Supplementary Information

Synthesis of photoactivable Pt(IV) prodrug loaded on $NaYF_4$ based upconversion nanoparticles functionalized with 2-deoxy-D-glucose and its evaluation for targeted cancer therapy

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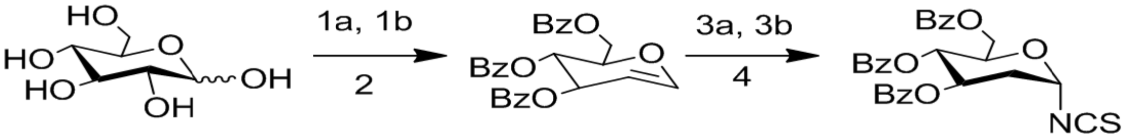
1 Synthesis of 2-deoxy-D-glucose derivatives and their characterization data: ^{1}H and ^{13}C{^{1}H} NMR spectra in $CDCl_3$

1a Synthesis of 2-deoxy-D-glucose isothiocyante



Scheme 1 — (1a) benzoyl chloride, pyridine; (1b) HBr (33%) in acetic acid, DCM; (2) Zn, NH_4Cl in acetonitrile, reflux; (3a) HBr (catalytic amount), Ac_2O, acetic acid; (3b) HBr (33%) in acetic acid, DCM; (4) KSCN, TBAB, reflux.

1b Synthesis of 1,2,3,4,5-penta-O-benzoyl-glucopyranose

To D-glucose (10 g, 60 mmol) in pyridine (40 ml) at 0 °C, benzoyl chloride (39 ml, 300 mmol) was added under argon atmosphere. The reaction was allowed to stir at room temperature for overnight. When the reaction completed, the reaction mixture was diluted with chloroform (50 ml) and washed with ice cooled HCl solution followed by washing with saturated aqueous solution of sodium carbonate. The organic layer was concentrated giving a fine white powder which was characterized with FT-IR, NMR spectroscopy and elemental analyses.

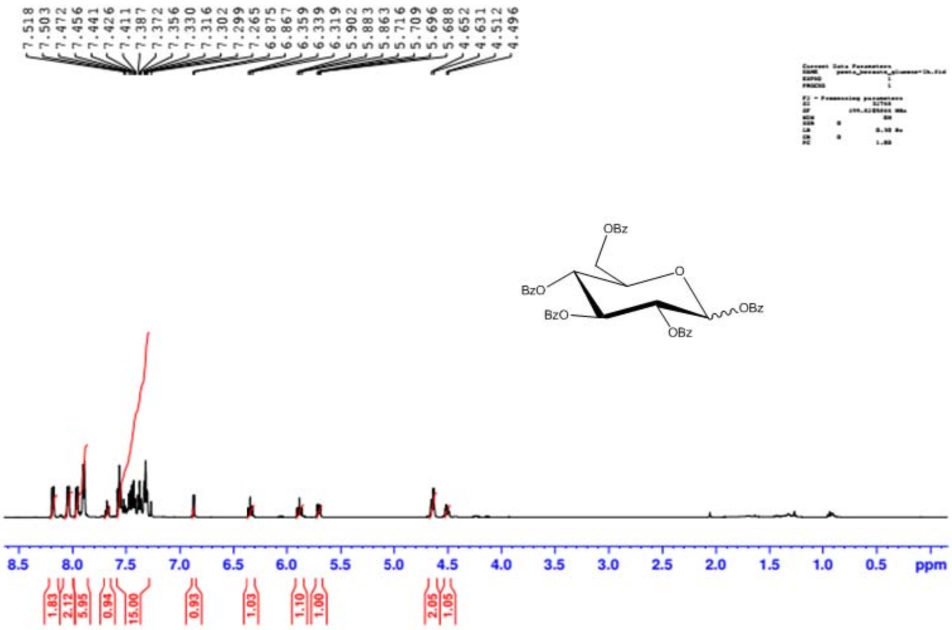


Fig. S1 — ^{1}H NMR spectrum of 1,2,3,4,5-penta-O-benzoyl-glucopyranose in $CDCl_3$

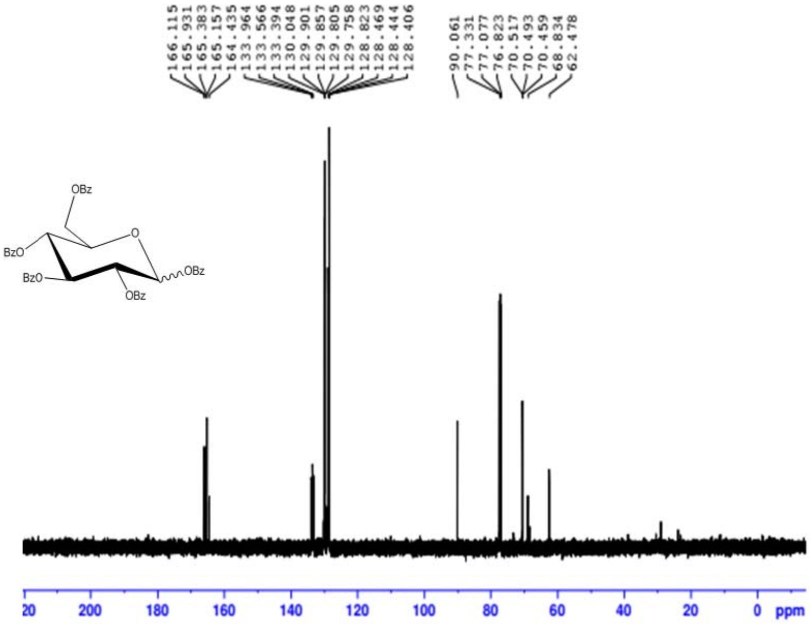


Fig. S2 — $^{13}C\{^{1}H\}$ NMR spectrum of 1,2,3,4,5-penta-O-benzoyl-glucopyranose in $CDCl_3$

1c Synthesis of2,3,4,5-tetra-O-benzoyl-glucopyranosyl bromide

Following the procedure as given in 1a, bromination of 1,2,3,4,5-penta-O-benzoyl-glucopyranose(5 g, 7 mmol) was done. A white precipitate obtained was characterized with FT-IR, NMR spectroscopy and elemental analyses.

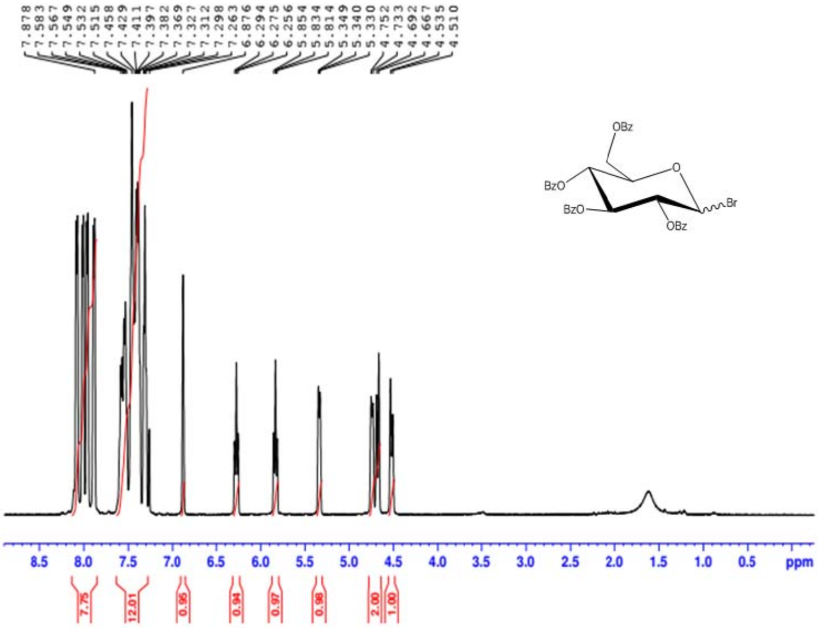


Fig. S3 — ^{1}H NMR spectrum of 2,3,4,5-tetra-O-benzoyl-glucopyranosyl bromide in $CDCl_3$

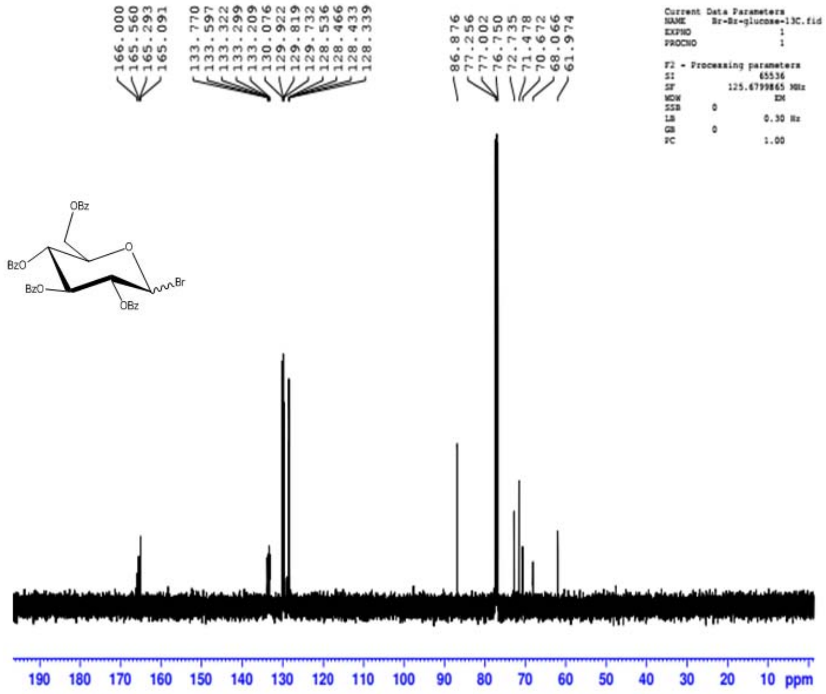


Fig. S4 — ^{13}C{^{1}H} NMR spectrum of 2,3,4,5-tetra-O-benzoyl-glucopyranosyl bromide in $CDCl_3$

1d Synthesis of 1-O-acetyl-3,4,5-tri-O-benzoyl-2-deoxyglycopyranose

To a compound 2,3,4,5-tetra-O-benzoyl-glucopyranosyl bromide (3 g, 5 mmol) dissolved in acetonitrile under an inert atmosphere of argon, To this reaction mixture the Zn metal powder (2.3 g, 40 mmol) and NH_4Cl (2 g, 40 mmol) were added. The resulted reaction mixture was refluxed till the completion of the reaction. After cooling to room temperature, the reaction mixture was filtered through Whatman filter paper (No. 41) and the solvent was evaporated. Further, the reaction is worked up with chloroform, concentrated and characterized with NMR spectroscopy.

To a solution of obtained compound (2 g) in acetonitrile (50 ml), acidic resin (DOWEX resin) (4 g), LiBr (4 g) was added. Later, water (4 ml) was added and stirred for 24h at room temperature. After completion of the reaction, the resin was removed by filtration and the filtrate was concentrated under reduced pressure. The reaction product was worked up with chloroform. The obtained compound was further dissolved in DCM (10 ml) and pyridine (5 ml) mixture. Acetic anhydride (10 ml) was added to the reaction mixture at 0 ^{o}C and allowed to stir overnight at room temperature. The reaction mixture was worked up with chloroform and used for next process without doing further purification.

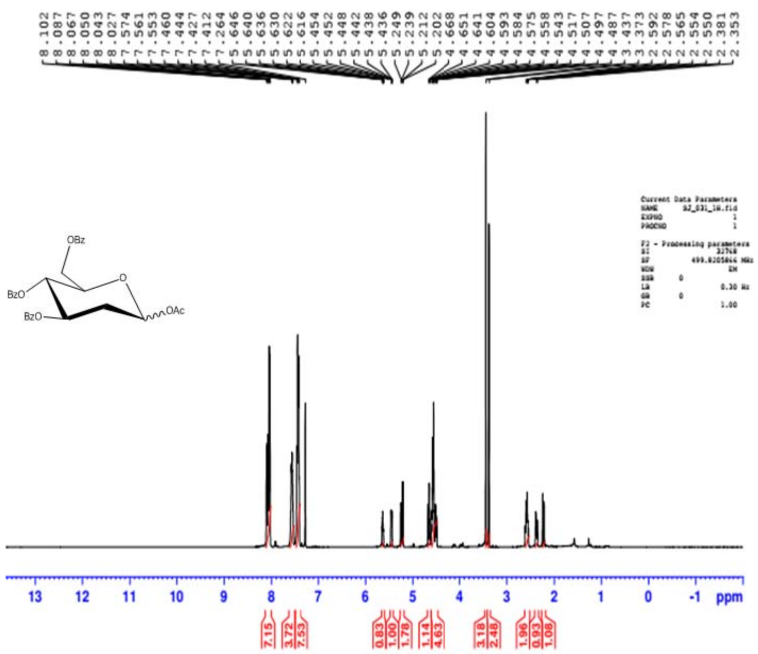


Fig. S5 — ^{1}H NMR spectrum of 1-O-acetyl-3,4,5-tri-O-benzoyl-2-deoxyglycopyranose in CDCl$_3$

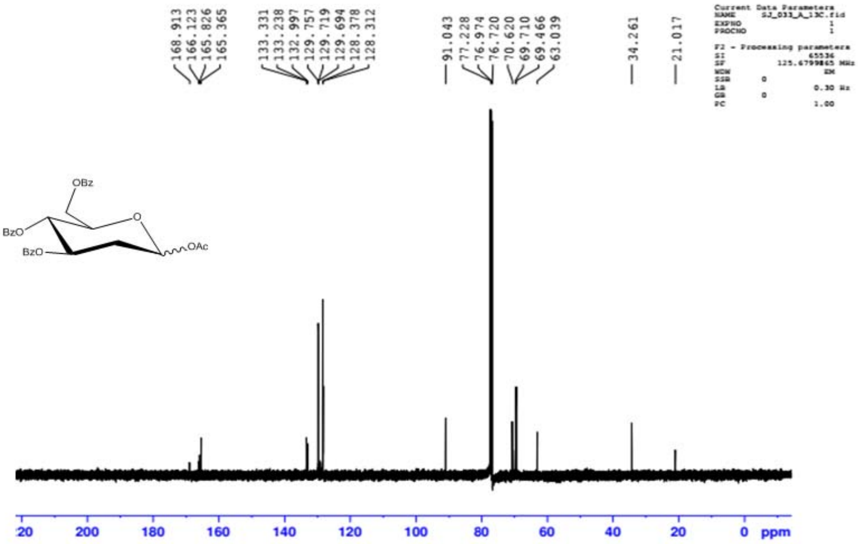


Fig. S6 — ^{13}C{^{1}H} NMR spectrum of 1-O-acetyl-3,4,5-tri-O-benzoyl-2-deoxyglycopyranose in CDCl$_3$

1e Synthesis of 3,4,5-tri-O-benzoyl-2-deoxyglycopyranosyl bromide

Following the procedure of bromination of earlier pyranosederivative (1 g) was done and without doing any further purification and the obtained compound was used for next reaction.

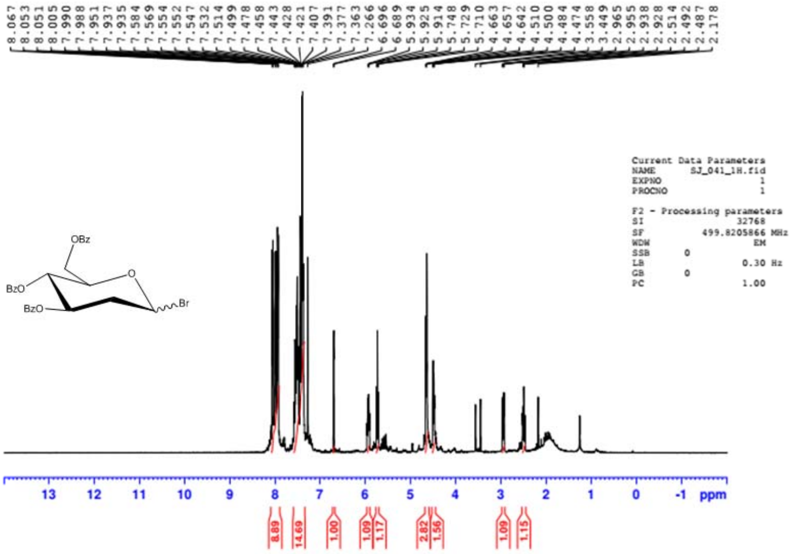


Fig. S7 — ^{1}H NMR spectrum of 3,4,5-tri-O-benzoyl-2-deoxyglycopyranosyl bromide in $CDCl_3$

1f Synthesis of 3,4,5-tri-O-benzoyl-2-deoxyglycopyranosyl thiocyanate

Potassium thiocyanate (2 mmol) and tetrabutylammonium bromide (TBAB) (1 mmol) were added to acetonitrile (40 ml) containing molecular sieves 4 Å (1.5 g). After stirring for 3 h, the 3,4,5-tri-O-benzoyl-2-deoxyglycopyranosyl bromide was added and refluxed for 3 h. After filtering the reaction mixture using Whatman filter paper no. 41, the organic layer was collected, worked up with chloroform and concentrated under reduced pressure and characterized with FT-IR, NMR spectroscopy and elemental analyses.

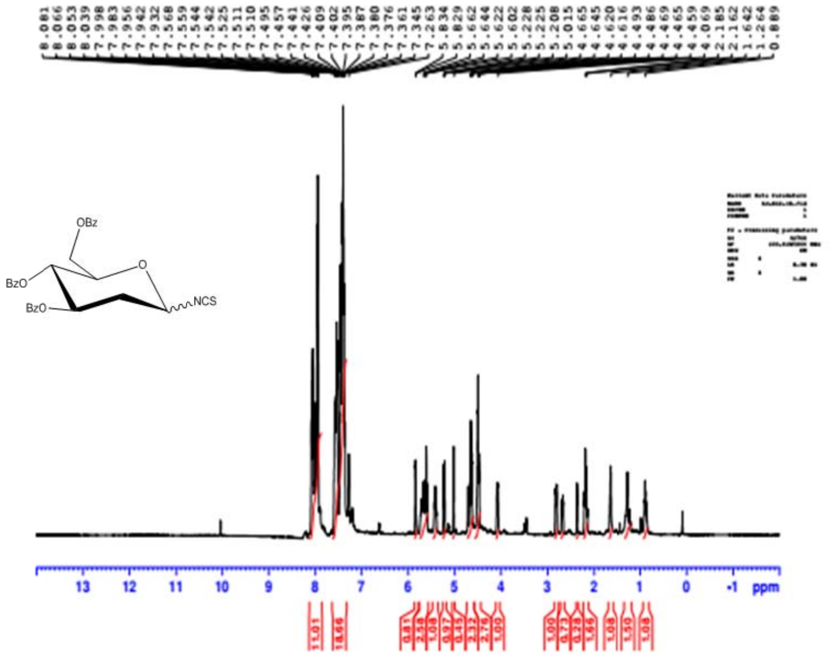
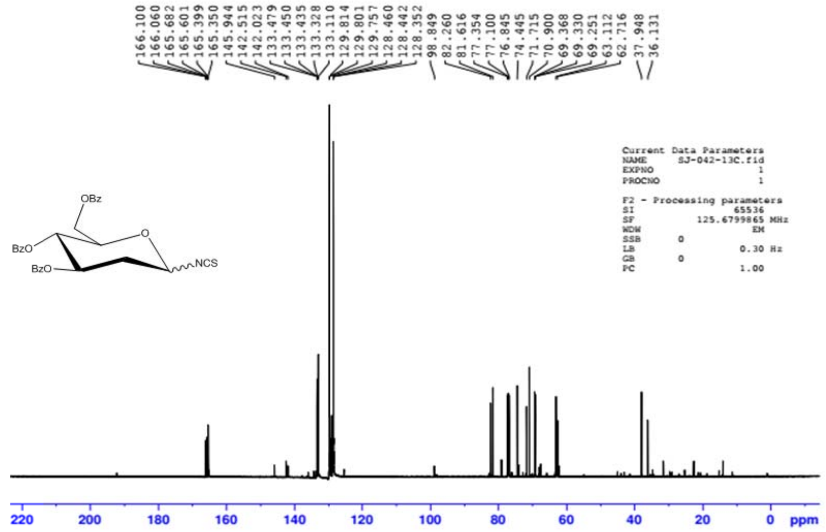


Fig. S8 — ^{1}H NMR spectrum of 3,4,5-tri-O-benzoyl-2-deoxyglycopyranosyl thiocyanate in $CDCl_3$



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PROCNO                  1

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Fig. S9 — $^{13}C\{^1H\}$ NMR spectrum of 3,4,5-tri-O-benzoyl-2-deoxyglycopyranosyl thiocyanate in $CDCl_3$

2 Characterization ofcis-$[PtI_2(NH_3)_2(OCOCH_2CH_2COOH)_2]$:$^1H$ and $^{13}C\{^1H\}$NMR spectral analyses

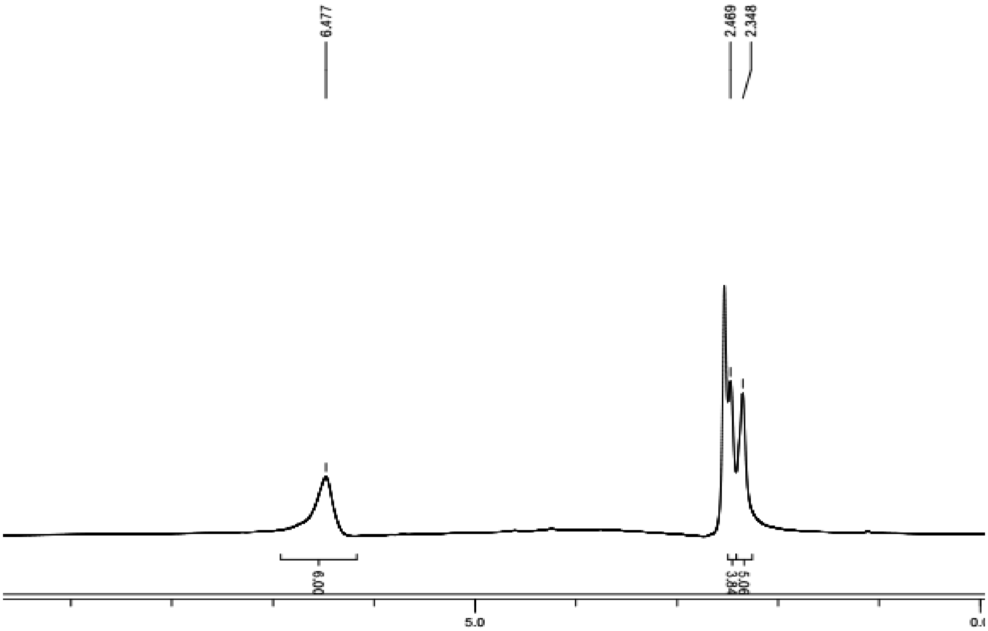

Fig. S10 — ^1H NMR spectrum of cis-$[PtI_2(NH_3)_2(OCOCH_2CH_2COOH)_2]$ in DMSO-d_6

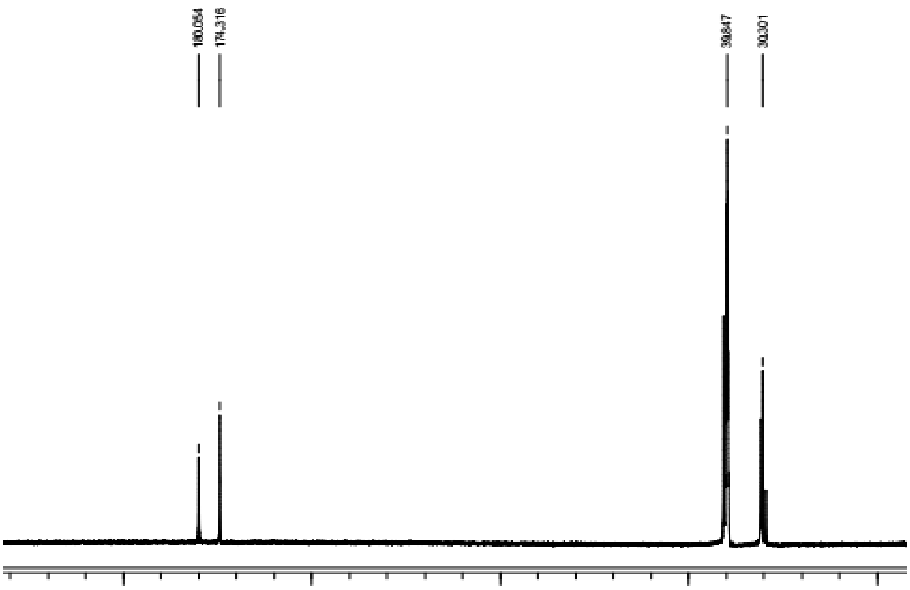

Fig. S11 — $^{13}C\{^{1}H\}$ spectrum of cis-$[PtI_2(NH_3)_2(OCOCH_2CH_2COOH)_2]$ in DMSO-d_6