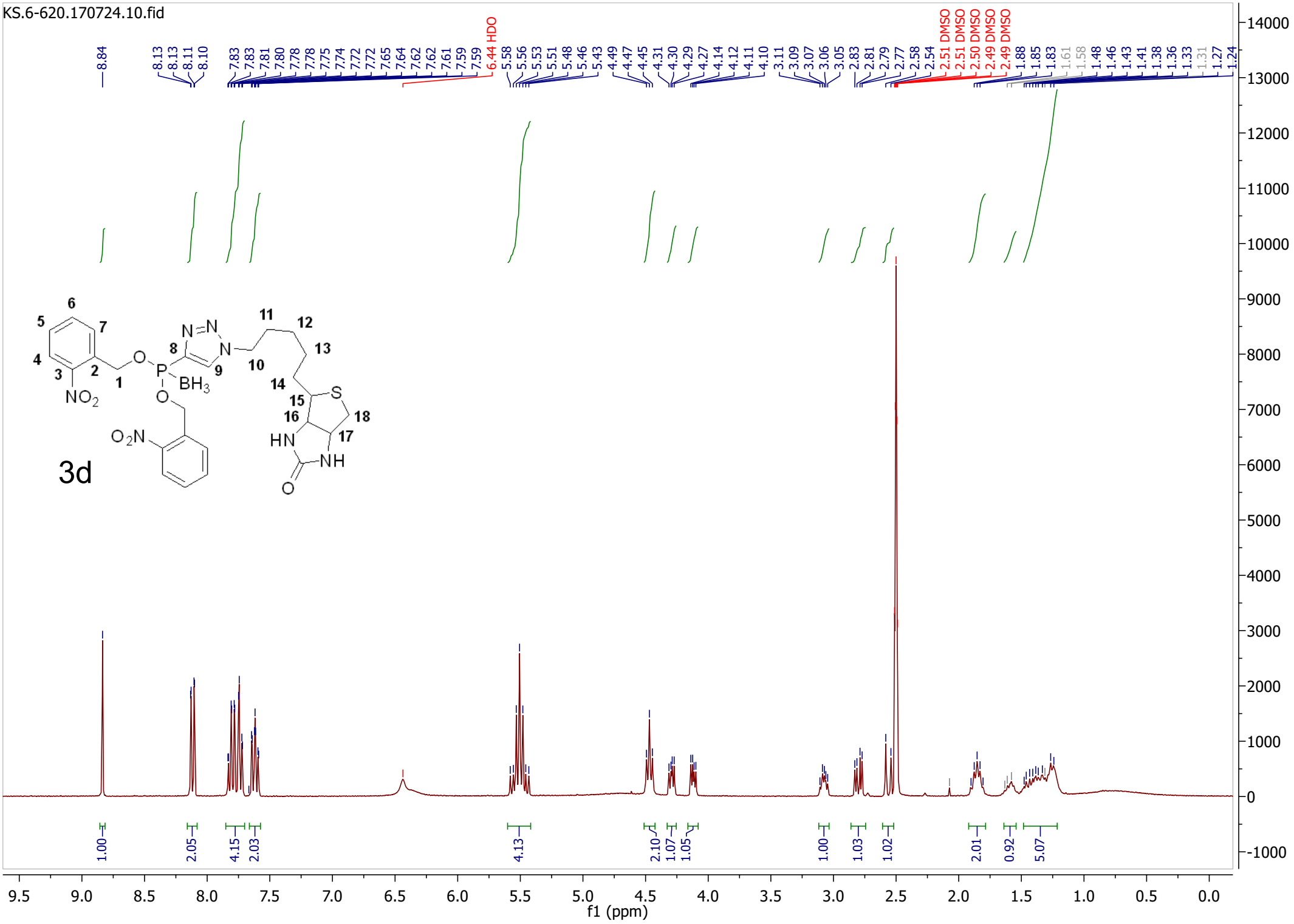
3c
NO2
O2N
BH3
f1 (ppm)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7.61
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1.38
1.36
1.33
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1.27
1.24
3d
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4.15
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f1 (ppm)

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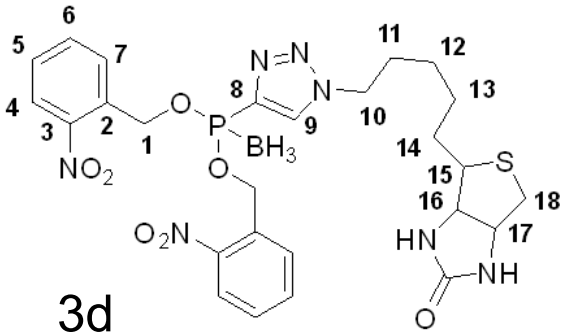

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f1 (ppm)

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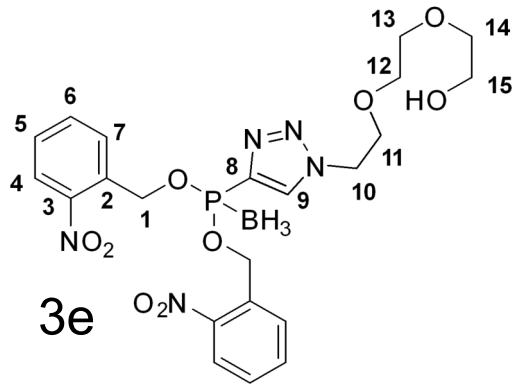

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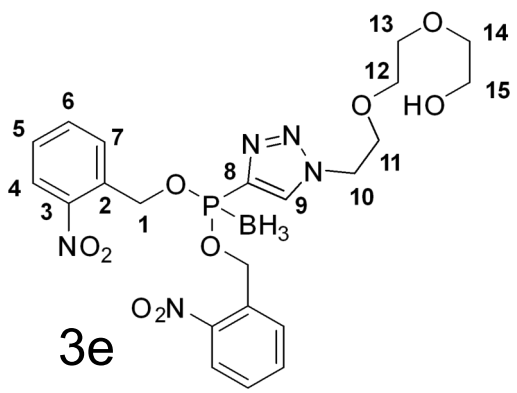

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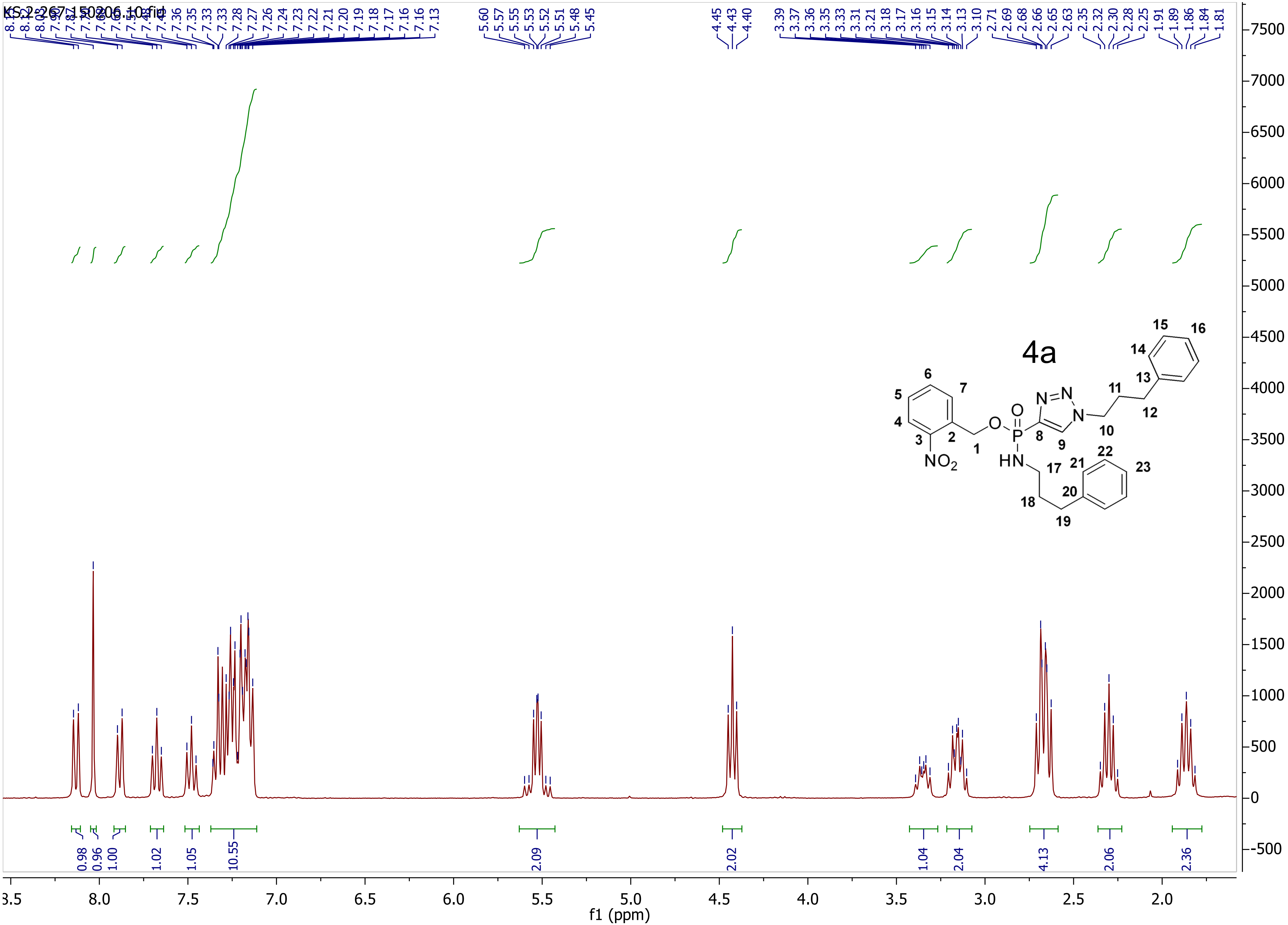

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4a
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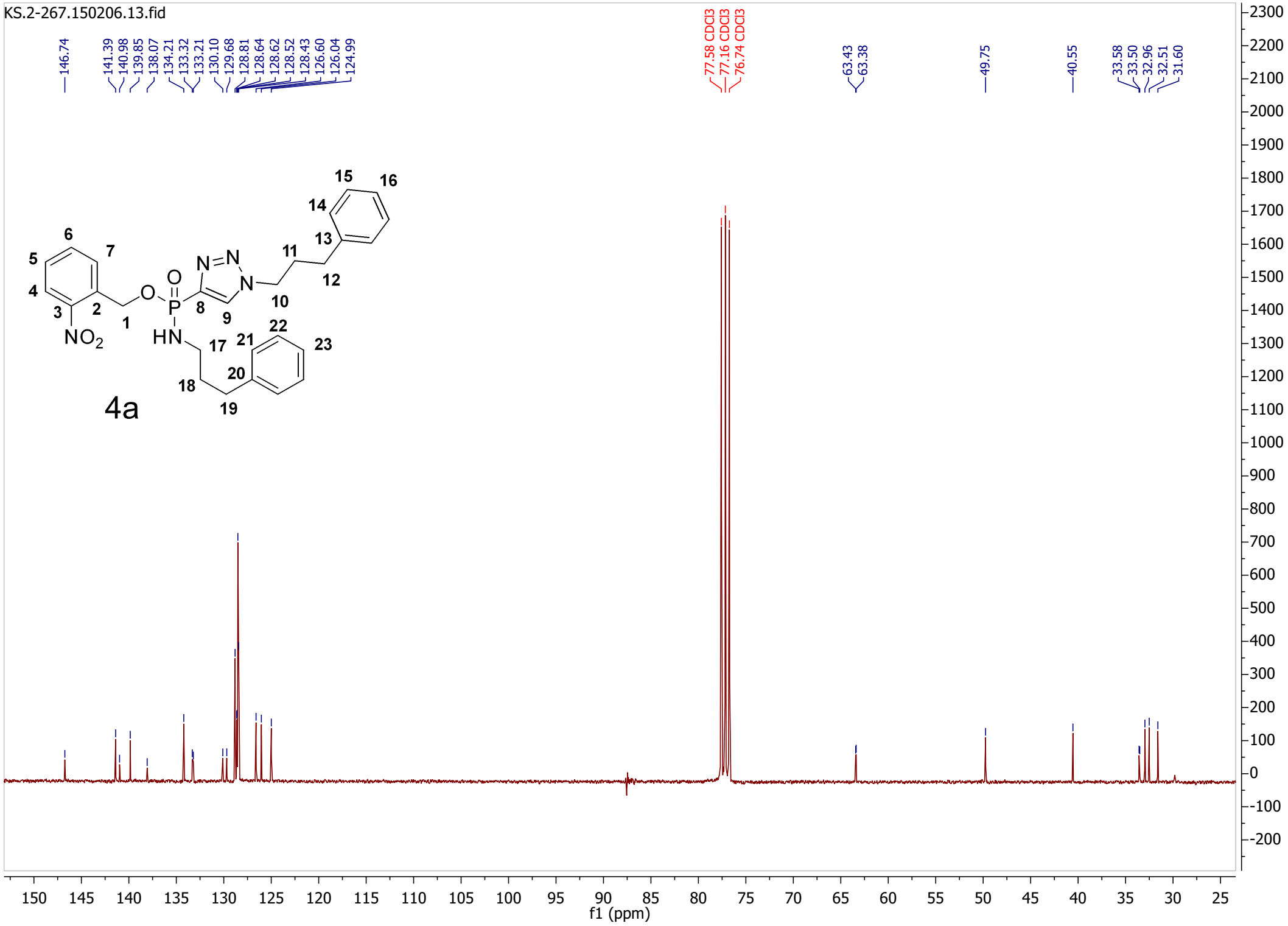
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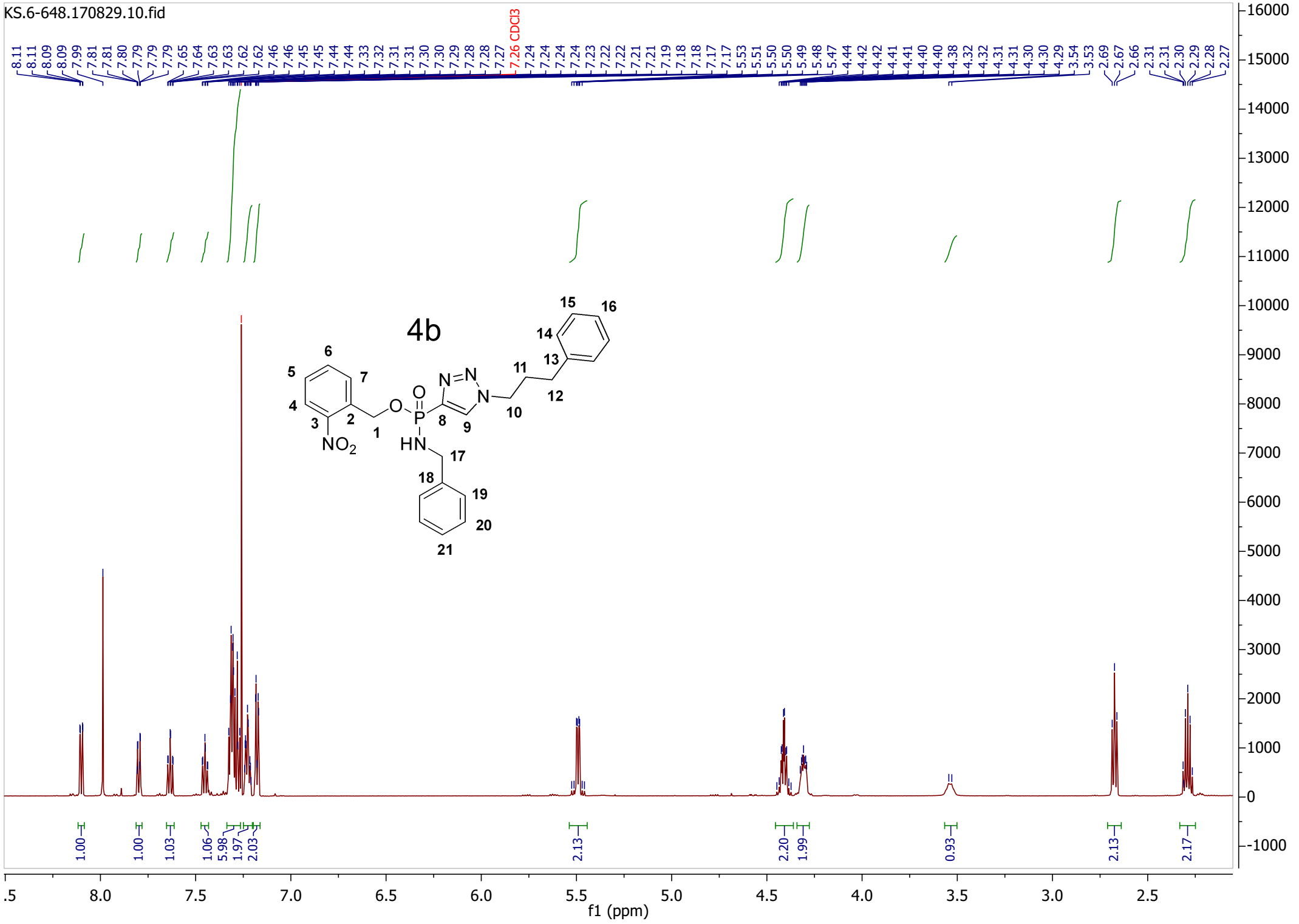
f1 (ppm)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4b
f1 (ppm)

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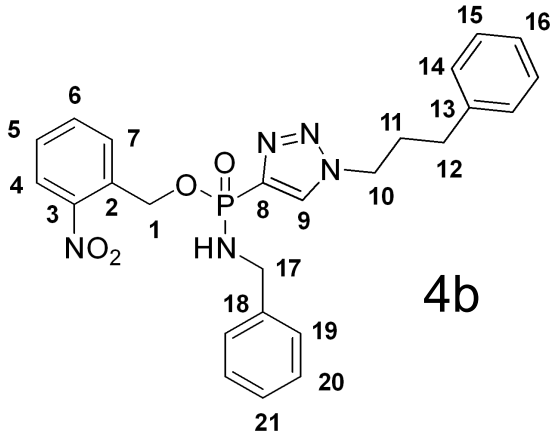

4b

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40000
35000
30000
25000
20000
15000
10000
5000
0

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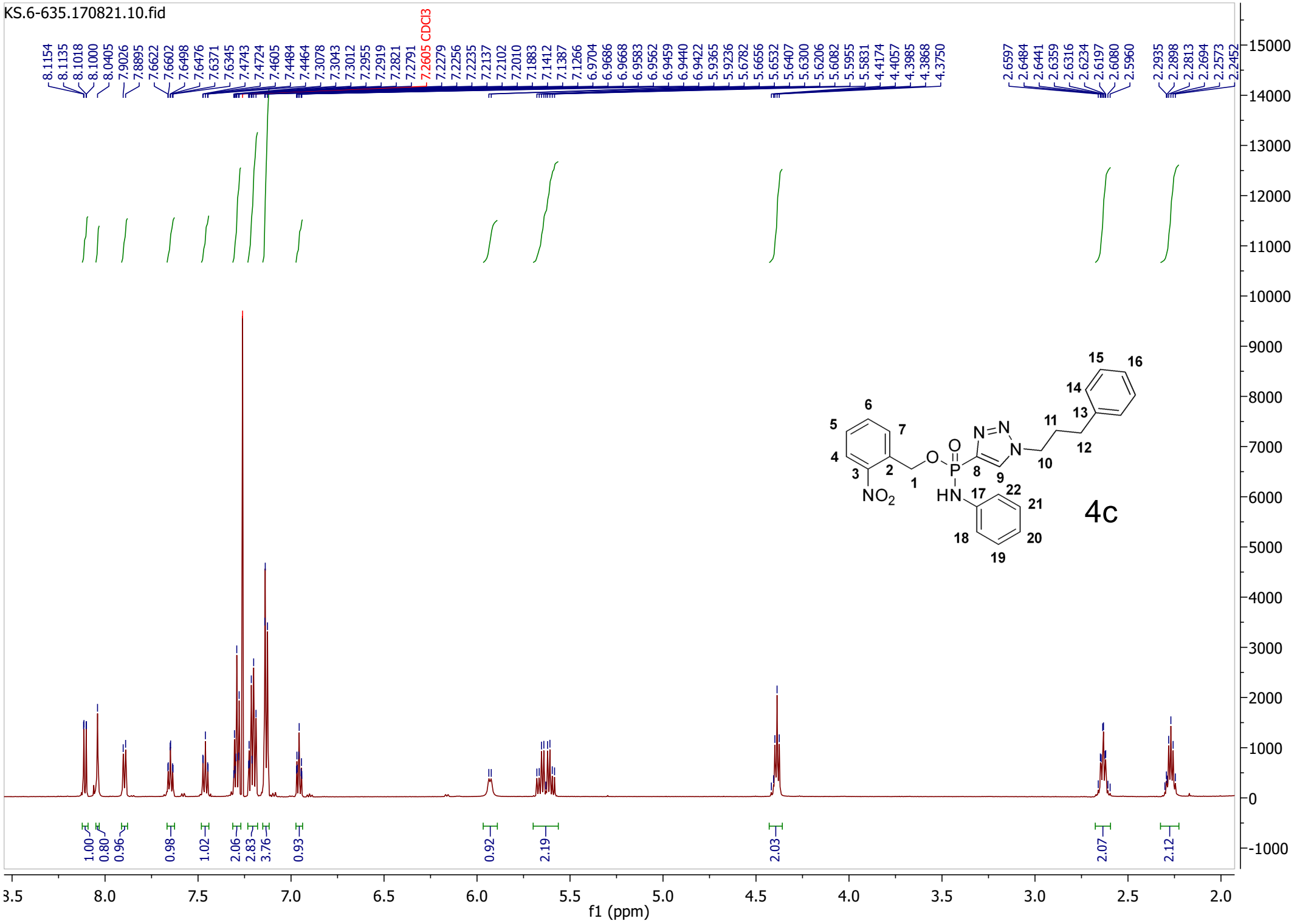
f1 (ppm)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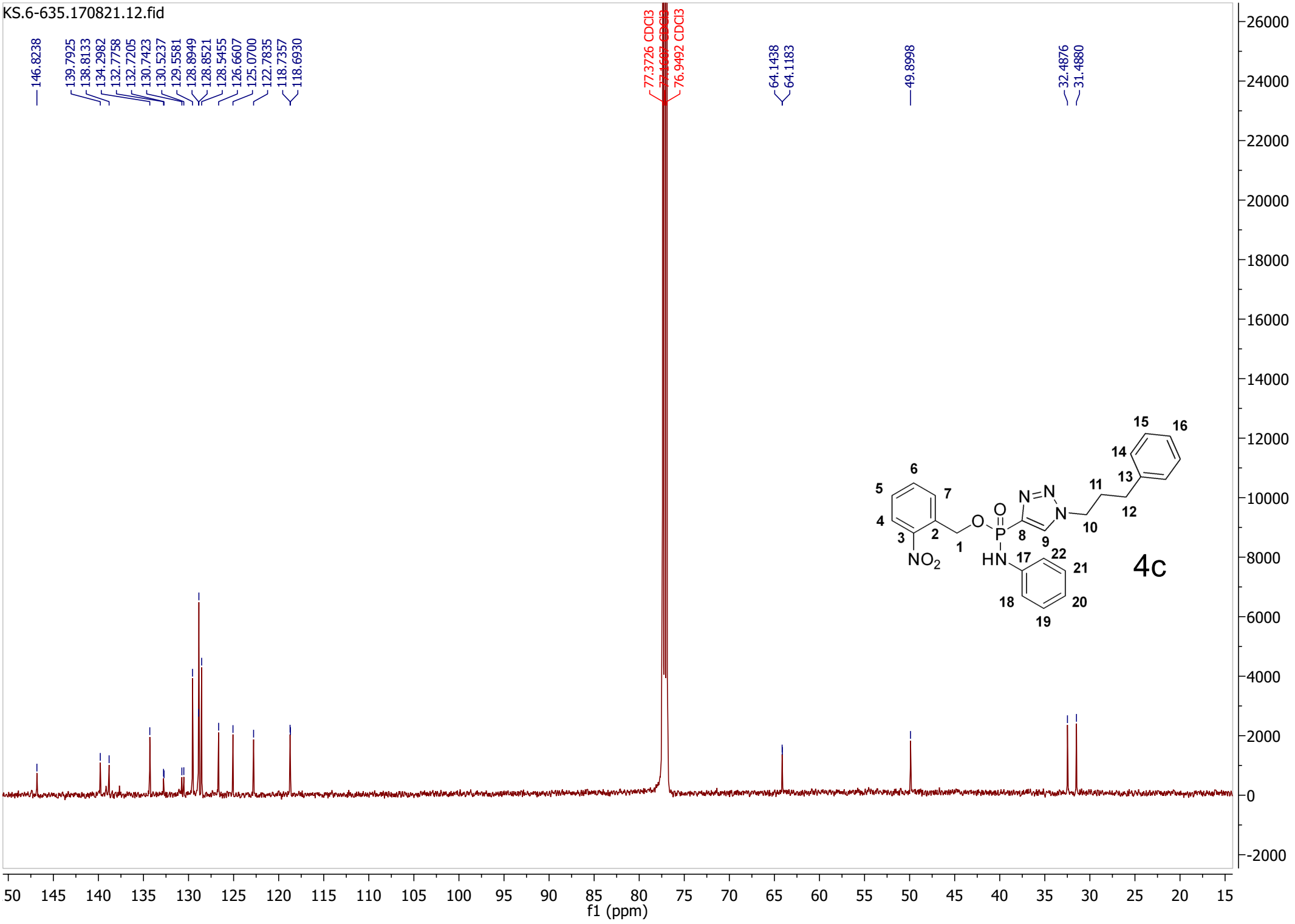
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4c
f1 (ppm)