



Supporting Information

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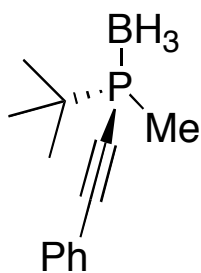
Synthesis and Enantioselectivity of P-Chiral Phosphine Ligands Possessing Alkynyl Groups

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General.

All solvents used in reactions were dried and purified according to standard procedure. NMR spectra were measured with JEOL JMN-GXS-500 (500 MHz) or JEOR JMN-LA-400 (400 MHz) spectrometer in CDCl₃. Chemical shifts were reported in δ ppm. Optical rotations were measured with JASCO DIP-370 polarimeter. Enantiomeric excesses were determined by HPLC analysis using Chiralcel AD, OJ-H, OD-H, OB, IA columns and varying concentrations of 2-propanol/hexane as the mobile phase. X-ray crystal structure data were collected using a Bruker SMART APEX II diffractometer with Mo-K α radiation. Silica gel (Kanto Chemical, Silica Gel 60N for flash chromatography) was used for column chromatography.

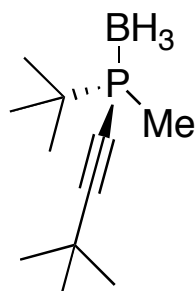
(*S*)-*tert*-Butylmethyl(phenylethynyl)phosphine–borane (**3a**)



To a solution of (*S*)-*tert*-butylmethylphosphine–borane (**1**) (>99% ee, 1.8 g, 15.4 mmol) in dry Et₂O (60 mL) was added *n*BuLi (11.6 mL of a 1.60 M solution in hexane, 18.5 mmol) at –78 °C under nitrogen, and the mixture was stirred for 15 min. 1,2-Dibromoethane (2.0 mL, 23.1 mmol) was added dropwise, and the reaction mixture was stirred at –78 °C. After 2 h, lithium phenylacetylide (30.8 mmol, 30 mL of Et₂O solution) was added to the reaction mixture, and the mixture was stirred at room temperature. After 1.5 h, the reaction was quenched with 1 M HCl. The mixture was extracted with EtOAc three times. The combined organic layers were washed with saturated NaHCO₃ and brine, and dried over Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (hexane/EtOAc = 5/1) to give (*S*)-*tert*-butylmethyl(phenylethynyl)phosphine–borane (**3a**) (97% ee, 2.8 g, 12.8 mmol, 83%) as white solid. ¹H NMR (500 MHz, CDCl₃) δ 0.42–0.98 (m, 4H), 1.29 (d, ³*J*(H,P) = 15.6 Hz, 9H), 1.51 (d, ²*J*(H,P) = 10.0 Hz, 3H), 7.33–7.37 (m, 2H), 7.41 (tt, ³*J*(H,H) = 15.3, ⁴*J*(H,H) = 1.7 Hz, 1H), 7.50–7.52 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 8.37 (d, *J*(CP) = 40 Hz), 24.96 (d, *J*(CP) = 4 Hz), 29.03 (d, *J*(CP) = 37 Hz), 79.42 (d,

$J(\text{CP}) = 90 \text{ Hz}$), 106.00 (d, $J(\text{CP}) = 12 \text{ Hz}$), 120.77, 128.42, 130.01, 132.20. ^{31}P NMR (162 MHz, CDCl_3) δ 18.0. HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{19}\text{BP}$ (M^+-H) 217.1320, found 217.1313. $[\alpha]_D^{22} = 0.97 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.0100 \text{ g cm}^{-3}$ in CHCl_3), HPLC: Daicel Chiralcel OD-H, Hexane/*i*PrOH = 199/1, Flow rate = 0.5 mL/min, UV = 254 nm, $t_R = 11.9 \text{ min}$ (*R*), $t_R = 13.1 \text{ min}$ (*S*).

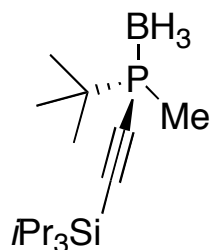
(*S*)-*tert*-Butyl(3,3-dimethyl-1-butyne)methylphosphine–borane (3b)



In a similar manner (*S*)-*tert*-butyl(3,3-dimethyl-1-butyne)methylphosphine–borane was prepared in 82% yield. ^1H NMR (400 MHz, CDCl_3) δ 0.23–0.89 (m, 3H), 1.21 (d, $^3J(\text{H,H}) = 15.1 \text{ Hz}$, 9H), 1.27 (s, 9H), 1.38 (d, $^2J(\text{H,H}) = 10.0 \text{ Hz}$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 8.54 (d, $J(\text{CP}) = 40 \text{ Hz}$), 24.77 (d, $J(\text{CP}) = 3 \text{ Hz}$), 28.62 (d, $J(\text{CP}) = 35 \text{ Hz}$), 30.20 (d, $J(\text{CP}) = 2 \text{ Hz}$), 68.70 (d, $J(\text{CP}) = 95 \text{ Hz}$), 116.79 (d, $J(\text{CP}) = 10 \text{ Hz}$). ^{31}P NMR (162 MHz, CDCl_3) δ 15.7. HRMS (FAB) calcd for $\text{C}_{11}\text{H}_{24}\text{BP}$ (M^++K) 237.1348, found 237.1351. $[\alpha]_D^{22} = 9.4 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$

($c = 0.0013 \text{ g cm}^{-3}$ in CHCl_3). Its enantiomeric excess was determined to be 98% ee by HPLC analysis. HPLC: Daicel Chiralpak IA, Hexane/*i*PrOH=1000/1, Flow rate = 0.5 mL/min, UV = 230 nm, $t_R = 13.7 \text{ min}$ (*R*), $t_R = 15.3 \text{ min}$ (*S*).

(*S*)-*tert*-Butylmethyl(triisopropylsilylethynyl)phosphine–borane (3c)



In a similar manner (*S*)-*tert*-butylmethyl(triisopropylsilylethynyl)phosphine–borane was prepared in 86% yield. ^1H NMR (400 MHz, CDCl_3) δ 0.27–0.73 (m, 3H), 1.09–1.10 (m, 21H), 1.24 (d, $^3J(\text{HP}) = 15.4 \text{ Hz}$, 9H), 1.43 (d, $^2J(\text{HP}) = 10.2 \text{ Hz}$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 8.45 (d, $J(\text{CP}) = 40 \text{ Hz}$), 10.90, 18.43, 24.82 (d, $J(\text{CP}) = 3 \text{ Hz}$), 28.62 (d, $J(\text{CP}) = 38 \text{ Hz}$), 98.26 (d, $J(\text{CP}) = 77 \text{ Hz}$), 113.26 (d, $J(\text{CP}) = 3 \text{ Hz}$). ^{31}P NMR (162 MHz, CDCl_3) δ 17.5. HRMS (FAB) calcd for $\text{C}_{16}\text{H}_{35}\text{BPSi}$ (M^+-H) 297.2342, found 297.2332. $[\alpha]_D^{22} = -8.9$

$\text{cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.0101 \text{ g cm}^{-3}$ in CHCl_3). Its enantiomeric excess was determined to be 98% ee by HPLC analysis. Daicel Chiralpak IA, Hexane/*i*PrOH = 1000/1, Flow rate = 0.5 mL/min, UV = 230 nm, $t_R = 11.0 \text{ min}$ (*R*), $t_R = 13.6 \text{ min}$ (*S*).

(*S*)-*tert*-Butylmethyl(trimethylsilylethynyl)phosphine–borane (3d)

In a similar manner (*S*)-*tert*-butylmethyl(trimethylsilylethynyl)phosphine–borane was prepared in 81% yield. ^1H NMR (400 MHz, CDCl_3) δ 0.22 (s, 9H), 1.23 (d, $^3J(\text{HP}) = 15.4 \text{ Hz}$, 9H), 1.42 (d, $^2J(\text{HP}) = 10.2 \text{ Hz}$, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 8.92 (d, $J(\text{CP}) = 40 \text{ Hz}$), 25.45 (d, $J(\text{CP}) = 4 \text{ Hz}$), 29.28 (d, $J(\text{CP}) = 38 \text{ Hz}$), 96.79 (d, $J(\text{CP}) = 77 \text{ Hz}$), 116.66 (d, $J(\text{CP})$

= 3 Hz). ^{31}P NMR (162 MHz, CDCl_3) δ 17.1. $[\alpha]_D^{22} = -1.59 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.0100 \text{ g cm}^{-3}$ in CHCl_3). Its enantiomeric excess was determined to be 99% ee by HPLC analysis. Daicel Chiralcel OJ-H, Hexane/*i*PrOH = 99/1, Flow rate = 0.5 mL/min, UV = 230 nm, $t_R = 8.8 \text{ min}$ (*R*), $t_R = 9.7 \text{ min}$ (*S*).

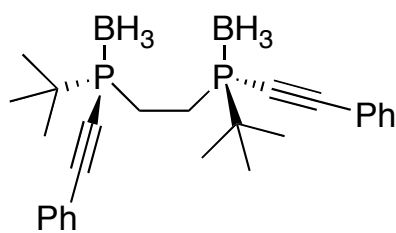
(*S*)-*tert*-Butylmethylphenylphosphine–borane (3e),^[1-4] (*S*)-*tert*-Butyl(*o*-methoxyphenyl)-methylphosphine–borane (3f),^[2,5] and (*S*)-Benzyl(*tert*-butyl)methylphosphine–borane (4b)^[6,7]

The absolute configurations and enantiomeric excesses of the products (**3e**, **3f**, and **4b**) were determined by HPLC analysis in comparison with the reported data.^[1-7] **3e**: Daicel Chiralcel OJ-H, Hexane/*i*PrOH = 9/1, Flow rate = 0.5 mL/min, UV = 230 nm, $t_R = 25.5 \text{ min}$ (*R*), $t_R = 27.7 \text{ min}$ (*S*); **3f**: Daicel Chiralcel OD-H, Hexane/*i*PrOH = 99/1, Flow rate = 0.5 mL/min, UV = 230 nm, $t_R = 11.0 \text{ min}$ (*R*), $t_R = 11.6 \text{ min}$ (*S*); **4b**: Daicel Chiralcel OD-H, Hexane/*i*PrOH = 9/1, Flow rate = 0.5 mL/min, UV = 230 nm, $t_R = 16.9 \text{ min}$ (*R*), $t_R = 18.9 \text{ min}$ (*S*).

(*S*)-*n*-Butyl(*tert*-butyl)methylphosphine–borane (4a)

The absolute configuration and the optical purity of compound **4a** ($[\alpha]_D = -4.1 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.010 \text{ g cm}^{-1}$ in CHCl_3)) were determined by comparison of the sign of rotation and specific rotation of the authentic sample ($[\alpha]_D = -4.5 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.010 \text{ g cm}^{-3}$ in CHCl_3)) prepared by the reaction of compound **1** with *n*BuLi and bromobutane.

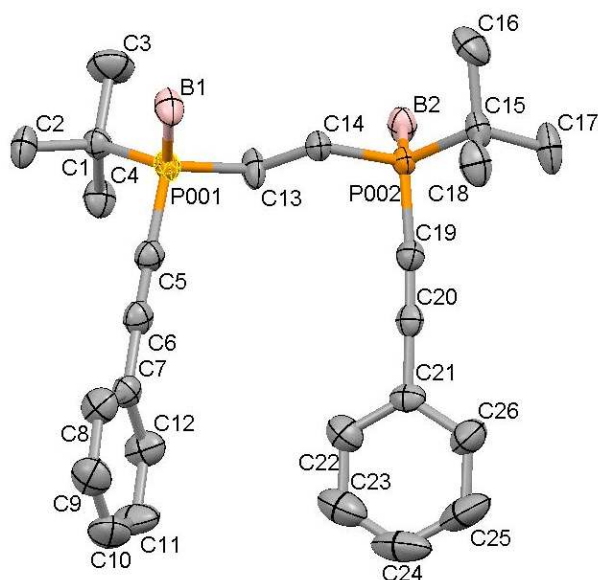
(*S,S*)-1,2-Bis(boranato(*tert*-butyl)(phenylethynyl)phosphino)ethane (6a)



To a solution of (*S*)-*tert*-butylmethyl(phenylethynyl)-phosphine–borane (**3a**) (97% ee, 0.95 g, 4.4 mmol) and TMEDA (0.8 mL, 5.2 mmol) in dry Et_2O (13 mL) was added *s*-BuLi (5.2 mL of a 1.0 M solution in hexane, 5.2 mmol) at $-78 \text{ }^\circ\text{C}$ under nitrogen, and the mixture was stirred for 1 h and $-50 \text{ }^\circ\text{C}$ for 10 min. Copper(II) chloride (1.5 g, 11 mmol) was added with vigorous stirring and the resulting mixture was gradually warmed to room temperature. After 2 h, the reaction was quenched with saturated NH_4Cl . The mixture was extracted with EtOAc three times. The combined organic layers were washed with brine, and dried over Na_2SO_4 . After filtration, the filtrate was concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (hexane/EtOAc = 4/1) to give (*S,S*)-1,2-bis(boranato(*tert*-butyl)(phenylethynyl)phosphino)ethane (**6a**) (0.69 g, 1.6 mmol, 73%) as white solid. ^1H NMR (400 MHz, CDCl_3) δ 0.57–0.80 (m, 6H), 1.32–1.35 (m, 18H), 2.13–2.28 (m, 4H), 7.29–7.32 (m, 4H), 7.41 (tt, $^3J(\text{H,H}) = 15.0 \text{ Hz}$, $^4J(\text{H,H}) = 2.5 \text{ Hz}$, 2H), 7.46–7.47 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 17.01 (d, $J(\text{CP}) = 34 \text{ Hz}$), 25.30 (t,

$J(\text{CP}) = 3 \text{ Hz}$), 30.11 (d, $J(\text{CP}) = 36 \text{ Hz}$), 77.88 (d, $J(\text{CP}) = 88 \text{ Hz}$), 107.38, 120.39, 128.48, 130.22, 132.24. ^{31}P NMR (162 MHz, CDCl_3) δ 29.6. $[\alpha]_{\text{D}}^{22} = 111 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.0100 \text{ g cm}^{-3}$ in CHCl_3).

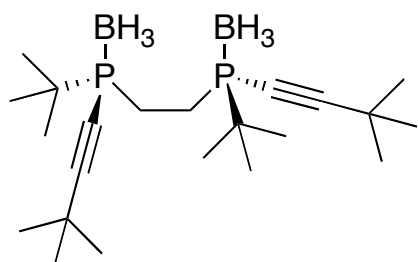
Recrystallization of compound **6a** from a mixed solvent of EtOAc and *n*-hexane gave analysis. Empirical prisms. Absolute configuration of this compound was determined by



single crystal X-ray Formula $\text{C}_{26}\text{H}_{48}\text{B}_2\text{P}_2$; Formula weight 444.20; Temperature 173 K; Wavelength 0.71073 Å; Crystal system Orthorhombic; Space group $P2(1)2(1)2$; Unit cell dimensions $a = 22.202(5) \text{ Å}$, $\alpha = 90^\circ$, $b = 10.932(3) \text{ Å}$, $\beta = 90^\circ$, $c = 11.379(3) \text{ Å}$, $\gamma = 90^\circ$; Volume 2761.8(11) Å³; $Z = 5$; Density (calculated) 1.335 Mg/m³; Crystal size 0.45 x 0.35 x 0.15 mm³; GOF = 1.034; Final R indices [$I > 2\sigma(I)$] $R1 = 0.0446$, $wR2 = 0.1045$; R indices (all data) $R1 =$

0.0524, $wR2 = 0.1095$; Absolute structure parameter 0.06(10). CCDC-641148.

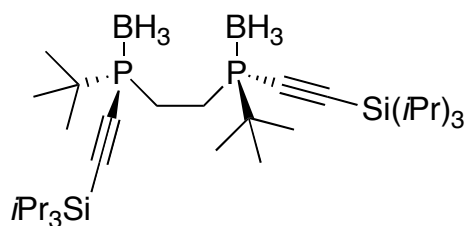
(*S,S*)-1,2-Bis(boranato(*tert*-butyl))(3,3-dimethyl-1-butynyl)phosphino)ethane (**6b**)



This compound was prepared in 73% yield by the oxidative coupling of **4b**. ^1H NMR (400 MHz, CDCl_3) δ 0.22–0.88 (m, 6H), 1.22–1.26 (d, $^3J(\text{H,P}) = 15.1 \text{ Hz}$, 18H), 1.28 (s, 18H), 1.94–2.02 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 17.05 (d, $J(\text{CP}) = 34 \text{ Hz}$), 25.12, 28.58, 29.58 (d, $J(\text{CP}) = 37 \text{ Hz}$), 30.26, 67.35 (d, $J(\text{CP}) = 93 \text{ Hz}$), 118.42 (d, $J(\text{CP}) = 10 \text{ Hz}$). ^{31}P NMR (162 MHz,

CDCl_3) δ 27.8. HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{46}\text{B}_2\text{P}_2$ ($\text{M}^+ + \text{K}$) 433.2906, found 433.2881. $[\alpha]_{\text{D}}^{22} = 19.4 \text{ cm}^3 \text{ g}^{-1} \text{ dm}^{-1}$ ($c = 0.0096 \text{ g cm}^{-3}$ in CHCl_3).

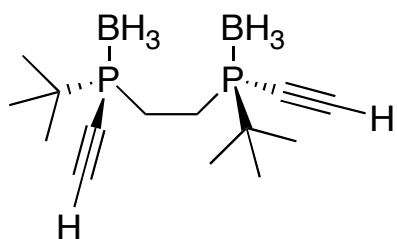
(*S,S*)-1,2-Bis(boranato(*tert*-butyl)triisopropylsilylethynylphosphino)ethane (**5c**)



This compound was prepared in 78% yield by the oxidative coupling of **4c**. ^1H NMR (400 MHz, CDCl_3) δ 0.27–0.73 (m, 6H), 1.06–1.14 (m, 42H), 1.25–1.29 (m, 18H), 1.98–2.13 (m, 4H). ^{13}C NMR

(100 MHz, CDCl₃) δ 10.92, 16.73 (d, $J(\text{CP}) = 32$ Hz), 18.50 (d, $J(\text{CP}) = 2$ Hz), 25.19, 29.63 (d, $J = 36$ Hz), 96.47 (d, $J = 74$ Hz), 115.49. ³¹P NMR (162 MHz, CDCl₃) δ 29.3. HRMS (FAB) calcd for C₃₂H₇₀B₂P₂Si₂ (M⁺+K) 633.4327, found 633.4327. $[\alpha]_D^{22} = 25.1$ cm³ g⁻¹ dm⁻¹ ($c = 0.0100$ g cm⁻³ in CHCl₃).

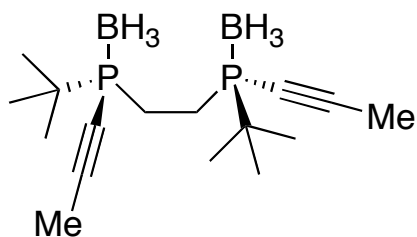
(*S,S*)-1,2-Bis(boranato(*tert*-butyl)ethynylphosphino)ethane (6d)



Tetrabutylammonium fluoride (0.4 mL of a 1.0 M solution in THF, 0.4 mmol) was added to (*S,S*)-1,2-bis(boranato(*tert*-butyl)(triisopropylsilylethynyl)phosphino)ethane (**6c**) (60 mg, 0.1 mmol) under nitrogen, and the mixture was stirred at room temperature. After 6 h, the reaction was quenched by the addition of water. The mixture was

extracted with EtOAc three times. The combined organic layers were washed with brine, and dried over Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (hexane/EtOAc = 3/1) to give (*S,S*)-1,2-bis(boranato(*tert*-butyl)ethynylphosphino)ethane (**6d**) (15 mg, 0.052 mmol, 52%) as white solid. ¹H NMR (400 MHz, CDCl₃) δ 0.24–0.92 (m, 6H), 1.27–1.31 (m, 18H), 2.01–2.15 (m, 4H), 3.08–3.10 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 16.31 (d, $J(\text{CP}) = 33$ Hz), 25.08, 29.66 (d, $J(\text{CP}) = 35$ Hz), 74.06 (d, $J(\text{CP}) = 81$ Hz), 96.28. ³¹P NMR (162 MHz, CDCl₃) δ 30.9. HRMS (FAB) calcd for C₁₄H₃₀B₂P₂Si₂ (M⁺+K) 321.1651, found 321.1662. $[\alpha]_D^{22} = -13.9$ cm³ g⁻¹ dm⁻¹ ($c = 0.0024$ g cm⁻³ in CHCl₃).

(*S,S*)-1,2-Bis(boranato(*tert*-butyl)(1-propynyl)phosphino)ethane (6e)

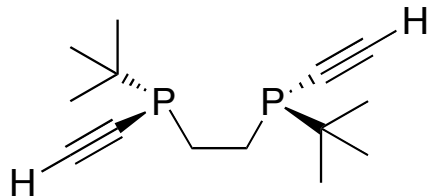


To a solution of (*S,S*)-1,2-bis(boranato(*tert*-butyl)ethynylphosphino)ethane (**6d**) 31 mg, 0.11 mmol) in THF (0.55 mL) was added *s*BuLi (0.28 mL of a 1.0 M solution in hexane, 0.28 mmol) at –78 °C under nitrogen, and the mixture was stirred for 1 h. Iodomethane (34 μL, 0.55 mmol) was added to the

solution with stirring and the mixture was warmed to room temperature during 2 h. The reaction was quenched with saturated NH₄Cl. The mixture was extracted with EtOAc three times. The combined organic layers were washed with brine, and dried over Na₂SO₄. After filtration, the filtrate was concentrated under reduced pressure, and the residue was purified by chromatography on silica gel (hexane/EtOAc = 4/1) to give (*S,S*)-1,2-bis(boranato(*tert*-butyl)(1-propynyl)phosphino)ethane (**6e**) (30 mg, 88%) as white solid. ¹H NMR (400 MHz, CDCl₃) δ 0.24–0.86 (m, 6H), 1.23–1.27 (m, 18H), 2.00–2.06 (m, 10H). ¹³C NMR (100 MHz,

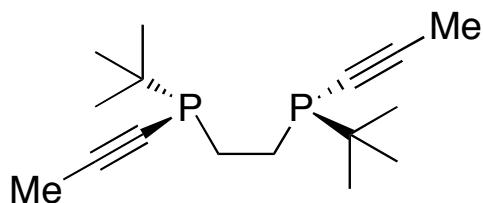
□□□□ ^{31}P NMR (202 MHz, CDCl_3) δ -13.09.

(*S,S*)-1,2-Bis(*t*-butyl(ethynyl)phosphino)ethane (5d)



^1H NMR (400 MHz, CDCl_3) δ 1.1–1.18 (m, 18H), 1.54–1.65 (m, 2H), 1.96–2.03 (m, 2H), 2.86 (s, CCH). (500 MHz, $\text{CDCl}_3/\text{CD}_3\text{OD}$) δ 1.14–1.18 (m, 18H), 1.55–1.65 (m, 2H), 1.96–2.03 (m, 2H) (The signal of CCH was not observed.). ^{13}C NMR (100 MHz, CDCl_3) δ 19.76, 27.31, 29.40, 83.30–83.53 (m), 93.52. ^{31}P NMR (202 MHz, CDCl_3) δ -14.25.

(*S,S*)-1,2-Bis(*tert*-butyl(1-propynyl)phosphino)ethane (5e)



^1H NMR (400 MHz, CDCl_3) δ 1.10–1.15 (m, 18H), 1.49–1.60 (m, 2H), 1.84–1.94 (m, 2H), 1.98 (s, 6H). (Diethyl ether was strongly bound to this ligand and could not be removed in vacuo). ^{13}C NMR (125 MHz, CDCl_3) δ 5.14, 20.36 27.39, 29.39 (d, $J(\text{CP}) = 3$ Hz), 76.61, 102.52. ^{31}P NMR (202 MHz, CDCl_3) δ -13.00.

General Procedure for Rhodium-Catalyzed Asymmetric Hydrogenation of Methyl (*Z*)- α -Acetamidocinnamate

A 50 mL-hydrogenation tube was charged with methyl (*Z*)- α -acetamidocinnamate (0.5 mmol). The tube was connected to the hydrogen tank via stainless steel tubing. The vessel was evacuated and filled with 1 atm of hydrogen gas (Nippon Sanso, 99.9999%). A solution of $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ (1.9 mg, 5.0 μmol) and (*S,S*)-1,2-bis(1-alkynyl(*tert*-butyl)phosphino)ethane (AlkynylIP*) (5.5 μmol) in degassed MeOH (1 mL) was added via a syringe to the tube, and the hydrogen pressure was increased to 1 atm. After 3 h, the reaction mixture was evaporated and the residue was purified by flash chromatography on silica gel using EtOAc as an eluent. The product was characterized by spectral data and analyzed by HPLC using a chiral column. The absolute configuration and enantiomeric excess of the product were determined by comparison of the retention times with reported values.⁸ Conditions for the HPLC analysis of *N*-acetylphenylalanine methyl ester: Chiralcel OJ, hexane/2-propanol = 9:1, 0.5 mL/min, wavelength = 254 nm, retention times: 22.3 min (*R*), 31.7 min (*S*).

General Procedure for Rhodium-Catalyzed Asymmetric 1,4-Addition of Organoboronic Acids to Enones

A solution of $[\text{Rh}(\text{nbd})_2]\text{BF}_4$ (1.9 mg, 10 μmol) and ligand (*S,S*)-1,2-bis(1-alkynyl(*tert*-butyl)phosphino)ethane (AlkynylP*) (11 μmol) in dioxane (1 mL) was stirred at 40 °C for 15 min under nitrogen. To the reaction mixture was added KOH (0.1 mL, 1.5M, 0.15 mmol) in water and the solution was stirred for 15 min. Arylboronic acid (1.0 mmol) and α,β -unsaturated carbonyl compound (0.50 mmol) was added to the solution. After stirring at 40 °C for 2 h, the reaction mixture was quenched with saturated NaHCO_3 and extracted with ether five times. The combined organic layers were dried over sodium sulfate and concentrated under reduced pressure. The residue was purified by preparative TLC (silica gel, hexane/EtOAc = 3/1). The products were characterized by their spectral data and analyzed by HPLC using chiral columns. The absolute configurations and ee values of the products were determined by comparison of the retention times with reported values.⁹

Conditions for the determination of the ee's by HPLC analysis. 3-Phenylcyclohexanone: Chiralcel OD-H, hexane:2-propanol = 98:2, 0.5 mL/min, wavelength 254 nm, retention times: 26.4 min (*S*), 28.2 min (*R*). 3-(4-Trifluoromethylphenyl)cyclohexanone: Chiralcel OJ, hexane:2-propanol = 98:2, 1.0 mL/min, wavelength 254 nm, retention times: 18.1 min (*R*), 20.5 min (*S*). 3-(4-Methoxyphenyl)cyclohexanone: Chiralcel OJ, hexane:2-propanol = 98:2, 1.0 mL/min, wavelength 254 nm, retention times: 34.6 min (*R*), 42.9 min (*S*). 3-Phenylcyclopentanone: Chiralcel OB, hexane:2-propanol = 98:2, 1.0 mL/min, wavelength 254 nm, retention times: 16.5 min (*S*), 22.4 min (*R*). 5-Methyl-4-phenylhexan-2-one: Chiralcel OJ, hexane:2-propanol = 98:2, 0.5 mL/min, wavelength 254 nm, retention times: 16.3 min (*R*), 20.0 min (*S*).

In a similar manner, 2-cyclohexenone (0.50 mmol) was reacted with phenylboronic acid in the presence of $[\text{Rh}(\text{nbd})_2]\text{BF}_4/t\text{Bu-BisP}^*$ (2 mol%) at 40 °C. The reaction was sluggish and after 2 h the reaction mixture was worked up to give 3-phenylcyclohexanone in 37% yield. The ee of this product was determined to be 20% by HPLC analysis.

General Procedure for the Alkylative Ring-Opening of Oxabenzonorbornadiene Derivatives

A solution of $\text{PdCl}_2(\text{cod})$ (1.1 mg, 8.0 μmol) and (*S,S*)-1,2-bis(1-alkynyl(*tert*-butyl)phosphino)ethane (AlkynylP*) (8.8 μmol) in CH_2Cl_2 (1 mL) was stirred at 40 °C under nitrogen for 15 min. To the solution was added a solution of oxabenzonorbornadiene (58 mg, 0.4 mmol) in CH_2Cl_2 (3 mL), followed by dimethylzinc (0.6 mL of 1.0 M hexane solution). The resulting solution was stirred at room temperature until completion of the reaction. The reaction was quenched by the addition of a few drops of water and the mixture was passed through a short plug of Celite and then concentrated. The residue was purified by preparative TLC (hexane/EtOAc).

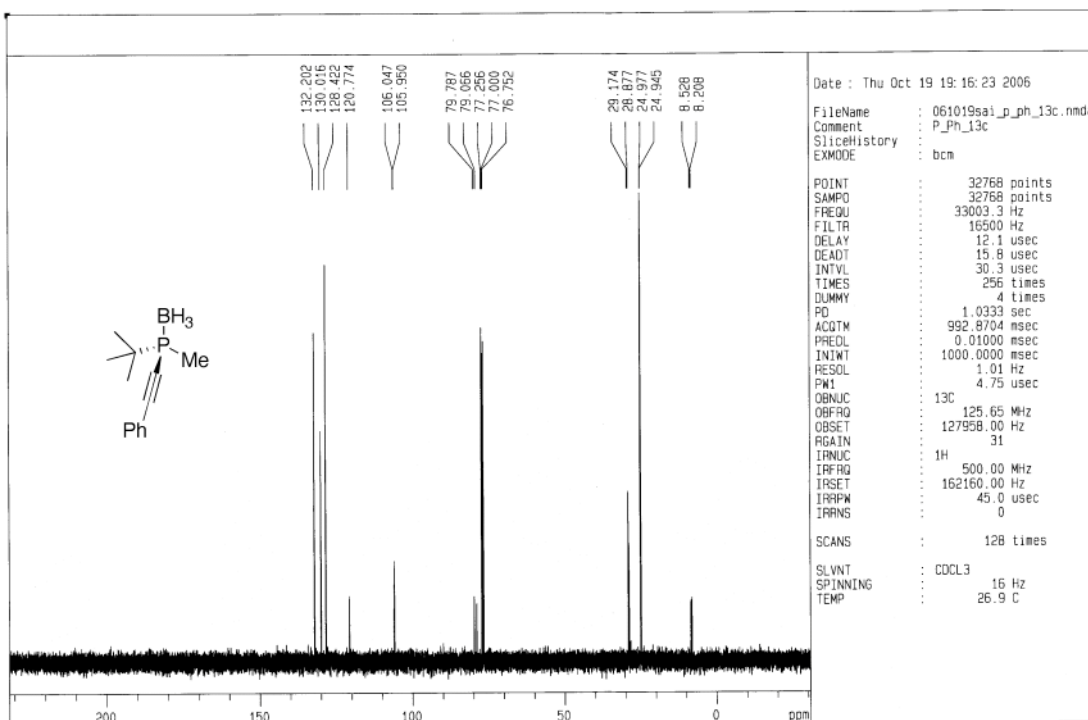
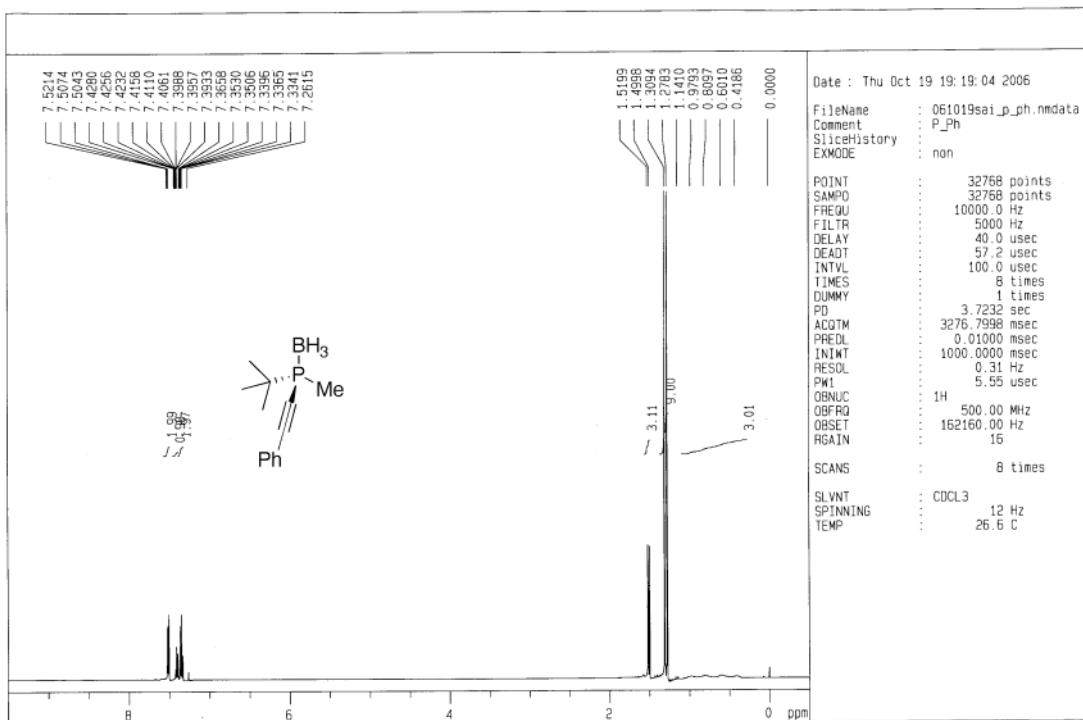
The products were characterized by their spectral data and analyzed by HPLC using chiral columns. The absolute configurations and ee values of the products were determined by comparison of the retention times with reported values.¹⁰

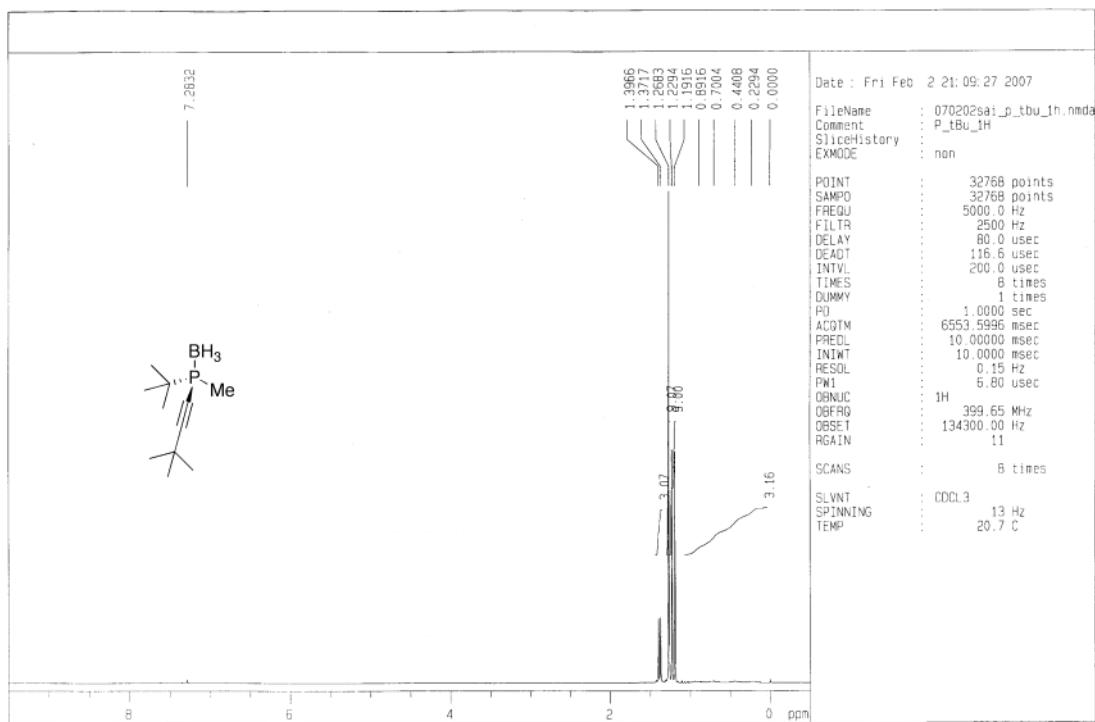
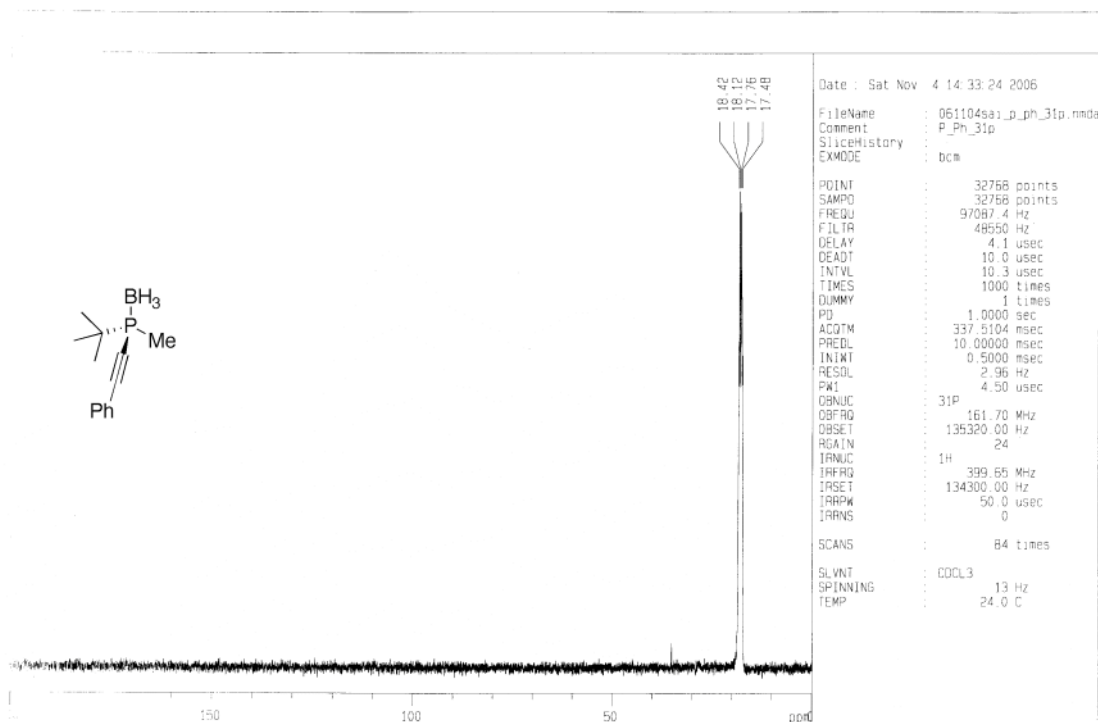
Conditions for the determination of the ee's by HPLC analysis. 2-Methyl-1,2-dihydronaphthalen-1-ol: Chiralcel OD-H, hexane:2-propanol = 199:1, 1 mL/min, wavelength 254 nm, retention times: 28.5 min (1*R*,2*R*), 30.6 min (1*S*,2*S*); 2-Ethyl-1,2-dihydronaphthalen-1-ol: Chiralcel OD-H, hexane:2-propanol = 199:1, 1 mL/min, wavelength 254 nm, retention times: 26.0 min (1*R*,2*R*), 29.6 min (1*S*,2*S*). 2-Methyl-1,2-dihydro-5,8-bis(methoxymethoxy)-naphthalen-1-ol: Chiralcel OD-H, hexane:2-propanol = 9:1, 1.0 mL/min, wavelength 254 nm, retention times: 9.0 min (1*R*,2*R*), 11.1 min (1*S*,2*S*). 2-Ethyl-1,2-dihydro-5,8-bis(methoxymethoxy)-naphthalen-1-ol: Chiralcel OD-H, hexane:2-propanol = 9:1, 0.5 mL/min, wavelength 254 nm, retention times: 15.5 min (1*R*,2*R*), 17.0 min (1*S*,2*S*).

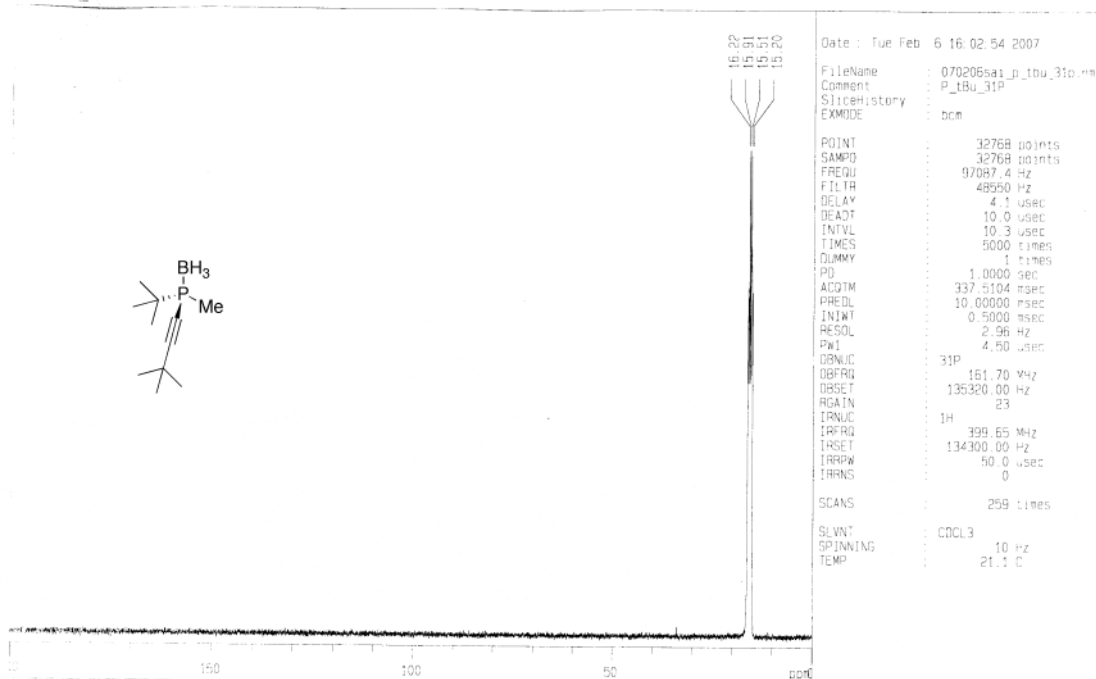
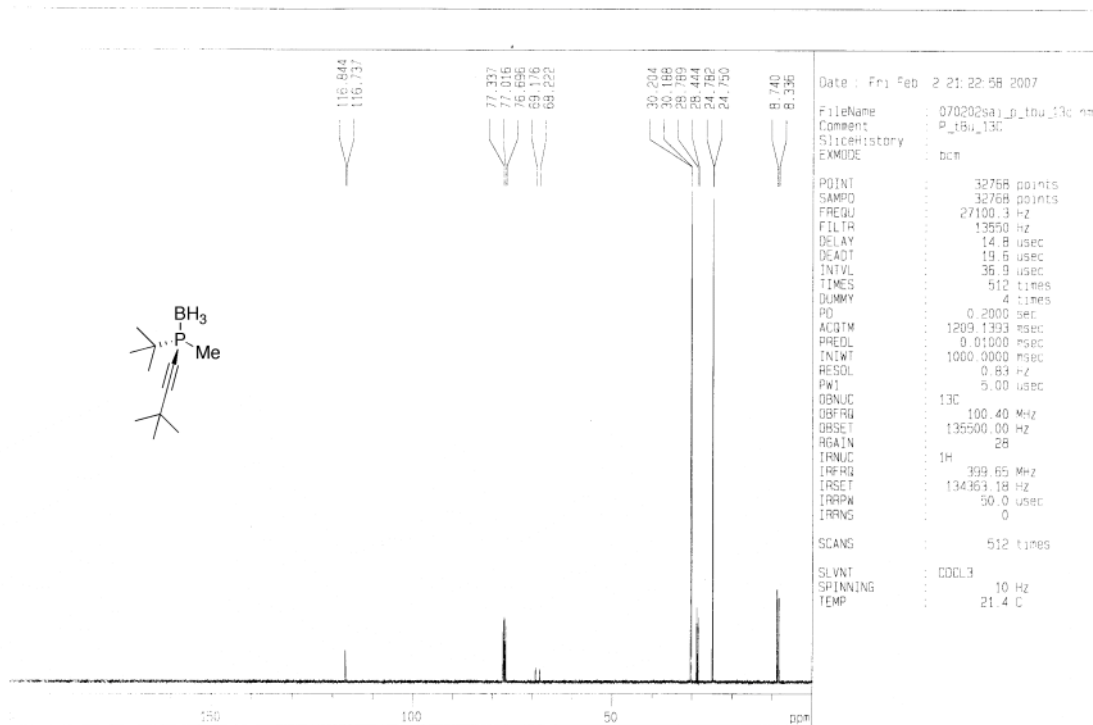
In a similar manner, oxabenzonorbornadiene (0.4 mmol) was reacted with diethylzinc in the presence of PdCl₂(cod)/*t*Bu-BisP* (2 mol%) at room temperature for 6 h to give (1*S*,2*S*)-2-ethyl-1,2-dihydronaphthalen-1-ol in 93% yield. The ee of this product was determined to be 94% by HPLC analysis.

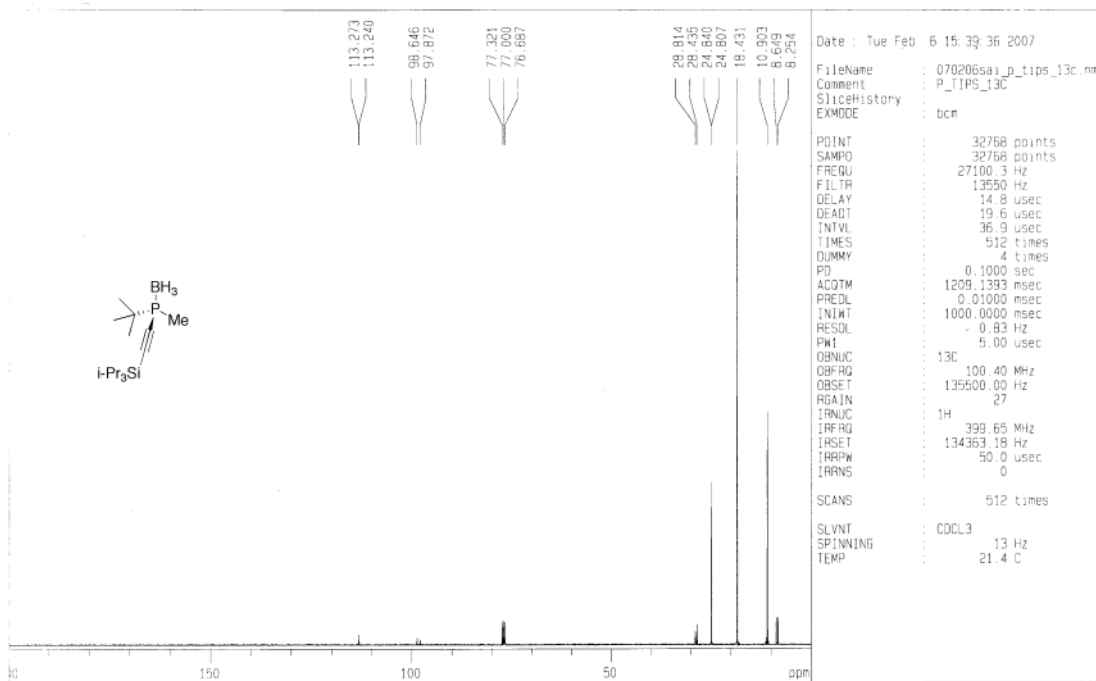
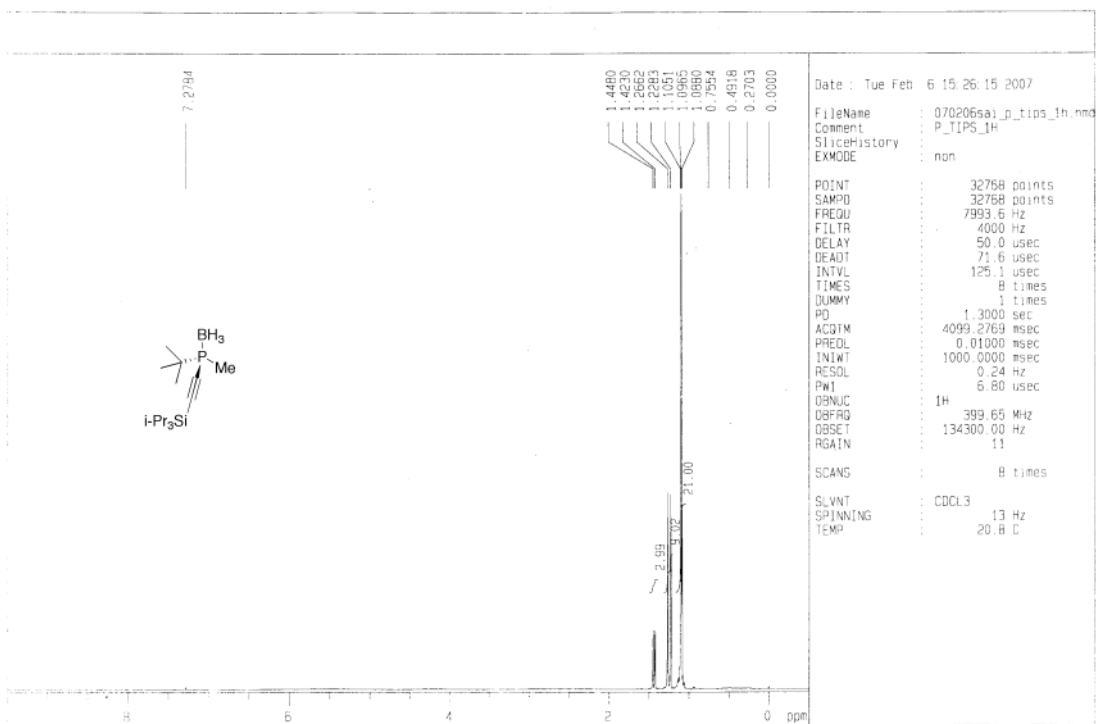
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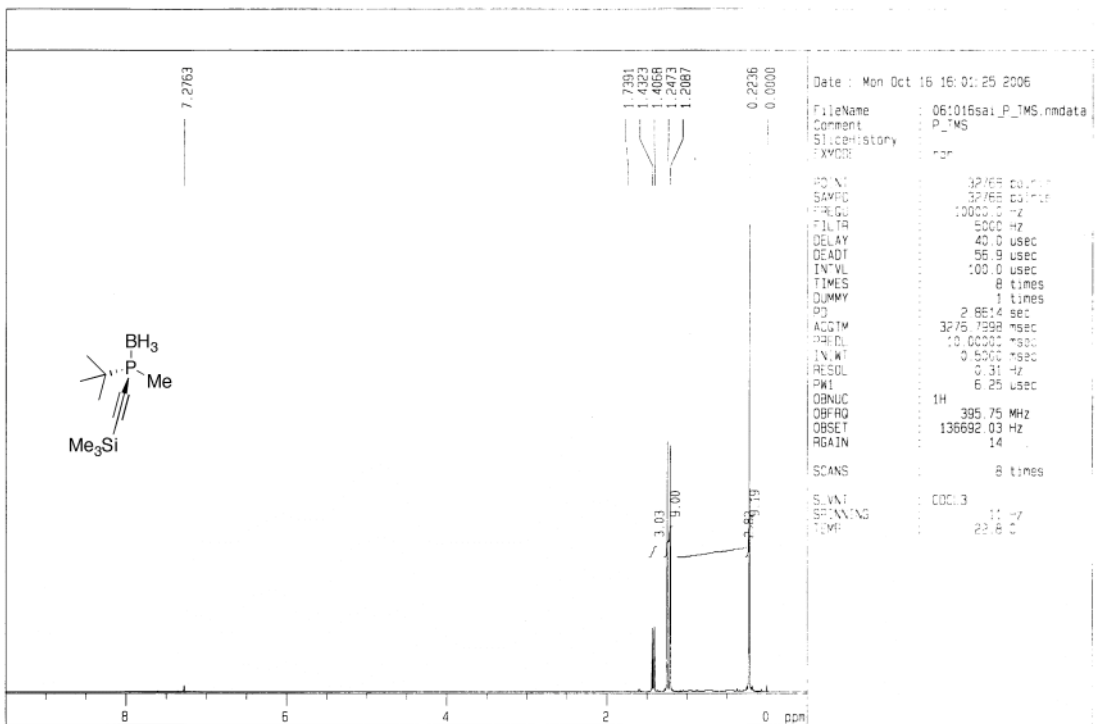
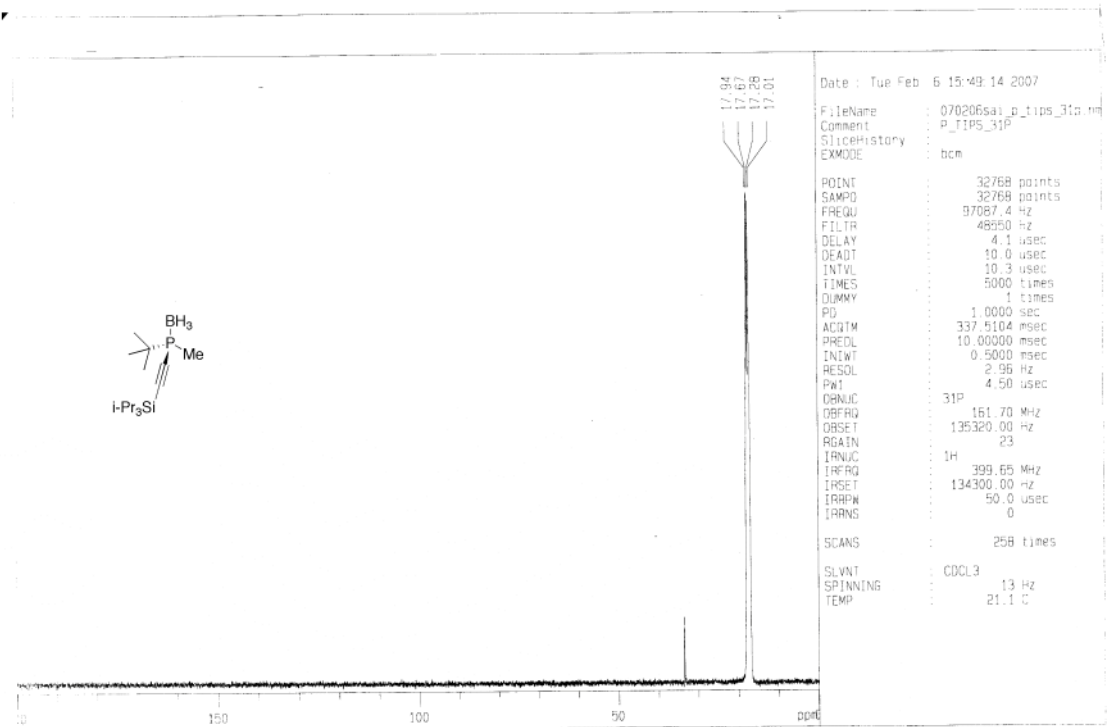
- [1] T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, *J. Am. Chem. Soc.* **1990**, *112*, 5244–5252.
- [2] T. Imamoto, M. Matsuo, T. Nonomura, K. Kishikawa, M. Yanagawa, *Heteroatom Chem.* **1993**, *4*, 475–486.
- [3] E. J. Corey, Z. Chen, G. J. Tanoury, *J. Am. Chem. Soc.* **1993**, *115*, 11000–11001.
- [4] M. Stankevic, K. M. Pietrusiewicz, *J. Org. Chem.* **2007**, *72*, 816–822.
- [5] Y. Takahashi, Y. Yamamoto, K. Katagiri, H. Danjo, K. Yamaguchi, T. Imamoto, *J. Org. Chem.* **2005**, *70*, 9009–9012.
- [6] T. Miura, H. Yamada, S. Kikuchi, T. Imamoto, *J. Org. Chem.* **2000**, *65*, 1877–1880.
- [7] H. Danjo, W. Sasaki, T. Miyazaki, T. Imamoto, *Tetrahedron Lett.* **2003**, *44*, 3467–3469.
- [8] Imamoto, T.; Watanabe, J.; Wada, Y.; Masuda, H.; Yamada, H.; Tsuruta, H.; Matsukawa, S.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 1635–1636.
- [9] Takaya, Y.; Ogasawara, M.; Hayashi, T.; Sakai, M.; Miyaura, N. *J. Am. Chem. Soc.* **1998**, *120*, 5579–5580.
- [10] Lautens, M.; Renaud, J.-L.; Hiebert, S. *J. Am. Chem. Soc.* **2000**, *122*, 1804–1805.

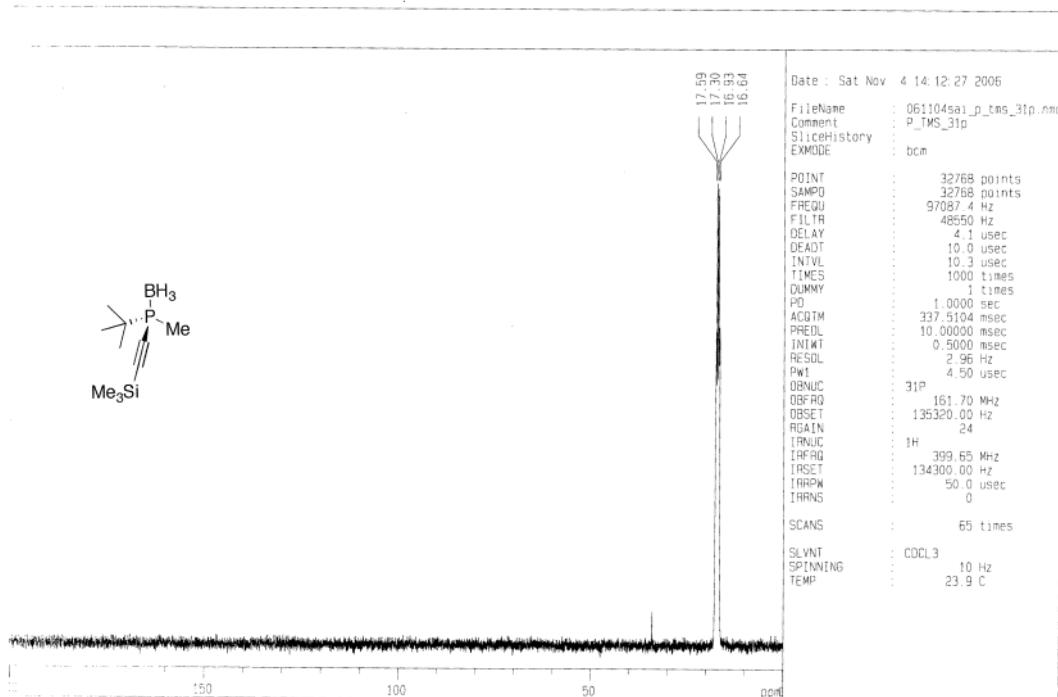
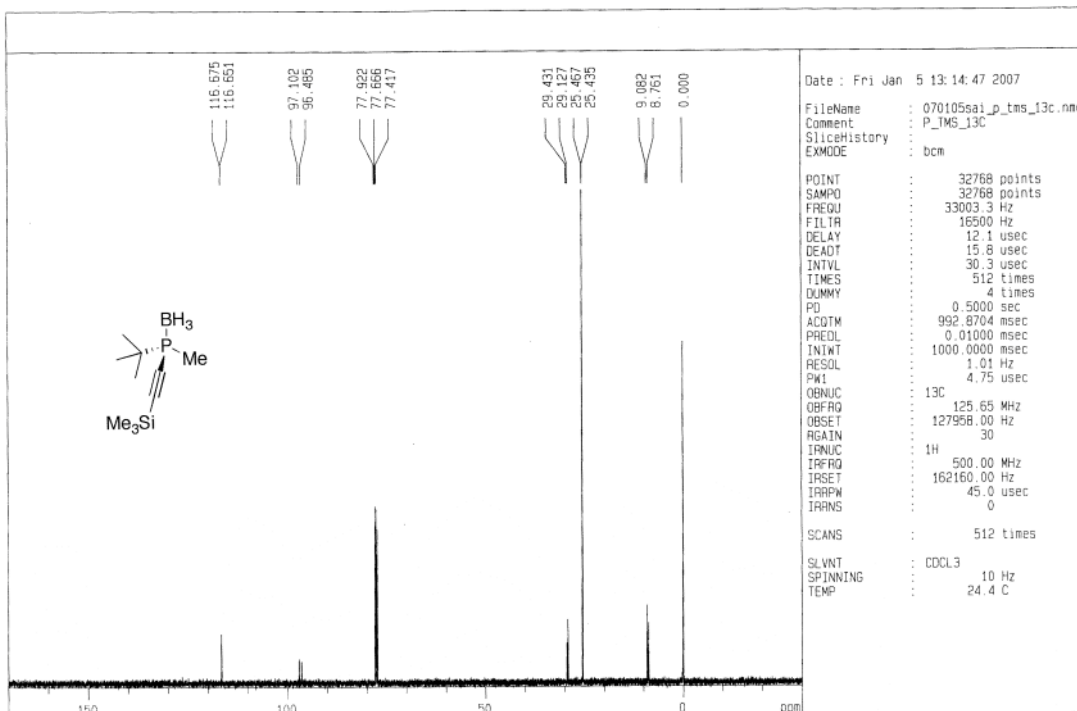


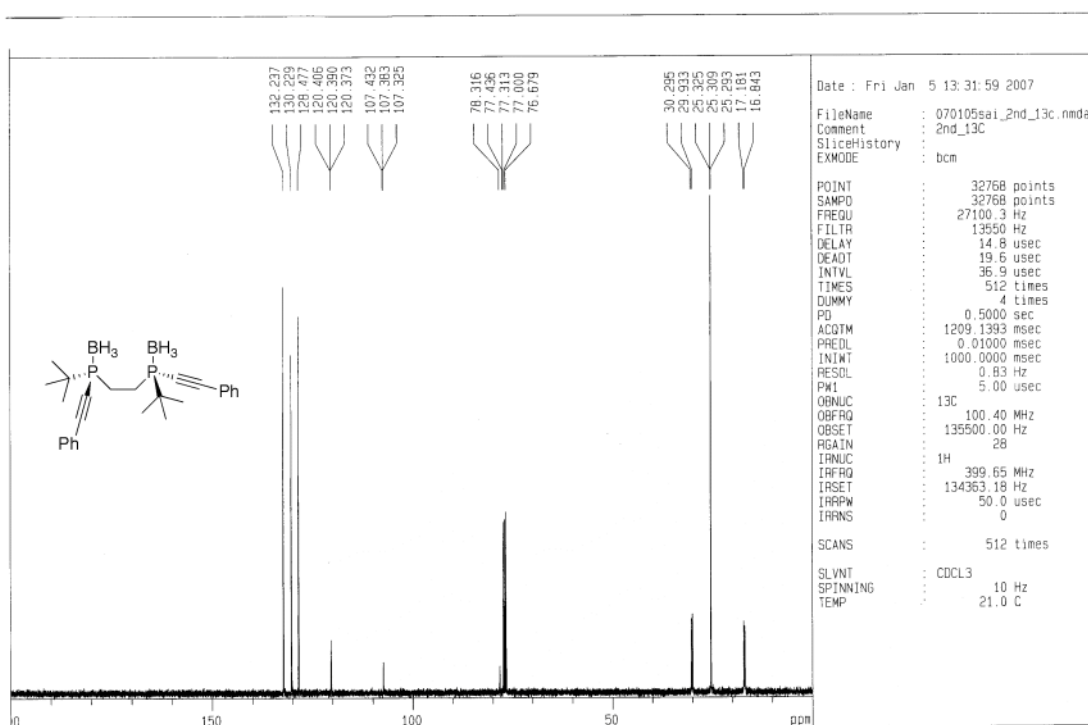
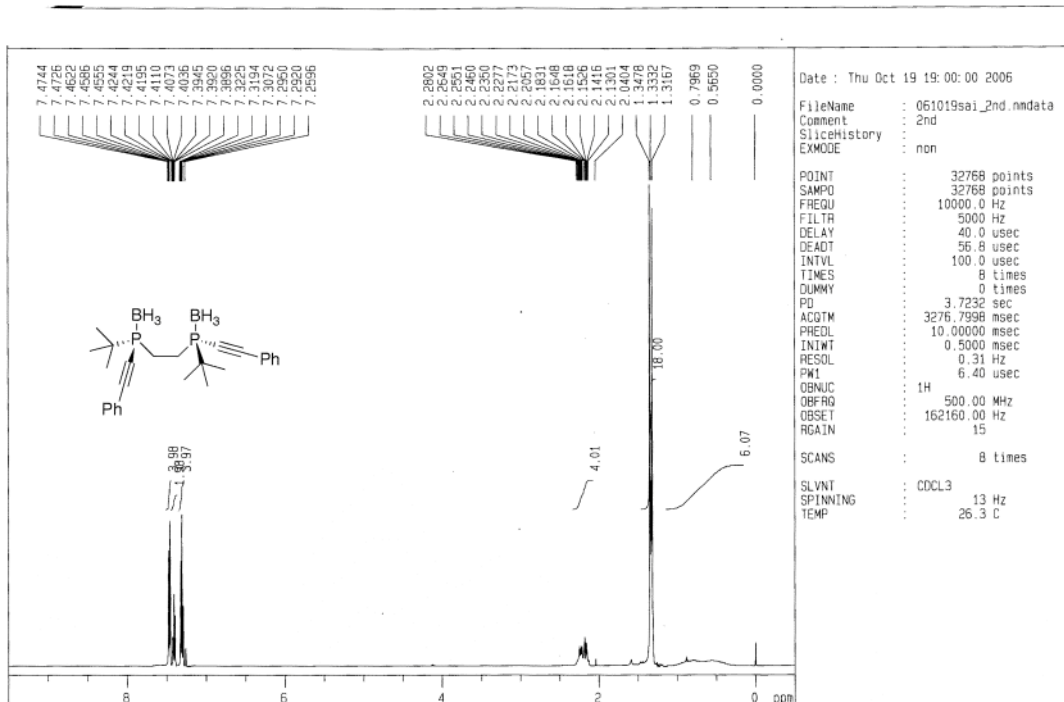


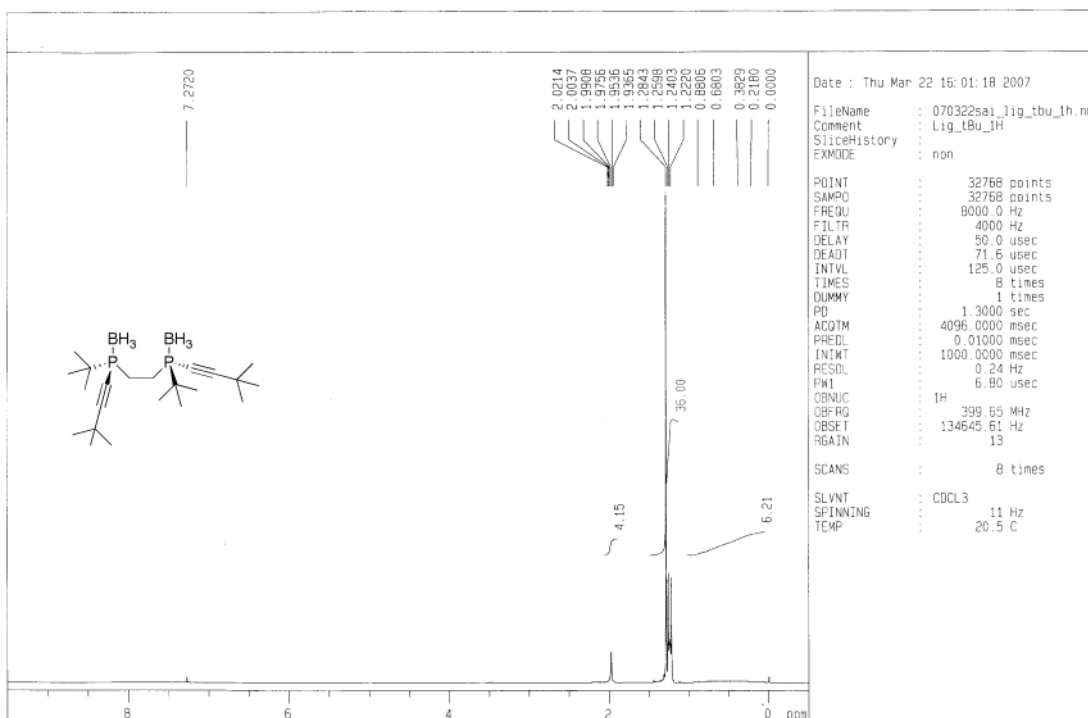
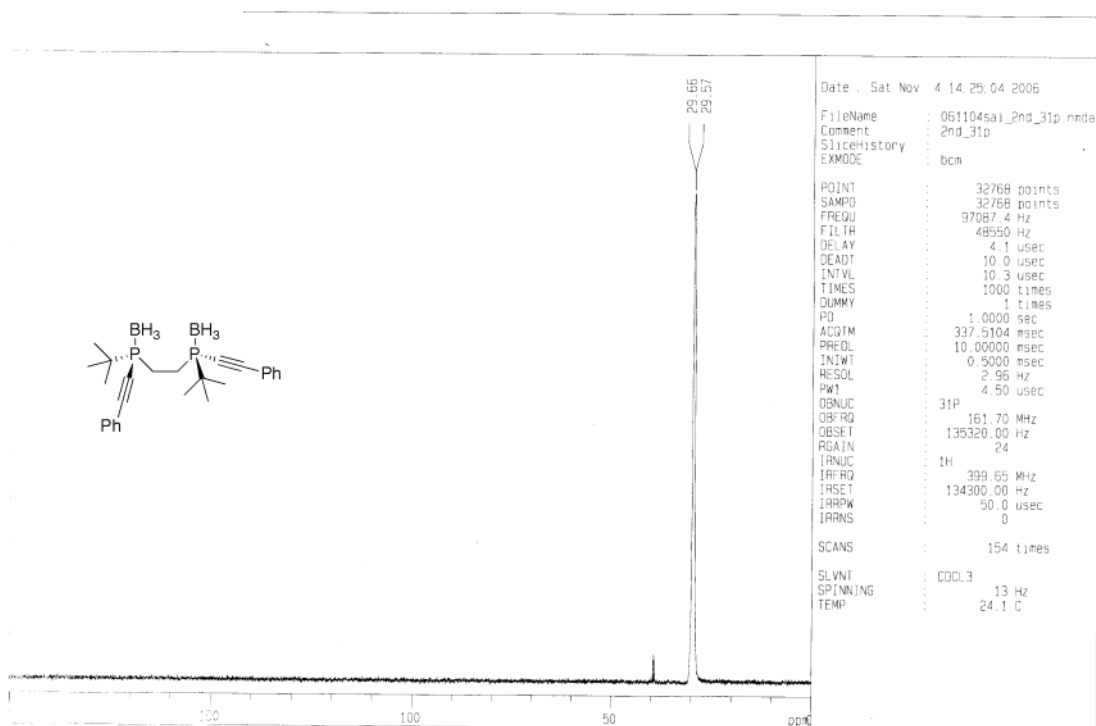


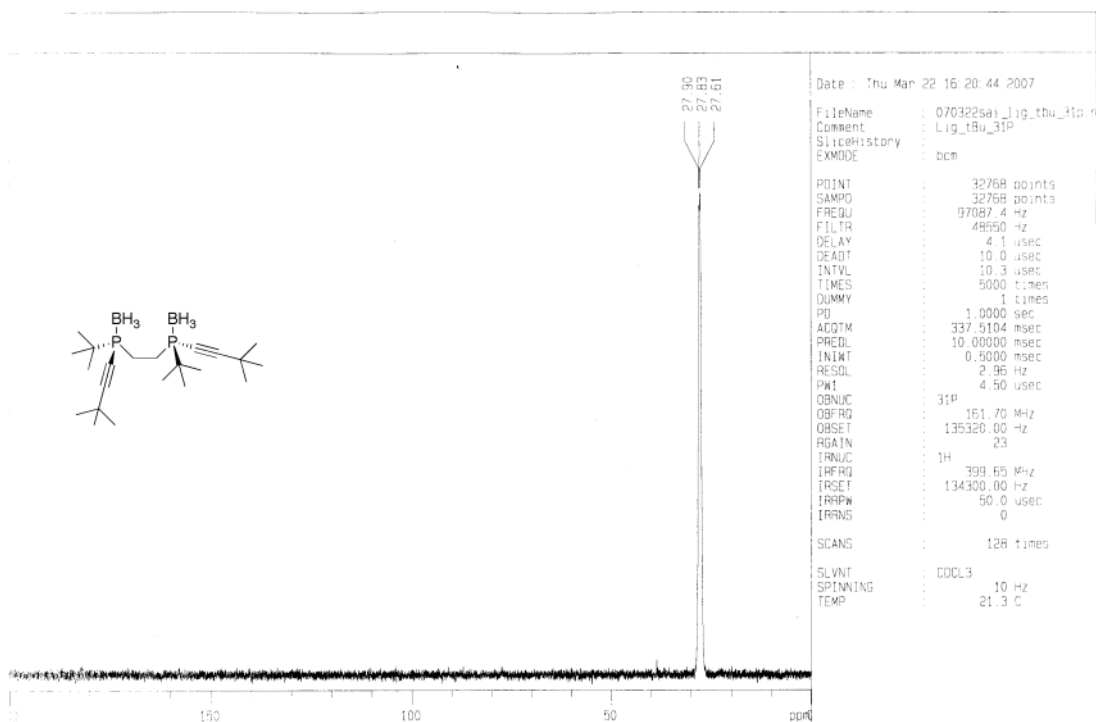
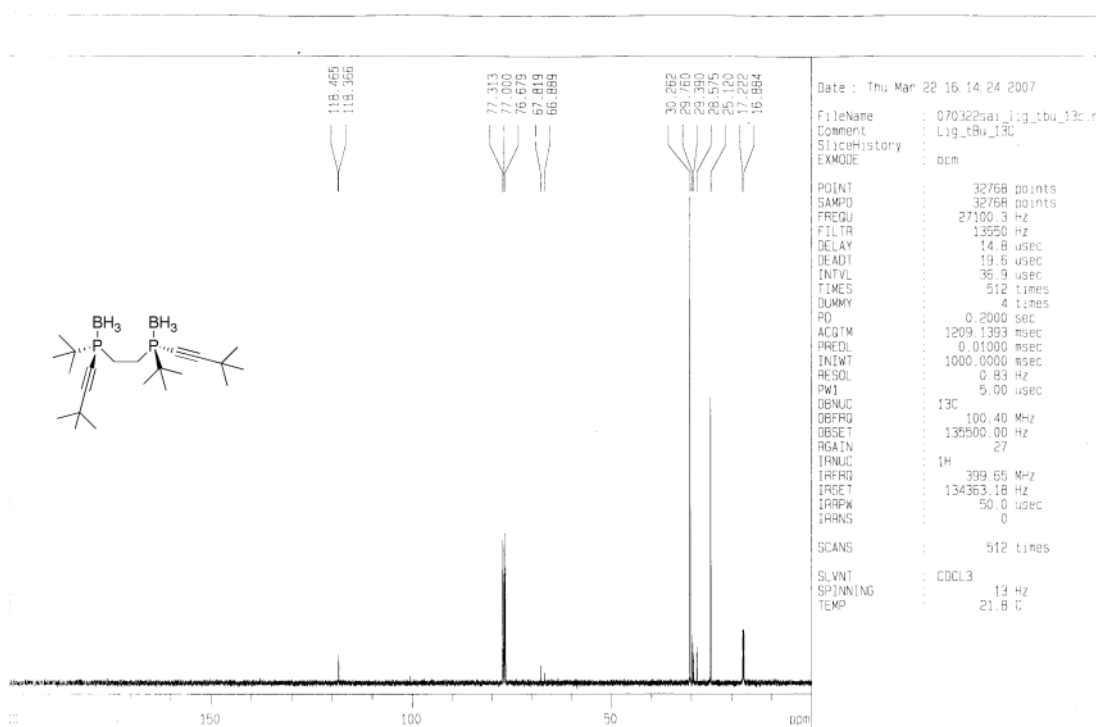


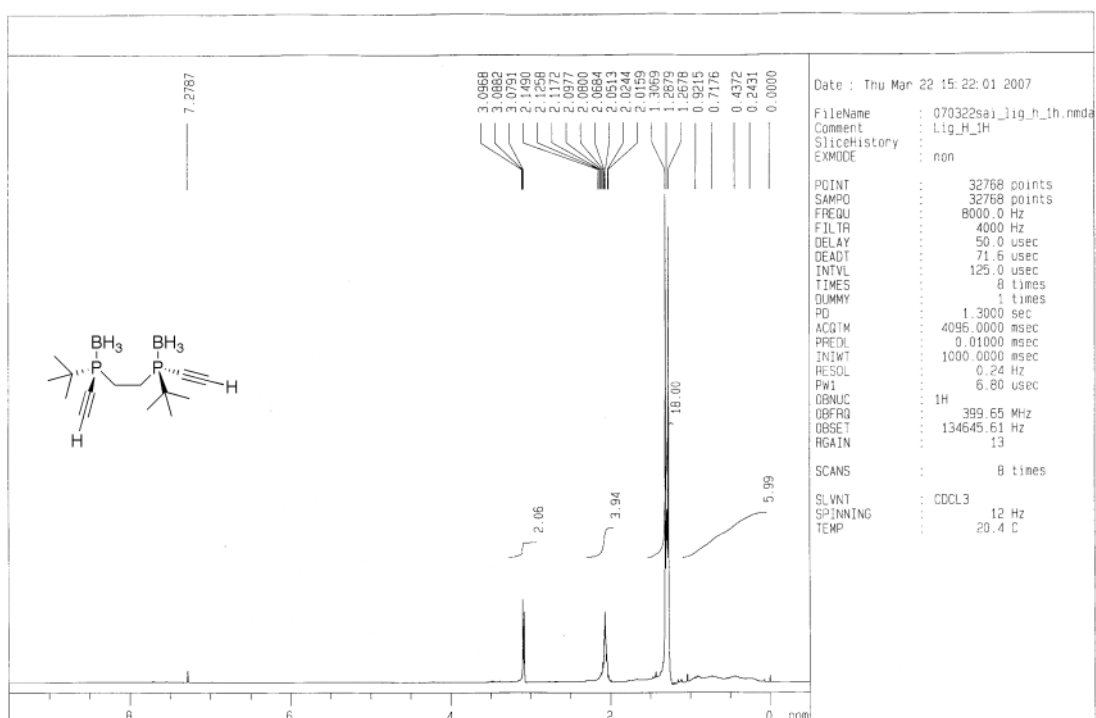
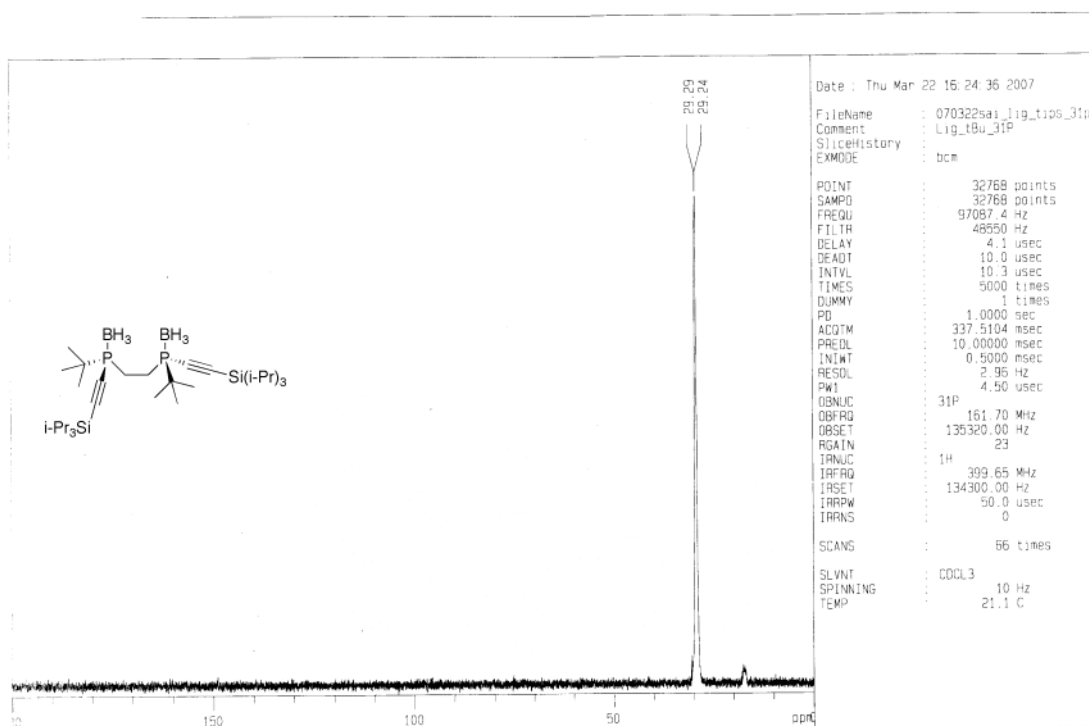


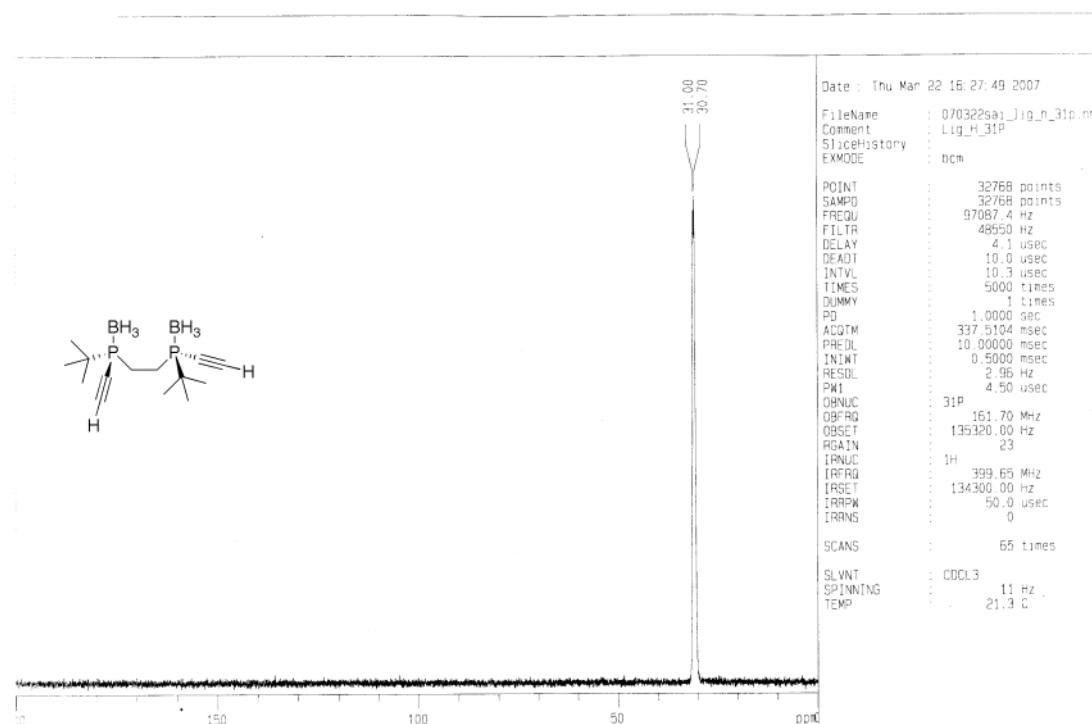
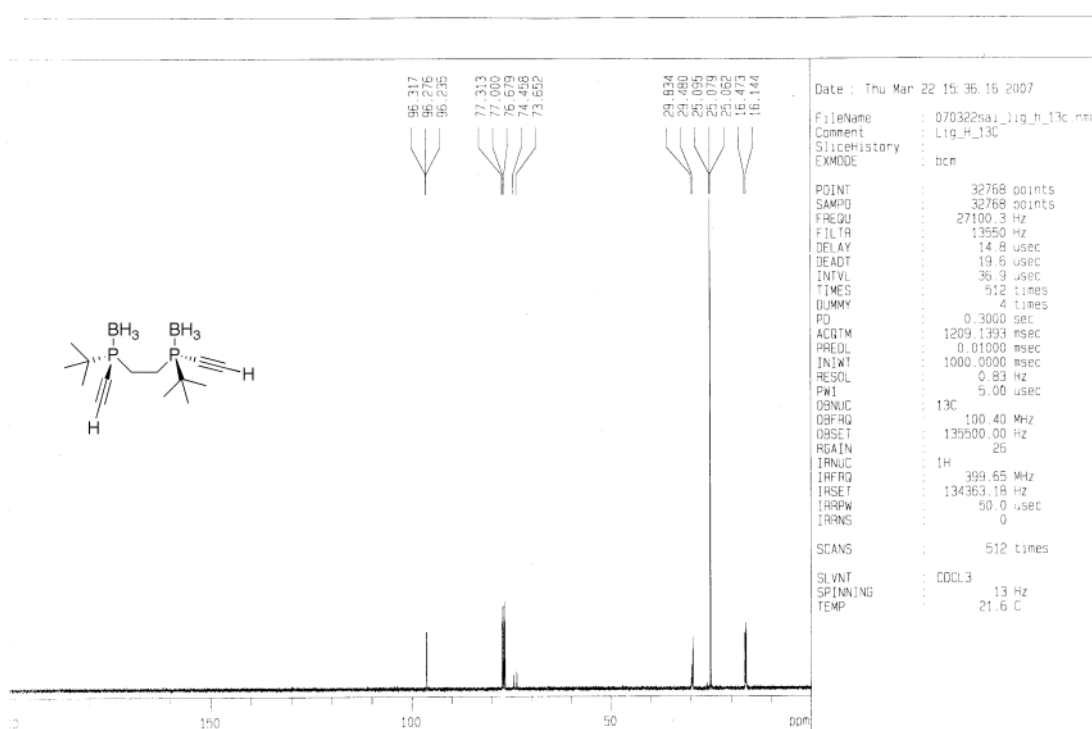


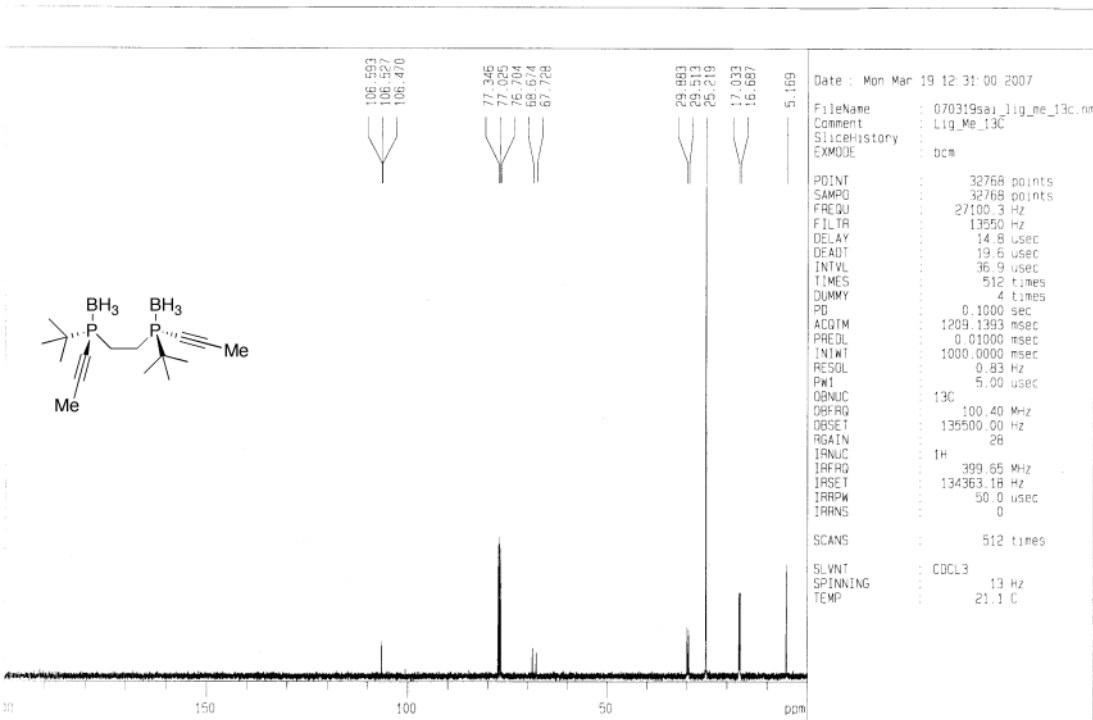
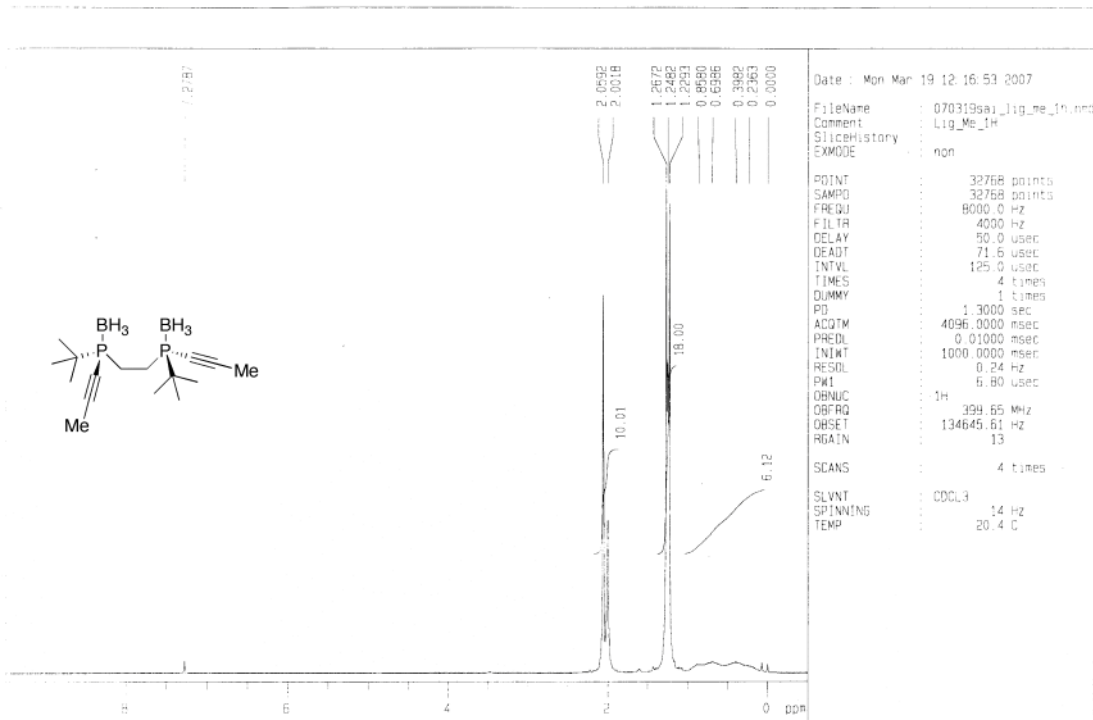


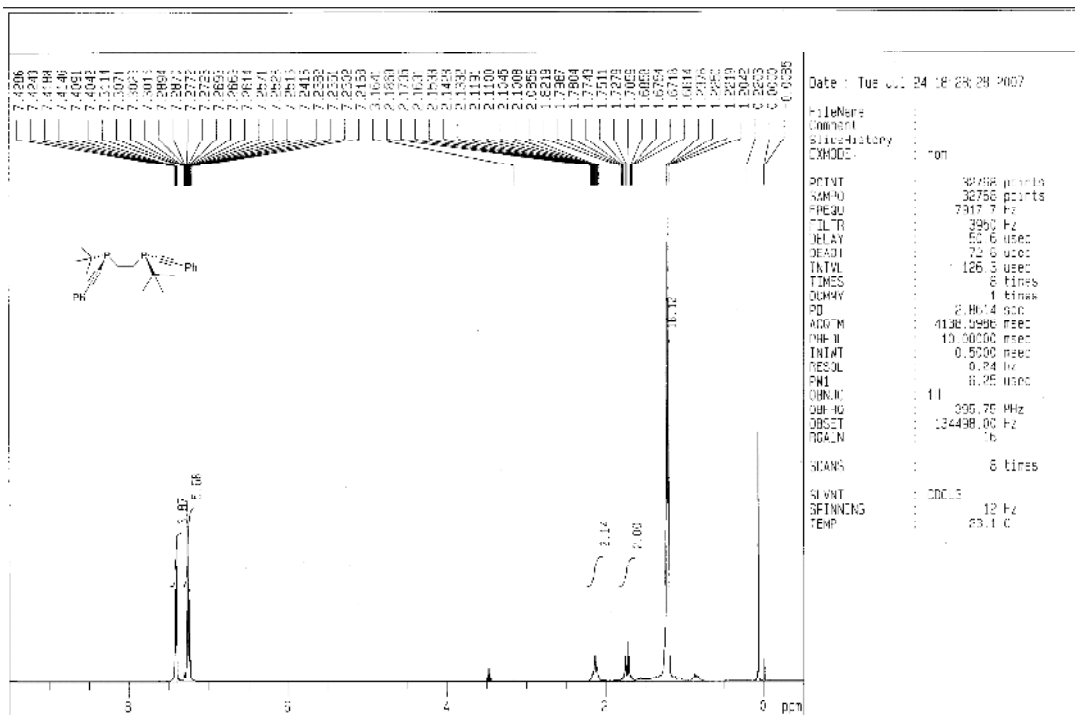
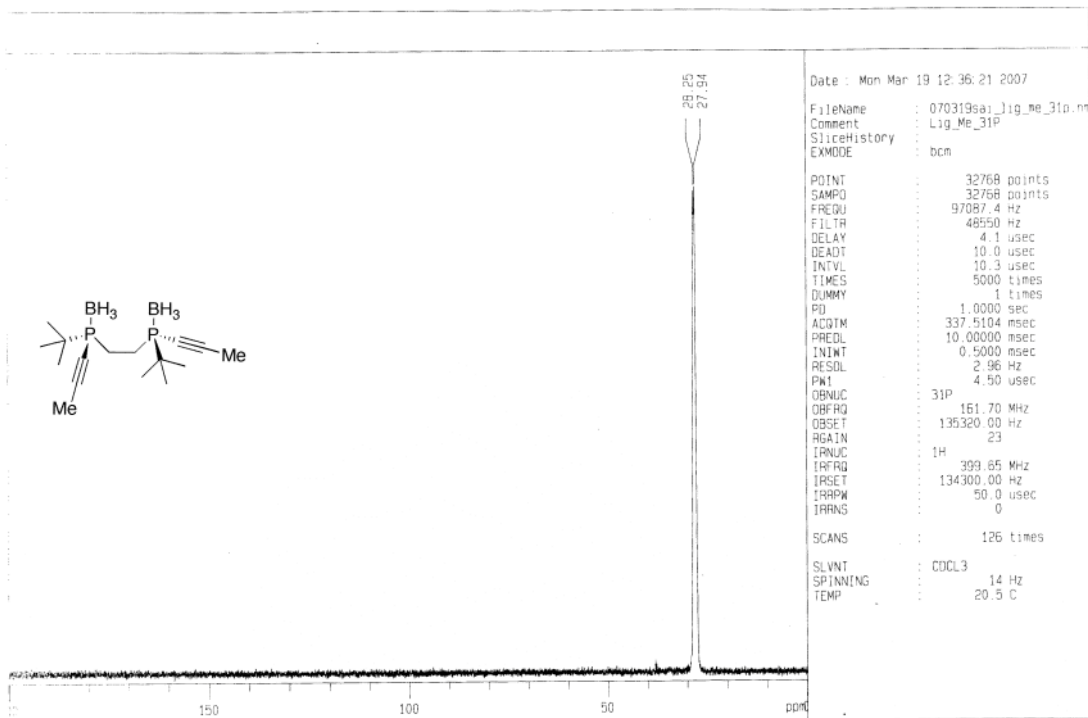


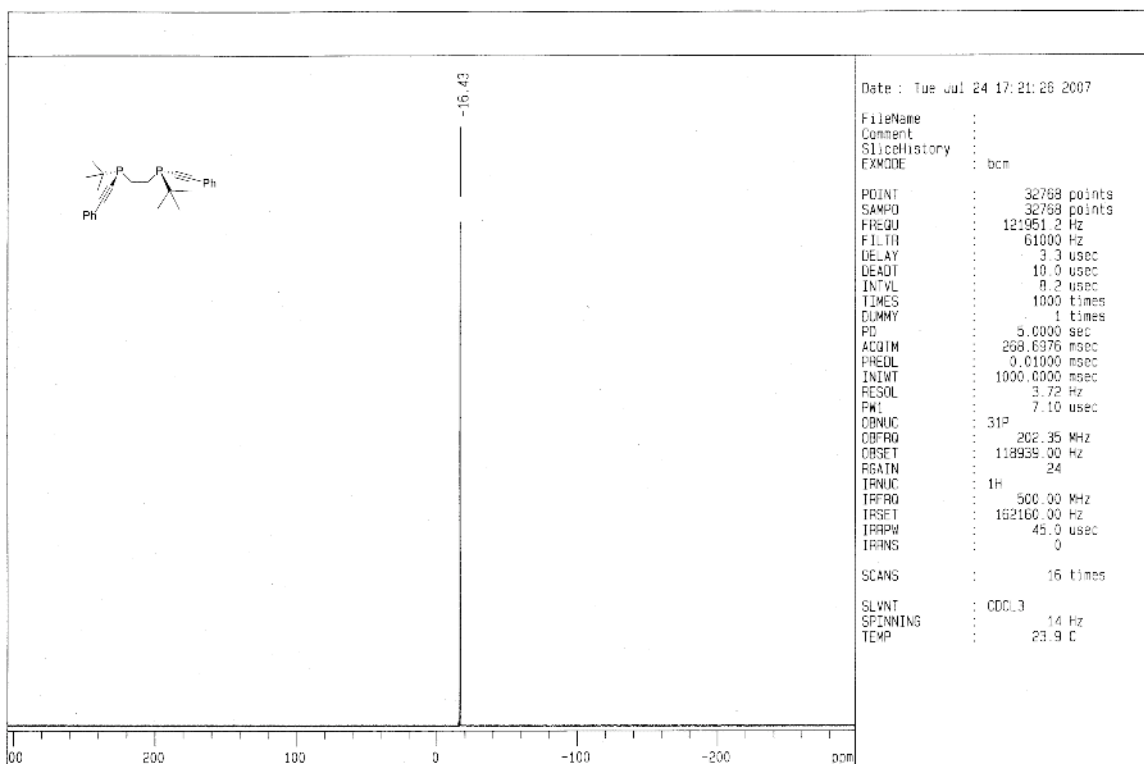
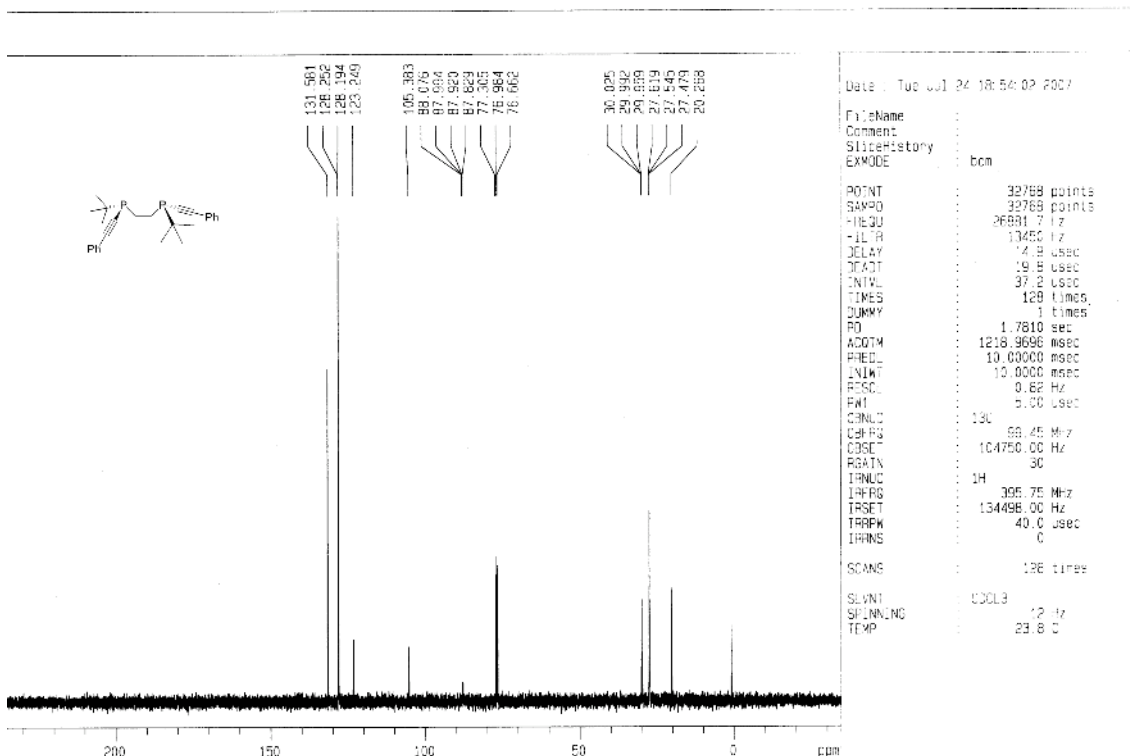


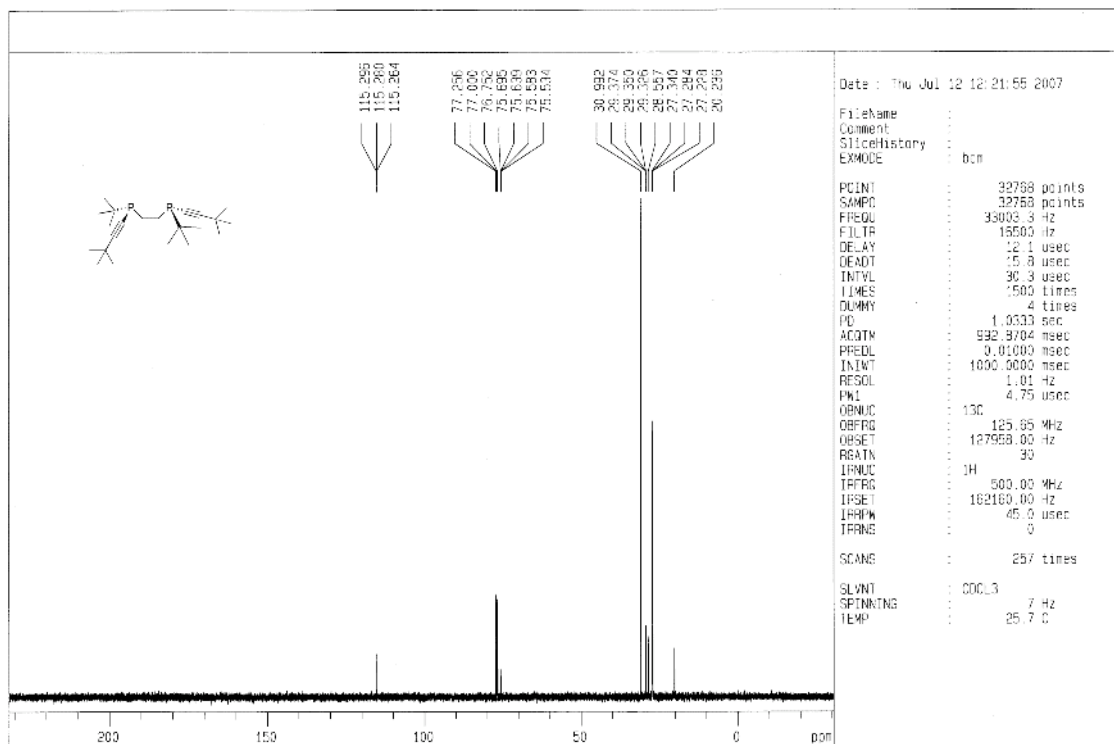
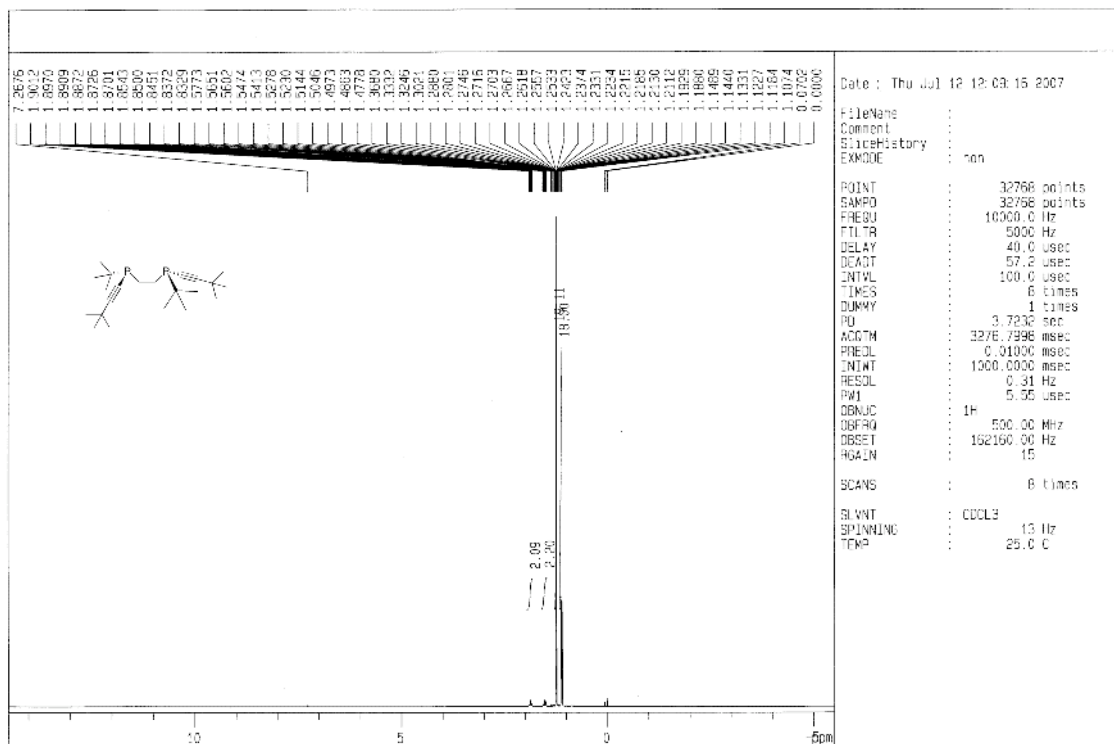


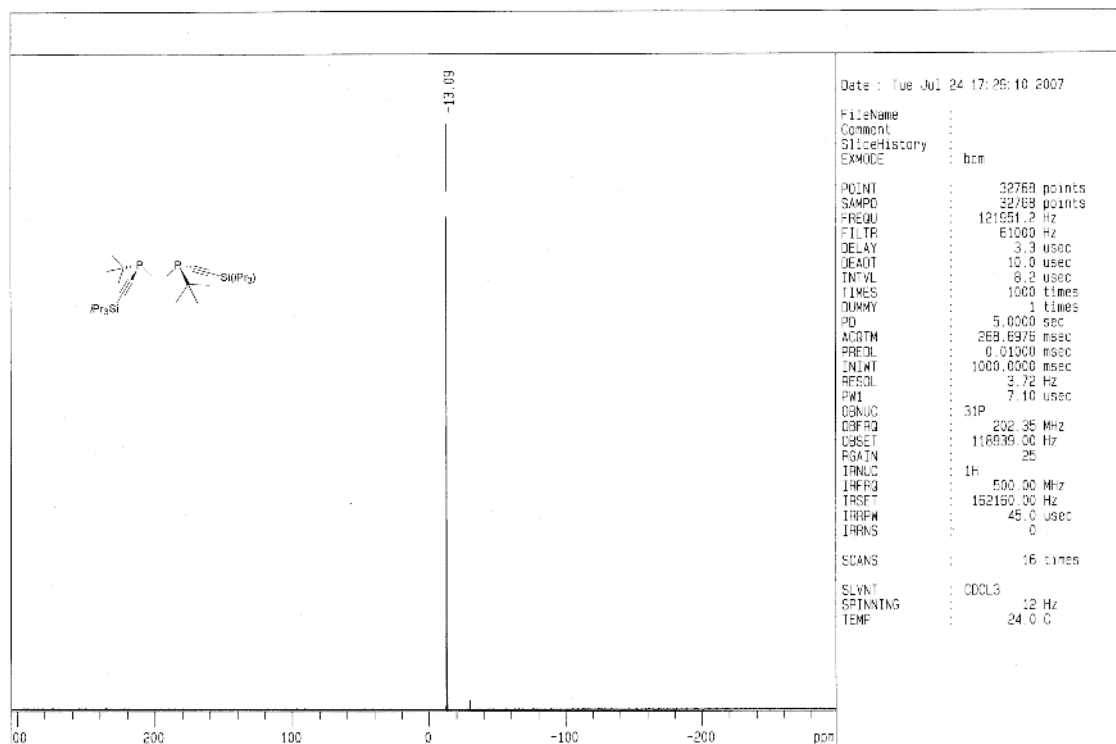
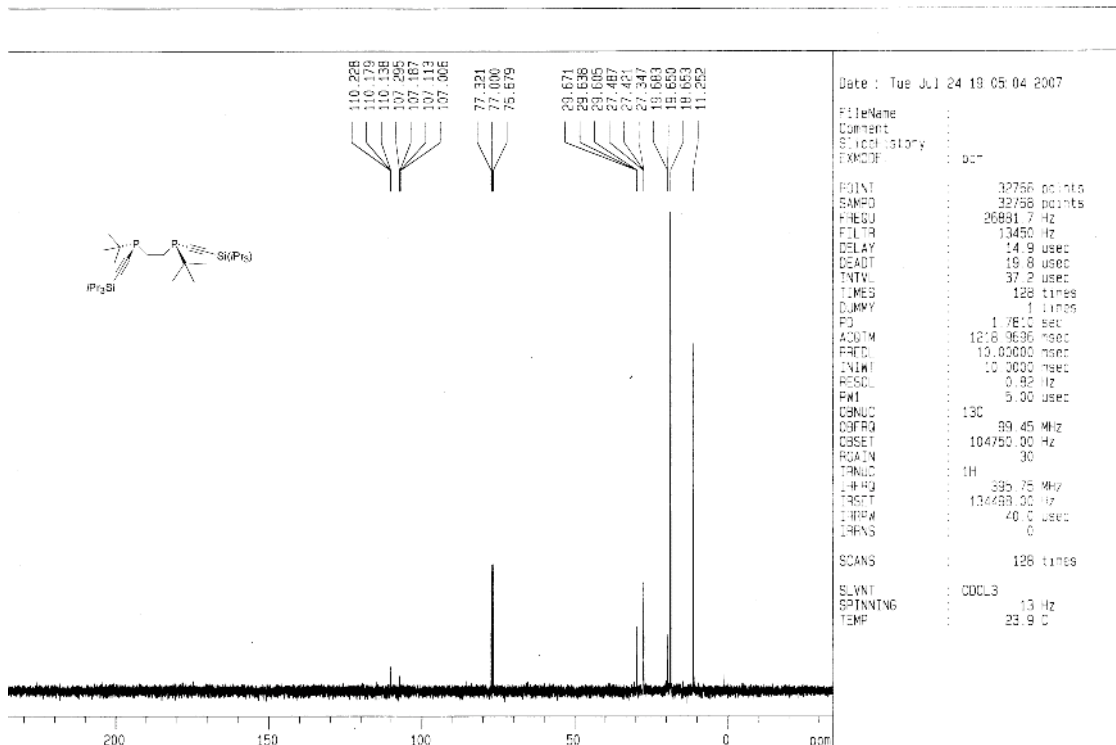


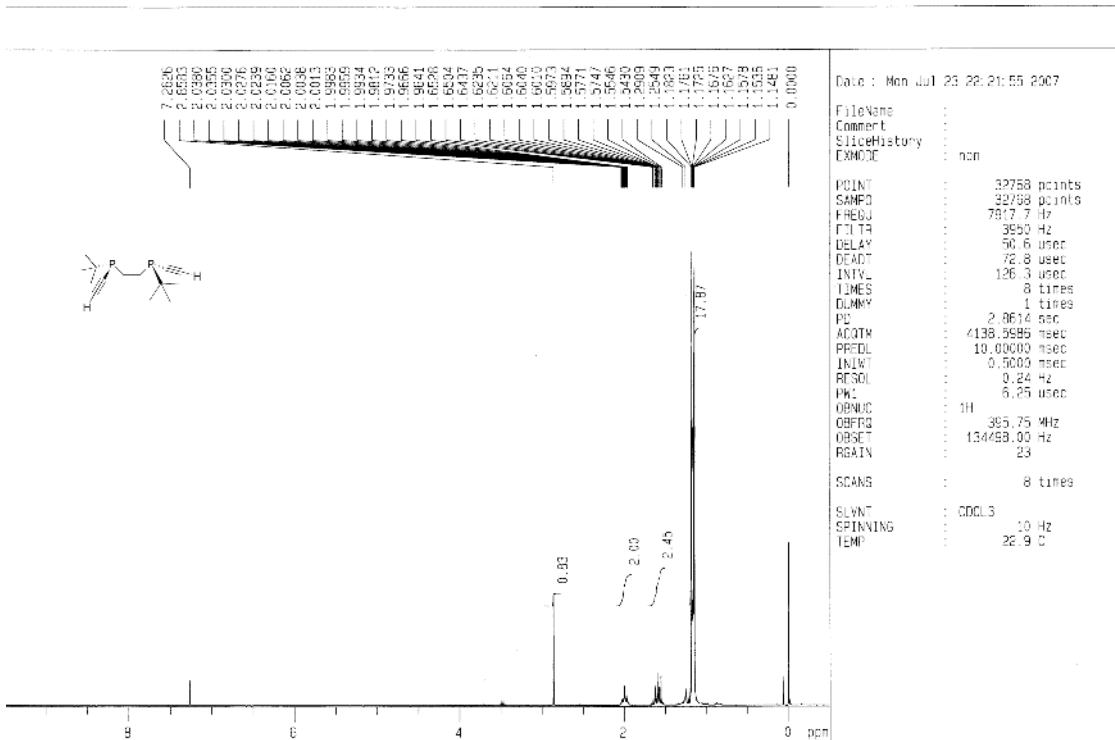












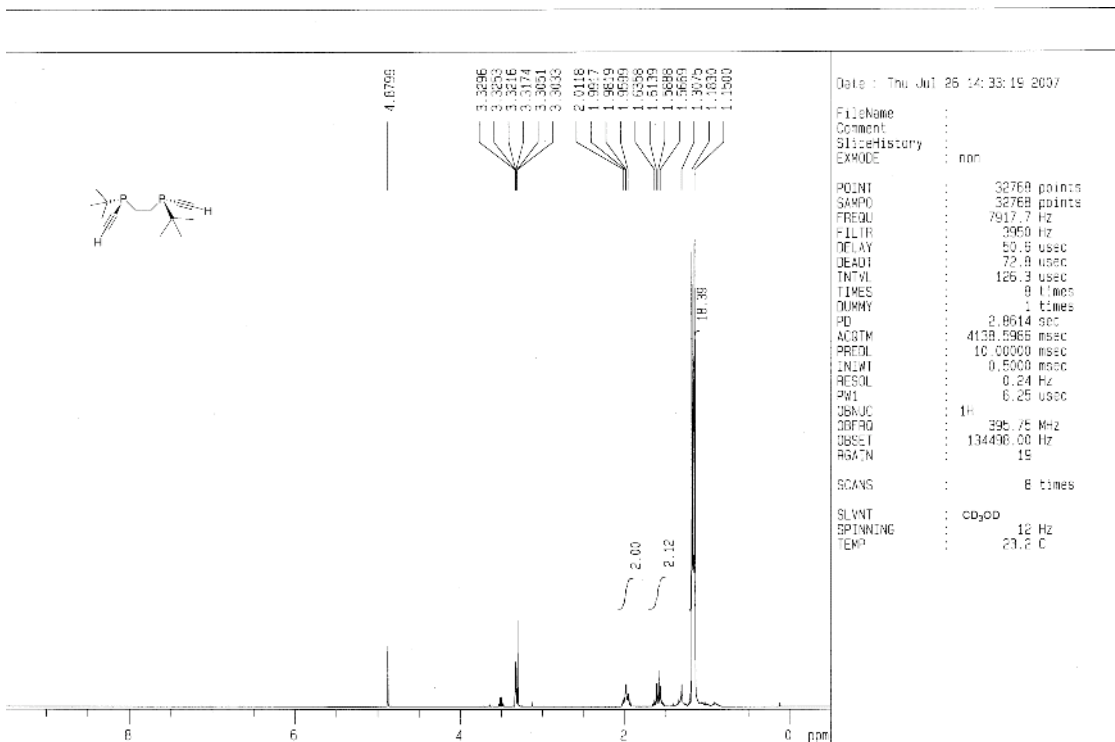
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