Supporting Information

Synthesis and Structure—Activity Relationship Study of Antimicrobial Auranofin against ESKAPE Pathogens

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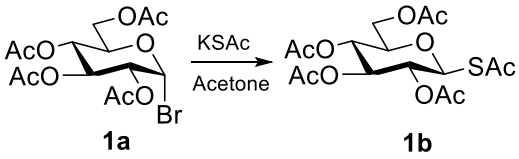
Synthesis of 1b.



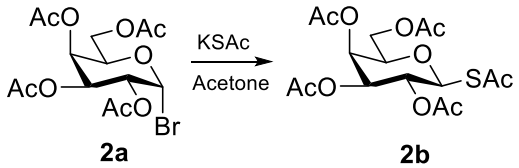
1a 1b

Scheme S1. Synthesis of compound **1b**.

2,3,4,6-Tetra-*O*-acetyl-1-*S*-acetyl-1-thio-β-D-glucopyranose (1b)

This compound was synthesized according to general procedure A from **1a** (1.52 g, 3.70 mmol) and purified by flash column chromatography (ethyl acetate:hexanes = 1:1) to give **1b** as a white solid (1.50 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.24-5.14 (m, 2H, H-3, H-1), 5.08 – 4.97 (m, 2H, H-2, H-4), 4.18 (dd, *J* = 12.5, 4.5 Hz, 1H, H-6a), 4.01 (dd, *J* = 12.5, 2.1 Hz, 1H, H-6b), 3.77 (ddd, *J* = 10.1, 4.4, 2.1 Hz, 1H, H-5), 2.30 (s, 3H, SAc), 1.98 (s, 3H, OAc), 1.94 (s, 3H, OAc), 1.93 (s, 3H, OAc), 1.91 (s, 3H, OAc). The NMR spectrum is consistent with published data.[1]

Synthesis of 2b.



2a 2b

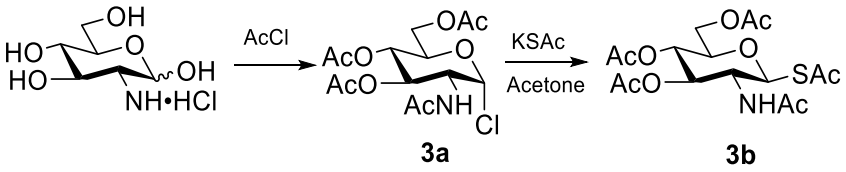
Scheme S2. Synthesis of compound **2b**.

2,3,4,6-Tetra-*O*-acetyl-1-*S*-acetyl-1-thio-*β*-D-galactopyranose (2b)

This compound was synthesized from compound **2a** (2.24 g, 3.22 mmol) according to general procedure A and purified by flash column chromatography (ethyl acetate:hexanes =1:1) to give **2b** (1.18 g, 90%) as a pale-yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46 (d, *J* = 3.3 Hz, 1H, H-4), 5.35 – 5.29 (t, *J* = 3.3 Hz, 1H, H-2), 5.25 (d, *J* = 10.4 Hz, 1H, H-1), 5.11 (dd, *J* = 9.7, 3.4 Hz, 1H, H-3), 4.18 – 4.02 (m, 3H, H-6a, H-6b, H-5), 2.39 (s, 3H),

2.15 (s, 3H, SAc), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.98 (s, 3H, OAc). The NMR spectrum is consistent with published data.[1]

Synthesis of 3b.



Scheme S3. Synthesis of compound **3b**.

3,4,6-Tri-*O*-acetyl-2-*N*-acetylamido-2-deoxy-α-D-glucopyranosyl chloride (3a)

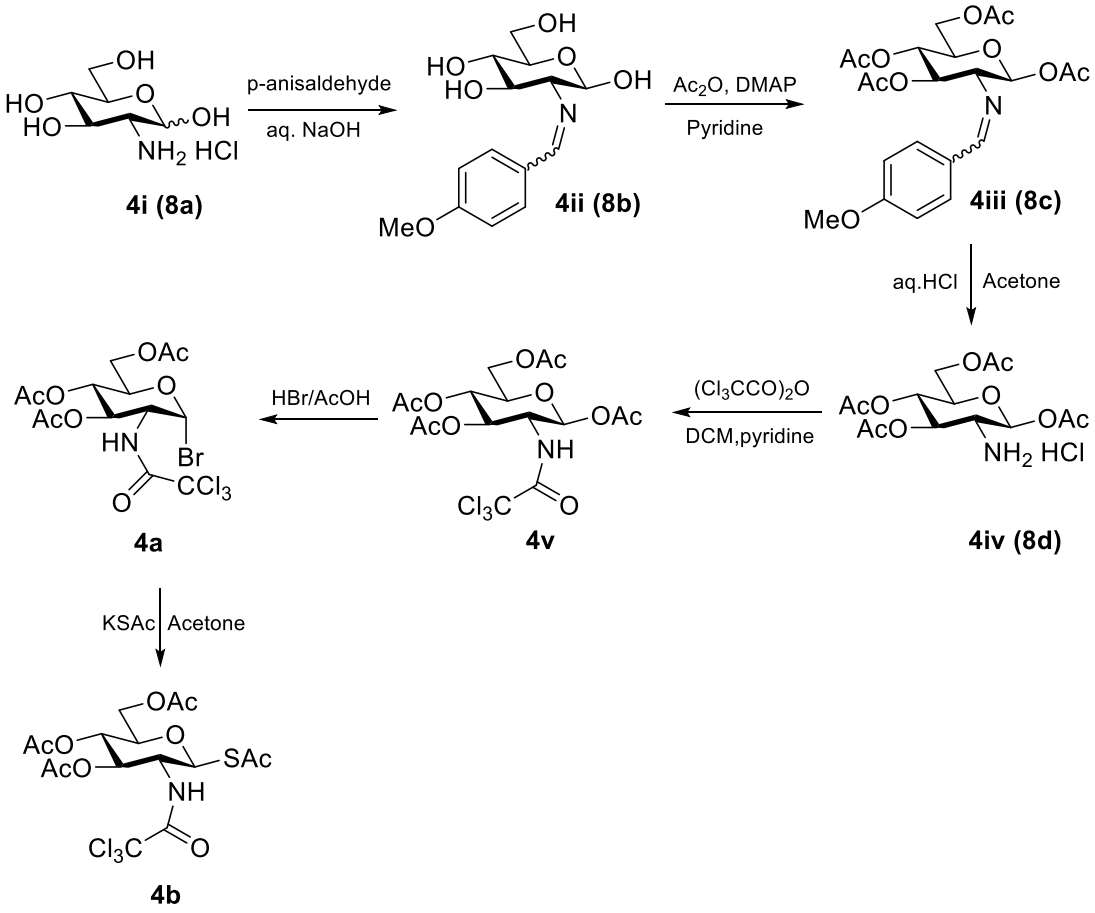
Prepared according to reported protocol.[2] Acetyl chloride (2.0 mL, 28.0 mmol) was added dropwise into a round-bottom flask containing *N*-acetylglucosamine (1.0 g, 4.52 mmol) at 0 °C. The mixture was stirred for 48 h under Ar at rt. DCM (200 mL) was added and the organic layer was washed by water, saturated sodium bicarbonate, brine and dried over $MgSO_4$. After removing the solvent, the residue was purified by flash column chromatography (ethyl acetate:hexanes = 3:1) to afford **3a** as a white solid (951 mg, 57%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.19 (d, *J* = 3.7 Hz, 1H, H-1), 5.79 (d, *J* = 8.7 Hz, 1H, NH), 5.32 (dd, *J* = 10.5, 9.6 Hz, 1H, H-3), 5.22 (t, *J* = 9.8 Hz, 1H, H-4), 4.53 (ddd, *J* = 10.7, 8.7, 3.7 Hz, 1H, H-2), 4.32 – 4.23 (m, 2H, H-6a, H-5), 4.17 – 4.10 (m, 1H, H-6b), 2.10 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.99 (s, 3H, NHAc).

3,4,6-Tri-*O*-acetyl-2-*N*-acetyl-*S*-acetyl-1-thio-*β*-D-glucosamine (3b)

This compound was synthesized according to general procedure A from **3a** (951 mg, 2.60 mmol), and purified by flash column chromatography (ethyl acetate:hexanes =2:1) to give **3b** as a pale yellow solid (925 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.58 (d, *J* = 9.7

Hz, 1H, NH), 5.15 (d, *J* = 10.8 Hz, 1H, H-1), 5.13 (t, *J* = 9.3 Hz, 1H, H-3), 5.09 (t, *J* = 9.5 Hz, 1H, H-4), 4.35 (q, *J* = 10.0 Hz, 1H, H-2), 4.24 (dd, *J* = 12.5, 4.5 Hz, 1H, H-6a), 4.10 (dd, *J* = 12.5, 2.2 Hz, 1H, H-6b), 3.78 (ddd, *J* = 9.6, 4.5, 2.2 Hz, 1H, H-5), 2.37 (s, 3H, SAc), 2.08 (s, 3H, OAc), 2.03 (s, 6H, 2×OAc), 1.92 (s, 3H, NHAc). The NMR spectrum is consistent with published data.[1]

Synthesis of 4b.



Scheme S4. Synthesis of compound **4b**.

2-Deoxy-2-[[(4-methoxyphenyl)methylene]amino]-β-D-glucopyranose (4ii)

Prepared according to a reported procedure.[3] D-Glucosamine hydrochloride **4i** (3.0 g, 13.9 mmol) was dissolved in 1 M NaOH (15 mL), and *p*-anisaldehyde (2.0 mL, 16.7 mmol) was added. The mixture was stirred at RT for 0.5 h then was briefly sonicated for 1 min, and was stirred for another 0.5 h. The white precipitate was filtered off, washed with cold water (30 mL) and EtOH/Et_2O (30 mL, 1:1, v/v), and dried under high-vacuum, yielding **4ii** as a white powder (3.71 g, 89%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.11 (s, 1H), 7.71 – 7.66 (m, 2H), 7.02 – 6.96 (m, 2H), 6.51 (d, *J* = 6.8 Hz, 1H), 4.90 (d, *J* = 5.3 Hz, 1H), 4.79 (d, *J* = 5.6 Hz, 1H), 4.69 (dd, *J* = 7.7, 6.7 Hz, 1H), 4.52 (t, *J* = 5.8 Hz, 1H), 3.80 (s, 3H), 3.73 (ddd, *J* = 11.6, 5.6, 2.2 Hz, 1H), 3.48 (dt, *J* = 11.8, 6.0 Hz, 1H), 3.45 – 3.37 (m, 1H), 3.23 (ddd, *J* = 9.7, 5.9, 2.2 Hz, 1H), 3.14 (ddd, *J* = 9.7, 8.7, 5.3 Hz, 1H), 2.79 (dd, *J* = 9.3, 7.6 Hz, 1H).

1,3,4,6-Tetra-*O*-acetyl-2-deoxy-2-[[(4-methoxyphenyl)-methylene]amino]-β-D-glucopyranose (4iii)

Prepared according to an adapted procedure.[3] To a cold mixture of **4ii** (4.0 g, 13.5 mmol,) and DMAP (0.06 g, 0.5 mmol) in pyridine (22 mL) was added acetic anhydride (12 mL) at 0 °C. The reaction was stirred overnight at RT. The reaction mixture was then poured into ice water. A large amount of precipitate formed. The precipitate was collected by filtration, and washed with water and Et_2O. After dried in vacuum overnight, **4iii** was obtained as a white powder (4.6 g, 74%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.28 (s, 1H), 7.74 – 7.60 (m, 2H), 7.07 – 6.93 (m, 2H), 6.06 (d, *J* = 8.2 Hz, 1H), 5.44 (t, *J* = 9.7 Hz, 1H), 4.97 (t, *J* = 9.7 Hz, 1H), 4.33 – 4.16 (m, 2H), 4.01 (dd, *J* = 12.3, 2.1 Hz, 1H), 3.80 (s, 3H), 3.44 (dd, *J* = 9.5, 8.6 Hz, 1H), 2.02 (s, 3H), 1.98 (s, 3H), 1.98 (s, 3H), 1.82 (s, 3H).

1,3,4,6-Tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranose hydrochloride (4iv)

Prepared according to a reported procedure.[3] To a solution of **4iii** (3.6 g, 7.73 mmol) in refluxing acetone (20 mL), 5 M aqueous solution of HCl (2 mL) was added dropwise. After 5 min, a white precipitate started to form. After vigorous stirring for 30 min, the reaction was cooled to RT, and the precipitate was filtered off, and washed successively with acetone and Et_2O. After drying in vacuum overnight, **4iv** was obtained as white powder (2.68 g, 90%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.75 (s, 3H, NH_3Cl), 5.90 (d, *J* = 8.6 Hz, 1H, H-1), 5.35 (dd, *J* = 10.4, 9.2 Hz, 1H, H-3), 4.93 (dd, *J* = 10.1, 9.2 Hz, 1H, H-4), 4.19 (dd, *J* = 12.5, 4.5 Hz, 1H, H-6a), 4.05 (ddd, *J* = 10.1, 4.5, 2.3 Hz, 1H, H-5), 4.00 (dd, *J* = 12.5, 2.3 Hz, 1H, H-6b), 3.57 (dd, *J* = 10.4, 8.7 Hz, 1H, H-2), 2.17 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.00 (s, 3H, OAc), 1.98 (s, 3H, OAc).

1,3,4,6-Tri-*O*-acetyl-2-*N*-trichloroactyl-*β*-D-glucosamine (4v)

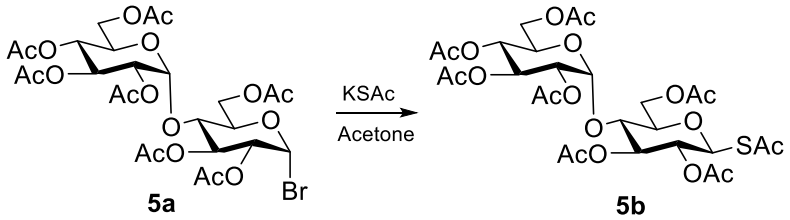
To a solution of **4iv** (1.00 g, 2.61 mmol) in 10 mL of DCM, pyridine (0.84 mL, 10.4 mmol) was added. The solution was brought to 0 °C. Trichloroacetic anhydride (1.21 g, 3.91 mmol) was added. The reaction was stirred overnight, then was poured into 50 mL of 1 M HCl solution followed by extraction with DCM (50 mL×3). The combined organic phase was washed by saturated $NaHCO_3$, brine, and dried over $MgSO_4$. After removal of the solvent, the residue was purified by flash column chromatography (ethyl acetate/hexanes=1:2) to afford **4v** as a white solid (1.25 g, 97%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 9.5 Hz, 1H, NH), 5.82 (d, *J* = 8.7 Hz, 1H, H-1), 5.40 (dd, *J* = 10.9, 9.4 Hz, 1H, H-3), 5.17 (t, *J* = 9.7 Hz, 1H, H-4), 4.37 – 4.25 (m, 2H, H-2, H-6a), 4.17 (dd, *J* = 12.5, 2.2 Hz, 2H, H-6b), 3.91 (ddd, *J* = 10.0, 4.9, 2.2 Hz, 1H, H-5), 2.12 (s, 3H, OAc),

2.11 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc). The NMR spectrum is consistent with published data.[4]

3,4,6-Tri-*O*-acetyl-2-*N*-trichloroactyl-*S*-acetyl-1-thio-*β*-D-glucosamine (4b)

To a solution of **4v** (350 mg, 0.71 mmol) in 3 mL of dry DCM, 4 mL of 33% wt HBr/AcOH solution was added dropwise at 0 °C. The reaction was brought to RT and was further stirred for 2 h. After diluting with 30 mL of DCM, the reaction mixture was poured into 60 mL of ice water and was extracted with DCM 3 times. The combined organic phase was washed by saturated $NaHCO_3$ solution, water, brine, and dried over Na_2SO_4. After removing the solvent by rotovap evaporation, the crude bromide product **4a** was obtained and was used immediately in the next step without further purification. To a solution of this crude **4a** in 8 mL of acetone, KSAc (162 mg, 1.42 mmol) was added. The reaction mixture was stirred at RT for 3 h. After removing the solvent by rotovap evaporation, 30 mL of DCM, 10 mL of water and 20 mL of brine were added to the residue. The mixture was extracted by DCM 2 times. The combined organic phase was dried over Na_2SO_4 then was purified by flash column chromatography (ethyl acetate/hexanes=1:2) to afford **4b** as an orange solid (285 mg, 79% over 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 9.8 Hz, 1H, NH), 5.55 (dd, *J* = 10.4, 9.6 Hz, 1H, H-3), 5.37 (d, *J* = 10.7 Hz, 1H, H-1), 5.18 (t, *J* = 9.8 Hz, 1H, H-4), 4.38 (q, *J* = 10.4 Hz, 1H, H-2), 4.27 (dd, *J* = 12.6, 5.1 Hz, 1H, H-6a), 4.15 (dd, *J* = 12.5, 2.2 Hz, 1H, H-6b), 3.92 (ddd, *J* = 10.1, 5.1, 2.2 Hz, 1H, H-5), 2.38 (s, 3H, SAc), 2.11 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.06 (s, 3H, OAc). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.14, 171.71, 170.68, 169.37, 162.20, 92.37, 80.88, 76.84, 73.42, 68.13, 62.15, 53.88, 30.85, 20.77, 20.63, 20.56.

Synthesis of 5b.

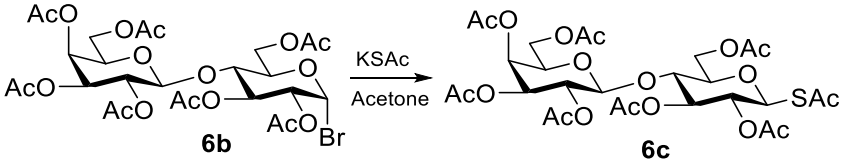


Scheme S5. Synthesis of compound **5b**.

2,3,4,6-Tetra-*O*-acetyl-*α*-D-glucopyranosyl (1→4)-2,3,6-tri-*O*-acetyl-l-*S*-acetyl-1-thio-*β*-D-glucopyranose (5b)

This compound was synthesized according to general procedure A and purified by flash column chromatography (ethyl acetate: hexanes =1:1) to give **5b** as a viscous solid in 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.38 (d, *J* = 3.7 Hz, 1H, H-1′), 5.37 – 5.23 (m, 3H, H-3′,H-3, H-1), 5.12 – 4.90 (m, 2H, H-4′, H-2), 4.84 (dd, *J* = 10.4, 4.0 Hz, 1H, H-2′), 4.43 (dd, *J* = 12.3, 2.3 Hz, 1H, H-6a), 4.30-4.12 (m, 2H, H-6b, H-6'a), 4.10 – 3.72 (m, 4H, H-6'b, H-4, H-5', H-5), 2.36 (s, 3H, SAc), 2.11 (s, 3H, SAc), 2.08 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.01 (s, 3H,OAc), 1.99 (s, 3H, OAc), 1.99 (s, 6H, OAc×2). The NMR spectrum is consistent with published data.[1]

Synthesis of 6b.

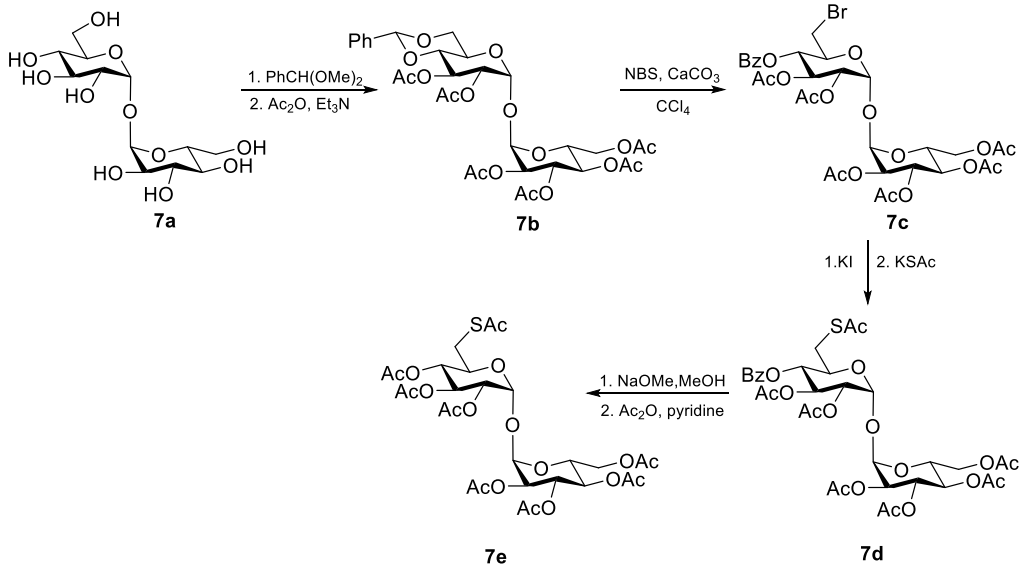


Scheme S6. Synthesis of compound **6b**.

2,3,4,6-Tetra-*O*-acetyl-*β*-D-galactopyranosyl (1→4)-2,3,6-tri-*O*-acetyl-l-*S*-acetyl-1-thio-*β*-D-glucopyranose (6b)

This compound was synthesized according to general procedure A, and purified by flash column chromatography (ethyl acetate/hexanes =1:1) to give **6b** as a viscous solid in 85% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (dd, *J* = 3.4, 1.0 Hz, 1H, H-4'), 5.25 (t, *J* = 9.1 Hz, 1H, H-3), 5.21 (d, *J* = 10.5 Hz, 1H, H-1), 5.11 (dd, *J* = 10.4, 7.9 Hz, 1H, H-2'), 5.04 (dd, *J* = 10.4, 9.2 Hz, 1H, H-2), 4.94 (dd, *J* = 10.4, 3.5 Hz, 1H, H-3'), 4.46 (d, *J* = 7.9 Hz, 1H, H-1'), 4.45 (dd, *J* = 12.1, 1.9 Hz, 1H, H-6'a), 4.16 – 4.04 (m, 3H, H-6a, H-6b, H-6'b), 3.89 – 3.84 (m, 1H, H-5'), 3.82 (dd, *J* = 9.9, 9.0 Hz, 1H, H-4), 3.75 (ddd, *J* = 10.0, 4.7, 1.9 Hz, 1H, H-5), 2.37 (s, 3H, SAc), 2.15 (s, 3H, OAc), 2.11 (s, 3H, OAc), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.96 (s, 3H, OAc). The NMR spectrum is consistent with published data.[1]

Synthesis of 7e.



Scheme S7. Synthesis of compound **7e**.

2,3,2',3',4',6'-*O*-Acetyl-4,6-di-*O*-benzylidene-α-D-trehalose (7b)

Prepared according to an adapted procedure.[5] Benzaldehyde dimethyl acetal (1.62 mL, 10.8 mmol), trehalose (2.05 g, 6.0 mmol) and *p*-toluenesulfonic acid monohydrate (0.23 g, 1.2 mmol) were added to DMF (30 mL). The mixture was stirred for 12 hours at 40 °C. After cooling to 0 °C, triethylamine (23.60 g, 232.0 mol) and DMAP (122 mg, 1.00 mmol) were added followed by Ac_2O (13.0 g, 116.0 mmol) dropwise. The reaction mixture was slowly warmed to RT and stirred overnight, after which it was poured into water, and extracted by ethyl acetate 3 times. The combined organic phase was washed by brine twice, and dried over Na_2SO_4. After removing the solvent, the residue was purified by column chromatography (ethyl acetate/hexanes = 1:1.5 to 1:1) twice to give the desire product as a white amorphous solid (1.60 g, 40%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 - 7.38 (m, 2H, Ar-H), 7.38 - 7.30 (m, 3H, Ar-H), 5.61 (t, *J* = 9.8 Hz, 1H, H-3'), 5.55 - 5.44 (m, 2H, H-3, PhC*H*), 5.37 (d, *J* = 3.7 Hz, 1H, H-1'), 5.27 (d, *J* = 3.7 Hz, 1H, H-1), 5.09 - 5.02 (m, 2H, H-2' and H-4'), 5.00 (dd, *J* = 10.2, 4.0 Hz, 1H, H-2),4.25 (dd, *J* = 12.2, 5.6 Hz, 1H; H-6a'), 4.17 (dd, *J* = 10.5, 4.9 Hz, 1H, H-6a), 4.09 (ddd, *J* = 10.3, 5.7, 2.2 Hz, 1H, H-5'), 4.01 (dd, *J* = 12.2, 2.2, 1H, H-6b'), 3.97 (td, *J* = 9.9, 4.9 Hz, 1 H, H-5), 3.75 (t, *J* = 10.4 Hz, 1H, H-6b), 3.69 (t, *J* = 9.6 Hz, 1H, H-4), 2.22 - 1.96 (m, 18H, OAc). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.76, 170.22, 170.03, 169.97, 169.78, 169.78, 136.87, 129.32, 128.41, 126.34, 101.96, 93.49, 92.35, 79.16, 77.43, 70.78, 70.24, 70.16, 69.06, 68.70, 68.28, 63.34, 61.94, 21.01, 20.84, 20.79, 20.79.

4-*O*-Benzoyl-6-bromo-2,3,2',3',4',6'-penta-*O*-acetyl-6-deoxy-α, α-D-trehalose (7c)

Prepared according to an adapted procedure.[5] Compound **7b** (1.44 g, 2.11 mmol) was added into 60 mL of CCl_4 containing NBS (413 mg, 2.32 mmol) and $CaCO_3$ (232 mg, 2.32 mmol). The mixture was refluxed at 77 °C for 3 hours. After cooling to room temperature,

the solution was washed with saturated $NaHCO_3$ and water. The organic phase was dried over Na_2SO_4, and the filtrate was concentrated in vacuum. The residue was purified by flash column chromatography (ethyl acetate/hexanes = 2:3) to give **7c** as a white solid (1.43 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 - 7.95 (d, *J* = 7.3 Hz, 2H, Ar-H), 7.63 (t, *J* = 7.3 Hz, 1H, Ar-H), 7.49 (t, *J* = 7.7 Hz, 2H, Ar-H), 5.71 (t, *J* = 9.8 Hz, 1H, H-3), 5.54 (t, *J* = 9.7 Hz, 1H, H-3'), 5.41 (d, *J* = 3.9 Hz, 1H, H-1), 5.38 (d, *J* = 3.9 Hz, 1H, H-1'), 5.21 - 5.00 (m, 4H, H-2, H-4', H-2' and H-4), 4.25 (m, 2H, H-5' and H-6a'), 4.16 - 3.97 (m, 2H, H-5 and H-6b'), 3.49 - 3.25 (m, 2H, H-6a and H-6b), 2.28 - 1.76 (m, 18H, OAc). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.81, 170.81, 170.24, 169.73, 169.65, 169.65, 165.59, 134.10, 130.17, 130.17, 128.91, 128.91, 128.65, 92.39, 91.98, 71.82, 70.48, 70.40, 70.29, 69.43, 69.43, 68.80, 68.45, 61.99, 30.75, 21.17, 20.92, 20.90, 20.81, 20.80, 20.78, 20.76.

4-*O*-Benzoyl-6-*S*-acetyl-2,3,2',3',4',6'-penta-*O*-acetyl -α, α-D-trehalose (7d)

Compound **7c** (2.95 g, 3.87 mmol) and KI (1.93 g, 11.6 mmol) was added to a round bottle flask containing 30 mL of DMF. After stirring at 60 °C for 4 h, the mixture was cooled to RT, and KSAc (1.33 g, 11.6 mmol) was added to the mixture. The reaction was stirred under Ar protection overnight. The resulting mixture was poured into 100 mL brine/100 mL water and extracted with ethyl acetate (100 mL×3). The combined organic layer was further washed with 200 mL brine and dried on $MgSO_4$, concentrated in vacuum. The residue was purified by column chromatography (ethyl acetate/hexanes = 1 to 1) to afford the product as a viscous solid (2.93 g, 96%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.3, 1.2 Hz, 1H, Ar-H), 7.60 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.47 (t, *J* = 7.8 Hz, 1H, Ar-H), 5.67 (dd, *J* = 9.8, 9.7 Hz, 1H, H-3), 5.52 (dd, *J* = 9.9, 9.6 Hz, 1H, H-3′), 5.34 (d, *J* = 3.9 Hz, 2H, H-1, H-1'), 5.20 (t, *J* = 9.7 Hz, 1H, H-4), 5.13 – 4.98 (m, 3H, H-2, H-2′, H-4′), 4.20 (dd, *J*

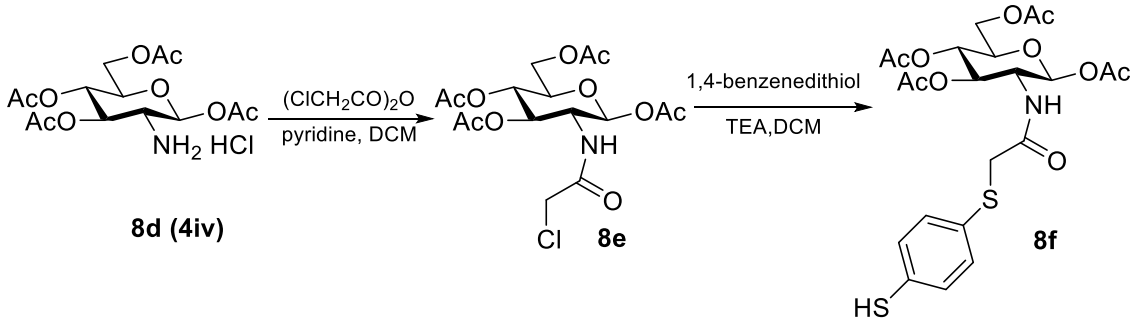
= 12.2, 6.0 Hz, 1H, H-6a'), 4.07 (dd, *J* = 12.2, 2.1 Hz, 1H, H-6b'), 4.03 – 3.90 (m, 2H, H-5, H-5′), 3.30 (dd, *J* = 14.2, 2.6 Hz, 1H, H-6a), 2.91 (dd, *J* = 14.5, 9.2 Hz, 1H, H-6b), 2.32 (s, 3H, SAc), 2.11 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.93 (s, 3H, OAc). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.64, 170.73, 170.01, 169.94, 169.85, 169.77, 169.70, 165.66, 133.78, 130.02, 128.95, 128.73, 91.26, 91.12, 72.03, 70.34, 70.31, 69.76, 69.60, 69.53, 68.72, 68.31, 61.93, 30.47, 30.27, 20.80, 20.72, 20.72, 20.72, 20.70, 20.70.

6-*S*-Acetyl-2,3,4,2',3',4',6'-hexa-*O*-acetyl-α,α-D-trehalose (7e)

Compound **7d** (1.44 g, 1.90 mmol) was dissolved in 50 mL methanol. NaOMe (113 mg, 2.09 mmol) in 3 mL methanol was added to the reaction under Ar protection. The reaction mixture was stirred overnight. After removing the solvent under vacuum, 7 mL of pyridine was added followed by addition of acetic anhydride (2.7 mL, 28.5 mmol) dropwise at 0° C. The reaction was stirred for 16 hours at RT. The reaction mixture was diluted by 100 mL ethyl acetate and poured into 100 mL of water. After extraction for 3 times by ethyl acetate, the combined organic layer was washed with 1 M HCl, saturated $NaHCO_3$, water, and brine, dried over $MgSO_4$. After removing the solvent, the residue was purified by column chromatography (ethyl acetate/hexanes = 1:1) to afford the product as a viscous solid (964 mg, 73% over 2 steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.44 (t, *J* = 9.7 Hz, 2H, H-4, H-4′), 5.27 (d, *J* = 3.9 Hz, 1H, H-1′), 5.24 (d, *J* = 3.8 Hz, 1H, H-1),5.05 – 4.89 (m,

4H, H-2, H-2′, H-3, H-3′), 4.16 (dd, *J* = 12.2, 6.0 Hz, 1H, H-6′a), 4.01 (dd, *J* = 12.2, 1.9 Hz, 1H, H-6′b), 3.94 (ddd, *J* = 10.0, 5.9, 1.7 Hz, 1H, H-5′), 3.89 – 3.80 (m, 1H, H-5), 3.15 (dd, *J* = 14.2, 2.6 Hz, 1H, H-6a), 2.93 (dd, *J* = 14.2, 7.9 Hz, 1H, H-6b), 2.32 (s, 3H, SAc), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.00 (s, 3H, OAc), 2.00 (s, 3H, OAc). ^{13}C NMR (50 MHz, $CDCl_3$) δ 194.73, 170.69, 169.96, 169.85, 169.83, 169.66, 91.45, 91.31, 71.07, 70.20, 70.12, 69.93, 69.70, 69.48, 68.68, 68.30, 61.92, 30.47, 29.93, 20.76, 20.76, 20.73, 20.67.

Synthesis of 8f.



8d (4iv) **8e** **8f**

Scheme S8. Synthesis of compound **8f**. Compounds **8a**-**8d** are identical to compounds **4i**-**4iv** (see **Scheme S4** and the procedures for their syntheses).

1,2,3,4-Tetra-*O*-acetyl-2-chloroacetamido-2-deoxy-β-D-glucopyranose (8e)

Prepared according to a reported procedure.[6] To a solution of **8d** (2.53 g, 6.51 mmol) in 30 mL of DCM, pyridine (0.84 mL, 10.4 mmol) was added. The solution was brought to 0 °C. Chloroacetic anhydride (1.67 g, 9.77 mmol) was added. The reaction solution was stirred overnight, then was poured into 50 mL 1 M HCl solution and was extracted by DCM (50

mL×3). The combined organic phase was washed by saturated $NaHCO_3$, brine, and dried over $MgSO_4$. After removing the solvent, the residue was purified by flash column chromatography (ethyl acetate/hexanes=2:3) to afford **8e** as a white solid (2.45 g, 89%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (d, *J* = 9.2 Hz, 1H, NH), 5.81 (d, *J* = 8.6 Hz, 1H, H-1), 5.28 (dd, *J* = 10.5, 9.3 Hz, 1H, H-3), 5.14 (t, *J* = 9.5 Hz, 1H, H-4), 4.29 (dd, *J* = 12.5, 4.7 Hz, 1H, H-6a), 4.22 (dt, *J* = 10.5, 9.0 Hz, 1H, H-2), 4.14 (dd, *J* = 12.5, 2.3 Hz, 1H, H-6b), 3.98 (d, *J* = 1.6 Hz, 2H, CH_2Cl), 3.85 (ddd, *J* = 9.8, 4.6, 2.3 Hz, 1H, H-5), 2.12 (s, 3H, OAc), 2.10 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.05 (s, 3H, OAc).

1,3,4,6-Tetra-*O*-acetyl-2-((4-mercaptophenyl) sulfanyl)acetamido-2-deoxy-β-D-glucopyranose (8f)

To a solution of compound **8e** (160 mg, 0.378 mmol) and 1,4-benzenedithiol (107 mg, 0.755 mmol) in 5 mL of DCM, TEA (42 mg, 0.415 mmol) was added. The reaction was stirred for 16 h. Then it was concentrated and directly purified by flash column chromatography (ethyl acetate/DCM = 1:1.2) to give the product as a colorless viscous solid (180 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 – 7.17 (m, 2H, Ar-H), 7.15 – 7.09 (m, 2H, Ar-H), 6.81 (d, *J* = 9.2 Hz, 1H, NH), 5.73 (d, *J* = 8.7 Hz, 1H, H-1), 5.24 (dd, *J* = 10.5, 9.3 Hz, 1H, H-3), 5.09 (t, *J* = 9.6 Hz, 1H, H-4), 4.27 (dd, *J* = 12.5, 4.6 Hz, 1H, H-6a), 4.18 (dt, *J* = 10.5, 9.1 Hz, 1H, H-2), 4.11 (dd, *J* = 12.5, 2.2 Hz, 1H, H-6b), 3.82 (ddd, *J* = 9.9, 4.6, 2.3 Hz, 1H, H-5), 3.53 (q, *J* = 16.6 Hz, 2H, SCH_2), 3.45 (s, 1H, SH), 2.08 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.95 (s, 3H, OAc), 1.88 (s, 3H, OAc). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.80, 170.74, 169.43, 169.30, 168.43, 131.72, 130.33, 130.06, 129.04, 92.28, 72.94, 72.18, 68.10, 61.76, 53.47, 37.60, 20.83, 20.81, 20.69, 20.57.

Determination of compound purity by absolute qHNMR with internal calibration

The purities of compounds **1**—**40** were determined by absolute qNMR following the "general guidelines for quantitative 1D ^{1}H NMR (qHNMR) experiments," provided by the *Journal of Medicinal Chemistry*.

The internal calibrant dimethyl sulfone ($DMSO_2$) was purchased from Sigma-Aldrich (product number: M81705, batch number: WXBC7924V). The purity of the internal calibrant ($\boldsymbol{P_{IC}}$) was 100.0% according to the "Certificate of Analysis" of this particular batch provided by the vendor. The absolute qHNMR with internal calibration was conducted on a Bruker Avance Spectrospin DRX500 spectrometer at 298K. The data were obtained at 90º pulse tip angle with an interpulse delay (D_1) of 60 s and an acquisition time of 3.2 s in a non-spinning mode. The FID was obtained following 64 scans of 256 K data points with a 20 ppm width spectral window. The data were processed with the MestReNova 9.0.1 software.

General procedure for qHNMR

Step 1: The weights of the sample ($\boldsymbol{m_S}$) and the internal calibrant ($\boldsymbol{m_{IC}}$) were measured on a semi-micro METTLER TOLEDO balance with 0.01 mg accuracy. Then they were fully dissolved in 650 μL of $CDCl_3$ or 600 μL of D_2O in a 2-mL vial. The resulting solution was transferred into a 5-mm standard NMR tube for analysis.

Step 2: After manual phase and baseline correction, the purest signals of the sample were integrated. The integral of the sample ($\boldsymbol{Int_t}$) was calculated as the average of all integrated

protons by dividing the sum of all those integrals by the number of protons that give rise the signals. By this procedure, the total number of protons ($\boldsymbol{n_t}$) is set to 1.

Step 3: The integral of the internal calibrant ($DMSO_2$, singlet at 3.0-3.2 ppm) and the number of protons that give rise to this signal were recorded as $\boldsymbol{Int_{IC}}$ and $\boldsymbol{n_{IC}}$ ($\boldsymbol{n_{IC}} = 6$).

Step 4: Calculate the molecular weights of the sample ($\boldsymbol{MW_t}$) and the internal calibrant ($\boldsymbol{MW_{IC}} = 94.13$ g/mol).

Step 5: Calculate the purity (***P***) of the sample according to the following equation:

$$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC}$$

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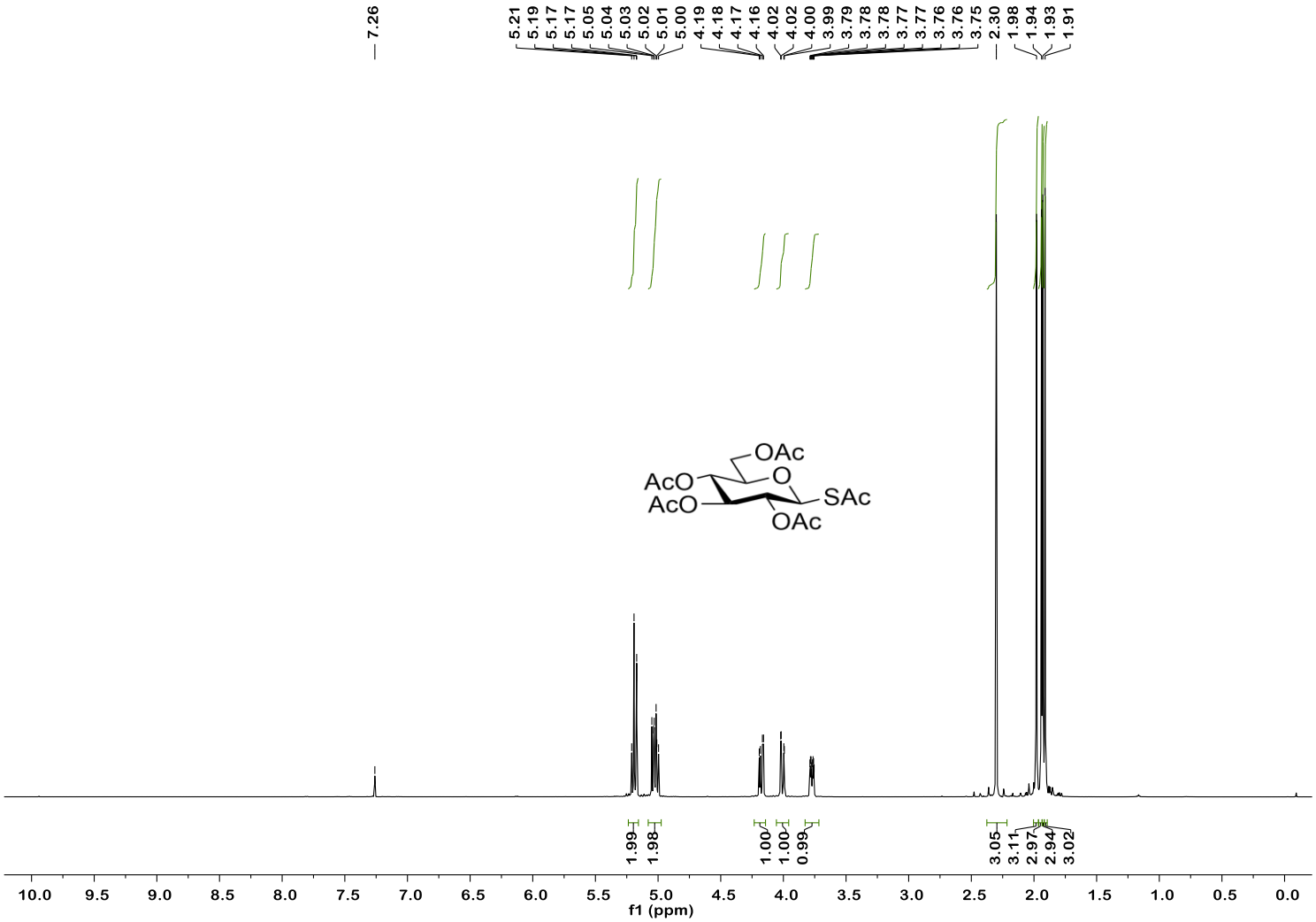


Figure S1. ^{1}H NMR spectrum of compound **1b** in $CDCl_3$.

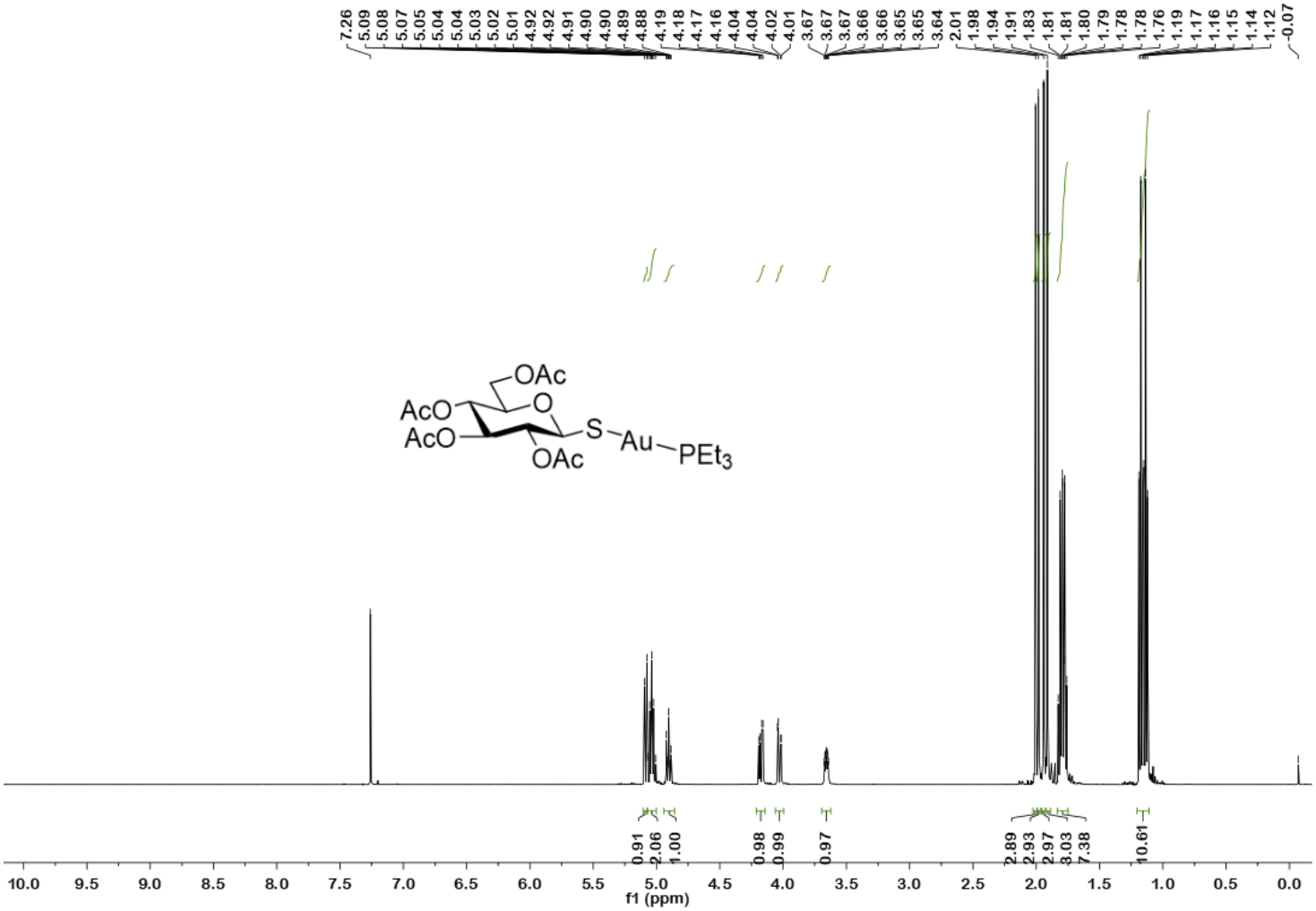


Figure S2. ^{1}H NMR spectrum of compound **1** in $CDCl_3$.

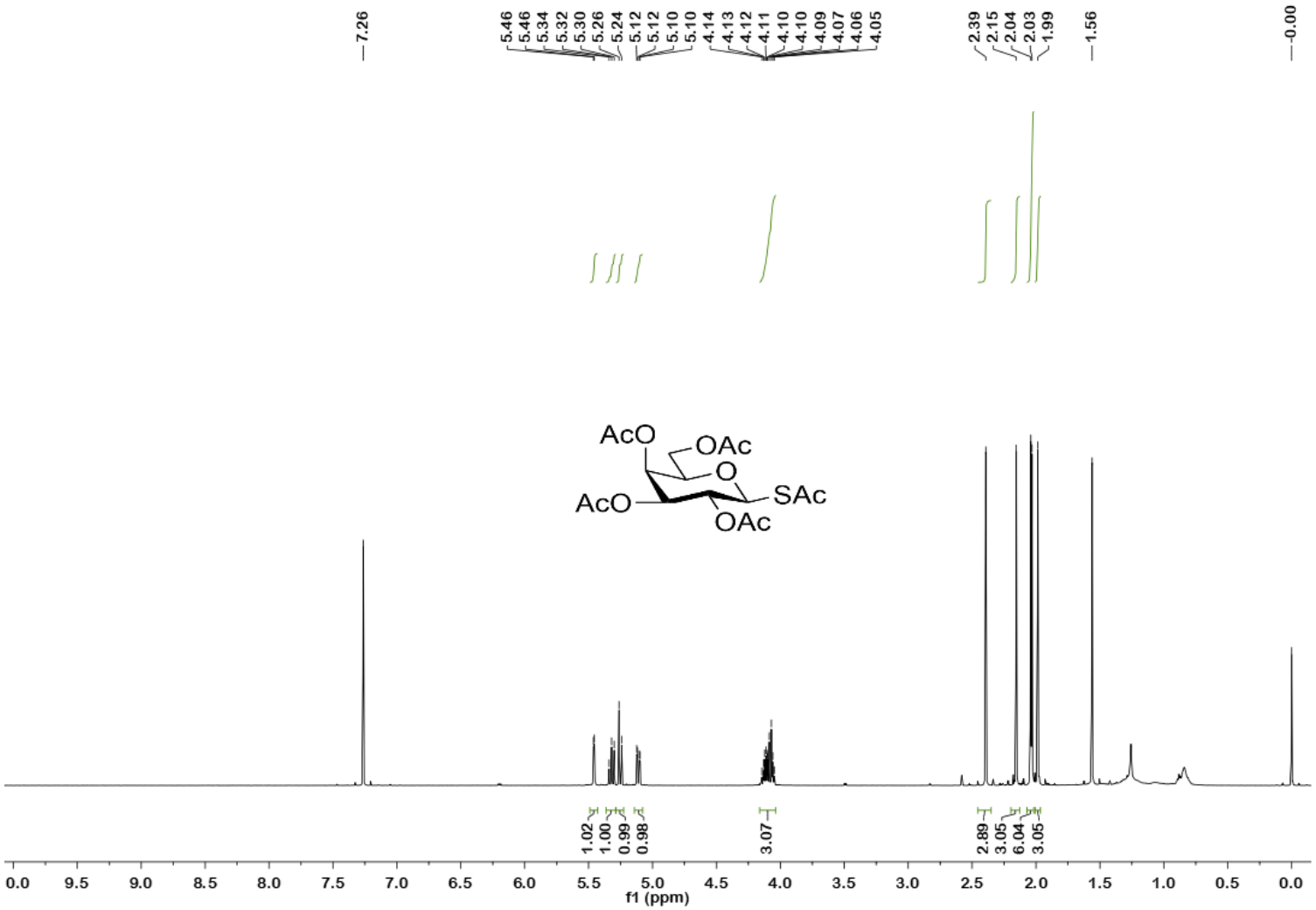


Figure S3. ^{1}H NMR spectrum of compound **2b** in $CDCl_3$.

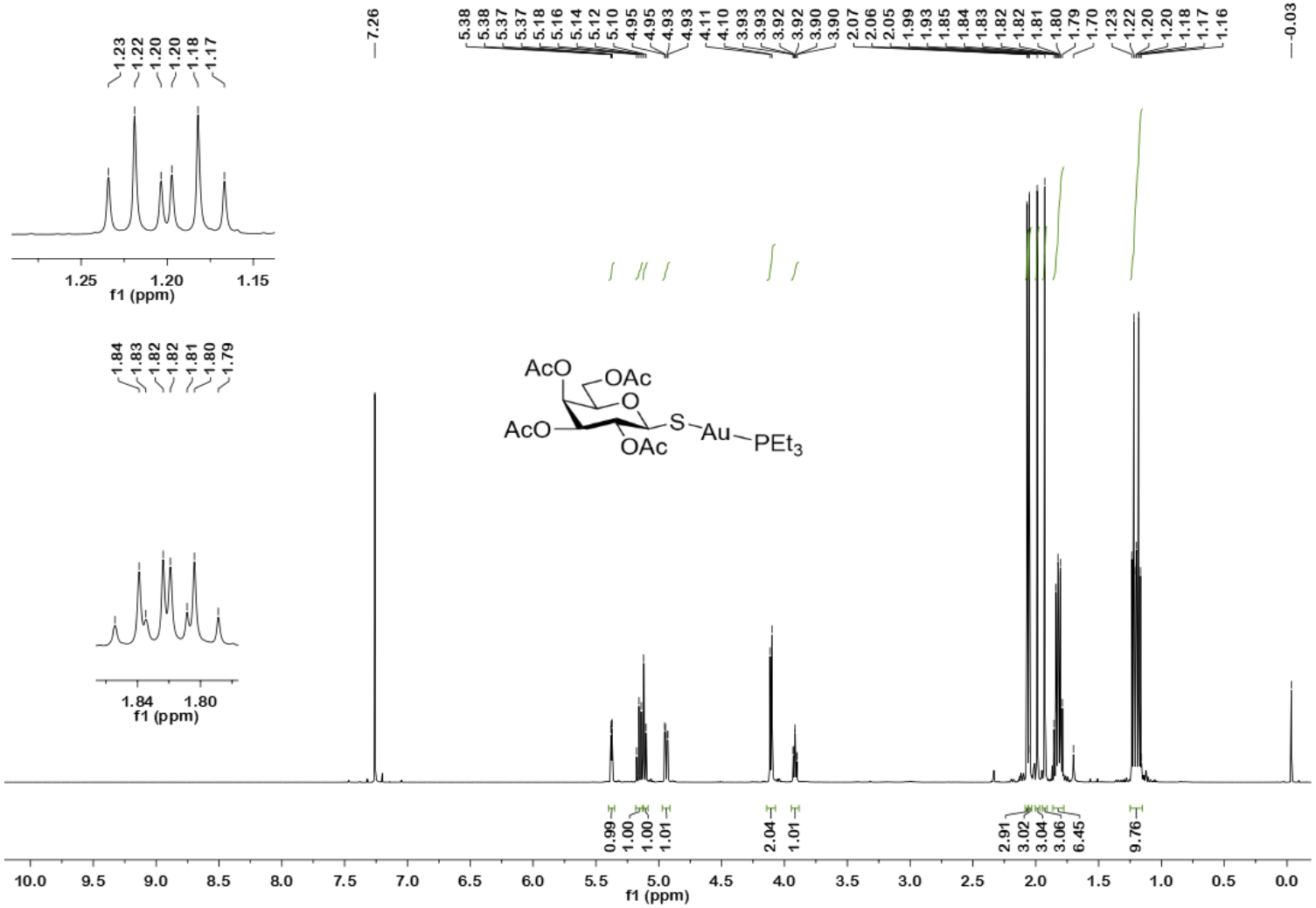


Figure S4. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

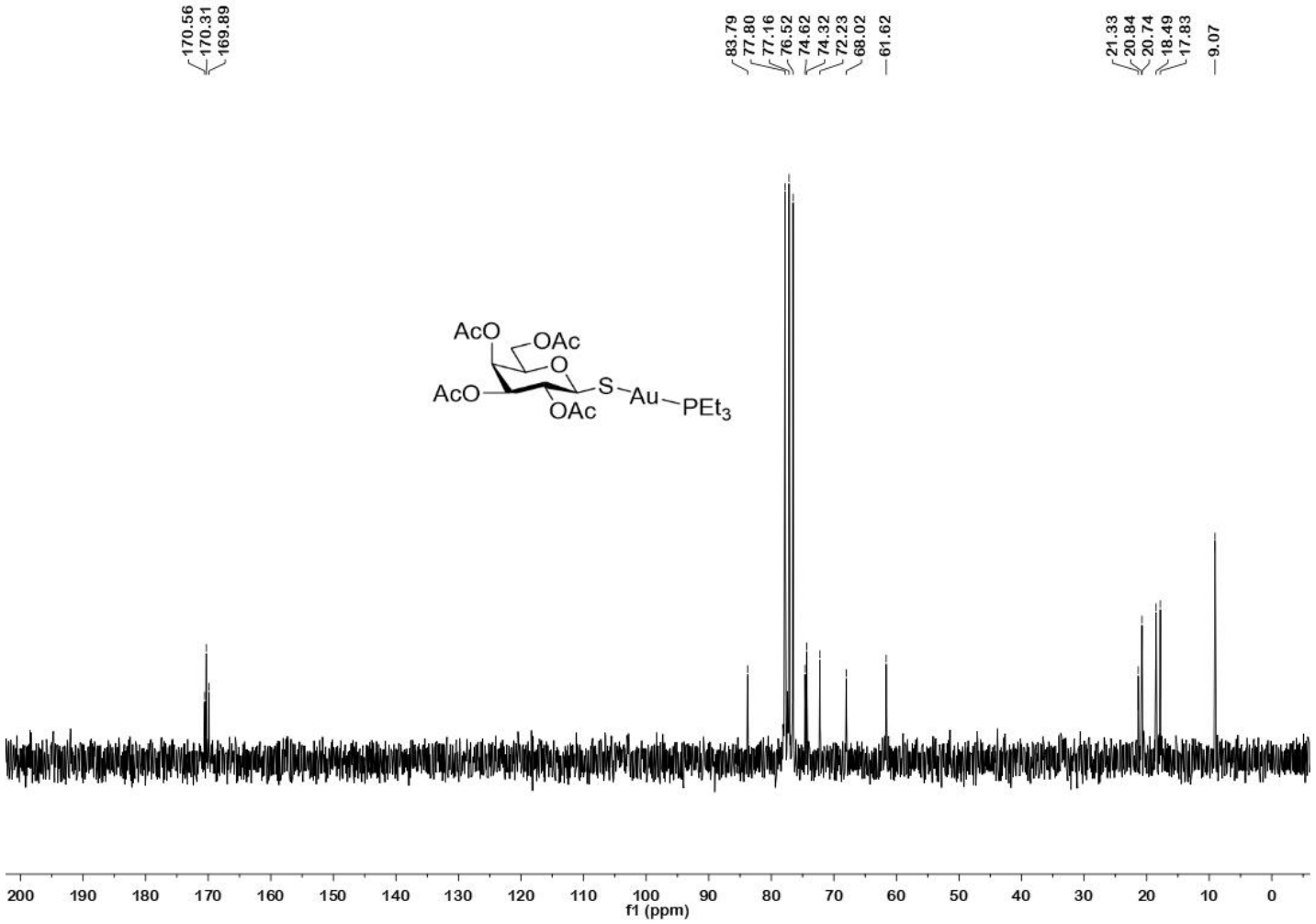


Figure S5. ^{13}C NMR spectrum of compound **2** in $CDCl_3$.

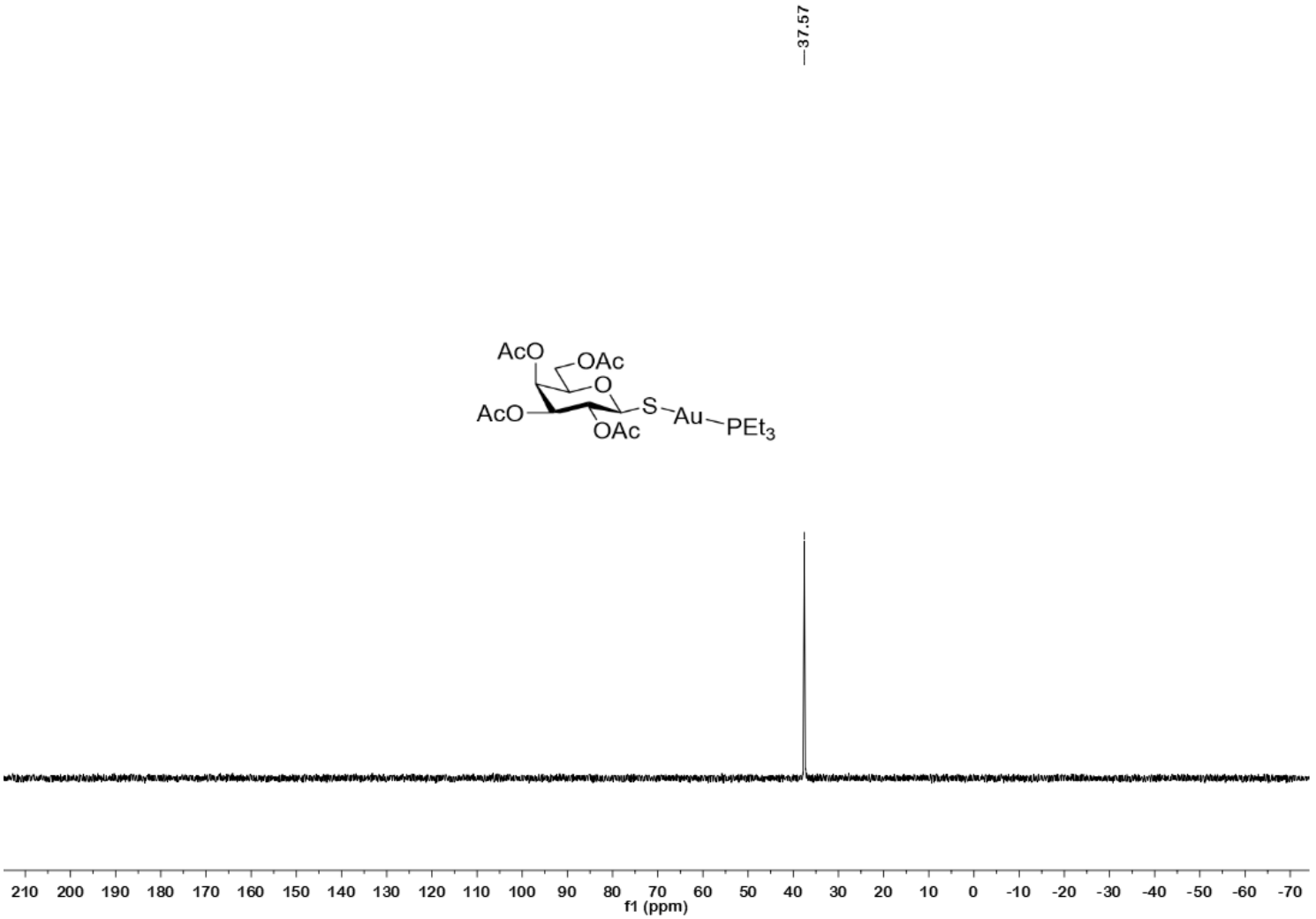


Figure S6. ^{31}P NMR spectrum of compound **2** in $CDCl_3$.

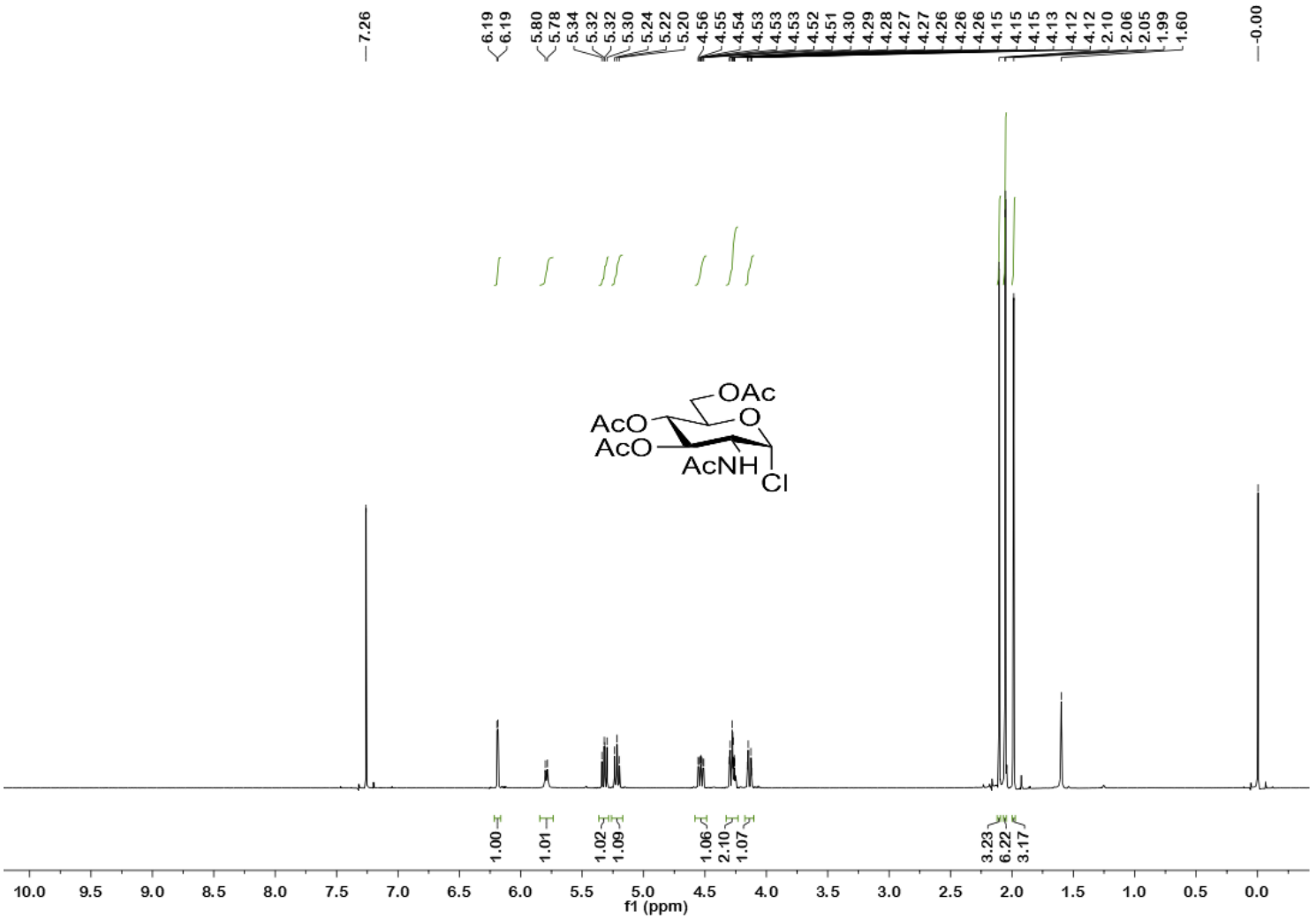


Figure S7. ^{1}H NMR spectrum of compound **3a** in $CDCl_3$.

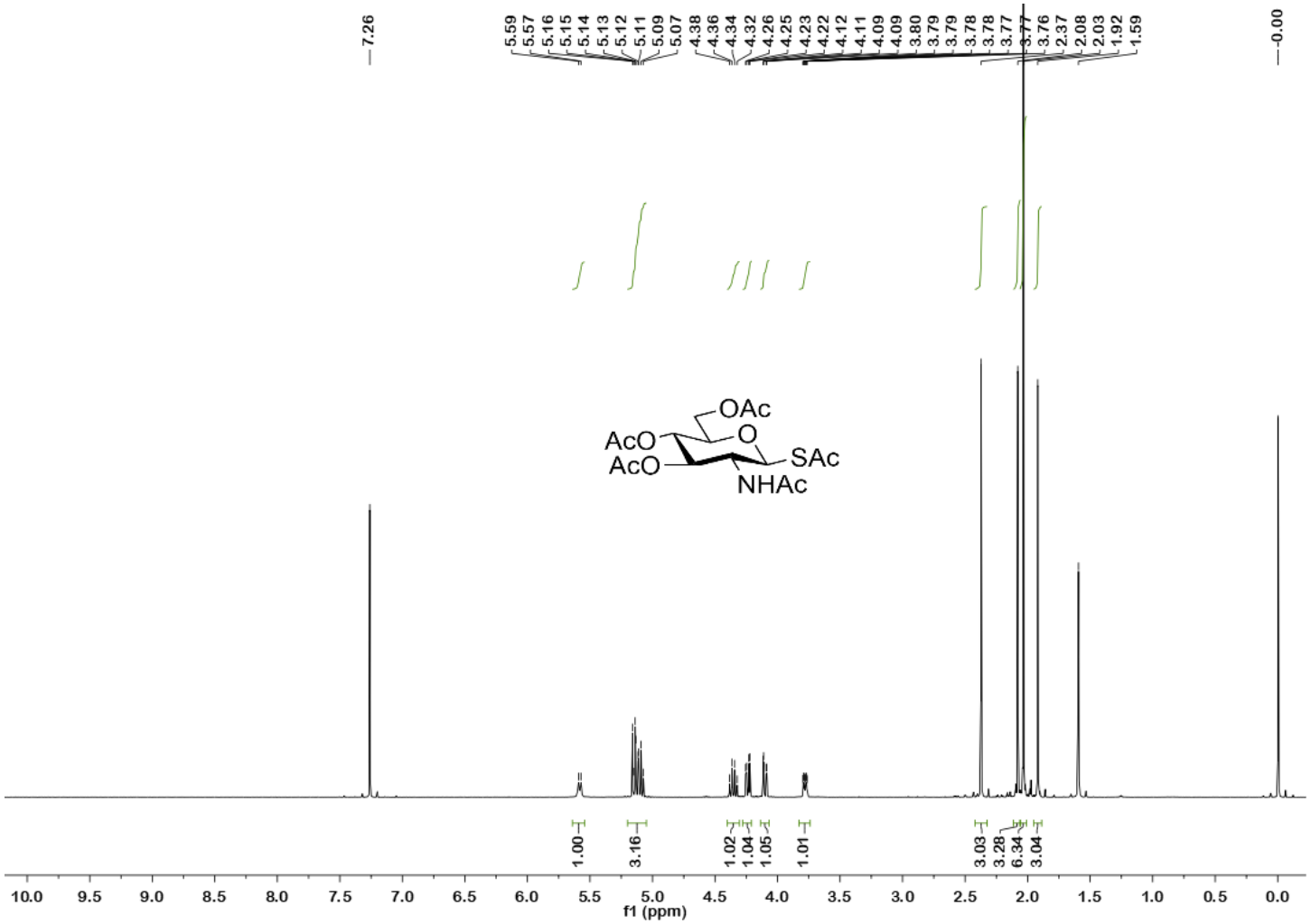


Figure S8. ^{1}H NMR spectrum of compound **3b** in $CDCl_3$.

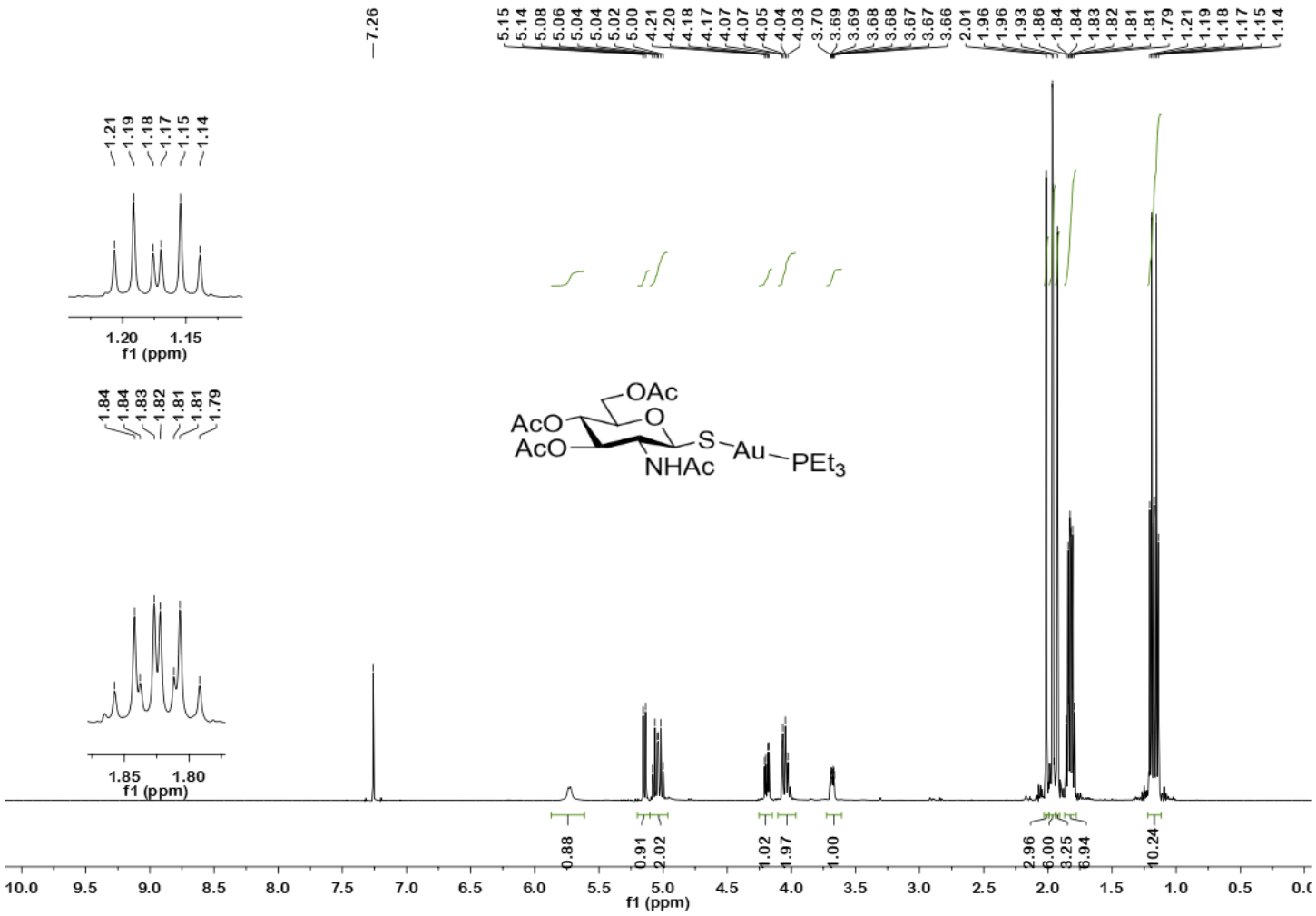


Figure S9. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

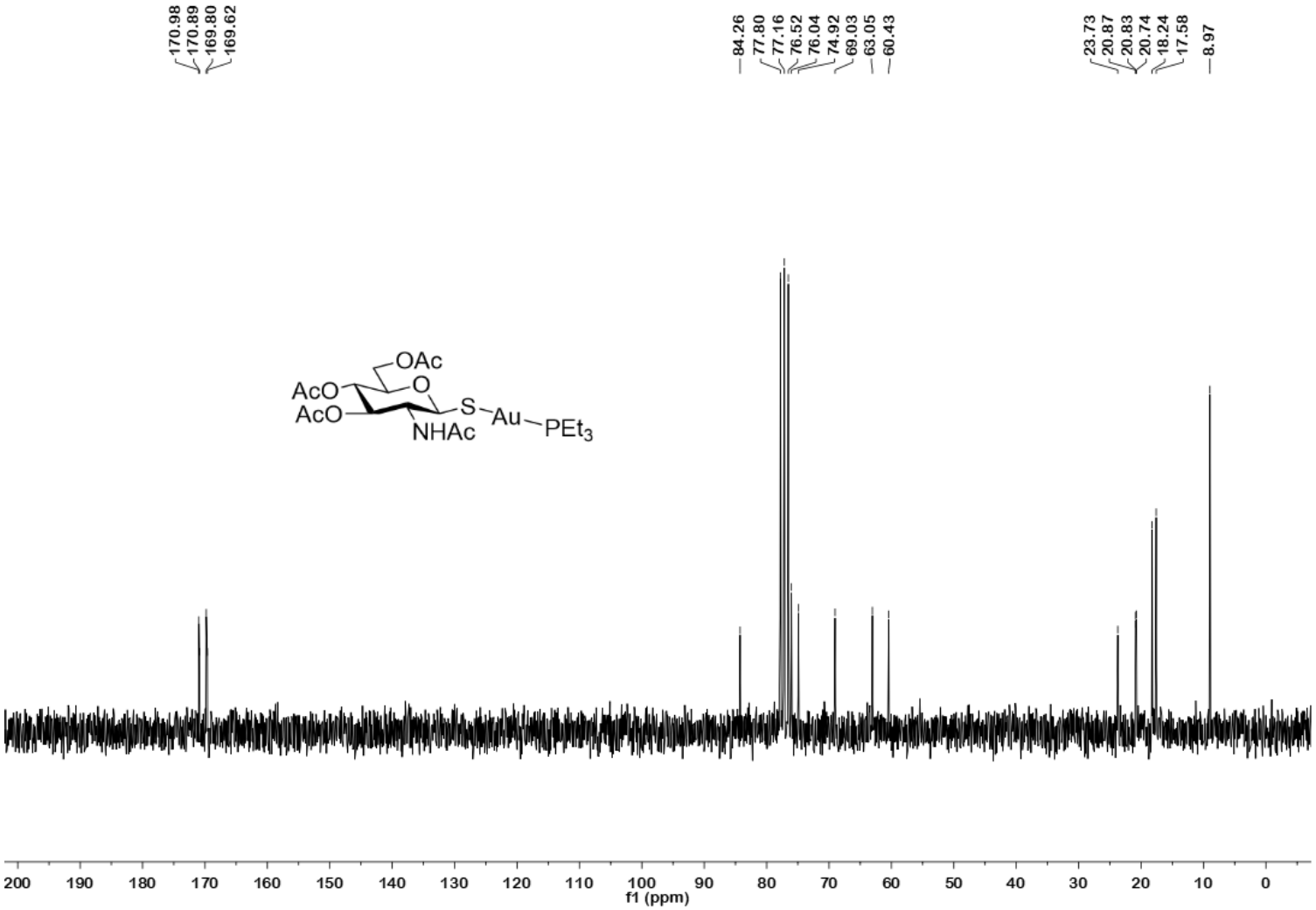


Figure S10. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

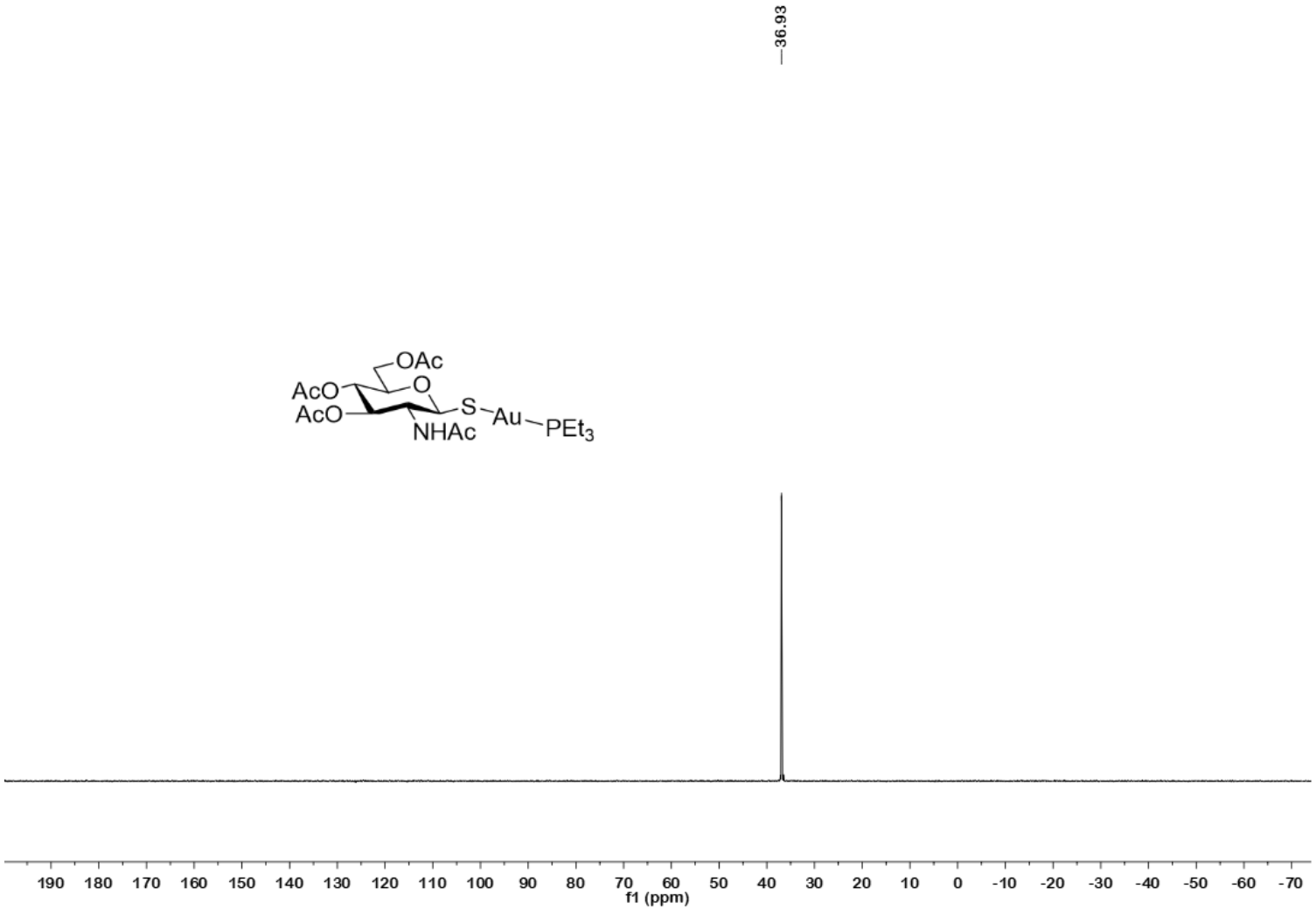


Figure S11. ^{31}P NMR spectrum of compound **3** in $CDCl_3$.

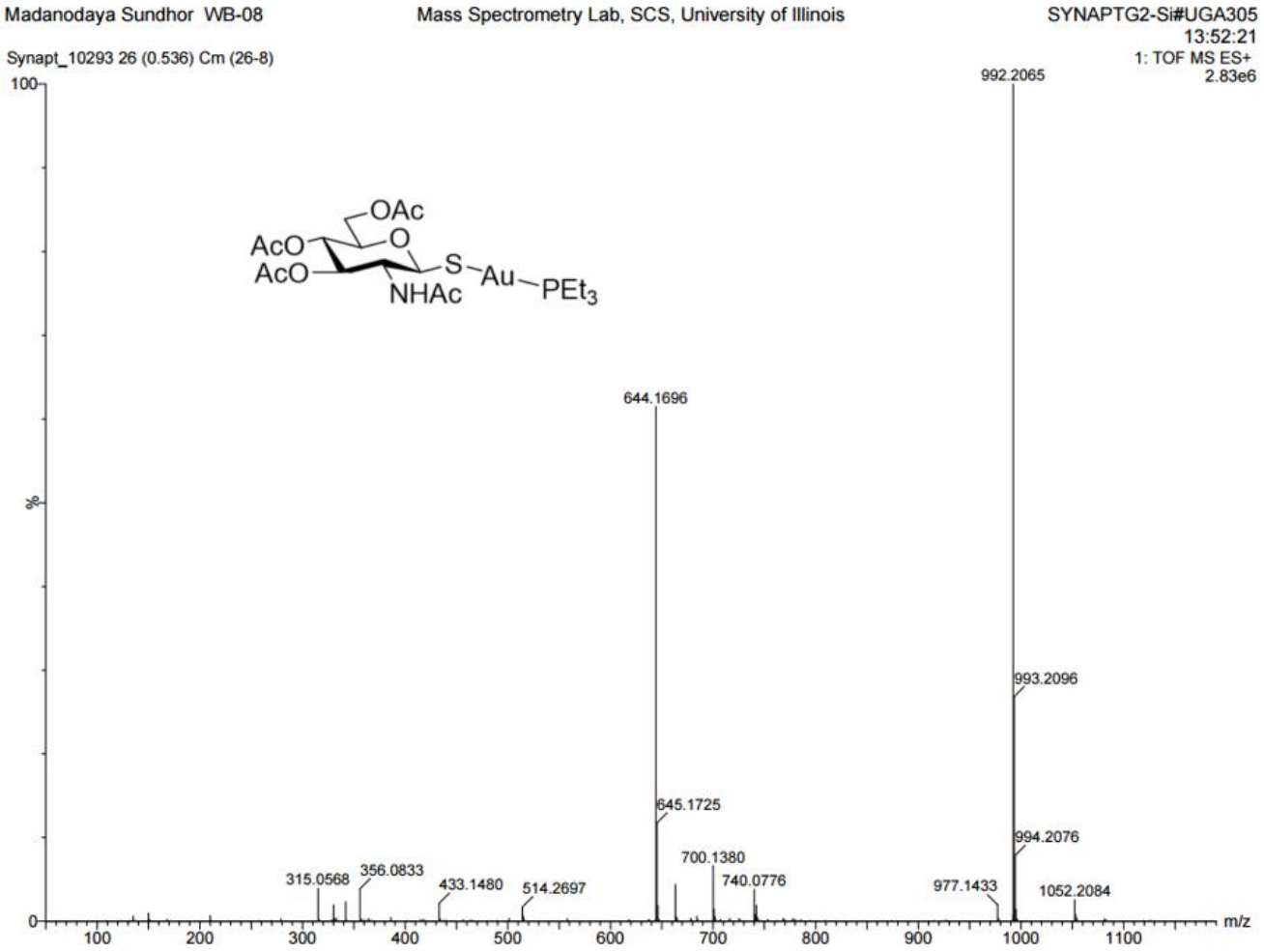


Figure S12. HRMS of compound **3**.

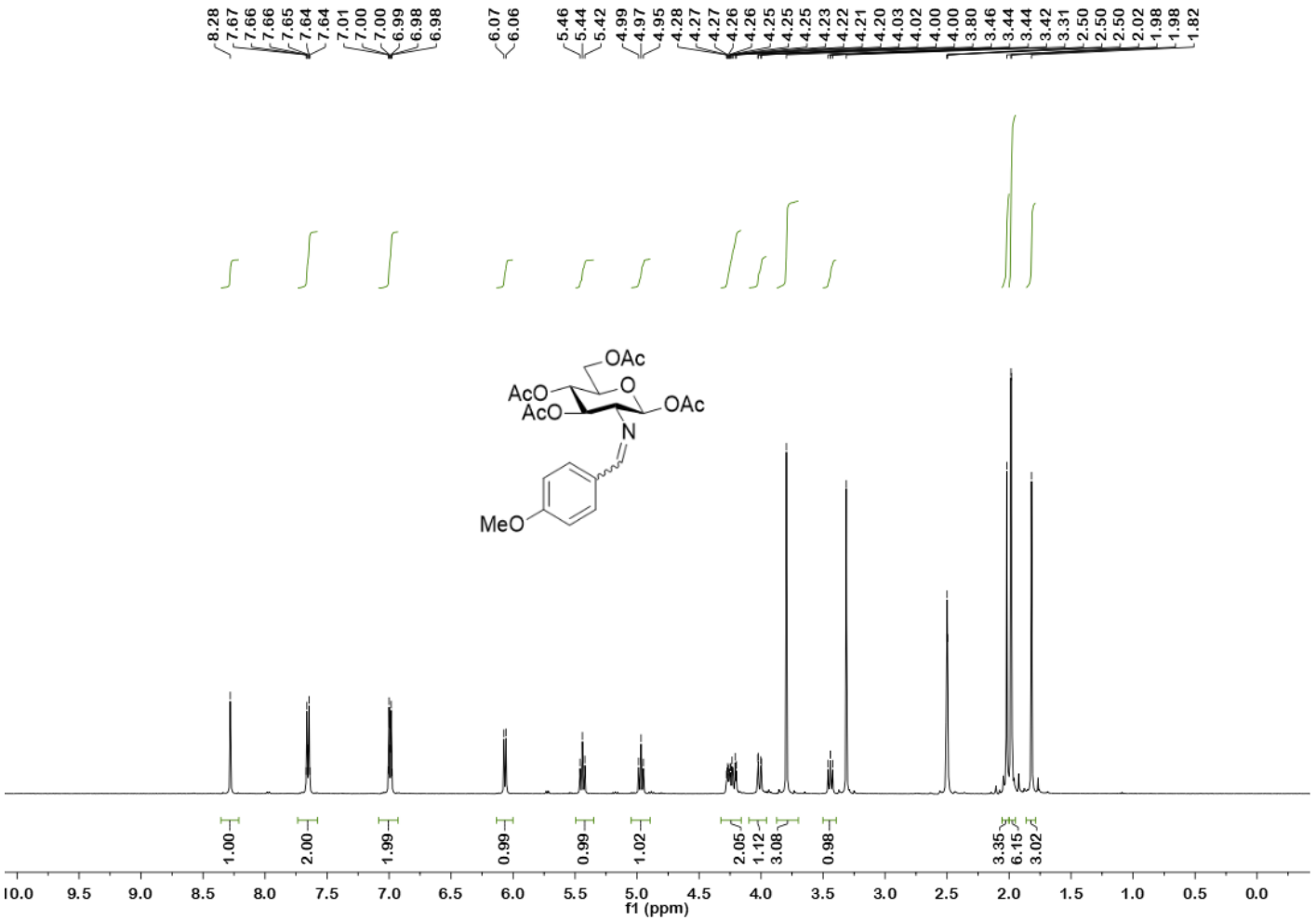


Figure S13. ^{1}H NMR spectrum of compound **4c** in DMSO-d_6.

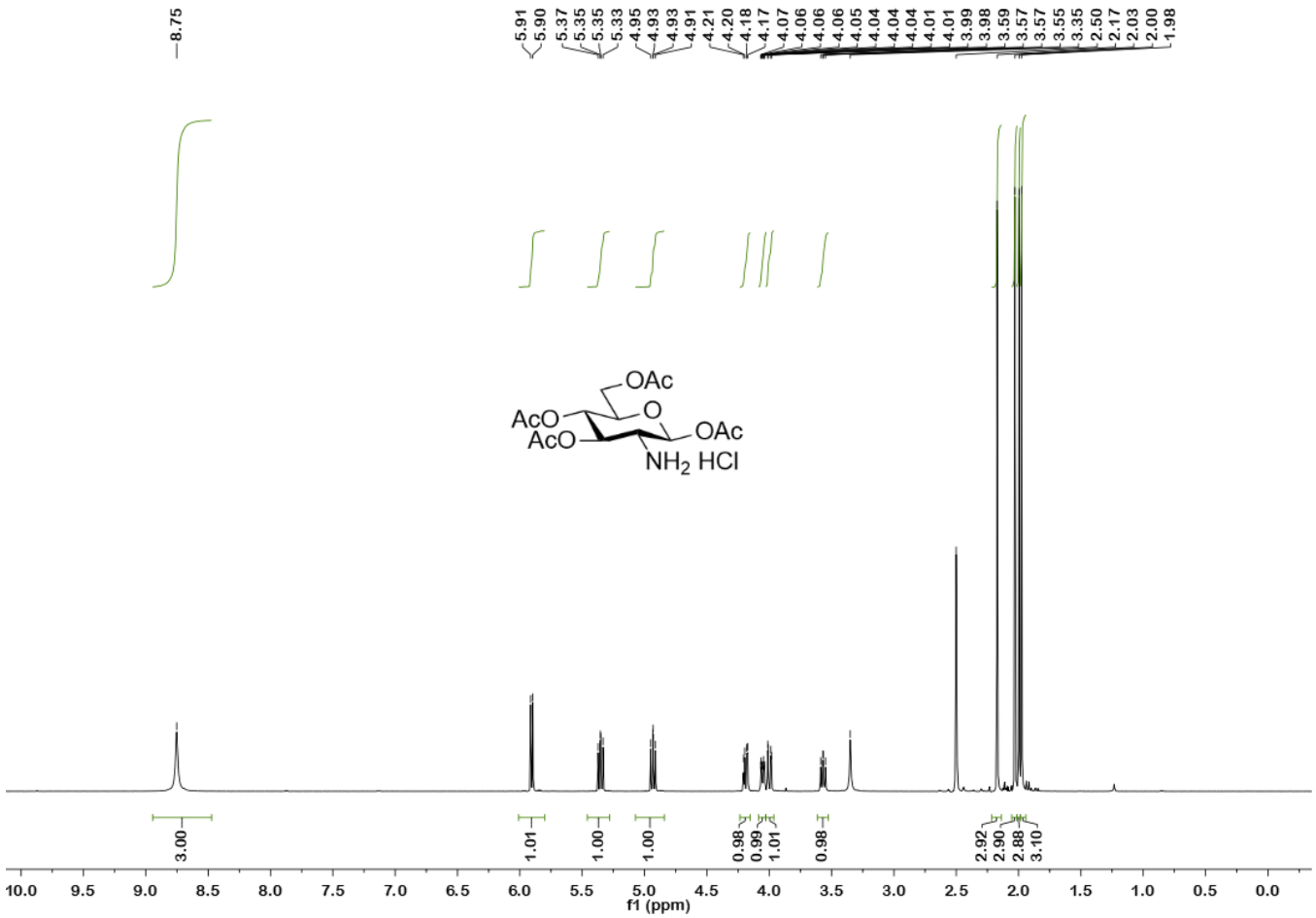


Figure S14. ^{1}H NMR spectrum of compound **4d** in DMSO-d_6.

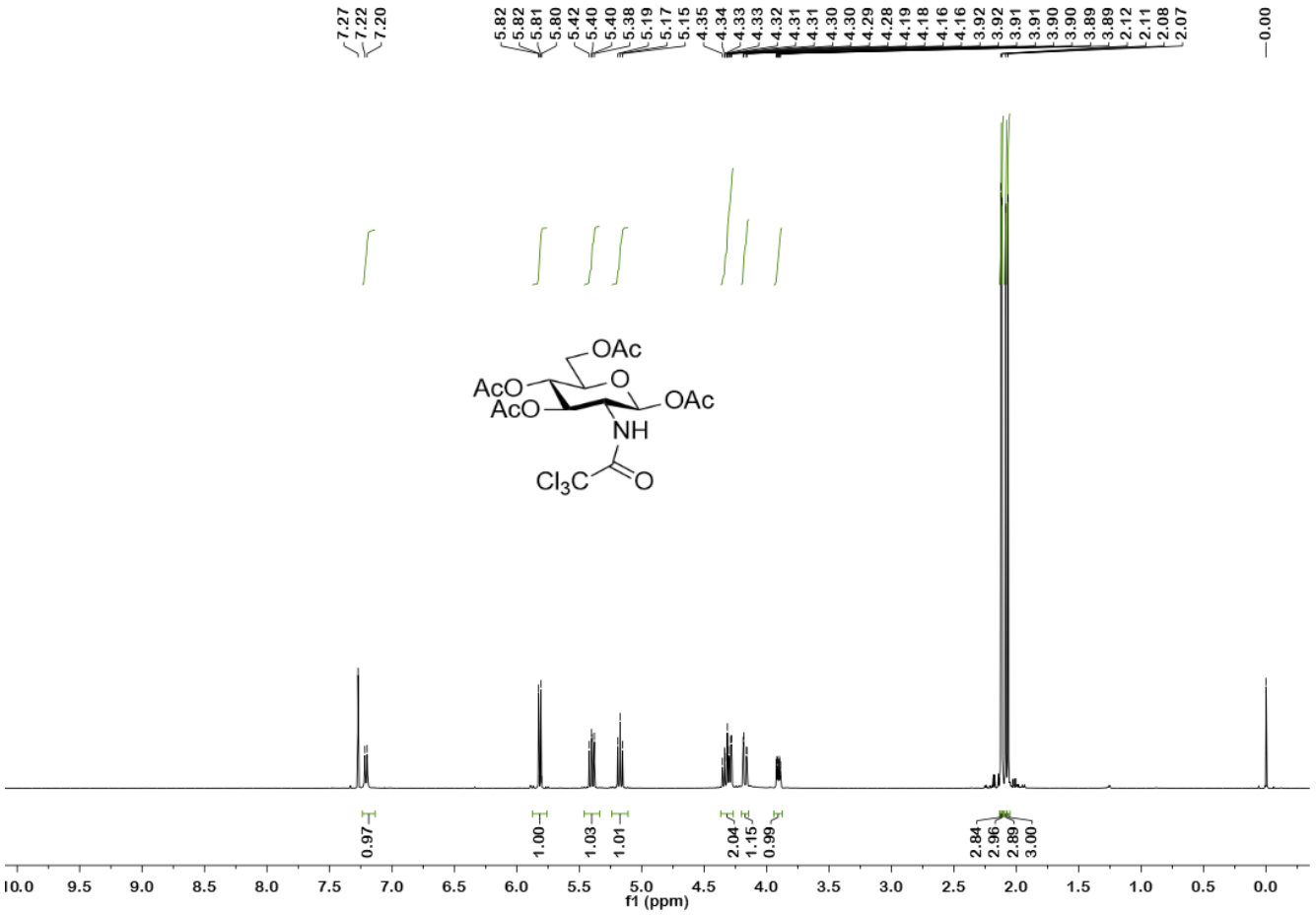


Figure S15. ^{1}H NMR spectrum of compound **4e** in $CDCl_3$.

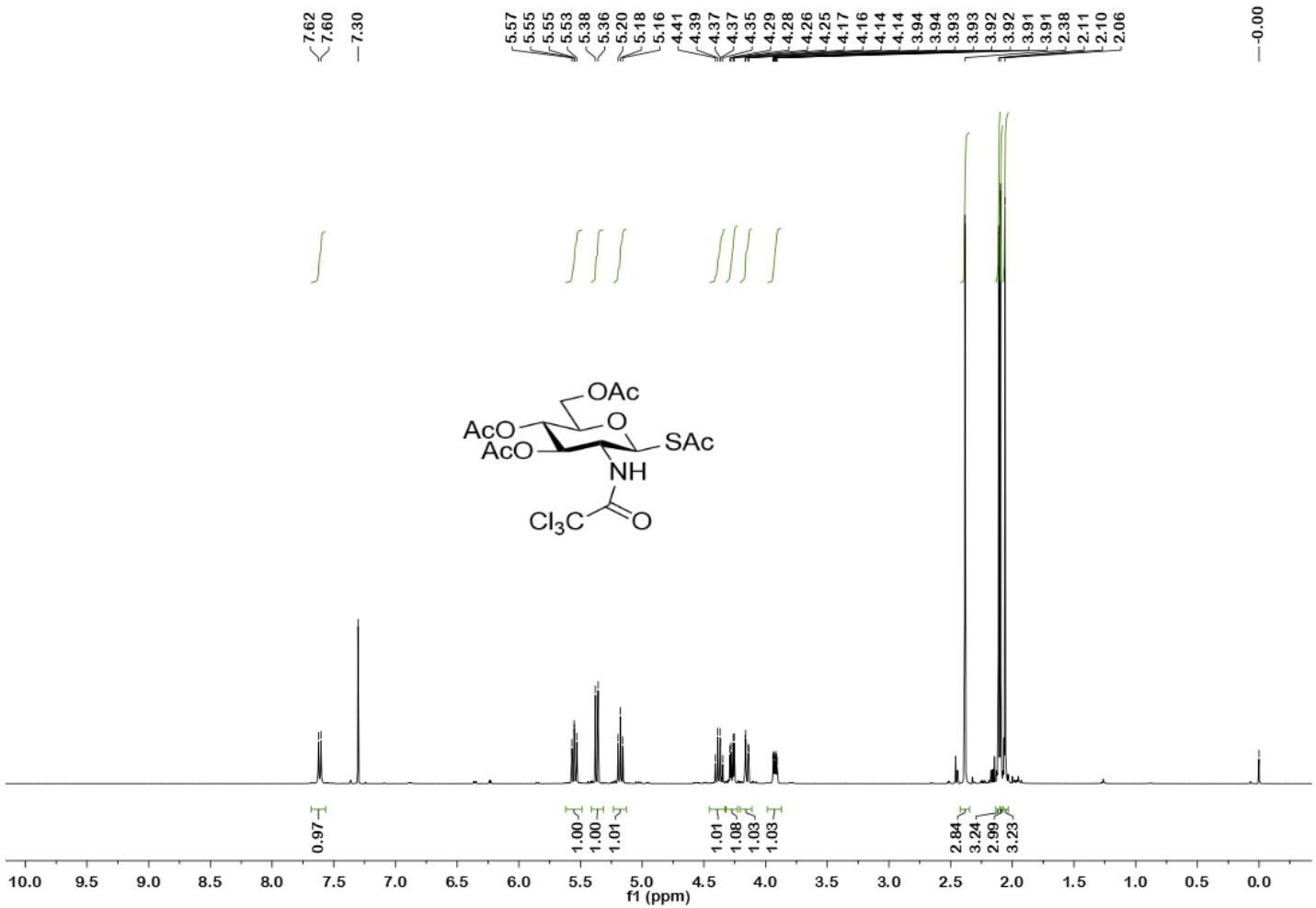


Figure S16. ^{1}H NMR spectrum of compound **4f** in $CDCl_3$.

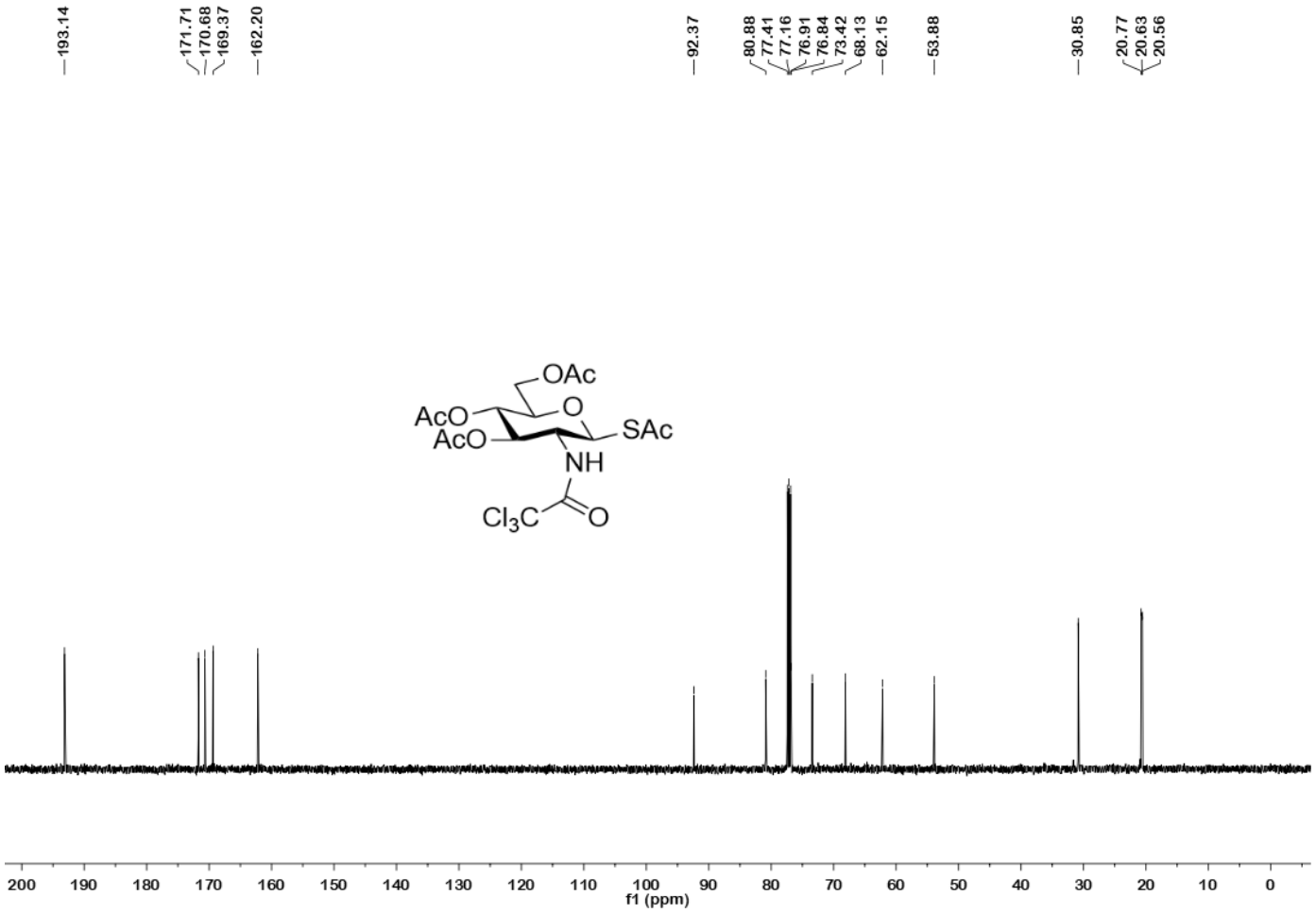


Figure S17. ^{13}C NMR spectrum of compound **4f** in $CDCl_3$.

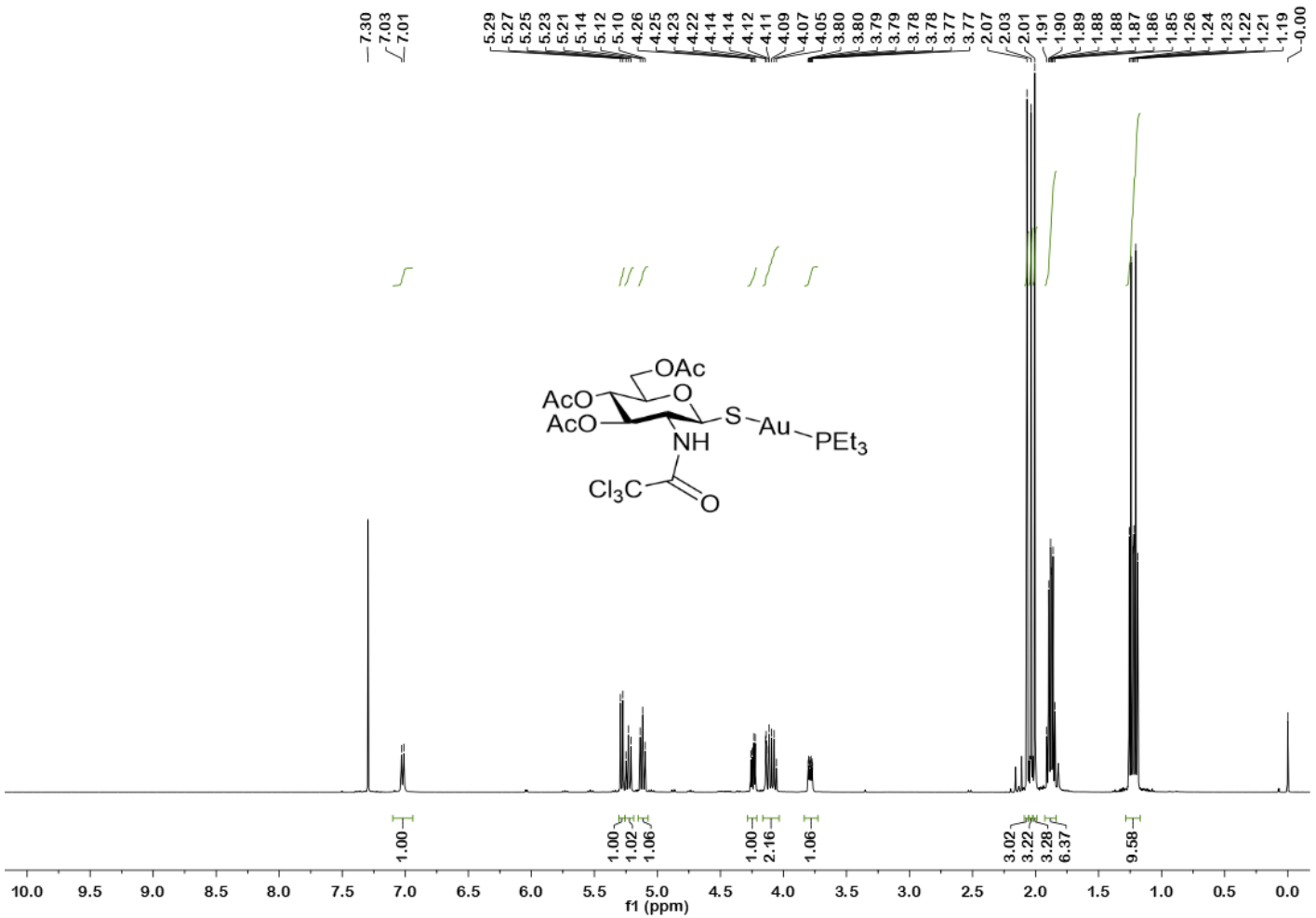


Figure S18. ^{1}H NMR spectrum of compound **4** in $CDCl_3$.

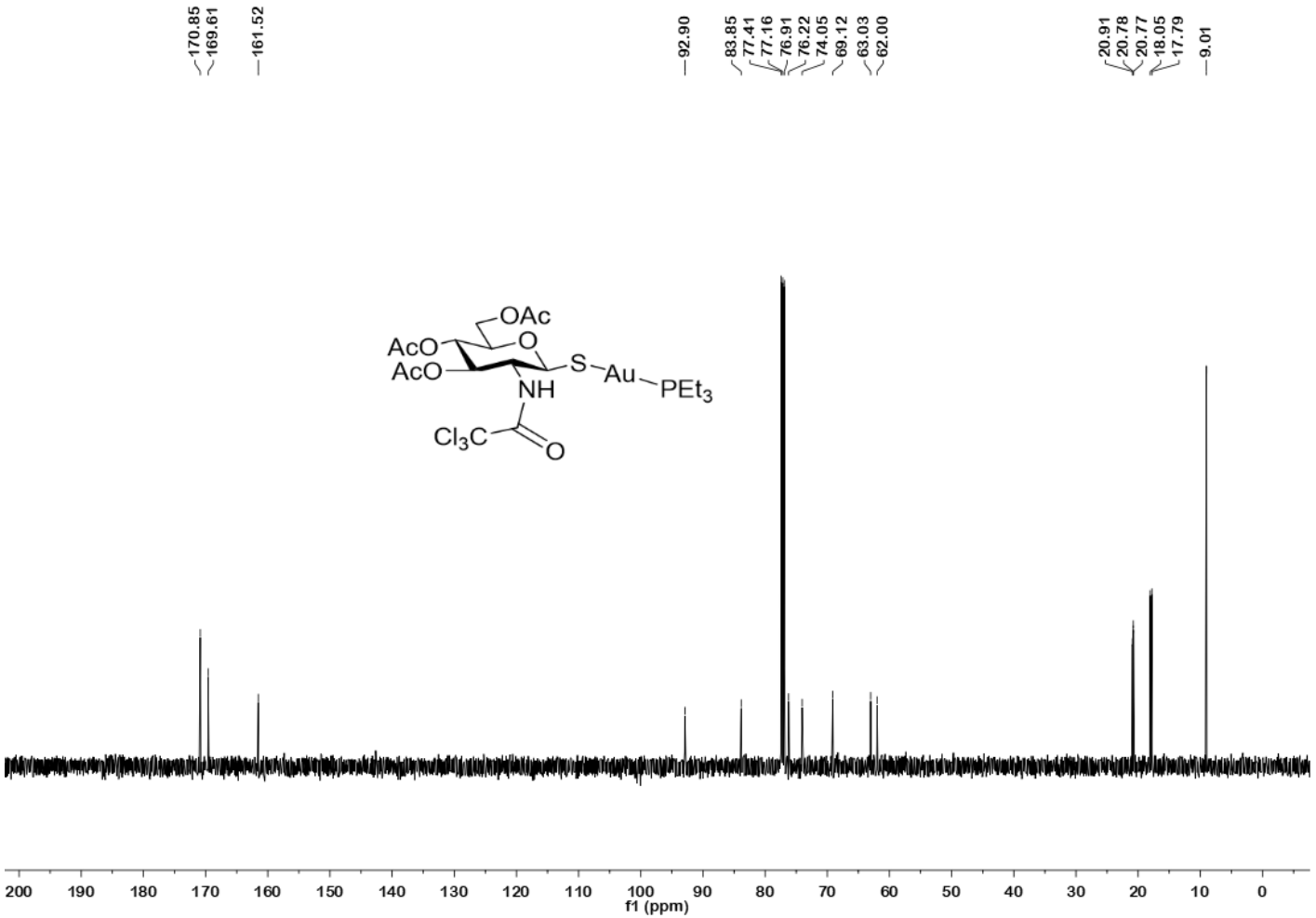


Figure S19. ^{13}C NMR spectrum of compound **4** in $CDCl_3$.

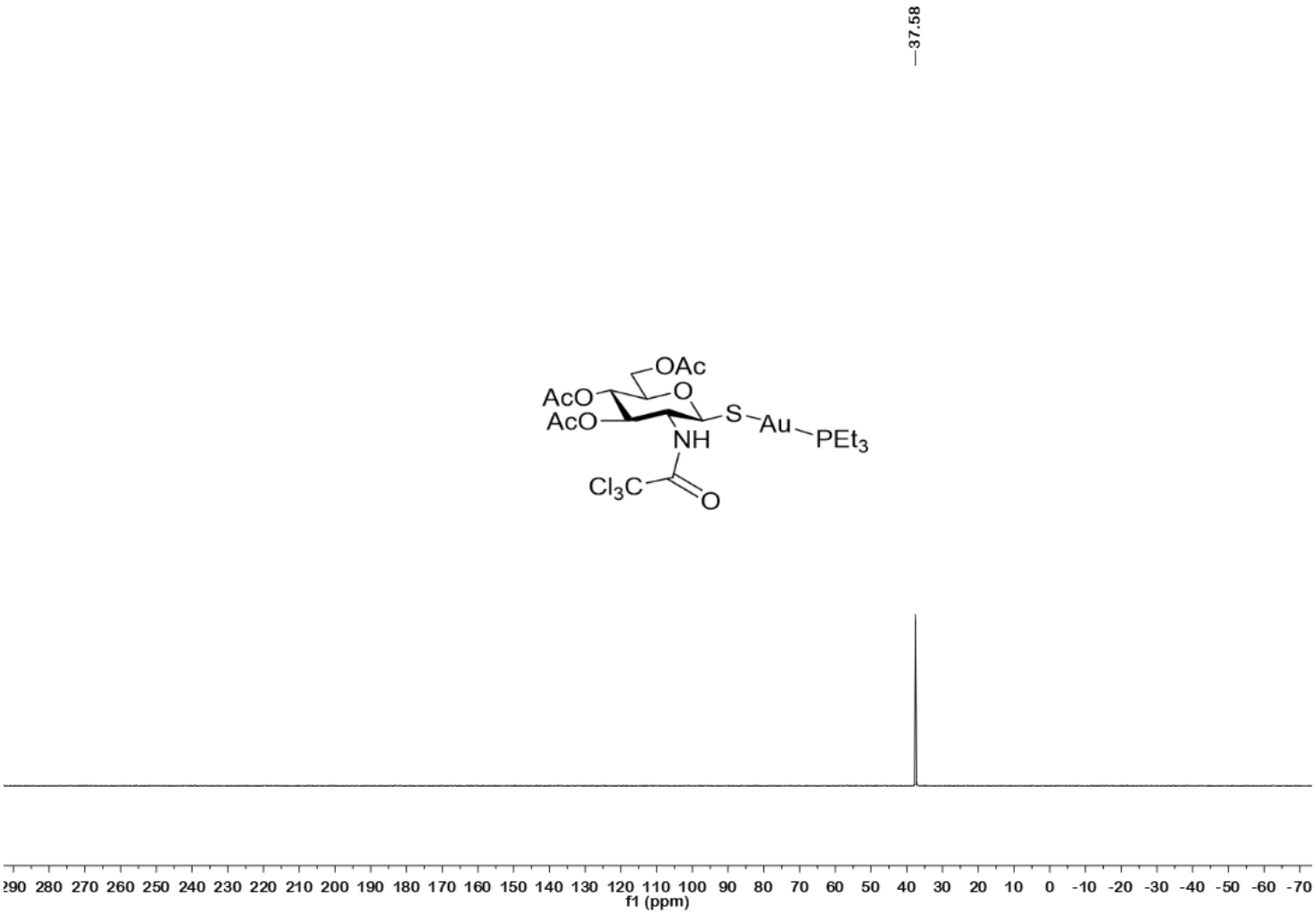


Figure S20. ^{31}P NMR spectrum of compound **4** in $CDCl_3$.

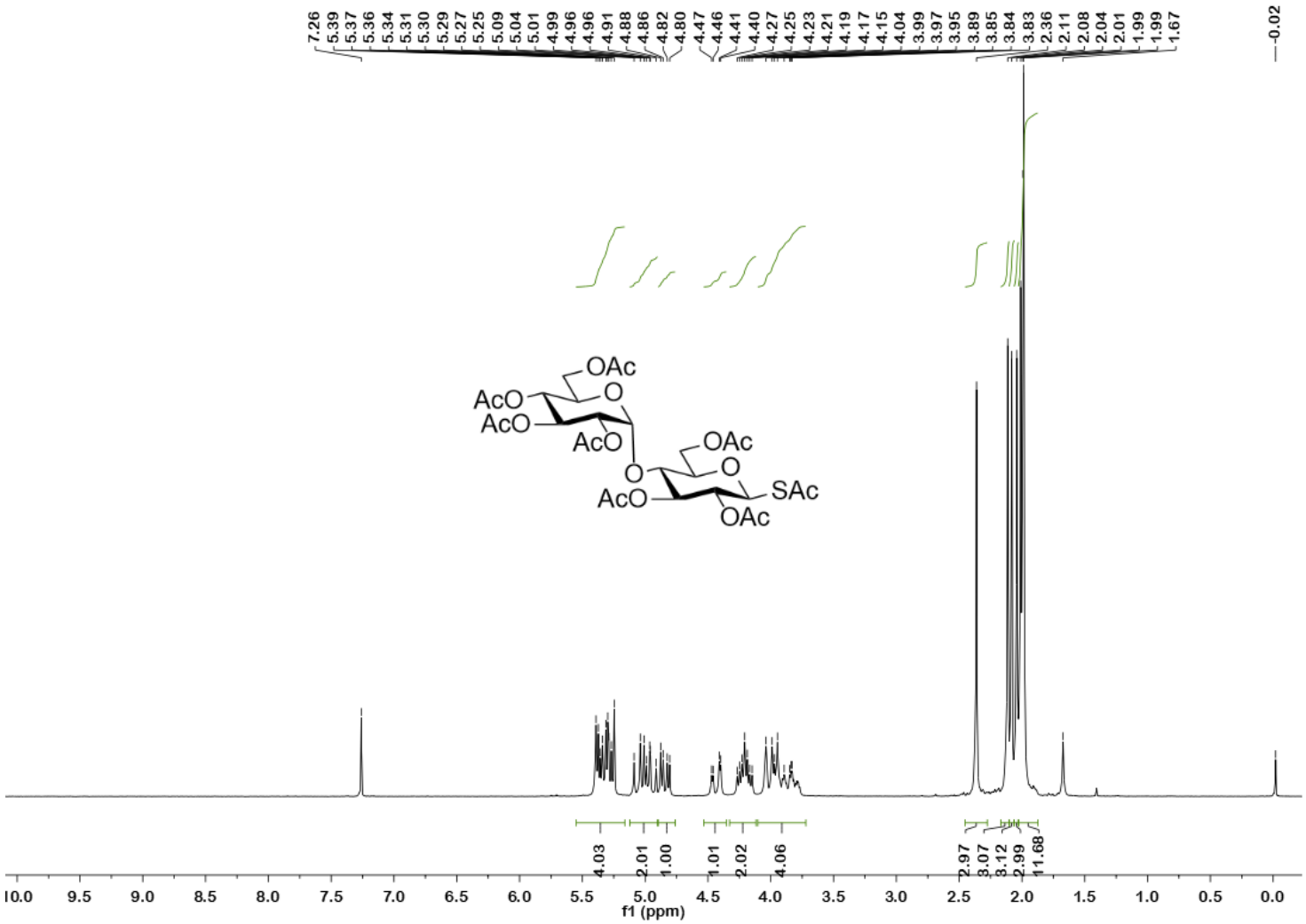


Figure S21. ^{1}H NMR spectrum of compound **5b** in $CDCl_3$.

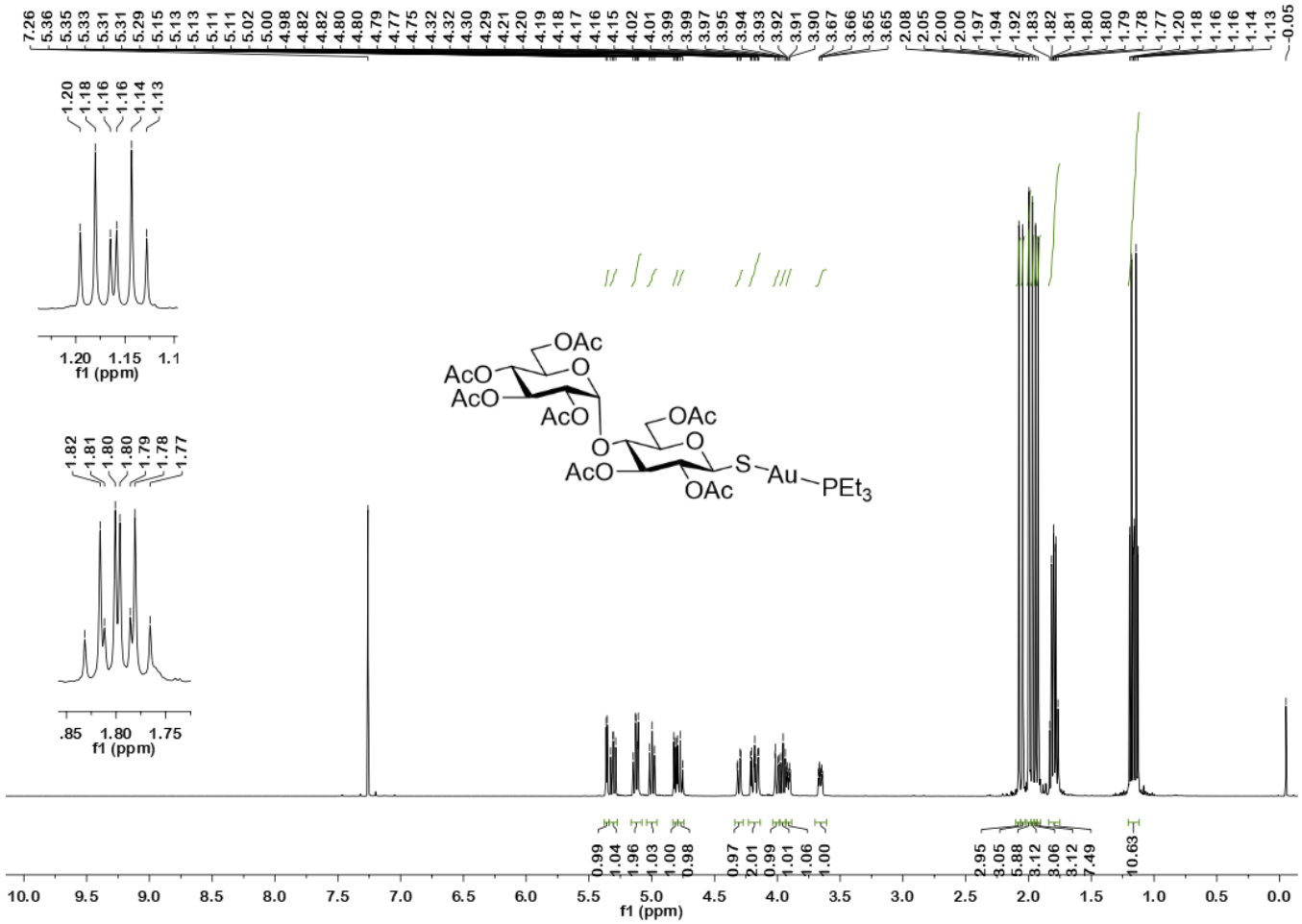


Figure S22. ^{1}H NMR spectrum of compound **5** in $CDCl_3$

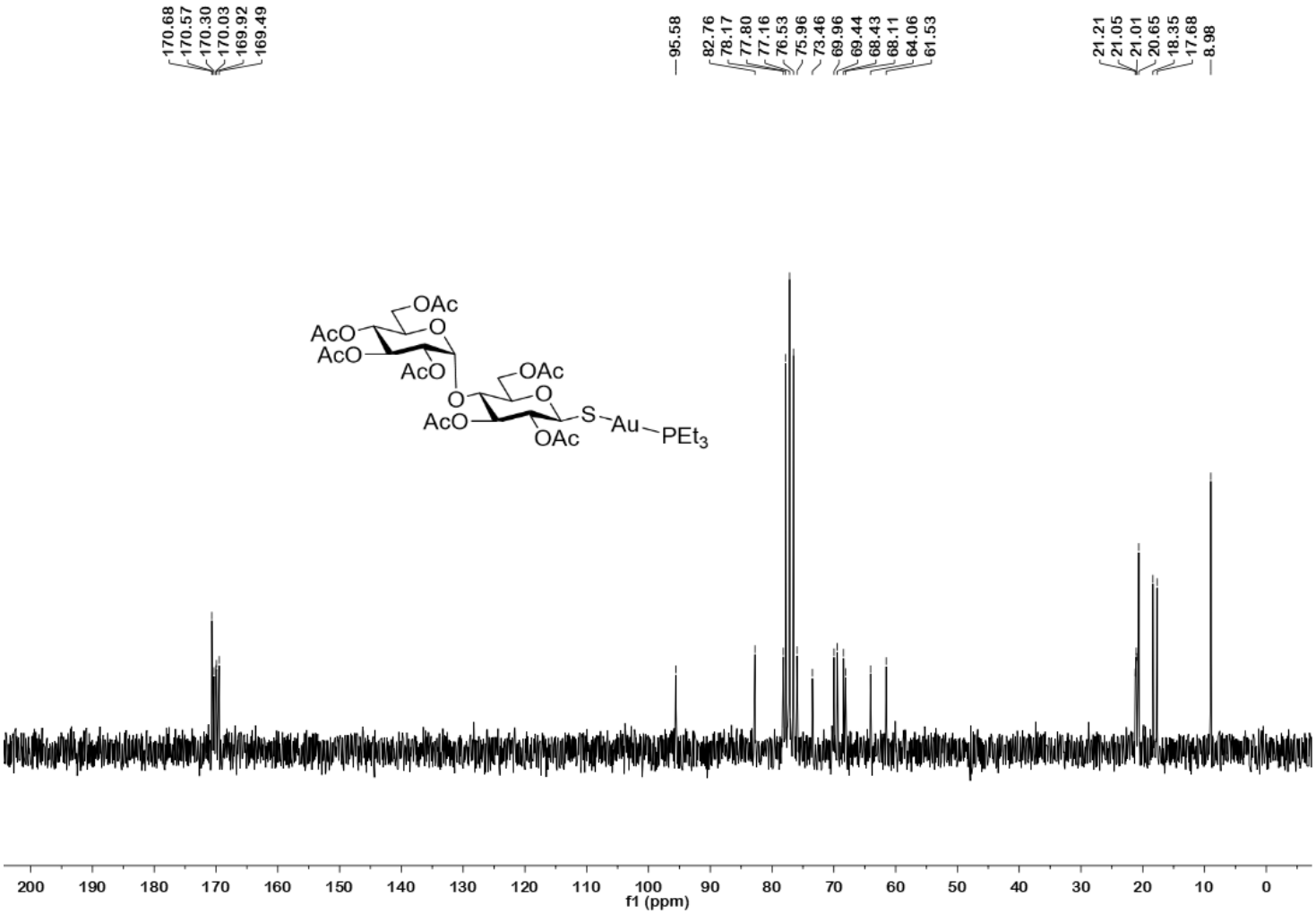


Figure S23. ^{13}C NMR spectrum of compound **5** in $CDCl_3$

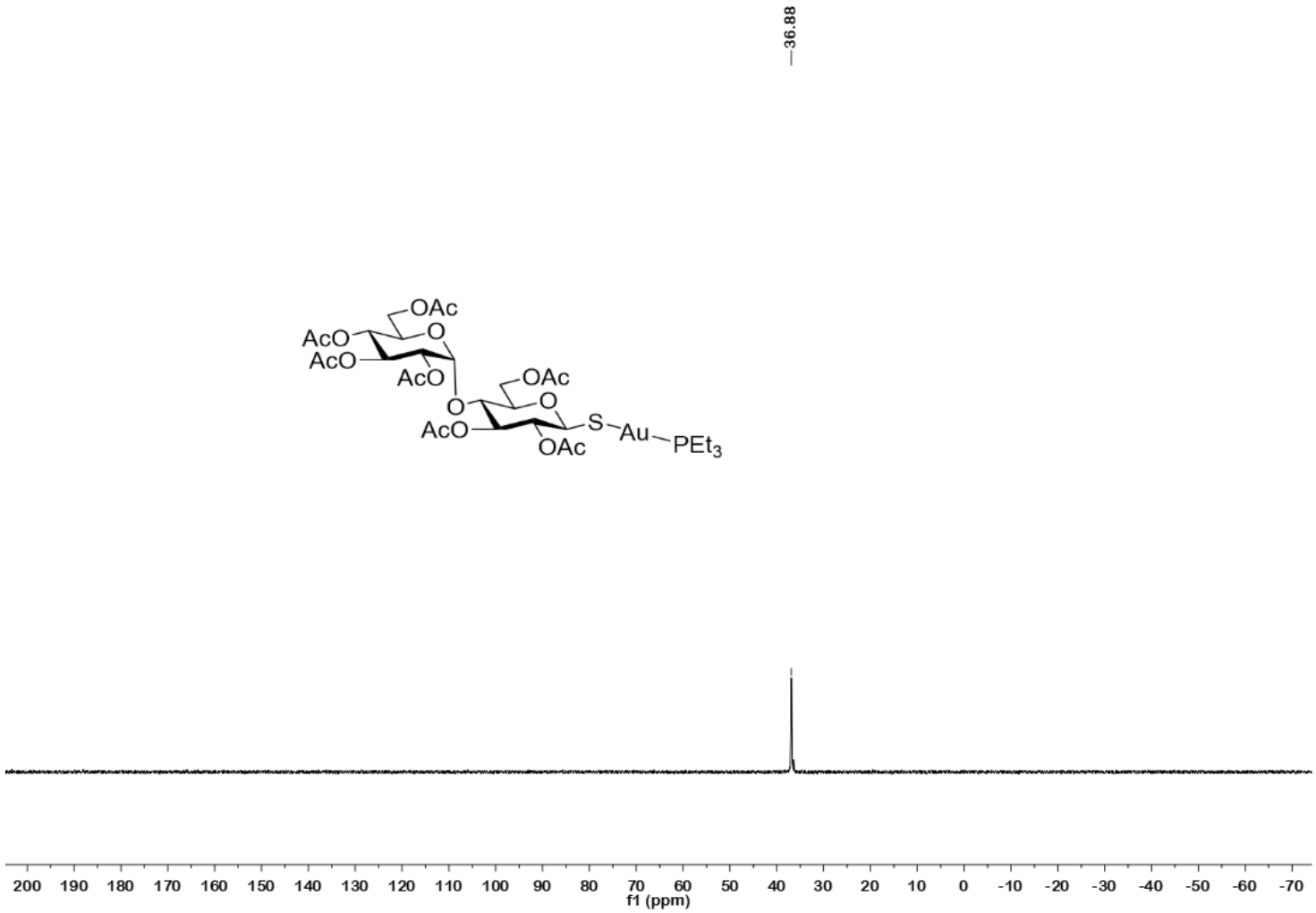


Figure S24. ^{31}P NMR spectrum of compound **5** in $CDCl_3$

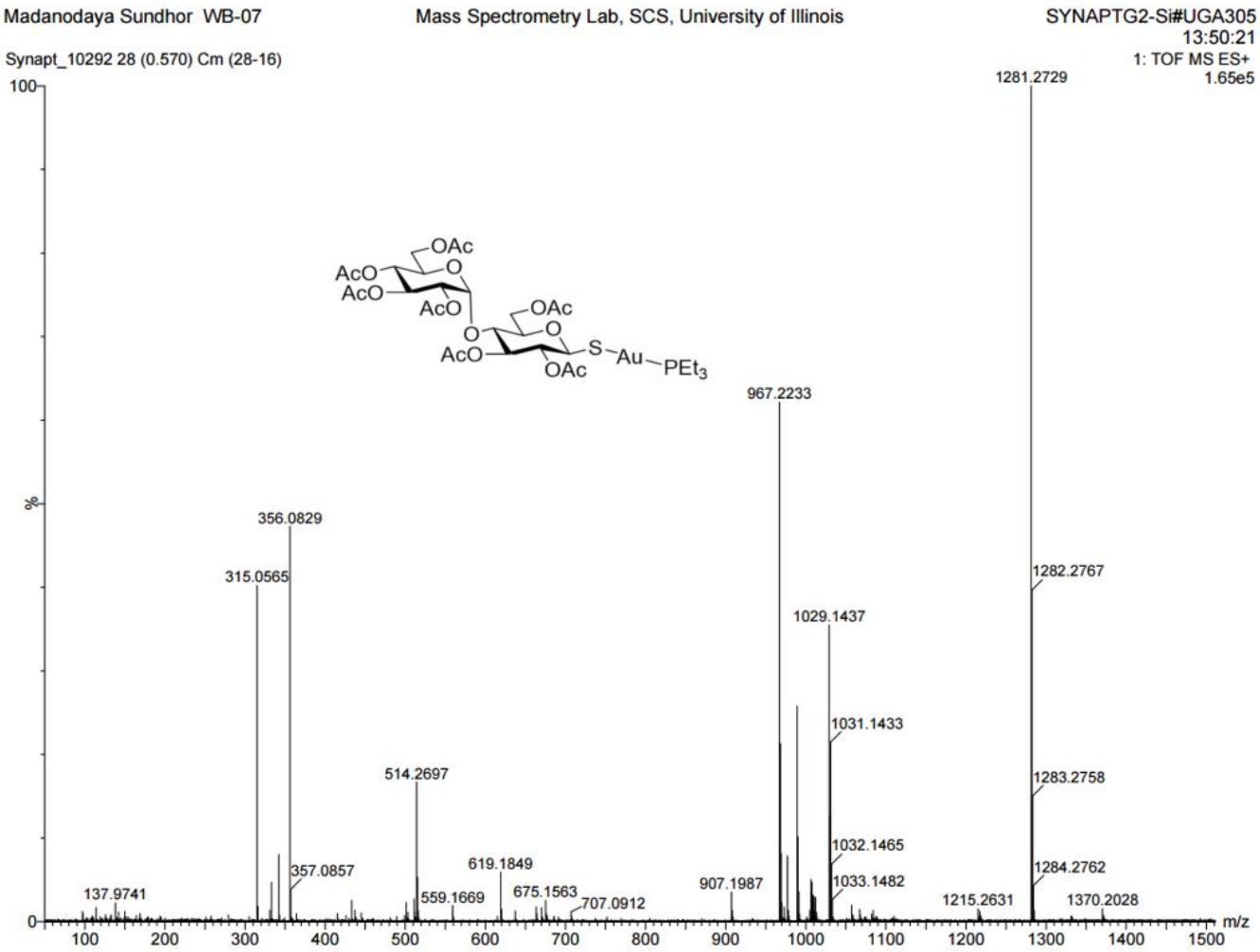


Figure S25. HRMS of compound **5.**

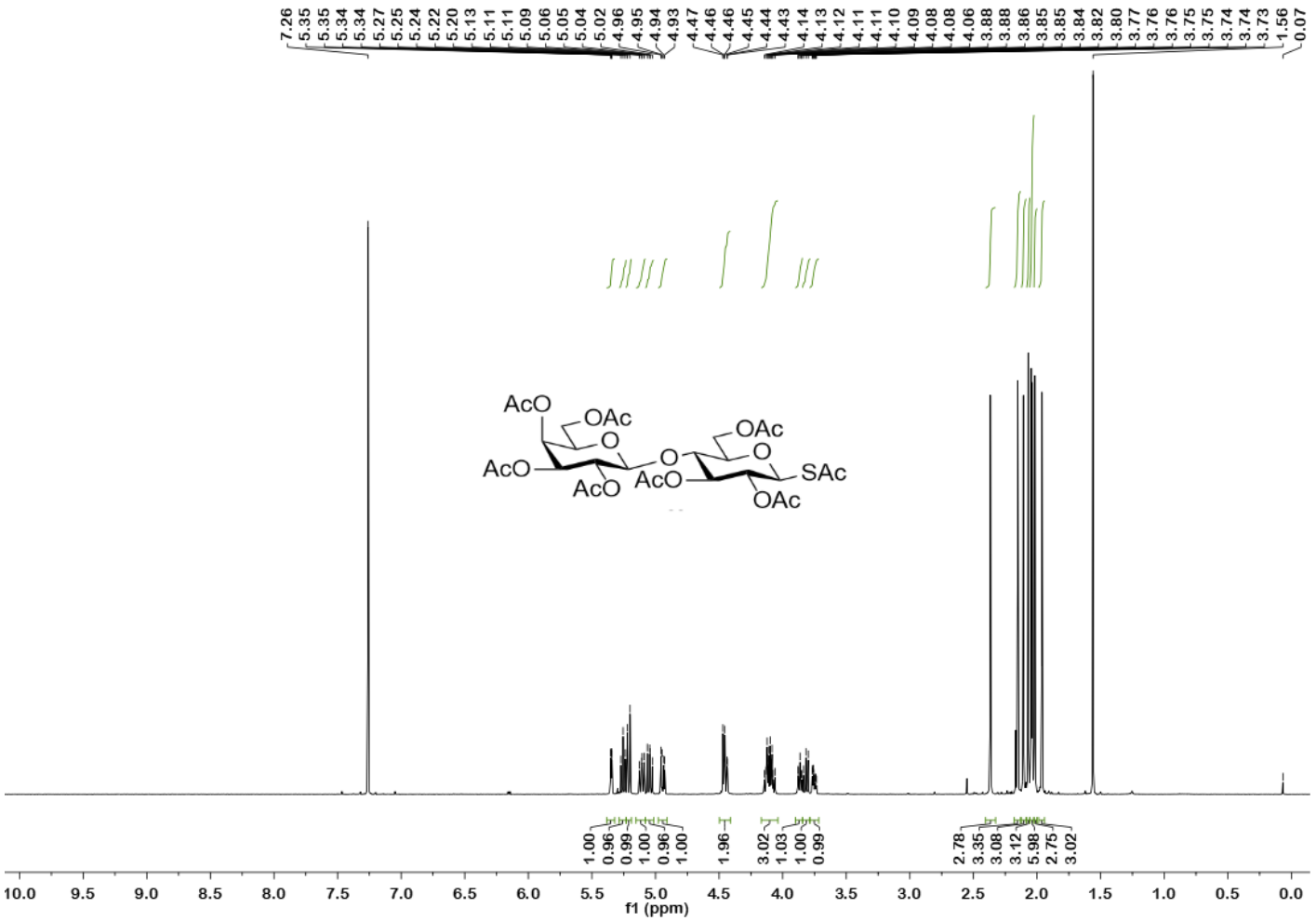


Figure S26. ^{1}H NMR spectrum of compound **6b** in $CDCl_3$.

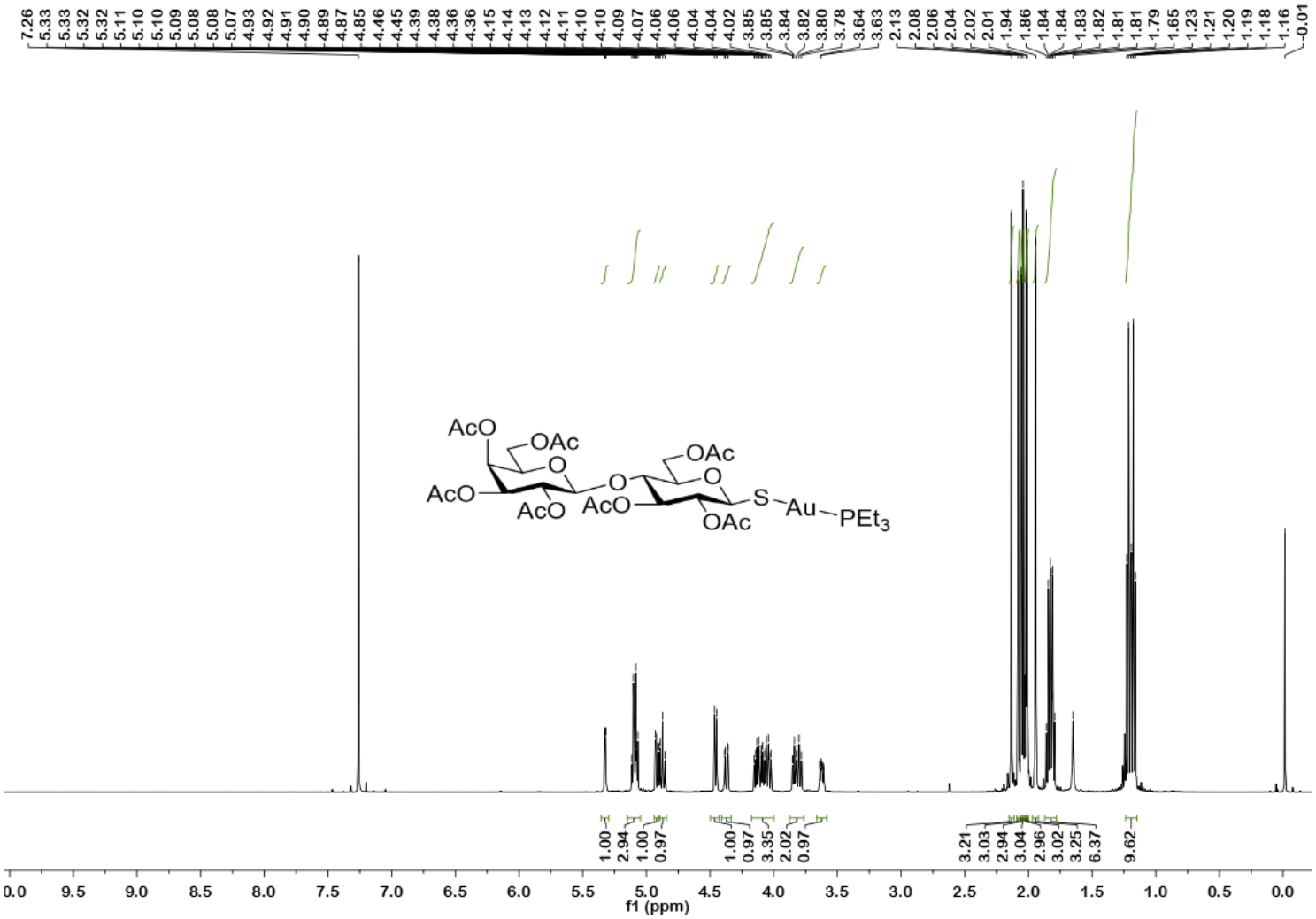


Figure S27. ^{1}H NMR spectrum of compound **6** in $CDCl_3$.

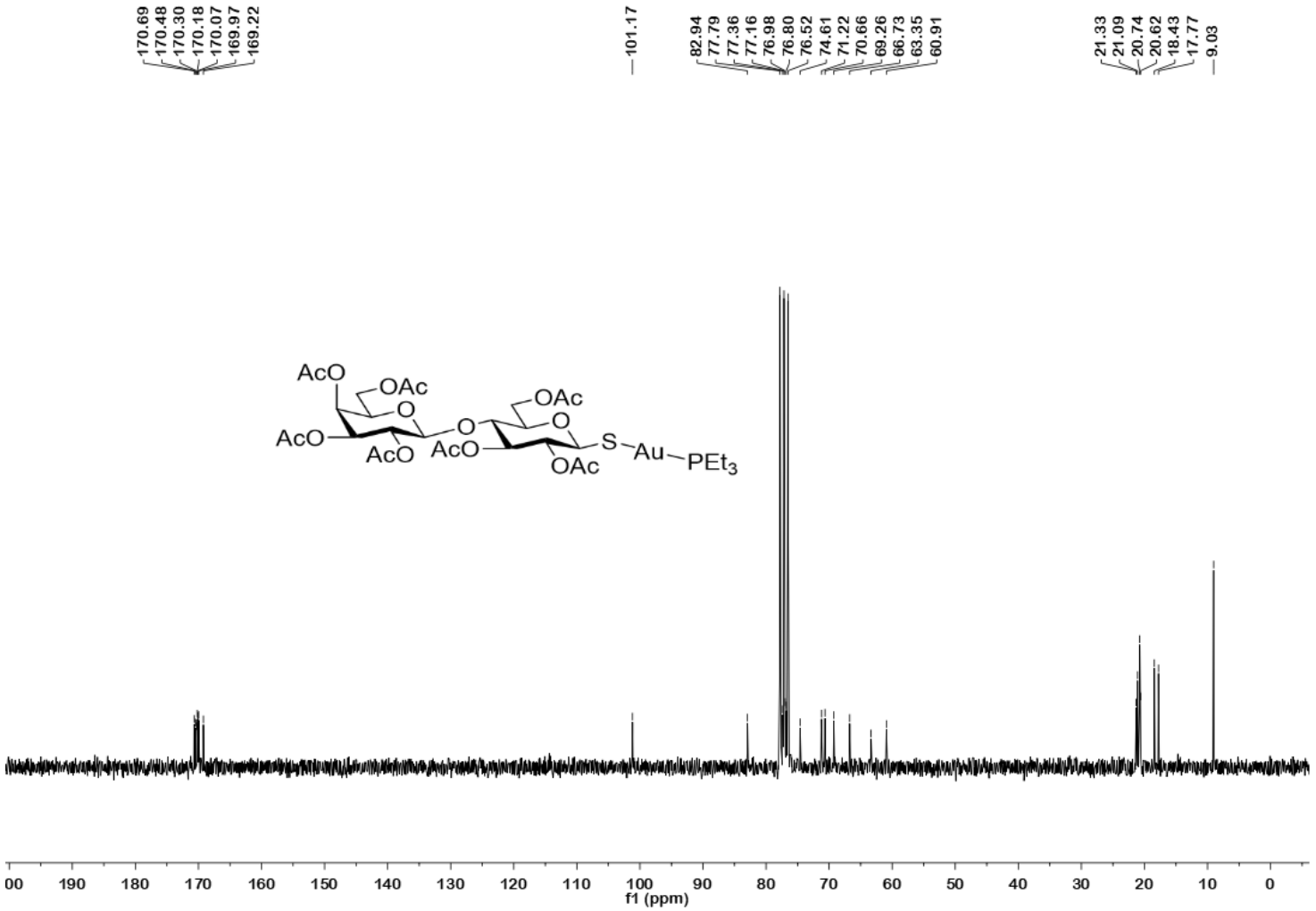


Figure S28. ^{13}C NMR spectrum of compound **6** in $CDCl_3$.

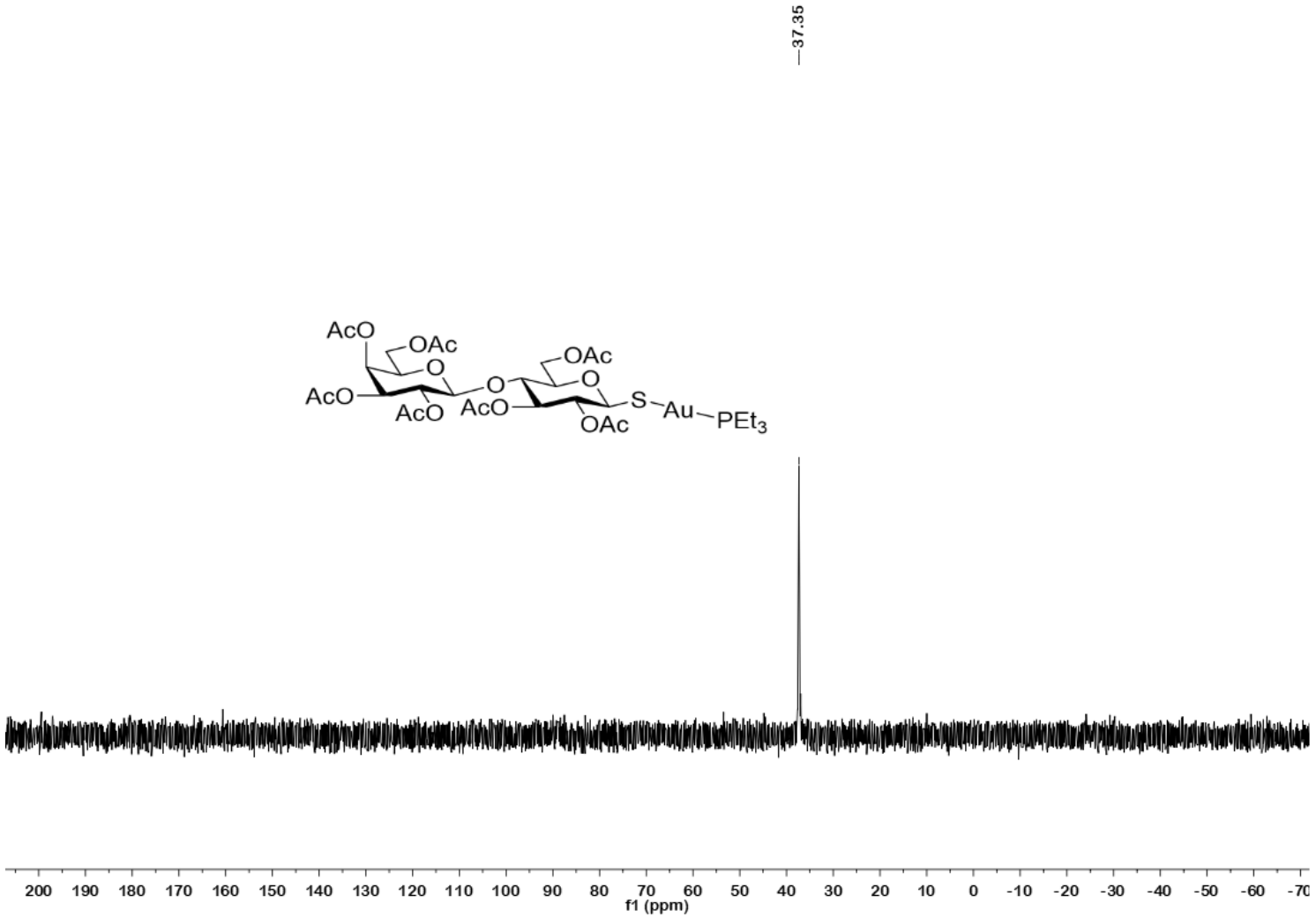


Figure S29. ^{31}P NMR spectrum of compound **6** in $CDCl_3$.

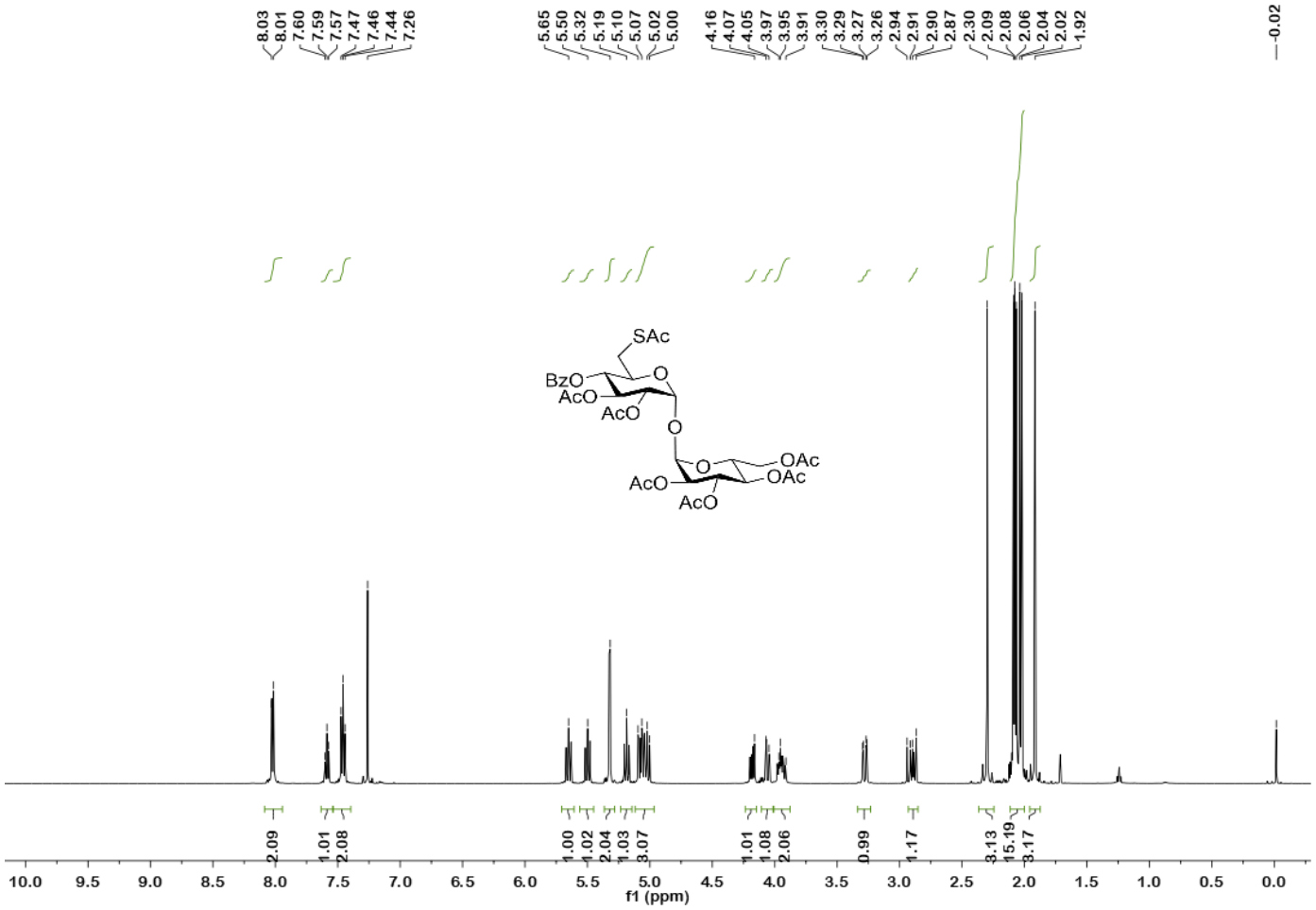


Figure S30. ^{1}H NMR spectrum of compound **7d** in $CDCl_3$.

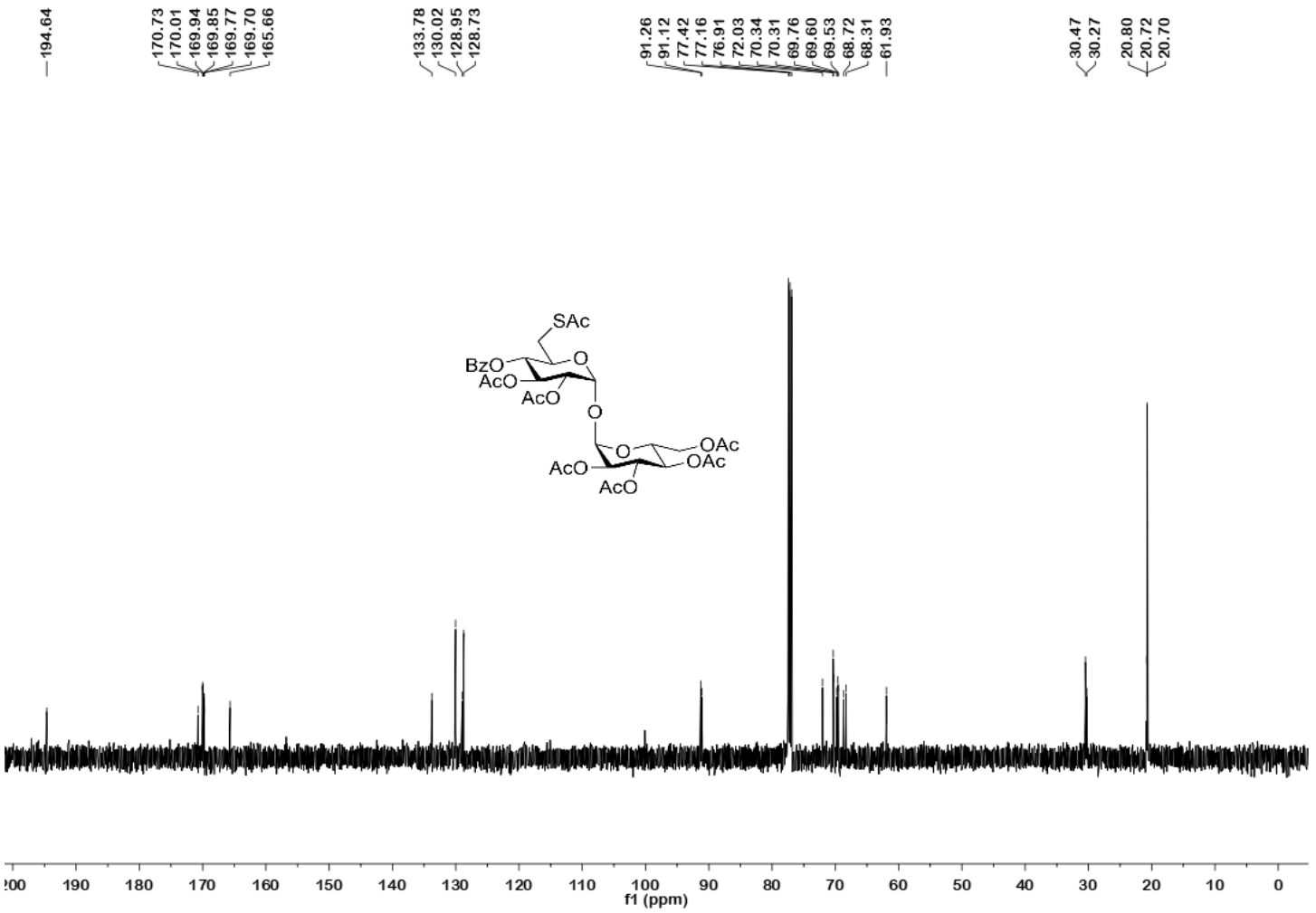


Figure S31. ^{13}C NMR spectrum of compound **7d** in $CDCl_3$.

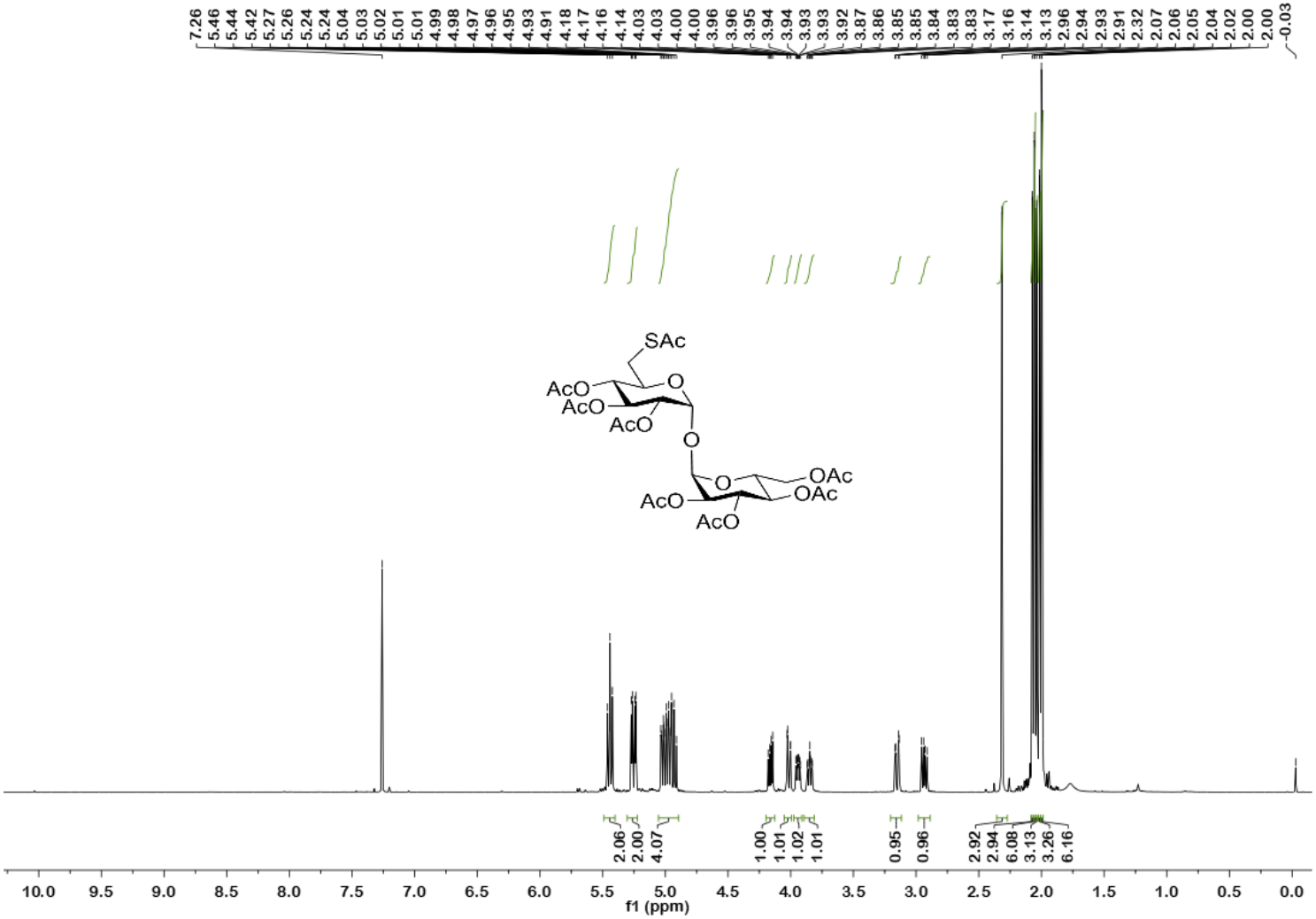


Figure S32. ^{1}H NMR spectrum of compound **7e** in $CDCl_3$.

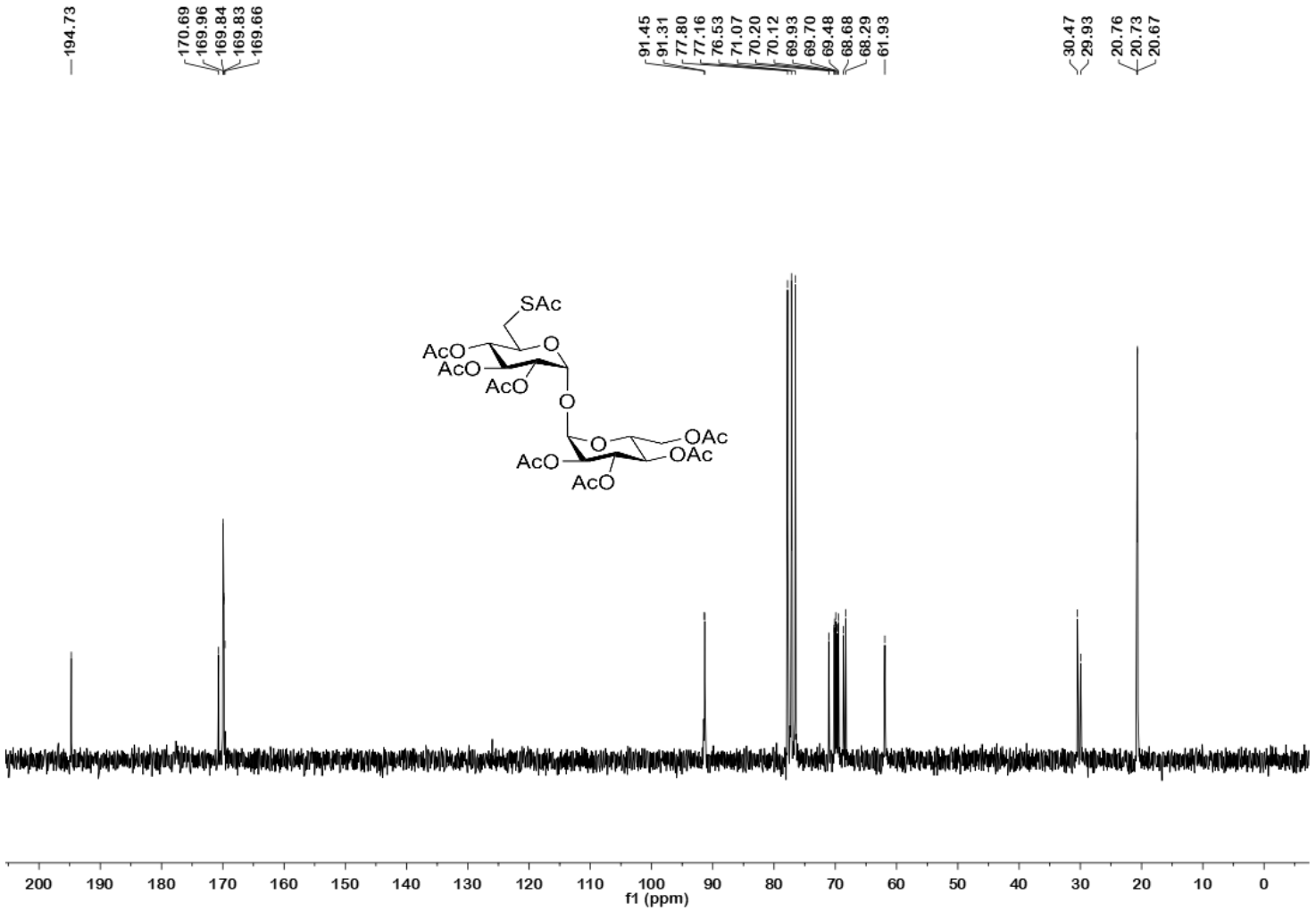


Figure S33. ^{13}C NMR spectrum of compound **7e** in $CDCl_3$.

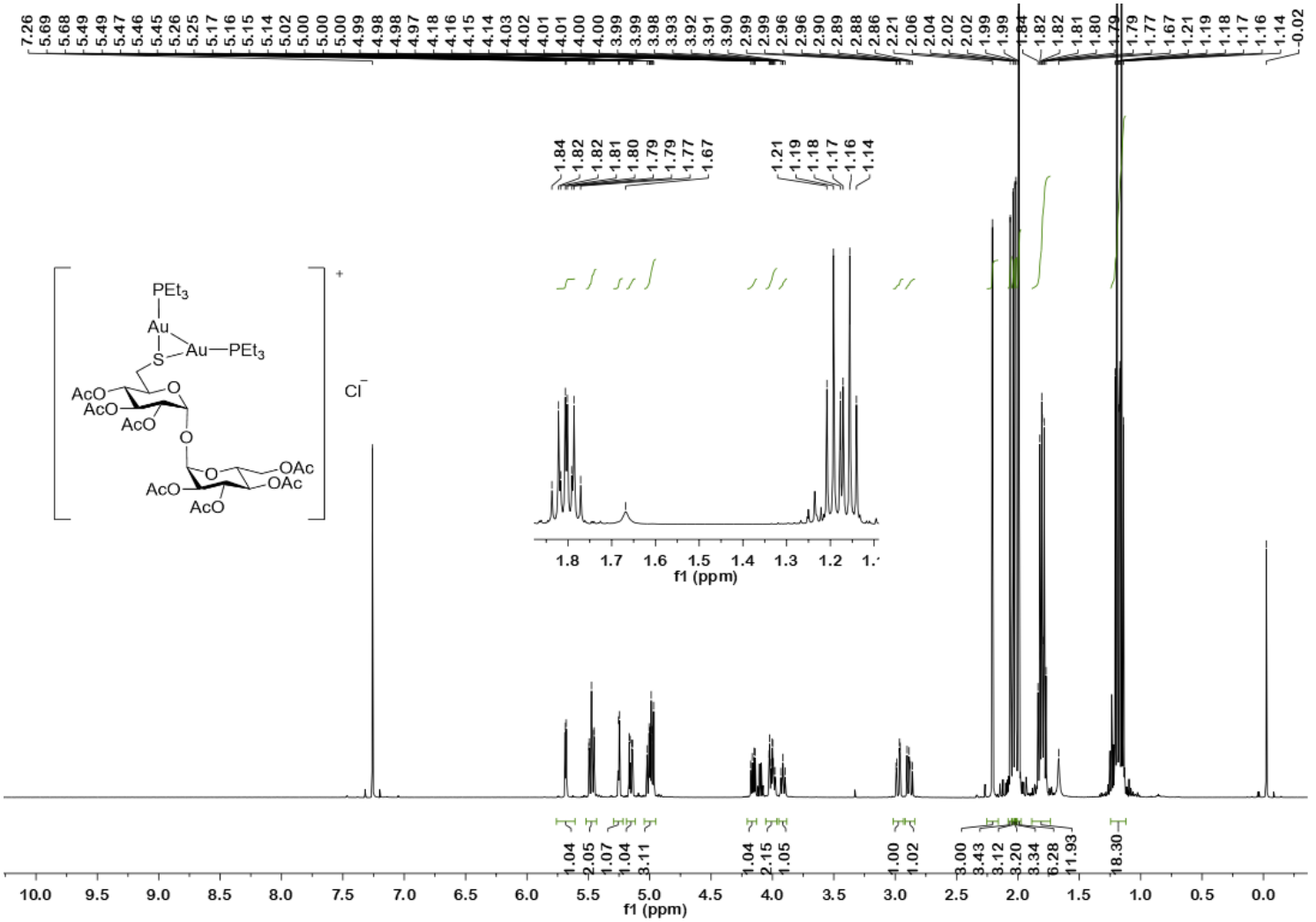


Figure S34. ^{1}H NMR spectrum of compound **7** in $CDCl_3$.

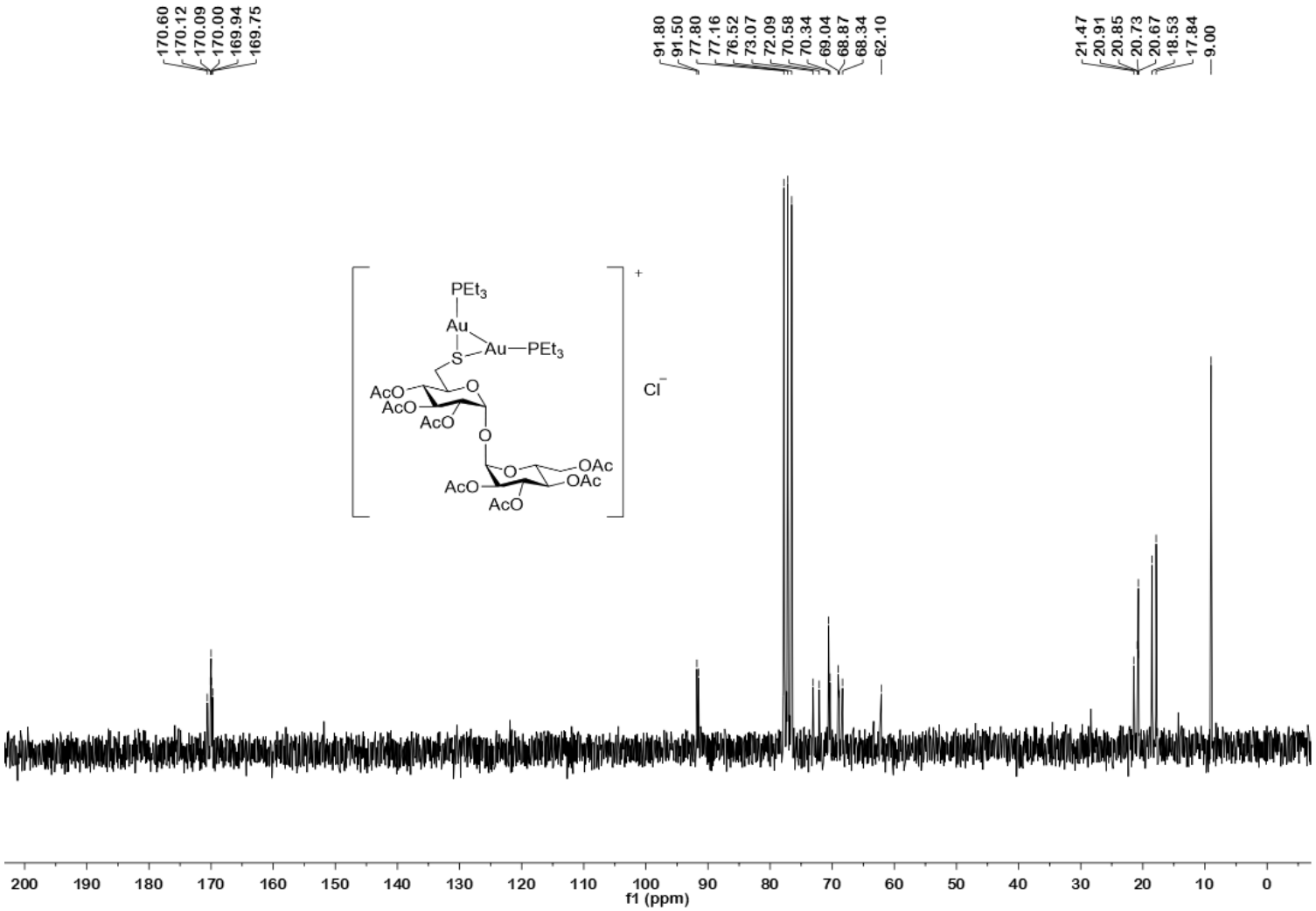


Figure S35. ^{13}C NMR spectrum of compound **7** in $CDCl_3$.

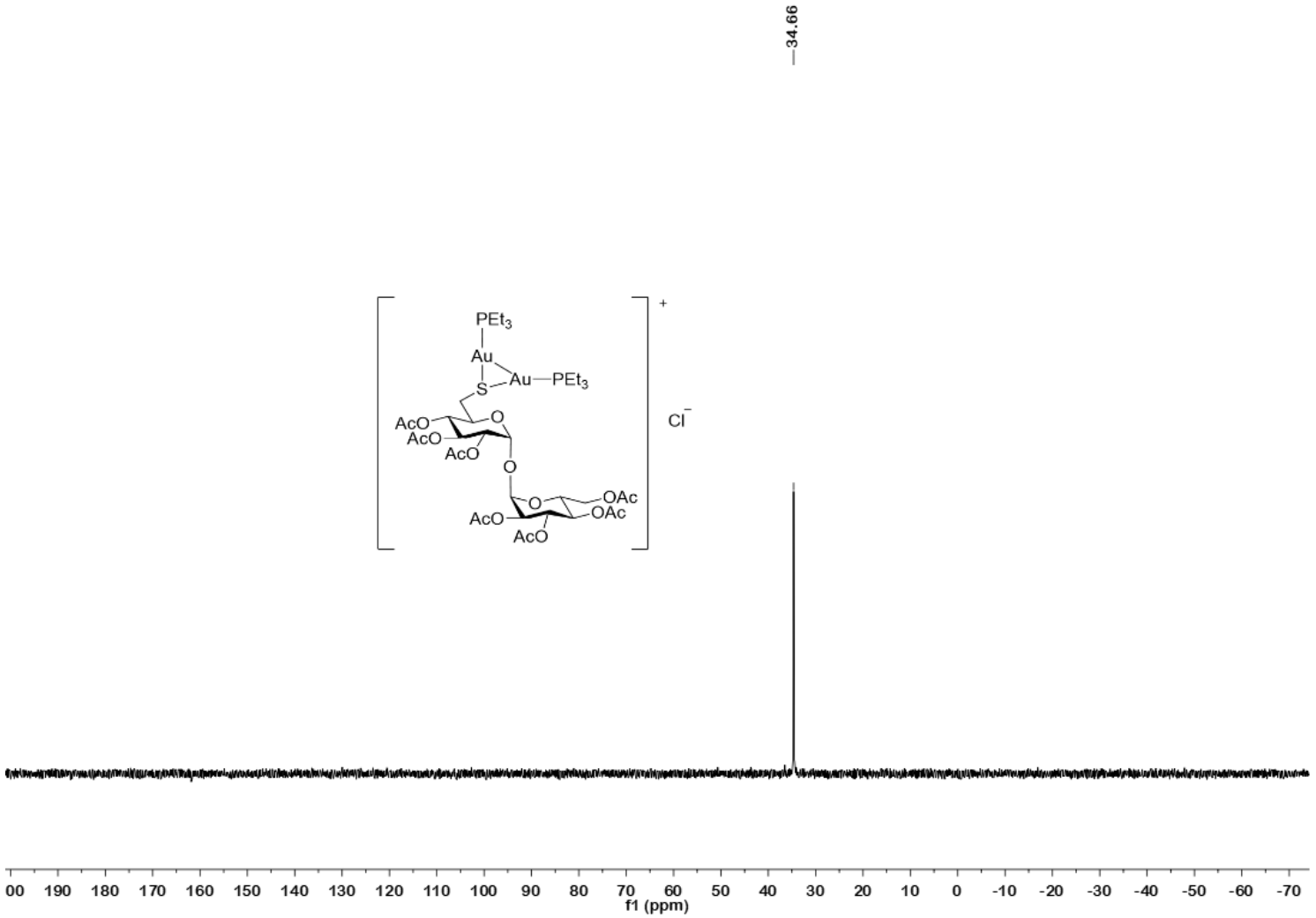


Figure S36. ^{31}P NMR spectrum of compound **7** in $CDCl_3$.

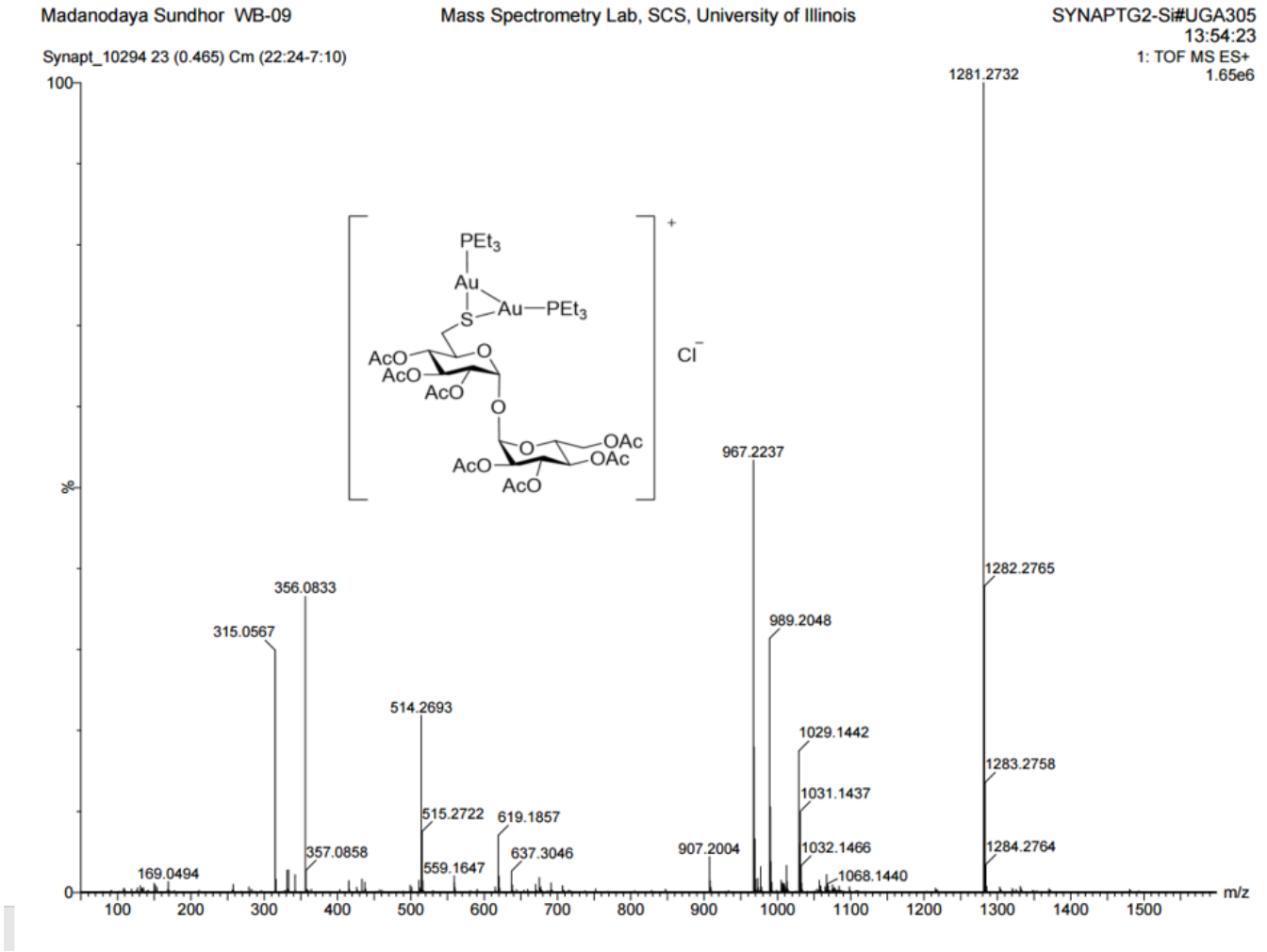


Figure S37. HRMS of compound **7**.

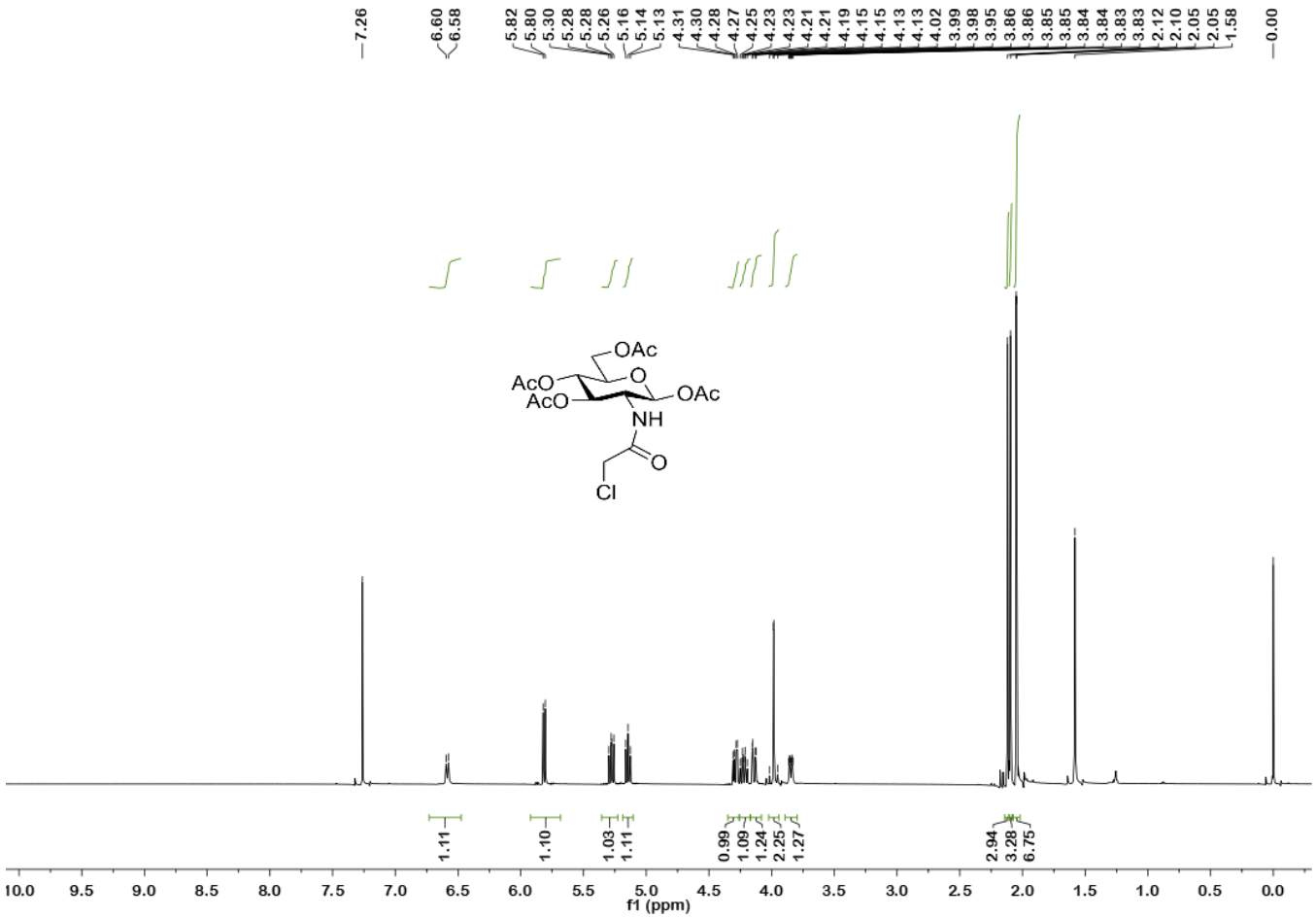


Figure S38. ^{1}H NMR spectrum of compound **8e** in $CDCl_3$

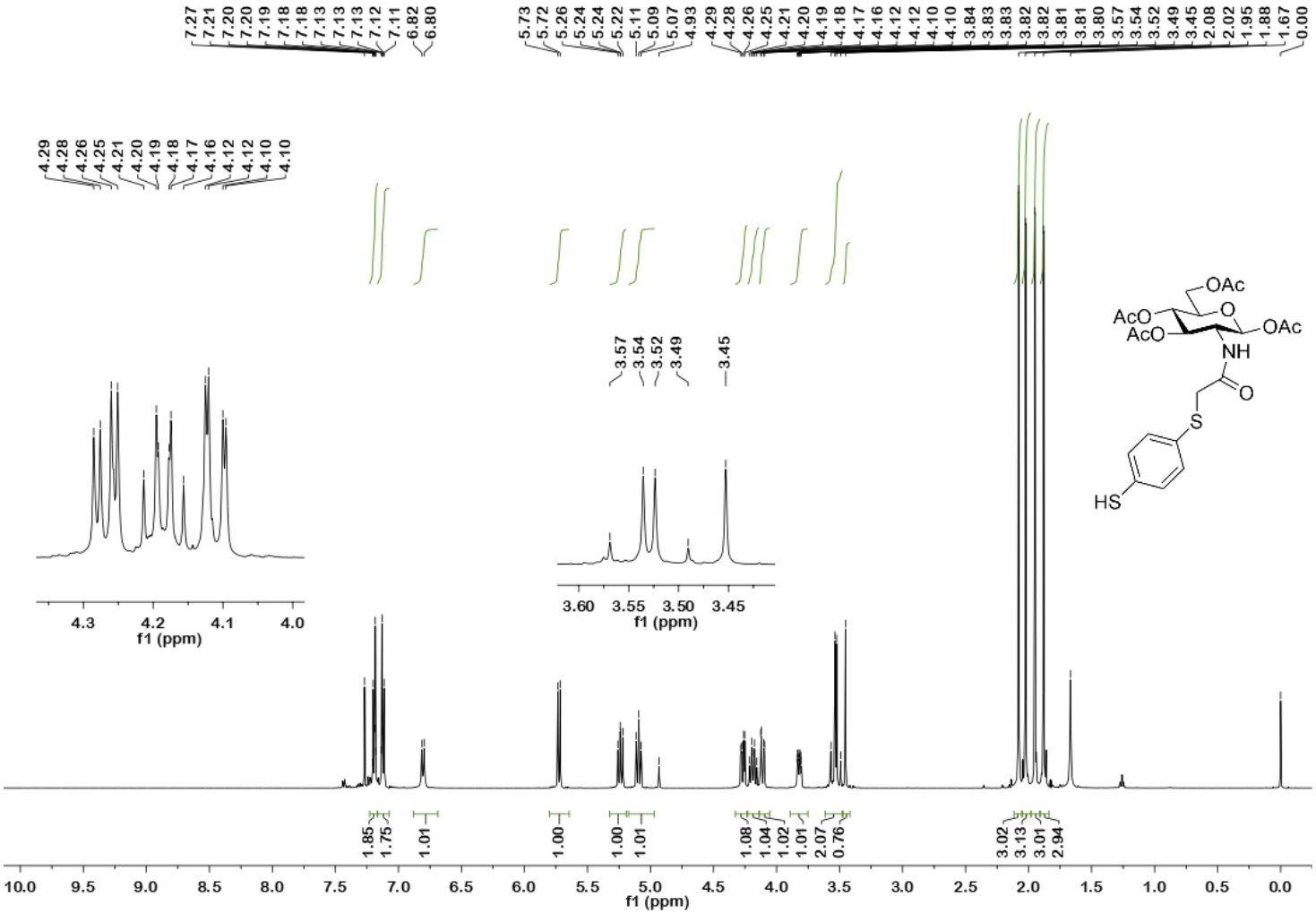


Figure S39. ^{1}H NMR spectrum of compound **8f** in $CDCl_3$

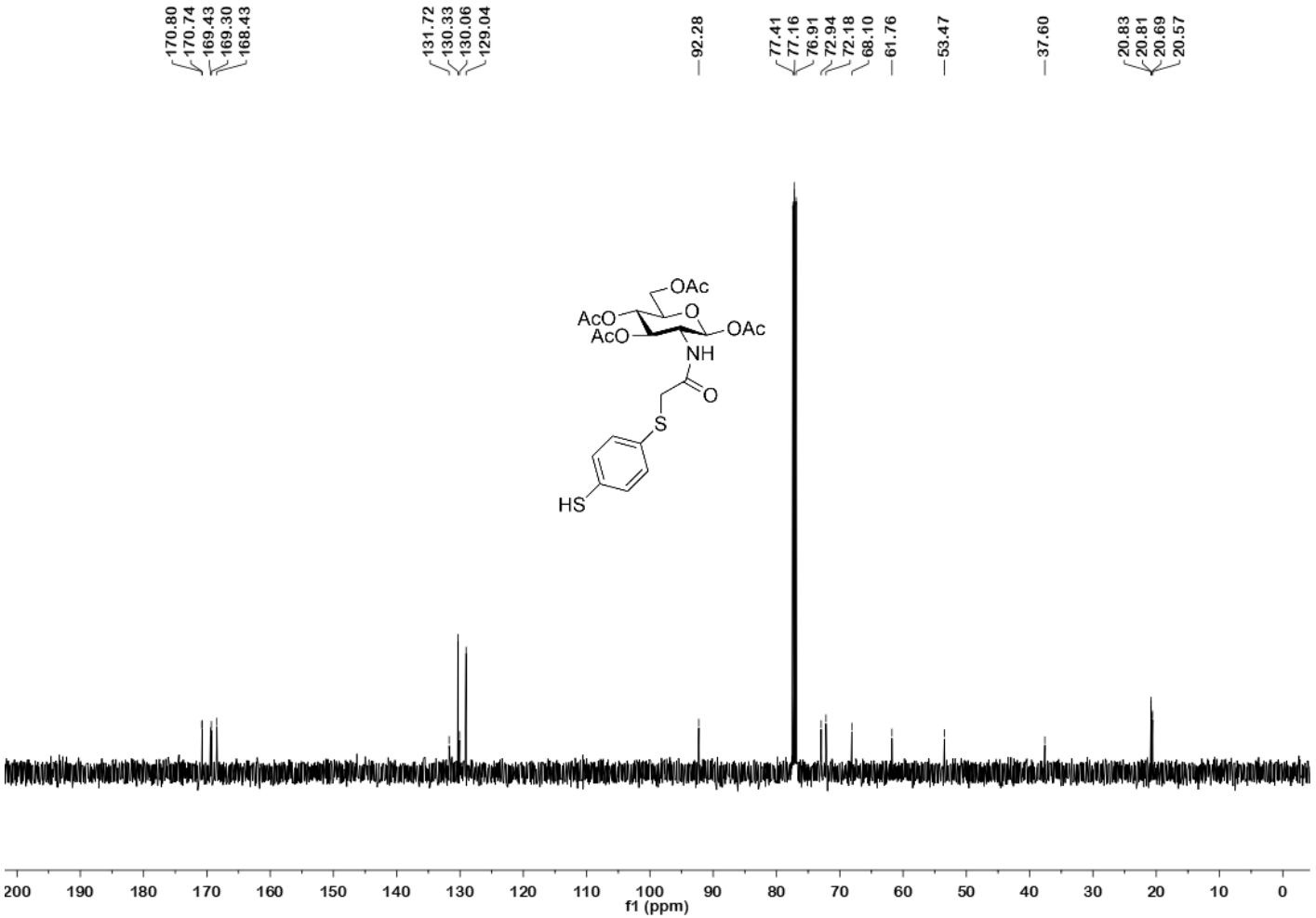


Figure S40. ^{13}C NMR spectrum of compound **8f** in $CDCl_3$

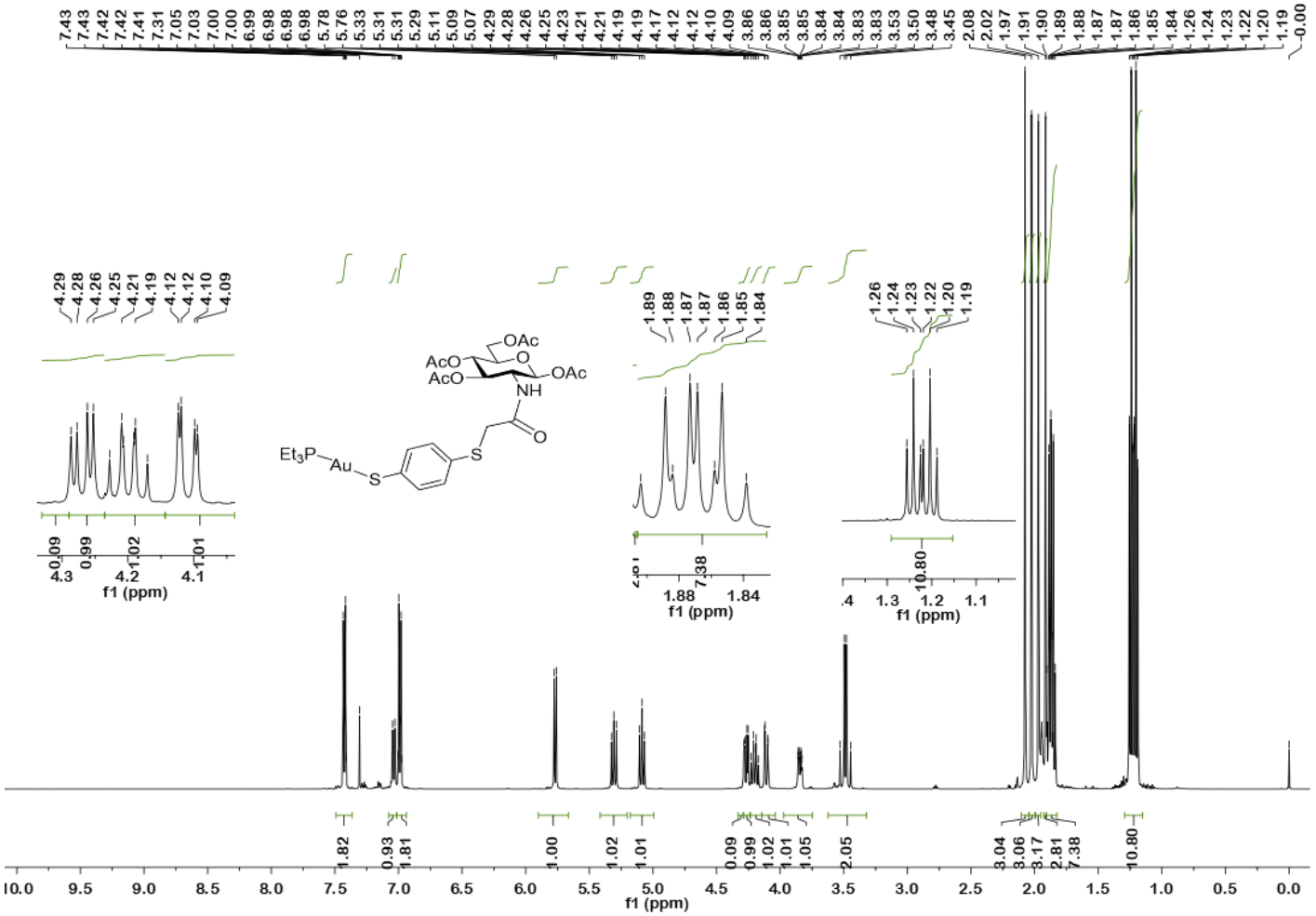


Figure S41. ^{1}H NMR spectrum of compound **8** in $CDCl_3$

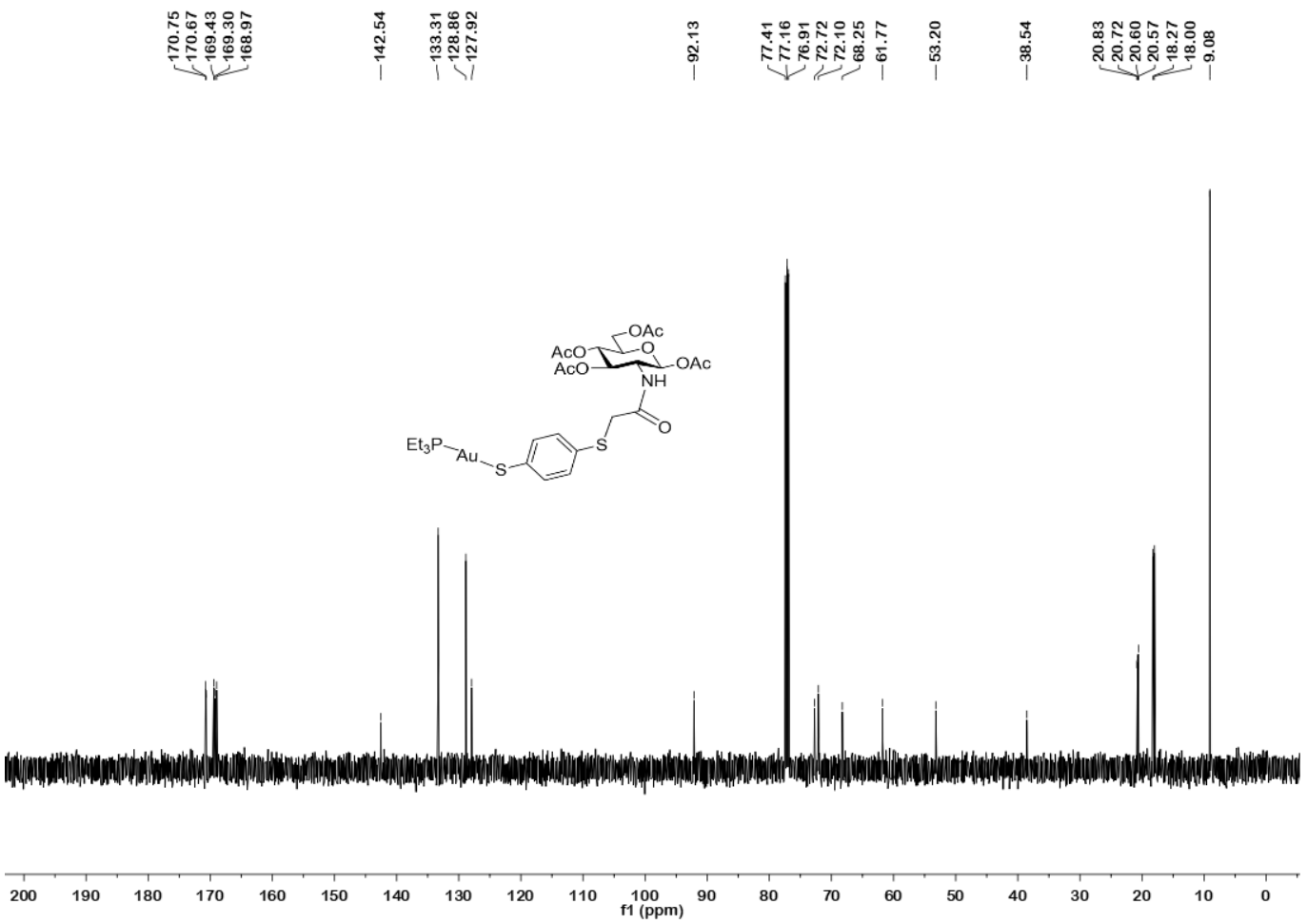


Figure S42. ^{13}C NMR spectrum of compound **8** in $CDCl_3$.

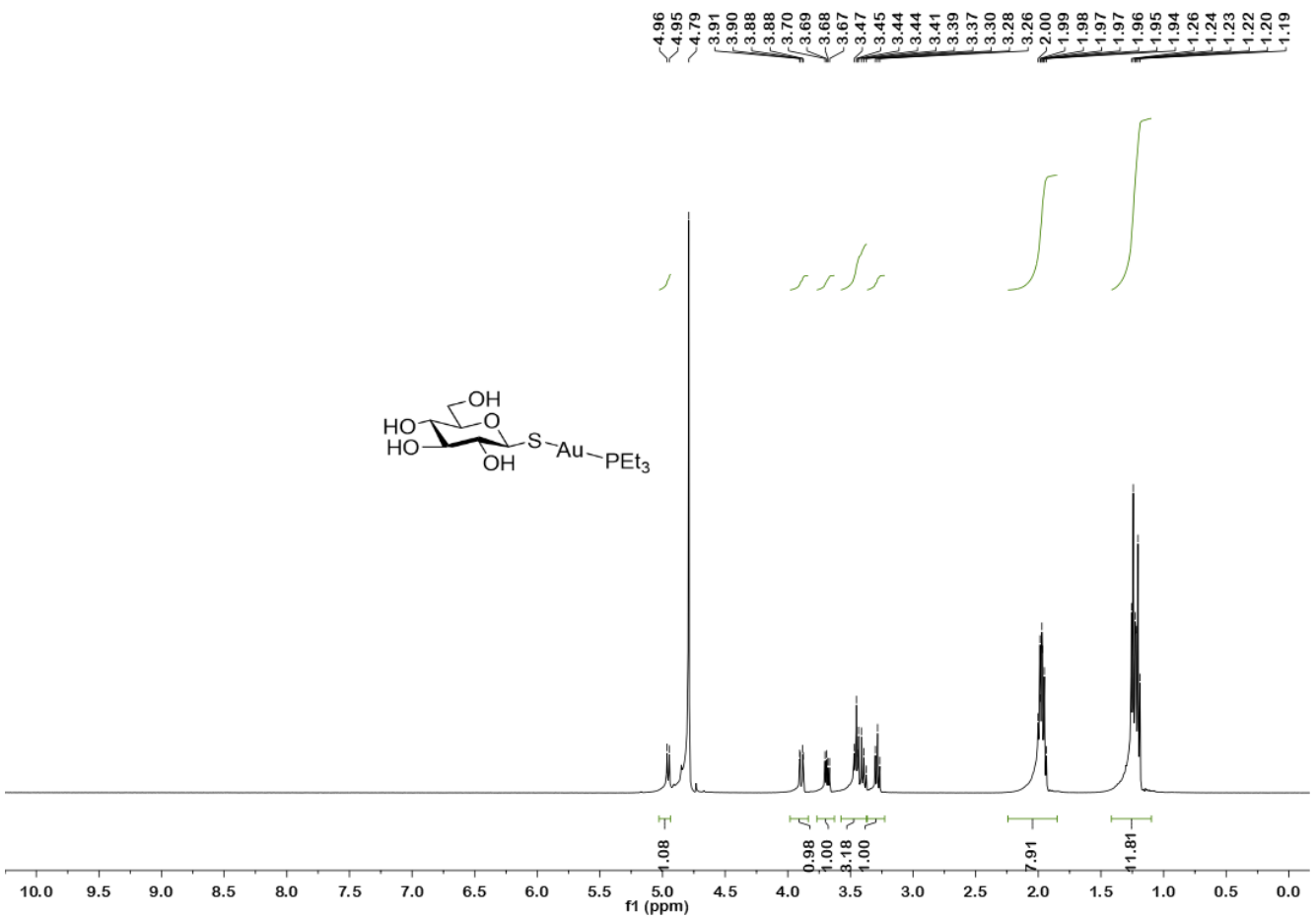


Figure S43. ^{1}H NMR spectrum of compound **9** in D_2O.

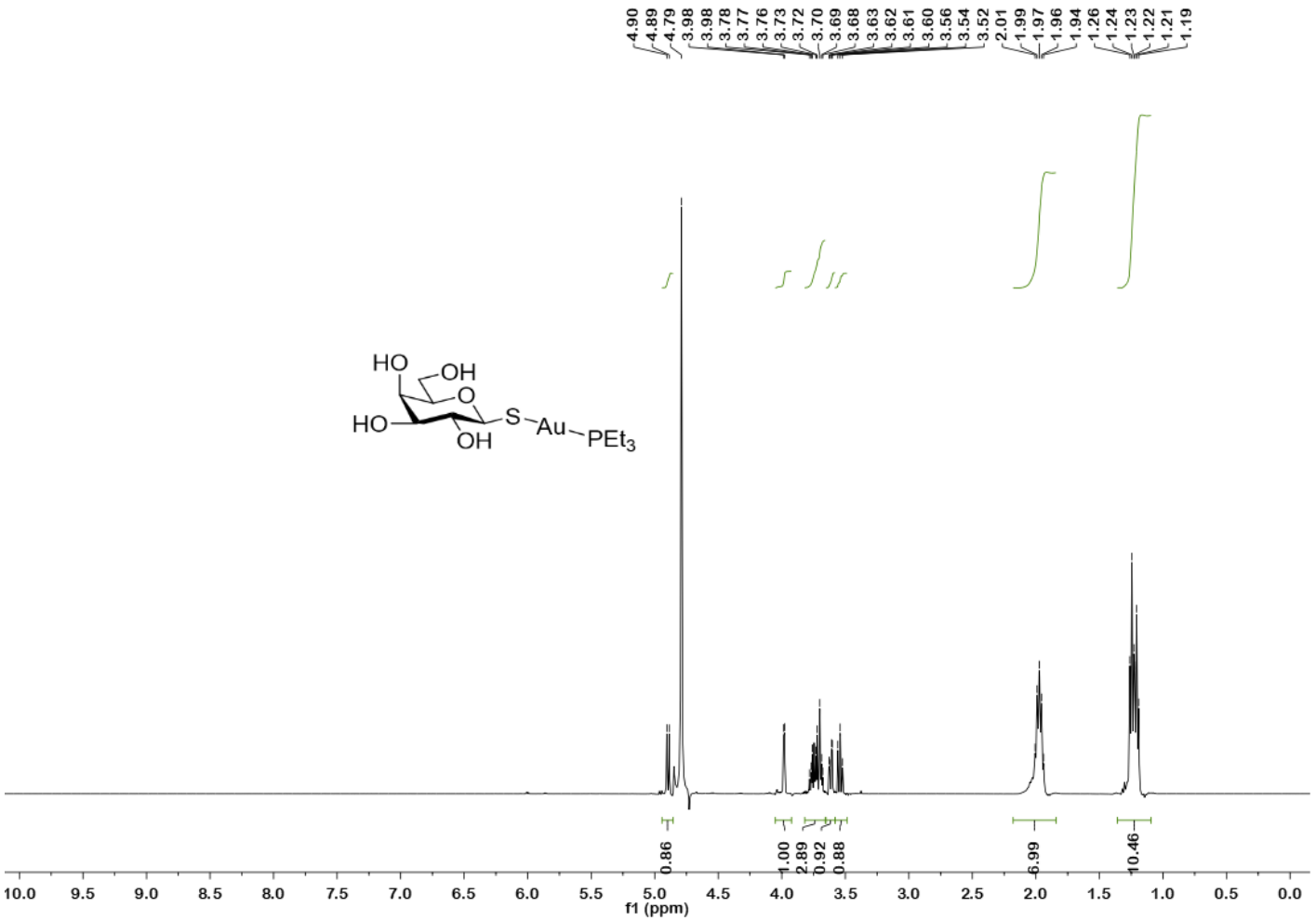


Figure S44. ^{1}H NMR spectrum of compound **10** in D_2O.

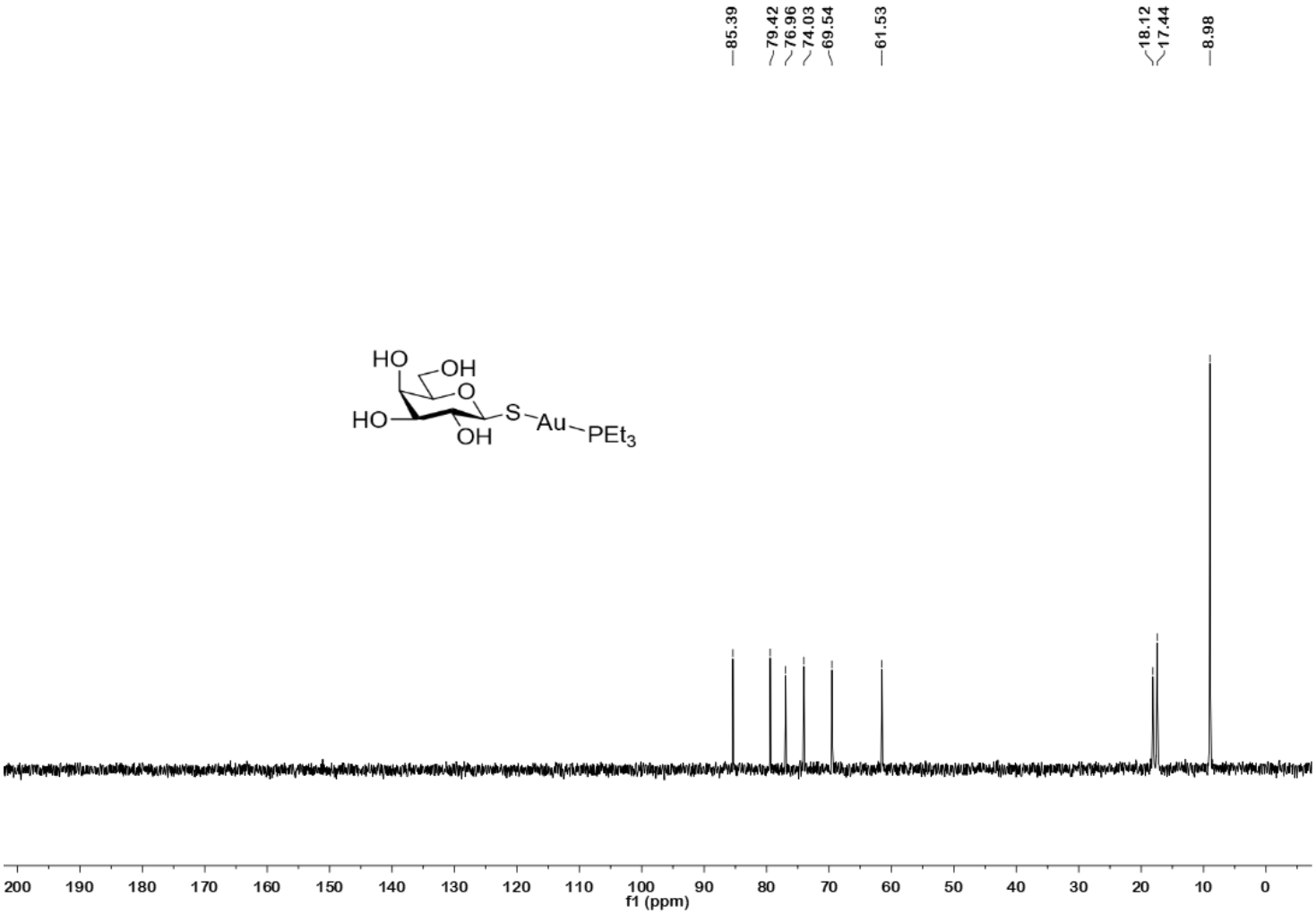


Figure S45. ^{13}C NMR spectrum of compound **10** in D_2O.

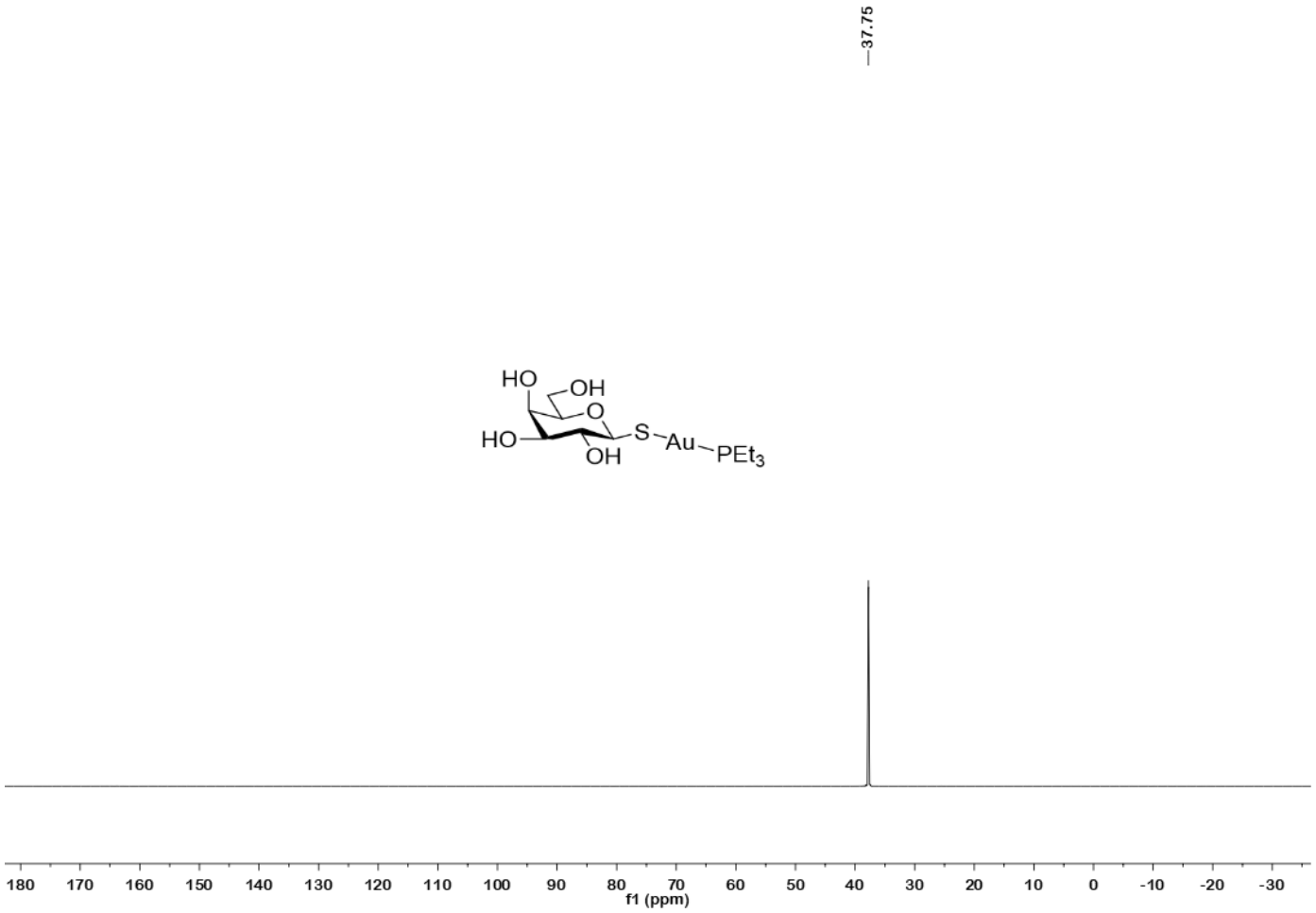


Figure S46. ^{31}P NMR spectrum of compound **10** in D_2O.

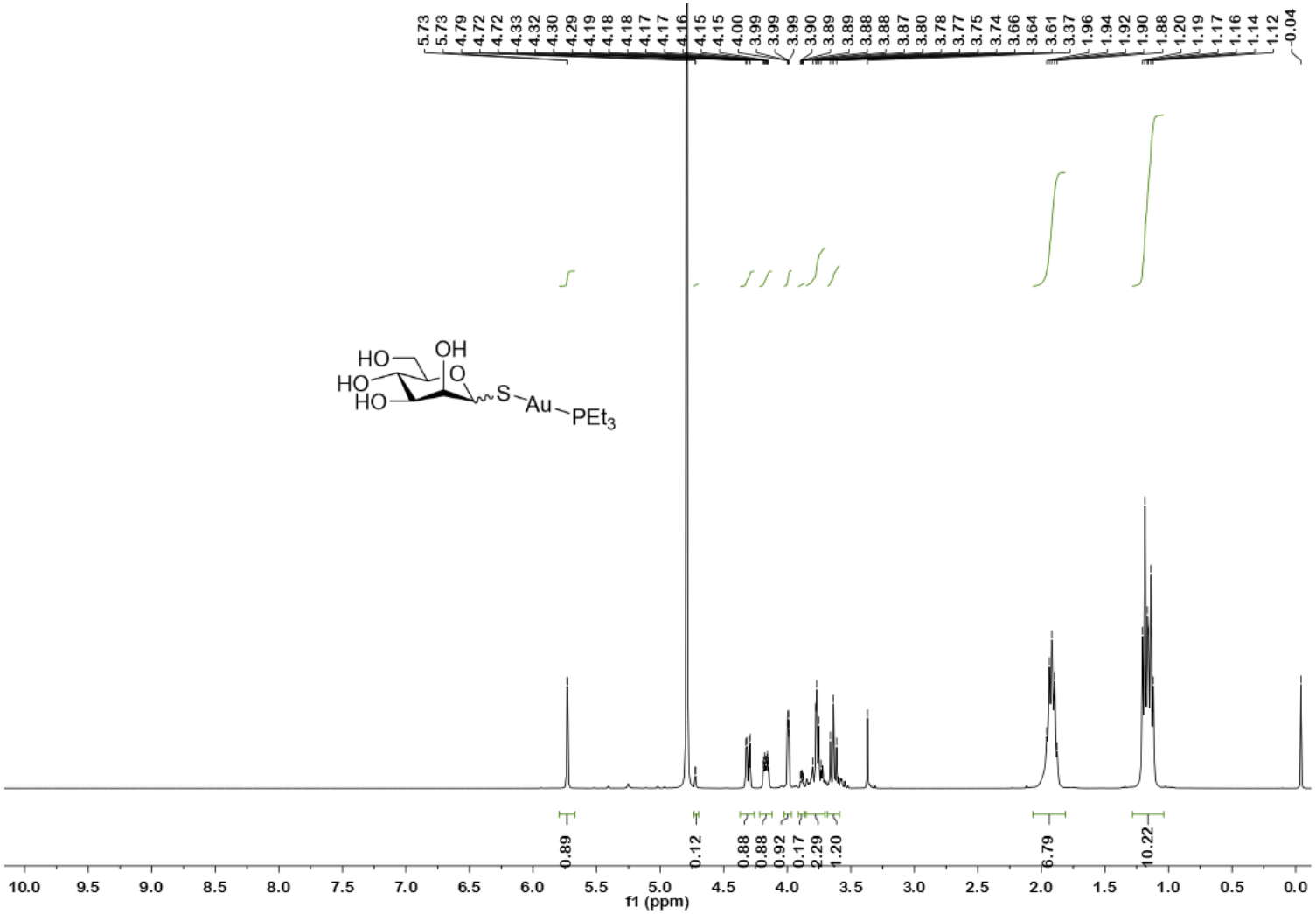


Figure S47. ^{1}H NMR spectrum of compound **11** in D_2O

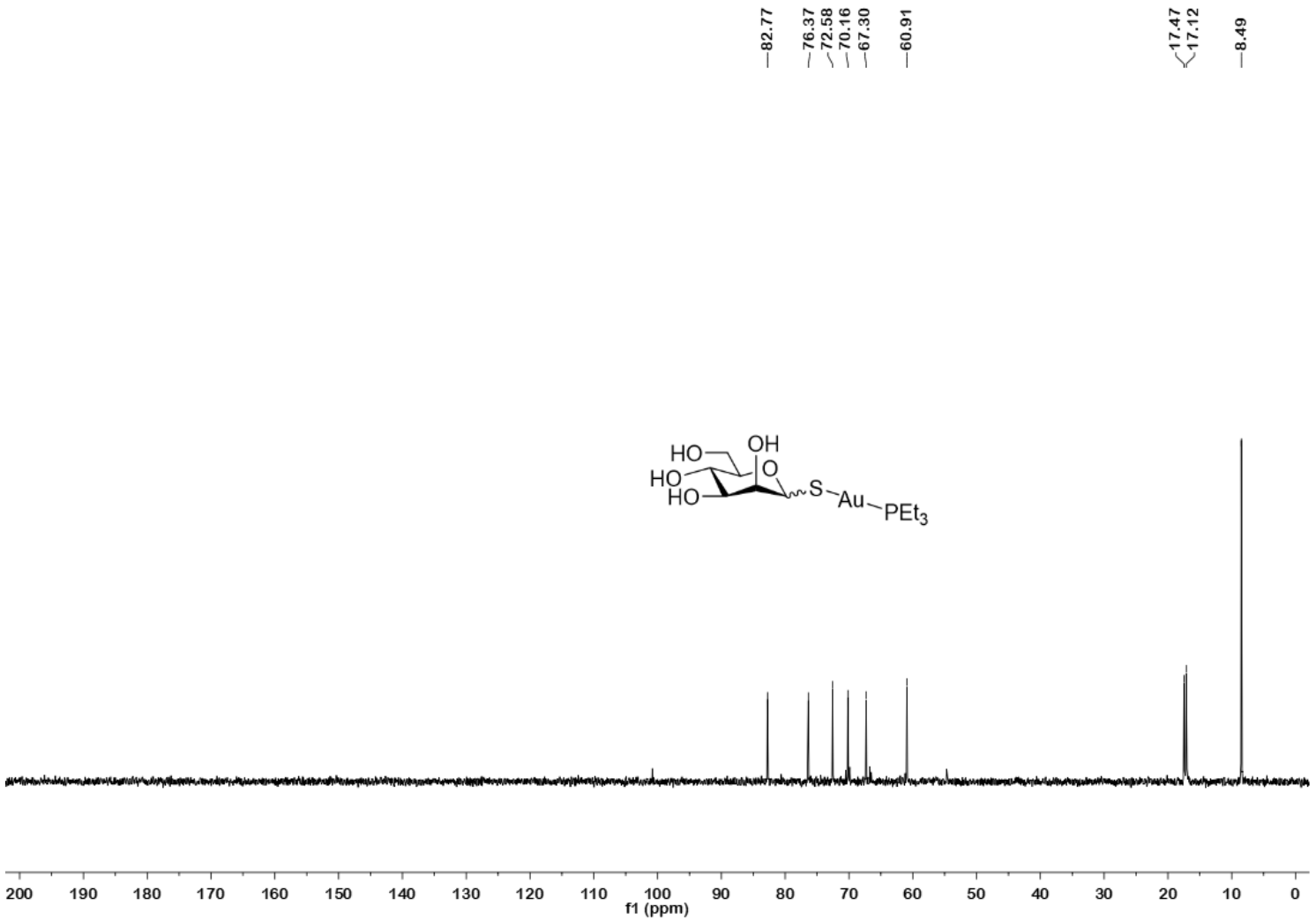


Figure S48. ^{13}C NMR spectrum of compound **11** in D_2O.

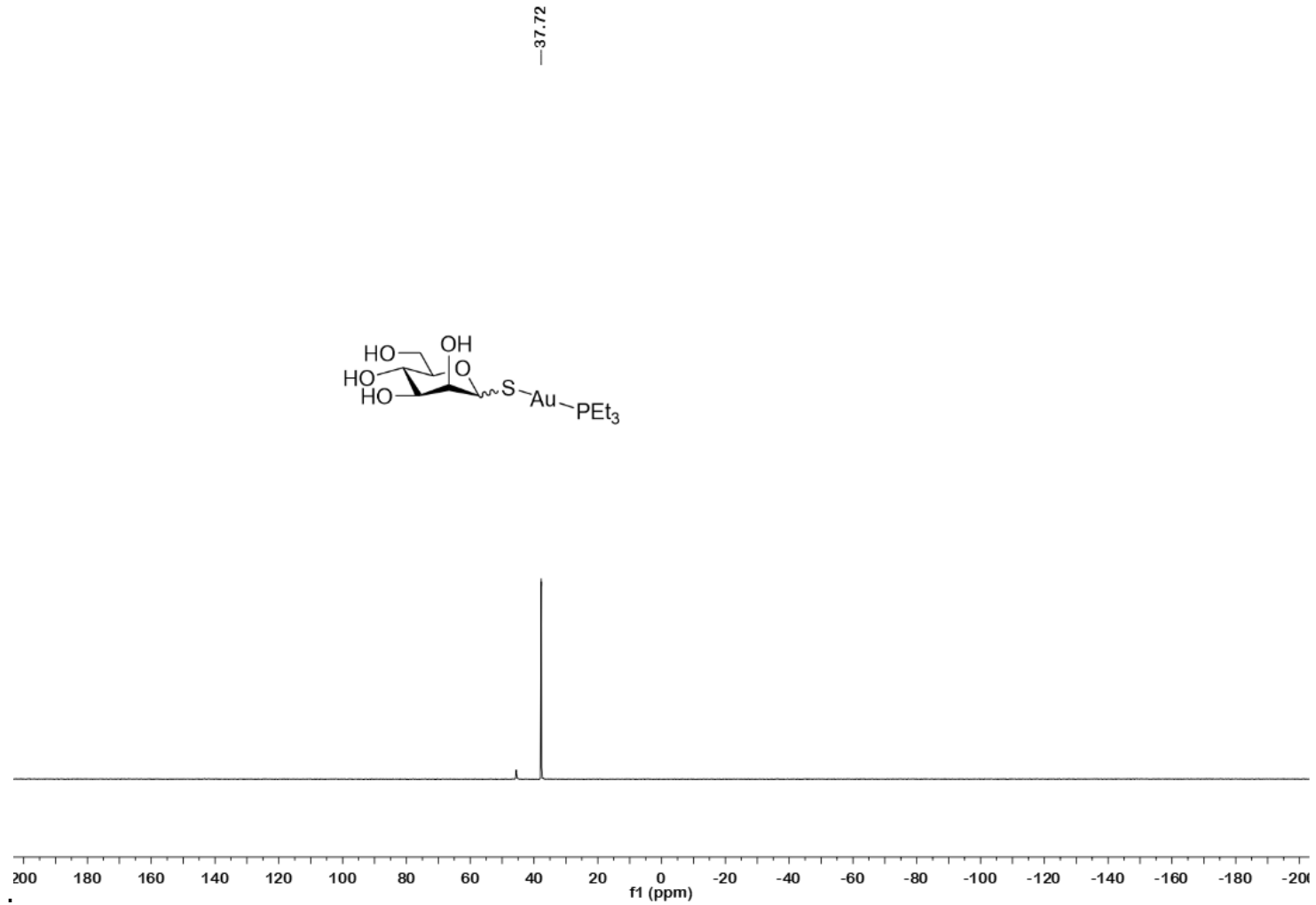


Figure S49. ^{31}P NMR spectrum of compound **11** in D_2O.

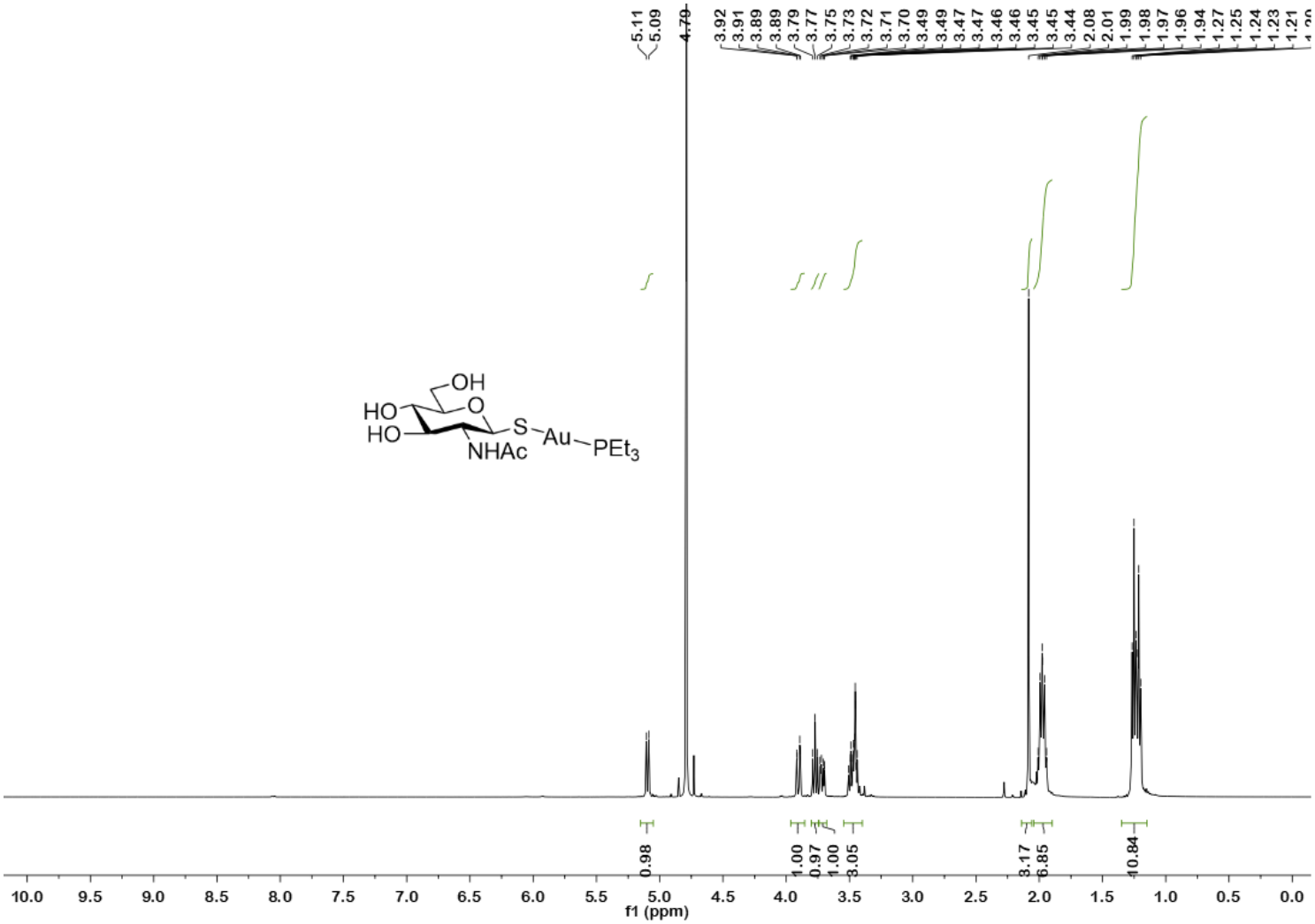


Figure S50. ^{1}H NMR spectrum of compound **12** in D_2O.

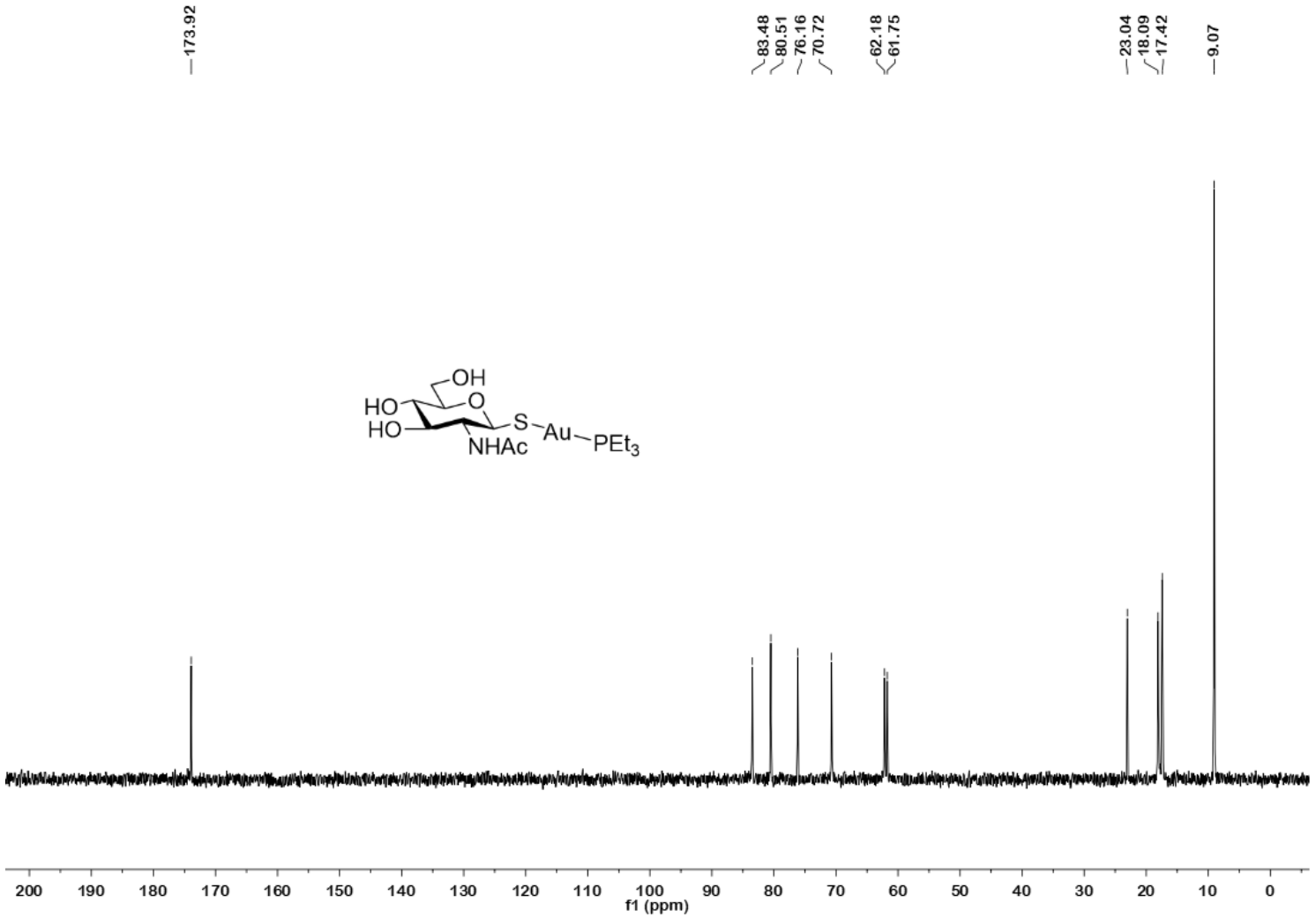


Figure S51. ^{13}C NMR spectrum of compound **12** in D_2O.

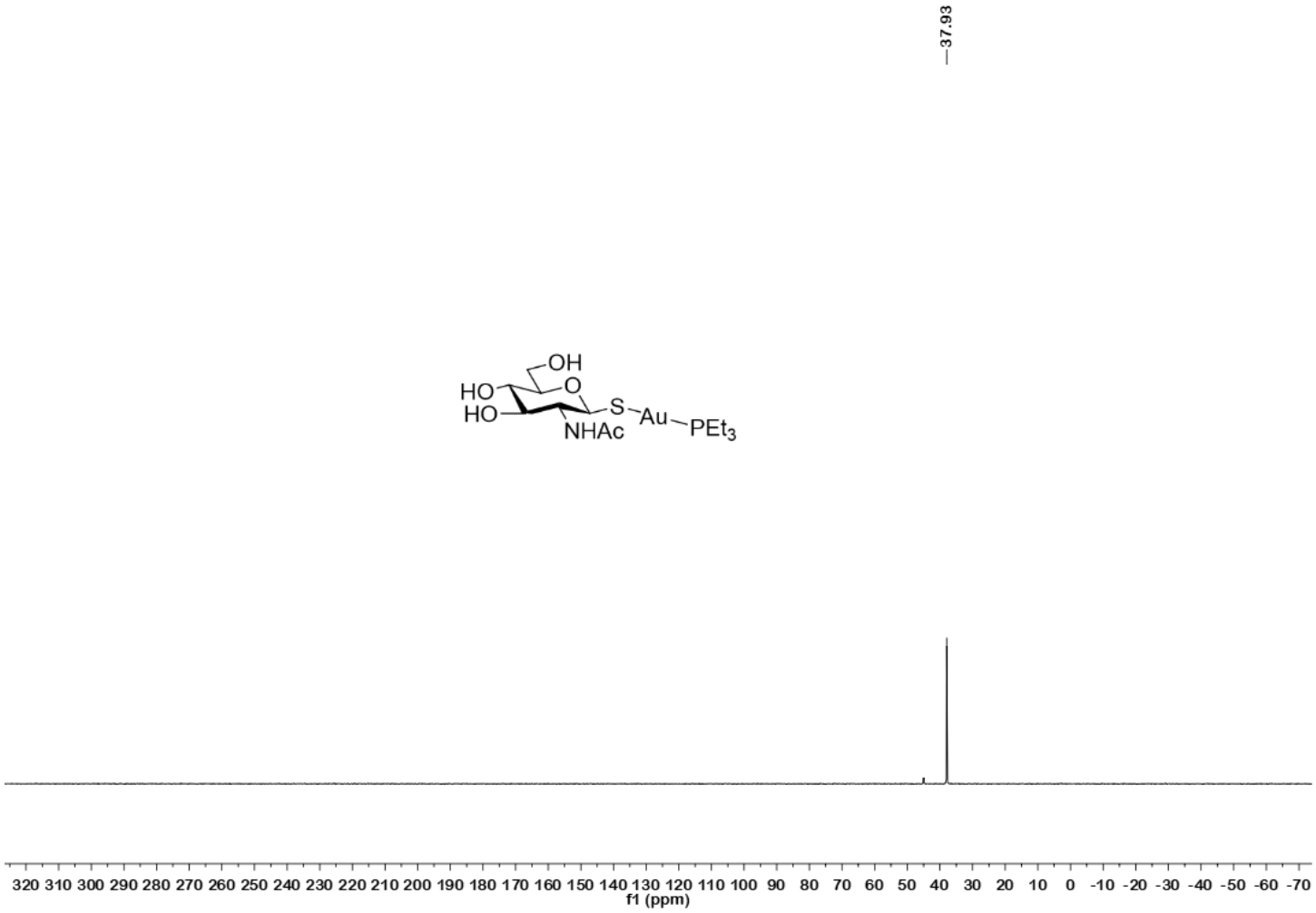


Figure S52. ^{31}P NMR spectrum of compound **12** in D_2O.

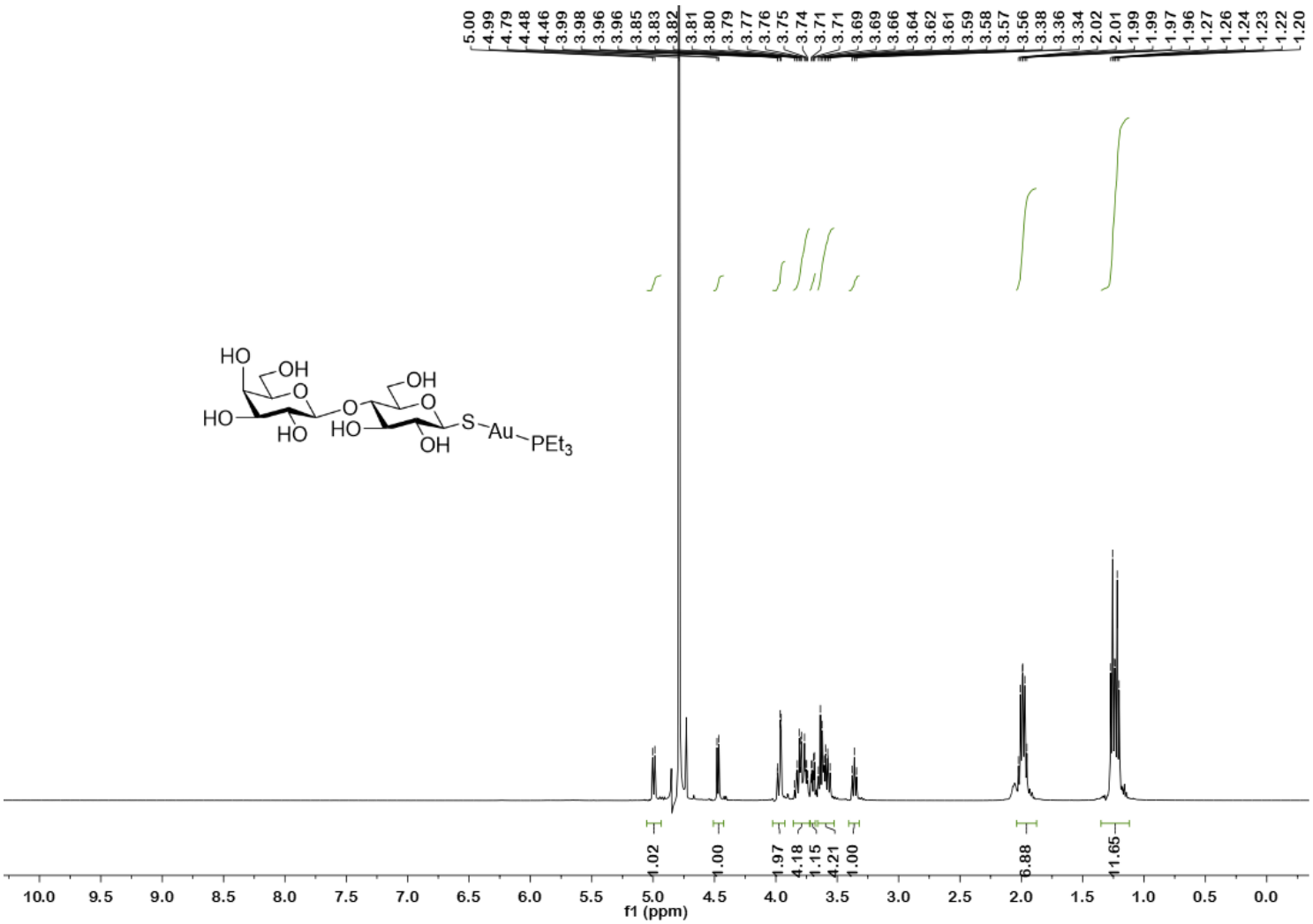


Figure S53. ^{1}H NMR spectrum of compound **13** in D_2O.

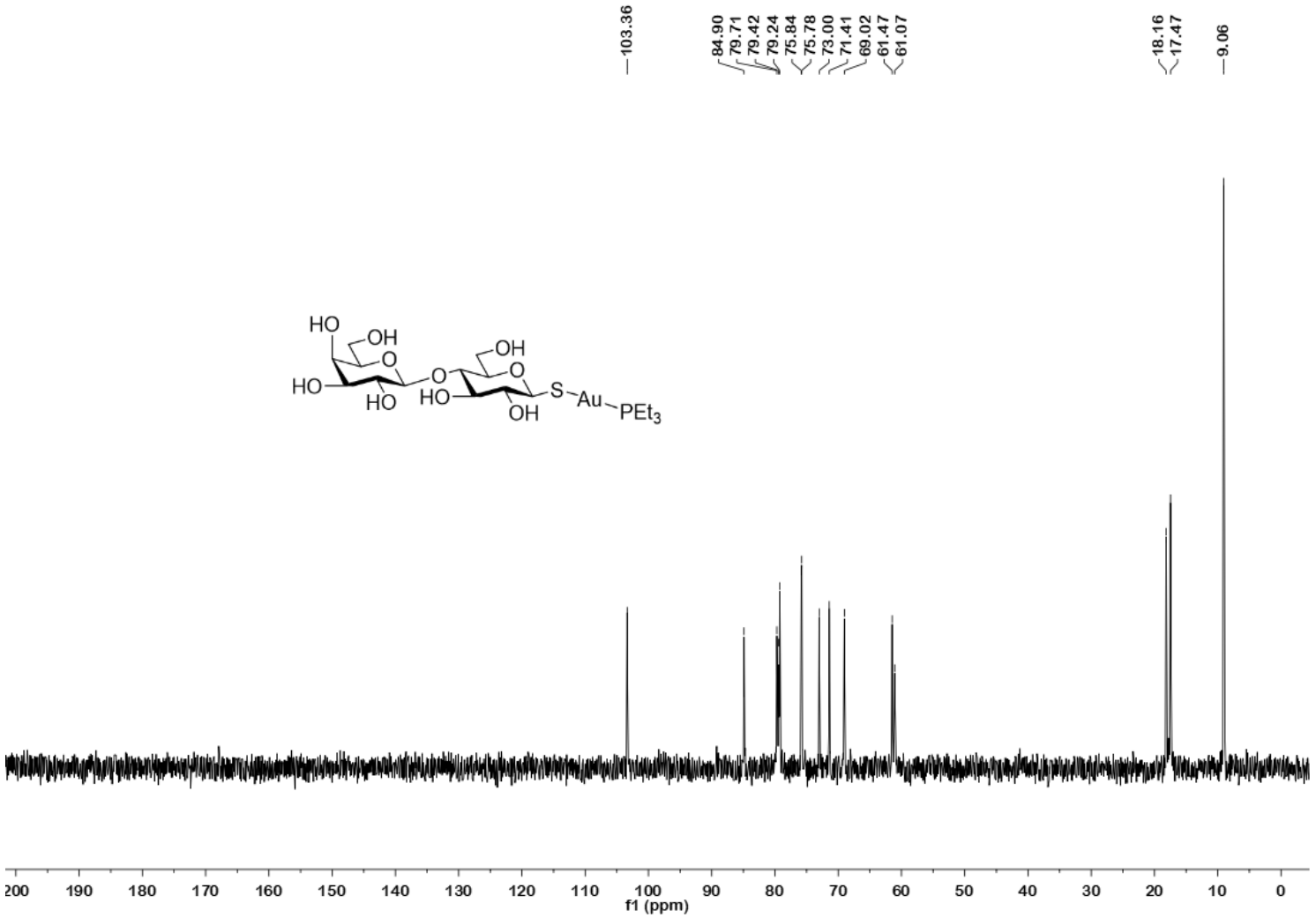


Figure S54. ^{13}C NMR spectrum of compound **13** in D_2O.

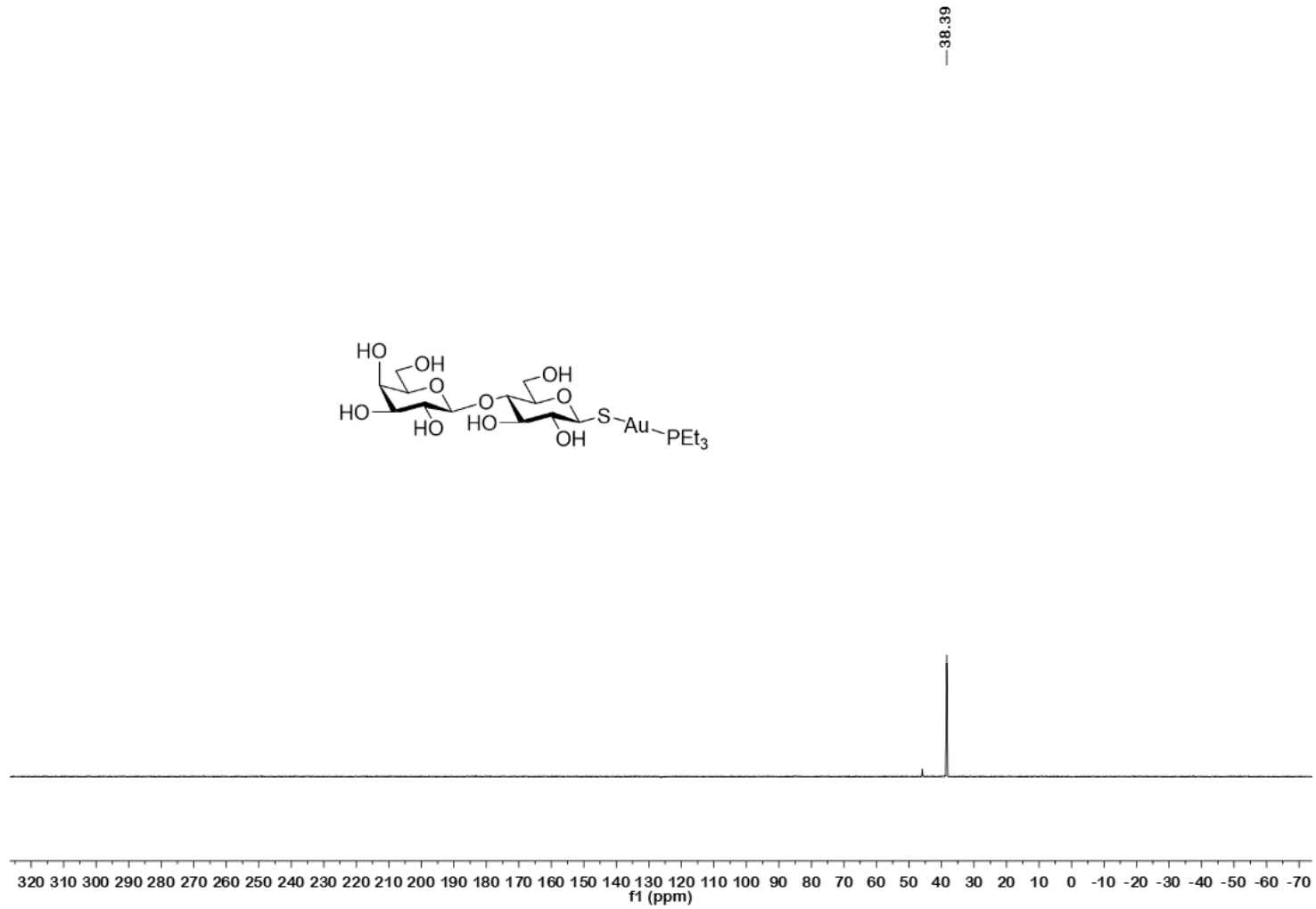


Figure S55. ^{31}P NMR spectrum of compound **13** in D_2O.

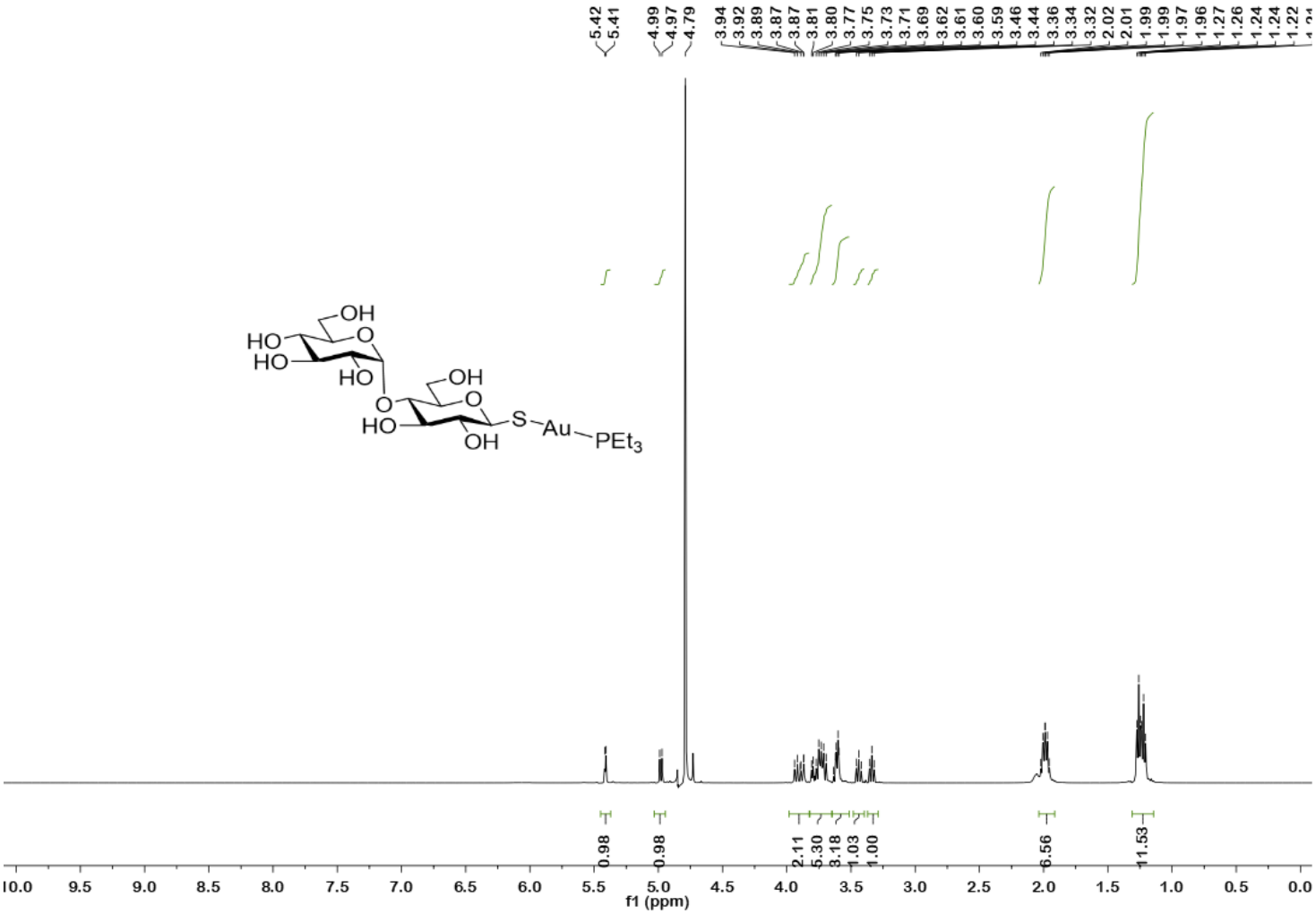


Figure S56. ^{1}H NMR spectrum of compound **14** in D_2O.

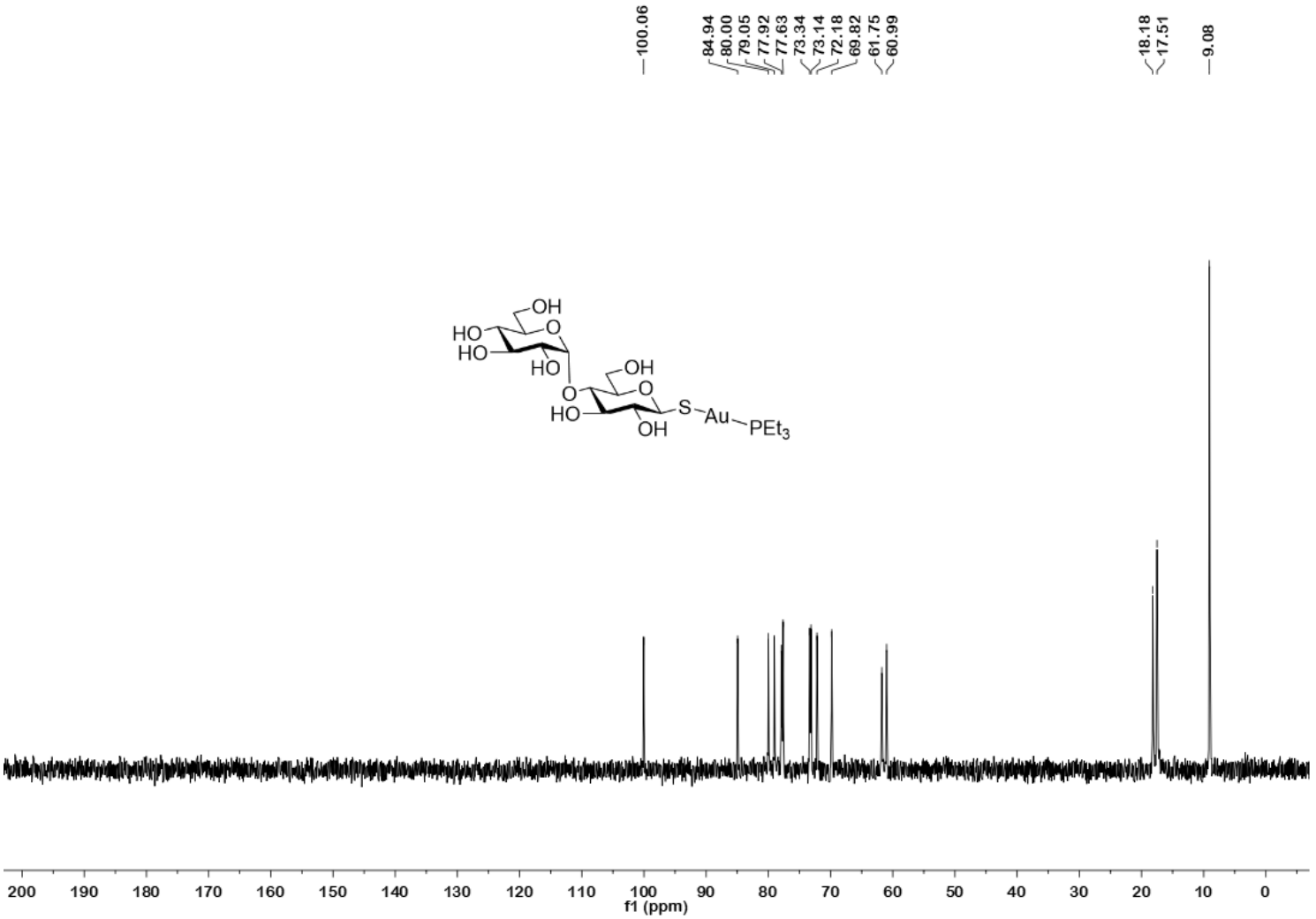


Figure S57. ^{13}C NMR spectrum of compound **14** in D_2O.

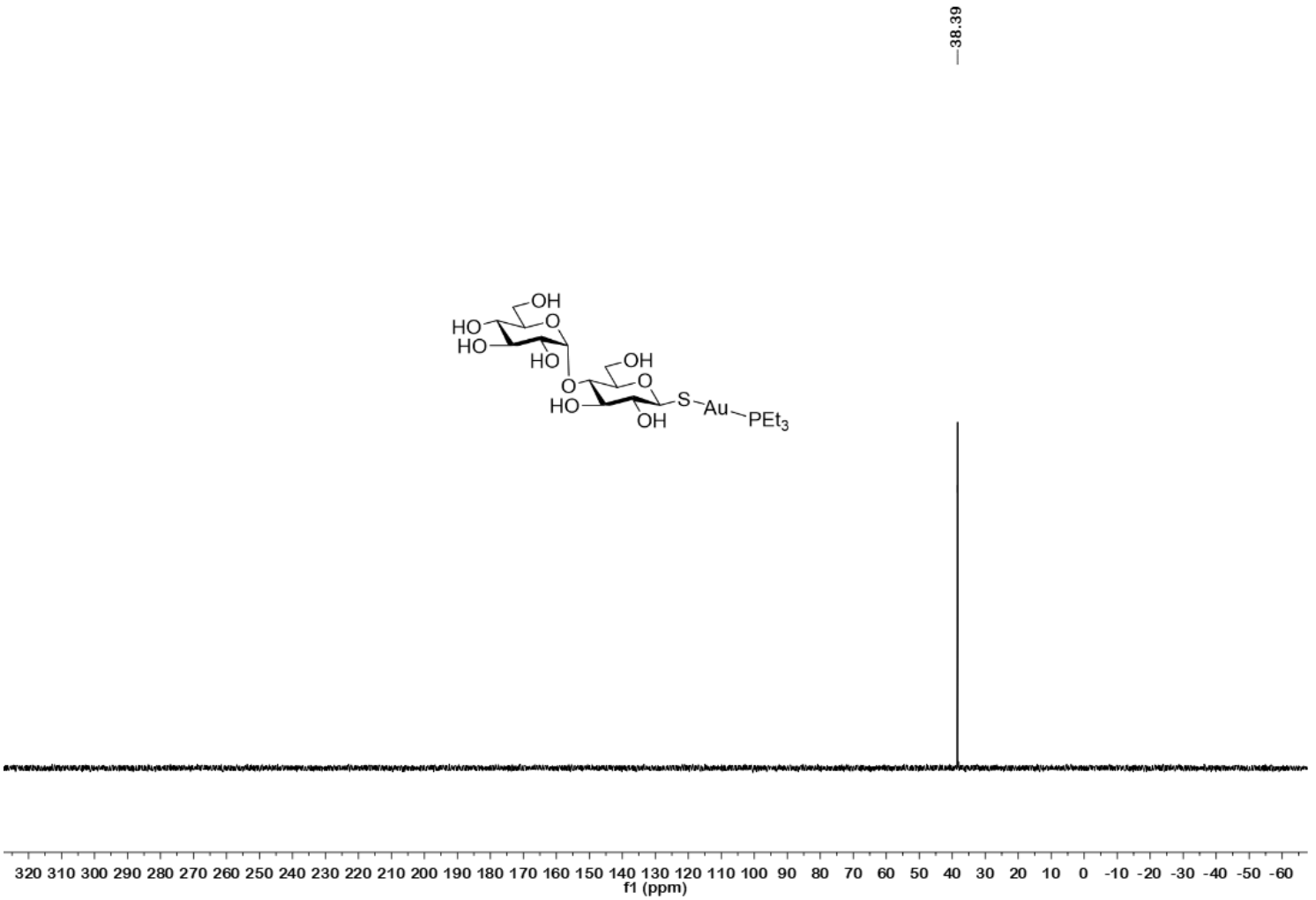


Figure S58. ^{31}P NMR spectrum of compound **14** in D_2O.

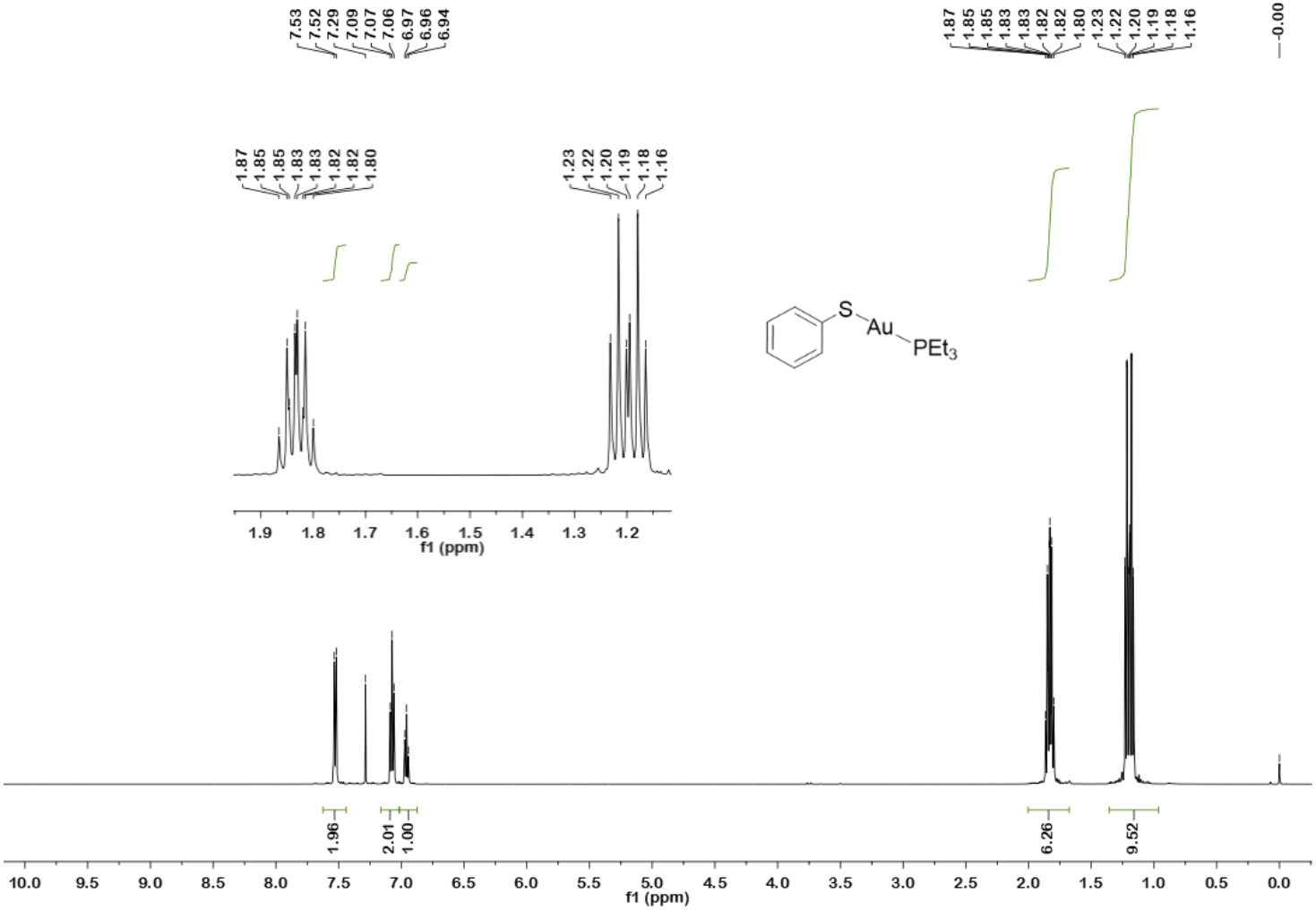


Figure S59. ^{1}H NMR spectrum of compound **15** in $CDCl_3$.

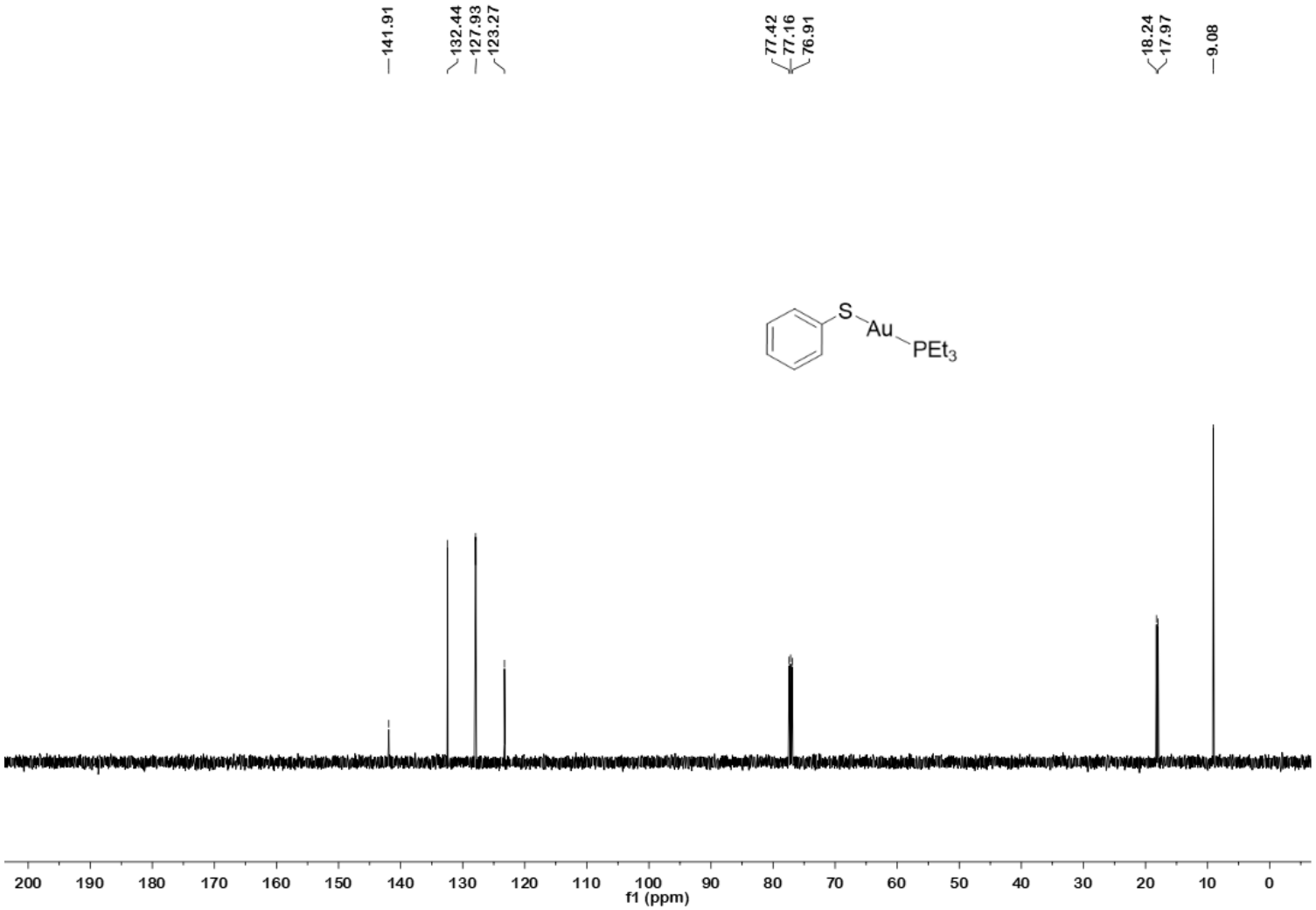


Figure S60. ^{13}C NMR spectrum of compound **15** in $CDCl_3$.

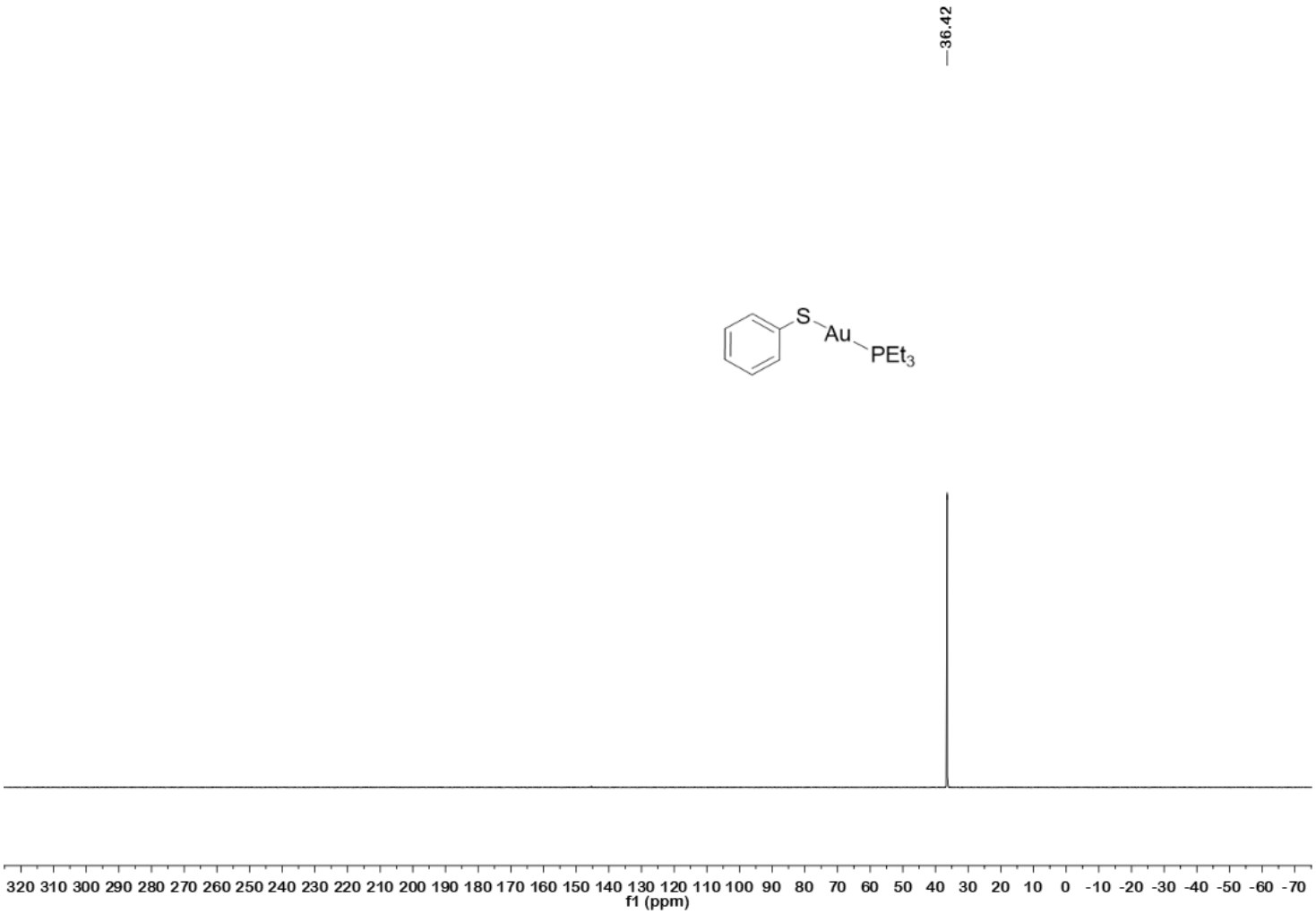


Figure S61. ^{31}P NMR spectrum of compound **15** in $CDCl_3$.

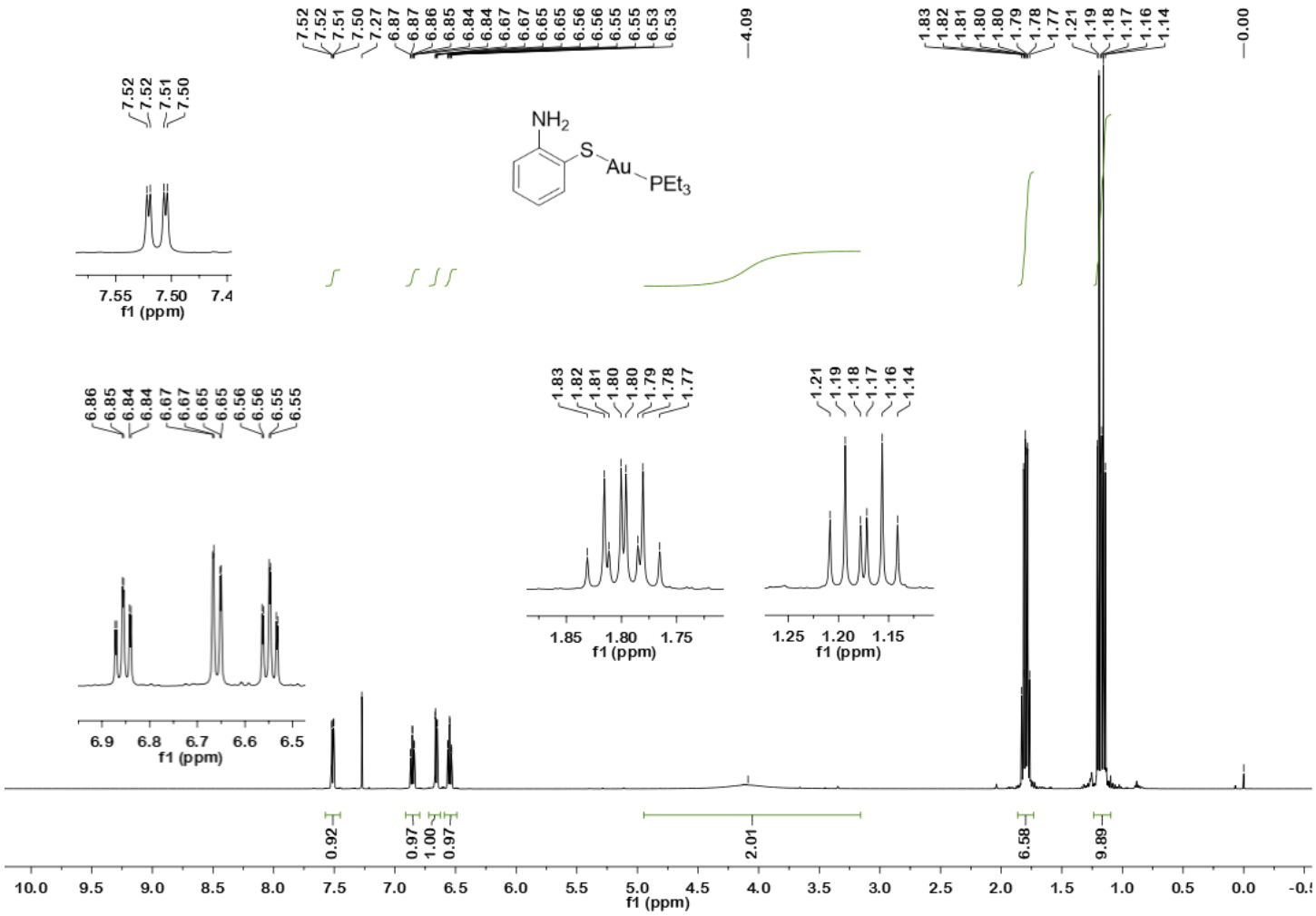


Figure S62. ^{1}H NMR spectrum of compound **16** in $CDCl_3$.

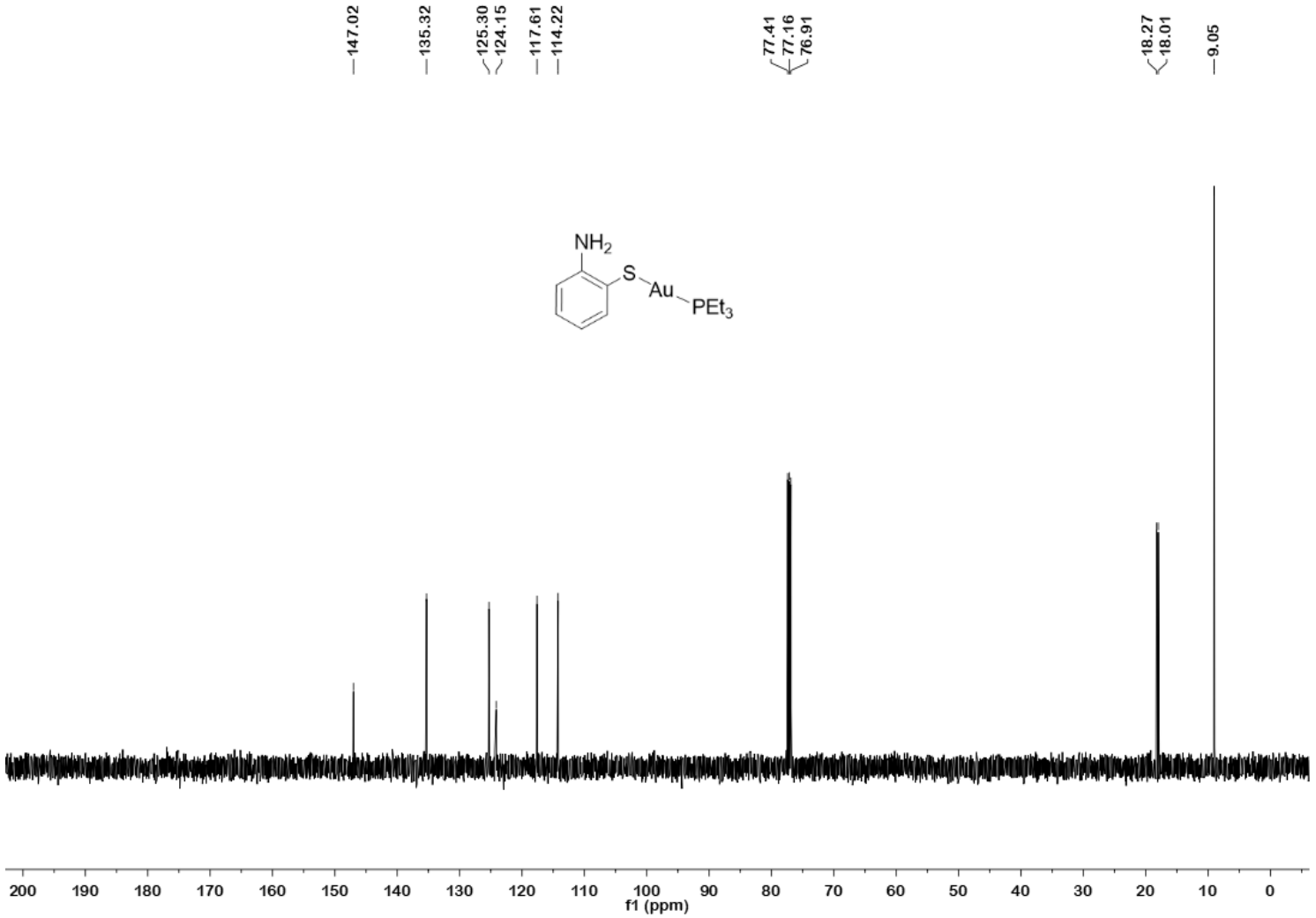


Figure S63. ^{13}C NMR spectrum of compound **16** in $CDCl_3$.

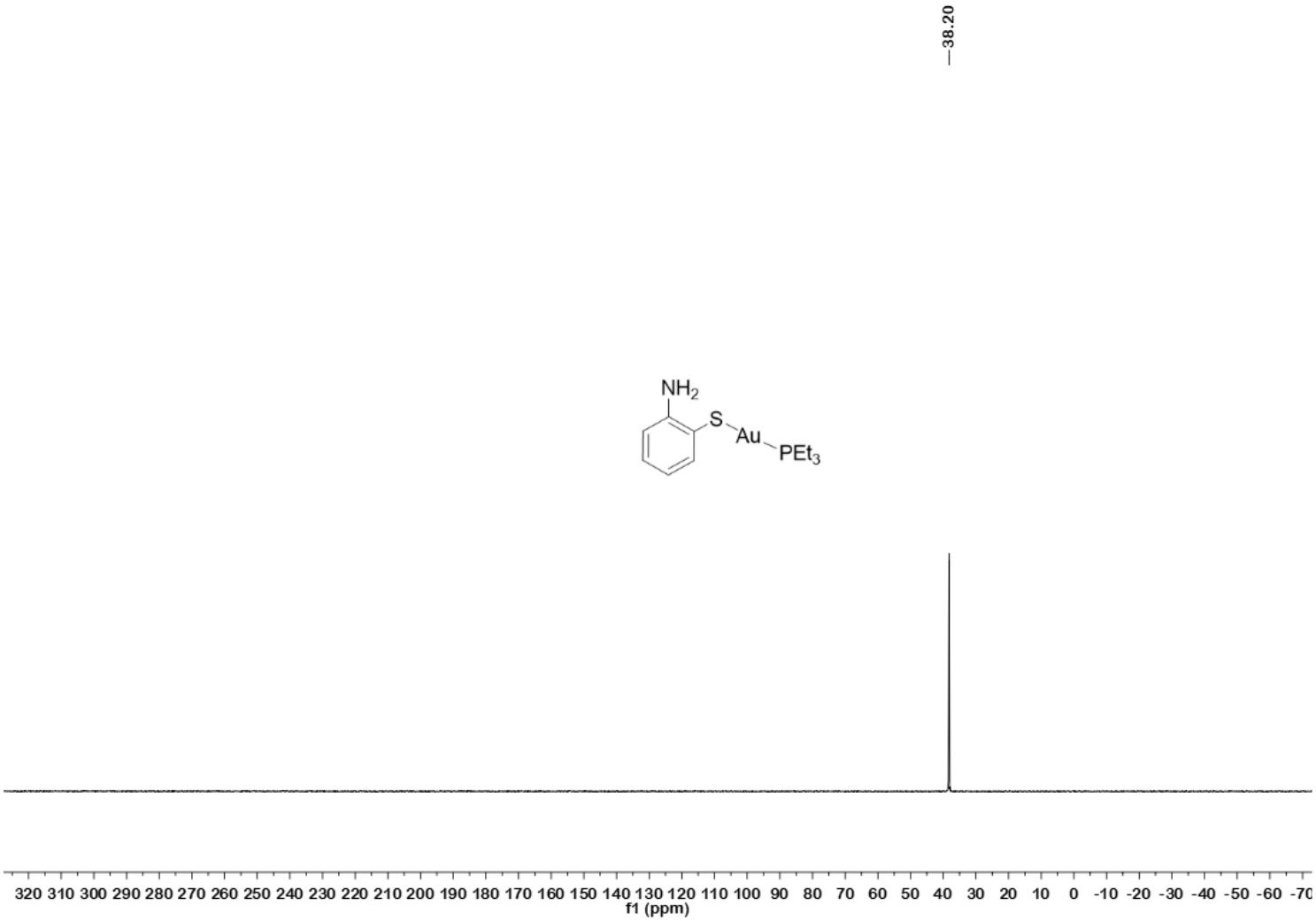


Figure S64. ^{31}P NMR spectrum of compound **16** in $CDCl_3$.

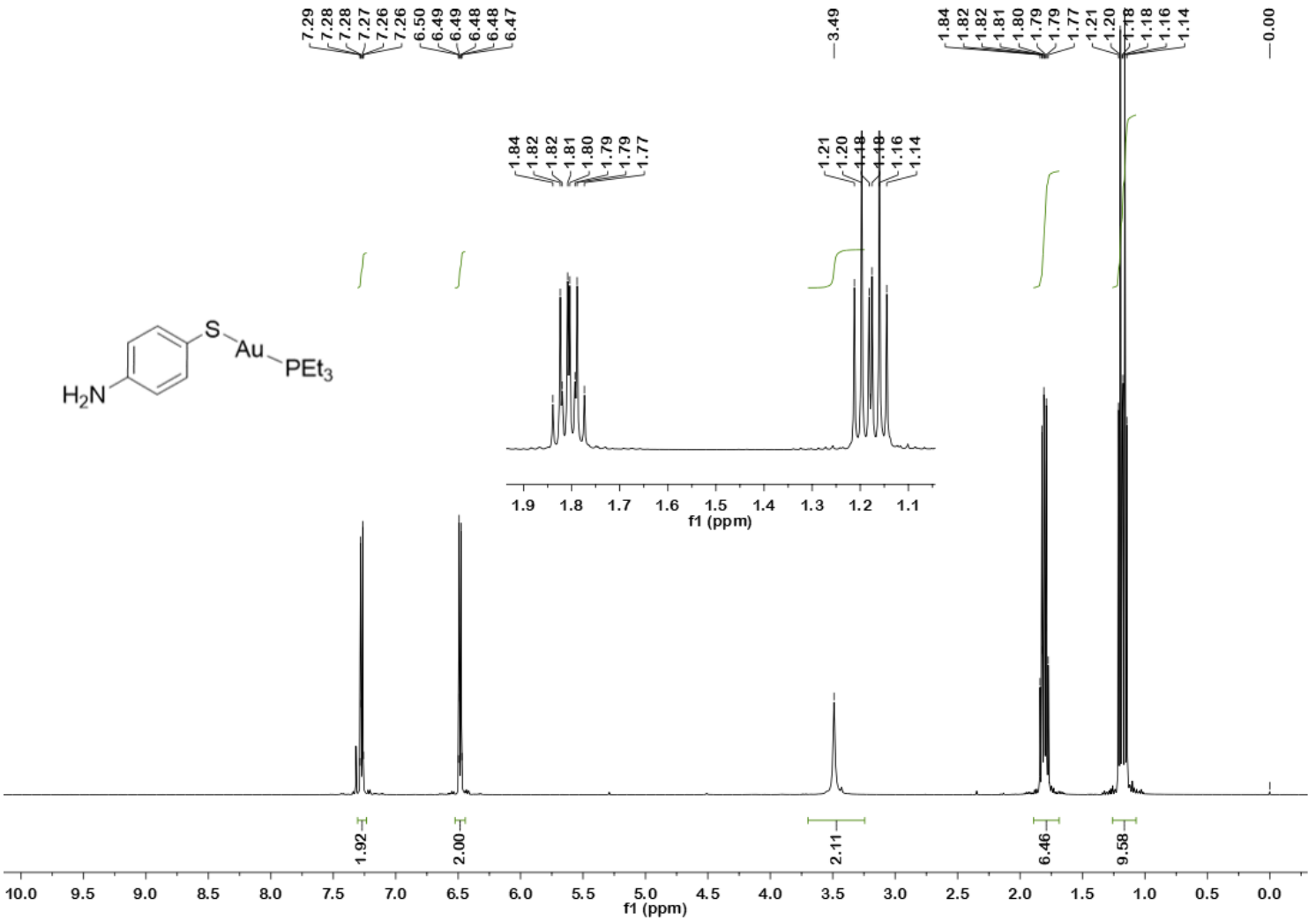


Figure S65. ^{1}H NMR spectrum of compound **17** in $CDCl_3$.

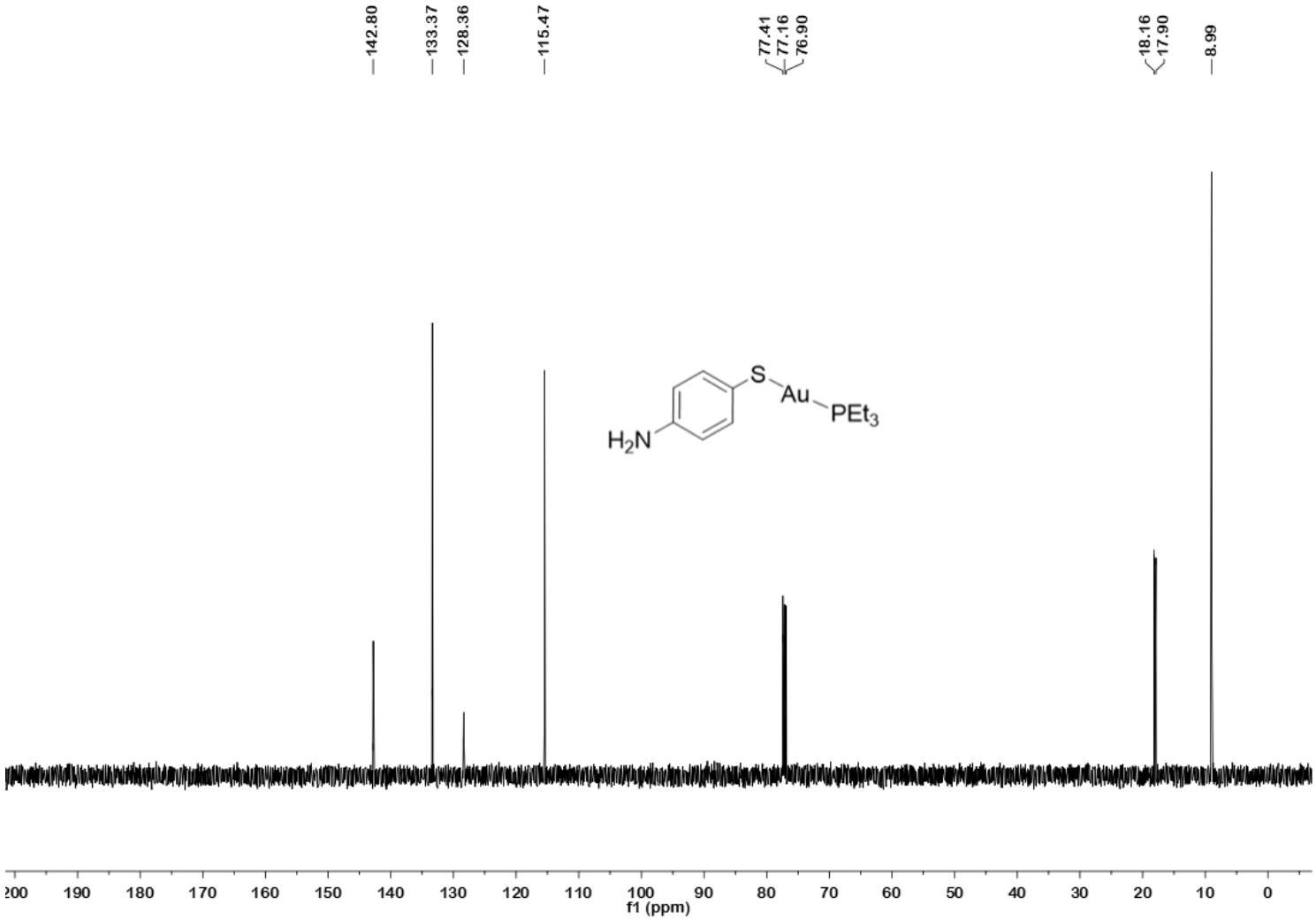


Figure S66. ^{13}C NMR spectrum of compound **17** in $CDCl_3$.

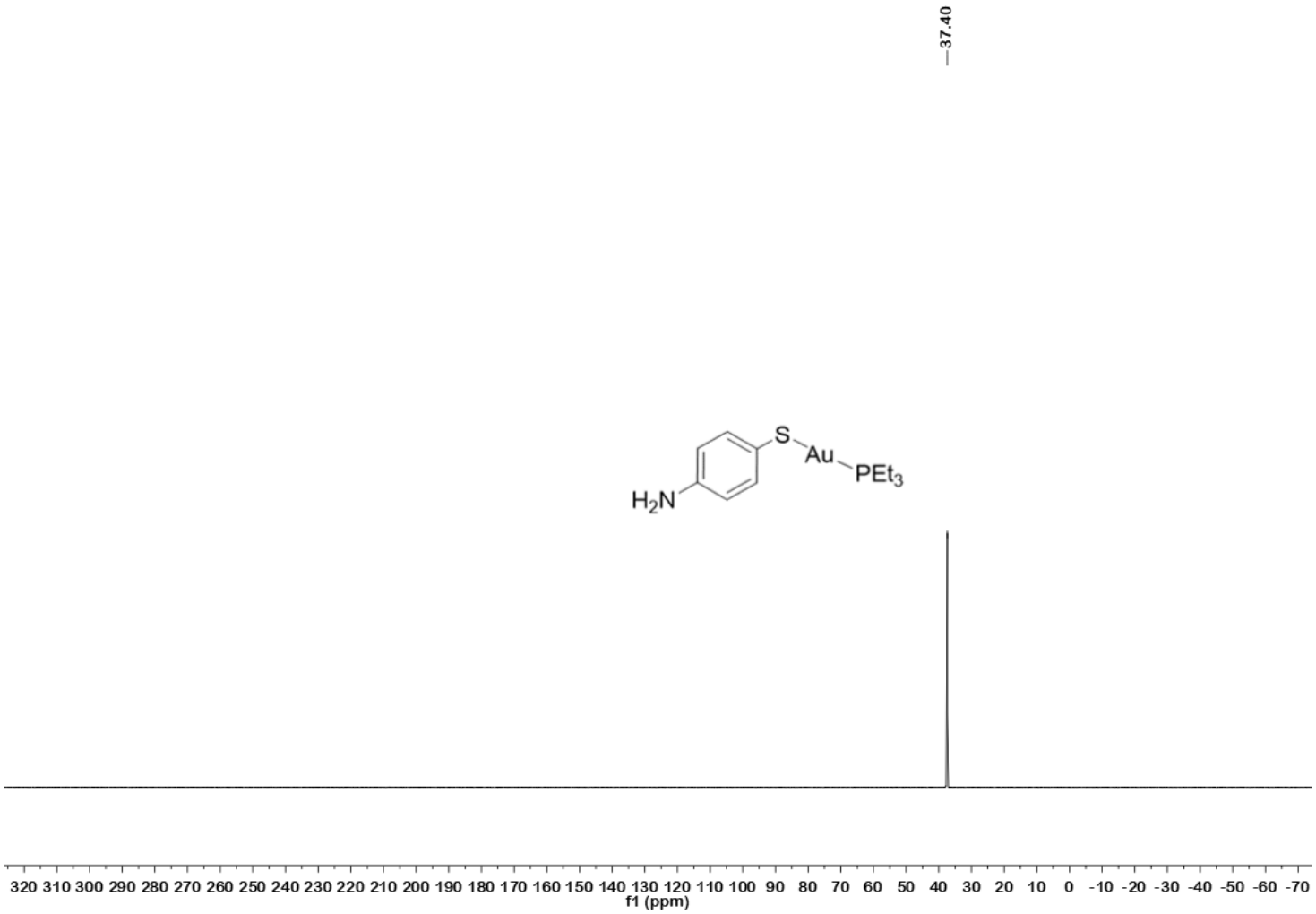


Figure S67. ^{31}P NMR spectrum of compound **17** in $CDCl_3$.

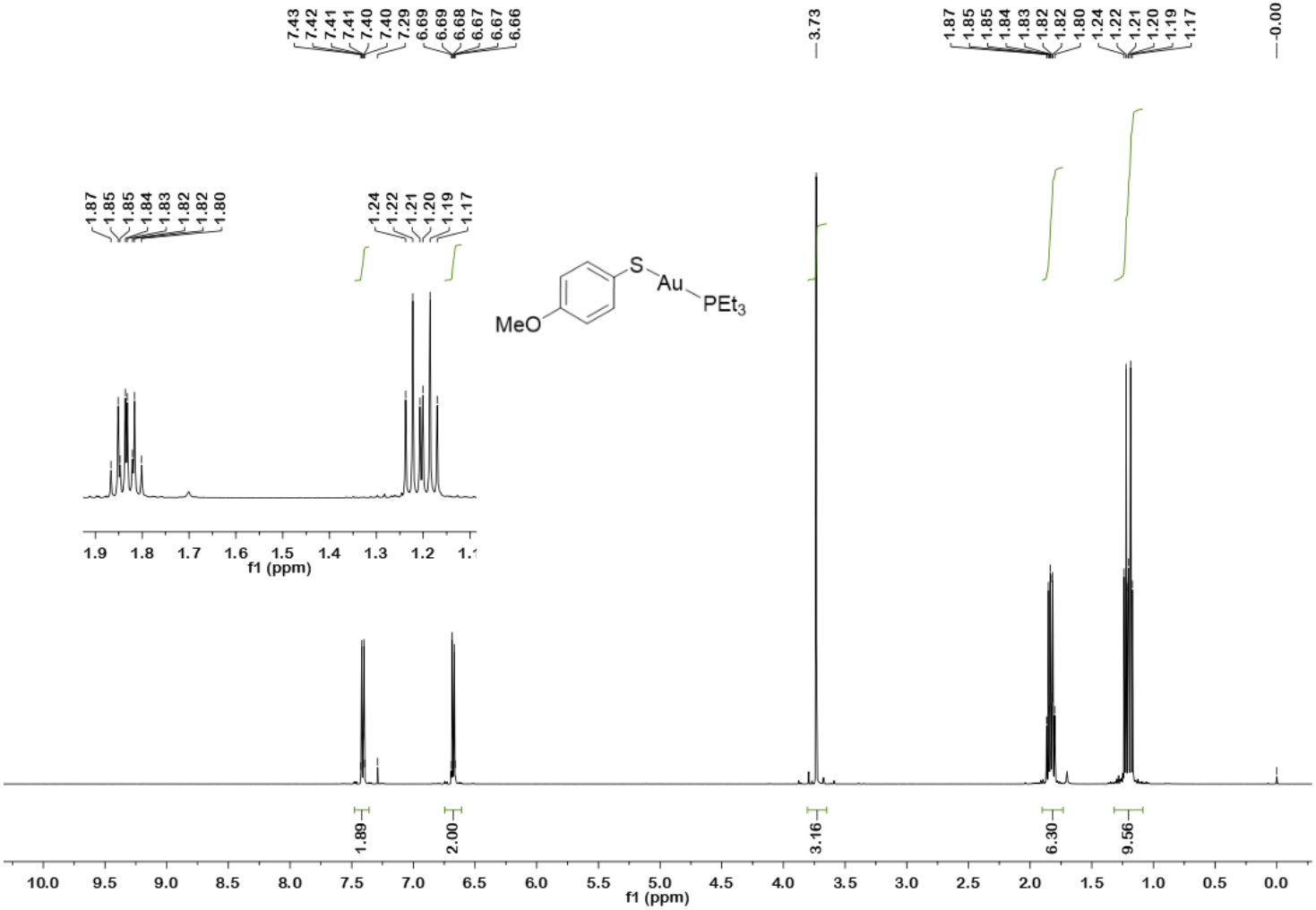


Figure S68. ^{1}H NMR spectrum of compound **18** in $CDCl_3$.

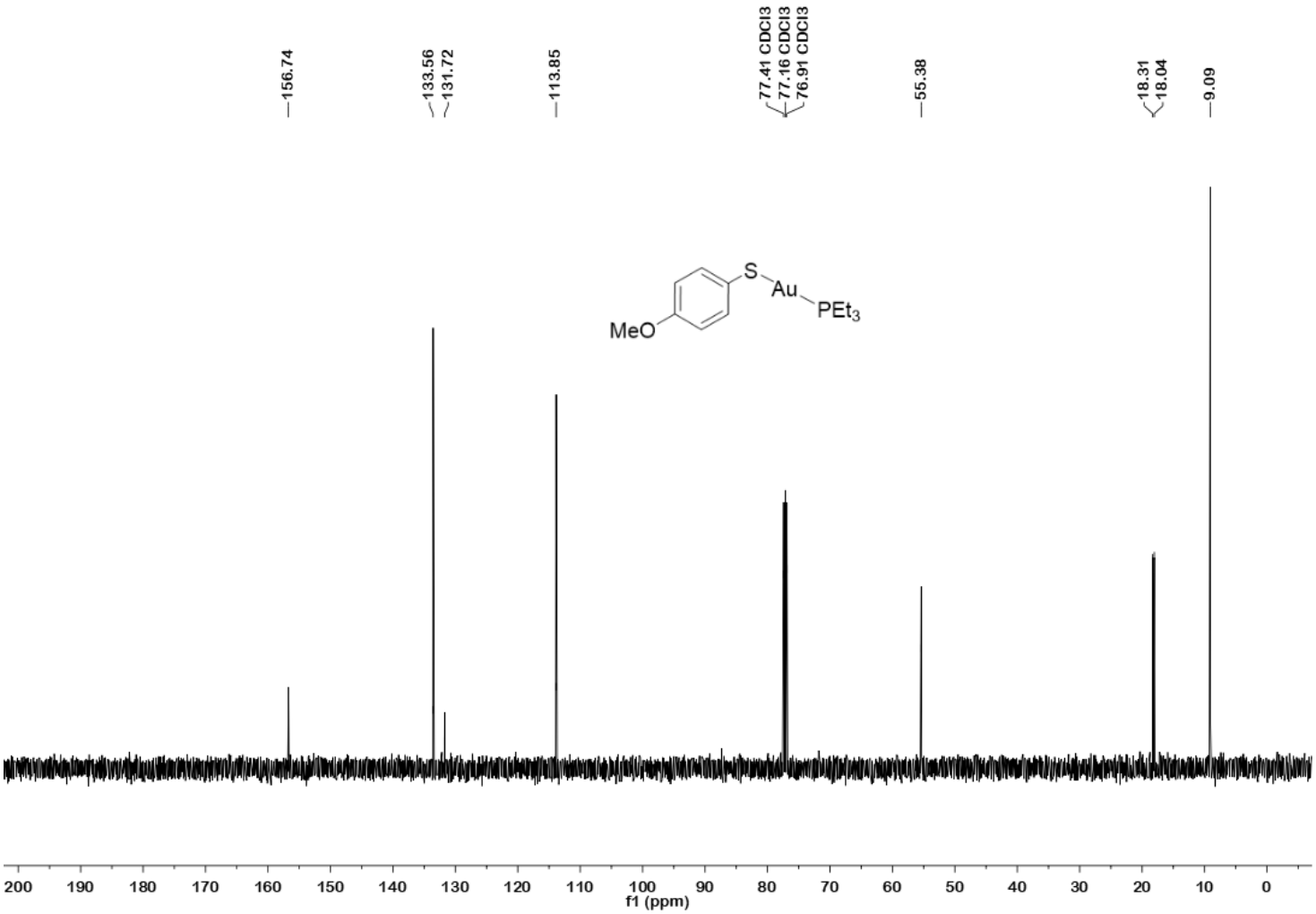


Figure S69. ^{13}C NMR spectrum of compound **18** in $CDCl_3$.

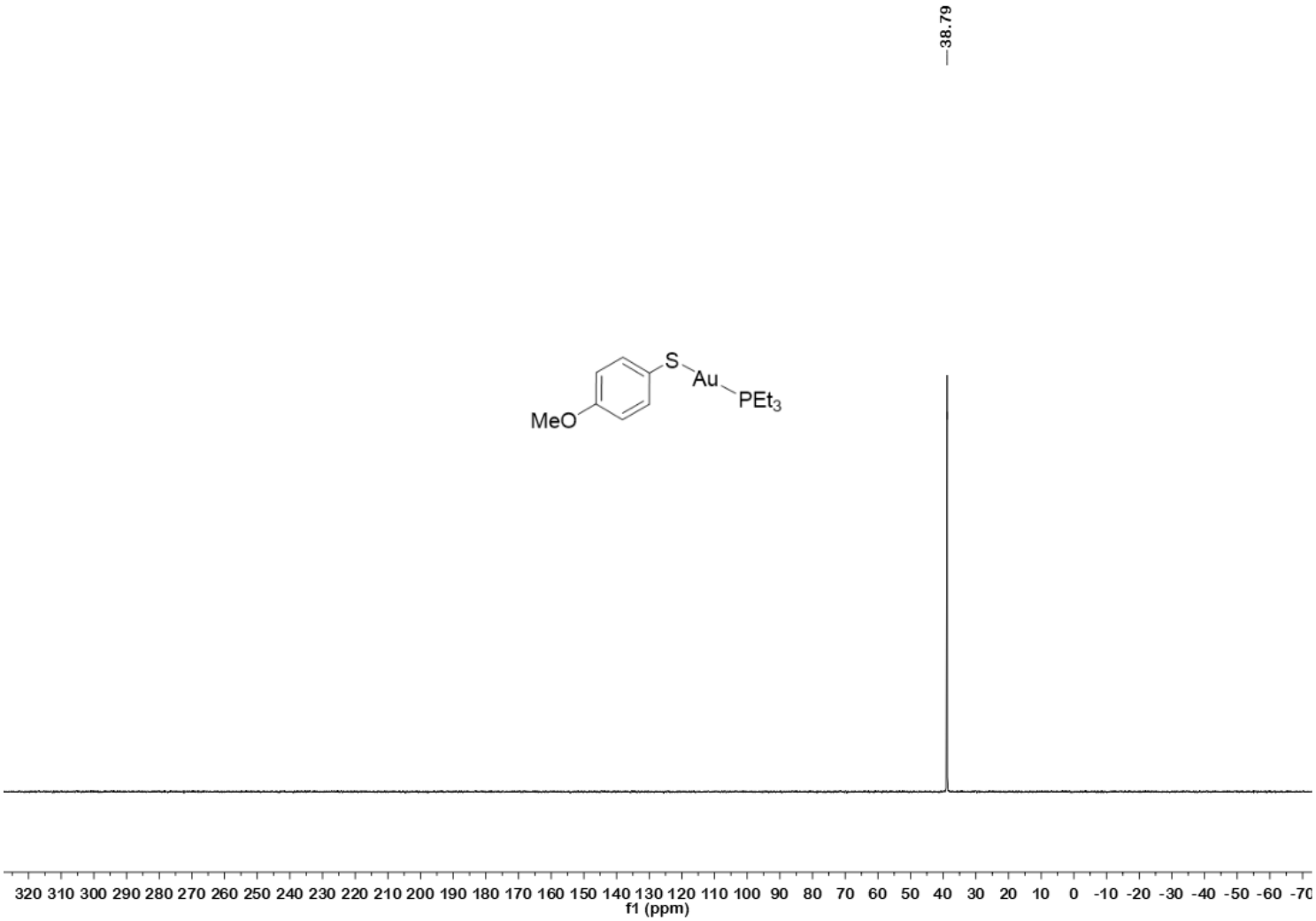


Figure S70. ^{31}P NMR spectrum of compound **18** in $CDCl_3$.

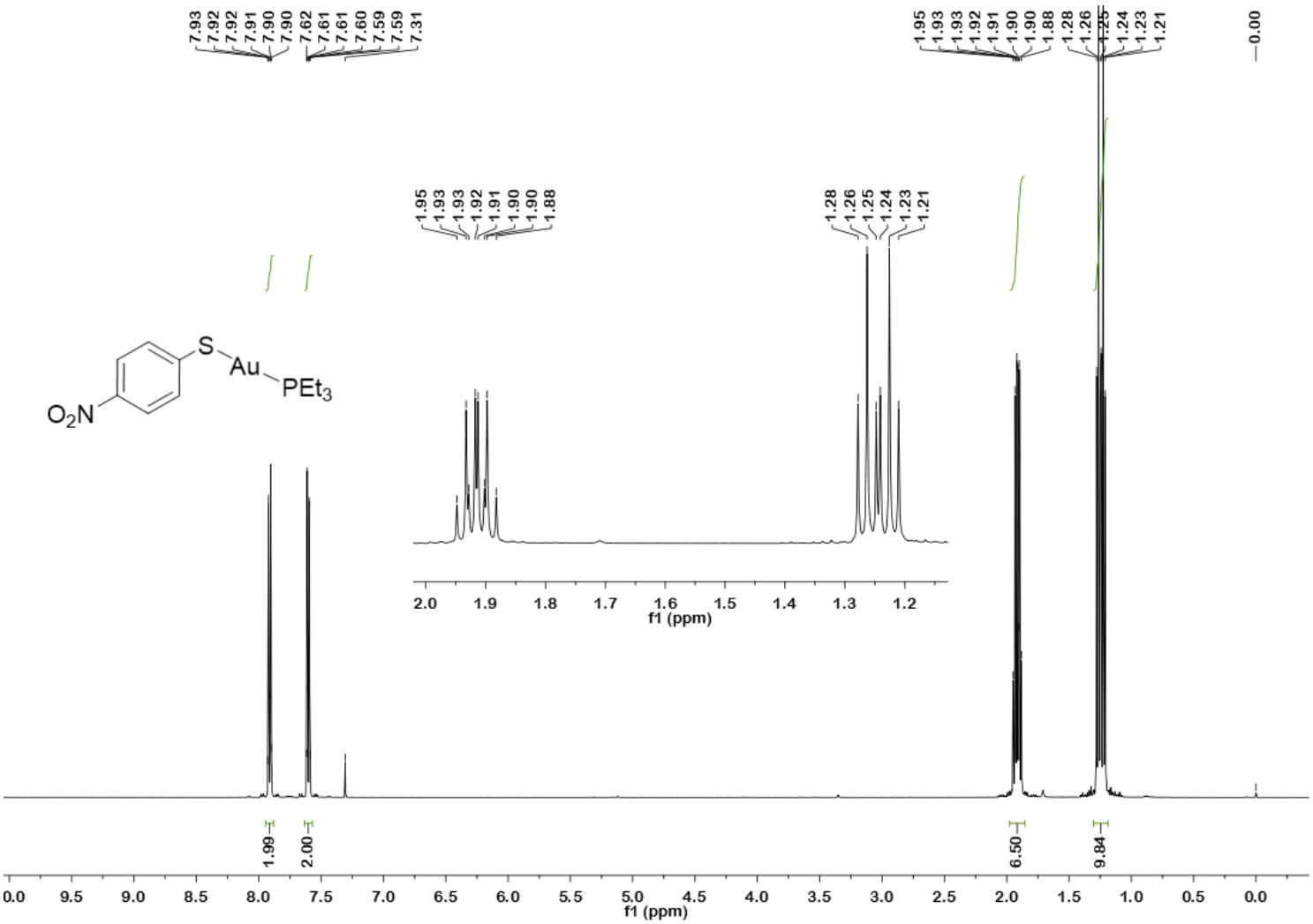


Figure S71. ^{1}H NMR spectrum of compound **19** in $CDCl_3$.

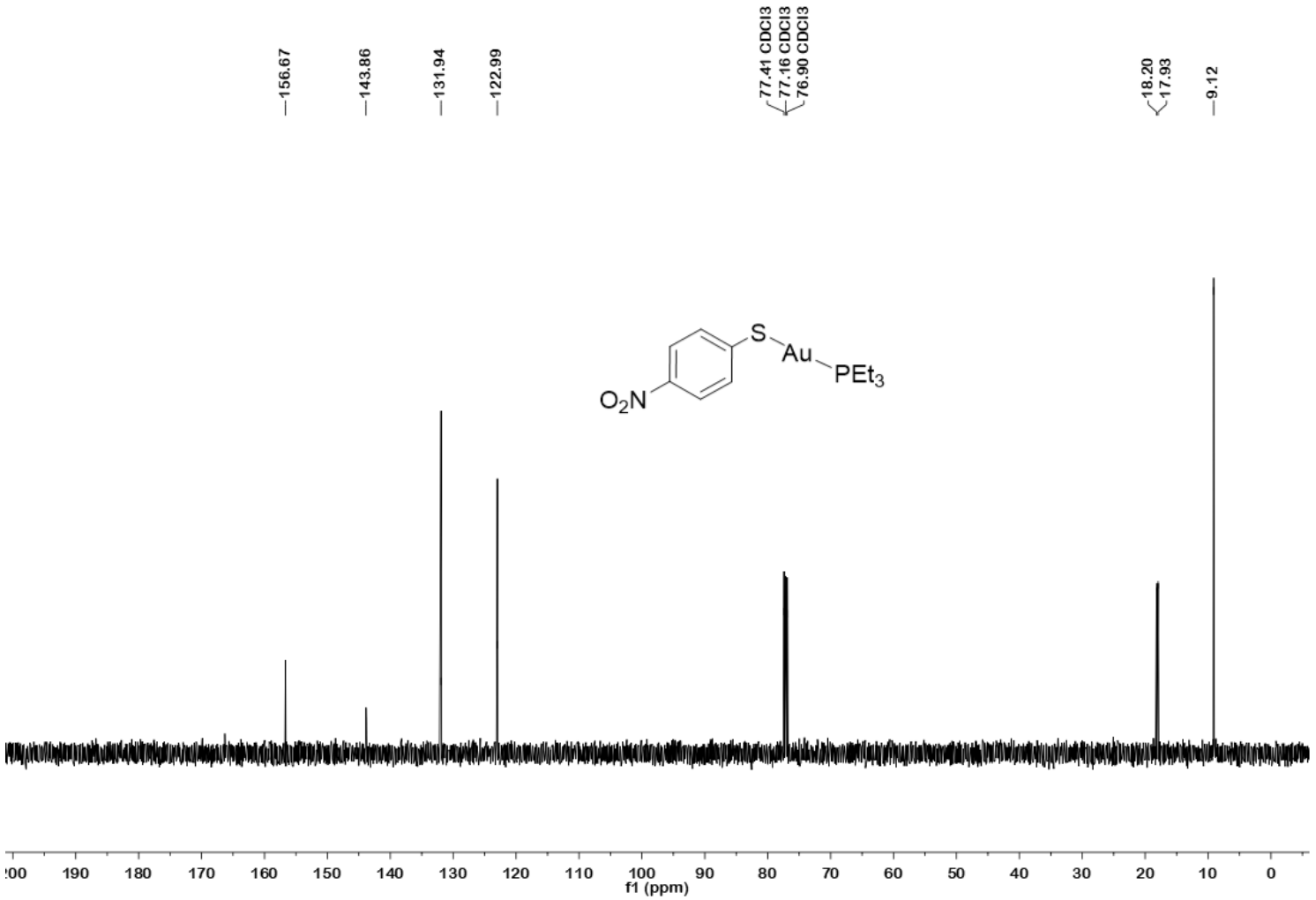


Figure S72. ^{13}C NMR spectrum of compound **19** in $CDCl_3$.

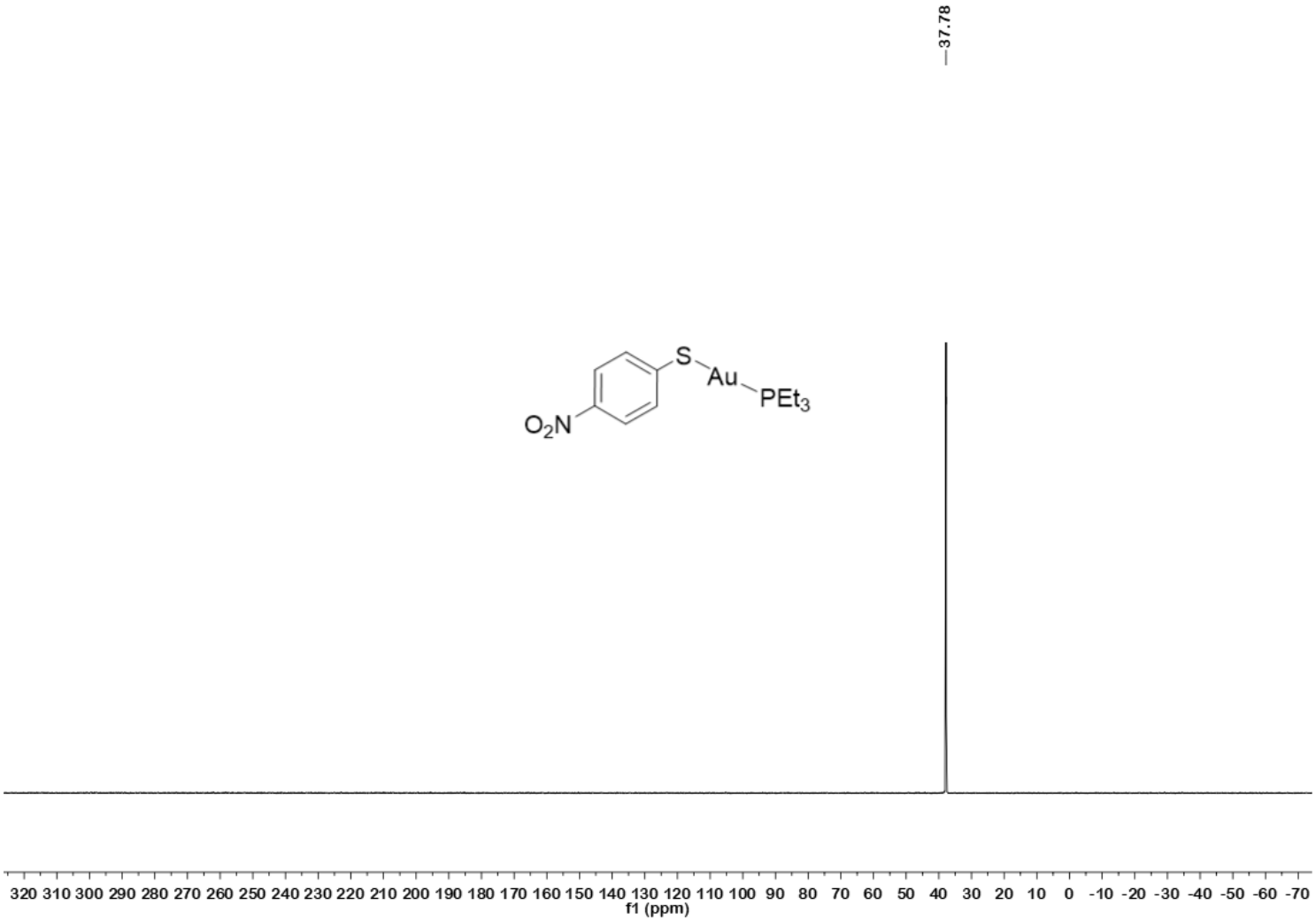


Figure S73. ^{31}P NMR spectrum of compound **19** in $CDCl_3$.

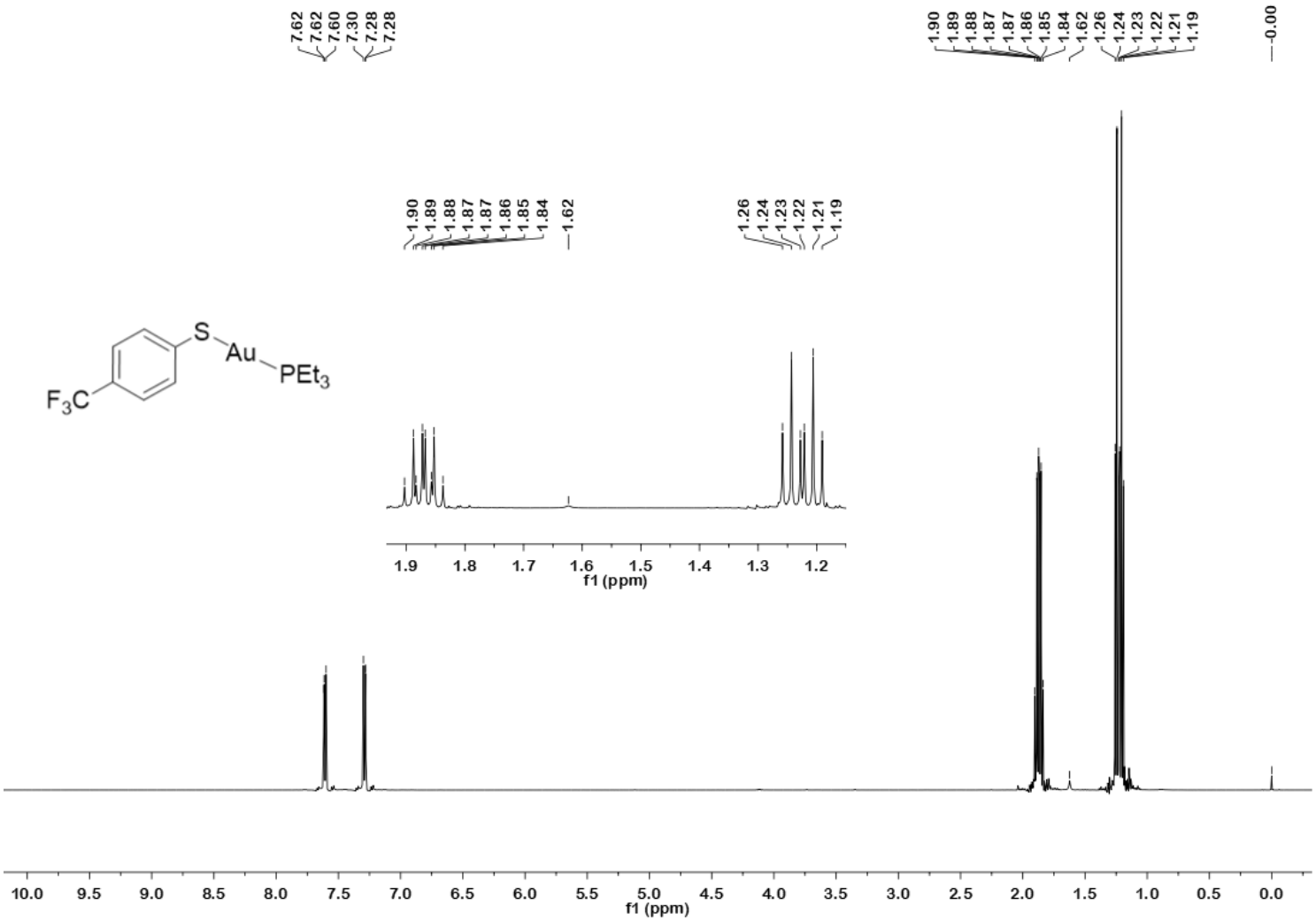


Figure S74. ^{1}H NMR spectrum of compound **20** in $CDCl_3$.

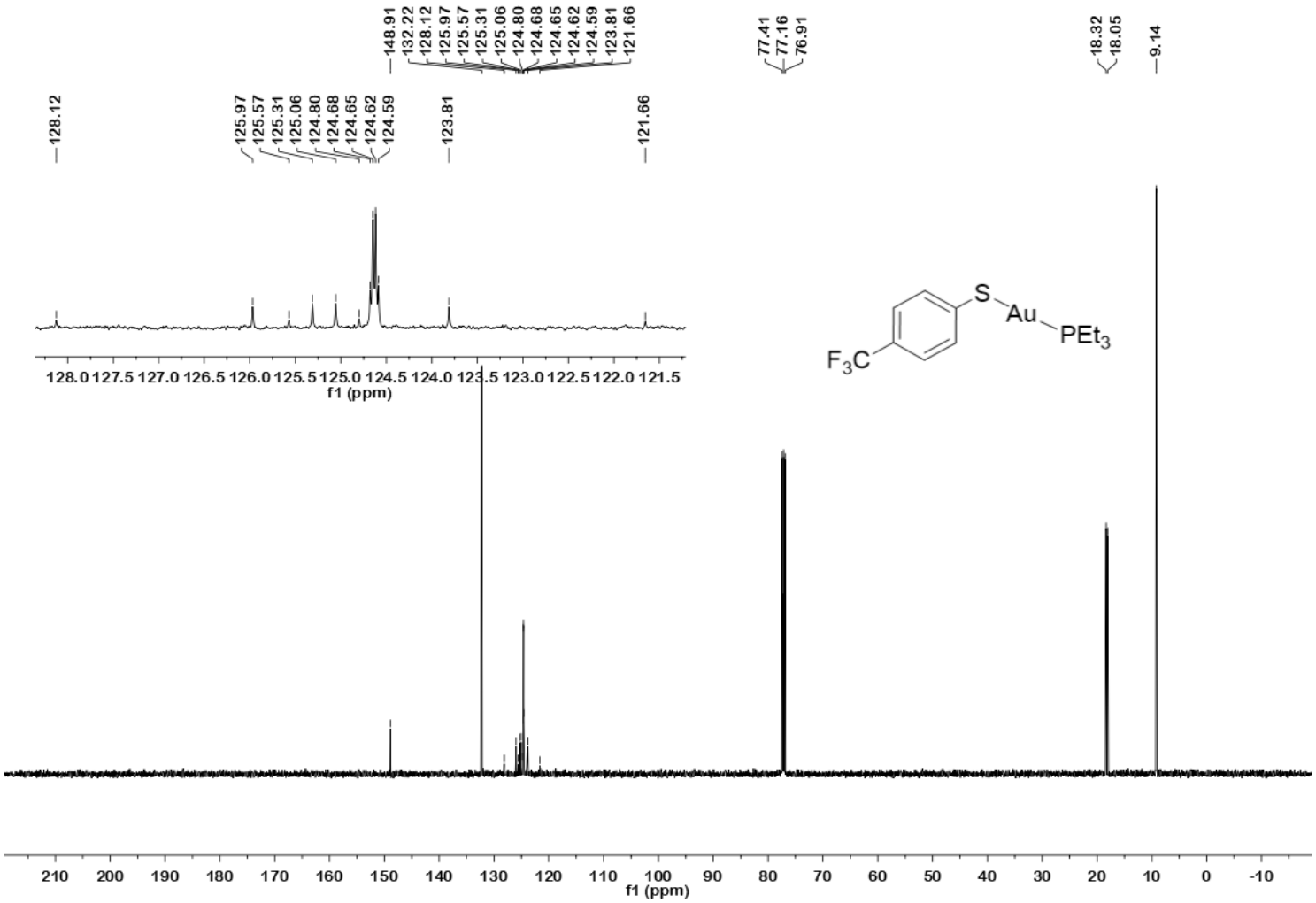


Figure S75. ^{13}C NMR spectrum of compound **20** in $CDCl_3$.

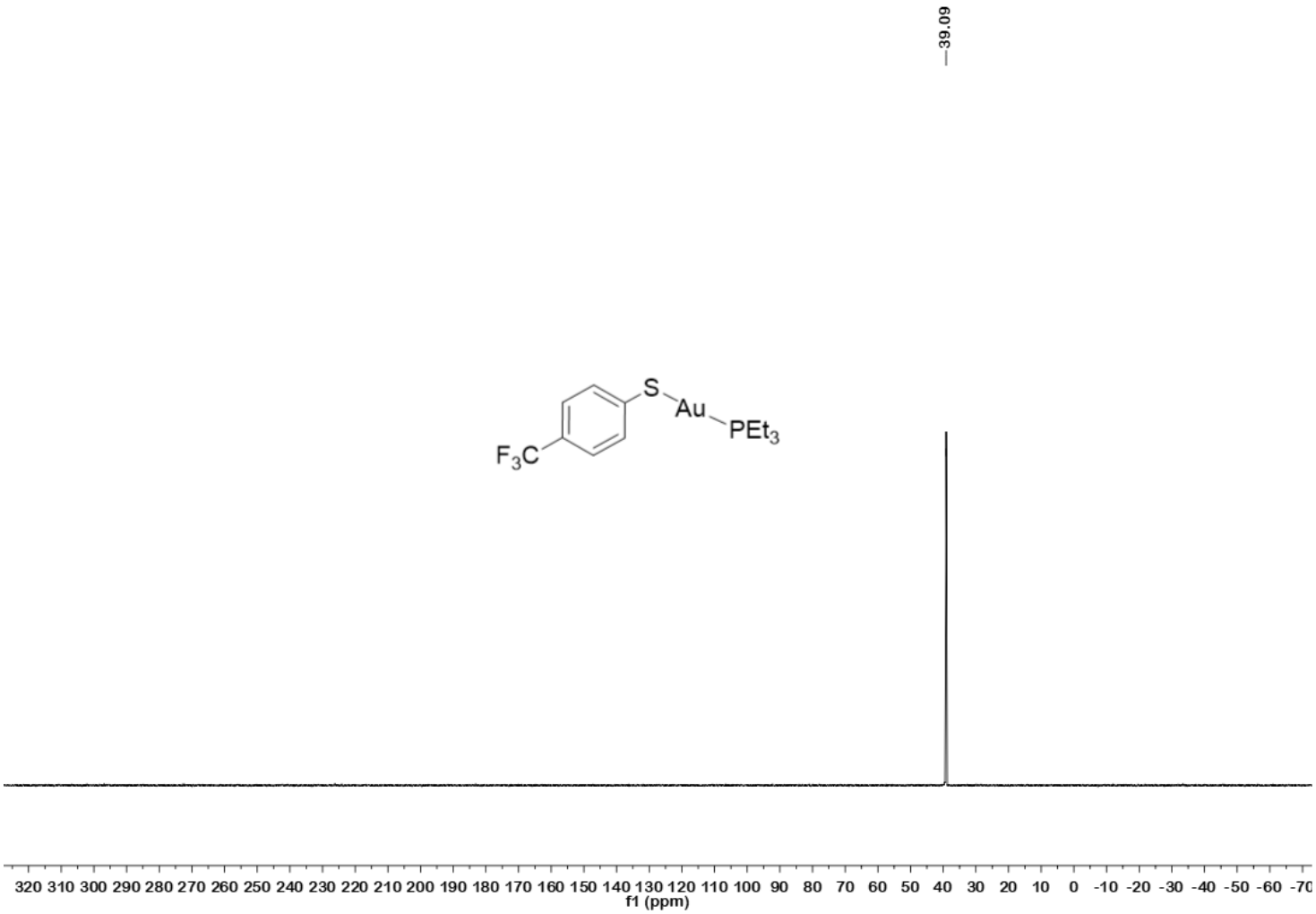


Figure S76. ^{31}P NMR spectrum of compound **20** in $CDCl_3$.

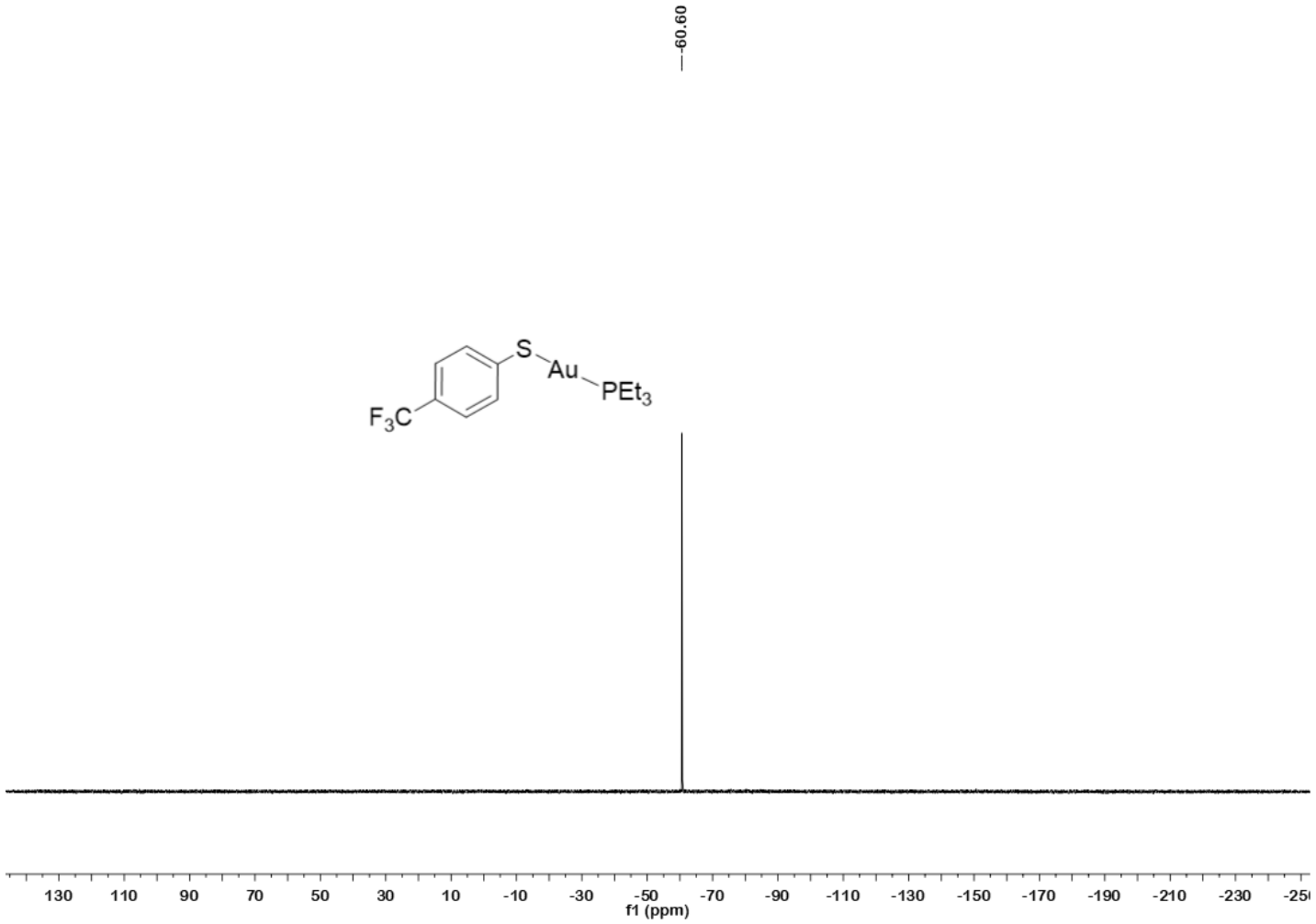


Figure S77. ^{19}F NMR spectrum of compound **20** in $CDCl_3$.

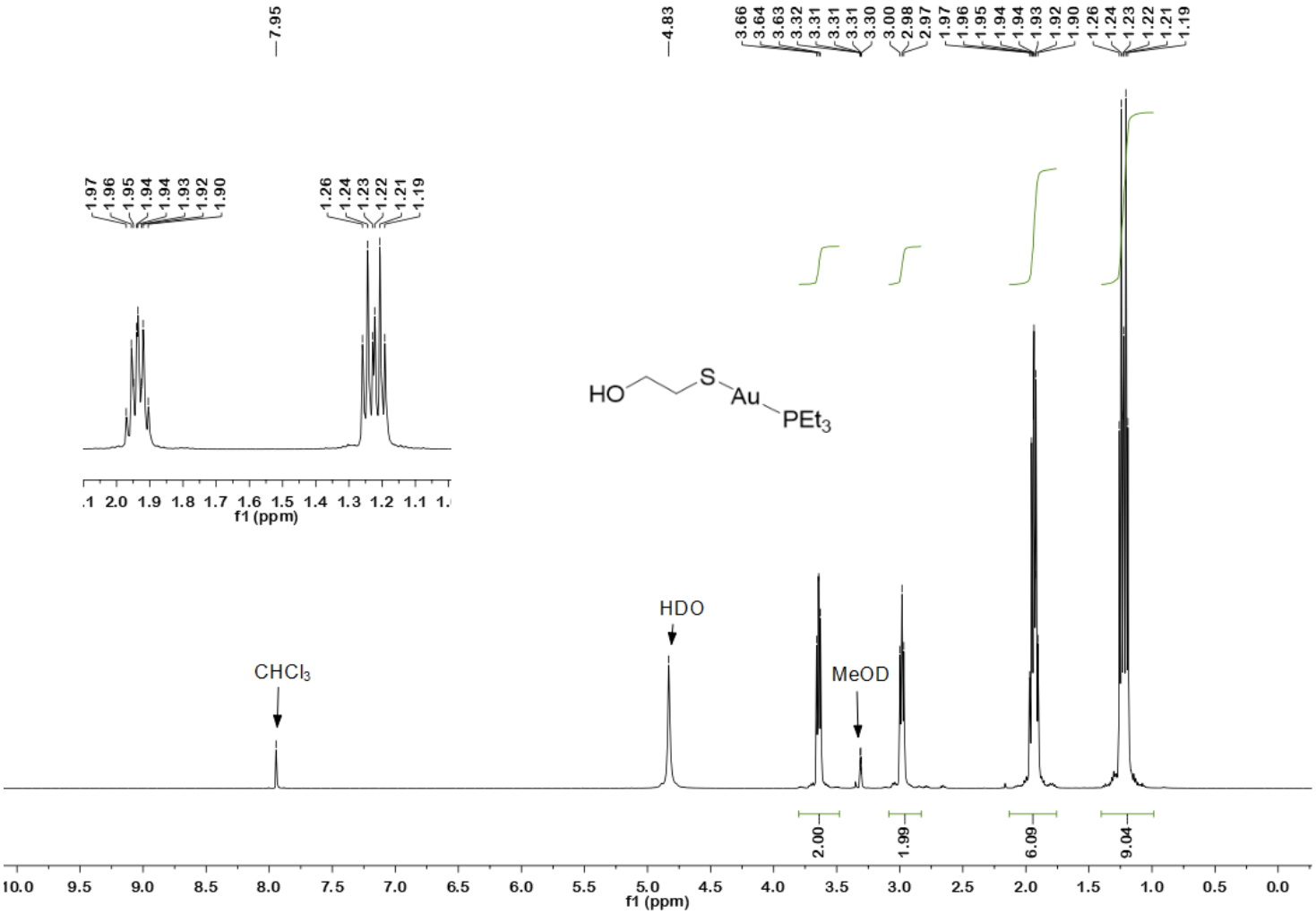


Figure S78. ^{1}H NMR spectrum of compound **21** in CD_3OD.

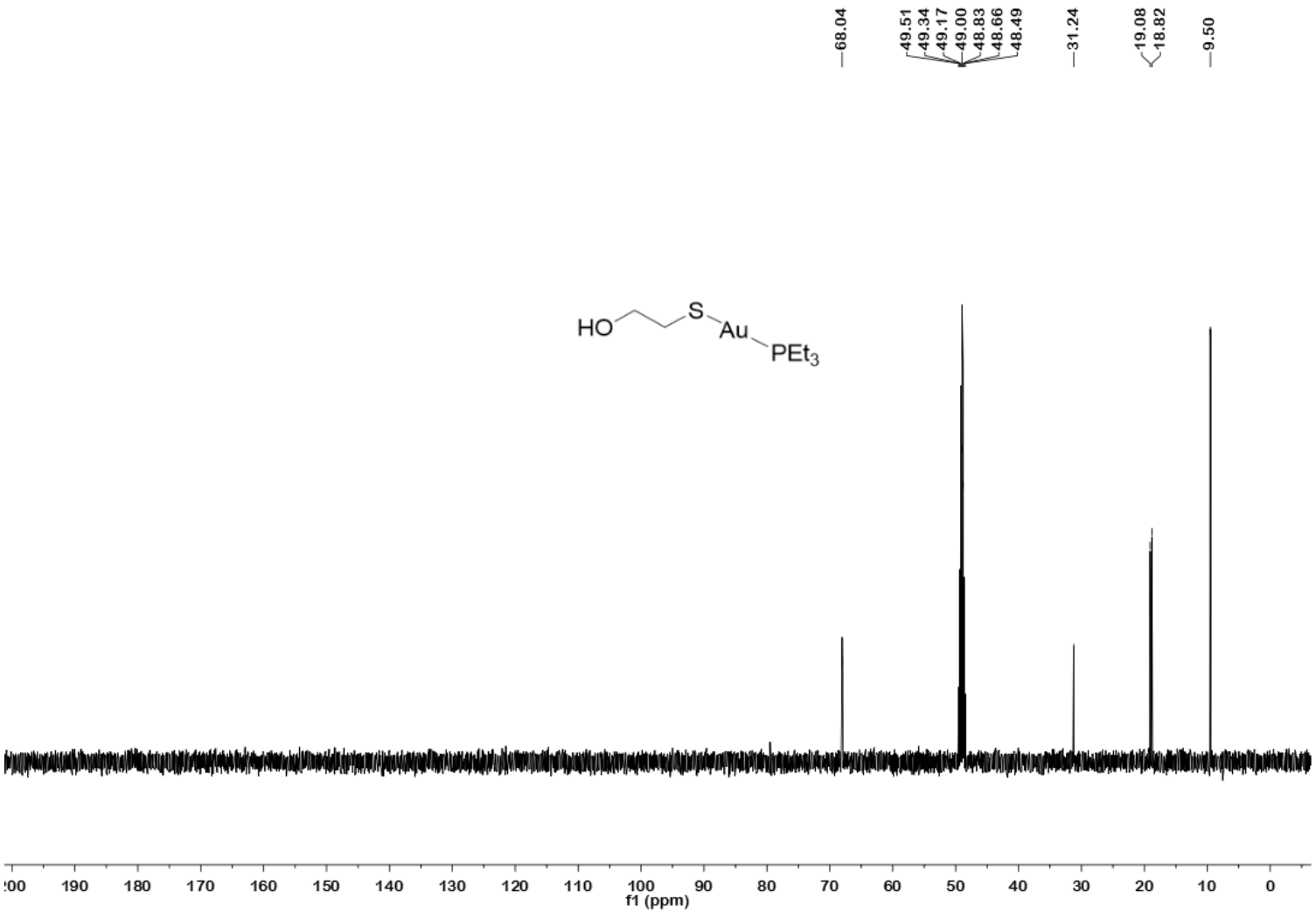


Figure S79. ^{13}C NMR spectrum of compound **21** in CD_3OD.

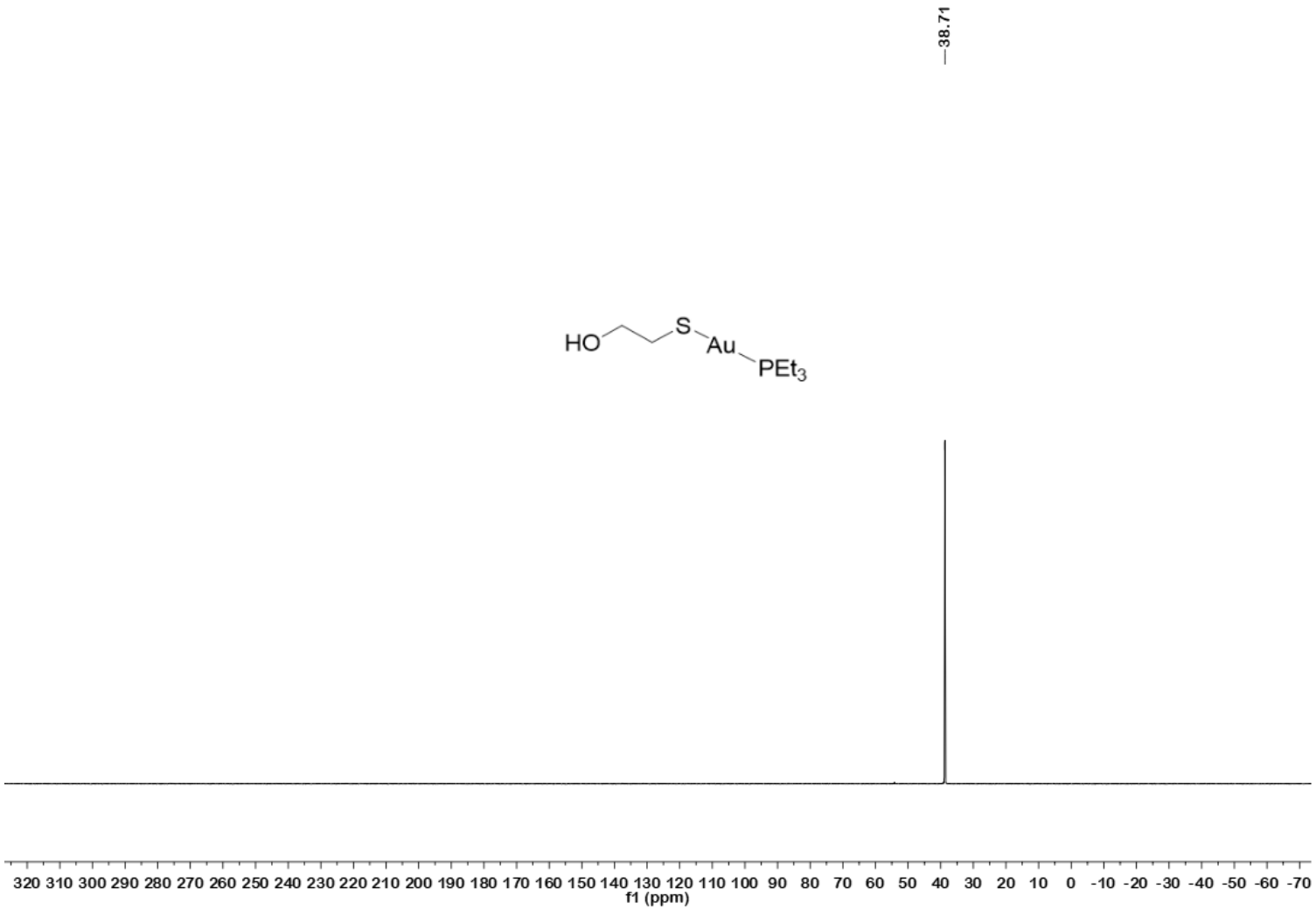


Figure S80. ^{31}P NMR spectrum of compound **21** in CD_3OD.

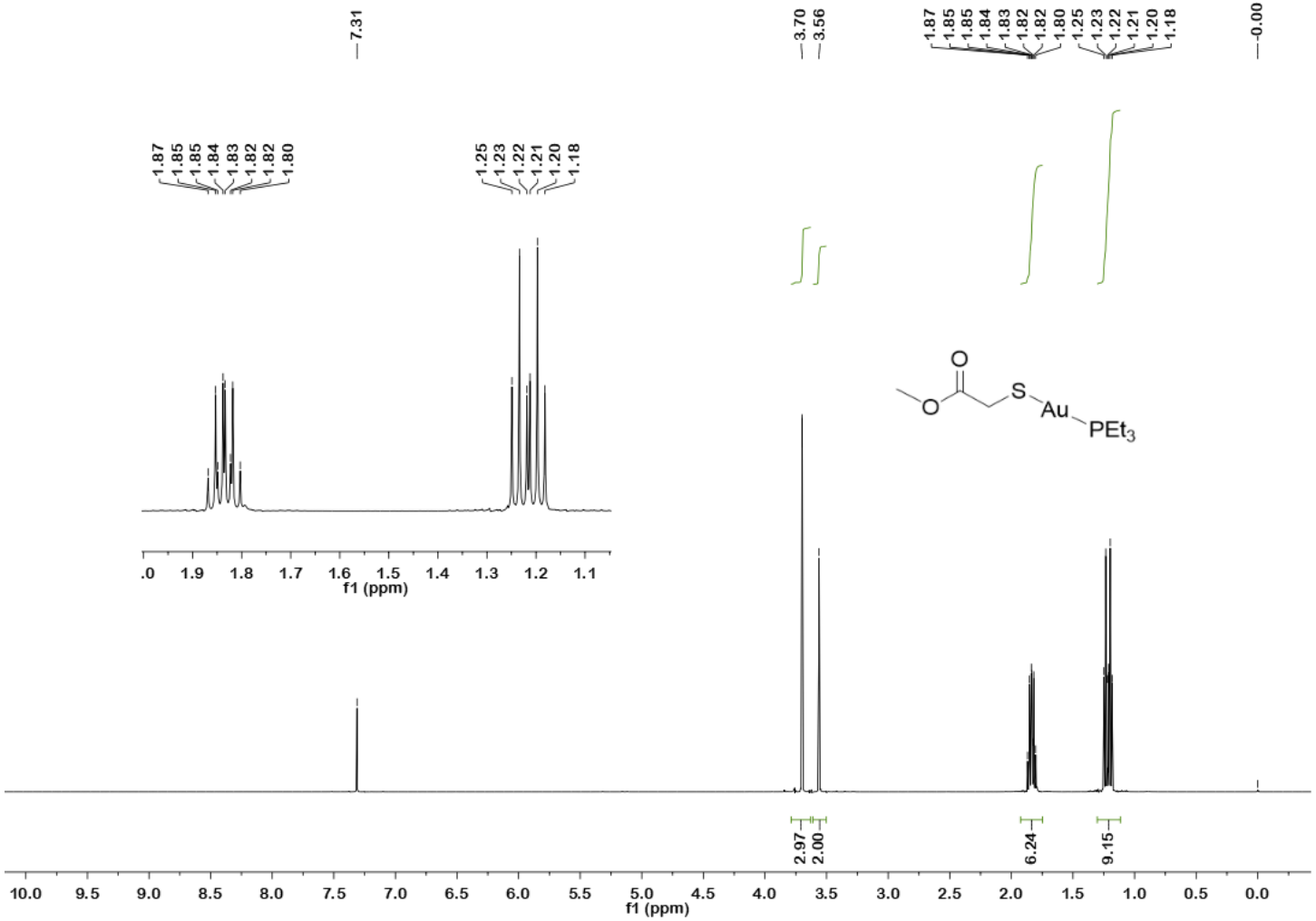


Figure S81. ^{1}H NMR spectrum of compound **22** in $CDCl_3$.

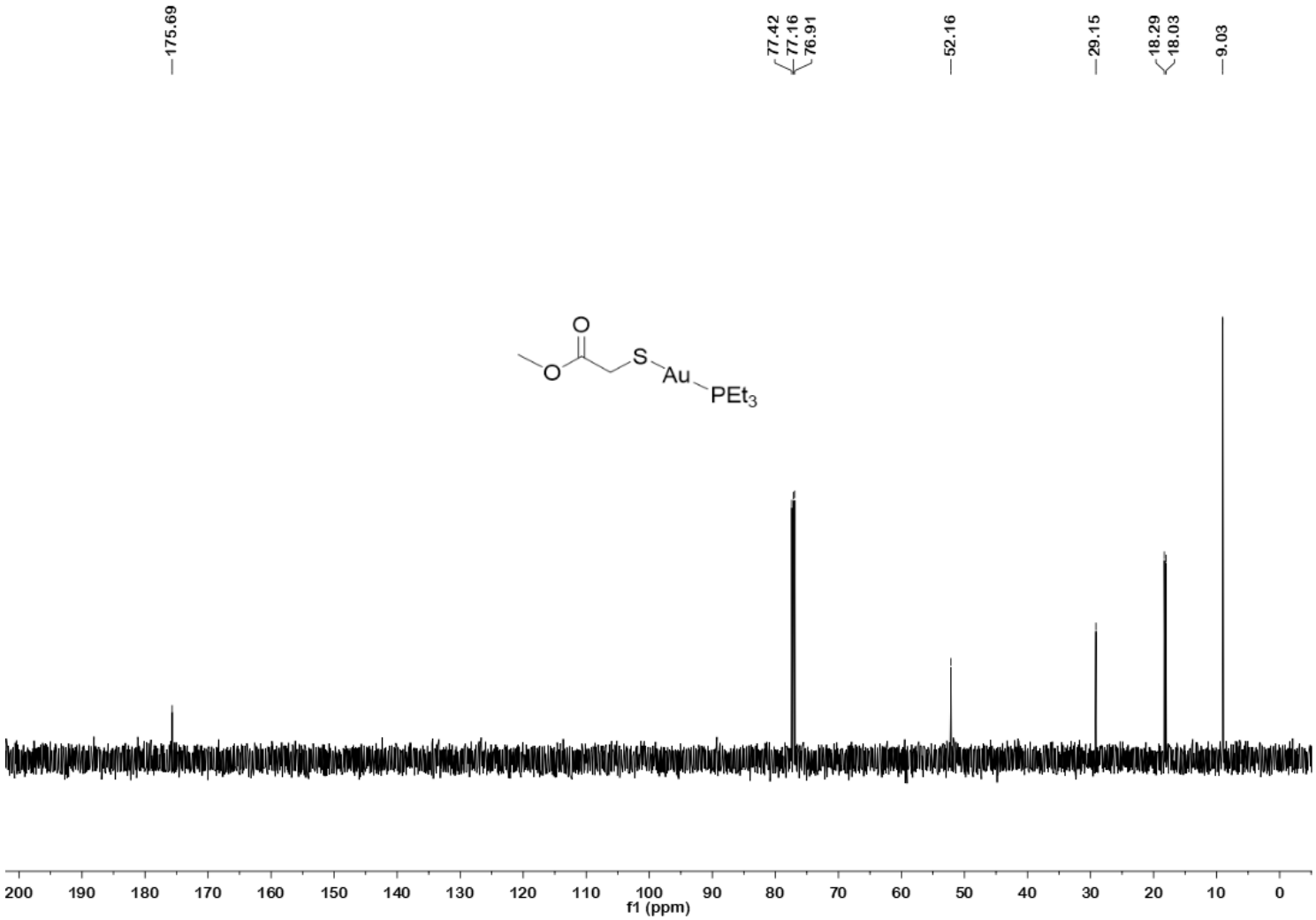


Figure S82. ^{13}C NMR spectrum of compound **22** in $CDCl_3$.

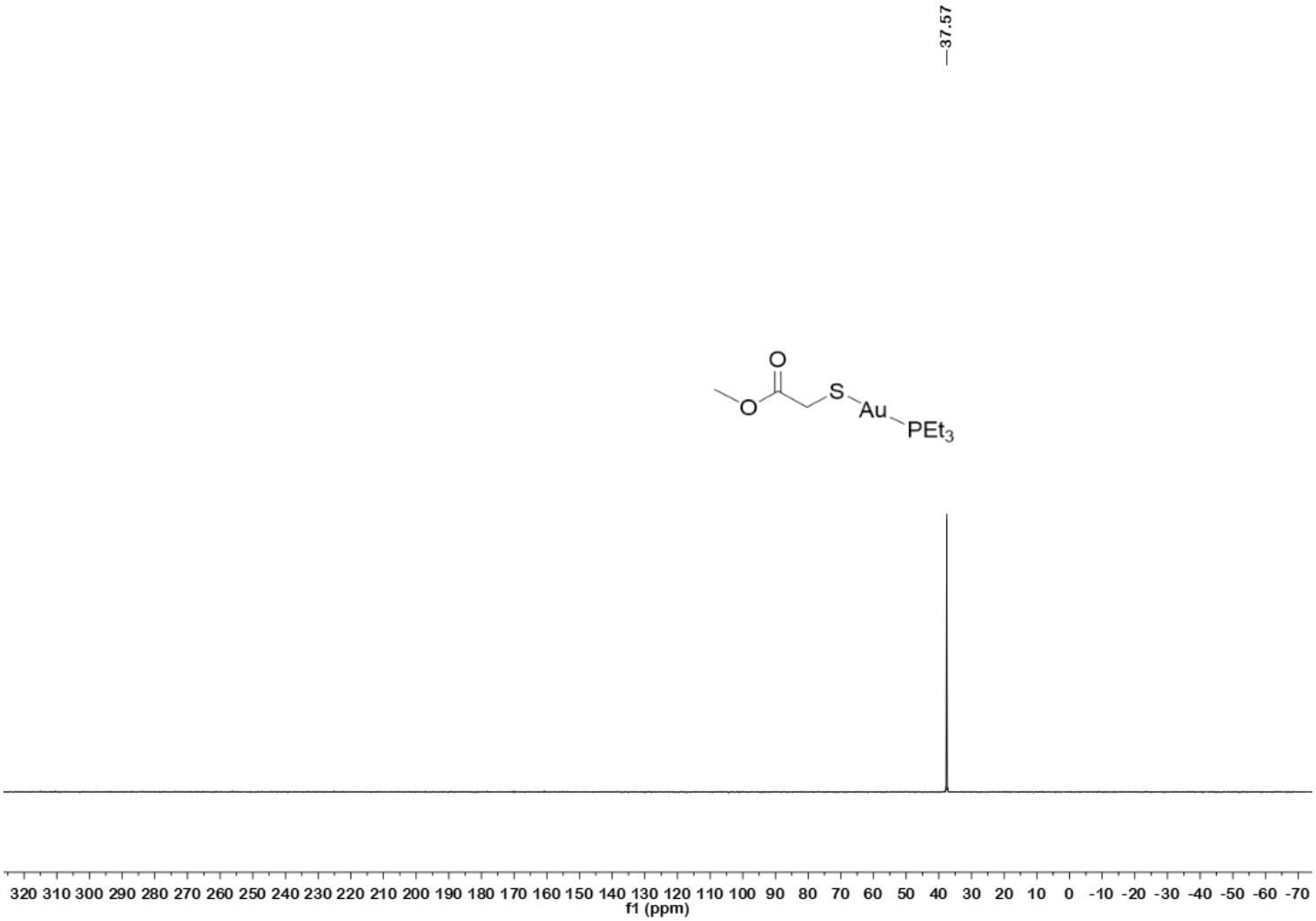


Figure S83. ^{31}P NMR spectrum of compound **22** in $CDCl_3$.

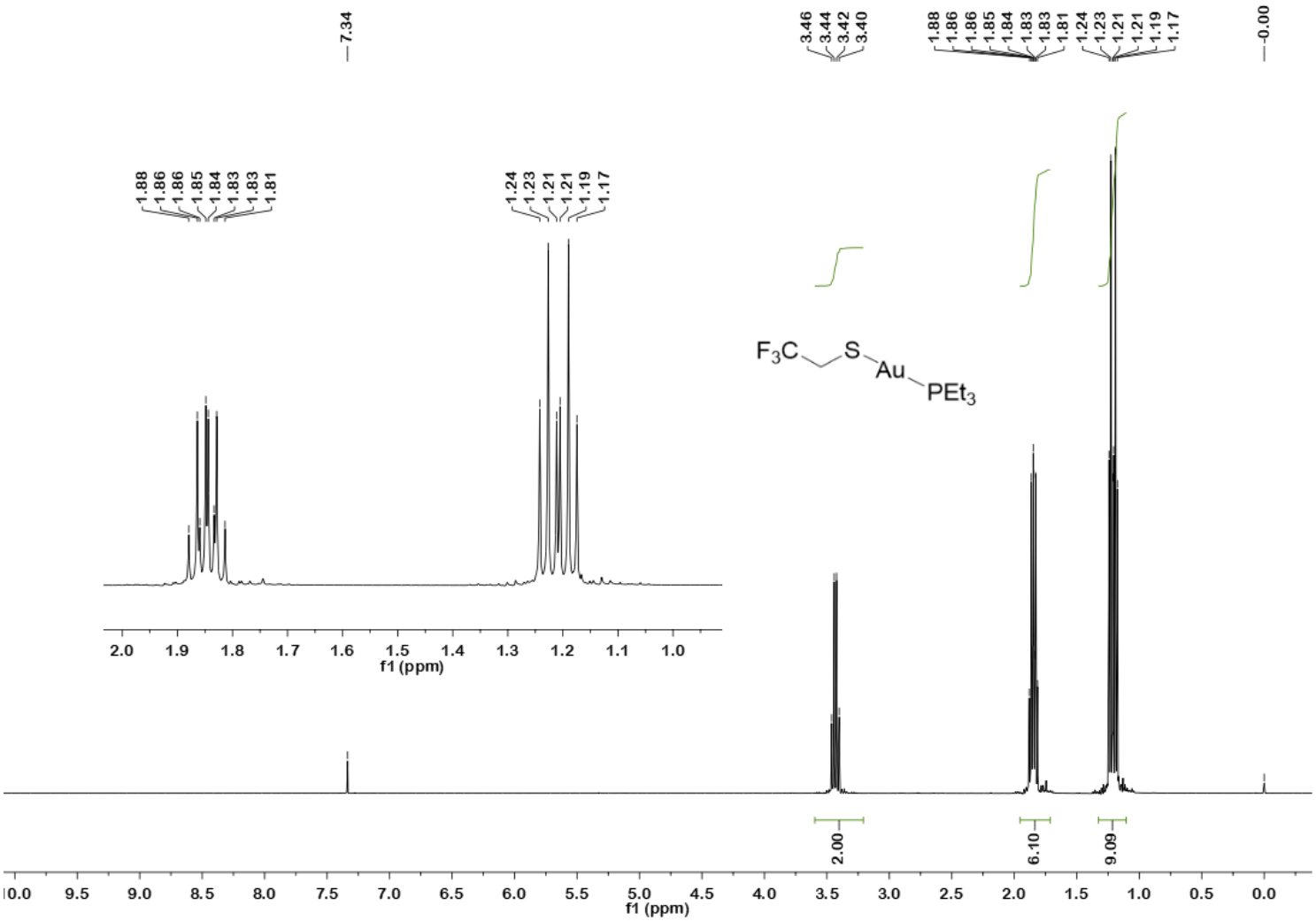


Figure S84. ^{1}H NMR spectrum of compound **23** in $CDCl_3$.

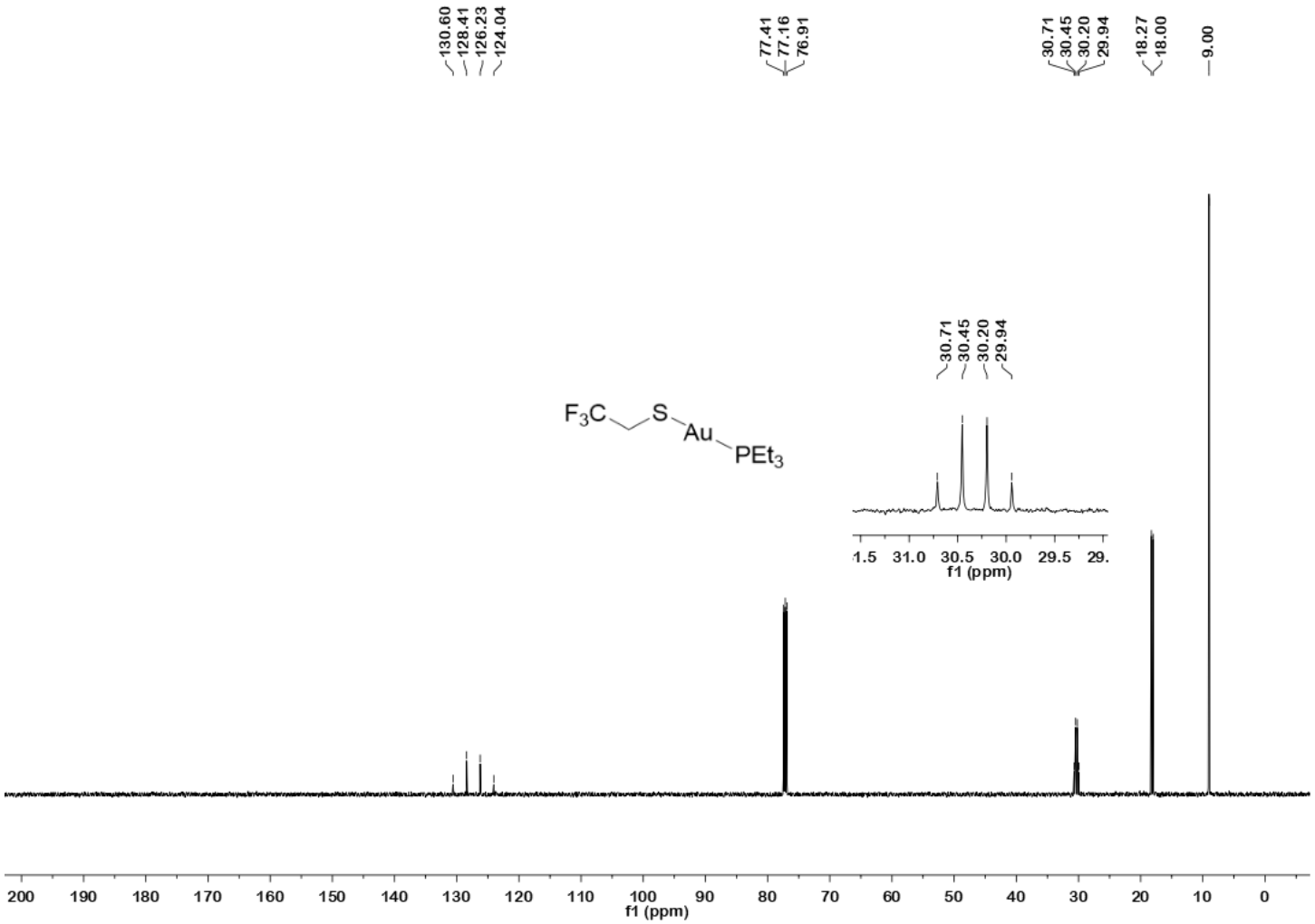


Figure S85. ^{13}C NMR spectrum of compound **23** in $CDCl_3$.

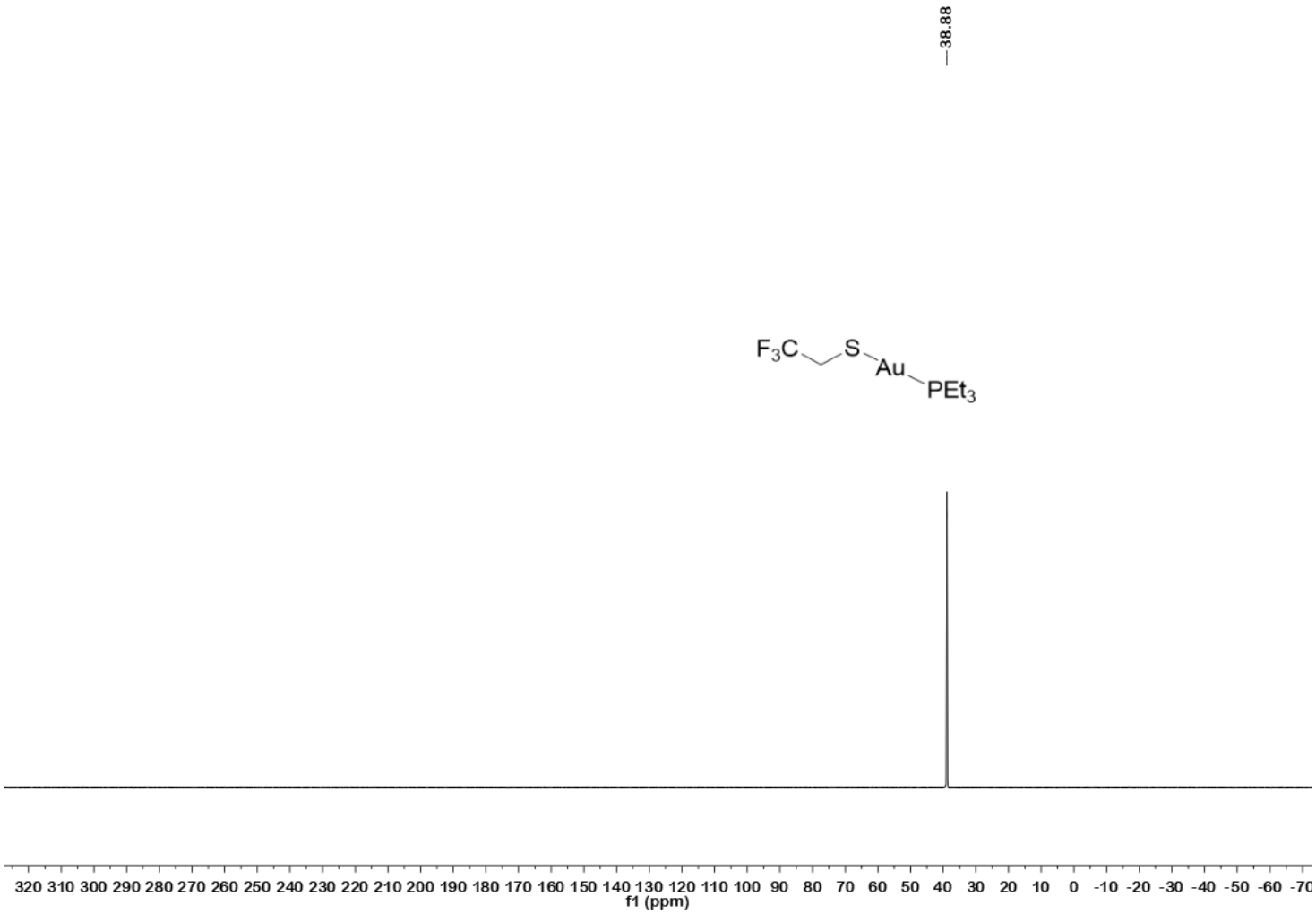


Figure S86. ^{31}P NMR spectrum of compound **23** in $CDCl_3$.

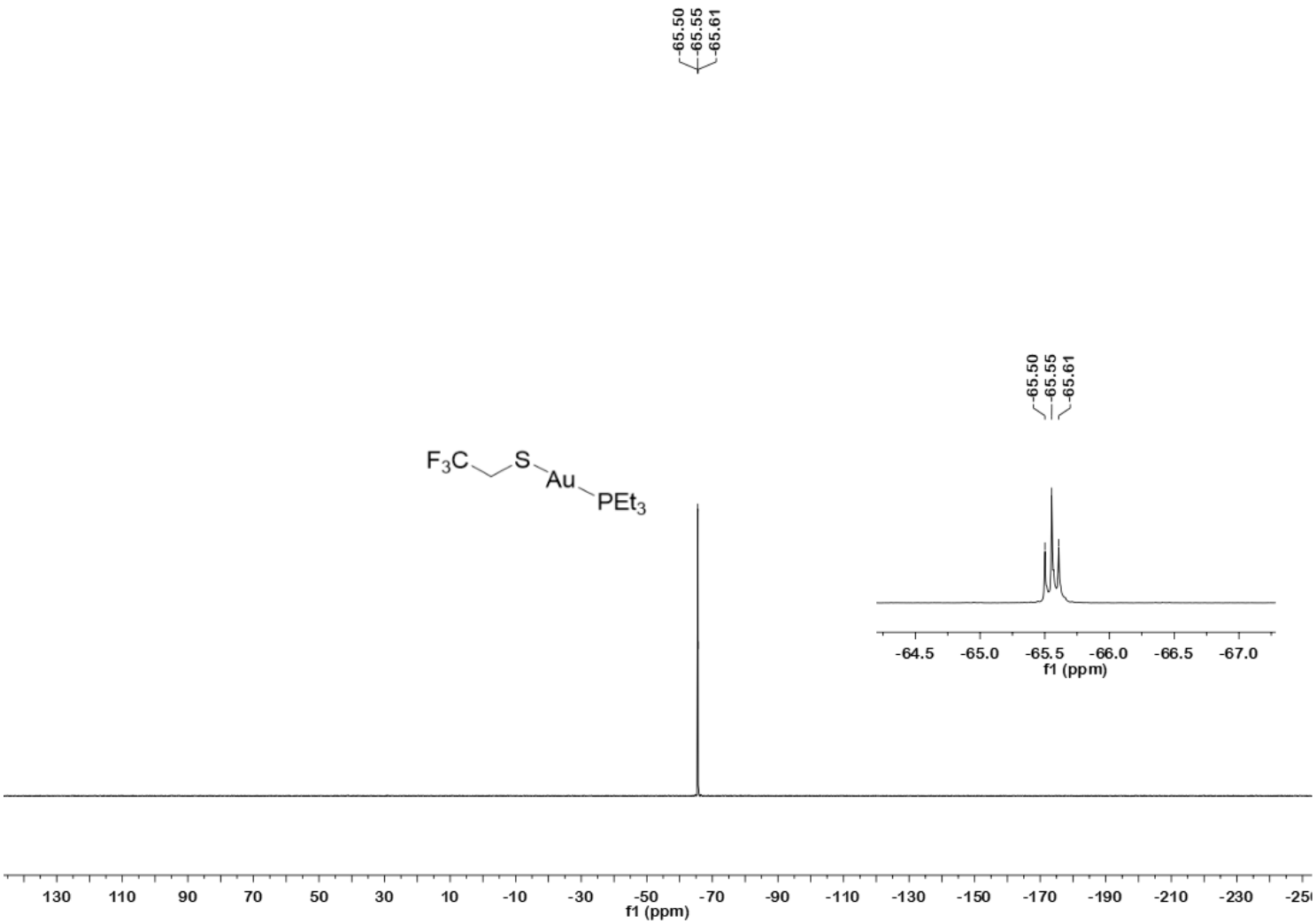


Figure S87. ^{19}F NMR spectrum of compound **23** in $CDCl_3$.

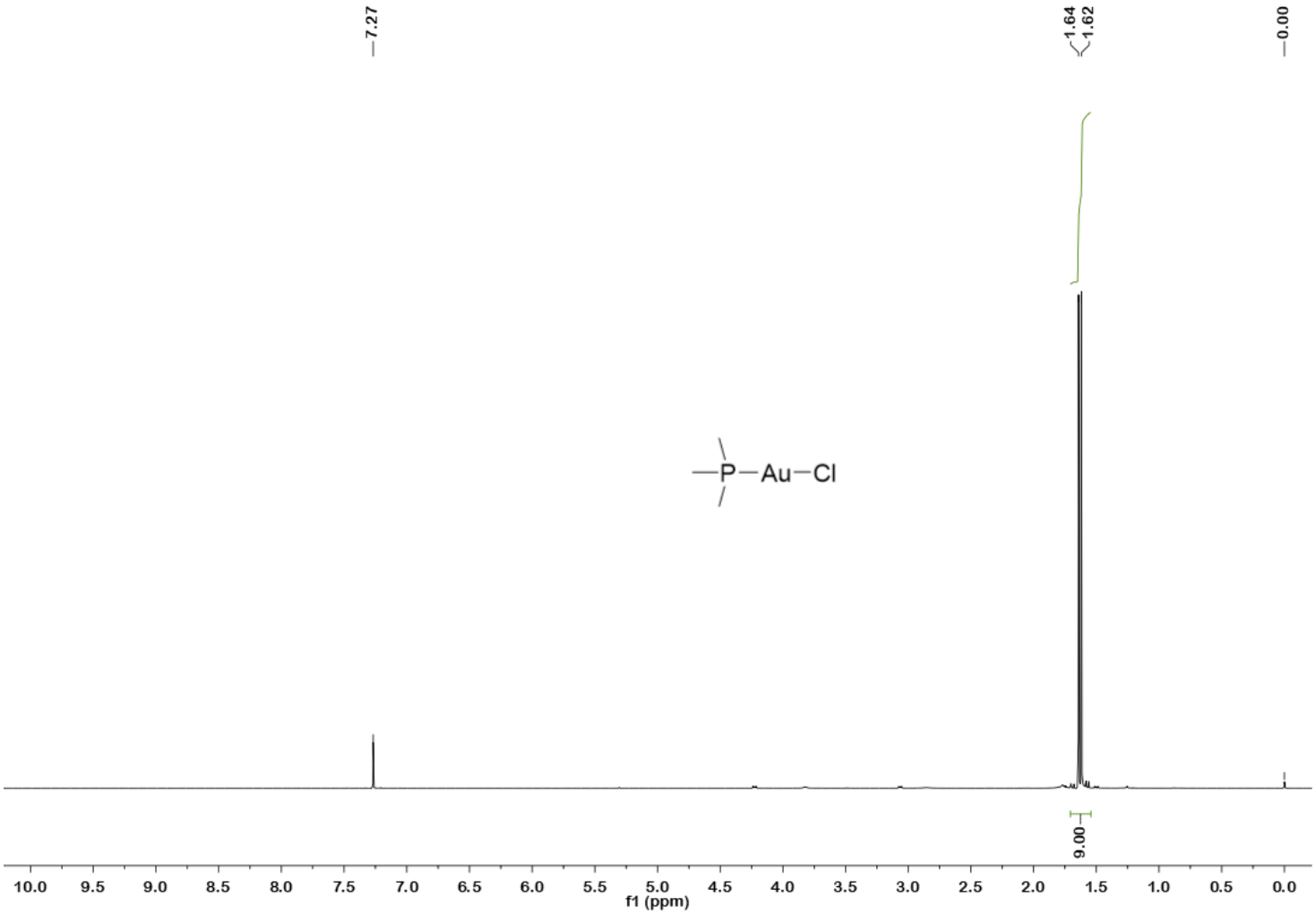


Figure S88. ^{1}H NMR spectrum of compound **24** in $CDCl_3$.

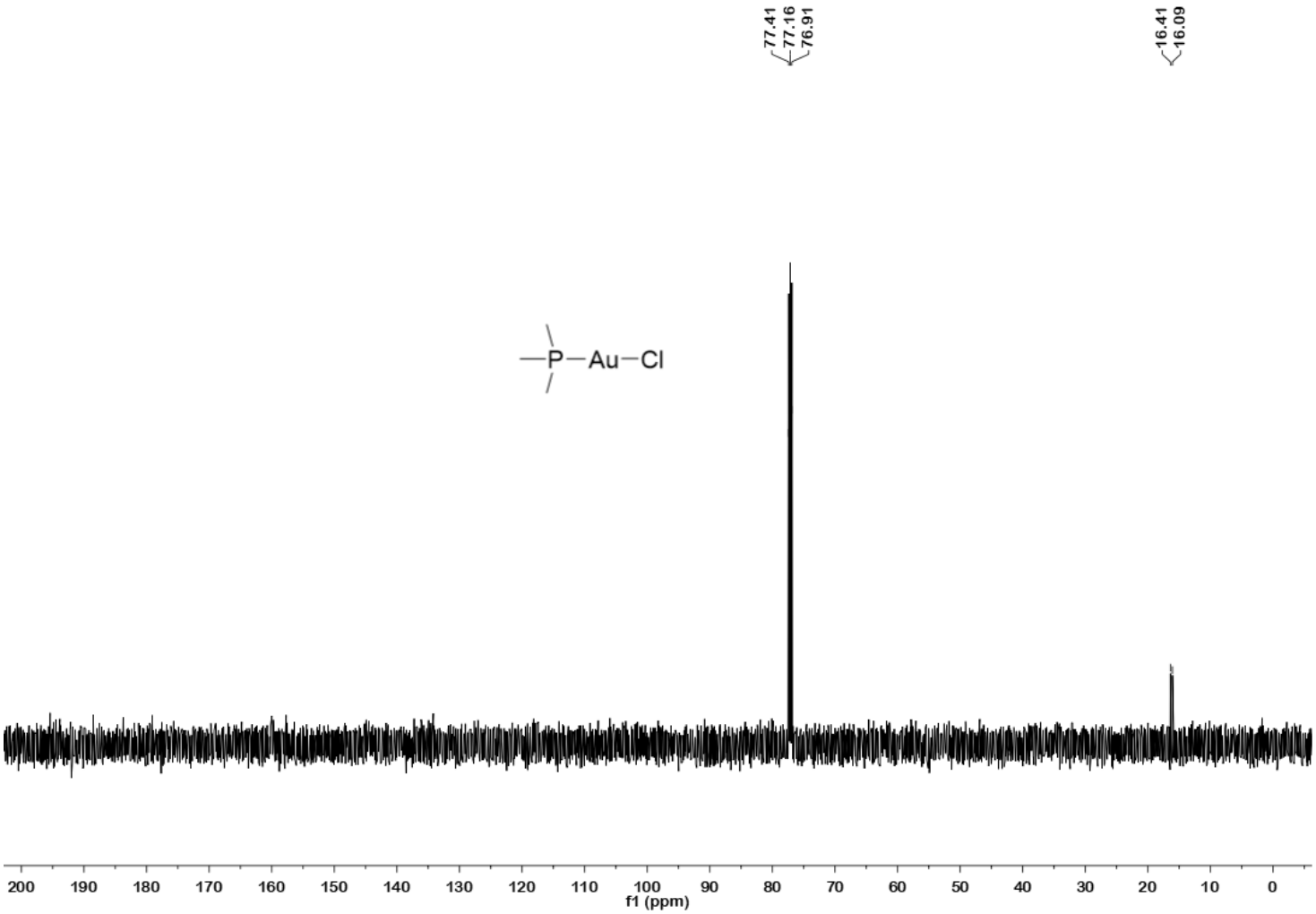


Figure S89. ^{13}C NMR spectrum of compound **24** in $CDCl_3$.

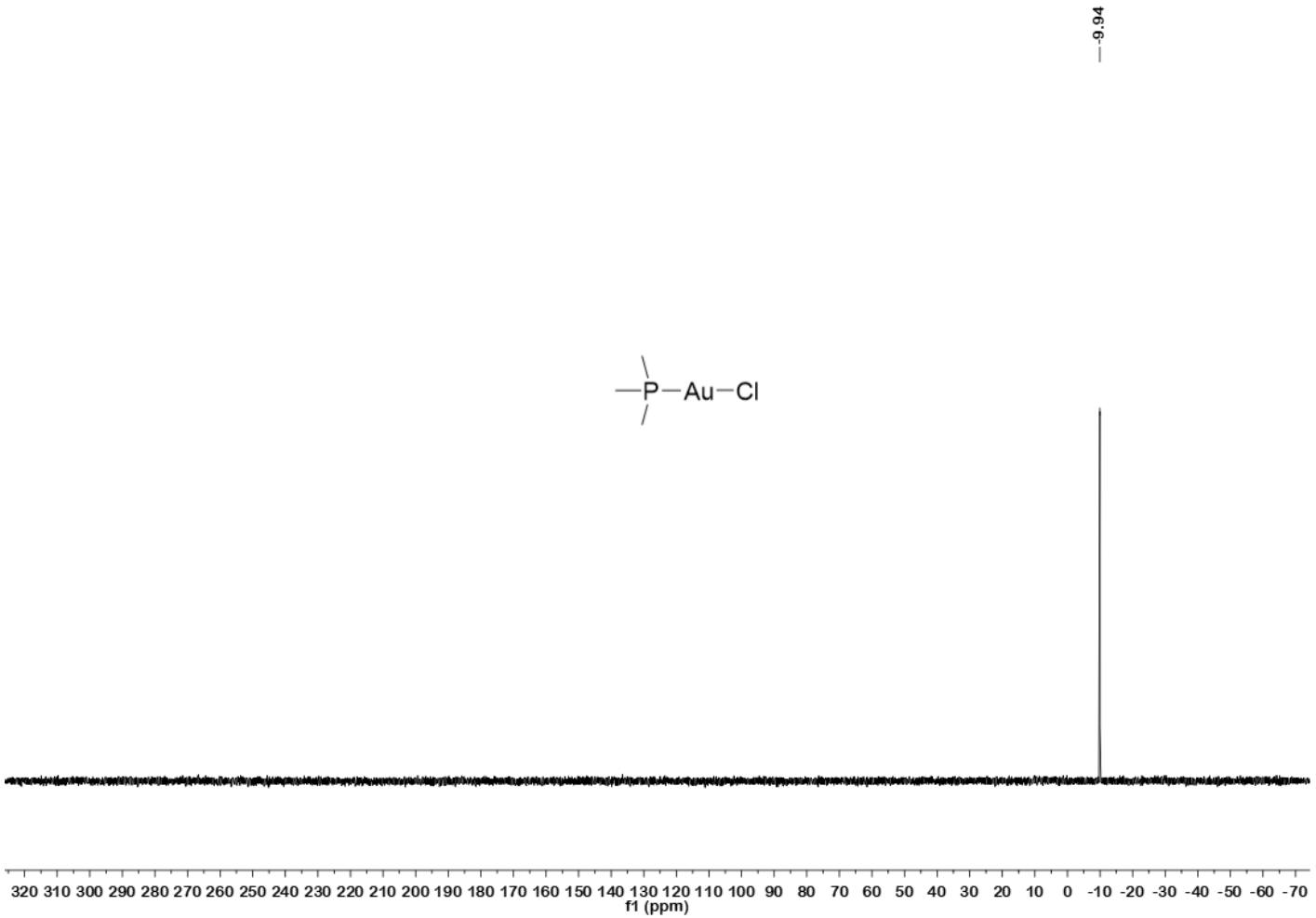


Figure S90. ^{31}P NMR spectrum of compound **24** in $CDCl_3$.

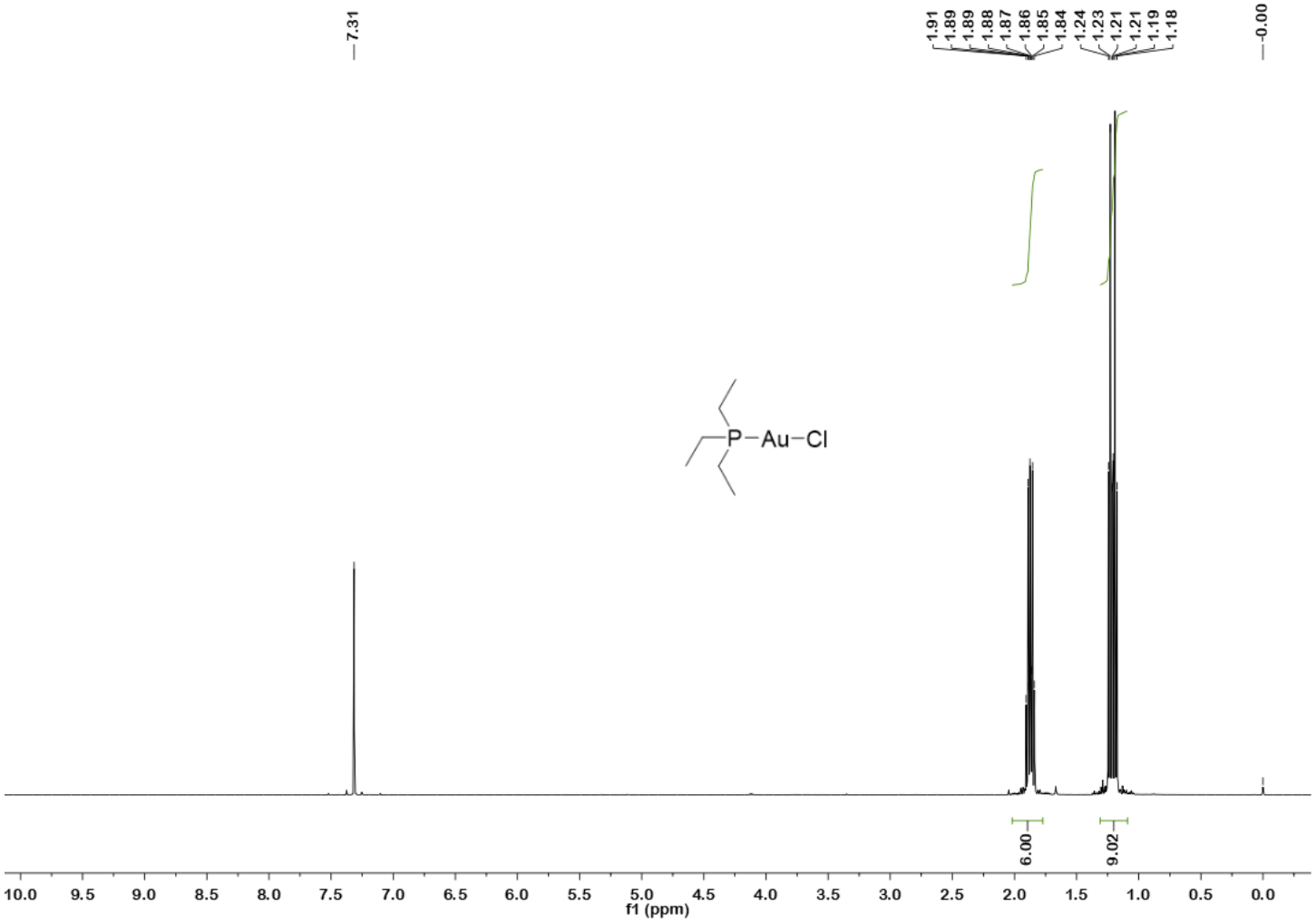


Figure S91. ^{1}H NMR spectrum of compound **25** in $CDCl_3$.

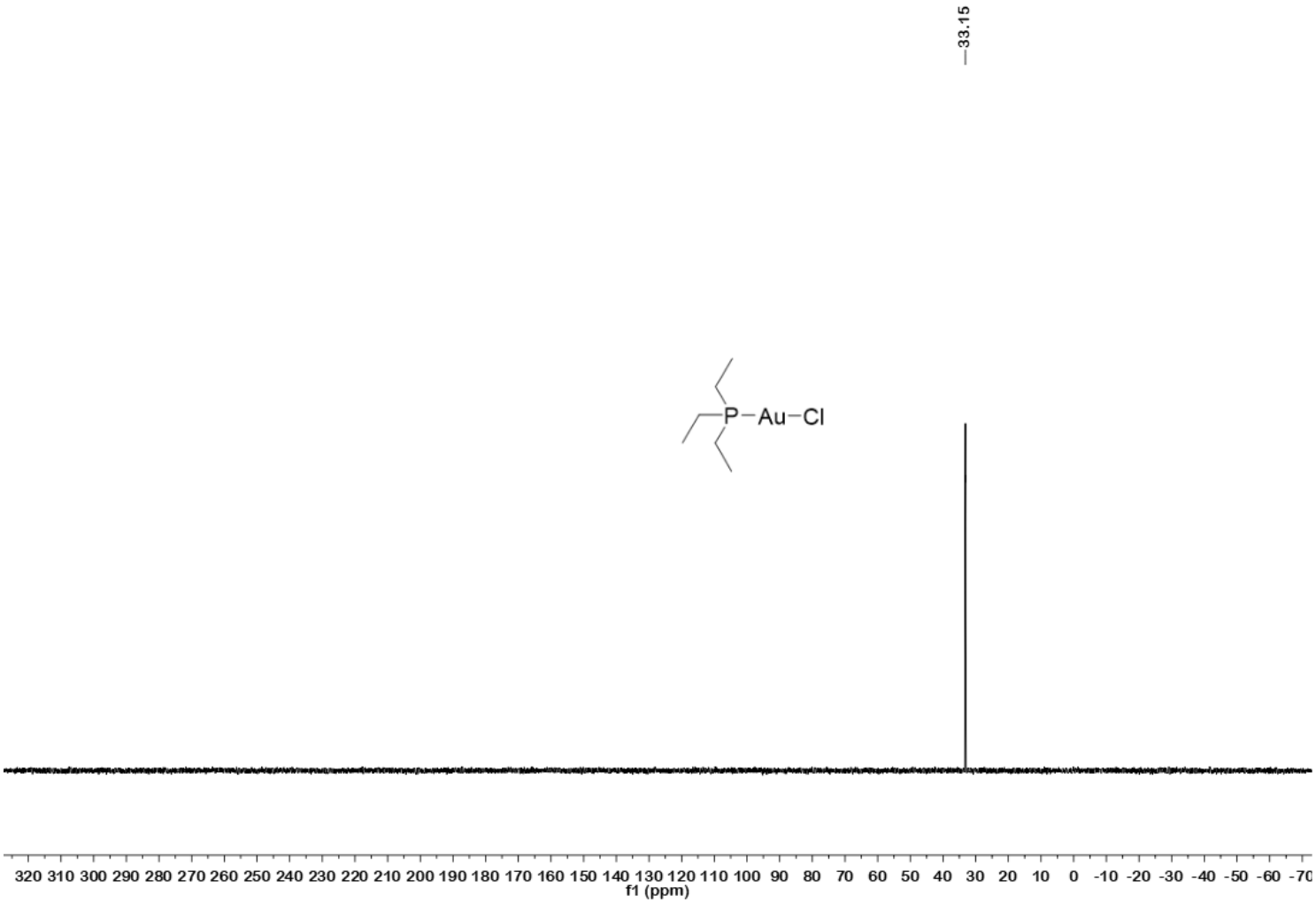


Figure S92. ^{31}P NMR spectrum of compound **25** in $CDCl_3$.

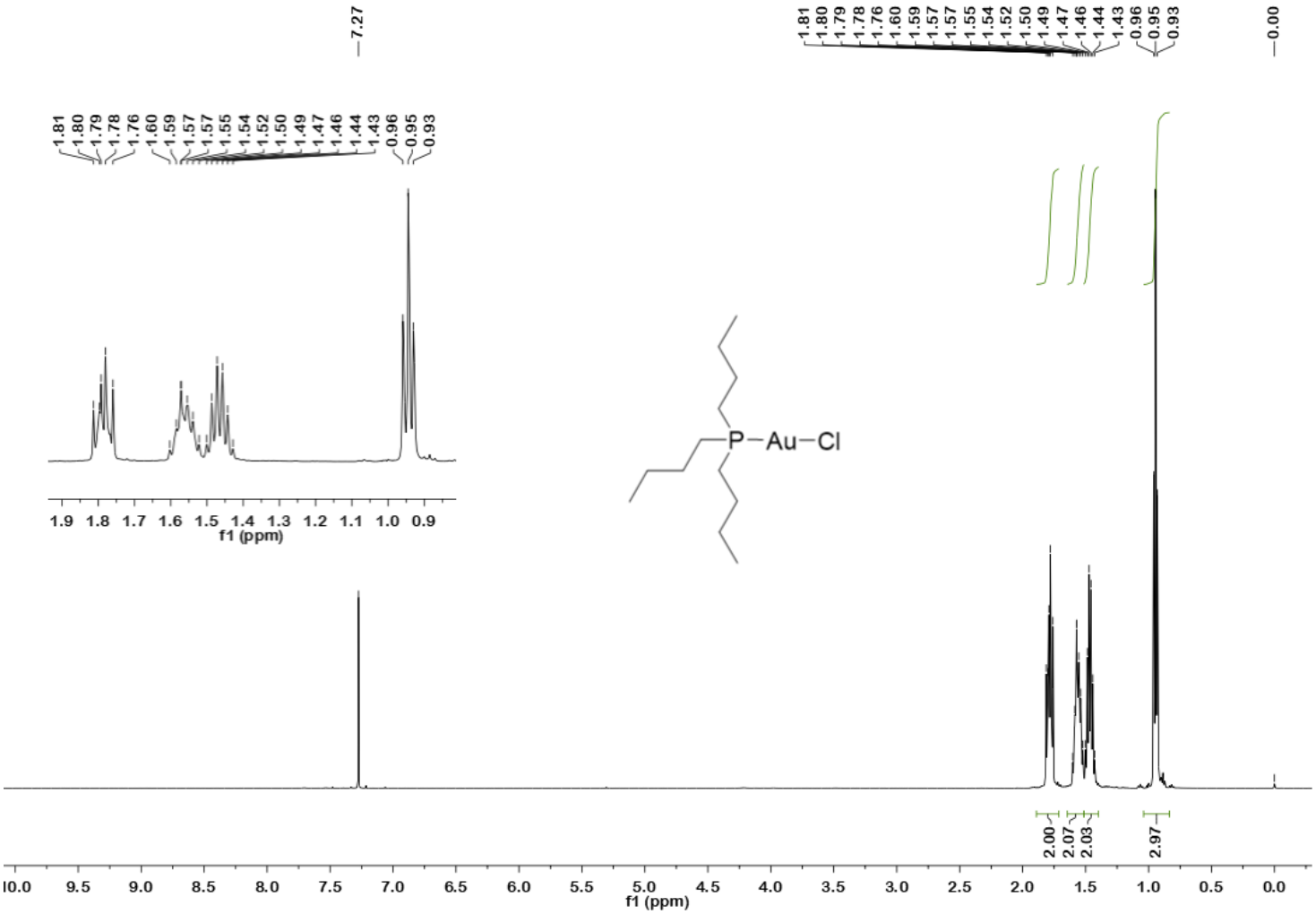


Figure S93. ^{1}H NMR spectrum of compound **26** in $CDCl_3$.

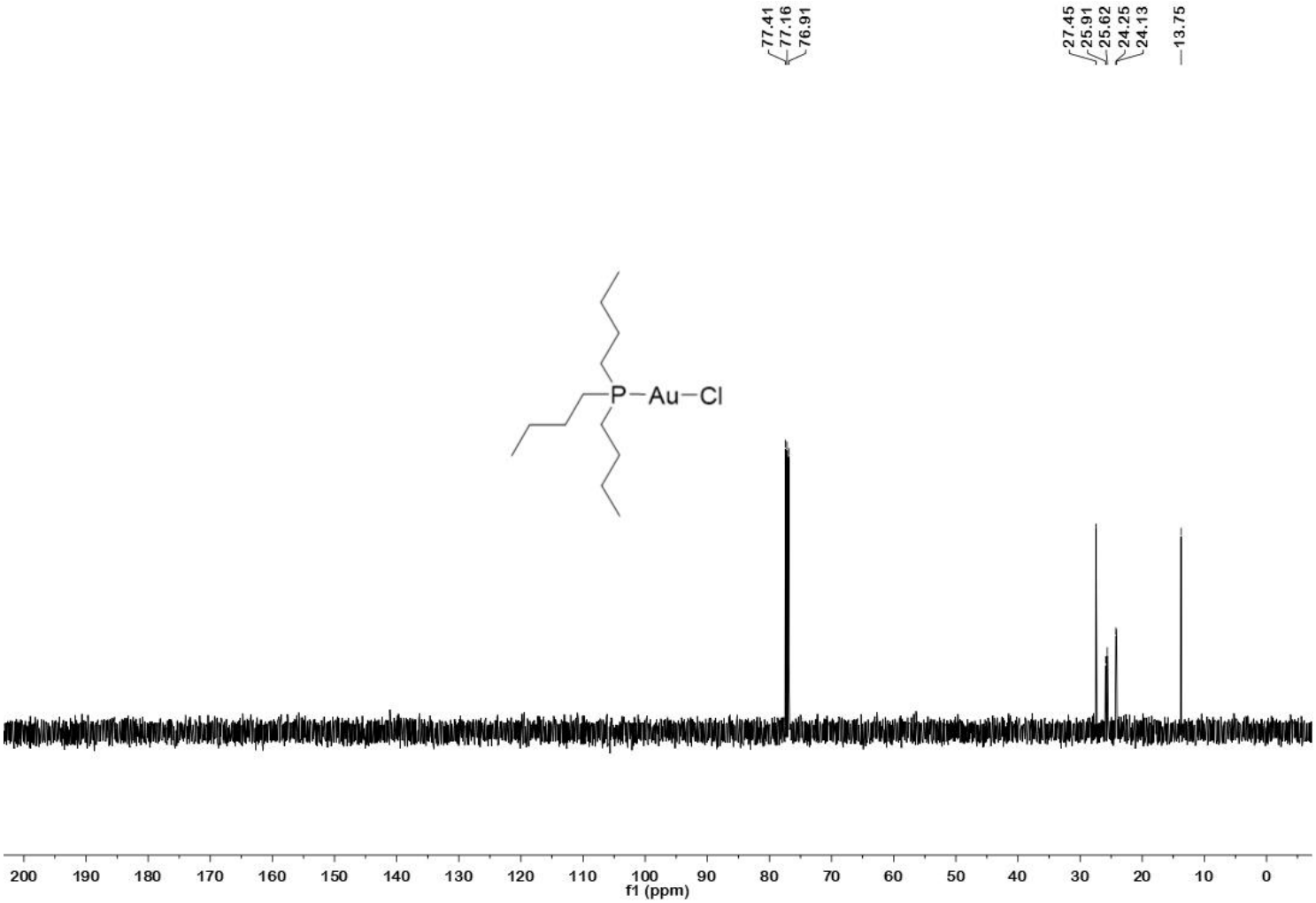


Figure S94. ^{13}C NMR spectrum of compound **26** in $CDCl_3$.

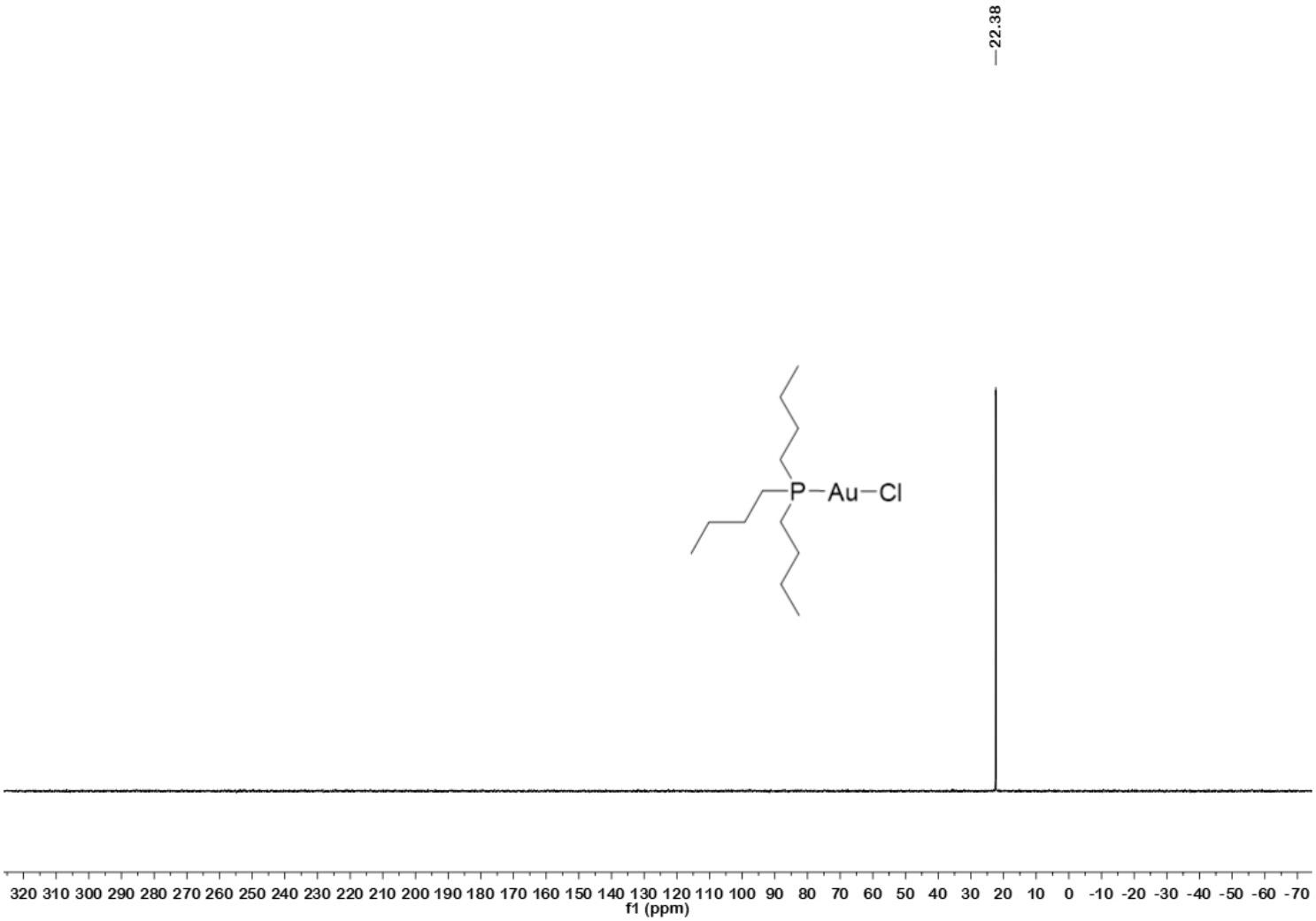


Figure S95. ^{31}P NMR spectrum of compound **26** in $CDCl_3$.

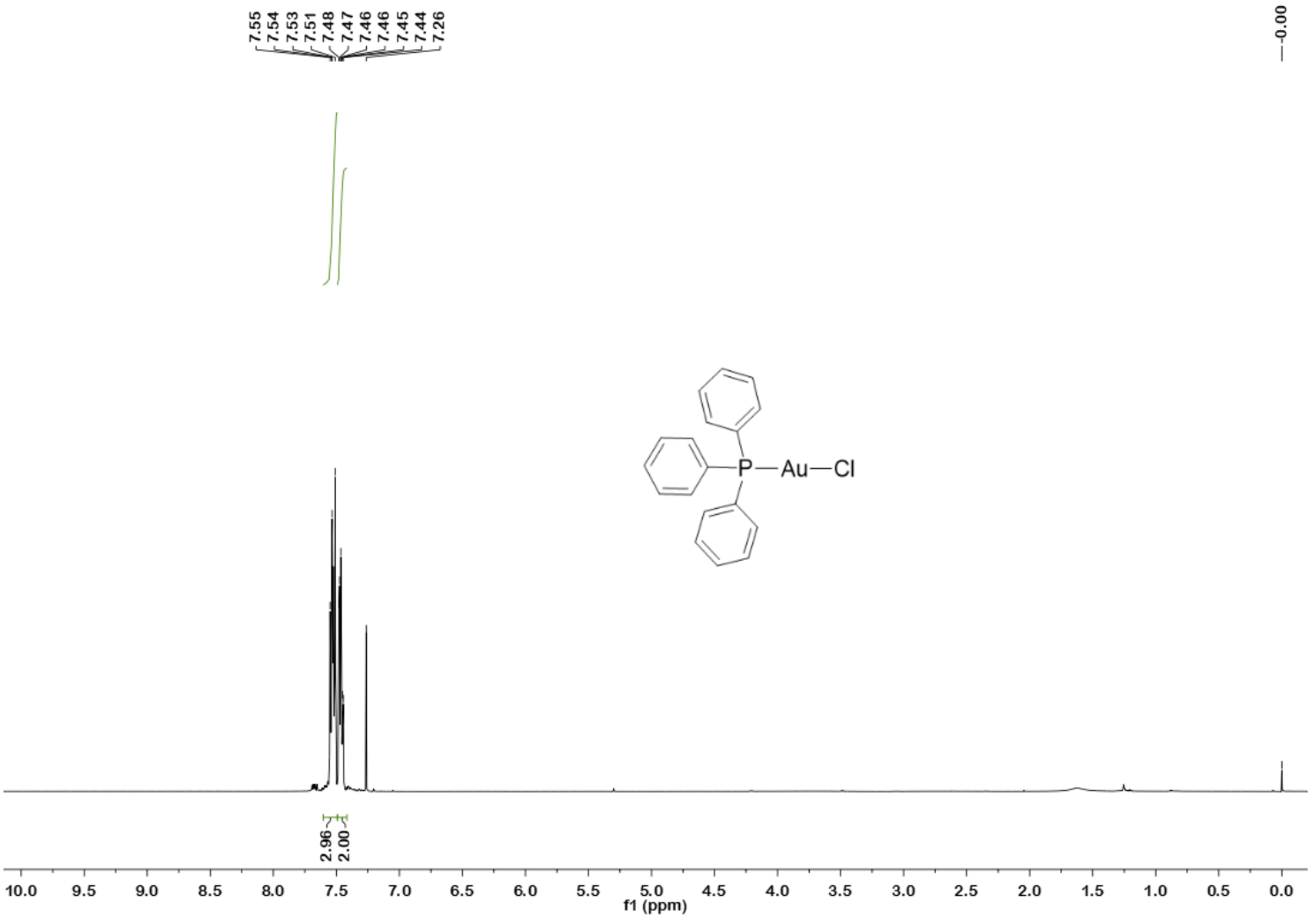


Figure S96. ^{1}H NMR spectrum of compound **27** in $CDCl_3$.

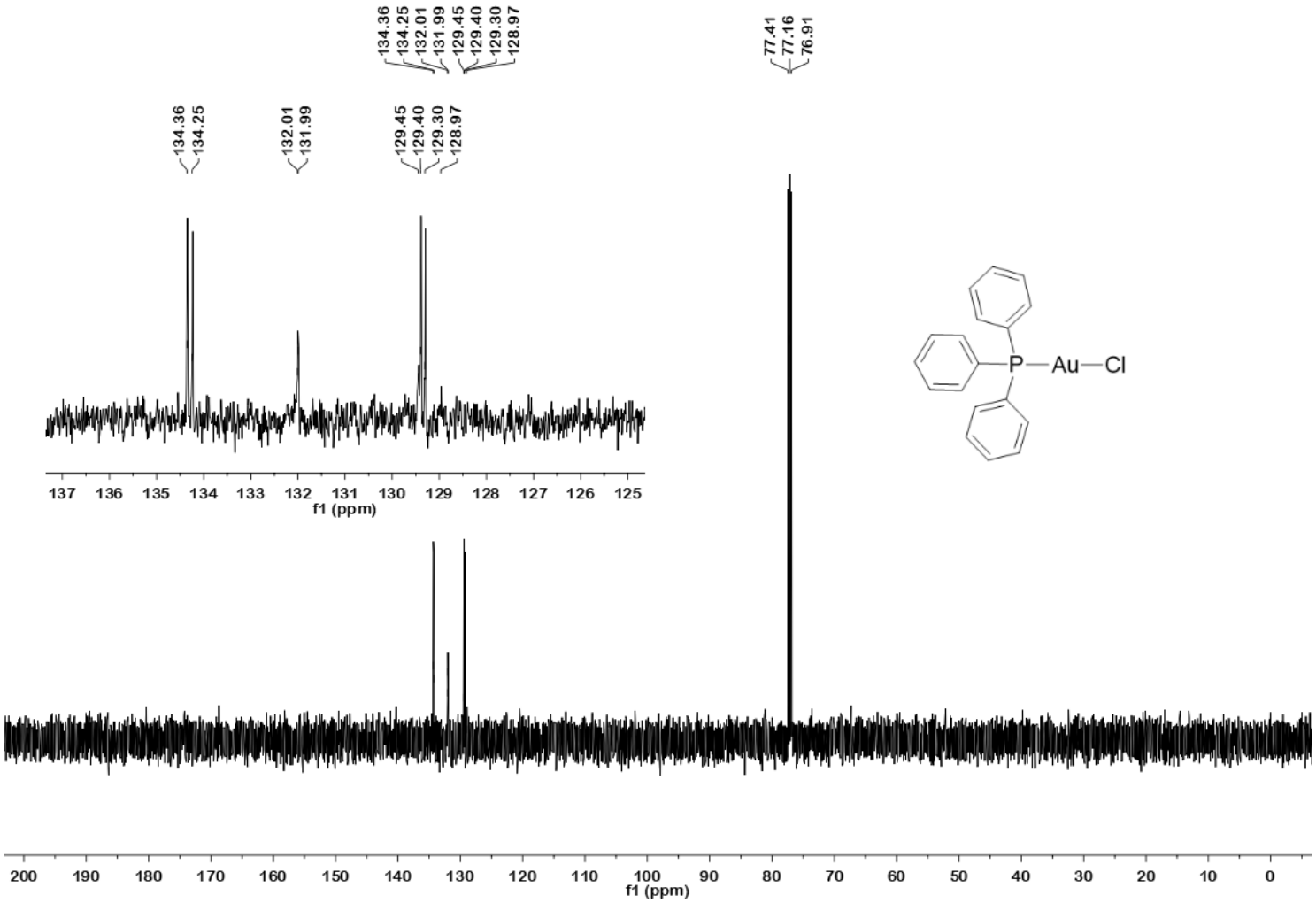


Figure S97. ^{13}C NMR spectrum of compound **27** in $CDCl_3$.

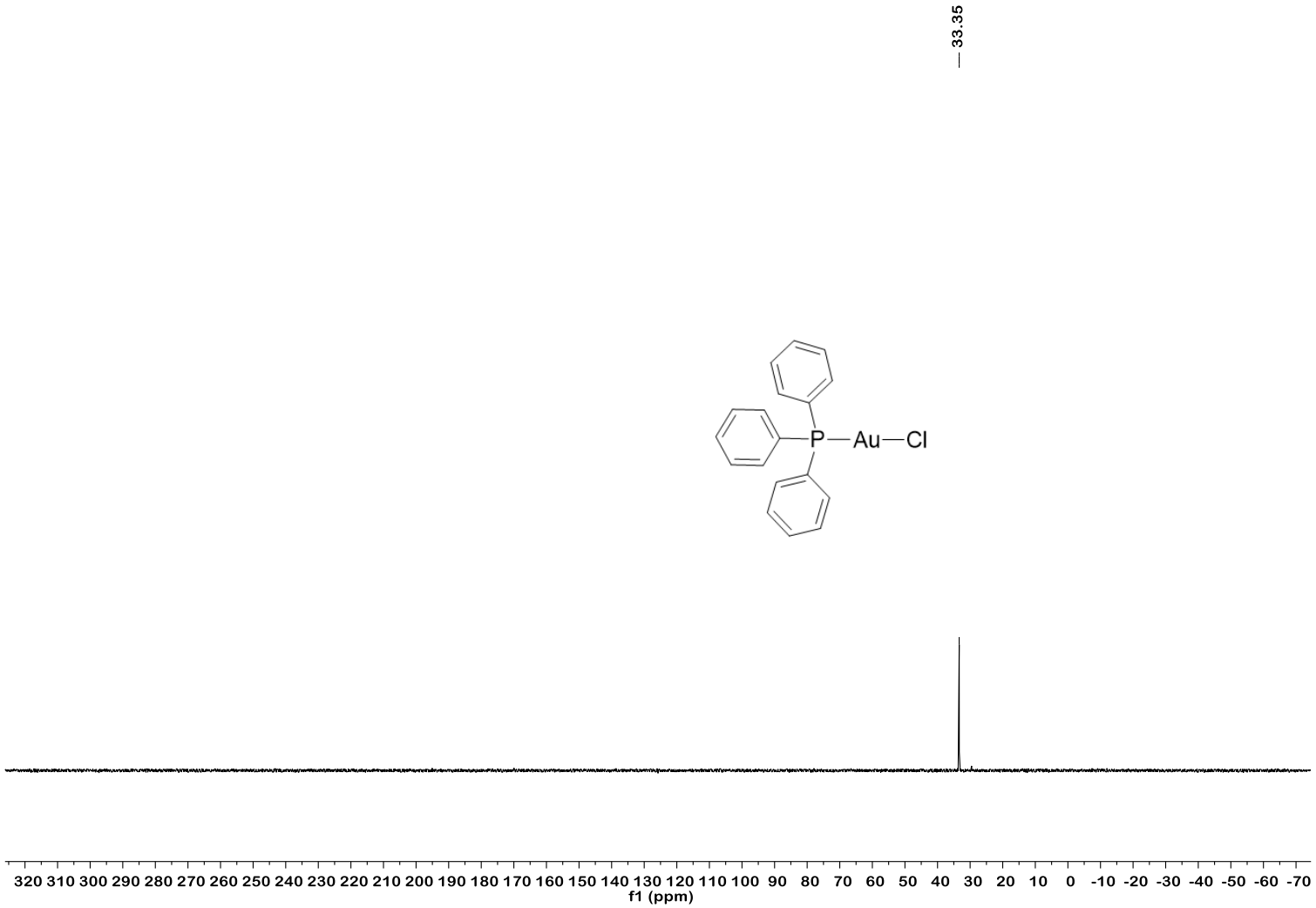


Figure S98. ^{31}P NMR spectrum of compound **27** in $CDCl_3$.

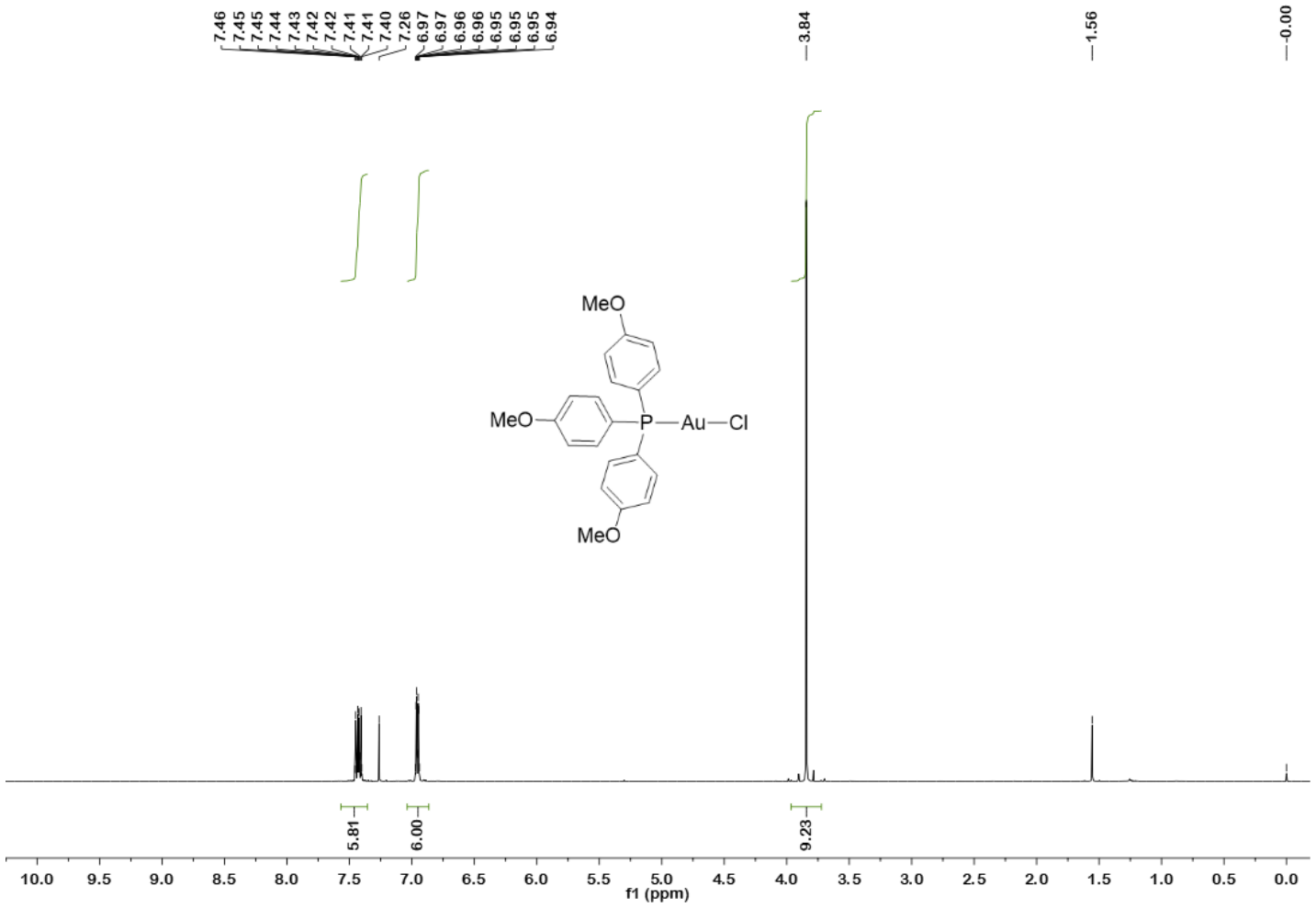


Figure S99. ^{1}H NMR spectrum of compound **28** in $CDCl_3$.

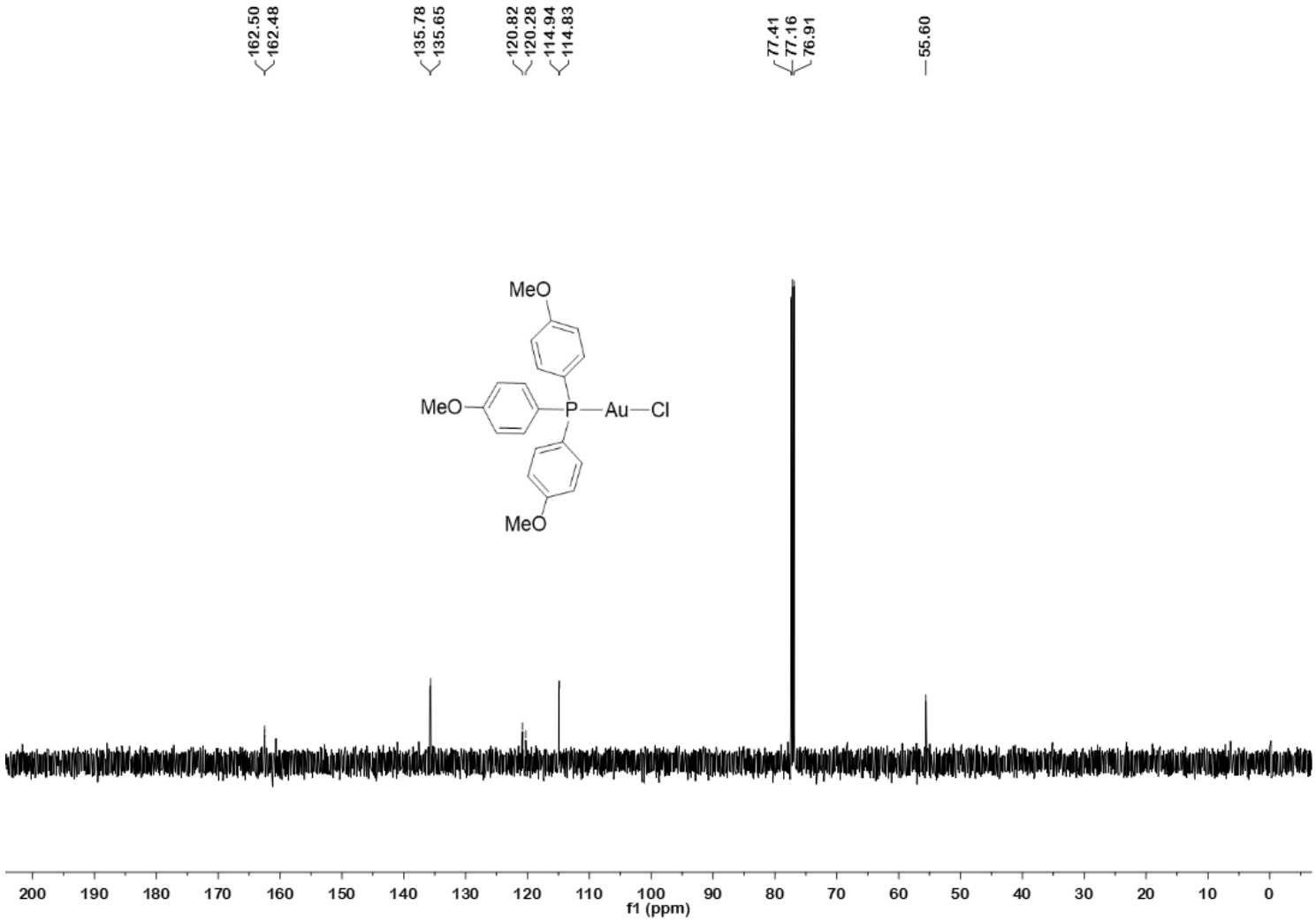


Figure S100. ^{13}C NMR spectrum of compound **28** in $CDCl_3$.

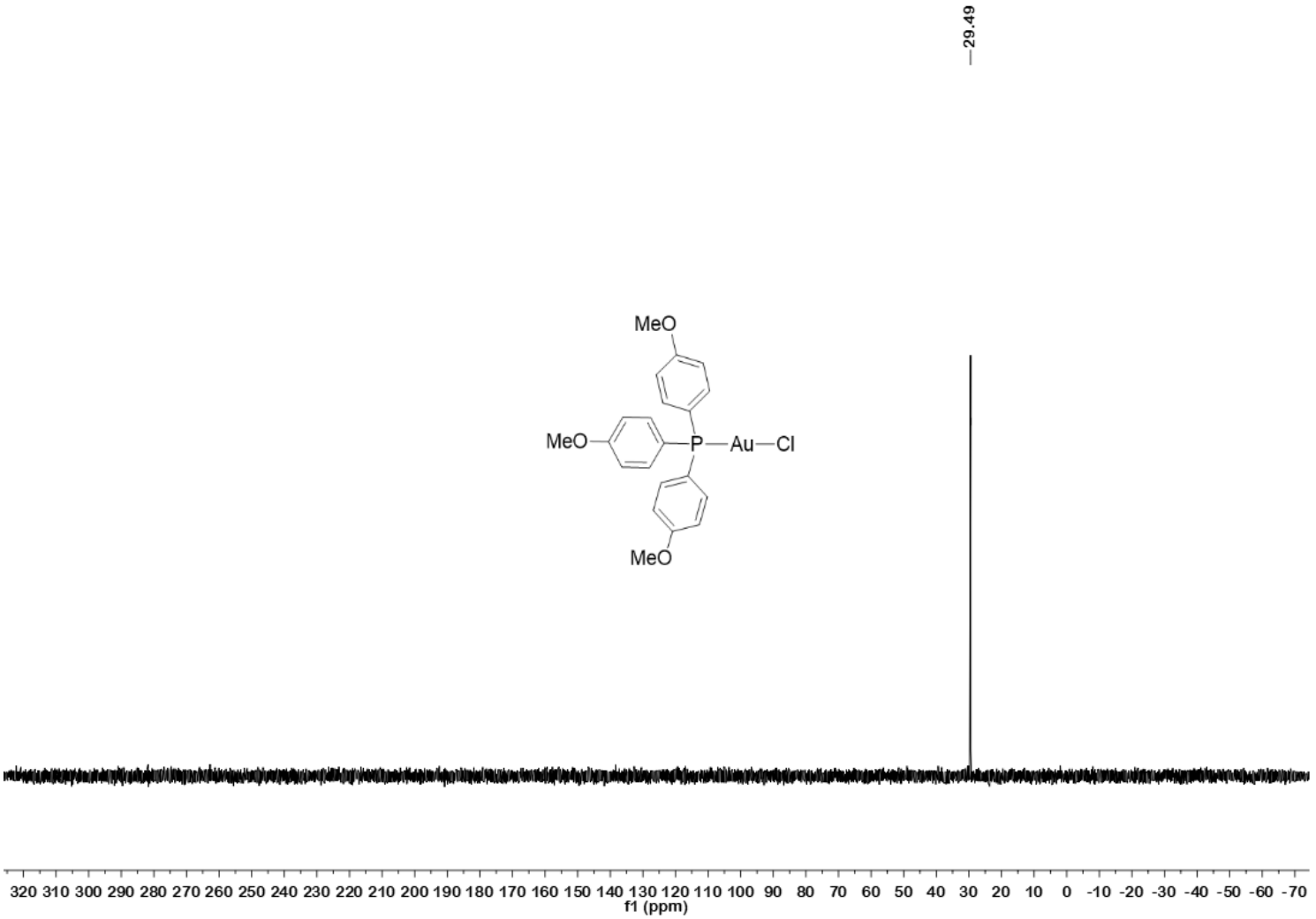


Figure S101. ^{31}P NMR spectrum of compound **28** in $CDCl_3$.

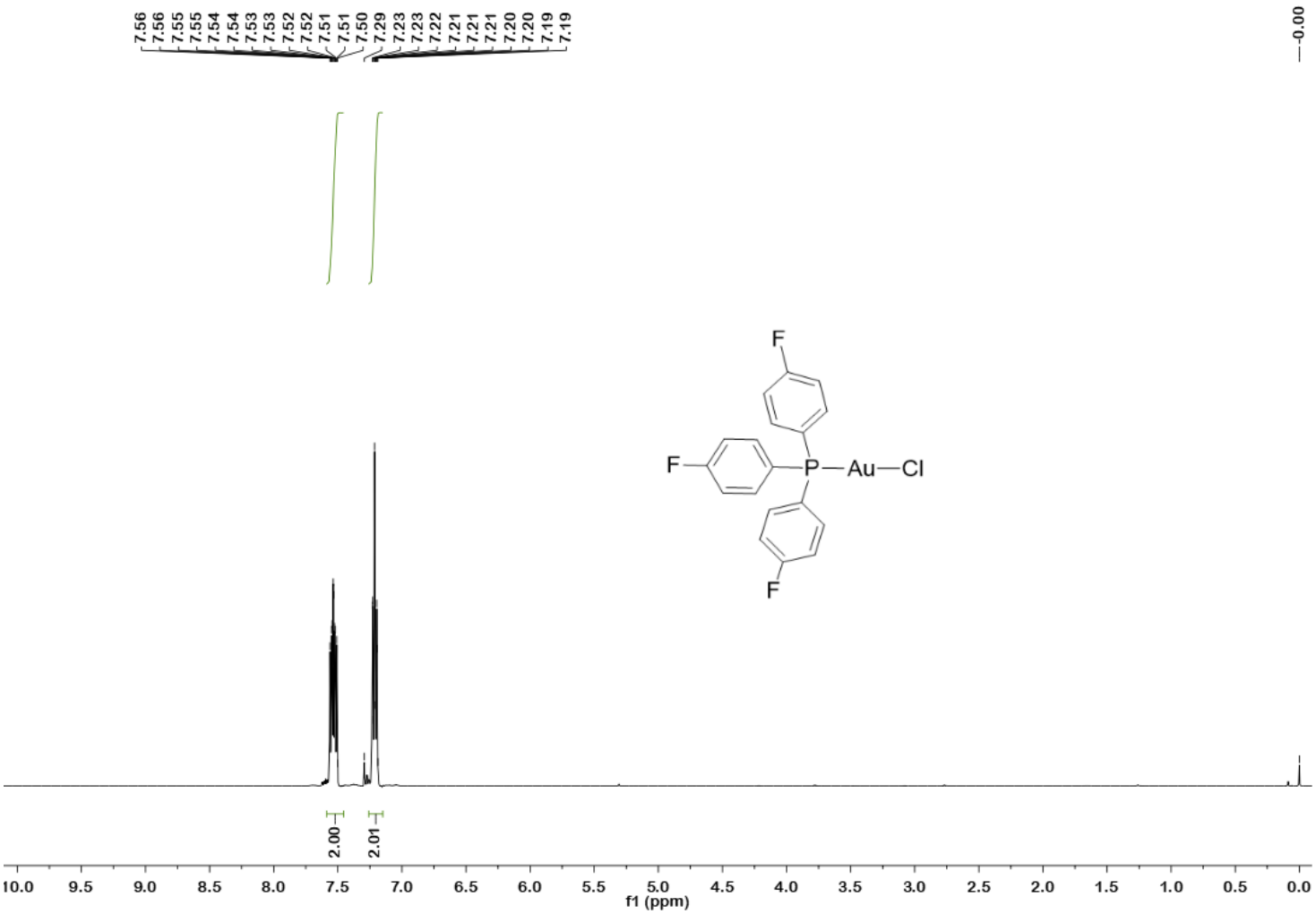


Figure S102. ^{1}H NMR spectrum of compound **29** in $CDCl_3$.

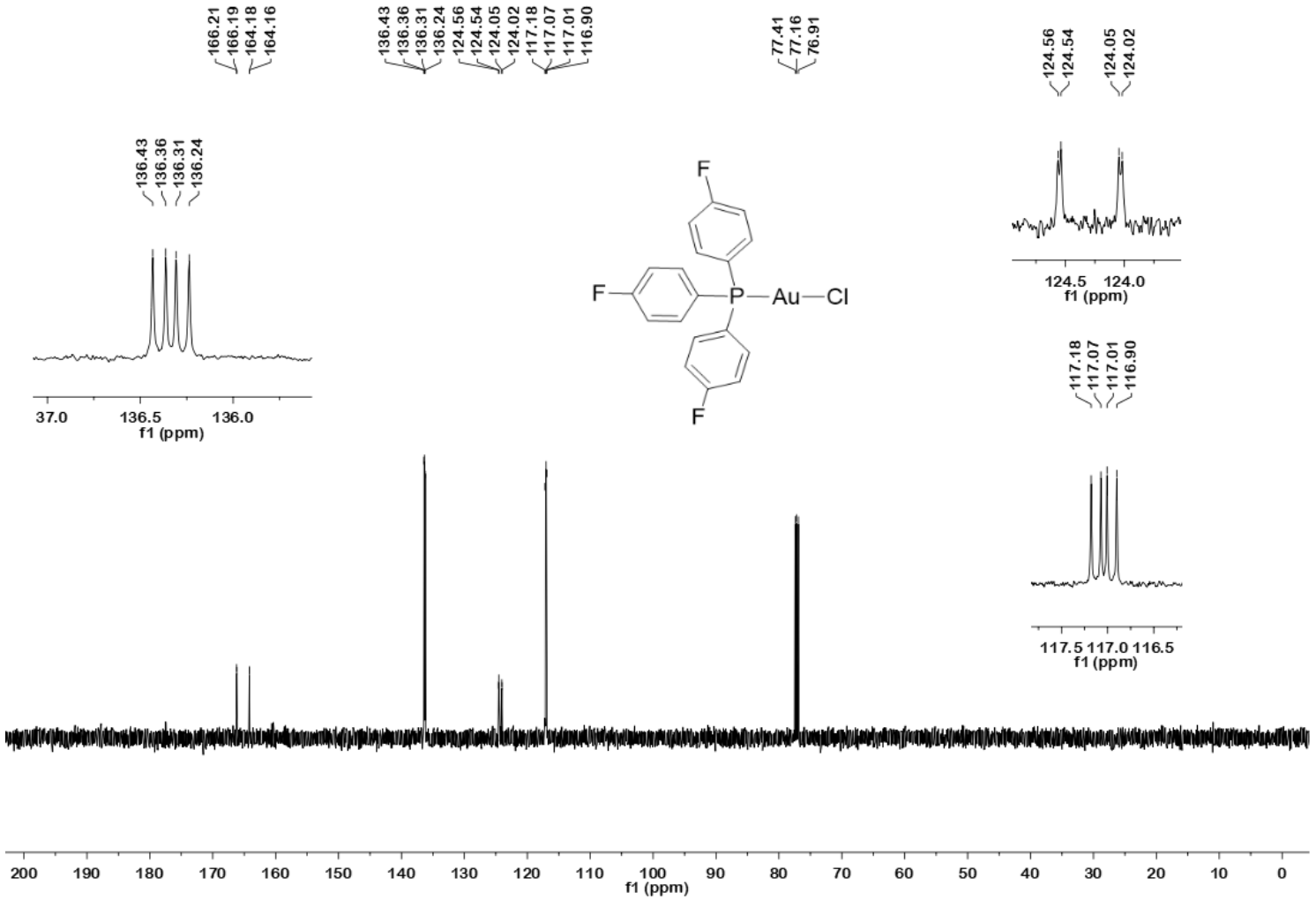


Figure S103. ^{13}C NMR spectrum of compound **29** in $CDCl_3$.

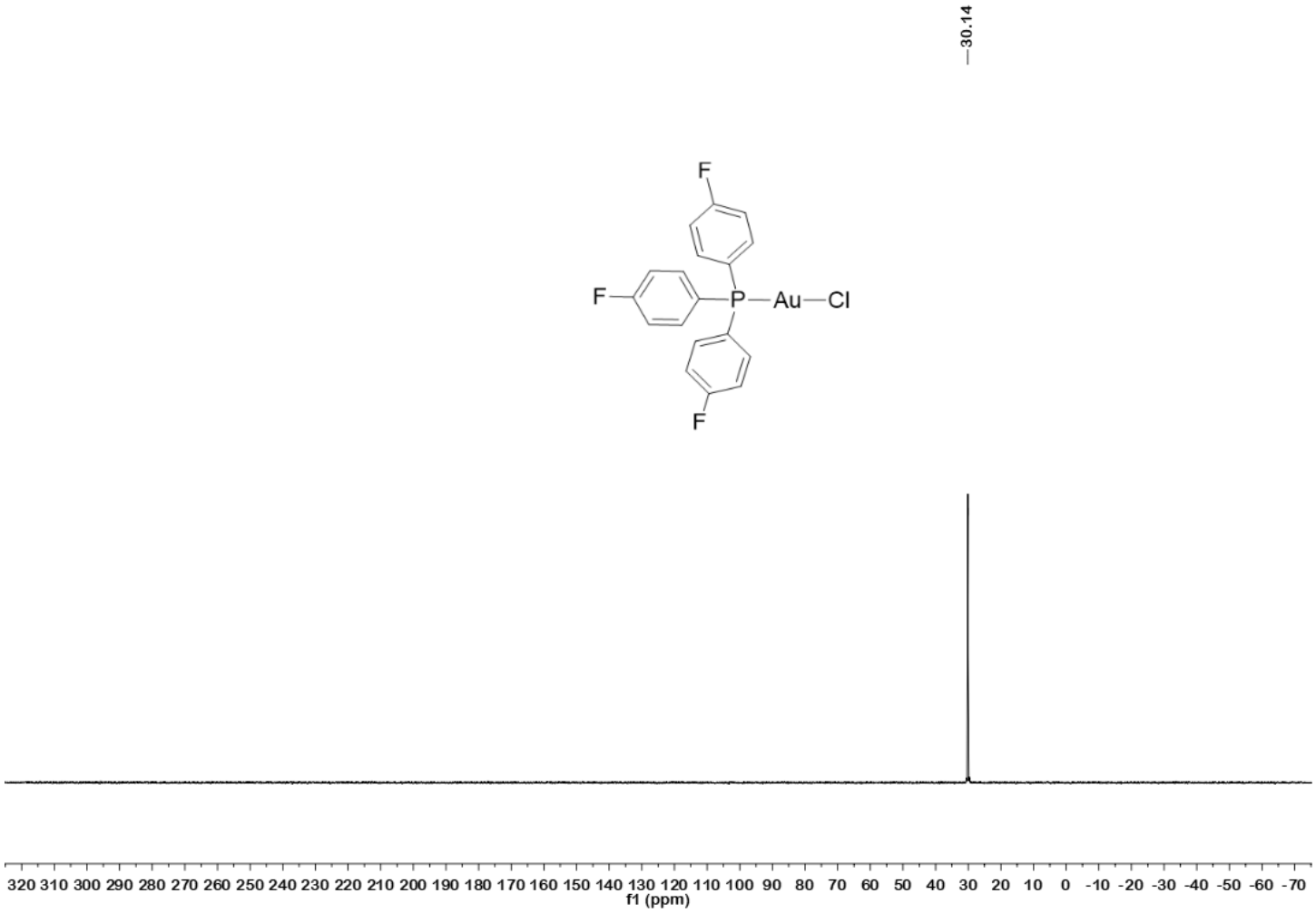


Figure S104. ^{31}P NMR spectrum of compound **29** in $CDCl_3$.

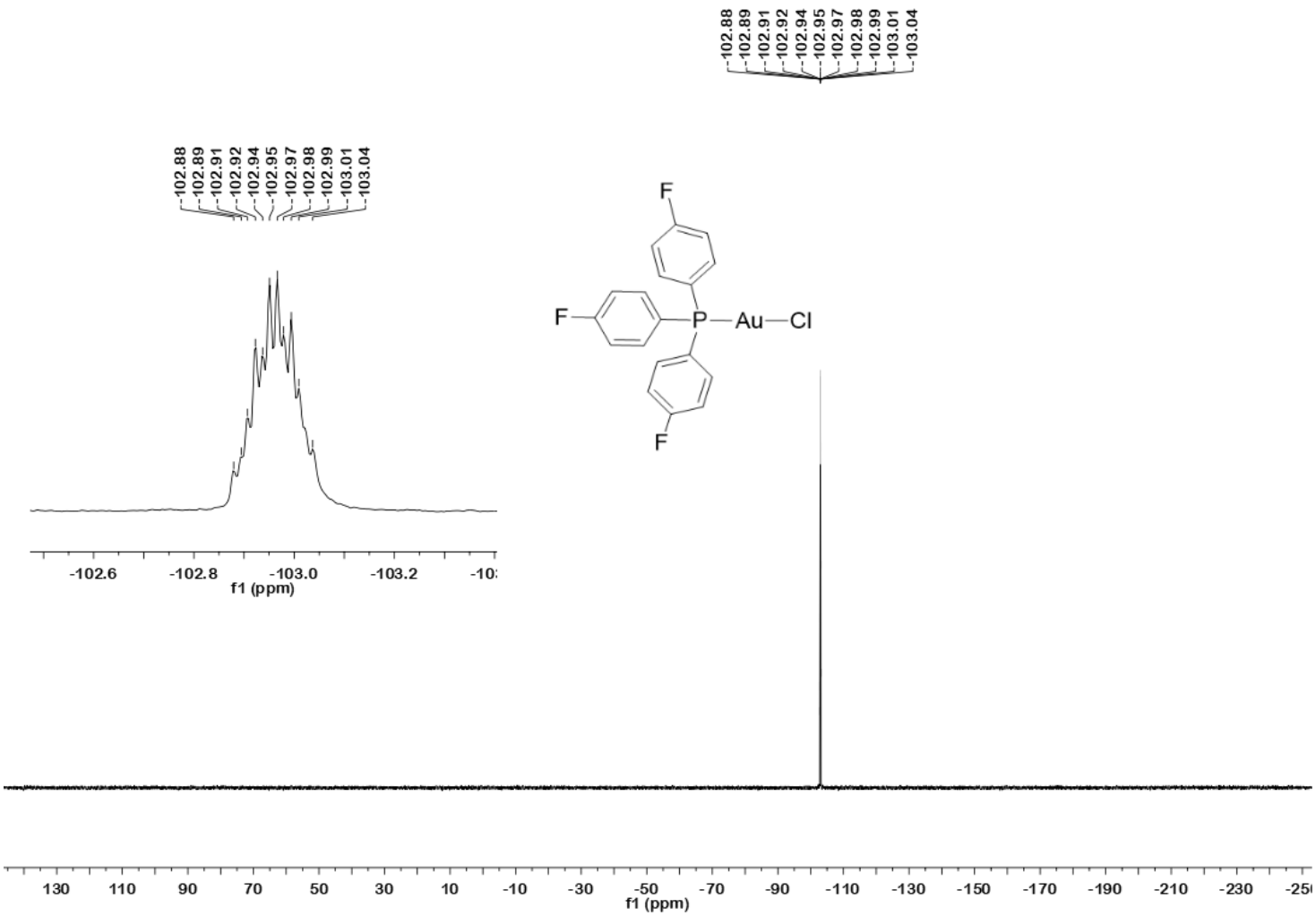


Figure S105. ^{19}F NMR spectrum of compound **29** in $CDCl_3$.

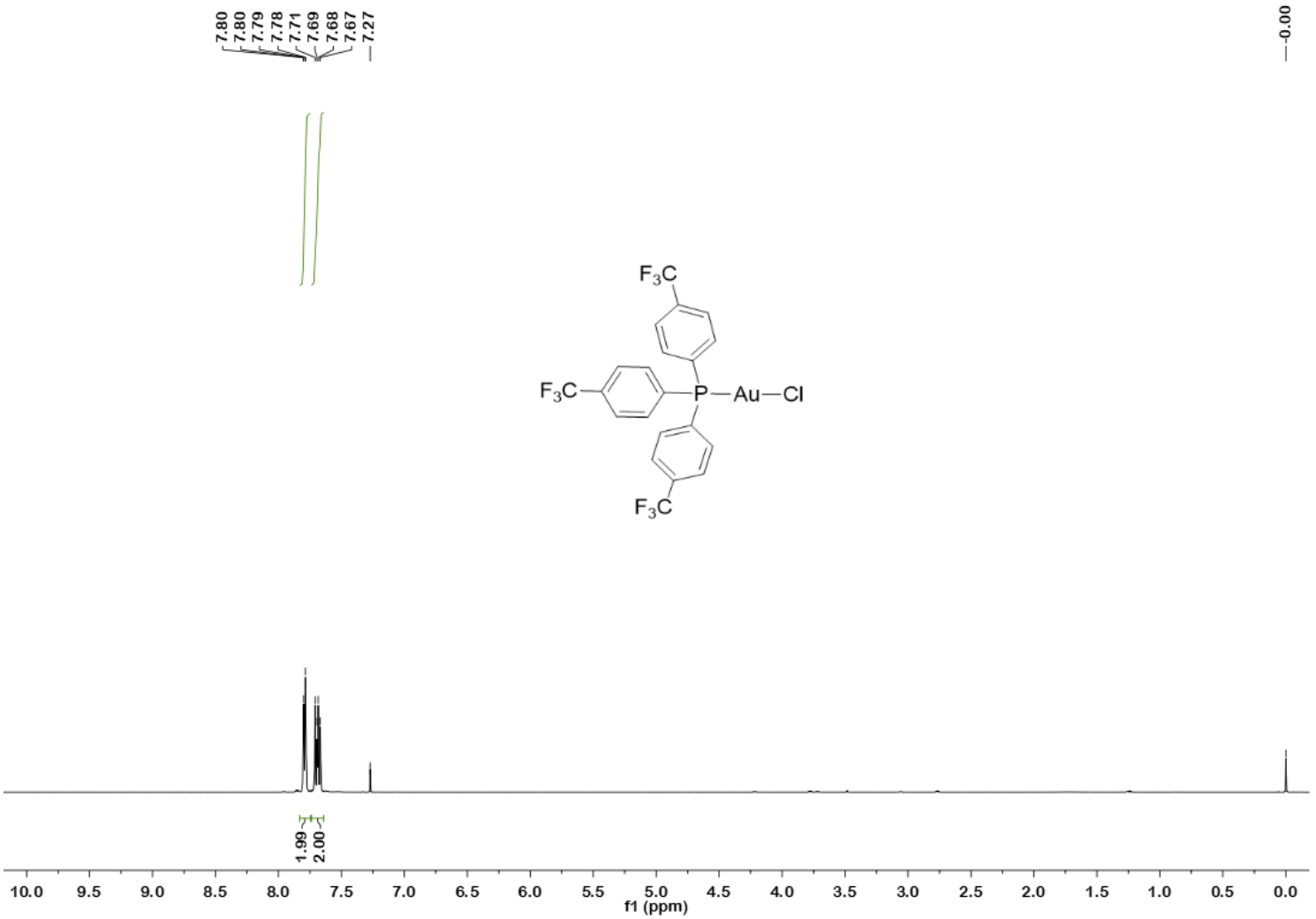


Figure S106. ^{1}H NMR spectrum of compound **30** in $CDCl_3$.

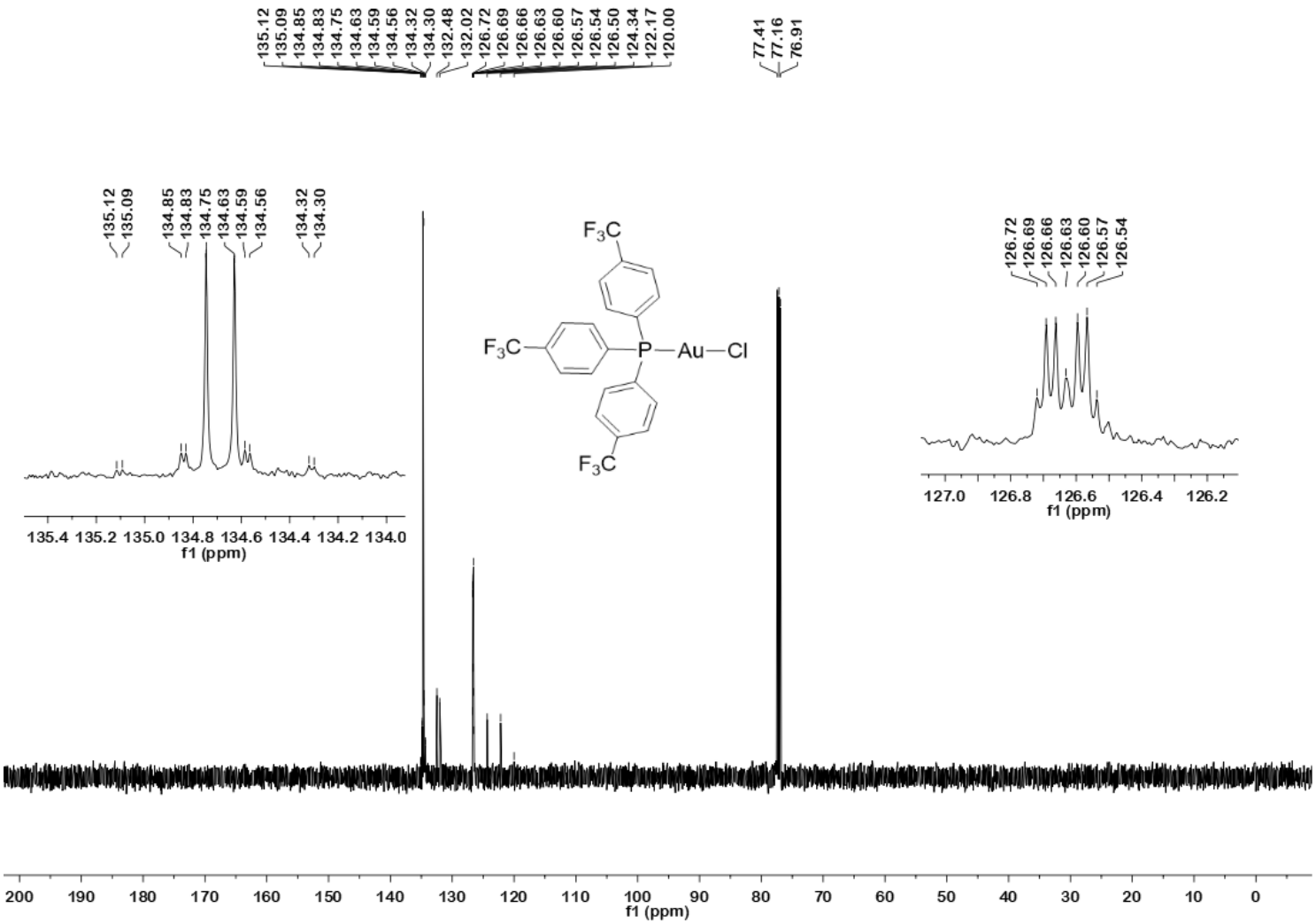


Figure S107. ^{13}C NMR spectrum of compound **30** in $CDCl_3$.

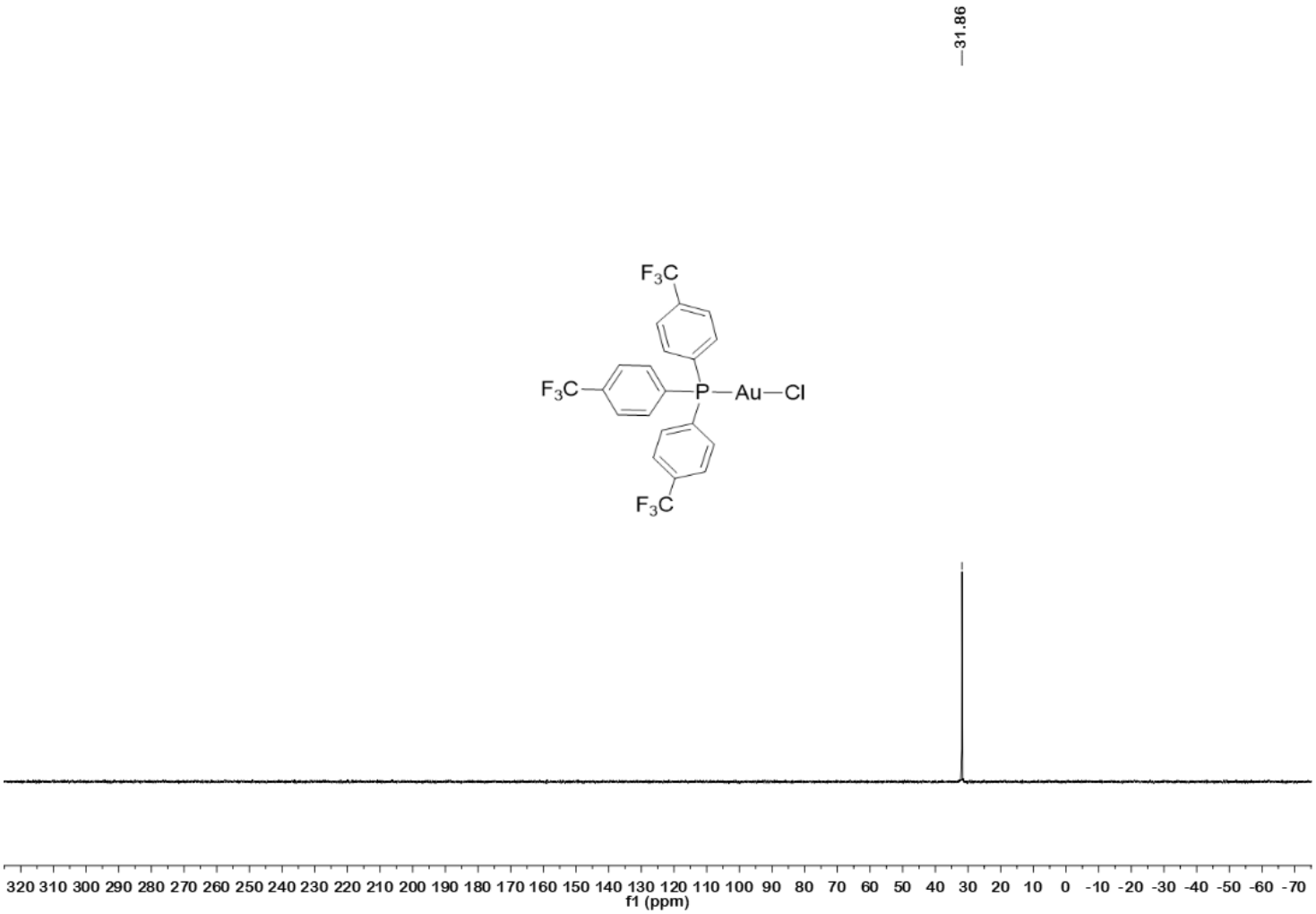


Figure S108. ^{31}P NMR spectrum of compound **30** in $CDCl_3$.

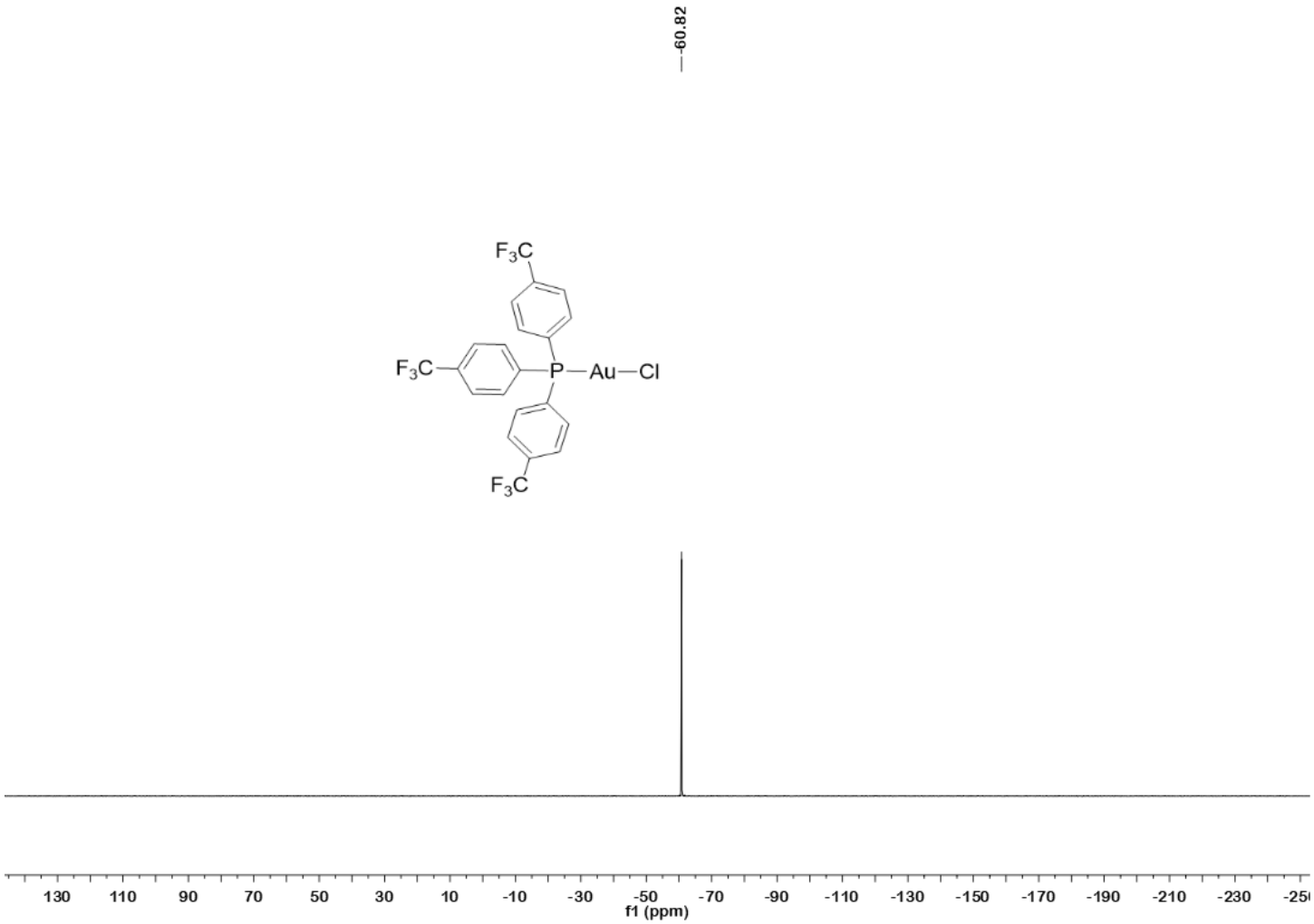


Figure S109. ^{19}F NMR spectrum of compound **30** in $CDCl_3$.

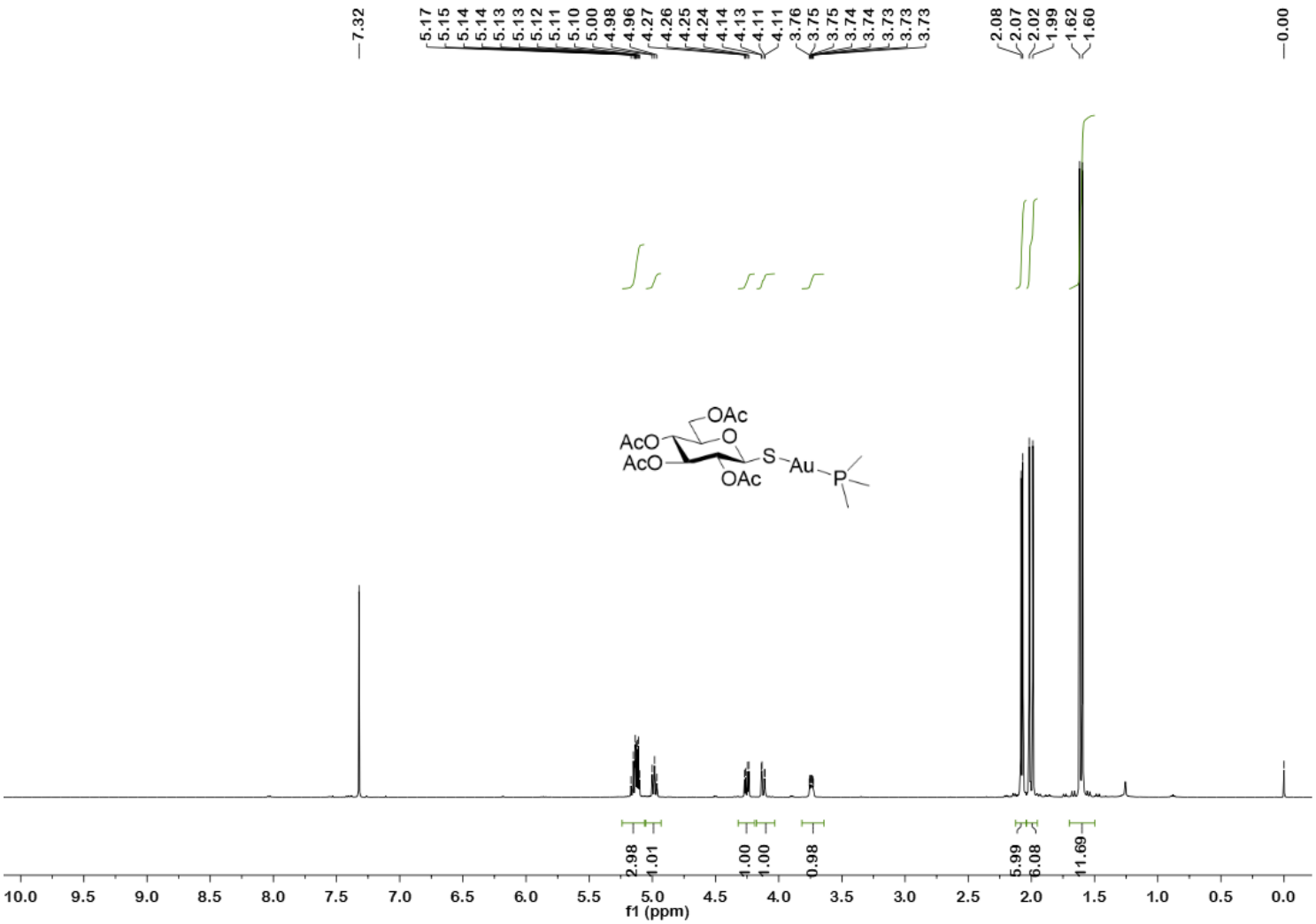


Figure S110. ^{1}H NMR spectrum of compound **31** in $CDCl_3$.

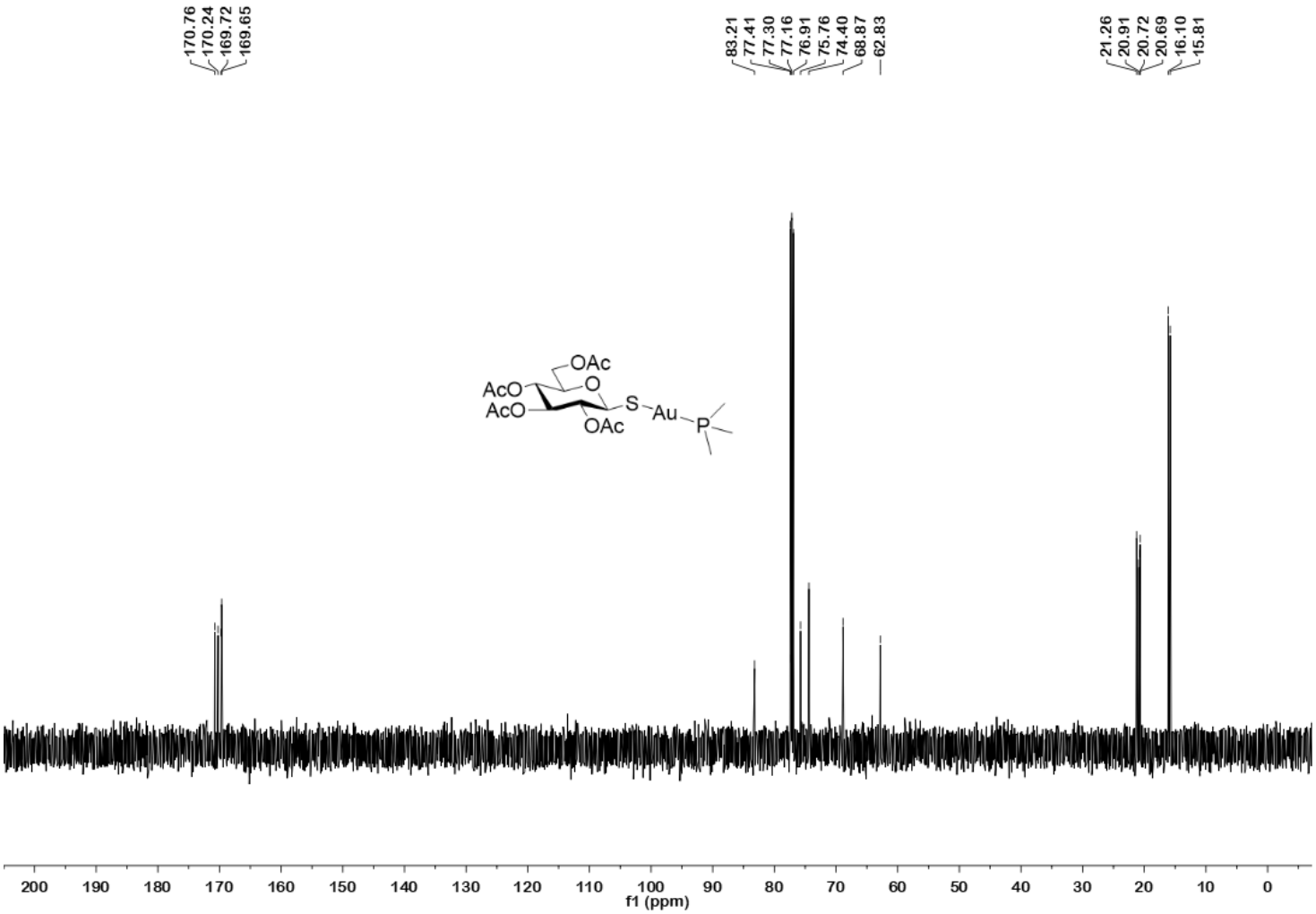


Figure S111. ^{13}C NMR spectrum of compound **31** in $CDCl_3$.

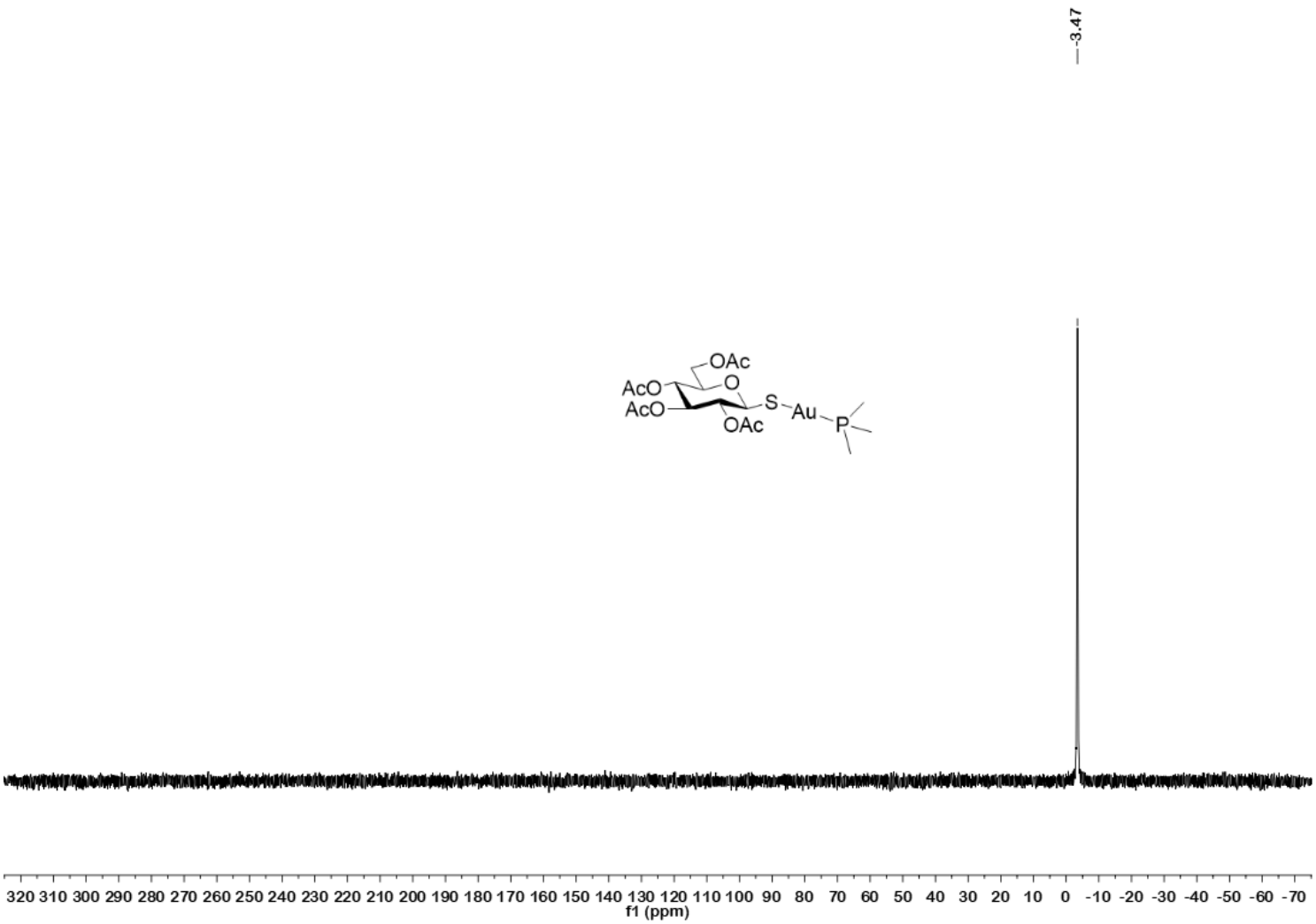


Figure S112. ^{31}P NMR spectrum of compound **31** in $CDCl_3$.

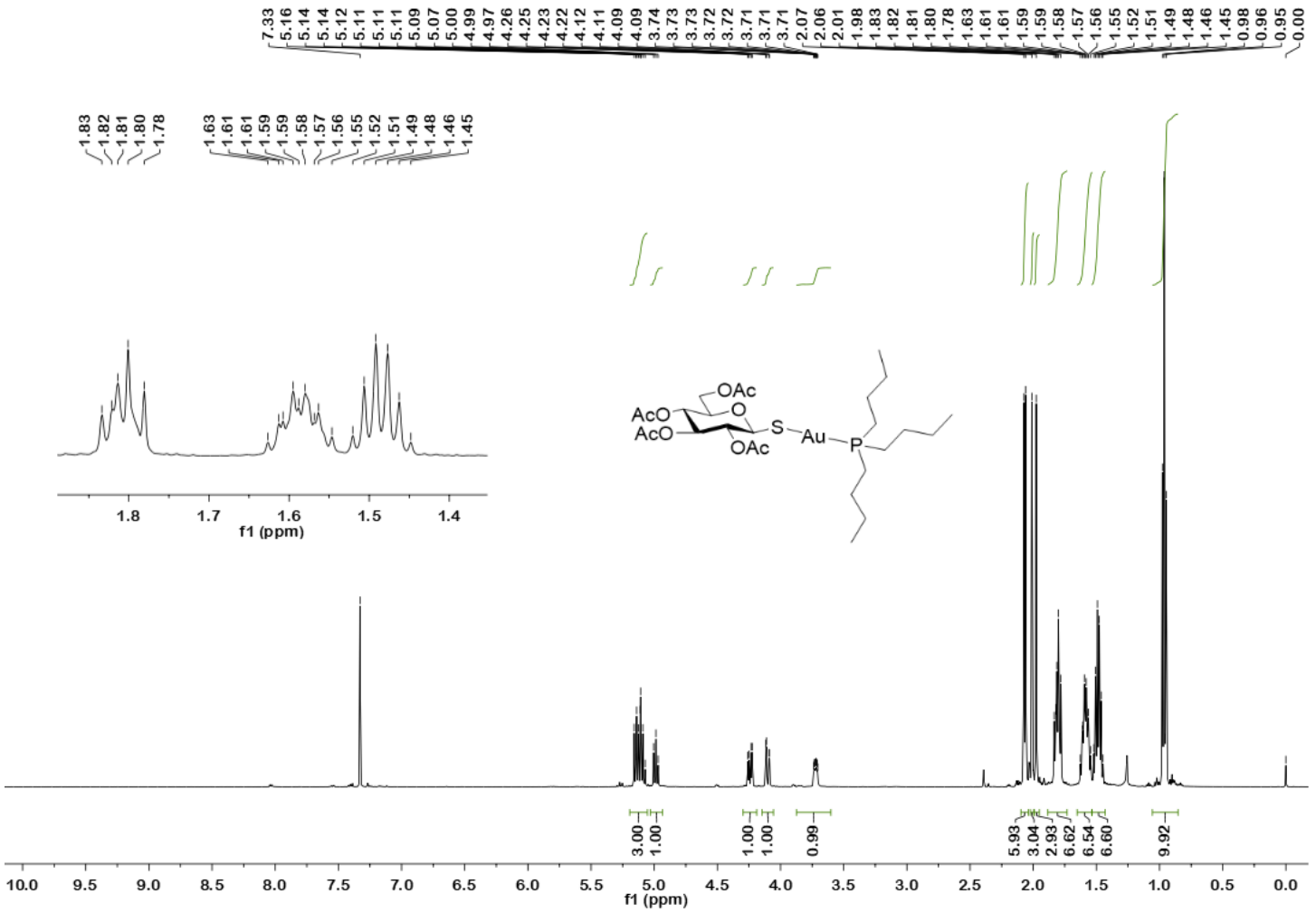


Figure S113. ^{1}H NMR spectrum of compound **32** in $CDCl_3$.

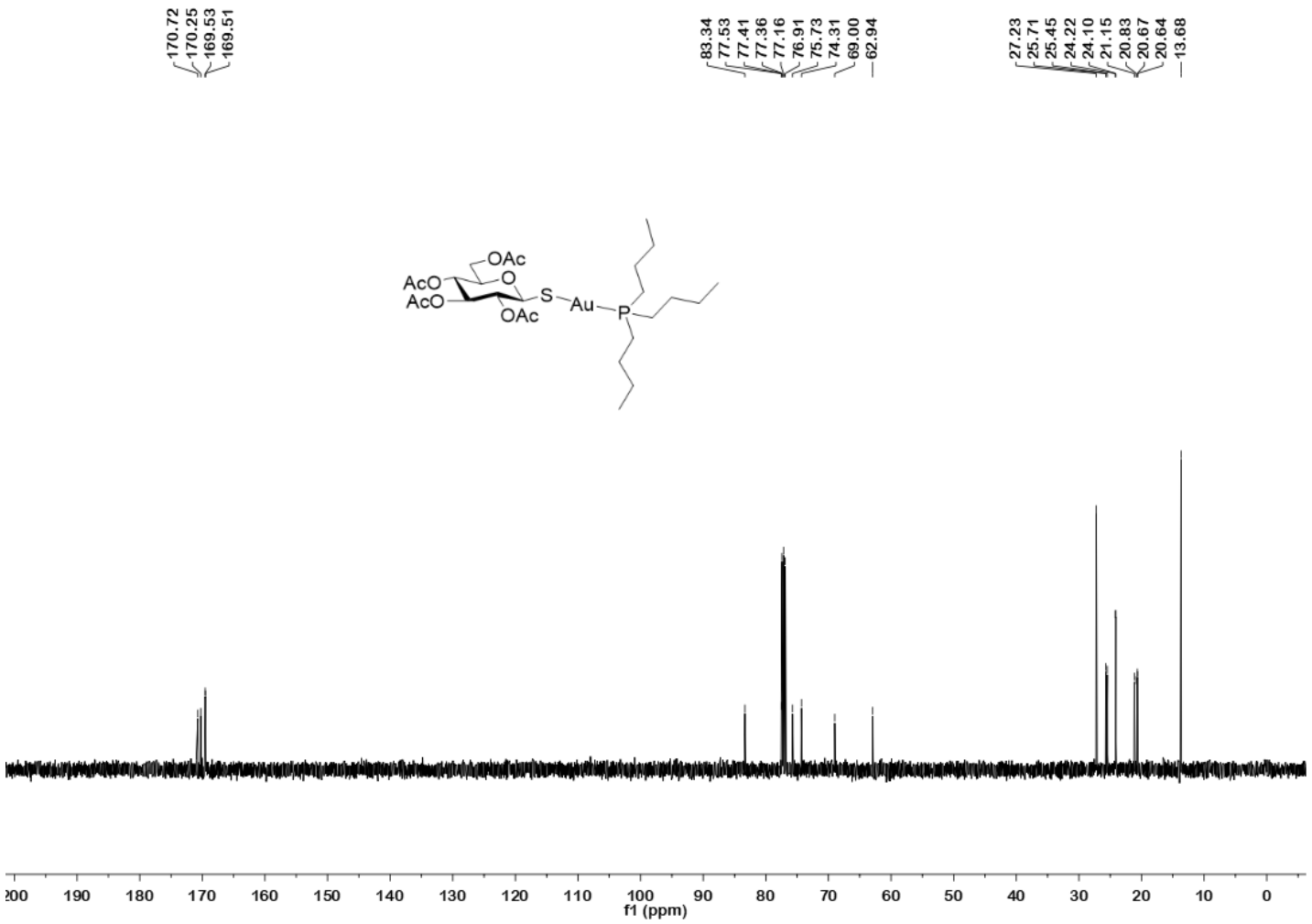


Figure S114. ^{13}C NMR spectrum of compound **32** in $CDCl_3$.

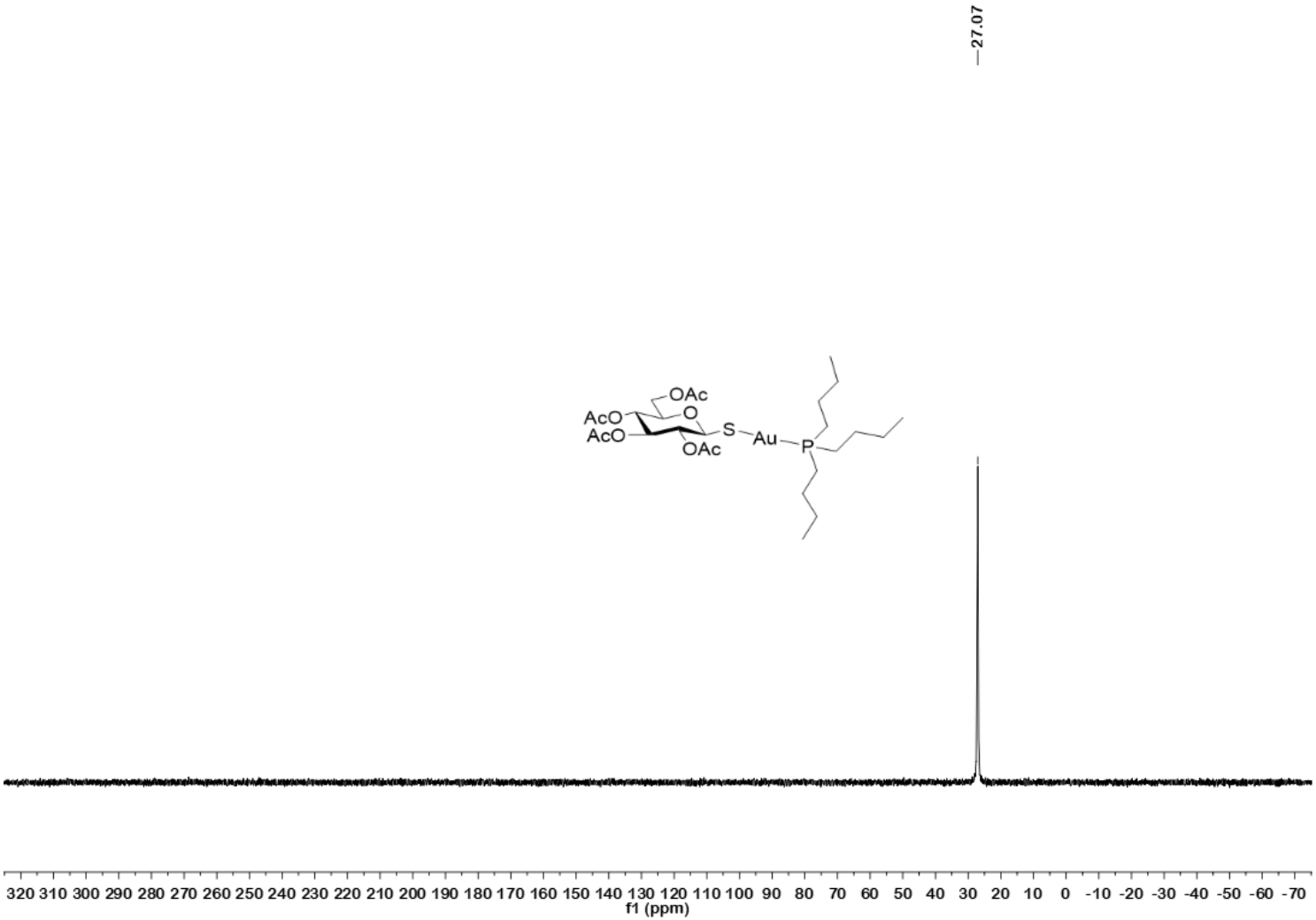


Figure S115. ^{31}P NMR spectrum of compound **32** in $CDCl_3$.

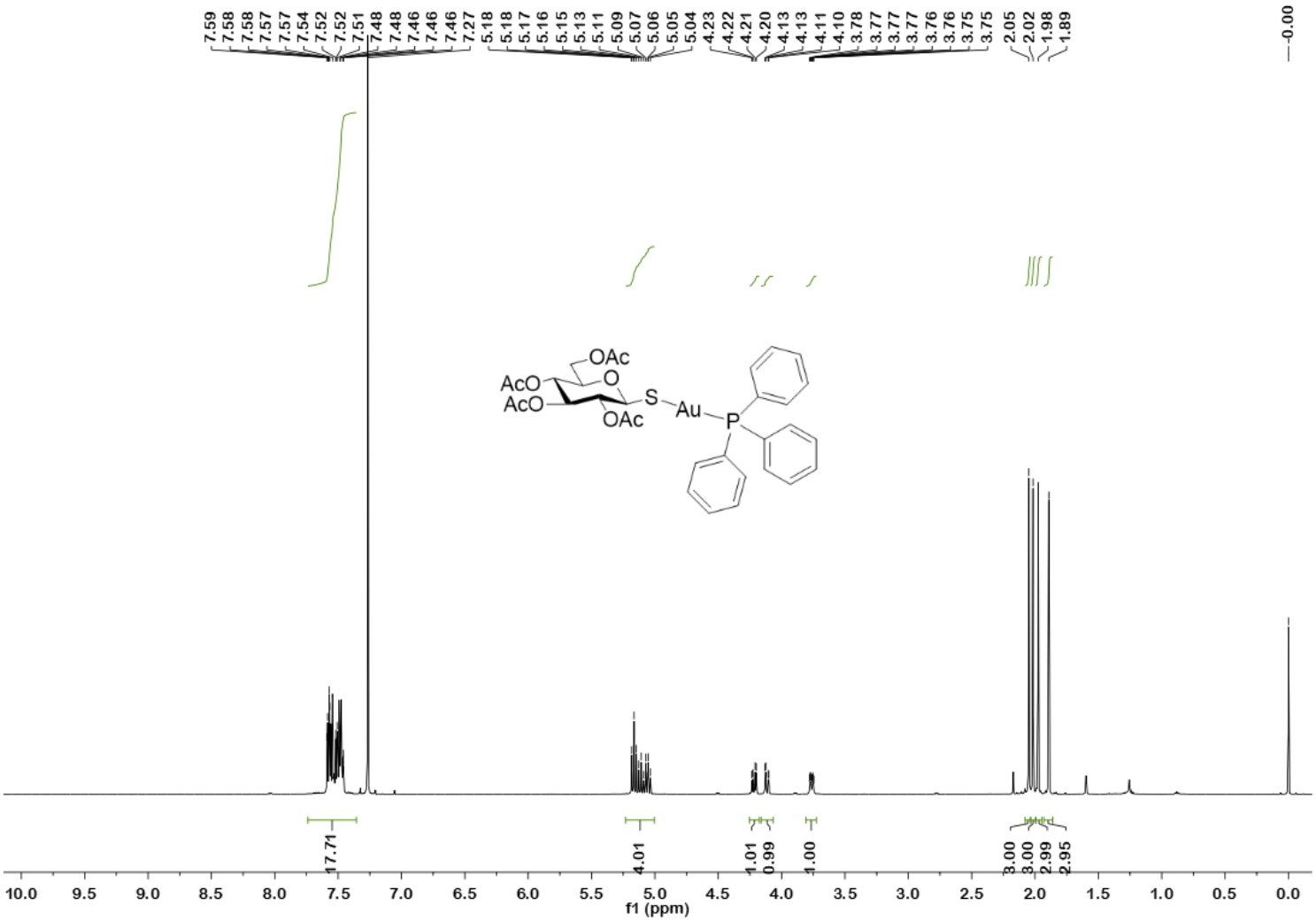


Figure S116. ^{1}H NMR spectrum of compound **33** in $CDCl_3$.

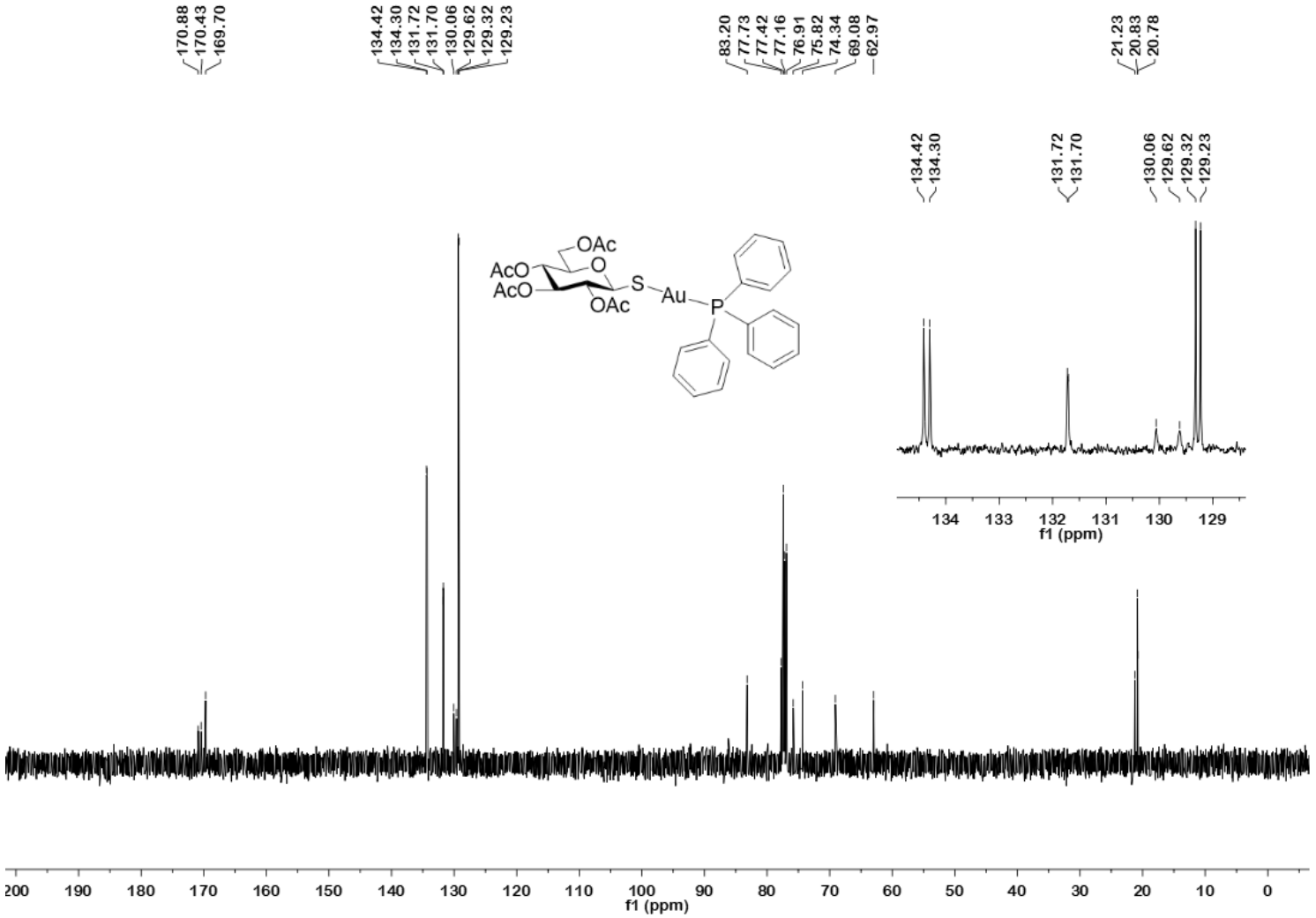


Figure S117. ^{13}C NMR spectrum of compound **33** in $CDCl_3$.

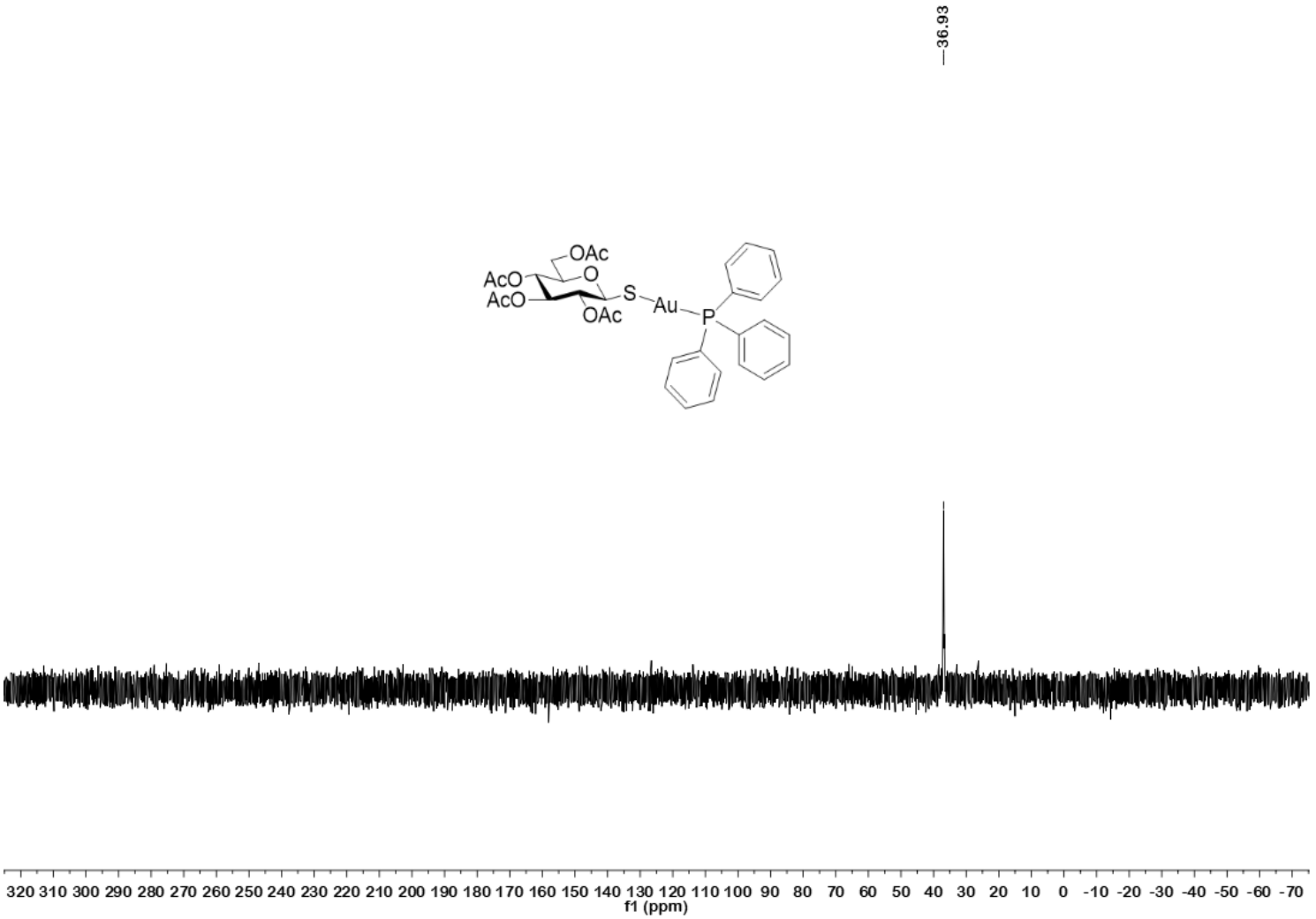


Figure S118. ^{31}P NMR spectrum of compound **33** in $CDCl_3$.

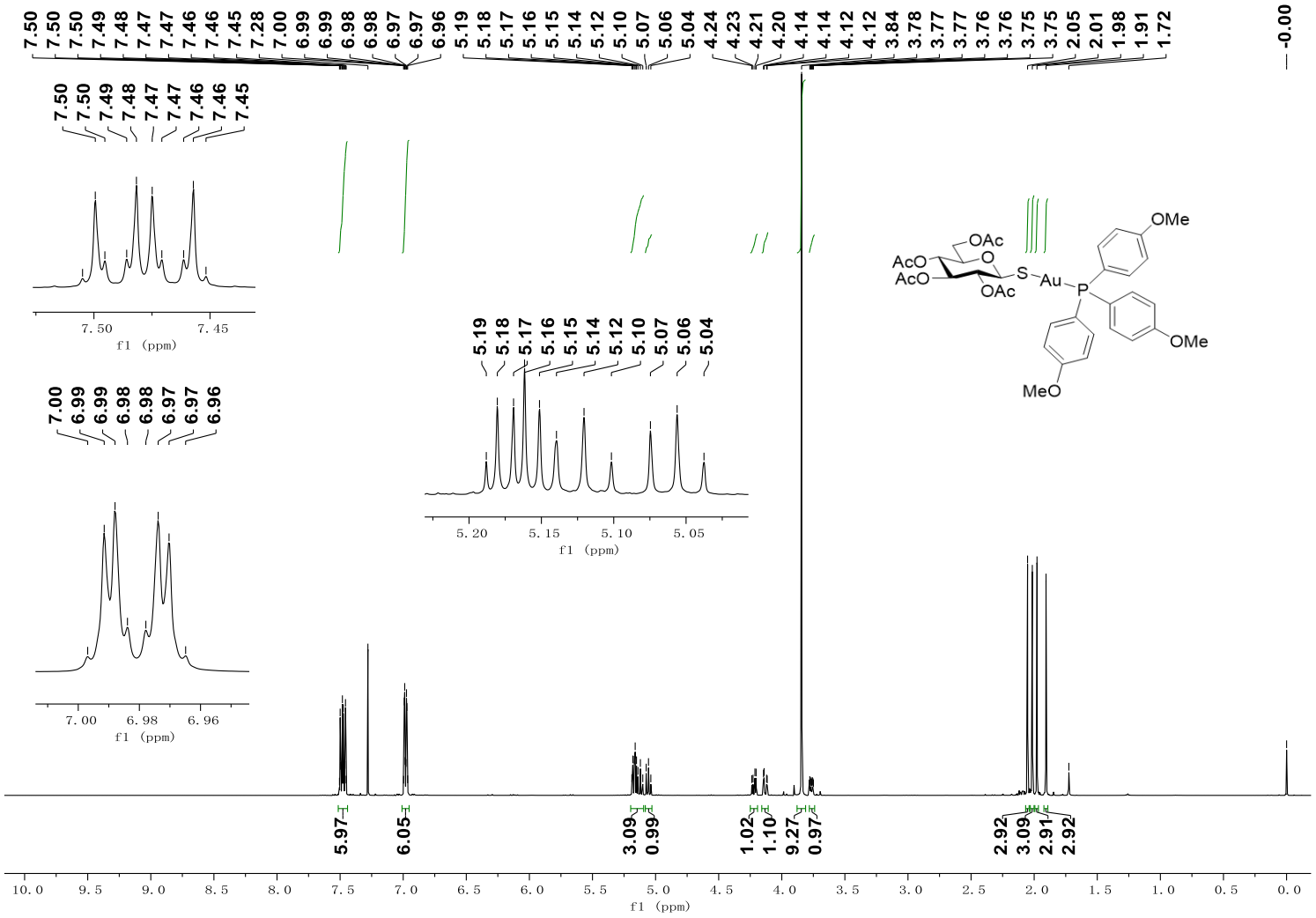


Figure S119. ^{1}H NMR spectrum of compound **34** in $CDCl_3$.

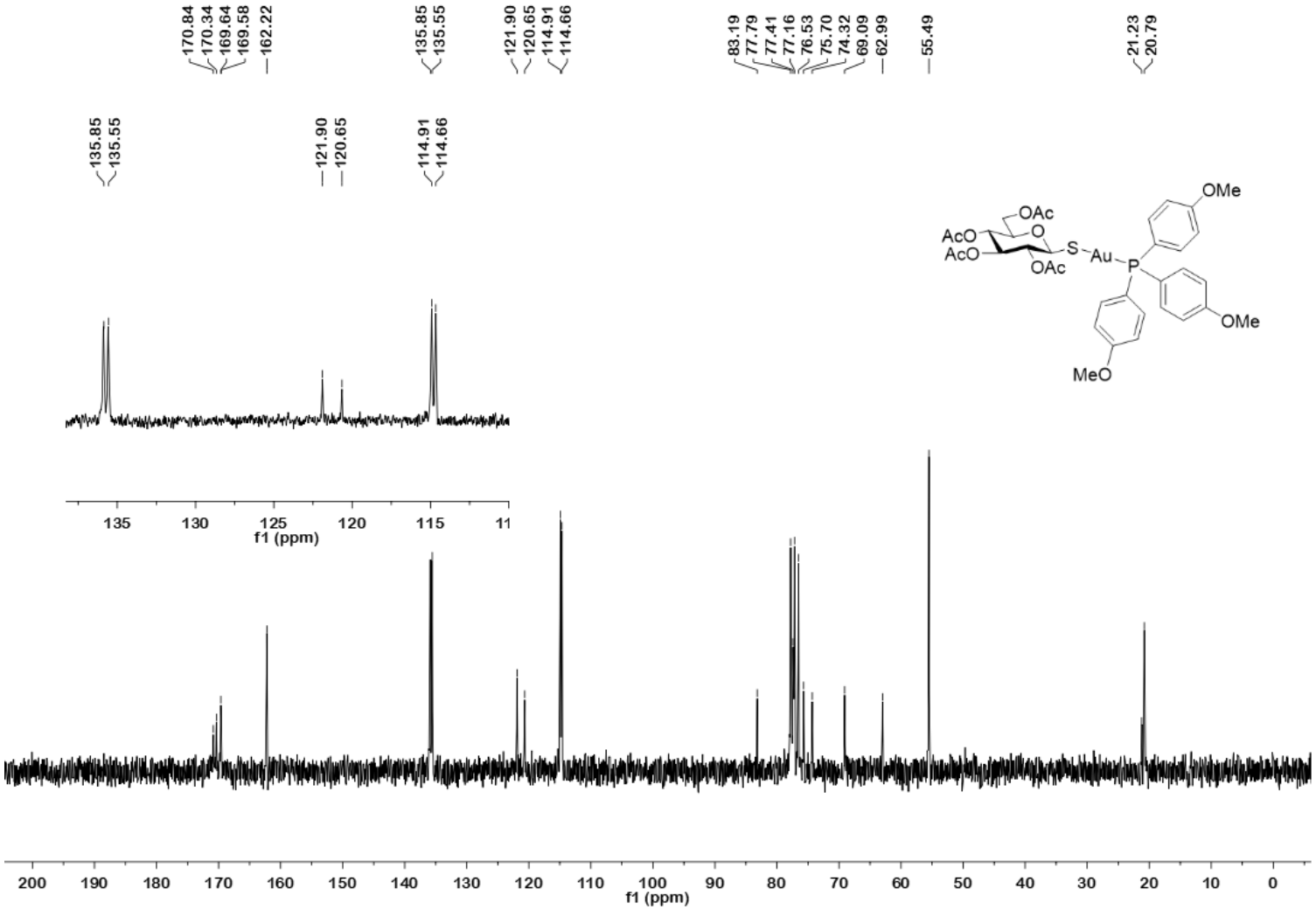


Figure S120. ^{13}C NMR spectrum of compound **34** in $CDCl_3$.

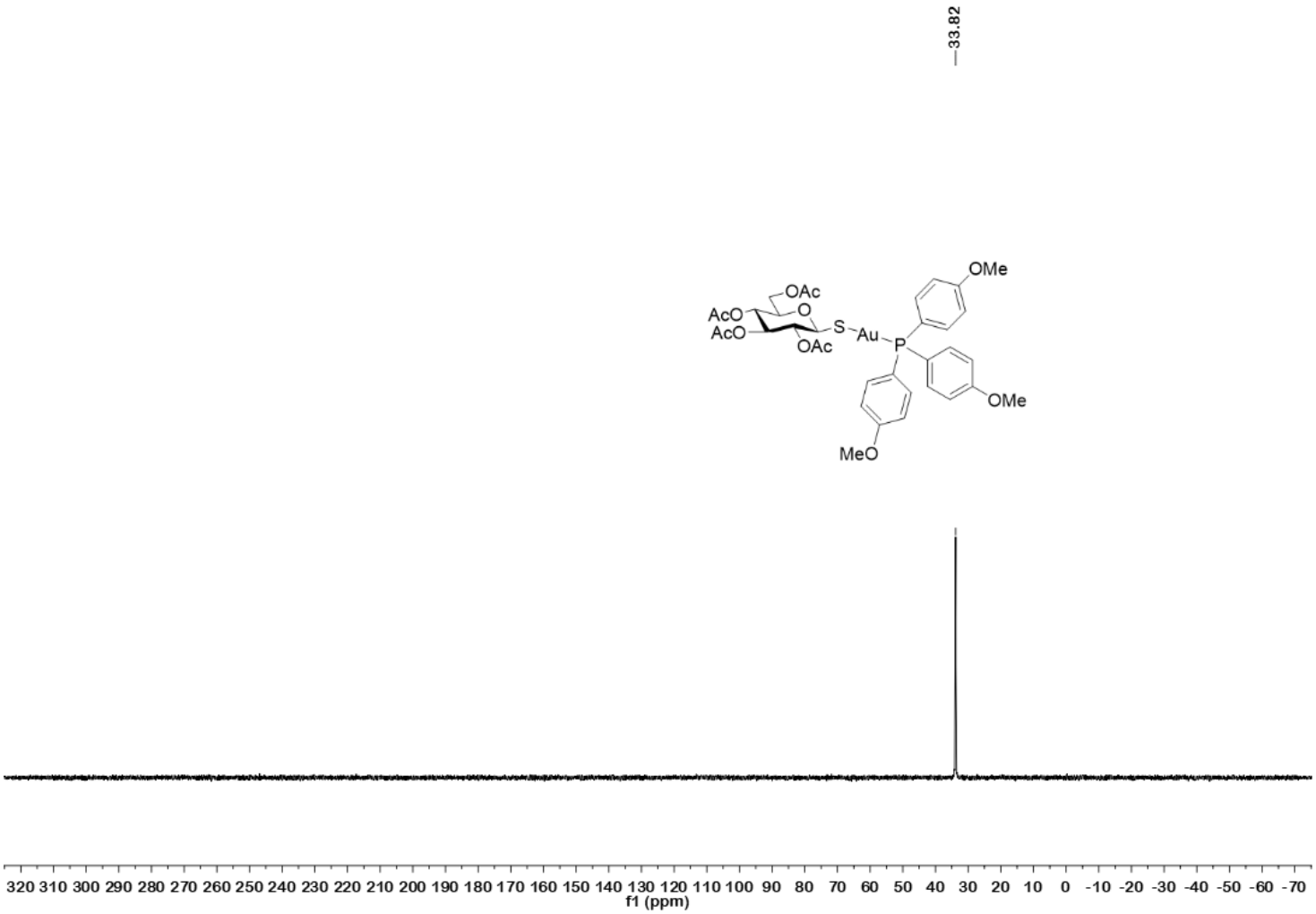


Figure S121. ^{31}P NMR spectrum of compound **34** in $CDCl_3$.

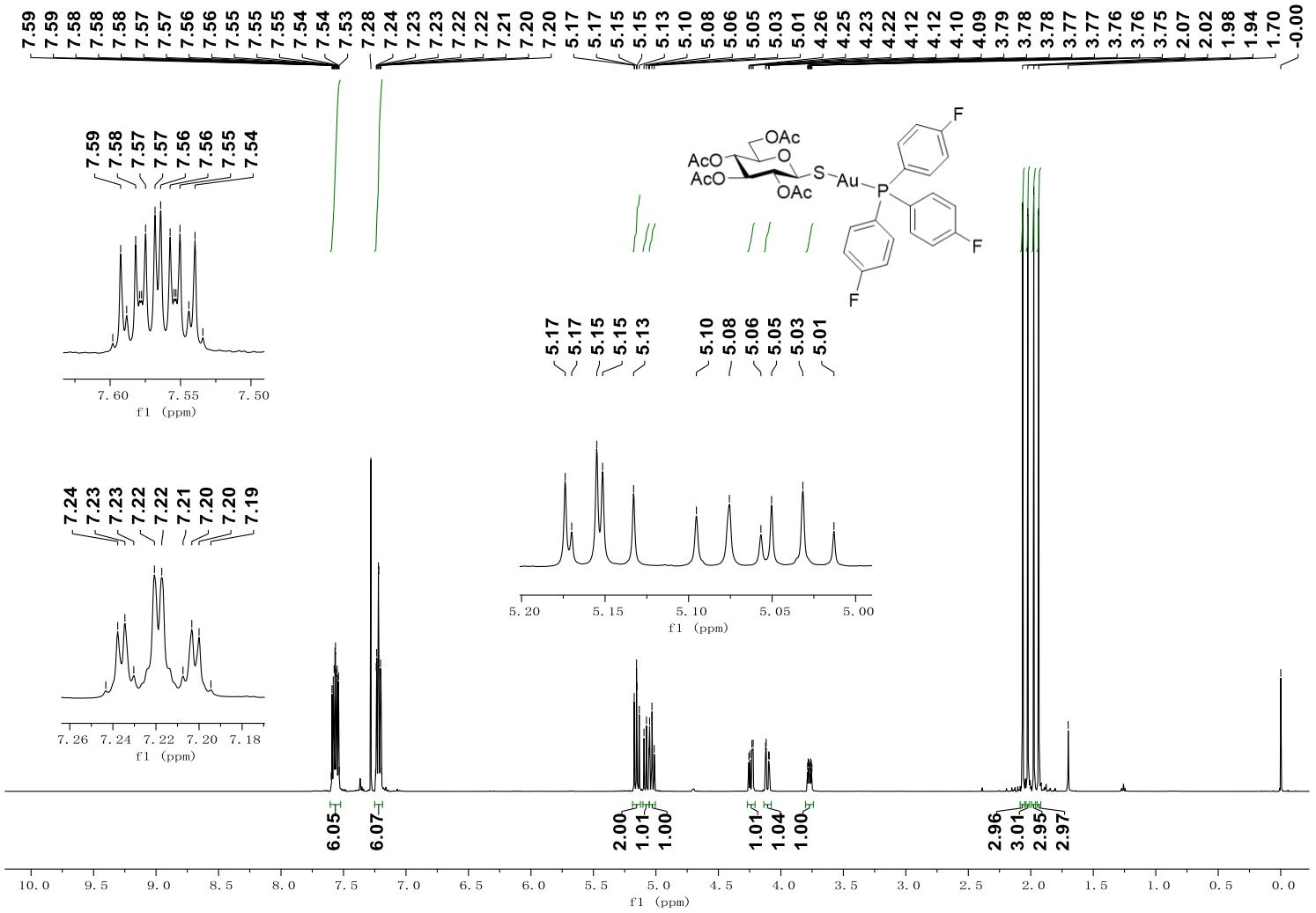


Figure S122. ^{1}H NMR spectrum of compound **35** in $CDCl_3$.

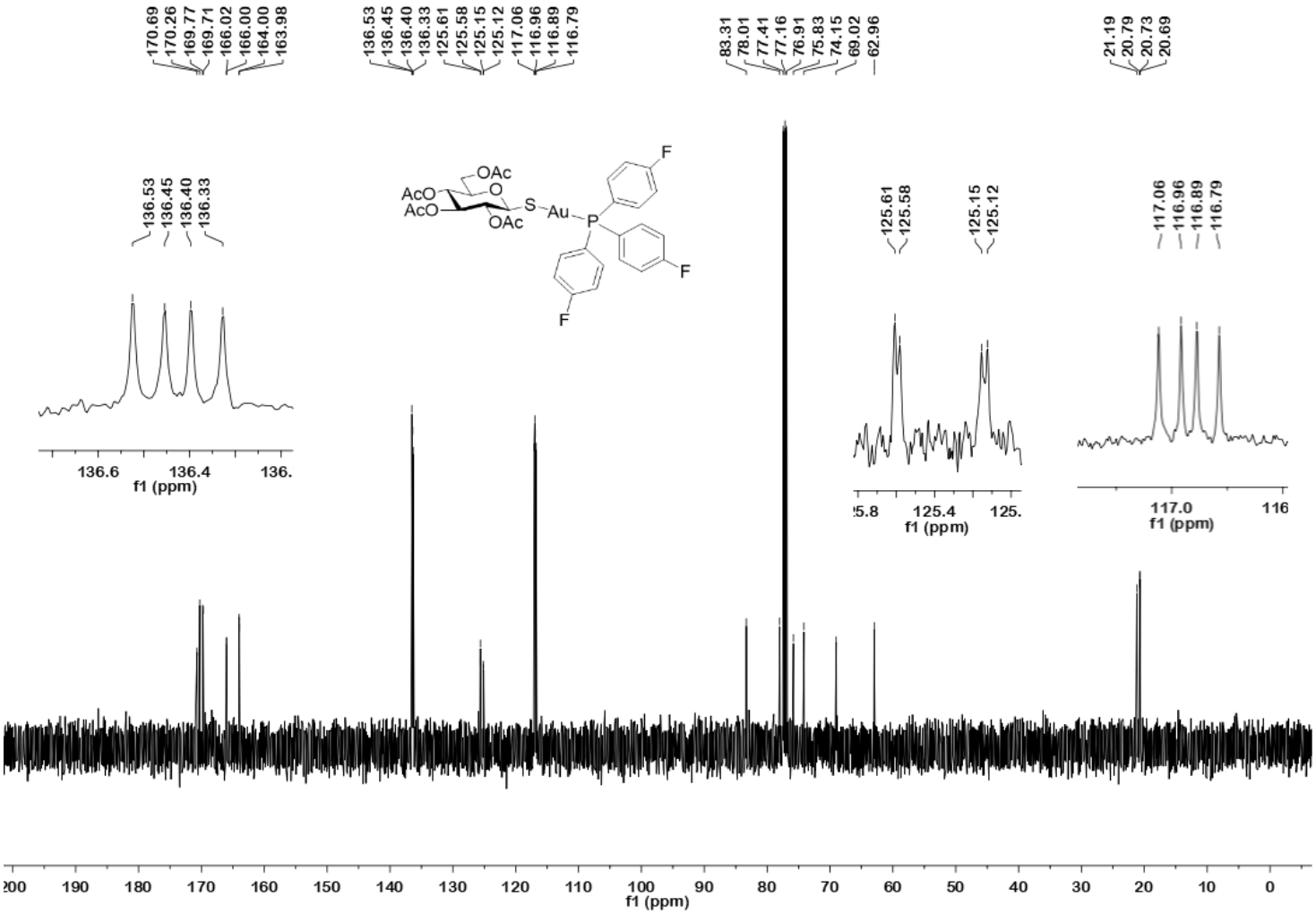


Figure S123. ^{13}C NMR spectrum of compound **35** in $CDCl_3$.

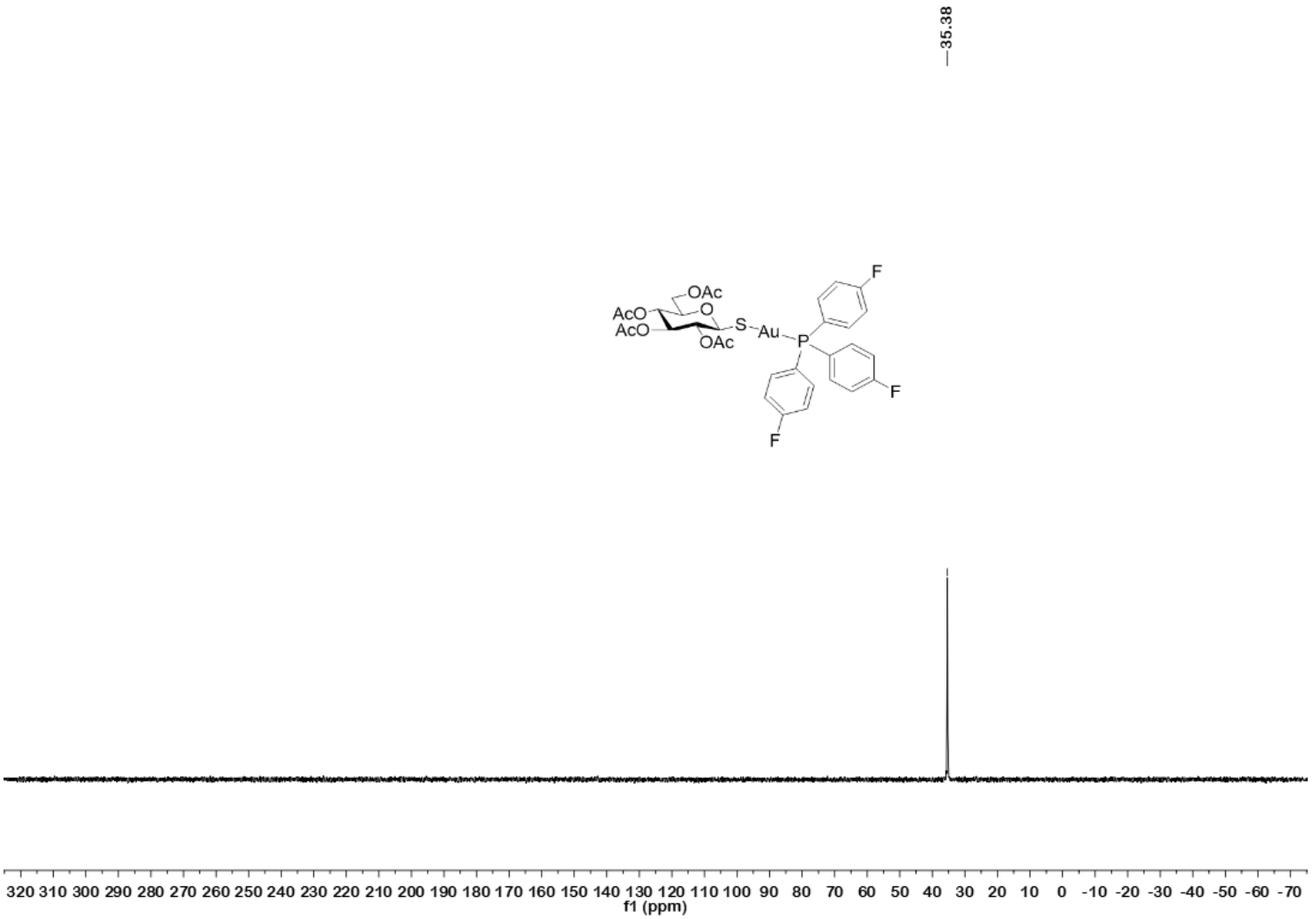


Figure S124. ^{31}P NMR spectrum of compound **35** in $CDCl_3$.

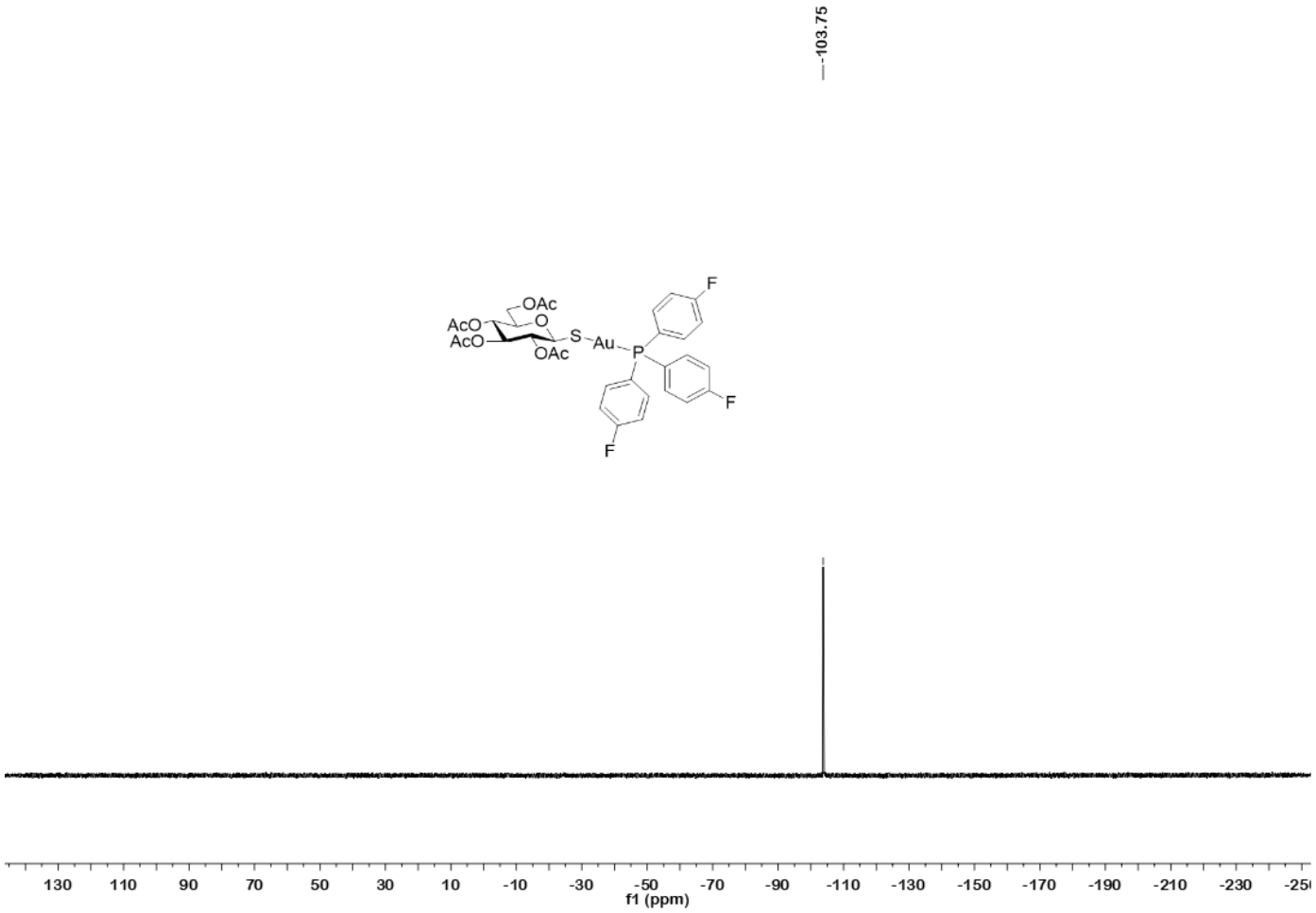


Figure S125. ^{19}F NMR spectrum of compound **35** in $CDCl_3$.

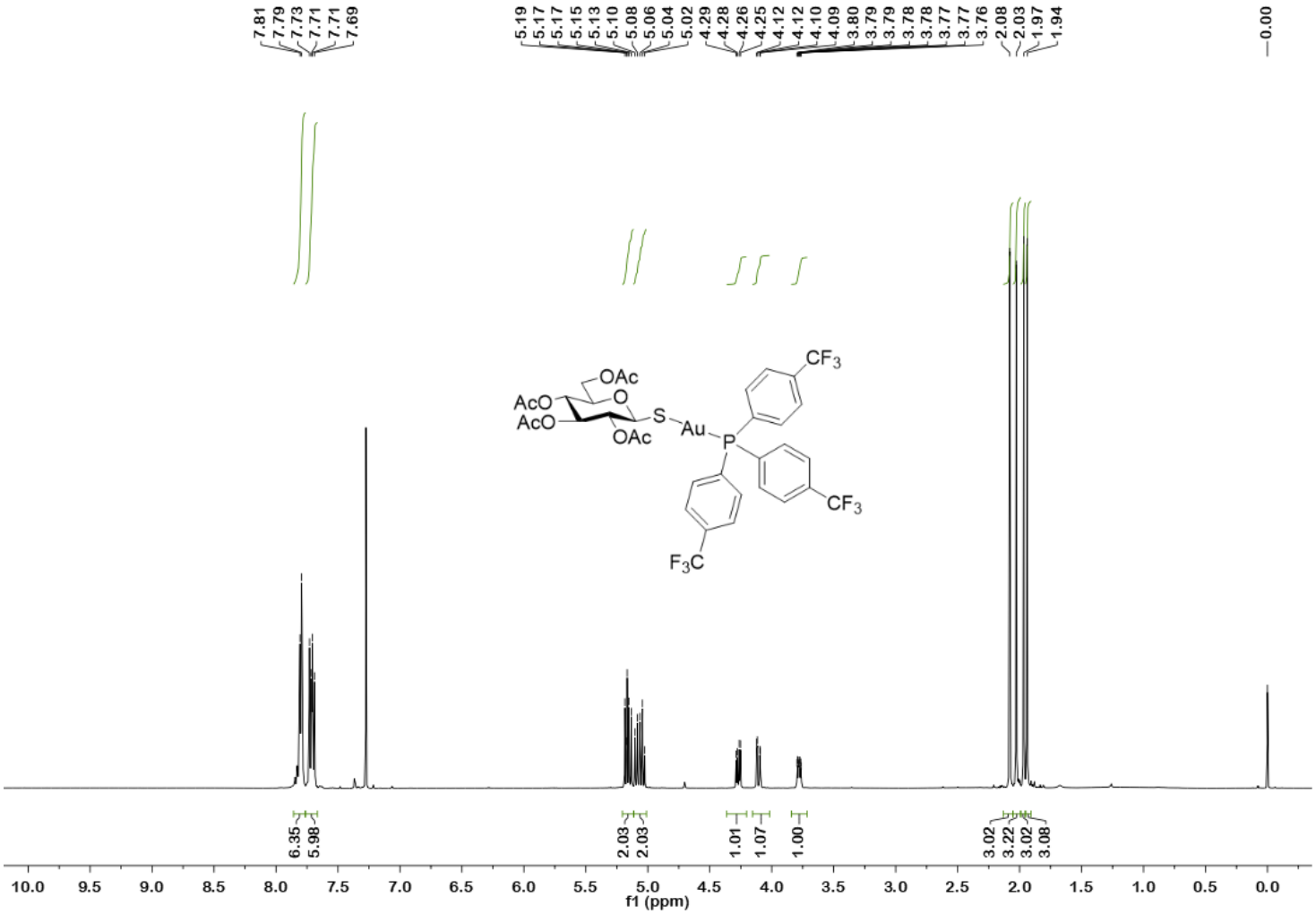


Figure S126. ^{1}H NMR spectrum of compound **36** in $CDCl_3$.

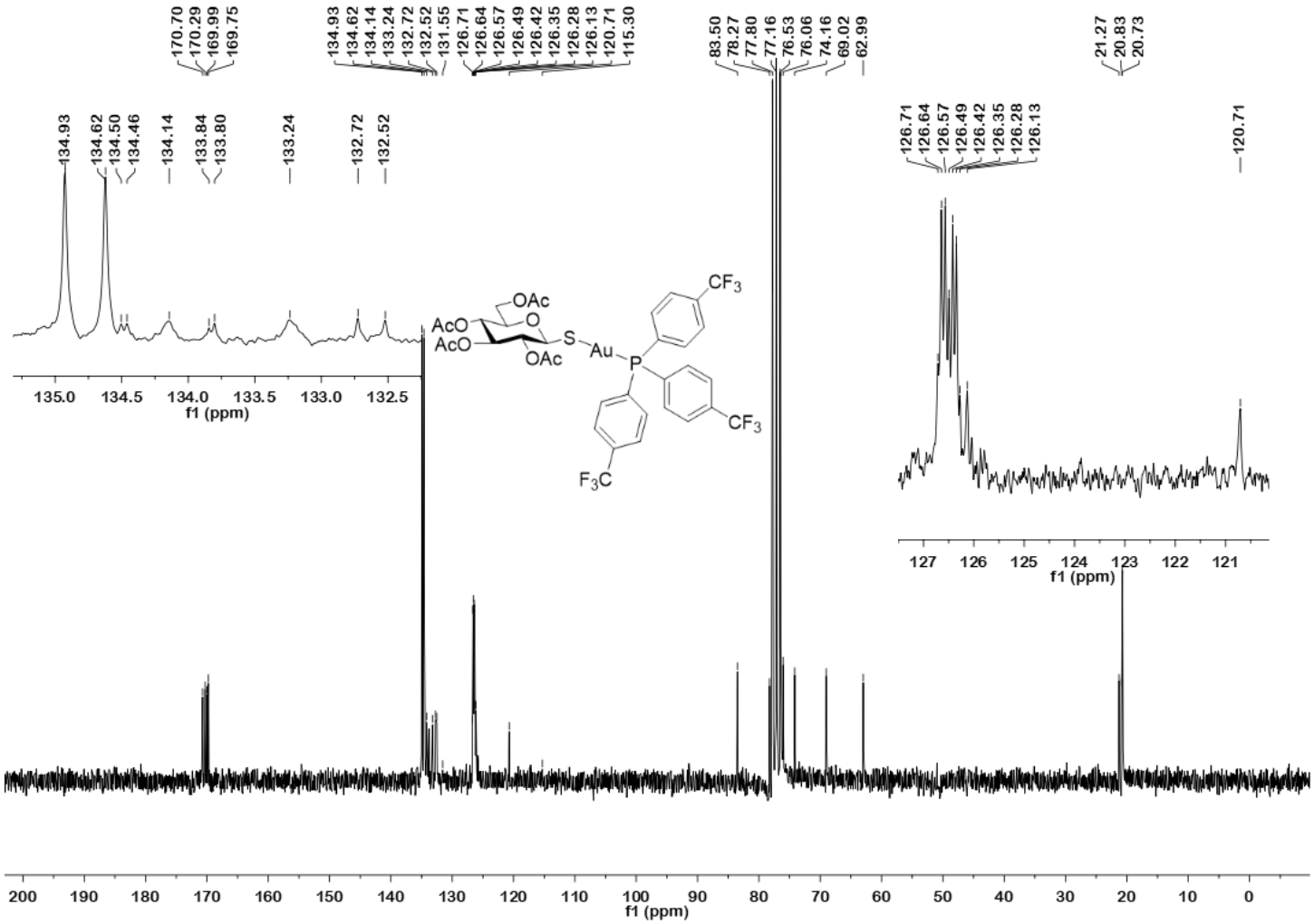


Figure S127. ^{13}C NMR spectrum of compound **36** in $CDCl_3$.

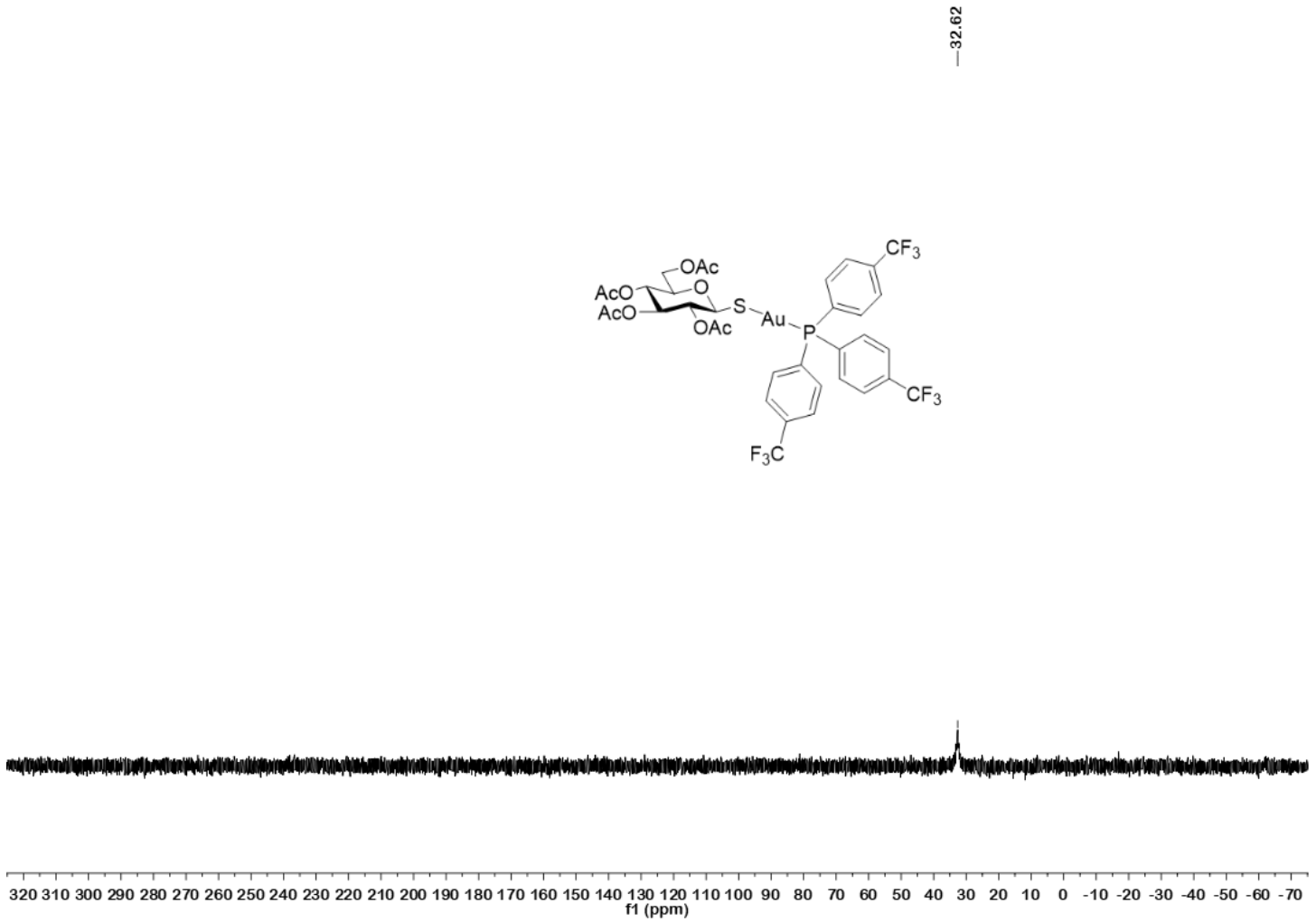


Figure S128. ^{31}P NMR spectrum of compound **36** in $CDCl_3$.

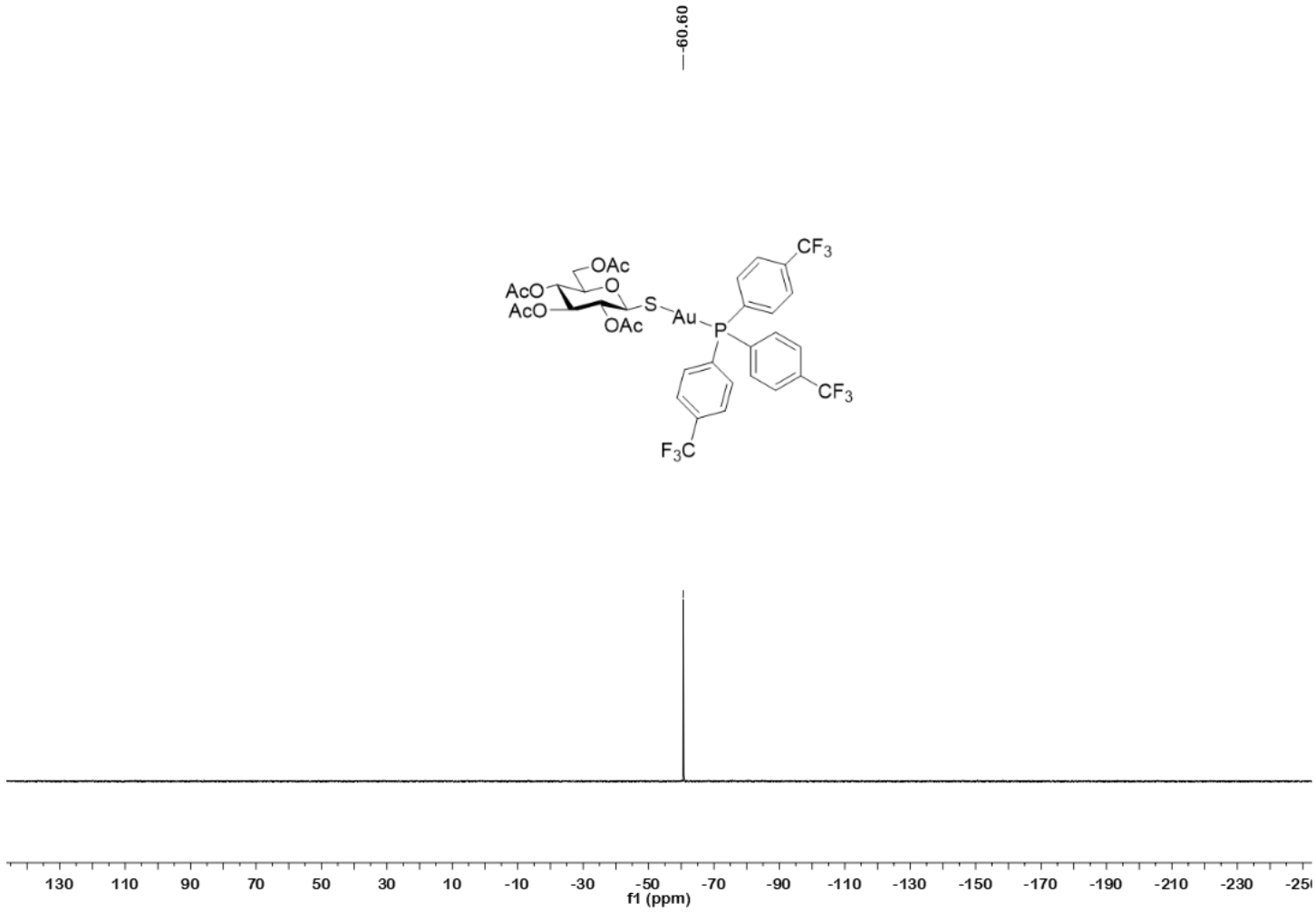


Figure S129. ^{19}F NMR spectrum of compound **36** in $CDCl_3$.

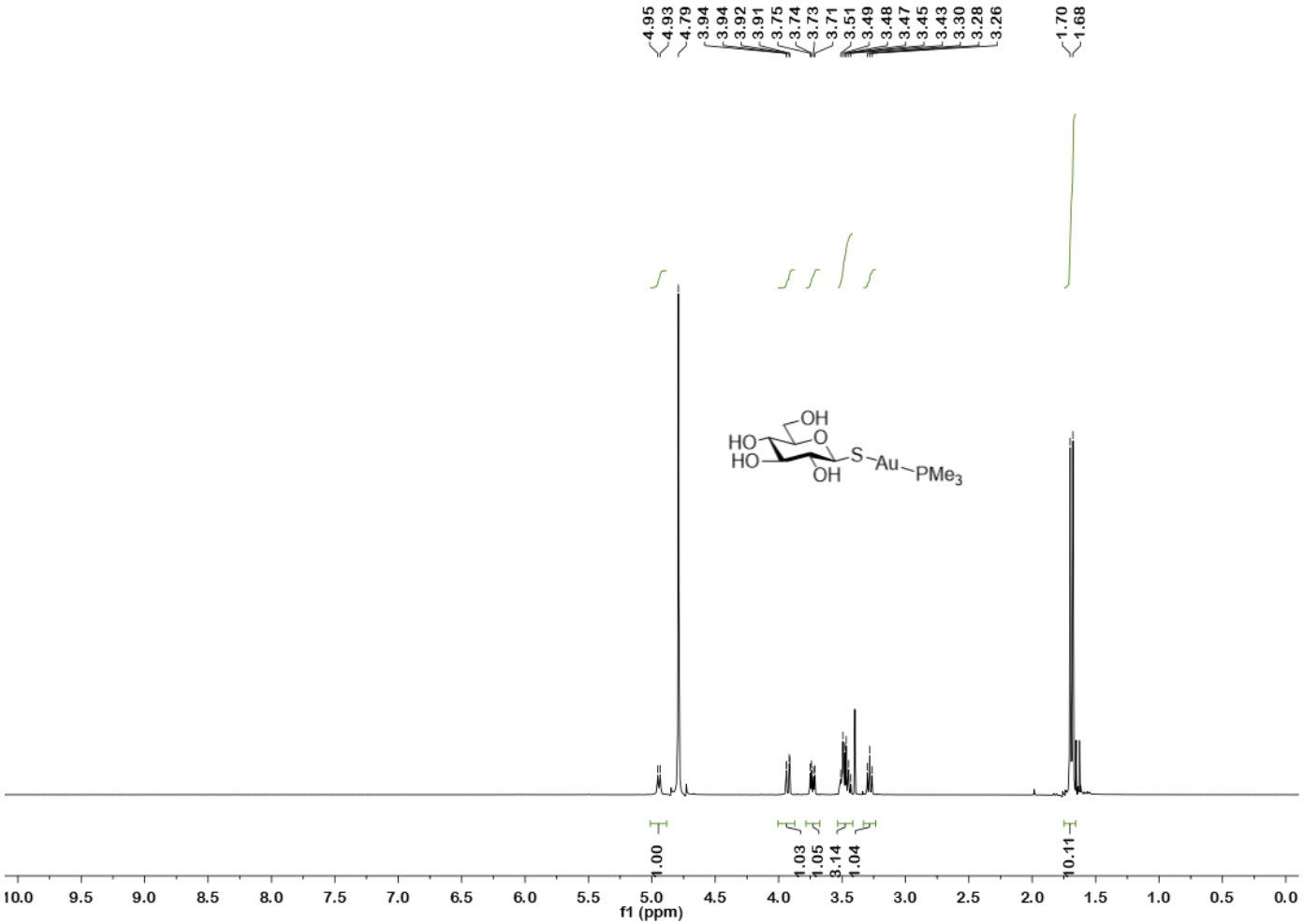


Figure S130. ^{1}H NMR spectrum of compound **37** in D_2O.

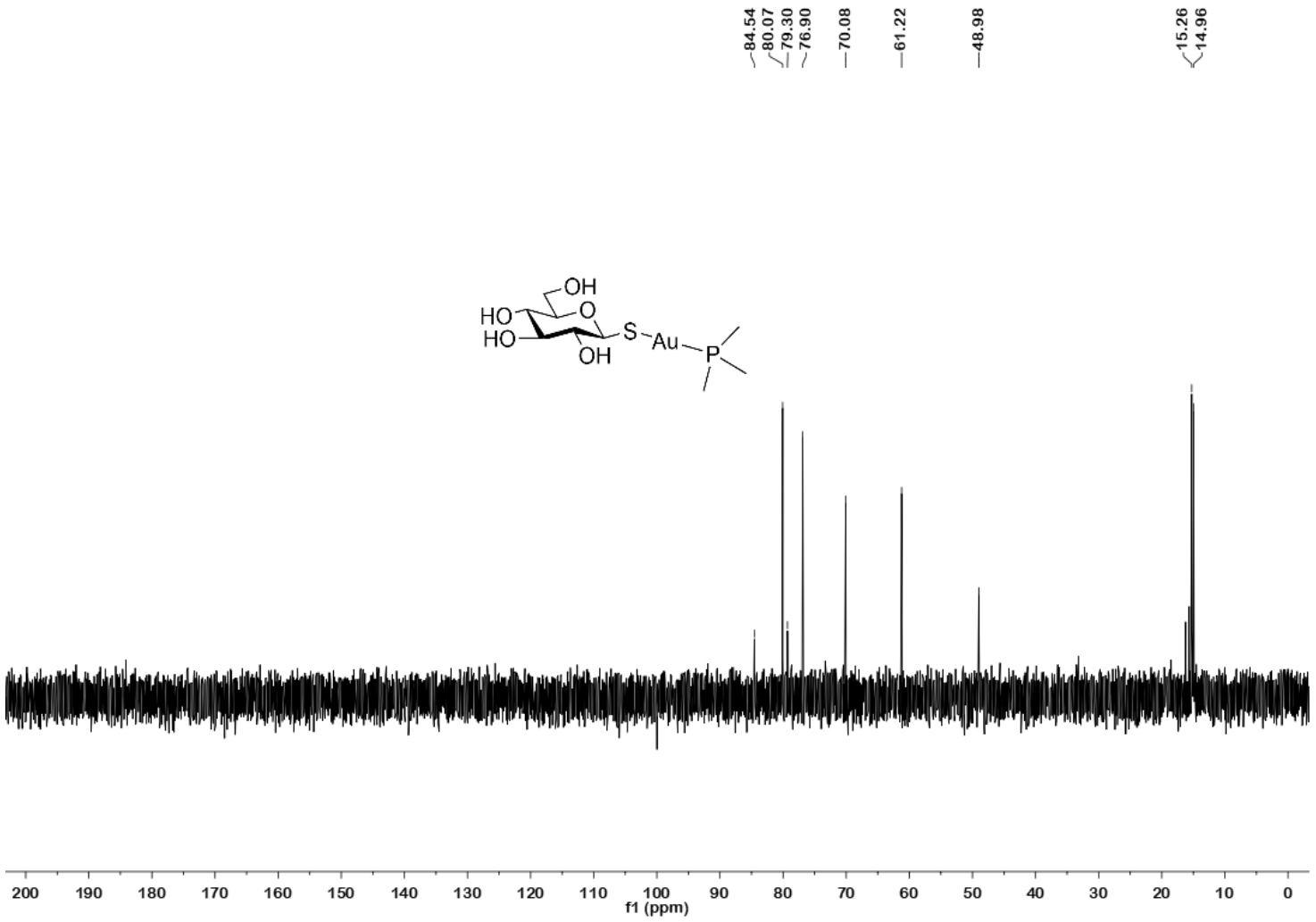


Figure S131. ^{13}C NMR spectrum of compound **37** in D_2O.

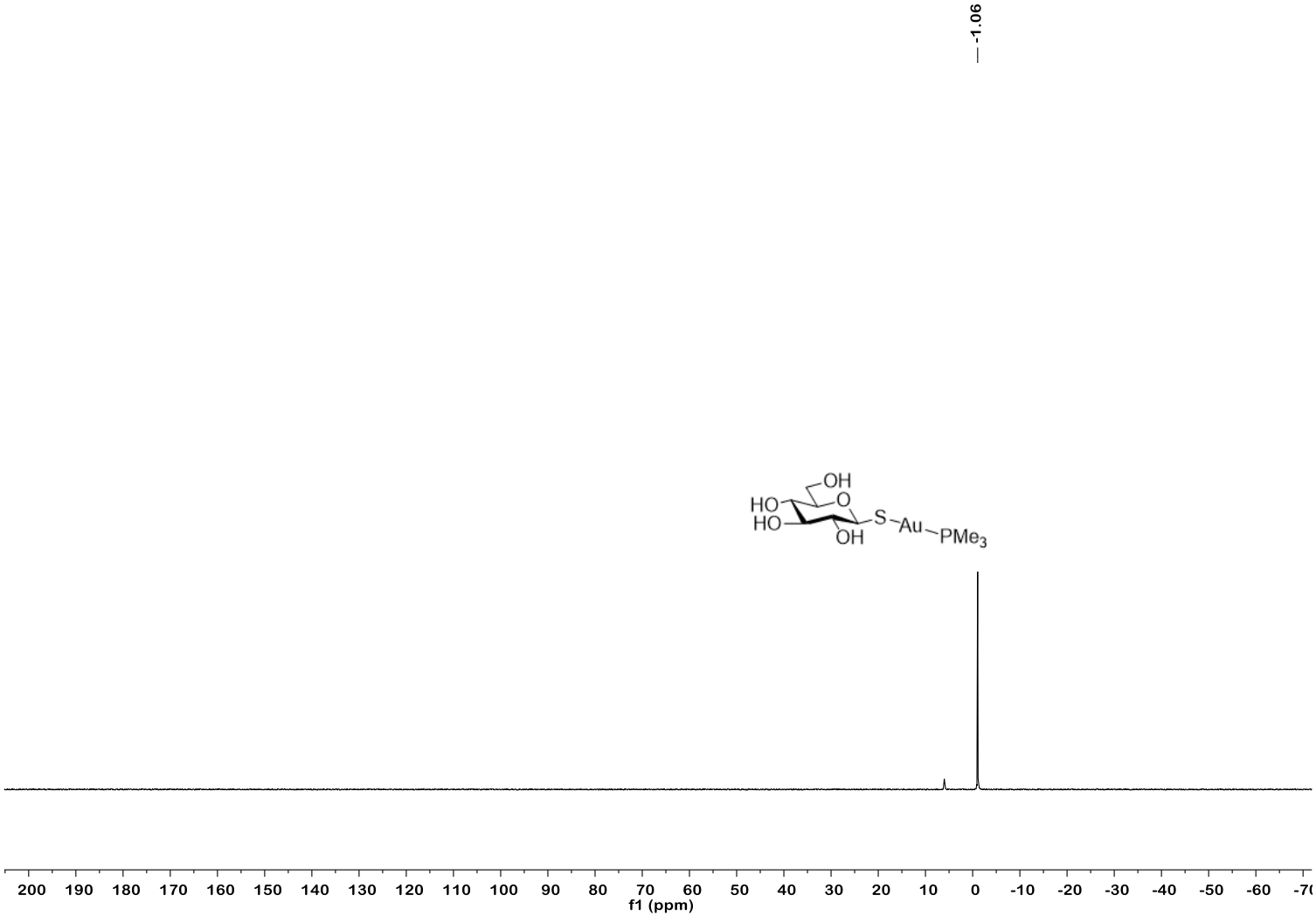


Figure S132. ^{31}P NMR spectrum of compound **37** in D_2O.

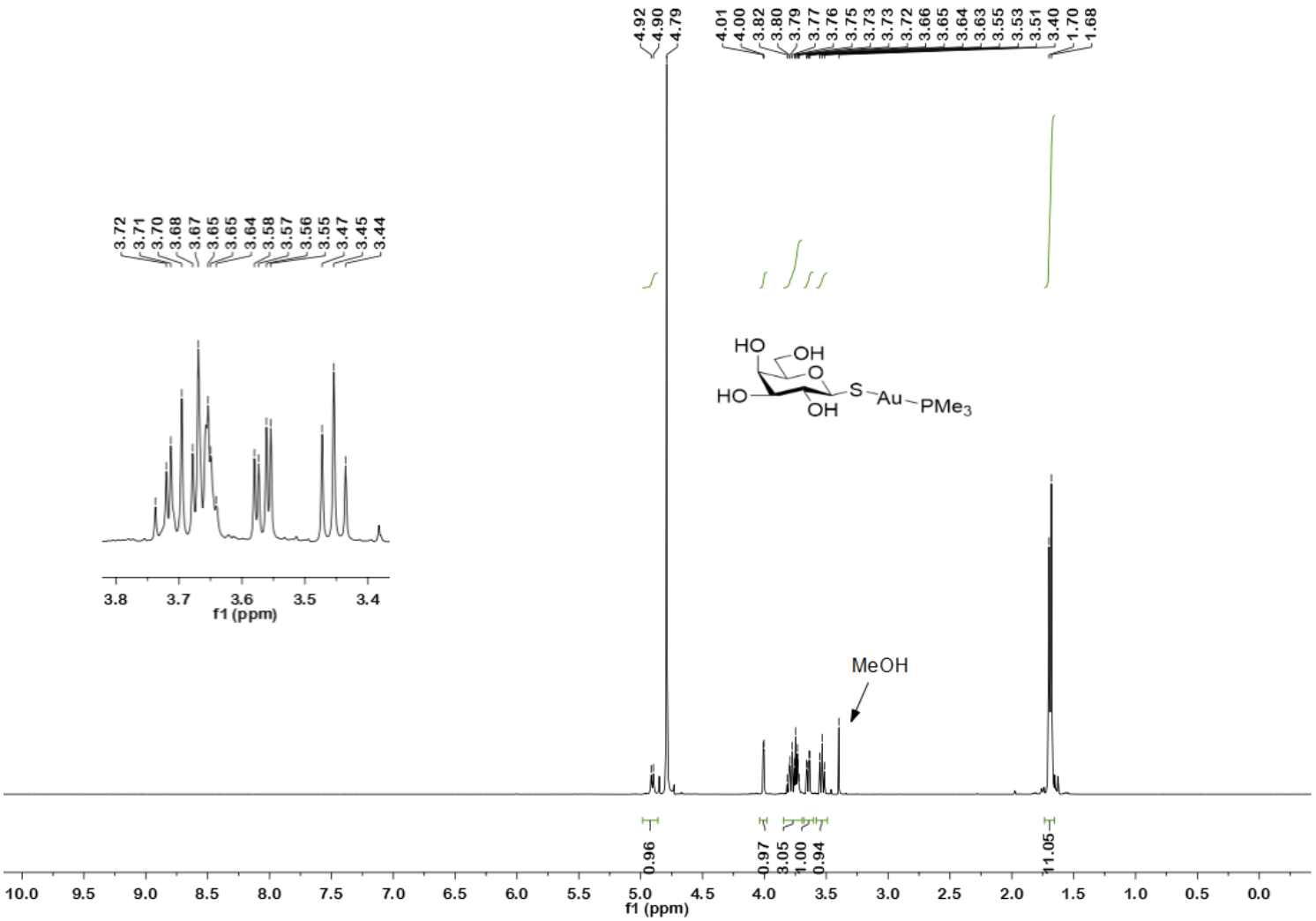


Figure S133. ^{1}H NMR spectrum of compound **38** in D_2O

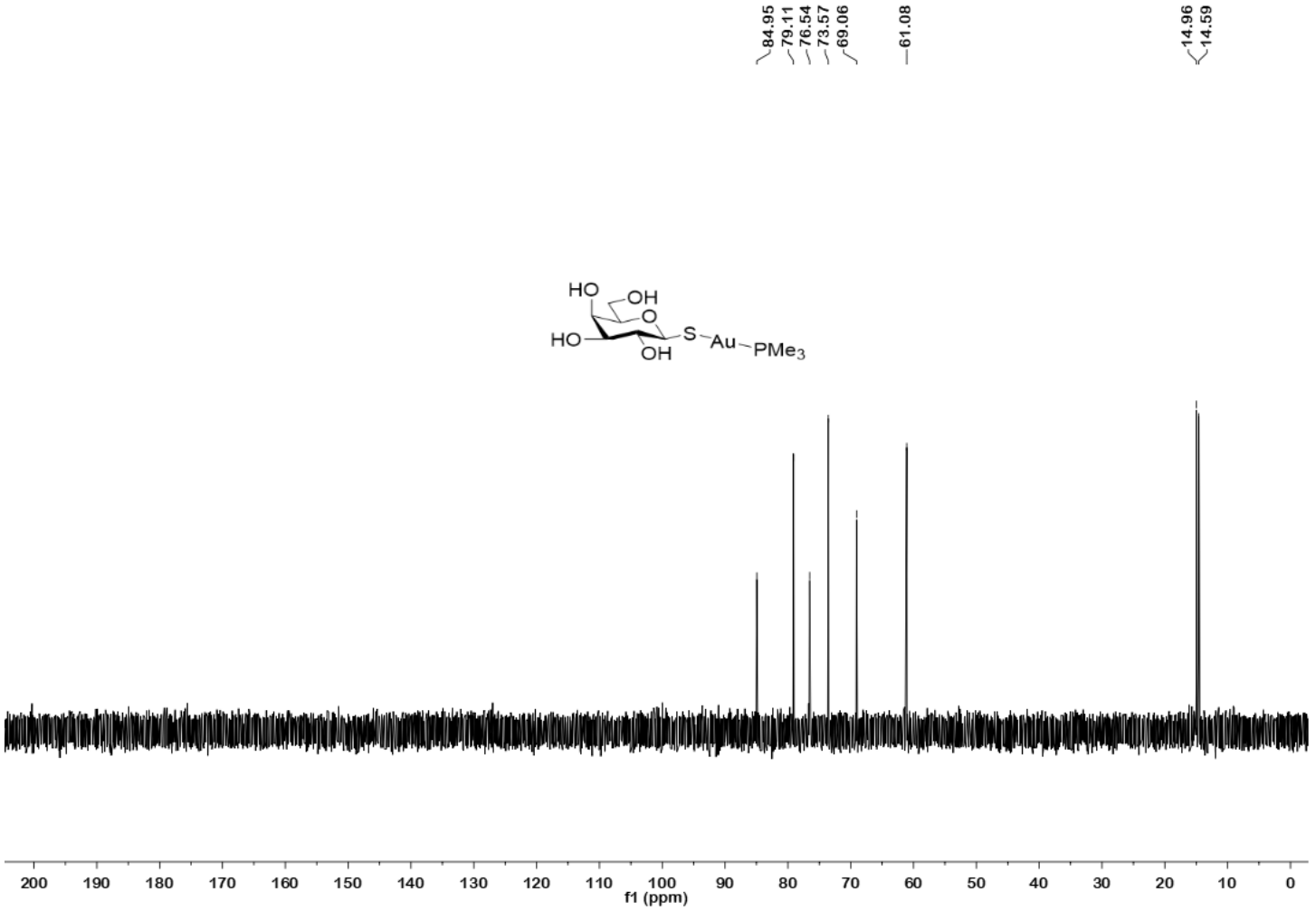


Figure S134. ^{13}C NMR spectrum of compound **38** in D_2O.

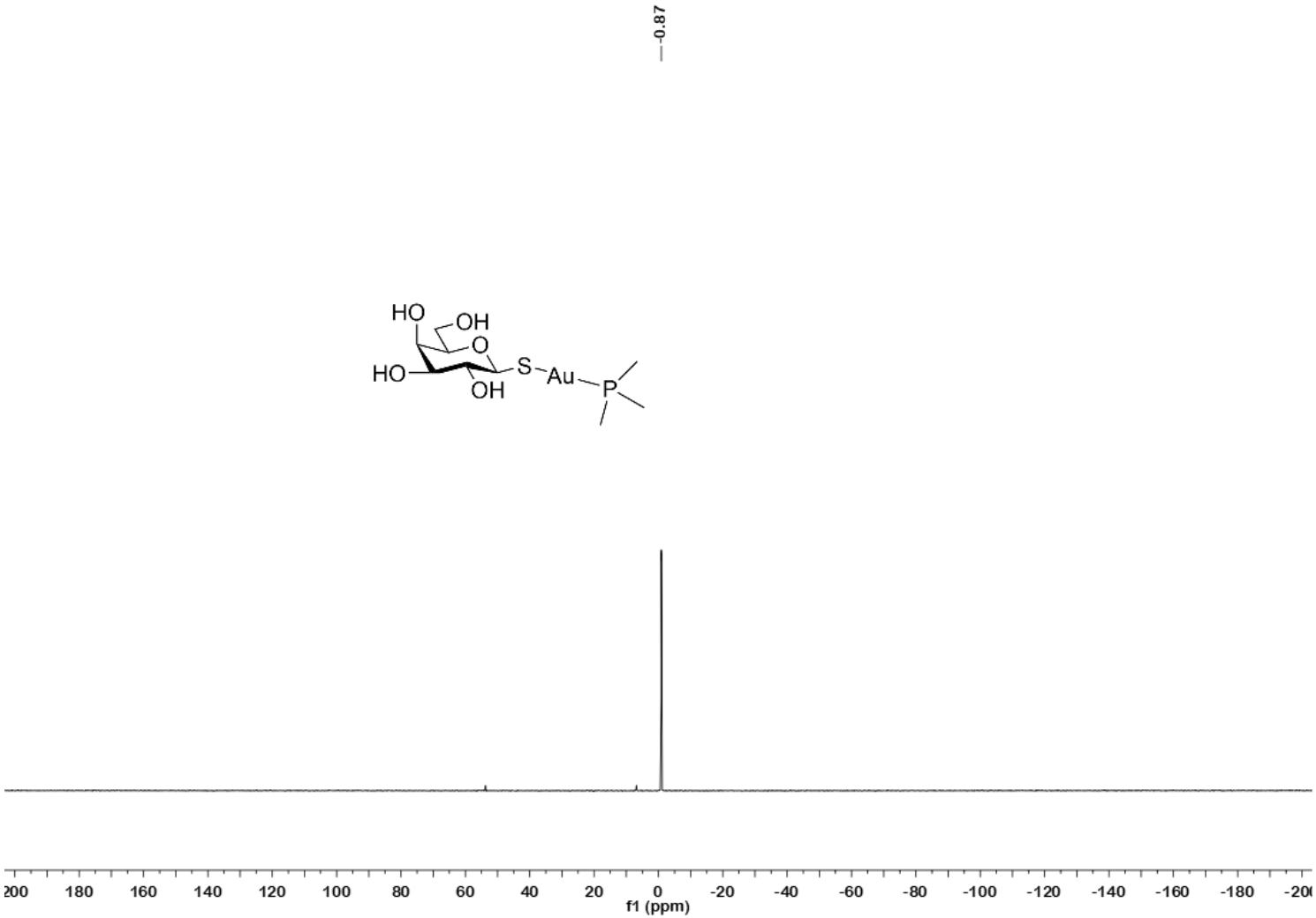


Figure S135. ^{31}P NMR spectrum of compound **38** in D_2O.

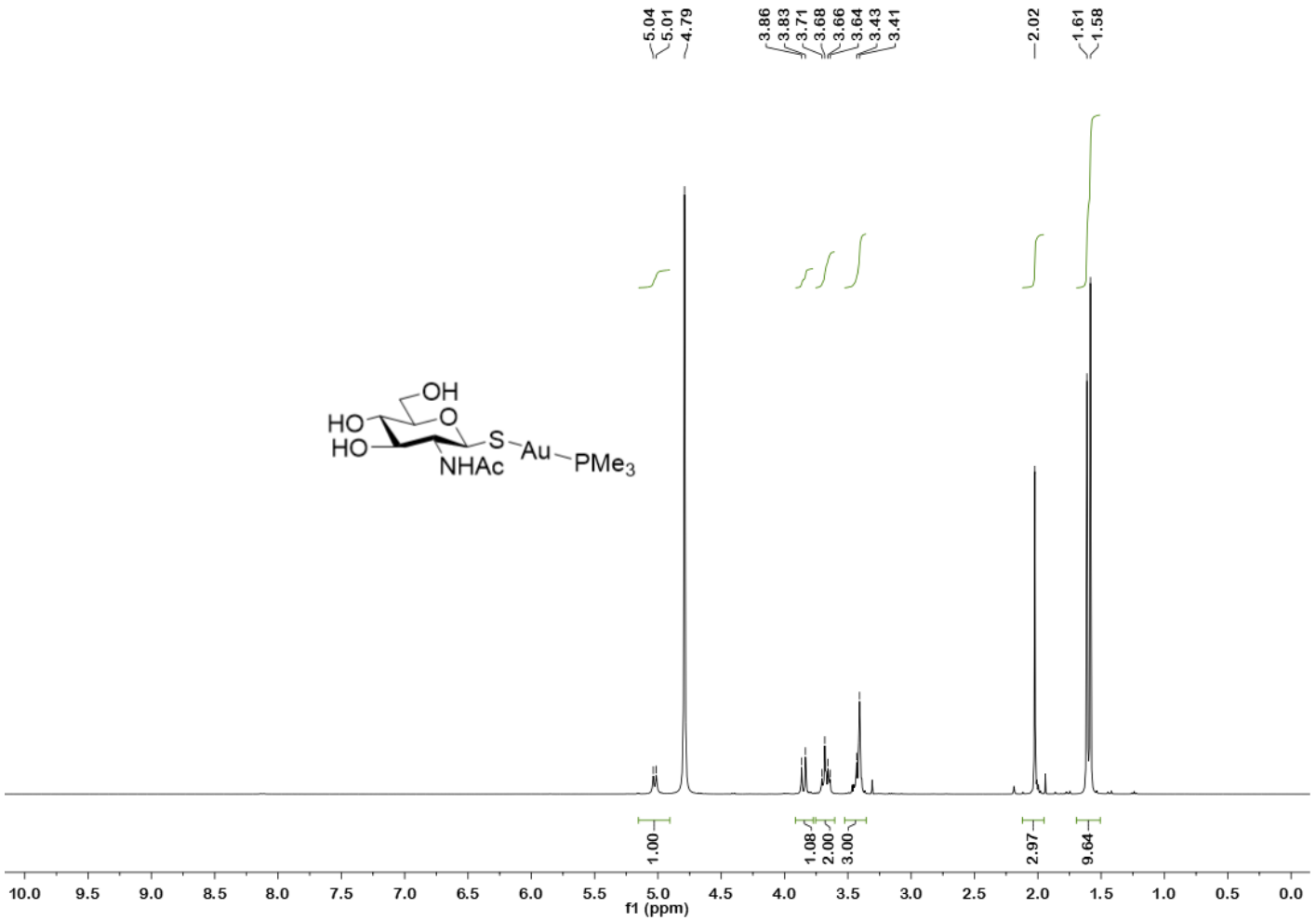


Figure S136. ^{1}H NMR spectrum of compound **39** in D_2O

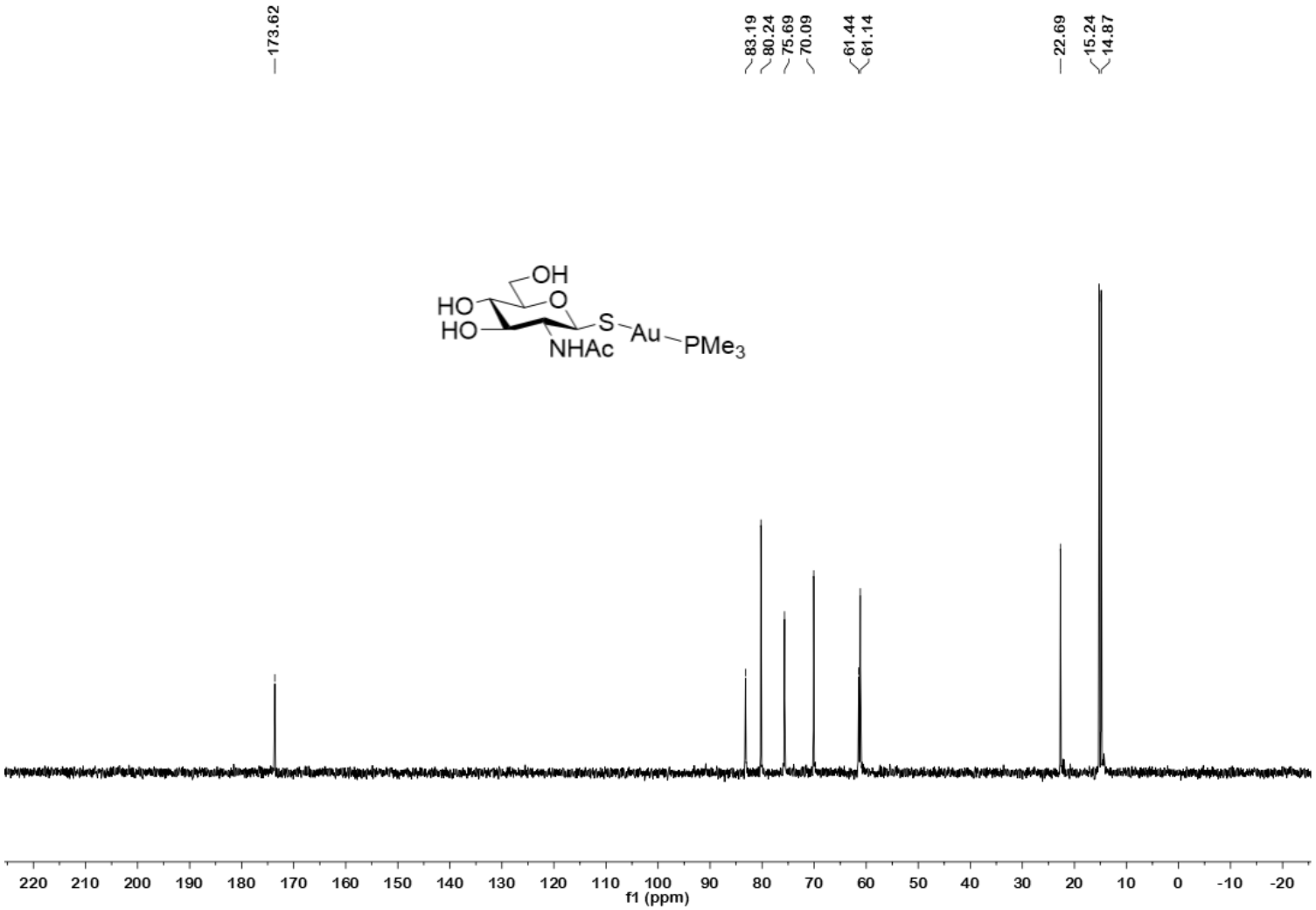


Figure S137. ^{13}C NMR spectrum of compound **39** in D_2O.

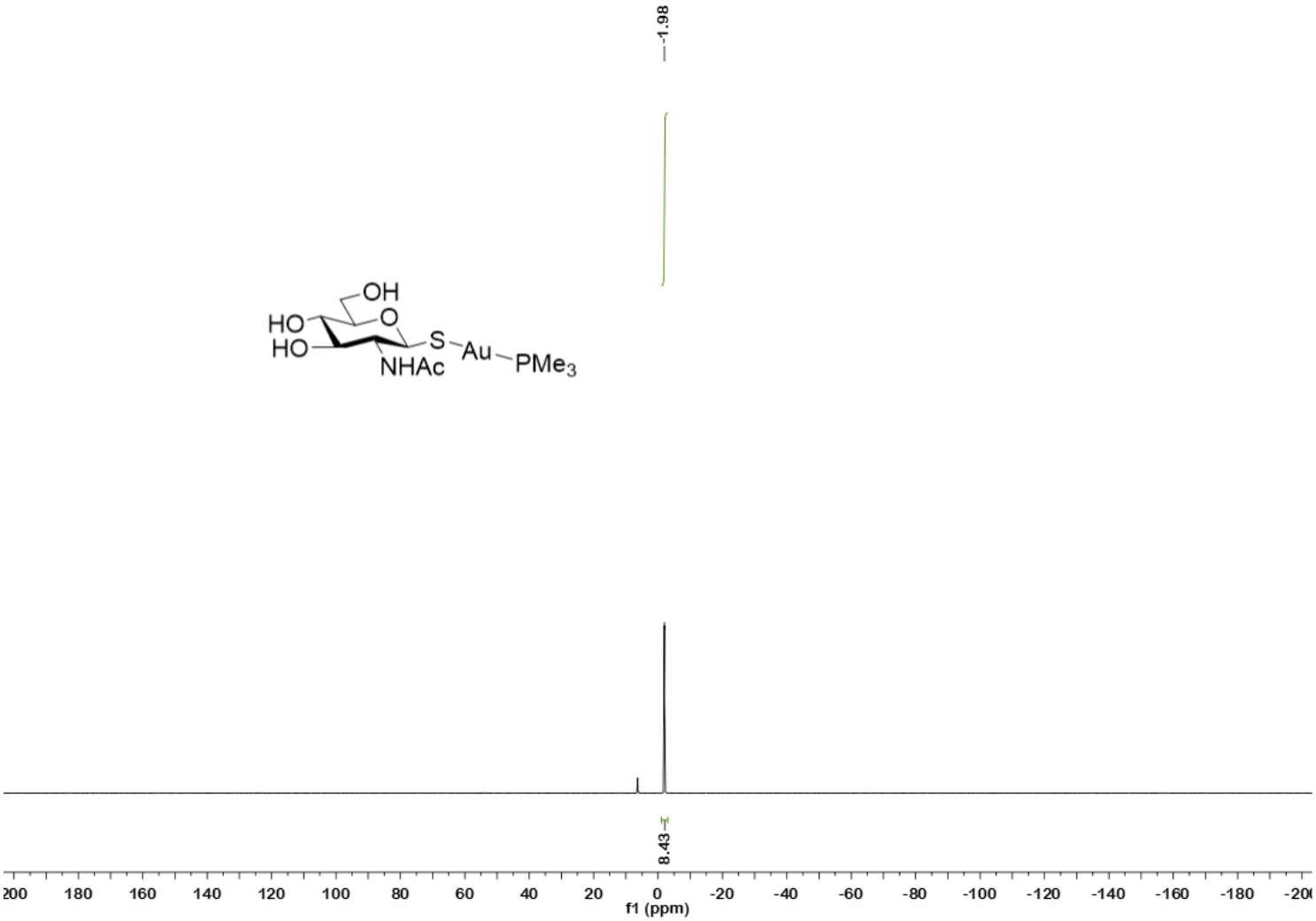


Figure S138. ^{31}P NMR spectrum of compound **39** in D_2O.

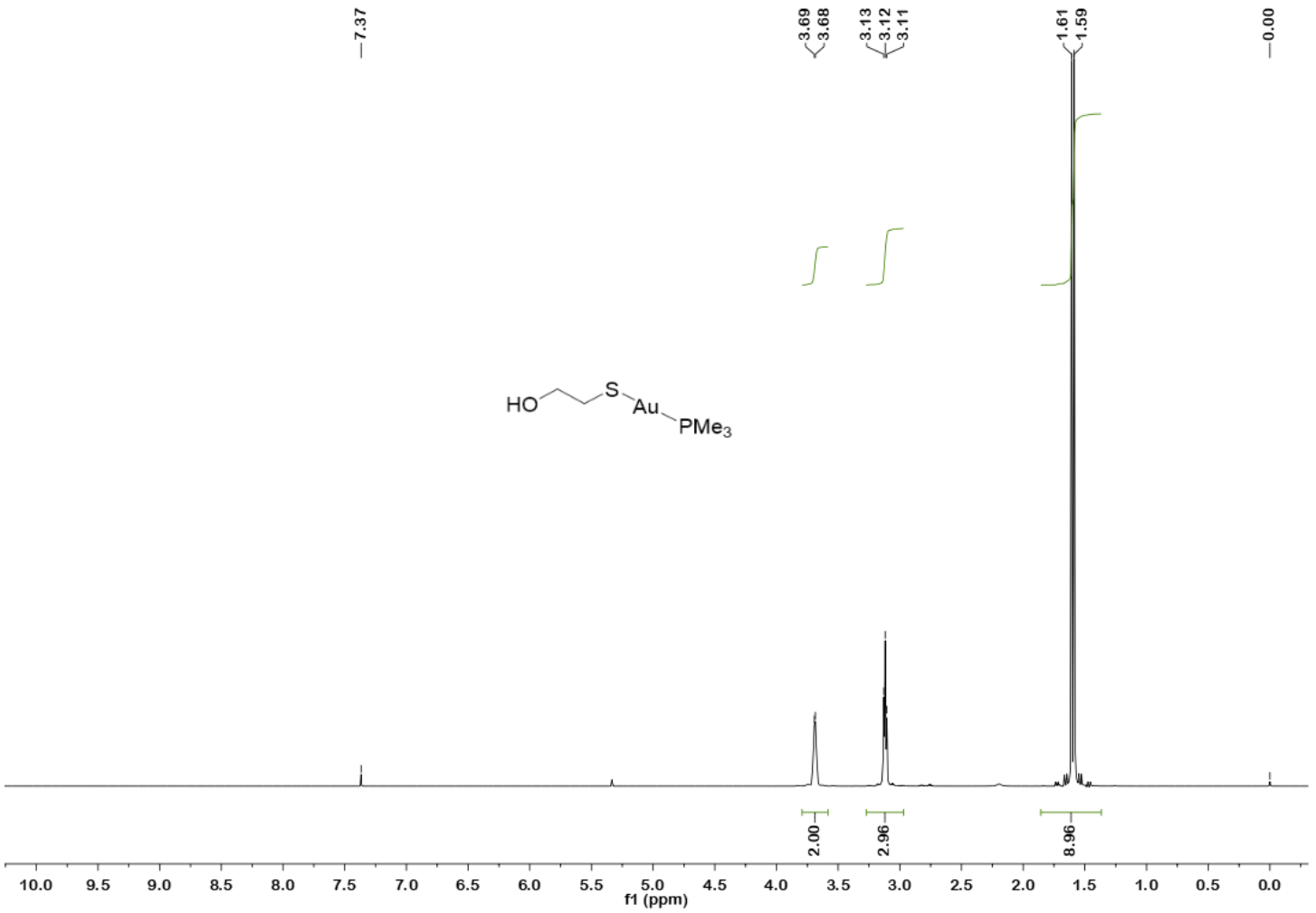


Figure S139. ^{1}H NMR spectrum of compound **40** in $CDCl_3$.

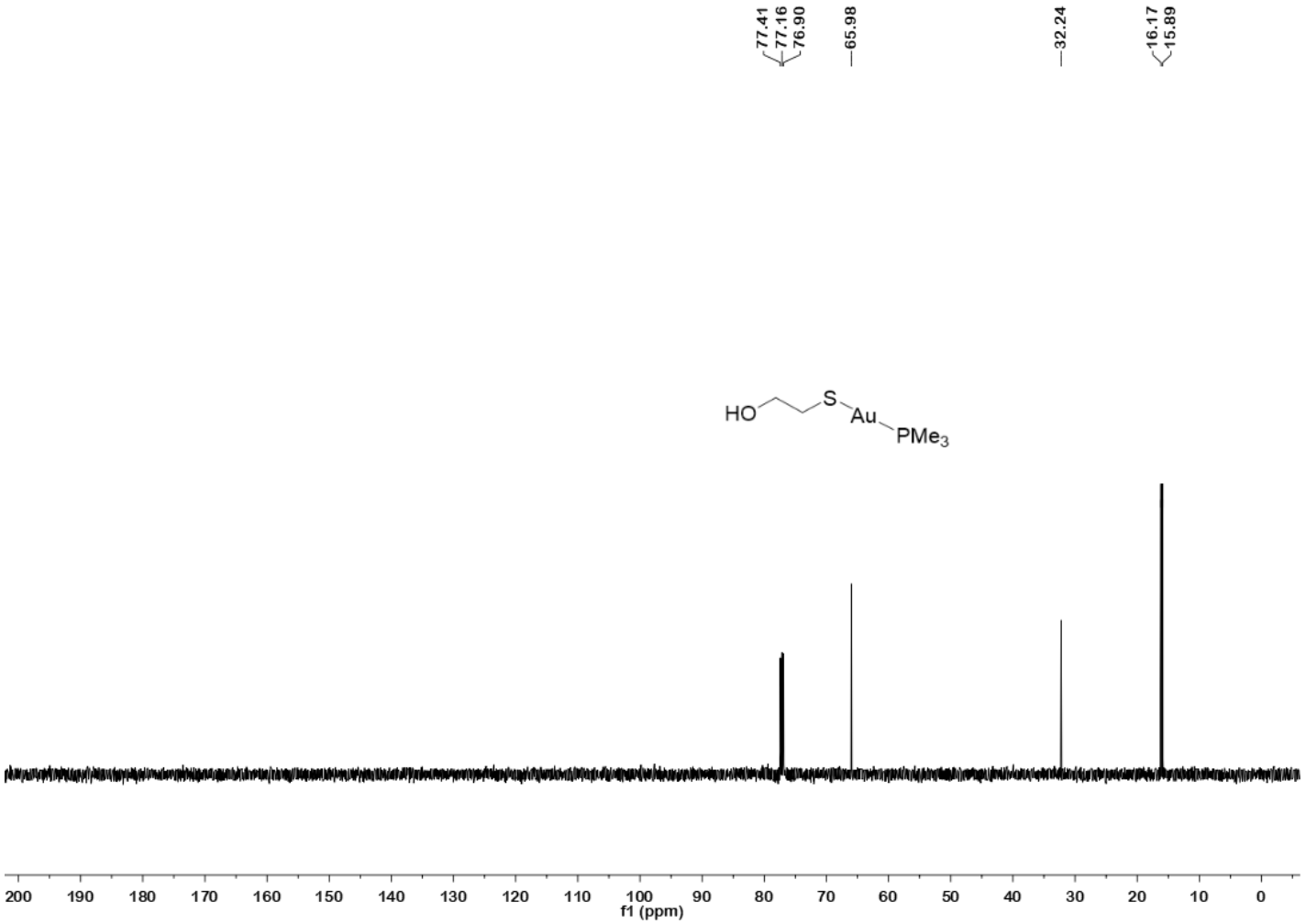


Figure S140. ^{13}C NMR spectrum of compound **40** in in $CDCl_3$.

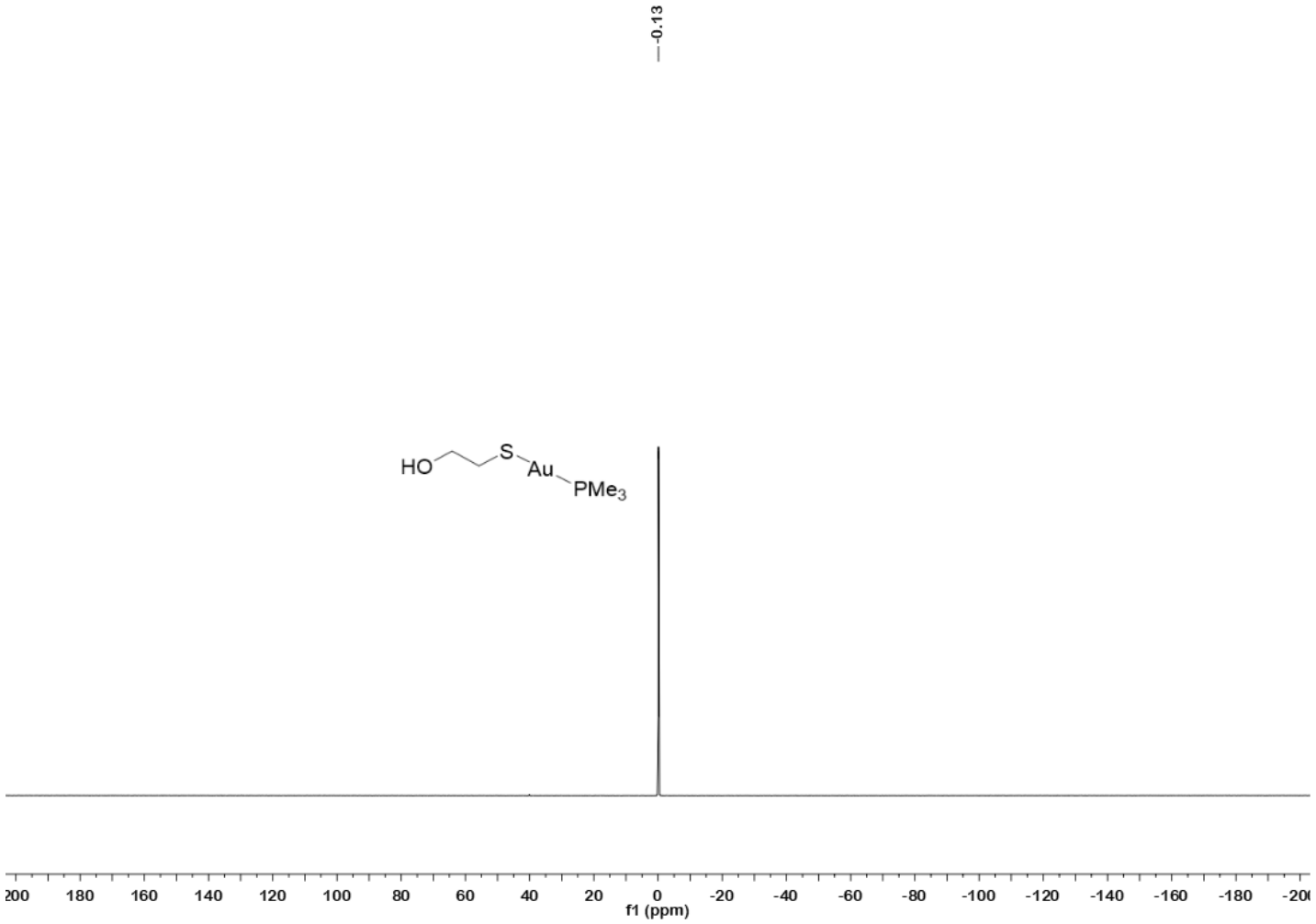
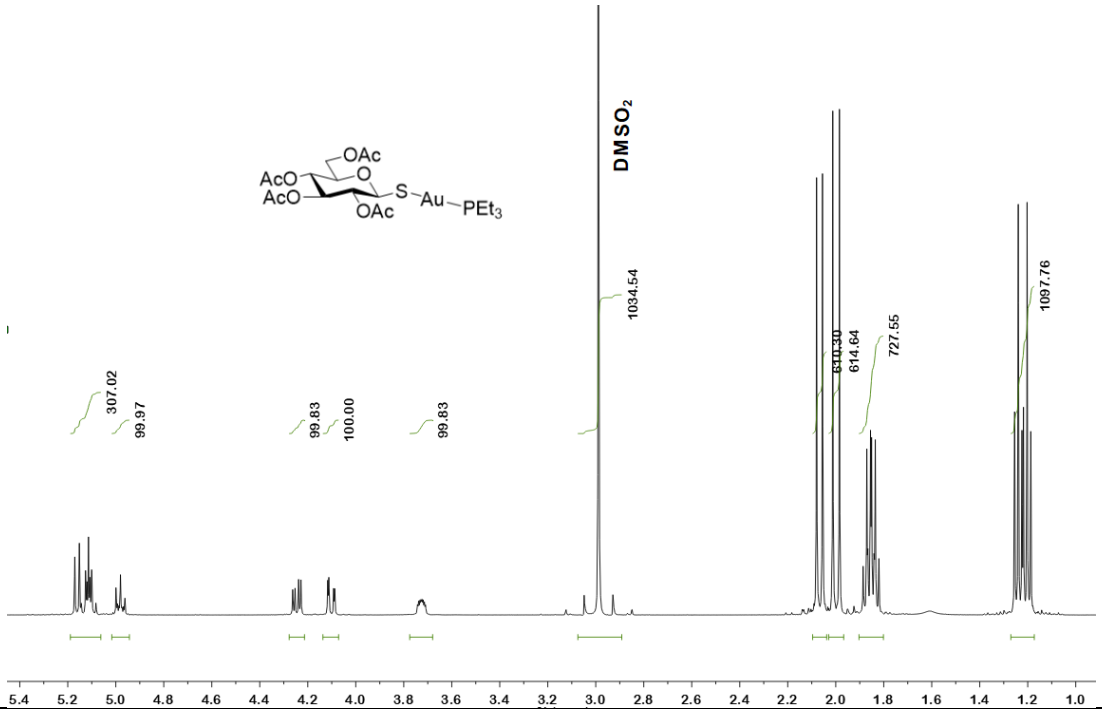


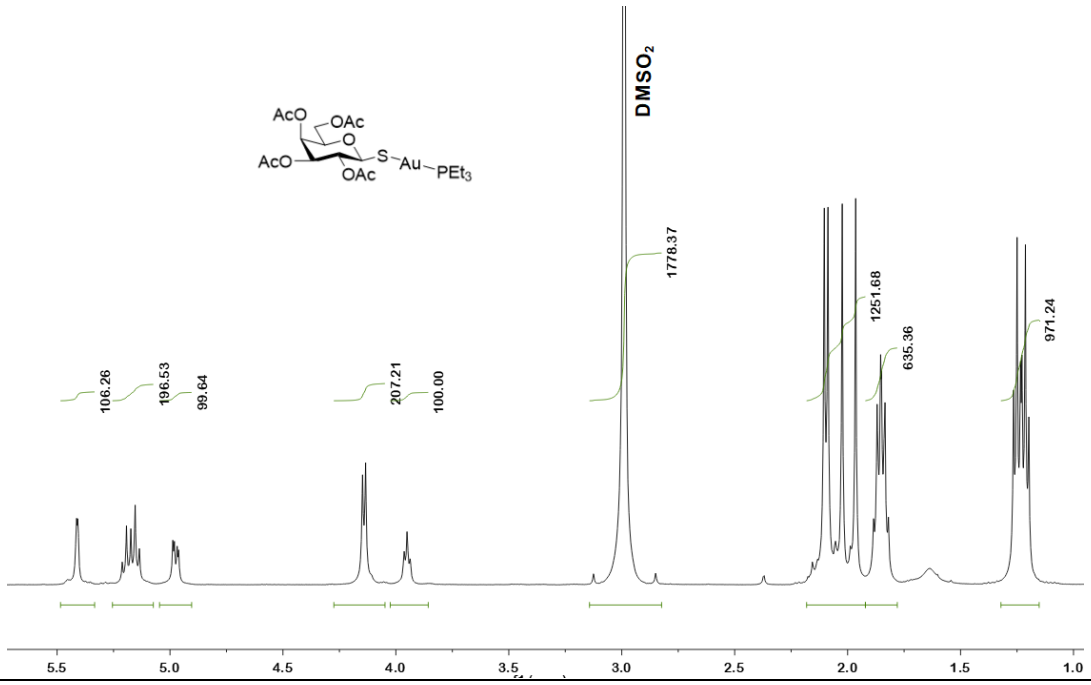
Figure S141. ^{31}P NMR spectrum of compound **40** in in $CDCl_3$.

Determination of purity of Compounds 1 – 40 by qHNMR.

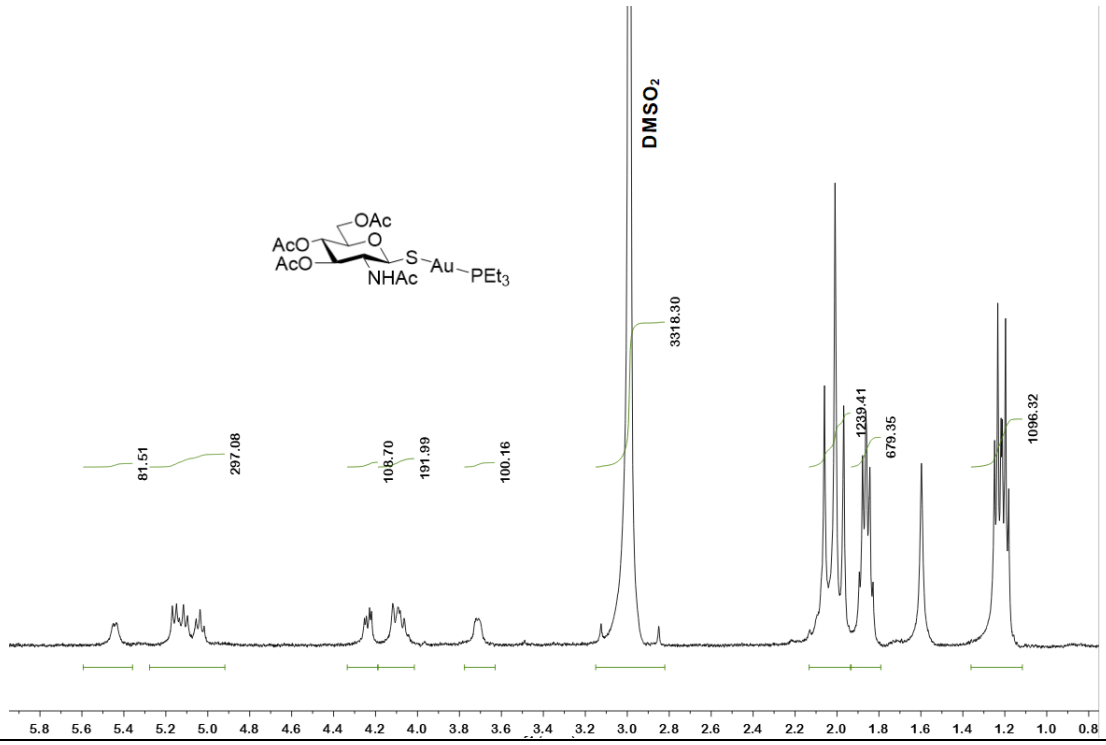
Compound **1** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 9.36 mg, $\boldsymbol{m_{IC}}$ = 1.93 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 110.49, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1034.54, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 678.48 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.1\ \%$
Note	The integral of target analyte was calculated as the average of signals at 5.19-5.07, 4.24, 4.10, 3.73, 2.08, 2.06, 2.01,1.98, 1.85 and 1.22 ppm.

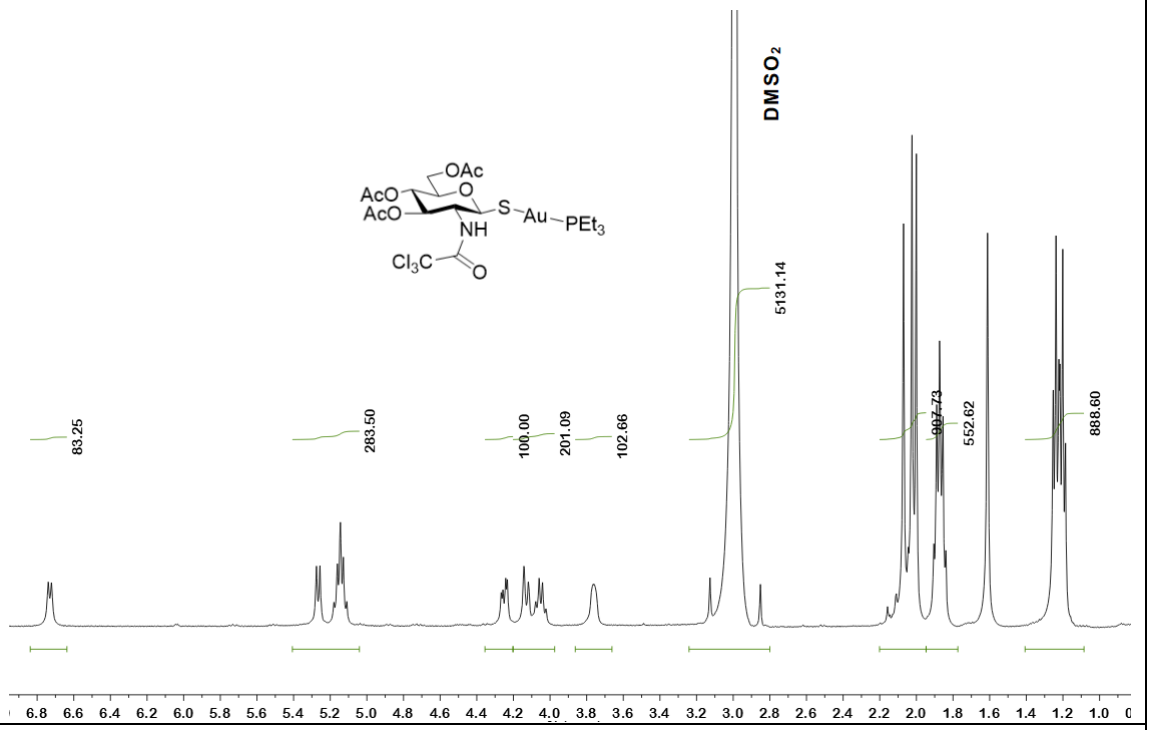
Compound **2** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 8.64 mg, $\boldsymbol{m_{IC}}$ = 3.21 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 104.94, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1778.37, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 678.48 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 94.8\%$
Note	The integral of target analyte was calculated as the average of signals at 5.41, 5.24-5.08, 4.97, 4.14, 3.95, 2.10, 2.09, 2.02, 1.96, 1.85 and 1.23 ppm.

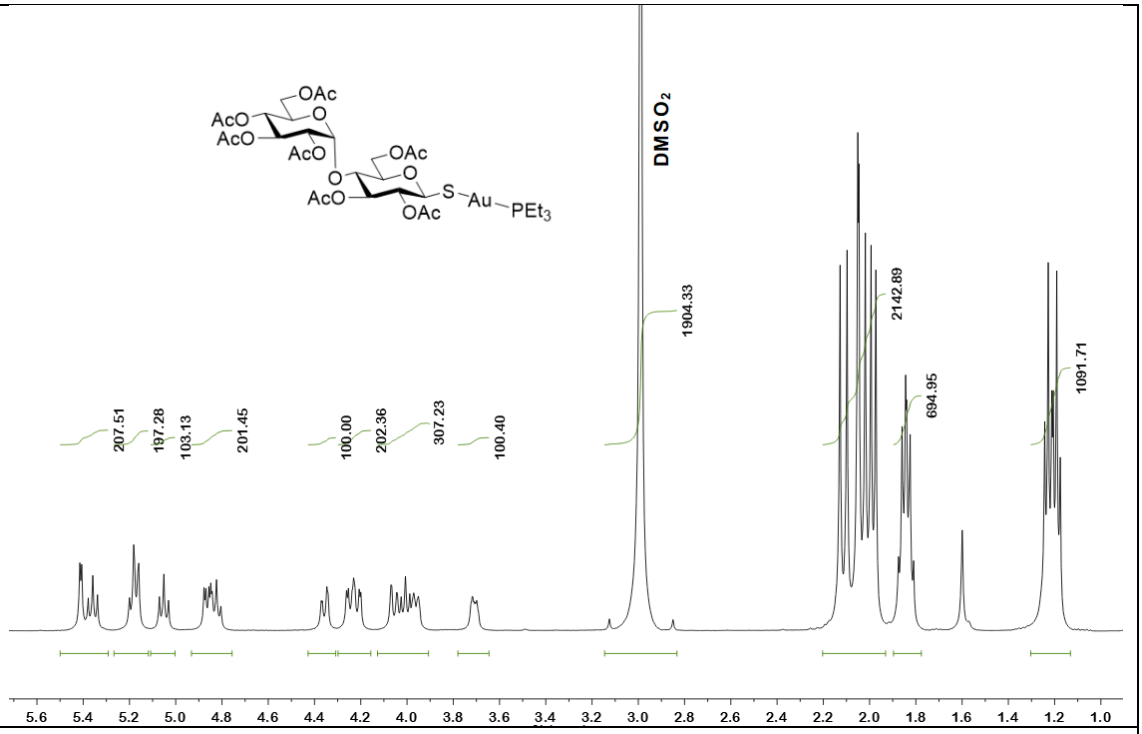
Compound **3** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 3.36 mg, $\boldsymbol{m_{IC}}$ = 2.25 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 109.21, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 3318.30, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 677.50 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.2\%$
Note	The integral of target analyte was calculated as the average of signals at 5.41, 5.24-5.08, 4.97, 4.14, 3.95, 2.10, 2.09, 2.02, 1.96, 1.85 and 1.23 ppm.

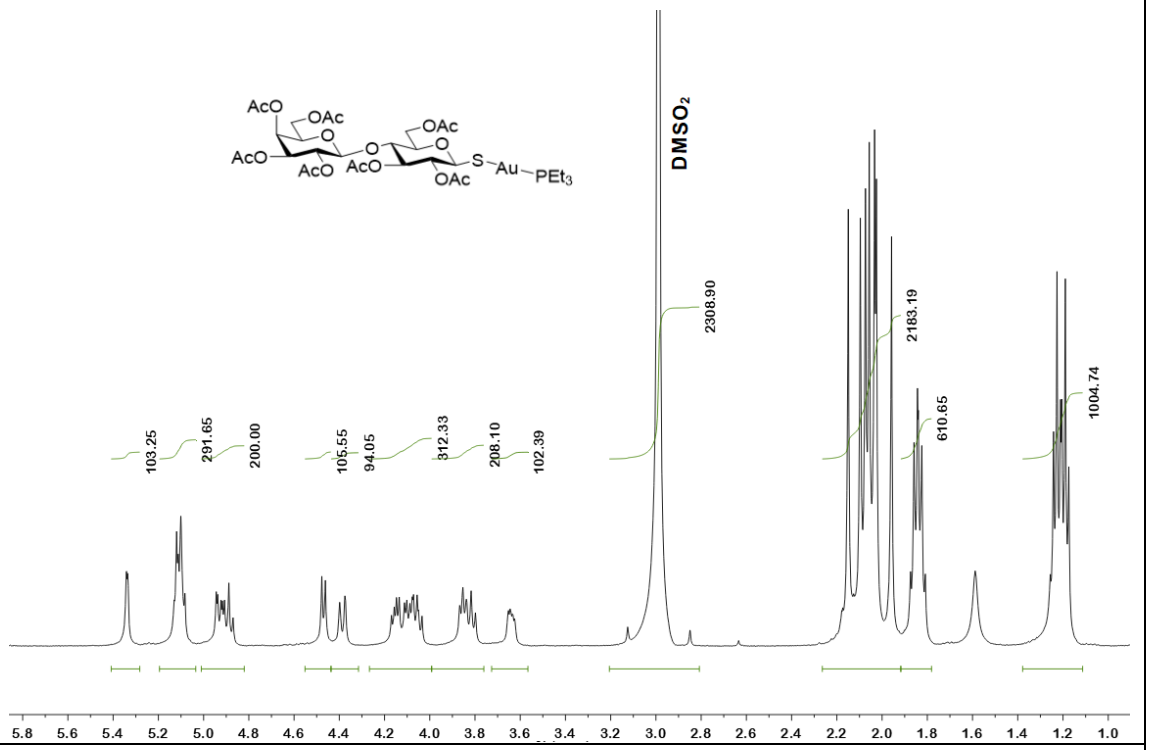
Compound **4** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 4.14 mg, $\boldsymbol{m_{IC}}$ = 4.22 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 98.18, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 5131.14, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 780.83 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 97.1\%$
Note	The integral of target analyte was calculated as the average of signals at 5.26, 5.14, 4.25, 4.13, 4.05 and 3.17 ppm.

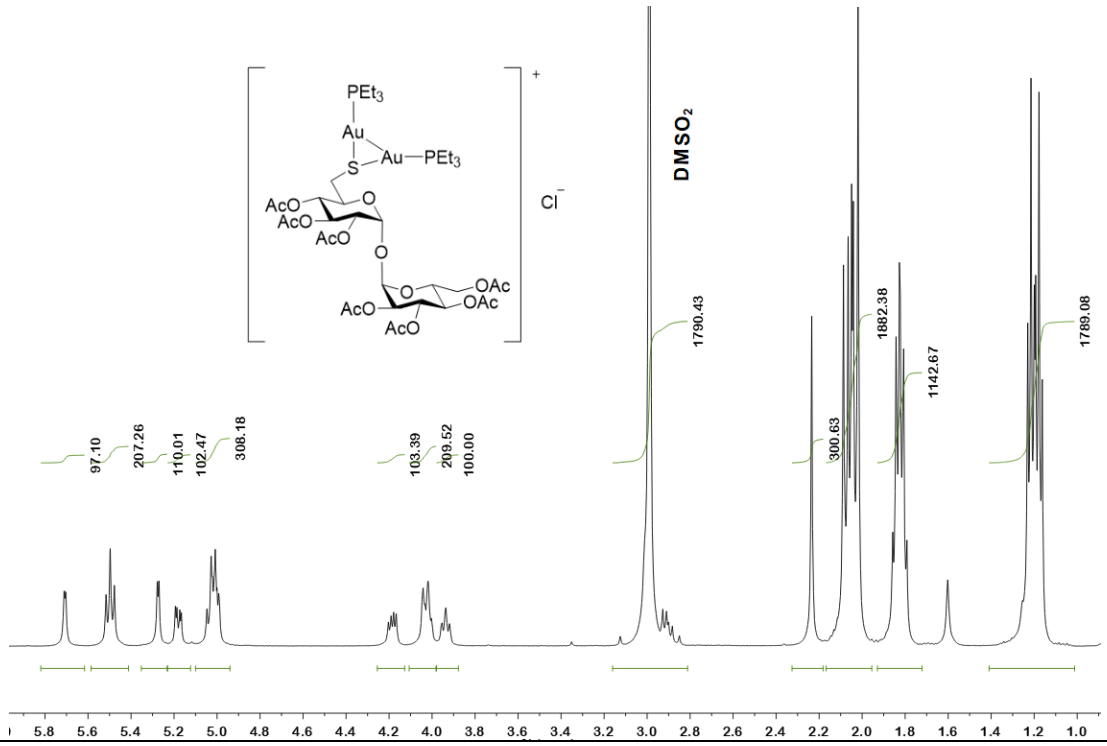
Compound **5** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 8.51 mg, $\boldsymbol{m_{IC}}$ = 2.36 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 107.33, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1904.33, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 966.74 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 96.3\%$
Note	The integral of target analyte was calculated as the average of signals at 5.41, 5.36, 5.23-5.13, 5.05, 4.86, 4.81, 4.36, 4.30-4.15, 4.06, 4.01, 3.96, 3.71, 2.13, 2.05, 2.02, 1.99, 1.97, 1.84 and 1.21 ppm.

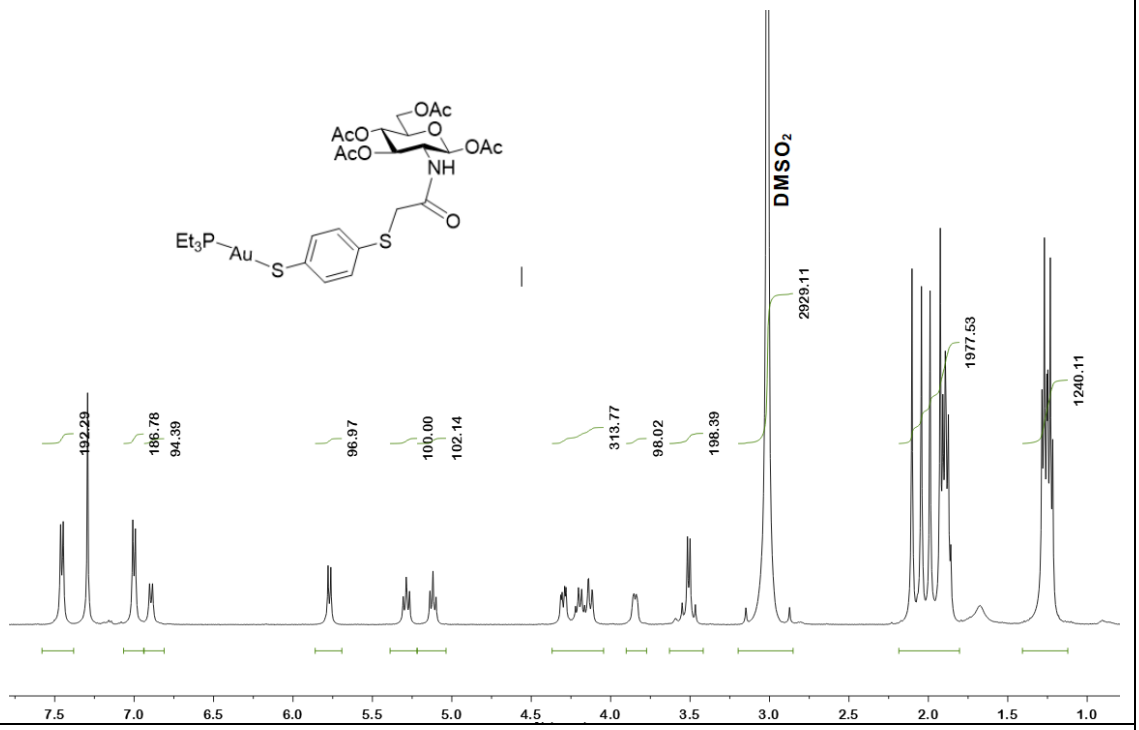
Compound **6** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 5.13 mg, $\boldsymbol{m_{IC}}$ = 1.76 mg, $\boldsymbol{P_{IC}}$= 100.0%
Step 2	$\boldsymbol{Int_t}$ = 104.32, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 2308.90, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 966.74 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.5\%$
Note	The integral of target analyte was calculated as the average of signals at 5.34, 5.20-5.05, 4.93, 4.86, 4.43, 3.95-3.75, 3.64, 2.15, 2.10, 2.07, 2.06, 2.03, 2.03, 1.96, 1.84 and 1.21 ppm.

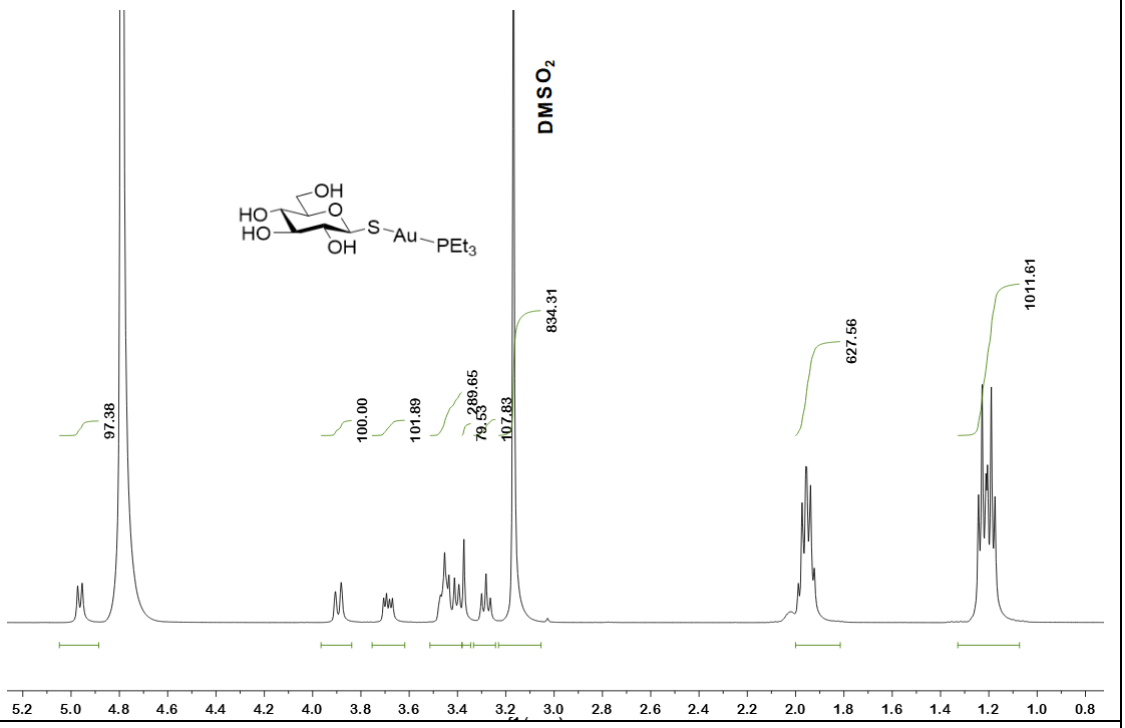
Compound **7** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 10.52 mg, $\boldsymbol{m_{IC}}$ = 1.88 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 100.83, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1588.77, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 1317.31 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.2\%$
Note	The integral of target analyte was calculated as the average of signals at and 1.21 ppm.

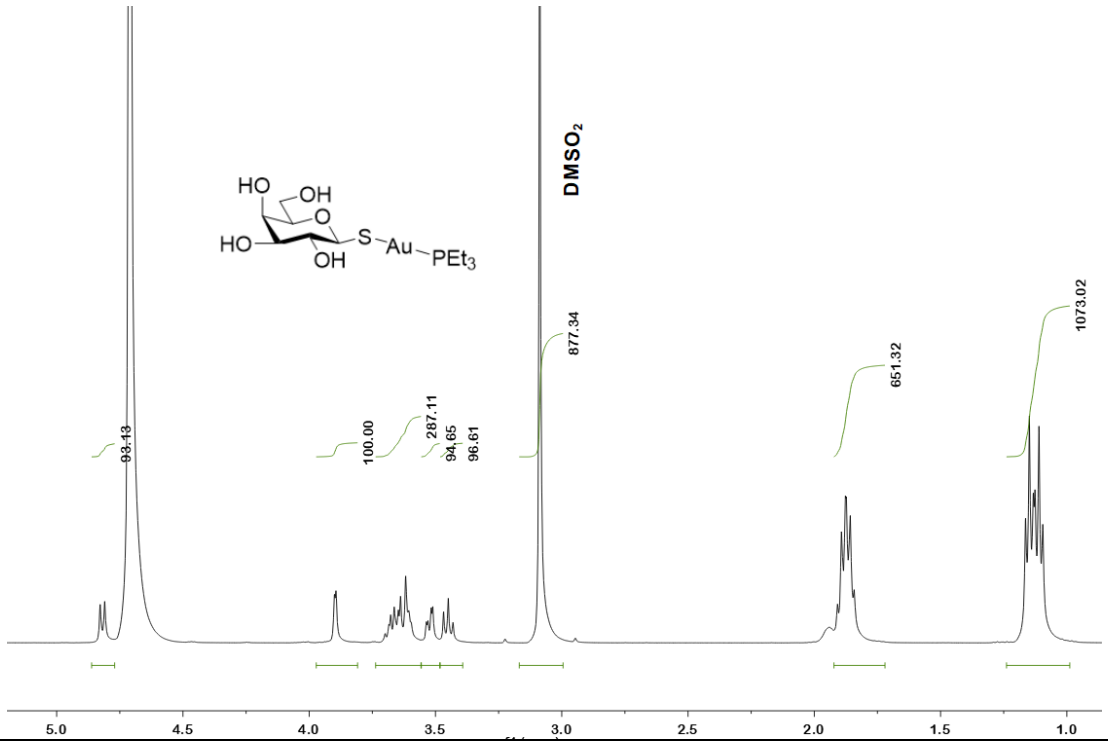
Compound **8** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 8.24 mg, $\boldsymbol{m_{IC}}$ = 4.02 mg, $\boldsymbol{P_{IC}}$= 100.0%
Step 2	$\boldsymbol{Int_t}$ = 112.65, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 2929.11, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 843.69 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.0\%$
Note	The integral of target analyte was calculated as the average of signals at 7.45, 7.00, 5.77, 5.29, 5.12, 4.3, 4.19, 4.13 3.85, 3.51, 2.10, 2.04, 1.99, ,1.92, 1.89 and 1.25 ppm.

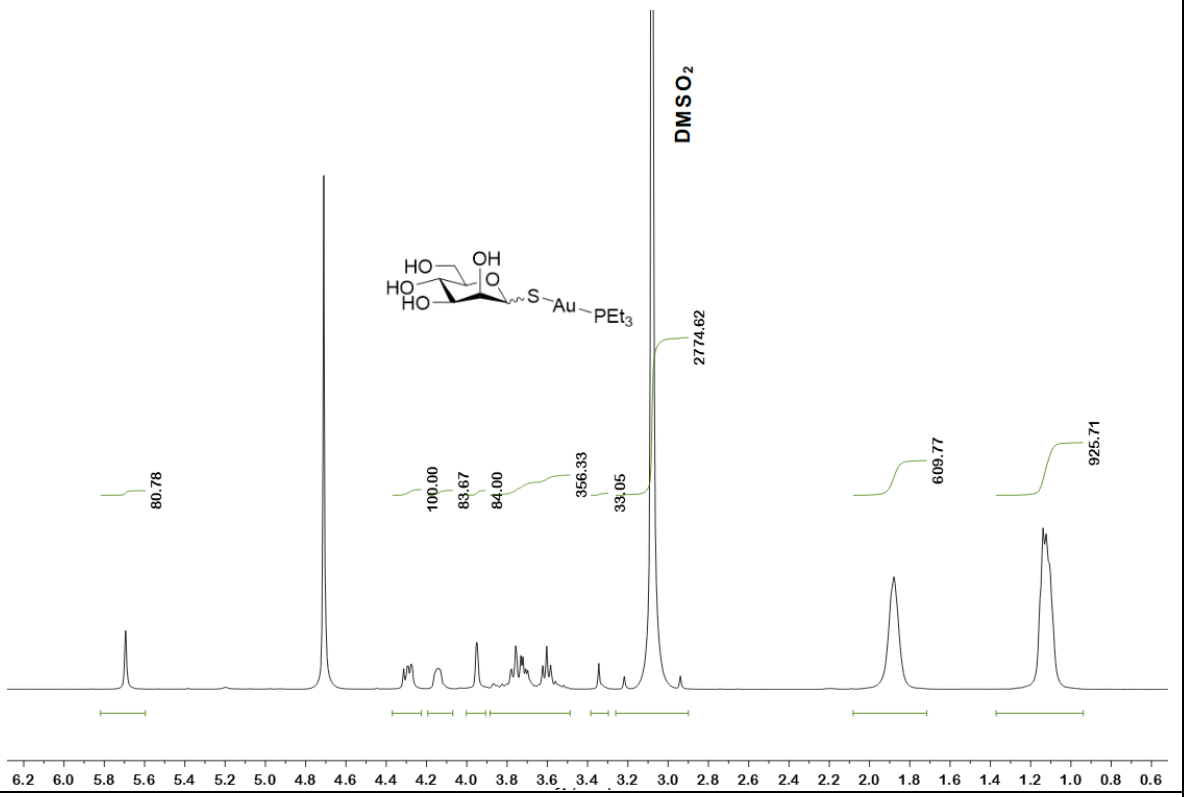
Compound **9** in D_2O with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 11.89 mg, $\boldsymbol{m_{IC}}$ = 2.73 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 109.13, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 834.31, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 510.34 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 97.7\ \%$
Note	The integral of target analyte was calculated as the average of signals at 4.96, 3.90, 3.69, 3.28 and 1.21 ppm.

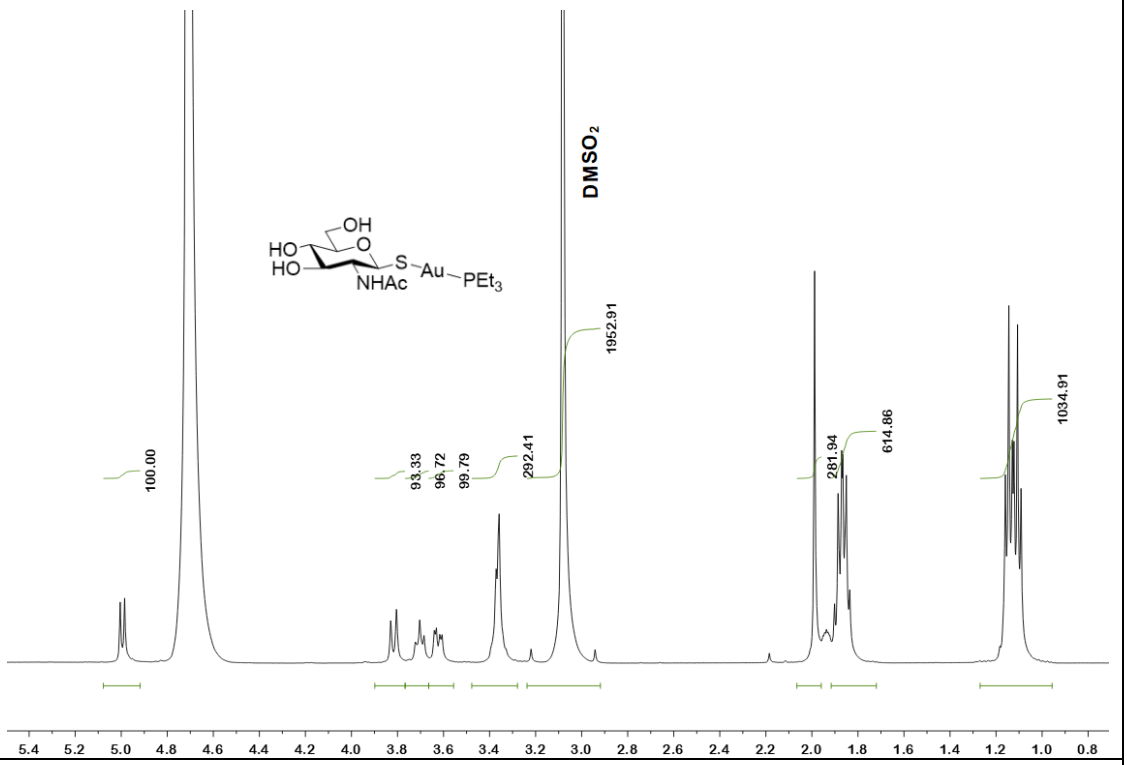
Compound **10** in D_2O with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 12.05 mg, $\boldsymbol{m_{IC}}$ = 2.84 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 110.09, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 877.34, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 510.34 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 96.2\ \%$
Note	The integral of target analyte was calculated as the average of signals at 3.98, 3.80-3.64, 3.60, 3.53 and 1.21 ppm.

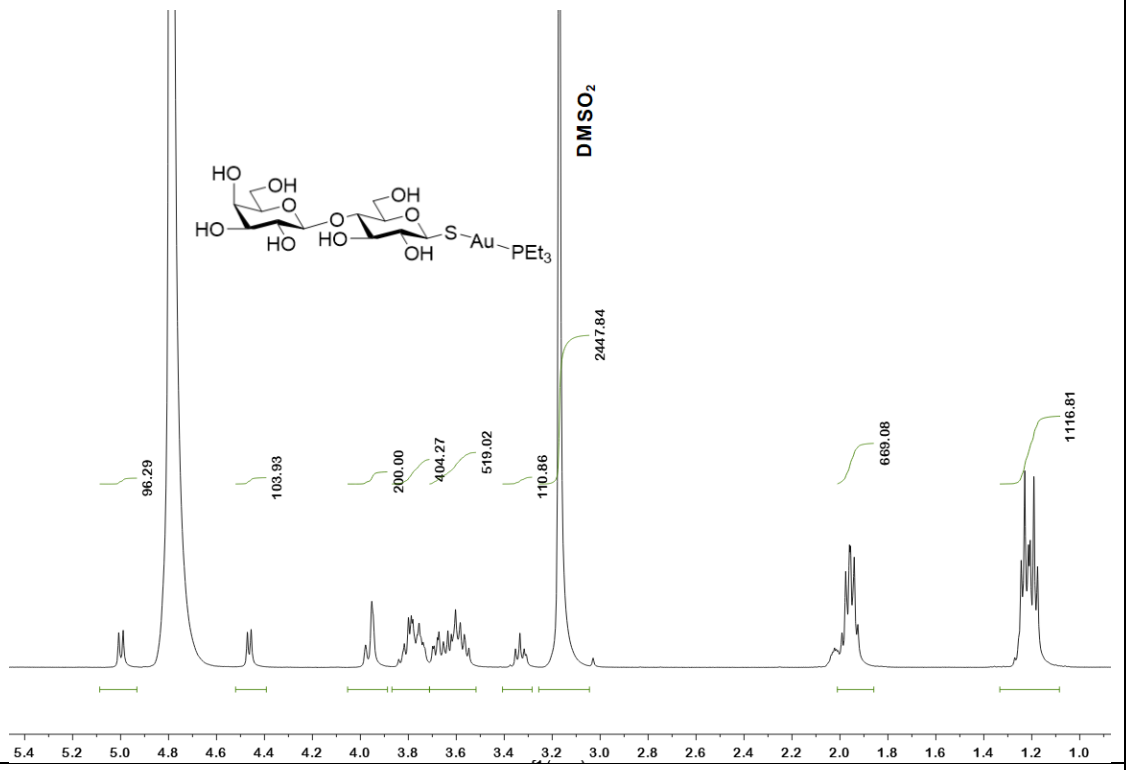
Compound **11** in D_2O with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 7.63 mg, $\boldsymbol{m_{IC}}$ = 6.19 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 102.17, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 2774.62, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 510.34 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 97.2\ \%$
Note	The integral of target analyte was calculated as the average of signals at 4.41-4.32, 1.96 and 1.20 ppm.

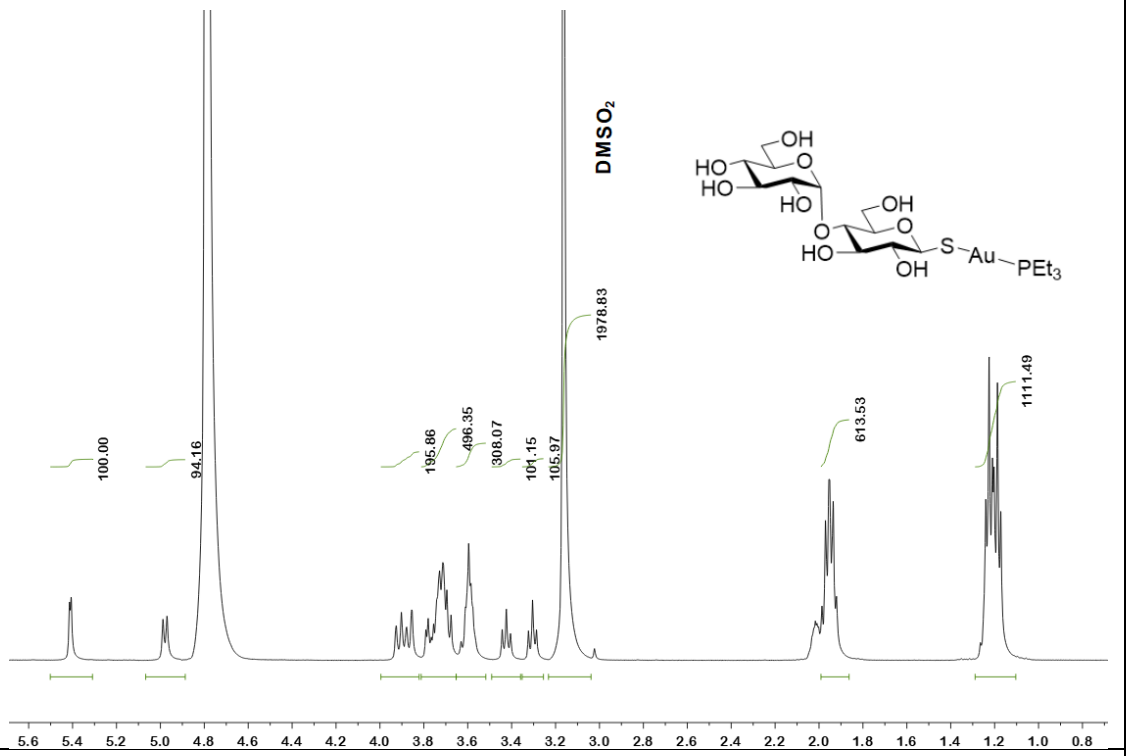
Compound **12** in D_2O with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 6.62 mg, $\boldsymbol{m_{IC}}$ = 3.32 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 107.32, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1952.91, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 551.39 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 96.9\ \%$
Note	The integral of target analyte was calculated as the average of signals at 5.07, 3.90, 3.78, 3.70, 3.53-3.35 and 1.20 ppm.

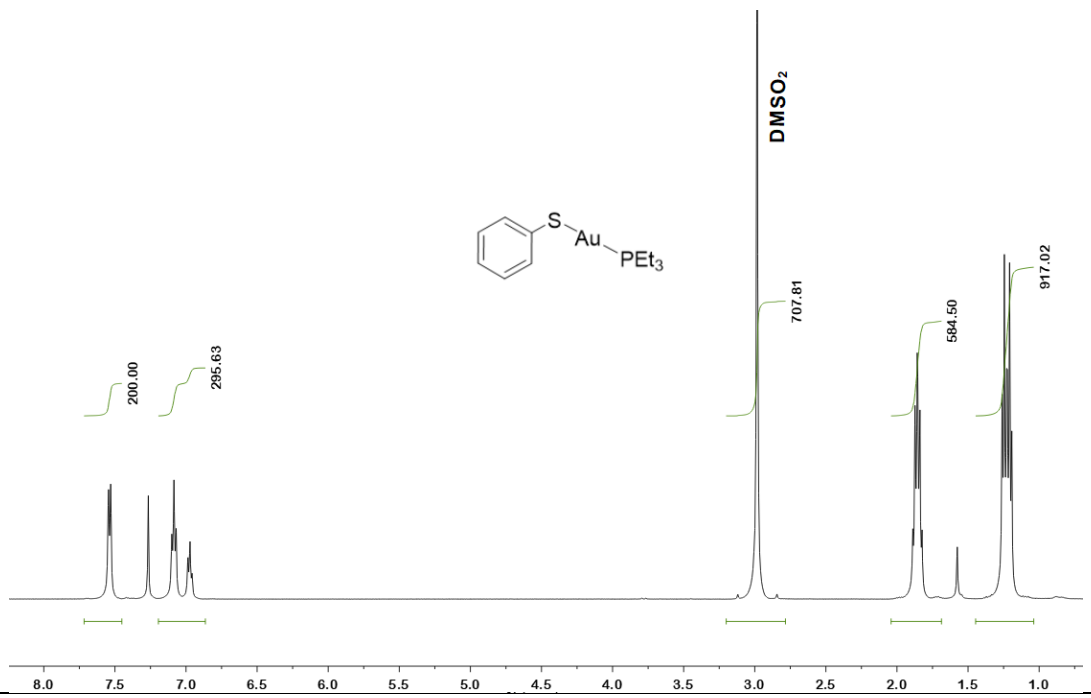
Compound **13** in D_2O with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 5.63 mg, $\boldsymbol{m_{IC}}$ = 2.76 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 110.92, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 2447.84, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 672.48 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.2\ \%$
Note	The integral of target analyte was calculated as the average of signals at 5.00, 4.47, 4.03-3.89, 3.86-3.71, 3.71-3.51 and 1.21 ppm.

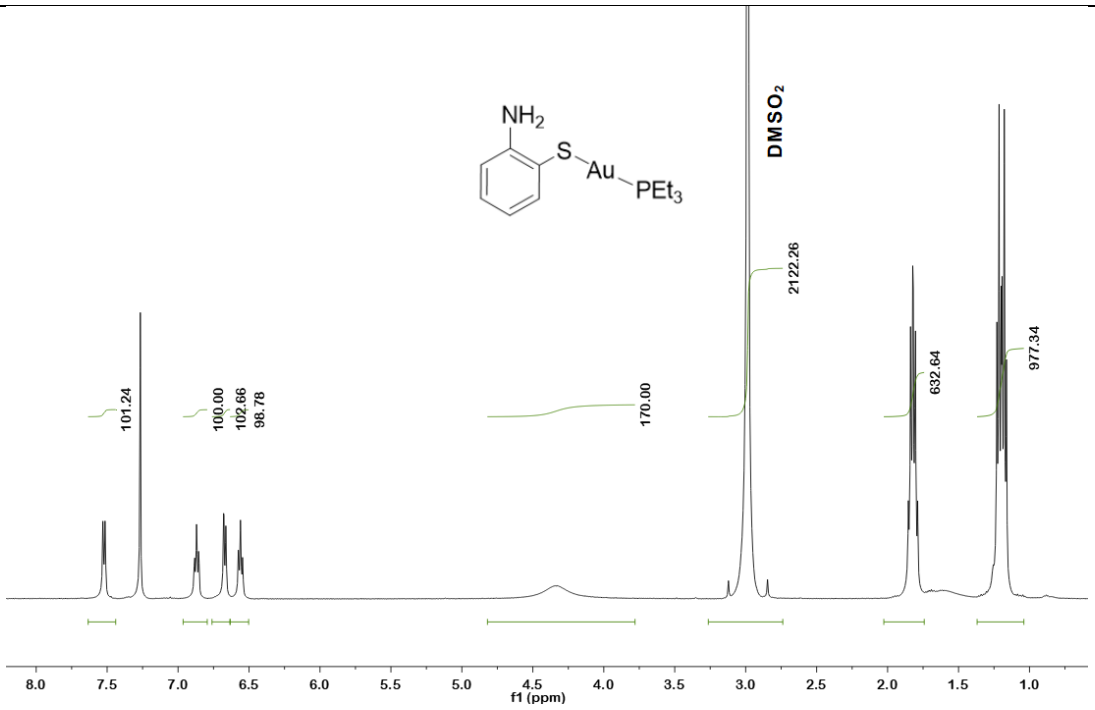
Compound **14** in D_2O with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 6.22 mg, $\boldsymbol{m_{IC}}$ = 2.52 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 109.26, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1978.83, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 672.48 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.9\%$
Note	The integral of target analyte was calculated as the average of signals at 5.41, 4.98, 3.91, 3.87, 3.81-3.65, 3.64-3.52, 3.42, 3.30 and 1.21 ppm.

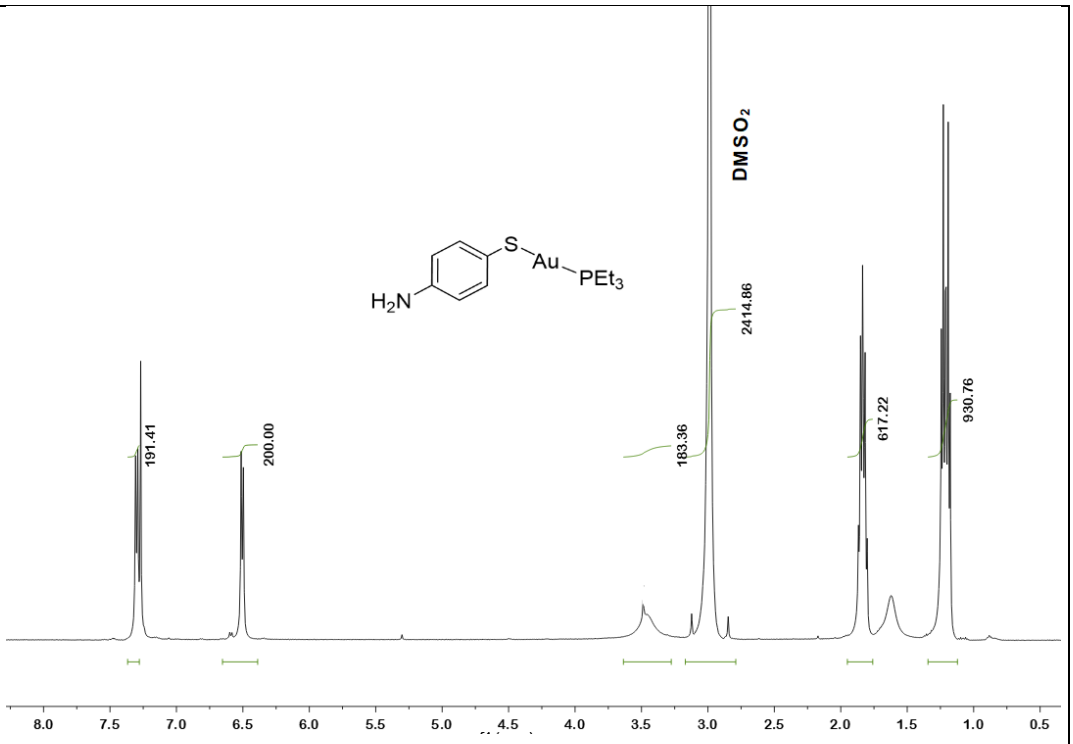
Compound **15** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 8.73 mg, $\boldsymbol{m_{IC}}$ = 2.19 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 99.86, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 707.81, $\mathbf{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 424.29 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.7\%$
Note	The integral of target analyte was calculated as the average of signals at 7.54, 7.09, 6.97, 1.86 and 1.23 ppm.

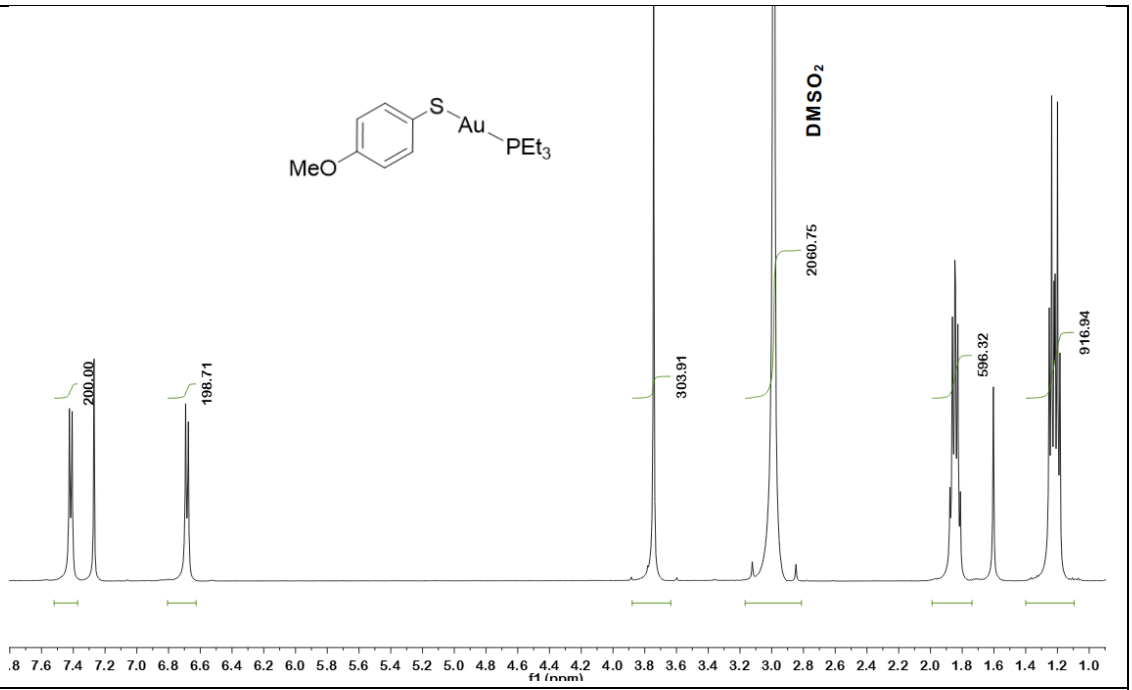
Compound **16** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 4.79 mg, $\boldsymbol{m_{IC}}$ = 3.45 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 103.53, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 2122.26, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 439.31 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 98.4\ \%$
Note	The integral of target analyte was calculated as the average of signals at 7.52,6.87,6.67,6.56 and 1.82 ppm

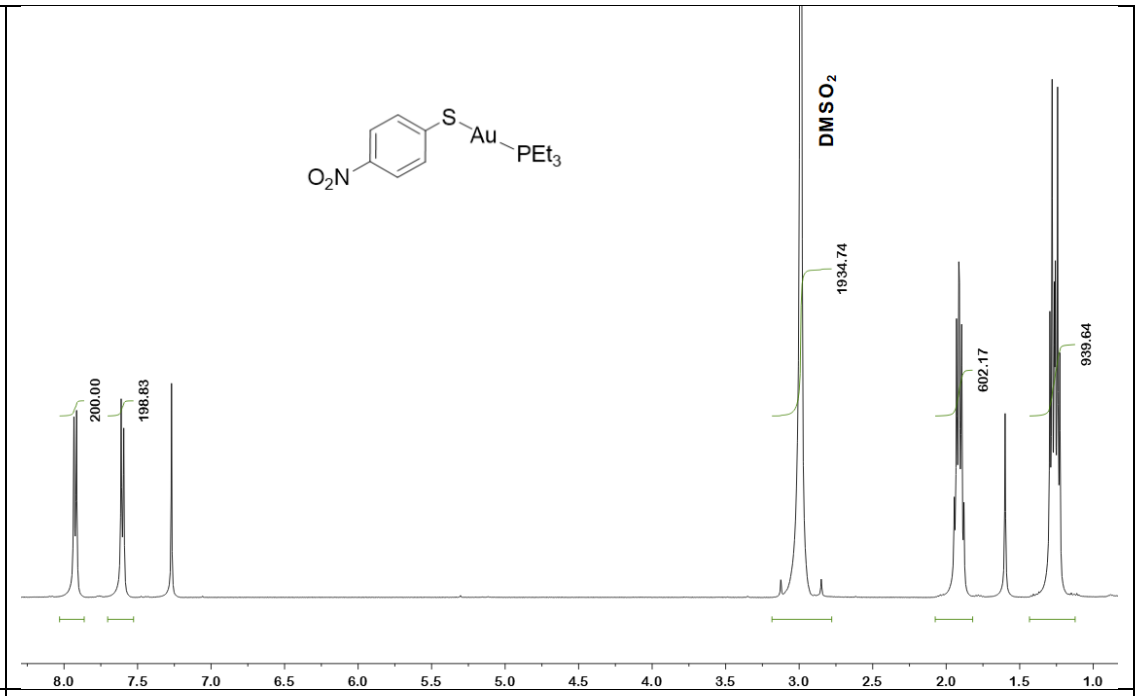
Compound **17** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 4.96 mg, $\boldsymbol{m_{IC}}$ = 4.08 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 102.82, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 2414.86, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 439.31 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 98.08\ \%$
Note	The integral of target analyte was calculated as the average of signals at 6.50, 1.83 and 1.21 ppm.

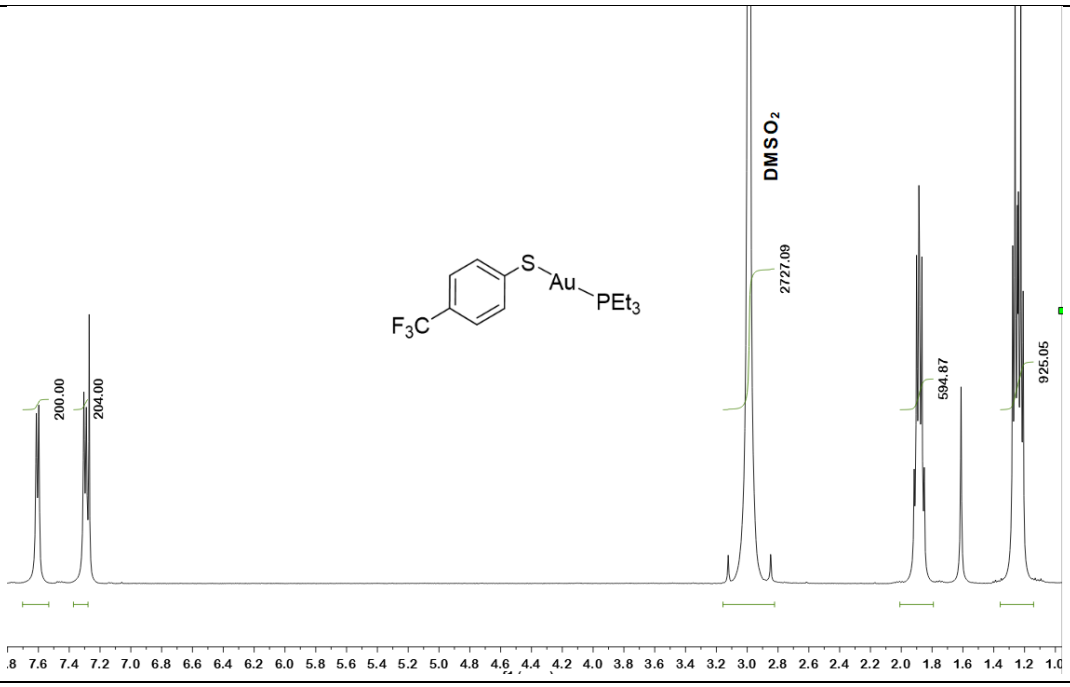
Compound **18** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 6.65 mg, $\boldsymbol{m_{IC}}$ = 4.66 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 100.70, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1030.38, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 454.32 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 99.2\ \%$
Note	The integral of target analyte was calculated as the average of signals at 7.41, 6.69, 3.74,1.84 and 1.22 ppm

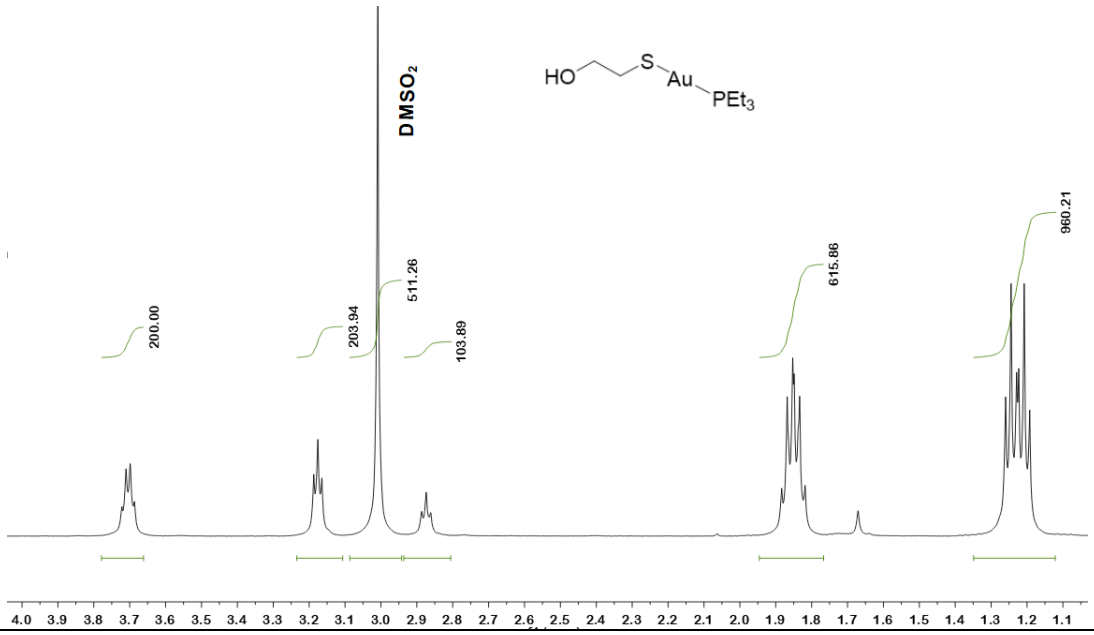
Compound **19** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 7.05 mg, $\boldsymbol{m_{IC}}$ = 4.40 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 102.14, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1934.74, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 469.29 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 98.6\ \%$
Note	The integral of target analyte was calculated as the average of signals at 7.92, 7.60,1.91 and 1.26 ppm

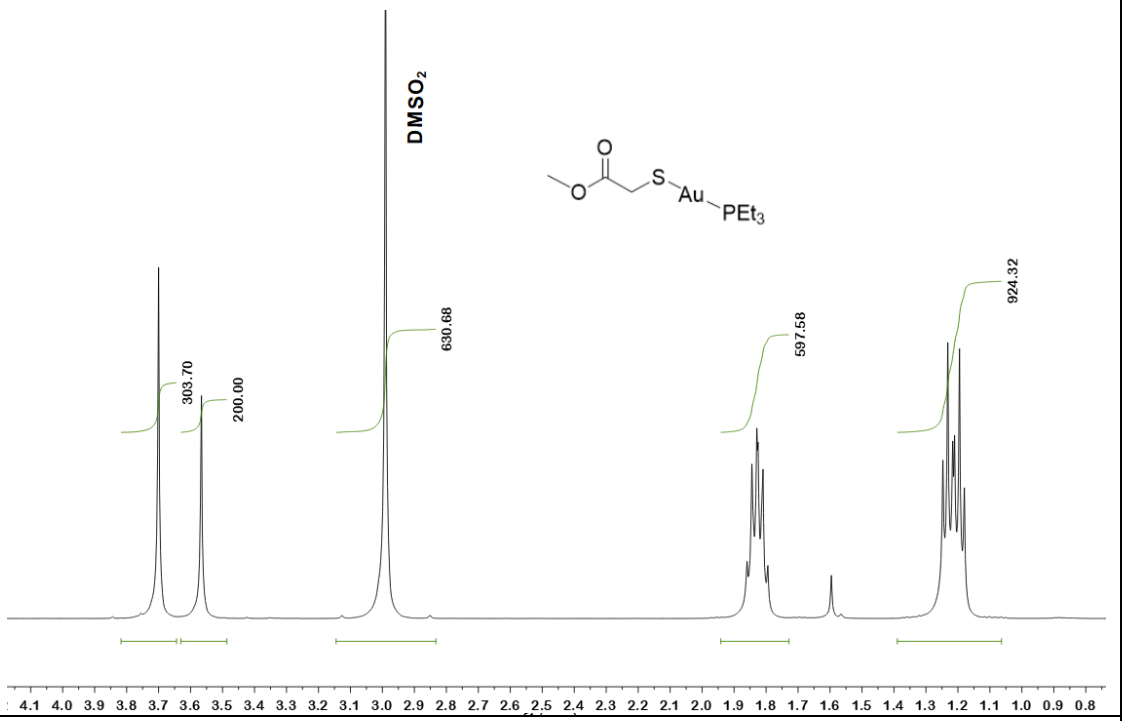
Compound **20** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 7.31 mg, $\boldsymbol{m_{IC}}$ = 6.49 mg, $\boldsymbol{P_{IC}}$ = 100%
Step 2	$\boldsymbol{Int_t}$ = 100.10, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 2754.38, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 492.29 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 101.2\%$
Note	The integral of target analyte was calculated as the average of signals at 1.89 and 7.61 ppm.

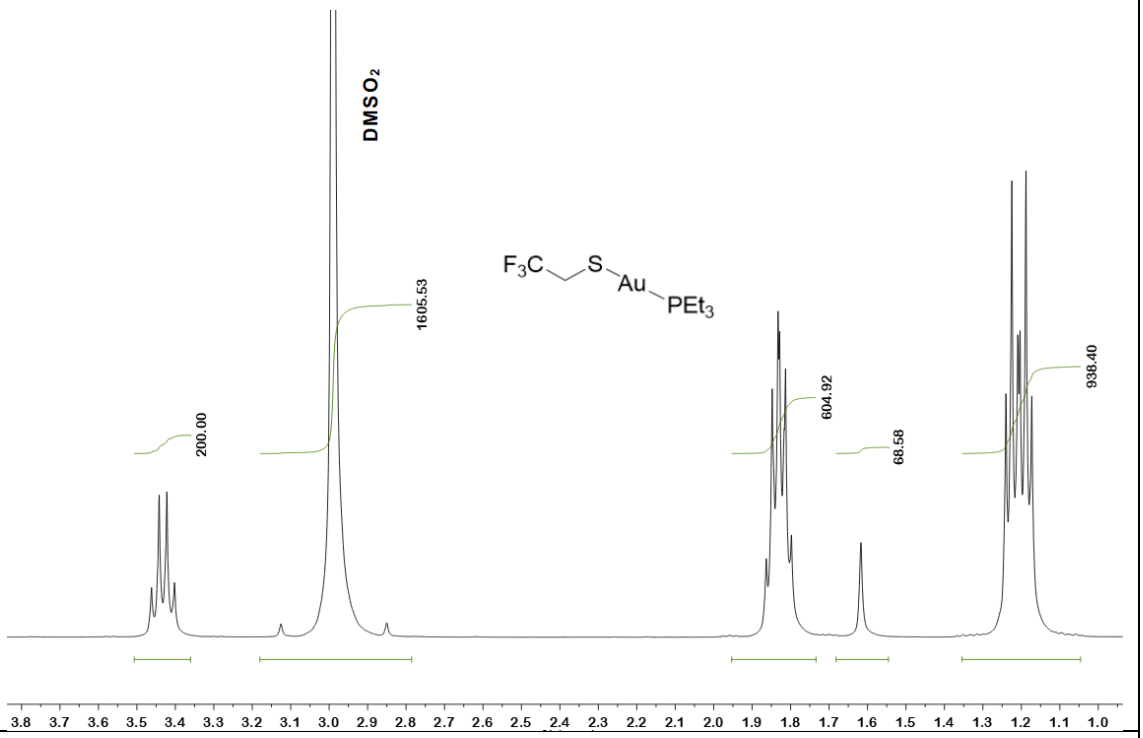
Compound **21** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 13.15 mg, $\boldsymbol{m_{IC}}$ = 2.52 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 104.21, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 511.26, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 392.25 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 97.7\%$
Note	The integral of target analyte was calculated as the average of signals at 3.71, 3.18, 1.85 and 1.22 ppm.

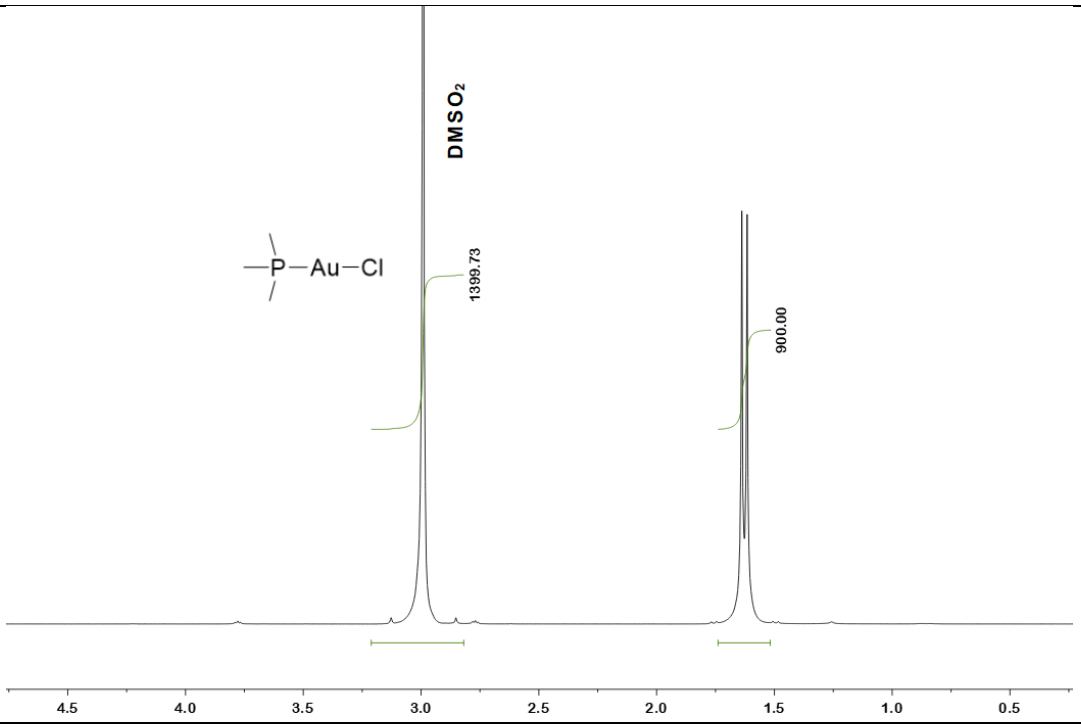
Compound **22** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 8.34 mg, $\boldsymbol{m_{IC}}$ = 1.93 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 101.48, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 630.68, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 420.26 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 99.4\ \%$
Note	The integral of target analyte was calculated as the average of signals at 3.70, 3.57, 1.83 and 1.21 ppm.

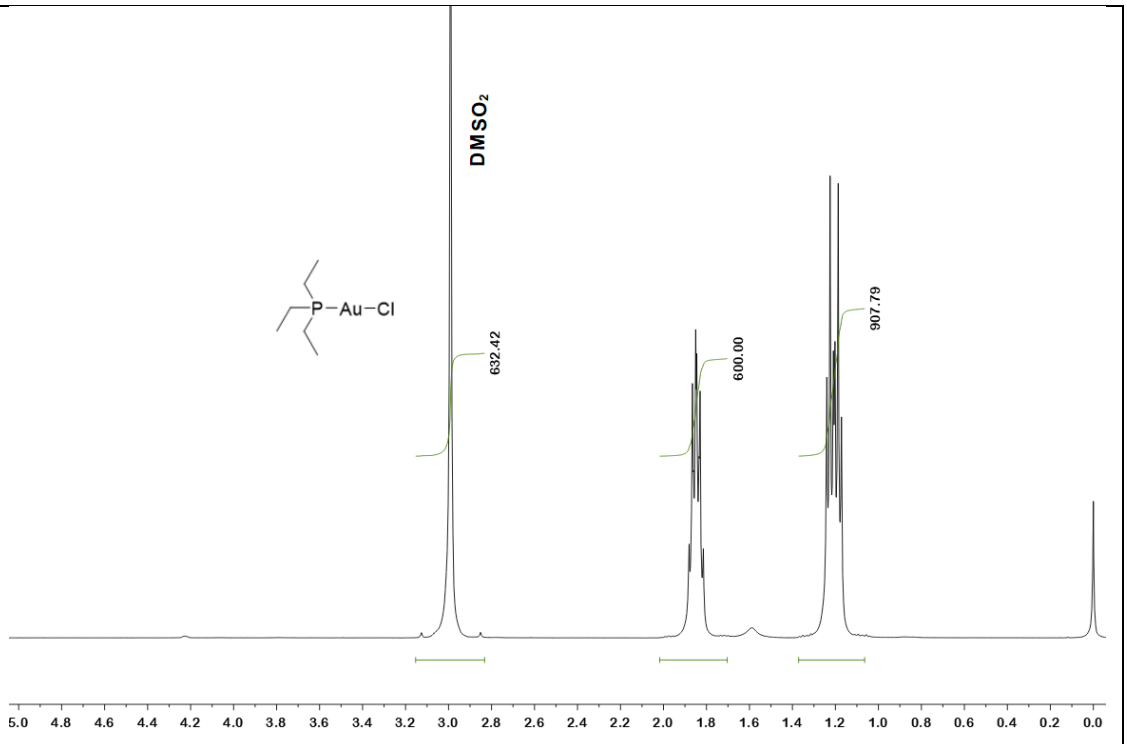
Compound **23** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 7.77 mg, $\boldsymbol{m_{IC}}$ = 4.60 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 100.61, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1605.53, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 430.22 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 101.7\%$
Note	The integral of target analyte was calculated as the average of signals at 3.43 and 1.83 ppm.

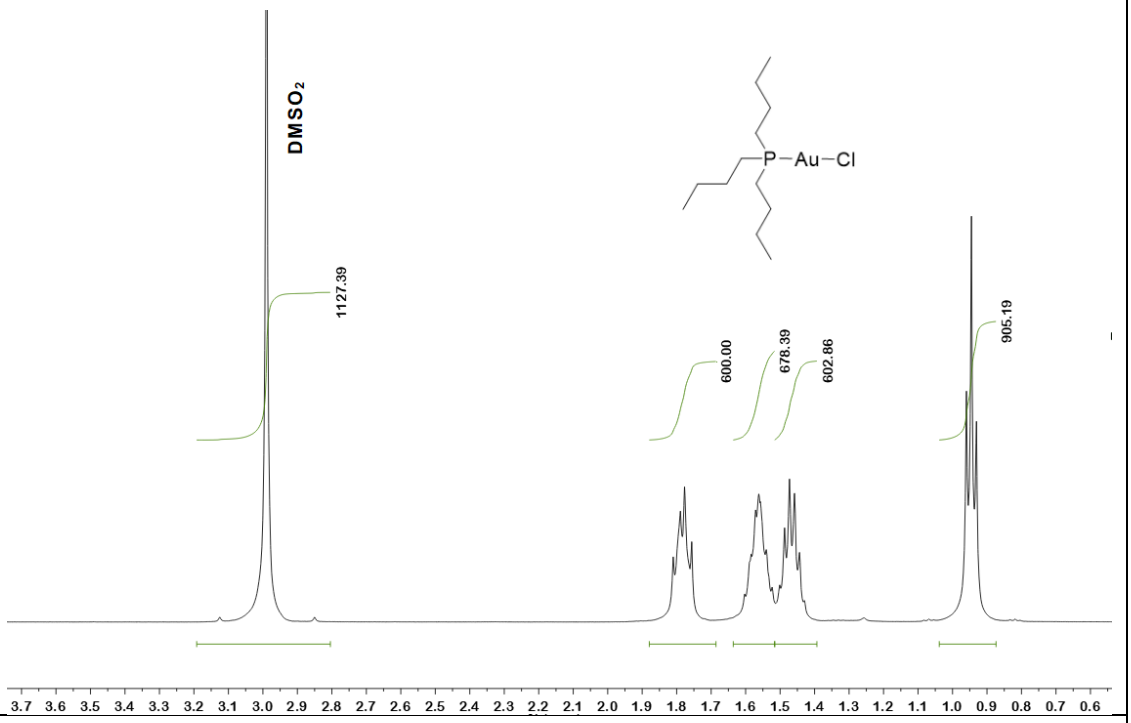
Compound **24** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 5.25 mg, $\boldsymbol{m_{IC}}$ = 4.04 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 100.00, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1399.73, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 308.50 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 100.2\ \%$

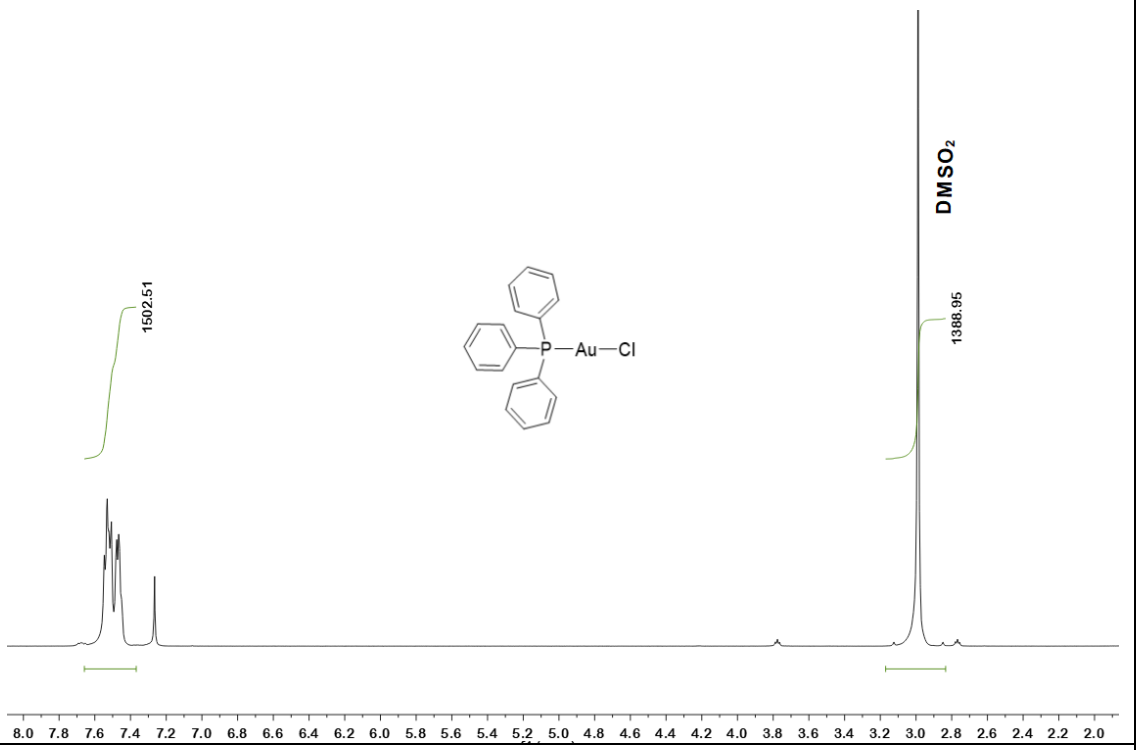
Compound **25** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 7.06 mg, $\boldsymbol{m_{IC}}$ = 1.93 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 100.52, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 632.42, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 350.58 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 97.1\%$
Note	The integral of target analyte was calculated as the average of signals 1.85, and 1.21 ppm.

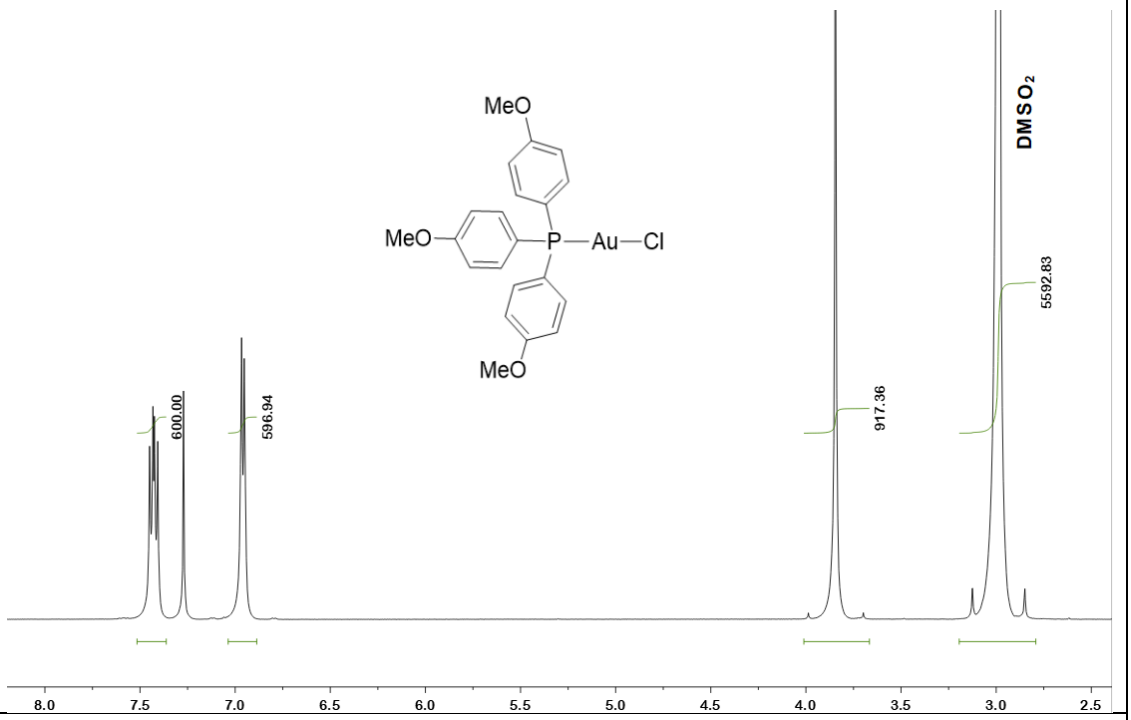
Compound **26** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 5.06 mg, $\boldsymbol{m_{IC}}$ = 2.04 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 100.38, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1127.39, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 434.74 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 99.5\%$
Note	The integral of target analyte was calculated as the average of signals at 1.78, 1.46 and 0.94 ppm.

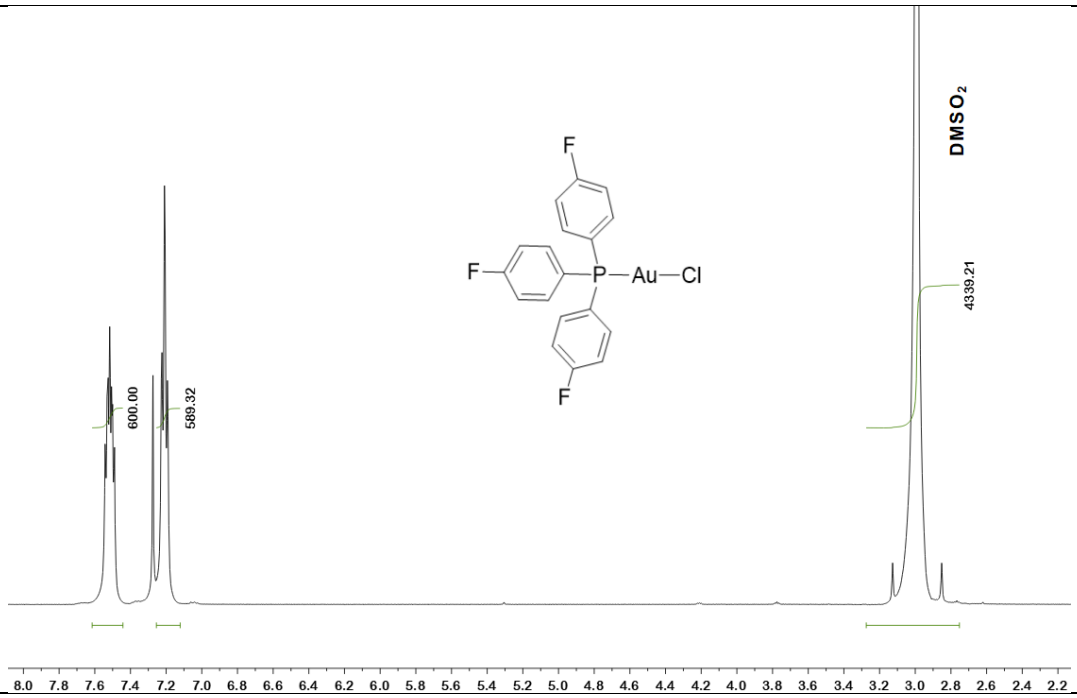
Compound **27** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 6.59 mg, $\boldsymbol{m_{IC}}$ = 2.86 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 100.00, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1388.95, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 494.71 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 98.5\%$
Note	The integral of target analyte was calculated as the average of signals 7.65-7.40 ppm.

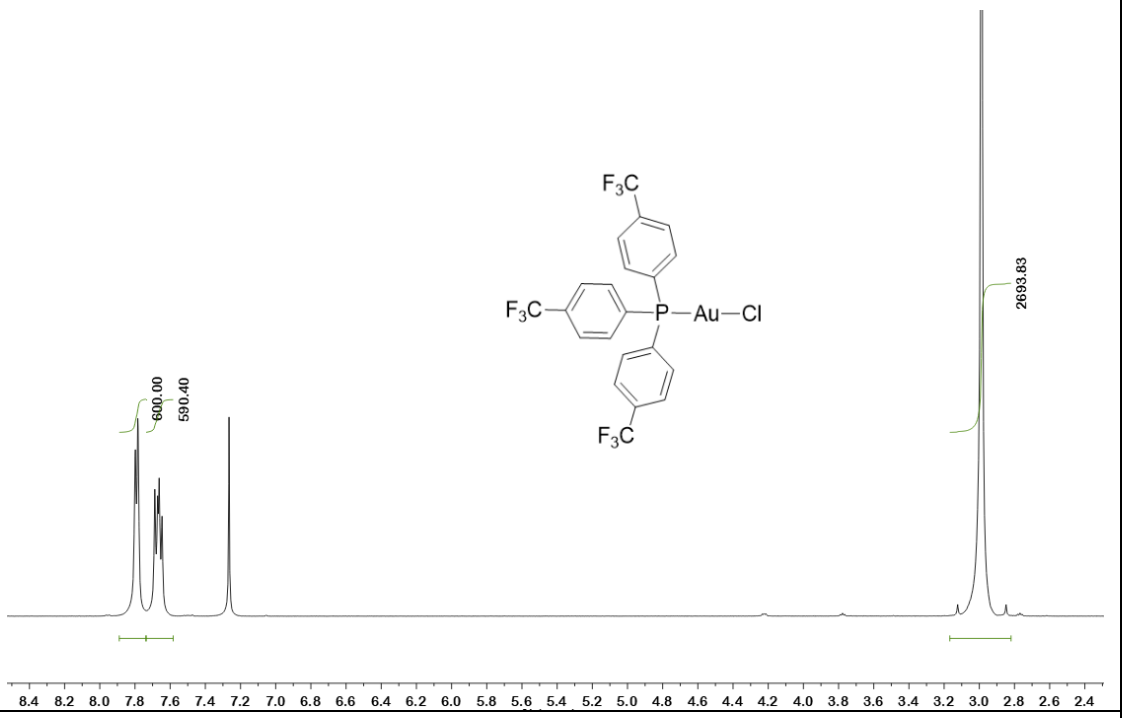
Compound **28** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 5.44 mg, $\boldsymbol{m_{IC}}$ = 7.97 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 100.68, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 5592.83, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 584.79 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 98.3\ \%$
Note	The integral of target analyte was calculated as the average of signals at 7.43, 6.96 and 3.85 ppm.

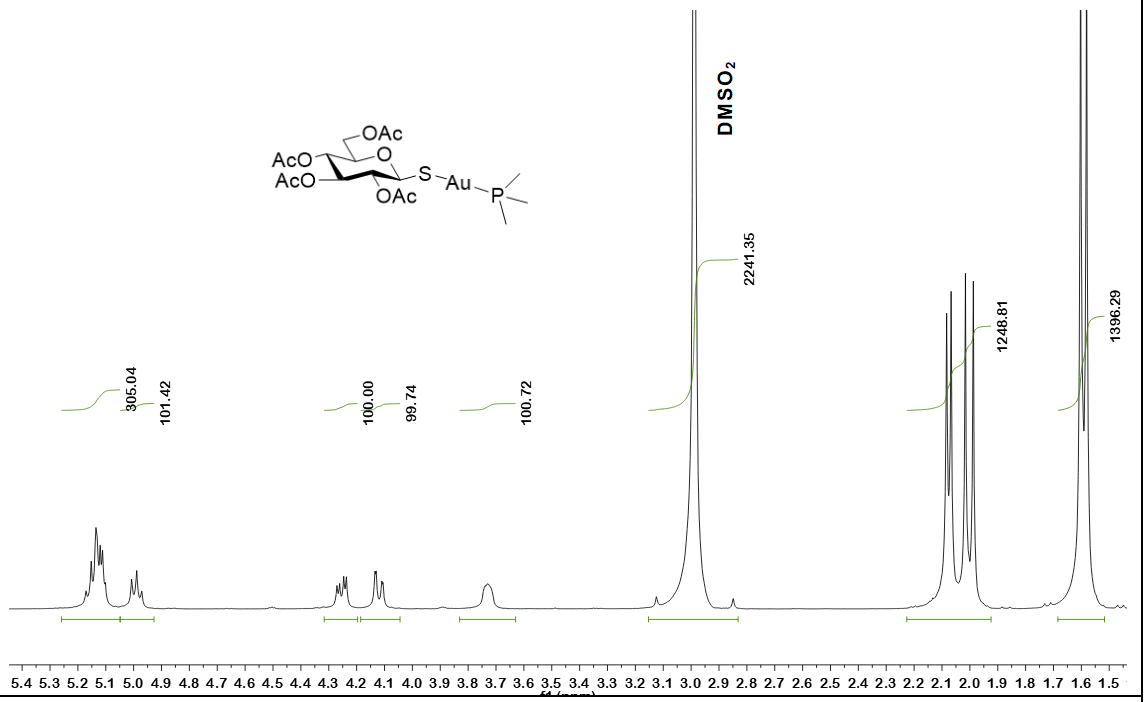
Compound **29** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 7.42 mg, $\boldsymbol{m_{IC}}$ = 8.93 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 100.00, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 4339.21, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 548.68 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 97.0\ \%$
Note	The integral of target analyte was calculated from signals at 7.52 ppm.

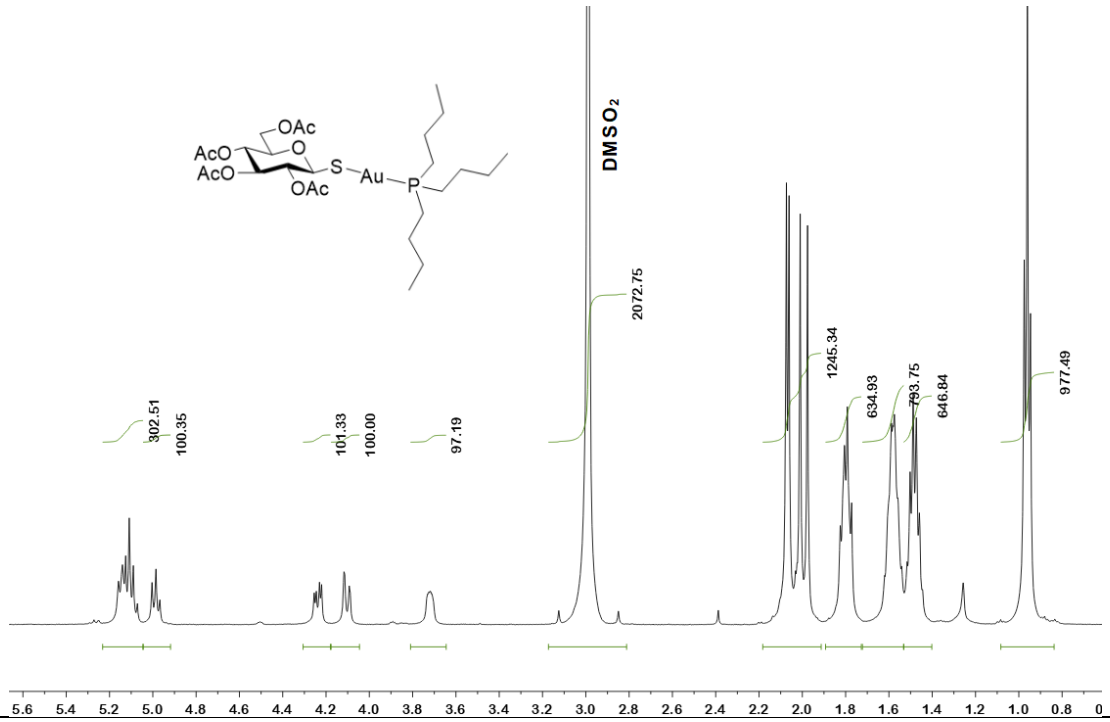
Compound **30** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 5.39 mg, $\boldsymbol{m_{IC}}$ = 3.31 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 99.20, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 2693.83, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 698.70 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 100.7\ \%$
Note	The integral of target analyte was calculated as the average of signals at 7.79 and 7.67 ppm.

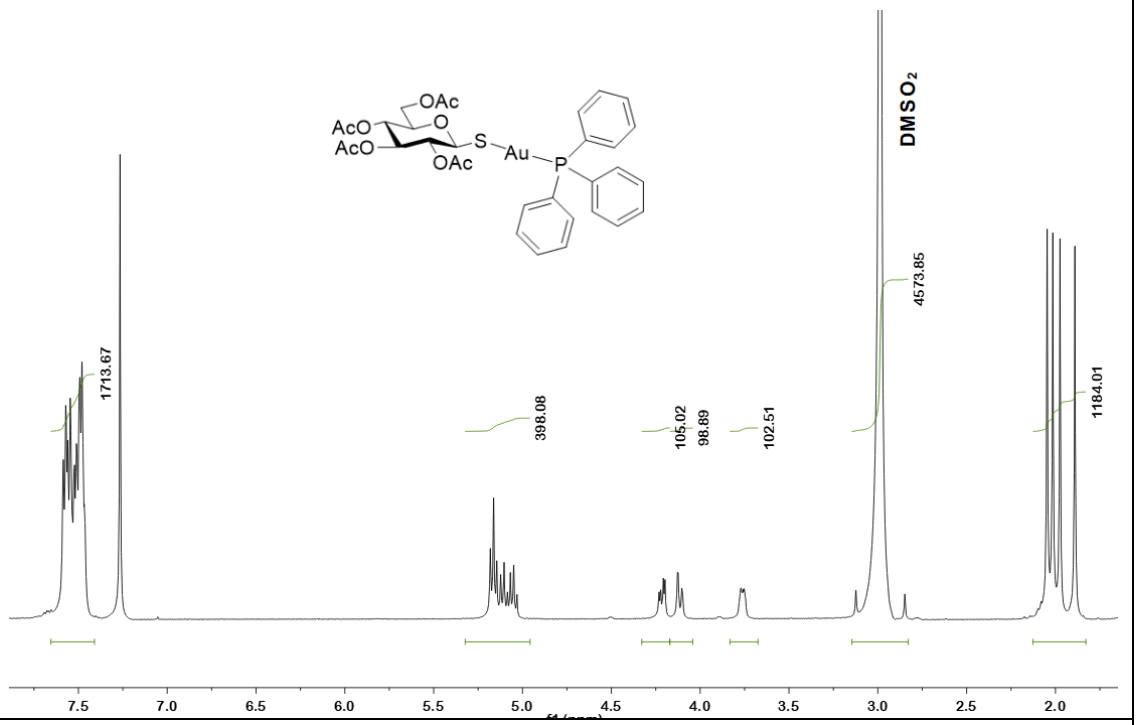
Compound **31** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 5.59 mg, $\boldsymbol{m_{IC}}$ = 2.85 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 102.93, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 2241.35 $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 636.40 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.0\%$
Note	The integral of target analyte was calculated as the average of signals at 5.20-5.06, 4.99, 4.26, 4.12, 3.73, 2.08, 2.07, 2.01 and 1.99 ppm.

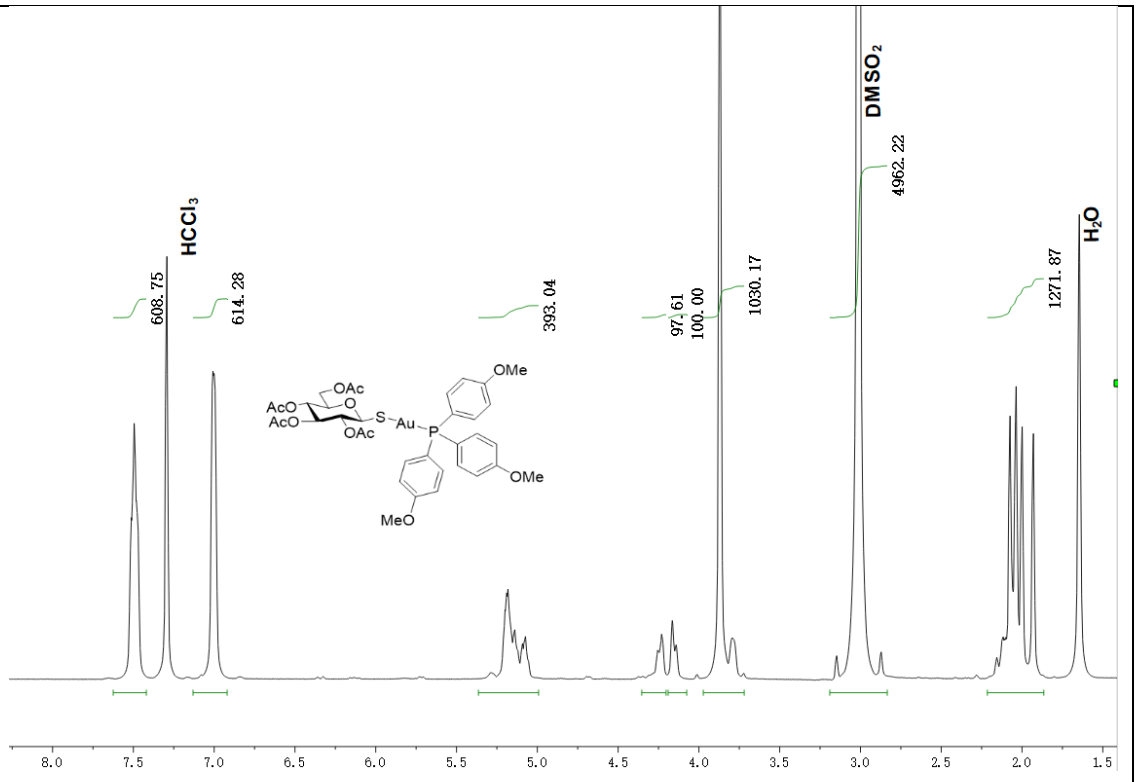
Compound **32** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 5.04 mg, $\boldsymbol{m_{IC}}$ = 1.97 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 105.15, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 2072.75, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 762.65 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 96.4\%$
Note	The integral of target analyte was calculated as the average of signals at 5.20-5.06, 4.98, 4.24, 4.10, 3.72, 2.07, 2.06, 2.01 1.98, 1.80,1.48 and 0.96 ppm.

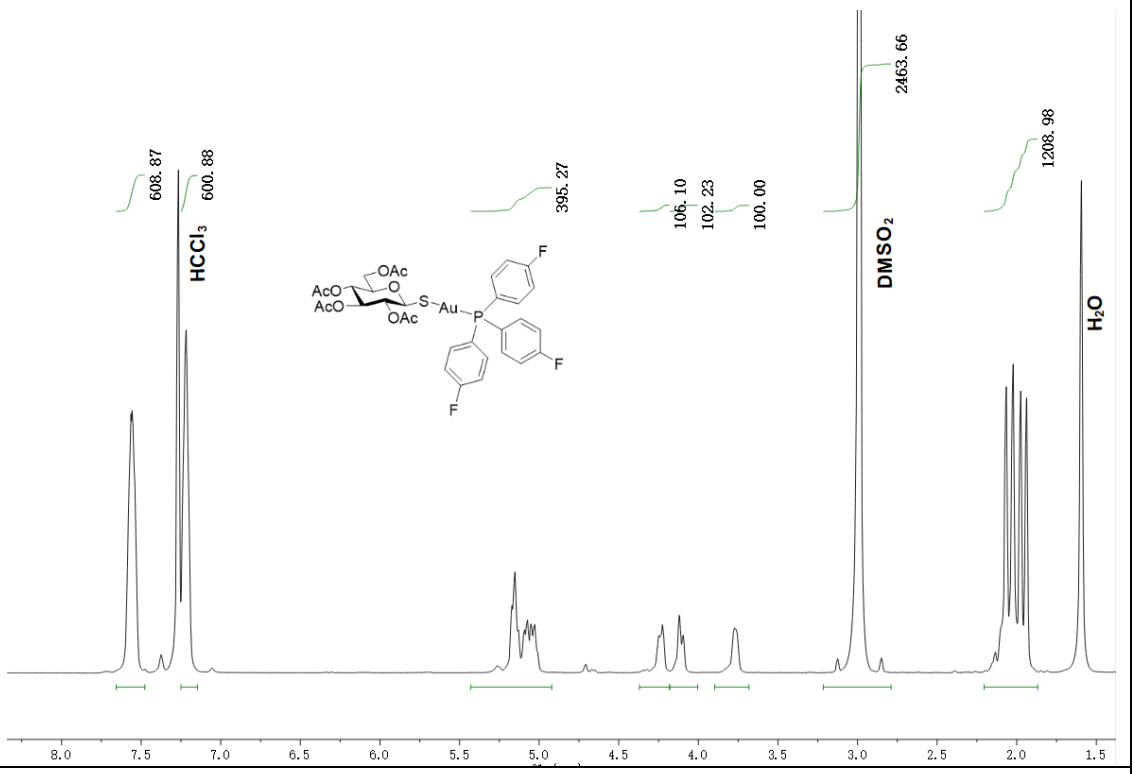
Compound **33** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 5.20 mg, $\boldsymbol{m_{IC}}$ = 4.09 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 105.95, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 4573.85, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 822.62 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.5\%$
Note	The integral of target analyte was calculated as the average of signals at 7.64-7.42, 5.23-5.01, 4.22, 4.11, 3.76, 2.05, 2.01, 1.97 and 1.89 ppm.

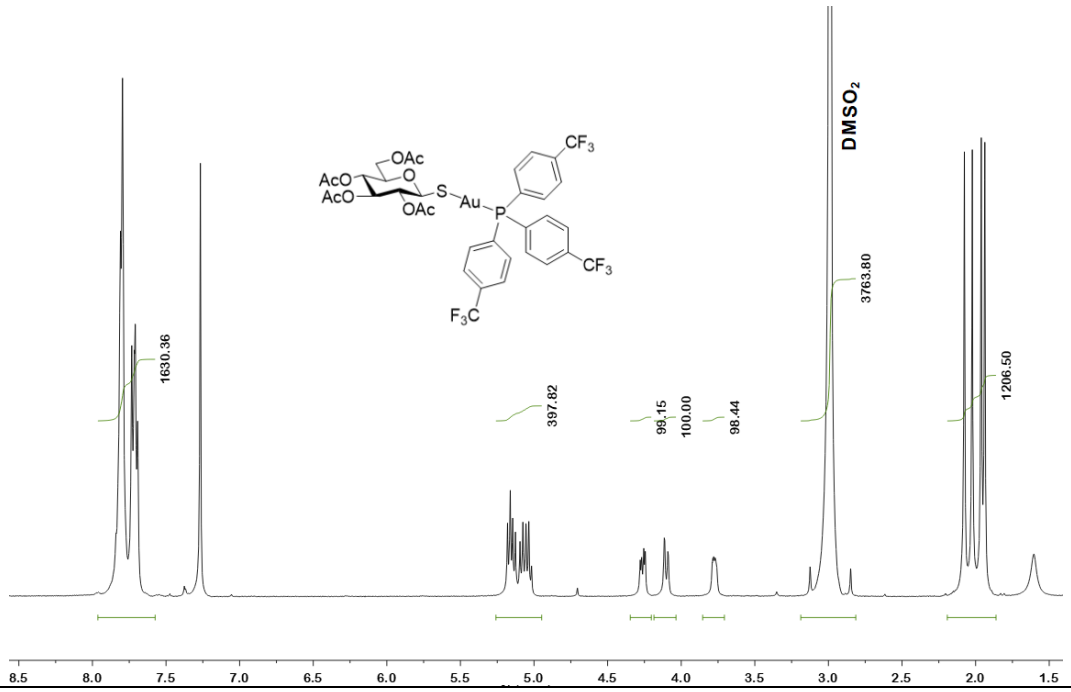
Compound **34** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 5.84 mg, $\boldsymbol{m_{IC}}$ = 4.65 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 102.89, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 4962.22, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 912.63 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 96.0\%$
Note	The integral of target analyte was calculated as the average of signals at 7.47, 6.98, 5.31-4.98, 4.22, 4.13, 3.85, 3.77, 2.05, 2.01, 1.98 and 1.91 ppm.

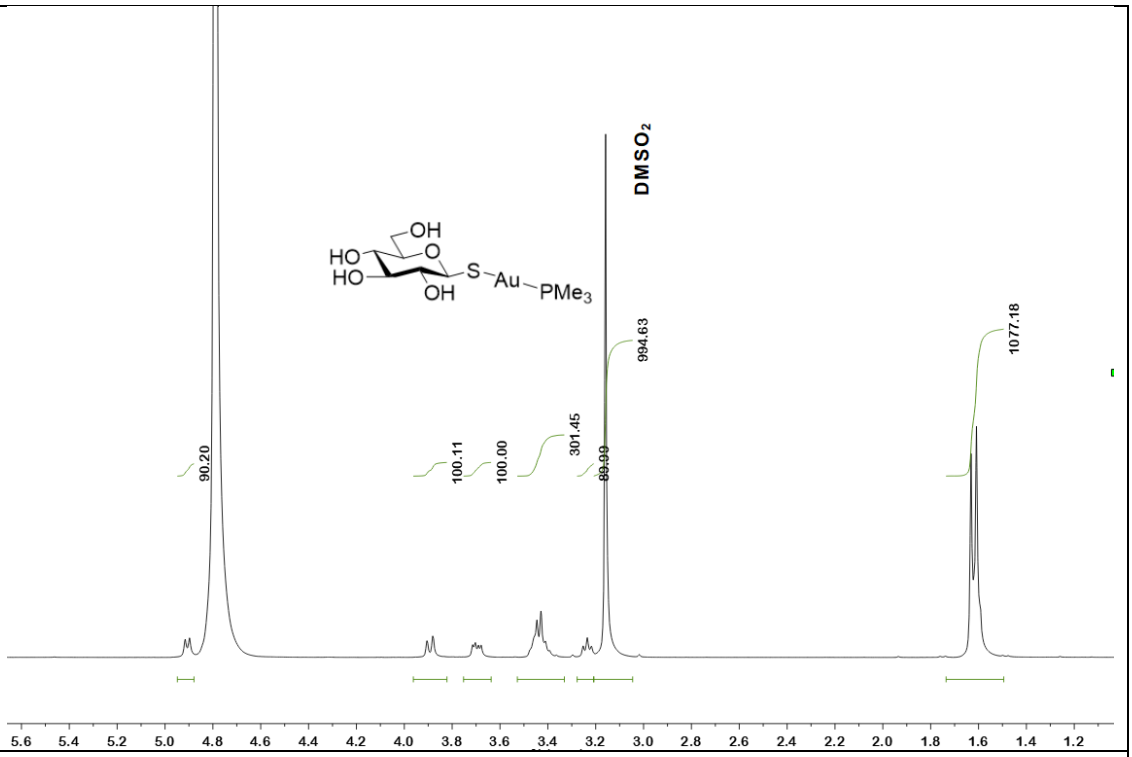
Compound **35** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 5.81 mg, $\boldsymbol{m_{IC}}$ = 2.42 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 100.86, $\mathbf{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 2463.66, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 876.59 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.3\%$
Note	The integral of target analyte was calculated as the average of signals at 7.56, 5.32-4.96, 4.24, 4.11, 3.77, 2.07, 2.02, 1.98, and 1.94 ppm.

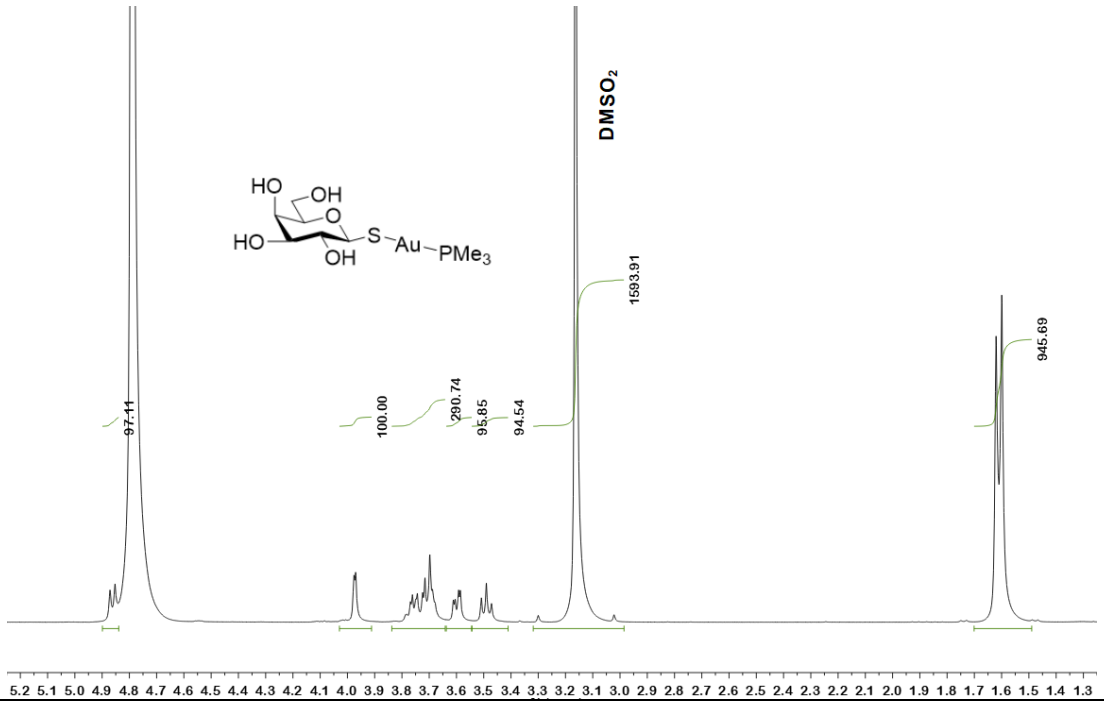
Compound **36** in $CDCl_3$ with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 7.49 mg, $\boldsymbol{m_{IC}}$ = 3.55 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 114.92, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 3763.80, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 1026.61 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 94.7\%$
Note	The integral of target analyte was calculated as the average of signals at 7.96-7.58, 5.26-4.97, 4.26, 4.10, 3.77, 2.08, 2.02, 1.96 and 1.94 ppm.

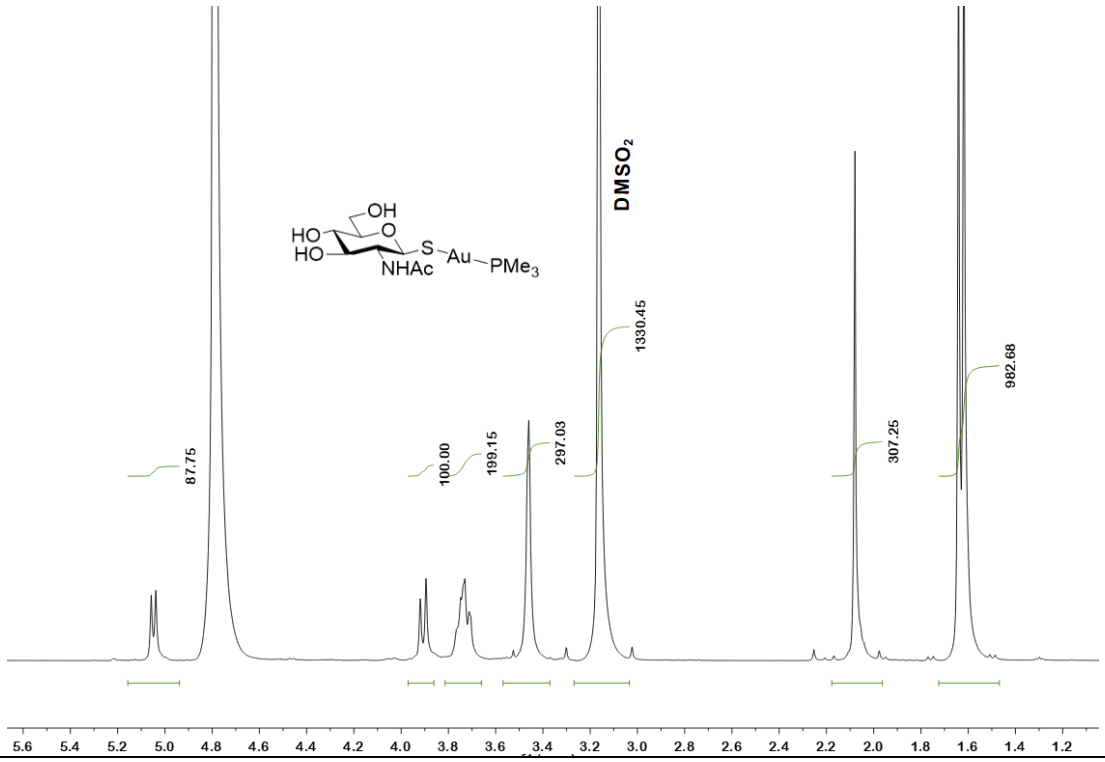
Compound **37** in D_2O with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 10.01 mg, $\boldsymbol{m_{IC}}$ = 2.81 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 112.77, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 994.63, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 468.25 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 95.0\%$
Note	The integral of target analyte was calculated as the average of signals 3.89, 3.69, 3.53-3.34 and 1.62 ppm.

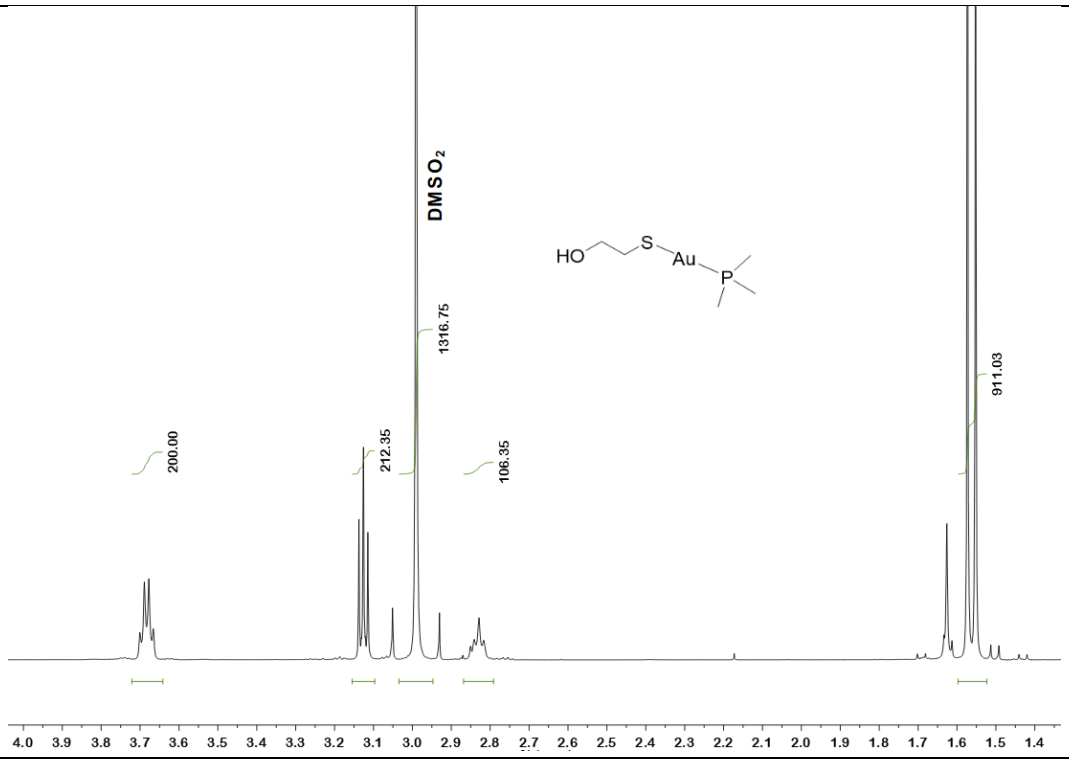
Compound **38** in D_2O with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 6.37 mg, $\boldsymbol{m_{IC}}$ = 3.22 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 101.79, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1593.91, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 468.25 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 96.4\%$
Note	The integral of target analyte was calculated as the average of signals 3.97, 3.82-3.64, 3.60, 3.49 and 1.61 ppm.

Compound **39** in D_2O with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	m_s = 11.47 mg, m_{IC} = 4.25 mg, P_{IC} = 100.0%
Step 2	Int_t = 104.78, n_t = 1
Step 3	Int_{IC} = 1330.45, n_{IC} = 6
Step 4	MW_t = 509.31 g/mol, MW_{IC} = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 94.7\ \%$
Note	The integral of target analyte was calculated as the average of signals 3.91, 3.81-3.65, 2.08 and 1.63 ppm.

Compound **40** in D_2O with the addition of dimethyl sulfone ($DMSO_2$, 100.0%) as internal standard (500 MHz).

	
Step 1	$\boldsymbol{m_s}$ = 7.05 mg, $\boldsymbol{m_{IC}}$ = 4.08 mg, $\boldsymbol{P_{IC}}$ = 100.0%
Step 2	$\boldsymbol{Int_t}$ = 101.80, $\boldsymbol{n_t}$ = 1
Step 3	$\boldsymbol{Int_{IC}}$ = 1316.75, $\boldsymbol{n_{IC}}$ = 6
Step 4	$\boldsymbol{MW_t}$ = 350.17 g/mol, $\boldsymbol{MW_{IC}}$ = 94.13 g/mol
Step 5	$P\ [\%] = \frac{n_{IC} \cdot Int_t \cdot MW_t \cdot m_{IC}}{n_t \cdot Int_{IC} \cdot MW_{IC} \cdot m_s} \cdot P_{IC} = 99.9\ \%$
Note:	The integral of target analyte was calculated as the average of signals at 3.68, 3.13 and 1.56 ppm.

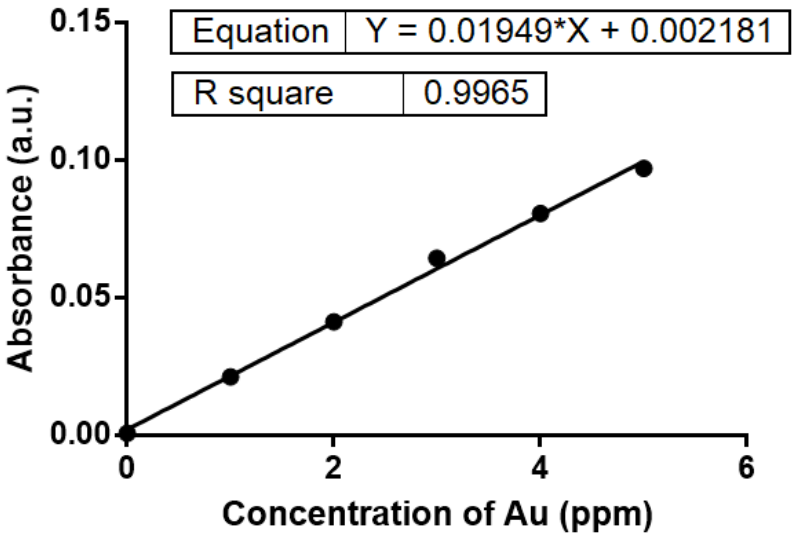


Figure S142. Calibration Curve A of compound **40** in *n*-octanol-saturated water.

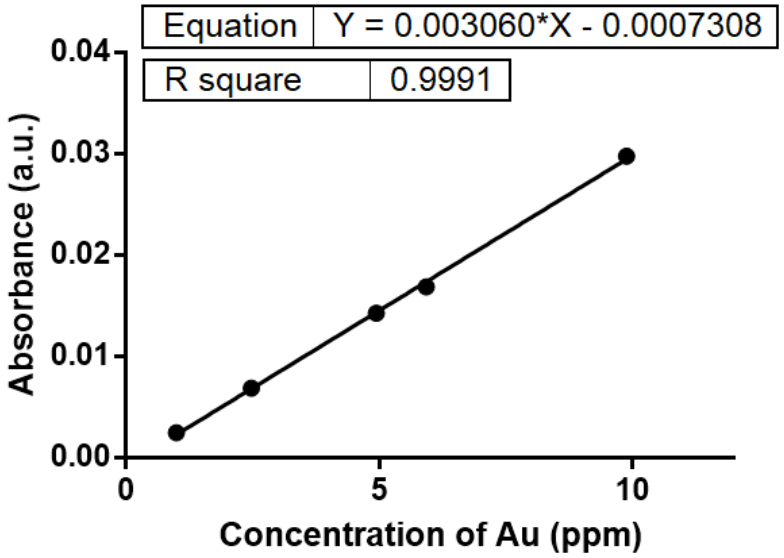


Figure S143. Calibration Curve B of compound **40** in water–saturated *n*-octanol.

Table S1. MIC/MBC (μg/mL)[a] of Group 1 analogs having varying thio sugar structures.

	A. baumannii NCTC 13420	*P. aeruginosa* NCTC 13437	*E. cloacae* NCTC 13405	K. pneumoniae ATCC 700603	*S. aureus* JE2 (USA300)	*E. faecium* ATCC 700221	*E. coli* ATCC 25922	Log P
1	32 (32)	256 (256)	128 (128)	256 (256)	0.03 (0.06)	0.12/0.06 (0.25)	16 (16)	0.56
2	32 (64)	256 (256)	256 (256)	>256 (>256)	0.03 (0.06)	0.12/0.25 (0.25)	16 (16)	0.38
3	16 (32)	128 (128)	32 (64)	128 (128)	0.03/0.06 (0.06)	0.06 (0.25)	8 (8)	0.26
4[f]	64 (128)	>256	>256	>256	0.008 (0.01)	0.06 (0.12)	16 (16)	1.01
5[f]	32 (32)	128 (128)	64 (64)	>256	0.008 (0.06)	0.03/0.06 (0.12)	16 (16)	0.45
6[g]	64 (128)	128 (128)	256 (256)	>256	0.03 (0.12)	0.12 (0.25)	32 (32)	1.04
7[c]	16 (16)	>256	32 (32)	>256	0.004/0.008 (0.008)	0.06 (0.12)	32 (32)	-0.28
8[f]	64/16 (16)	>256	128/256	>256	0.03/0.008 (0.12)	0.03/0.06 (0.25)	128/>256 (128)	-0.36
9	32/8 (128)	256 (256)	64 (64)	256 (256)	0.03/0.06 (0.25)	0.06 (1)	16 (16)	-0.81
10	16 (16)	128 (128)	32 (32)	128 (128)	0.01 (0.06)	0.06/0.12 (0.25)	8 (8)	-0.73
11	16 (32)	256 (256)	64 (128)	256 (256)	0.01/0.03 (0.06)	0.03/0.06 (0.25)	8 (8)	-0.59
12	8/16 (64)	256 (256)	64 (128)	256 (256)	0.008 (0.03)	0.03/0.06 (0.25)	4/2 (4)	-0.89
13	16/32 (128)	256 (256)	128 (128)	256 (256)	0.01/0.03 (0.06)	0.06 (0.25)	16 (16)	-1.81
14	16 (16)	256 (256)	128 (128)	>256 (>256)	0.03/0.06 (0.06)	0.06/0.12 (0.25)	8 (8)	-1.69

[a]Assays were repeated twice. Only one value is presented unless both data are shown.

Lowest precipitation concentration at [b]4, [c]8, [d]16, [e]32 [f]64, [g]128 μg/mL.

Table S2. MIC/MBC (μg/mL)[a] of Group 2 analogs having an aromatic or aliphatic thiol ligand.

	A. baumannii **NCTC 13420**	***P. aeruginosa*** **NCTC 13437**	***E. cloacae*** **NCTC 13405**	**K. pneumoniae ATCC 700603**	***S. aureus*** **JE2 (USA300)**	***E. faecium*** **ATCC 700221**	***E. coli*** **ATCC 25922**	**Log P**
1	32 (32)	256 (256)	128 (128)	256 (256)	0.03 (0.06)	0.12/0.06 (0.25)	16 (16)	0.56
15[f]	32/8 (>256)	128 (128)	32 (256)	>256 (>256)	0.008 (0.25)	0.25 (0.5)	64 (64)	2.20
16[g]	8/16 (8)	128 (128)	8/32 (16/32)	64 (64)	0.004 (0.25)	0.01 (0.06)	16 (16)	0.61
17[d]	8 (8)	64 (64)	16 (16)	16 (16)	0.01/0.03 (0.03)	0.01 (0.06)	4 (4)	1.36
18[f]	16 (16)	128 (128)	64 (64)	64 (64)	0.008 (0.12)	0.01/0.06 (0.12)	16 (16)	2.01
19[e]	>256	>256	>256	>256	0.0002/0.008 (0.008)	0.03/0.06 (0.25)	>256	>3.28
20[e]	256 (>256)	>256	>256	>256	0.01/0.06 (0.12)	0.01 (0.12)	>256	>3.18
21[e]	4 (32)	16 (16)	4/2 (32)	8 (8)	0.01 (0.01)	0.06/0.12 (0.25)	4 (4)	1.19
22[d]	8 (32)	128 (128)	16 (64)	32 (32)	0.002/0.007 (0.01)	0.06/0.12 (0.25)	32 (32)	1.75
23[g]	32/16 (64)	64 (64)	16 (64)	64 (64)	0.004 (0.06)	0.25 (0.5)	32 (32)	2.08

[a]Assays were repeated twice. Only one value is presented unless both data are shown.

Lowest precipitation concentration at [b]4, [c]8, [d]16, [e]32 [f]64, [g]128 μg/mL.

Table S3. MIC/MBC (μg/mL)[a] of Group 3 analogs having a trialkyl- or triaryl-phosphine ligand.

	A. baumannii **NCTC 13420**	***P. aeruginosa*** **NCTC 13437**	***E. cloacae*** **NCTC 13405**	**K. pneumoniae ATCC 700603**	***aureus*JE2 (USA300)**	***E. faecium*** **ATCC 700221**	***E. coli*** **ATCC 25922**	**Log P**
24	4/2 (4)	16 (16)	1 (1)	4/2 (4)	0.03/0.06 (0.5)	0.12 (1)	2 (2)	0.16
25	8/4 (8)	32 (64)	8 (8)	16 (16)	0.004/0.007 (0.06)	0.03/0.06 (0.25)	8 (8)	1.74
26[e]	64/32 (64)	32 (32)	>256	64 (64)	1 (2)	2 (2)	>256	>3.99
27[d]	64/8 (258)	>256	>256	>256	0.5/1 (2)	2 (2)	>256	>3.94
28[c]	>256	>256	>256	>256	1 (2)	2 (2)	>256	>4.09
29[d]	32/16 (128)	>256	>256	>256	0.5 (2)	1/2 (2)	>256	>4.04
30[e]	>256	>256	>256	>256	2/1 (8)	>256	>256	>3.94
31[g]	8/4 (64)	64 (64)	2 (2)	8 (8)	0.06 (0.12)	0.12/0.25 (0.5)	4 (4)	0.35
1	32 (32)	256 (256)	128 (128)	256 (256)	0.03 (0.06)	0.12/0.06 (0.25)	16 (16)	0.56
32[e]	64 (>256)	>256	>256	>256	2 (2)	4/2 (2)	>256	>4.32
33[c]	>256	>256	>256	>256	1/2 (2)	4 (4)	>256	>3.87
34[c]	>256	>256	>256	>256	1 (2)	4/2 (4)	>256	>3.03
35[c]	>256	>256	>256	>256	1 (2)	4/2 (4)	>256	>3.04
36[e]	>256	>256	>256	>256	4 (8)	32 (64)	>256	>3.55

[a]Assays were repeated twice. Only one value is presented unless both data are shown.

Lowest precipitation concentration at [b]4, [c]8, [d]16, [e]32 [f]64, [g]128 μg/mL.

Table S4. MIC/MBC (μg/mL)[a] of analogs having trimethylphosphine ligand.

	A. baumannii **NCTC 13420**	***P. aeruginosa*** **NCTC 13437**	***E. cloacae*** **NCTC 13405**	**K. pneumoniae ATCC 700603**	***S. aureus*** **JE2 (USA300)**	***E. faecium*** **ATCC 700221**	***E. coli*** **ATCC 25922**	**Log P**
1	32 (32)	256 (256)	128 (128)	256 (256)	0.03 (0.06)	0.12/0.06 (0.25)	16 (16)	0.56
31[g]	8/4 (64)	64 (64)	2 (2)	8 (8)	0.06 (0.12)	0.12/0.25 (0.5)	4 (4)	0.35
37	8/2 (8)	>256	2/4 (8)	16 (16)	0.12/0.25 (0.5)	0.12/0.25 (0.25)	4 (4)	-1.63
38	8/4 (8)	>256 (>256)	2 (2)	16 (16)	0.12 (0.12)	0.12/0.25 (0.25)	4 (4)	-1.88
39	8/4 (8)	>256 (>256)	4/8 (8)	16 (64)	0.25 (0.25)	0.12/0.25 (0.25)	4/16 (16)	-2.03
40[f]	2/1 (8)	32/8 (32)	1 (1)	4 (8)	0.12 (0.25)	0.12 (0.12)	0.5/2 (4)	-0.15

[a]Assays were repeated twice. Only one value is presented unless both data are shown.

Lowest precipitation concentration at [b]4, [c]8, [d]16, [e]32 [f]64, [g]128 μg/mL.

Table S5. IC_{50} (μg/mL)[a] of auranofin and analogs against A549 cells.

1	**2**	**3**	**4**	**5**	**6**	**7**
7.7±1.3	10.5±0.2	30.9±5.8	7.9±0.1	15.2±0.3	29.8±3.2	14.4±0.0
8	**9**	**10**	**11**	**12**	**13**	**14**
15.8±0.1	30.2±0.1	16.9±0.5	17.2±1.1	29.2±4.8	32.9±4.6	31.0±2.4
15	**16**	**17**	**18**	**19**	**20**	**21**
4.3±0.2	7.5±0.1	6.5±1.1	7.2±0.7	5.5±1.3	3.1±0.2	7.3±1.7
22	**23**	**24**	**25**	**26**	**27**	**28**
6.4±2.4	4.6±0.2	15.9±0.7	9.5±0.1	4.7±0.0	12.0±1.8	9.4±1.7
29	**30**	**31**	**32**	**33**	**34**	**35**
13.2±1.0	85.6±26.1	13.1±2.3	2.5±0.3	3.1±0.1	3.8±0.1	2.9±0.1
36	**37**	**38**	**39**	**40**		
18.3±2.2	52.2±1.0	43.0±3.7	35.5±0.9	12.3±3.1		

[a]Data are presented as mean±S.E.M. from two independent experiments.