

Alkylgold Complexes by the Intramolecular Aminouration of Unactivated Alkenes

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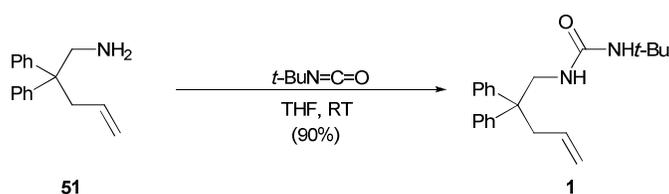
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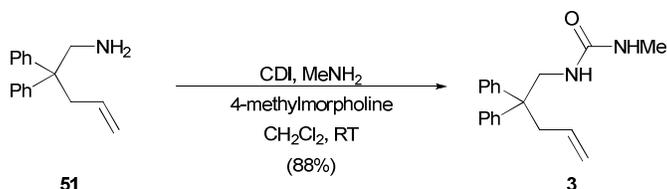
I. General Information: Unless otherwise noted commercial materials were used without further purification. Dichloromethane (DCM) and chloroform utilized in gold(I)-catalyzed reactions was used as received from Aldrich Chemical Company. Gold(I)-catalyzed reactions were conducted in two dram vials equipped with a magnetic stir bar, fitted with a threaded cap, and protected from ambient light. All other reactions were conducted in flame-dried glassware under an inert (N_2) atmosphere with magnetic stirring and dried solvent. Solvents were dried by passage through an activated alumina column under nitrogen. Phosphine gold(I) chloride complexes and $[(Ph_3PAu)_3O]BF_4$ complexes were prepared according to procedures previously described.^{1,2} Alkene substrates were prepared according to the methods of Widenhoefer.^{3,4} Thin-layer chromatography (TLC) analysis was performed using Merck silica gel 60 F254 TLC plates, and visualized by staining with I_2 , and UV. Flash column chromatography was carried out on Merck 60 silica gel (32 – 63 μm) or MicroSolv Basic Alumina (50 – 200 μm). 1H and ^{13}C NMR spectra were recorded with Bruker AVB-400, AVQ-400, DRX-500, and AV-600 spectrometers and chemical shifts are reported in ppm, relative to $CHCl_3$ (7.26 ppm for 1H , and 77.23 ppm for ^{13}C), unless otherwise noted. Mass spectral and analytical data were obtained via the QB3/College of Chemistry Mass Spectrometry Facility operated by the College of Chemistry, University of California, Berkeley.

II. Substrate Synthesis

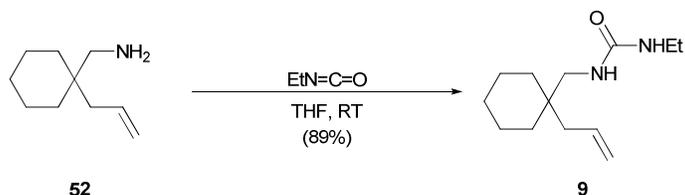


tert-Butyl Urea **1**: Amine **51** (0.237 g, 1.0 mmol) was dissolved in THF (2 mL) at room temperature, then *tert*-butyl isocyanate (0.08 mL, 1.0 mmol) was added slowly and the solution was allowed to stir overnight. The reaction was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (0 – 10% EtOAc in hexanes with 2% MeOH) to provide **1** (0.300 g, 90%) as a fluffy white solid: 1H NMR (600 MHz, $CDCl_3$) δ 7.29 (s, 4H), 7.22 – 7.17 (m, 6H), 5.43 (ddt, 1H, $J = 17.1, 10.1, 7.1$ Hz), 5.01 – 4.95 (m, 2H), 4.03 (dt, 1H, $J = 1.2, 0.6$ Hz), 3.85 (d, 2H, $J = 5.9$ Hz), 3.78 (s, 1H), 2.87 (d, 2H, $J = 7.1$ Hz), 1.19 (s, 9H) ppm; ^{13}C NMR

(150 MHz, CDCl₃) δ 157.2, 145.7, 134.0, 128.2, 128.1, 126.3, 118.4, 50.3, 50.2, 47.0, 41.9, 29.4 ppm. HRMS (ESI) calc'd for [C₂₂H₂₉ON₂]⁺: m/z 337.2274, found 337.2283.

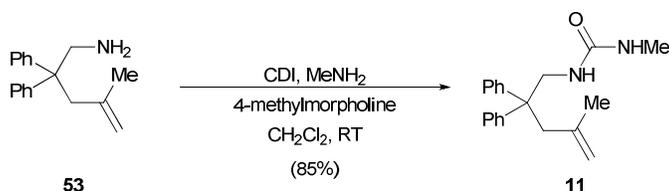


Methyl Urea **3**: Amine **51** (0.237 g, 1.0 mmol) and 4-methylmorpholine (0.22 mL, 2.0 mmol) were dissolved in CH₂Cl₂ (3.0 mL) was added dropwise over 10 minutes to a solution of carbonyl diimidazole (0.243 g, 1.5 mmol) in CH₂Cl₂ (10.0 mL) at -10 °C. After slowly warming to room temperature over 1 hour, the solution was recooled to -10 °C, and methylamine (0.50 mL, 33% in EtOH, 4.0 mmol) was added and the solution warmed to room temperature overnight. The reaction mixture was diluted with CH₂Cl₂ (30 mL), and washed with 1 N HCl (15 mL), water (15 mL), and brine (15 mL). The organic layer was then dried over MgSO₄, filtered, and concentrated *in vacuo*. The residue was suspended in CH₂Cl₂ (2.0 mL) and then pentanes was added (30 mL), giving a voluminous white precipitate, which was collected by suction filtration, washing with pentanes, then collected and dried under vacuum, providing **3** (0.2587 g, 88% yield) as a fluffy white solid: ¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.28 (m, 4H), 7.23 – 7.15 (m, 6H), 5.44 (ddt, 1H, J = 17.2, 10.1, 7.1 Hz), 5.01 – 4.97 (m, 2H), 4.18 (brs, 1H), 3.91 (brs, 1H), 3.87 (d, 2H, J = 5.2 Hz), 2.87 (d, 2H, J = 7.1 Hz), 2.61 (d, 3H, J = 4.9 Hz) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 158.7, 145.6, 134.0, 128.3, 128.1, 126.5, 118.5, 50.4, 47.2, 41.8, 27.2 ppm; HRMS (ESI) calc'd for [C₁₉H₂₃N₂O]⁺: m/z 295.1810, found 295.1812.

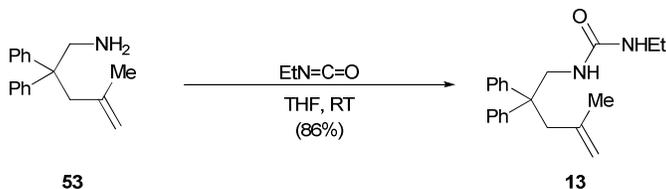


Ethyl Urea **9**: Amine **52** (0.153 g, 1.0 mmol) was dissolved in THF (2 mL) at room temperature, then ethyl isocyanate (0.08 mL, 1.0 mmol) was added slowly and the solution was allowed to stir overnight. The reaction was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (10 – 14% EtOAc in hexanes with 2% MeOH) to provide **9** (0.200

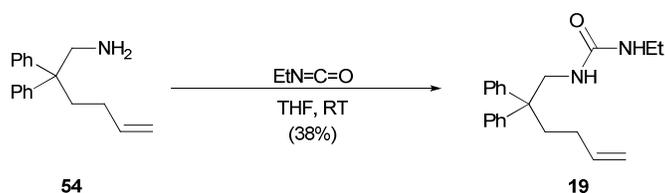
g, 89%) as a fluffy white solid: ^1H NMR (600 MHz, CDCl_3) 5.80 (m, 1H), 5.08 (m, 4H), 3.16 (m, 2H), 3.05 (d, 2H, $J = 6.1$ Hz), 2.03 (d, 2H, $J = 7.4$ Hz), 1.48 – 1.33 (m, 6H), 1.33 – 1.22 (m, 5H), 1.09 (td, 3H, $J = 7.2, 1.8$ Hz) ppm; ^{13}C NMR (150 MHz, CDCl_3) 159.0, 134.9, 117.1, 46.7, 40.3, 36.9, 35.1, 33.3, 26.2, 21.4, 15.5 ppm; HRMS (ESI) calc'd for $[\text{C}_{13}\text{H}_{24}\text{ON}_2]^+$: m/z 224.1889, found 224.1888.



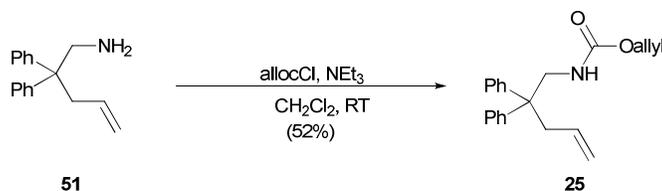
Methyl Urea 11: Amine **53** (0.251 g, 1.0 mmol) and 4-methylmorpholine (0.22 mL, 2.0 mmol) were dissolved in CH_2Cl_2 (3.0 mL) was added dropwise over 10 minutes to a solution of carbonyl diimidazole (0.243 g, 1.5 mmol) in CH_2Cl_2 (10.0 mL) at -10 °C. After slowly warming to room temperature over 1 hour, the solution was recooled to -10 °C, and methylamine (0.50 mL, 33% in EtOH, 4.0 mmol) was added and the solution was warmed to room temperature overnight. The reaction mixture was diluted with CH_2Cl_2 (30 mL), and washed with 1 N HCl (15 mL), water (15 mL), and brine (15 mL). The organic layer was then dried over MgSO_4 , filtered, and concentrated *in vacuo*. The residue was suspended in CH_2Cl_2 (2.0 mL) and then pentanes was added (30 mL), giving a voluminous white precipitate, which was collected by suction filtration, washing with pentanes, then collected and dried under vacuum, providing **11** (0.2633 g, 85% yield) as a fluffy white solid: ^1H NMR (500 MHz, CDCl_3) δ 7.31 – 7.23 (m, 4H), 7.23 – 7.19 (m, 6H), 4.84 (s, 1H), 4.66 (s, 1H), 4.28 (brs, 1H), 3.93 (d, 2H, $J = 5.0$ Hz), 3.90 (brs, 1H), 2.86 (s, 2H), 2.59 (d, 3H, $J = 4.8$ Hz), 1.04 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 158.7, 146.1, 141.9, 128.2, 126.5, 116.3, 49.9, 46.7, 44.7, 27.1, 24.3 ppm; HRMS (ESI) calc'd for $[\text{C}_{20}\text{H}_{25}\text{N}_2\text{O}]^+$: m/z 309.1967, found 309.1966.



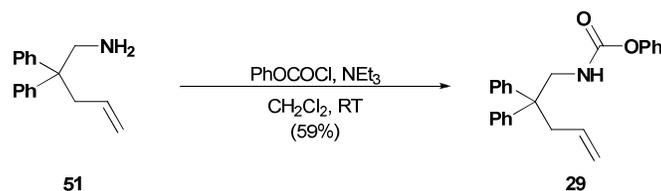
Ethyl Urea **13**: Amine **53** (0.241 g, 1.0 mmol) was dissolved in CH₂Cl₂ (10 mL) at room temperature, then ethyl isocyanate (0.08 mL, 1.0 mmol) was added slowly and the solution was allowed to stir overnight. The reaction was quenched by the addition of 1 N HCl (20 mL) and extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were washed with H₂O (10 mL) and brine (10 mL), dried over MgSO₄, filtered and concentrated *in vacuo*. The residue was purified by crystallization from CH₂Cl₂/hexanes to provide **13** (0.2658g, 86%) as a fluffy white solid: ¹H NMR (500 MHz, CDCl₃) 7.31 – 7.23 (m, 4H), 7.23 – 7.19 (m, 6H), 4.87 (s, 1H), 4.69 (s, 1H), 4.11 (brs, 1H), 3.97 (d, 2H, *J* = 5.6 Hz), 3.10 – 3.02 (m, 2H), 2.90 (s, 2H), 1.07 (s, 3H), 1.05 (t, 3H, *J* = 7.2 Hz) ppm; ¹³C NMR (150 MHz, CDCl₃) δ 157.9, 146.1, 141.8, 128.2, 128.1, 126.5, 116.2, 49.9, 46.7, 44.8, 35.3, 24.3, 15.3 ppm; HRMS (ESI) calc'd for [C₂₁H₂₇ON₂]⁺: *m/z* 323.2118, found 323.2130.



Ethyl Urea **19**: To amine **54** (0.616 g, 2.45 mmol) in THF (6.0 mL) was added dropwise ethyl isocyanate (0.193 mL, 2.45 mmol) and stirred overnight. The reaction mixture was concentrated *in vacuo* to giving an off-white solid. The residue was recrystallized in toluene yielding a voluminous white precipitate, which was collected under suction filtration and dried under vacuum, providing **19** (0.2993 g, 38% yield) as a fluffy white solid: ¹H NMR (400 MHz, CDCl₃) d 7.36 – 7.30 (m, 4H), 7.27 – 7.22 (m, 6H), 5.78 (ddt, 1H, *J* = 17.1, 10.2, 6.8 Hz), 4.98 (dd, 1H, *J* = 17.1, 1.8 Hz), 4.93 (d, 1H, *J* = 10.2 Hz), 4.15 (t, 1H, *J* = 5.3 Hz), 3.96 (d, 2H, *J* = 5.5 Hz), 3.86 (t, 1H, *J* = 5.7 Hz), 3.15 (dq, 2H, *J* = 7.2, 5.6 Hz), 2.21 – 2.17 (m, 2H), 1.87 – 1.81 (m, 2H), 1.07 (t, 3H, *J* = 7.2 Hz) ppm; ¹³C NMR (100 MHz, CDCl₃) d 158.0, 146.0, 138.8, 128.3, 128.1, 126.4, 114.4, 50.6, 47.1, 36.5, 35.4, 28.7, 15.4 ppm; IR (neat): 3329, 1624, 1495, 1282, 1141, 703 cm⁻¹; HRMS (ESI) calc'd for [C₂₁H₂₇ON₂]⁺: *m/z* 323.2118, found 323.2124.



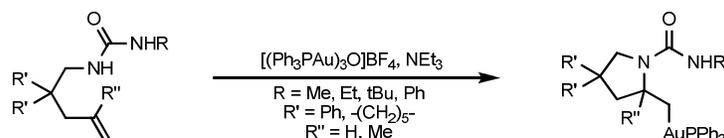
Allyl Carbamate **25**: Amine **51** (0.593 g, 2.5 mmol) and triethylamine (0.52 mL, 3.75 mmol) were combined in CH_2Cl_2 (10 mL) and cooled to 0 °C. Then allyl chloroformate (0.29 mL, 2.75 mmol) was added dropwise and the solution was allowed to slowly warm to room temperature overnight. The reaction was quenched by the addition of 0.5 N HCl (20 mL) and extracted with Et_2O (3×10 mL). The combined organic layers were washed with sat. aq. NaHCO_3 (10 mL) and brine (10 mL), dried over MgSO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (10% EtOAc in hexanes) to give **25** (0.4223, 52%) as a colorless viscous oil that solidified upon standing: ^1H NMR (500 MHz, CDCl_3) δ 7.32 – 7.28 (m, 4H), 7.24 – 7.20 (m, 2H), 7.17 (d, 4H, $J = 7.6$ Hz), 5.87 (m, 1H), 5.43 (m, 1H), 5.24 (d, 1H, $J = 17.3$ Hz), 5.18 (d, 1H, $J = 10.4$ Hz), 4.51 (d, 2H, $J = 5.5$ Hz), 4.30 (s, 1H), 3.92 (d, 2H, $J = 5.9$ Hz), 2.87 (d, 2H, $J = 6.9$ Hz) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 156.1, 145.2, 133.7, 132.9, 128.3, 128.0, 126.5, 118.7, 117.8, 65.6, 50.1, 47.6, 41.7 ppm; HRMS (ESI) calc'd for $[\text{C}_{21}\text{H}_{24}\text{O}_2\text{N}]^+$: m/z 322.1808, found 322.1802.



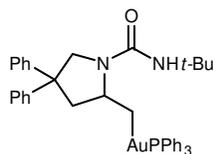
Phenyl Carbamate **29**: Amine **51** (0.593 g, 2.5 mmol) and triethylamine (0.52 mL, 3.75 mmol) were combined in CH_2Cl_2 (10 mL) and cooled to 0 °C. Then phenyl chloroformate (0.38 mL, 3.0 mmol) was added dropwise and the solution was allowed to slowly warm to room temperature overnight. The reaction was quenched by the addition of 0.5 N HCl (20 mL) and extracted with Et_2O (3×10 mL). The combined organic layers were washed with sat. aq. NaHCO_3 (10 mL) and brine (10 mL), dried over MgSO_4 , filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (8% EtOAc in hexanes) to give **29** (0.5262, 59%) as an amorphous solid. At room temperature in CDCl_3 , **29** exists as a 6:1 mixture of rotomers. Spectroscopic data is reported only for the major rotomer: ^1H NMR (500 MHz,

CDCl_3) δ 7.40 – 7.35 (m, 6H), 7.32 – 7.25 (m, 6H), 7.22 (t, 1H, $J = 7.3$ Hz), 7.09 (d, 2H, $J = 8.1$ Hz), 5.55 – 5.46 (m, 1H), 5.09 (d, 1H, $J = 17.3$ Hz), 5.05 (d, 1H, $J = 10.5$ Hz), 4.68 (brs, 1H), 4.05 (d, 2H, $J = 6.0$ Hz), 2.98 (d, 2H, $J = 7.0$ Hz) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 154.5, 151.0, 145.1, 133.6, 129.3, 128.4, 128.0, 126.7, 125.3, 121.5, 118.9, 50.3, 47.8, 41.9 ppm; HRMS (ESI) calc'd for $[\text{C}_{24}\text{H}_{24}\text{O}_2\text{N}]^+$: m/z 358.1808, found 358.1802.

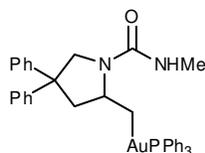
III. Urea Aminoauration



General Procedure for cyclization of urea substrates to pyrrolidines: Urea (100 μmol) and triethylamine (200 μmol) were combined in CDCl_3 (1.0 mL) and let stir for five minutes before the addition of the gold trimer (40 μmol) in one portion. After 12 hours, the reaction mixture was concentrated to dryness. The residue was then suspended in EtOAc and filtered through a pad of basic alumina, then concentrated *in vacuo*. Alternatively, the crude reaction mixture was diluted with chloroform (20 mL), washed with sat. aq. NaHCO_3 (10 mL), dried (MgSO_4) and concentrated to yield a crude foam.

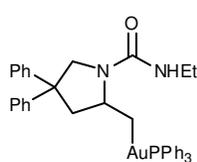


Alkyl Gold 2: From *t*-butyl urea **1**. Purified by flash column chromatography on basic alumina (5% EtOAc in toluene with 1% NEt_3) to afford **2** (80%) as a white foam: ^1H NMR (600 MHz, CDCl_3) δ 7.48 (m, 9H), 7.39 (m, 6H), 7.21 (m, 10H), 4.94 (dd, 1H, $J = 11.5, 2.0$ Hz), 4.48 (s, 1H), 4.02 (m, 1H), 3.52 (d, 1H, $J = 11.6$ Hz), 2.95 (m, 1H), 2.74 (dd, 1H, $J = 12.1, 9.7$ Hz), 1.76 (m, 1H), 1.66 (m, 1H), 1.37 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 156.8, 146.8, 146.4, 134.2 (d, $J_{31\text{P}-13\text{C}} = 13.7$ Hz), 131.2 (d, $J_{31\text{P}-13\text{C}} = 47.7$ Hz), 130.99 (d, $J_{31\text{P}-13\text{C}} = 4.4$ Hz), 128.9 (d, $J_{31\text{P}-13\text{C}} = 10.6$ Hz) 128.3, 128.2, 127.1, 127.0, 126.0, 125.7, 58.5 (d, $J_{31\text{P}-13\text{C}} = 3$ Hz), 54.8, 52.2, 52.1, 50.4, 37.1 (d, $J_{31\text{P}-13\text{C}} = 92$ Hz), 36.8, 29.8 ppm; ^{31}P NMR (240 MHz, CDCl_3) δ 45.4 ppm; HRMS (ESI) calc'd for $[\text{C}_{40}\text{H}_{43}\text{AuN}_2\text{OP}]^+$: m/z 795.2773, found 795.2791.

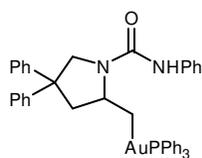


Alkyl Gold 4: From methyl urea **3**. Purified by flash column chromatography on basic alumina (10% EtOAc in toluene with 1% NEt_3) to afford **4** (59%) as a

white foam: ^1H NMR (600 MHz, CDCl_3) δ 7.47 (m, 8H), 7.43 – 7.36 (m, 6H), 7.31 – 7.21 (m, 9H), 7.21 – 7.15 (m, 1H), 7.12 (m, 1H), 4.94 (d, 1H, $J = 11.4$ Hz), 4.51 (q, 1H, $J = 4.6$ Hz), 4.13 – 3.99 (m, 1H), 3.60 (d, 1H, $J = 11.4$ Hz), 3.00 (ddd, 1H, $J = 12.1, 6.3, 1.5$ Hz), 2.81 (d, 3H, $J = 4.6$ Hz), 2.70 (dd, 1H, $J = 12.1, 9.6$ Hz), 1.76 (ddd, 1H, $J = 12.3, 8.7, 3.1$ Hz), 1.61 (ddd, 1H, $J = 13.0, 8.7, 8.4$ Hz) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 157.9, 146.8, 146.3, 134.2 (d, $J_{31\text{P}-13\text{C}} = 13.7$ Hz), 131.2 (d, $J_{31\text{P}-13\text{C}} = 50.0$ Hz), 131.0, 129.0 (d, $J_{31\text{P}-13\text{C}} = 10.6$ Hz), 128.3, 128.2, 127.1, 126.9, 126.0, 125.7, 58.5 (d, $J_{31\text{P}-13\text{C}} = 2.5$ Hz), 55.2, 52.2, 52.0, 37.10 (d, $J_{31\text{P}-13\text{C}} = 92.0$ Hz), 27.3 ppm; ^{31}P NMR (160 MHz, CDCl_3) δ 45.6 ppm; HRMS (ESI) calc'd for $[\text{C}_{37}\text{H}_{37}\text{AuN}_2\text{OP}]^+$: m/z 753.2309, found 753.2319.

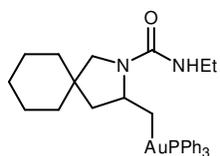


Alkyl Gold **6**: From ethyl urea **5**. Purified by flash column chromatography on basic alumina (5% EtOAc in toluene with 1% NEt_3) to afford **6** (63%) as a white foam: ^1H NMR (600 MHz, CDCl_3) δ 7.53 – 7.46 (m, 8H), 7.45 – 7.39 (m, 6H), 7.30 – 7.25 (m, 9H), 7.20 – 7.17 (m, 1H), 7.15 – 7.13 (m, 1H), 4.96 (d, 1H, $J = 10.4$ Hz), 4.53 (t, 1H, $J = 5.4$ Hz), 4.13 – 4.02 (m, 1H), 3.60 (d, 1H, $J = 11.5$ Hz), 3.38 – 3.25 (m, 1H), 3.00 (ddd, 1H, $J = 12.1, 6.0, 2.1$ Hz), 2.73 (dd, 1H, $J = 12.2, 9.6$ Hz), 1.79 (ddd, 1H, $J = 12.4, 9.0, 3.1$ Hz), 1.65 (dt, 1H, $J = 13.0, 8.5$ Hz), 1.13 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 157.3, 146.9, 146.4, 134.2 (d, $J_{31\text{P}-13\text{C}} = 13.7$ Hz), 131.2 (d, $J_{31\text{P}-13\text{C}} = 47.7$ Hz), 131.0 (d, $J_{31\text{P}-13\text{C}} = 2.2$ Hz), 129.0 (d, $J_{31\text{P}-13\text{C}} = 10.6$ Hz), 128.3, 127.1, 126.9, 126.0, 125.8, 58.5 (d, $J_{31\text{P}-13\text{C}} = 3.0$ Hz), 55.2, 52.2, 52.1, 37.1 (d, $J_{31\text{P}-13\text{C}} = 92.0$ Hz), 35.4, 16.0 ppm; ^{31}P NMR (160 MHz, CDCl_3) δ 45.6 ppm; HRMS (ESI) calc'd for $[\text{C}_{38}\text{H}_{39}\text{AuN}_2\text{OP}]^+$: m/z 767.2466, found 767.2474.

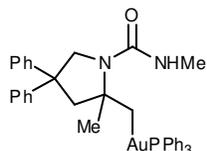


Alkyl Gold **8**: From phenyl urea **7**. Purified by flash column chromatography on basic alumina (1% EtOAc in toluene with 1% NEt_3) to afford **8** (66%) as a white foam: ^1H NMR (600 MHz, CDCl_3) δ 7.55 – 7.45 (m, 10H), 7.45 – 7.37 (m, 6H), 7.35 (d, 2H, $J = 7.8$ Hz), 7.33 – 7.20 (m, 10H), 7.16 (t, 1H, $J = 7.3$ Hz), 6.99 (t, 1H, $J = 7.4$ Hz), 6.71 (brs, 1H), 5.01 (d, 1H, $J = 11.4$ Hz), 4.35 – 4.31 (m, 1H), 3.70 (d, 1H, $J = 11.4$ Hz), 3.09 (ddd, 1H, $J = 12.2, 5.9, 2.0$ Hz), 2.81 (dd, 1H, $J = 12.2, 9.6$ Hz), 1.88 (ddd, 1H, $J = 12.9, 9.1, 3.1$ Hz), 1.81 (ddd, 1H, $J = 12.9, 8.2, 8.1$ Hz) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 154.2, 146.6, 146.0, 139.9, 134.2 (d, $J_{31\text{P}-13\text{C}} = 13.8$ Hz), 131.1 (d, $J_{31\text{P}-13\text{C}} = 48.6$ Hz), 131.0 (d, $J_{31\text{P}-13\text{C}}$

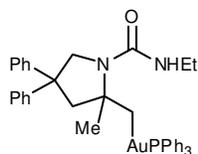
= 2.0 Hz), 129.0 (d, $J_{31\text{P}-13\text{C}} = 10.9$ Hz), 128.7, 128.4, 128.4, 127.1, 126.8, 126.2, 126.0, 122.0, 119.1, 58.9 (d, $J_{31\text{P}-13\text{C}} = 2.8$ Hz), 55.1, 52.1, 51.9, 37.4 ($J_{31\text{P}-13\text{C}} = 92.2$ Hz) ppm; ^{31}P NMR (160 MHz, CDCl_3) δ 45.5 ppm; HRMS (ESI) calc'd for $[\text{C}_{42}\text{H}_{39}\text{AuN}_2\text{OP}]^+$: m/z 815.2466, found 815.2471.



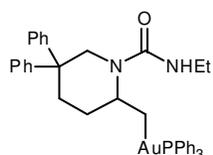
Alkyl Gold **10**: From ethyl urea **9**. Purified by flash column chromatography on basic alumina (5% EtOAc in toluene with 1% NEt_3) to afford **10** (49%) as white foam: ^1H NMR (600 MHz, CDCl_3) δ 7.54 – 7.43 (m, 15H), 4.45 (m, 1H), 4.21 (m, 1H), 3.77 (d, $J = 10.6$ Hz, 1H), 3.32 – 3.18 (m, 2H), 2.98 (d, $J = 10.7$ Hz, 1H), 2.23 (dd, $J = 12.3, 7.1$ Hz, 1H), 1.74 (ddd, $J = 12.6, 9.0, 3.5$ Hz, 1H), 1.56 (dt, $J = 12.6, 8.8$ Hz, 2H), 1.48 – 1.21 (m, 10H), 1.10 (t, $J = 7.2$ Hz, 3H) ppm; ^{13}C NMR (150 MHz, CDCl_3): δ 157.6, 134.2 (d, $J_{31\text{P}-13\text{C}} = 13.7$ Hz), 131.3 (d, $J_{31\text{P}-13\text{C}} = 47.3$ Hz), 130.96 (d, $J_{31\text{P}-13\text{C}} = 2.0$ Hz), 128.95 (d, $J_{31\text{P}-13\text{C}} = 10.6$ Hz), 58.5 (d, $J_{31\text{P}-13\text{C}} = 2.6$ Hz), 40.4, 37.9 (d, $J_{31\text{P}-13\text{C}} = 91.9$ Hz), 37.0, 35.3, 34.7, 26.4, 24.0, 22.9, 15.9 ppm; ^{31}P NMR (240 MHz, CDCl_3) δ 45.8 ppm; HRMS (ESI) calc'd for $[\text{C}_{31}\text{H}_{39}\text{AuNO}_2\text{P}]^+$: m/z 683.2460, found 683.2483.



Alkyl Gold **12**: From methyl urea **11**. Purified by flash column chromatography on basic alumina (5% EtOAc in toluene! with 1% NEt_3) to afford **12** (60%) as white foam: ^1H NMR (600 MHz, CDCl_3) δ 7.53 – 7.42 (m, 9H), 7.42 – 7.33 (m, 8H), 7.31 – 7.24 (m, 6H), 7.22 – 7.16 (m, 1H), 7.12 (dd, 1H, $J = 18.3, 11.0$ Hz), 4.84 (d, 1H, $J = 11.4$ Hz), 4.65 (brs, 1H), 3.84 (d, 1H, $J = 11.4$ Hz), 3.28 (d, 1H, $J = 12.3$ Hz), 2.86 (d, 1H, $J = 4.7$ Hz), 2.81 (d, 1H, $J = 12.3$ Hz), 1.91 (dd, 1H, $J = 13.0, 9.1$ Hz), 1.75 (dd, 1H, $J = 12.4, 9.1$ Hz), 1.15 (s, 1H) ppm; ^{13}C NMR (151 MHz, CDCl_3) δ 157.6, 147.8, 146.8, 134.2 (d, $J_{31\text{P}-13\text{C}} = 13.8$ Hz), 131.2 (d, $J_{31\text{P}-13\text{C}} = 47.6$ Hz), 131.0 (d, $J_{31\text{P}-13\text{C}} = 2.2$ Hz), 129.0 (d, $J_{31\text{P}-13\text{C}} = 10.6$ Hz), 128.3, 128.2, 127.2, 127.0, 125.8, 125.7, 66.5, 58.6, 56.1, 50.1, 47.8 (d, $J_{31\text{P}-13\text{C}} = 92.6$ Hz), 31.6 (d, $J_{31\text{P}-13\text{C}} = 5.2$ Hz), 27.31 ppm; ^{31}P NMR (160 MHz, CDCl_3) δ 45.4 ppm; HRMS (ESI) calc'd for $[\text{C}_{38}\text{H}_{39}\text{AuN}_2\text{OP}]^+$: m/z 767.2466, found 767.2443.

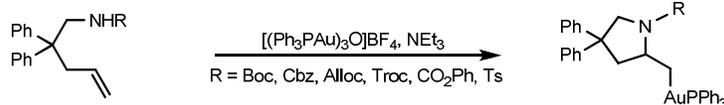


Alkyl Gold **14**: From ethyl urea **13**. Purified by flash column chromatography on basic alumina (5% EtOAc in toluene with 1% NEt₃) to afford **14** (40%) as white foam: ¹H NMR (500 MHz, CDCl₃) δ 7.54 – 7.42 (m, 9H), 7.42 – 7.34 (m, 8H), 7.31 – 7.24 (m, 6H), 7.18 (dd, 1H, *J* = 13.4, 6.3 Hz), 7.13 (dd, 1H, *J* = 16.4, 9.1 Hz), 4.86 (d, 1H, *J* = 11.4 Hz), 4.67 (brs, 1H), 3.85 (d, 1H, *J* = 11.4 Hz), 3.44 – 3.28 (m, 3H), 2.82 (dd, *J* = 12.2, 1.6 Hz, 1H), 1.93 (dd, *J* = 13.0, 9.1 Hz, 1H), 1.74 (dd, *J* = 12.8, 7.9 Hz, 1H), 1.16 (s, 3H), 1.15 (t, 3H, *J* = 7.3 Hz) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 156.9, 147.9, 146.8, 134.3 (d, *J*_{31P-13C} = 13.8 Hz), 131.2 (d, *J*_{31P-13C} = 47.6 Hz), 131.0 (d, *J*_{31P-13C} = 2.2 Hz), 129.0 (d, *J*_{31P-13C} = 10.6 Hz), 128.3, 128.2, 127.2, 127.0, 125.8, 125.7, 66.4 (d, *J*_{31P-13C} = 4.5 Hz), 58.7, 56.0, 47.9 (d, *J*_{31P-13C} = 92.6 Hz), 47.5, 35.3, 31.6 (d, *J*_{31P-13C} = 5.2 Hz), 15.9 ppm; ³¹P NMR (160 MHz, CDCl₃) δ 45.3 ppm; HRMS (ESI) calc'd for [C₃₉H₄₁AuN₂OP]⁺: *m/z* 781.2617, found 781.2620.



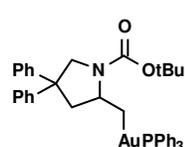
Alkyl Gold **20**: To a solution of ethyl urea **19** (0.027 g, 0.084 mmol) and triethylamine (24 μL, 0.17 mmol) in DCM (0.5 mL) was added [(Ph₃P₃Au)₃O]BF₄ and stirred overnight. The reaction was diluted with DCM (3 mL) and washed with saturated NaHCO₃ (2 × 3 mL), dried over MgSO₄, filtered, and concentrated *in vacuo*, to yield a yellow foam. The crude material was purified by flash column chromatography on basic alumina (40:20:1 toluene/DCM/EtOAc with 1% NEt₃) to afford **20** (20 mg, 30% yield) as a white foam: ¹H NMR (600 MHz, CD₂Cl₂) δ 7.52 – 7.44 (m, 17H), 7.28 – 7.24 (m, 4H), 7.17 – 7.08 (m, 4H), 5.07 (dd, 1H, *J* = 13.9, 2.3 Hz), 4.67 (t, 1H, *J* = 5.2 Hz), 4.23 (br s, 1H), 3.30 (d, 1H, *J* = 13.9 Hz), 3.25 – 3.19 (m, 1H), 3.15 – 3.08 (m, 1H), 2.91 (dt, 1H, *J* = 13.3, 3.42 Hz), 2.43 – 2.40 (m, 1H), 1.74 – 1.60 (m, 4H), 1.03 (t, 3H, *J* = 7.2 Hz) ppm; ¹³C NMR (150 MHz, CD₂Cl₂) δ 157.4, 148.6, 145.9, 134.2 (d, *J*_{31P-13C} = 13.7 Hz), 131.3 (d, *J*_{31P-13C} = 47.5 Hz), 131.0, 128.9 (d, *J*_{31P-13C} = 10.5 Hz), 128.0, 128.0, 128.0, 126.7, 125.75, 125.4, 46.6, 45.4, 35.6, 30.8 (d, *J*_{31P-13C} = 93.4 Hz), 30.4, 30.4, 29.5, 15.4 ppm; ³¹P NMR (160 MHz, CD₂Cl₂) δ 45.4 ppm; IR (neat): 3449, 2092, 1624.3, 1496, 1435, 1272, 1124, 1027, 1011 cm⁻¹; HRMS (ESI) calc'd for [C₃₉H₄₁AuN₂OP]⁺: *m/z* 781.2617, found 781.2625.

IV. Carbamate Aminoauration

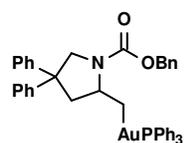


General Procedure for the aminoauration of carbamate, sulfonyl and acetamide substrates:

Protected amine (100 μmol) and triethylamine (200 μmol) were combined in CDCl_3 (1.0 mL) and let stir for five minutes before the addition of the gold trimer (40 μmol) in one portion. After 12 hours, the reaction mixture was diluted with CHCl_3 (10 mL) and washed with H_2O (2×5 mL). The organic layer was then dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was then suspended in EtOAc and filtered through a pad of basic alumina, the concentrated *in vacuo*.

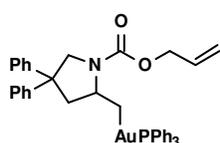


Alkyl Gold 22: From *t*-butyl carbamate **21**. Purified by flash chromatography on silica gel (gradient: 5% – 10% EtOAc in pentanes with 0.5% NEt_3) to afford **22** (53%) as a white foam. ^1H NMR shows a 3:1 mixture of rotomers in C_6D_6 , confirmed by heating to 60 $^\circ\text{C}$, where peaks coalesced to broad singlets. Major rotomer: ^1H NMR (600 MHz, CDCl_3 , 298 K) δ 7.45 – 7.35 (m, 8H), 7.13 – 7.07 (m, 4H), 7.01 – 6.91 (m, 13H), 5.14 (d, 1H, $J = 11.5, 1.4$ Hz), 4.89 – 4.83 (m, 1H), 3.90 (d, 1H, $J = 11.5$ Hz), 3.07 (ddd, 1H, $J = 12.1, 6.3, 1.8$ Hz), 2.91 (dd, 1H, $J = 12.1, 9.9$ Hz), 2.62 (ddd, 1H, $J = 12.5, 8.4, 8.0$ Hz), 2.44 (ddd, 1H, $J = 11.3, 8.4, 1.7$ Hz), 1.60 (s, 9H) ppm; ^{13}C NMR (150 MHz, C_6D_6 , 298 K) δ 155.1, 147.3, 146.7, 134.2 (d, $J_{31\text{P}-13\text{C}} = 13.8$ Hz), 131.7 (d, $J_{31\text{P}-13\text{C}} = 46.2$ Hz), 130.5, 128.8 (d, $J_{31\text{P}-13\text{C}} = 10.5$ Hz), 128.2, 128.2, 127.2, 127.1, 125.7, 125.6, 77.4, 59.7 (d, $J_{31\text{P}-13\text{C}} = 3.5$ Hz), 55.8, 52.9, 51.4, 39.1 (d, $J_{31\text{P}-13\text{C}} = 91.7$ Hz), 28.6 ppm; ^{31}P NMR (240 MHz, C_6D_6 , 298 K) δ 45.7 ppm; Minor rotomer: ^1H NMR (600 MHz, CDCl_3 , 298 K) δ 7.45 – 7.35 (m, 8H), 7.13 – 7.07 (m, 4H), 7.01 – 6.91 (m, 13H), 5.09 – 5.02 (m, 1H), 4.80 (d, 1H, $J = 11.0$ Hz), 3.98 (d, 1H, $J = 11.0$ Hz), 3.13 (dd, 1H, $J = 11.5, 6.7$ Hz), 2.80 (app t, 1H, $J = 9.1$ Hz), 2.74 (dd, 1H, $J = 11.5, 10.6$ Hz), 2.53 – 2.58 (m, 1H), 1.53 (s, 9H) ppm; ^{31}P NMR (240 MHz, C_6D_6 , 298 K) δ 45.6 ppm; HRMS (ESI) calc'd for $[\text{C}_{40}\text{H}_{42}\text{AuNO}_2\text{P}]^+$: m/z 796.2626, found 796.2613.



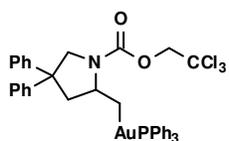
Alkyl Gold 24: From benzyl carbamate **23**. Purified by flash chromatography on silica gel (gradient: 10% – 20% EtOAc in pentanes with 0.5% NEt_3) to afford **24** (49%) as an off-white foam. ^1H NMR shows a 1.5:1 mixture of rotomers in CDCl_3 , confirmed by heating to 60 $^\circ\text{C}$ in C_6D_6 where peaks coalesced to broad singlets. Major

rotomer: ^1H NMR (600 MHz, CDCl_3 , 298 K) δ 7.53 – 7.46 (m, 10H), 7.43 – 7.32 (m, 9H), 7.31 – 7.13 (m, 11H), 5.24 (d, 1H, $J = 13.0$ Hz), 5.22 (d, 1H, $J = 13.0$ Hz), 4.77 (dd, 1H, $J = 11.5, 1.7$ Hz), 4.52 – 4.43 (m, 1H), 3.75 (d, 1H, $J = 11.5$ Hz), 3.02 – 3.07 (m, 1H), 2.67 (dd, 1H, $J = 12.3, 9.8$ Hz), 1.95 (ddd, 1H, $J = 11.9, 9.1, 2.7$ Hz), 1.87 – 1.82 (m, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3 , 298 K) δ 155.5, 146.8, 146.1, 137.8, 134.3 (d, $J_{31\text{P}-13\text{C}} = 13.4$ Hz), 131.4 (d, $J_{31\text{P}-13\text{C}} = 46.9$ Hz), 130.9 (d, $J_{31\text{P}-13\text{C}} = 2.1$ Hz), 128.9 (d, $J_{31\text{P}-13\text{C}} = 10.3$ Hz), 128.9, 128.4, 128.3, 128.3, 127.9, 127.3, 127.1, 126.8, 126.1, 125.9, 66.2, 60.0 (d, $J_{31\text{P}-13\text{C}} = 2.4$ Hz), 55.8, 52.7, 51.0, 37.8 (d, $J_{31\text{P}-13\text{C}} = 92.1$ Hz) ppm; ^{31}P NMR (240 MHz, CDCl_3 , 298 K) δ 45.8 ppm; Minor rotomer: ^1H NMR (600 MHz, CDCl_3 , 298 K) δ 7.53 – 7.46 (m, 10H), 7.43 – 7.32 (m, 9H), 7.31 – 7.13 (m, 11H), 5.35 (d, 1H, $J = 12.5$ Hz), 5.07 (d, 1H, $J = 12.5$ Hz), 4.63 (dd, 1H, $J = 11.45, 1.2$ Hz), 4.52 – 4.43 (m, 1H), 3.79 (d, 1H, $J = 11.4$ Hz), 3.02 – 3.07 (m, 1H), 2.57 (dd, 1H, $J = 12.4, 9.8$ Hz), 2.08 (ddd, 1H, $J = 11.8, 9.2, 2.6$ Hz), 1.85 – 1.79 (m, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3 , 298 K) δ 154.3, 146.8, 146.2, 137.8, 134.2 (d, $J_{31\text{P}-13\text{C}} = 13.6$ Hz), 131.6 (d, $J_{31\text{P}-13\text{C}} = 46.5$ Hz), 130.9 (d, $J_{31\text{P}-13\text{C}} = 1.8$ Hz), 129.2 (d, $J_{31\text{P}-13\text{C}} = 11.8$ Hz), 128.5, 128.3, 128.3, 127.7, 127.3, 127.1, 126.8, 126.1, 125.9, 66.2, 60.6 (d, $J_{31\text{P}-13\text{C}} = 2.7$ Hz), 55.8, 52.8, 50.1, 36.7 (d, $J_{31\text{P}-13\text{C}} = 91.8$ Hz) ppm; ^{31}P NMR (240 MHz, CDCl_3 , 298 K) δ 45.7 ppm; HRMS (ESI) calc'd for $[\text{C}_{43}\text{H}_{40}\text{AuNO}_2\text{P}]^+$: m/z 830.2476, found 830.2457.

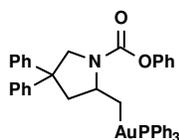


Alkyl Gold **26**: From allyl carbamate **25**. Purified by flash chromatography on silica gel (gradient: 10% – 20% EtOAc in pentanes with 0.5% NEt_3) to afford **26** (37%) as a white foam. ^1H NMR shows a 1.5:1 mixture of rotomers in CDCl_3 , confirmed by heating to 60 °C in C_6D_6 where peaks coalesced to broad singlets. Major rotomer: ^1H NMR (600 MHz, CDCl_3 , 298 K) δ 7.53 – 7.46 (m, 10H), 7.43 – 7.39 (m, 6H), 7.32 – 7.19 (m, 8H), 7.17 – 7.13 (m, 1H), 6.01 – 5.93 (m, 1H), 5.31 (dd, 1H, $J = 17.1, 1.4$ Hz), 5.14 (dd, 1H, $J = 10.6, 1.4$ Hz), 4.76 – 4.58 (m, 3H), 4.43 – 4.37 (m, 1H), 3.73 (d, 1H, $J = 11.4$ Hz), 3.08 – 3.03 (m, 1H), 2.66 (dd, 1H, $J = 12.5, 9.9$ Hz), 1.96 (ddd, 1H, $J = 12.0, 9.1, 2.8$ Hz), 1.84 – 1.75 (m, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3 , 298 K) δ 155.4, 146.9, 146.1, 134.3 (d, $J_{31\text{P}-13\text{C}} = 14.0$ Hz), 133.8, 132.0, 131.4 (d, $J_{31\text{P}-13\text{C}} = 46.7$ Hz), 130.9 (d, $J_{31\text{P}-13\text{C}} = 1.7$ Hz), 129.0 (d, $J_{31\text{P}-13\text{C}} = 10.4$ Hz), 128.9, 128.3, 127.0, 126.8, 126.1, 125.9, 116.2, 65.2, 60.0 (d, $J_{31\text{P}-13\text{C}} = 2.7$ Hz), 55.7, 52.7, 51.0, 37.6 (d, $J_{31\text{P}-13\text{C}} = 91.6$ Hz) ppm; ^{31}P NMR (240 MHz, CDCl_3 , 298 K) δ 45.8 ppm; Minor rotomer: ^1H NMR (600 MHz, CDCl_3 , 298 K) δ 7.53 – 7.46 (m, 10H), 7.43 –

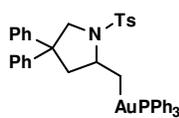
7.39 (m, 6H), 7.32 – 7.19 (m, 8H), 7.17 – 7.13 (m, 1H), 6.01 – 5.93 (m, 1H), 5.29 (dd, 1H, $J = 17.1, 1.3$ Hz), 5.14 (dd, 1H, $J = 10.4, 1.3$ Hz), 4.76 – 4.58 (m, 3H), 4.53 – 4.46 (m, 1H), 3.80 (d, 1H, $J = 11.3$ Hz), 3.08 – 3.03 (m, 1H), 2.56 (dd, 1H, $J = 12.3, 9.6$ Hz), 2.05 (ddd, 1H, $J = 12.0, 9.2, 2.6$ Hz), 1.84 – 1.73 (m, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3 , 298 K) δ 154.1, 146.9, 146.3, 143.1 (d, $J_{31\text{P}-13\text{C}} = 13.4$ Hz), 133.9, 132.0, 131.6 (d, $J_{31\text{P}-13\text{C}} = 47.0$ Hz), 130.9 (d, $J_{31\text{P}-13\text{C}} = 1.5$ Hz), 129.3 (d, $J_{31\text{P}-13\text{C}} = 11.8$ Hz), 128.9, 128.3, 127.0, 126.8, 126.1, 125.9, 116.7, 65.1, 60.5 (d, $J_{31\text{P}-13\text{C}} = 1.9$ Hz), 55.8, 52.9, 50.1, 37.8 (d, $J_{31\text{P}-13\text{C}} = 91.6$ Hz) ppm; ^{31}P NMR (240 MHz, CDCl_3 , 298 K) δ 45.7 ppm; HRMS (ESI) calc'd for $[\text{C}_{39}\text{H}_{38}\text{AuNO}_2\text{P}]^+$: m/z 780.2313, found 780.2300.



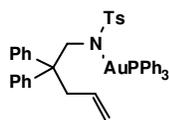
Alkyl Gold **28**: From trichloromethyl carbamate **27**. Purified by flash chromatography on silica gel (gradient: 5% – 10% EtOAc in pentanes with 0.5% NEt_3) to afford **28** (43%) as a white foam. ^1H NMR shows a 1.3:1 mixture of rotomers in CDCl_3 , confirmed by heating to 60 °C in C_6D_6 where peaks coalesced to broad singlets. Major rotomer: ^1H NMR (600 MHz, CDCl_3 , 298 K) δ 7.54 – 7.47 (m, 9H), 7.45 – 7.39 (m, 6H), 7.33 – 7.20 (m, 9H), 7.17 – 7.14 (m, 1H), 4.85 (d, 1H, $J = 12.1$ Hz), 4.83 (d, 1H, $J = 12.1$ Hz), 4.77 (dd, 1H, $J = 11.5, 2.3$ Hz), 4.60 – 4.54 (m, 1H), 3.79 (d, 1H, $J = 11.5$ Hz), 3.10 – 3.06 (m, 1H), 2.69 (dd, 1H, $J = 12.5, 9.8$ Hz), 1.98 – 1.94 (m, 2H) ppm; ^{13}C NMR (150 MHz, CDCl_3 , 298 K) δ 153.7, 146.6, 145.7, 134.2 (d, $J_{31\text{P}-13\text{C}} = 13.8$ Hz), 131.4 (d, $J_{31\text{P}-13\text{C}} = 47.1$ Hz), 130.9, 129.0 (d, $J_{31\text{P}-13\text{C}} = 10.5$ Hz), 128.4, 128.4, 127.0, 126.8, 126.2, 126.0, 96.2, 74.6, 60.5 (d, $J_{31\text{P}-13\text{C}} = 3.2$ Hz), 55.9, 52.8, 50.7, 37.6 (d, $J_{31\text{P}-13\text{C}} = 91.6$ Hz) ppm; ^{31}P NMR (240 MHz, CDCl_3 , 298 K) δ 45.8 ppm. Minor rotomer: ^1H NMR (600 MHz, CDCl_3 , 298 K) δ 7.54 – 7.47 (m, 9H), 7.45 – 7.39 (m, 6H), 7.33 – 7.20 (m, 9H), 7.17 – 7.14 (m, 1H), 5.03 (d, 1H, $J = 12.0$ Hz), 4.75 (dd, 1H, $J = 11.4, 2.3$ Hz), 4.58 (d, 1H, $J = 12.0$ Hz), 4.53 – 4.48 (m, 1H), 3.86 (d, 1H, $J = 11.4$ Hz), 3.12 – 3.08 (m, 1H), 2.59 (dd, 1H, $J = 12.6, 9.8$ Hz), 2.06 (ddd, 1H, $J = 12.2, 9.1, 3.0$ Hz), 1.81 (dt, 1H, $J = 12.2, 8.5$ Hz) ppm; ^{13}C NMR (150 MHz, CDCl_3 , 298 K) δ 152.1, 146.5, 145.7, 134.2 (d, $J_{31\text{P}-13\text{C}} = 13.8$ Hz), 134.4 (d, $J_{31\text{P}-13\text{C}} = 47.1$ Hz), 130.9, 129.0 (d, $J_{31\text{P}-13\text{C}} = 10.5$ Hz), 128.4, 128.4, 127.0, 126.8, 126.2, 126.1, 96.4, 74.4, 61.0 (d, $J_{31\text{P}-13\text{C}} = 2.6$ Hz), 55.8, 52.9, 50.0, 36.3 (d, $J_{31\text{P}-13\text{C}} = 91.9$ Hz) ppm; ^{31}P NMR (240 MHz, CDCl_3 , 298 K) δ 45.8 ppm; HRMS (ESI) calc'd for $[\text{C}_{38}\text{H}_{35}\text{AuNO}_2\text{PCl}_3]^+$: m/z 870.1151, found 870.1131.



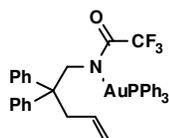
Alkyl Gold **30**: From phenyl carbamate **29**. Purified by flash chromatography on silica gel (gradient: 10% – 20% EtOAc in pentanes with 0.5% NEt₃) to afford **30** (69%) as a white foam. ¹H NMR shows a 2:1 mixture of rotomers in CDCl₃, confirmed by heating to 60 °C in C₆D₆ where peaks coalesced to broad singlets. Major rotomer: ¹H NMR (600 MHz, CDCl₃, 298 K) δ 7.56 – 7.47 (m, 9H), 7.44 – 7.27 (m, 16H), 7.23 – 7.16 (m, 5H), 4.78 (dd, 1H, *J* = 11.4, 2.1 Hz), 4.64 – 4.58 (m, 1H), 3.82 (d, 1H, *J* = 11.4 Hz), 3.12 (ddd, 1H, *J* = 12.2, 6.3, 2.2 Hz), 2.72 (dd, 1H, *J* = 12.5, 9.8 Hz), 2.06 – 2.02 (m, 1H), 1.95 (dt, 1H, *J* = 12.3, 8.5 Hz) ppm; ¹³C NMR (150 MHz, CDCl₃, 298 K) δ 153.9, 152.1, 146.7, 145.9, 134.3 (d, *J*_{31P-13C} = 13.7 Hz), 131.3 (d, *J*_{31P-13C} = 47.2 Hz), 137.0 (d, *J*_{31P-13C} = 2.1 Hz), 129.0, 129.0 (d, *J*_{31P-13C} = 10.8 Hz), 128.4, 128.4, 127.1, 126.8, 126.2, 126.0, 124.6, 121.9, 60.6 (d, *J*_{31P-13C} = 2.7 Hz), 55.8, 52.7, 50.8, 37.7 (d, *J*_{31P-13C} = 91.3 Hz) ppm; ³¹P NMR (240 MHz, CDCl₃, 298 K) δ 45.9 ppm; Minor rotomer: ¹H NMR (600 MHz, CDCl₃, 298 K) δ 7.56 – 7.47 (m, 9H), 7.44 – 7.27 (m, 16H), 7.23 – 7.16 (m, 4H), 7.12 (d, 2H, *J* = 7.1 Hz), 4.83 (dd, 1H, *J* = 11.4, 1.8 Hz), 4.64 – 4.58 (m, 1H), 3.96 (d, 1H, *J* = 11.4 Hz), 3.17 – 3.12 (m, 1H), 2.63 (dd, 1H, *J* = 12.6, 9.8 Hz), 2.08 – 2.05 (m, 1H), 1.91 (dt, 1H, *J* = 12.2, 8.4 Hz) ppm; ¹³C NMR (150 MHz, CDCl₃, 298 K) δ 152.5, 151.8, 146.7, 146.0, 134.3 (d, *J*_{31P-13C} = 13.6 Hz), 130.9 (d, *J*_{31P-13C} = 2.0 Hz), 129.0 (d, *J*_{31P-13C} = 10.6 Hz), 128.4, 128.4, 127.1, 126.8, 126.2, 126.1, 124.6, 121.9, 60.9 (d, *J*_{31P-13C} = 3.0 Hz), 56.3, 53.1, 50.8, 36.6 (d, *J*_{31P-13C} = 91.5 Hz) ppm; ³¹P NMR (240 MHz, CDCl₃, 298 K) δ 45.8 ppm; HRMS (ESI) calc'd for [C₄₂H₃₈AuNO₂P]⁺: *m/z* 816.2325, found 816.2300.



Alkyl Gold **33**: From tosylamide **31**. Purified by flash chromatography on silica gel (10% EtOAc in pentanes with 0.5% NEt₃) to afford **33** (29%) as a white foam: ¹H NMR (600 MHz, CDCl₃) δ 7.69 (d, 2H, *J* = 8.2 Hz), 7.54 – 7.41 (m, 8H), 7.31 – 7.29 (m, 3H), 7.26 – 7.11 (m, 8H), 7.09 (d, 2H, *J* = 8.2 Hz), 4.53 (dd, 1H, *J* = 10.3, 1.1 Hz), 4.52 – 4.46 (m, 1H), 3.93 (d, 1H, *J* = 10.3 Hz), 3.08 (ddd, 1H, *J* = 12.5, 6.0, 1.1 Hz), 2.58 (dd, 1H, *J* = 12.5, 9.5 Hz), 2.33 (s, 3H), 2.05 (ddd, 1H, *J* = 12.3, 8.9, 3.4 Hz), 1.52 (ddd, 1H, *J* = 11.8, 10.1, 8.9 Hz) ppm; ¹³C NMR (150 MHz, CDCl₃) δ 146.8, 145.6, 141.7, 139.1, 134.3 (d, *J*_{31P-13C} = 13.7 Hz), 131.4 (d, *J*_{31P-13C} = 47.2 Hz), 131.0 (d, *J*_{31P-13C} = 2.2 Hz), 129.1, 129.0 (d, *J*_{31P-13C} = 10.5 Hz), 128.3, 127.0, 127.0, 126.9, 126.1, 125.9, 64.6 (d, *J*_{31P-13C} = 1.5 Hz), 58.3, 52.5, 51.2, 37.4 (d, *J*_{31P-13C} = 90.5 Hz), 21.4 ppm; ³¹P NMR (240 MHz, CDCl₃) δ 45.34 ppm; HRMS (ESI) calc'd for [C₄₂H₄₀AuNO₂PS]⁺: *m/z* 850.2203, found 850.2177.

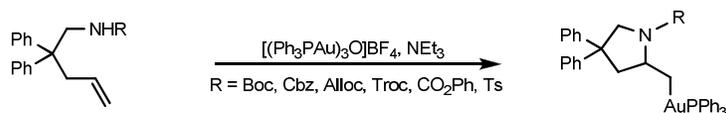


Gold Tosylamide **35** was independently synthesized by the following method: In the glove box, sodium hydride (1.9 mg, 0.075 mmol, 1 equiv) was added to a solution of tosylamide **31** (30 mg, 0.075 mmol, 1 equiv) in THF (1 mL). The solution was stirred until gas evolution ceased (30 min). Triphenylphosphine gold chloride (37 mg, 0.075 mmol, 1 equiv) was added and the reaction mixture was stirred for 30 min. The resulting white suspension was filtered through a glass microfilter fiber plug and concentrated in vacuo to yield **31** as an off-white solid (50 mg, 79%): ¹H NMR (600 MHz, d₈-THF) δ 7.81 (d, 2H, *J* = 8.1 Hz), 7.55 (ddt, 3H, *J* = 9.4, 5.3, 1.8 Hz), 7.49 (m, 6H), 7.42 (m, 6H), 7.13 (m, 6H), 6.93 (dd, 4H, *J* = 8.2, 7.5 Hz), 6.77 (t, 2H, *J* = 7.3 Hz), 5.70 (m, 1H), 4.74 (m, 2H), 4.11 (s, 2H), 3.10 (d, 2H, *J* = 7.1 Hz), 2.35 (s, 3H) ppm; ¹³C NMR (150 MHz, d₈-THF): δ 147.0, 143.0, 139.5, 135.2, 134.35 (d, *J*_{31P-13C} = 13.9 Hz), 131.30 (d, *J*_{31P-13C} = 2.7 Hz), 129.8 (d, *J*_{31P-13C} = 60.5 Hz), 128.7 (d, *J*_{31P-13C} = 11.5 Hz), 128.38, 128.35, 127.5, 126.9, 125.3, 116.3, 55.6, 50.5, 41.6, 20.3 ppm; ³¹P NMR (240 MHz, d₈-THF) δ 31.7 ppm; HRMS (ESI) calc'd for M+(Ph₃P)₂Au⁺ [C₆₀H₅₄AuNO₂PS]⁺: *m/z* 1308.2676, found 1308.2713.

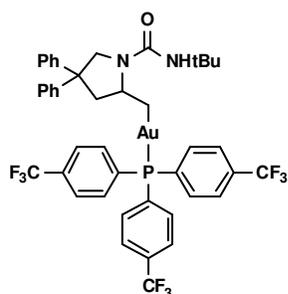


Gold Amide **36** was independently synthesized by the following method: In the glove box, sodium hydride (1.9 mg, 0.075 mmol, 1 equiv) was added to a solution of amide **32** (25 mg, 0.075 mmol, 1 equiv) in THF (1 mL). The solution was stirred until gas evolution ceased (30 min). Triphenylphosphine gold chloride (37 mg, 0.075 mmol, 1 equiv) was added and the reaction mixture was stirred for 30 min. The resulting white suspension was filtered through a glass microfilter fiber plug and concentrated in vacuo to yield **36** as an off-white solid (45 mg, 76%): ¹H NMR (600 MHz, d₈-THF) δ 7.56 (t, 3H, *J* = 7.1 Hz), 7.50 (t, 6H, *J* = 6.7 Hz), 7.35 (m, 6H), 7.19 (d, 4H, *J* = 7.7 Hz), 6.97 (t, 4H, *J* = 7.5 Hz), 6.77 (t, 2H, *J* = 7.1 Hz), 4.70 (m, 2H), 4.57 (s, 2H), 2.89 (d, 2H, *J* = 6.7 Hz) ppm; ¹³C NMR (150 MHz, d₈-THF) δ 163.6 (m) 147.5, 135.7, 134.2 (d, *J*_{31P-13C} = 13.7 Hz), 131.6, 128.90, 128.85 (d, *J*_{31P-13C} = 11.6 Hz), 128.6 (d, *J*_{31P-13C} = 46.2 Hz), 127.5, 125.4, 116.1, 54.5, 51.5, 41.4 ppm; ³¹P NMR (240 MHz, d₈-THF) δ 31.2 ppm; HRMS (ESI) calc'd for M+(Ph₃P)₂Au⁺ [C₅₅H₄₇AuNO₂PCl₃]⁺: *m/z* 1250.2411, found 1250.2434.

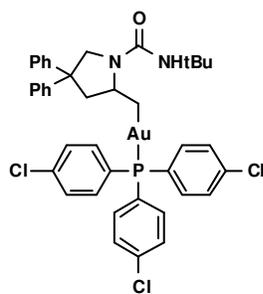
V. Aminoauration with Alternate Ligands



General Procedure for the aminoauration with arylphosphine ligands: *t*-Butyl urea **2** (100 μmol) and triethylamine (200 μmol) were combined in CDCl_3 (1.0 mL) and let stir for five minutes before the addition of the gold trimer (40 μmol) in one portion. After 12 hours, the reaction mixture was diluted with CHCl_3 (10 mL) and washed with H_2O (2×5 mL). The organic layer was then dried over Na_2SO_4 , filtered and concentrated *in vacuo*. The residue was then suspended in EtOAc and filtered through a pad of basic alumina, the concentrated *in vacuo*.

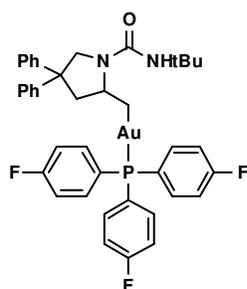


Trifluoromethyl Phosphine **39**: Purified by flash column chromatography on basic alumina (99:1 toluene/EtOAc with 1% NEt_3) to afford **39** (68%) as a white foam: ^1H NMR (600 MHz, CDCl_3) δ 7.66 (d, 6H, $J = 6.9$ Hz), 7.64 – 7.58 (m, 6H), 7.35 – 7.21 (m, 9H), 7.18 – 7.13 (m, 1H), 4.94 (d, 1H, $J = 11.4$ Hz), 4.41 (brs, 1H), 4.28 – 4.16 (m, 1H), 3.51 (d, 1H, $J = 11.4$ Hz), 2.95 (ddd, 1H, $J = 12.1, 6.0, 2.2$ Hz), 2.77 (dd, 1H, $J = 12.1, 9.5$ Hz), 1.90 – 1.73 (m, 2H), 1.38 (s, 9H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 156.6, 146.9, 146.3, 134.6 (d, $J_{31\text{P}-13\text{C}} = 15.0$ Hz), 134.2 (d, $J_{31\text{P}-13\text{C}} = 44.2$ Hz), 133.7 (qd, $J_{19\text{F}-13\text{C}} = 33.6$ Hz, $J_{31\text{P}-13\text{C}} = 1.8$ Hz), 128.4, 128.3, 127.0, 126.8, 126.2 (dq, $J_{31\text{P}-13\text{C}} = 11.2$ Hz, $J_{19\text{F}-13\text{C}} = 3.9$ Hz), 125.8, 123.3 (q, $J_{19\text{F}-13\text{C}} = 273.5$ Hz), 57.8 (d, $J_{31\text{P}-13\text{C}} = 4.0$ Hz), 54.9, 52.1, 52.0, 50.5, 33.0 (d, $J_{31\text{P}-13\text{C}} = 93.4$ Hz), 29.8 ppm; ^{31}P NMR (160 MHz, CDCl_3) δ 45.3 ppm; HRMS (ESI) calc'd for $[\text{C}_{43}\text{H}_{40}\text{AuF}_9\text{N}_2\text{OP}]^+$: m/z 999.2400, found 999.2406.



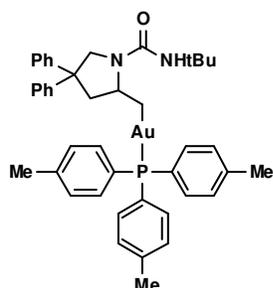
Chloro Phosphine **40**: Purified by flash column chromatography on basic alumina (99:1 toluene/EtOAc with 1% NEt_3) to afford **40** (67%) as a red foam: ^1H NMR (600 MHz, CDCl_3) δ 7.39 – 7.31 (m, 11H), 7.30 – 7.20 (m, 10H), 7.15 – 7.10 (m, 1H), 4.92 (dd, 1H, $J = 11.5, 2.2$ Hz), 4.40 (s, 1H), 4.17 – 4.05 (m, 1H), 3.47 (d, 1H, $J = 11.5$ Hz), 2.91 (ddd, 1H, $J = 12.0, 6.0, 2.2$ Hz), 2.71 (dd, 1H, $J = 12.0, 9.6$ Hz), 1.75 – 1.70 (m, 1H), 1.36 (s, 1H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 156.6, 146.8, 146.3, 138.1 (d, $J_{31\text{P}-13\text{C}} = 2.2$ Hz), 135.3, (d, $J_{31\text{P}-13\text{C}} = 15.2$ Hz), 129.5, (d, $J_{31\text{P}-13\text{C}} = 11.2$ Hz), 128.9 (d, $J_{31\text{P}-13\text{C}} = 47.8$ Hz),

128.4, 128.2, 127.0, 126.8, 126.2, 125.8, 58.0 (d, $J_{31\text{P}-13\text{C}} = 3.6$ Hz), 54.8, 52.1, 52.0, 50.4, 37.5 (d, $J_{31\text{P}-13\text{C}} = 92.9$ Hz), 29.8 ppm; ^{31}P NMR (160 MHz, CDCl_3) δ 44.1 ppm; HRMS (ESI) calc'd for $[\text{C}_{40}\text{H}_{40}\text{AuN}_2\text{OPCl}_3]^+$: m/z 891.1604, found 891.1614.



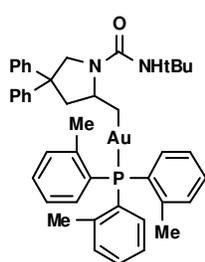
Fluorophosphine 41: Purified by flash column chromatography on basic alumina (99:1 toluene/EtOAc with 1% NEt_3) to afford **41** (75%) as a faint pink foam: ^1H NMR (500 MHz, CDCl_3) δ 7.49 – 7.44 (m, 6H), 7.36 – 7.22

(m, 9H), 7.17 – 7.08 (m, 7H), 4.95 (dd, 1H, $J = 11.5, 1.3$ Hz), 4.45 (brs, 1H), 4.19 – 4.11 (m, 1H), 3.51 (d, $J = 11.5$ Hz, 1H), 2.94 (ddd, 1H, $J = 12.1, 6.0, 2.0$ Hz), 2.75 (dd, $J = 12.1, 9.7$ Hz, 1H), 1.74 – 1.71 (m, 2H), 1.39 (s, 9H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 164.6 (d, $J_{19\text{F}-13\text{C}} = 253.7$ Hz), 156.7, 146.9, 146.4, 136.3 (dd, $J_{31\text{P}-13\text{C}} = 15.7, J_{19\text{F}-13\text{C}} = 8.6$ Hz), 128.4, 128.3, 127.1, 127.0, 126.6 (d, $J_{31\text{P}-13\text{C}} = 51.8$ Hz), 126.2, 125.8, 116.6 (dd, $J_{19\text{F}-13\text{C}} = 21.5, J_{31\text{P}-13\text{C}} = 11.8$ Hz), 58.1 (d, $J_{31\text{P}-13\text{C}} = 1.9$ Hz), 54.8, 52.1, 52.1, 50.4, 37.4 (d, $J_{31\text{P}-13\text{C}} = 93.0$ Hz), 29.8 ppm; ^{31}P NMR (160 MHz, CDCl_3) δ 43.6 ppm; HRMS (ESI) calc'd for $[\text{C}_{40}\text{H}_{40}\text{AuN}_2\text{OPF}_3]^+$: m/z 849.2490, found 849.2496.



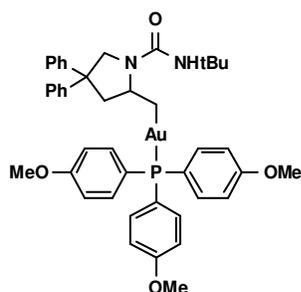
para-Methyl Phosphine 42: Purified by flash column chromatography on

basic alumina (99:1 toluene/EtOAc with 1% NEt_3) to afford **42** (72%) as an off-white foam: ^1H NMR (600 MHz, CDCl_3) δ 7.42 – 7.38 (m, 6H), 7.34 – 7.24 (m, 8H), 7.24 – 7.16 (m, 7H), 7.16 – 7.13 (m, 1H), 4.96 (dd, 1H, $J = 11.6, 1.5$ Hz), 4.50 (s, 1H), 4.08 – 3.96 (m, 1H), 3.53 (d, 1H, $J = 11.6$ Hz), 3.00 – 2.92 (m, 1H), 2.75 (dd, 1H, $J = 12.0, 9.8$ Hz), 2.40 (s, 9H), 1.76 (ddd, 1H, $J = 12.4, 8.4, 3.8$ Hz), 1.64 (ddd, 1H, $J = 12.9, 8.4, 8.3$ Hz), 1.39 (s, 9H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 156.9, 146.9, 146.5, 141.2, (d, $J_{31\text{P}-13\text{C}} = 2.2$ Hz), 134.1 (d, $J_{31\text{P}-13\text{C}} = 14.0$ Hz), 129.7 (d, $J_{31\text{P}-13\text{C}} = 10.9$ Hz), 128.3 (d, $J_{31\text{P}-13\text{C}} = 49.6$ Hz), 128.2, 128.2, 127.2, 127.1, 126.0, 125.7, 58.6 (d, $J_{31\text{P}-13\text{C}} = 2.9$ Hz), 54.76, 52.24, 52.11, 50.37, 36.9 (d, $J_{31\text{P}-13\text{C}} = 92.1$ Hz), 29.8, 21.4 ppm; ^{31}P NMR (160 MHz, CDCl_3) δ 43.7 ppm; HRMS (ESI) calc'd for $[\text{C}_{43}\text{H}_{49}\text{AuN}_2\text{OP}]^+$: m/z 837.3243, found 837.3258.



ortho-Methyl Phosphine 43: Purified by flash column chromatography on basic alumina (49:1 toluene/EtOAc with 1% NEt_3) to afford **43** (73%) as a

white foam: ^1H NMR (500 MHz, CDCl_3) δ 7.40 (t, 3H, $J = 7.5$ Hz), 7.29 (m, 3H), 7.27 – 7.19 (m, 6H), 7.19 – 7.07 (m, 7H), 6.87 (dd, 3H, $J = 10.7, 8.0$ Hz), 4.89 (dd, 1H, $J = 11.5, 1.7$ Hz), 4.38 (s, 1H), 3.87 – 3.79 (m, 1H), 3.36 (d, 1H, $J = 11.5$ Hz), 2.85 (ddd, 1H, $J = 12.0, 5.9, 2.0$ Hz), 2.67 (s, 9H), 2.56 (dd, 1H, $J = 12.0, 9.7$ Hz), 1.70 (ddd, 1H, $J = 12.8, 8.8, 2.5$ Hz), 1.53 (dt, $J = 12.8, 8.8$ Hz, 1H), 1.32 (s, 9H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 156.8, 146.8, 146.4, 143.0 (d, $J_{31\text{P}-13\text{C}} = 14.1$ Hz), 133.6 (d, $J_{31\text{P}-13\text{C}} = 7.2$ Hz), 131.9 (d, $J_{31\text{P}-13\text{C}} = 8.2$ Hz), 131.0 (d, $J_{31\text{P}-13\text{C}} = 1.9$ Hz), 128.2, 128.2, 127.9 (d, $J_{31\text{P}-13\text{C}} = 45.4$ Hz), 127.1, 127.0, 126.5 (d, $J_{31\text{P}-13\text{C}} = 8.2$ Hz), 126.0, 125.7, 58.7 (d, $J_{31\text{P}-13\text{C}} = 2.6$ Hz), 54.5, 52.1, 51.9, 50.3, 33.8 (d, $J_{31\text{P}-13\text{C}} = 91.3$ Hz), 29.7, 23.5 (d, $J_{31\text{P}-13\text{C}} = 9.9$ Hz) ppm; ^{31}P NMR (160 MHz, CDCl_3) δ 34.7 ppm; HRMS (ESI) calc'd for $[\text{C}_{43}\text{H}_{49}\text{AuN}_2\text{OP}]^+$: m/z 837.3243, found 837.3255.



Methoxy Phosphine **44**: Purified by flash column chromatography on

basic alumina (9:1 pentanes/EtOAc with 1% NEt_3) to afford **44** (56%)

as a white foam: ^1H NMR (600 MHz, CDCl_3) δ 7.41 – 7.36 (m, 6H),

7.31 – 7.20 (m, 8H), 7.20 – 7.16 (m, 1H), 7.12 (t, 1H, $J = 7.0$ Hz), 6.87

(d, $J = 7.5$ Hz, 6H), 4.94 (d, 1H, $J = 11.7$ Hz), 4.48 (s, 1H), 4.02 (d, 1H,

$J = 8.1$ Hz), 3.81 (s, 9H), 3.52 (d, 1H, $J = 11.6$ Hz), 2.95 – 2.89 (m,

1H), 2.76 (dd, 1H, $J = 11.9, 9.9$ Hz), 1.69 (ddd, 1H, $J = 12.8, 9.1, 2.7$ Hz), 1.61 (ddd, 1H, $J =$

13.1, 9.1, 8.2 Hz), 1.36 (s, 9H) ppm; ^{13}C NMR (150 MHz, CDCl_3) δ 161.6 (d, $J_{31\text{P}-13\text{C}} = 2.0$ Hz),

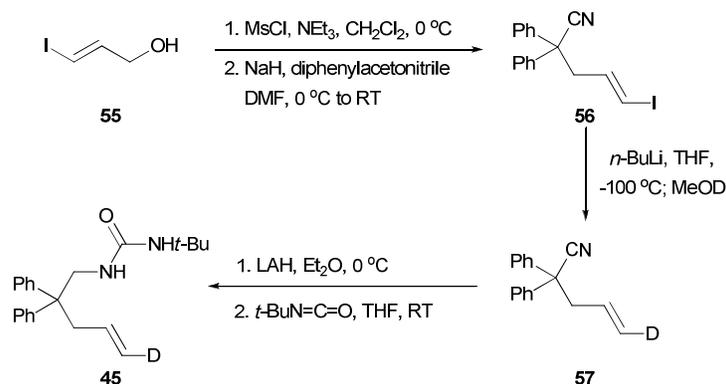
156.9, 147.0, 146.5, 135.6 (d, $J_{31\text{P}-13\text{C}} = 15.2$ Hz), 128.3, 128.2, 127.2, 127.1, 126.0, 125.7, 123.0

(d, $J_{31\text{P}-13\text{C}} = 52.8$ Hz), 114.6 (d, $J_{31\text{P}-13\text{C}} = 11.7$ Hz), 58.5 (d, $J_{31\text{P}-13\text{C}} = 3.3$ Hz), 55.4, 54.8, 52.2,

52.1, 50.4, 37.1 (d, $J_{31\text{P}-13\text{C}} = 92.4$ Hz), 29.8 ppm; ^{31}P NMR (160 MHz, CDCl_3) δ 42.2 ppm;

HRMS (ESI) calc'd for $[\text{C}_{43}\text{H}_{49}\text{AuN}_2\text{O}_4\text{P}]^+$: m/z 885.3090, found 885.3097.

VI. Isotopic Labelling Studies

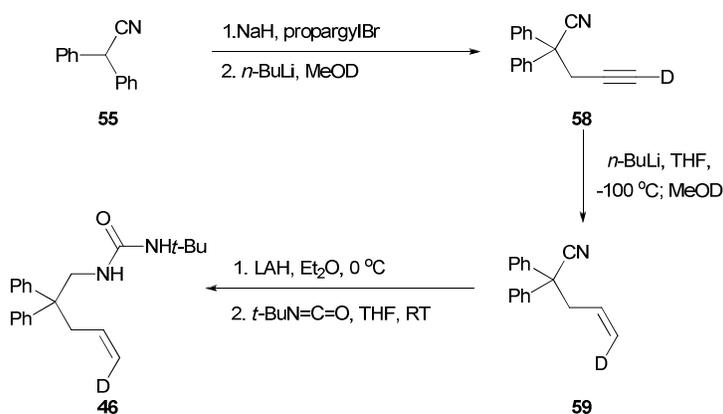


Vinyl Iodide **56**: Mesyl chloride (1.8 mL, 22.8 mmol, 1.2 equiv) was added dropwise to a solution of (E)-prop-2-ene-1-ol⁵ (**55**) (3.5 g, 19 mmol) and triethylamine (3.96 mL, 28.5 mmol, 1.5 equiv) in DCM (30 mL) at 0 °C. The solution was stirred at 0 °C for 30 min at which point TLC indicated complete reaction. The reaction mixture was poured onto sat. aq. NaHCO₃/Brine (50 mL, 1:3), extracted with DCM (3 x 50 mL), washed with sat. aq. NaHCO₃/Brine (50 mL, 1:3), dried (MgSO₄) and concentrated to yield 4.24 g (E)-prop-2-ene-1-methanesulfonate as a clear yellow oil. The crude oil was used without further purification. Diphenylacetonitrile (2.85 g, 14.7 mmol) in DMF (10 mL) was via cannula to a suspension of NaH (600 mg, 15 mmol) in DMF (2 mL) at 0 °C. The solution was warmed to 23 °C and stirred until gas evolution ceased (~30 min). The solution was re-cooled to 0 °C and (E)-prop-2-ene-1-methanesulfonate (4.2 g, 16 mmol) was added. The solution was warmed to 23 °C and stirred overnight. The reaction was quenched on sat. aq. NH₄Cl (50 mL), extracted with Et₂O (4 x 50 mL), washed with water (4 x 50 mL), dried (MgSO₄) and concentrated to yield a crude yellow oil (2.8 g). The crude oil was purified by column chromatography (SiO₂; 0-4% EtOAc/Hex; 1% inc; collect at 2%) to yield 2.1 g clear oil contaminated with ~5% diphenylacetonitrile. The clear oil was dissolved in EtOAc (4 mL) and diluted with hexanes (50 mL) and allowed to recrystallize by slow evaporation. The crystals were collected by filtration and washed with cold hexanes to yield **56** (1.5 g, 4.2 mmol, 28%) as clear colorless crystals: ¹H NMR (600 MHz, CDCl₃) δ 7.41-7.37 (m, 8H), 7.34-7.31 (m, 2H), 6.46 (dt, 1H, *J* = 7.7, 1.6 Hz), 6.28 (dt, 1H, *J* = 7.6, 6.4 Hz), 3.24 (dd, 2H, *J* = 6.3, 1.7 Hz).

Olefin **57**: Deuterium was incorporated by the method of Seebach.⁶ To a solution of **56** (294 mg, 0.82 mmol) in dry THF at -90 °C was added *n*-BuLi (315 μL, 0.82 mmol, 1 equiv). The solution

was quenched with MeOD (0.2 mL, from an ampule). The solution was diluted with ethyl acetate (50 mL), washed with water (15 mL), dried with MgSO₄ and concentrated to yield **57** (185 mg, 0.79 mmol, 96%, 98% D) as a clear oil: ¹H NMR (600 MHz, CDCl₃) δ 7.42-7.36 (m, 8H), 7.32-7.30 (m, 2H), 5.73 (dt, 1H, *J* = 16.9, 7.1 Hz), 5.23-5.20 (m, 1H), 3.16 (dd, 2H, *J* = 7.0, 1.2 Hz); ¹³C NMR (150 MHz, CDCl₃) δ 139.74, 131.67, 128.85, 127.94, 121.96, 120.14 (t, *J* = 22 Hz), 51.73, 43.90.

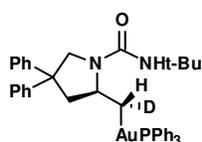
t-Butyl urea **45**: Compound **57** was reduced with LAH and treated with *tert*-butylisocyanate according to the methods of Widenhoefer^{3,4} to yield **45**: ¹H NMR (600 MHz, CDCl₃) δ 7.30 – 7.18 (m, 10H), 5.43 (dt, 1H, *J* = 16.8, 7.2 Hz), 4.98 (d, 1H, *J* = 17.1 Hz), 4.05 (s, 1H), 3.85 (d, 3H, *J* = 5.8 Hz), 2.87 (d, 2H, *J* = 7.0 Hz), 1.26 (s, 9H) ppm; ²H NMR (92 MHz, CDCl₃) δ 4.97 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 157.2, 145.7, 133.9, 128.2, 128.1, 126.3, 118.1 (t, *J* = 22 Hz), 50.3, 50.2, 47.1, 41.8, 29.4 ppm; HRMS (ESI) calc'd for [C₂₂H₂₈DON₂]⁺: *m/z* 338.2337, found 338.2343.



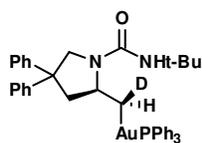
Olefin **59**: Alkyne **58** (98% D) was prepared according to the methods of Chang⁷. A solution of alkyne **58** (100 mg, 0.43 mmol), ethylene diamine (30 μ L, 0.43 mmol) and Pd/CaCO₃ (5 mg, 0.0025 mmol, 0.6 mol%) in THF (5 mL) was stirred rapidly under H₂ (1 atm) for 50 min. TLC showed complete conversion to a higher R_f spot. The reaction mixture was filtered thru celite, washed with EtOAc (3 x 10 mL), concentrated in vacuo to yield 110 mg crude clear yellow oil. ¹H NMR showed alkene **59** with approximately ~15% E/Z isomerization: ¹H NMR (600 MHz, CDCl₃) δ 7.42-7.34 (m, 8H), 7.32-7.28 (m, 2H), 5.72-5.69 (m, 1H), 5.16 (d, 1H, *J* = 10.2 Hz), 3.14 (d, 2H, *J* = 7.0 Hz).

t-Butyl urea **46**: Compound **59** was reduced with LAH and treated with *tert*-butylisocyanate according to the methods of Widenhoefer^{3,4} to yield **45**: ¹H NMR (600 MHz, CDCl₃) δ 7.30 (t, 4H, *J* = 7.6 Hz), 7.20 (m, 6H), 5.42 (m, 1H), 4.95 (d, 1H, *J* = 10.2 Hz), 3.97 (s, 1H), 3.85 (d, 2H, *J* = 5.9 Hz), 3.73 (s, 1H), 2.87 (d, 2H, *J* = 7.1 Hz), 1.26 (s, 9H) ppm; ²H NMR (92 MHz, CDCl₃) δ 4.93 (s, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 157.2, 145.7, 133.9, 128.2, 128.1, 126.3, 118.1 (t, *J* = 22 Hz), 50.3, 50.2, 47.1, 41.8, 29.4 ppm; HRMS (ESI) calc'd for [C₂₂H₂₈DON₂]⁺: *m/z* 338.2337, found 338.2349.

Synthesis of the Deuterated Aminoauration Products: Protected amine (100 μmol) and triethylamine (200 μmol) were combined in CDCl₃ (1.0 mL) and let stir for five minutes before the addition of the gold trimer (40 μmol) in one portion. After 12 hours, the reaction mixture was diluted with CHCl₃ (10 mL) and washed with H₂O (2 × 5 mL). The organic layer was then dried over Na₂SO₄, filtered and concentrated *in vacuo*. The residue was then suspended in EtOAc and filtered through a pad of basic alumina, the concentrated *in vacuo*.

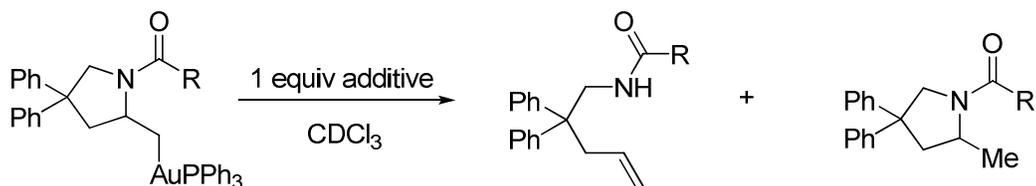


47: From *t*-butyl urea **45**. Purified by flash column chromatography on basic alumina (5% EtOAc in toluene with 1% NEt₃) to afford **47** (80%) as a white foam: ¹H NMR (600 MHz, CDCl₃) δ 7.49 – 7.44 (m, 9H), 7.40 – 7.37 (m, 6H), 7.27–7.11 (m, 10H), 4.92 (dd, 1H, *J* = 11.5, 2.2 Hz), 4.45 (s, 1H), 3.99 (m, 1H), 3.50 (d, 1H, *J* = 11.6 Hz), 2.72 (dd, 1H, *J* = 12.1, 9.7 Hz), 1.61 (t, 1H, *J* = 8.4 Hz), 1.36 (s, 9H); ²H NMR (92 MHz, CDCl₃) δ 1.64 (br s, 1H); HRMS (ESI) calc'd for [C₄₀H₄₂DAuN₂OP]⁺: *m/z* 796.2836, found 796.2856.



48: From *t*-butyl urea **46**. Purified by flash column chromatography on basic alumina (5% EtOAc in toluene with 1% NEt₃) to afford **47** (80%) as a white foam: ¹H NMR (500 MHz, CDCl₃) δ 7.52 – 7.46 (m, 9 H), 7.42 – 7.38 (m, 6H), 7.30 – 7.13 (m, 10H), 4.95 (dd, 1H, *J* = 11.5, 2.2 Hz), 4.48 (s, 1H), 4.03 (m, 1H), 3.53 (d, 1H, *J* = 11.5 Hz), 2.95 (m, 1 H), 2.75 (dd, 1H, *J* = 12.1, 9.7 Hz), 1.75 (dd, 1H, *J* = 9.0, 2.2 Hz), 1.38 (s, 9H); ²H NMR (92 MHz, CDCl₃) δ 1.54 (br s, 1H); HRMS (ESI) calc'd for [C₄₀H₄₂DAuN₂OP]⁺: *m/z* 796.2836, found 796.2853.

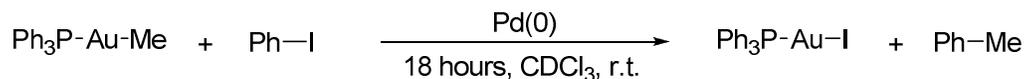
VII. Acid Screens



entry	R	additive	time/h	% alkyl gold	% alkene	% pyrrolidine
1	NH <i>t</i> -Bu	TsOH	1	40	60	0
			15	0	0	100
2		HCl	1	0	100	0
3		NH ₄ Cl	1	0	100	0
4	OPh	TsOH	1	54	46	0
			15	53	46	0
5		HCl	1	75	23	0
			15	61	34	0
6		PPTS	1	0	100	0
			15	0	100	0
7		AcOH	1	100	0	0
			15	88	11	0

Acid Studies Procedure: Acid source (1 equiv) was added to a solution of alkyl gold (5 mg, 0.0063 mmol) in CDCl₃ (0.6 mL). The reactions were monitored by ¹H and ³¹P NMR at the times indicated, and the yields were determined by ¹H NMR versus 1,3,5-trimethoxybenzene as an internal standard.

VIII. Palladium Cross-Coupling Model System



entry	Pd source	% conversion ^a
1	Pd(PPh ₃) ₄	decomp
2	Pd ₂ (dba) ₃	decomp
3	Pd ₂ (dba) ₃ , PPh ₃	no reaction
4	Pd ₂ (dba) ₃ , PCy ₃	no reaction
5	Pd ₂ (dba) ₃ , dppb	trace
6	Pd ₂ (dba) ₃ , DPEPHOS	47%
7	PdCl ₂ (MeCN) ₂ , DPEPHOS	trace
8	Pd₂(dba)₃, XANTPHOS	84%
9	PdCl ₂ (MeCN) ₂ , XANTPHOS	9%

^a conversions determined by ¹H NMR versus internal standard

Palladium Catalyzed Cross Coupling of Organogold species: In a vial, the palladium source (10 mol%) and ligand (10 mol%) were dissolved in CDCl₃. After 2 minutes, iodobenzene (300 mol%) was added and let stir at room temperature for 30 minutes. The solution of the palladium complex was then added to a solution of methyltriphenylphosphine gold (100 mol%) and an internal standard (1,3,5-trimethoxybenzene) in CDCl₃. The reaction was monitored by ¹H NMR for the formation of toluene and the disappearance of the alkyl gold species.

Attempts to use these conditions with isolated alkylgolds (such as **2**, **10**, **14**, **22**, and **31**) lead only to recovery of the precursor olefin with trace amounts of cross-coupled products.

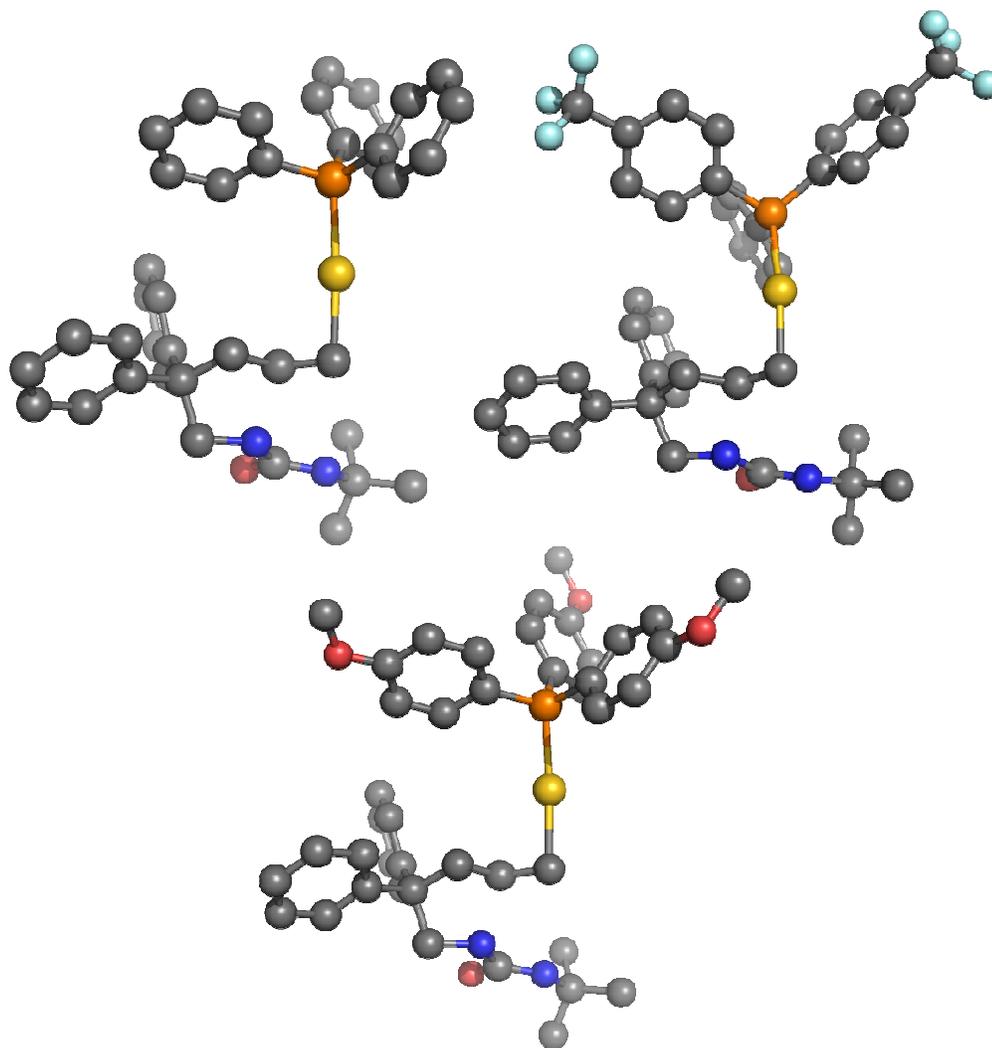
IX. Computational Methods

Calculations were performed using density functional theory (DFT) with the M06 functional,⁸ as implemented in Jaguar 7.6.110⁹. All calculations used the Hay and Wadt small core-valence relativistic effective-core-potential¹⁰ (ECP) for Au. The LACVP** basis set was used for all geometry optimizations and LACV3P++**(2f) for energies. LACV3P++**(2f) utilizes the LACV3P++** basis set as implemented in Jaguar plus a double-zeta f-shell with exponents from Martin and Sundermann.¹¹ All electrons were described for all other atoms using the 6-31G** for geometry optimizations and 6-311++G** basis set for electronic energies.^{12,13} For each optimized structure, the M06 analytic Hessian was calculated to obtain the vibrational frequencies, which in turn were used to obtain the zero point energies and free energy corrections (without translational or rotational components). Solvent corrections were based on single point self-consistent Poisson-Boltzmann continuum solvation calculations (using the LACVP** basis set) for CHCl₃ ($\epsilon = 4.81$ and $R_0 = 2.52$ Å) using the PBF¹⁴ module in Jaguar. Natural Bond Orbital¹⁵ analyses were performed using the NBO 5.0 code¹⁶ as implemented in Jaguar 7.6.110 on M06/LACV3P++**(2f) wavefunctions.

(I) Energetics

Au(I)PPh ₃	Single Point Gas Phase M06 LACV3P**++(+f)	LACVP** M06	LACVP** gas phase Optimization M06-I			H (Kcal/mol)	ΔH
			ESCF	Vsolv	Hvib		
N(Me)₃	-174.3830031	-2.7055	4	74.685	70.835	-109351.029	
HN(Me)₃	-174.7490744	-51.0074	4.161	84.083	72.358	-109619.4851	
Au(IP(Ph)₃	ESCF	Vsolv	Hvib	ZPE	Svib	H (Kcal/mol)	ΔH
open	-2210.682343	-33.5817	23.63	496.548	162.27	-1386734.243	0
TS	-2210.663	-33.3478	21.536	497.865	145.582	-1386722.648	11.59
closed no H	-2210.278211	-11.5249	22.634	488.825	158.193	-1386467.308	-1.52
Au(IP(Ph(CF₃))₃	ESCF	Vsolv	Hvib	ZPE	Svib	H (Kcal/mol)	ΔH
open Au CF₃	-3221.771653	-37.7694	30.215	508.074	210.938	-2021188.568	0.00
TS Au CF₃	-3221.75129	-37.5259	30.323	504.675	219.848	-2021178.837	9.73
Closed AuCF₃ no H	-3221.380253	-12.6964	29.716	498.13	210.695	-2020928.331	-8.22
Au(IP(Ph(MeO))₃	ESCF	Vsolv	Hvib	ZPE	Svib	H (Kcal/mol)	ΔH
Open MeO	-2554.174155	-35.0171	27.865	560.378	188.483	-1602212.023	0.00
TS MeO	-2554.152527	-35.0585	27.887	558.678	199.579	-1602200.17	11.85
closed MeO no H	-2553.768395	-14.9129	27.392	551.437	184.025	-1601946.715	-3.15

(II) Transitions Structures



(III) XYZ of Intermediates and Transition Structures

1. PPh3

P(Ph)3Au Substrate			P(Ph)3Au TS				
Au1	7.5130230470	-3.3765863857	2.6050911882	C1	3.1718092582	6.4177354199	8.5515813321
C2	6.2884683098	-0.5928800298	3.9344655311	C2	2.8144404017	7.7656219282	8.6891637960
C3	4.8363087193	-1.1285742094	3.7195116763	H3	3.2761993907	3.5169615557	8.0457999745
C4	4.6760454350	-1.4210083734	2.2095394921	C4	1.8789670406	8.1447896192	9.6442154773
N5	3.3617079700	-1.8422820621	1.8325470059	H5	1.6053998223	9.1915183875	9.7529838372
C6	2.5952532117	-1.0535530611	0.9841967064	C6	1.2884752488	7.1827459073	10.4621650043
N7	1.3065280282	-1.5029675791	0.8381309810	H7	0.5534133029	7.4797103453	11.2041268100
O8	3.0763505810	-0.0958701422	0.3885114595	C8	1.6407150465	5.8438630495	10.3282221542
P9	6.9198903438	-5.1934160997	1.2559057680	H9	1.1835244132	5.0939055460	10.9665180919
C10	2.8202902436	-4.3210457975	-0.6366534985	C10	2.5806779350	5.4576045591	9.3768106731
C11	2.9625671562	-5.4326738678	0.1882922317	H11	2.8509236391	4.4094482361	9.2736761010
C12	4.1959706899	-5.7259234512	0.7671228748	C12	4.3418599260	4.1774884255	7.1378268540
C13	5.2949734905	-4.8994710305	0.5120334948	C13	3.3210223833	3.6116621754	6.3641690474
C14	5.1454542824	-3.7772589856	-0.3167539742	H14	2.6200094152	4.2607256022	5.8400079500
C15	3.9130405394	-3.4923374164	-0.8894862209	C15	3.2009316885	2.2310616959	6.2706891531
C16	9.8953143515	-5.9489535845	-2.1598670881	H16	2.4053555236	1.7963398518	5.6732442607
C17	10.3503829365	-5.5463559527	-0.9059867974	C17	4.1066731976	1.4077524680	6.9370307653
C18	9.4413901885	-5.2901363587	0.1130865622	H18	4.0169416405	0.3283387903	6.8586077157
C19	8.0690085534	-5.4419272655	-0.1185480470	C19	5.1306130645	1.9664161581	7.6965570336
C20	7.6146684736	-5.8453722757	-1.3797729781	H20	5.8397167526	1.3238414965	8.2103102943
C21	8.5314019467	-6.0967776880	-2.3954215365	C21	5.2513763808	3.3487268265	7.8016203757
C22	6.6480380442	-9.1487430235	3.5869917057	H22	6.0509943196	3.7819995517	8.3974294427
C23	6.6464342896	-9.1573990788	2.1924620835	C23	6.0140525532	6.4093411117	7.9723195326
C24	6.7445808388	-7.9642097494	1.4860917648	H24	7.0808940240	6.6396659947	7.0970542206
C25	6.8418271508	-6.7479867859	2.1769176800	C25	6.9109815553	6.6136168823	6.0219118803
C26	6.8564301691	-6.7458528088	3.5753771386	C26	8.3492869798	6.9008337933	7.6012306250
C27	6.7544361710	-7.9439206827	4.2765973060	H27	9.1761171453	7.0781539162	6.9202077131
C28	4.3491970222	-4.6439276163	6.2265384774	C28	8.5559927736	6.9417754114	8.9778309612
C29	4.3545089299	-4.7843199980	4.8454036945	H29	9.5467019463	7.1506336452	9.3707175808
C30	4.5116114997	-3.6657256642	4.0244441776	C30	7.4949922216	6.7221253375	9.8526569558
C31	4.6371192802	-2.3826487219	4.5699546712	H31	7.6566348025	6.7585134438	10.9258079422
C32	4.6222024061	-2.2588437629	5.9668695377	C32	6.2239865675	6.4551477272	9.3552381638
C33	4.4884730165	-3.3734040679	6.7858649436	H33	5.3948773319	6.2843866398	10.0385350163
C34	1.8446071256	1.9099452697	4.5490585653	C34	3.0411505752	8.0682363863	3.5384482631
C35	1.5569988779	0.5638684205	4.7553579319	H35	3.9056756627	8.2347878492	2.922262330
C36	2.5274931576	-0.4045944198	4.5190687573	H36	2.3108530014	7.3777618849	3.1066775127
C37	3.8090855784	-0.0512781305	4.0797908113	C37	2.5053295249	9.2354153325	4.1668484913
C38	4.0786667342	1.3026403636	3.8644530293	H38	3.2349813118	10.0021058950	4.4467662189
C39	3.1099710463	2.2738402509	4.1007655796	C39	1.3010988465	9.1980763722	5.0593762423
C40	0.2592858303	-0.6997940524	0.1660573658	H40	0.5454258872	8.5141214590	4.6471812297
C41	-1.0222535878	-1.5200819442	0.2704477191	H41	1.5958687721	8.7869106829	6.0315667828
C42	0.6265166098	-0.5062018396	-1.3026963209	C42	0.7420478971	10.6206298171	5.2166784288
C43	0.0862481650	0.6477875727	0.8669329320	H43	0.5474034011	11.0936627956	3.7538283863
H44	6.5864293318	0.0280667351	3.0811813401	C44	-0.4462688882	10.7956292309	3.4109419561
H45	6.2738055925	0.0763320063	4.8076775226	H45	0.6435308274	12.1725830357	3.602263906
H46	4.8691145601	-0.5062631234	1.6396130279	C46	-0.5923586168	10.6585936567	5.9482329232
H47	5.4353723866	-2.1597811581	1.8871546866	C47	-1.0862952452	9.5712764338	6.6716597327
H48	1.8535650898	-4.0871953488	-1.0757856664	H48	-0.5372472577	8.6323746120	6.7016839422
H49	2.1126001813	-6.0805179015	0.3829343163	C49	-2.2857461171	9.6738769935	7.3736230123
H50	4.3034589239	-6.5978225179	1.4086120693	H50	-2.6553416246	8.8186997953	7.9323839430
H51	5.9962527471	-3.1231157225	4.5055164656	C51	-3.0044579148	10.8633011579	7.3638435578
H52	3.7963595807	-2.6082991312	-1.5106217556	H52	-3.9372322405	10.9427869549	7.9140368765
H53	10.6064015709	-6.1431004462	-2.9572051333	C53	-2.5174434453	11.9556413223	6.6498947847
H54	11.4139940610	-5.4263746480	-0.7240687812	H54	-3.0673264437	12.8922727182	6.6441537367
H55	9.7928071474	-4.9711439106	1.0937483910	C55	-1.3189095039	11.8546439720	5.9553755116
H56	6.5493772800	-5.9562898334	-1.5684691673	H56	-0.9283310372	12.7232543328	5.4271622299
H57	8.1769129557	-6.4066448177	-3.3738727156	C57	1.7460614863	11.4553924066	6.0283206783
H58	6.5730187696	-10.0835368380	4.1343039807	C58	2.0396435710	11.0105399063	7.3256129750
H59	6.5718446866	-10.0968592614	1.6529578372	H59	1.5249618949	10.1316854483	7.7125818253
H60	6.7490710680	-7.9744677238	0.3976248693	C60	2.9382600596	11.6895457774	8.1359332662
H61	6.9385326921	-5.8022062115	4.1144803473	H61	3.1462718601	11.3242087224	9.1391016546
H62	6.7625920169	-7.9337838919	5.3628703673	C62	3.5601498138	12.8460423197	7.6674410090
H63	0.9592320196	-2.0985306770	1.5775778853	H63	4.2626885489	13.3842972626	8.2967251239
H64	4.2260605826	-5.5129685767	6.8664641997	C64	3.2636214835	13.3067482379	6.3919986733
H65	4.2343160694	-5.7658832065	4.3925148817	H65	3.7349893161	14.2108629745	6.0171673618
H66	4.5175247035	-3.8147324950	2.9453710404	C66	2.3644292637	12.6189190008	5.5753210205
H67	4.6957020302	-1.2678271904	6.4110333331	H67	2.1780875592	12.9989851465	4.5771729399
H68	4.4788323802	-3.2510831500	7.8652457290	C68	2.5004784348	11.2641847087	2.1692012544
H69	1.0892611718	2.6674265854	4.7345758132	C69	4.4192921110	11.0650087111	10.5808956391
H70	0.5726704198	0.2631799892	5.1046564320	C70	4.0698583673	12.2907377062	-0.2560415185
H71	2.2885858305	-1.4520893611	4.6928186137	H71	3.2998583048	12.0529712771	-0.9953114460
H72	5.0518928114	1.6162639189	3.4939771789	H72	4.9594805582	12.6319474945	-0.7918156183
H73	3.3474125466	3.3193496082	3.9282308783	C73	3.7120622585	13.1097455653	0.3690797495
H74	-0.9089910154	-2.4960113787	-0.2142680702	C74	5.4693946242	11.4002432810	1.6380793473
H75	-1.3102621319	-1.6854784583	1.3156832813	H75	5.1149022556	12.1877450094	2.3073787790
H76	-1.8491153429	-0.9965359792	-0.2160810708	H76	6.3879646597	11.7509480582	1.1598669339
H77	0.7714565743	-1.4740088515	-1.7949664501	H77	5.7191981096	10.5169929790	2.2373762656
H78	-0.1831382308	0.0170030548	-1.8206408477	C78	4.8992598484	9.9287851806	-0.3126036609
H79	1.5415709991	0.0779041200	-1.4048361112	H79	5.1491673996	9.0346899305	0.2717619236
H80	-0.6857015429	1.2434671223	0.3695340499	H80	5.8019509104	10.2300971940	-0.8482435589
H81	-0.2163296751	0.5084782617	1.9106791654	H81	4.1430935687	9.6596116307	-1.0570409648
H82	1.0215521505	1.2125547103	0.8519760343	N82	1.5506829581	10.4262170937	2.8951642138
H83	2.9206320988	-2.5845095407	2.3537799639	H83	3.1927211093	10.5541557322	1.2560040090
C84	8.6000232315	-1.6145040714	3.6461344652	N84	3.0716865647	9.5501643018	1.2537122814
H85	8.8573195781	-0.9167532523	2.8512757524	Au8	4.3974251097	5.9802013109	7.2839306071
H86	9.4166803448	-2.1758765127	4.0937438660	P86	3.8065232624	7.0668164189	5.3024659045
C87	7.3631070316	-1.5832861443	4.2371361546	O87	2.6260115730	12.4427012186	2.4361944950
H88	7.1976320663	-2.2190573935	5.1095884077	H88	1.1200433159	9.7450824783	2.2757148659
P(Ph)3Au Product							
C1	4.6041446799	7.3917442840	8.4467720694	C1	3.1718092582	6.4177354199	8.5515813321
C2	4.7691166584	8.7405744777	8.1120478576	C2	2.8144404017	7.7656219282	8.6891637960
H3	4.9652270071	9.0135270539	7.0752367049	H3	3.2761993907	3.5169615557	8.0457999745
C4	4.6608176046	9.7260306768	9.0898237414	C4	1.8789670406	8.1447896192	9.6442154773
H5	4.7769993890	10.7705153444	8.8148706835	H5	1.6053998223	9.1915183875	9.7529838372
C6	4.3841756679	9.3738969535	10.4076254026	C6	1.2884752488	7.1827459073	10.4621650043
H7	4.292597297	10.1435001981	11.1691381645	H7	0.5534133029	7.4797103453	11.2041268100
C8	4.2103868931	8.0330869547	10.7477999233	C8	1.6407150465	5.8438630495	10.3282221542
H9	3.9834843395	7.7556617375	11.7735705755	H9	1.1835244132	5.0939055460	10.9665180919
C10	4.3132333105	7.0468895944	9.7735212460	C10	2.5806779350	5.4576045591	9.3768106731
H11	4.1547166966	6.0021289931	10.0369580988	H11	2.8509236391	4.4094482361	9.2736761010
C12	3.3384729067	4.9954730562	7.5590955882	C12	4.3418599260	4.1774884255	7.1378268540

C13	2.0458648907	5.3748567429	7.1728917705
H14	1.9077690696	6.2955363422	6.6045373508
C15	0.9530242512	4.5809780867	7.4979560756
H16	-0.0441048149	4.8834115642	7.1883323676
C17	1.1398172169	3.3944494786	8.2037964267
H18	0.2867911121	2.7691726246	8.4521298575
C19	2.4211914100	3.0065518046	8.5829257291
H20	2.5696696505	2.0789861151	9.1291320881
C21	3.5190001732	3.8017529726	8.2644007652
H22	4.5189832921	3.4924198103	8.5617654814
C23	6.2056698691	5.1490717002	7.4587729377
C24	6.5632496329	4.1983753887	6.4925061773
H25	5.9624042206	4.0969273284	5.5899349428
C26	7.6747654777	3.3875083408	6.6831985860
H27	7.9395617975	2.6499410914	5.9309103822
C28	8.4513109461	3.5278336124	7.8314833297
H29	9.3239566221	2.8975370468	7.9777339387
C30	8.1128562115	4.4815758376	8.7859466591
H31	8.7208549776	4.5980778449	9.6787979557
C32	6.9938439430	5.2904570969	8.6046849571
H33	6.7339820643	6.0328712274	9.3553593949
C34	3.4774735314	8.2636540226	3.4378932653
H35	4.2679142923	8.6426216909	2.7794452816
H36	2.8236656458	7.6357704770	2.8194217294
C37	2.6571979600	9.3772792458	4.0764112390
H38	3.3238763123	10.0628419022	4.6324285159
C39	1.6015491734	8.8458156034	5.0483656284
H40	1.2053819353	7.8916130346	4.6700119132
H41	2.0339004200	8.6541556669	6.0385390589
C42	0.4950366243	9.9069621624	5.0527673220
C43	0.4460008885	10.2056482003	3.5440926952
H44	-0.1160680562	9.4055141120	3.0408881802
H45	-0.0131303743	11.1557392363	3.2620873210
C46	-0.8332797658	9.4195218772	5.5931898071
C47	-0.9457845357	8.2638666426	6.3697421424
H48	-0.0584418011	7.6720198665	6.5875758428
C49	-2.1775536821	7.8649234385	6.8833887015
H50	-2.2433520951	6.9636047730	7.4928335585
C51	-3.3192473755	8.6149296296	6.6245617865
H52	-4.2806698133	8.3045074149	7.0247472766
C53	-3.2199563941	9.7716077068	5.8546580573
H54	-4.1054149667	10.3684874995	5.6521040256
C55	-1.9885557077	10.1702498097	5.3501016002
H56	-1.9121899176	11.0862386811	4.7665470294
C57	0.9701200426	11.1050120360	5.8809776819
C58	1.2251593649	10.9082091578	7.2443746225
H59	1.0617950130	9.9228334625	7.6806230082
C60	1.6685701807	11.9465613660	8.0530464241
H61	1.8527614053	11.7654513461	9.1099188523
C62	1.8726393914	13.2136127440	7.5107435840
H63	2.2199946586	14.0300811038	8.1387375085
C64	1.6251358971	13.4222839099	6.1592043758
H65	1.7843831238	14.4048037754	5.7213797852
C66	1.1762792025	12.3798612073	5.3483528723
H67	1.0039105150	12.5742585342	4.2919892903
C68	2.3481153950	11.3170289357	2.4937566474
C69	4.4696745695	12.5644575460	2.0277581001
C70	4.1688991144	12.9588286919	0.5832496073
H71	4.4249304835	12.1426238702	-0.0992150731
H72	4.7580619609	13.8389170209	0.3030162508
H73	3.1092913390	13.1893245428	0.4651100790
C74	4.1284793444	13.7152026131	2.9769763105
H75	3.0695205848	13.9722630406	2.8966985109
H76	4.7216971284	14.6035181043	2.7334892011
H77	4.3390084892	13.4363374923	4.0156518257
C78	5.9436427658	12.1954666067	2.1669200858
H79	6.1875952991	11.9109601869	3.1975558035
H80	6.5771768028	13.0455176674	1.8983613357
H81	6.2041777499	11.3588695131	1.5093407284
N82	1.8459302656	10.1996597663	3.1417509497
N83	3.7149701612	11.3548773942	2.3931280045
H84	4.2402060364	10.6336595611	2.8611133526
P85	4.7072198196	6.1264309691	7.1352832821
Au86	4.2658962355	7.1395927832	5.0283088010
O87	1.6140104716	12.1960514005	2.0329730010

2. AuP(PhMeO)3

P(PhMeO)3Au Substrate				P(PhMeO)3Au TS			
Au1	7.4829884099	-3.3852194937	2.5031638057	C1	3.0971750655	6.3838962047	8.6240630542
C2	6.1644465062	-0.6561589305	4.0338909274	C2	2.6416261965	7.7082674425	8.7488372387
C3	4.7345807485	-1.1150766338	3.6089439988	H3	3.0608579163	8.4853542846	8.1061100521
C4	4.7339618582	-1.1915767638	2.0595428391	C4	1.6774197960	8.0432763017	9.6814356552
N5	3.48288238490	-1.5405251335	1.4562429623	H5	1.3178727436	9.0632754719	9.7892301754
C6	2.6713498420	-0.5461227142	0.9050982311	C6	1.1390601805	7.0539995923	10.5203111374
N7	1.4595484676	-1.0346067256	0.4885815517	C8	1.5795090945	5.7314511904	10.4039529860
O8	3.0385942486	0.6181950503	0.8133670537	H9	1.1716335548	4.9528905777	11.0389175820
P9	7.0710143584	-5.2207967556	1.1048659067	C10	2.5502275464	5.4079171918	9.4605515710
C10	2.7468563174	-4.6609579139	-0.3556490171	H11	2.8826379837	4.3754148921	9.3748397457
C11	3.0685275500	-5.8021021737	0.3847320077	C12	4.3628001807	4.2112349102	7.1791946094
C12	4.3877279700	-6.0130684523	0.7818120552	C13	3.3145541185	3.6397504824	6.4371518841
C13	5.3898980866	-5.0997230494	0.4502696020	H14	2.5471561586	4.2829158907	6.0071116388
C14	5.0549586194	-3.9725416379	-0.3213482342	C15	3.2420874461	2.2741865391	6.2476412551
C15	3.7542454649	-3.7598899683	-0.7311020266	H16	2.4367422441	1.8217894057	5.6778842581
C16	9.8869606470	-5.4369774581	-2.5258348399	C17	4.2320680246	1.4375643824	6.7869317651
C17	10.3572777455	-4.9663570691	-1.2898306154	C19	5.2855942688	1.9930894482	7.5206789659
C18	9.5036042491	-4.8971162803	-0.2076054007	H20	6.0621185918	1.3633000920	7.9407410719
C19	8.1625955685	-5.3005455252	-0.3239816538	C21	5.3425409484	3.3708847443	7.7116073404
C20	7.7036549601	-5.7712928606	-1.5593923293	H22	6.1669864844	3.7919701811	8.2827401688
C21	8.5532138828	-5.8430233838	-2.6563013938	C23	5.9668267356	6.4154003326	8.1789399505
C22	7.1487521991	-9.1313466917	3.5228852397	C24	7.0776037316	6.7099740037	7.3720120986
C23	7.3875194848	-9.1586396778	2.1396724121	H25	6.9597507815	6.7540794519	6.2901856956
C24	7.3980025473	-7.9836230056	1.4133942532	C26	8.3173435213	6.9424991235	7.9355767488
C25	7.1750526918	-6.7507096759	2.0498545158	H27	9.1846489034	7.1713776826	7.3251957290
C26	6.9547910165	-6.7329271906	3.4308362967	C28	8.4746174099	6.8913777417	9.3283511192
C27	6.9310506381	-7.9085434070	4.1702659190	H31	7.3734061220	6.6111017994	10.1458975876
C28	3.9468614199	-4.9023620906	5.5844765412	H31	7.4767792717	6.5774254555	11.2247161166
C29	4.1010115648	-4.8694655759	4.2048460086	C32	6.1320575040	6.3755161852	9.5669124585
C30	4.3511491964	-3.6601723030	3.5529661477	H33	5.2799935915	6.1581214040	10.2080756274
C31	4.4304288394	-2.4593042747	4.2652606541	C34	3.1643911482	8.1178620280	3.6069840591
C32	4.2614794975	-2.5092390929	5.6565441886	H35	4.0410780807	8.2781628536	2.9761722926
C33	4.0300169771	-3.7133219269	6.3098696441	H36	2.4567459016	7.3942624799	3.1920815726
C34	1.6971944074	1.8361068006	4.5328561742	C37	2.5997462344	9.2842427906	4.2013645943
C35	1.3664476117	0.4885360160	4.4325542101	H38	3.3035207927	10.0819192172	4.4573067071
C36	2.3537254295	-0.4551875693	4.1760046896	C39	1.3858671091	9.2383151267	5.0813000762
C37	3.6907207263	-0.0746535247	4.0127913424	H40	0.6585114719	8.5162098748	4.6836548938
C38	4.0068636620	1.2824933029	4.1092938850	H41	1.6815151544	8.8655857400	6.0688760767
C39	3.0212118048	2.2288479784	4.3718932906	C42	0.7833293912	10.6460141938	5.1949126918
C40	0.4881096192	-0.2193882163	-0.2716083718	C43	0.5842101528	11.0706112101	3.7199376415
C41	-0.6691451533	-1.1571983486	-0.6017278036	H44	-0.4048001635	10.7487243351	3.3842210678
C42	1.1128303507	0.3090009795	-1.5632894133	H45	0.6621570986	12.1463331460	3.5548380798
C43	-0.0013080016	0.9306104561	0.6047630037	C46	-0.5531460173	10.6647561608	5.9211095490
H44	6.5483510820	0.0761057370	3.1330152710	C47	-1.0339122563	9.5752990296	6.6496370261
H45	6.0757199829	-0.1233278496	4.9925910752	H48	-0.4648820059	8.6492025432	6.6984987220
H46	4.9872564129	-0.200555946	1.6691532044	C49	-2.2419523171	9.6625108321	7.3387509793
H47	5.5245764152	-1.8901798512	1.7213373338	H50	-2.5984699227	8.8075904252	7.9063959889
H48	2.3045815270	-6.5196446791	0.6638817488	C51	-2.9852631330	10.8361469101	7.3053303023
H49	4.6306081852	-6.8958563437	1.3701115732	H52	-3.9251453959	10.9035053161	7.8451000228
H50	5.8225927296	-3.2465695967	-0.5863932144	C53	-2.5131506125	11.9296914001	6.5829638790
H51	3.4809181528	-2.8822989530	-1.3095342555	H54	-3.0820344345	12.8547068922	6.5588567386
H52	11.3928157823	-4.6510680813	-1.2166568520	C55	-1.3053195947	11.8447688598	5.9303184785
H53	9.8727613187	-4.5189609989	0.7449105040	H56	-0.9251954717	12.7143045847	5.3684540308
H54	6.6658790141	-6.0774879050	-1.6728861706	C57	1.7656977983	11.5274255456	5.9812167027
H55	8.1729631410	-6.200540076	-3.6049041712	C58	2.0368018844	11.1578175121	7.3060133282
H56	7.5639162988	-10.1185044356	1.6654238542	H59	1.5132456829	10.3043291592	7.7346835618
H57	7.5851486632	-8.0159212376	0.3417838938	C60	2.9297499666	11.8756224239	8.0880262269
H58	6.7844730862	-5.7835671318	3.93911759165	H61	3.1205993738	11.5653536315	9.1126462065
H59	6.7534618453	-7.8666083108	5.2394897146	C62	3.5667037168	12.9984417991	7.5619972788
H60	1.4175303099	-2.0280095079	0.2987847390	H63	4.2633043922	13.5684718717	8.1696049925
H61	3.7496402704	-5.8418688750	6.0933973575	C64	3.2944989532	13.3855160642	6.2568502105
H62	4.0284147969	-5.7842892353	3.6199881792	H65	3.7797649441	14.2618805083	5.8364822586
H63	4.4761848824	-3.6734951477	2.4725856606	C66	2.4038909392	12.6560915705	5.4673002734
H64	4.2907390693	-1.5826078917	6.2266267360	H67	2.2371169745	12.9753677911	4.4438557592
H65	3.899625097	-3.7244665786	7.3884879546	C68	2.4876085739	11.2277763682	2.0837431515
H66	0.9274585399	2.576882880	4.7332114138	C69	4.2802209317	11.0473136895	0.3498666242
H67	0.3350340968	0.1684335296	4.5535495436	C70	3.7657200339	12.1822859722	-0.5290754786
H68	2.0810446631	-1.5059277462	4.1015099144	H71	2.9579557190	11.8366324706	-1.1802006717
H69	5.0289372523	1.6226180994	3.9594790508	C72	4.5770798807	12.5505009299	-1.1628307567
H70	3.2907403901	3.2787070442	4.4420063661	H73	3.3971363031	13.0143162165	0.0725013405
H71	-0.3359302807	-1.9807939440	-1.2453157056	C74	5.3943910788	11.5284136845	1.2762914319
H72	-1.1076170470	-1.5821689436	0.3080875594	H75	5.0451502742	12.3366816862	1.9226672620
H73	-1.4558881385	-0.6182609555	-1.1360298546	H76	6.2373531910	11.9028514306	0.6888695931
H74	1.4587412146	-0.5192474352	-2.1927054449	H77	5.7602241571	10.7099848434	1.9062366498
H75	0.3774637888	0.8811367724	-2.1381298782	C78	4.7631146069	9.8872867032	-0.5109415378
H76	1.9616191850	0.9591164169	-1.3429367676	H79	5.1266612183	9.0549747790	0.1034104217
H77	-0.7502231833	1.5193547878	0.0656903204	H80	5.5912449693	10.2113364406	-1.1448298335
H78	-0.4610766278	0.5472489766	1.5210627694	H81	3.9673662932	9.5171119092	-1.1650320235
H79	0.8249921107	1.5879164410	0.8819885941	N82	1.6048894262	10.3957225028	2.8893712229
H80	3.0195386634	-2.3732739260	1.7895034872	N83	3.1604546840	10.5032836504	1.1670426089
C81	8.4662455475	-1.7014872462	3.7779650424	H84	3.0860814084	9.4962979130	1.2123518952
H82	8.7866487351	-0.9263307016	3.0842149168	P85	4.3881067981	6.0039762266	7.4102261996
H83	9.2425320937	-2.3261377183	4.2138066419	Au86	3.8818523254	7.1377146326	5.4260820468
C84	7.1941211541	-1.7055394589	4.2850448849	O87	2.5803192409	12.4232759098	2.2864114241
H85	6.9544071260	-2.4354778857	5.0621141726	H88	1.1945346353	9.6564616051	2.3258910203
X86	7.8584480084#	-1.5941588249#	3.9949542816#	O88	4.0802011934	0.1211637488	6.5376658709
O87	1.4932745866	-4.3132235445	-0.7332233378	C87	5.0672719128	-0.7620063346	7.0463426514
O88	7.1528506209	-10.3291887133	4.1363938737	N82	0.2054811991	7.4758312782	11.3973687599
O89	10.7892993876	-5.4498608089	-3.5233419109	C89	-0.3480087099	6.5128369268	12.2812455042
C90	10.3573745723	-5.8937405483	-4.8020329659	O90	9.7212649676	9.782773227	9.7828741340
C91	0.4369855431	-5.2105409011	-0.4133341454	C91	9.9329321849	7.0760198734	11.1849377848
C92	6.9153290726	-10.5368204267	5.5363449669	C92	-1.0572581903	7.0523505503	12.9069157560
H93	6.9594963652	-11.4051543845	5.8264936431	H93	-0.8731659378	5.7211442622	11.7337459635
H94	7.6815912751	-9.7944861544	6.0823255958	H94	0.4248968486	6.0602788980	12.9138214183
H95	5.9259618230	-9.9522221303	5.7807616156	H95	4.7658920965	-1.7605142316	6.7335283915
H96	11.2257224506	-5.8157198820	-5.4538998777	H96	6.0576881684	-0.5342169687	6.6346316222
H97	10.0183310071	-6.9355564161	-4.7690201780	H97	5.1143226518	-0.7220060879	8.1411952469
H98	9.5507547272	-5.2615507368	-5.1909917507	H98	10.9909037557	7.2838577898	11.3367060044
H99	-0.4701781020	-4.7630203446	-0.8168353620	H99	9.3345575621	7.8298628289	11.7100483350
H100	0.5973662299	-6.1907012049	-0.8761002818	H100	9.6955004739	6.0839056426	11.5870956886
H101	0.3326305484	-					

C4	3.8479225798	9.3041695586	9.3378937324
H5	4.2499360219	10.2721559352	9.6217100026
C6	2.5070650561	9.0224302019	9.6307132352
C7	1.9642723423	7.7878580589	9.2704098678
H8	0.9264681902	7.5537662054	9.4835953108
C9	2.7541939844	6.8579091338	8.5988835373
H10	2.3113705439	5.9065329658	8.3089773338
C11	4.2674964783	4.4269763296	7.3524986814
C12	3.2087902248	4.0584183211	6.5062630523
H13	2.9184985934	4.7277564355	5.6955376942
C14	2.5276270691	2.8684352918	6.6939816152
H15	1.7037070589	2.5798932074	6.0490479768
C16	2.9006227909	2.0061836811	7.7319757632
C17	3.9665238027	2.3473847711	8.5705085300
H18	4.2776372598	1.6858916446	9.3719066367
C19	4.6353785769	3.5516176388	8.3765284916
H20	5.4603357803	3.8086768686	9.0379915959
C21	6.6845203386	5.9590610207	7.8623579917
C22	7.7851986547	5.7523572341	7.0164275596
H23	7.6291713933	5.7007802251	5.9404808133
C24	9.0621298851	5.6209593938	7.5313430023
H25	9.9200881127	5.4620925485	6.8859064056
C26	9.2705785126	5.7028929808	8.9133079657
C27	8.1888572259	5.9243878532	9.7713026927
H28	8.3350029205	6.0029445764	10.8433262936
C29	6.9093403627	6.0501597251	9.2398107176
H30	6.0717806866	6.2323534655	9.9109553441
C31	3.6892536999	8.1207115140	3.4129391060
H32	4.4474862159	8.5025322468	2.7181800976
H33	3.0686763007	7.4142748258	2.8458672384
C34	2.7970267034	9.2232424622	3.9767396296
H35	3.4168681026	10.0719209613	4.3170602174
C36	1.9360762538	8.7444075954	5.1471372185
H37	1.6425728087	7.7016943972	4.9575006469
H38	2.4879469523	8.7598748665	6.0952894507
C39	0.6960730037	9.6450725465	5.1331927016
C40	0.4342181734	9.6599736498	3.6183902890
H41	-0.0581319359	8.7198355324	3.3296275691
H42	-0.1872115561	10.4823223649	3.2562817412
C43	-0.4760999007	9.1031219180	5.9284844271
C44	-0.3961776041	7.9375491181	6.6943663480
H45	0.5300816587	7.3685502933	6.7213430626
C46	-1.4849775067	7.5015019792	7.4483921688
H47	-1.3985119770	6.5923366307	8.0405065696
C48	-2.6729354301	8.2240162749	7.4477951179
H49	-3.5209049669	7.8869405300	8.0382013387
C50	-2.7659389503	9.3878410656	6.6858339439
H51	-3.6881285477	9.9639511222	6.6810933308
C52	-1.6781995148	9.8212935861	5.9394793316
H53	-1.7448536827	10.7456055552	5.3673427846
C54	1.0735068955	11.0249127644	5.6795949066
C55	1.4482497199	11.1095767264	7.0255195710
H56	1.4463561883	10.2014147160	7.6249874199
C57	1.8159317171	12.3164963688	7.6035712909
H58	2.0986016611	12.3443945983	8.6538655267
C59	1.8182553924	13.4780557407	6.8332965073
H60	2.1076142456	14.4285513409	7.2746182659
C61	1.4470553063	13.4102940655	5.4952929952
H62	1.4473751054	14.3099155748	4.8841417262
C63	1.0746165376	12.1952943477	4.9179691939
H64	0.7956115708	12.1753577938	3.8662712522
C65	2.0097905658	10.7796666975	2.1357834651
C66	3.8281874924	12.1573797092	1.1075570849
C67	3.2745639073	12.1984858500	-0.3162511505
H68	3.555840164	11.2938726987	-0.8645476183
H69	3.6792681027	13.0644786250	-0.8520750587
H70	2.1862704822	12.2691482956	-0.2996252883
C71	3.4459237617	13.4326204953	1.8632254147
H72	2.3589283480	13.5323083375	1.9126893593
H73	3.8535243515	14.3155825512	1.3582452678
H74	3.8389589903	13.4103363934	2.8859934720
C75	5.3464700911	12.0138108197	1.0657709478
H76	5.7724165943	11.9883234330	2.0759055483
H77	5.7948469910	12.8598827881	0.5372297591
H78	5.6409942249	11.0958566718	0.5450611414
N79	1.7683104582	9.7583019162	3.0391412644
N80	3.3290372567	10.9693024749	1.8183635666
H81	4.0164627929	10.4082504605	2.2966695904
P82	5.0261101862	6.0650638828	7.1367876746
Au83	4.5702347832	7.0703770683	5.0163607983
O84	1.0984032946	11.4564990514	1.6485381075
O86	1.8110530894	10.0192050911	10.2335286181
C87	0.4062013803	9.8518333017	10.3401403152
O88	2.1727528251	0.8680741556	7.8426111889
C89	2.5120458011	-0.0172569231	8.8921558058
O90	10.5552593611	5.5629385723	9.3217541589
C91	10.8065740989	5.6378166180	10.7116920652
H92	1.8128310098	-0.8500264806	8.8237703374
H93	3.5371950090	-0.3949129202	8.7880374298
H94	2.4101347145	0.4621651646	9.8741789398
H95	11.8801512054	5.4959970335	10.8330106271
H96	10.5212155414	6.6145789492	11.1226177686
H97	10.2727381211	4.8524017228	11.2618910261
H98	0.0230061934	10.7874880356	10.7472789348
H99	-0.0523693634	9.6659630175	9.3584656752
H100	0.1473380282	9.0282341697	11.0179303336

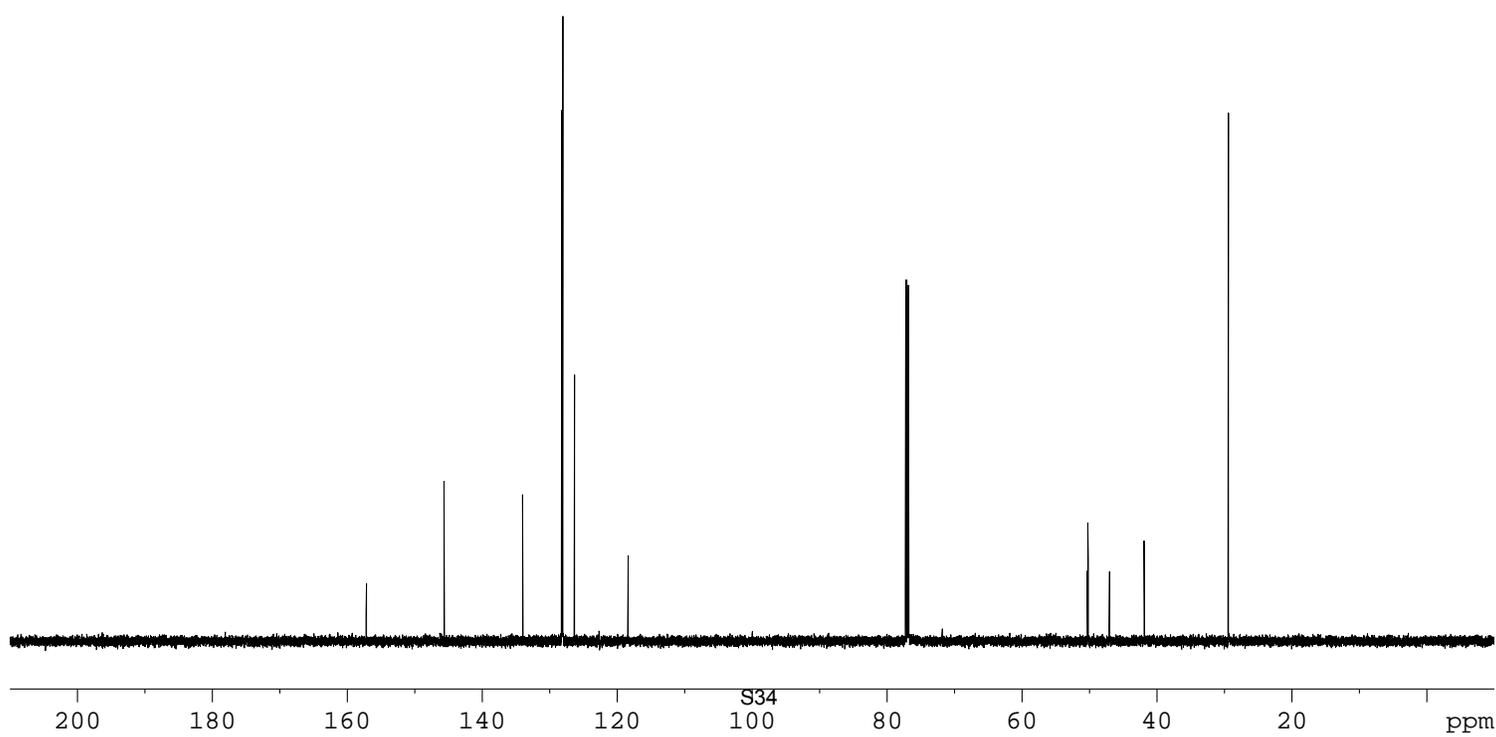
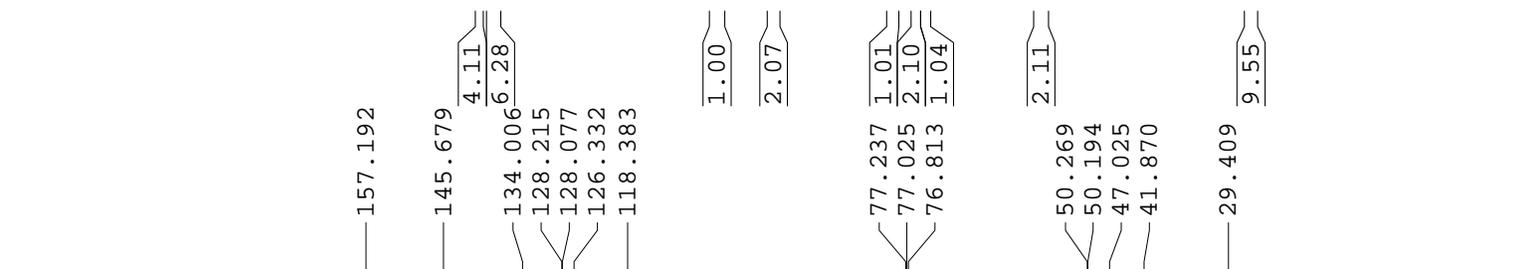
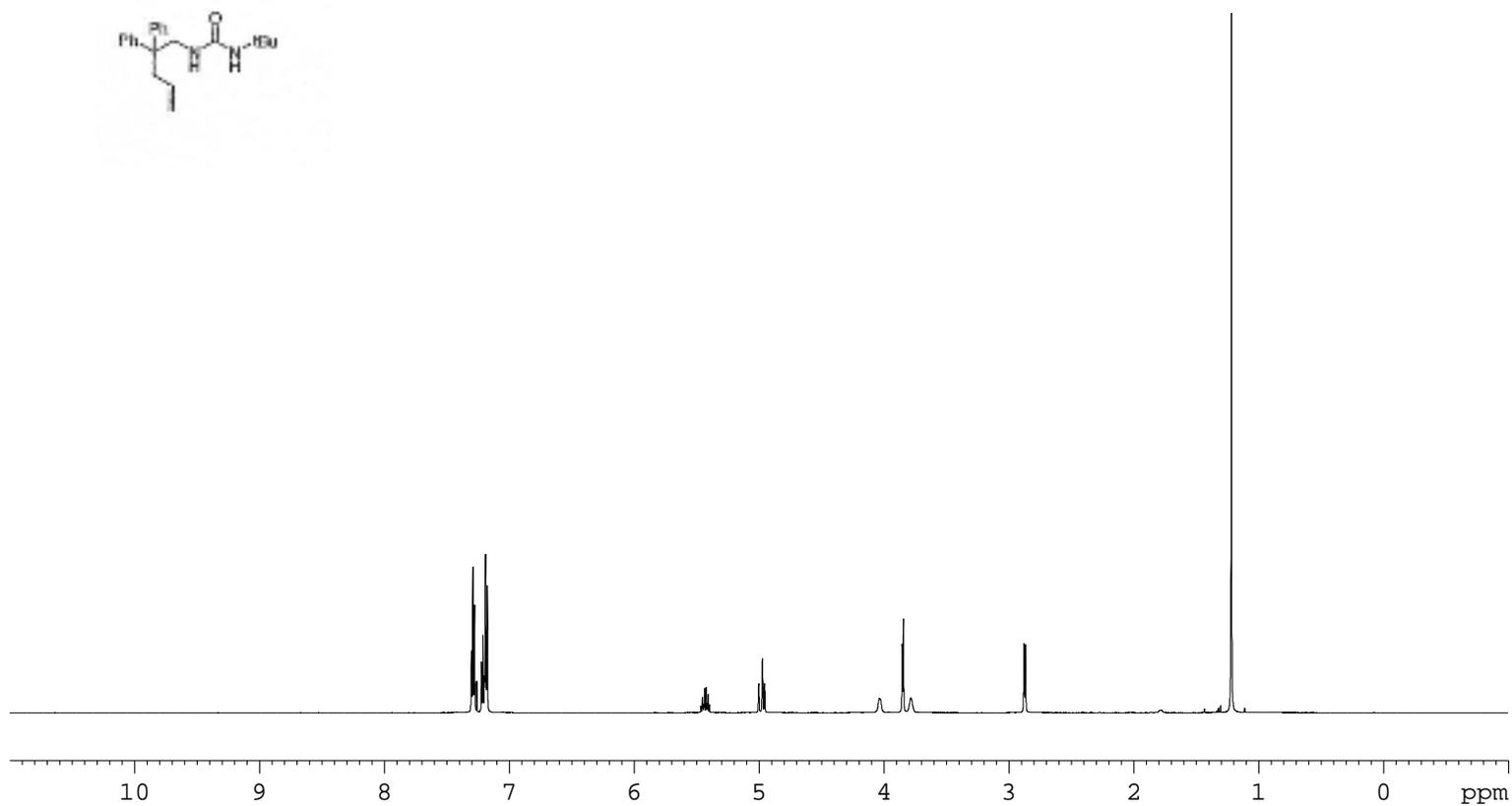
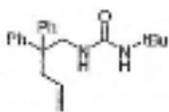
3. AuP(PhCF₃)₃

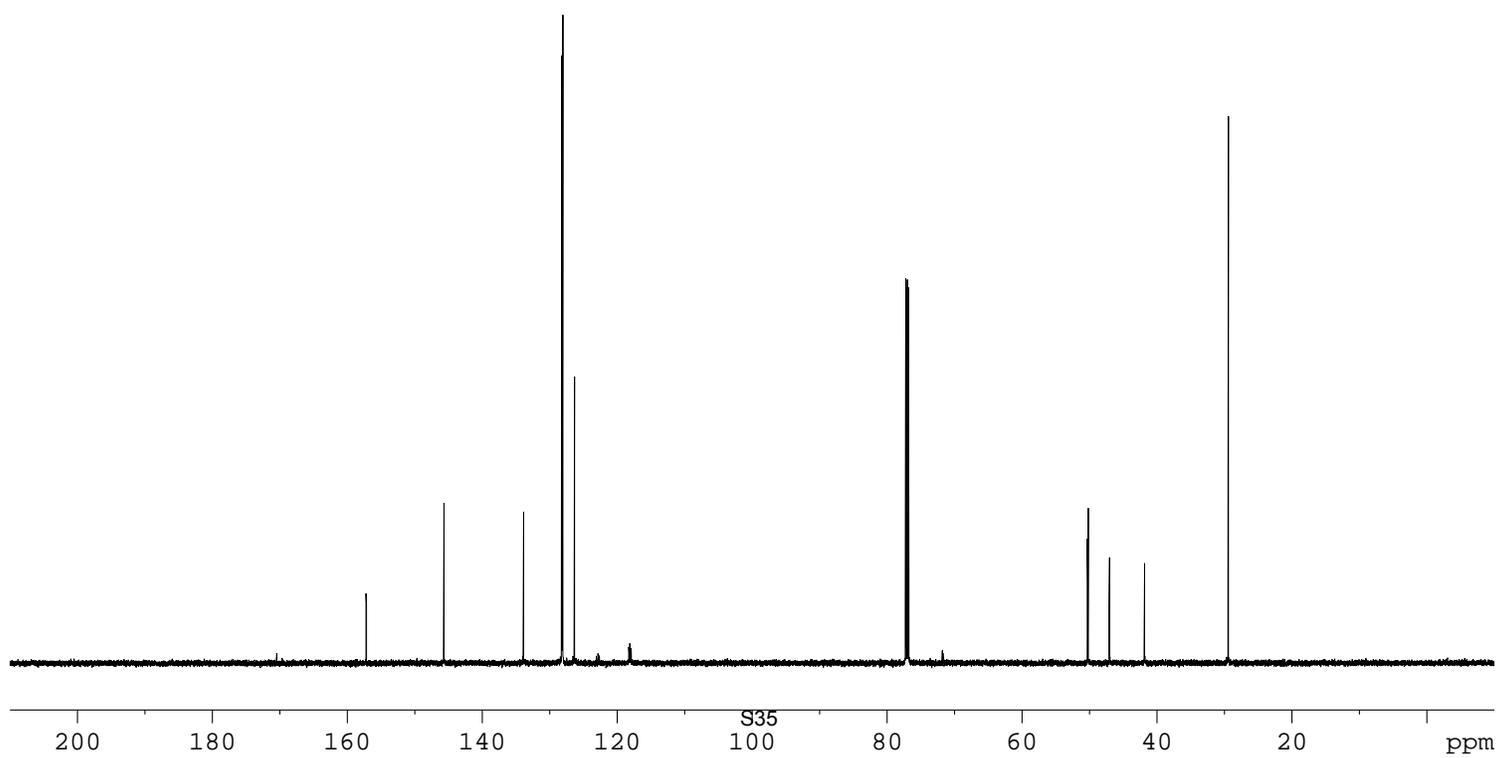
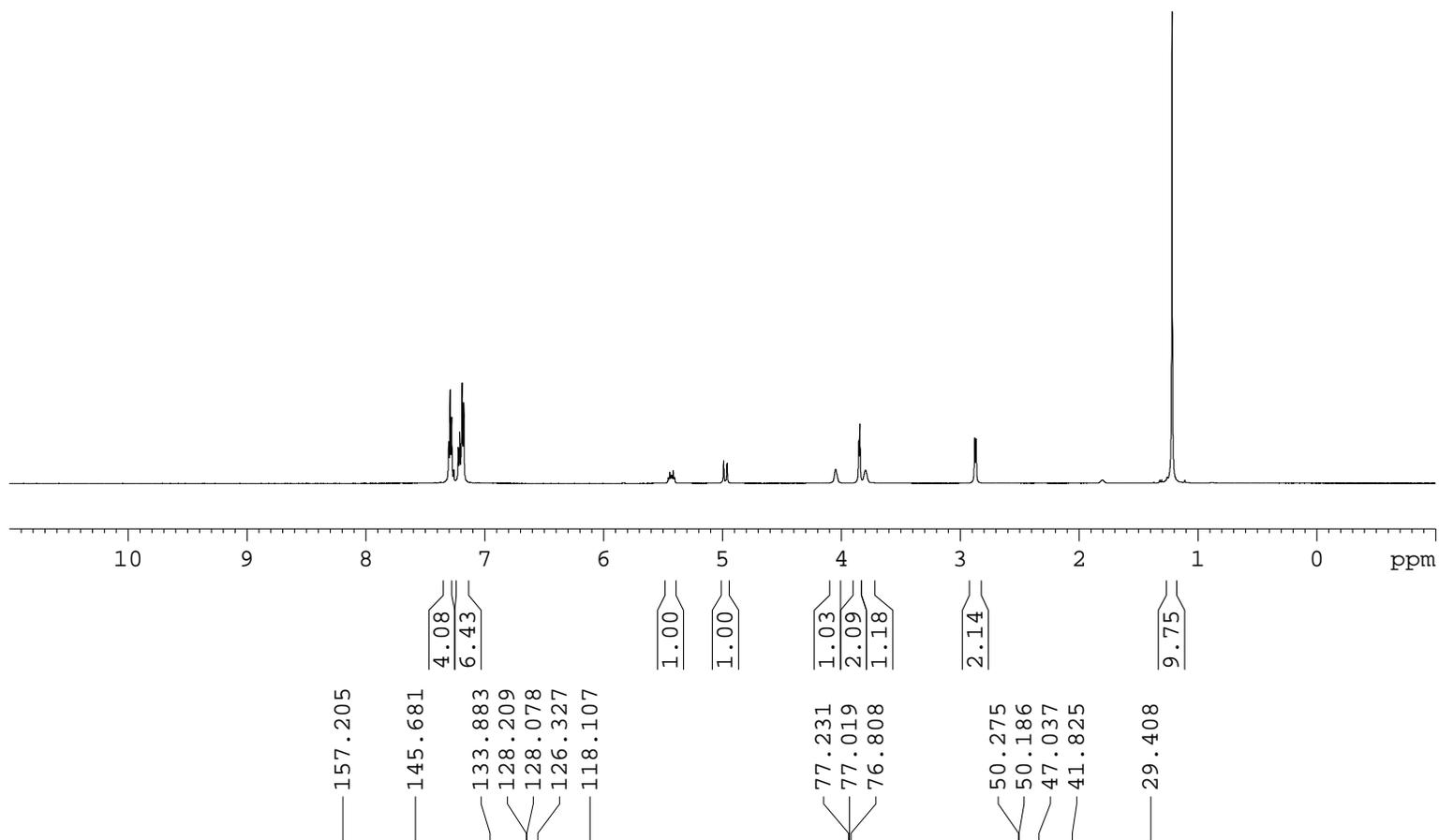
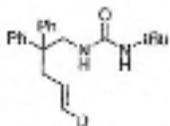
P(PhCF ₃) ₃ Au Substrate				P(PhCF ₃) ₃ Au TS			
Au1	7.4582854827	-3.3107274509	2.5473468481	C1	2.9923566975	5.7622427483	8.4329732982
C2	6.1552306161	-6.0033746979	4.0447801126	C2	2.3728531007	6.9591725150	8.8212675312
C3	4.7363749745	-1.1346512607	3.6594869197	H3	2.5737023956	7.8747313045	8.2642925604
C4	4.7057957875	-1.2421130967	2.1173914401	C4	1.5179777205	6.9788457953	9.9102682472
N5	3.4336797466	-1.6009307496	1.5586800951	H5	1.0358308026	7.9038166641	10.2168761002
C6	2.7313028373	-0.6364287800	0.8175681693	C6	1.2643581006	5.7982564096	10.6139142546
N7	1.4665446770	-1.0209851750	0.4937377334	C8	1.8706404305	4.6084755079	10.2315952119
O8	3.2637279522	0.4085595627	0.4614101026	H9	1.6628635163	3.6979877877	10.7834367652
P9	7.0195802352	-5.1476233798	1.1633830108	C10	2.7362384349	4.5875511898	9.1400765241
C10	2.7752205176	-4.6649176721	-0.5263143627	H11	3.2063484411	3.6531950522	8.8439642278
C11	3.0964471861	-5.8304663062	0.1680291512	C12	4.7466394740	4.1559331285	6.7737170403
C12	4.3812752888	-6.0127867507	0.6653614655	C13	4.0731610881	3.2400451239	5.9552490995
C13	5.3480658905	-5.0198999090	0.4699303775	H14	3.1836580794	3.5517152588	5.4104027403
C14	5.0217565713	-3.8594631829	-0.2424647621	C15	4.5411837625	1.9400979195	5.8365173041
C15	3.7382428886	-3.6821535130	-0.7430951459	H16	4.0251416304	1.2253485037	5.2021764214
C16	9.8655220573	-5.6407981139	-2.4046232240	C17	5.6899424689	1.5519896996	6.5262554002
C17	10.3659010443	-5.2700916848	-1.1556166940	C19	6.3703117799	2.4588120719	7.3323654086
C18	9.4992341332	-5.0991107567	-0.0873371100	H20	7.2678078942	2.1467159093	7.8553232661
C19	8.1246883063	-5.3069864901	-0.2615396750	C21	5.9001863069	3.7609639765	7.4570166412
C20	7.6300242960	-5.6798606576	-1.5155404336	H22	6.4376924642	4.4683556602	8.0832993039
C21	8.5024674949	-5.8450690418	-2.5857551854	C23	5.4245086632	6.9240329177	7.4153713047
C22	7.0757302722	-0.9943858820	3.5076538056	C24	6.0256537723	7.6964995605	6.4178208993
C23	7.2187901056	-9.1142339560	2.1190181598	H25	5.6621641417	7.6354979300	5.3927651713
C24	7.2326049122	-9.7247116699	1.4066644595	C26	7.0700443392	8.5572491171	6.7308163359
C25	7.1022724732	-6.7037862953	2.0841038261	H27	7.5236768308	9.1749071014	5.9628951695
C26	6.9794206087	-6.6918086240	3.4764836364	C28	7.5136443613	8.6508026085	8.0455572885
C27	6.9597781387	-7.8871270395	4.1876377636	C30	6.9205120420	7.8852309957	9.0494524305
C28	4.1471451157	-9.3730633566	5.6898024402	H31	7.2686065165	7.9783500380	10.0749790136
C29	4.1726757431	-4.8949710689	4.3018721104	C32	5.8764690758	7.0258060351	8.7376161323
C30	4.3625727826	-3.6829613678	3.6334927169	H33	5.3986387812	6.4466659269	9.5250464347
C31	4.5083140284	-2.4834878224	4.3399619251	C34	2.0122781047	7.9275660674	3.5611520684
C32	4.4650865912	-2.5390979352	5.7406590726	H35	2.7169460491	7.7749183730	2.7408559692
C33	4.2954332717	-3.7457360579	6.4081290895	H36	0.9999229835	7.5893971752	3.3313634941
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P(PhCF ₃) ₃ Au product							
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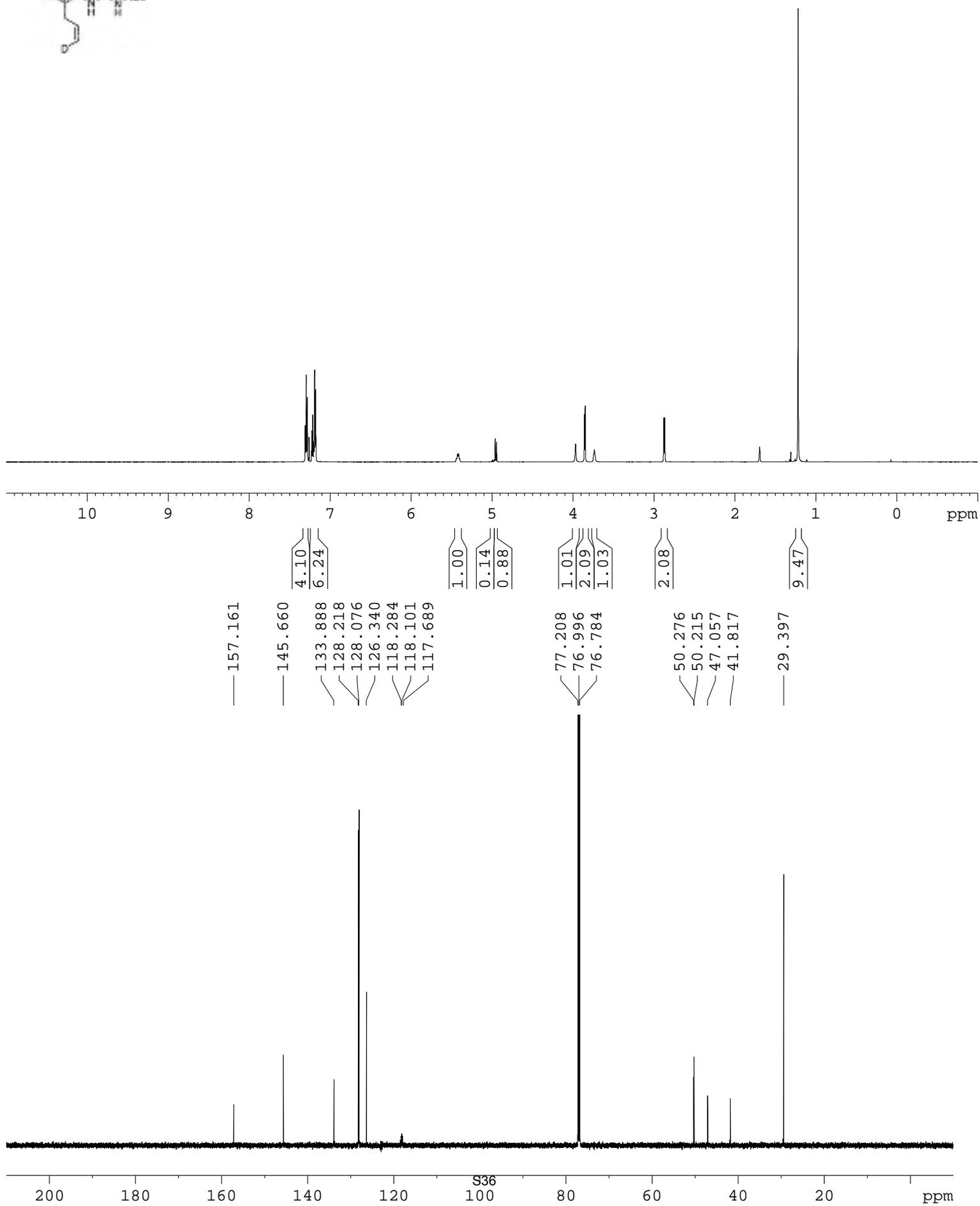
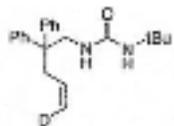
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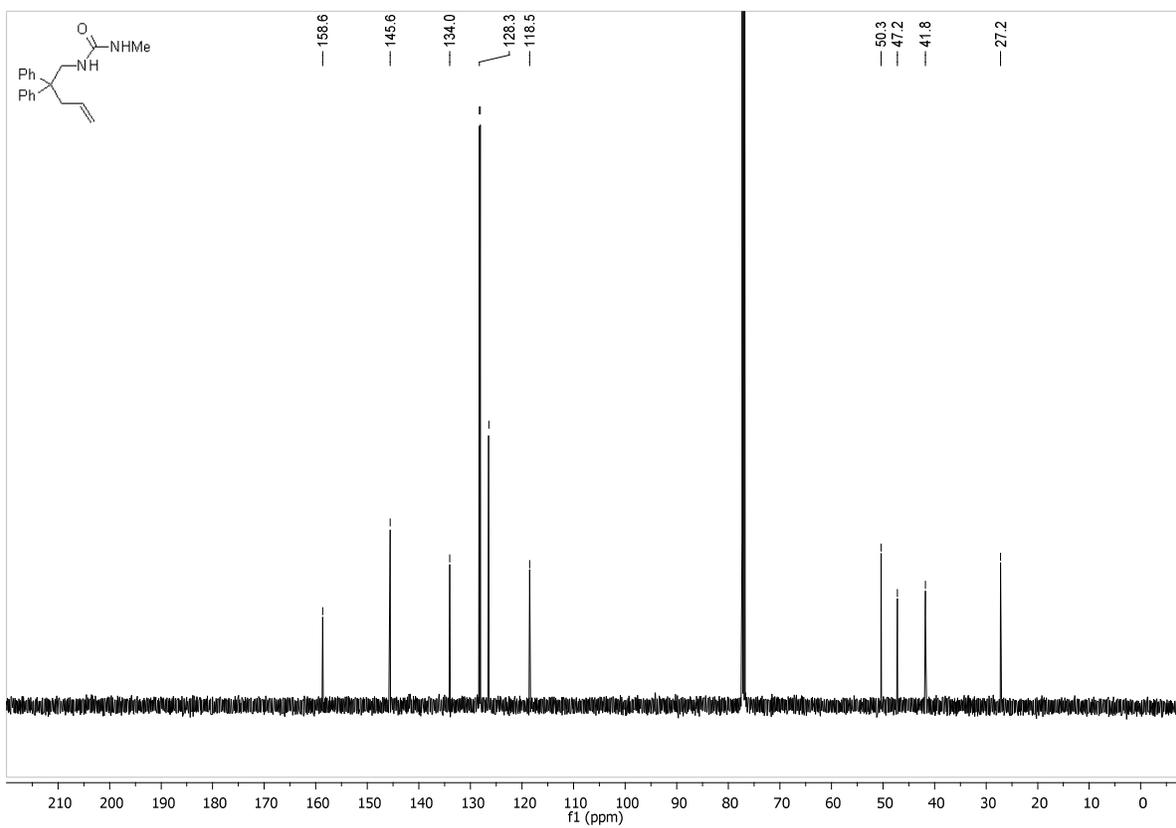
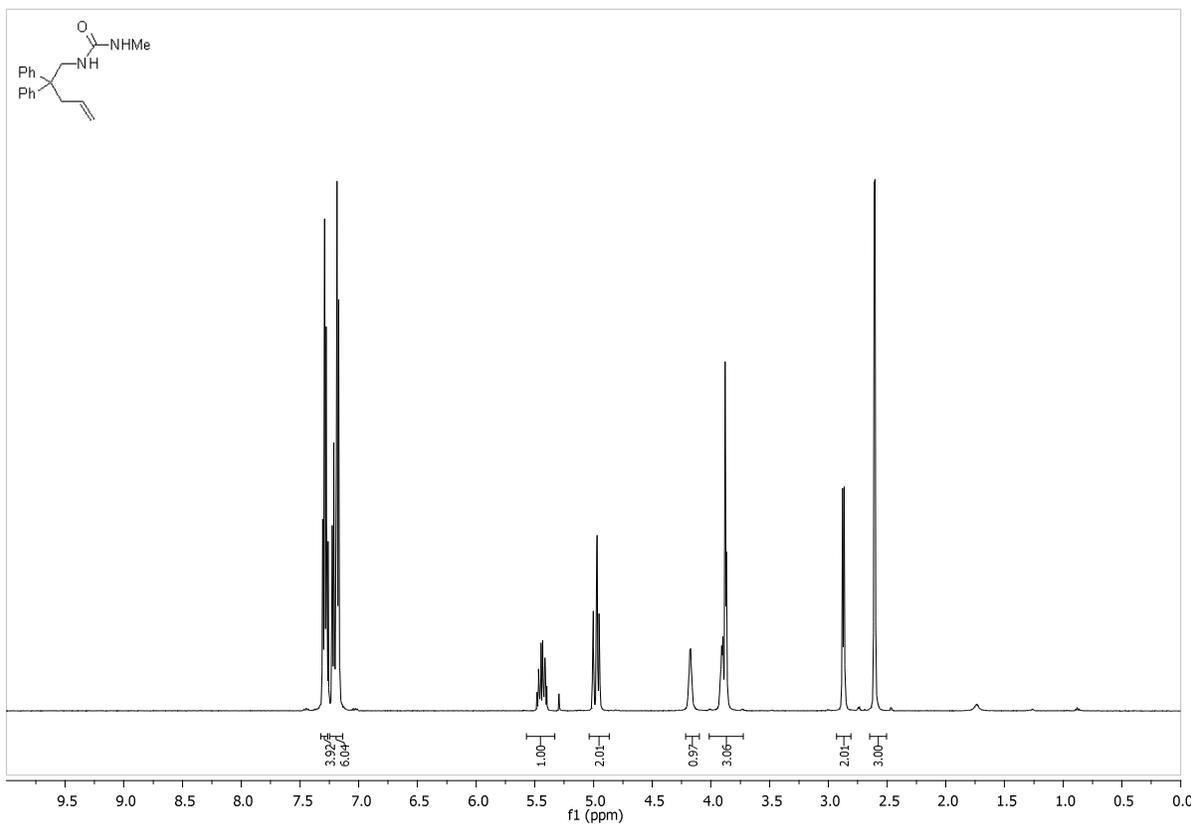
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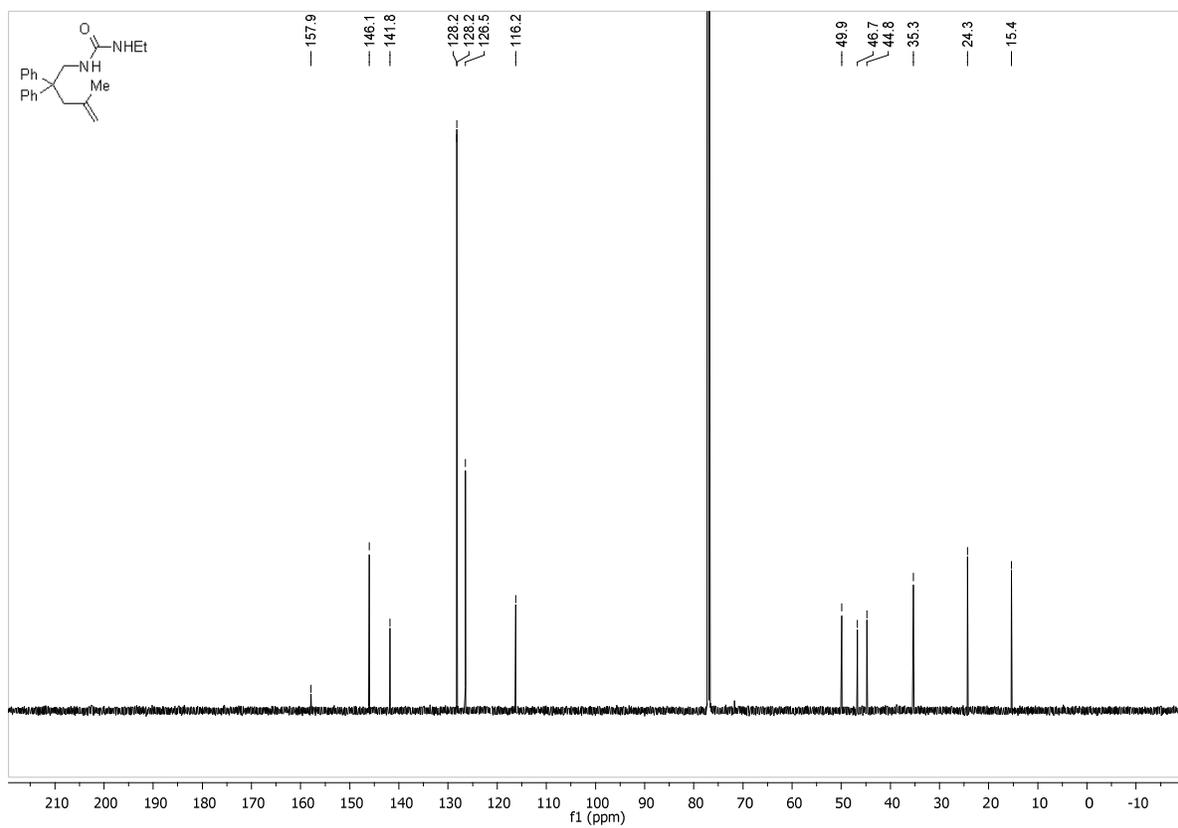
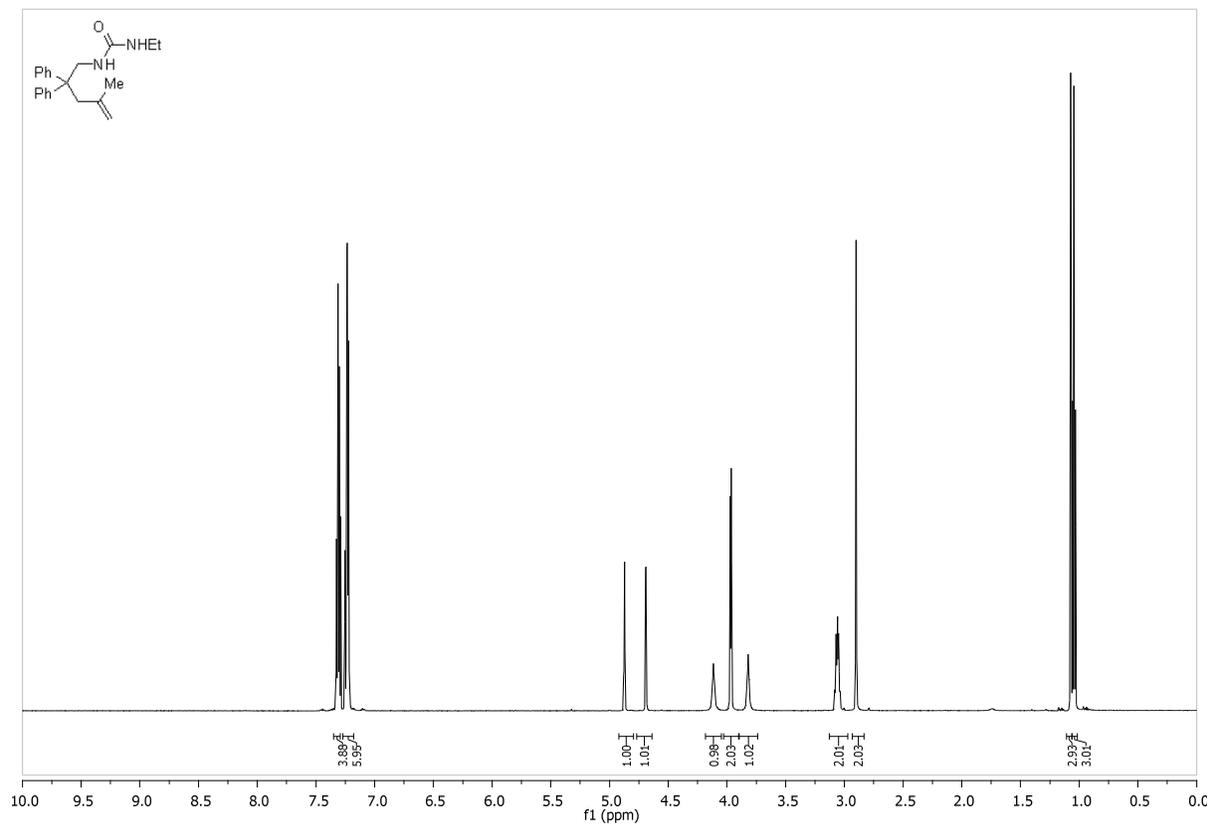
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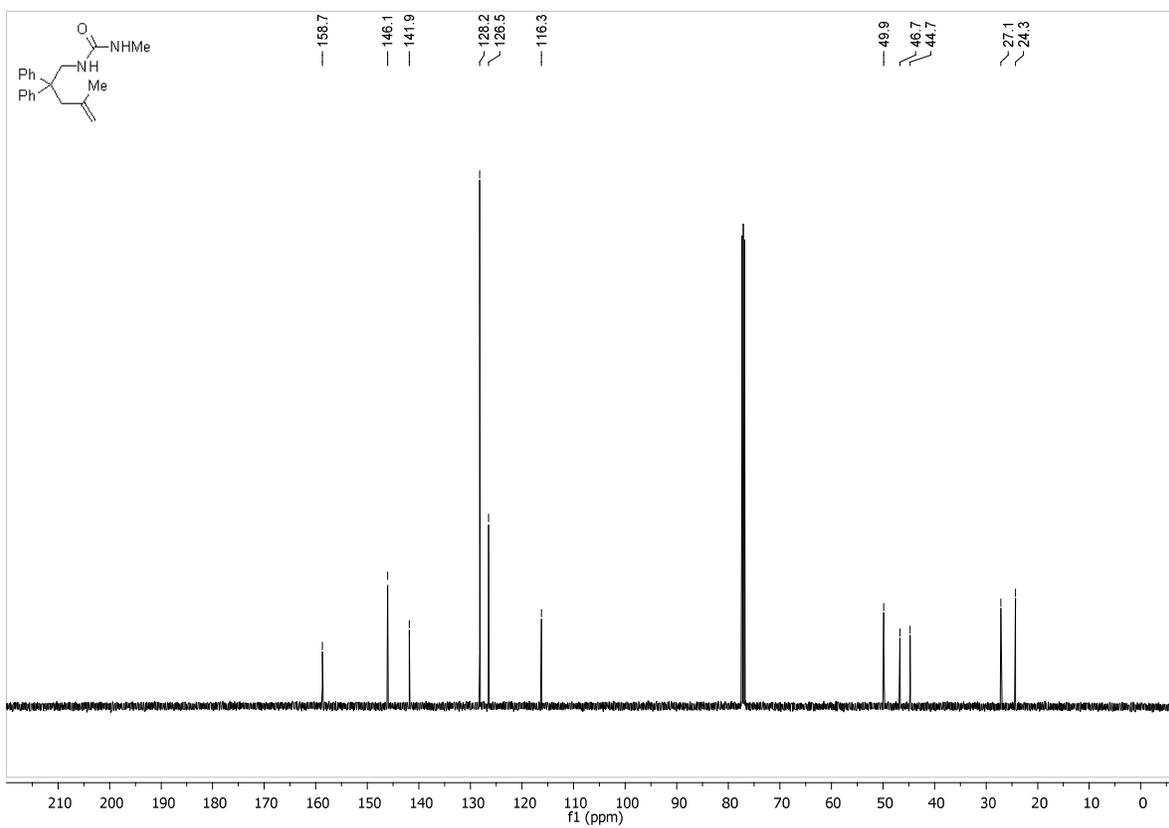
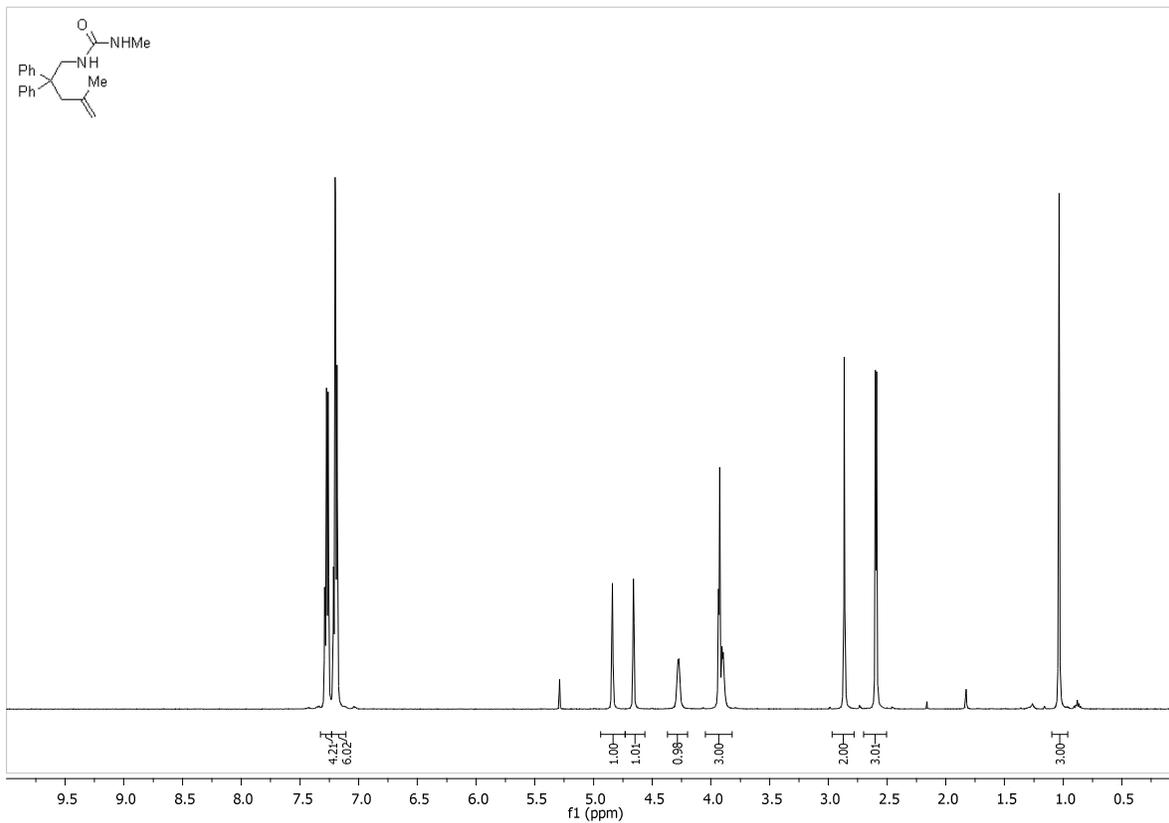


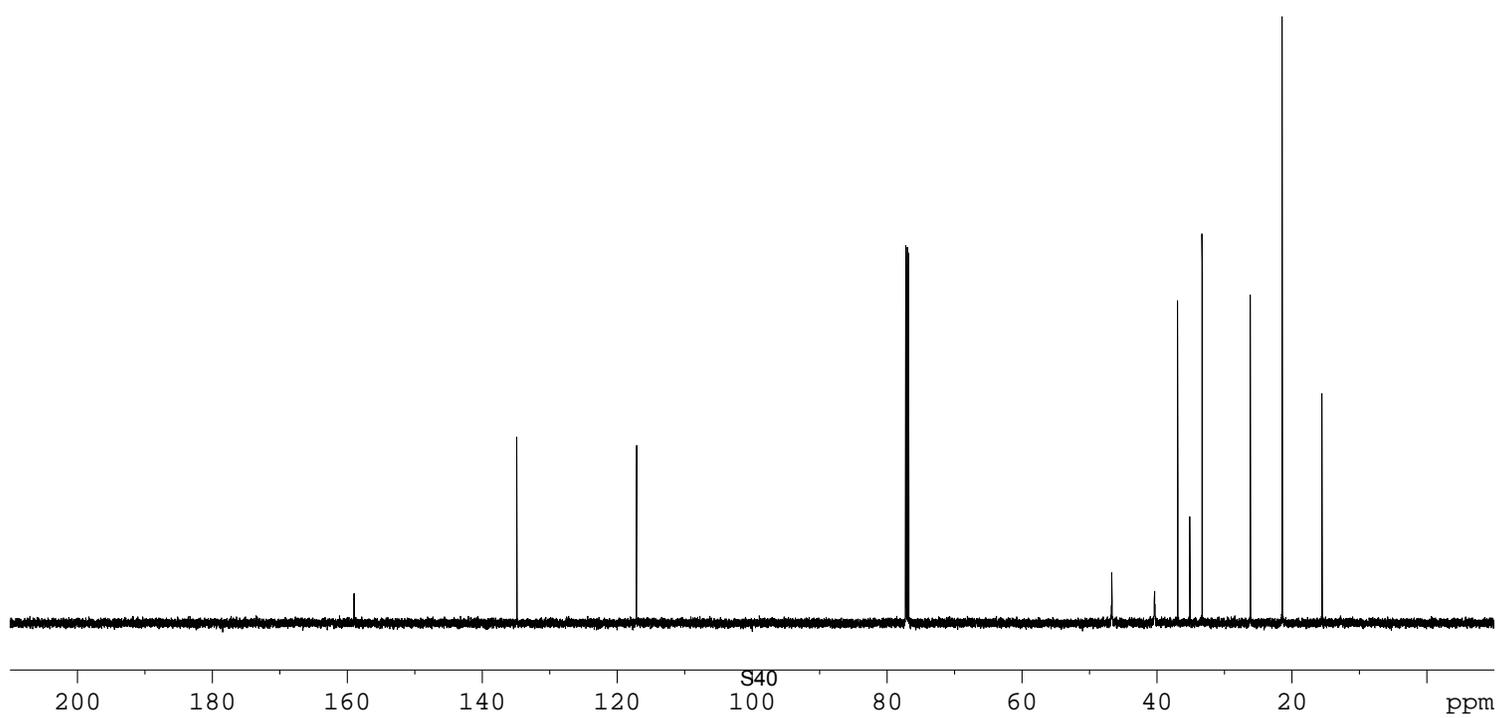
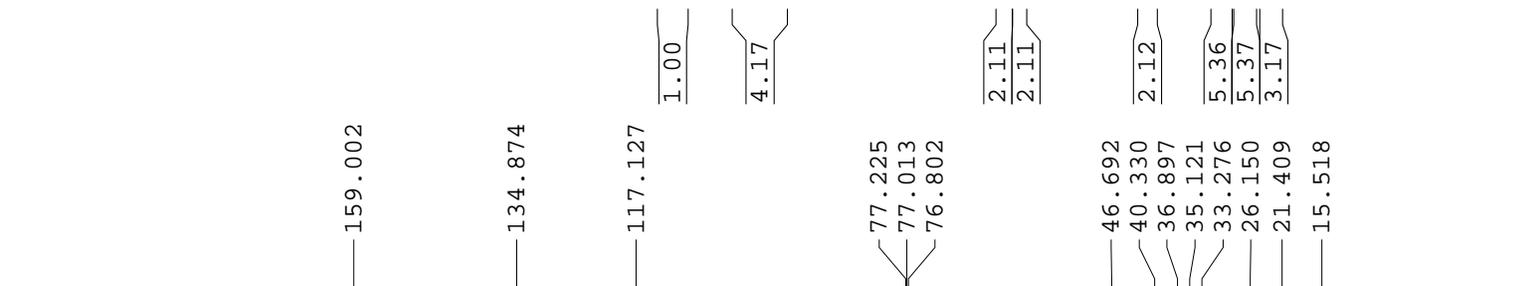
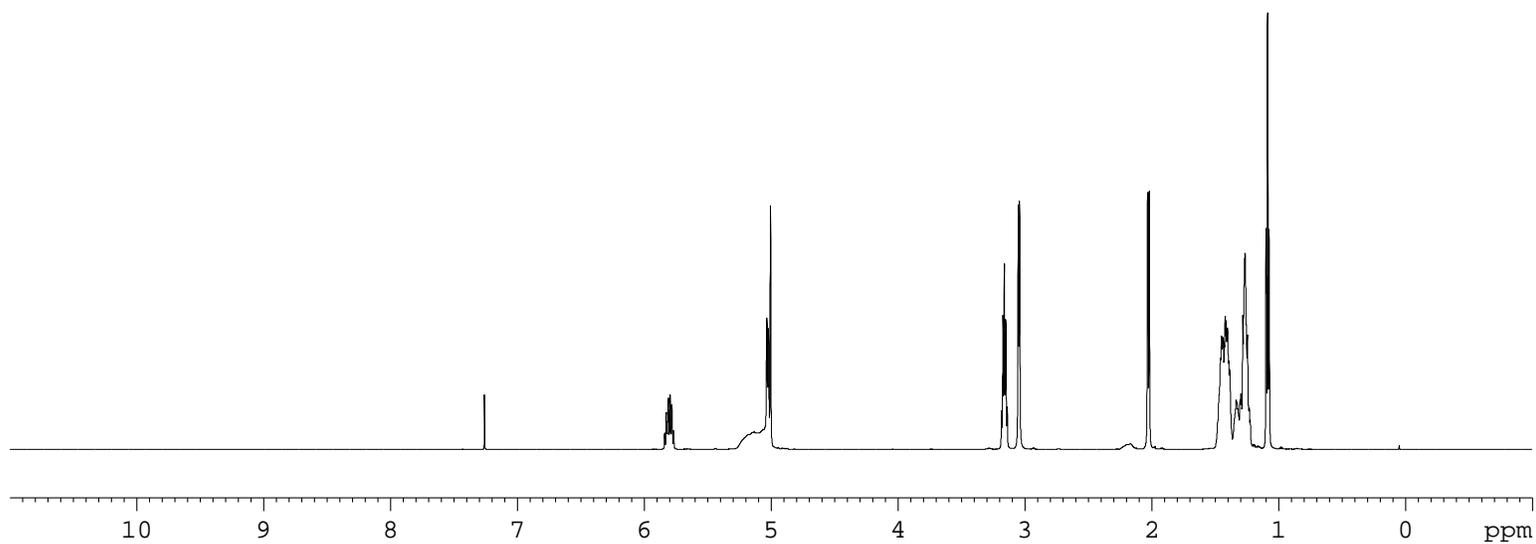
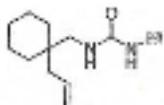


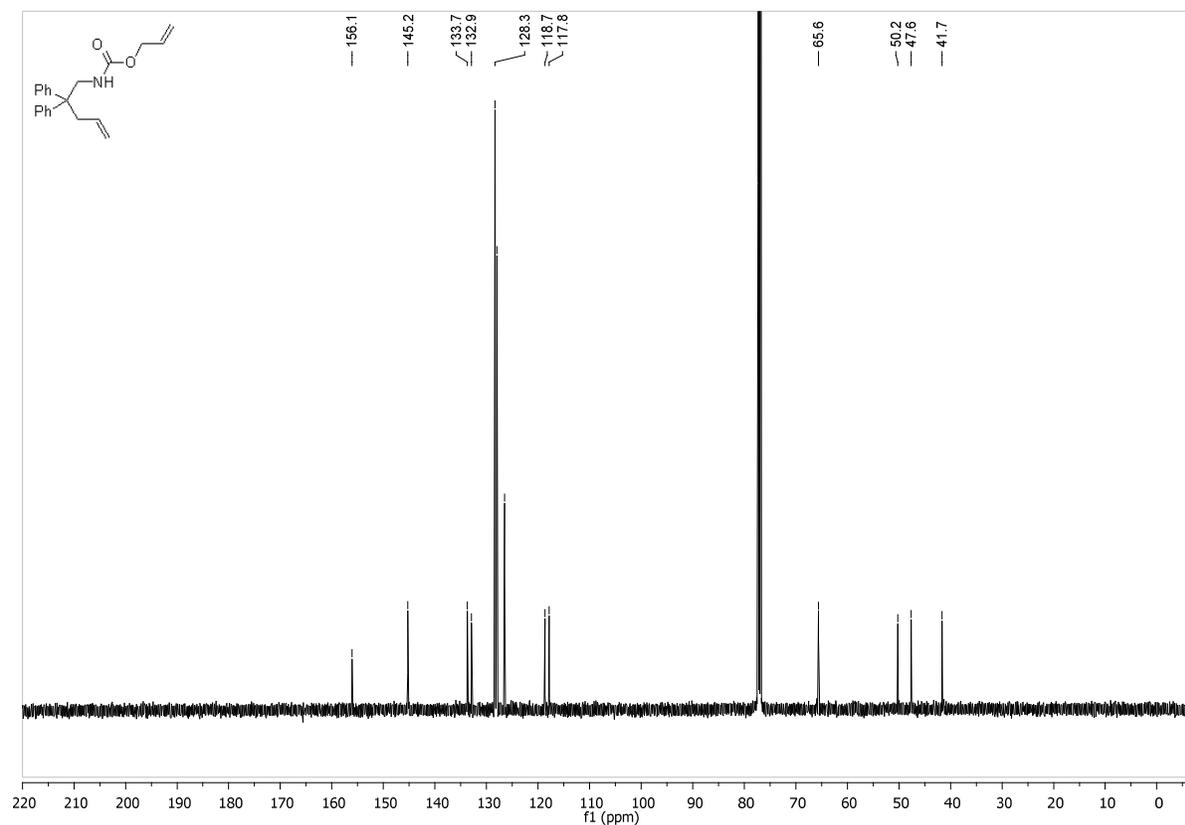
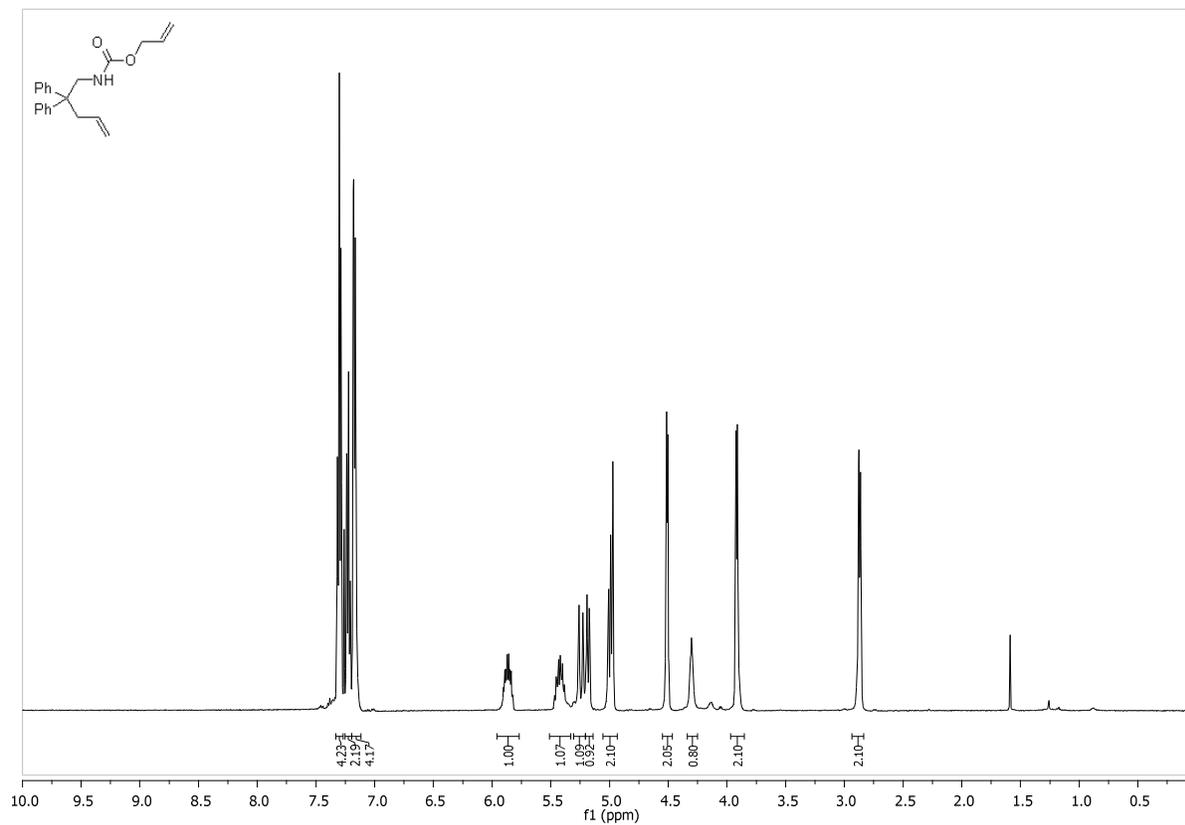


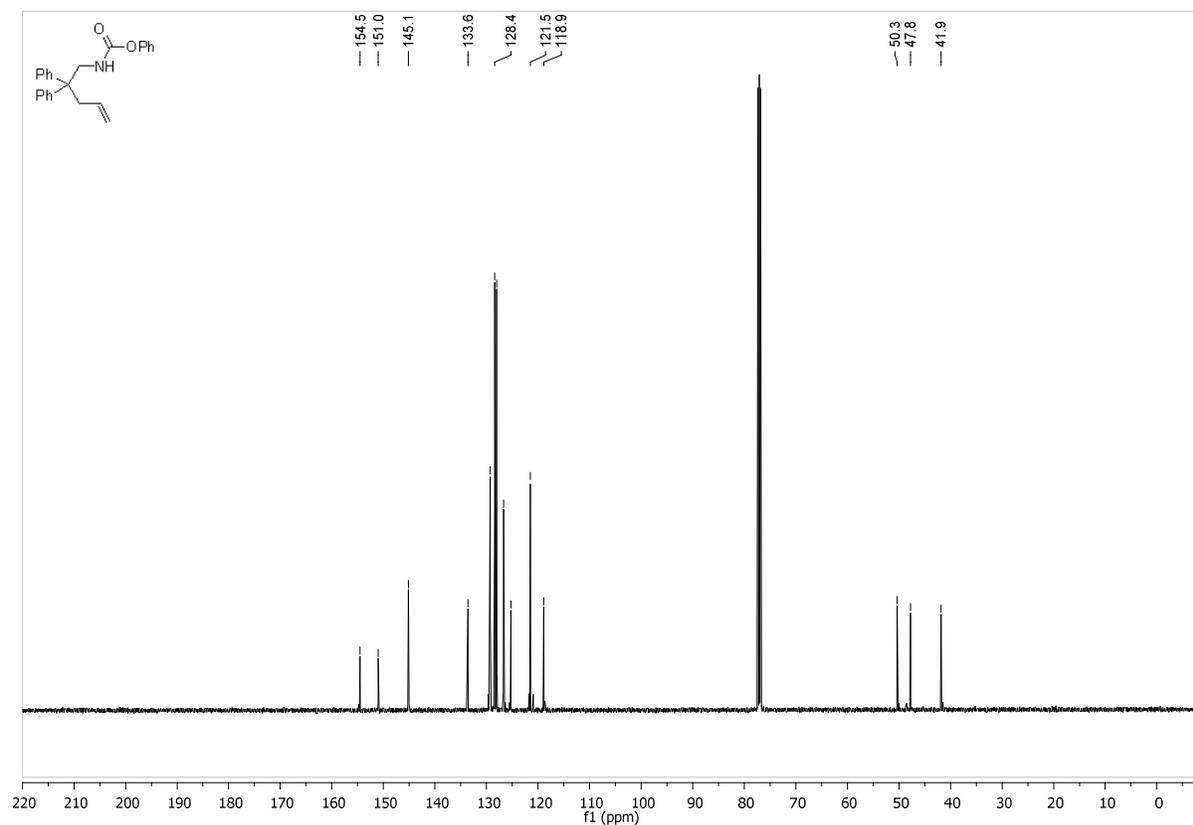
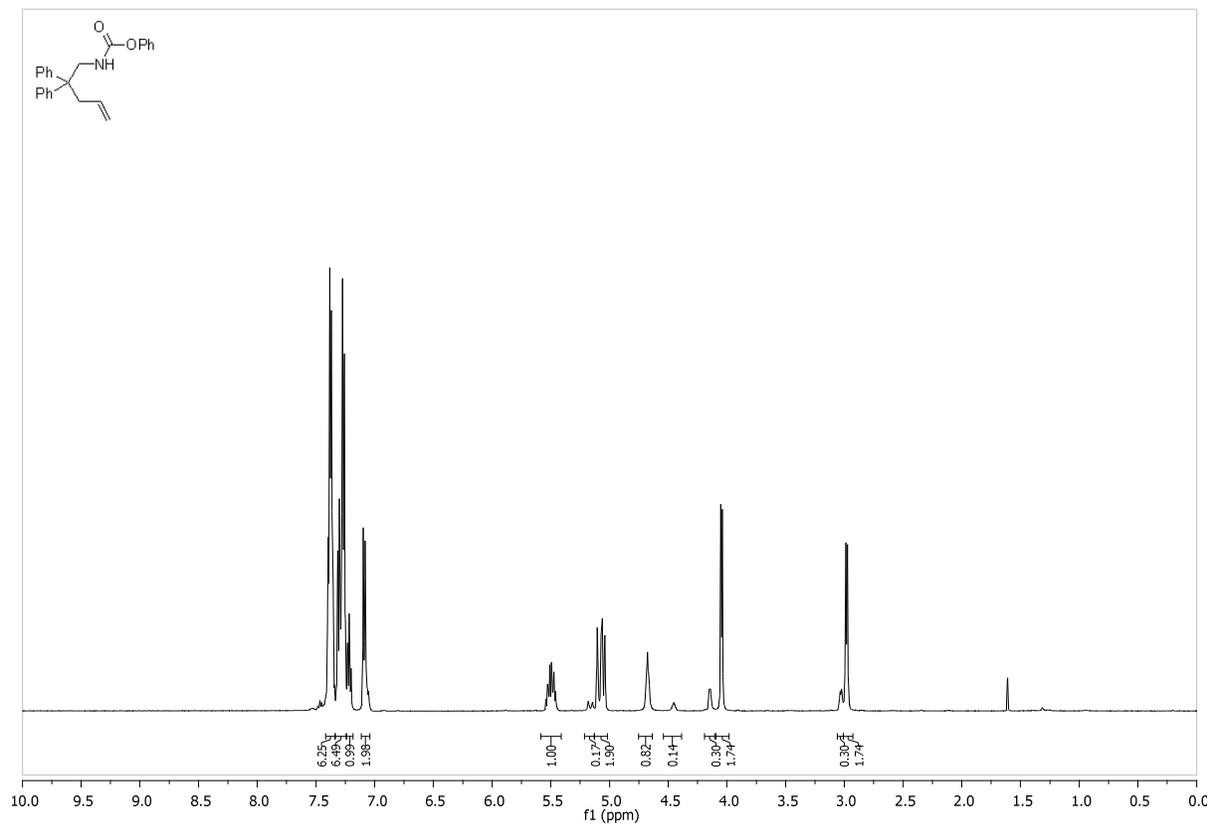


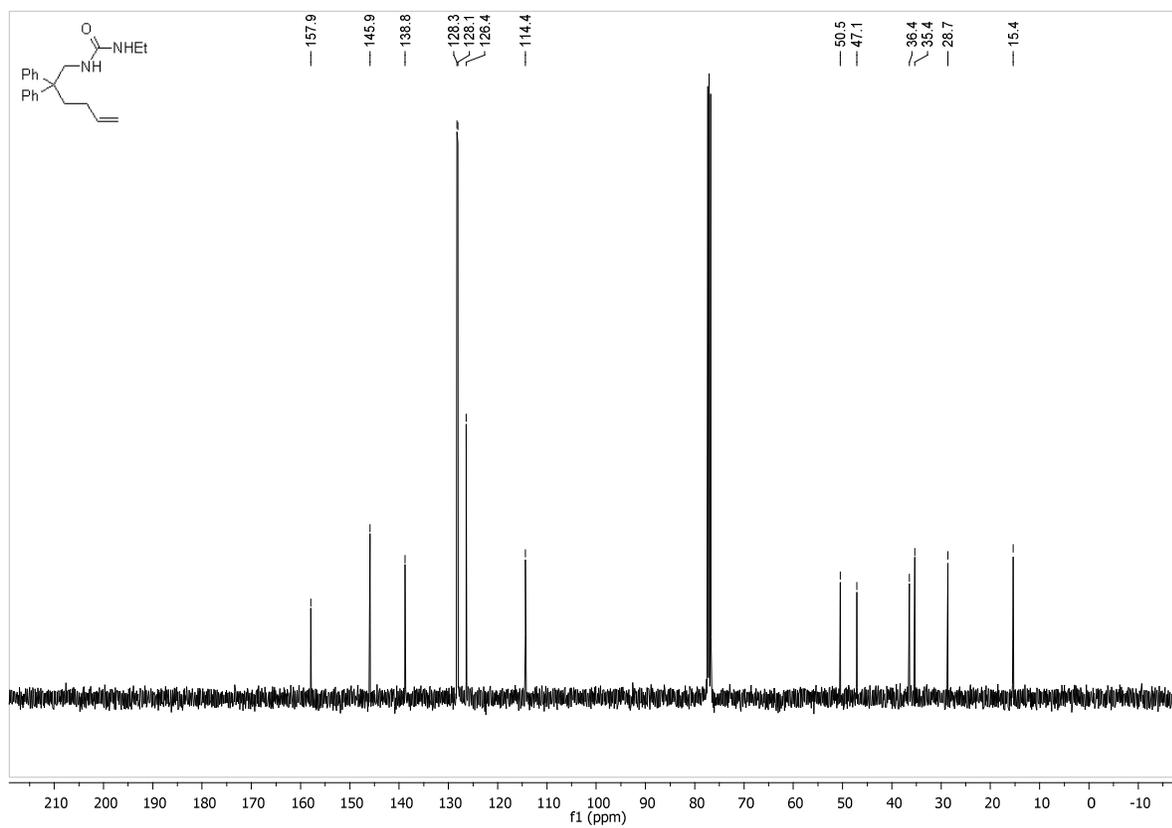
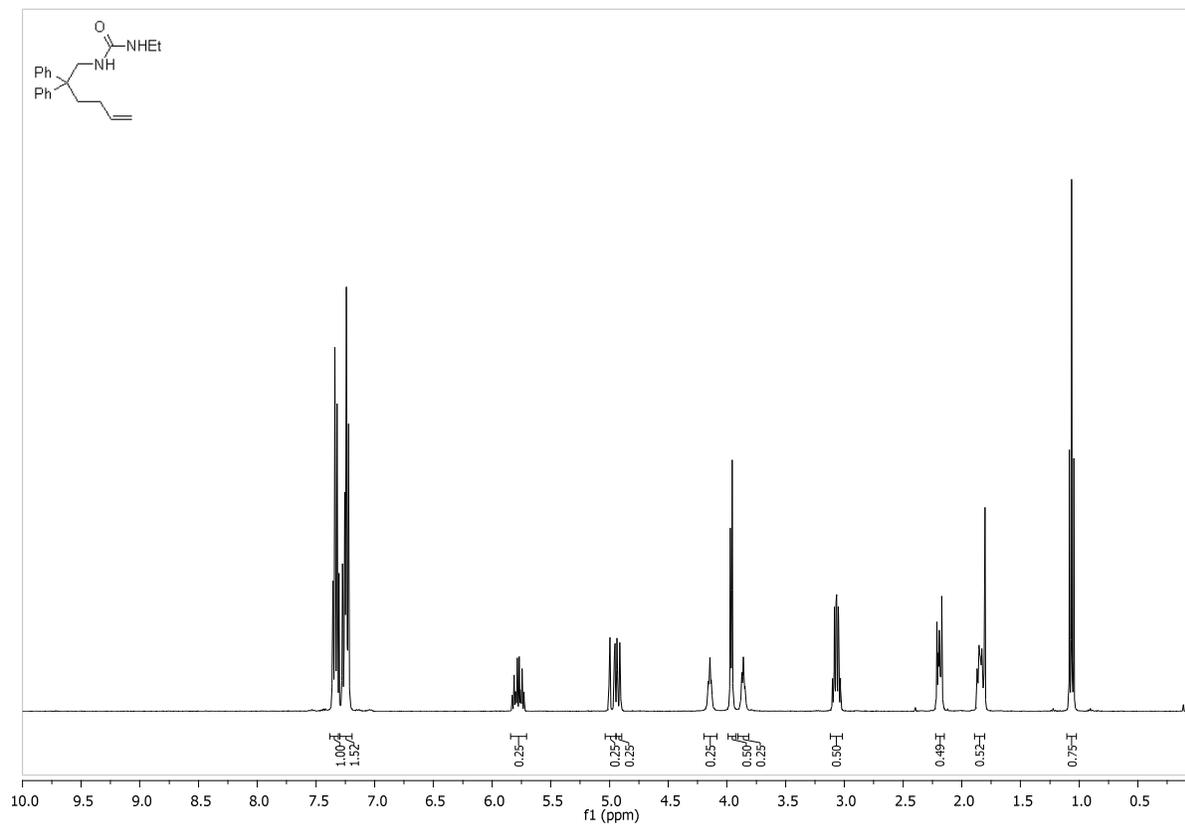


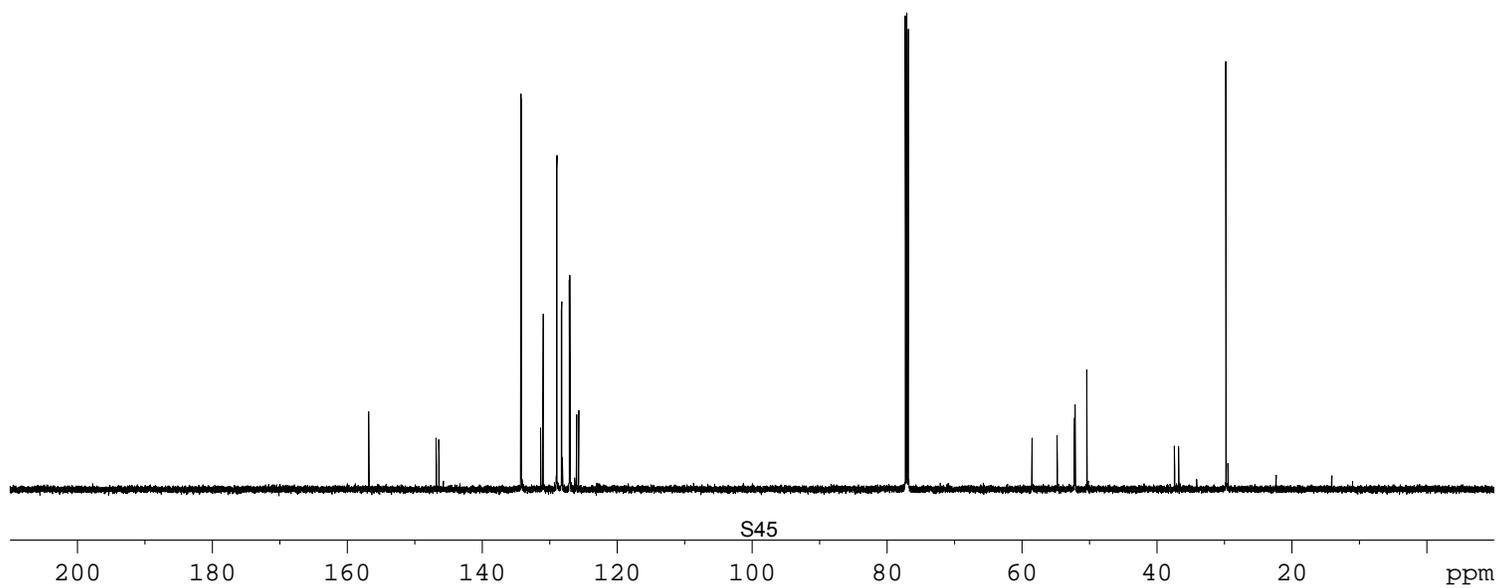
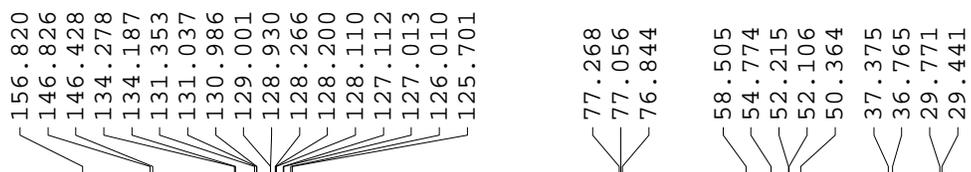
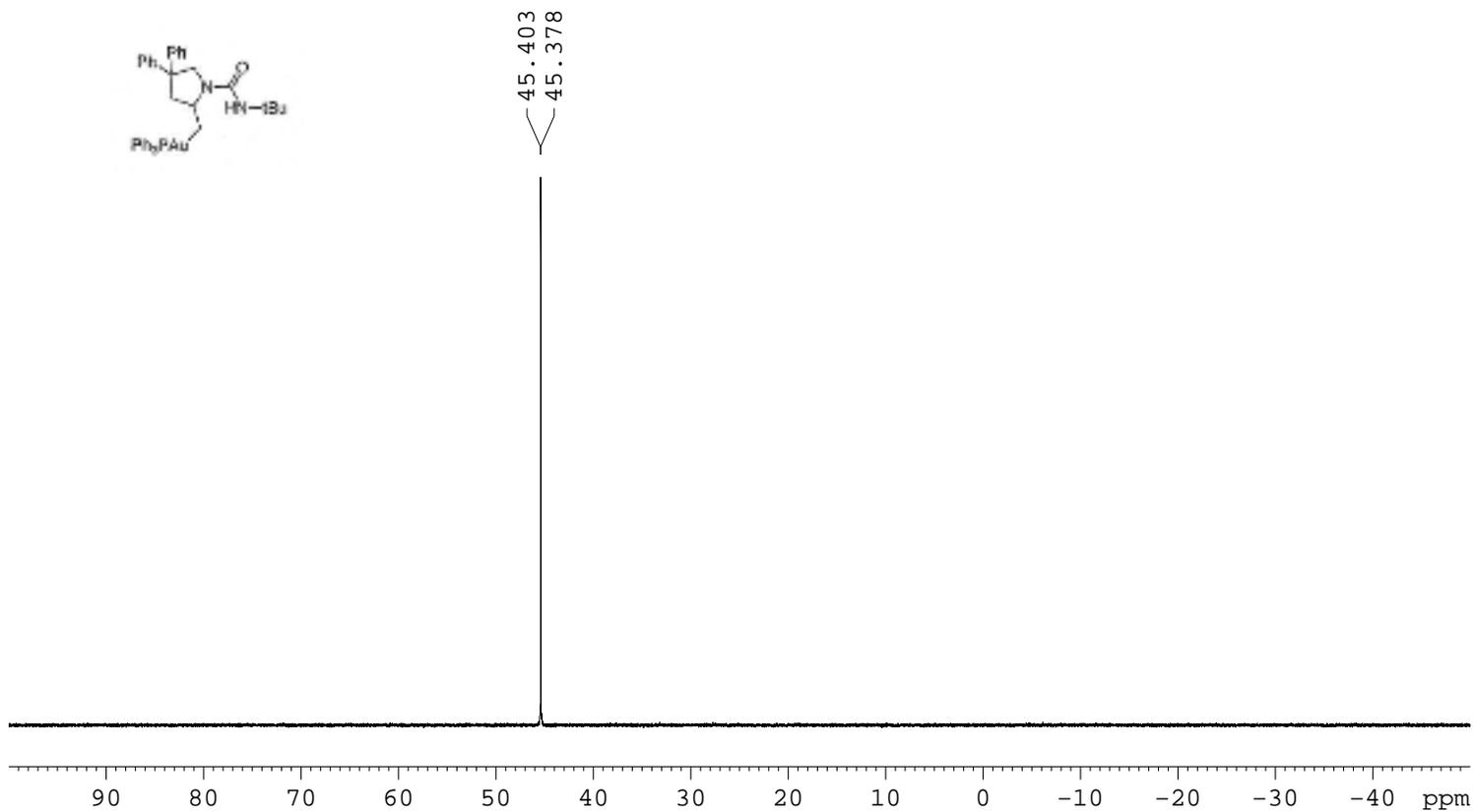
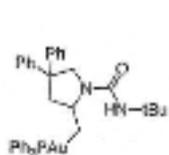


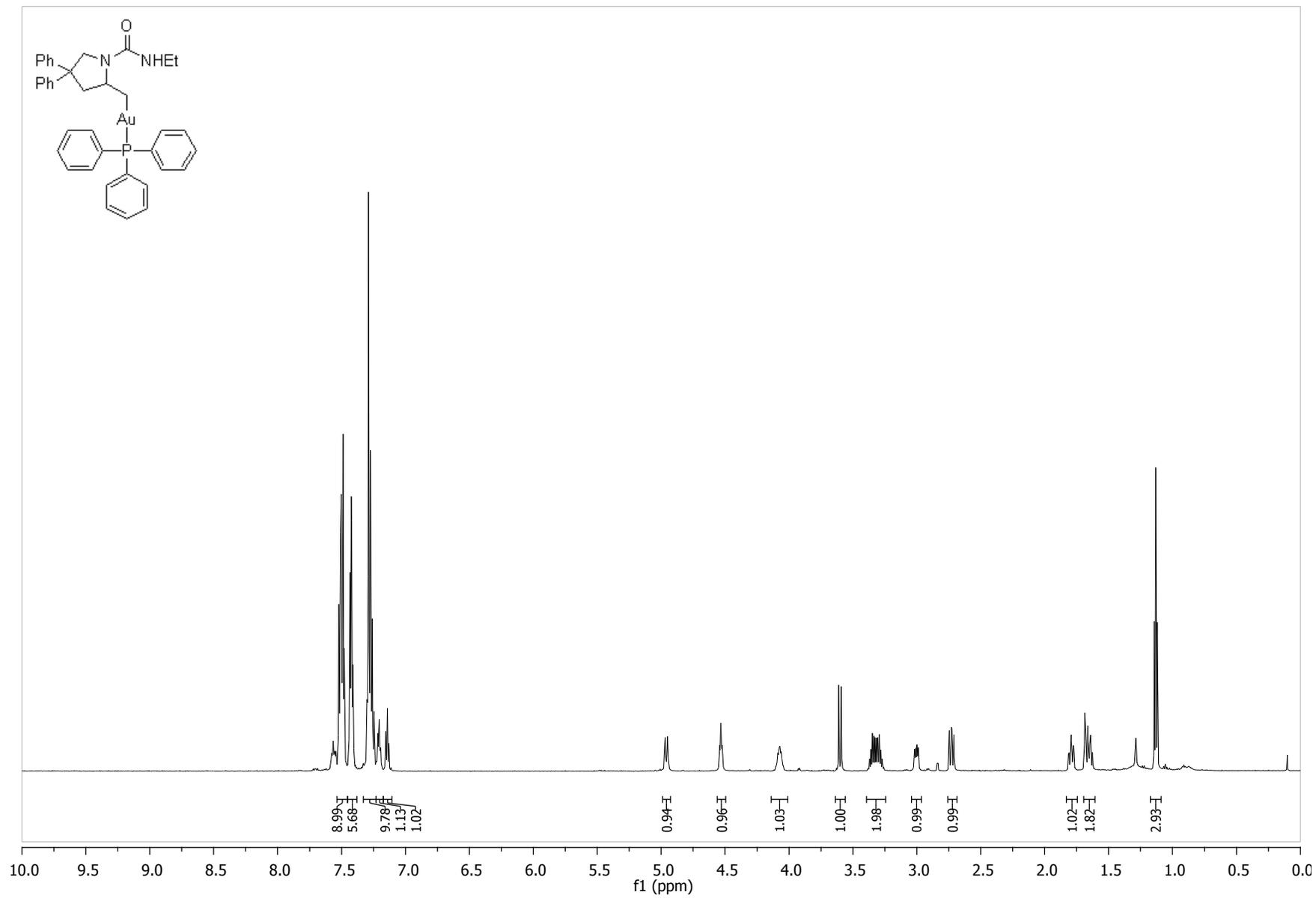


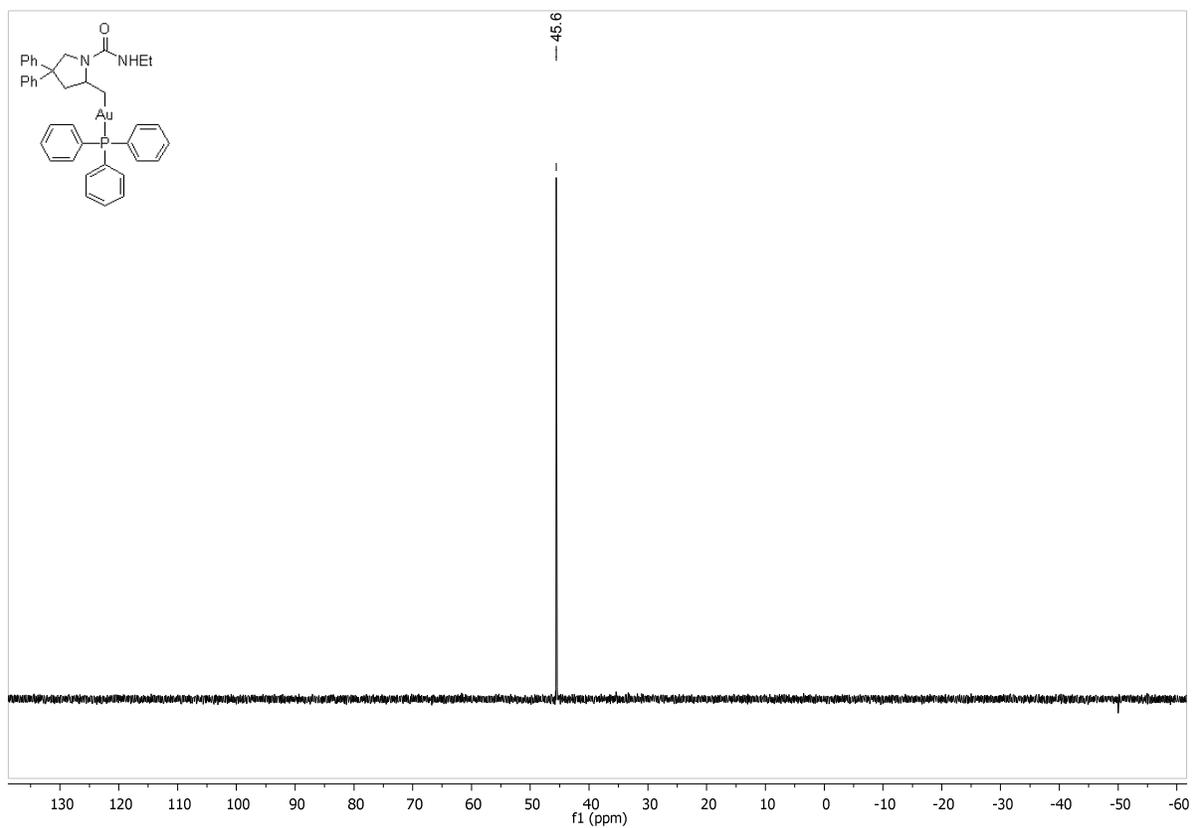
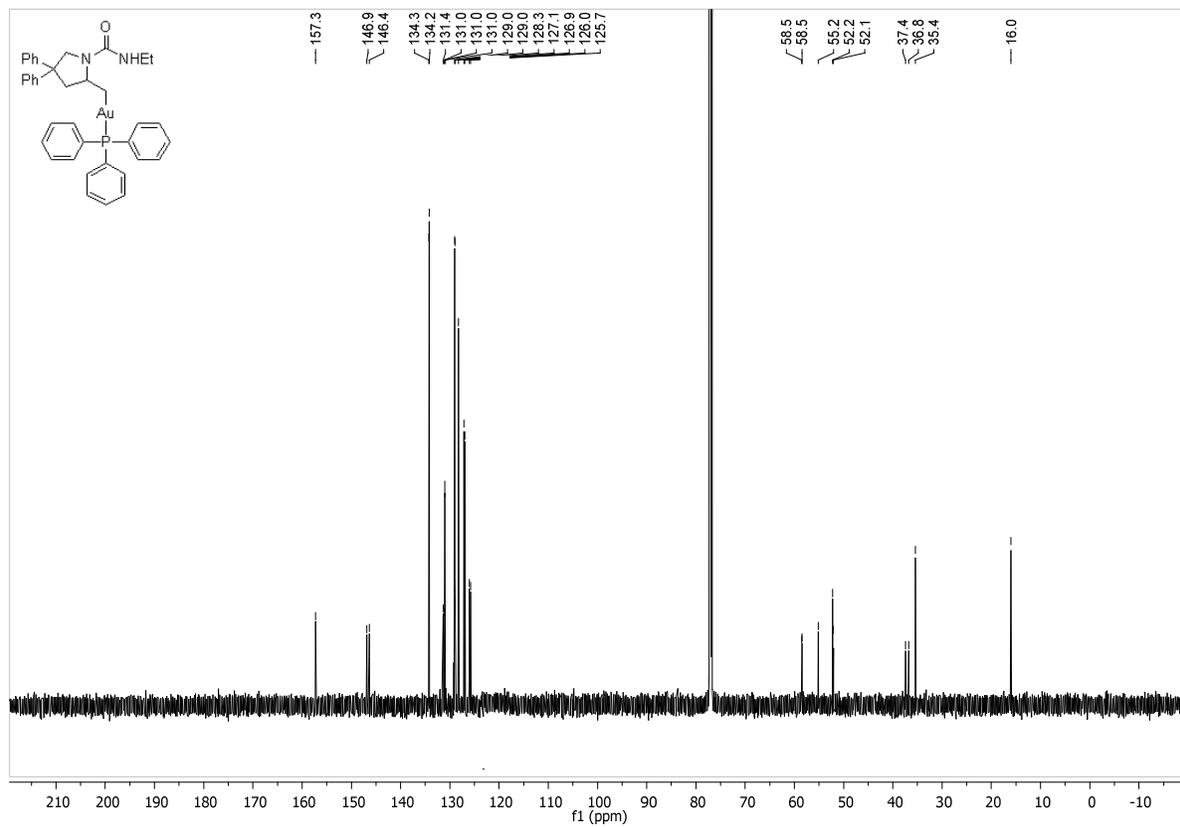


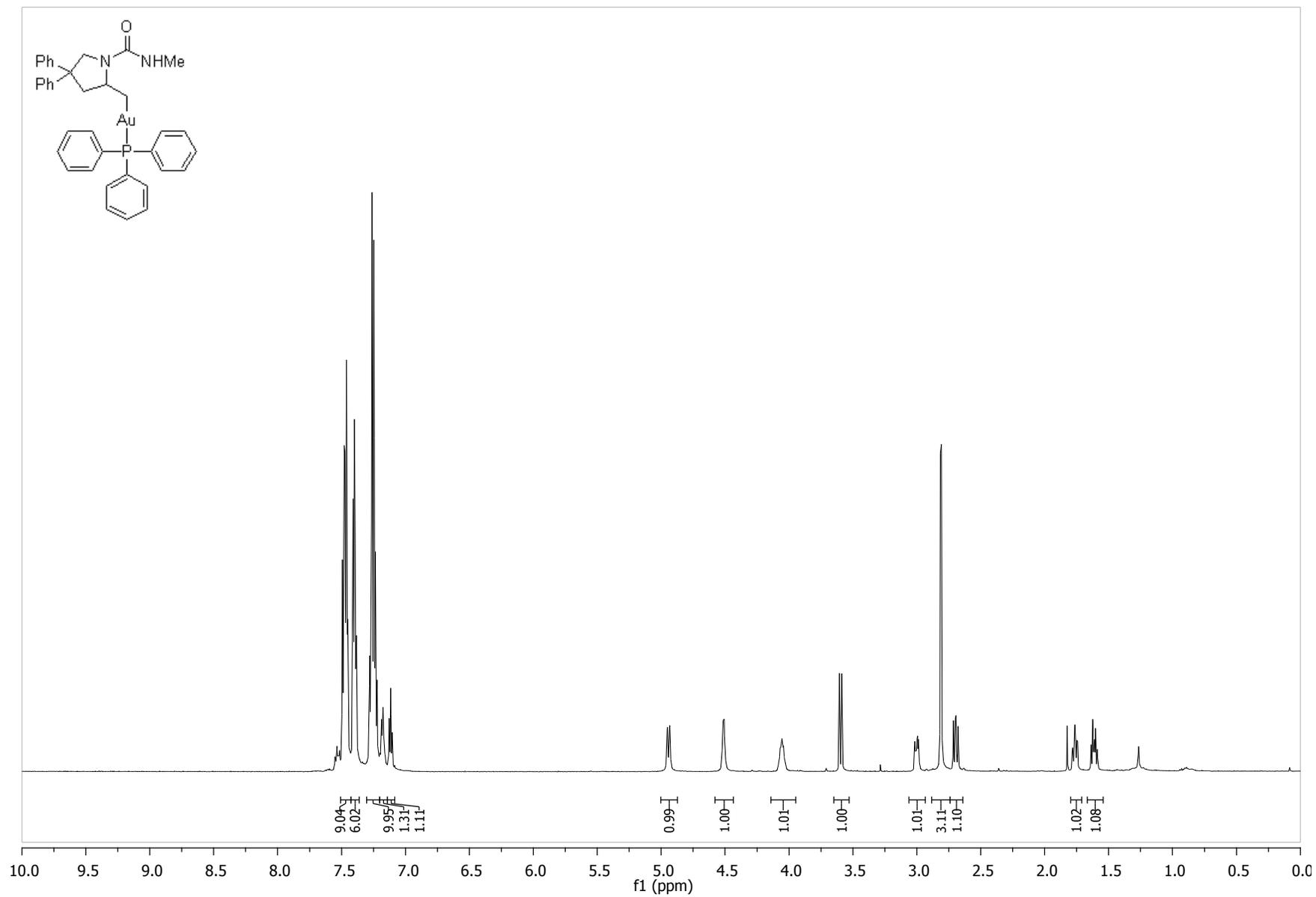


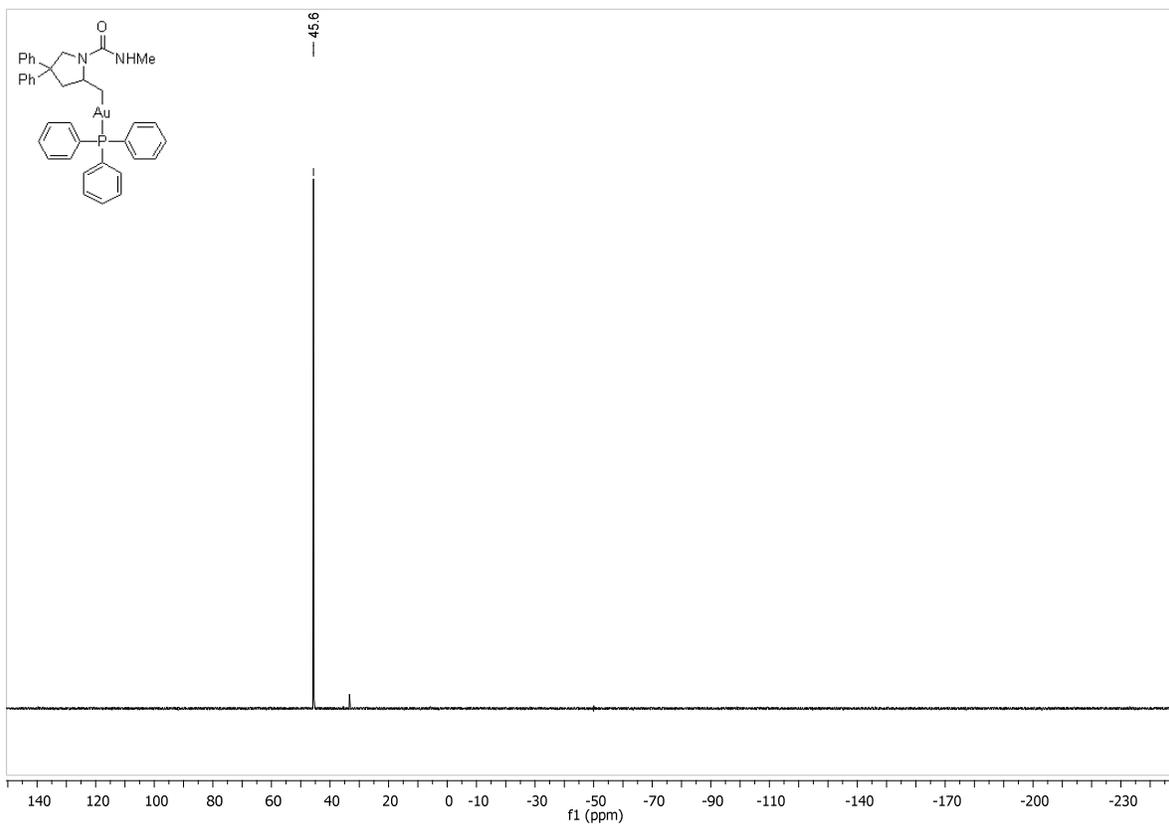
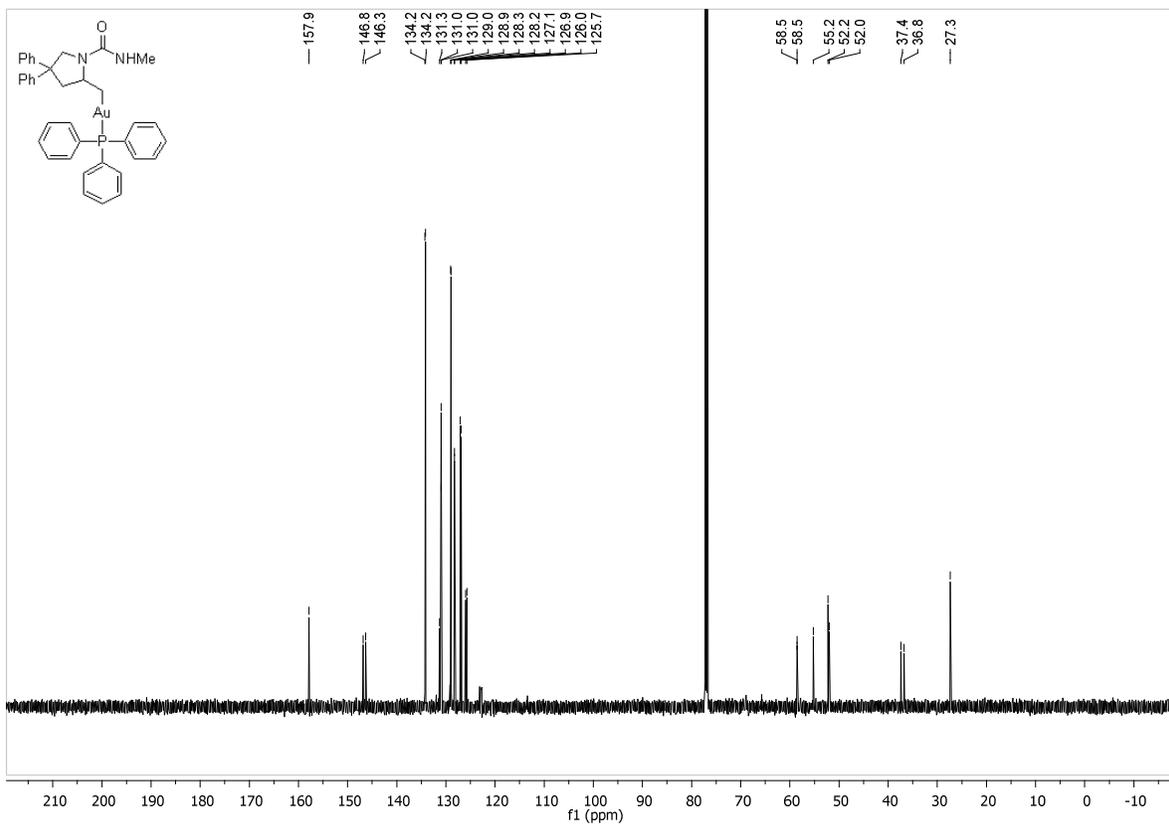


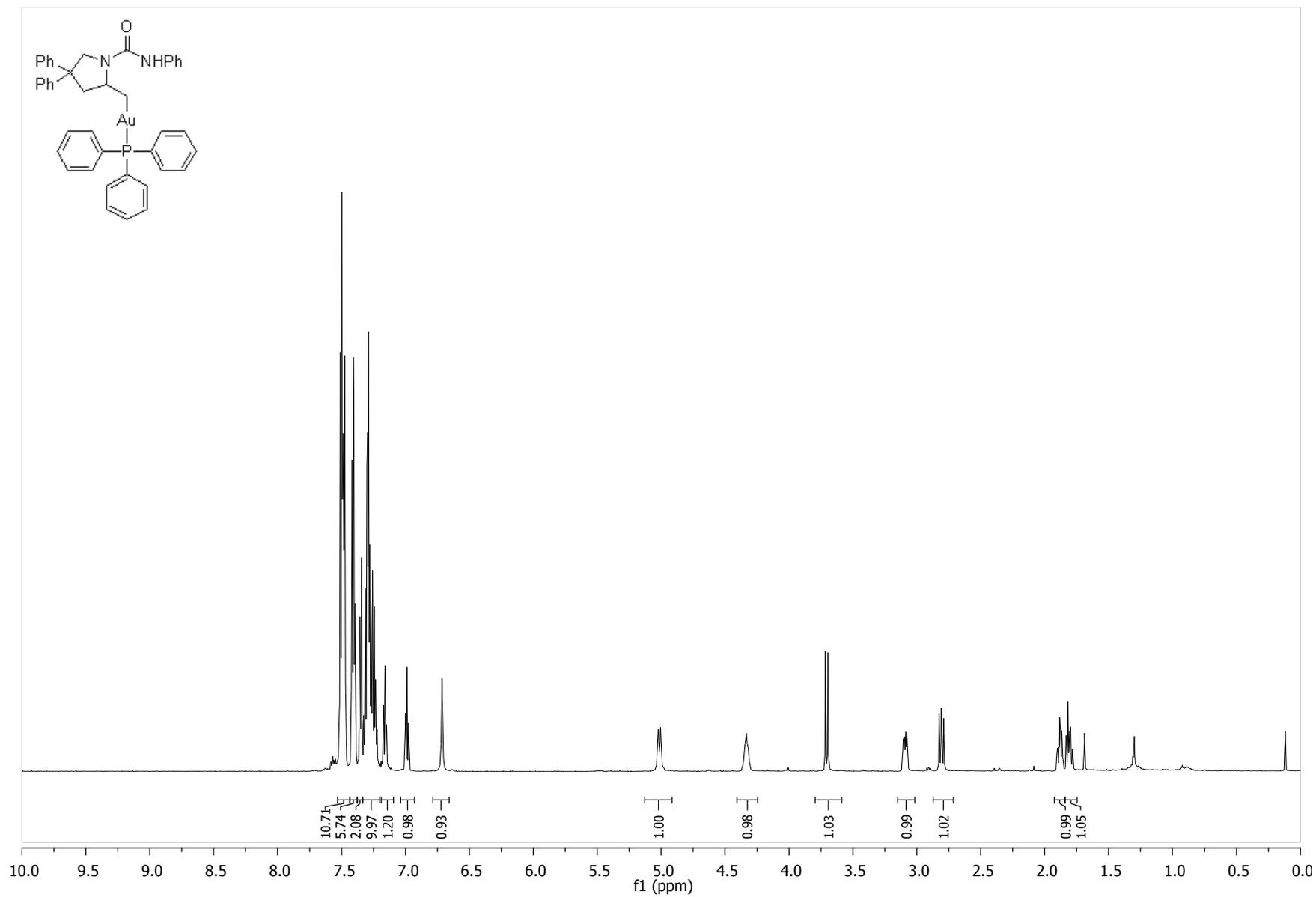


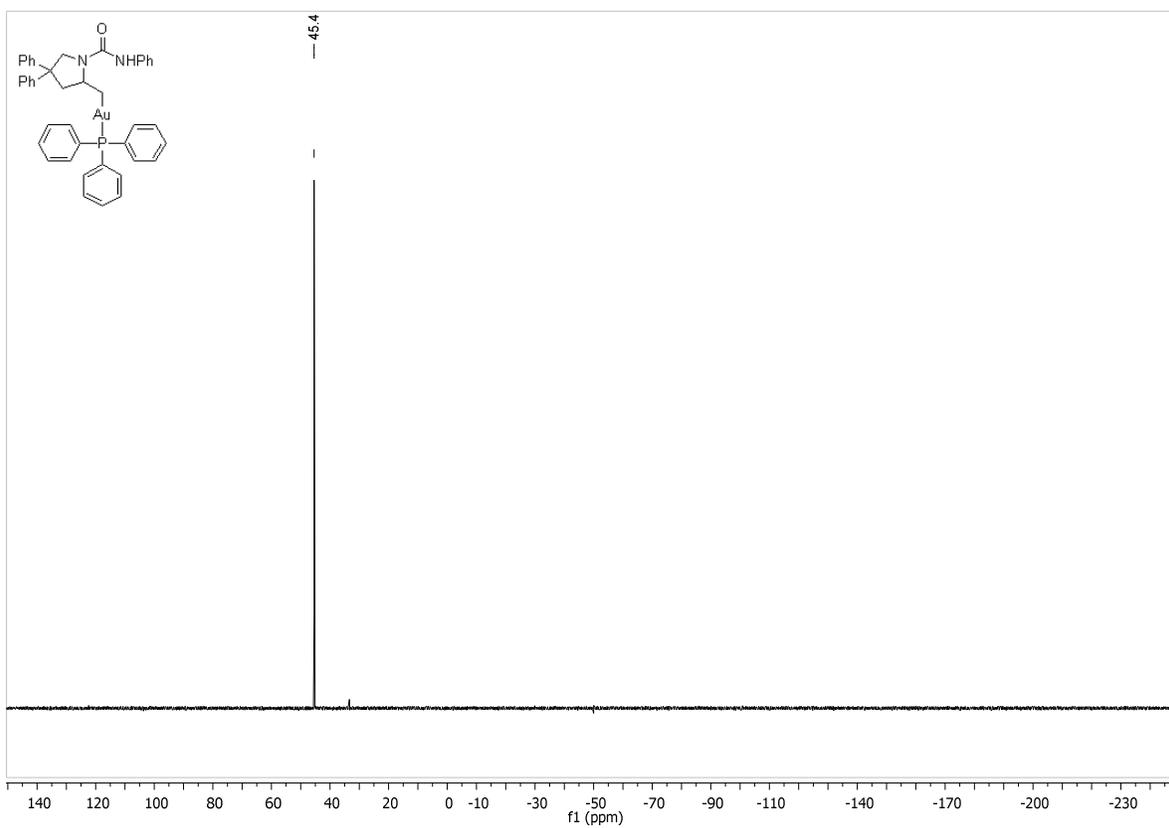
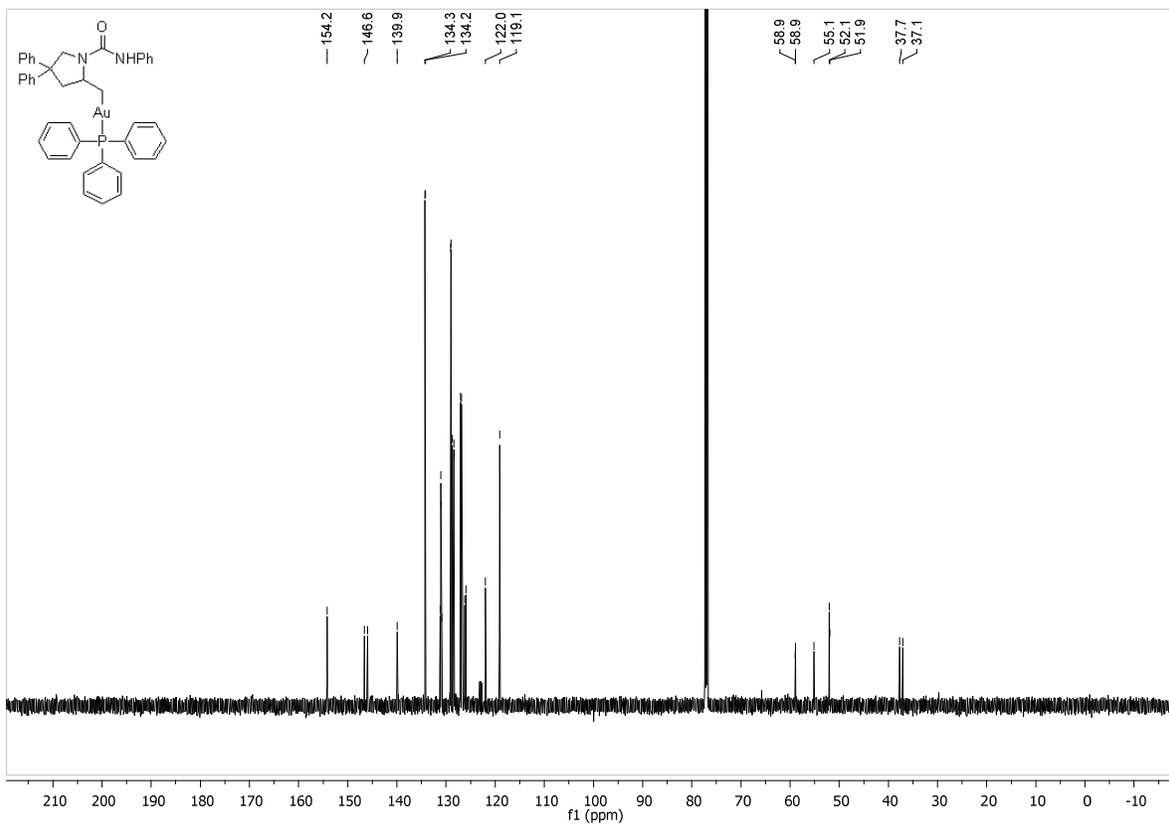


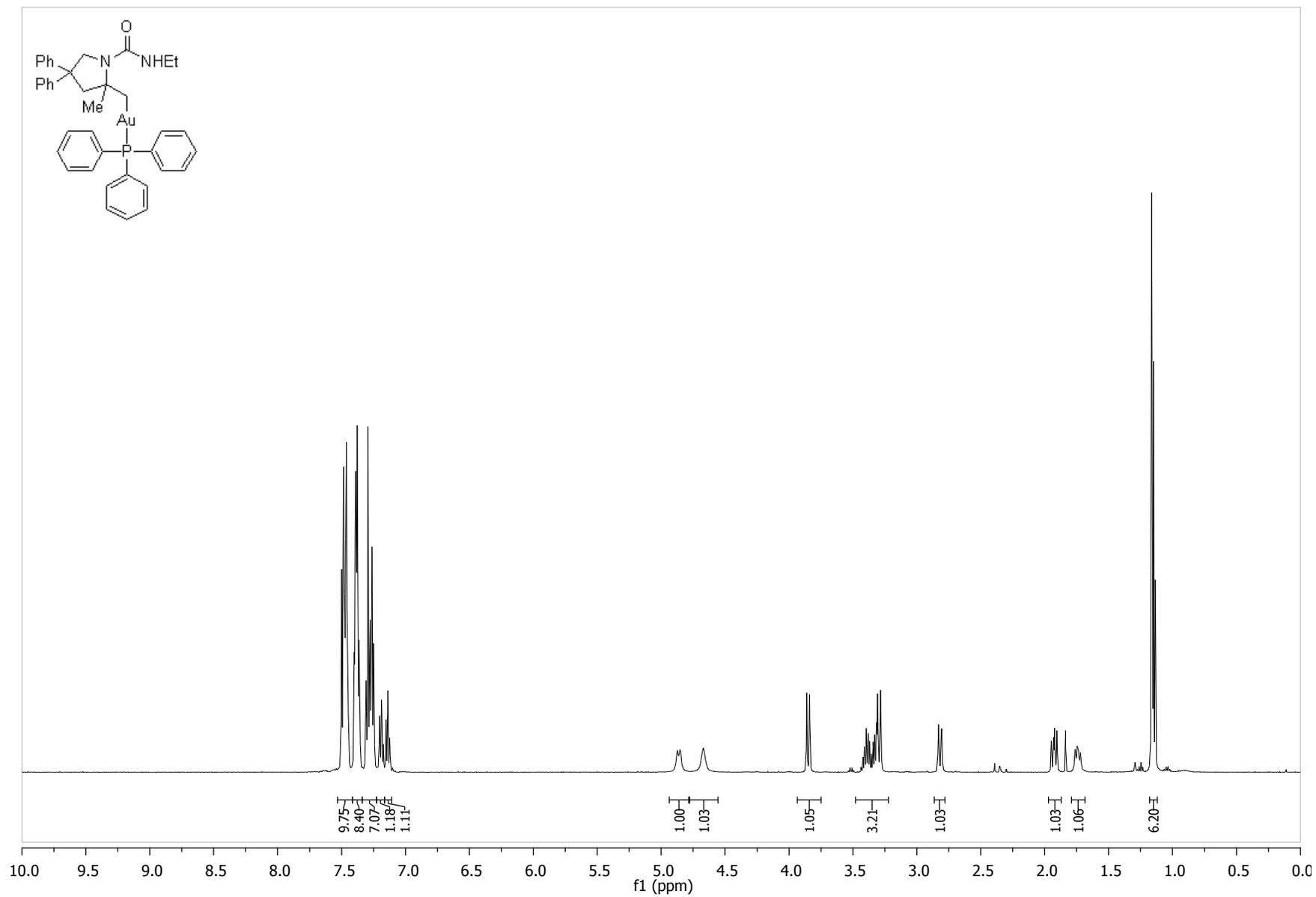


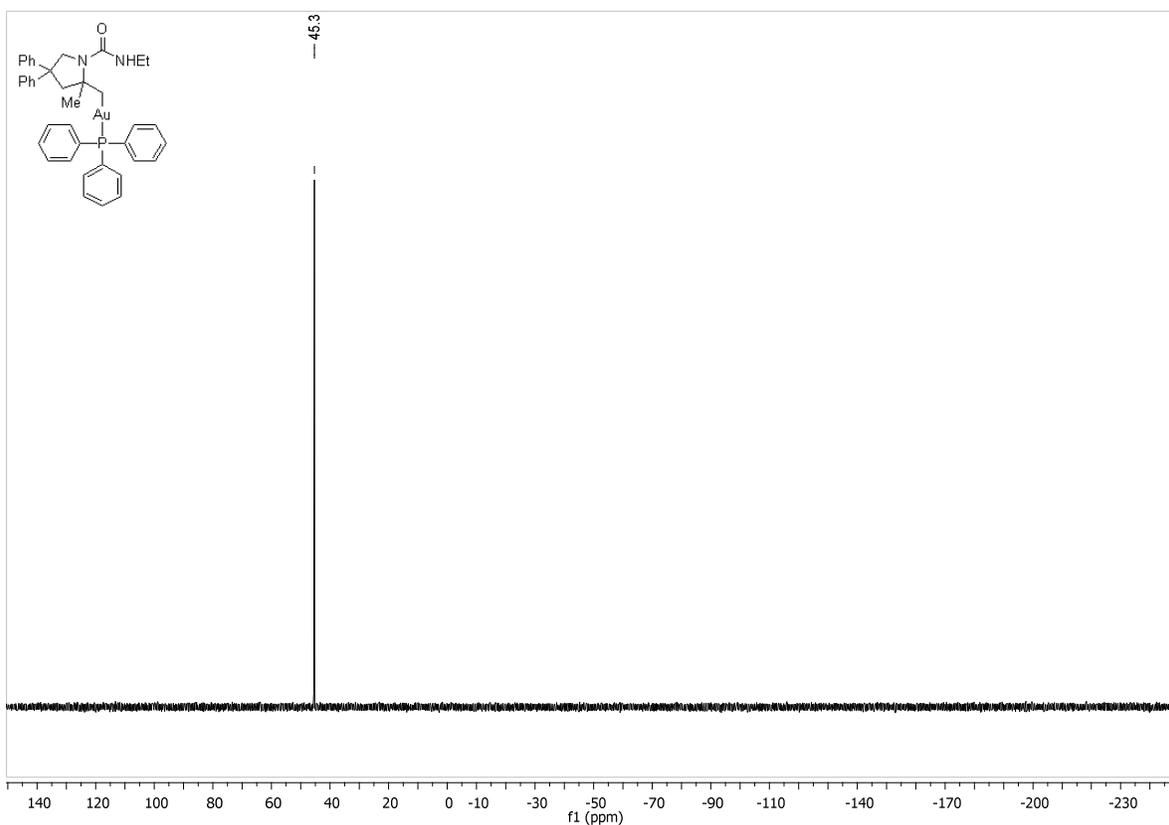
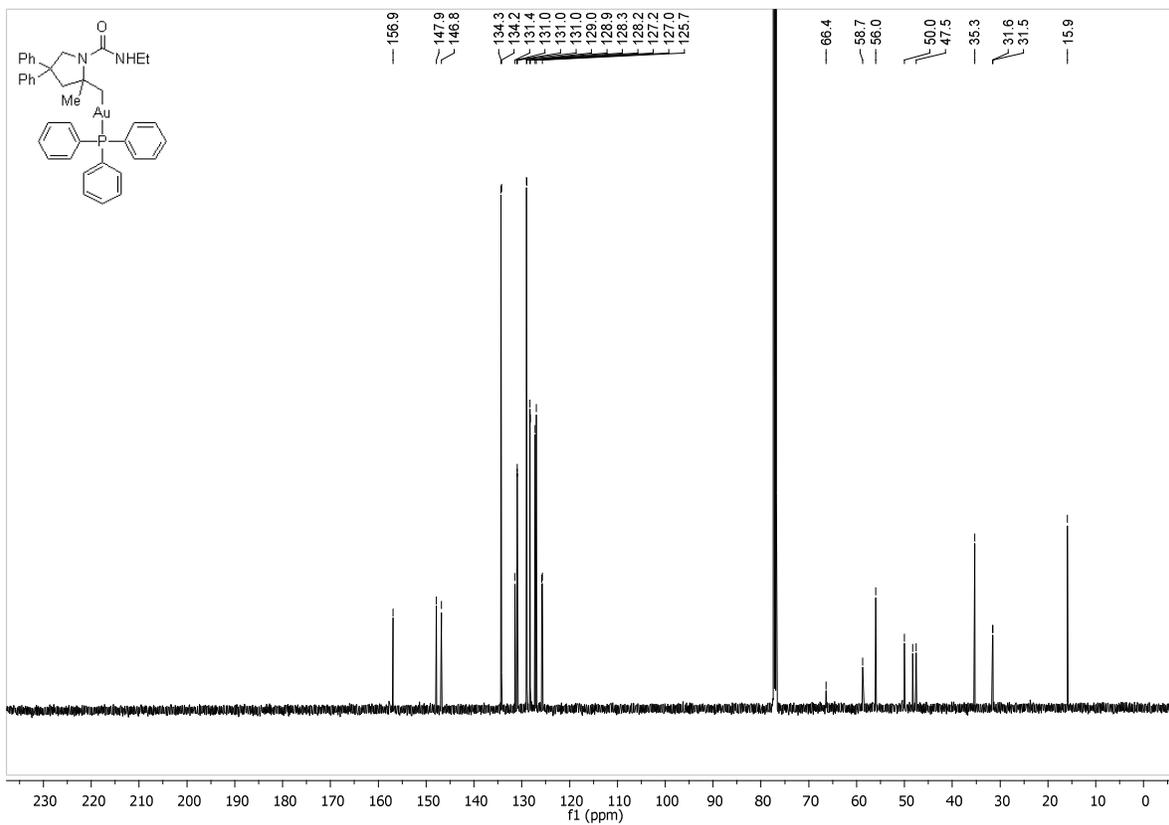


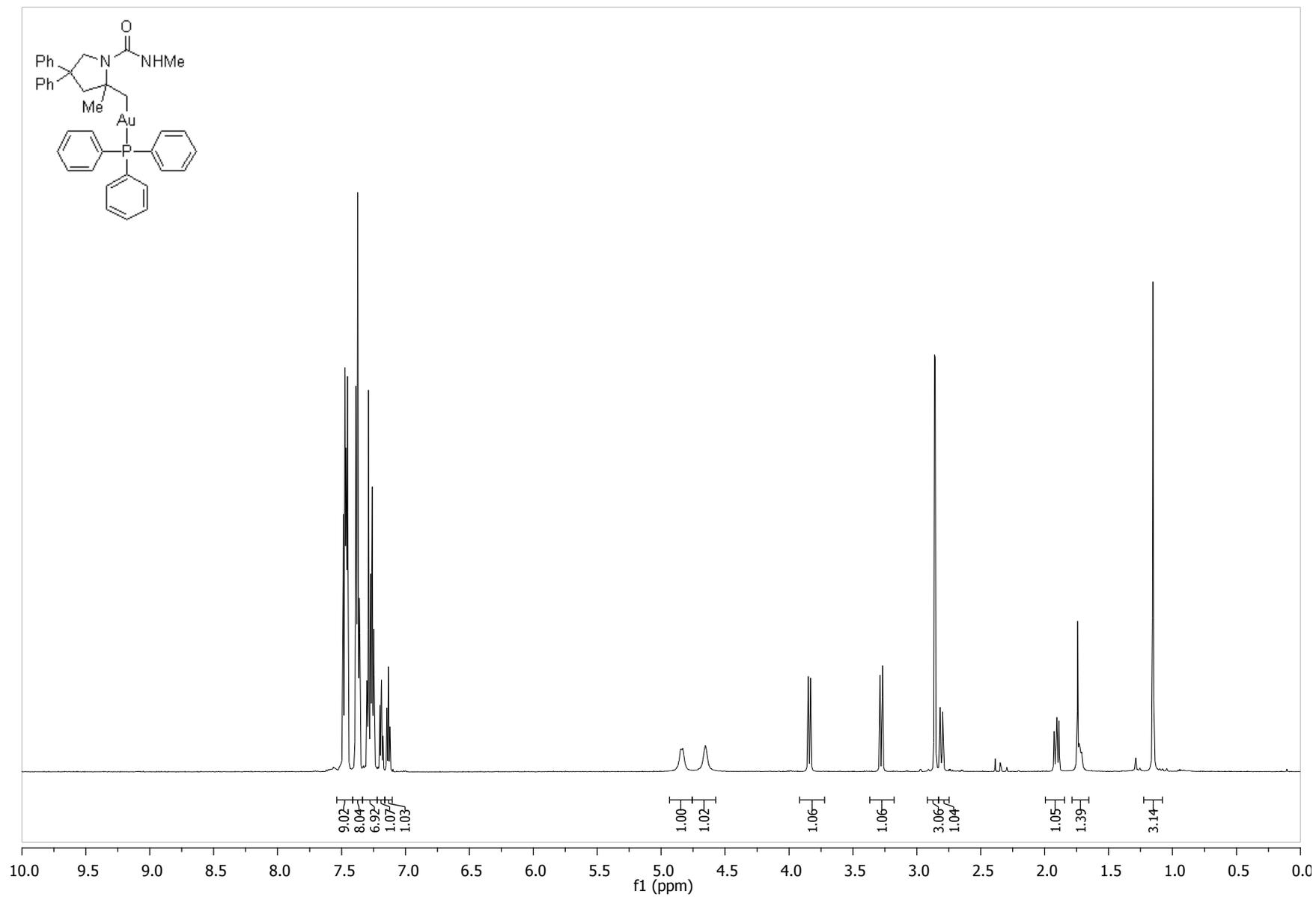


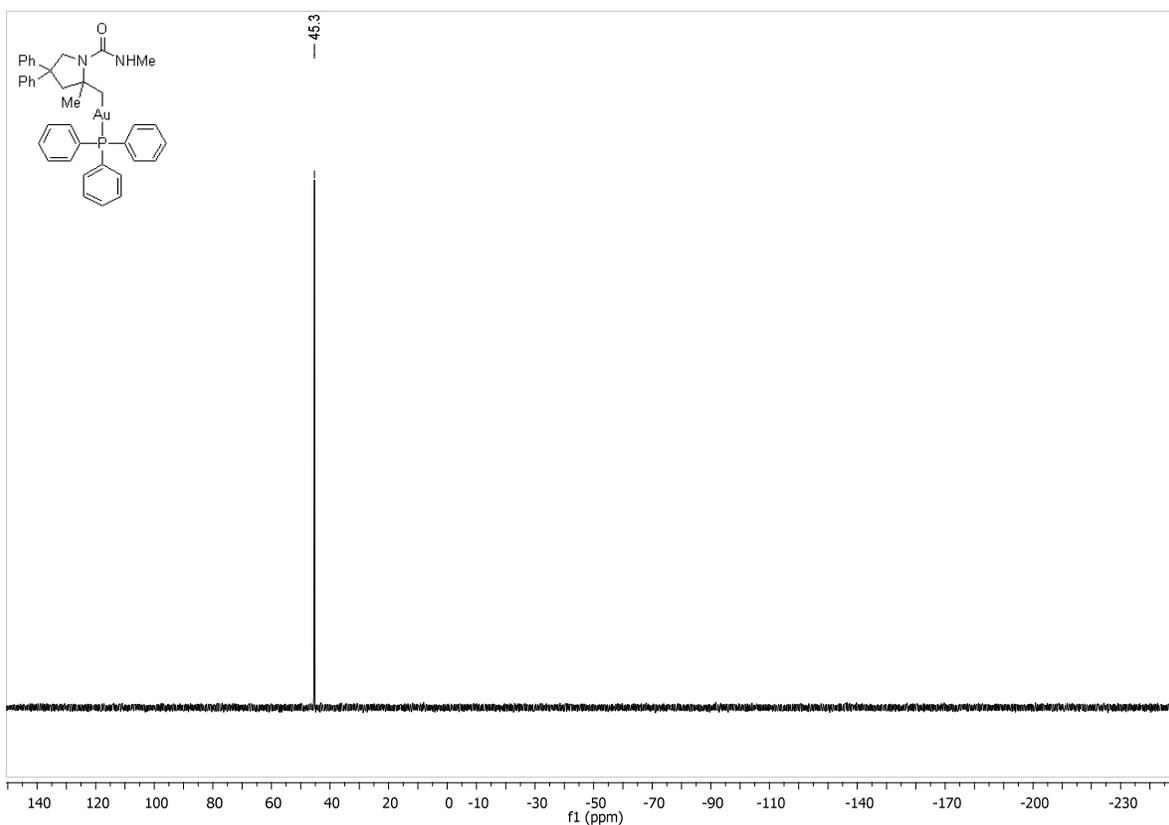
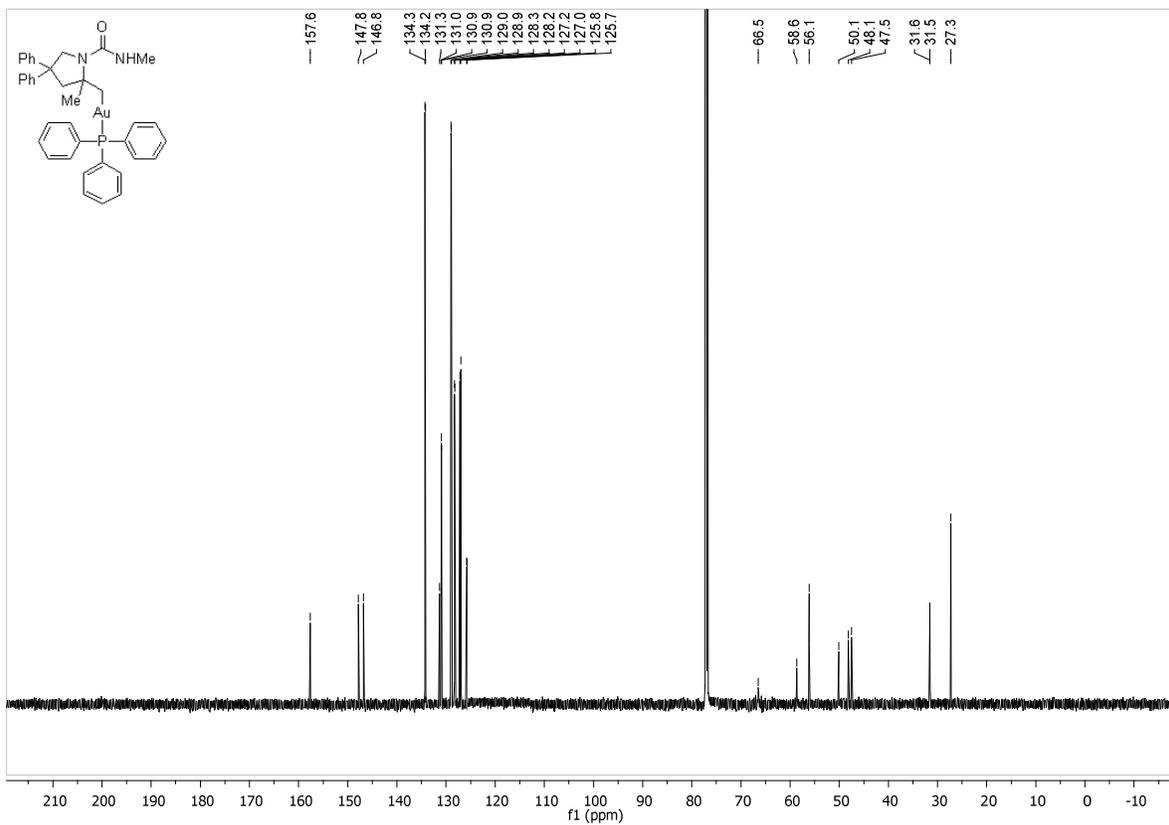


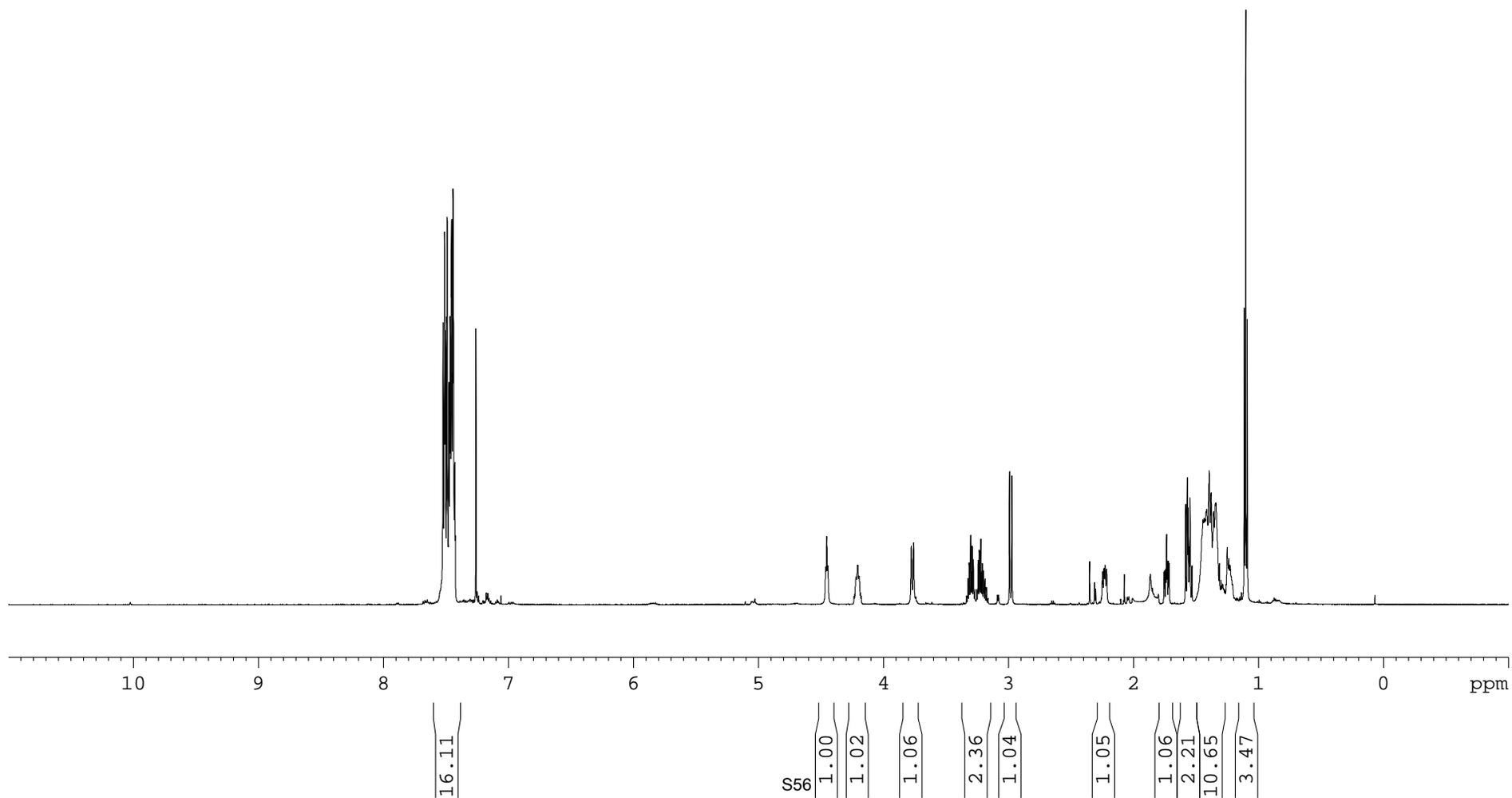
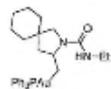


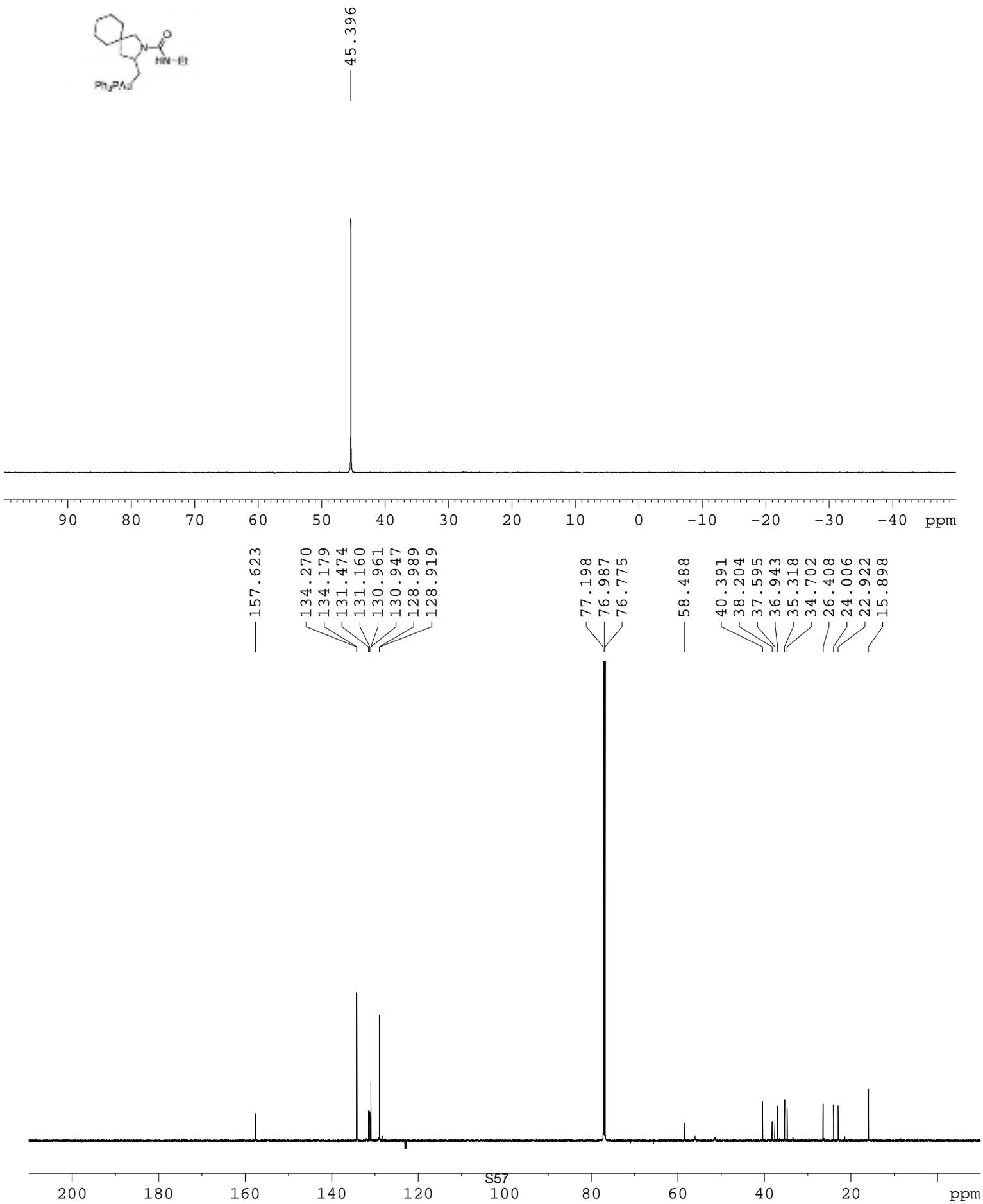
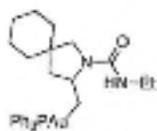


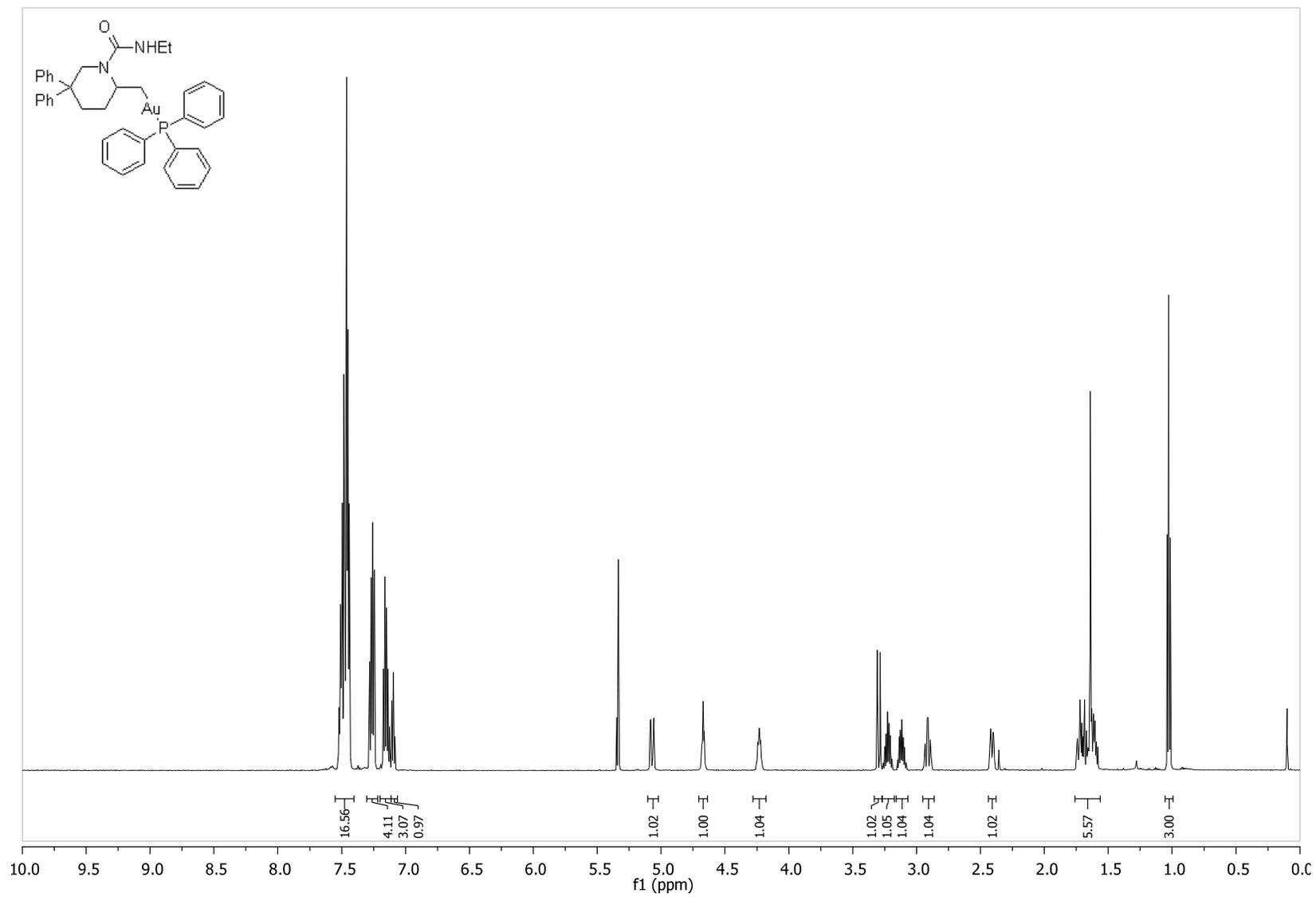


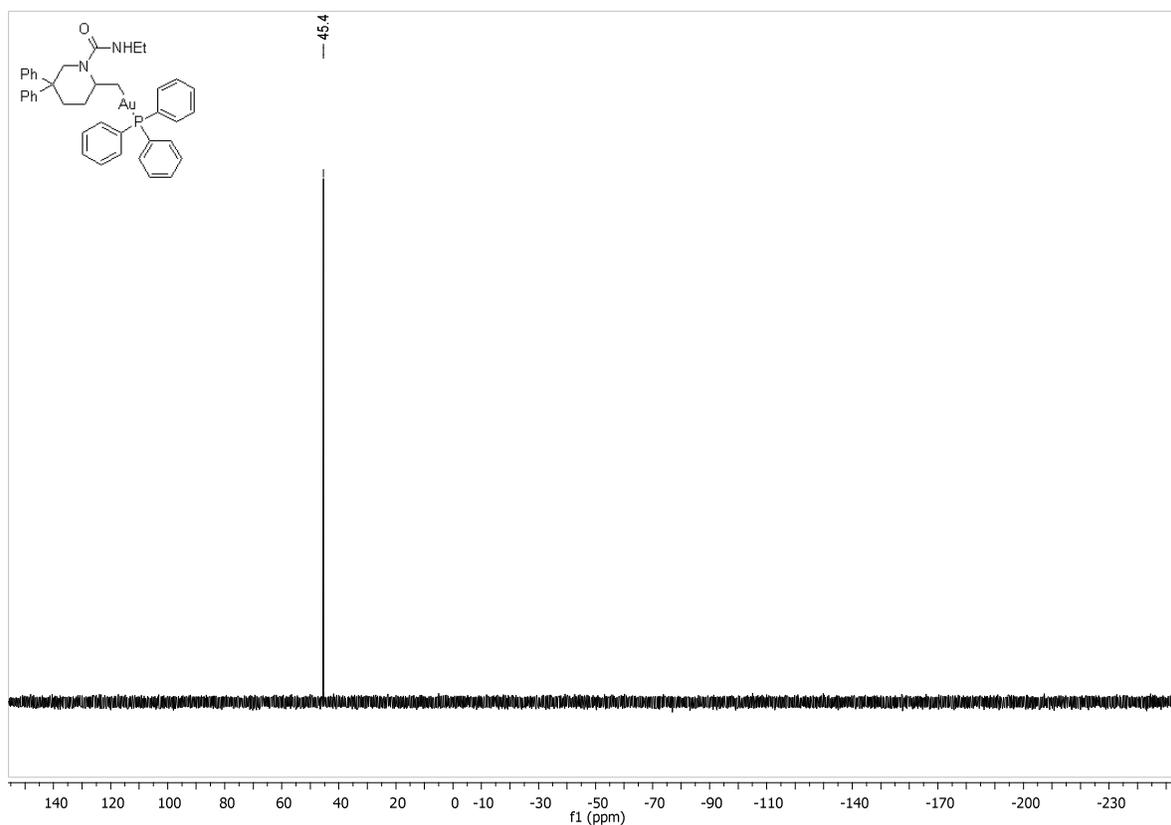
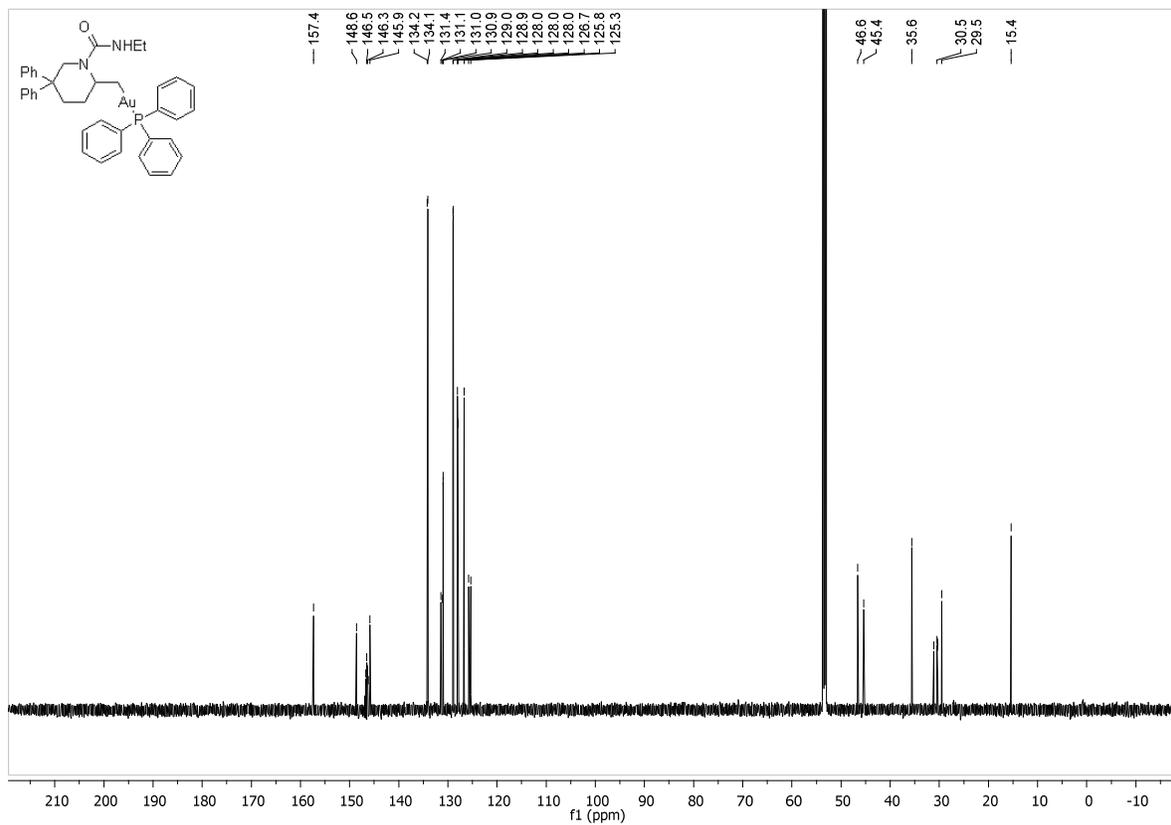


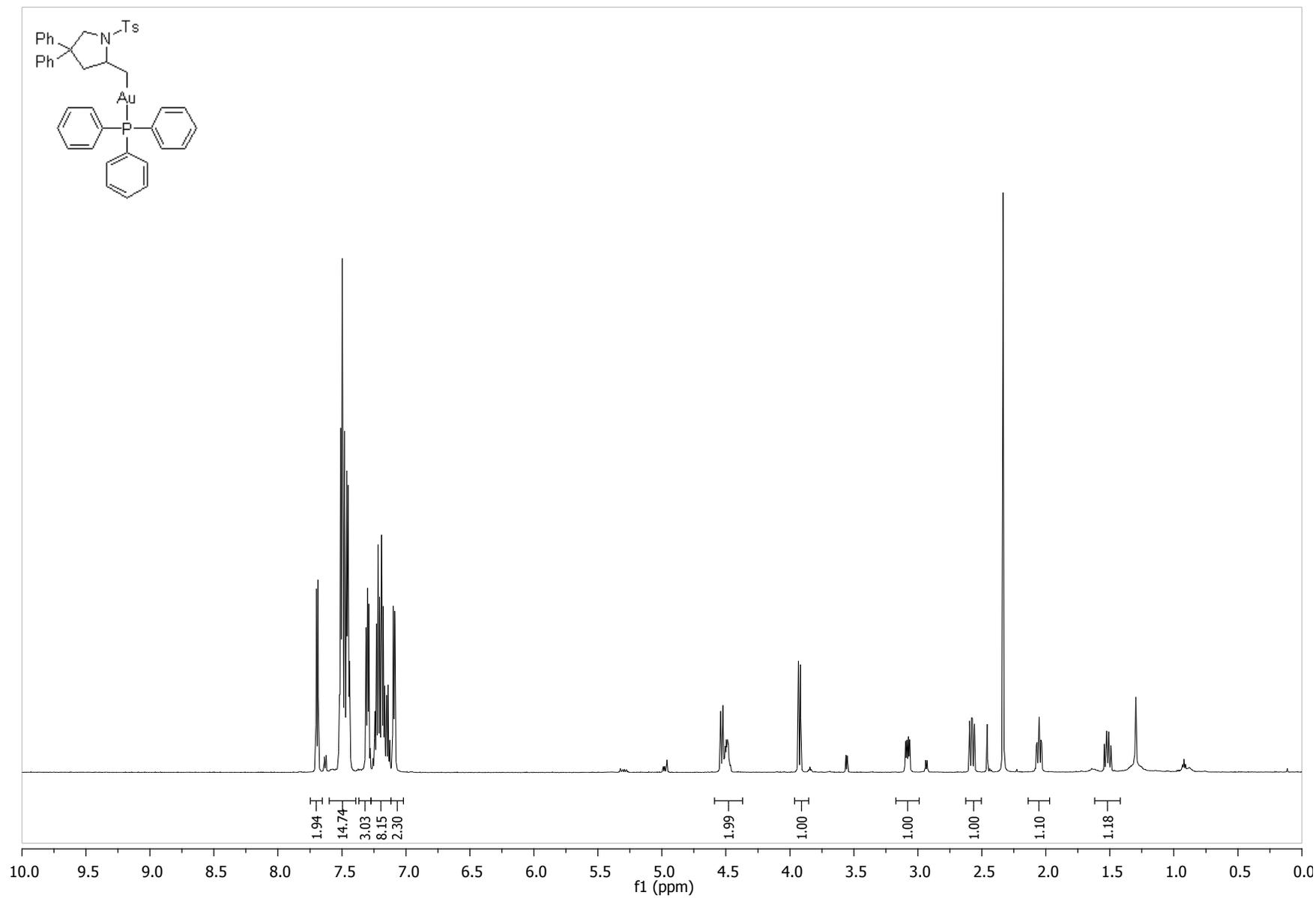


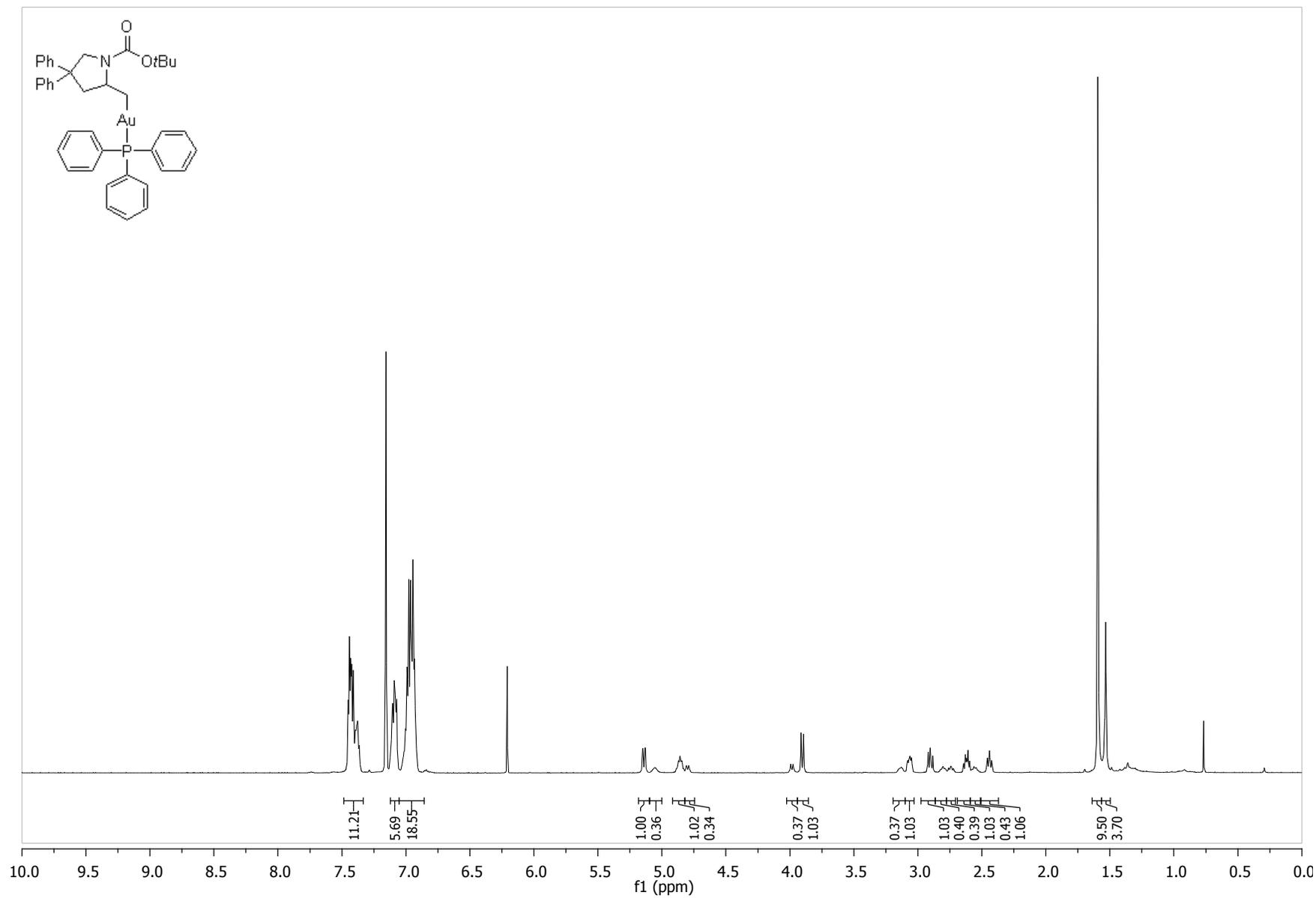


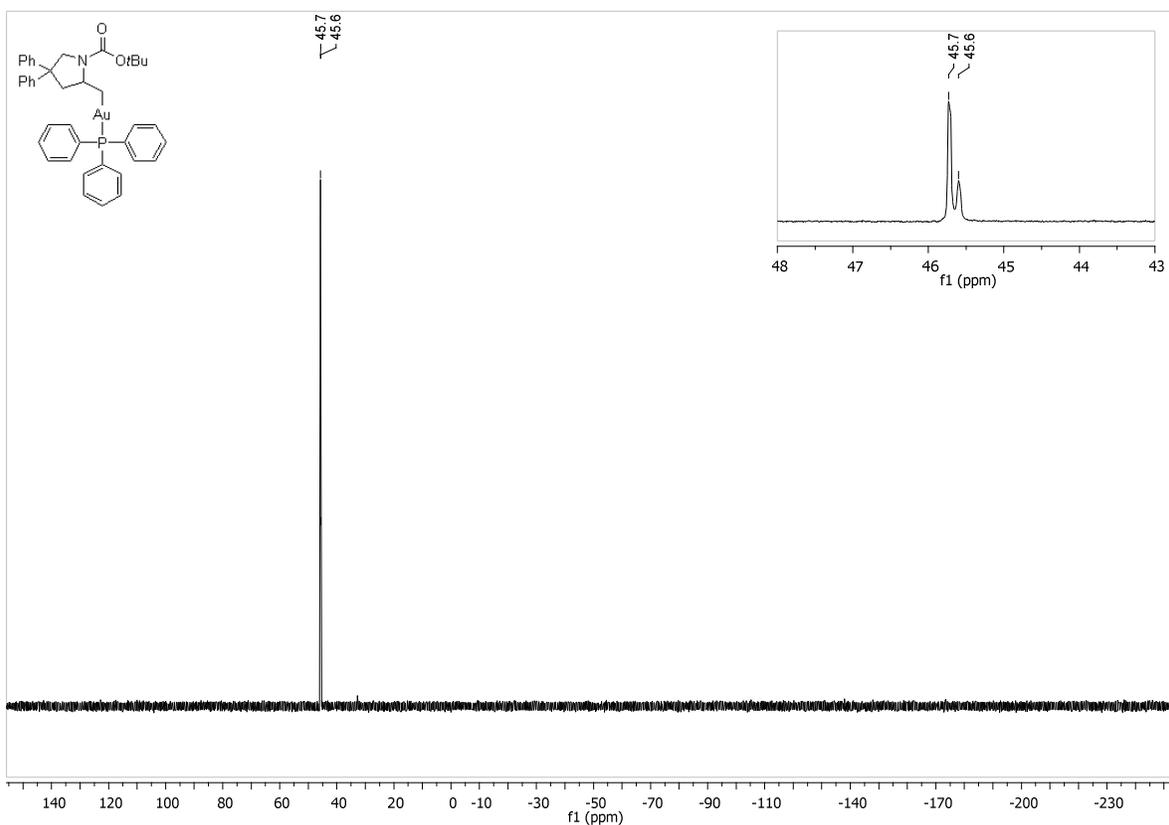
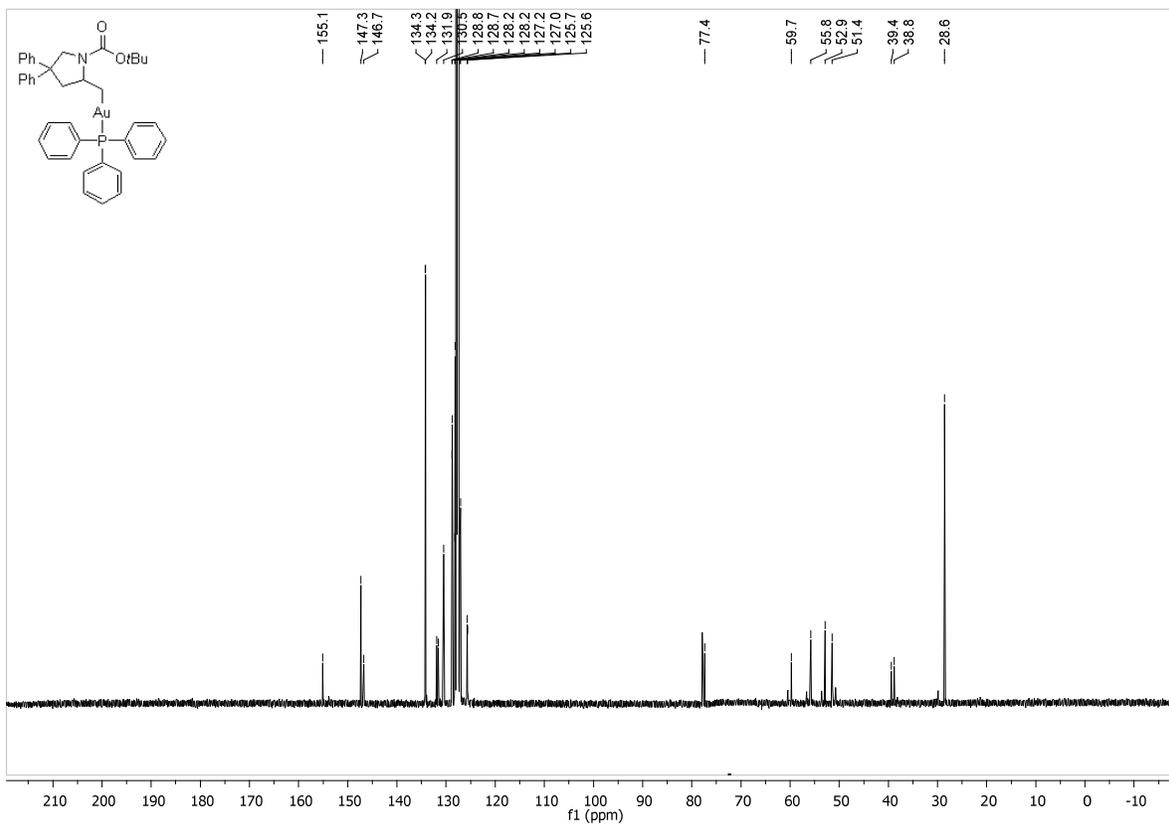


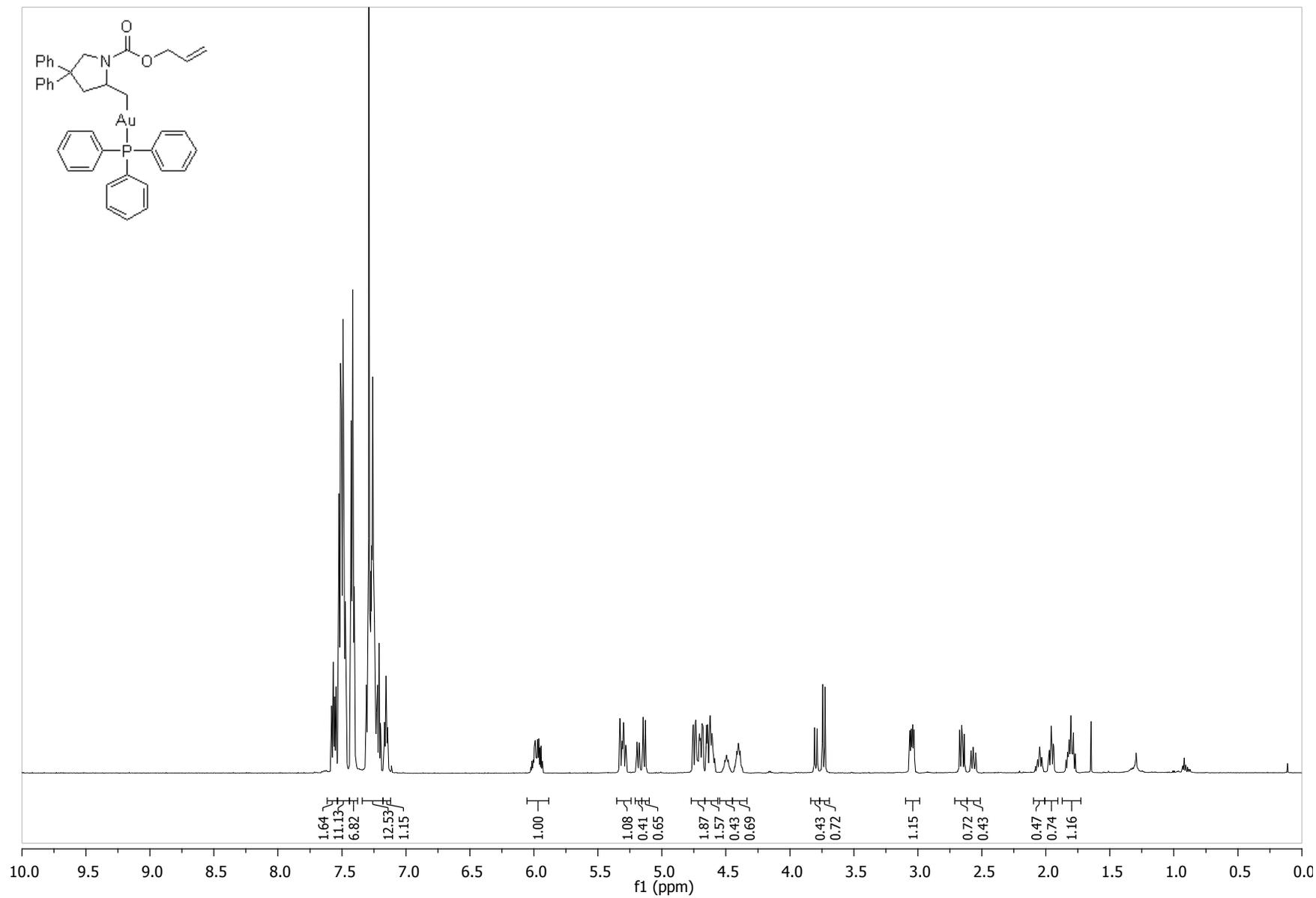


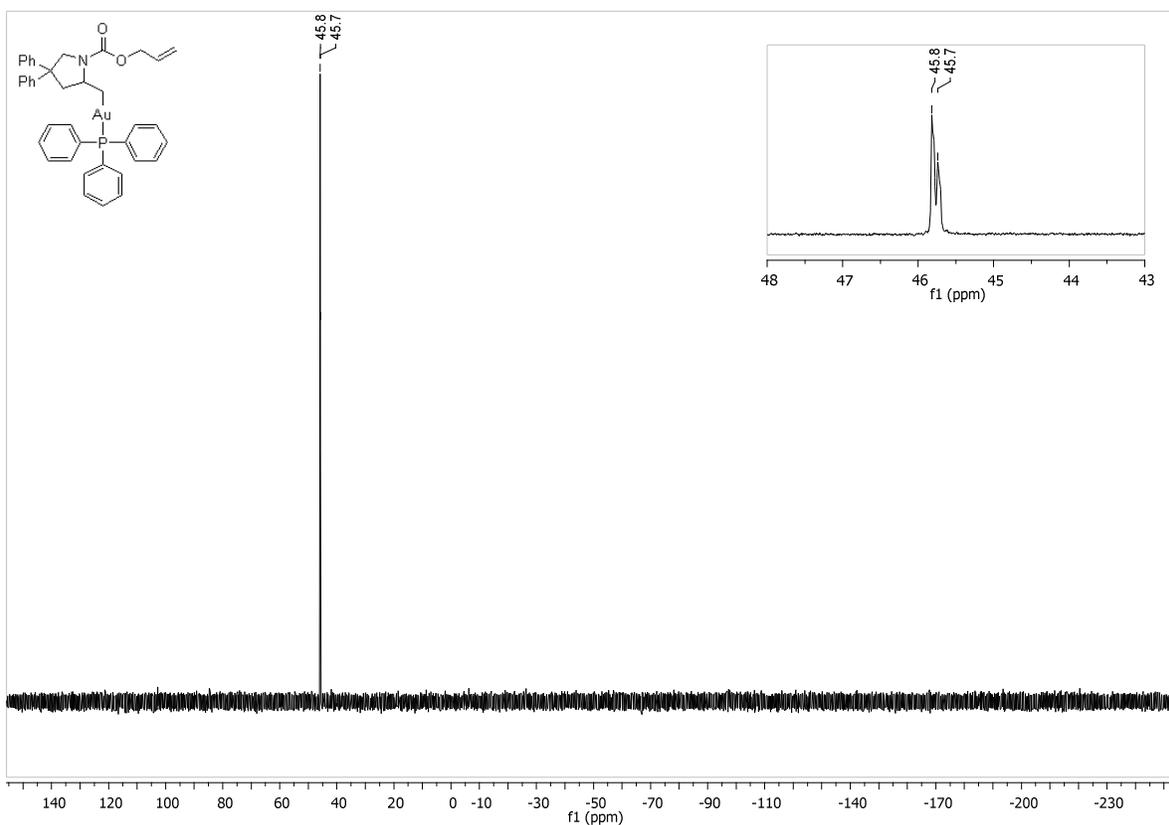
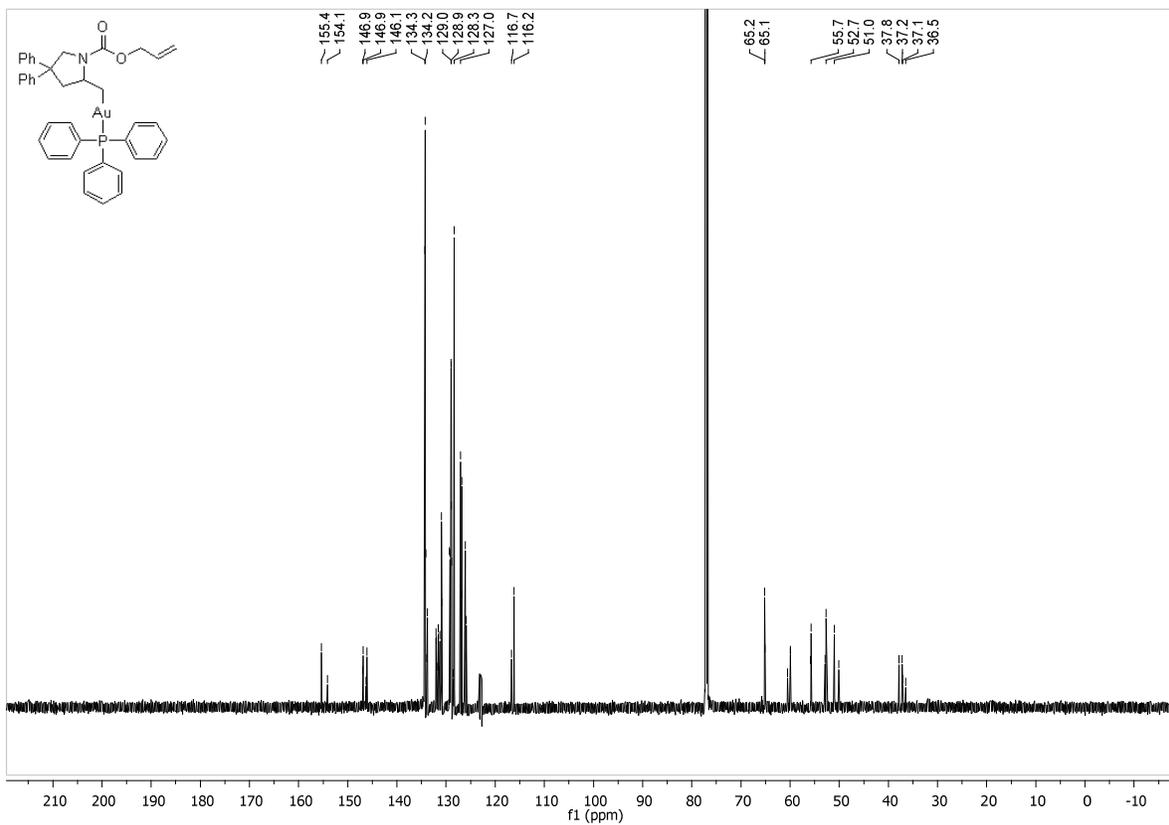


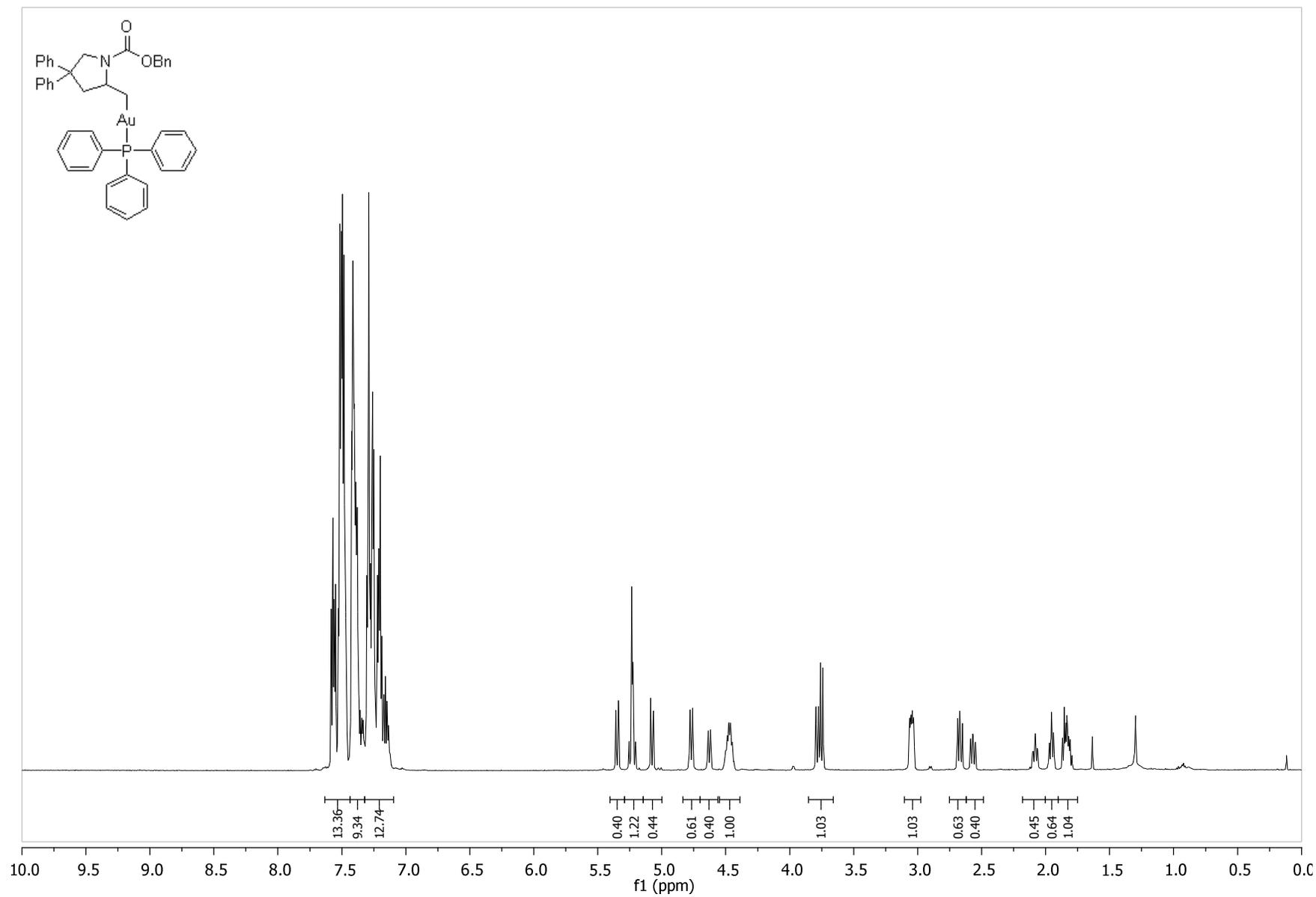


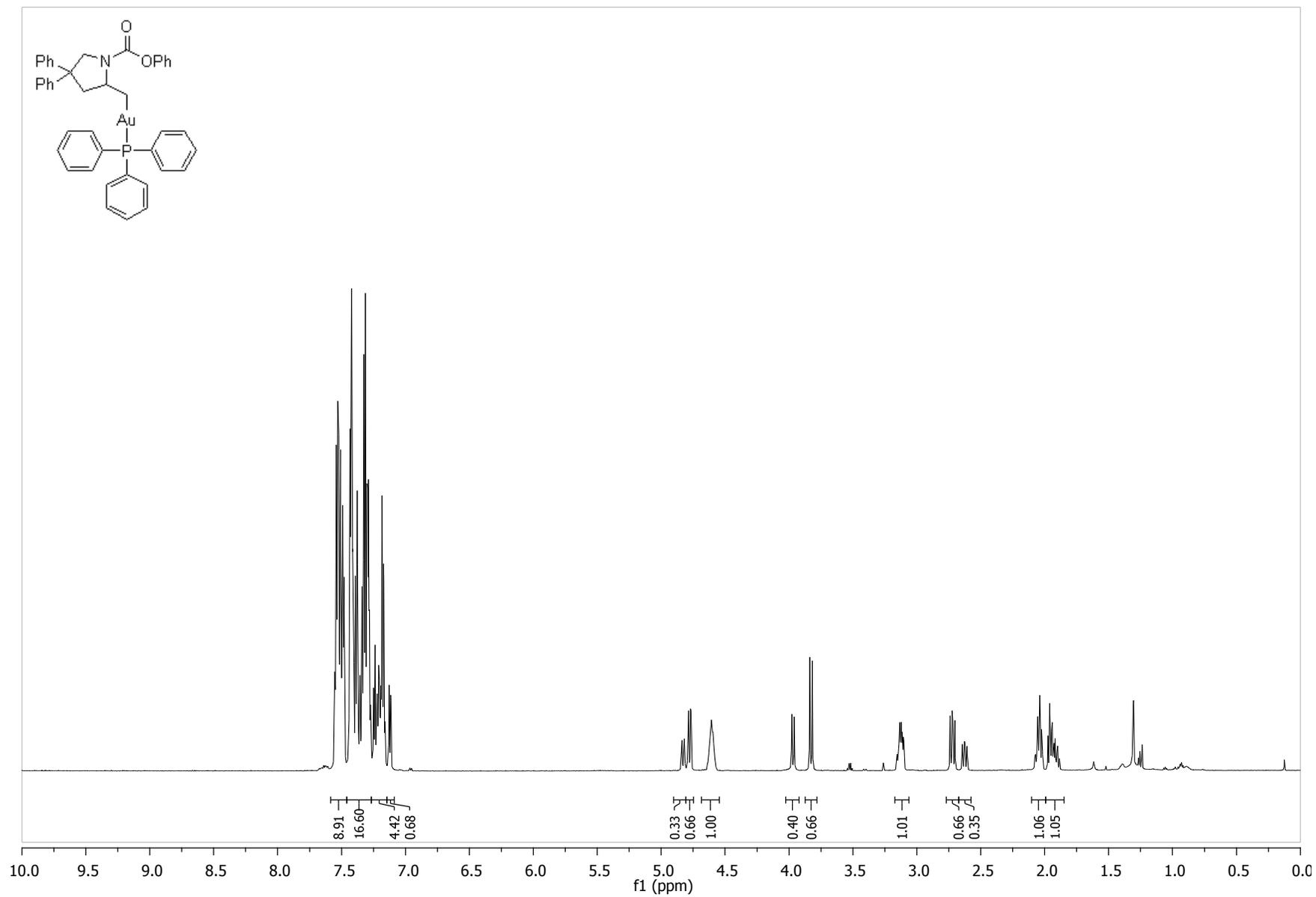


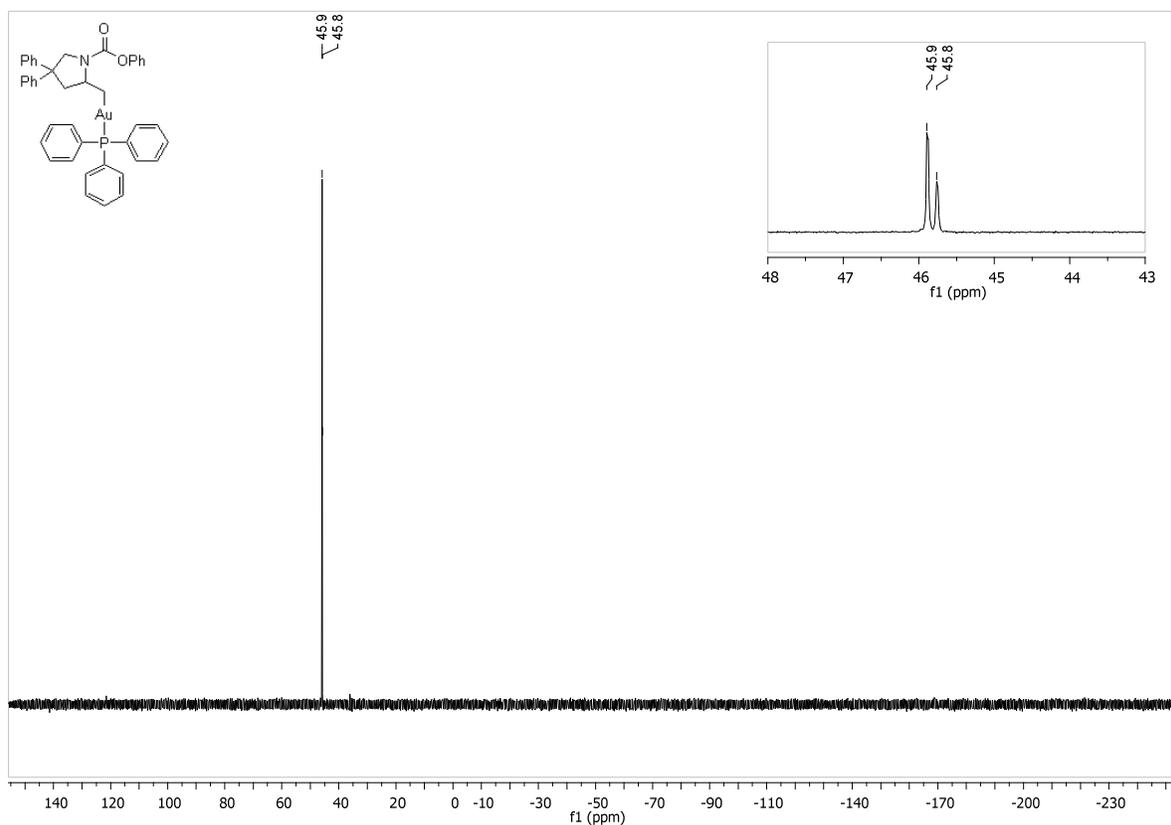
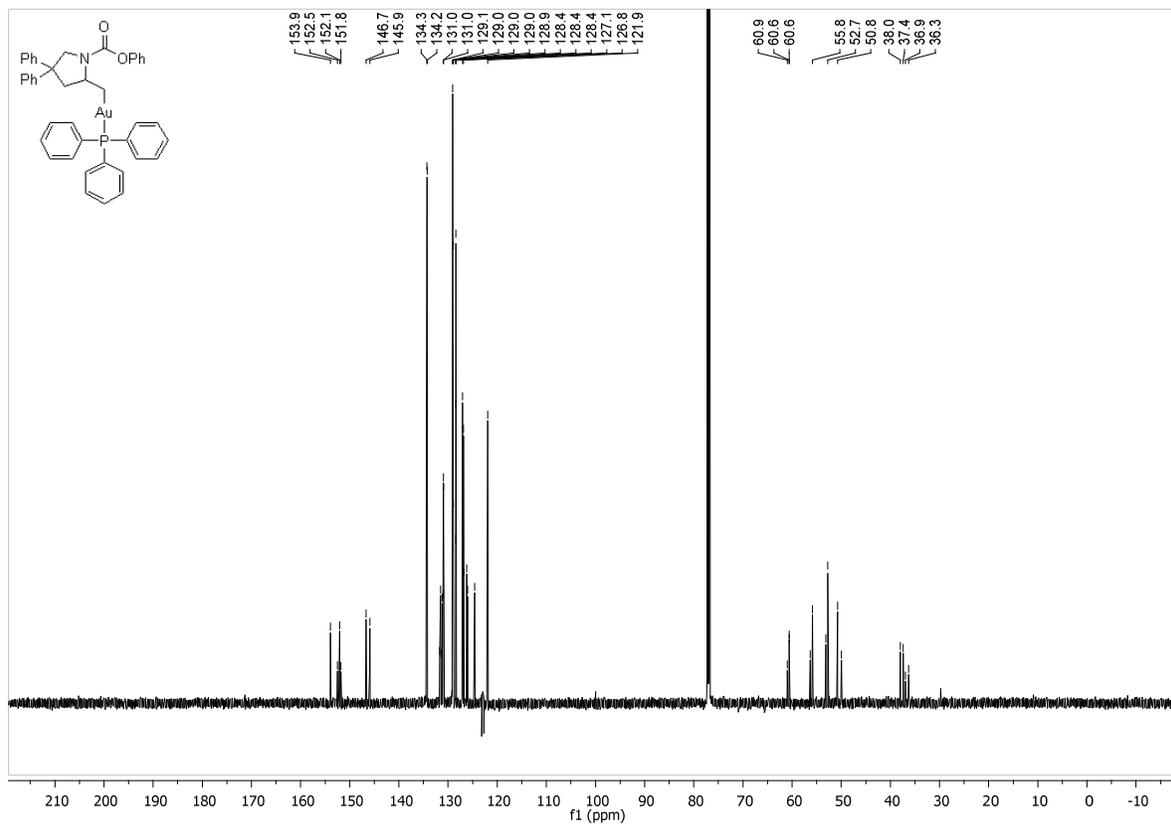


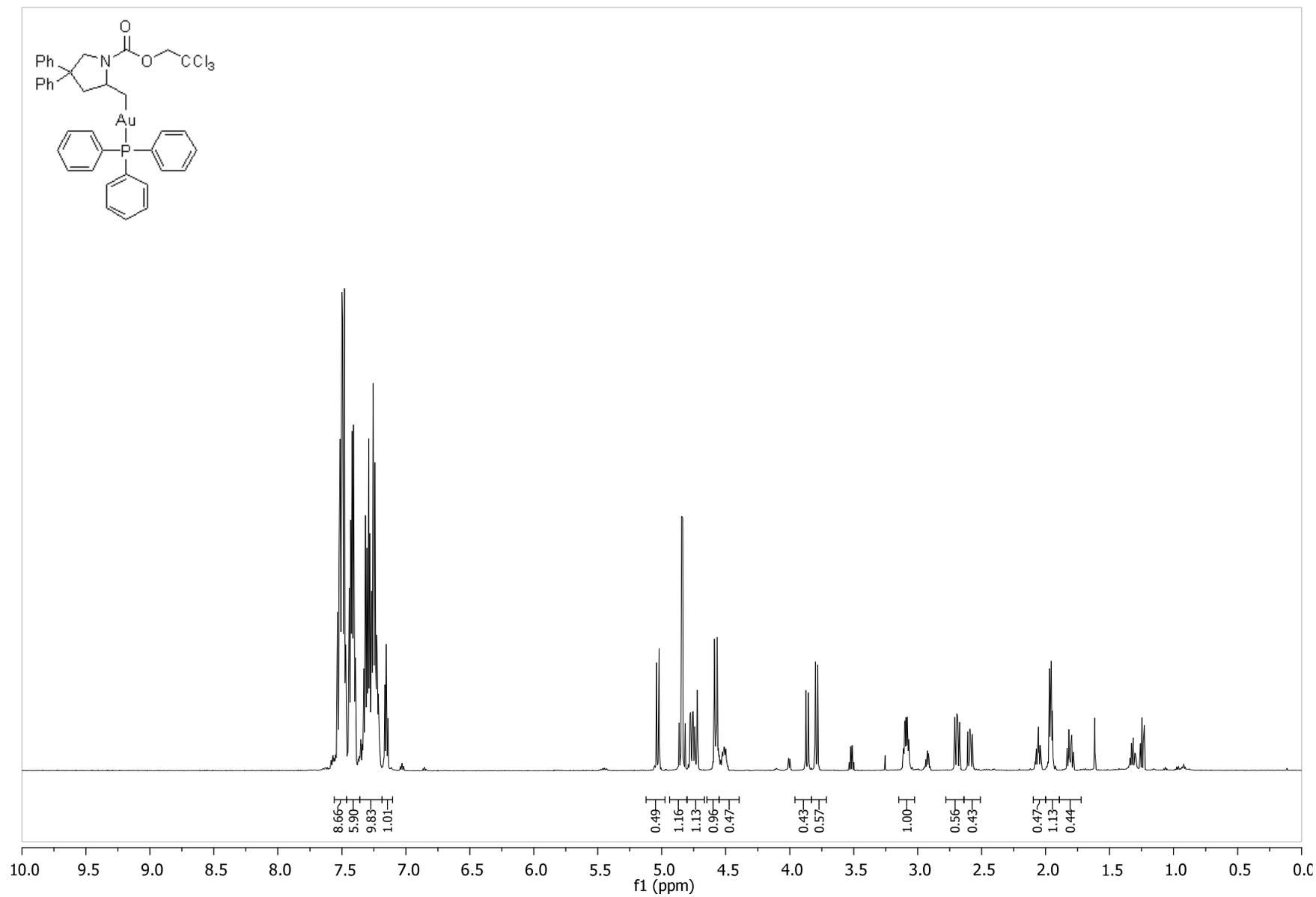


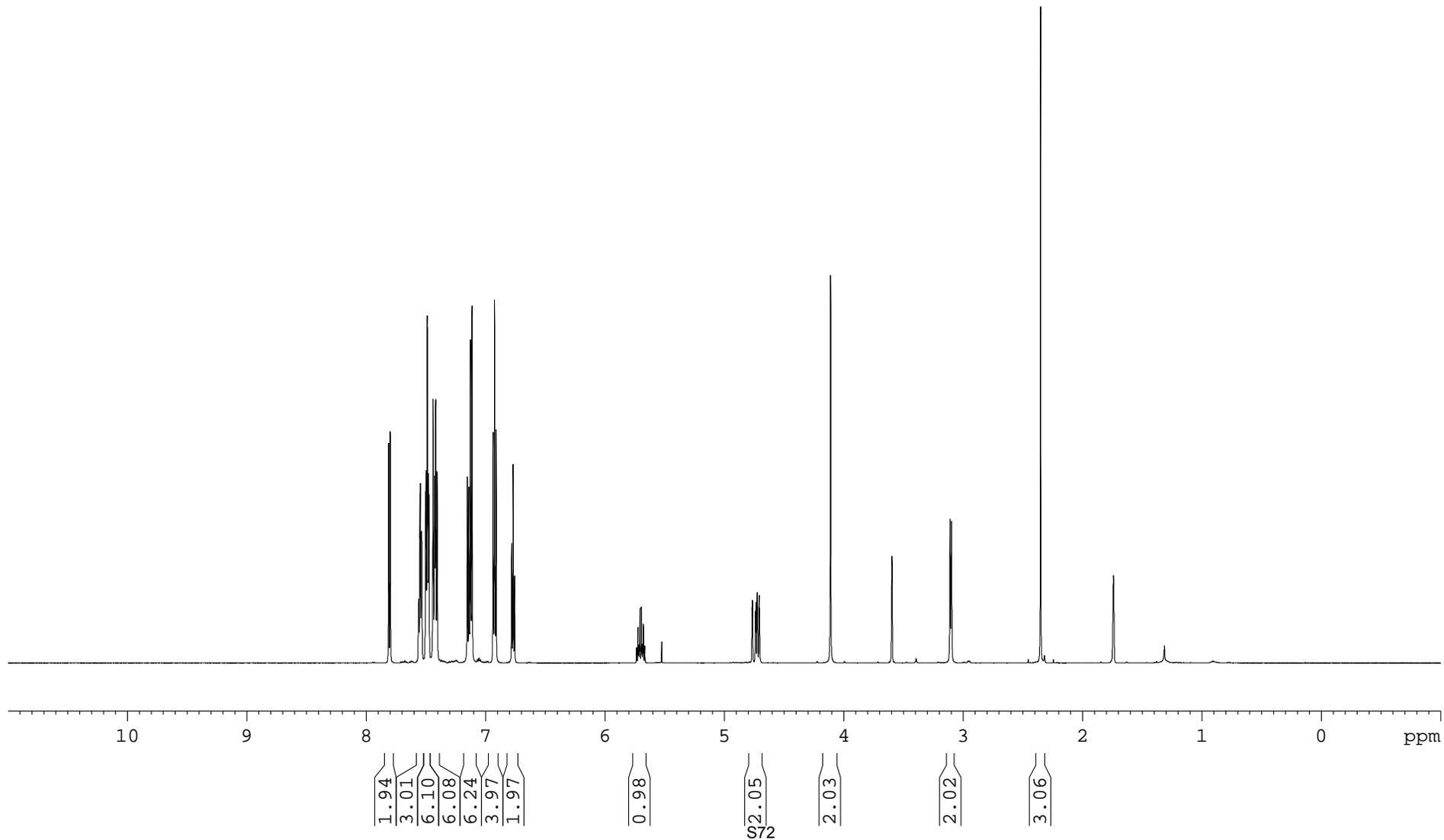


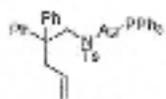




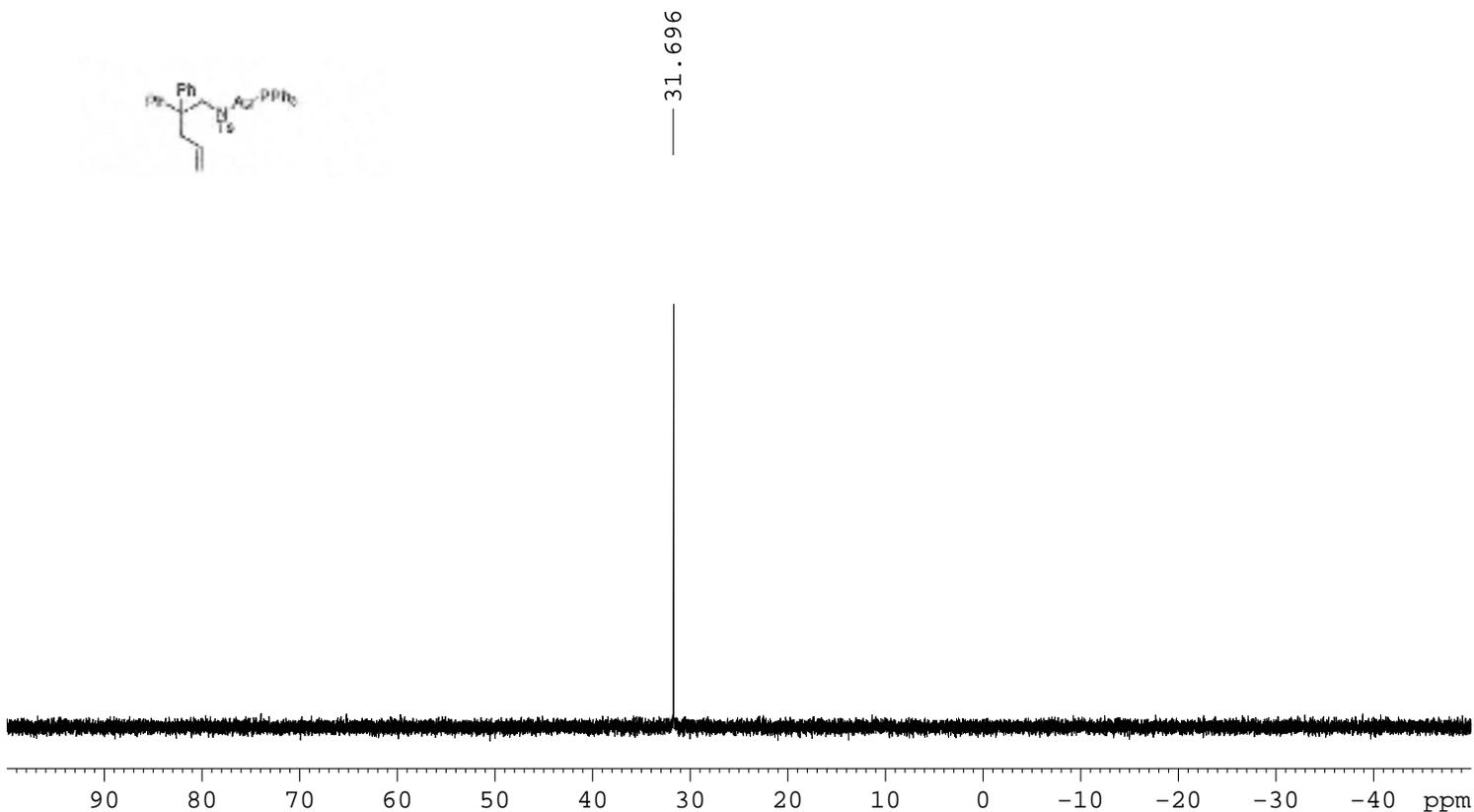




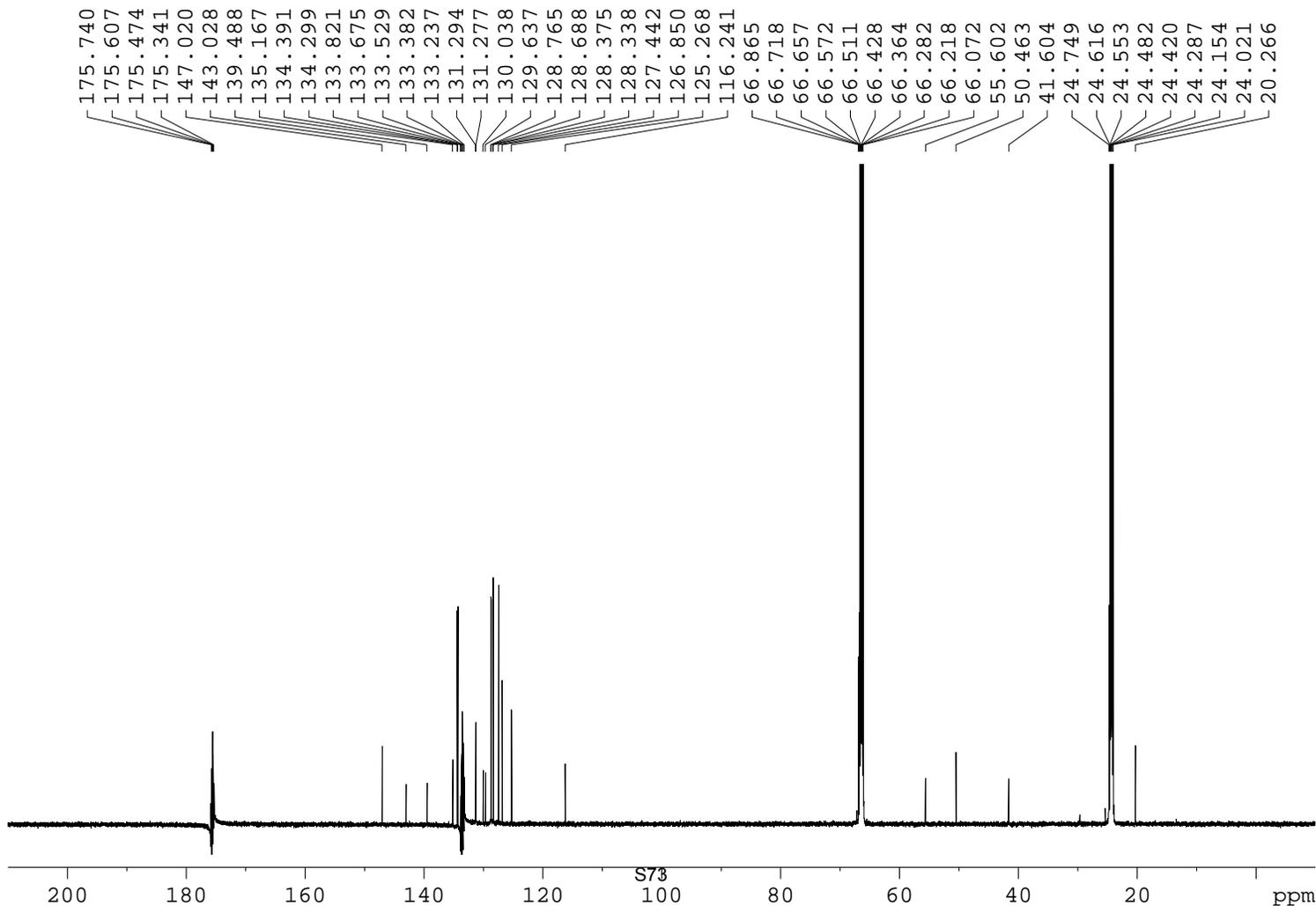


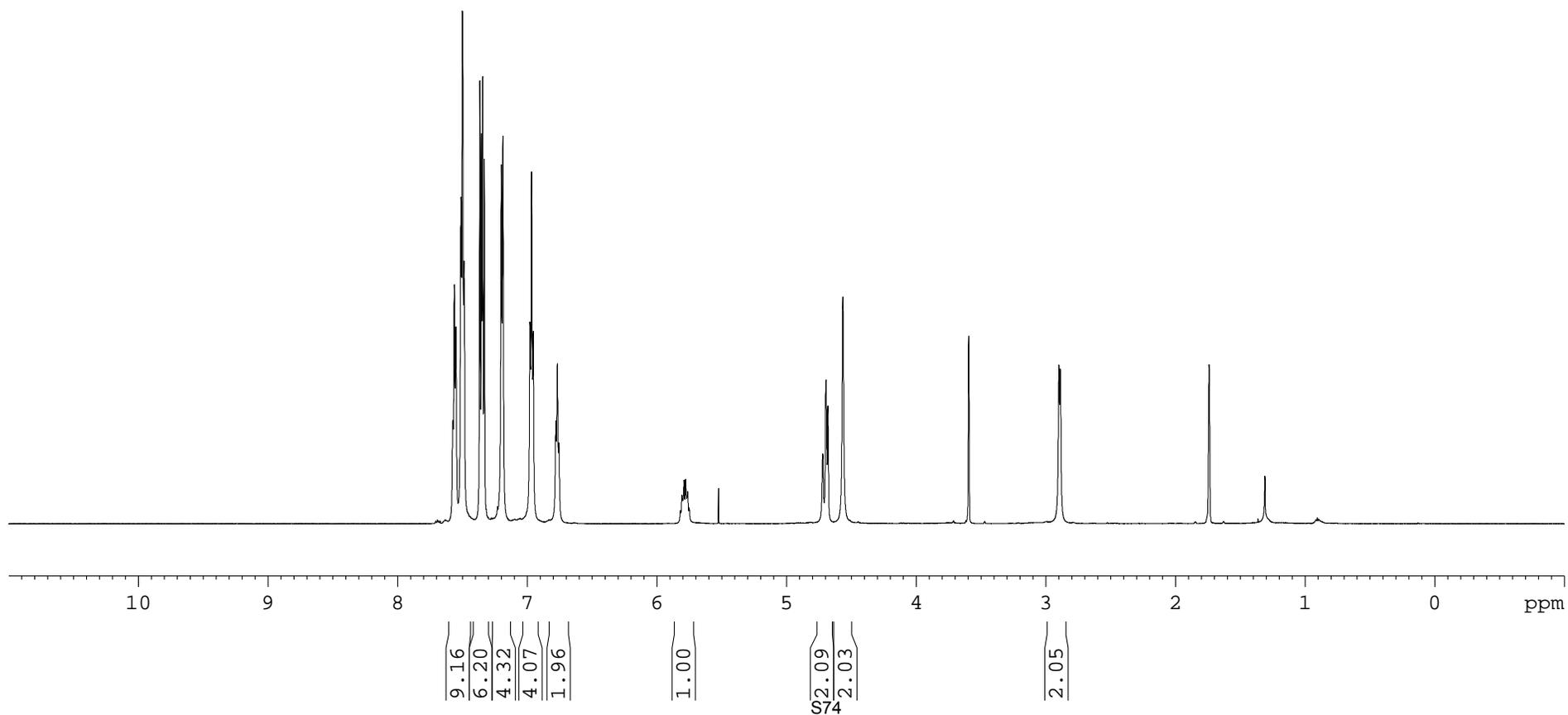
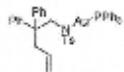


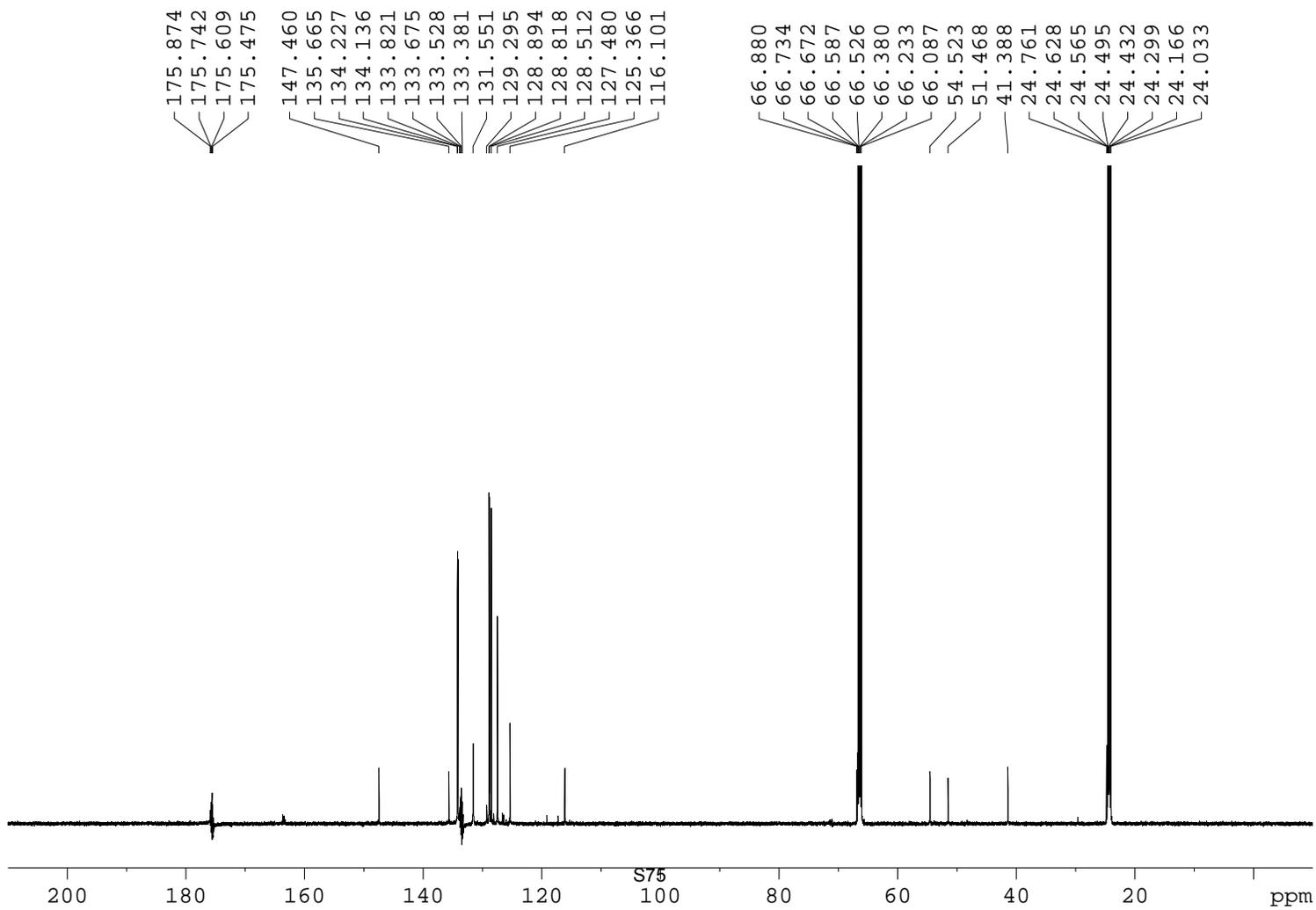
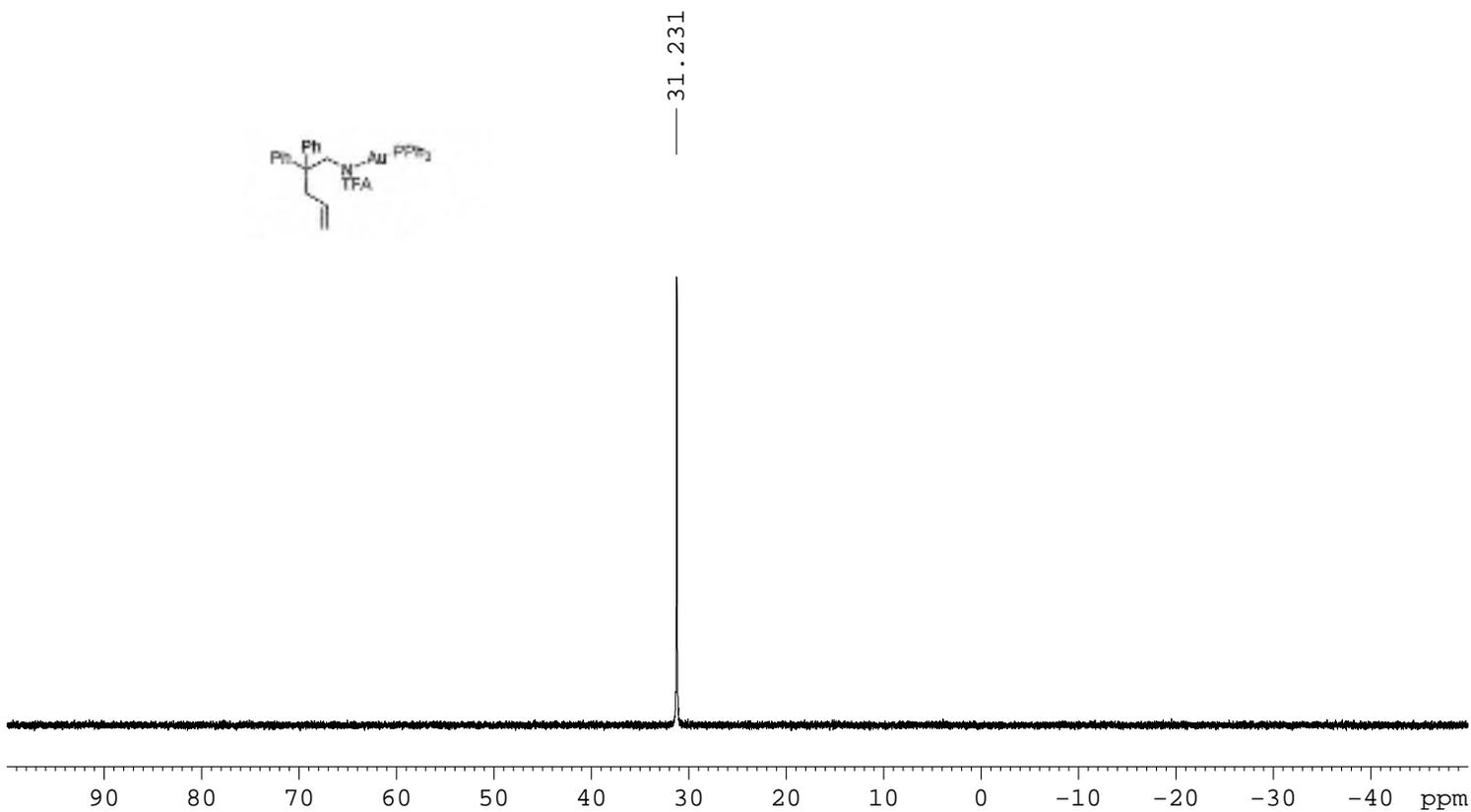
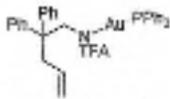
31.696

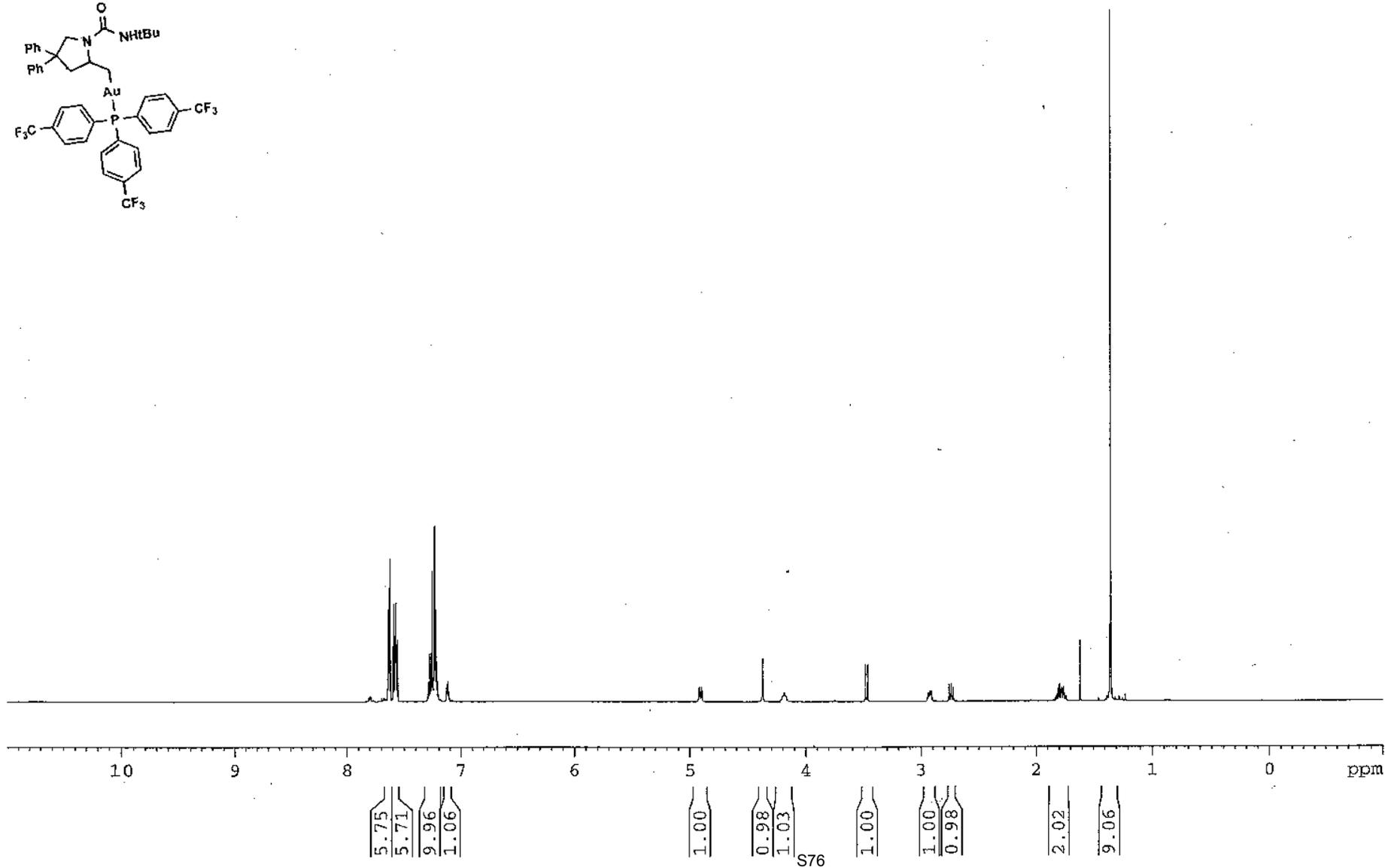
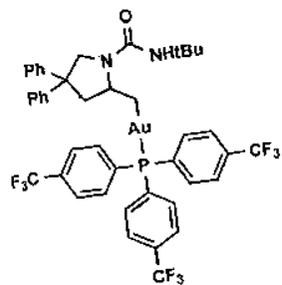
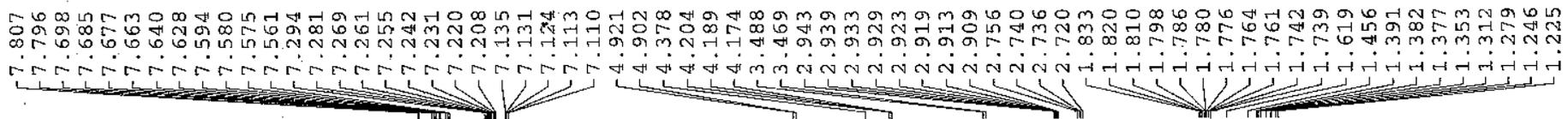


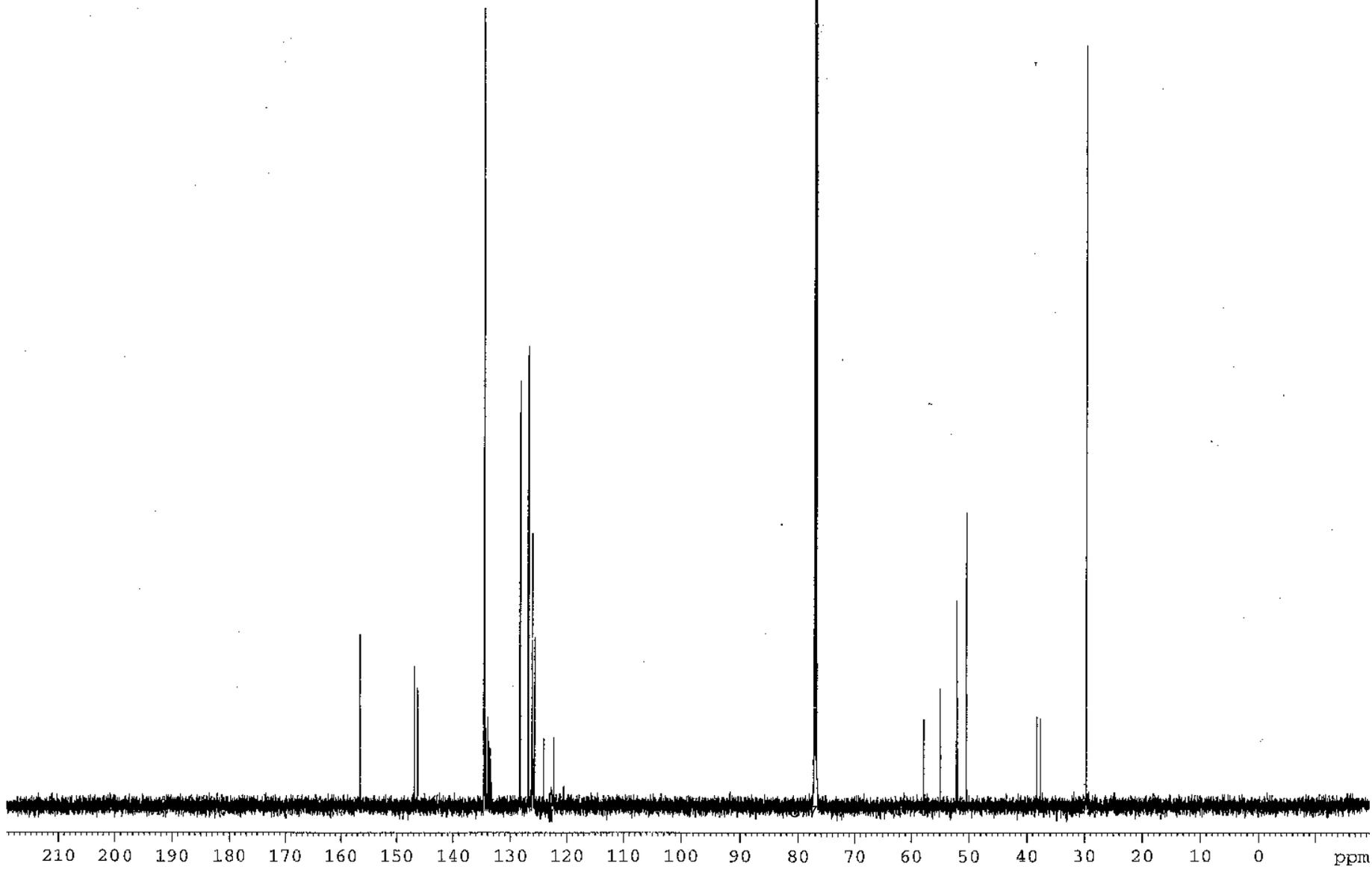
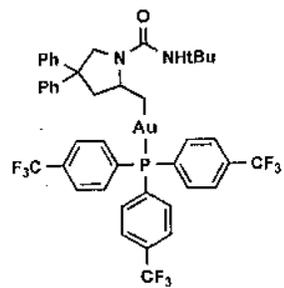
- 175.740
- 175.607
- 175.474
- 175.341
- 147.020
- 143.028
- 139.488
- 135.167
- 134.391
- 134.299
- 133.821
- 133.675
- 133.529
- 133.382
- 133.237
- 131.294
- 131.277
- 130.038
- 129.637
- 128.765
- 128.688
- 128.375
- 128.338
- 127.442
- 126.850
- 125.268
- 116.241
- 66.865
- 66.718
- 66.657
- 66.572
- 66.511
- 66.428
- 66.364
- 66.282
- 66.218
- 66.072
- 55.602
- 50.463
- 41.604
- 24.749
- 24.616
- 24.553
- 24.482
- 24.420
- 24.287
- 24.154
- 24.021
- 20.266

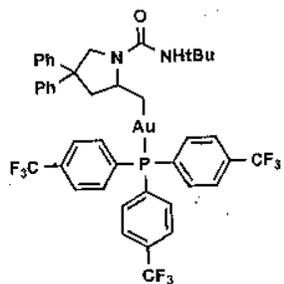












45.44
45.31

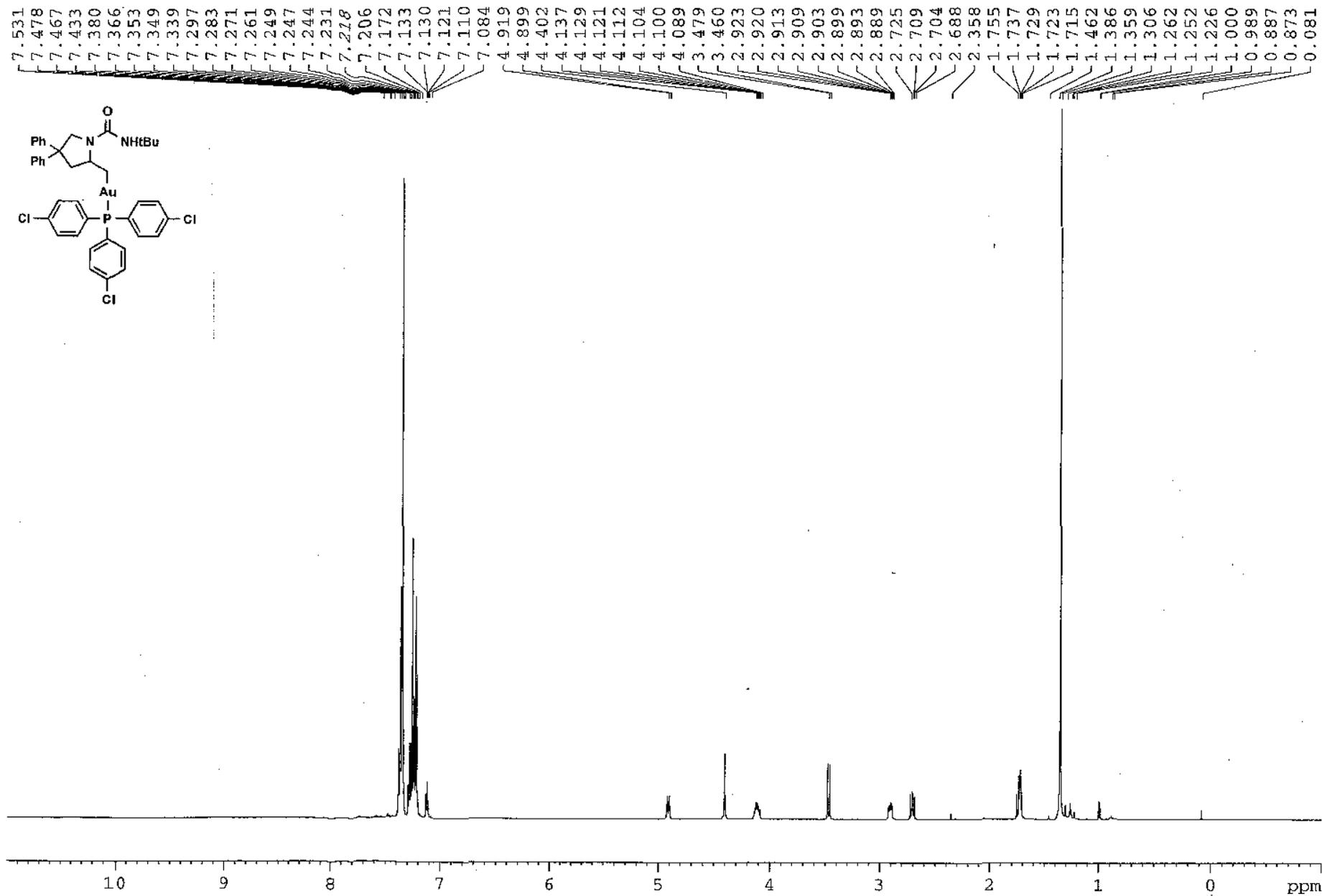
```
NAME      web2-104-recrys
EXPNO     3
PROCNO    1
Date_     20090916
Time      13.44
INSTRUM   AVA-400
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD        131072
SOLVENT   CDC13
NS        32
DS        0
SWH       64935.066 Hz
FIDRES    0.495415 Hz
AQ        1.0093044 sec
RG        16384
DW        7.700 usec
DE        6.00 usec
TE        295.1 K
D1        1.79999995 sec
D11       0.03000000 sec
TD0       1
```

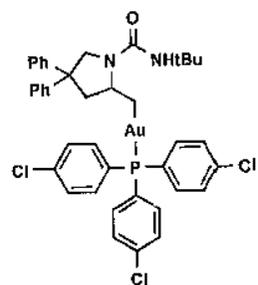
```
===== CHANNEL f1 =====
NUC1      31P
P1        8.10 usec
PL1       -1.00 dB
PL1W      25.29822159 W
SFO1      161.9674742 MHz
```

```
===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2      1H
PCPD2     70.00 usec
PL2       -3.00 dB
PL12      15.68 dB
```

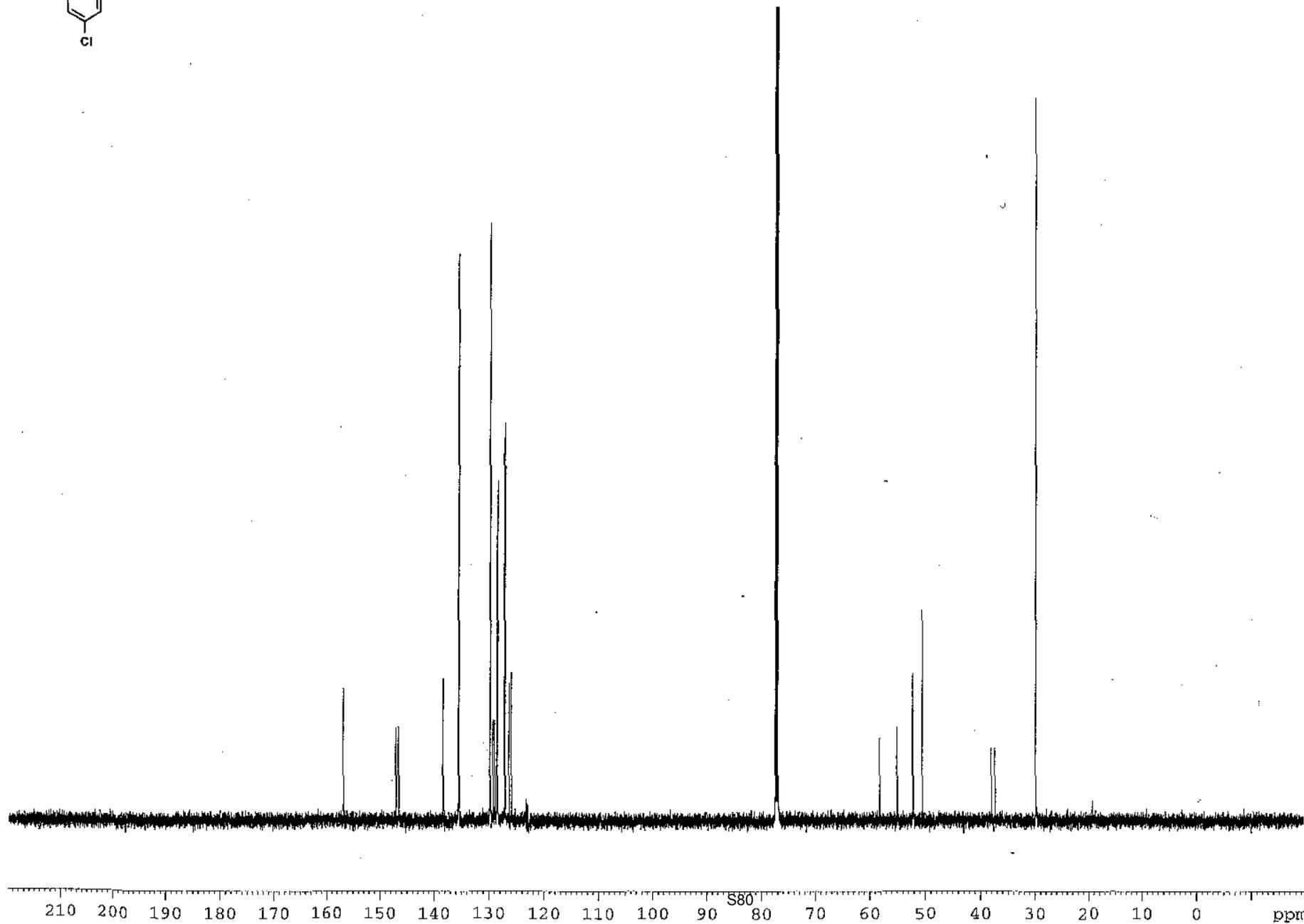
S78

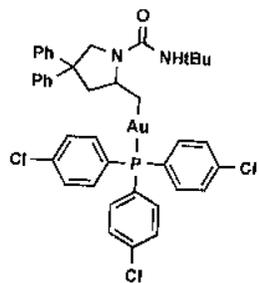
80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 ppm





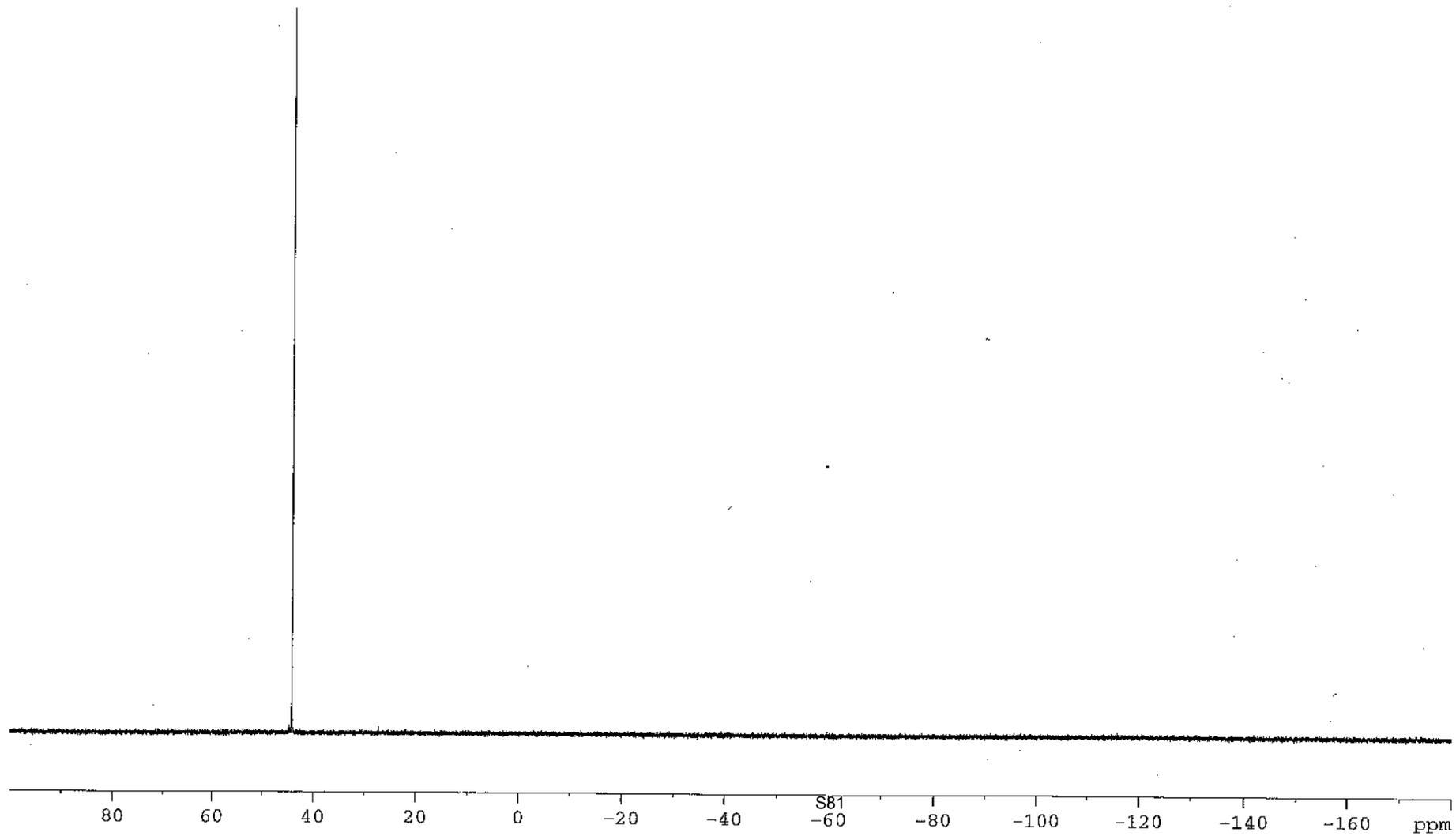
156.61
146.82
146.33
138.11
135.31
135.21
129.57
129.50
129.04
128.72
128.34
128.23
128.04
127.04
126.88
126.11
125.7

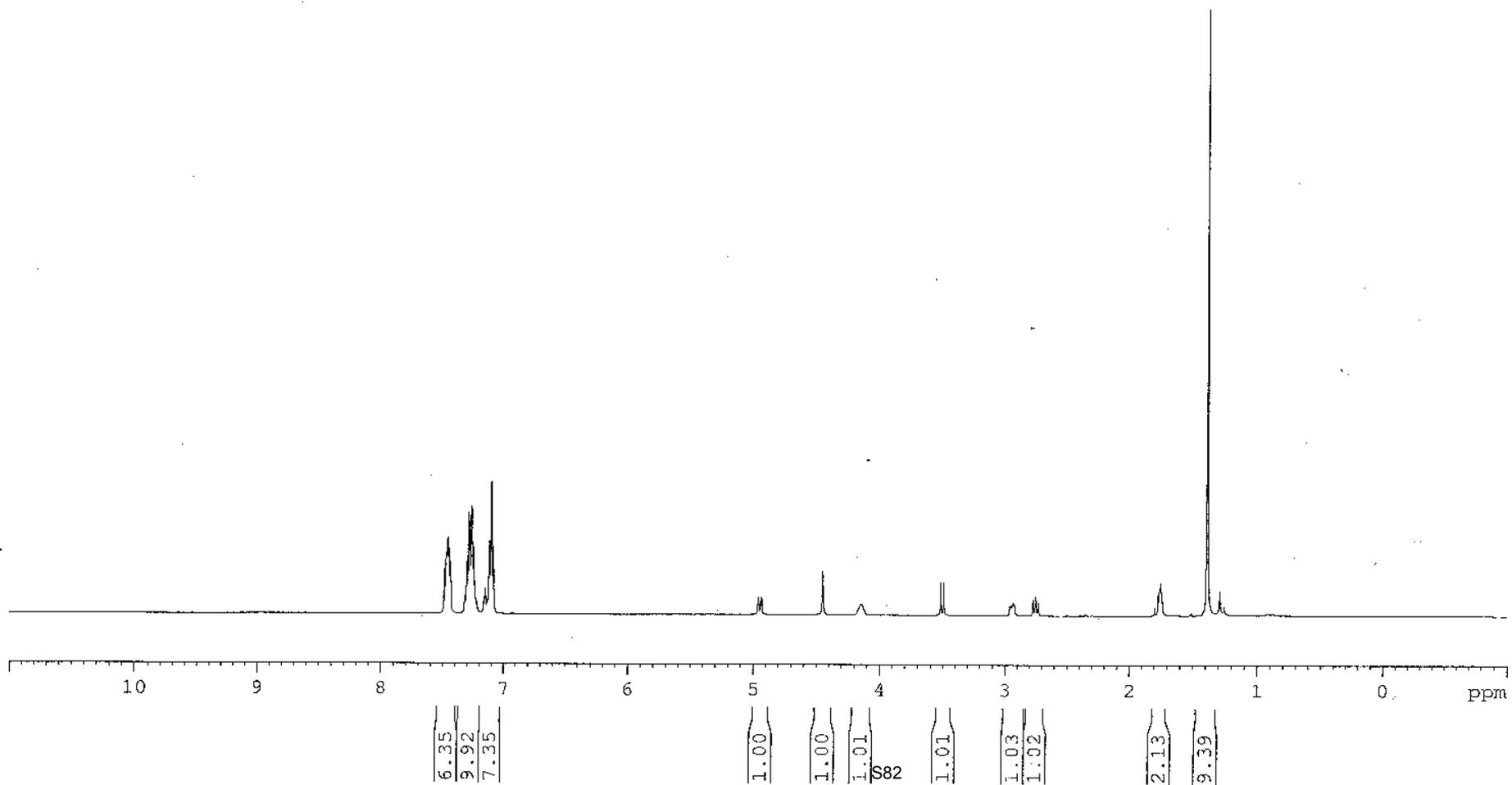
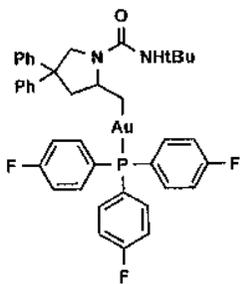


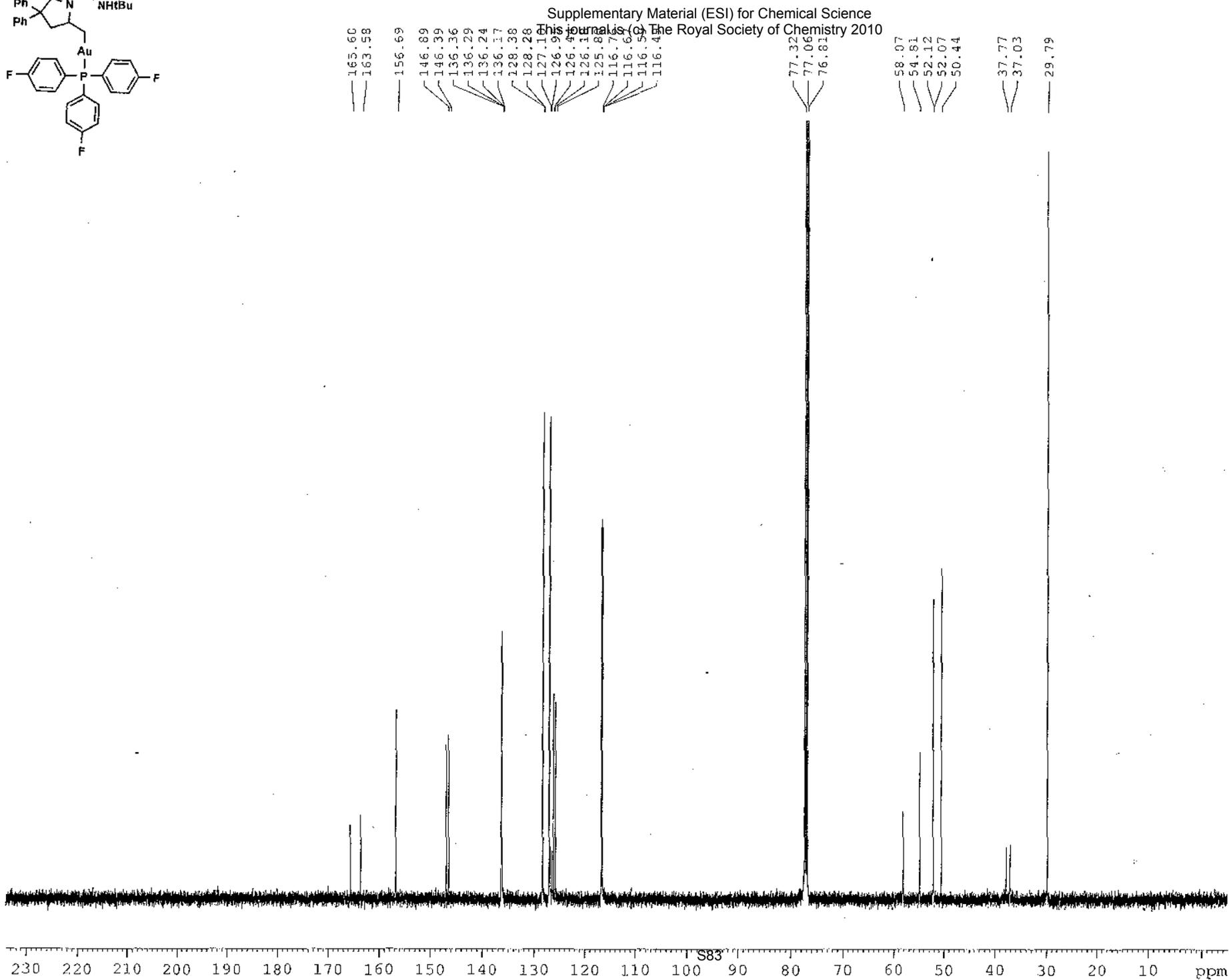
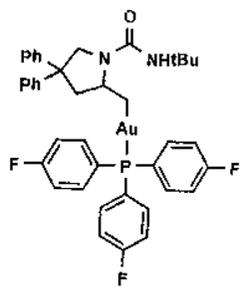


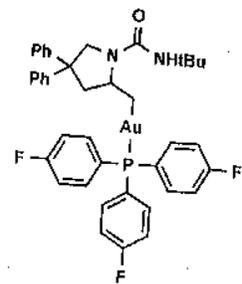
44.82
44.54
44.20
44.07
43.91

— 27.15



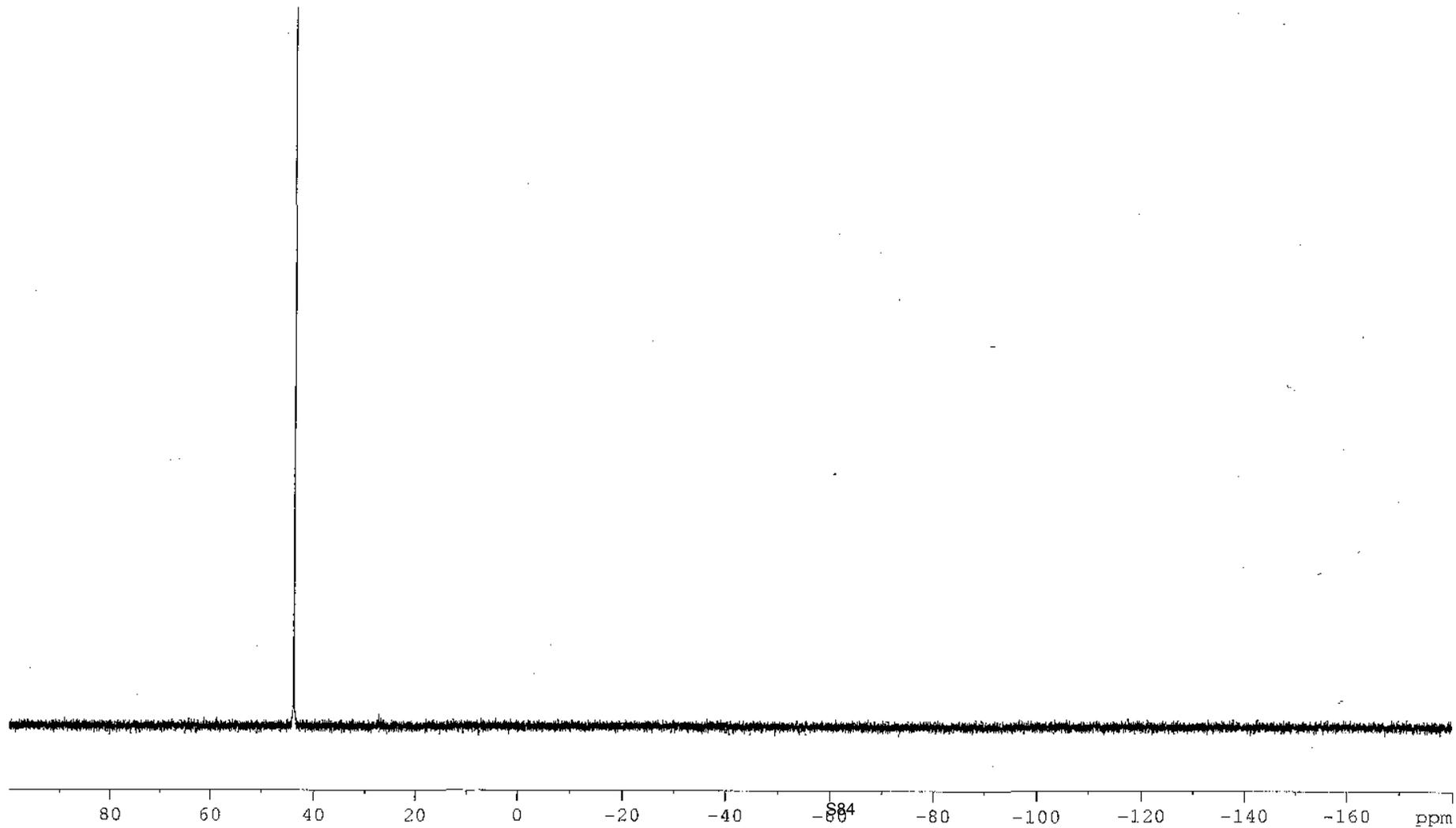


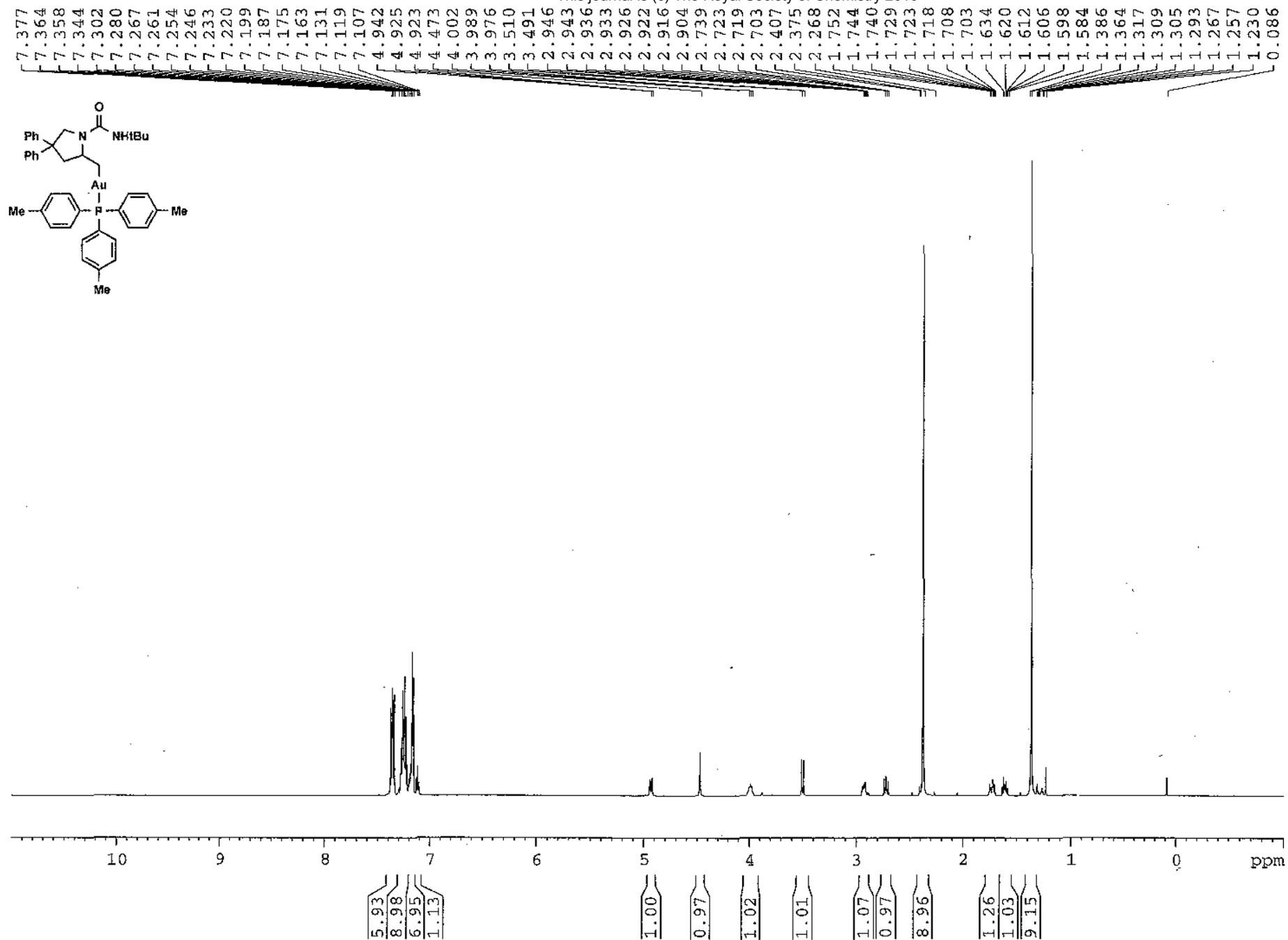


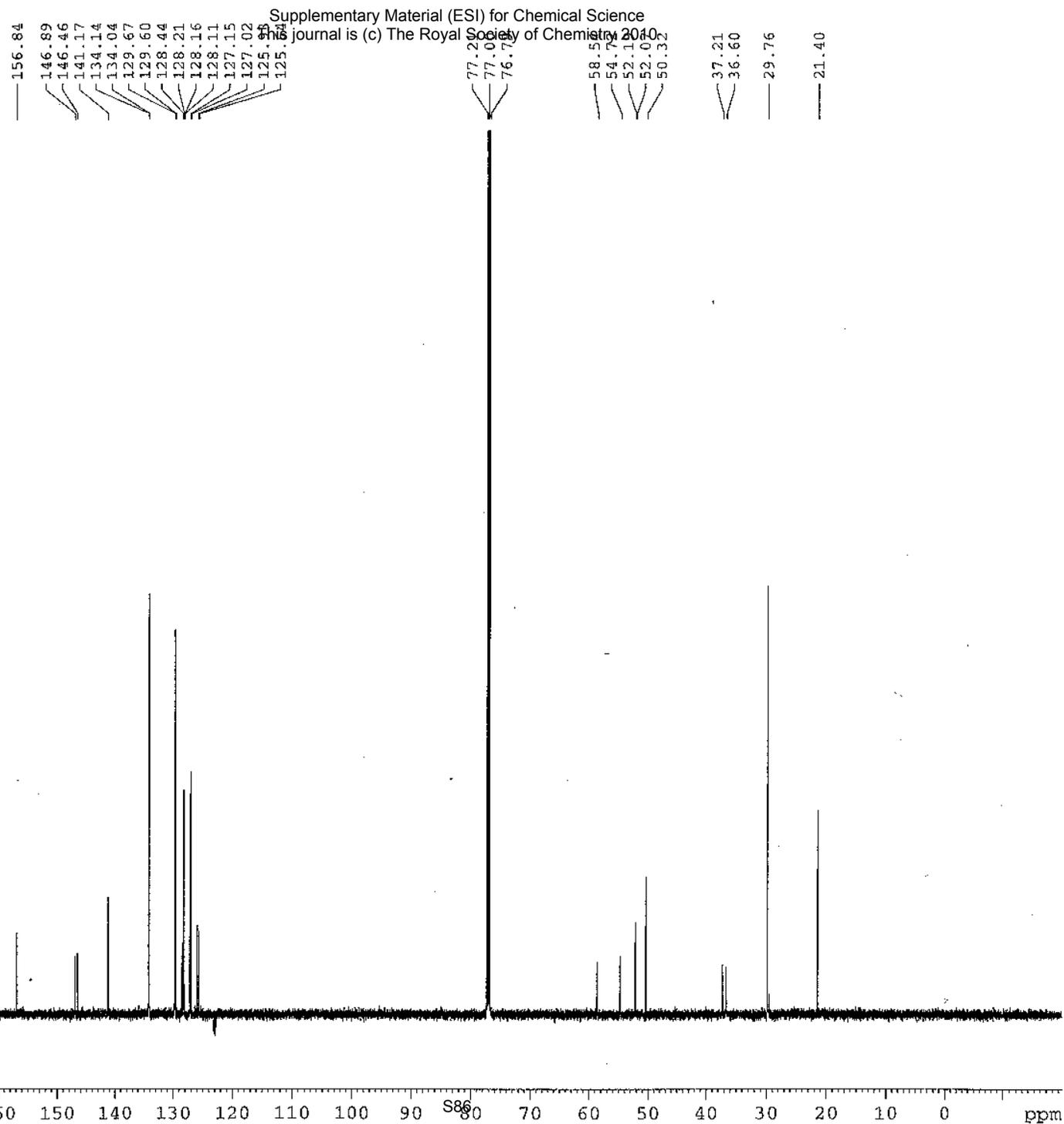
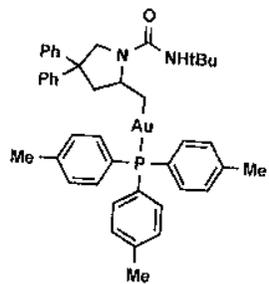


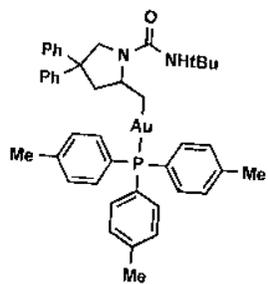
— 43.61

— 27.00

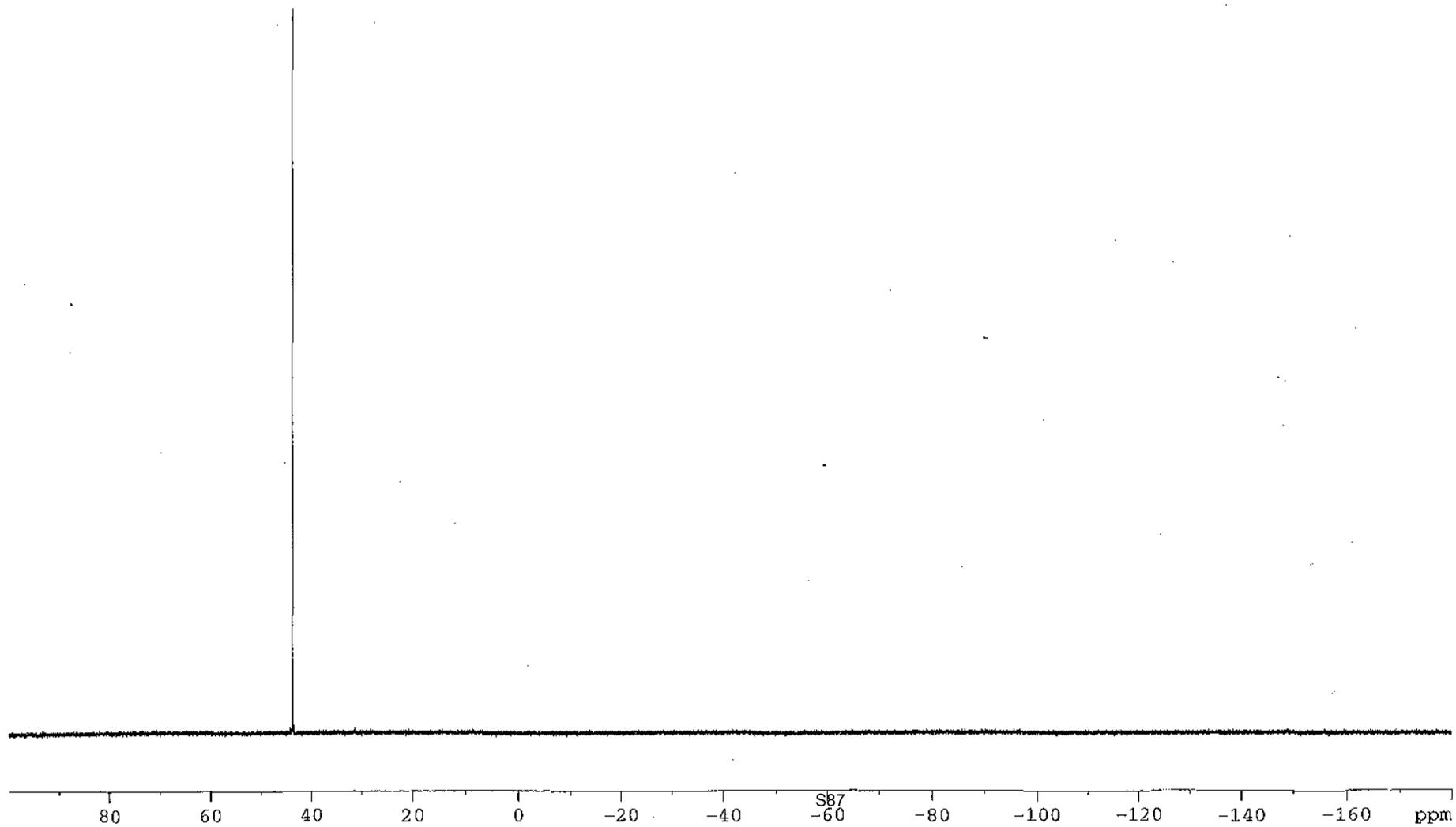


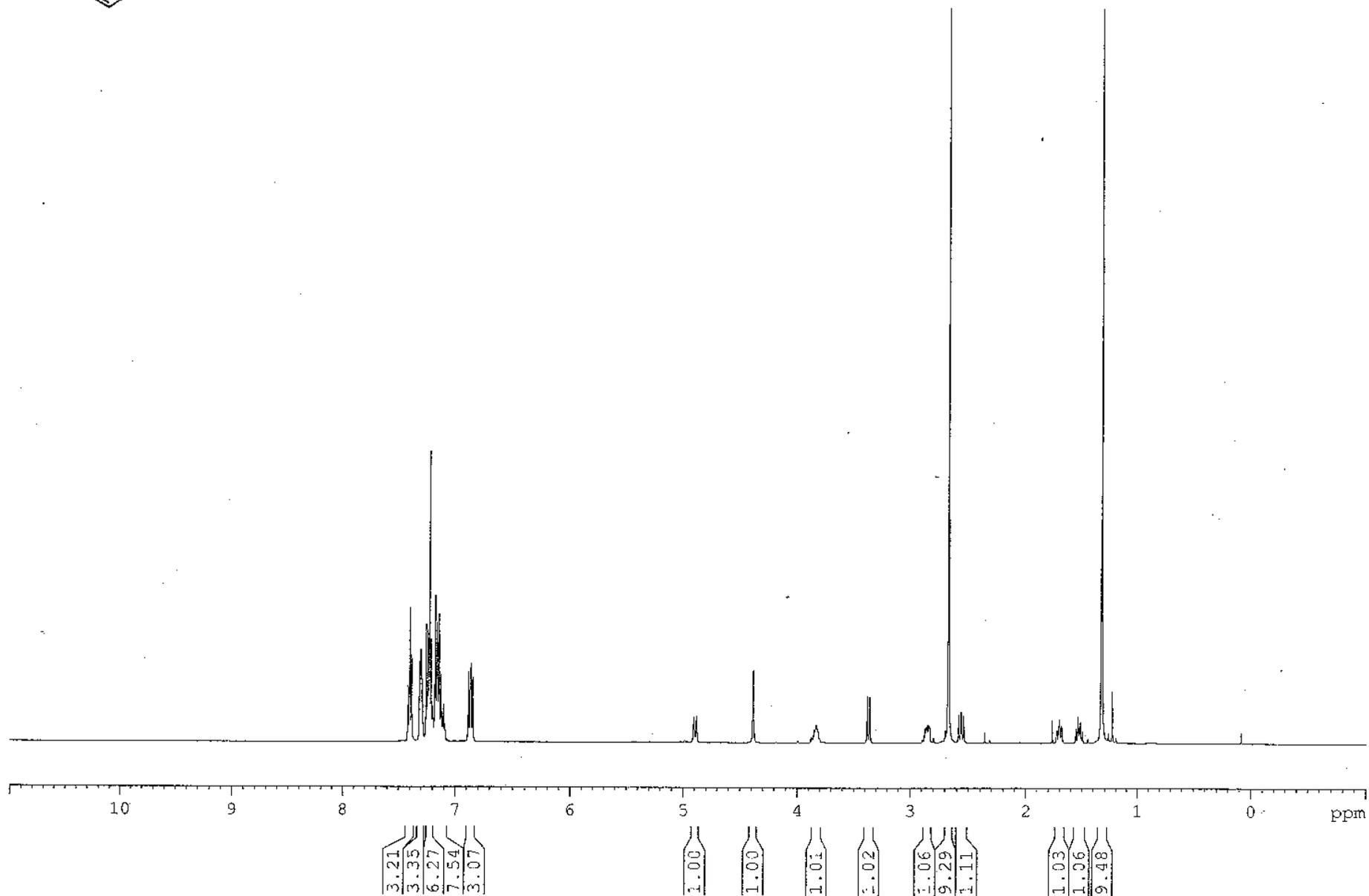
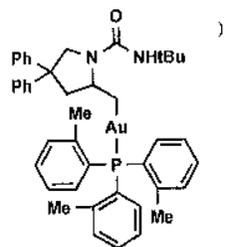






44.23
43.96
43.80
43.70
43.67
43.63
43.50







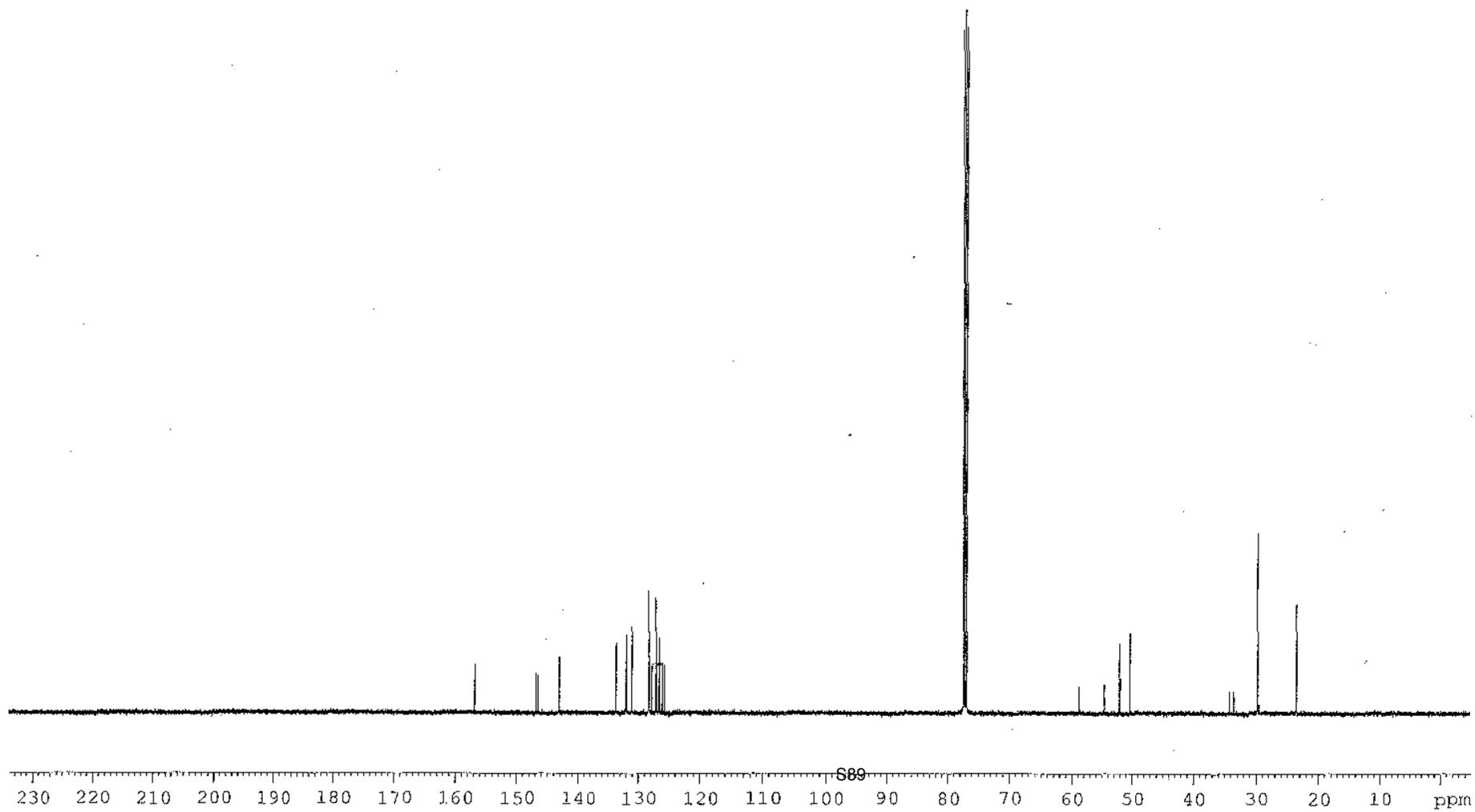
Supplementary Material (ESI) for Chemical Science
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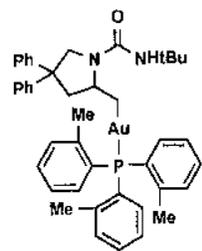
156.75
 146.79
 146.43
 143.07
 142.96
 133.65
 133.59
 131.97
 131.90
 131.03
 131.02
 128.24
 128.21
 128.19
 127.79
 127.11
 126.98
 126.51
 126.50
 126.02
 125.76

77.32
 77.07
 76.82

58.71
 54.54
 52.09
 51.87
 50.29

34.17
 33.44
 29.71
 23.51
 23.43





— 34.73

