

Electronic Supporting Information

for

Iridium-promoted conversion of chlorosilanes to alkynyl derivatives, based on Cl/I exchange and C_{sp}-H bond activation in “one-pot” reaction sequence

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1. Procedures and NMR data of synthesized compounds

Synthesis of dimethyl[bis(phenylethynyl)]silane – SiMe₂(C≡CPh)₂ (1, Table 3)

A thick-wall, vacuum glass Schlenk's reactor (50 mL), equipped with a magnetic stirrer was charged, under argon atmosphere, with 1.93 g (14.4 mmol) of anhydrous lithium iodide (LiI) and 20 mL of anhydrous and deoxidized C₆H₅CF₃. Whereupon, to the mixture obtained, 0.77 g of Me₂SiCl₂ (6 mmol), 2,48 g of NEt(*i*-Pr)₂ (19.2 mmol), 1.41 g of PhC≡CH (14.4 mmol) and 34.04 mg of the complex [$\{\text{Ir}(\mu\text{-Cl})(\text{CO})_2\}_2$] (0.06 mmol) were successively added under the flow of argon. The reactor was placed in oil bath and the reaction was conducted at 90 °C upon vigorous stirring. The reaction was carried out until complete conversion of silicon reagent, typically 24 h. The mixture was analyzed on GC and GC/MS at the beginning and after 24 h. Conversion and yield were calculated using the internal standard calculation method (the solvent pick was used as a internal standard). After the reaction completion, in order to remove the catalyst and ammonium salt from the reaction mixture, the solvent and unreacted substrates were evaporated at a reduced pressure and then 30 mL of pentane was added. The resulting suspension was filtered off and the resulting deposit was rinsed with two portions of pentane. The solvent was initially evaporated from the filtrate, and the residual product was distilled by means of the "trap-to-trap" technique at a reduced pressure giving 1.52 g of the final product. Dimethylbis(phenylethynyl) silane was obtained with a yield 97%. Analysis calculated for C₁₈H₁₆Si C 83.02; H 6.19; found C 83.10; H 6.22.

¹H NMR (300 MHz, CDCl₃, 300 K) δ(ppm) = 7.41 (m, 4H, m-Ph-); 7.22 (m, 6H, o,p-Ph-); 0.39 (s, 6H, -SiMe₂-). ¹³C NMR (74.46 MHz, C₆D₆, 300 K) δ(ppm) = 132.28, 128.99, 128.34, 122.79 (-Ph), 106.05 (≡SiC≡C-), 90.75 (≡SiC≡C-), 0.64 (-SiMe₂-). ²⁹Si NMR (119.23 MHz, C₆D₆, 300 K) δ(ppm) = -39.35.

Synthesis of methylphenyl[bis(phenylethynyl)]silane – SiMePh(C≡CPh)₂ (2, Table 3)

Following the procedure used for preparation of compound 1 (Table 3), a reaction was carried out between:

- 1.93 g (14.4 mmol) of LiI
 - 1.15 g (6 mmol) of (Me)(Ph)SiCl₂
 - 1.71 g (16.8 mmol) of PhC≡CH
 - 2,48 g (19.2 mmol) of NEt(*i*-Pr)₂
- in the presence of:
- 68.08 mg (0.12 mmol) of the complex [$\{\text{Ir}(\mu\text{-Cl})(\text{CO})_2\}_2$]

The residual product was purified by flash chromatography using column filled with silica, using hexane/Et₂O (95/5 %) as mobile phase. 1.84 g of diphenyl(phenylethynyl)vinylsilane was obtained (yield of 95%).

Analysis calculated for C₂₃H₁₈Si; C 85.66; H 5.63; found C 85.72; H 5.66;

¹H NMR (300 MHz, CDCl₃, 300 K) δ(ppm) = 7.92 (m, 2H, m-Ph-); 7.60 (m, 2H, m-Ph-) 7.50 (m, 3H, o,p-Ph-); 7.37 (m, 3H, o,p-Ph-); 0.78 (s, 6H, =SiMe-). ¹³C NMR (74.46 MHz, C₆D₆, 300 K) δ(ppm) = 134.28, 133.78, 132.34, 130.19, 129.17, 128.36, 128.20, 122.63 (-Ph), 107.52 (≡SiC≡C-), 89.15 (≡SiC≡C-), 0.28 (=SiMe-). ²⁹Si NMR (119.23 MHz, C₆D₆, 300 K) δ(ppm) = -43.65.

Synthesis of diphenyl[bis(phenylethynyl)]silane – SiPh₂(C≡CPh)₂ (3, Table 3)

Following the procedure used for preparation of compound 1 (Table 3), a reaction was carried out for 72h at 100 °C between:

- 1.93 g (14.4 mmol) of LiI
- 1.52 g (6 mmol) of Ph₂SiCl₂
- 1.71 g (16.8 mmol) of PhC≡CH
- 2,48 g (19.2 mmol) of NEt(*i*-Pr)₂

in the presence of:

- 68.08 mg (0.12 mmol) of the complex [{Ir(μ-Cl)(CO)₂ }₂]

The residual product was purified by flash chromatography using column filled with silica, using hexane/Et₂O (95/5 %) as mobile phase. After purification 2.08 g of diphenylbis(phenylethynyl)silane was obtained (yield of 90%).

Analysis calculated for C₂₈H₂₀Si; C 87.45; H 5.24; found C 87.52; H 5.29

¹H NMR (300 MHz, CDCl₃, 300 K) δ(ppm) = 7.95 (m, 5H, Ph-); 7.68 (m, 3H, Ph-) 7.55 (m, 8H, Ph-); 7.44 (m, 4H, Ph-). ¹³C NMR (74.46 MHz, C₆D₆, 300 K) δ(ppm) = 134.57, 132.62, 132.50, 131.19, 129.87, 128.50, 128.34, 121.67 (Ph-), 110.06 (≡SiC≡C-), 87.20 (≡SiC≡C-). ²⁹Si NMR (119.23 MHz, C₆D₆, 300 K) δ(ppm) = -43.68.

Synthesis of dimethyl{bis(trimethylsilyl)ethynyl}silane – SiMe₂(C≡CSiMe₃)₂ (4, Table 3)

Following the procedure used for preparation of compound 1 (Table 3), a reaction was carried out between:

- 1.93 g (14.4 mmol) of LiI

- 0.77 g (6 mmol) of Me_2SiCl_2
- 1.65 g (16.8 mmol) of $\text{Me}_3\text{SiC}\equiv\text{CH}$
- 2,48 g (19.2 mmol) of $\text{NEt}(i\text{-Pr})_2$

in the presence of:

- 34.04 mg (0.06 mmol) of the complex $[\{\text{Ir}(\mu\text{-Cl})(\text{CO})_2\}_2]$

1.45 g of dimethyl{(trimethylsilyl)ethynylsilane was obtained (yield of 96%).

Analysis calculated for $\text{C}_{12}\text{H}_{24}\text{Si}_3$; C 57.06; H 9.58; found C 57.12; H 5.32

^1H NMR (300 MHz, CDCl_3 , 300 K) $\delta(\text{ppm}) = 0.31$ (s, 6H, $-\text{SiMe}_2-$); 0.17 (s, 18H, $-\text{SiMe}_3$).

^{13}C NMR (74.46 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = 115.36$ ($\equiv\text{Si}\underline{\text{C}}\equiv\text{C}-$), 109.84 ($\equiv\text{Si}\text{C}\equiv\underline{\text{C}}$ -), 0.56 ($-\text{SiMe}_2-$), -0.08 ($-\text{SiMe}_3$). ^{29}Si NMR (119.23 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = -18.41$ ($-\text{SiMe}_3$), -42.68 ($-\text{SiMe}_2-$).

Synthesis of methylphenyl{bis(trimethylsilyl)ethynyl}silane – $\text{SiMePh}(\text{C}\equiv\text{CSiMe}_3)_2$ (5, Table 3)

Following the procedure used for preparation of compound 1, a reaction was carried out between:

- 1.93 g (14.4 mmol) of LiI
- 1.15 g (6 mmol) of $(\text{Me})(\text{Ph})\text{SiCl}_2$
- 1.65 g (16.8 mmol) of $\text{Me}_3\text{SiC}\equiv\text{CH}$
- 2,48 g (19.2 mmol) of $\text{NEt}(i\text{-Pr})_2$

in the presence of:

- 34.04 mg (0.06 mmol) of the complex $[\{\text{Ir}(\mu\text{-Cl})(\text{CO})_2\}_2]$

1.79 g of methylphenyl{(trimethylsilyl)ethynyl}silane was obtained (yield of 95%).

Analysis calculated for $\text{C}_{17}\text{H}_{26}\text{Si}_3$; C 64.89; H 8.33; found C 64.97; H 8.36

^1H NMR (300 MHz, CDCl_3 , 300 K) $\delta(\text{ppm}) = 7.74$ (m, 2H, m-Ph-) 7.42 (m, 3H, o,p-Ph-);

0.55 (s, 6H, $=\text{SiMe}-$); 0.22 (s, 18H, $-\text{SiMe}_3$). ^{13}C NMR (74.46 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = 134.24$, 134.09, 130.07, 128.07 ($-\text{Ph}$), 117.30 ($\equiv\text{Si}\underline{\text{C}}\equiv\text{C}-$), 107.93 ($\equiv\text{Si}\text{C}\equiv\underline{\text{C}}$ -), 0.40 ($=\text{SiMe}-$), -0.11 ($-\text{SiMe}_3$). ^{29}Si NMR (119.23 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = -17.97$ ($-\text{SiMe}_3$), -46.91 ($=\text{SiMe}-$).

Synthesis of diphenylbis(trimethylsilyl)ethynyl)silane – SiPh₂(C≡CSiMe₃)₂ (6, Table 3)

Following the procedure used for preparation of compound 1 (Table 3), a reaction was carried out for 72h at 100 °C between:

- 1.93 g (14.4 mmol) of LiI
- 1.52 g (6 mmol) of Ph₂SiCl₂
- 1.65 g (16.8 mmol) of Me₃SiC≡CH
- 2,48 g (19.2 mmol) of NEt(*i*-Pr)₂

in the presence of:

- 68.08 mg (0.12 mmol) of the complex [{Ir(μ-Cl)(CO)₂ }₂]

The residual product was purified by flash chromatography using column filled with silica and using hexane/Et₂O (95/5 %) as mobile phase. After purification 2.08 g of diphenylbis(trimethylsilyl)ethynyl)silane was obtained (yield of 96%).

Analysis calculated for C₂₂H₂₈Si₃; C 70.14; H 7.49; found C 70.26; H 7.54

¹H NMR (300 MHz, CDCl₃, 300 K) δ(ppm) = 7.82 (m, 4H, *m*-Ph-) 7.49 (m, 6H, *o,p*-Ph-); 0.32 (s, 18H, -SiMe₃). ¹³C NMR (74.46 MHz, C₆D₆, 300 K) δ(ppm) = 134.55, 134.21, 132.54, 131.89, 131.13, 128.48, 128.29 (-Ph), 120.82 (≡SiC≡C-), 105.40 (≡SiC≡C-), -0.27 (-SiMe₃). ²⁹Si NMR (119.23 MHz, C₆D₆, 300 K) δ(ppm) = -16.71 (-SiMe₃), -21.20 (-SiPh₂-).

Synthesis of methylbis(trimethylsilyl)ethynyl]vinylsilane – SiMe(C≡CSiMe₃)₂(CH=CH₂) (10, Table 3)

Following the procedure used for preparation of compound 1 (Table 3), a reaction was carried out between:

- 1.93 g (14.4 mmol) of LiI
- 0.85 g (6 mmol) of (Me)(H₂C=CH)SiCl₂
- 1.65 g (16.8 mmol) of Me₃SiC≡CH
- 2,48 g (19.2 mmol) of NEt(*i*-Pr)₂

in the presence of:

- 34.04 mg (0.06 mmol) of the complex [{Ir(μ-Cl)(CO)₂ }₂]

1.54 g of methyl[bis(trimethylsilyl)ethynyl]vinylsilane was obtained (yield of 96%).

Analysis calculated for C₁₃H₂₄Si₃; C 59.01; H 9.14; found C 59.10; H 9.18

¹H NMR (300 MHz, CDCl₃, 300 K) δ(ppm) = 6.07 (m, 3H, -CH=CH₂); 0.37 (s, 3H, =SiMe-); 0.18 (s, 18H, -SiMe₃). ¹³C NMR (74.46 MHz, C₆D₆, 300 K) δ(ppm) = 135.20 (≡SiCH=C_H), 133.48 (≡SiC_H=CH₂), 116.76 (≡SiC≡C-SiMe₃), 107.71 (≡SiC≡C-SiMe₃), -0.12 (-SiMe₃), -

0.59 (=SiMe-). ^{29}Si NMR (119.23 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = -18.12$ (-SiMe₃), -49.45 (=SiMe-).

Synthesis of 1,1,3,3-tetramethyl-1,3-bis(phenylethynyl)disiloxane – {(PhC≡C)Me₂Si}₂O (12, Table 3)

Following the procedure used for preparation of compound 1 (Table 3), a reaction was carried out between:

- 1.93 g (14.4 mmol) of LiI
- 1.22 g (6 mmol) of ClMe₂SiOSiMe₂Cl
- 1.71 g (16.8 mmol) of PhC≡CH
- 2,48 g (19.2 mmol) of NEt(*i*-Pr)₂

in the presence of:

- 34.04 mg (0.06 mmol) of the complex [{Ir(μ-Cl)(CO)₂ }₂]

1.20 g of 1,1,3,3-tetramethyl-1,3-bis(phenylethynyl)disiloxane was obtained (yield of 60%).

Analysis calculated for C₂₀H₂₂OSi₂; C 71.80; H 6.63; found C 71.91; H 6.69

^1H NMR (300 MHz, CDCl₃, 300 K) $\delta(\text{ppm}) = 7.45$ (m, 4H, *m*-Ph); 6.90 (m, 6H, *o,p*-Ph); 0.50 (s, 12H, -CH₃); ^{13}C NMR (74.46 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = 132.42$, 132.34; 129.00, 128.50 (-Ph), 123.28 (-C≡C-SiMe₂O-); 91.27 (-C≡C-SiMe₂O-); 2.42 (-SiMe₂-).

Synthesis of 1,1,3,3-tetramethyl-1,3-bis{(trimethylsilyl)ethynyl}disiloxane – {(Me₃SiC≡C)Me₂Si}₂O (13, Table 3)

Following the procedure used for preparation of compound 1 (Table 3), a reaction was carried out between:

- 1.93 g (14.4 mmol) of LiI
- 1.22 g (6 mmol) of ClMe₂SiOSiMe₂Cl
- 1.65 g (16.8 mmol) of Me₃SiC≡CH
- 2,48 g (19.2 mmol) of NEt(*i*-Pr)₂

in the presence of:

- 34.04 mg (0.06 mmol) of the complex [{Ir(μ-Cl)(CO)₂ }₂]

1.33 g of 1,1,3,3-tetramethyl-1,3-bis{(trimethylsilyl)ethynyl}disiloxane was obtained (yield of 68%).

Analysis calculated for C₁₄H₃₀OSi₄; C 51.47; H 9.26; found C 51.60; H 9.31

The NMR data identical with those presented in our previous publication [1].

Synthesis of chlorodimethyl(phenylethynyl)silane – SiClMe₂(C≡CPh) (1, Table 4)

A thick-wall, vacuum glass Schlenk's reactor (50 mL), equipped with a magnetic stirrer was charged, under argon atmosphere, with 1.93 g (14.4 mmol) of anhydrous lithium iodide (LiI) and 30 mL of anhydrous and deoxidized C₆H₅CF₃. Whereupon, to the mixture obtained, 5.57 g of Me₂SiCl₂ (43.2 mmol), 2.98 g of NEt(*i*-Pr)₂ (23.04 mmol), 1.47 g of PhC≡CH (14.4 mmol) and 40.85 mg of the complex [Ir(μ-Cl)(CO)₂]₂ (0.072 mmol) were successively added under the flow of argon. The reactor was placed in oil bath and the reaction was conducted at 70 °C upon vigorous stirring. The reaction was carried out until complete conversion of silicon reagent, typically 24 h. The reaction mixture was analyzed on GC and GC/MS at the beginning and after this time. Conversion and yield were calculated using the internal standard calculation method (the solvent pick was used as a internal standard). After the reaction completion, in order to remove the catalyst, ammonium salt from the reaction mixture the solvent and unreacted substrates were evaporated at a reduced pressure and then 30 mL of pentane was added. The resulting suspension was filtered off and the resulting deposit was rinsed with two portions of pentane. The solvent was initially evaporated from the filtrate, and the residual product was distilled by means of the "trap-to-trap" technique at a reduced pressure giving 1.82 g of the final product. Chlorodimethyl(phenylethynyl)silane was obtained with a yield 65%.

Analysis calculated for C₁₀H₁₁ClSi C 61.68; H 5.69; found C 61.78; H 5.73.

¹H NMR (300 MHz, CDCl₃, 300 K) δ(ppm) = □7.53 (m, 2H, *m*-Ph-); 7.35 (m, 3H, *o,p*-Ph-); 0.69 (s, 6H, -SiMe₂-). ¹³C NMR (75.46 MHz, C₆D₆, 300 K) δ(ppm) = 132.30; 129.52; 128.44; 121.93 (-Ph); 107.03 (Ph-C≡C-SiClMe₂); 89.83 (Ph-C≡C-SiClMe₂); 3.90 (-SiClMe₂). ²⁹Si NMR (119.23 MHz, C₆D₆, 300 K) δ(ppm) = 0.34.

Synthesis of chlorodiphenyl(phenylethynyl)silane – SiClPh₂(C≡CPh) (2, Table 4)

Following the procedure used for preparation of SiClMe₂(C≡CPh) (1, Table 4), a reaction was carried out for 48h at 90 °C between:

- 0.97 g (7.2 mmol) of LiI
- 1.82 g (7.2 mmol) of Ph₂SiCl₂
- 1.47 g (7.2 mmol) of PhC≡CH
- 1.49 g (11.52 mmol) of NEt(*i*-Pr)₂

in the presence of:

- 20.42 mg (0.036 mmol) of the complex [$\{\text{Ir}(\mu\text{-Cl})(\text{CO})_2\}_2$]
2.06 g of chlorodiphenyl(phenylethynyl)silane was obtained (yield of 90 %).
Analysis calculated for $\text{C}_{20}\text{H}_{15}\text{ClSi}$; C 75.33; H 4.74; found C 75.41; H 4.77;
 ^1H NMR (300 MHz, CDCl_3 , 300 K) $\delta(\text{ppm}) = 7.90$ (m, 4H, *m*- Ph_2ClSi -); 7.65 (m, 2H, *m*-Ph-); 7.52 (m, 6H, *o,p*- Ph_2ClSi -); 7.41 (m, 3H, *o,p*-Ph-). ^{13}C NMR (74.46 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = 134.58$; 132.66; 132.51; 131.18; 129.86; 128.50; 128.34; 121.71 (-Ph); 110.06 (Ph-C \equiv C-SiClPh $_2$); 87.22 (Ph-C \equiv C-SiClPh $_2$). ^{29}Si NMR (119.23 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = -19.13$.

Synthesis of chlorodimethyl{(trimethylsilyl)ethynyl}silane – $\text{SiCl}(\text{Me})_2(\text{C}\equiv\text{CSiMe}_3)$ (3, Table 4)

Following the procedure used for preparation of $\text{SiClMe}_2(\text{C}\equiv\text{CPh})$ (1, Table 4), a reaction was carried out between:

- 3.86 g (28.8 mmol) of LiI
- 11.14 g (86.4 mmol) of Me_2SiCl_2
- 2.82 g (28.8 mmol) of $\text{Me}_3\text{SiC}\equiv\text{CH}$
- 5.96 g (46.08 mmol) of $\text{NEt}(i\text{-Pr})_2$

in the presence of:

- 81.70 mg (0.144 mmol) of the complex [$\{\text{Ir}(\mu\text{-Cl})(\text{CO})_2\}_2$]

After the reaction completion, in order to remove the catalyst, ammonium salt from the reaction mixture the solvent and unreacted substrates were evaporated at a reduced pressure and then 30 mL of pentane was added. The resulting suspension was filtered off and the resulting deposit was rinsed with two portions of pentane. The solvent was initially evaporated from the filtrate, and the residual product was distilled by fractional distillation under argon at atmospheric pressure giving 3.3 g of chlorodimethyl{(trimethylsilyl)ethynyl}silane (yield of 60%).

Analysis calculated for $\text{C}_7\text{H}_{15}\text{ClSi}_2$; C 44.06; H 7.92; found C 44.17; H 7.98.

^1H NMR (300 MHz, CDCl_3 , 300 K) $\delta(\text{ppm}) = 0.53$ (s, 6H, - SiClMe_2); 0.17 (s, 9H, - SiMe_3).
 ^{13}C NMR (74.46 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = 116.88$; 108.42 ($\text{Me}_3\text{Si-C}\equiv\text{C-SiClMe}_2$); 3.82 (- SiClMe_2); -0.29 (- SiClMe_2). ^{29}Si NMR (119.23 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = -1.74$ (- SiClMe_2); -17.56 (- SiMe_3).

Synthesis of chlorodiphenyl{(trimethylsilyl)ethynyl}silane – $\text{SiCl}(\text{Ph})_2(\text{C}\equiv\text{CSiMe}_3)$ (4, Table 4)

Following the procedure used for preparation $\text{SiClMe}_2(\text{C}\equiv\text{CPh})$ (1, Table 4), a reaction was carried out for 48h at 90 °C between:

- 0.97 g (7.2 mmol) of LiI
- 1.82 g (7.2 mmol) of Ph_2SiCl_2
- 0.7 g (7.2 mmol) of $\text{Me}_3\text{SiC}\equiv\text{CH}$
- 1.49 g (11.52 mmol) of $\text{NEt}(i\text{-Pr})_2$

in the presence of:

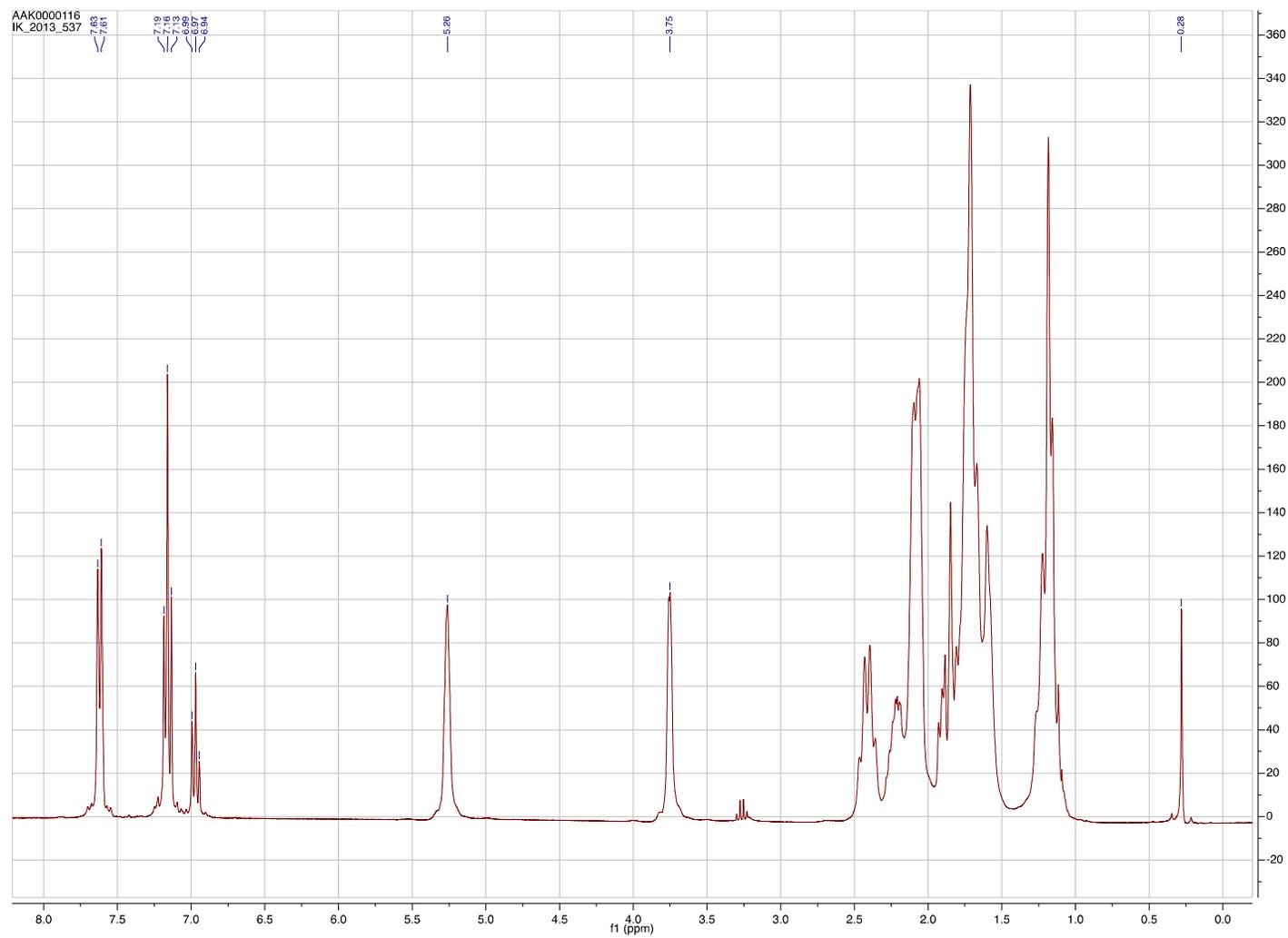
- 40.85 mg (0.072 mmol) of the complex $[\{\text{Ir}(\mu\text{-Cl})(\text{CO})_2\}_2]$

1.93 g of chlorodiphenyl{(trimethylsilyl)ethynyl}silane was obtained (yield of 85%).

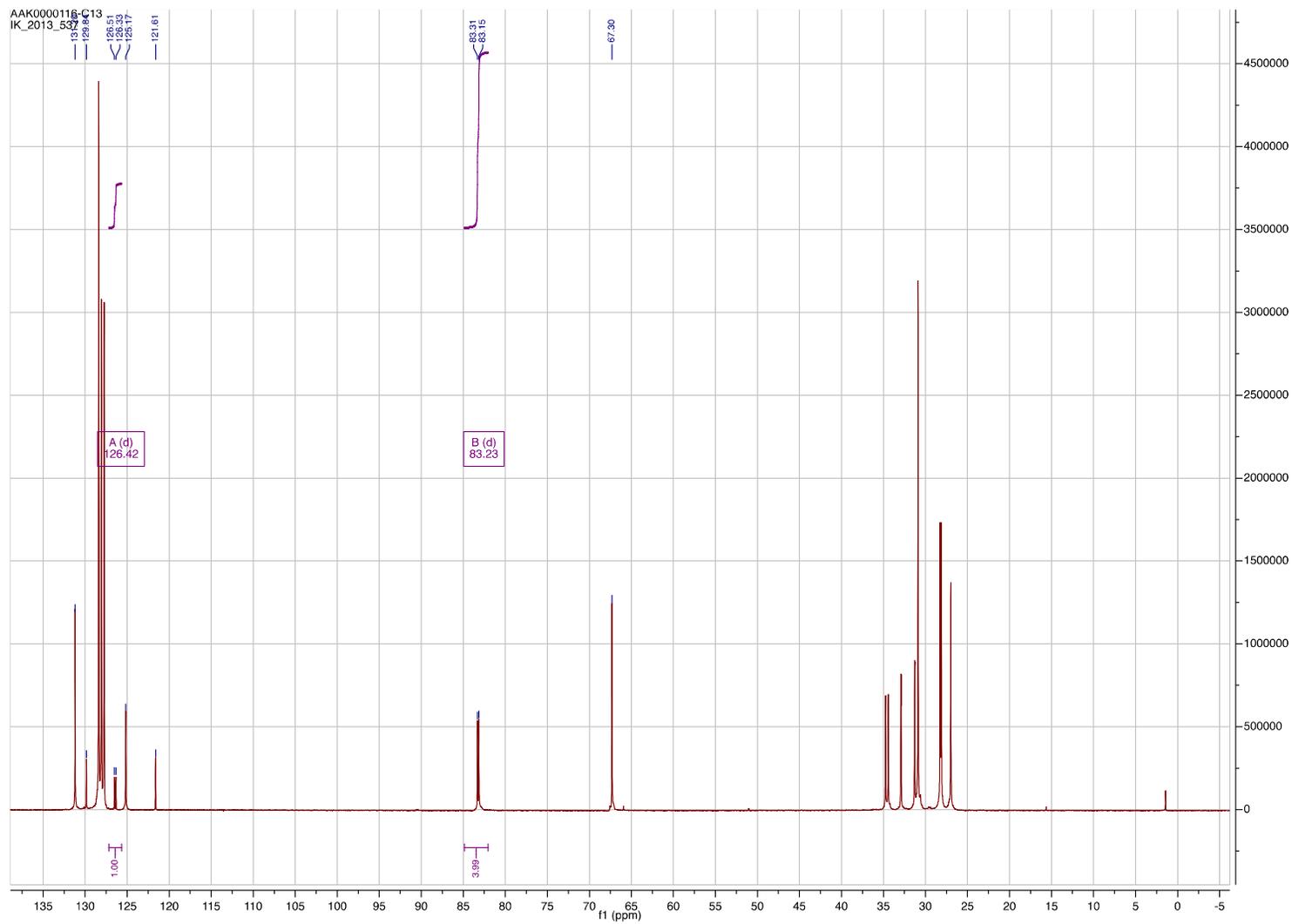
Analysis calculated for $\text{C}_{17}\text{H}_{19}\text{ClSi}_2$; C 64.83; H 6.08; found C 64.90; H 6.15;

^1H NMR (300 MHz, CDCl_3 , 300 K) $\delta(\text{ppm}) = 7.82$ (m, 4H, *m*-Ph-); 7.49 (m, 6H, *o,p*-Ph-); 0.32 (s, 9H, - SiMe_3). ^{13}C NMR (74.46 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = 134.55$; 134.21; 131.13; 128.29 (-Ph); 120.82; 105.40 ($\text{Me}_3\text{Si-C}\equiv\text{C-SiClPh}_2$); -0.27 (- SiMe_3). ^{29}Si NMR (119.23 MHz, C_6D_6 , 300 K) $\delta(\text{ppm}) = -16.71$ (- SiMe_3); -21.17 (- SiClMe_2).

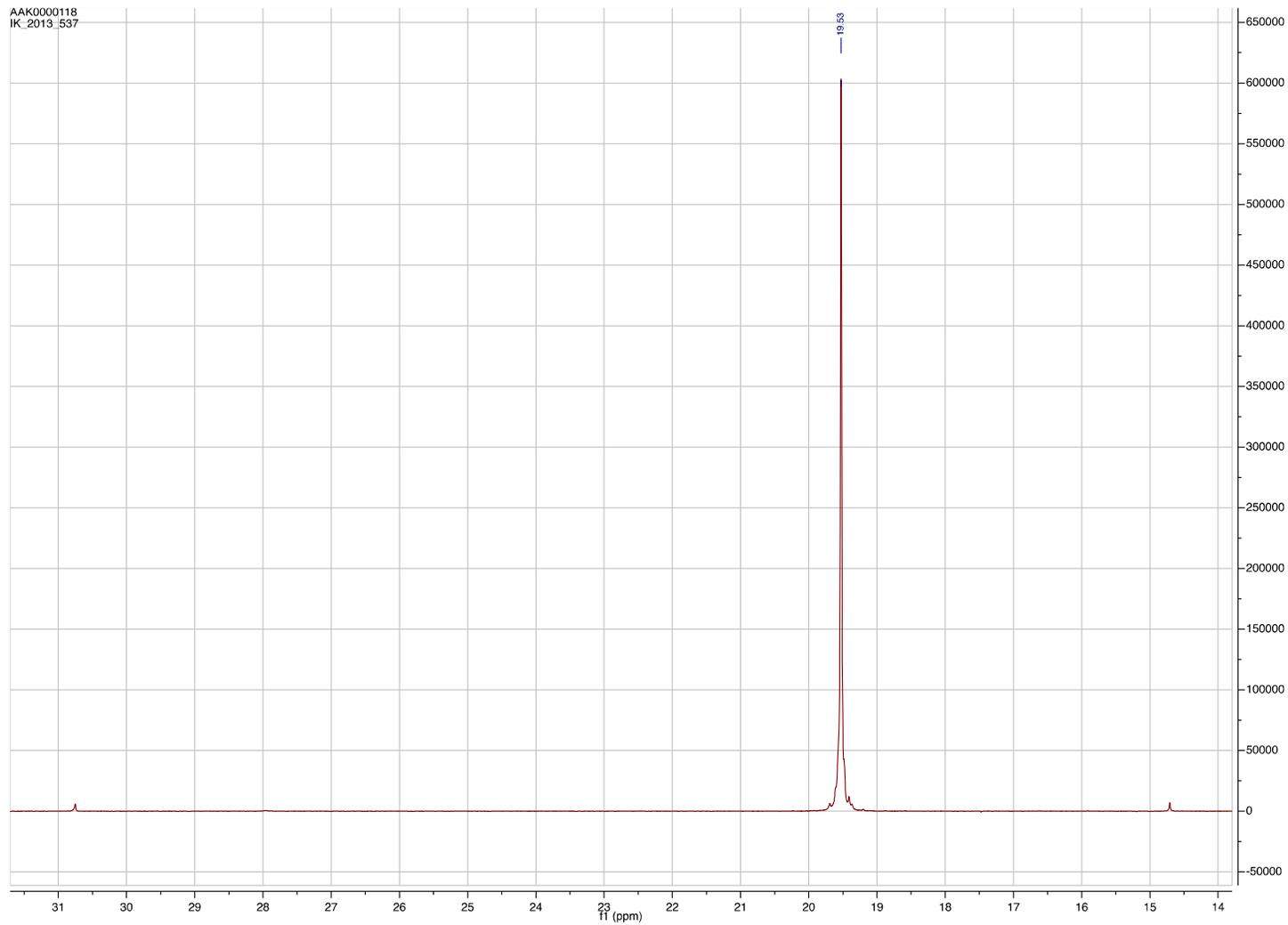
¹H NMR spectrum of A



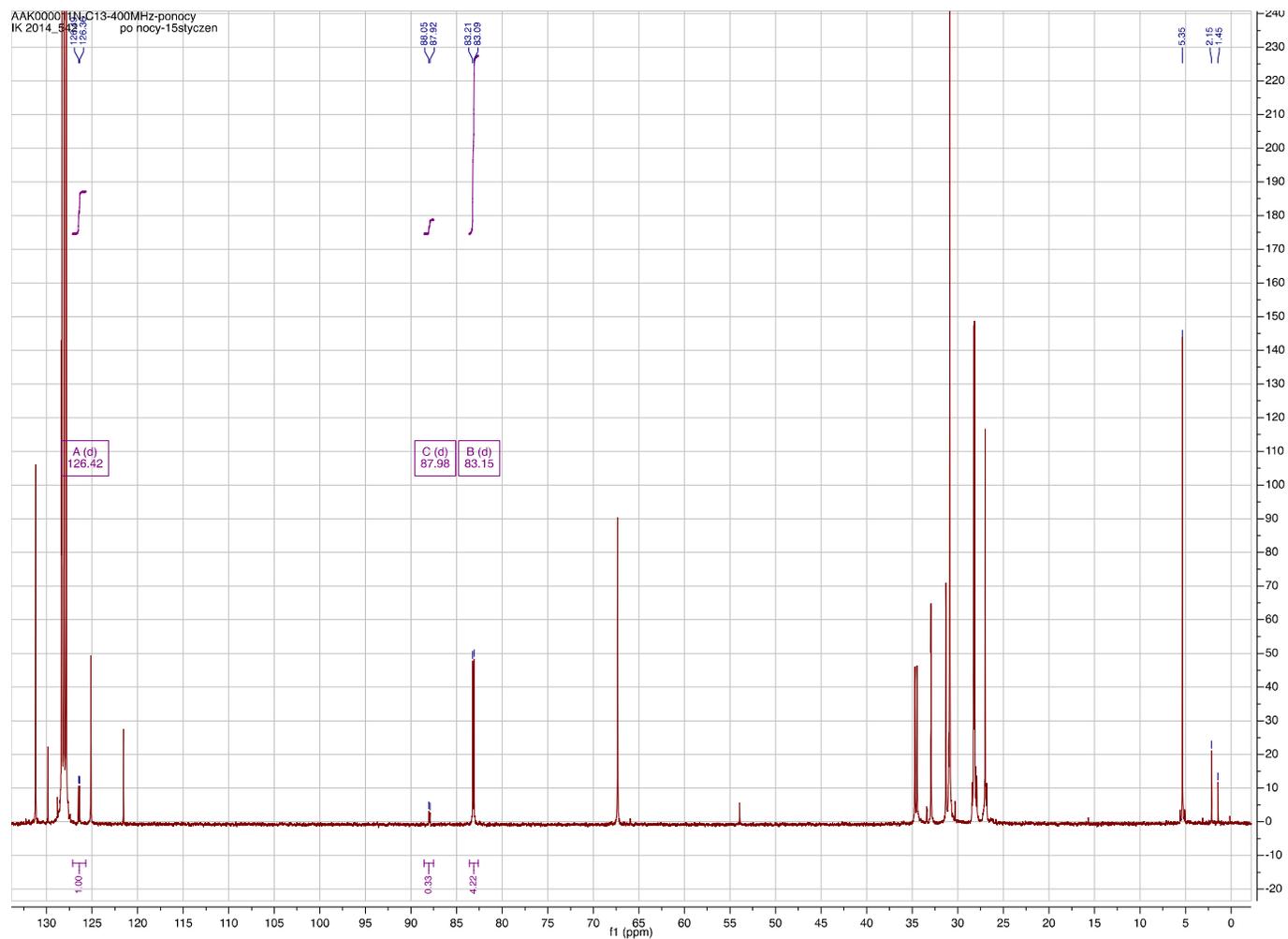
¹³C NMR spectrum of A



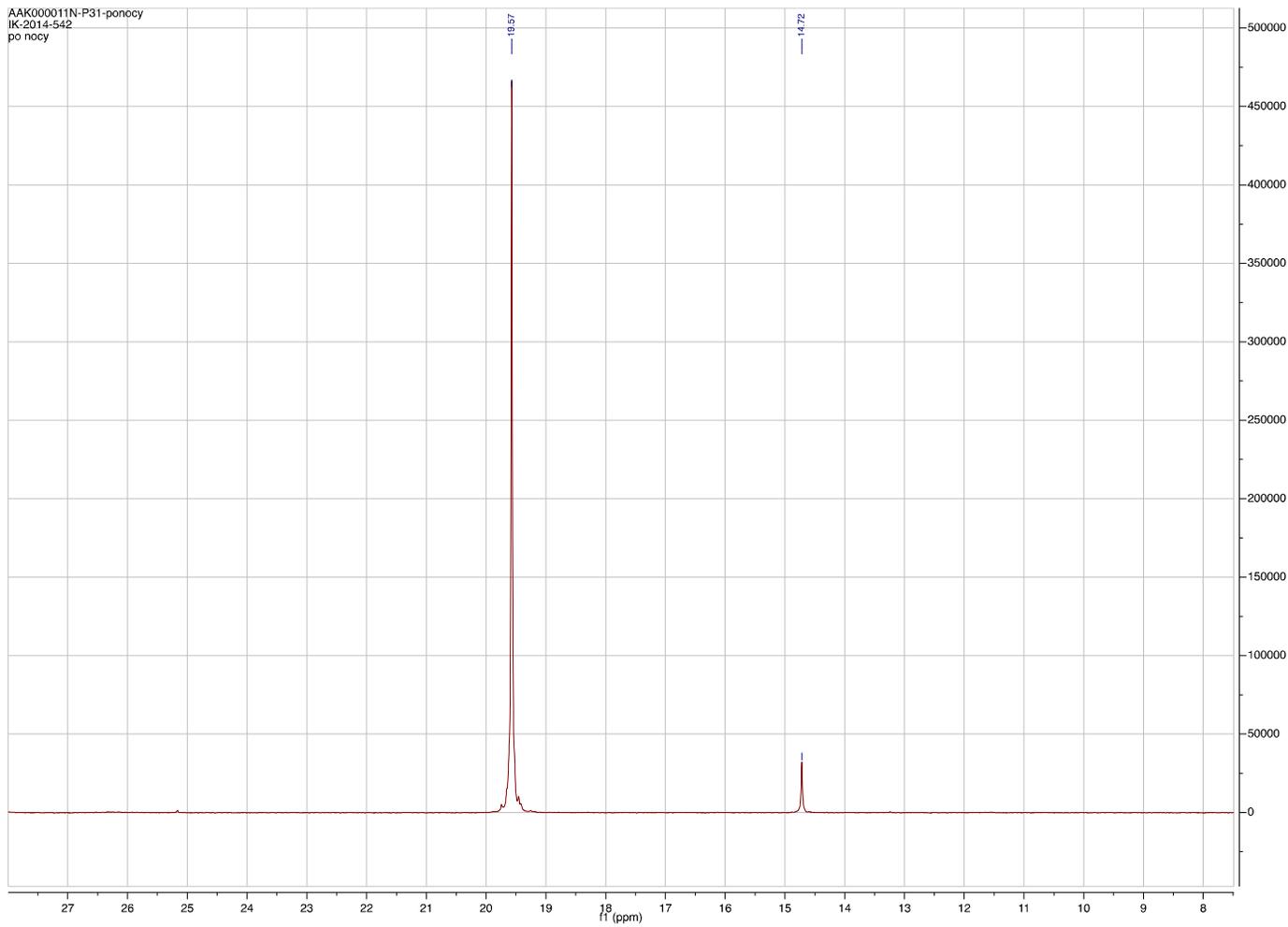
³¹P NMR spectrum of A



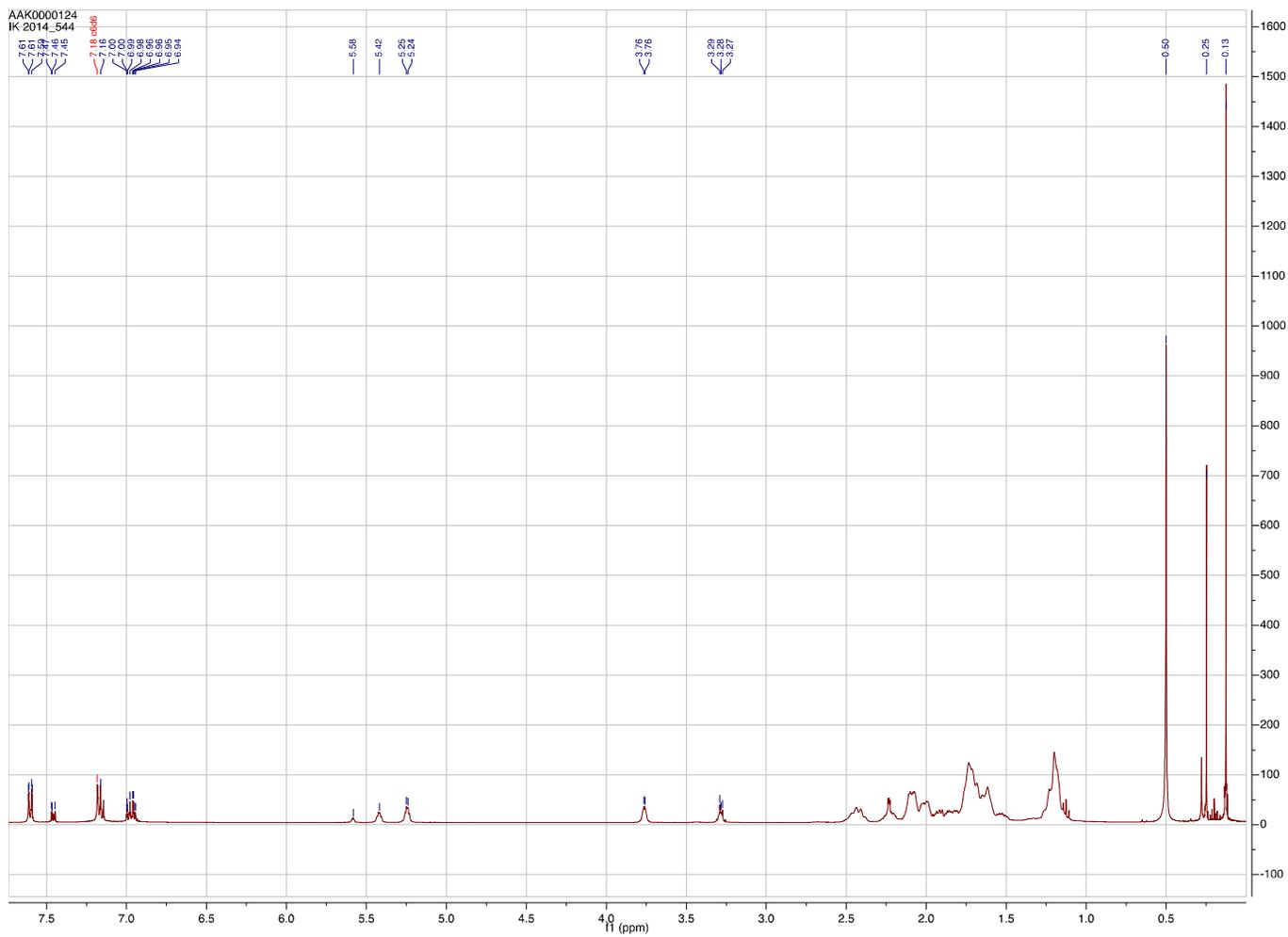
¹³C NMR spectrum



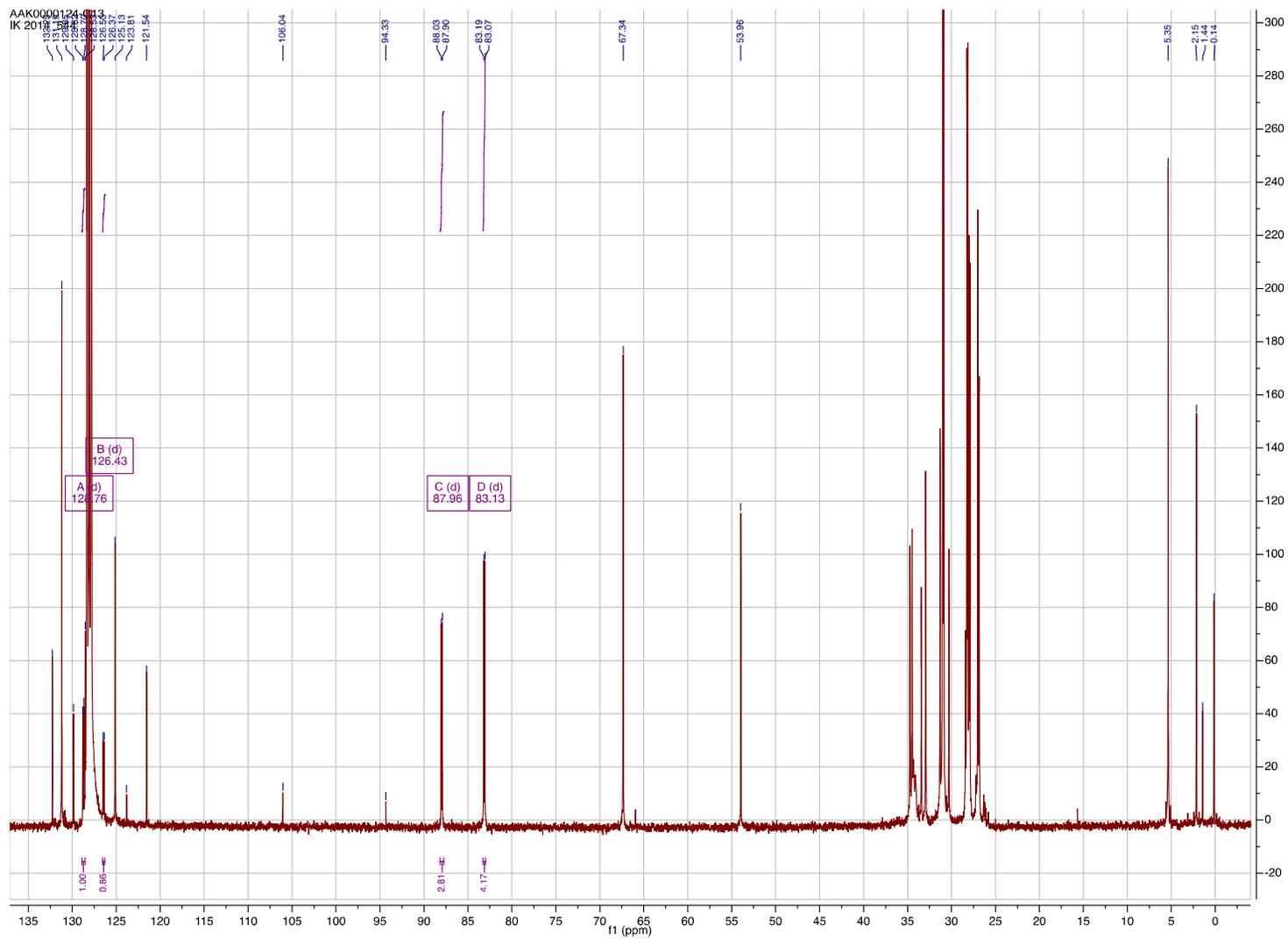
³¹P NMR spectrum



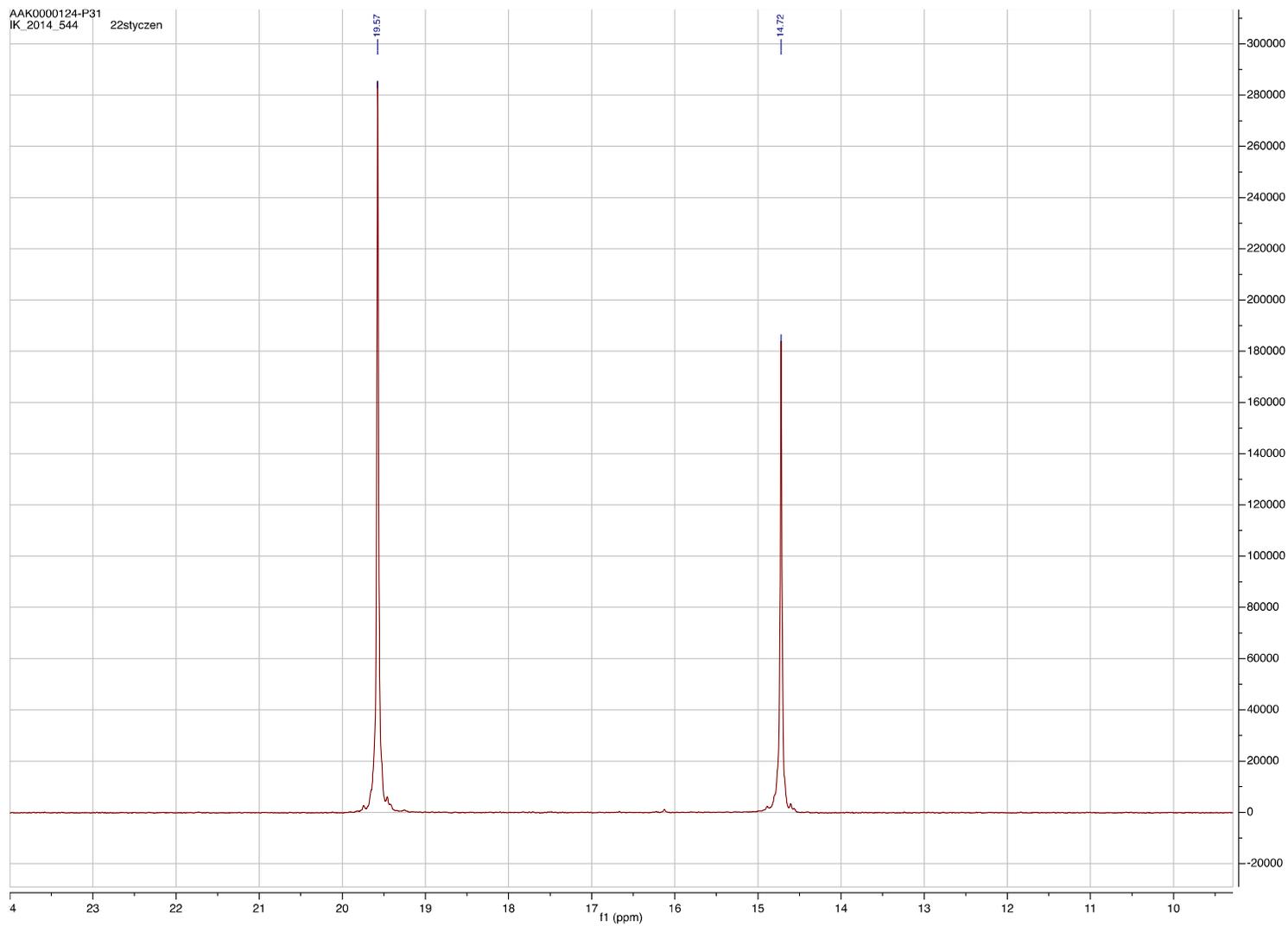
b) after 24h of reaction at 50°C
¹H NMR spectrum



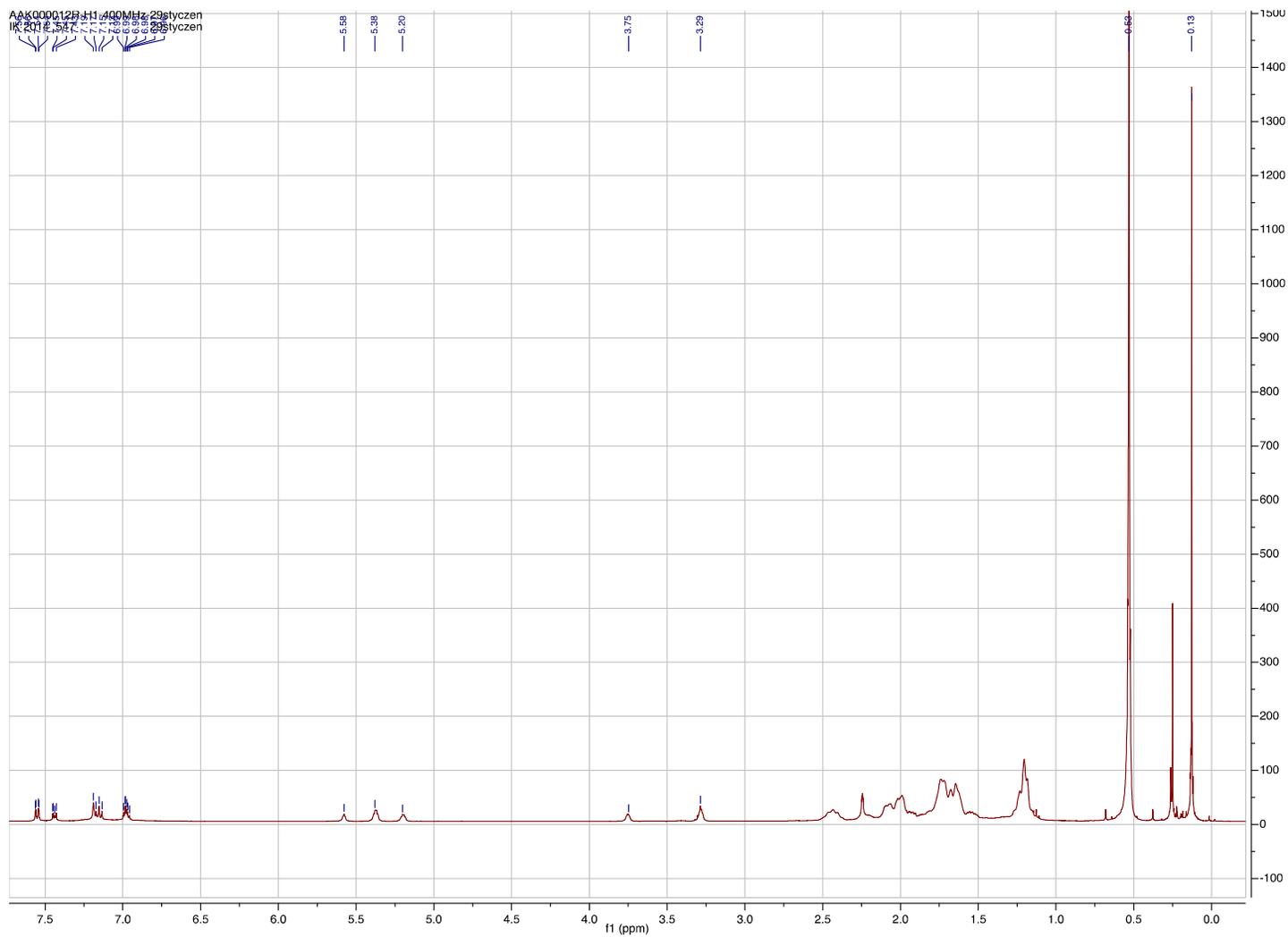
¹³C NMR spectrum



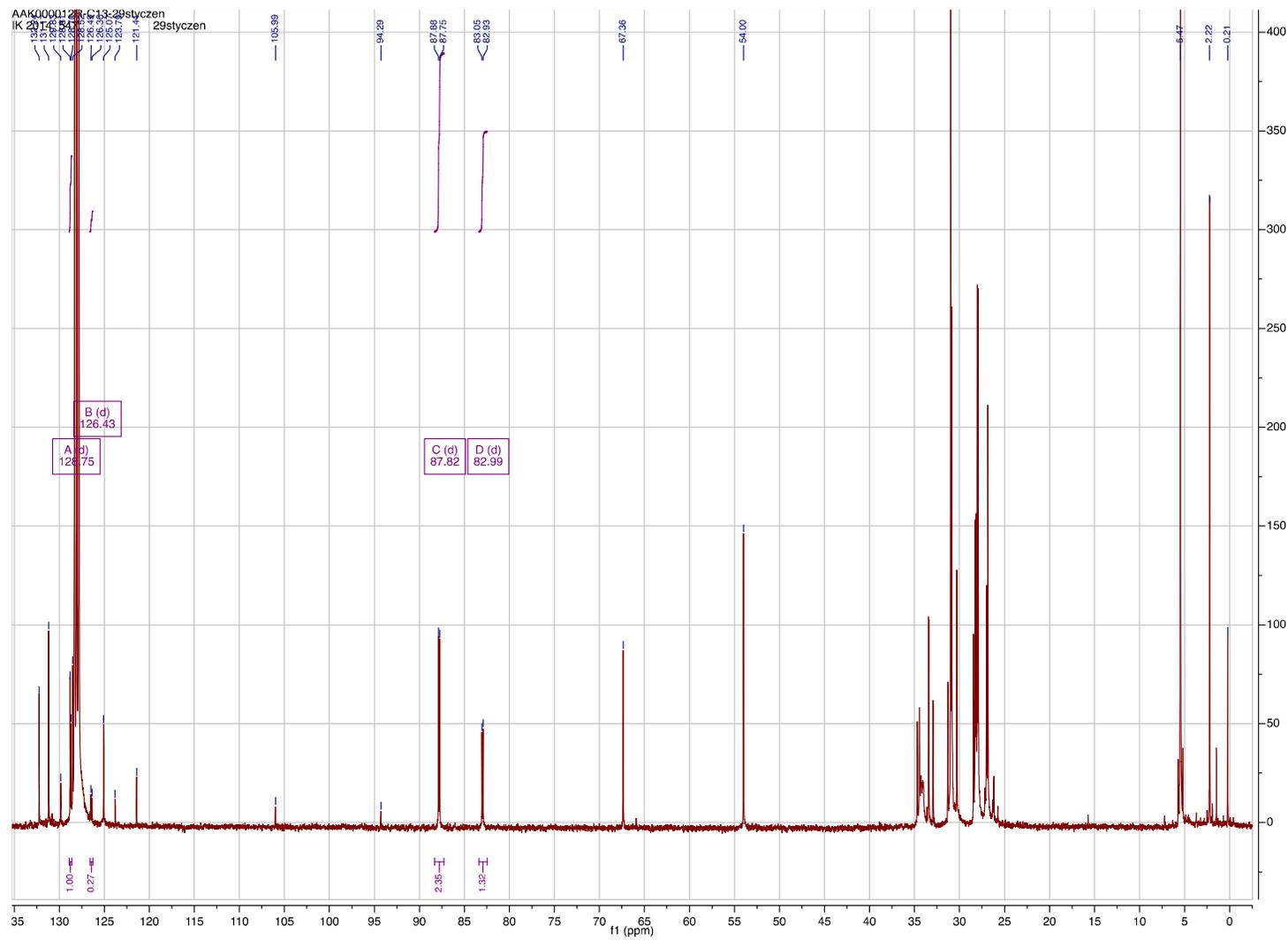
³¹P NMR spectrum



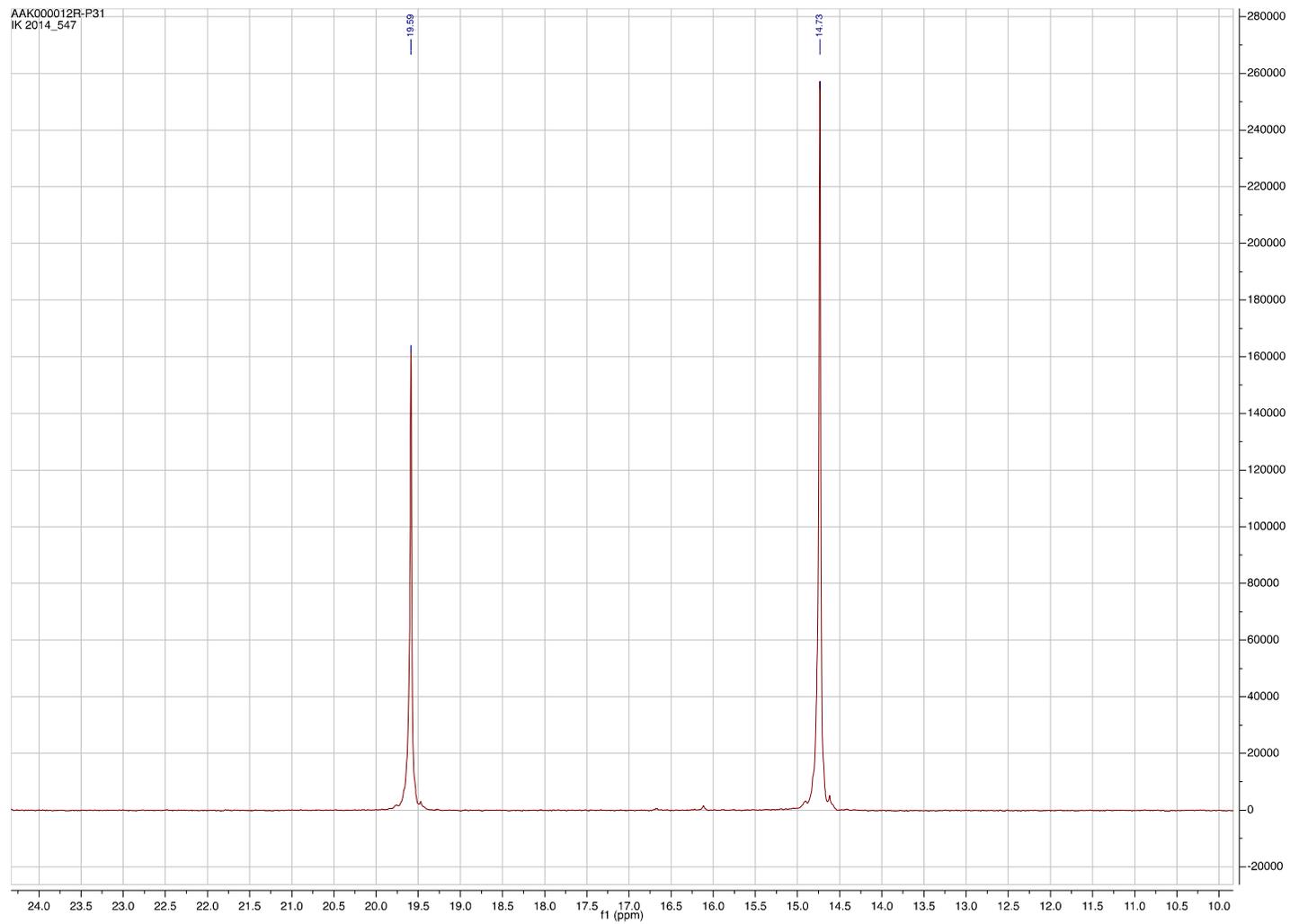
c) after 24 hours of the reaction at room temperature from the addition of Me₃Si-I two equivalents
¹H NMR spectrum



¹³C NMR spectrum



³¹P NMR spectrum



2. References

1. Kownacki, I.; Marciniak, B.; Dudzic, B.; Kubicki, M. *Organometallics* **2011**, *30*, 2539–2545