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Room Temperature Alkynylation of *H*-Phosphi(na)tes and Secondary Phosphine Oxides with Ethynylbenziodoxolones (EBX) Reagents

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(60 pages)

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1. General Method

All chemicals were purchased from Acros, Aldrich, Fluka, VWR, Aplichem, Maybrige, TCI or Merck and used as such unless stated otherwise. Chromatographic purification was performed as flash chromatography using Macherey-Nagel silica 40-63, 60 Å, using the solvents indicated as eluent with 0.1-0.5 bar pressure. TLC was performed on Merck silica gel 60 F_{254} TLC glass plates or aluminium plates and visualized with UV light, permanganate stain, CAN stain or Anisaldehyde stain.Melting points were measured on a Büchi B-540 melting point apparatus using open glass capillaries, the data is uncorrected. ^{1}H-NMR spectra were recorded on a Brucker DPX-400 400 MHz spectrometer in chloroform-d, DMSO-d_6 or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 7.26 ppm, the internal DMSO signal at 2.50 ppm or the internal methanol signal at 3.30 ppm as standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quadruplet, qi = quintet, m = multiplet or unresolved, br = broad signal, app = apparent, coupling constant(s) in Hz, integration, interpretation).^{13}C-NMR spectra were recorded with ^{1}H-decoupling on a Bruker DPX-400 100 MHz spectrometer in chloroform-d, DMSO-d_6 or CD_3OD, all signals are reported in ppm with the internal chloroform signal at 77.0 ppm, the internal DMSO signal at 39.5 ppm or the internal methanol signal at 49.0 ppm as standard. ^{31}P-NMR spectra were recorded on a Brucker DPX-400 162 MHz spectrometer in chloroform-d. ^{19}F-NMR spectra were recorded on a Brucker DPX-400 376 MHz spectrometer in chloroform-d. No internal standard was used for ^{31}P-NMR and ^{19}F-NMR spectra. Infrared spectra were recorded on a JASCO FT-IR B4100 spectrophotometer with an ATR PRO410-S and a ZnSe prisma and are reported as cm^{-1} (w = weak, m = medium, s = strong, br = broad). Gas chromatographic and low resolution mass spectrometric measurements were performed on a Perkin-Elmer Clarus 600 gas chromatographer and mass spectrometer using a Perkin-Elmer Elite fused silica column (length: 30 m, diameter: 0.32 mm) and Helium as carrier gas. High resolution mass spectrometric measurements were performed by the mass spectrometry service of ISIC at the EPFL on a MICROMASS (ESI) Q-TOF Ultima API.

2. Synthesis of Reagents and Starting Materials

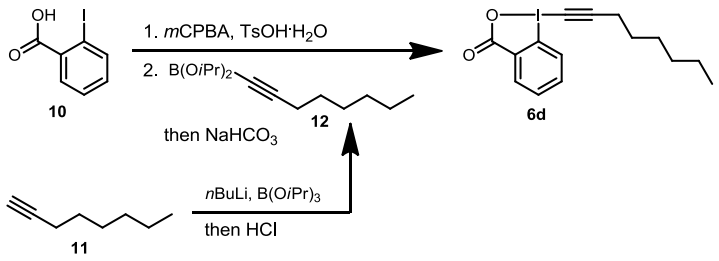
TIPS-EBX (**6a**), Ph-EBX (**6b**) and *t*Bu-EBX (**6c**) were made using our reported protocols.[1] *n*Hex-EBX (**6d**) was made using a reported procedure.[2]

Diethyl phosphite (**5a**), dimethyl phosphite (**5b**), dibenzyl phosphite (**5c**), ethyl phenylphosphinate (**5e**), phenyl phosphoric acid (**5i**), di-phenylphosphine oxide (**8a**), 3'-Azido-3'-deoxythymidine, Di-*tert*-butylphosphine oxide (**8h**) are commercially available from Sigma-Aldrich or TCI.

Dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (**5d**), *tert*-butyl(phenyl)phosphine oxide (**8e**), (2*R*,5*R*)-2,5-diphenylphospholane 1-oxide (**8f**), and dicyclohexylphosphine oxide (**8g**) were generously given by Dr. Pavel Donets and Prof. Nicolai Cramer from the Laboratory of Asymmetric Catalysis and Synthesis at EPFL.

Allyl phenylphosphinate (**5f**),[3] (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl phenylphosphinate (**5g**),[4] di-p-tolylphosphine oxide (**8b**),[5] bis(4-fluorophenyl)phosphine oxide (**8c**),[4] dibutylphosphine oxide (**8d**),[4] *t*-butyl(phenyl)phosphine oxide (**8e**), were made using reported literature procedures.

Octynyl-1,2-benziodoxol-3(1*H*)-one (6d)



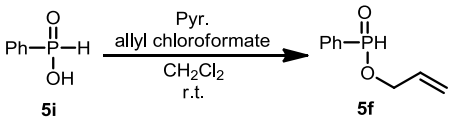
Following a slightly modified procedure,[6] a solution of 1-octyne (**11**) (747 mg, 6.78 mmol, 1.00 eq.) and dry diethyl ether (7.0 mL) was cooled to -78 °C, at which temperature 1.6 M *n*BuLi in hexanes (4.24 mL, 6.78 mmol, 1.00 eq.) was added dropwise. The mixture was stirred at -78 °C for 90 minutes and then canullated into a to -78 °C pre-cooled solution consisting of triisopropyl borate (1.56 mL, 6.78 mmol, 1.00 eq.) and dry diethyl ether (7.0 mL). The reaction mixture was stirred at -78 °C for 2 hours, after which 2.0 M HCl in diethyl ether (3.73 mL, 7.46 mmol, 1.10 eq.) was added. The cooling bath was removed and the mixture was stirred for an additional 60 minutes. After filtration and solvent removal, Kugelrohr distillation (75 °C at 0.6 mbar) furnished pure diisopropyloct-1-ynylboronate (**12**, 940 mg, 3.95 mmol, 58% yield) as a colorless liquid. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 4.55 (hept, 2H, *J* = 6.2 Hz, CHO), 2.27 (t, 2H, *J* = 7.0 Hz,

[1] (a) Brand, J. P.; Waser, J. *Synthesis* **2012**, *44*, 1155. (b) Brand, J. P.; Chevalley, C.; Scopelliti, R.; Waser, J. *Chem. Eur. J.* **2012**, *18*, 5655.
[2] Meouma, J. B.; Olofsson, B. *Chen. Eur J.* **2012**, *18*, 3690.
[3] Fourgeaud, P.; Midrier, C.; Vors, J.-P.; Volle, J.-N.; Pirat, J.-L.; Virieux, D. *Tetrahedron* **2010**, *66*, 758.
[4] Xu, Q.; Zhao, C.-Q.; Han, L.-B. *J. Am. Chem. Soc*. **2008**, *130*, 12648.
[5] Busacca, C. A.; Lorenz, J. C.; Grinberg, N.; Haddad, N.; Hrapchak, M.; Latil, B.; Lee, H.; Sabila, P.; Saha, A.; Sarvestani, M.; Chen, S.; Varsolona, R.; Wei, X. ; Senanayake, C. H. *Org. Lett.* **2005**, *7*, 4277.
[6] Brown, H. C.; Bhat, N. G.; Srebnik, M. *Tetrahedron Lett.* **1988**, *29*, 2631.

propargylic CH_2), 1.60-1.48 (m, 2H, CH_2), 1.45-1.24 (m, 6H, CH_2), 1.19 (d, 12H, J = 6.2 Hz, ^{i}Pr CH_3), 0.89 (t, 3H, J = 6.9 Hz, hexyl CH_3). The values of the ^{1}H NMR spectrum are in accordance with reported literature data.[6]

Following a slightly modified procedure,[2] 2-iodobenzoic acid (**10**) (692 mg, 2.79 mmol, 1.00 eq.), *para*-toluenesulfonic acid monohydrate (TsOH•H_2O, 531 mg, 2.79 mmol, 1.00 eq.) and *meta*-chloroperoxybenzoic acid (*m*CPBA-70%, 756 mg, 3.07 mmol, 1.10 eq.) were dissolved in dichloromethane (4.5 mL) and 2,2,2-trifluoroethanol (4.5 mL). The mixture was stirred at room temperature under nitrogen for 1 hour, after which diisopropyloct-1-ynylboronate (**12**, 930 mg, 3.90 mmol, 1.40 eq.) was added in one portion. The reaction mixture was stirred for 2 hours at room temperature, filtered and concentrated *in vacuo*. The resulting oil was dissolved in dichloromethane (30 mL) and under vigorous stirring, saturated aq. $NaHCO_3$ (30 mL) was added. The mixture was stirred for 15 minutes, the two layers were separated and the aqueous layer was extracted with additional portions of dichloromethane (3 x 10 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was purified by flash column chromatography (ethyl acetate) to afford **6d** (940 mg, 2.64 mmol, 95%) as a white solid. R_f (EtOAc) = 0.25. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.42-8.35 (m, 1H, Ar*H*), 8.20-8.13 (m, 1H, Ar*H*), 7.78-7.69 (m, 2H, Ar*H*), 2.59 (t, 2H, J = 7.1 Hz, CCCH_2), 1.70-1.58 (m, 2H, CH_2), 1.51-1.39 (m, 2H, CH_2), 1.38-1.26 (m, 4H, CH_2), 0.94-0.86 (m, 3H, CH_2CH_3). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 166.7, 134.7, 132.5, 131.7, 131.6, 126.3, 115.7, 109.9, 39.4, 31.3, 28.7, 28.3, 22.6, 20.6, 14.1. The characterization data is in accordance with reported literature values.[7]

Allyl phenylphosphinate (5f)



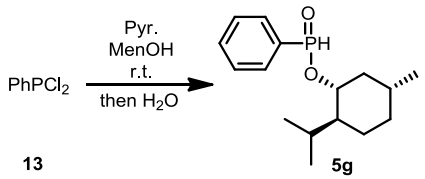
5i **5f**

Product **5f** was made by using the known procedure reported by Virieux and co-workers.[3] Pyridine (3.0 mL, 36 mmol) was added to a stirring solution of phenylphosphinic acid (5.17 g, 36.4 mmol) and allyl chloroformate (4.0 mL, 36 mmol) in CH_2Cl_2 (70 mL) at room temperature. This reaction was stirred for 30 min. Once gas evolution was stopped, the resulting mixture was heated at reflux for 15 min, and cooled down to room temperature. 0.1 N aqueous solution (50 mL) was added to the resulting mixture, and stirred for 30 min. The organic layer was separated, washed with water (2 * 50 mL), and dried over Na_2SO_4. The resulting solution was filtered and organic solvent was removed under reduced pressure. The remaining oil was distilled under vacuum to give pure **5f** (3.93 g, 21.6 mmol, 59%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.85 (m, 2H, Ph H), 7.65 – 7.61 (m, 1H, Ph H), 7.65 (d, J = 400 Hz, 1H, PH), 7.56 – 7.52 (m, 2H, Ph H), 5.97 (ddtd, J = 17.0, 10.3, 5.6, 0.8 Hz, 1H, alkene CH), 5.46 – 5.35 (m, 1H), 5.28 (dt, J = 10.5, 1.1 Hz,

[7] Huang, H.; Zhang, G.; Gong, L.; Zhang, S.; Chen, Y. *J. Am. Chem. Soc.*, **2014**, *136*, 2280.

1H, alkene CH_2), 4.60 (dddt, J = 16.1, 9.5, 5.5, 1.6 Hz, 2H, CH_2O). The characterization data is in accordance with reported literature values.[3]

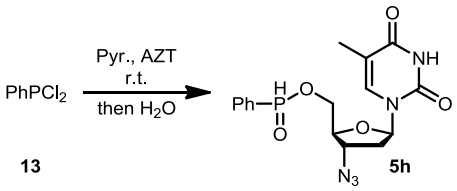
(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl phenylphosphinate (5g)[4]



13 5g

Product **5g** was made by using the known procedure reported by Han and co-workers.[4] $PhPCl_2$ (**13**) (4.34 mL, 32.0 mmol) in dry Et_2O (10 mL) was added to a mixture of pyridine (2.59 mL, 32.0 mmol) and *R*-menthol (5.0 g, 32 mmol) in dry Et_2O (30 mL) at 0 ^{0}C, and the resulting solution was stirred at room temperature overnight. H_2O (3 mL) was added, and the reaction mixture was washed with H_2O and extracted with hexane (60 mL * 3 times). The organic layer was separated, dried over $MgSO_4$, and filtrated. The organic solvent was removed under reduced pressure to give a crude oil. The oil was distilled under vacuum to give the pure adduct **5g** (5.2 g, 19 mmol, 58%). The diastereomeric ratio is 1:1.6 calculated based on integration of peaks in ^{31}P-NMR. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, J = 485 Hz, 1H, PH), 7.80 (ddt, J = 14.1, 8.2, 1.3 Hz, 2H, Ph H), 7.67 – 7.57 (m, 1H, Ph H), 7.56 – 7.47 (m, 2H, Ph H), 4.29 (td, J = 10.5, 4.5 Hz, 1H, CHO), 2.38 – 2.04 (m, 2H, CH or CH_2), 1.79 – 1.62 (m, 2H, CH or CH_2), 1.47 (ddt, J = 13.1, 6.7, 3.4 Hz, 2H, CH or CH_2), 1.36 – 1.19 (m, 1H, CH or CH_2), 1.04 – 0.78 (m, 11H, CH, CH_2 and CH_3). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 21.3, 22.7. The characterization data is in accordance with reported literature values.[4]

((2S,3S,5R)-3-Azido-5-(5-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2H)-yl)tetrahydrofuran-2-yl)methyl phenylphosphinate (5h)

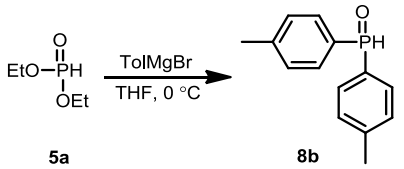


13 5h

Product **5h** was made by using the known procedure reported by Han and co-workers.[4] $PhPCl_2$ (**13**) (0.16 mL, 1.2 mmol) in dry Et_2O (2 mL) was added to a mixture of pyridine (0.19 mL, 2.3 mmol) and AZT (0.30 g, 1.1 mmol) in dry Et_2O (6 mL) at 0 ^{0}C, and the resulting solution was stirred at room temperature overnight. H_2O (2 mL) was added, and the reaction mixture was washed with H_2O (5 mL) and extracted with EtOAc (5 mL * 5 times). The organic layer was separated, dried over $MgSO_4$, and filtrated. The organic solvent was removed under reduced pressure to give a crude

gel. The crude gel was purified by column chromatography ($MeOH/CH_2Cl_2$ 1/10) to give the product **5h** as a pale brown gel (0.20 g, 0.52 mmol, 47%, ca. 95% purity). **R*f*** 0.25 ($MeOH/CH_2Cl_2$ 1/8, $KMnO_4$). The diastereomeric ratio is 1:1 which was calculated based on integration of peaks in ^{1}H-NMR at 7.14 and 6.85 ppm. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 490 Hz, 1H, PH), 7.67 (dd, *J* = 14.1, 8.3, 2.5, 1.4 Hz, 2H, Ph H), 7.52 – 7.45 (m, 1H, Ph H), 7.43 – 7.34 (m, 2H, Ph H), 7.14 (s, 0.5H, CH thymine, 1. diastereoisomer), 6.85 (s, 0.5H, CH thymine, 2. diastereoisomer), 6.08 (dt, *J* = 11.4, 6.5 Hz, 1H, CHON), 4.40 – 4.16 (m, 3H, CH_2O and CHO), 3.94 (dq, *J* = 8.1, 3.7 Hz, 1H, CHN_3), 2.35 – 2.17 (m, 2H, CH_2), 1.70 (s, 1.5H, Me thymine, 1. diastereoisomer), 1.58 (s, 1.5H, Me thymine, 2. diastereoisomer). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 163.9, 150.3, 142.6, 136.8, 132.7 (d, *J* = 3.0 Hz), 132.1, 130.7 (d, *J* = 12.1 Hz), 128.6 (d, *J* = 13.9 Hz), 126.7, 111.2, 85.5 (d, *J* = 186.0 Hz), 60.9 (d, *J* = 183.5 Hz), 37.3, 12.5. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 22.2.[8] **IR** 3662(m), 2989(s), 2107(w), 1693(m), 1408(m), 1255(m), 1067(s), 894 (m).

Di-p-tolylphosphine oxide (8b)[5]

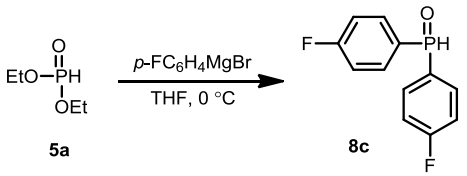


5a **8b**

Product **8b** was made by using the known procedure reported by Busacca and co-workers.[5] A solution of diethylphosphite (**5a**) (1.5 mL, 12 mmol) in 10 mL THF was added dropwise to 1.0 M TolMgBr in THF (38.4 mL) at 0 ^{0}C. The resulting solution was stirred at 0 ^{0}C degree for 15 min and at room temperature for 30 min, and cooled down to 0 ^{0}C again before 0.1 N HCl aqueous solution (10 mL) was added. TBME (30 mL) was added to the resulting mixture and stirred for 5 min. The upper organic layer was decanted from the gel. CH_2Cl_2 (35 mL) was subsequently added to the gel and stirred for 5 min. The resulting mixture was then filtered through a celite pad, washing the pad with CH_2Cl_2 (35 mL). The organic layer was separated. All combined organic solutions were dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a crude solid. The solid was recrystallized from boiling EtOAc (15 mL) to give the corresponding **8b** as a colorless solid (2.3 g, 9.8 mmol, 84%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 500 Hz, 1H, PH), 7.60 (ddd, *J* = 13.7, 8.1, 1.6 Hz, 4H, Tol CH), 7.35 – 7.29 (m, 4H, Tol CH), 2.43 (s, 6H, Me). The characterization data is *not* in accordance with reported literature values, as the tolyl Me peak was missing in the reported data.[5] The other peaks are corresponding.

[8] The phosphorous signal of both diastereoisomers was overlapping.

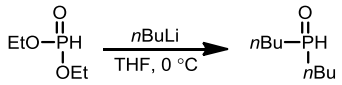
Bis(4-fluorophenyl)phosphine oxide (8c)[4]



5a 8c

Product **8c** was made by using the known procedure reported by Busacca and co-workers.[5] Diethylphosphite (**5a**) (1.0 mL, 7.7 mmol) in 8 mL THF was added dropwise to a solution of *p*-FC_6H_4MgBr in 10 mL THF (prepared from 0.64 g Mg (26 mmol) with 2.81 mL *p*-FC_6H_4Br (25.6 mmol)) at 0 ^{0}C. The resulting solution was stirred at 0 ^{0}C degree for 15 min and at room temperature for 30 min, and cooled down to 0 ^{0}C again before 0.1 N HCl aqueous solution (10 mL) was added. TBME (25 mL) was added to the resulting mixture and stirred for 5 min. The upper organic layer was decanted from the gel. CH_2Cl_2 (25 mL) was subsequently added to the gel and stirred for 5 min. The resulting mixture was then filtered through a celite pad, washing the pad with CH_2Cl_2 (25 mL). The organic layer was separated. All combined organic solutions were dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a crude oil. The crude oil was purified by column chromatography (pentane/EtOAc 2.5/1) to give the product **8c** as a colorless oil (1.4 g, 5.7 mmol, 73%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 485 Hz, 1H, PH), 7.72 (ddd, *J* = 13.1, 8.6, 5.5 Hz, 4H, Ar CH), 7.28 – 7.19 (m, 4H, Ar CH). The characterization data is in accordance with reported literature values.[5]

Dibutylphosphine oxide (8d)[5]



5a 8d

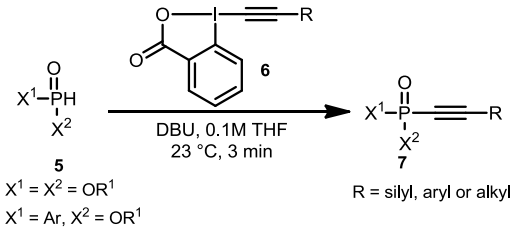
Product **8d** was made by using the known procedure reported by Busacca and co-workers.[5]A solution of diethylphosphite (**5a**) (3.0 mL, 23 mmol) in 10 mL THF was added dropwise to 2.5 M *n*BuLi in THF (30.7 mL, 77.0 mmol) at 0 ^{0}C. The resulting solution was stirred at 0 ^{0}C degree for 15 min and at room temperature for 30 min, and cooled down to 0 ^{0}C again before 0.1 N HCl aqueous solution (20 mL) was added. TBME (40 mL) was added to the resulting mixture and stirred for 5 min. The upper organic layer was decanted from the gel. CH_2Cl_2 (50 mL) was subsequently added to the gel and stirred for 5 min. The resulting mixture was then filtered through a celite pad, washing the pad with CH_2Cl_2 (50 mL). The organic layer was separated. All combined organic solutions were dried over $MgSO_4$ and the solvent was removed under reduced pressure to give a crude gel. The gel was recrystallized from boiling hexane (15 mL) to give **8d** as a colorless solid (3.3 g, 20 mmol, 87%). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.59 – 6.19 (dm, *J* = 446 Hz, 1H, PH), 1.92 – 1.51 (m, 8H, CH_2), 1.51 – 1.37 (m, 4H, CH_2), 0.93 (t, *J* = 7.3 Hz, 6H, CH_3). The characterization data is in accordance with reported literature values.[5]

3. Alkynylation Reaction

Optimization procedure:

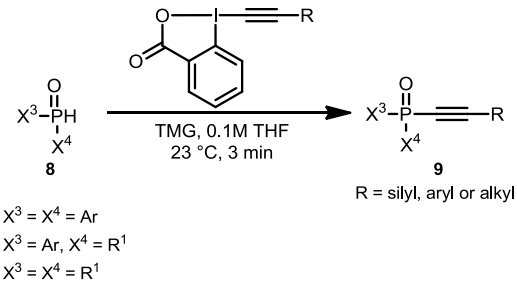
To a stirring solution of TIPS-EBX (**6a**) (1.1 – 1.2 equiv) and base (1.1 – 2.0 equiv) in solvent (0.1 M) was added diethyl phosphite **5a** (7.3 mg, 0.050 mmol, 1.0 equiv). The resulting solution was then stirred at r.t for 3 or 90 min. Subsequently 1M HCl (3 mL) and EtOAc (3 mL) were added to quench the resulting mixture. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 mL * 3). All combined organic layers were washed with sat. $NaHCO_3$ (5 mL * 2), dried over $MgSO_4$, and removed under reduced pressure to give a crude adduct. Yield (%) based on ^{1}H-NMR with 1,3,5-trimethoxybenzene as internal reference. Pure product **7a** was further obtained by column chromatographic purification. **R*f*** 0.55 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for purification.

General procedure A:



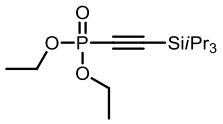
To a stirring solution of TIPS-, Ph-, *t*Bu- or *n*Hex-EBX **6** (1.1 equiv) and DBU (1.5 equiv) in THF (0.1 M) was added phosphite or phosphinate **5** (0.15–0.29 mmol, 1.0 equiv). The resulting solution was then stirred at r.t for 3 min. Subsequently 1M HCl (3 mL) and EtOAc (3 mL) were added to quench the resulting mixture. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 mL * 3). All combined organic layers were washed with sat. $NaHCO_3$ (5 mL * 2), dried over $MgSO_4$, and removed under reduced pressure to give a crude adduct. The pure corresponding product was obtained by column chromatographic purification.

General procedure B:



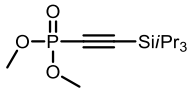
To a stirring solution of TIPS-, Ph-, *t*Bu- or *n*Hex-EBX **6** (1.5 equiv) and TMG (1.5 equiv) in THF (0.1 M) was added phosphine oxide **8** (0.15–0.29 mmol, 1.0 equiv). The resulting solution was then stirred at r.t for 3 min. Subsequently 1M HCl (3 mL) and EtOAc (3 mL) were added to quench the resulting mixture. The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 mL * 3). All combined organic layers were washed with sat. $NaHCO_3$ (5 mL * 2), dried over $MgSO_4$, and removed under reduced pressure to give a crude adduct. The pure corresponding product was obtained by column chromatographic purification.

Diethyl ((triisopropylsilyl)ethynyl)phosphonate (7a)



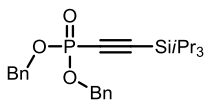
H-phosphite **5a** (45 mg, 0.32 mmol) and TIPS-EBX (**6a**) were used in general procedure A. **10a** was obtained as a colorless gel (91 mg, 0.28 mmol, 90% yield). **R*f*** 0.55 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 4.15 (dd, *J* = 8.9, 7.1, 0.7 Hz, 4H, CH_2O), 1.36 (td, *J* = 7.1, 0.7 Hz, 6H, ethyl CH_3), 1.15 – 1.04 (m, 21H, TIPS). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 106.5 (d, *J* = 37.6 Hz), 96.4 (d, *J* = 269.7 Hz), 63.1 (d, *J* = 5.5 Hz), 17.7, 16.06 (d, *J* = 6.9 Hz), 10.8. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ -8.5. **IR** 3669(s), 2998(s), 2361(s), 2180(w), 1408(s), 1252(s), 1079(s), 883(s), 819(m). **HRMS** (ESI) calcd for $C_{15}H_{32}O_3PSi^+$ $[M+H]^+$ 319.1853, found 319.1857.

Dimethyl ((triisopropylsilyl)ethynyl)phosphonate (7b)



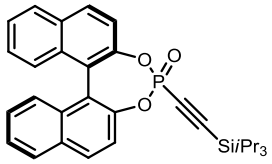
H-phosphite **5b** (35 mg, 0.32 mmol) and TIPS-EBX (**6a**) were used in general procedure A. **7b** was obtained as a colorless gel (79 mg, 0.27 mmol, 85% yield). **R*f*** 0.55 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 4.12 (d, *J* = 8.9 Hz, 6H, Me), 1.45 – 1.17 (m, 21H, TIPS). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 107.9 (d, *J* = 37.9 Hz), 94.6 (d, *J* = 273.0 Hz), 53.4 (d, *J* = 5.6 Hz), 18.4, 10.8. ^{31}P-NMR (162 MHz, $CDCl_3$) δ -5.2. **IR** 3674(s), 2989(s), 2361(s), 2180(w), 1251(s), 1081(s), 893(m), 822(m). **HRMS** (ESI) calcd for $C_{13}H_{28}O_3PSi^+$ $[M+H]^+$ 291.1540, found 291.1541.

Dibenzyl ((triisopropylsilyl)ethynyl)phosphonate (7c)



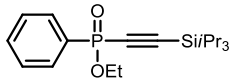
H-phosphite **5c** (88 mg, 0.32 mmol) and TIPS-EBX (**6a**) were used in general procedure A. **7c** was obtained as a colorless gel (126 mg, 0.283 mmol, 89% yield). **R*f*** 0.7 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 2/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.30 (m, 10H, CH Ph), 5.14 (d, *J* = 8.5 Hz, 4H, Bn CH_2), 1.25 – 0.97 (m, 21H, TIPS). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 135.5 (d, *J* = 7.5 Hz), 128.5, 128.5, 127.8, 107.8 (d, *J* = 38.3 Hz), 95.8 (d, *J* = 274.7 Hz), 68.5 (d, *J* = 5.2 Hz), 18.5, 10.8. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ -8.0. **IR** 3674(s), 2972(s), 2902(s), 2361(s), 2180(w), 1933(w), 1454(m), 1394(s), 1251(s), 1056(s), 881(s), 785(w). **HRMS** (ESI) calcd for $C_{25}H_{36}O_3PSi^+$ $[M+H]^+$ 443.2166, found 443.2172.

4-((Triisopropylsilyl)ethynyl)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (7d)



H-phosphite **5d** (60 mg, 0.18 mmol) and TIPS-EBX (**6a**) were used in general procedure A. **7d** was obtained as a colorless gel (80 mg, 0.16 mmol, 86% yield). **R*f*** 0.8 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 3/1 was used as the eluting solvents for purification. **$[\alpha]_D^{23.0}$** -63.7(c = 0.44, $CHCl_3$). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 8.09 – 7.92 (m, 4H, Ar H), 7.63 (dd, *J* = 8.8, 1.1 Hz, 1H, Ar H), 7.58 – 7.47 (m, 3H, Ar H), 7.46 – 7.29 (m, 4H, Ar H), 1.15 – 1.00 (m, 21H, TIPS). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 146.7 (d, *J* = 10.9 Hz), 145.4 (d, *J* = 9.1 Hz), 132.3 (d, *J* = 9.3 Hz), 131.9 (d, *J* = 4.9 Hz), 131.4, 130.9, 128.5 (d, *J* = 11.4 Hz), 127.2 (d, *J* = 28.1 Hz), 126.7 (d, *J* = 3.7 Hz), 125.9, 121.8 (dd, *J* = 13.6, 2.6 Hz), 120.9 (dd, *J* = 27.4, 3.0 Hz), 111.3 (d, *J* = 39.5 Hz), 93.2 (d, *J* = 294.2 Hz), 18.4, 10.8.[9] **^{31}P-NMR** (162 MHz, $CDCl_3$) δ -1.91. **IR** 3669(s), 2991(s), 2361(s), 2180(w), 1934(w), 1407(s), 1251(s), 1076(s), 893(s). **HRMS** (ESI) calcd for $C_{31}H_{34}O_3PSi^+$ $[M+H]^+$ 513.2009, found 513.2003.

Ethyl phenyl((triisopropylsilyl)ethynyl)phosphinate (7e)

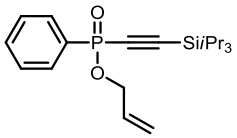


H-phosphinate **5e** (54 mg, 0.32 mmol) and TIPS-EBX (**6a**) were used in general procedure A. **7e** was obtained as a colorless gel (85 mg, 0.24 mmol, 76% yield). **R*f*** 0.5 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 2/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.90 (ddd, *J* = 14.4, 7.5, 1.4 Hz, 2H, Ar H), 7.56 (dd, *J* = 7.5, 1.4 Hz, 1H, Ar H), 7.48 (d, *J* = 3.8 Hz, 2H, Ar H), 4.36 – 4.17 (m, 2H, ethyl CH_2), 1.40 (t, *J* = 7.0 Hz, 3H, ethyl CH_3), 1.21 – 0.98 (m, 21H, TIPS). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 132.6 (d, *J* = 3.1 Hz), 131.2 (d, *J* = 170.3 Hz), 130.9 (d, *J* = 11.3 Hz), 128.4 (d, *J* = 14.9 Hz), 109.2 (d, *J* = 26.4 Hz), 99.8 (d, *J* = 192.3 Hz), 62.3 (d, *J* = 6.6 Hz), 18.4, 16.3 (d, *J* = 6.9 Hz), 10.9. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 8.1. **IR** 3674(s), 3392(w), 3228(w), 2972(s), 2361(s), 2180(w), 1933(w), 1452(m), 1394(s),

[9] Not all aromatic signals were resolved.

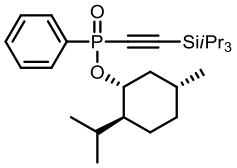
1250(s), 1053(s), 881(s), 801(m). **HRMS** (ESI) calcd for $C_{19}H_{32}O_2PSi^+$ $[M+H]^+$ 351.1904, found 351.1909.

Allyl phenyl((triisopropylsilyl)ethynyl)phosphinate (7f)



H-phosphinate **5f** (58 mg, 0.32 mmol) and TIPS-EBX (**6a**) were used in general procedure A. **7f** was obtained as a colorless gel (100 mg, 0.285 mmol, 87% yield). **R*f*** 0.6 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.97 – 7.81 (m, 2H, Ph CH), 7.59 – 7.51 (m, 1H, Ph CH), 7.50 – 7.43 (m, 2H, Ph CH), 5.98 (ddt, *J* = 17.1, 10.7, 5.5 Hz, 1H, alkene CH), 5.37 (dq, *J* = 17.1, 1.5 Hz, 1H, alkene CH_2), 5.23 (dq, *J* = 10.3, 1.3 Hz, 1H, alkene CH_2), 4.66 (ddt, *J* = 7.0, 4.1, 1.6 Hz, 2H, CH_2O), 1.19 – 0.98 (m, 21H, TIPS). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 132.8 (d, *J* = 3.0 Hz), 132.6 (d, *J* = 7.4 Hz), 130.9 (d, *J* = 11.4 Hz), 130.9 (d, *J* = 170.5 Hz), 128.5 (d, *J* = 15.0 Hz), 118.2, 109.7 (d, *J* = 26.8 Hz), 99.5 (d, *J* = 193.5 Hz), 66.4 (d, *J* = 6.2 Hz), 18.4, 10.9. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 8.6. **IR** 3676(s), 2964(s), 2361 (s), 2125(w), 1923(w), 1452(m), 1407(s), 1251(s), 1057(s), 881(s), 792(m). **HRMS** (ESI) calcd for $C_{20}H_{32}O_2PSi^+$ $[M+H]^+$ 362.1830, found 363.1904.

(*1R,2S,5R*)-2-Isopropyl-5-methylcyclohexyl phenyl((triisopropylsilyl)ethynyl)phosphinate (7g)

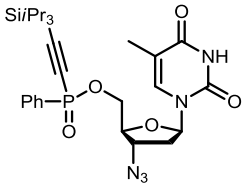


H-phosphinate **5g** (108 mg, 0.372 mmol) and TIPS-EBX (**6a**) were used in general procedure A. **7g** was obtained as a colorless gel (119 mg, 0.264 mmol, 71% yield). The diastereomeric ratio is 1:1, which was calculated based on integration of peaks in ^{31}P-NMR. **R*f*** 0.8 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 2.5/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.90 (dddd, *J* = 14.3, 8.4, 4.1, 1.4 Hz, 2H, Ph CH), 7.59 – 7.52 (m, 1H, Ph CH), 7.48 (tdd, *J* = 6.8, 3.9, 1.4 Hz, 2H, Ph CH), 4.46 (tdd, *J* = 10.8, 7.8, 4.4 Hz, 1H, CHO), 2.62 – 2.34 (m, 1H, aliphatic H), 1.79 – 1.62 (m, 2H, aliphatic H), 1.36 – 1.21 (m, 2H, aliphatic H), 1.20 – 1.04 (m, 25H, aliphatic H and TIPS), 0.98 – 0.86 (m, 9H, aliphatic H and TIPS). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 132.9 (d, *J* = 170.5 Hz), 132.4, 132.4, 132.1, 130.9, 130.8, 130.6, 128.3 (d, *J* = 15.0 Hz), 109.3 (d, *J* = 26.0 Hz), 108.6 (d, *J* = 26.2 Hz), 101.3 (d, *J* = 190.7 Hz), 100.5 (d, *J* = 190.7 Hz), 79.6 (d, *J* = 8.1 Hz), 78.5 (d, *J* = 7.9 Hz), 48.6, 48.6, 48.5, 43.7, 42.6, 34.1 (d, *J* = 2.8 Hz), 31.7, 31.6, 25.8, 25.5, 23.1, 23.0, 21.9, 21.9, 21.0 (d, *J* = 2.0 Hz), 18.5, 18.4, 17.7, 16.2, 15.6, 12.3, 11.0 (d, *J* = 1.9 Hz).[10] **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 7.1, 5.1. **IR** 3674(s), 2988(s),

[10] Not all aliphatic signals were resolved.

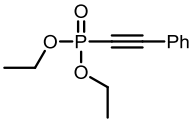
2361(s), 2180(w), 1453(m), 1407(s), 1250(s), 1079(s), 882(s), 787(m). **HRMS** (ESI) calcd for $C_{27}H_{45}O_2PSi^+$M+H) 461.2926, found 461.2998.

3'-Azido-3'-deoxythymidinyl phenyl((triisopropylsilyl)ethynyl)phosphinate (7h)



H-phosphinate **5h** (172 mg, 0.443 mmol) and TIPS-EBX (**6a**) were used in general procedure A. **7h** was obtained as a colorless gel (176 mg, 0.313 mmol, 70% yield). The diastereomeric ratio is 1:1.3, which was calculated based on average integration of peaks in ^{1}H-NMR at 7.42 and 7.23 ppm, and ^{31}P-NMR. **R*f*** 0.45 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 2.5/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 9.14 (s, 1H, NH), 7.90 (ddd, *J* = 14.5, 7.9, 6.4 Hz, 2H, Ph CH), 7.64 (td, *J* = 7.4, 1.6 Hz, 1H, Ph CH), 7.58 – 7.49 (m, 2H, Ph CH), 7.42 (s, 0.4H, CH thymine, 1. diastereoisomer), 7.23 (s, 0.6H) , CH thymine, 2. diastereoisomer, 6.36 – 6.11 (m, 1H, CHON), 4.56 – 4.27 (m, 3H, CHO and CH_2O), 4.12 (dd, *J* = 8.7, 3.4 Hz, 1H, CHN_3), 2.44 (dtd, *J* = 13.6, 6.4, 3.7 Hz, 1H, CH_2), 2.21 (ddt, *J* = 23.2, 14.1, 7.3 Hz, 1H, CH_2), 1.75 (s, 1.3H, Me thymine, 1. diastereoisomer), 1.64 (s, 1.7H, Me thymine, 2. diastereoisomer), 1.23 – 1.00 (m, 21H, TIPS). **^{13}C-NMR** ($CDCl_3$, 100MHz) δ 163.7, 163.6, 150.3, 150.2, 135.0, 134.8, 133.5, 133.5, 130.8 (d, *J* = 11.9 Hz), 130.8 (d, *J* = 11.7 Hz), 130.5, 129.2, 128.8 (d, *J* = 15.2 Hz), 111.8 (d, *J* = 26.7 Hz), 111.5, 111.4, 99.3 (d, *J* = 196.0 Hz), 98.1 (d, *J* = 196.0 Hz), 84.6 , 84.6, 82.5 (d, *J* = 7.1 Hz), 82.4 (d, *J* = 7.6 Hz), 65.1, 65.0, 64.9, 60.8, 60.7, 37.7, 37.6, 18.4 (d, *J* = 1.9 Hz), 12.3, 12.3, 10.9. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 10.4, 10.0. **IR** 3668(m), 2972(s), 2361(m), 2180(w), 1699(w), 1453(m), 1407(s), 1250(s), 1076(s), 882(m). **HRMS** (ESI) calcd for $C_{19}H_{28}NSi^+$ (M+H) 572.2379, found 572.2570.

Diethyl (phenylethynyl)phosphonate (7j)[11]

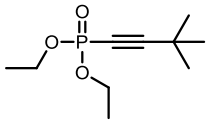


H-phosphite **5a** (26 mg, 0.18 mmol) and Ph-EBX (**6b**) were used in general procedure A. **7j** was obtained as a colorless gel (30 mg, 0.13 mmol, 69% yield). **R*f*** 0.45 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.52 (m, 2H, Ph CH), 7.50 – 7.32 (m, 3H, Ph CH), 4.37 – 4.13 (m, 4H, Et CH_2), 1.40 (td, *J* = 7.1, 0.7 Hz, 6H, Et CH_3). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 132.6 (d, *J* = 2.5 Hz), 130.7, 128.6, 119.6 (d, *J* = 5.6 Hz), 99.1 (d, *J* = 52.9 Hz), 79.8 (d, one peak mixing with $CDCl_3$), 63.3 (d, *J* = 5.5 Hz), 16.2 (d, *J* = 7.0 Hz). **^{31}P-NMR** (162 MHz, $CDCl_3$) δ -6.0. **IR**

[11] Wang, Y.; Gan, J.; Liu, L.; Yuan, H.; Gao, Y.; Liu Y.; Zhao, Y. *J. Org. Chem*, **2014**, *79*, 3678.

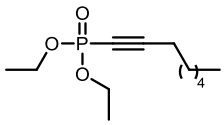
3674(s), 3344(m), 2973(s), 2361(s), 2180(w), 1452(s), 1374(s), 1251(s), 1051(s), 881(m). The characterization data is in accordance with reported literature values.[11]

Diethyl (3,3-dimethylbut-1-yn-1-yl)phosphonate (7k)



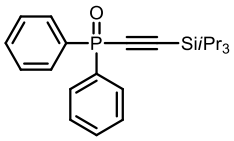
H-phosphite **5a** (46 mg, 0.32 mmol) and *t*Bu-EBX (**6c**) were used in general procedure A. **7k** was obtained as a colorless gel (58 mg, 0.27 mmol, 80% yield). **R*f*** 0.55 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 4.17 – 4.02 (m, 4H, Et CH_2), 1.33 (td, *J* = 7.1, 0.8 Hz, 6H, Et CH_3), 1.25 (s, 9H, ^{t}Bu). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 110.2 (d, *J* = 50.8 Hz), 68.7 (d, *J* = 301.8 Hz), 62.8 (d, *J* = 5.5 Hz), 29.8, 27.9, 16.0. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ -5.7. **IR** 3676(s), 2988(s), 2361(s), 2180(w), 1407(m), 1394(s), 1251(s), 1083(s), 893(m), 798(m). **HRMS** (ESI) calcd for $C_{10}H_{19}O_3P^+$ (M+H) 219.1071, found 219.1150.

Diethyl oct-1-yn-1-ylphosphonate (7l)



H-phosphite **5a** (23 mg, 0.16 mmol) and *n*Hex-EBX (**6d**) were used in general procedure A. **7l** was obtained as a colorless gel (34.5 mg, 0.14 mmol, 86% yield). **R*f*** 0.3 (pentane/EtOAc 1/2, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 4.29 – 3.99 (m, 4H, Et CH_2), 2.33 (td, *J* = 7.2, 4.4 Hz, 2H, propargyl CH_2), 1.66 – 1.49 (m, 2H, CH_2), 1.47 – 1.15 (m, 12H, CH_2 and ethyl CH_3), 0.88 (dd, *J* = 7.5, 6.1 Hz, 3H, Me). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 103.2 (d, *J* = 52.9 Hz), 70.4 (d, *J* = 303.2 Hz), 62.9 (d, *J* = 5.5 Hz), 31.1, 28.4, 27.4 (d, *J* = 2.2 Hz), 22.4, 19.2 (d, *J* = 4.5 Hz), 16.1 (d, *J* = 7.1 Hz), 14.0. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ -6.1. **IR** 3662(s), 2988(w), 2207(w), 1394(m), 1251(m), 1057(s), 893(m). **HRMS** (ESI) calcd for $C_{12}H_{24}O_3P^+$ (M+H) 247.1458, found 247.1470.

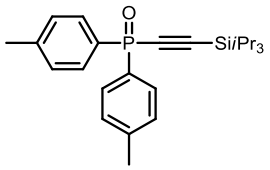
Diphenyl((triisopropylsilyl)ethynyl)phosphine oxide (9a)



H-phosphine oxide **8a** (48.7 mg, 0.233 mmol) and TIPS-EBX (**6a**) were used in general procedure B. **9a** was obtained as a colorless gel (81 mg, 0.21 mmol, 91% yield). **R*f*** 0.5 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for

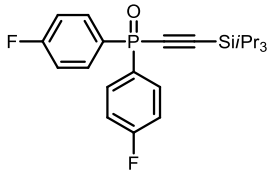
purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.85 (ddd, *J* = 13.8, 8.3, 1.5 Hz, 4H, Ph CH), 7.55 – 7.48 (m, 2H, Ph CH), 7.48 – 7.41 (m, 4H, Ph CH), 1.21 – 1.00 (m, 21H, TIPS). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 133.2 (d, *J* = 120.9 Hz), 132.1 (d, *J* = 2.9 Hz), 130.9 (d, *J* = 11.2 Hz), 128.5 (d, *J* = 13.5 Hz), 113.4 (d, *J* = 18.8 Hz), 101.1 (d, *J* = 151.5 Hz), 18.5, 11.0. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 6.9. **IR** 3674(s), 2991(s), 2361(s), 2121(w), 1934(w), 1407(s), 1251(s), 1081(s), 893(s), 791(m). **HRMS** (ESI) calcd for $C_{23}H_{32}OPSi^+$ $[M+H]^+$ 383.1955, found 383.1957.

Di-p-tolyl((triisopropylsilyl)ethynyl)phosphine oxide (9b)



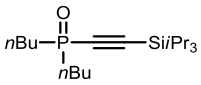
H-phosphine oxide **8b** (53.7 mg, 0.233 mmol) and TIPS-EBX (**6a**) were used in general procedure B. **9b** was obtained as a colorless gel (85 mg, 0.21 mmol, 89% yield). **R*f*** 0.45 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 13.6, 8.1 Hz, 4H, Ar CH), 7.24 (dd, *J* = 8.1, 3.0 Hz, 4H, Ar CH), 2.36 (s, 6H, Me), 1.22 – 1.01 (m, 21H, TIPS). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 142.5 (d, *J* = 3.0 Hz), 130.8 (d, *J* = 11.6 Hz), 129.5, 129.2 (d, *J* = 13.8 Hz), 112.4 (d, *J* = 18.8 Hz), 101.5 (d, *J* = 150.4 Hz), 21.5, 18.4, 11.0. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 7.2. **IR** 3674(s), 3319(w), 3227(w), 2972(s), 2361(s), 2190(w), 1933(w), 1452(m), 1407(s), 1251(s), 1056(s), 893(s), 803(w). **HRMS** (ESI) calcd for $C_{25}H_{36}OPSi^+$ $[M+H]^+$ 411.2268, found 411.2267.

Bis(4-fluorophenyl)((triisopropylsilyl)ethynyl)phosphine oxide (9c)



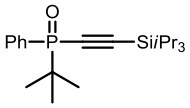
H-phosphine oxide **8c** (45 mg, 0.18 mmol) and TIPS-EBX (**9a**) were used in general procedure B. **9c** was obtained as a colorless gel (70 mg, 0.17 mmol, 93% yield). **R*f*** 0.5 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.76 (m, 4H, Ar CH), 7.15 (td, *J* = 8.7, 2.3 Hz, 4H, Ar CH), 1.20 – 1.03 (m, 21H, TIPS). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 165.3 (dd, *J* = 254.0, 3.5 Hz), 133.4 (dd, *J* = 12.9, 8.9 Hz), 129.0 (dd, *J* = 125.1, 3.4 Hz), 116.1 (dd, *J* = 21.6, 14.8 Hz), 114.3 (d, *J* = 19.6 Hz), 100.7 (d, *J* = 154.4 Hz), 18.48, 10.99. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 4.6. **^{19}F-NMR** (376 MHz, $CDCl_3$) δ -106.0. **IR** 3674(s), 3391(m), 3226(m), 2958(s), 2361 (s), 2125(w), 1933(w), 1082(s), 893(s), 802(w). **HRMS** (ESI) calcd for $C_{23}F_2H_{30}OPSi^+$ $[M+H]^+$ 419.1766, found 419.1767.

Dibutyl((triisopropylsilyl)ethynyl)phosphine oxide (9d)



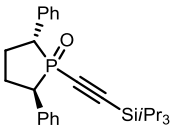
H-phosphine oxide **8d** (39 mg, 0.23 mmol) and TIPS-EBX (**6a**) were used in general procedure B. **9d** was obtained as a colorless liquid (69 mg, 0.20 mmol, 86% yield, 95% purity). **R*f*** 0.5 ($MeOH/CH_2Cl_2$ 1/10, $KMnO_4$); $MeOH/CH_2Cl_2$ 3/100 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 1.95 – 1.76 (m, 4H, Bu CH_2), 1.75 – 1.57 (m, 4H, Bu CH_2), 1.46 (h, *J* = 7.3 Hz, 4H, Bu CH_2), 1.16 – 1.02 (m, 21H, TIPS), 0.93 (t, *J* = 7.3 Hz, 6H, Me). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 109.3 (d, *J* = 15.6 Hz), 31.2 (d, *J* = 78.9 Hz), 24.2 (d, *J* = 3.7 Hz), 23.9 (d, *J* = 15.6 Hz), 18.4, 13.6, 10.9.[12] **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 25.3. **IR** 3675(m), 3385(m), 2972(sh), 2902(s), 2361(s), 2180(w), 1921(w), 1453(m), 1394(s), 1251(s), 1051(sh), 881(s), 8020(w). **HRMS** (ESI) calcd for $C_{19}H_{40}OPSi^+$ $[M+H]^+$ 343.2581, found 343.2584.

***tert*-Butyl(phenyl)((triisopropylsilyl)ethynyl)phosphine oxide (9e)**



H-phosphine oxide **8e** (45 mg, 0.25 mmol) and TIPS-EBX (**6a**) were used in general procedure B. **9e** was obtained as a colorless gel (78 mg, 0.22 mmol, 87% yield). **R*f*** 0.45 (pentane/EtOAc 2/1, $KMnO_4$); pentane/EtOAc 2/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.86 (ddd, *J* = 11.9, 8.3, 1.4 Hz, 2H, Ph CH), 7.56 – 7.50 (m, 1H, Ph CH), 7.45 (tdd, *J* = 7.0, 3.1, 1.6 Hz, 2H, Ph CH), 1.27 – 1.04 (m, 30H, TIPS and ^{t}Bu). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 132.0, 131.9, 129.4 (d, *J* = 108.0 Hz), 128.0 (d, *J* = 12.2 Hz), 111.5 (d, *J* = 14.1 Hz), 99.5 (d, *J* = 132.5 Hz), 33.7 (d, *J* = 82.4 Hz), 23.7, 18.5, 11.0. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 29.8. **IR** 3674(s), 3390(w), 3226(w), 2988(s), 2361(s), 2195(w), 1933(w), 1452(m), 1394(s), 1251(s), 1056(s), 880(s). **HRMS** (ESI) calcd for $C_{21}H_{36}OPSi^+$ $[M+H]^+$ 363.2268, found 363.2268.

(*2R*,*5R*)-2,5-Diphenyl-1-((triisopropylsilyl)ethynyl)phospholane 1-oxide (9f)

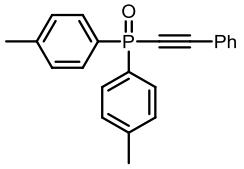


H-phosphine oxide **8f** (45 mg, 0.18 mmol) and TIPS-EBX (**6a**) were used in general procedure B. **9f** was obtained as a colorless gel (68 mg, 0.15 mmol, 89% yield). **R*f*** 0.6 (pentane/EtOAc 1/1,

[12] One of ethynyl carbons is not strong enough to be recorded.

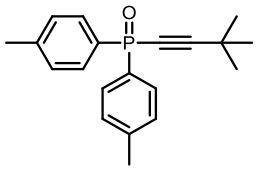
$KMnO_4$); pentane/EtOAc 2/1 was used as the eluting solvents for purification. $[\alpha]_D^{23.0}$ +2.2 (c = 0.2, $CHCl_3$). **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.36 – 7.13 (m, 10H, Ph CH), 3.57 (ddd, *J* = 24.7, 12.5, 7.1 Hz, 1H, CHPh), 3.35 (td, *J* = 12.2, 7.6 Hz, 1H, CHPh), 2.63 – 2.19 (m, 3H, CH_2), 2.16 – 1.99 (m, 1H, CH_2), 0.88 (m, 21H, TIPS). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 135.5 (dd, *J* = 43.1, 5.7 Hz), 128.8 (d, *J* = 5.5 Hz), 128.6 (dd, *J* = 10.5, 2.3 Hz), 127.7 (d, *J* = 5.4 Hz), 127.0 (dd, *J* = 21.4, 2.8 Hz), 112.8 (d, *J* = 13.5 Hz), 100.0 (d, *J* = 132.1 Hz), 50.5 (d, *J* = 33.4 Hz), 49.8 (d, *J* = 33.4 Hz), 31.1 (d, *J* = 9.5 Hz), 27.3 (d, *J* = 11.3 Hz), 18.3, 10.7. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 36.3. **IR** 3671(m), 2987(s), 2361(m), 2180(w), 1407(s), 1251(s), 1059(s), 893(m). **HRMS** (ESI) calcd for for $C_{27}H_{38}OPSi^+$ $[M+H]^+$ 437.2424, found 437.2425.

(Phenylethynyl)di-p-tolylphosphine oxide (9i)



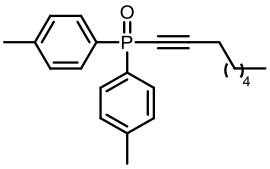
H-phosphine oxide **8b** (31 mg, 0.13 mmol) and Ph-EBX (**6b**) were used in general procedure B. **9i** was obtained as a colorless solid (32 mg, 0.10 mmol, 72% yield). **R*f*** 0.5 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluted solvents for purification. **Mp** 78 °C; **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 13.7, 8.1 Hz, 4H, Ar CH), 7.62 – 7.56 (m, 2H, Ar CH), 7.47 – 7.41 (m, 1H, Ar CH), 7.37 (tt, *J* = 6.7, 1.6 Hz, 2H, Ar CH), 7.29 (dd, *J* = 8.1, 3.0 Hz, 4H, Ar CH), 2.40 (s, 6H, Me). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 142.8 (d, *J* = 3.0 Hz), 132.5, 132.5, 131.0 (d, *J* = 11.7 Hz), 130.5, 129.4 (d, *J* = 13.9 Hz), 128.6, 120.2 (d, *J* = 4.1 Hz), 105.0 (d, *J* = 29.8 Hz), 83.3 (d, *J* = 169.0 Hz), 21.7. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 9.2. **IR** ν 3675(s), 3344(s), 2973(s), 2891(s), 2361(s), 2180(w), 1407(s), 1251(s), 1072(s), 894(s). **HRMS** (ESI) calcd for $C_{22}H_{20}OP^+$ $[M+H]^+$ 331.1246, found 331.1245.

3,3-Dimethylbut-1-yn-1-yl)di-p-tolylphosphine oxide (9j)



H-phosphine oxide **8b** (47 mg, 0.20 mmol) and *t*Bu-EBX (**6c**) were used in general procedure B. **9j** was obtained as a colorless gel (55 mg, 0.17 mmol, 87% yield). **R*f*** 0.4 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 13.6, 8.0 Hz, 4H, Ar CH), 7.25 (dd, *J* = 8.0, 2.8 Hz, 4H, Ar CH), 2.38 (s, 6H, Ar Me), 1.31 (s, 9H, ^{t}Bu). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 142.3, 130.8 (d, *J* = 11.6 Hz), 130.6 (d, *J* = 124.1 Hz), 129.2 (d, *J* = 13.8 Hz), 116.1 (d, *J* = 28.8 Hz), 73.4 (d, *J* = 173.7 Hz), 30.0, 28.4, 21.6. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 7.9. **IR** 3674(s), 2988(s), 2361(s), 2177(w), 1933(w), 1452(m), 1407(s), 1252(s), 1230(s), 1066(s), 893(s), 778(w). **HRMS** (ESI) calcd for $C_{20}H_{24}OP^+$ (M+H) 311.1486, found 311.1565.

Oct-1-yn-1-yldi-p-tolylphosphine oxide (9k)



H-phosphine oxide **8b** (37.7 mg, 0.163 mmol) and *n*Hex-EBX (**6d**) were used in general procedure B. **9k** was obtained as a colorless gel (47 mg, 0.14 mmol, 85% yield). **R*f*** 0.35 (pentane/EtOAc 1/1, $KMnO_4$); pentane/EtOAc 1/1 was used as the eluting solvents for purification. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 13.6, 8.1 Hz, 4H, Ar H), 7.33 – 7.21 (m, 4H, Ar H), 2.50 – 2.35 (m, 8H, 2*CH_3C$_6$H$_4$ + CH_2), 1.70 – 1.56 (m, 2H, CH_2), 1.50 – 1.38 (m, 2H, CH_2), 1.36 – 1.21 (m, 4H, CH_2), 0.96 – 0.83 (m, 3H, Me). **^{13}C-NMR** (101 MHz, $CDCl_3$) δ 142.5 (d, *J* = 3.0 Hz), 130.9 (d, *J* = 11.6 Hz), 129.7, 129.2 (d, *J* = 13.8 Hz), 109.3 (d, *J* = 30.4 Hz), 75.2 (d, *J* = 174.4 Hz), 31.2, 28.5, 27.6 (d, *J* = 1.8 Hz), 22.5, 21.6, 19.8 (d, *J* = 3.2 Hz), 14.0. **^{31}P-NMR** (162 MHz, $CDCl_3$) δ 8.1. **IR** 3662(s), 2988(s), 2193(s), 1394(m), 1407(s), 1252(s), 1057(s), 893(s), 809(w). **HRMS** (ESI) calcd for $C_{22}H_{28}OP^+$ (M+H) 339.1872, found 339.1888

4. Spectra of New Compounds

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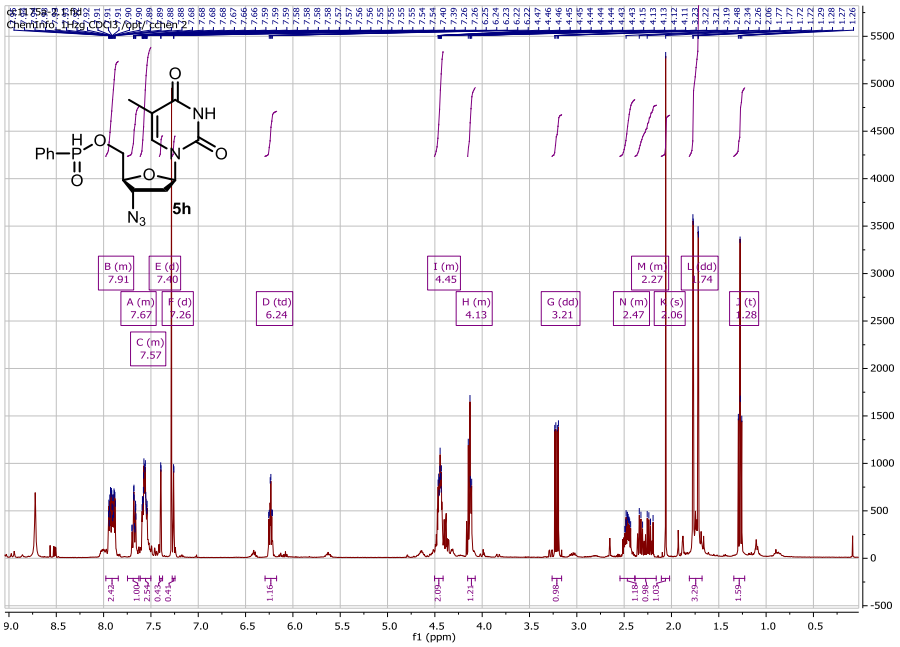
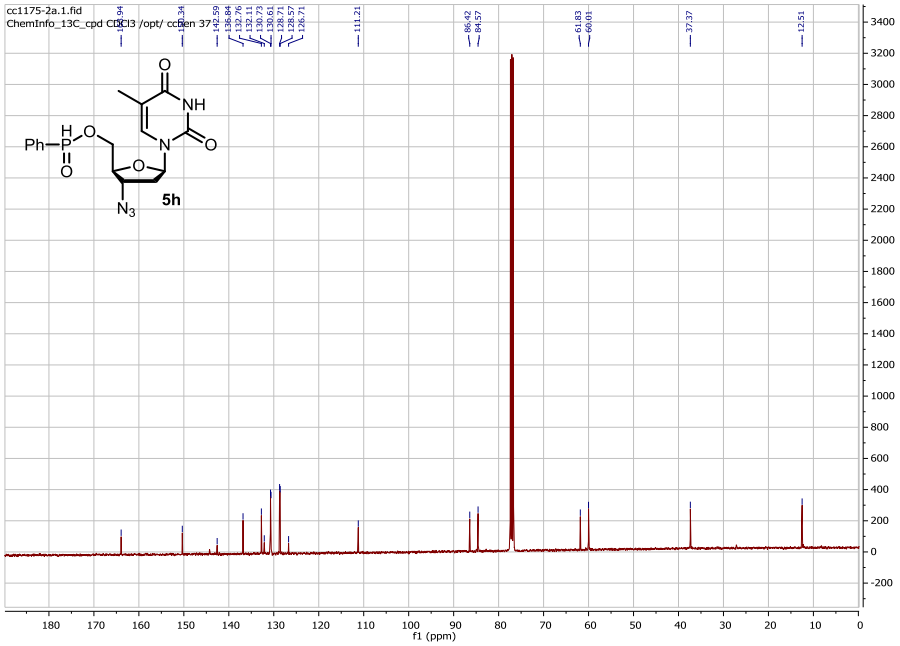
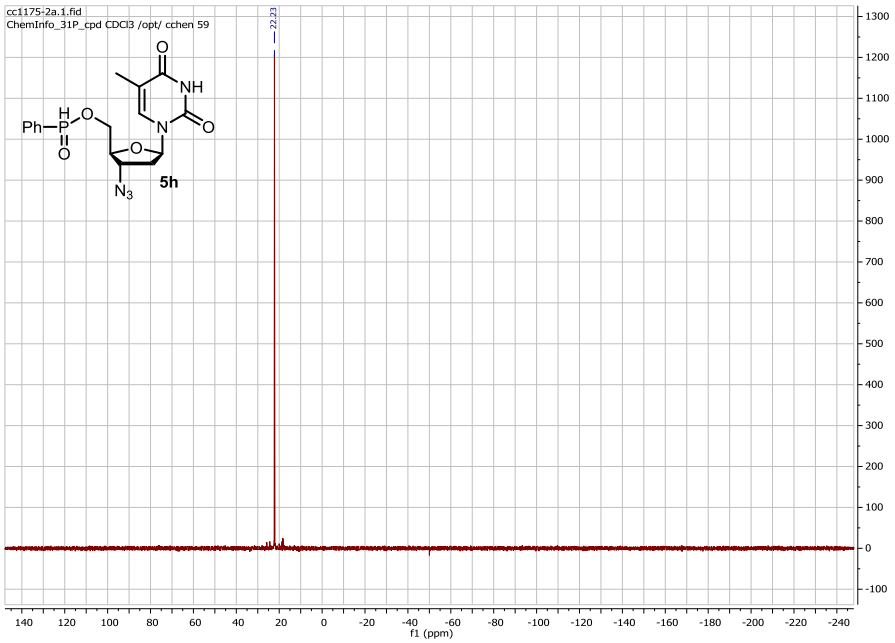
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **5h**

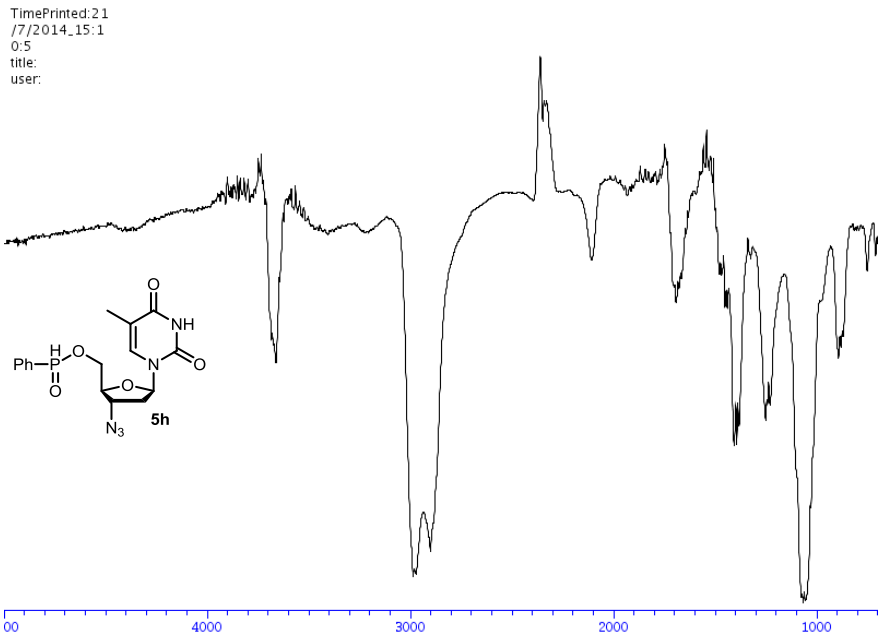


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **5h**

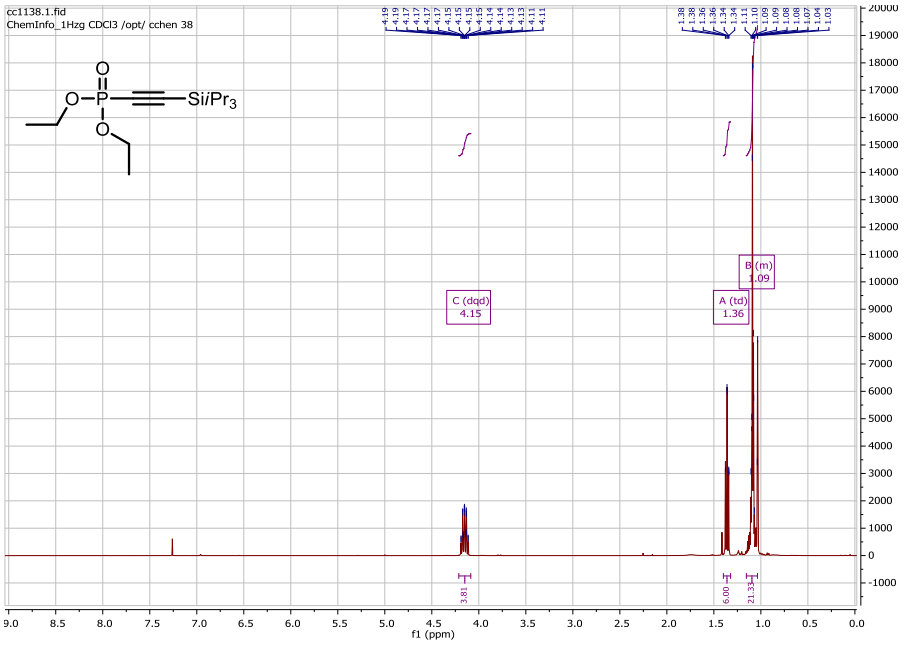


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **5h**

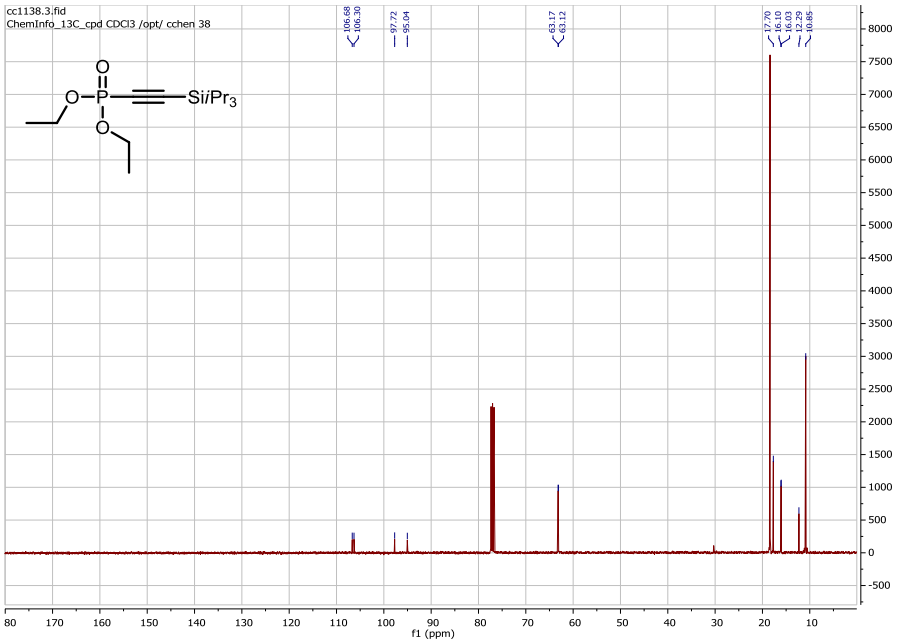




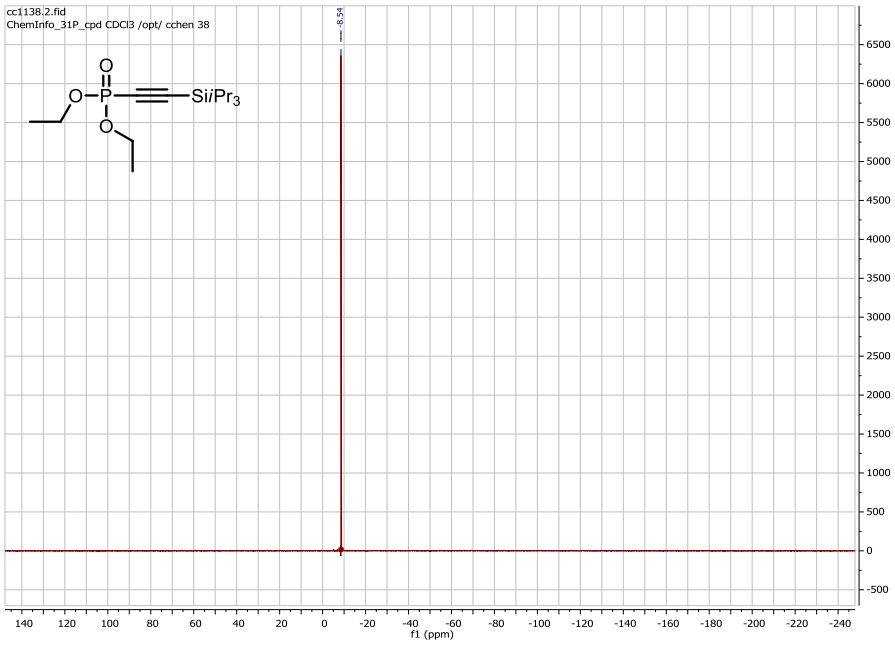
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7a**

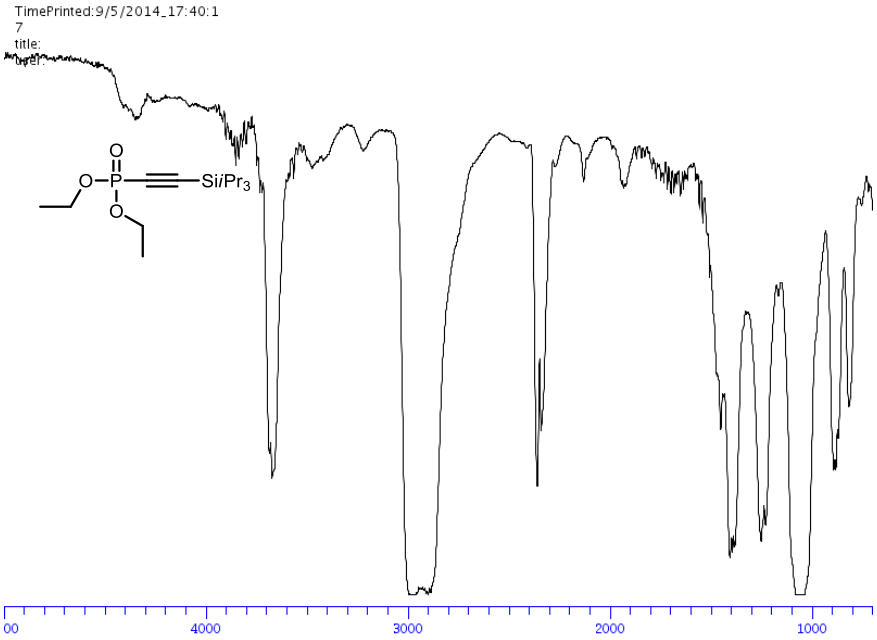


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7a**

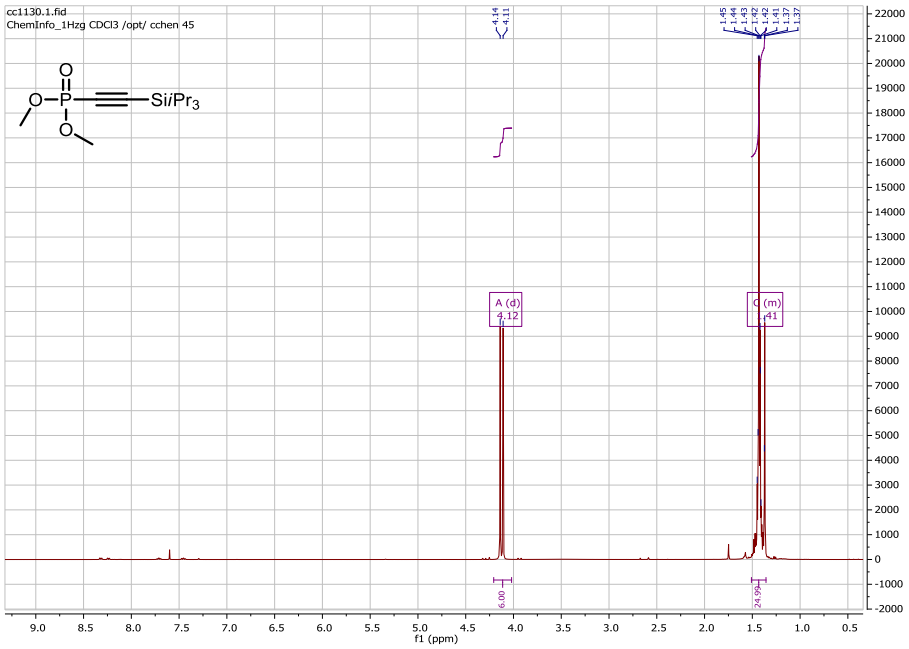


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **7a**

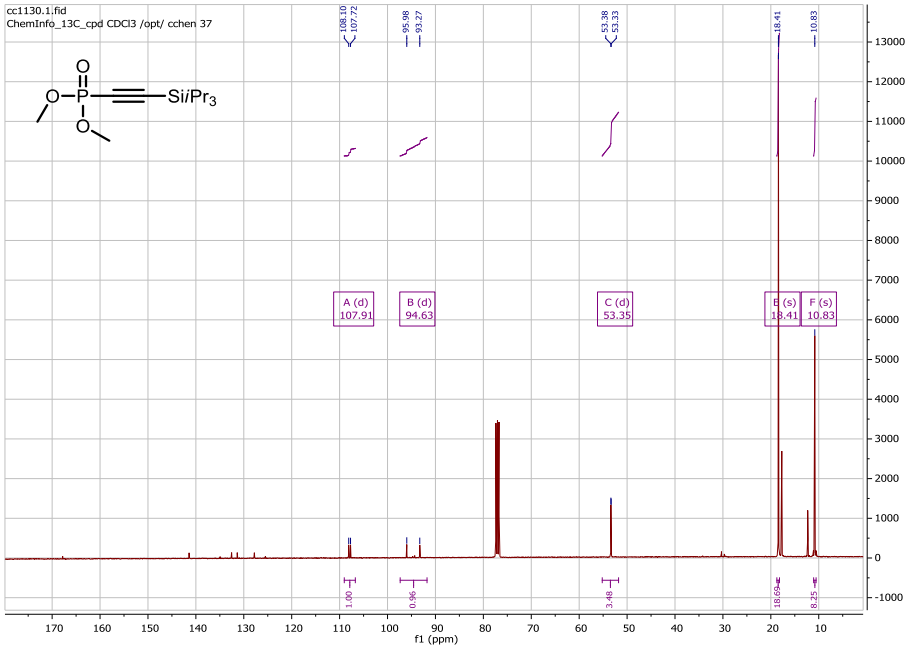




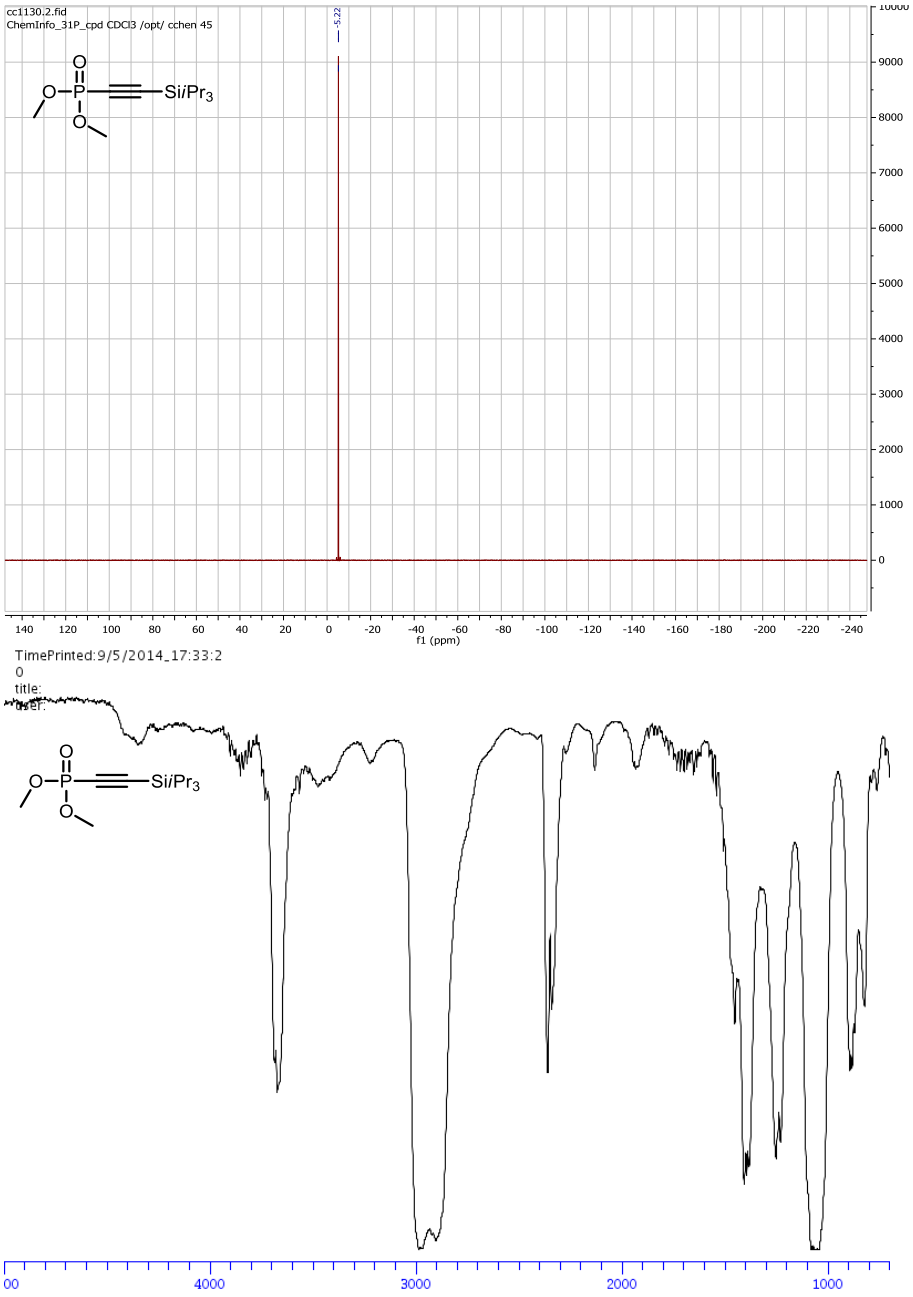
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7b**



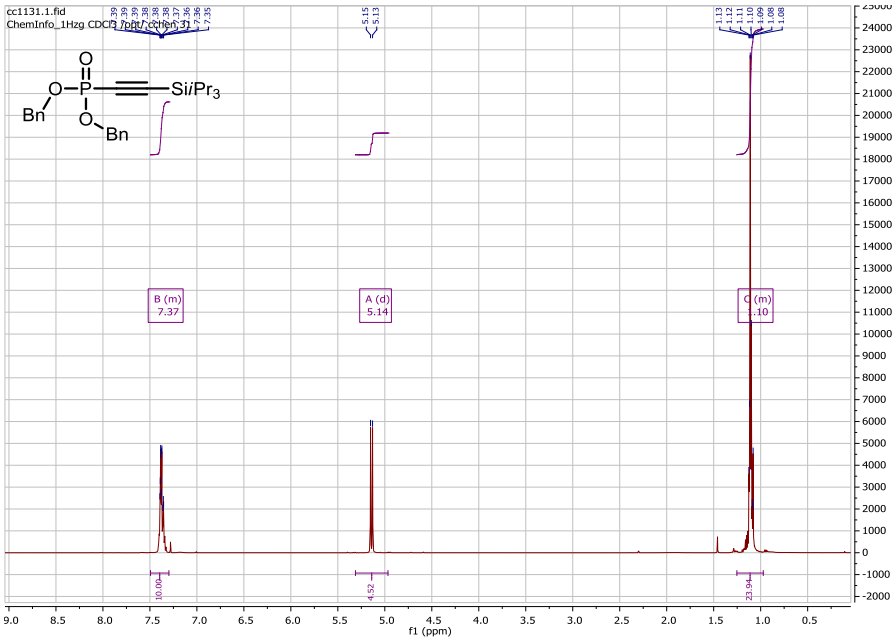
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7b**



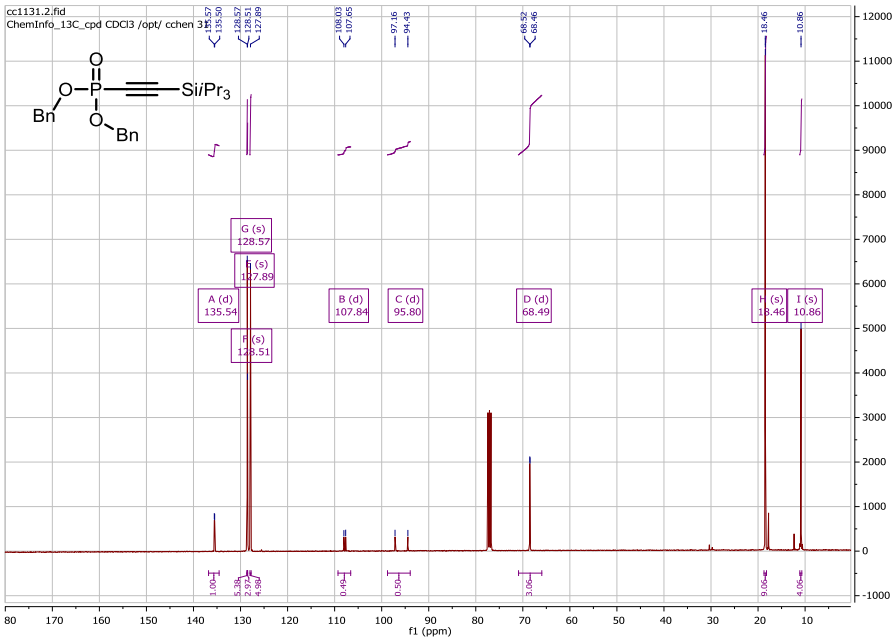
^{31}P-NMR (162 MHz, $CDCl_3$) of compound **7b**



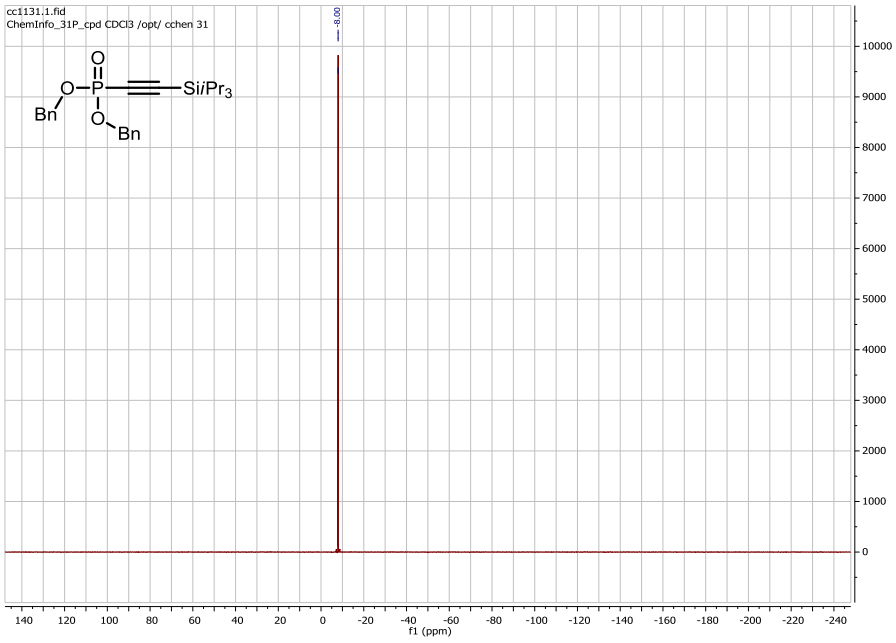
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7c**

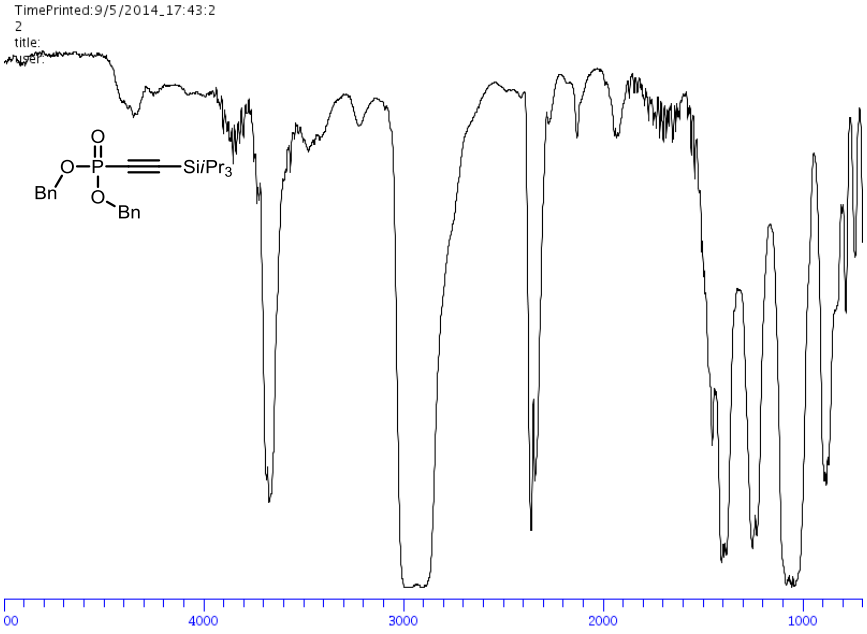


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7c**

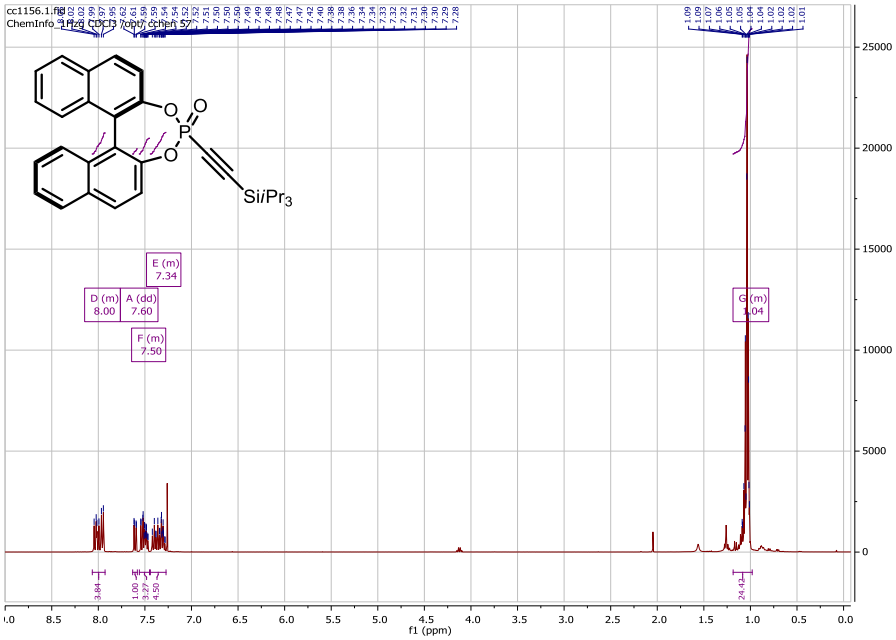


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **7c**

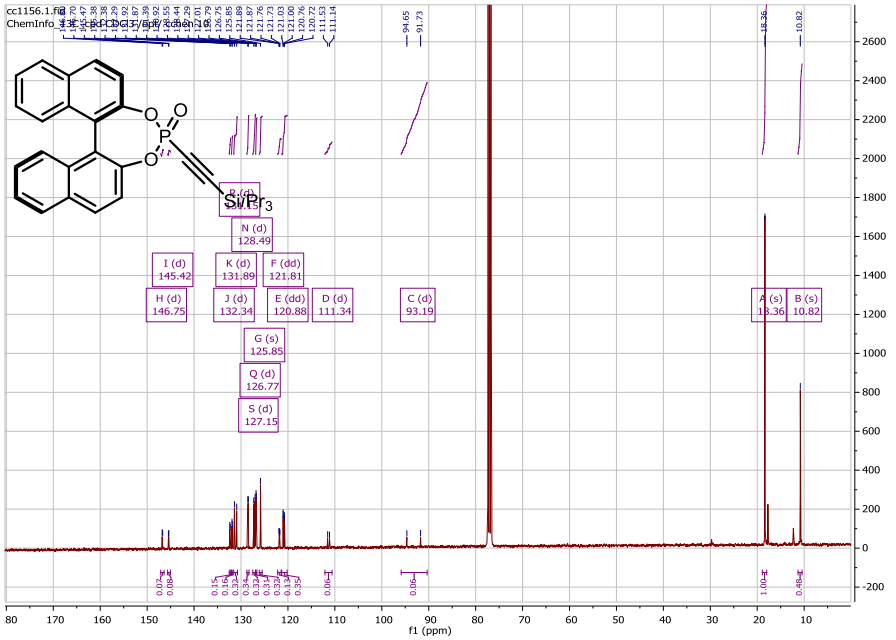




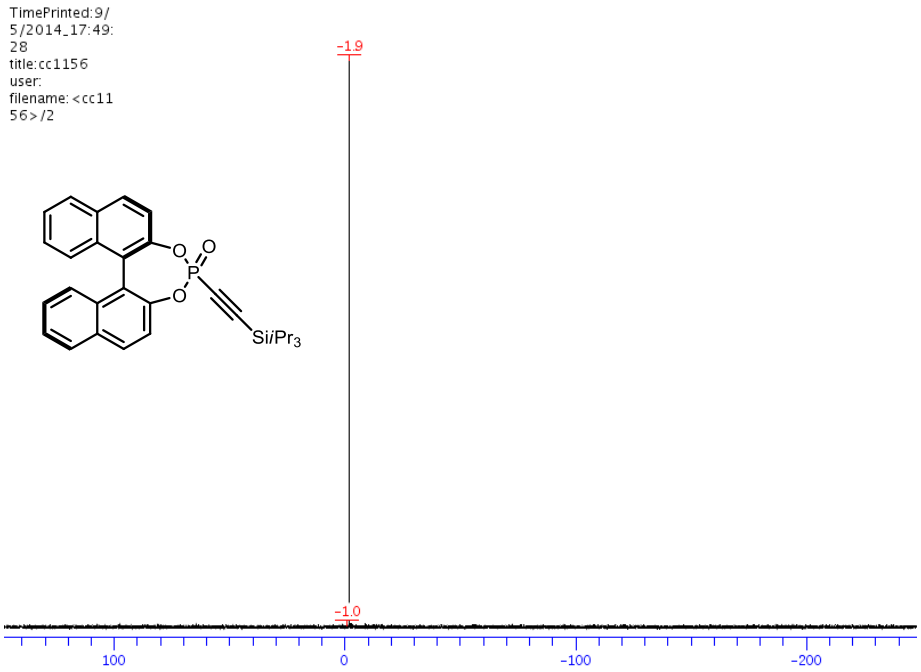
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7d**

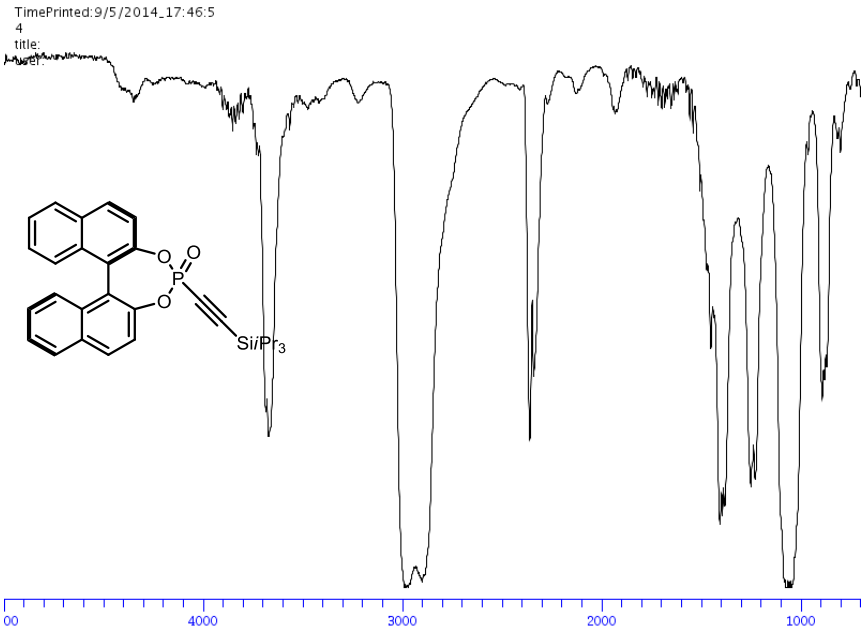


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7d**

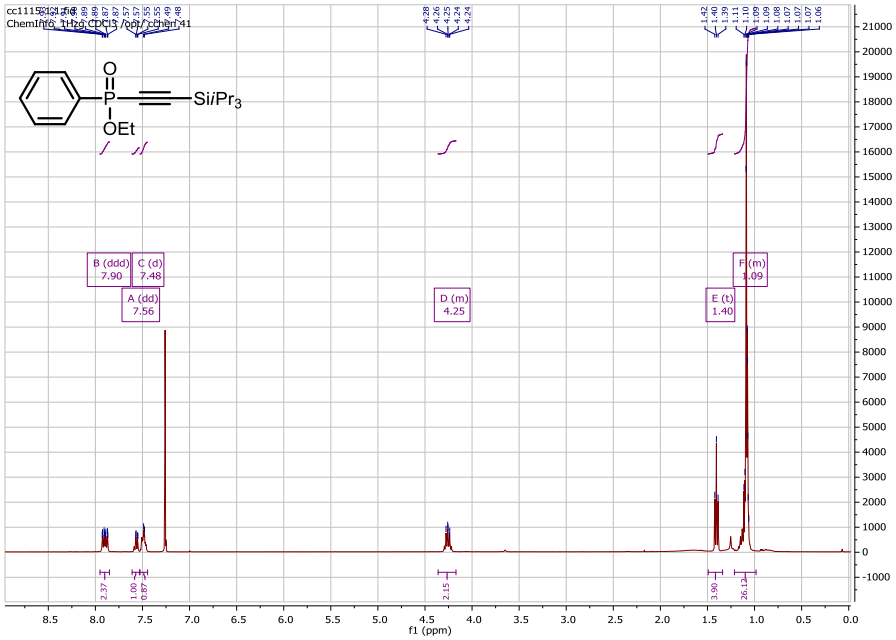


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **7d**

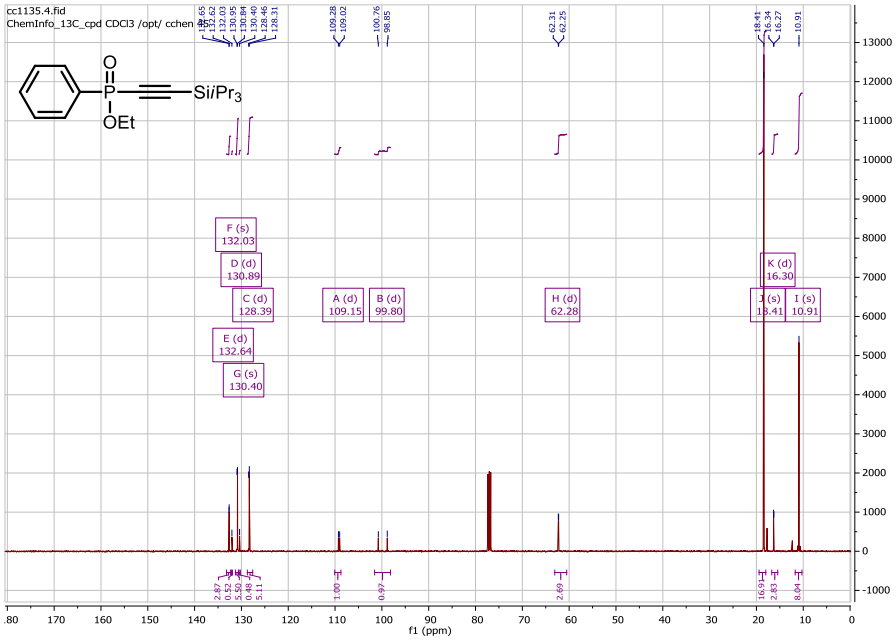




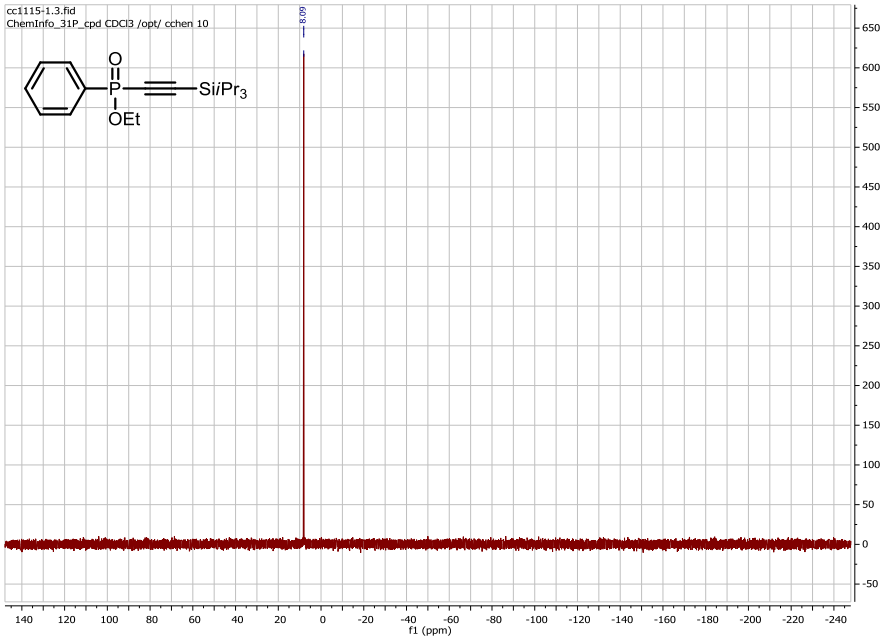
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7e**

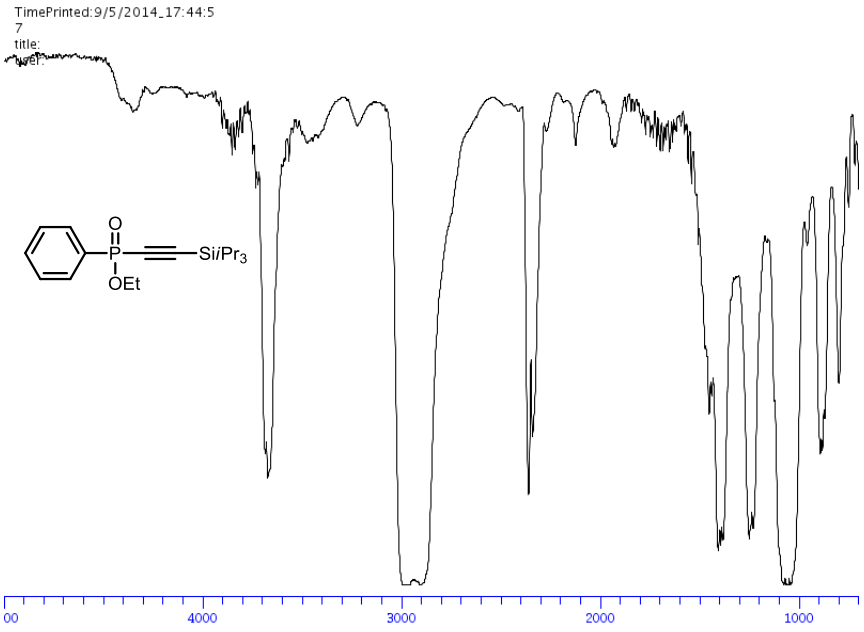


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7e**

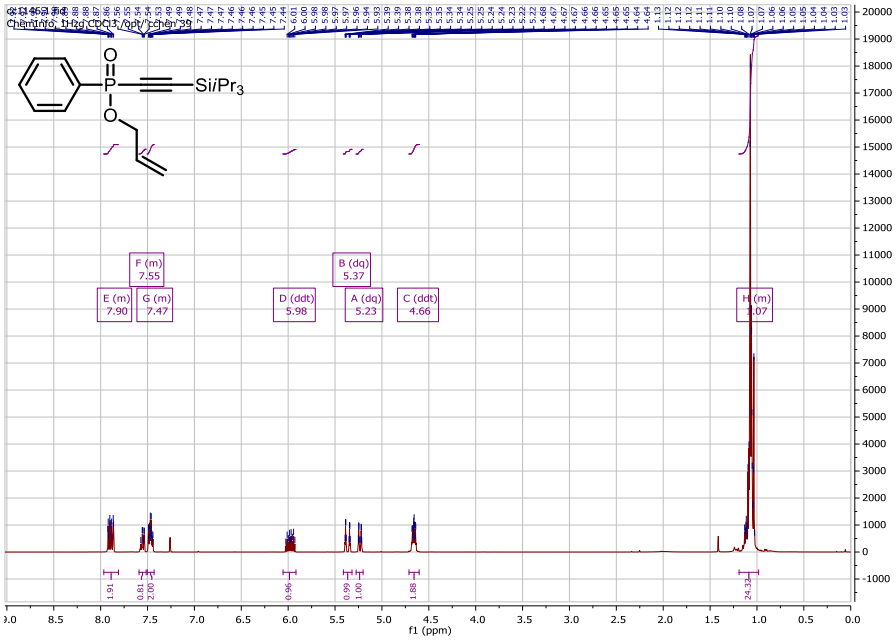


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **7e**

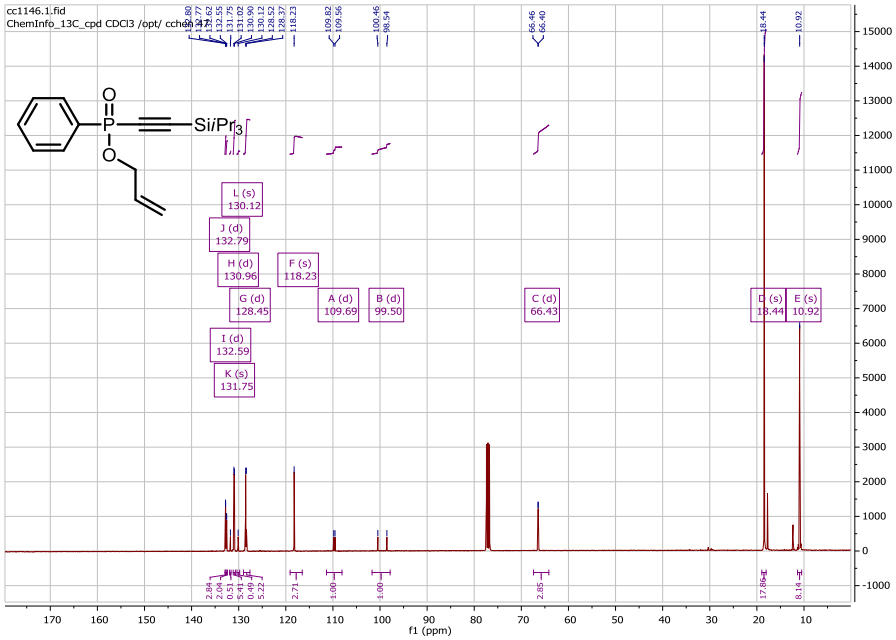




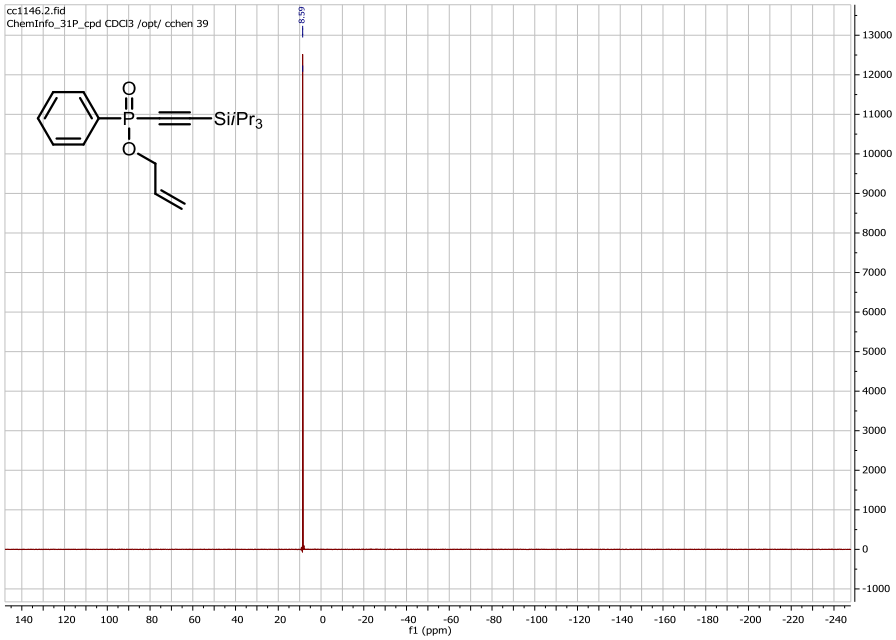
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7f**

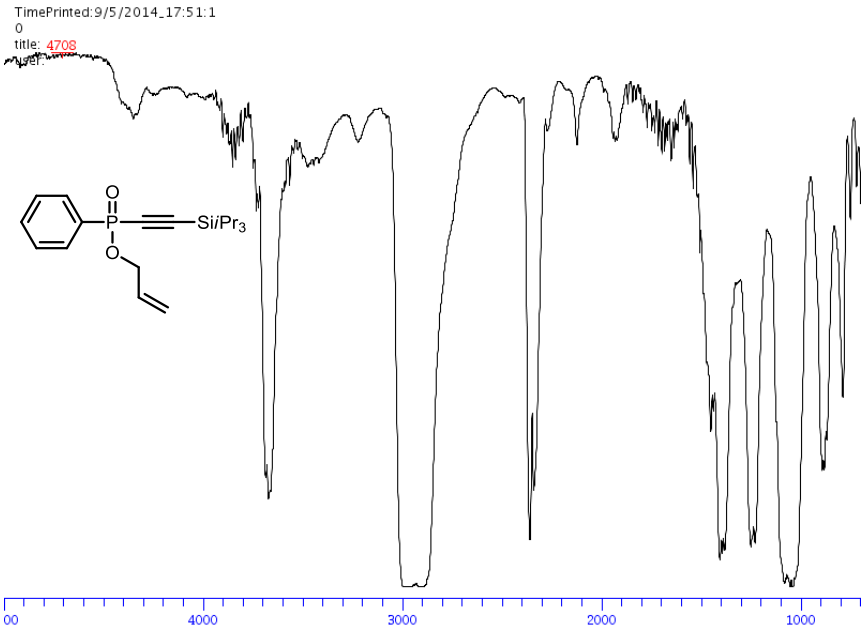


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7f**

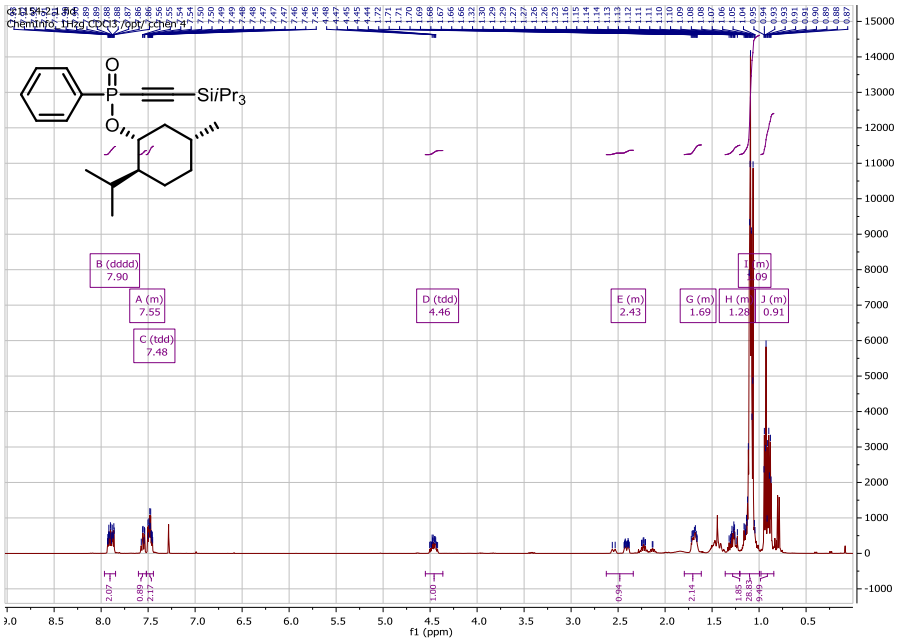


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **7f**

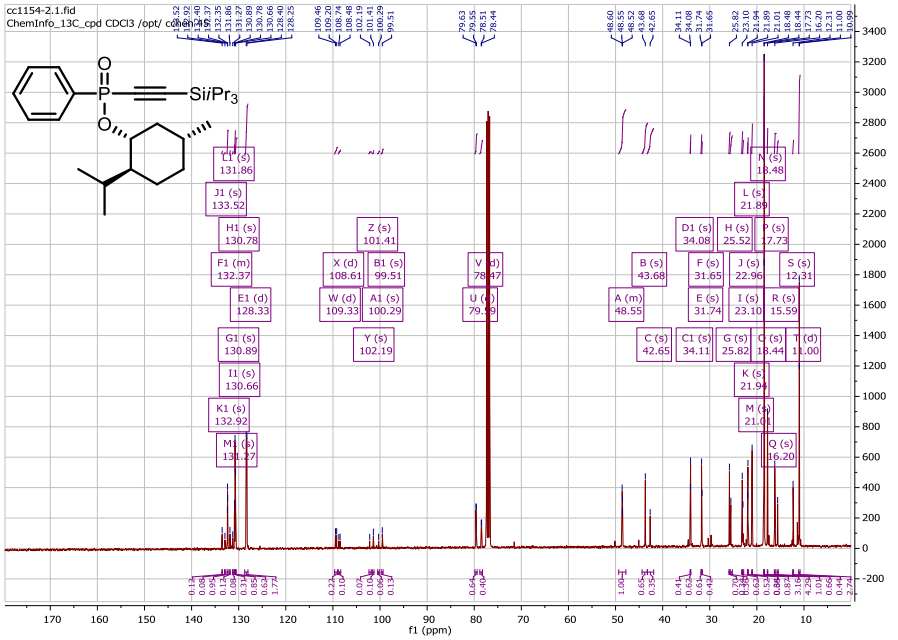




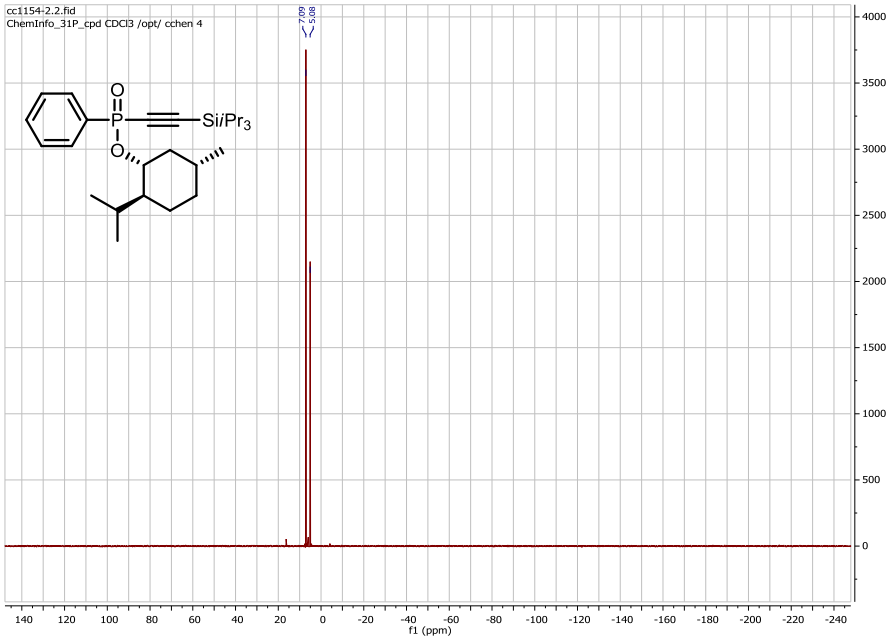
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7g**

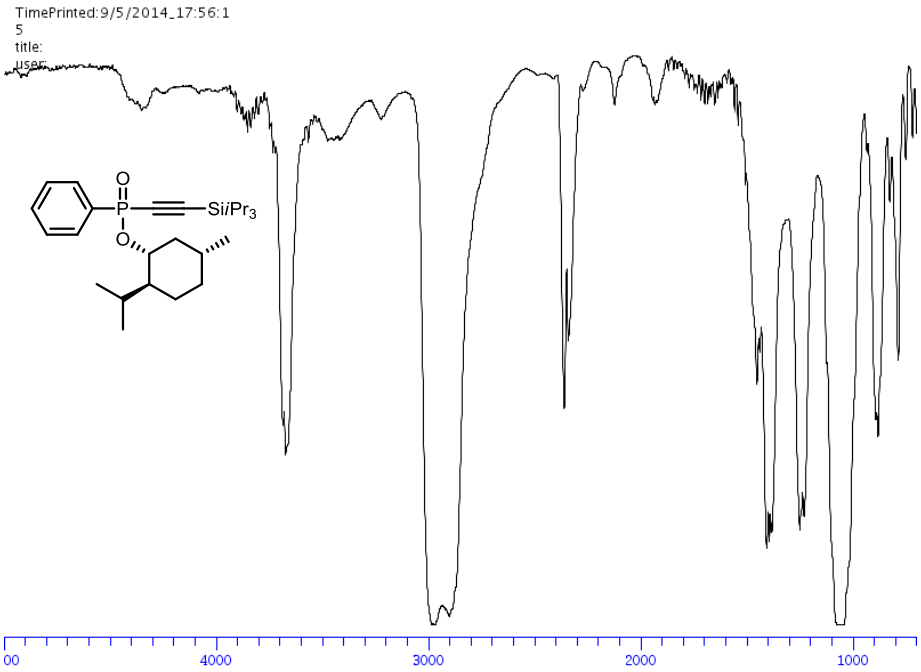


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7g**

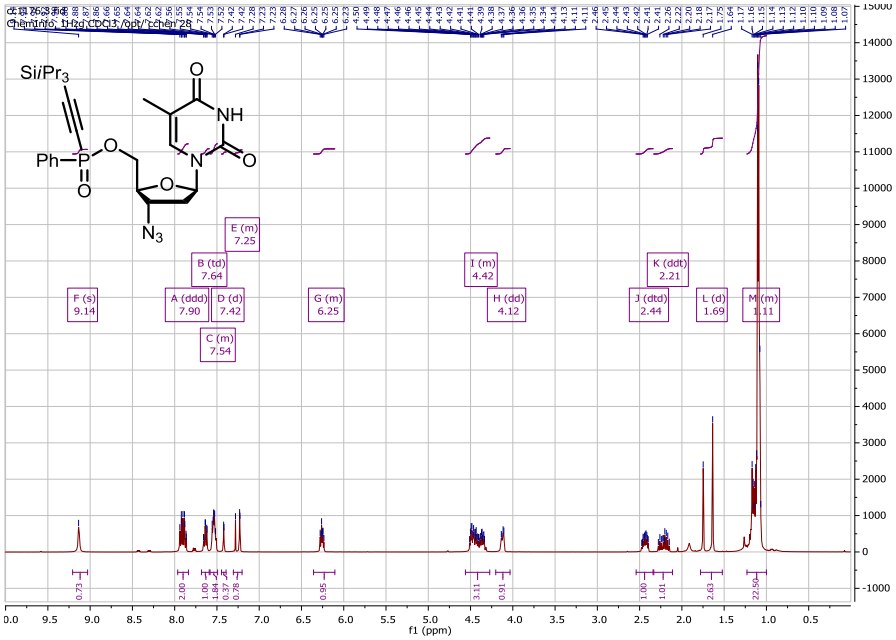


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **7g**

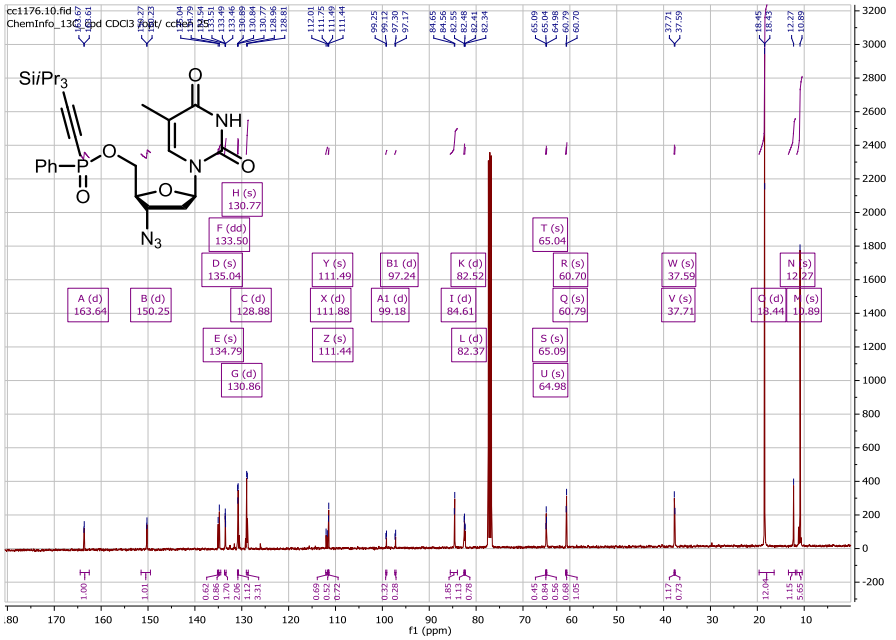




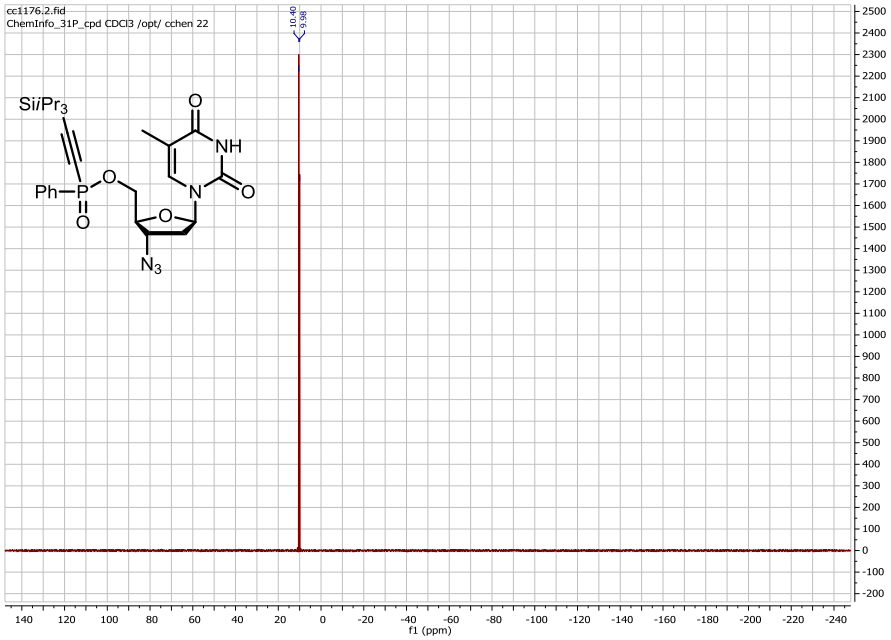
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7h**

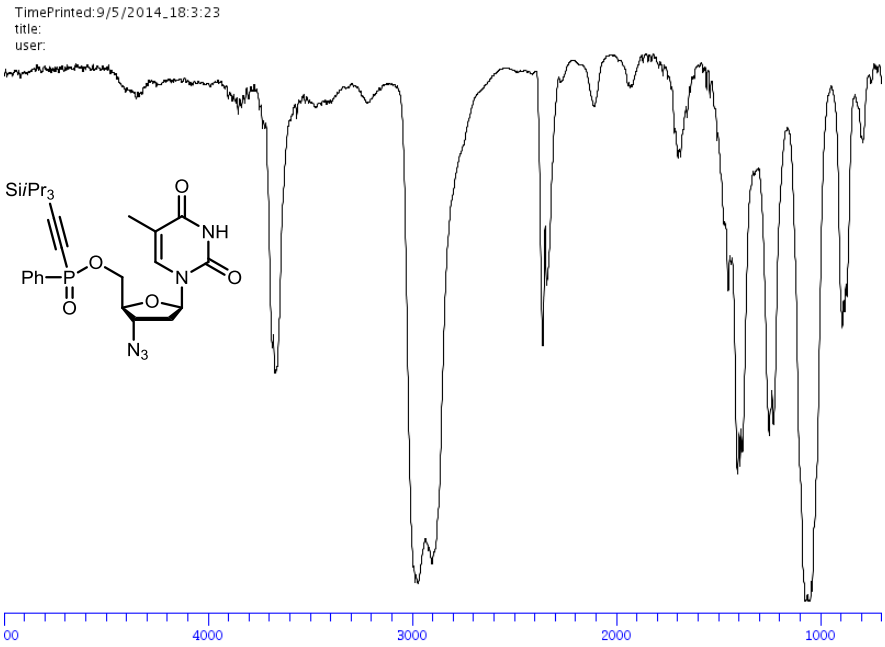


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7h**

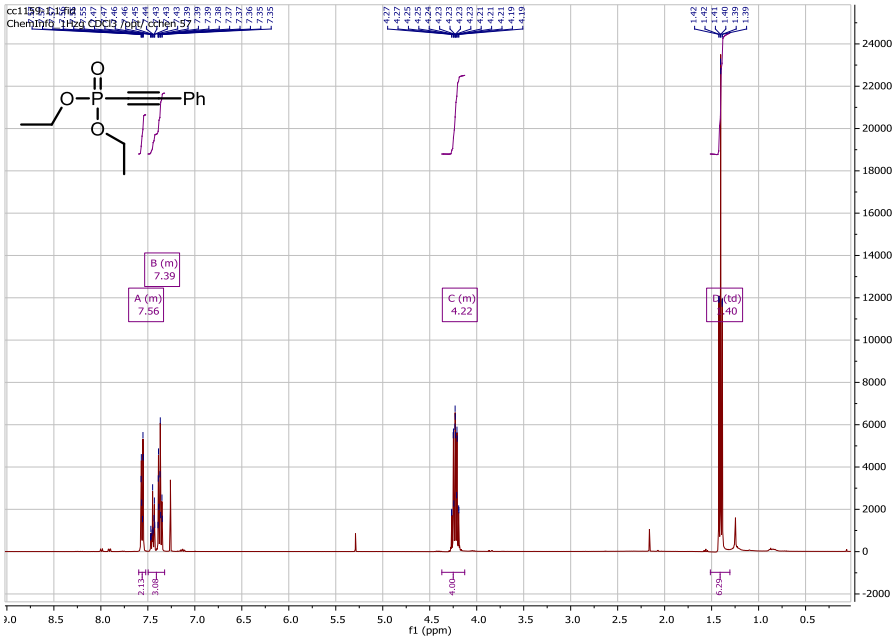


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **7h**

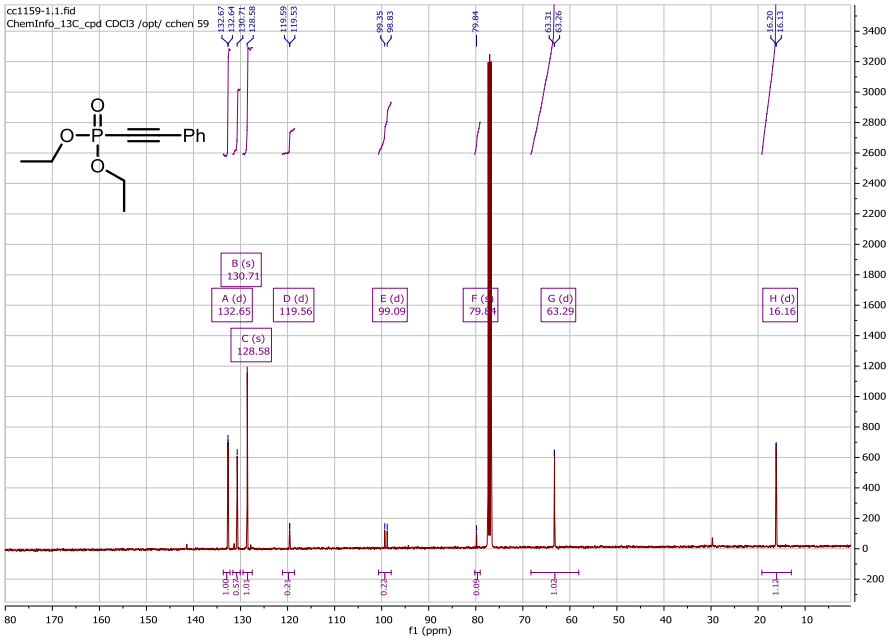




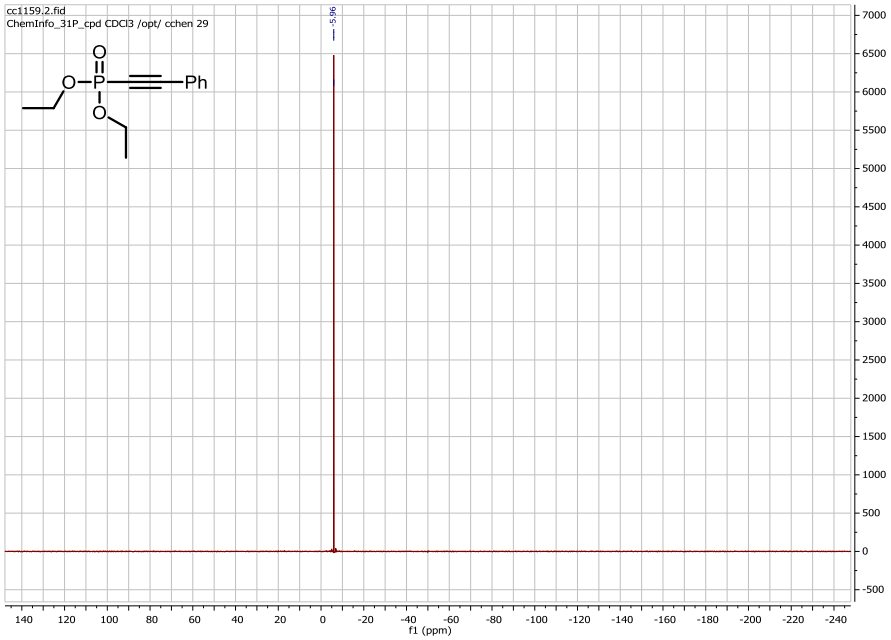
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7j**

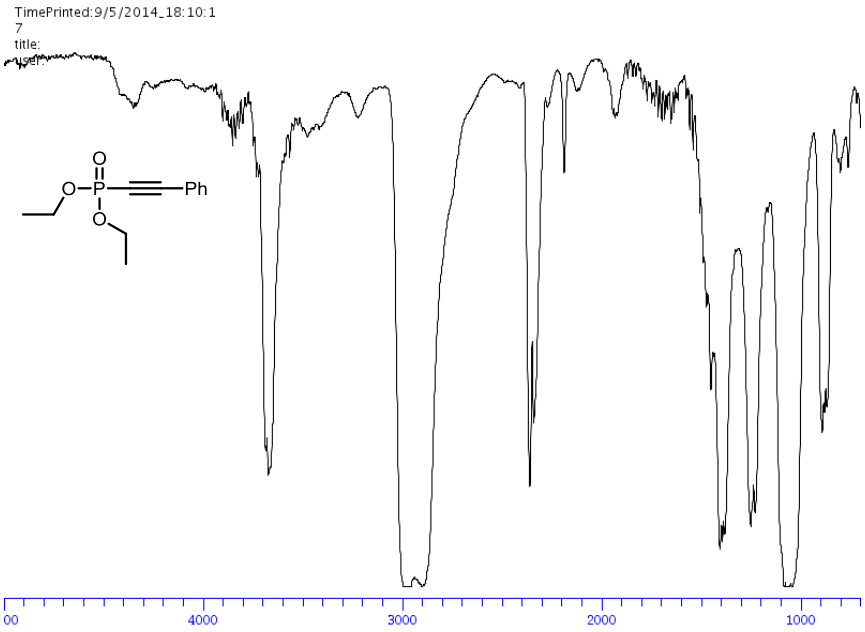


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7j**

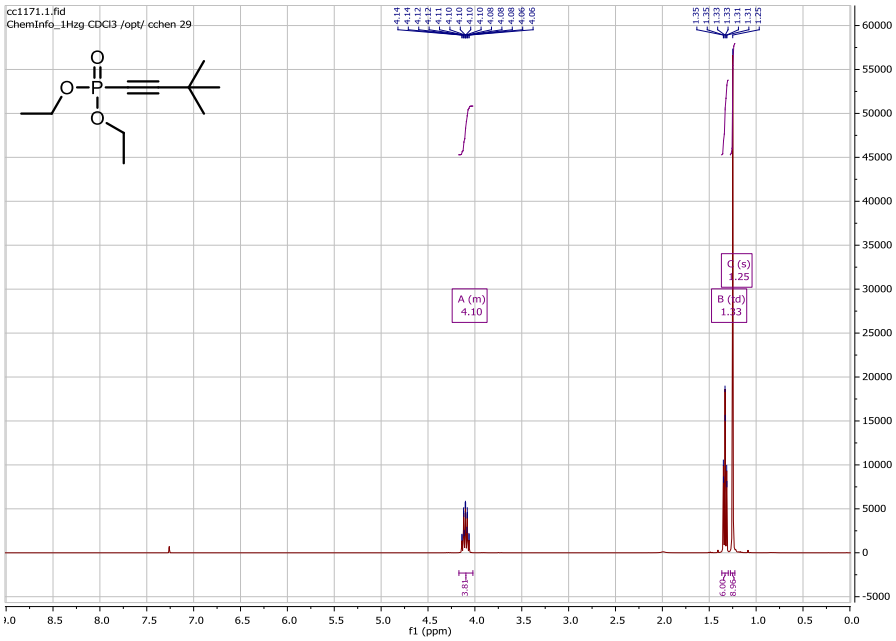


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **7j**

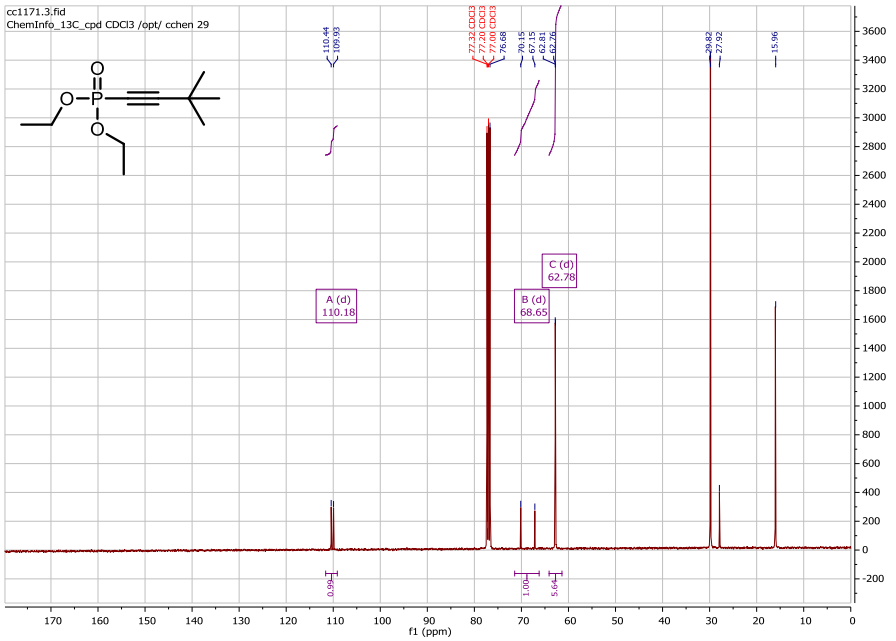




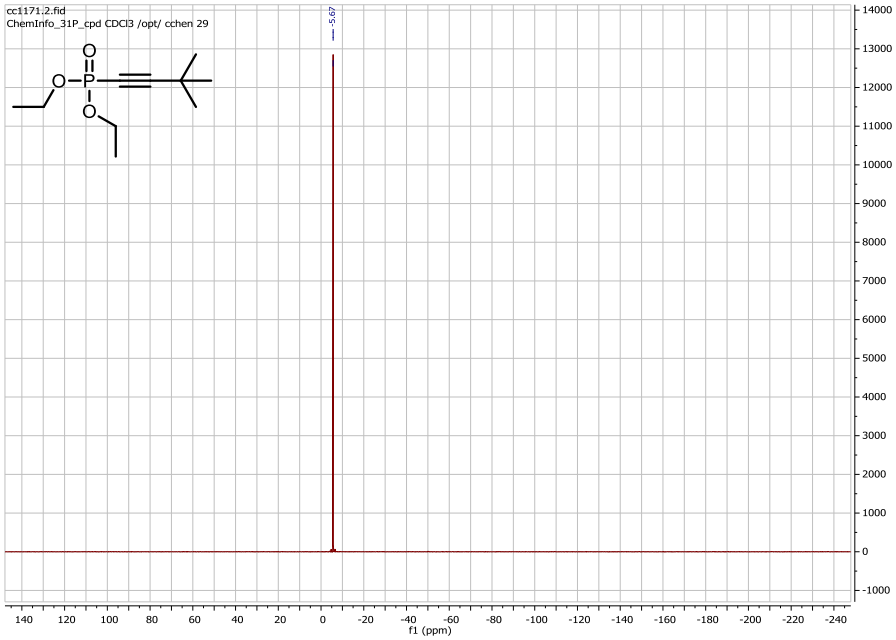
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7k**

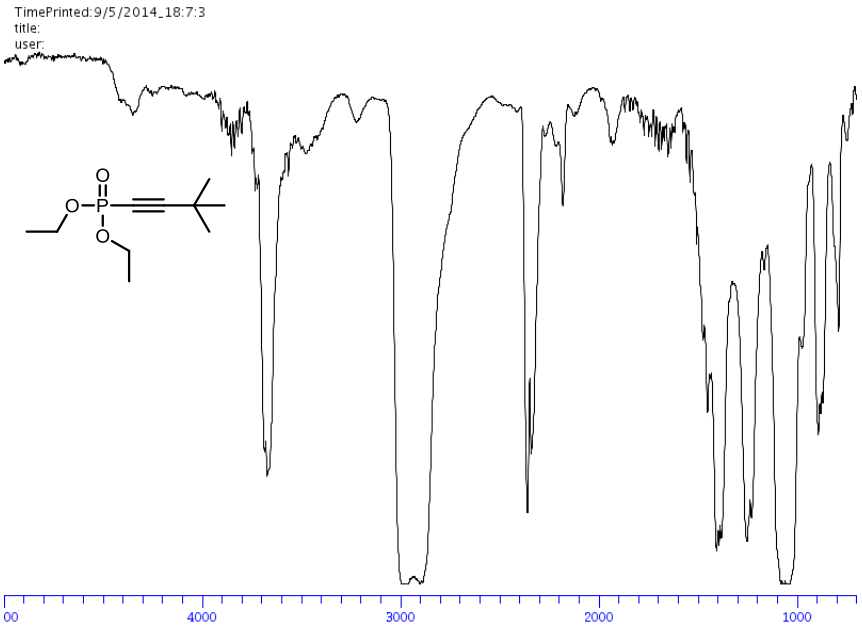


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7k**

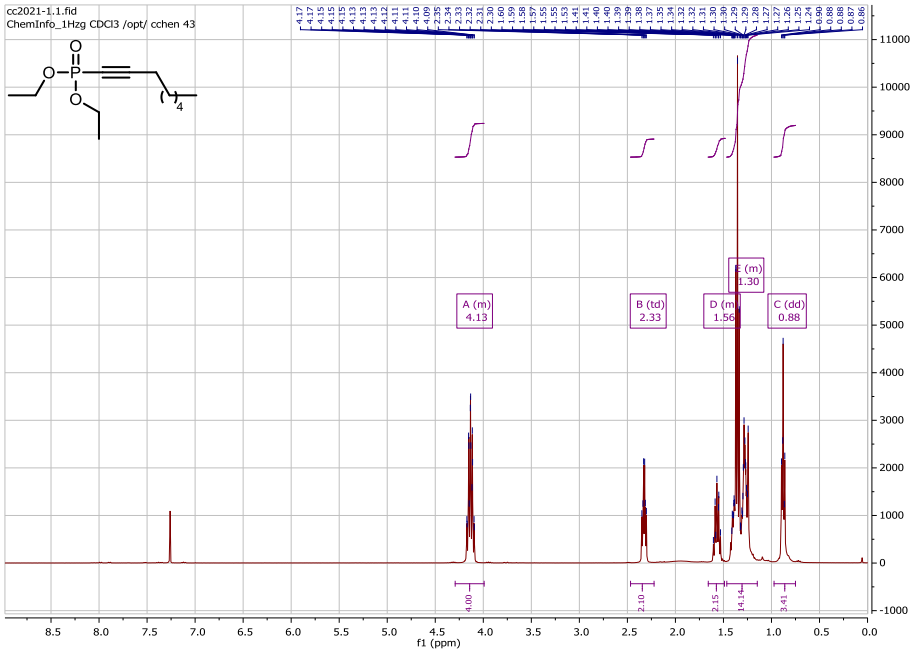


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **7k**

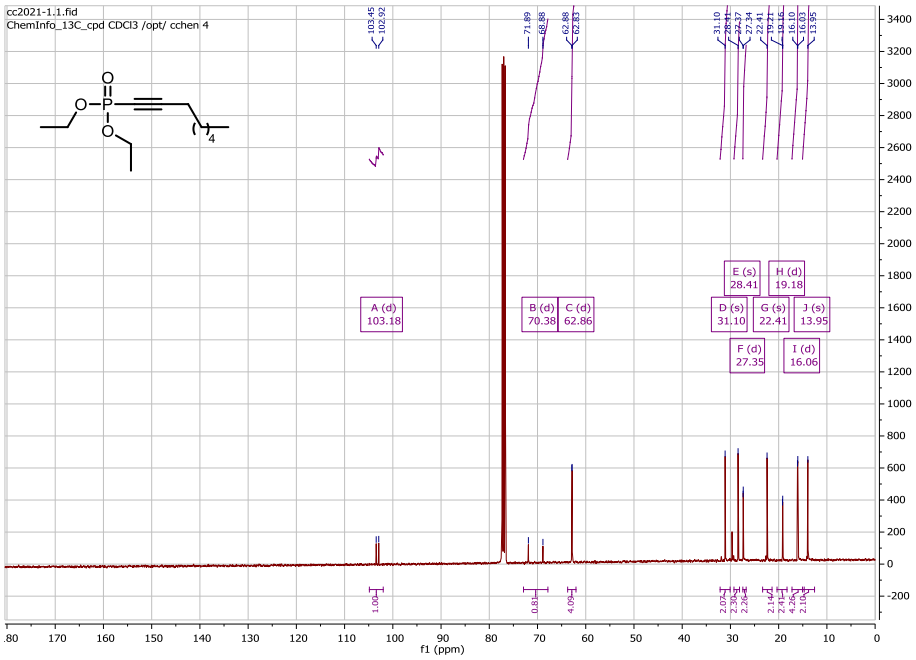




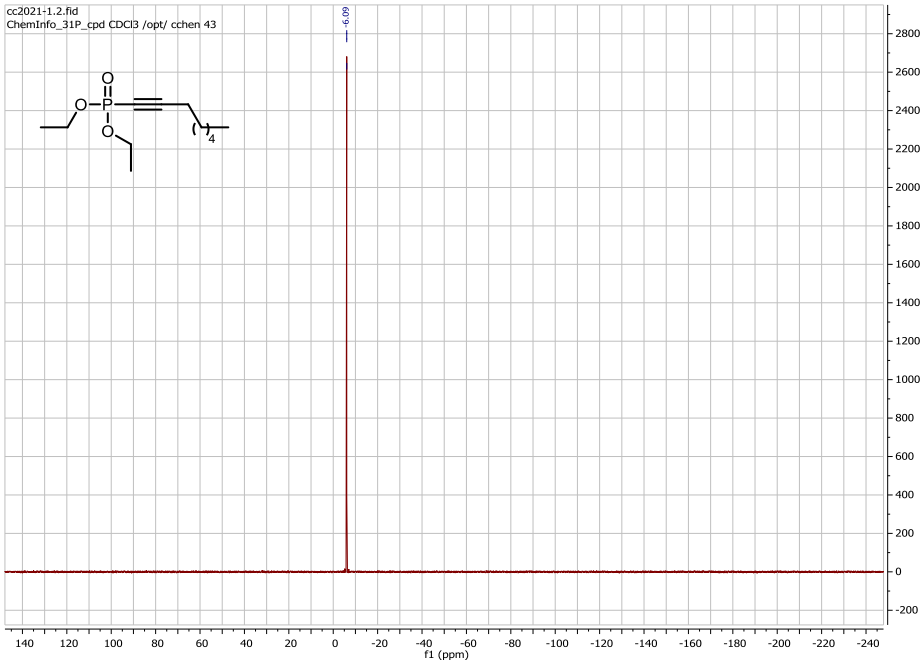
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **7l**

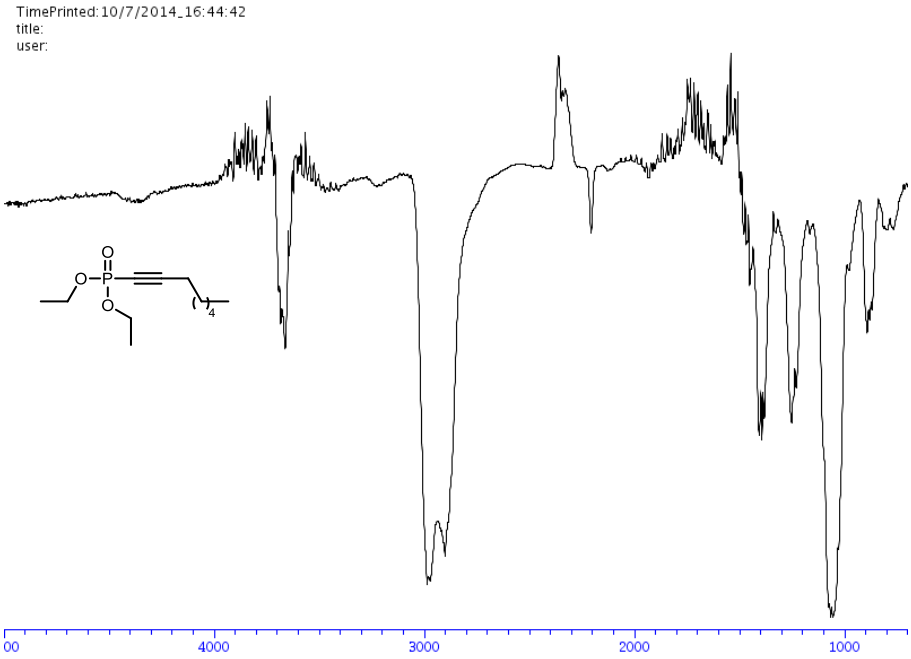


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **7l**

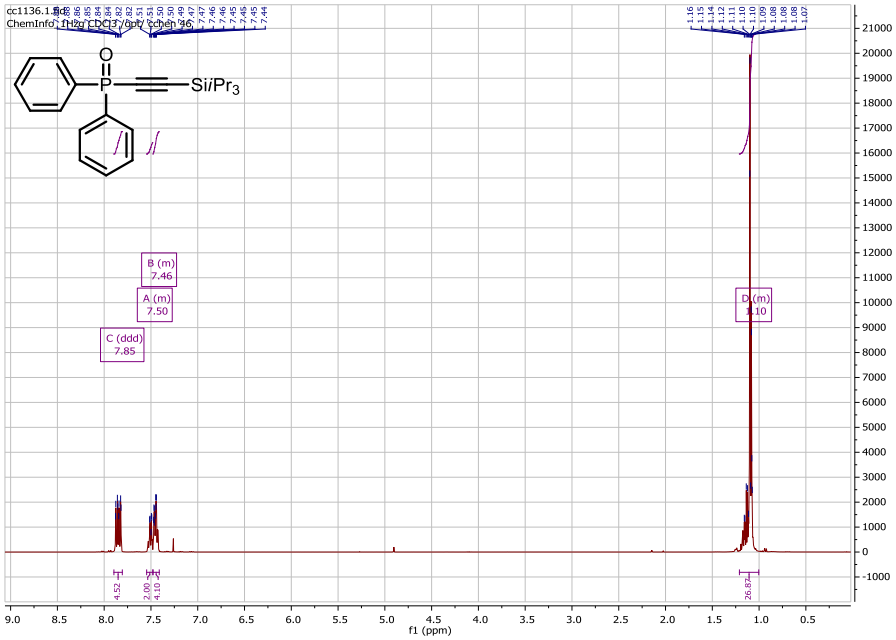


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **7l**

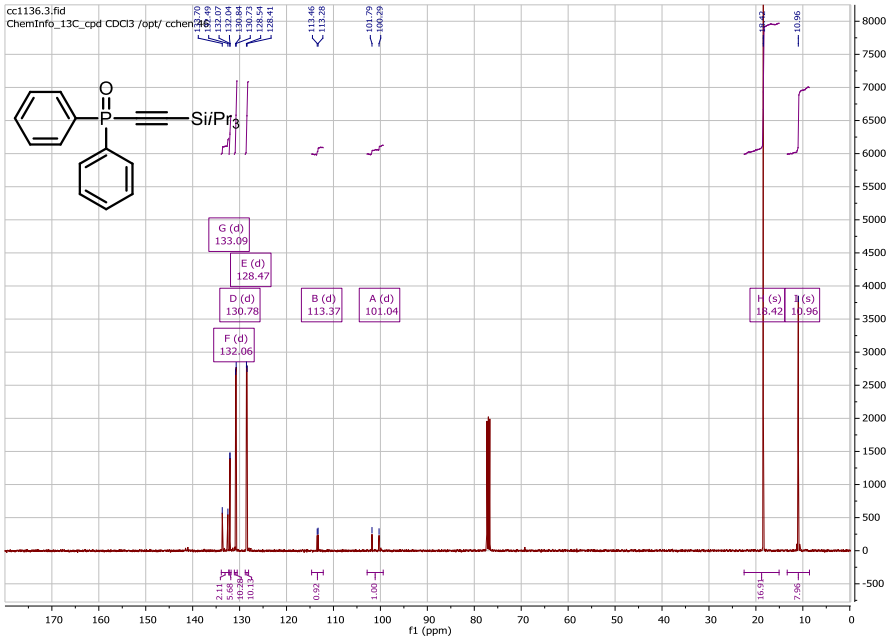




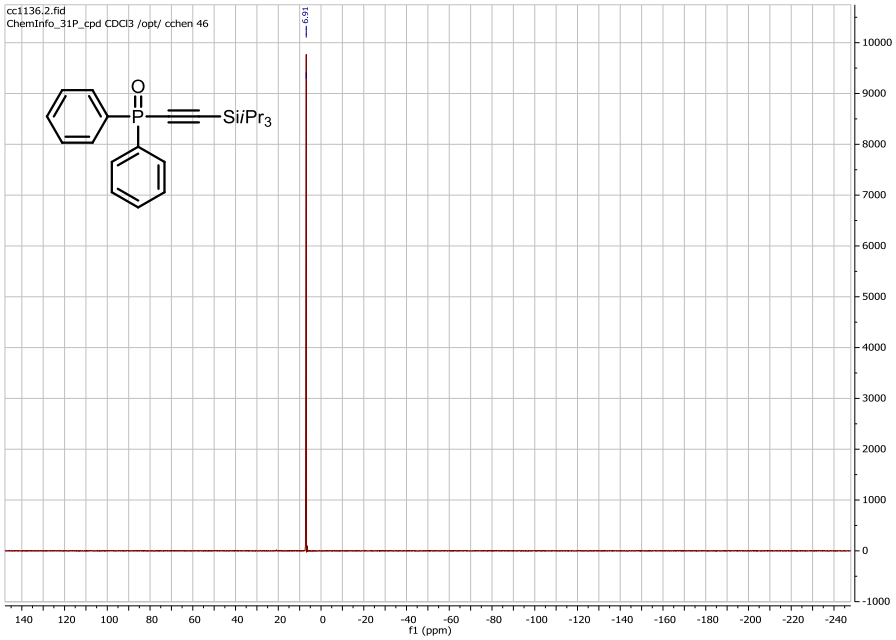
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **9a**

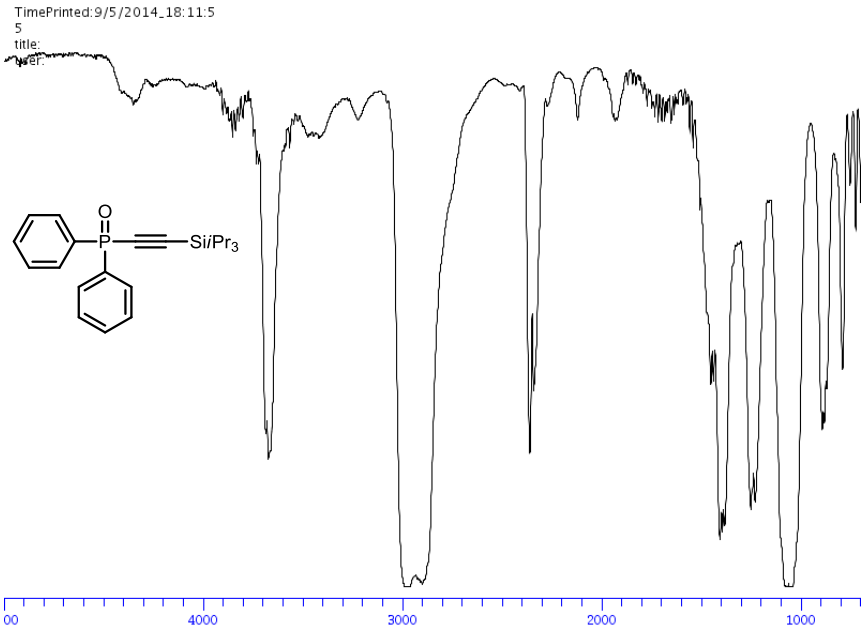


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **9a**

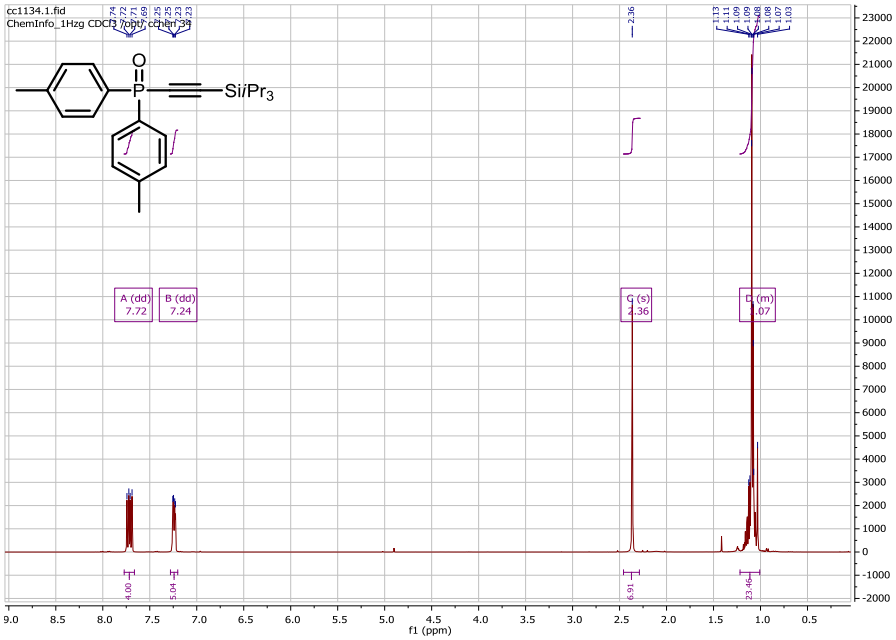


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **9a**

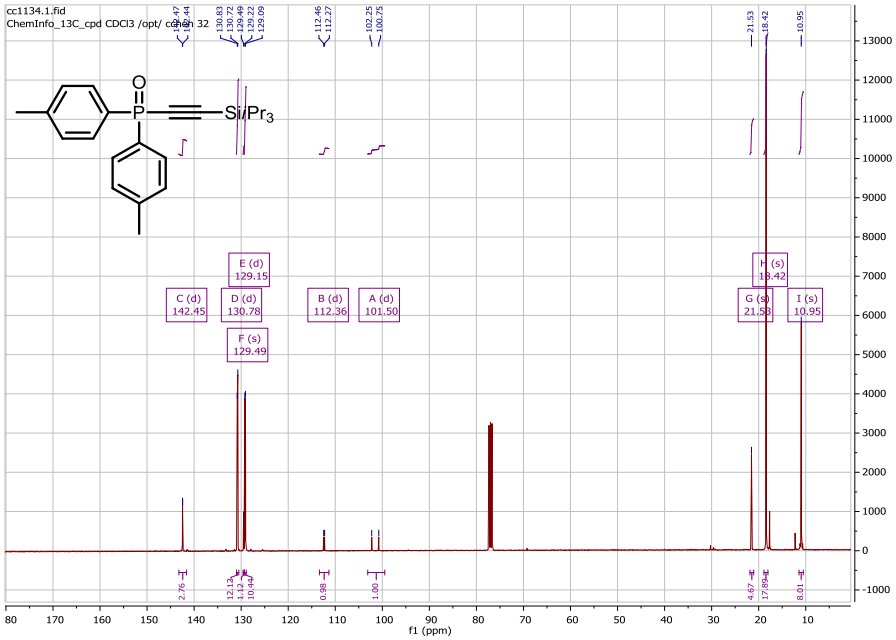




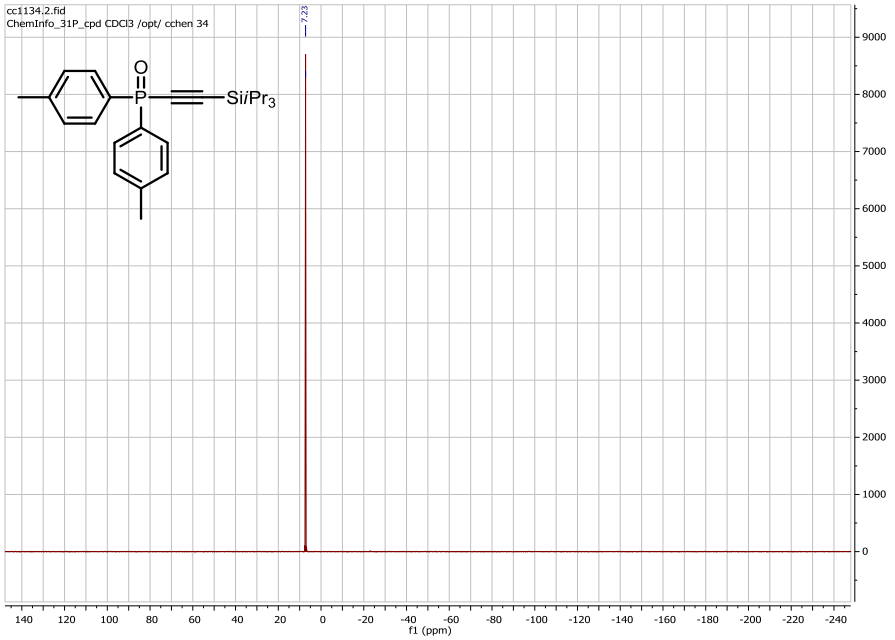
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **9b**

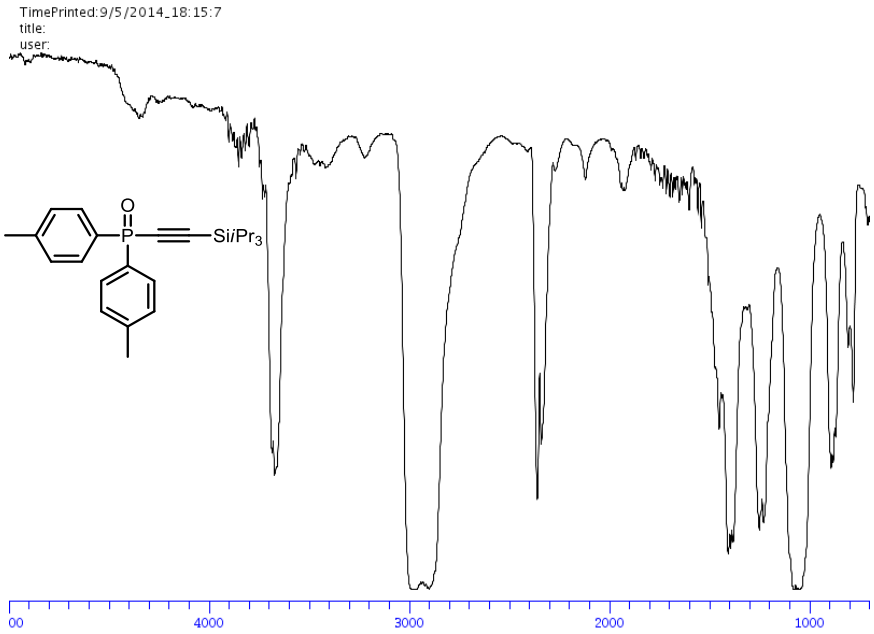


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **9b**

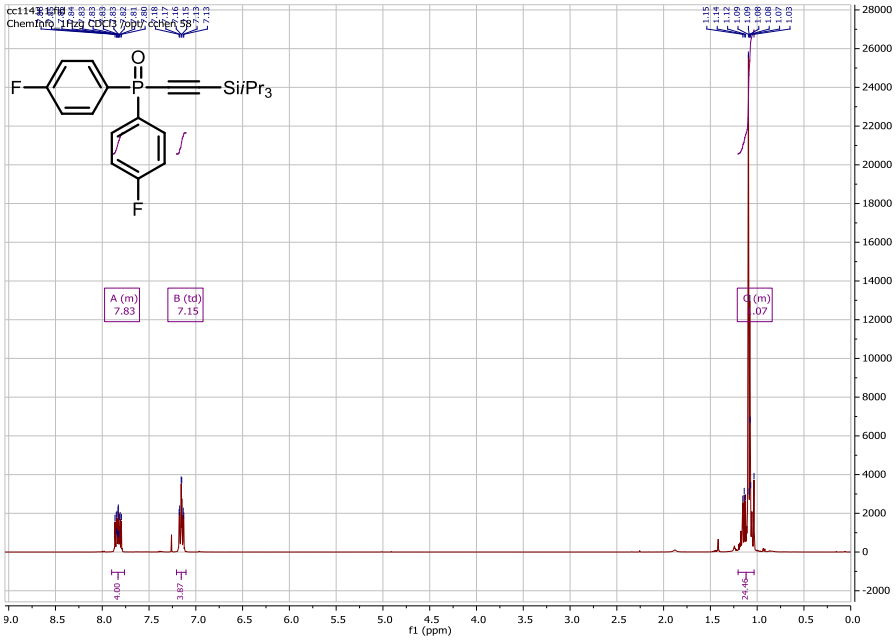


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **9b**

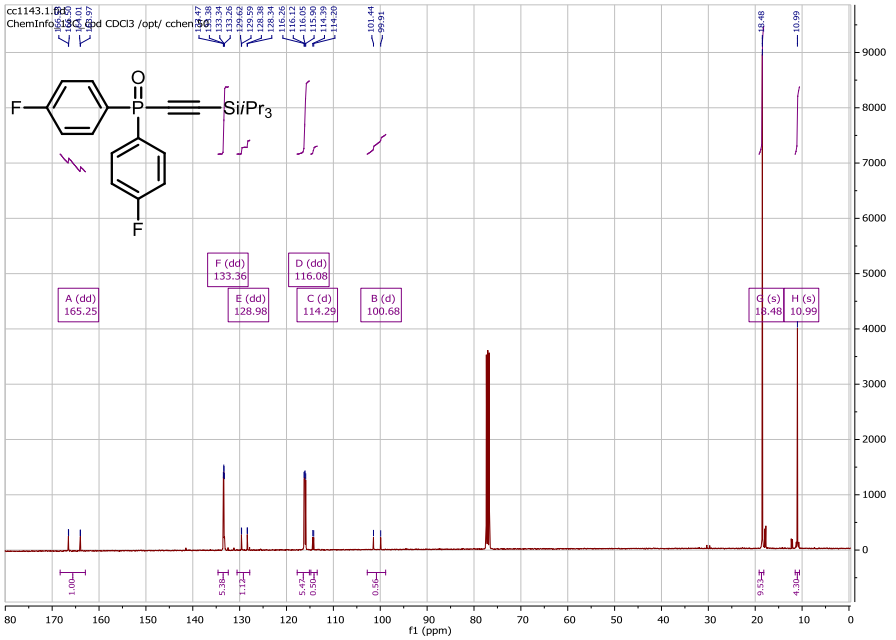




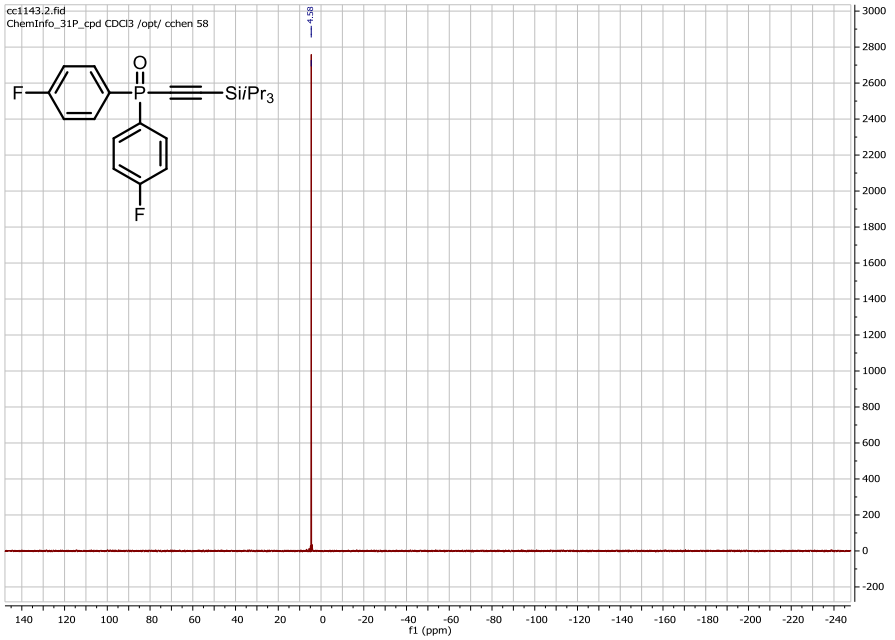
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **9c**



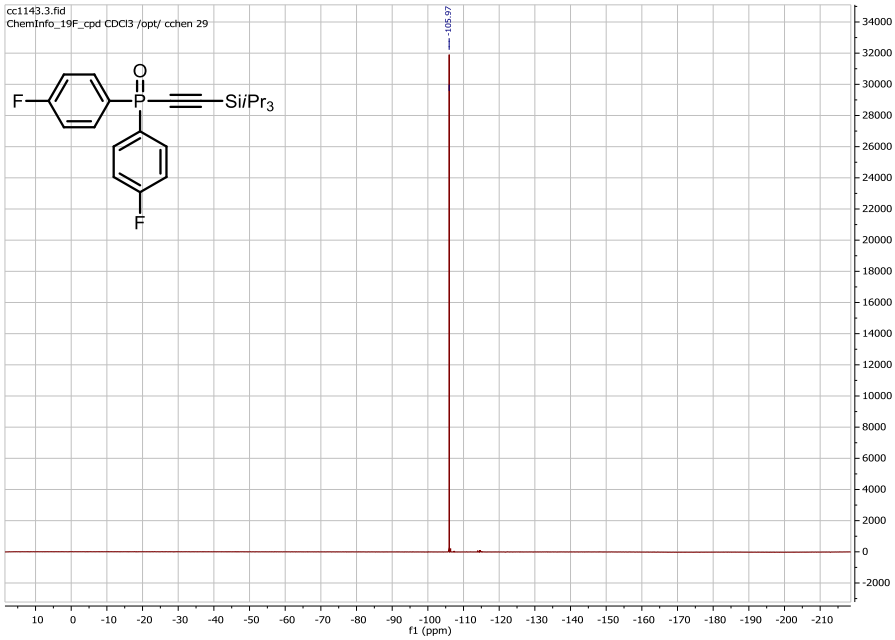
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **9c**

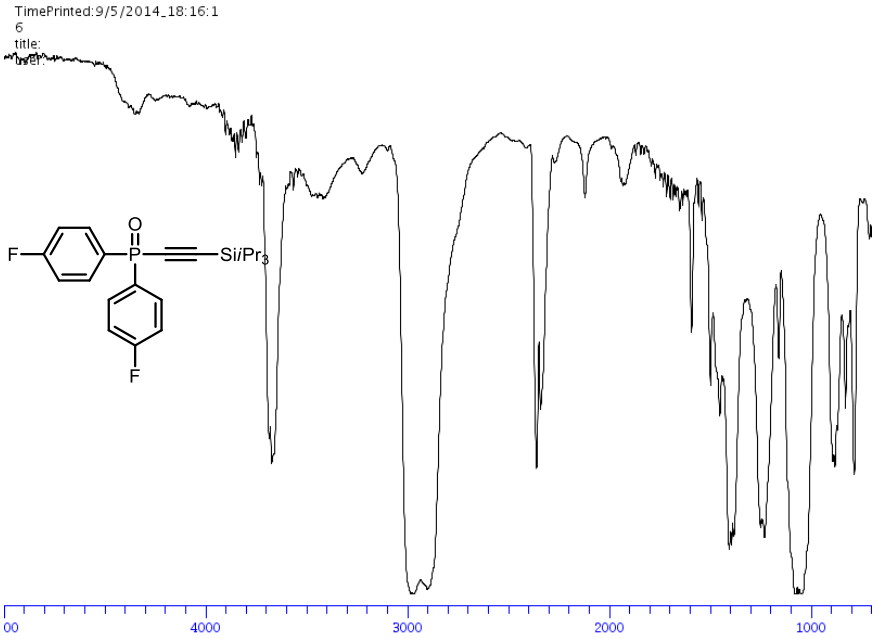


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **9c**

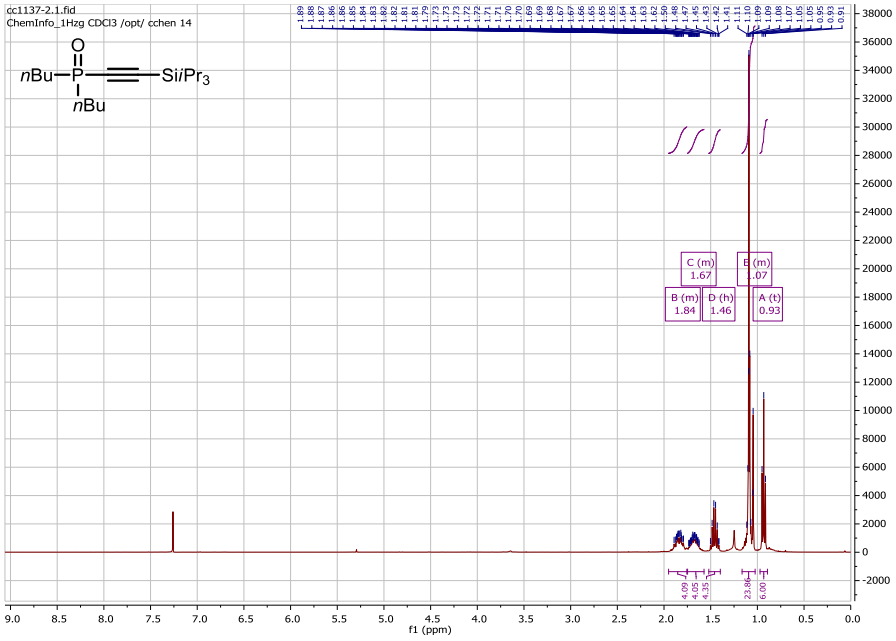


^{19}F-NMR (376 MHz, $CDCl_3$) of compound **9c**



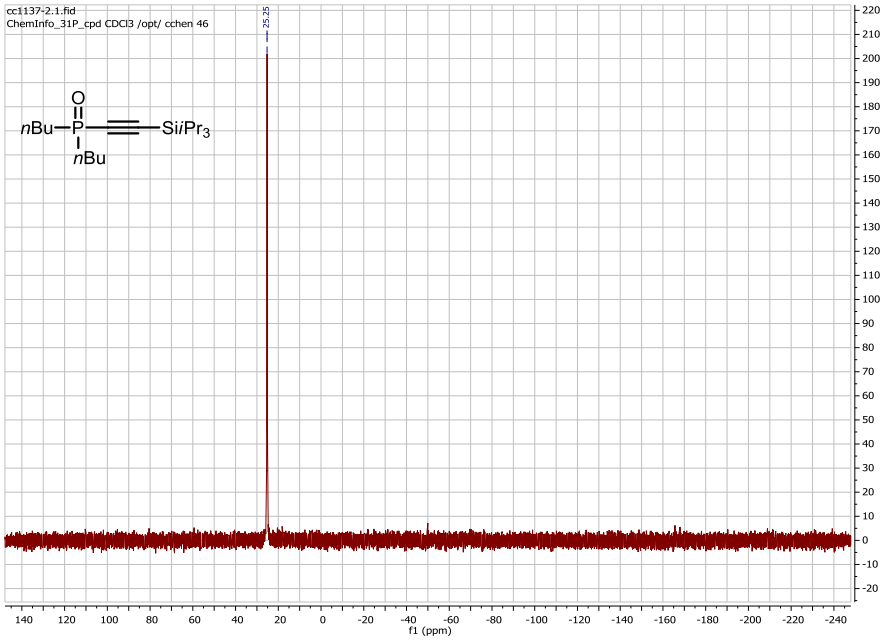


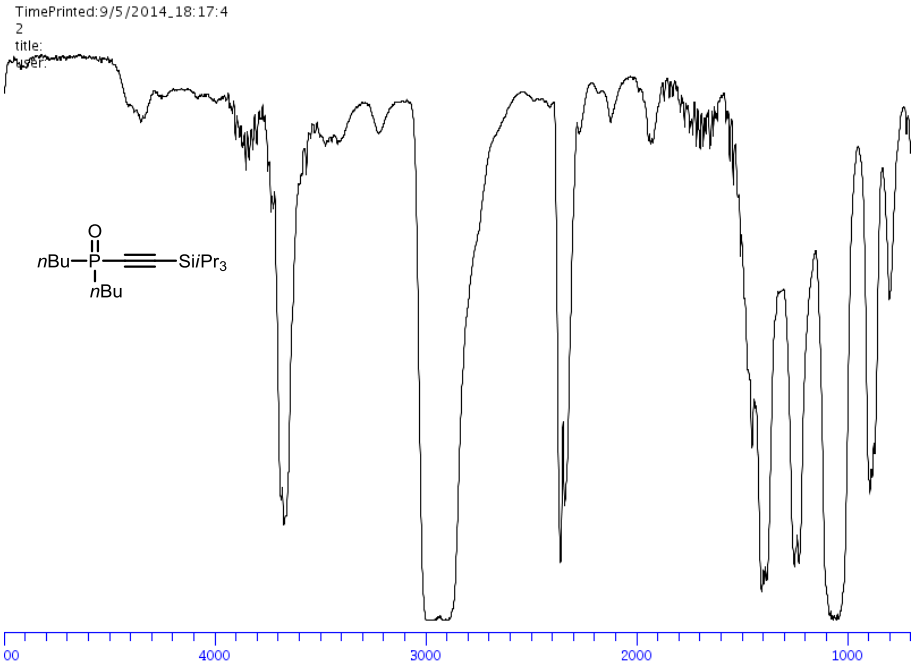
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **9d**



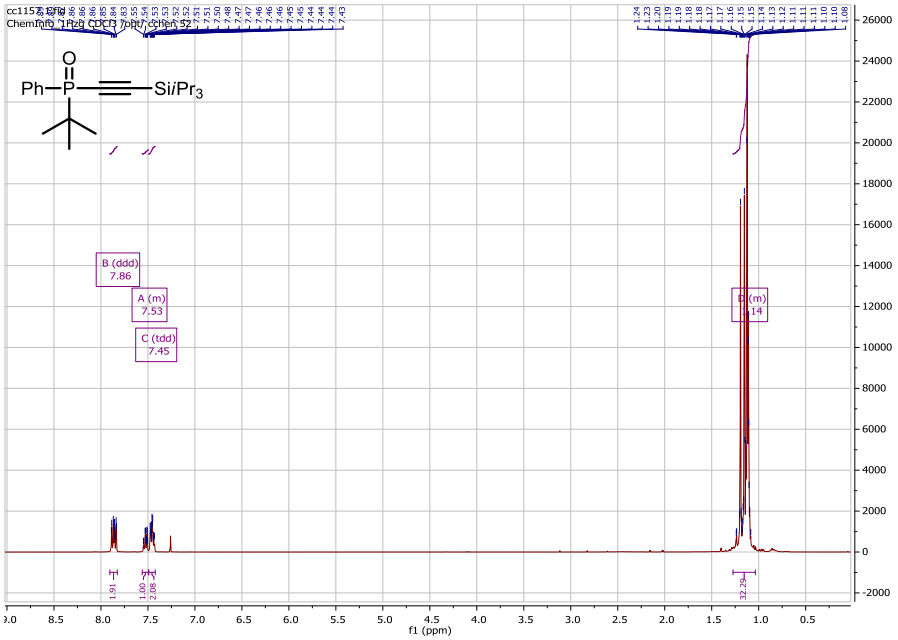
^{13}C-NMR (101 MHz, $CDCl_3$) of compound **9d**

^{31}P-NMR (162 MHz, $CDCl_3$) of compound **9d**

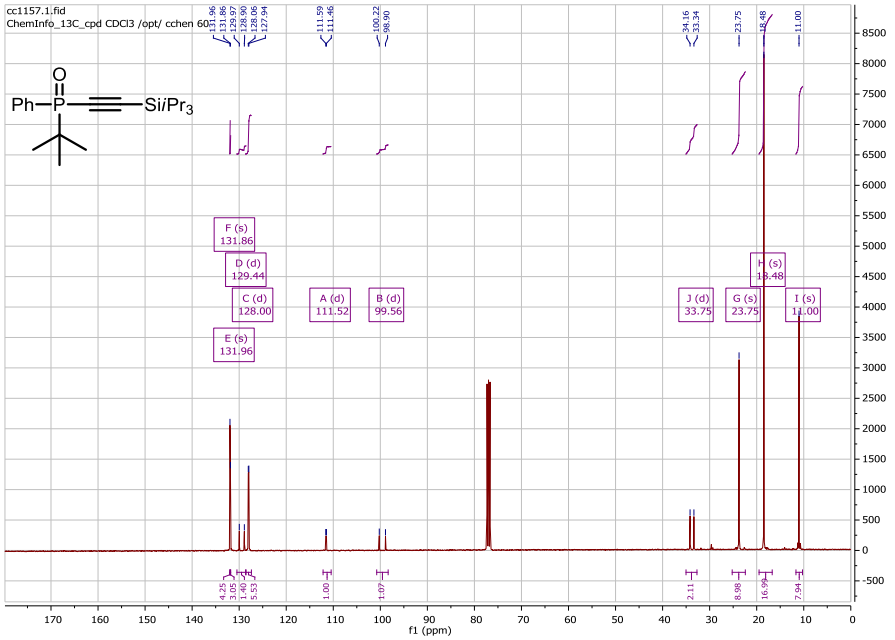




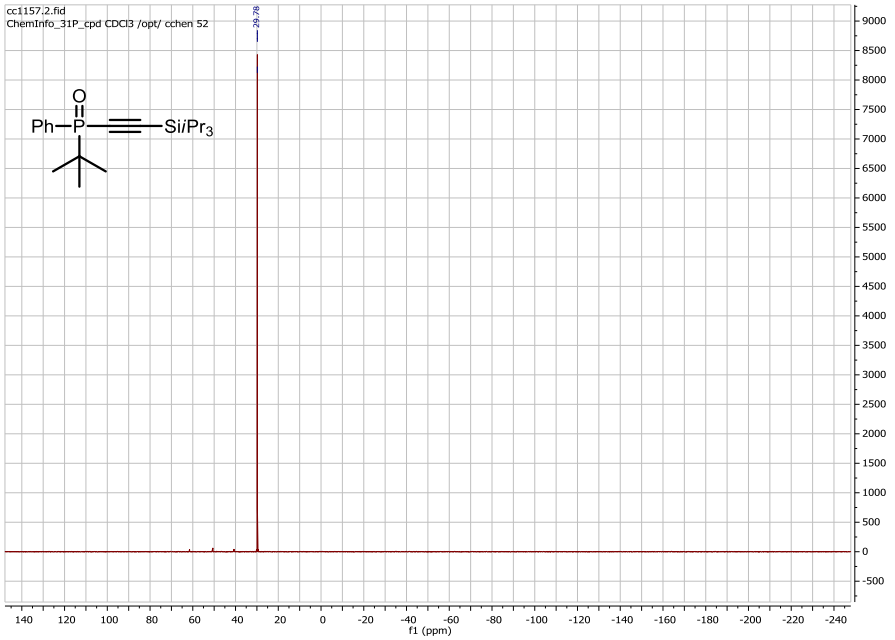
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **9e**

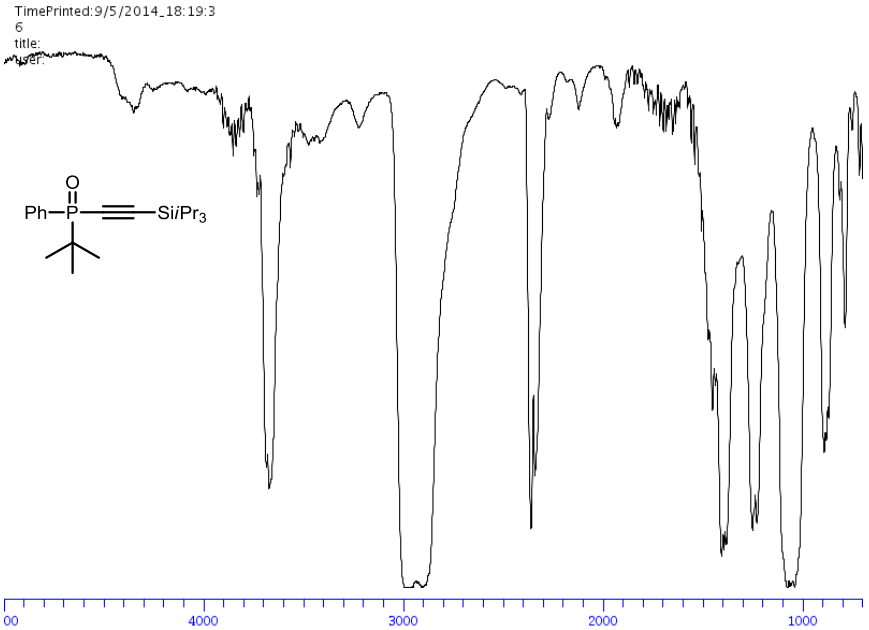


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **9e**

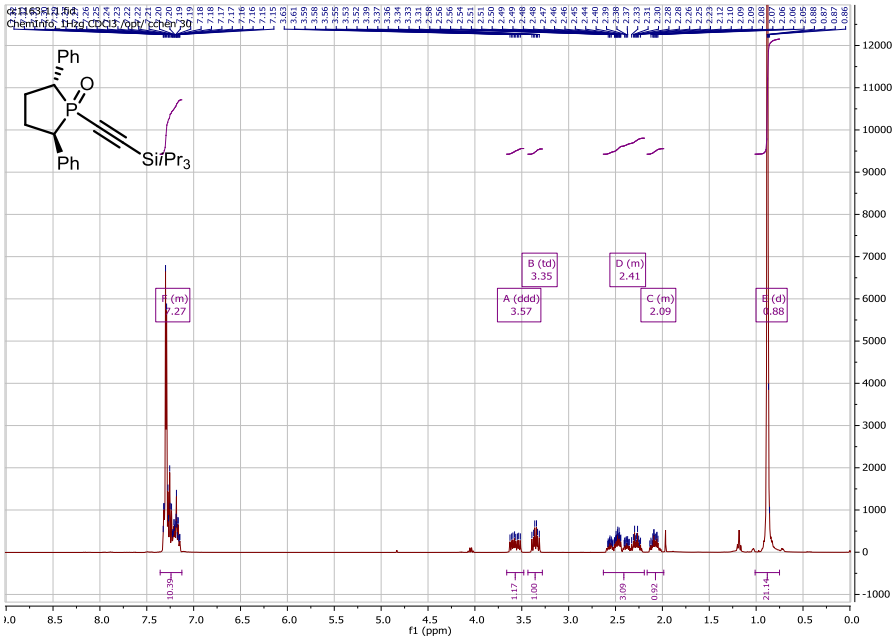


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **9e**

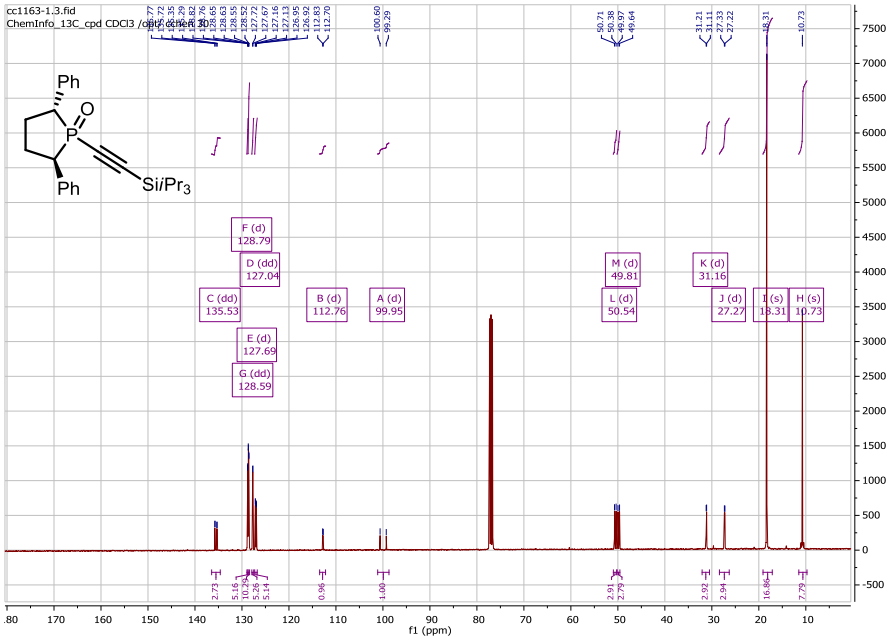




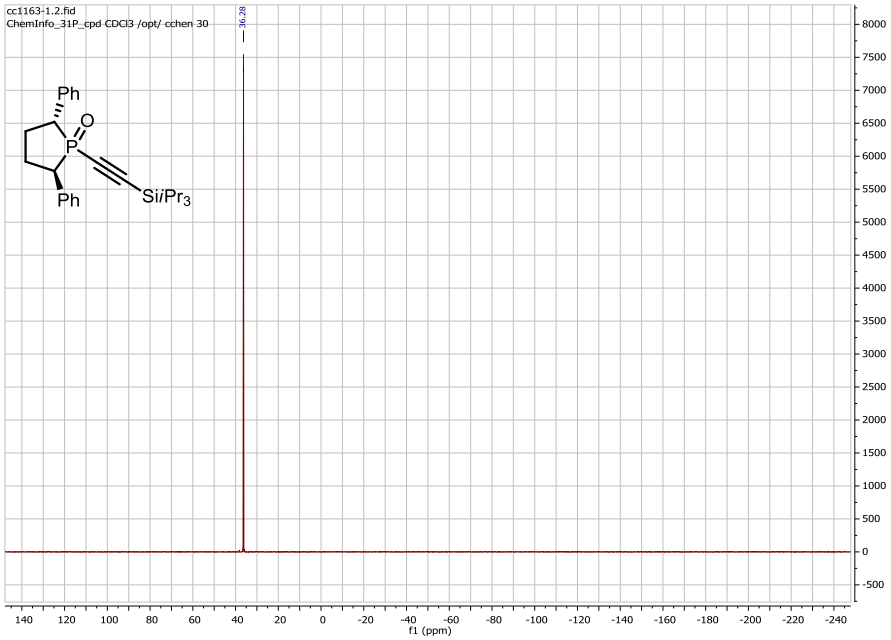
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **9f**

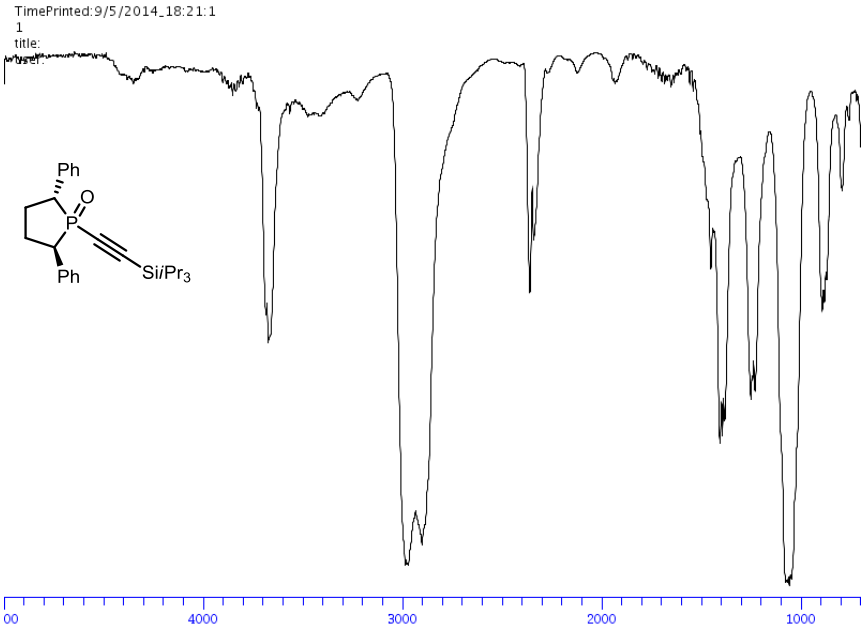


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **9f**

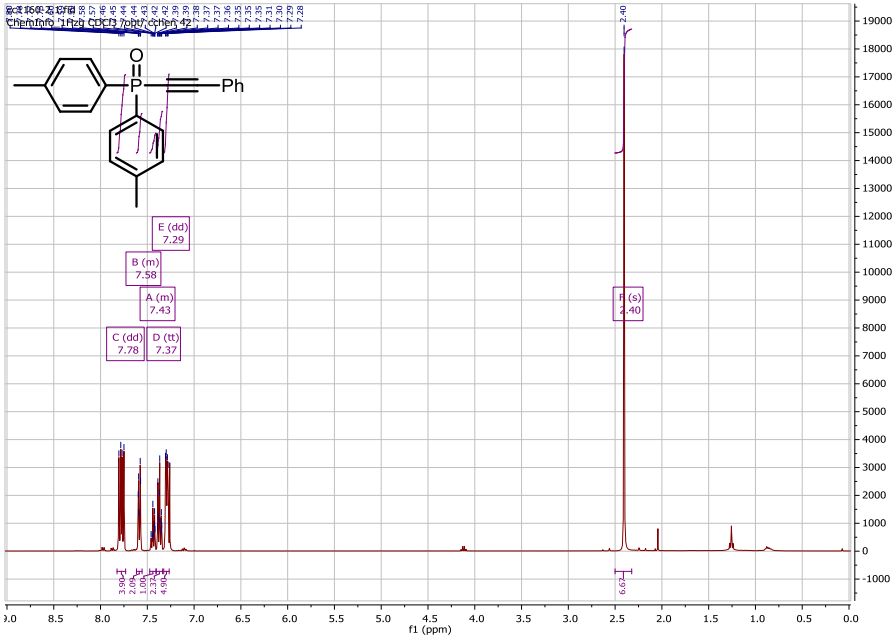


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **9f**

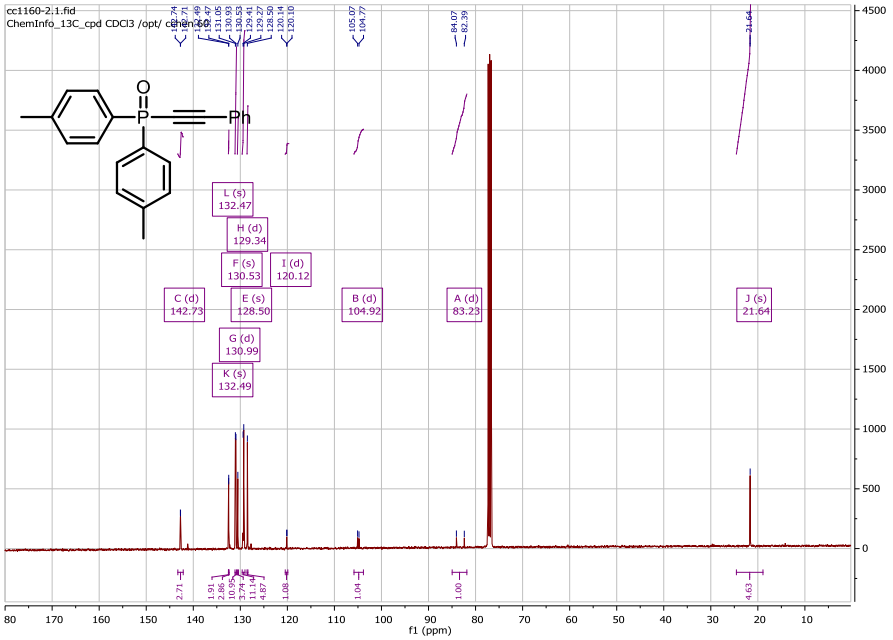




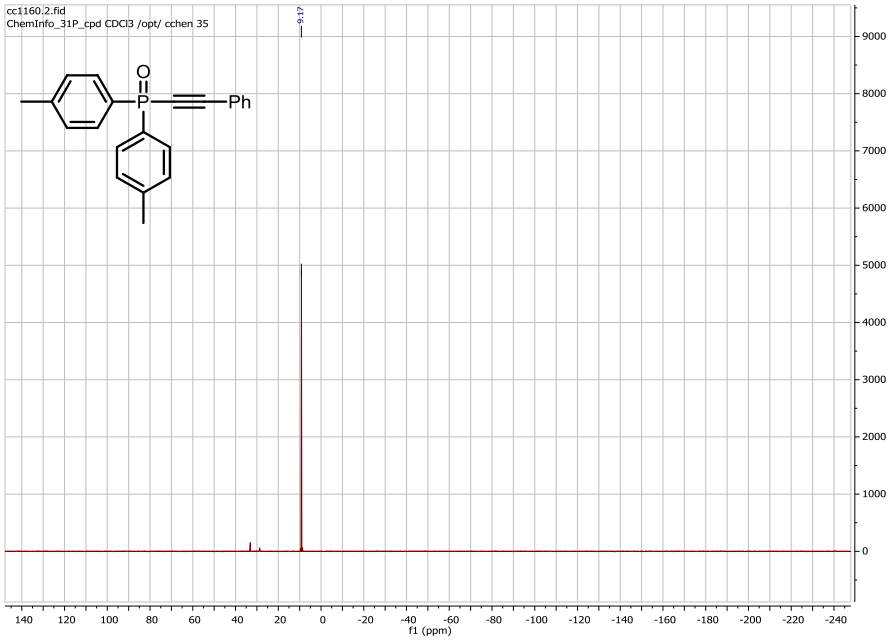
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **9i**

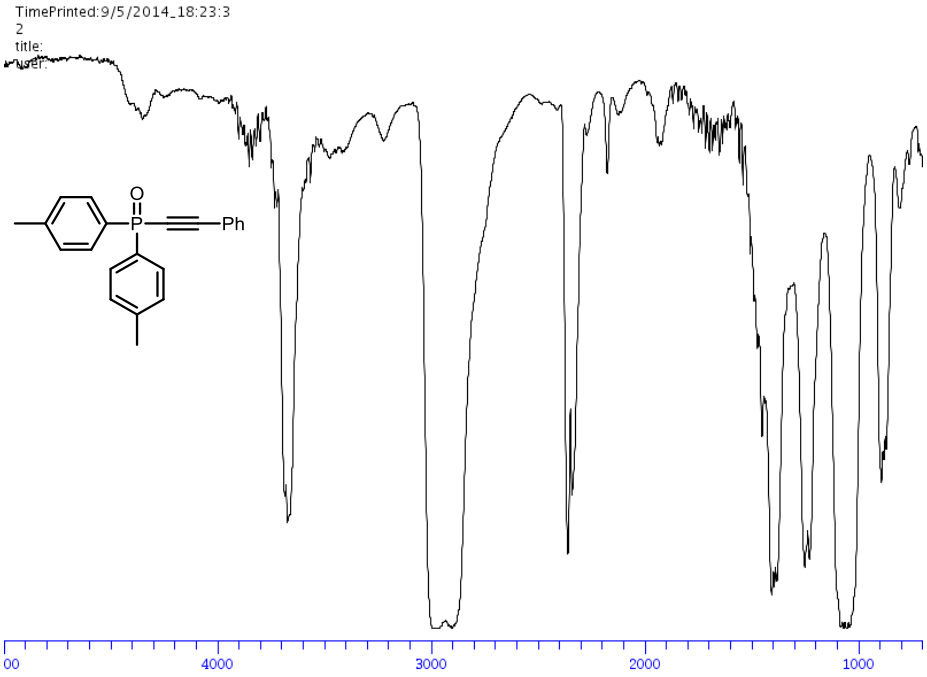


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **9i**



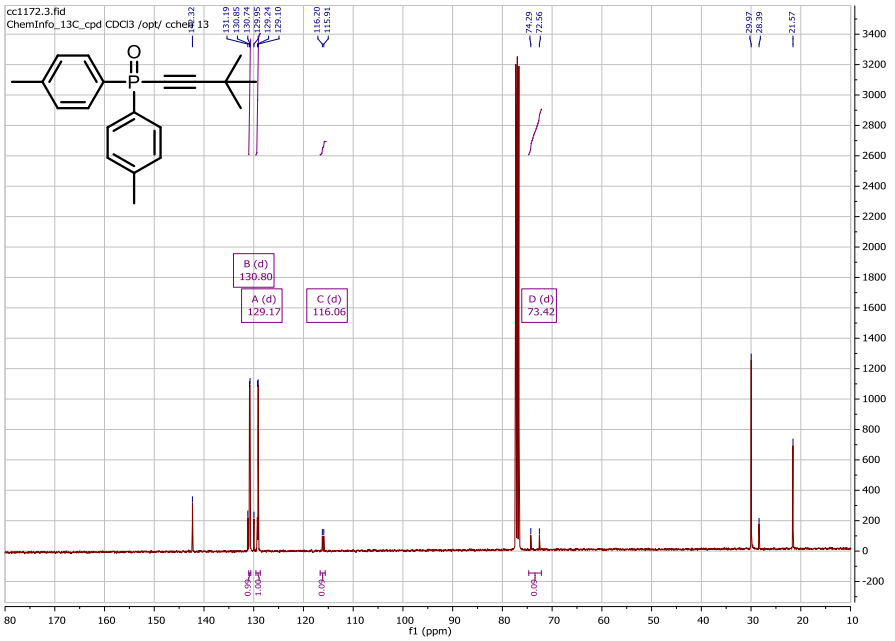
^{31}P-NMR (162 MHz, $CDCl_3$) of compound **9i**



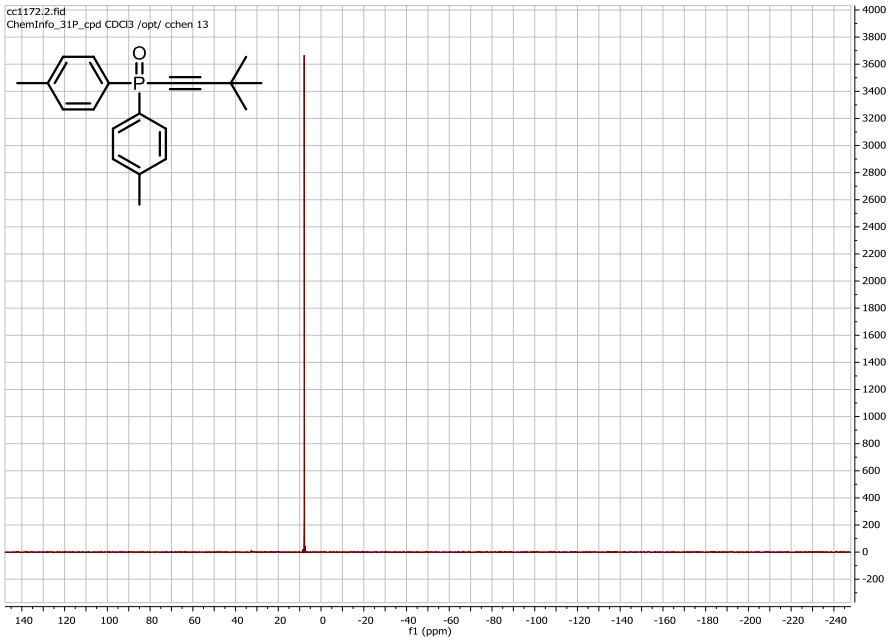


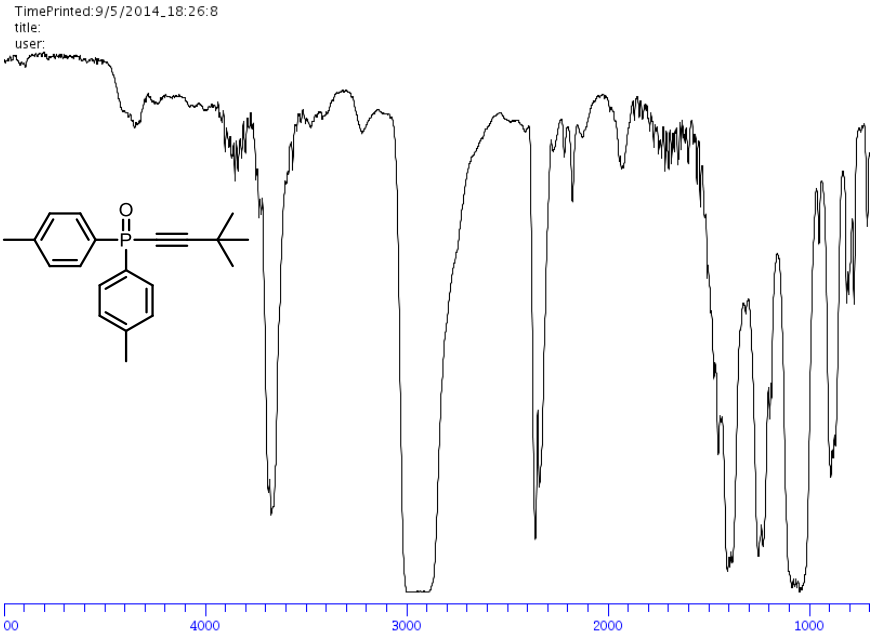
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **9j**

^{13}C-NMR (101 MHz, $CDCl_3$) of compound **9j**

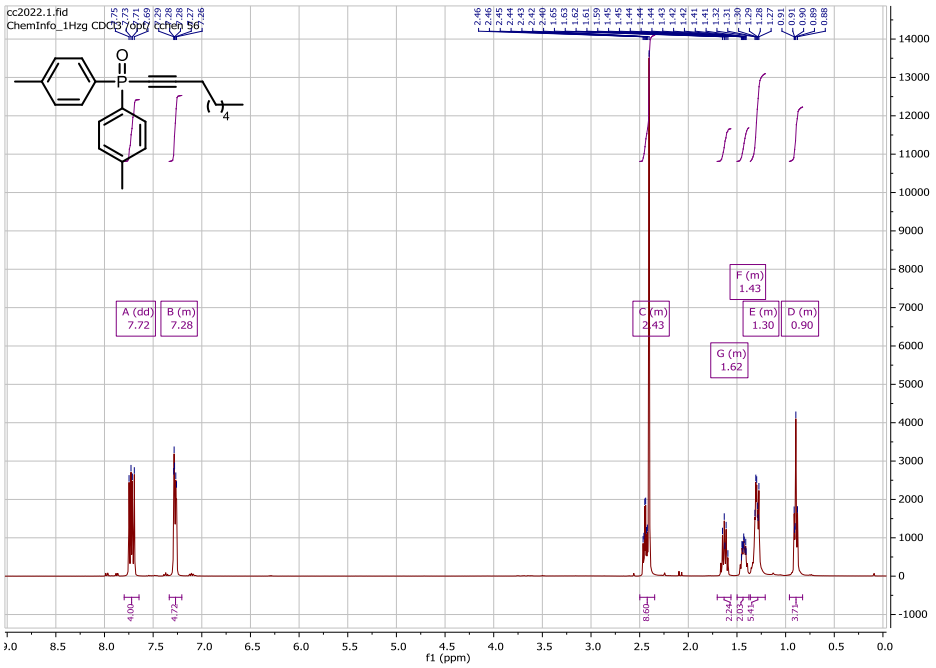


^{31}P-NMR (162 MHz, $CDCl_3$) of compound **9j**

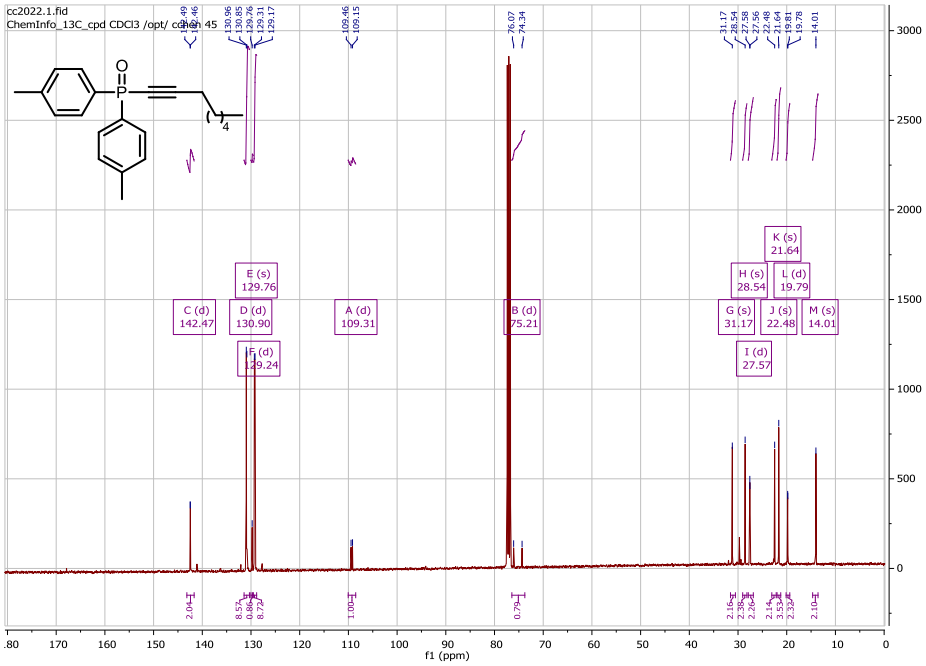




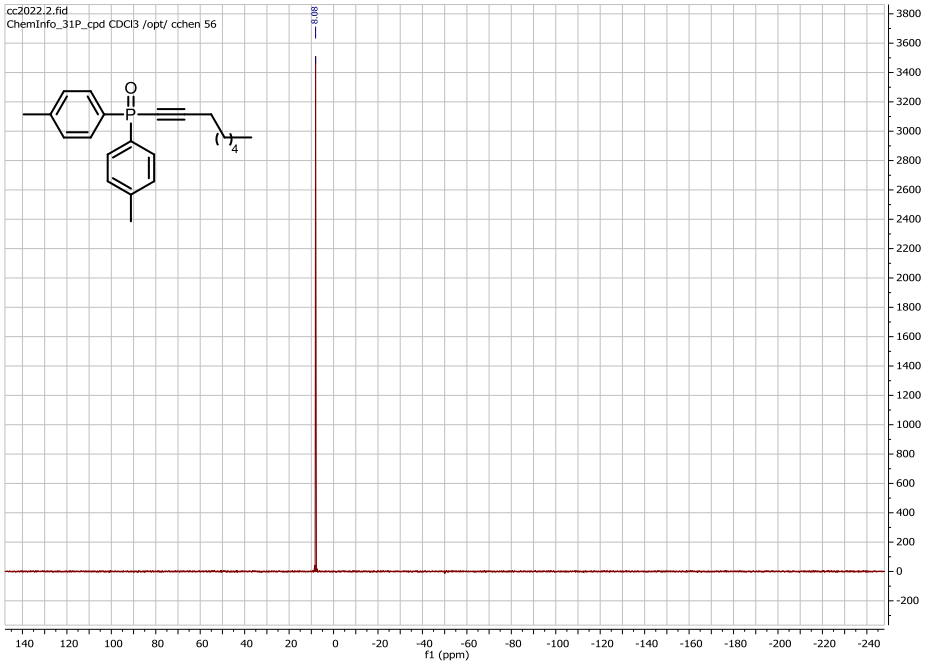
^{1}H-NMR (400 MHz, $CDCl_3$) of compound **9k**

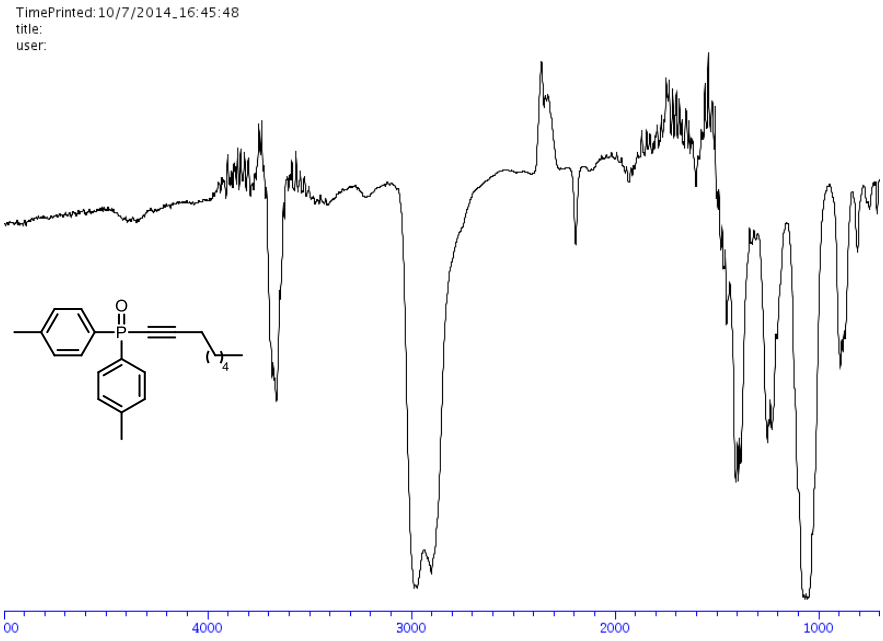


^{13}C-NMR (101 MHz, $CDCl_3$) of compound **9k**



^{31}P-NMR (162 MHz, $CDCl_3$) of compound **9k**

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